

Supporting Information

Sc(OTf)₃-mediated 1,3-dipolar cycloaddition–ring cleavage–rearrangement: a highly stereoselective access to *Z*-β-enaminonitriles

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Experimental

General methods and materials. Proton nuclear magnetic resonance spectra (^1H NMR) and carbon nuclear magnetic resonance spectra (^{13}C NMR) were recorded at 500 MHz and 125 MHz, respectively, using CDCl_3 as reference standard (δ 7.26 ppm) for ^1H NMR and (δ 77.04 ppm) for ^{13}C NMR. HRMS (ion trap) were recorded using APCI or ESI. Melting points are uncorrected. Column chromatography was performed on silica gel (300-400 mesh). Unless otherwise noted, all reagents were obtained commercially and used without further purification.

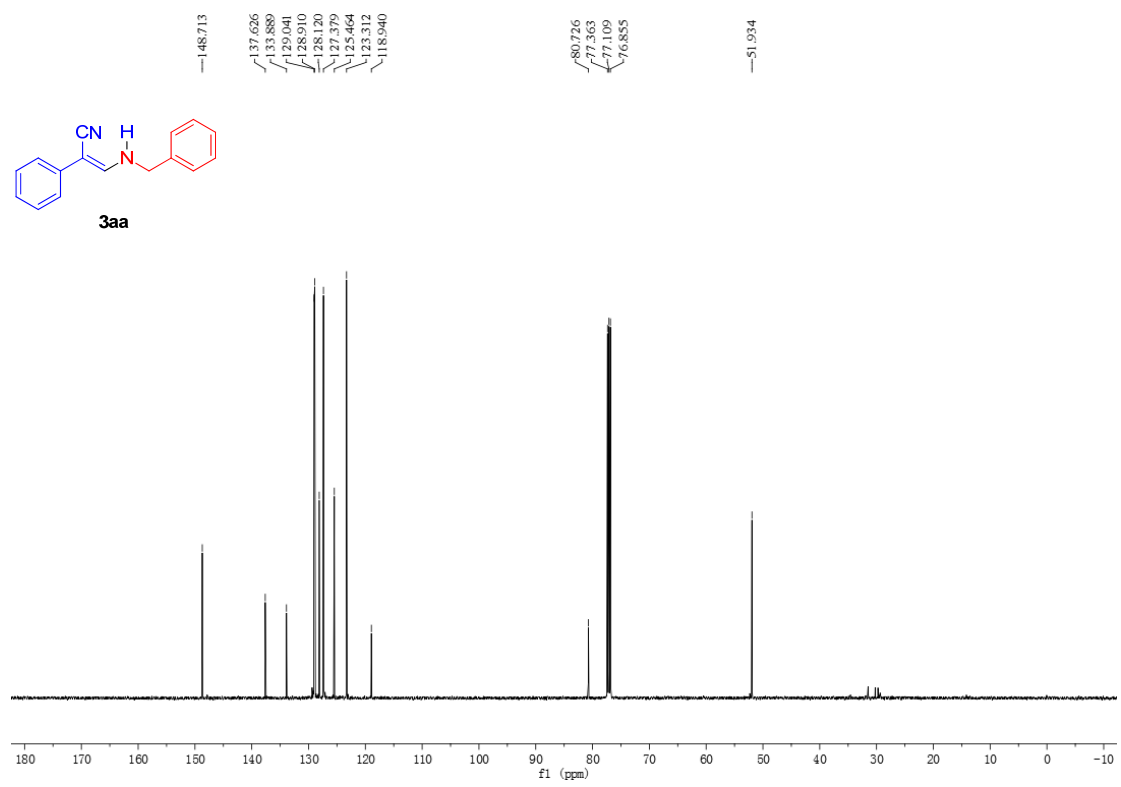
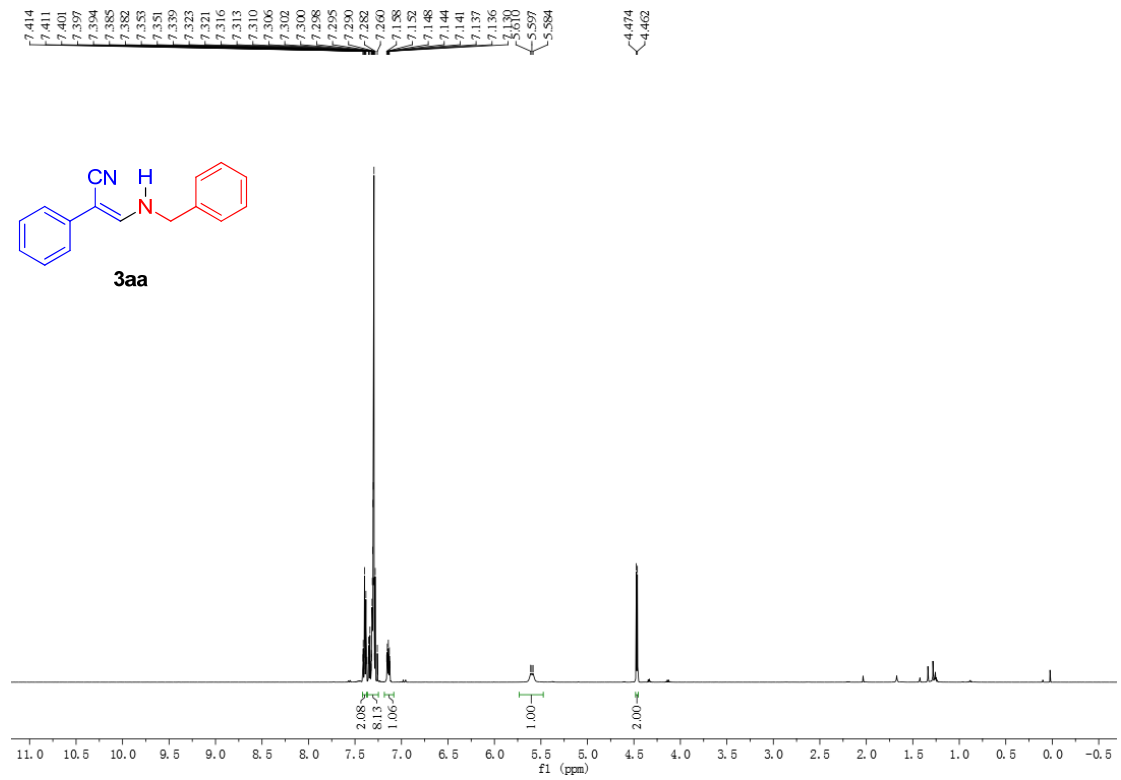
The α , β -unsaturated nitriles **1b**¹, **1c**¹, **1d**¹, **1f**¹, **1h**¹, **1i**¹, **1j**¹ and the azides **2b**², **2c**², **2d**³, **2e**³, **2f**⁴, **2g**⁴, **2h**², **2i**⁵, **2j**², **2k**³, **2l**⁵, **2m**⁶, **2n**², **2o**³ were synthesized as previously reported in the literature.

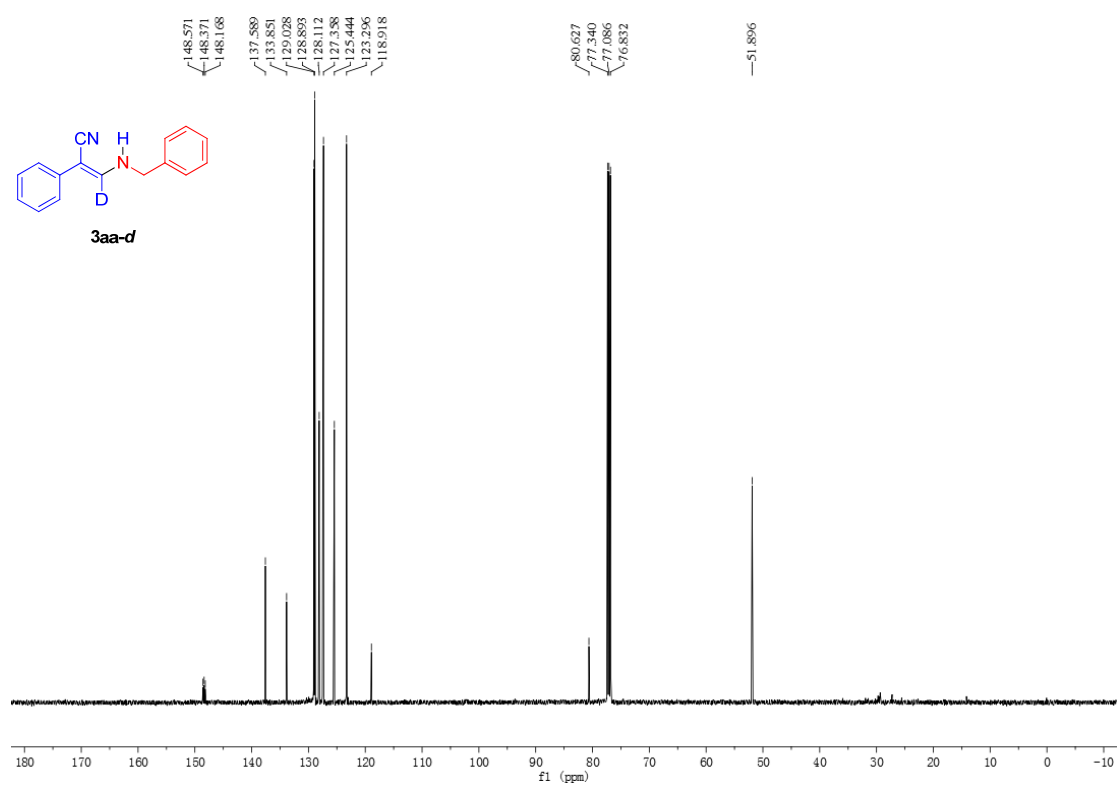
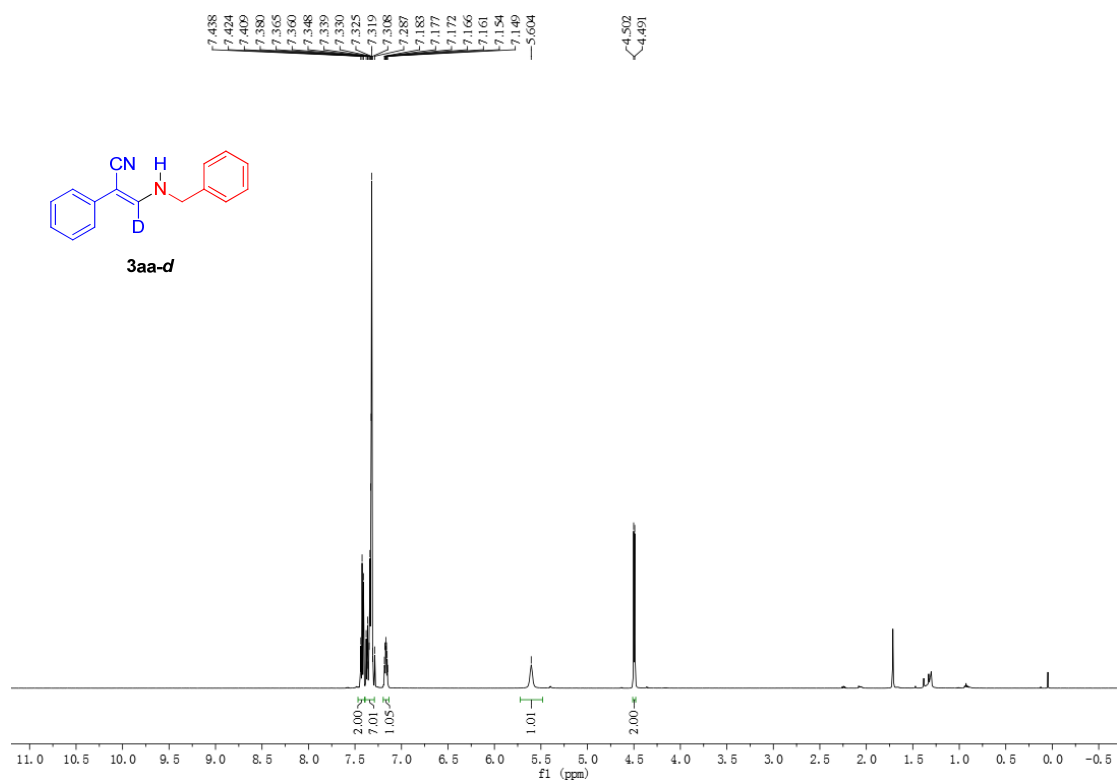
General experimental procedure for synthesis of *Z*- β -enaminonitriles **3.** A mixture of α , β -unsaturated nitriles (1.0 equiv, 1 mmol), azide (1.2 equiv, 1.2 mmol), $\text{Sc}(\text{OTf})_3$ (0.05 equiv, 0.05 mmol), and 2 mL of toluene was refluxed at 110 °C for 12 h. The progress of the reaction was monitored by thin-layer chromatography. The mixture was then cooled and evaporated under reduced pressure. The target product **3** was purified by column chromatography on silica gel using a mixture of ethyl acetate and petroleum ether.

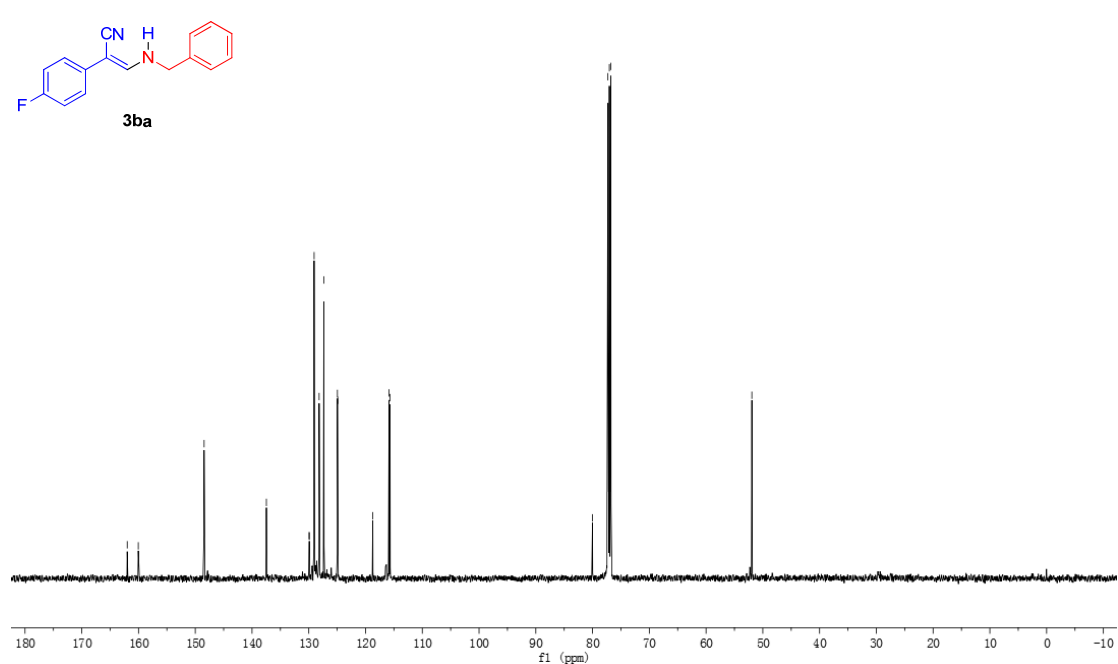
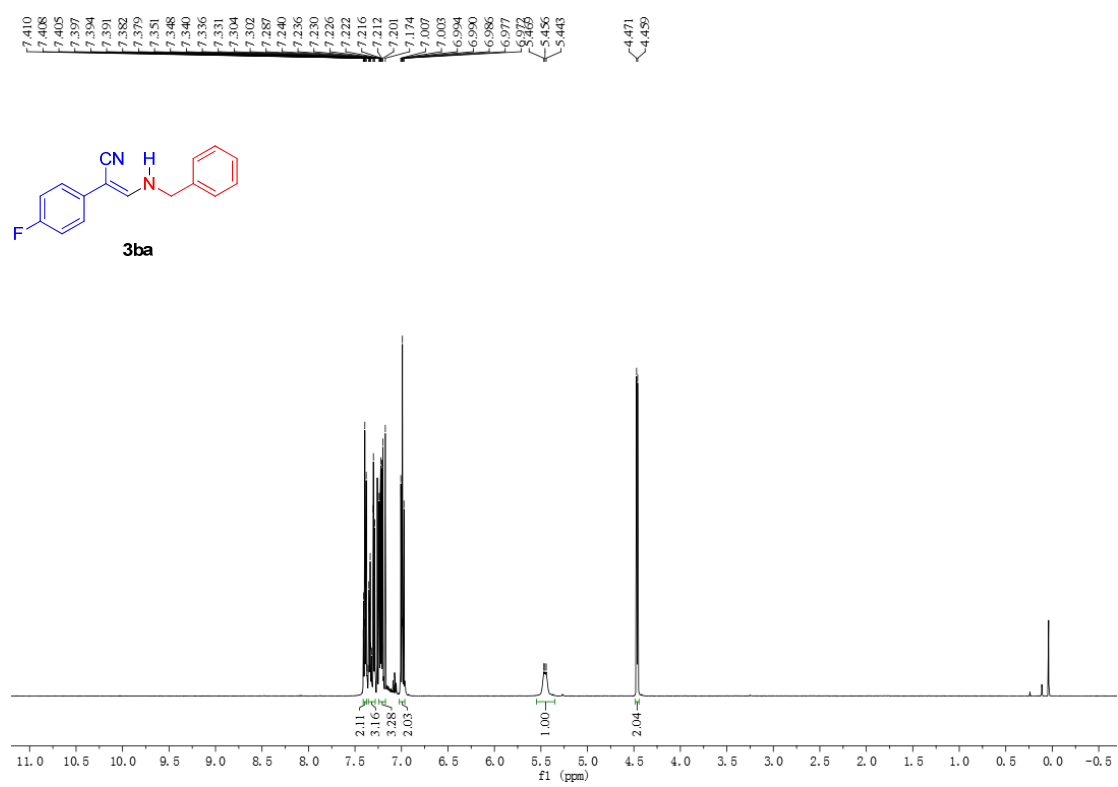
[CAUTION: Sufficient care has to be exercised while handling organic azides because of their explosive nature.]

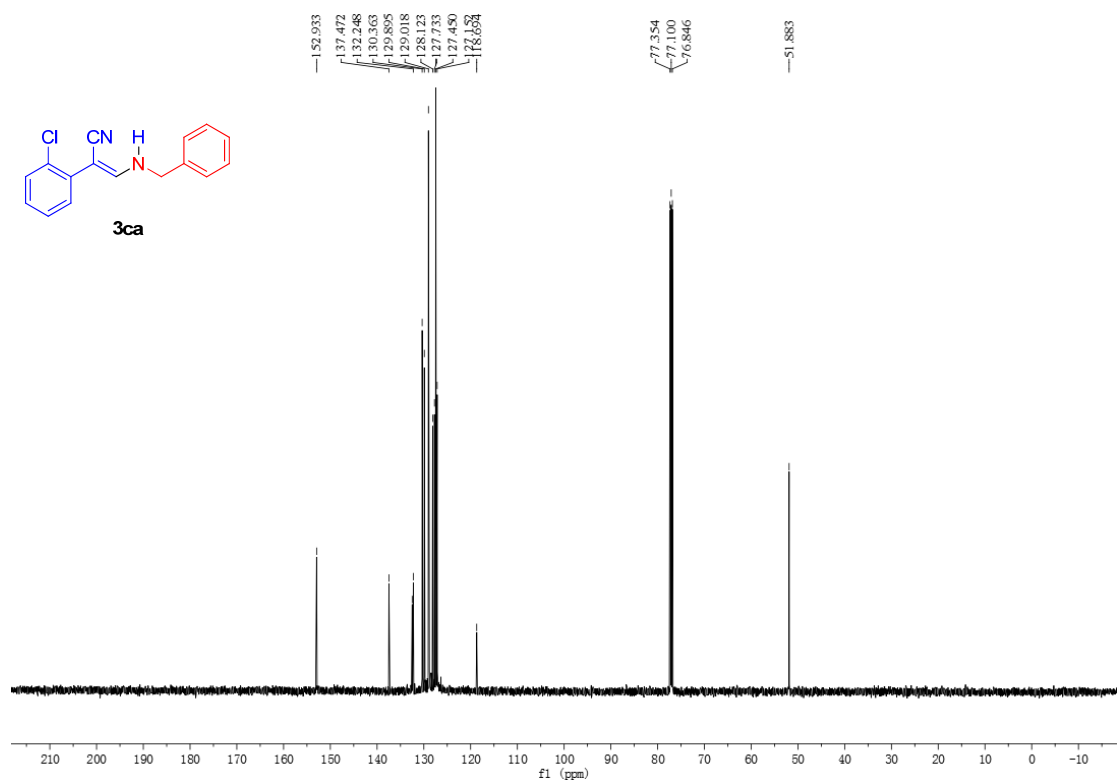
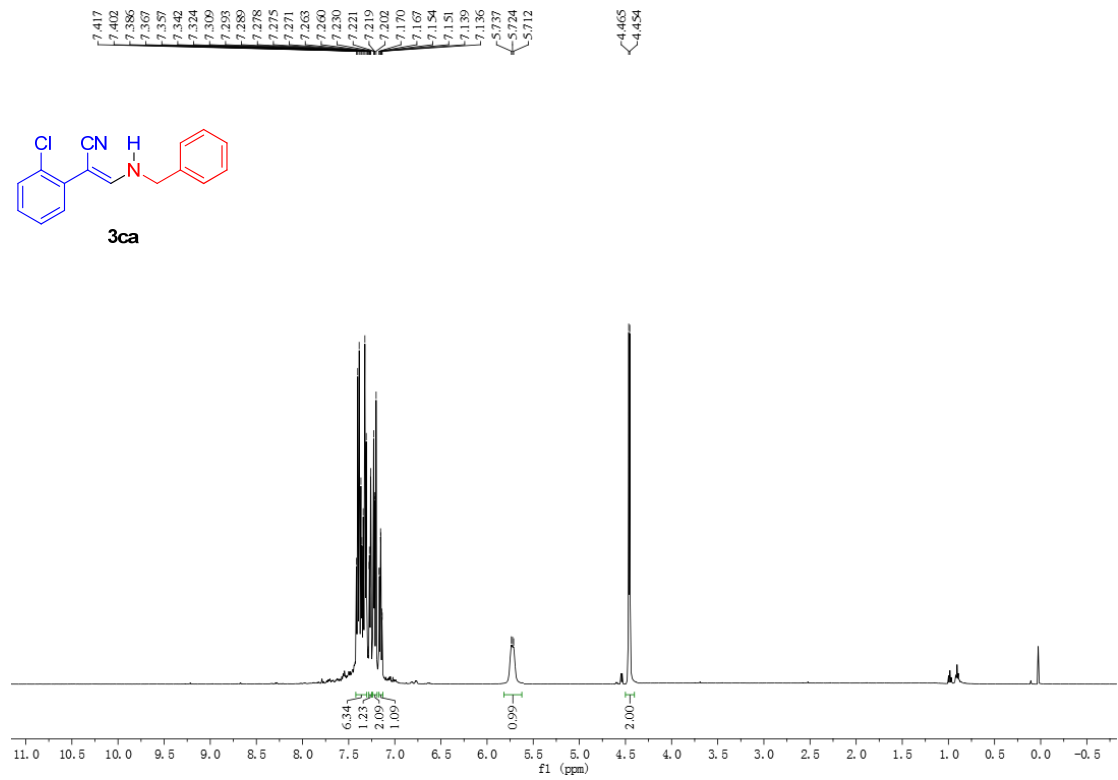
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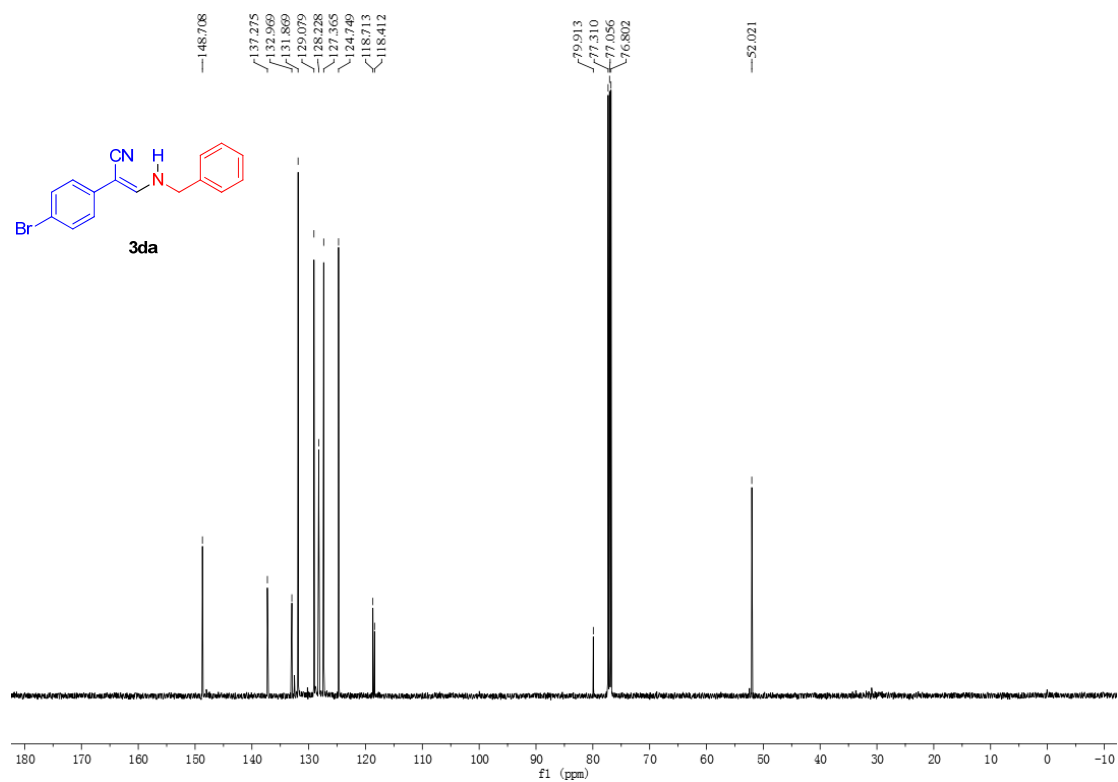
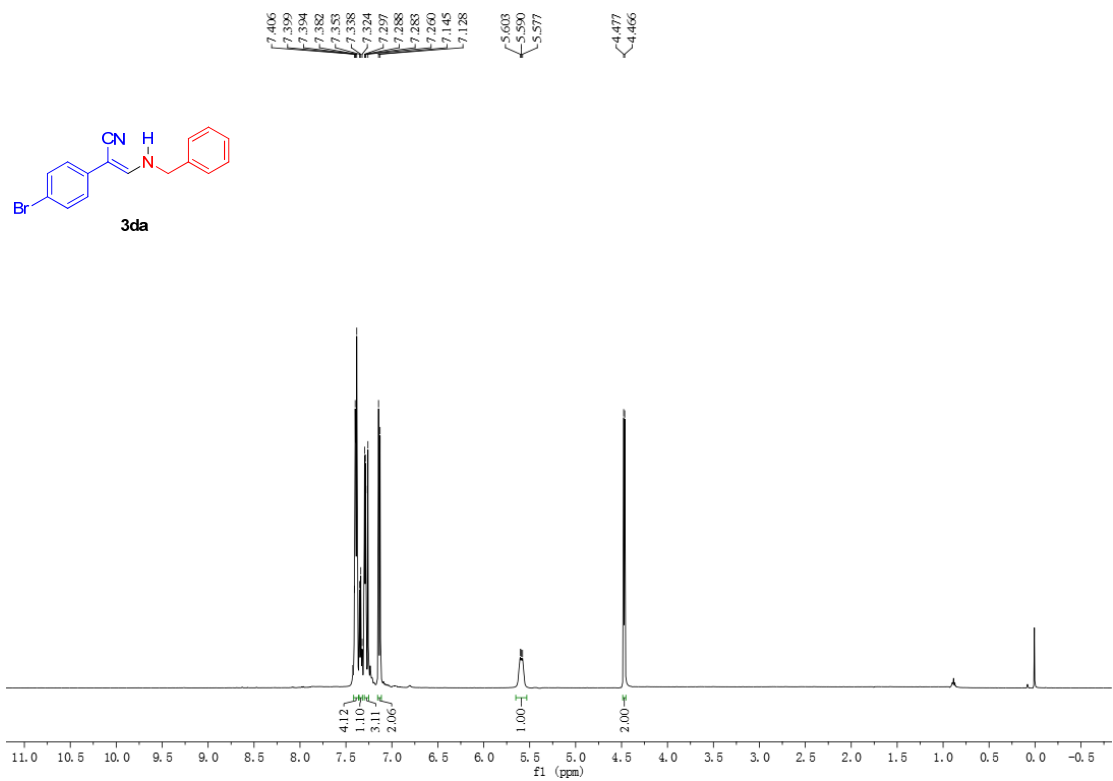
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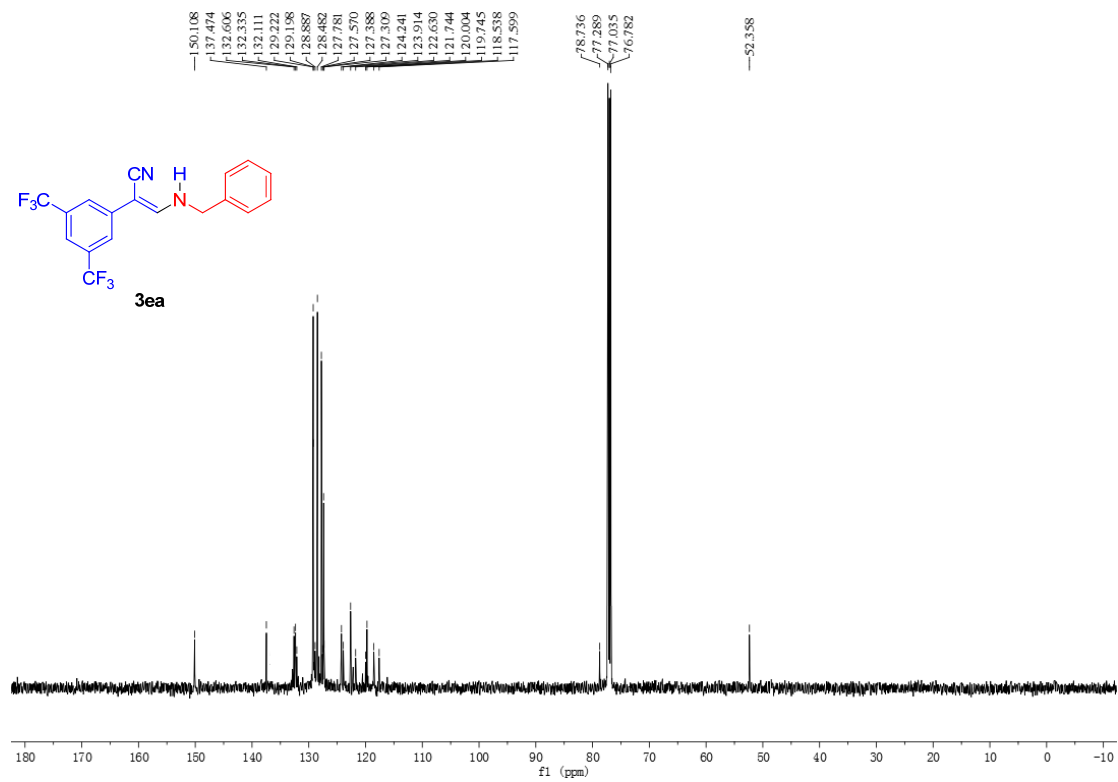
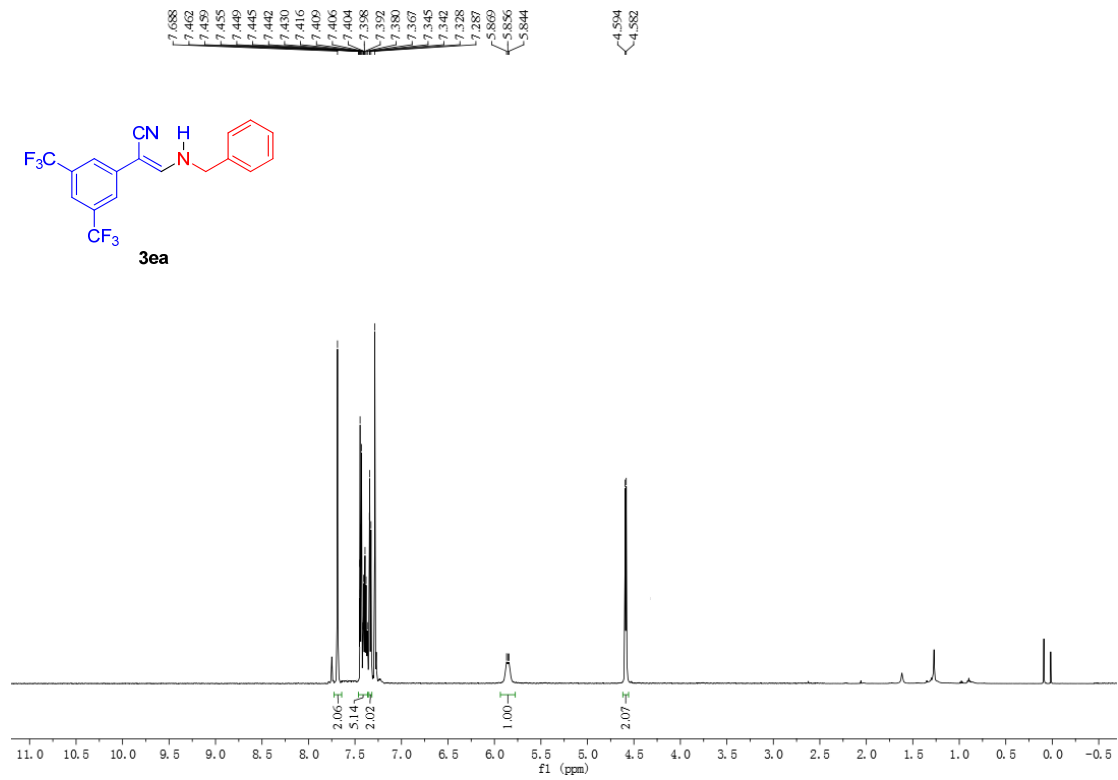


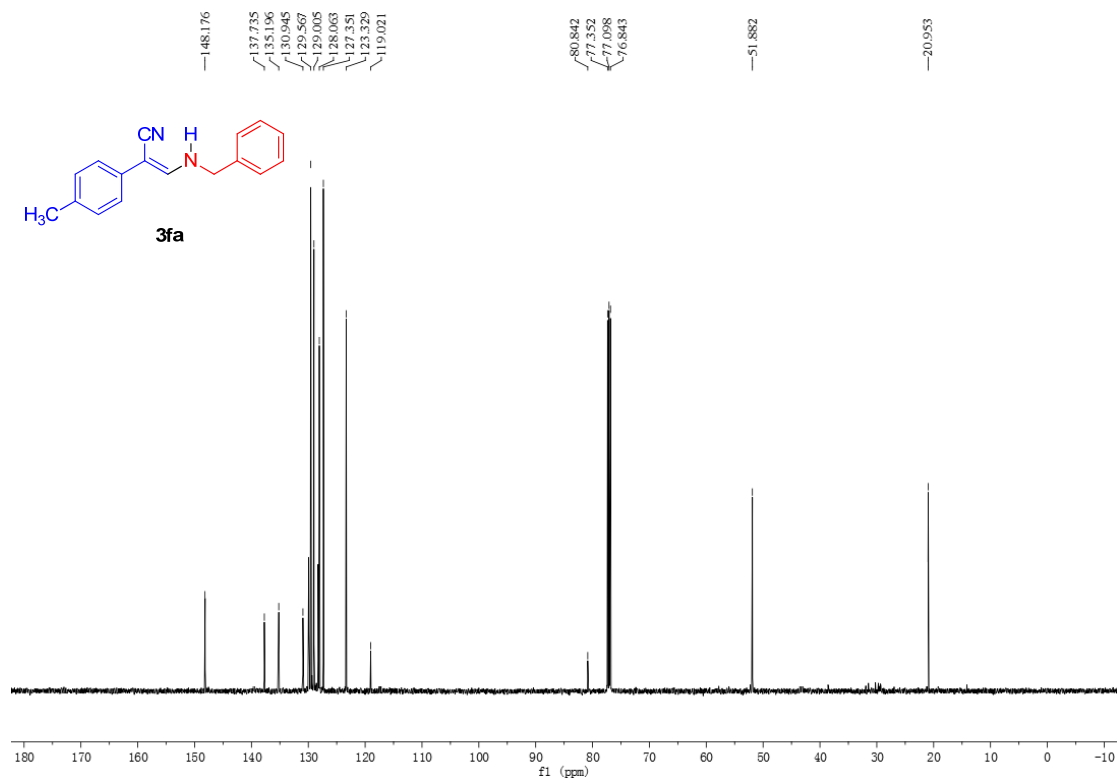
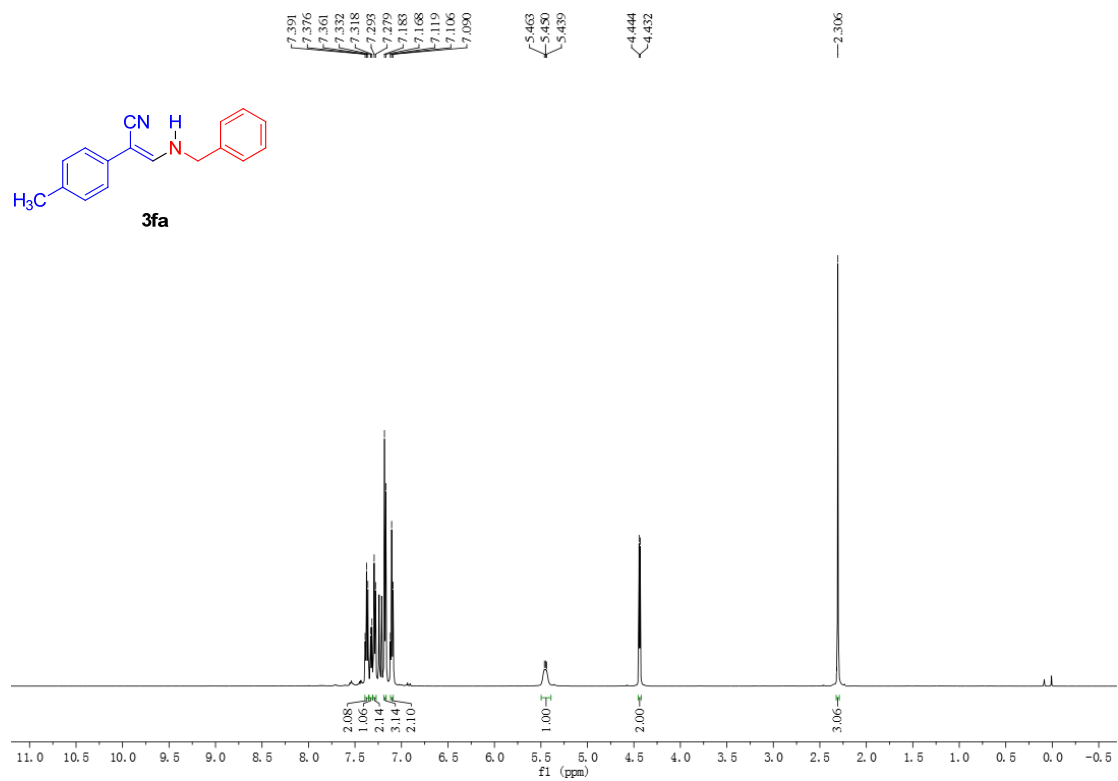


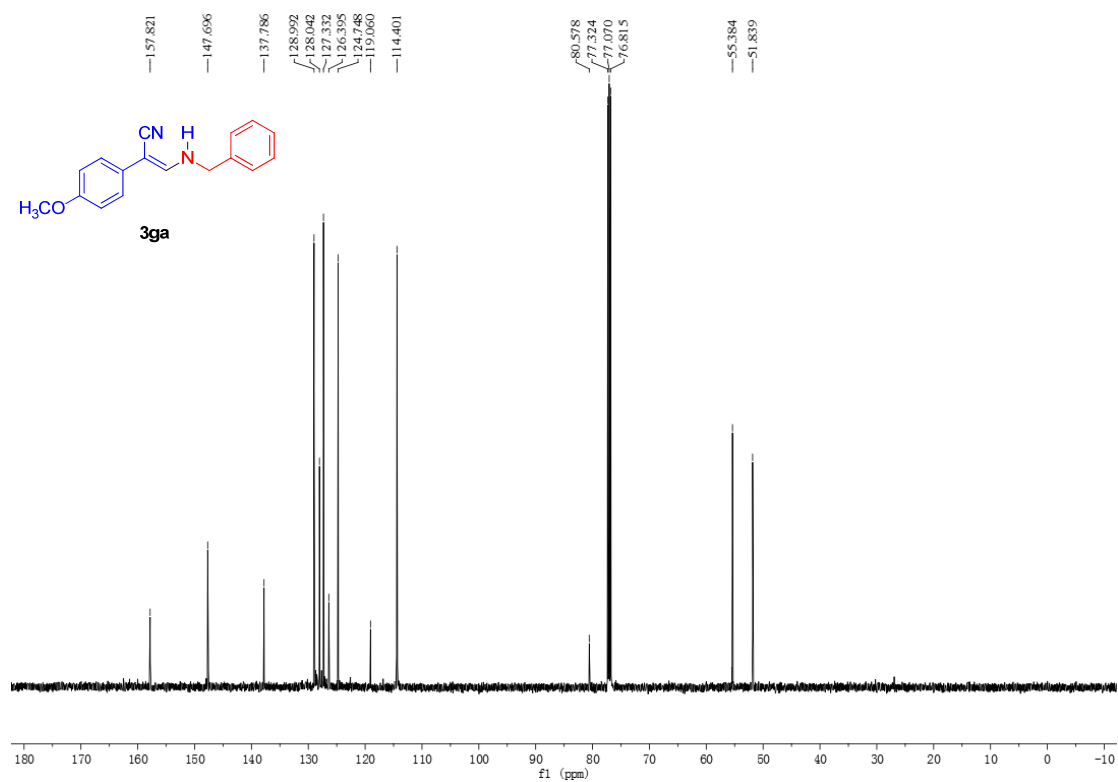
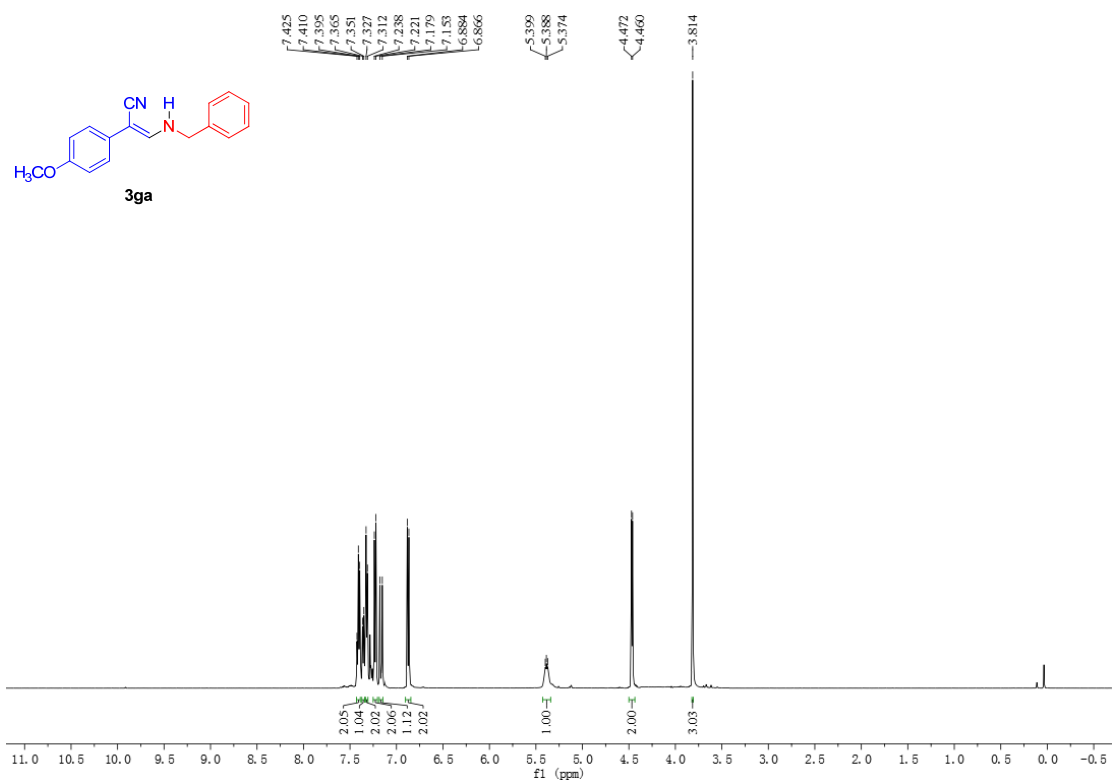


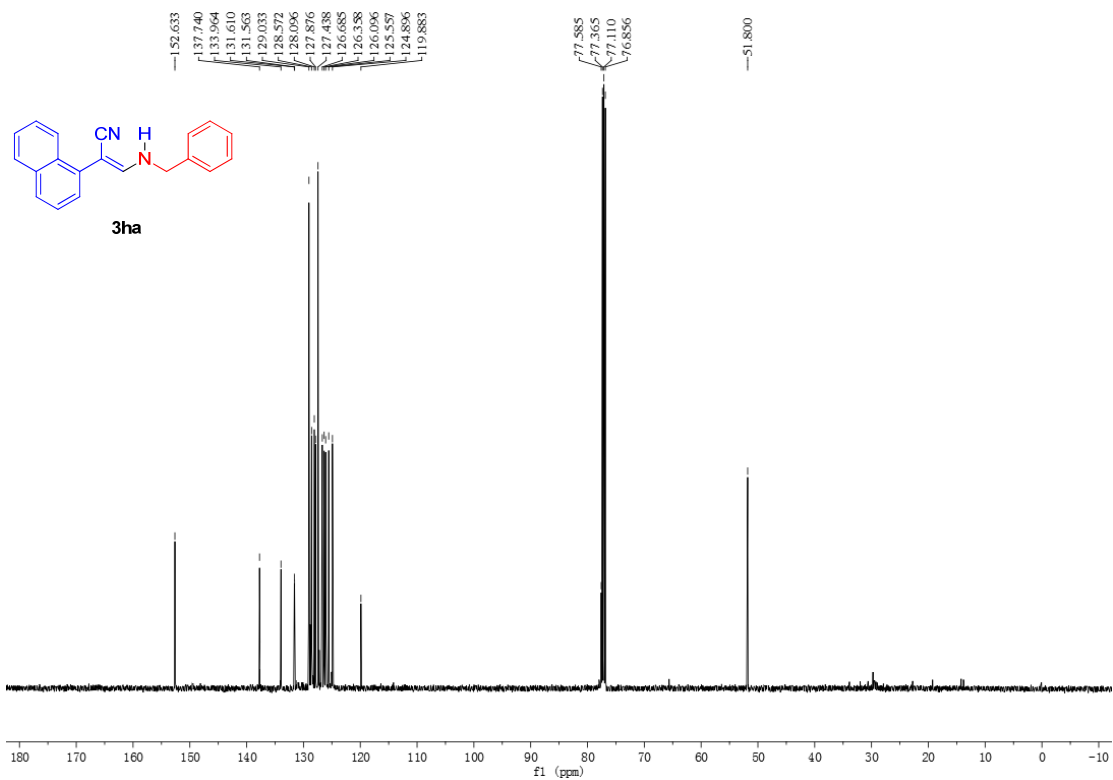
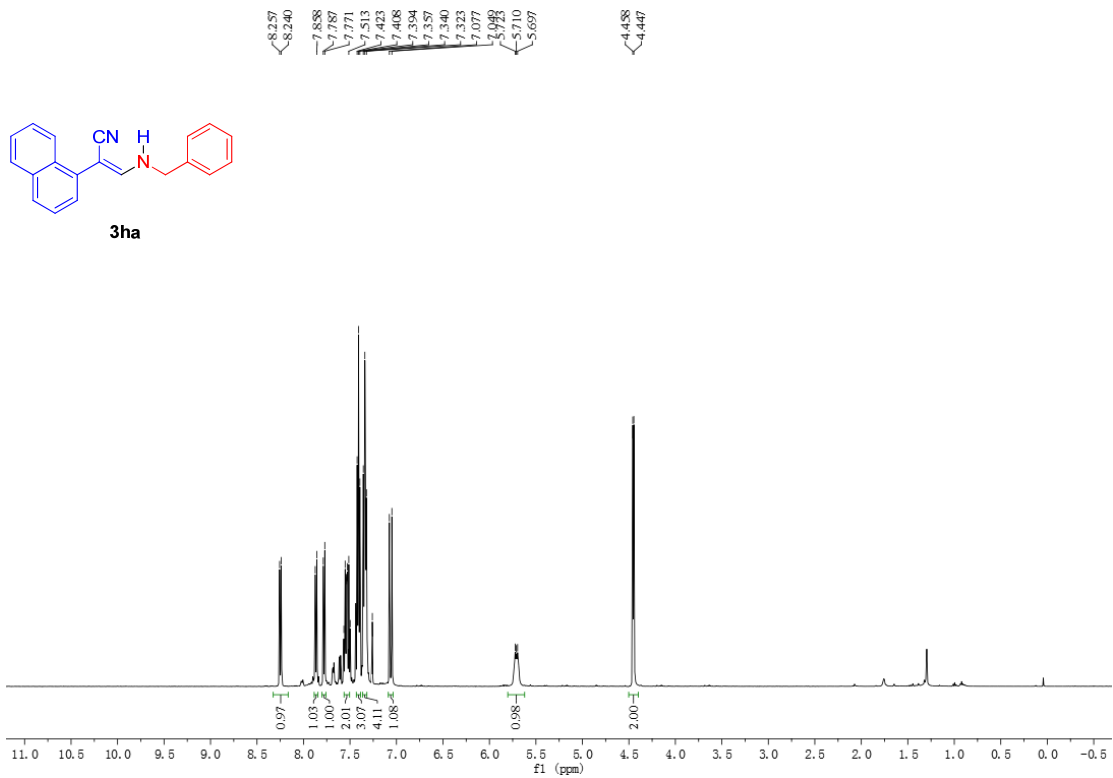


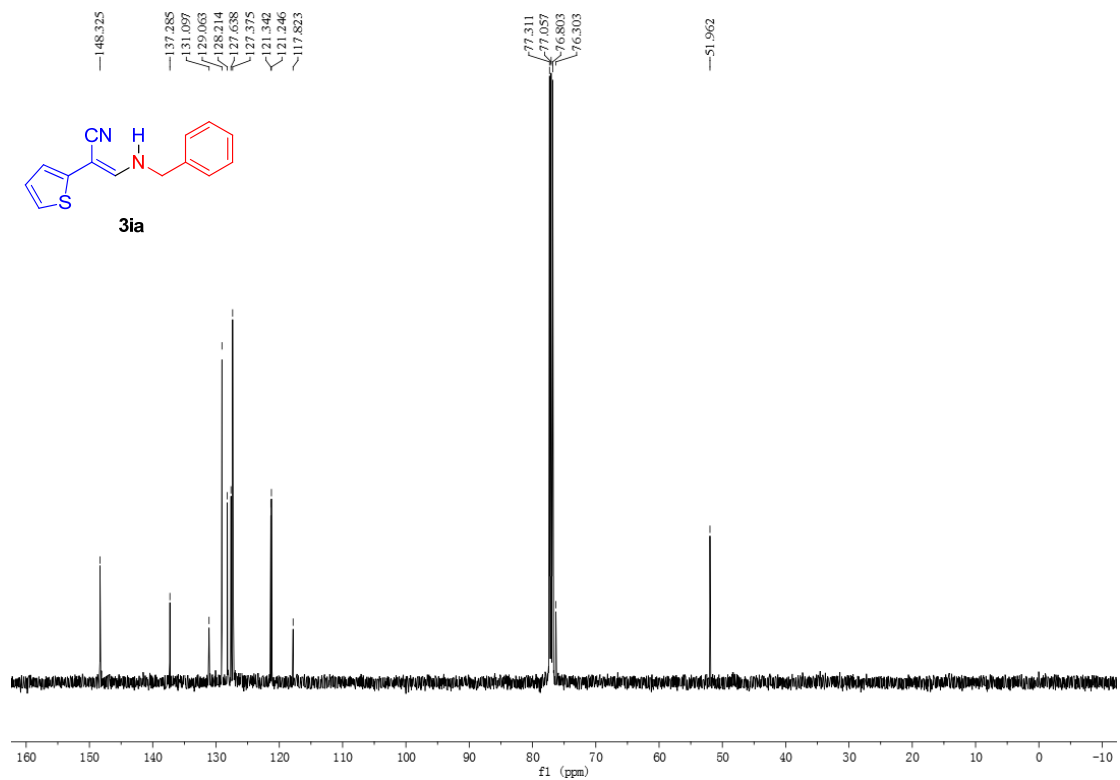
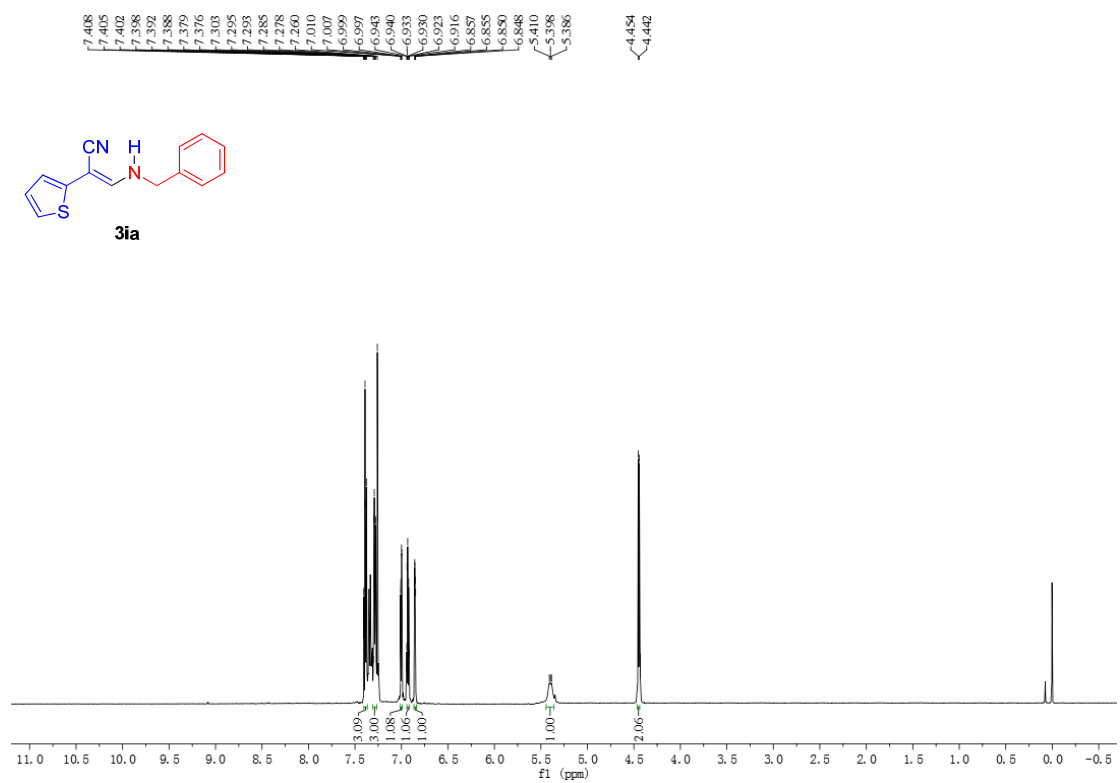


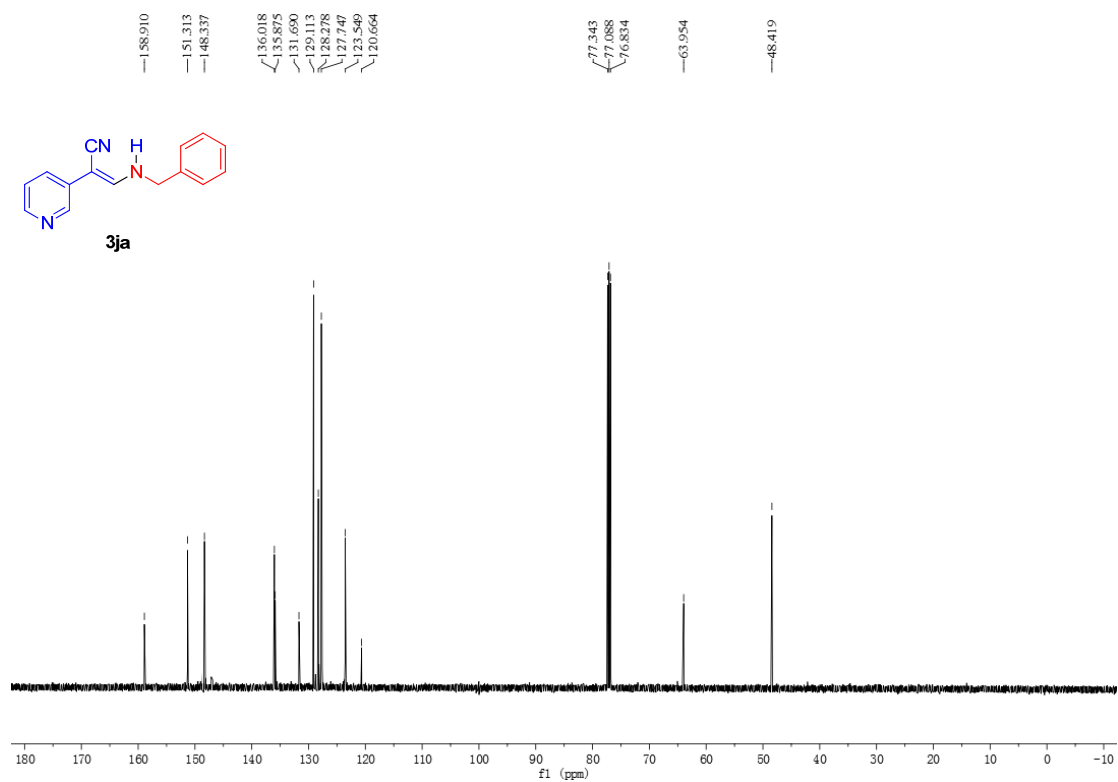
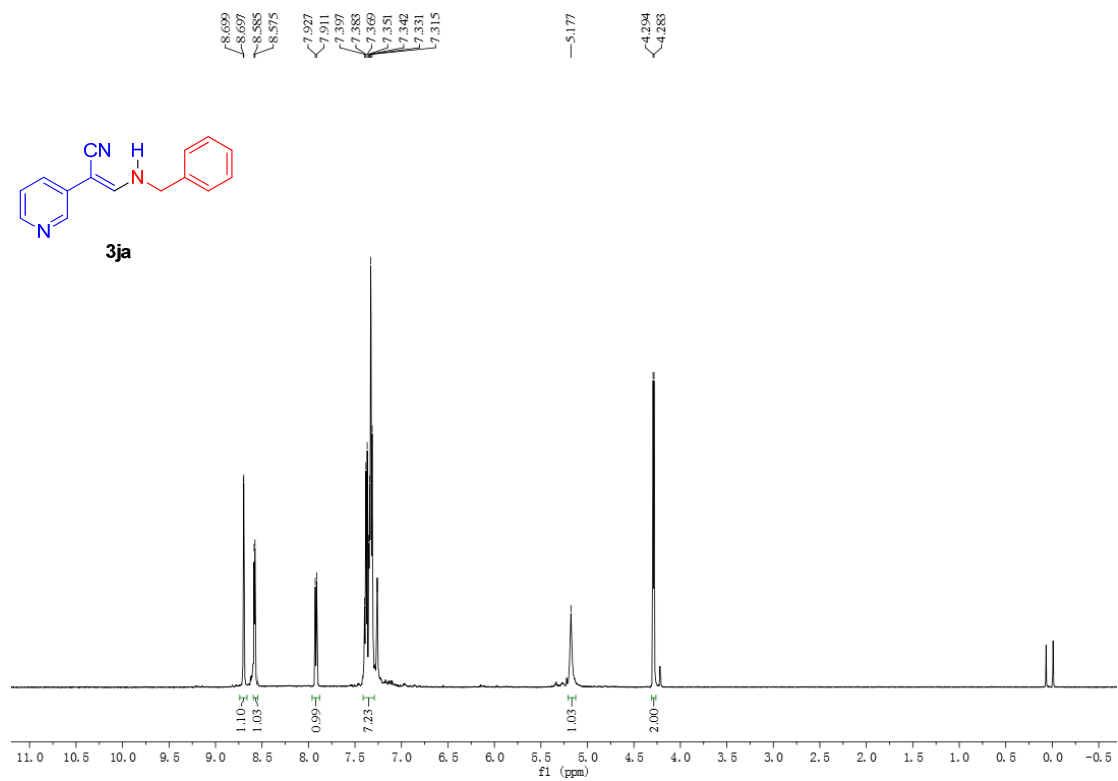


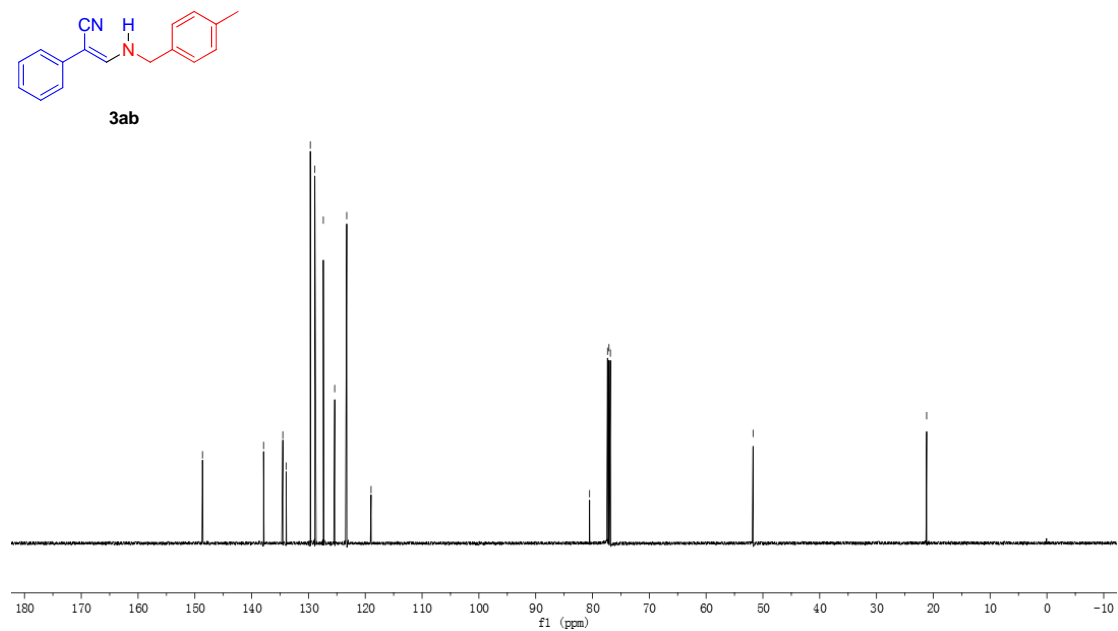
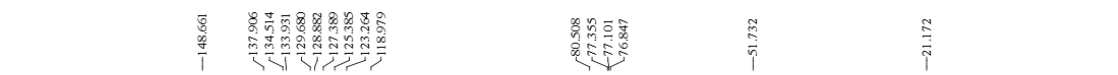
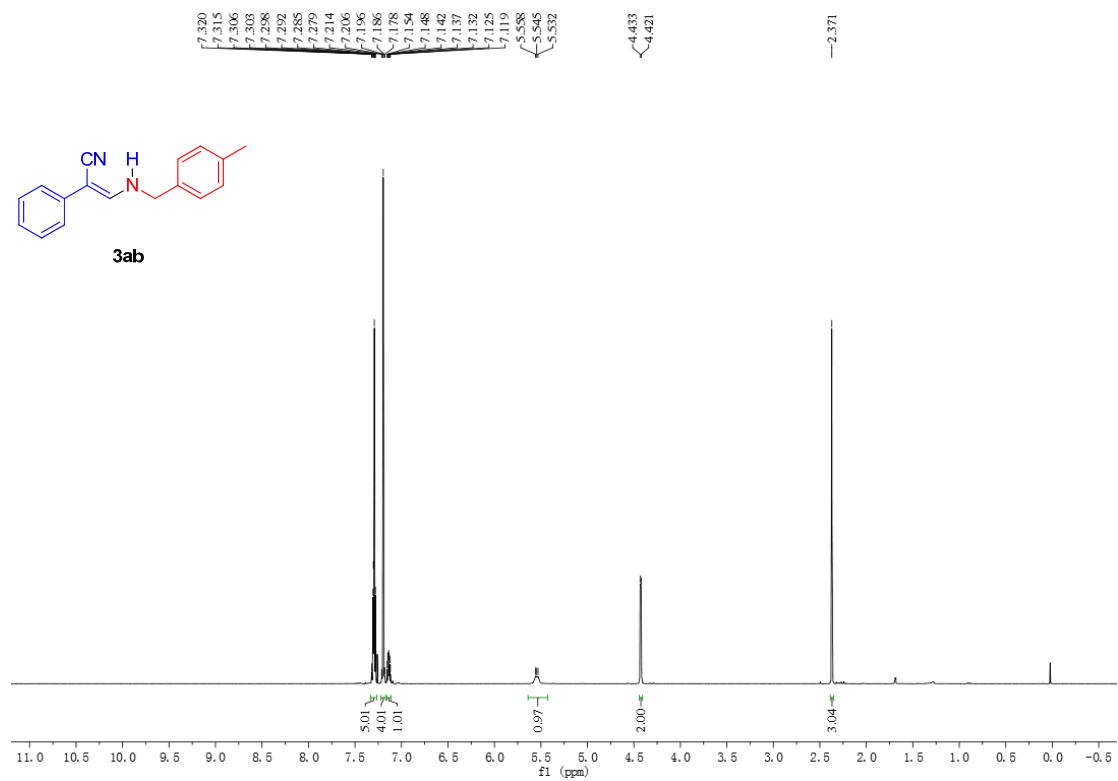


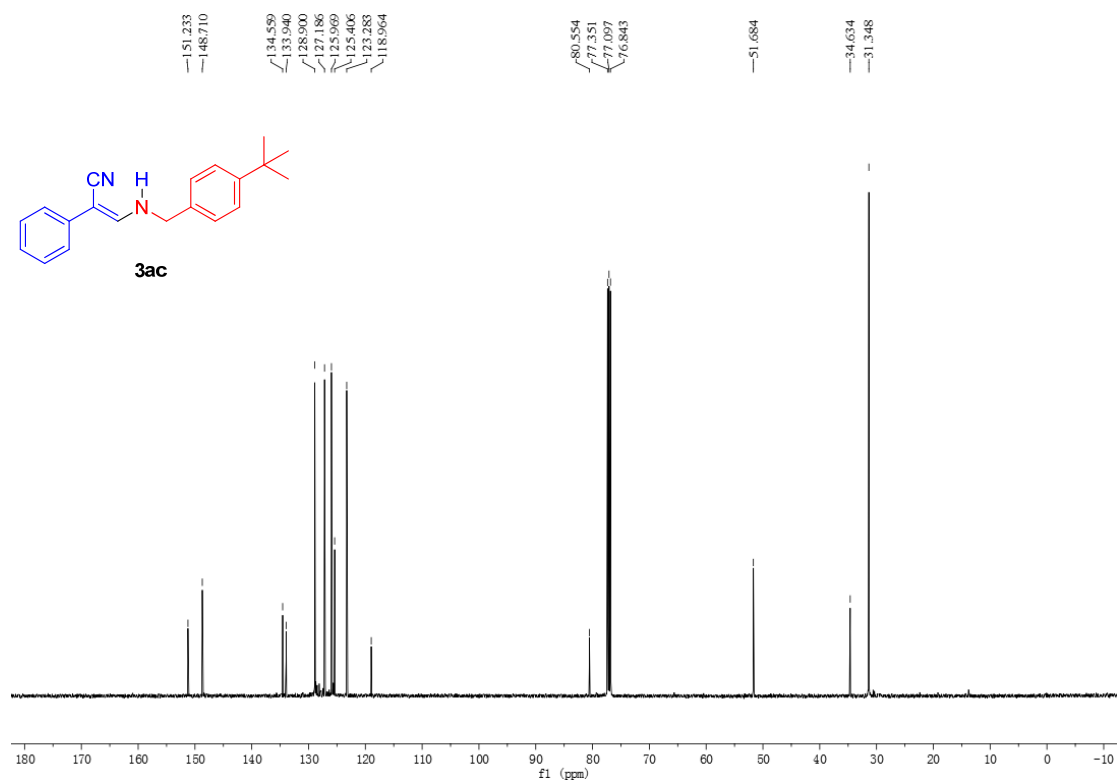
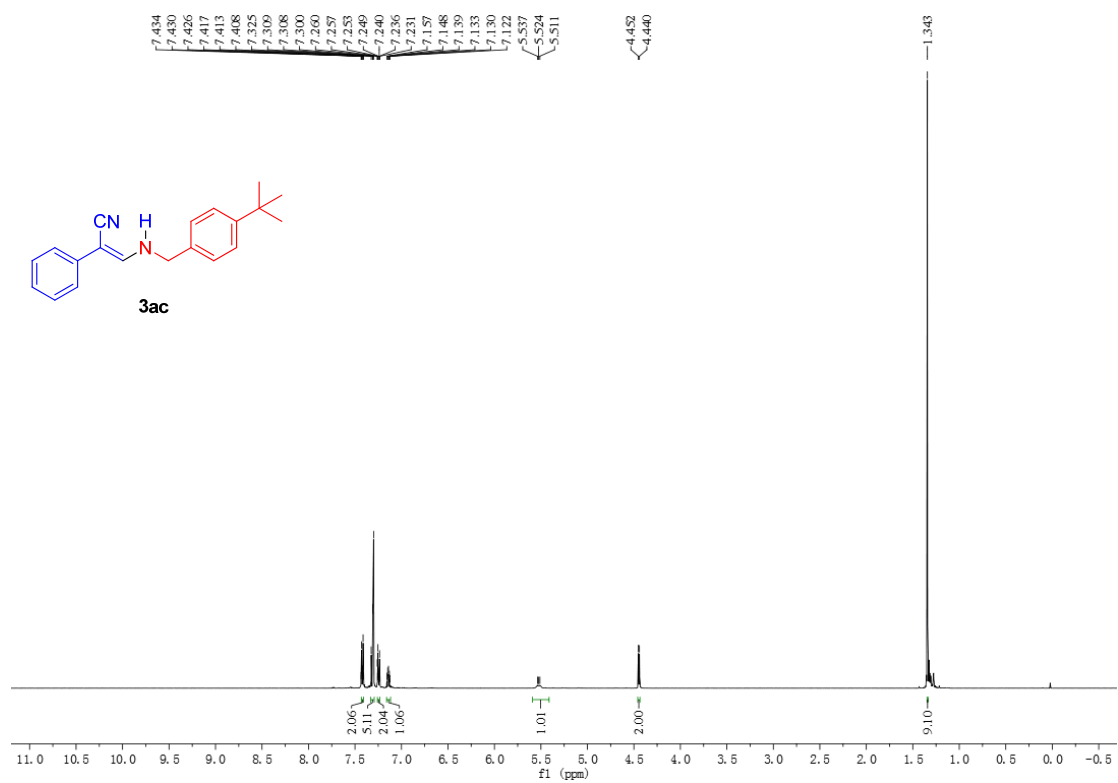


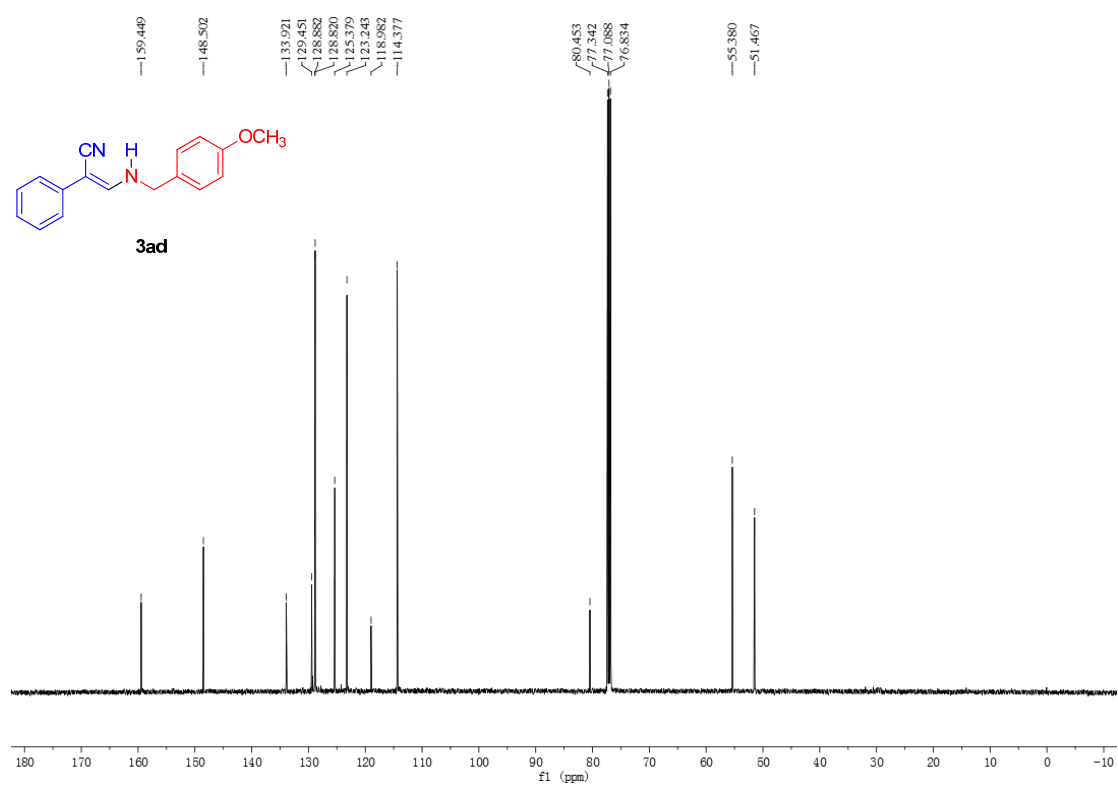
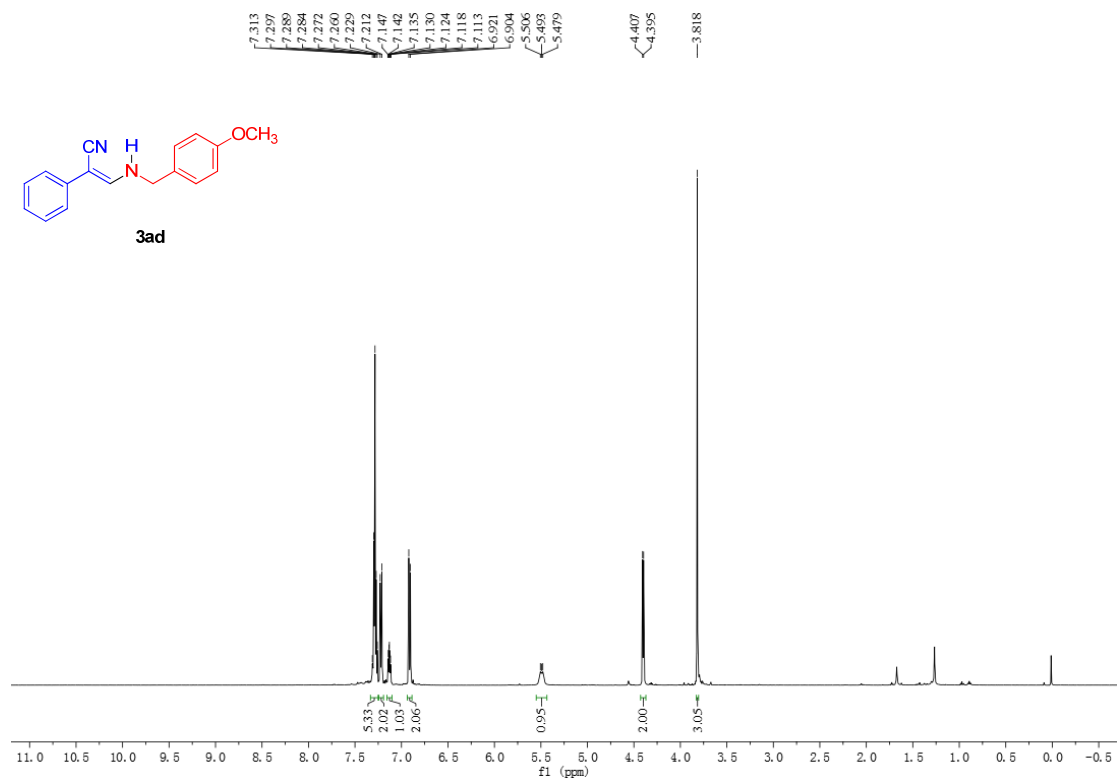


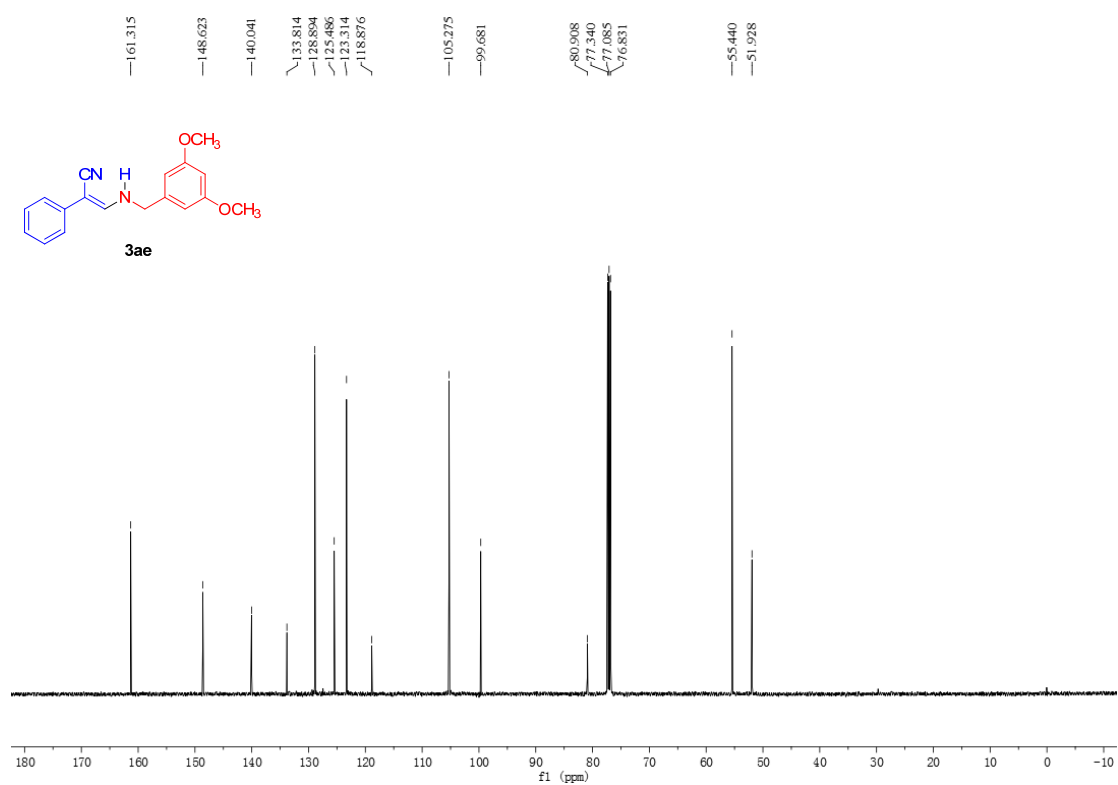
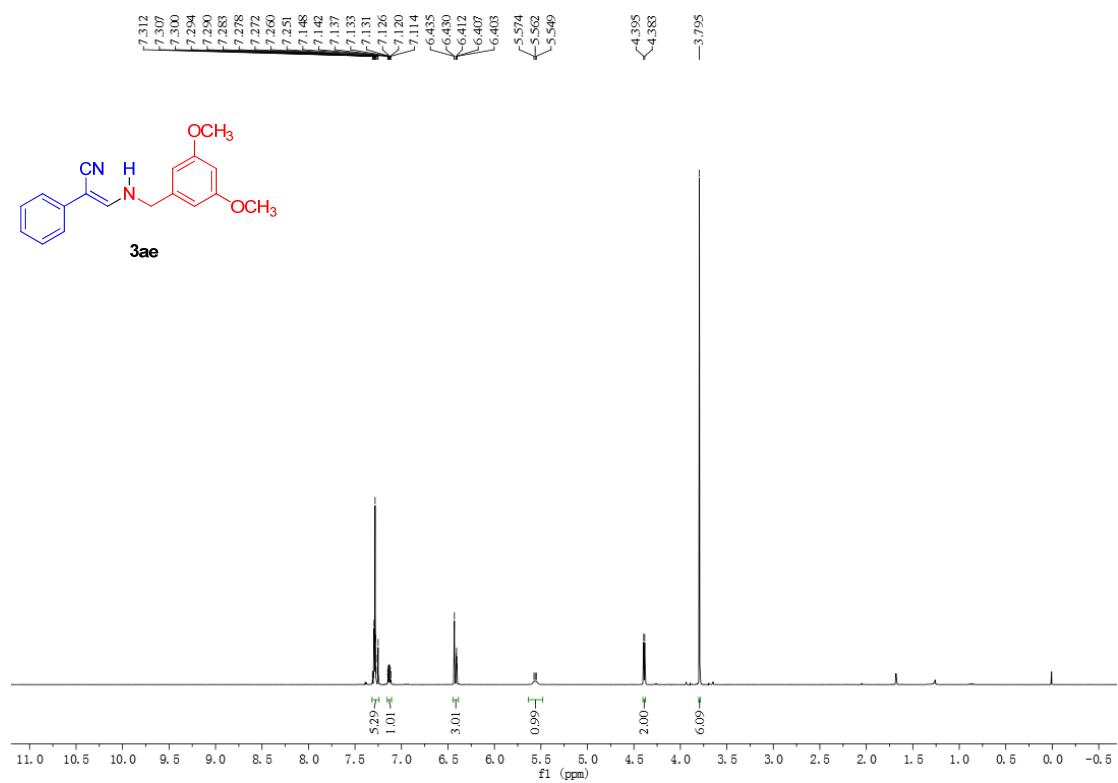


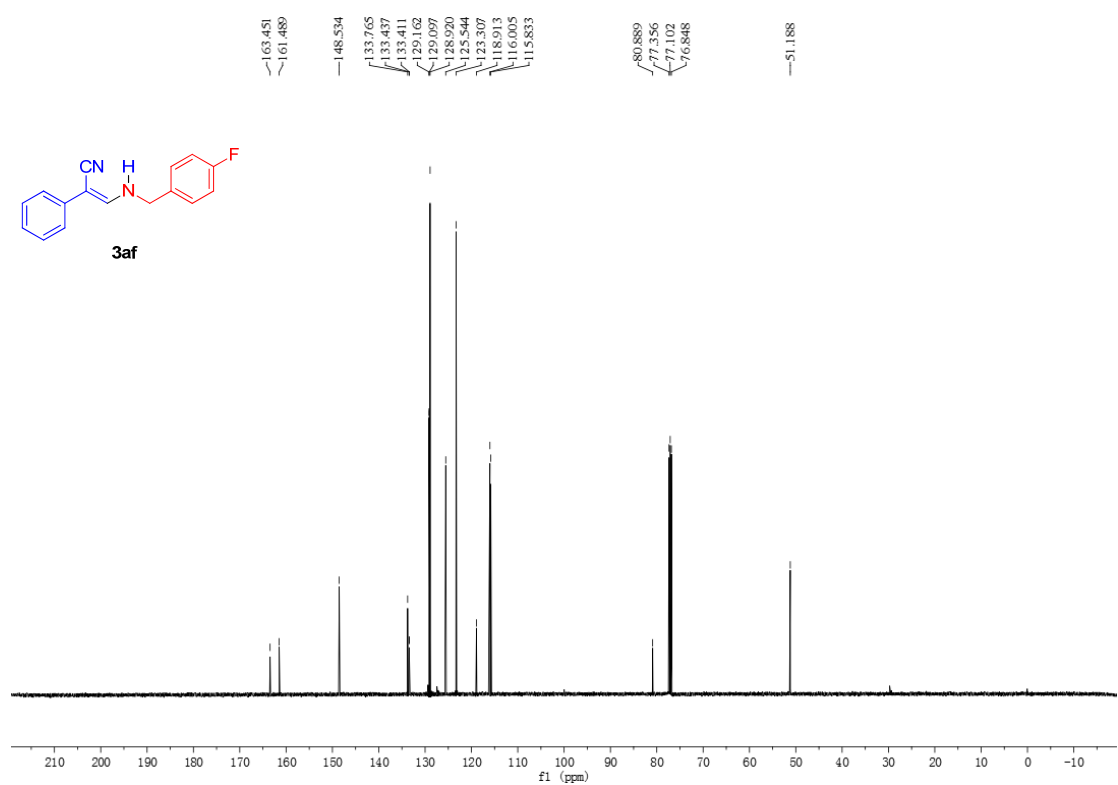
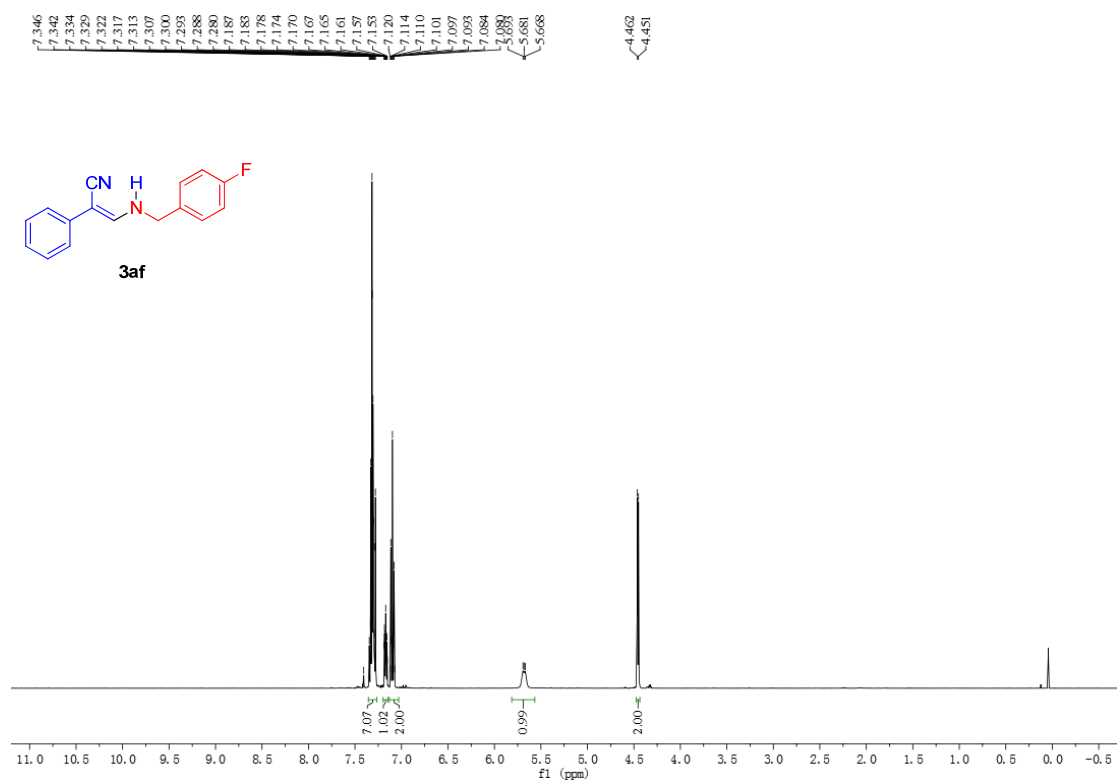


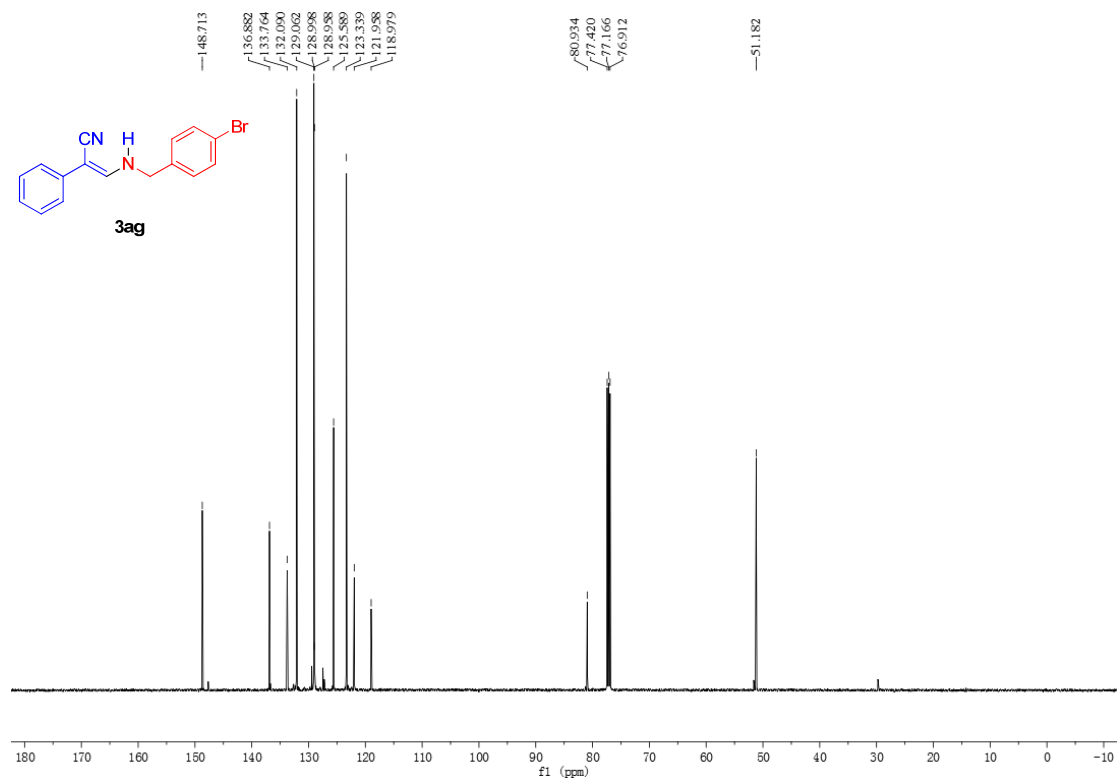
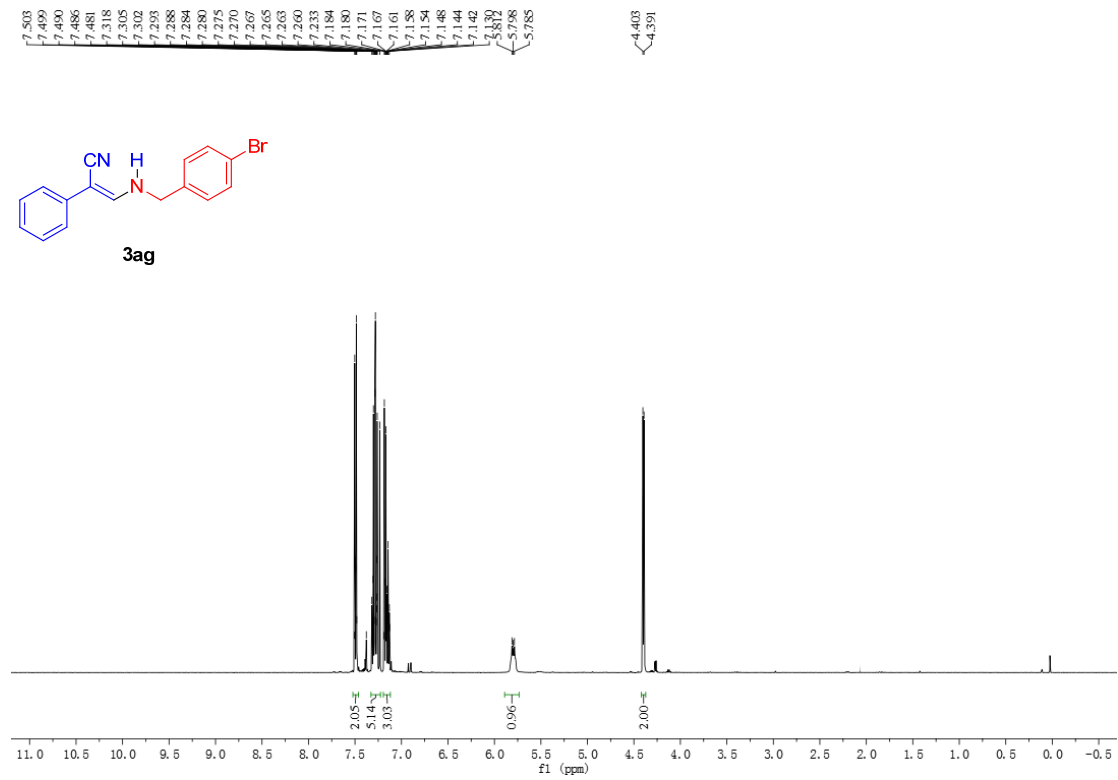




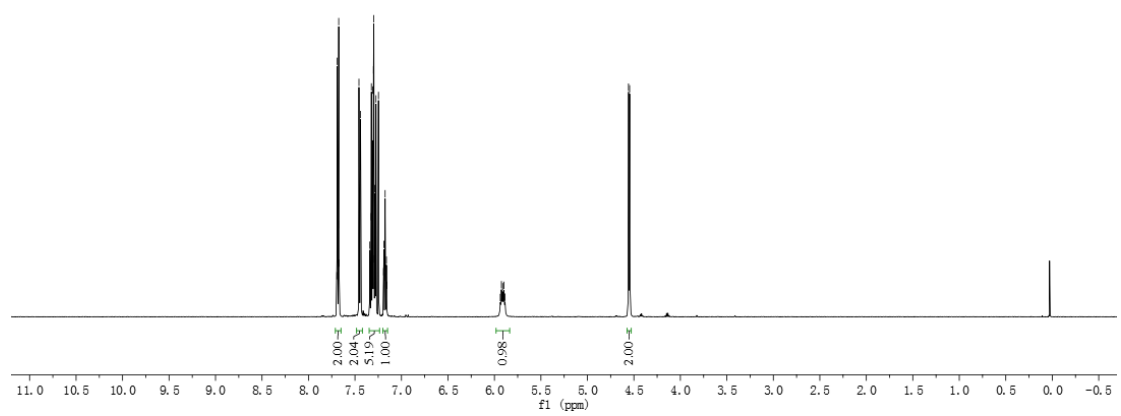
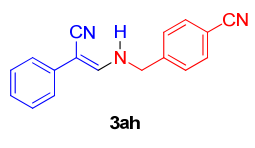




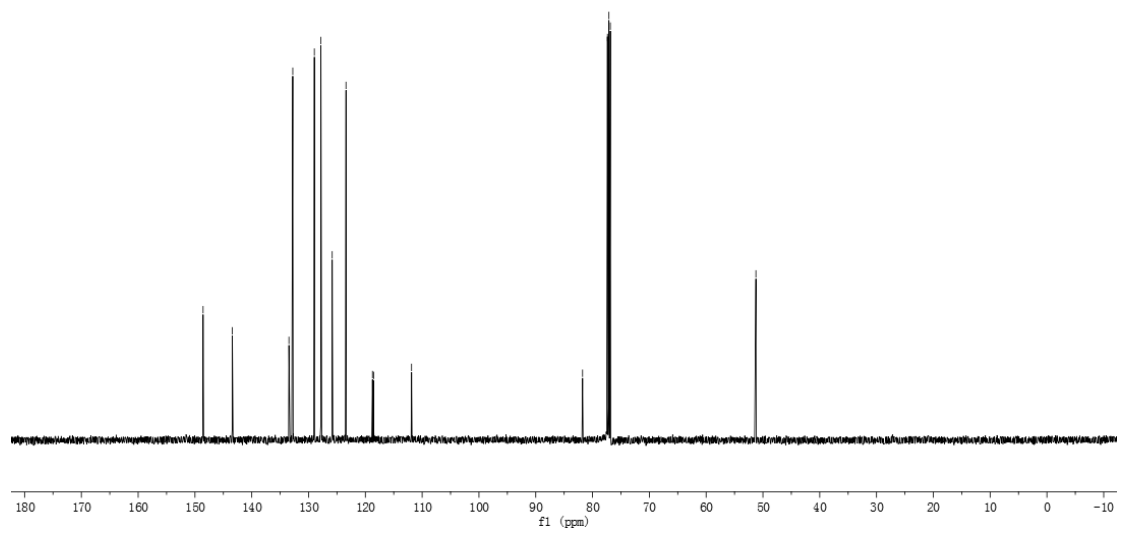
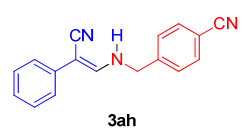


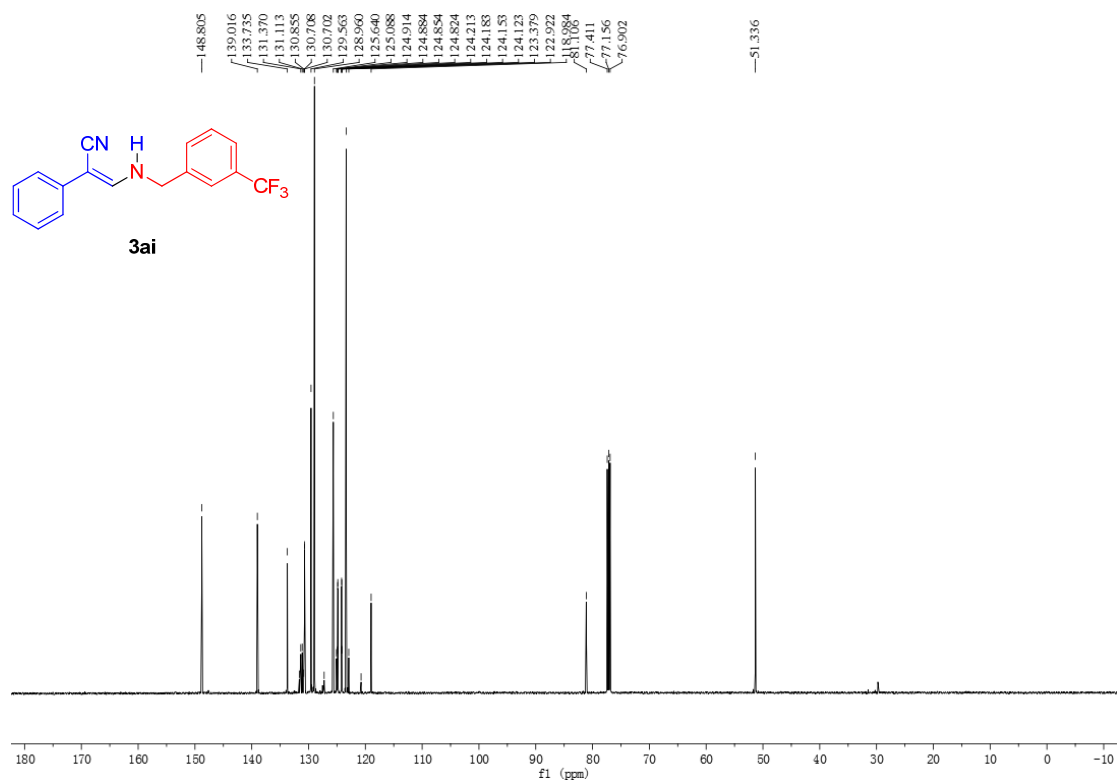
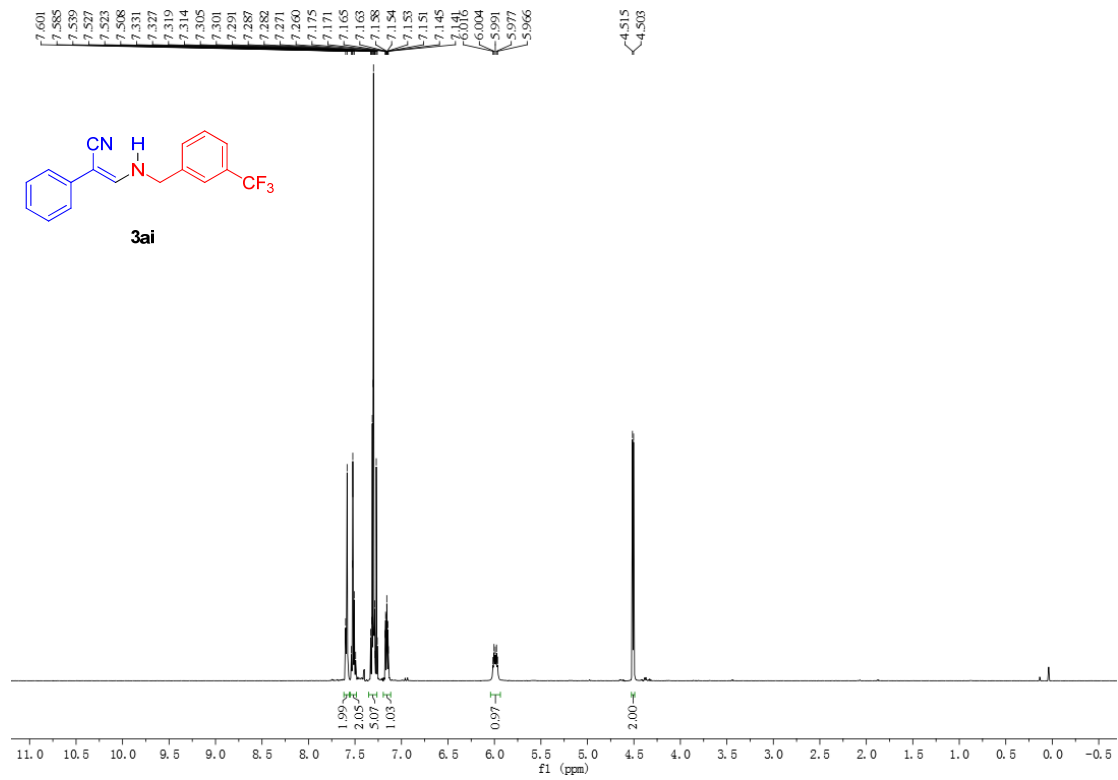


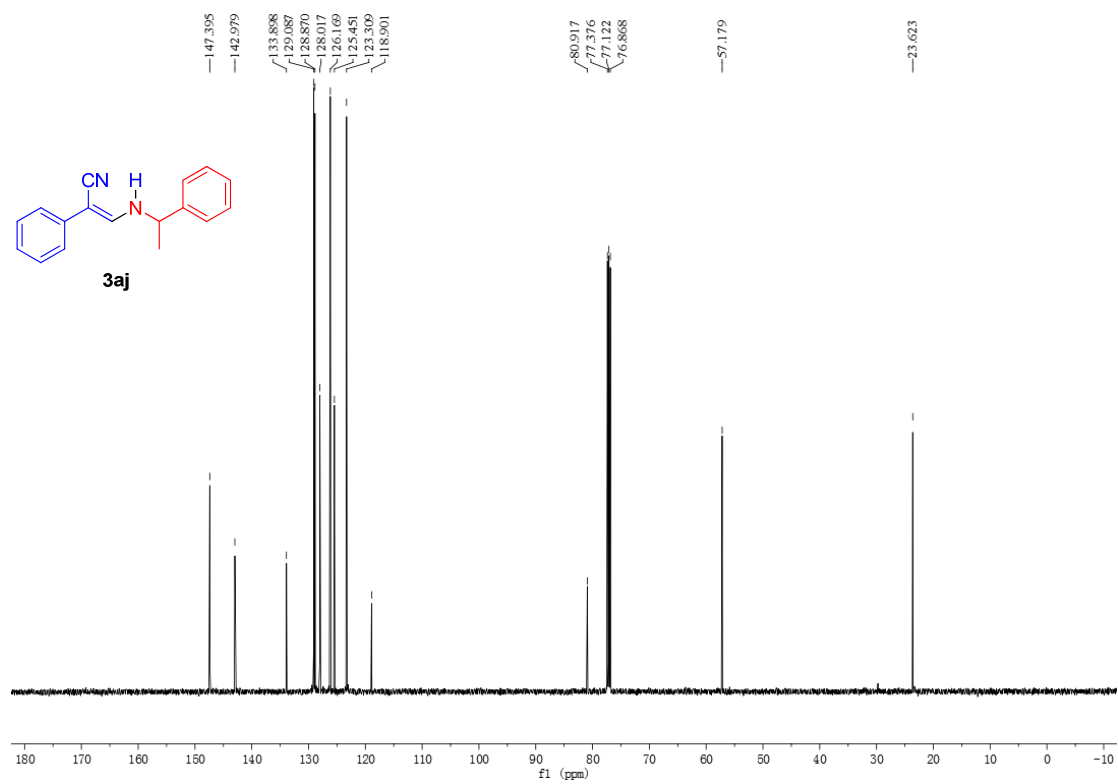
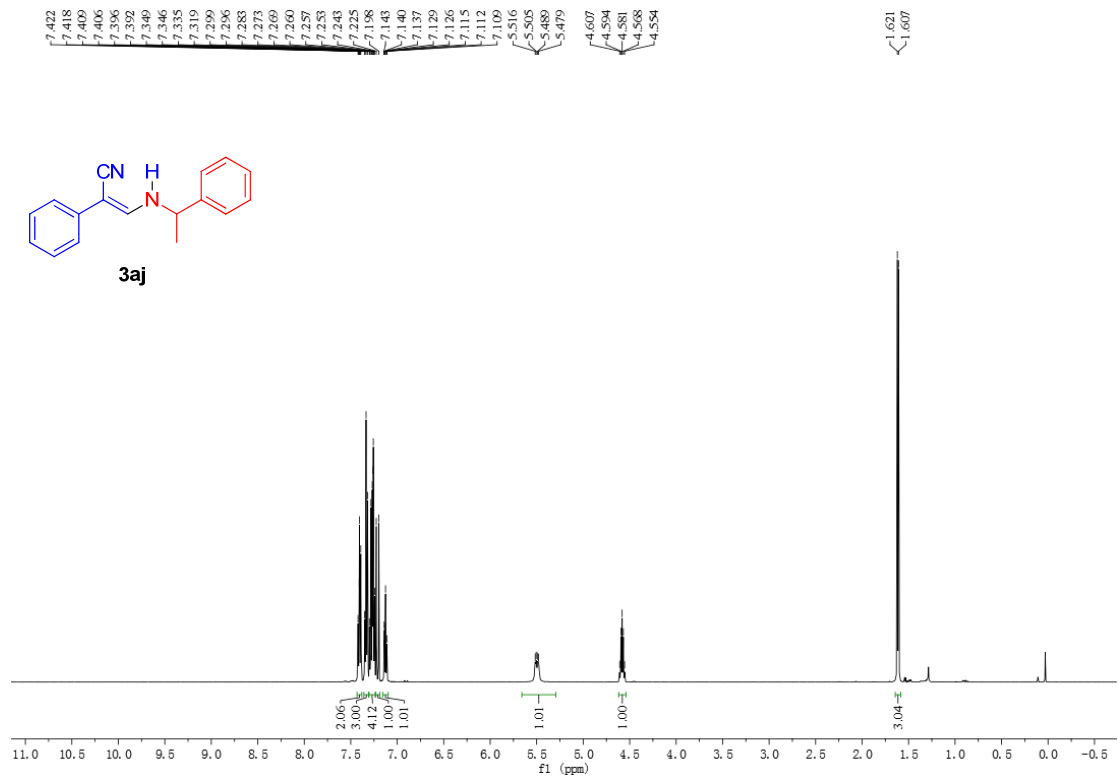
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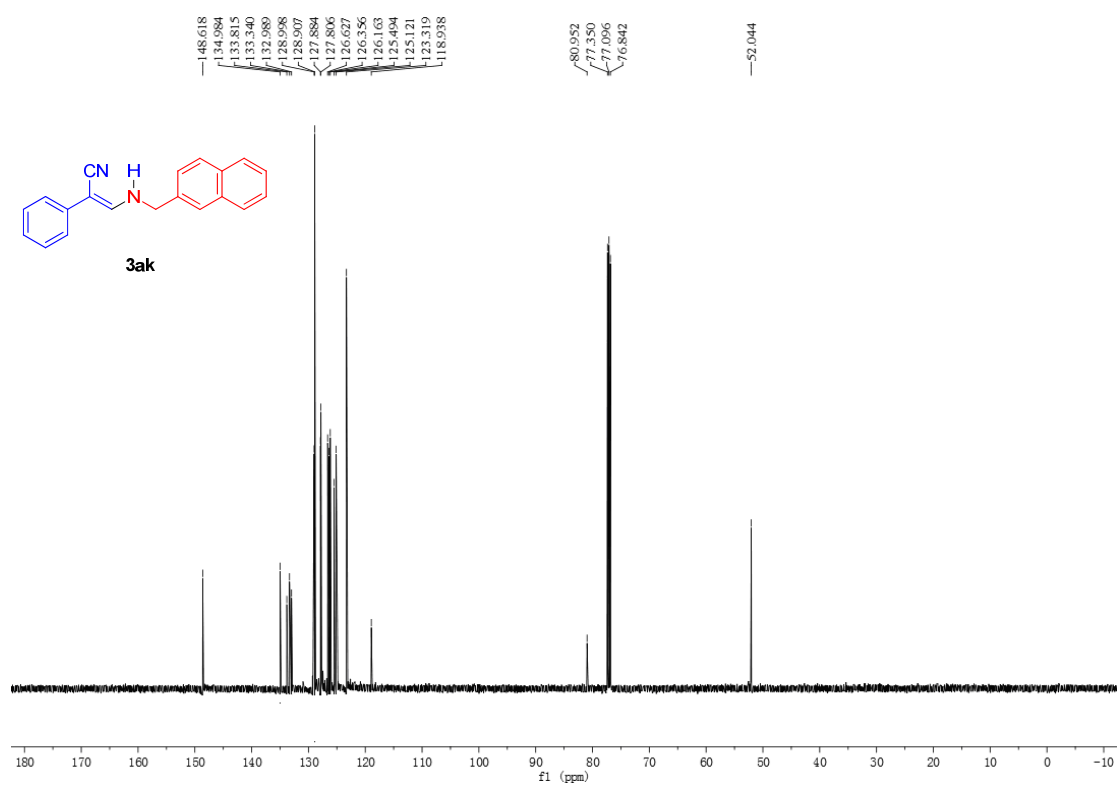
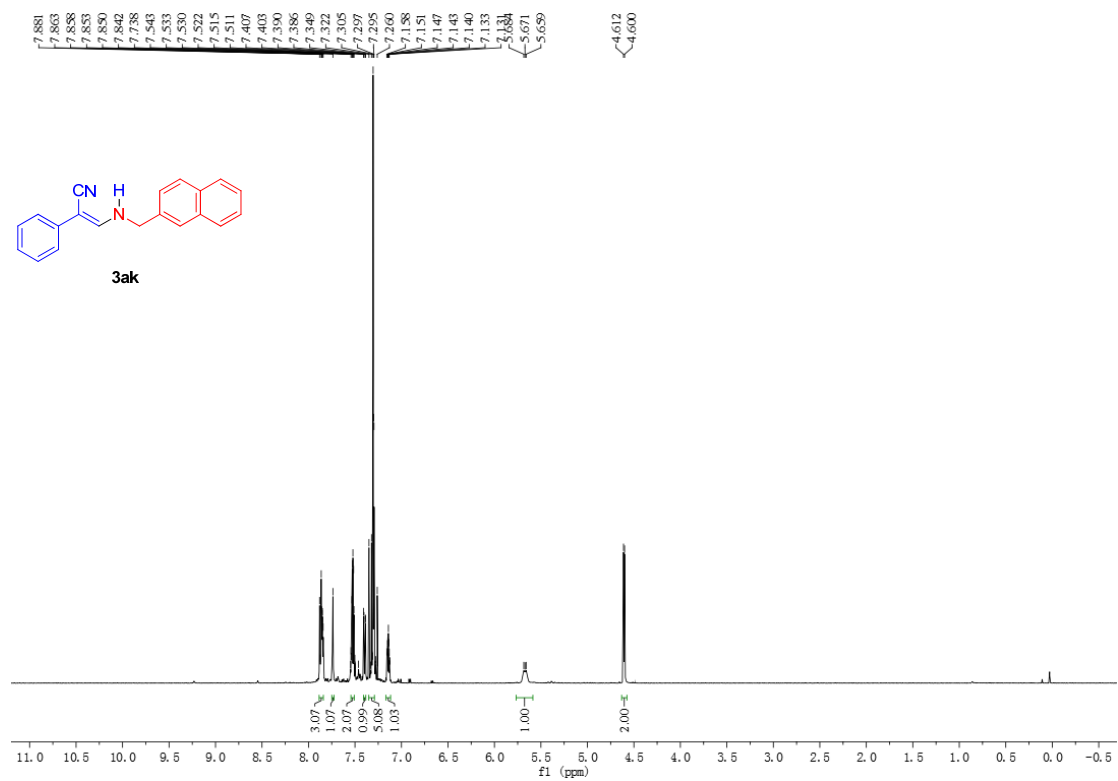


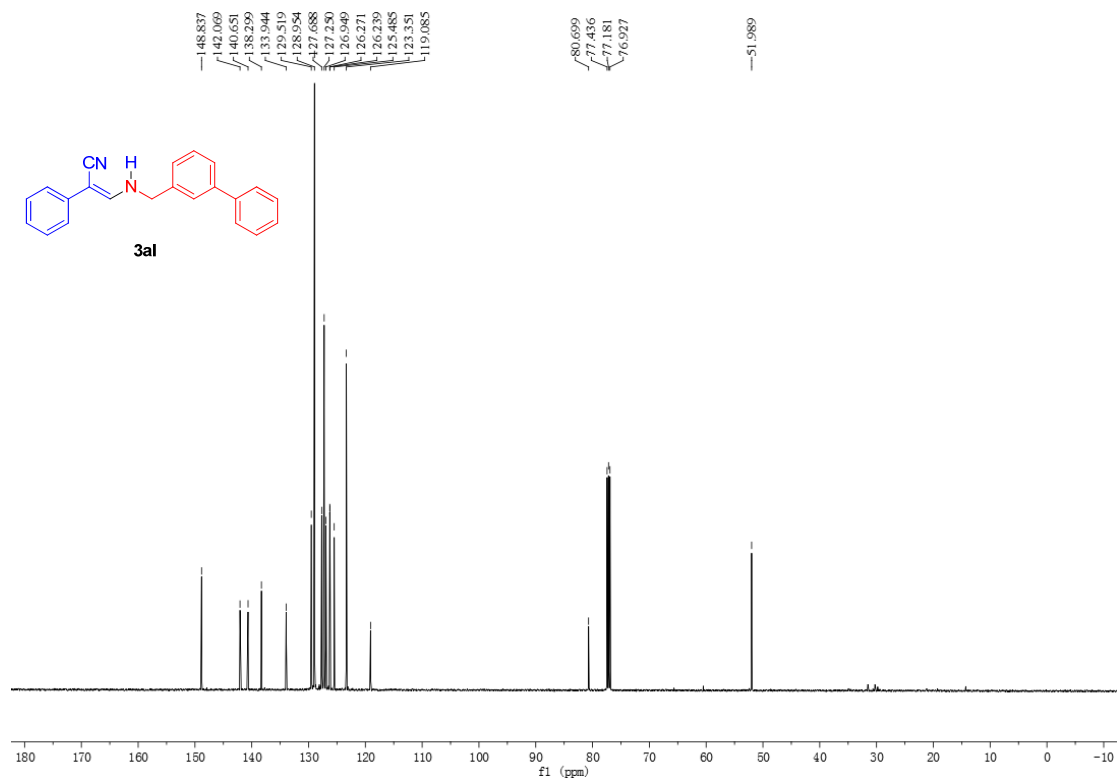
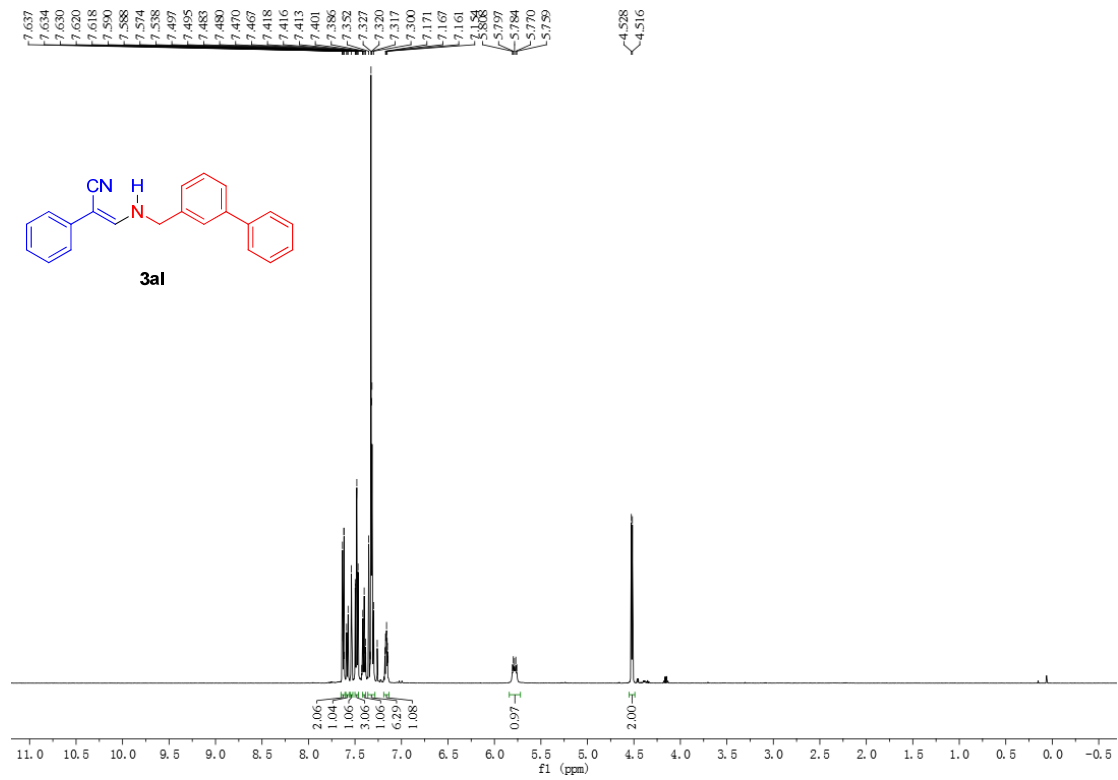
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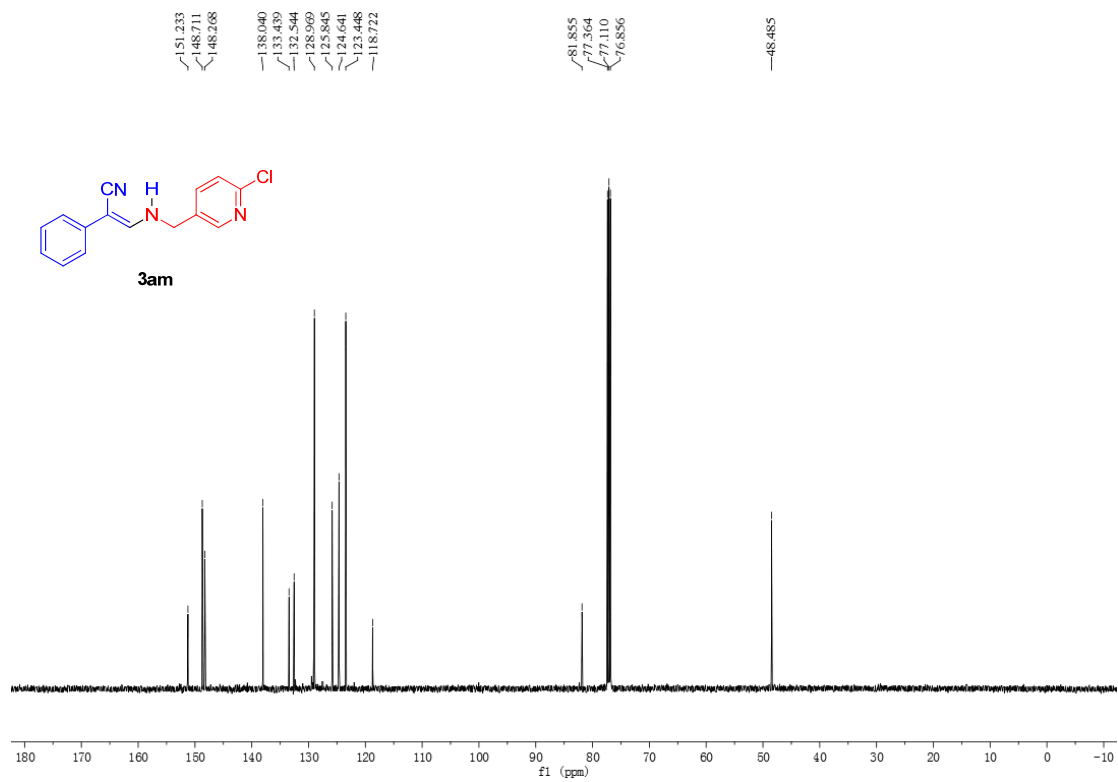
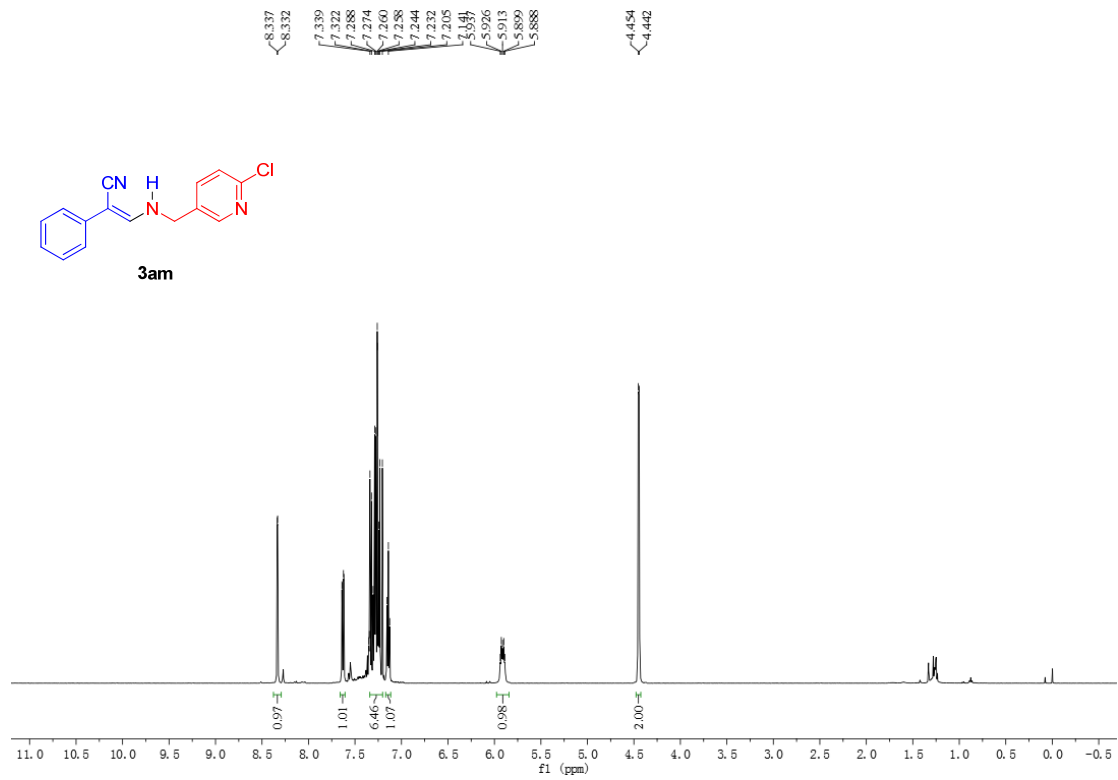


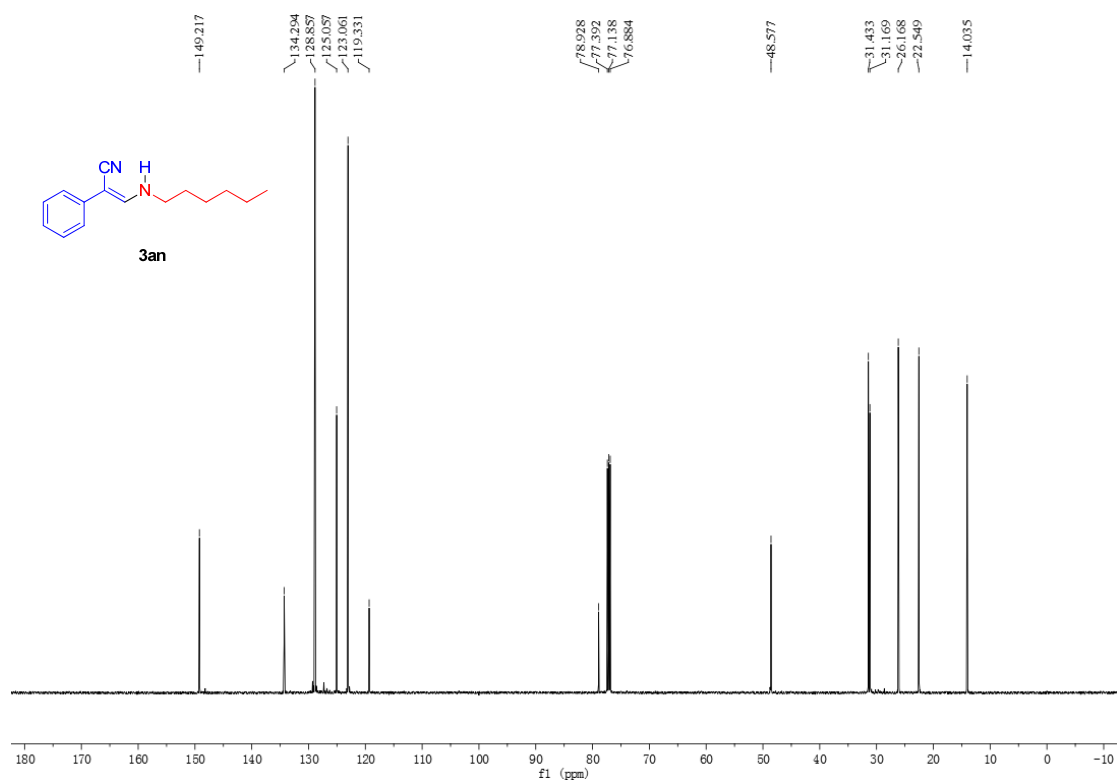
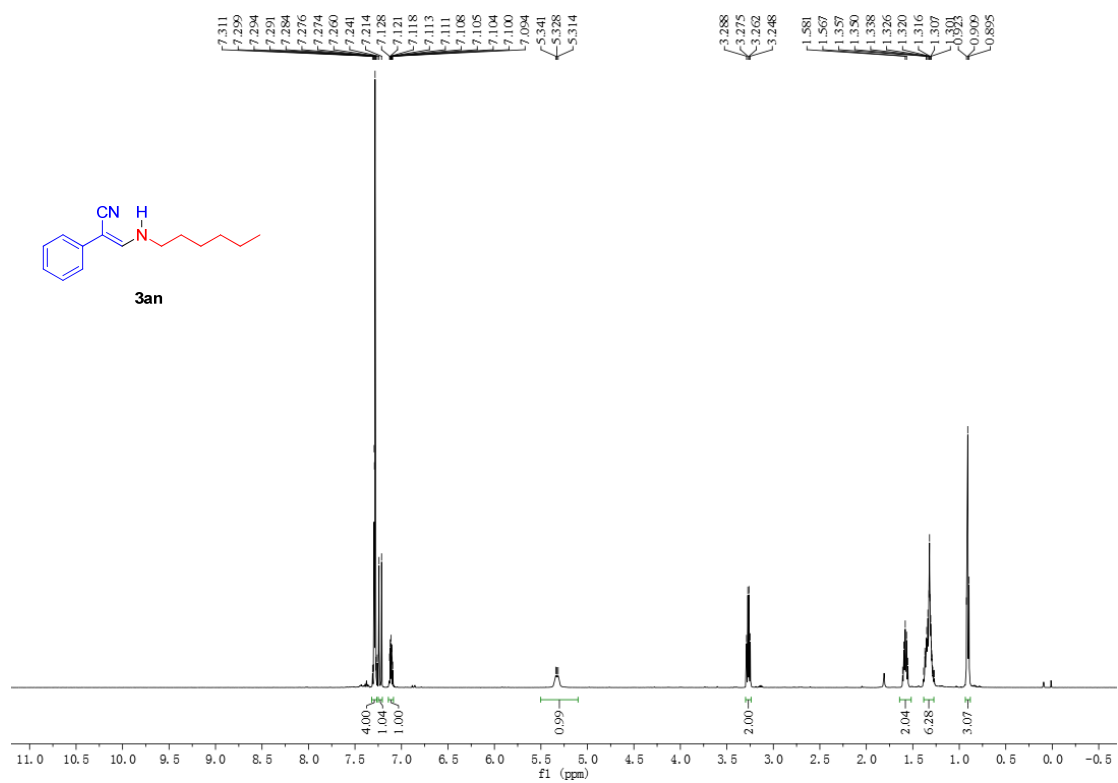


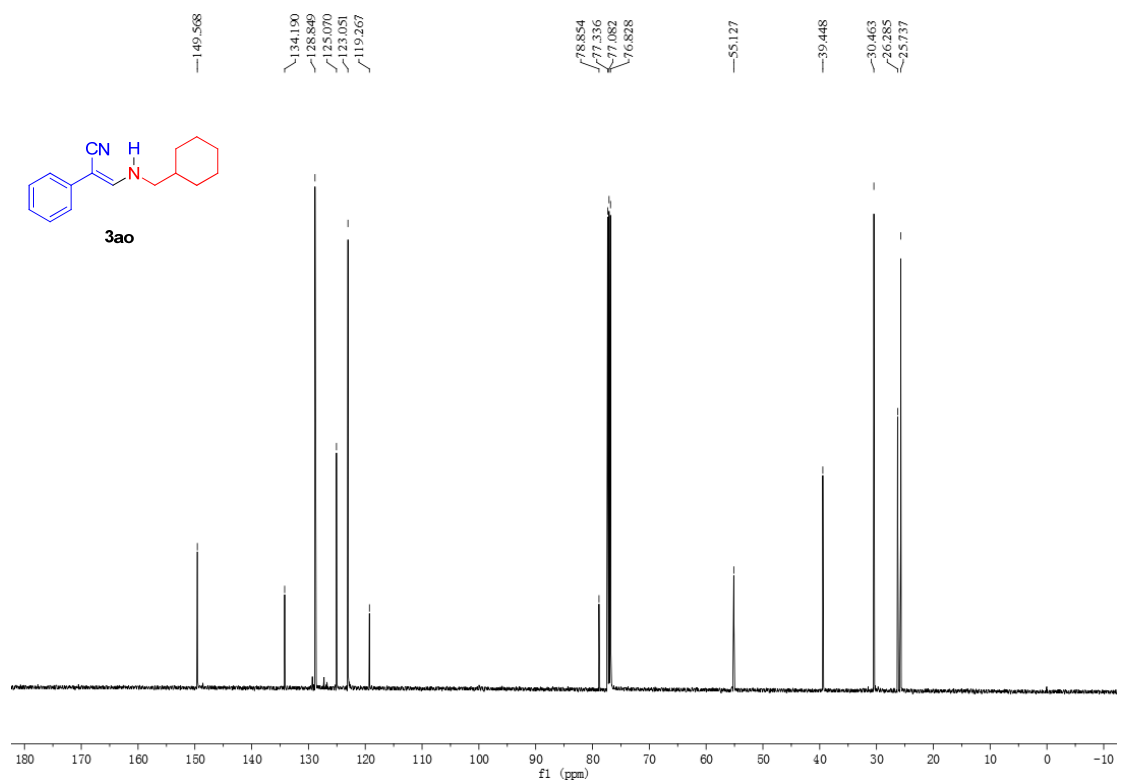
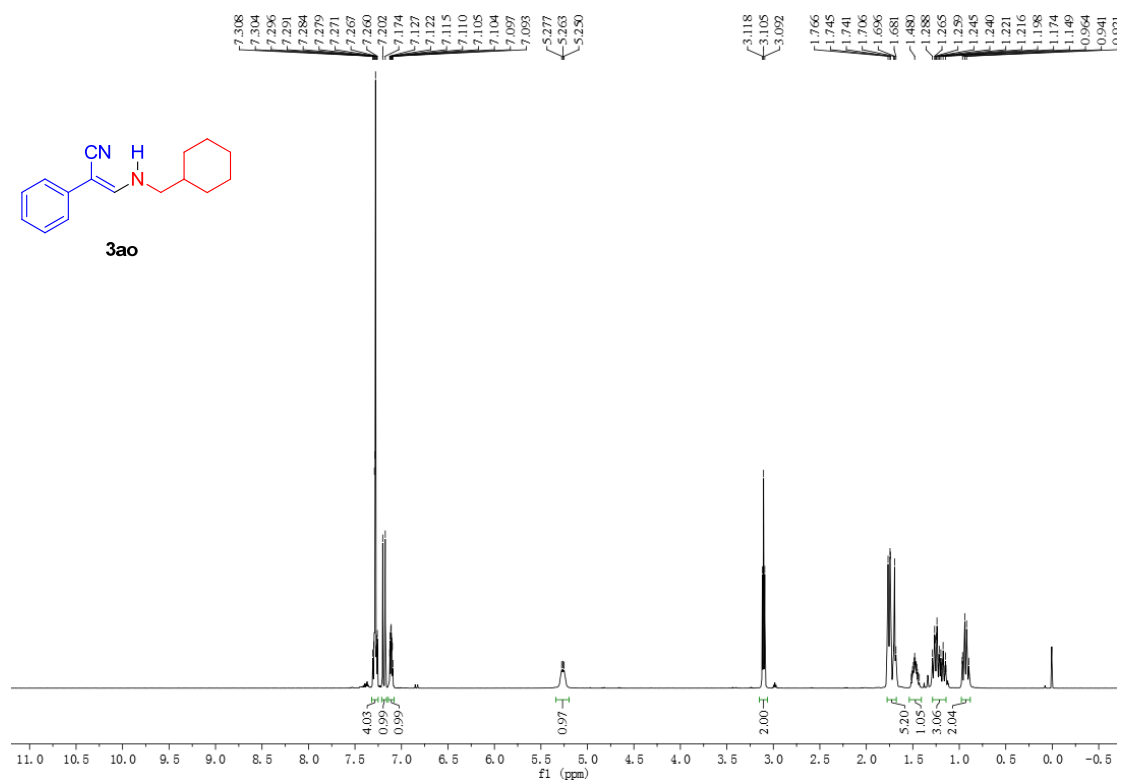




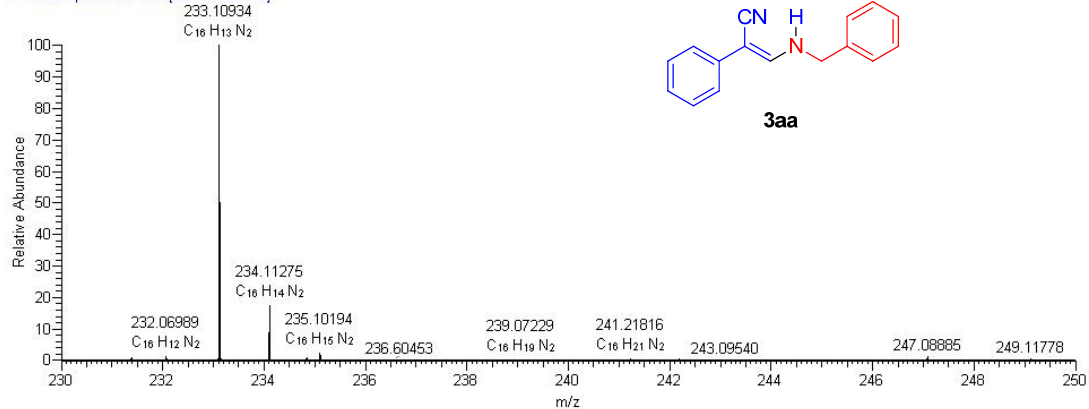




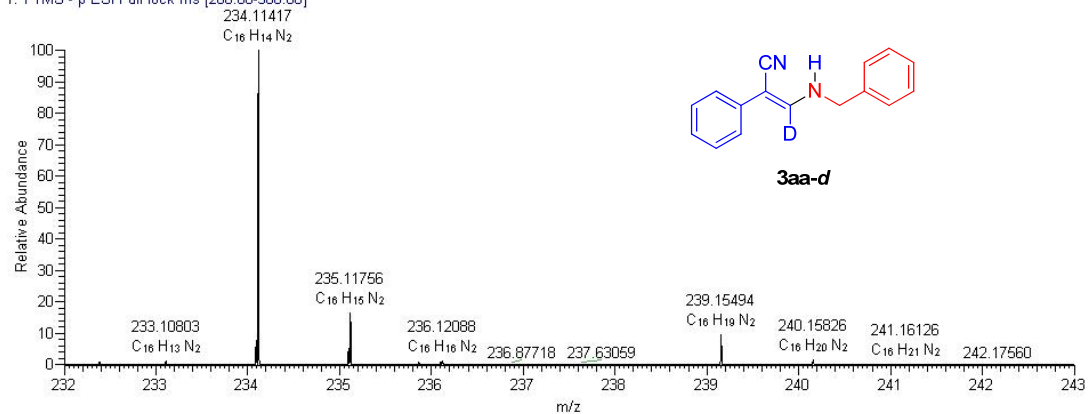




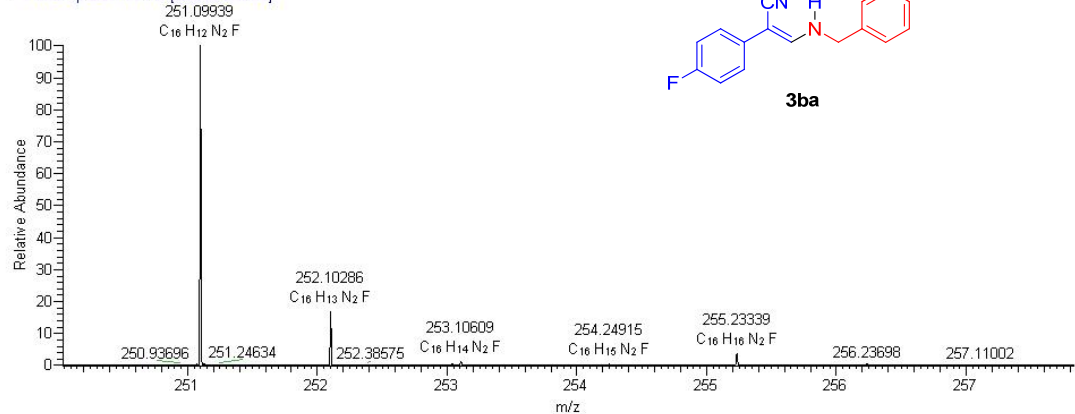
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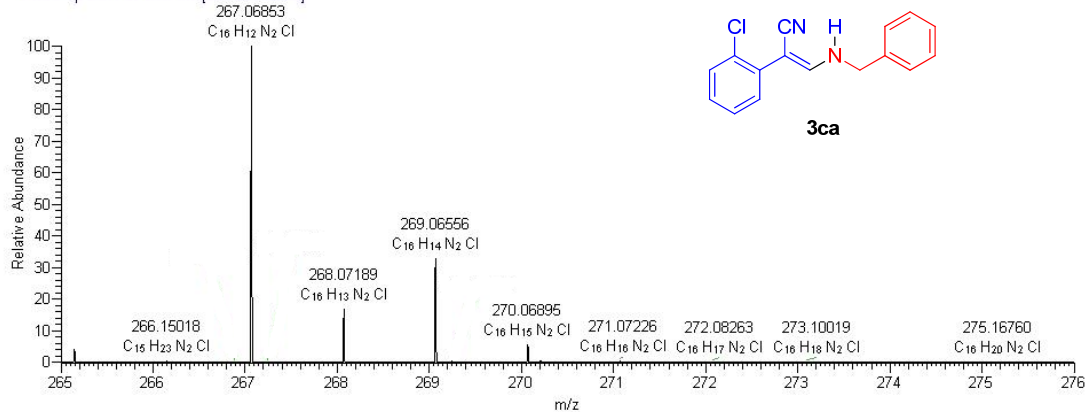
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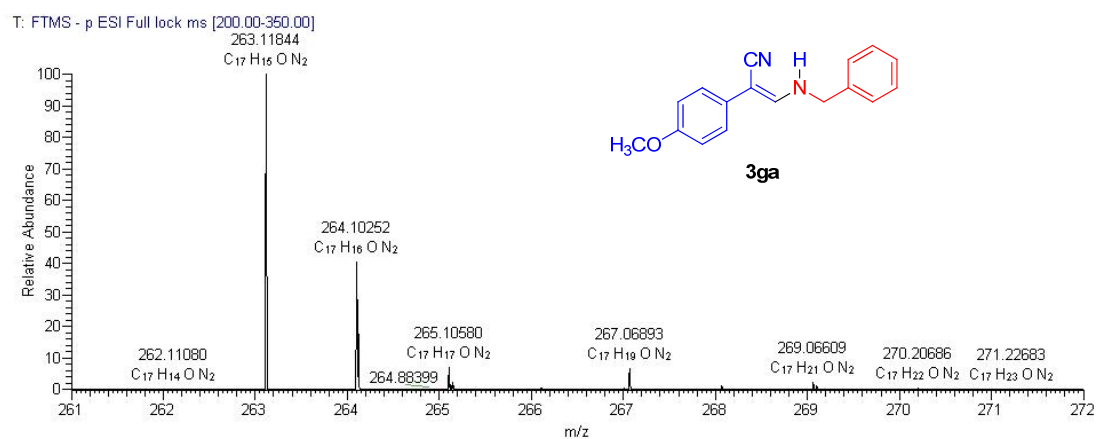
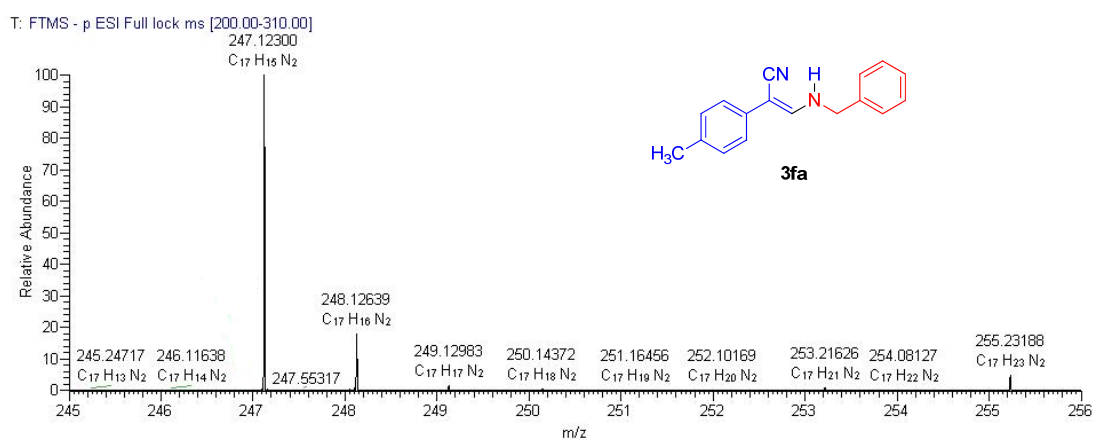
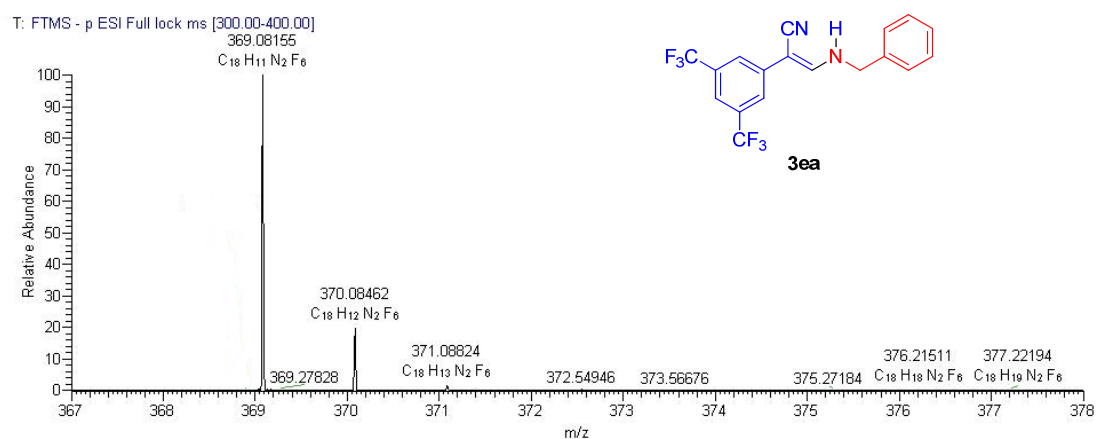
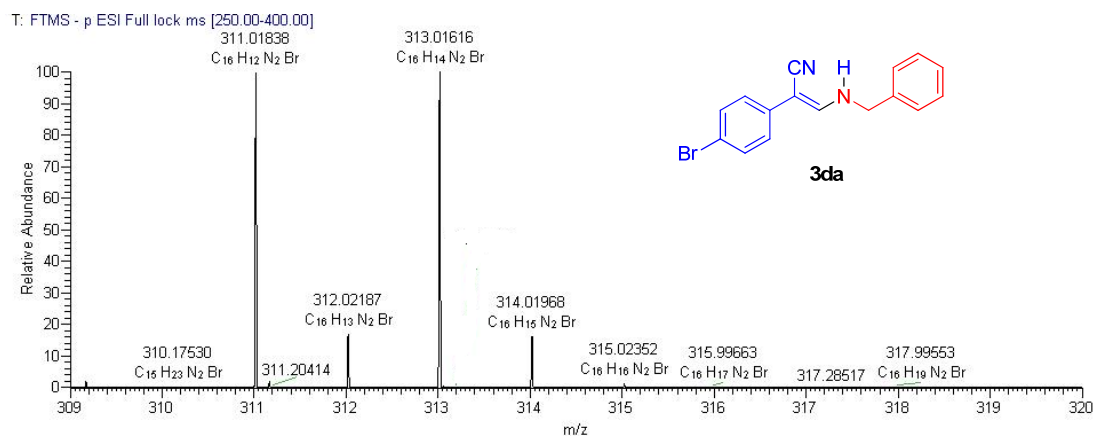


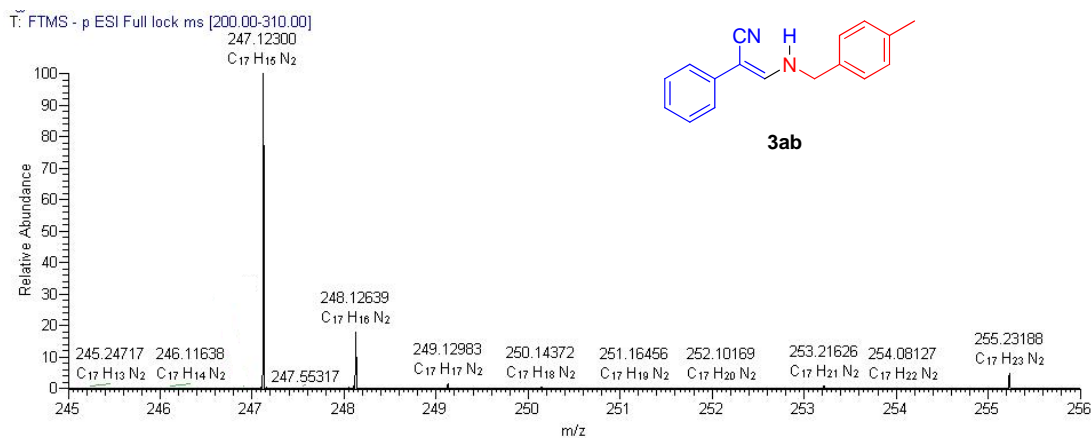
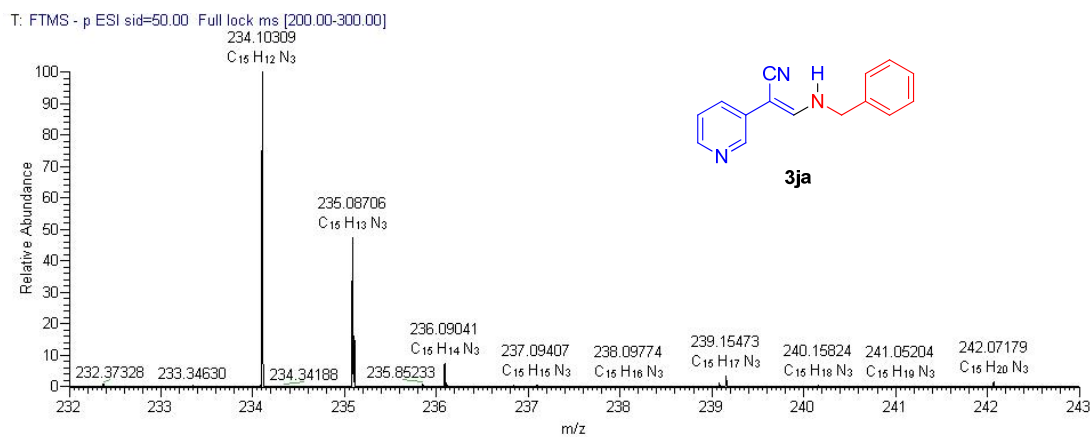
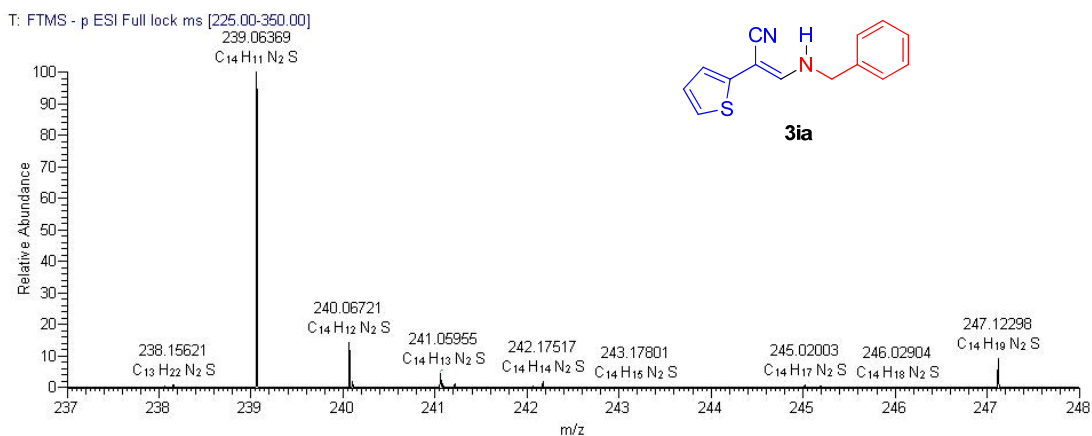
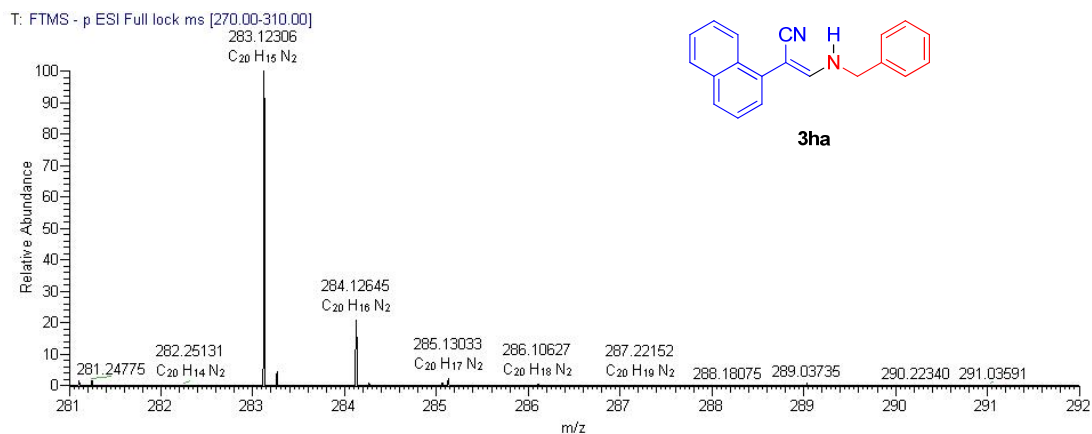
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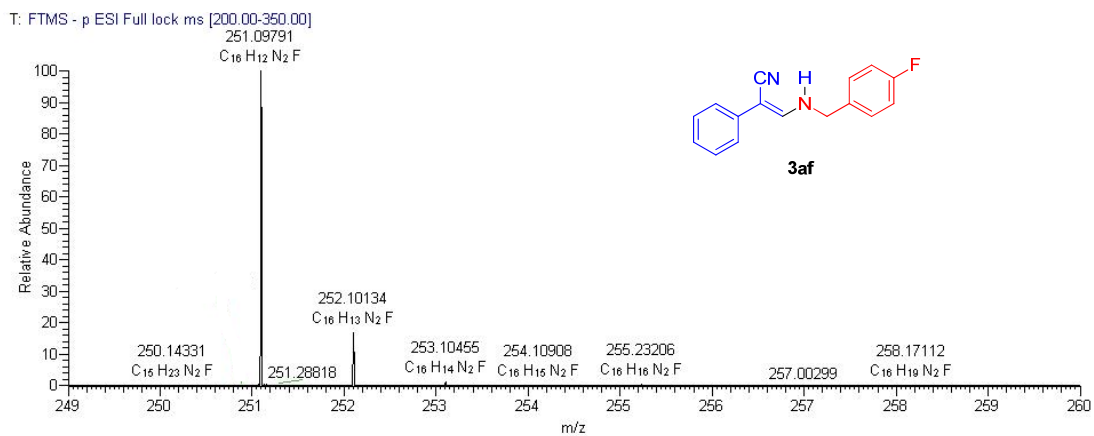
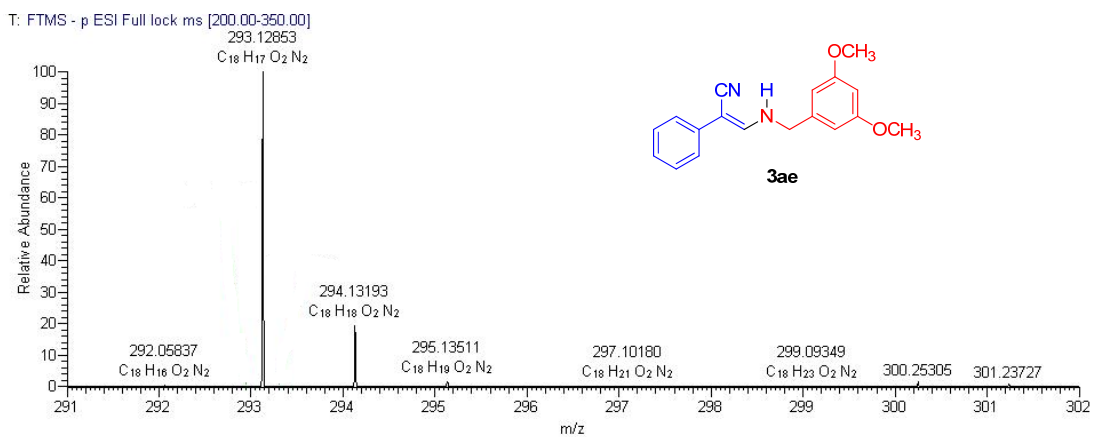
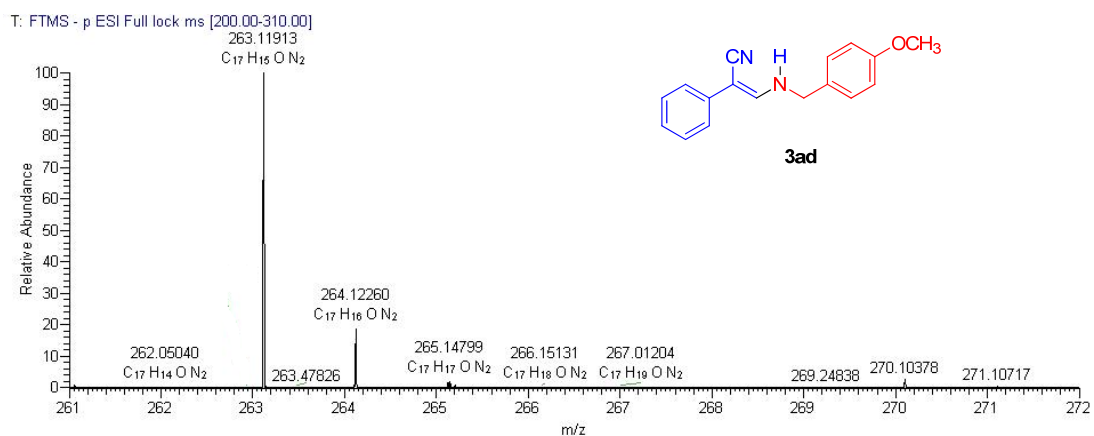
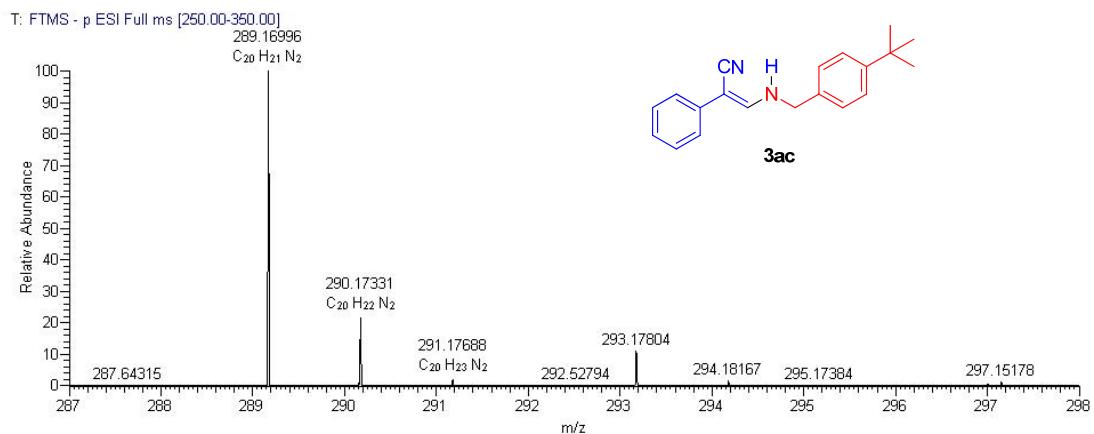


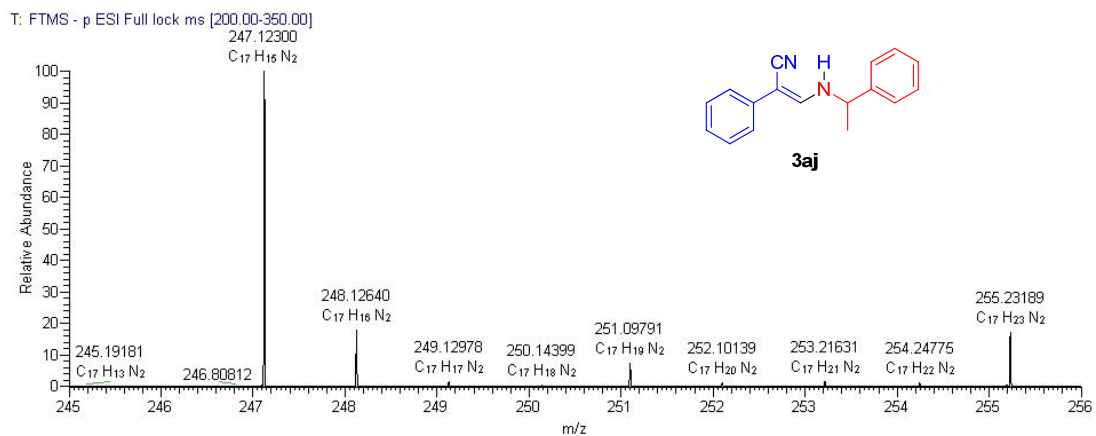
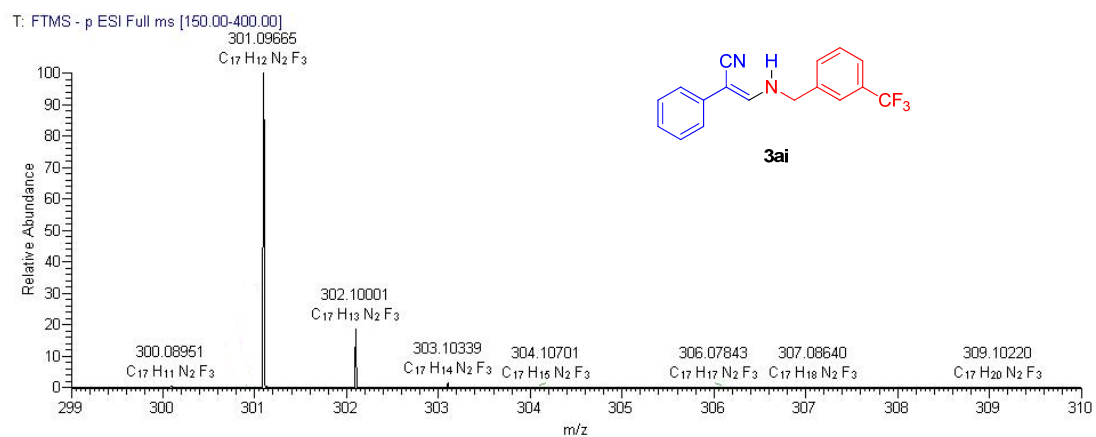
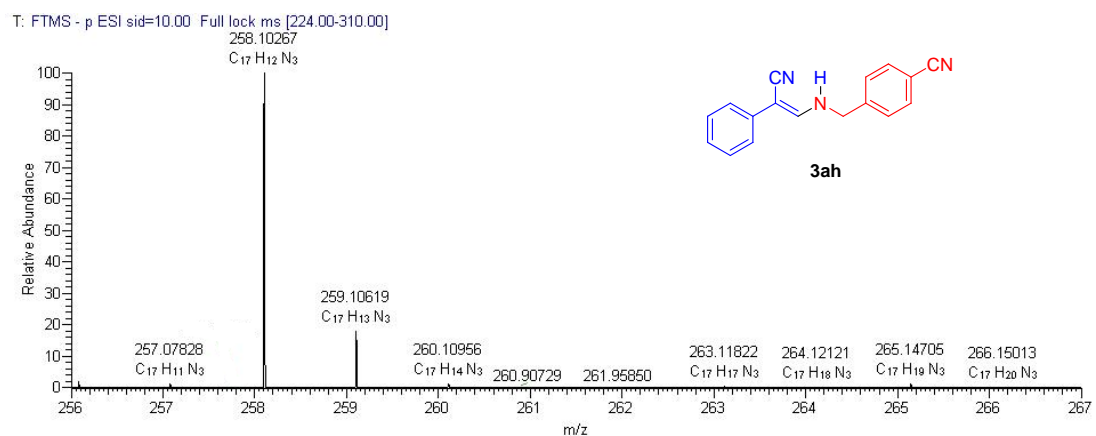
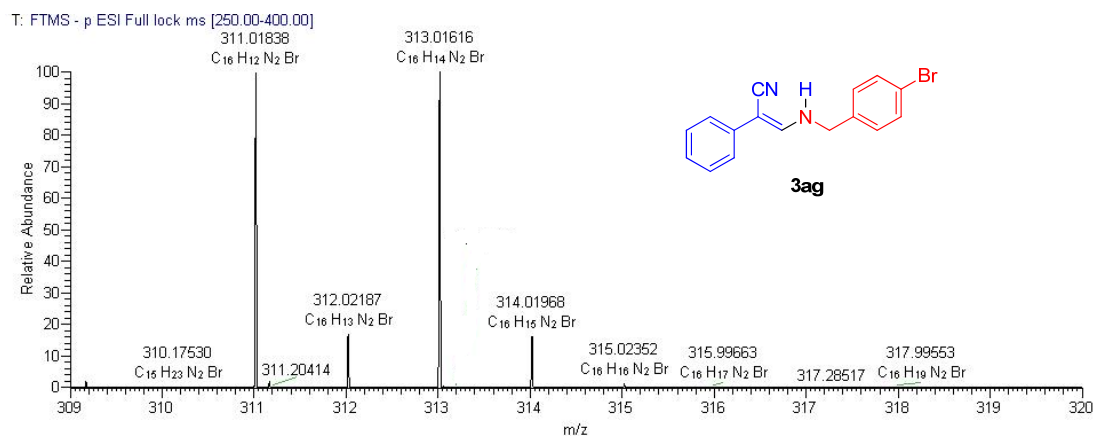
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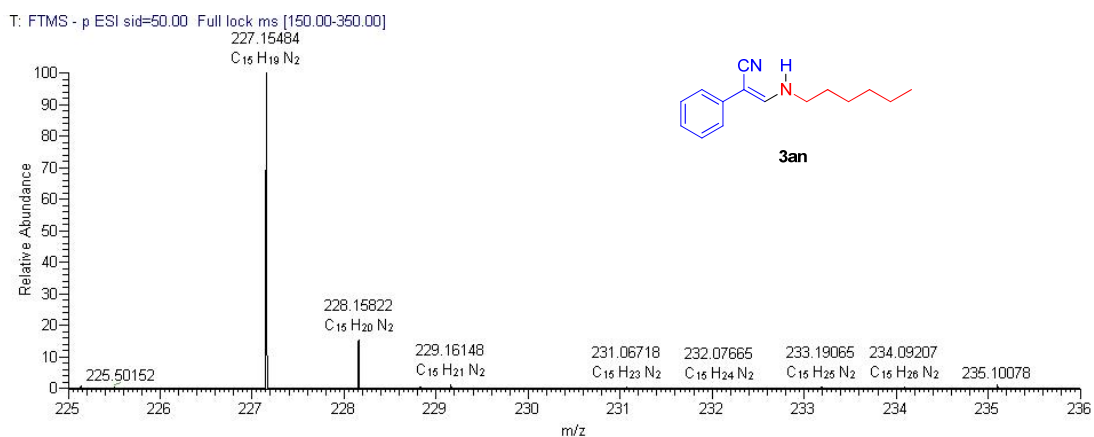
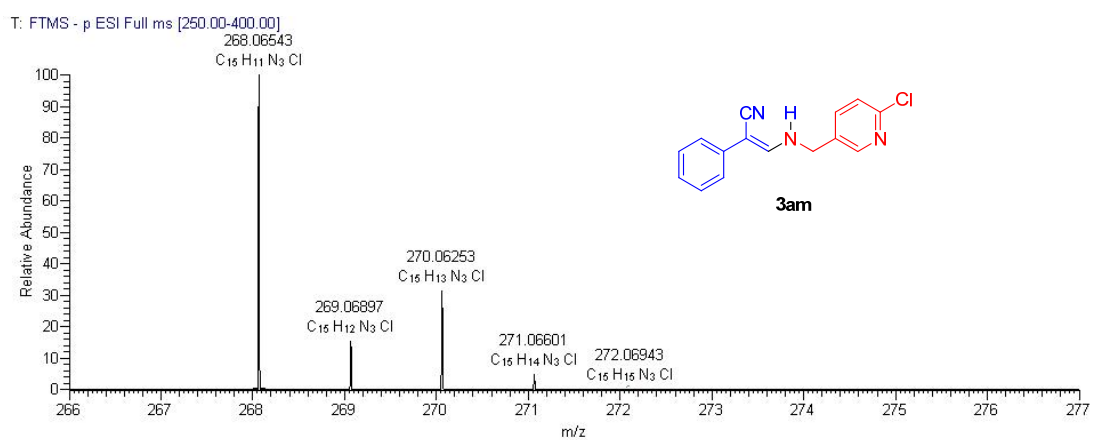
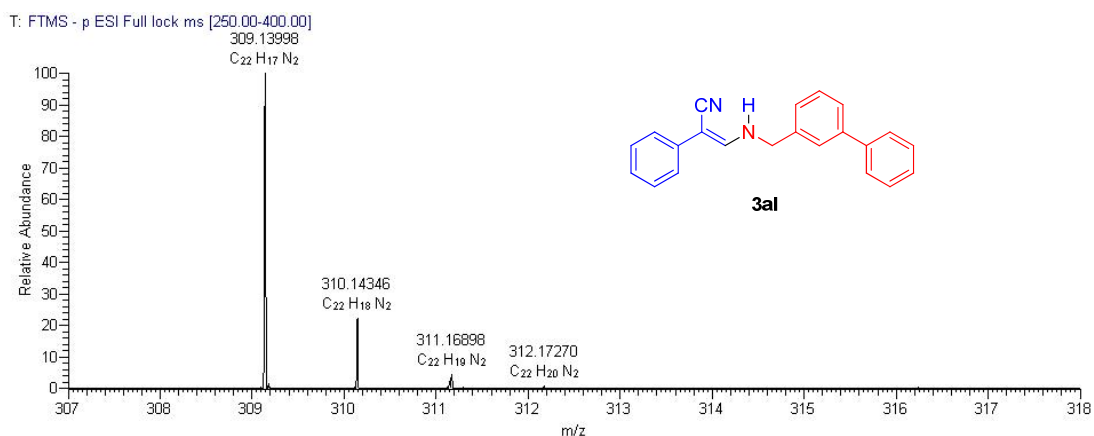
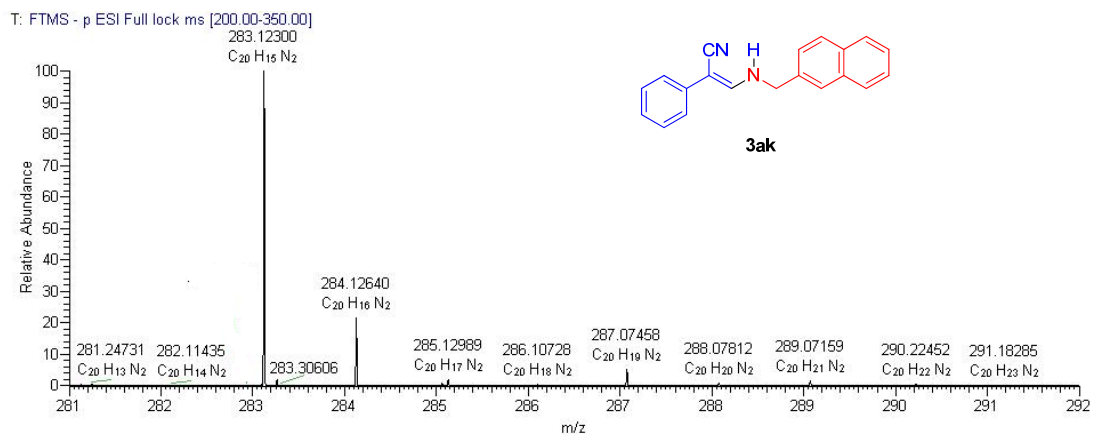












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