

Supplementary Material

On-column reduction of aldehyde with diMe-Imd-BH₃: simultaneous reaction and purification by flash chromatography

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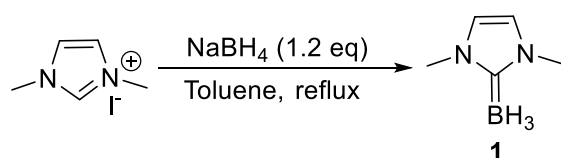
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1. General Information

All the commercial reagents were used without further purification. ^1H and ^{13}C NMR spectra were recorded on Bruker 400 UltraShieldTM spectrometer (400 MHz for ^1H NMR, 101 MHz for ^{13}C NMR); IR spectra were recorded on a Nicolet Avatar 370 DTGS spectrometer. High-resolution mass spectrometry (HRMS) was recorded on a Q-TOF (AB SCIEX X500R with ESI source, and Agilent 7250 with EI source), which combines quadrupole precursor ion selection and a high-resolution accurate-mass (HR/AM) Time of Flight mass analyzer to deliver mass accuracy. Flash chromatography was packed with SiO_2 (silica gel 60, 200–300 mesh) or alimina (neutral, 200–300 mesh). Melting points were recorded on the microscope with hot plate with thermometer.

2. Preparation of 1,3-dimethylimidazol-2-ylidene borane (diMe-Imd-BH₃, **1**)



To a suspension of 1,3-dimethylimidazole iodide (11.202 g, 50.00 mmol) in toluene (50 mL) was added sodium borohydride (2.282 g, 60.32 mmol) was added. The system was purged with nitrogen three times. The mixture was heated to reflux and heated for 13 hours. Before cooling, the reaction solution was decanted, and the remaining solid residue was dissolved in dichloromethane and filtered. The filtrate was combined with the decanted solution, and the mixture was concentrated under reduced pressure. The crude product was purified by column chromatography to afford a white solid (3.794 g, 34.50 mmol, 69% yield).

1,3-Dimethylimidazol-2-ylidene borane (**1**)

White solid. M.p. 135.8–137.0 °C (ref^[1] 134–137 °C); R_f = 0.39 (PE/EA 1:1).

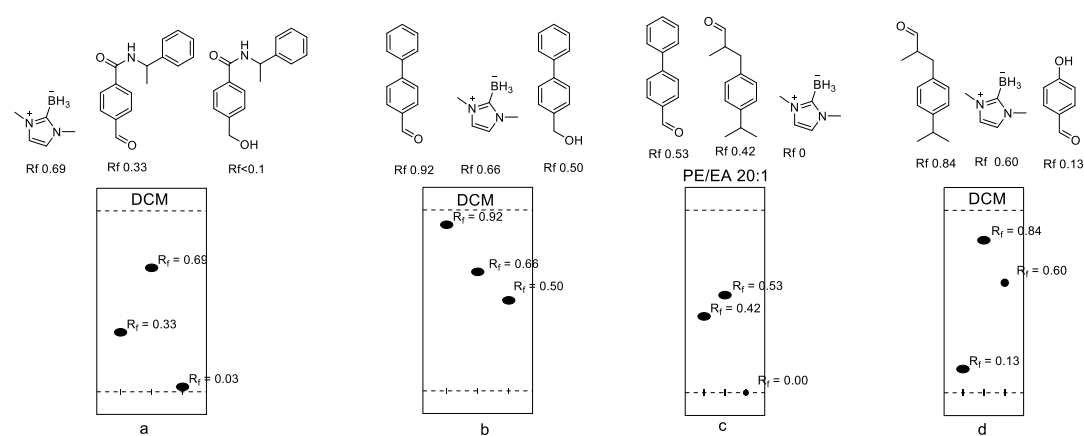
^1H NMR (400 MHz, CDCl_3) δ 6.79 (s, 2H), 3.73 (s, 6H), 1.00 (q, $J_{\text{B-H}}$ = 86.4 Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3): δ 120.0, 36.1; ^{11}B NMR (128 MHz, CDCl_3): δ -37.5 (q, J = 86.1 Hz), .

3. General Procedure for the Reduction of Aldehydes with diMe-Imd-BH₃ and Quenching with Diluted HCl

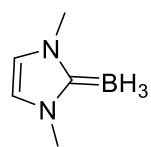
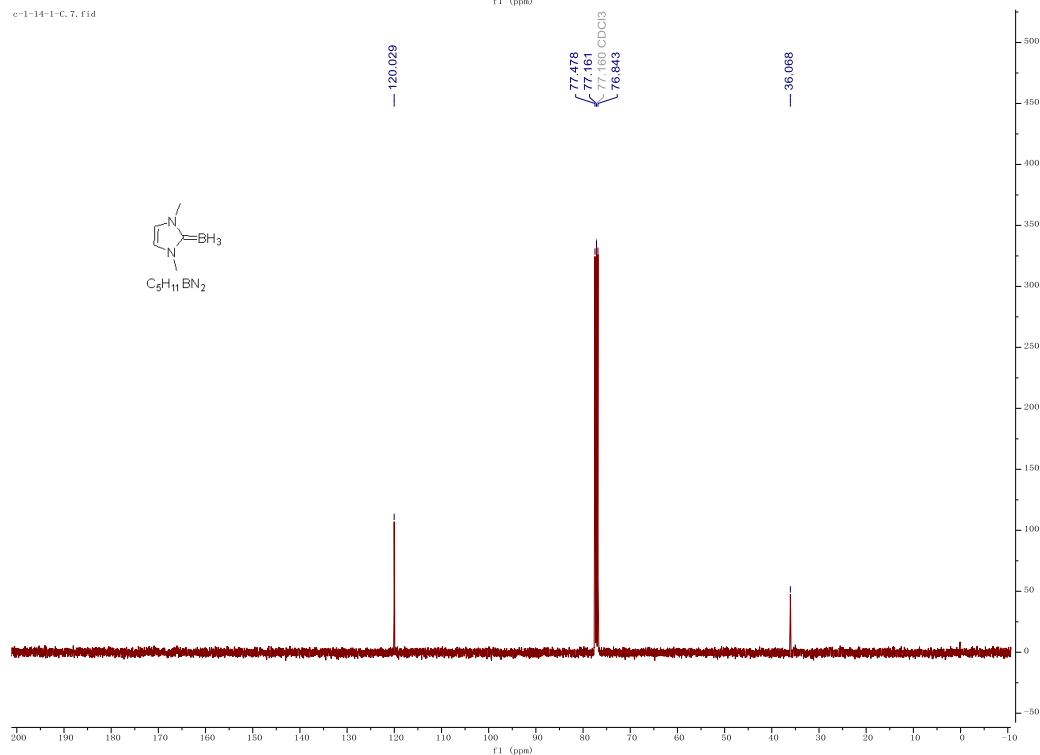
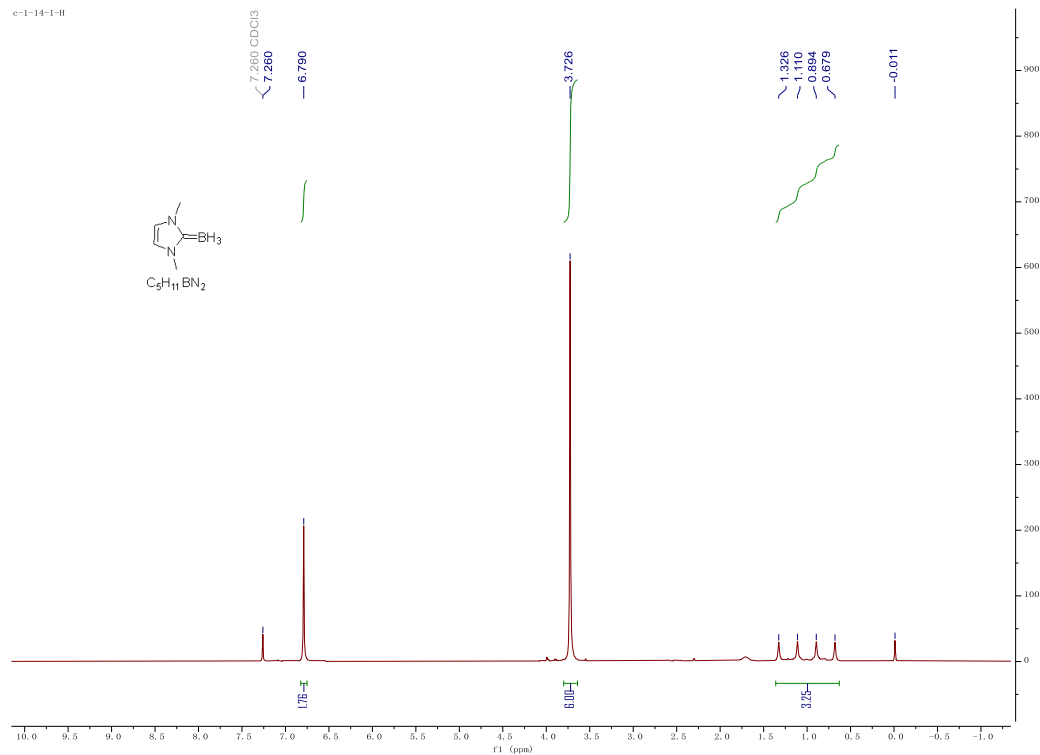
To a solution of aldehyde **2** (1.0 mmol) in acetonitrile (5 mL) was added diMe-Imd-BH₃ (**1**, 1.0 mmol). The system was purged with nitrogen three times and the mixture was stirred at room

temperature for 8 hours. The reaction was monitored by TLC. Upon completion, diluted HCl (1:5, 5 mL) was added, and the mixture was stirred for 10 minutes. The acetonitrile was then removed under reduced pressure, and the aqueous phase was extracted with methyl *tert*-butyl ether (MTBE, 15 mL*3). The combined organic layers were washed with saturated sodium bicarbonate (5 mL), water (5 mL), and brine (10 mL), then dried over anhydrous sodium sulfate. The crude product was concentrated and purified by flash chromatography to afford the desired alcohol **3**.

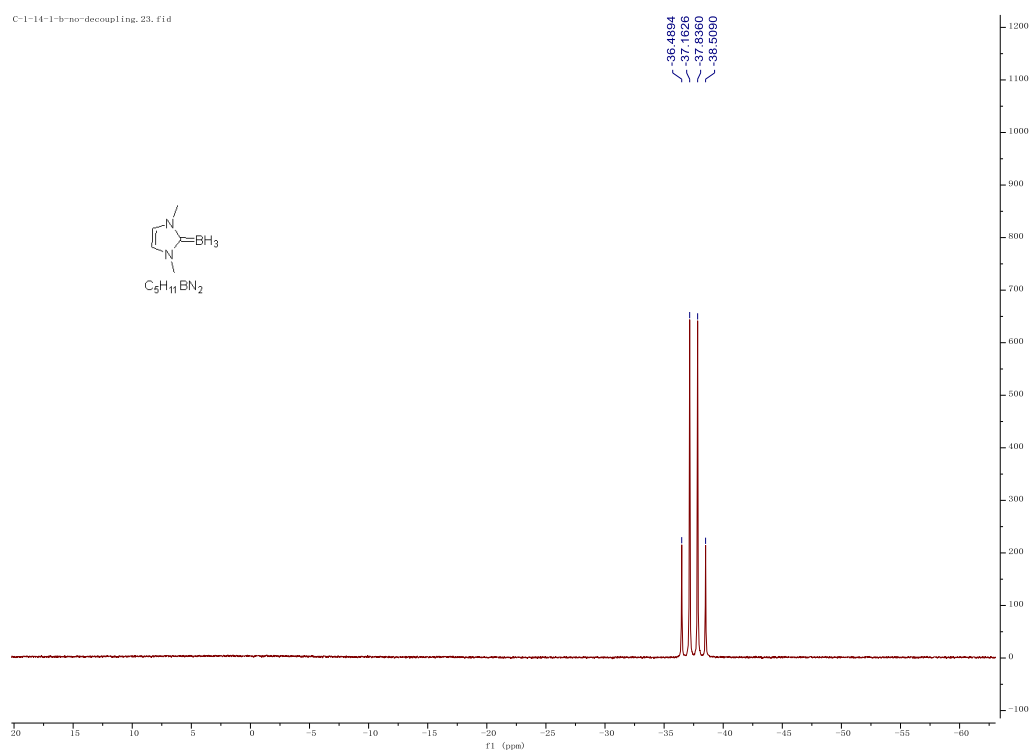
4. Thin Layer Chromatography (TLC) Profiles of Selected Compounds



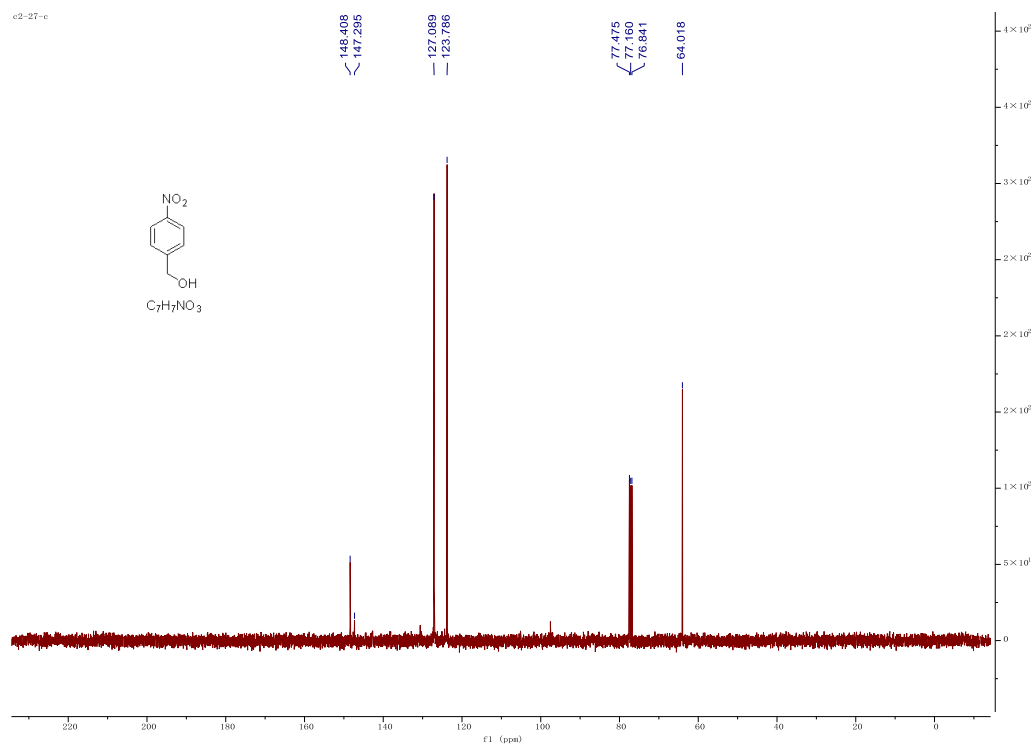
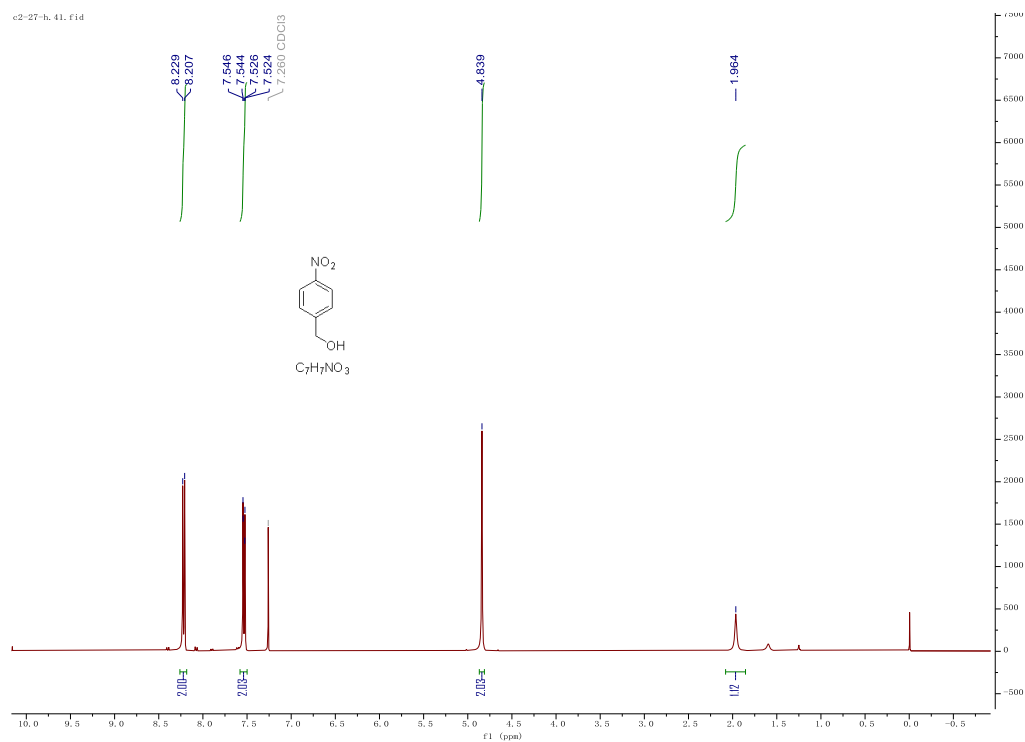
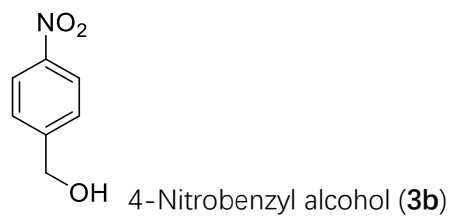
5. Copies of NMR spectra of products

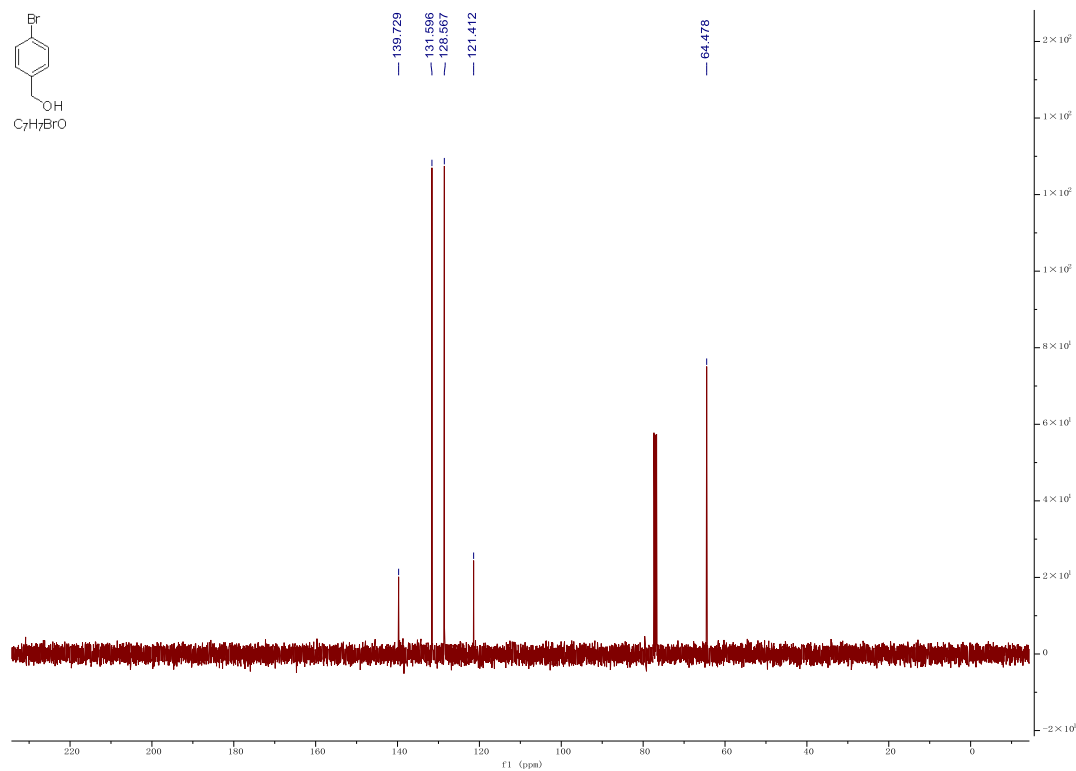
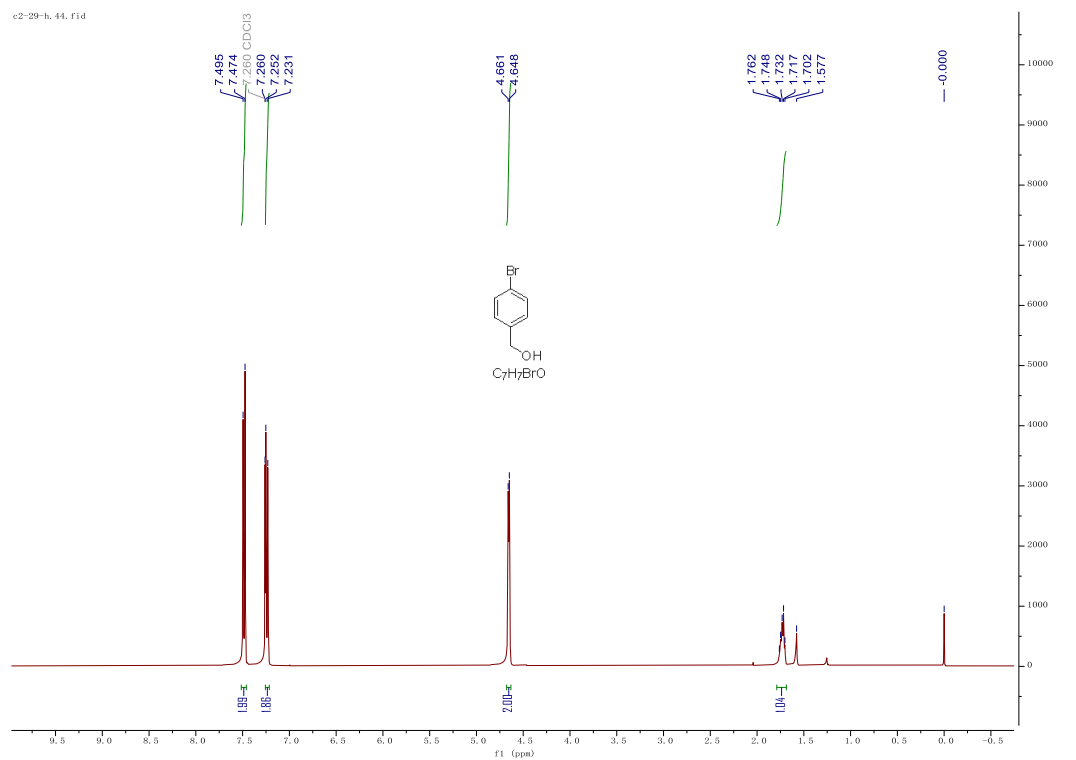
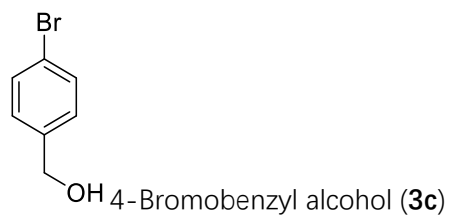
1,3-Dimethylimidazol-2-ylidene borane (**1**)

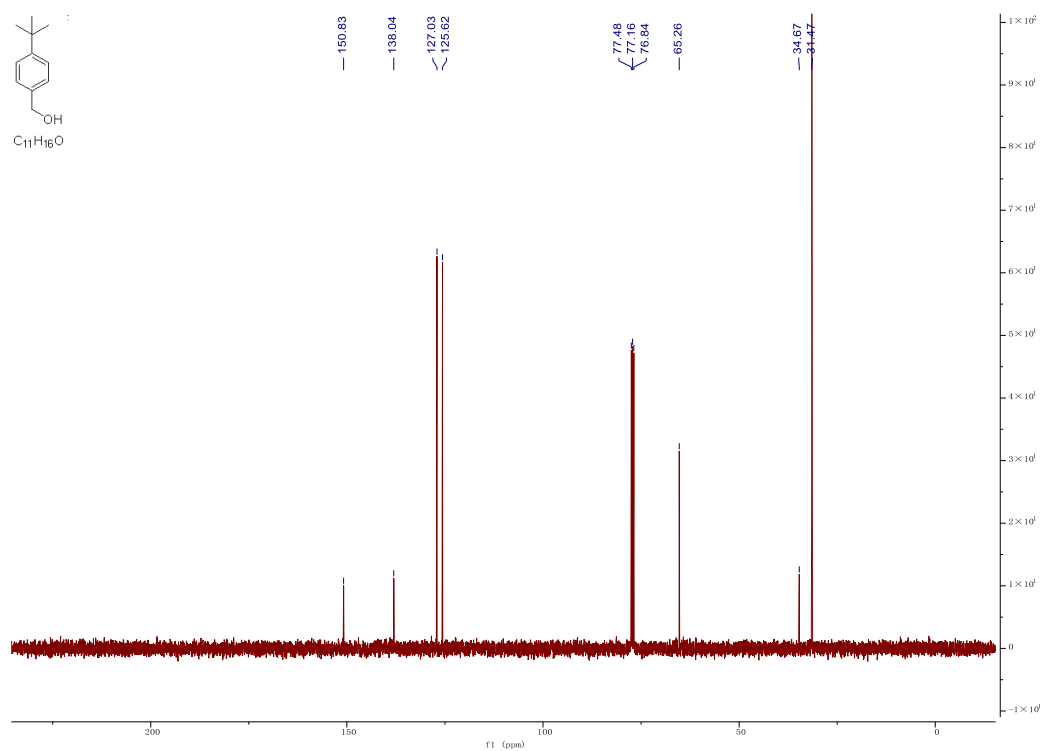
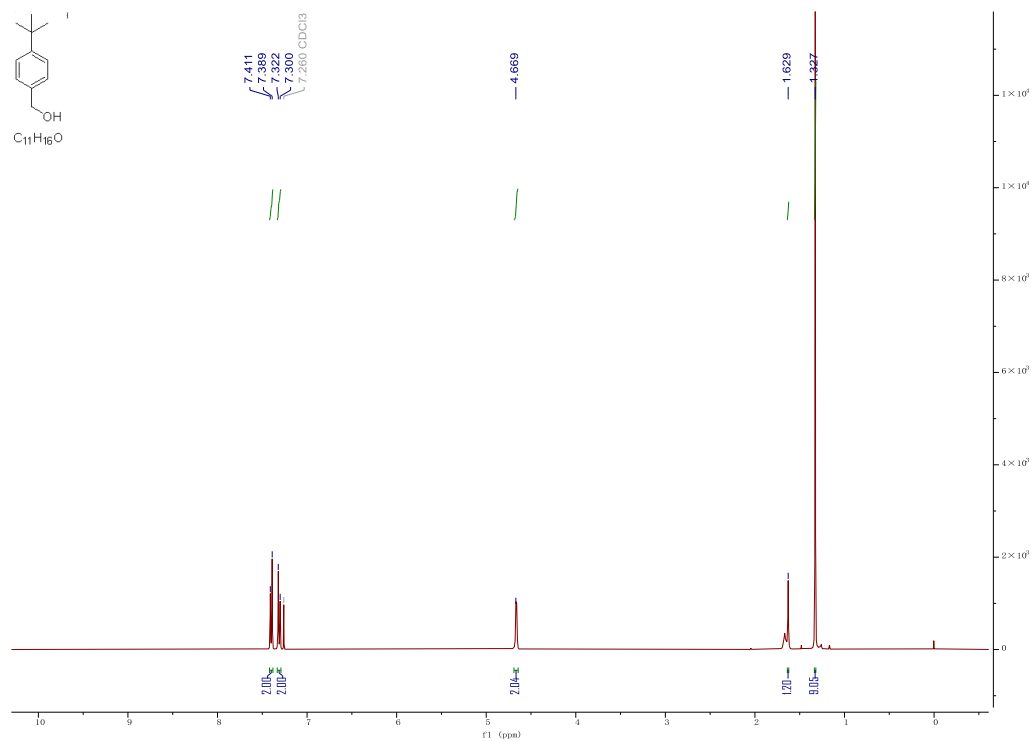
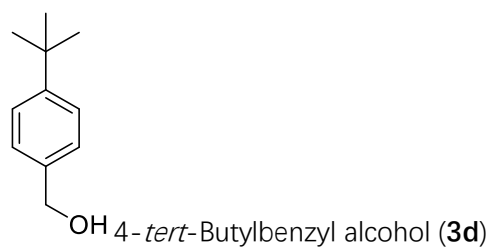
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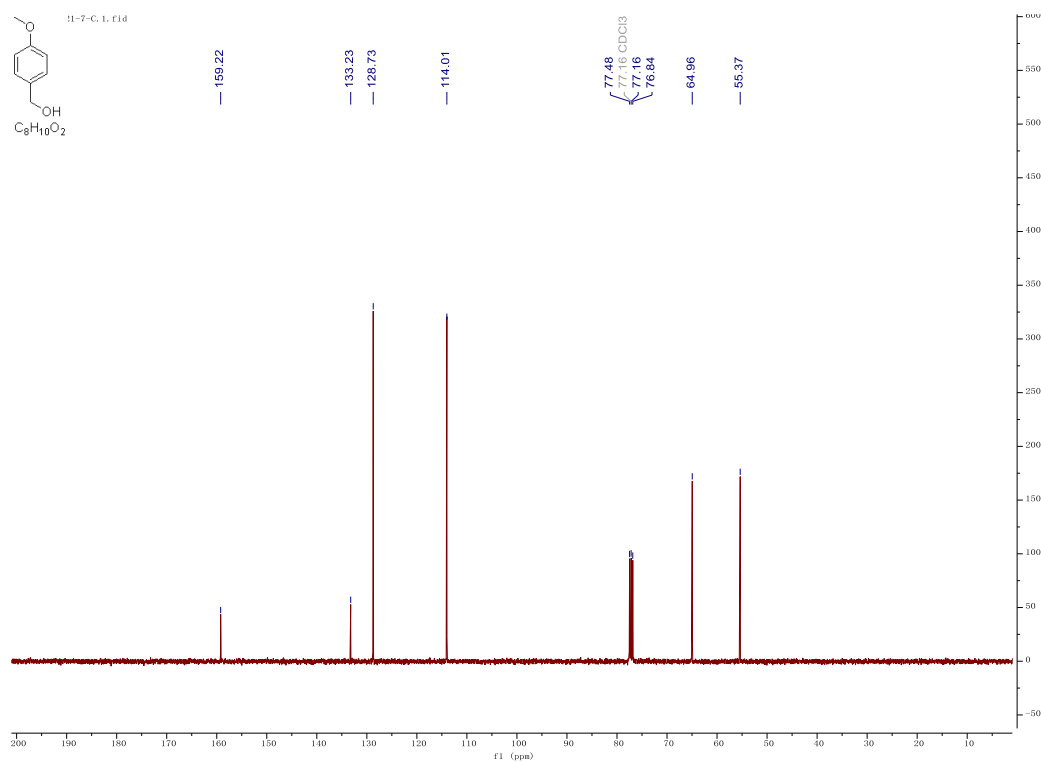
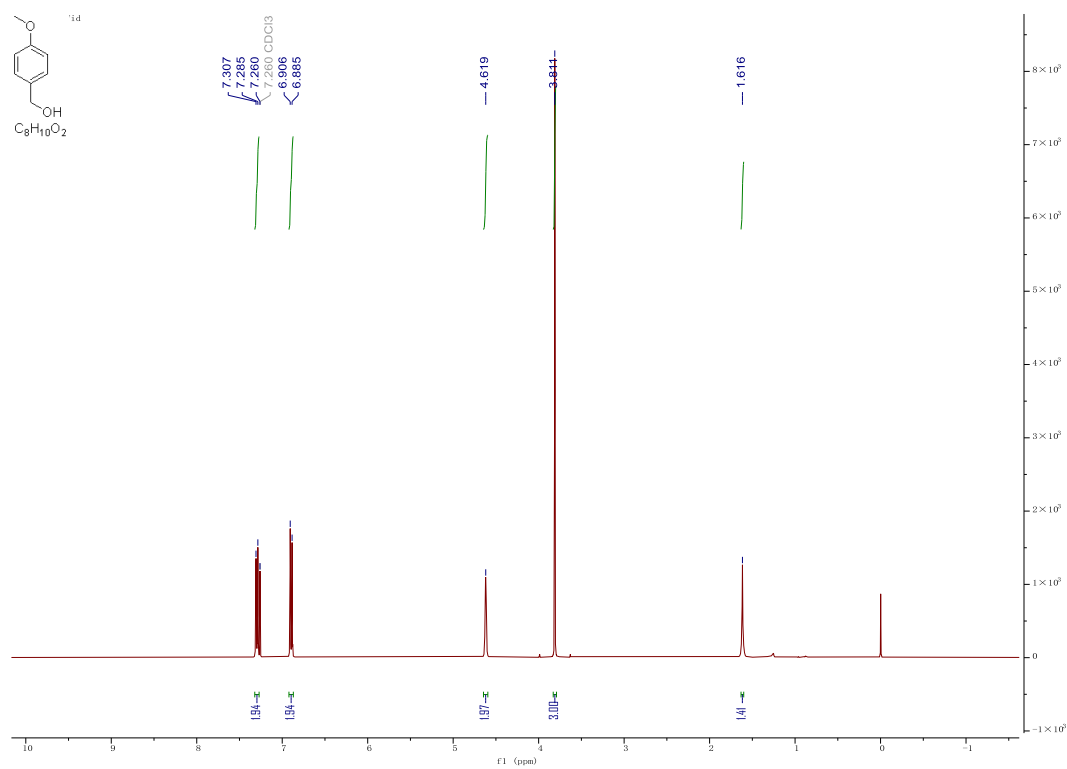
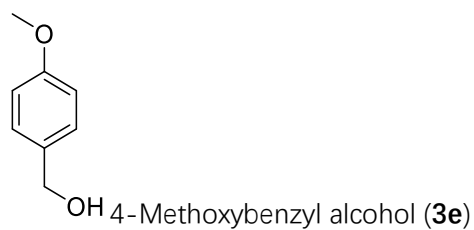


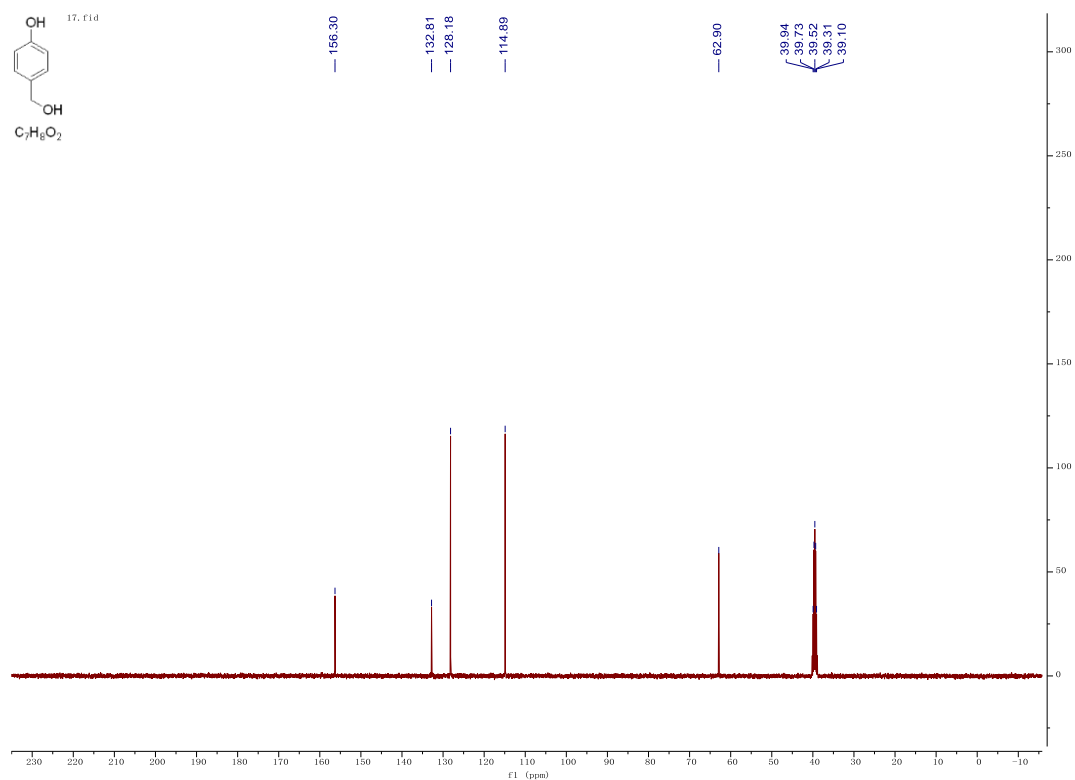
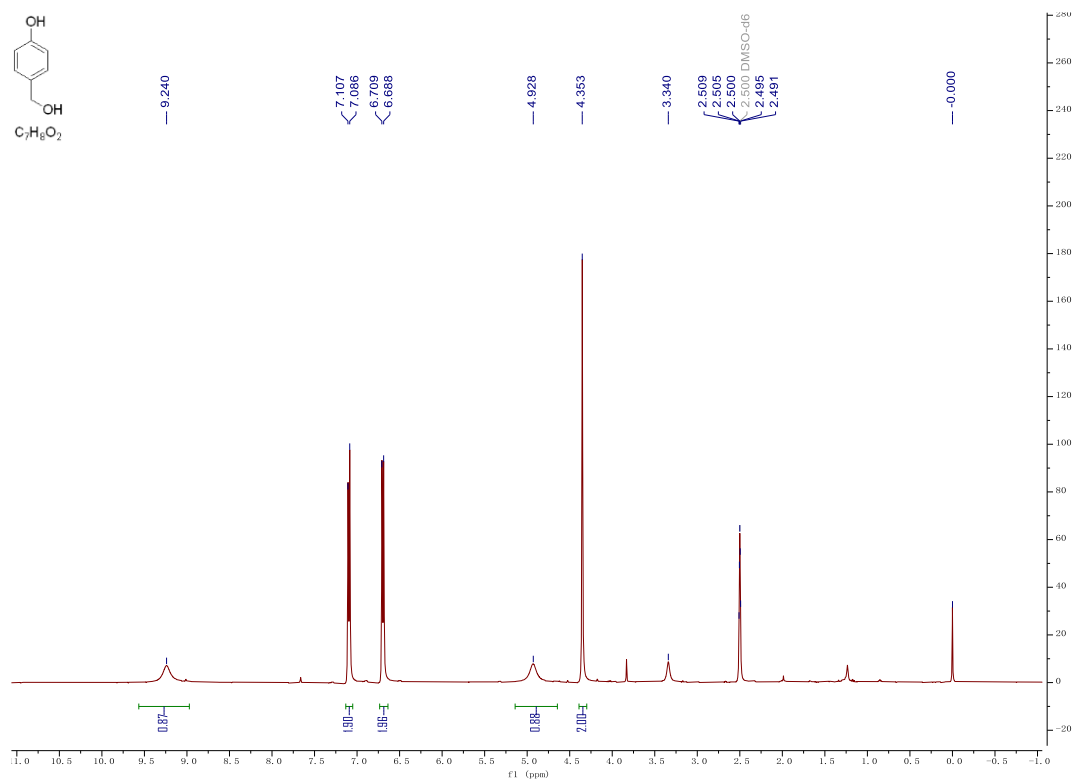
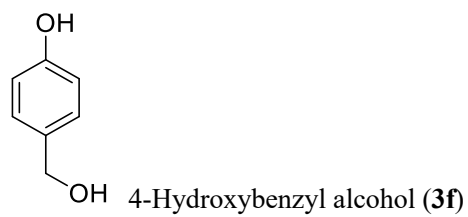


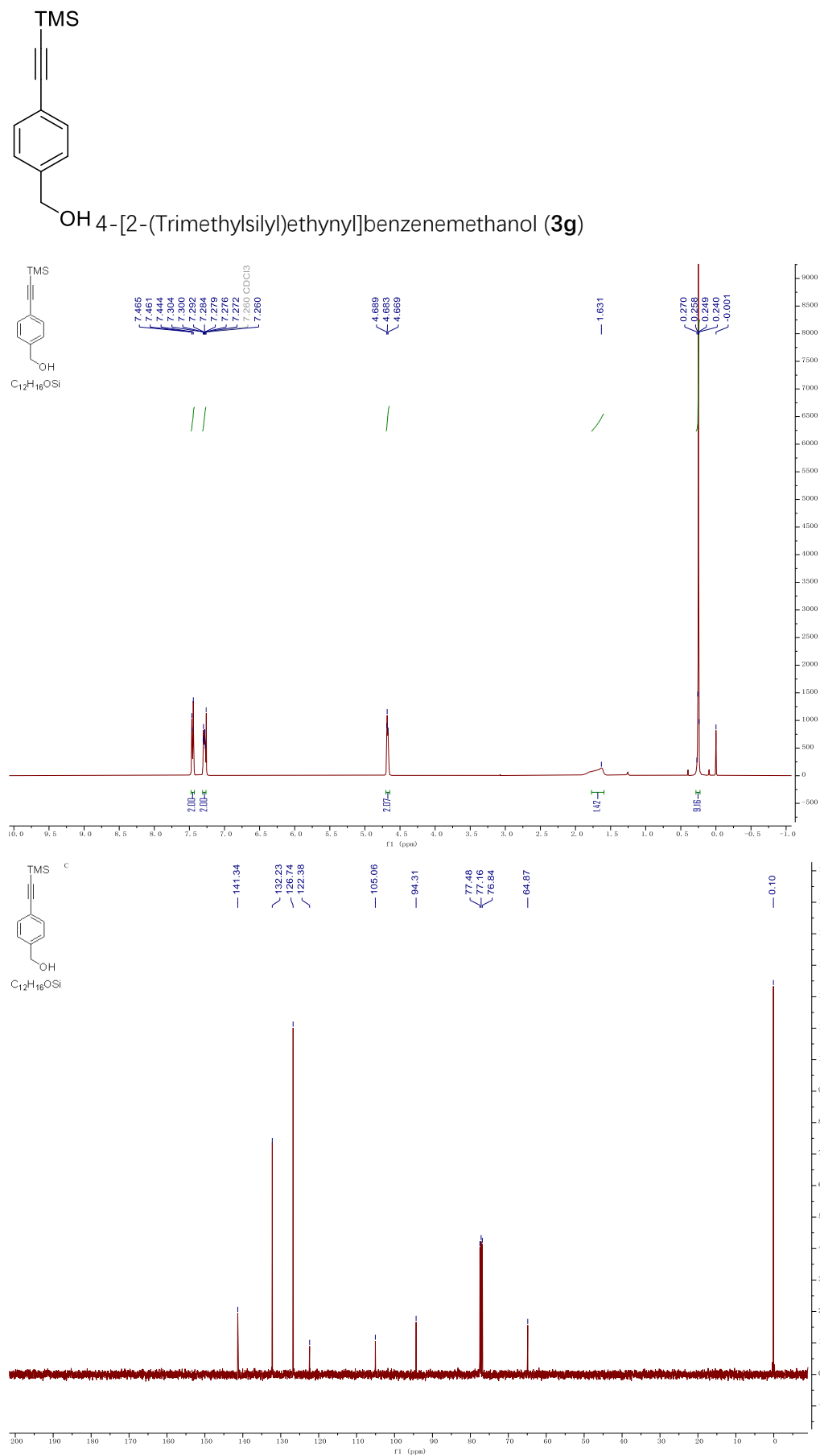


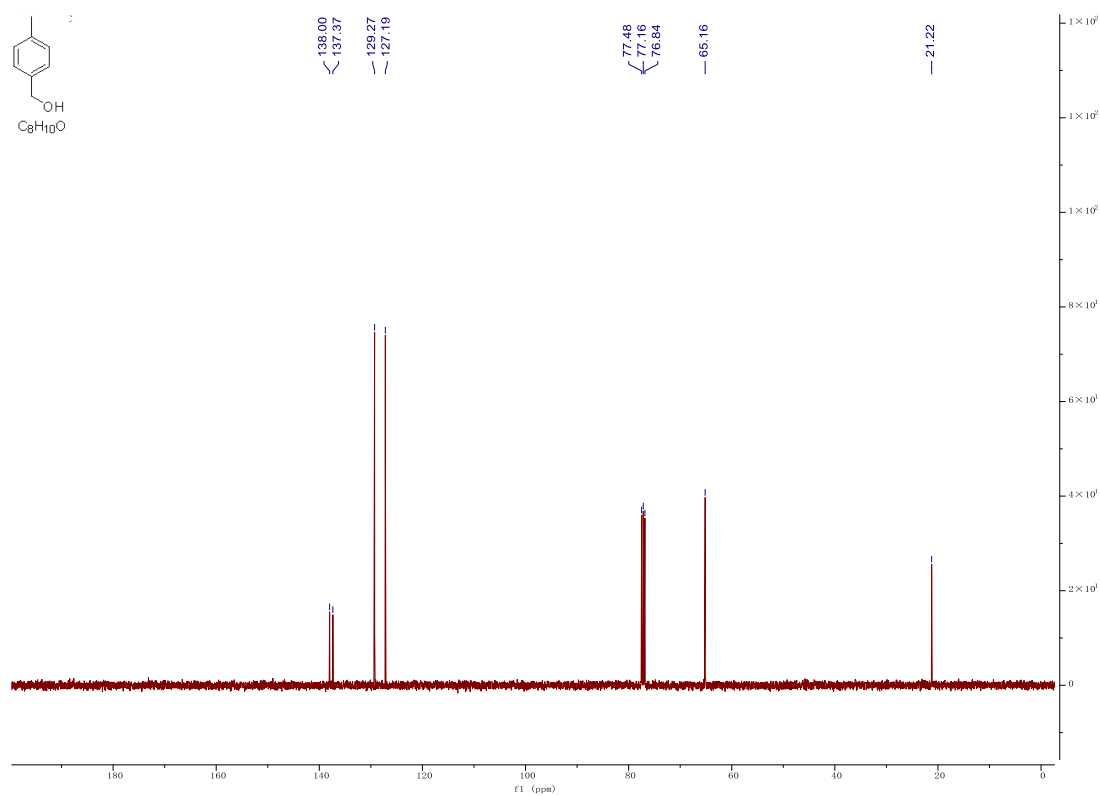
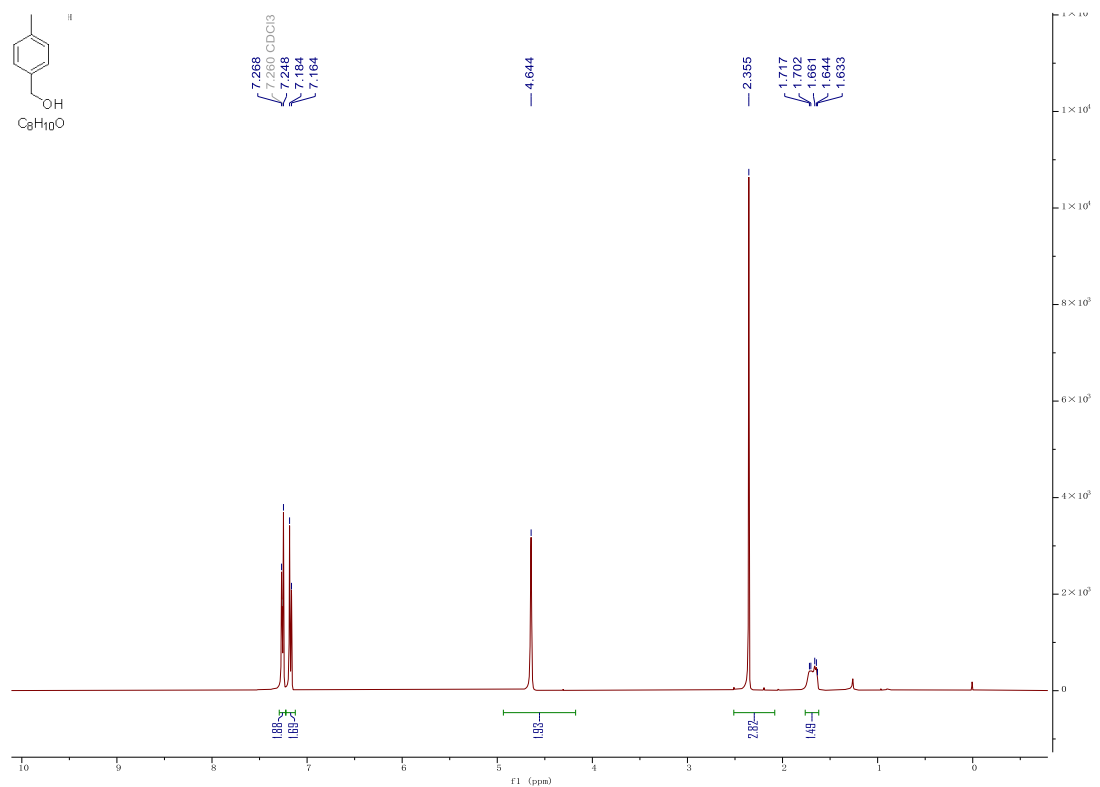
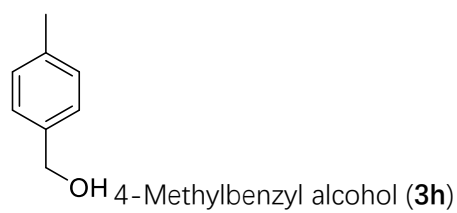


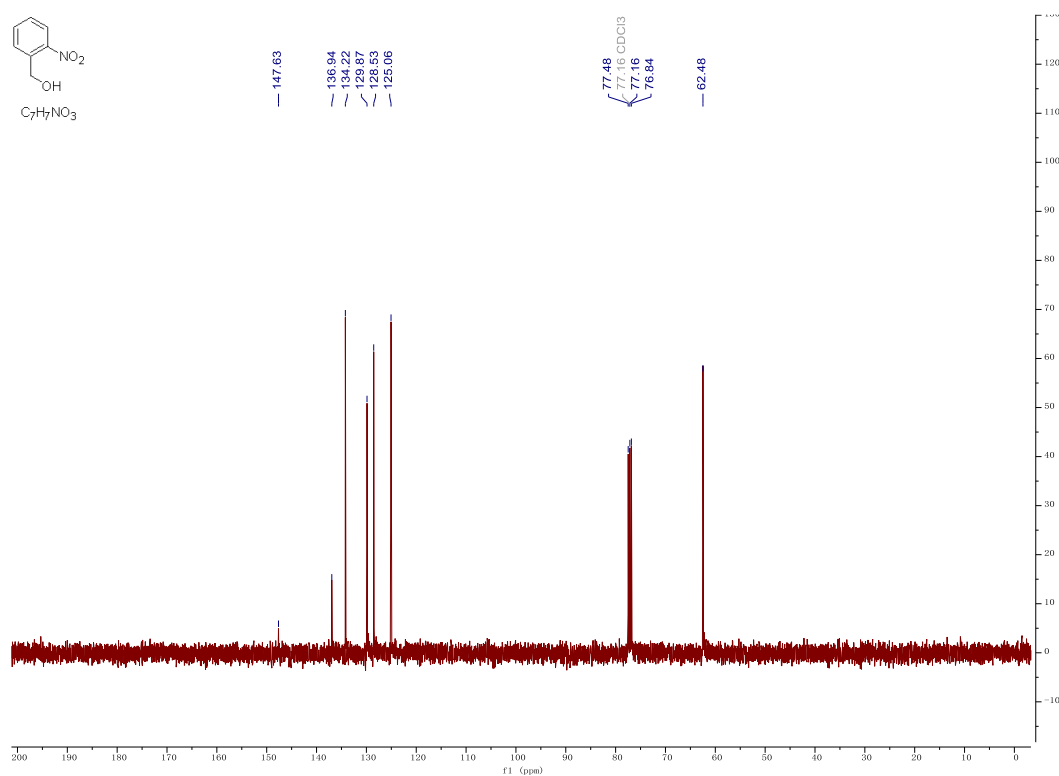
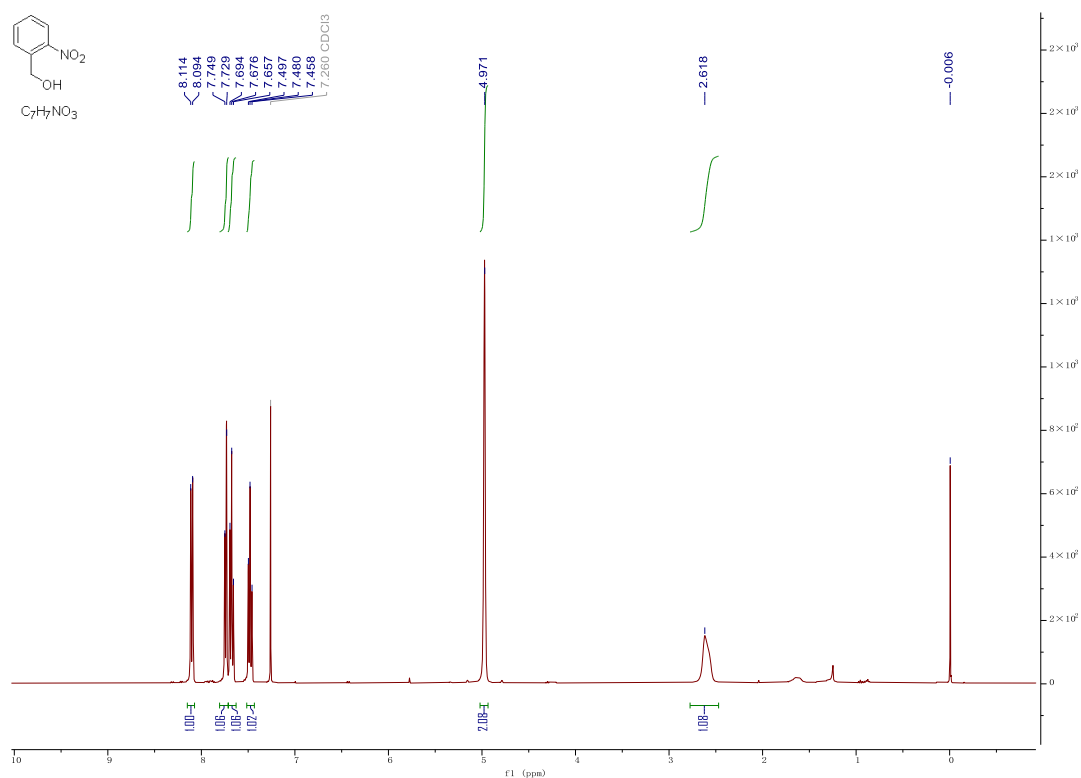
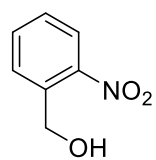


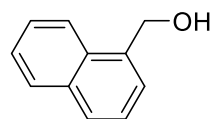




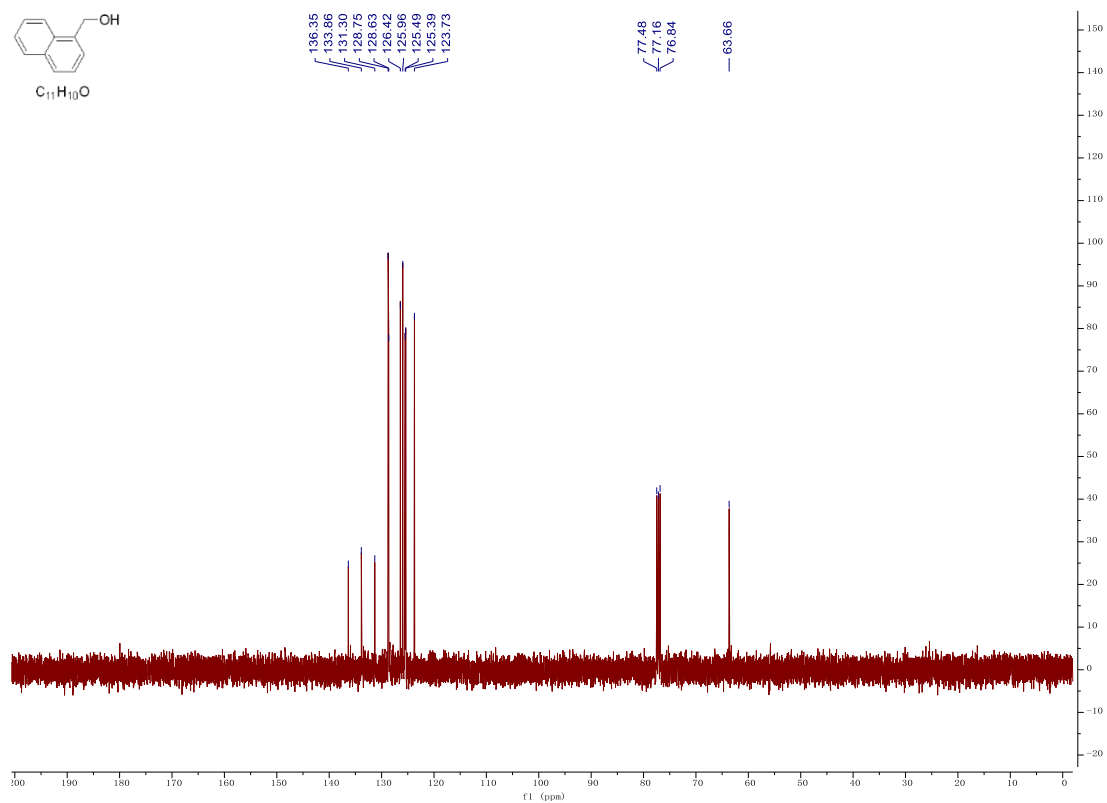
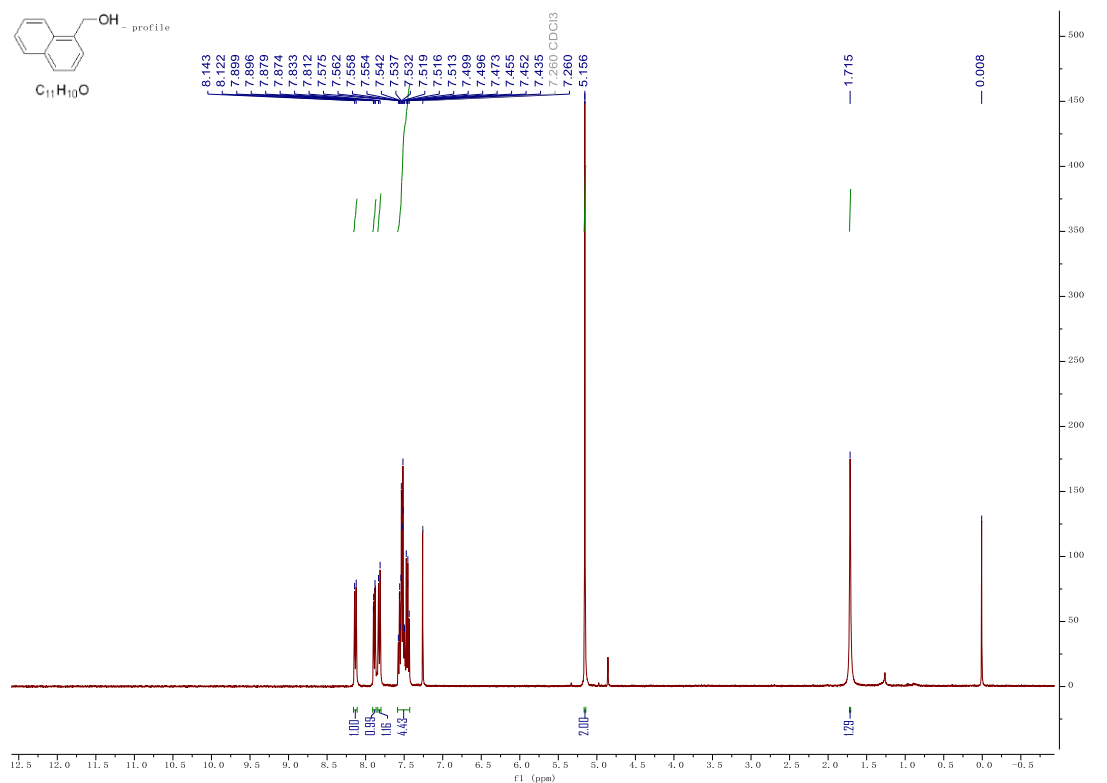


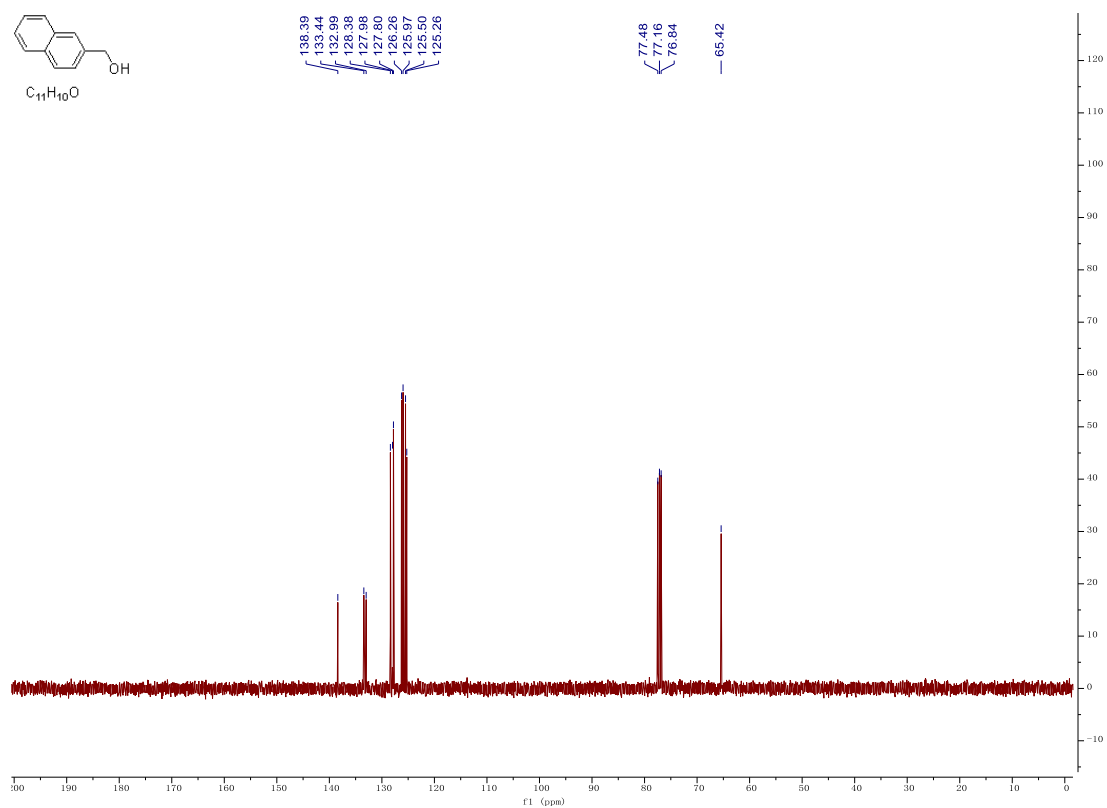
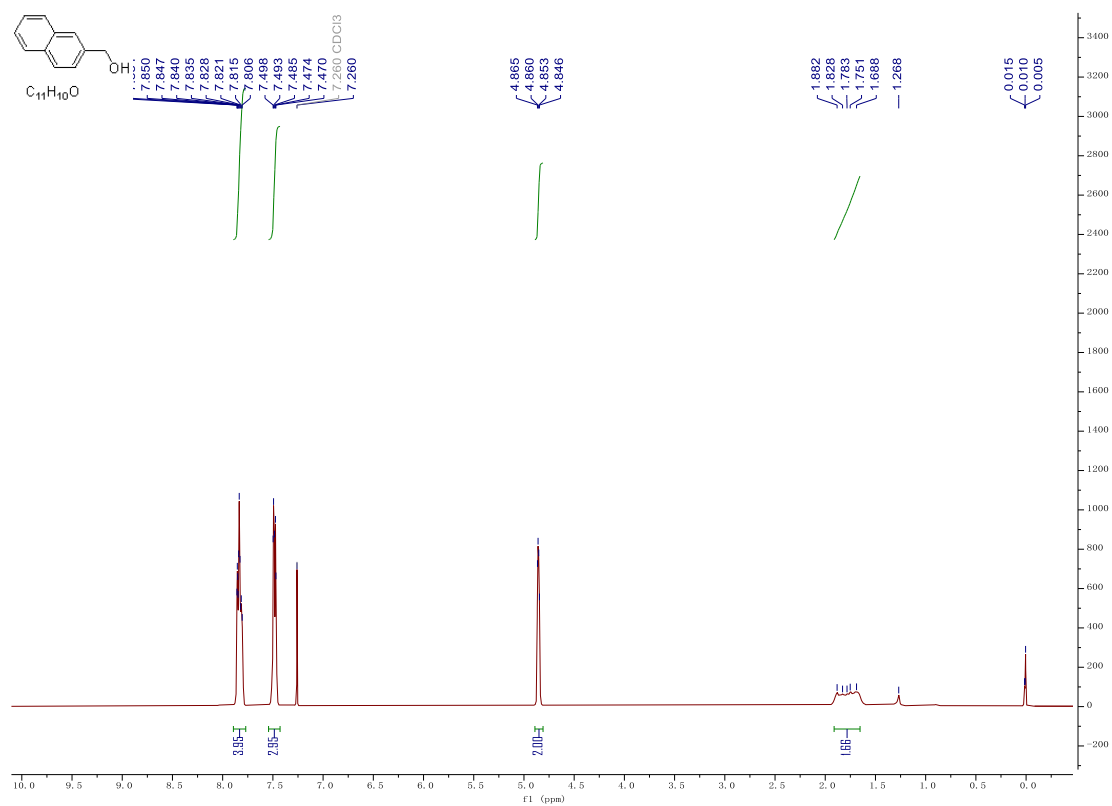
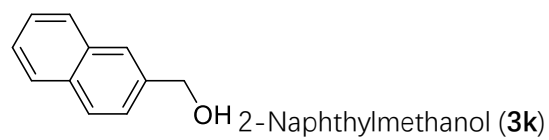


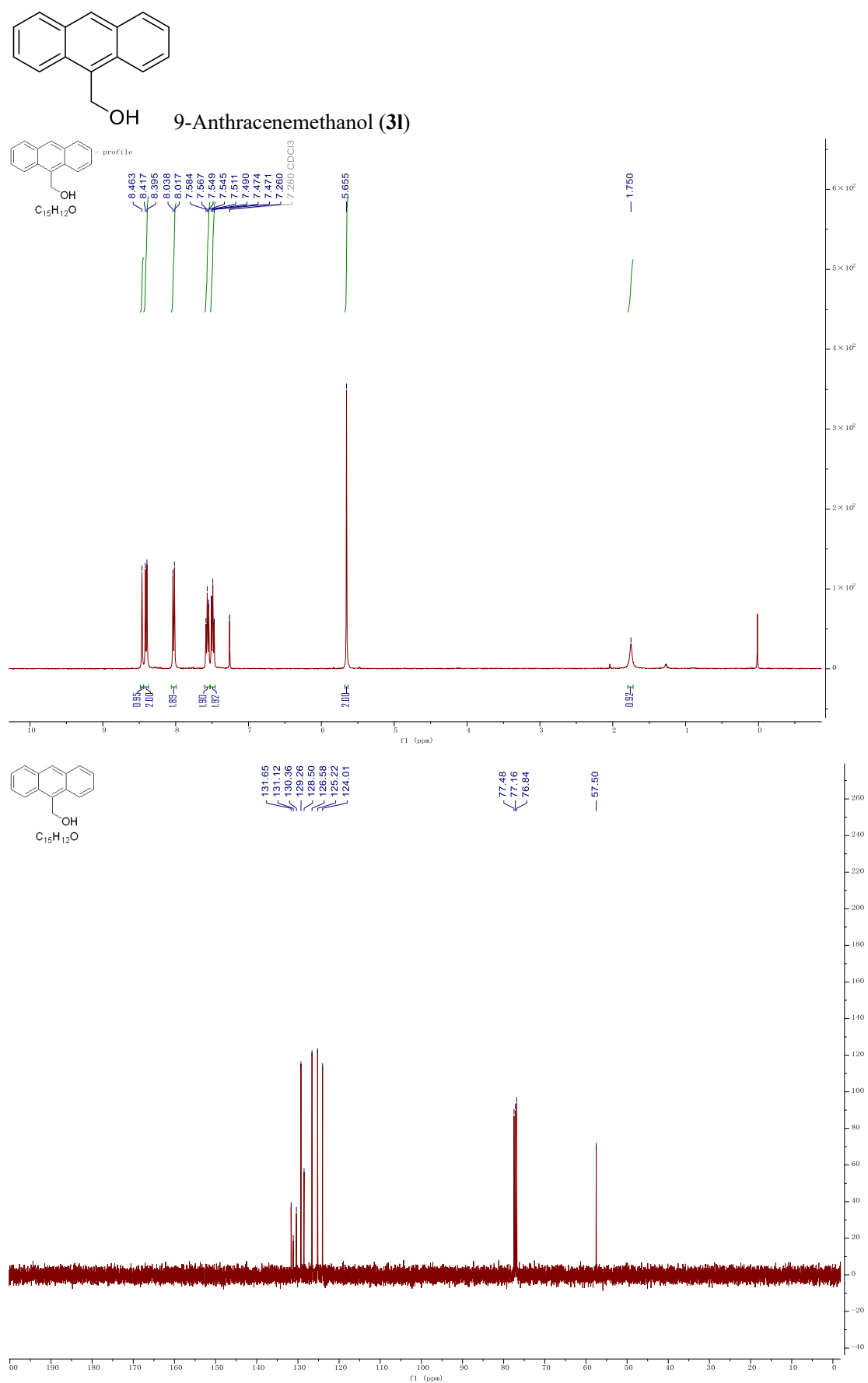


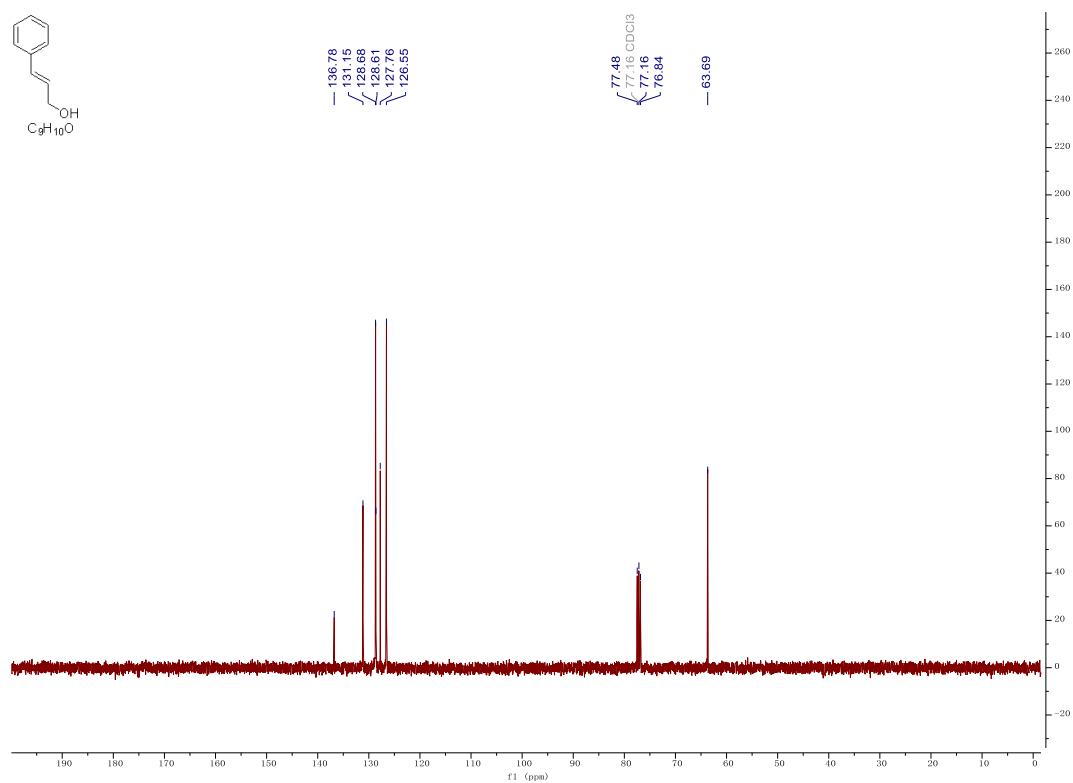
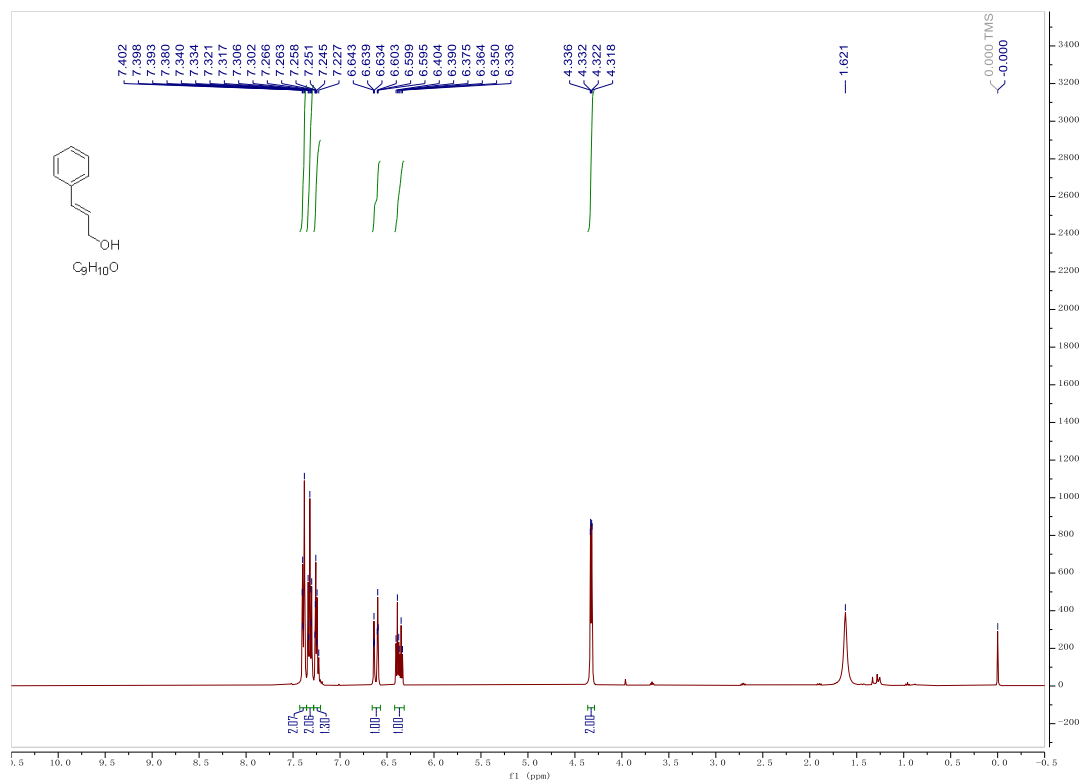
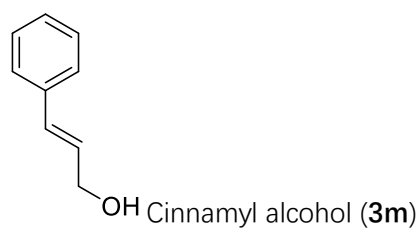


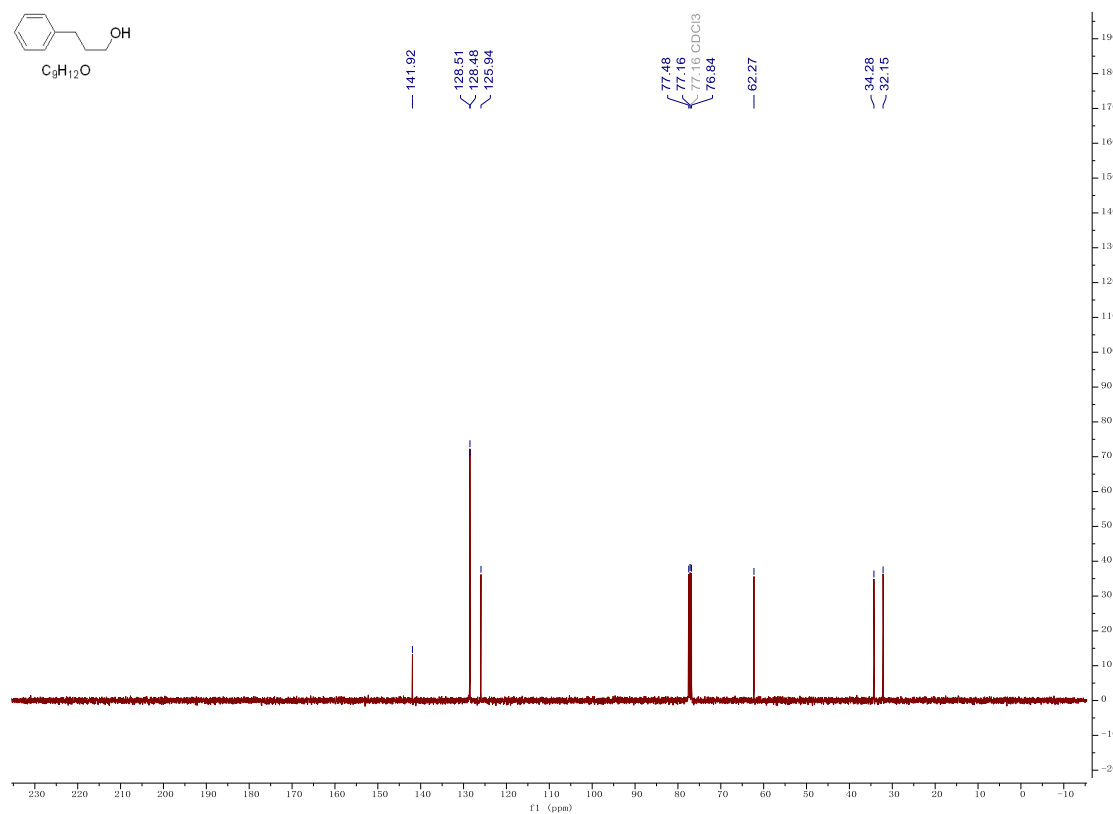
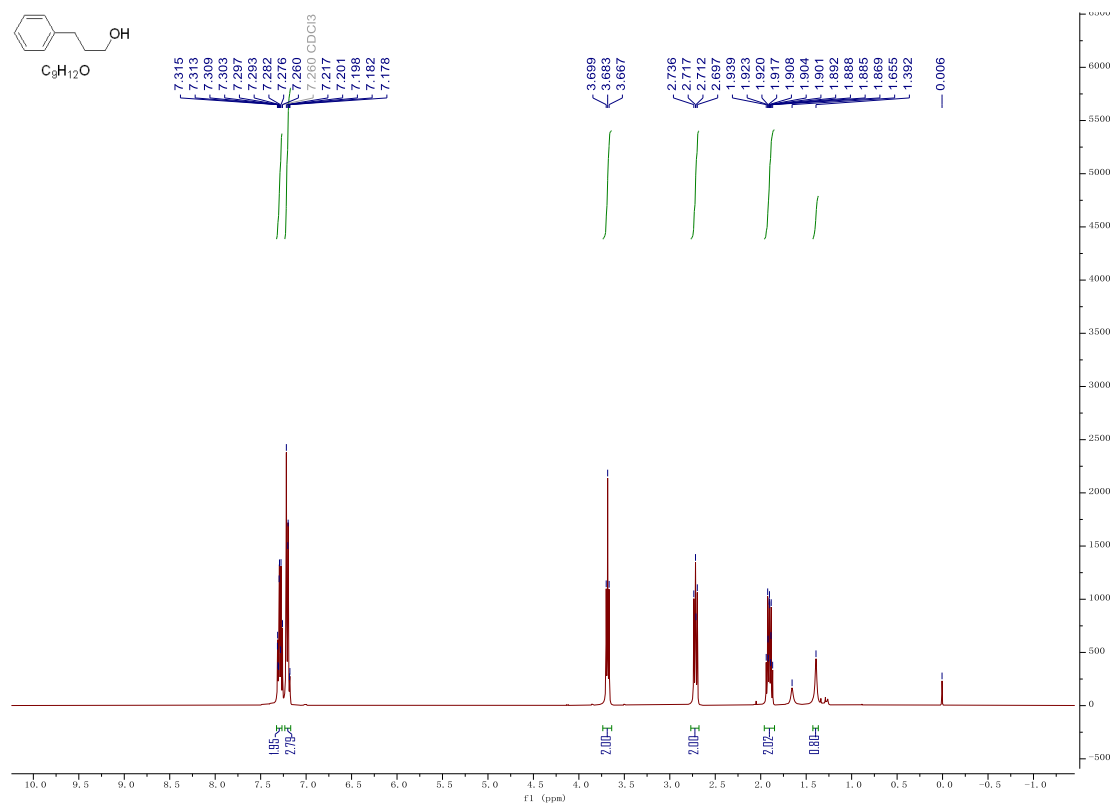
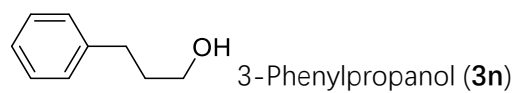
1-Naphthylmethanol (3j)

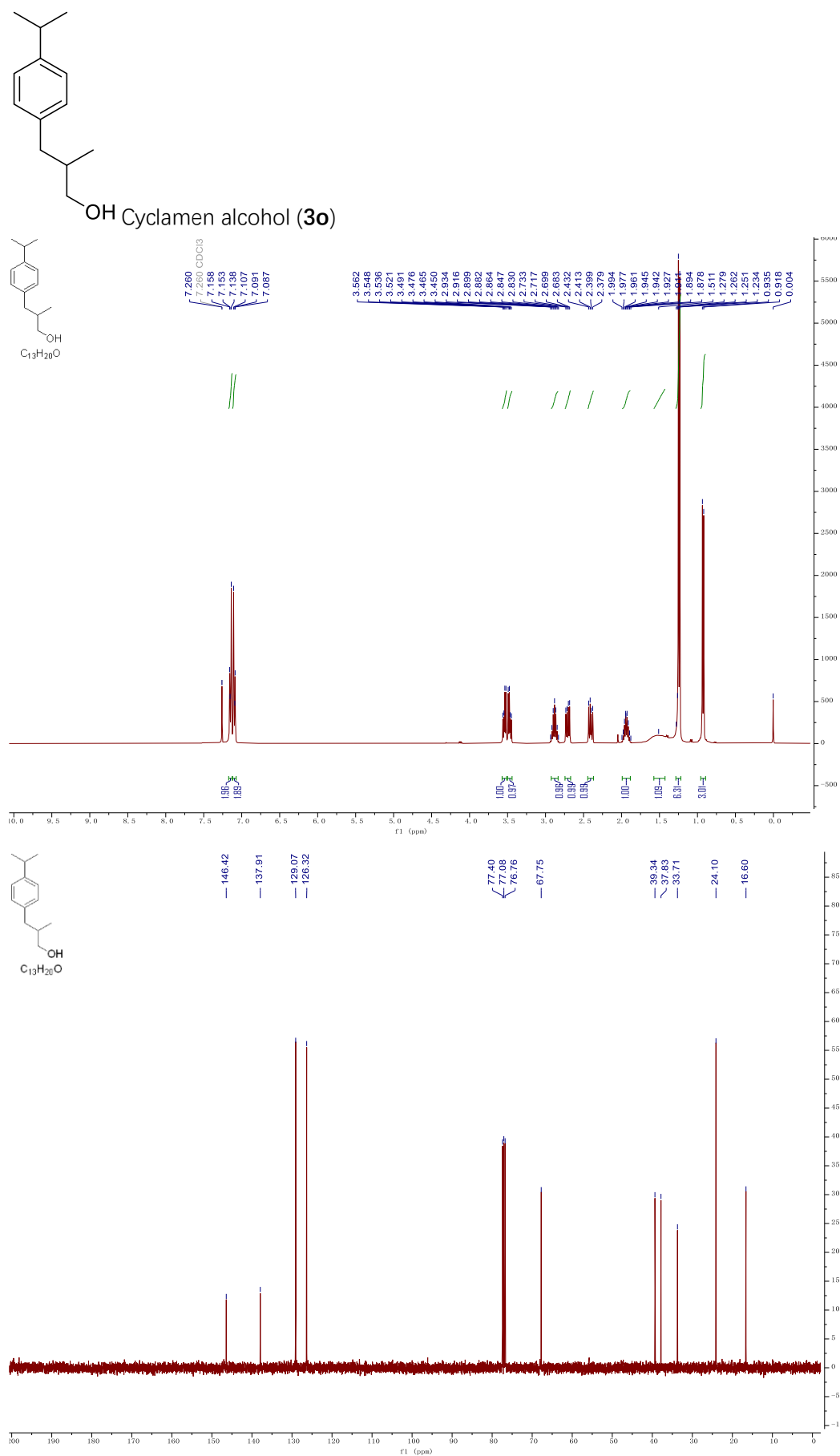


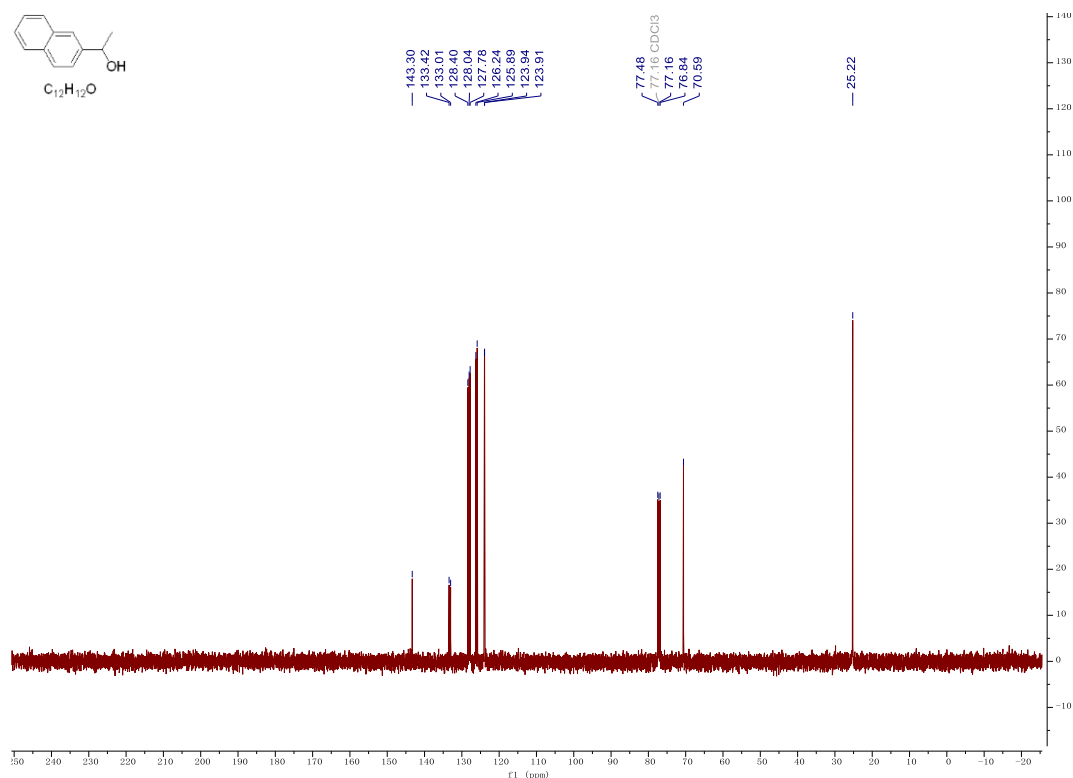
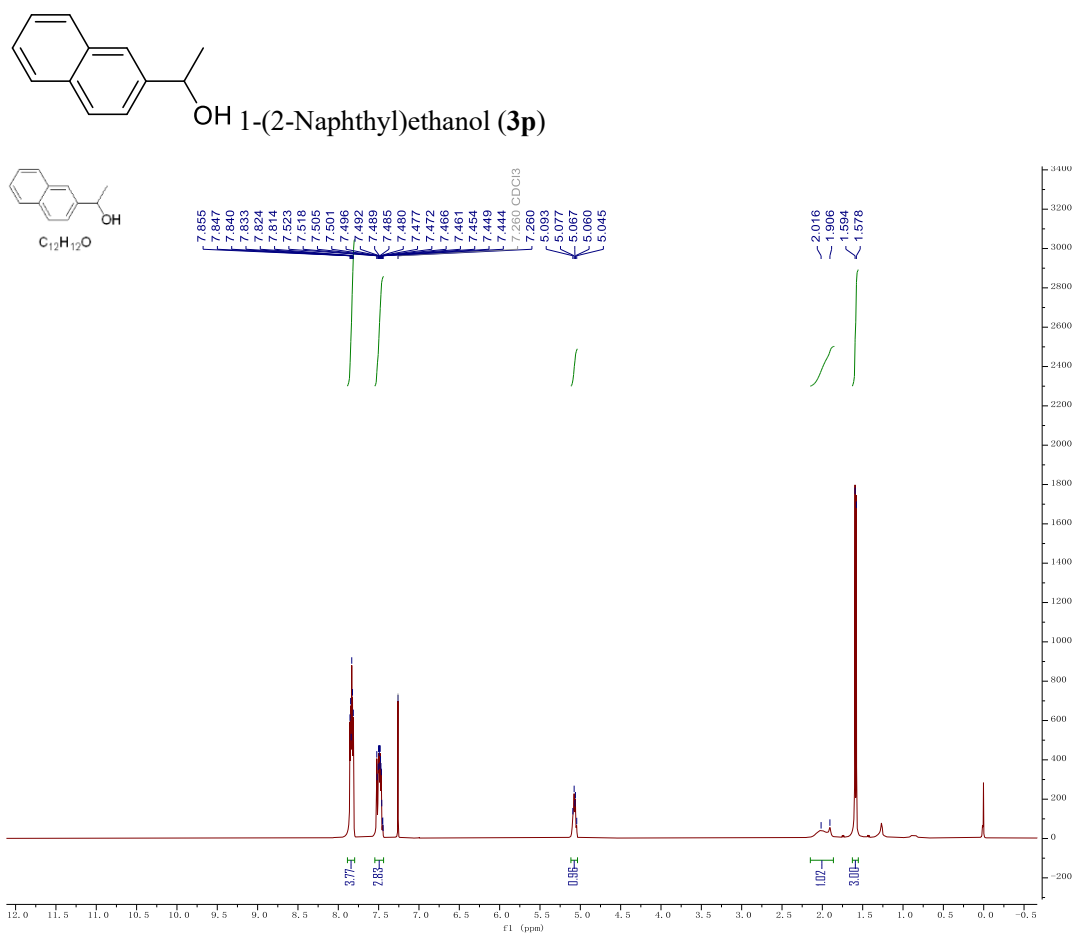


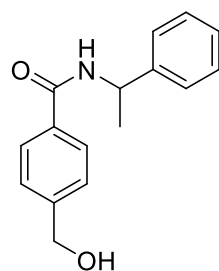
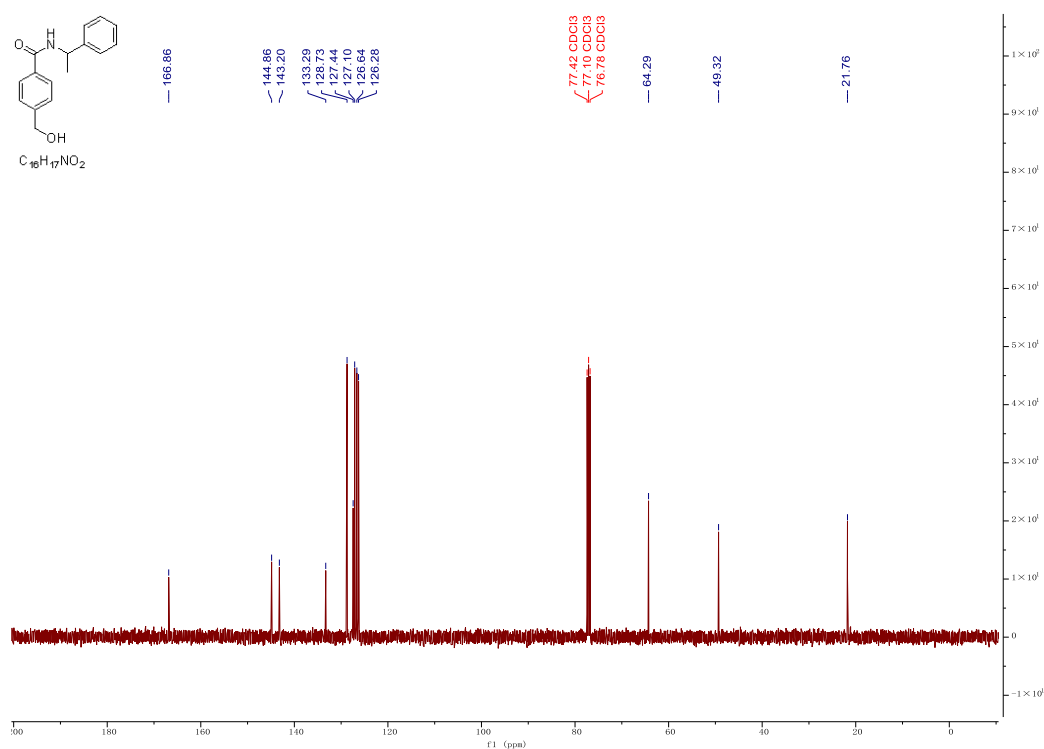
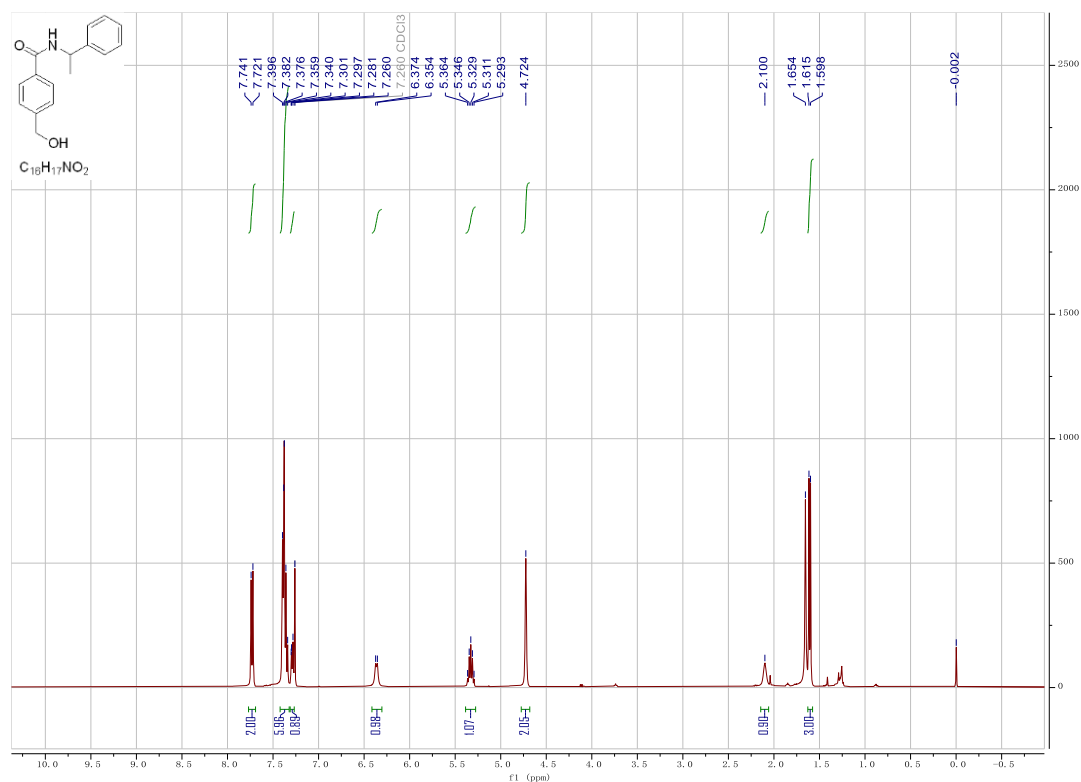










4-Hydroxymethyl-*N*-(1-phenylethyl)benzamide (3q)

6. References

- [1] J. C. Walton, M. M. Brahmi, L. Fensterbank, E. Lacôte, M. Malacria, Q. Chu, S.-H. Ueng, A. Solovyeu, D. P. Curran, *J. Am. Chem. Soc.* **2010**, *132*, 2350-2358.