Supporting Information

Rh(III)-catalyzed C–H oxidative *ortho*-olefination of arenes using 7-azaindole as a directing group and utilization in the construction of new tetracyclic heterocycles containing 7-azaindole skeleton

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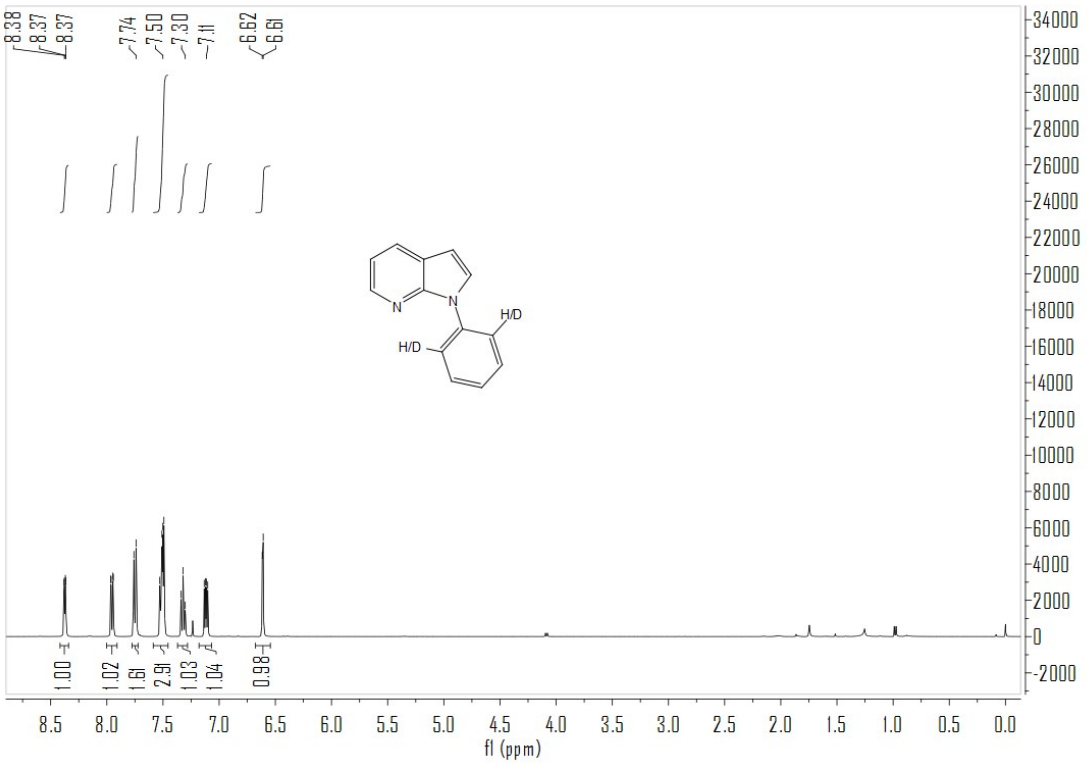
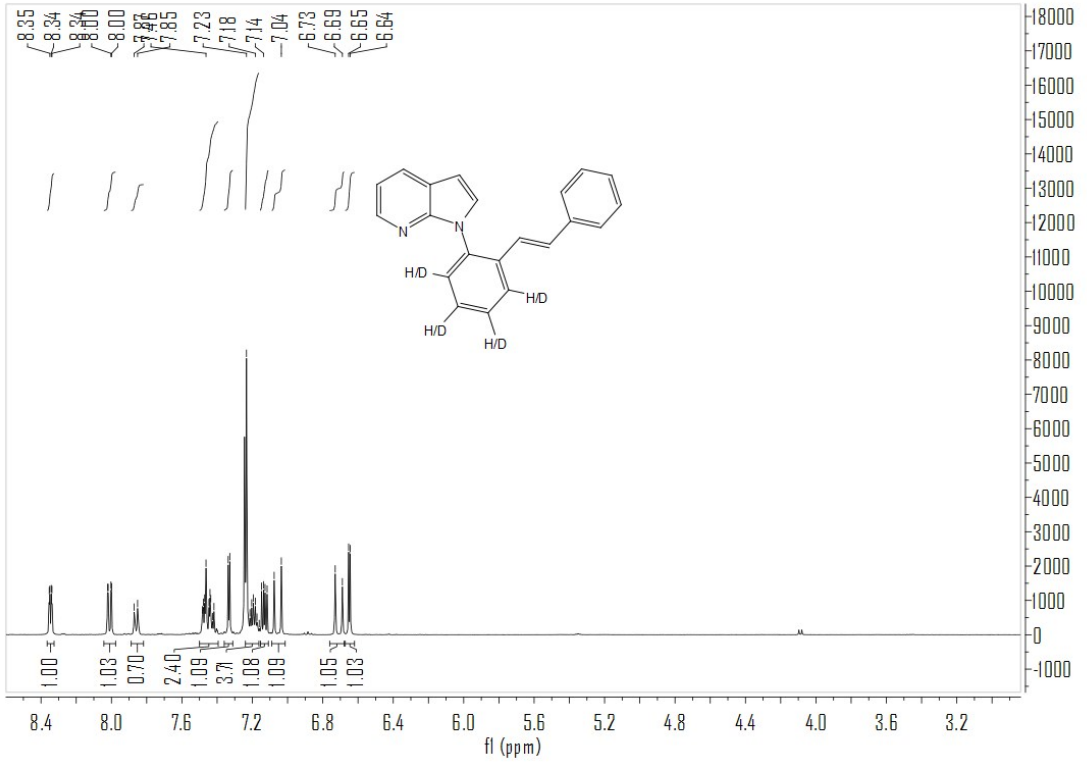
Content

Deuterium-Labeling Result and Kinetic Isotope Effect

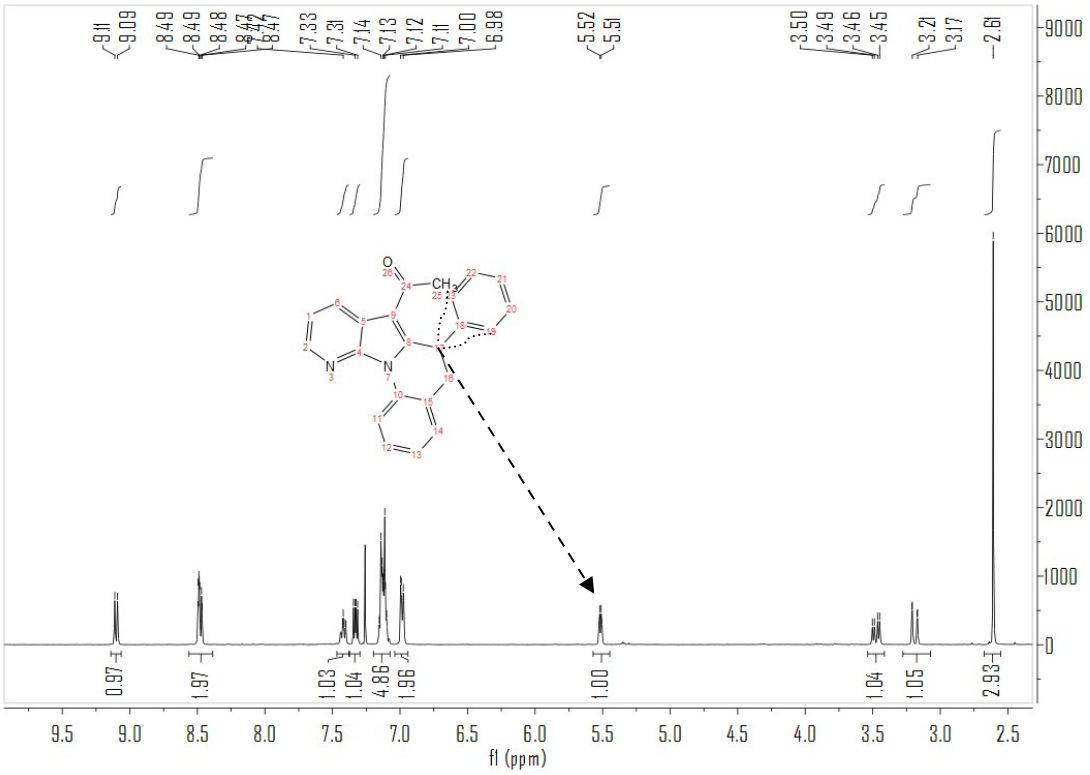
H/D exchange experiments

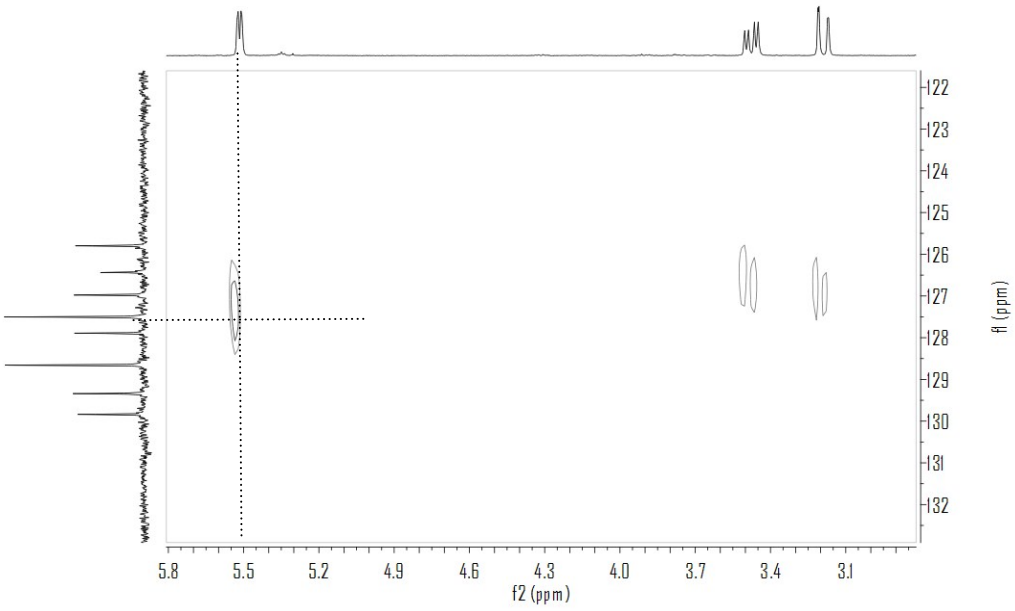


KIE experiments



Identification of product 4a (^{1}H, ^{13}C, HMBC)





General Procedure for starting materials

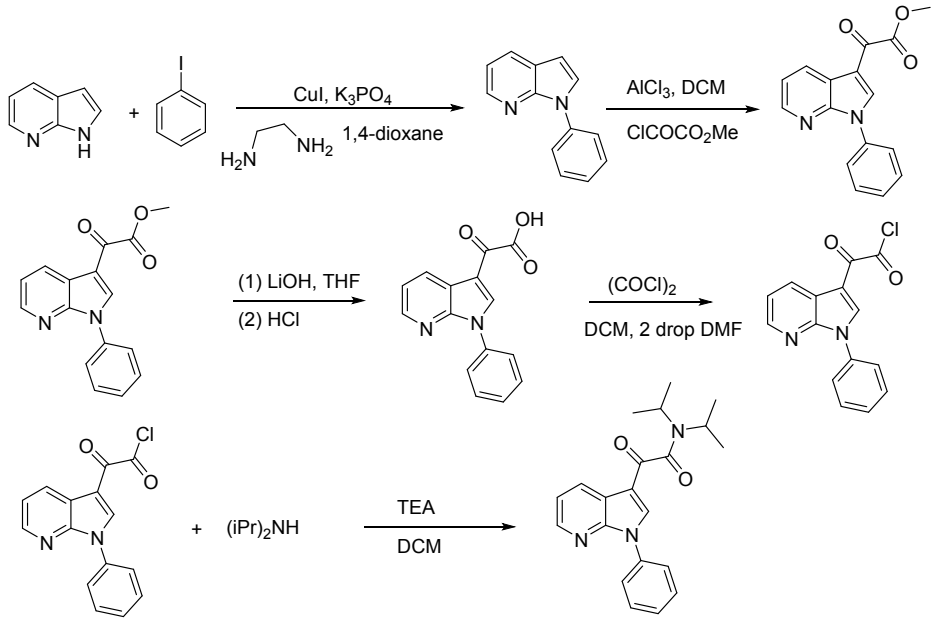
1. All of the starting materials were known according to the reported literature[1-4], except for **1m**.

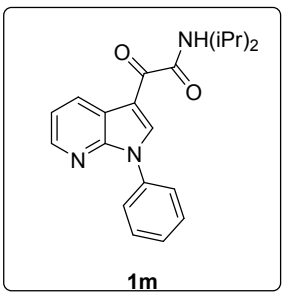
(1) G. Y. Qian, X. H. Hong, B. X. Liu, H. Mao and B. Xu, *Org. Lett.* 2014, **16**, 5294-5297.

(2) Z. X. Zhang, Z. Yang, H. Wong, J. L. Zhu, N. A. MeanWell, J. F. Kadow and T. Wang, *J. Org. Chem*. 2002, **67**, 6226-6227.

(3) S. S. Li, C. Q. Wang, H. Lin, X. M. Zhang and L. Dong, *Org. Lett*. 2015, **17**, 3018-3021.

(4) B. Liu, X. Wang, Z. M. Ge and R. T. Li, *Org. Biomol. Chem*. 2016, **14**, 2944-2949.

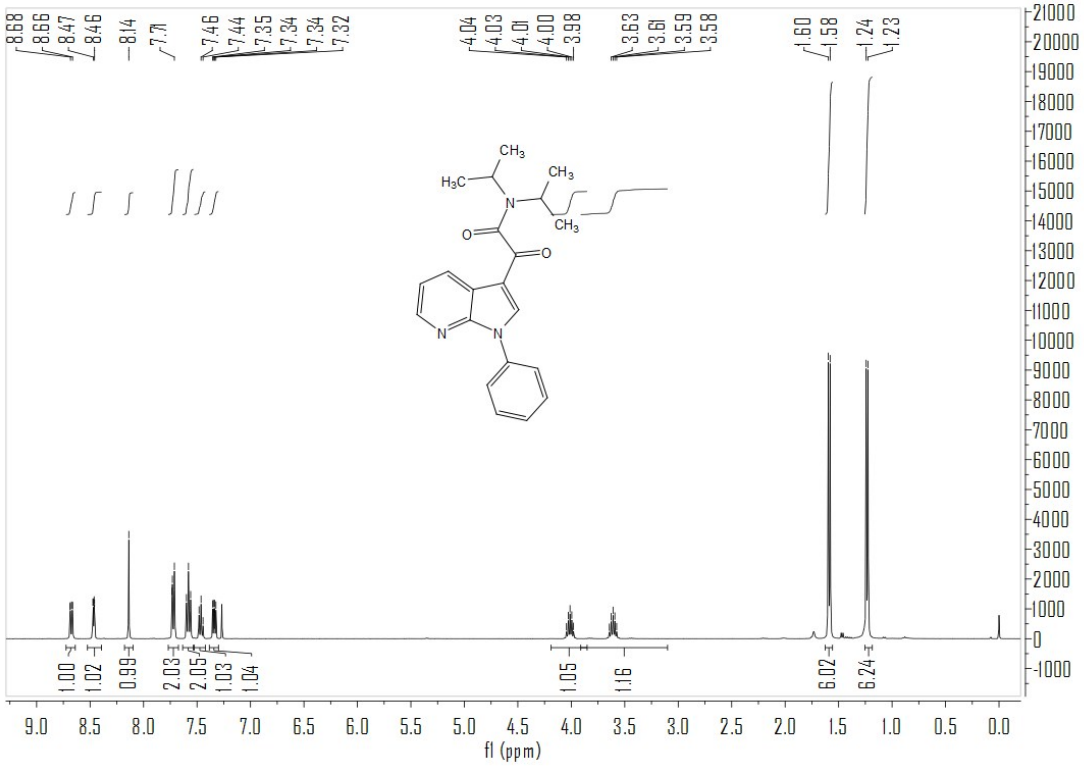




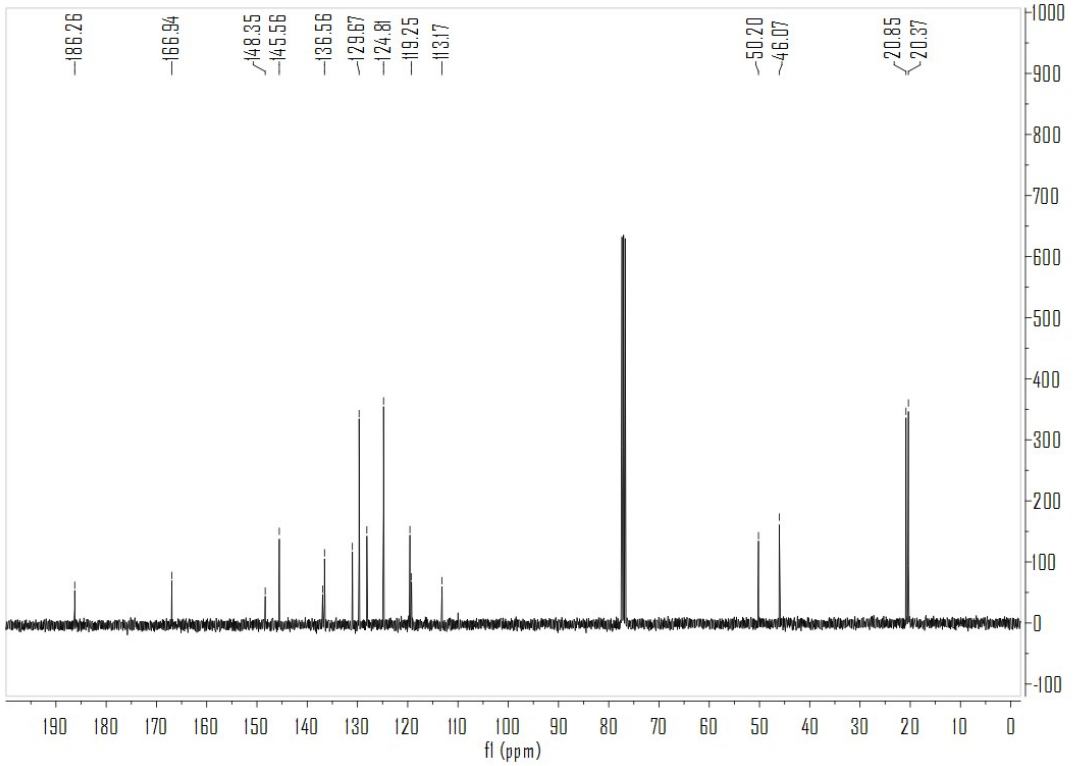
White solid, ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, J = 7.9, 1.5 Hz, 1H), 8.47 (dd, J = 4.7, 1.6 Hz, 1H), 8.14 (s, 1H), 7.77 – 7.67 (m, 2H), 7.58 (t, J = 7.8 Hz, 2H), 7.46 (t, J = 7.4 Hz, 1H), 7.34 (dd, J = 7.9, 4.7 Hz, 1H), 4.01 (dt, J = 13.3, 6.6 Hz, 1H), 3.61 (dt, J = 13.7, 6.8 Hz, 1H), 1.59 (d, J = 6.8 Hz, 6H), 1.23 (d, J = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 186.3, 166.9, 148.4, 145.6, 136.9, 136.6, 131.0, 129.7, 128.1, 124.8, 119.6, 119.3, 113.2, 50.2, 46.1, 20.9, 20.4. HRMS m/z (ESI) calcd for $C_{21}H_{24}N_3O_2$ $(M+H)^+$: 350.1863, found 350.1855.

^{1}H NMR and ^{13}C NMR Spectra ($CDCl_3$, ^{1}H 400 MHz, ^{13}C 100 MHz)

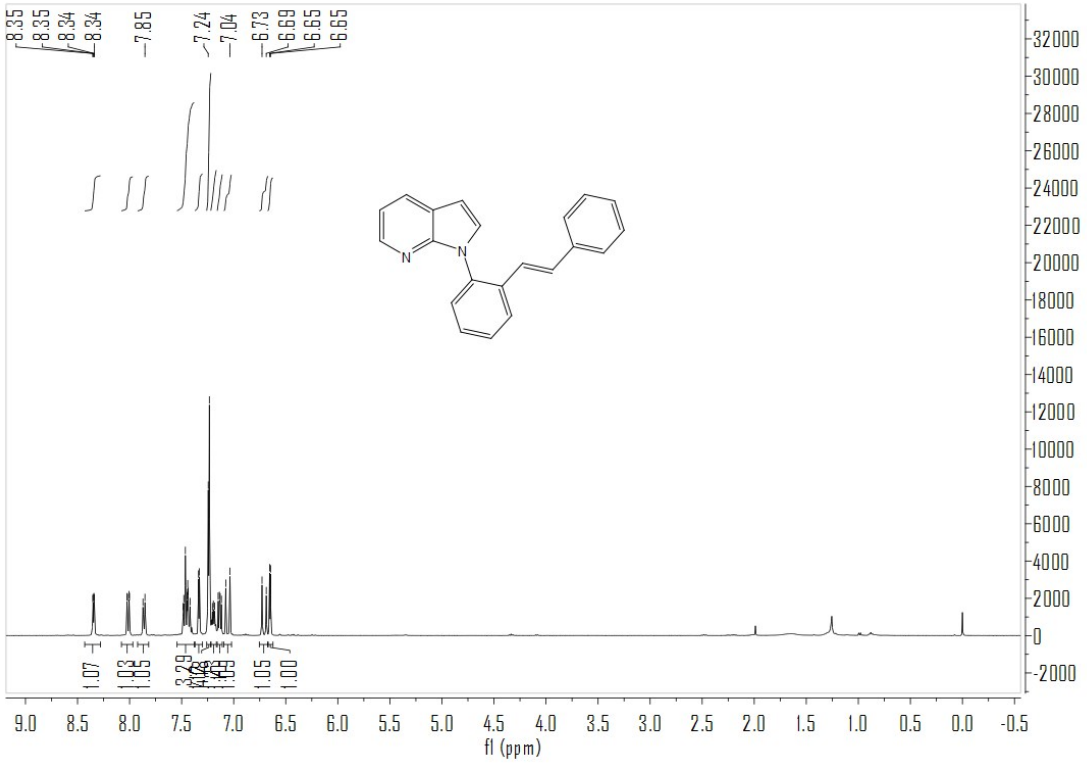
^{1}H NMR of 1m



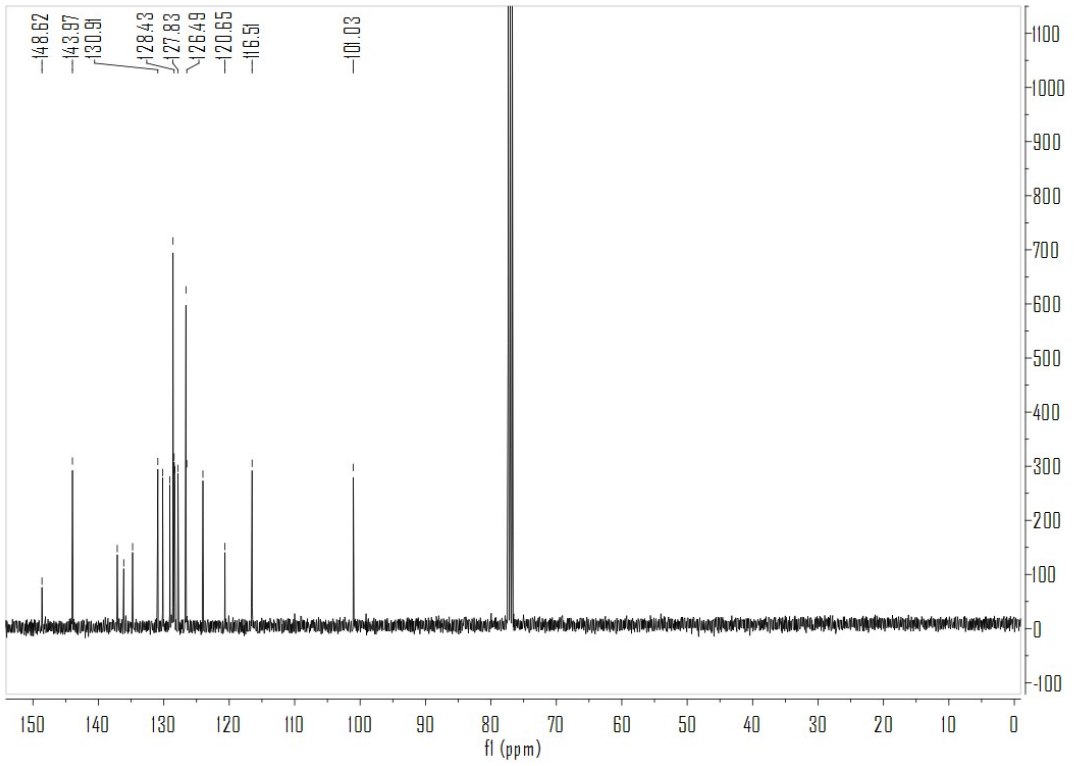
^{13} C NMR of 1m



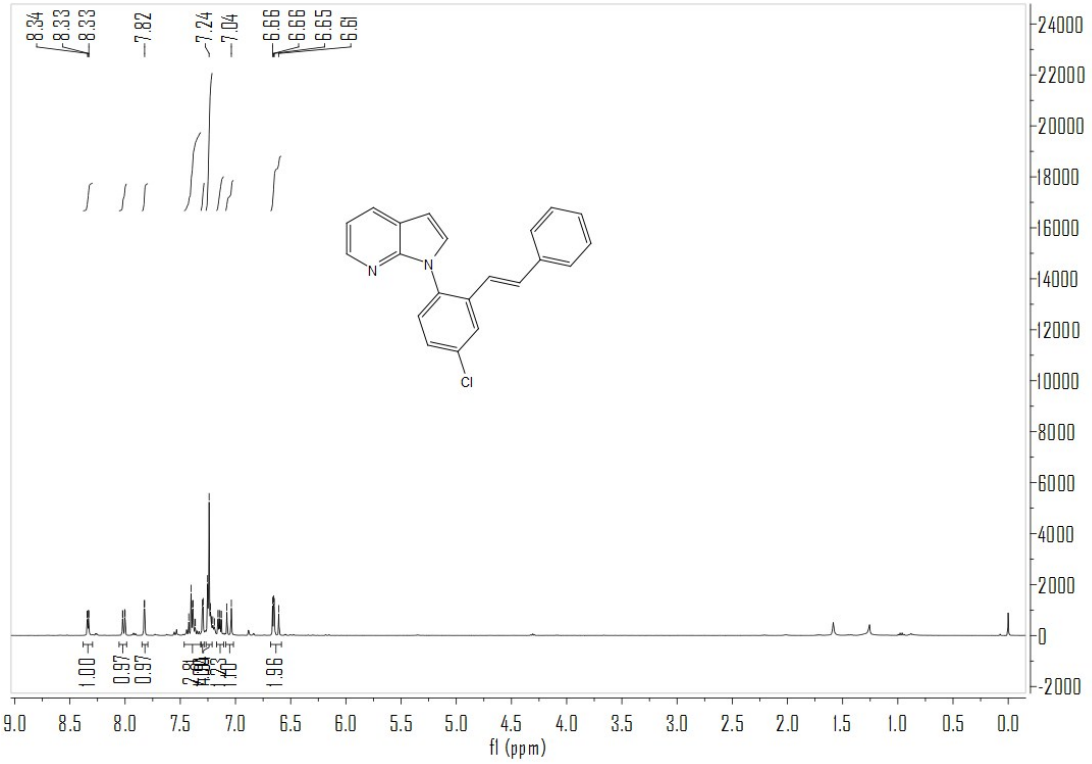
^{1}H NMR of 3a



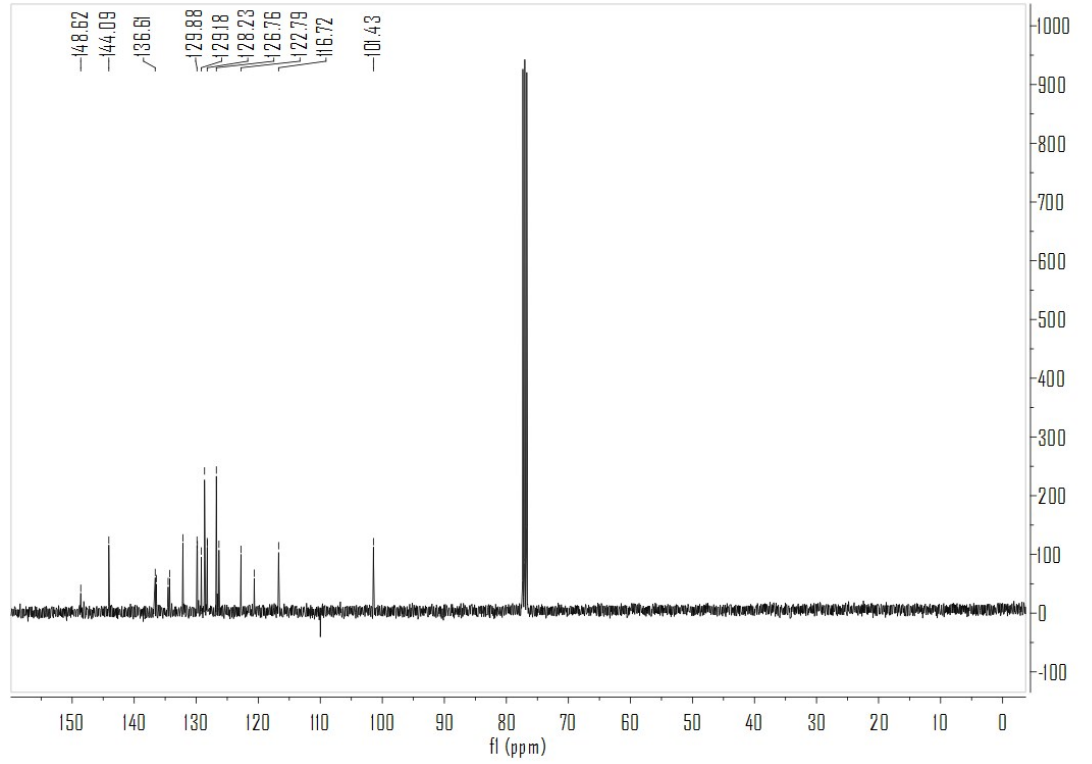
^{13} C NMR of 3a



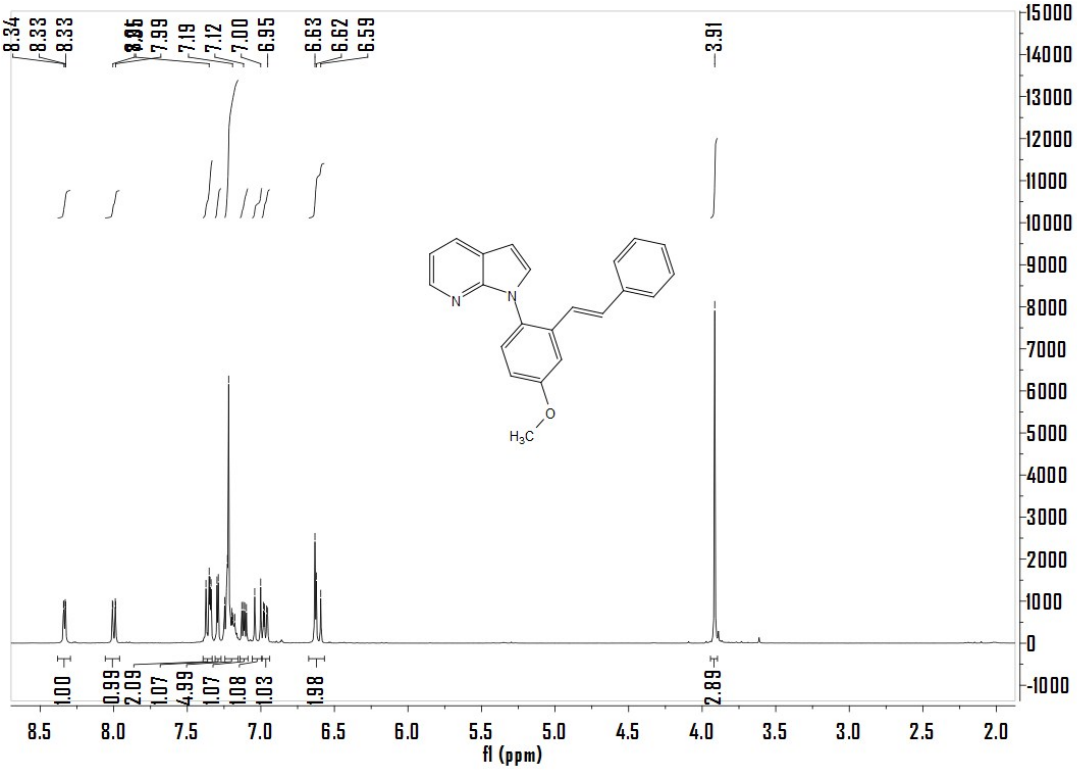
^{1}H NMR of 3b



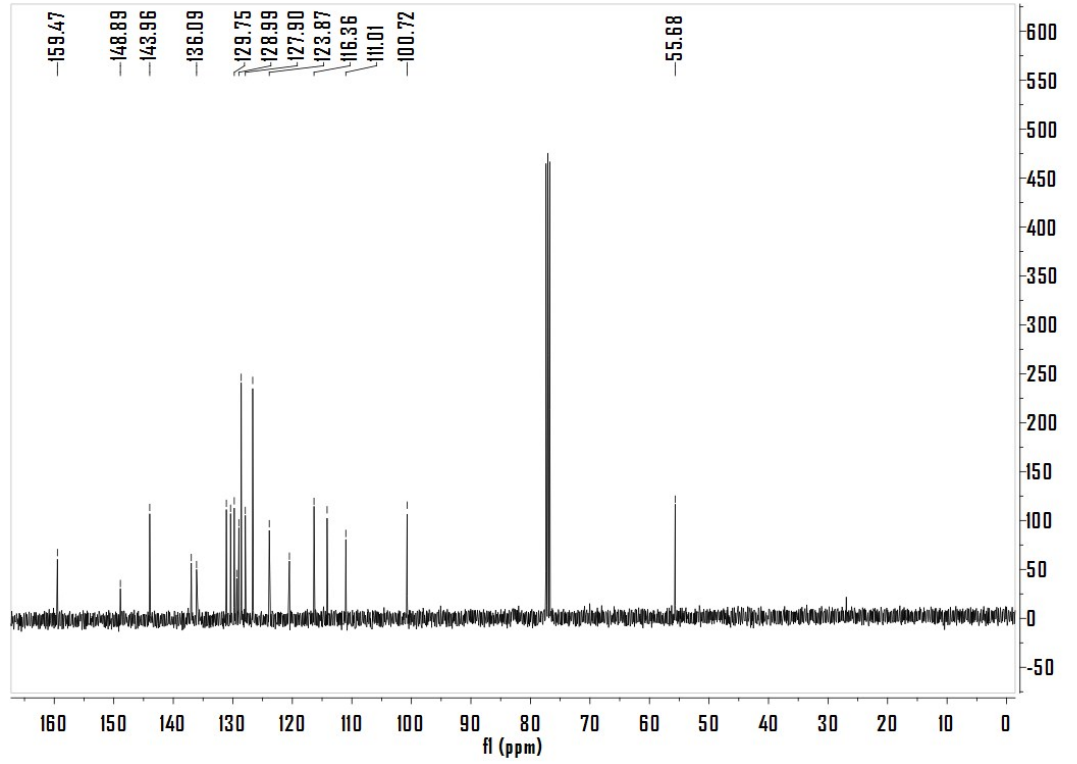
^{13} C NMR of 3b



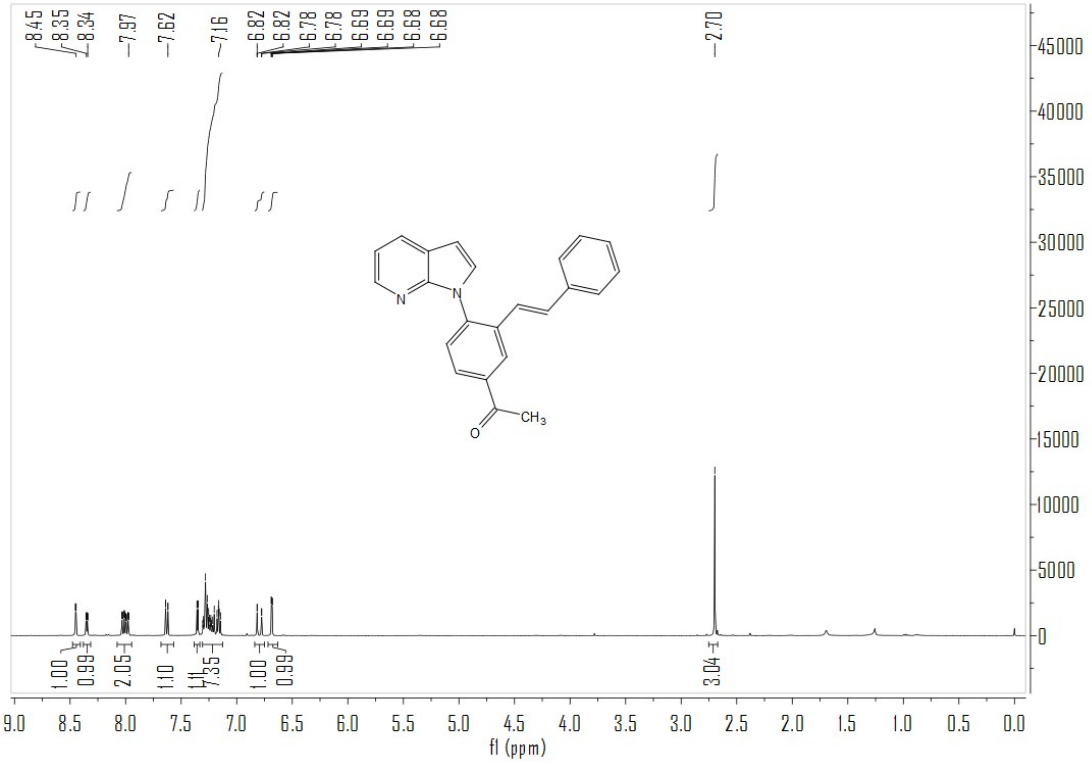
[1]H NMR of 3c



[13] C NMR of 3c



[1]H NMR of 3d



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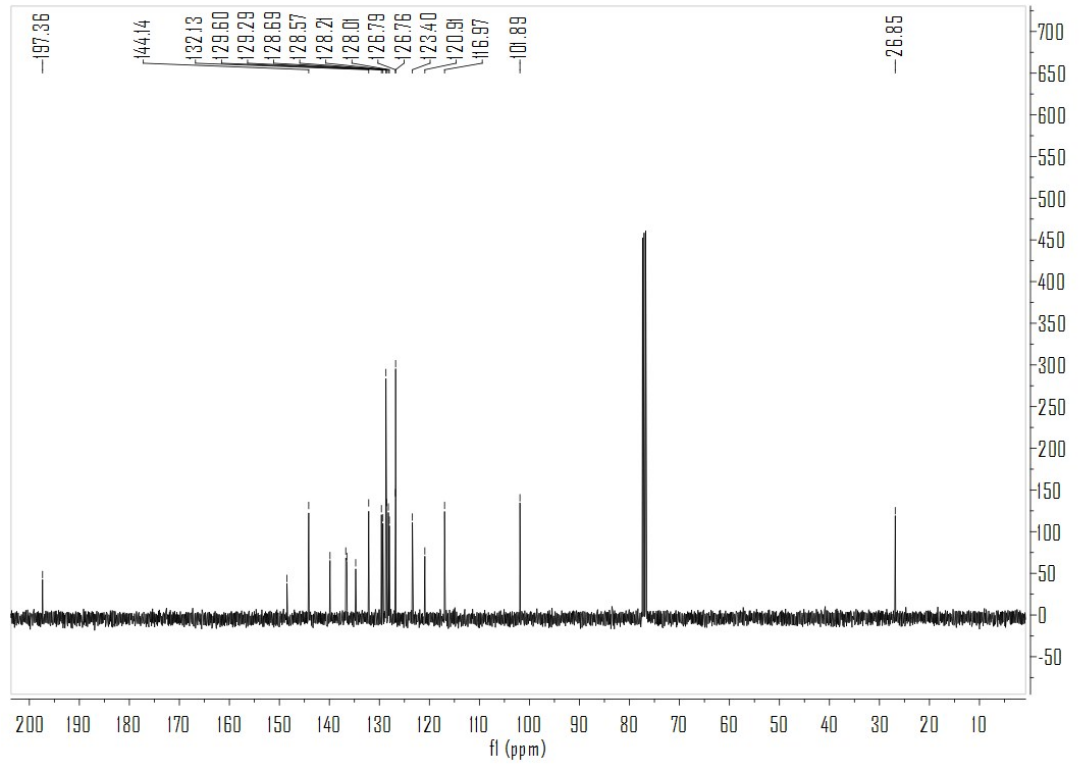
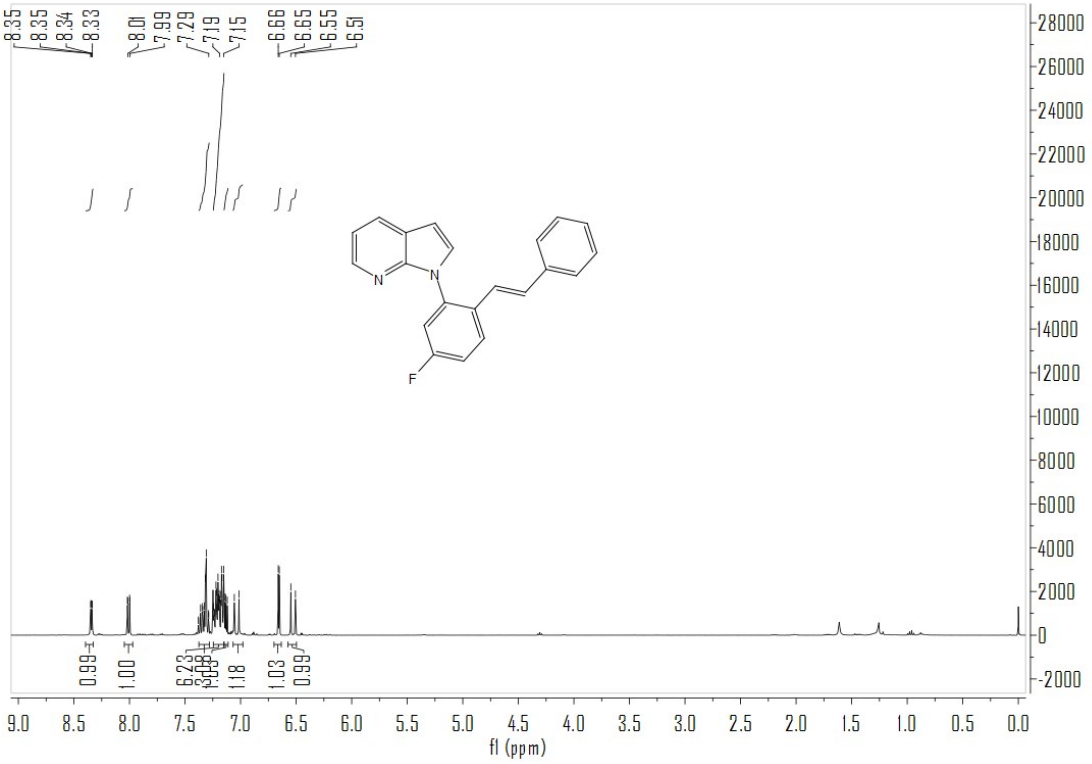


[1]H NMR of 3e



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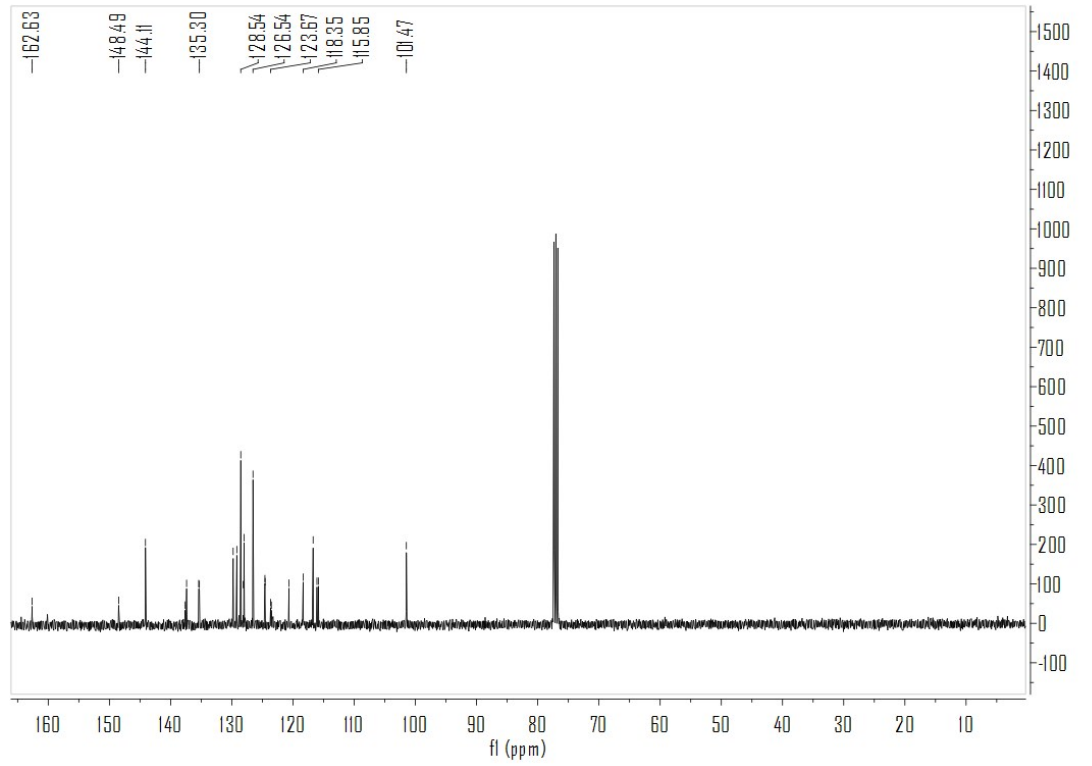
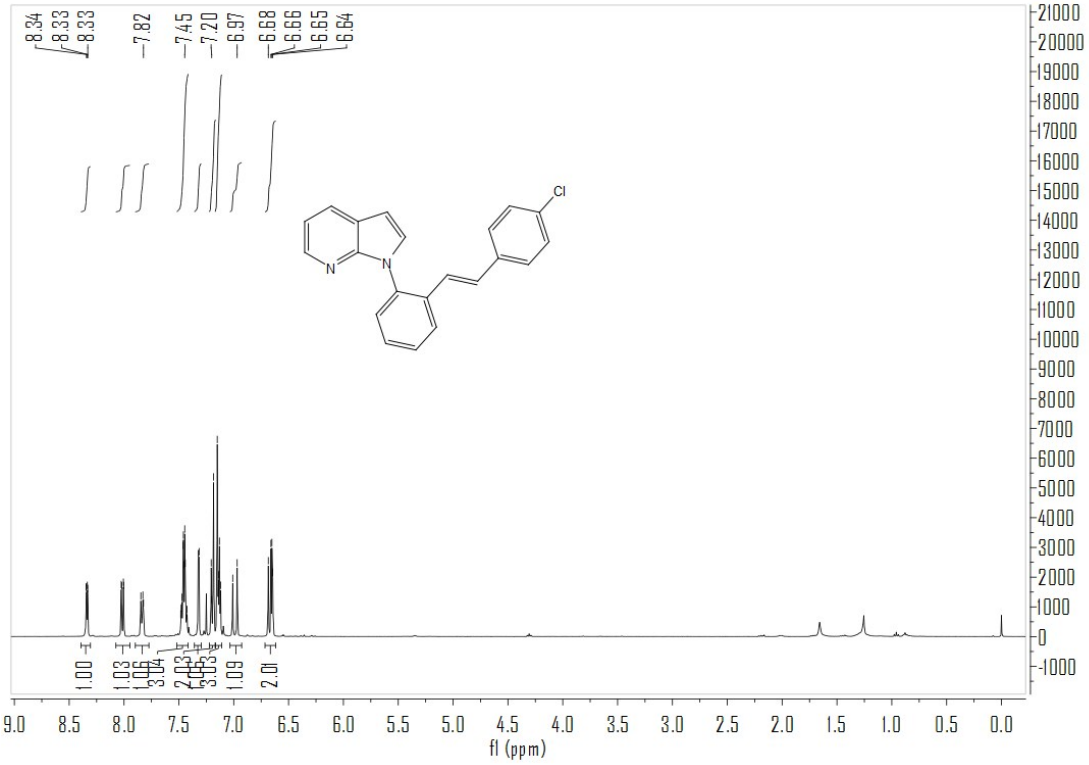
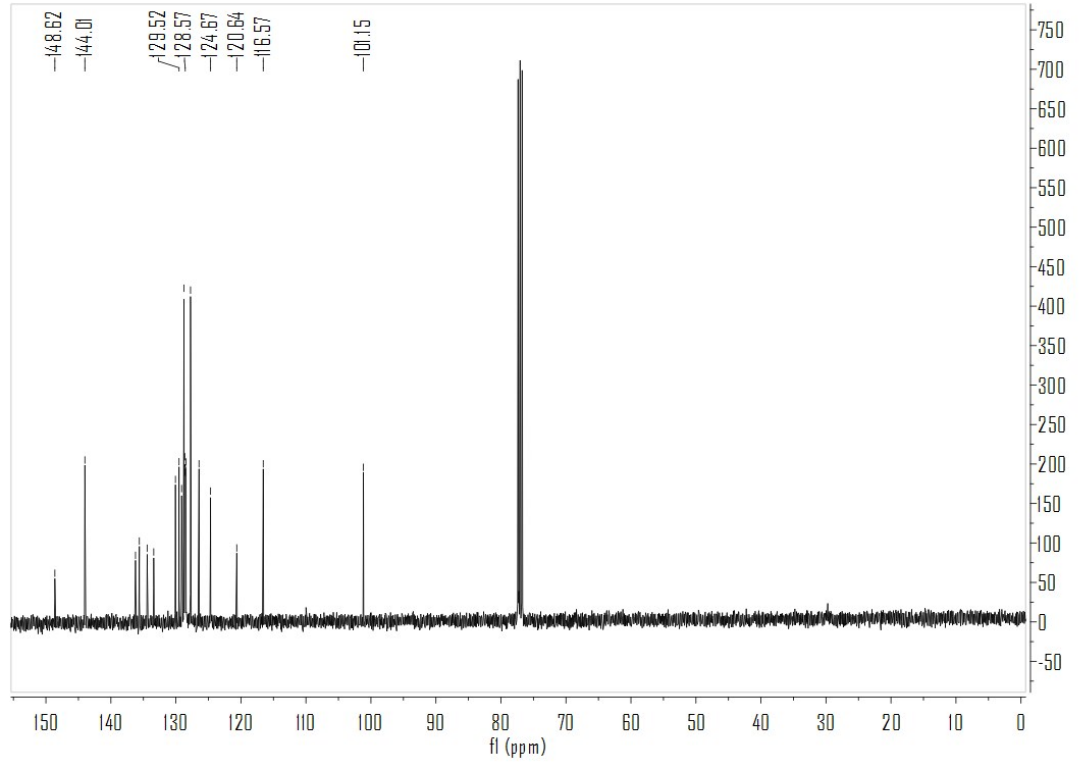


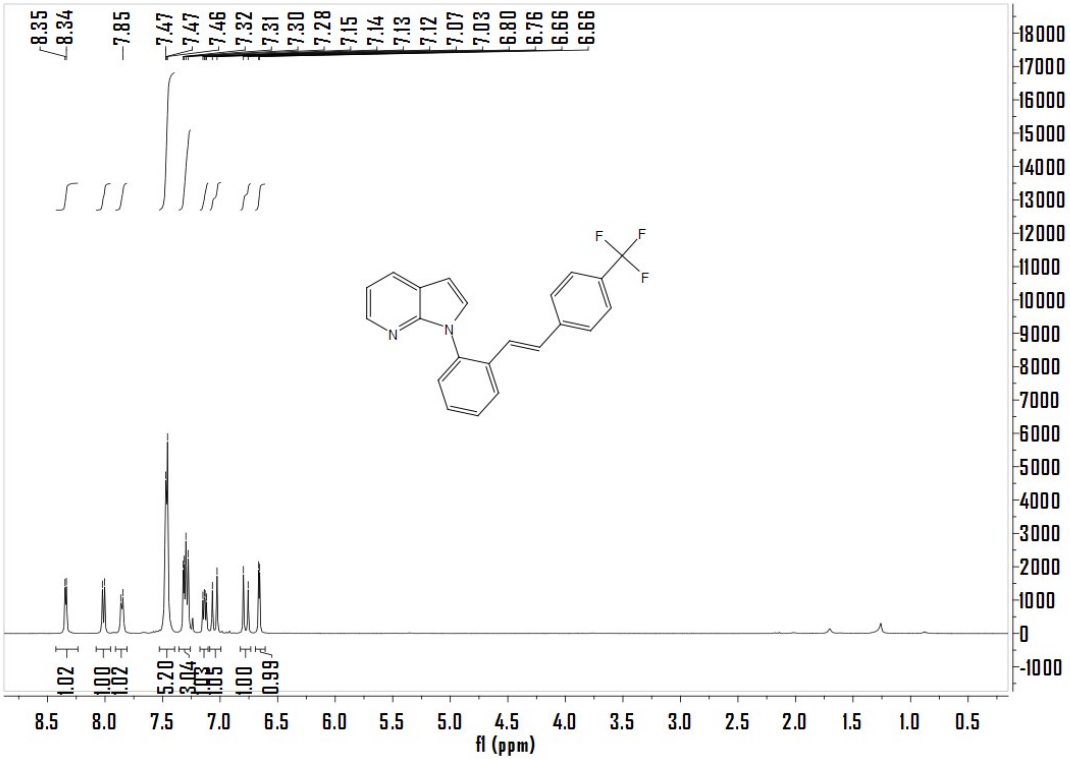
^{1}H NMR of 3f



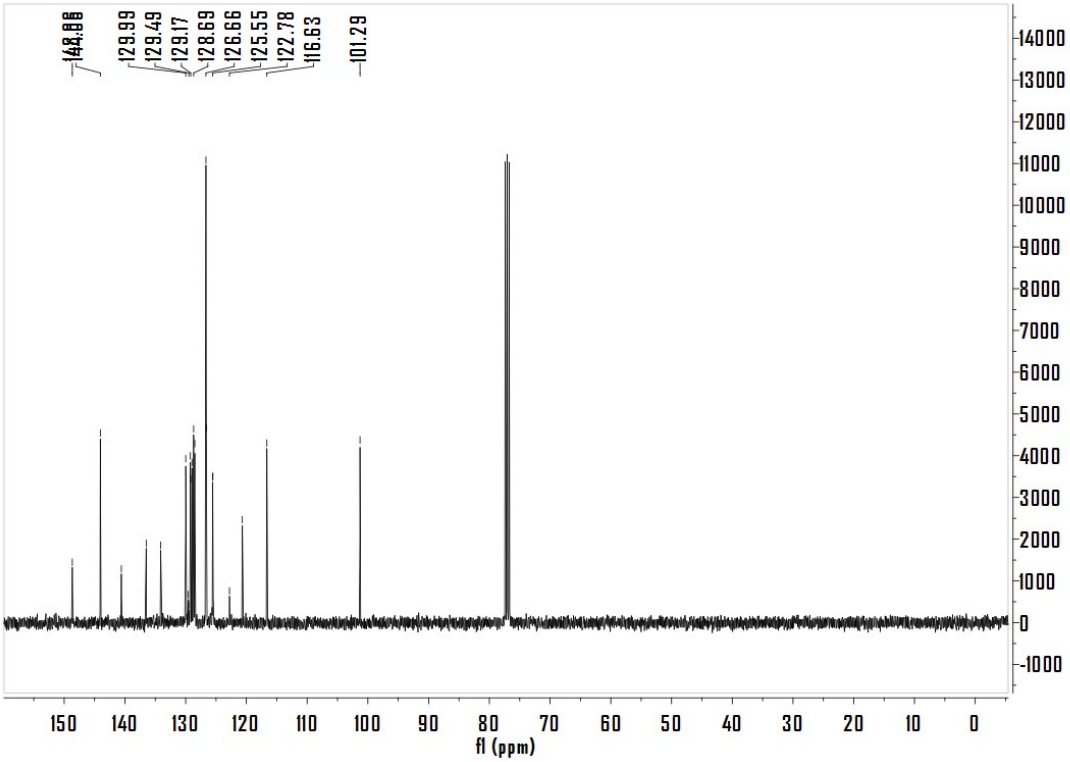
^{13} C NMR of 3f



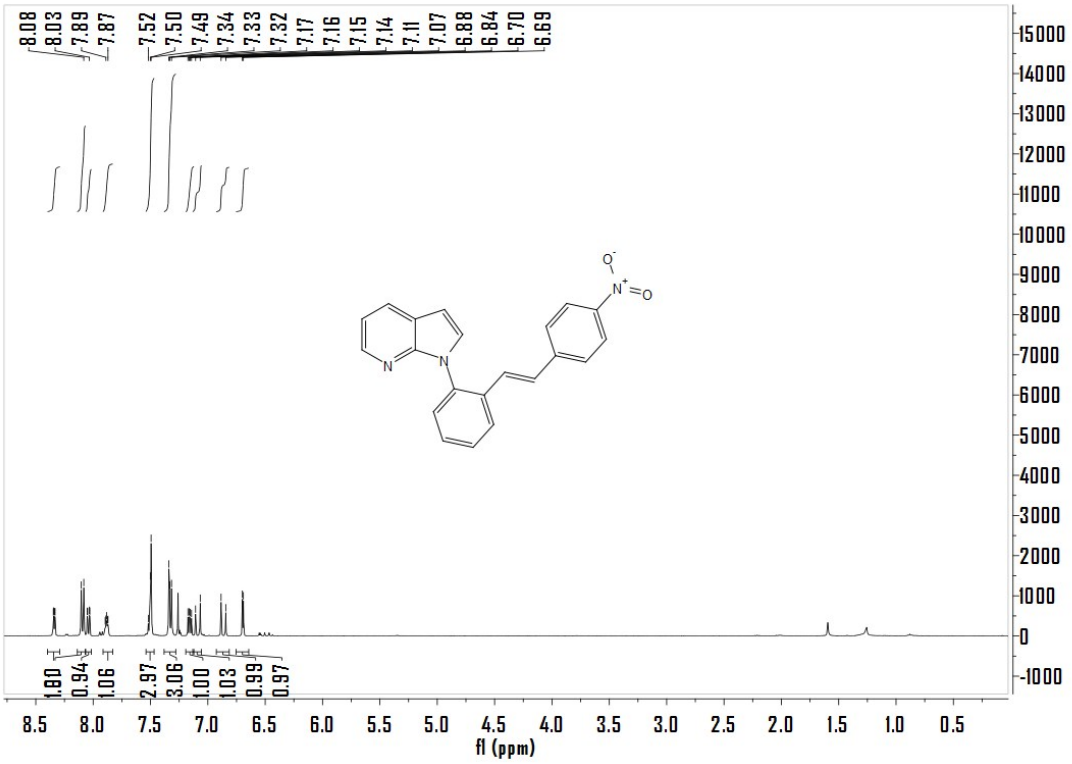
^{1}H NMR of 3g



^{13} C NMR of 3g



^{1}H NMR of 3h



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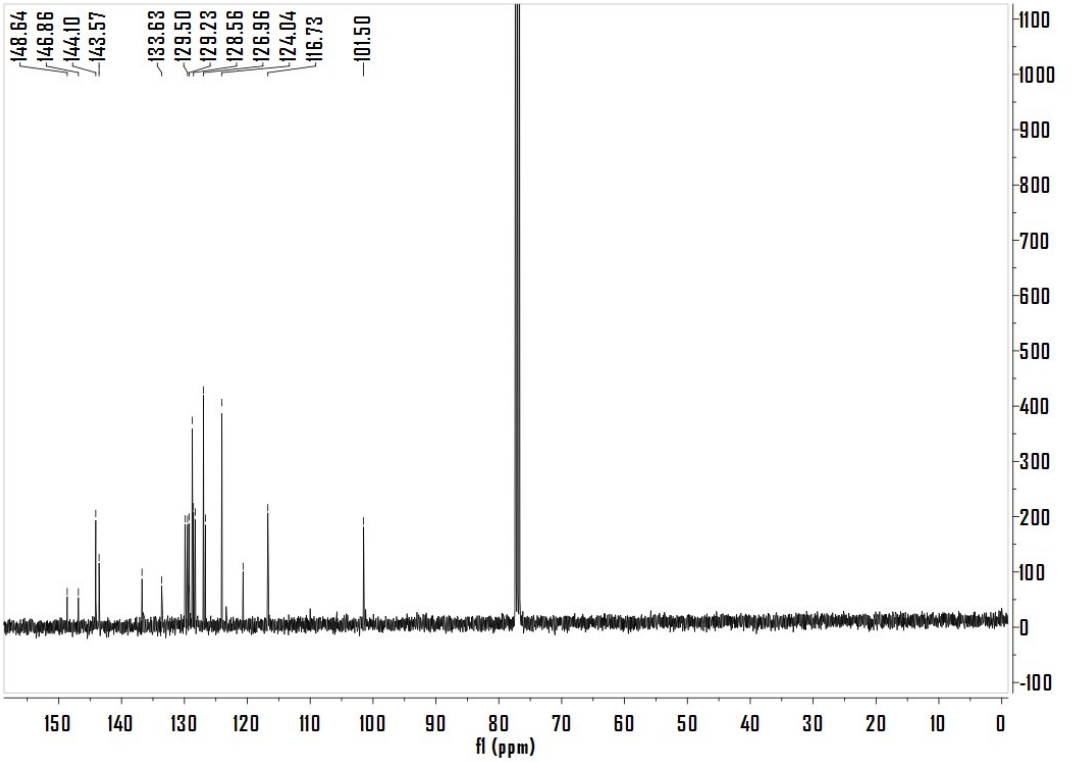
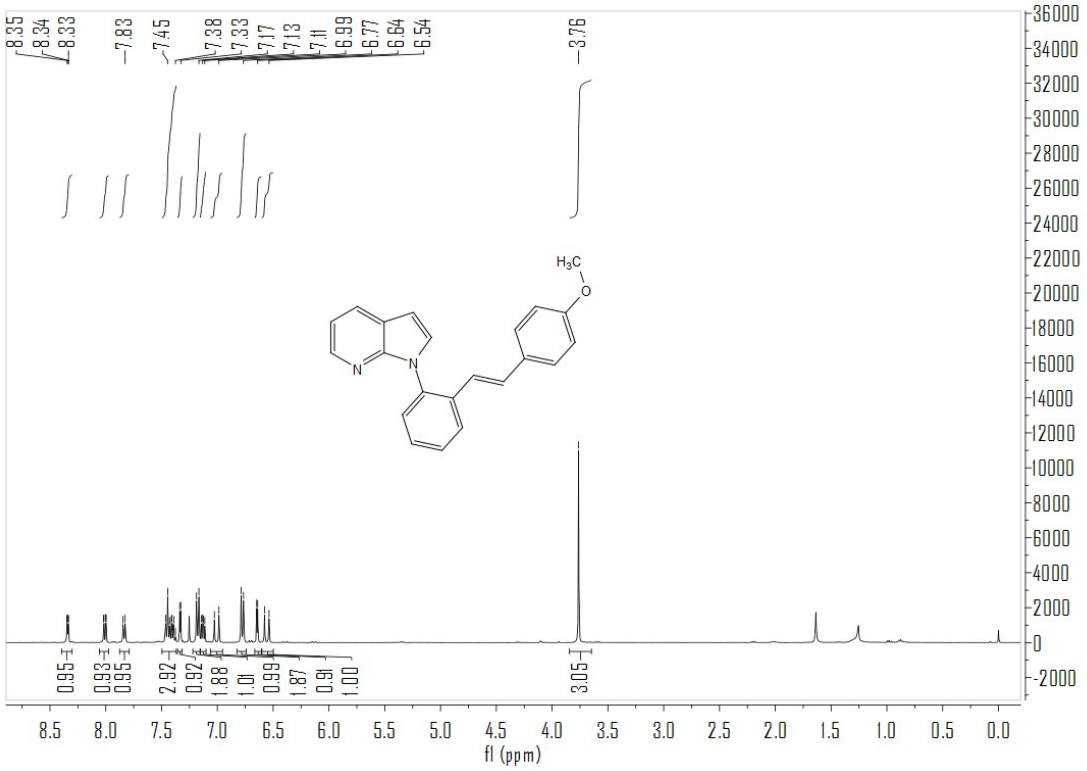


[1]H NMR of 3i



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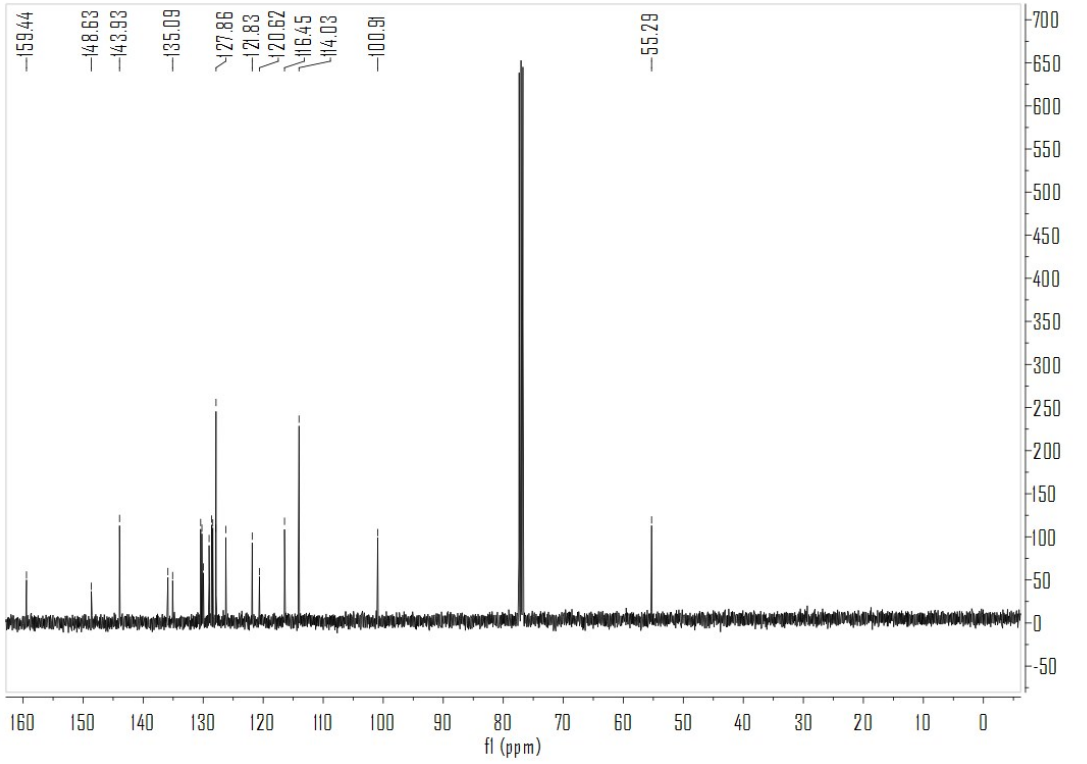
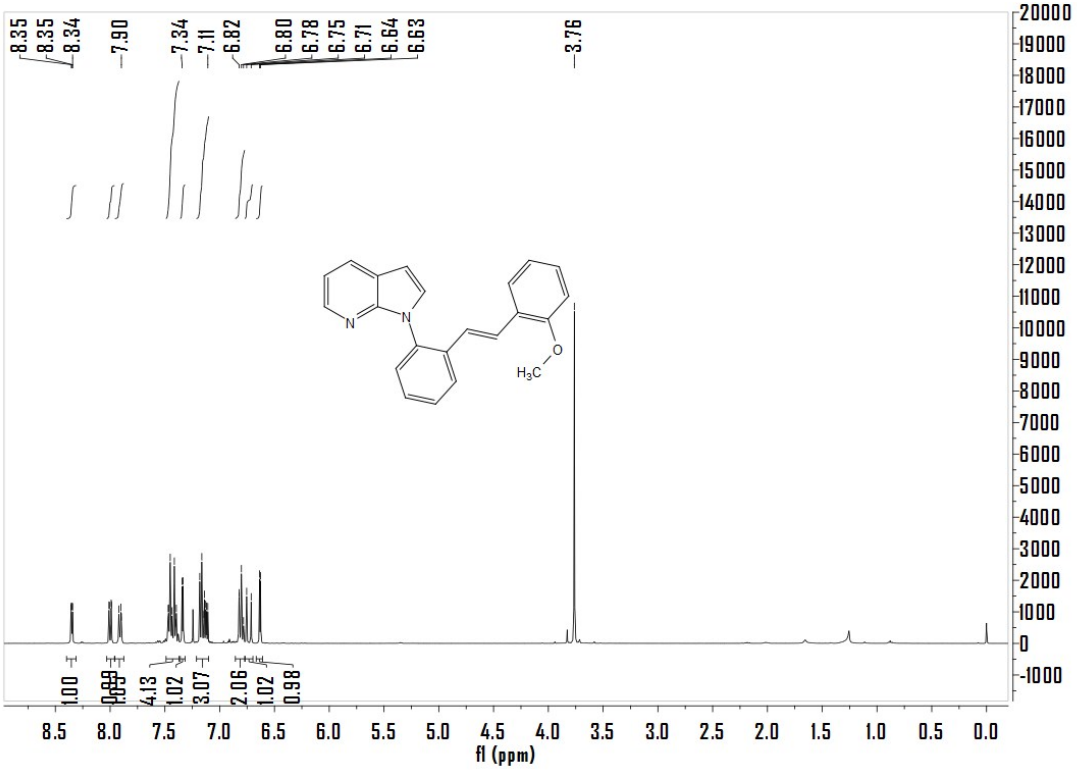


^{1}H NMR of 3j



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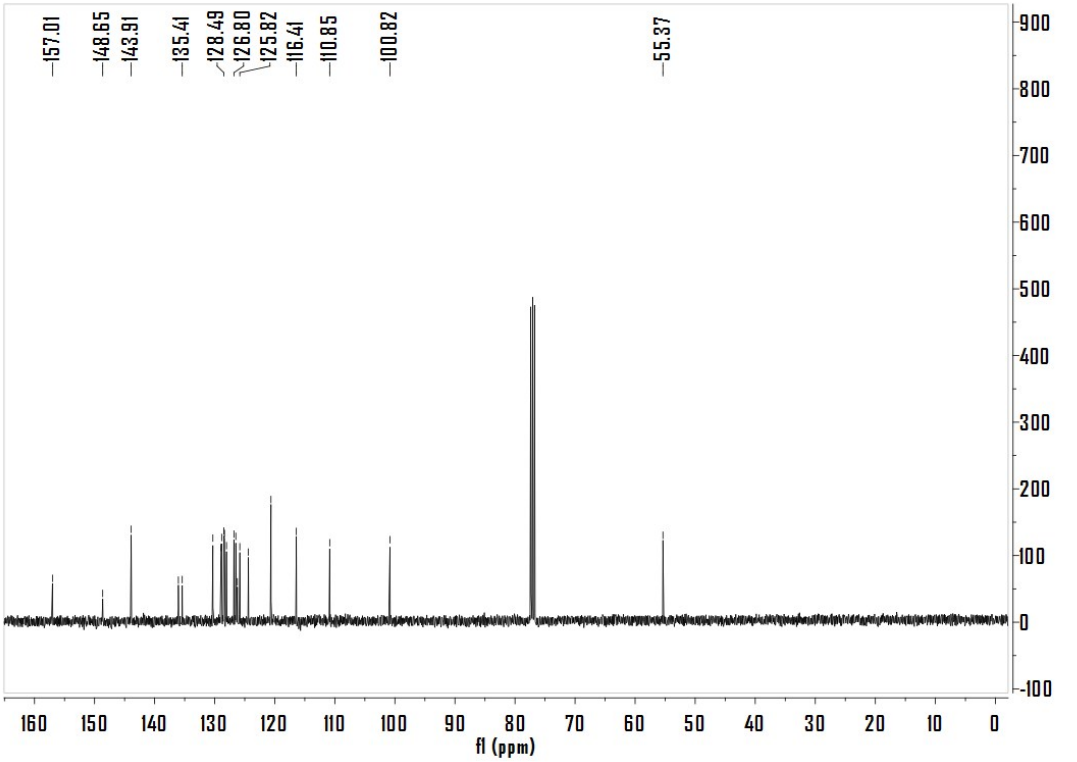
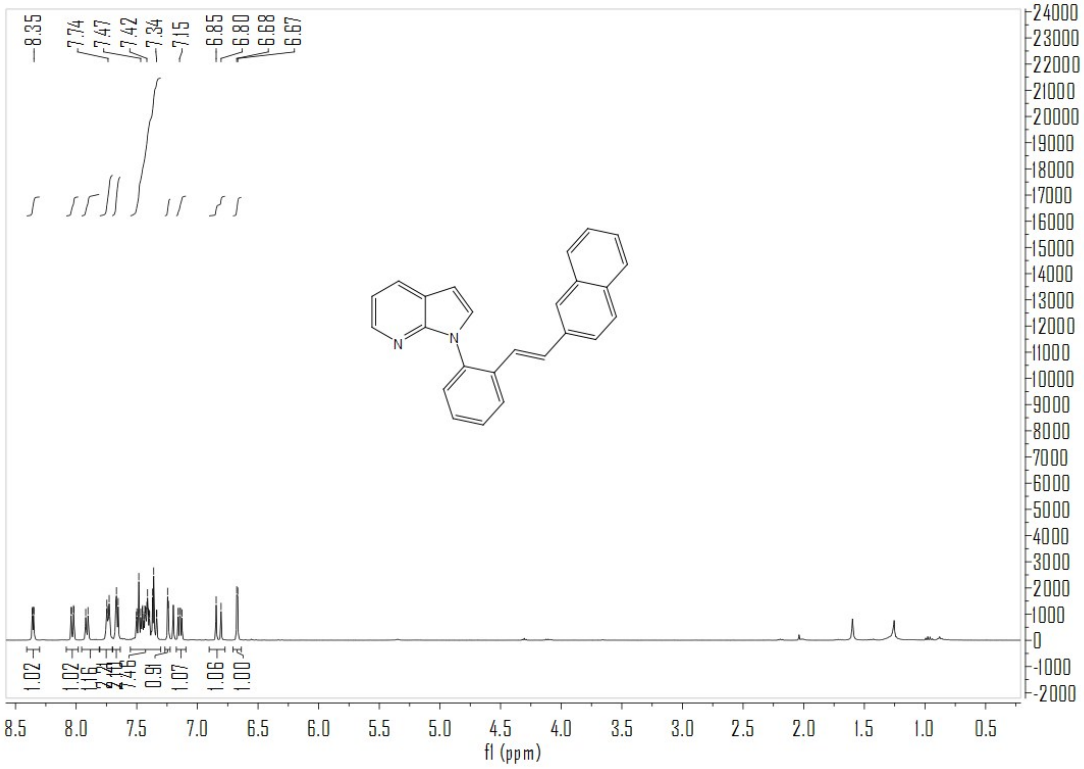


^{1}H NMR of 3k



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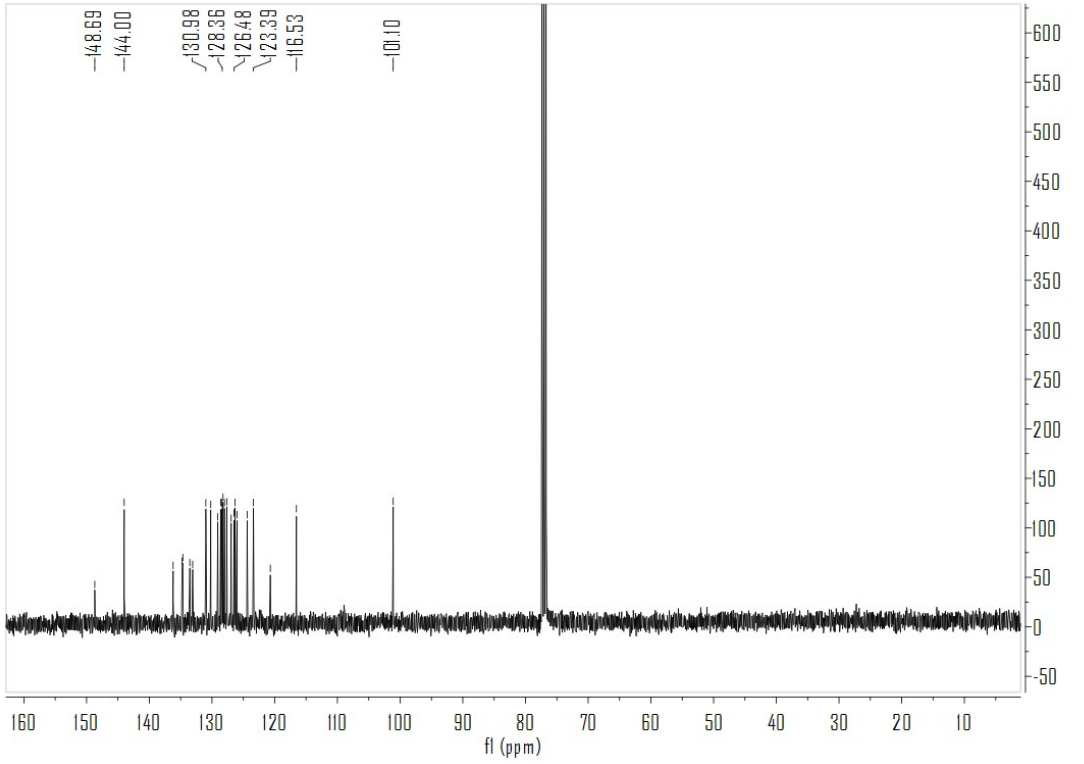
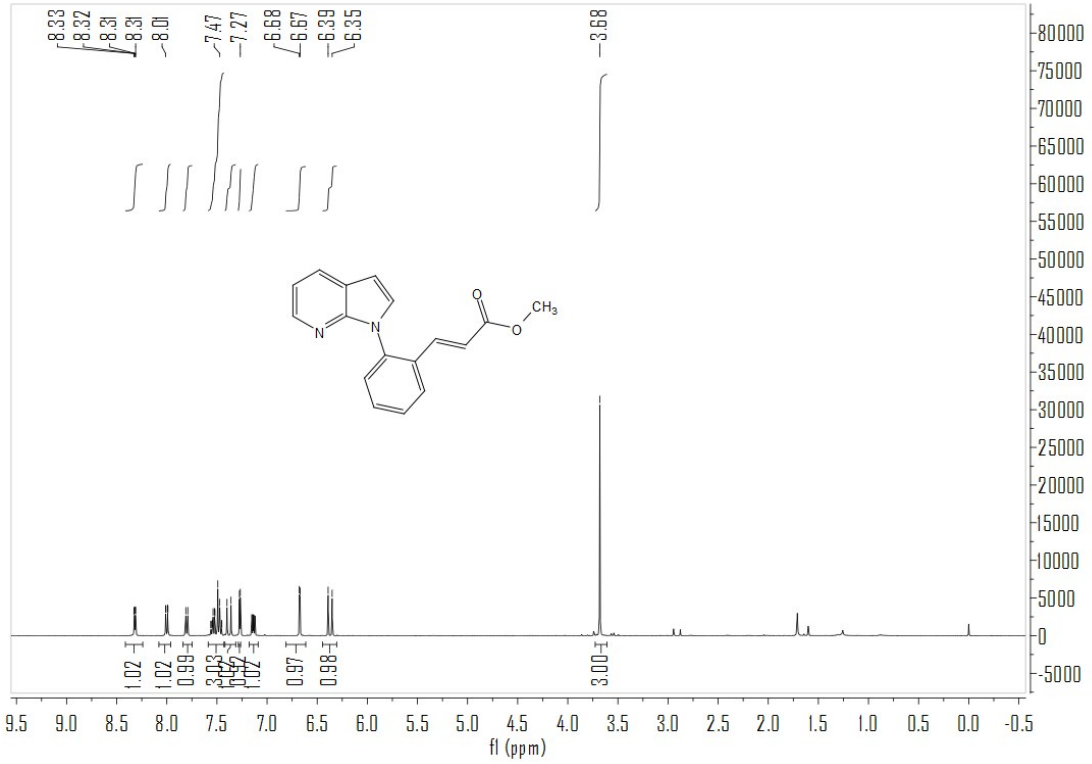


^{1}H NMR of 3l



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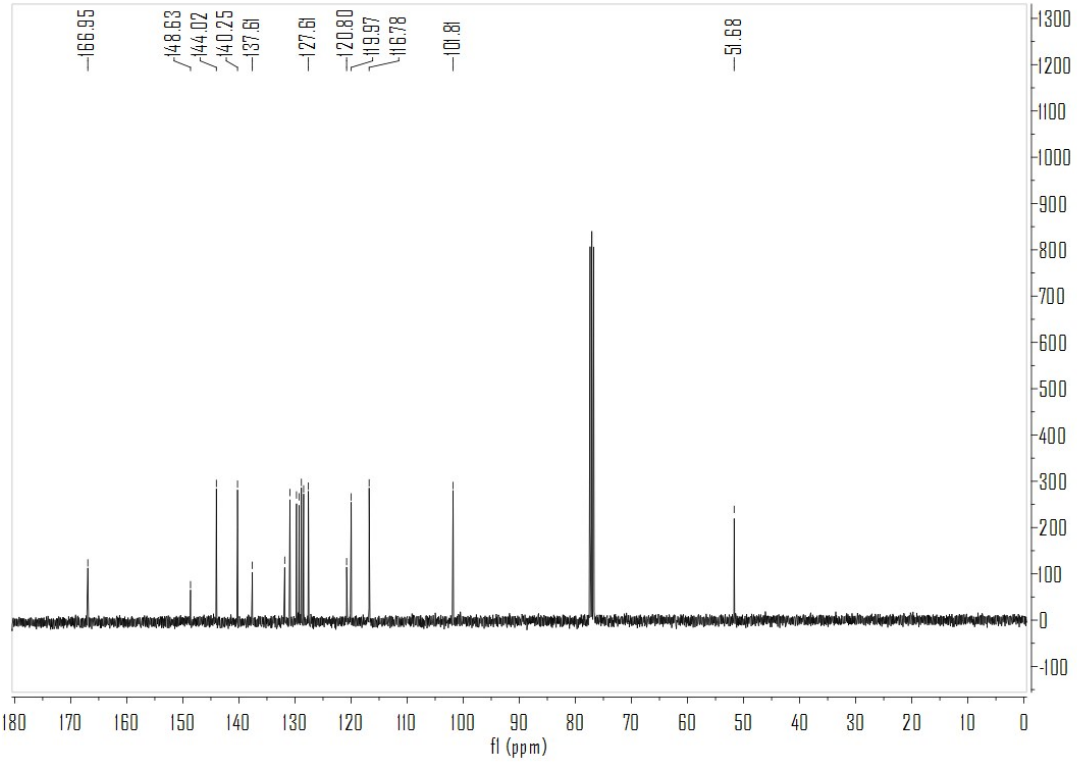

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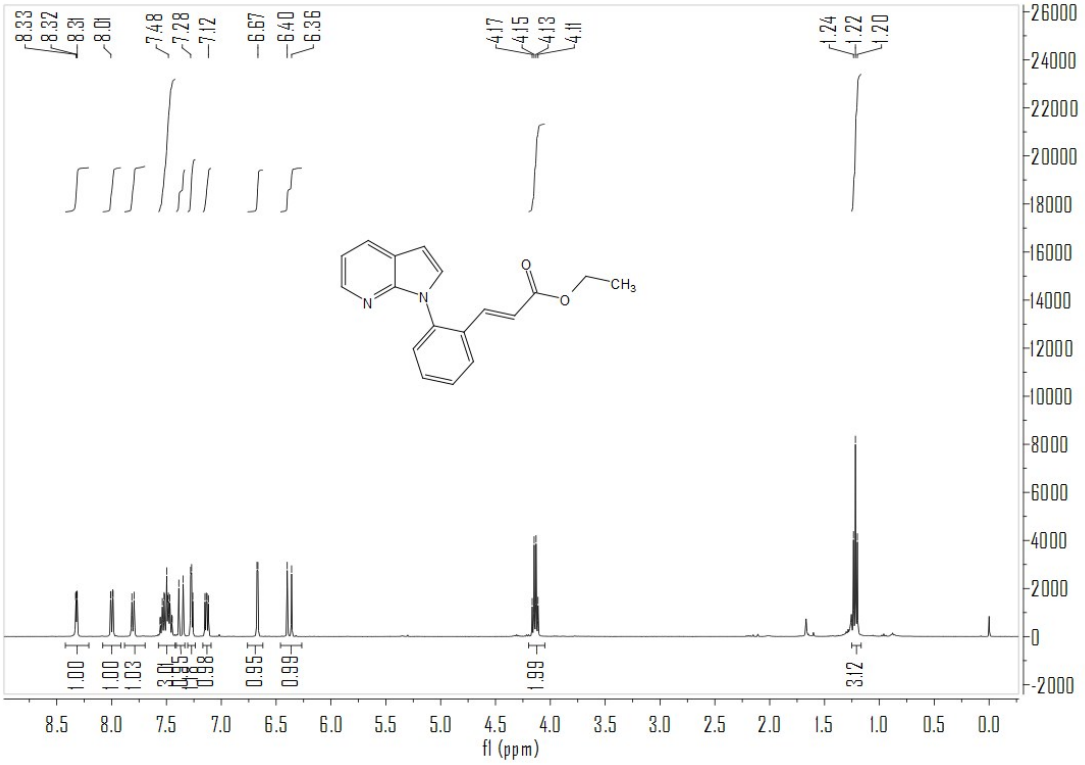

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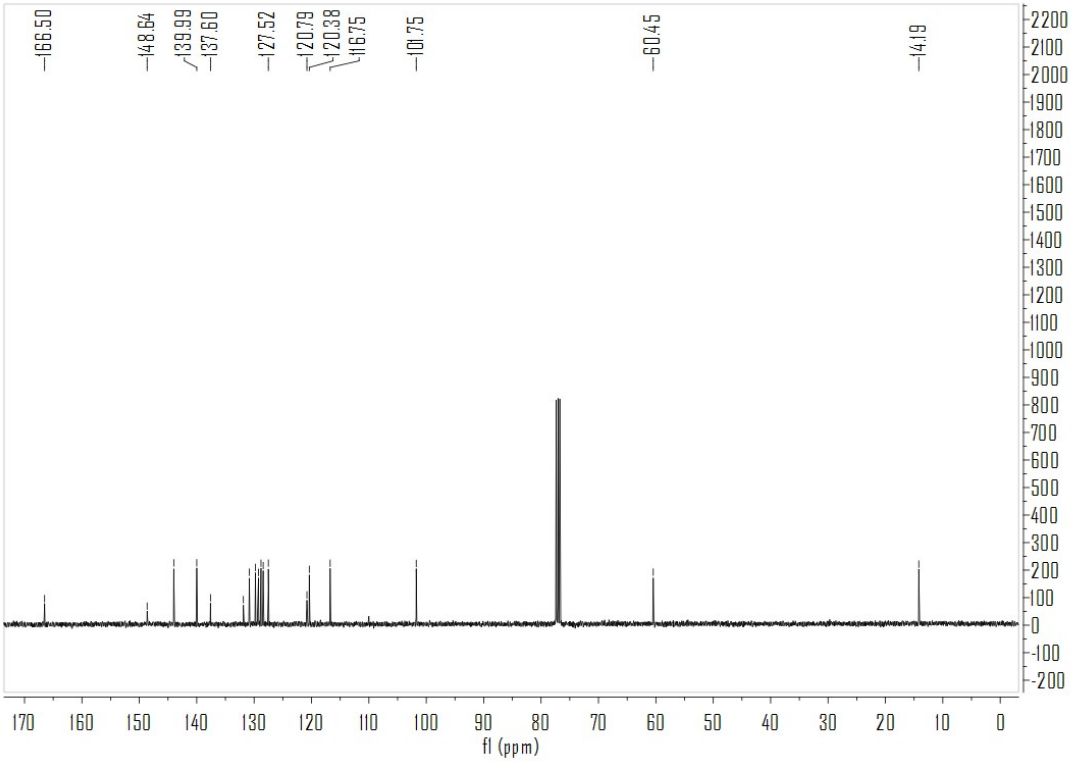
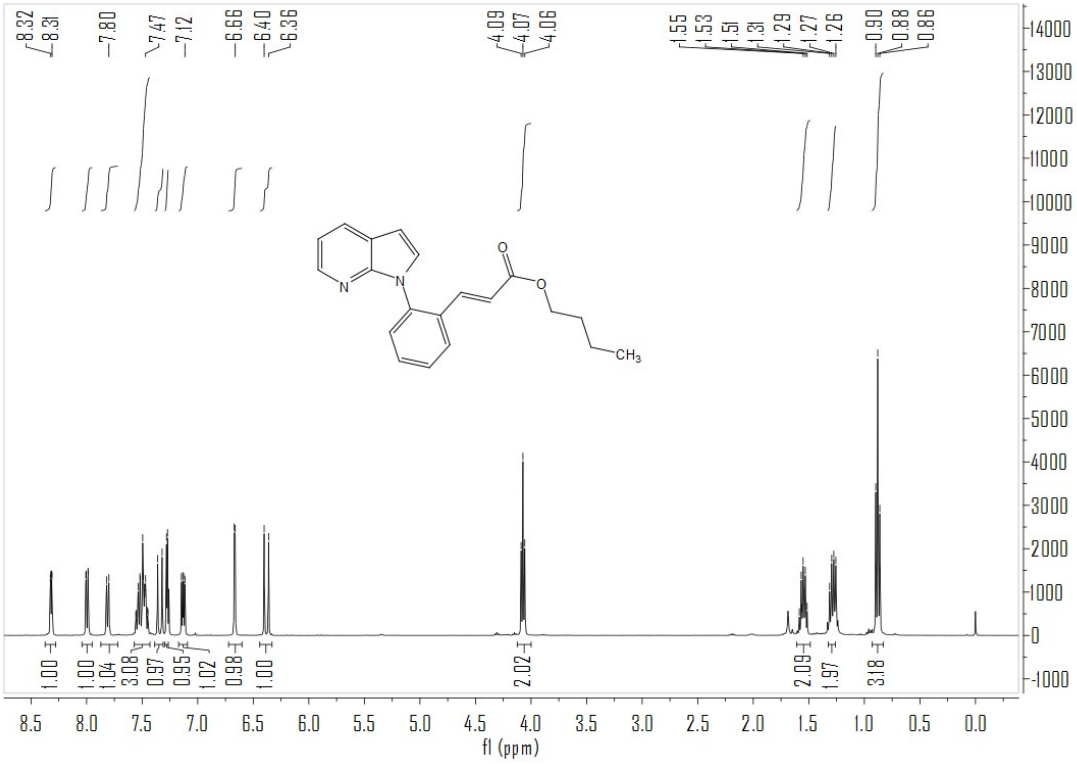
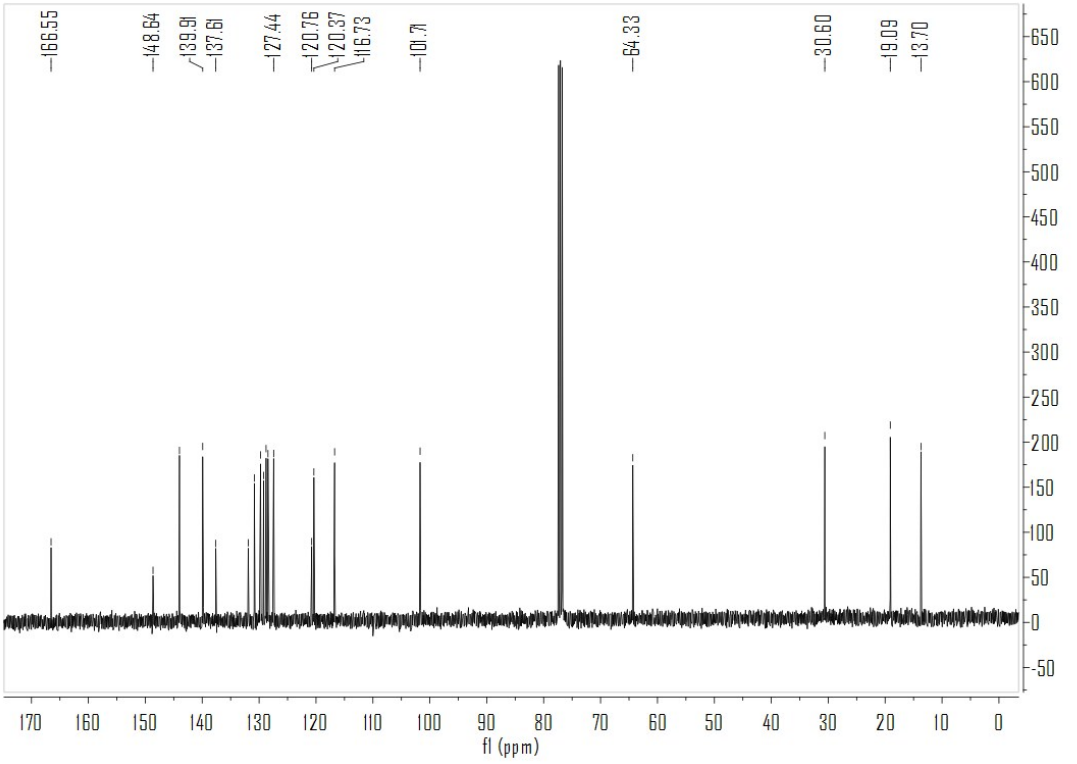


^{1}H NMR of 3n



^{13} C NMR of 3n



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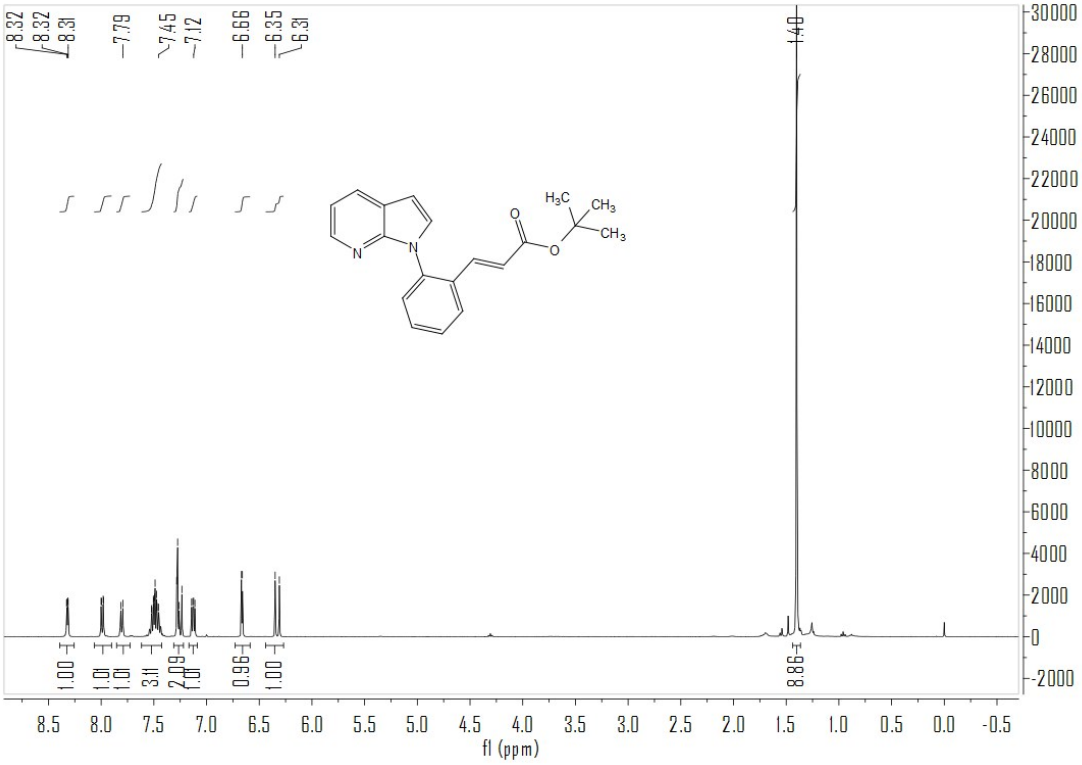

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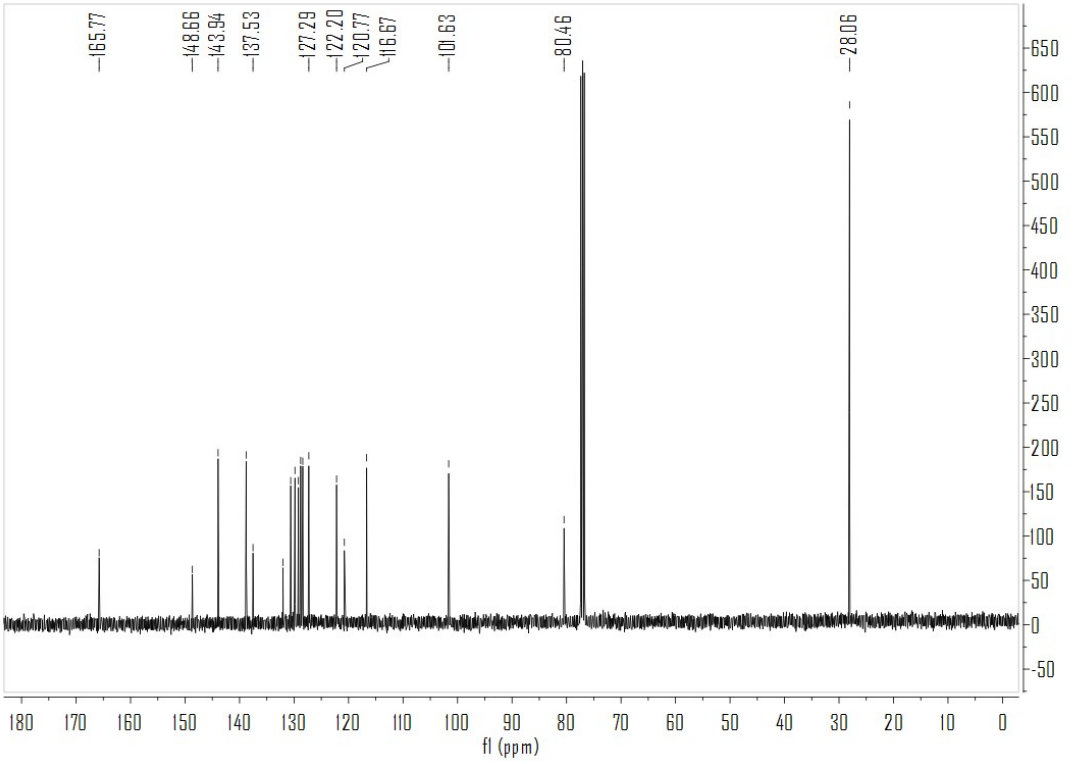
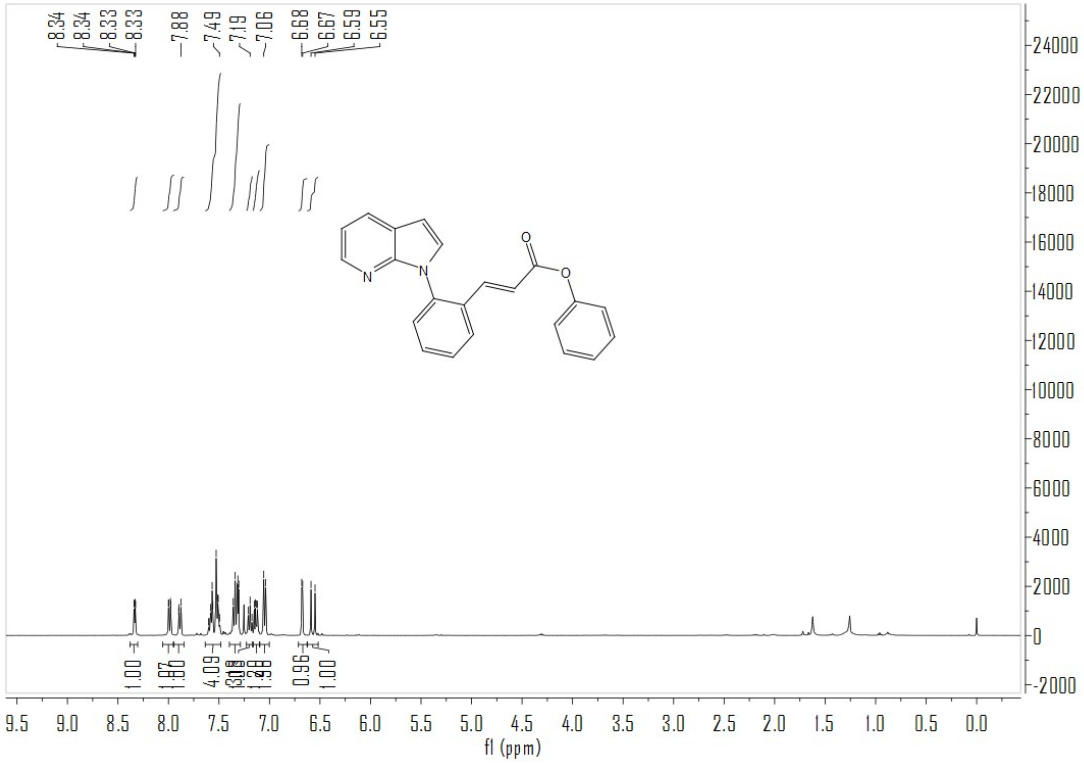


[1]H NMR of 3p



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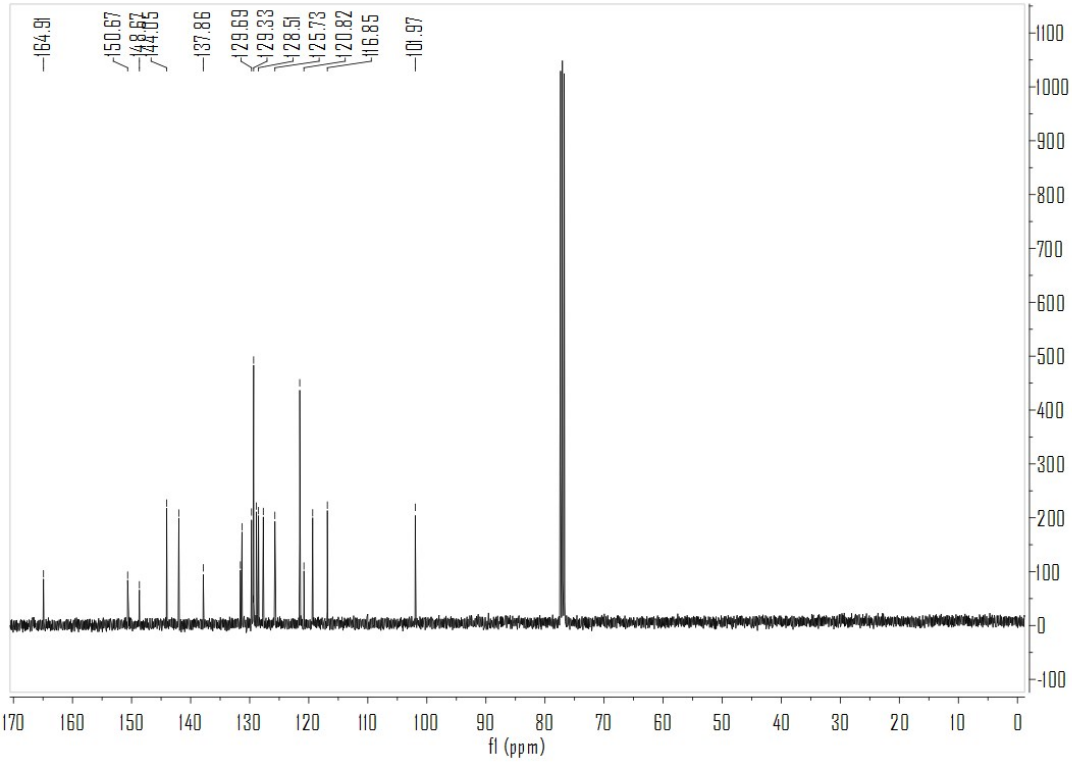

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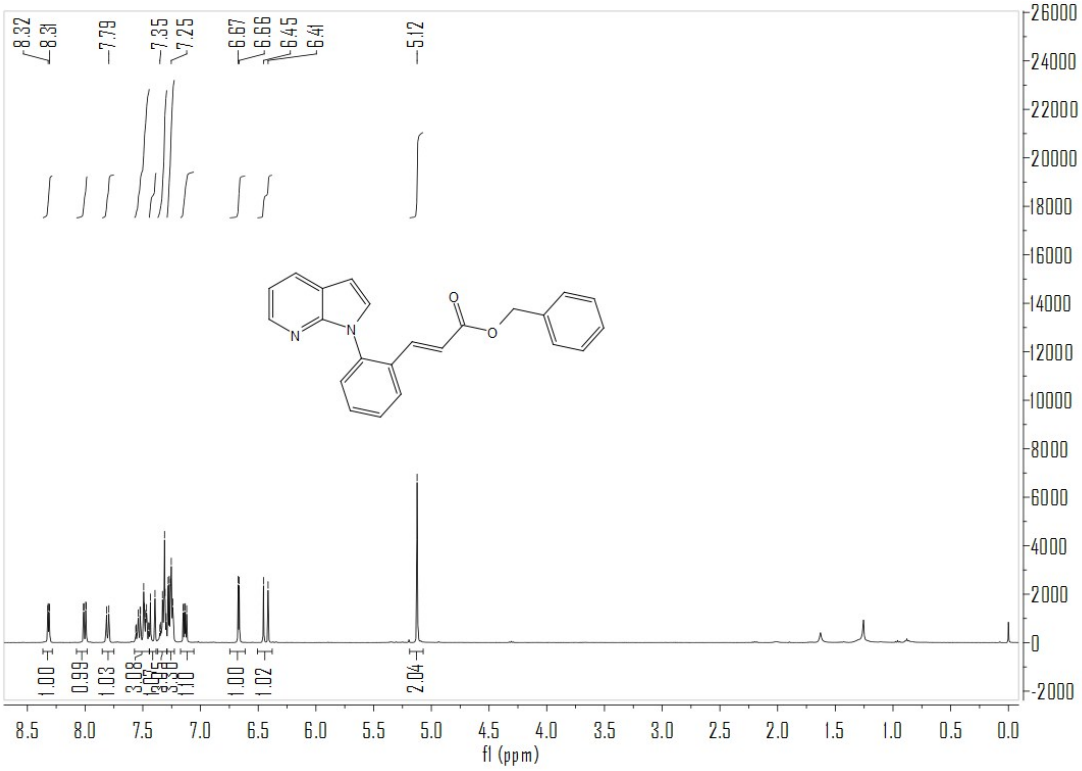
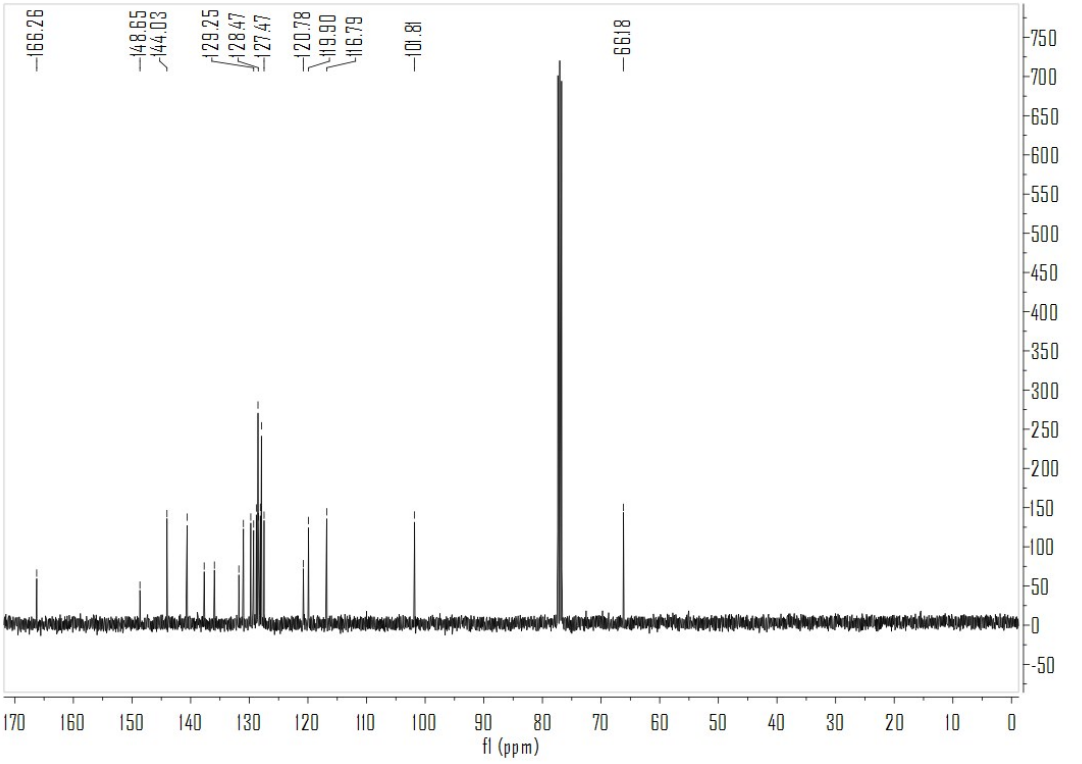
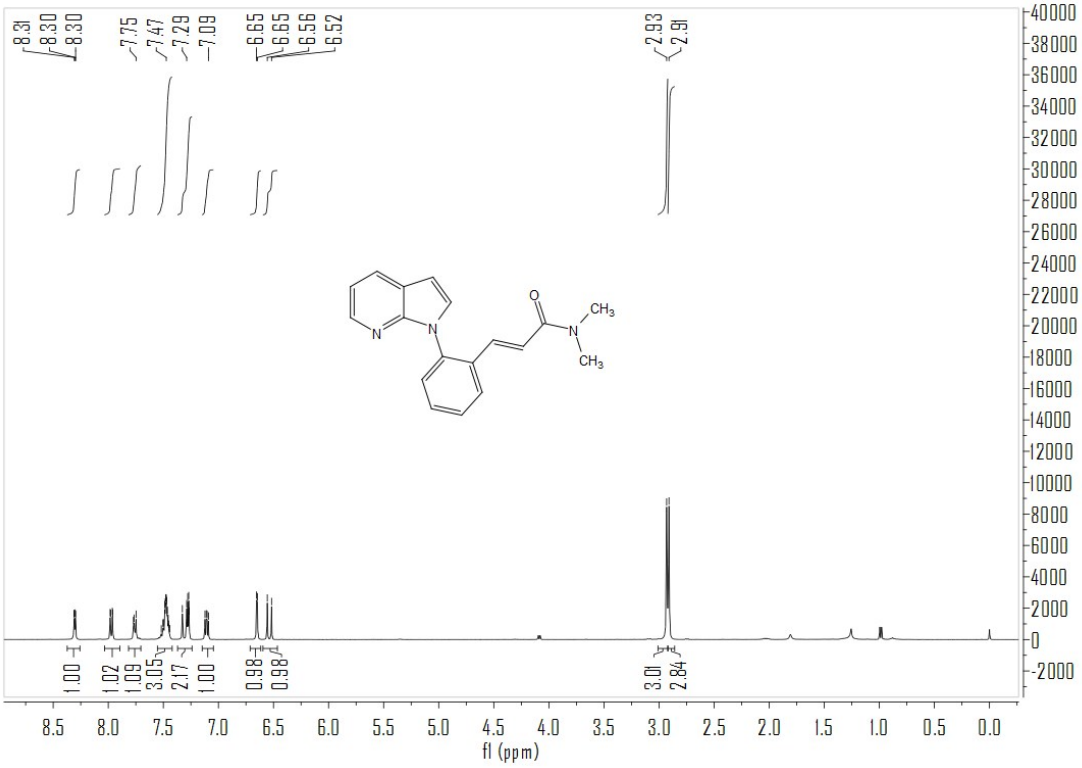


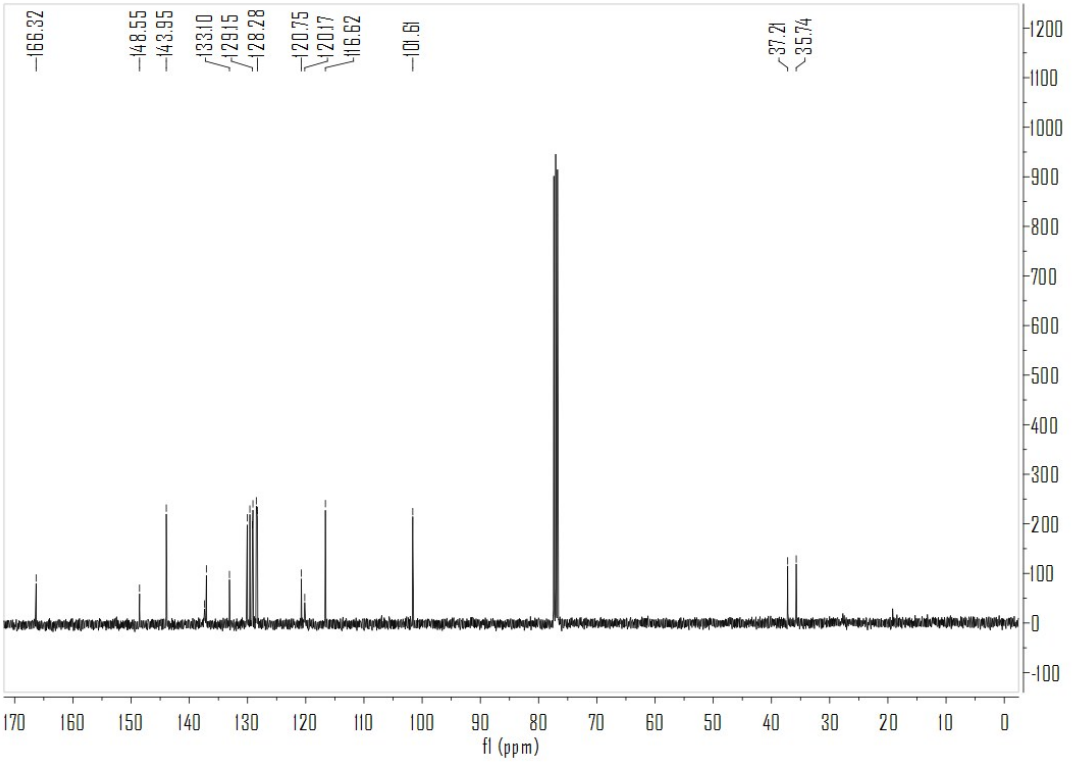
[13] C NMR of 3q



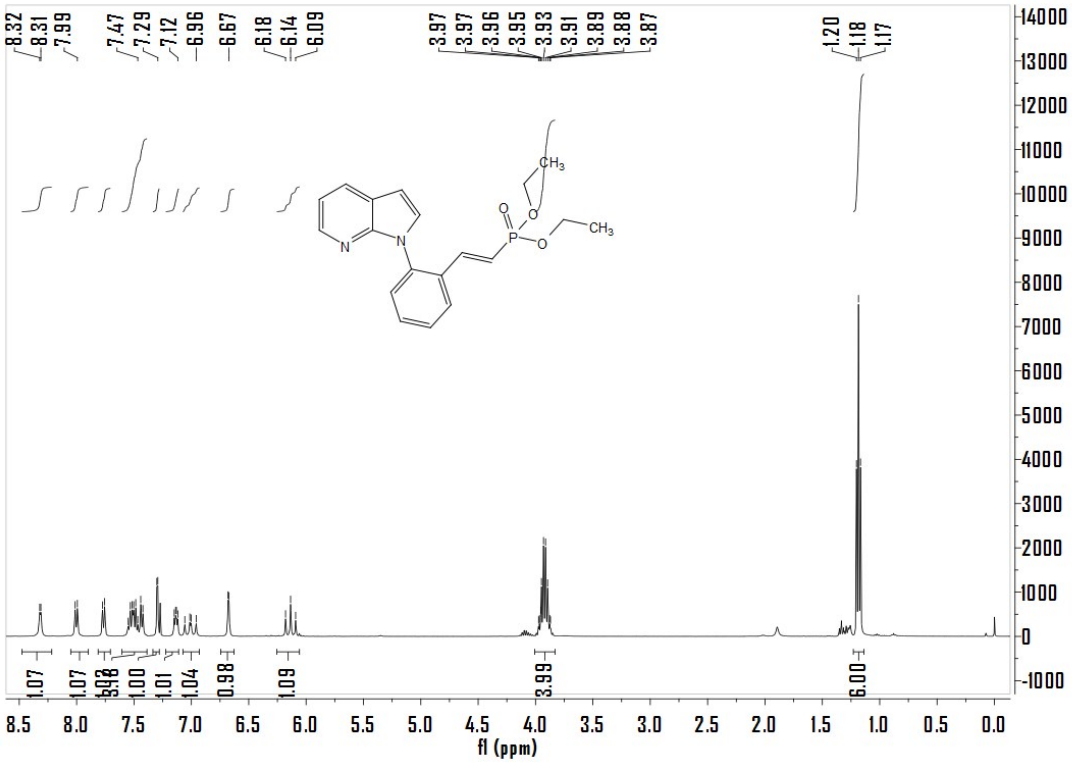
^{1}H NMR of 3r



^{13} C NMR of 3r



^{1}H NMR of 3s



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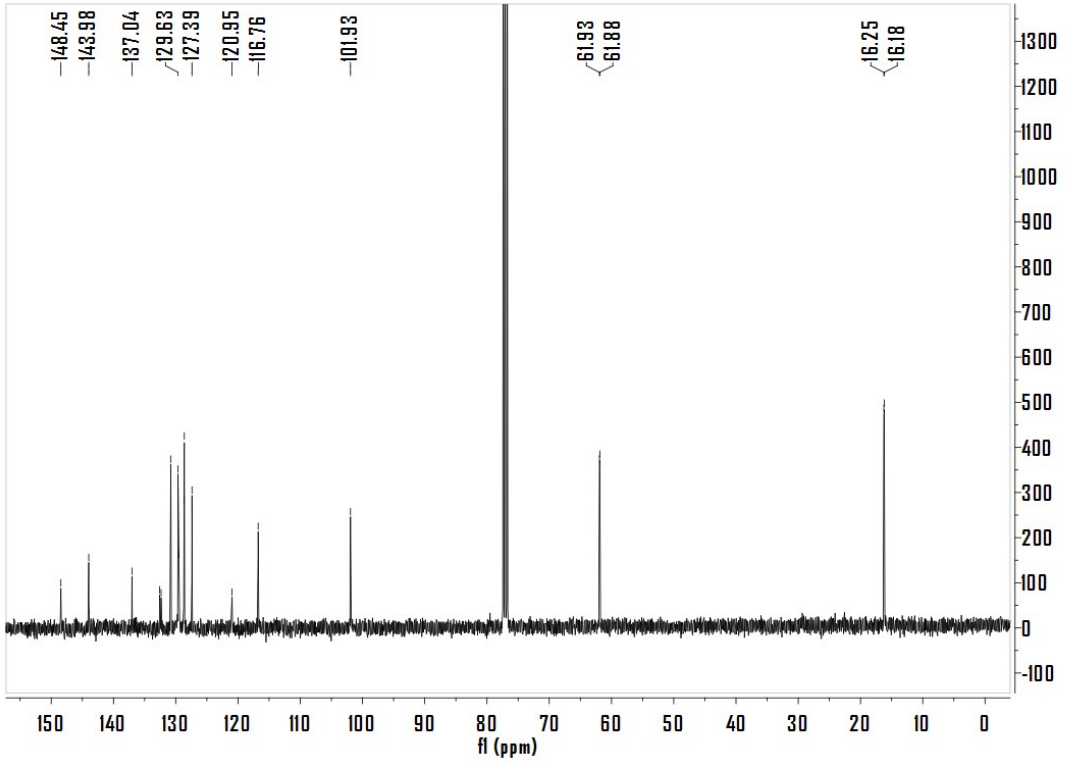
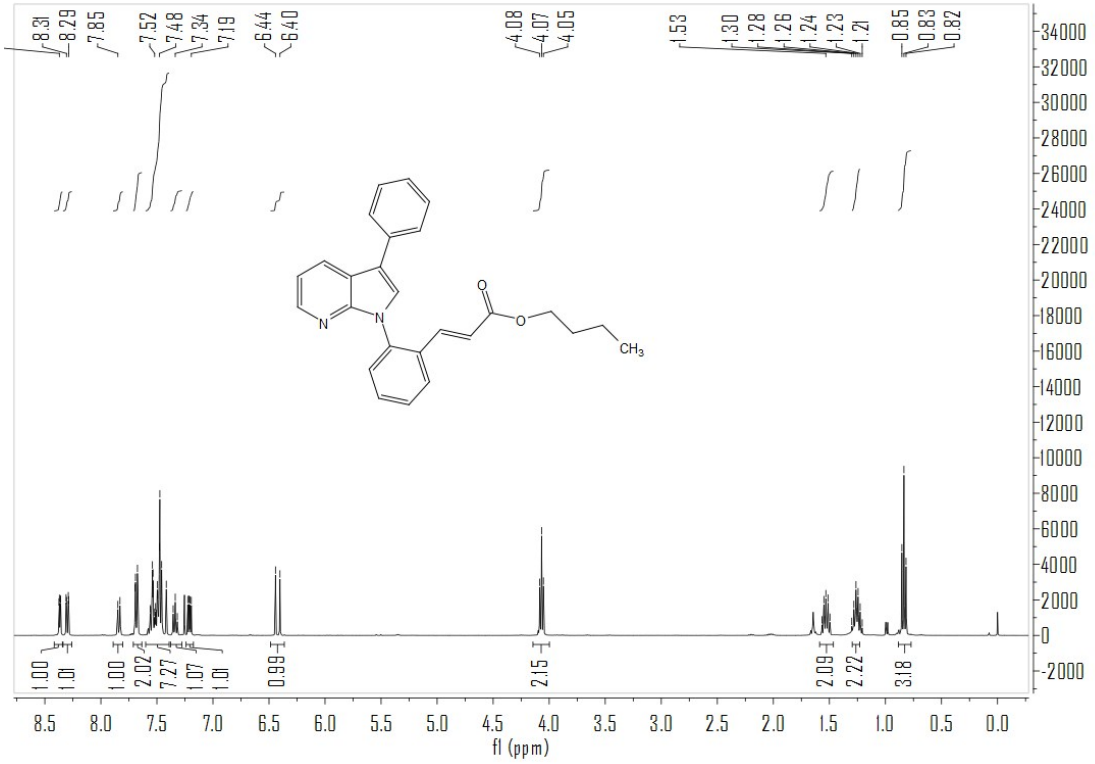


^{1}H NMR of 3t



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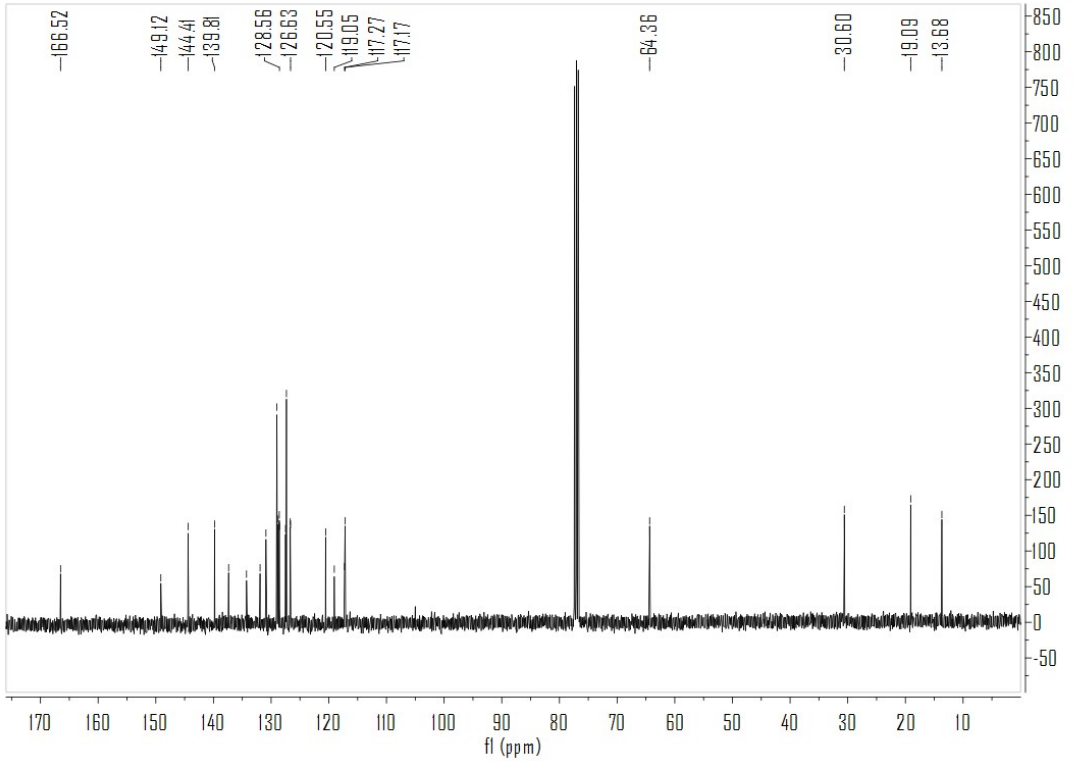
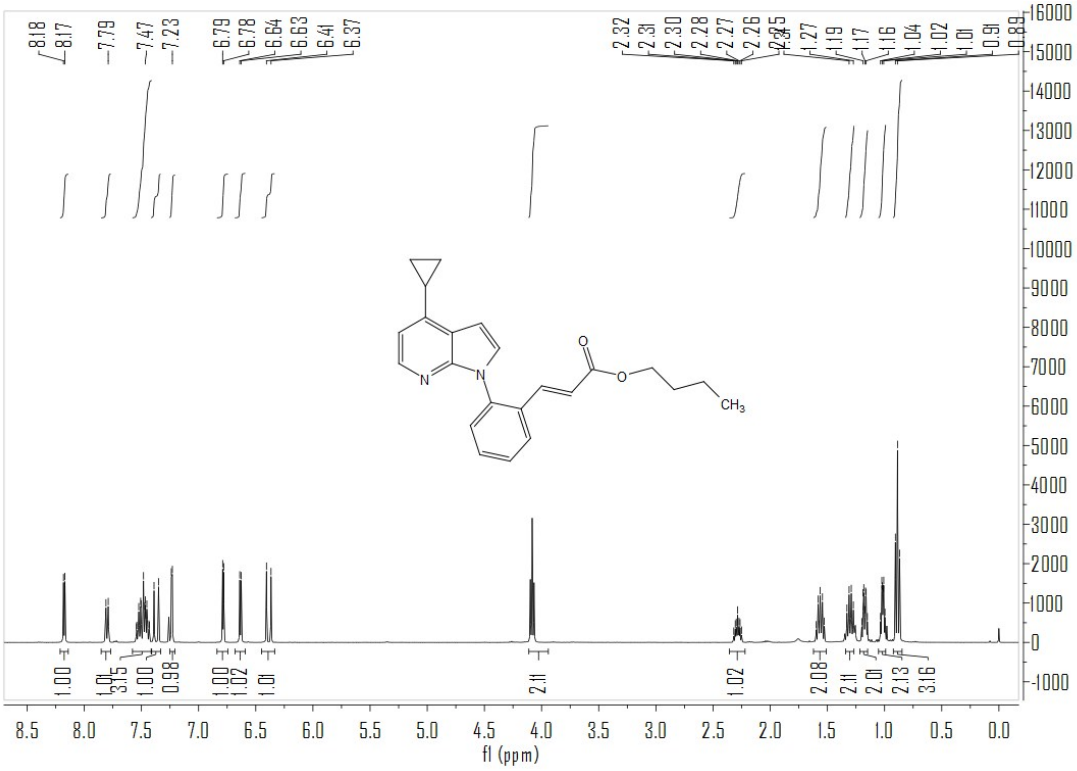
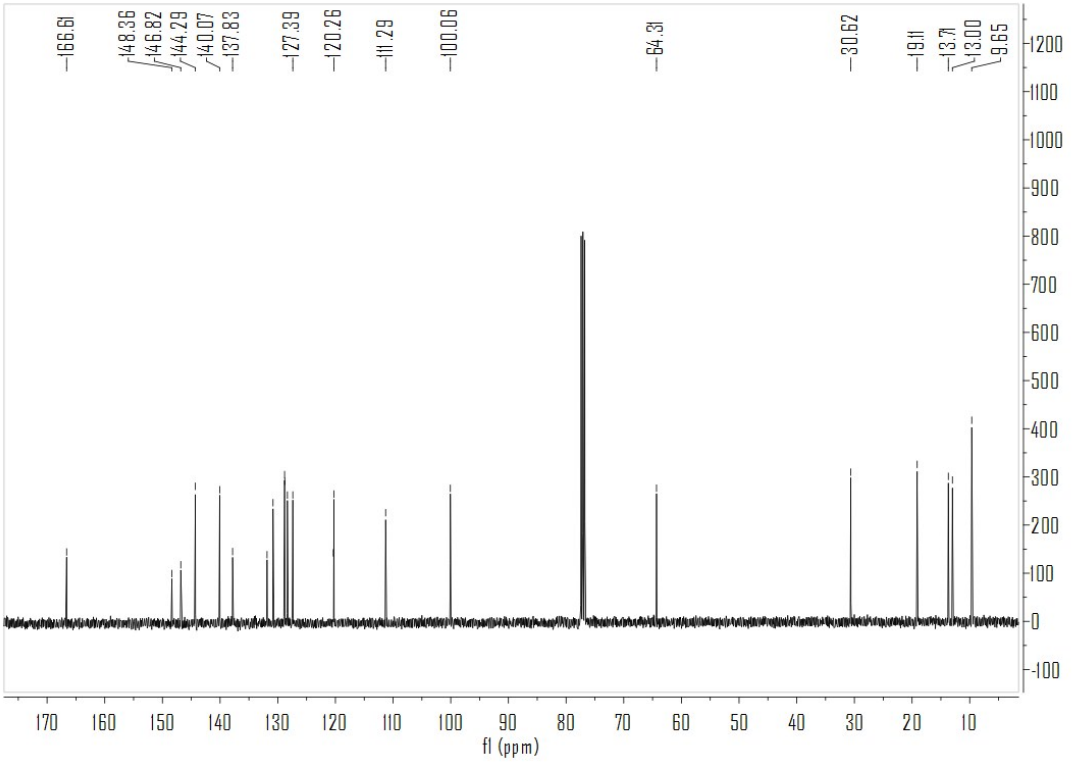


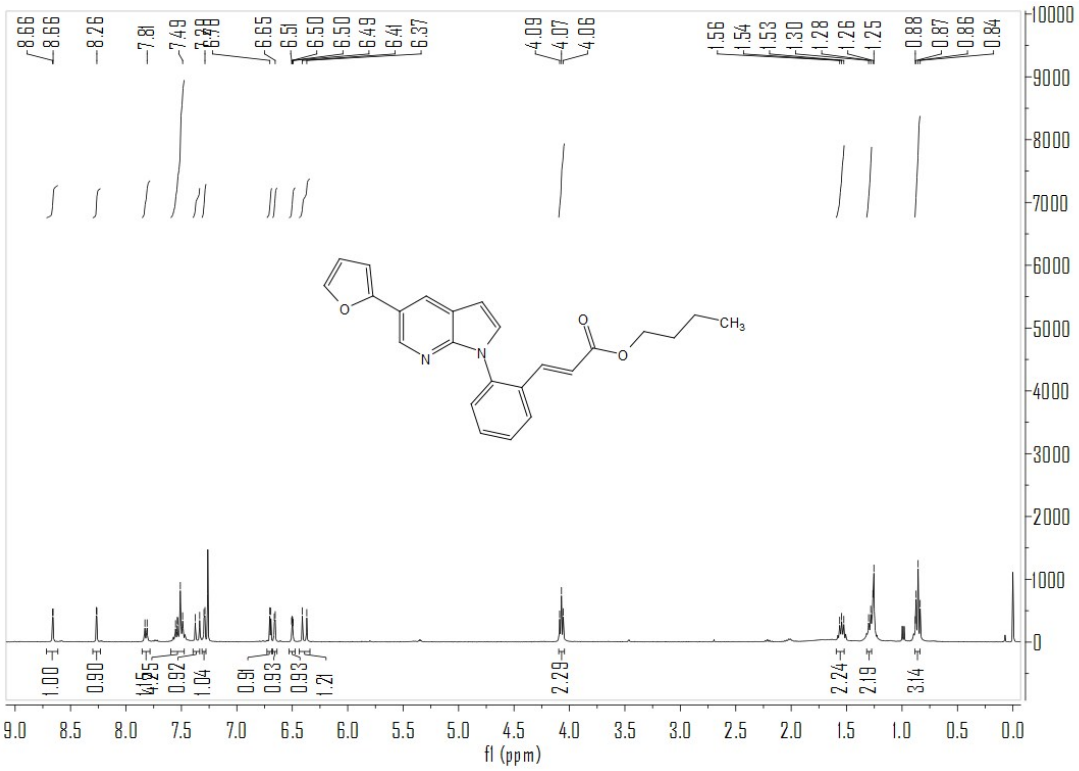
[1]H NMR of 3u



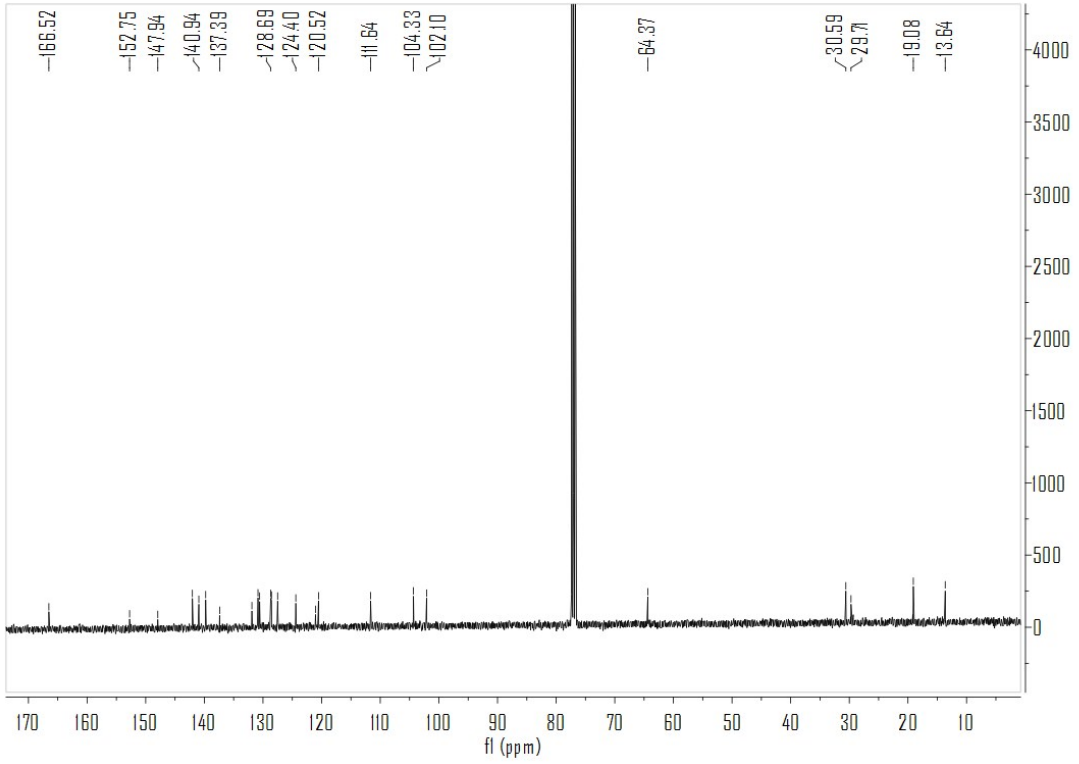
[13] C NMR of 3u



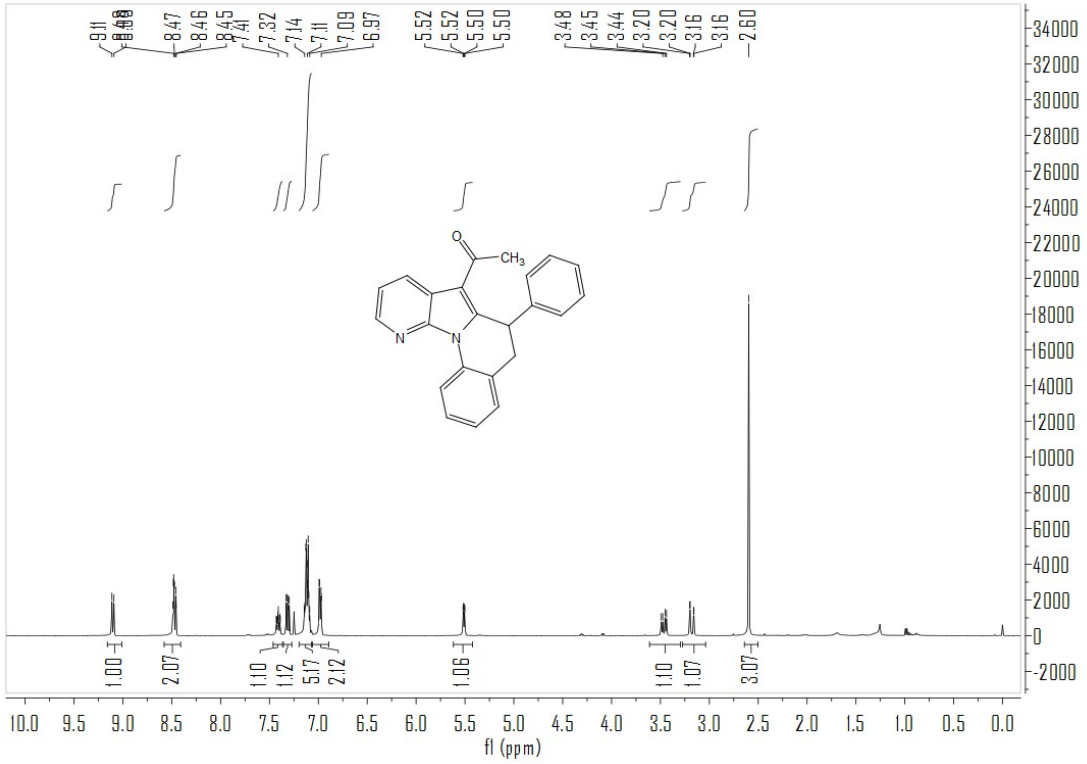
[1]H NMR of 3v



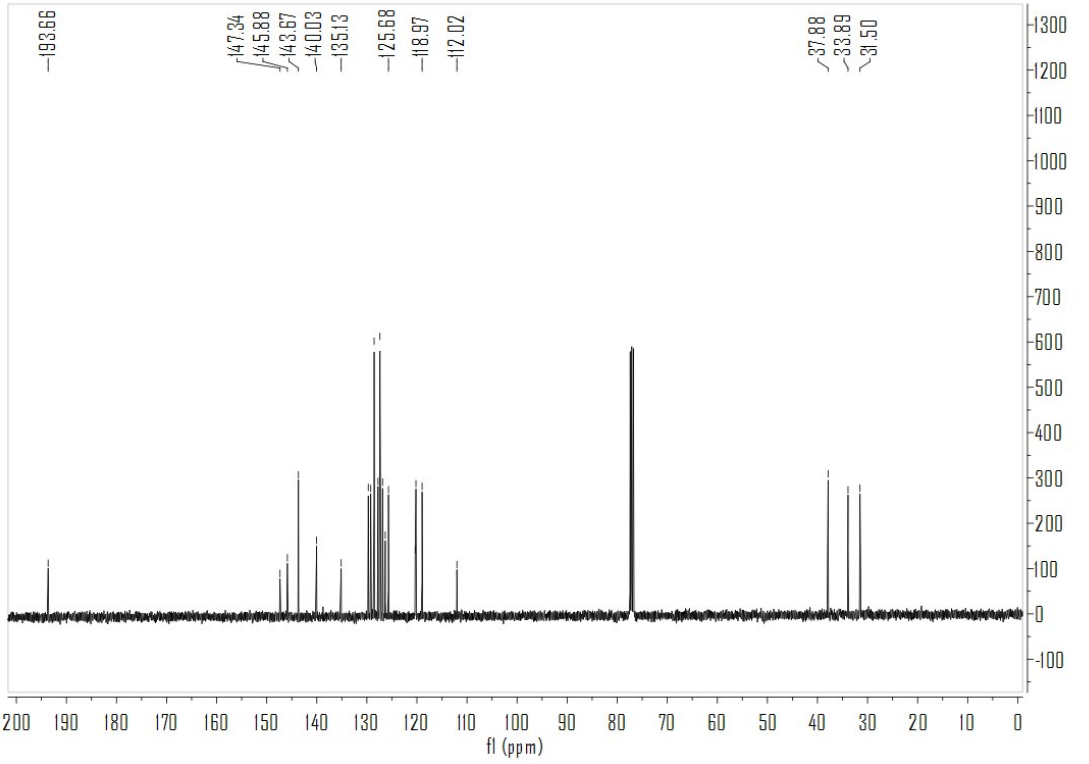
[13] C NMR of 3v



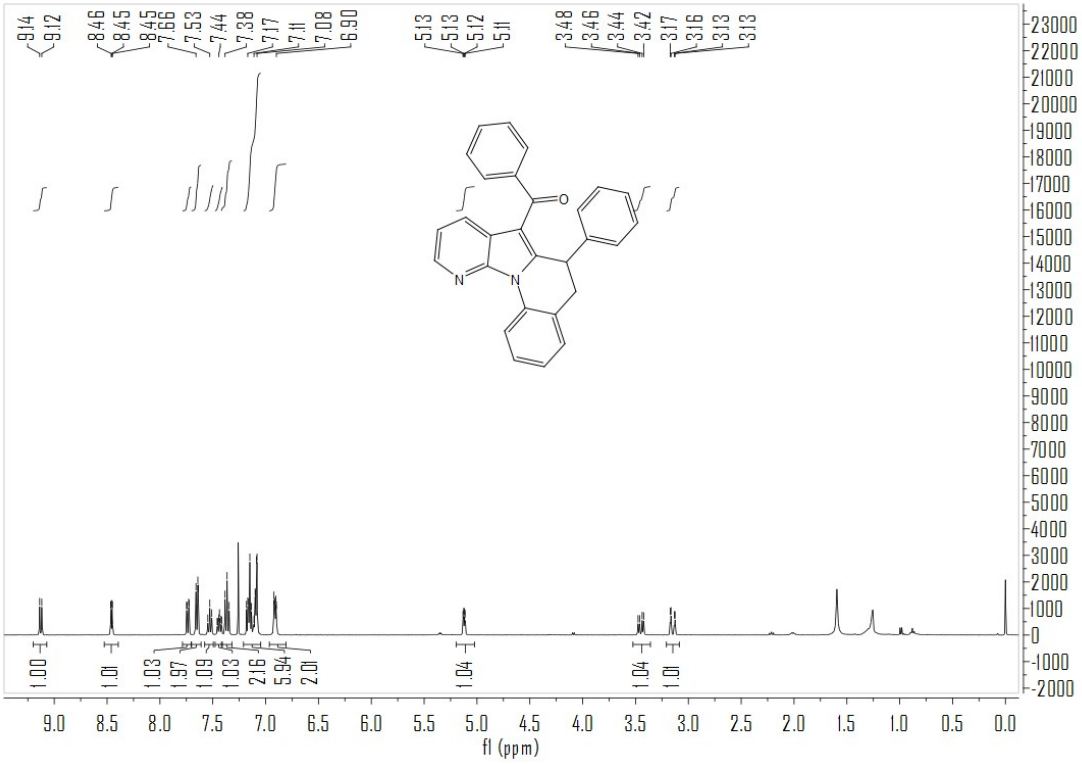
^{1}H NMR of 4a



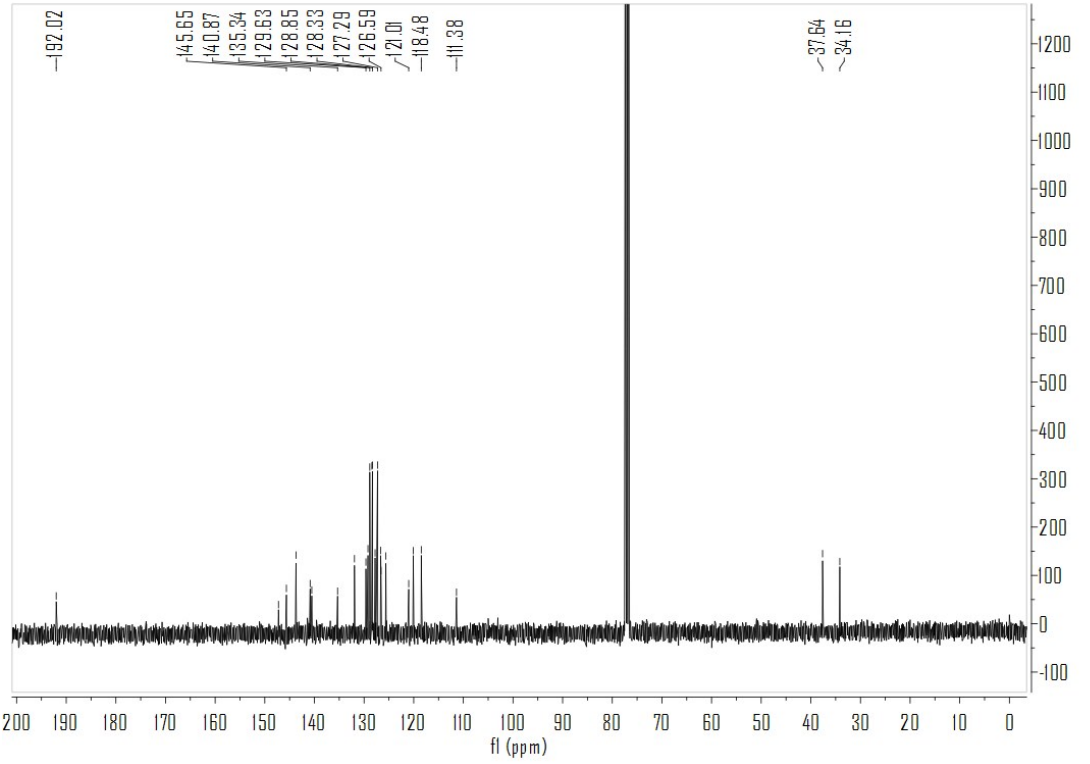
^{13} C NMR of 4a



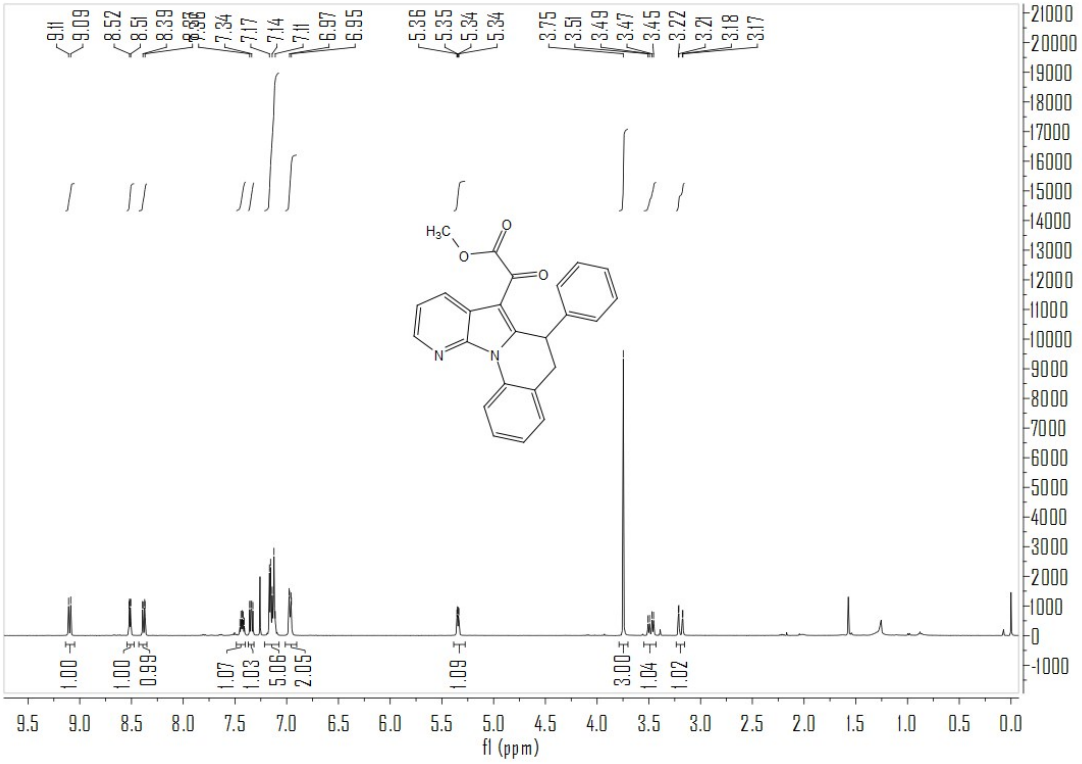
^{1}H NMR of 4b



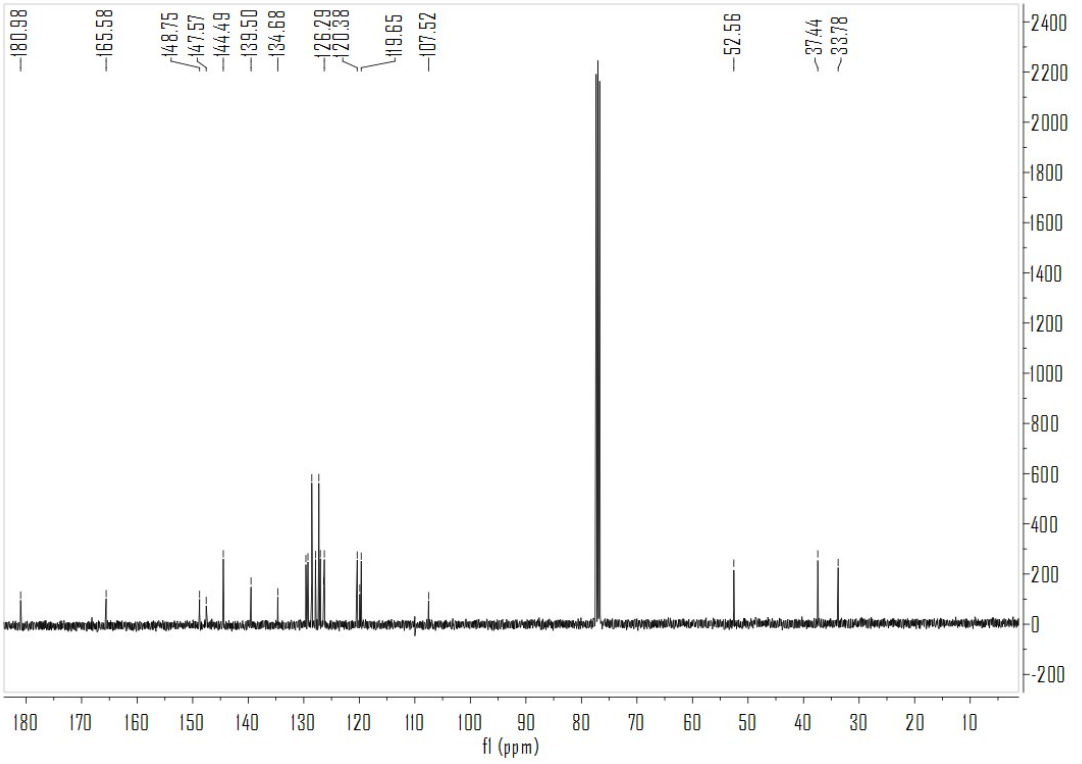
^{13} C NMR of 4b



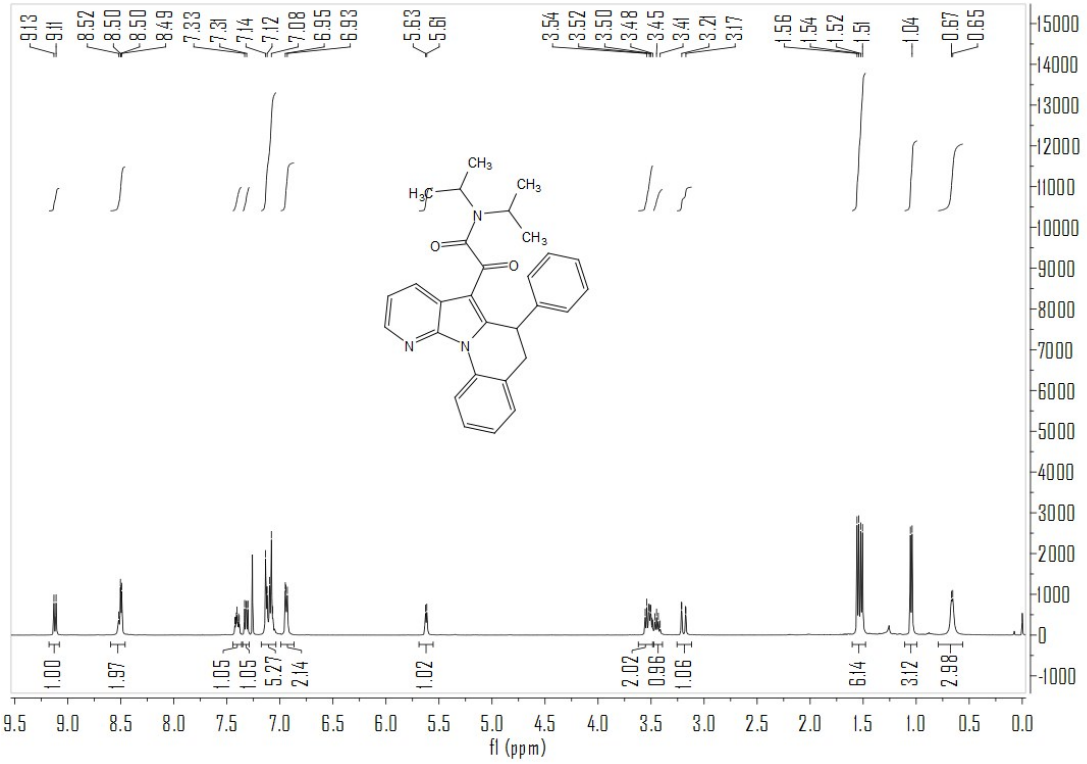
[1]H NMR of 4c



[13] C NMR of 4c



[1]H NMR of 4d



[13] C NMR of 4d