

Nickel-Catalyzed Direct C3-Acylation of 2*H*-Indazoles with Aldehydes

*Yan-Ling Liu, You-Lu Pan, Gang-Jian Li, Hai-Feng Xu, Jian-Zhong Chen**

College of Pharmaceutical Sciences, Zhejiang University, 866 Yuhangtang Rd., Hangzhou, 310058, China

Supporting Information

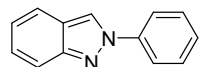
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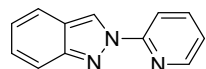
General procedure for the preparation of 2*H*-indazoles.^[1]

NaN₃ (1.19 g, 18.26 mmol), CuI (173.90 mg, 0.913 mmol), 2-bromobenzaldehyde (1.07 mL, 9.13 mmol), TMEDA (137.00 μ L, 9.13 mmol) and anilines (10.96 mmol) were reacted in 20.00 mL of DMSO in pressure tubes. The reaction mixture was heated to 120 °C for 12 h. After cooling, the mixture was poured into the EtOAc (50.0mL) and washed with water (3 \times 25.0 mL), brine (3 \times 25.0 mL), then dried over MgSO₄ and was passed through a Celite. Evaporation of the solvent under reduced pressure provided the crude product, which was purified by column chromatography (Petroleum ether : EtOAc = 15:1) to afford the final product.

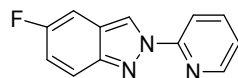
Characterization of 2*H*-indazoles.



2-Phenyl-2*H*-indazole (1a). General procedure. Yellow solid. ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.^[2] ¹H NMR (500 MHz, CDCl₃): δ 8.38 (s, 1H), 7.89 (d, J = 7.64 Hz, 1H), 7.79 (d, J = 8.74 Hz, 1H), 7.69 (d, J = 8.46 Hz, 1H), 7.50 (t, J = 7.91 Hz, 2H), 7.38 (t, J = 7.42 Hz, 1H), 7.31 (dd, J = 8.15, 7.19 Hz, 1H), 7.10 (dd, J = 8.06, 7.00 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ 149.86, 140.61, 129.57, 127.90, 126.83, 122.48, 121.03, 120.40, 118.01, 77.30, 77.04, 76.79.

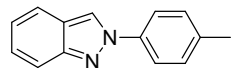


2-(Pyridin-2-yl)-2*H*-indazole (1b1). General procedure. Pale yellow solid. ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.^[2] ¹H NMR (500 MHz, CDCl₃): δ 9.10 (d, J = 0.94 Hz, 1H), 8.50 (dd, J = 4.80, 1.03 Hz, 1H), 8.28 (d, J = 8.24 Hz, 1H), 7.89 (dt, J = 8.13, 7.86, 1.81 Hz, 1H), 7.79-7.70 (m, 2H), 7.35-7.30 (m, 1H), 7.29 (dd, J = 7.37, 4.83 Hz, 1H), 7.10 (ddd, J = 8.43, 6.56, 0.75 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ 151.93, 150.36, 148.32, 138.83, 127.57, 122.74, 122.70, 121.21, 120.61, 118.09, 114.12, 77.30, 77.05, 76.80.

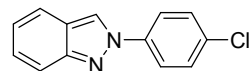


5-Fluoro-2-(pyridin-2-yl)-2*H*-indazole (1b2). General procedure. Yellow solid. ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.^[2] ¹H NMR (500 MHz, CDCl₃): δ 8.97 (d, J = 0.79 Hz, 1H), 8.41 (ddd, J = 4.79, 1.74, 0.73 Hz, 1H), 7.80 (ddd, J = 8.22, 7.45, 1.84 Hz, 1H), 7.66-7.62 (m, 1H), 7.20 (ddt, J = 8.91, 5.98, 2.82 Hz, 2H), 7.05 (dt, J = 9.25, 9.23, 2.43 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ 158.70, 156.78, 150.64, 147.31,

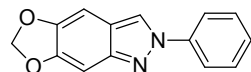
146.72, 137.88, 121.88, 119.69, 119.62, 119.20, 119.12, 118.55, 118.31, 112.90, 102.34, 102.14, 76.26, 76.01, 75.75.



2-(*p*-Tolyl)-2*H*-indazole (1b3). General procedure 1. Brown solid. ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.^[2] ¹H NMR (500 MHz, CDCl₃): δ 8.34 (d, *J* = 0.81 Hz, 1H), 7.81-7.73 (m, 3H), 7.68 (td, *J* = 8.36, 0.83 Hz, 1H), 7.36-7.27 (m, 3H), 7.09 (ddd, *J* = 8.37, 6.61, 0.69 Hz, 1H), 2.41 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ 149.70, 138.34, 137.90, 130.09, 126.65, 122.75, 122.32, 120.88, 120.33, 120.27, 117.92, 77.29, 77.04, 76.79.



2-(4-Chlorophenyl)-2*H*-indazole (1b4). General procedure 1. Brown solid. ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.^[2] ¹H NMR (500 MHz, CDCl₃): δ 8.35 (d, *J* = 0.77 Hz, 1H), 7.85-7.81 (m, 2H), 7.77 (dd, *J* = 8.81, 0.83 Hz, 1H), 7.68 (d, *J* = 8.48 Hz, 1H), 7.49-7.46 (m, 2H), 7.32 (ddd, *J* = 8.77, 6.59, 0.99 Hz, 1H), 7.11 (ddd, *J* = 8.39, 6.62, 0.65 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ 149.93, 139.05, 133.59, 129.71, 127.16, 122.76, 122.03, 120.40, 120.32, 117.94, 77.32, 77.07, 76.81.

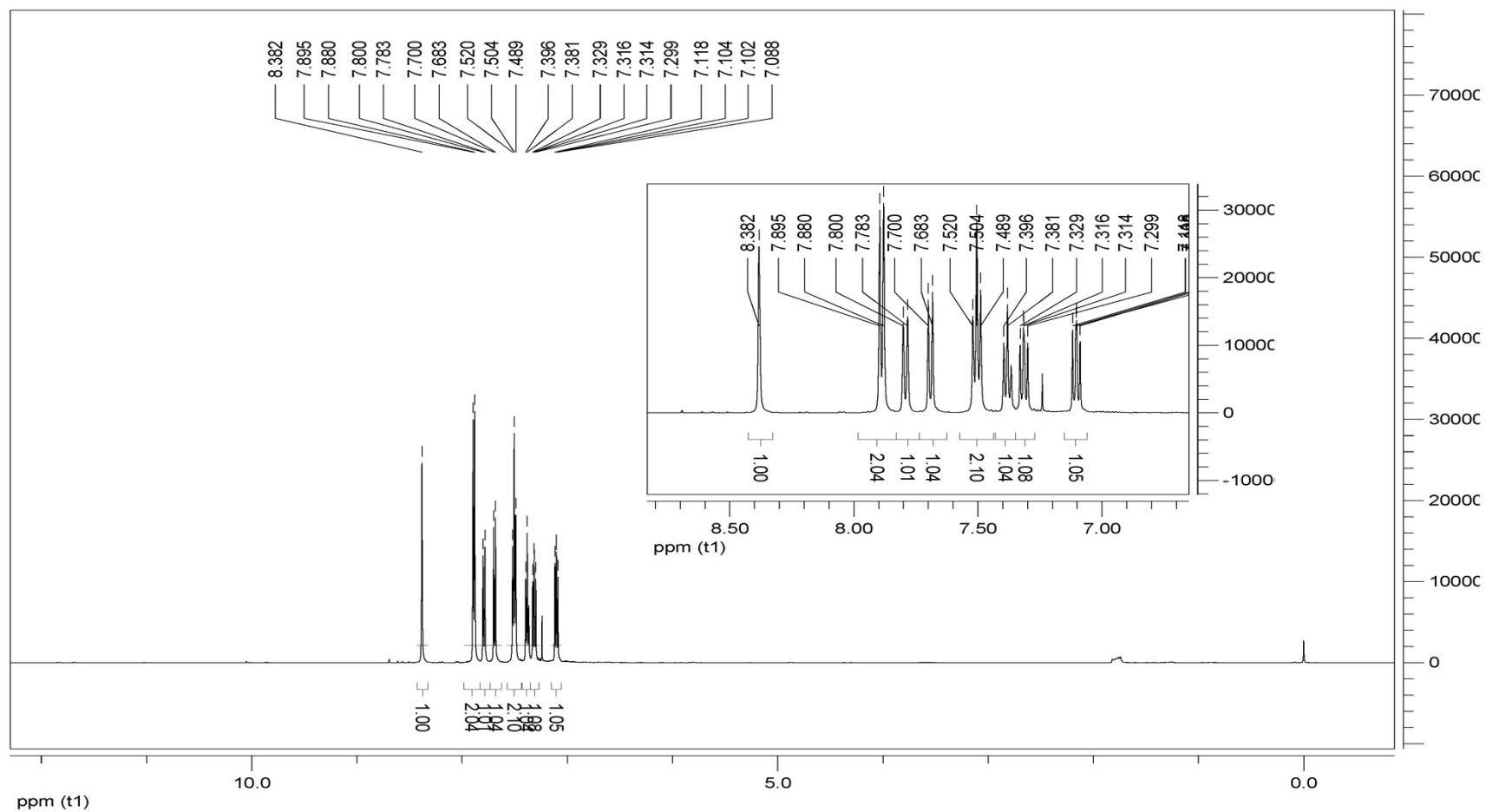
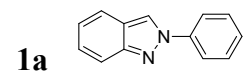


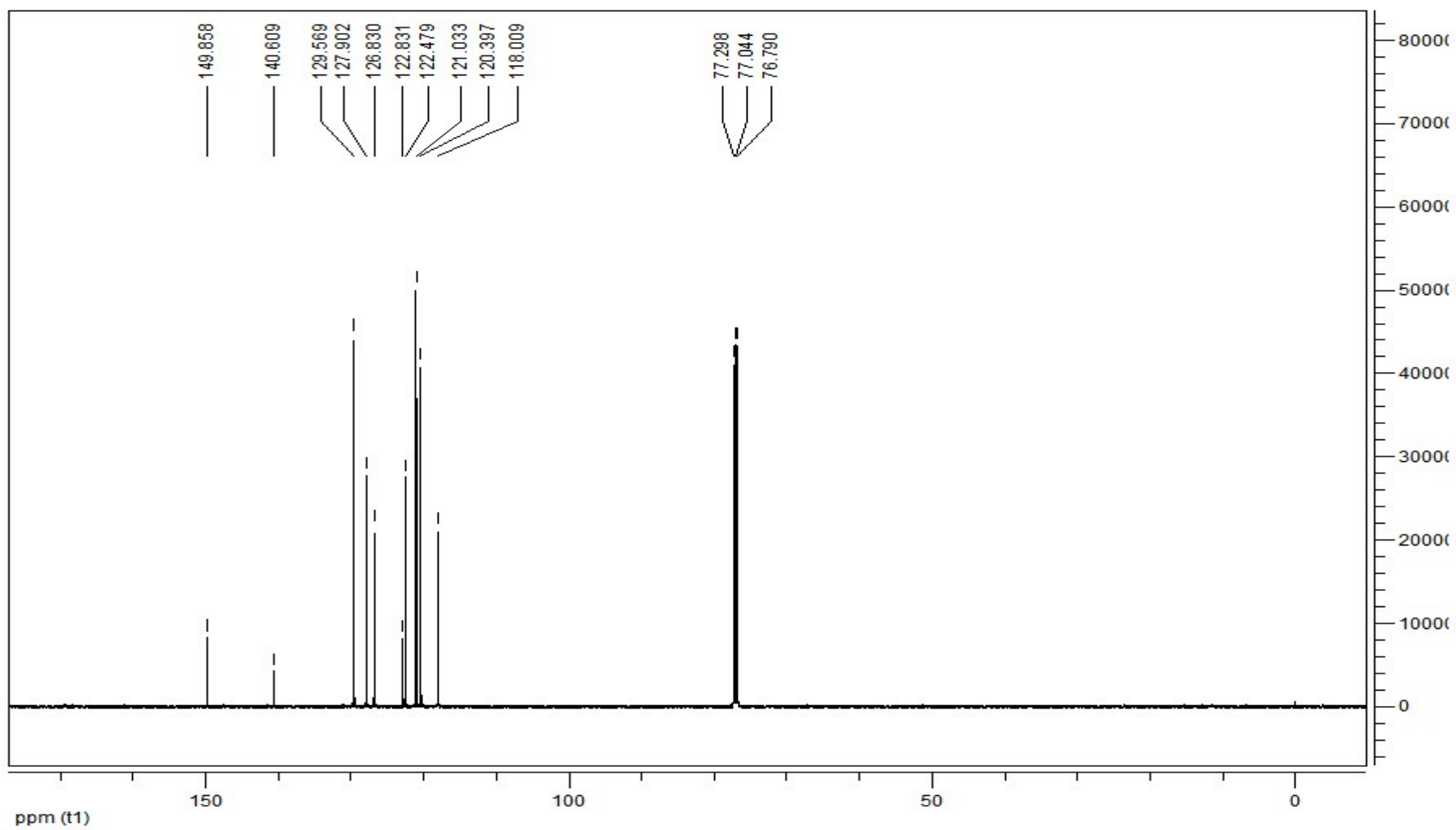
2-Phenyl-2*H*-[1,3]dioxolo[4,5-*f*]indazole (1b5). General procedure 1. Yellow solid. ¹H NMR and ¹³C NMR spectra for this compound are consistent with previously reported literature data.^[2] ¹H NMR (500 MHz, CDCl₃): δ 8.17 (d, *J* = 0.68 Hz, 1H), 7.82-7.79 (m, 2H), 7.48 (dd, *J* = 10.75, 5.23 Hz, 2H), 7.33 (t, *J* = 7.42 Hz, 1H), 7.03 (s, 1H), 6.88 (s, 1H), 5.96 (s, 2H). ¹³C NMR (126 MHz, CDCl₃): δ 149.73, 147.44, 146.11, 140.51, 129.52, 127.13, 120.06, 119.68, 118.59, 101.01, 94.88, 94.20, 77.32, 77.06, 76.81.

references

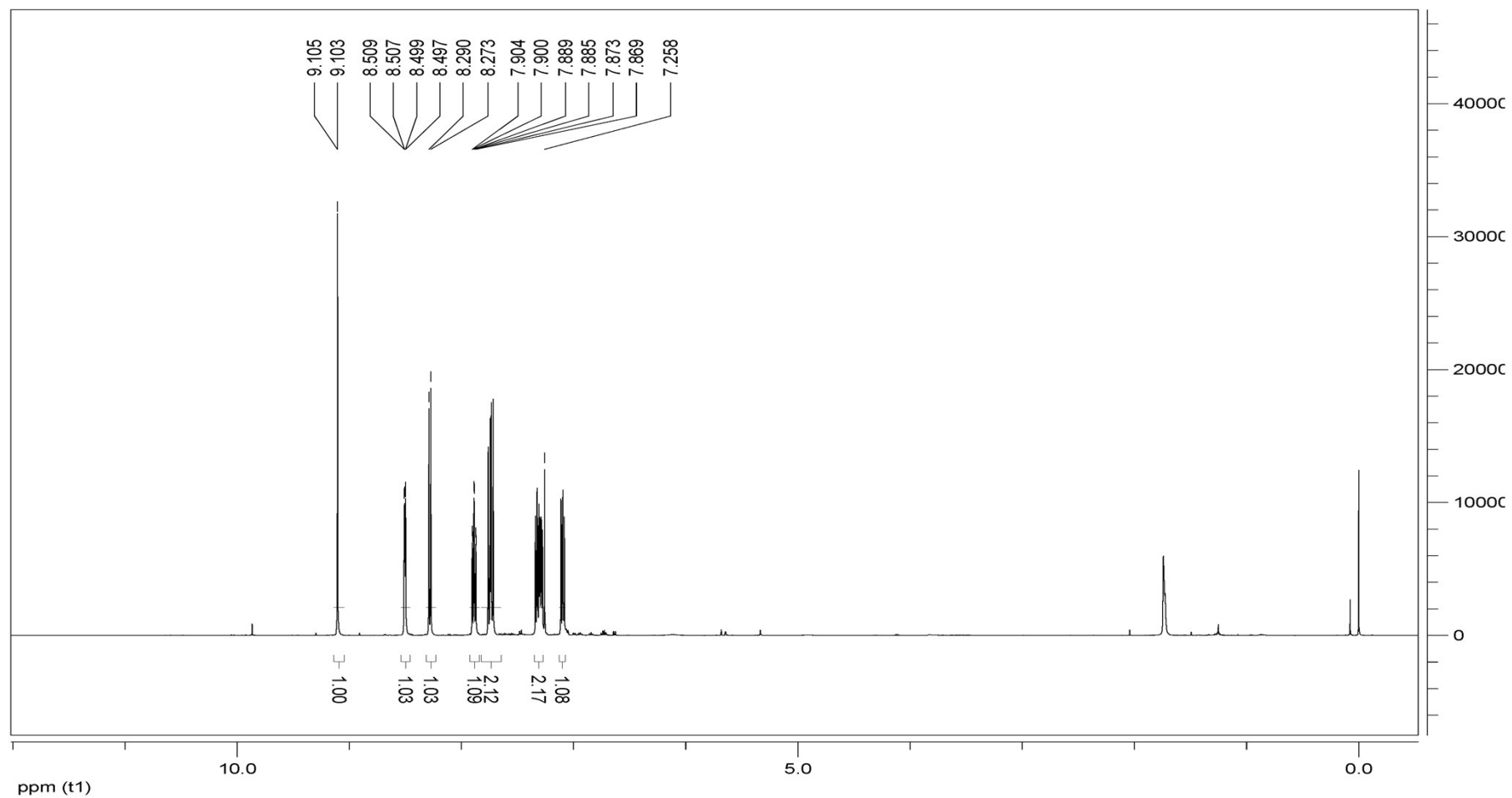
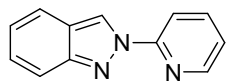
- [1] M. R. Kumar, A. Park, N. Park and S. Lee, *Organic Letters*, 2011, **13**, 3542-3545.
- [2] G. Bogonda, H. Y. Kim and K. Oh, *Organic Letters*, 2018, 2711-2715.

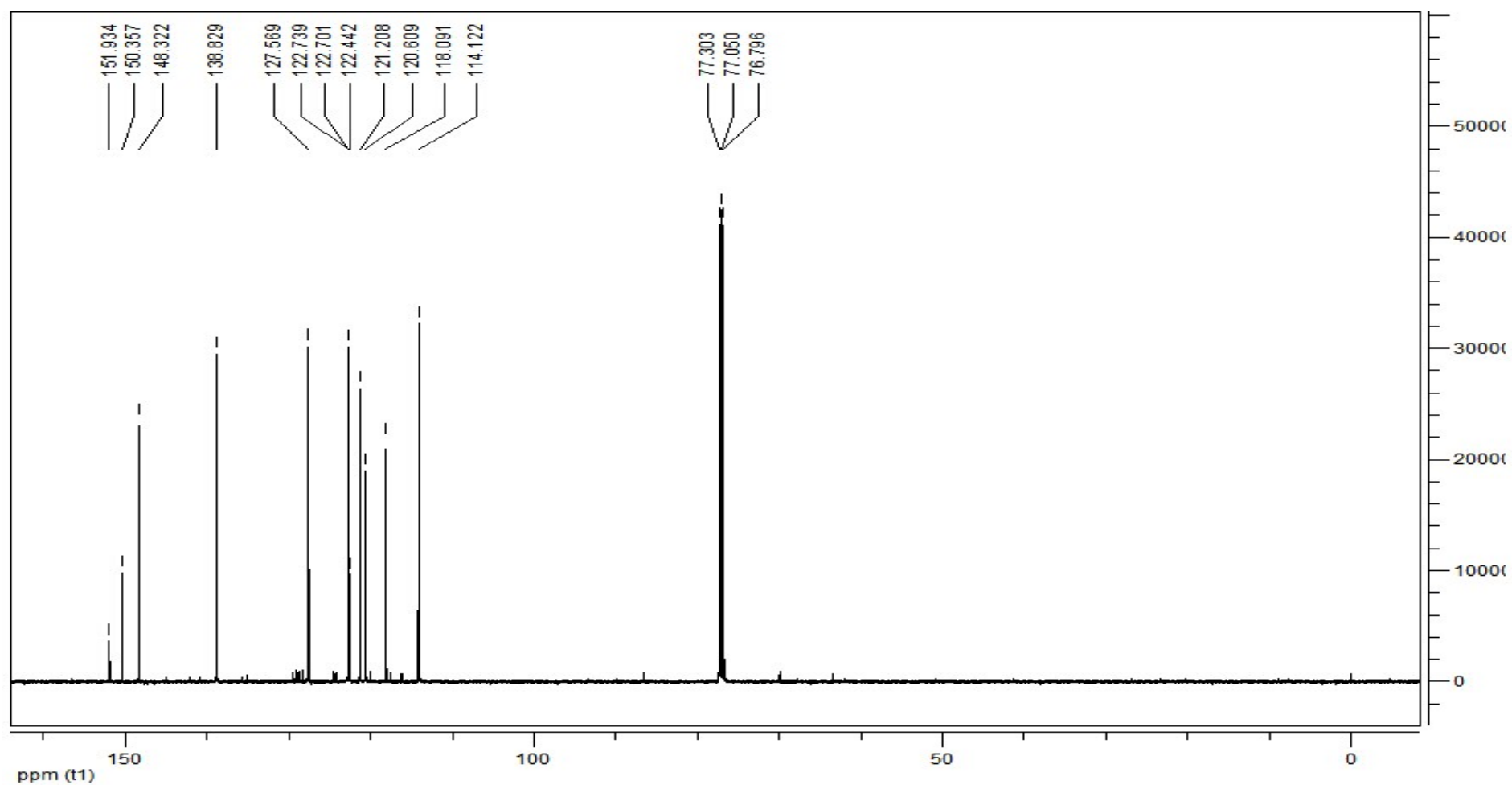
¹H and ¹³C NMR Spectra



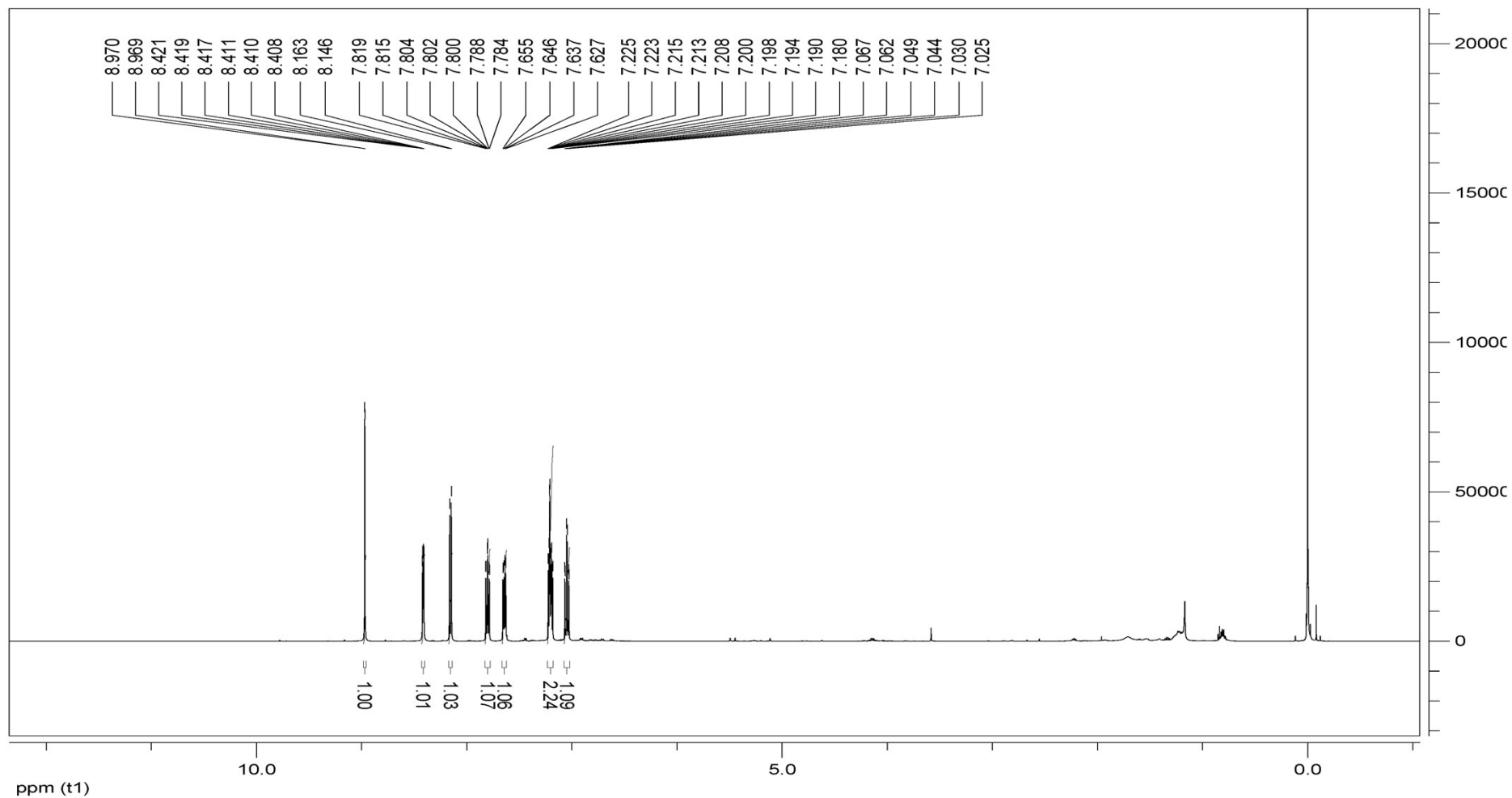
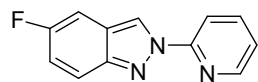


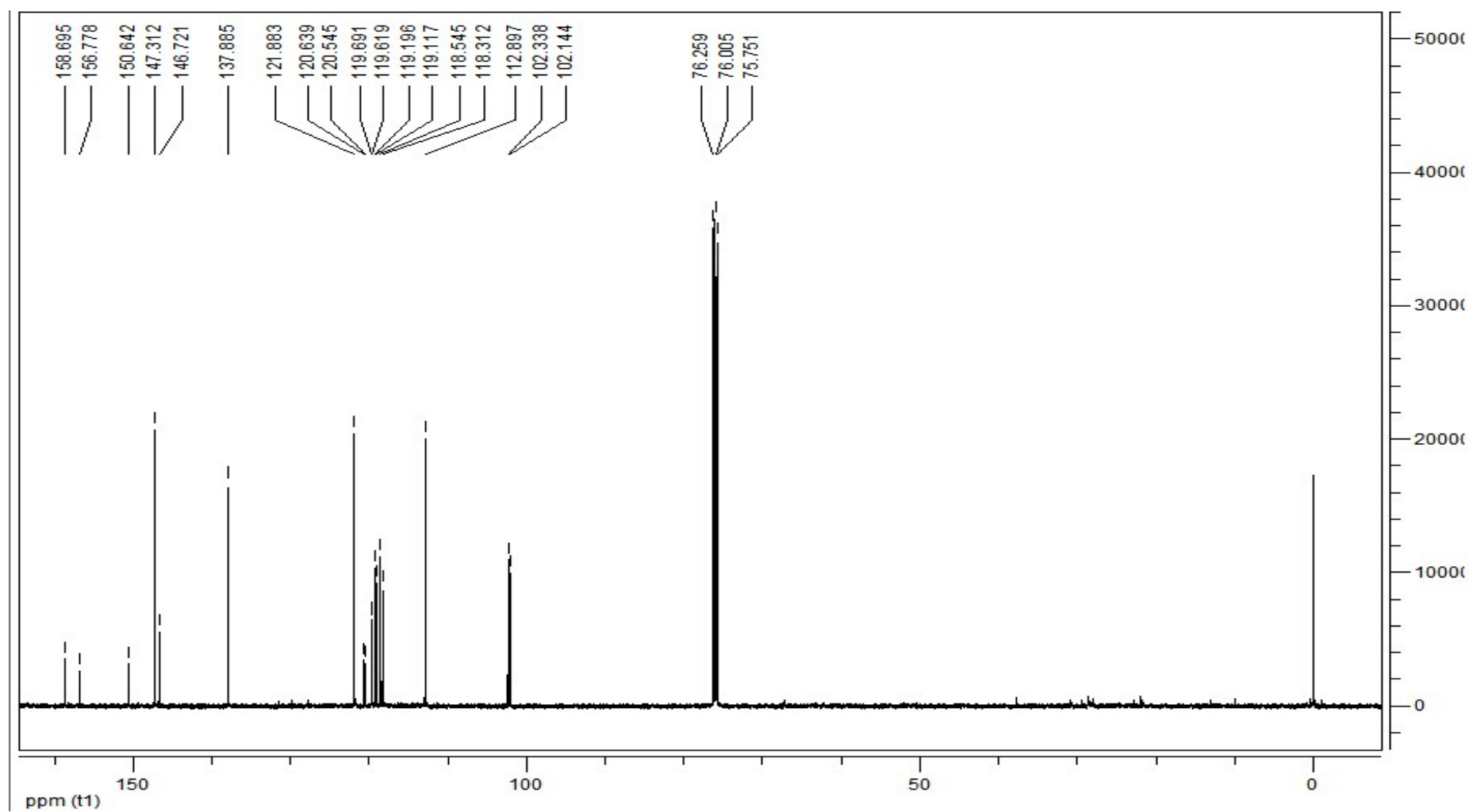
1b1



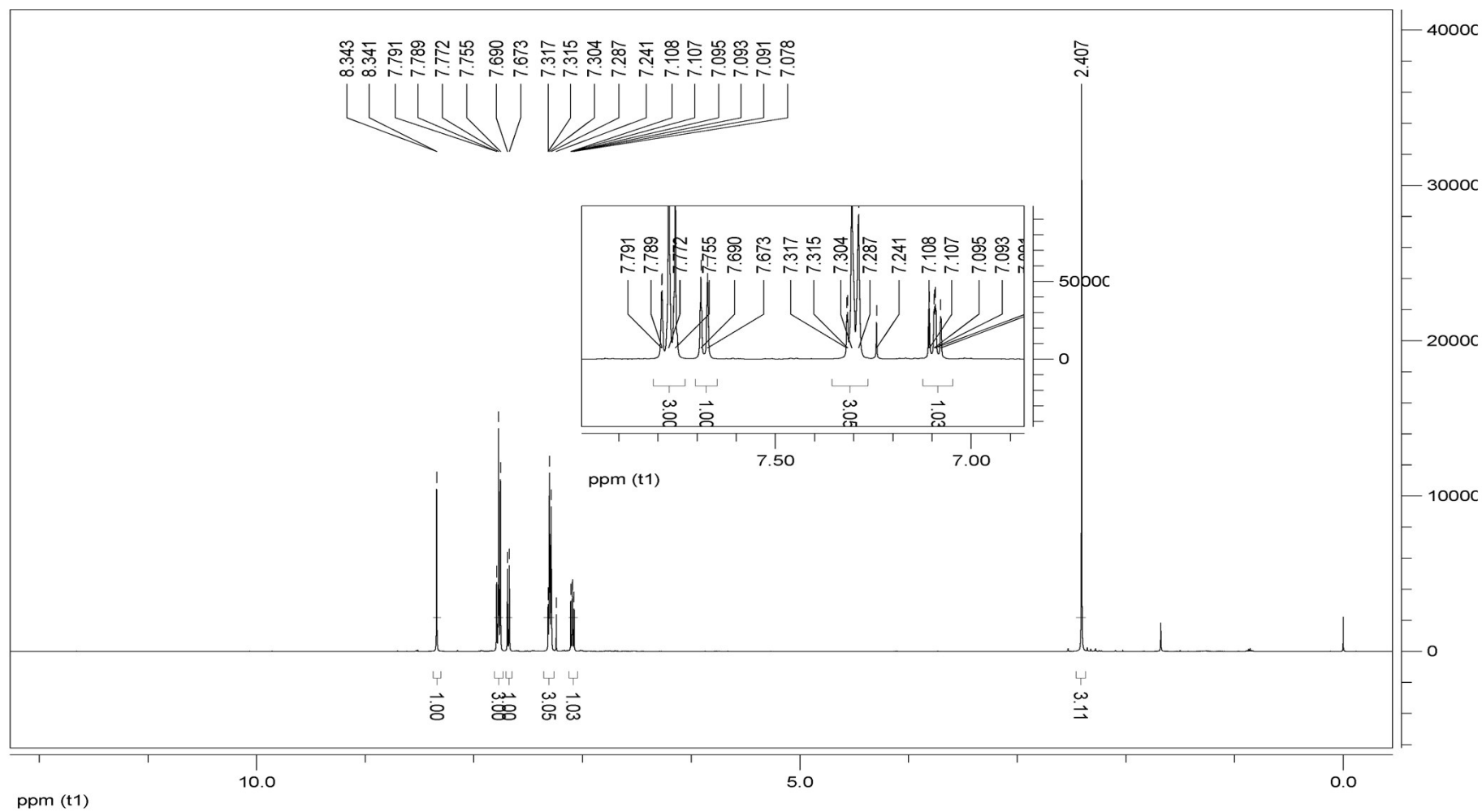
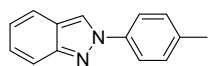


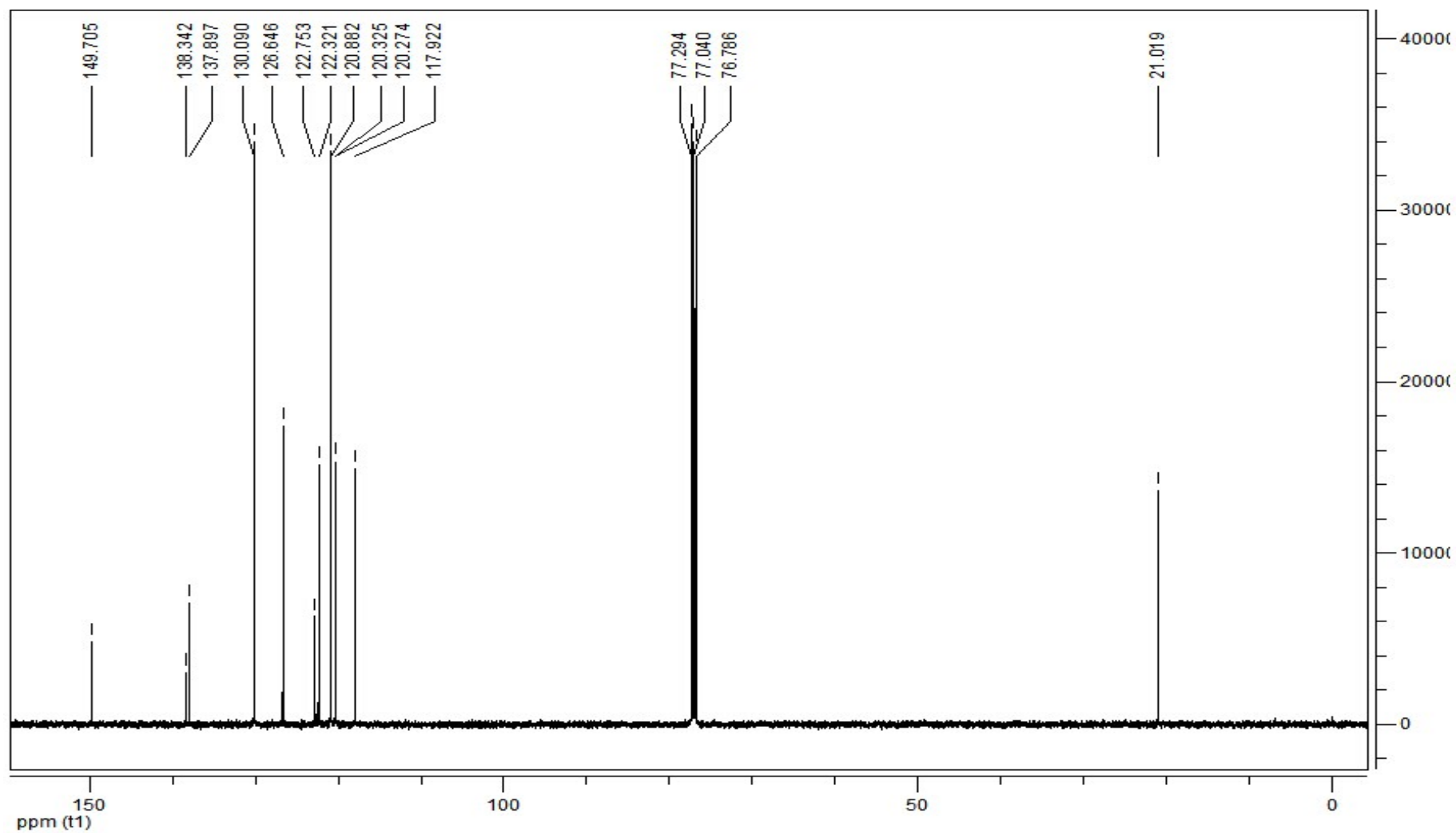
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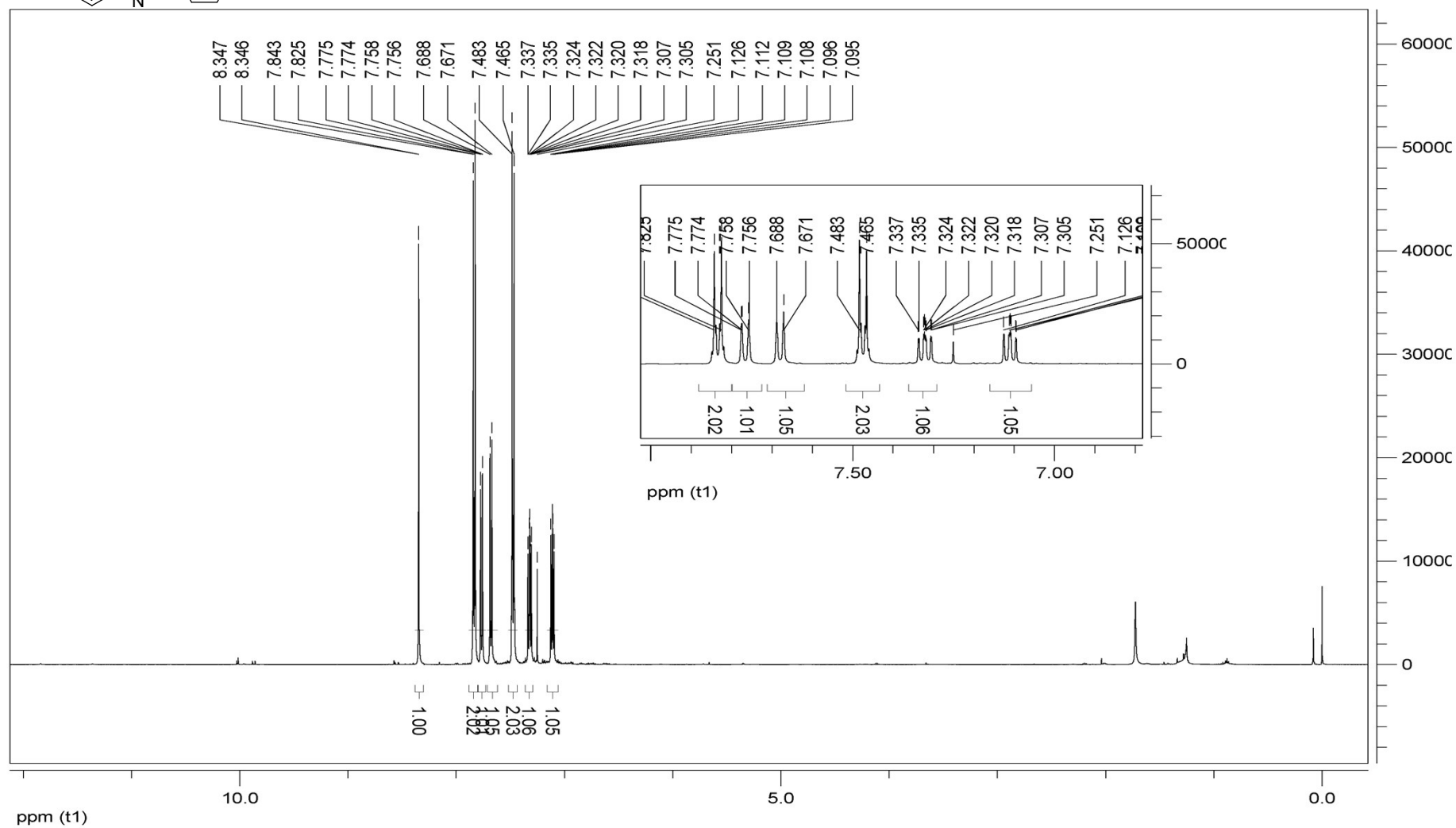
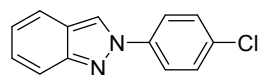


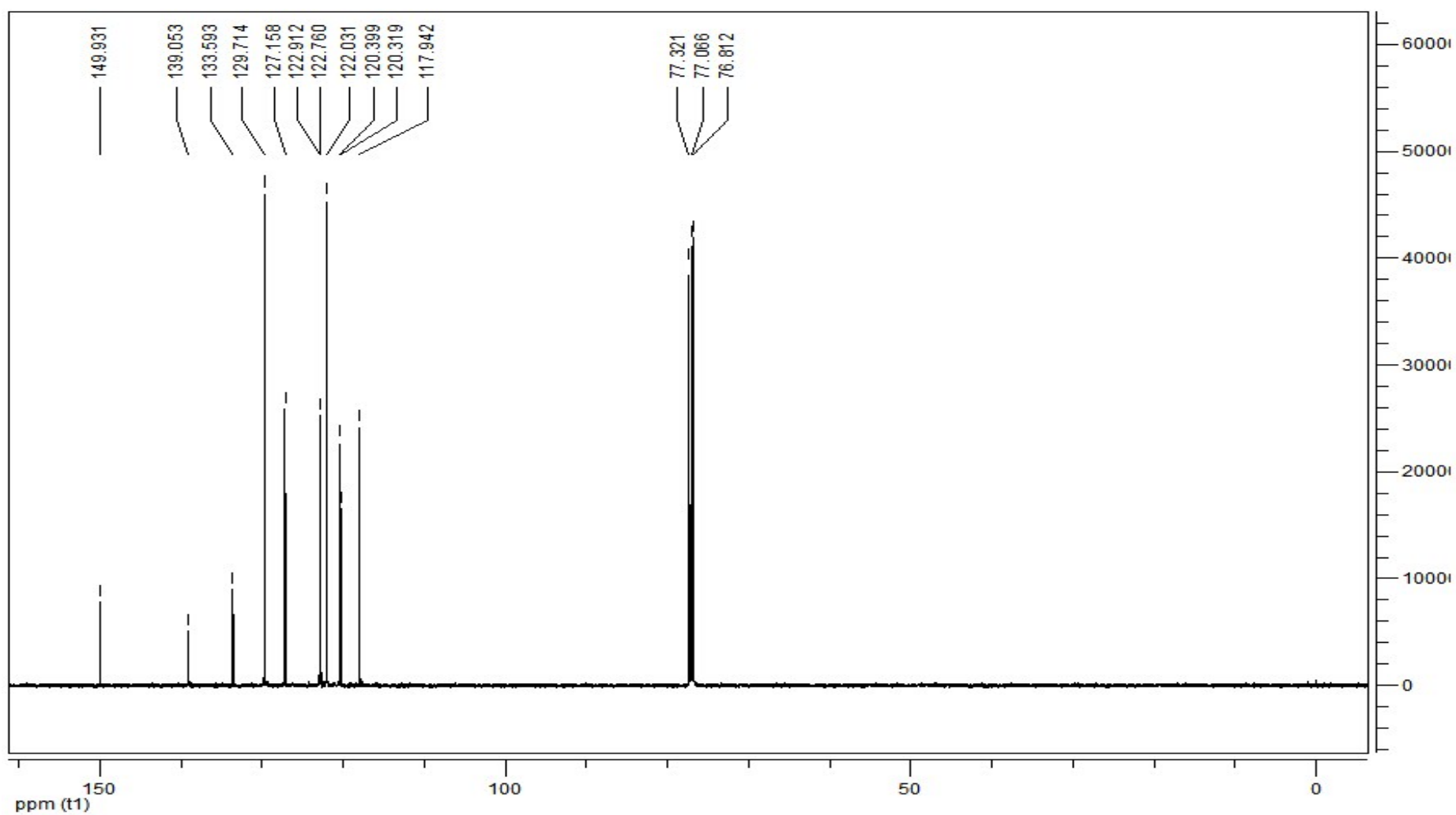
1b3





1b4





1b5

