Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information for

Access to quinolinones via DMAP-catalysed cascade reaction of 2-substituted benzoic acids with organic azides

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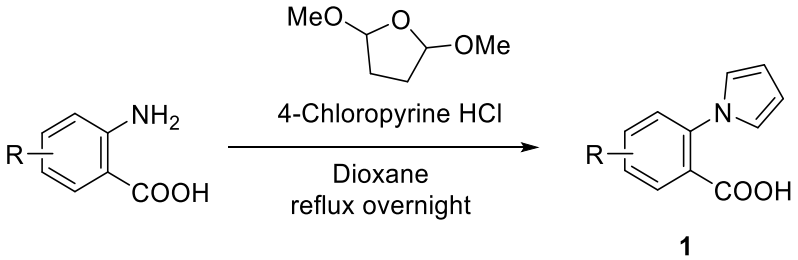
1. General Information

Unless otherwise noted, materials were purchased from commercial suppliers (Alfa, TCI and Sigma-Aldrich etc.), and used without further purification. All the solvents were treated according to general methods. All reactions were monitored by thin-layer chromatography (TLC) on silica gel plates using UV light as visualizing agent (if applicable). Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR spectra were recorded on 400 and 600 MHz spectrophotometers. Chemical shifts are reported in delta (δ (ppm)) units in parts per million (ppm) relative to the singlet (0 for tetramethylsilane (TMS). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration. ^{13}C NMR spectra were recorded on Varian Mercury 100 MHz with complete proton spectrophotometers ($CDCl_3$: 77.0 ppm, DMSO: 39.6 ppm). The high resolution mass spectra (HRMS) measured on a Shimadzu LCMS-IT-TOF mass spectrometer or DIONEX UltiMate 3000 & Bruker Compact TOF mass spectrometer by ESI. Measured values are reported to 4 decimal places of the calculated value. The calculated values are based on the most abundant isotope. An oil bath was used for synthesis of aromatic acids, and a heating module was used for preparation of compounds **3aa-xa**, **5aa-ea**, **9**, **11-13**, **15**.

2. Preparation of Substrates

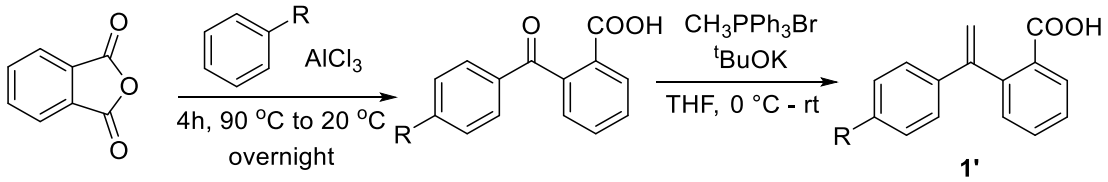
2.1 General procedure for preparation of 2-(1-Pyrrolyl)benzoicacid (1a-1n)[1]



1

Mixture of *o*-aminobenzoic acid derivatives (10.0 mmol), tetrahydro-2,5-dimethoxy-furan (1.0 equiv), and 4-chloropyridine hydrochloride (1.0 equiv) in dioxane (30 mL) was heated to reflux overnight. The reaction mixture passed through celite and washed with H_2O, and extracted with DCM. The separated organic layer was dried and evaporated in vacuo. Purification by flash column chromatography (PE/EA = 1:1) afforded the product **1**.

2.2 General procedure for preparation of 2-(1-phenylethenyl)benzoic acid (1r-1x)[2]



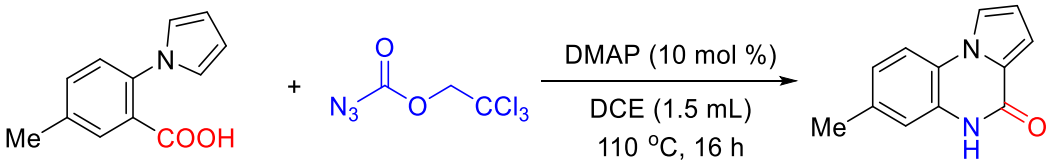
1'

Into an oven-dried two-necked round-bottomed flask, equipped with a magnetic stirrer and a reflux condenser, was placed the corresponding anhydride (10.0 mmol) under the N_2 atmosphere. The substituted benzene derivative (25 mL) was added via syringe. Then, aluminum chloride (4.0 g, 30.0 mmol) was added slowly (in portions) and the resulting mixture was heated at 90 ℃ for 4 h. After this, the resulting suspension was stirred overnight at room temperature. The reaction was quenched carefully with HCl 1M (10 mL) at 0 ℃ and extracted with ethyl acetate. The combined organic layers were treated with NaOH 1M (20 mL). The aqueous layer was acidified with concentrated HCl (37% w/w) until pH= 1, resulting in a milky white suspension. This was extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The resulting product was used in the next step without further purification.

In an oven-dried round-bottomed flask was added methyltriphenylphosphonium bromide (3.6 g, 10.0 mmol) and the system was evacuated and filled with N_2 (three times). After this, dry THF (35 mL) was added and the solution was stirred at 0 ℃. Then potassium tert-butoxide (1.9 g, 20.0 mmol) was added slowly and the suspension turned yellow. This resulting suspension was stirred under N_2 atmosphere for 30 min at 0 ℃. The previously obtained ketoacid product (5.0 mmol) was dissolved in dry THF (5 mL) and added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched carefully with HCl 1M (20 mL) at 0 ℃ and extracted with ethyl acetate. The combined organic layers were treated with NaOH 1M (35 mL). The aqueous layer was acidified with concentrated HCl (37% w/w) until pH= 1, resulting in a milky white suspension. This was extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by column chromatography.

3. General Procedure and Spectral Data of the Products

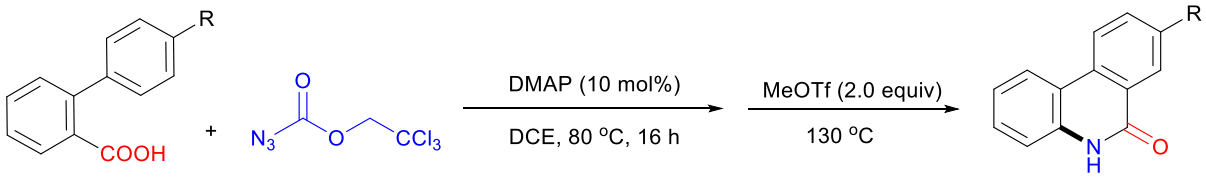
3.1 General procedure for the synthesis of (3aa-3oa, 3ra-xa, 5aa-5ea)



1a **2a** **3aa**

A 10 mL screw-cap vial was charged with aromatic acids **1a** (40.2 mg, 0.2 mmol), azidoformate **2a** (52 uL, 0.4 mmol), DMAP (2.4 mg, 10 mol%), and DCE (3 mL). The mixture was stirred at 110 °C for 16 h, as monitored by TLC analysis. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3:1) directly to give the desired product **3aa** in 91% isolated yield as a yellow solid. Other products **3ba-oa**, **3ra-xa**, **5aa-ea** were prepared according to the above procedure. (Note: a heating module was used as the heating source.).

3.2 General procedure for the synthesis of 3pa and 3qa



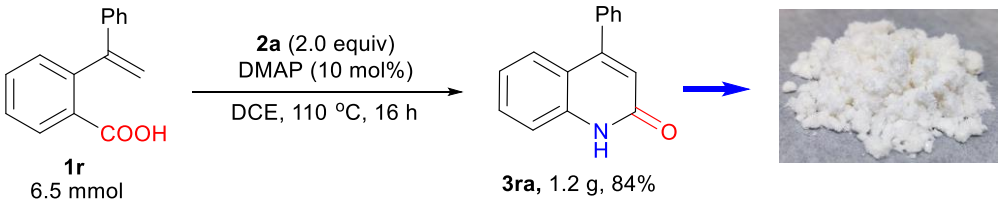
1p, R = H
1q, R = OMe

2a

3pa, R = H, 52%
3qa, R = OMe, 40%

A 10 mL screw-cap vial was charged with aromatic acids **1p** (39.6 mg, 0.2 mmol), azidoformate **2** (52 uL, 0.4 mmol), DMAP (2.4 mg, 10 mol%), and DCE (3 mL). The mixture was stirred at 80 °C for 2 h. Then, MeOTf (46 uL, 0.4 mmol) was added into the reaction mixture, and the resulting reaction mixture stirred at 130 °C for 14 h. After cooling down, the crude reaction mixture was purified by flash chromatography to give the desired product **3pa** in 52 % isolated yield as a white solid. **3qa** was obtained in 40 % according to the same procedure. (Note: a heating module was used as the heating source.).

3.3 Gram-scale reaction for the synthesis of 3ra



Mixture of 2-(1-phenylethenyl) benzoic acid (1.5 g, 6.5 mmol), 2,2,2-Trichloroethyl carbonazidate (1.7 mL, 13 mmol), and DMAP (78 mg, 10 mol%) in DCE (50 mL) was heated to 110 °C for 16 h. After cooling down, the crude reaction mixture was purified by flash chromatography to give product **3ra** (1.2 g) in 84% isolated yield as a white solid.

Procedure and Results of Sensitivity Assessment of Reaction 3ra:

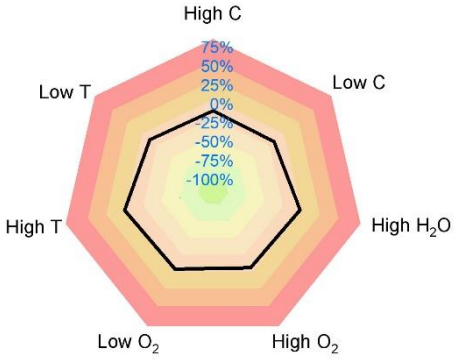
Standard conditions: n = 0.2 mmol, c = 0.067 M, V = 3 mL, T = 110 ℃

Stock solution: n = 2.0 mmol, c = 0.074 M, V = 27 mL, **1r**: 448.0 mg, **2a**: 520 μL, DMAP: 24.0 mg, DCE: 27 mL.

Preparation of sensitivity assessment of reaction 3ra

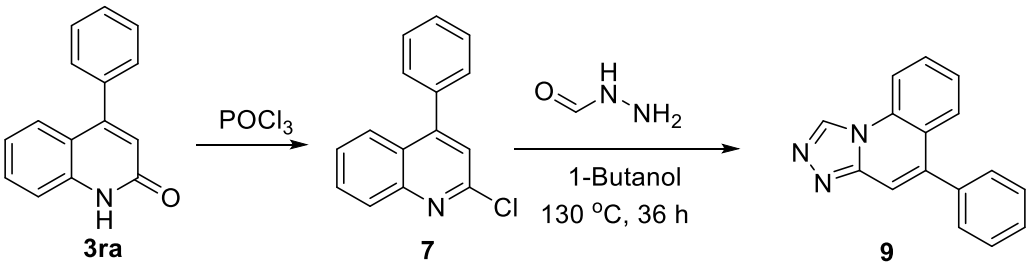
Number	Experiment	Preparation	Yield	Deviation
1	High C	2.7 mL stock sol.	80%	-15%
2	Low C	2.7 mL stock sol. + 0.6 mL DCE	78%	-17%
3	High H_2O	2.7 mL stock sol. + 0.3 mL DCE + 30 μL H_2O	92%	-2%
4	High O_2	2.7 mL stock sol. + 0.3 mL DCE, under O_2	88%	-6%
5	Low O_2	2.7 mL stock sol. + 0.3 mL DCE, under N_2, degassed	90%	-4%
6	High T	2.7 mL stock sol. + 0.3 mL DCE, T=120 ℃	94%	0
7	Low T	2.7 mL stock sol. + 0.3 mL DCE, T=100 ℃	82%	-13%
8	Control	2.7 mL stock sol. + 0.3 mL DCE	94%	

Radar diagram:



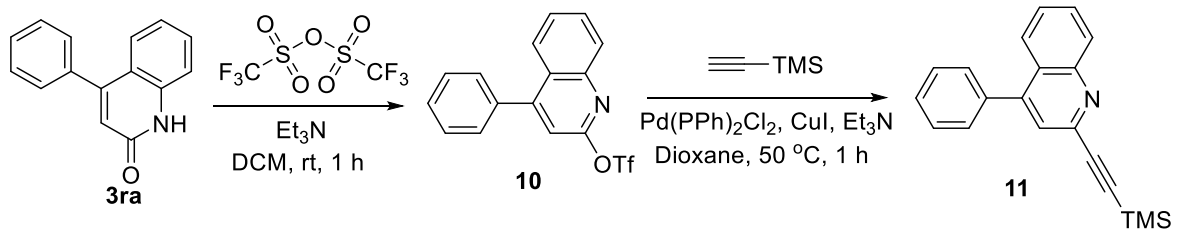
The assessment of this reaction revealed a slight dependence on the concentration and temperature. A change in water, O_2 or N_2 caused medium effects, whereas the scalability and random errors were found to be weakly influencing parameters.

3.4 Synthesis of compound 9, 11–13 and 15



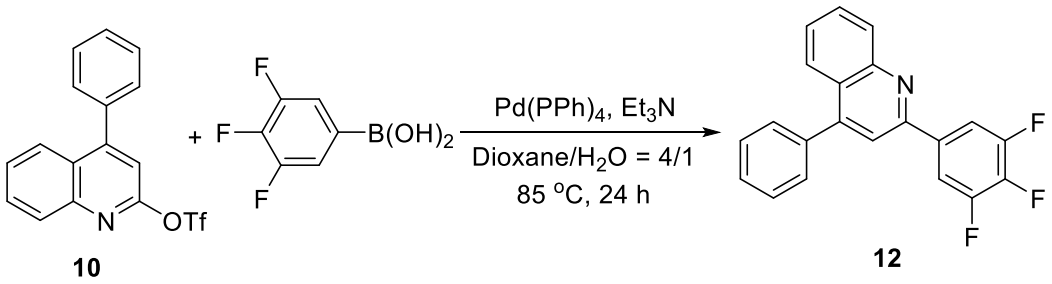
Compound **3ra** (44.3 mg, 0.2 mmol) was added to a 10 mL screw-cap vial. $POCl_3$ (1 mL) was carefully added to the vial under a blanket of nitrogen. The reaction mixture was heated to 80 ℃ for 5 h. Remove the excess of reactive under vacuum, dissolve the residue carefully in water at 0 ℃ and make the resulting solution basic with 30% aqueous ammonium hydroxide solution (pH = 9-10). Filter the precipitate and solubilize in methylene chloride. Dry the organic layer over Na_2SO_4 and filter and evaporate to dry to obtain the product **7** as a white liquid in 77% yield.

Dissolve 2-Chloro-4-phenylquinoline (23.9 mg, 0.1 mmol) and formohydrazide (7.0 mg, 0.1 mmol) in *n*-butylalcohol (2 mL) in a screw-cap vial under a blanket of nitrogen. The reaction mixture was stirred under reflux for 36 h. Remove solvents under reduced pressure and extract the residue twice with 5 mL dichloromethane. Wash the organic layer three times with water and dry over anhydrous $MgSO_4$. Remove the solvents, purify the products by silica gel column chromatography to give product **8** as an orange solid in 84% yield (dichloromethane/methanol = 20:1).

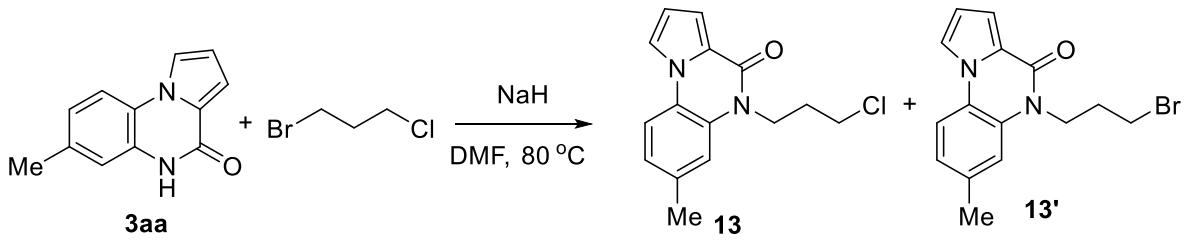


A suspension of 4-phenyl-1H-quinolin-2-one **3ra** (221.3 mg, 1.0 mmol) in anhydrous DCM (10 mL) was cooled to 0 ℃ in an ice bath, and DBU (228.3 mg, 1.5 mmol) was added under N_2 atmosphere. After 10 min of stirring, Tf_2O (338.4 mg, 1.2 mmol) was added and the resulting mixture was stirred for an additional 1 h, poured into water, and extracted three times with EtOAc. The combined organic phases were washed with sat. aq $NaHCO_3$, dried over Na_2SO_4, filtered, and concentrated in vacuo. The resulting solid was washed with Et_2O to give 200 mg (56% yield) of pure product as a yellow liquid.

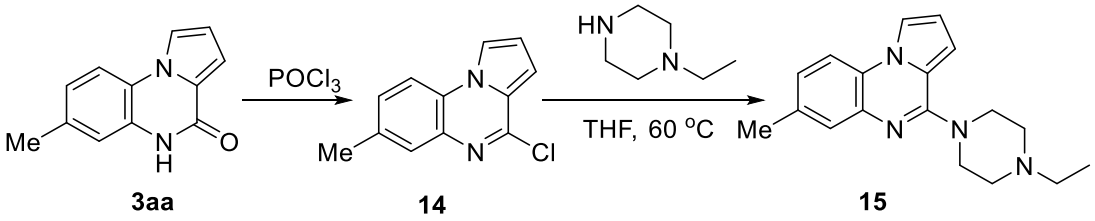
Triflate **10** (38 mg, 0.1 mmol), ethynyltrimethylsilane (15 mg, 0.15 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 10 mol %), CuI (2 mg, 10 mol %), and Et_3N (31 mg, 0.3 mmol) were mixed in dioxane (2 mL), and heated in a screw-cap vial under N_2 atmosphere at 50 ℃ for 1 h using oil bath heating (monitored by TLC). After the reaction was complete, the solvent was evaporated and the crude product was purified by flash chromatography on silica gel to give 24 mg (80 % yield) of compound **11** as a white solid.



Triflate **10** (38 mg, 0.1 mmol), 3,4,5-Trifluorophenyl boronic acid (26.5 mg, 1.5 equiv), and Et_3N (31 mg, 3.0 equiv) were mixed in dioxane/water (v/v = 4:1, 2 mL). The screw-cap vial was flushed with N_2, and $Pd(PPh_3)_4$ (5 mg, 5 mol %) was added, and the mixture was stirred at 85 ℃ for 24 h using oil bath heating (monitored by TLC). The solvent was evaporated, and the residue was redissolved in EtOAc and filtered through celite. The resulting solution was washed with 1 M aq NaOH three times and twice with water, dried over $MgSO_4$, filtered and concentrated in the vacuo. The crude product was purified by flash chromatography on silica gel to give 30 mg (90%) of product **12** as a white solid.



7-Methylpyrrolo [1,2-a] quinoxalin-4 (5H) -one (39.6 mg, 0.2 mmol) was dissolved in anhydrous DMF (2 mL) in a 10 mL screw-cap vial. NaH (4.8 mg, 0.2 mmol) was carefully added to the vial under a blanket of nitrogen. The reaction mixture was allowed to react for 2 h at room temperature after which 1-bromo-3-chloropropane (38.8 mg, 0.24 mmol) was added and the mixture was heated to 80 ℃ overnight. The reaction mixture was diluted with ethyl acetate and washed with H_2O, brine, dried over Na_2SO_4, then filtered and concentrated. The crude mixture was purified by flash chromatography to give a mixture of product **13** and **13'** as a white solid (40.9 mg, 73% yield, 4:1).

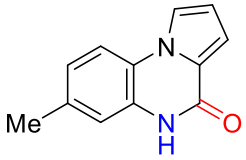


7-Methylpyrrolo [1,2-a] quinoxalin-4-(5H)-one **3aa** (39.6 mg, 0.2 mmol) was added to a 10 mL screw-cap vial. $POCl_3$ (1 mL) was carefully added to the vial under a blanket of nitrogen. The reaction mixture was heated to 80 ℃ for 7 h. Remove the excess of reactive under vacuum, dissolve the residue carefully in water at 0 ℃ and make the resulting solution basic with 30% aqueous ammonium hydroxide solution (pH = 9-10). Filter the precipitate and solubilize in methylene chloride. Dry the organic layer over Na_2SO_4 and filter and evaporate to dry to obtain the product **14** as a yellow solid in 85% yield.

Compound **14** (21.6 mg, 0.1 mmol) and 1-Ethylpiperazine (57.0 mg, 0.5mmol) was dissolved in THF (1 mL) in a 10 mL screw-cap vial. The reaction mixture was heated to 80 ℃ for 12 h. The solution was cooled and purified by flash chromatography to give product **15** as a white solid in 68% yield.

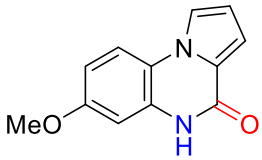
3.5 Spectral data of the products 3aa-xa, 5aa-ea, 9, 11–13 and 15[1-3]

Product 3aa (known compound, CAS: 159548-95-5)



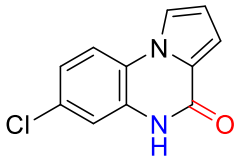
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3aa** as a yellow solid (36.2 mg, 91% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.15 (s, 1H), 7.69 – 7.68 (m, 1H), 7.55 (d, *J* = 2.7 Hz, 1H), 7.30 – 7.29 (m, 1H), 7.11 (s, 1H), 7.04 (d, *J* = 8.3 Hz, 1H), 6.70 (t, *J* = 8.3 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 155.6, 135.5, 128.9, 123.8, 123.5, 121.0, 118.3, 116.8, 115.3, 113.0, 111.58, 21.2.

Product 3ba (known compound, CAS: 160657-07-8)



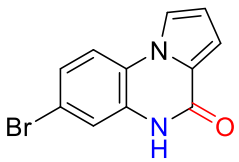
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 1:1), yielding of **3ba** as a brown-yellow solid (30.4 mg, 71% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.18 (s, 1H), 8.11 (s, 1H), 7.98 (d, *J* = 8.8 Hz, 1H), 6.99 (d, *J* = 4.0 Hz, 1H), 6.86 – 6.79 (m, 2H), 6.64 (t, *J* = 3.3 Hz, 1H), 3.79 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 157.4, 155.6, 130.1, 123.0, 118.2, 117.3, 116.5, 112.7, 111.4, 109.4, 101.2, 55.9.

Product 3ca (known compound, CAS: 160657-02-3)



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ca** as a yellow solid (33.8 mg, 78% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.37 (s, 1H), 8.20 (s, 1H), 8.09 (d, *J* = 8.7 Hz, 1H), 7.31 (d, *J* = 2.3 Hz, 1H), 7.27 – 7.24 (m, 1H), 7.06 (d, *J* = 2.3 Hz, 1H), 6.71 (t, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 155.3, 130.3, 129.7, 123.4, 122.6, 122.1, 119.00, 117.2, 116.1, 113.5, 112.3.

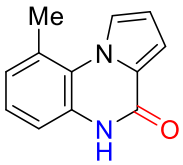
Product 3da (known compound, CAS: 931325-46-1)



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3da** as a brown-yellow solid (44.0 mg, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.36 (s, 1H), 8.20 – 8.19 (m, 1H),

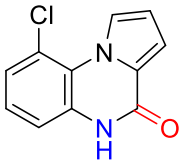
8.02 (d, *J* = 8.8 Hz, 1H), 7.45 (d, *J* = 2.2 Hz, 1H), 7.37 (dd, *J* = 8.7, 2.2 Hz, 1H), 7.07 – 7.06 (m, 1H), 6.71 (t, *J* = 2.8 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 155.2, 130.5, 125.4, 123.4, 122.4, 119.0 (overlap), 117.7, 117.42 113.5, 112.3.

Product 3ea (known compound, CAS: 251649-48-6)



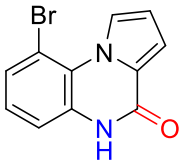
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ea** as a brown-yellow solid (27.8 mg, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.24 (s, 1H), 8.17 (s, 1H), 7.19 – 7.15 (m, 2H), 7.09 (d, *J* = 3.9 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 1H), 6.68 (t, *J* = 3.4 Hz, 1H), 2.78 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 155.2, 130.2, 127.0, 126.6, 125.5, 125.1, 123.1, 122.8, 115.5, 112.7, 111.5, 23.5.

Product 3fa (known compound, CAS: 159548-98-8)



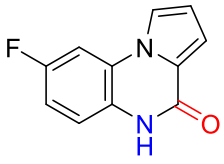
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3fa** as a brown-yellow solid (32.0 mg, 73% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.52 (s, 1H), 8.83 – 8.82 (m, 1H), 7.33 – 7.2 (m, 3H), 7.15 (dd, *J* = 4.0, 1.5 Hz, 1H), 6.73 (t, *J* = 3.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 154.9, 132.0, 126.4, 125.9, 125.3, 123.0, 121.1, 120.7, 116.5, 113.0, 112.4.

Product 3ga



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ga** as a yellow solid (43.8 mg, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.44 (s, 1H), 9.00 (d, *J* = 1.6 Hz, 1H), 7.45 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 8.1 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.69 (t, *J* = 3.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 154.8, 132.1, 129.6, 126.8, 125.4, 122.4, 121.8, 117.1, 112.6 (overlap), 108.9. M.P.: 185.0 – 185.5 °C HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_7BrN_2O$: 284.9634; found: 284.9646.

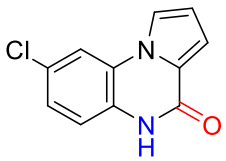
Product 3ha (known compound, CAS: 159548-97-7)



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ha** as a brown-yellow solid (20.6 mg, 51% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.31 (s, 1H), 8.20 (s, 1H), 8.08 (dd, *J* =

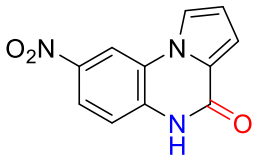
10.0, 2.7 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.20 – 7.15 (m, 1H), 7.07 – 7.03 (m, 1H), 6.72 (t, *J* = 3.5 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 158.0 (d, *J* = 236.4 Hz) 155.1, 125.6 (d, *J* = 2.2 Hz), 123.6 (t, *J* = 5.3 Hz), 119.1, 118.2 (d, *J* = 9.0 Hz), 113.6, 113.2, 113.0, 112.2, 103.0 (d, *J* = 27.9 HZ). ^{19}F NMR (376 MHz, DMSO) δ = -119.1.

Product 3ia (known compound, CAS: 160657-04-5)



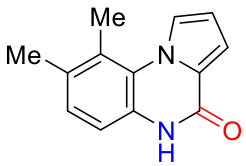
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ia** as a brown-yellow solid (35.4 mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.45(s, 1H), 8.34 – 8.33 (m, 2H), 7.43 – 7.40 (m, 1H), 7.35 (d, *J* = 8.6 Hz, 1H), 7.13 – 7.11 (m, 1H), 6.70 (t, *J* = 3.9 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 155.3, 127.9, 127.0, 125.9, 124.0, 123.5, 119.2, 118.4, 115.4, 113.7, 112.4.

Product 3ja



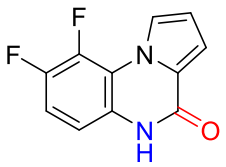
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 2:1), yielding of **3ja** as a yellow solid (25.8 mg, 56% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.82 (s, 1H), 8.94 (d, *J* = 2.4 Hz, 1H), 8.49 (dd, *J* = 2.9, 1.4 Hz, 1H), 8.18 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.42 (d, *J* = 9.0 Hz, 1H), 7.11 (dd, *J* = 3.9, 1.4 Hz, 1H), 6.75 (t, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 155.3, 142.4, 134.9, 123.3, 123.0, 121.7, 120.2, 117.2, 114.0, 113.1, 111.6. M.P.: 180.0 – 180.5 °C HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_7N_3O_3$: 230.0560; found: 230.0567.

Product 3ka



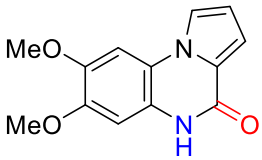
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 2:1), yielding of **3ka** as a yellow solid (37.4 mg, 88% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.08 (s, 1H), 8.09 (dd, *J* = 3.0, 1.5 Hz, 1H), 7.04 (d, *J* = 8.2 Hz, 1H), 7.01 – 6.97 (m, 2H), 6.59 (dd, *J* = 3.9, 2.9 Hz, 1H), 2.55 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 155.3, 132.3, 128.2, 127.5, 125.2, 125.2, 123.9, 123.2, 114.4, 112.5, 111.7, 21.1, 18.3. M.P.: 204.0 – 206.0 °C HRMS (ESI): m/z $[M+K]^+$ calcd for $C_{13}H_{12}N_2O$: 251.0581; found: 251.0580.

Product 3la



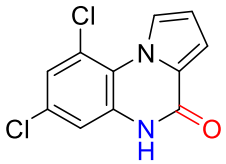
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 2:1), yielding of **3la** as a yellow solid (22.0 mg, 50% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.33 (s, 1H), 8.34 (dd, *J* = 11.7, 7.6 Hz, 1H), 8.16 (s, 1H), 7.24 (dd, *J* = 11.2, 7.6 Hz, 1H), 7.05 (d, *J* = 3.7 Hz, 1H), 6.71 (t, *J* = 3.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 155.1, 148.4 (d, *J* = 14.7 Hz), 146.2 (dd, *J* = 47.4, 13.6 Hz), 144.1 (d, *J* = 12.4 Hz), 125.8 (d, *J* = 6.9 Hz), 123.3, 119.5 (d, *J* = 8.5 Hz), 119.3, 113.6, 112.3, 105.2 (q, *J* = 15.2 Hz). ^{19}F NMR (376 MHz, DMSO) δ = -141.0 (d, *J* = 23.7 Hz), -144.2 (d, *J* = 23.5 Hz). M.P.: 108.0 – 108.5 °C HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{11}H_6F_2N_2O$: 243.0340; found: 243.0341.

Product 3ma



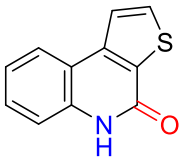
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 1:1), yielding of **3ma** as a brown-yellow solid (38.2 mg, 78% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.04 (s, 1H), 8.19 (s, 1H), 7.62 (s, 1H), 6.97 (d, *J* = 3.9 Hz, 1H), 6.87 (s, 1H), 6.64 (t, *J* = 3.4 Hz, 1H), 3.86 (s, 3H), 3.77 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 155.3, 147.5, 145.4, 123.4, 122.2, 118.2, 116.2, 112.6, 111.1, 100.5, 100.1, 56.9, 56.1. M.P.: 170.0 – 170.5 °C HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{12}N_2O_3$: 267.0740; found: 267.0741.

Product 3na



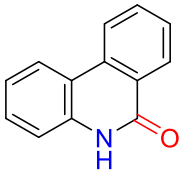
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 2:1), yielding of **3na** as a brown-yellow solid (40.8 mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.57 (s, 1H), 8.79 (s, 1H), 7.45 (s, 1H), 7.30 (s, 1H), 7.17 (d, *J* = 4.0 Hz, 1H), 6.74 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 154.7, 132.9, 129.4, 125.0, 124.6, 123.1, 122.2, 120.0, 115.7, 113.3, 112.8. M.P.: 110.0 – 110.5 °C HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{11}H_6Cl_2N_2O$: 252.9930; found: 252.9944.

Product 3oa (known compound, CAS: 35621-15-9)



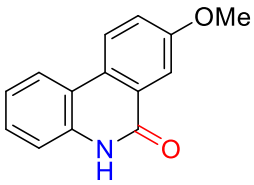
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3oa** as a gray-black solid (12.4 mg, 31% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.91 (s, 1H), 8.19 (t, *J* = 7.0 Hz, 2H), 8.09 (d, *J* = 5.1 Hz, 1H), 7.54 – 7.45 (m, 2H), 7.29 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 158.2, 143.5, 137.8, 134.7, 130.5, 129.5, 124.7, 124.0, 122.7, 117.4, 116.6.

Product 3pa (known compound, CAS: 1015-89-0)



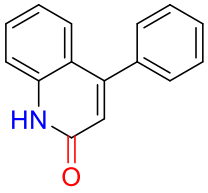
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3pa** as a white solid (15.6 mg, 40% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.71 (s, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.40 (d, *J* = 8.1 Hz, 1H), 8.33 (d, *J* = 7.9 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.66 (t, *J* = 7.5 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 161.3, 137.0, 134.7, 133.3, 130.0, 128.4, 127.9, 126.1, 123.7, 123.1, 122.7, 118.0, 116.6.

Product 3qa (known compound, CAS: 38088-95-8)



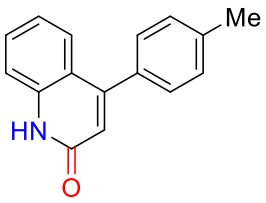
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 1:1), yielding of **3qa** as a white solid (12.0 mg, 27% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.73 (s, 1H), 8.45 (d, *J* = 8.9 Hz, 1H), 8.31 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 2.8 Hz, 1H), 7.47 – 7.41 (m, 2H), 7.35 (d, *J* = 8.1 Hz, 1H), 7.25 (t, *J* = 7.5 Hz, 1H), 3.92 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 161.0, 159.5, 135.9, 128.9, 128.1, 127.6, 125.0, 123.1, 122.7, 122.1, 118.2, 116.4, 109.2, 55.9.

Product 3ra (known compound, CAS: 5855-57-2)



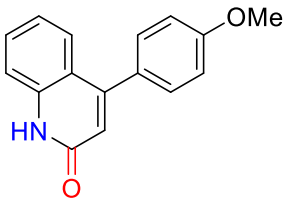
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ra** as a white solid (42.0 mg, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.91 (s, 1H), 7.54 – 7.47 (m, 4H), 7.46 (d, *J* = 6.5 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.39 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 161.8, 152.0, 139.8, 137.2, 131.0, 129.2 (overlap), 129.1, 126.6, 122.3, 121.7, 118.8, 116.3.

Product 3sa (known compound, CAS: 106015-76-3)



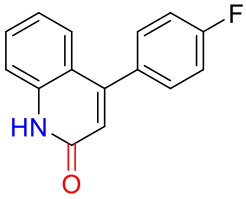
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3sa** as a white solid (37.2 mg, 79% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.88 (s, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.43 – 7.35 (m, 6H), 7.14 (t, *J* = 7.7 Hz, 1H), 6.37 (s, 1H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 161.8, 152.0, 139.8, 138.7, 134.3, 131.0, 129.7, 129.1, 126.6, 122.3, 121.5, 118.9, 116.2, 21.3.

Product 3ta (known compound, CAS: 37118-72-2)



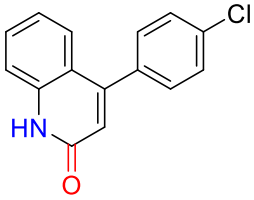
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 1:1), yielding of **3ta** as a white solid (35.2 mg, 70% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.87 (s, 1H), 7.52 (t, *J* = 7.1 Hz, 1H), 7.47 – 7.39 (m, 4H), 7.18 – 7.09 (m, 3H), 6.38 (s, 1H), 3.85 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 166.6, 164.9, 156.4, 144.6, 135.7, 135.3, 134.1, 131.4, 127.0, 126.1, 123.7, 121.0, 119.3, 60.5.

Product 3ua (known compound, CAS: 106015-75-2)



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ua** as a yellow solid (30.6 mg, 64% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.91 (s, 1H), 7.54 (t, *J* = 8.3, 3H), 7.42 – 7.35 (m, 4H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.41 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 162.8 (d, *J* = 244.3 Hz), 161.7, 150.9, 139.8, 133.5 (d, *J* = 3.2 Hz), 131.4 (d, *J* = 8.6 Hz), 131.1, 126.5, 122.4, 122.0, 118.8, 116.3, 116.2, 116.0. ^{19}F NMR (376 MHz, DMSO) δ = -113.0.

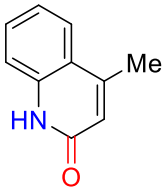
Product 3va (known compound, CAS: 106015-76-3)



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3va** as a white solid (46.2 mg, 91% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.95 (s, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.57 – 7.51 (m, 3H), 7.39 (dd, *J* = 22.6, 8.1 Hz, 2H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.43 (s, 1H). ^{13}C NMR (101 MHz, DMSO) δ = 161.6, 150.7, 139.8, 136.0, 134.1, 131.1 (overlap), 129.2

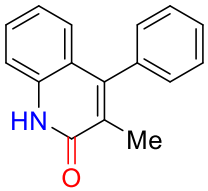
(overlap), 126.4, 122.4, 122.0, 118.6, 116.3.

Product 3wa (known compound, CAS: 607-66-9)

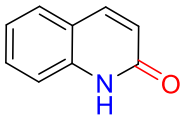


The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3wa** as a white solid (25.8 mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.63 (s, 1H), 7.71 (d, *J* = 8.0 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 8.2 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 6.42 (s, 1H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, DMSO) δ = 162.1, 148.4, 139.1, 130.7, 125.2, 122.1, 121.3, 120.0, 18.9.

Product 3xa (known compound, CAS: 37118-75-5)



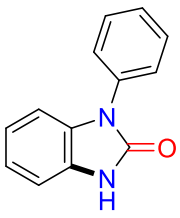
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3xa** as a white solid (30.0 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 12.59 (s, 1H), 7.56 – 7.42 (m, 5H), 7.26 (d, *J* = 7.0 Hz, 2H), 7.09 – 7.04 (m, 2H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 164.6, 148.9, 137.1, 137.0, 129.3, 128.8, 128.7, 128.0, 127.5, 126.8, 122.2, 121.1, 116.0, 14.4.



Product 3ya (known compound, CAS: 59-31-4)

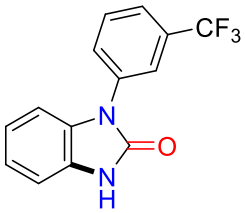
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 4:1 to 3:1), yielding of **3ya** as a yellow solid (11.5 mg, 40 % yield). ^{1}H NMR (600 MHz, DMSO-d6) δ = 11.76 (s, 1H), 7.91 (d, J = 9.5 Hz, 1H), 7.66 (d, J = 7.5 Hz, 1H), 7.53 – 7.48 (m, 1H), 7.32 (d, J = 8.2 Hz, 1H), 7.18 (t, J = 7.5 Hz, 1H), 6.51 (d, J = 9.5 Hz, 1H). ^{13}C NMR (151 MHz, DMSO) δ = 162.4, 140.7, 139.3, 130.8, 128.3, 122.4, 122.2, 119.6, 115.6.

Product 5aa (known compound, CAS: 14813-85-5)



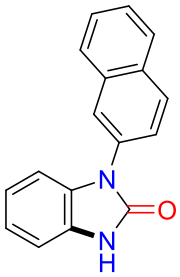
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1 to 4:1), yielding of **5aa** as a white solid (22.4 mg, 53% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.16 (s, 1H), 7.59 – 7.52 (m, 4H), 7.47 – 7.40 (m, 1H), 7.10 – 7.05 (m, 2H), 7.04 – 6.97 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ = 153.7, 135.0, 130.5, 129.9, 128.9, 127.8, 126.4, 122.3, 121.4, 109.6, 108.6.

Product 5ba (known compound, CAS: 1526961-90-9)



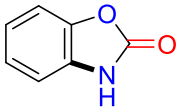
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1 to 4:1), yielding of **5ba** as a white solid (50.2 mg, 90% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.31 (s, 1H), 7.95 (s, 1H), 7.90 (d, *J* = 6.7 Hz, 1H), 7.85 – 7.78 (m, 2H), 7.11 (d, *J* = 2.8 Hz, 2H), 7.09 – 7.01 (m, 2H). ^{13}C NMR (101 MHz, DMSO) δ = 153.5, 135.9, 131.2, 130.6 (q, *J* = 32.0 Hz), 130.1, 129.9, 129.0, 125.6, 124.3 (q, *J* = 3.8 Hz), 123.0 (q, *J* = 4.1 Hz), 122.7, 121.5, 120.3 (q, *J* = 270.1 Hz), 109.2 (q, *J* = 120.4 Hz). ^{19}F NMR (376 MHz, $CDCl_3$) δ = -62.6.

Product 5ca



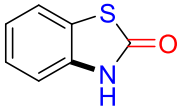
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1 to 4:1), yielding of **5ca** as a yellow solid (33.4 mg, 64% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.23 (s, 1H), 8.09 – 8.01 (m, 2H), 8.00 – 7.98 (m, 2H), 7.66 – 7.63 (m, 1H), 7.58 – 7.56 (m, 2H), 7,12 – 6.99 (m, 4H). ^{13}C NMR (101 MHz, DMSO) δ = 153.9, 133.6, 132.5, 132.2, 130.5, 129.6, 128.9, 128.3, 128.2, 127.2, 127.0, 124.7, 124.5, 122.4, 121.5, 109.7, 108.8.

Product 5da (known compound, CAS: 59-49-4)



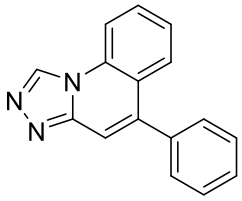
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1 to 5:1), yielding of **5da** as a white solid (18.0 mg, 67% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.67 (s, 1H), 7.22 (d, *J* = 7.8 Hz, 1H), 7.18 – 7.11 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 156.1, 143.9, 129.4, 124.2, 122.8, 110.2, 110.2.

Product 5ea (known compound, CAS: 59-49-4)



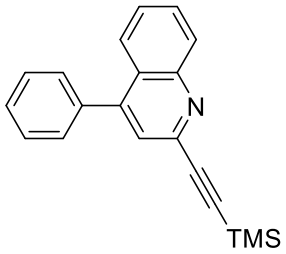
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 10:1 to 5:1), yielding of **5ea** as a white solid (19.4 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 10.17 (s, 1H), 7.41 (d, *J* = 7.8 Hz, 1H), 7.31 – 7.25 (m, 1H), 7.20 – 7.13 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 173.2, 135.4, 126.5, 123.9, 123.3, 122.5, 111.8.

Product 9 (known compound, CAS: 1108713-24-1)



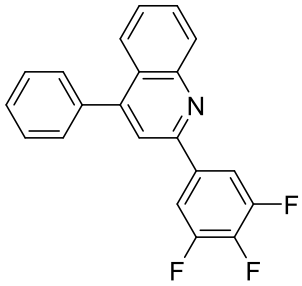
The crude product was purified by column chromatography (SiO_2, dichloromethane/methanol = 20:1), yielding of **9** as a orange solid (34.5 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 9.32 (s, 1H), 8.08 (d, *J* = 8.3 Hz, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.77 – 7.70 (m, 1H), 7.61 (s, 1H), 7.56 – 7.47 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 148.0, 141.9, 137.4, 134.5, 130.5, 130.0, 129.4 (overlap), 128.8, 128.7, 128.5, 126.3, 123.5, 115.8, 114.1.

Product 11



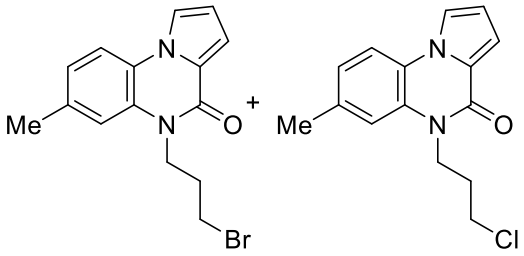
The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 5:1), yielding of **11** as a white solid (24.0 mg, 80% yield).^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 8.5 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.72 (t, *J* = 8.4, Hz, 1H), 7.55 – 7.47 (m, 7H), 0.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.3, 152.2, 146.5, 141.0, 133.5 (overlap), 133.1 (overlap), 132.3, 130.9, 129.6, 129.3, 128.3, 107.9, 99.3, 3.4. M.P.: 140.0 – 141.0 °C HRMS (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{19}NSi$: 324.1179; found: 324.1181.

Product 12



The crude product was purified by column chromatography (SiO_2, petroleum ether/ethyl acetate = 20:1 to 5:1), yielding of **12** as a white solid (30.0 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.21 (d, *J* = 8.7 Hz, 1H), 7.93 – 7.85 (m, 3H), 7.76 (t, *J* = 8.4, 1H), 7.71 (s, 1H), 7.59 – 7.49 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 153.1 (m), 152.8 (dd, *J* = 10.2, 4.0 Hz), 150.4 (dd, *J* = 10.2, 3.9 Hz), 149.9, 148.6, 141.9, 139.3 (t, *J* = 15.6 Hz), 138.0, 135.6 (m), 130.1 (d, *J* = 14.8 Hz), 129.5, 128.7, 128.6, 127.0, 126.1, 125.8, 118.2, 111.5 (d, *J* = 22.2 Hz), 111.4 (d, *J* = 9.9 Hz). M.P.: 174.0 – 174.5 °C HRMS (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{12}F_3N$: 336.0995; found: 336.0990.

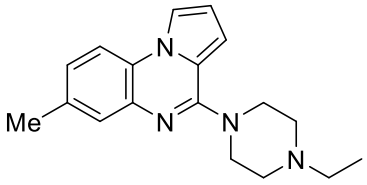
Product 13



13+13', 73% (4:1)

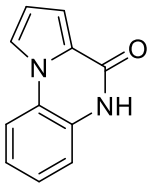
The crude product was purified by column chromatography (SiO_2, petroleum ether /ethyl acetate = 20:1 to 5:1)), yielding of a mixture of **13** and **13'** as a yellow solid (40.9 mg, 73% yield, 4:1). ^{1}H NMR (400 MHz, $CDCl_3$, **13+13'**) δ = 7.63 – 7.58 (m, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.05 (d, *J* = 8.3 Hz, 1H), 6.65 (t, *J* = 3.3 Hz, 1H), 4.41 (t, *J* = 7.4 Hz, 2H), 3.72 (t, *J* = 6.3 Hz, 2H), 2.47 (s, 3H), 2.25 – 2.21 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 155.7, 135.8, 129.1, 123.7, 122.9, 122.0, 115.9, 114.7, 113.1, 112.5, 42.8, 40.0, 38.9, 30.9, 30.5, 21.5.

Product 15



The crude product was purified by column chromato-graphy (SiO_2, petroleum ether/ethyl acetate = 20:1 to 3:1), yielding of **15** as a white solid (20.0 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.75 (d, *J* = 2.8 Hz, 1H), 7.59 (d, *J* = 8.3 Hz, 1H), 7.48 (s, 1H), 7.06 (d, *J* = 8.2 Hz, 1H), 6.77 – 6.73 (m, 1H), 6.72 (t, *J* = 3.4 Hz, 1H), 3.83 (t, *J* = 5.0 Hz, 4H), 2.65 (t, *J* = 5.0 Hz, 4H), 2.51 (q, *J* = 7.2 Hz, 2H), 2.42 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 152.7, 136.0, 134.8, 127.4, 125.0, 123.7, 120.1, 114.2, 113.0, 112.2, 106.5, 52.9, 52.5, 47.9, 21.1, 11.9.

Product 18 (known compound, CAS: 6025-68-9)



The crude product was purified by column chromato-graphy (SiO_2, petroleum ether/ethyl acetate = 20:1 to 3:1), yielding of **15** as a white solid (5.2 mg, 14% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ = 11.27 (s, 1H), 8.21 – 8.18 (m, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.04 – 7.02 (m, 1H), 6.69 (t, *J* = 3.3 Hz, 1H).

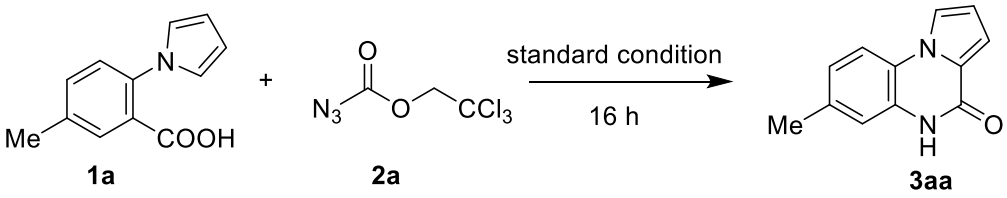
References:

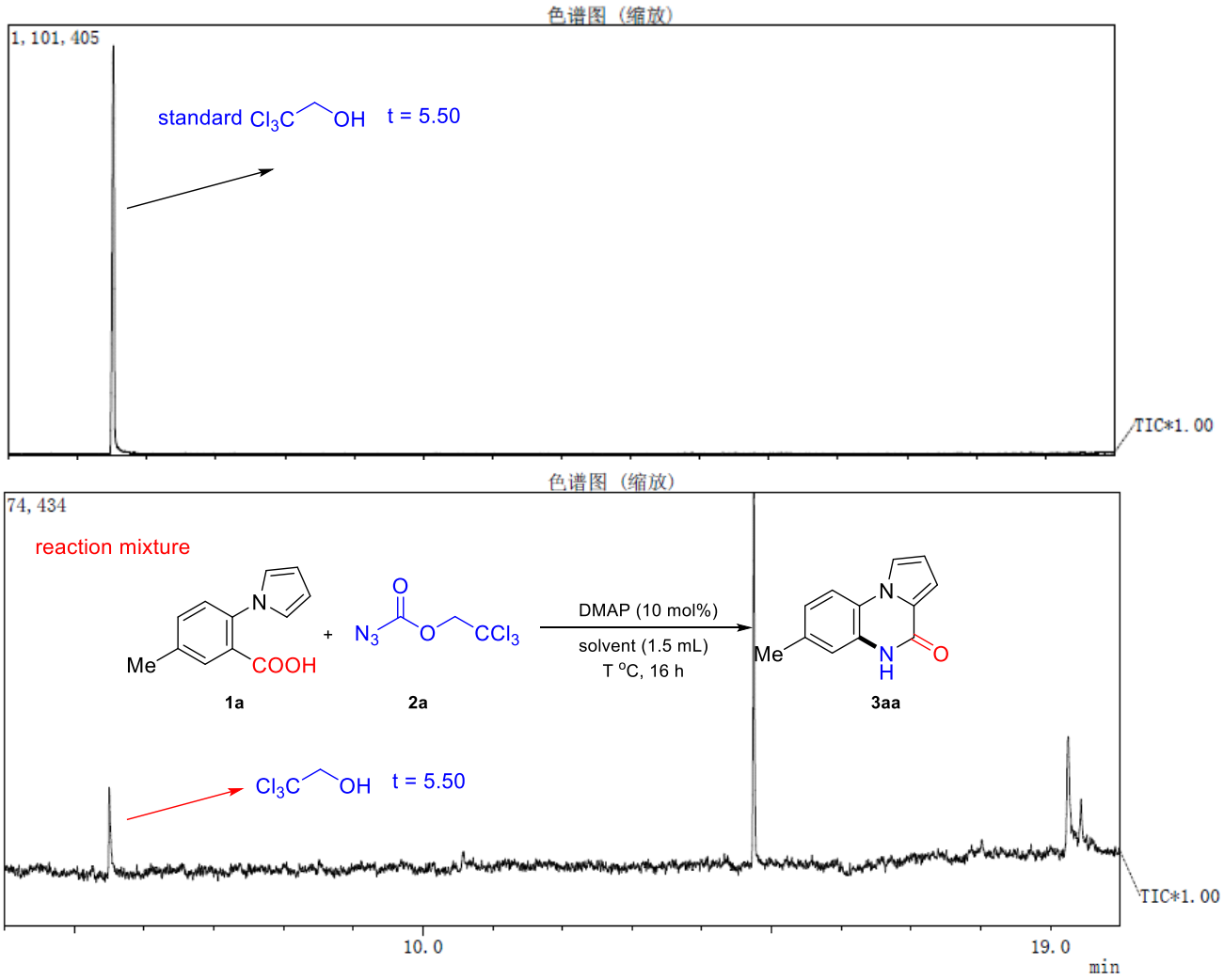
[1] Wei, Z.; Zhang, J.; Yang, H.; Jiang, G. Brønsted Acid-Catalyzed Asymmetric Ring-Closing Alkylation of Inert N-substituted Pyrroles with α, β-Unsaturated Ketones *Adv. Synth. Catal.* **2019**, 361, 3694-3697.

[2] Diego, F. B.; Jose, G. G. Metal-Free Arylation-Lactonization Sequence of γ-Alkenoic Acids Using Anilines as Aryl Radical Precursors. *Eur. J. Org. Chem*. **2019**, 47, 7735-7744.

[3] Nan, J.; Chen, P.; Gong, X.; Hu, Y.; Ma, Q.; Wang, B.; Ma, Y. M. Metal-Free C–H[5+1]Carbonylation of 2-Alkenyl/Pyrrolylanilines Using Dioxazolones as Carbonylating Reagents. *Org. Lett.* **2021**, 23, 3761–3766.

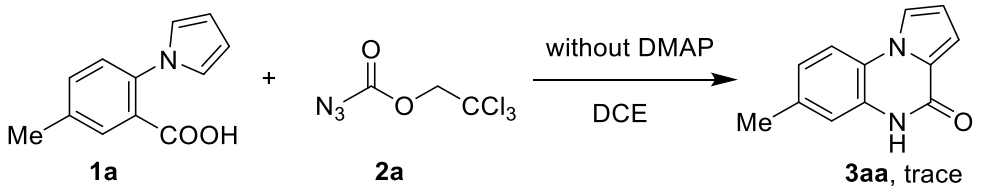
4. Mechanistic Studies



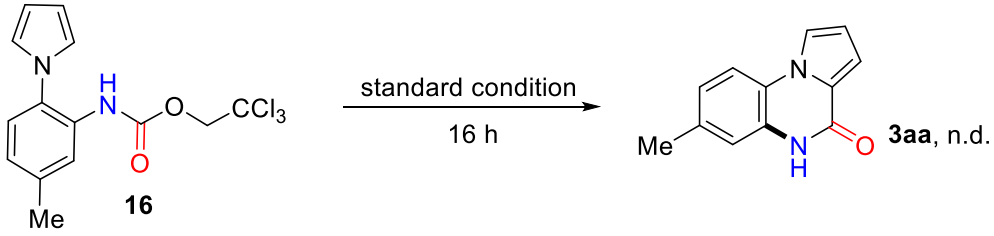


1a (20.1 mg, 0.1 mmol), DMAP (1.2 mg, 10 mol%) and **2a** (26 uL, 0.2 mmol) were dissolved in DCE (1.5 mL). Then, the mixture was stirred at 110 °C for 16 h.

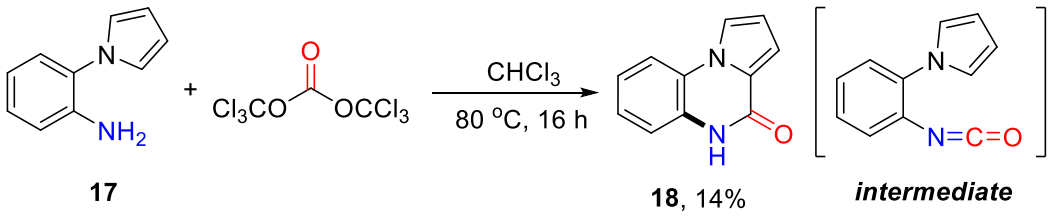
The by-product 2,2,2-trichloroethan-1-ol can be successfully detected by the analysis of the crude reaction mixture via gas chromatography, which supports the proposed mechanism in the manuscript.



1a (20.1 mg, 0.1 mmol) and **2a** (26 uL, 0.2 mmol) were dissolved in DCE (1.5 mL). Then, the mixture was stirred at 110 °C for 16 h. ***As a result, only trace amount of 3aa can be detected. The result demonstrated the importance of DMAP in this reaction, which acts as an effective promoter for the azido transfer process.***



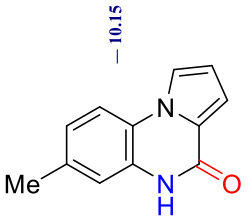
16 (20.0 mg, 0.06 mmol) was dissolved in DCE (1.5 mL). Then, the mixture was stirred at 110 °C for 16 h, as monitored by TLC analysis. ***The direct decarboxylative amination product 16 failed to give 3aa, suggesting it is not the intermediate in current reaction.***

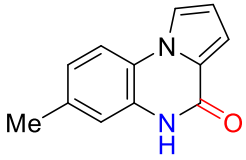


17 (31.6 mg, 0.2 mmol) and bis(trichloromethyl) carbonate (326.4 mg, 1.1 mmol) were dissolved in $CHCl_3$ (2.0 mL). Then, the mixture was stirred at 80 °C for 16 h, as monitored by TLC analysis and purified by flash chromatography. ***The desired cyclization product can be obtained in 14% yield, indicating the intermediacy of an isocyanate in this reaction.***

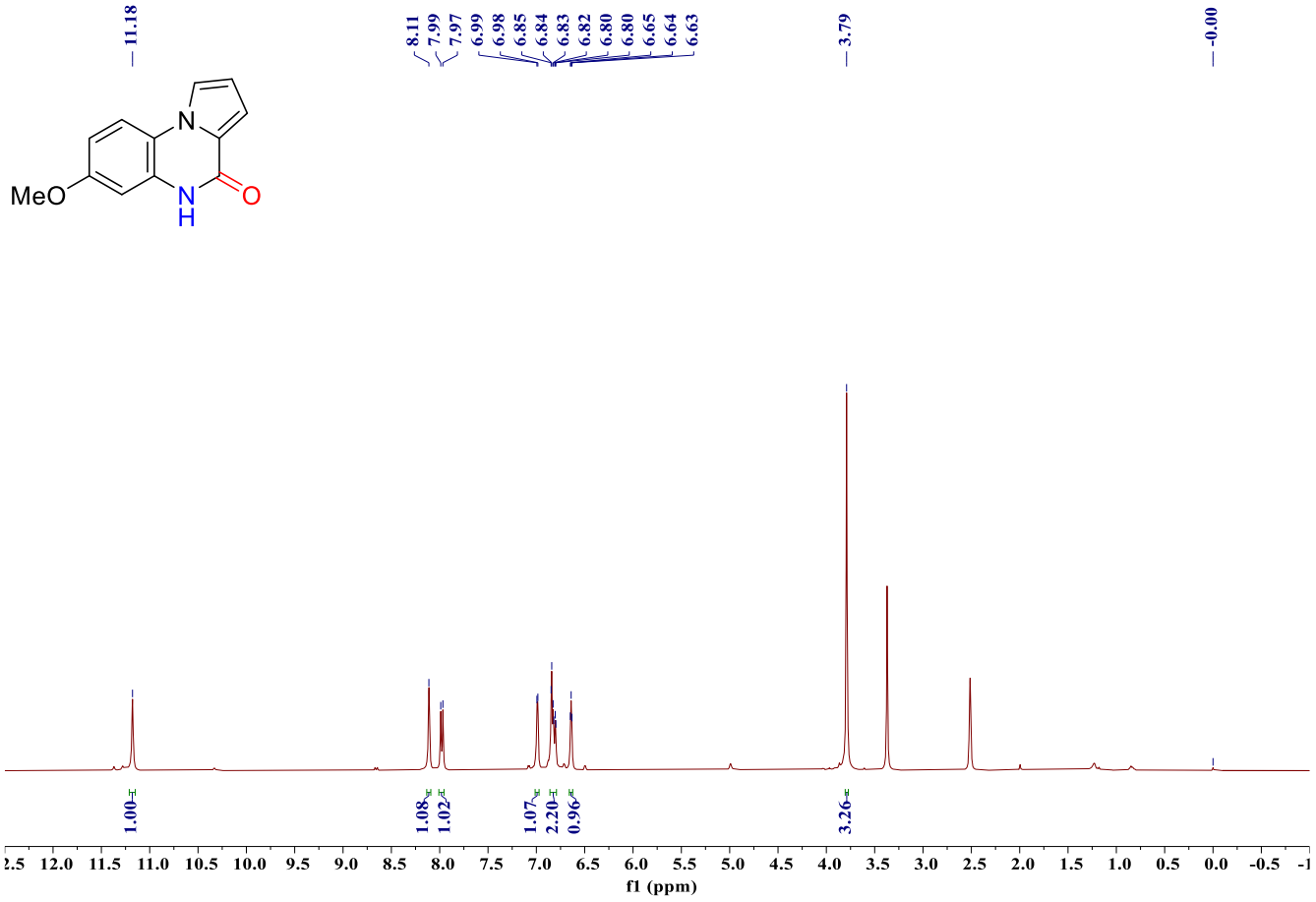
5. NMR Spectra of products 3aa-ya, 3ab-3ag, 9, 11–13 and 15

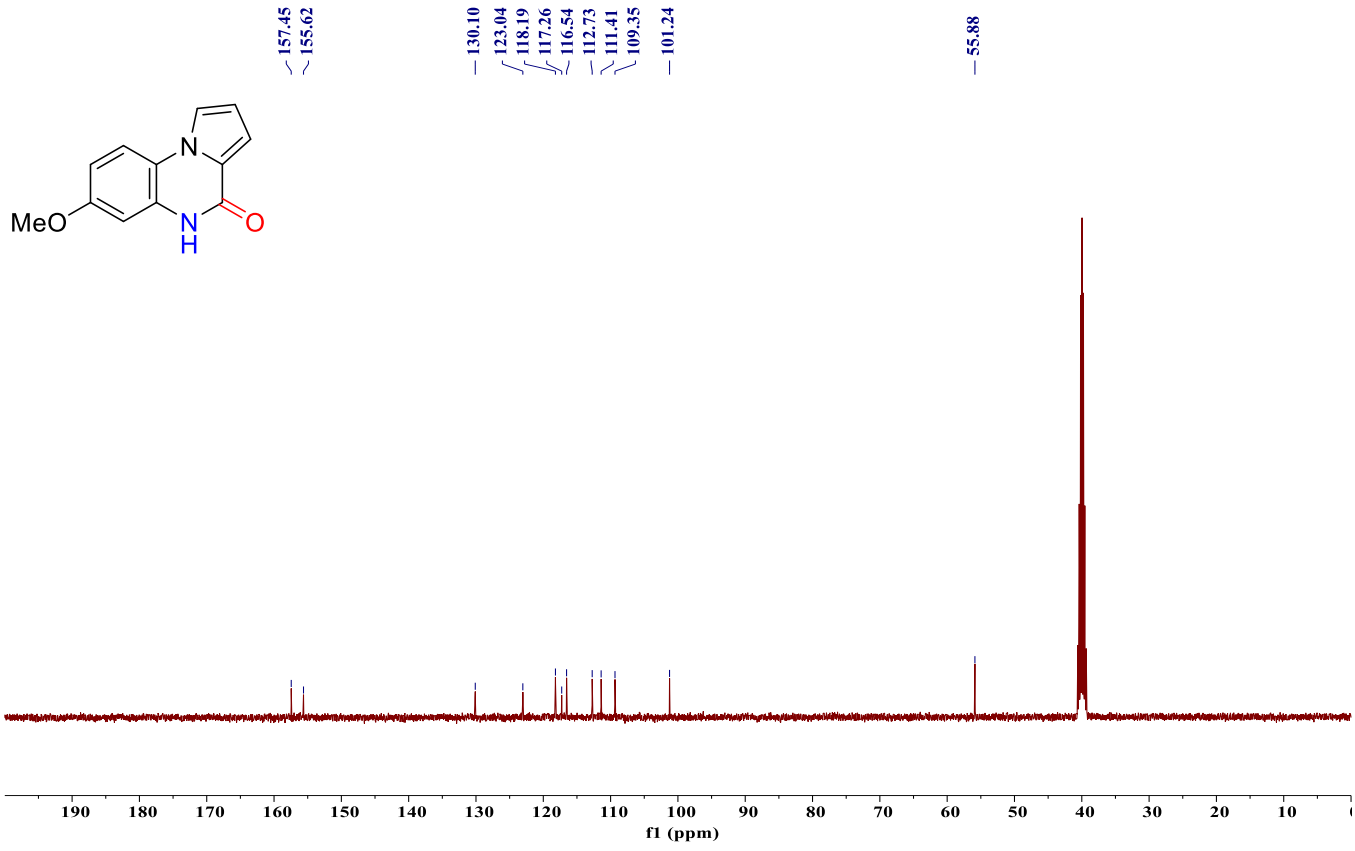
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3aa



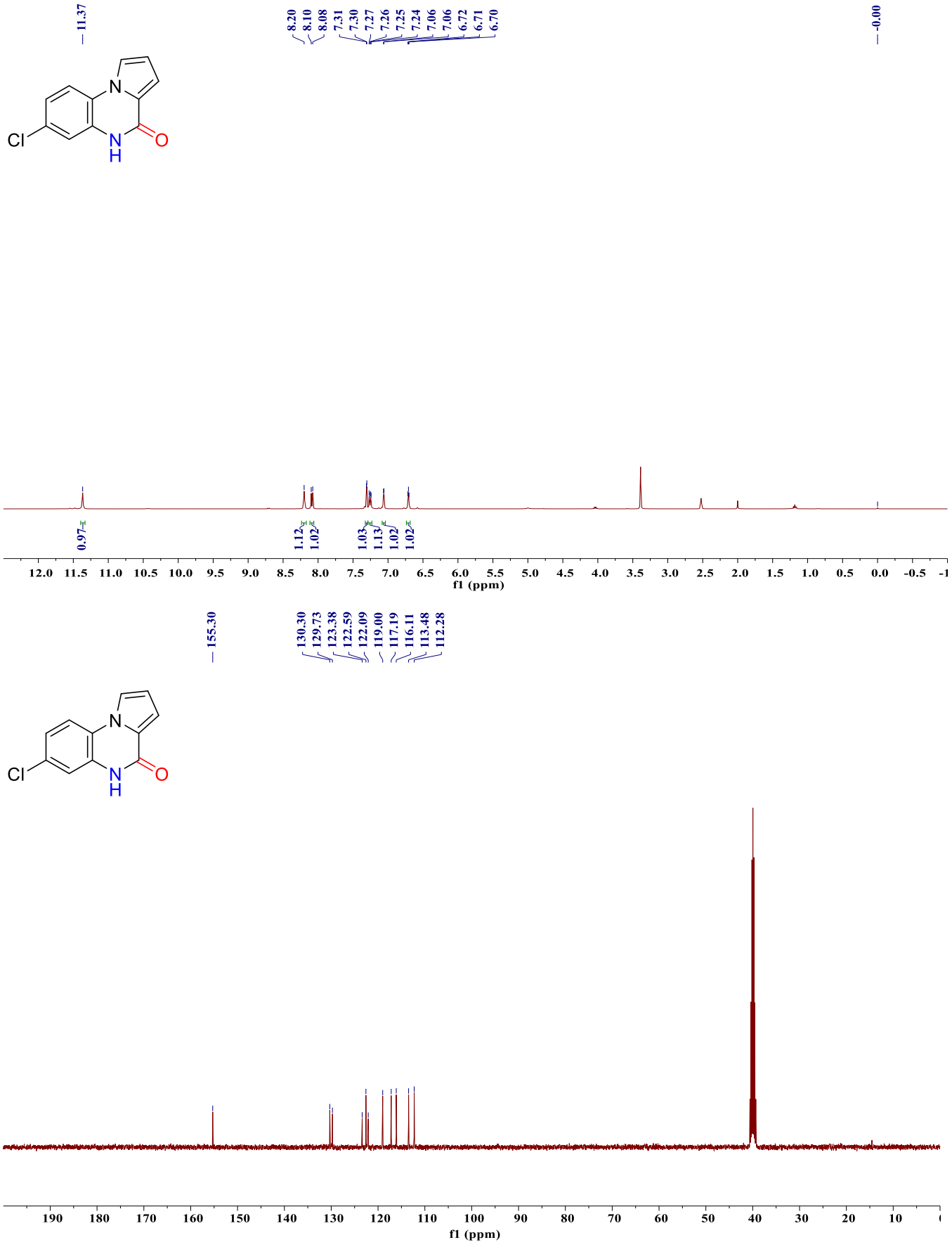


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ba

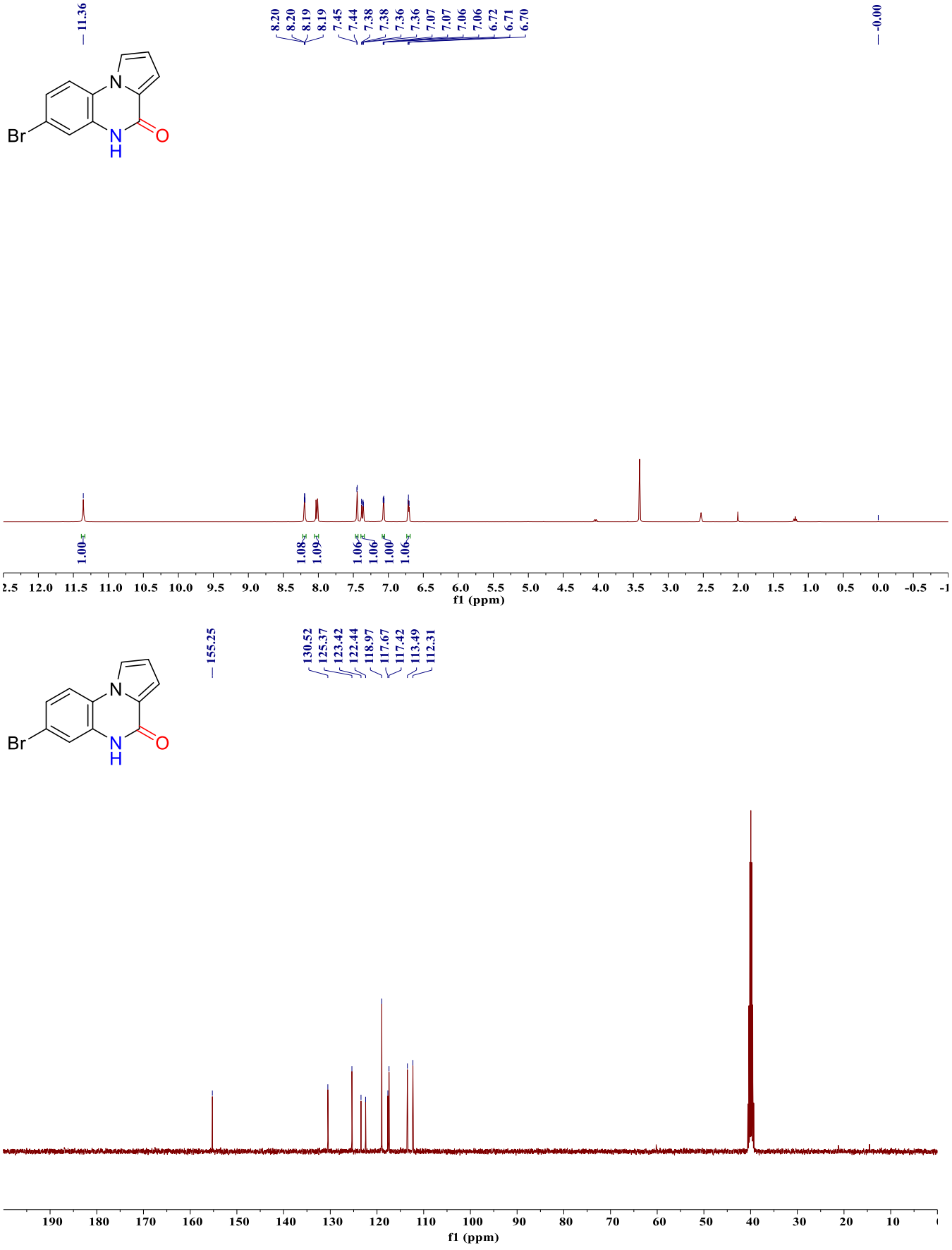




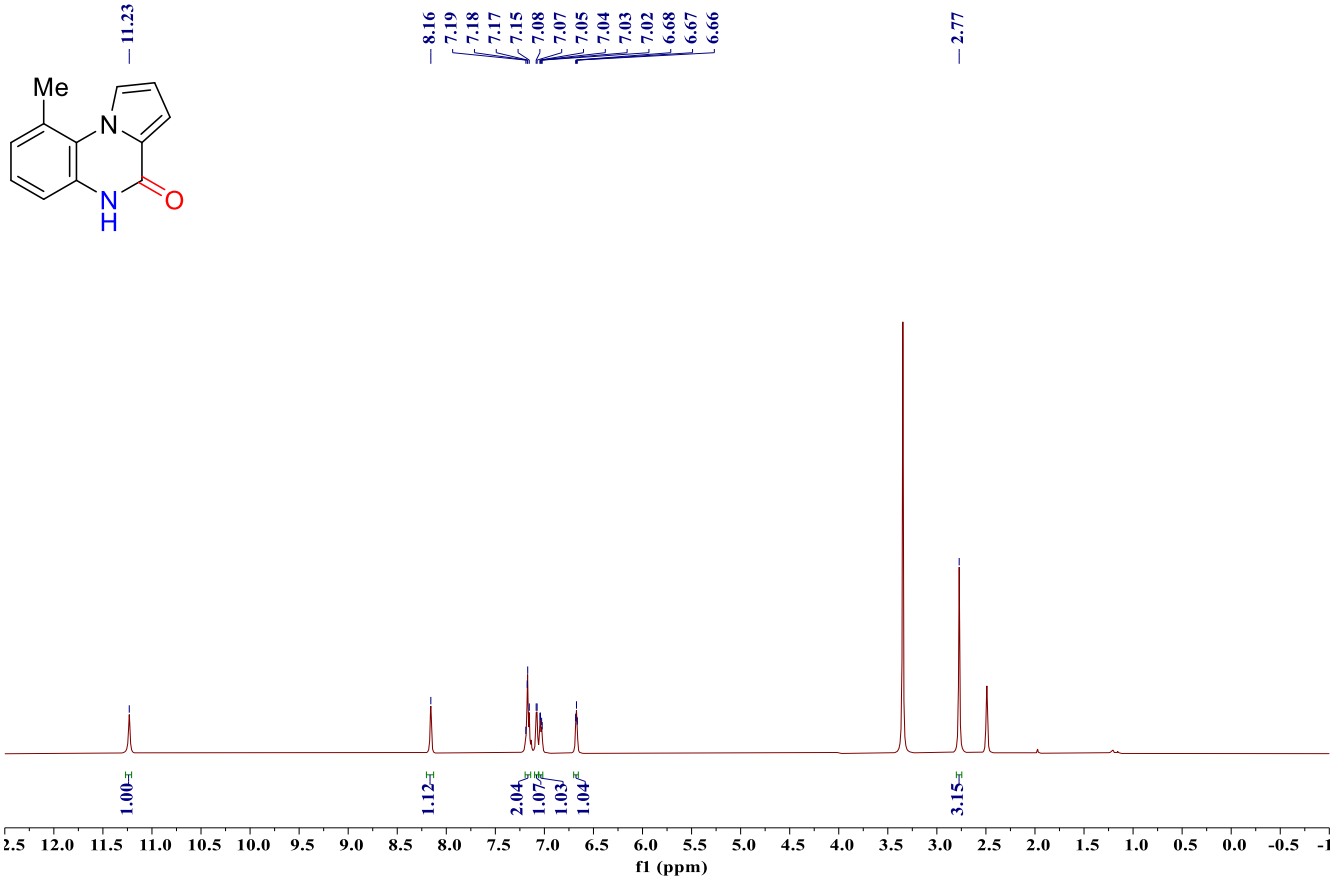
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ca

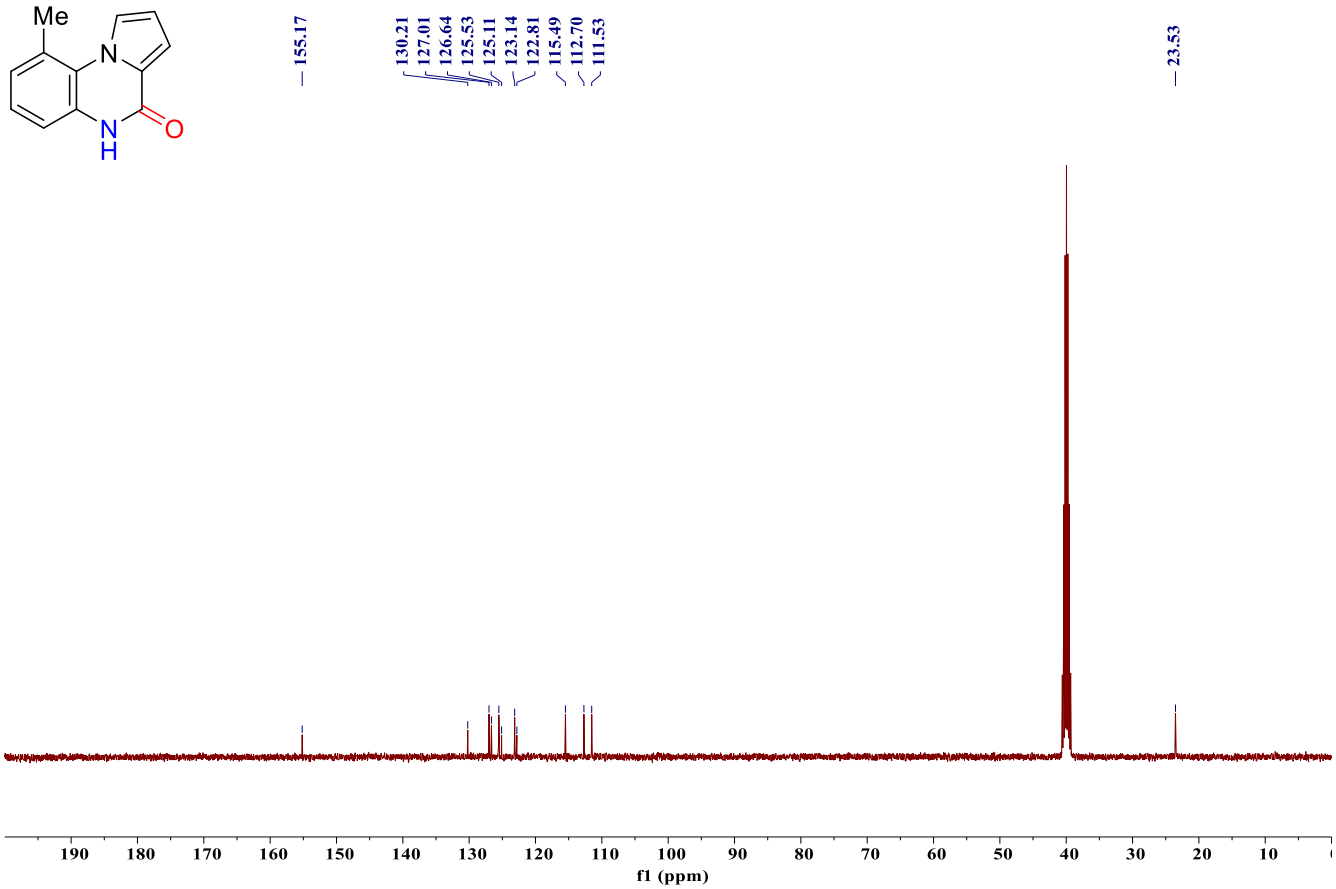


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3da

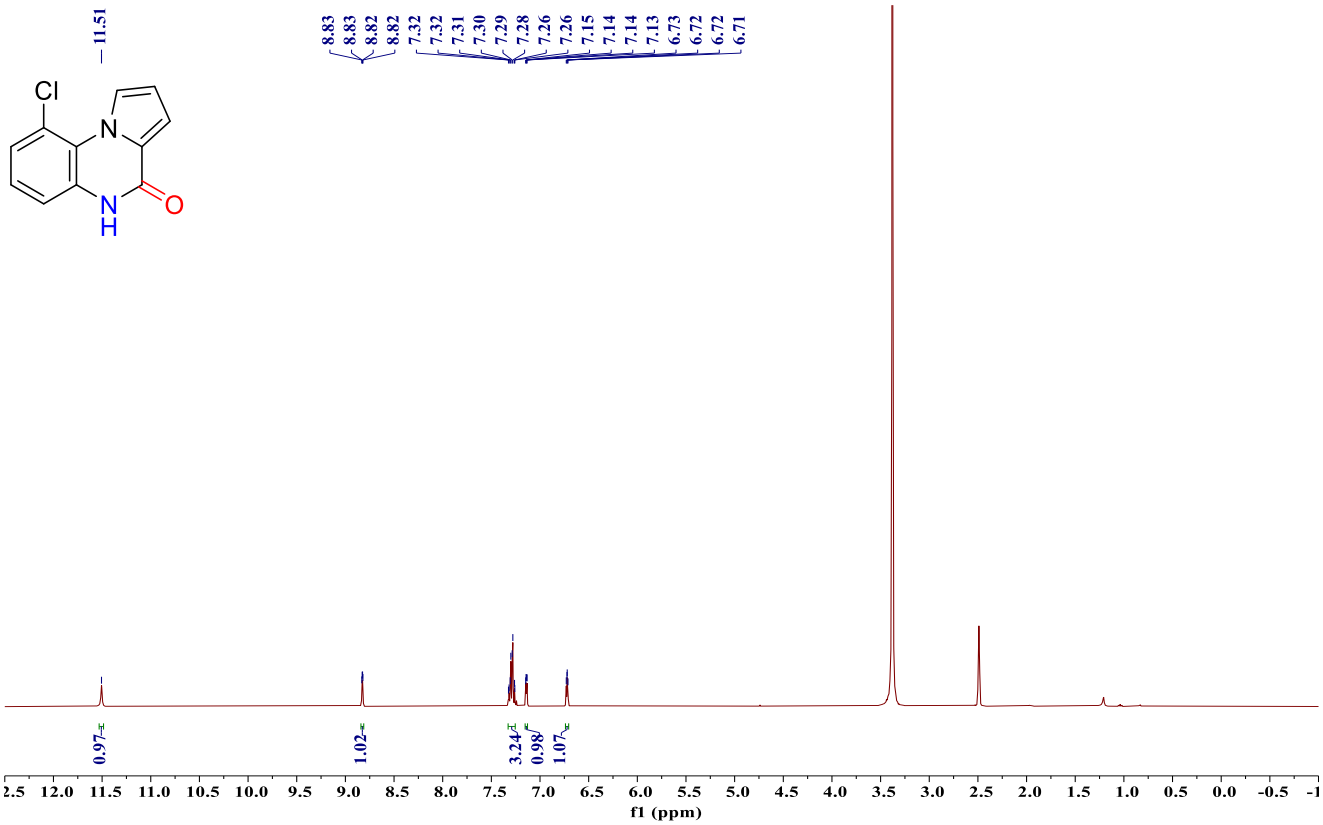


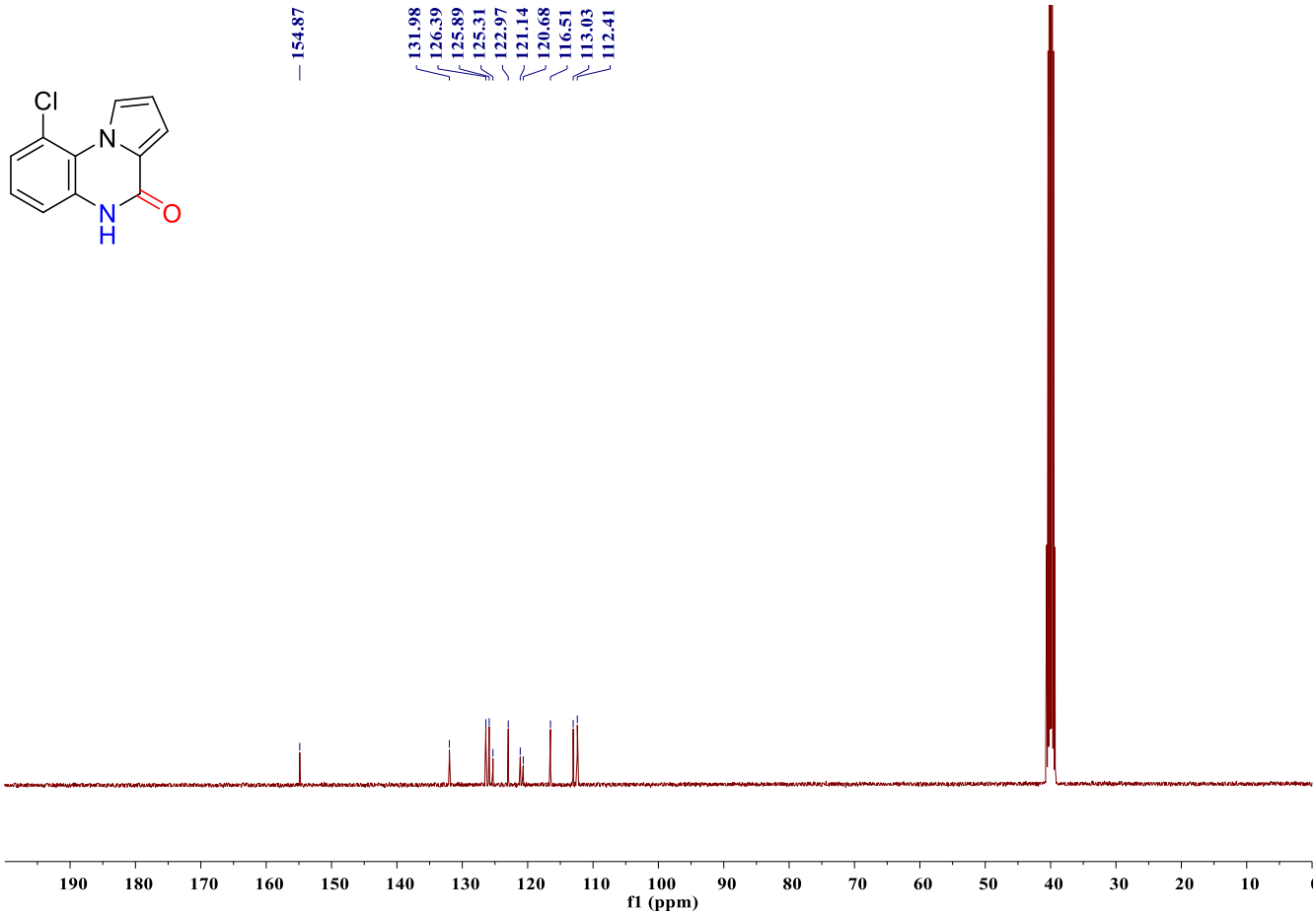
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ea



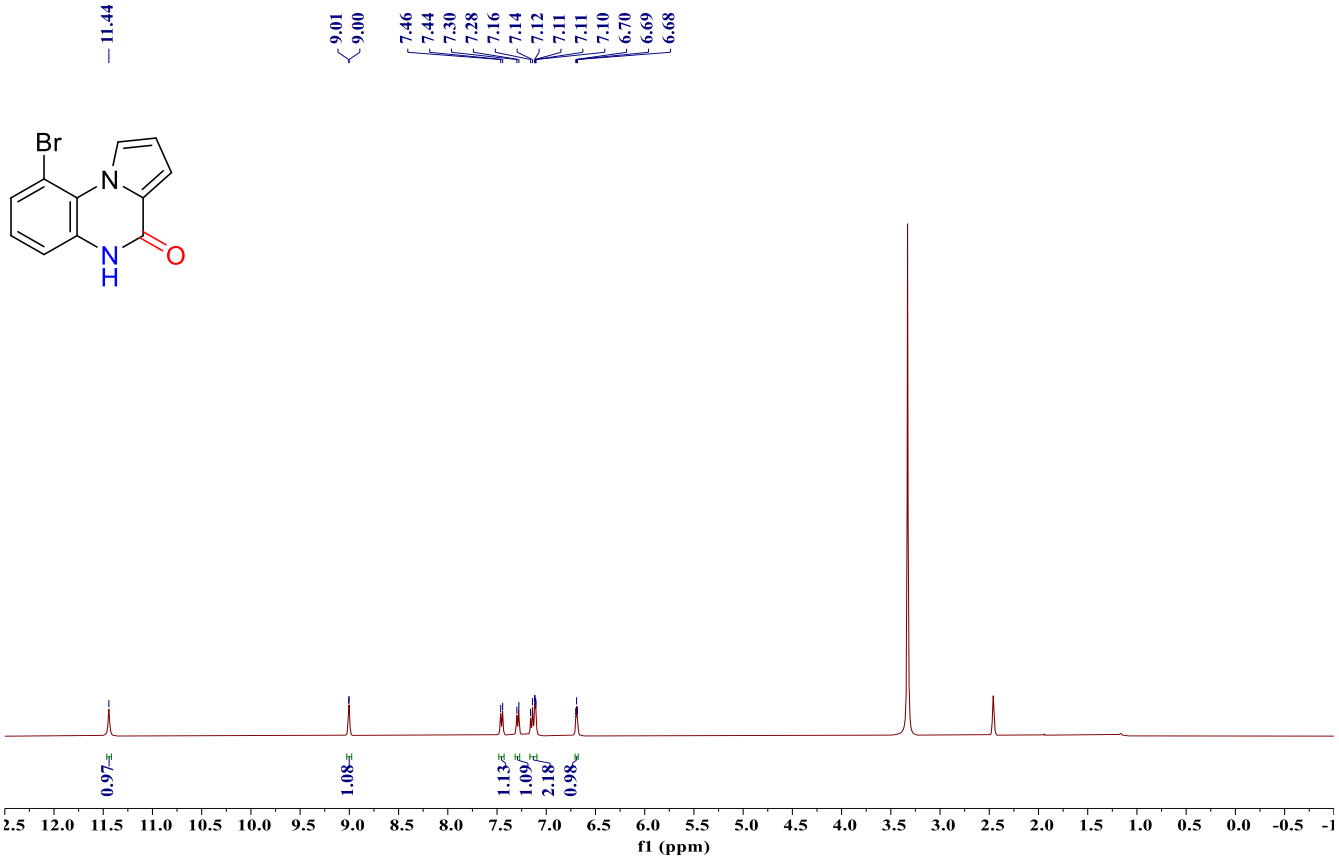


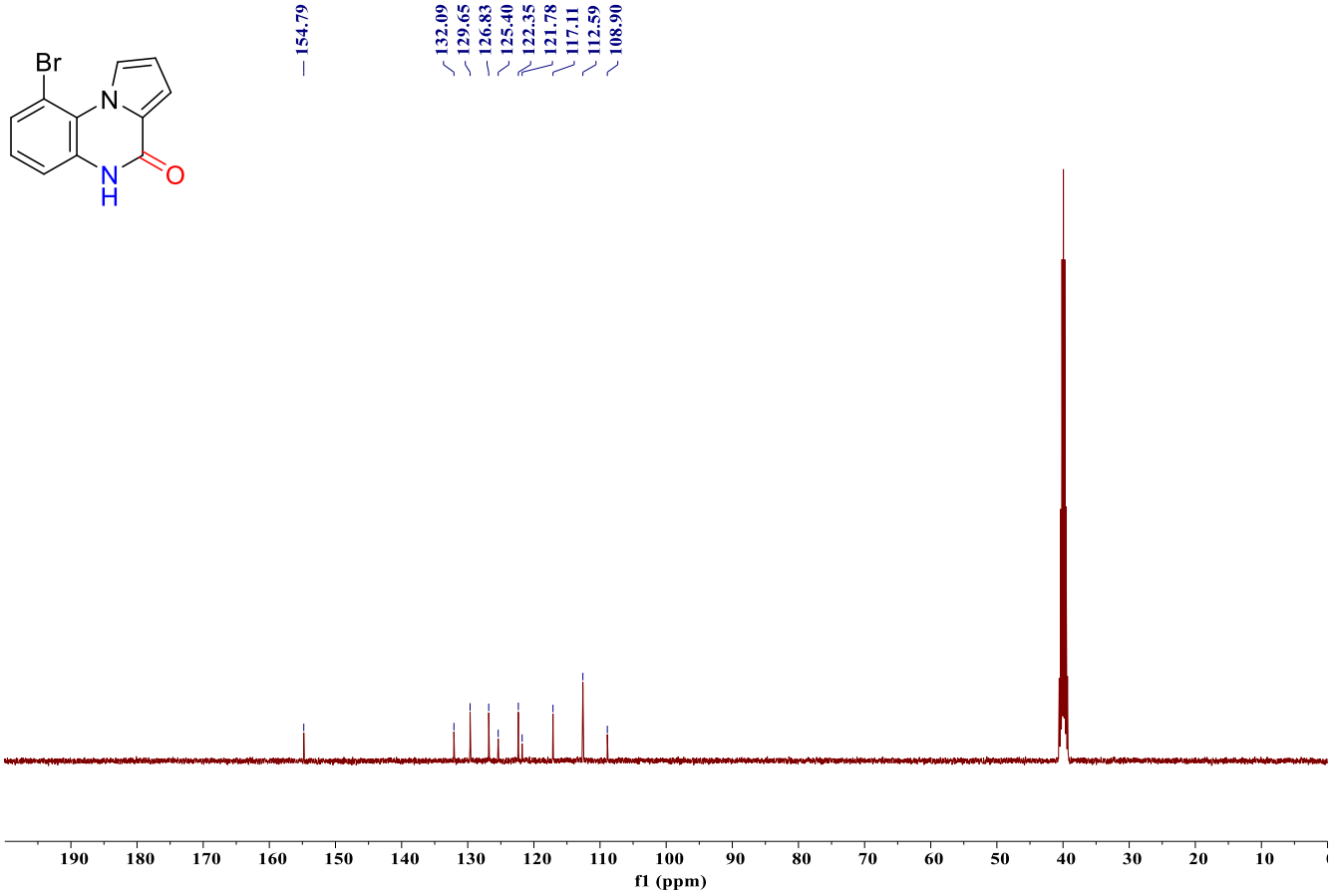
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3fa



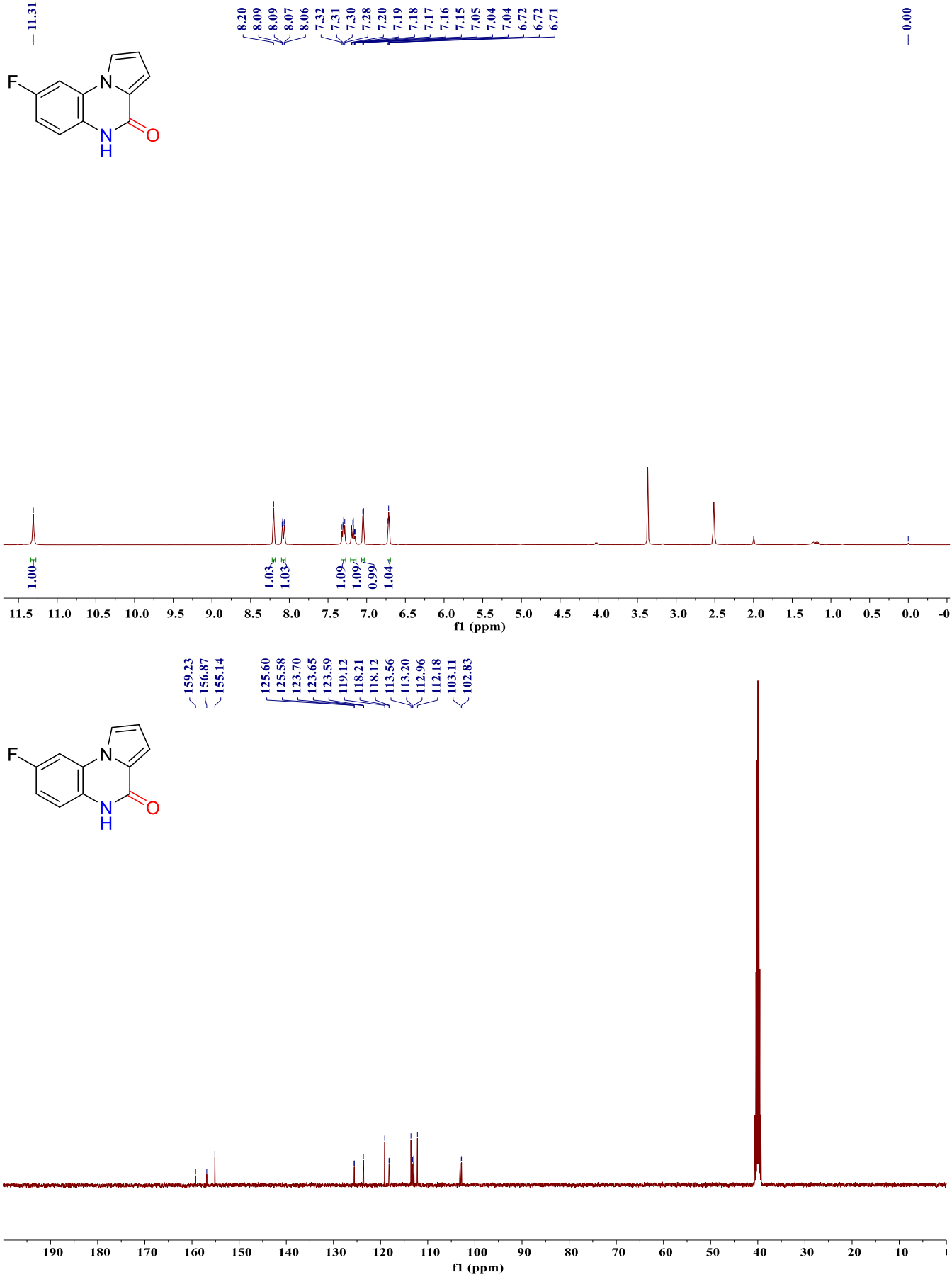


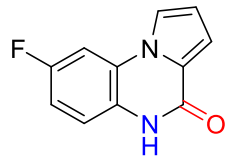
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ga





^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (376 MHz, DMSO) spectra of product 3ha

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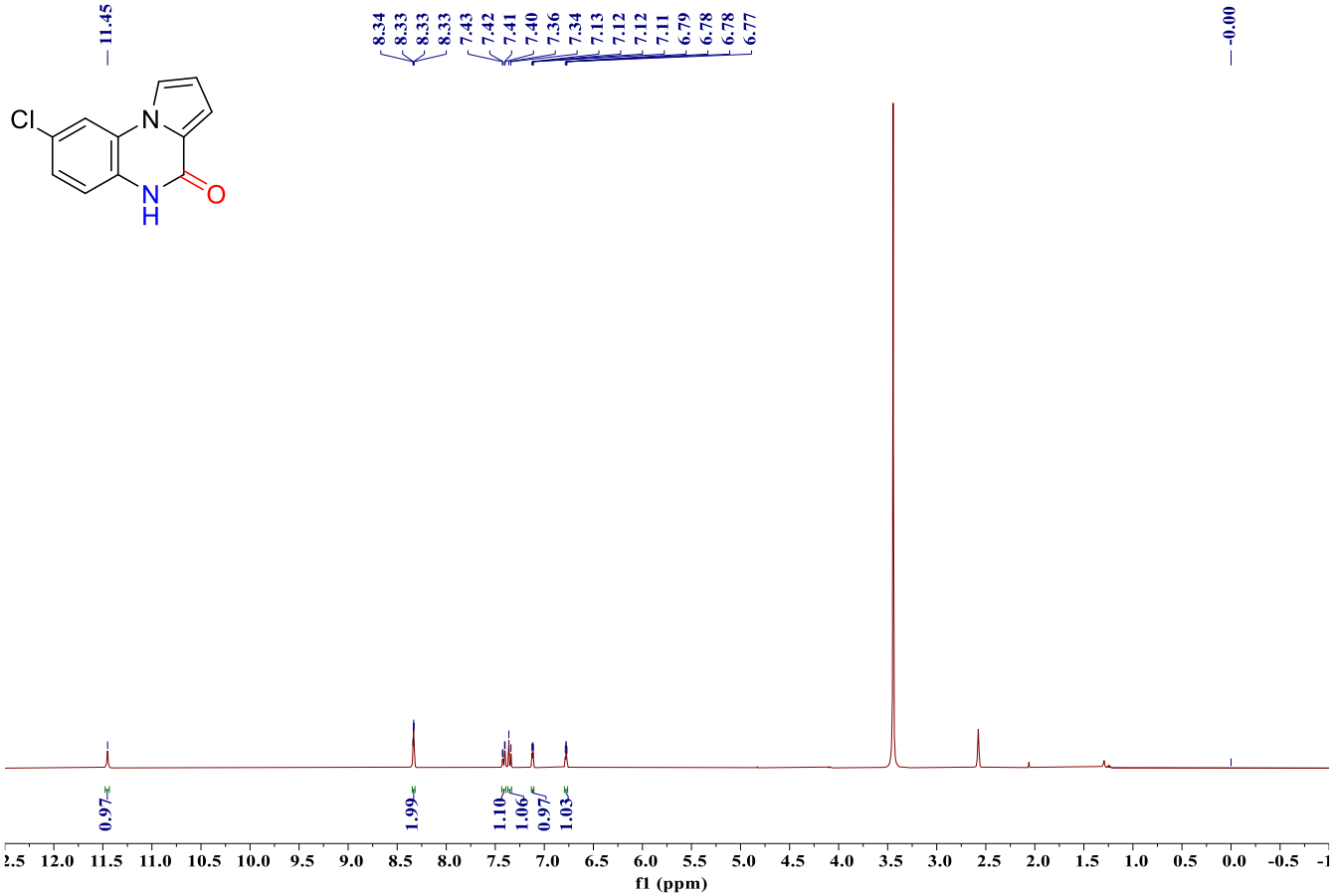
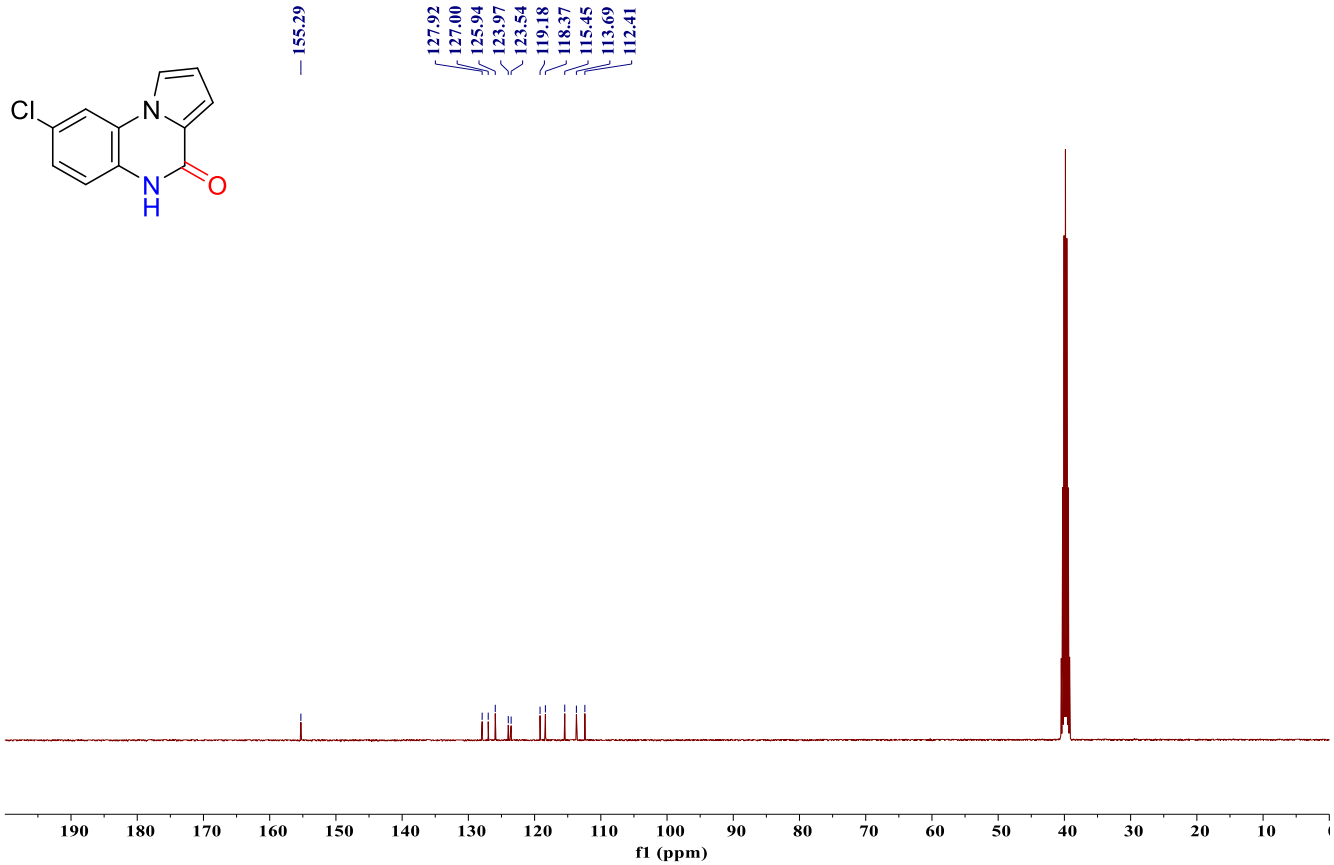
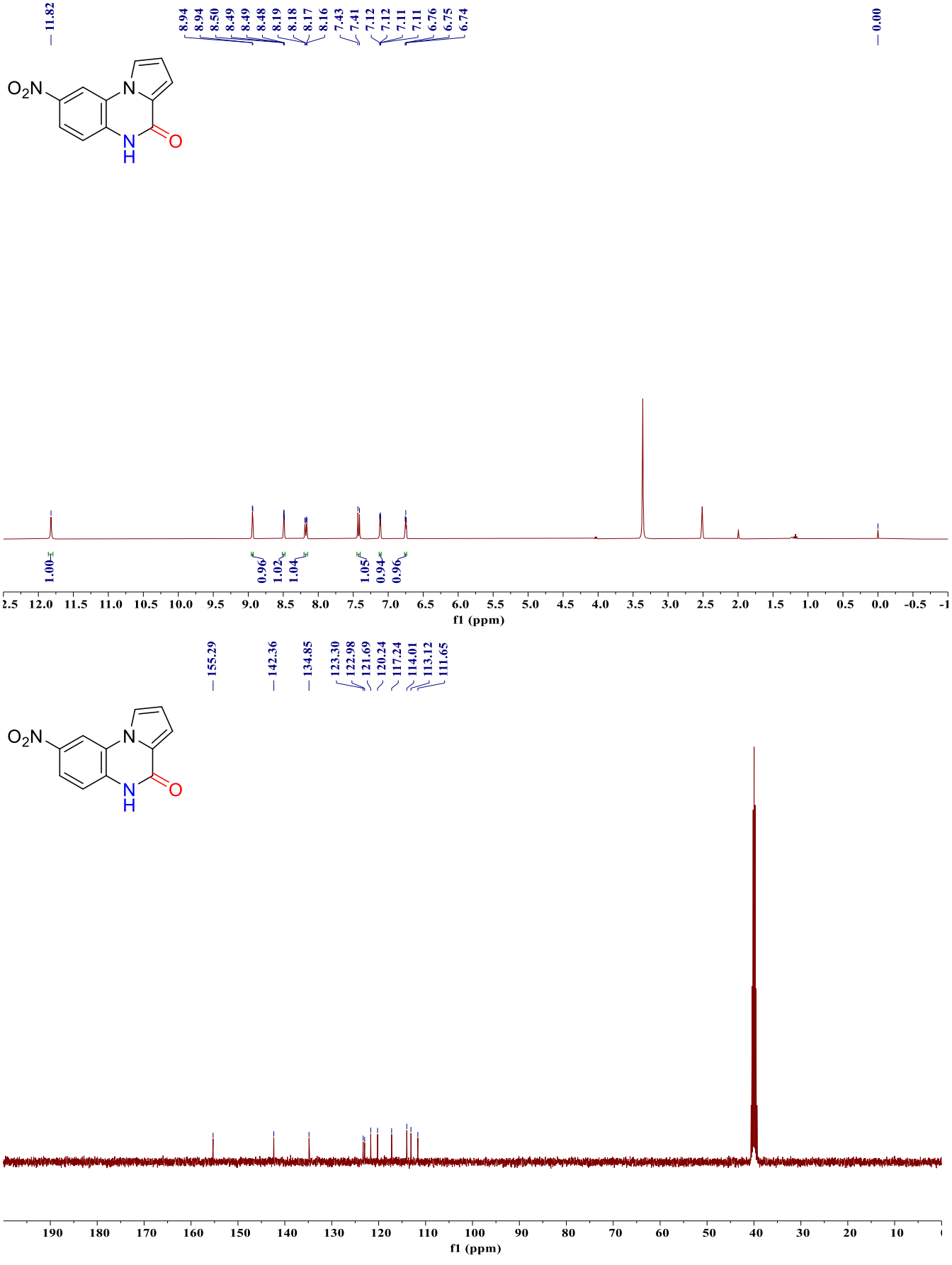
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ia

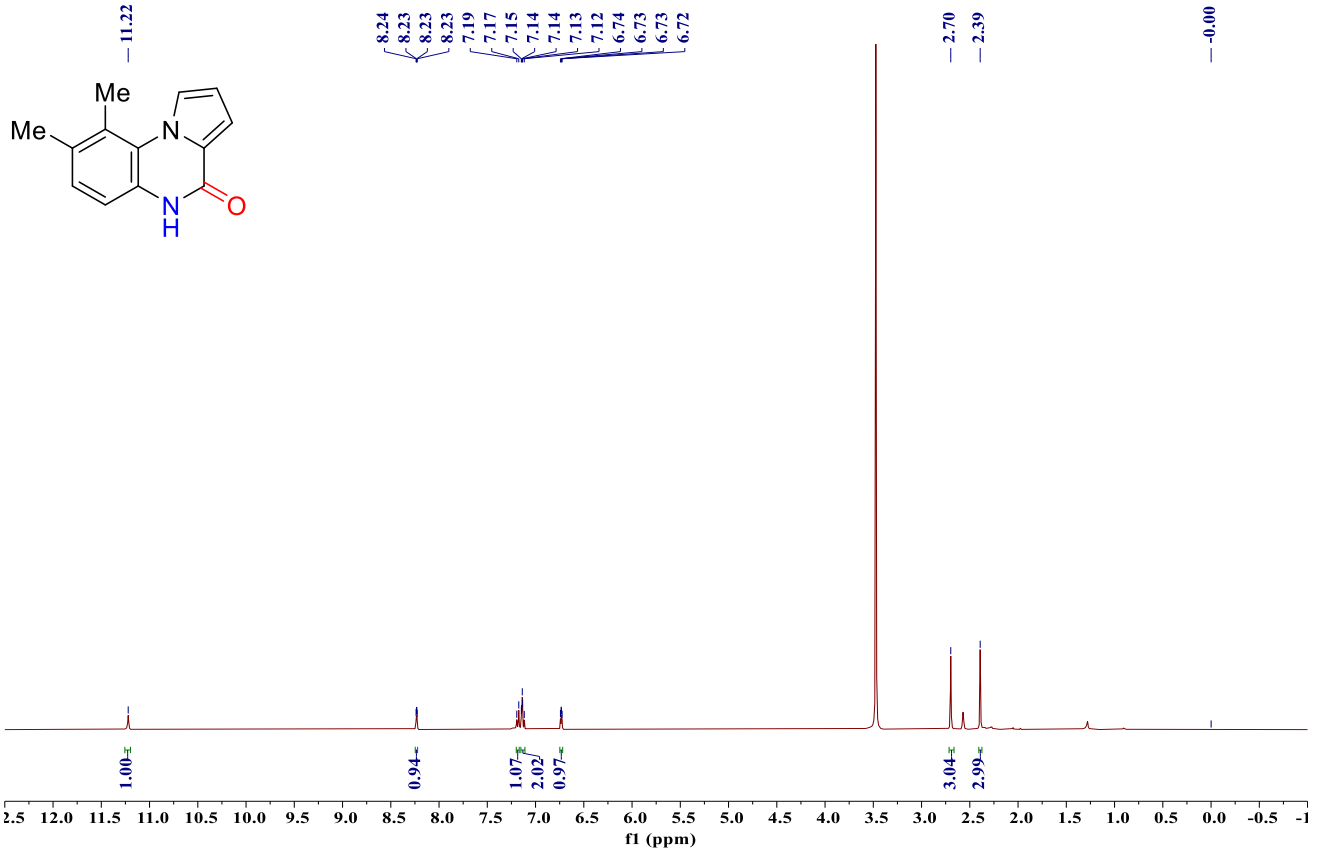


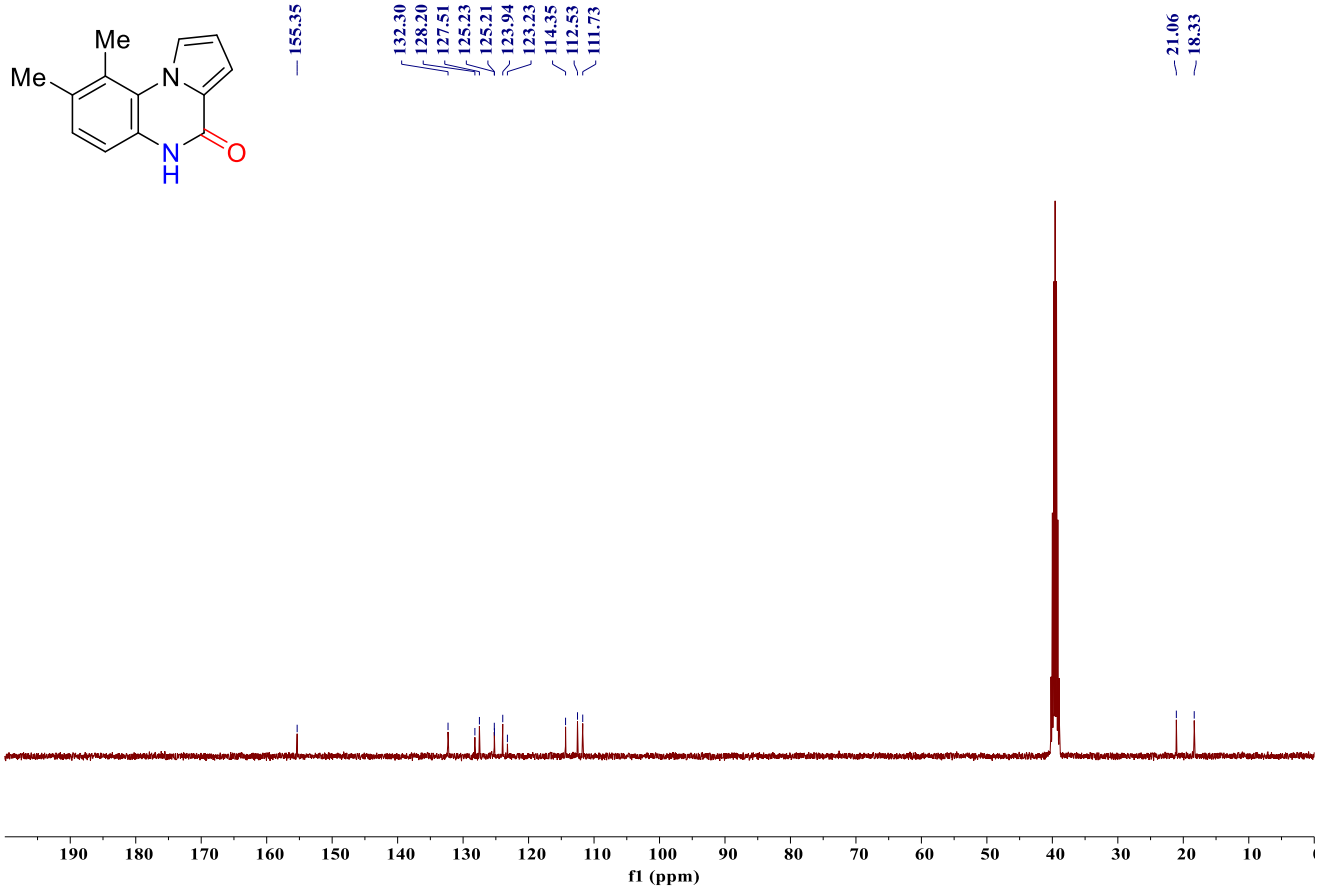


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ja

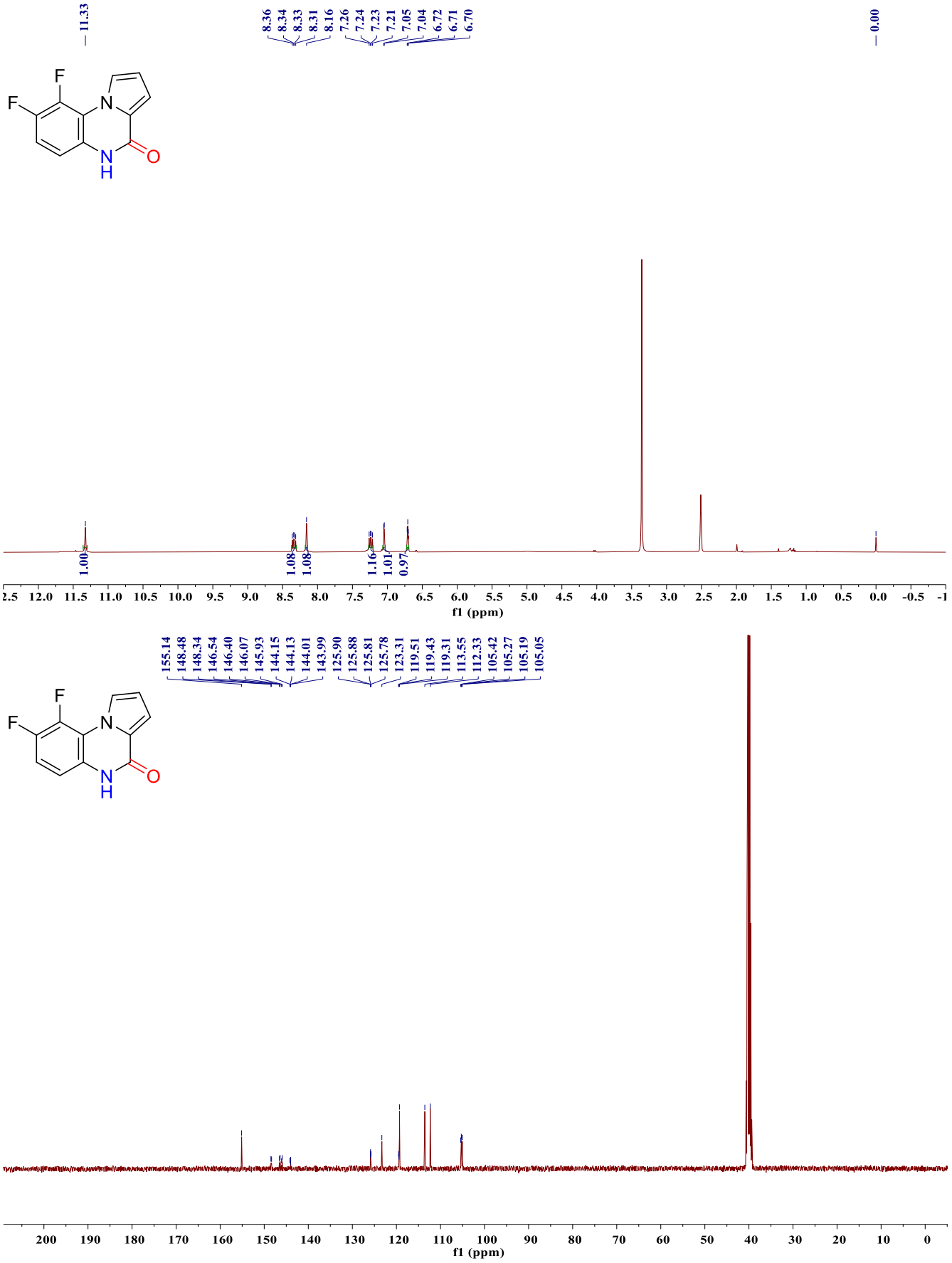


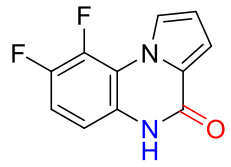
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ka





^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (376 MHz, DMSO) spectra of 3la

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-144.26
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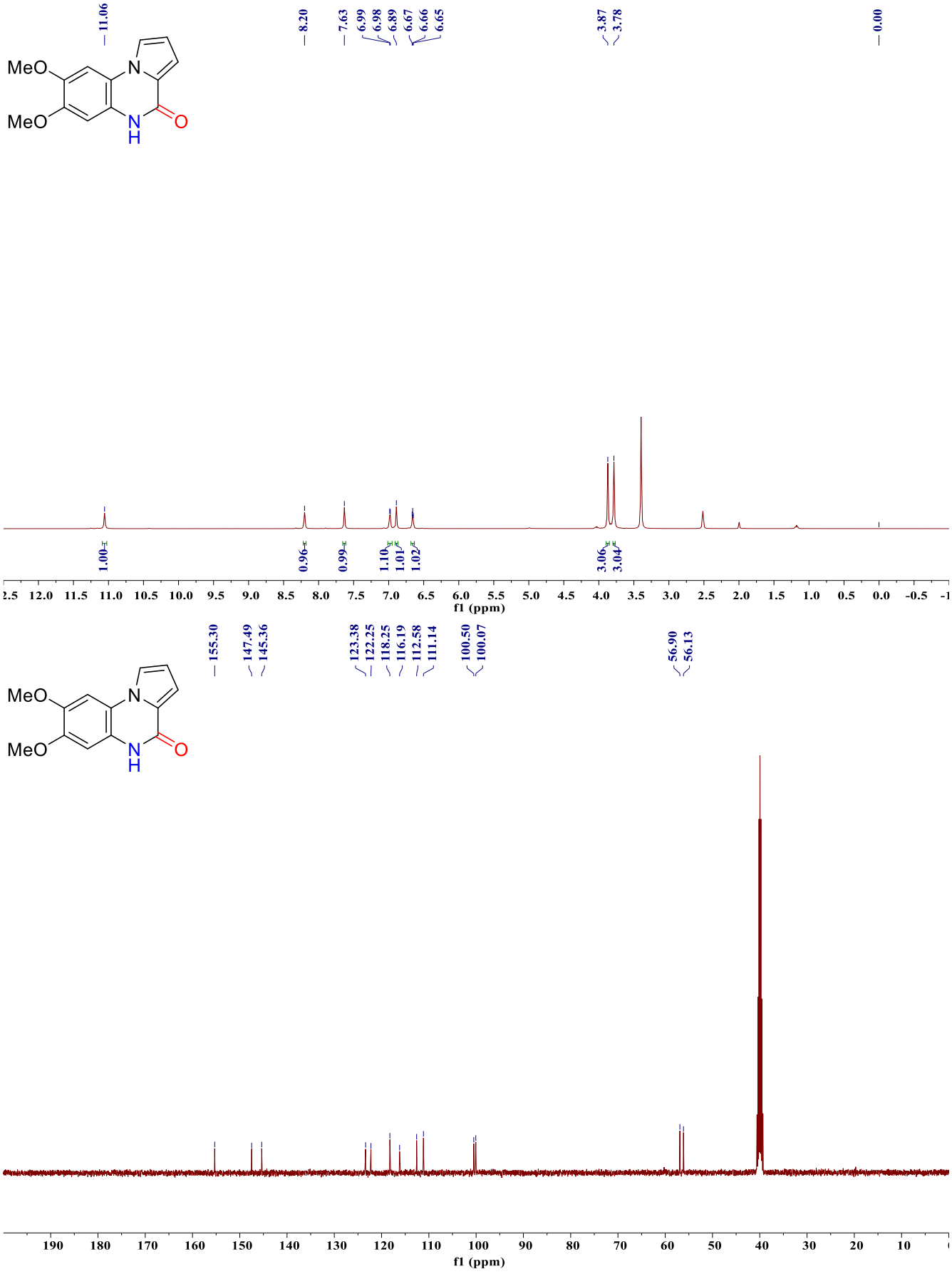
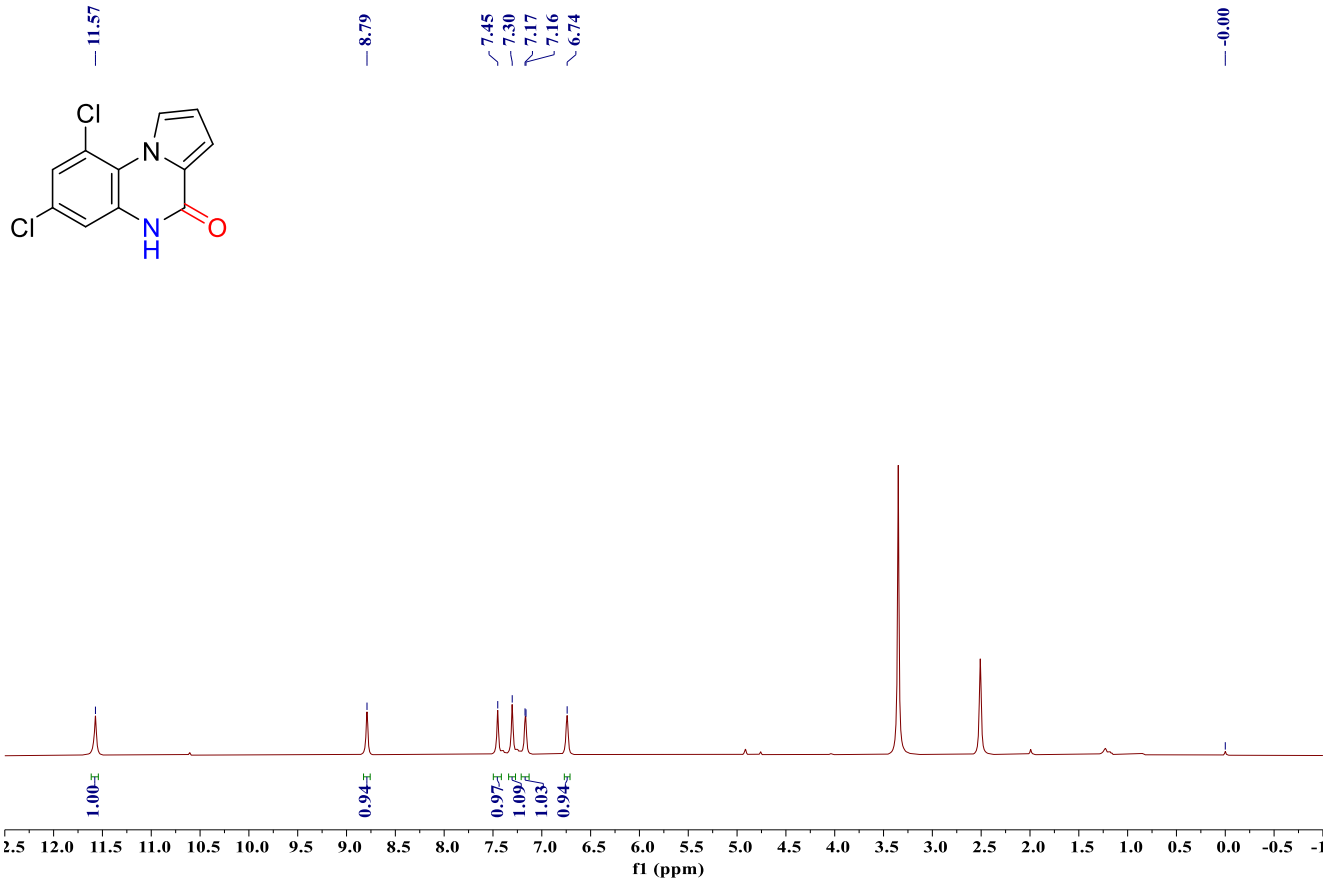
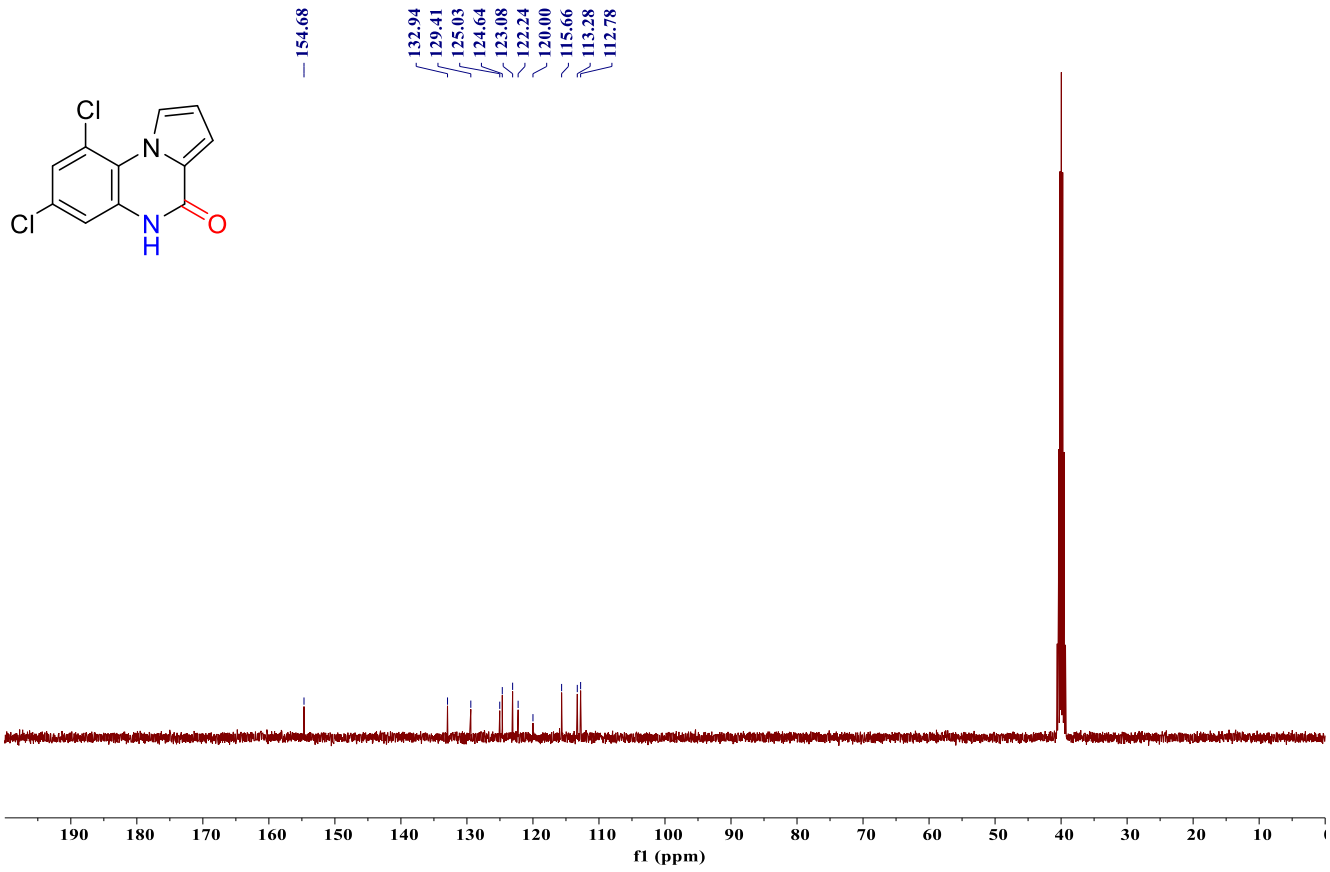
f1 (ppm)

^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ma

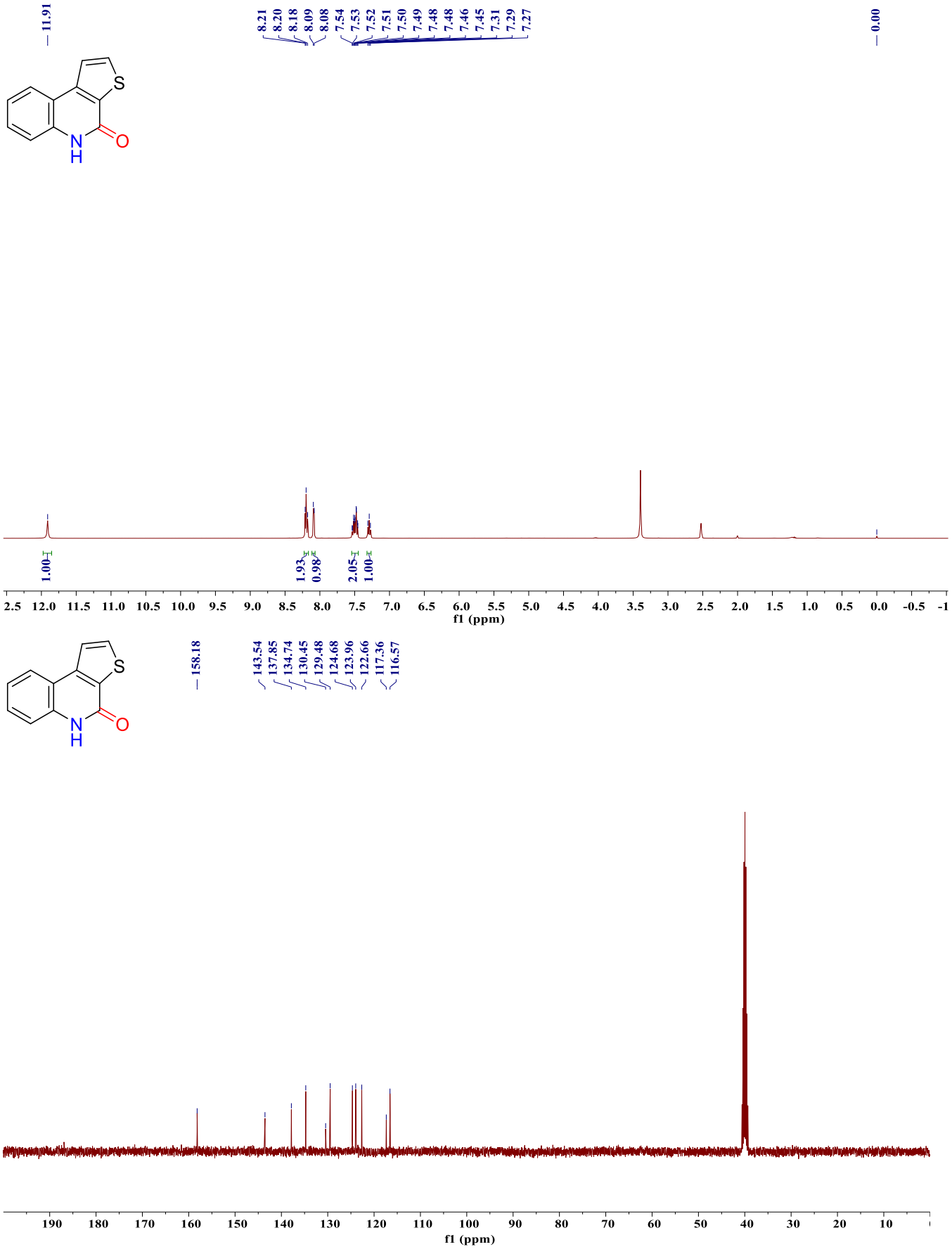


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3na

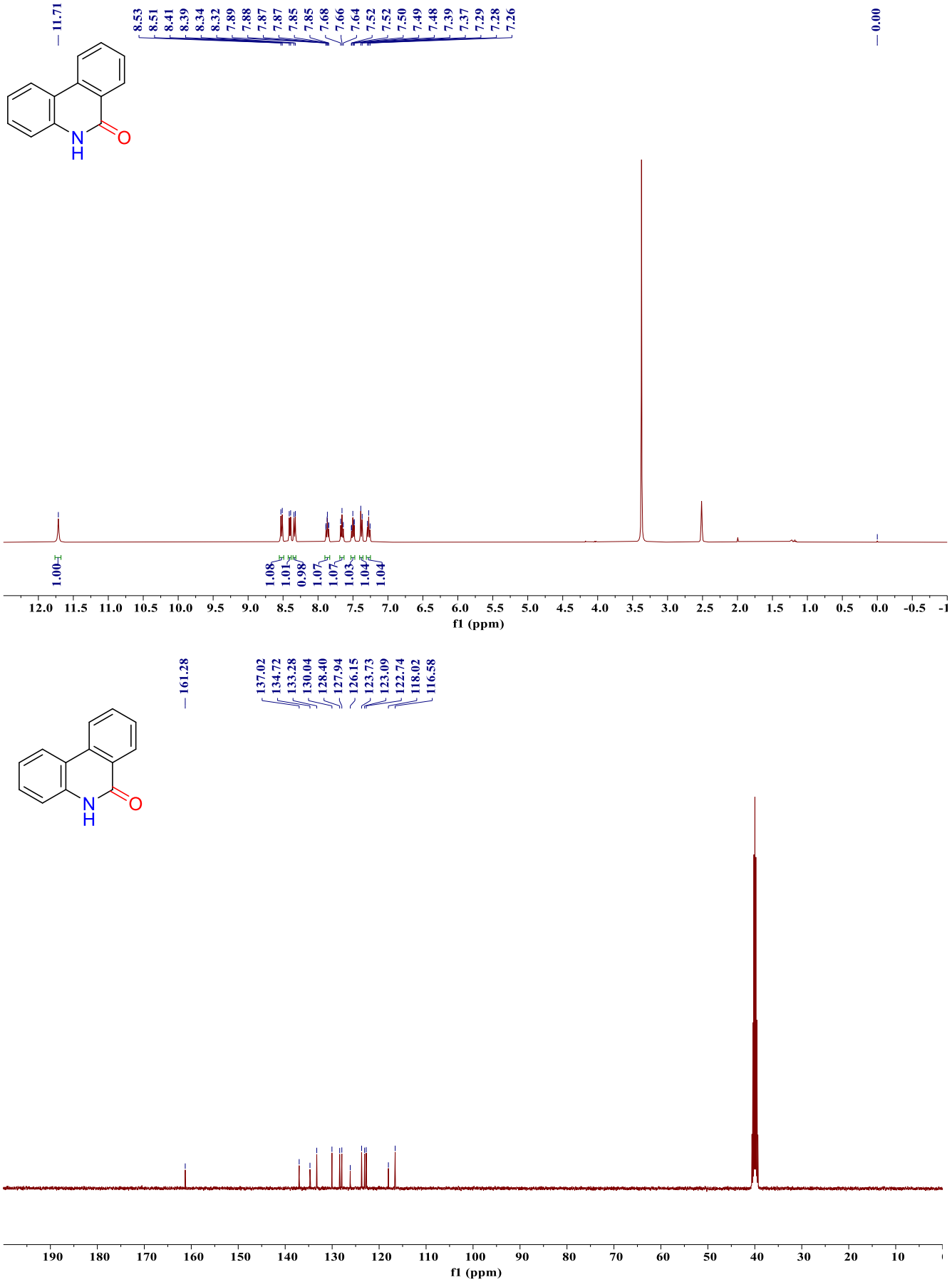




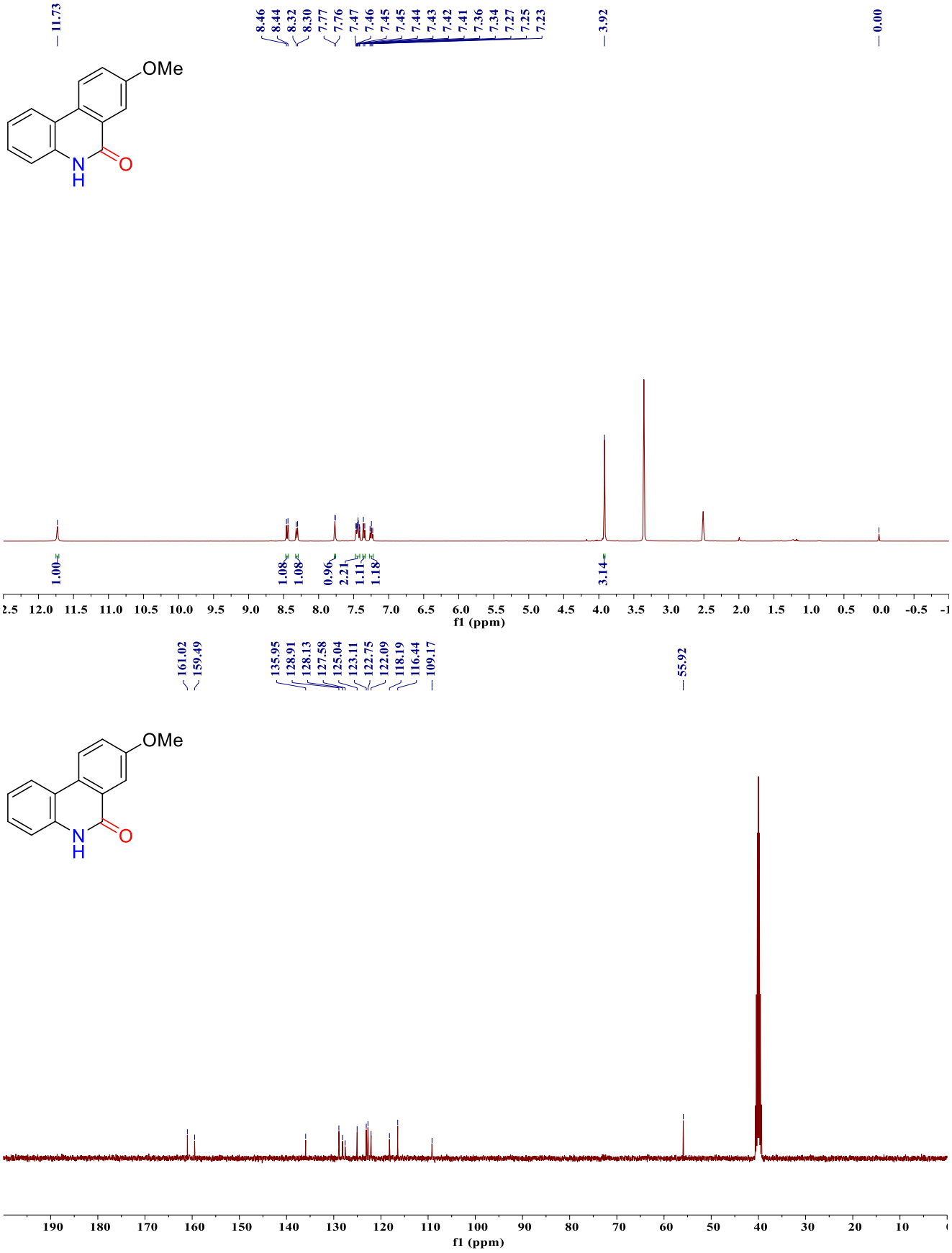
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3oa



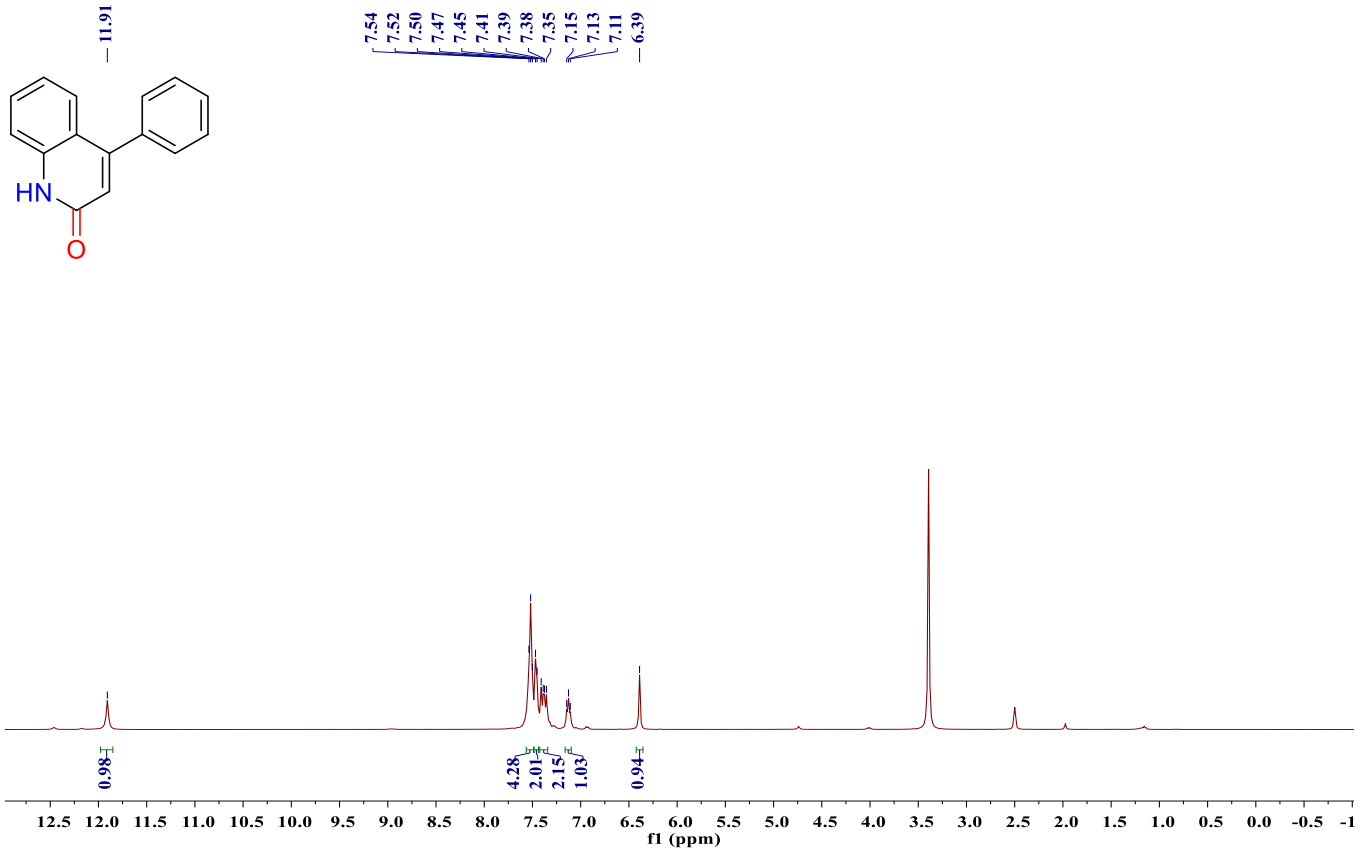
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3pa

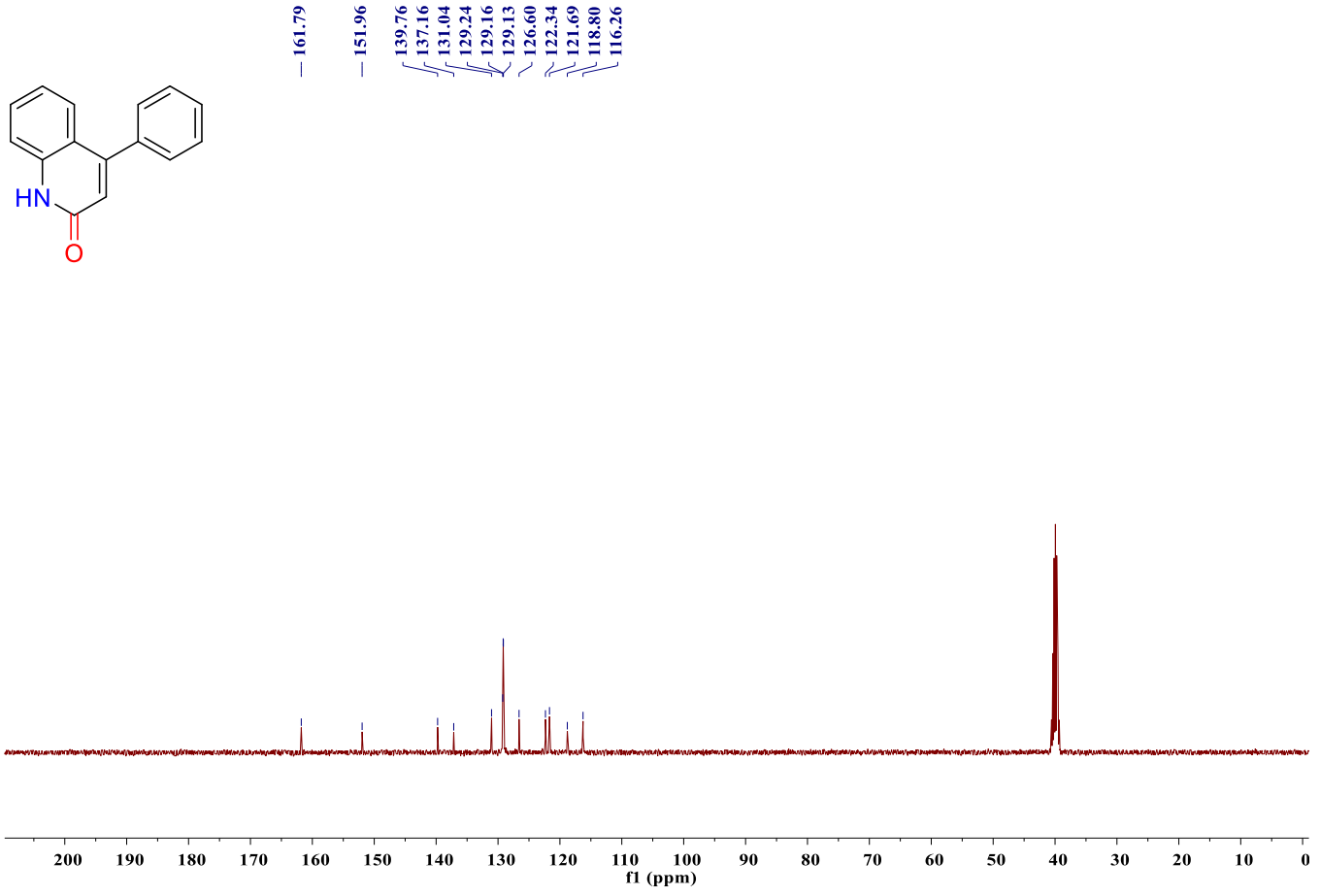


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3qa

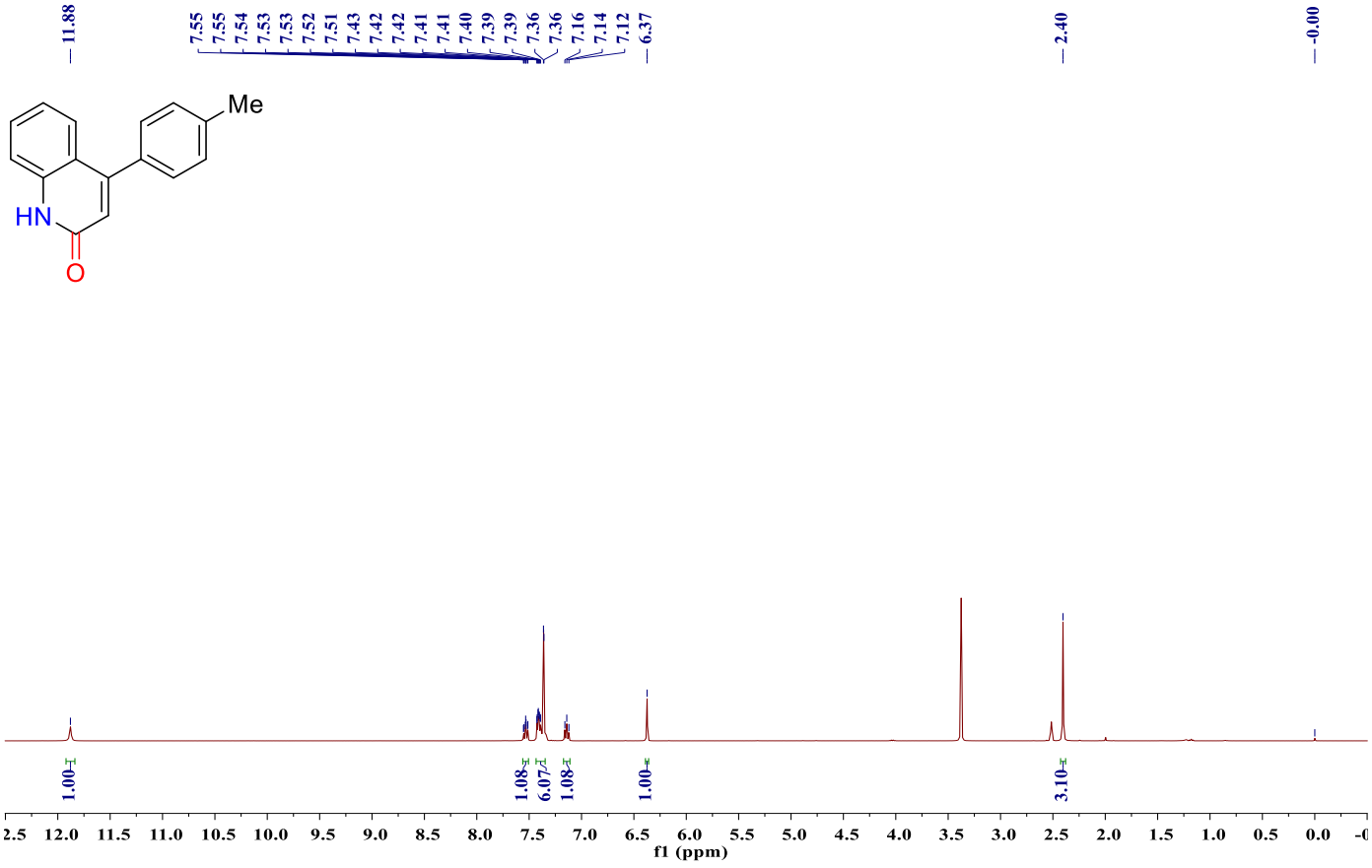


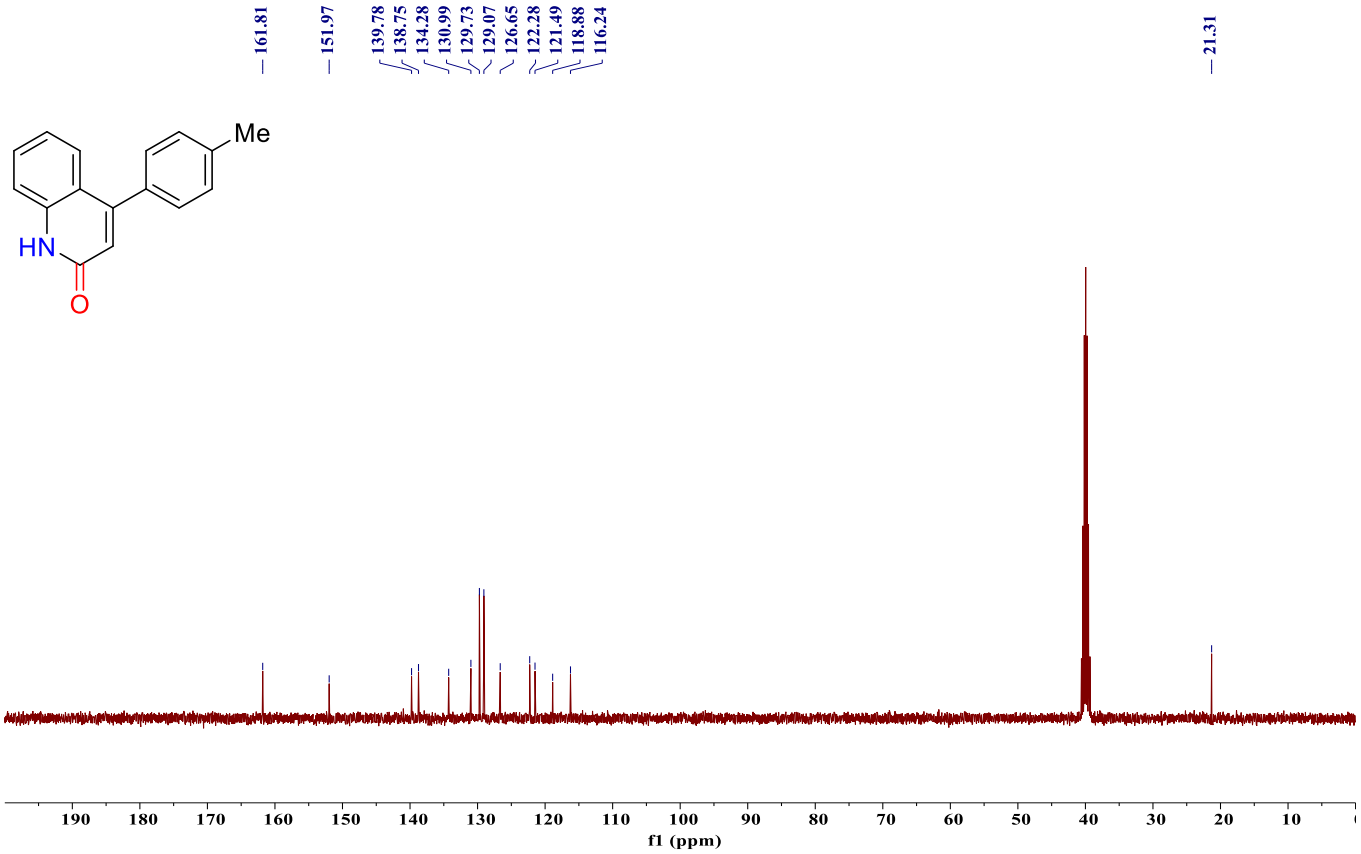
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ra



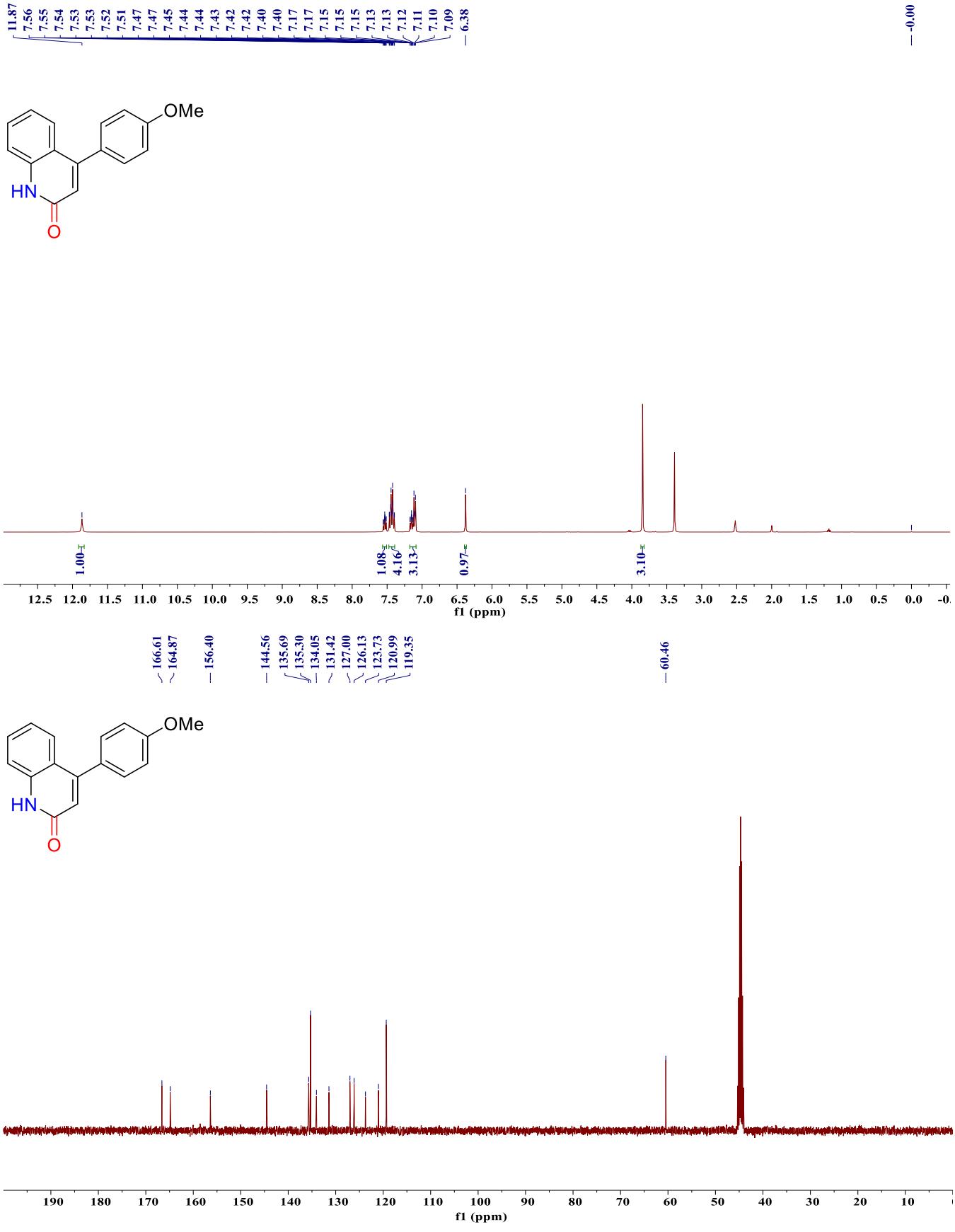


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3sa

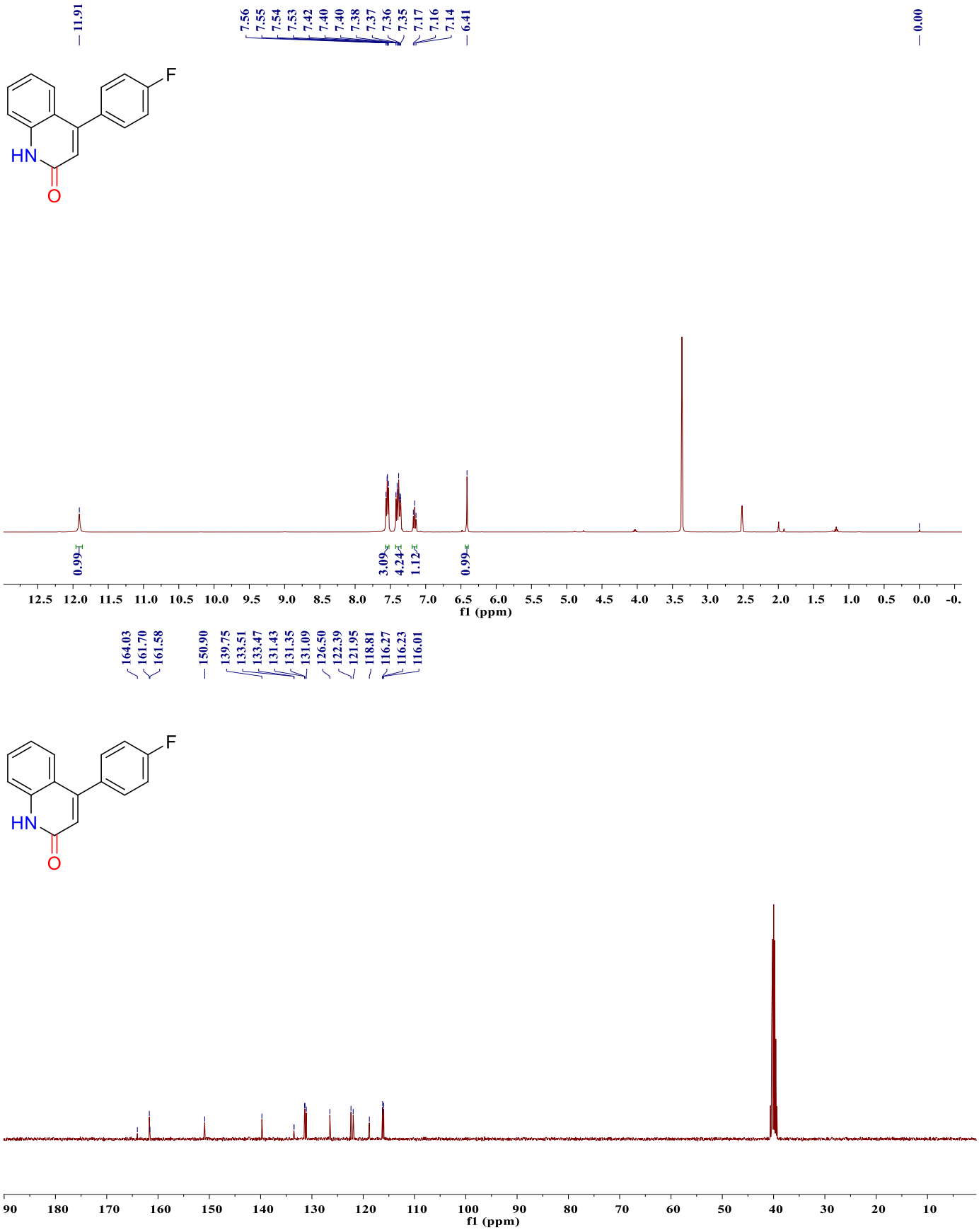


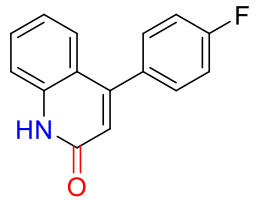


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ta



^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (376 MHz, DMSO) spectra of 3ua




F
HN
O

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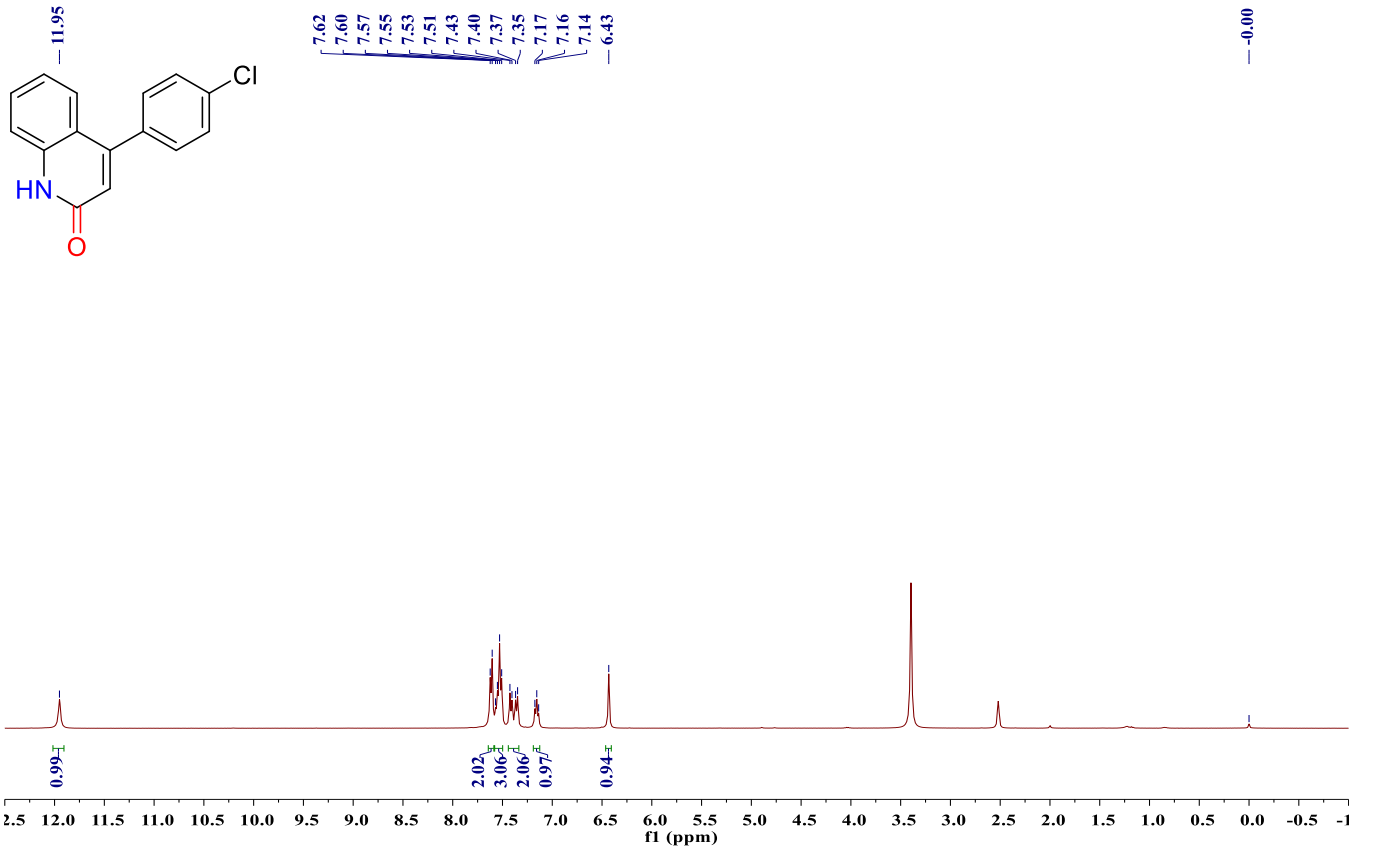
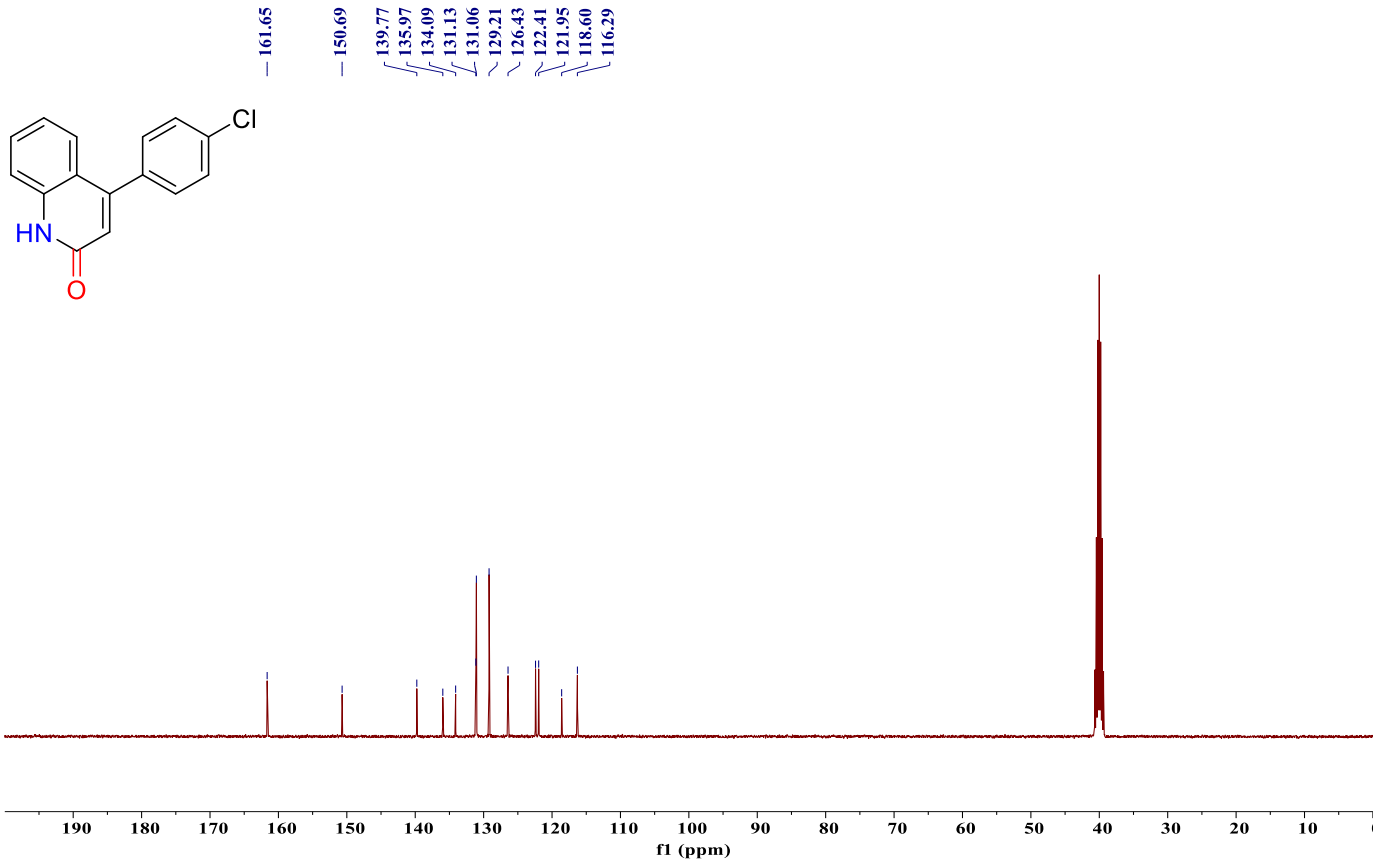
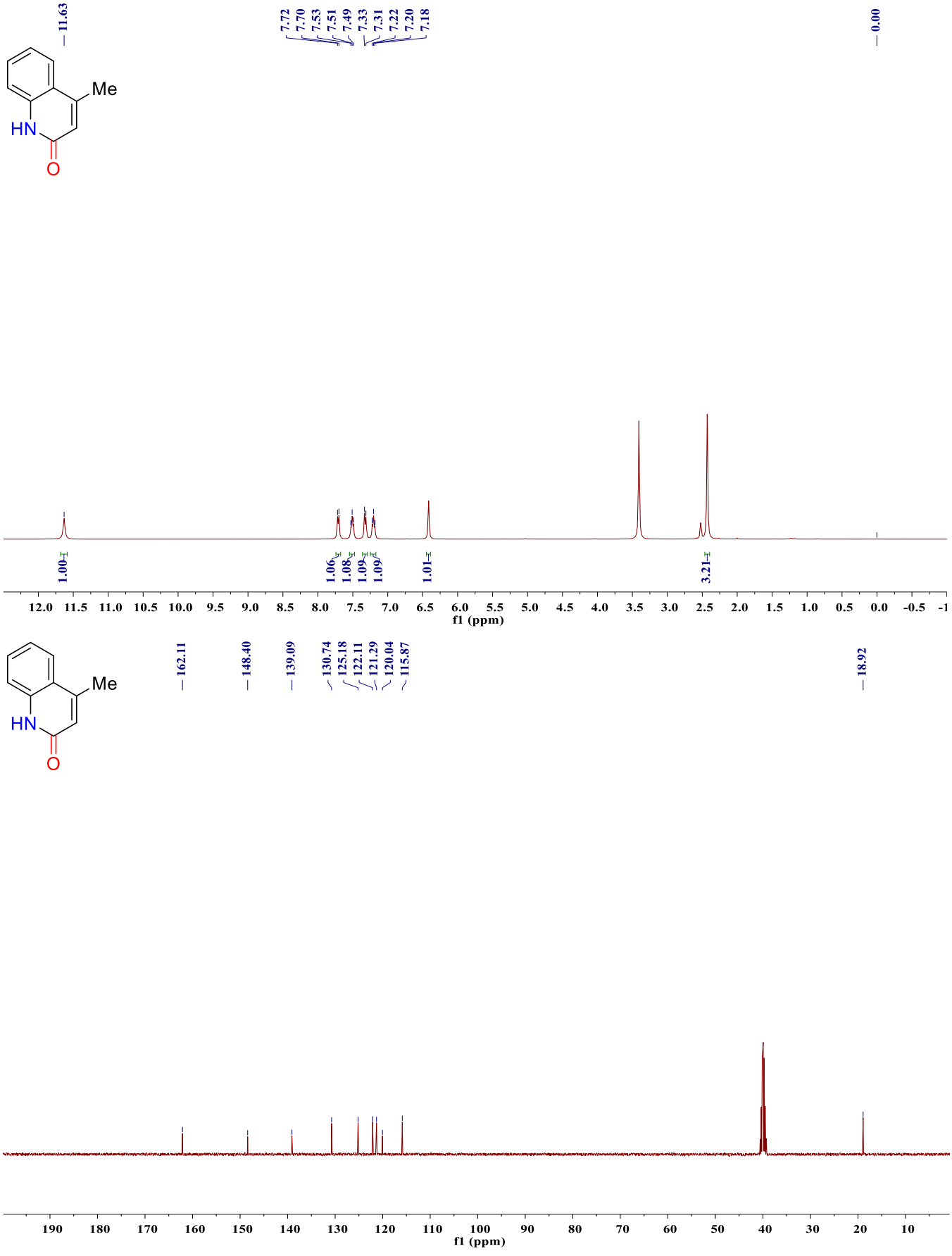
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3va

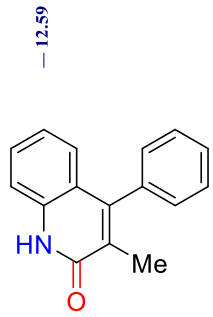


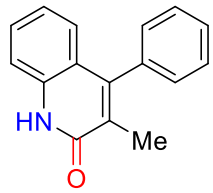


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3wa

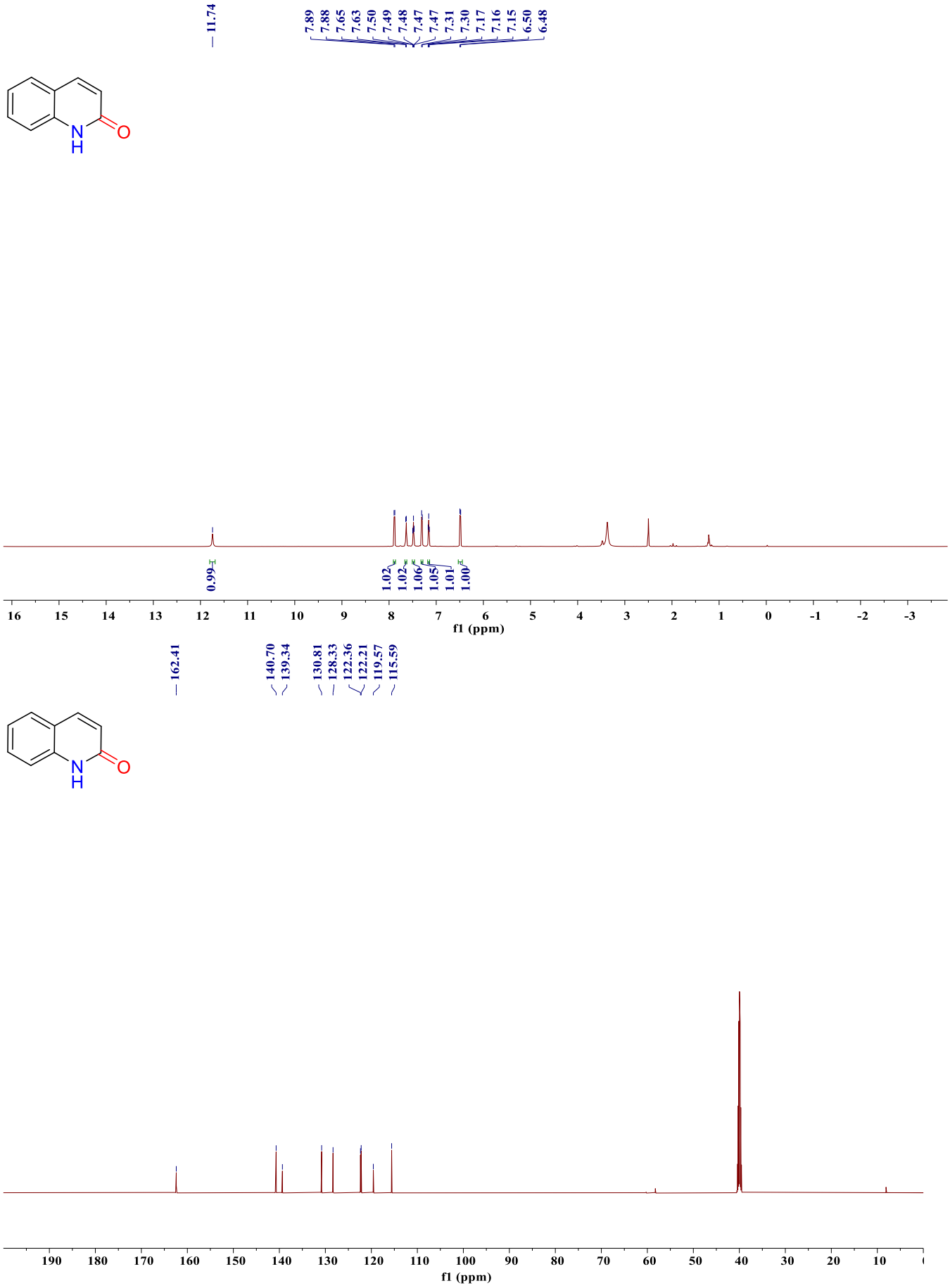


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 3xa

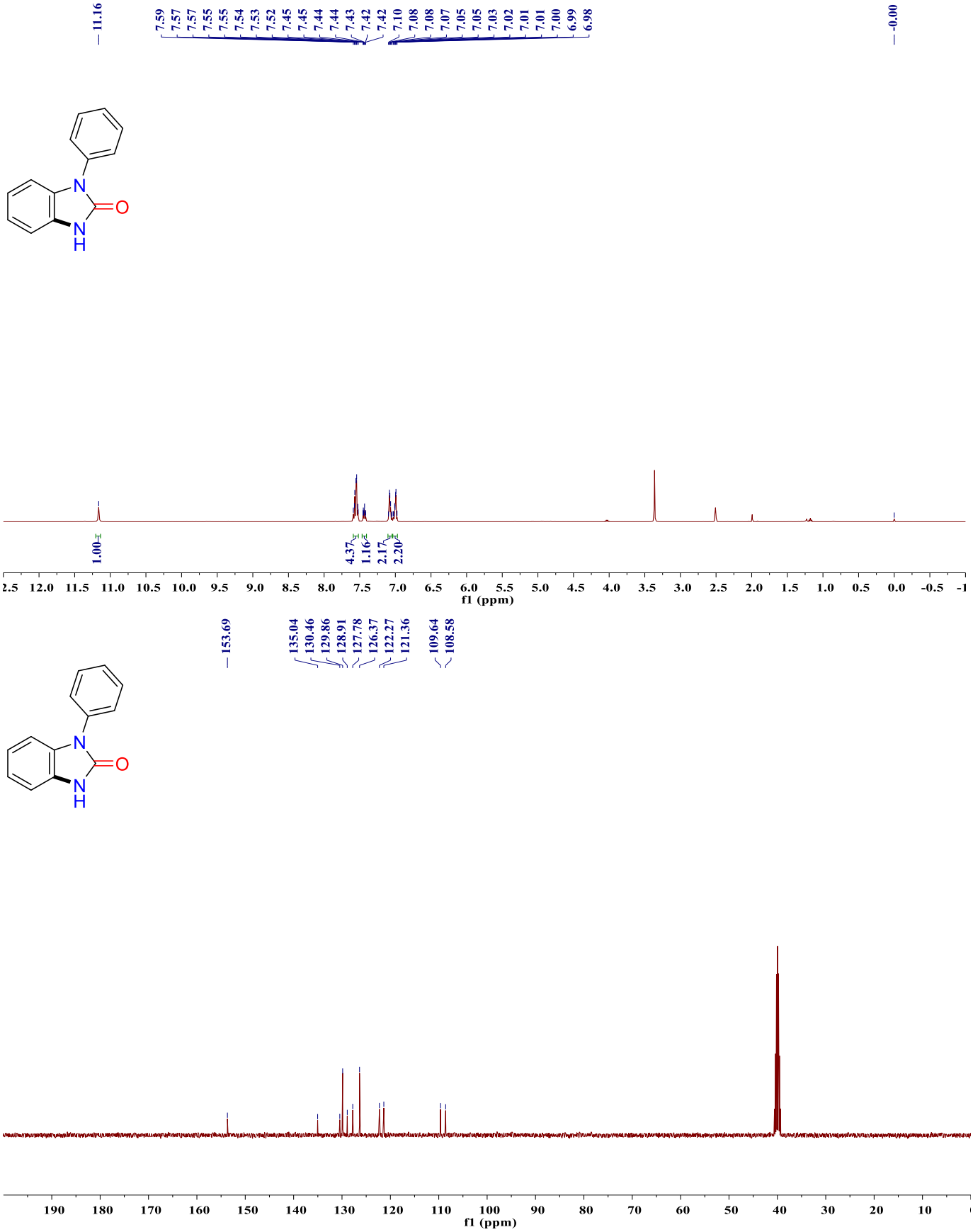




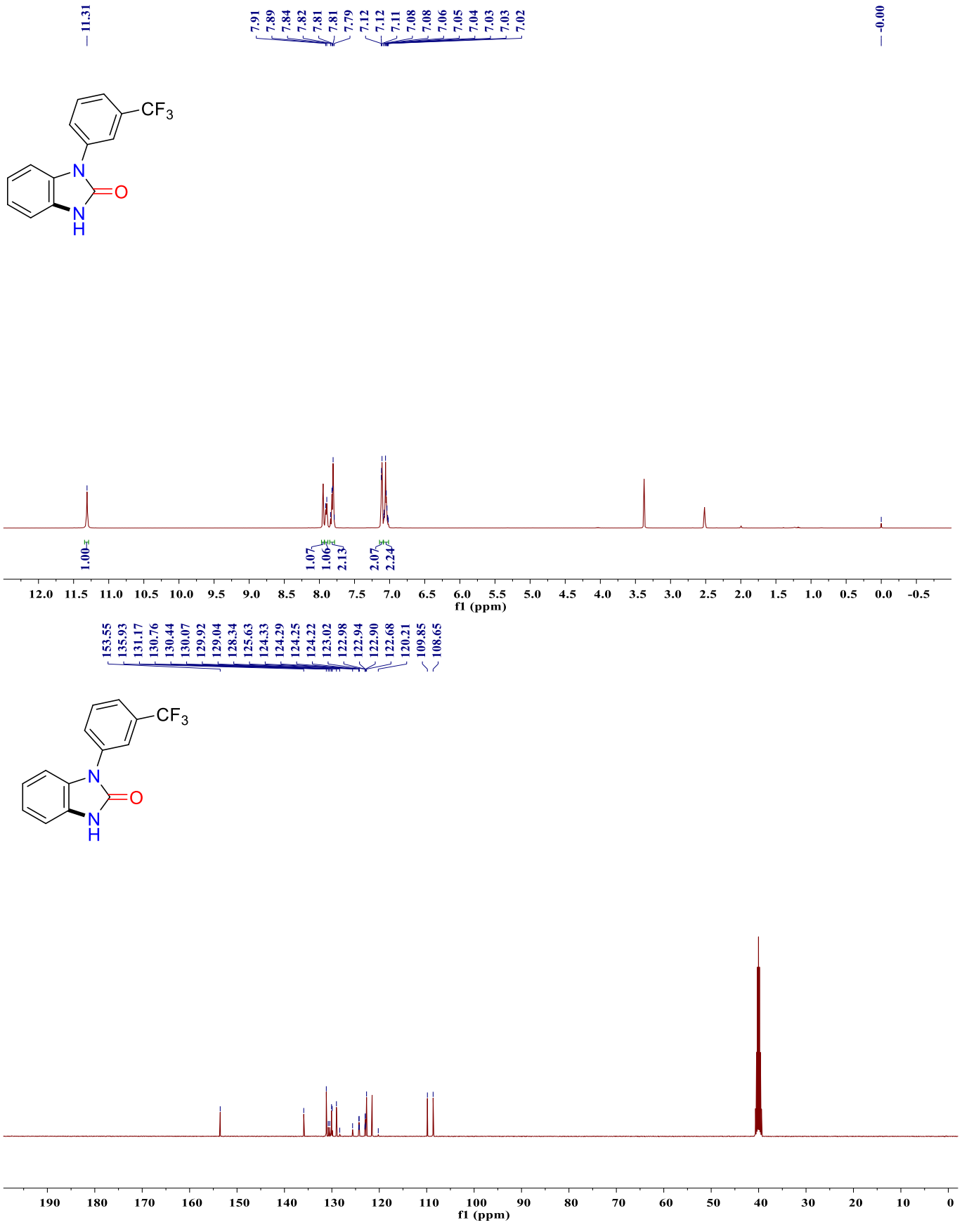
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 3ya

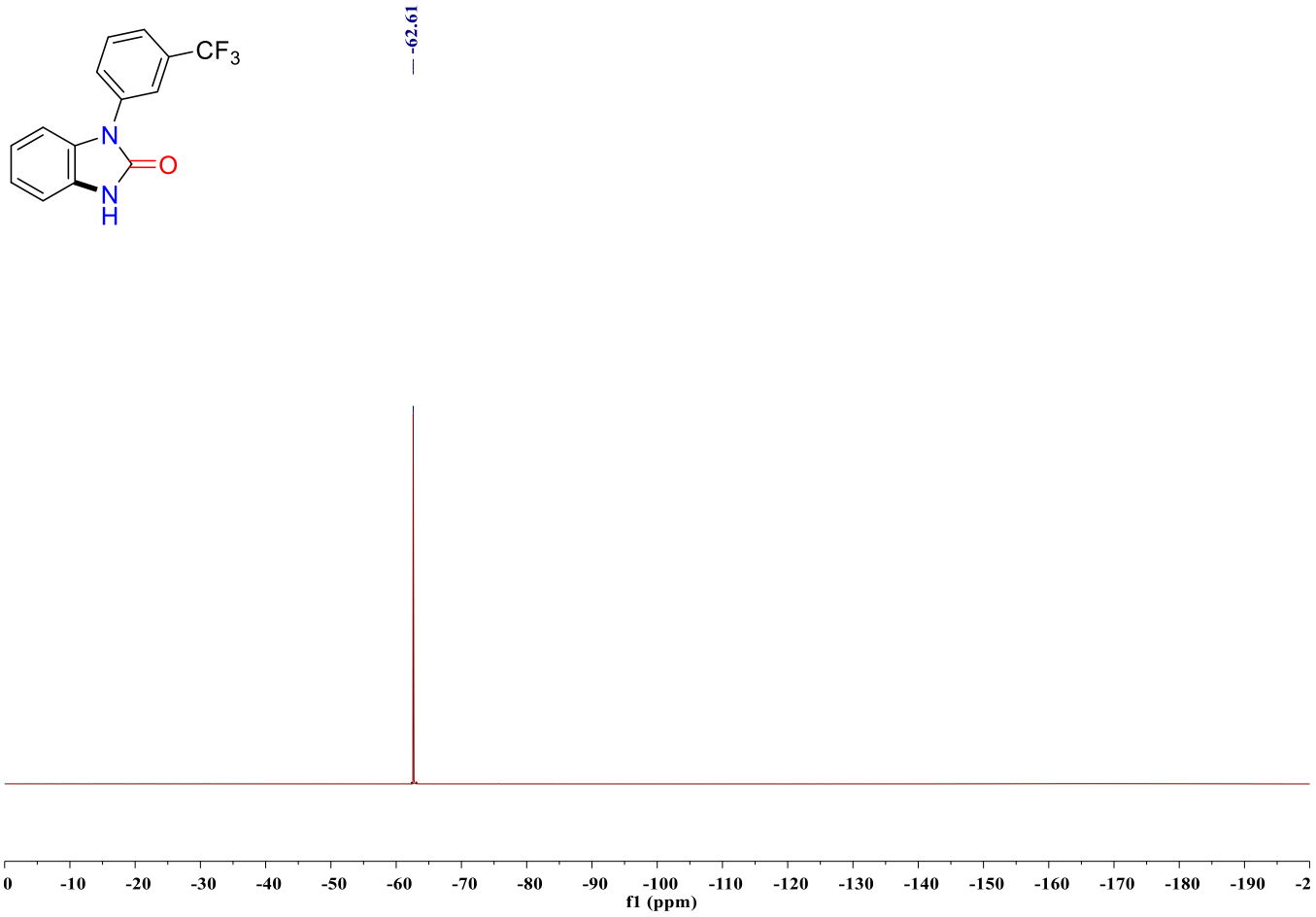


^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 5aa



^{1}H NMR (400 MHz, DMSO-d_6), ^{13}C NMR (100 MHz, DMSO) and ^{19}F NMR (376 MHz, DMSO) spectra of 5ba




CF3
N
O
N
H
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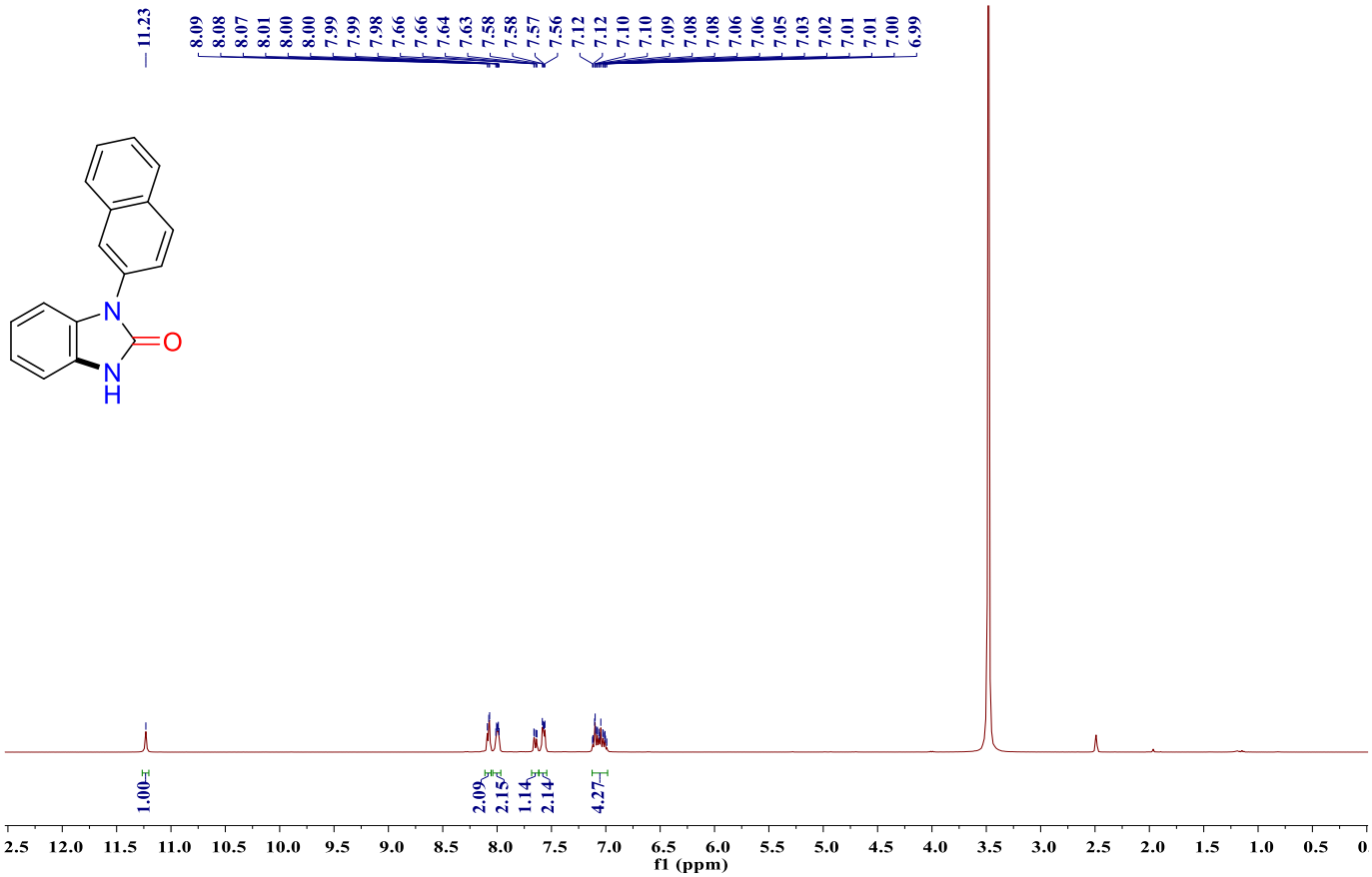
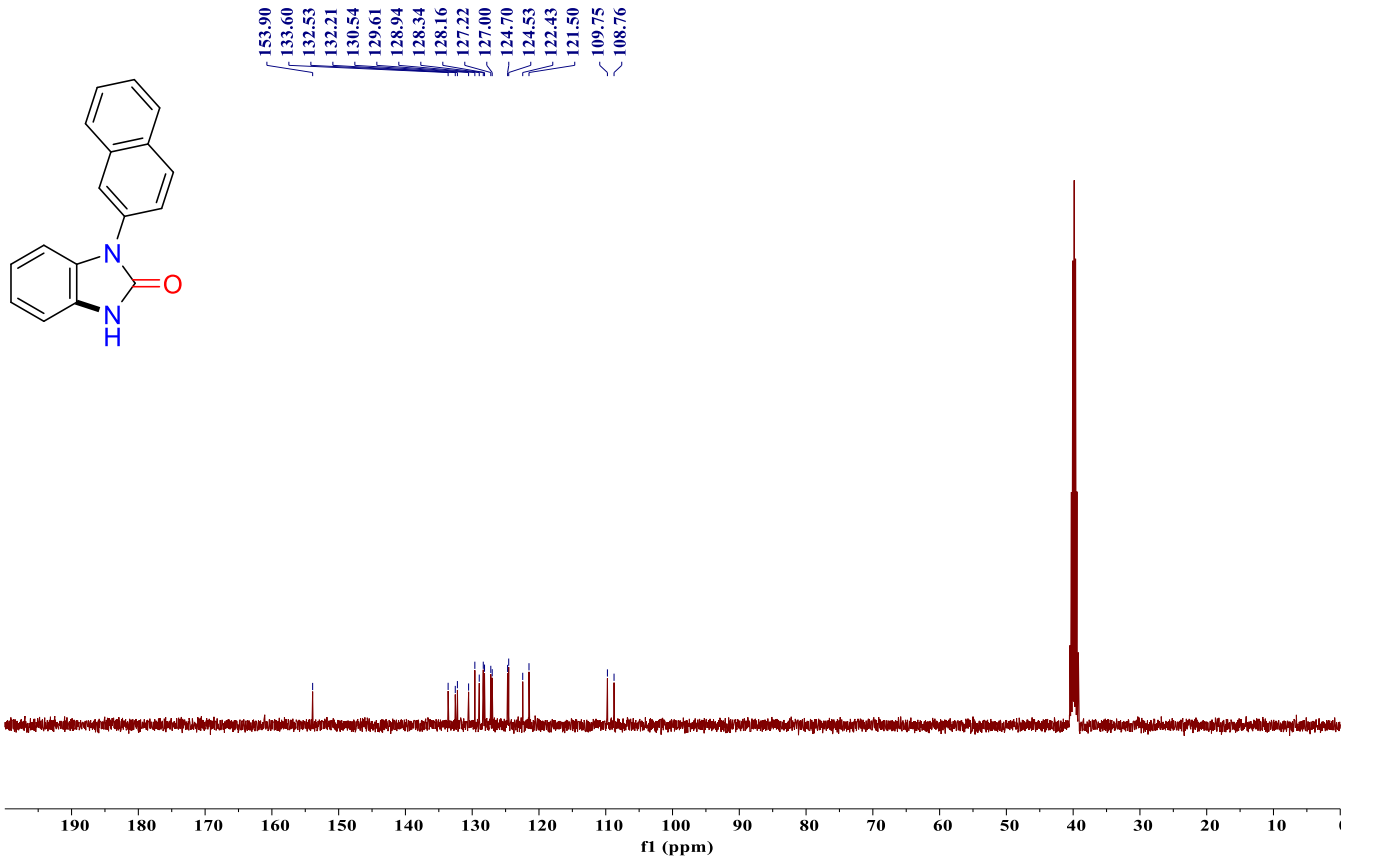
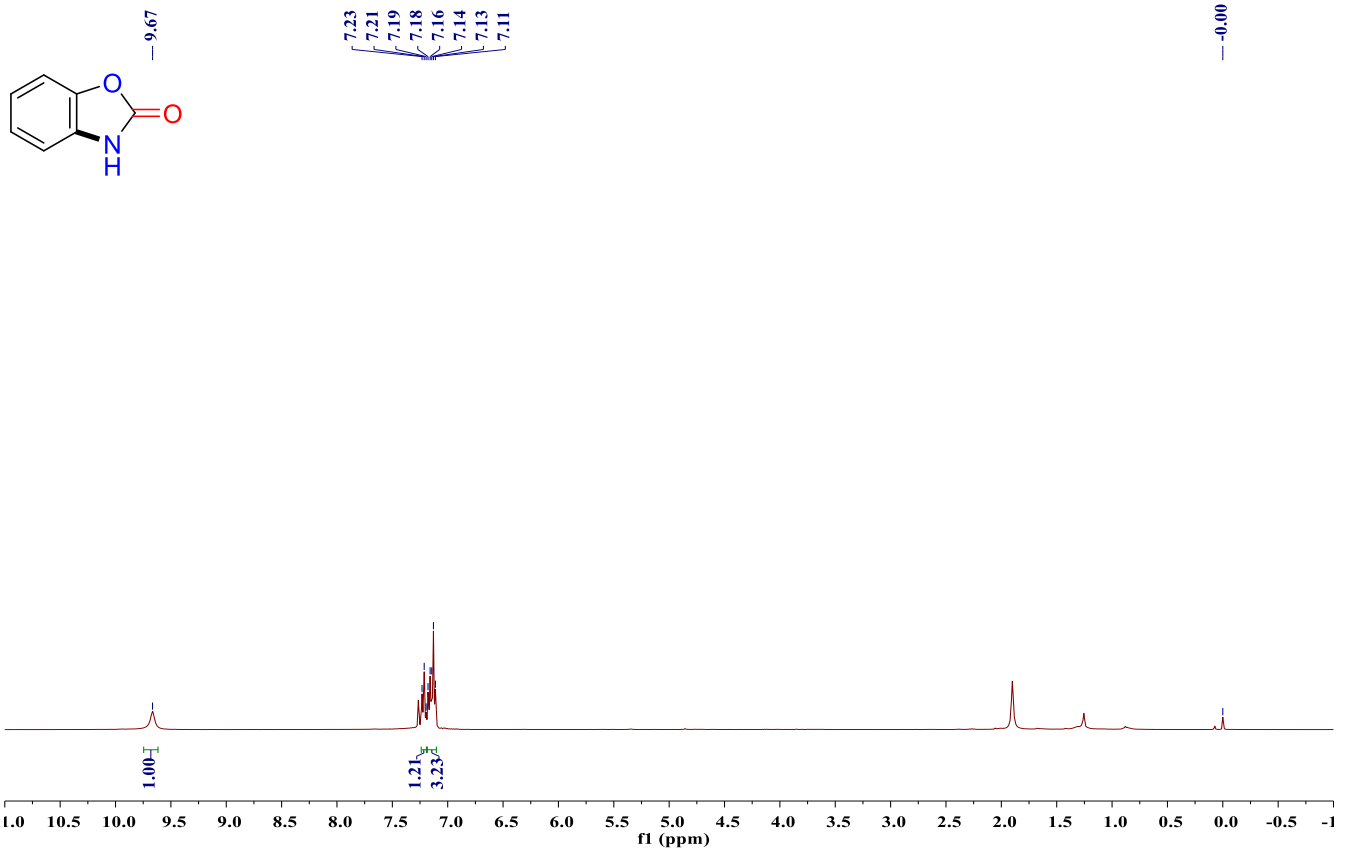
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-2
f1 (ppm)

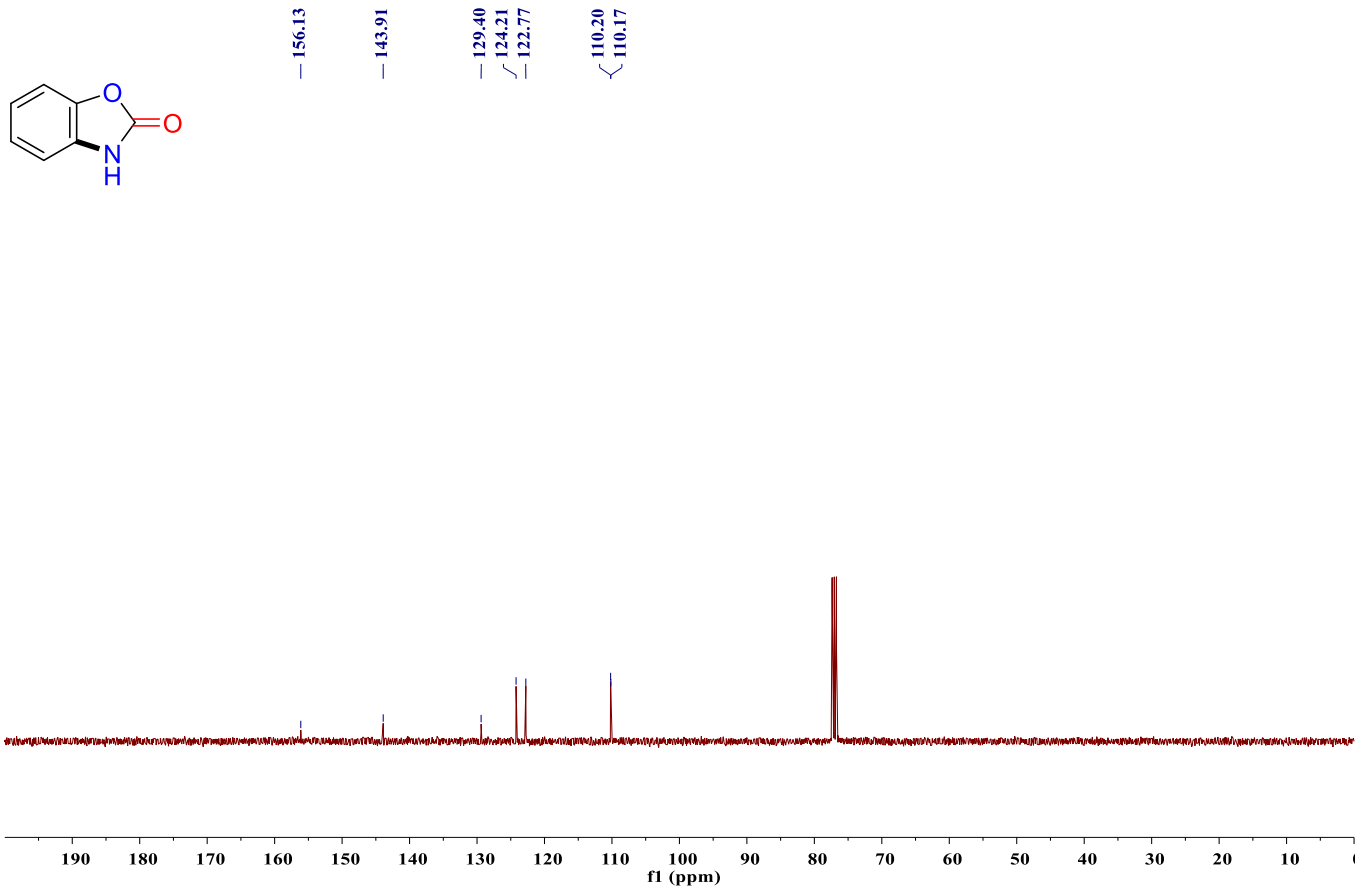
^{1}H NMR (400 MHz, DMSO-d_6) and ^{13}C NMR (100 MHz, DMSO) spectra of product 5ca



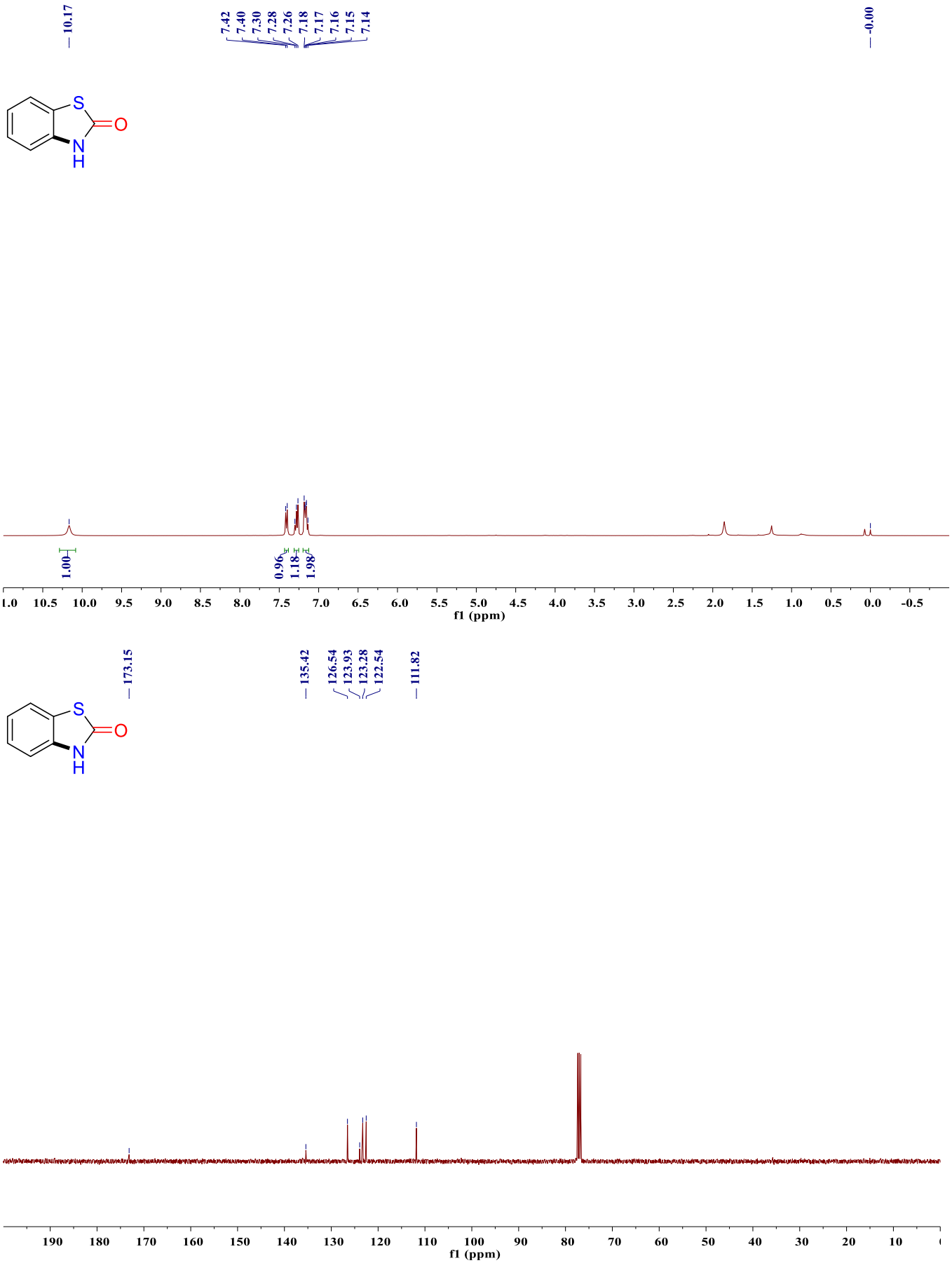


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5da

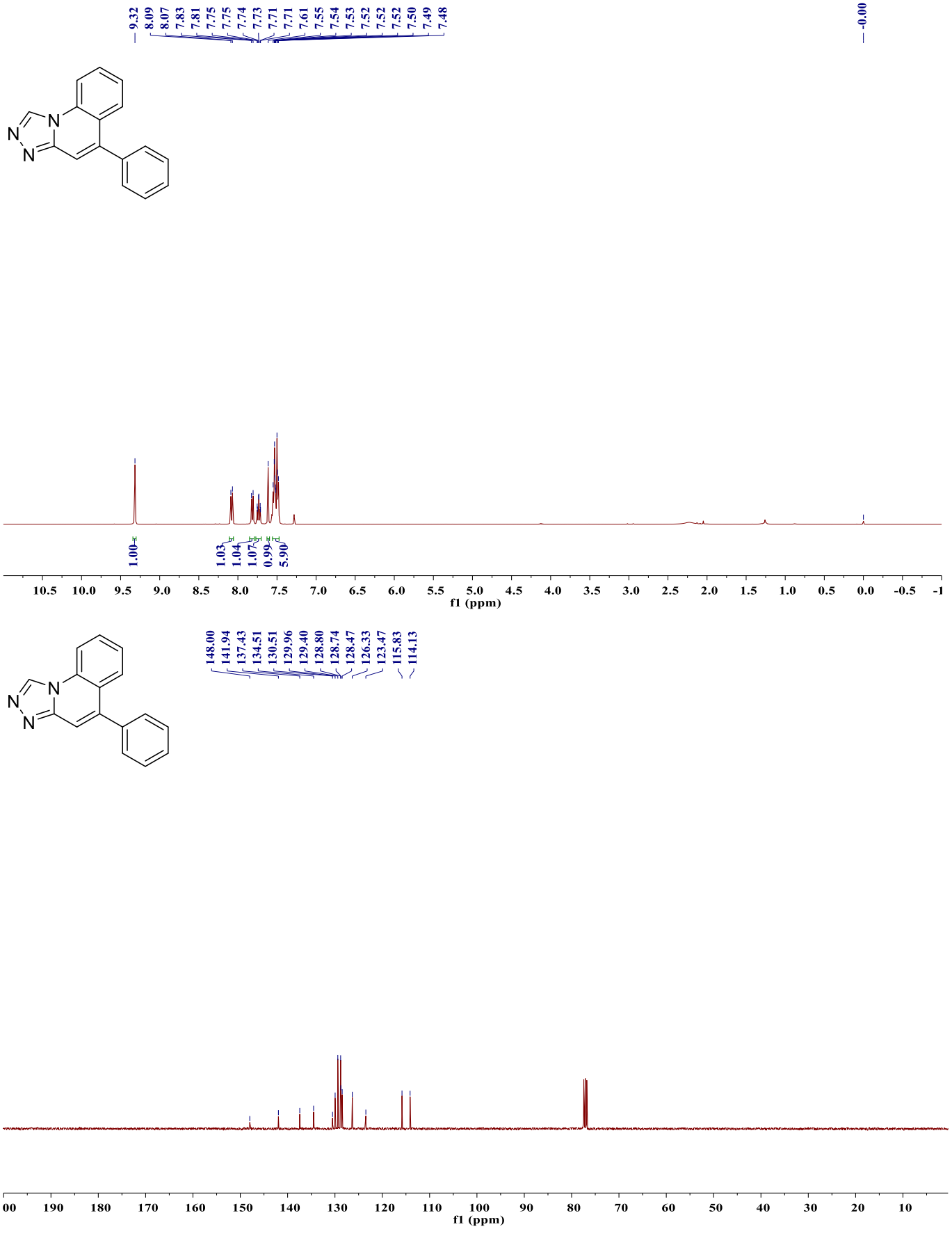




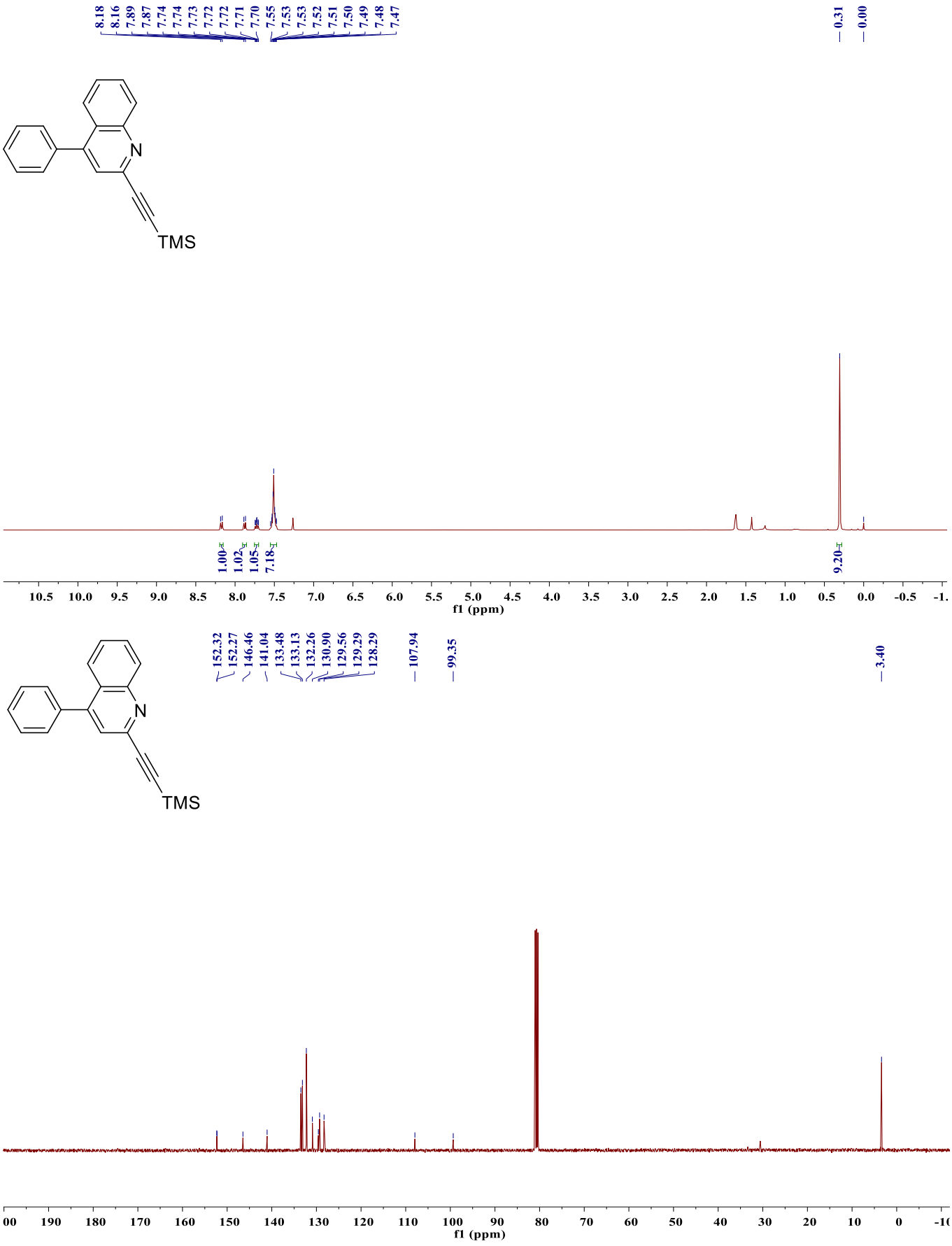
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5ea



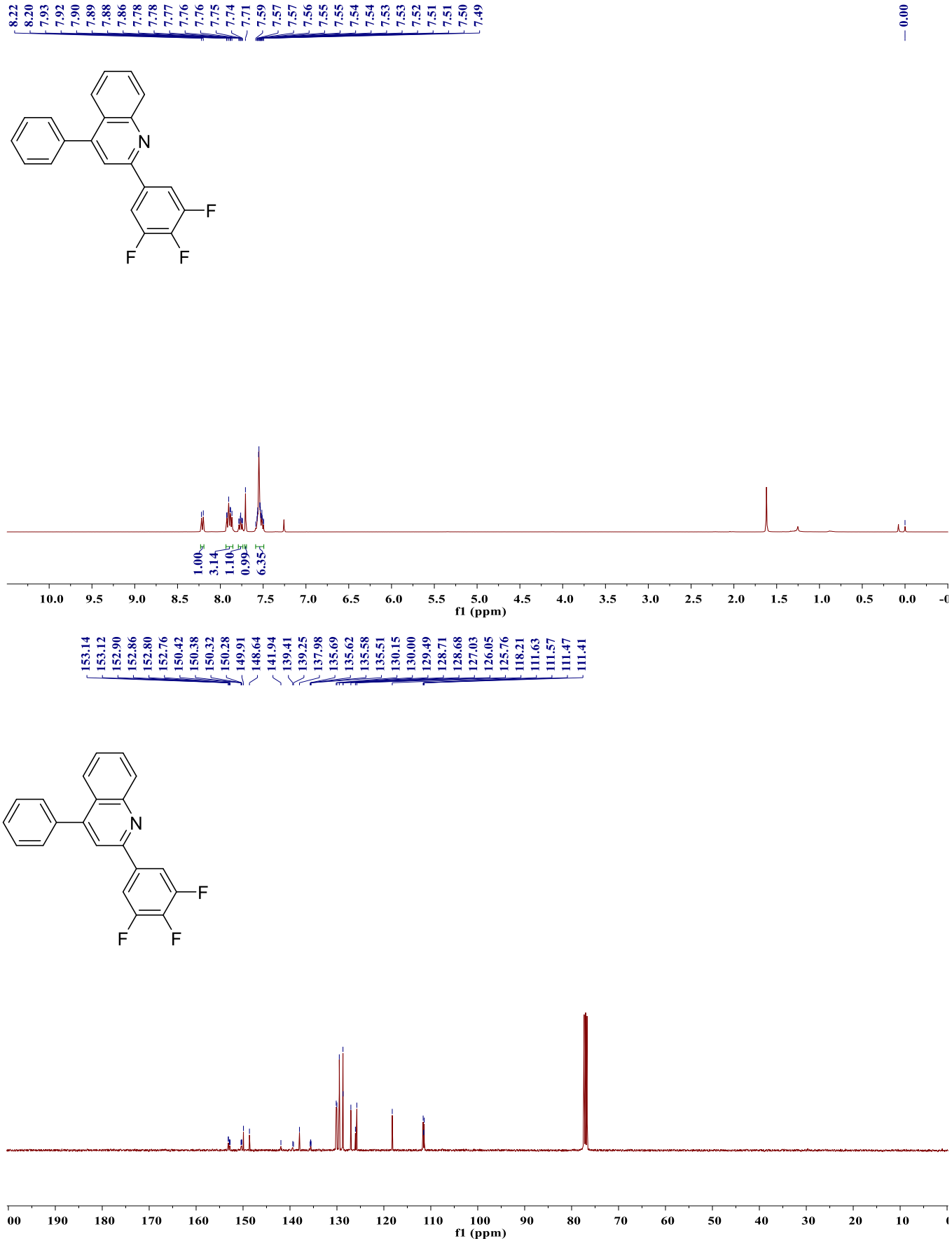
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 9



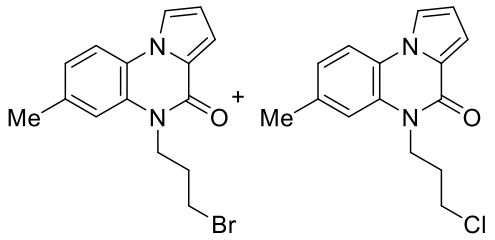
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 11



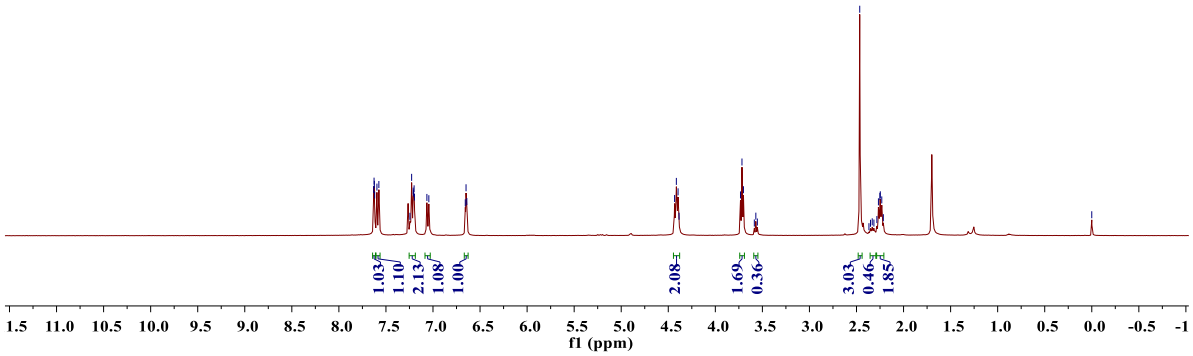
^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 12

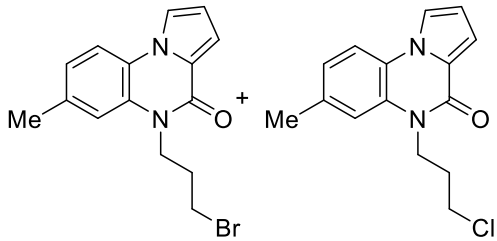


^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 13+13'

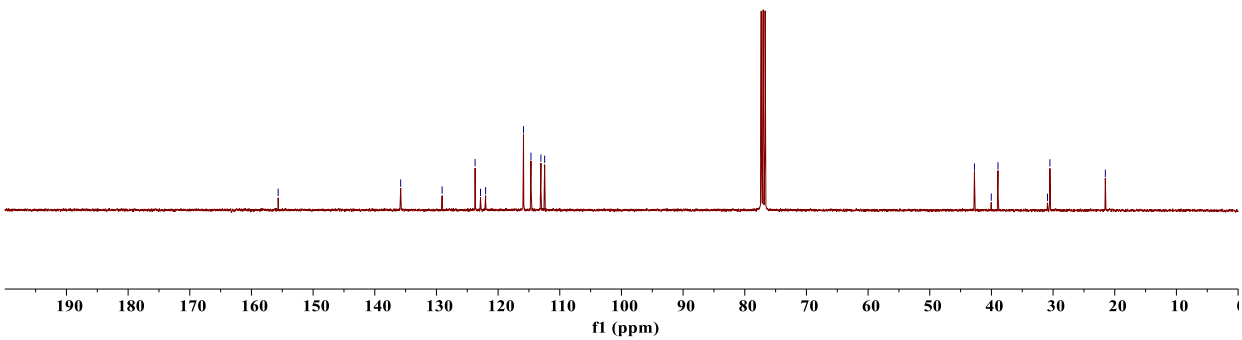


13+13', 73% (4:1)

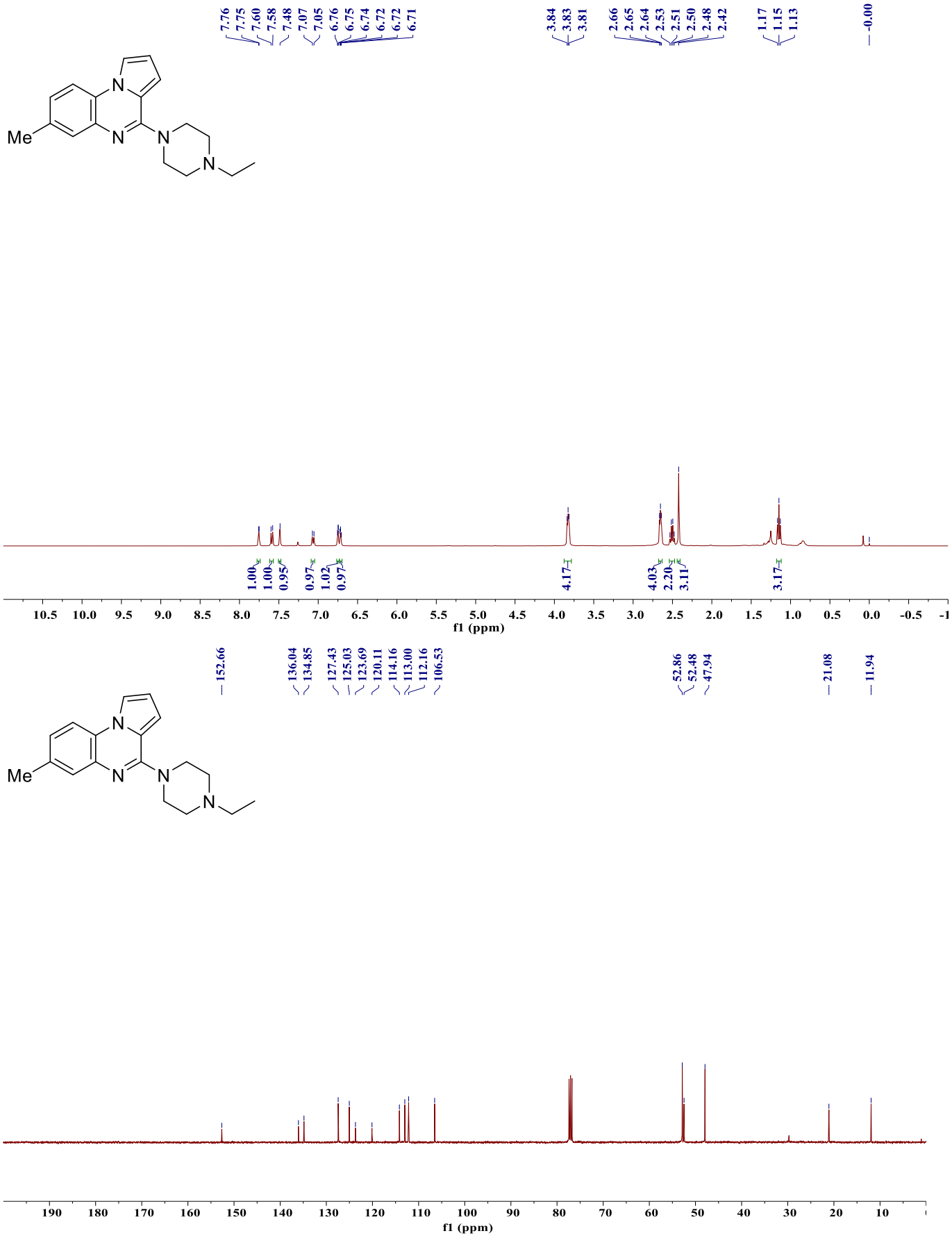




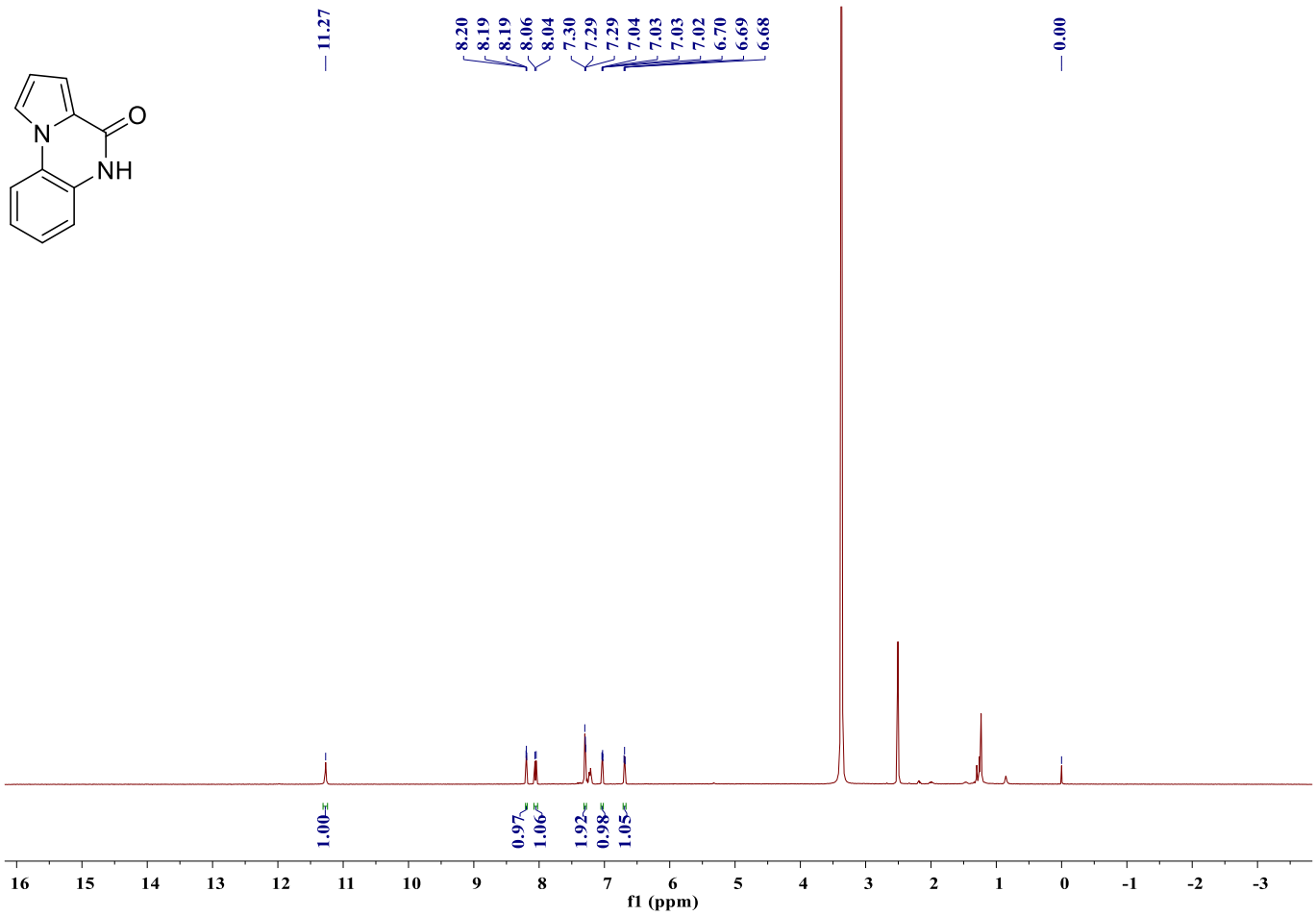
13+13', 73% (4:1)



^{1}H NMR (400 MHz, $CDCl_3$) and ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 15



^{1}H NMR (400 MHz, DMSO-d_6) spectra of product 18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8.19
8.06
8.04
7.30
7.29
7.29
7.04
7.03
7.03
7.02
6.70
6.69
6.68
0.00
1.00
0.97
1.06
1.92
0.98
1.05
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
f1 (ppm)
N
O
NH