

Non-directed Oxidative Annulation of 2-Arylindazoles with Electron Deficient Olefins *via* Visible Light Photocatalysis

Krishna Kanta Das and Alakananda Hajra*^a

^aDepartment of Chemistry, Visva-Bharati (A Central University), Santiniketan 731235, India;
Tel./Fax: +913463 261526; E-mail: alakananda.hajra@visva-bharati.ac.in

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1. General Information:

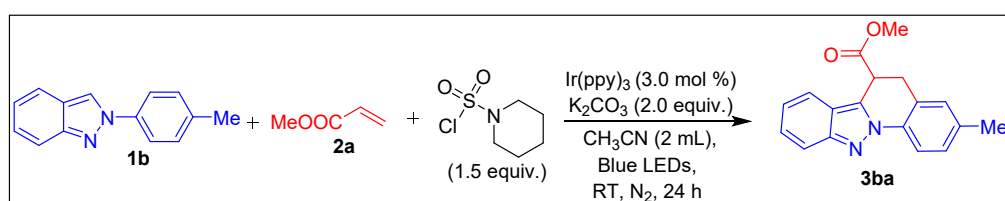
All reagents were purchased from commercial sources and used without further purification. ¹H NMR spectra were determined on 400 MHz spectrometer as solutions in CDCl₃. Chemical shifts are expressed in parts per million (δ) and the signals were reported as s (singlet), d (doublet), t (triplet), m (multiplet) and coupling constants (*J*) were given in Hz. ¹³C{¹H} NMR spectra were recorded at 100 MHz in CDCl₃ solution. Chemical shifts as internal standard is referenced to CDCl₃ (δ = 7.26 for ¹H and δ = 77.16 for ¹³C{¹H} NMR) for as internal standard. Thin-layer chromatography (TLC) was performed on Merck pre-coated silica gel 60 F254 aluminum sheets with detection under UV light at 254 nm. Chromatographic separations were carried out on silica gel (60-120 mesh or 100–200 mesh). All 2-arylidazoles¹ were prepared by the reported methods. All solvents were dried and distilled before use. Commercially available solvents were freshly distilled before the reaction. All reactions involving moisture sensitive reactants were executed using oven dried glassware. Melting points (M.p.) were determined after recrystallization of solid compounds from a solution of dichloromethane/petroleum ether (1:3).

2. Light Information: Kessil 34 W blue LED (Model No. H150-BLUE) was used as a light source for light promoted reactions. Rating of LED: 24VDC 1.5A 34W. Model: H150-BLUE. Range of wavelength: 450-530 nm. Manufacturer: Kessil, 1689 Regatta blvd, Richmond, CA 94804 (www.kessil.com).

3. Reaction Setup: The Borosilicate glass tube was used to carry out light-promoted reaction. The reaction tube was kept 7 cm apart from the exposed of Kessil 34 W blue LED. Regular fan was used to keep up the temperature 28 to 30 °C during the reaction. We did not use any filter.

4. Experimental Procedures:

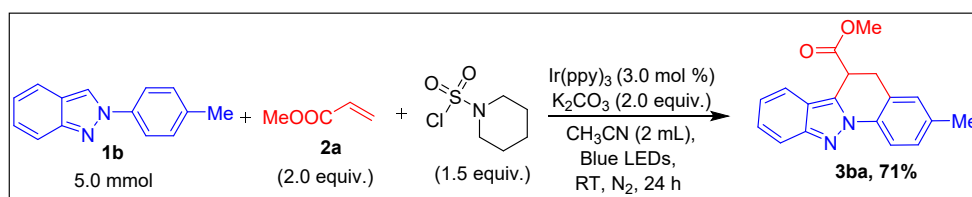
4.1. Typical Experimental Procedure for 3ba:



A mixture of 2-(*p*-tolyl)-2*H*-indazole (**1b**) (0.25 mmol, 52.0 mg), Ir(ppy)₃ (3 mol%, 4.9 mg), and K₂CO₃ (2.0 equiv., 69.1 mg) was taken in an oven dried screw-capped reaction tube. Then the reaction vessel was evacuated and filled with nitrogen for three times. Then methyl acrylate (**2a**) (2.0 equiv., 43.0 mg), piperidine-1-sulfonyl chloride (1.5 equiv., 68.8 mg), and CH₃CN (2 mL) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under a nitrogen atmosphere for 24 h. The progress of the reaction was monitored by TLC, the reaction was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate.

5. Gram-Scale Preparations:

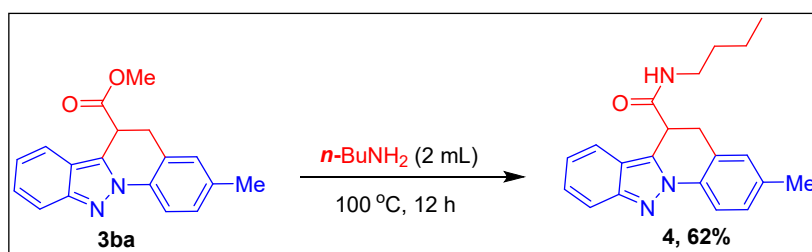
5.1. Synthesis of 3ba on 5.0 mmol Scale:



A mixture of 2-(*p*-tolyl)-2*H*-indazole (**1b**) (5.0 mmol, 1.04 g), Ir(ppy)₃ (3 mol%, 98.1 mg), and K₂CO₃ (2.0 equiv., 1.3 g) was taken in an oven dried reaction vessel. Then the reaction vessel was evacuated and filled with nitrogen for three times. Then methyl acrylate (**2a**) (2.0 equiv., 860 mg), piperidine-1-sulfonyl chloride (1.5 equiv., 1.3 g), and CH₃CN (20 mL) were added to an oven-dried reaction vessel (round bottom flask) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under a nitrogen atmosphere for 24 h. The progress of the reaction was monitored by TLC, the reaction was cooled to room temperature and extracted with ethyl acetate. The organic phase was dried over anhydrous Na₂SO₄. The crude residue was obtained after evaporating the solvent in vacuum and was purified by column chromatography on silica gel using a mixture of petroleum ether and ethyl acetate as an eluting solvent to afford the pure product **3ba** (1.03 g, 71%) as a yellow solid.

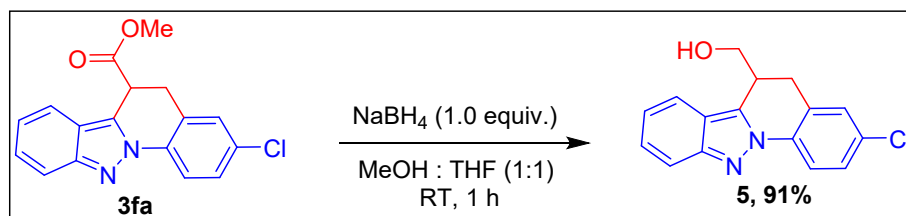
6. Synthetic Transformations:

6.1: Transformation of ester group to amide group:²



In a flame dried reaction tube methyl 3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (**3ba**, 0.2 mmol, 58.4 mg) was added in *n*-BuNH₂ (2 mL) and heated at 100 °C in an oil bath for 12 h. Then the product formation of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous Na₂SO₄, concentrated and the crude mixture was purified by a flash column chromatography on silica gel (60-120 mesh) using 18% ethyl acetate in hexane on silica gel to afford the corresponding product **4** (41.3 mg, 62%) as yellowish white solid.

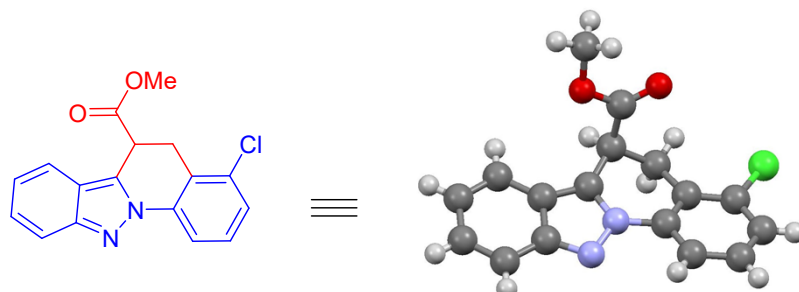
6.2: Transformation of ester group to alcohol group:³



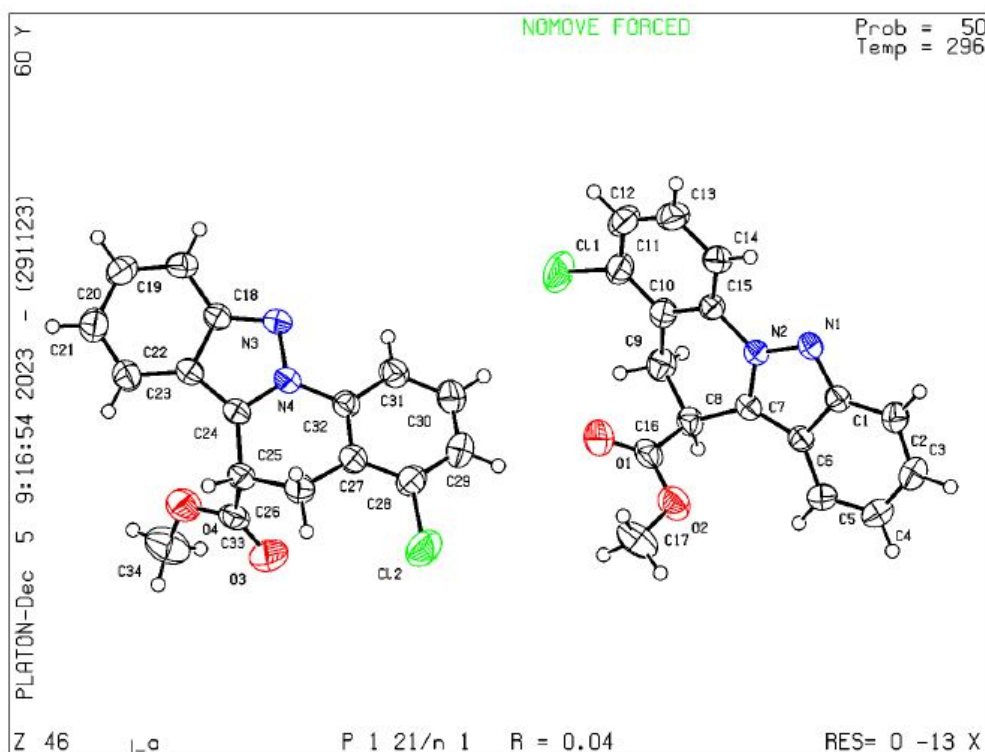
In a flame dried reaction tube methyl 3-chloro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (**3fa**, 0.2 mmol, 62.5 mg,) and NaBH₄ (1.0 equiv., 7.5 mg) was added in dry solvent MeOH : THF (1:1) (2 mL) at room temperature for 1 h. Then the product formation of the reaction was monitored by TLC. After the reaction was completed, the reaction mixture was evaporating the solvent in vacuum. The reaction mixture was diluted with ethyl acetate and washed with brine. The organic layer was dried over anhydrous Na₂SO₄, concentrated and the crude mixture was purified by a flash column chromatography on silica gel (60-120 mesh) using 20% ethyl acetate in hexane on silica gel to afford the corresponding product **5** (51.8 mg, 91%) as brown solid.

7. Structure determination (X-ray crystallographic data for **3ia**):

The pale yellow crystal of **3ia** was obtained by crystallization from a solution in dichloromethane/petroleum ether after purification by column chromatography. Chemical Formula: $C_{17}H_{14}ClN_2O_2$.



Datablock J_a - ellipsoid plot



View of ORTEP (with 50% probability) diagram for the structure Methyl 4-chloro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (**3ia**).

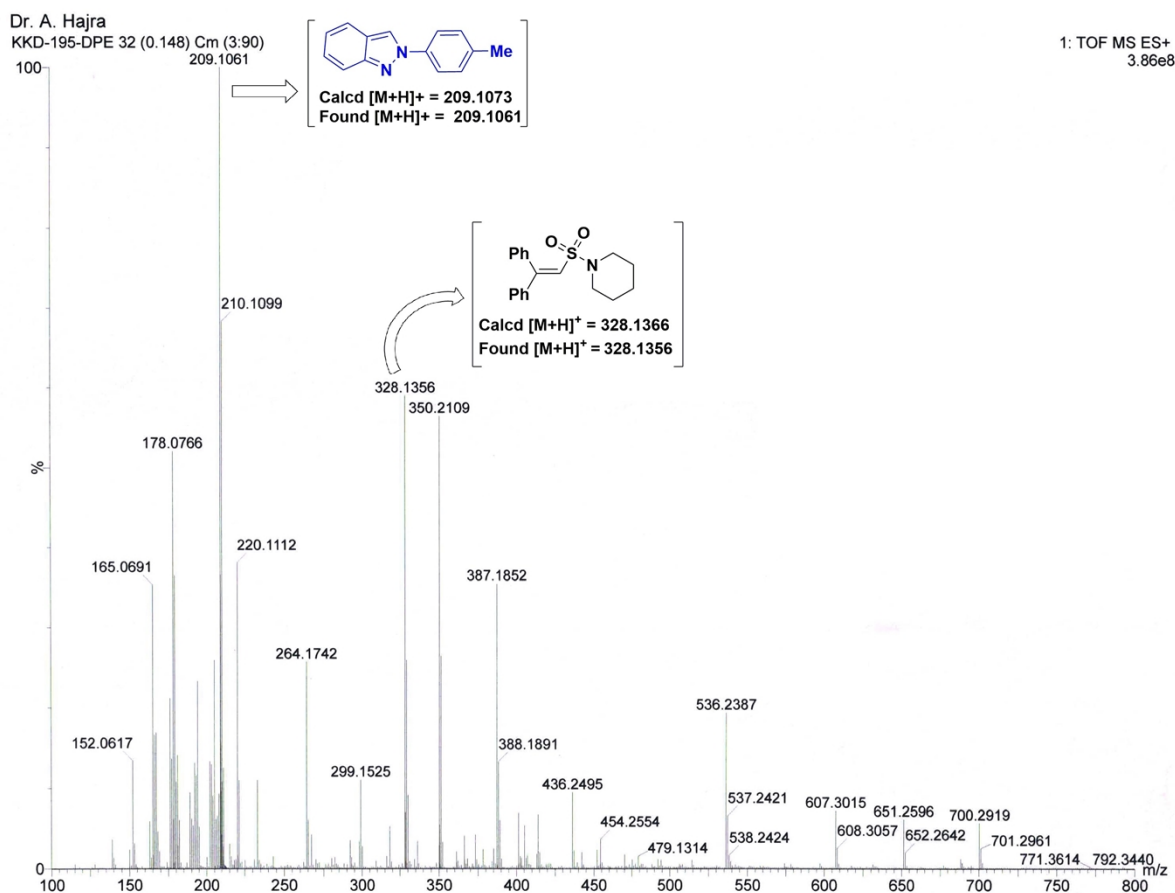
Wavelength	0.71073 Å	
Formula	C ₁₇ H ₁₄ ClN ₂ O ₂	
Crystal system	Monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 11.441(2) Å	α = 90.0°
	b = 13.070(2) Å	β = 105.086(4) °
	c = 20.184(3) Å	γ = 90.0°
Volume	2914.2 Å ³	
Z	8	
R factor (%)	4.49 %	

The crystallographic data have been deposited with the Cambridge Crystallographic Data centre as a supplementary publication with a CCDC reference number 2345181.

8. Radical Trapping Experiment & Reaction intermediate:

8.1 Radical Trapping Experiment:

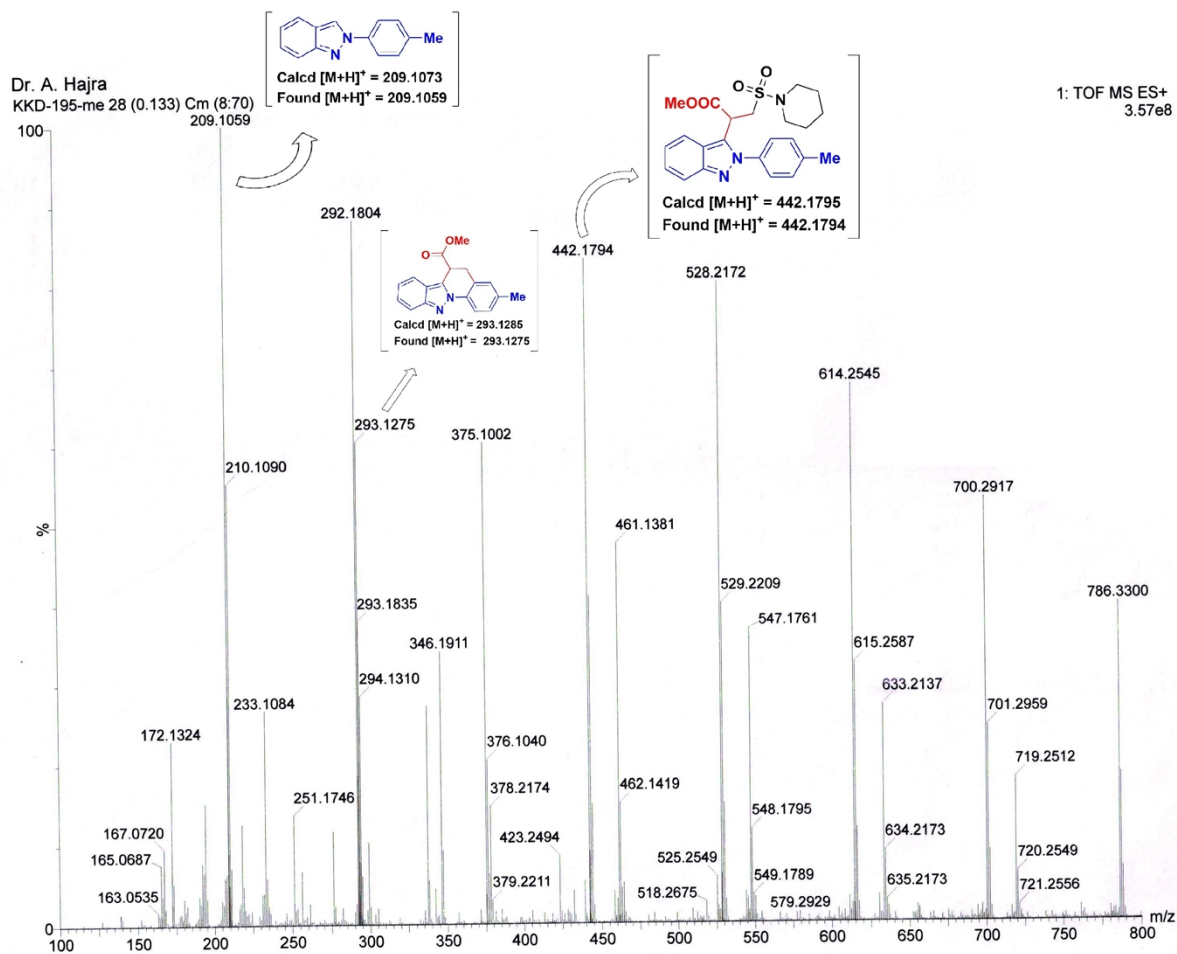
A mixture of 2-(*p*-tolyl)-2*H*-indazole (**1b**) (0.25 mmol, 52.0 mg), Ir(ppy)₃ (3 mol%, 4.9 mg), and K₂CO₃ (2.0 equiv., 69.1 mg) was taken in an oven dried screw-capped reaction tube. Then the reaction vessel was evacuated and filled with nitrogen for three times. Then methyl acrylate (**2a**) (2.0 equiv., 43.0 mg), piperidine-1-sulfonyl chloride (1.5 equiv., 68.8 mg), DPE (3.0 equiv., 135.1 mg) and CH₃CN (2 mL) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under a nitrogen atmosphere for 24 h. After that, the reaction mixture was run for HRMS analysis showed that HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₁₉H₂₂NO₂S]⁺: 328.1366; found: 328.1356, we confirmed that DPE trapped radical adduct was found.



HRMS spectra of DPE adduct

8.2 Reaction intermediate detected by HRMS:

A mixture of 2-(*p*-tolyl)-2*H*-indazole (**1b**) (0.25 mmol, 52.0 mg), Ir(ppy)₃ (3 mol%, 4.9 mg), and K₂CO₃ (2.0 equiv., 69.1 mg) was taken in an oven dried screw-capped reaction tube. Then the reaction vessel was evacuated and filled with nitrogen for three times. Then methyl acrylate (**2a**) (2.0 equiv., 43.0 mg), piperidine-1-sulfonyl chloride (1.5 equiv., 68.8 mg) and CH₃CN (2 mL) were added to an oven-dried reaction vessel (tube) equipped with a magnetic stirrer, and the reaction vessel was irradiated with Kessil 34 W blue LED at room temperature under a nitrogen atmosphere for 5 h. After that, the reaction mixture was run for HRMS analysis shows the possible involvement of intermediate (**F**) in the reaction pathway. HRMS (ESI-TOF) *m/z*: [M + H]⁺ Calcd for [C₂₃H₂₈N₃O₄S]⁺: 442.1795; found: 442.1794, we confirmed that reaction intermediate (**F**) was formed.



HRMS spectra of intermediate (F)

9. Fluorescence Quenching Studies:⁴

1.0×10^{-5} M Ir(ppy)₃ solution was prepared in CH₃CN for Photoluminescence studies where as other substrates like a) 2-(*p*-tolyl)-2*H*-indazole (**1b**), b) piperidine-1-sulfonyl chloride and c) methyl acrylate (**2a**) in CH₃CN have been made maintaining 1.0×10^{-2} M concentration.

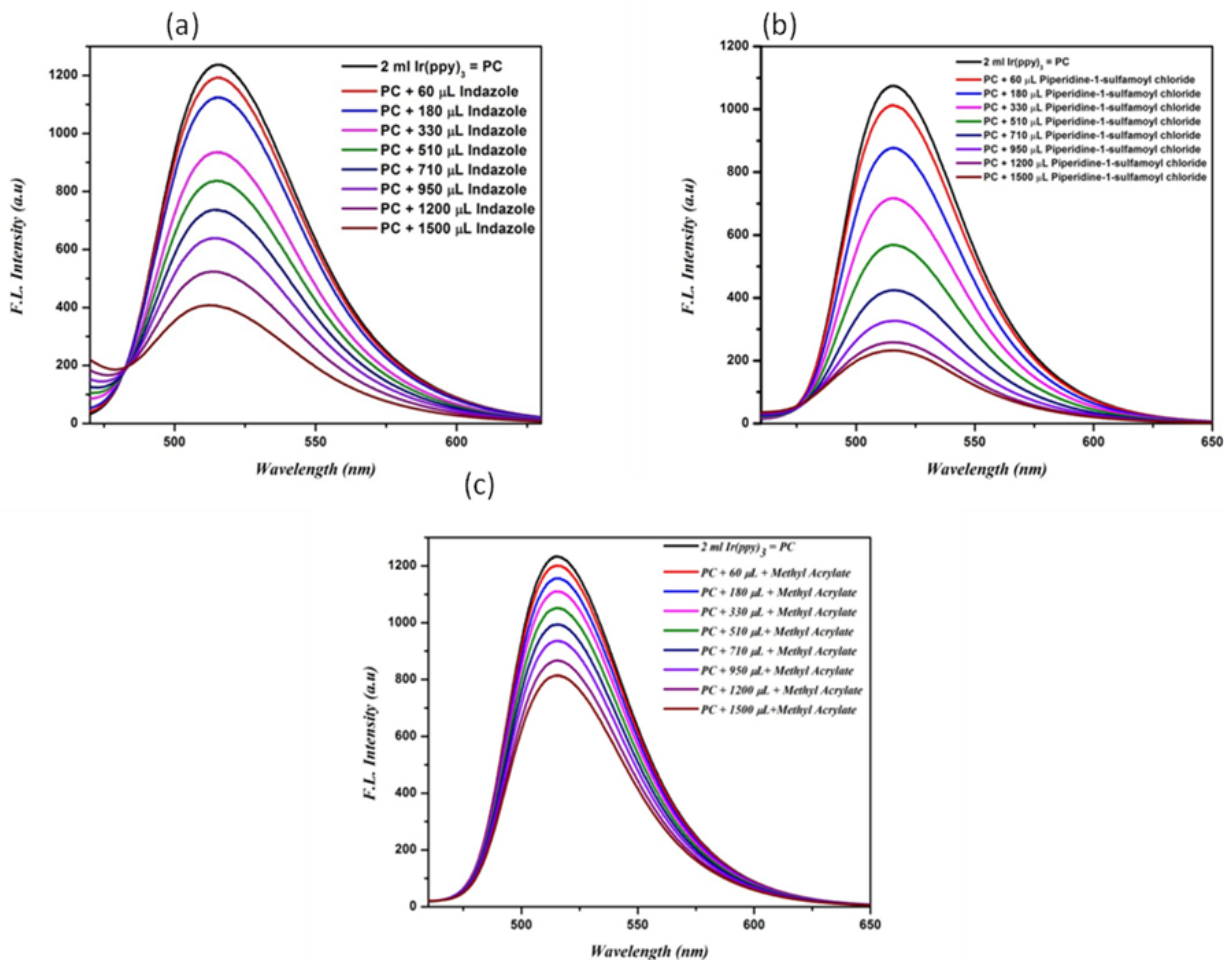


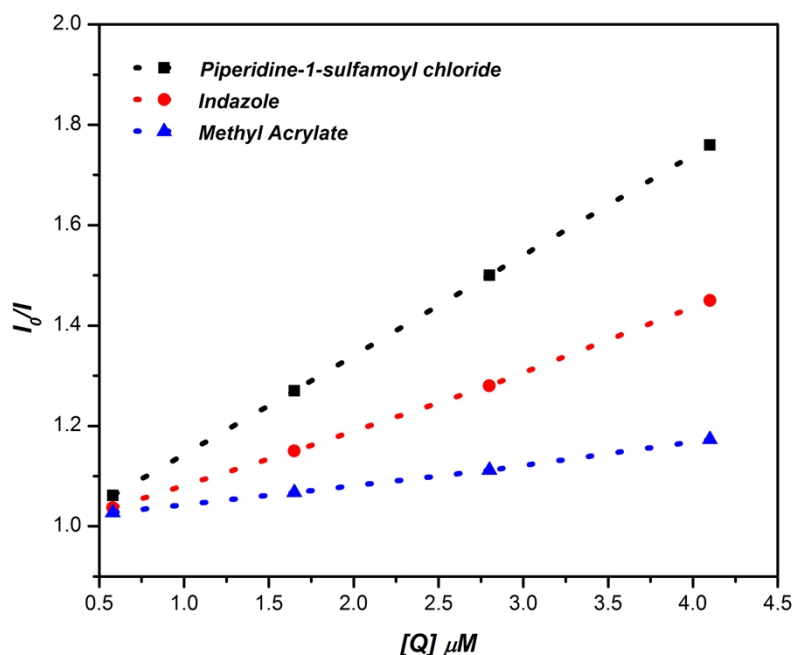
Fig (S1): Change in Fluorescence intensity of Ir(ppy)₃ (1.0×10^{-5} M in CH₃CN) upon incremental addition of a) 2-(*p*-tolyl)-2*H*-indazole (**1b**), b) piperidine-1-sulfonyl chloride and c) methyl acrylate (**2a**). Excitation wavelength = 380 nm.

The quenching phenomena of the photocatalyst in presence of different substrates are explained by the Stern-Volmer plot with the help equation (i).

$$(I_0/I) = K_{SV} [Q] + 1 \quad \text{-----(i)}$$

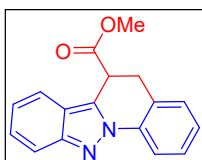
Here, I_0 and I represent the fluorescence intensity of Ir(ppy)₃ in absence and presence of the quencher respectively, K_{SV} is Stern-Volmer quenching constant and $[Q]$ is the concentration of the quencher. If the I_0/I versus $[Q]$ plot are linear, K_{SV} can be estimated accurately. In case of piperidine-1-sulfonyl chloride K_{SV} value obtained from Stern volmer plot is 1.98×10^5 M⁻¹. It has been observed that the emission intensity of Ir(ppy)₃, which is largely quenched by

the gradual addition of piperidine-1-sulfonyl chloride, is moderately affected by the addition of **1b** and slightly affected by the addition of **2a**.

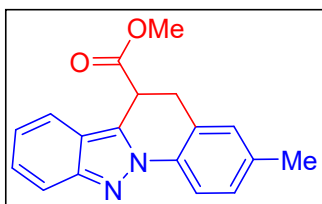


Fig(S2): Stern-Volmer plot from the steady state fluorescence emission of Ir(ppy)₃ in presence of quencher in CH₃CN at 300 K obtained from Fig. (S1).

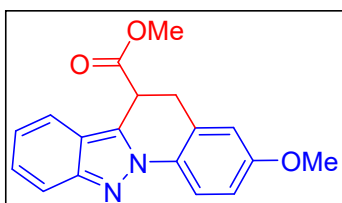
10. Characterization Data for the Synthesized Products:



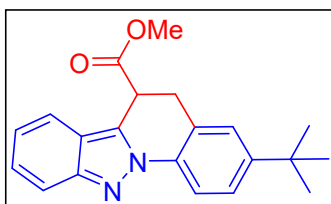
Methyl 5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3aa): Yellow solid (71%, 49.3 mg); $R_f = 0.50$ (PE/EA = 86 : 14), M.p. 92-93 °C; ¹H NMR (400 MHz, CDCl₃): δ 8.20 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 9.2$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.42 (t, $J = 8.0$ Hz, 1H), 7.37-7.33 (m, 2H), 7.31-7.27 (m, 1H), 7.13-7.09 (m, 1H), 4.52-4.50 (m, 1H), 3.64 (s, 3H), 3.55-3.50 (m, 1H), 3.37-3.31 (m, 1H); ¹³C{¹H} NMR (100 MHz, CDCl₃): δ 171.0, 149.1, 136.0, 128.8, 128.4, 127.5, 127.4, 127.3, 125.9, 122.5, 120.5, 119.7, 118.0, 117.9, 52.8, 38.0, 28.6; HRMS (ESI-TOF) m/z : $[M + H]^+$ Calcd for $[C_{17}H_{15}N_2O_2]^+$: 279.1128; found: 279.1110.



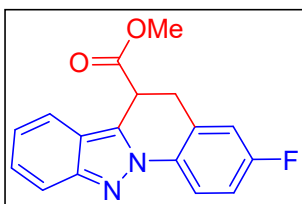
Methyl 3-methyl-5,6-dihydroindazol[2,3-a]quinoline-6-carboxylate (3ba): Yellow solid (84%, 61.3 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 102-103 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.33-7.29 (m, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.16 (s, 1H), 7.11-7.07 (m, 1H), 4.50-4.47 (m, 1H), 3.64 (s, 3H), 3.49-3.44 (m, 1H), 3.32-3.26 (m, 1H), 2.38 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.1, 149.1, 137.2, 133.8, 129.4, 128.9, 128.8, 127.1, 125.7, 122.2, 120.5, 119.6, 119.3, 117.8, 52.7, 38.0, 28.6, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_2]^+$: 293.1285; found: 293.1290.



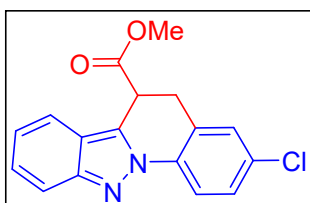
Methyl 3-methoxy-5,6-dihydroindazol[2,3-a]quinoline-6-carboxylate (3ca): Yellow solid (54%, 41.6 mg); $R_f = 0.50$ (PE/EA = 80 : 20), M.p. 106-107 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.12 (d, $J = 8.8$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.34-7.30 (m, 1H), 7.12-7.08 (m, 1H), 6.94-6.91 (m, 1H), 6.88 (d, $J = 2.4$ Hz, 1H), 4.51-4.48 (m, 1H), 3.85 (s, 3H), 3.64 (s, 3H), 3.51-3.46 (m, 1H), 3.34-3.28 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.0, 158.7, 148.7, 129.6, 127.5, 127.1, 126.6, 122.2, 120.5, 119.5, 119.3, 117.6, 114.4, 113.2, 55.6, 52.8, 37.9, 28.8; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3]^+$: 309.1234; found: 309.1235.



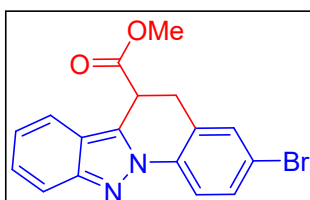
Methyl 3-(tert-butyl)-5,6-dihydroindazol[2,3-a]quinoline-6-carboxylate (3da): Yellow solid (92%, 76.8 mg); $R_f = 0.50$ (PE/EA = 86 : 14), M.p. 109-110 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.42 (d, $J = 8.4$ Hz, 1H), 7.34-7.29 (m, 2H), 7.09 (t, $J = 8.0$ Hz, 1H), 4.51-4.48 (m, 1H), 3.66 (s, 3H), 3.54-3.49 (m, 1H), 3.35-3.30 (m, 1H), 1.35 (s, 9H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.2, 150.5, 149.0, 133.7, 127.1, 125.7, 125.4, 125.3, 122.2, 120.5, 119.6, 117.9, 117.7, 117.5, 52.8, 38.1, 34.8, 31.4, 28.8; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{21}\text{H}_{23}\text{N}_2\text{O}_2]^+$: 335.1754; found: 335.1745.



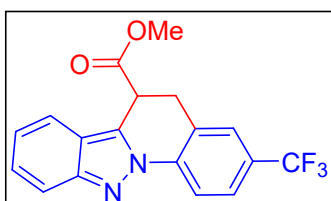
Methyl 3-fluoro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ea): Yellow solid (75%, 55.5 mg); $R_f = 0.50$ (PE/EA = 86 : 14), M.p. 99-100 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.18-8.15 (m, 1H), 7.74 (d, $J = 9.2$ Hz, 1H), 7.61 (d, $J = 8.8$ Hz, 1H), 7.34-7.30 (m, 1H), 7.13-7.07 (m, 3H), 4.53-4.50 (m, 1H), 3.64 (s, 3H), 3.53-3.48 (m, 1H), 3.35-3.29 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.7, 161.4 (C-F, $^1J_{\text{C-F}} = 247.0$ Hz), 149.2, 132.4, 128.2 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 127.4, 126.9, 122.5, 120.6, 119.8 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 119.6, 117.9, 115.8 (C-F, $^1J_{\text{C-F}} = 23.0$ Hz), 115.1 (C-F, $^2J_{\text{C-F}} = 22.0$ Hz), 52.9, 37.7, 28.5; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{14}\text{FN}_2\text{O}_2]^+$: 297.1034; found: 297.1017.



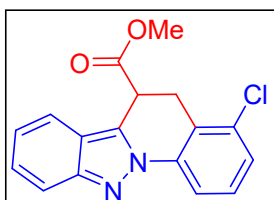
Methyl 3-chloro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3fa): Yellow solid (73%, 56.9 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 113-114 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.12 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.39-7.35 (m, 2H), 7.33-7.30 (m, 1H), 7.13-7.09 (m, 1H), 4.52-4.50 (m, 1H), 3.64 (s, 3H), 3.51-3.46 (m, 1H), 3.34-3.28 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.7, 149.4, 134.7, 132.7, 128.8, 128.5, 127.6, 127.5, 127.2, 122.7, 120.7, 119.6, 119.4, 118.0, 52.9, 37.7, 28.3; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{14}\text{ClN}_2\text{O}_2]^+$: 313.0738; found: 313.0747.



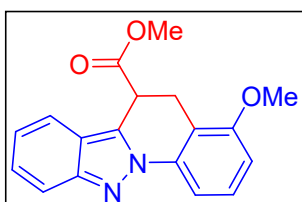
Methyl 3-bromo-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ga): Yellow solid (51%, 45.5 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 125-126 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.60 (d, $J = 8.8$ Hz, 1H), 7.55-7.51 (m, 2H), 7.34-7.30 (m, 1H), 7.13-7.09 (m, 1H), 4.52-4.49 (m, 1H), 3.65 (s, 3H), 3.52-3.47 (m, 1H), 3.35-3.29 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.6, 149.4, 135.1, 131.7, 131.5, 127.9, 127.6, 127.2, 122.7, 120.6, 120.7, 120.6, 119.7, 118.0, 52.9, 37.8, 28.3; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{14}\text{BrN}_2\text{O}_2]^+$: 357.0233; found: 357.0241.



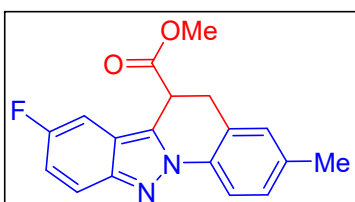
Methyl 3-(trifluoromethyl)-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ha): Greenish yellow solid (64%, 55.4 mg); $R_f = 0.50$ (PE/EA = 84 : 16), M.p. 128-129 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.30 (d, $J = 8.4$ Hz, 1H), 7.74 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 1H), 7.62 (d, $J = 8.4$ Hz, 2H), 7.36-7.32 (m, 1H), 7.14-7.11 (m, 1H), 4.57-4.54 (m, 1H), 3.65 (s, 3H), 3.61-3.56 (m, 1H), 3.41-3.35 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.5, 149.8, 138.5, 128.7, (q, $J = 33.0$ Hz), 128.0, 127.8, 126.5, 125.8, (q, $J = 4.0$ Hz), 123.9 (d, $J = 270.0$ Hz), 122.5, 120.8, 119.8, 118.3, 118.1, 52.9, 37.6, 28.4; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{14}\text{F}_3\text{N}_2\text{O}_2]^+$: 347.1002; found: 347.0991.



Methyl 4-chloro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ia): Yellow solid (81%, 63.3 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 121-122 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.17-8.13 (m, 1H), 7.73 (d, $J = 8.4$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.37-7.31 (m, 3H), 7.13-7.09 (m, 1H), 4.56-4.53 (m, 1H), 3.86-3.81 (m, 1H), 3.67 (s, 3H), 3.29-3.23 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.7, 149.6, 137.2, 133.9, 128.7, 128.0, 127.7, 127.2, 124.4, 122.7, 120.5, 119.7, 118.0, 116.7, 52.9, 37.4, 25.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{14}\text{ClN}_2\text{O}_2]^+$: 313.0738; found: 313.0727.

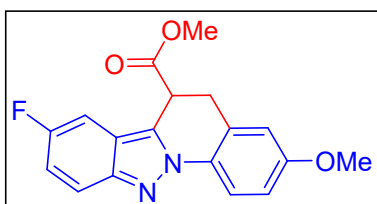


Methyl 4-methoxy-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ja): Yellow solid (77%, 59.3 mg); $R_f = 0.50$ (PE/EA = 80 : 20), M.p. 110-111 °C; ^1H NMR (400 MHz, CDCl_3): δ 7.85 (d, $J = 8.0$ Hz, 1H), 7.77-7.74 (m, 1H), 7.60 (d, $J = 8.4$ Hz, 1H), 7.38-7.29 (m, 2H), 7.12-7.07 (m, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 4.51-4.48 (m, 1H), 3.91 (s, 3H), 3.73-3.68 (m, 1H), 3.65 (s, 3H), 3.16-3.10 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.3, 157.0, 149.1, 136.7, 128.4, 127.3, 122.3, 120.4, 119.7, 117.9, 114.5, 110.5, 109.3, 103.0, 56.0, 52.8, 37.6, 21.6; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3]^+$: 309.1234; found: 309.1214.

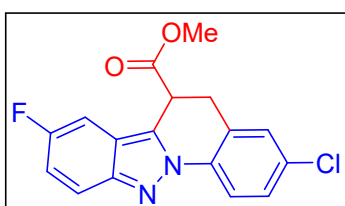


Methyl 8-fluoro-3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ka): Brown solid (85%, 65.9 mg); $R_f = 0.50$ (PE/EA = 84 : 16), M.p. 112-113 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.02 (d, $J = 8.0$ Hz, 1H), 7.73-7.70 (m, 1H), 7.21-7.15 (m, 3H), 7.13-7.08 (m, 1H), 4.43-4.40 (m, 1H), 3.65 (s, 3H), 3.49-3.44 (m, 1H), 3.31-3.26 (m, 1H), 2.38 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.9, 158.6 (C-F, $^1J_{\text{C-F}} = 239.0$ Hz), 146.5, 137.4, 133.7, 129.4,

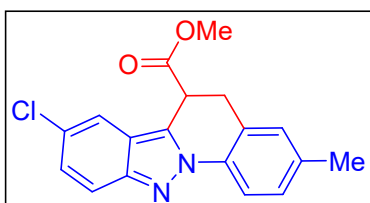
129.0, 127.2 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 125.7, 120.1 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 119.8, 118.6 (C-F, $^2J_{\text{C-F}} = 28.0$ Hz), 117.7, 102.2 (C-F, $^2J_{\text{C-F}} = 25.0$ Hz), 52.8, 37.9, 28.5, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{16}\text{FN}_2\text{O}_2]^+$: 311.1190; found: 311.1188.



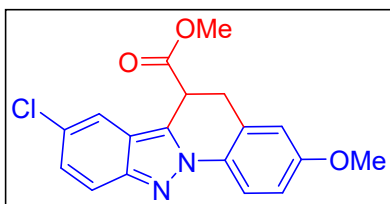
Methyl 8-fluoro-3-methoxy-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3la): Yellow solid (76%, 62.0 mg); $R_f = 0.50$ (PE/EA = 81 : 19), M.p. 104-105 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.8$ Hz, 1H), 7.72-7.69 (m, 1H), 7.18-7.15 (m, 1H), 7.12-7.07 (m, 1H), 6.93-6.88 (m, 2H), 4.43-4.40 (m, 1H), 3.85 (s, 3H), 3.66 (s, 3H), 3.50-3.45 (m, 1H), 3.33-3.27 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.9, 158.8, 158.6 (C-F, $^1J_{\text{C-F}} = 240.0$ Hz), 146.3, 129.7, 127.5, 126.6 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 119.9, 119.8 (C-F, $^3J_{\text{C-F}} = 10.0$ Hz), 119.2, 118.3 (C-F, $^2J_{\text{C-F}} = 29.0$ Hz), 114.3, 113.3, 102.1 (C-F, $^2J_{\text{C-F}} = 24.0$ Hz), 55.6, 52.8, 37.9, 28.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{16}\text{FN}_2\text{O}_3]^+$: 327.1139; found: 327.1126.



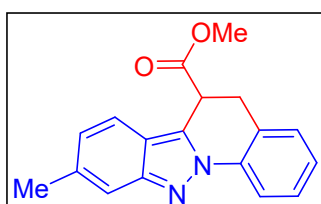
Methyl 3-chloro-8-fluoro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ma): White solid (84%, 69.5 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 117-118 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.08 (d, $J = 8.4$ Hz, 1H), 7.72-7.68 (m, 1H), 7.38-7.36 (m, 2H), 7.18-7.16 (m, 1H), 7.15-7.10 (m, 1H), 4.45-4.43 (m, 1H), 3.66 (s, 3H), 3.51-3.46 (m, 1H), 3.33-3.28 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.5, 158.7 (C-F, $^1J_{\text{C-F}} = 240.0$ Hz), 146.7, 134.5, 132.9, 128.7 (C-F, $^2J_{\text{C-F}} = 36.0$ Hz), 127.6, 127.3 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 120.1 (C-F, $^3J_{\text{C-F}} = 9.0$ Hz), 120.0, 119.3, 119.2, 119.1, 102.2 (C-F, $^2J_{\text{C-F}} = 24.0$ Hz), 53.0, 37.6, 28.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{13}\text{ClFN}_2\text{O}_2]^+$: 331.0644; found: 331.0624.



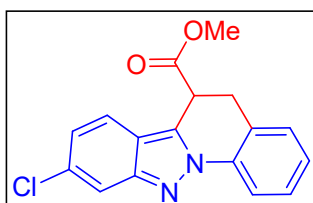
Methyl 8-chloro-3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3na): Brown solid (82%, 66.9 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 107-108 °C; ^1H NMR (400 MHz, CDCl_3): δ 8.02 (d, $J = 8.0$ Hz, 1H), 7.68 (d, $J = 8.8$ Hz, 1H), 7.57 (d, $J = 1.6$ Hz, 1H), 7.24-7.19 (m, 2H), 7.16 (s, 1H), 4.44-4.41 (m, 1H), 3.65 (s, 3H), 3.49-3.44 (m, 1H), 3.31-3.26 (m, 1H), 2.38 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.8, 147.4, 137.6, 133.6, 129.5, 129.0, 128.4, 127.9, 126.8, 125.7, 121.0, 119.4, 118.4, 117.9, 52.9, 37.9, 28.4, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{O}_2]^+$: 327.0895; found: 327.0886.



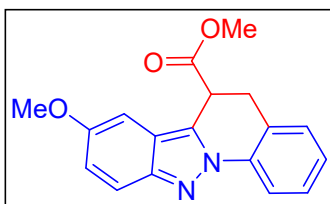
Methyl 8-chloro-3-methoxy-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (30a): Yellow solid (61%, 52.1 mg); $R_f = 0.50$ (PE/EA = 80 : 20), M.p. 150-151 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.8$ Hz, 1H), 7.67 (d, $J = 9.2$ Hz, 1H), 7.57 (d, $J = 1.6$ Hz, 1H), 7.24-7.21 (m, 1H), 6.93-6.88 (m, 2H), 4.44-4.42 (m, 1H), 3.85 (s, 3H), 3.65 (s, 3H), 3.50-3.45 (m, 1H), 3.33-3.27 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.7, 158.9, 147.3, 129.6, 128.2, 127.7, 127.5, 126.1, 121.0, 119.3, 118.3, 114.3, 113.3, 55.6, 52.9, 37.8, 28.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{16}\text{ClN}_2\text{O}_3]^+$: 343.0844; found: 343.0833.



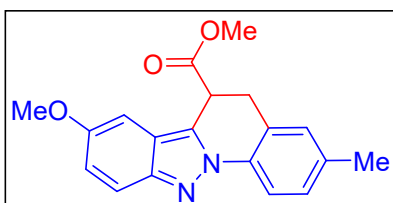
Methyl 9-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3pa): Yellow solid (89%, 65.0 mg); $R_f = 0.50$ (PE/EA = 86 : 14), M.p. 76-77 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.15 (d, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 9.2$ Hz, 2H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 7.2$ Hz, 1H), 7.26-7.22 (m, 1H), 6.95-6.93 (m, 1H), 4.48-4.45 (m, 1H), 3.64 (s, 3H), 3.52-3.47 (m, 1H), 3.34-3.29 (m, 1H), 2.45 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.1, 149.9, 137.3, 136.2, 128.7, 128.3, 127.2, 126.9, 125.7, 125.4, 119.1, 119.0, 117.8, 116.3, 52.7, 38.0, 28.6, 22.45; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_2]^+$: 293.1285; found: 293.1267.



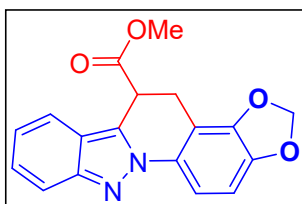
Methyl 9-chloro-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3qa): Brown solid (87%, 68.0 mg); $R_f = 0.50$ (PE/EA = 85 : 15), M.p. 98-99 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.15 (d, $J = 8.0$ Hz, 1H), 7.73 (d, $J = 1.2$ Hz, 1H), 7.54 (d, $J = 9.2$ Hz, 1H), 7.41 (t, $J = 8.0$ Hz, 1H), 7.35 (d, $J = 7.2$ Hz, 1H), 7.30-7.25 (m, 1H), 7.06-7.03 (m, 1H), 4.49-4.46 (m, 1H), 3.64 (s, 3H), 3.54-3.49 (m, 1H), 3.36-3.30 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.7, 149.4, 135.8, 133.1, 128.8, 128.5, 128.0, 127.5, 125.8, 123.9, 121.0, 119.1, 118.0, 116.9, 52.9, 37.9, 28.4; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{14}\text{ClN}_2\text{O}_2]^+$: 313.0738; found: 313.0747.



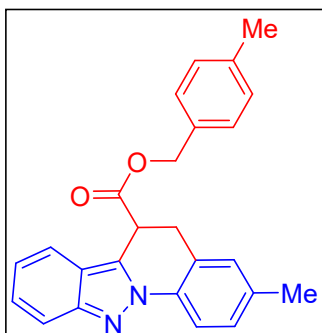
Methyl 8-methoxy-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3ra): Brown solid (73%, 56.2 mg); $R_f = 0.50$ (PE/EA = 80 : 20), M.p. 103-104 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.12 (d, $J = 8.0$ Hz, 1H), 7.65 (d, $J = 9.2$ Hz, 1H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.33 (d, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.2$ Hz, 1H), 7.03-7.01 (m, 1H), 6.77 (d, $J = 2.0$ Hz, 1H), 4.46-4.44 (m, 1H), 3.86 (s, 3H), 3.64 (s, 3H), 3.52-3.47 (m, 1H), 3.35-3.30 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.2, 155.5, 146.2, 136.2, 128.8, 128.3, 126.8, 126.1, 125.6, 122.4, 120.4, 119.4, 117.6, 95.6, 55.5, 52.7, 37.9, 28.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{17}\text{N}_2\text{O}_3]^+$: 309.1234; found: 309.1217.



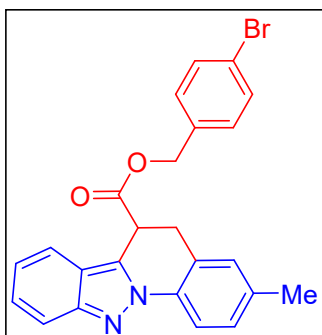
Methyl 8-methoxy-3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3sa): Yellow solid (90%, 72.5 mg); $R_f = 0.50$ (PE/EA = 80 : 20), M.p. 128-129 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.99 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 9.2$ Hz, 1H), 7.18 (d, $J = 8.4$ Hz, 1H), 7.13 (s, 1H), 7.02-7.00 (m, 1H), 6.77 (d, $J = 2.0$ Hz, 1H), 4.44-4.41 (m, 1H), 3.85 (s, 3H), 3.63 (s, 3H), 3.47-3.42 (m, 1H), 3.30-3.25 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.3, 155.4, 146.0, 136.7, 134.0, 129.3, 128.9, 125.8, 125.5, 122.1, 120.4, 119.3, 117.4, 95.6, 55.4, 52.7, 37.9, 28.7, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_3]^+$: 323.1390; found: 323.1388.



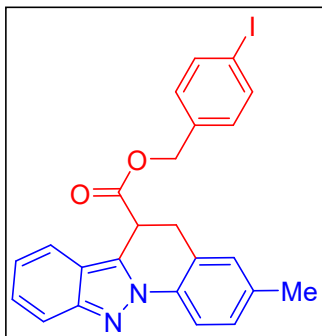
Methyl 6,7-dihydro-[1,3]dioxolo[4,5-f]indazolo[2,3-a]quinoline-7-carboxylate (3ta): Greenish yellow solid (83%, 66.9 mg); $R_f = 0.50$ (PE/EA = 78 : 22), M.p. 123-124 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 7.74-7.70 (m, 2H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.32-7.28 (m, 1H), 7.11-7.07 (m, 1H), 6.80 (s, 1H), 6.02-6.00 (m, 2H), 4.46-4.43 (m, 1H), 3.64 (s, 3H), 3.43-3.38 (m, 1H), 3.26-3.21 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 171.0, 148.8, 147.6, 146.6, 130.5, 127.0, 126.7, 122.3, 120.5, 119.5, 119.3, 117.7, 108.5, 101.8, 100.2, 52.8, 37.9, 28.7; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{18}\text{H}_{15}\text{N}_2\text{O}_4]^+$: 323.1026; found: 323.1022.



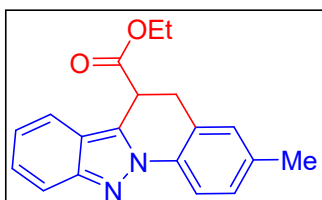
4-Methylbenzyl 3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3bb): Yellow solid (94%, 89.9 mg); $R_f = 0.50$ (PE/EA = 83 : 17), M.p. 96-97 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.33-7.29 (m, 1H), 7.21 (d, $J = 8.4$ Hz, 1H), 7.12 (s, 1H), 7.06 (t, $J = 8.0$ Hz, 3H), 6.99 (d, $J = 8.4$ Hz, 2H), 5.06-4.98 (m, 2H), 4.51-4.49 (m, 1H), 3.47-3.41 (m, 1H), 3.32-3.27 (m, 1H), 2.37 (s, 3H), 2.32 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.4, 149.0, 138.1, 137.2, 133.8, 132.2, 129.4, 129.2, 128.9, 128.1, 127.1, 125.7, 122.2, 120.5, 119.7, 117.88, 117.83, 67.2, 38.3, 28.6, 21.3, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{25}\text{H}_{23}\text{N}_2\text{O}_2]^+$: 383.1754; found: 383.1747.



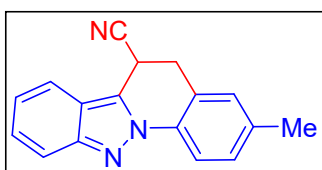
4-Bromobenzyl 3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3bc): White solid (76%, 85.0 mg); $R_f = 0.50$ (PE/EA = 84 : 16), M.p. 112-113 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.07 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.55 (d, $J = 8.4$ Hz, 1H), 7.35-7.30 (m, 3H), 7.22 (d, $J = 8.4$ Hz, 1H), 7.10-7.06 (m, 2H), 6.89 (d, $J = 8.4$ Hz, 2H), 5.00-4.93 (m, 2H), 4.53-4.51 (m, 1H), 3.46-3.41 (m, 1H), 3.35-3.29 (m, 1H), 2.38 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.2, 148.9, 137.4, 134.2, 133.7, 131.6, 129.5, 129.4, 129.0, 127.3, 127.0, 125.6, 122.4, 122.3, 120.5, 119.5, 117.9, 117.8, 66.4, 38.1, 28.6, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{24}\text{H}_{20}\text{BrN}_2\text{O}_2]^+$: 447.0703; found: 447.0690.



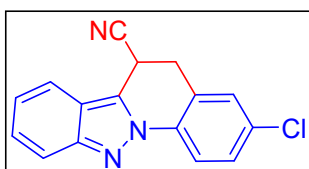
4-Iodobenzyl 3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3bd): White solid (96%, 118.6 mg); $R_f = 0.50$ (PE/EA = 84 : 16), M.p. 124-125 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.05 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.56-7.53 (m, 3H), 7.34-7.29 (m, 1H), 7.22 (d, $J = 8.0$ Hz, 1H), 7.10-7.05 (m, 2H), 6.75 (d, $J = 8.4$ Hz, 2H), 4.99-4.91 (m, 2H), 4.52-4.50 (m, 1H), 3.45-3.40 (m, 1H), 3.33-3.28 (m, 1H), 2.38 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.2, 149.0, 137.6, 137.2, 134.8, 133.8, 129.6, 129.4, 129.0, 127.1, 126.8, 125.6, 122.3, 120.5, 119.5, 117.9, 117.8, 94.0, 66.4, 38.1, 28.6, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{24}\text{H}_{20}\text{IN}_2\text{O}_2]^+$: 495.0564; found: 495.0551.



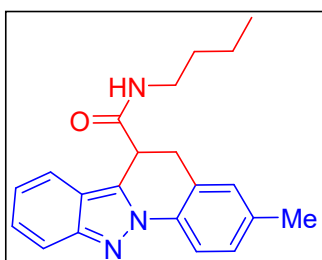
Ethyl 3-methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carboxylate (3be): Gummy liquid (77%, 58.9 mg); $R_f = 0.50$ (PE/EA = 85 : 15); $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.06 (d, $J = 8.0$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.61 (d, $J = 8.4$ Hz, 1H), 7.33-7.29 (m, 1H), 7.20 (d, $J = 8.0$ Hz, 1H), 7.16 (s, 3H), 7.11-7.07 (m, 1H), 4.48-4.45 (m, 1H), 4.16-4.02 (m, 2H), 3.48-3.43 (m, 1H), 3.32-3.27 (m, 1H), 2.38 (s, 3H), 1.13 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 170.6, 149.0, 137.2, 133.8, 129.3, 128.9, 127.3, 127.1, 125.8, 122.2, 120.5, 119.7, 117.85, 117.82, 61.7, 38.2, 28.6, 21.2, 14.1; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{19}\text{H}_{19}\text{N}_2\text{O}_2]^+$: 307.1441; found: 307.1440.



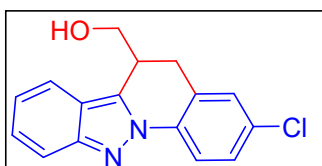
3-Methyl-5,6-dihydroindazolo[2,3-a]quinoline-6-carbonitrile (3bf): Brown solid (72%, 46.7 mg); $R_f = 0.50$ (PE/EA = 83 : 17), M.p. 147-148 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.08 (d, $J = 8.0$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 1H), 7.76 (d, $J = 8.8$ Hz, 1H), 7.37-7.33 (m, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.17 (t, $J = 8.8$ Hz, 2H), 4.62 (t, $J = 7.6$ Hz, 1H), 3.41 (d, $J = 7.2$ Hz, 2H), 2.40 (s, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.2, 137.8, 133.6, 129.9, 129.4, 127.5, 123.6, 123.2, 122.0, 119.8, 119.0, 118.2, 118.1, 117.4, 30.2, 24.9, 21.2; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{17}\text{H}_{14}\text{N}_3]^+$: 260.1182; found: 260.1166.



3-chloro-5,6-dihydroindazolo[2,3-a]quinoline-6-carbonitrile (3fg): Yellowish white solid (61%, 42.6 mg); $R_f = 0.50$ (PE/EA = 83 : 17), M.p. 154-155 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.10 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.8$ Hz, 1H), 7.59 (d, $J = 8.4$ Hz, 1H), 7.44-7.41 (m, 1H), 7.35-7.29 (m, 2H), 7.11-7.08 (m, 1H), 4.64 (t, $J = 7.6$ Hz, 1H), 3.42 (d, $J = 7.6$ Hz, 2H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.3, 133.9, 133.7, 130.1, 129.5, 127.6, 123.8, 123.3, 122.1, 119.9, 199.1, 118.3, 118.2, 117.5, 30.3, 24.9; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{16}\text{H}_{11}\text{ClN}_3]^+$: 280.0636; found: 280.0648.



***N*-Butyl-3-methyl-5,6-dihydroindazolo[2,3-*a*]quinoline-6-carboxamide (4):** Yellowish white solid (62%, 51.6 mg); $R_f = 0.50$ (PE/EA = 76 : 24), M.p. 169-170 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.03 (d, $J = 8.0$ Hz, 1H), 7.768 (d, $J = 8.8$ Hz, 1H), 7.58 (d, $J = 8.4$ Hz, 1H), 7.36-7.33 (m, 1H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.17-7.12 (m, 2H), 5.23 (s, 1H), 4.32-4.29 (m, 1H), 3.70-3.65 (m, 1H), 3.29-3.23 (m, 1H), 3.07-3.02 (m, 2H), 2.37 (s, 3H), 1.20-1.15 (m, 2H), 1.01-0.95 (m, 2H), 0.71 (t, $J = 7.6$ Hz, 3H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 169.4, 149.2, 137.6, 133.7, 129.9, 128.9, 127.9, 127.4, 126.2, 122.9, 120.6, 118.9, 118.2, 117.7, 39.6, 39.1, 31.3, 29.0, 21.2, 19.7, 13.6; HRMS (ESI-TOF) m/z : $[\text{M} + \text{H}]^+$ Calcd for $[\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}]^+$: 334.1914; found: 334.1900.

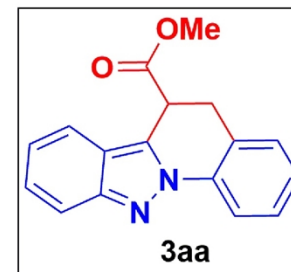
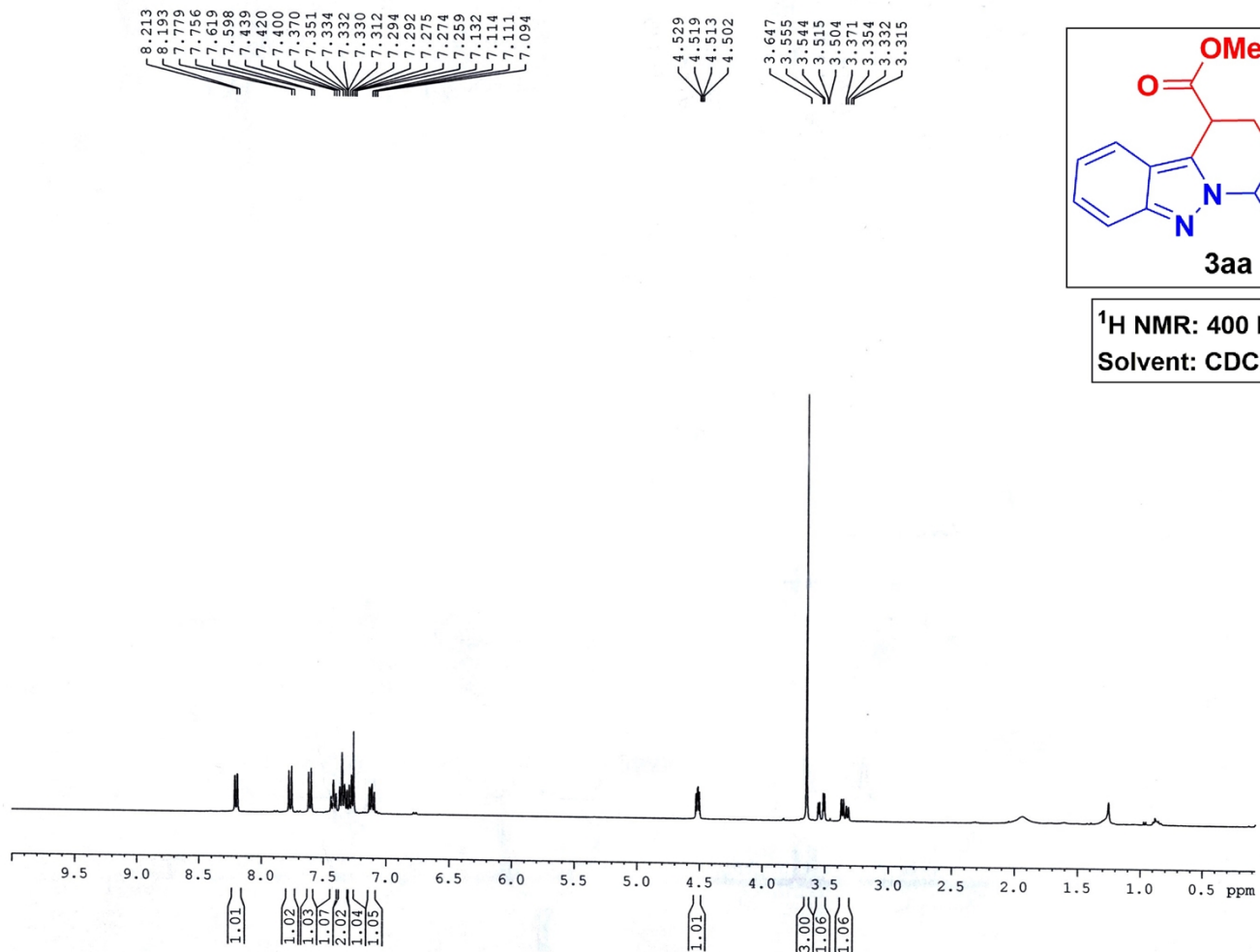


3-Chloro-5,6-dihydroindazolo[2,3-*a*]quinolin-6-ylmethanol (5): Brown solid (91%, 64.8 mg); $R_f = 0.50$ (PE/EA = 74 : 28), M.p. 95-96 °C; $^1\text{H NMR}$ (400 MHz, CDCl_3): δ 8.04 (d, $J = 8.4$ Hz, 1H), 7.67-7.62 (m, 2H), 7.34-7.27 (m, 3H), 7.07-7.04 (m, 1H), 3.83-3.72 (m, 3H), 3.25-3.20 (m, 1H), 3.16-3.12 (m, 1H); $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, CDCl_3): δ 149.2, 134.7, 132.5, 131.4, 129.2, 128.26, 128.23, 127.6, 122.3, 120.5, 119.8, 119.1, 117.7, 63.4, 34.9, 27.5; HRMS (ESI-TOF) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $[\text{C}_{16}\text{H}_{13}\text{ClN}_2\text{ONa}]^+$: 307.0609; found: 307.0609.

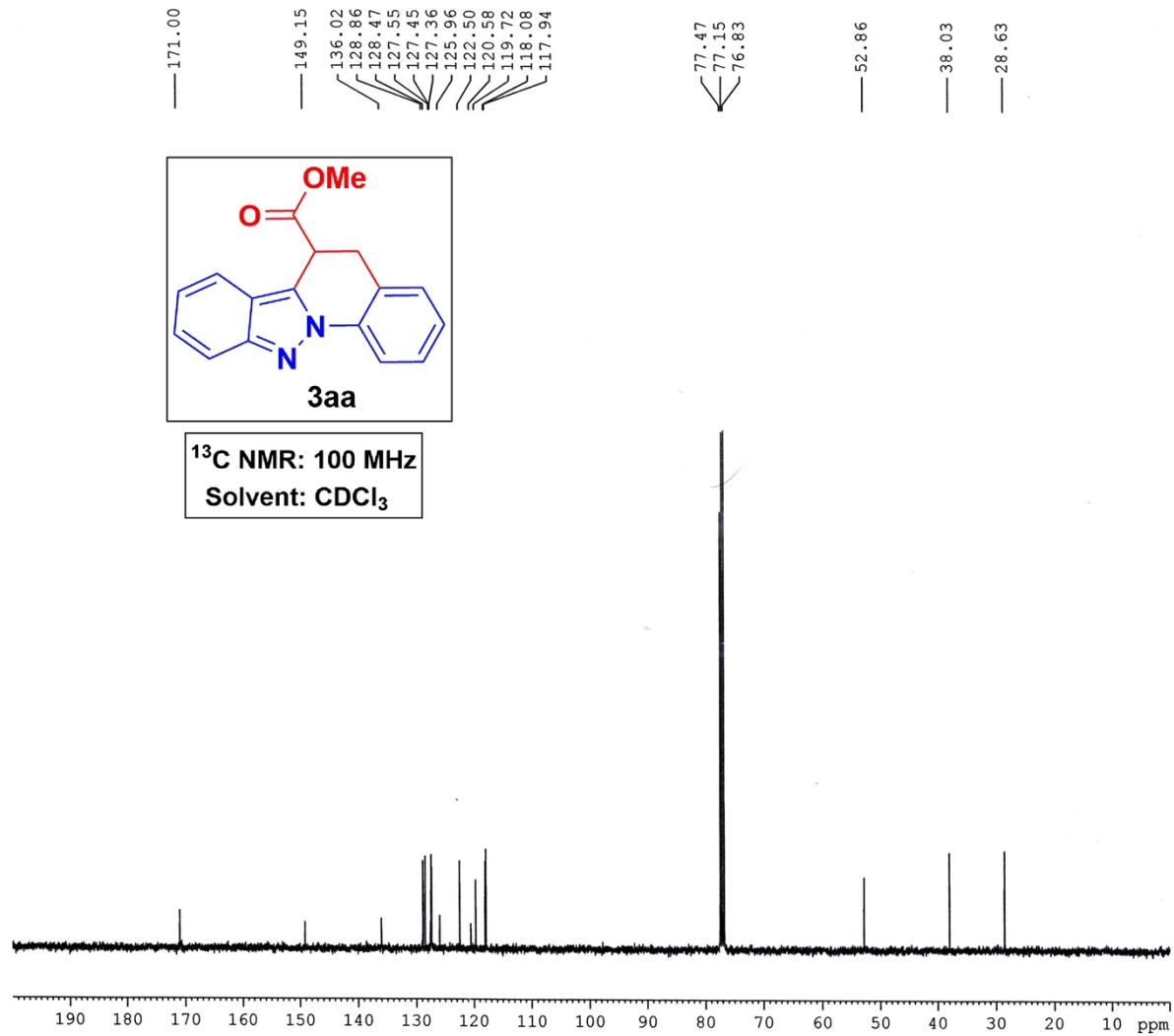
11. References:

- (1) (a) M. R. Kumar, A. Park, N. Park and S. Lee, *Org. Lett.*, 2011, **13**, 3542–3545; (b) G.; Bogonda, H. Y. Kim and K. Oh, *Org. Lett.*, 2018, **20**, 2711–2715.
- (2) S. Bhattacharjee and A. Hajra, *Org. Lett.*, 2023, **25**, 4183–4187.
- (3) D. S. Nipate, N. Meena, P. N. Swami, K. Rangan and A. Kumar, *Chem. Commun.*, 2024, **60**, 344–347.
- (4) (a) M. J. Cabrera-Afonso, A. Sookezian, S. O. Badir, M. E. Khatib and G. A. Molander, *Chem. Sci.*, 2021, **12**, 9189–9195; (b) A. Sookezian and G. A. Molander, *Org. Lett.*, 2023, **25**, 1014–1019.

12. NMR Spectra for the Synthesized Products



¹H NMR: 400 MHz
Solvent: CDCl₃



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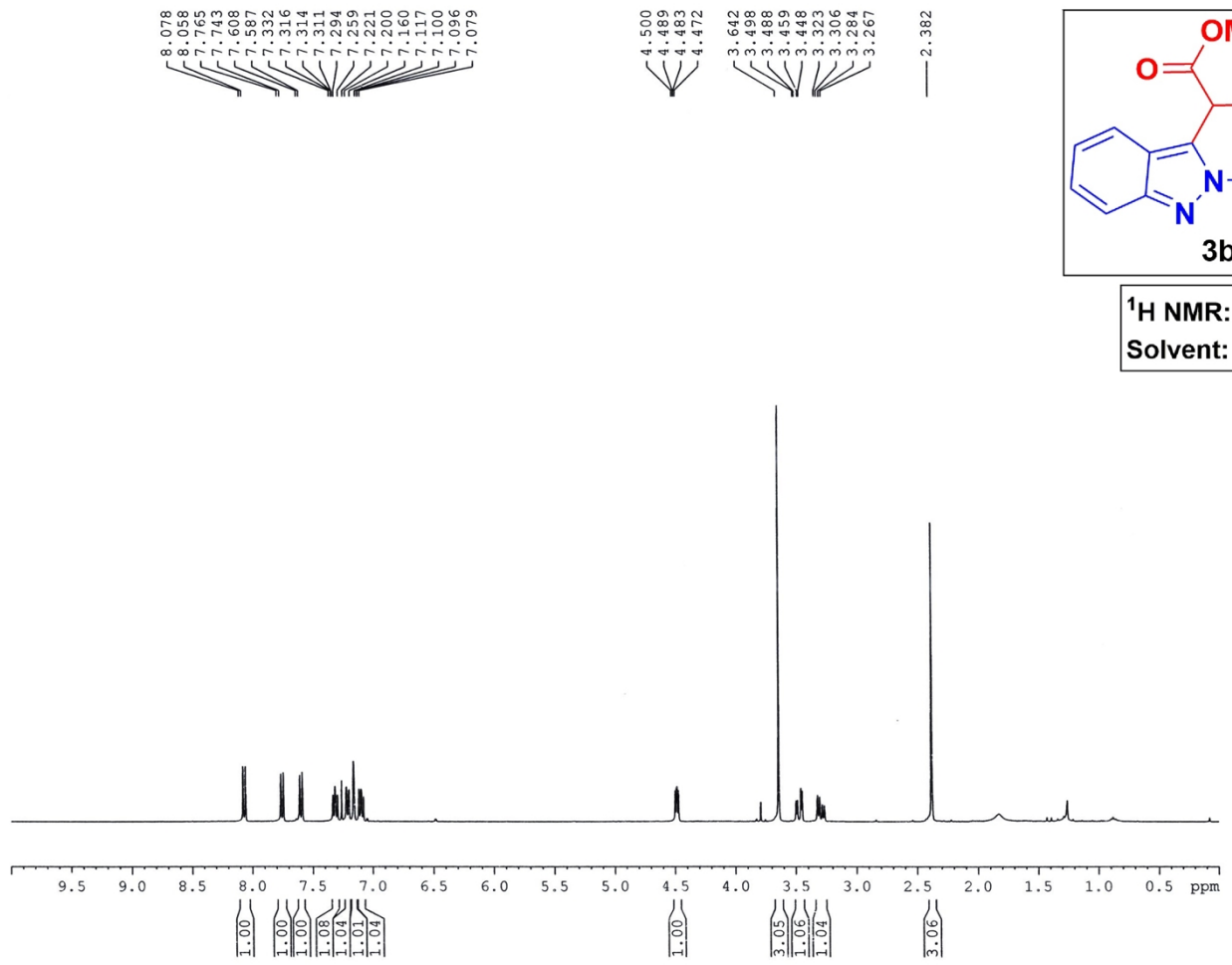
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EXNO      443
PROCNO    1

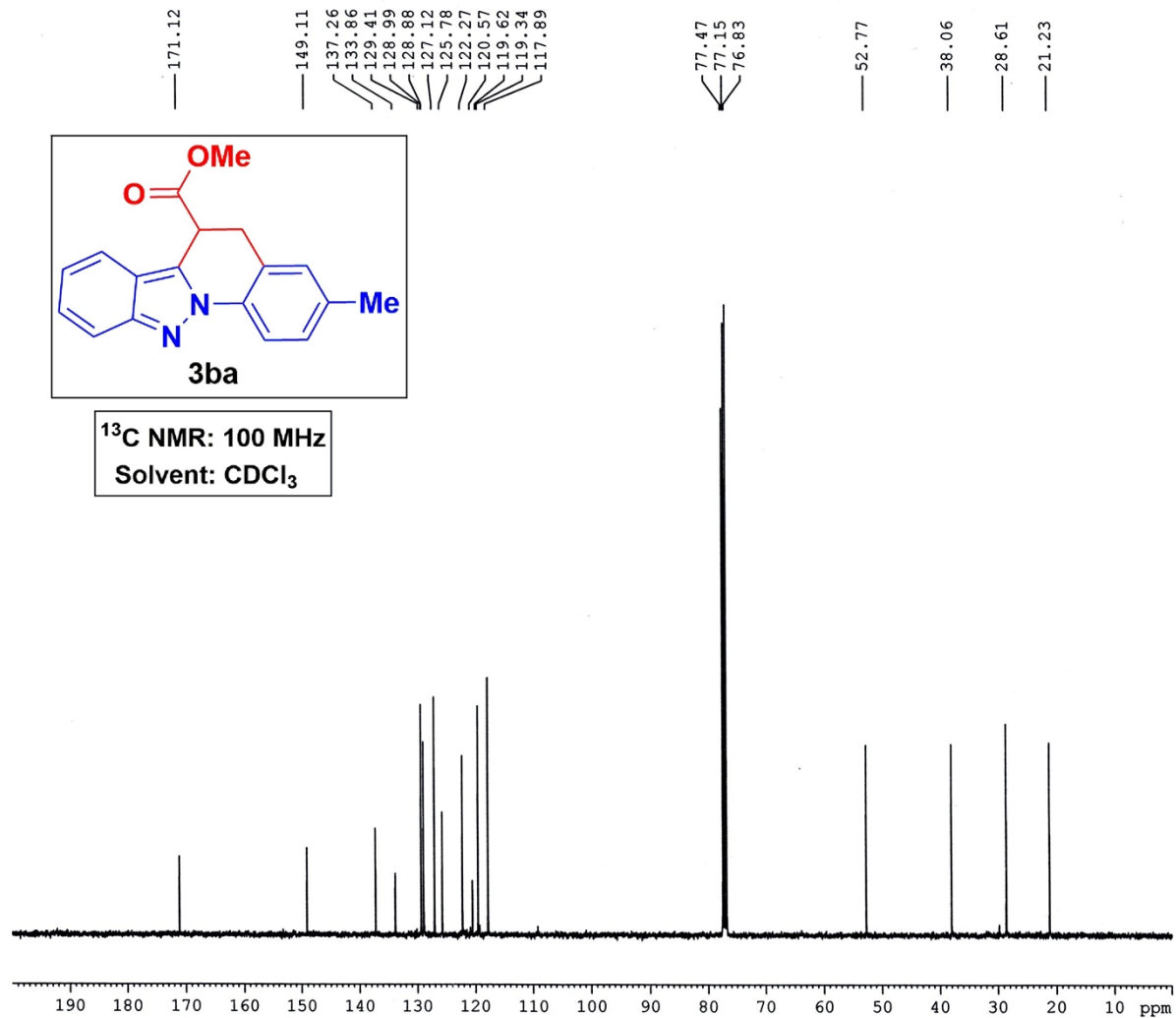
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TD         32768
SOLVENT   CDCl3
NS         420
DS         2
SWH       24038.461 Hz
FIDRES    0.733596 Hz
AQ        0.6815744 sec
RG        186.42
LW        20.800 usec
DE        6.50 usec
TE        292.5 K
D1        2.00000000 sec
D11       0.03000000 sec
TD0       1

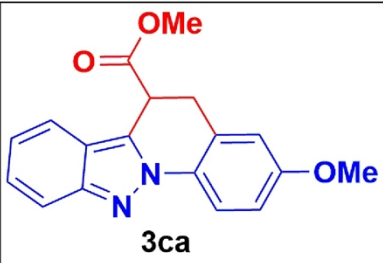
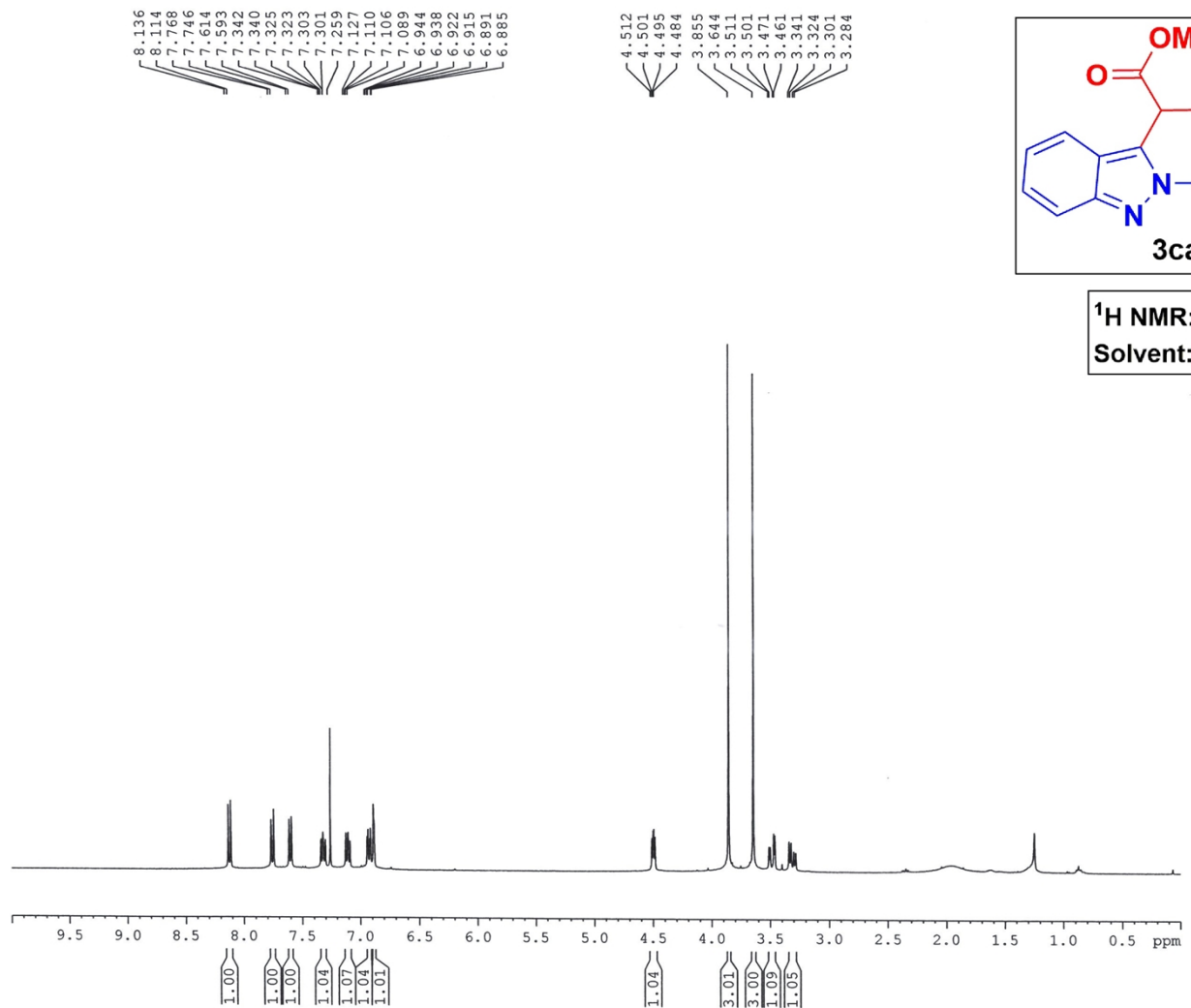
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NUC1     13C
P1       8.90 usec
PLW1     54.00000000 W

----- CHANNEL f2 -----
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NUC2     1H
CPDPRG2  waltz16
PCPD2    90.00 usec
PLW2     12.00000000 W
PLW12    0.32231000 W
PLW13    0.16212000 W

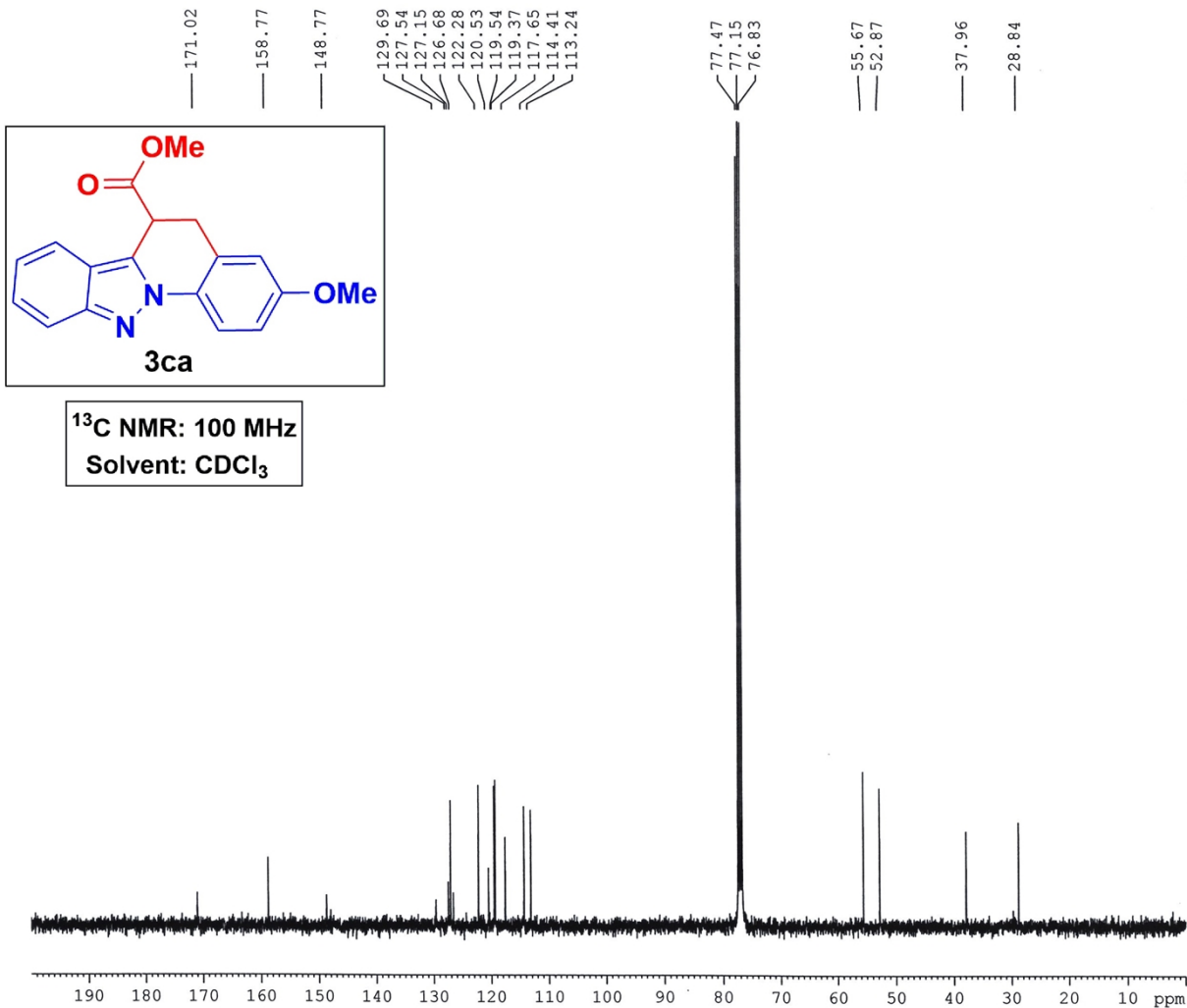
F2 - Processing parameters
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GB       0
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¹H NMR: 400 MHz
Solvent: CDCl₃



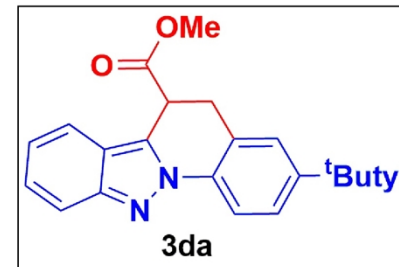
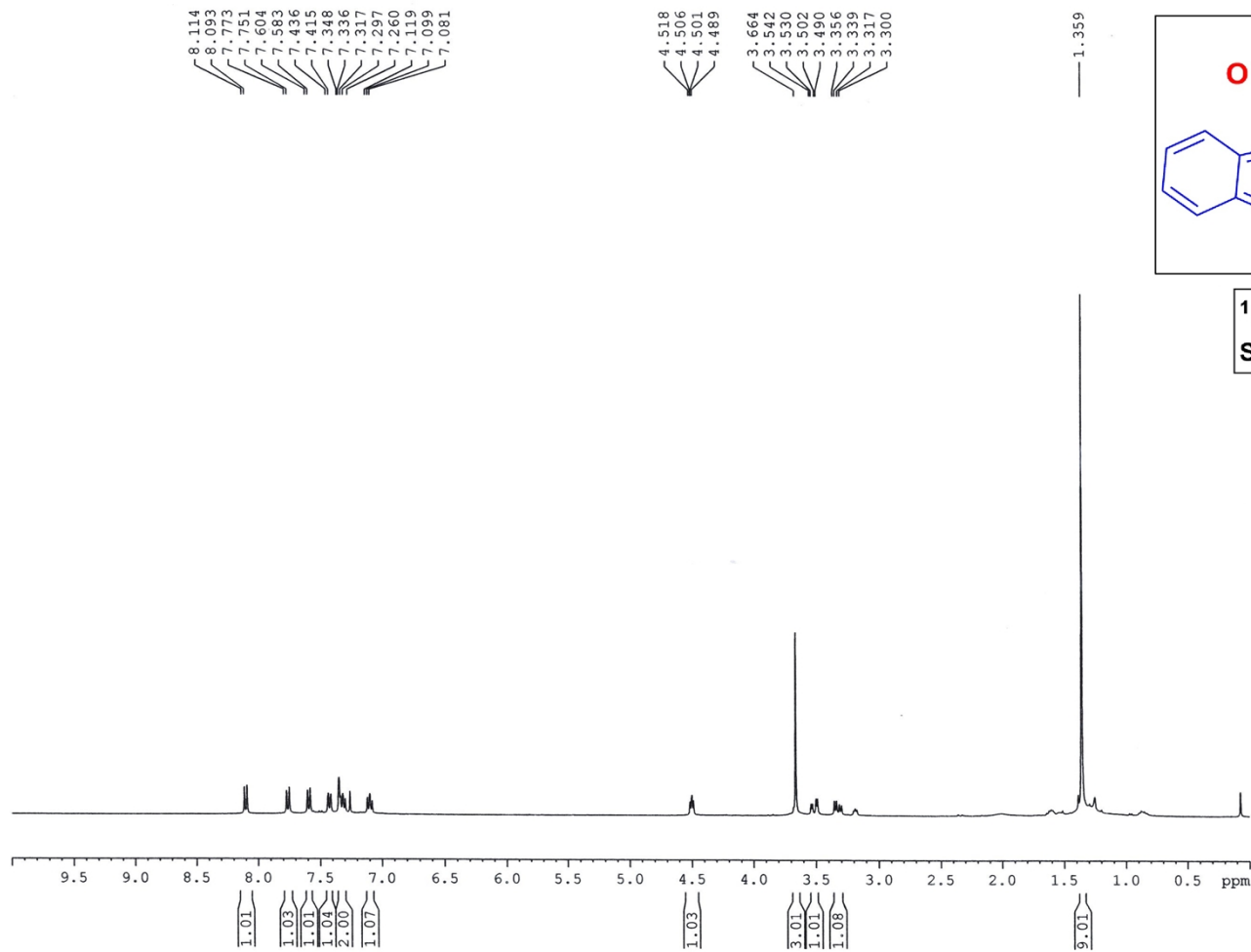
Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 444
 PROCNO 1

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 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 520
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 291.7 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

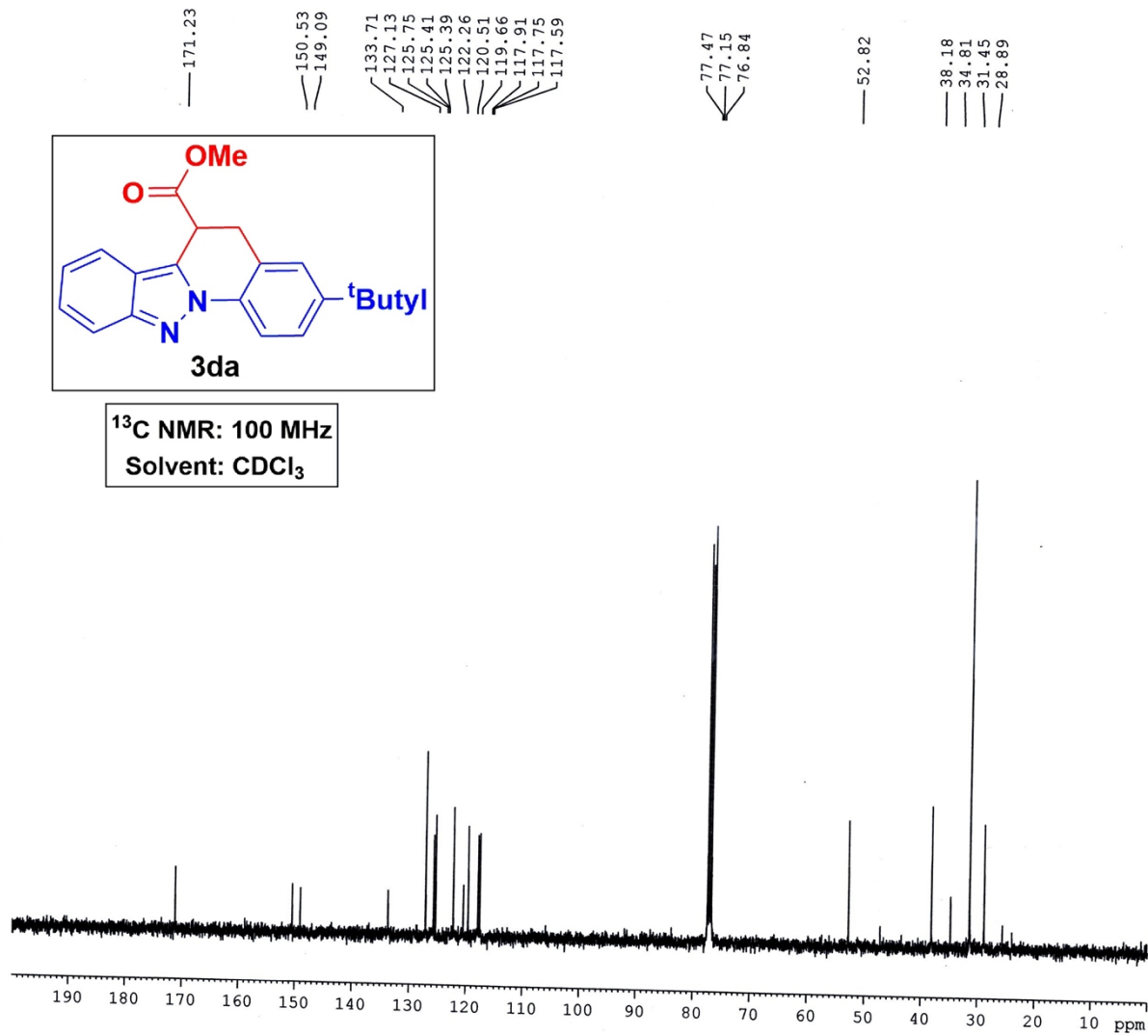
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 NUC1 13C
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 NUC2 1H
 CPDPRG[2] waltz16
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 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
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 SF 100.6177872 MHz
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 LB 1.00 Hz
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 PC 1.40



¹H NMR: 400 MHz
Solvent: CDCl₃



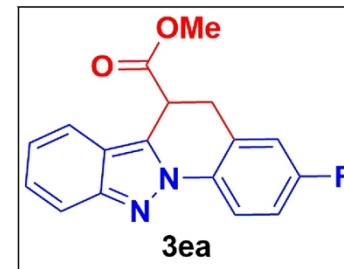
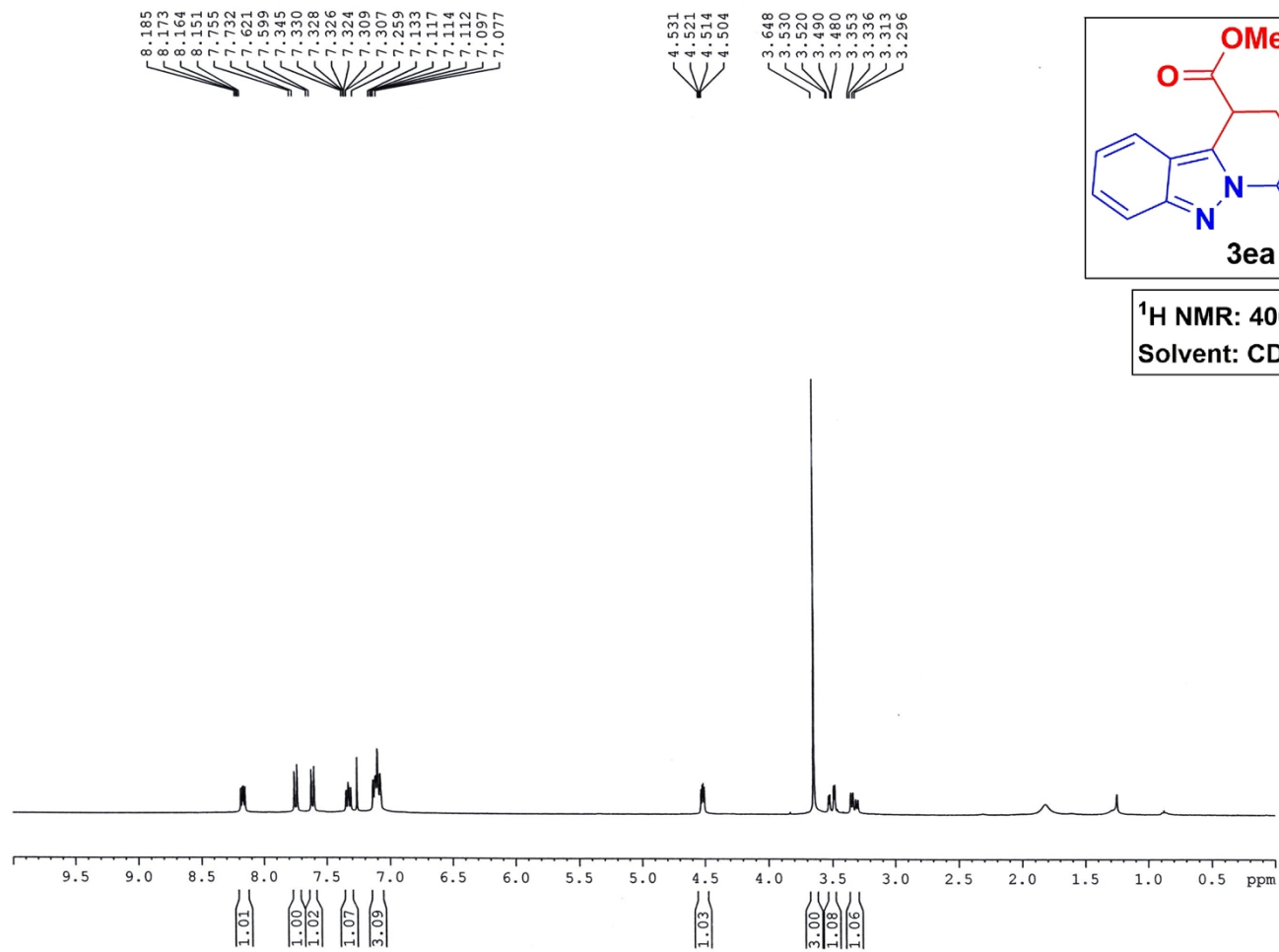
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 EXPNO 3
 PROCNO 1

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 PULPROG zgpg30
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 SOLVENT CDCl3
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 FIDRES 0.733596 Hz
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 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

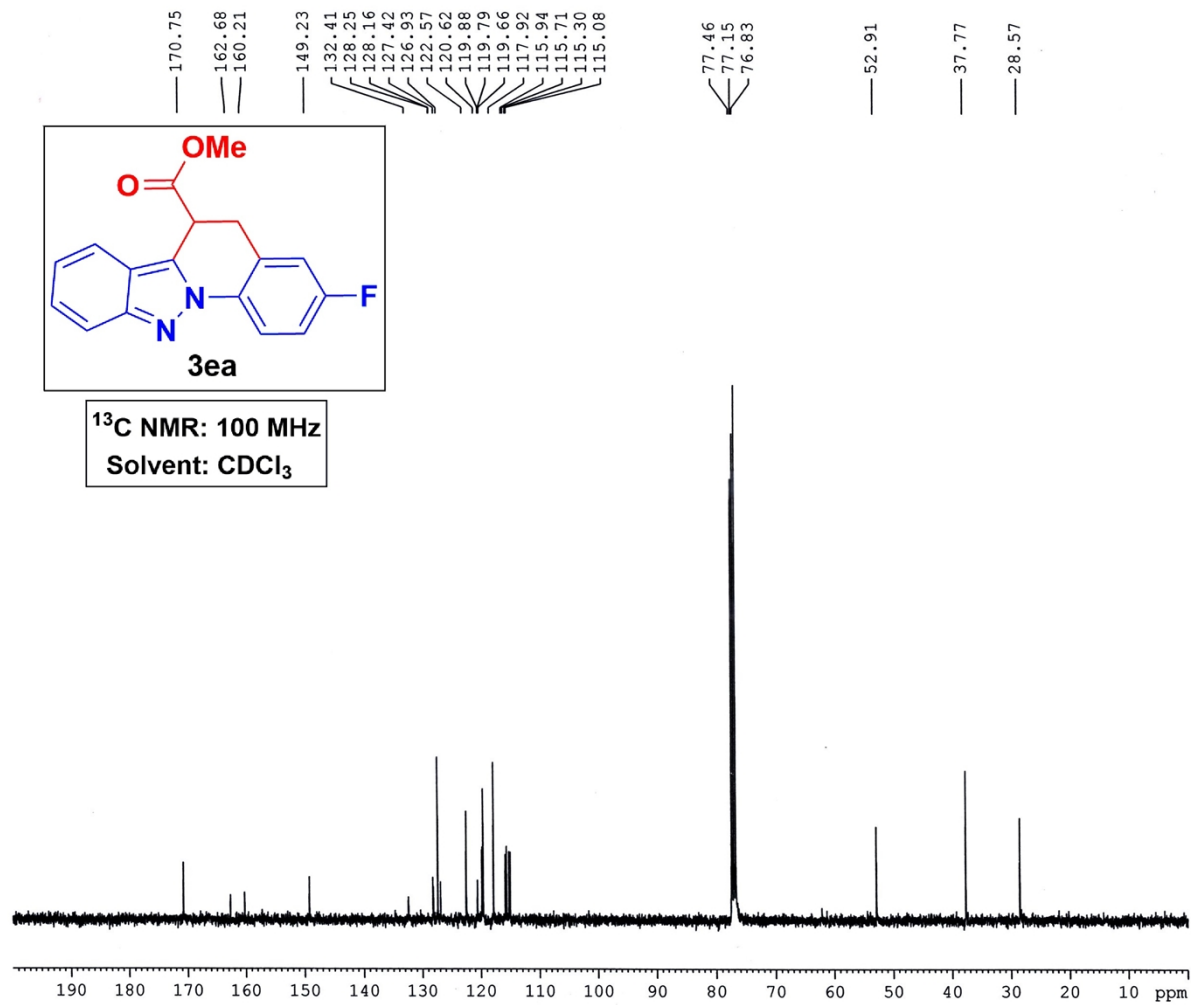
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 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
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 SF 100.6177880 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



**¹H NMR: 400 MHz
Solvent: CDCl₃**



Current Data Parameters
NAME Dr. A HAJRA-2023-13C
EXPNO 421
PROCNO 1

F2 - Acquisition Parameters
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Time 11.49
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PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 380
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 294.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

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NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W

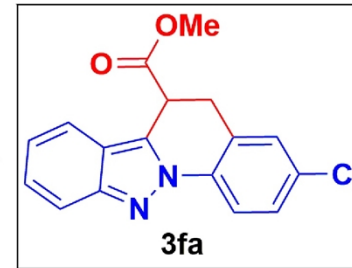
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PLW13 0.16212000 W

F2 - Processing parameters
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WDW EM
SSB 0
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GB 0
PC 1.40

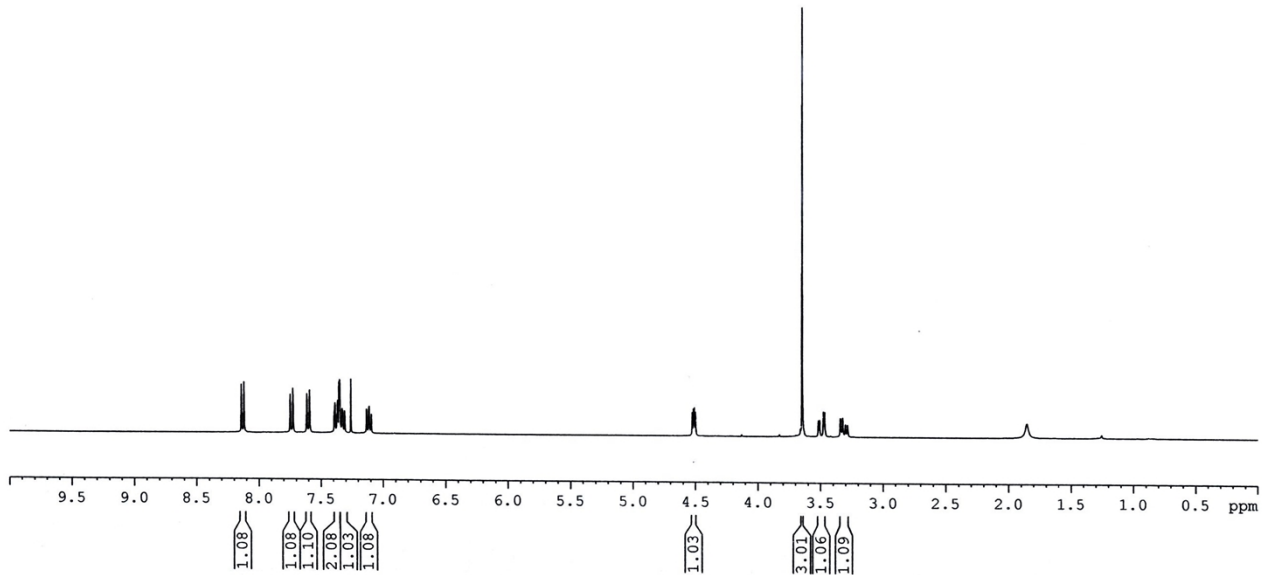
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7.311
7.309
7.259
7.133
7.115
7.112
7.096

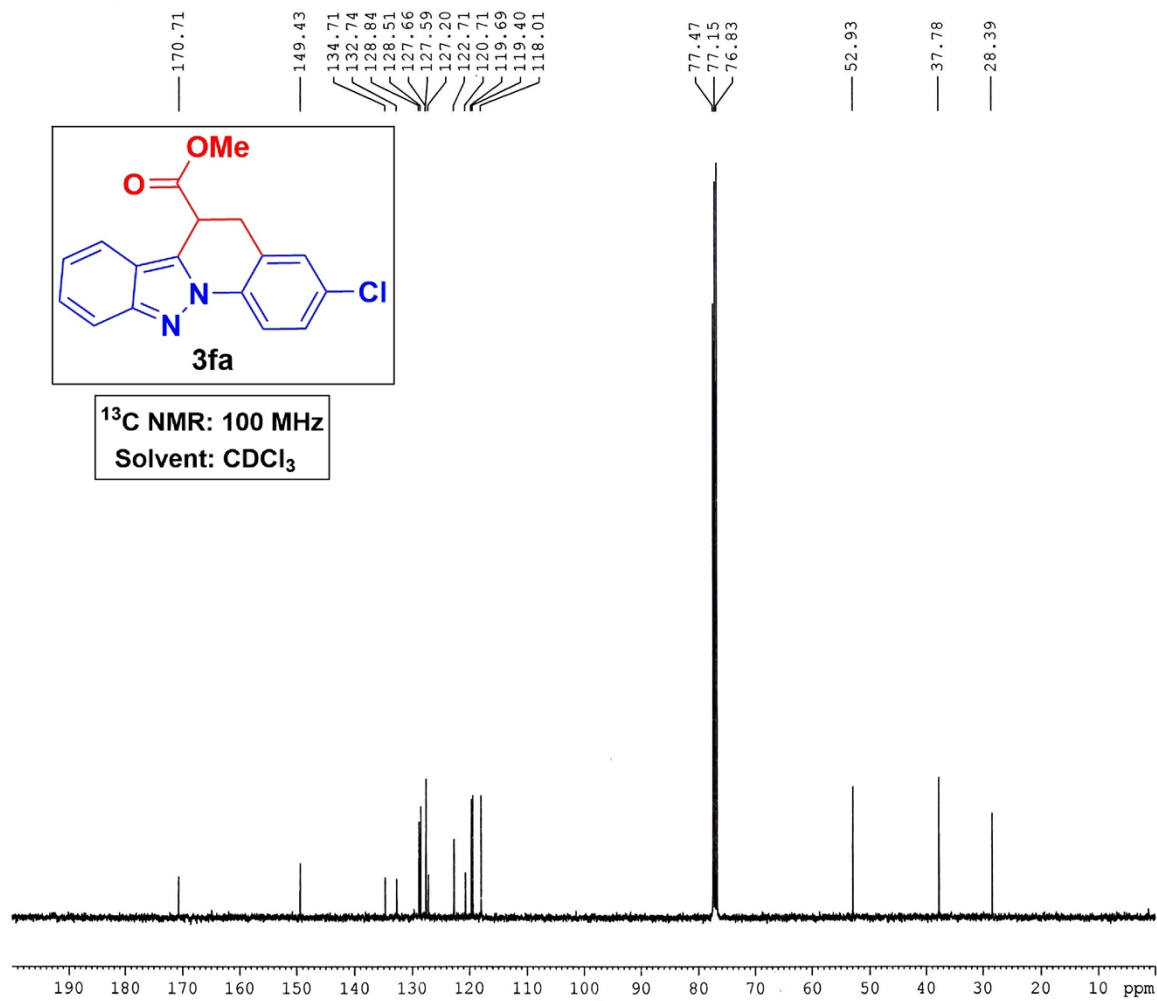
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4.517
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3.285



$^1\text{H NMR}$: 400 MHz
Solvent: CDCl_3





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Current Data Parameters
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EXPNO     347
PROCNO    1

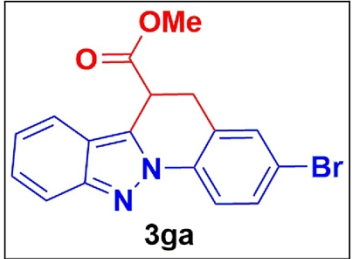
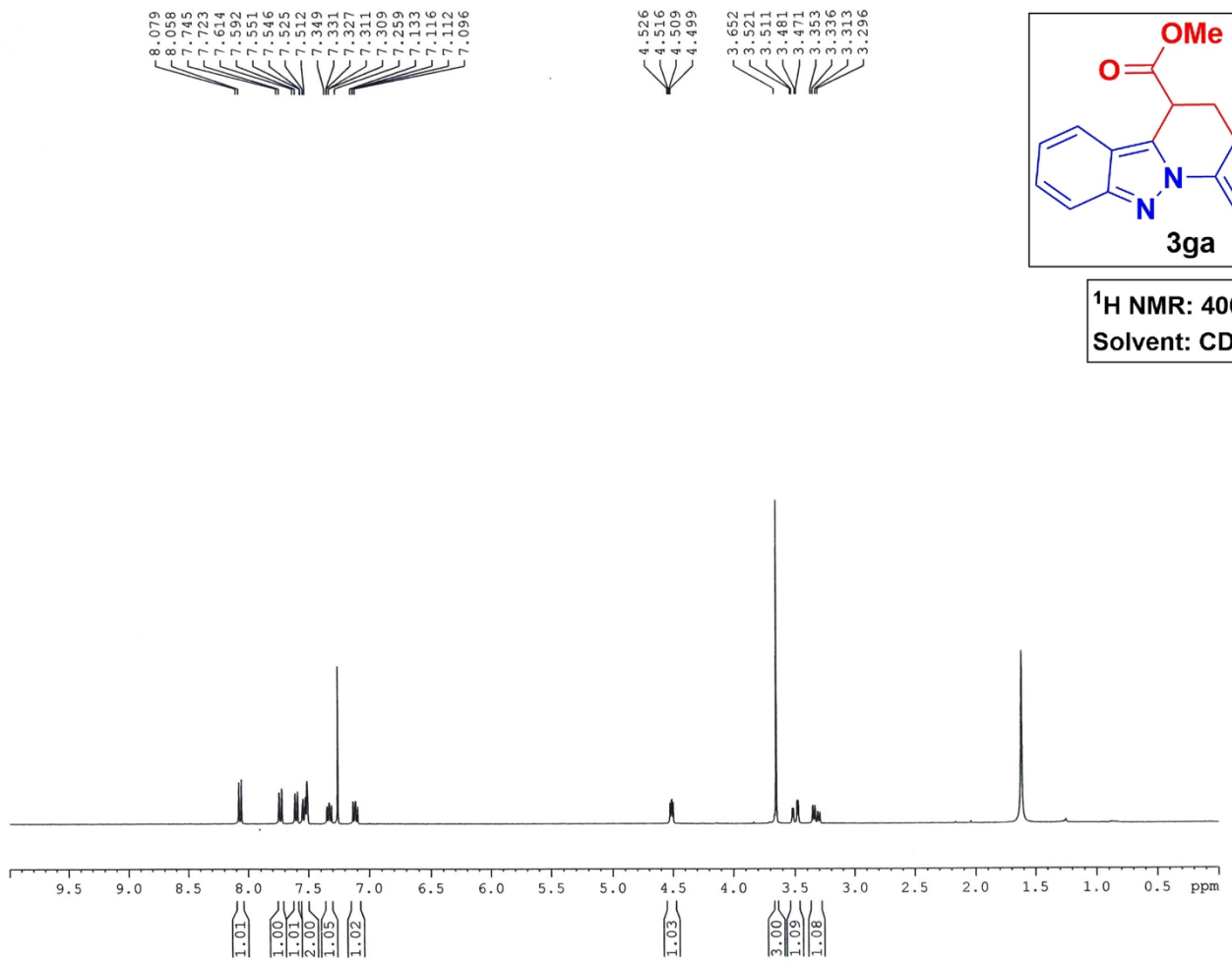
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SOLVENT   CDCl3
NS         950
DS         2
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6815744 sec
RG         186.42
DW         20.800 usec
DE         6.50 usec
TE         296.7 K
D1         2.0000000 sec
D11        0.03000000 sec
TDO        1

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NUC1       13C
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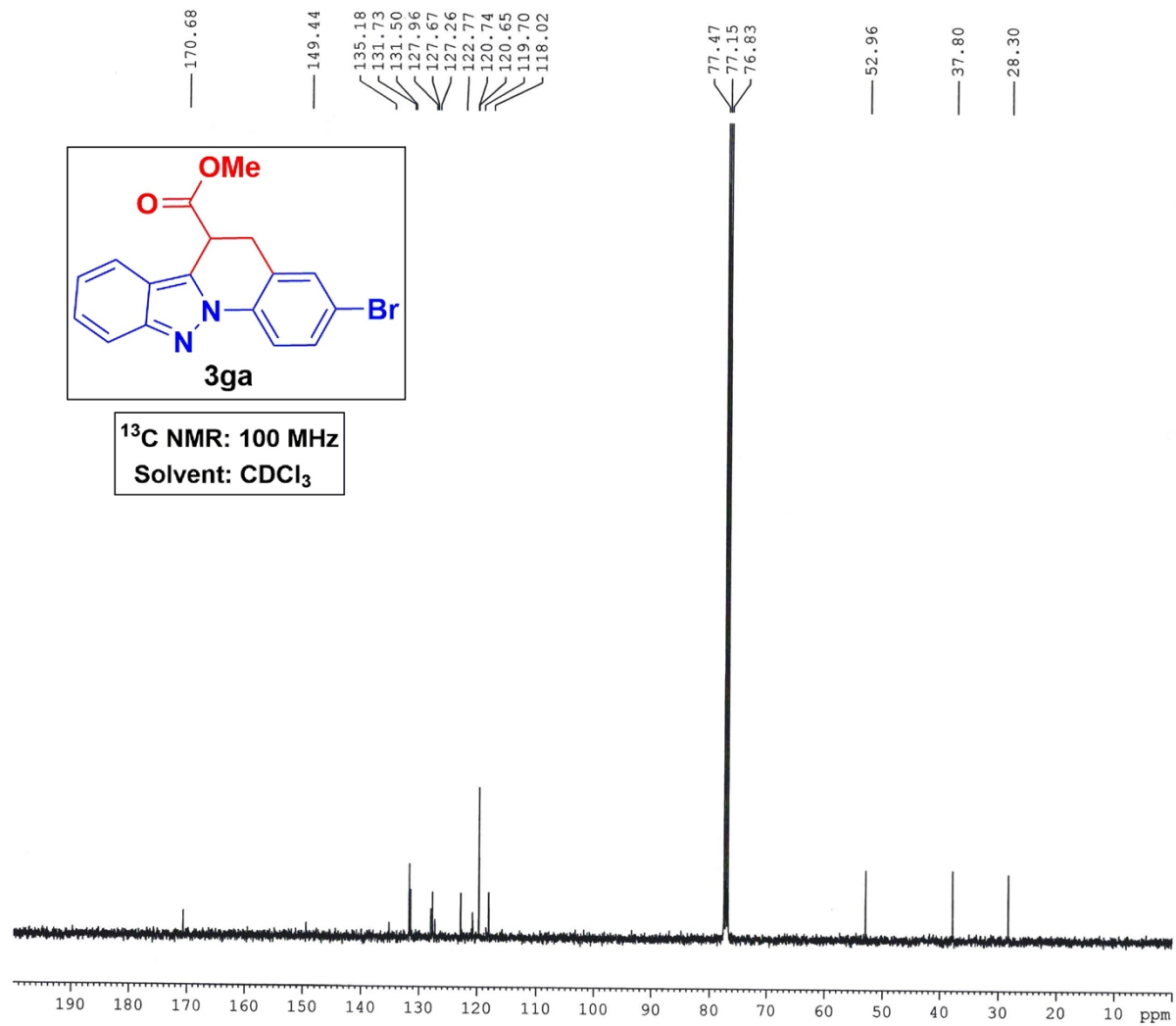
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PLW2      12.00000000 W
PLW12     0.32231000 W
PLW13     0.16212000 W

F2 - Processing parameters
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SF         100.6177858 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

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**¹H NMR: 400 MHz
Solvent: CDCl₃**



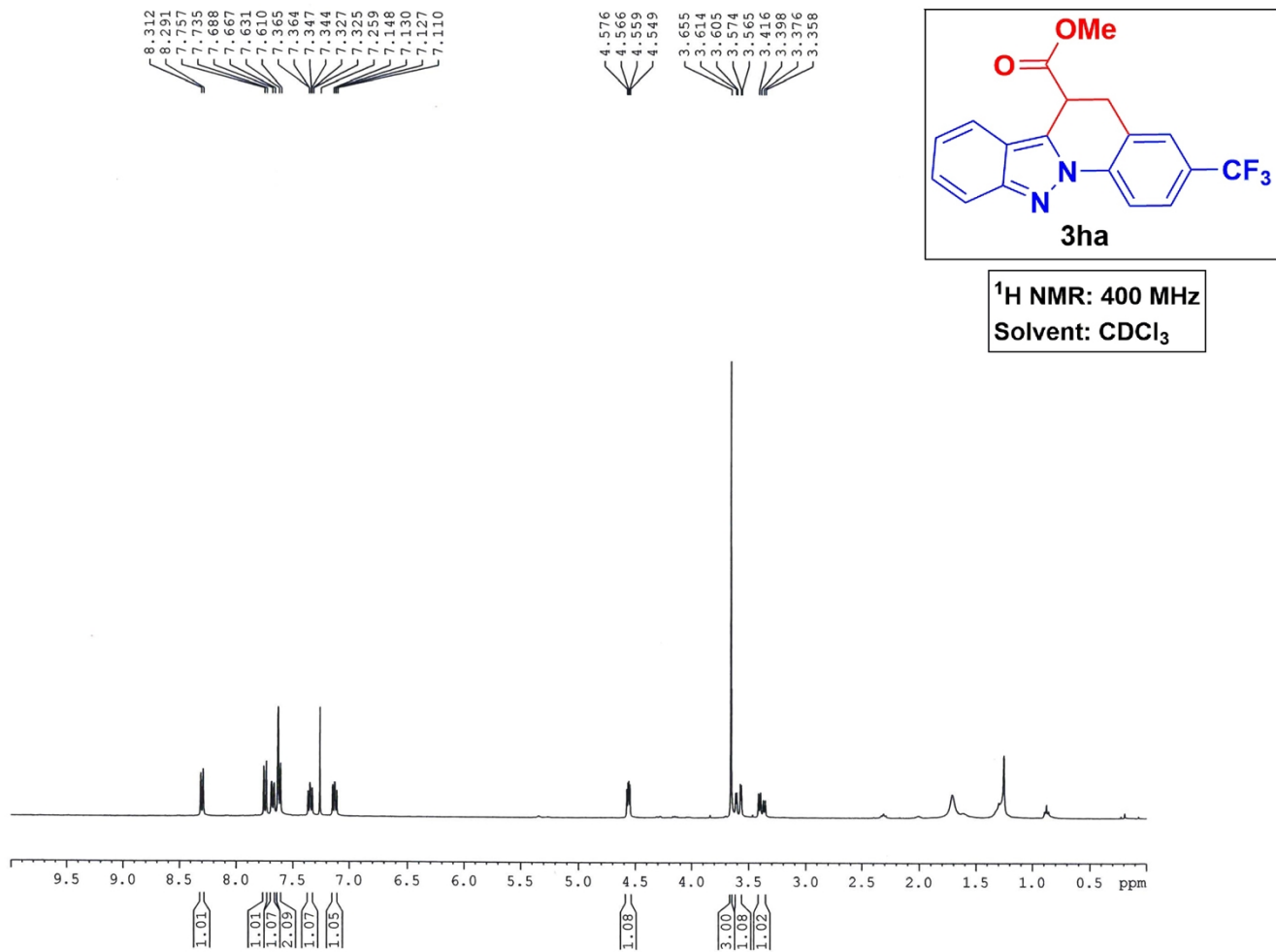
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 NAME Dr. A HAJRA-2023-13C
 EXPNO 377
 PROCNO 1

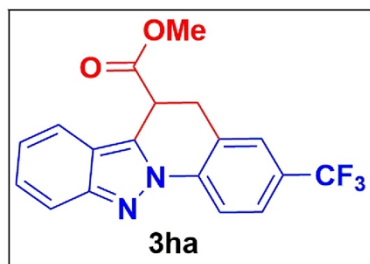
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 PULPROG zgpg30
 TD 32768
 SOLVENT CDC13
 NS 1024
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 296.5 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
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 P1 8.90 usec
 PLW1 54.00000000 W

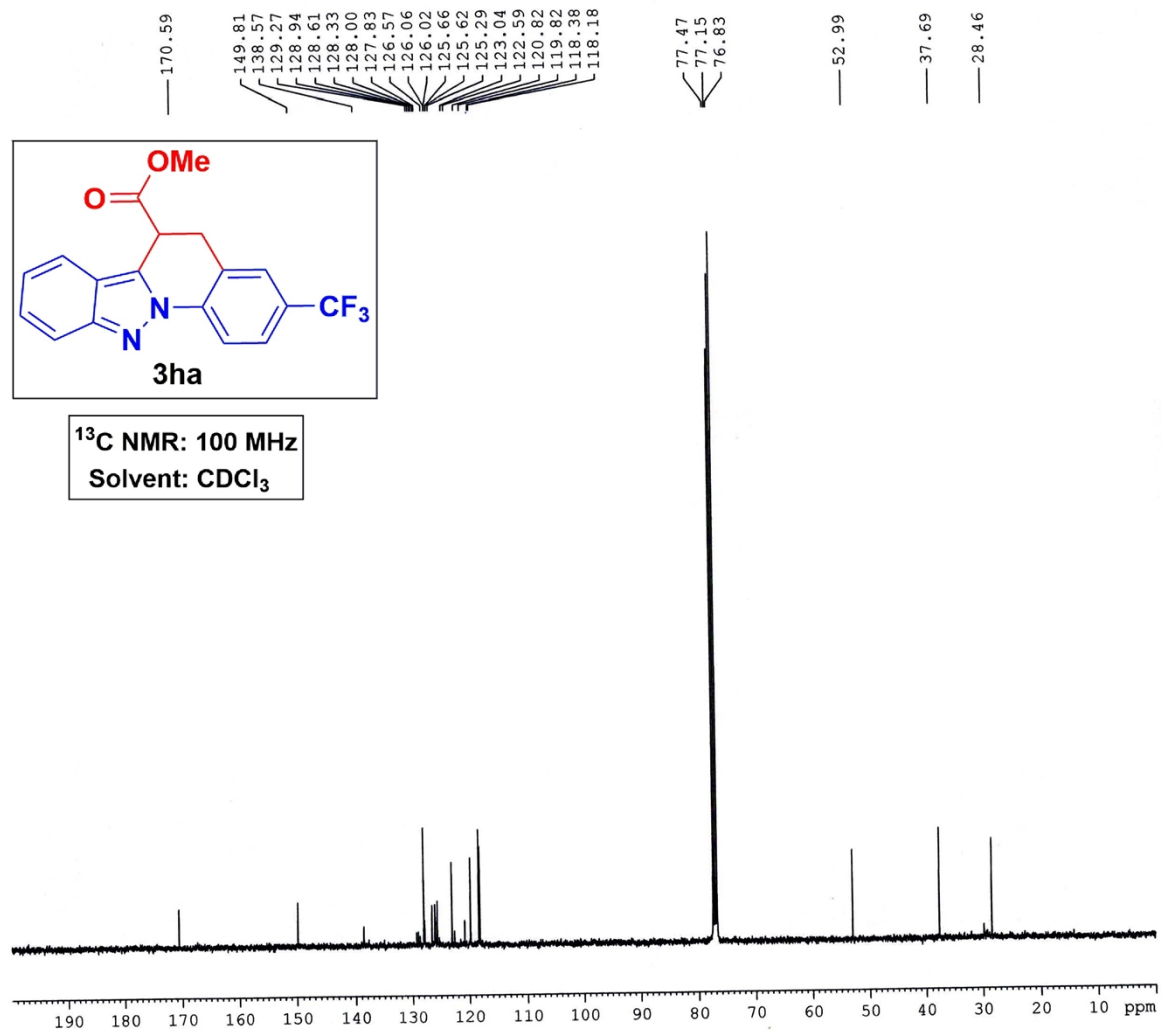
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 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
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 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





¹³C NMR: 100 MHz
Solvent: CDCl₃



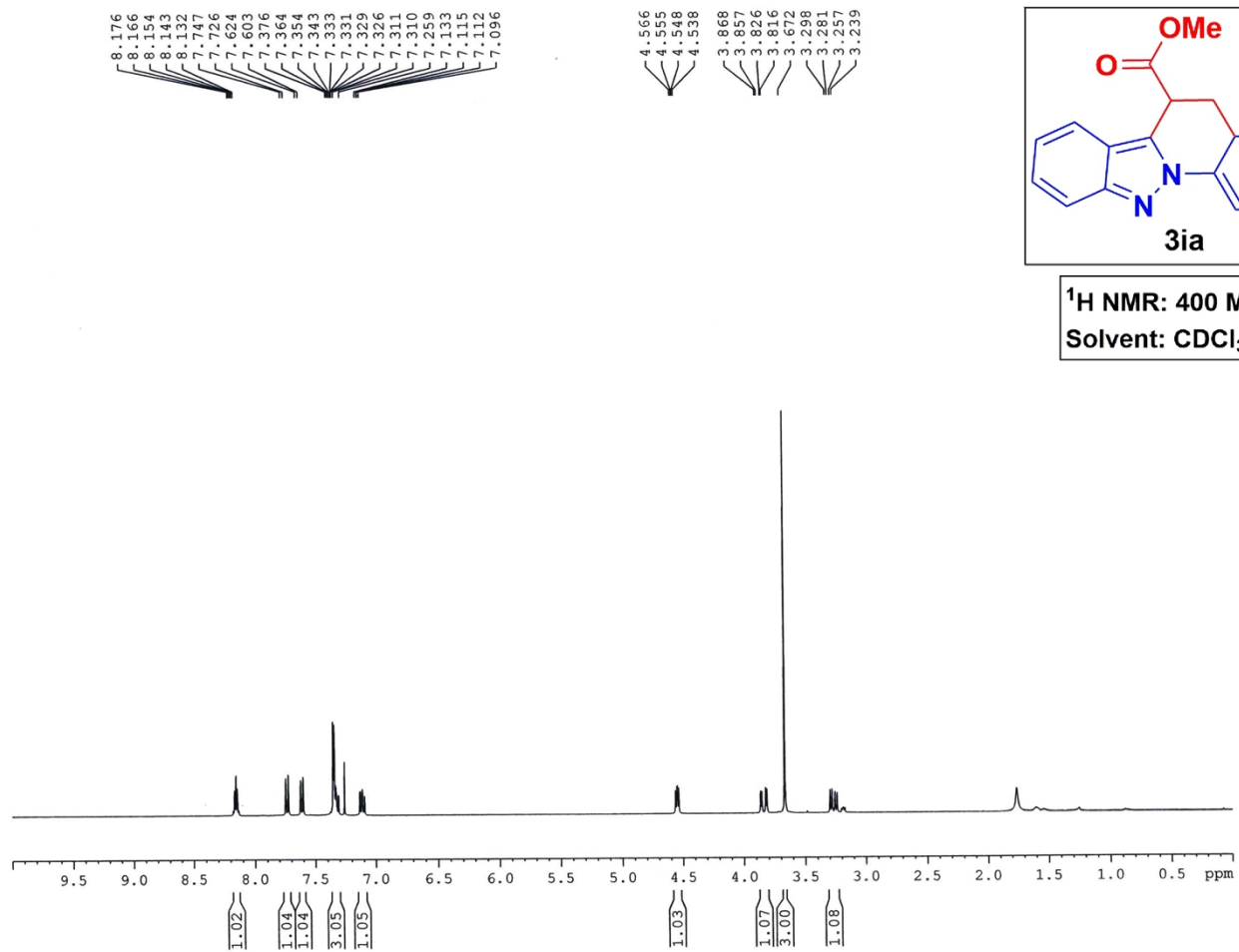
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NAME Dr. A HAJRA-2023-13C
EXPNO 426
PROCNO 1

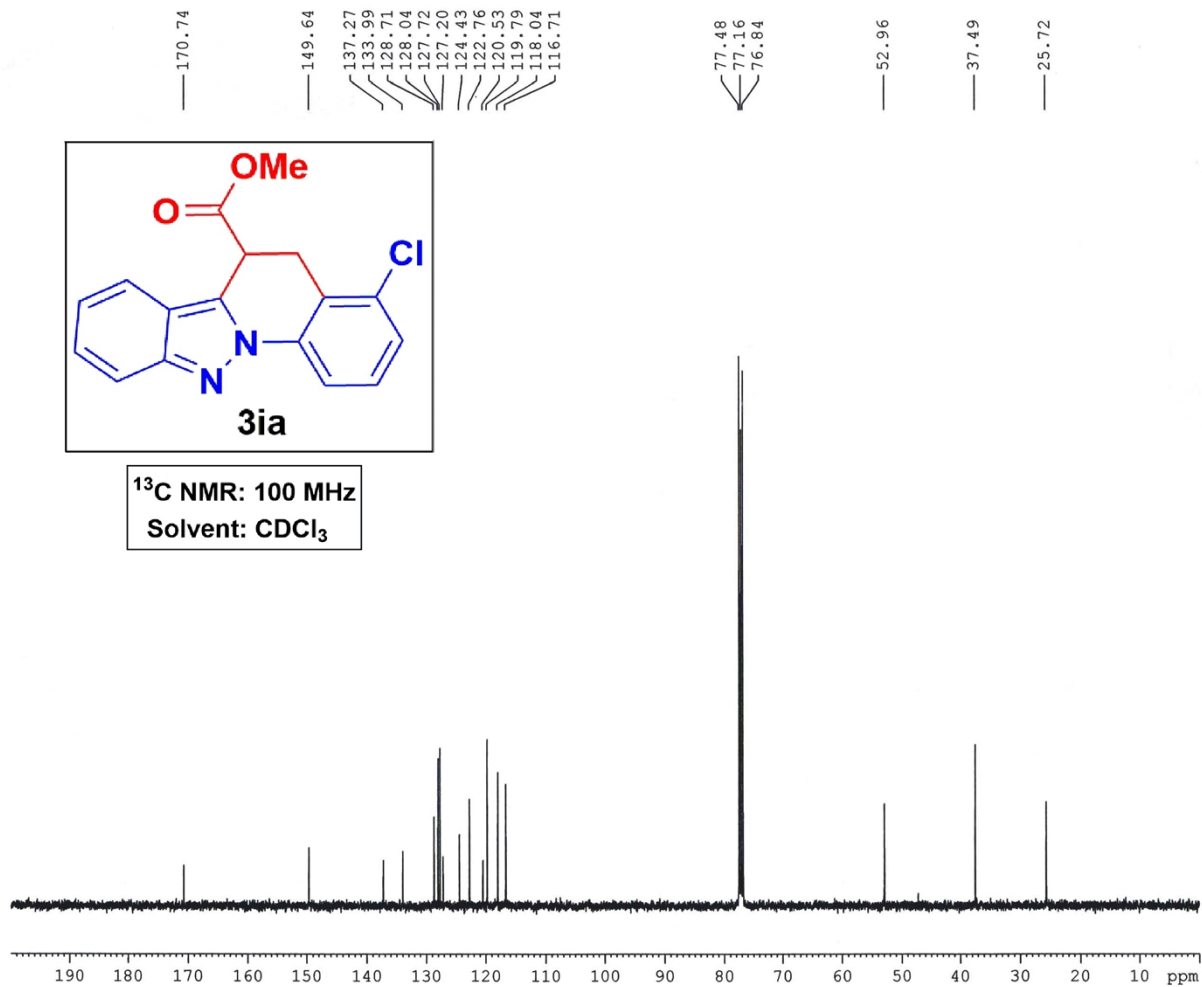
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PULPROG zgpg30
TD 32768
SOLVENT CDCl3
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DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 296.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TDO 1

----- CHANNEL f1 -----
SFO1 100.6278588 MHz
NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W

----- CHANNEL f2 -----
SFO2 400.1516006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.32231000 W
PLW13 0.16212000 W

F2 - Processing parameters
SI 16384
SF 100.6177857 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





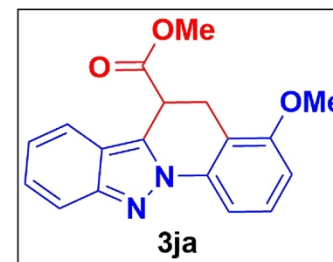
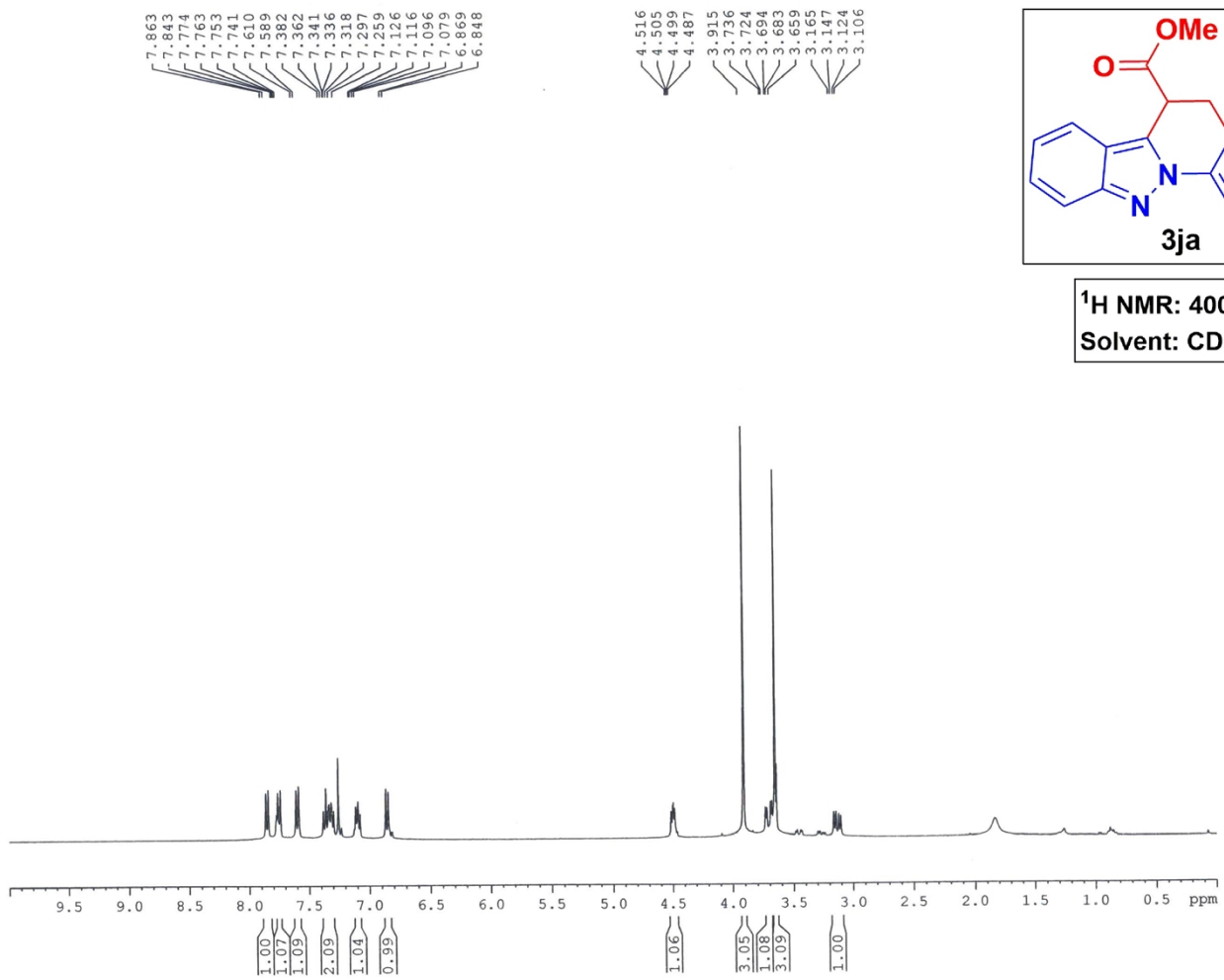
Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 393
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20230927
 Time 12.05
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 450
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 296.2 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TD0 1

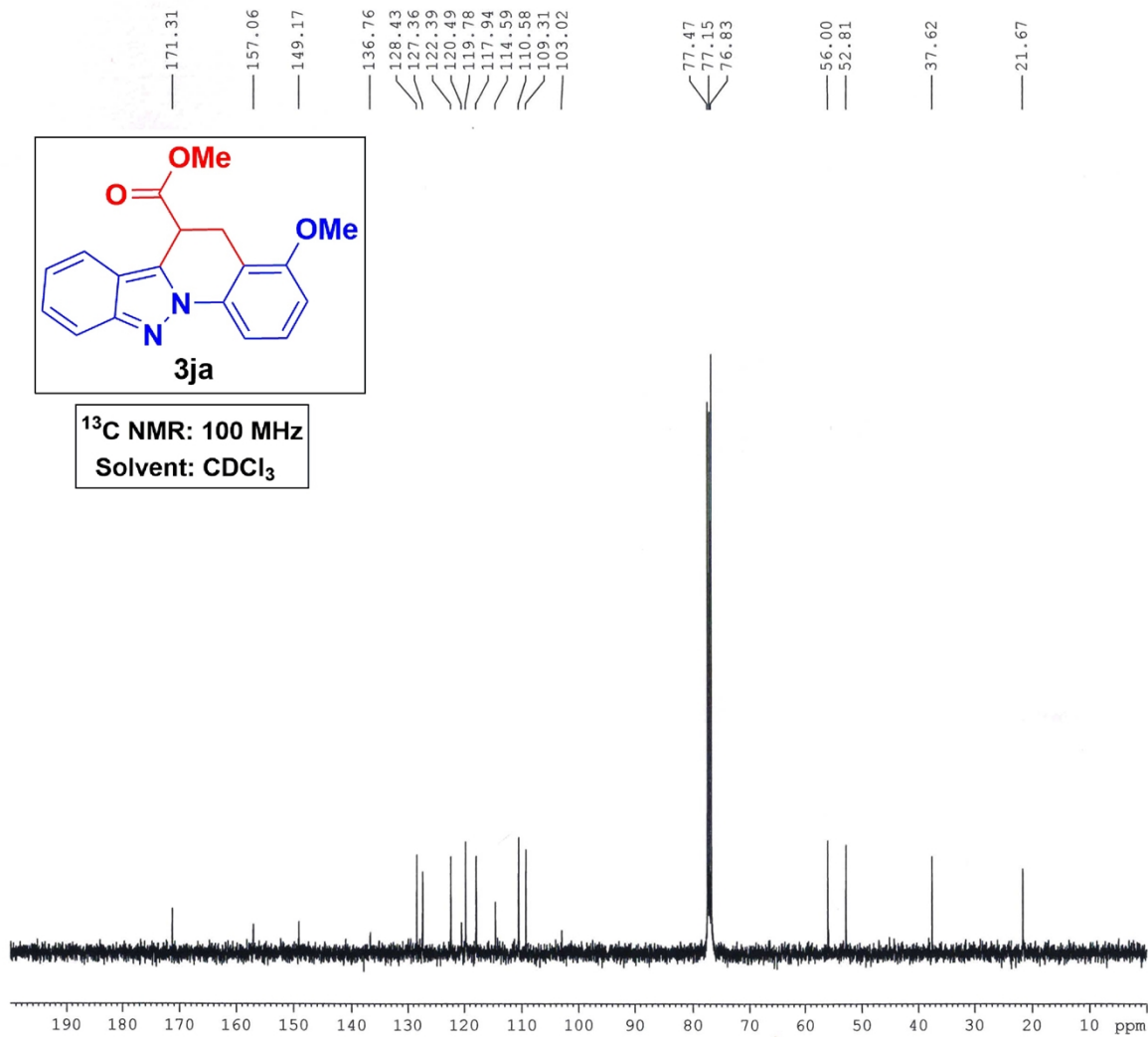
===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.0000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.0000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177858 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 EC 1.40



¹H NMR: 400 MHz
Solvent: CDCl₃



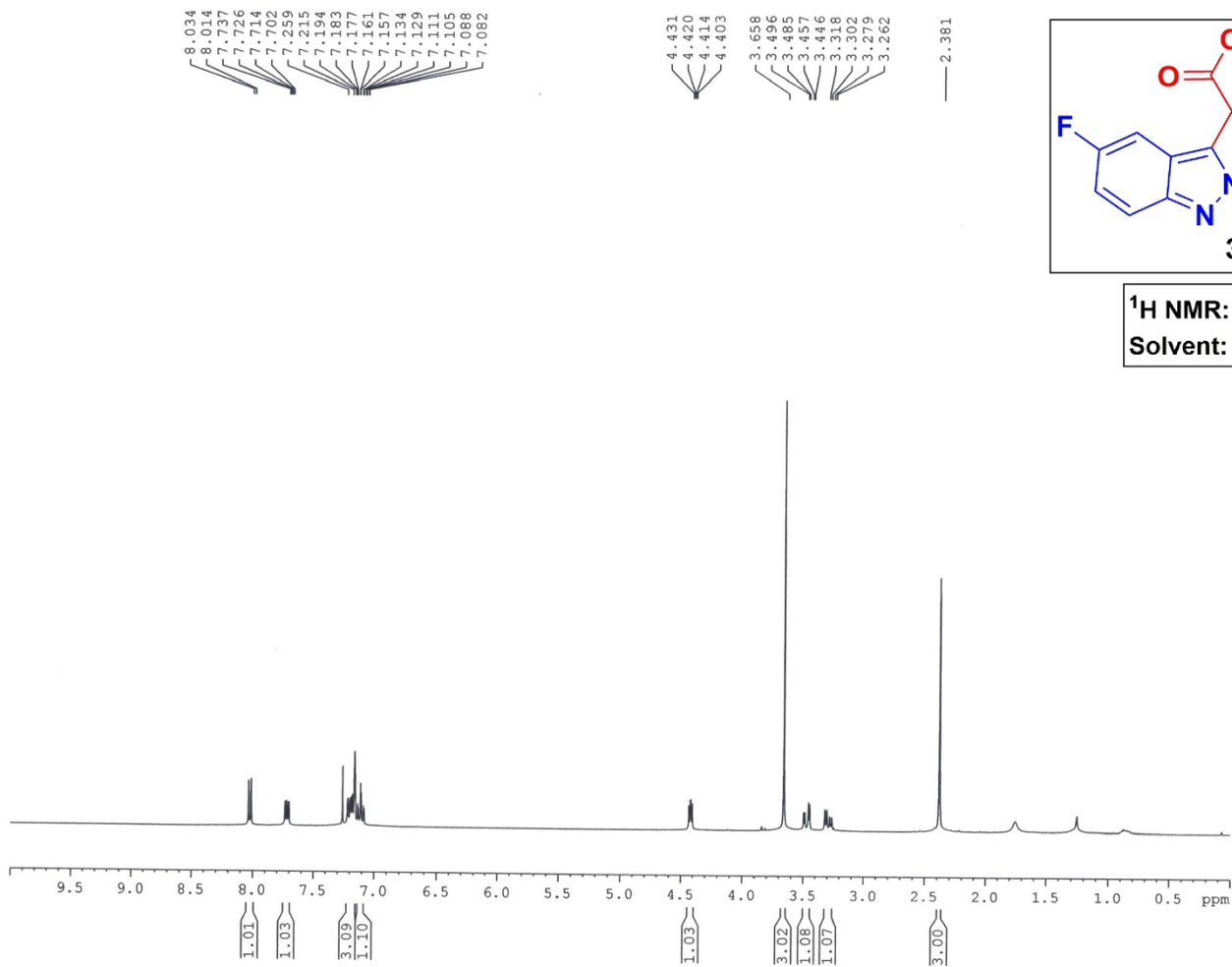
Current Data Parameters
 NAME Dr. A HAJRA-2024-13C
 EXPNO 32
 PROCNO 1

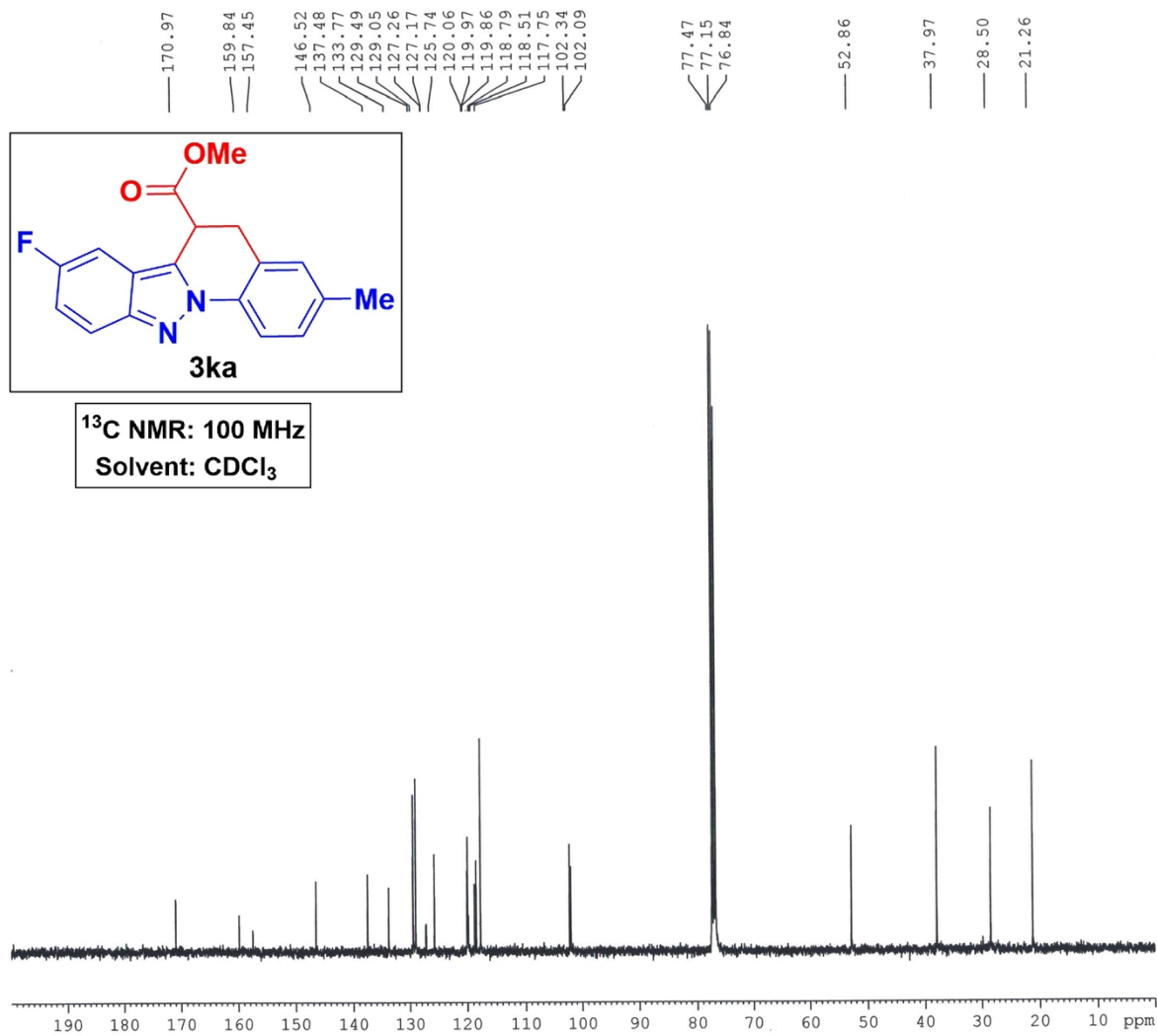
F2 - Acquisition Parameters
 Date 20240205
 Time 10.50
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 320
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 293.9 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177868 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





Current Data Parameters
NAME Dr. A HAJRA-2023-13C
EXPNO 441
PROCNO 1

F2 - Acquisition Parameters
Date_ 20231201
Time 10.57
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 950
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 294.5 K
D1 2.0000000 sec
D11 0.0300000 sec
TD0 1

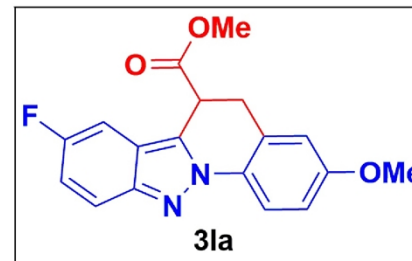
===== CHANNEL f1 =====
SFO1 100.6278588 MHz
NUC1 13C
P1 8.90 usec
PLW1 54.0000000 W

===== CHANNEL f2 =====
SFO2 400.1516006 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 12.0000000 W
PLW12 0.32231000 W
PLW13 0.16212000 W

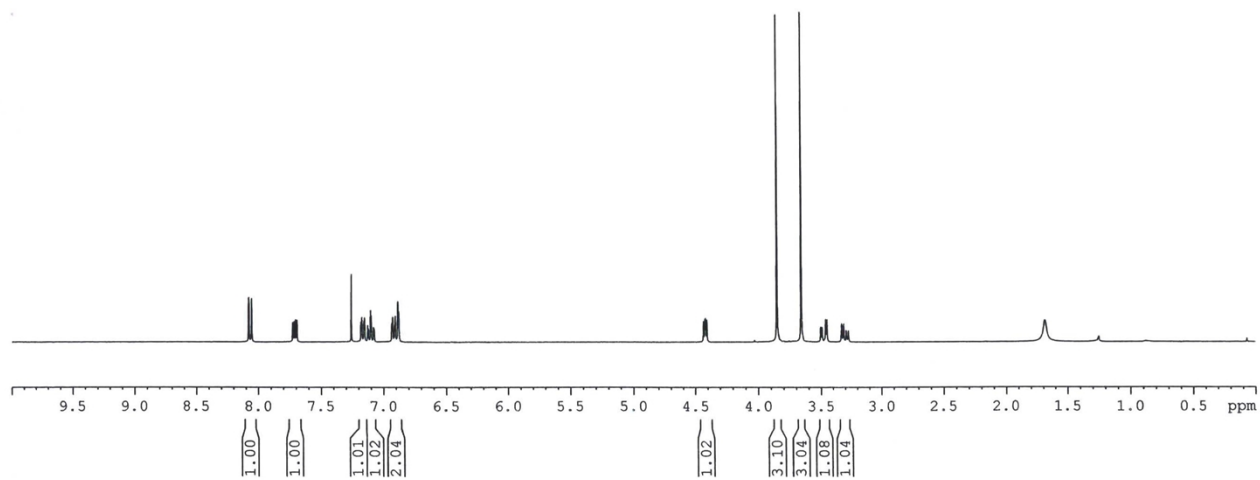
F2 - Processing parameters
SI 16384
SF 100.6177858 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

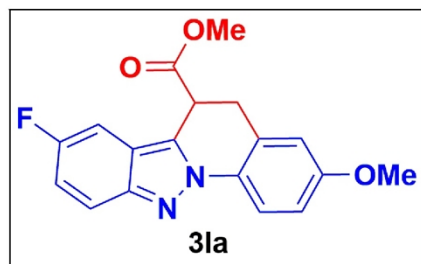
8.078
8.056
7.728
7.716
7.704
7.693
7.260
7.182
7.176
7.160
7.154
7.128
7.122
7.105
7.099
7.082
7.076
6.935
6.929
6.913
6.907
6.896
6.880

4.434
4.424
4.418
4.407
3.853
3.660
3.502
3.492
3.463
3.452
3.331
3.314
3.291
3.274

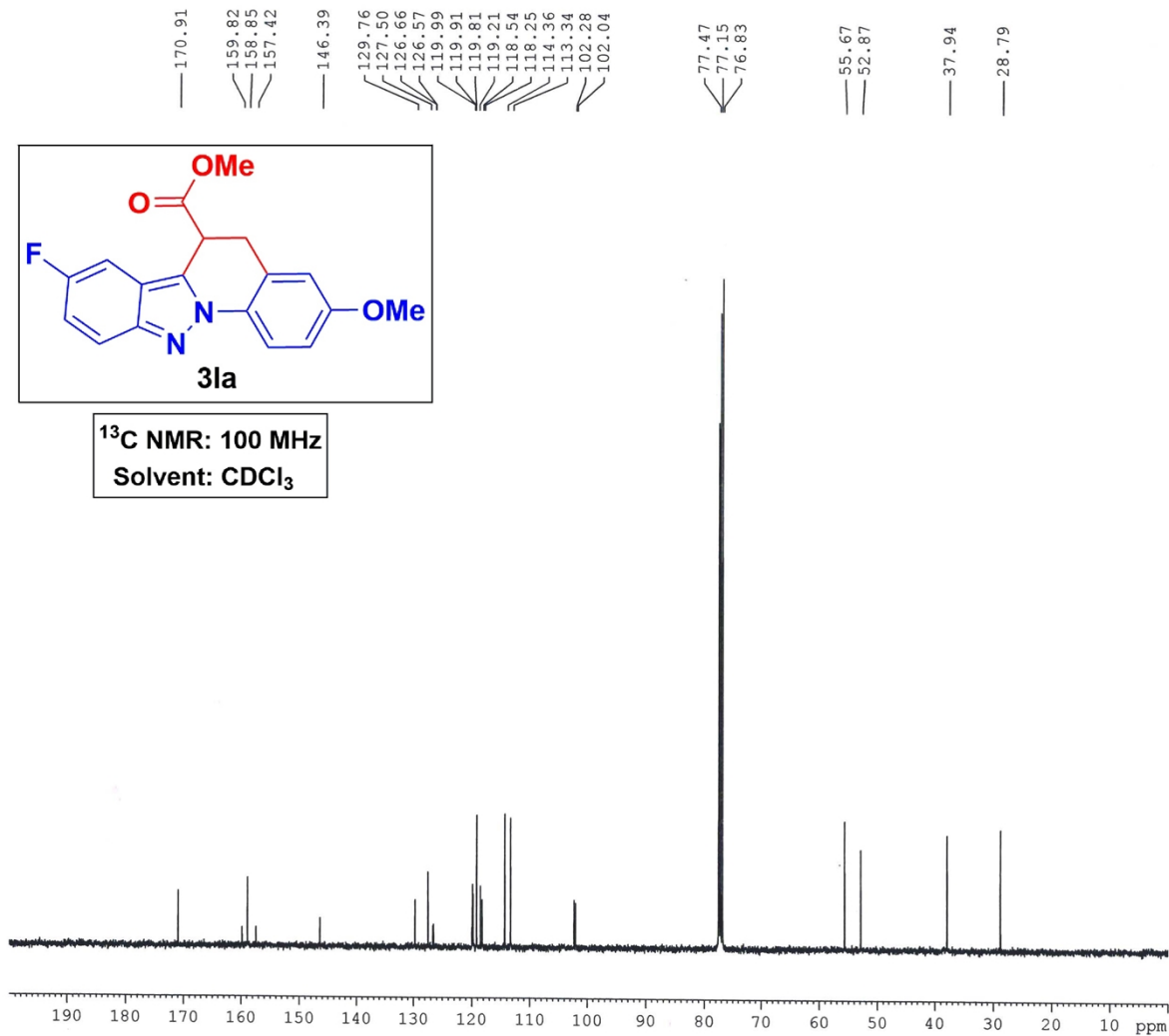


¹H NMR: 400 MHz
Solvent: CDCl₃





¹³C NMR: 100 MHz
Solvent: CDCl₃



Current Data Parameters
 NAME Dr. A HA.FRA-2023-13C
 EXPNO 367
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20230915
 Time 12.24
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 950
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 296.5 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

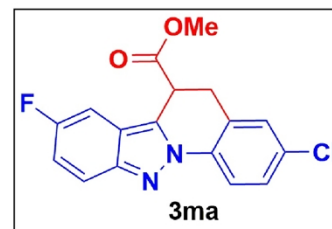
===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.0000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 12.0000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

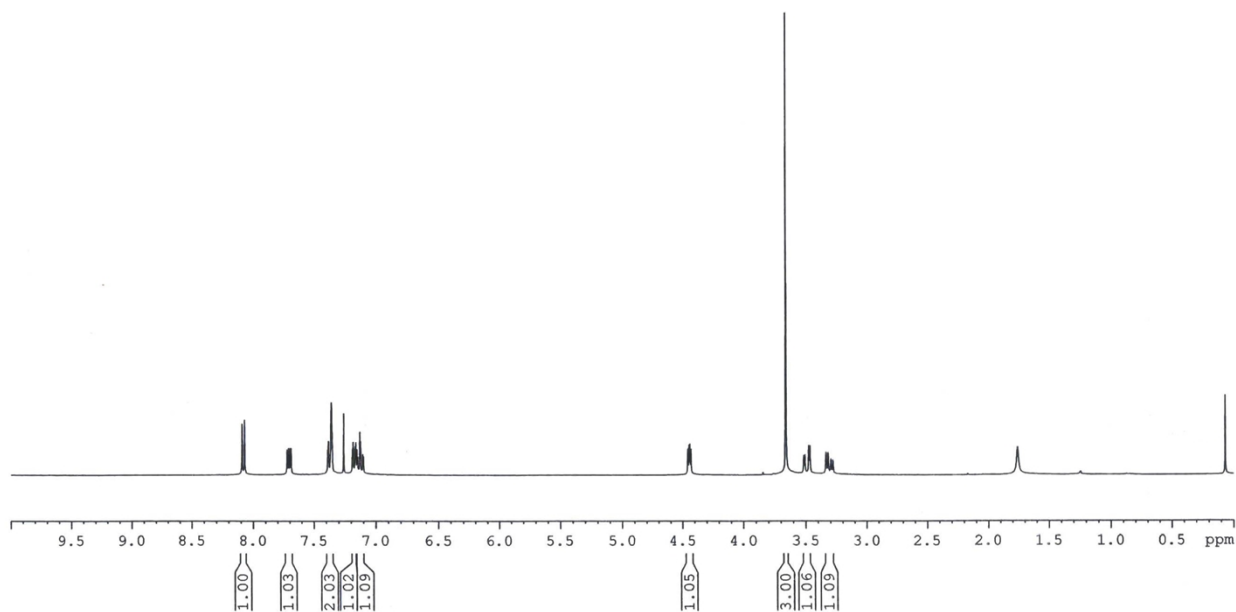
F2 - Processing parameters
 SI 16384
 SF 100.6177858 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

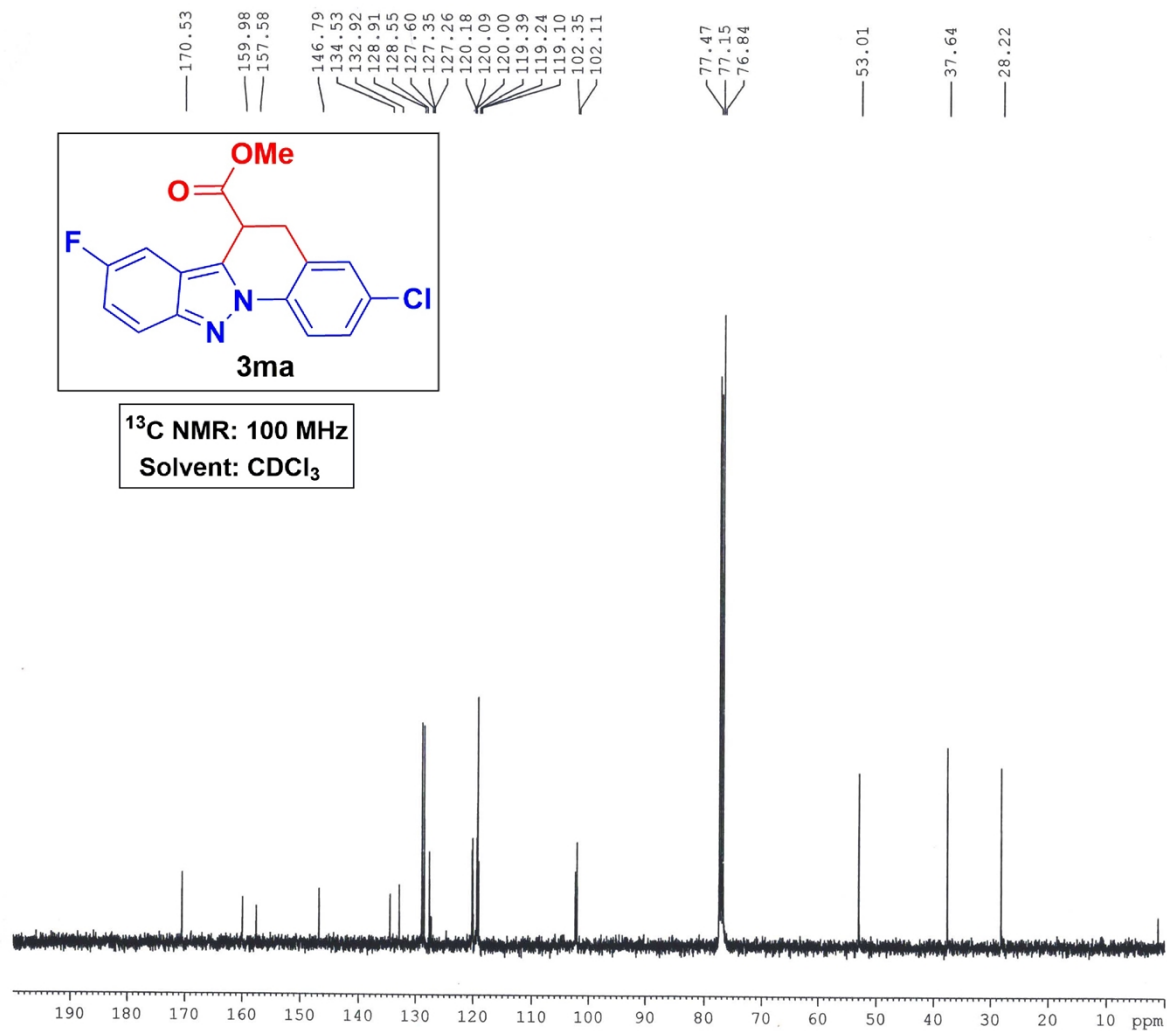
8.091
8.070
7.724
7.713
7.700
7.689
7.388
7.360
7.259
7.189
7.184
7.167
7.161
7.152
7.146
7.129
7.123
7.106
7.100

4.458
4.448
4.441
4.431
3.662
3.517
3.507
3.477
3.467
3.337
3.320
3.297
3.280



**¹H NMR: 400 MHz
Solvent: CDCl₃**





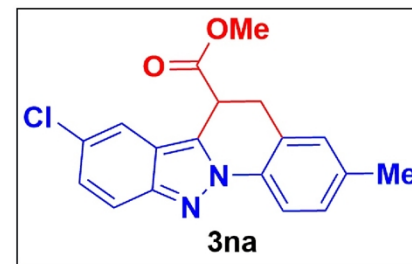
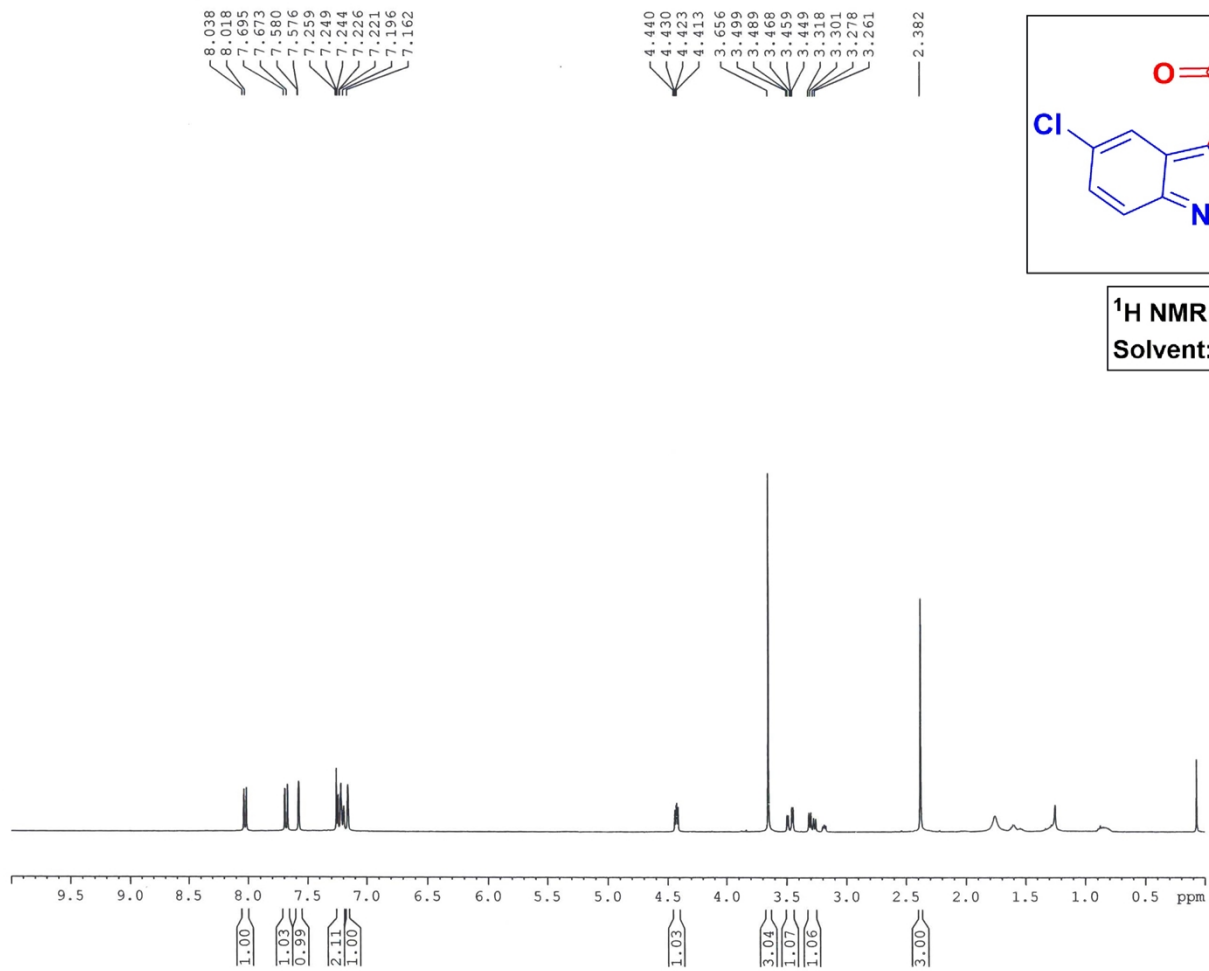
Current Data Parameters
NAME Dr. A HAJRA-2024-13C
EXPNO 30
PROCNO 1

F2 - Acquisition Parameters
Date 20240202
Time 13.20
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 340
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 290.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

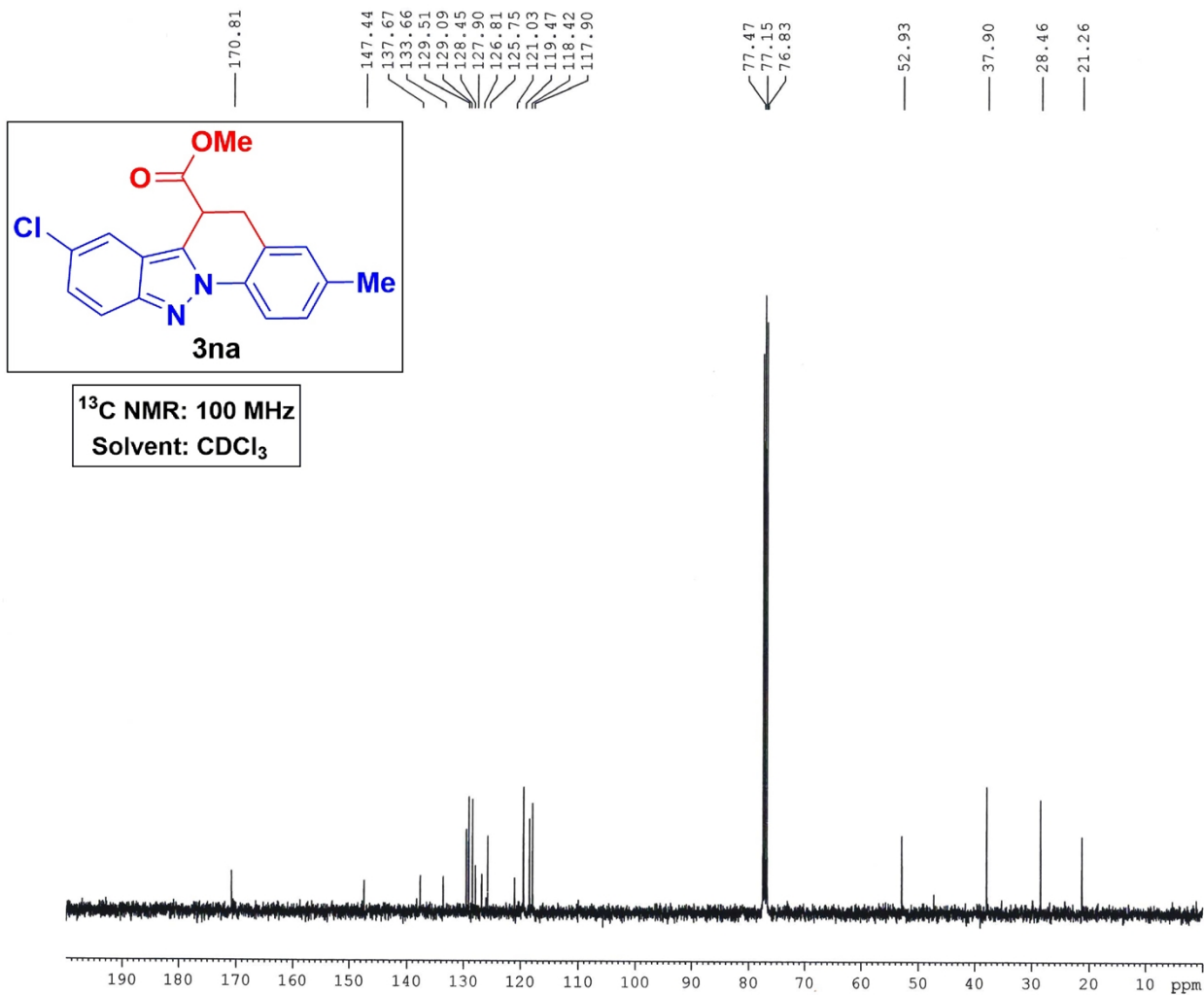
===== CHANNEL f1 =====
SFO1 100.6278588 MHz
NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W

===== CHANNEL f2 =====
SFO2 400.1516006 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.32231000 W
PLW13 0.16212000 W

F2 - Processing parameters
SI 16384
SF 100.6177881 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



¹H NMR: 400 MHz
Solvent: CDCl₃



Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 388
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20230926
 Time_ 12.29
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 170
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 297.1 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

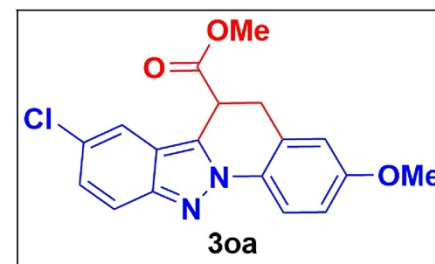
===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.0000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.0000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

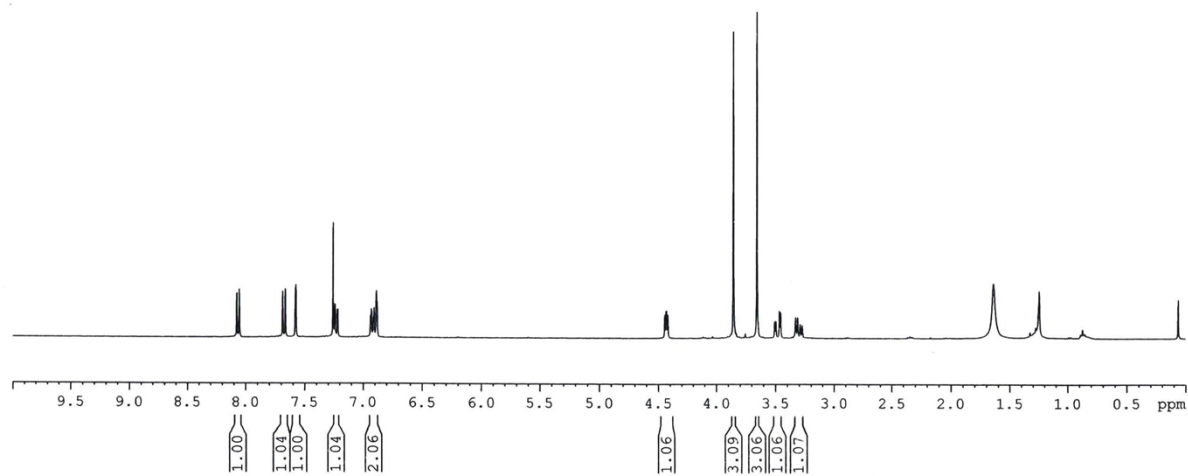
F2 - Processing parameters
 SI 16384
 SF 100.6177858 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

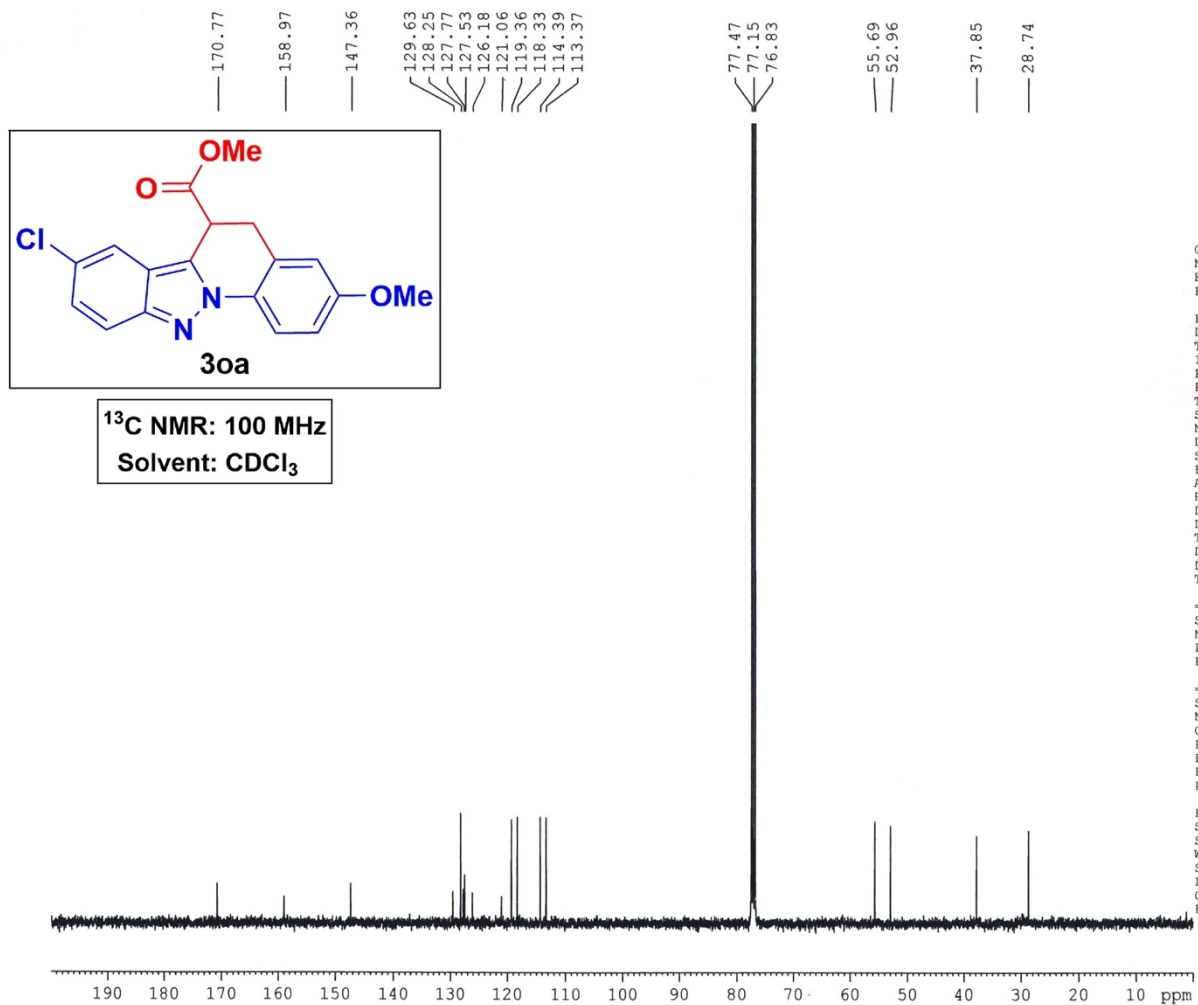
8.078
8.056
7.688
7.665
7.580
7.576
7.260
7.245
7.241
7.222
7.218
6.938
6.931
6.916
6.909
6.889
6.883

4.447
4.437
4.430
4.420
3.856
3.657
3.509
3.499
3.469
3.459
3.333
3.316
3.293
3.276



¹H NMR: 400 MHz
Solvent: CDCl₃





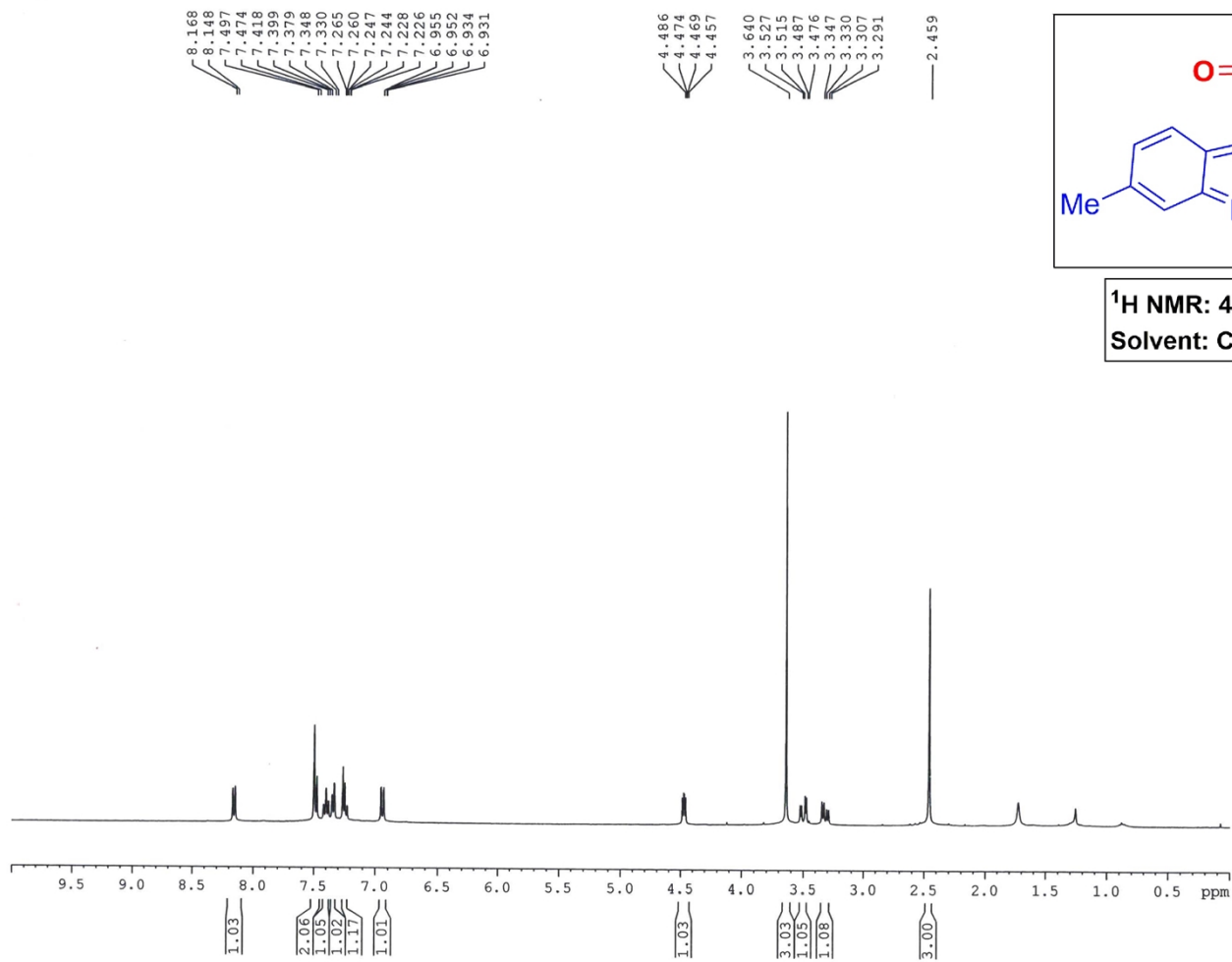
Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 352
 PROCNO 1

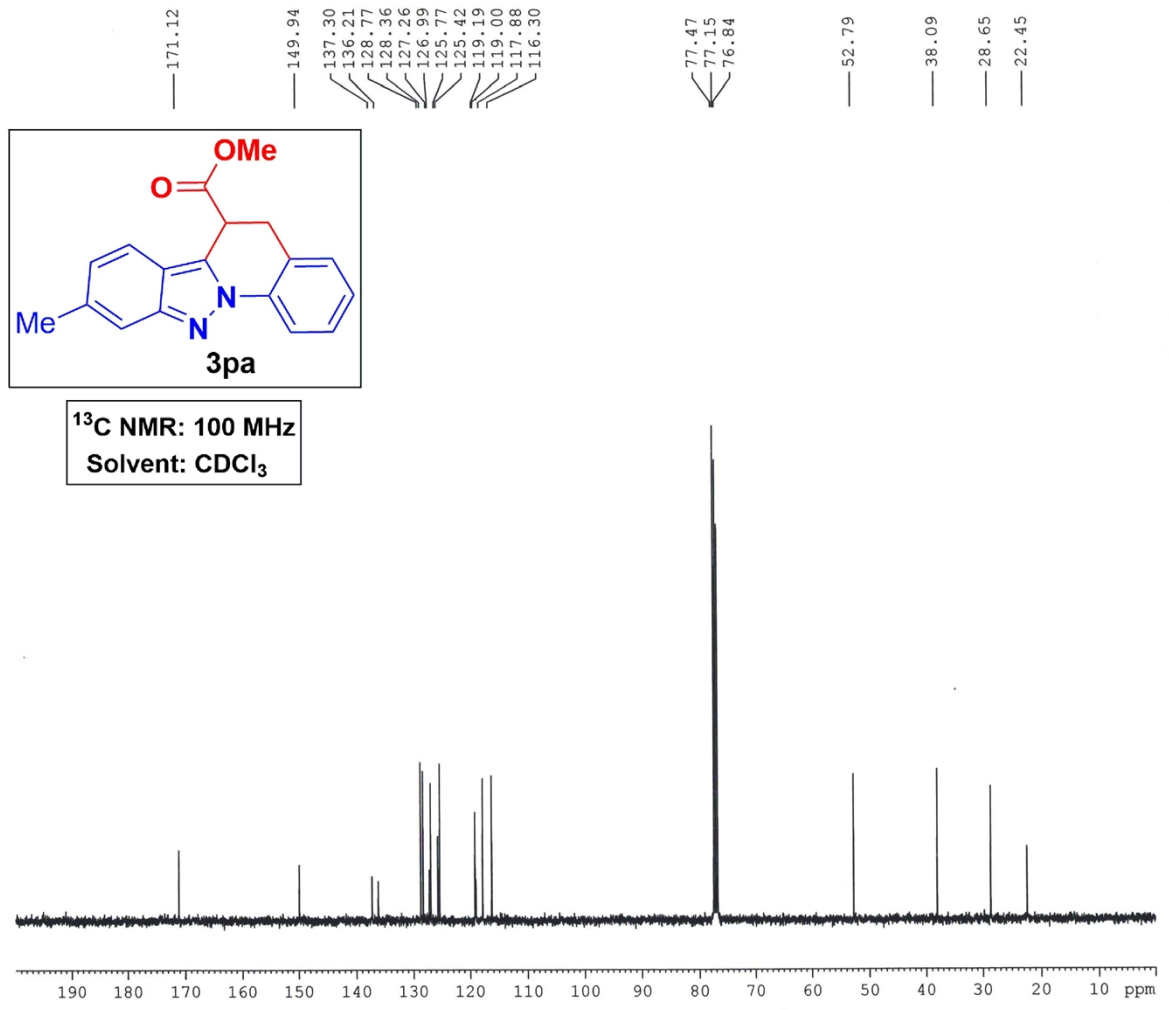
F2 - Acquisition Parameters
 Date 20230907
 Time 18.27
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 1024
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 294.9 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177859 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40





```

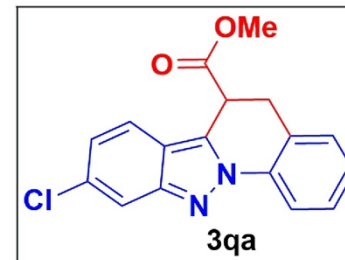
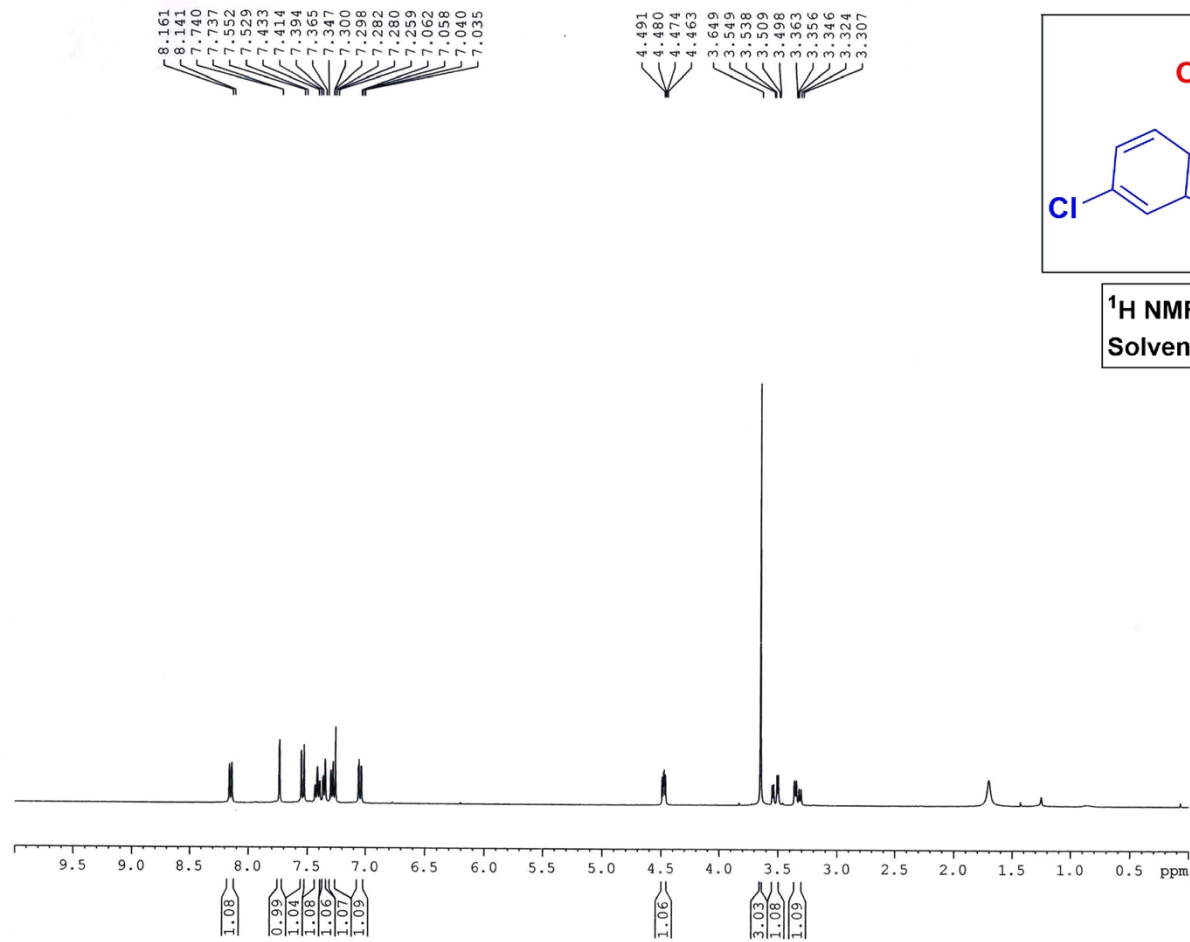
Current Data Parameters
NAME      Dr. A HAJRA-2023-13C
EXPNO     418
PROCNO    1

F2 - Acquisition Parameters
Date_     20231103
Time      9.33
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         280
DS         2
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6815744 sec
RG         186.42
DW         20.800 usec
DE         6.50 usec
TE         293.8 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

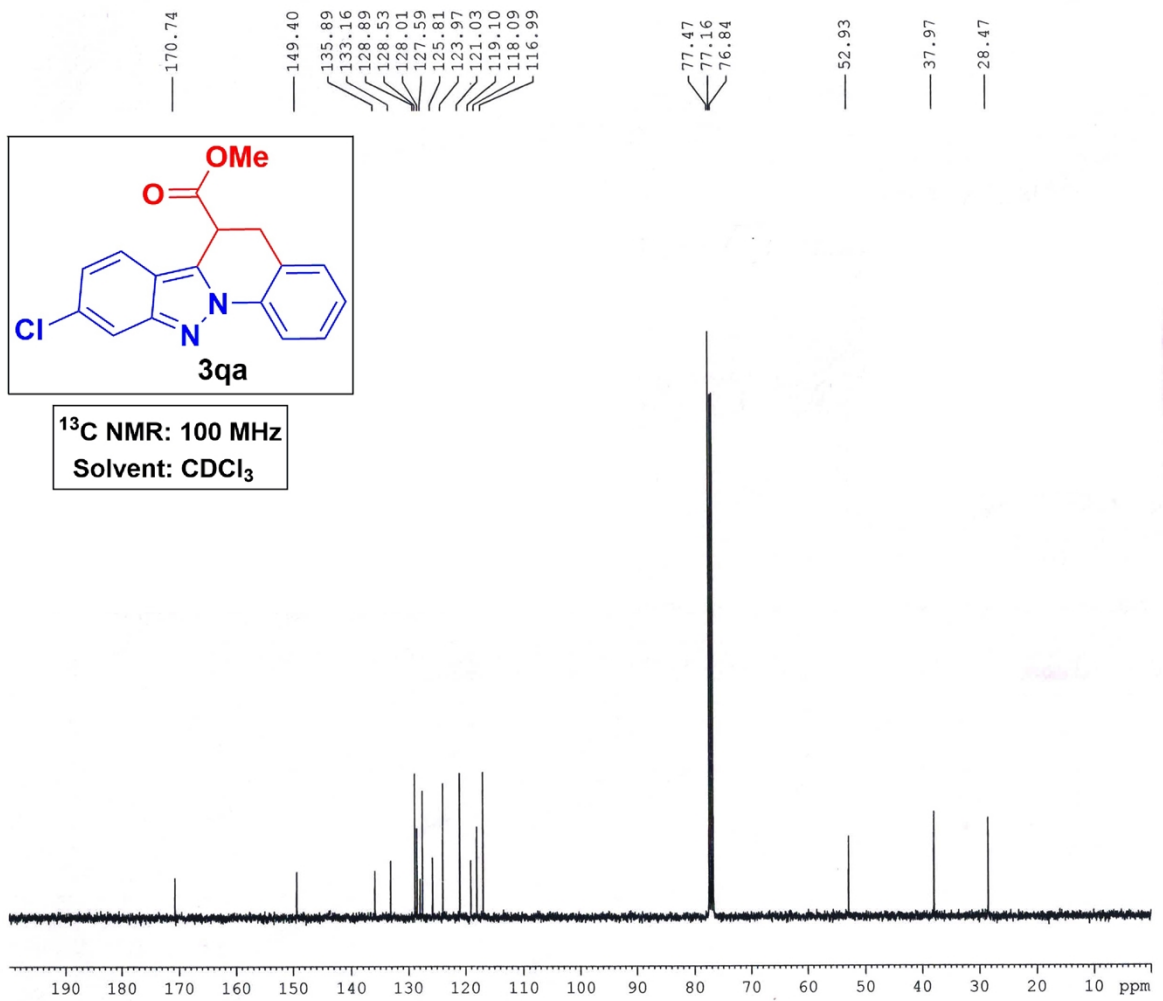
----- CHANNEL f1 -----
SFO1      100.6278588 MHz
NUC1       13C
P1         8.90 usec
PLW1       54.00000000 W

----- CHANNEL f2 -----
SFO2      400.1516006 MHz
NUC2       1H
CPDPRG[2] waltz16
PCPD2      90.00 usec
PLW2       12.00000000 W
PLW12      0.32231000 W
PLW13      0.16212000 W

F2 - Processing parameters
SI         16384
SF         100.6177873 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```

¹H NMR: 400 MHz
Solvent: CDCl₃



```

Current Data Parameters
NAME      Dr. A HAJRA-2023-13C
EXPNO     359
PROCNO    1

F2 - Acquisition Parameters
Date_     20230914
Time      10.24
INSTRUM   spect
PROBHD    5 mm PABBO BB/
FULPROG   zgpg30
TD         32768
SOLVENT   CDC13
NS         520
DS         2
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6815744 sec
RG         186.42
DW         20.800 usec
DE         6.50 usec
TE         295.1 K
D1         2.00000000 sec
D11        0.03000000 sec
TDO        1

----- CHANNEL f1 -----
SFO1      100.6278588 MHz
NUC1       13C
P1         8.90 usec
PLW1       54.00000000 W

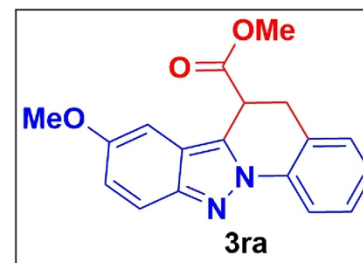
----- CHANNEL f2 -----
SFO2      400.1516006 MHz
NUC2        1H
CPDPRG2    waltz16
PCPD2      90.00 usec
PLW2       12.00000000 W
PLW2       0.32231000 W
PLW3       0.16212000 W

F2 - Processing parameters
SI         16384
SF         100.6177858 MHz
WDW        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40

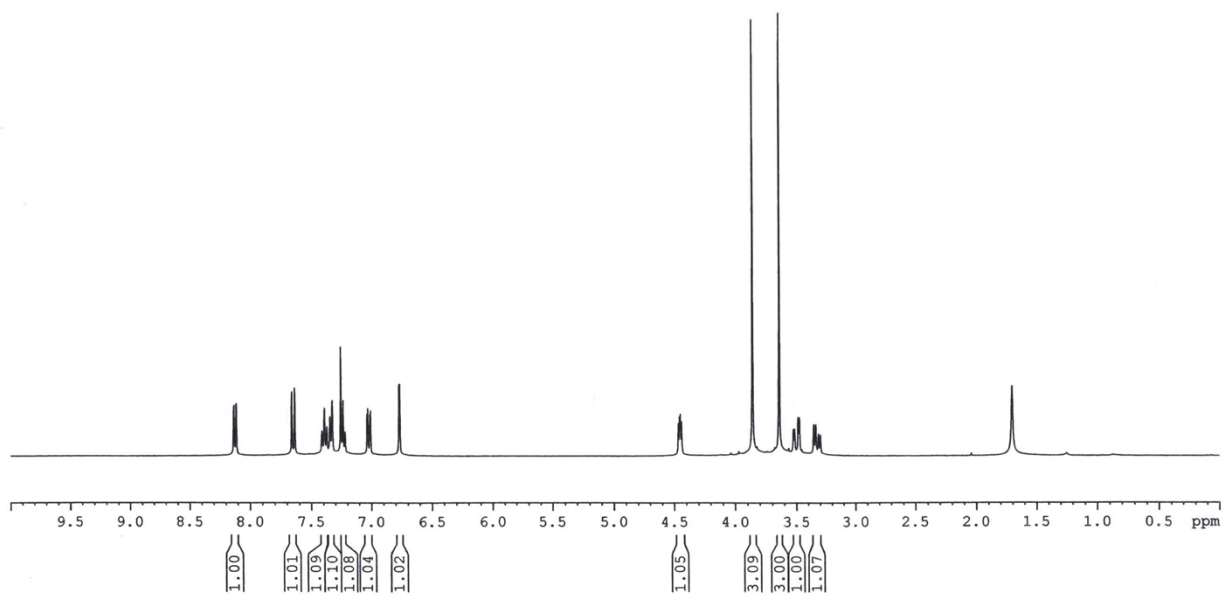
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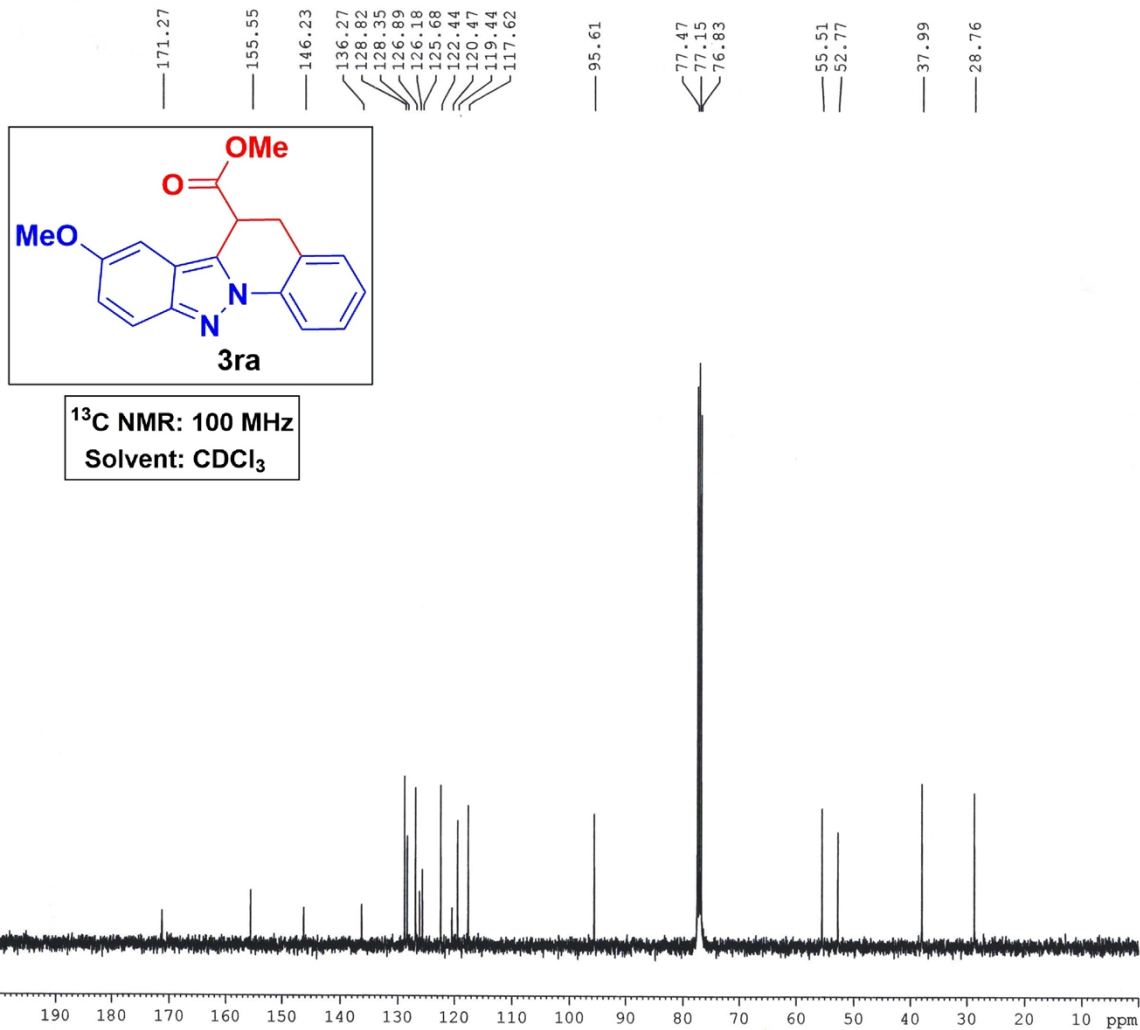
8.134
8.114
7.662
7.639
7.412
7.394
7.374
7.347
7.328
7.259
7.239
7.221
7.039
7.033
7.016
7.010
6.773
6.768

4.467
4.457
4.451
4.440
3.861
3.643
3.526
3.516
3.487
3.477
3.356
3.339
3.317
3.300



^1H NMR: 400 MHz
Solvent: CDCl_3





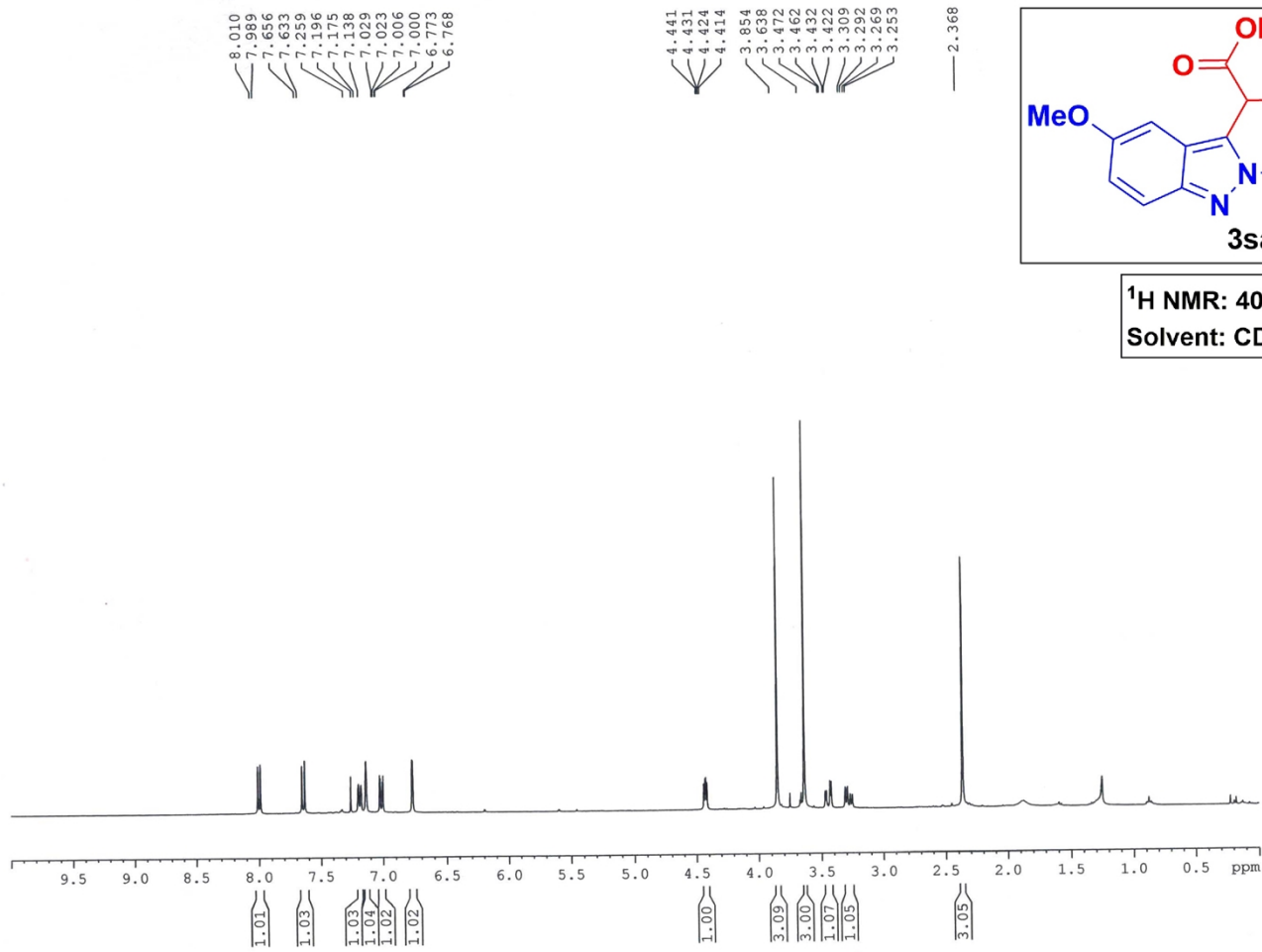
Current Data Parameters
NAME Dr. A HAJRA-2024-13C
EXPNO 29
PROCNO 1

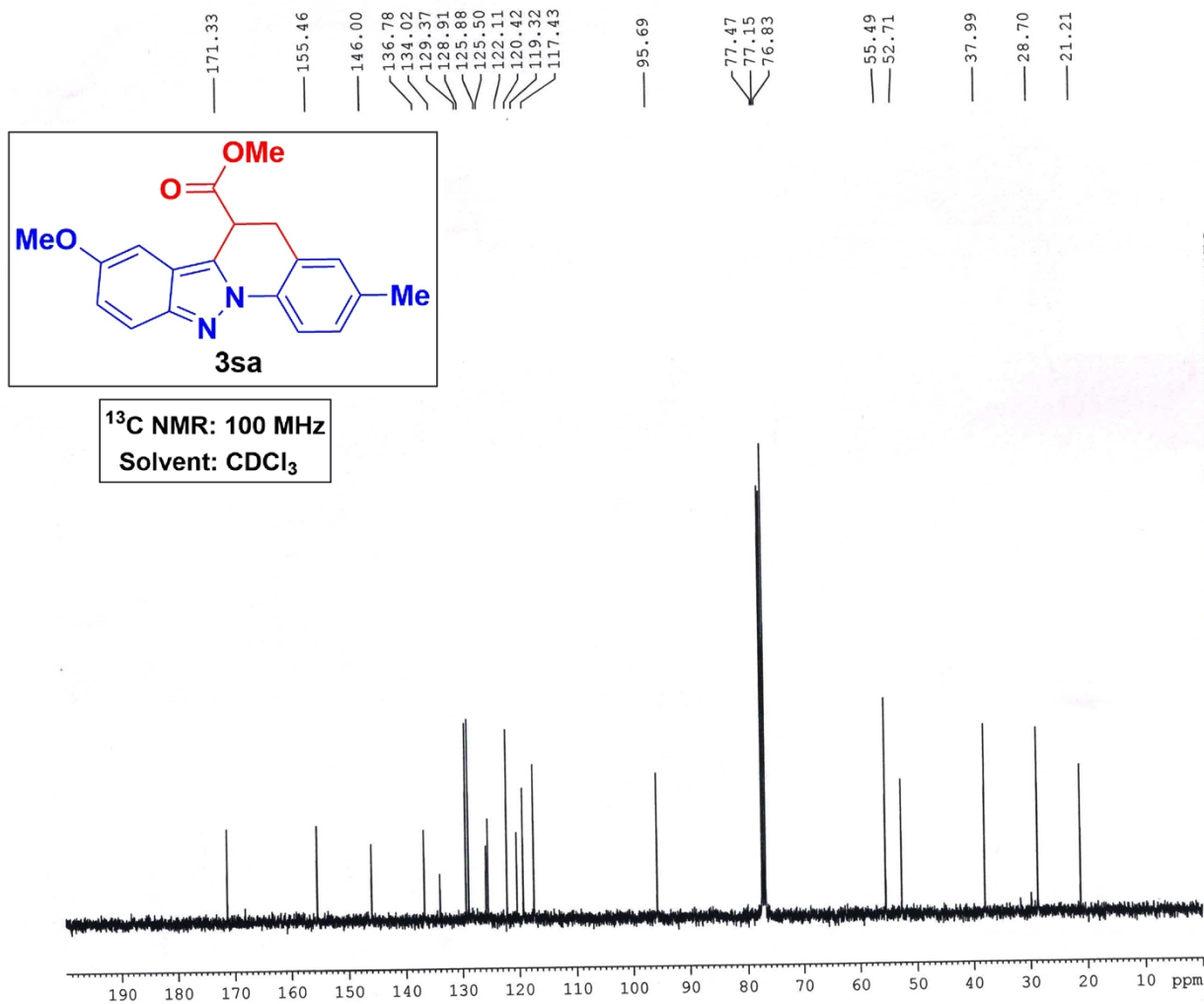
F2 - Acquisition Parameters
Date_ 20240201
Time_ 17.08
INSTRUM spect
PROBHD 5 mm FAPBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 320
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 292.5 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

===== CHANNEL f1 =====
SFO1 100.6278588 MHz
NUC1 13C
P1 8.90 usec
PLW1 54.00000000 W

===== CHANNEL f2 =====
SFO2 400.1516006 MHz
NUC2 1H
CFPRG[2] waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.32231000 W
PLW13 0.16212000 W

F2 - Processing parameters
SI 16384
SF 100.6177873 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 429
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20231107
 Time 17.31
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 180
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 295.6 K
 D1 2.0000000 sec
 D11 0.0300000 sec
 TDO 1

===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

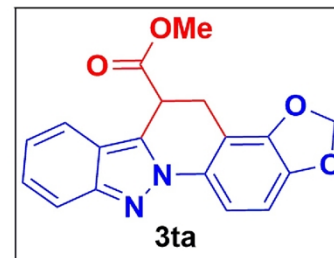
===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 ECPD2 90.00 usec
 PLW2 12.00000000 W
 ELW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177883 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

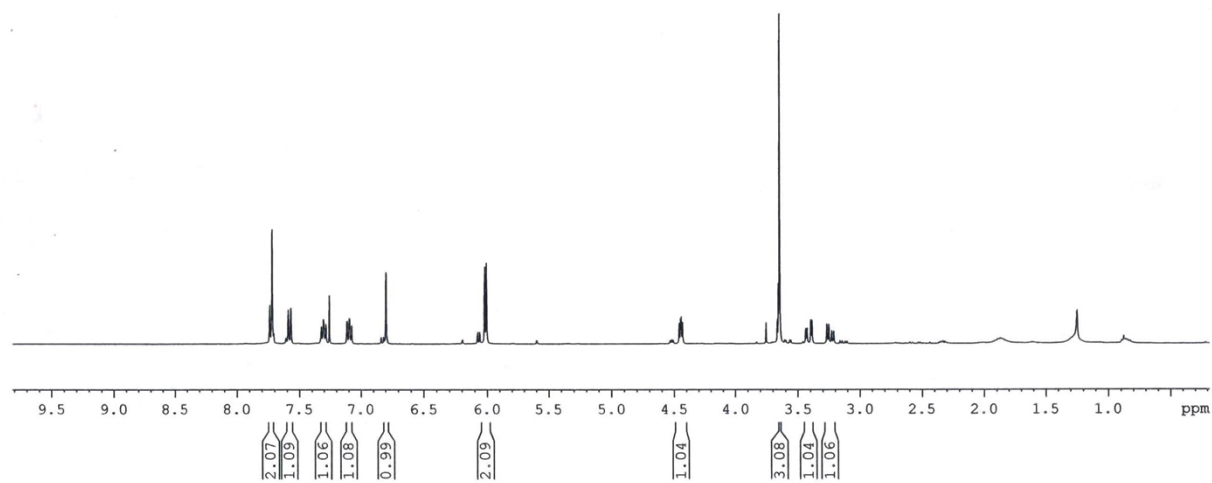
7.741
7.729
7.723
7.721
7.707
7.611
7.593
7.572
7.325
7.317
7.307
7.305
7.302
7.294
7.288
7.286
7.259
7.114
7.098
7.095
7.077
6.799
6.023
6.019
6.008
6.004

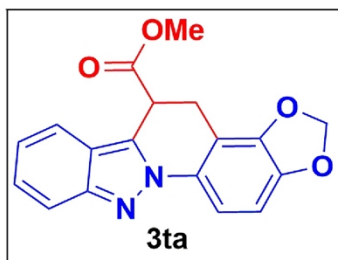
4.460
4.449
4.443
4.433

3.647
3.438
3.428
3.399
3.388
3.269
3.252
3.229
3.212

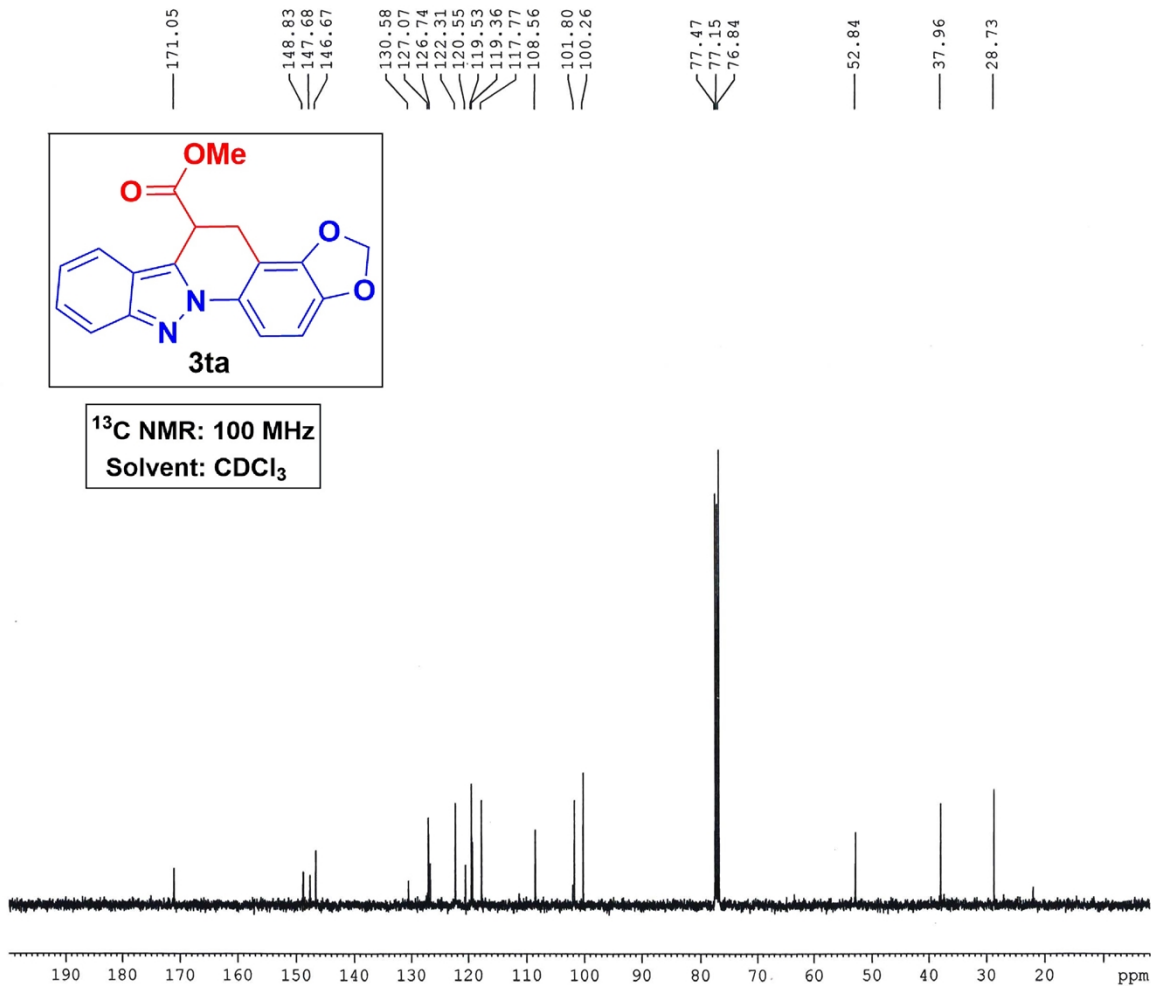


¹H NMR: 400 MHz
Solvent: CDCl₃





¹³C NMR: 100 MHz
Solvent: CDCl₃



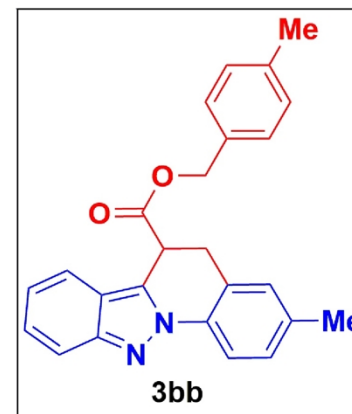
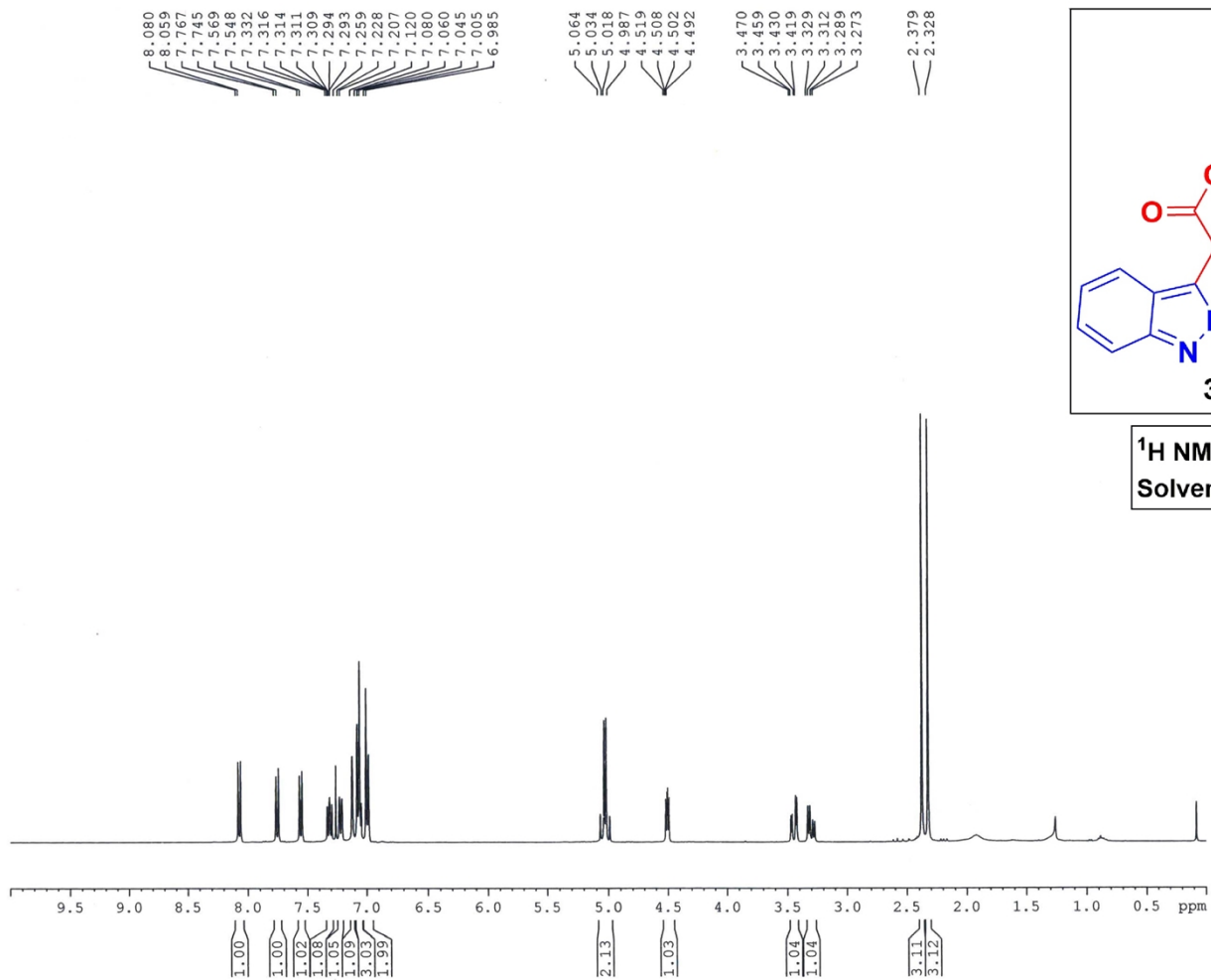
Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 447
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20231209
 Time 16.47
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 190
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 291.5 K
 D1 2.0000000 sec
 D11 0.03000000 sec
 TDO 1

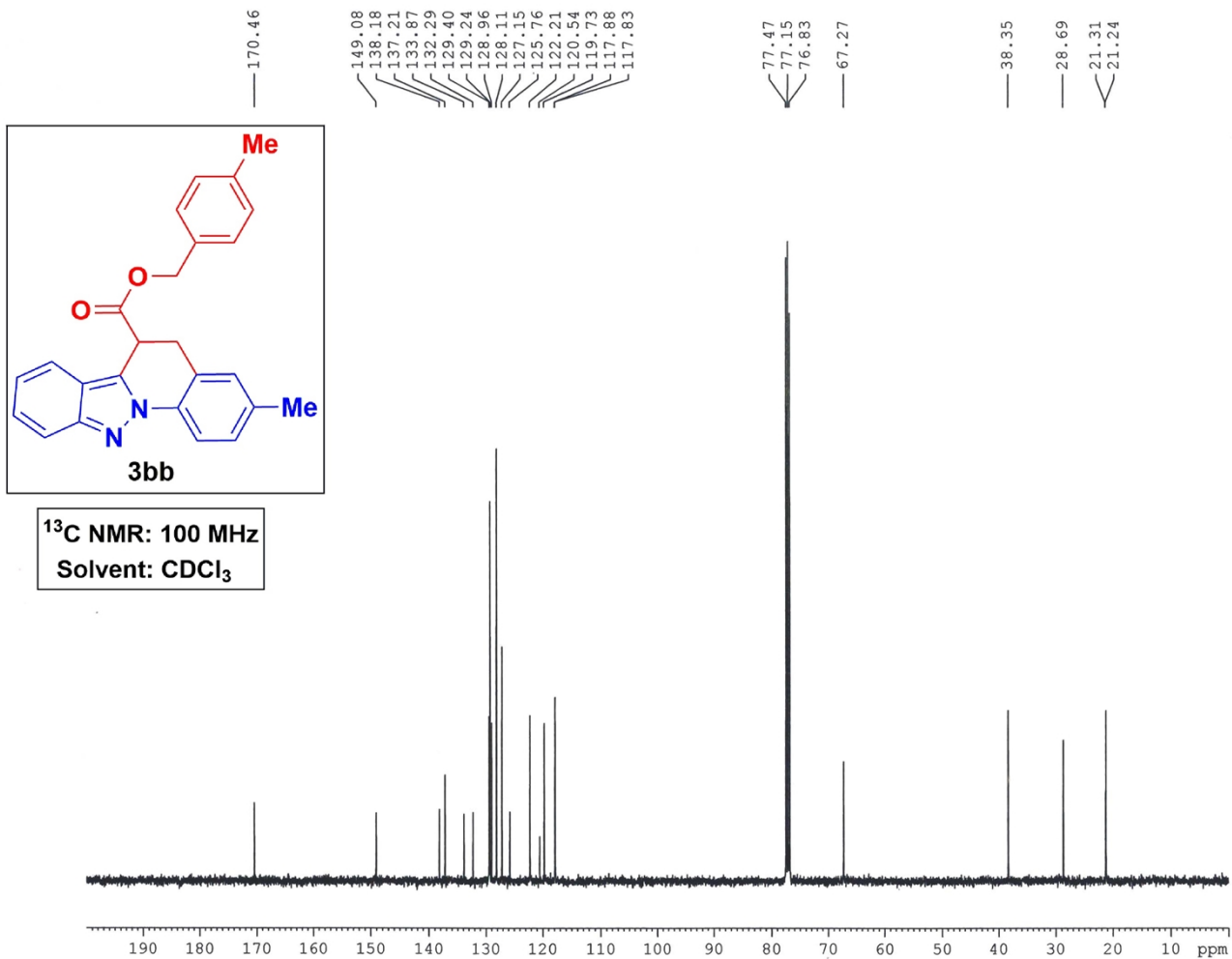
===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.0000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 12.0000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177881 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



¹H NMR: 400 MHz
Solvent: CDCl₃



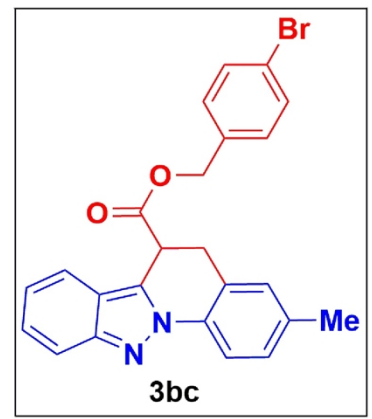
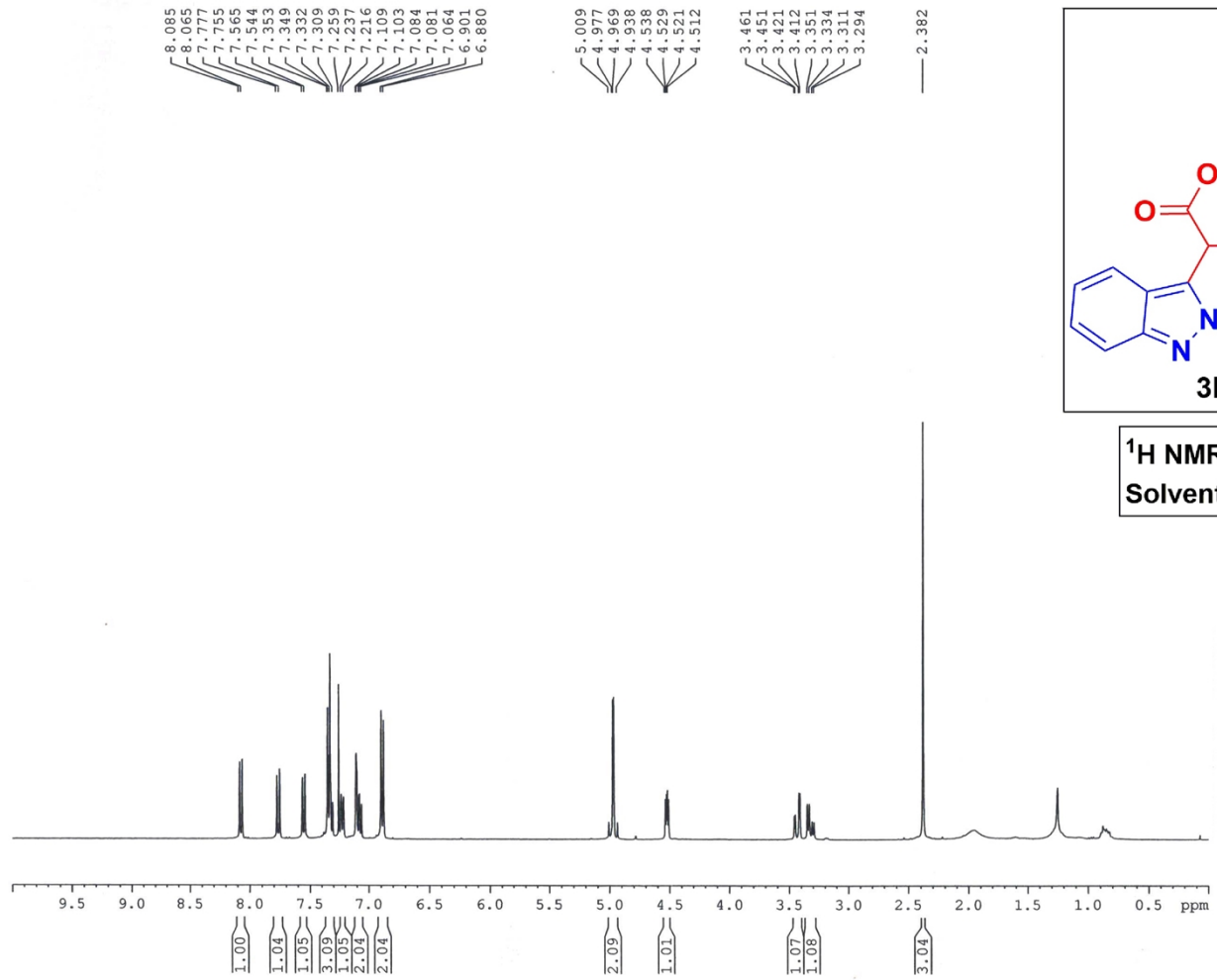
Current Data Parameters
 NAME Dr. A HAJRA-2023-13C
 EXPNO 456
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20231224
 Time_ 12.07
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 520
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 292.0 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

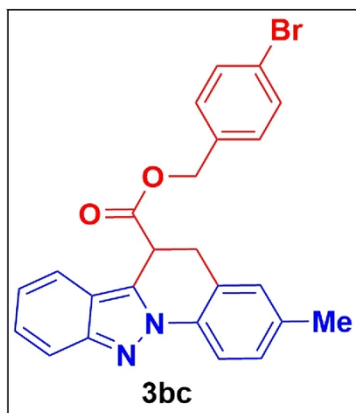
===== CHANNEL f1 =====
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

===== CHANNEL f2 =====
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

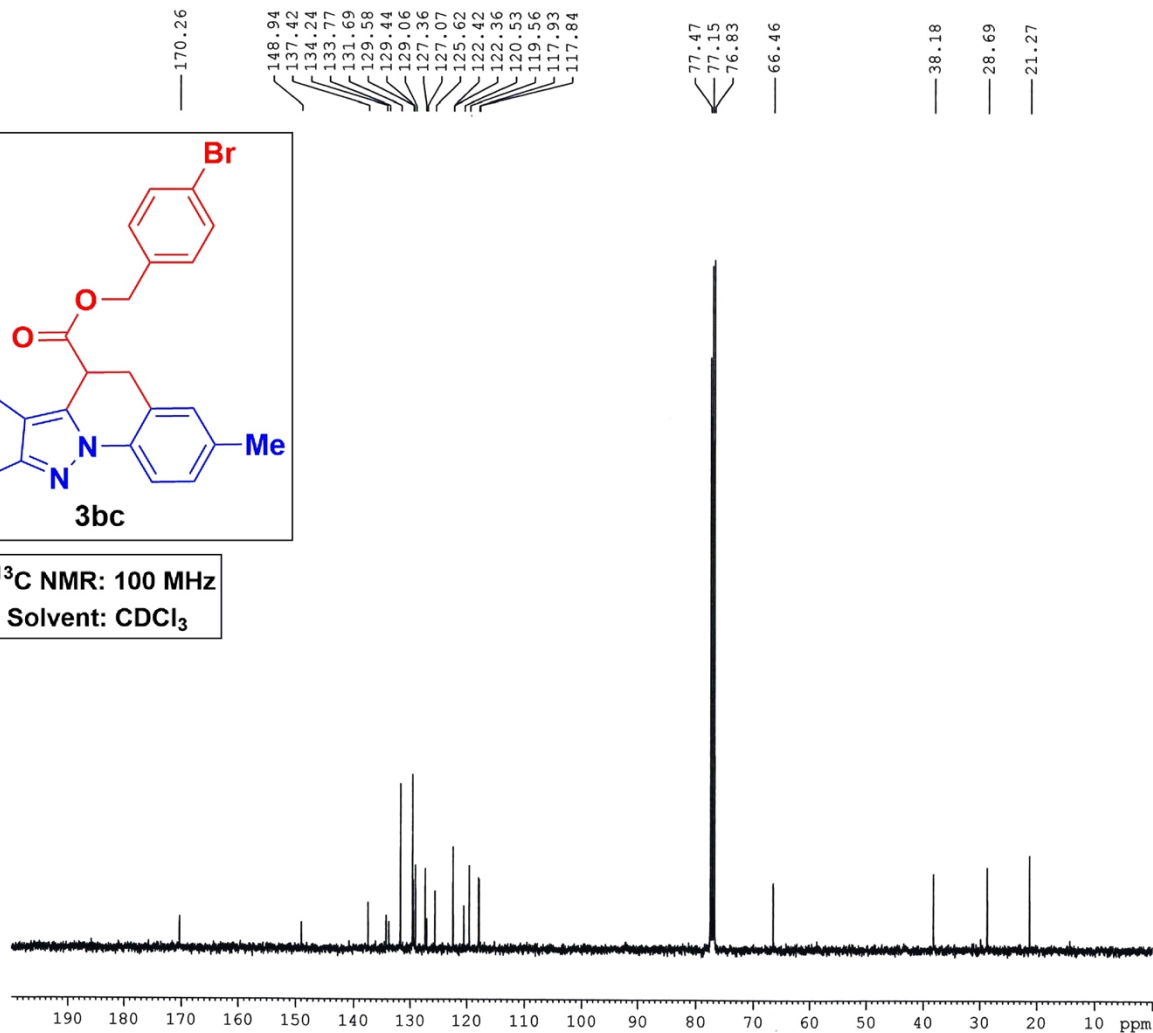
F2 - Processing parameters
 SI 16384
 SF 100.6177889 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



**¹H NMR: 400 MHz
Solvent: CDCl₃**



¹³C NMR: 100 MHz
Solvent: CDCl₃



```

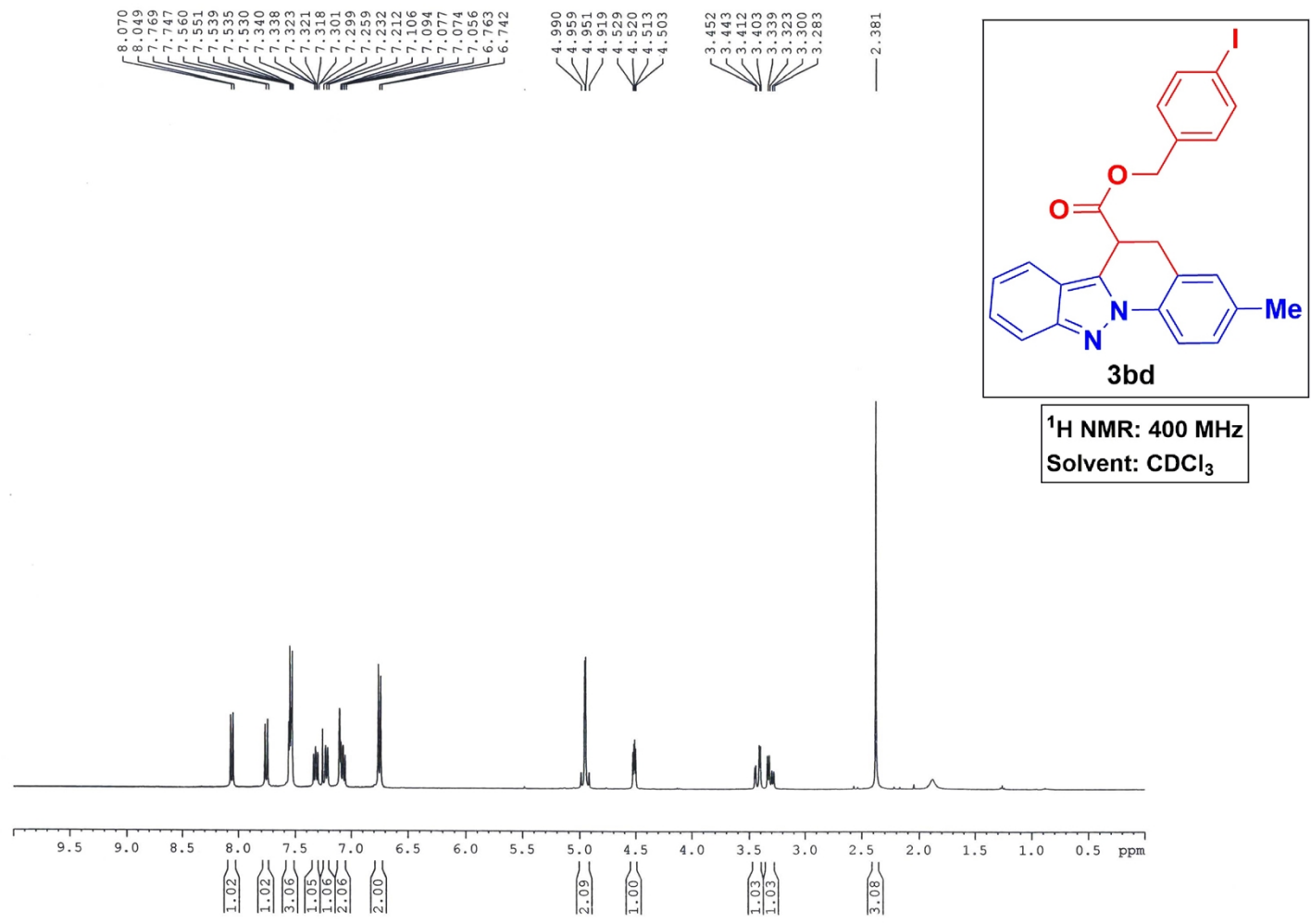
Current Data Parameters
NAME      Dr. A HAJRA-2024-13C
EXPNO    10
PROCNO    1

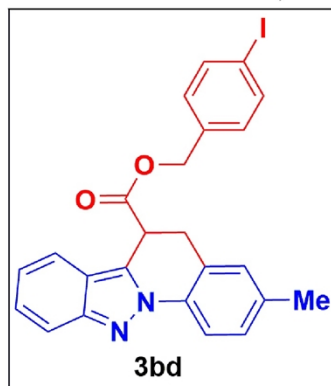
F2 - Acquisition Parameters
Date_     20240113
Time      11.21
INSTRUM   spect
PROBHD    5 mm PABBO BB/
PULPROG   zgpg30
TD         32768
SOLVENT   CDCl3
NS         620
DS         2
SWH        24038.461 Hz
FIDRES     0.733596 Hz
AQ         0.6815744 sec
RG         186.42
DW         20.800 usec
DE         6.50 usec
TE         291.9 K
D1         2.00000000 sec
D11        0.03000000 sec
TD0        1

===== CHANNEL f1 =====
SFO1      100.6278588 MHz
NUC1       13C
P1         8.90 usec
PLW1       54.00000000 W

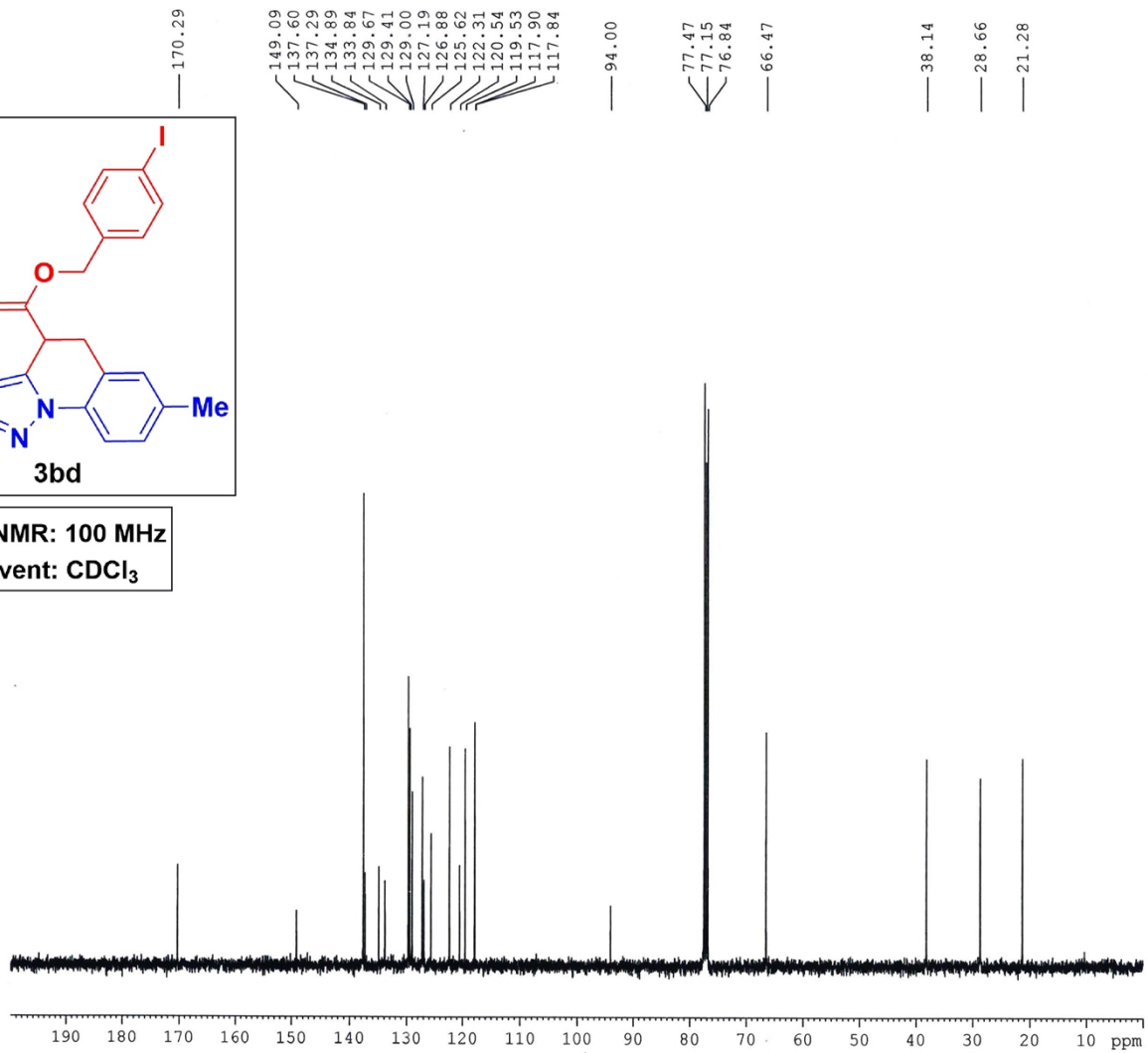
===== CHANNEL f2 =====
SFO2      400.1516006 MHz
NUC2       1H
CPDPRG2    waltz16
PCPD2      90.00 usec
PLW2       12.00000000 W
PLW12      0.32231000 W
PLW13      0.16212000 W

F2 - Processing parameters
SI         16384
SF         100.6177873 MHz
WLB        EM
SSB        0
LB         1.00 Hz
GB         0
PC         1.40
  
```





¹³C NMR: 100 MHz
Solvent: CDCl₃



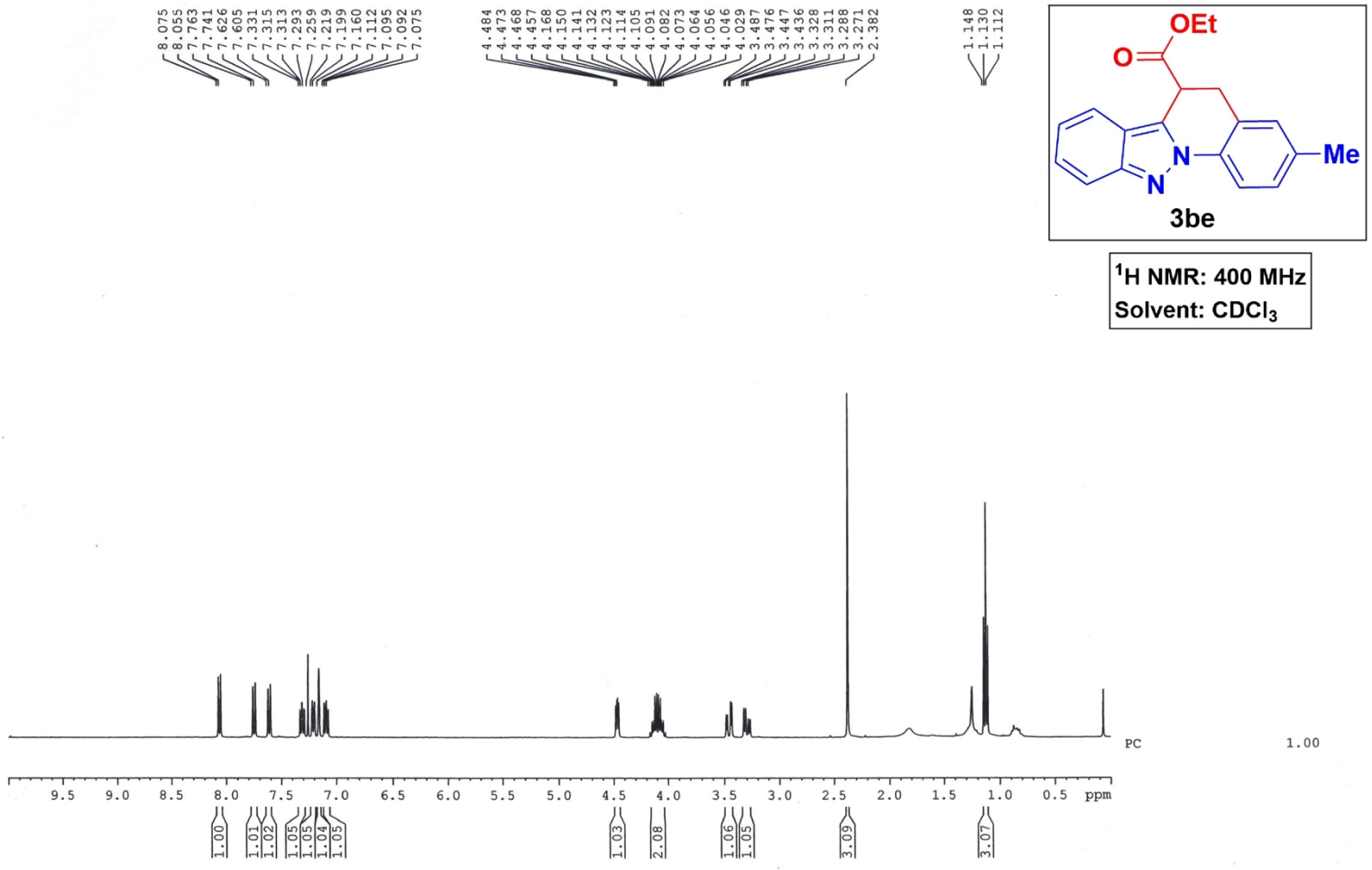
Current Data Parameters
 NAME Dr. A HAJRA-2024-13C
 EXPNO 17
 PROCNO 1

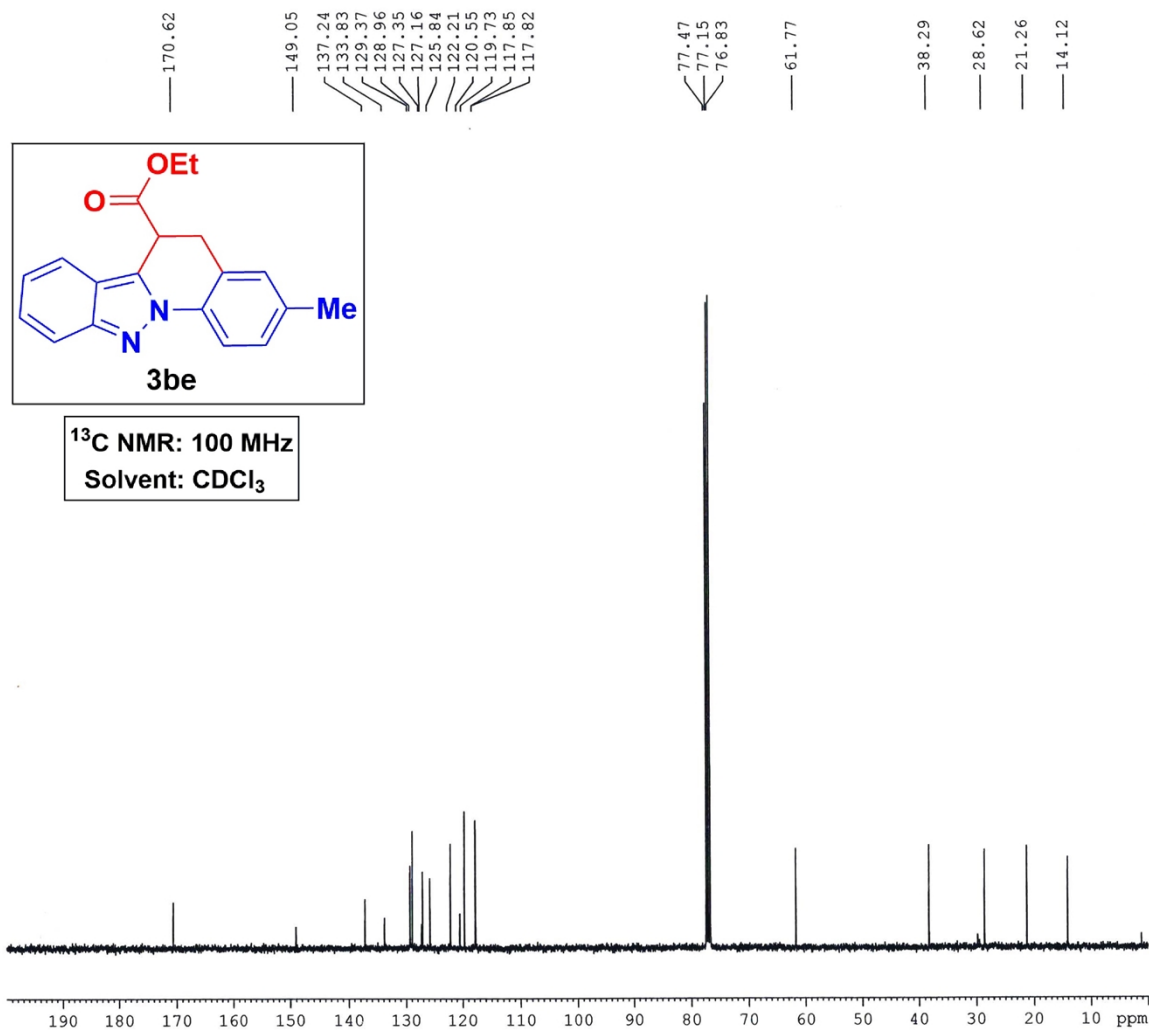
F2 - Acquisition Parameters
 Date_ 20240124
 Time 18.08
 INSTRUM spect
 FROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 200
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 290.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

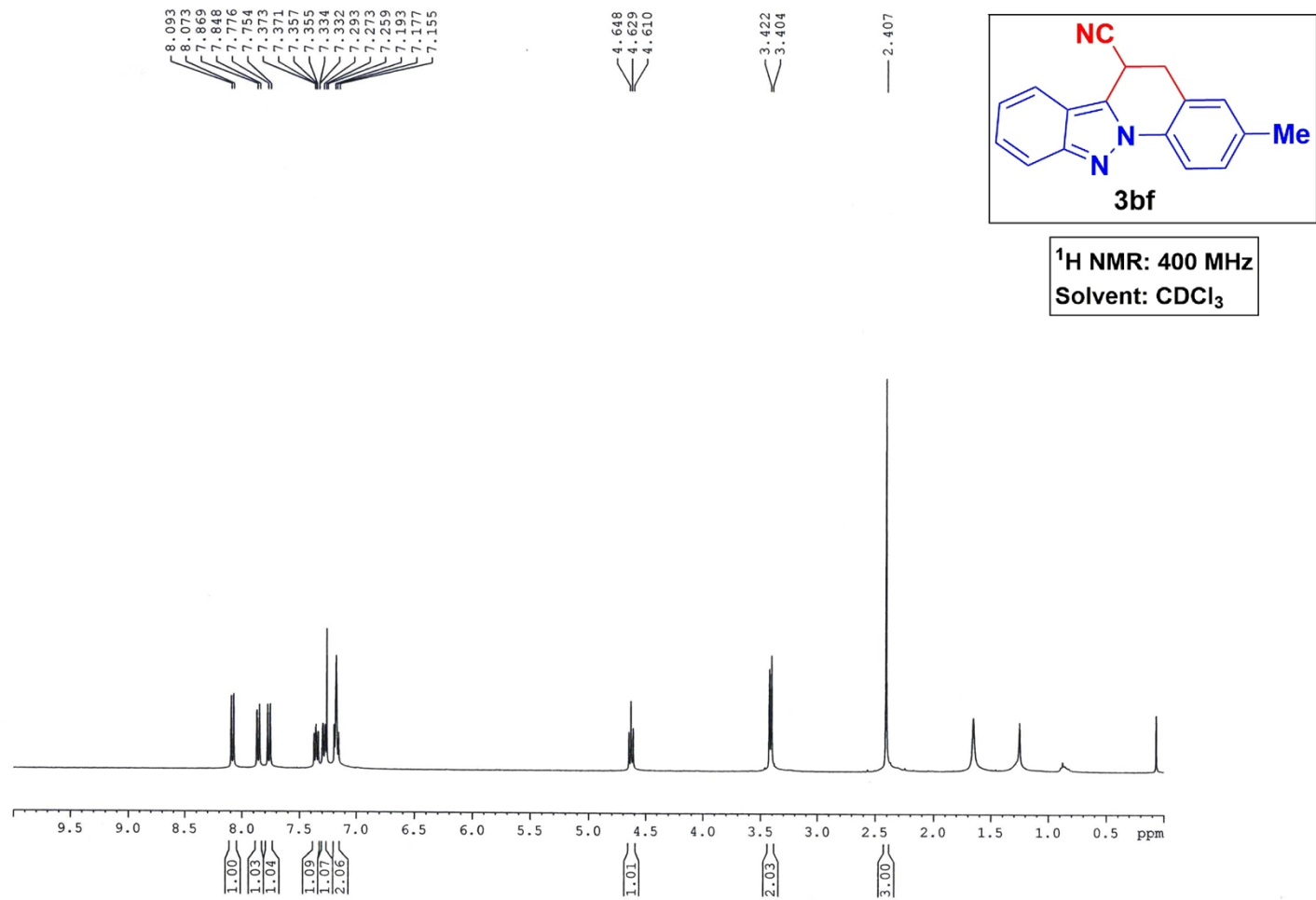
----- CHANNEL f1 -----
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

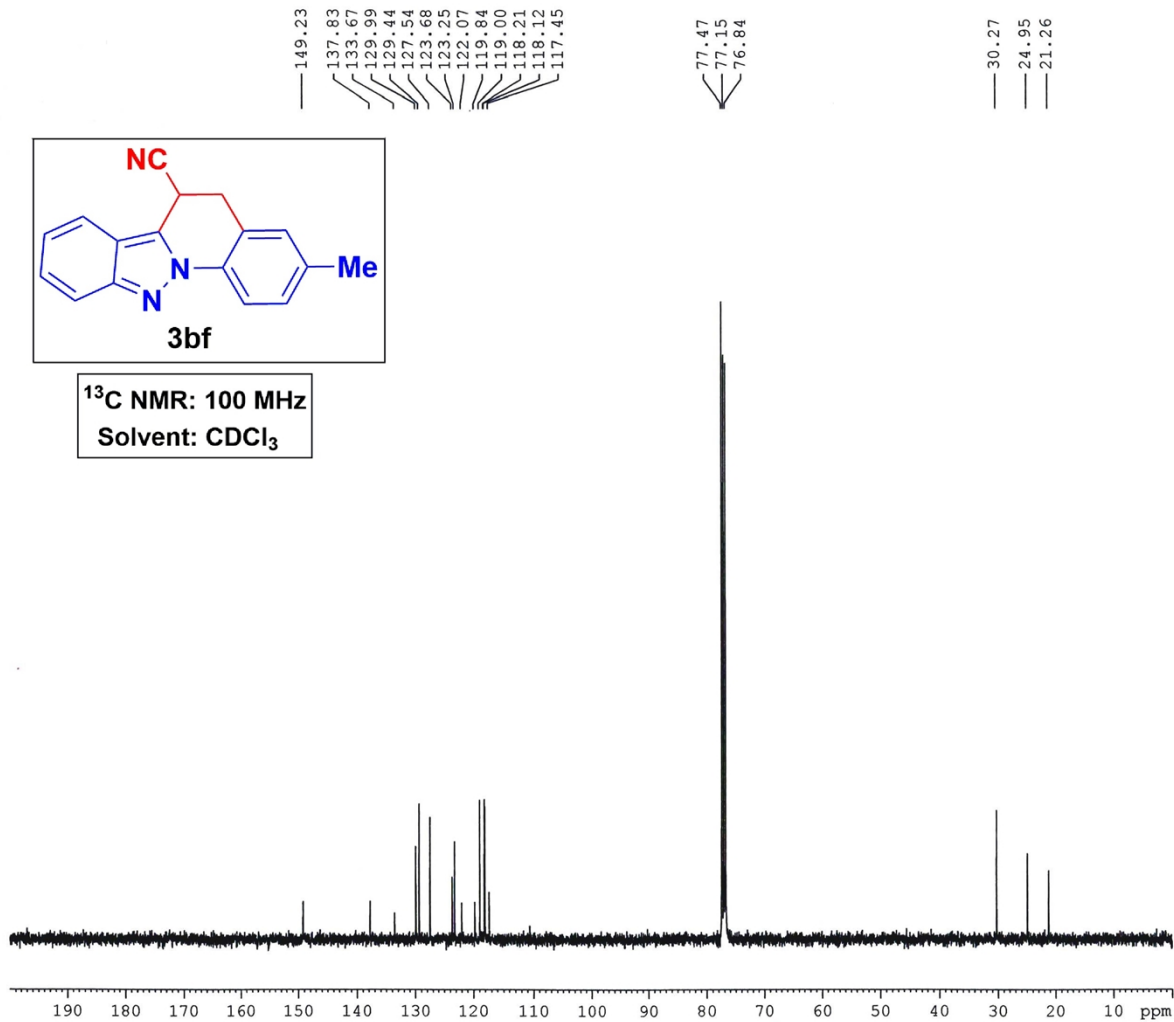
----- CHANNEL f2 -----
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177909 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40









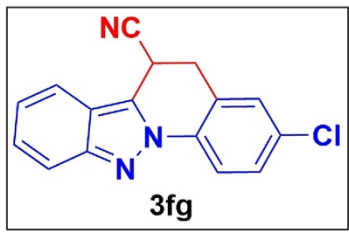
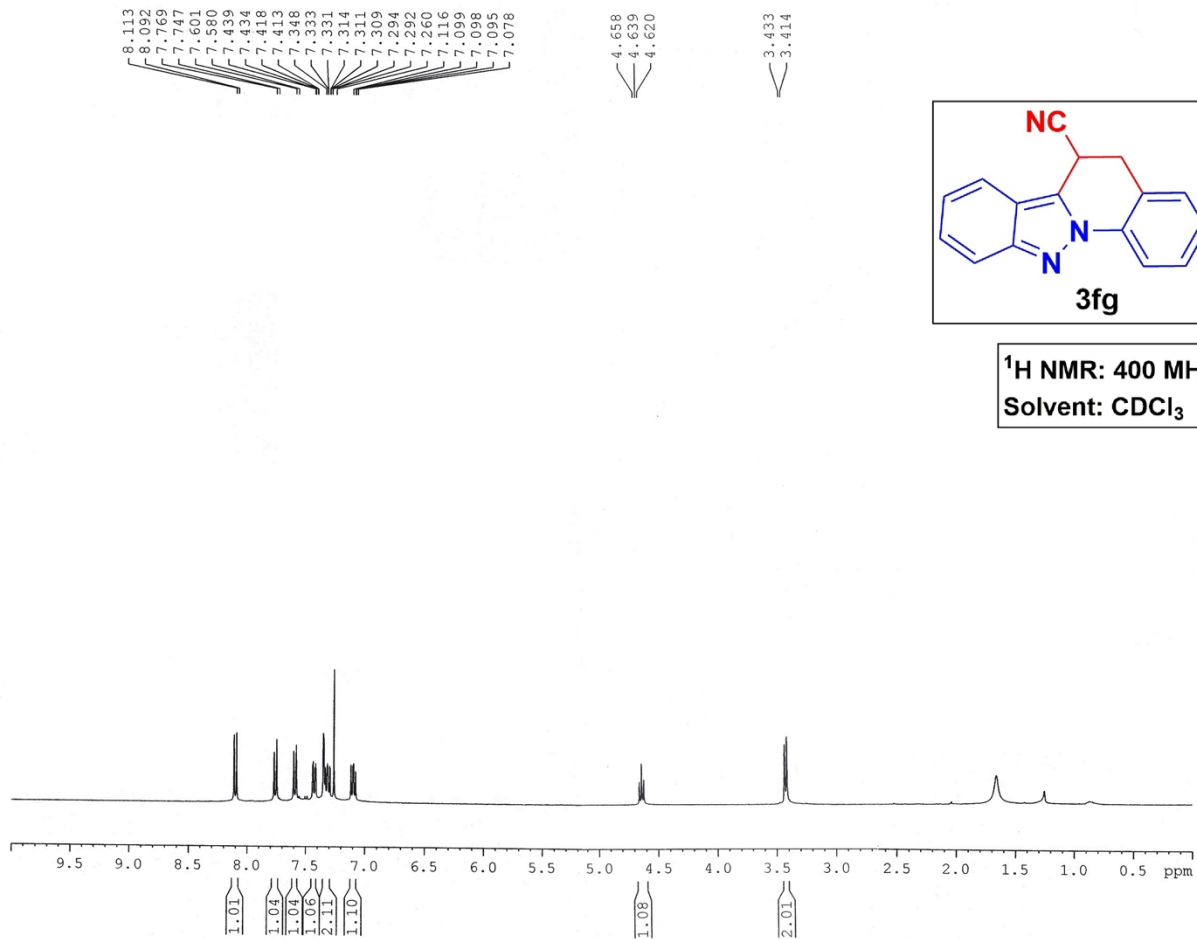
Current Data Parameters
NAME Dr. A HAJRA-2024-13C
EXPNO 15
PROCNO 1

F2 - Acquisition Parameters
Date_ 20240122
Time_ 10.58
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 32768
SOLVENT CDCl3
NS 480
DS 2
SWH 24038.461 Hz
FIDRES 0.733596 Hz
AQ 0.6815744 sec
RG 186.42
DW 20.800 usec
DE 6.50 usec
TE 290.1 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

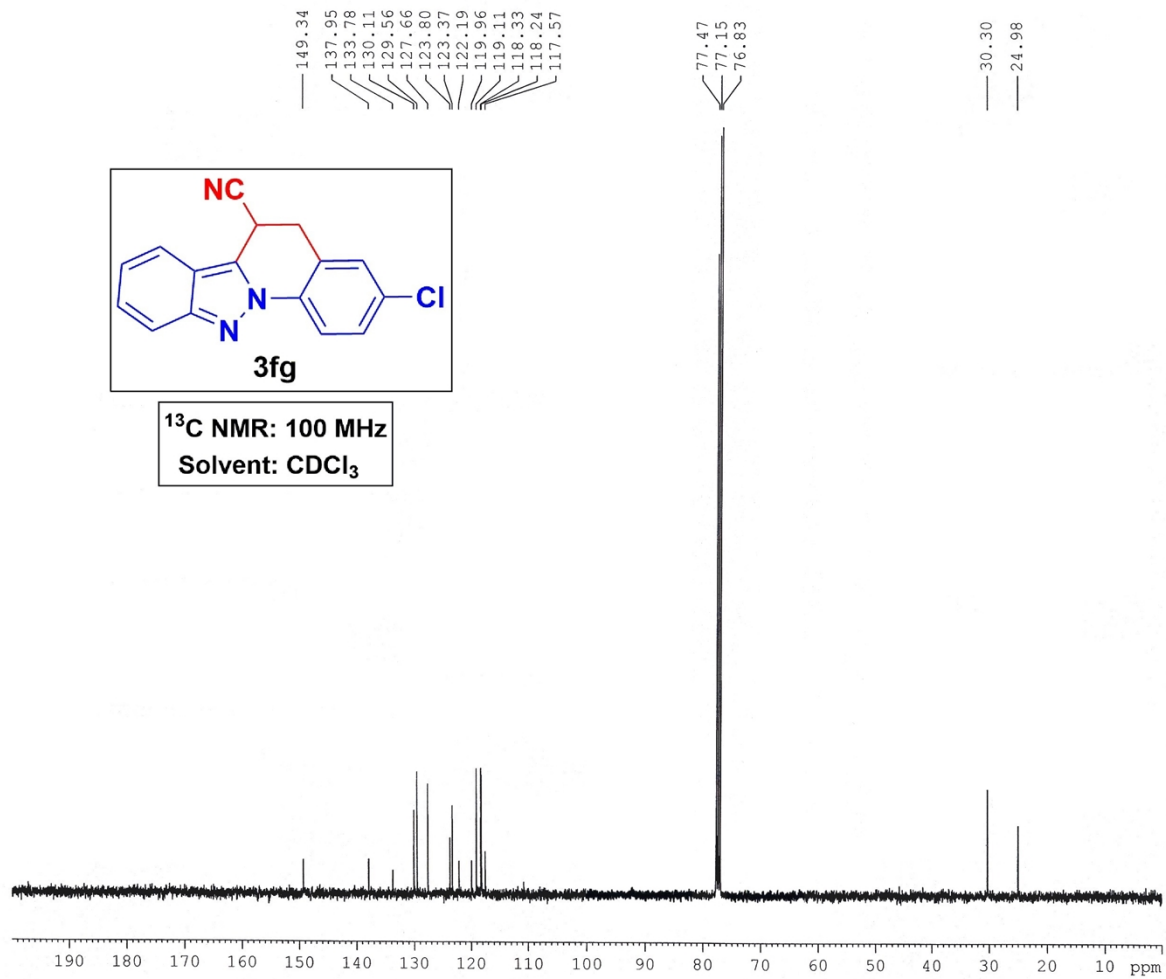
----- CHANNEL f1 -----
SFO1 100.6278588 MHz
NUC1 13C
P1 8.90 usec
PLW1 54.0000000 W

----- CHANNEL f2 -----
SFO2 400.1516006 MHz
NUC2 1H
PCPD2 waltz16
PCPD2 90.00 usec
PLW2 12.0000000 W
PLW12 0.32231000 W
PLW13 0.16212000 W

F2 - Processing parameters
SI 16384
SF 100.6177877 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



¹H NMR: 400 MHz
 Solvent: CDCl₃



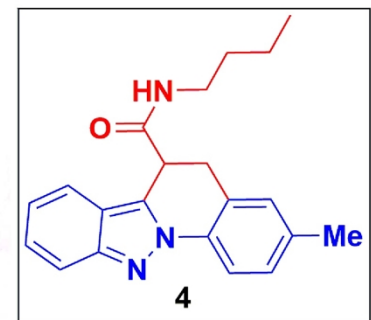
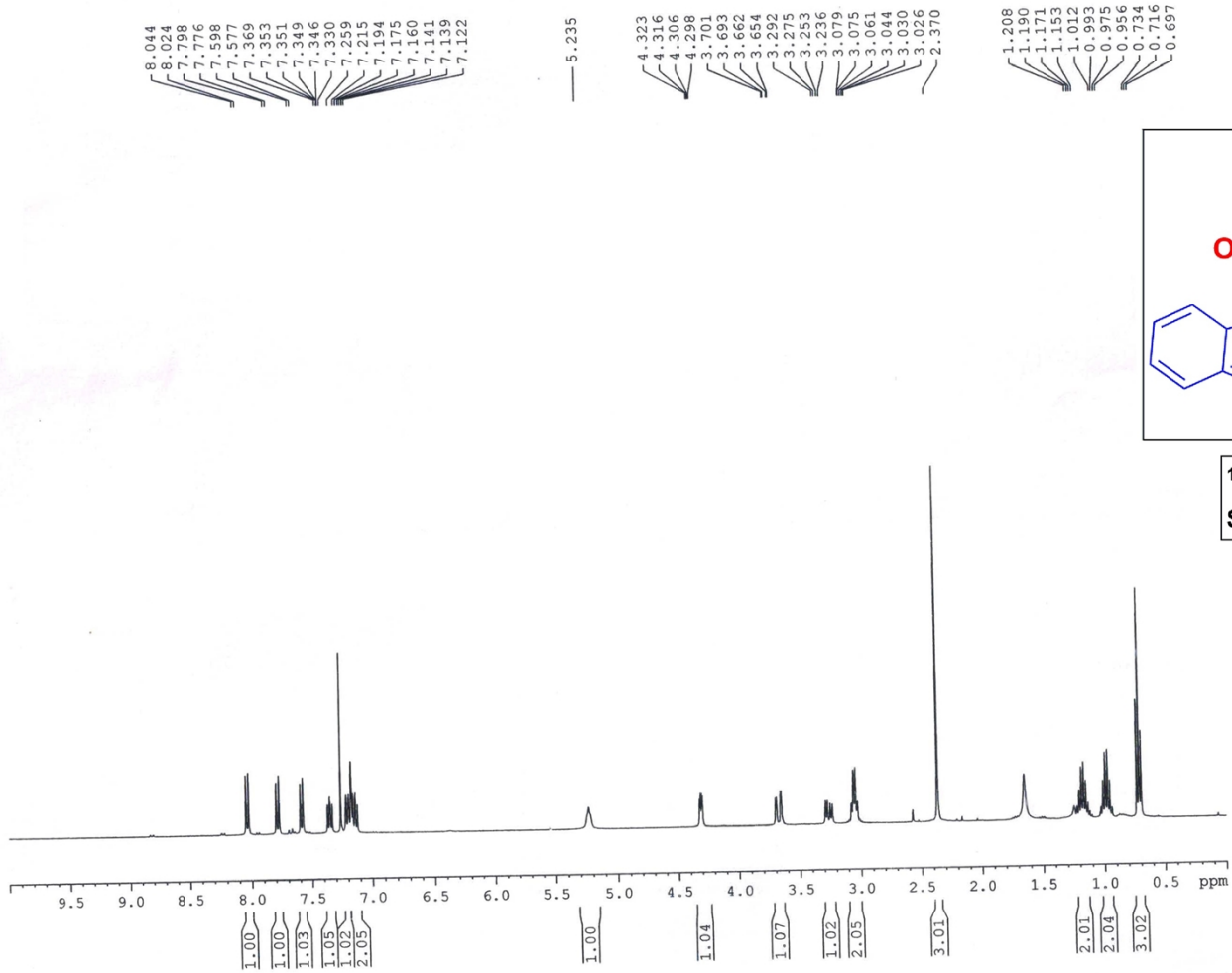
Current Data Parameters
 NAME Dr. A HAJRA-2024-13C
 EXPNO 237
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20240816
 Time 9.37
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 510
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 298.1 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TDO 1

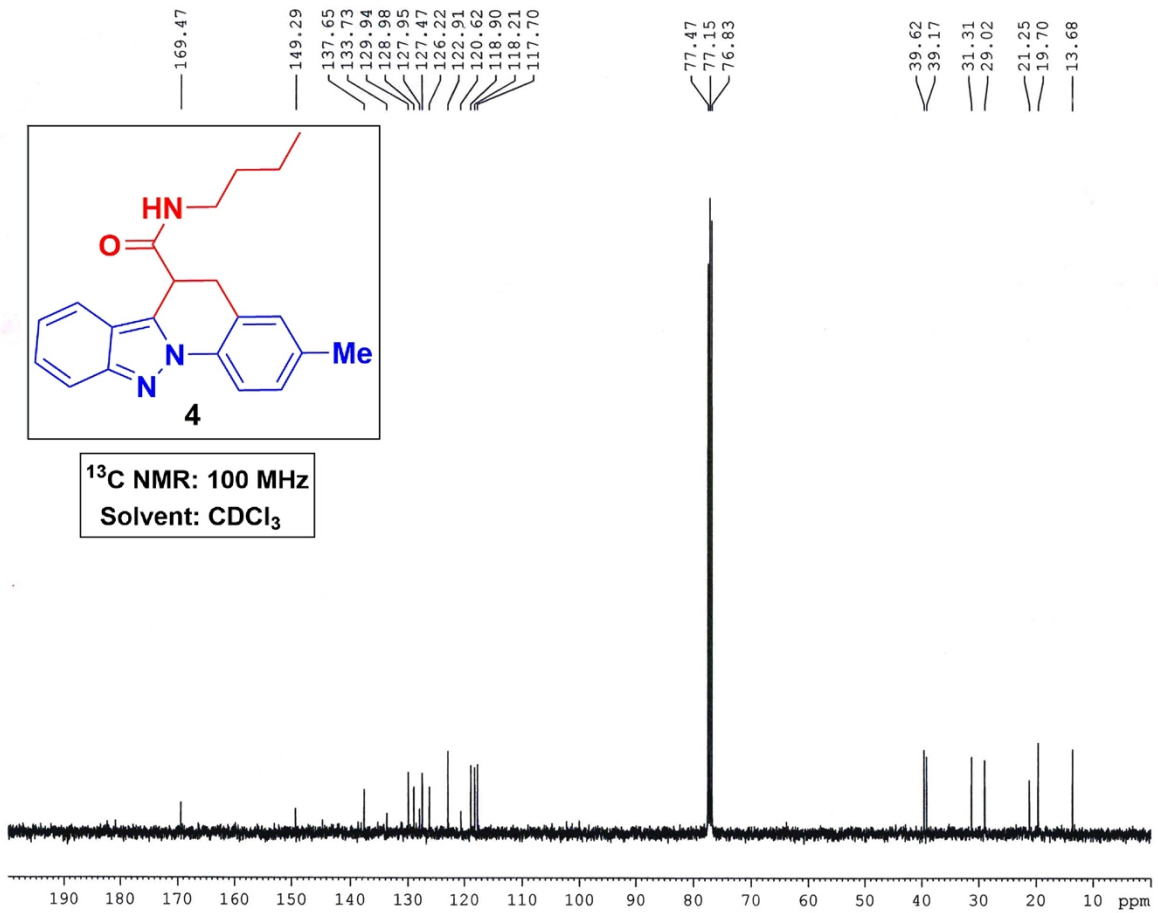
----- CHANNEL f1 -----
 SFO1 100.6278588 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

----- CHANNEL f2 -----
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG[2] waltz16
 PCPD2 90.00 usec
 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

F2 - Processing parameters
 SI 16384
 SF 100.6177844 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



¹H NMR: 400 MHz
Solvent: CDCl₃



Current Data Parameters
 NAME Dr. A HAJRA-2024-13C
 EXPNO 58
 PROCNO 1

F2 - Acquisition Parameters
 Date 20240308
 Time 11.12
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 32768
 SOLVENT CDCl3
 NS 320
 DS 2
 SWH 24038.461 Hz
 FIDRES 0.733596 Hz
 AQ 0.6815744 sec
 RG 186.42
 DW 20.800 usec
 DE 6.50 usec
 TE 294.6 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

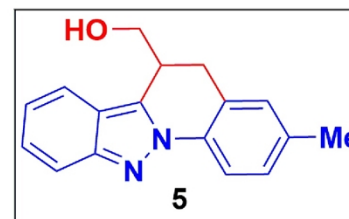
----- CHANNEL f1 -----
 SFO1 100.6278568 MHz
 NUC1 13C
 P1 8.90 usec
 PLW1 54.00000000 W

----- CHANNEL f2 -----
 SFO2 400.1516006 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 90.00 usec
 PLW2 12.00000000 W
 PLW12 0.32231000 W
 PLW13 0.16212000 W

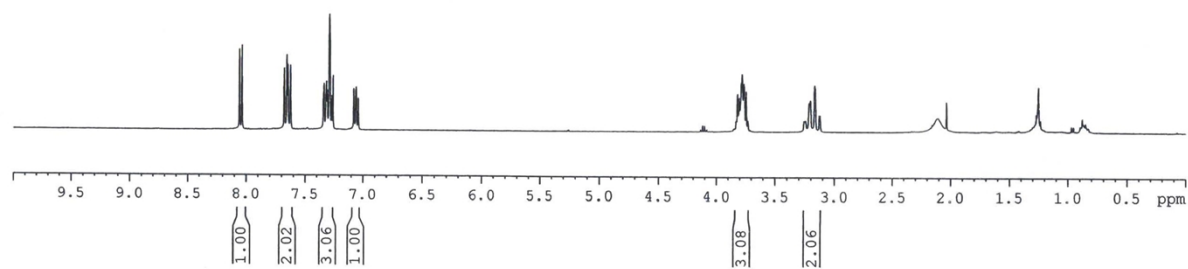
F2 - Processing parameters
 SI 16384
 SF 100.6177858 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

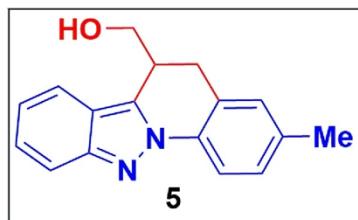
8.058
8.037
7.678
7.656
7.647
7.625
7.342
7.337
7.320
7.315
7.309
7.291
7.271
7.260
7.079
7.061
7.059
7.042

3.831
3.820
3.812
3.805
3.796
3.791
3.787
3.780
3.768
3.764
3.761
3.743
3.729
3.256
3.245
3.215
3.204
3.168
3.163
3.128
3.123

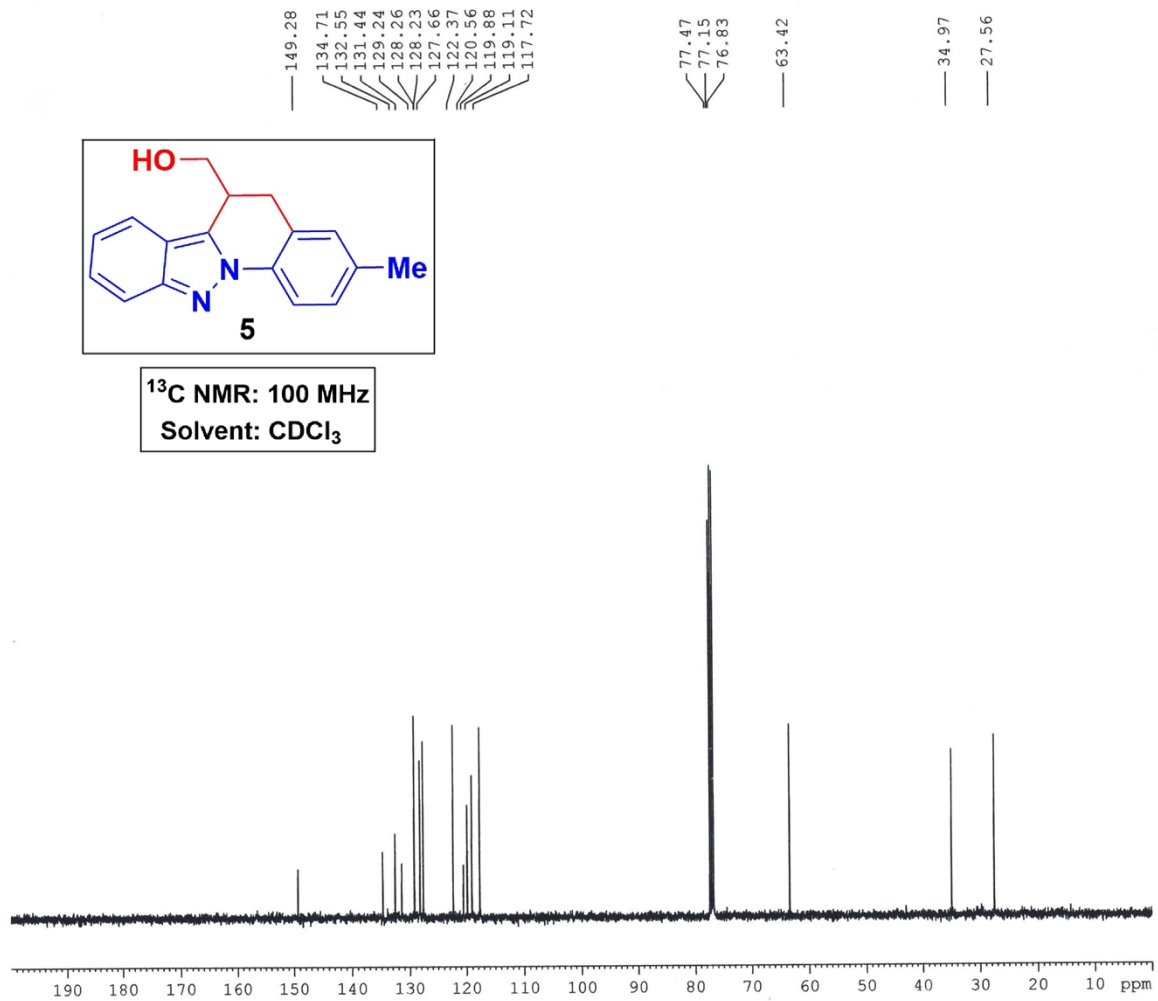


¹H NMR: 400 MHz
Solvent: CDCl₃





¹³C NMR: 100 MHz
Solvent: CDCl₃



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Current Data Parameters
NAME      Dr. A HAJRA-2024-13C
EXPNO    62
PROCNO   1

F2 - Acquisition Parameters
Date_    20240313
Time     17.58
INSTRUM  spect
PROBHD   5 mm PABBO BB/
PULPROG  zgpg30
TD       32768
SOLVENT  CDCl3
NS       280
DS       2
SWH      24038.461 Hz
FIDRES   0.733596 Hz
AQ       0.6815744 sec
RG       186.42
DW       20.800 usec
DE       6.50 usec
TE       295.5 K
D1       2.0000000 sec
D11      0.0300000 sec
TD0      1

===== CHANNEL f1 =====
SFO1     100.6278588 MHz
NUC1      13C
P1       8.90 usec
PLW1     54.0000000 W

===== CHANNEL f2 =====
SFO2     400.1516006 MHz
NUC2      1H
CPDPRG[2] waltz16
PCPD2    90.00 usec
PLW2     12.0000000 W
PLW12    0.32231000 W
PLW13    0.16212000 W

F2 - Processing parameters
SI       16384
SF       100.6177873 MHz
WDW      EM
SSB      0
LB       1.00 Hz
GB       0
PC       1.40

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