Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.
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Efficient and metal Free synthesis of 2-aroyl 7-azaindoles via thermally induced denitrogenative intramolecular annulation of 1,2,3,4-tetrazolopyridines

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Supporting Information

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1. General Information

Reagents: All commercial reagents and KSM used in this study were purchased from Sigma-Aldrich, BLD Pharmatech India, and Thermo Fischer Scientific.

Solvents: All solvents used in this study were purchased from Finar India.

Reaction: Unless otherwise specified, all reaction was performed in oven-dried glassware (Borosil and Biotage seal tube vial)

Chromatography: Thin layer chromatography (TLC) was carried out on a silica gel 60 F254 pre-coated glass plate. Flash chromatography was carried out using silica gel (100-200mesh, Rankem) eluting with a mixture of n-Hexane and ethyl acetate. **LCMS** were recorded in Water Acquity UPLC- H Class equipped with PDA and attached with QDa detector, Column temperature: 30°C, Auto sampler temperature: 15°C,Mobile Phase A : 0.1 % Formic acid in Milli Q water (pH= 2.70), Mobile Phase B : 0.1% Formic acid in Milli Q water : Acetonitrile (10:90), Mobile phase gradient details: T = 0 min (97% A, 3% B) flow : 0.8 mL/min; T = 0.75 min (97% A, 3% B) flow : 0.8 mL/min; gradient to T = 2.7 min (2% A, 98% B) flow : 0.8 mL/min; gradient to T = 3 min (0% A, 100% B) flow : 1mL/min; T = 3.5 min (0% A, 100% B) flow : 1 mL/min; gradient to T= 3.51 min (97% A, 3% B) flow : 0.8 mL/min; end of run at T = 4 min (97% A, 3% B), Flow rate: 0.8 mL/min, Run Time:- 4 min.

UV Detection Method: - PDA

Mass parameter:

Probe:-ESI, Mode of Ionisation :- positive and negative, Cone voltage :-10V and 30V, capillary voltage:- 0.8 KV, Extractor Voltage:- 1KV, Rf Lens:- 0.1,Temperature of source:- 120°C,Temperature of Probe:- 600°C, Cone Gas Flow:- Default , Desolvation Gas flow:- Default

NMR Spectroscopy: ^{1}H and ^{13}C NMR were recorded in Bruker Advance Neo Ascend 400MHz using $CDCl_3$ and DMSO-*d6.* Data were reported as follow: s = singlet, d = doublet, t = triplet, dd= doublet of doublets, m = multiplate and br s = broad singlet.

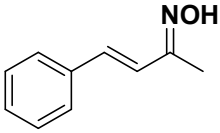
Elemental analysis: Elemental analysis was carried out in the Elementar Vario Micro Cube instrument.

X-Ray: X-ray diffraction data were collected on a Bruker D8 QUEST diffractometer.

IR: IR spectrums were recorded using Shimadzu-IR spirit.

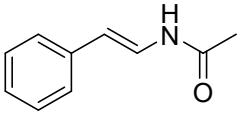
2. Experimental procedures

Step-1 Synthesis of (2E,3E)-4-phenylbut-3-en-2-one oxime (i)[1]



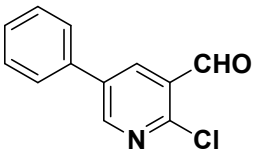
To a stirred solution of (E)-4-phenylbut-3-en-2-one (CAS # 1896-62-4) (80g, 547.23 mmol) in EtOH (800ml) was added pyridine (108.12g, 1360.91 mmol) at room temperature. After 15 min of stirring hydroxylamine hydrochloride (50.47g, 820.84 mmol) was added and the reaction mixture was stirred at 60°C for 2 h. The reaction mixture was then diluted with water, extracted with ethyl acetate (2 × 750 mL), and washed with 1N HCl solution (300ml). The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under a reduced vacuum to afford CMP-i. off-white solid (77g, 87%). **m/z:** 162.02 $(M+H)^+$ **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.56-7.50 (m, 1H), 7.37-7.22 (m, 5H), 7.22-7.17 (m, 1H), 6.10 (d, J = 14.4Hz, 1H), 2.13 (s, 3H).

Step-2 Synthesis of (E)-N-styrylacetamide ii[2]



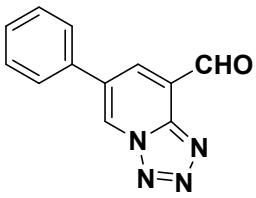
CMP-i (77g, 477.66 mmol), $Zn(OTf)_2$ (34.77g, 95.53 mmol), and phthalic anhydride (7.07g, 47.76 mmol) were dissolved in acetonitrile (700mL) and the reaction mixture was heated at 55 °C for 12 h. After the indicated time, the reaction mixture was diluted with water and extracted in ethyl acetate (2 × 750 mL). The organic layer was then evaporated and the residue was purified by column chromatography (0-10% ethyl acetate: hexane) to afford CMP- ii. Pale yellow solid. (43 g, 55%); **m/z:** 162.01 (M+1) **^{1}H NMR (400MHz, $CDCl_3$)** δ 7.56-7.53 (m, 1H), 7.39 (br s, 1H), 7.37-7.28 (m, 3H), 7.22-7.17 (m, 2H), 6.12 (d, J= 14.4Hz, 1H), 2.13 (s, 3H)

Step-3 Synthesis of 2-chloro-5-phenylnicotinaldehyde (1)[3]



Three neck RBF equipped with a condenser and magnetic stirrer were added DMF (40mL) and cooled to 0 °C. $POCl_3$ (100mL) was added dropwise with stirring over a period of 1 h. The reaction mixture was then stirred at room temperature for 1 h followed by portion-wise addition of compound ii (20g, 124.20 mmol). The resulting brown reaction mixture was then heated at 90 °C for 2 h. After completion of the reaction, the reaction mixture was cooled and poured into crushed ice water, neutralized with solid NaOAc. The crude solid was filtered and purified via normal phase column chromatography (0-7% ethyl acetate: hexane) to afford 2-chloro-5-phenylnicotinaldehyde as a pale yellow solid (13g, 48%). **m/z:** 218.01 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 10.52 (s, 1H), 8.84 (d, J = 2.4Hz, 1H), 8.43 (d, J = 2.8Hz, 1H), 7.64-7.61 (m, 2H), 7.56-7.28 (m, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 189.53, 151.84, 150.42, 136.23, 135.60, 134.60, 129.27, 128.98, 128.35, 127.02. Anal. Calcd for $C_{12}H_8ClNO$: C, 66.22; H, 3.70; N, 6.44 Found; C, 66.72; H, 3.80; N, 6.52.

Step-4 Synthesis of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (2)

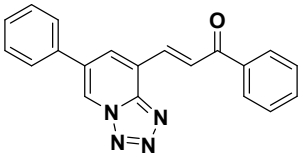


An oven-dried vial equipped with a stir bar was charged with CMP-1 (3g, 13.81 mmol), NaN_3 (27.63 mmol), and DMF (30 mL) and heated at 55 °C for 6h. After an indicated time, the reaction mixture was poured into crushed ice water and the resulting solid was filtered, washed with brine solution, and dried under vacuum to afford compound 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde. Brown solid (2.6g, 84.69%). **m/z:** 224.05 (M+1), **^{1}H NMR (400MHz, $CDCl_3$)** δ 10.827 (s, 1H), 9.21 (d, *J*= 1.6Hz, 1H), 8.57 (d, *J*= 1.6Hz, 1H), 7.71-7.61 (m, 2H), 7.59-7.57 (m, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 187.89, 162.26, 145.05, 138.09, 133.60, 129.62, 129.30, 127.63, 127.35, 123.14. Anal. Calcd for $C_{12}H_8N_4O$: C, 64.28; H, 3.60; N, 24.99 Found; C, 63.86; H, 3.48; N, 24.83.

General procedure-A for Synthesis of substituted chalcones (4a-n)

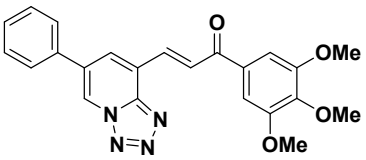
To a well-stirred solution of compound-2 (1 mmol) and appropriate acetophenone (**3a-n**, 1 mmol) in MeOH (5mL) was added 10% KOH (0.2mL) and stirred at room temperature for an appropriate time (1-2h). After completion of the reaction as indicated by TLC, the reaction mixture was poured into crushed ice water and acidified with 1N HCl (pH 4). The resulting solid was filtered and recrystallized in ethanol to afford Chalcones (4a-n).

(E)-1-phenyl-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4a).



Compound 6a was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2 g, 0.89 mmol) and acetophenone (3a, 0.107g, 0.89mmol) as per above general procedure-A to give (E)-1-phenyl-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as a grey solid (4a, 0.2g, 68%). **m/z**: 327.10 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.11 (d, *J*= 15.6Hz, 1H), 8.98 (d, *J*= 1.6Hz, 1H), 8.25-8.23 (m, 2H), 8.08 (d, *J* = 1.2Hz, 1H), 8.03 (d, *J* =15.6Hz, 1H), 7.69-7.65 (m, 3H), 7.62-7.54 (m, 5H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 189.17, 146.13, 137.17, 136.83, 135.24, 134.08, 133.59, 130.28, 129.22, 129.01, 128.41, 128.17, 127.40, 123.84, 122.80. Anal. Calcd for $C_{20}H_{14}N_4O$: C, 73.61; H, 4.32; N, 17.17 Found; C, 74.01; H, 4.48; N, 17.26.

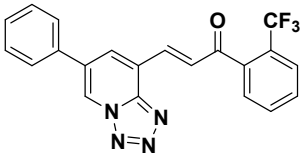
((E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(3,4,5-trimethoxyphenyl) prop-2-en-1-one (4b).



Compound 6b was prepared using general procedure-A from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (3b, 0.15 g, 0.68 mmol) and 3′,4′,5′-trimethoxyacetophenone (0.187g, 0.68mmol) as per above general procedure-A to give ((E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one as a white solid (**4b**, 0.18g, 67%). **m/z**: 417.34 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.10 (d, *J*= 15.6Hz, 1H), 8.98 (d, *J*= 1.6Hz, 1H), 8.079 (s, 1H), 7.98 (d, *J*= 15.2Hz, 1H), 7.69-7.67 (m, 2H), 7.60-7.56 (m, 3H), 7.505 (s, 2H), 4.036 (s, 6H), 3.99 (s, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 188.21, 152.99, 152.78, 146.20, 145.81, 142.39, 141.86, 136.56, 134.86, 134.77,

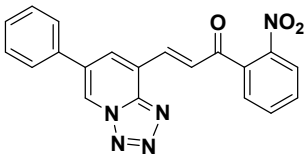
134.12, 132.91, 132.53, 131.94, 130.28, 130.11, 129.31, 129.23, 129.13, 128.99, 128.40, 127.99, 127.42, 127.31, 60.25, 60.11, 56.17, 556.07 Anal. Calcd for $C_{23}H_{20}N_4O_4$: C, 66.34; H, 4.84; N, 13.45 Found; C, 66.29; H, 4.75; N, 13.40.

(E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(2-(trifluoromethyl)phenyl) prop-2-en-1-one (4c).



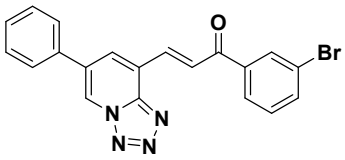
Compound 4c was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2 g, 0.89 mmol) and 2'-(trifluoromethyl)acetophenone (3c ,0.167g, 0.89mmol) as per above general procedure-A to give (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one as off white solid (4c, 0.23g, 65%). **m/z**: 395.22 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.98 (s, 1H), 8.45 (d, *J*= 16Hz, 1H), 8.039 (s, 1H), 7.84-7.78 (m, 3H), 7.74-7.66 (m, 5H), 7.64-7.55 (m, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 194.38, 145.80, 140.25, 137.91, 136.38, 133.87, 132.71, 132.35, 130.85, 130.11, 129.17, 128.44, 127.31, 126.89, 126.85, 126.40, 126.08, 125.08, 124.30, 122.36, 122.16. Anal. Calcd for $C_{21}H_{13}F_3N_4O$: C, 63.96; H, 3.32; N, 14.21 Found; C, 63.87; H, 3.27; N, 14.14.

(E)-1-(2-nitrophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4d).



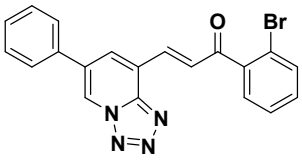
Compound 4d was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.15g, 0.68mmol) and 2'-Nitroacetophenone (3d, 0.11g, 0.68mmol) as per above general procedure-A to give (E)-1-(2-nitrophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as reddish brown solid (4d, 0.13g, 57%). m/z: 372.25 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.79 (s, 1H), 8.702 (s, 1H), 8.30 (d, *J*= 8.4Hz, 1H), 8.17 (d, *J*= 16.4Hz, 1H), 7.99-7.92 (m, 1H), 7.90—7.89 (m, 3H), 7.81-7.76 (m, 2H), 7.57-50 (m, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 192.39, 138.92, 136.13, 134.96, 134.79, 133.91, 131.83, 131.73, 130.12, 129.16, 129.13, 129.04, 127.31, 124.76, 124.21, 122.18. Anal. Calcd for $C_{20}H_{13}N_5O_3$: C, 64.69; H, 3.53; N, 18.86 Found; C, 64.52; H, 3.39; N, 18.79.

(E)-1-(3-bromophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4e).



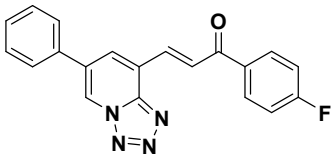
Compound 4e was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.15g, 0.68mmol) and 3-bromoacetophenone (3e, 0.13g, 0.68mmol) as per above general procedure-A to give (E)-1-(3-bromophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4e, 0.18g, 67%), **m/z**: 406.20 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.04 (s, 1H), 9.00-8.99 (m, 1H), 8.33-8.32 (m, 1H), 8.18 (d, *J*= 7.6Hz, 1H), 8.09 (s, 1H), 8.06 (d, *J*= 15.2Hz, 1H), 7.80-7.78 (m, 1H), 7.69-7.68 (m, 2H), 7.63-7.50 (m, 3H), 7.48-7.46 (m, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 188.03, 131.36, 130.81, 130.29, 129.23, 129.15, 127.70, 127.50, 127.43, 124.05, 122.63, 122.45. Anal. Calcd for $C_{20}H_{13}BrN_4O$: C, 59.28; H, 3.23; N, 13.83 Found; C, 59.14; H, 3.18; N, 13.77.

(E)-1-(2-bromophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4f)



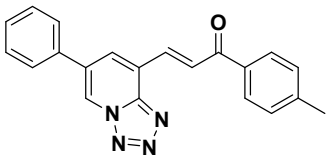
Compound 4f was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.15g, 0.68mmol) and 2-bromoacetophenone (3f, 0.13g, 0.68mmol) as per above general procedure-A to give (E)-1-(2-bromophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4f, 0.18g, 66%). **m/z**: 406.15 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.97 (d, J = 5.6Hz, 1H), 8.58 (d, J = 16Hz, 1H), 8.04 (s, 1H), 7.83 (d, J= 15.6Hz, 1H), 7.73 (dd, J_1=1.2Hz and J_2=1.2Hz, 1H), 7.67-7.63 (m, 2.5H), 7.61-7.55 (m, 3.5H), 7.50-7.49 (m, 1H), 7.48-7.46 (m, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 194.10, 145.85, 140.26, 139.12, 136.18, 133.90, 133.29, 133.23, 132.00, 130.15, 129.27, 129.11, 129.14, 128.02, 127.34, 124.19, 122.53, 118.60. Anal. Calcd for $C_{20}H_{13}BrN_4O$: C, 59.28; H, 3.23; N, 13.83 Found; C, 59.20; H, 3.16; N, 13.72.

(E)-1-(4-fluorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4g)



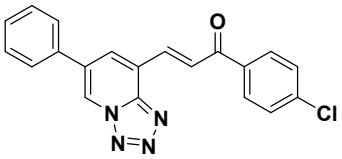
Compound 4g was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 4′-Fluoroacetophenone (3g, 0.12g, 0.89mmol) as per above general procedure-A to give (E)-1-(4-fluorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4g, 0.19g, 63%). **m/z**: 345.02 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.10 (d, J= 15.6Hz, 1H), 8.99 (d, J= 1.6Hz, 1H), 8.30-8.27 (m, 2H), 8.086 (s, 1H), 8.02 (d, J= 15.6Hz, 1H), 7.68 (dd, J_1=1.6Hz and J_2=1.2Hz, 2H), 7.62-7.7.55 (m, 3H), 7.26-7.24 (m, 2H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 187.63, 166.47, 163.96, 146.11, 136.88, 135.16, 134.06, 133.86, 132.77, 132.68, 131.49, 131.40, 130.26, 129.21, 129.12, 128.22, 128.16, 127.84, 127.39, 126.90. Anal. Calcd for $C_{20}H_{13}FN_4O$: C,69.76; H, 3.81; N, 16.27 Found; C, 69.65; H, 3.69; N, 15.96.

(E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(p-tolyl)prop-2-en-1-one (4h)



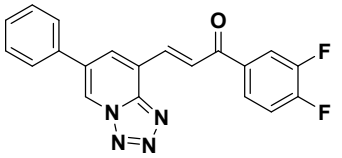
Compound 4h was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 4′-methylacetophenone (3h, 0.12g, 0.89mmol) as per above general procedure to give-A (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(p-tolyl)prop-2-en-1-one as off white solid (4h, 0.15g, 60%). **m/z**: 341.15 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.11 (d, J= 15.6Hz, 1H), 8.97 (d, J= 1.2Hz, 1H), 8.15 (d, J= 8Hz, 2H), 8.072 (s, 1H), 8.01 (d, J= 15.6Hz, 1H), 7.68 (dd, J_1=1.6Hz and J_2=1.2Hz, 2H), 7.62-7.7.55 (m, 3H), 7.38 (d, J= 8Hz, 2H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 188.53, 146.16, 144.17, 136.49, 135.08, 134.68, 134.11, 130.29, 129.66, 129.22, 129.13, 128.57, 128.19, 127.42, 123.77, 122.86, 21.25. Anal. Calcd for $C_{21}H_{16}N_4O$: C, 74.10; H, 4.74; N, 16.46 Found; C, 74.01; H, 4.36; N, 16.41.

(E)-1-(4-chlorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4i)



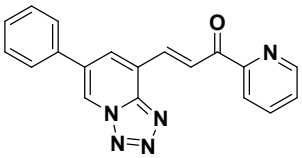
Compound 4i was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 4′-chloroacetophenone (3i, 0.14g, 0.89mmol) as per above general procedure-A to give (E)-1-(4-chlorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4i, 0.23g, 69%). **m/z**: 361.70 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.07 (d, J = 15.6Hz, 1H), 8.99 (s, 1H), 8.18 (d, J= 8.4Hz, 2H), 8.08 (s, 1H), 8.01 (d, J = 15.2Hz, 1H), 7.68-7.60 (m, 2H), 7.58-7.47 (m, 5H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 188.10, 146.11, 138.51, 137.22, 135.80, 135.34, 134.06, 130.23, 130.27, 129.23, 129.14, 127.75, 127.39, 123.96, 122.67. Anal. Calcd for $C_{20}H_{13}ClN_4O$: C, 66.58; H, 3.63; N, 15.53 Found; C, 65.45; H, 3.59; N, 15.41.

(E)-1-(3,4-difluorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4j)



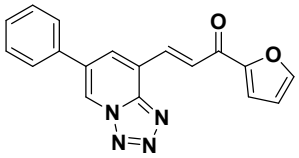
Compound 4j was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 3′,4’-difluoroacetophenone (3j, 0.14g, 0.89mmol) as per above general procedure-A to give (E)-1-(3,4-difluorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4j, 0.21g, 66%). **m/z**: 363.22 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.06 (d, J= 15.6Hz, 1H), 9.00 (s, 1H), 8.09-8.05 (m, 3H) 8.033-7.994 (d, J= 15.6Hz, 1H), 7.68 (dd, J_1 = 1.6Hz and J_2 = 1.2Hz, 2H), 7.63-7.54 (m, 3H), 7.42-7.35 (m, 1H); **^{13}C NMR 1400MHz, DMSO-*d6*)** δ 186.94, 151.59, 151.47, 151.02, 150.89, 148.55, 148.42, 149.17, 137.29, 135.01, 134.68, 134.07, 130.29, 129.23, 129.15, 127.42-127.38, 126.43-126.32, 124.07, 122.56, 118.46, 118.28, 117.7, 117.56. Anal. Calcd for $C_{20}H_{12}F_2N_4O$: C, 66.30; H, 3.34; N, 15.46 Found; C, 66.16; H, 3.19; N, 15.39.

(E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(pyridin-2-yl)prop-2-en-1-one (4k).



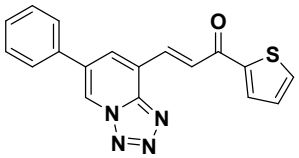
Compound 4k was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 2’-acetylpyridine (3k, 0.11g, 0.89mmol) as per above general procedure-A to give (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(pyridin-2-yl)prop-2-en-1-one as brown solid (4k, 0.21g, 72%). **m/z**: 327.22 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 9.47 (d, J = 16Hz, 1H), 8.98 (d, J = 0.8Hz, 1H), 8.87 (d, J = 4Hz, 1H) 8.24 (d, J = 7.6Hz, 1H), 8.16 (s, 1H), 8.124 (s, 1H), 7.93 (m, 1H), 7.68 (d, J = 7.2Hz, 2H), 7.62-7.54 (m, 4H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 189.20, 153.11, 149.41, 149.09, 145.93, 137.84, 137.52, 137.23, 136.49, 134.05, 130.21, 129.23, 129.12, 127.94-127.78, 127.37, 123.80, 123.05, 122.69, 121.31. Anal. Calcd for $C_{19}H_{13}N_5O$: C, 69.71; H, 4.00; N, 21.39 Found; C, 69.61; H, 3.92; N, 21.45.

(E)-1-(furan-2-yl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4l)



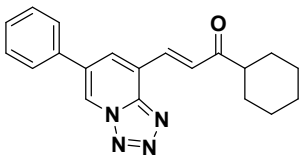
Compound 4l was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 2-Furyl methyl ketone (3l, 0.1g, 0.89mmol) as per above general procedure-A to give (E)-1-(furan-2-yl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4l, 0.2g, 70%). **m/z**: 317.16 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.98 (d, J = 1.2Hz, 1H), 8.88 (d, J = 16.4Hz, 1H) 8.07 (s, 1H), 8.05 (d, J = 1.2Hz, 1H) 7.77 (d, J = 1.2Hz, 1H), 7.68-7.62 (m, 2H), 7.61-7.55 (m, 4H), 6.99-6.68 (m, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 176.62, 152.83, 148.79, 146.06, 135.98, 135.41, 134.07, 130.26, 129.23, 127.89, 126.90, 123.86, 122.61, 119.52, 113.22. Anal. Calcd for $C_{18}H_{12}N_4O_2$: C, 68.35; H, 3.82; N, 17.71 Found; C, 68.27; H, 3.85; N, 17.75.

(E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(thiophen-2-yl)prop-2-en-1-one (4m).



Compound 4m was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and 2-acetylthiophene (3m, 0.11g, 0.89mmol) as per above general procedure-A to give (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(thiophen-2-yl)prop-2-en-1-one as off white solid (4m, 0.16g, 54%). m/z: 333.22 $(M+H)^+$, **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.98 (s, 1H), 8.97 (d, J = 14Hz, 1H) 8.17 (dd, J_1 =1.2Hz and J_2 = 0.8Hz, 1H), 8.07 (d, J= 1.2Hz, 1H) 8.01 (d, J= 15.6Hz, 1H), 7.8 (dd, J_1 = 0.8Hz and J_2 =1.2Hz, 1H), 7.68-7.66 (m, 2H), 7.62-7.55 (m, 4H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 181.30, 146.20, 145.85, 144.71, 136.29, 136.01, 135.06, 134.12, 133.73, 130.30, 129.24, 128.07, 127.43, 123.93, 122.63. Anal. Calcd for $C_{18}H_{12}N_4OS$: C, 65.05; H, 3.64; N, 16.86; S, 9.65 Found; C, 64.89; H, 3.58; N, 16.90; S, 9.60.

(E)-1-cyclohexyl-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4n)

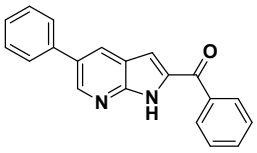


Compound 4n was prepared from a mixture of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (0.2g, 0.89mmol) and cyclohexyl methyl ketone (3n, 0.11g, 0.89mmol) as per above general procedure-A to give (E)-1-cyclohexyl-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one as off white solid (4n, 0.21g, 70%). **m/z**: 305.35 (M+1), **^{1}H NMR (400MHz, $CDCl_3$)** δ 8.95 (d, J = 1.2Hz, 1H), 8.26 (d, J = 15.6Hz, 1H) 8.00 (s, 1H), 7.80 (d, J = 16Hz, 1H) 7.66-7.61 (m, 2H), 7.60-754 (m, 3H), 2.76-2.70 (m, 1H), 2.05-2.02 (m, 2H), 1.98-1.86 (m, 2H), 1.77-1.74 (m, 1H), 1.59-1.35 (m, 4H), 1.35-1.27 (m, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 202.32, 145.93, 135.25, 134.96, 134.07, 131.03, 130.16, 129.21, 129.12, 127.34, 123.60, 122.79, 48.45, 28.09, 25.47, 25.10. Anal. Calcd for $C_{20}H_{20}N_4O$: C, 72.27; H, 6.06; N, 16.86 Found; C, 72.18; H, 5.99; N, 16.80.

General procedure-B for Synthesis of 7-Azaindole derivatives (5a-n)

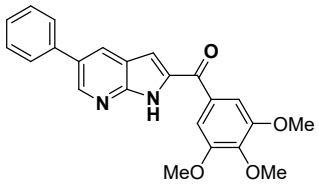
An oven-dried seal tube containing appropriate chalcone (4a-n) and Dowtherm-A was heated at 210-220 ^{o}C for 1-2h. After completion of the reaction as indicated by TLC, the reaction mixture was allowed to cool at room temperature, and the obtained solid was filtered, washed with hexane, and recrystallized using ethanol to afford the required 7-Azaindole (5a-n)

Phenyl(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5a)



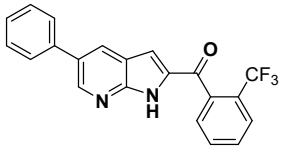
Compound **5a** was prepared from (E)-1-phenyl-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (**4a**, 0.2g, 0.61mmol) and Dowtherm-A (10 mL) as per above general procedure-B. White solid (0.13 g, 73%); mp >350 °C **m/z**: 299.20 $(M+H)^+$,**^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.66 (s, 1H), 8.79 (d, J = 1.2Hz, 1H), 8.42 (d, J =2Hz, 1H), 7.96 (d, J = 7.6Hz, 2H), 7.73 (t, J = 7.6Hz, 3H) 7.62 (t, J =7.2Hz, 2H), 7.52 (t, J=7.6Hz, 2H), 7.40 (t, J=7.2Hz, 1H), 7.16 (s, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 186.68, 148.88, 146.94, 138.27, 137.59, 135.10, 132.56, 129.58, 129.07, 128.66, 127.28, 126.94, 119.25, 110.97. IR (KBr, ν_{max}, cm^{-1}): 3029, 2788, 1645, 1497, 1315, 944. Anal. Calcd for $C_{20}H_{14}N_2O$: C, 80.52; H, 4.73; N, 9.39 Found; C, 80.47; H, 4.79; N, 9.42.

(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)(3,4,5-trimethoxyphenyl)methanone (5b)



Compound **5b** was prepared (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(3,4,5-trimethoxyphenyl)prop-2-en-1-one (4b, 0.15g, 0.38mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.11 g, 77%); mp >350 °C; **m/z**: 389.31 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.61 (s, 1H), 8.78 (d, J = 2.4Hz, 1H), 8.41 (d, J = 2Hz, 1H), 7.75 (d, J = 7.2Hz, 2H), 7.52 (t, J=7.6Hz, 2H), 7.40 (t, J = 7.6Hz, 1H), 7.29 (s, 1H), 7.25 (s, 2H), 3.89 (s, 6H), 3.80 (s, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 185.53, 152.71, 148.81, 146.74, 141.32, 138.28, 135.07, 132.66, 129.46, 129.11, 129.06, 127.24, 126.88, 119.27, 110.63, 106.73, 60.18, 56.07. IR (KBr, ν_{max}, cm^{-1}): 3023, 2834, 1634, 1495, 1335, 1134, 1004. Anal. Calcd for $C_{23}H_{20}N_2O_4$: C, 71.12; H, 5.19; N, 7.21 Found; C, 71.00; H, 4.98; N, 7.06.

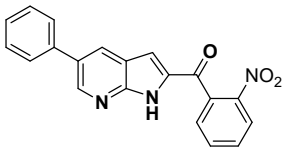
(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)(2-(trifluoromethyl)phenyl)methanone (5c)



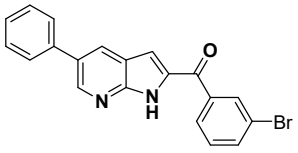
Compound **5c** was prepared (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(2-(trifluoromethyl)phenyl)prop-2-en-1-one (4c, 0.2g, 0.50mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.13 g, 64%); mp >350 °C; **m/z**: 367.22 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.84 (s, 1H), 8.81 (d, J = 2Hz, 1H), 8.36 (d, J = 2.4Hz, 1H), 7.97 (d, J = 1.6Hz, 1H), 7.83 (m, 3H), 7.72 (d, J = 1.2Hz, 2H), 7.50 (t, J=7.6Hz, 2H), 7.40 (t, J=7.6Hz, 2H), 6.82 (d, J = 2.4Hz, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 186.33, 149.23, 147.70, 138.10, 136.97, 136.95, 135.53, 132.27, 130.80, 129.79, 129.38, 129.04, 128.92, 127.31, 126.92, 126.77, 126.72, 126.67, 126.35, 126.04, 125.10, 122.38, 119.09,

112.38. IR (KBr, ν_{max}, cm^{-1}): 2956, 2851, 1643, 1491, 1316, 1137, 1003. Anal. Calcd for $C_{21}H_{13}F_3N_2O$: C, 68.85; H, 3.58; N, 7.65 Found; C, 68.76; H, 3.48; N, 7.52.

(2-nitrophenyl)(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5d)



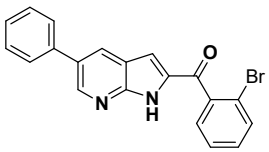
Compound **5d** was prepared E)-1-(2-nitrophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4d, 0.1g, 0.27mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Brown solid (0.062 g, 68%); mp >350 °C; **m/z**: 344.27 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.87 (s, 1H), 8.80 (d, *J* = 2.4Hz, 1H), 8.33 (d, *J* = 2Hz, 1H), 8.29 (m, 1H), 8.01 (t, *J*=7.6Hz, 1H), 7.90 (m, 2H), 7.72 (d, *J* = 7.2Hz, 2H), 7.50 (t, *J*=7.2Hz, 2H), 7.39 (t, *J* = 7.2Hz, 1H), 6.85 (d, *J* = 2Hz, 1H); **^{13}C NMR (400MHz, DMSO-*d6*)** δ 184.49, 149.19, 147.53, 146.83, 138.10, 135.22, 134.58, 134.19, 131.74, 129.79, 129.52, 129.26, 129.05, 127.32, 126.94, 124.75, 122.72, 119.08, 112.16, 110.73. IR (KBr, ν_{max}, cm^{-1}): 3029, 2836, 1651, 1524, 1497, 1354, 1005. Anal. Calcd for $C_{20}H_{13}N_3O_3$: C, 69.97; H, 3.82; N, 12.24 Found; C, 68.81; H, 3.73; N, 12.14.



(3-bromophenyl)(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5e)

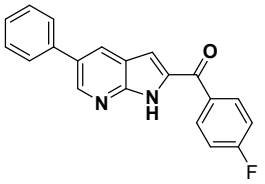
Compound 5**e** was prepared (E)-1-(3-bromophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4e, 0.1g, 0.25mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.070 g, 75%); mp >350 °C; **m/z**: 378.18 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.72 (s, 1H), 8.80 (d, *J* = 2Hz, 1H), 8.44 (d, *J* = 2Hz, 1H), 8.50 (s, 1H), 7.96 (t, *J* = 8.4Hz, 2H), 7.74 (d, *J* = 7.2Hz, 2H), 7.59 (t, *J* = 8Hz, 1H), 7.52 (t, *J*= 7.6Hz, 2H), 7.40 (t, *J* = 7.2Hz, 1H), 7.19 (s, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 185.15, 149.0, 147.27, 139.68, 138.20, 135.14, 134.66, 131.33, 130.89, 129.66, 129.31, 129.09, 128.09, 127.32, 126.93, 121.88, 119.22, 111.49. IR (KBr, ν_{max}, cm^{-1}): 3029, 2886, 1645, 1418, 1251, 1009, 693. Anal. Calcd for $C_{20}H_{13}BrN_2O$: C, 63.38; H, 3.47; N, 7.43 Found; C, 63.30; H, 3.41; N, 7.31.

(2-bromophenyl)(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5f)



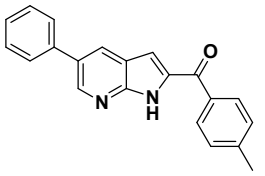
Compound **5f** was prepared (E)-1-(2-bromophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4f, 0.1g, 0.25mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.063 g, 68%); mp >350 °C; **m/z**: 378.10 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.81 (s, 1H), 8.80 (d, *J* = 2Hz, 1H), 8.37 (d, *J* = 2Hz, 1H), 7.80 (d, *J* = 7.2Hz, 1H), 7.71 (d, *J* = 7.6Hz, 2H), 7.64 (m, 2H), 7.58 (m, 4H), 7.40 (t, *J*=8.4Hz, 1H), 6.82 (s, 1H); **^{13}C NMR (400MHz, DMSO-*d6*)** δ 186.64, 149.28, 147.62, 139.64, 138.11, 135.21, 133.01, 131.90, 129.74, 129.38, 129.21, 129.05, 127.56, 127.31, 126.92, 119.16, 118.87, 112.34. IR (KBr, ν_{max}, cm^{-1}): 3025, 2837, 1651, 1466, 1305, 1001, 697. Anal. Calcd for $C_{20}H_{13}BrN_2O$: C, 63.68; H, 3.47; N, 7.43 Found; C, 63.49; H, 3.38; N, 7.31.

(4-fluorophenyl)(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5g)



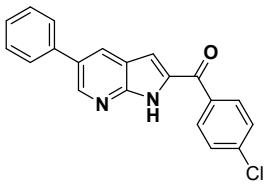
Compound **5g** was prepared (E)-1-(4-fluorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4g, 0.1g, 0.32mmol)and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.056 g, 61%); mp >350 °C; **m/z**: 317.19 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.67 (s, 1H), 8.79 (d, *J* = 2Hz, 1H), 8.41 (d, *J* = 2Hz, 1H), 8.065-8.029 (q, 2H), 7.74 (d, *J* = 7.6Hz, 2H), 7.67 (F coupled, 0.5H), 7.53-7.40 (m, 5H), 7.38 (br F coupled 0.5H), 7.17 (s, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 185.23, 165.88, 163.39, 148.85, 146.97, 140.16, 138.23, 134.92, 134.13, 134.10, 131.95, 131.86, 129.59, 129.11, 129.06, 128.90, 127.39, 127.27, 126.92, 126.66, 119.21, 115.83, 115.61, 110.87. IR (KBr, ν_{max}, cm^{-1}): 3026, 2888, 2831, 1643, 1430, 1296, 1155, 1009. Anal. Calcd for $C_{20}H_{13}FN_2O$: C, 75.94; H, 4.14; N, 8.86 Found; C, 75.82; H, 4.29; N, 9.01.

(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)(p-tolyl)methanone (5h)



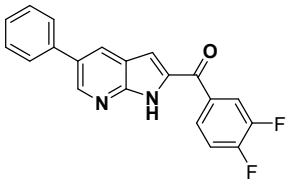
Compound **5h** was prepared (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(p-tolyl)prop-2-en-1-one (4h, 0.13g, 0.38mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.082 g, 66%); mp >350 °C; **m/z**: 313.15 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.61 (s, 1H), 8.78 (d, *J* = 2Hz, 1H), 8.41 (d, *J*=2Hz, 1H), 7.87 (d, *J*=8Hz, 2H), 7.74 (d, *J* = 7.2Hz, 2H), 7.51 (t, *J* = 7.2Hz, 2H), 7.41 (m, 3H), 7.15 (d, *J* = 2Hz, 1H), 2.44 (s, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 186.23, 148.76, 146.7, 142.93, 138.28, 135.21, 134.88, 129.50, 129.19, 129.04, 127.23, 126.90, 119.22, 110.41, 21.15. IR (KBr, ν_{max}, cm^{-1}): 3028, 2834, 2778, 1645, 1430, 1310, 1006. Anal. Calcd for $C_{21}H_{16}N_2O$: C, 80.75; H, 5.16; N, 8.97 Found; C, 80.61; H, 5.02; N, 9.03.

(4-chlorophenyl)(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5i)



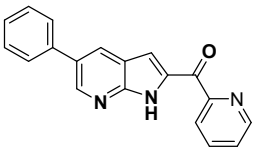
Compound **5i** was prepared from ((E)-1-(4-chlorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4i, 0.12g, 0.33mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.072 g, 65%); mp >350 °C; **m/z**: 333.60 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.69 (s, 1H), 8.80 (d, *J* = 1.6Hz, 1H), 8.42 (d, *J* = 1.6Hz, 1H), 7.97 (d, *J* = 8.4Hz, 2H), 7.72-7.75 (m, 4H), 7.51 (t, *J* = 7.2Hz, 2H), 7.40 (m, 1H), 7.188 (s, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 185.43, 148.91, 147.11, 138.19, 137.43, 136.20, 134.80, 130.92, 129.63, 129.15, 129.06, 128.77, 127.29, 126.92, 119.19, 111.09. IR (KBr, ν_{max}, cm^{-1}): 3029, 2844, 2772, 1648, 1486, 1298, 1004, 835. Anal. Calcd for $C_{20}H_{13}ClN_2O$: C, 72.18; H, 3.94; N, 8.42 Found; C, 72.08; H, 3.83; N, 8.33.

(3,4-difluorophenyl)(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5j)



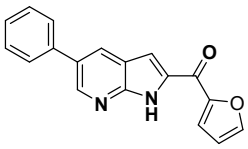
Compound **5j** was prepared from (E)-1-(3,4-difluorophenyl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4j, 0.13g, 0.35mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.085 g, 72%); mp >350 °C; **m/z**: 335.16 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.71 (s, 1H), 8.80 (d, *J*=2.4Hz, 1H), 8.42 (d, *J* = 2.4Hz, 1H), 8.03-8.05 (m, 1H), 7.85 (br s ,1H), 7.73-7.66 (m, 3H), 7.51 (t, *J*=7.6Hz, 2H), 7.40 (t, *J* = 7.6Hz, 1H), 7.23 (s, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 188.14, 148.96, 147.23, 138.17, 134.87, 134.50, 129.65, 129.20, 129.07, 127.30, 126.92, 126.79, 126.76, 126.72, 119.19, 118.51, 118.33, 118.02, 117.84, 111.43. IR (KBr, ν_{max}, cm^{-1}): 3028, 2845, 1645, 1428, 1285, 1173, 1011. Anal. Calcd for $C_{20}H_{12}F_2N_2O$: C, 71.85; H, 3.62; N, 8.38 Found; C, 71.75; H, 3.55; N, 8.27.

(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)(pyridin-2-yl)methanone (5k)



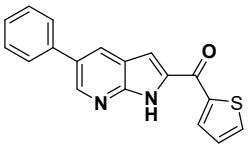
Compound **5k** was prepared from (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(pyridin-2-yl)prop-2-en-1-one (4k, 0.15g, 0.45mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Brown solid (0.075 g, 45%); mp >350 °C; **m/z**: 300.10 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.59 (s, 1H), 8.86-8.85 (m, 1H), 8.80 (d, *J* = 2.4Hz, 1H), 8.48 (d, *J* = 2Hz, 1H), 8.12 (m, 2H), 7.93 (d, *J* = 2Hz, 1H), 7.74 (m, 3H), 7.51 (t, *J* = 7.6Hz, 2H), 7.41 (m, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 183.36, 154.53, 149.47, 149.14, 147.68, 138.74, 138.24, 135.01, 130.51, 129.99, 129.91, 129.54, 127.73, 127.70, 127.41, 124.15, 123.89, 119.08, 119.06, 113.56. IR (KBr, ν_{max}, cm^{-1}): 3025, 2845, 1645, 1453, 1293, 1007. Anal. Calcd for $C_{19}H_{13}N_3O$: C, 76.24; H, 4.38; N, 14.04 Found; C, 76.13; H, 4.24; N, 13.89.

furan-2-yl(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5l)



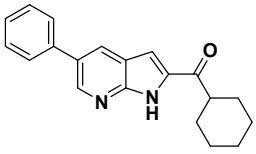
Compound **5l** was prepared from (E)-1-(furan-2-yl)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4l, 0.15g, 0.47mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.080 g, 62%); mp >350 °C; **m/z**: 289.20 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.61 (s, 1H), 8.77 (d, *J* = 2Hz, 1H), 8.45 (d, *J* = 2Hz, 1H), 8.17 (s, 1H), 7.75 (d, *J* = 7.2Hz, 2H), 7.684 (s, 1H), 7.64 (d, *J* = 3.2Hz, 1H), 7.52 (t, *J*=7.6Hz, 2H), 7.42-7.38 (m, 1H), 6.86-6.85 (m, 1H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 172.06, 151.63, 148.59, 148.19, 146.85, 138.26, 134.39, 129.56, 129.06, 128.90, 127.27, 126.94, 119.49, 119.39, 112.84, 109.13. IR (KBr, ν_{max}, cm^{-1}): 3027, 2886, 2781, 1631, 1470, 1305, 1261, 935. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 74.99; H, 4.20; N, 9.72 Found; C, 74.81; H, 4.08; N, 9.62.

(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)(thiophen-2-yl)methanone (5m)



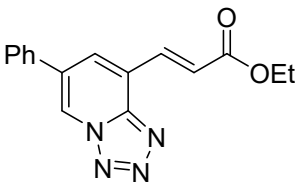
Compound **5m** was prepared from (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)-1-(thiophen-2-yl)prop-2-en-1-one (4m, 0.13g, 0.39mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.066 g, 54%); mp >350 °C; **m/z**: 305.15 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.64 (s, 1H), 8.78 (d, *J* = 2Hz, 1H), 8.42 (d, *J* = 2Hz, 1H), 8.16-8.13 (m, 2H), 7.76-7.74 (m, 2H), 7.53-7.50 (m, 3H), 7.42-7.35 (m, 2H), 7.42-7.38 (m, 1H); **^{13}C NMR (400MHz, DMSO-*d6*)** δ 177.99, 149.17, 147.25, 142.71, 138.74, 135.45, 135.31, 134.42, 130.51, 130.07, 129.56, 129.49, 129.36, 127.76, 127.42, 119.79, 119.07, 109.44. IR (KBr, ν_{max}, cm^{-1}): 3040, 2887, 2834, 1613, 1422, 1300, 1023. Anal. Calcd for $C_{12}H_{12}N_2O_2$: C, 71.03; H, 3.97; N, 9.20, S, 10.53 Found; C, 70.91; H, 3.85; N, 8.81, S, 10.37.

(cyclohexyl(5-phenyl-1H-pyrrolo[2,3-b]pyridin-2-yl)methanone (5n)



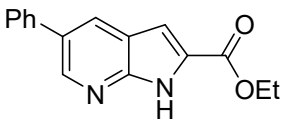
Compound **5n** was prepared from (E)-1-cyclohexyl-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)prop-2-en-1-one (4n, 0.1g, 0.30mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.072 g, 79%); mp >350 °C; **m/z**: 305.20 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 13.24 (s, 1H), 8.73 (d, *J* = 2Hz, 1H), 8.37 (d, *J* = 2Hz, 1H), 7.73 (d, *J* = 7.2Hz, 2H), 7.52-7.46 (m, 3H), 7.41-7.37 (m, 1H), 1.86-1.69 (m, 5H), 1.48-1.33 (m, 4H), 1.26 (br s, 2H); **^{13}C NMR (400MHz, DMSO-*d6*)** δ 196.11, 148.75, 146.46, 138.32, 135.25, 129.36, 129.03, 128.82, 127.20, 126.92, 119.25, 107.45, 45.31, 29.35, 25.46, 25.08. IR (KBr, ν_{max}, cm^{-1}): 2928, 2853, 1651, 1427, 1287, 1005. Anal. Calcd for $C_{20}H_{20}N_2O$: C, 78.92; H, 6.62; N, 9.20 Found; C, 78.81; H, 6.49; N, 8.91.

ethyl (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)acrylate (6a)



To a stirred solution of 6-phenyltetrazolo[1,5-a]pyridine-8-carbaldehyde (2, 0.2 g, 1.3 mmol) in anhydrous CH_3CN (6 mL), (ethoxycarbonylmethylene)triphenylphosphorane (0.51 g, 1.5 mmol) was added in one portion. The resulting solution was stirred at ambient temperature overnight and then concentrated. The residue was column-chromatographed using 10% EA in hexane to afford the desired compound as off white solid. **m/z**: 294.31 $(M+H)^+$,

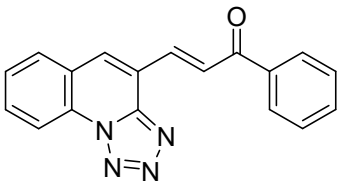
ethyl 5-phenyl-1H-pyrrolo[2,3-b]pyridine-2-carboxylate (7a)



Compound **7a** was prepared from ethyl (E)-3-(6-phenyltetrazolo[1,5-a]pyridin-8-yl)acrylate (6a, 0.1g, 0.34mmol) and Dowtherm-A (10 mL) as per above general procedure-B. Off-white solid (0.061 g, 65%); mp >350 °C; **m/z**: 266.31 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.594 (s, 1H), 8.73 (d, *J*= 2Hz, 1H), 8.36 (d, *J* = 2.4 Hz, 1H), 7.73 (d, *J* = 7.2Hz, 2H), 7.50 (t, *J* = 7.6Hz, 2H), 7.39 (t, *J*= 7.6 Hz, 1H), 7.216 (s, 1H), 4.39-4.33 (q, 2H), 1.35 (t, *J* = 7.2Hz, 3H); **^{13}C NMR (100MHz, DMSO-*d6*)** δ 160.89, 148.34, 145.84, 138.32, 129.36, 129.02, 128.59,

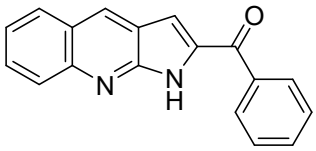
128.36, 127.20, 126.92, 119.02, 106.72, 60.72, 14.20. IR (KBr, ν_{max}, cm^{-1}): 2923, 2853, 1716, 1443, 1286, 1024.

(E)-1-phenyl-3-(tetrazolo[1,5-a]quinolin-4-yl)prop-2-en-1-one (6b)



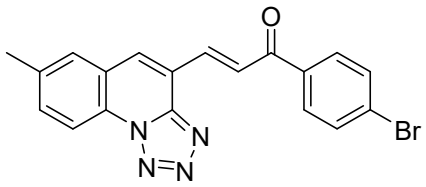
Compound **6b** was prepared from Tetrazolo [1,5-a] quinoline-4-carbaldehyde (1.58 g, 8mmol) and acetophenone (0.93ml, 8mmol) as per above general procedure-A. Off-white solid (1.68 g, 72%). **m/z**: 300.1 $(M+H)^+$,

phenyl(1H-pyrrolo[2,3-b]quinolin-2-yl)methanone (7b)



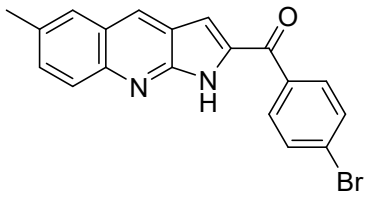
Compound **7b** was prepared from (E)-1-phenyl-3-(tetrazolo[1,5-a]quinolin-4-yl)prop-2-en-1-one (6b, 1g, 3.3mmol) and Dowtherm-A (25 mL) as per above general procedure-B. Off-white solid (0.16 g, 17%); mp >350 °C; **m/z**: 273.3 $(M+H)^+$, **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.39 (s, 1H), 8.83 (s, 1H), 8.10 (d, J = 8.4 Hz, 2H), 8.00 (d, J = 8 Hz, 2H), 7.76 (m, 2H), 7.65 (t, J = 7.6 Hz, 2H), 7.48 (t, J = 7.2 Hz, 2H), 7.31 (s, 1H); **^{13}C NMR (100MHz DMSO-*d6*)** δ 186.96, 150.38, 147.27, 137.98, 132.79, 131.57, 129.33, 128.96, 127.53, 124.61, 123.12, 121.01, 110.54. IR (KBr, ν_{max}, cm^{-1}): 3209, 3122, 1632, 1447, 1301, 1003.

(E)-1-(4-bromophenyl)-3-(7-methyltetrazolo[1,5-a]quinolin-4-yl)prop-2-en-1-one (6c)



Compound **6b** was prepared from 7-methyl tetrazolo [1,5-a] quinoline-4-carbaldehyde (1.g, 8mmol) and 4-bromo acetophenone (0.9ml, 8mmol) as per above general procedure-A. Off-white solid (1.5 g, 81%). **m/z**: 394.1 $(M+H)^+$

(4-bromophenyl)(6-methyl-1H-pyrrolo[2,3-b]quinolin-2-yl)methanone (7c)

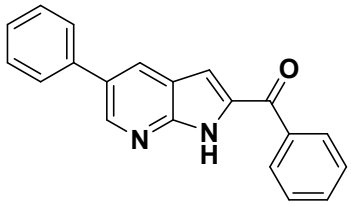


Compound **7c** was prepared from (E)-1-(4-bromophenyl)-3-(7-methyltetrazolo[1,5-a]quinolin-4-yl)prop-2-en-1-one (6c, 1.17g, 3mmol) and Dowtherm-A (25 mL) as per above general procedure-B. Off-white solid (0.14 g, 13%); mp >350 °C; **m/z**: 365.23 $(M+H)^+$; mp >350 °C; **^{1}H NMR (400MHz, DMSO-*d6*)** δ 12.34 (s, 1H), 8.71 (s, 1H), 7.93-7.81 (m, 3H), 7.88-7.83 (m, 3H), 7.58 (d, J = 8.8 Hz, 1H), 7.30 (s, 1H); **^{13}C NMR (100MHz DMSO-*d6*)** δ 185.91, 150.09, 146.10, 137.50, 136.43, 132.25, 131.92, 130.69, 127.34,126.70, 124.67, 120.92, 110.72. IR (KBr, ν_{max}, cm^{-1}): 3215, 3095, 1626, 1435, 1296, 1005, 693

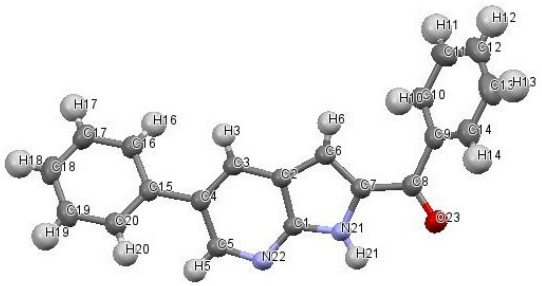
References

1. K. Taku, Xu Pengu, I. Satoshi, Z. Lei, K. Shu, *Chem. Commun*., 2014, **50**, 9336
2. X. Ze-feng, Z. Teng, H. Wenjun, *Tetrahedron*, 2019, **75**, 3113
3. R. Amresh, P. Perumal, *Synthetic Communications*, 2000, **30 (13)**, 2269

3. X-Ray crystal data



CMP-2a



The crystal of 5a was obtained by dissolving 20mg of a compound in 1mL DMF upon slow volatilization. A total of 2316 frames were collected. The total exposure time was 6.43 hours. The frames were integrated with the Bruker SAINT software package using a narrow-frame algorithm.

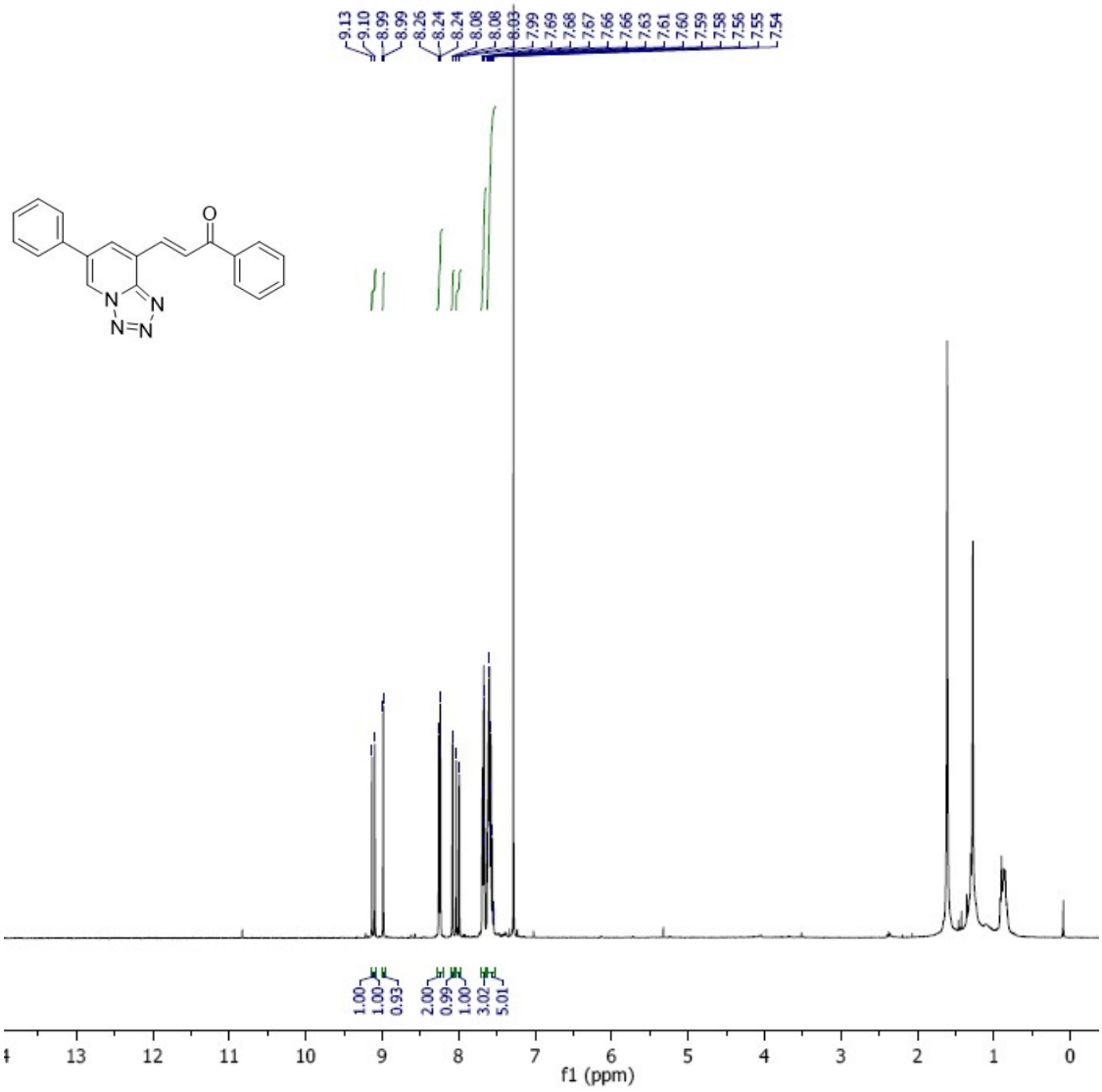
Table S2: Crystal data and Structure refinement of 5a

Chemical formula	$C_{20}H_{14}N_2O$
Formula weight	298.33 g/mol
Temperature	273(2) K
Wavelength	0.71073 Å
Crystal size	0.043 x 0.249 x 0.435 mm
Crystal habit	clear light colourless plate
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	a = 4.045(3) Å α = 80.01(2)° b = 12.408(11) Å β = 88.13(2)° c = 15.626(14) Å γ = 87.10(2)°
Volume	771.2(12) $Å^3$
Z	2
Density (calculated)	1.285 g/cm^3
Absorption coefficient	0.081 mm^{-1}
F(000)	312
Theta range for data collection	2.30 to 28.76°
Index ranges	-3<=h<=5, -16<=k<=16, -21<=l<=20
Reflections collected	17994
Independent reflections	3901 [R(int) = 0.0397]
Coverage of independent reflections	97.2%
Absorption correction	Multi-Scan
Refinement method	Full-matrix least-squares on F^2
Refinement Program	SHELXL-2018/3 (Sheldrick, 2018)
Structure solution technique	direct methods
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)_2$

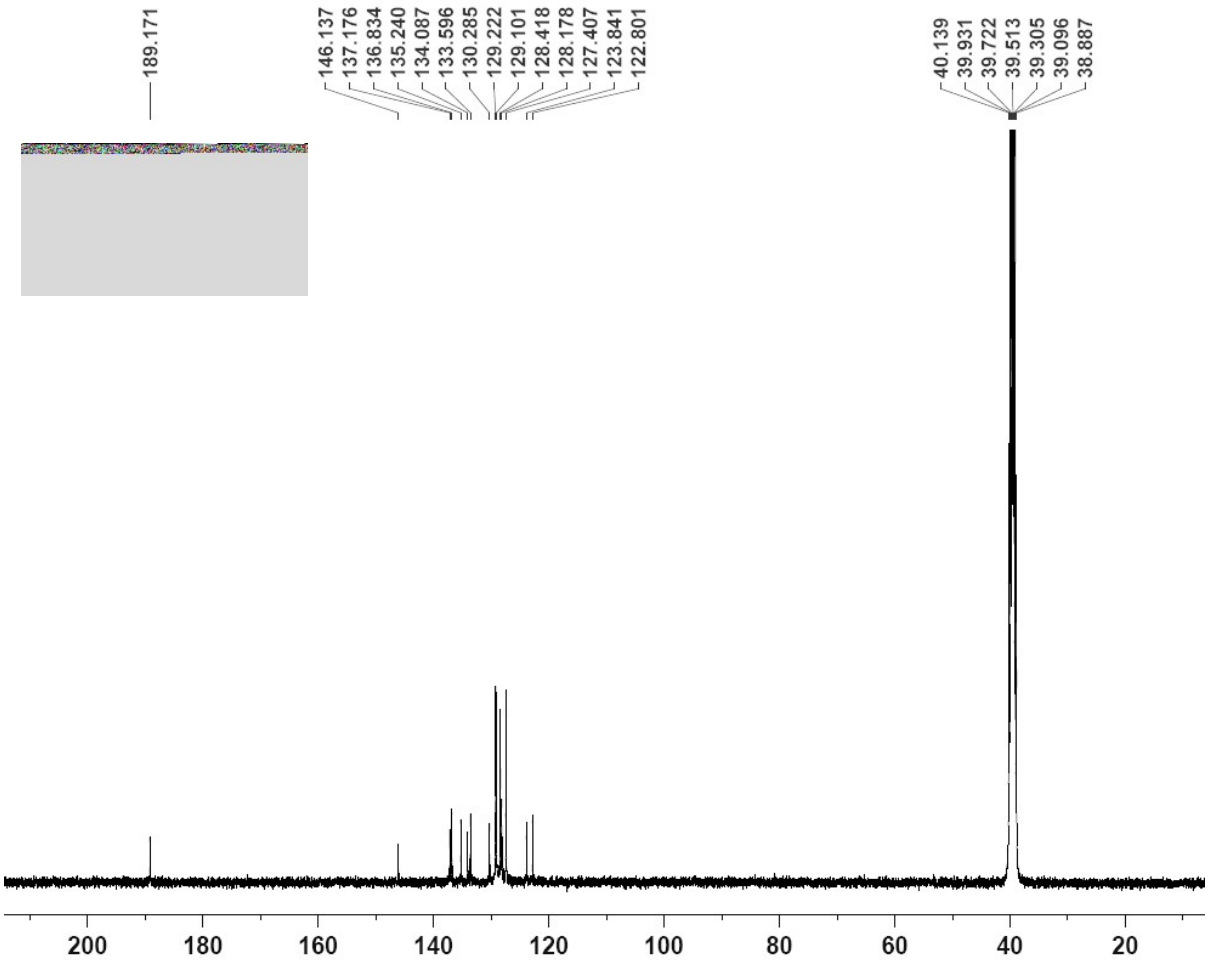
Data / restraints / parameters	3901 / 0 / 208
Goodness-of-fit on F^2	1.360
Final R indices	3231 data; I>2σ(I) R1 = 0.0471, wR2 = 0.1670 all data R1 = 0.0566, wR2 = 0.1785
Weighting scheme	$w= 1/[\sigma^2(F_o^2)+(0.1000P)^2]$ where $P=(F_o^2+2F_o^2)/3$
Largest diff. peak and hole	0.221 and -0.217 eÅ^{-3}
R.M.S. deviation from mean	0.054 eÅ^{-3}

4. ^{1}H and ^{13}C NMR spectra

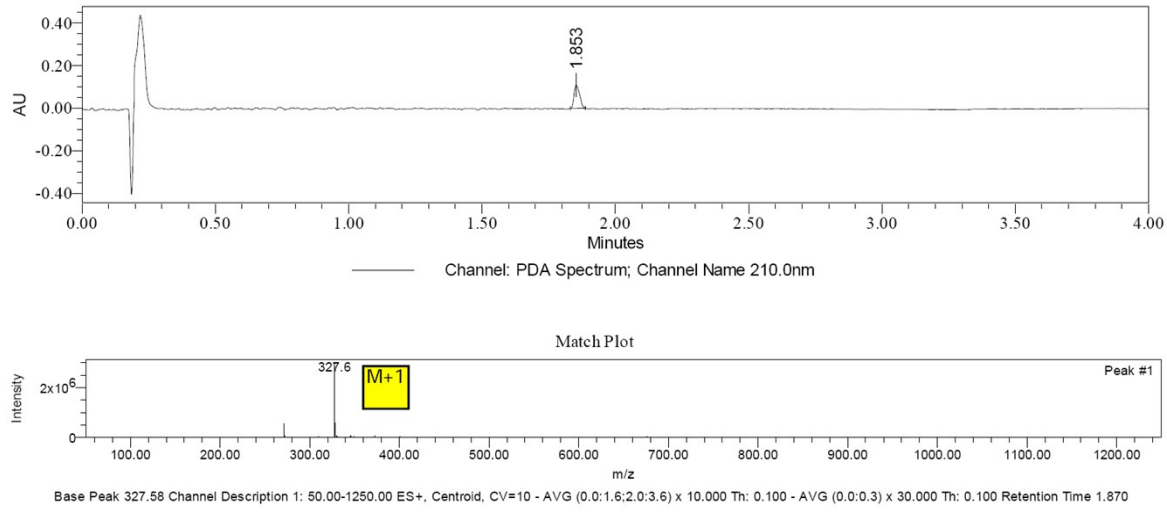
^{1}H NMR of Compound-4a



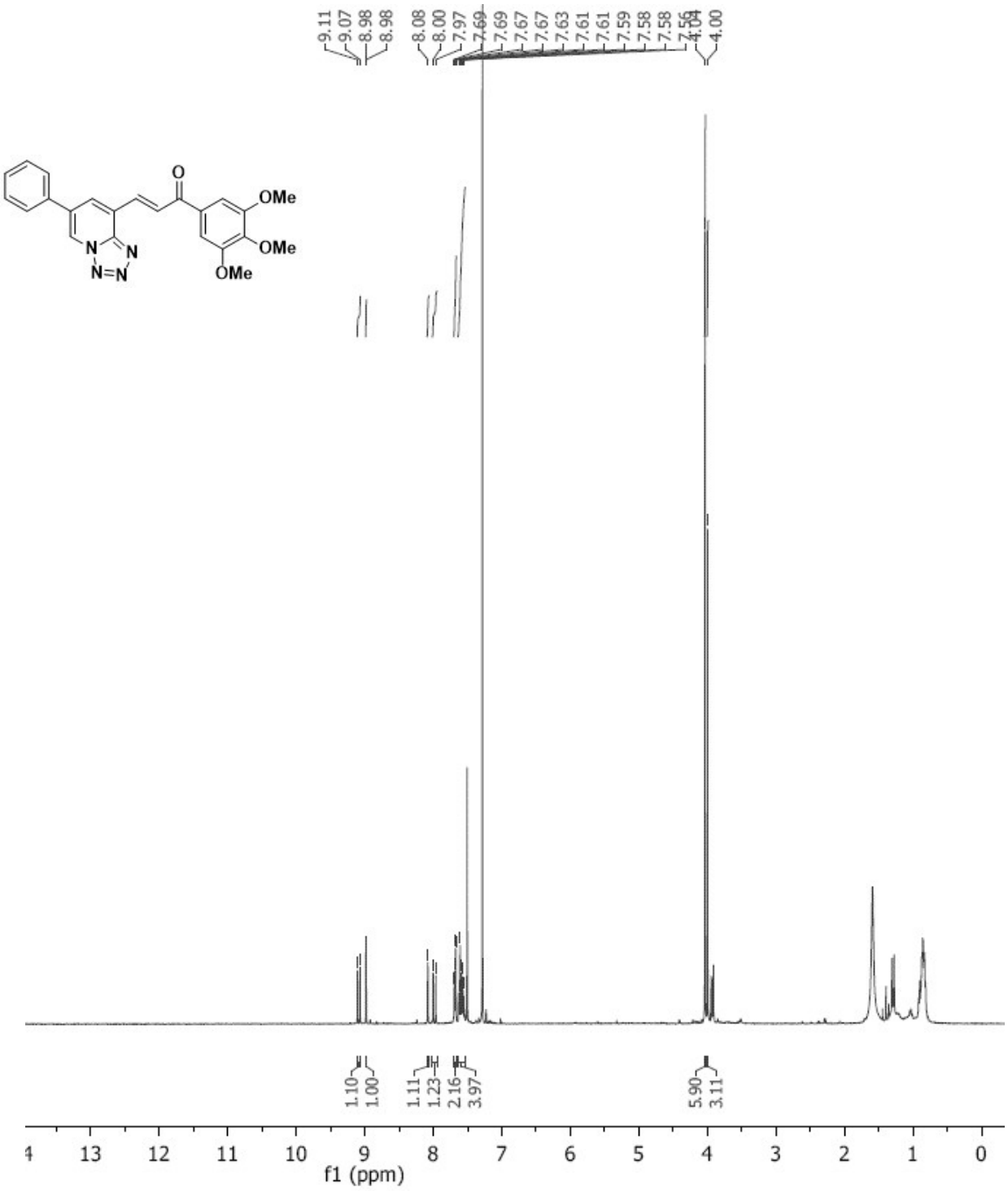
^{13}C NMR of Compound-4a



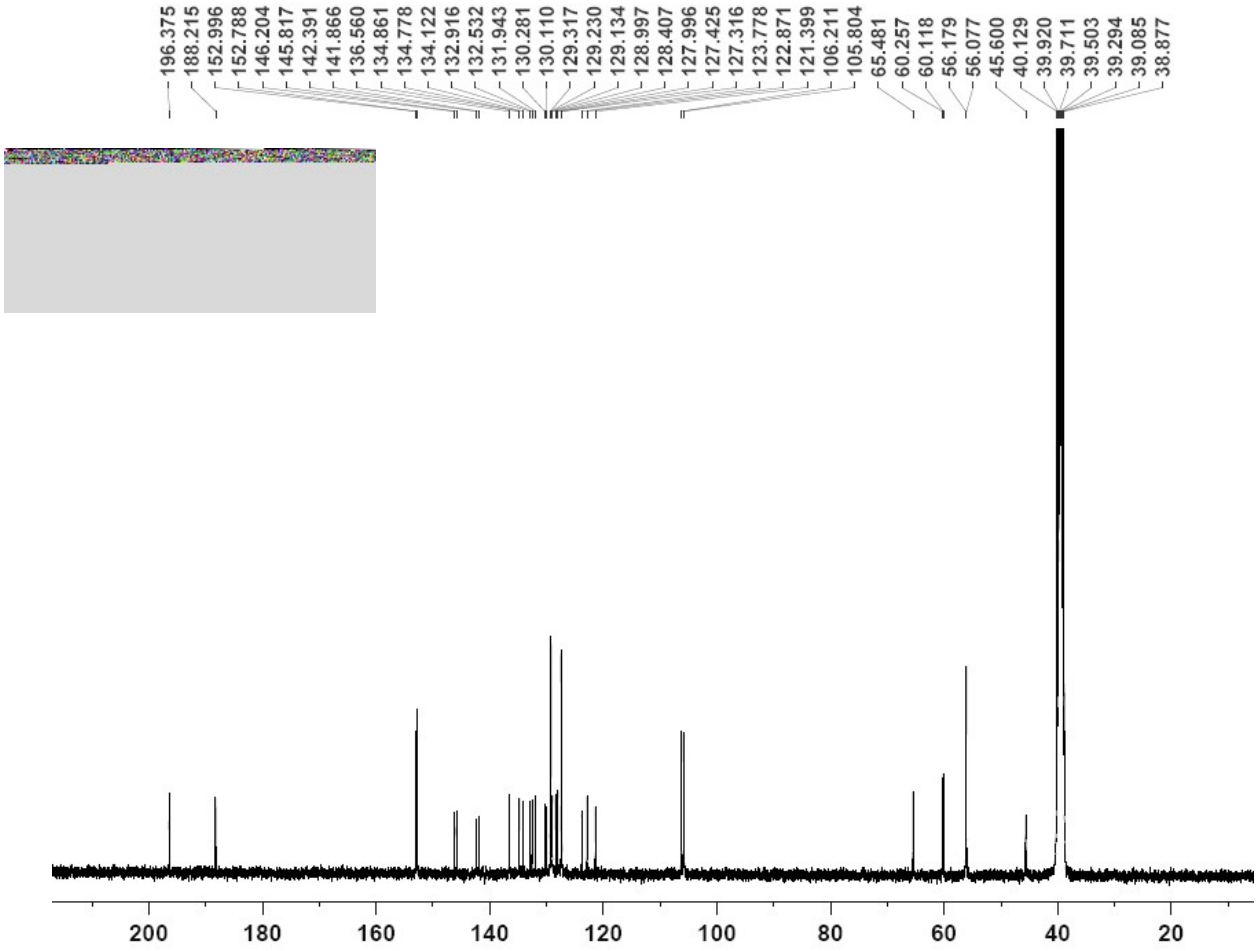
LCMS of Compound-4a



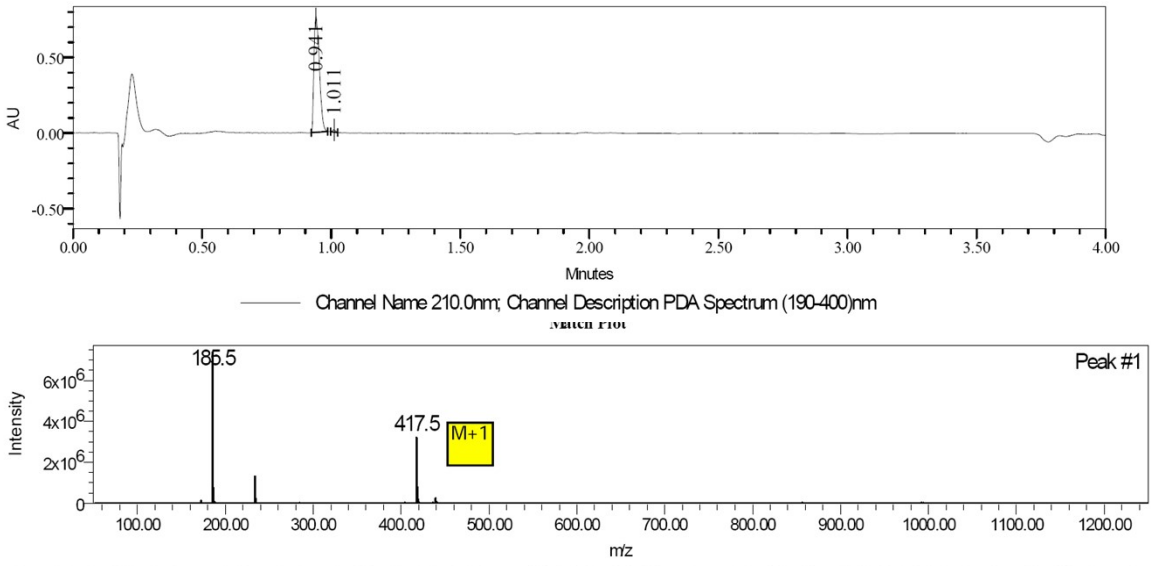
^{1}H NMR of Compound-4b



^{13}C NMR of Compound-4b

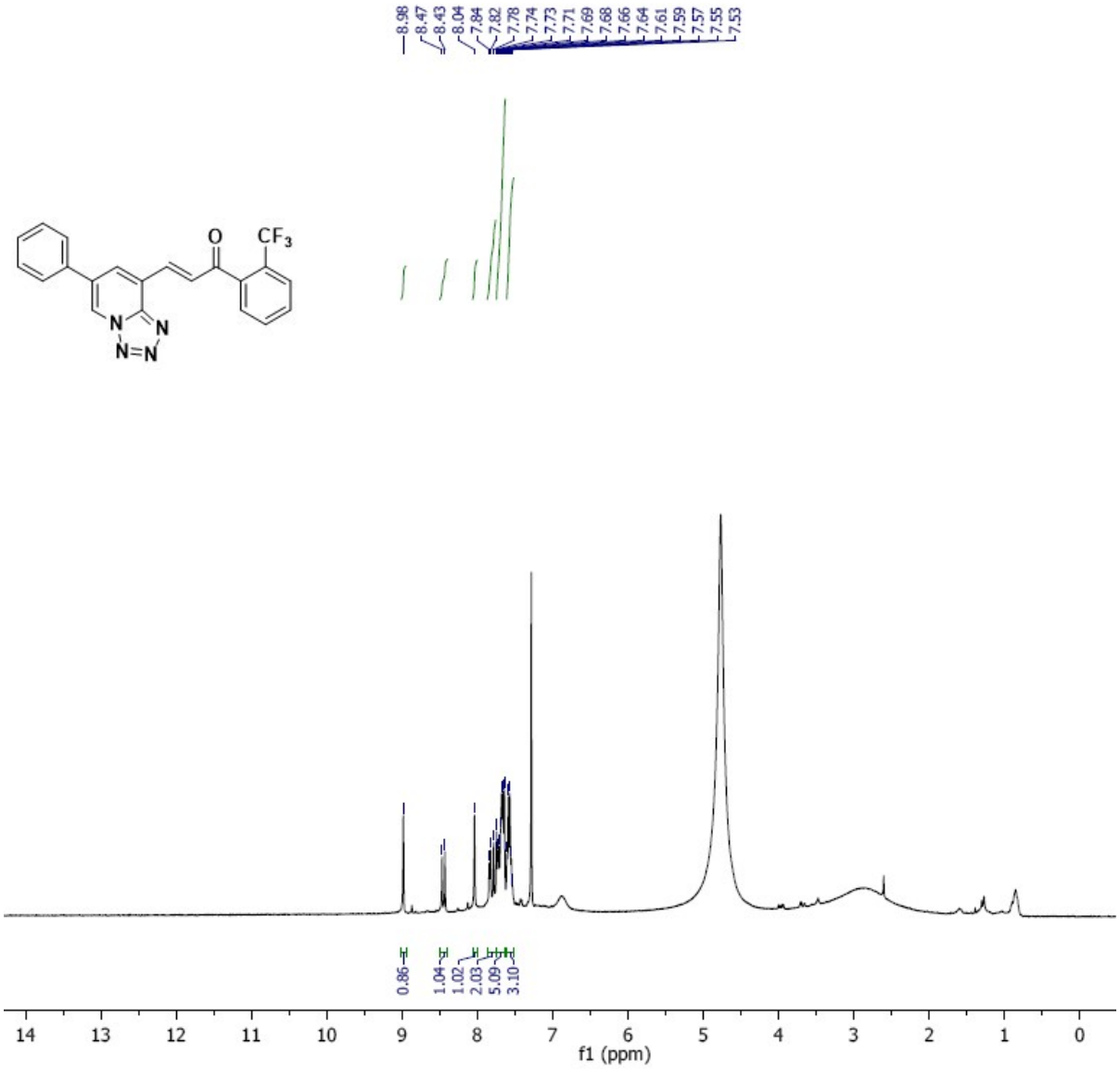


LCMS of Compound-4b

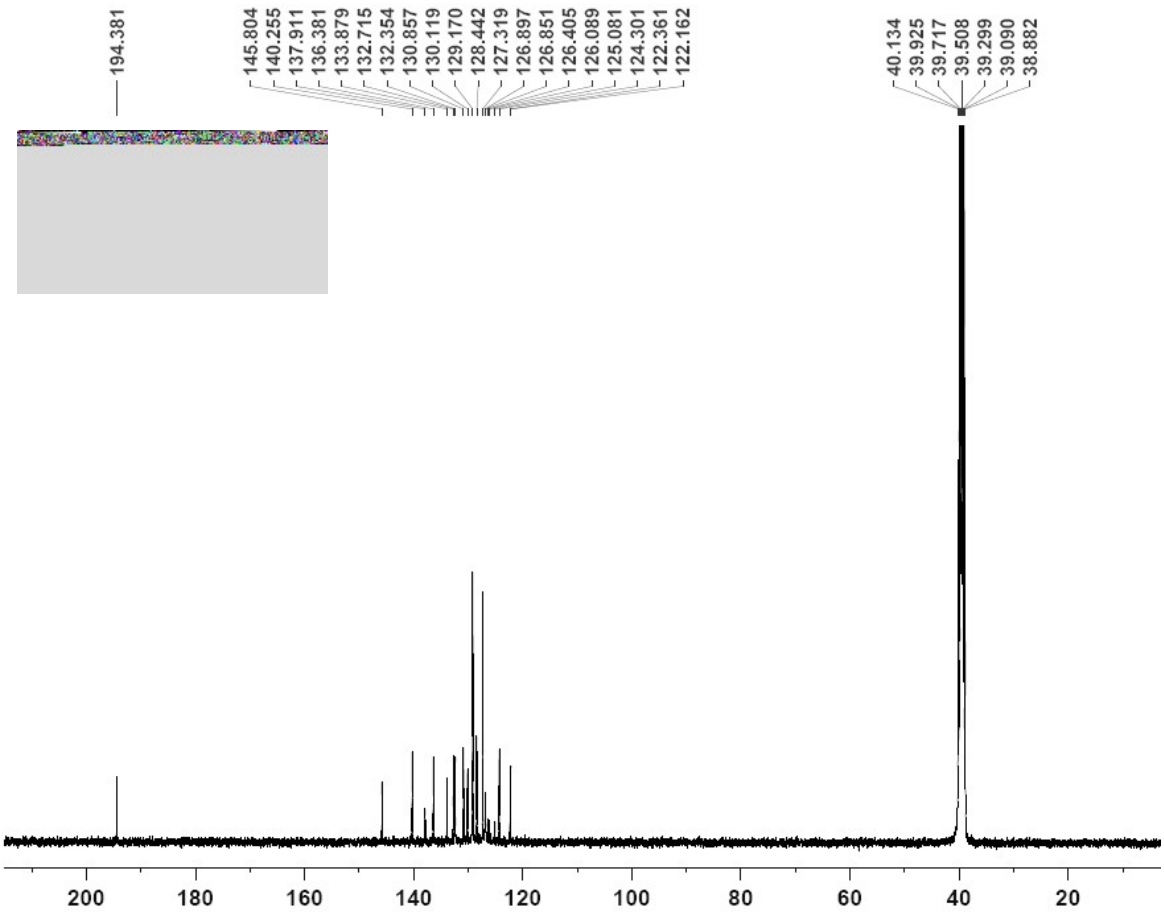


Base Peak 185.48 Channel Description 2: QDa Positive(+) Scan (50.00-1250.00)Da, Centroid, CV=30 - AVG (1.4:3.9;0.1:0.8) x 30.000 Retention Time 0.965

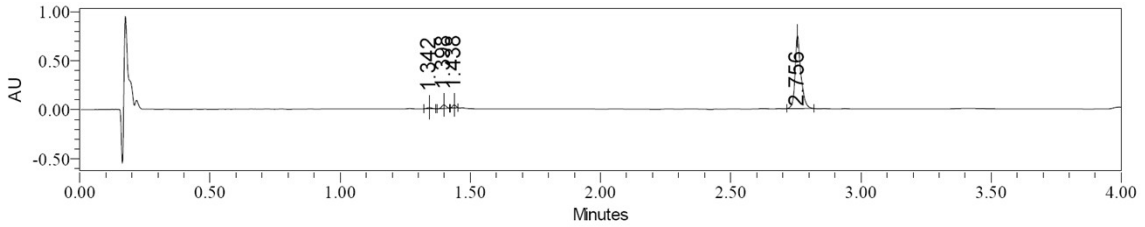
[1]H NMR of Compound-4c

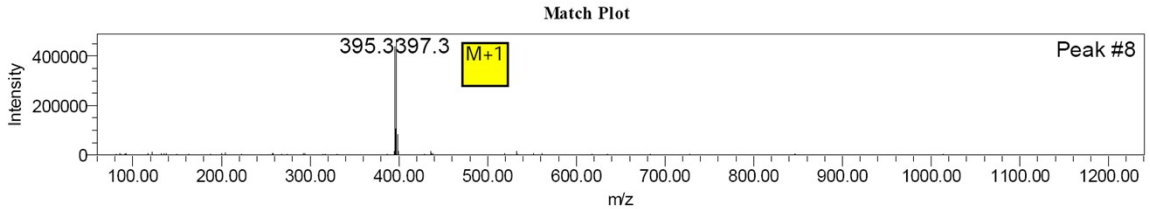


^{13}C NMR of Compound-4c



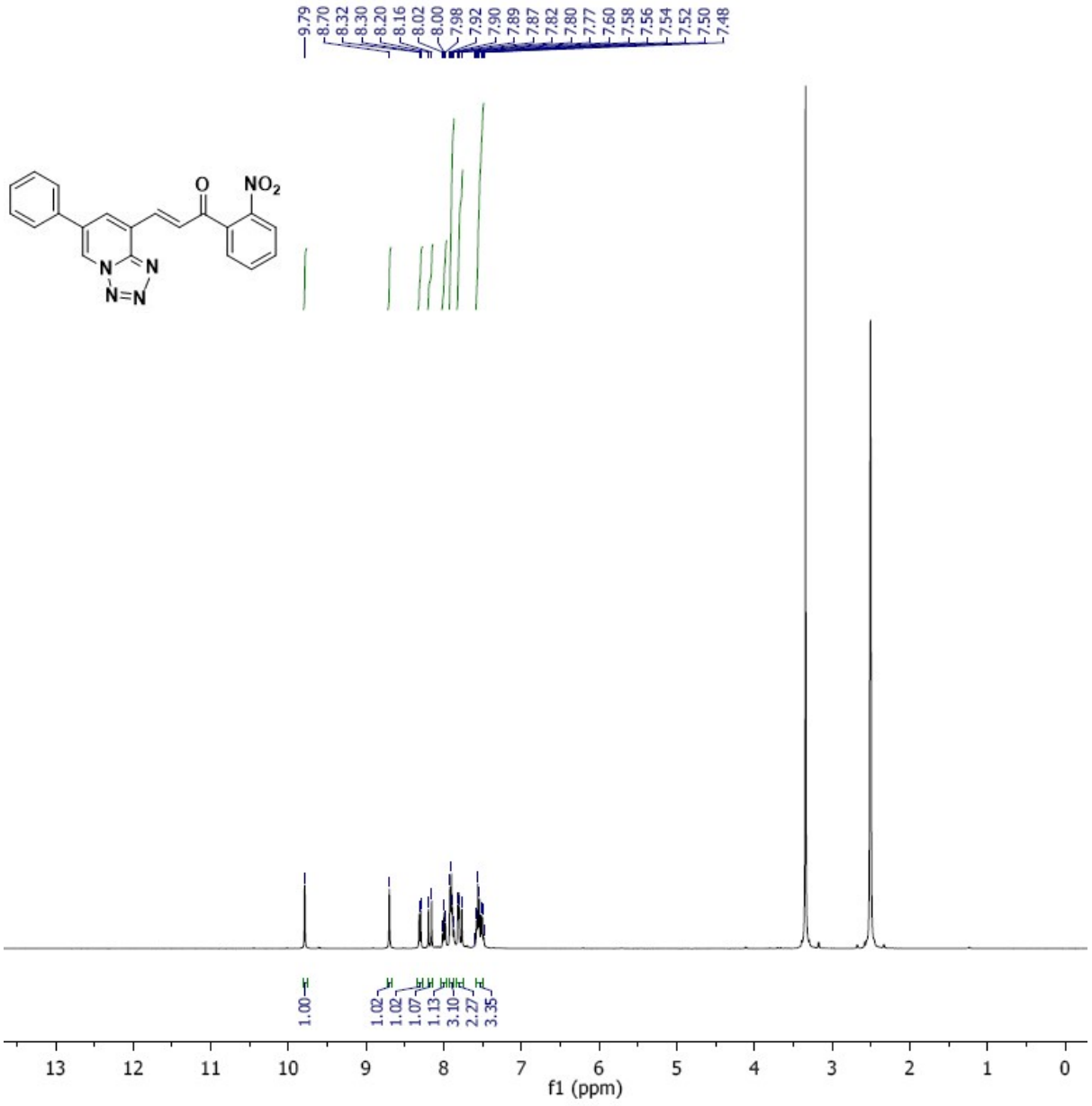
LCMS of Compound-4c



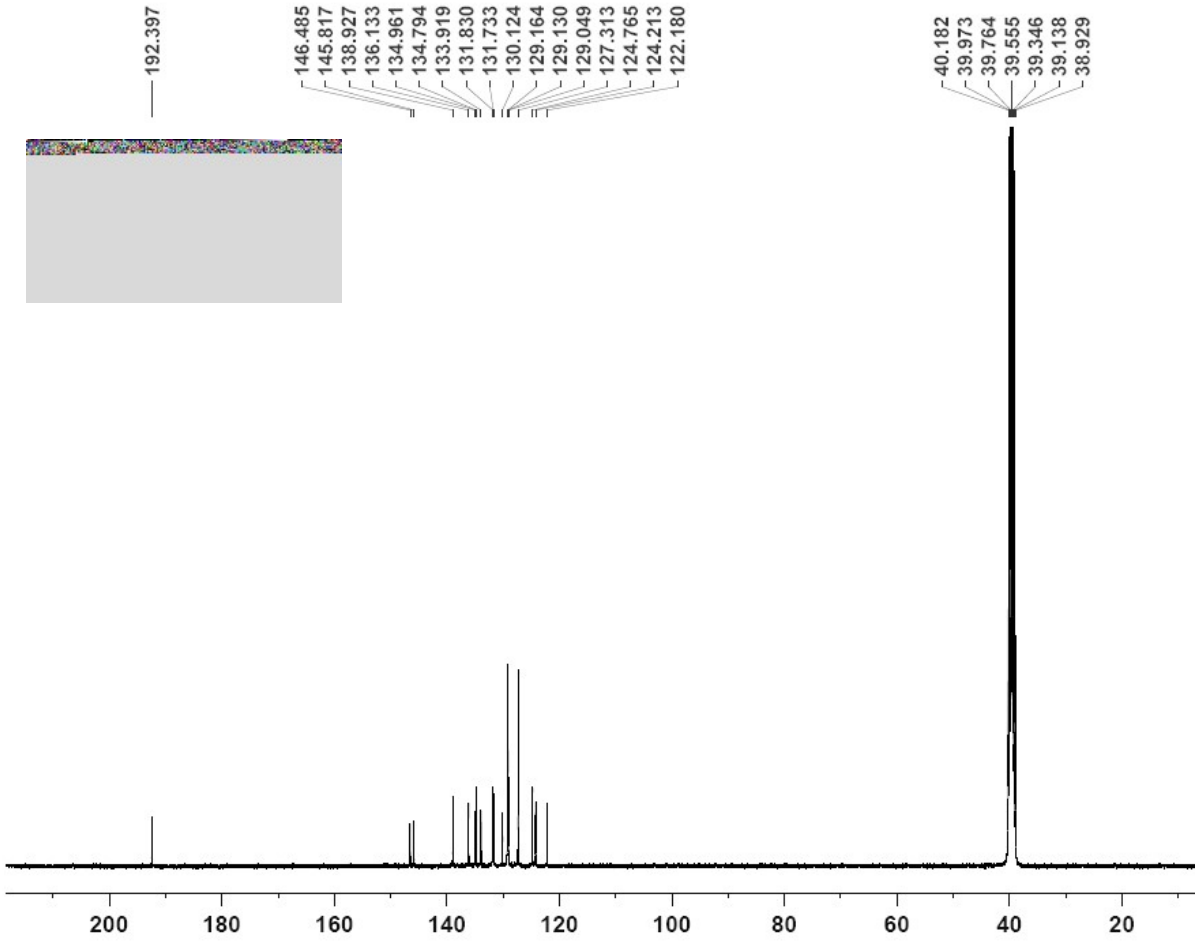


Base Peak 397.34 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.1:0.2;3.5:3.9) x 21.000 Th: 0.010 Retention Time 2.766

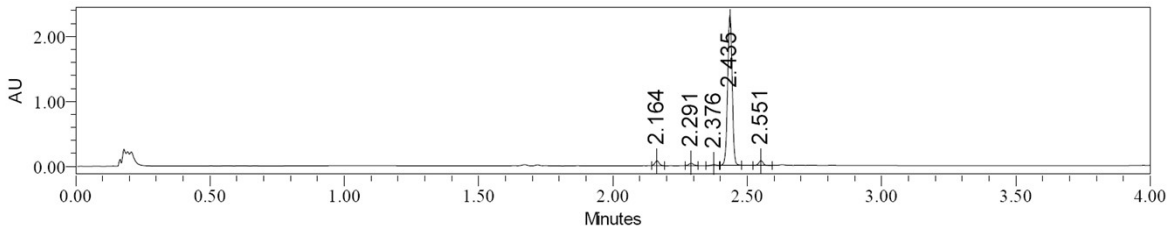
[1]H NMR of Compound-4d

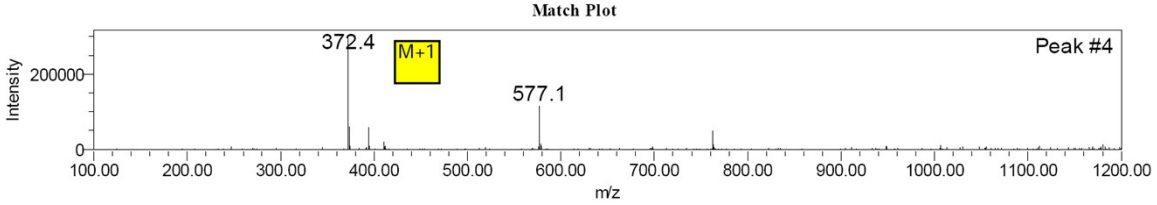


^{13}C NMR of Compound-4d



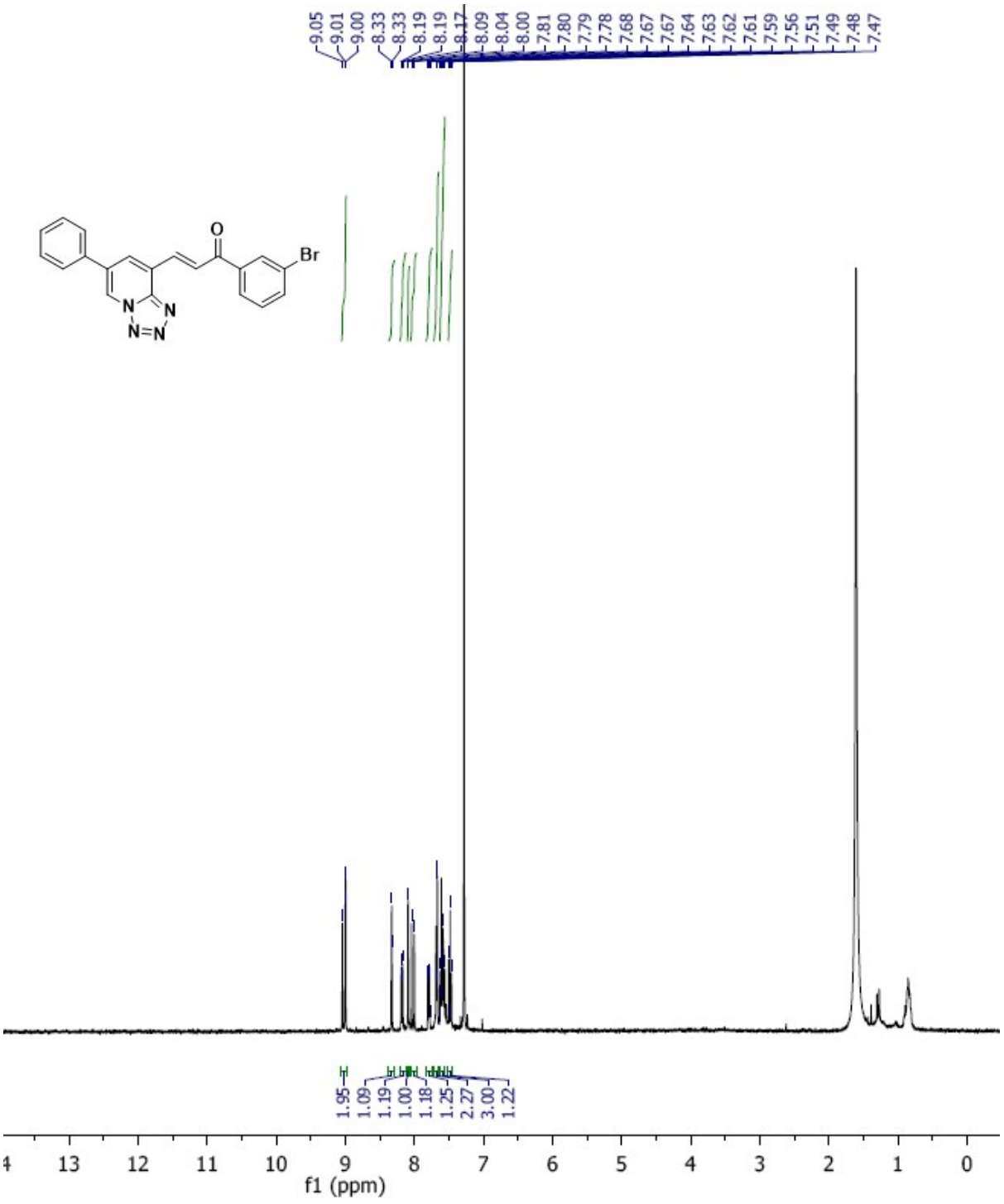
LCMS of Compound-4d



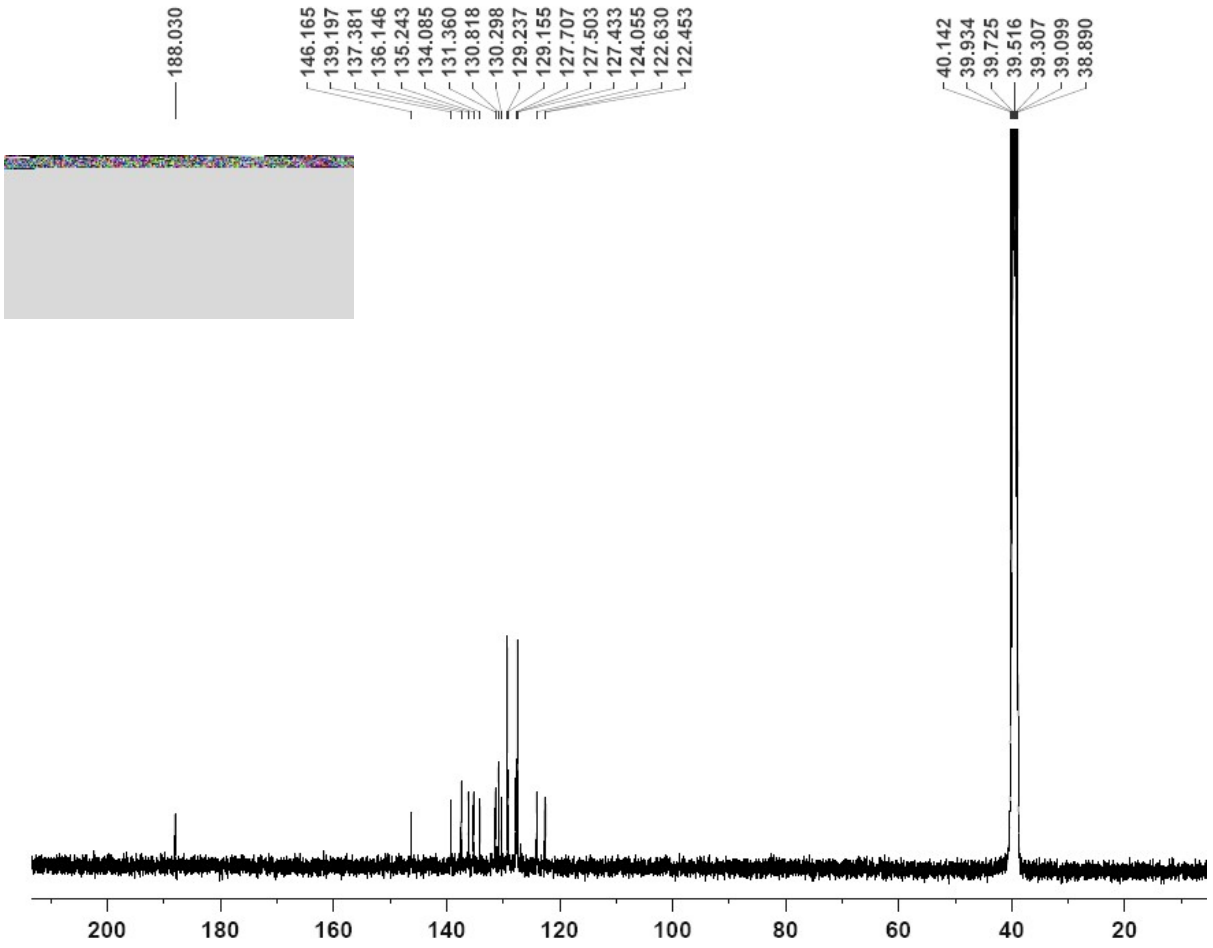


Base Peak 372.45 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:0.8;2.9:4.0) x 20.000 Th: 0.010 - AVG (0.0:1.8;2.8:3.1) x 20.000 Th: 0.010 Retention Time 2.442

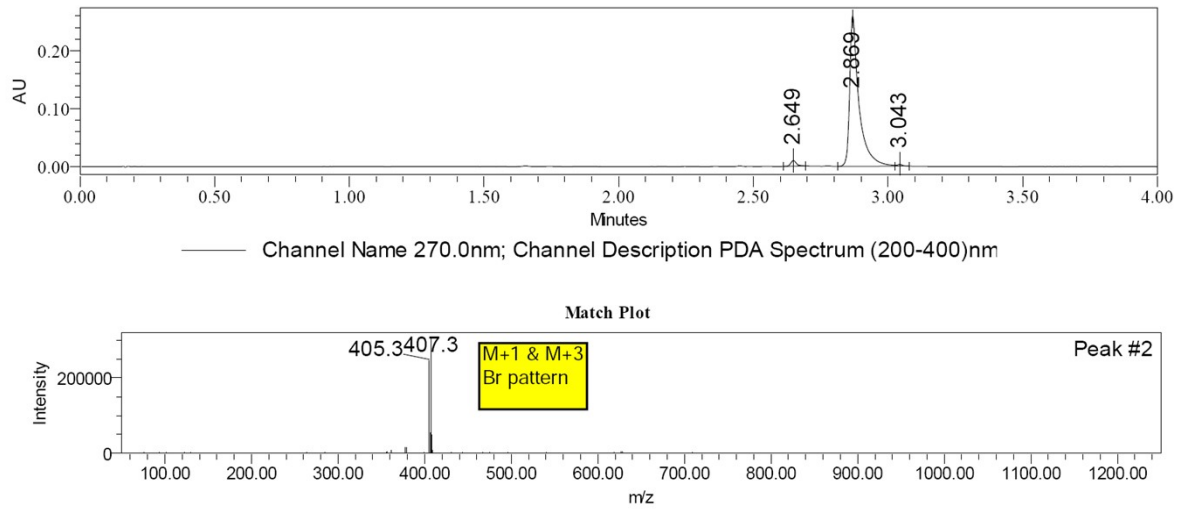
^{1}H NMR of Compound-4e



^{13}C NMR of Compound-4e

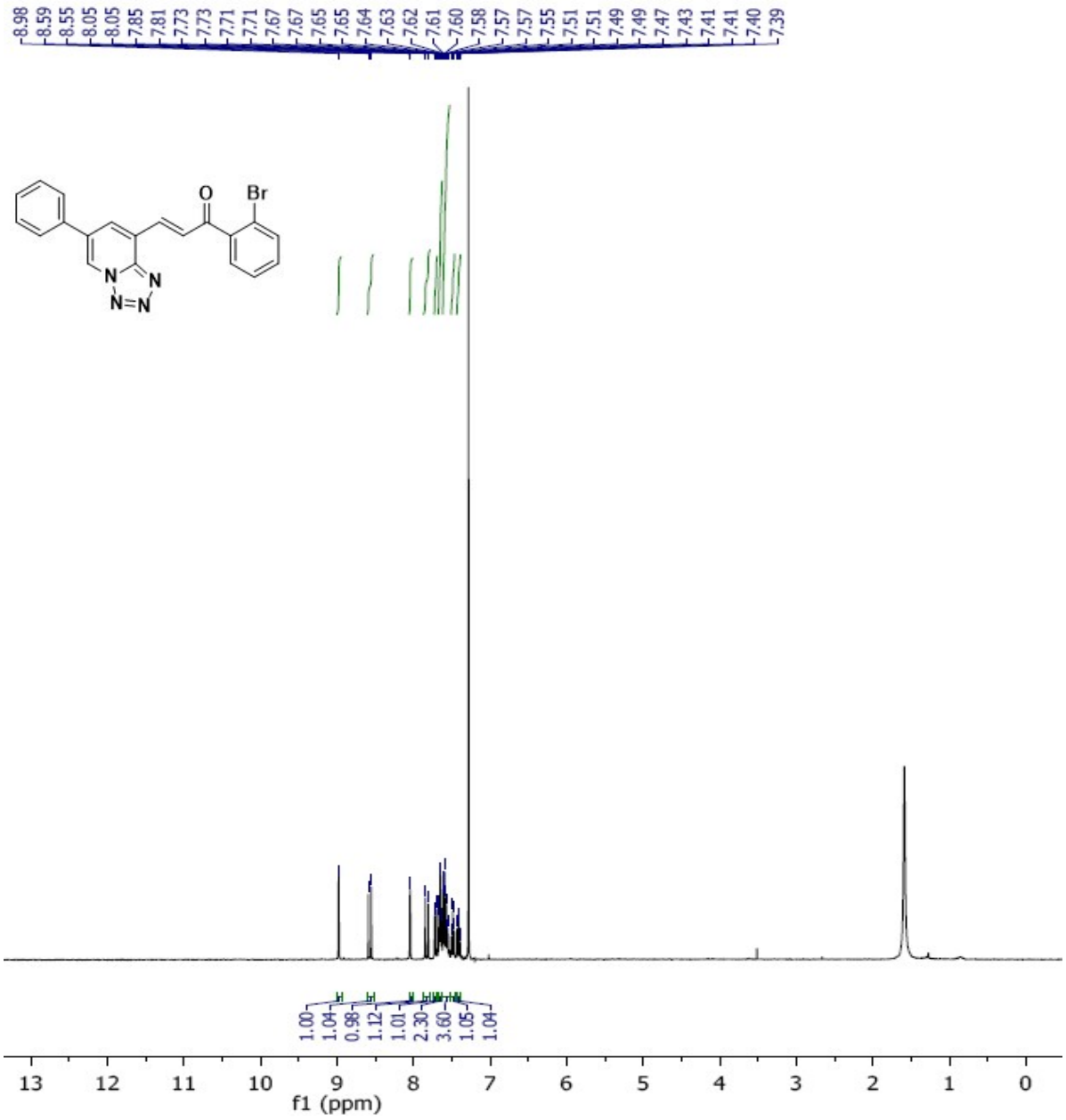


LCMS of Compound-4e

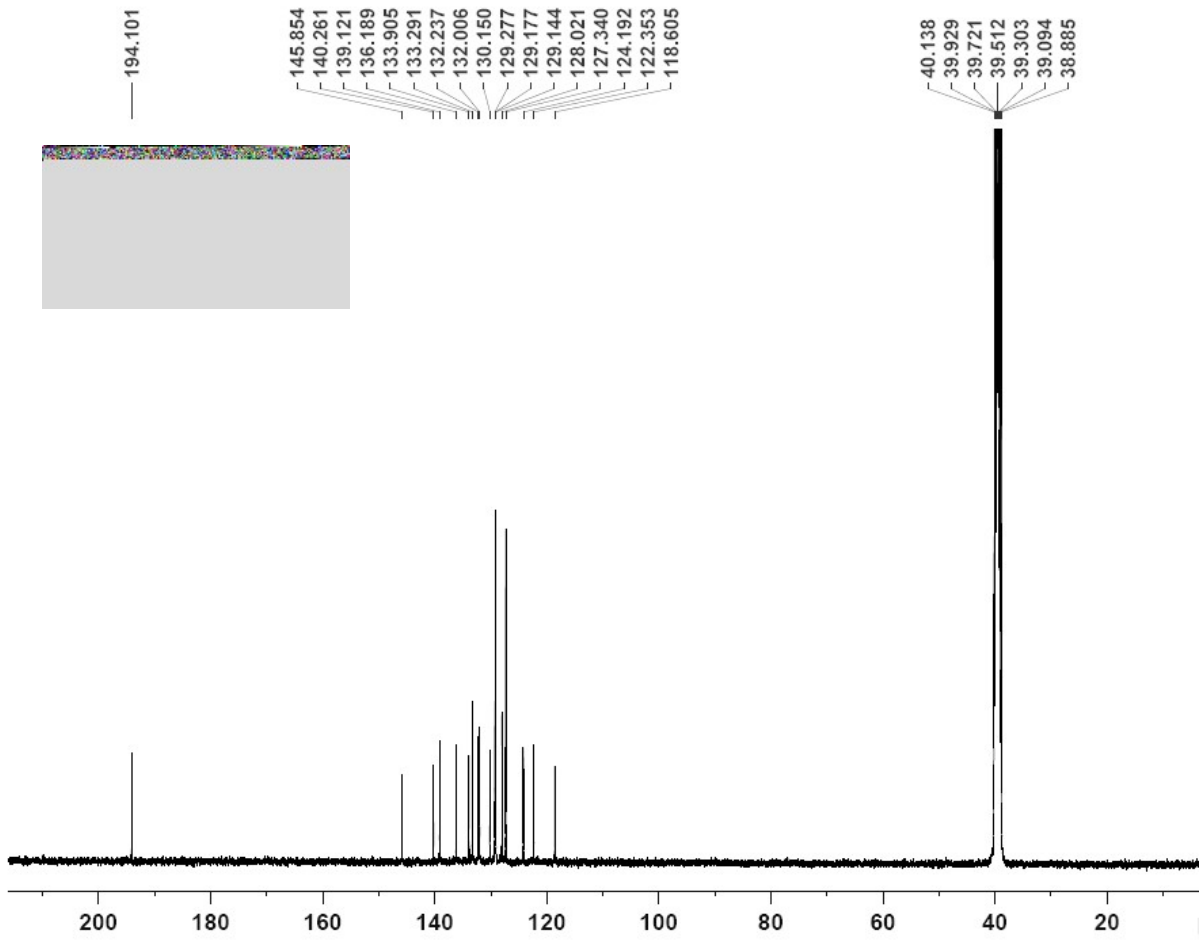


Base Peak 407.33 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.1:0.6;3.5:4.0) x 21.000 Th: 0.010 Retention Time 2.875

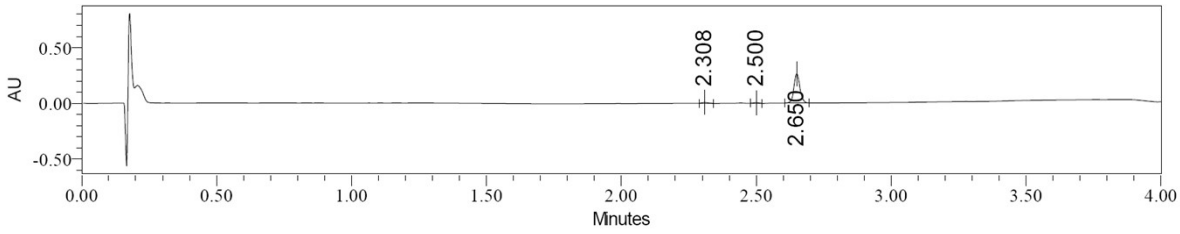
^{1}H NMR of Compound-4f

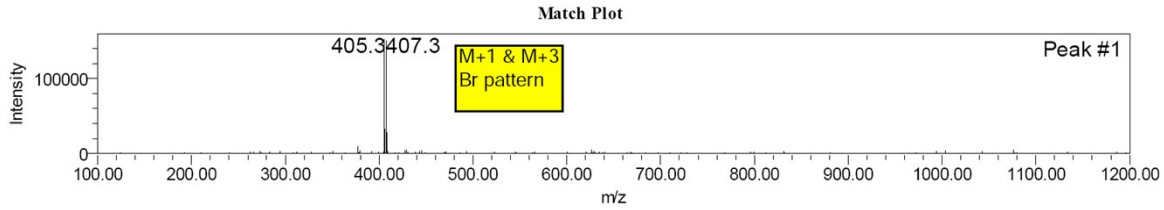


^{13}C NMR of Compound-4f



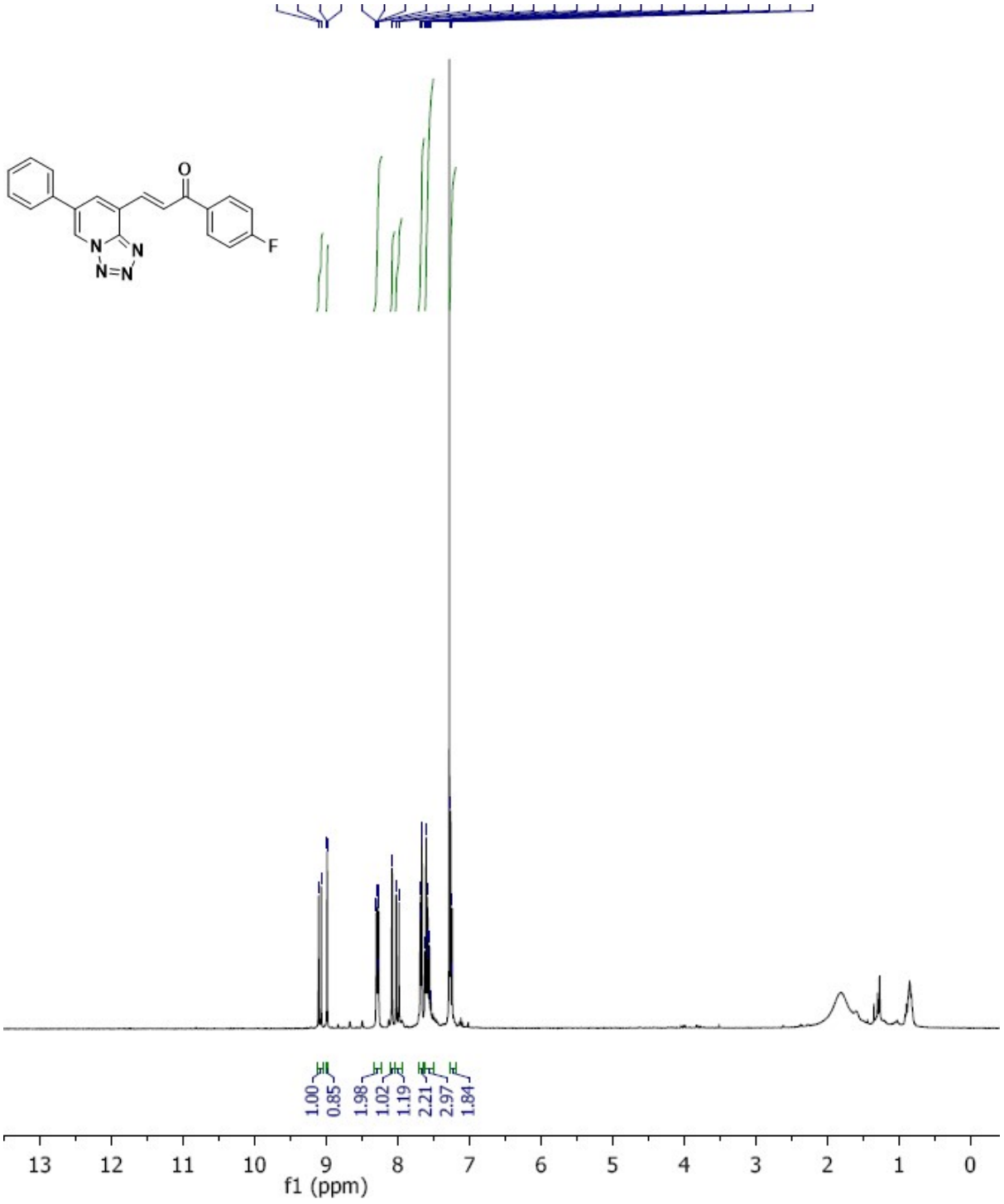
LCMS of Compound-4f



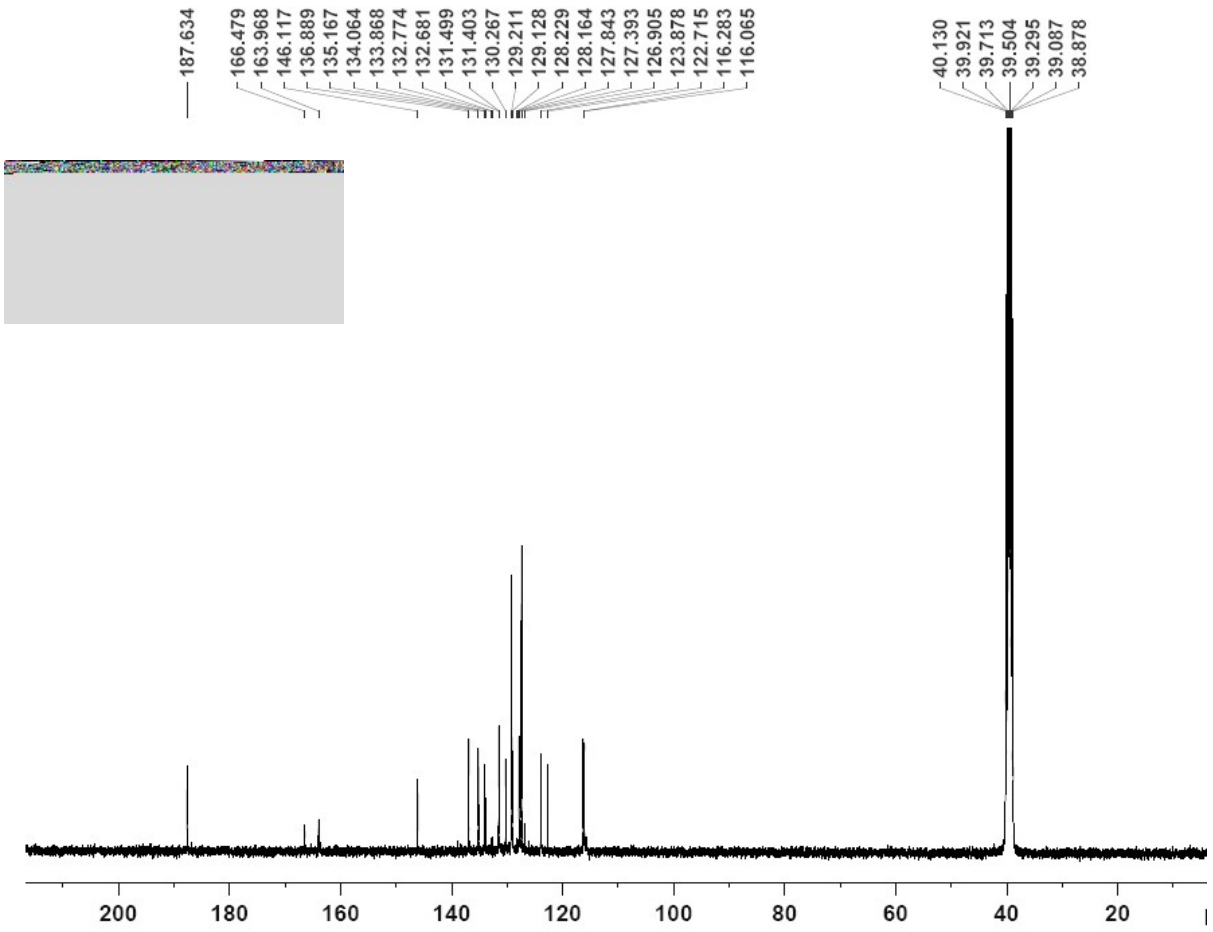


Base Peak 405.33 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.5;2.8:4.0) x 20.000 Th: 0.010 Retention Time 2.656

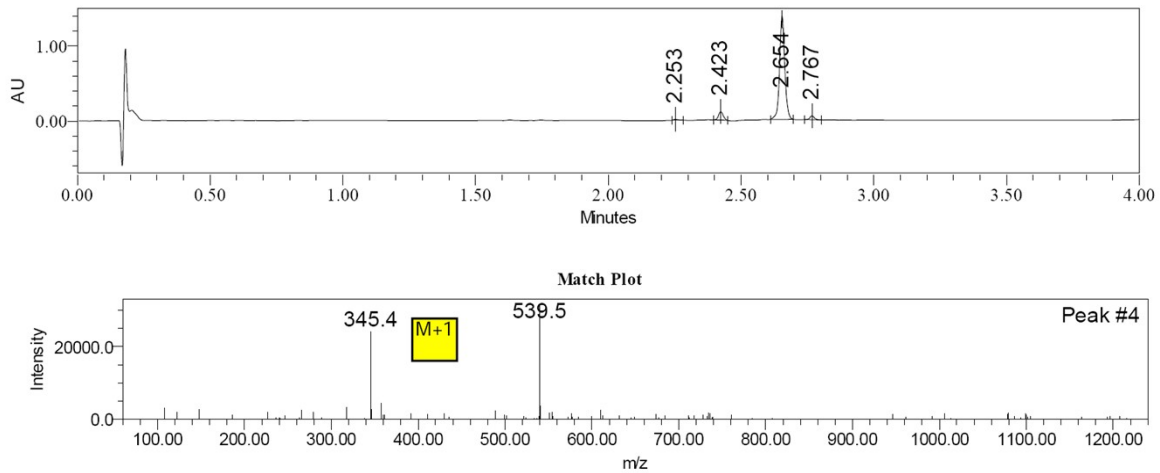
^{1}H NMR of Compound-4g



^{13}C NMR of Compound-4g

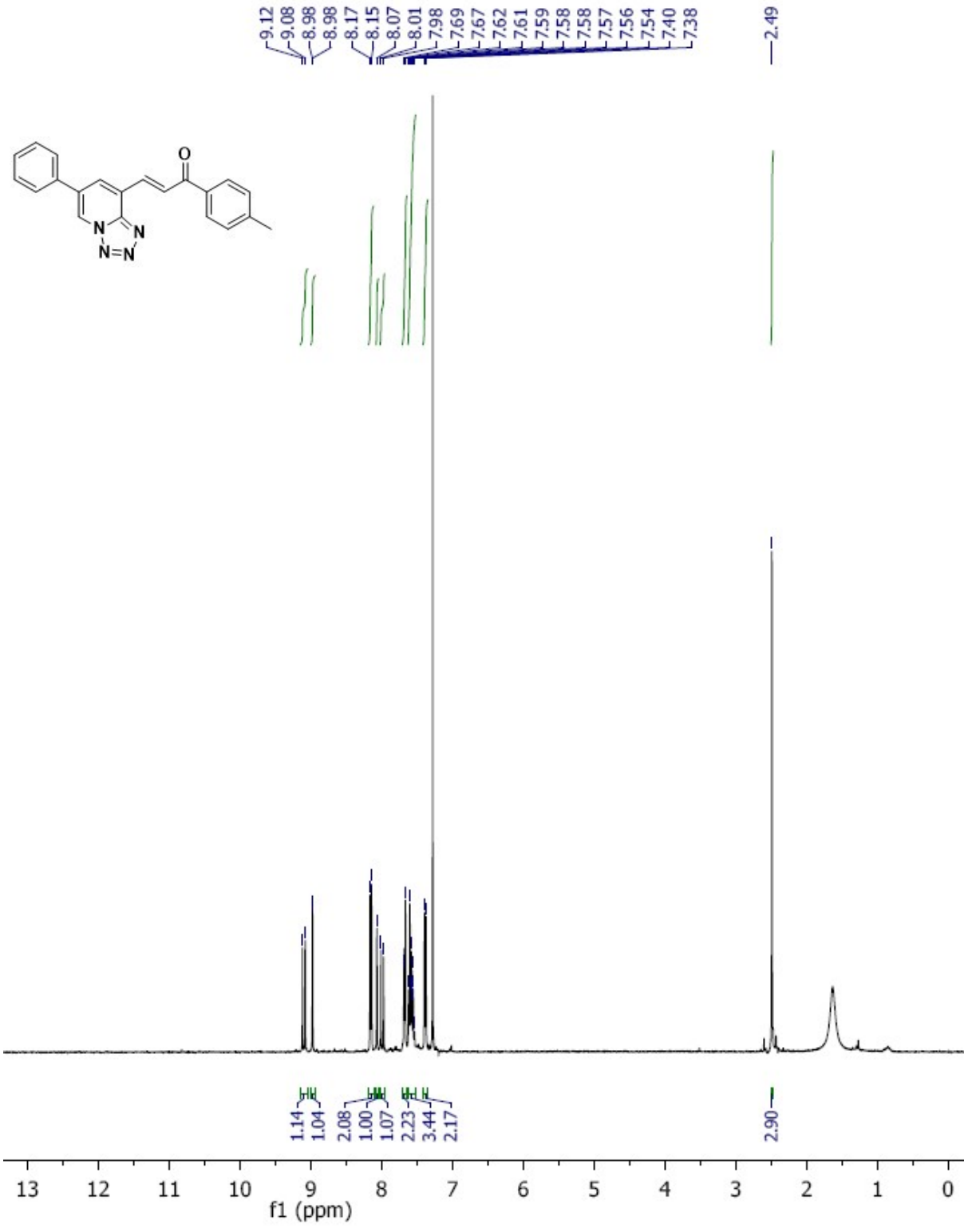


LCMS of Compound-4g

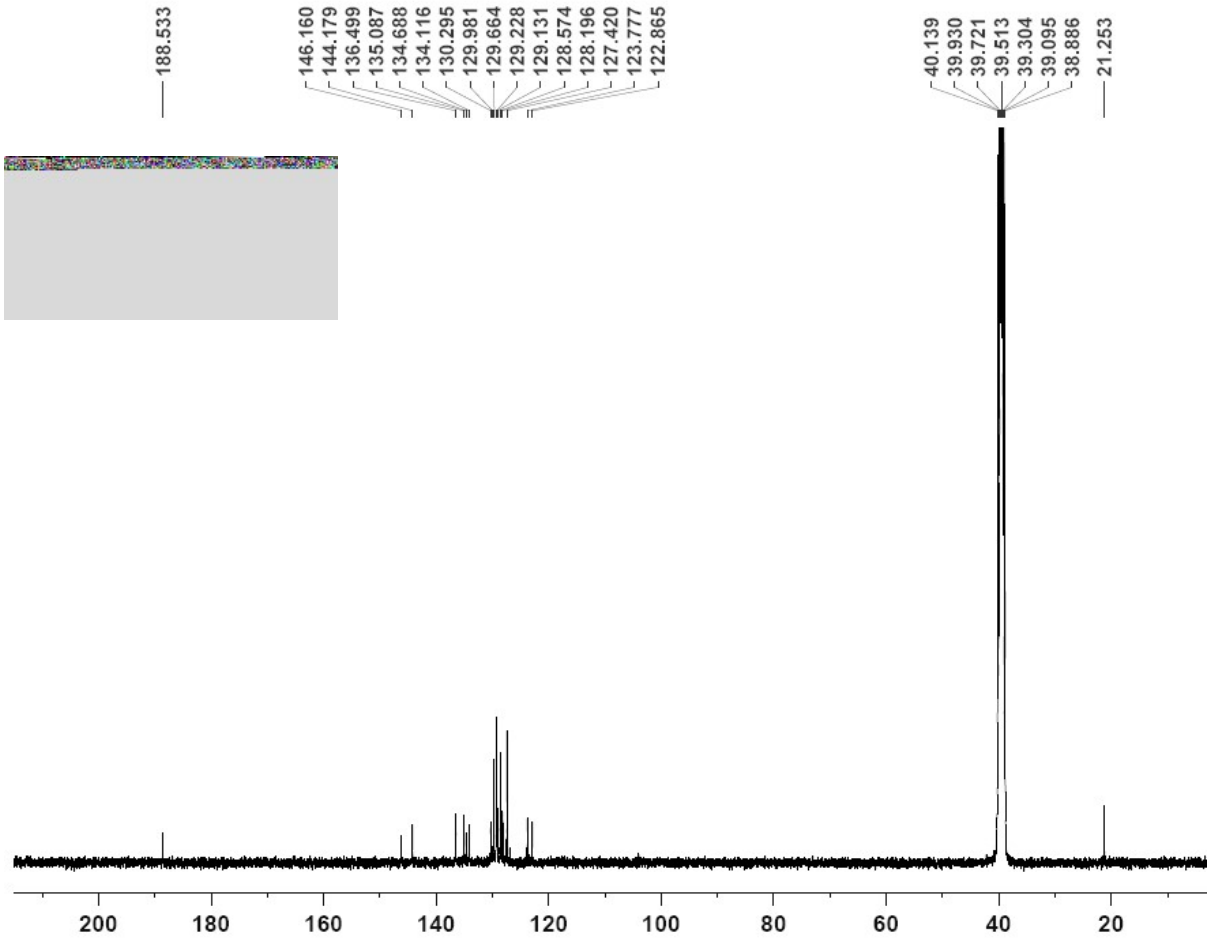


Base Peak 539.49 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:1.6;3.5:4.0) x 20.000 Th: 0.010 Retention Time 2.617

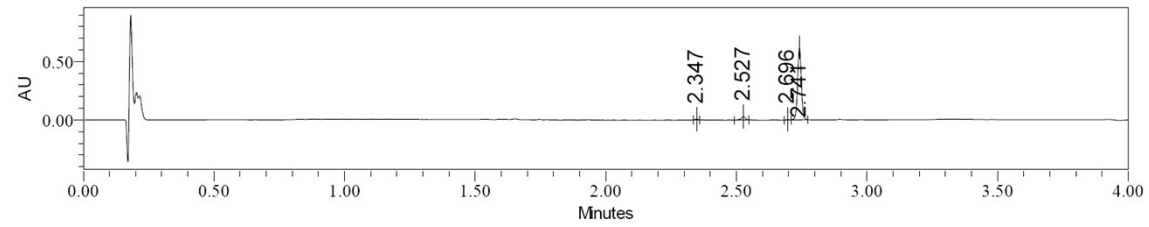
^{1}H NMR of Compound-4h

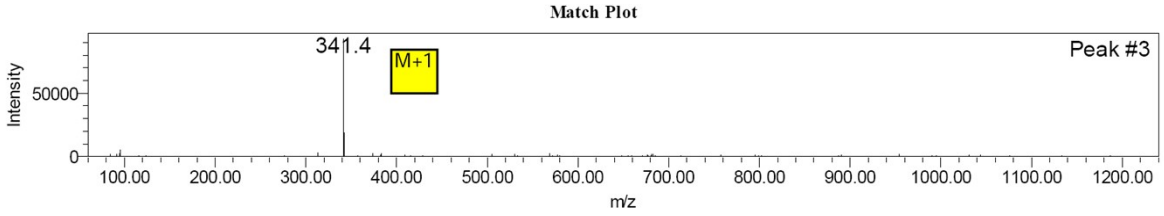


^{13}C NMR of Compound-4h



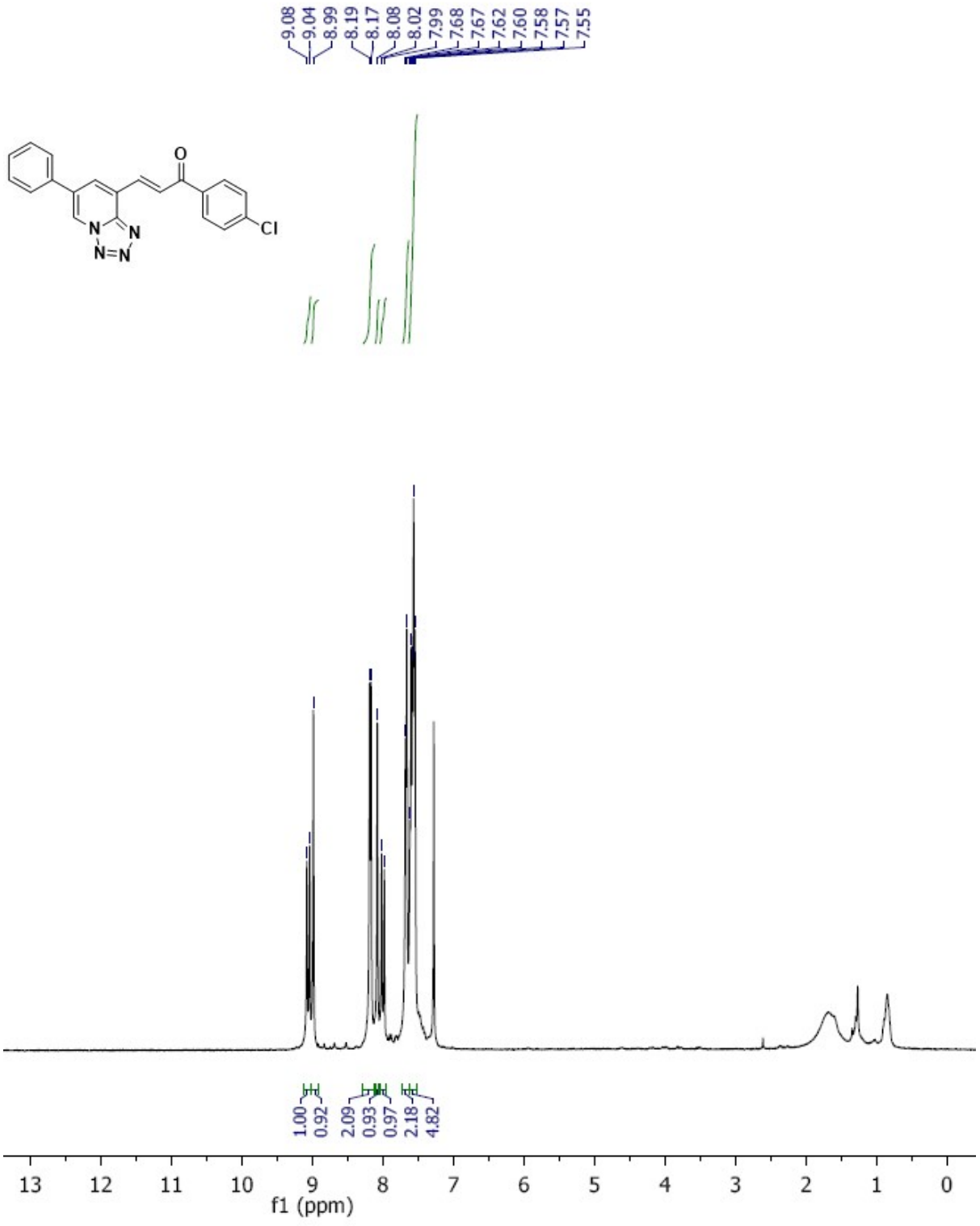
LCMS of Compound-4h



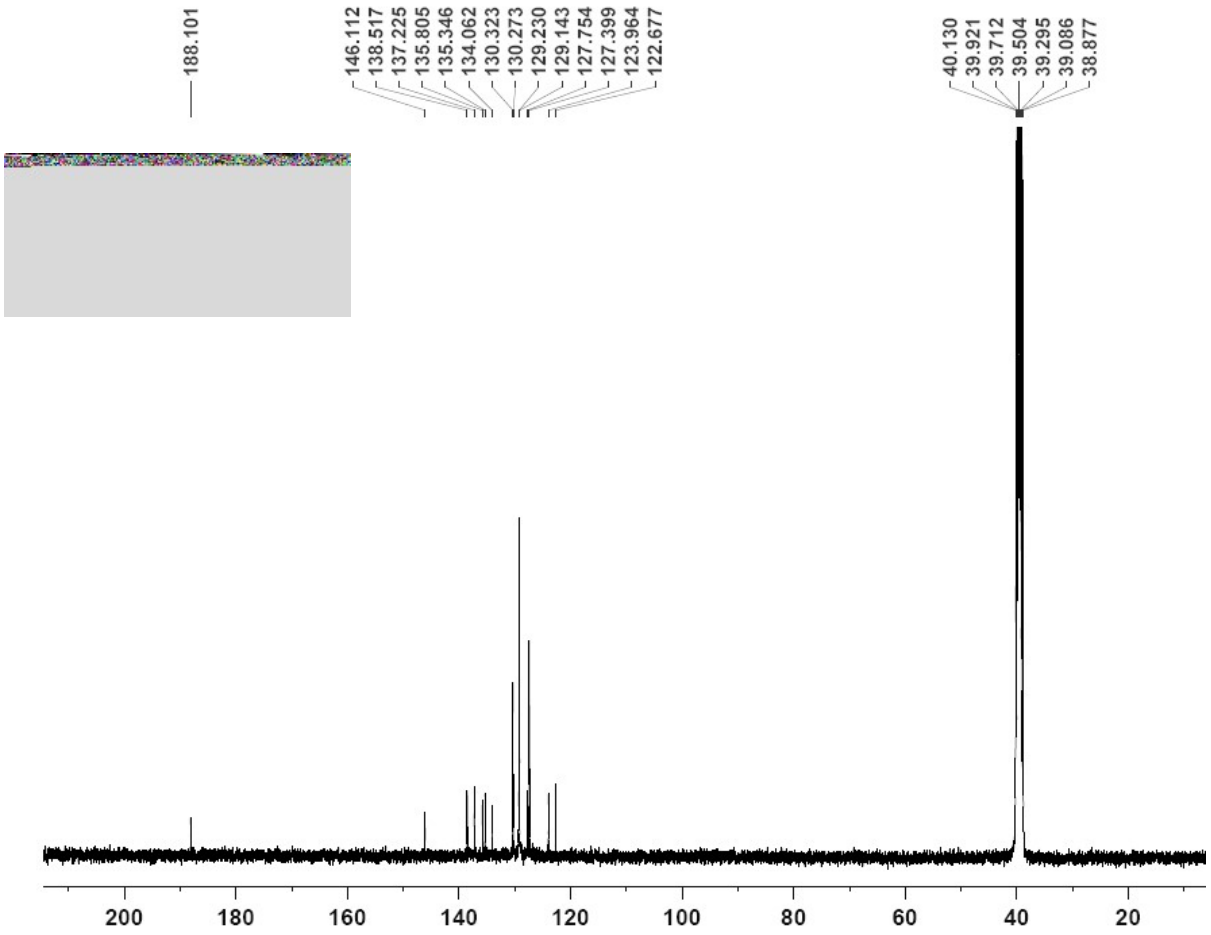


Base Peak 341.38 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.2;2.8:4.0) x 20.000 Th: 0.010 Retention Time 2.749

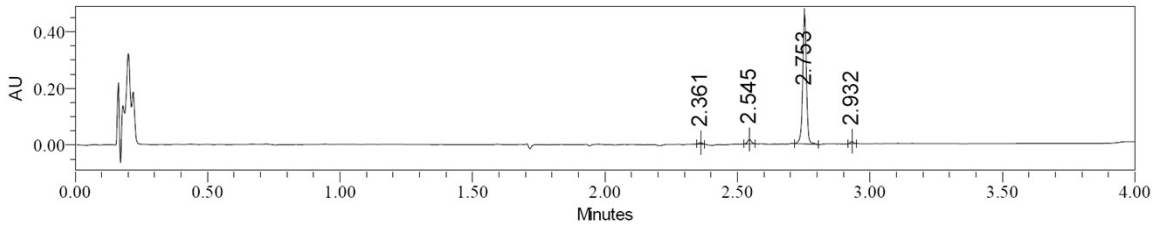
^{1}H NMR of Compound-4i

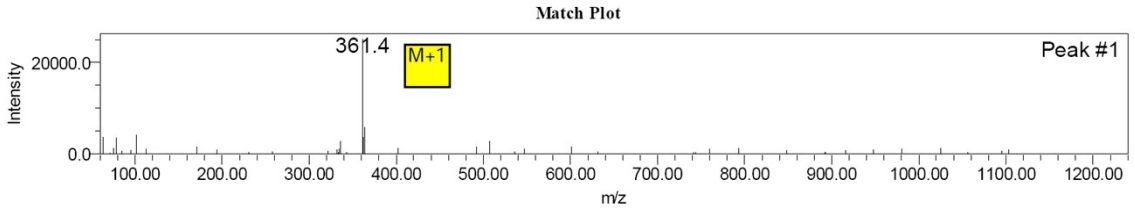


^{13}C NMR of Compound-4i



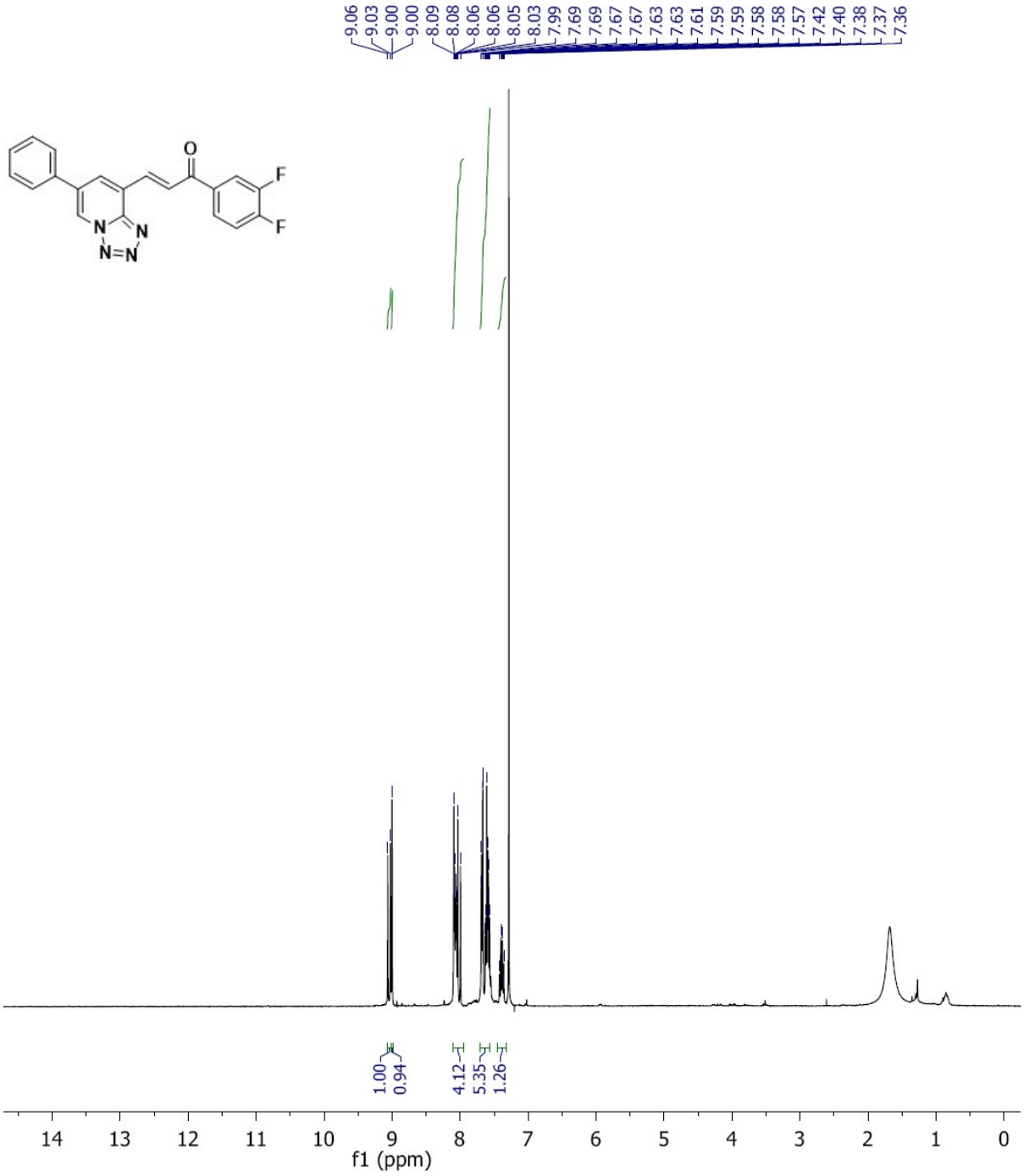
LCMS of Compound-4i



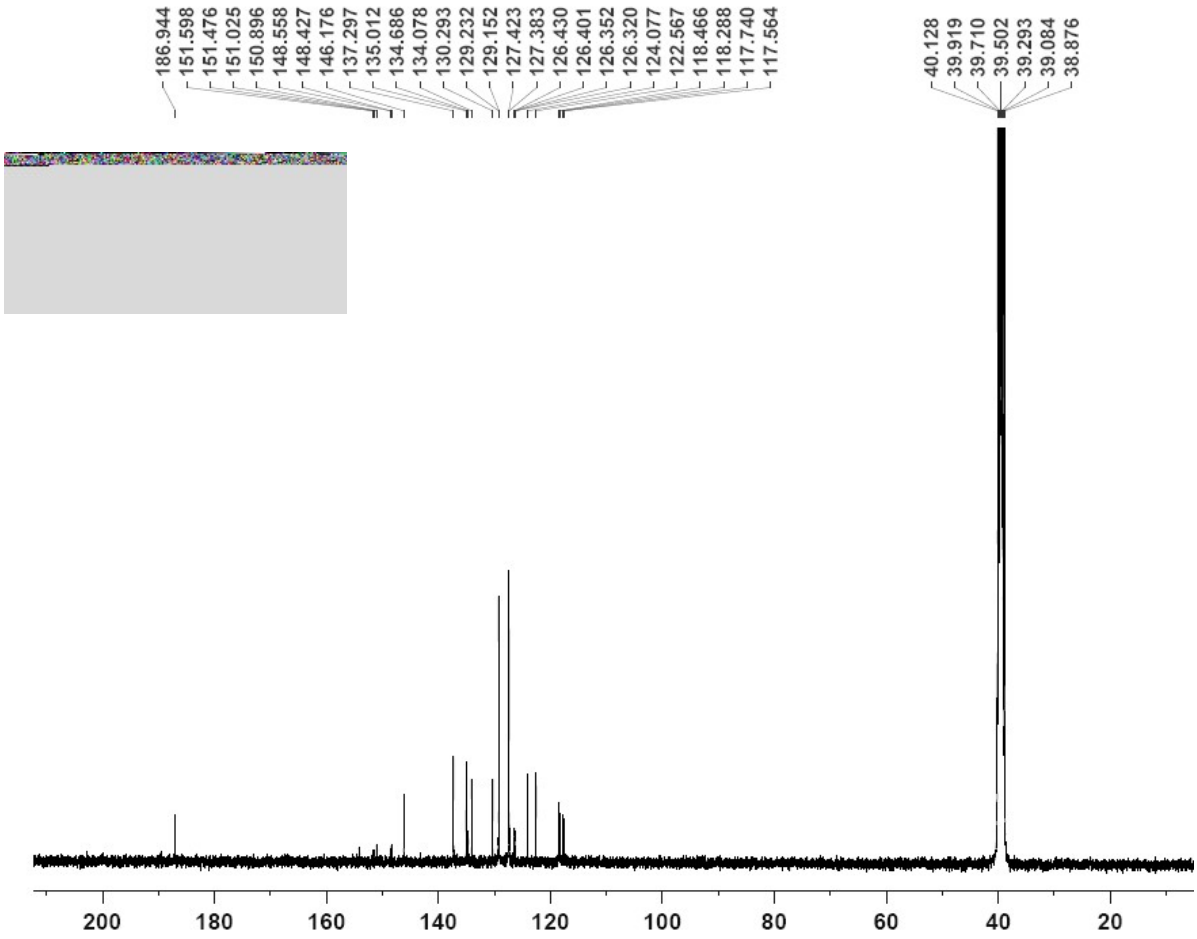


Base Peak 361.41 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.3;3.0:4.0) x 20.000 Th: 0.010 Retention Time 2.760

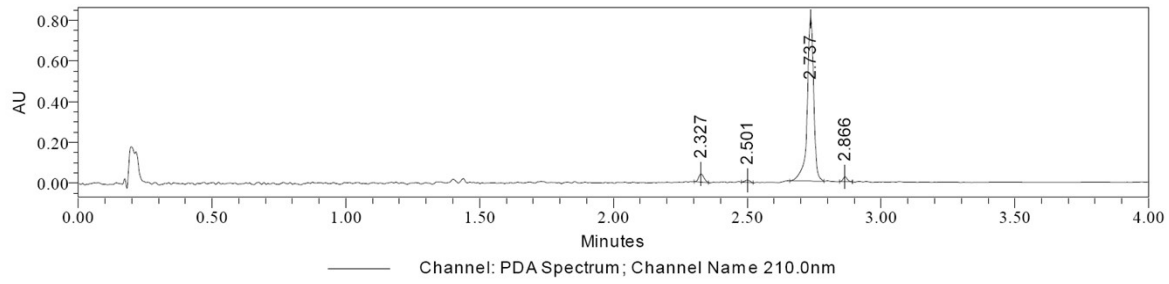
^{1}H NMR of Compound-4j



^{13}C NMR of Compound-4j

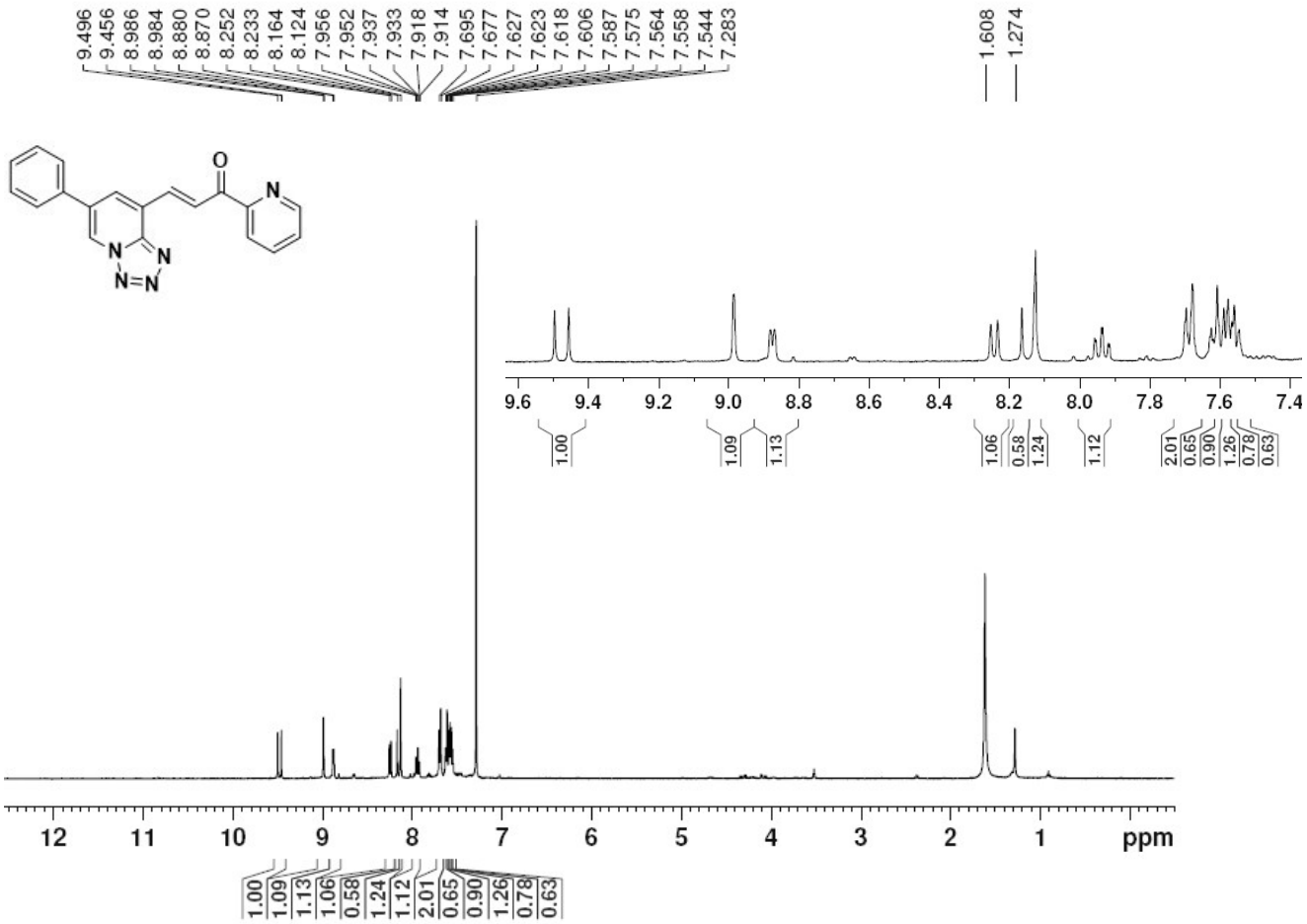


LCMS of Compound-4j

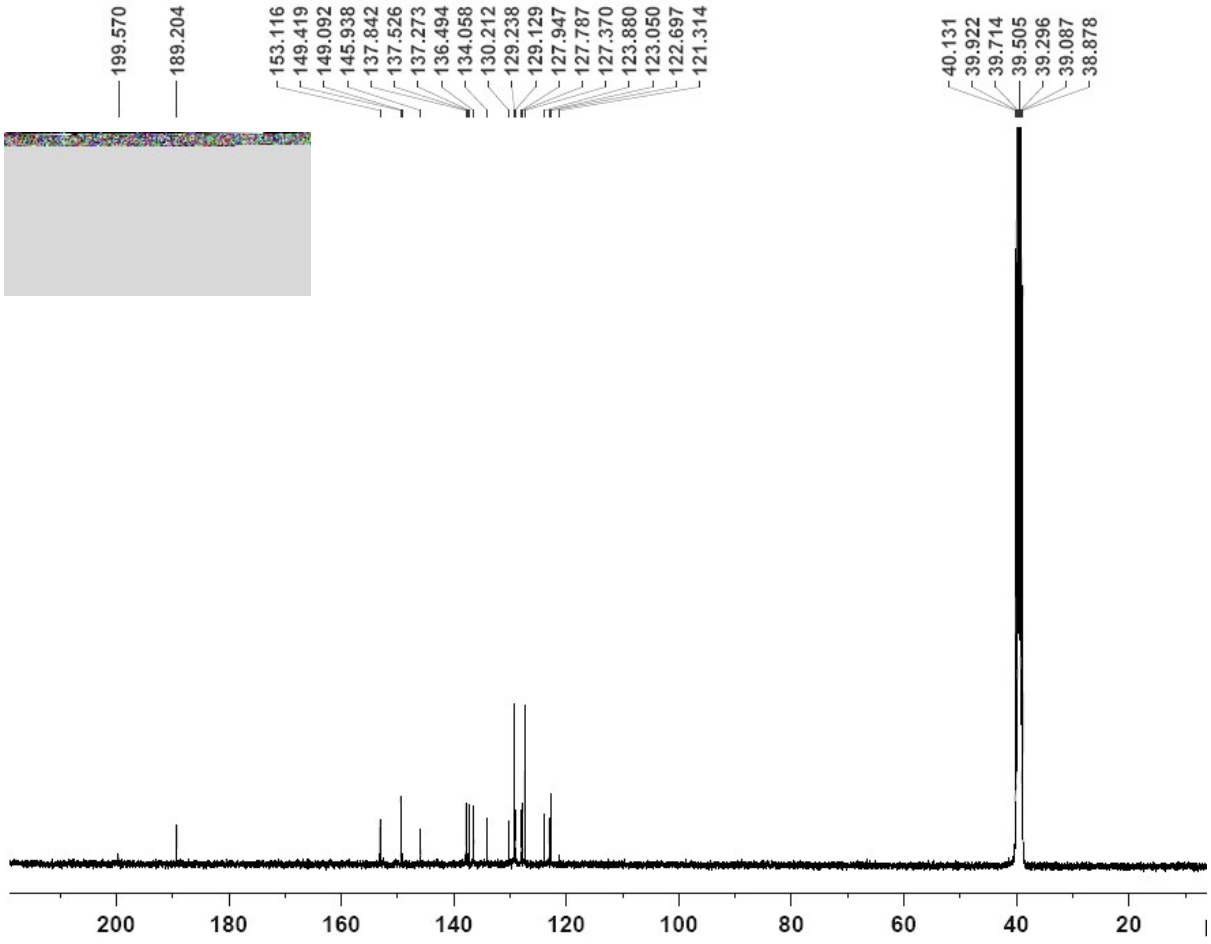


Due to presence of di-Fluoro, desired mass was not observed in LCMS

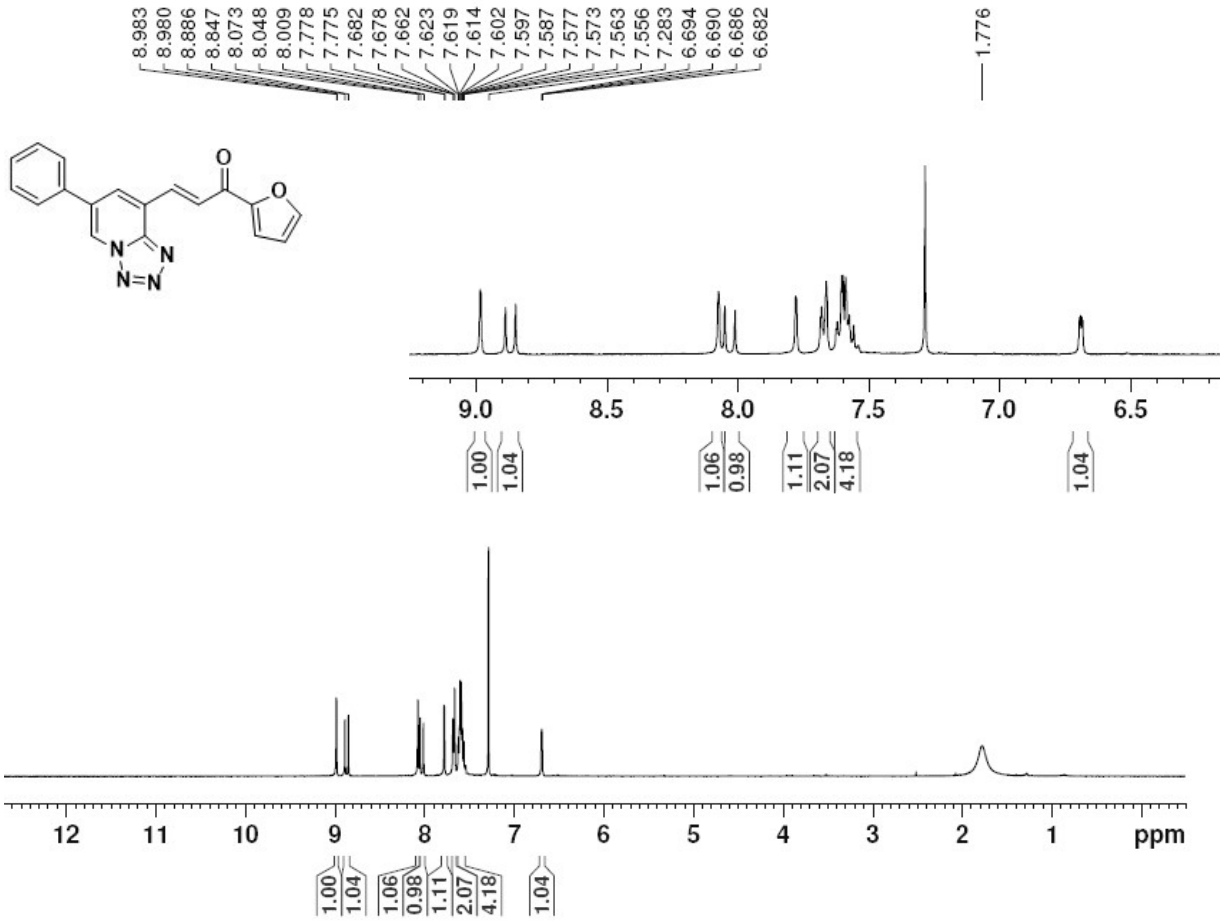
[1]H NMR of Compound-4k



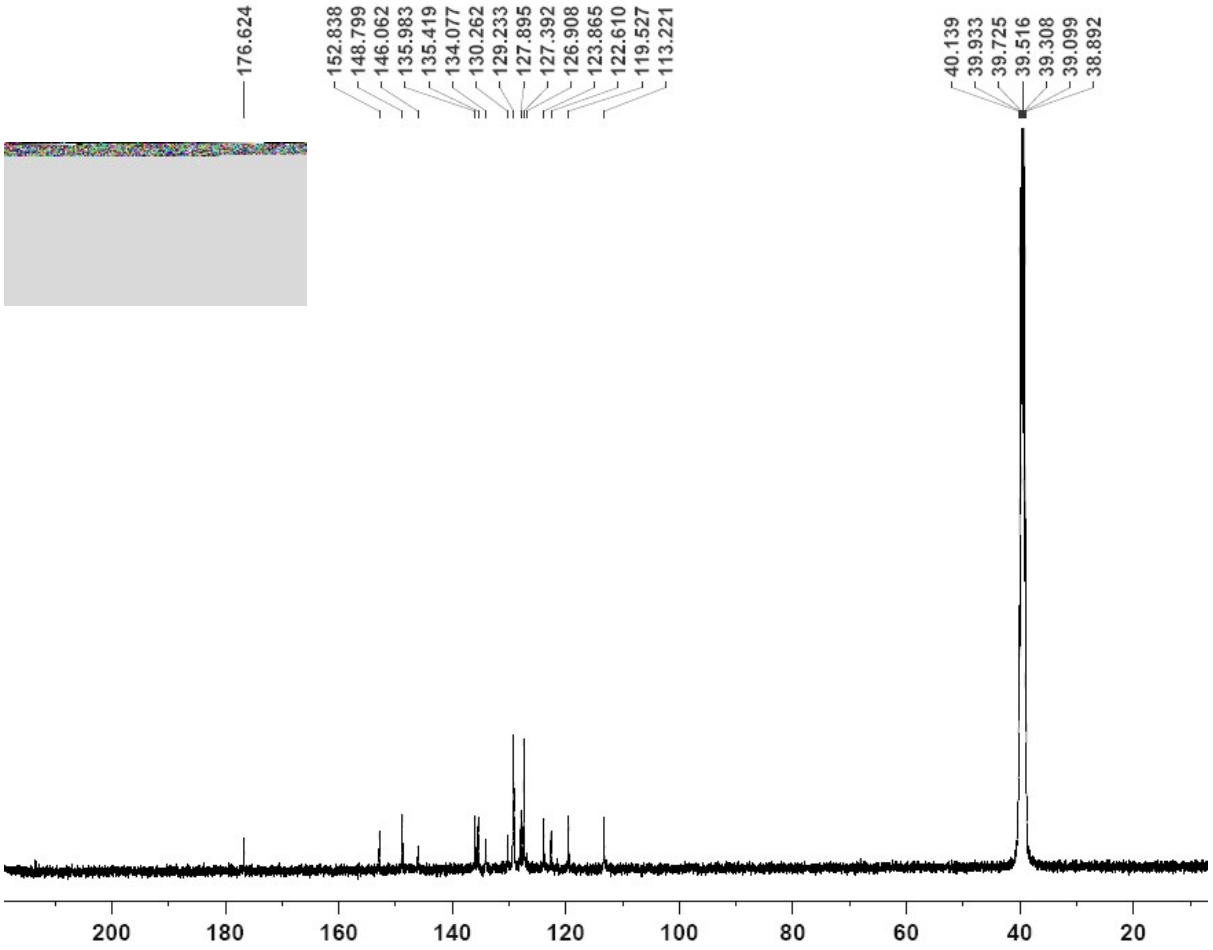
^{13}C NMR of Compound-4k



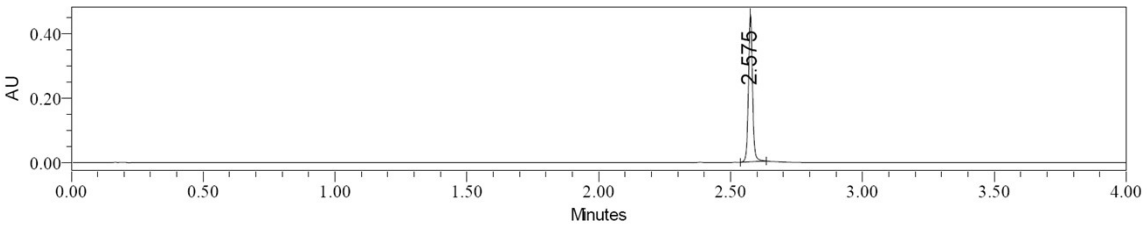
^{1}H NMR of Compound-4l

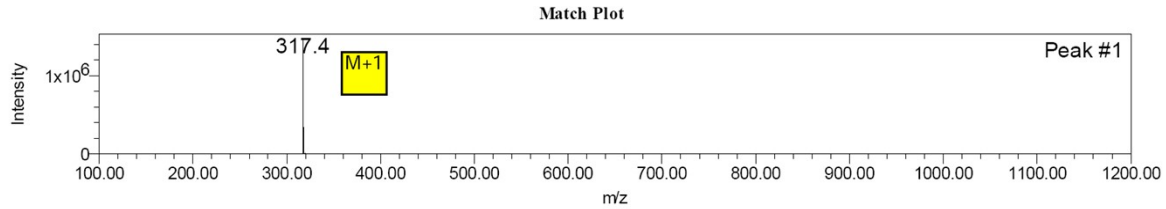


^{13}C NMR of Compound-4l



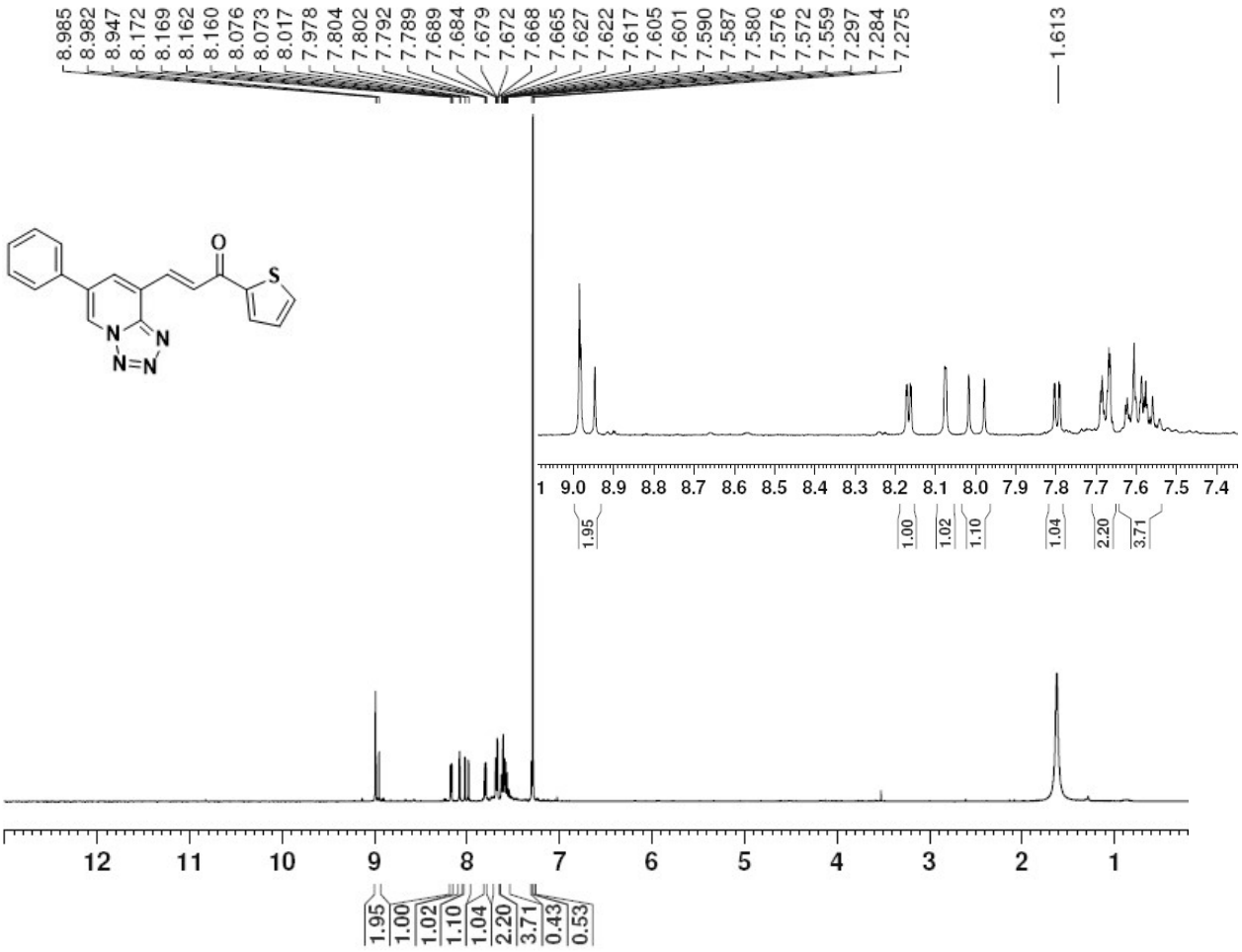
LCMS of Compound-4l



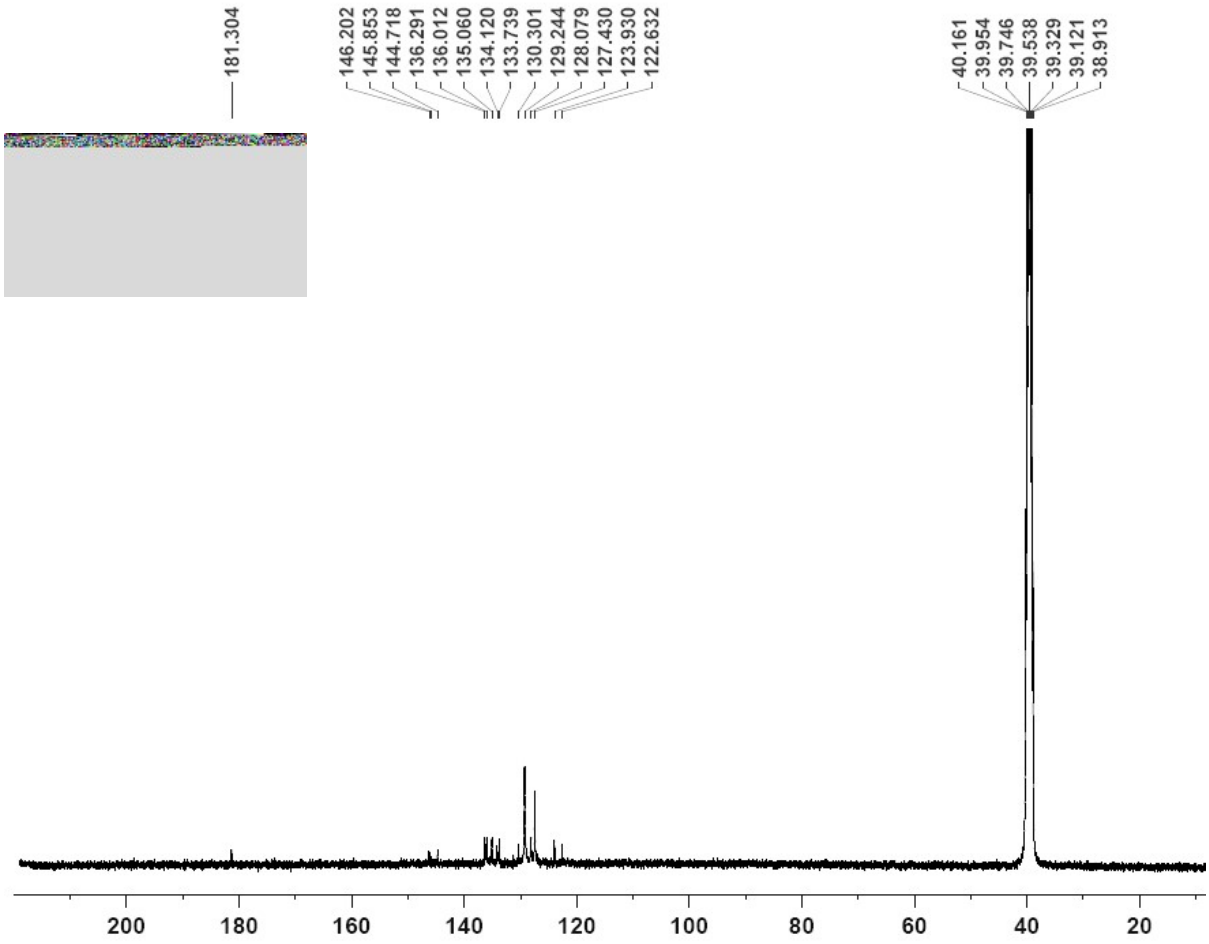


Base Peak 317.36 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (2.8:4.0;0.0:1.2) x 30.000 Retention Time 2.583

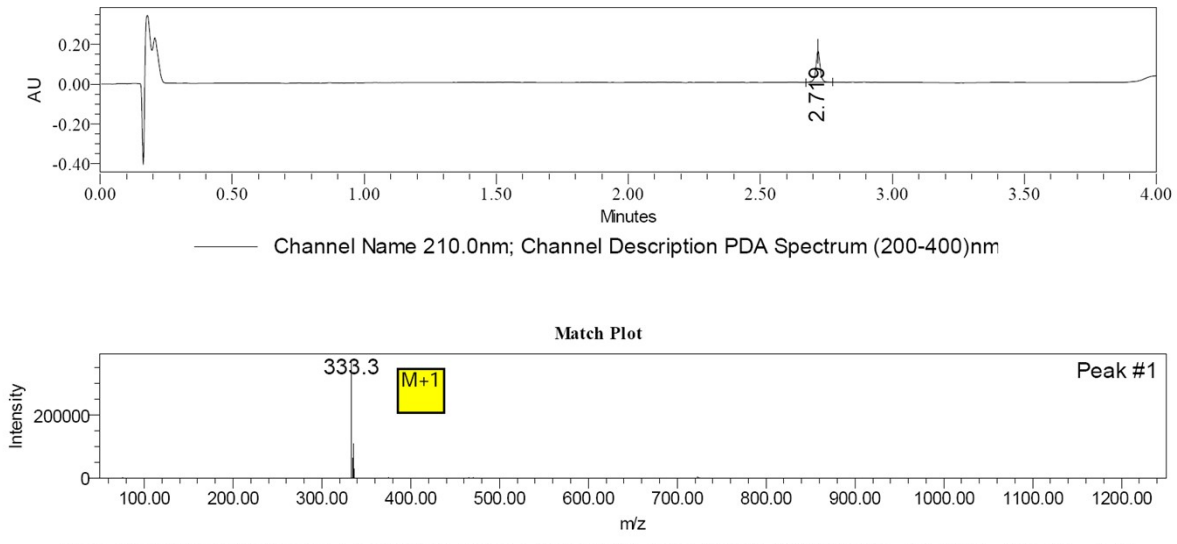
^{1}H NMR of Compound-4m



^{13}C NMR of Compound-4m

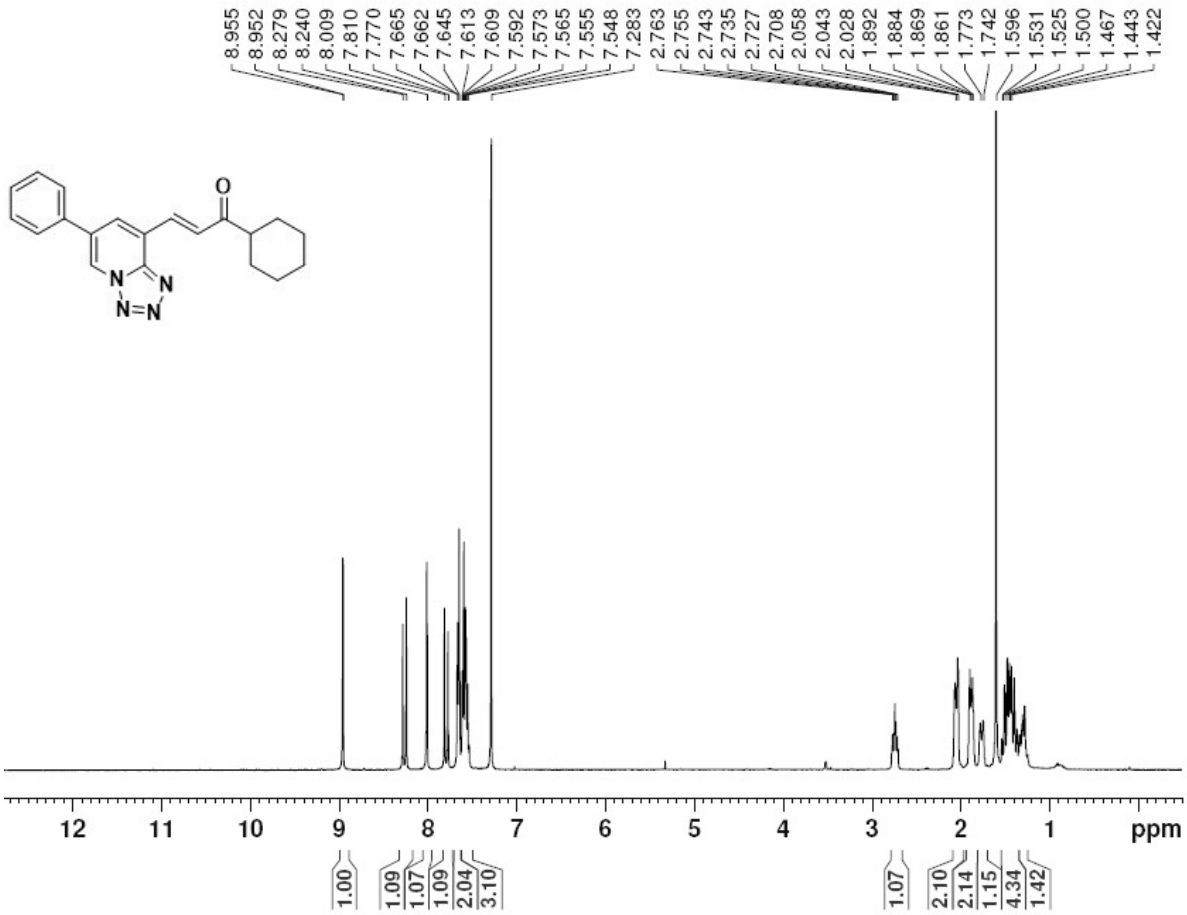


LCMS of Compound-4m

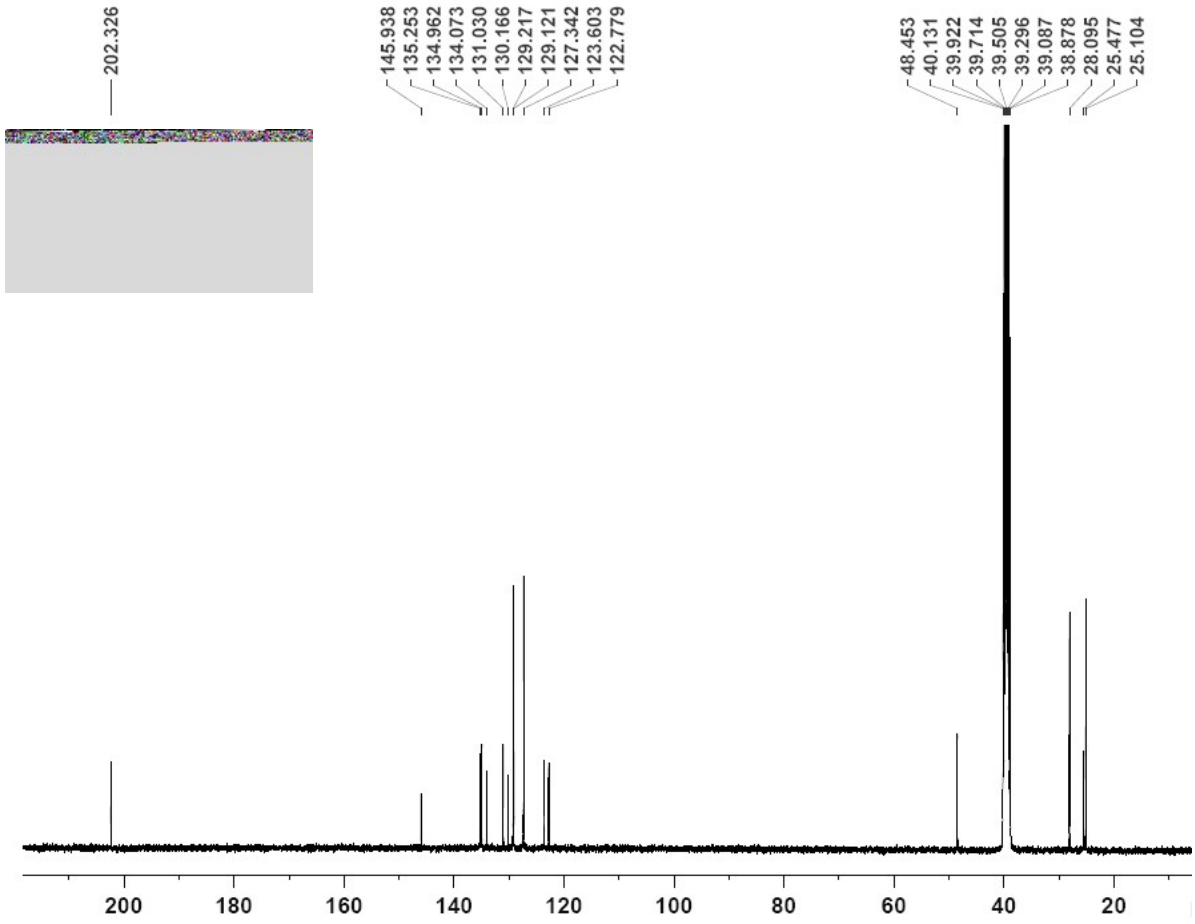


Base Peak 333.33 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.6;2.8:4.0) x 20.000 Th: 0.010 Retention Time 2.726

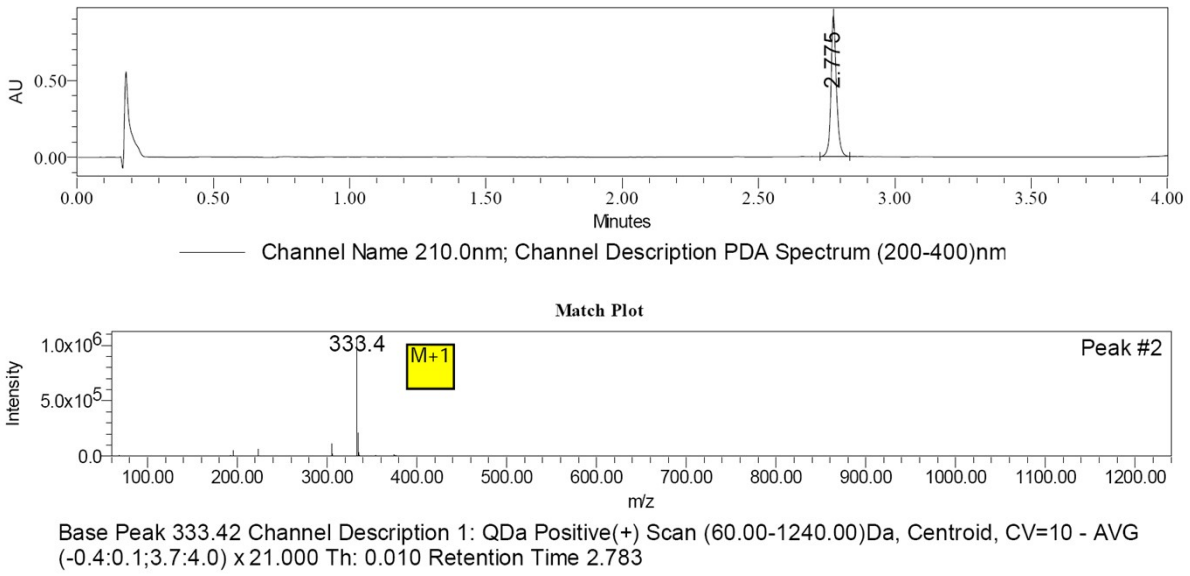
^{1}H NMR of Compound-4n



^{13}C NMR of Compound-4n

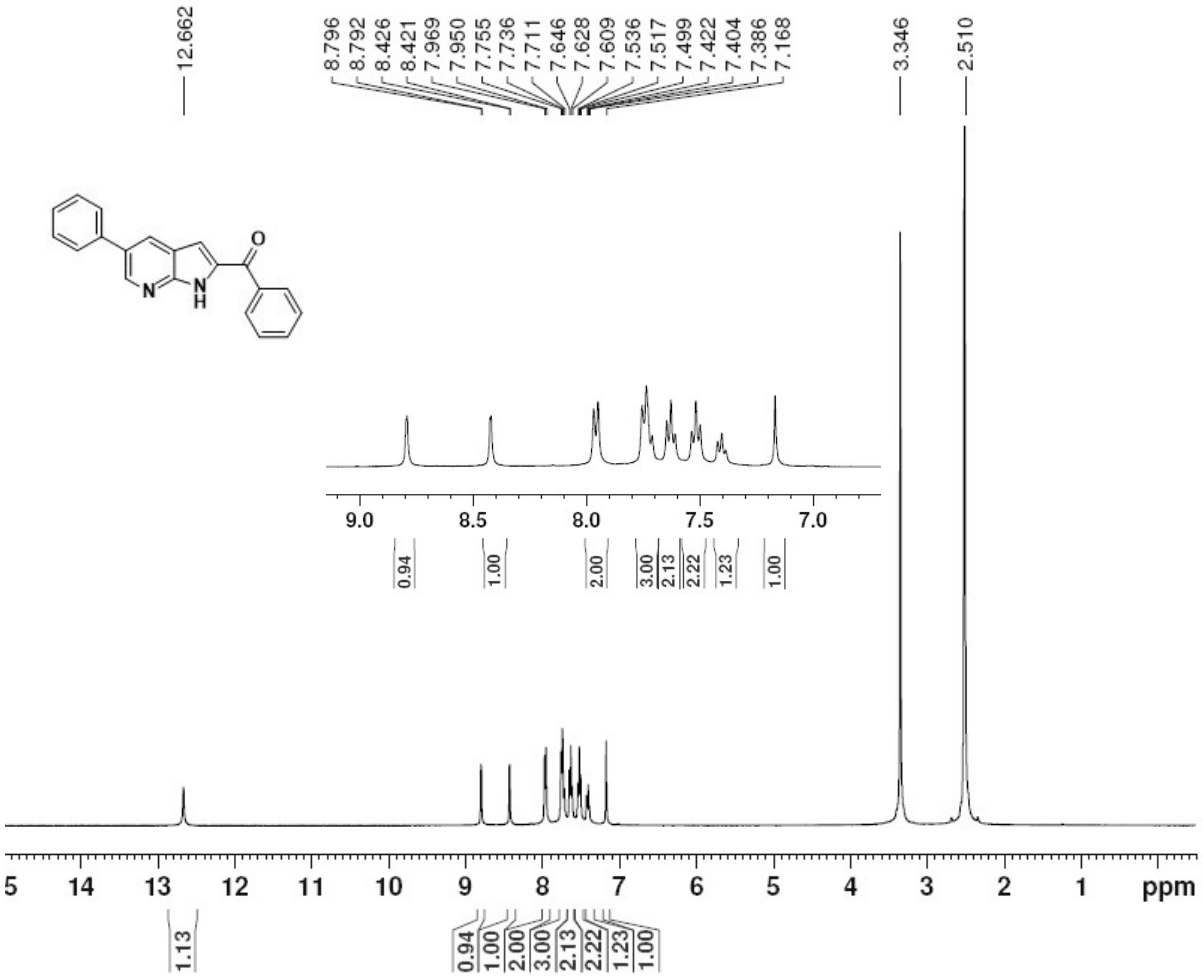


LCMS of Compound-4n

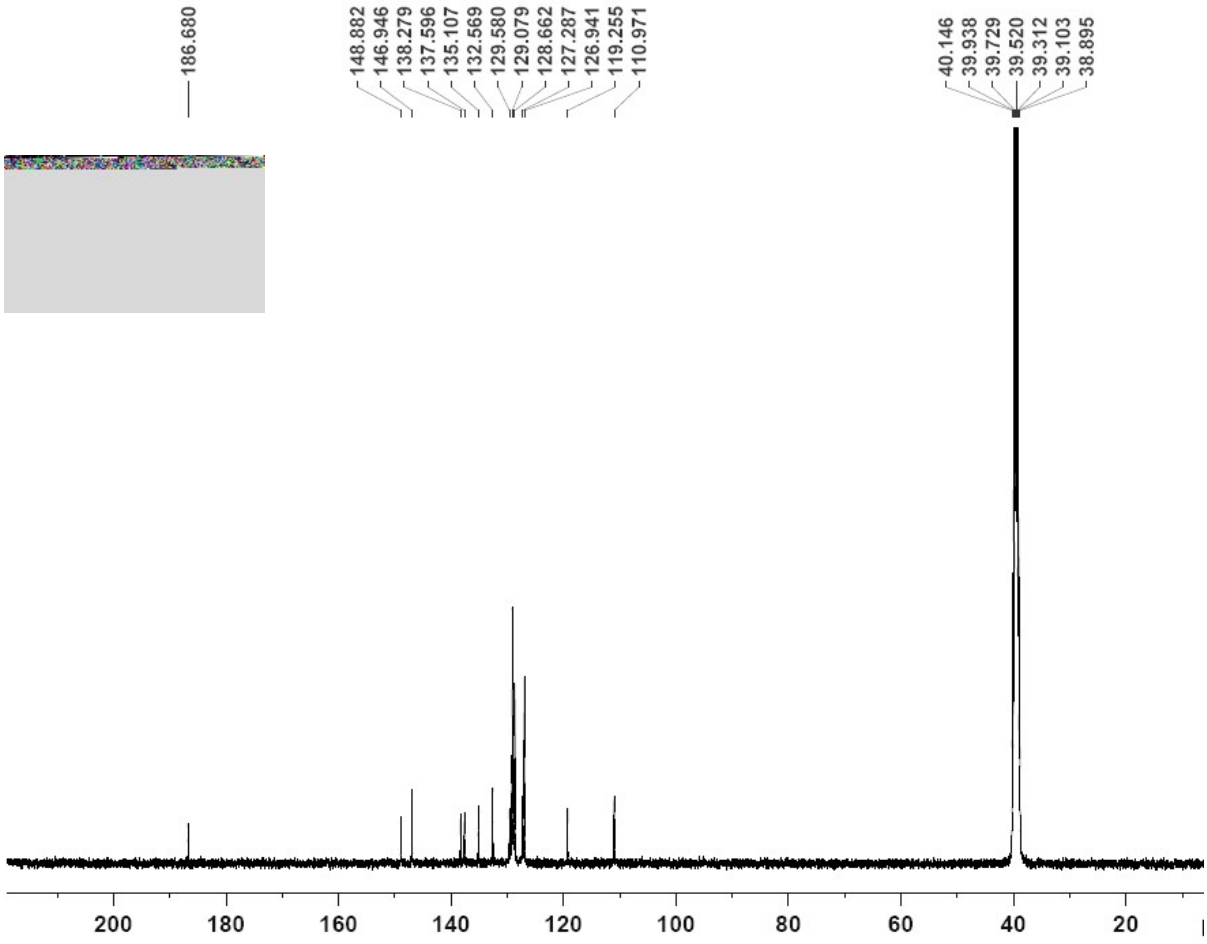


Base Peak 333.42 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (-0.4:0.1;3.7:4.0) x 21.000 Th: 0.010 Retention Time 2.783

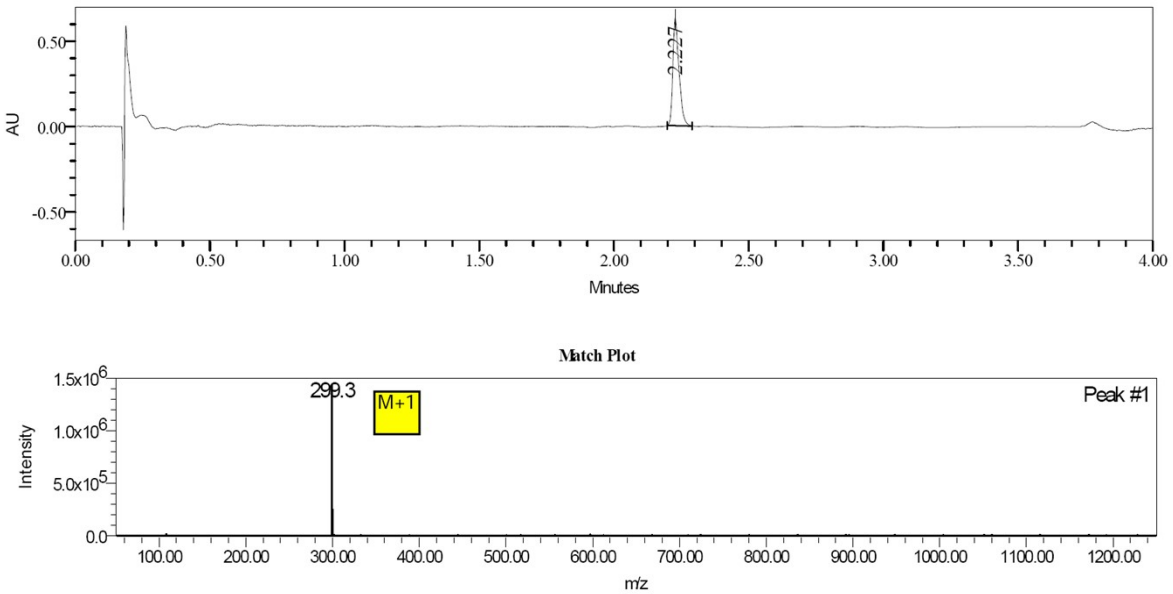
^{1}H NMR of Compound-5a



^{13}C NMR of Compound-5a

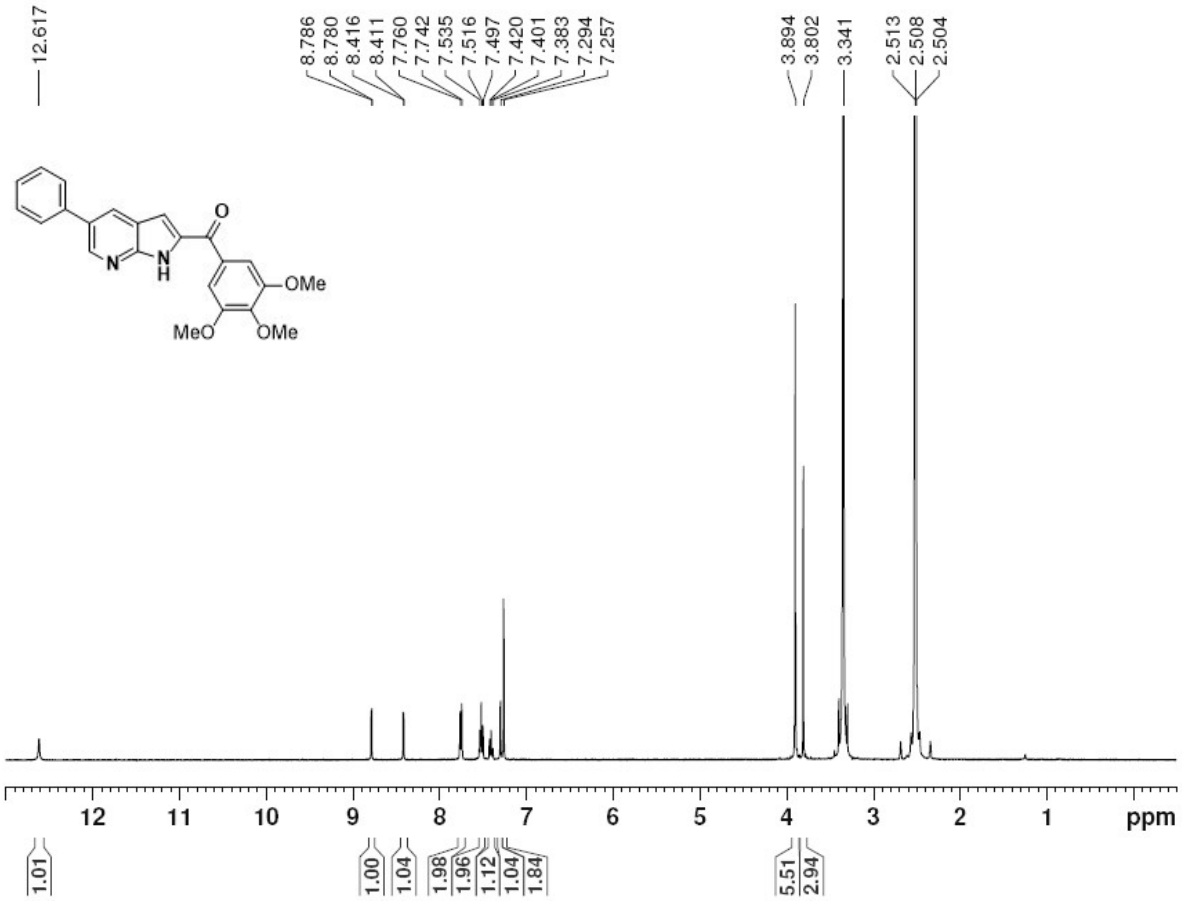


LCMS of Compound-5a

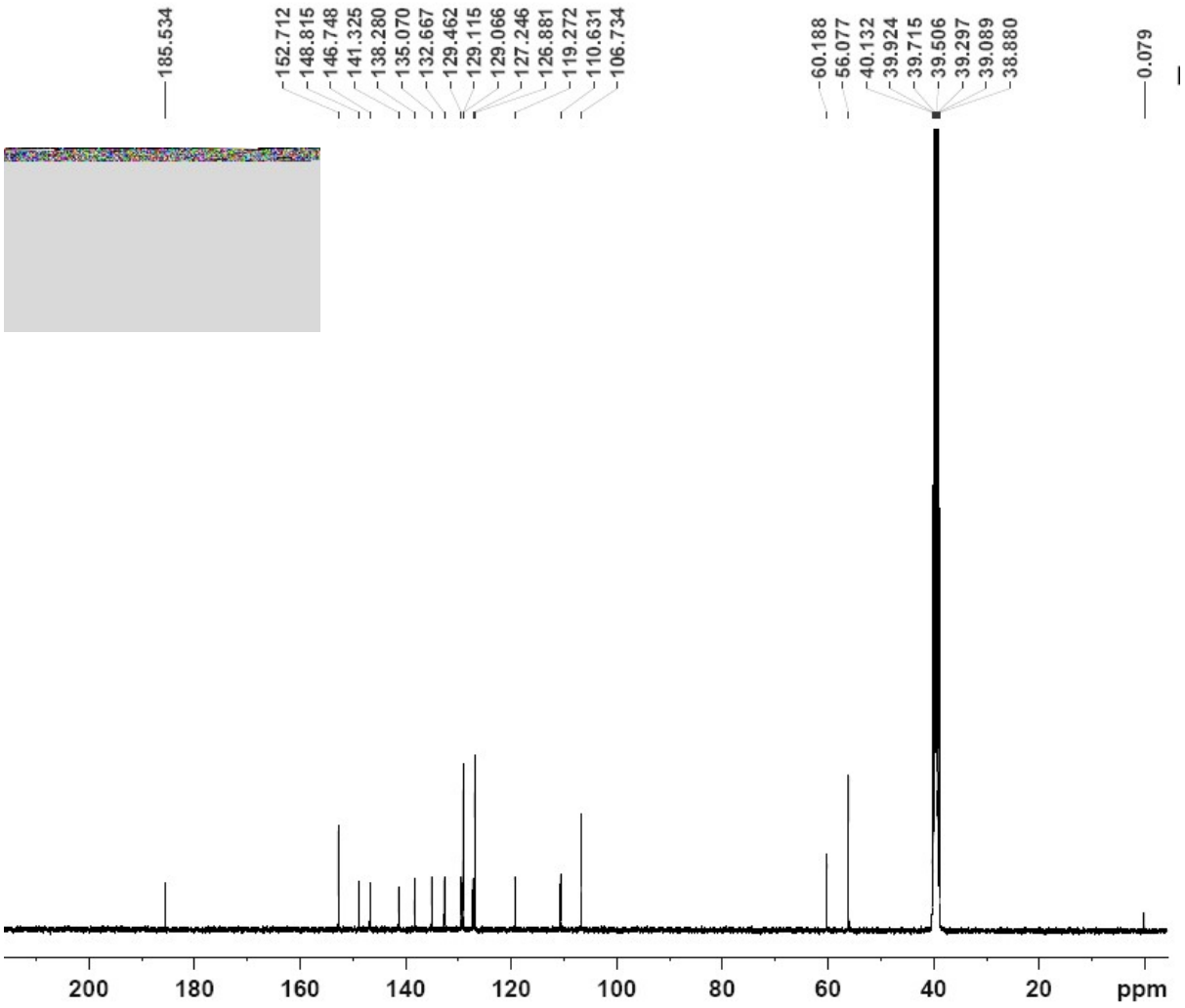


Base Peak 299.25 Channel Description 1: QDa Positive(+) Scan (50.00-1250.00)Da, Centroid, CV=10 - AVG (2.4:3.9;0.3:2.1) x 20.000 Th: 0.200
Retention Time 2.258

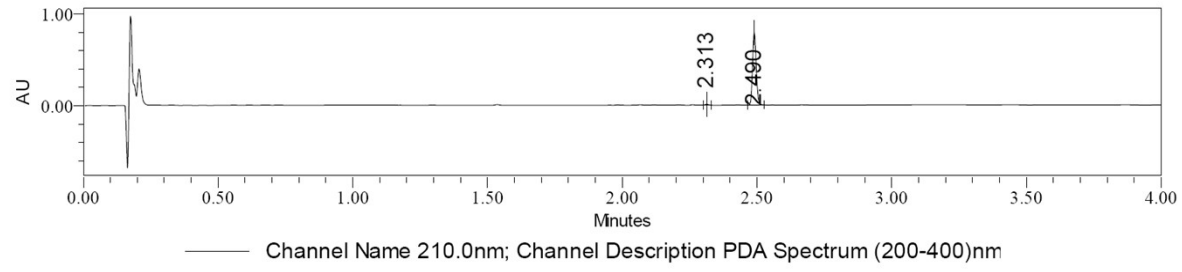
[1]H NMR of Compound-5b

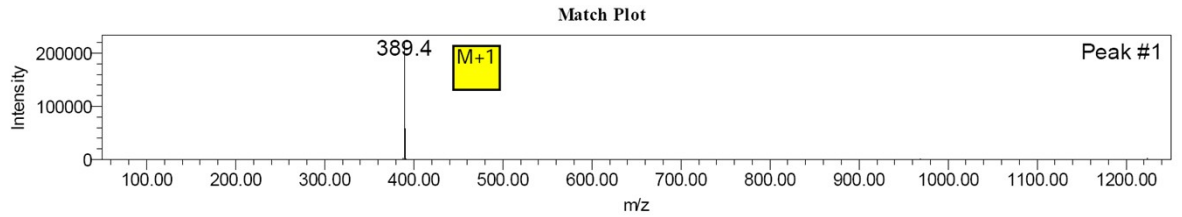


^{13}C NMR of Compound-5b



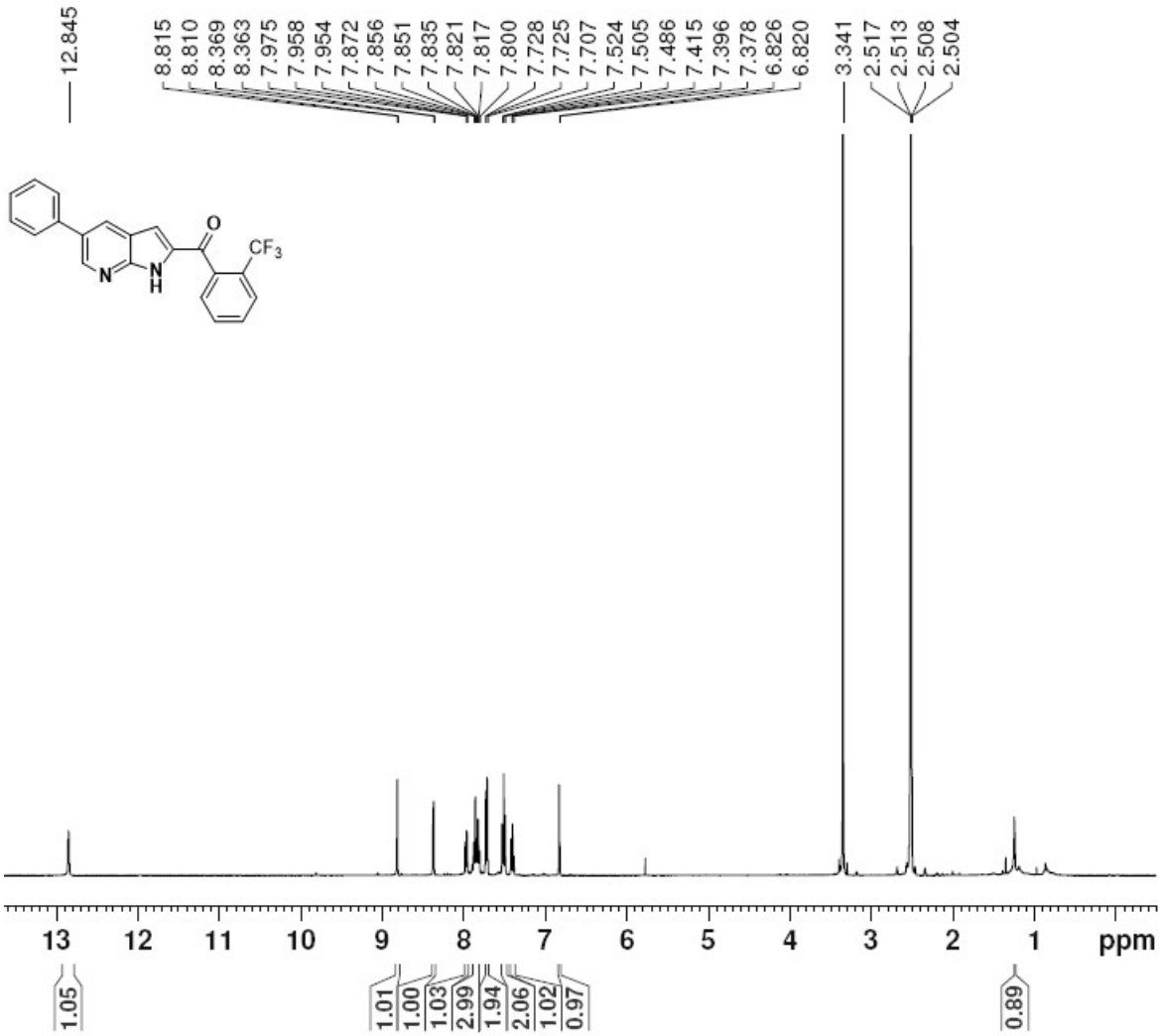
LCMS of Compound-5b



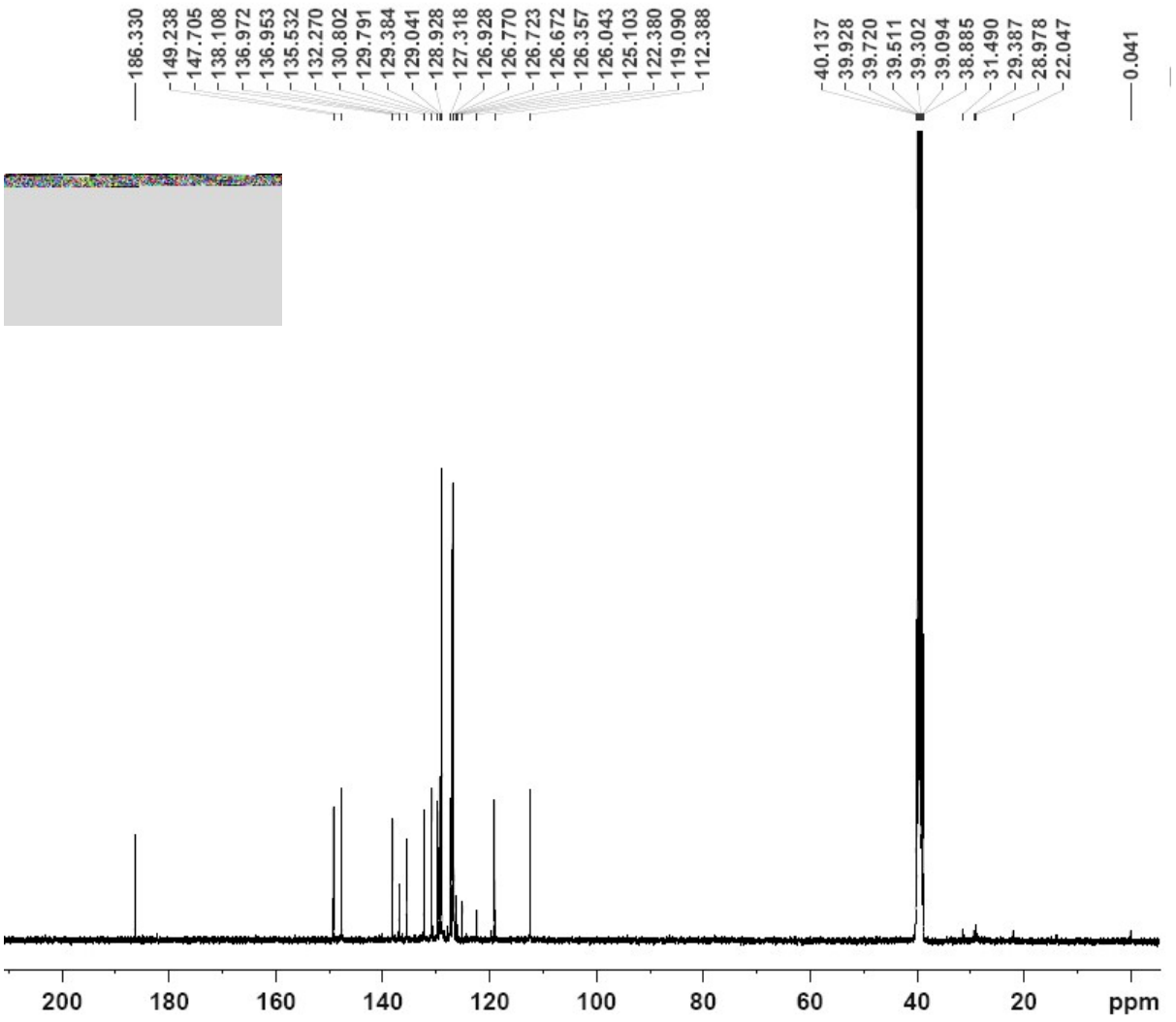


Base Peak 389.44 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:1.9;2.8:3.9) x 20.000 Th: 0.200 - AVG (0.1:0.5;1.6:2.4;2.6:3.9) x 50.000 Th: 0.200 Retention Time 2.498

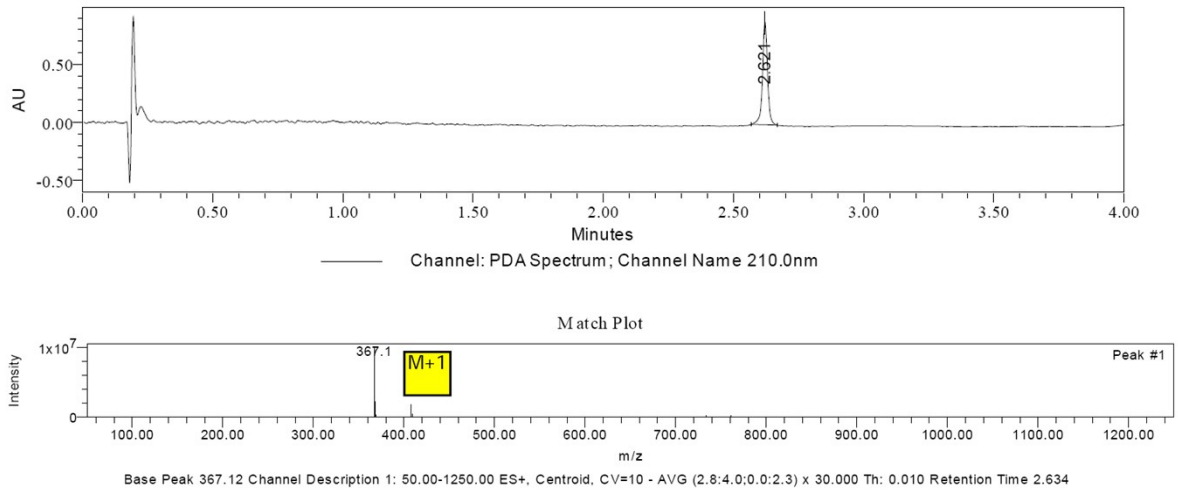
^{1}H NMR of Compound-5c



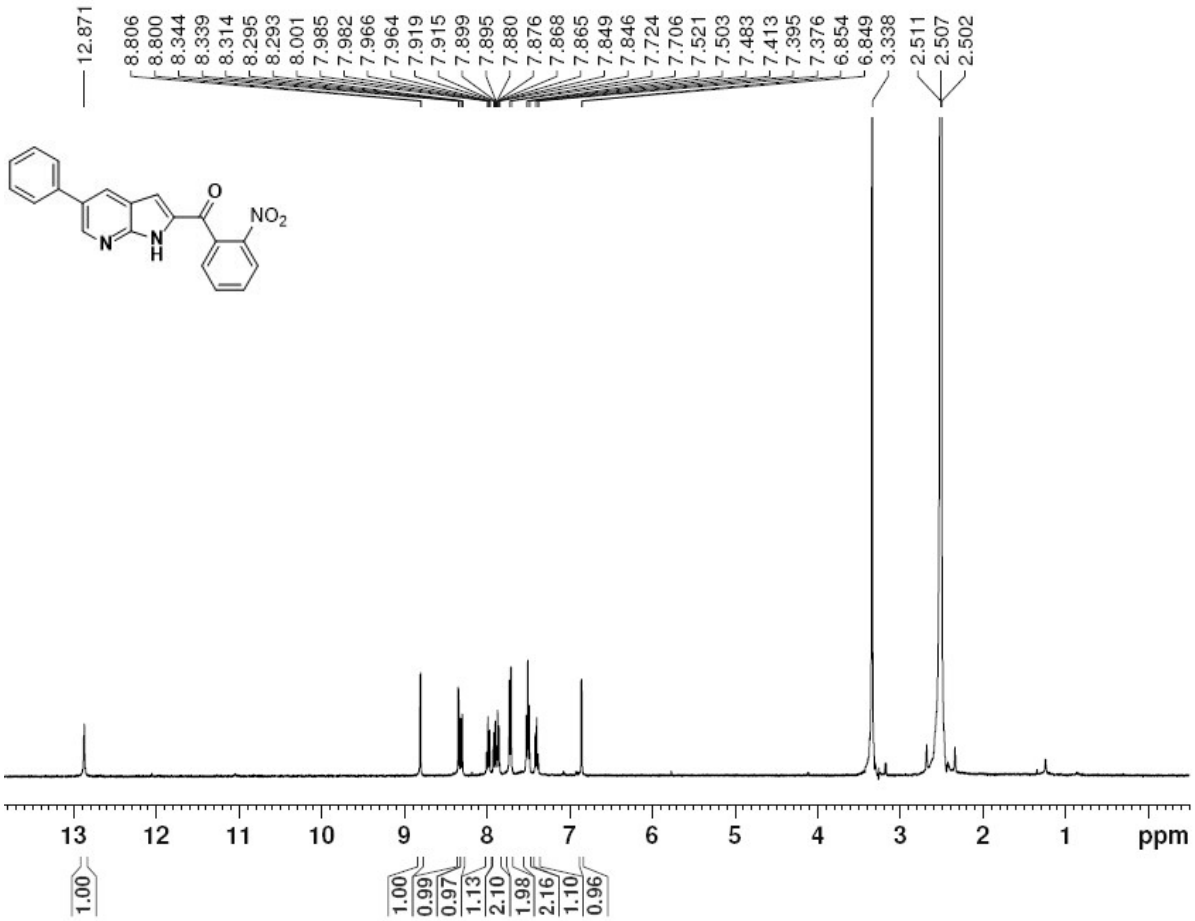
^{13}C NMR of Compound-5c



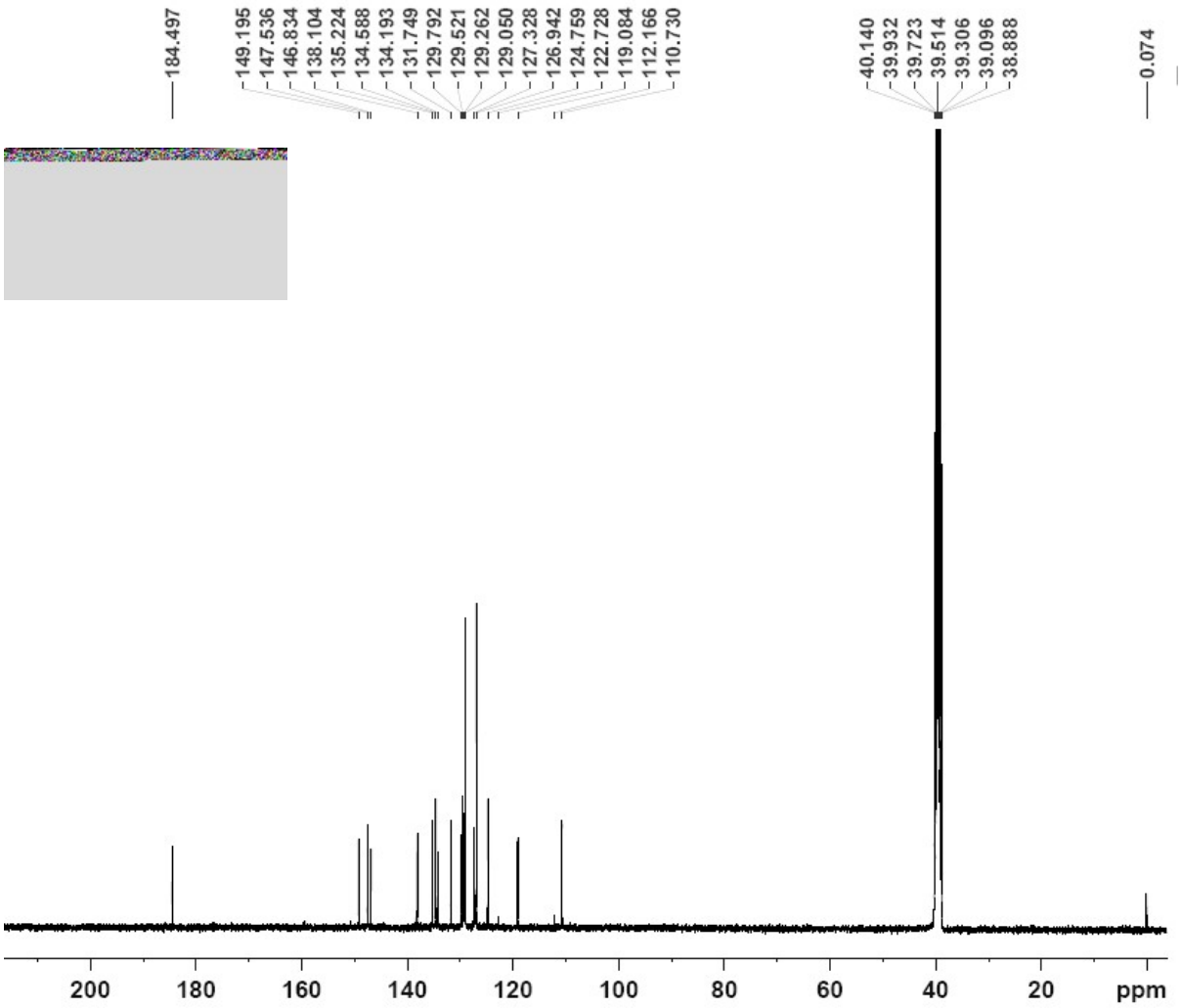
LCMS of Compound-5c



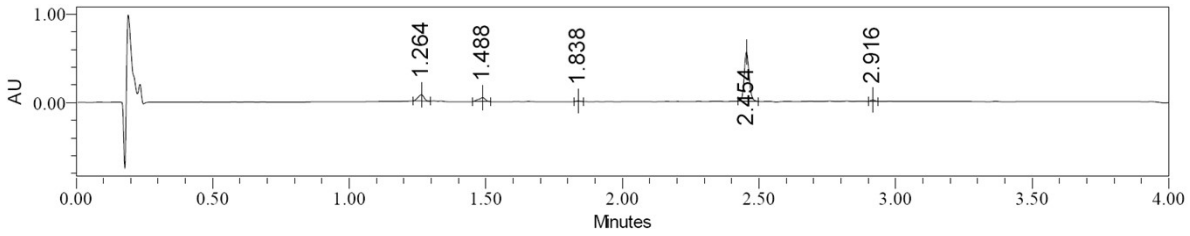
[1]H NMR of Compound-5d

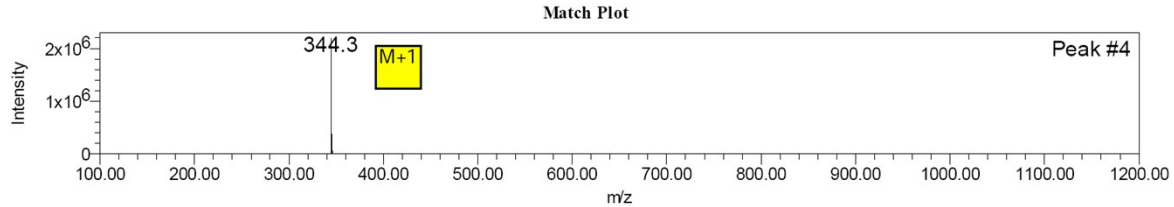


^{13}C NMR of Compound-5d



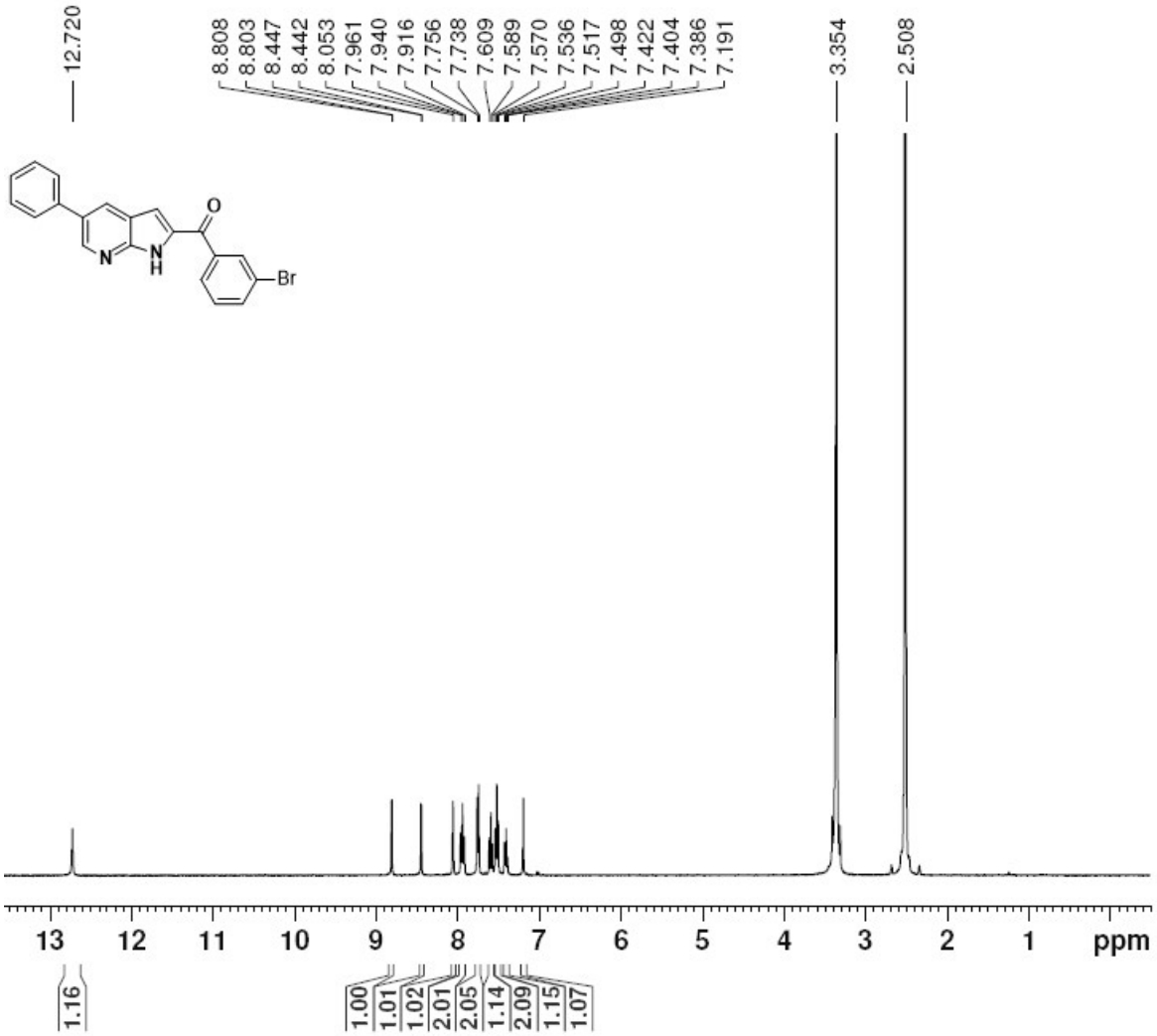
LCMS of Compound-5d



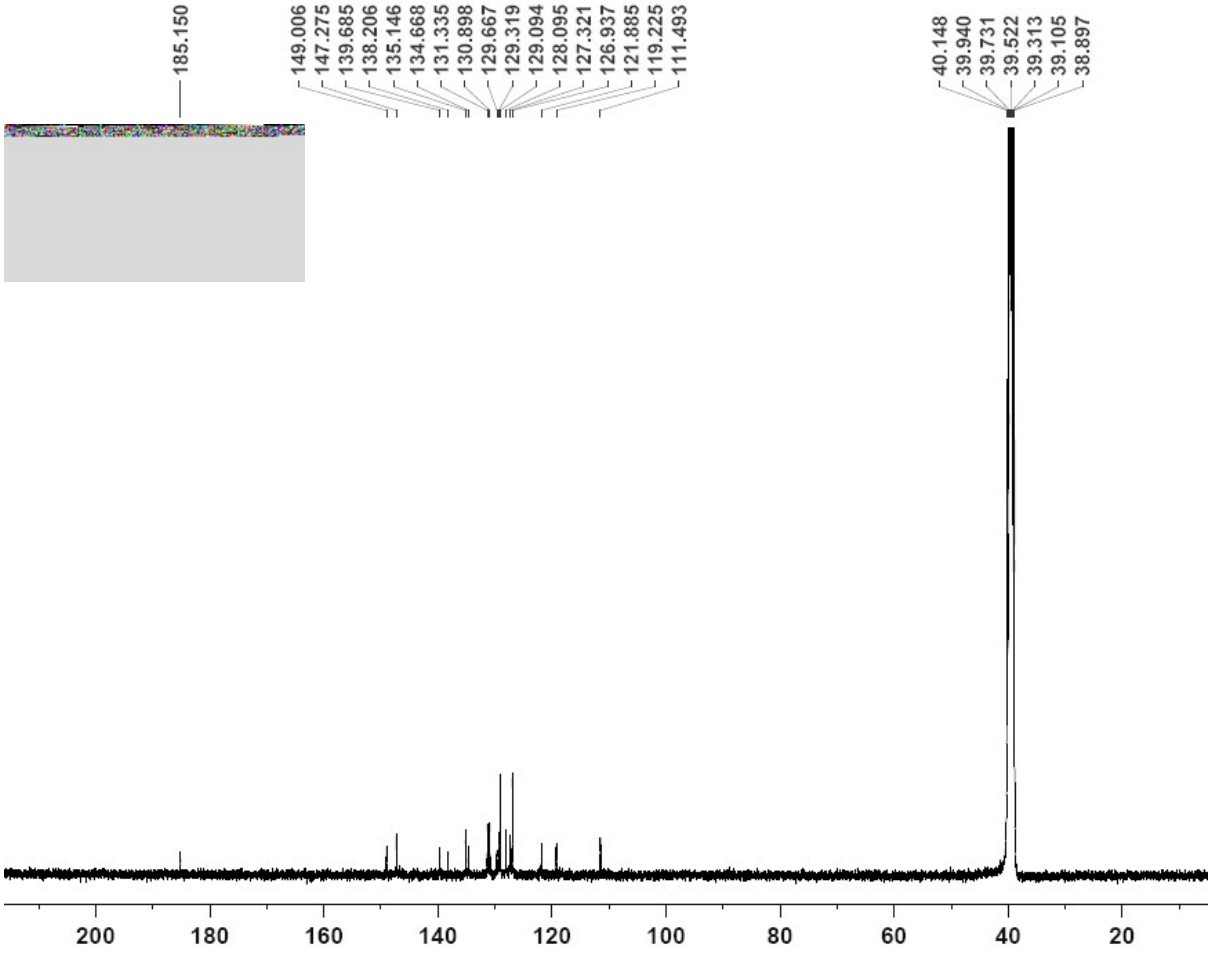


Base Peak 344.35 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:1.2;3.0:4.0;1.9:2.4;2.7:2.9) x 20.000 Th: 0.010 Retention Time 2.463

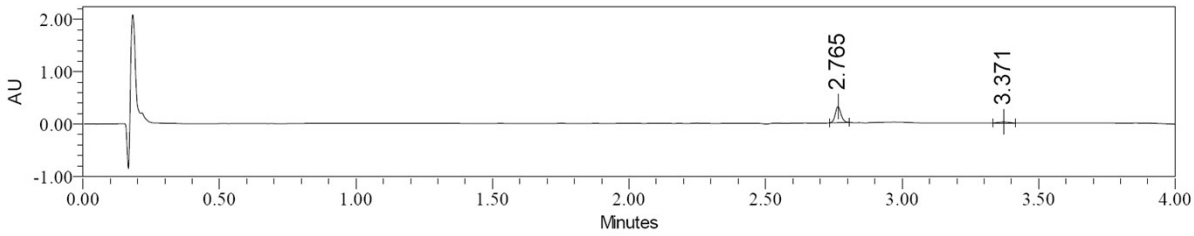
[1]H NMR of Compound-5e

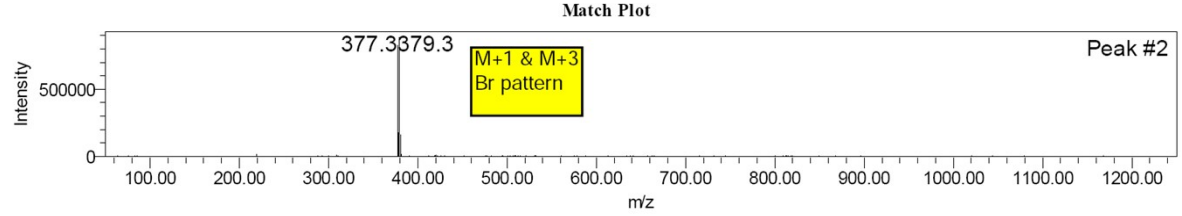


^{13}C NMR of Compound-5e



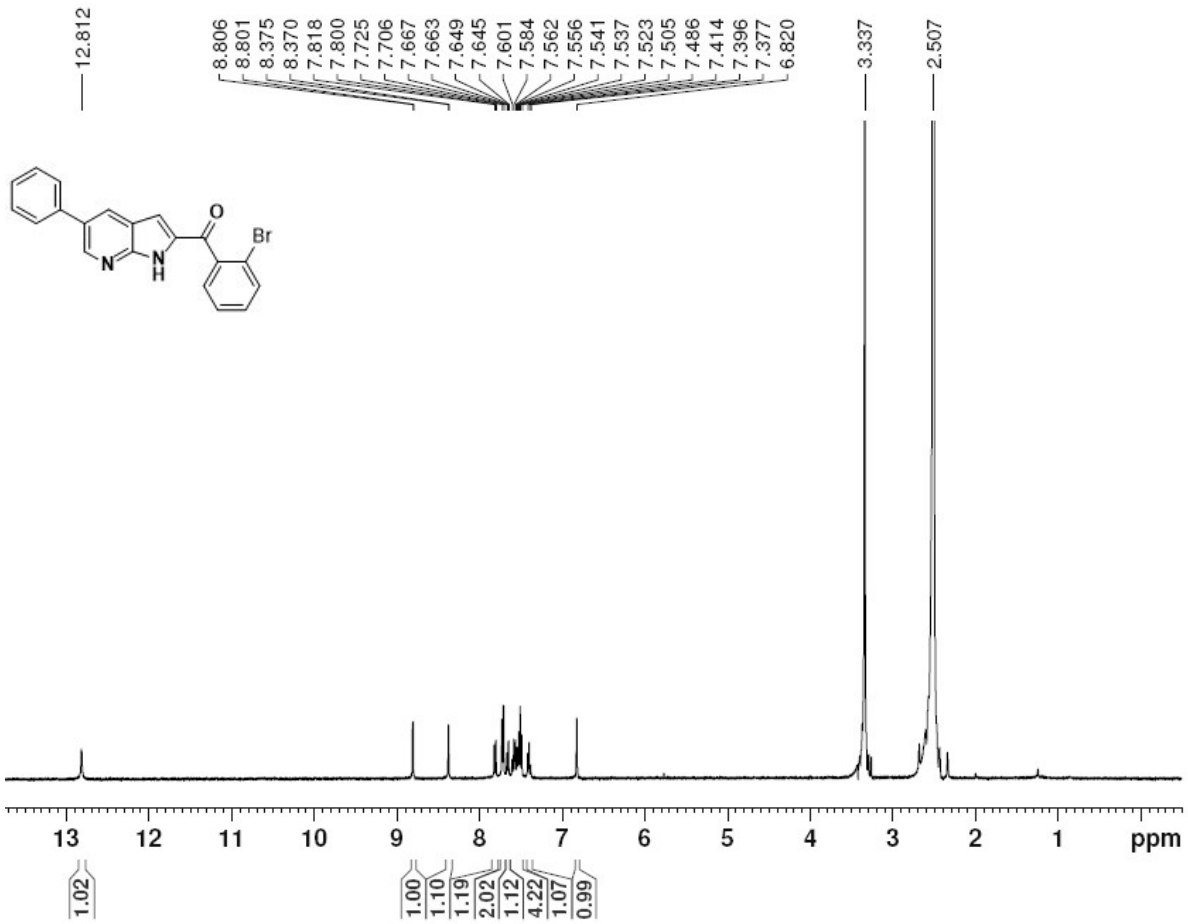
LCMS of Compound-5e



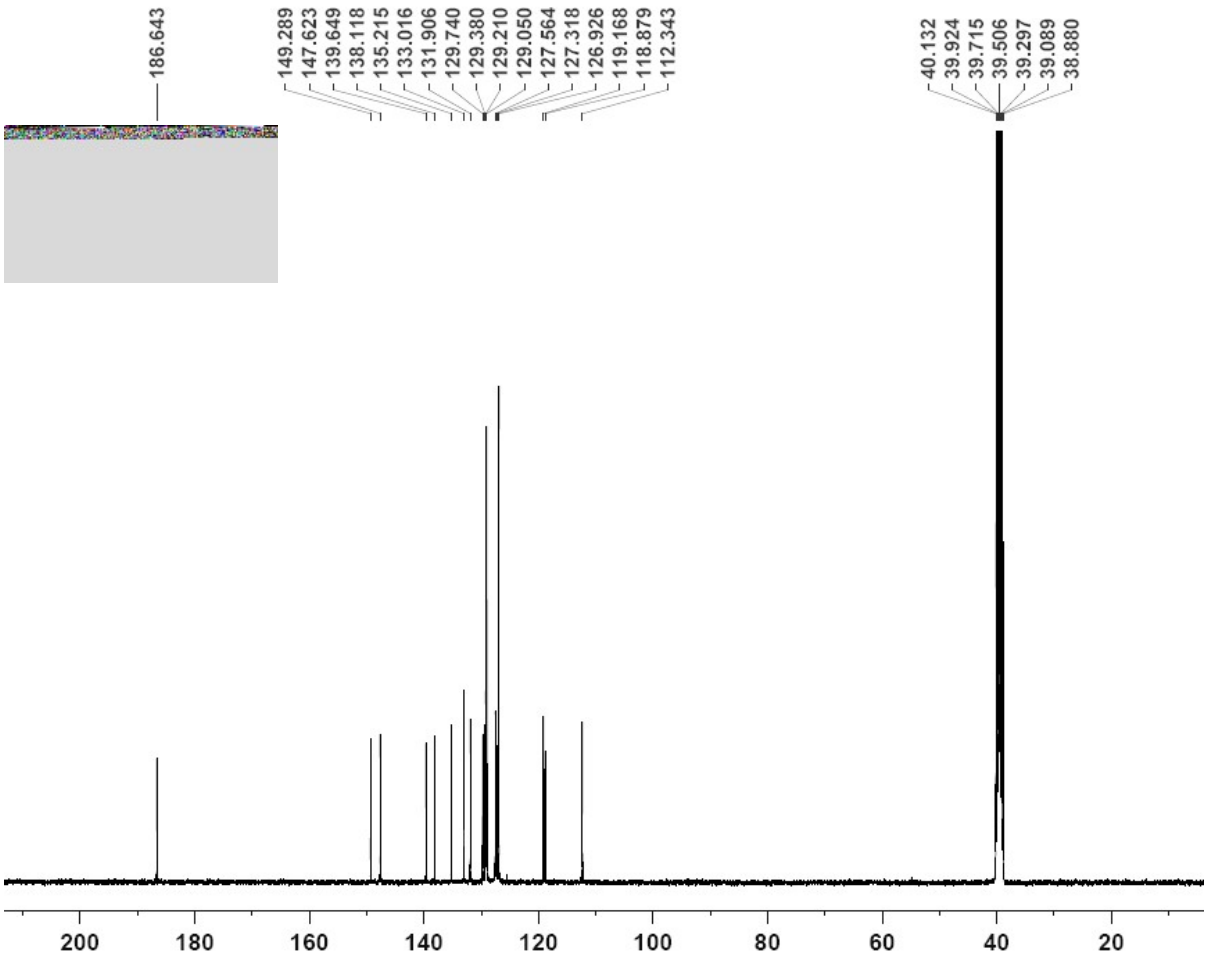


Base Peak 379.32 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.5:1.8;3.6:4.0) x 30.000 Th: 0.010 Retention Time 2.775

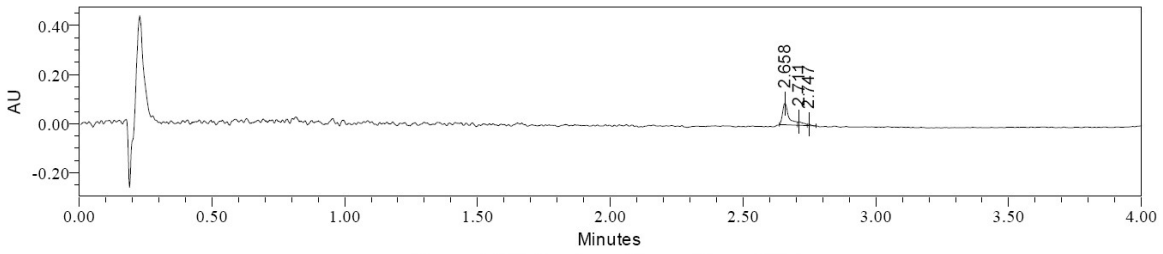
[1]H NMR of Compound-5f

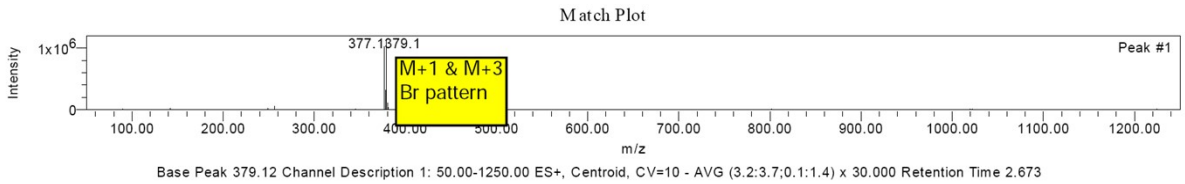


^{13}C NMR of Compound-5f

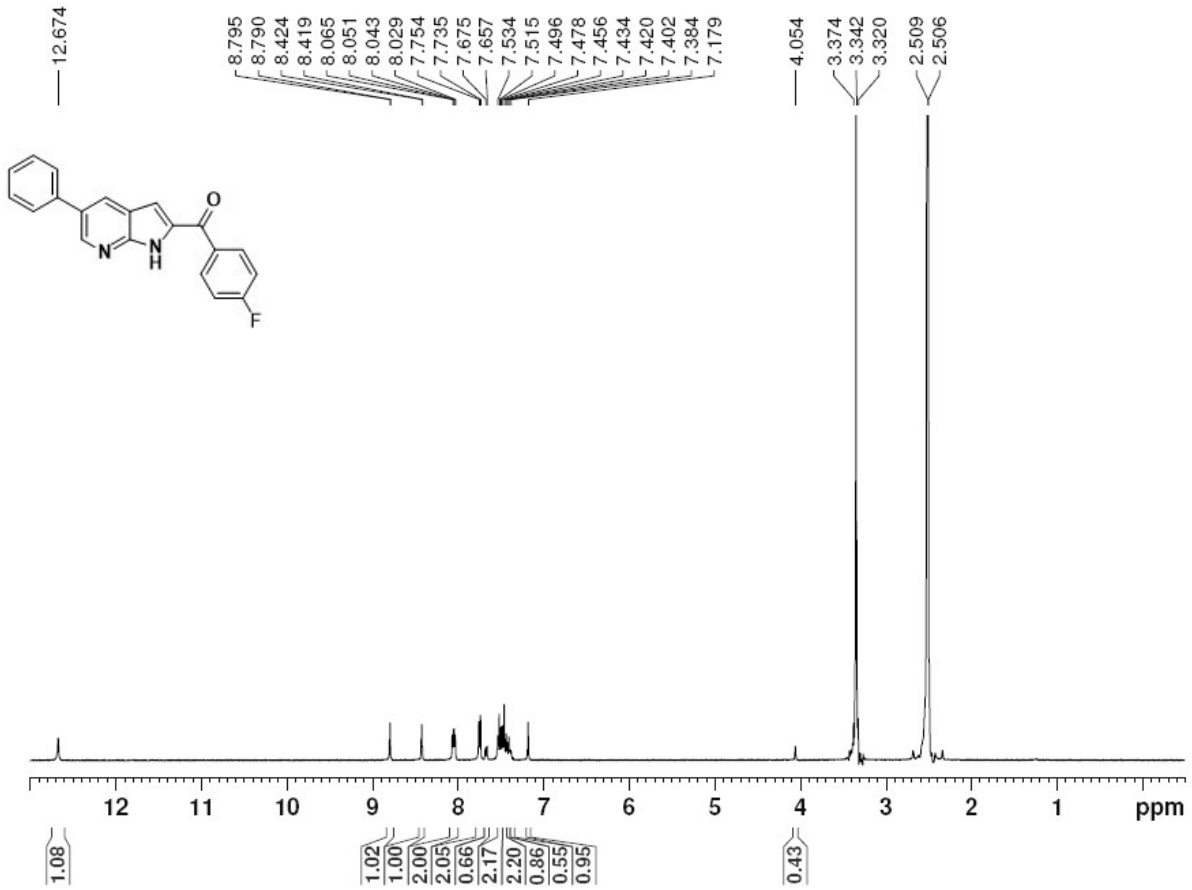


LCMS of Compound-5f

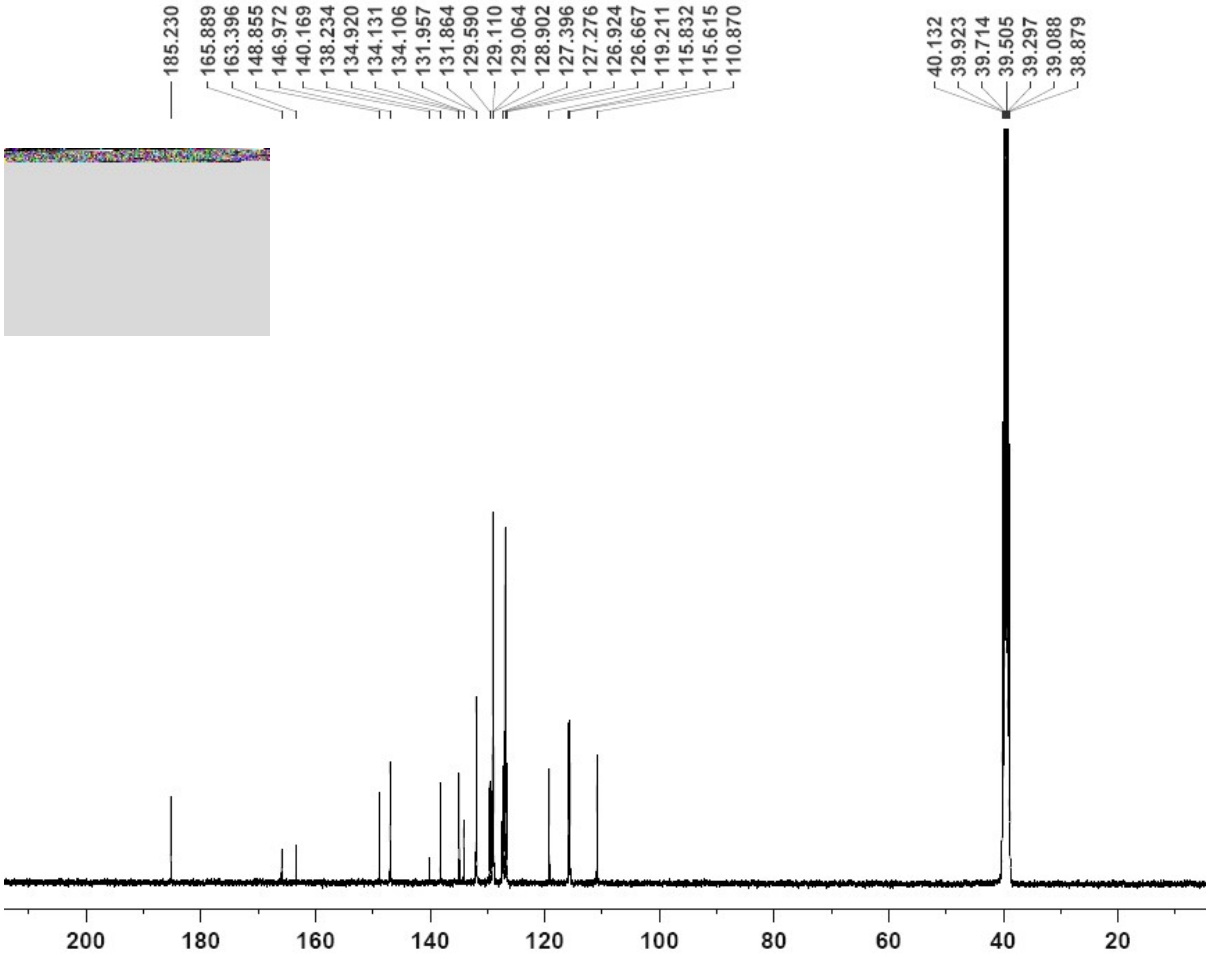




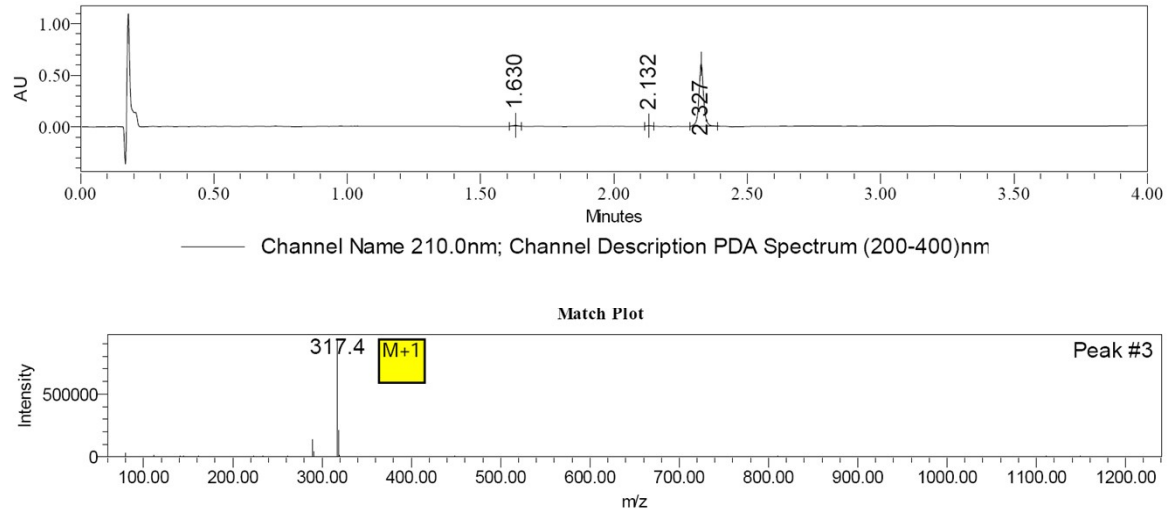
[1]H NMR of Compound-5g



^{13}C NMR of Compound-5g

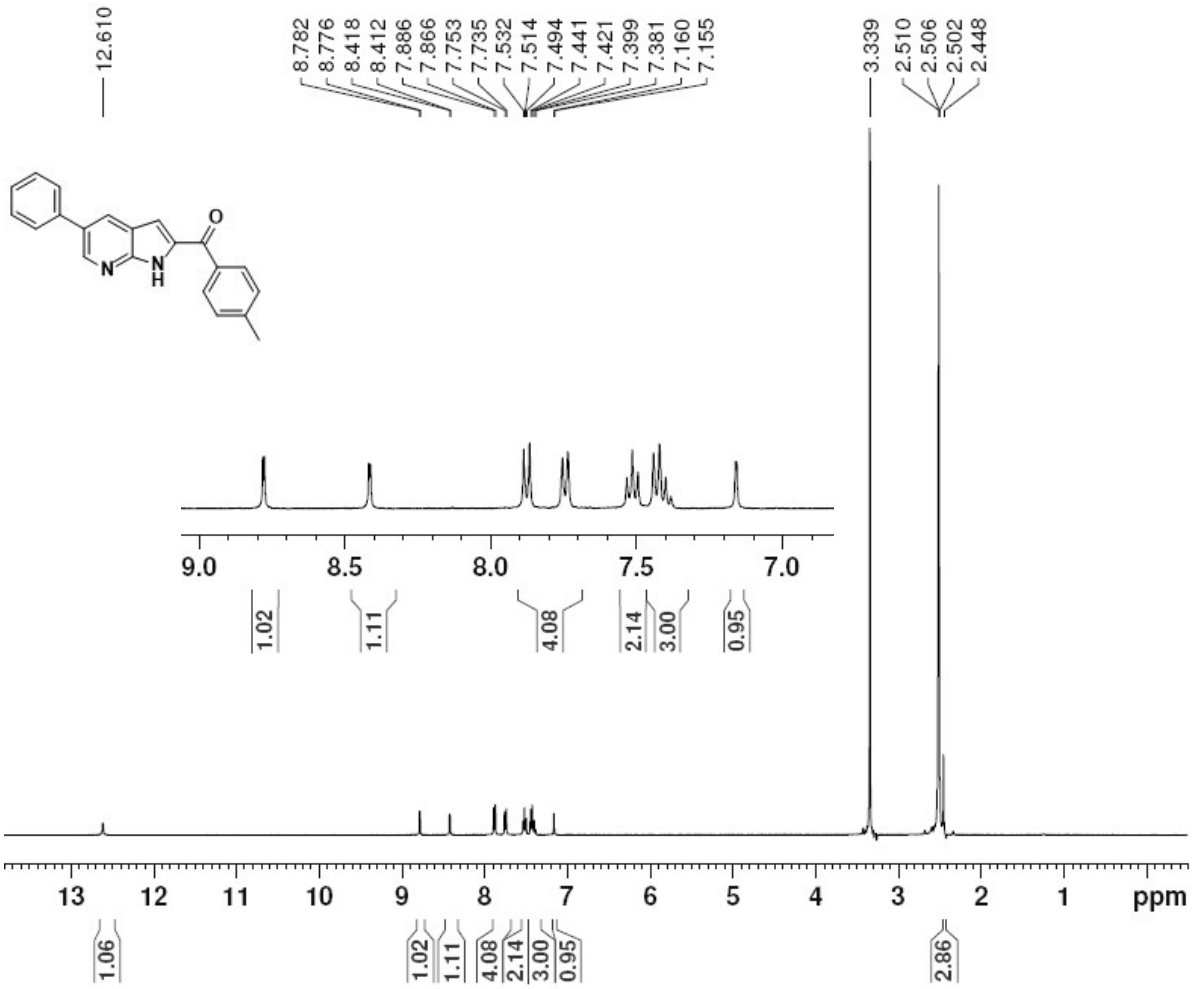


LCMS of Compound-5g

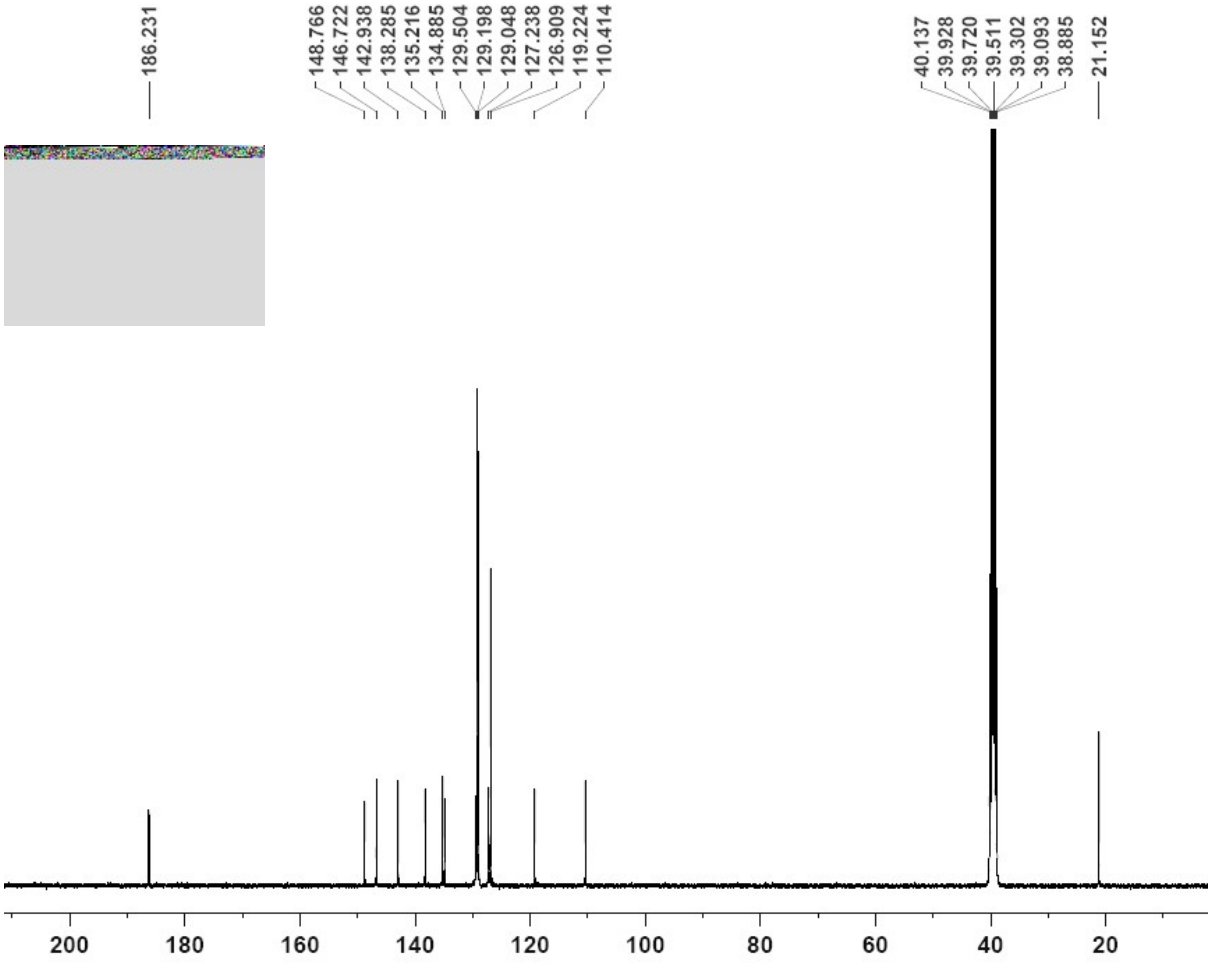


Base Peak 317.37 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.1:1.2;2.5:4.0) x 20.000 Th: 0.100 Retention Time 2.336

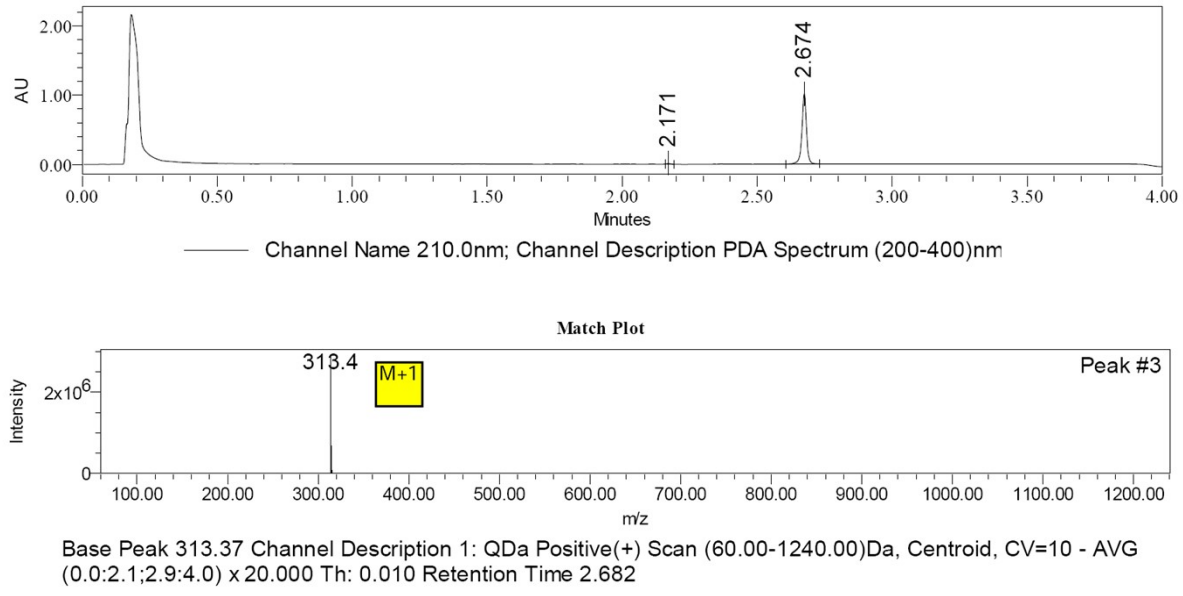
[1]H NMR of Compound-5h



^{13}C NMR of Compound-5h

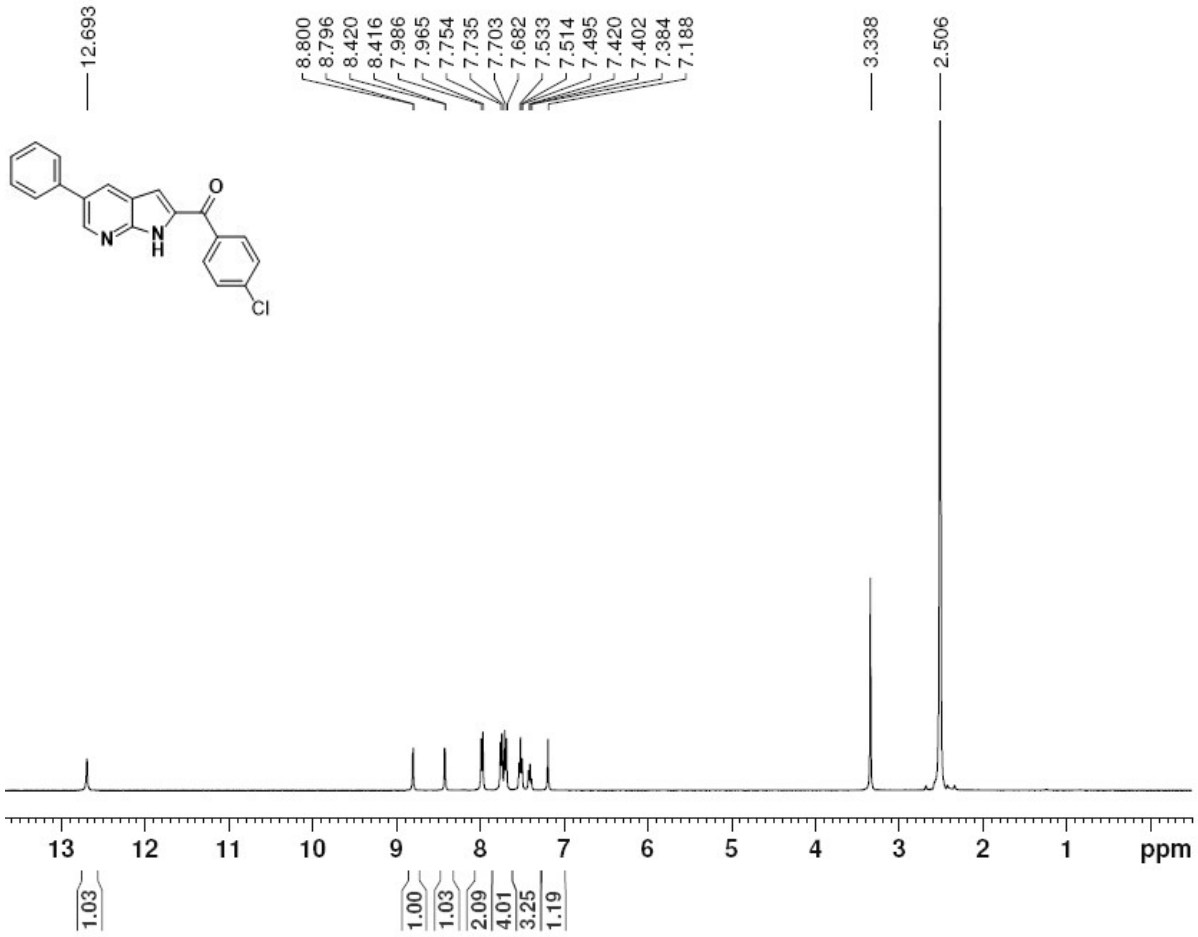


LCMS of Compound-5h

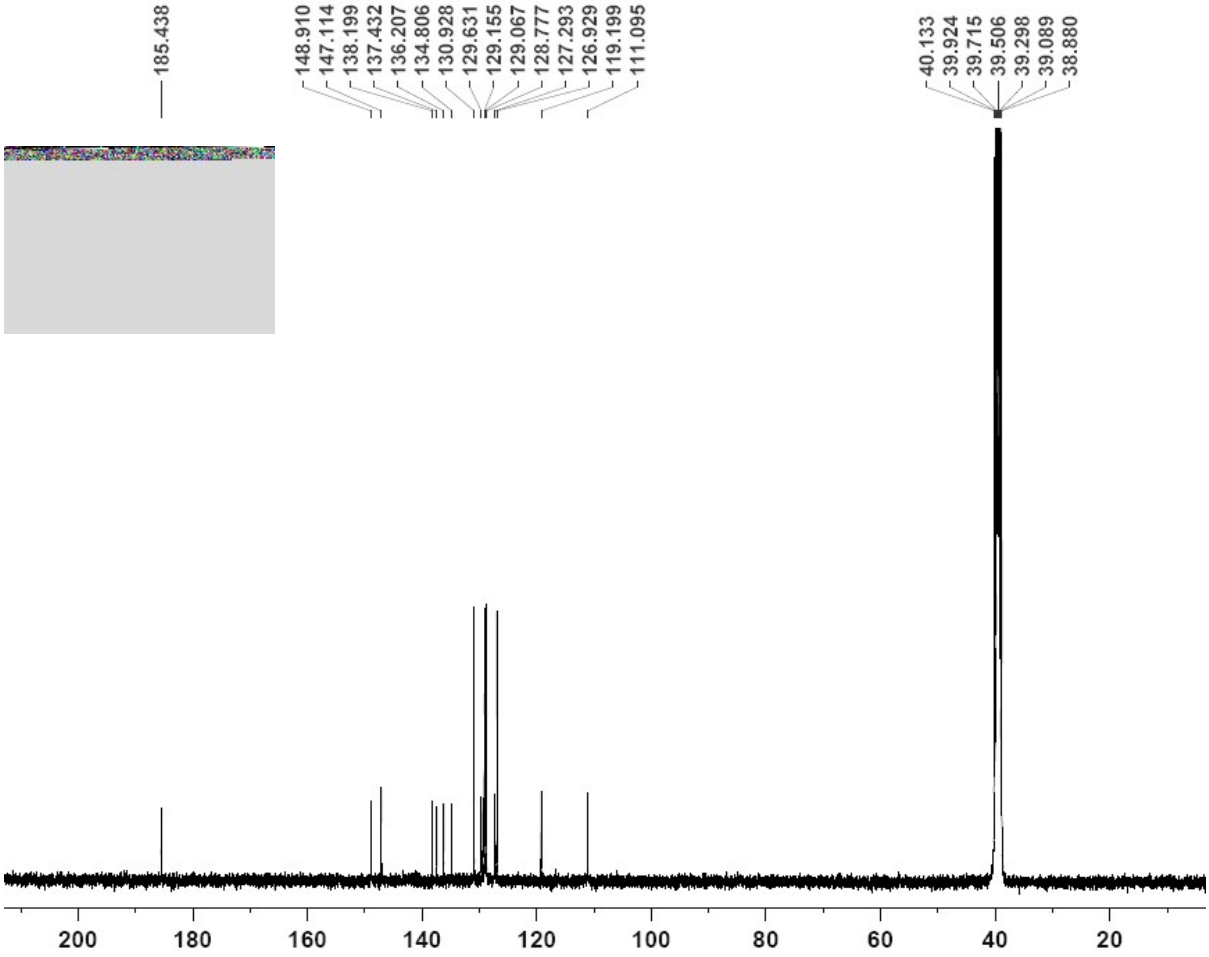


Base Peak 313.37 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.1;2.9:4.0) x 20.000 Th: 0.010 Retention Time 2.682

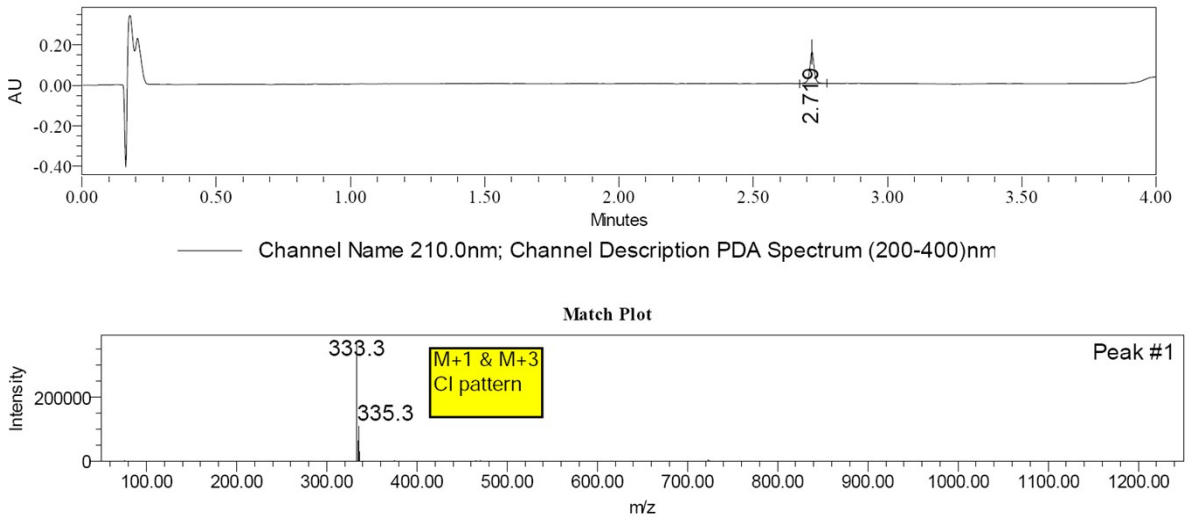
^{1}H NMR of Compound-5i



^{13}C NMR of Compound-5i

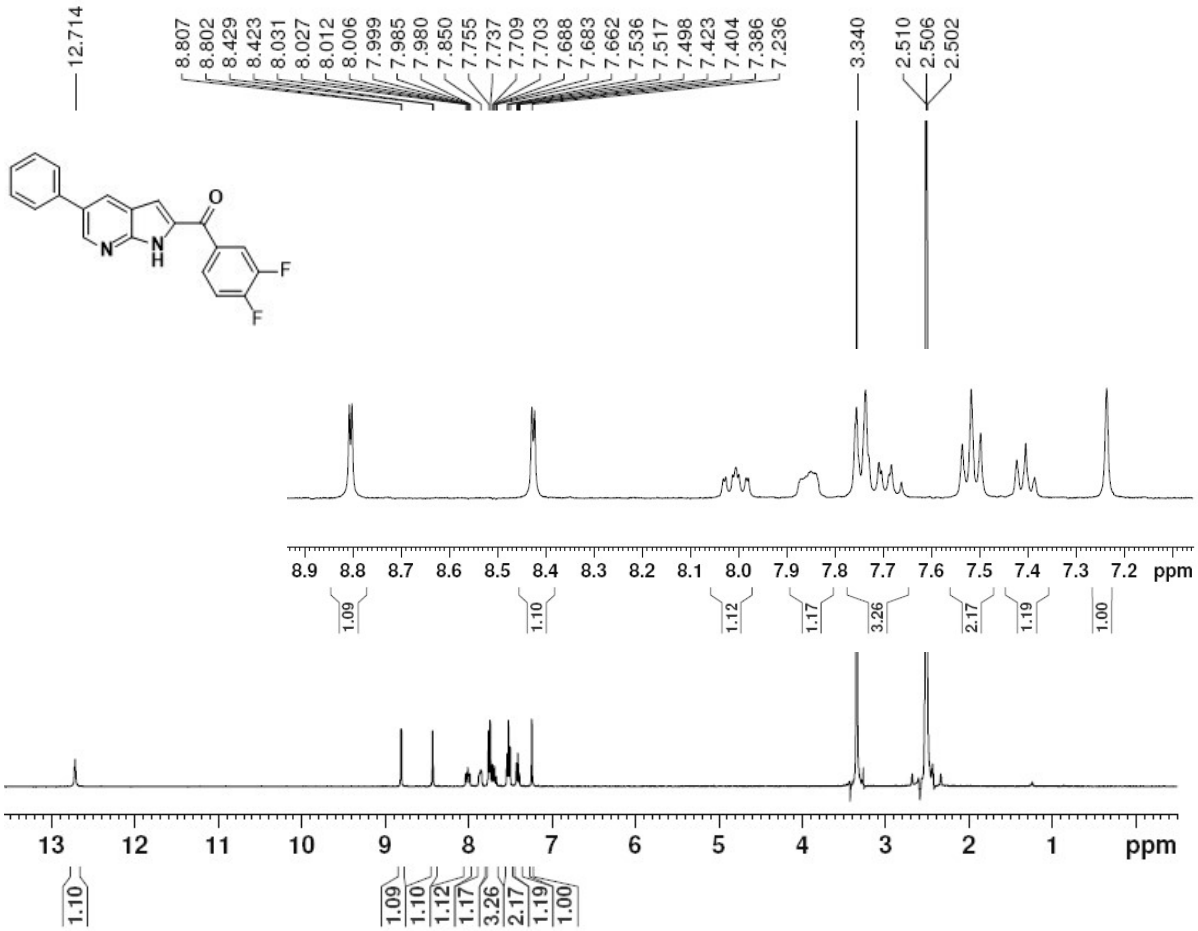


LCMS of Compound-5i

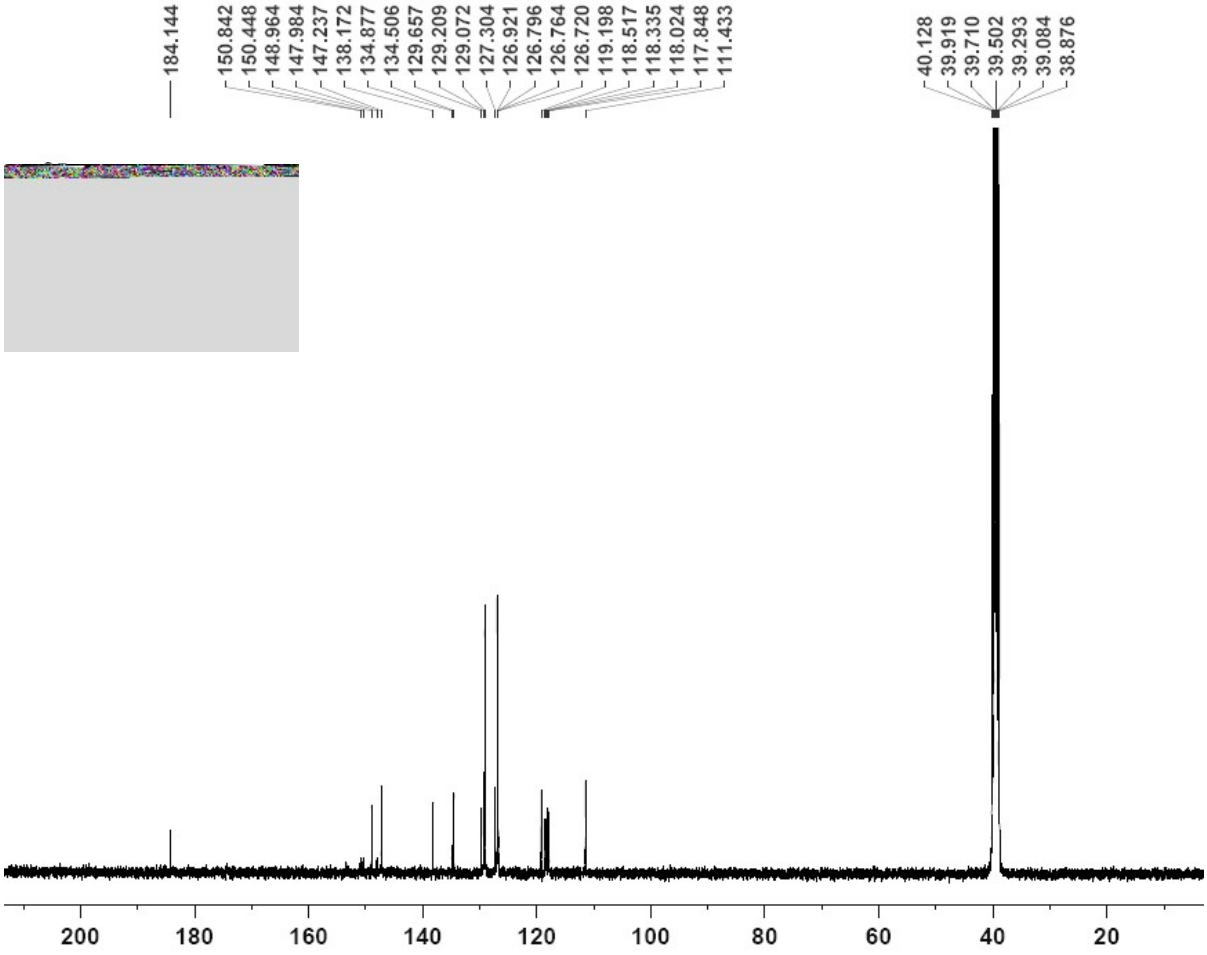


Base Peak 333.33 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.6;2.8:4.0) x 20.000 Th: 0.010 Retention Time 2.726

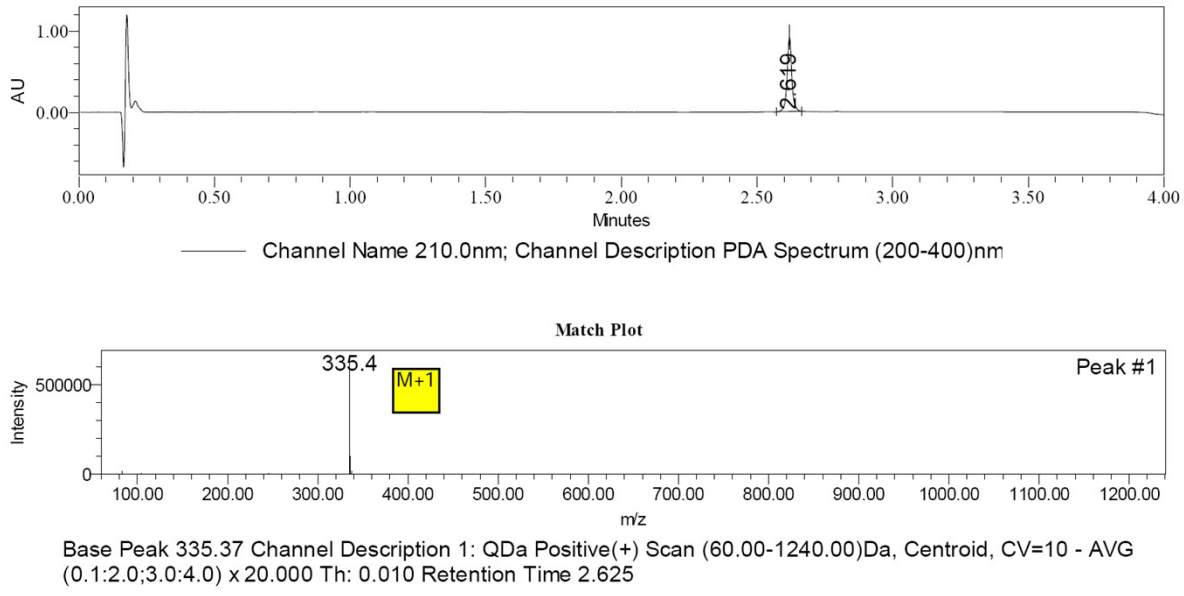
[1]H NMR of Compound-5j



^{13}C NMR of Compound-5j

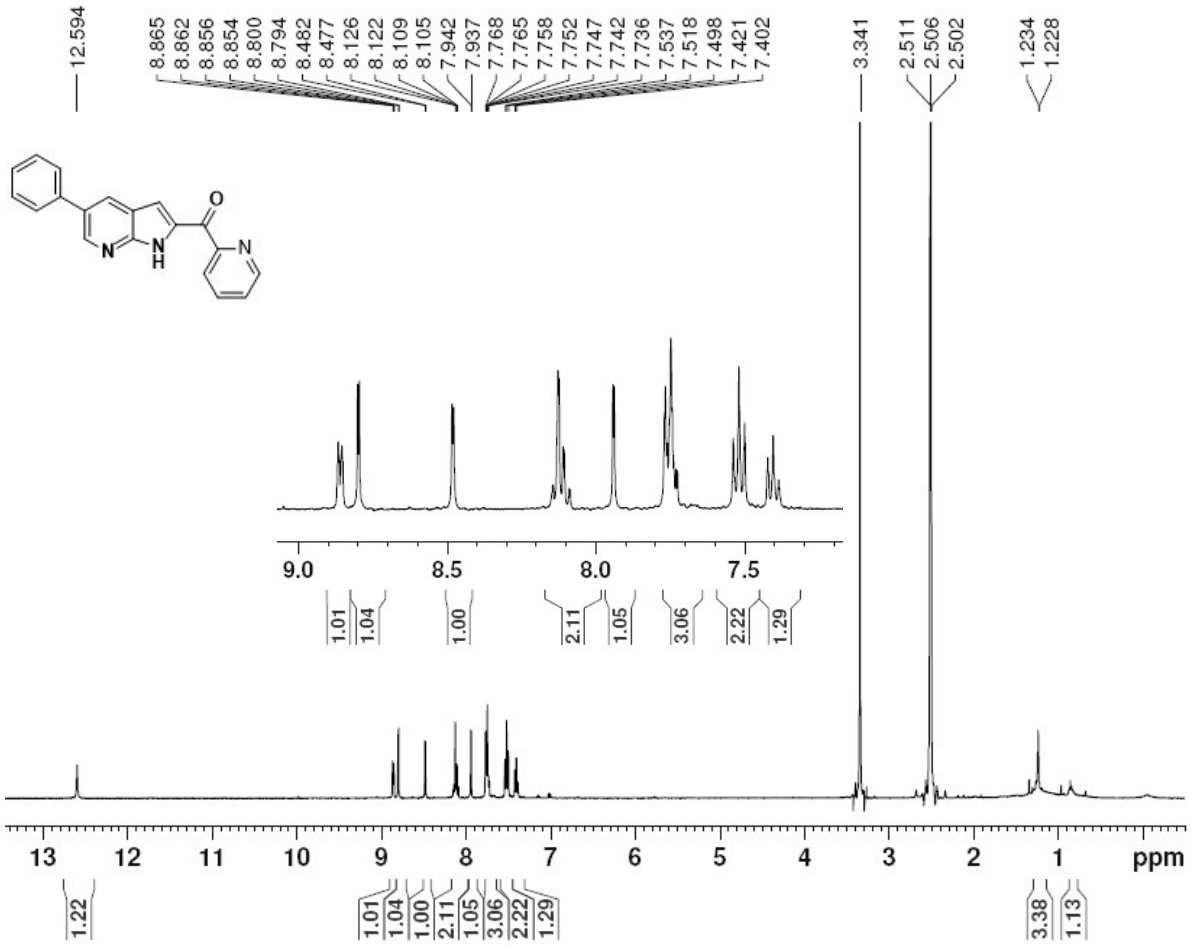


LCMS of Compound-5j

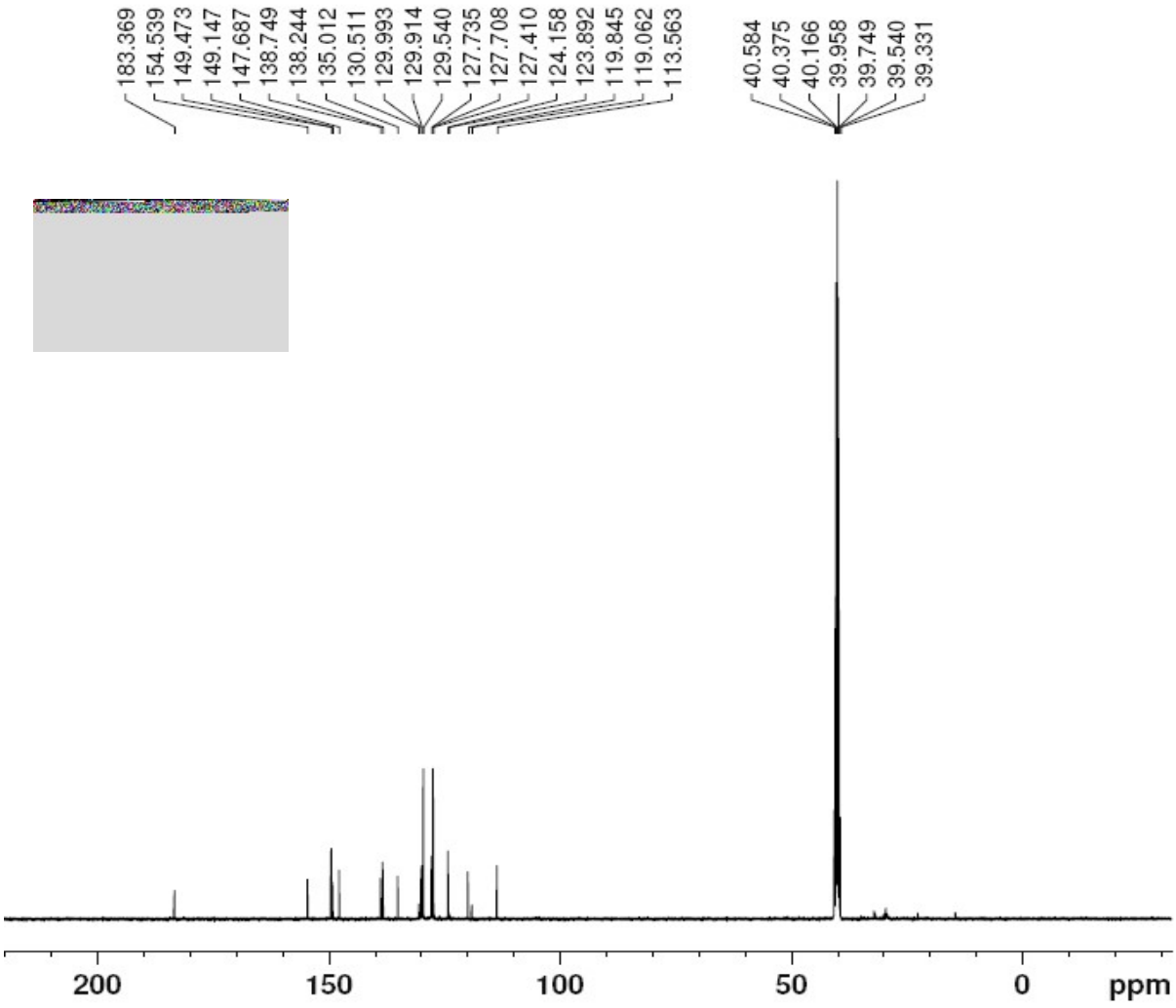


Base Peak 335.37 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.1:2.0;3.0:4.0) x 20.000 Th: 0.010 Retention Time 2.625

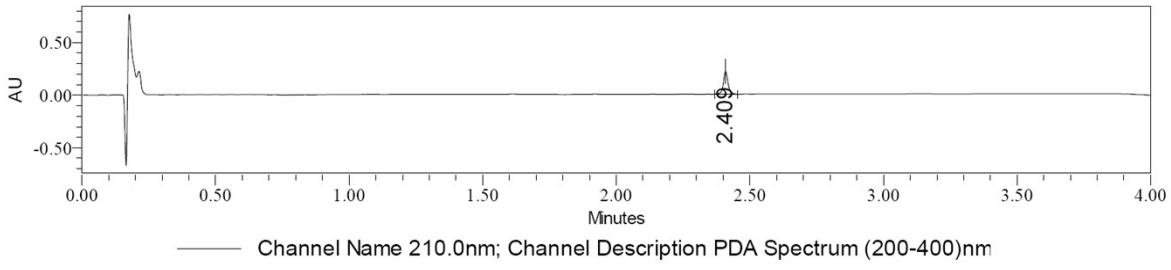
[1]H NMR of Compound-5k

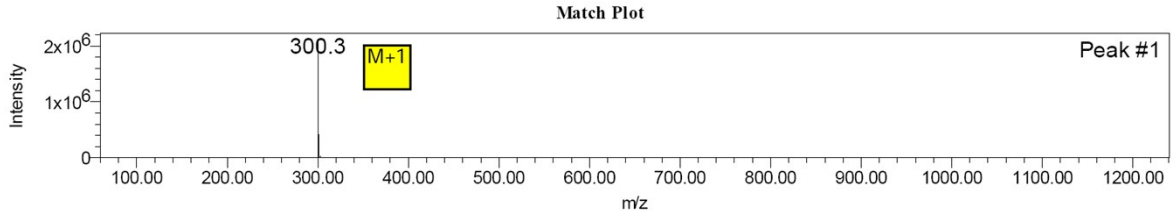


^{13}C NMR of Compound-5k



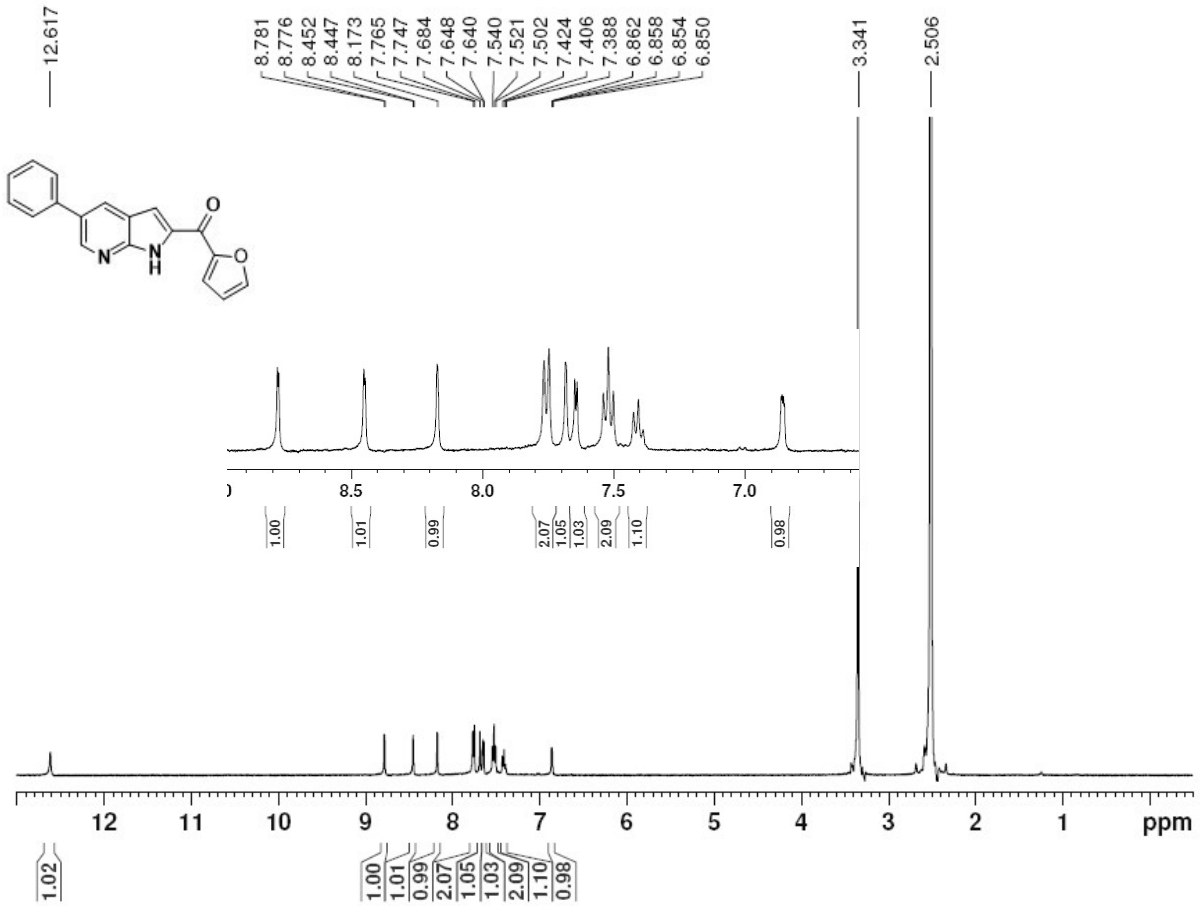
LCMS of Compound-5k



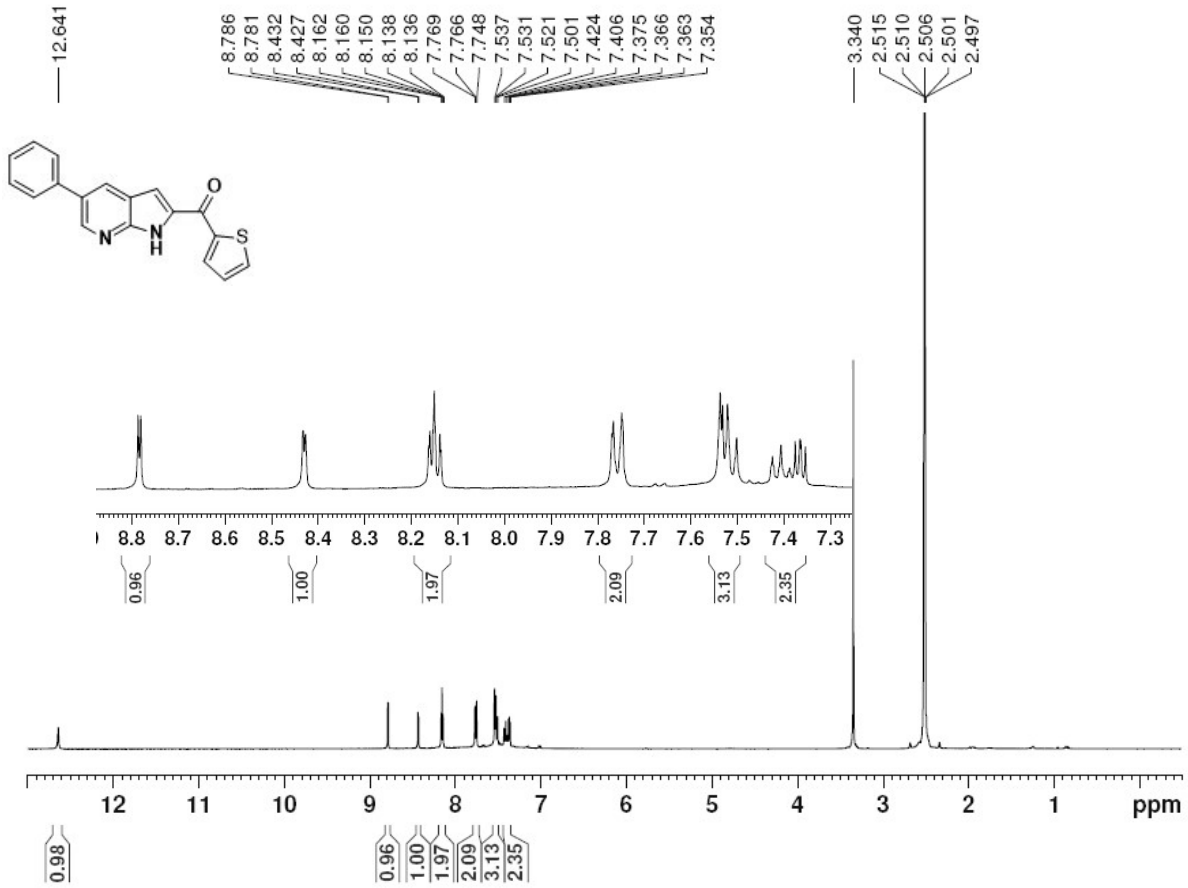


Base Peak 300.32 Channel Description 1: QDa Positive(+) Scan (60.00-1240.00)Da, Centroid, CV=10 - AVG (0.0:2.3;2.5:4.0) x 20.000 Th: 0.010 Retention Time 2.418

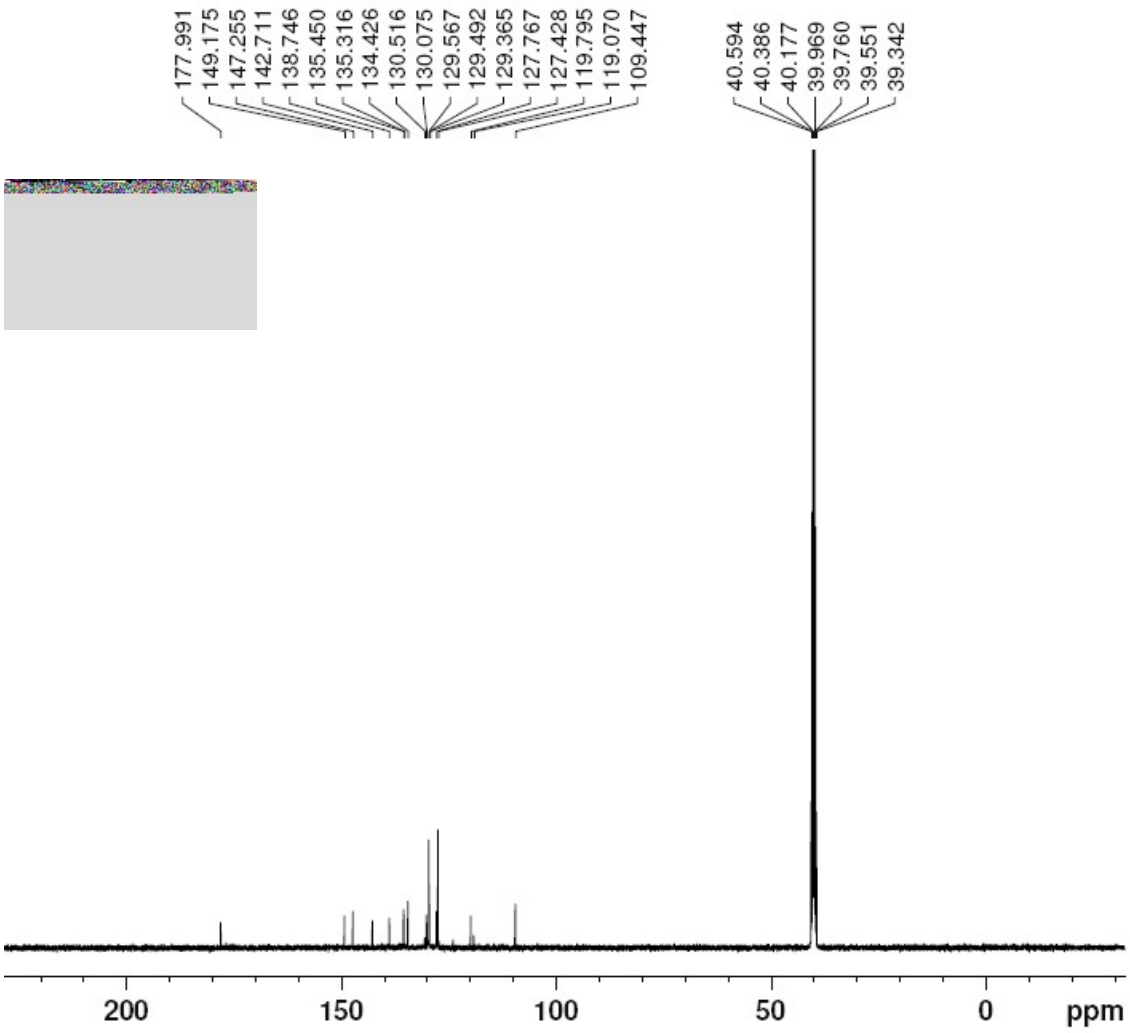
[1]H NMR of Compound-5l



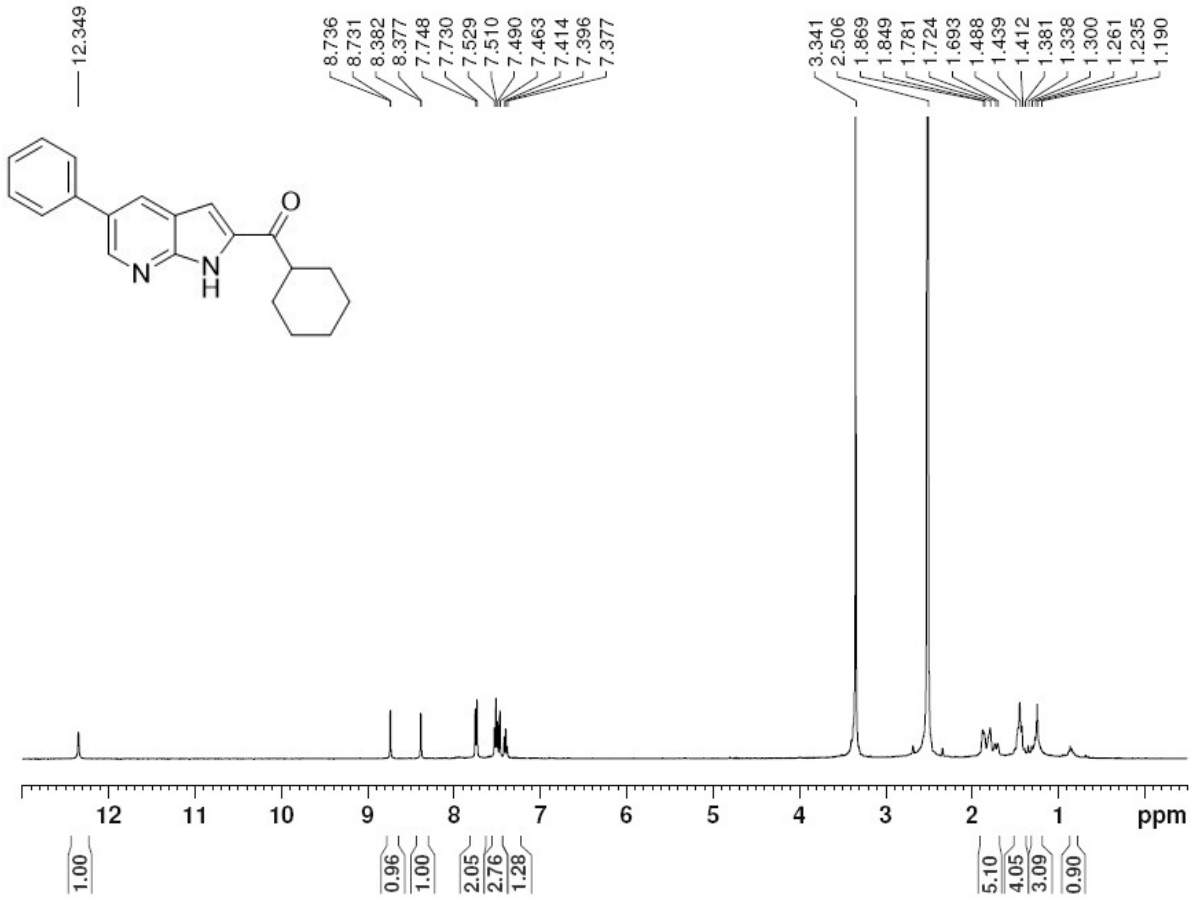
[1]H NMR of Compound-5m



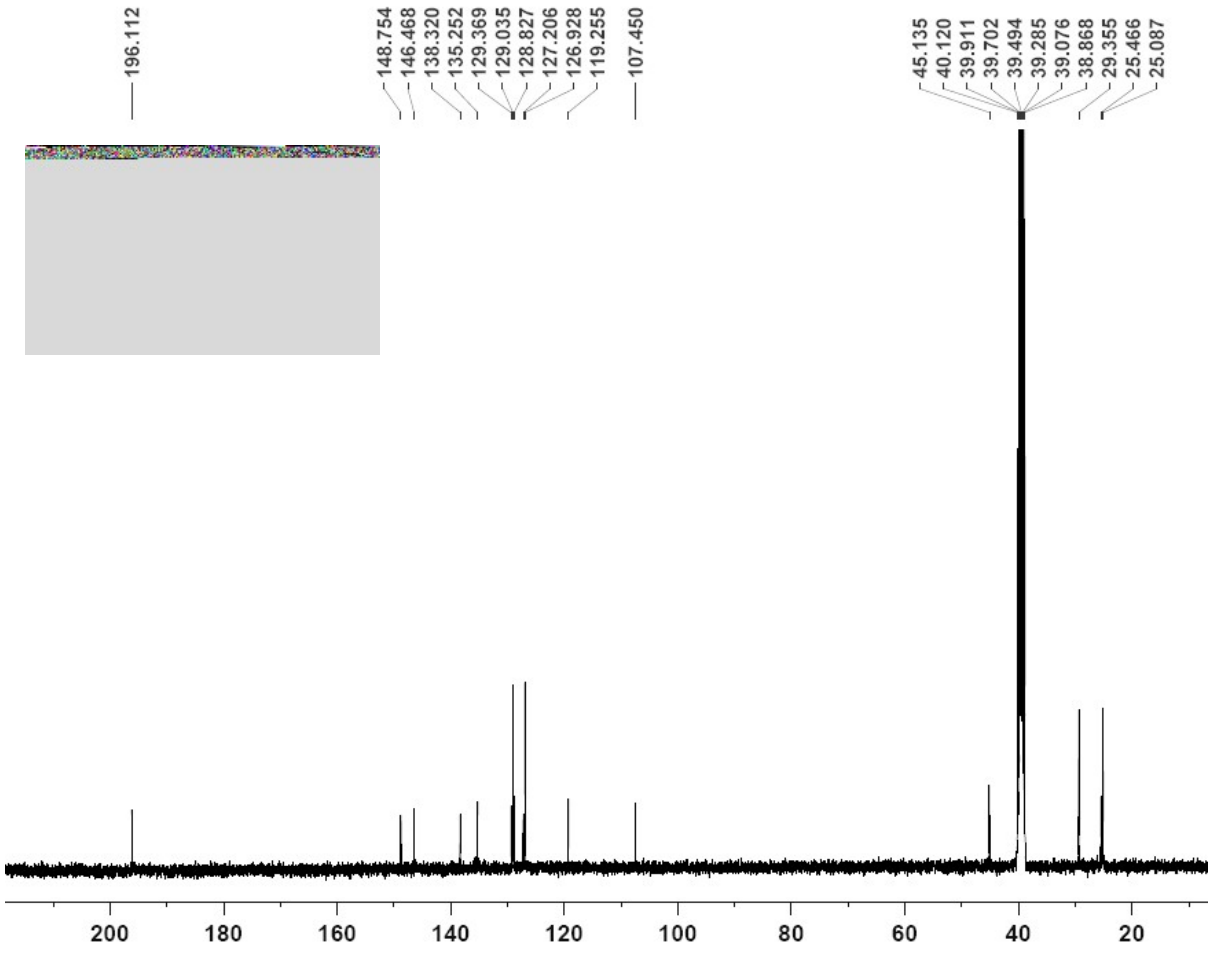
^{13}C NMR of Compound-5m



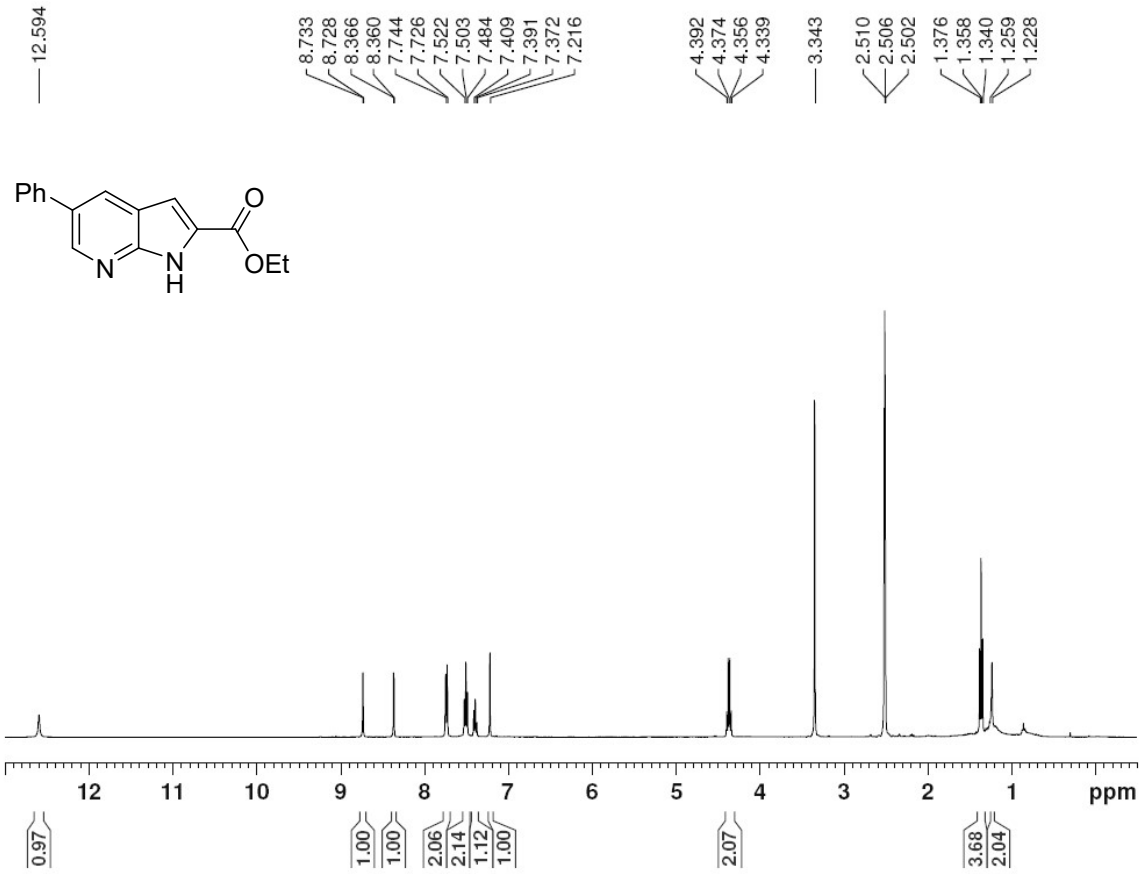
[1]H NMR of Compound-5n



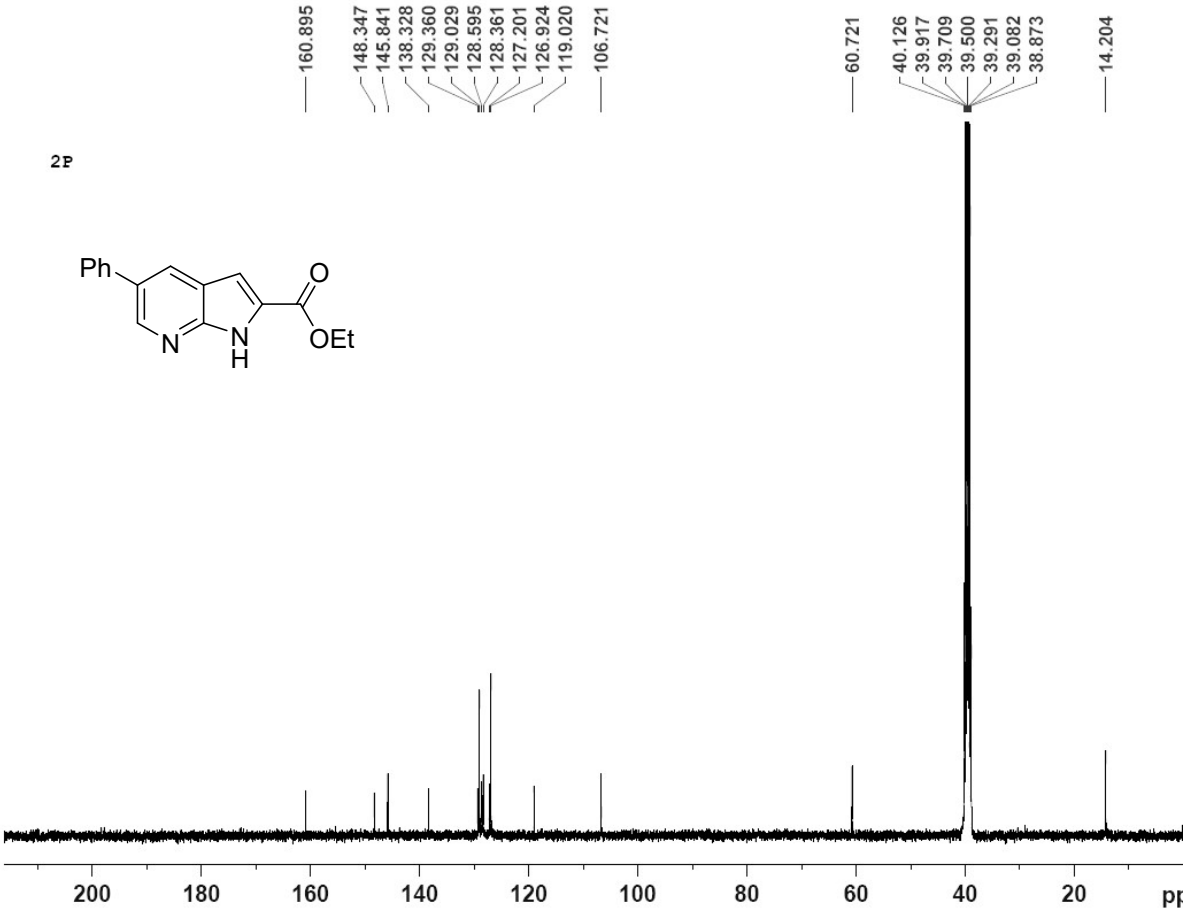
^{13}C NMR of Compound-5n



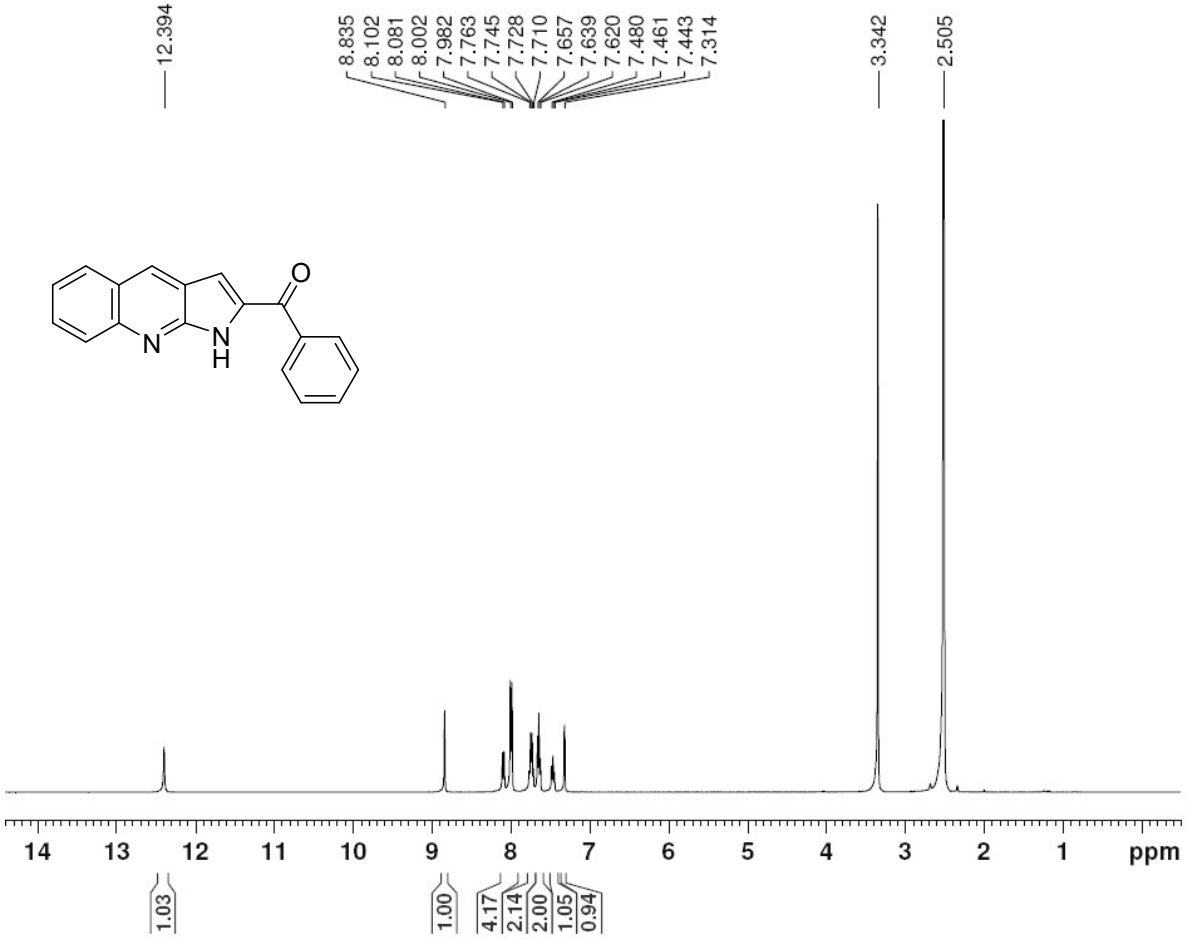
^{1}H NMR of Compound-7a



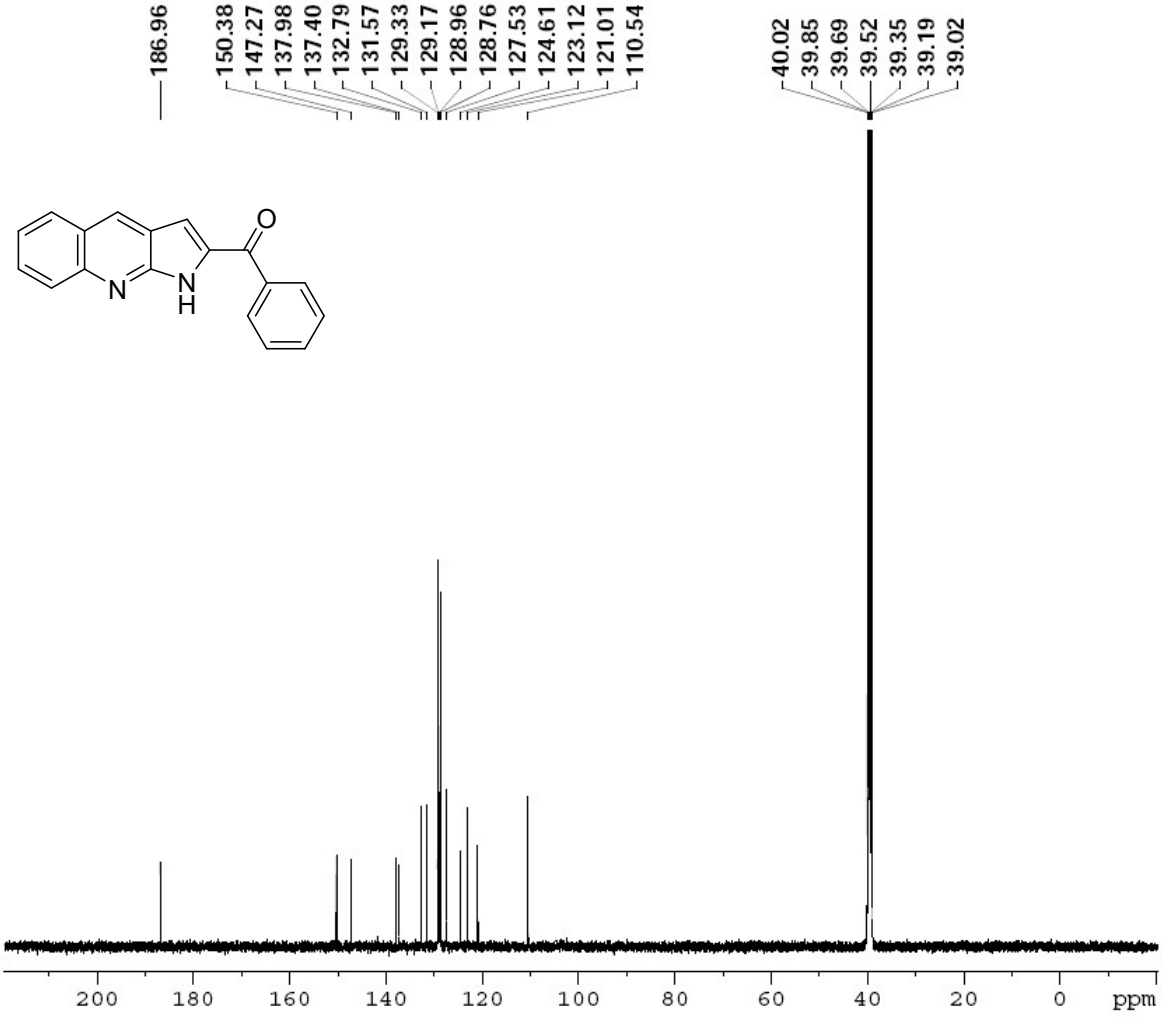
^{13}C NMR of Compound-7a



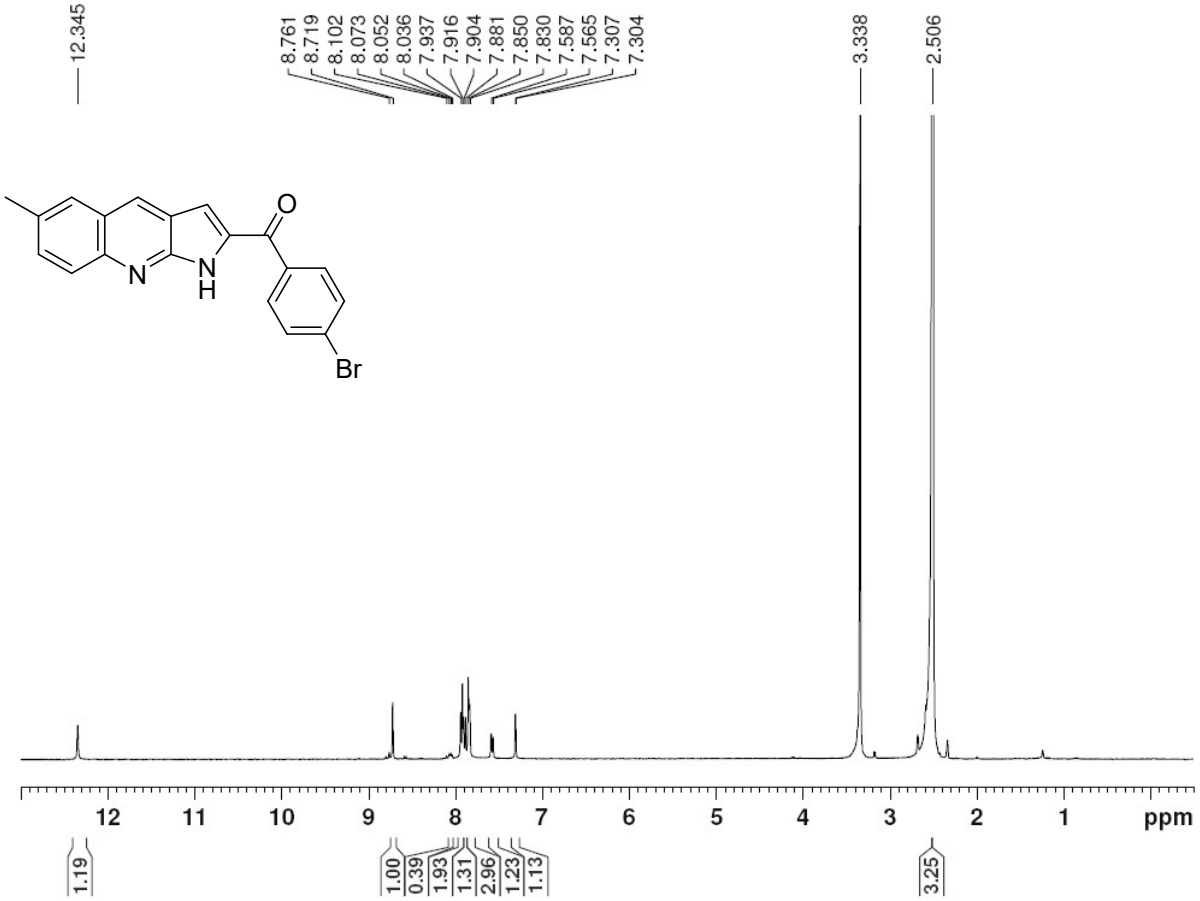
[1]H NMR of Compound-7b



^{13}C NMR of Compound-7b



^{1}H NMR of Compound-7c



^{13}C NMR of Compound-7c