Supporting Information

Tris(pentafluorophenyl)borane-Catalyzed Formal Cyanoalkylation of Indoles with Cyanohydrins

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1. NMR studies

^{1}H NMR monitoring of the decomposition of acetone cyanohydrin (2a): Solutions of acetone cyanohydrin **(2a)** (0.1 mmol) in the presence and absence of $B(C_6F_5)_3$ (0.005 mmol) in MeCN-d_3 (0.5 mL) were prepared and transferred into a sealed NMR tube. After subjection of them to indicated conditions, the resulting ^{1}H NMR spectra are shown in Figure S1. To confirm the generation of HCN, a 200 μL sample of the mixture (iv) was added to 500 μL $CDCl_3$, and the resulting ^{1}H NMR spectrum was compared to the reported data.[1] The analytical data was in excellent agreement with the reported data.

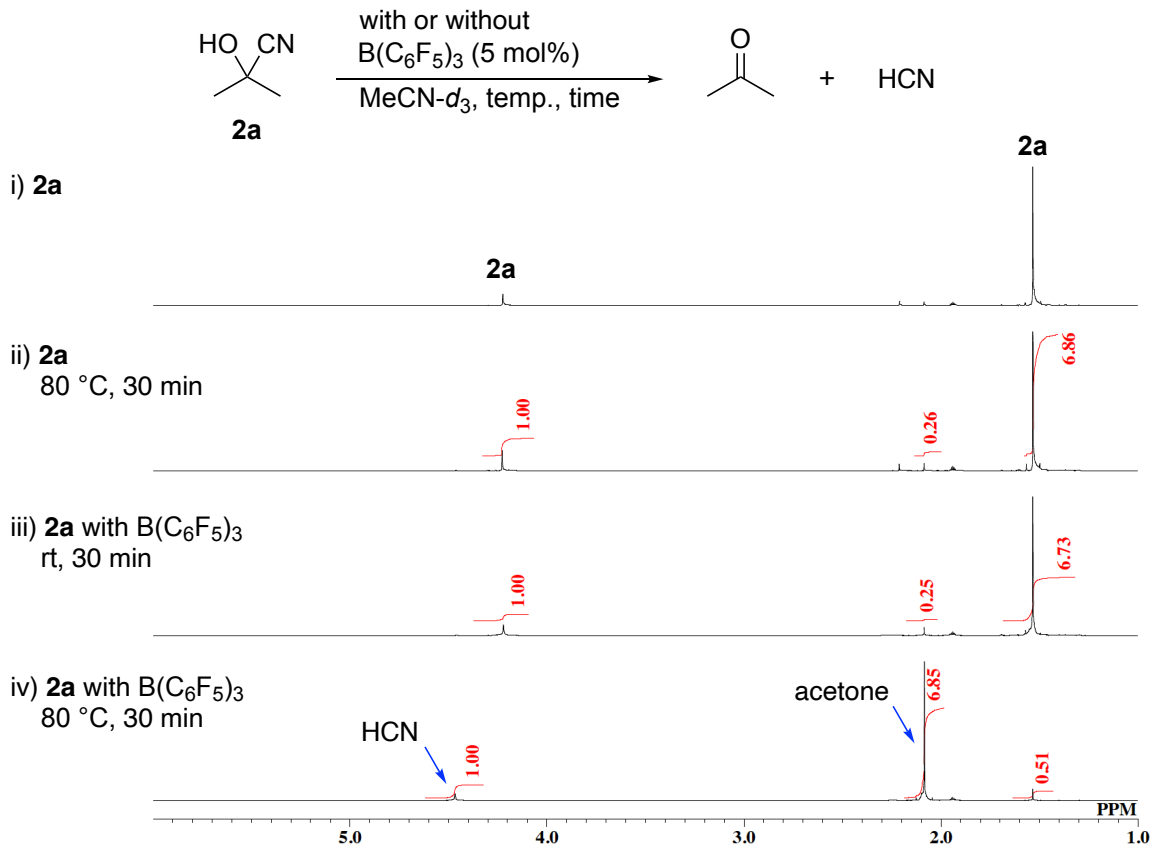


Figure S1. ^{1}H NMR spectra in MeCN-d_3: i) **2a**. ii) **2a** after stirring at 80 °C for 30 min. iii) Mixture of **2a** and $B(C_6F_5)_3$ (5 mol%) after stirring at room temperature for 30 min. iv) Mixture of **2a** and $B(C_6F_5)_3$ (5 mol%) after stirring 80 °C for 30 min.

^{1}H NMR monitoring of the decomposition of mandelonitrile (2e): Solutions of mandelonitrile **(2e)** (0.1 mmol) in the presence and absence of $B(C_6F_5)_3$ (0.005 mmol) in MeCN-d_3 (0.5 mL) were prepared and transferred into a sealed NMR tube. After subjection of them to indicated conditions, the resulting ^{1}H NMR spectra are shown in Figure S2.

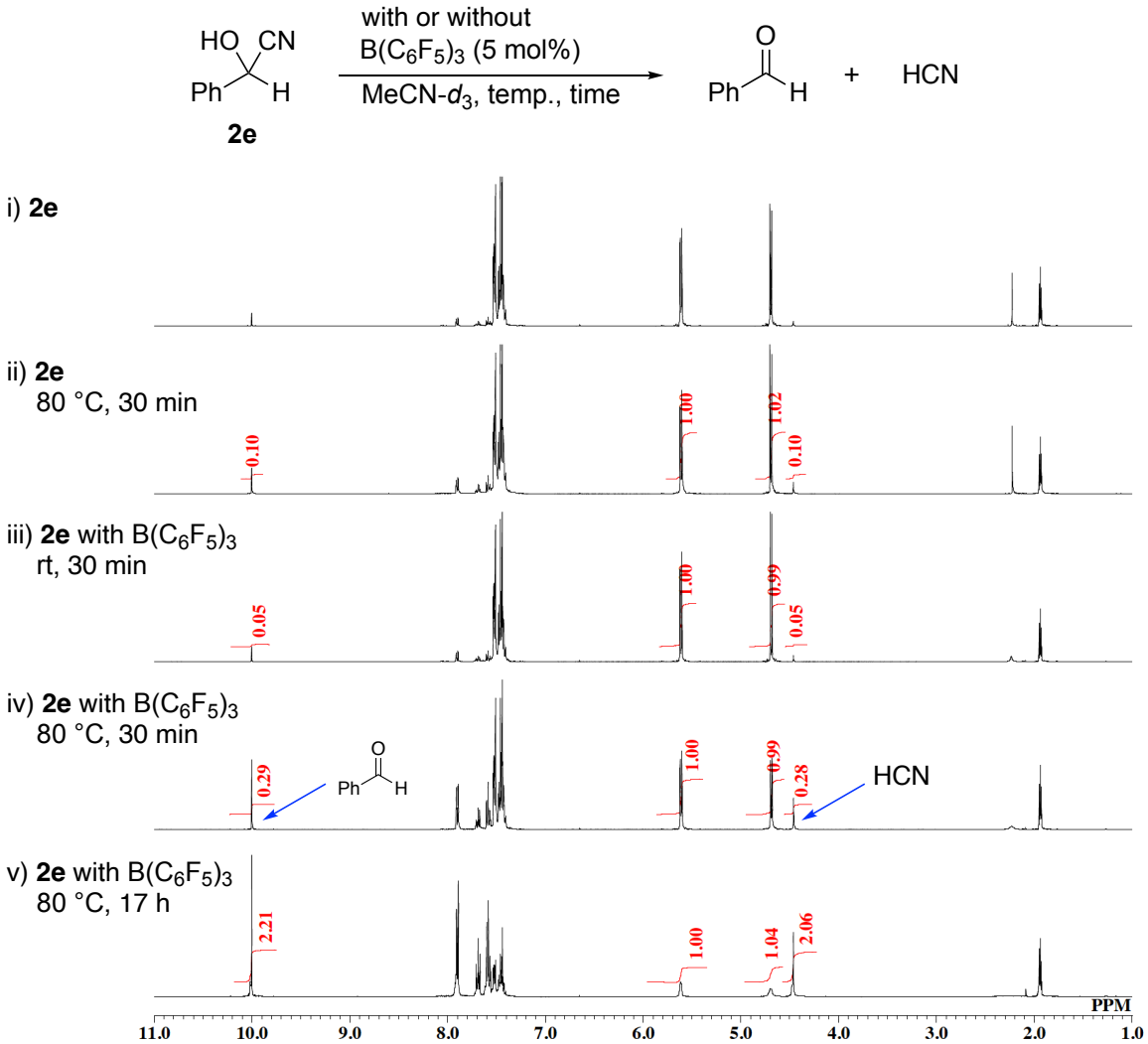


Figure S2. ^{1}H NMR spectra in MeCN-d_3: i) **2e**. ii) **2e** after stirring at 80 °C for 30 min. iii) Mixture of **2e** and $B(C_6F_5)_3$ (5 mol%) after stirring at room temperature for 30 min. iv) Mixture of **2e** and $B(C_6F_5)_3$ (5 mol%) after stirring 80 °C for 30 min. v) Mixture of **2e** and $B(C_6F_5)_3$ (5 mol%) after stirring 80 °C for 17 h.

NMR monitoring of a mixture of mandelonitrile (2e) and $B(C_6F_5)_3$: A solution of mandelonitrile **(2e)** (0.1 mmol) and $B(C_6F_5)_3$ (0.1 mmol) in toluene-d_8 (0.5 mL) was prepared and transferred into a sealed NMR tube. The resulting ^1H, $^{13}C\{^1H\}$, ^{11}B, and $^{19}F\{^1H\}$ NMR spectra are shown in Figures S3–6.[2]

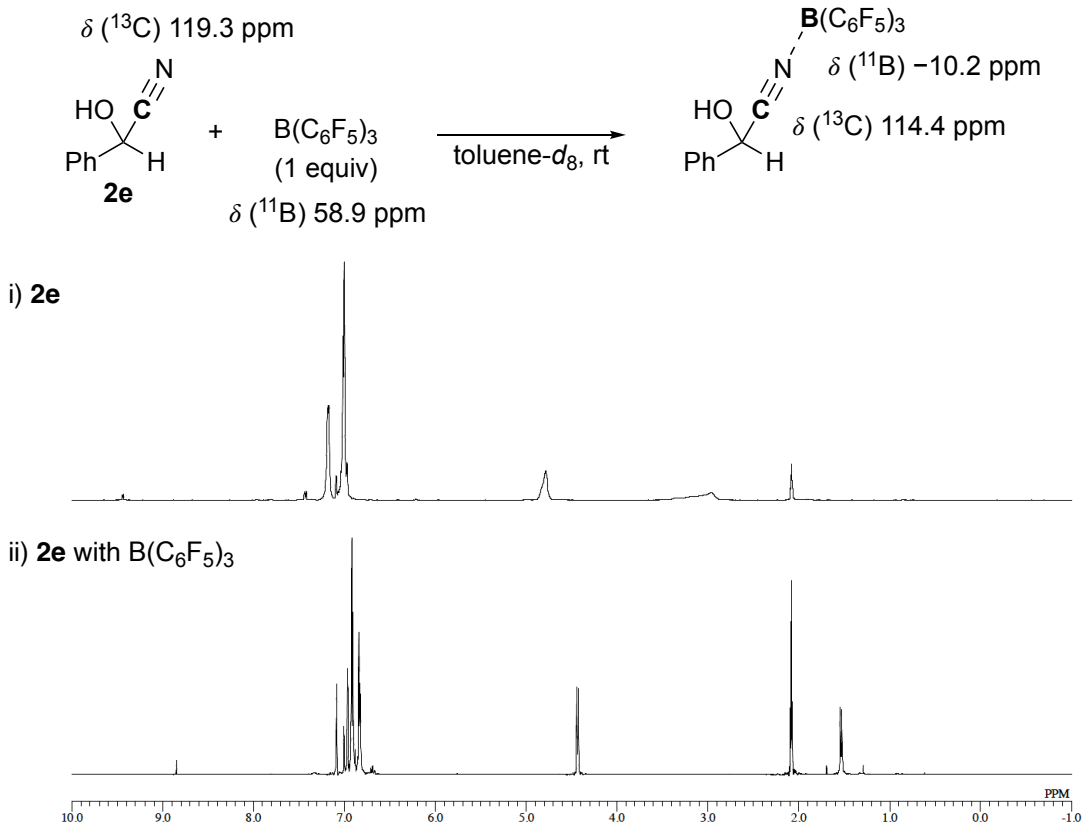


Figure S3. ^1H NMR spectra in toluene-d_8: i) **2e**. ii) Mixture of **2e** and $B(C_6F_5)_3$ (1 equiv).

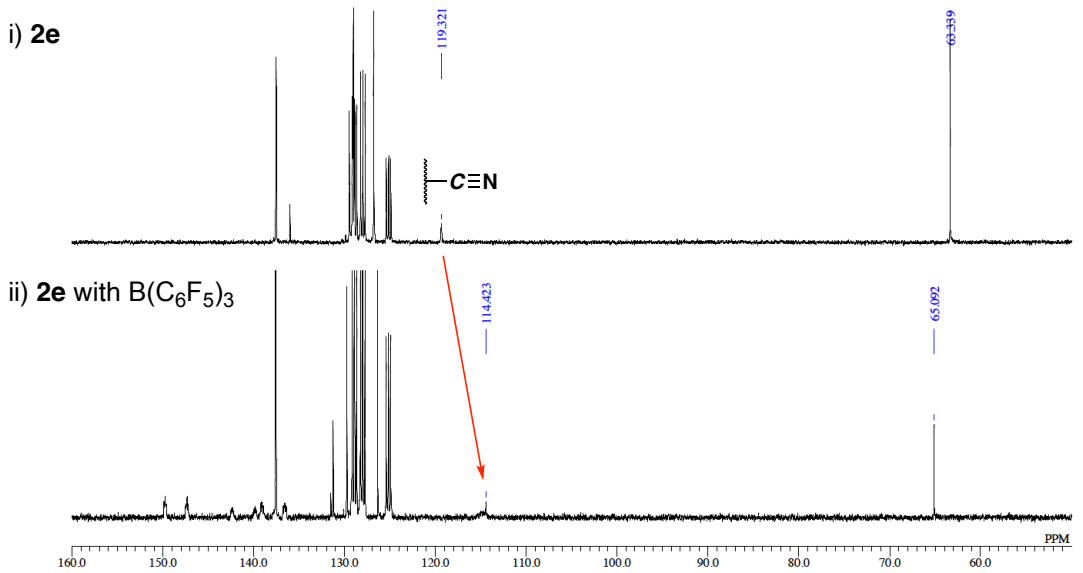


Figure S4. $^{13}C\{^1H\}$ NMR spectra in toluene-d_8: i) **2e**. ii) Mixture of **2e** and $B(C_6F_5)_3$ (1 equiv).

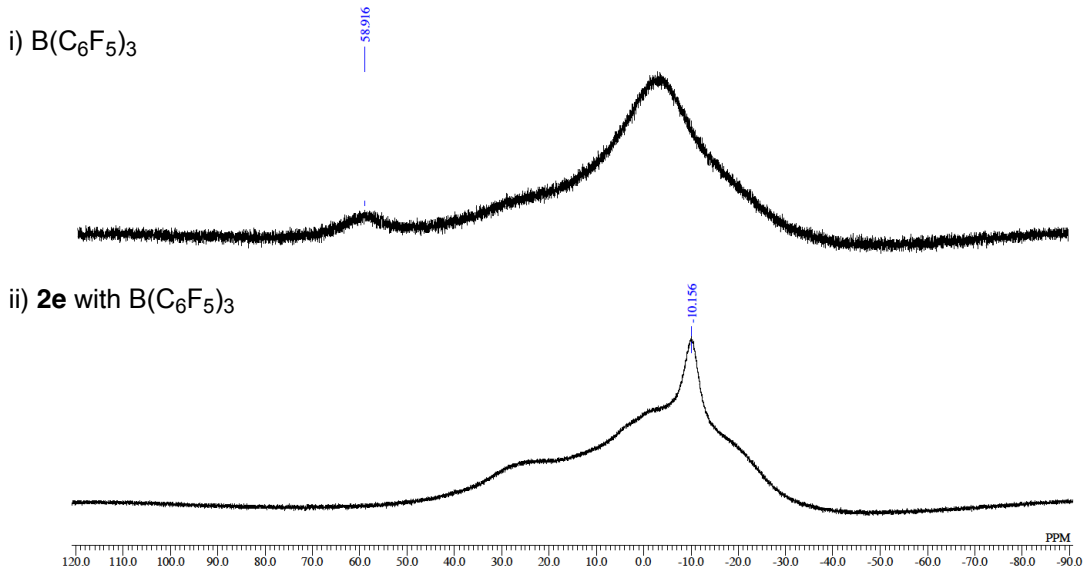


Figure S5. ^{11}B NMR spectra in toluene-d_8: i) $B(C_6F_5)_3$ ii) Mixture of **2e** and $B(C_6F_5)_3$ (1 equiv).

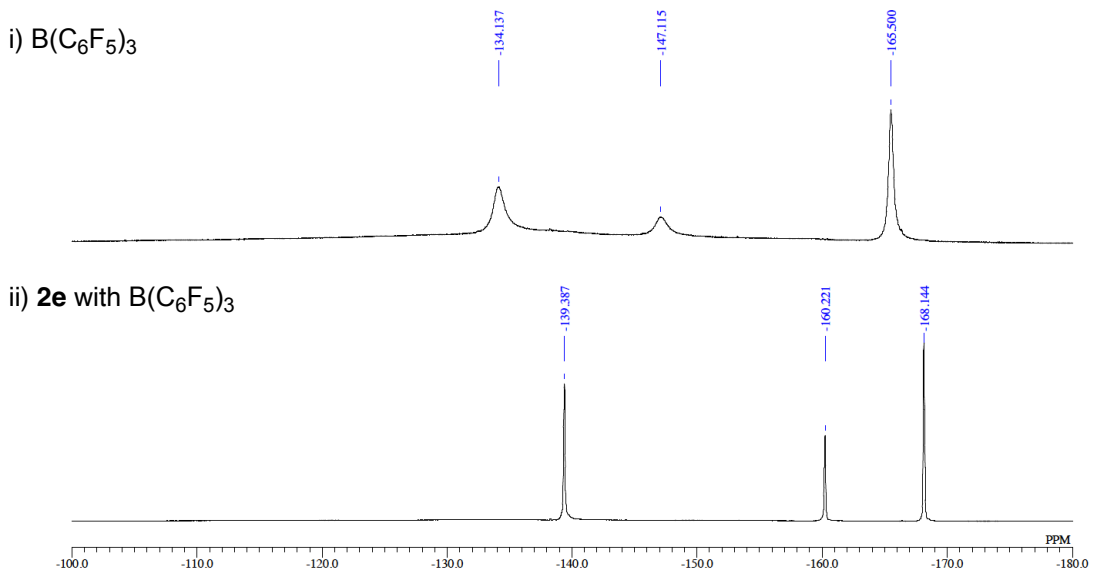


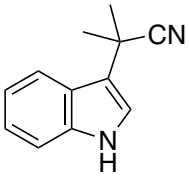
Figure S6. ^{19}F{^{1}H} NMR spectra in toluene-d_8: i) $B(C_6F_5)_3$. ii) Mixture of **2e** and $B(C_6F_5)_3$ (1 equiv).

2. References

(1) For ^{1}H NMR spectrum of HCN, see: M. Köckinger, C. A. Hone, C. O. Kappe, *Org. Lett.* **2019**, *21*, 5326.

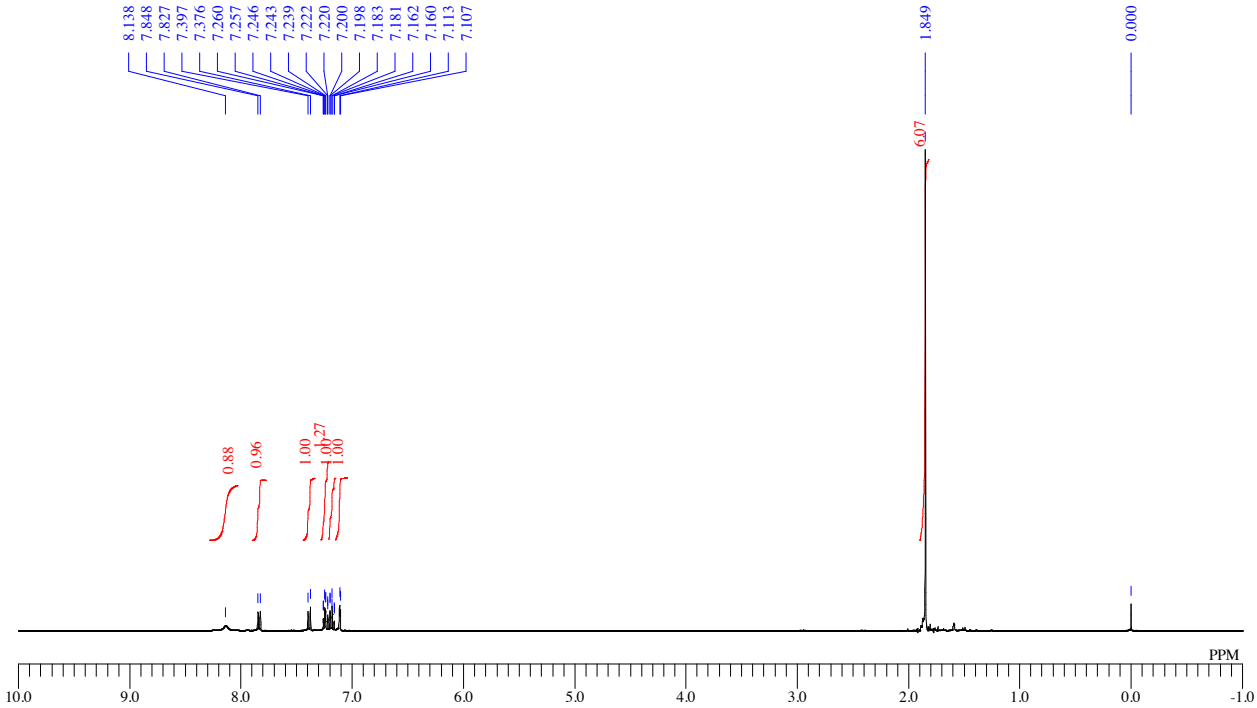
(2) For NMR spectra of $B(C_6F_5)_3$ in toluene-d_8, see: A. Bismuto, G. S. Nichol, F. Duarte, M. J. Cowley, S. P. Thomas, *Angew. Chem. Int. Ed.* **2020**, *59*, 12731.

3. NMR spectra

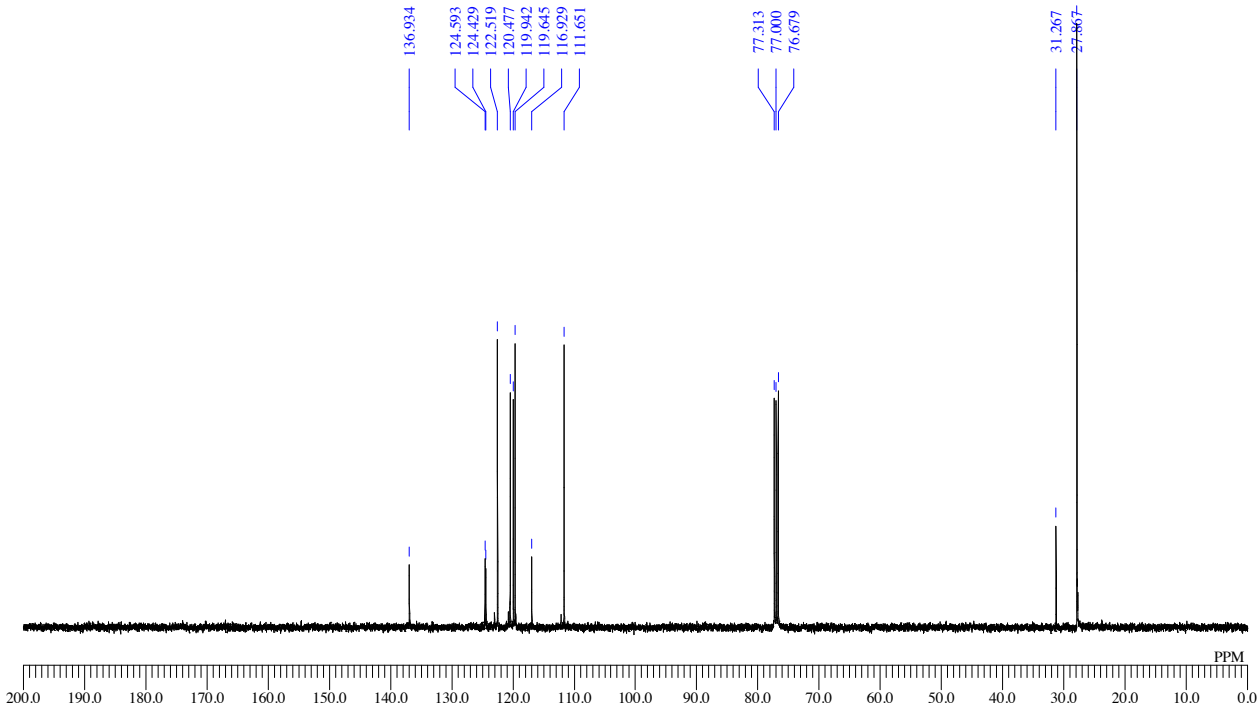


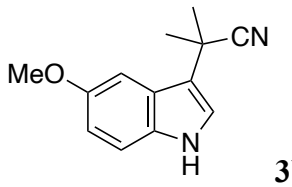
3aa

^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





3ba

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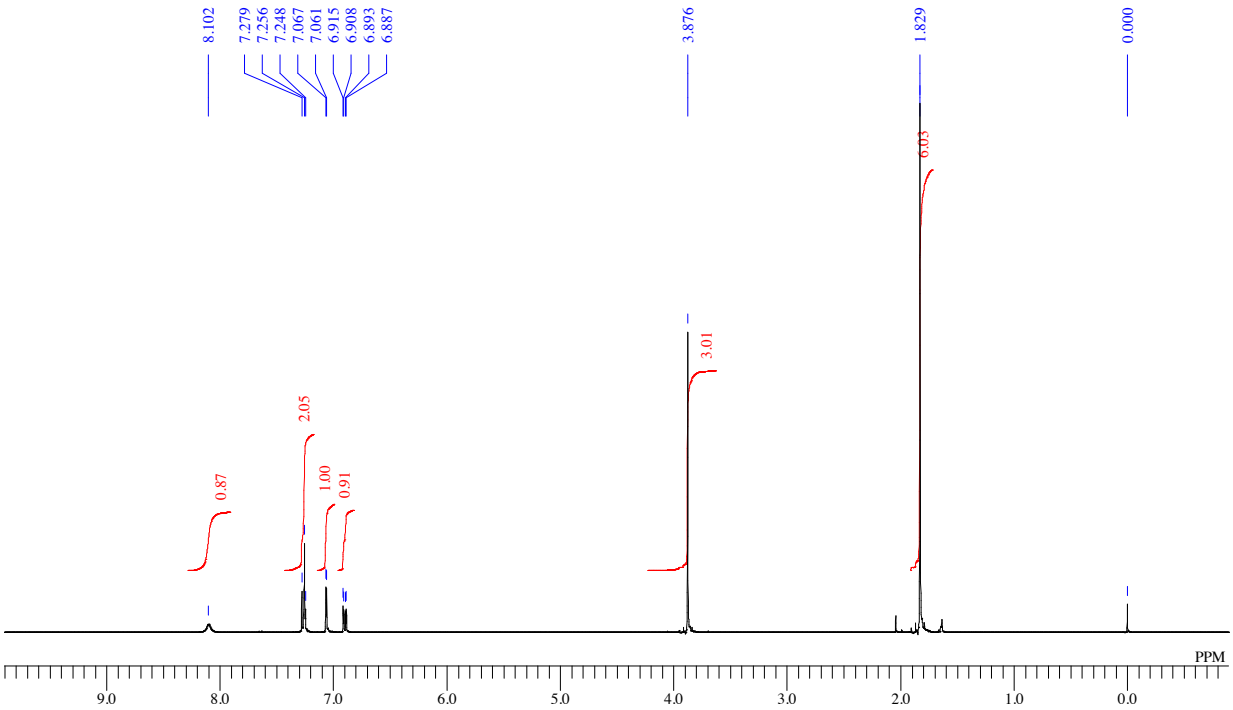
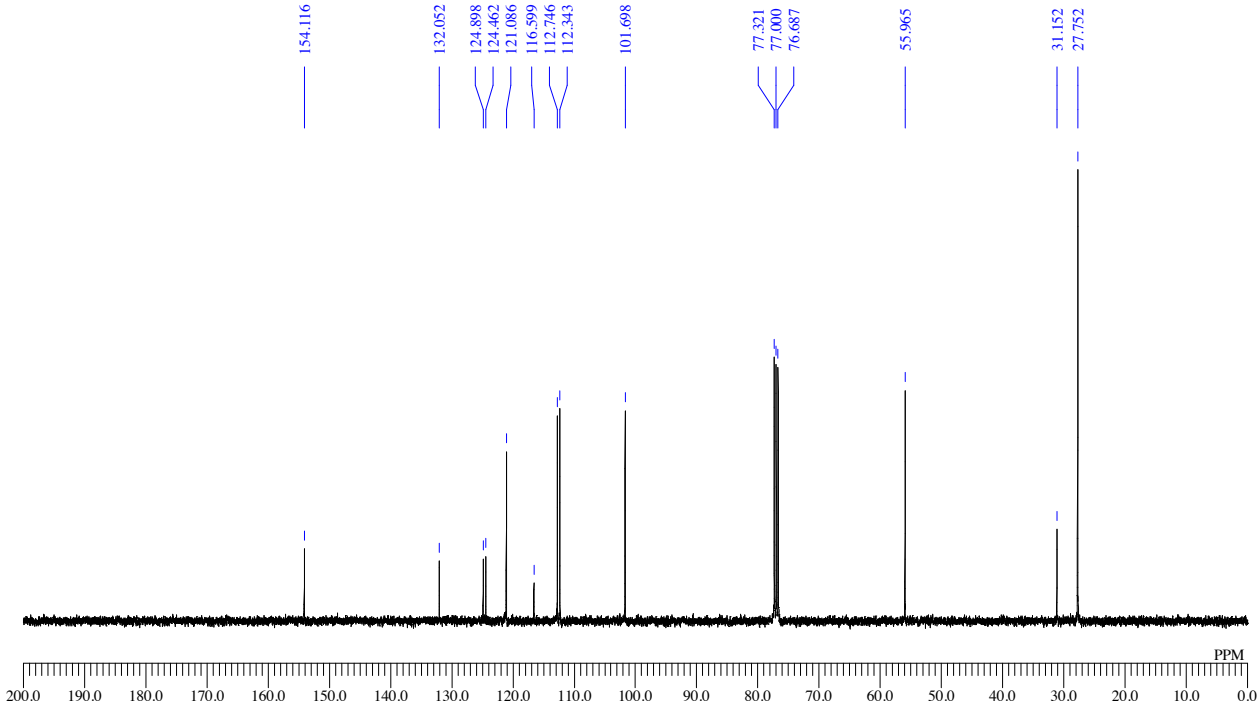
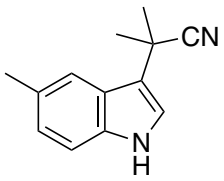


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





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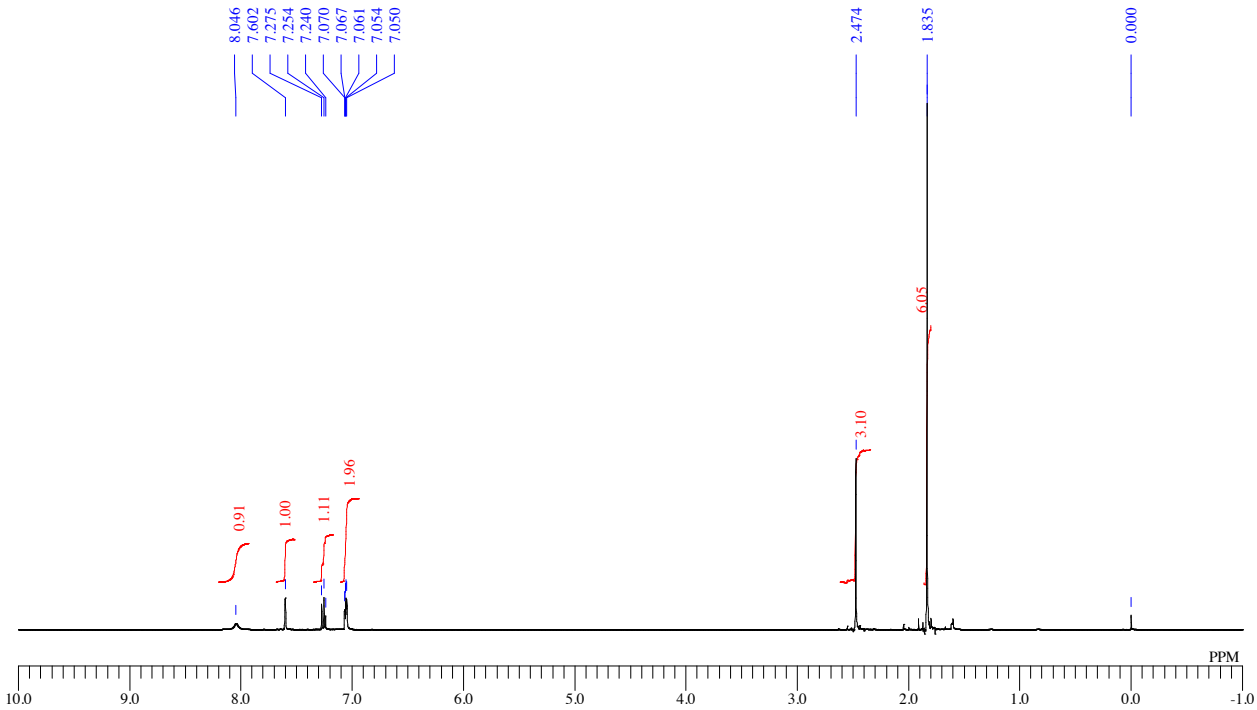
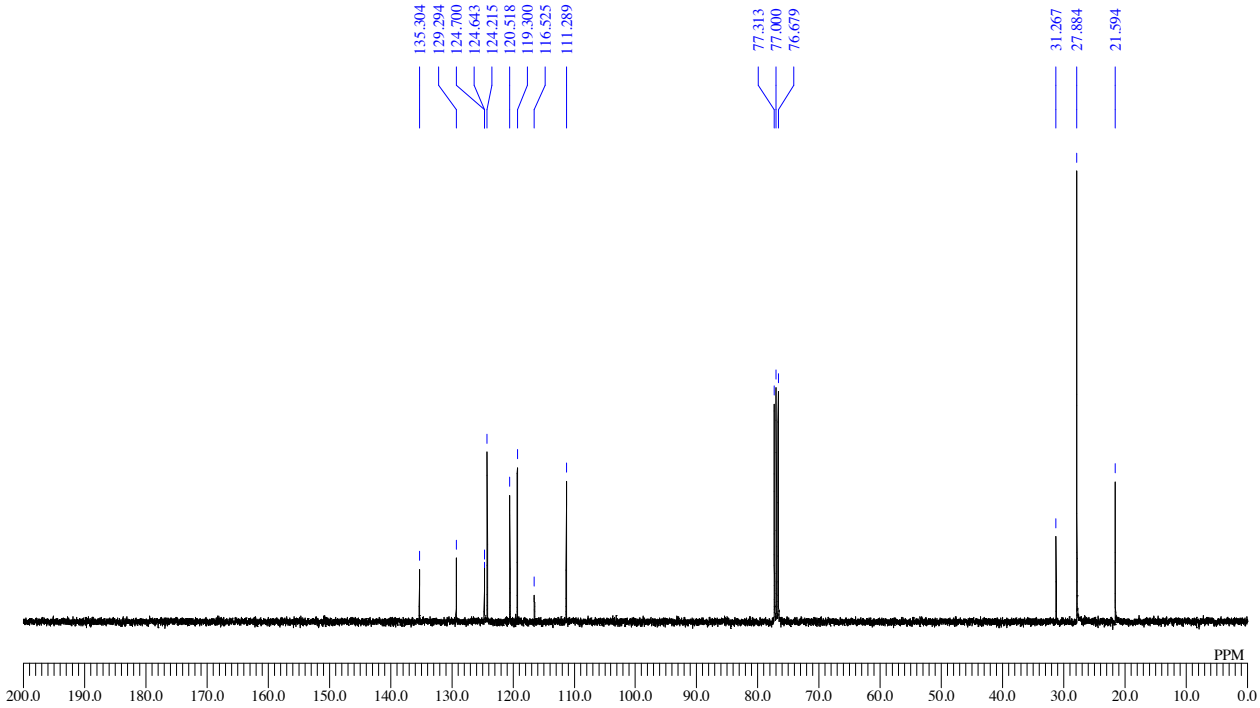
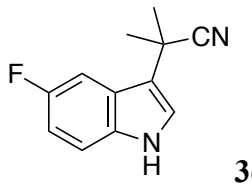


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





3da

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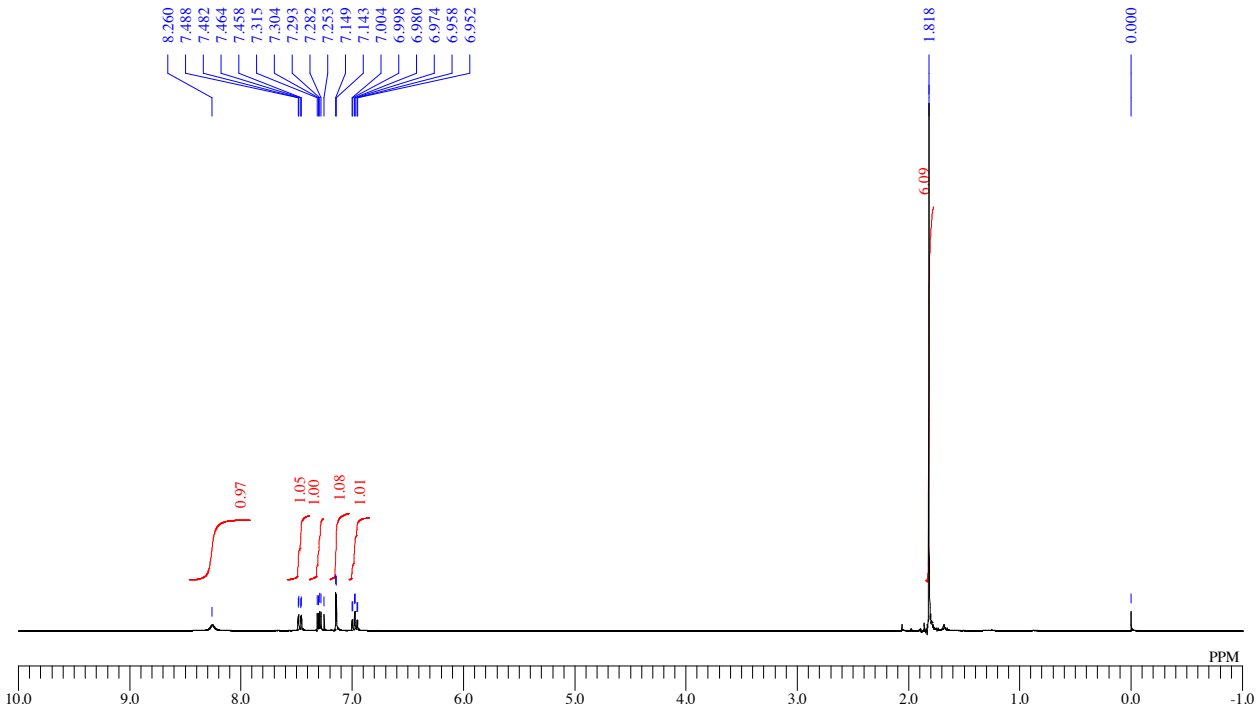
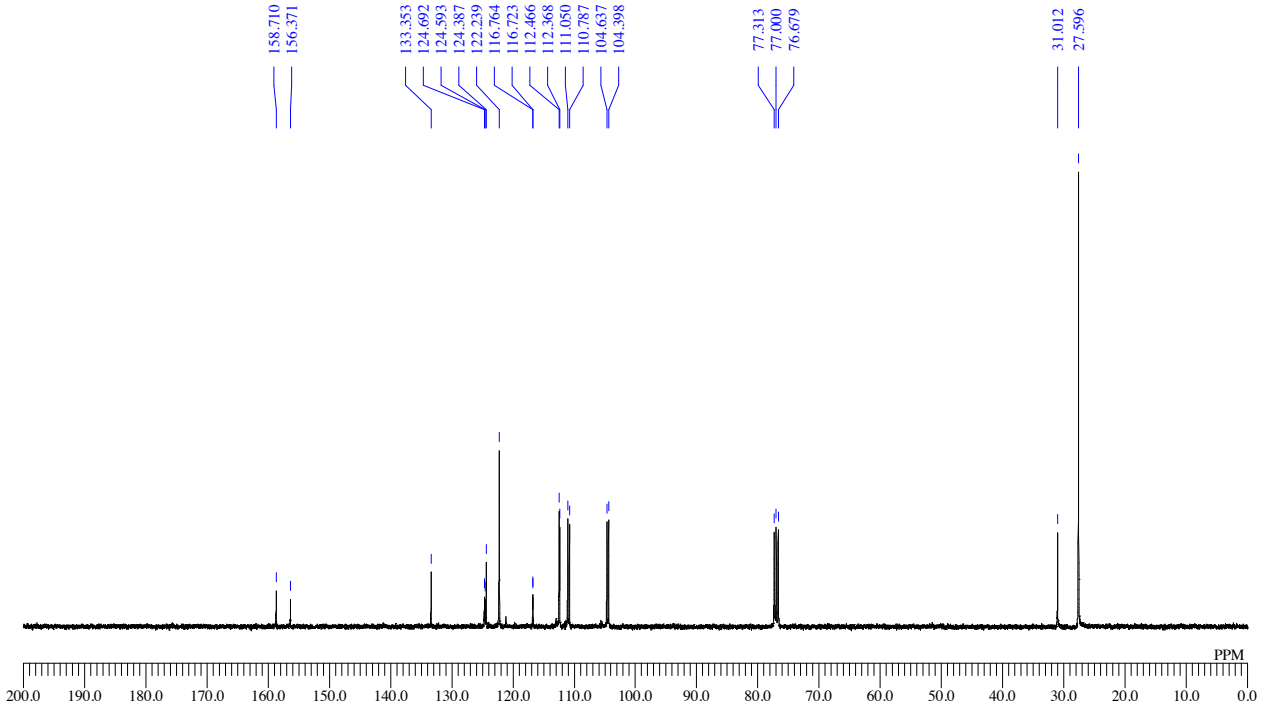
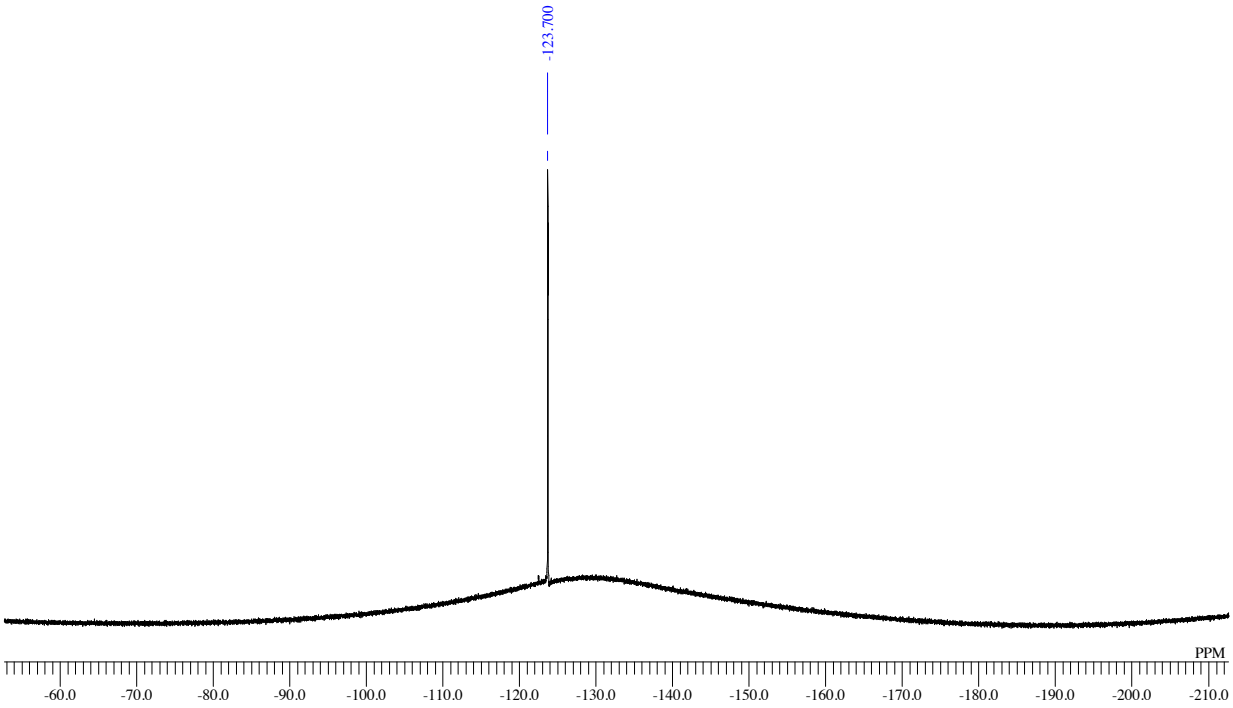
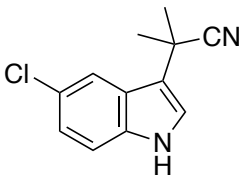


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



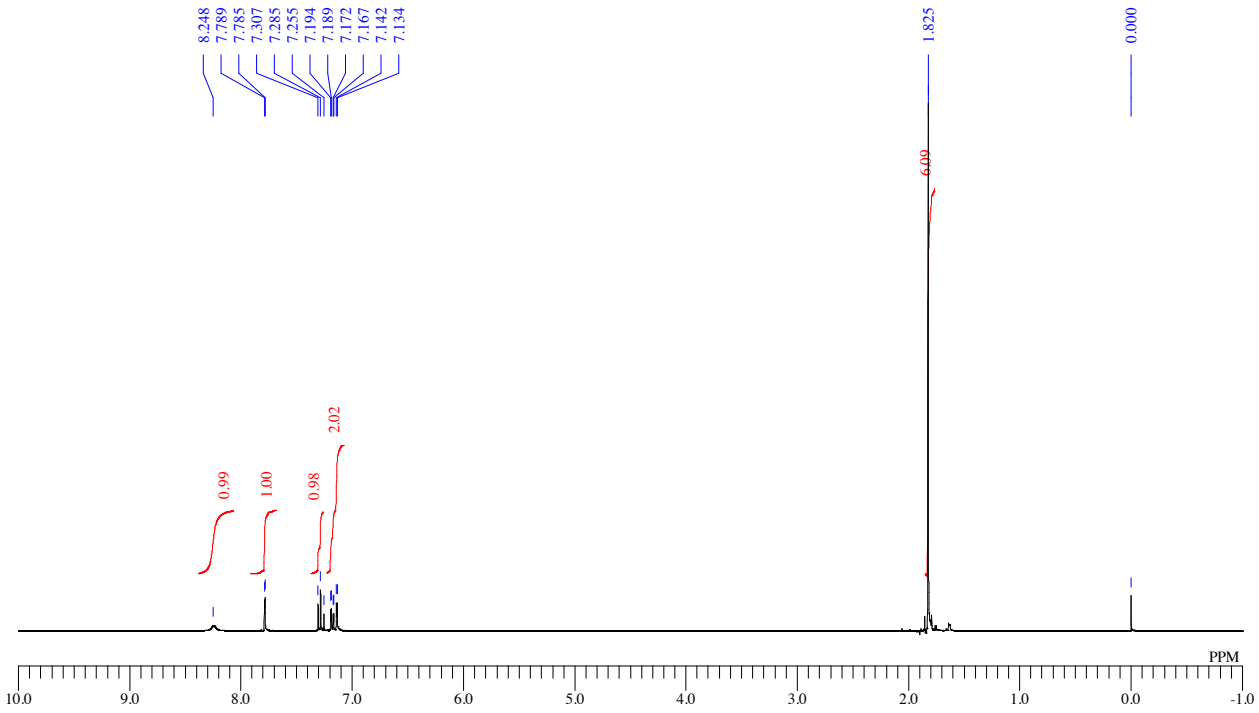
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



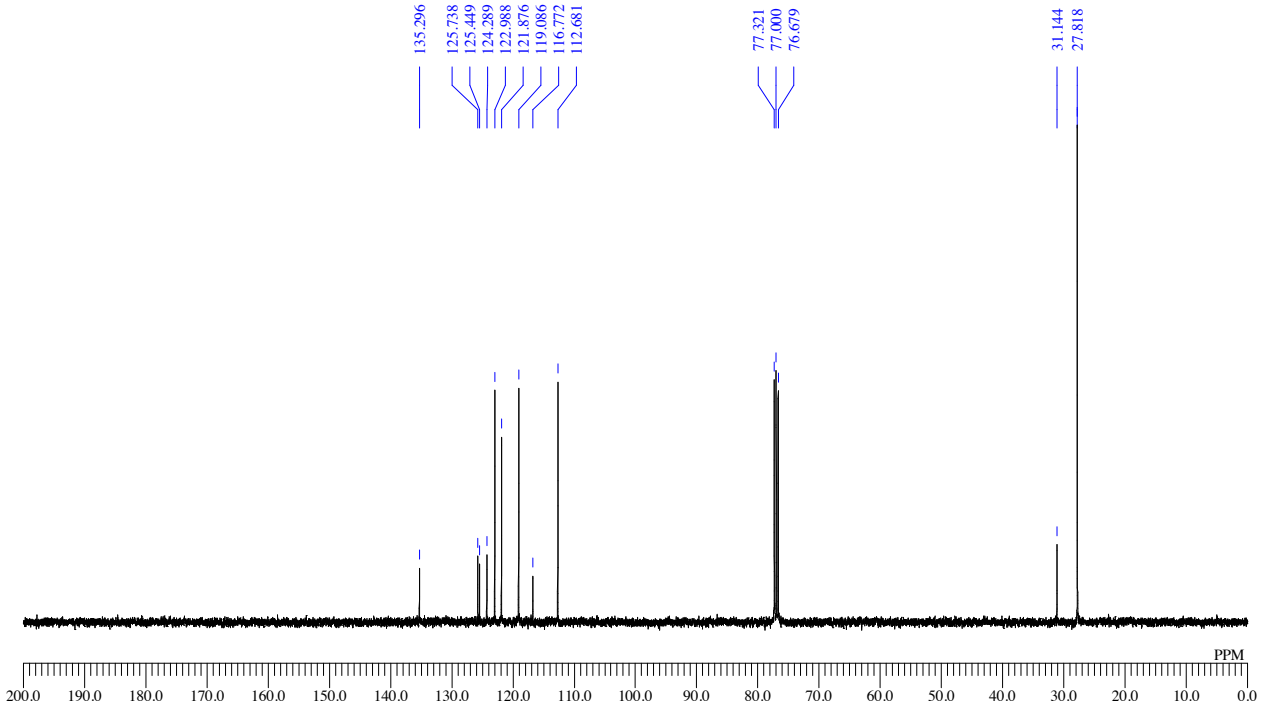


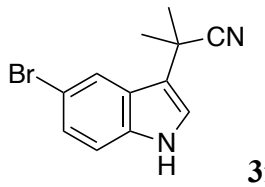
3ea

^{1}H NMR: (400 MHz, $CDCl_3$)



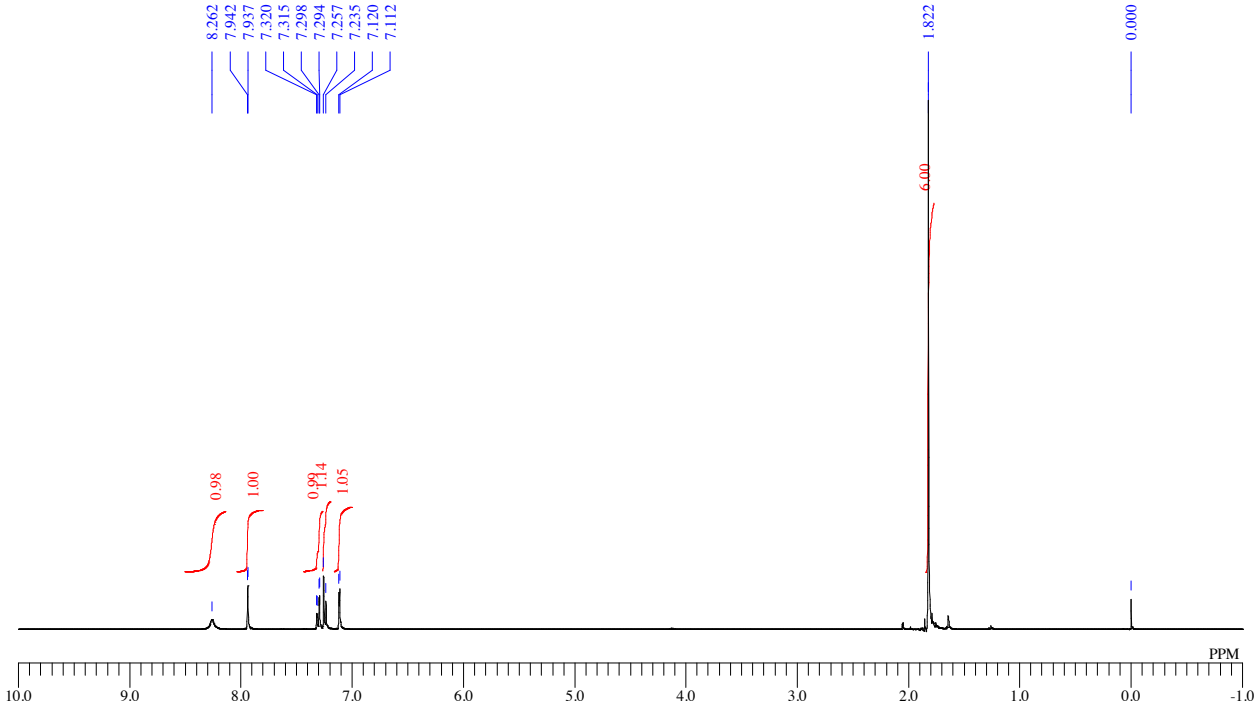
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



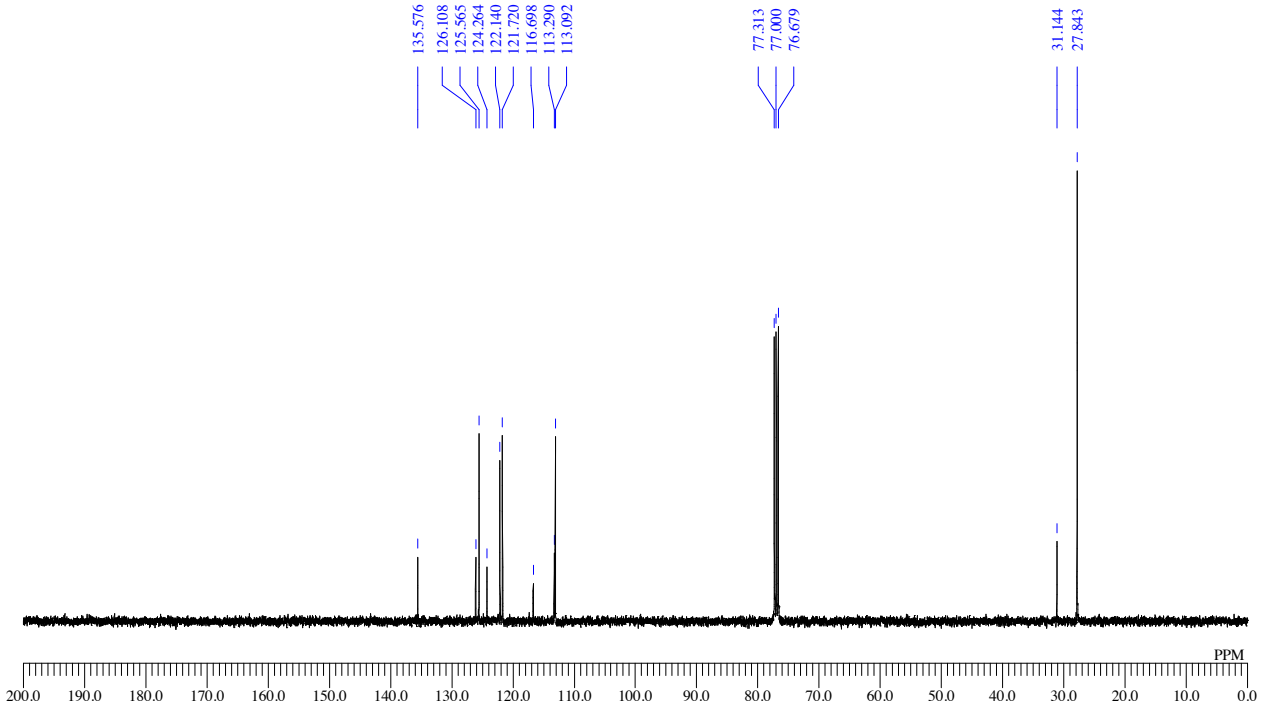


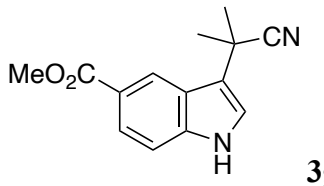
3fa

^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





3ga

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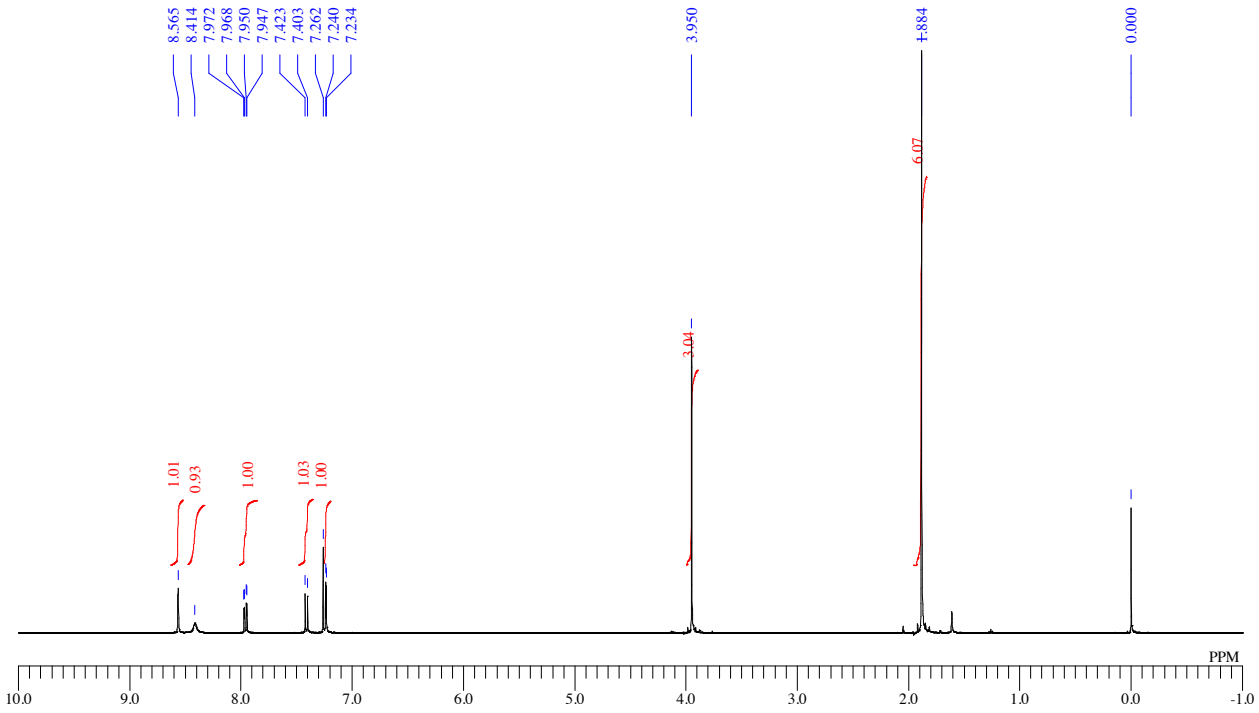

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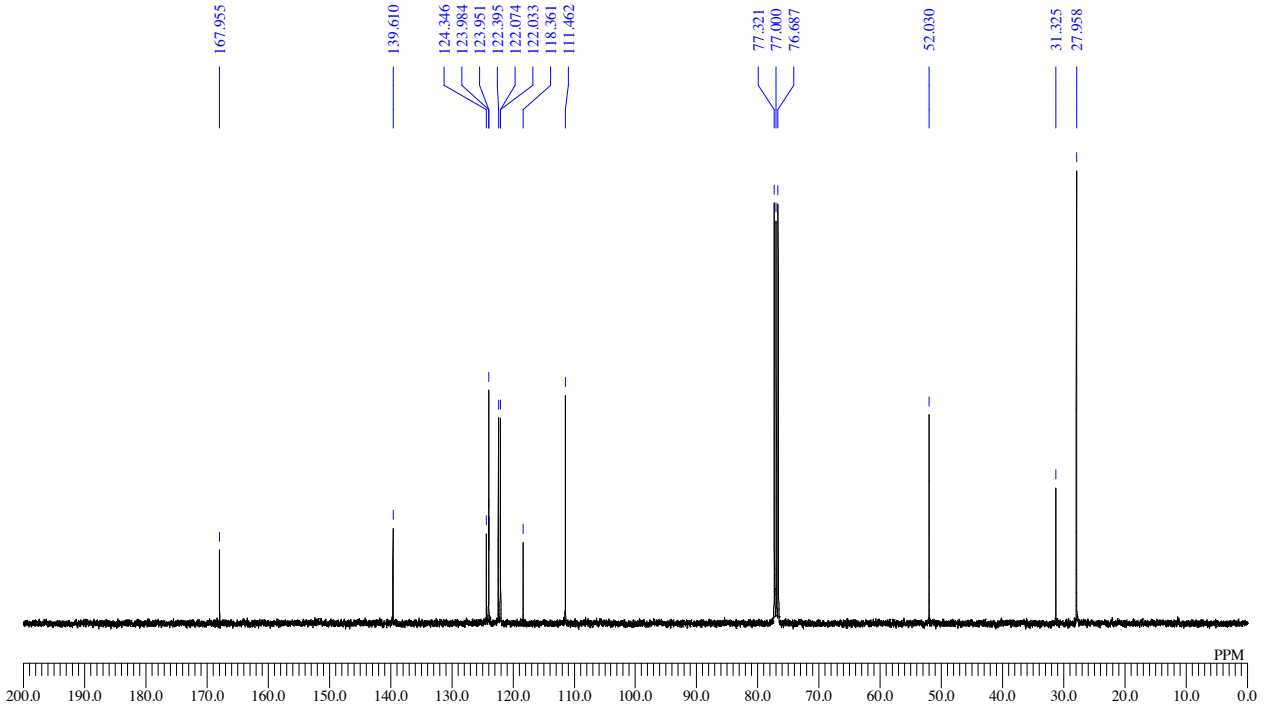

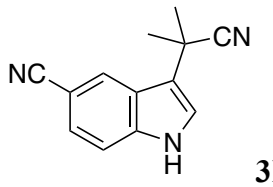

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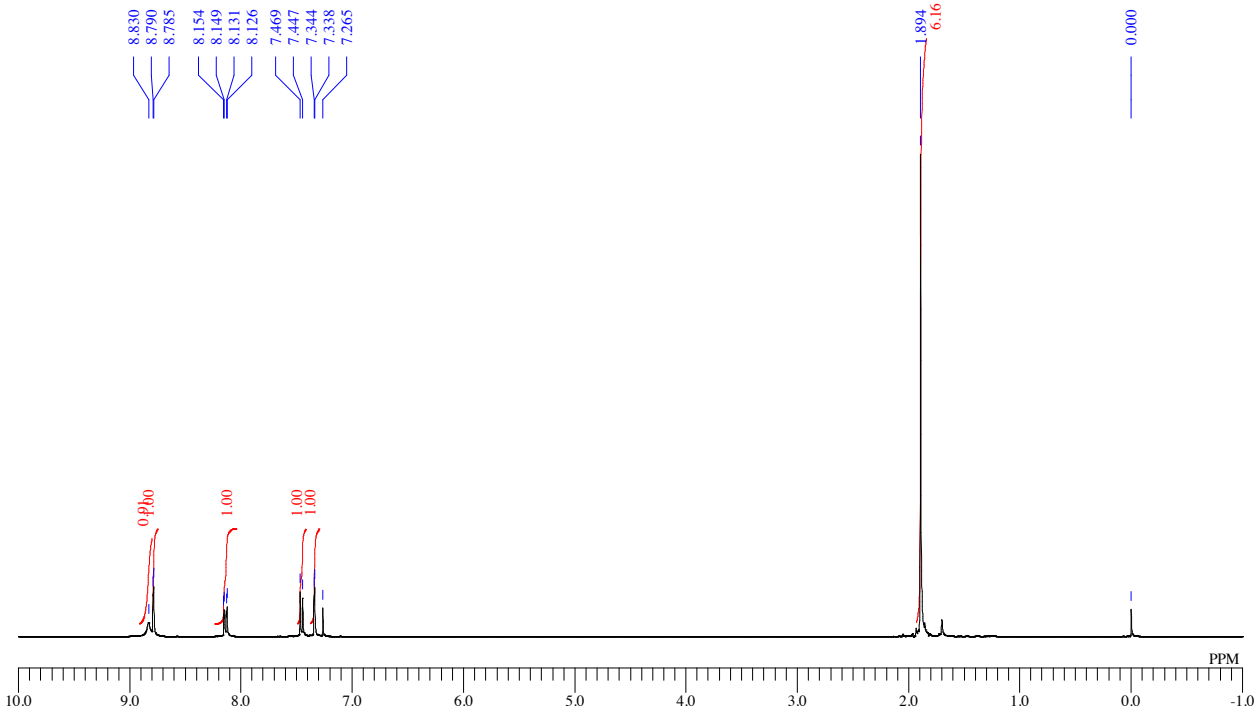
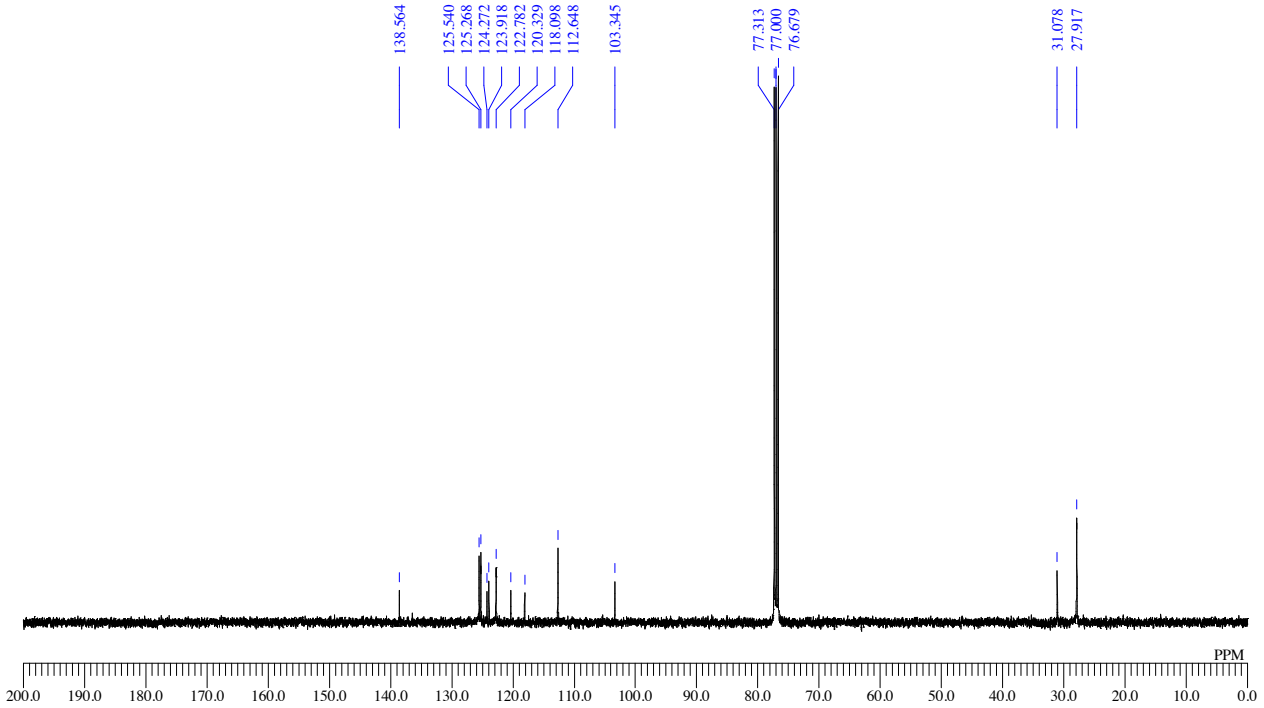
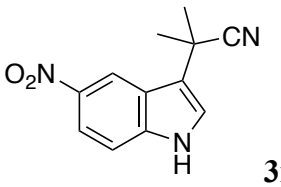


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





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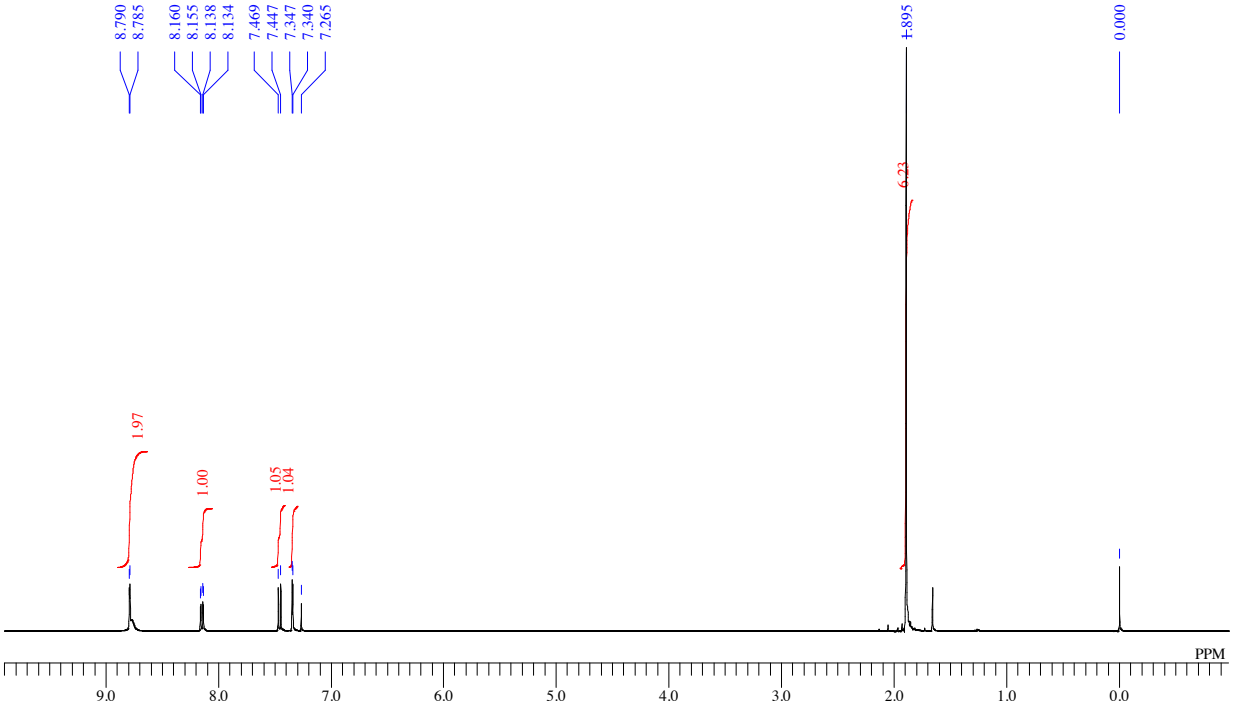

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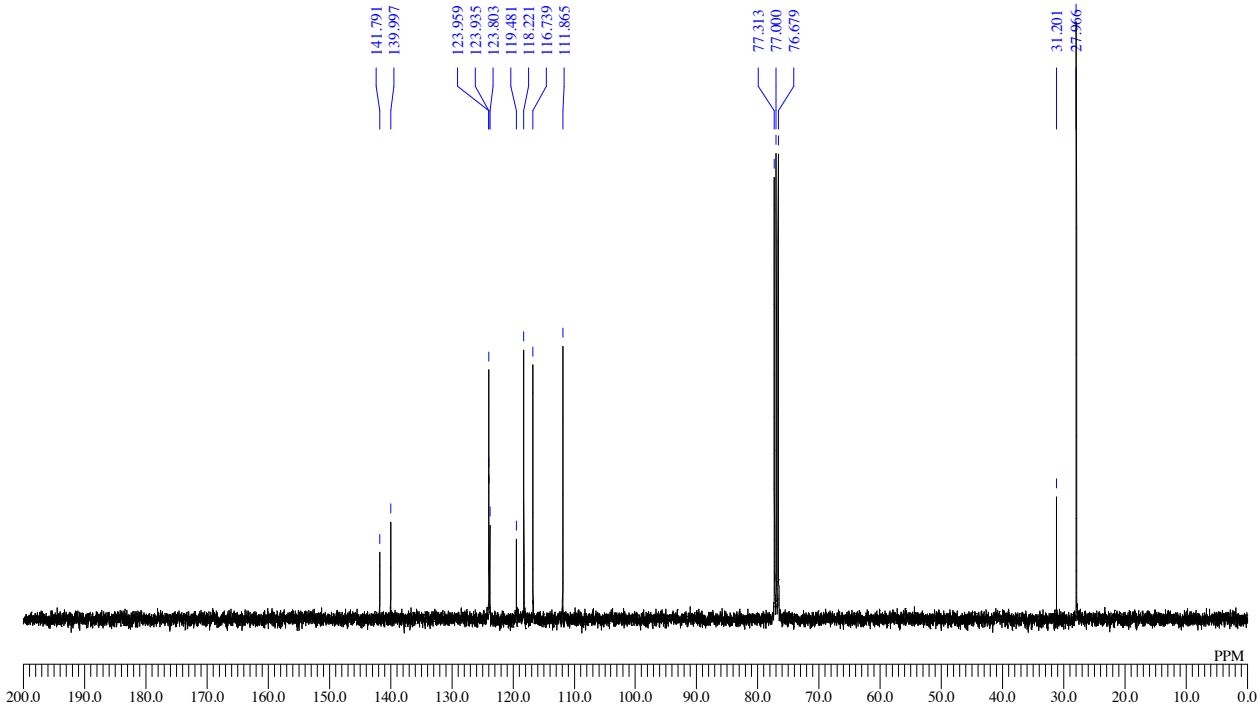

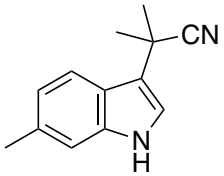

3ja

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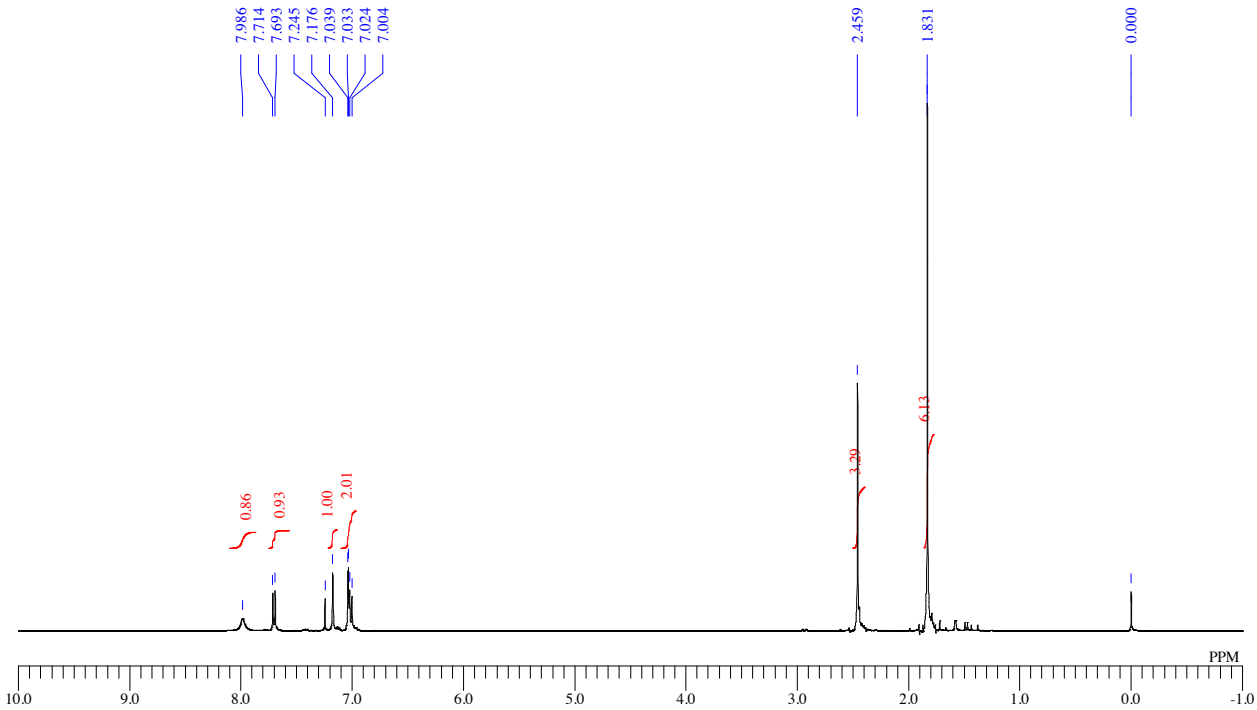

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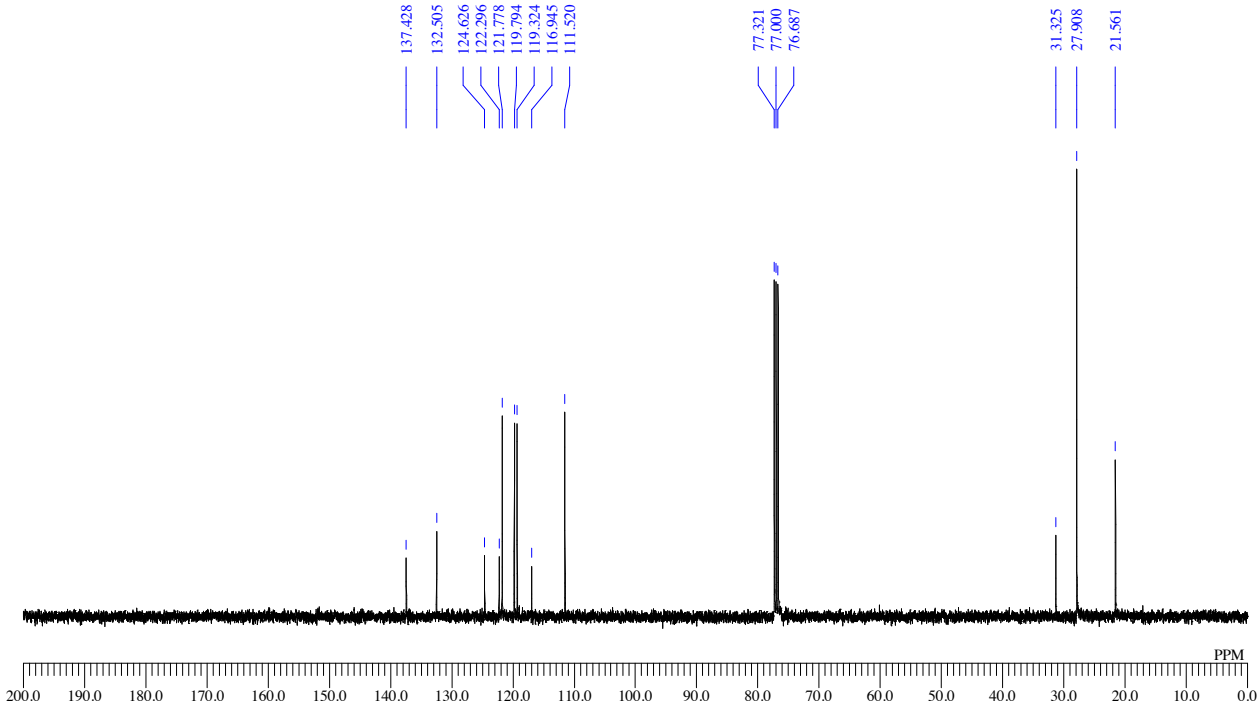

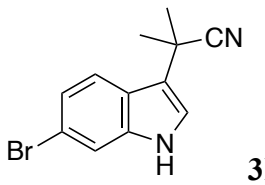

3ka

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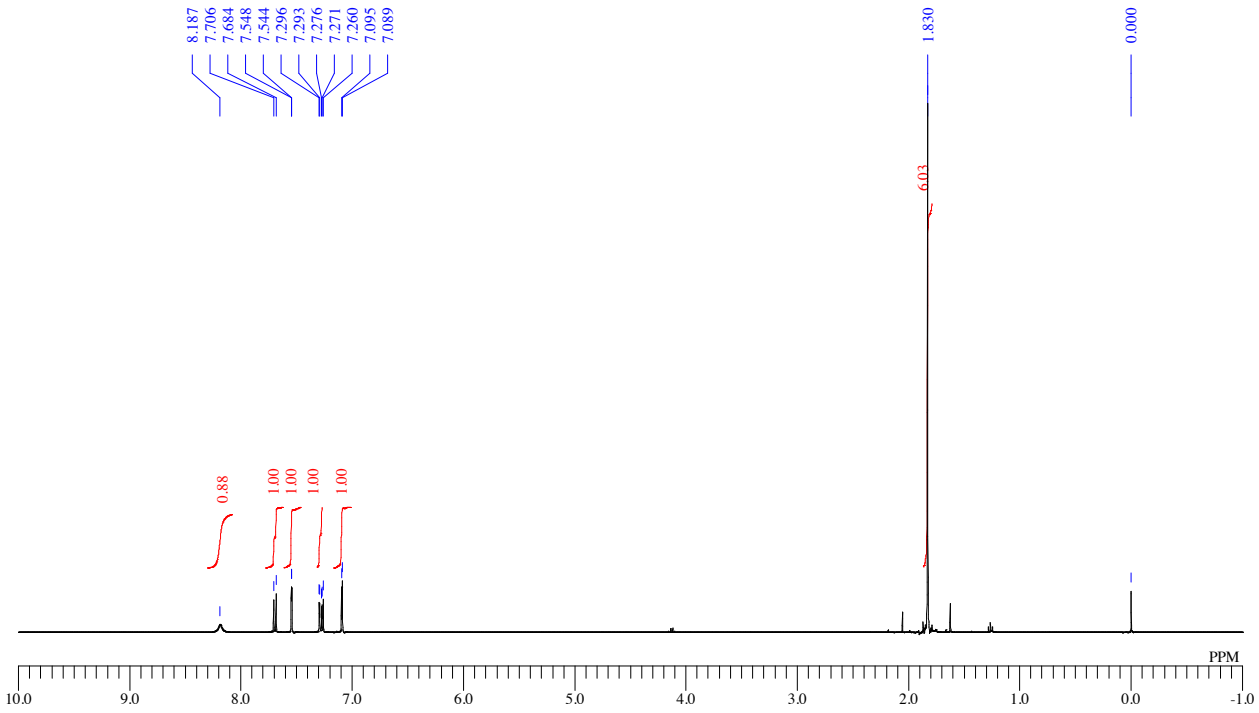

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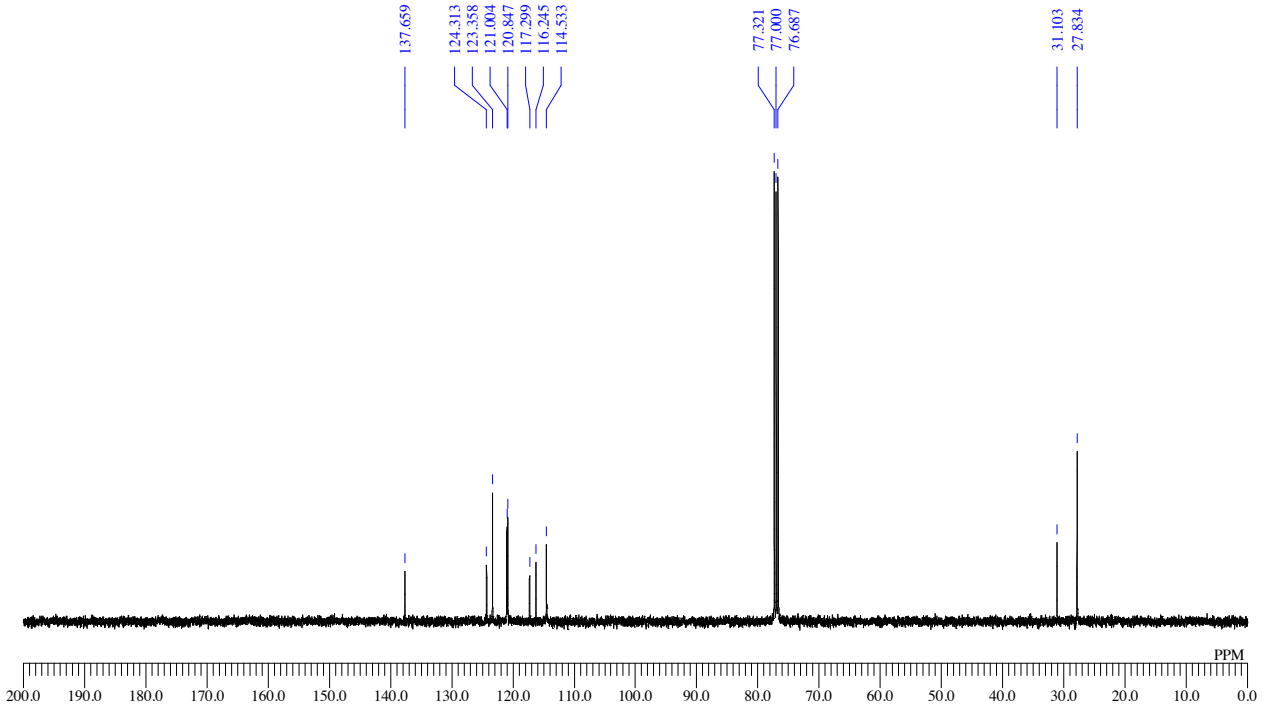

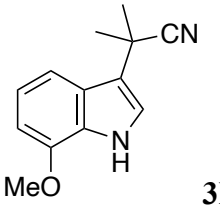

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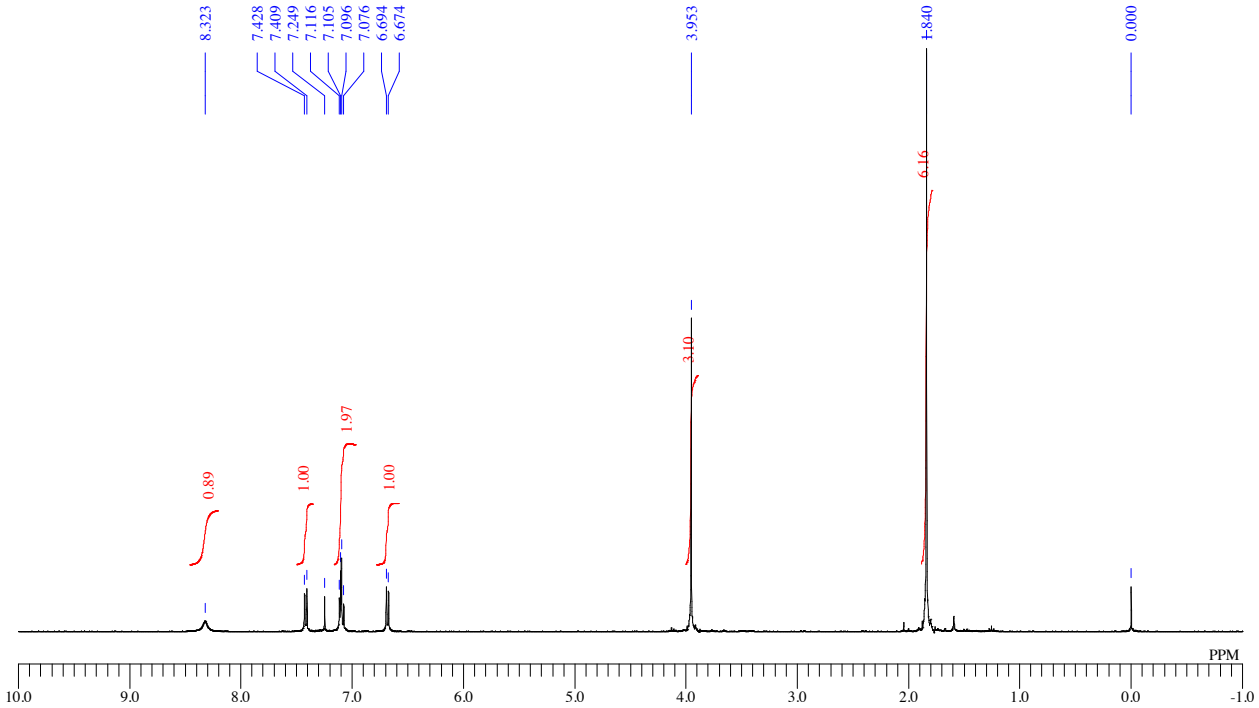
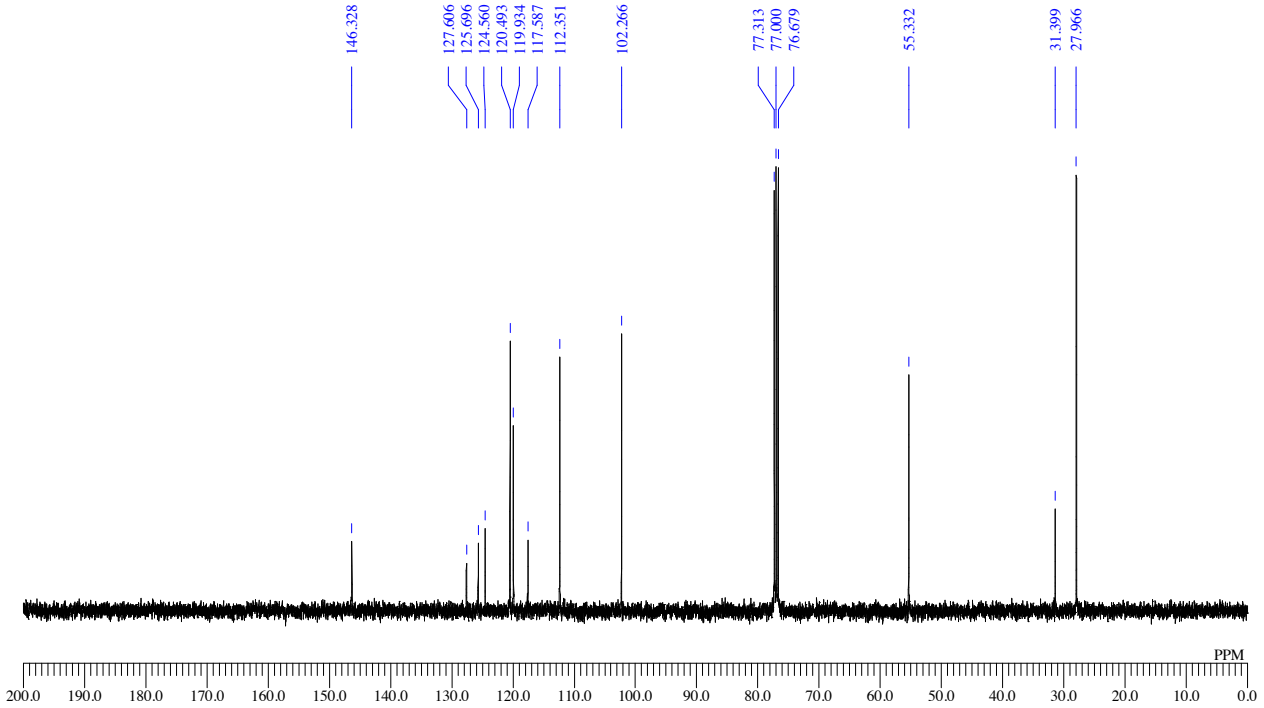
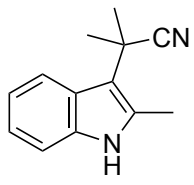


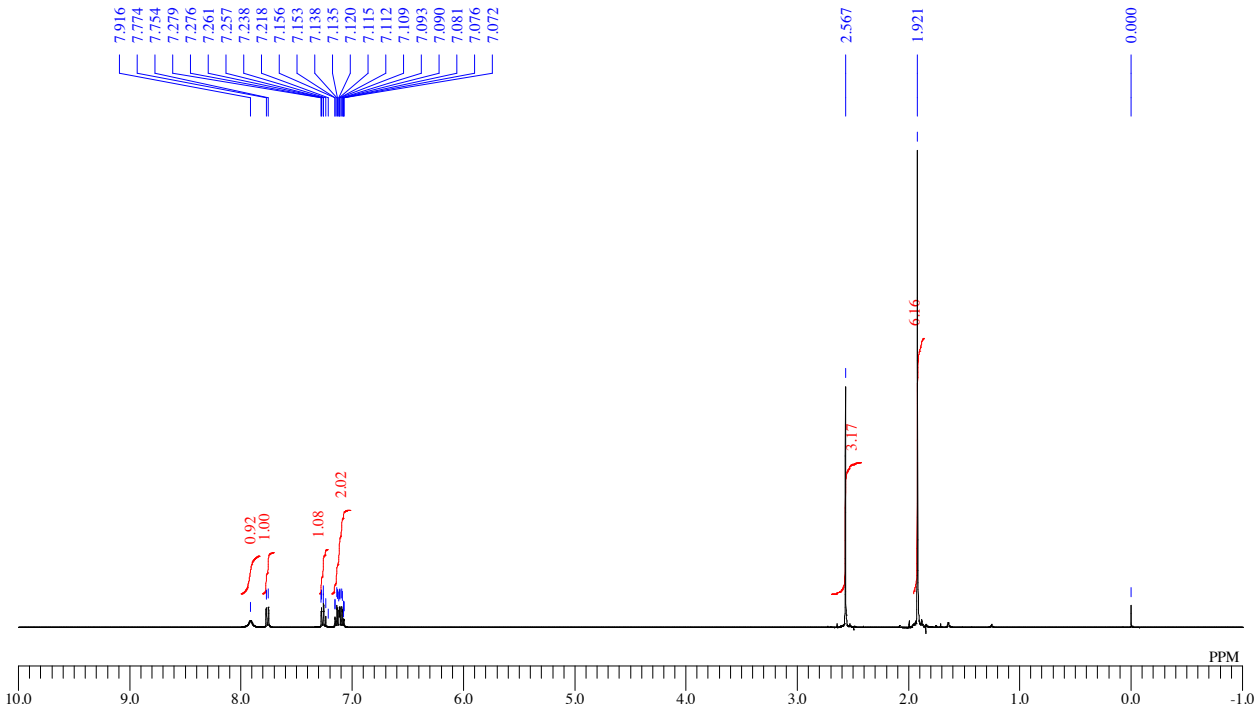
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



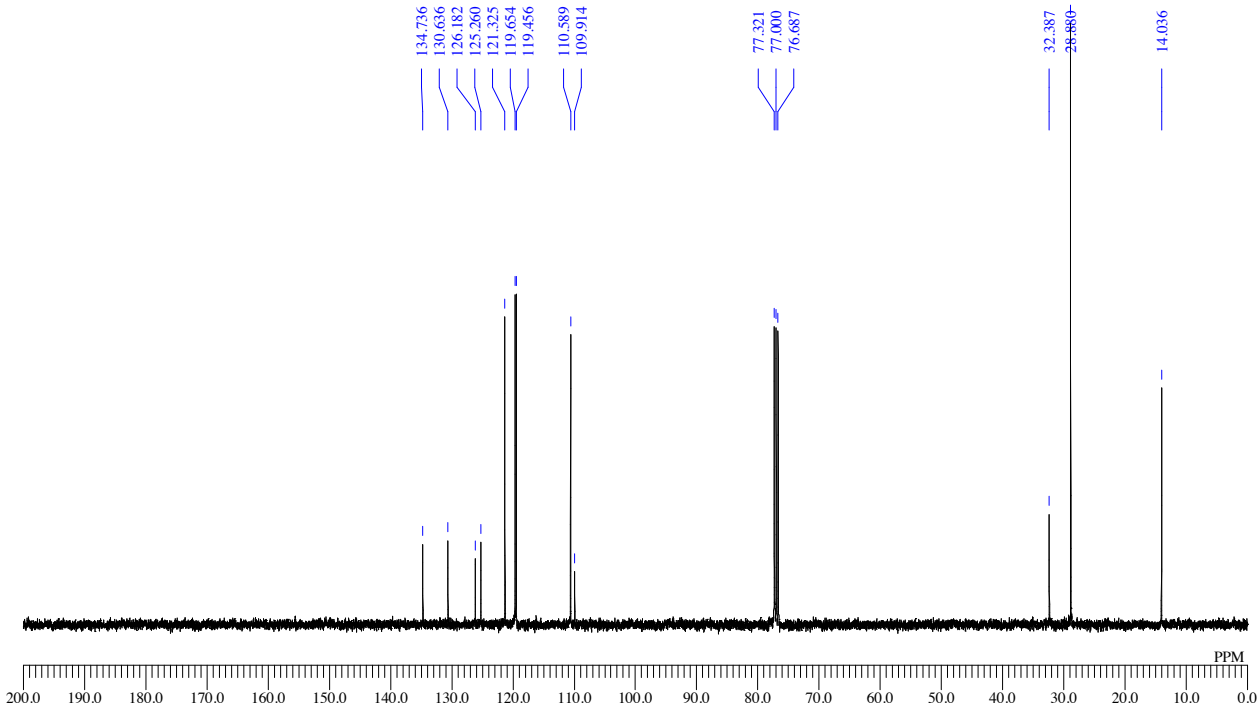


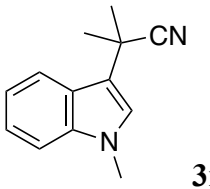
3ma

^{1}H NMR: (400 MHz, $CDCl_3$)



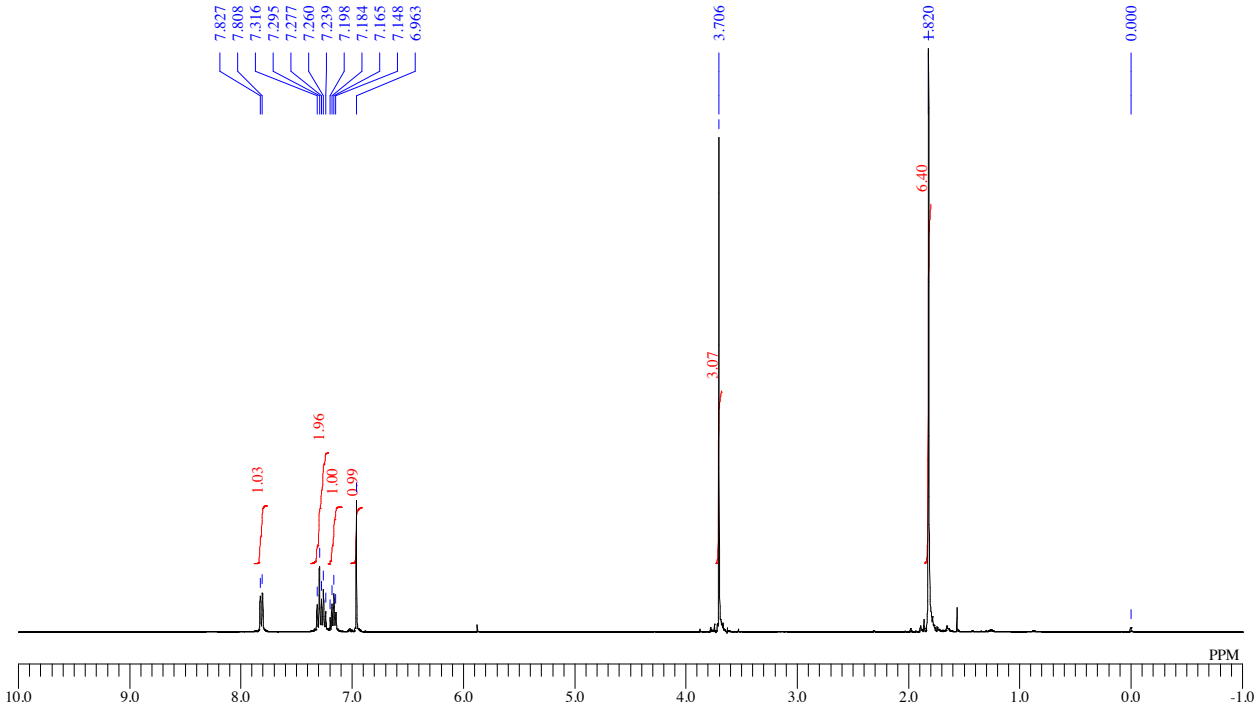
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



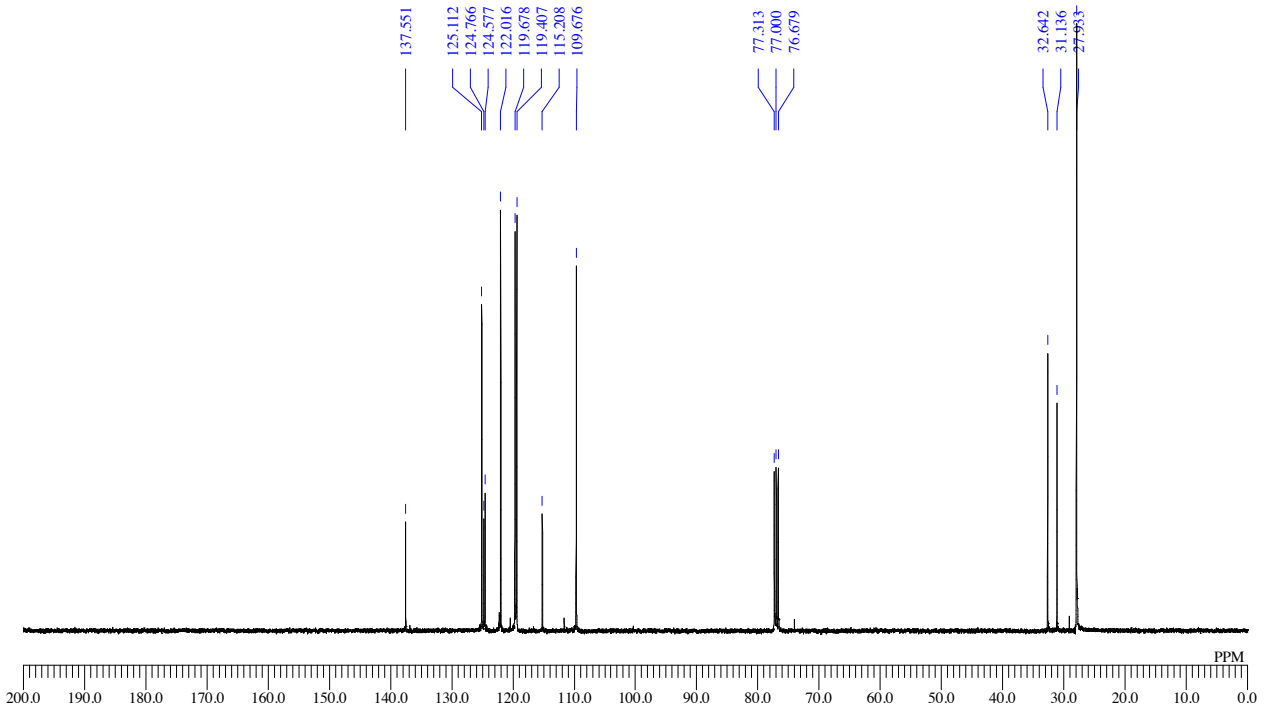


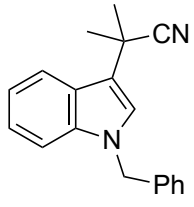
3na

^{1}H NMR: (400 MHz, $CDCl_3$)



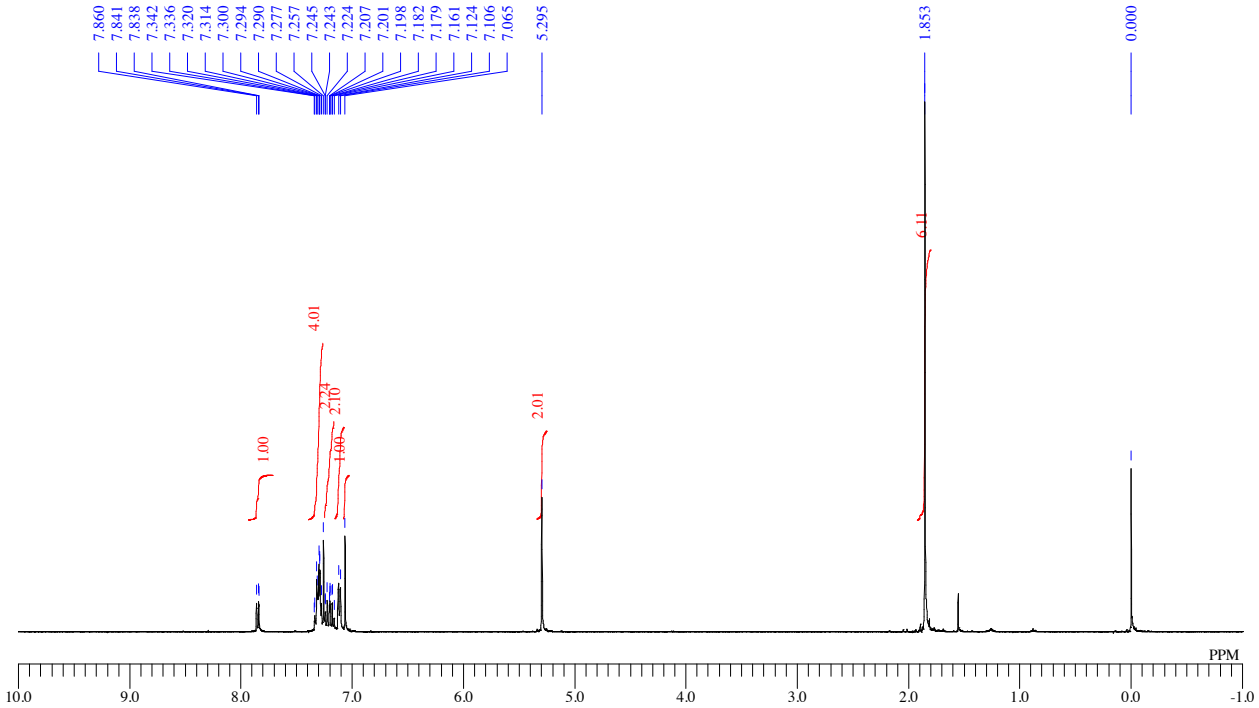
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



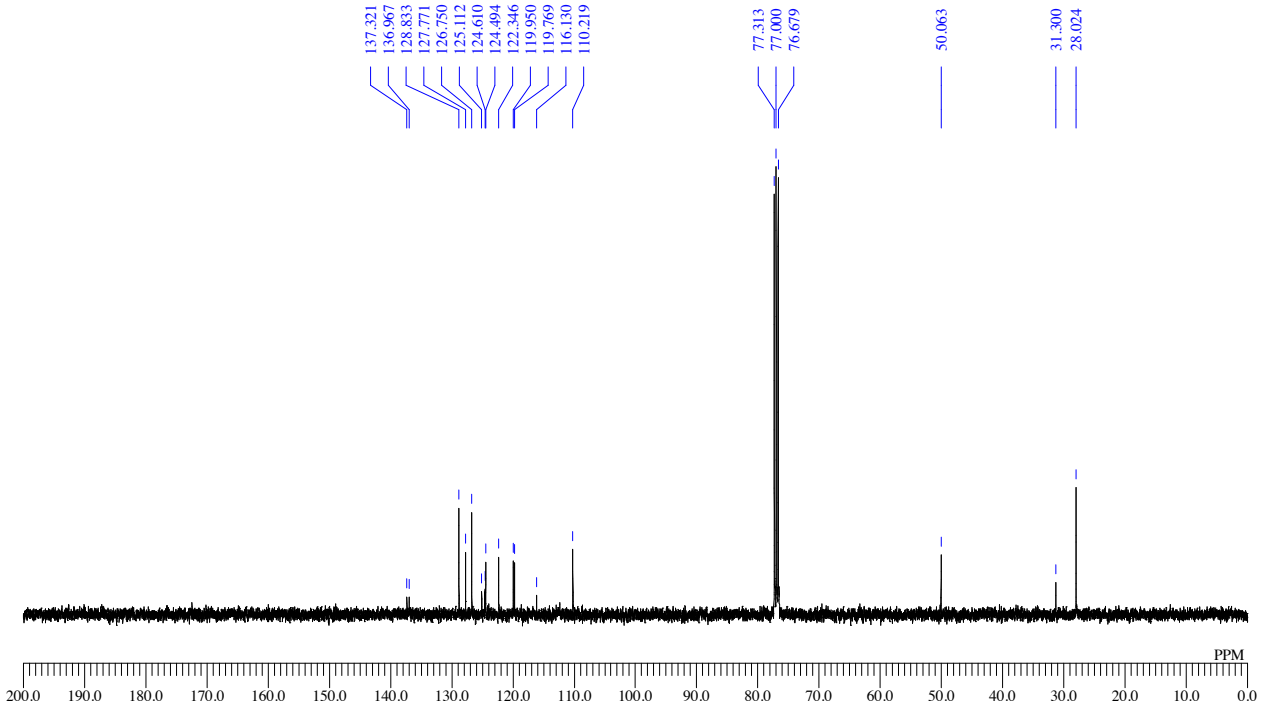


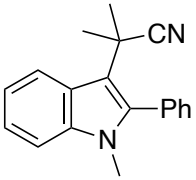
3oa

^{1}H NMR: (400 MHz, $CDCl_3$)



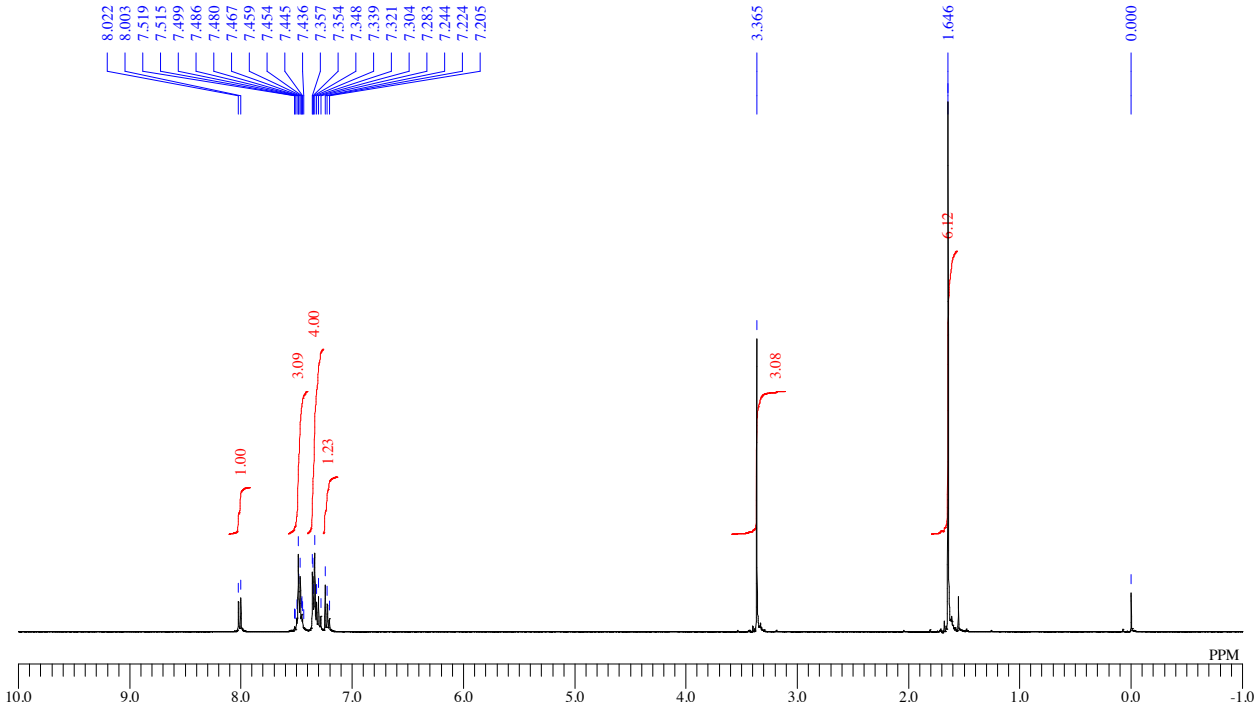
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



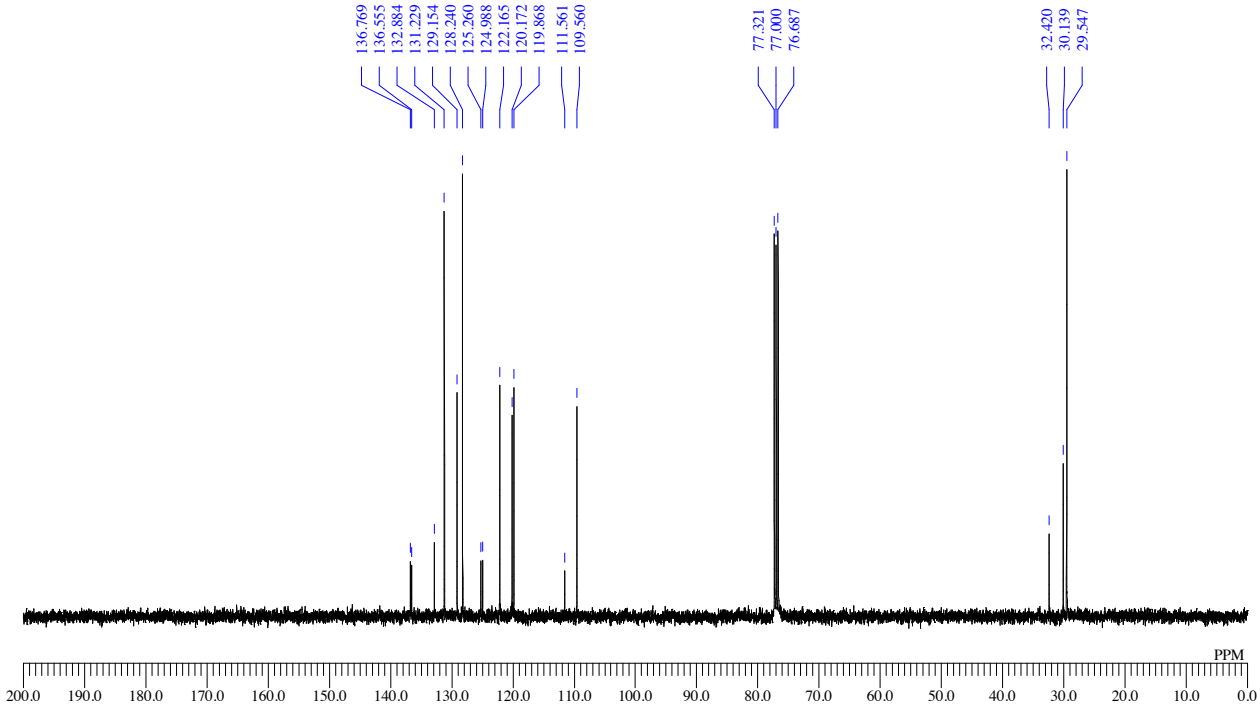


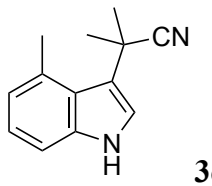
3pa

^{1}H NMR: (400 MHz, $CDCl_3$)



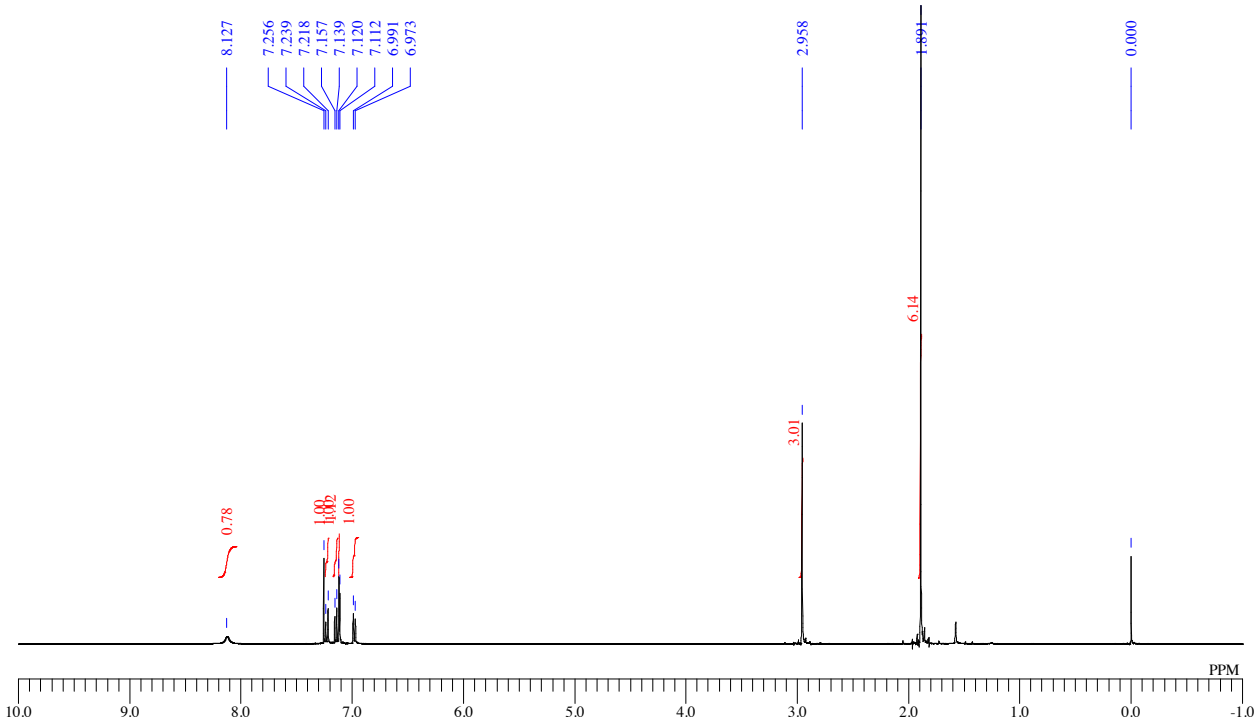
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



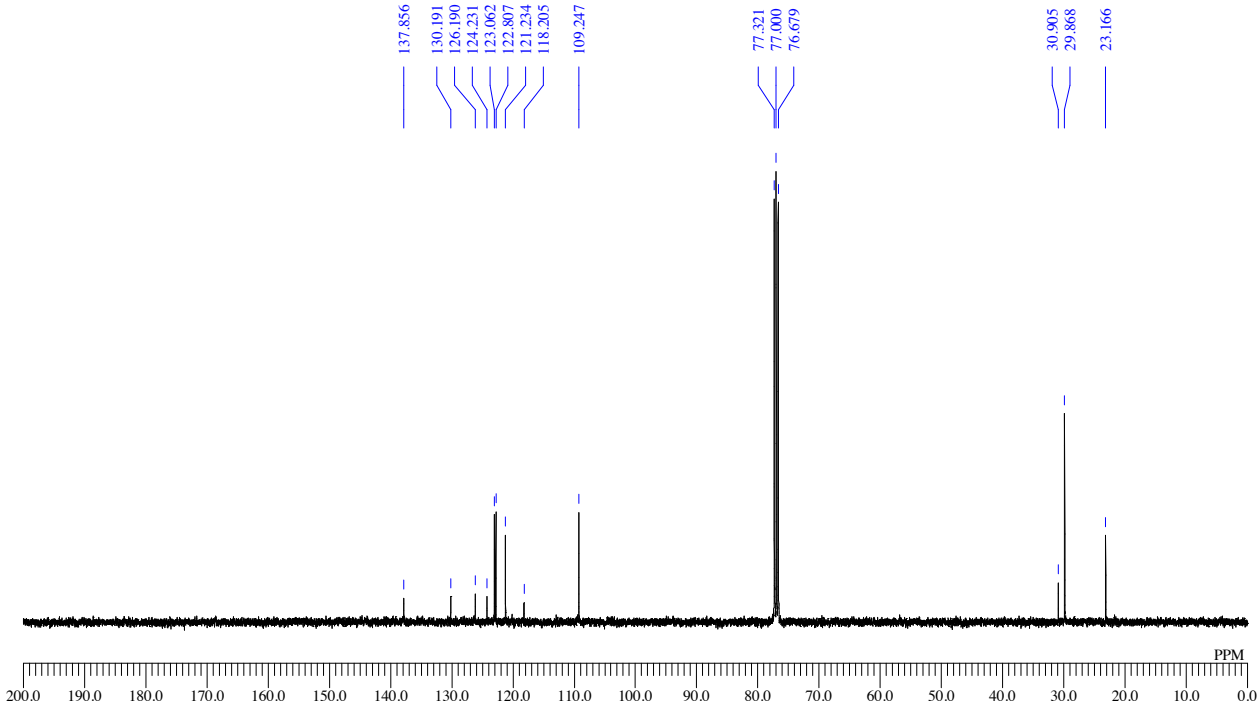


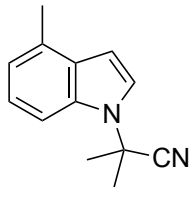
3qa

^{1}H NMR: (400 MHz, $CDCl_3$)



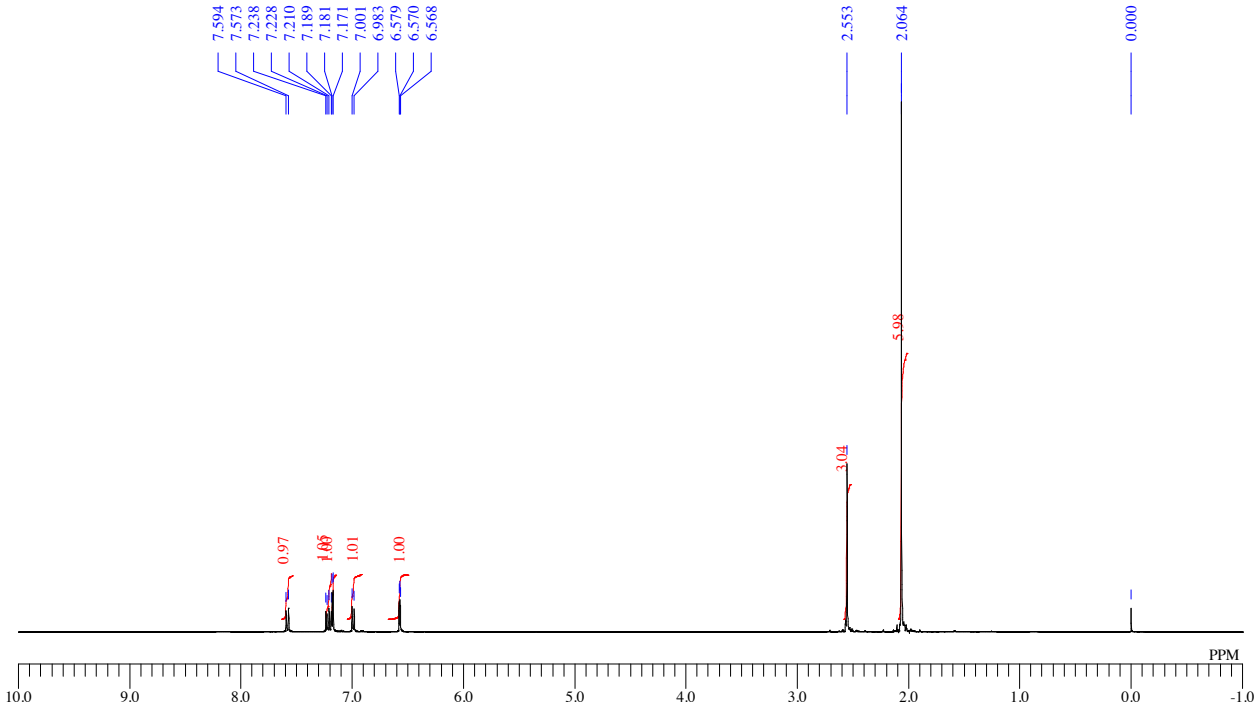
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



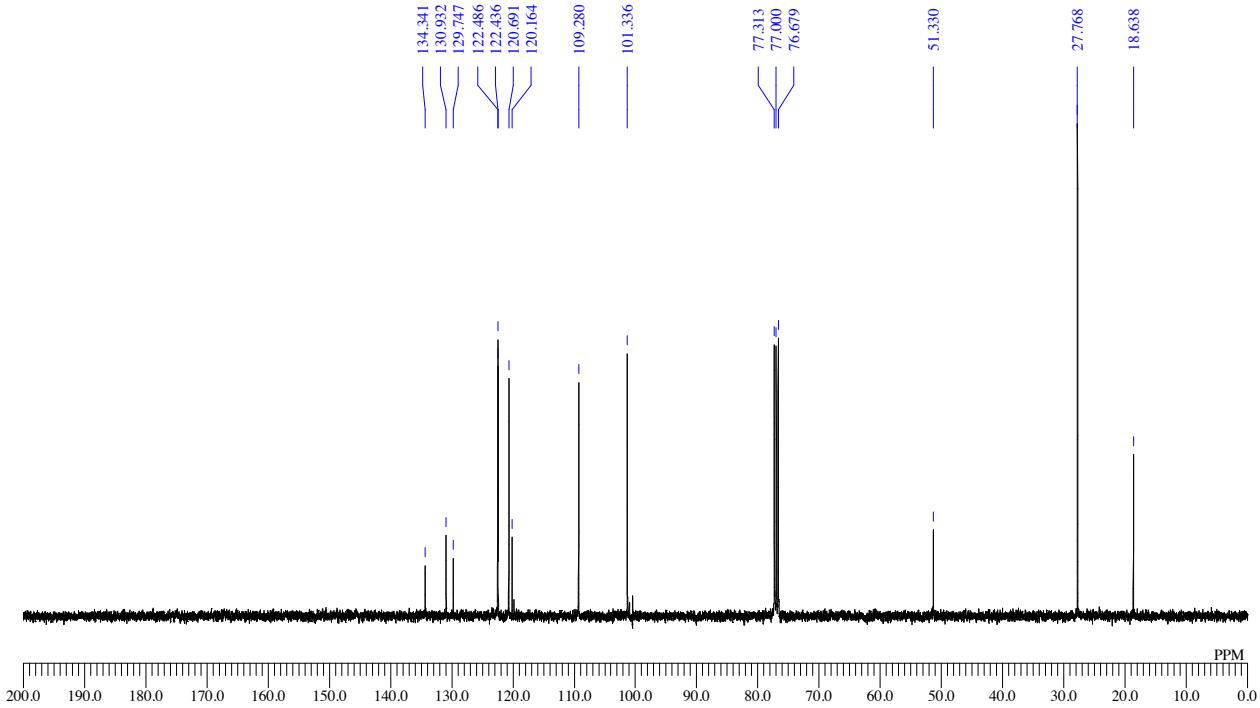


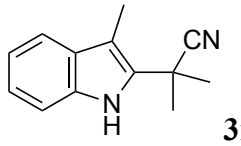
3qa'

^{1}H NMR: (400 MHz, $CDCl_3$)



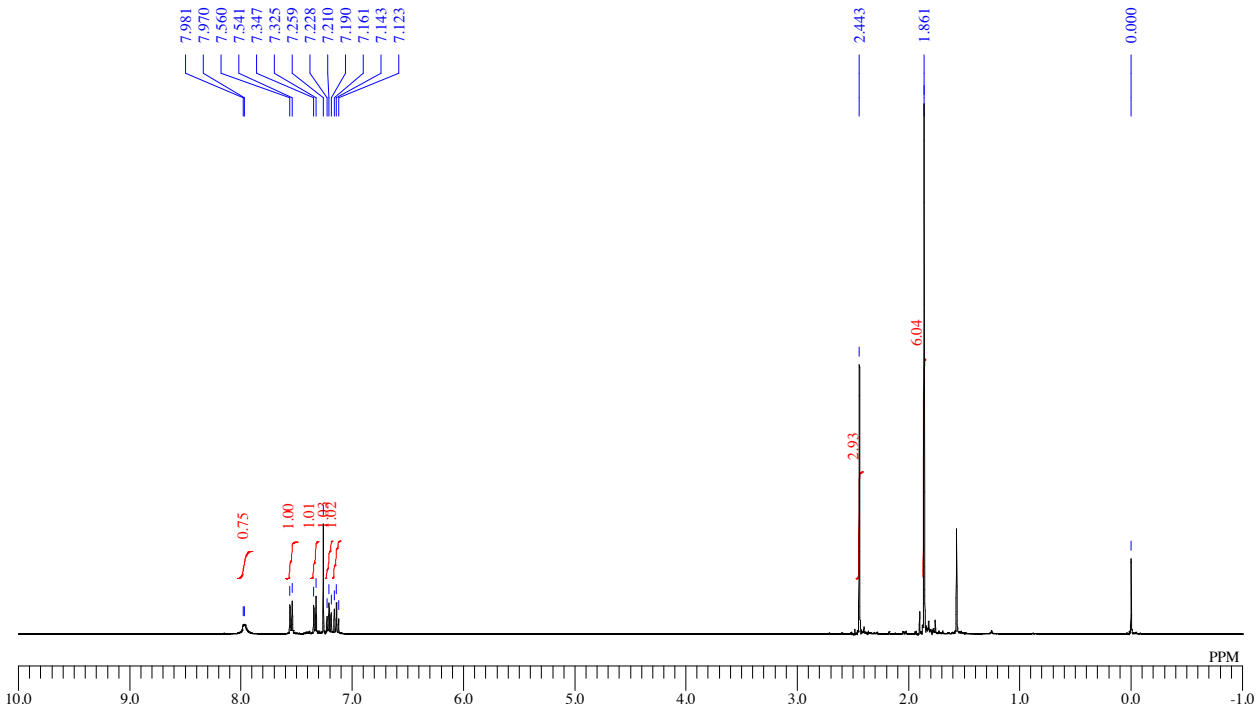
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



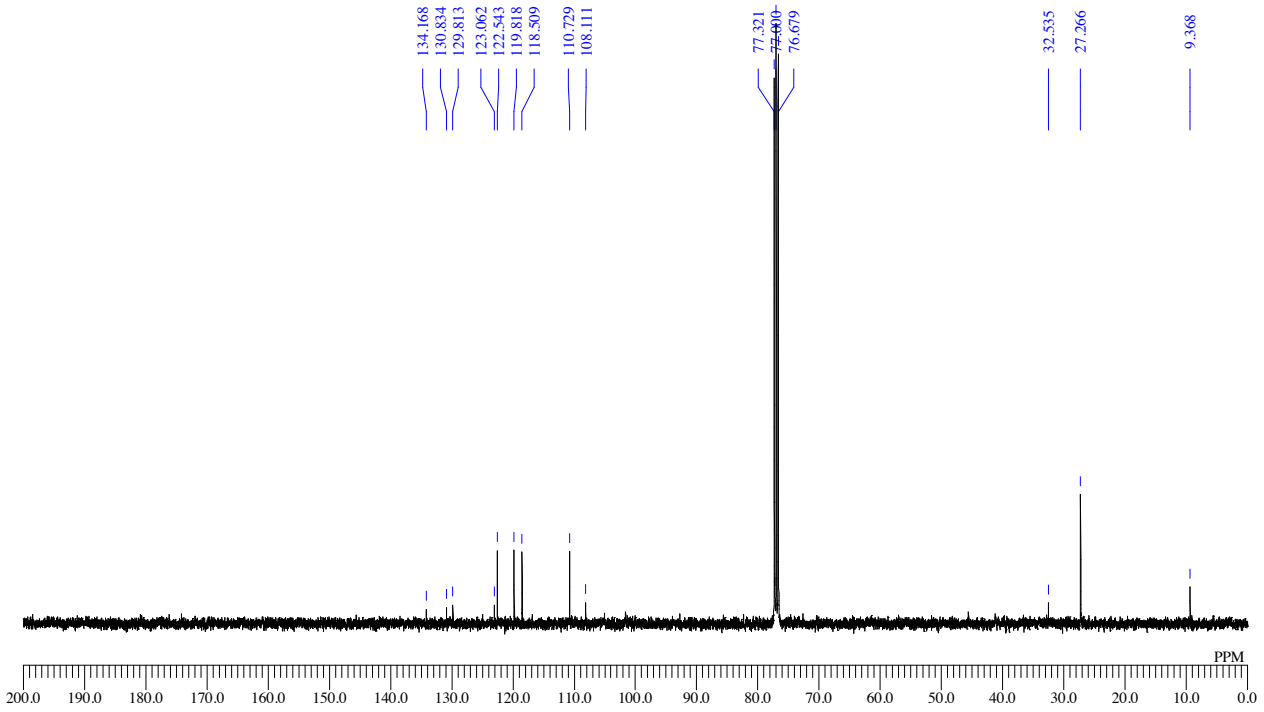


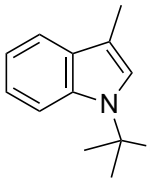
3ra

^{1}H NMR: (400 MHz, $CDCl_3$)



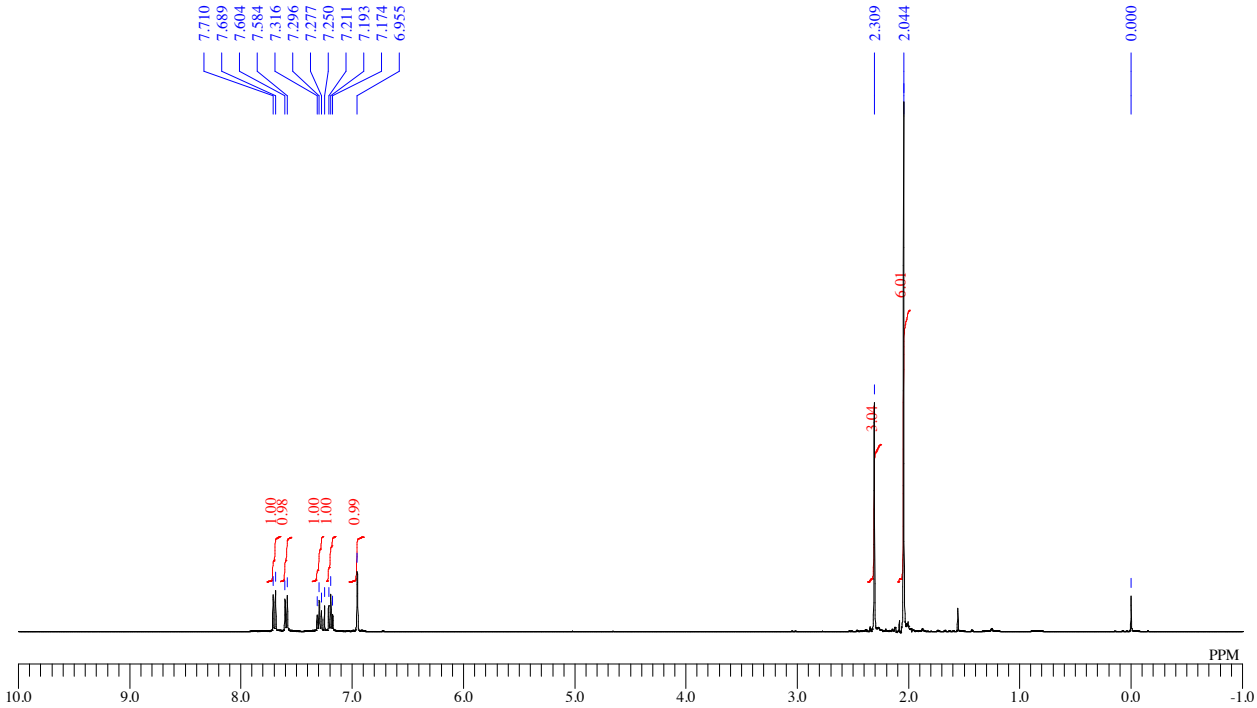
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



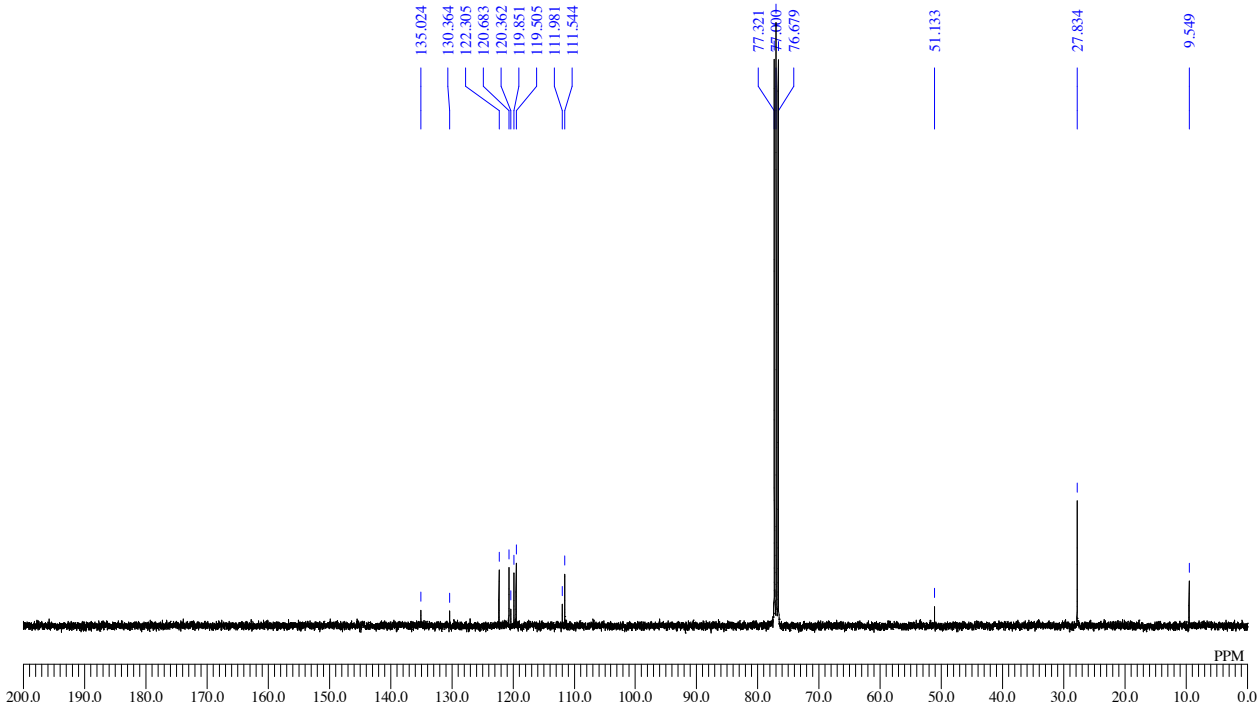


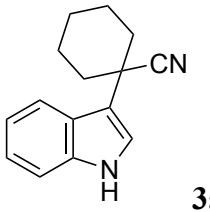
3ra'

^{1}H NMR: (400 MHz, $CDCl_3$)



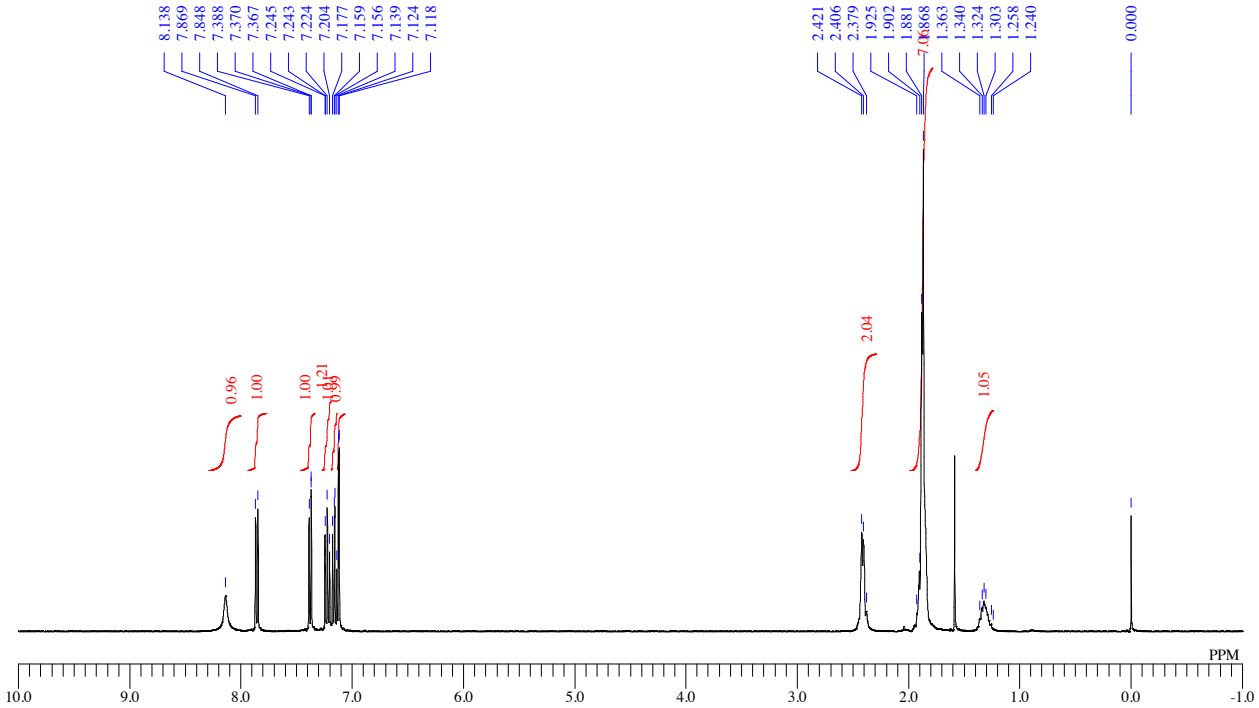
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



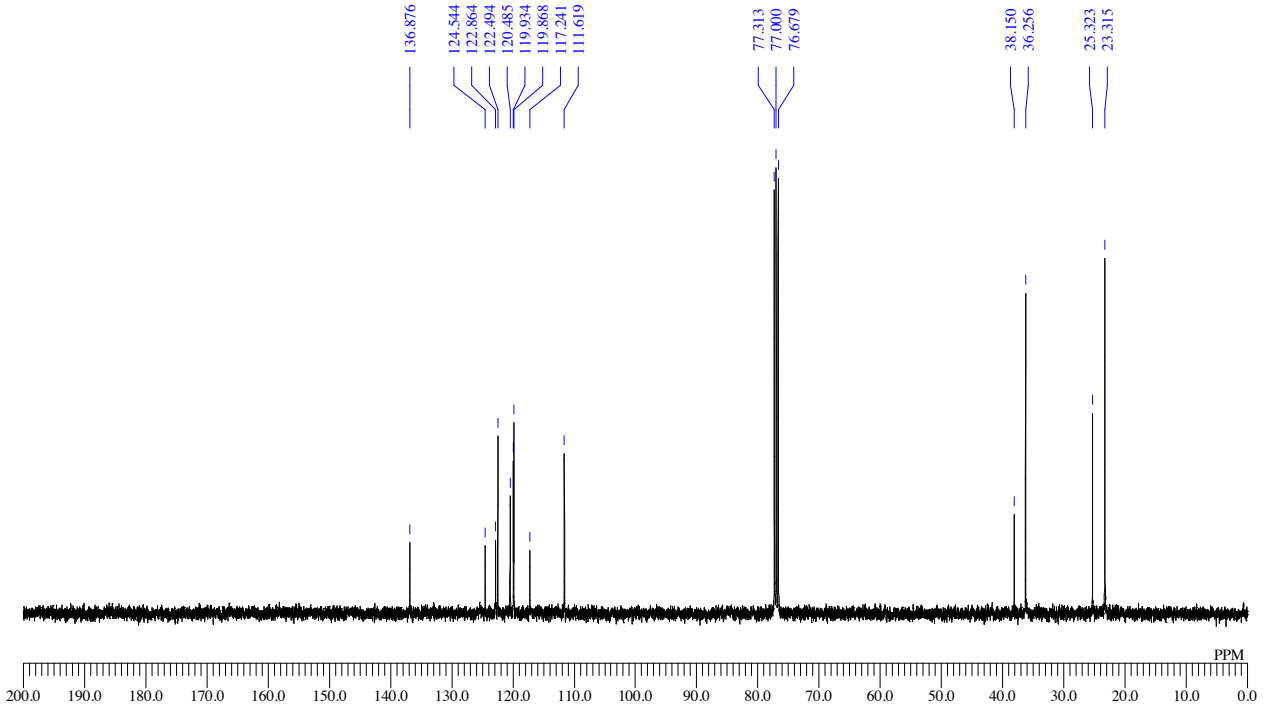


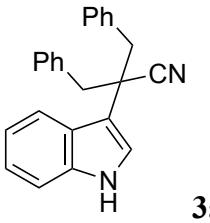
3ab

^{1}H NMR: (400 MHz, $CDCl_3$)



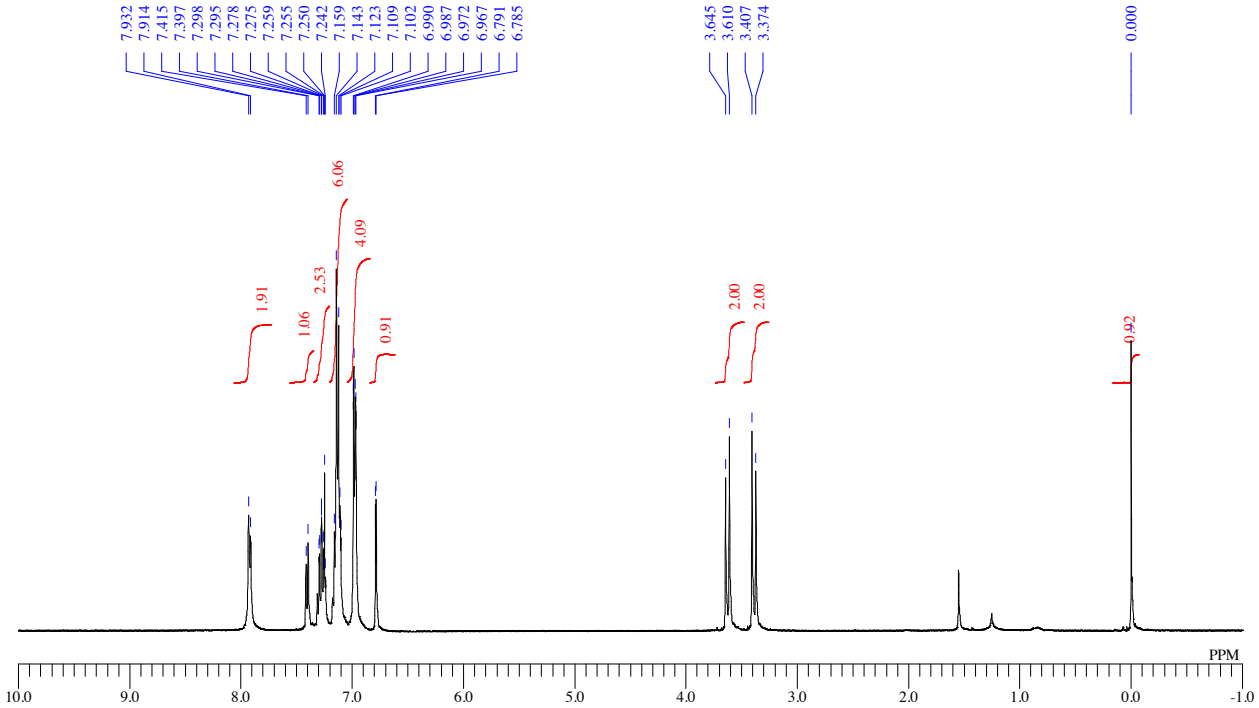
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



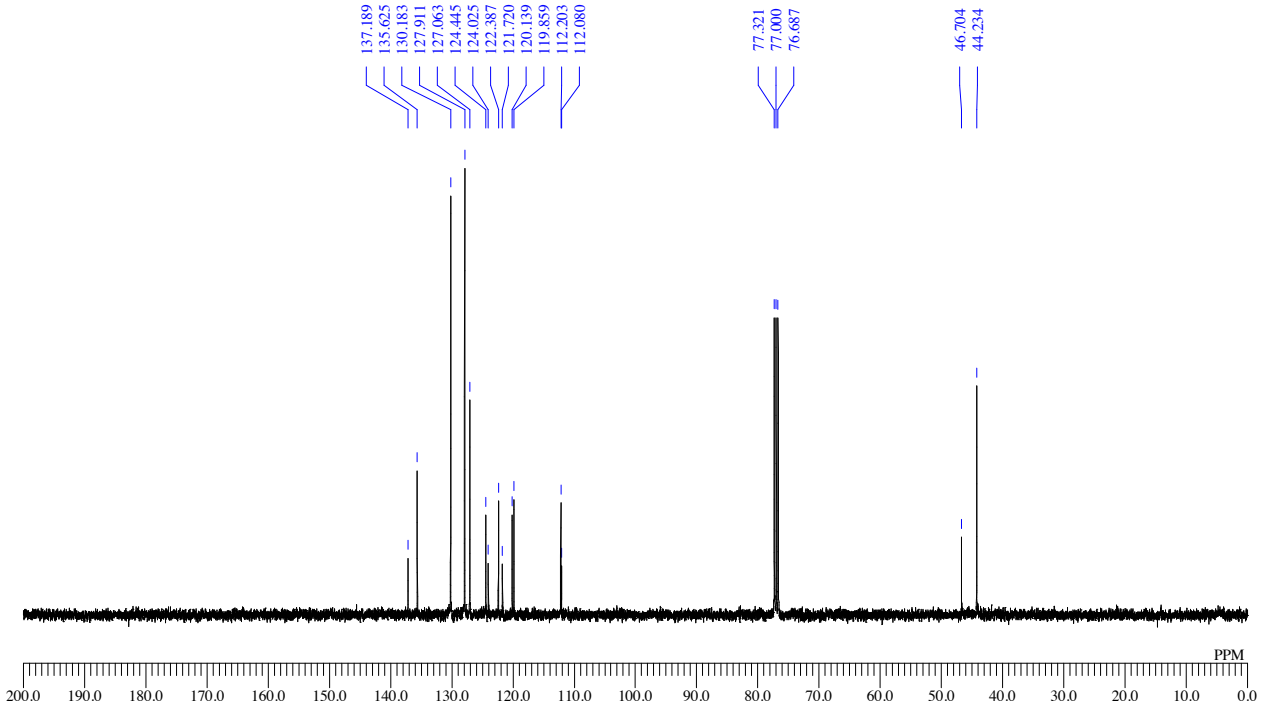


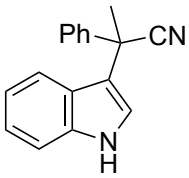
3ac

^{1}H NMR: (400 MHz, $CDCl_3$)



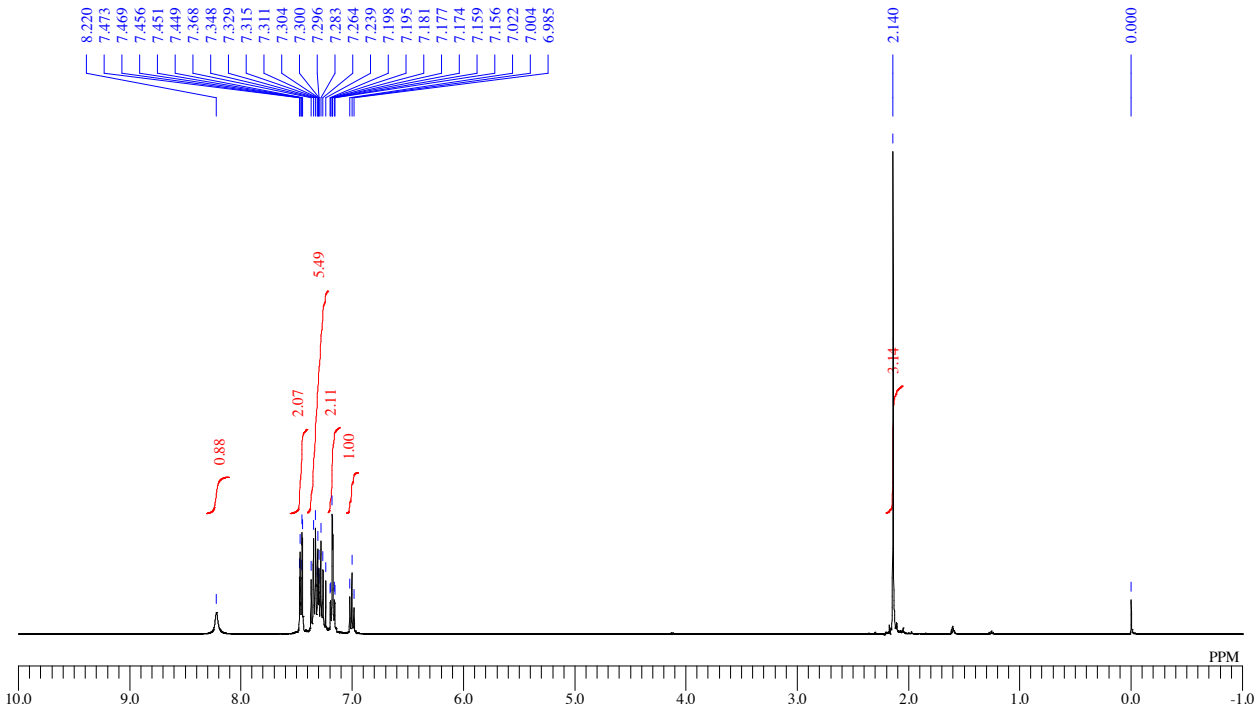
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



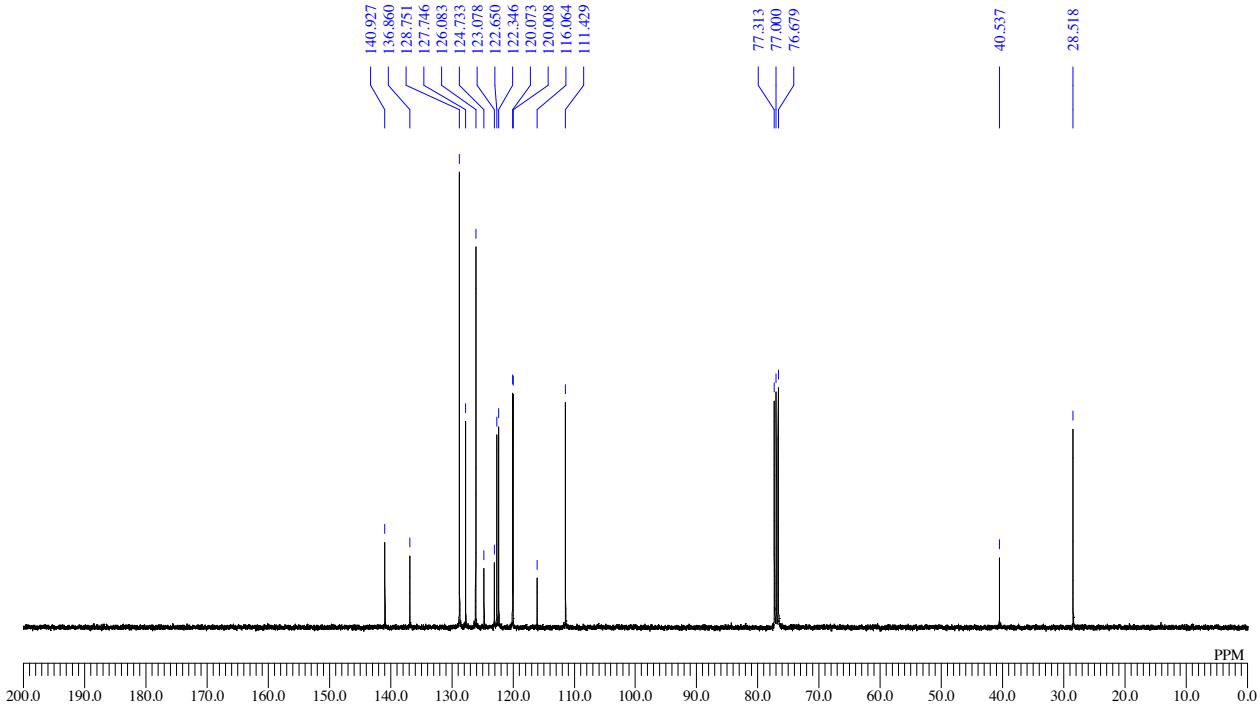


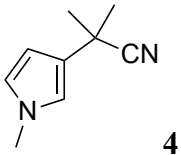
3ad

^{1}H NMR: (400 MHz, $CDCl_3$)



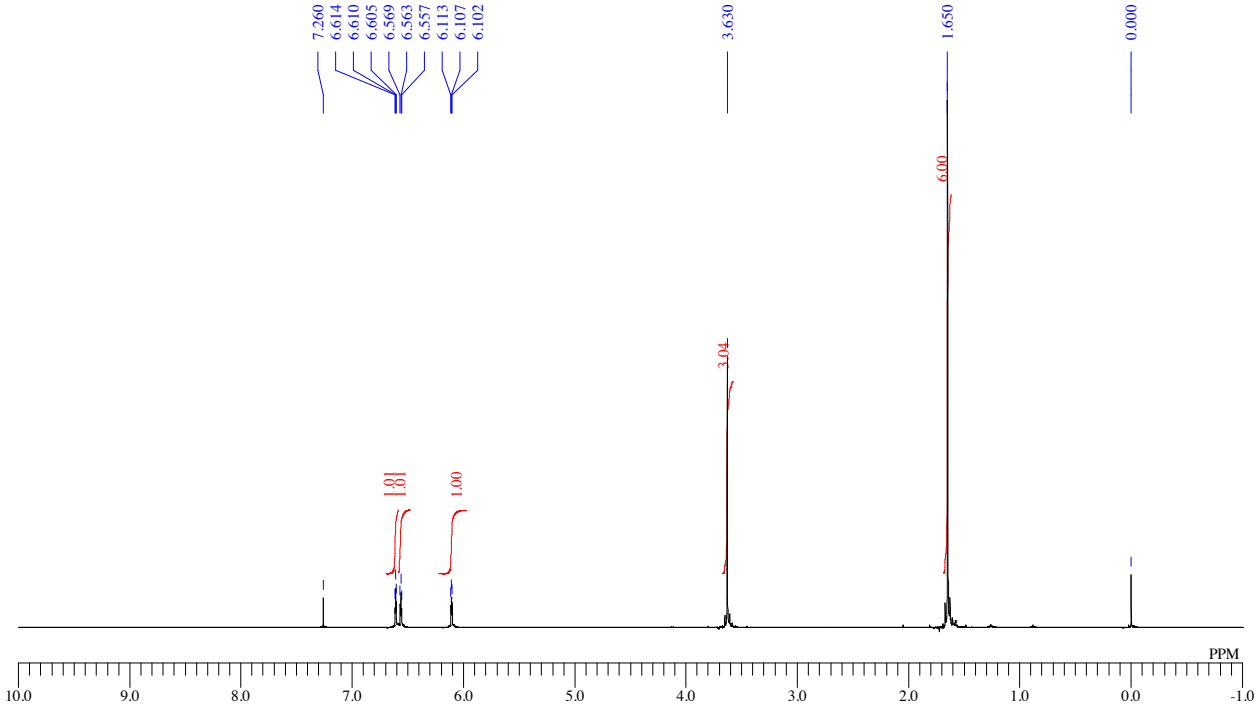
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



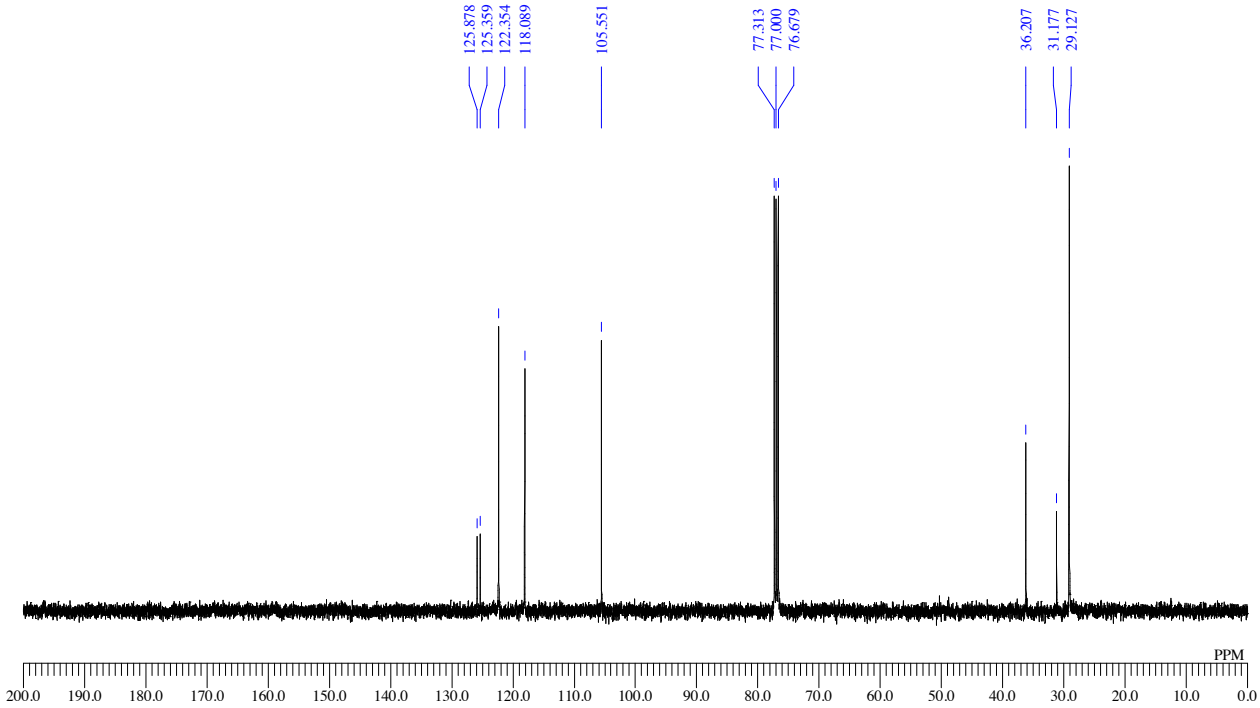


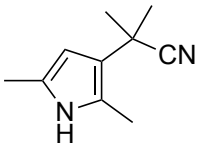
4

^{1}H NMR: (400 MHz, $CDCl_3$)



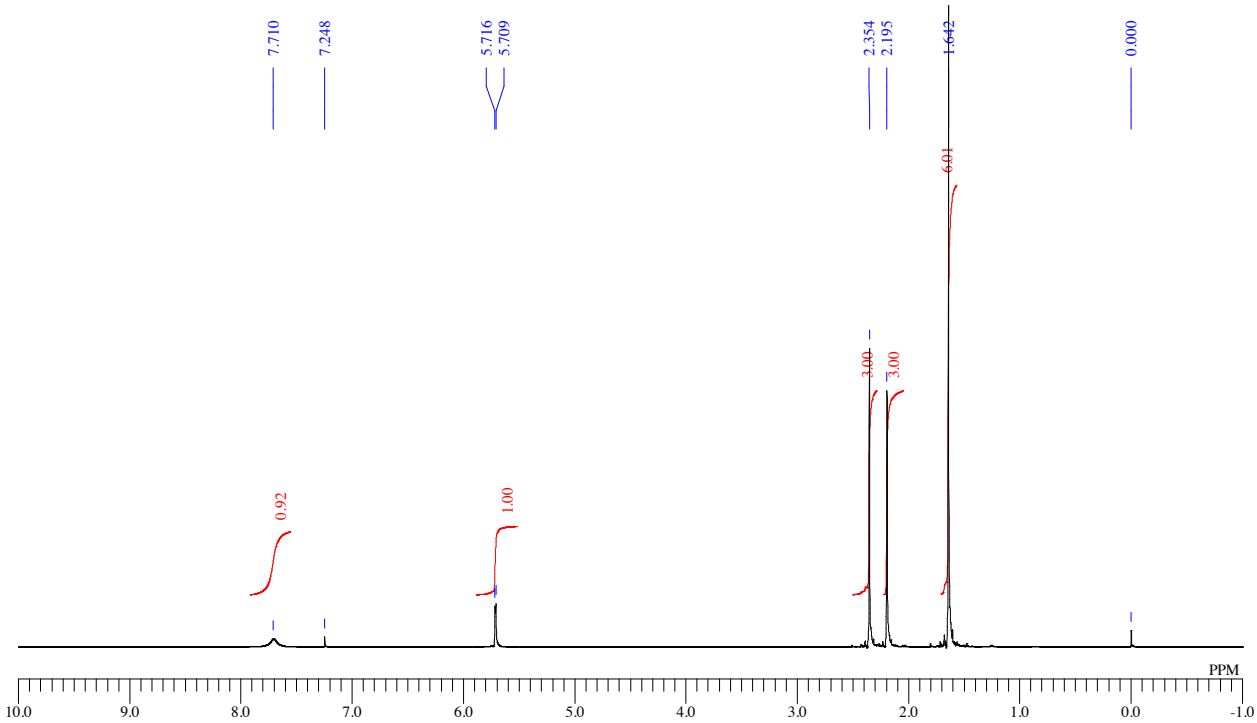
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



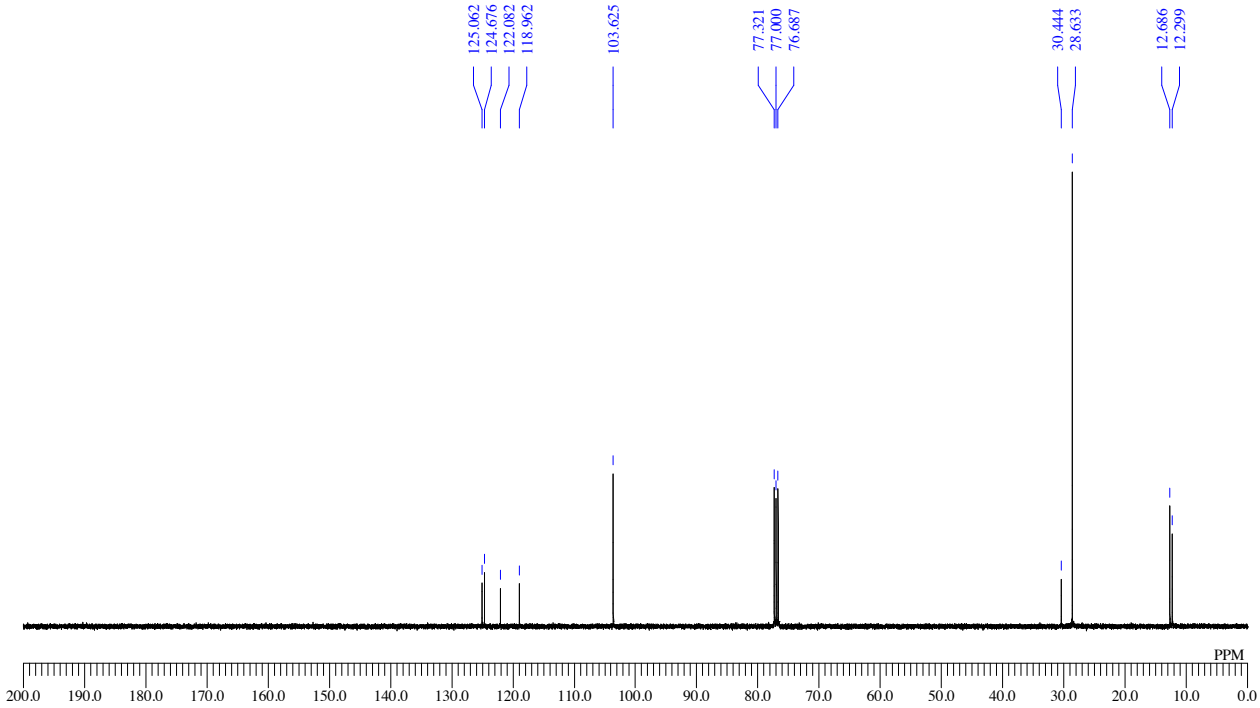


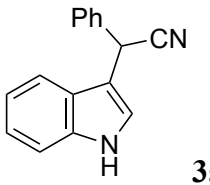
5

^{1}H NMR: (400 MHz, $CDCl_3$)



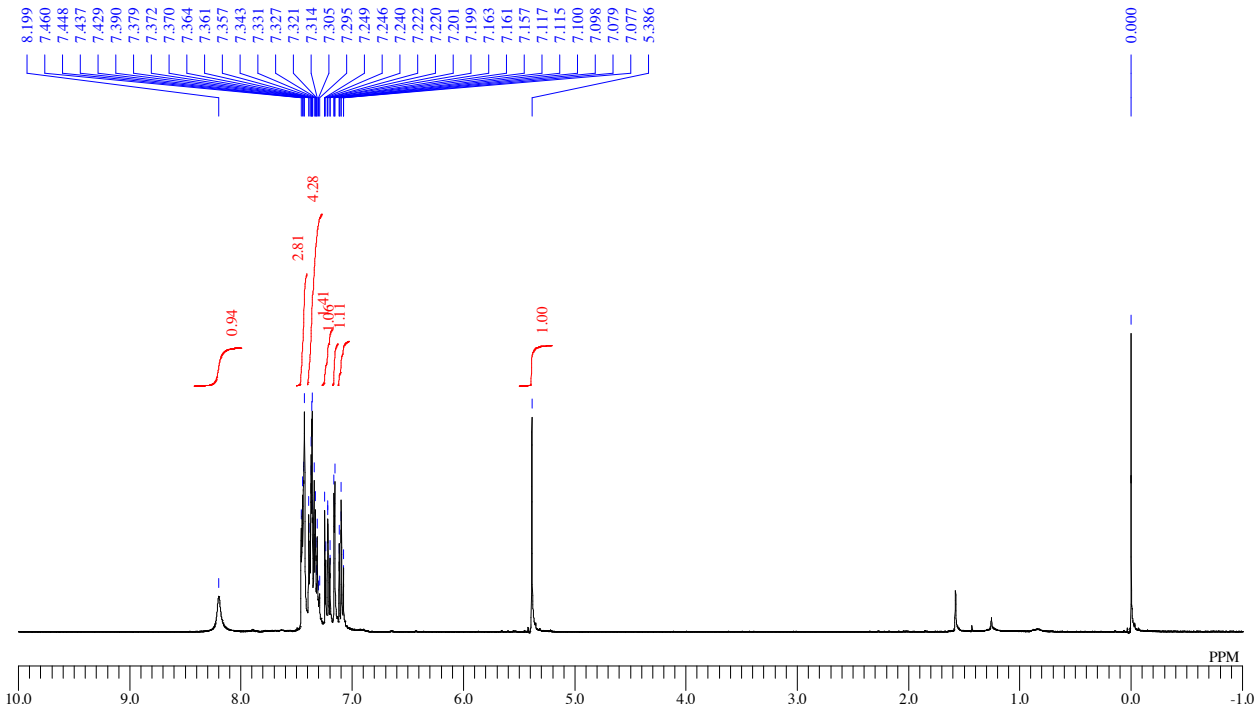
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



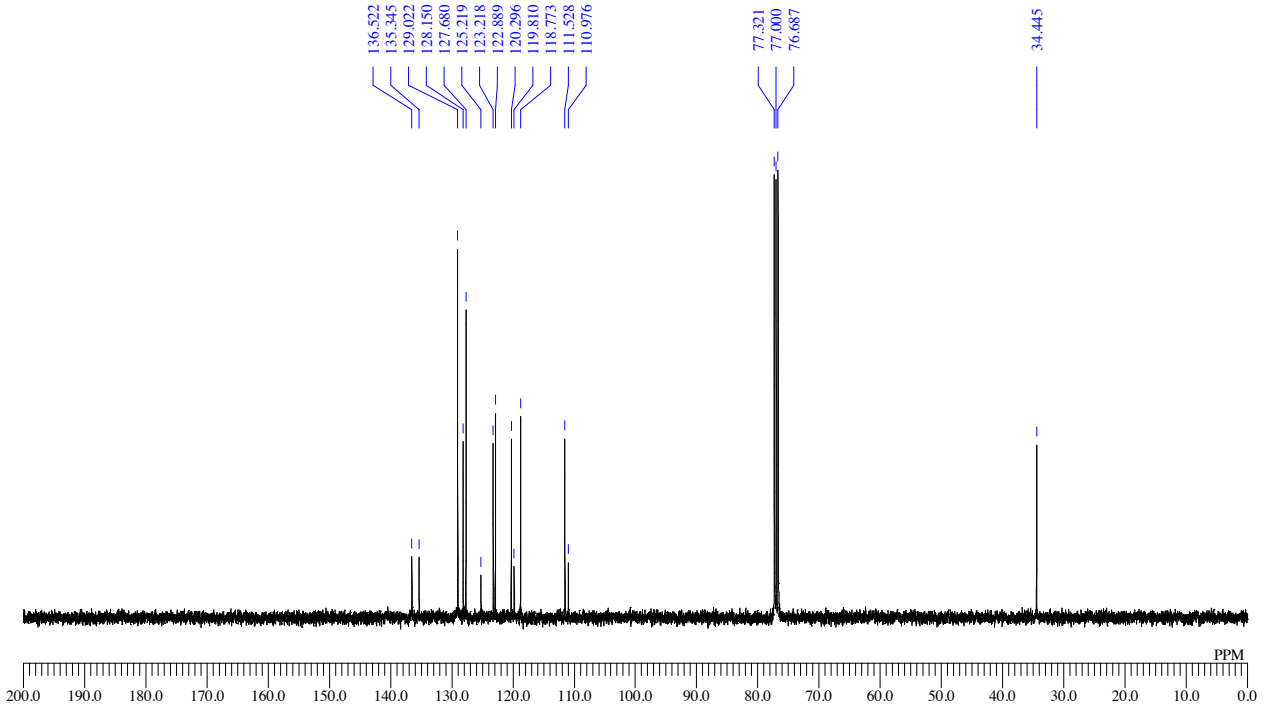


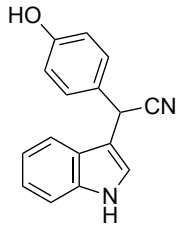
3ae, 10aa

^{1}H NMR: (400 MHz, $CDCl_3$)



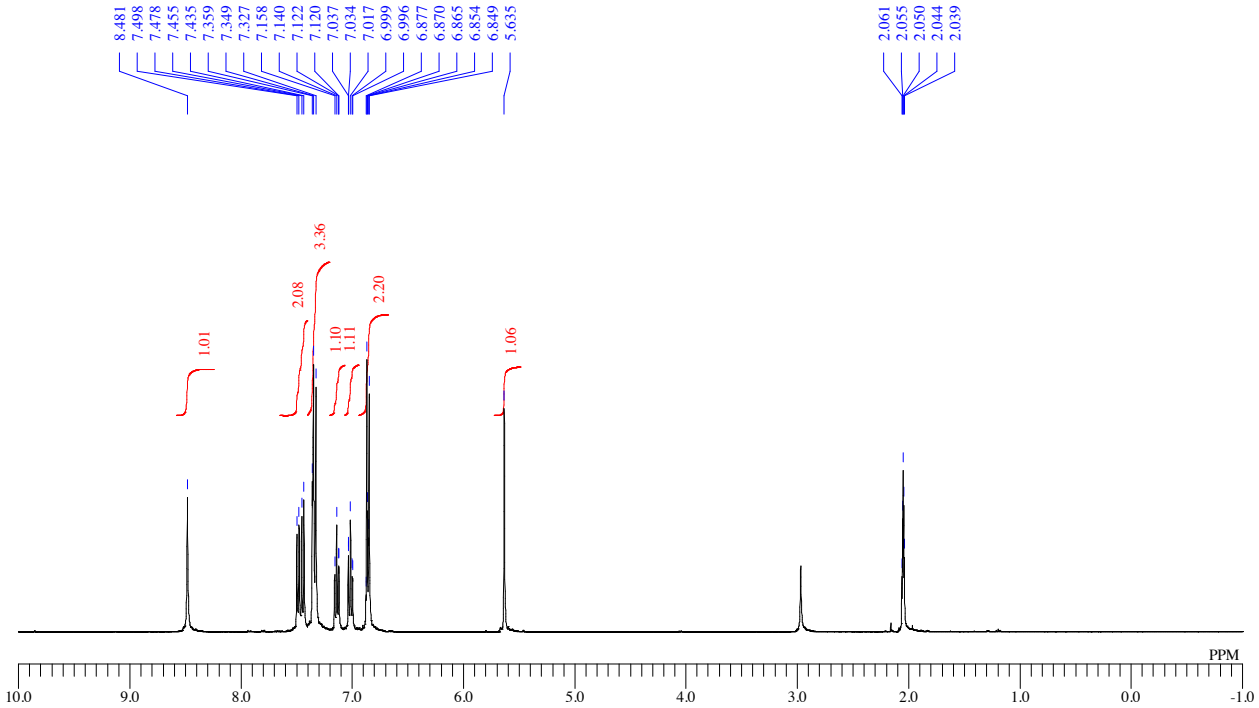
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



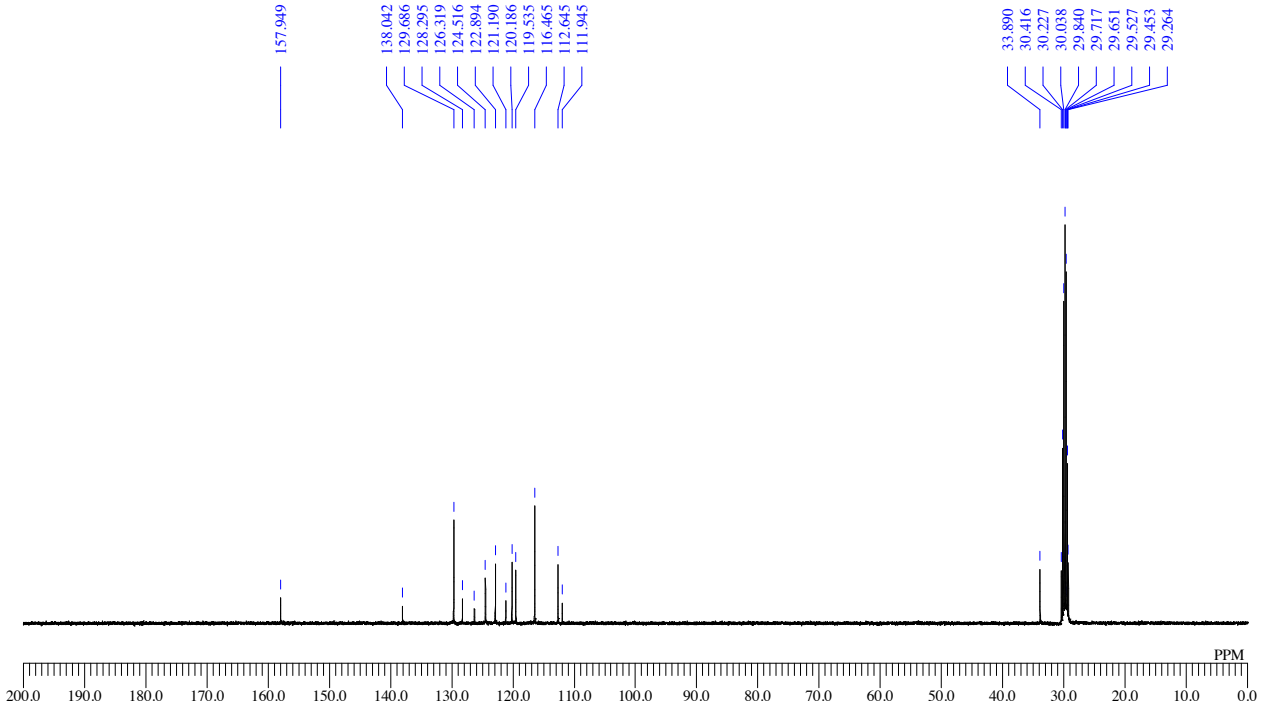


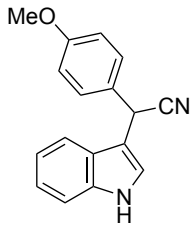
10ab

^{1}H NMR: (400 MHz, acetone-d_6)



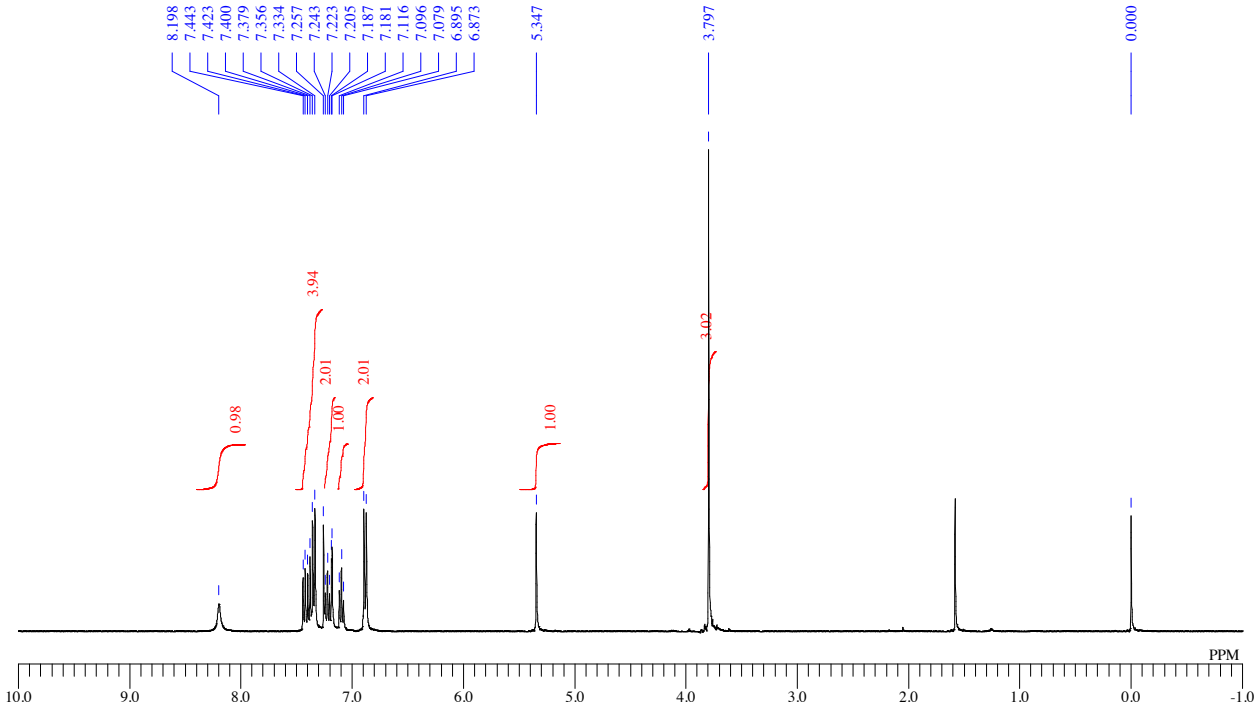
^{13}C{^{1}H} NMR: (100 MHz, acetone-d_6)



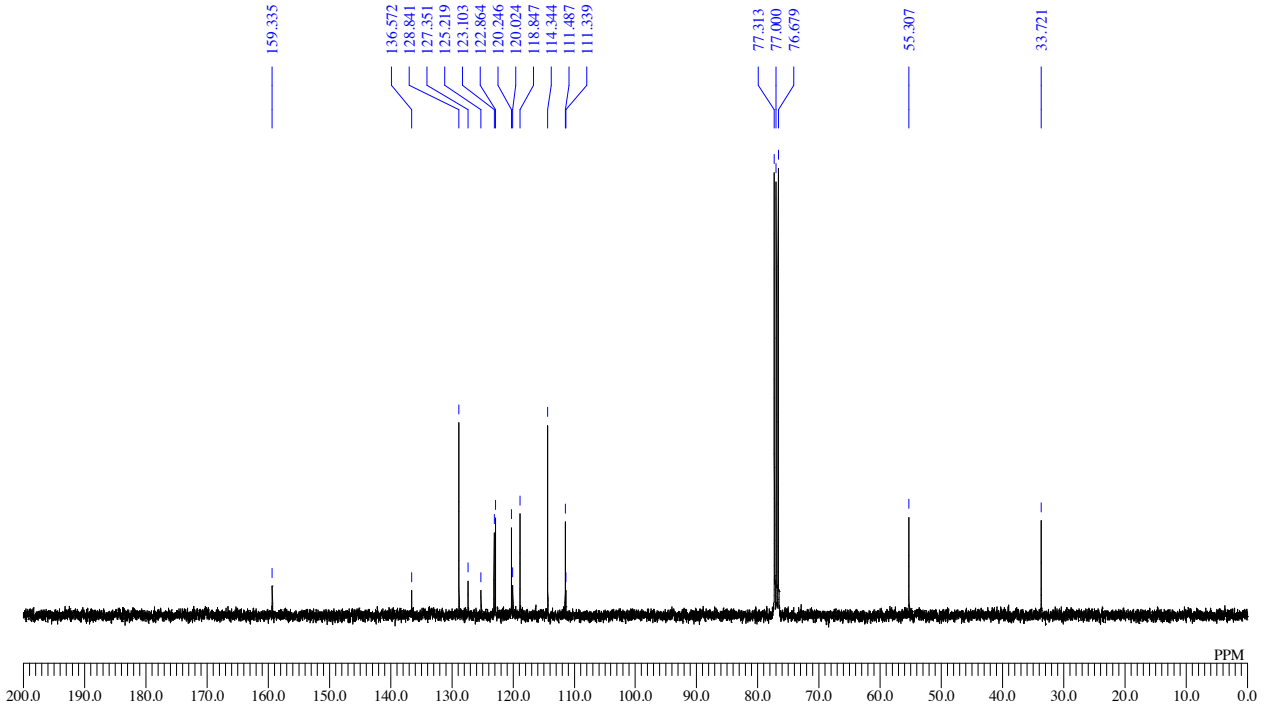


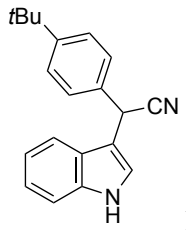
10ac

^{1}H NMR: (400 MHz, $CDCl_3$)



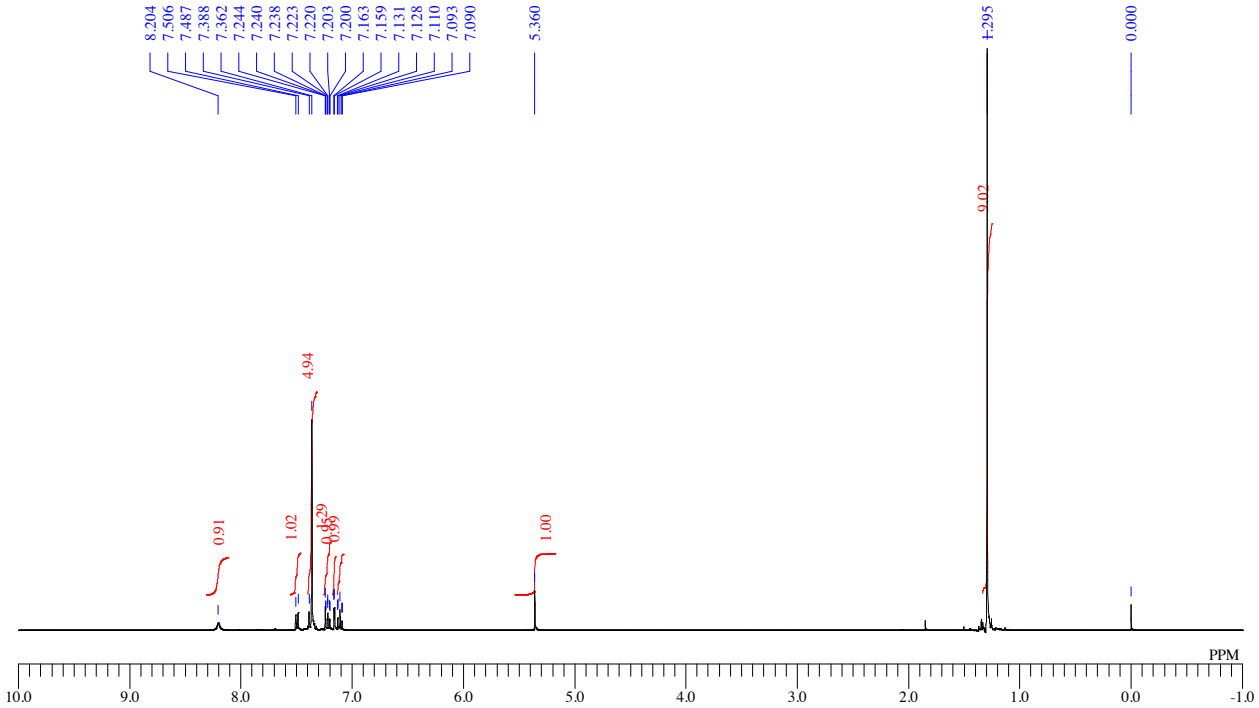
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



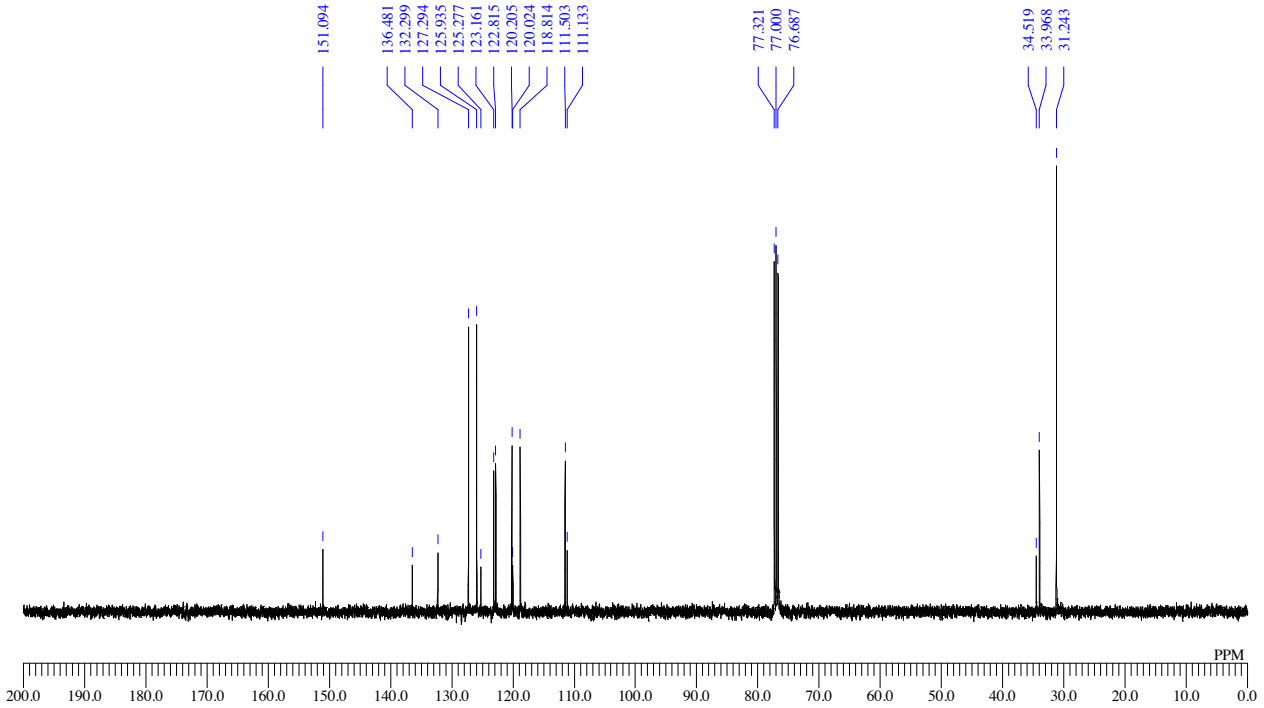


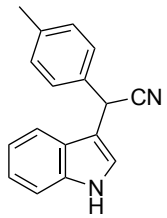
10ad

^{1}H NMR: (400 MHz, $CDCl_3$)



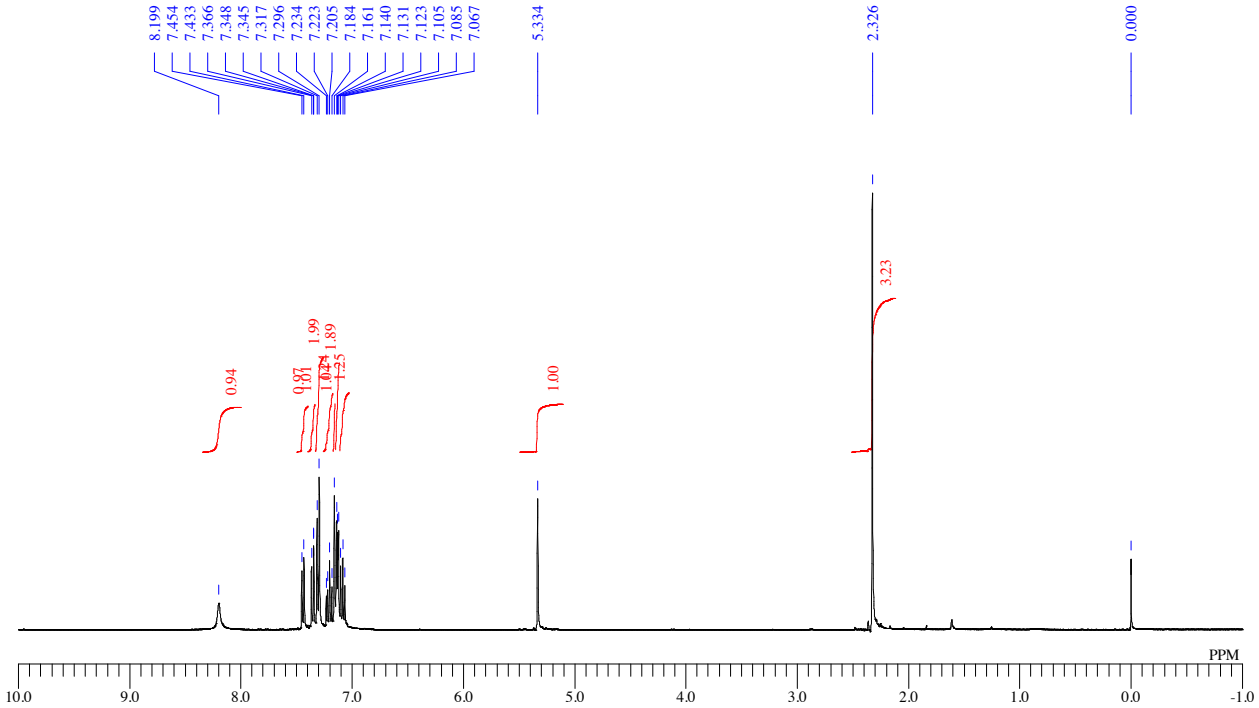
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



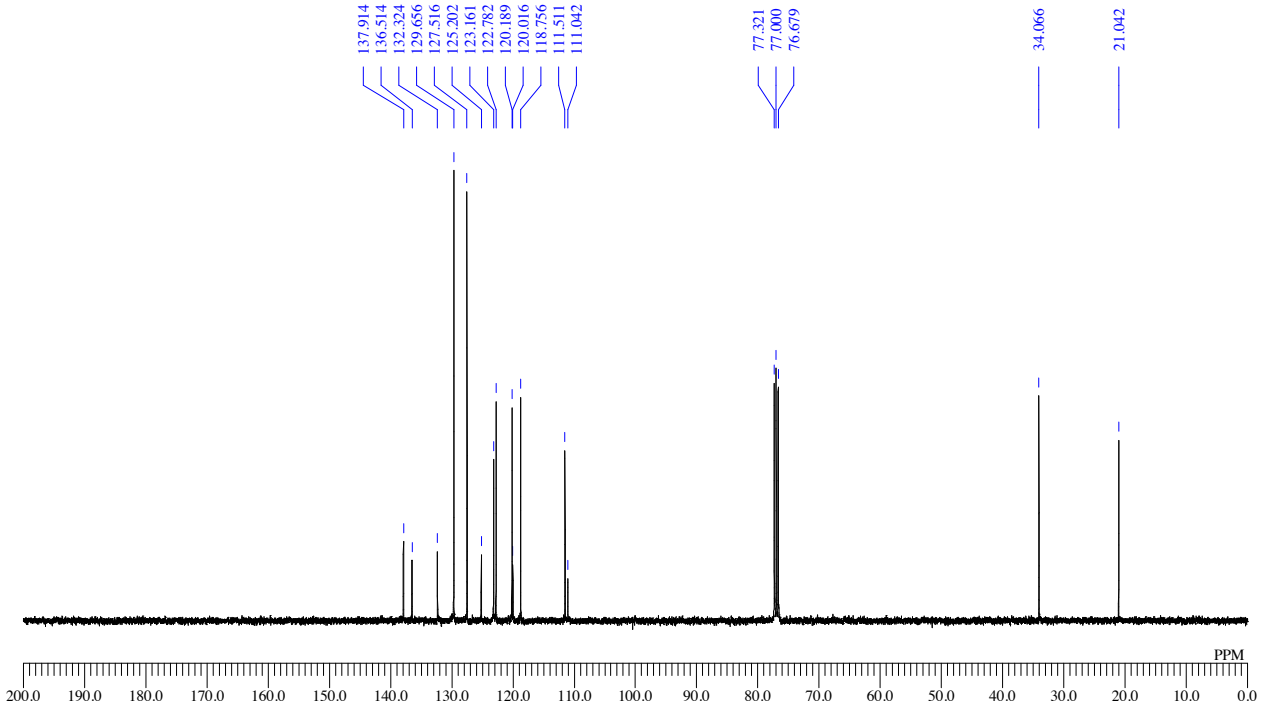


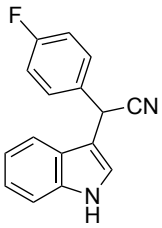
10ae

^{1}H NMR: (400 MHz, $CDCl_3$)



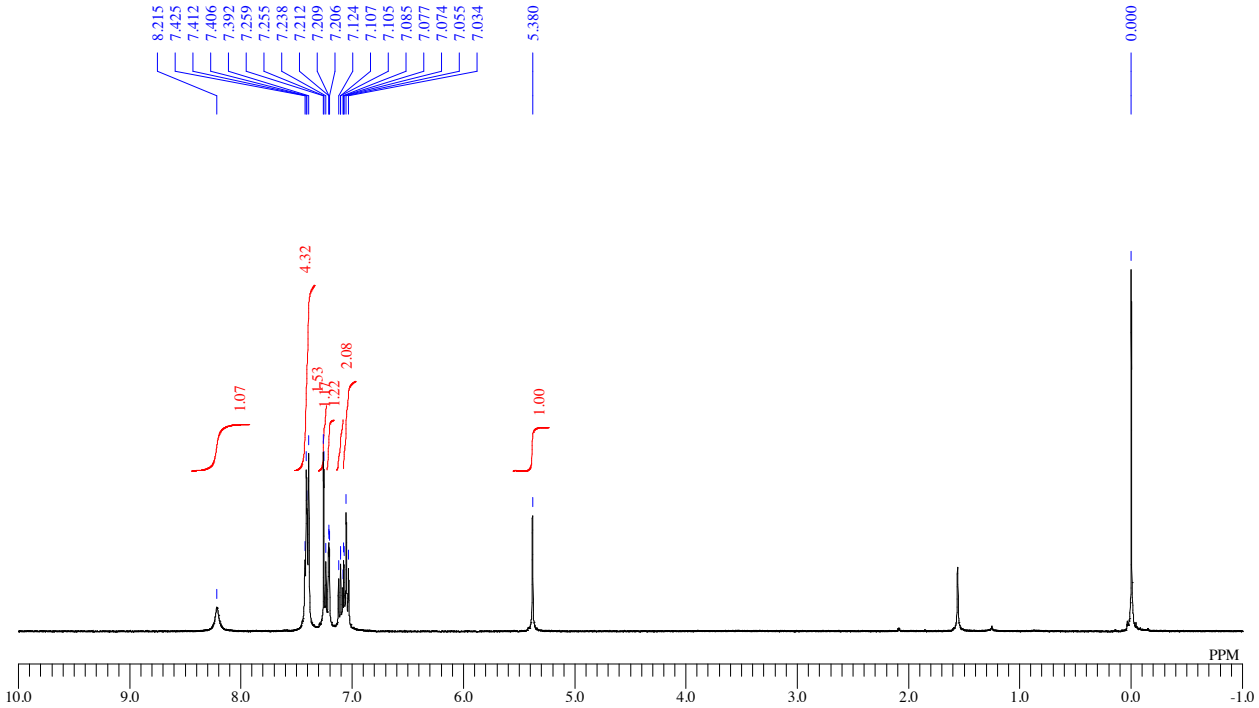
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



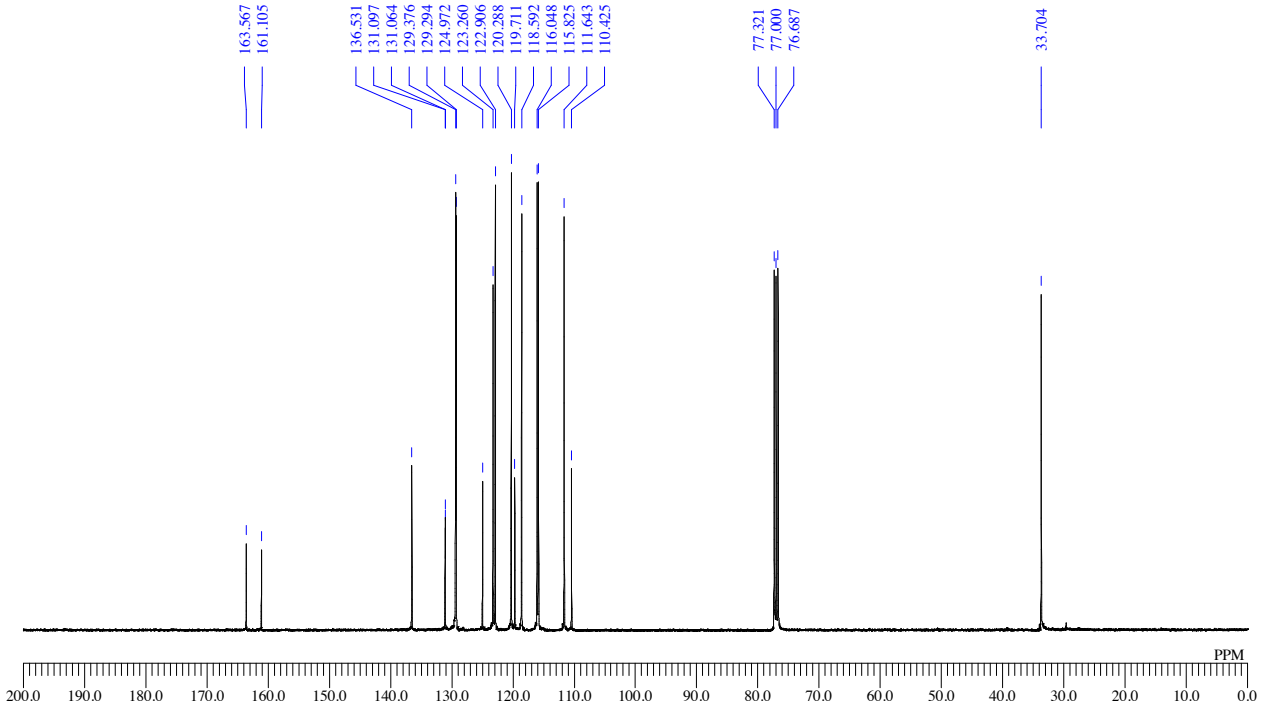


10af

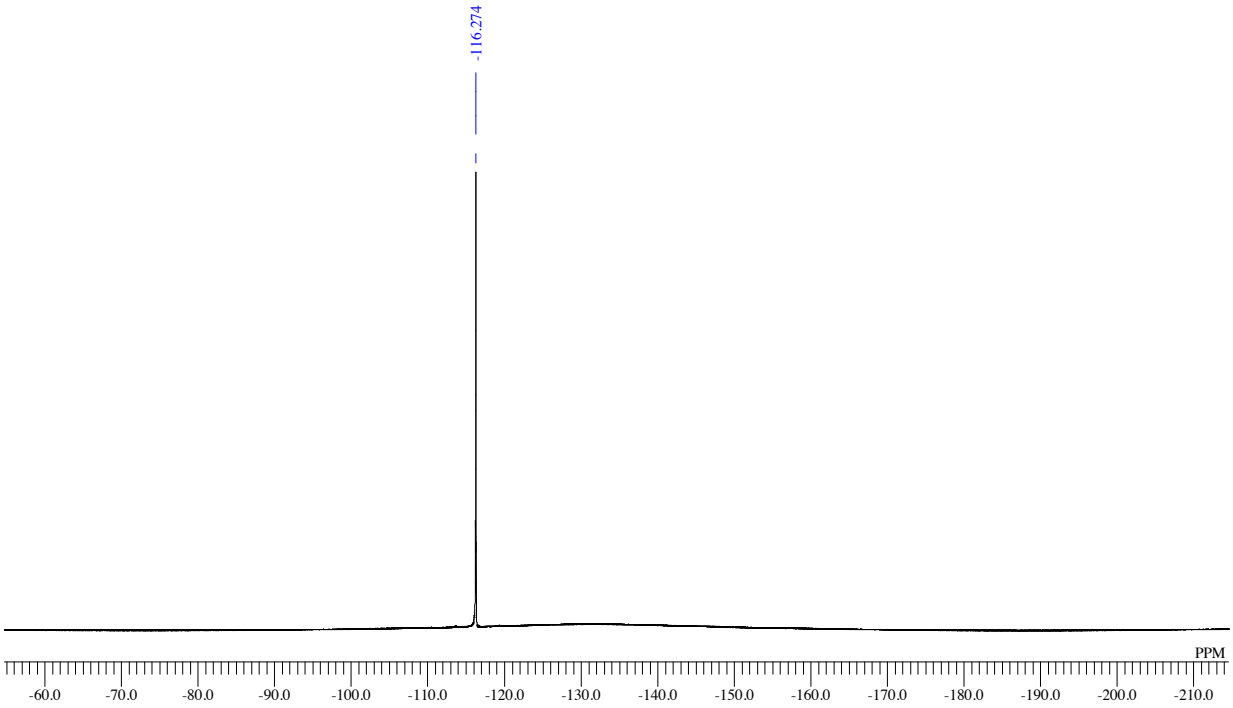
^{1}H NMR: (400 MHz, $CDCl_3$)

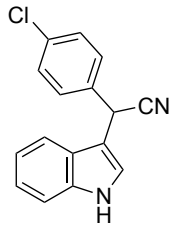


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



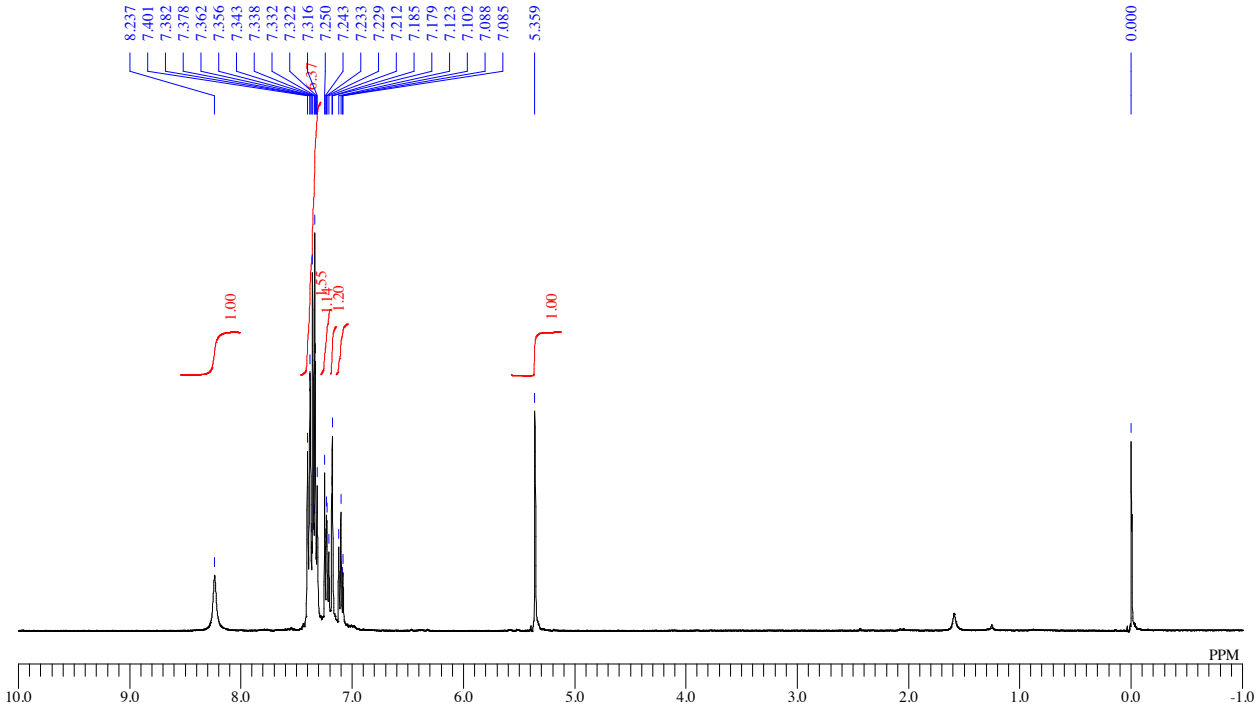
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



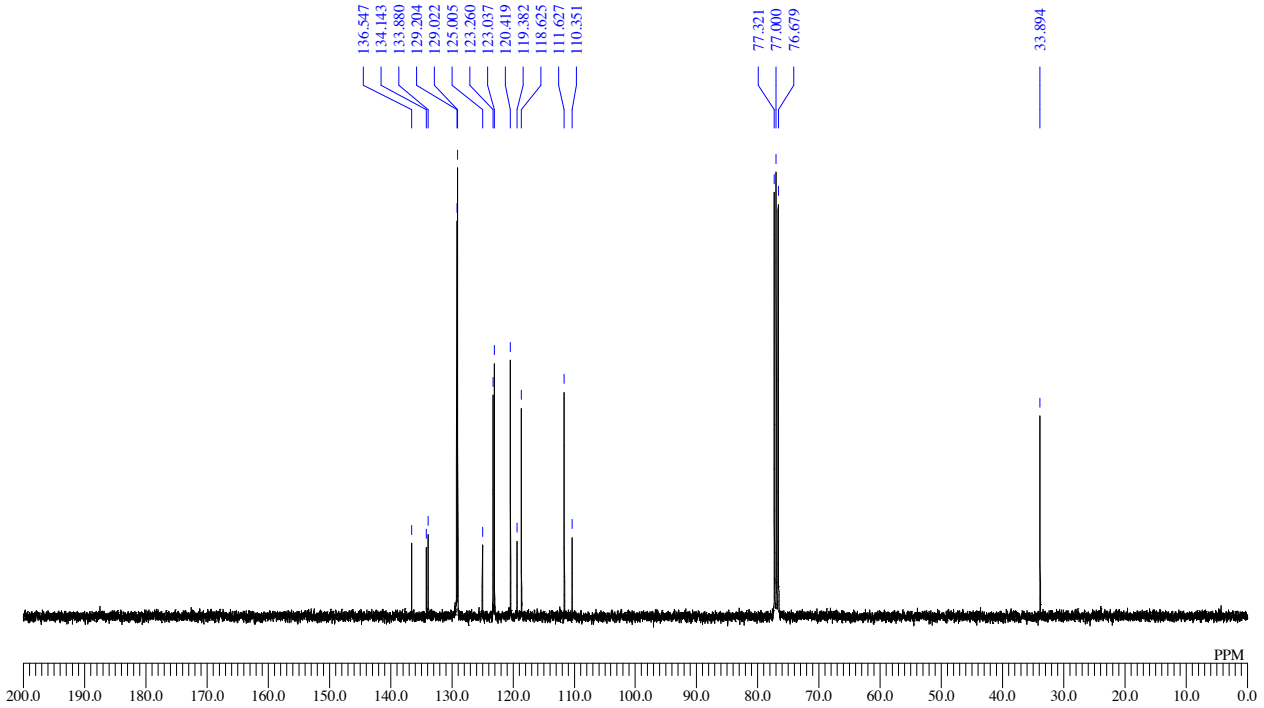


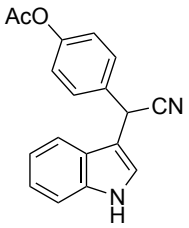
10ag

^{1}H NMR: (400 MHz, $CDCl_3$)



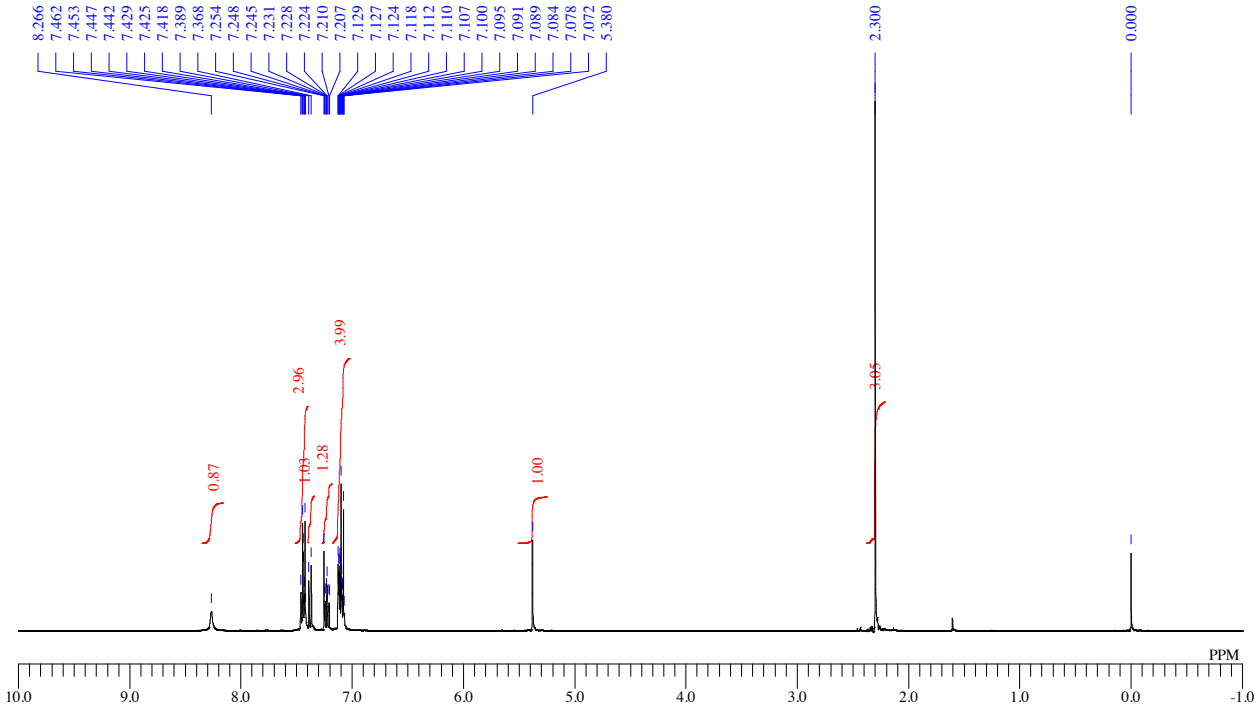
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



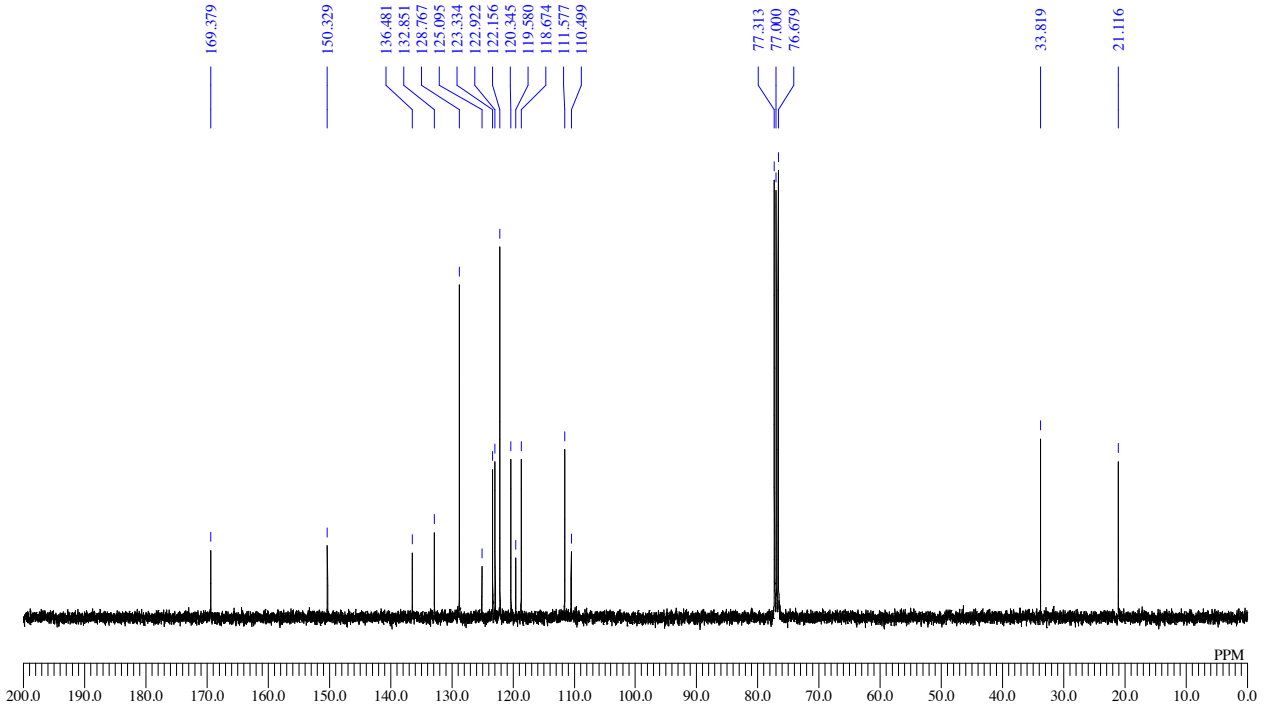


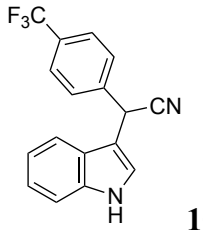
10ah

^{1}H NMR: (400 MHz, $CDCl_3$)



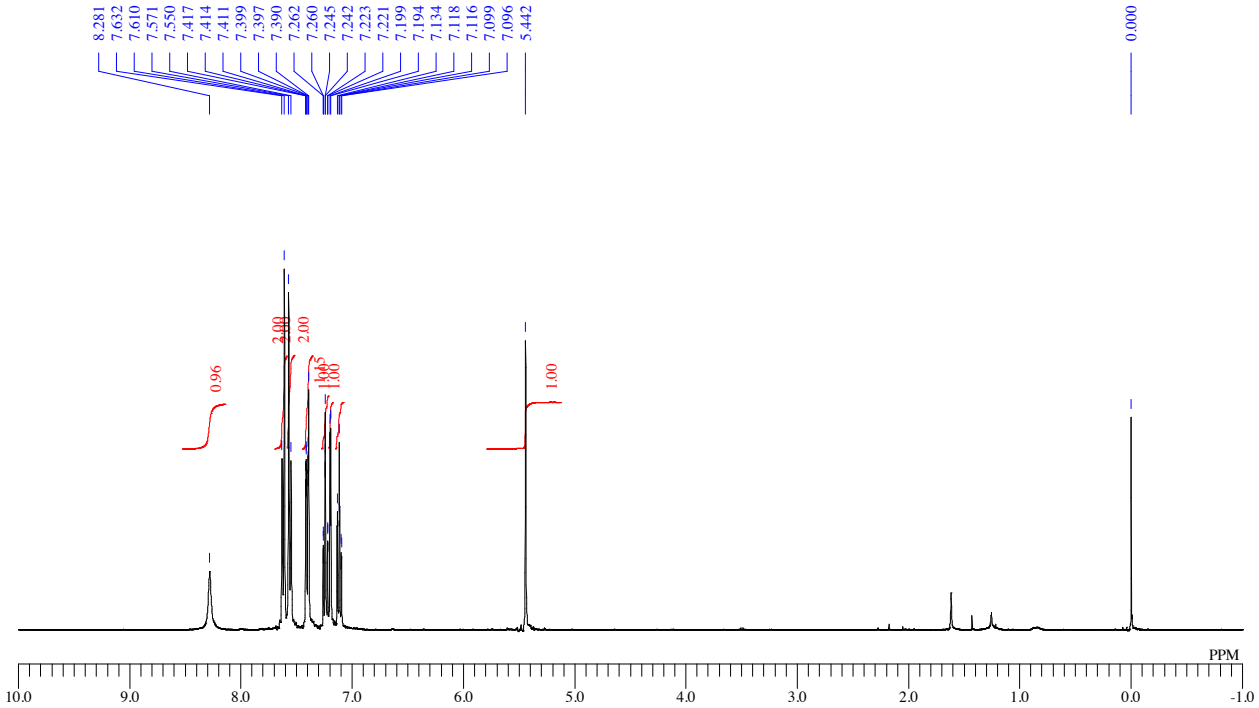
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



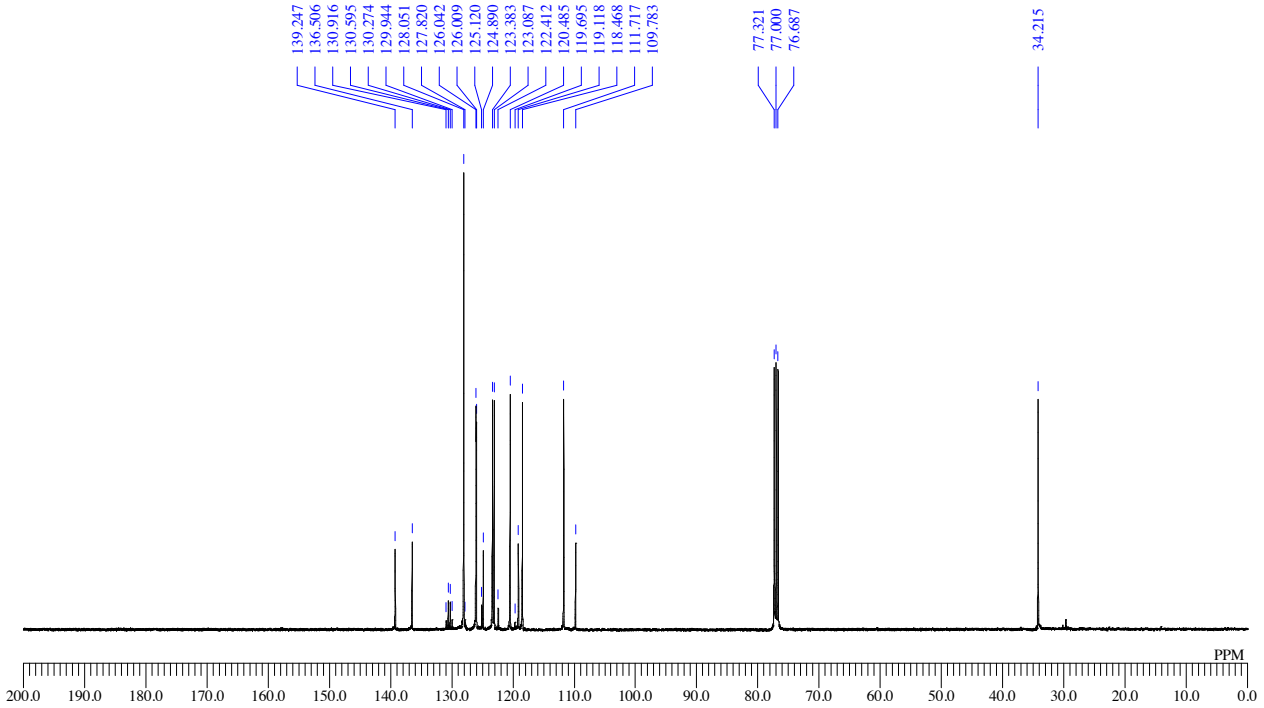


10ai

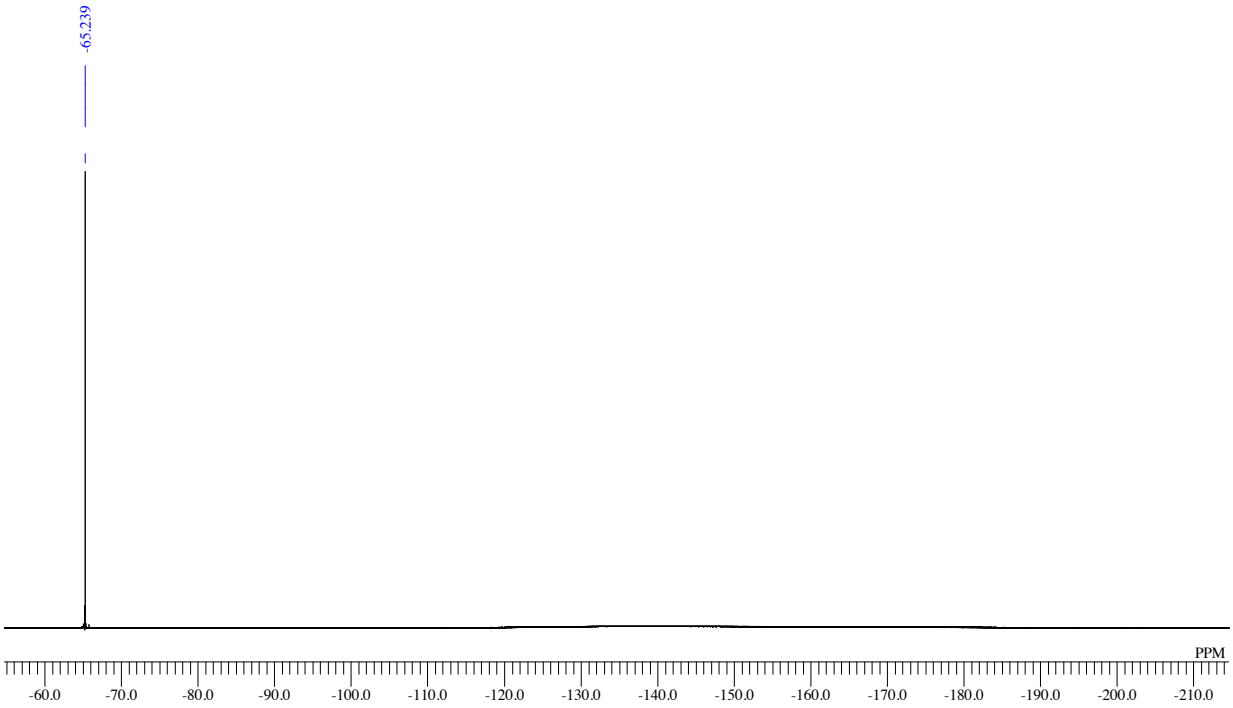
^{1}H NMR: (400 MHz, $CDCl_3$)

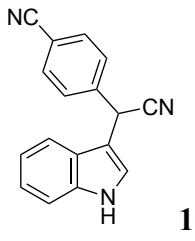


^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



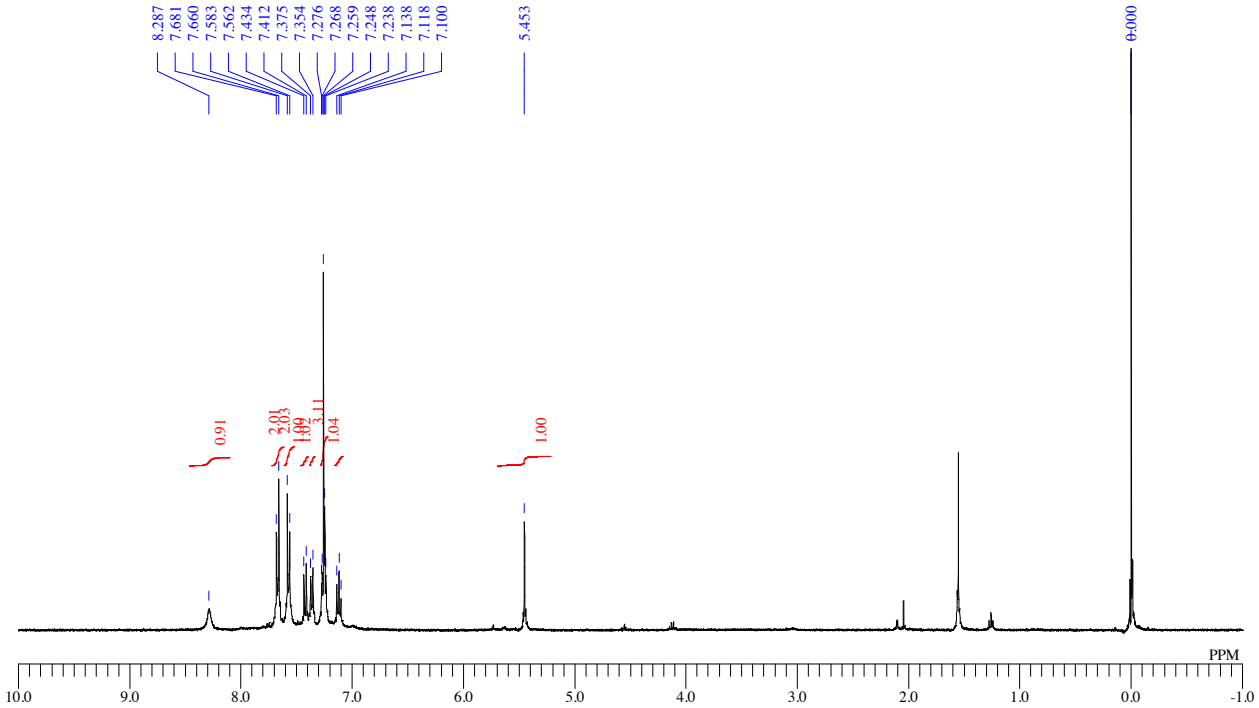
$^{19}F\{^{1}H\}$ NMR: (377 MHz, $CDCl_3$)



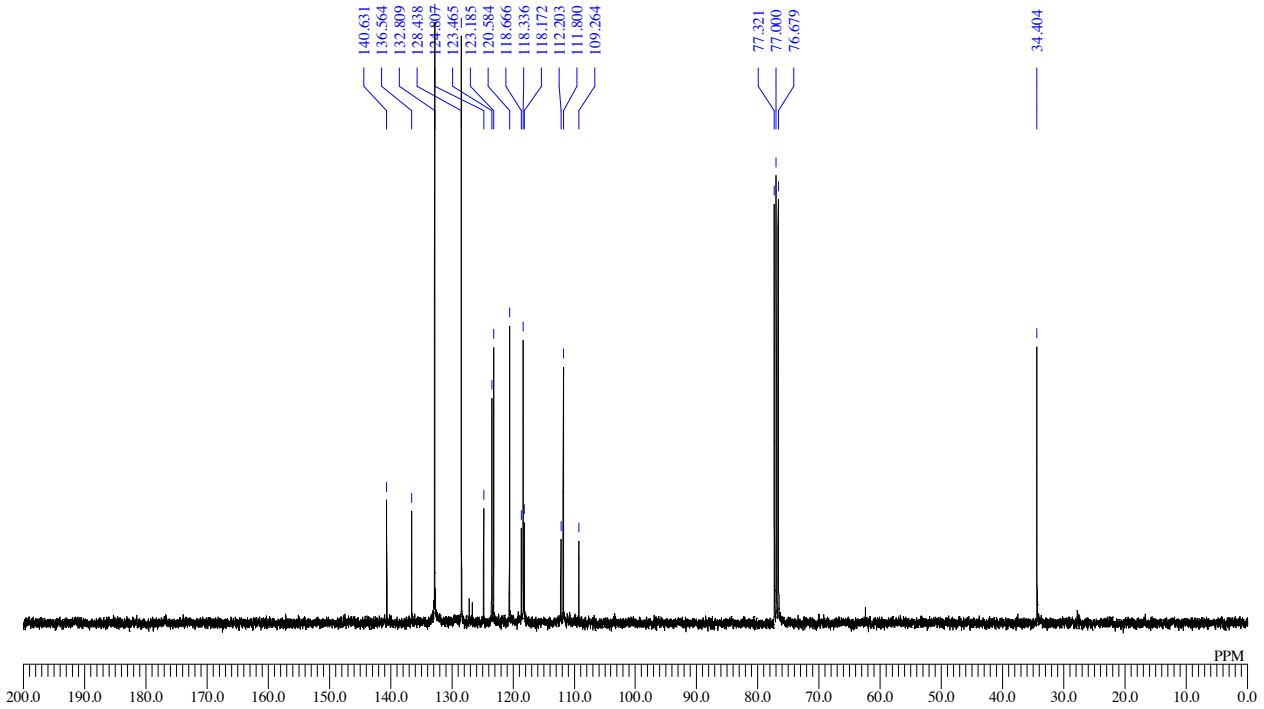


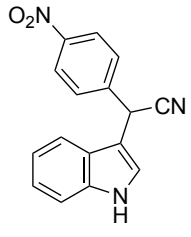
10aj

^{1}H NMR: (400 MHz, $CDCl_3$)



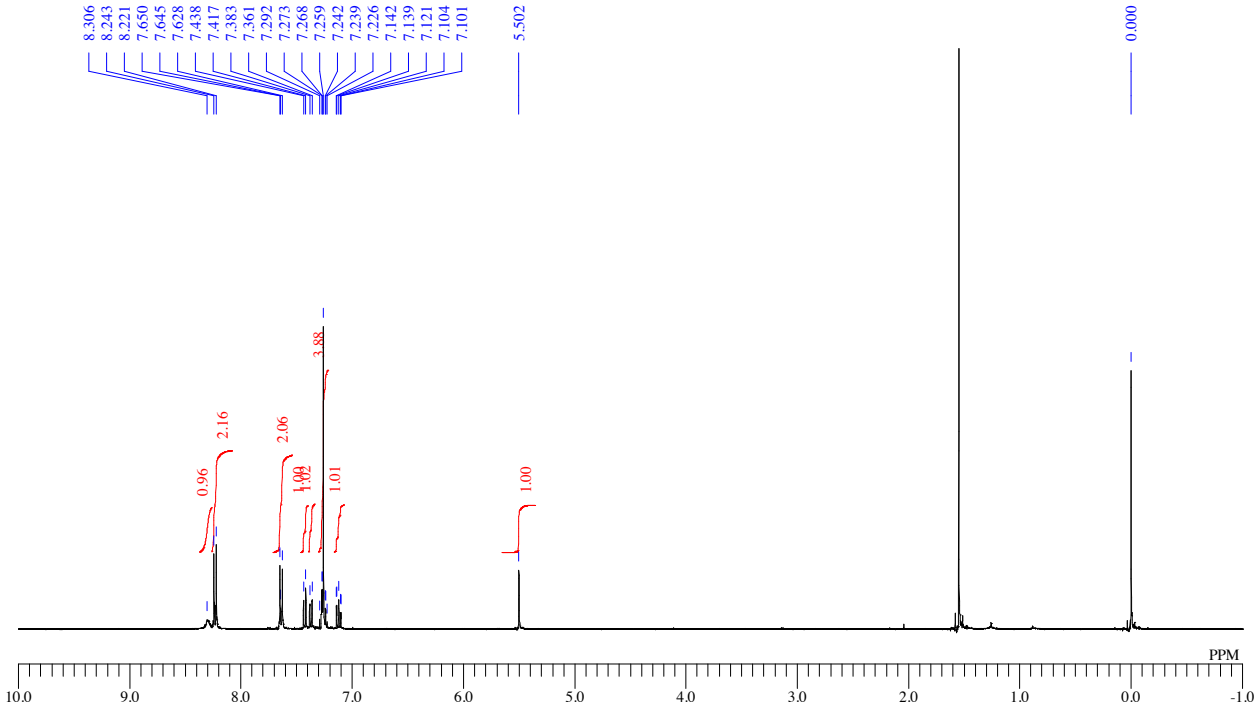
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



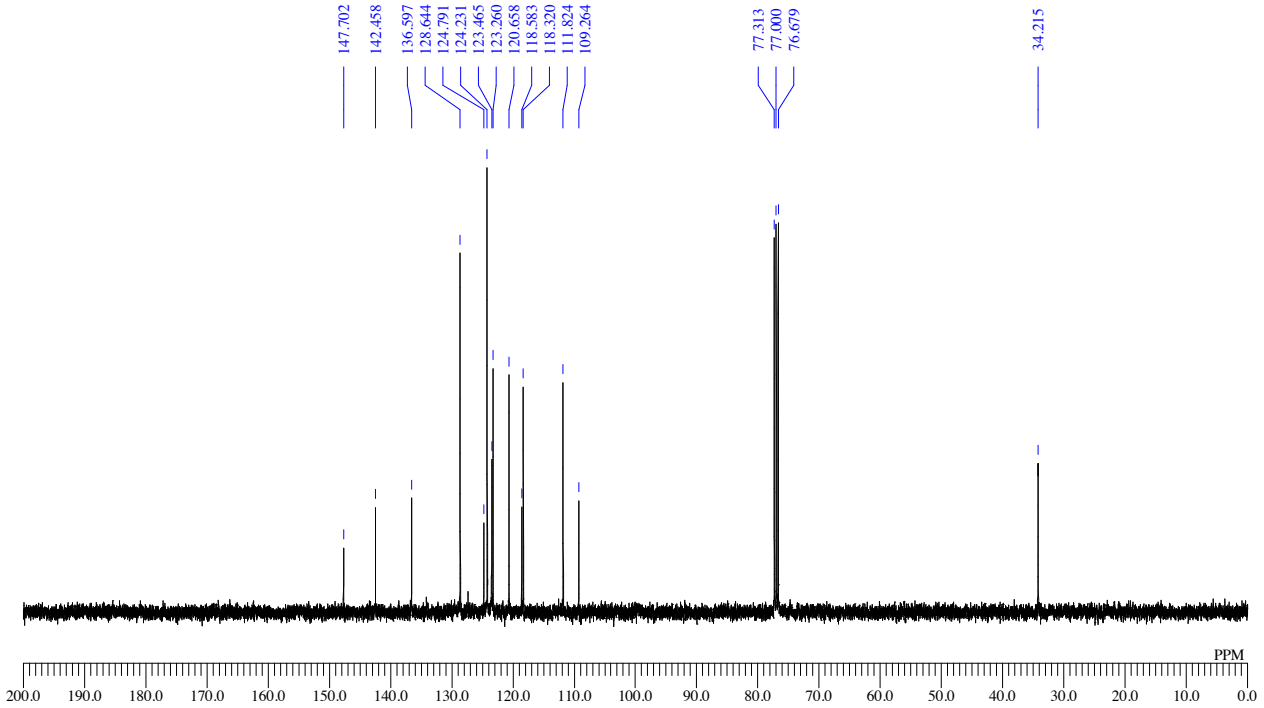


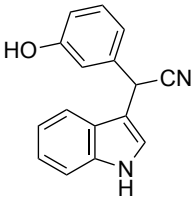
10ak

^{1}H NMR: (400 MHz, $CDCl_3$)



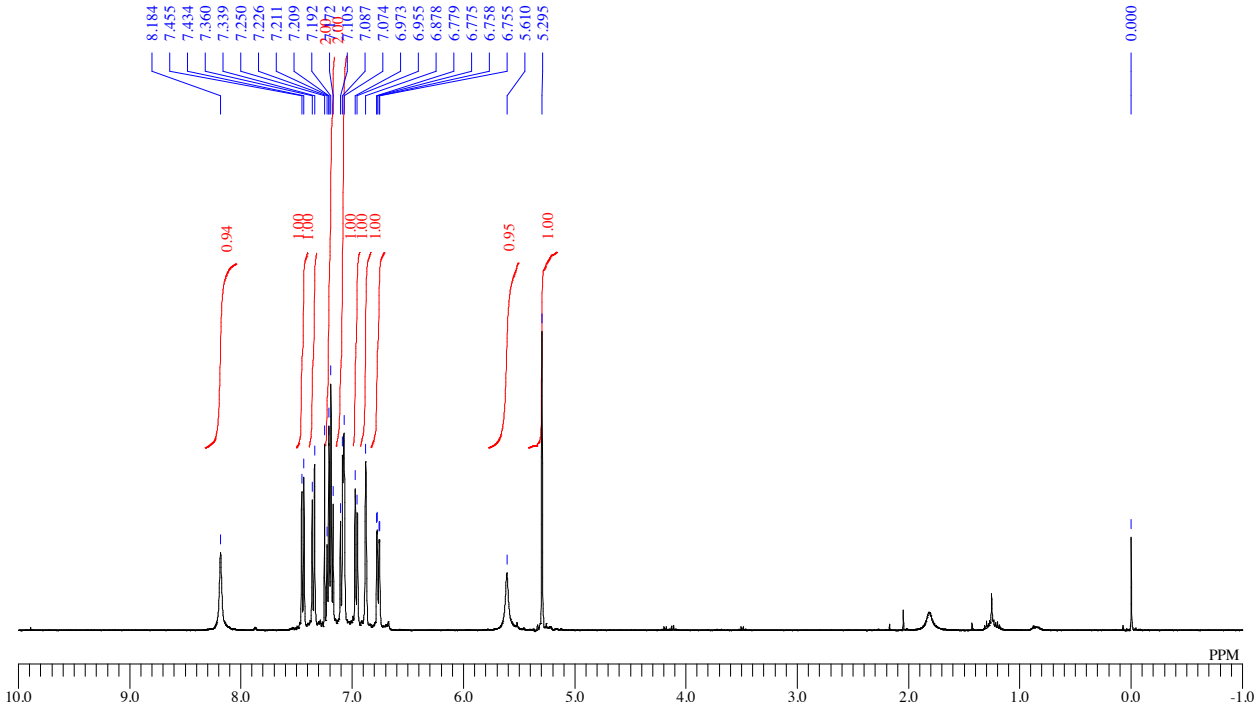
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



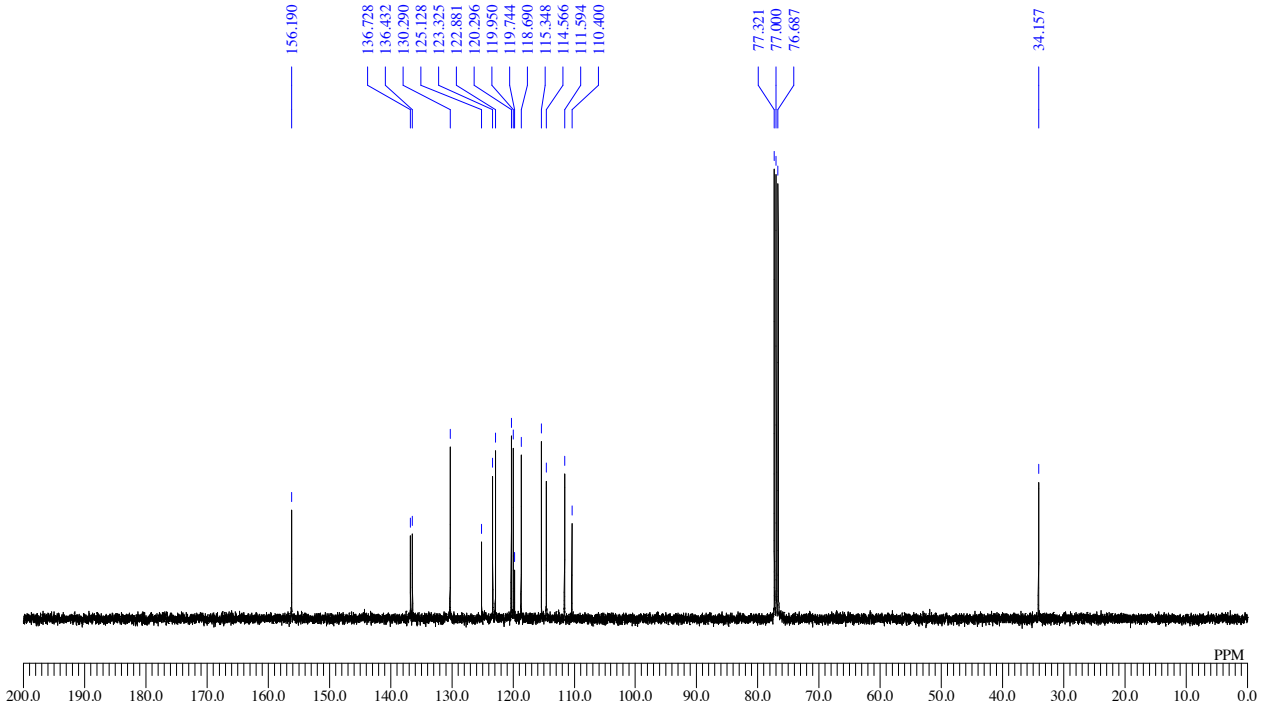


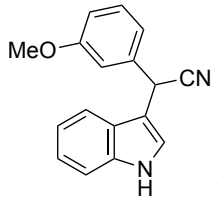
10al

^{1}H NMR: (400 MHz, $CDCl_3$)



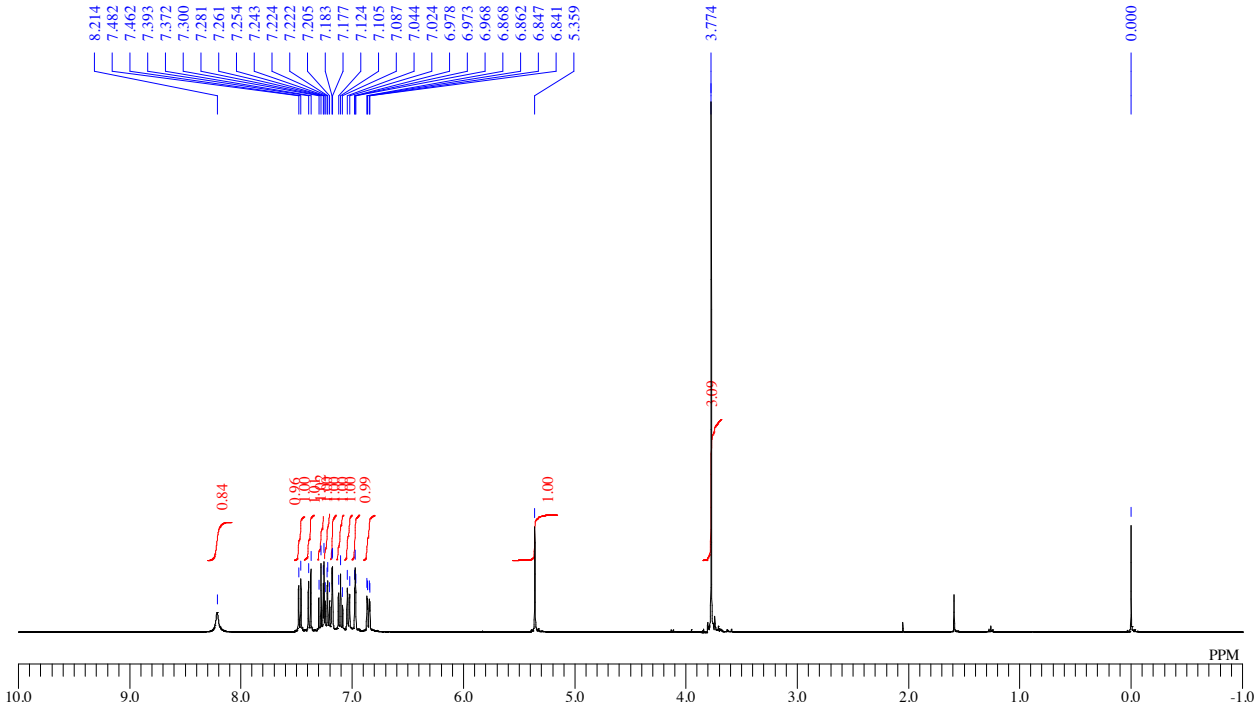
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



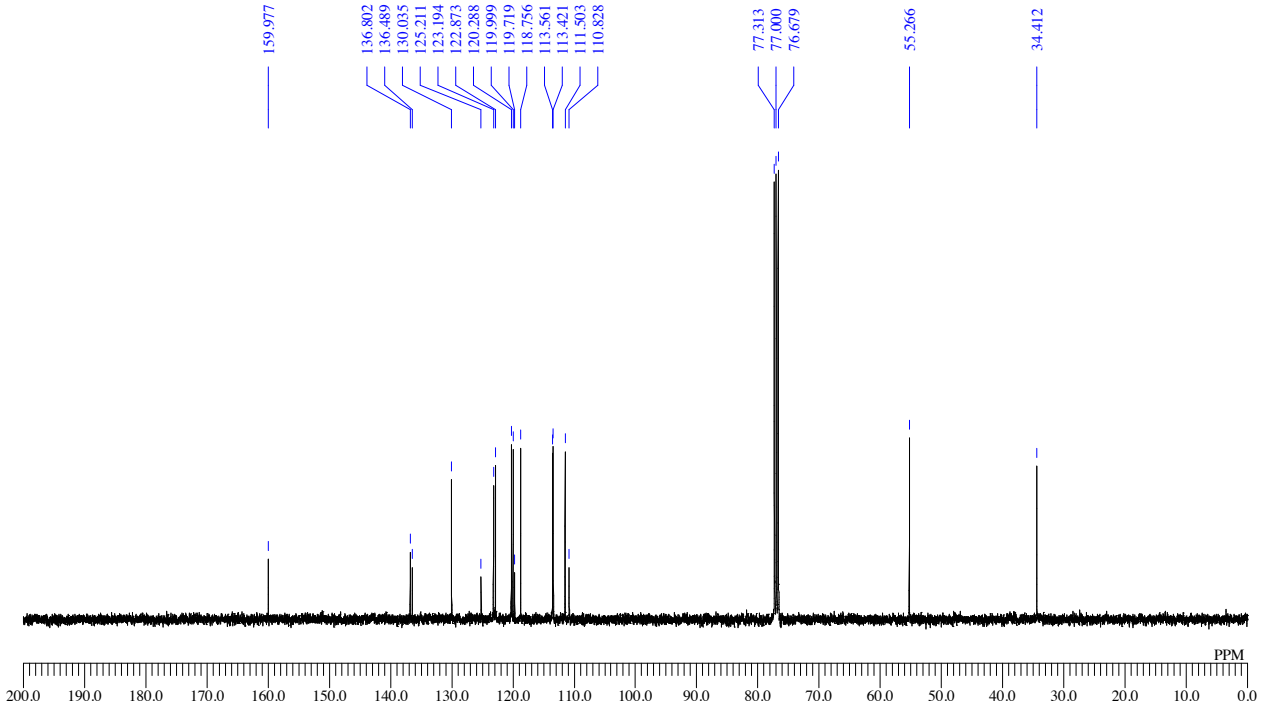


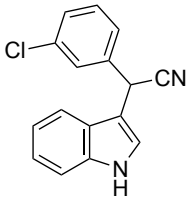
10am

^{1}H NMR: (400 MHz, $CDCl_3$)



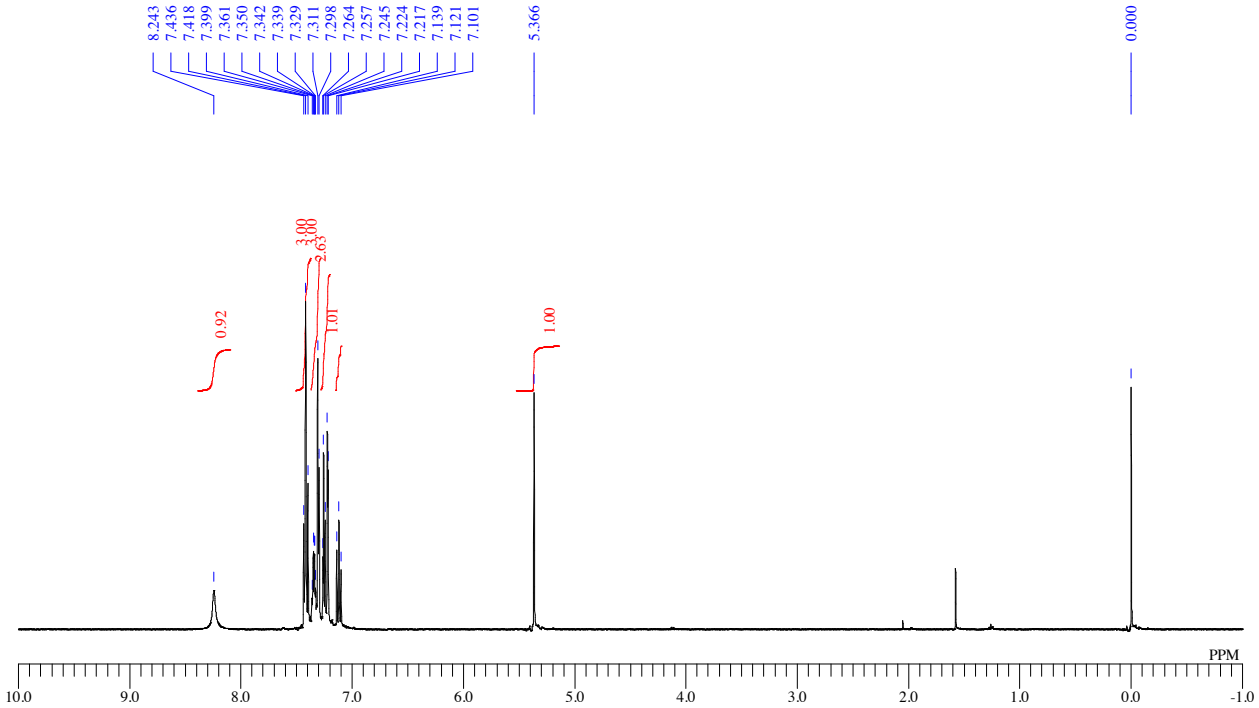
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



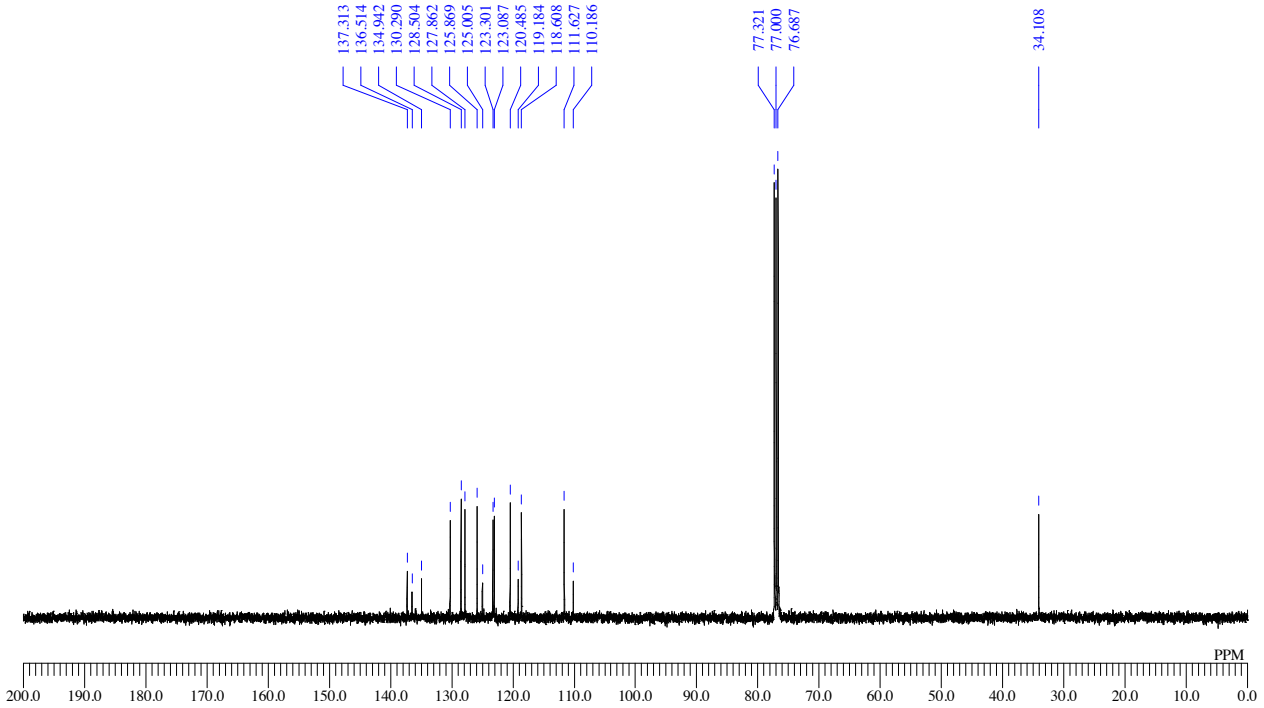


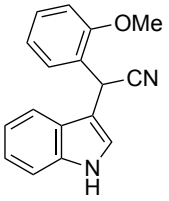
10an

^{1}H NMR: (400 MHz, $CDCl_3$)



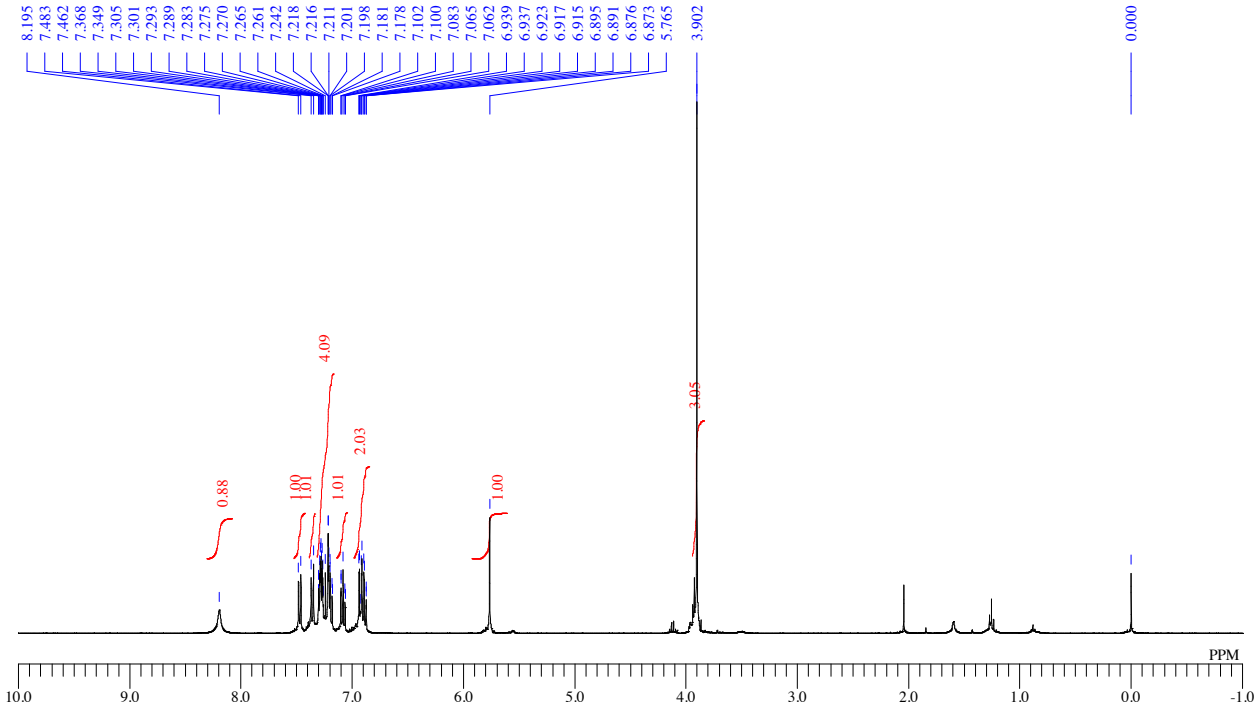
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



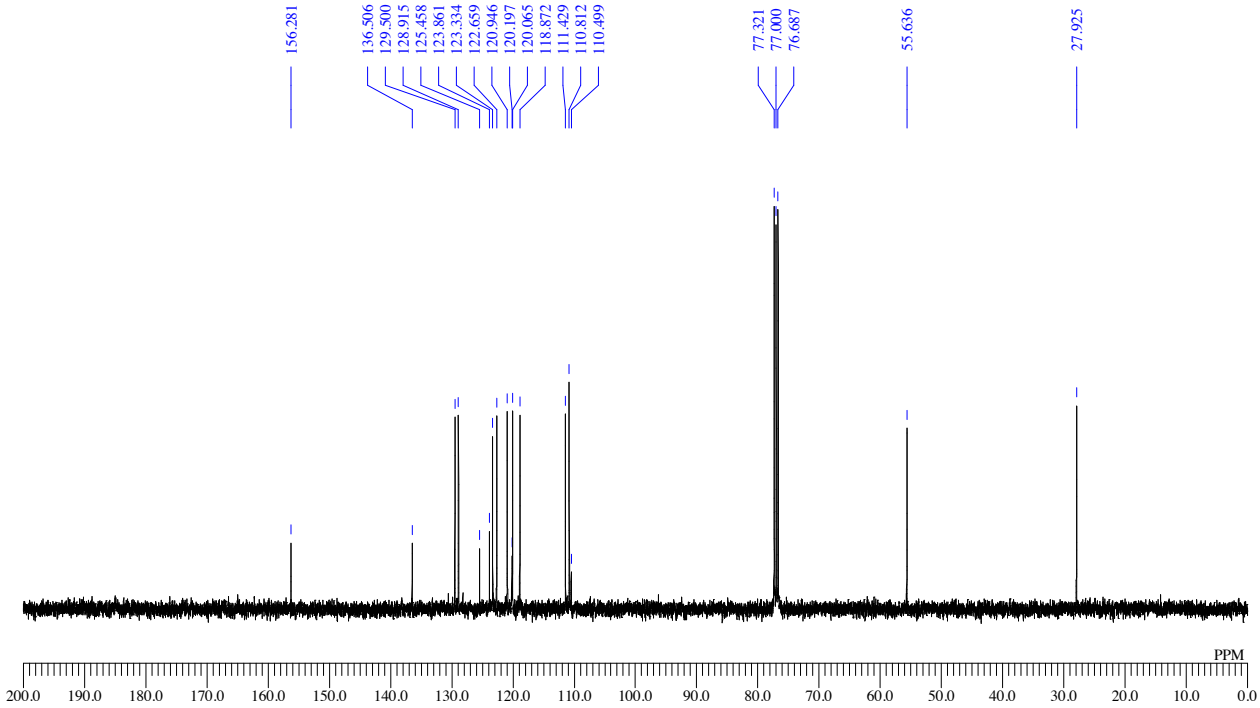


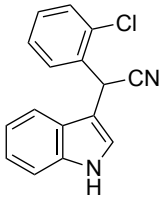
10ao

^{1}H NMR: (400 MHz, $CDCl_3$)



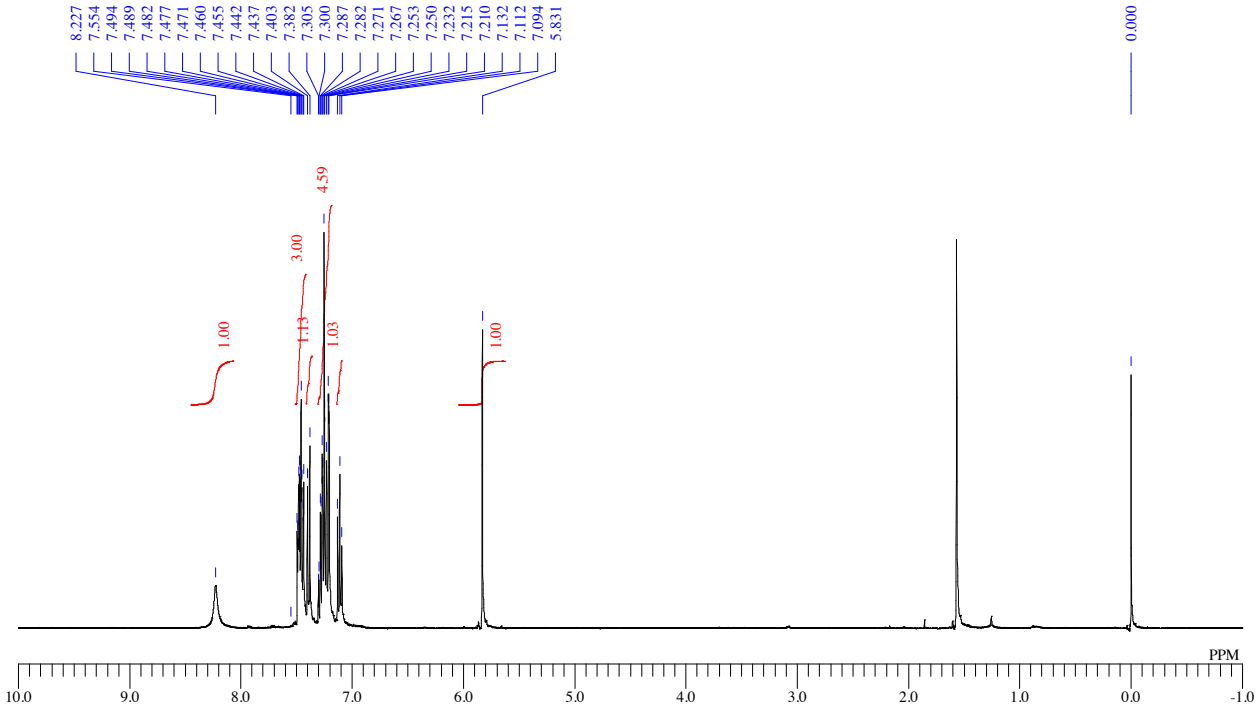
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



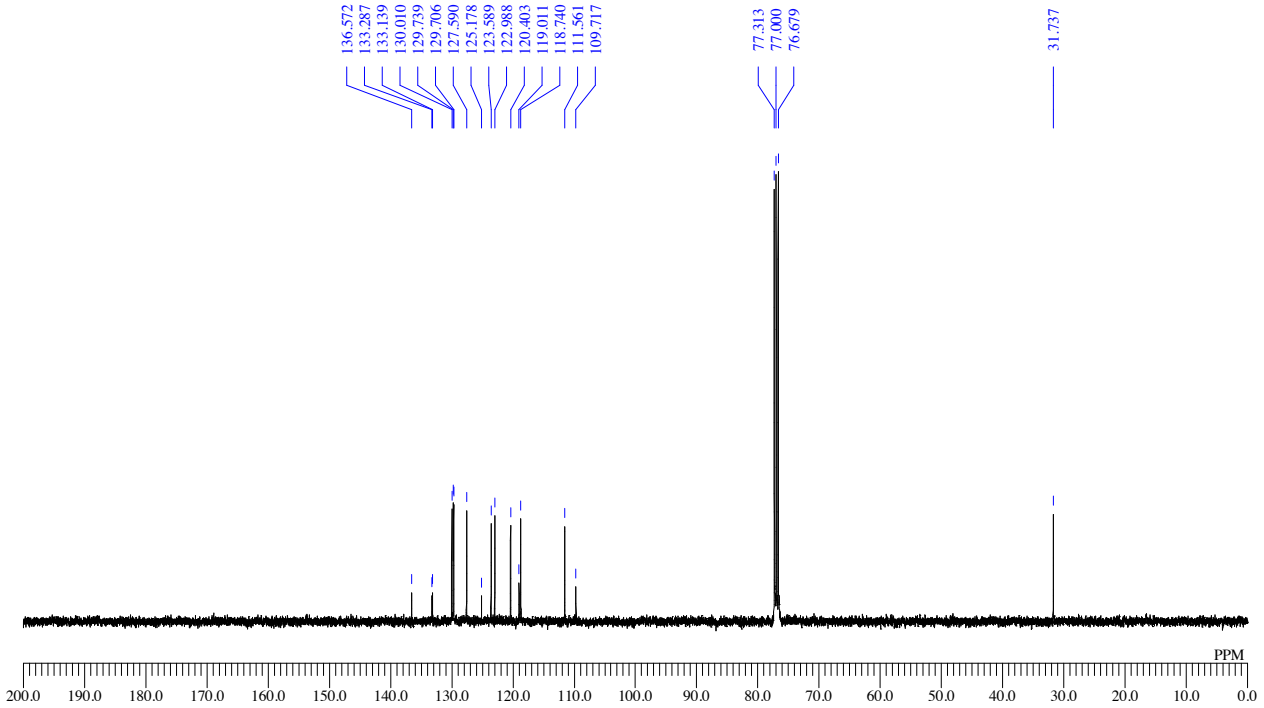


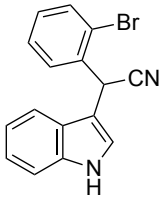
10ap

^{1}H NMR: (400 MHz, $CDCl_3$)



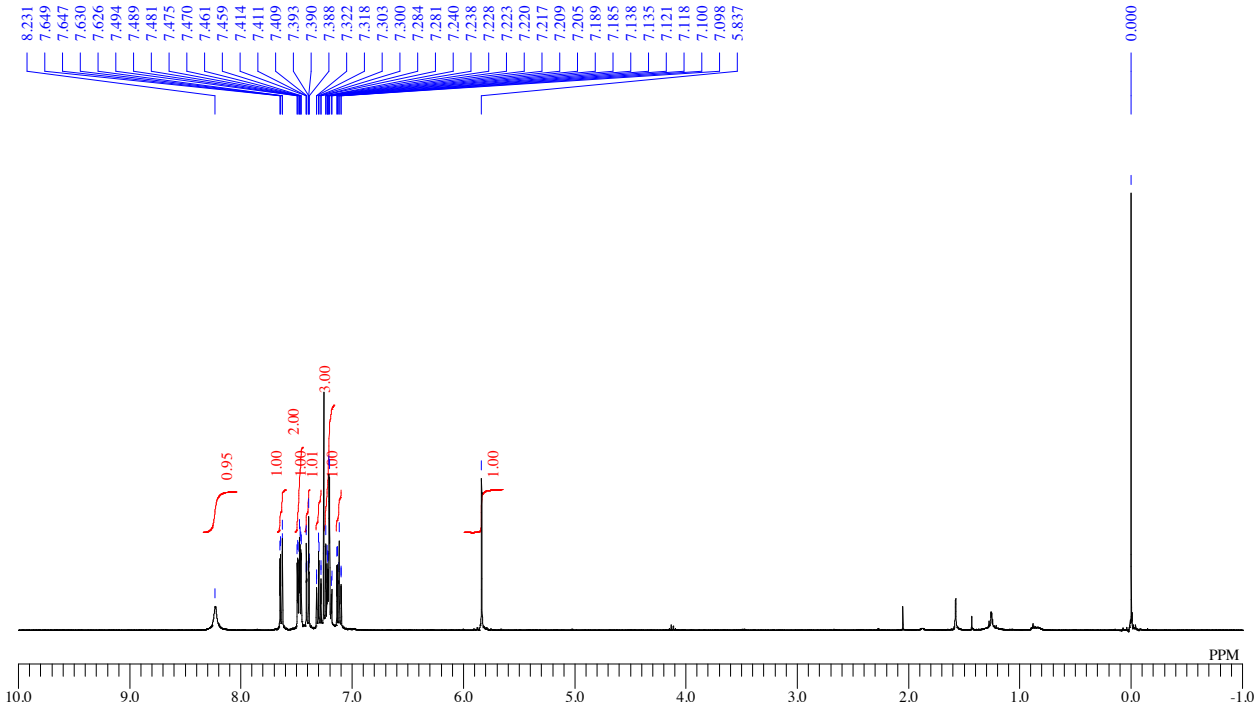
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



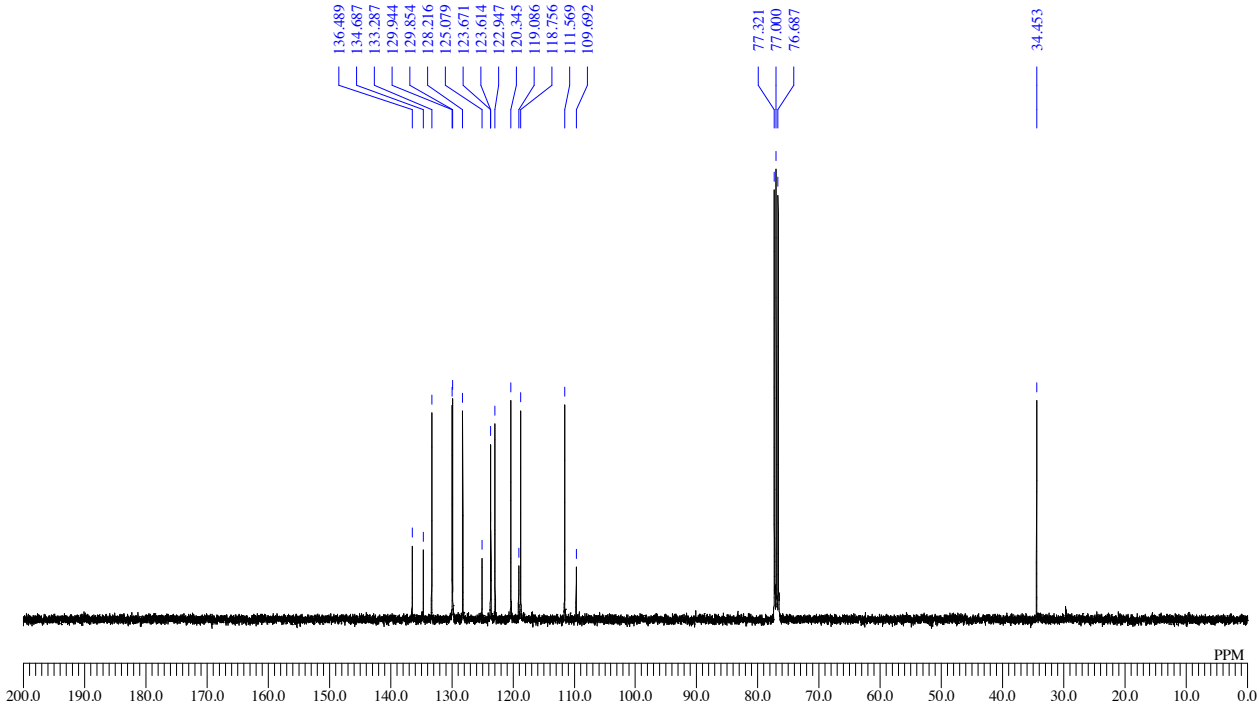


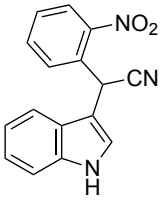
10aq

^{1}H NMR: (400 MHz, $CDCl_3$)



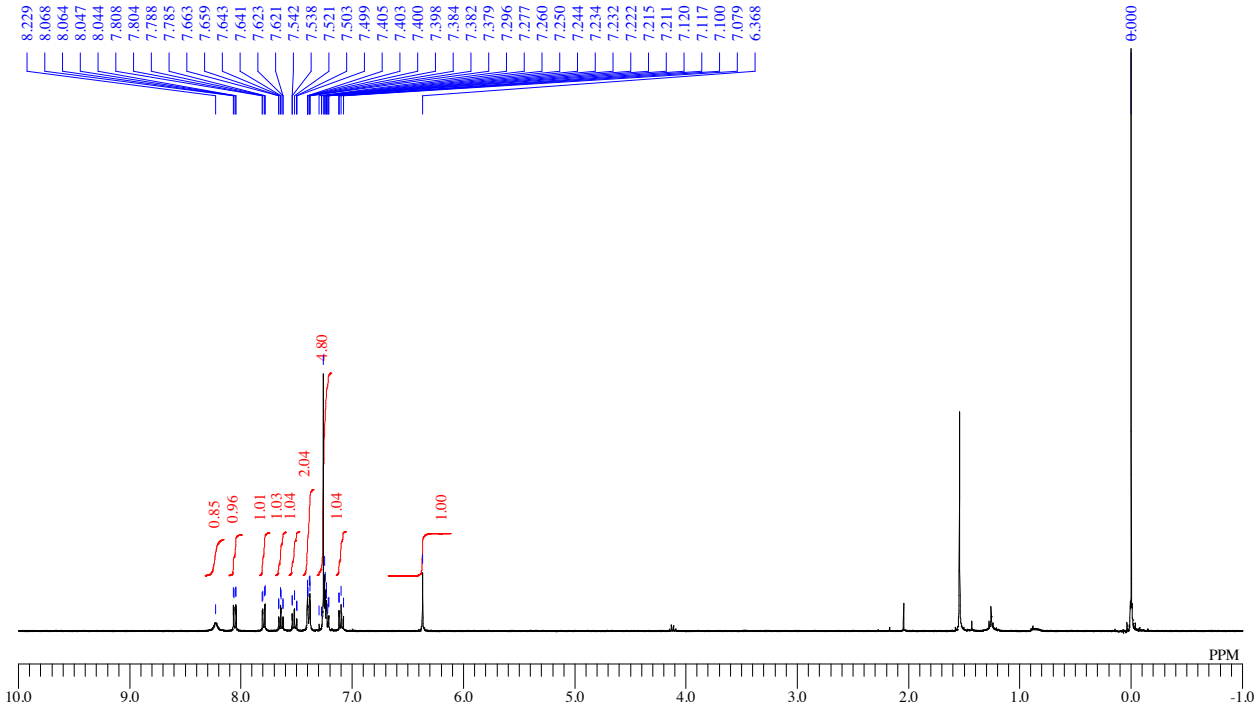
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



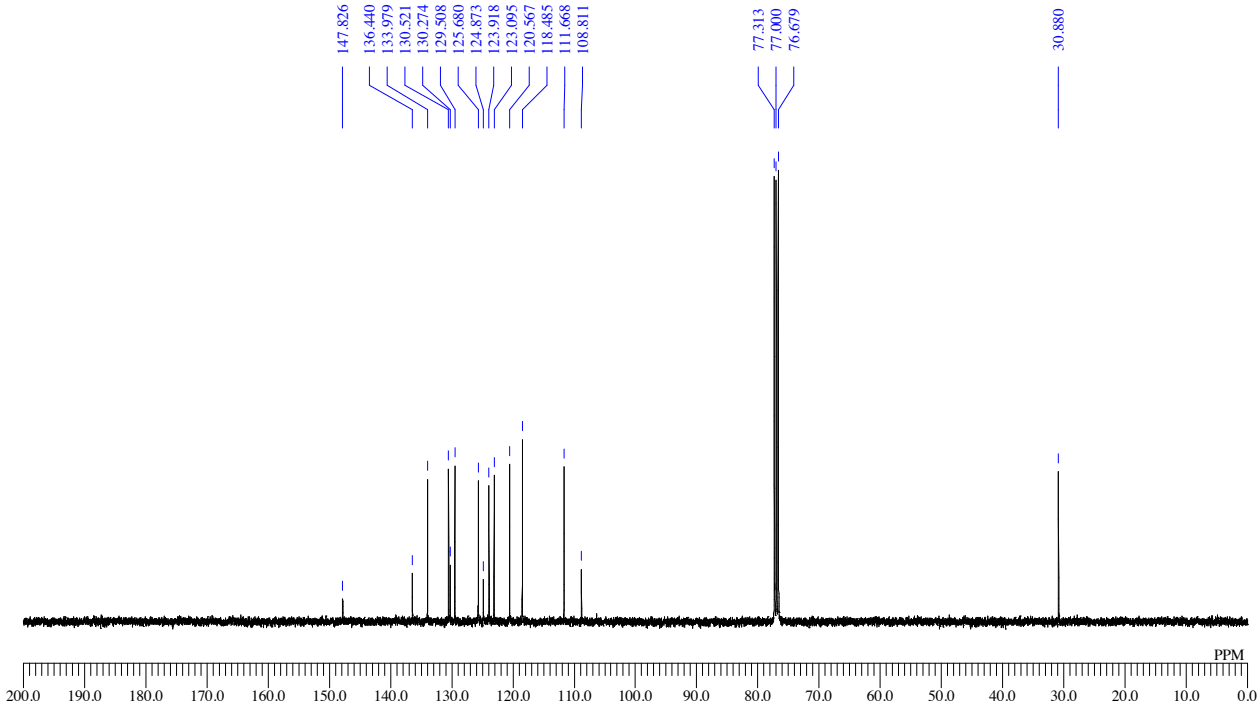


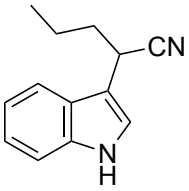
10ar

^{1}H NMR: (400 MHz, $CDCl_3$)



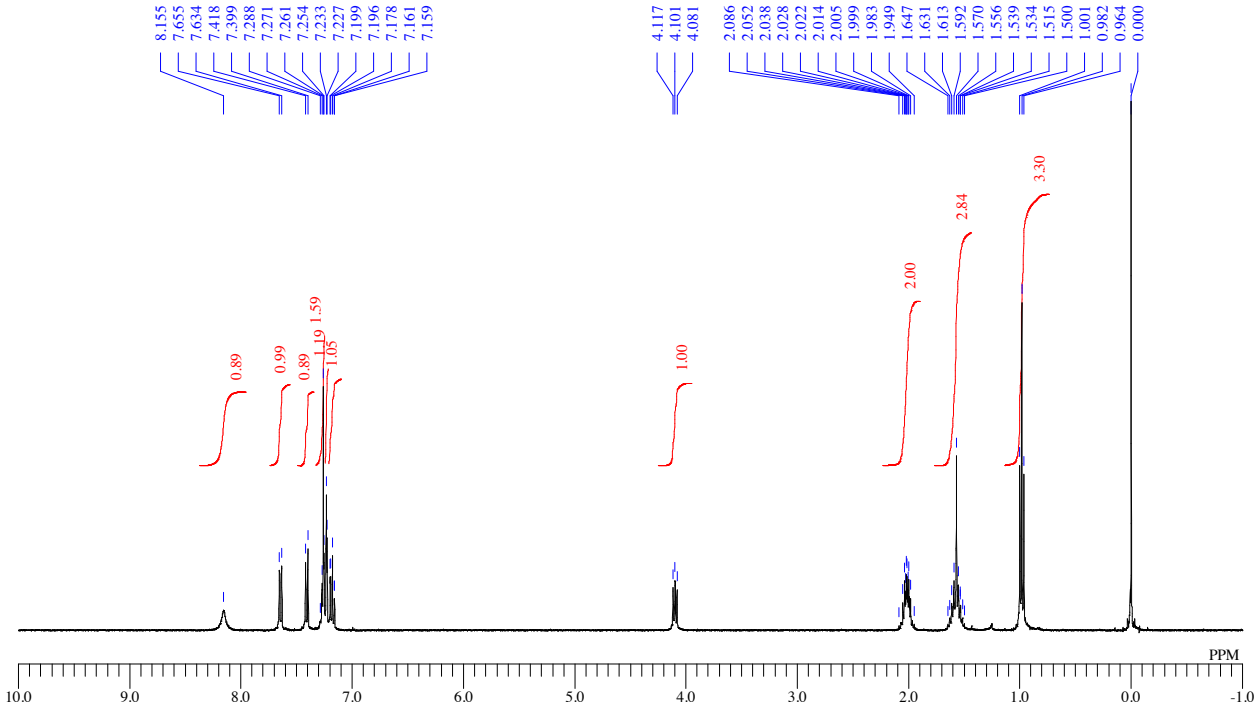
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



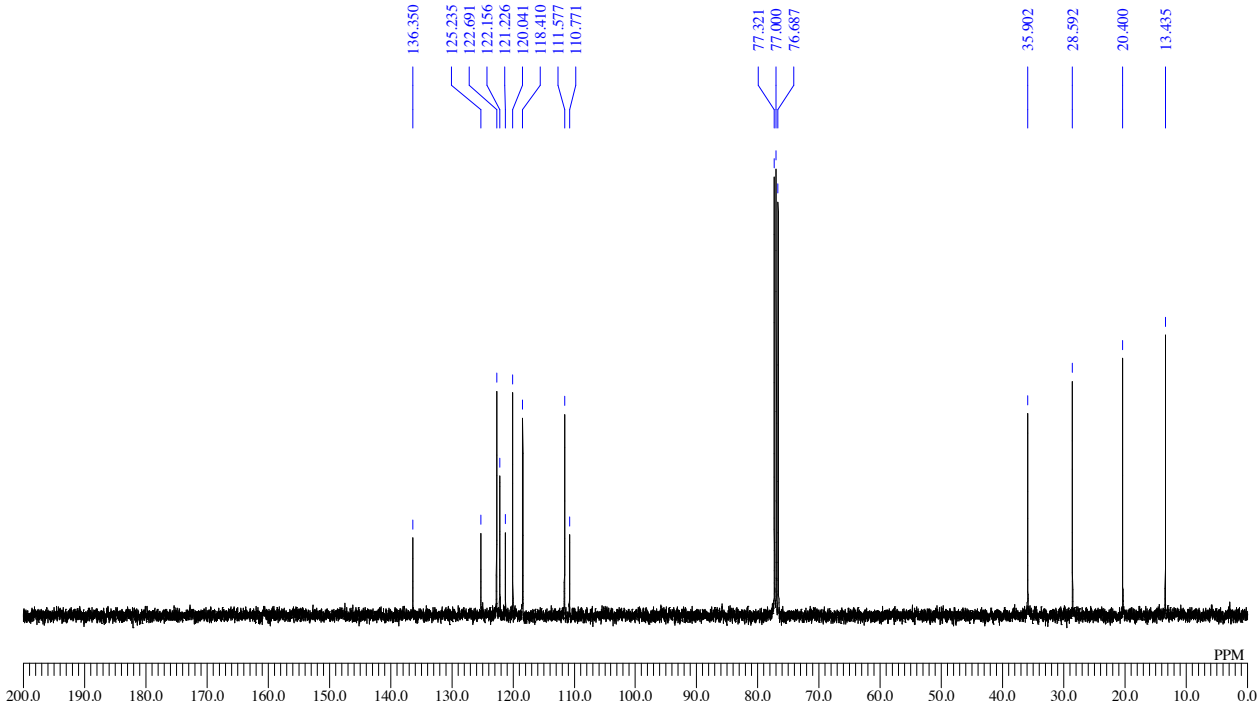


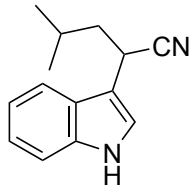
10as

^{1}H NMR: (400 MHz, $CDCl_3$)



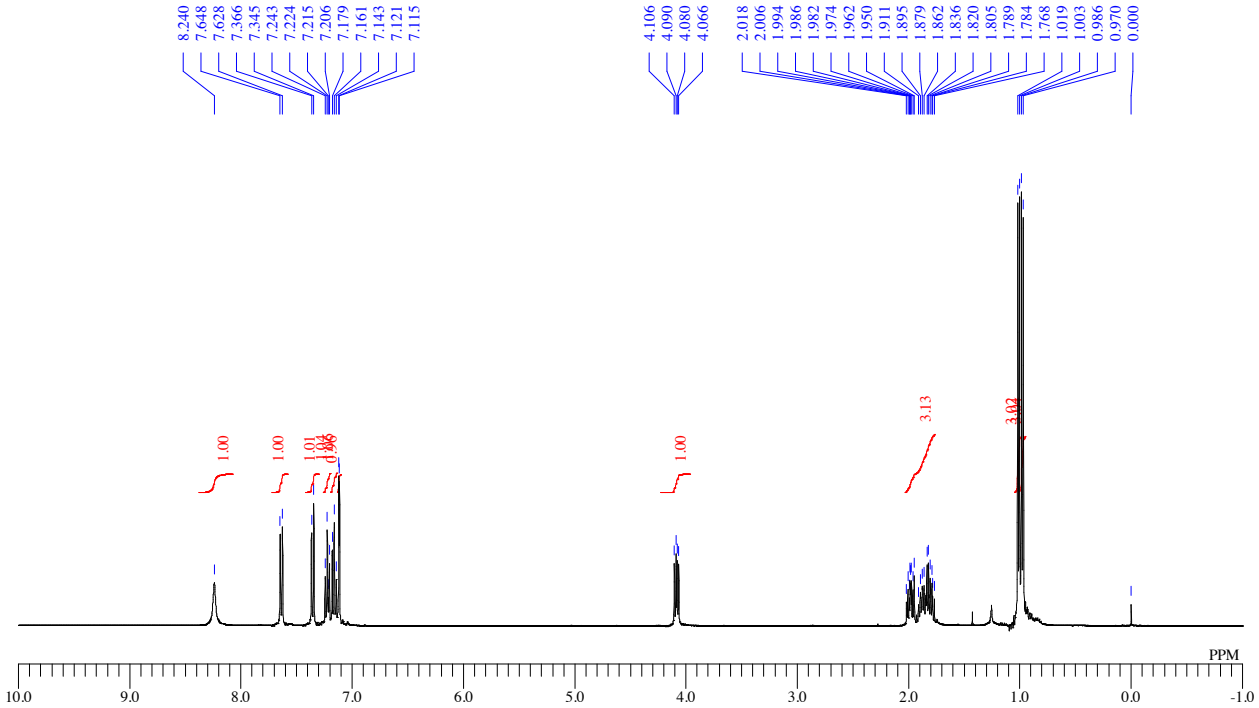
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)



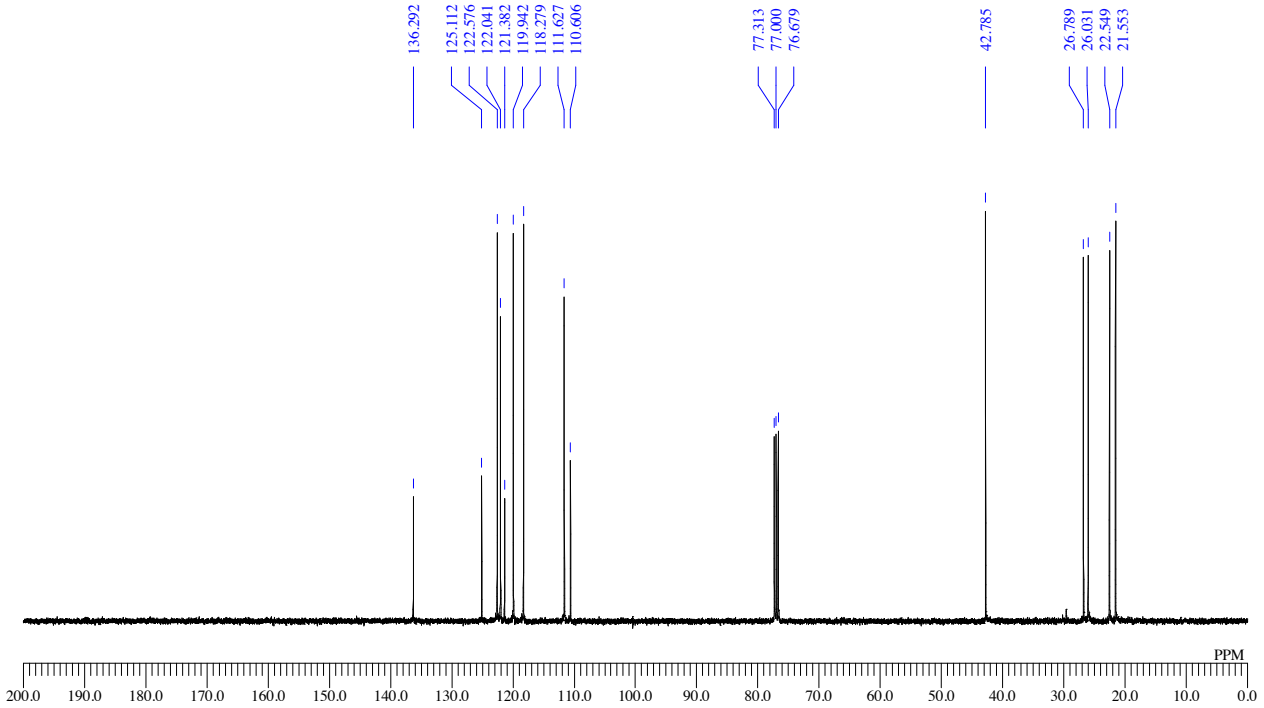


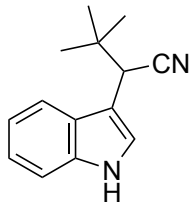
10at

^{1}H NMR: (400 MHz, $CDCl_3$)



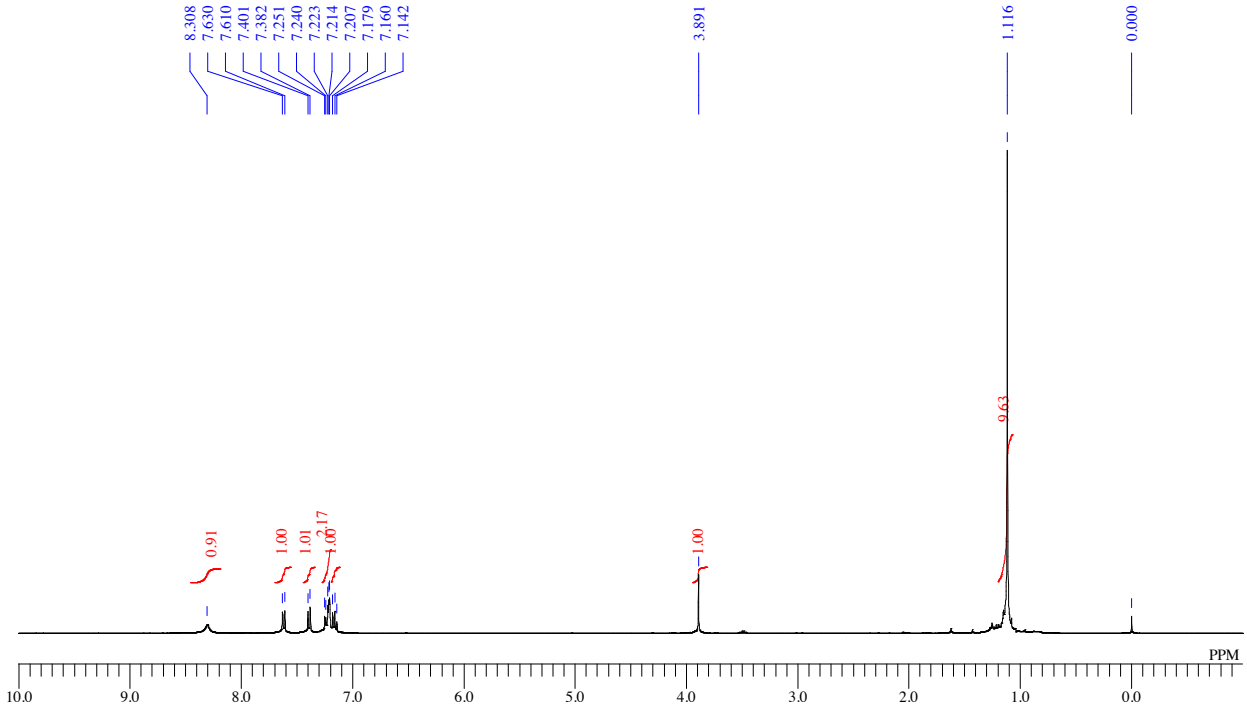
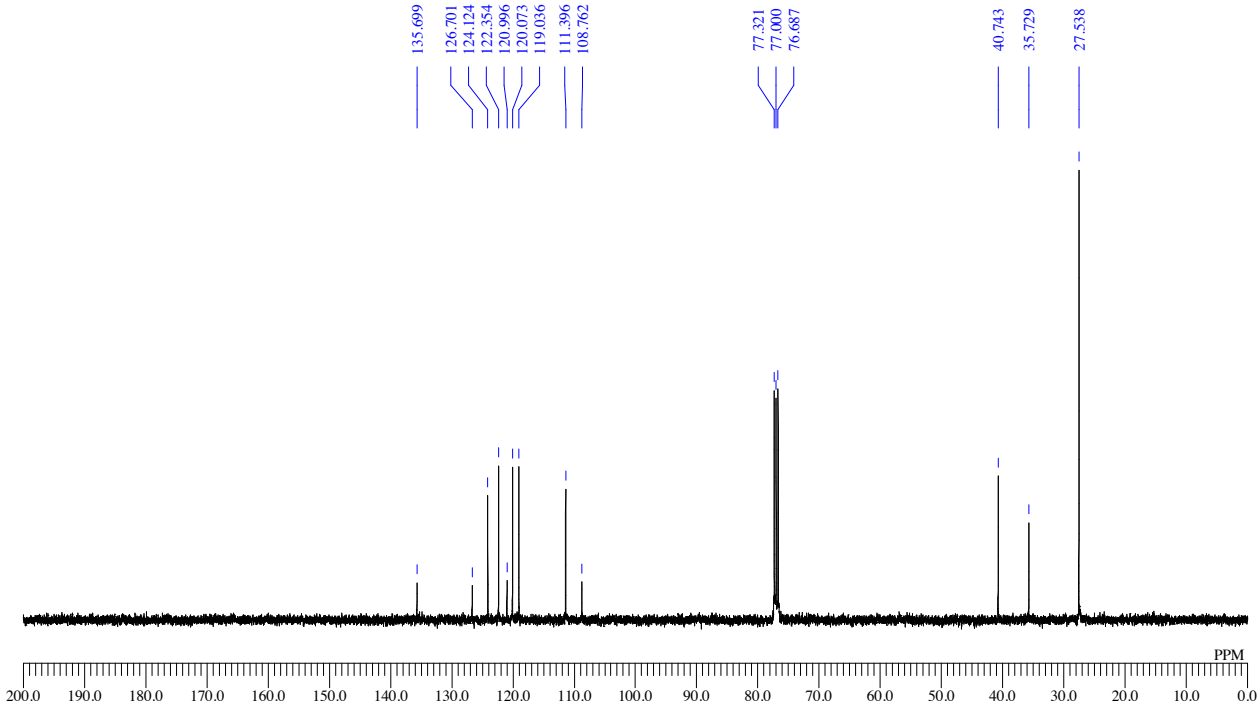
^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)





10au

^{1}H NMR: (400 MHz, $CDCl_3$)



^{13}C{^{1}H} NMR: (100 MHz, $CDCl_3$)