Supplementary Information

Electron-donor-acceptor complex between two intermediates enables a N-N bond cleavage cascade process to access 2,3-difunctionalized pyridines

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General information

All materials were purchased from commercial sources (Acros, Aldrich, Adamas, Casmart) and used without any further treatment unless otherwise stated. When required, unless specifically mentioned, dry solvents were obtained directly prior to use by distillation from CaH_2 or sodium/benzophenone. All reactions were performed in oven-dried glassware under an argon atmosphere unless otherwise noted. Removal of solvents *in vacuo* was achieved using both a GreatWall® rotary evaporator (bath temperatures up to 45 °C) at a pressure of either 15 mmHg (diaphragm pump) or 0.1 mmHg (oil pump), as appropriate, and a high vacuum line at room temperature Reactions requiring anhydrous conditions were run under a dry atmosphere of nitrogen or argon. Flash column chromatography (FCC) was performed using silica gel (Qindao Haiyang, 200-300). Thin layer chromatography (TLC) was performed using aluminium backed $60F_{254}$ silica plates. Visualization was achieved by UV fluorescence or a basic $KMnO_4$ solution and heat. ^1H nuclear magnetic resonance (^1H NMR) spectra were recorded on a Bruker Avance 400 MHz or 600 MHz spectrometer. ^{13}C NMR spectra were recorded at 101 MHz or 151 MHz as stated. ^1H chemical shifts are reported in ppm relative to solvent peak, $CDCl_3$ (δ = 7.26 ppm), DMSO-d_6 (δ = 2.50 ppm), Acetone-d_6 (δ = 2.05 ppm) and Methanol-d_4 (δ = 3.31 ppm). ^{13}C chemical shifts are reported in ppm using $CDCl_3$ (δ = 77.16 ppm), DMSO-d_6 (δ = 39.52 ppm), Acetone-*d6* (δ = 29.84, 206.26 ppm) and Methanol-d_4 (δ = 49.00 ppm). The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. High-resolution mass spectra (HRMS) were recorded on BioTOFQ. GC-MS analyses were performed on 7000C Triple Quadrupole GC–MS system (Agilent Technologies, Palo Alto, CA, USA).

Figure S1. Reaction set-up for irradiation with 36 W Fluorescent Lamp.

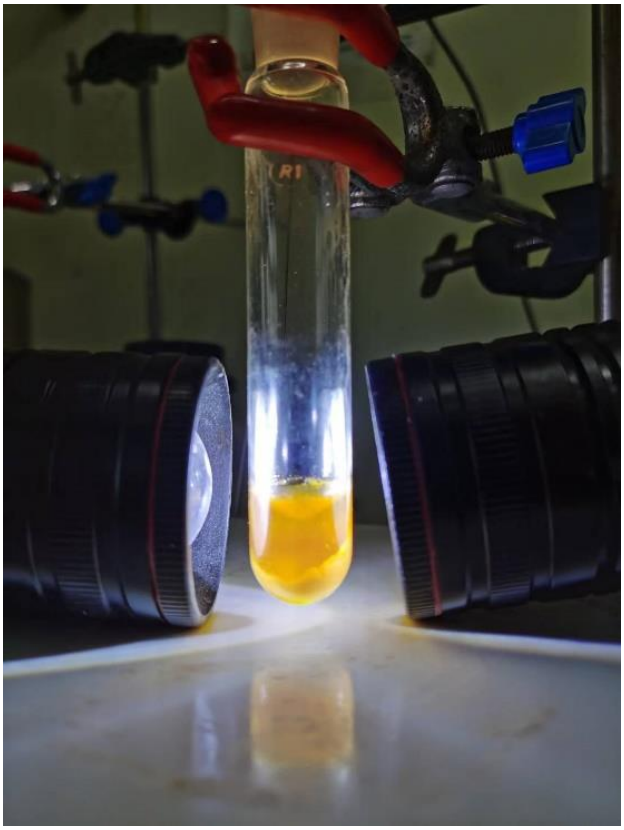
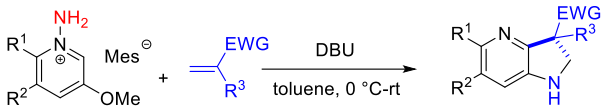


Figure S2. Reaction set-up for irradiation with white LEDs

Figure S3. Reaction set-up for irradiation with Sunlight

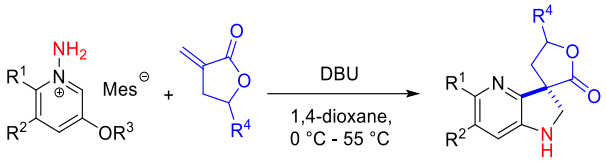
Figure S4. Reaction set-up for irradiation with UV/Green/Blue LED.

General Procedure A: for reactions between *N*-aminopyridine derivatives and α,β-unsaturated compounds



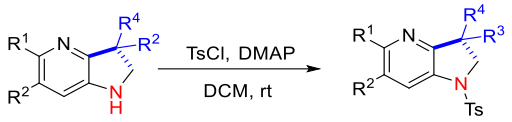
To a stirring suspension of *N*-aminopyridines (1.0 equiv.) and α, β-unsaturated compounds (1.2 equiv.) in toluene (0.05 - 0.075 M), DBU (1.5 to 2.0 equiv.) was added dropwise at 0 °C under the irradiation of visible-light. Then the reaction mixture was stirred at ambient temperature for 4 h. Upon completion as detected by TLC, the resulting mixture was poured into 10 mL saturated sodium bicarbonate solution, extracted with 5 mL ethyl acetate for 3 times, and washed with 10 mL brine, the solvent was removed by rotary evaporation and the residue was purified though FCC to obtain the product.

General Procedure B: for reactions between *N*-aminopyridine derivatives and γ-butyrolactones



To a stirring suspension of *N*-aminopyridines (1.0 equiv.) and γ-butyrolactone (1.2 equiv.) in 1,4-dioxane (0.05 - 0.075 M), DBU (1.5 to 2.0 equiv.) was added dropwise at 0 °C under the irradiation of visible-light. Then the reaction mixture was allowed to raise temperature to 55 °C and stirred for 4 h. Upon completion as detected by TLC, the resulting mixture were poured into saturated 10 mL sodium bicarbonate solution, extracted with 5 mL ethyl acetate for 3 times and washed with 10 mL brine, solvent was removed by rotary evaporation and the residue was purified though FCC to obtain the product.

General Procedure C: for reactions between 4-Azaindoline and Tosyl chloride

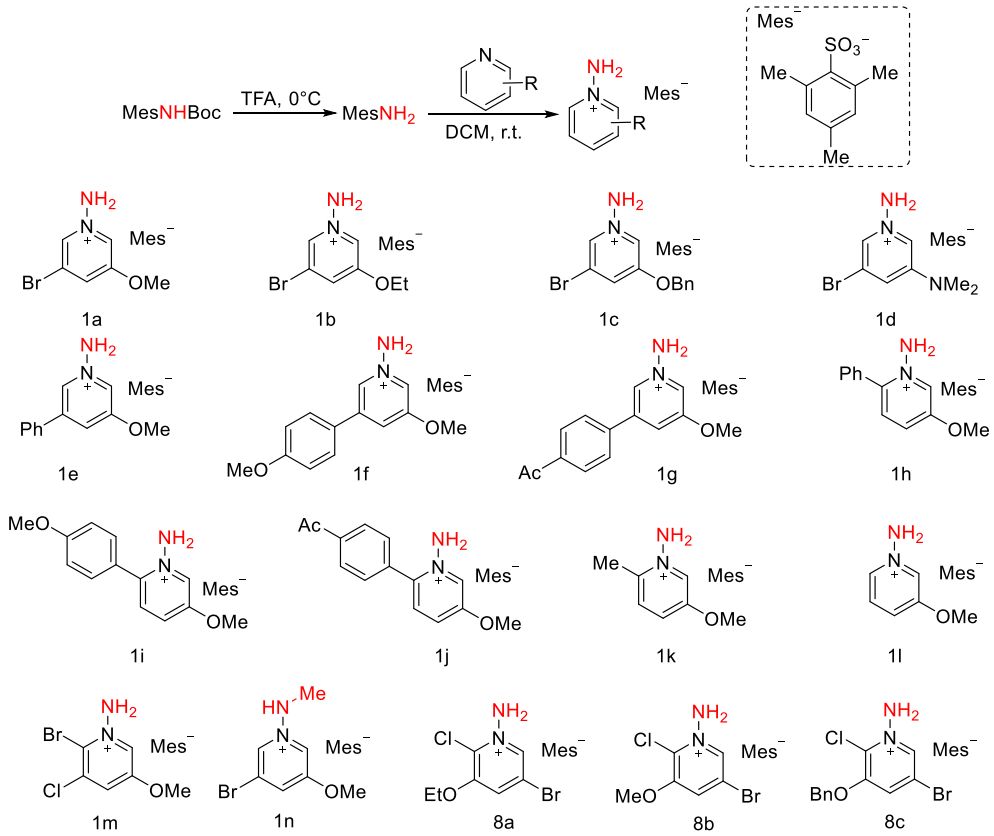


To a stirring suspension of 4-azaindoline derivatives (1.0 equiv.) in DCM (0.05 - 0.075 M) was added TsCl (1.05 equiv.) and DMAP (1.1 equiv.). Then the resulting mixture was allowed to stir at ambient temperature and monitored by TLC. Upon completion, solvent was removed by rotary evaporation and the residue was purified though FCC to obtain the products.

Due to some products are easy to decomposed, so we launched this procedure to protect free amine in the case of the 4-azaindoline products are unstable.

Substrate synthesis

Synthesis of substituted pyridinium salts (1a - 1n and 8a - 8c)



Scheme S1. Substituted pyridines involved in this study.

Preparation of *O*-Mesitylenesulfonylhydroxylamine (MSH)

MSH was prepared according to a literature procedure[1] with a slight modification.

tert-Butyl ((mesitylsulfonyl)oxy) carbamate was added to the stirring trifluoroacetic acid (TFA) (0.3 M) at 0 °C, the resulting reaction mixture was stirred at the same temperature and monitored by TLC. After completion, the mixture was poured into ice-water and filtered through Büchner funnel. The filter cake was rinsed with cold water until the pH ≈ 7, the obtained white solid was then redissolved into CH_2Cl_2 and dried over Na_2SO_4, filtered through celite®, the filter cake was rinsed with CH_2Cl_2 to make a solution of $MesONH_2$ (**MSH**) in CH_2Cl_2 (around 0.13 M).

Preparation of pyridinium salts

Pyridine (1.0 equiv.) was added to the **MSH** (1.0- 1.20 equiv.) (*vide infra*) solution (around 0.13 M in CH_2Cl_2) at 0 °C and stirred for 10 minutes. Then the resulting reaction mixture was allowed to be stirred at ambient temperature and monitored by TLC. Upon completion, solvent was removed by rotary evaporation and the residue was rinsed with hexane. Solid was collected though filtration and dried over

vacuum to afford the desired product which was used for the next step without further purification. Pyridinium salts **1a** - **1c**, **1f** and **8a** were prepared according to literatures procedure and the spectroscopic properties were consistent with the data available in the literature.[2] Pyridinium slats **1h** - **1m, 8b and 8c** were directly used in the reaction without collecting the spectroscopic data due to the poor solubility.

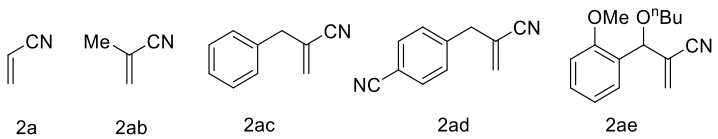
1d: ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.12 (d, J = 1.5 Hz, 1H), 8.09 (t, J = 2.0 Hz, 1H), 7.69 (s, 1H), 6.88 (s, 2H), 3.11 (s, 6H), 2.63 (s, 6H), 2.26 (s, 3H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 148.44, 139.43, 138.75, 136.83, 130.32, 125.26, 122.84, 121.26, 38.74, 21.88, 19.44. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_7H_{11}{}^{79}BrN_3^+$: 216.0131; found: 216.0135.

1e: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.81 (s, 1H), 8.61 (s, 1H), 8.17 (s, 1H), 7.88 - 7.81 (m, 2H), 7.61 - 7.55 (m, 2H), 6.75 (s, 2H), 4.05 (s, 3H), 2.50 (s, 6H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.40, 142.88, 140.58, 136.92, 136.36, 133.67, 130.72, 129.89, 128.92, 127.93, 125.03, 122.55, 57.91, 23.18, 20.74. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{12}H_{13}N_2O^+$: 201.1028; found: 201.1031.

1g: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.89 (s, 1H), 8.66 (s, 1H), 8.59 (br. s, 1H), 8.25 (s, 1H), 8.12 (d, J = 8.2 Hz, 2H), 8.00 (d, J = 8.3 Hz, 2H), 6.74 (s, 2H), 4.06 (s, 3H), 2.66 (s, 3H), 2.50 (s, 7H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 198.05, 158.41, 139.38, 138.15, 137.80, 136.87, 136.35, 130.36, 129.52, 129.23, 128.33, 125.63, 122.98, 58.00, 27.43, 23.18, 20.74. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{14}H_{15}N_2O_2^+$: 243.1134; found: 243.1141.

1n: ^{1}H NMR (400 MHz, Methanol-d_4) δ 8.77 (d, J = 2.00 Hz, 1H), 8.66 (d, J = 2.44 Hz, 1H), 8.13 (d, J = 2.36 Hz, 1H), 6.87 (s, 3H), 4.02 (d, J = 1.70 Hz, 3H), 2.64 (d, J = 1.72 Hz, 9H), 2.25 (s, 4H). ^{13}C NMR (101 MHz, Methanol-d_4) δ 158.81, 139.38, 138.91, 136.81, 132.35, 130.43, 128.64, 127.00, 122.15, 57.30, 37.67, 22.05, 19.62, 17.14. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_7H_{10}{}^{79}BrN_2O^+$: 216.9971; found: 216.9977.

Substituted acrylonitriles (2a - 2ae)



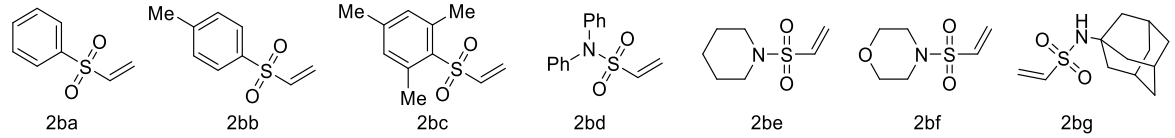
Scheme S2. Substituted acrylonitriles involved in this study.

Substituted acrylonitrile **2a** is commercially available and directly used without further purification, **2ab**[3]**, 2ac - 2ad**[4] were prepared according to literature procedures and the spectroscopic properties of

which are consistent with the data available in the literatures.

2ae was prepared according to a literature procedure[5]: A clean and dry 100 mL round-bottom flask was charged with 2-methoxybenzaldehyde (10.0 mmol) and acrylates/nitrile (15.0 mmol) followed by DABCO (5.0 mmol). The reaction mixtures were kept for 2 days at room temperature. After completion of the reactions, reaction mixtures were further purified by column chromatography using 20−30% ethyl acetate/hexanes as an eluent to provide the corresponding MBH alcohol (5.7 mmol, 57%). The mixture of the MBH alcohol (5.5 mmol), 1-bromobutane (22 mmol) and Ag_2O (5.5 mmol) was stirred at room temperature for 24 h. Ether (30 ml) was added and the mixture was well stirred and filtered. After removal of the solvent, the residue was subjected to flash chromatography using a silica gel column with dichloromethane as the eluent to afford **2ae** (4.6 mmol, 84%) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.33 (ddd, *J* = 8.6, 7.5, 1.8 Hz, 1H), 7.05 (td, *J* = 7.5, 1.0 Hz, 1H), 6.89 (d, *J* = 8.0 Hz,1H), 5.99- 5.94 (m, 2H), 5.34 (s, 1H), 3.85 (s, 3H), 3.51 (ddt, *J* = 27.0, 9.1, 6.5 Hz, 2H), 1.65 (dq, *J* = 8.6, 6.6 Hz, 2H), 1.53 – 1.39 (m, 2H), 0.96 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.61, 130.34, 129.49, 127.11, 126.26, 124.92, 120.98, 117.27, 110.45, 74.90, 69.32, 55.36, 31.80, 19.38, 13.92. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{15}H_{19}NNaO_2$: 268.1313; found: 268.1314.

Substituted γ-butyrolactone and vinylsulfonyl aromatics (2ba – 2bg)

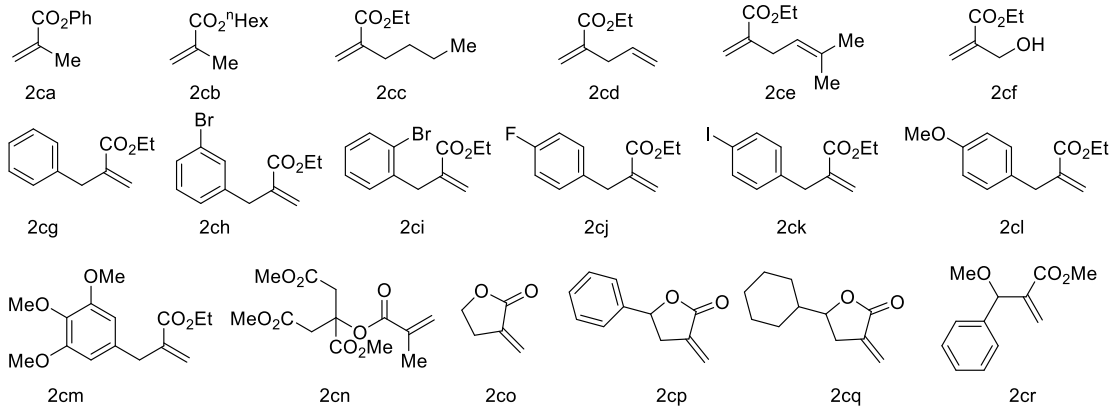


Scheme S3. α, β-Unsaturated sulfones and sulfamides involved in this study.

Unsaturated compound **2ba** is commercially available and directly used without further purification, **2bb** - **2bc**[6], **2bd**[7], **2be**[8], and **2bf**[9] were prepared according to a literature procedure and the spectroscopic properties of which are consistent with the data available in the literatures.

2bg was prepared according to a literature procedure[8]: 2-Chloroethanesulfonyl chloride (326 mg, 2 mmol) was added dropwise to a stirred solution of amantadine (302 mg, 2 mmol) and Et_3N (973 μL, 7 mmol) in DCM at 0 ºC. After addition, stirring was continued at 0 ºC overnight. The mixture was then diluted with DCM, washed with brine, dried over Na_2SO_4, and concentrated. Crude mixture was purified by silica gel column chromatography (10% ethyl acetate/hexanes) to give **2bg** (290 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.64 (dd, *J* = 16.5, 9.9 Hz, 1H), 6.24 (d, *J* = 16.5 Hz, 1H), 5.83 (d, *J* = 9.9 Hz, 1H), 4.31 (s, 1H), 2.14 – 2.07 (m, 3H), 1.94 (d, *J* = 2.9 Hz, 6H), 1.66 (p, *J* = 4.2, 3.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.07, 124.24, 55.12, 43.33, 35.90, 29.57. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{12}H_{19}NNaO_2S$: 264.1034; found: 264.1030.

Substituted α, β-unsaturated esters (2ca - 2cn)

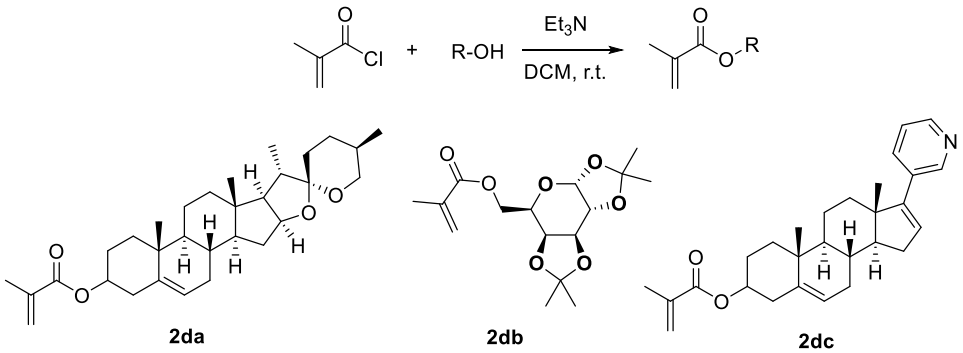


Scheme S4. Substituted α,β-unsaturated esters involved in this study.

Substituted α,β-unsaturated esters **2ca**, **2cb** and **2co** are commercially available and directly used without further purification. **2cc**[10], **2cd**[11], **2ce**[12], **2cf**[13], **2cg**[14], **2ch**[15], **2ci**[16], **2cj - 2cl**[17], **2cm**[18], **2cp**[19] and **2cq**[20] were prepared according to literature procedures and the spectroscopic properties of which are consistent with the data available in the literatures.

2cn was prepared as follow: to a solution of methacryloyl chloride (475 μL, 5 mmol) and trimethyl citrate (1170 mg, 5 mmol) in DCM, was added Et_3N (973 μL, 7 mmol) dropwise. The reaction mixture was stirred at room temperature overnight. The mixture was then washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. Crude mixture was purified by silica gel column chromatography with 5% ethyl acetate/hexanes to give **2cn** (967 mg, 64%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.14 (s, 1H), 5.64 (t, *J* = 1.7 Hz, 1H), 3.80 (s, 3H), 3.69 (s, 6H), 3.36 (d, *J* = 15.4 Hz, 2H), 3.27 (d, *J* = 15.4 Hz, 2H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.90, 169.25, 165.61, 135.41, 127.08, 52.96, 51.88, 38.49, 17.95. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{13}H_{18}NaO_8$: 325.0900; found: 325.0900.

Esterification of bioactive products



Scheme S5. Derivatives of bioactive products involved in this study.

To a solution of methacryloyl chloride (5 mmol) and the corresponding alcohol (5 mmol) in DCM, was added Et_3N (7 mmol) dropwise. The reaction mixture was stirred at room temperature overnight. The mixture was then washed with saturated $NaHCO_3$ solution, dried over Na_2SO_4 and concentrated. Crude mixture was purified by silica gel column chromatography with 5% ethyl acetate/hexanes to give the desire products.

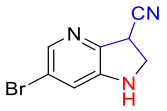
2da: 1350 mg, 57%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.10 (s, 1H), 5.55 (s, 1H), 5.41 (d, *J* = 4.9 Hz, 1H), 4.69 (tdd, *J* = 10.8, 6.4, 4.3 Hz, 1H), 4.44 (td, *J* = 7.8, 6.4 Hz, 1H), 3.54 - 3.46 (m, 1H), 3.40 (t, *J* = 10.9 Hz, 1H), 2.42 - 2.36 (m, 2H), 2.07 - 1.98 (m, 2H), 1.96 (s, 3H), 1.94 - 1.83 (m, 3H), 1.61 - 1.57 (m, 20H), 1.37 - 1.09 (m, 4H), 1.08 (s, 3H) 1.00 (d, *J* = 7.0 Hz, 3H), 0.81 (t, *J* = 3.2 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.89, 139.77, 136.87, 124.97, 122.37, 109.28, 80.82, 74.14, 66.85, 62.10, 56.46, 49.96, 41.63, 40.27, 39.75, 38.10, 36.98, 36.78, 32.07, 31.86, 31.43, 30.31, 28.82, 27.75, 20.83, 19.38, 18.33, 17.14, 16.28, 14.52. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{31}H_{47}O_4$: 483.3474; found: 483.3471.

2db: 689 mg, 41%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.15 (s, 1H), 5.58 (t, *J* = 1.6 Hz, 1H), 5.55 (d, *J* = 5.0 Hz, 1H), 4.64 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.37 - 4.31 (m, 2H), 4.31 - 4.24 (m, 2H), 4.09 (ddd, *J* = 7.1, 4.8, 1.8 Hz, 1H), 1.96 (d, *J* = 1.3 Hz, 3H), 1.52 (s, 3H), 1.47 (s, 3H), 1.35 (d, *J* = 4.5 Hz, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.25, 136.07, 125.83, 109.66, 108.78, 96.30, 71.12, 70.71, 70.53, 66.11, 63.64, 25.97, 25.95, 24.99, 24.47, 18.29. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{16}H_{25}O_7$: 329.1600; found: 329.1601.

2dc: 1669 mg, 80%. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 2.2 Hz, 1H), 8.48 (d, *J* = 4.8 Hz, 1H), 7.67 (dt, *J* = 8.0, 2.0 Hz, 1H), 7.24 (dd, *J* = 8.0, 4.9 Hz, 1H), 6.11 (s, 1H), 6.02 (dd, *J* = 3.2, 1.7 Hz, 1H), 5.56 (s, 1H), 5.45 (d, *J* = 5.1 Hz, 1H), 4.73 - 4.62 (m, 1H), 2.41 (q, *J* = 7.1, 6.5 Hz, 2H), 2.38 - 2.19 (m, 1H), 2.14 - 2.03 (m, 3H), 1.98 - 1.86 (m, 5H), 1.80 - 1.73 (m, 1H), 1.72 - 1.63 (m, 2H), 1.63 - 1.57 (m, 1H), 1.57 - 1.42 (m, 1H), 1.32 - 1.18 (m, 1H), 1.18 - 1.09 (m, 1H), 1.07 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.89, 151.63, 147.83, 147.77, 140.09, 136.84, 133.79, 133.01, 129.32, 125.04, 123.07, 122.30, 74.10, 57.47, 50.25, 47.34, 38.14, 36.93, 36.82, 35.21, 31.81, 31.53, 30.42, 27.74, 20.83, 19.31, 18.36, 16.58. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{28}H_{36}NO_2$: 418.2746; found: 418.2748.

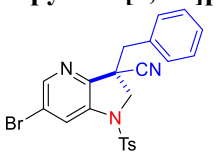
Spectral data of 4-azaindolines

6-Bromo-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3a)



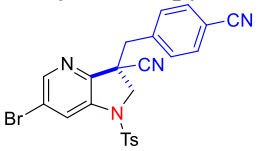
Compound 3a was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2aa** (8 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 35% EtOAc/hexanes) afforded **3a** (20.7 mg, 93%) as a white solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.86 (d, J = 2.0 Hz, 1H), 7.14 (d, J = 1.9 Hz, 1H), 5.73 (br. s, 1H), 4.52 (dd, J = 10.2, 7.6 Hz, 1H), 4.10 - 4.00 (m, 1H), 3.90 - 3.79 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 146.80, 145.01, 138.85, 120.76, 118.47, 117.70, 50.00, 32.33. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_8H_7{}^{79}BrN_3$: 223.9823; found: 223.9810.

3-Benzyl-6-bromo-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3b)



Compound 3b was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ac** (17.2 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 1.1 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) to give **3b** (34.1 mg, 73%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.37 (d, J = 2.0 Hz, 1H), 8.08 (d, J = 1.9 Hz, 1H), 7.67 (d, J = 8.4 Hz, 2H), 7.38 - 7.31 (m, 5H), 7.18 - 7.11 (m, 2H), 4.15 (d, J = 11.2 Hz, 1H), 3.92 (d, J = 11.2 Hz, 1H), 3.36 (d, J = 13.8 Hz, 1H), 2.96 (d, J = 13.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.10, 146.20, 145.87, 136.91, 133.06, 132.70, 130.43, 130.06, 128.96, 128.17, 127.21, 124.55, 121.84, 118.68, 55.81, 45.12, 42.38, 21.67. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{22}H_{19}{}^{79}BrN_3O_2S$: 468.0381; found: 468.0376.

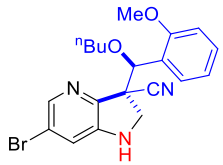
6-Bromo-3-(4-cyanobenzyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3c)



Compound 3c was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ad** (20.2 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) to give **3c** (78%, 38.4 mg) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.34 (d, J = 1.9 Hz, 1H), 8.06 (d, J = 1.9 Hz, 1H), 7.66 (d, J = 8.1 Hz, 2H), 7.60 (d, J = 7.9 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 7.24 (d, J = 8.0 Hz, 2H), 4.07 (d, J = 11.2 Hz, 1H), 3.97 (d, J = 11.2 Hz, 1H), 3.36 (d, J = 13.8 Hz, 1H), 3.10 (d, J = 13.8 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.20, 146.27, 146.15, 138.40, 136.95, 132.56, 130.91,

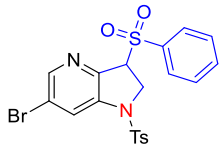
130.51, 127.21, 124.64, 122.21, 118.28, 118.16, 112.31, 55.94, 44.68, 42.16, 21.72. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{23}H_{18}{}^{79}BrN_4O_2S$: 493.0334; found: 493.0328.

6-Bromo-3-(butoxy(2-methoxyphenyl)methyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3d)



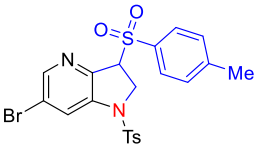
Compound 3d was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ae** (29.4 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **3d** (26.7 mg, 65%) as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.83 (d, J = 1.9 Hz, 1H), 7.49 (dd, J = 7.7, 1.7 Hz, 1H), 7.30 - 7.24 (m, 1H), 6.97 (d, J = 1.9 Hz, 1H), 6.90 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 8.3 Hz, 1H), 6.13 (s, 1H), 5.05 (s, 1H), 3.79 (d, J = 10.6 Hz, 1H), 3.65 (dd, J = 10.7, 2.3 Hz, 1H), 3.53 (s, 3H), 3.27 - 3.16 (m, 2H), 1.42 (dq, J = 13.2, 6.5 Hz, 2H), 1.28 - 1.20 (m, 2H), 0.80 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 157.70, 147.14, 145.95, 137.91, 130.26, 128.36, 124.11, 121.37, 120.82, 120.38, 117.40, 111.09, 75.29, 69.26, 55.66, 52.03, 50.84, 31.51, 19.11, 14.07. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{20}H_{22}{}^{79}BrN_3O_2Na$: 438.0793; found: 438.0783.

6-Bromo-3-(phenylsulfonyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (4a)



Compound 4a was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ba** (20.2 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) to give **4a** (37.0 mg, 75%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 8.25 (d, J = 1.9 Hz, 1H), 7.91 (d, J = 1.9 Hz, 1H), 7.74 - 7.69 (m, 2H), 7.69 - 7.64 (m, 3H), 7.50 (dd, J = 8.3, 7.2 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 4.68 (dd, J = 9.9, 3.3 Hz, 1H), 4.62 (dd, J = 12.5, 3.3 Hz, 1H), 4.11 (dd, J = 12.5, 10.0 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 145.60, 145.49, 143.03, 139.38, 136.11, 134.58, 132.94, 130.29, 129.34, 129.11, 127.31, 123.53, 122.15, 65.29, 49.62, 21.69. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{20}H_{18}{}^{79}BrN_2O_4S_2$: 492.9891; found: 492.9883.

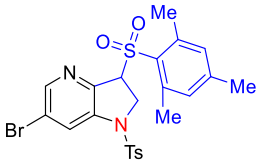
6-Bromo-1,3-ditosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (4b)



Compound 4b was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2bb** (21.8 mg,

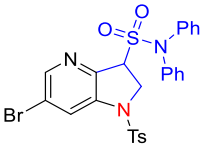
0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) to give **4b** (36.9 mg, 73%) as a white solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.21 - 8.20 (m, 1H), 7.91 (t, J = 1.4 Hz, 1H), 7.85 (d, J = 8.1 Hz, 2H), 7.57 (d, J = 7.9 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 5.05 (dd, J = 10.0, 3.2 Hz, 1H), 4.56 (dd, J = 12.3, 3.2 Hz, 1H), 4.34 (dd, J = 12.3, 10.0 Hz, 1H), 2.44 (s, 6H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 145.55, 145.46, 144.69, 144.51, 139.37, 134.16, 133.25, 130.28, 129.65, 129.27, 127.50, 122.61, 121.20, 64.96, 49.79, 20.72. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{21}H_{20}{}^{79}BrN_2O_4S_2$: 507.0048; found: 507.0049.

6-Bromo-3-(mesitylsulfonyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (4c)



Compound 4c was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2bc** (25.0 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) to give **4c** (36.8 mg, 69%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dd, J = 10.0, 2.0 Hz, 2H), 7.75 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.95 (s, 2H), 4.67 (dd, J = 9.9, 3.3 Hz, 1H), 4.60 (dd, J = 12.5, 3.4 Hz, 1H), 4.15 (dd, J = 12.4, 9.9 Hz, 1H), 2.41 (s, 3H), 2.37 (s, 6H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.40, 145.03, 144.31, 143.55, 141.05, 139.85, 133.33, 132.40, 130.53, 130.18, 127.44, 123.57, 121.98, 64.38, 48.74, 22.92, 21.68, 21.18. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{23}H_{24}{}^{79}BrN_2O_4S_2$: 535.0361; found: 535.0363.

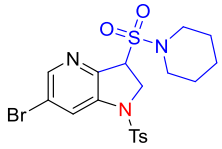
6-Bromo-*N*,*N*-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-sulfonamide (4d)



Compound 4d was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2bd** (31.1 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give **4d** (44.9 mg, 77%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (d, J = 1.9 Hz, 1H), 8.05 (d, J = 1.9 Hz, 1H), 7.71 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.0 Hz, 4H), 7.37 - 7.24 (m, 8H), 4.89 (dd, J = 10.3, 3.8 Hz, 1H), 4.59 (dd, J = 12.4, 3.8 Hz, 1H), 4.20 (dd, J = 12.4, 10.3 Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.46, 145.42, 143.26, 140.88, 139.76, 133.01, 130.24, 129.42, 128.81, 127.83, 127.34, 123.76,

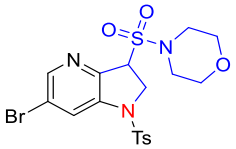
122.28, 61.45, 50.31, 21.67. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{26}H_{22}{}^{79}BrN_3O_4S_2Na$: 606.0133; found: 606.0128.

6-Bromo-3-(piperidin-1-ylsulfonyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (4e)



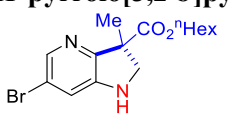
Compound 4e was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2be** (21.0 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give **4e** (40.4 mg, 81%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 2.0 Hz, 1H), 8.09 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.60 (dd, *J* = 10.0, 3.5 Hz, 1H), 4.49 (dd, *J* = 12.2, 3.5 Hz, 1H), 4.12 (dd, *J* = 12.2, 10.1 Hz, 1H), 3.37 - 2.96 (m, 4H), 2.44 (s, 3H), 1.61 - 1.51 (m, 7H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.55, 145.18, 144.25, 139.39, 132.99, 130.26, 127.39, 123.57, 121.82, 62.22, 50.56, 47.33, 25.97, 23.64, 21.68. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{19}H_{22}{}^{79}BrN_3O_4S_2Na$: 522.0133; found: 522.0132.

4-((6-Bromo-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridin-3-yl)sulfonyl)morpholine (4f)



Compound 4f was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2bf** (21.2 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give **4f** (29.6 mg, 59%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 (d, *J* = 1.9 Hz, 1H), 8.11 (d, *J* = 1.9 Hz, 1H), 7.80 - 7.73 (m, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 4.64 (dd, *J* = 10.1, 3.5 Hz, 1H), 4.51 (dd, *J* = 12.4, 3.5 Hz, 1H), 4.15 (dd, *J* = 12.4, 10.1 Hz, 1H), 3.65 (tdt, *J* = 14.7, 9.4, 3.1 Hz, 4H), 3.34 (ddd, *J* = 12.7, 6.4, 3.2 Hz, 2H), 3.16 (ddd, *J* = 12.6, 6.4, 3.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.64, 145.21, 143.86, 139.44, 132.90, 130.30, 127.39, 123.76, 122.07, 66.80, 62.26, 50.37, 46.42, 21.69. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{18}H_{20}{}^{79}BrN_3O_5S_2Na$: 523.9925; found: 523.9922.

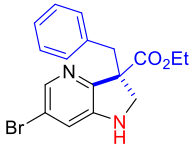
Hexyl 6-bromo-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5a)



Compound 5a was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2cb (**20.7 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **5a** (27.5 mg, 81%) as an off-brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.91 (t, *J* = 1.6 Hz, 1H),

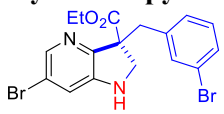
6.95 (t, J = 1.4 Hz, 1H), 4.16 (d, J = 9.5 Hz, 1H), 4.10 (tt, J = 7.4, 3.7 Hz, 2H), 3.99 (br. s, 1H), 3.45 (d, J = 9.5 Hz, 1H), 1.61 - 1.52 (m, 5H), 1.28 - 1.15 (m, 6H), 0.84 (t, J = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.35, 145.40, 120.07, 117.97, 65.73, 57.39, 51.97, 31.30, 28.44, 25.37, 22.50, 22.03, 13.96. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{15}H_{22}{}^{79}BrN_2O_2$:341.0865; found: 341.0861.

Ethyl 3-benzyl-6-bromo-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5b)



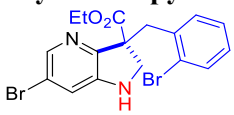
Compound 5b was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2cg** (22.8 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **5b** (28.7 mg, 80%) as a colorless oil. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.85 (d, J = 2.0 Hz, 1H), 7.25 - 7.21 (m, 3H), 7.13 - 7.07 (m, 2H), 6.93 (s, 1H), 5.37 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.07 (d, J = 10.0 Hz, 1H), 3.74 (dd, J = 10.1, 2.0 Hz, 1H), 3.49 (d, J = 13.7 Hz, 1H), 3.28 (d, J = 13.8 Hz, 1H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 171.80, 150.81, 147.19, 137.64, 137.18, 130.08, 128.05, 126.53, 120.03, 116.29, 60.98, 56.77, 52.82, 40.51, 13.56. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{18}{}^{79}BrN_2O_2$: 361.0552; found: 361.0559.

Ethyl 6-bromo-3-(3-bromobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5c)



Compound 5c was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ch** (32.2 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **5c** (35.0 mg, 80%) as a brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.80 (d, J = 2.0 Hz, 1H), 7.38 (dt, J = 8.0, 1.4 Hz, 1H), 7.18 (dd, J = 4.8, 3.0 Hz, 2H), 7.01 (d, J = 7.6 Hz, 1H), 6.88 (d, J = 2.0 Hz, 1H), 6.10 (s, 1H), 4.11 (q, J = 7.1 Hz, 2H), 3.89 (dd, J = 10.3, 1.5 Hz, 1H), 3.60 (dd, J = 10.3, 1.8 Hz, 1H), 3.33 (s, 1H), 3.19 (d, J = 13.6 Hz, 1H), 1.14 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.14, 150.48, 147.63, 140.03, 137.16, 133.05, 130.59, 129.93, 129.43, 121.74, 120.58, 116.35, 61.63, 56.51, 53.03, 14.48. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{17}{}^{79}Br_2N_2O_2$: 438.9657; found: 438.9650.

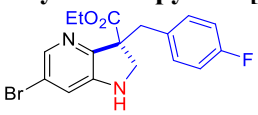
Ethyl 6-bromo-3-(2-bromobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5d)



Compound 5d was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ci** (32.2 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **5d** (33.4 mg, 76%) as a brown solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.82 (d, J = 1.9 Hz, 1H), 7.60 (dd, J = 7.9, 1.4 Hz, 1H), 7.21 (td, J = 7.5, 1.4 Hz, 1H), 7.14 (td, J = 7.6, 1.8 Hz, 1H), 6.93 (d, J = 1.9 Hz, 2H), 6.91 (d, J = 1.8 Hz, 1H), 6.16 (s, 1H), 4.10 (q, J = 7.1 Hz, 2H), 4.03 (d, J = 7.1 Hz, 1H), 4.00 - 3.96 (m,

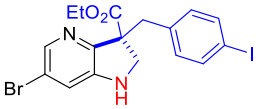
1H), 3.67 (d, *J* = 14.6 Hz, 1H), 3.55 (dd, *J* = 10.3, 1.9 Hz, 1H), 3.33 (s, 1H), 1.99 (s, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.28, 170.81, 150.31, 147.59, 137.40, 136.76, 133.17, 131.30, 129.19, 128.06, 125.95, 120.63, 116.57, 61.71, 60.23, 56.33, 53.29, 21.23, 14.55, 14.37. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{17}{}^{79}Br_2N_2O_2$: 438.9657; found: 438.9651.

Ethyl 6-bromo-3-(4-fluorobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5e)



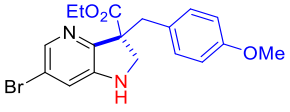
Compound 5e was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2cj** (25.0 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **5e** (29.5 mg, 78%) as a yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (d, *J* = 2.0 Hz, 1H), 7.12 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.02 - 6.95 (m, 2H), 6.93 (d, *J* = 2.0 Hz, 1H), 5.37 (br. s, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 4.07 (d, *J* = 10.1 Hz, 1H), 3.73 (d, *J* = 10.2 Hz, 1H), 3.45 (d, *J* = 13.9 Hz, 1H), 3.29 (d, *J* = 13.8 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d6) δ 171.77, 161.75 (d, J = 241 Hz), 150.70, 147.20, 137.75, 133.19 (d, J = 3.2 Hz), 131.86 (d, J = 8.0 Hz), 120.05, 116.40, 114.62 (d, *J* = 21.3 Hz), 61.01, 56.72, 52.77, 39.61, 13.54. ^{19}F NMR (376 MHz, Acetone-d_6) δ -118.07 (tt, *J* = 9.6, 5.4 Hz). ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{16}{}^{79}BrFN_2O_2$: 379.0457; found: 379.0464.

Ethyl 6-bromo-3-(4-iodobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5f)



Compound 5f was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ck** (37.9 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) afforded **5f** (41.3 mg, 85%) as an off-yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.84 (s, 1H), 7.59 (d, *J* = 7.9 Hz, 2H), 6.95 - 6.87 (m, 3H), 5.39 (s, 1H), 4.16 (q, *J* = 7.1 Hz, 2H), 4.07 (d, *J* = 10.2 Hz, 1H), 3.72 (d, *J* = 10.2 Hz, 1H), 3.41 (d, *J* = 13.7 Hz, 1H), 3.26 (d, *J* = 13.8 Hz, 1H), 1.20 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 171.73, 150.56, 147.24, 137.71, 137.11, 137.08, 132.44, 120.11, 116.38, 91.65, 61.08, 56.53, 52.86, 39.91, 13.55. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{17}{}^{79}BrIN_2O_2$: 486.9518; found: 486.9529.

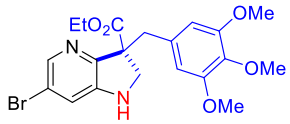
Ethyl 6-bromo-3-(4-methoxybenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5g)



Compound 5g was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2ck** (26.4 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) afforded **5g** (32.4 mg, 83%) as an off-yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.78 (d, *J* = 2.7 Hz, 1H), 6.92 (dd, *J* = 8.7, 2.6 Hz, 2H), 6.86 (s, 1H), 6.76 (dd, *J* = 8.7, 2.6 Hz, 2H), 6.08 (br. s, 1H), 4.09 (dt, *J* = 8.4, 5.9 Hz, 2H), 3.86 (dd, *J* = 10.1, 2.8 Hz, 1H), 3.68 (d, *J* = 2.8 Hz, 3H), 3.57 (dd, *J* = 10.2, 2.8 Hz, 1H),

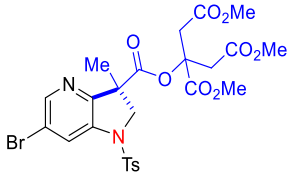
3.32 - 3.24 (m, 1H), 3.12 (dd, J = 13.8, 2.8 Hz, 1H), 1.13 (td, J = 7.2, 2.6 Hz, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.32, 158.40, 150.81, 147.61, 137.08, 131.37, 128.96, 120.41, 116.20, 113.94, 61.46, 56.82, 55.36, 52.77, 14.49. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{18}H_{20}{}^{79}BrN_2O_3$: 391.0657; found: 391.0655.

Ethyl 6-bromo-3-(3,4,5-trimethoxybenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5h)



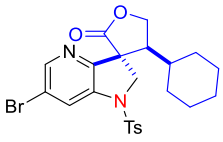
Compound 5h was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2cm** (33.6 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) afforded **5h** (32.4 mg, 72%) as an off-yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.85 (d, J = 1.9 Hz, 1H), 6.88 (d, J = 2.0 Hz, 1H), 6.27 (s, 2H), 5.31 (s, 1H), 4.18 (qt, J = 7.1, 3.6 Hz, 2H), 4.04 (dd, J = 10.2, 1.5 Hz, 1H), 3.76 (dd, J = 10.1, 2.2 Hz, 1H), 3.67 (s, 6H), 3.65 (s, 3H), 3.28 (s, 2H), 1.21 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 172.12, 152.95, 151.04, 147.57, 137.42, 137.01, 132.46, 120.02, 116.13, 107.42, 61.00, 59.54, 56.74, 55.25, 52.68, 40.75, 13.59. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{20}H_{24}{}^{79}BrN_2O_5$: 451.0869; found: 451.0878.

Trimethyl 2-((6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonyl)oxy) propane-1,2,3-tricarboxylate (5i)



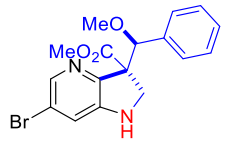
Compound 5i was prepared by the **general procedure A: 7** (44.0 mg, 0.10 mmol), **2cn** (36 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) to give **5i** (48.8 mg, 78%) as a white solid.^{1}H NMR (400 MHz, Acetone-d_6) δ 8.26 (d, J = 1.9 Hz, 1H), 8.01 (d, J = 2.0 Hz, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.1 Hz, 2H), 4.51 (d, J = 10.9 Hz, 1H), 3.87 (d, J = 10.9 Hz, 1H), 3.68 (s, 3H), 3.63 (s, 3H), 3.60 (s, 3H), 3.12 - 2.99 (m, 4H), 2.43 (s, 3H), 1.45 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 169.95, 168.76, 168.44, 168.34, 152.61, 145.50, 144.77, 137.36, 133.51, 130.25, 127.45, 122.83, 119.83, 78.98, 58.92, 52.32, 51.33, 51.29, 50.91, 38.23, 38.00, 21.08, 20.61. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{25}H_{28}{}^{79}BrN_2O_{10}S$: 626.0648; found: 626.0653.

5'-Chloro-4-cyclohexyl-6'-ethoxy-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (5j)



Compound 5j was prepared by the **general procedure B: 1a** (44.0 mg, 0.10 mmol), **2cq** (20.9 mg, 0.12 mmol), DBU (31 μL, 0.2 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **5j** (19.3 mg, 40%) as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 8.30 (d, J = 1.9 Hz, 1H), 7.92 (d, J = 2.0 Hz, 1H), 7.75 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 4.43 (t, J = 8.2 Hz, 1H), 4.19 (d, J = 11.5 Hz, 1H), 4.06 (d, J = 11.7 Hz, 1H), 2.34 (s, 3H), 2.17 - 2.07 (m, 2H), 1.83 (d, J = 13.0 Hz, 1H), 1.66 (d, J = 12.5 Hz, 2H), 1.60 (d, J = 11.8 Hz, 1H), 1.46 - 1.38 (m, 2H), 1.19 - 1.07 (m, 3H), 0.99 - 0.77 (m, 2H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.45, 153.23, 145.91, 136.68, 132.81, 130.84, 127.79, 124.18, 120.69, 82.54, 57.56, 52.90, 42.24, 29.26, 27.22, 26.18, 25.48, 25.46, 21.49. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{23}H_{26}{}^{79}BrN_2O_4S$: 505.0797; found: 505.0793.

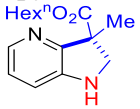
Methyl 6-bromo-3-(methoxy(phenyl)methyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5k)



Compound 5k was prepared by the **general procedure A: 1a** (44.0 mg, 0.10 mmol), **2cr** (24.7 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 40% EtOAc/hexanes) to give the product **5k** (19.6 mg, 52%, 5:1 *d.r.*) as an off-white solid. NMR Spectroscopic data for the major one: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, J = 2.0 Hz, 1H), 7.33 (d, J = 1.7 Hz, 5H), 6.97 (d, J = 1.9 Hz, 1H), 5.28 (s, 1H), 4.19 (d, J = 9.8 Hz, 1H), 4.03 (d, J = 9.8 Hz, 1H), 3.68 (s, 3H), 3.21 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.14, 147.69, 146.48, 140.00, 137.54, 128.44, 127.92, 127.46, 120.60, 118.13, 83.04, 62.84, 57.60, 52.73, 48.70. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{17}{}^{79}BrN_2O_3H$: 377.0501; found: 377.0495.

NMR Spectroscopic data for the major one: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.02 (d, J = 1.9 Hz, 0.2 H), 7.30 (s, 1H), 7.07 (dd, J = 6.7, 2.9 Hz, 3H), 6.69 (d, J = 1.9 Hz, 2H), 5.33 (d, J = 8.7 Hz, 1H), 4.35 (d, J = 10.7 Hz, 1H), 3.92 (s, 3H), 3.90 (d, J = 19.7 Hz, 1H), 3.34 (s, 3H).

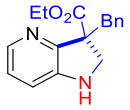
Hexyl 3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6a)



Compound 6a was prepared by the **general procedure A: 1l** (44.0 mg, 0.10 mmol), **2cb** (24.7 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 40% EtOAc/hexanes) to give the product **6a** (18.1 mg, 69%) as an off-white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 4.9 Hz, 1H), 6.97 (dd, J = 7.9, 4.9 Hz, 1H), 6.90 (d, J = 7.9 Hz, 1H), 4.21 - 4.08 (m, 3H), 3.81 (br. s, 1H), 3.46 (d, J = 9.5 Hz, 1H), 1.66 (s, 3H), 1.60 (q, J = 6.8 Hz, 2H), 1.26 (t, J = 5.3 Hz, 6H), 0.87 (t, J = 6.5 Hz, 3H). ^{13}C

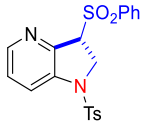
NMR (101 MHz, Chloroform-*d*) δ 173.83, 153.21, 144.13, 139.86, 122.75, 115.91, 65.55, 57.07, 52.55, 31.33, 28.47, 25.36, 22.50, 22.04, 13.97. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{15}H_{22}N_2O_2$: 263.1760; found: 263.1754.

Ethyl 3-benzyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6b)



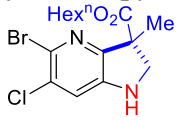
Compound 6b was prepared by the **general procedure A: 1l** (44.0 mg, 0.10 mmol), **2cg** (24.7 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 40% EtOAc/hexanes) to give the product **6b** (17.5 mg, 62%) as a colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 4.9 Hz, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 7.33 - 7.25 (m, 1H), 7.23 - 7.18 (m, 3H), 6.96 - 6.91 (m, 2H), 4.80 (d, *J* = 11.4 Hz, 1H), 4.34 - 4.23 (m, 3H), 3.59 (d, *J* = 14.0 Hz, 1H), 3.47 (d, *J* = 14.0 Hz, 1H), 1.27 (t, *J* = 7.11 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.72, 152.81, 147.01, 136.26, 135.10, 129.71, 128.54, 127.38, 125.05, 123.70, 62.48, 56.84, 53.72, 53.70, 41.15, 14.05. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{17}H_{19}N_2O_2$: 283.1447; found: 283.1441.

3-(Phenylsulfonyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (6c)



Compound 6c was prepared by the **general procedure A: 1l** (44.0 mg, 0.10 mmol), **2ba** (24.7 mg, 0.12 mmol), DBU (31 μL, 0.2 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **6c** (16.6 mg, 40%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 4.9 Hz, 1H), 7.66 (dq, *J* = 24.1, 8.7 Hz, 6H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, *J* = 8.3, 4.9 Hz, 1H), 4.76 (dd, *J* = 10.1, 3.2 Hz, 1H), 4.60 (dd, *J* = 12.5, 3.3 Hz, 1H), 4.10 - 4.00 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 145.24, 144.32, 138.19, 137.36, 134.13, 133.20, 130.11, 129.19, 128.97, 127.50, 124.40, 120.61, 65.55, 49.20, 20.59. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{20}H_{19}N_2O_4S_2$: 415.0786; found: 415.0787.

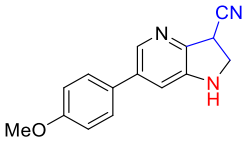
Hexyl 5-bromo-6-chloro-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6d)



Compound 6d was prepared by the **general procedure A: 1m** (44.0 mg, 0.10 mmol), **2cb** (24.7 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 40% EtOAc/hexanes) to give the product **6d** (20.9 mg, 56%) as an off-white solid.^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.94 (s, 1H), 4.14 (q, *J* = 7.7, 6.7 Hz, 3H), 4.03 (br. s, 1H), 3.51 (d, *J* = 9.7 Hz, 1H), 1.66 - 1.55 (m, 5H), 1.33 - 1.21 (m, 6H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.06, 152.15, 144.71, 131.90,

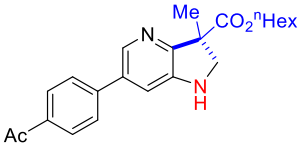
128.10, 117.50, 65.81, 57.88, 51.96, 31.33, 28.43, 25.40, 22.51, 21.95, 13.99. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{15}H_{20}{}^{79}Br^{35}ClN_2O_2Na$: 397.0294; found: 397.0290.

6-(4-Methoxyphenyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (6e)



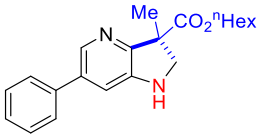
Compound 6e was prepared by the **general procedure A: 1f** (43.0 mg, 0.10 mmol), **2aa** (8 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) afforded **6e** (20.1 mg, 80%) as a brown solid.^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 1.9 Hz, 1H), 7.58 (d, J = 8.6 Hz, 2H), 7.09 (d, J = 2.0 Hz, 1H), 7.38 (d, J = 8.6 Hz, 2H), 6.20 (s, 1H), 4.69 (dd, J = 10.1, 7.4 Hz, 1H), 3.88 (td, J = 9.9, 1.6 Hz, 1H), 3.80 (s, 3H), 3.71 (ddd, J = 9.7, 7.4, 2.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 159.79, 146.02, 144.60, 136.90, 136.51, 130.37, 128.53, 120.22, 114.96, 113.45, 55.68, 49.72, 32.50. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{15}H_{14}N_3O$: 252.1137; found:252.1129.

Hexyl 6-(4-methoxyphenyl)-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6f)



Compound **6f** was prepared by the **general procedure A**: **1g** (44.2 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 8% EtOAc/hexanes) afforded **6f** (33.1 mg, 87%) as a brown solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.11 - 8.06 (m, 3H), 7.76 (d, J = 8.2 Hz, 2H), 7.18 (s, 1H), 5.41 (s, 1H), 4.17 (d, J = 9.7 Hz, 1H), 4.12 (t, J = 6.5 Hz, 2H), 3.54 (d, J = 9.7 Hz, 1H), 2.63 (s, 3H). 1.61 - 1.56 (m, 5H), 1.33 - 1.26 (m, 6H), 0.86 (t, J = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 196.58, 173.33, 154.18, 143.32, 136.87, 136.35, 134.76, 128.84, 127.06, 112.64, 64.65, 57.17, 52.07, 31.17, 25.86, 25.26, 22.32, 21.60, 13.35. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{23}H_{29}N_2O_3$: 381.2178; found: 381.2173.

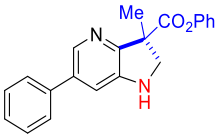
Hexyl 3-methyl-6-phenyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6g)



Compound 6g was prepared by the **general procedure A: 1e** (40.0 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **6g** (24.7 mg, 73%) as an off-white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.18 (s, 1H), 7.55 (d, J = 7.9 Hz, 2H), 7.46 (t, J = 7.5 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.08 (s, 1H), 4.24 (d, J = 9.5 Hz, 1H), 4.18 (td, J = 6.7, 3.6 Hz, 2H), 3.94 (br. s, 1H), 3.52 (d, J = 9.5 Hz, 1H), 1.71 (s, 3H), 1.67 - 1.60 (m, 2H), 1.29 - 1.25 (m, 6H), 0.87 (t, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.81, 152.26, 144.36, 138.69, 138.67, 136.47, 128.89, 127.79, 127.22, 114.55, 65.65, 57.40, 53.44, 52.32, 31.33, 28.49, 25.39,

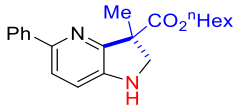
22.50, 22.14, 13.96. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{21}H_{27}N_2O_2$: 339.2073; found: 339.2056.

Phenyl 3-methyl-6-phenyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6h)



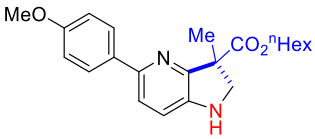
Compound 6h was prepared by the **general procedure A: 1e** (40.0 mg, 0.10 mmol), **2ca** (19 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **6h** (25.1 mg, 76%) as a yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.03 (d, J = 1.8 Hz, 1H), 7.64 (dd, J = 7.4, 1.7 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.45-7.36 (m, 3H), 7.26 (t, J = 7.4 Hz, 1H), 7.10 (d, J = 1.9 Hz, 1H), 7.07 (d, J = 7.7 Hz, 2H), 6.16 (d, J = 2.0 Hz, 1H), 4.20 (dd, J = 10.0, 2.1 Hz, 1H), 3.56 (dd, J = 10.0, 1.7 Hz, 1H), 1.62 (s, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.84, 152.87, 151.12, 145.75, 138.58, 136.61, 136.11, 130.03, 129.47, 128.27, 127.33, 126.42, 122.00, 113.18, 57.04, 52.23, 22.63. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{21}H_{19}N_2O_2$: 331.1447; found: 331.1455.

Hexyl 3-methyl-5-phenyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6i)



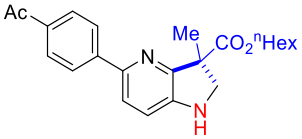
Compound 6i was prepared by the **general procedure A: 5b** (40.0 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **6i** (30.1 mg, 89%) as a yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, J = 7.6 Hz, 2H), 7.48 - 7.38 (m, 3H), 7.31 (t, J = 7.2 Hz, 1H), 6.95 (d, J = 8.0 Hz, 1H), 4.24 - 4.13 (m, 3H), 3.86 (br. s, 1H), 3.50 (d, J = 9.6, 1H), 1.70 (s, 3H), 1.63 (dq, J = 14.0, 6.8, 6.3 Hz, 2H), 1.34 - 1.21 (m, 6H), 0.84 (t, J = 6.4 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.10, 153.56, 148.07, 142.89, 139.81, 128.47, 127.39, 126.00, 119.56, 116.28, 65.43, 57.36, 52.69, 31.38, 28.59, 25.48, 22.48, 22.12, 13.98. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{21}H_{27}N_2O_2$: 339.2073; found: 339.2056.

Hexyl 5-(4-methoxyphenyl)-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6j)



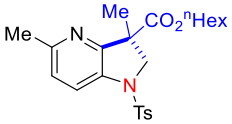
Compound 6j was prepared by the **general procedure A: 1i** (43.0 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **6j** (32.8 mg, 89%) as a off-white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, J = 7.7 Hz, 2H), 7.36 (d, J = 7.6 Hz, 1H), 6.93 (d, J = 7.7 Hz, 3H), 4.14 (m, 3H), 3.84 (s, 3H), 3.47 (t, J = 9.9 Hz, 1H), 1.67 (s, 3H), 1.62 - 1.55 (m, 2H), 1.31 - 1.19 (m, 6H), 0.82 (t, J = 8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.74, 159.53, 127.25, 118.86, 116.71, 113.87, 65.41, 57.38, 55.34, 52.62, 31.39, 28.59, 25.47, 22.48, 22.10, 14.00. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{22}H_{28}N_2O_3$: 369.2178; found: 369.2173.

Hexyl 5-(4-acetylphenyl)-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6k)



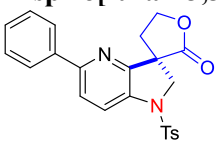
Compound 6k was prepared by the **general procedure A: 1j** (44.2 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **6k** (28.9 mg, 76%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 9.0 Hz, 2H), 8.01 (d, *J* = 8.7 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 1H), 6.96 (d, *J* = 8.3 Hz, 1H), 4.24 (d, *J* = 9.5 Hz, 1H), 4.17 (ddt, *J* = 10.8, 6.6, 4.3 Hz, 2H), 3.53 (d, *J* = 9.5 Hz, 1H), 2.64 (s, 3H), 1.71 (s, 3H),1.61 (dt, *J* = 8.2, 6.5 Hz, 2H), 1.33 - 1.17 (m, 6H), 0.83 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.92, 173.87, 153.88, 146.07, 144.14, 143.62, 135.73, 128.73, 125.76, 120.35, 115.66, 65.50, 57.27, 52.57, 31.36, 28.57, 26.67, 25.46, 22.48, 22.18, 13.97. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{23}H_{29}N_2O_3$: 381.2178; found: 381.2174.

Phenyl 3,5-dimethyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6l)



Compound 6l was prepared by the **general procedure A: 1k** (34.0 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) afforded **6l** (22.0 mg, 51%) as a colorless oil.^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 8.3 Hz, 1H), 7.70 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 6.6 Hz, 2H), 7.01 (d, *J* = 8.3 Hz, 1H), 4.40 (d, *J* = 10.9 Hz, 1H), 4.02 (dt, *J* = 10.7, 6.6 Hz, 1H), 3.93 (dt, *J* = 10.7, 6.6 Hz, 1H), 3.71 (d, *J* = 10.9 Hz, 1H), 2.48 (s, 3H), 2.40 (s, 3H), 1.43 (s, 3H), 1.50-1.38 (m, 2H), 1.34 – 1.10 (m, 6H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.45, 153.91, 153.75, 144.52, 133.54, 133.49, 129.80, 127.38, 122.50, 121.92, 65.68, 59.25, 51.48, 31.26, 28.26, 25.26, 23.71, 22.72, 22.48, 21.57, 13.96. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{23}H_{31}N_2O_4S$: 431.2005; found: 431.1945.

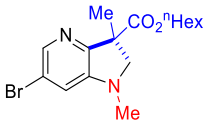
5'-Phenyl-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (6m)



Compound 6m was prepared by the **general procedure B: 1h** (40.0 mg, 0.10 mmol), **2co** (11 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 10% EtOAc/hexanes) afforded **6m** (21.4 mg, 51%) as a colorless

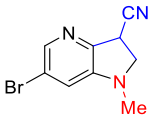
oil. **6m** is a mixture of rotamers (major: minor = 2:1); NMR Spectroscopic data for the major one: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 - 7.89 (m, 2H), 7.74 (d, *J* = 8.1 Hz, 2H), 7.70 (dd, *J* = 8.4, 5.6 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 3H), 4.93 - 4.83 (m, 1H), 4.49 - 4.30 (m, 2H), 4.04 (d, *J* = 11.3 Hz, 1H), 2.41 (s, 3H), 2.39 - 2.30 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.20, 153.30, 145.12, 137.93, 134.32, 133.16, 130.09, 128.75, 127.42, 126.39, 122.65, 120.43, 66.19, 57.06, 51.67, 36.27, 21.64. ESI-HRMS (m/z): $[M+H]^{+}$calcd for $C_{23}H_{21}N_2O_4S$: 421.1220; found: 421.1217. NMR Spectroscopic data for the minor one: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 4.78 - 4.66 (m, 1H), 2.32 - 2.26 (m, 1H), 1.59 (s, 1H).

Hexyl 6-bromo-1,3-dimethyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6n)



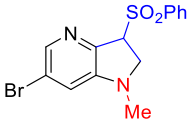
Compound 6n was prepared by the **general procedure A: 1h** (40.0 mg, 0.10 mmol), **2cb** (23 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 20% EtOAc/hexanes) to give the product **6n** (25.1 mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.8 Hz, 1H), 6.78 (d, *J* = 1.8 Hz, 1H), 4.14 (td, *J* = 6.7, 1.91 Hz, 2H), 4.01 (dd, *J* = 9.3, 1.6 Hz, 1H), 3.25 (dd, *J* = 9.4, 1.6 Hz, 1H), 2.81 (d, *J* = 1.6 Hz, 3H), 1.64 - 1.57 (m, 5H), 1.26 (d, *J* = 5.2 Hz, 6H), 0.92 - 0.84 (m, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.14, 152.43, 147.00, 138.40, 120.45, 115.15, 65.75, 64.93, 51.48, 34.75, 31.30, 28.43, 25.36, 22.50, 21.89, 13.95. ESI-HRMS (m/z): $[M+H]^{+}$calcd for $C_{16}H_{24}{}^{79}BrN_2O_2$: 355.1021; found: 355.1025.

6-Bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (6o)



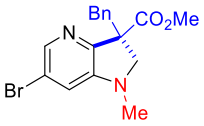
Compound 6o was prepared by the **general procedure A: 1h** (40.0 mg, 0.10 mmol), **2aa** (8 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) to give the product **6o** (11 mg, 46%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.85 (d, *J* = 1.9 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 4.52 (dd, *J* = 9.8, 7.6 Hz, 1H), 3.95 (t, *J* = 9.7 Hz, 1H), 3.72 (dd, *J* = 9.6, 7.6 Hz, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 147.74, 145.65, 138.26, 121.10, 118.09, 115.79, 57.05, 33.84, 31.88. ESI-HRMS (m/z): $[M+H]^{+}$calcd for $C_9H_9{}^{79}BrN_3$: 237.9980; found: 237.9970.

6-Bromo-1-methyl-3-(phenylsulfonyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (6p)



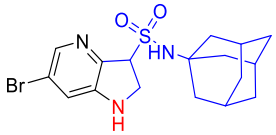
Compound 6p was prepared by the **general procedure A: 1h** (40.0 mg, 0.10 mmol), **2ba** (20.1 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) to give the product **6p** (26.4 mg, 75%). ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.77 - 7.64 (m, 4H), 7.64 - 7.53 (m, 2H), 6.87 (d, J = 1.9 Hz, 1H), 4.91 (dd, J = 9.8, 3.0 Hz, 1H), 4.16 (dd, J = 11.9, 3.0 Hz, 1H), 3.87 (dd, J = 11.9, 9.9 Hz, 1H), 2.76 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 149.27, 143.39, 138.07, 137.54, 133.83, 129.23, 128.68, 121.70, 114.95, 66.38, 54.14, 33.15. ESI-HRMS (m/z): [M+H]$^+$calcd for $C_{14}H_{14}{}^{79}BrN_2O_2S$: 352.9959; found: 352.9952.

Methyl 3-benzyl-6-bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6q)



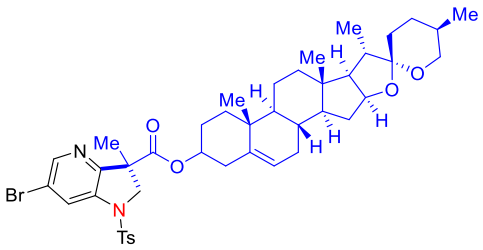
Compound 6q was prepared by the **general procedure A: 1h** (40.0 mg, 0.10 mmol), **2cb** (22 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 8% EtOAc/hexanes) to give the product **6q** (23.4 mg, 65%). ^{1}H NMR (400 MHz, Methanol-d_4) δ 7.79 (d, J = 1.9 Hz, 1H), 7.25 - 7.16 (m, 3H), 7.05 - 7.01 (m, 2H), 6.88 (d, J = 1.8 Hz, 1H), 3.91 (d, J = 10.0 Hz, 1H), 3.75 (s, 3H), 3.54 (d, J = 10.0 Hz, 1H), 3.46 (d, J = 13.7 Hz, 1H), 3.25 (d, J = 13.6 Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 172.12, 150.18, 147.40, 138.31, 136.51, 129.76, 128.37, 126.92, 120.99, 115.15, 60.67, 56.71, 52.88, 41.25, 34.53, 29.70. ESI-HRMS (m/z): [M+H]$^+$calcd for $C_{17}H_{18}{}^{79}BrN_2O_2$: 361.0551; found: 361.0516.

***N*-(Adamantan-1-yl)-6-bromo-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-sulfonamide (7a)**



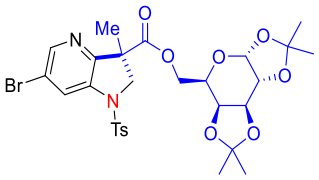
Compound 7a was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2bg** (28.7 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give **7a** (25.1 mg, 61%) as an off-white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.76 (d, J = 2.0 Hz, 1H), 7.01 (s, 1H), 6.98 (d, J = 2.0 Hz, 1H), 6.32 (d, J = 2.1 Hz, 1H), 4.68 (t, J = 7.1 Hz, 1H), 3.91 (dd, J = 7.3, 1.7 Hz, 2H), 2.02 (s, 3H), 1.88 (d, J = 3.0 Hz, 6H), 1.59 (d, J = 3.4 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.22, 144.68, 137.47, 121.19, 116.56, 66.03, 54.30, 47.93, 43.09, 36.10, 29.51. ESI-HRMS (m/z): [M+H]$^+$calcd for $C_{17}H_{23}{}^{79}BrN_3O_2S$: 412.0694; found: 412.0696.

(5'*R*,6*aR*,6*bS*,8*aS*,8*bR*,9*S*,10*R*,11*aS*,12*aS*,12*bS*)-5',6a,8a,9-Tetramethyl-1,3,3',4,4',5,5',6,6a,6b,6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl 6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (7b)



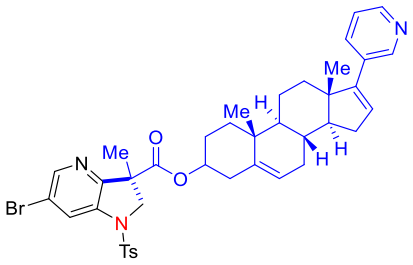
Compound 7b was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2da** (57.8 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **7b** (37.9 mg, 47%) as a white solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.24 (d, J = 2.1 Hz, 1H), 8.03 (d, J = 2.0 Hz, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.49 (d, J = 8.0 Hz, 2H), 5.39 - 5.32 (m, 1H), 4.48 - 4.34 (m, 3H), 3.91 (d, J = 11.0 Hz, 1H), 3.45 - 3.39 (m, 1H), 3.31 (t, J = 10.9 Hz, 1H), 2.43 (d, J = 3.0 Hz, 3H), 2.13 - 2.02 (m, 8H), 2.02 - 1.83 (m, 4H), 1.82 - 1.48 (m, 8H), 1.45 (s, 3H), 1.42 - 1.02 (m, 8H), 1.01 (s, 3H), 0.96 (d, J = 7.0 Hz, 3H), 0.94 - 0.86 (m, 1H), 0.83 (s, 3H), 0.78 (d, J = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.65, 154.00, 145.39, 145.38, 144.80, 139.54, 139.51, 137.19, 133.68, 130.19, 127.43, 122.97, 122.95, 122.28, 122.26, 119.60, 108.64, 80.53, 74.89 (d, J = 2.7 Hz), 66.33, 62.60, 59.48, 56.31, 50.90, 50.02, 41.49, 40.10, 39.51, 37.53, 37.45, 36.75, 36.66, 36.52, 31.83, 31.63, 31.35, 30.22, 27.21, 21.64, 20.71, 20.69, 20.65, 18.77, 16.56, 15.74, 14.13. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{43}H_{56}{}^{79}BrN_2O_6S$: 807.3042; found: 807.3049.

((3a*R*,5*R*,5a*S*,8a*S*,8b*R*)-2,2,7,7-Tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-5-yl)methyl 6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (7c)



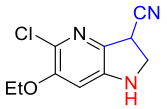
Compound 7c was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2db** (39.4 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **7c** (27.4 mg, 42%) as an off-yellow solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 8.23 (dd, J = 3.6, 2.0 Hz, 1H), 7.98 (dd, J = 9.2, 2.0 Hz, 1H), 7.86 (t, J = 8.8 Hz, 2H), 7.48 (d, J = 8.1 Hz, 2H), 5.43 (dd, J = 8.3, 5.0 Hz, 1H), 4.64 – 4.53 (m, 2H), 4.34 (dt, J = 4.5, 2.1 Hz, 1H), 4.14 - 4.05 (m, 2H), 3.95 - 3.83 (m, 2H), 2.44 (s, 3H), 1.47 (s, 3H), 1.42 (s, 3H), 1.38 (s, 3H), 1.33 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 171.27, 145.27, 144.99, 144.89, 137.23, 133.69, 130.19, 130.16, 127.51, 127.40, 123.15, 122.98, 109.05, 109.00, 108.30, 70.74, 70.66, 70.42, 65.80, 65.52, 64.12, 59.55, 59.47, 50.90, 25.41, 24.28, 23.65, 21.49, 21.36, 20.63, 13.45. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{28}H_{34}{}^{79}BrN_2O_9S$: 653.1168; found: 653.1178.

(8*R*,9*S*,10*R*,13*S*,14*S*)-10,13-Dimethyl-17-(pyridin-3-yl)-2,3,4,7,8,9,10,11,12,13,14,15-dodecahydro-1*H*-cyclopenta[a]phenanthren-3-yl 6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (7d)



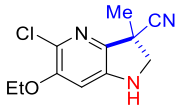
Compound 7d was prepared by the **general procedure A: 1a** (40.2 mg, 0.10 mmol), **2dc** (50.0 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **7d** (31.8 mg, 43%) as a white solid. ^{1}H NMR (400 MHz, Acetone-d_6) , 8.45 (dd, J = 4.8, 1.6 Hz, 1H), 8.25 (t, J = 2.0 Hz, 1H), 8.04 (t, J = 1.6 Hz, 1H), 7.87 (dd, J = 8.3, 1.5 Hz, 2H), 7.77 (dt, J = 7.9, 2.0 Hz, 1H), 7.49 (d, J = 8.1 Hz, 2H), 7.31 (dd, J = 8.0, 4.7 Hz, 1H), 6.08 (dt, J = 3.3, 2.1 Hz, 1H), 5.41 (ddd, J = 9.2, 5.1, 2.4 Hz, 1H), 4.45 (dd, J = 11.0, 2.3 Hz, 1H), 4.43 - 4.39 (m, 1H) 3.92 (d, J = 10.9 Hz, 1H), 2.44 (s, 3H), 2.34 - 2.26 (m, 1H), 2.09 – 2.05 (m, 4H), 1.95 - 1.47 (m, 5H), 1.46 (s, 1H), 1.33 - 1.18 (m, 2H), 1.09 (s, 3H), 1.06 (s, 3H), 0.97 - 0.80 (m, 1H). ^{13}C NMR (101 MHz, Acetone-d_6) δ 170.65, 151.86, 147.94, 147.70, 145.38, 144.82, 144.80, 139.91, 137.21, 133.69, 133.34, 132.66, 130.19, 128.83, 127.43, 123.05, 122.96, 122.25, 119.60, 74.88, 59.49, 57.54, 50.91, 50.30, 47.14, 37.56, 36.69, 36.60, 35.09, 31.42, 31.29, 30.34, 27.21, 27.13, 21.63, 20.67, 18.71, 15.98. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{40}H_{45}{}^{79}BrN_3O_4S$: 742.2314; found:742.2325.

5-Chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (9a)



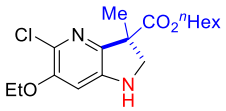
Compound 9a was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2aa** (8 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9a** (13.6 mg, 62%) as an off-white solid. ^{1}H NMR (400 MHz, Chloroform-d) δ 6.59 (s, 1H), 4.27 (dd, J = 9.8, 7.1 Hz, 1H), 4.07 (q, J = 7.0 Hz, 2H), 4.00 (d, J = 9.8 Hz, 1H), 3.93 (dd, J = 9.8, 7.0 Hz, 1H), 1.49 (t, J = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-d) δ 152.15, 144.63, 134.02, 118.24, 103.58, 65.23, 50.73, 32.50, 14.51. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{10}H_{11}{}^{35}ClN_3O$: 224.0591; found: 224.0574.

5-Chloro-6-ethoxy-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (9b)



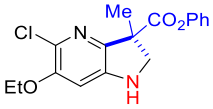
Compound 9b was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2ab** (10 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9b** (17.8 mg, 75%) as an off-white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.56 (s, 1H), 4.09 - 4.00 (m, 3H), 3.58 (d, *J* = 9.7 Hz, 1H), 1.73 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 152.04, 144.16, 138.39, 130.87, 121.44, 103.45, 65.17, 58.81, 39.90, 28.21, 23.18, 14.55. ESI-HRMS (m/z): $[M+H]^{+}$calcd for $C_{11}H_{12}{}^{35}ClN_3O$: 238.0747; found: 238.0741.

Hexyl 5-chloro-6-ethoxy-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9c)



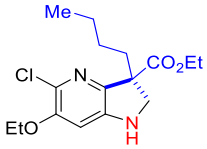
Compound 9c was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2ca** (19.4 mg, 0.2 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9c** (22.6 mg, 68%) as an off-brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) 6.59 (s, 1H), 4.16 (d, *J* = 9.8 Hz, 1H), 4.11 (t, *J* = 6.7 Hz, 2H), 4.04 (d, *J* = 6.8 Hz, 2H), 3.58 (d, *J* = 9.7 Hz, 1H), 3.05 (br. s, 1H) 1.61 (s, 3H), 1.45 (t, *J* = 6.9 Hz, 2H), 1.56 (t, *J* = 6.6 Hz, 1H), 1.48 - 1.39 (m, 5H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.61, 151.00, 143.53, 103.97, 65.67, 65.11, 58.00, 51.82, 31.35, 28.45, 25.40, 22.51, 21.94, 14.63, 13.99. ESI-HRMS (m/z): $[M+H]^{+}$calcd for $C_{17}H_{26}{}^{35}ClN_2O_3$: 341.1632; found: 341.1630.

Phenyl 5-chloro-6-ethoxy-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9d)



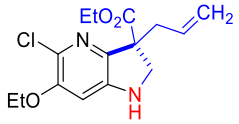
Compound 9d was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2cb** (20.7 mg, 0.2 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9d** (26.5 mg, 78%) as an off-yellow solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 (t, *J* = 7.9 Hz, 2H), 7.22 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.8 Hz, 2H), 6.59 (s, 1H), 4.33 (d, *J* = 9.8 Hz, 1H), 4.06 (qd, *J* = 7.0, 1.3 Hz, 2H), 3.61 (d, *J* = 9.8 Hz, 1H), 3.08 (br. s, 1H), 1.77 (s, 3H), 1.48 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.30, 151.23, 150.93, 144.67, 142.61, 130.29, 129.33, 125.88, 121.48, 103.41, 65.05, 58.04, 51.96, 22.11, 14.64. ESI-HRMS (m/z): $[M+H]^{+}$calcd for $C_{17}H_{18}{}^{35}ClN_2O_3$: 333.1006; found: 333.1001.

Ethyl 3-butyl-5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9e)



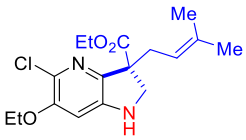
Compound 9e was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2cc** (18.7 mg, 0.2 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9e** (21.8 mg, 67%) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.53 (s, 1H), 4.29 - 4.16 (m, 3H), 4.05 (q, *J* = 7.0 Hz, 2H), 3.56 (d, *J* = 9.8 Hz, 1H), 1.94 – 1.80 (m, 1H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.38 - 1.23 (m, 6H), 0.90 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.91, 150.99, 144.90, 141.79, 103.05, 64.98, 61.42, 55.94, 55.04, 35.70, 29.72, 26.89, 22.95, 14.65, 14.21, 13.99. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{16}H_{24}{}^{35}ClN_2O_3$: 327.1476; found: 327.1477.

Ethyl 3-allyl-5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9f)



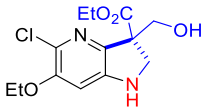
Compound 9f was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2cd** (16.9 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9f** (18.3 mg, 59%) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.53 (s, 1H), 5.75 - 5.60 (m, 1H), 5.20 - 5.06 (m, 2H), 4.23 (qd, *J* = 7.1, 1.5 Hz, 2H), 4.16 (d, *J* = 10.0 Hz, 1H), 4.06 (q, *J* = 7.0 Hz, 2H), 3.63 (d, *J* = 9.9 Hz, 1H), 2.98 (dd, *J* = 14.1, 7.4 Hz, 1H), 2.69 (dd, *J* = 14.1, 7.0 Hz, 1H), 1.48 (t, *J* = 7.0 Hz, 3H), 1.28 (t, *J* = 3.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.51, 151.12, 145.09, 133.21, 118.88, 103.01, 64.98, 61.59, 55.42, 54.25, 40.02, 29.72, 14.64, 14.21. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{15}H_{20}{}^{35}ClN_2O_3$: 311.1162; found: 311.1157.

Ethyl 5-chloro-6-ethoxy-3-(3-methylbut-2-en-1-yl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9g)



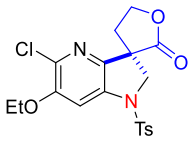
Compound 9g was prepared by the **general procedure A: 8** (44.0 mg, 0.10 mmol), **2ce** (20.0 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) afforded **9g** (16.6 mg, 49%) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.53 (s, 1H), 5.03 - 4.99 (m, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.15 (d, *J* = 8.4 Hz, 1H), 4.11 - 4.00 (m, 2H), 3.55 (d, *J* = 9.8 Hz, 1H), 2.94 (dd, *J* = 14.7, 7.5 Hz, 1H), 2.61 (dd, *J* = 14.7, 7.2 Hz, 1H), 1.68 (s, 3H), 1.63 (s, 3H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.26 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.79, 151.01, 145.01, 141.71, 135.39, 118.68, 103.09, 64.98, 64.39, 61.46, 56.07, 54.40, 34.07, 26.00, 18.10, 14.65, 14.19. ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{17}H_{24}{}^{35}ClN_2O_3$:339.1476; found: 339.1480.

Ethyl 6-bromo-3-(hydroxymethyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9h)



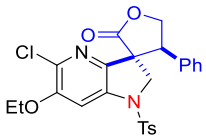
Compound 9h was prepared by the **general procedure F: 8** (44.0 mg, 0.10 mmol), **2cf** (15.7 mg, 0.2 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 40% EtOAc/hexanes) afforded **9h** (19.5 mg, 65%) as a brown solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.57 (d, *J* = 1.1 Hz, 1H), 4.24 (qq, *J* = 6.8, 3.5 Hz, 2H), 4.15 (d, *J* = 11.3 Hz, 1H), 4.09 - 4.00 (m, 3H), 3.92 - 3.84 (m, 2H), 2.96 (br. s, 1H), 1.47 (t, *J* = 7.0 Hz, 3H), 1.27 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 172.67, 151.51, 145.66, 139.81, 103.20, 65.26, 65.02, 61.82, 57.52, 14.60, 14.13. ESI-HRMS (m/z): $[M+H]^+$ calcd for $C_{13}H_{18}{}^{35}ClN_2O_4$:301.0955; found: 301.0957.

5'-Chloro-6'-ethoxy-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (9i)



Compound 9i was prepared by the **general procedure B: 8** (44.0 mg, 0.10 mmol), **2co** (11 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) to give **9i** (21.1 mg, 51%) as a white solid. ^{1}H NMR (400 MHz, Acetone-d_6) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.60 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 2H), 4.54 (td, *J* = 8.8, 7.0 Hz, 1H), 4.39 (td, *J* = 8.7, 3.5 Hz, 1H), 4.38 - 4.25 (m, 3H), 4.16 (d, *J* = 11.6 Hz, 1H), 2.51 - 2.42 (m, 1H), 2.40 (s, 3H), 2.28 (ddd, *J* = 12.9, 7.0, 3.4 Hz, 1H), 1.48 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (151 MHz, Acetone-d_6) δ 176.75, 152.55, 146.32, 144.16, 137.52, 135.93, 134.04, 131.08, 128.51, 108.83, 66.73, 66.34, 59.10, 51.63, 36.07, 21.50, 14.78. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{19}H_{20}{}^{35}ClN_2O_5$: 423.0782; found: 423.0780.

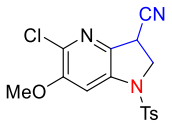
6'-Bromo-4-phenyl-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (9j)



Compound 9j was prepared by the **general procedure B: 8** (44.0 mg, 0.10 mmol), **2cp** (20.9 mg, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 30% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **9j** (22.8 mg, 47%) as a white solid. ^{1}H NMR (600 MHz, DMSO-d_6) δ 7.76 (d, *J* = 8.4 Hz, 2H), 7.53 (s, 1H), 7.45 (d, *J* = 7.5 Hz, 2H), 7.42 - 7.35 (m, 5H), 5.70 (dd, *J* = 10.2, 6.3 Hz, 1H), 4.28 (d, *J* = 11.8 Hz, 1H), 4.11 (d, *J* = 11.9 Hz, 1H), 3.99

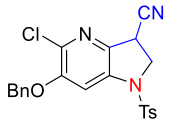
(s, 3H), 2.34 (s, 3H). ^{13}C NMR (151 MHz, DMSO-d_6) δ 175.70, 152.49, 145.80, 143.28, 138.62, 136.57, 134.41, 132.53, 130.78, 129.24, 129.05, 127.96, 127.06, 107.81, 79.32, 58.04, 57.35, 52.84, 42.82, 29.47, 21.53. ESI-HRMS (m/z): $[M+Na]^+$calcd for $C_{24}H_{22}{}^{35}ClN_2O_5S$: 485.0938; found: 485.0934.

5-Chloro-6-methoxy-1-tosyl-2,3-dihydro-1H-pyrrolo[3,2-b]pyridine-3-carbonitrile (9k)



Compound 9k was prepared by the **general procedure B: 8** (43.5 mg, 0.10 mmol), **2aa** (8 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 40% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **9j** (22.9 mg, 63%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 (d, *J* = 8.4 Hz, 2H), 7.58 (s, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 4.33 - 4.26 (m, 1H), 4.13 (qd, *J* = 6.4, 3.7 Hz, 2H), 4.03 (s, 3H), 2.45 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 153.01, 145.99, 137.07, 136.69, 135.43, 132.51, 130.50, 127.25, 116.46, 107.44, 56.83, 52.36, 31.39, 21.69. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{16}H_{15}{}^{35}ClN_3O_3S$: 364.0523; found: 364.0514.

6-(Benzyloxy)-5-chloro-1-tosyl-2,3-dihydro-1H-pyrrolo[3,2-b]pyridine-3-carbonitrile (9l)



Compound 9l was prepared by the **general procedure B: 8** (51.2 mg, 0.10 mmol), **2cp** (8 μL, 0.12 mmol), DBU (23 μL, 0.15 mmol) were employed. FCC (eluent: 25% EtOAc/hexanes) to give the crude product was directly used in **general procedure C:** TsCl (21.1 mg, 0.11 mmol), DMAP (13.4 mg, 0.11 mmol) were employed. FCC (eluent: 15% EtOAc/hexanes) afforded **9j** (25.9 mg, 59%) as a white solid. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.57 - 7.36 (m, 5H), 7.32 (d, *J* = 8.40 Hz, 1H), 7.20 (d, *J* = 8.09 Hz, 2H), 5.36 (dd, *J* = 12.8, 2.0 Hz, , 2H), 4.24 (dd, *J* = 10.20, 9.16 Hz, 1H), 4.16 - 4.02 (m, 2H), 2.42 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.59, 145.73, 137.04, 136.71, 135.55, 135.02, 132.13, 130.38, 129.09, 128.63, 127.31, 127.17, 116.46, 109.15, 71.16, 52.23, 31.33, 22.67, 14.14. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{22}H_{19}{}^{35}ClN_3O_3S$: 440.0836; found: 440.0833.

X-ray crystallographic data

	9a-Ts	**4b**	**9c-Ts**
CCDC number	2222506	2222507	2222508
Empirical formula	$C_{17}H_{16}ClN_3O_3S$	$C_{21}H_{19}BrN_2O_4S_2$, C_3H_6O	$C_{24}H_{23}ClN_2O_5S$
Formula weight	377.84	565.49	486.95
Temperature (K)	293 (2)	293 (2)	293 (2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	monoclinic	triclinic	triclinic
Space group	*P1*	*P1*	*C1*
a (Å)	11.4261(5)	8.1423(8)	21.5028(18)
b (Å)	9.6846 (4)	12.2839(8)	9.2793(6)
c (Å)	16.4306 (7)	12.9853(9)	24.775(2)
α (˚)	90	92.802(6)	90
β (˚)	103.775 (4)	98.268(7)	108.353(10)
γ (˚)	90	103.730(7)	90
Volume (Å^3)	1765.86 (13)	1243.89(18)	4691.9(7)
Z	4	2	8
Calculated density (g/cm^3)	1.421	1.510	1.379
Absorption coefficient (mm^{-1})	0.356	1.858	0.290
F(000)	784	580	2032
Crystal size (mm)	0.35 × 0.3 × 0.25	0.35 × 0.30 × 0.25	0.35 × 0.30 × 0.25
θ range (deg)	3.247 to **26.370**	3.182 to **26.370**	3.027 to **26.370**
Limiting indices	$-12 \le h \le 14$	$-9 \le h \le 10$	$-26 \le h \le 26$
	$-12 \le k \le 6$	$-13 \le k \le 15$	$-7 \le k \le 11$
	$-18 \le l \le 20$	$-16 \le l \le 16$	$-30 \le l \le 18$
Reflections collected	8593 [R_{int} = 0.0232]	10277 [R_{int} = 0.0350]	10760 [R_{int} = 0.0454]
Completeness to θ = **26.305**	0.998	0.998	0.998
Data / restraints / parameters	**3599** / 0 / 228	**5093** / 0 / 311	**4793**/0/301
Goodness of fit on F^2	1.048	1.001	1.050
R_1[a], wR_2[b] [$I > 2\sigma(I)$]	R_1 = 0.0605 wR_2 =0.1036	R_1 = 0.1004 wR_2 =0.1130	R_1 = 0.1341 wR_2 =0.2256
R_1[a], wR_2[b] (all data)	R_1 = 0.0444 wR_2 = 0.1133	R_1 = 0.0543 wR_2 = 0.1347	R_1 = 0.2551 wR_2 = 0.1480
Largest diff. peak and hole (e. Å^{-3})	0.287 and -0.345	0.381 and -0.419	0.691 and -0.311

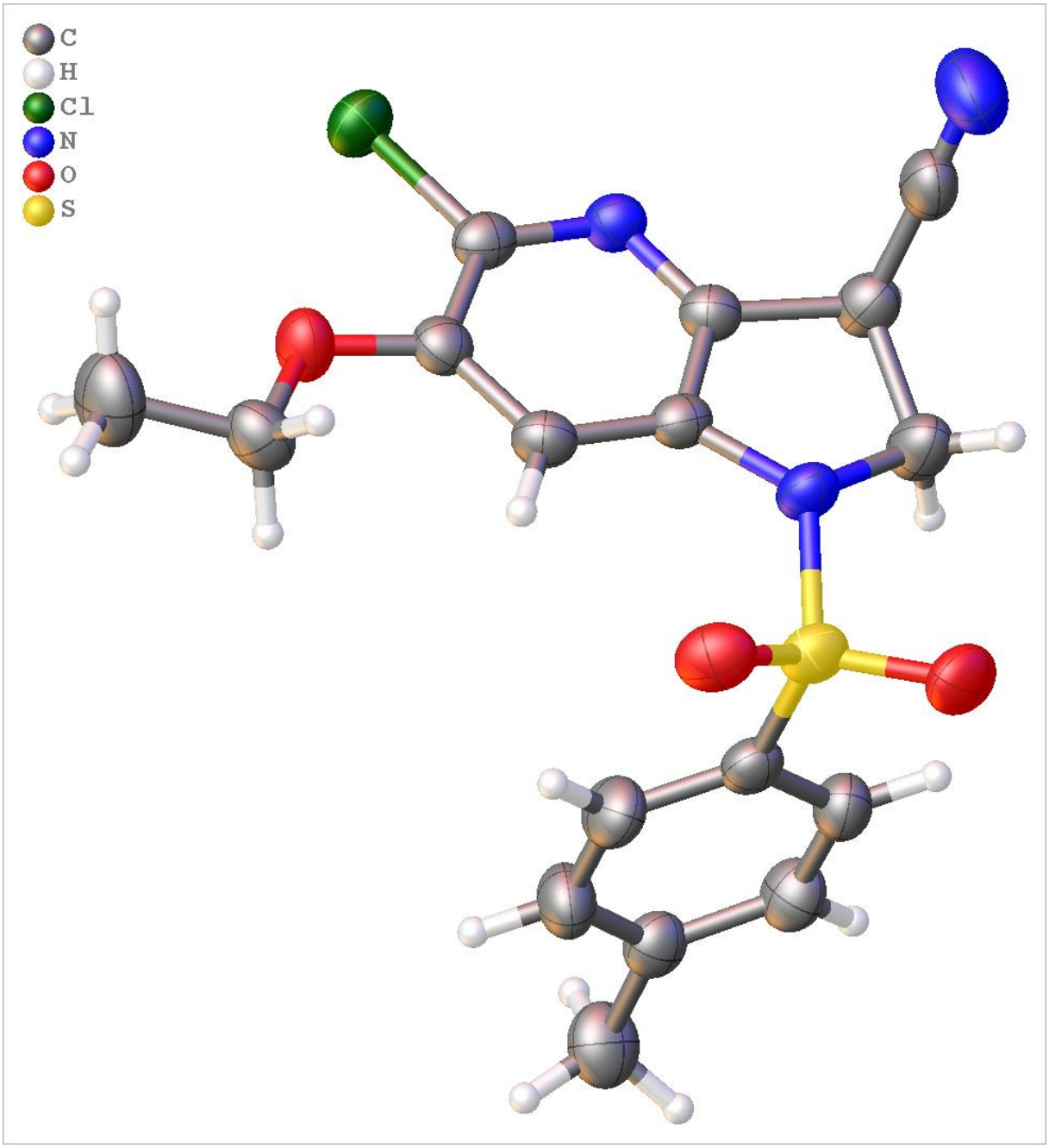


Figure S5. Crystal structure of **9a-Ts.**

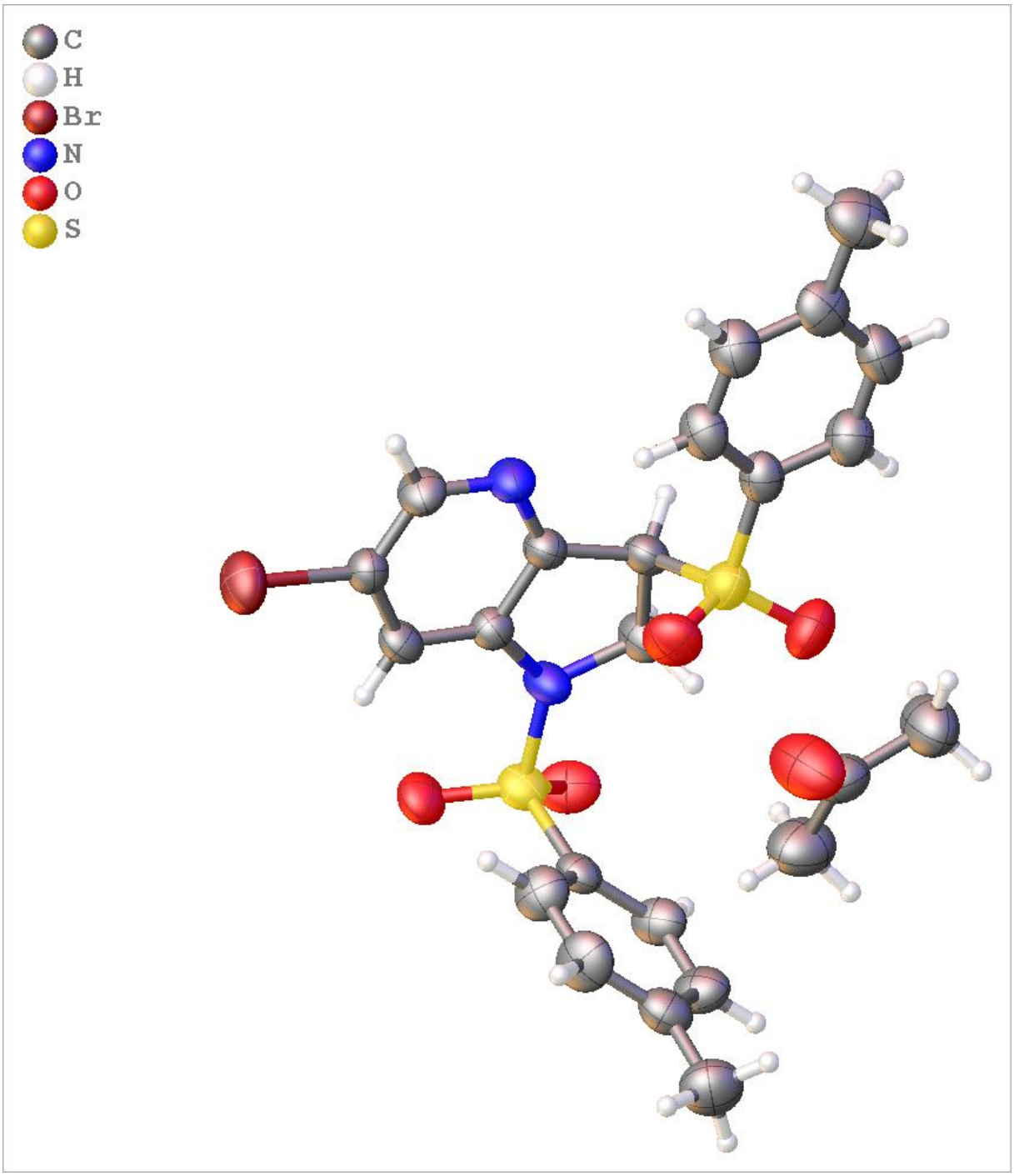


Figure S6. Crystal structure of **4b**

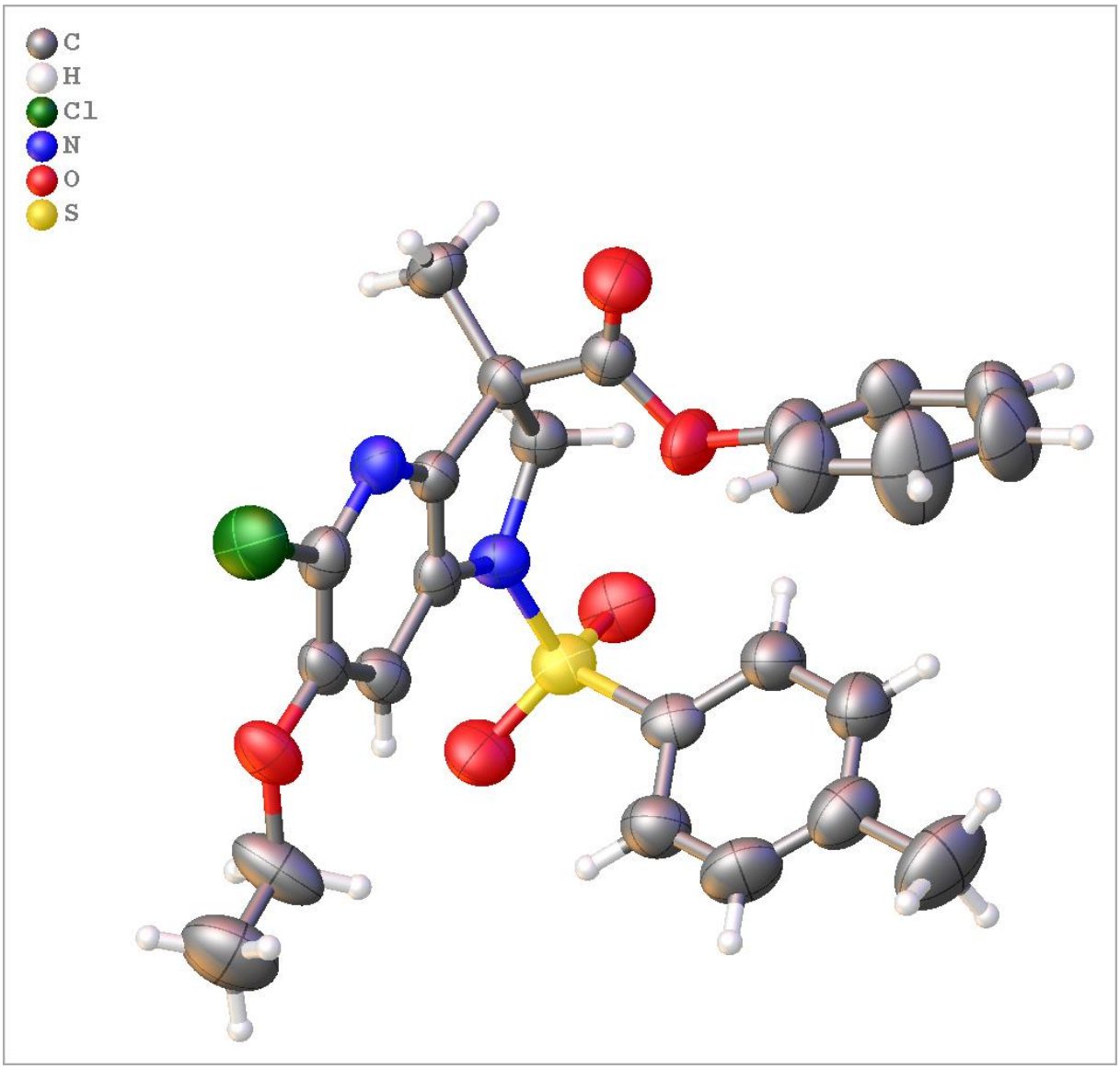


Figure S7. Crystal structure of **9c-Ts.**

Mechanism research

UV-VIS study

The UV-Vis spectra were recorded with the MAPADA P4 UV/VIS Spectrophotometer in different solvents, using the same concentration as in the reaction conditions.

UV-VIS study of 1a, 2a and DBU in Toluene

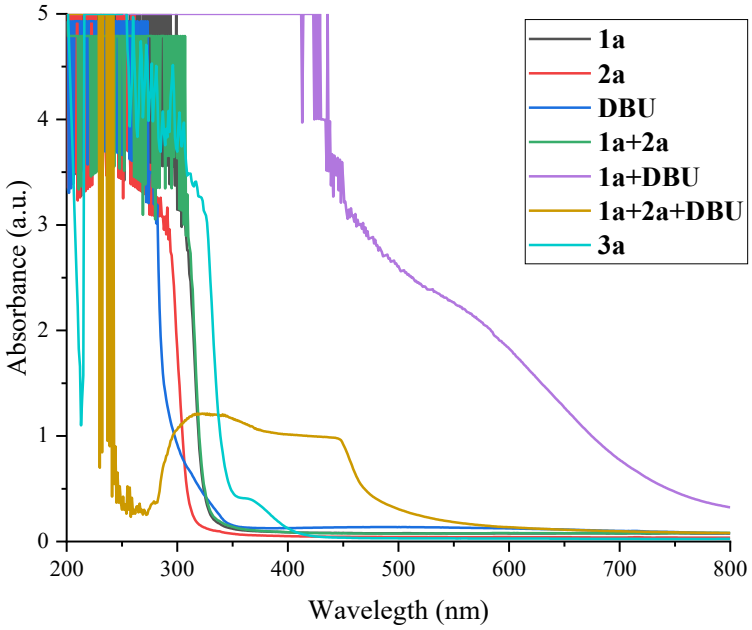


Figure S8. UV-Vis absorption spectra of **1a** (0.05 M) and **2a** (0.06 M) in toluene in presence of DBU (0.075 M). **1a** was partially dissolved.

UV-VIS study of 1a, 2a and DBU in acetonitrile

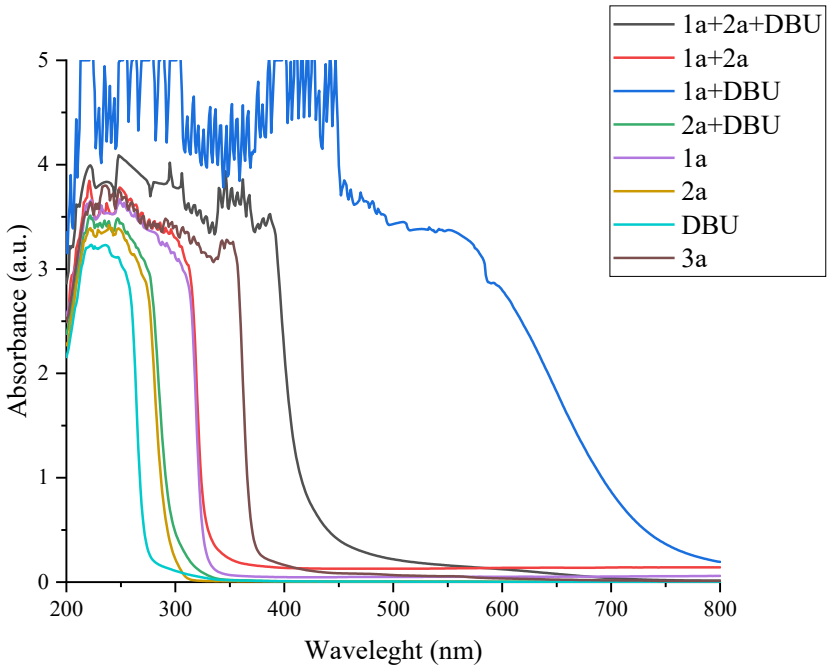


Figure S9. UV-VIS absorption spectra of **1a** (0.05 M) and **2a** (0.06 M) in acetonitrile in presence of DBU (0.075 M). **1a** was dissolved.

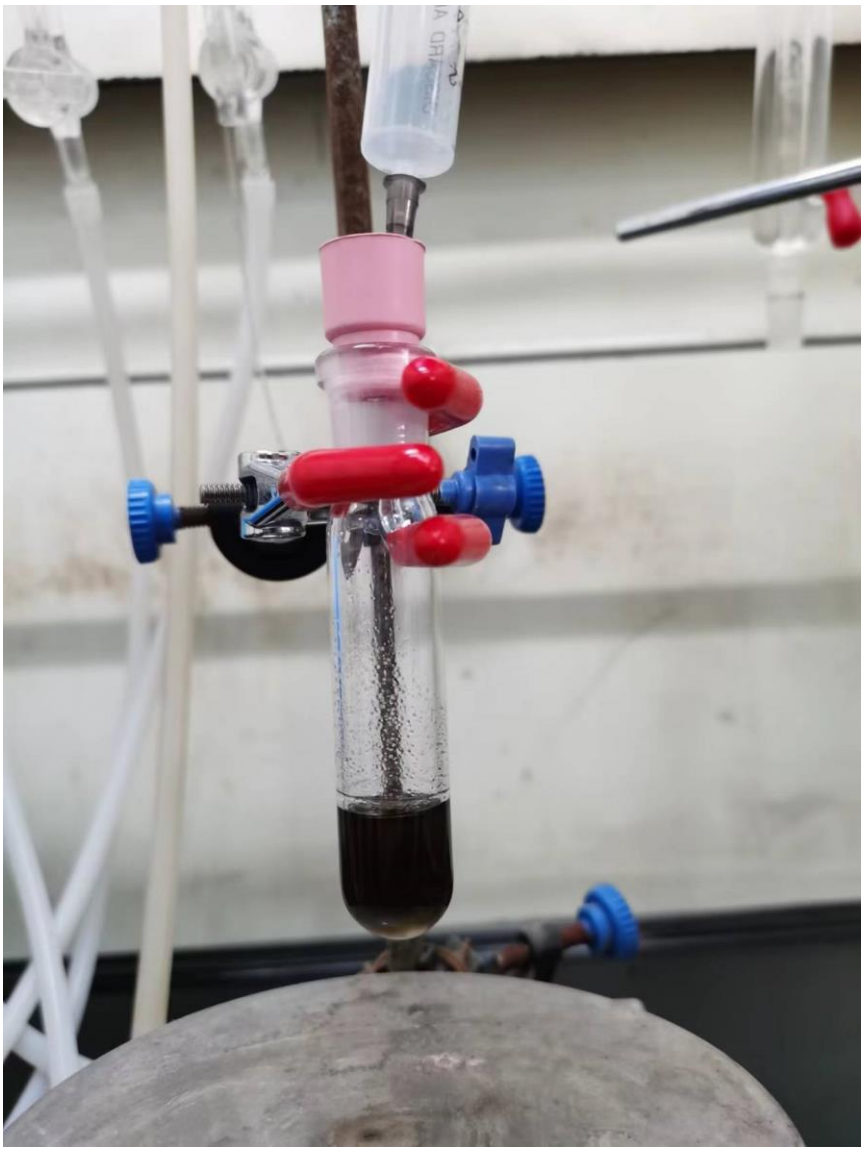


Figure S10. **1a** (0.05 M) and **DBU** (0.075 M) in toluene.

UV-VIS study of 12a, 1n, 1a and their mixtures

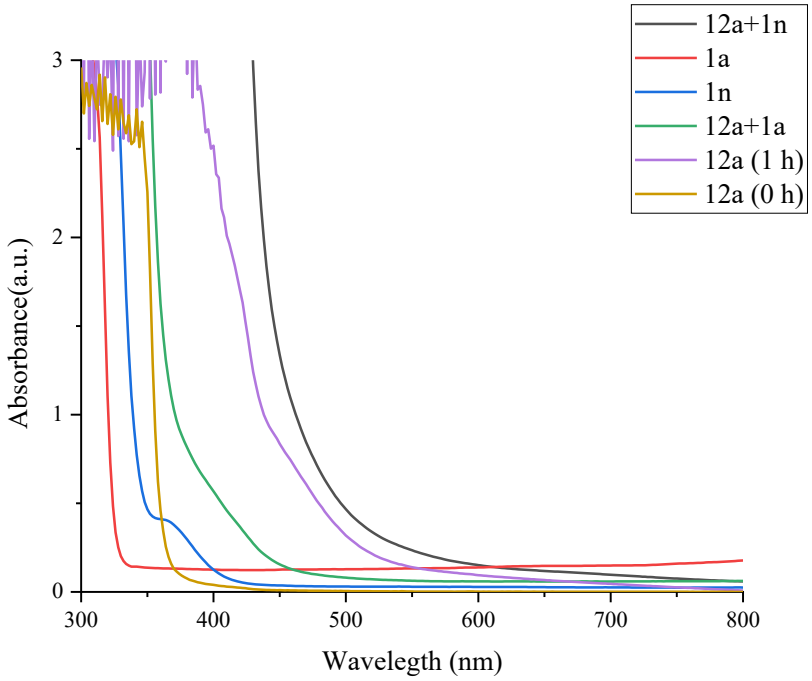


Figure S11. UV-VIS absorption spectra of **12a** (0.05 M), **1a** (0.05 M), **1n** (0.05 M) and their mixture (**12a**+**1a** or **12a**+**1n**) in acetonitrile. **1a** was partially dissolved.

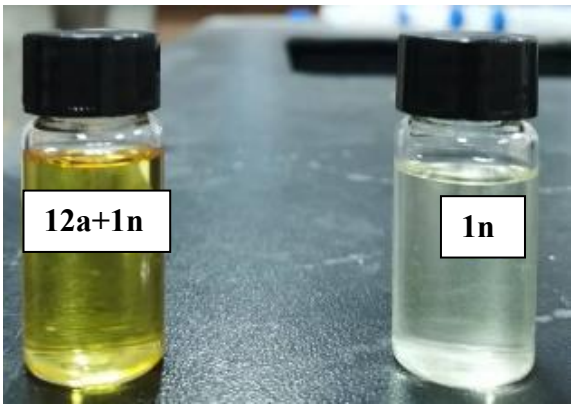


Figure S12. Left: the solvent of **12a** (0.05 M) + **1n** (0.05 M) in acetonitrile. Right: **1n** (0.05 M) in acetonitrile.

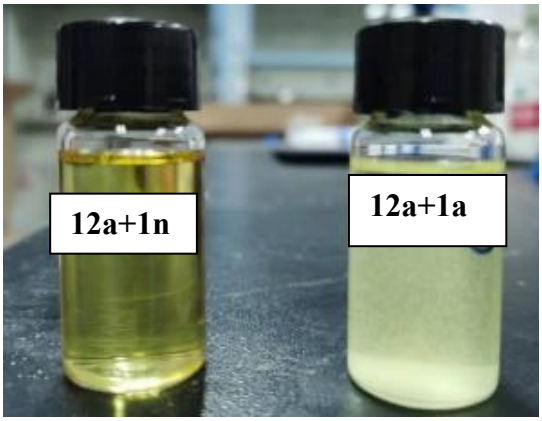


Figure S13. Left: the solvent of **12a** (0.05 M) + **1n** (0.05 M) in acetonitrile. Right: **12a** (0.05 M) + **1a** (0.05 M) in acetonitrile.

Comparison of UV-VIS spectra between 12a+1n and 1a+2a+DBU

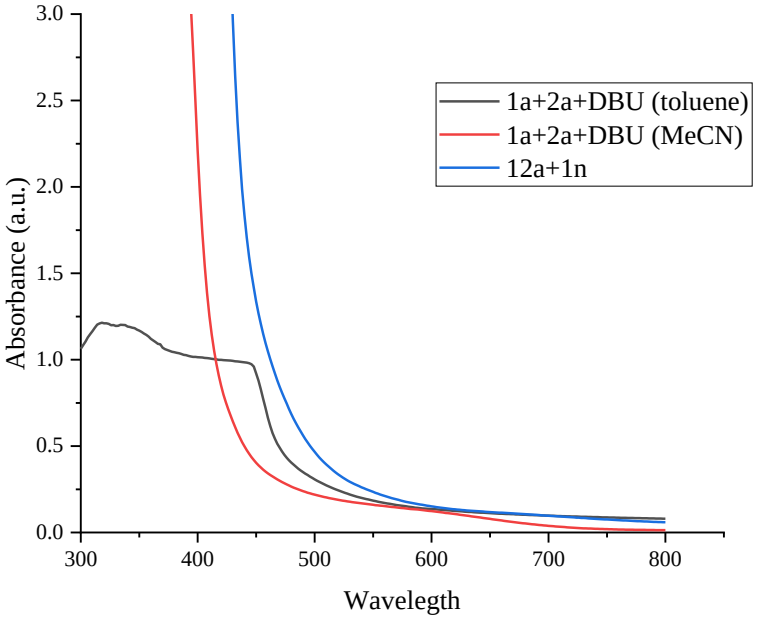


Figure S14. UV-VIS absorption spectra of **12a** (0.05 M) + **1n** (0.05 M) and **12a** (0.05 M) +**1a** (0.06 M) +**DBU** (0.075 M) in acetonitrile/toluene. **1a** was partially dissolved.

Light-on/off experiment

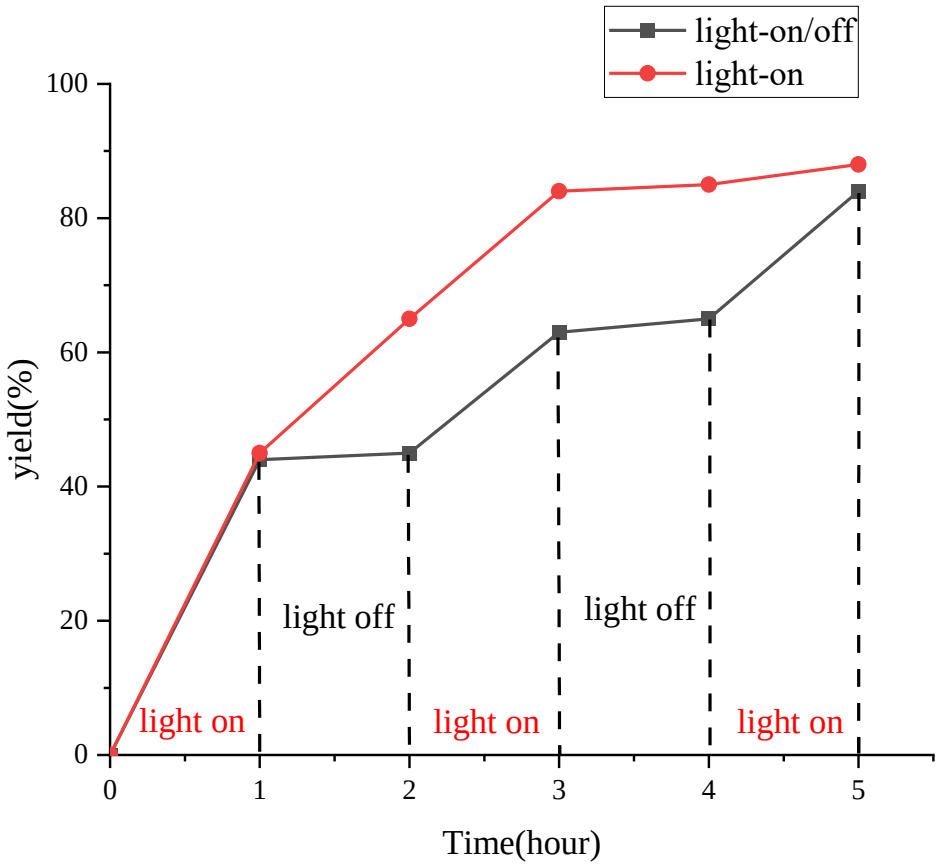


Figure S15. Light-on/off experiment of **1a**, **2a** and DBU in toluene. Redline is the yield of reaction continuous irradiated by visible-light. Blackline is the yield of reaction under irradiation of visible-light in the first, third and fifth hour.

CV study

Measurement conditions

A cylindrical three-electrode cell wass equipped with a glassy carbon working electrode, a 25 mm platinum wire as the counter electrode and Ag/AgCl (3.0 M NaCl) electrode as the reference electrode. The scan rate for the experiment was 50 mV/s/ The solution of pyridinium salt (10 mM) and *n*-Bu_4NPF_6 (100 mM) in Dry MeCN was degassed by Ar gas bubbling before the measurement, and the cyclic voltammetry was carried out under Ar atmosphere at room temperature. The experiment was measured by ElectraSyn 2.0, IKA.

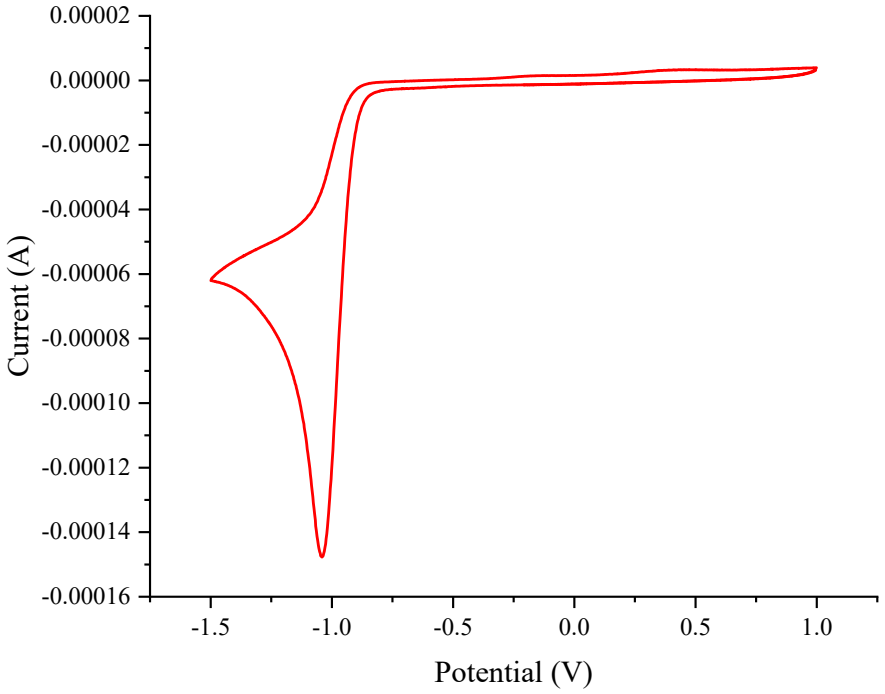


Figure S16. CV spectrum of **1a**

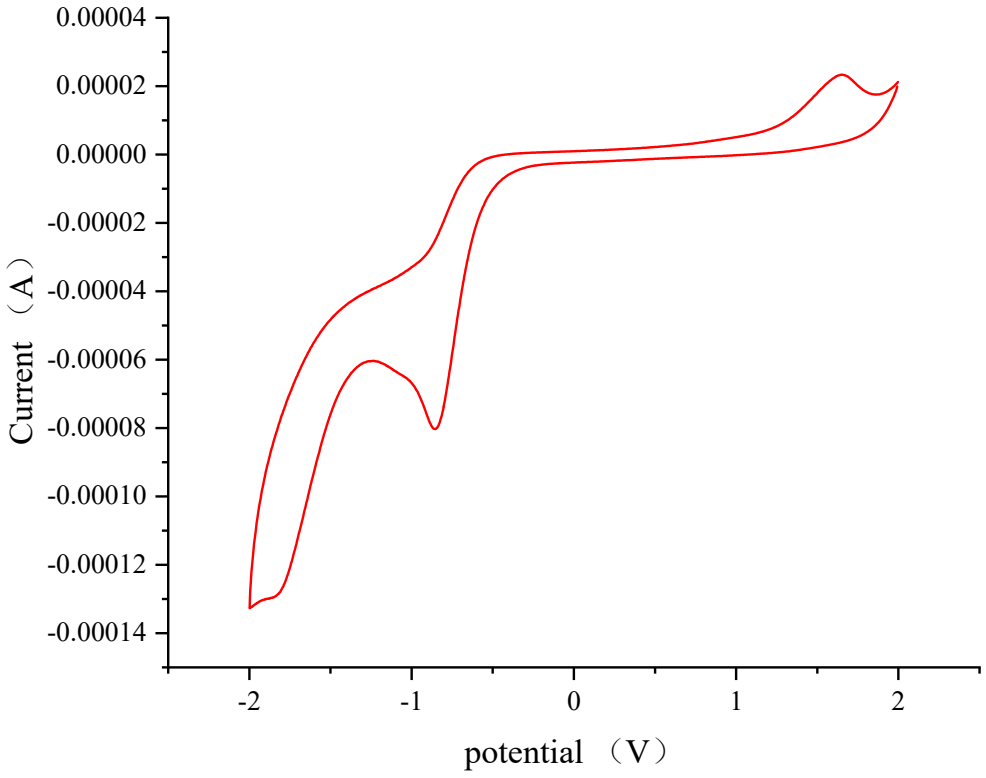
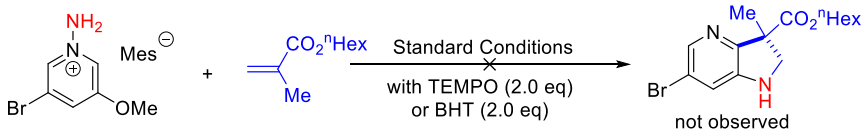


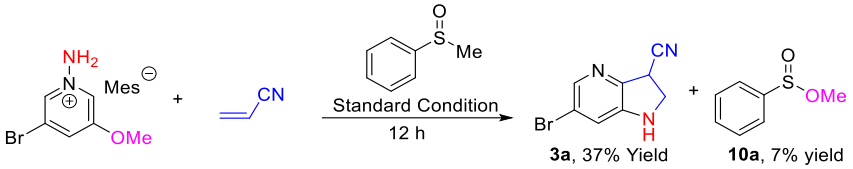
Figure S17. CV spectrum of **1n**

Radical inhibition reaction by TEMPO or BHT



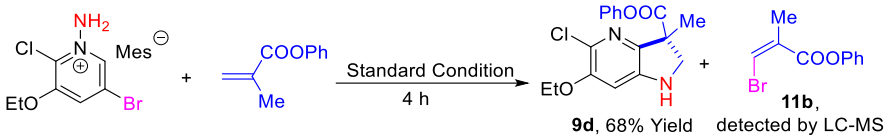
To a stirring suspension of *N*-aminopyridines **1a** (40.2 mg, 0.1 mmol), α,β-unsaturated esters (19.5 mg, 0.12 mmol) and TEMPO (31.3 mg, 0.2 mmol) or BHT (44.0 mg, 0.2 mmol) in toluene, DBU (25 μL, 0.15 mmol) was added dropwise at 0 °C under the irradiation of visible-light. Then the reaction mixture was stirred at ambient temperature for 4 h. The resulting mixture were poured into saturated sodium bicarbonate solution, extracted with ethyl acetate and washed with brine. Solvent was removed by rotary evaporation. TLC detected that no desired product was formed, which was further confirmed by HRMS analysis of the crude reaction mixture.

Radical trap reaction

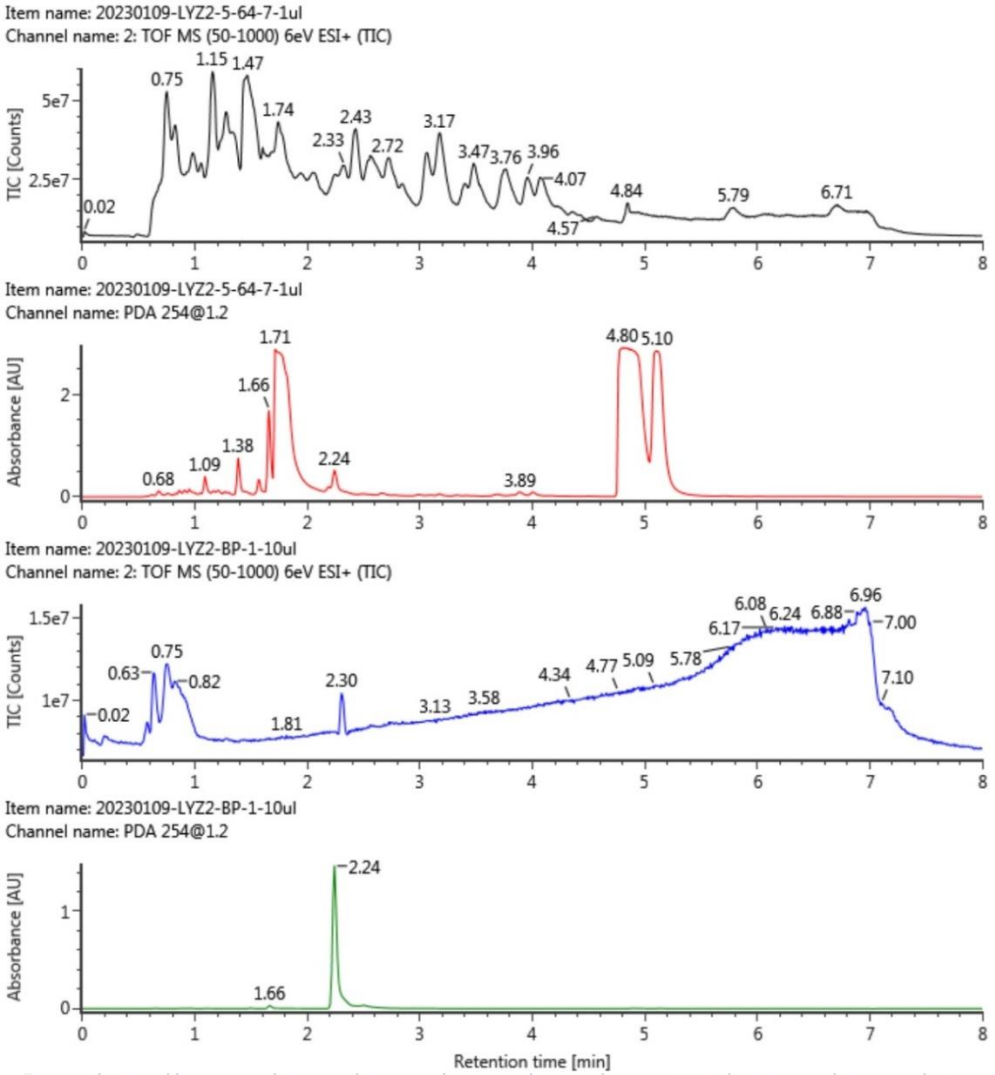


To a stirring suspension of *N*-aminopyridines **1a** (201 mg, 0.5 mmol), acrylonitrile (40 μL, 0.6 mmol) and methyl phenyl sulfone (156.0 mg, 1.0 mmol) in toluene, DBU (125 μL, 0.75 mmol) was added dropwise at 0 °C under the irradiation of visible-light. Then the reaction mixture was stirred at ambient temperature. Upon completion (12 h) as detected by TLC, the resulting mixture were poured into saturated sodium bicarbonate solution, extracted with ethyl acetate and washed with brine, solvent was removed by rotary evaporation and the residue was purified though FCC (eluent: 15% to 40% EtOAc/hexanes) to obtain the product **3a** (41.3 mg, 37%) and **10a** (5.3 mg, 7%).

10a: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.75 – 7.66 (m, 2H), 7.58 – 7.52 (m, 3H), 3.48 (s, 3H). ESI-HRMS (m/z): $[M+H]^+$calcd for $C_7H_9O_2S$: 157.0323; found:157.0321. The spectroscopic properties were consistent with the data available in the literature.[22]



To a stirring suspension of *N*-aminopyridines **8** (225 mg, 0.5 mmol) and phenyl methacrylate (97 μL, 0.6 mmol) in toluene, DBU (125 μL, 0.75 mmol) was added dropwise at 0 °C under the irradiation of visible-light. Then the reaction mixture was stirred at ambient temperature. Upon completion (4 h) as detected by TLC, the resulting mixture was concentrated under vacuum and the residue was directly send for LC-MS analysis.



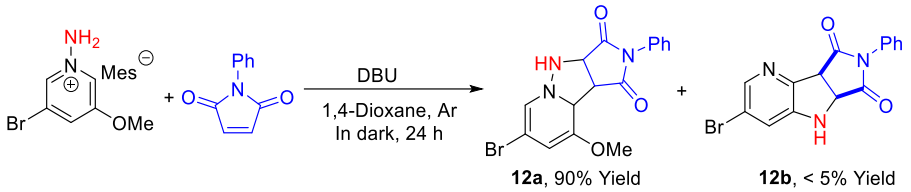
Com...	Identi...	Neutral...	Ob...	Observe...	Mass er...	Mass...	Observed RT...	Detector c...	Response	Adducts
LYZ	Ident...	239.97859	239.9799	262.9691	1.3	5.0	3.48	1357	1357	+Na

Com...	Identi...	Neutral...	Ob...	Observe...	Mass er...	Mass...	Observed RT...	Detector c...	Response	Adducts
LYZ	Ident...	239.97859	239.9788	240.9860	0.2	0.7	2.32	128506	58033	+H

Figure S18. LC-MS for detecting **11b**

The retention time for **11b** is at 2.24 min, the HRMS for HRMS: [M+H]+calcd for $C_{10}H_{10}BrO_2$: 240.9864; found: 240.9860; [M+Na]+calcd for $C_{10}H_9BrO_2Na$: 262.9684; found: 262.9691.

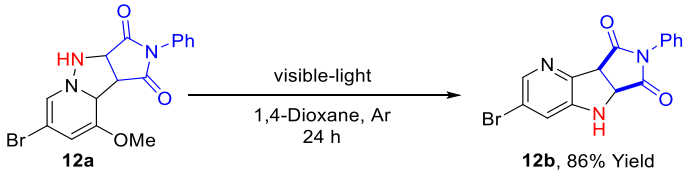
Identification of the intermediate



To a stirring suspension of *N*-aminopyridines **1a** (80.4 mg, 0.2 mmol) and N-phenylmaleimide **11** (41.6 mg, 0.24 mmol) in 1,4-dioxane, DBU (50 μL, 0.30 mmol) was added dropwise at 0 °C with the flask warped by aluminum film. Then the reaction mixture was stirred overnight at ambient temperature. Upon completion (24 h) as detected by TLC, the resulting mixture were poured into saturated sodium bicarbonate solution, extracted with ethyl acetate and washed with brine, solvent was removed by rotary evaporation and the residue was purified though FCC (eluent: 50% EtOAc/hexanes) to obtain the product **12a** (67.5 mg, 90%).

12a: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 – 7.45 (m, 2H), 7.42 (t, J = 6.7 Hz, 1H), 7.15 – 7.08 (m, 2H), 5.96 (s, 1H), 5.82 (d, J = 6.6 Hz, 1H), 5.25 (s, 1H), 4.45 (t, J = 7.5 Hz, 1H), 4.04 (d, J = 7.3 Hz, 1H), 3.72 (t, J = 8.1 Hz, 1H), 3.61 (d, J = 1.2 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.63, 173.63, 152.22, 132.76, 131.65, 129.33, 128.91, 127.36, 98.02, 91.53, 64.94, 62.51, 55.99, 53.32. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{16}H_{15}{}^{81}BrN_3O_3$: 378.0276; found: 378.0274.

Transformation of the intermediate to product



12a (37.5 mg, 0.1 mmol) was dissolved into 1,4-dioxane (2 mL) and stirred with the irradiation of visible-light at ambient temperature under argon atmosphere. Upon completion (24 h) as detected by TLC, the resulting mixture were poured into saturated sodium bicarbonate solution, extracted with ethyl acetate and washed with brine, solvent was removed by rotary evaporation and the residue was purified though FCC (eluent: 50% EtOAc/hexanes) to obtain the product **12b** (29.5 mg, 86%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.87 (d, J = 2.0 Hz, 1H), 7.53 – 7.38 (m, 4H), 7.29 – 7.22 (m, 2H), 7.08 (d, J = 2.0 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.25, 173.21, 146.65, 144.63, 138.79, 132.65, 129.44, 129.03, 127.48, 120.98, 117.32, 60.35, 49.46. ESI-HRMS (m/z): $[M+H]^+$calcd for $C_{15}H_{11}BrN_3O_2$: 344.0035; found:344.0032.

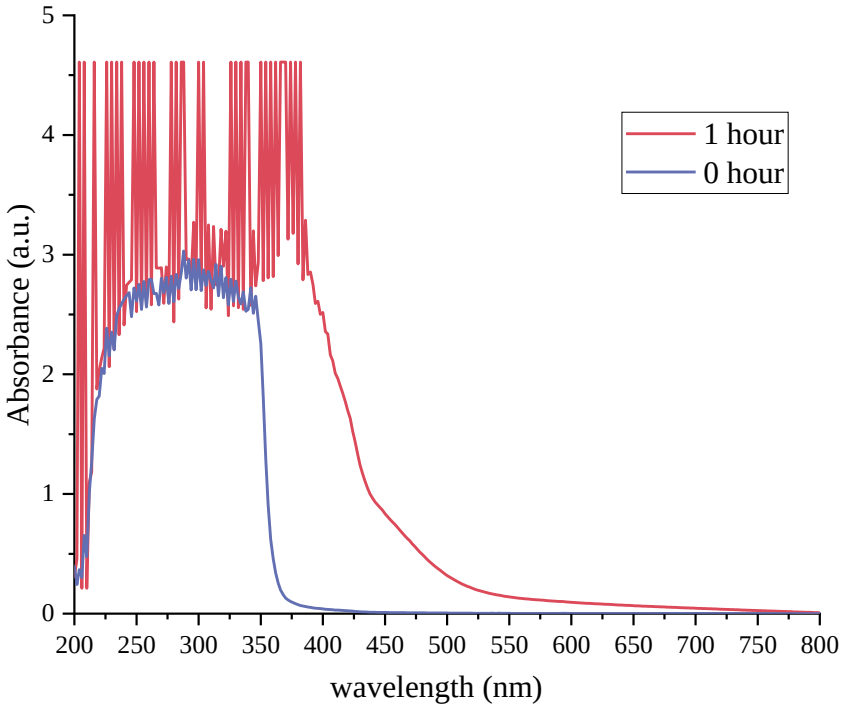
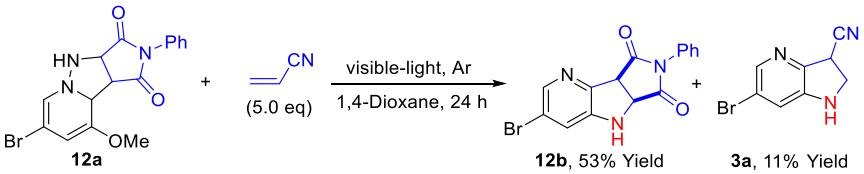


Figure S19. UV-VIS spectrum of **12a** in dioxane at 0 hour and 1 hour

Cross-over reaction



12a (37.5 mg, 0.1 mmol) and acrylonitrile (26.6 mg, 0.5 mmol) was stirred in 1,4-dioxane under the irradiation of visible-light. Upon completion (24 h) as detected by TLC, the resulting mixture was poured into saturated sodium bicarbonate solution, extracted with ethyl acetate and washed with brine, solvent was removed by rotary evaporation and the residue was purified though FCC (eluent: 50% EtOAc/hexanes) to obtain the product **12b** (18.2 mg, 53%) and **1a** (2.5 mg, 11%).

Computational details

All molecular geometries were optimized without constraints via DFT calculations using the (U)B3LYP functional[18] with Grimme's D3(BJ) dispersion correction[19]. The Def2-SVP was chosen to describe all atoms. Frequency calculations were carried out at the same level of theory to identify all of the stationary points as transition states (one imaginary frequency) or as minima (zero imaginary frequency) and to provide the thermal correction to free energies at 298.15 K and 1 atm. The higher accuracy single-point energy calculations were performed at the B3LYP-D3(BJ) level with the Def2-TZVPP for all atoms. The time-dependent density functional theory (TD-DFT) with CAM-B3LYP-D3(BJ)/6-311+G(d,p) level[20], is employed to calculated the excitation energy of related molecules. The continuum solvent model PCM[21] with toluene as the solvent, was used in all the calculations toluene. All calculations were performed with the *Gaussian 16* software package.[22]

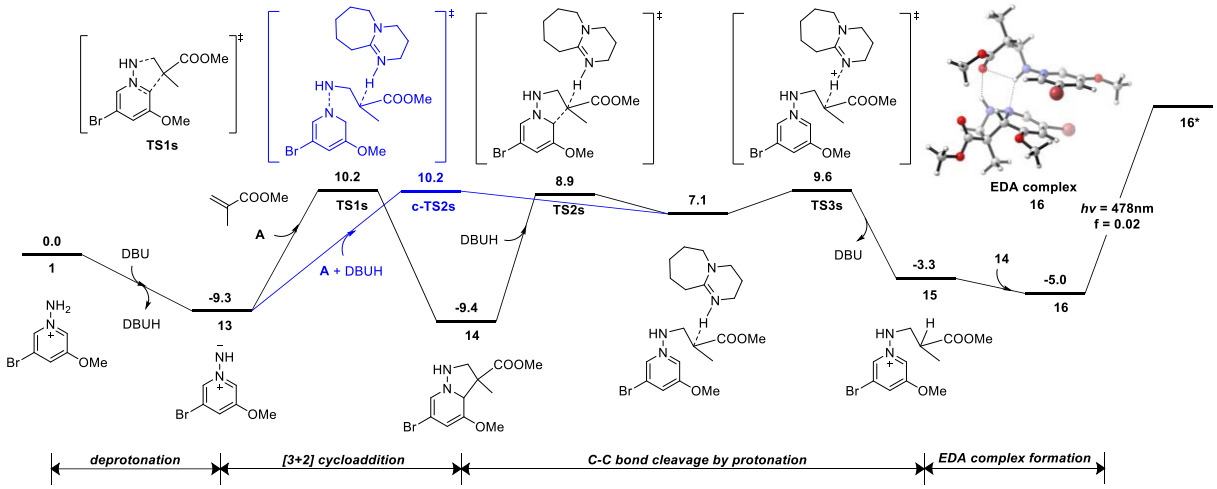


Figure S20. DFT calculation for the formation of intermediate **14** and **15.**

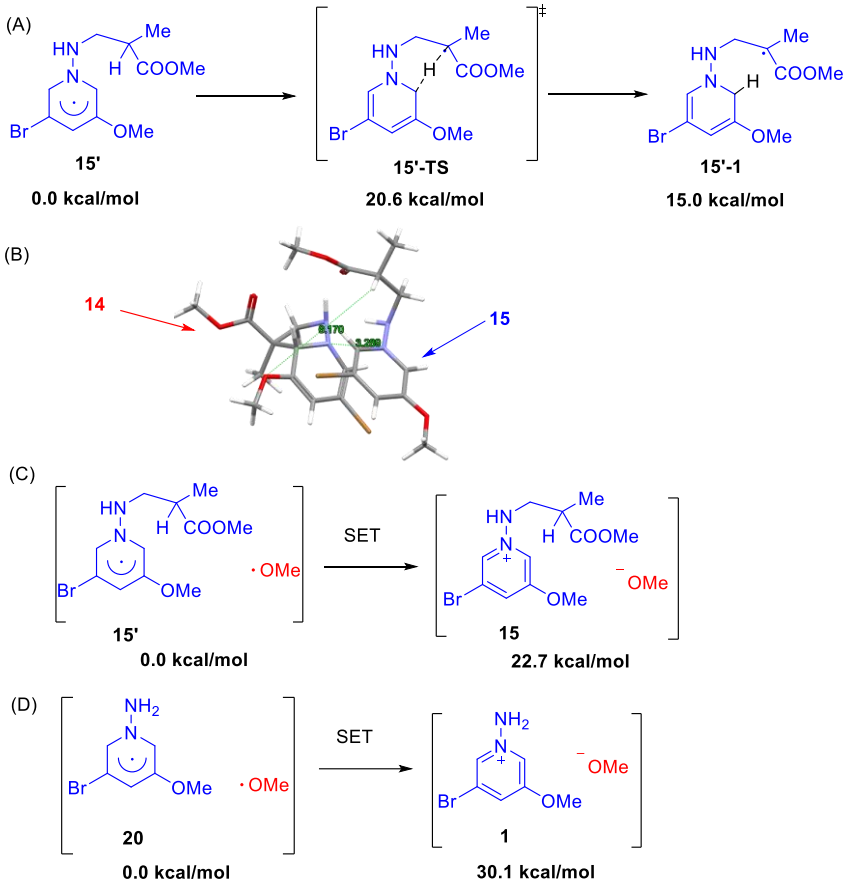


Figure S21. DFT calculation of transformation of pyridinium radicals. (A) 1,5-HAT process of **16'**. Energy barrier is 20.6 kcal/mol. (B) Distance between methoxy group (**14**) and α-H (**15**) in EDA complex. (C) methoxy radical oxidize **15'** to **15**. (D) methoxy radical oxidize **20** to **1**.

As most of the 4-azaindoline products are yielded over 50%, we believe that pyridinium radical **15'** should be re-cycled to **14** or **15**. To verify this hypothesis, we launched a series of calculations. The 1,5-HAT process of **15'** needs overcome an energy barrier of 20.6 kcal/mol (**Figure S20A**), which are not likely to happen at room temperature. While methoxy radical directly capture proton alone with radical radical coupling to form **14** would more likely to be underway without undergo a transition state at some specific geometry (**Figure S20B**). The distance between two moieties of EDA complex is 3.2 Å and distance between the methoxy group (in **14**) and α-H (in **15**) is 6.2 Å. According to the calculation result, this distance is suitable for proton capture by methoxy radical. Besides, we also calculated the energy differences of SET process between pyridine radicals and methoxy radical, both of these processes needed high energy to finish the electron transfer, which are not likely to happen at room temperature (**Figures S20C, S 20D**).

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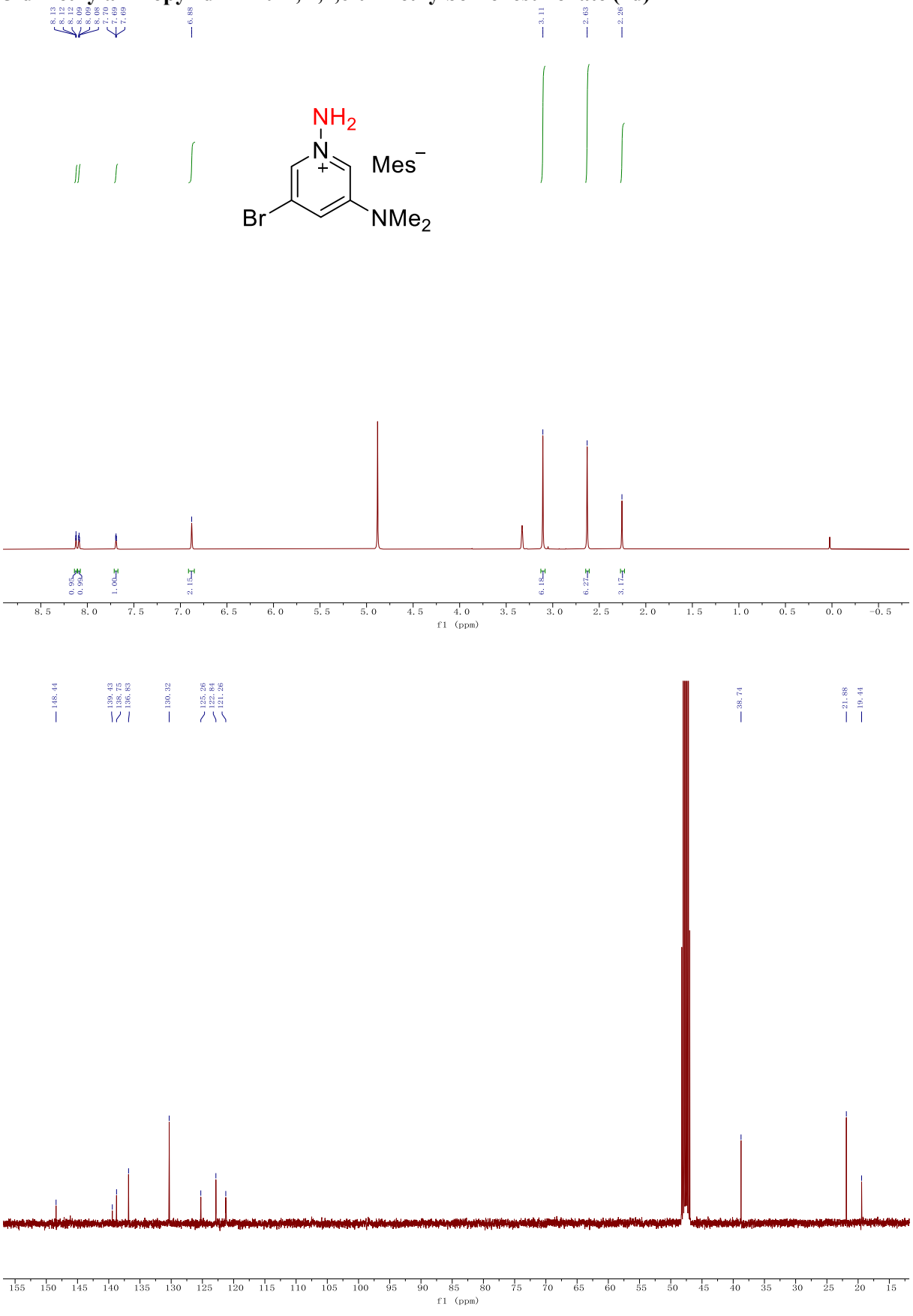
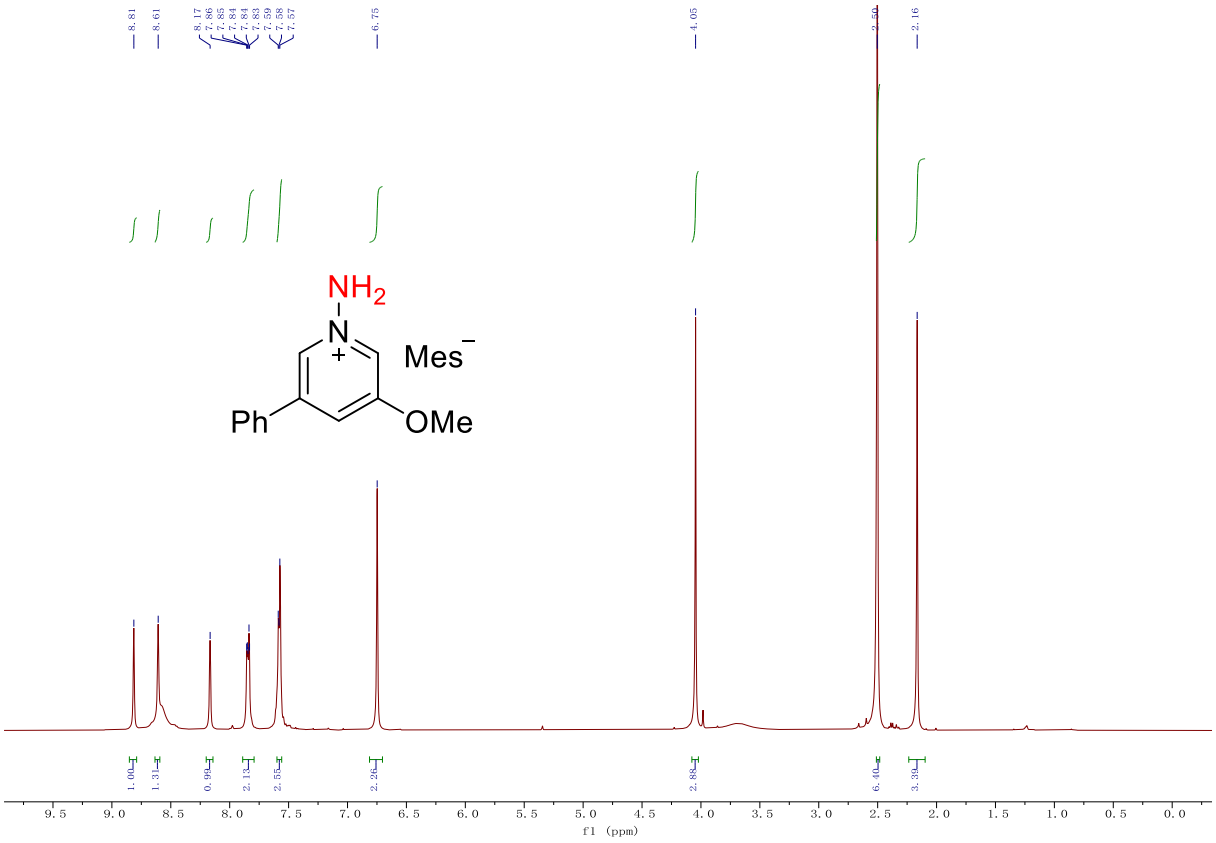
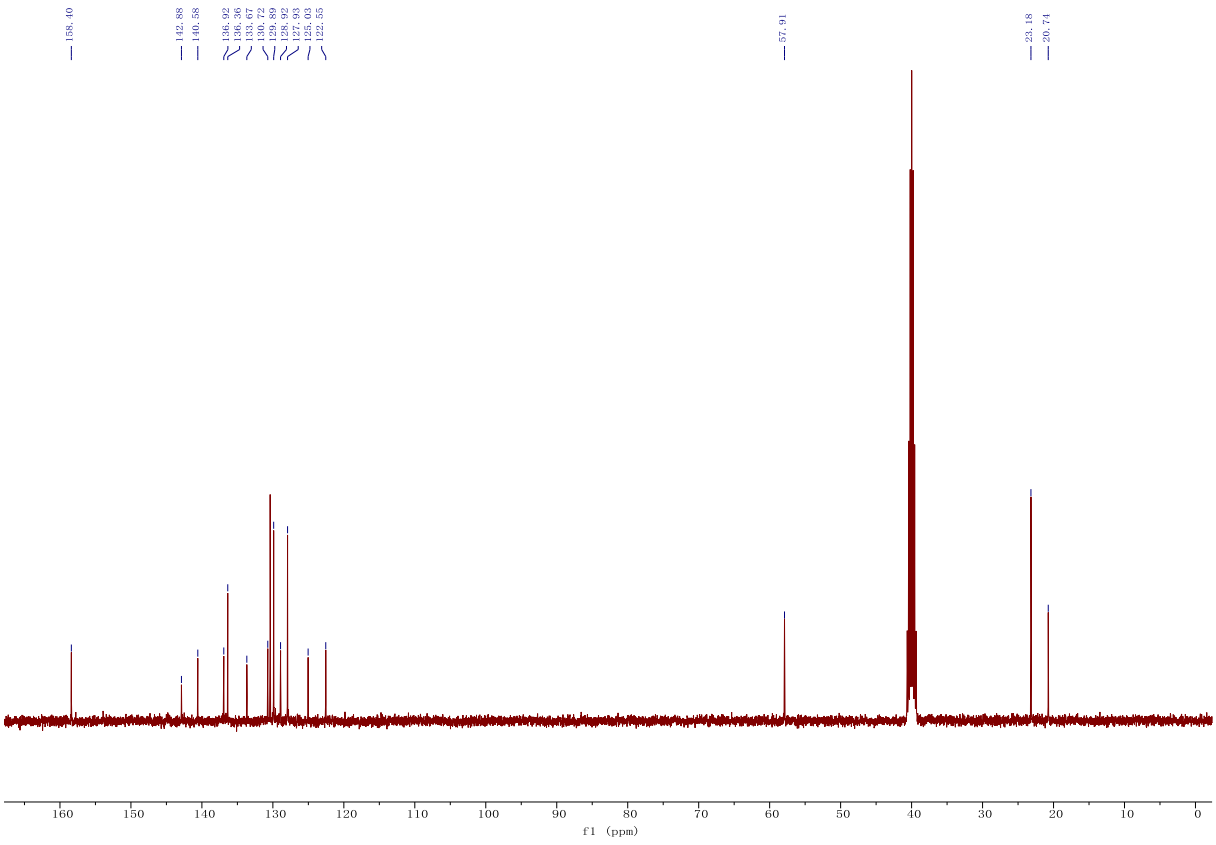
Copies of NMR Spectra

^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 1-amino-3-bromo-5-dimethylaminopyridin-1-ium, 2,4,6-trimethylbenzenesulfonate (1d)

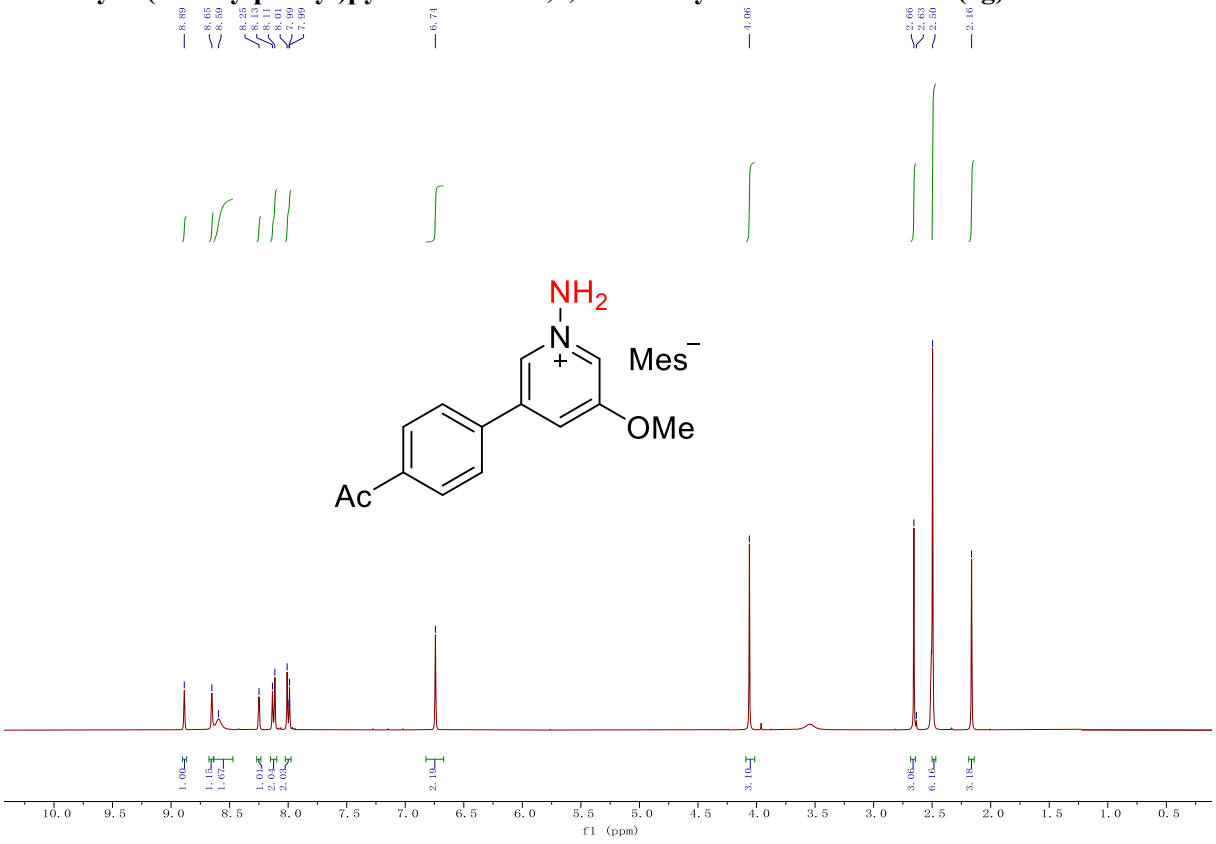


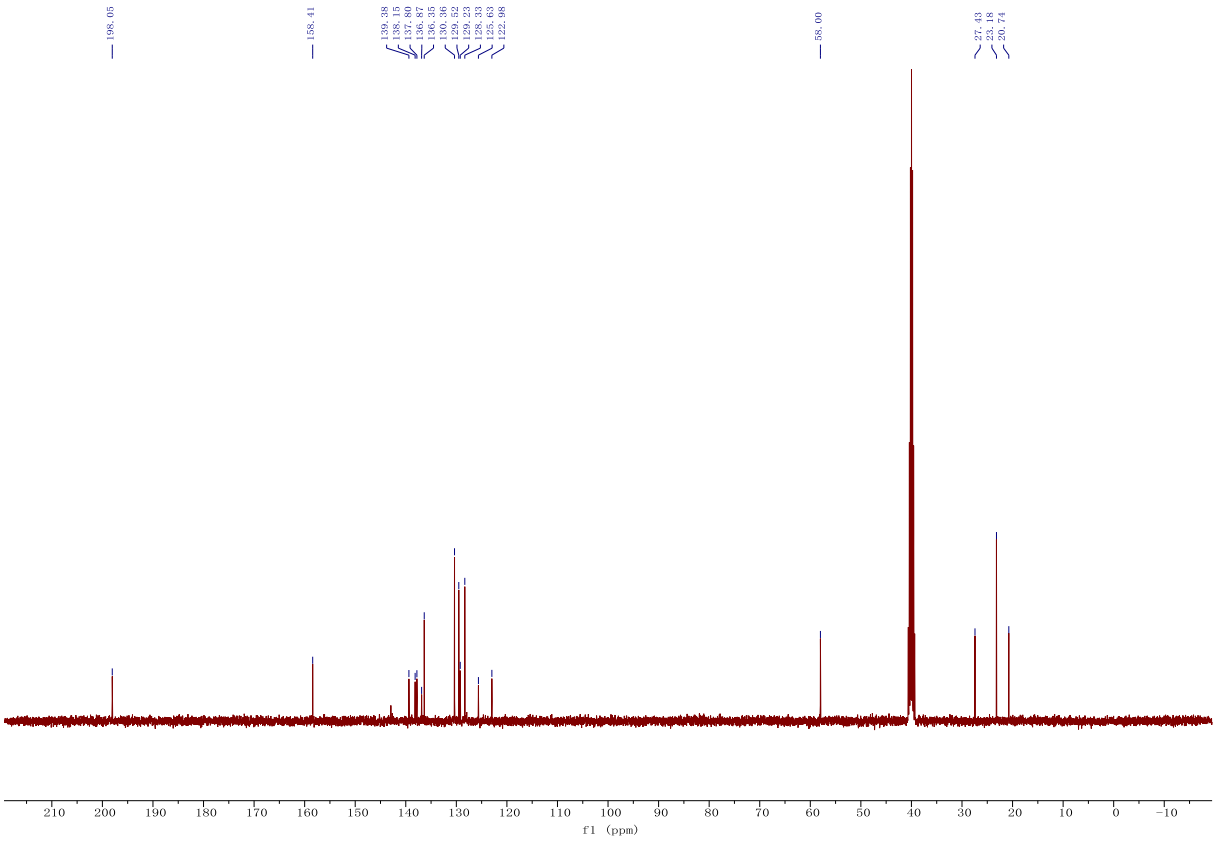
^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 1-amino-3-methoxy-5-phenylpyridin-1-ium 2,4,6-trimethylbenzene- sulfonate (1e)



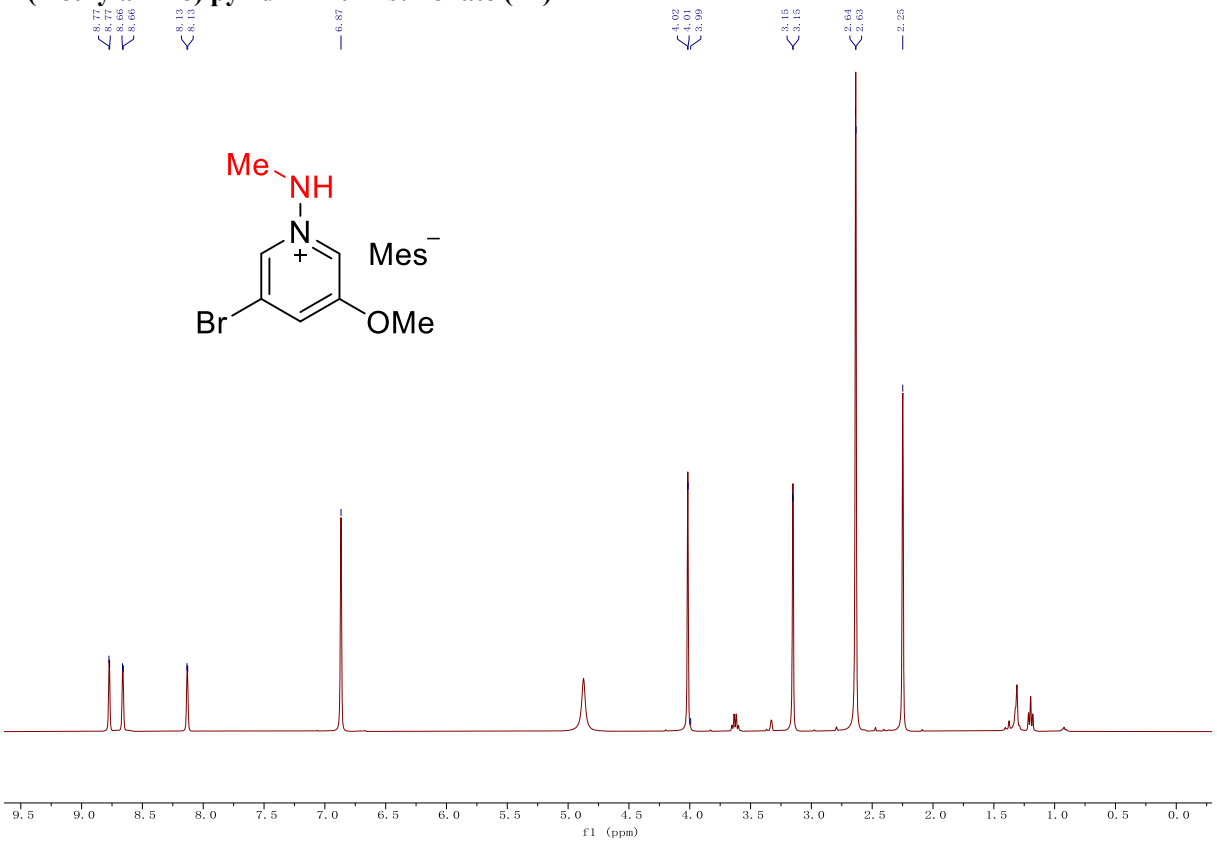


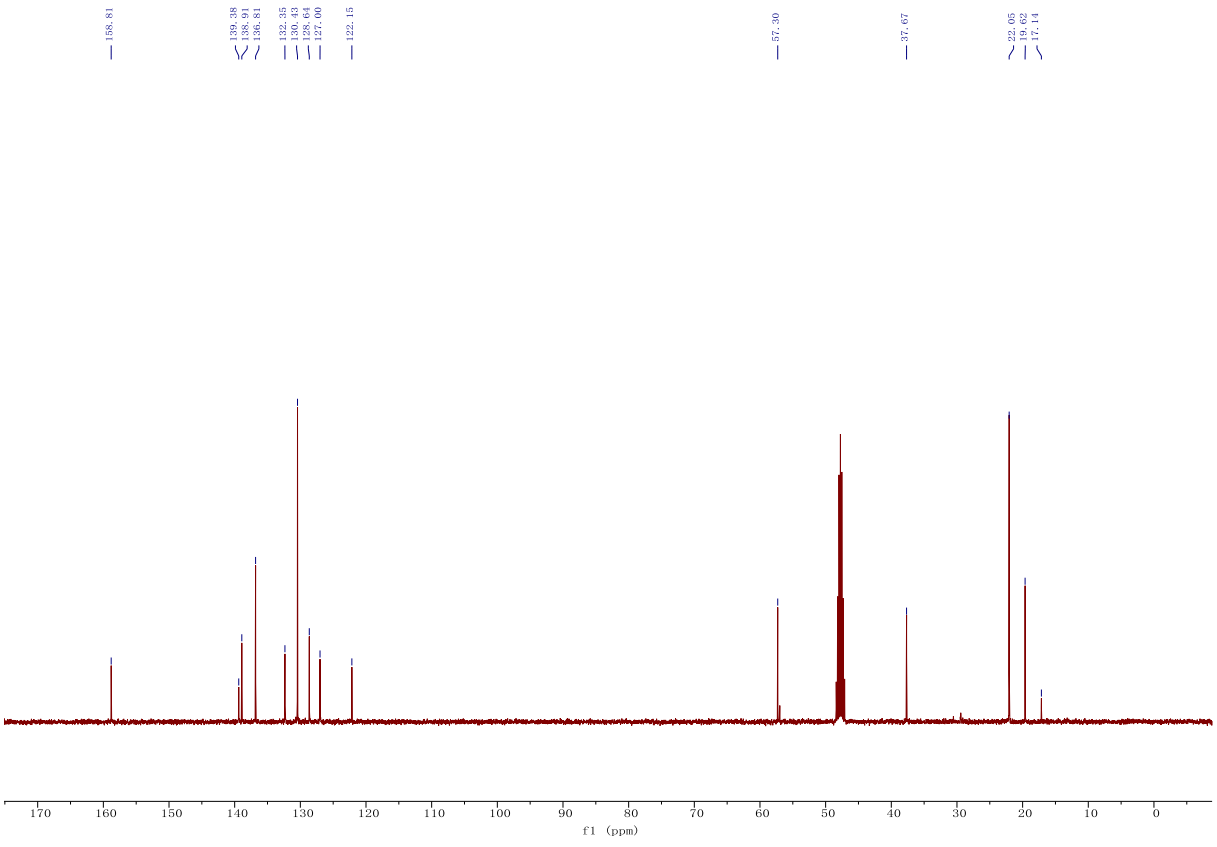
^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 1-amino-3-methoxy-5-(4-acetylphenyl)pyridin-1-ium 2,4,6-trimethylbenzene- sulfonate (1g)



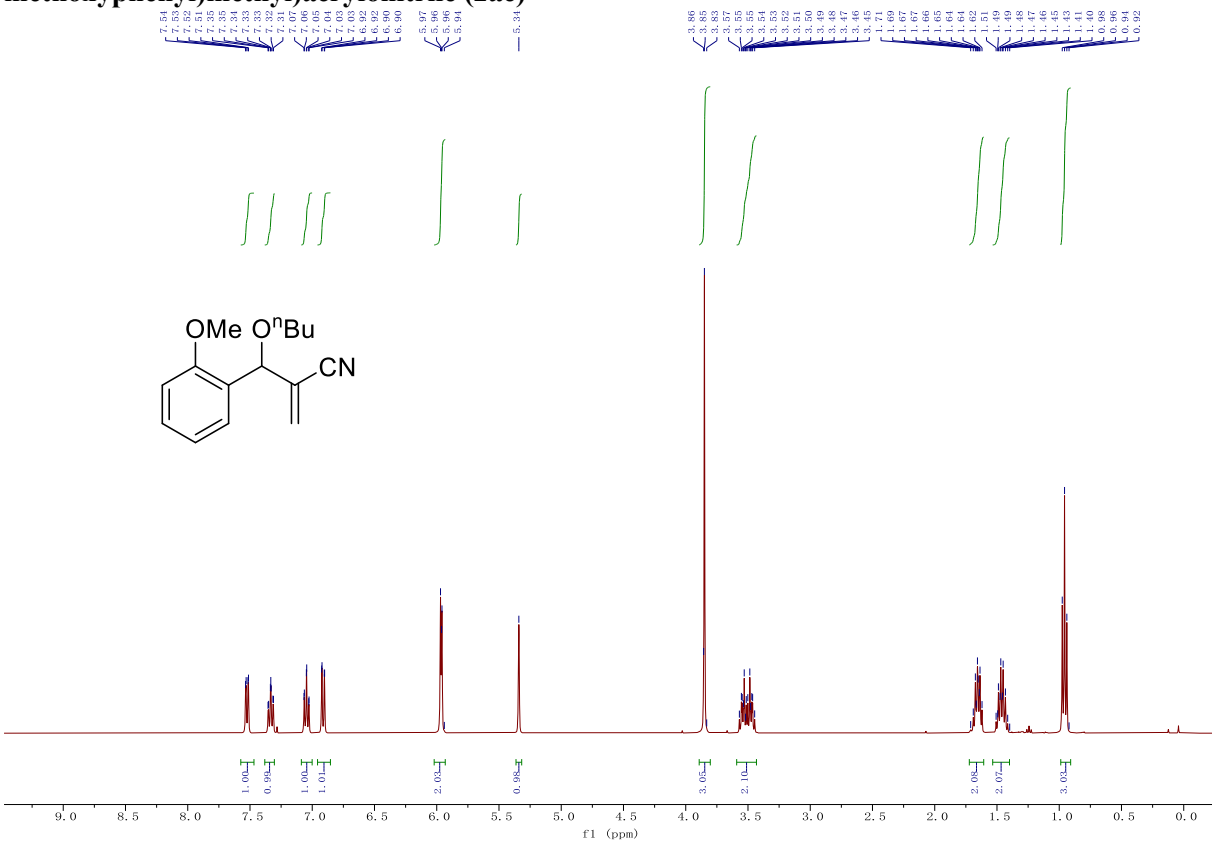


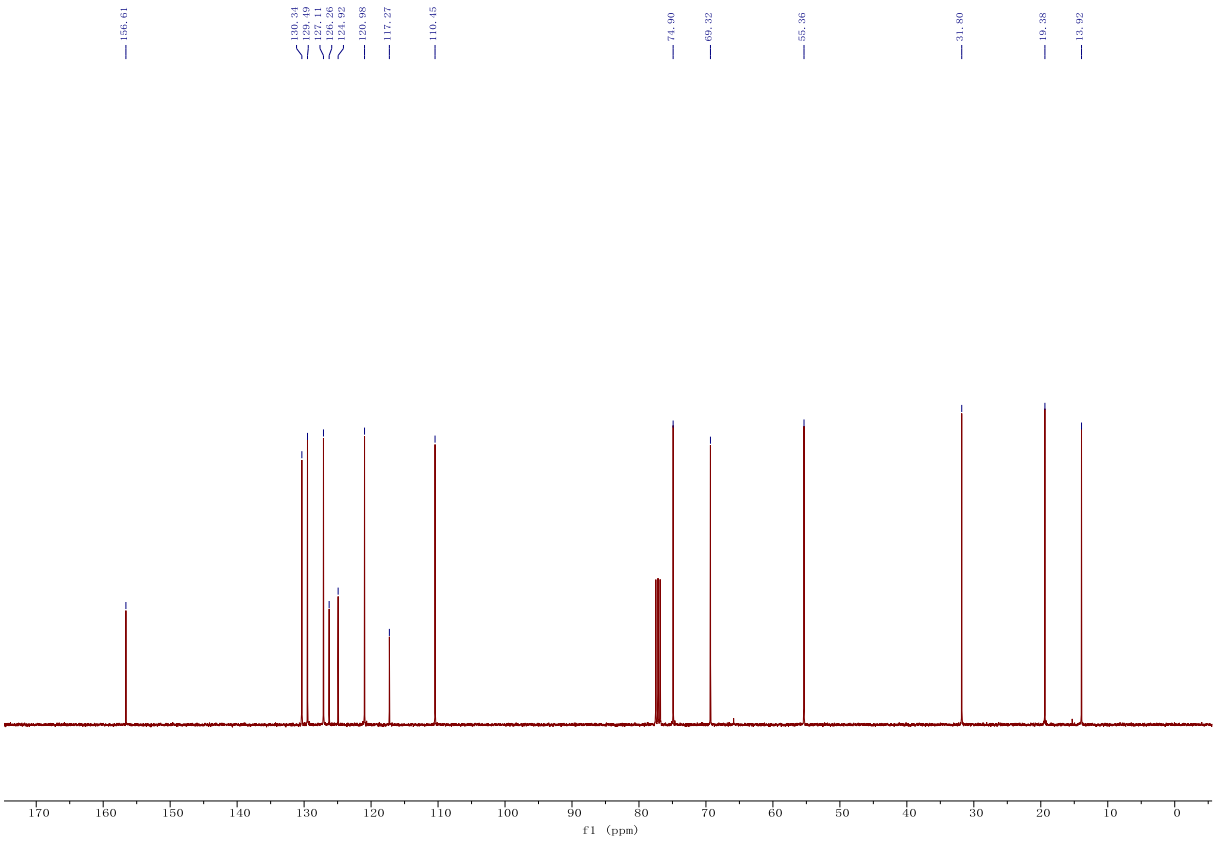
^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 3-bromo-5-methoxy-1-(methylamino) pyridin-1-ium-sulfonate (1n)



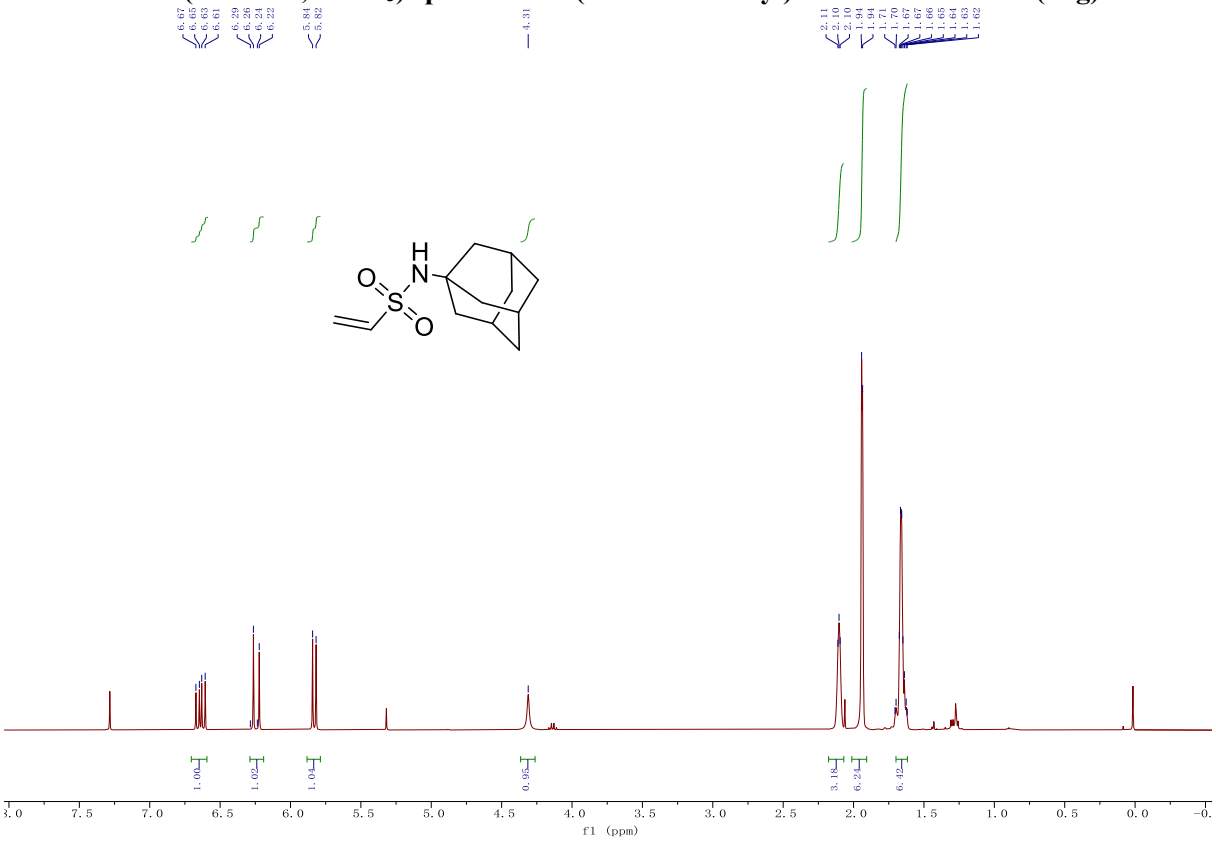


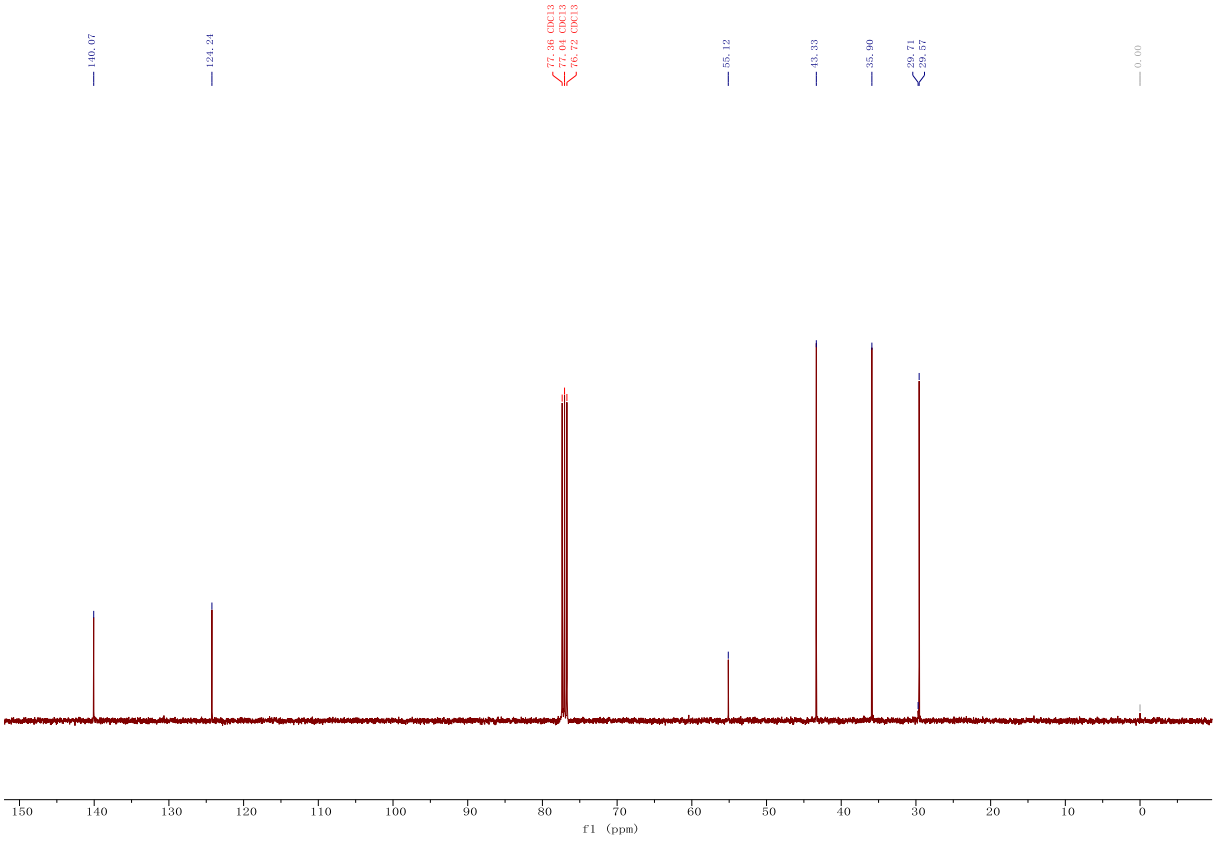
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 2-(butoxy(2-methoxyphenyl)methyl)acrylonitrile (2ae)



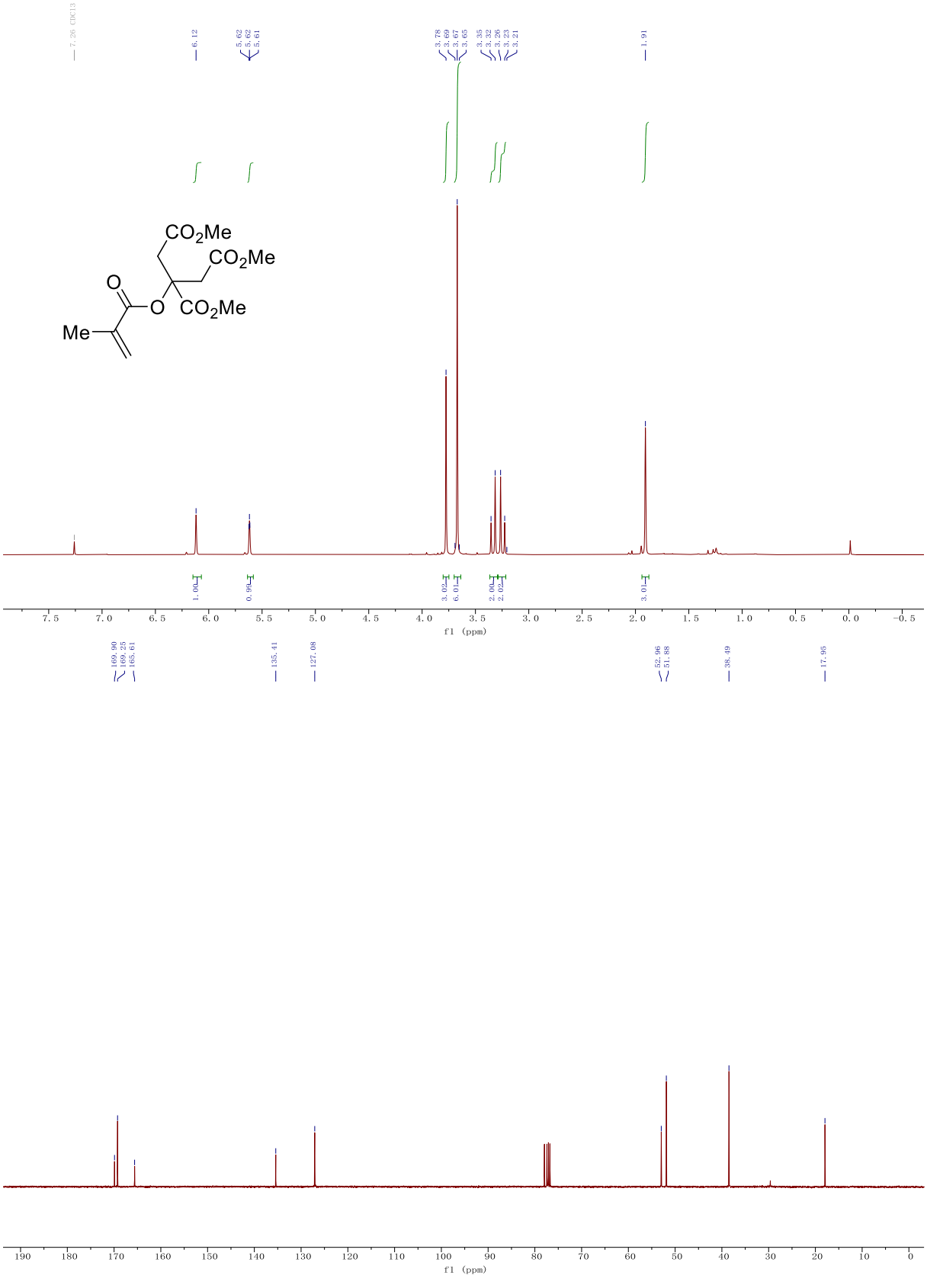


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of *N*-(adamantan-1-yl)ethenesulfonamide (2bg)

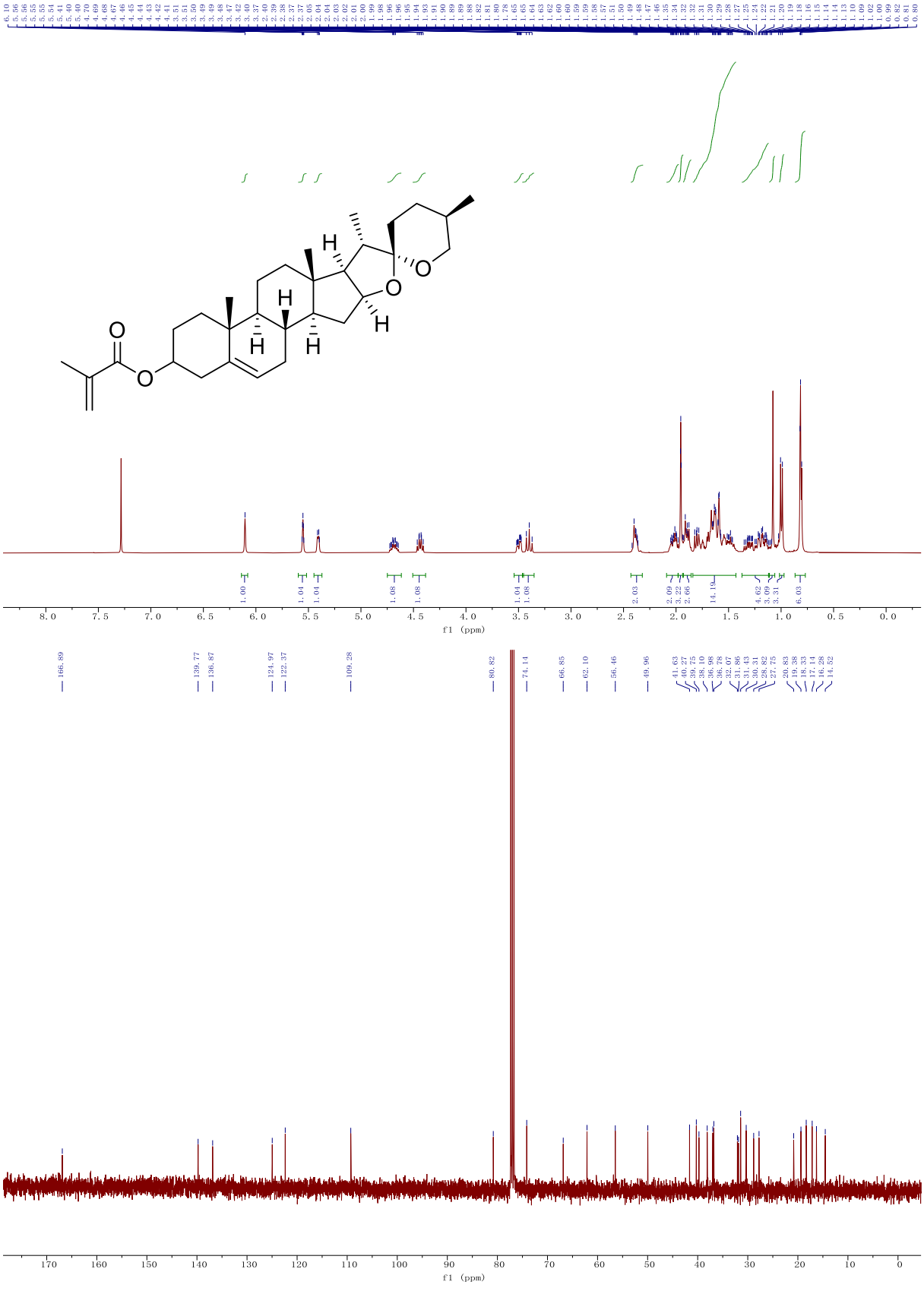




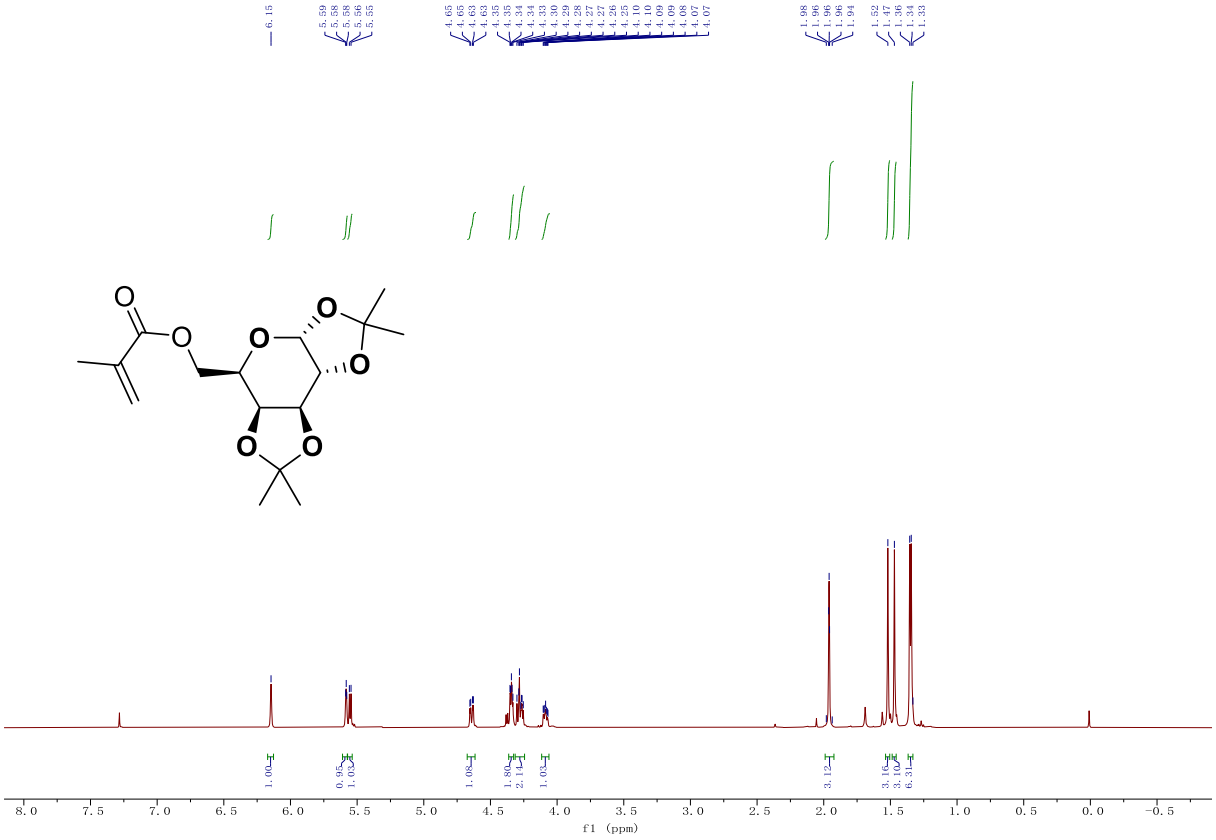
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of trimethyl 2-(methacryloyloxy)propane-1,2,3-tricarboxylate (2cn)

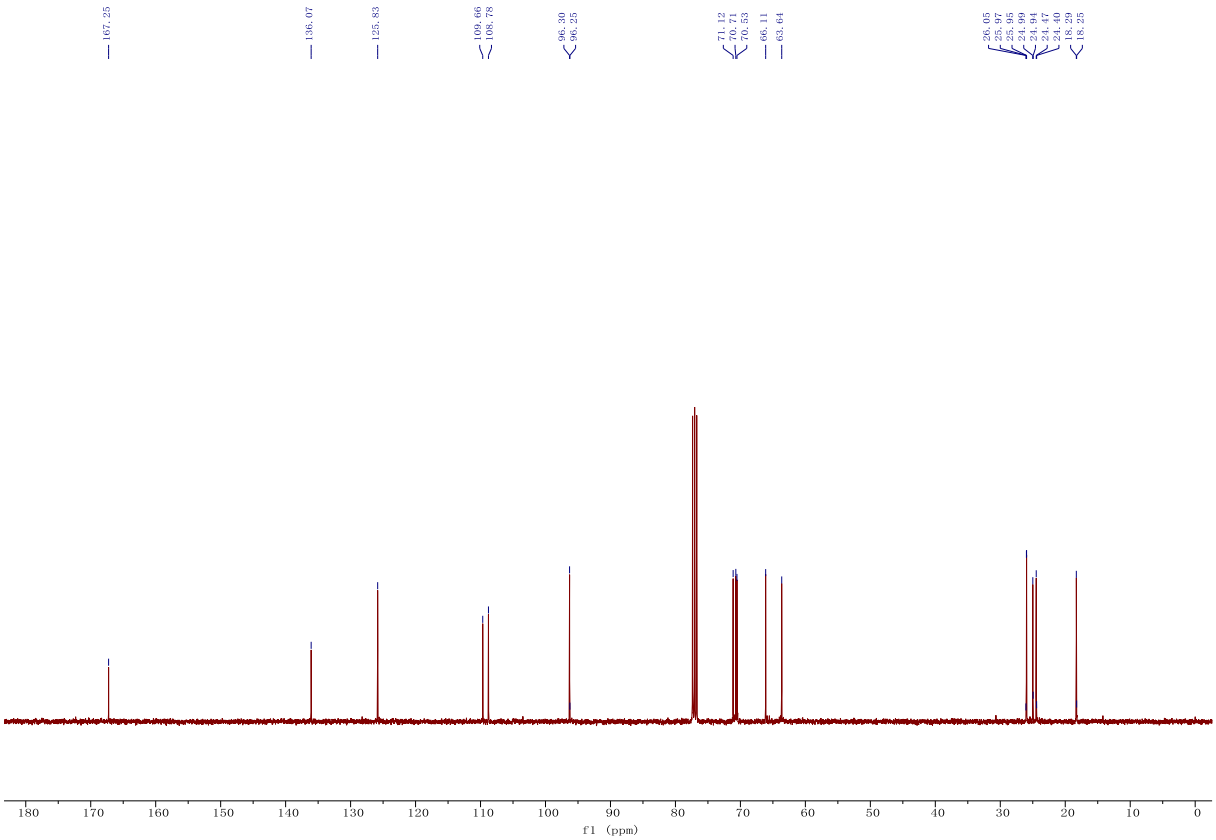


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of (5'*R*,6*aR*,6*bS*,8*aS*,8*bR*,9*S*,10*R*,11*aS*,12*aS*,12*bS*)-5',6a,8a,9-tetramethyl-1,3,3',4,4',5,5',6,6a,6b, 6',7,8,8a,8b,9,11a,12,12a,12b-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-4-yl methacrylate (2da)



^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ((3*aR*,5*R*,5*aS*,8*aS*,8*bR*)-2,2,7,7-tetramethyltetrahydro-5*H*-bis([1,3]dioxolo)[4,5-*b*:4',5'-*d*]pyran-5-yl)methyl methacrylate (2db)





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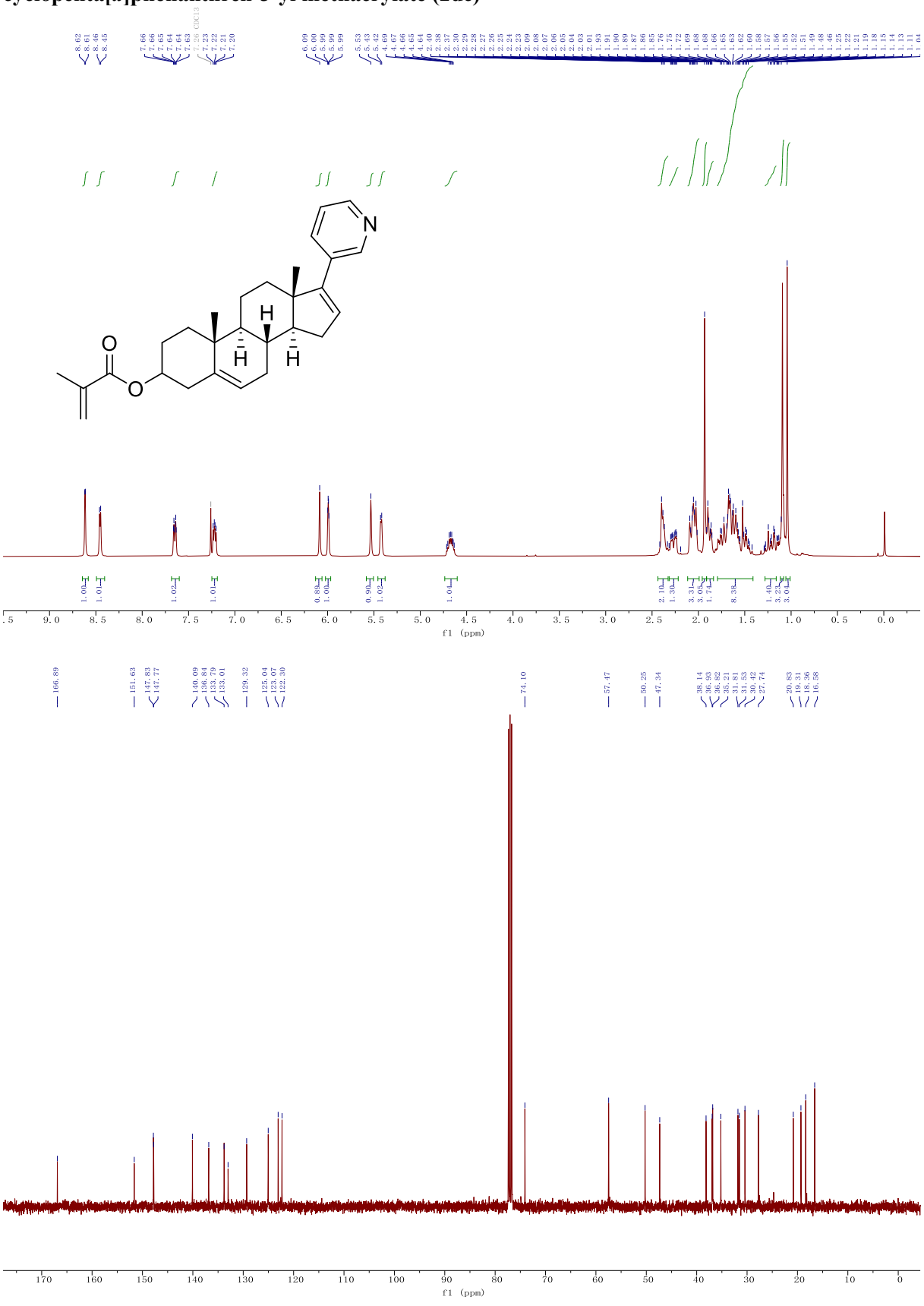
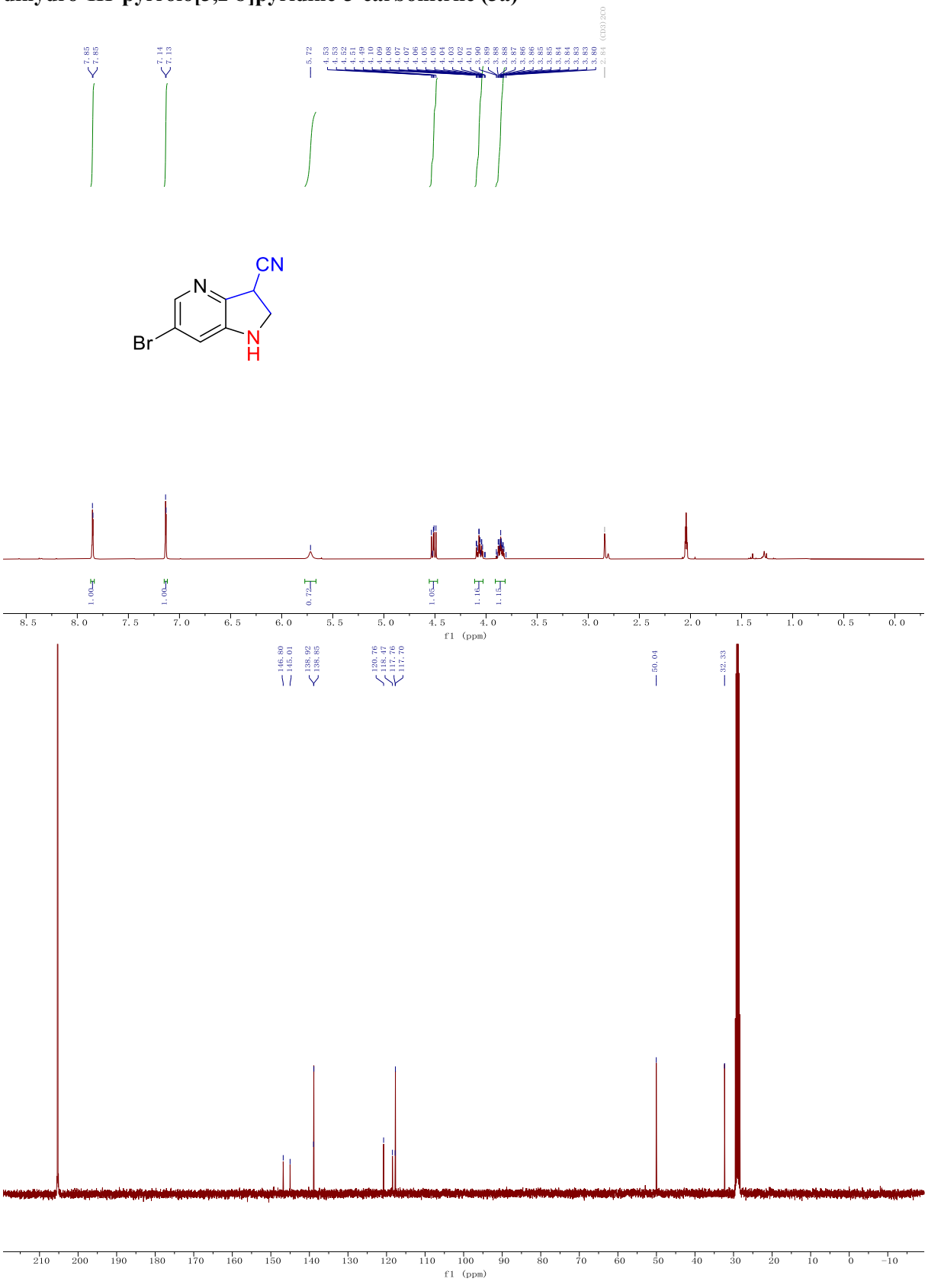
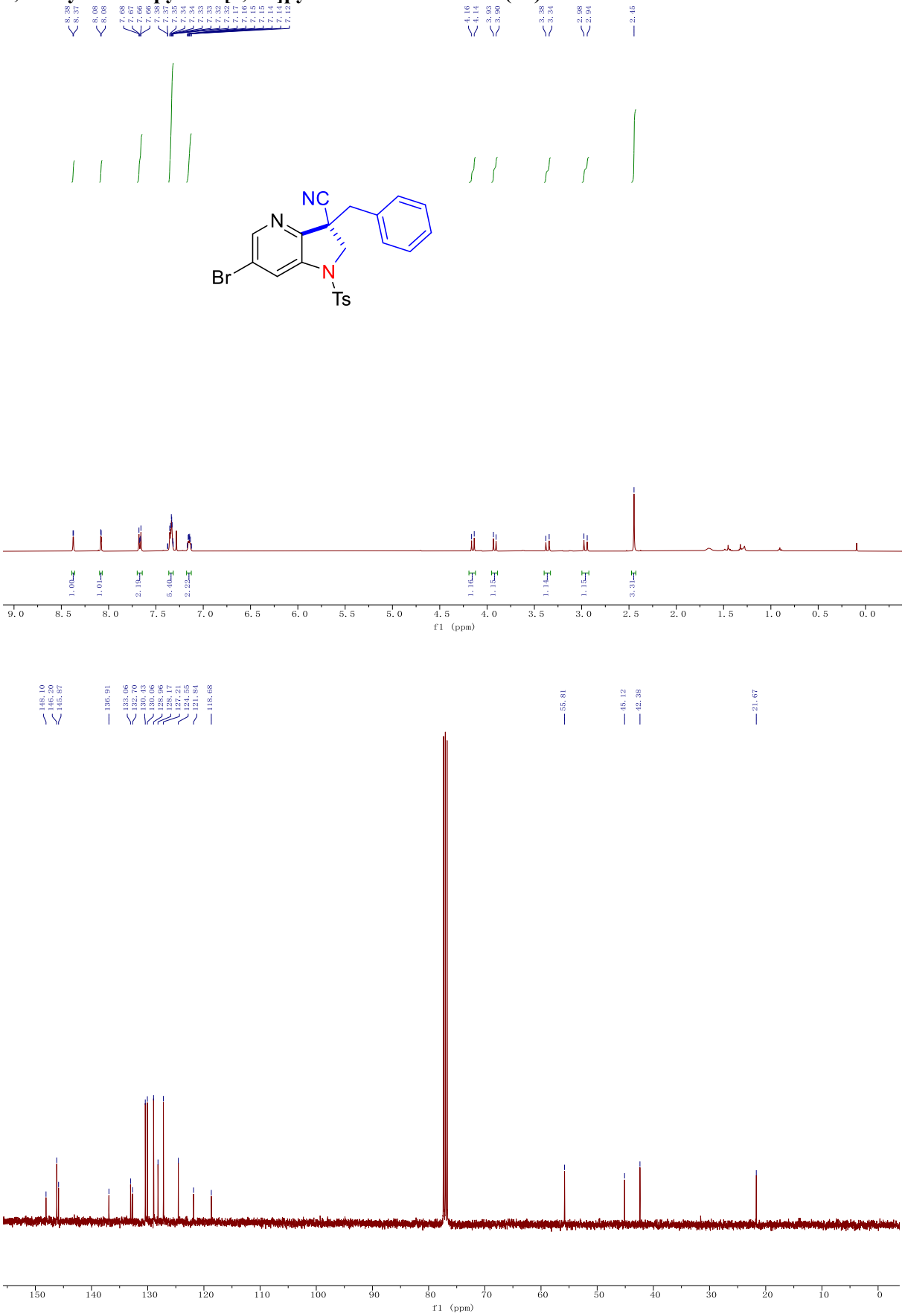


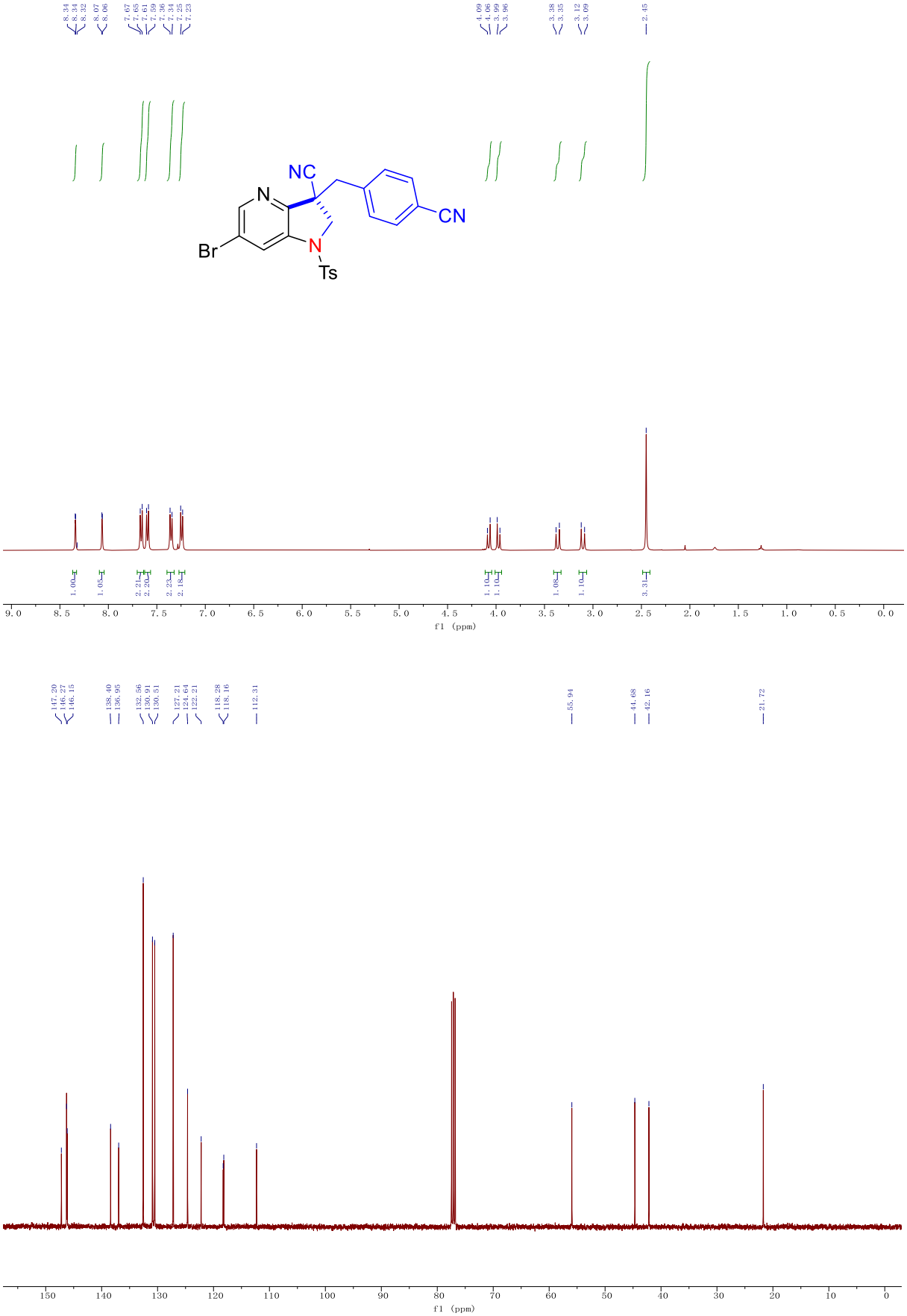
^{1}H NMR (400MHz, Acetone-*d6*) and ^{13}C NMR (101MHz, Acetone-*d6*) spectra of 6-bromo-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3a)



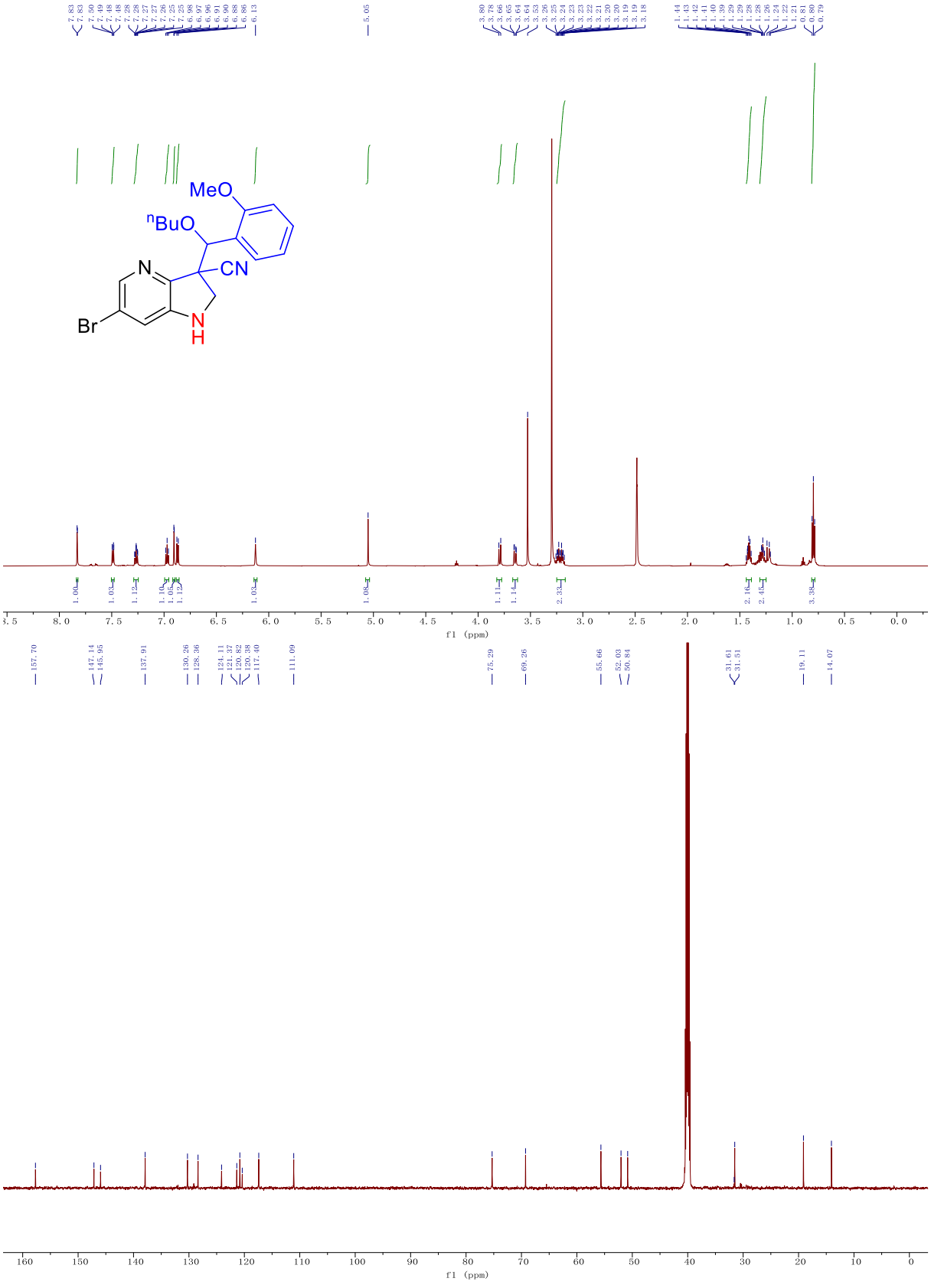
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 3-benzyl-6-bromo-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3b)



^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 6-bromo-3-(4-cyanobenzyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3c)



^{1}H NMR (600MHz, DMSO-*d6*) and ^{13}C NMR (151MHz, DMSO-*d6*) spectra of 6-bromo-3-(butoxy(2-methoxyphenyl)methyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (3d)



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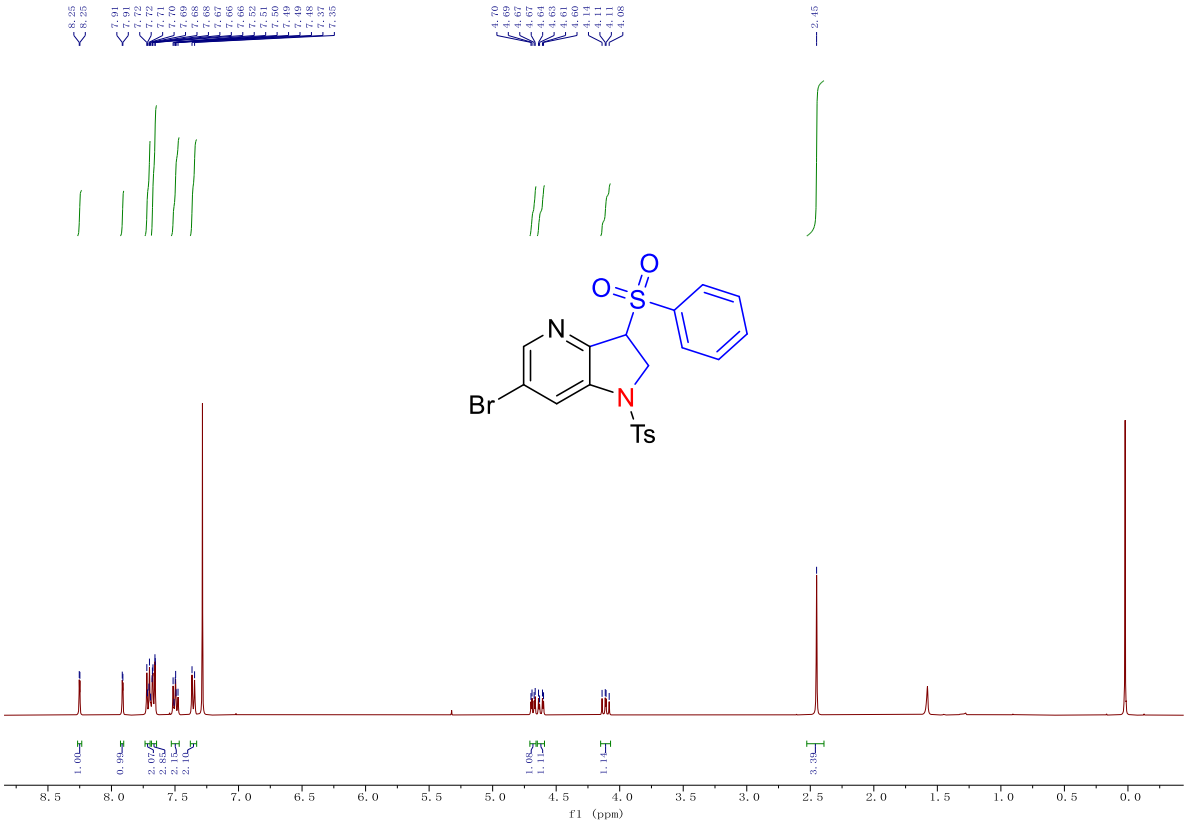
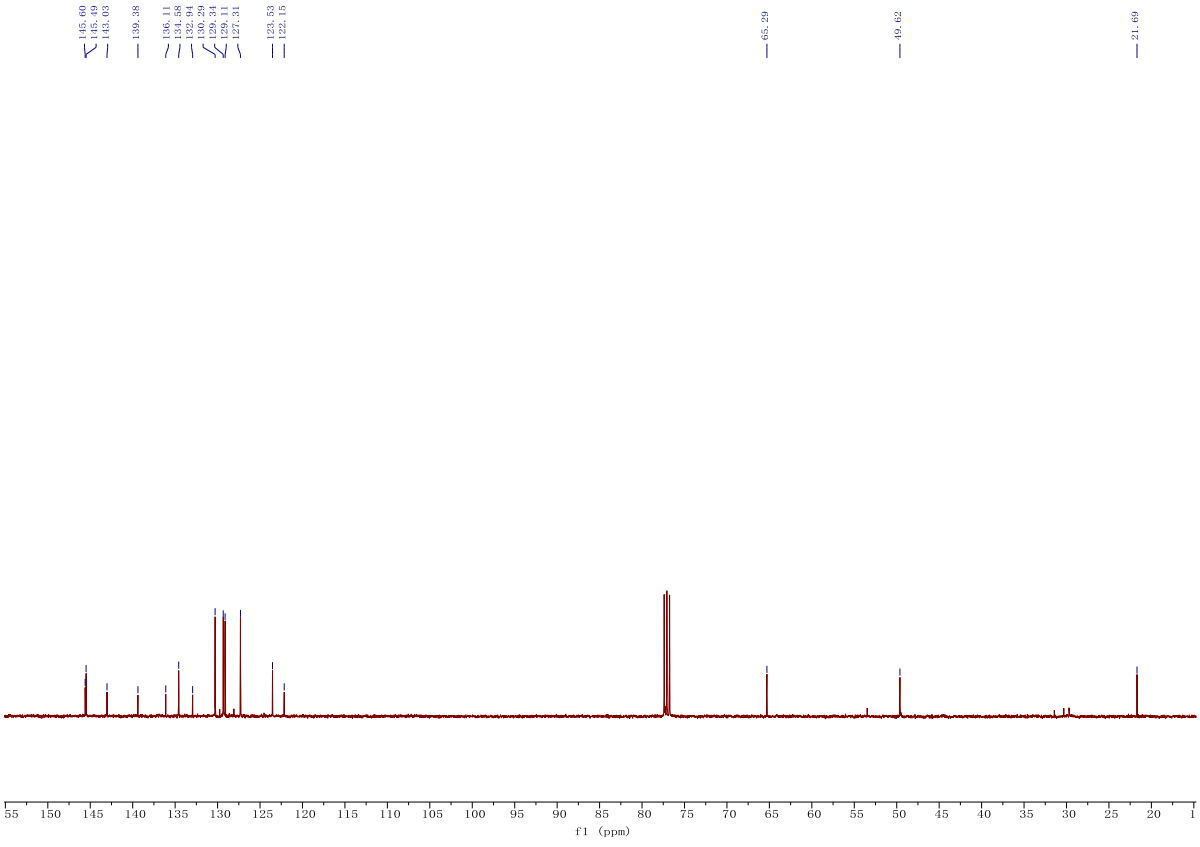
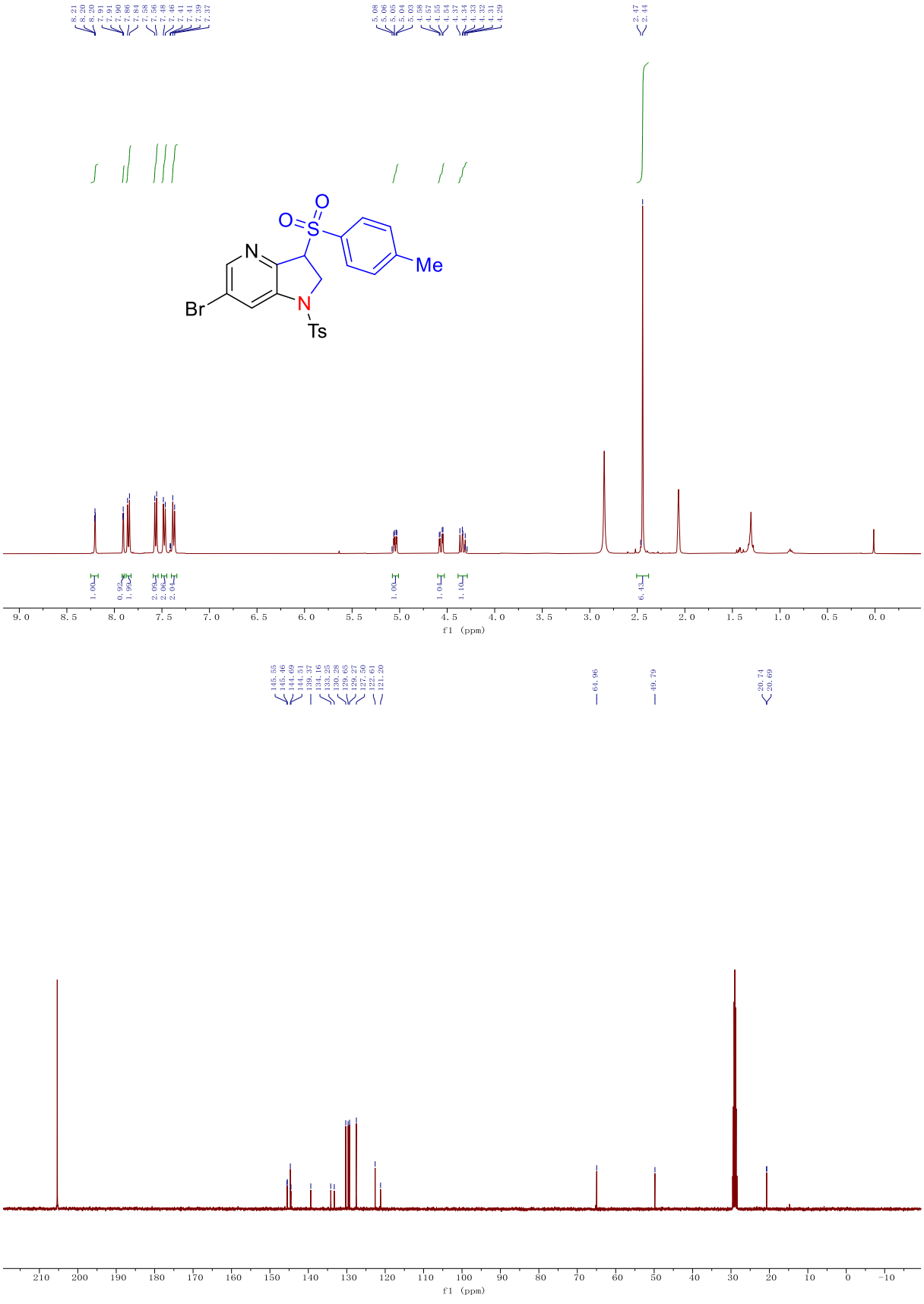




^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 6-bromo-1,3-ditosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (4b)



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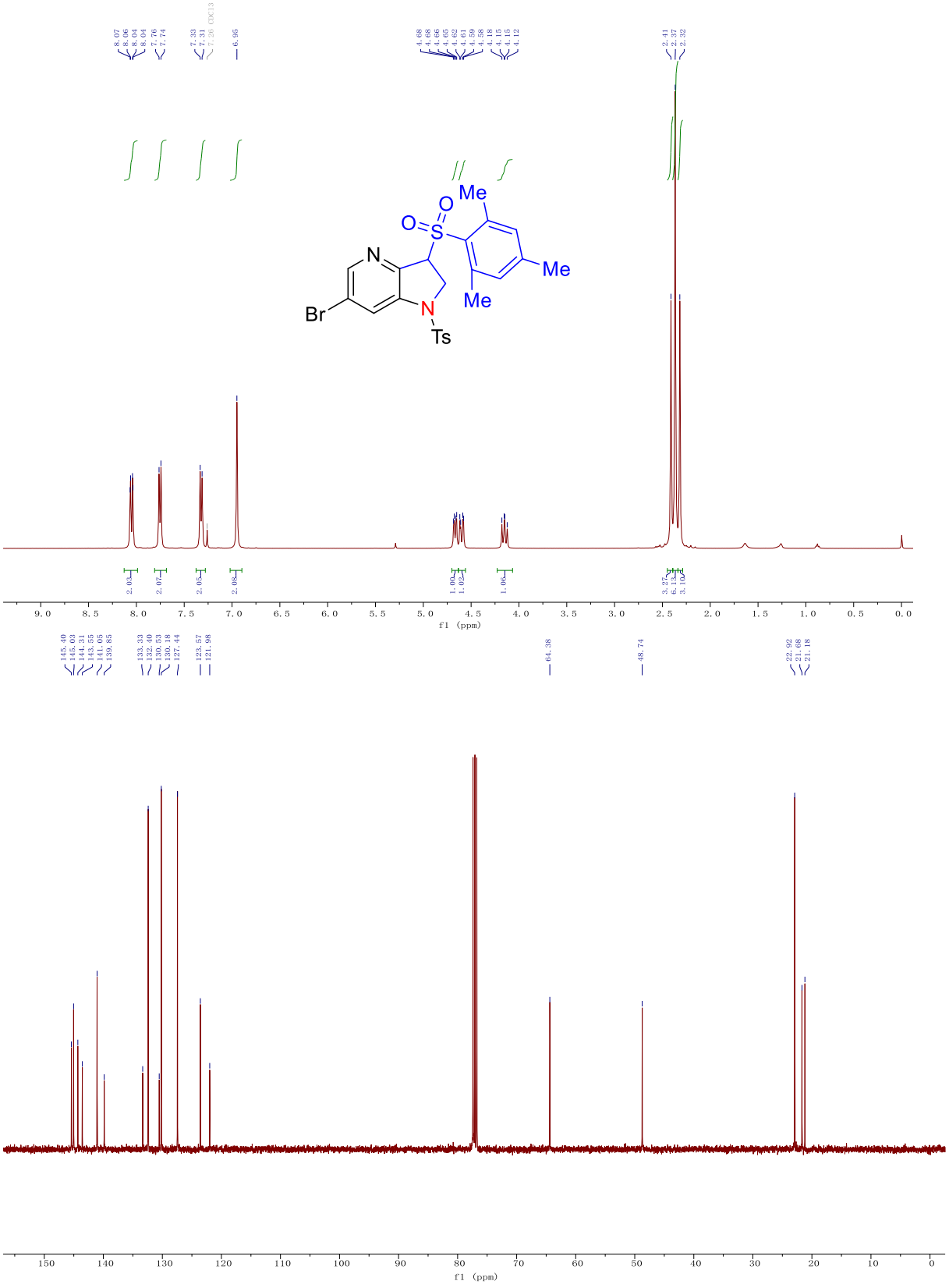

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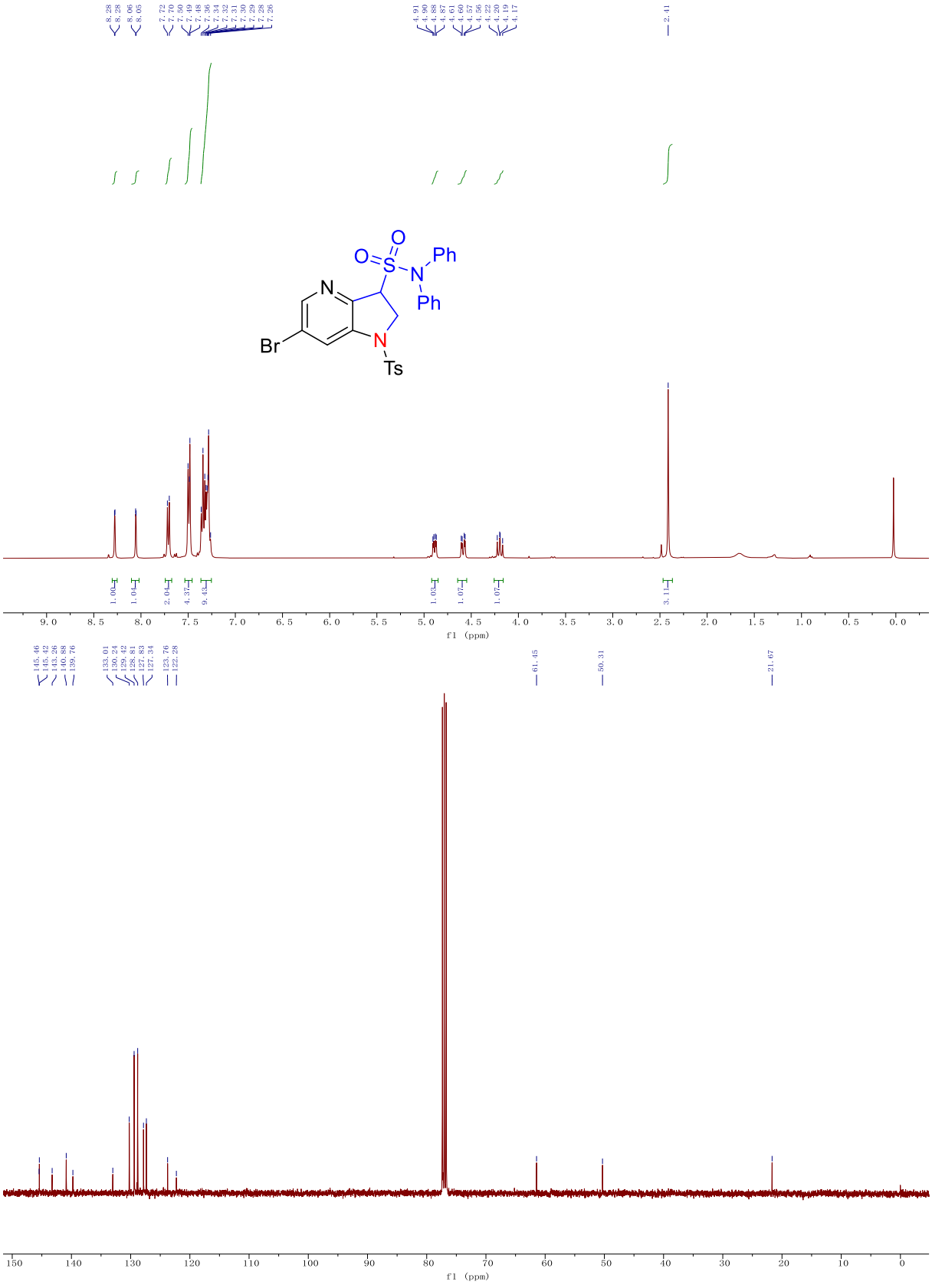

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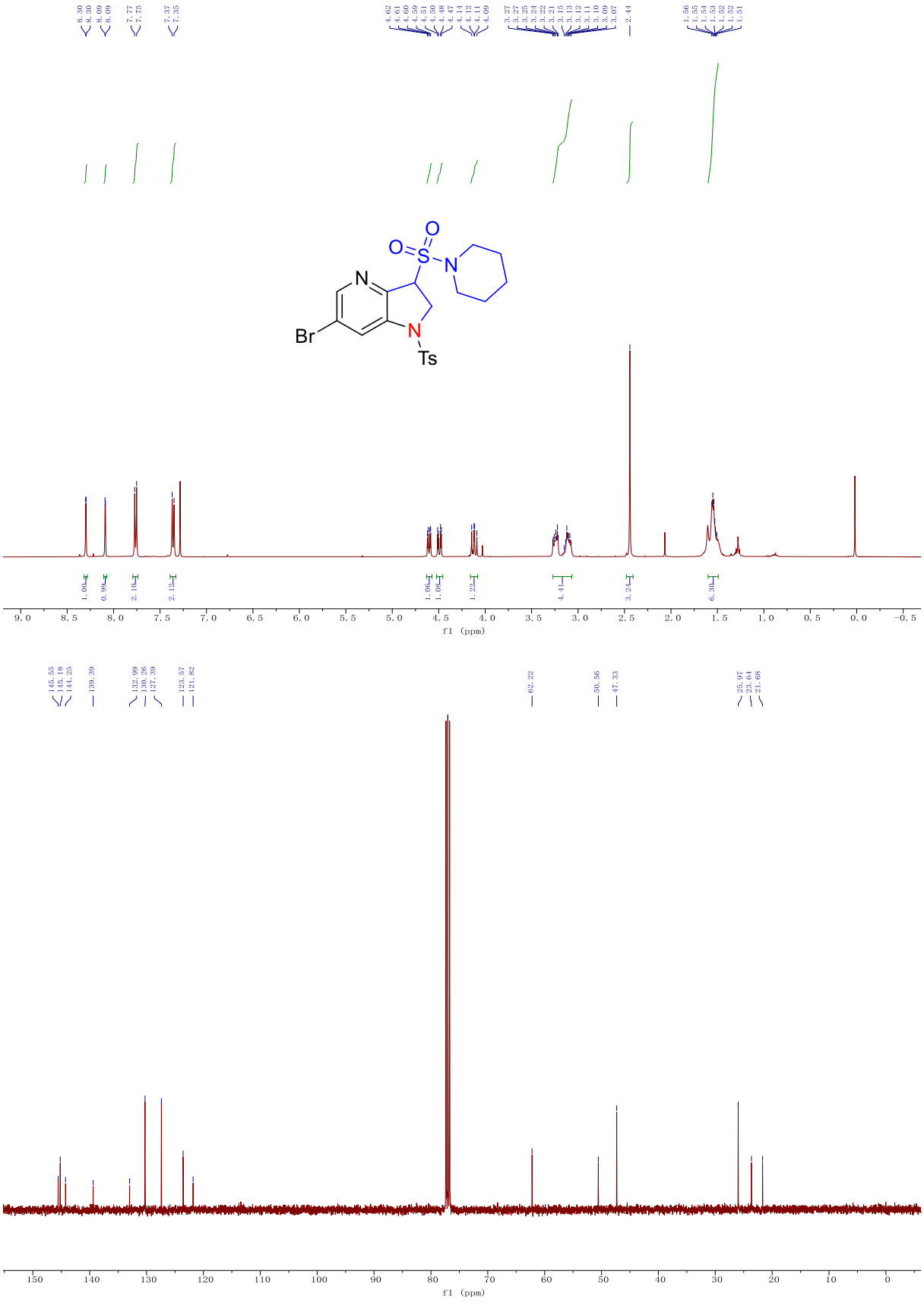
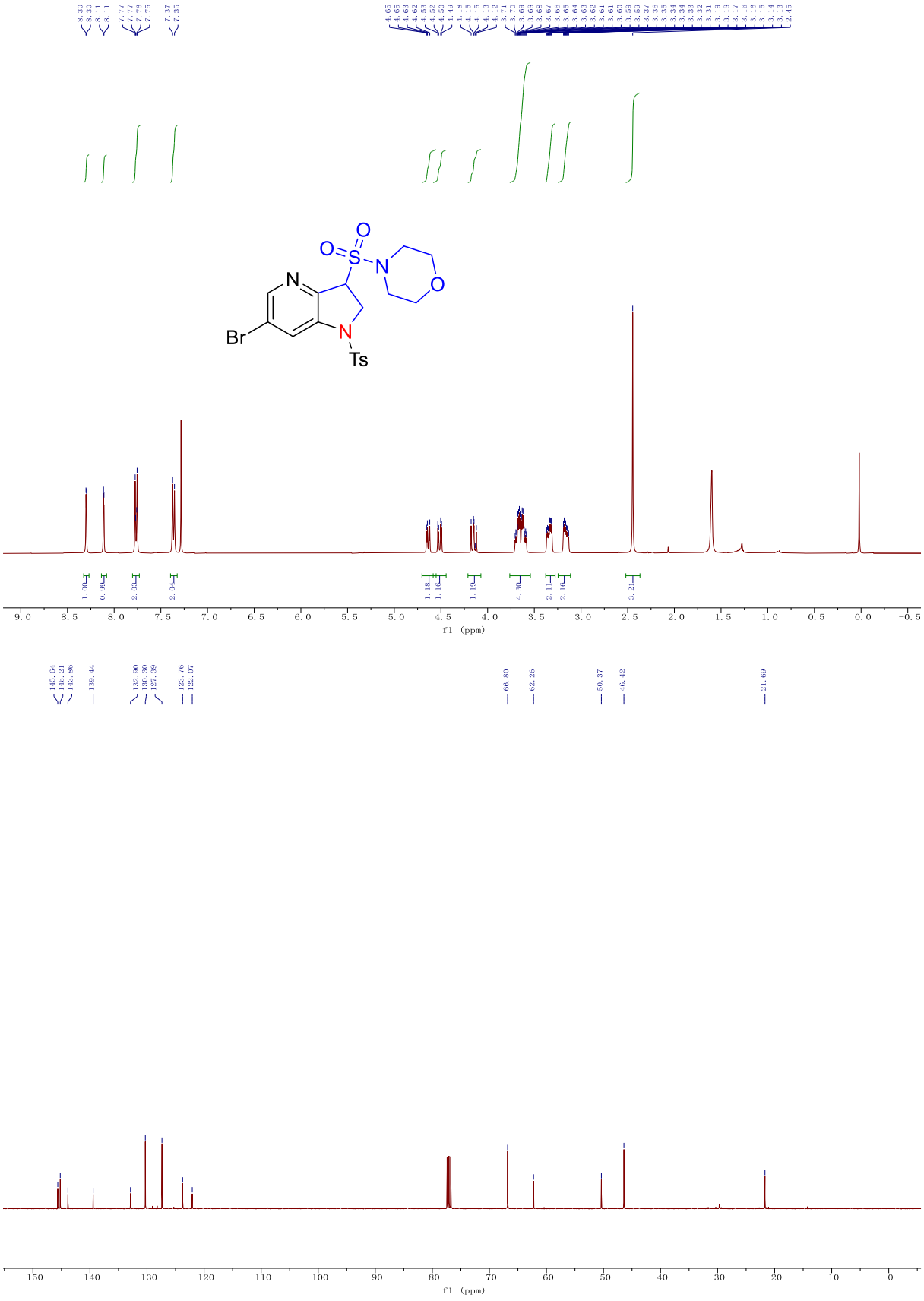
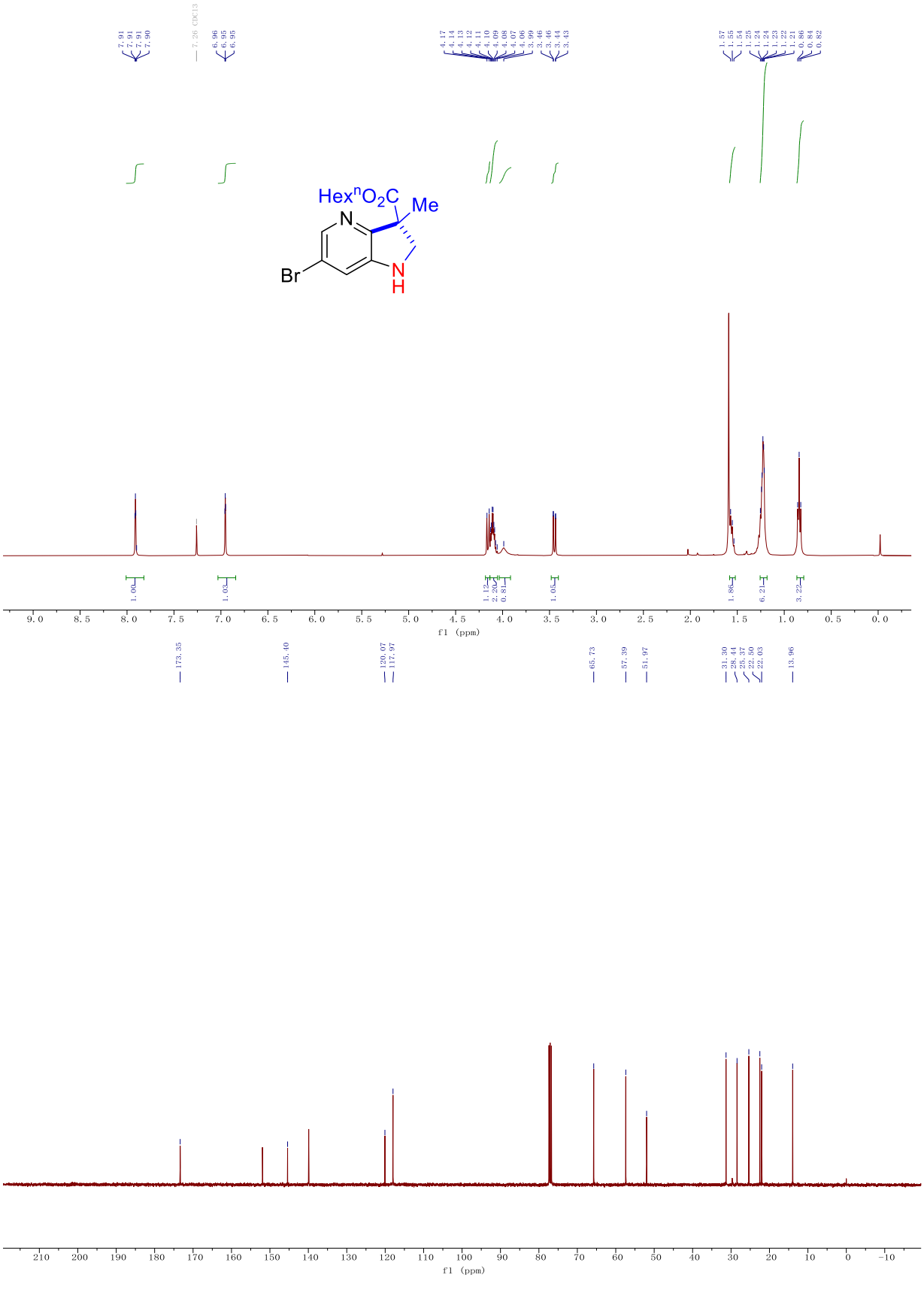


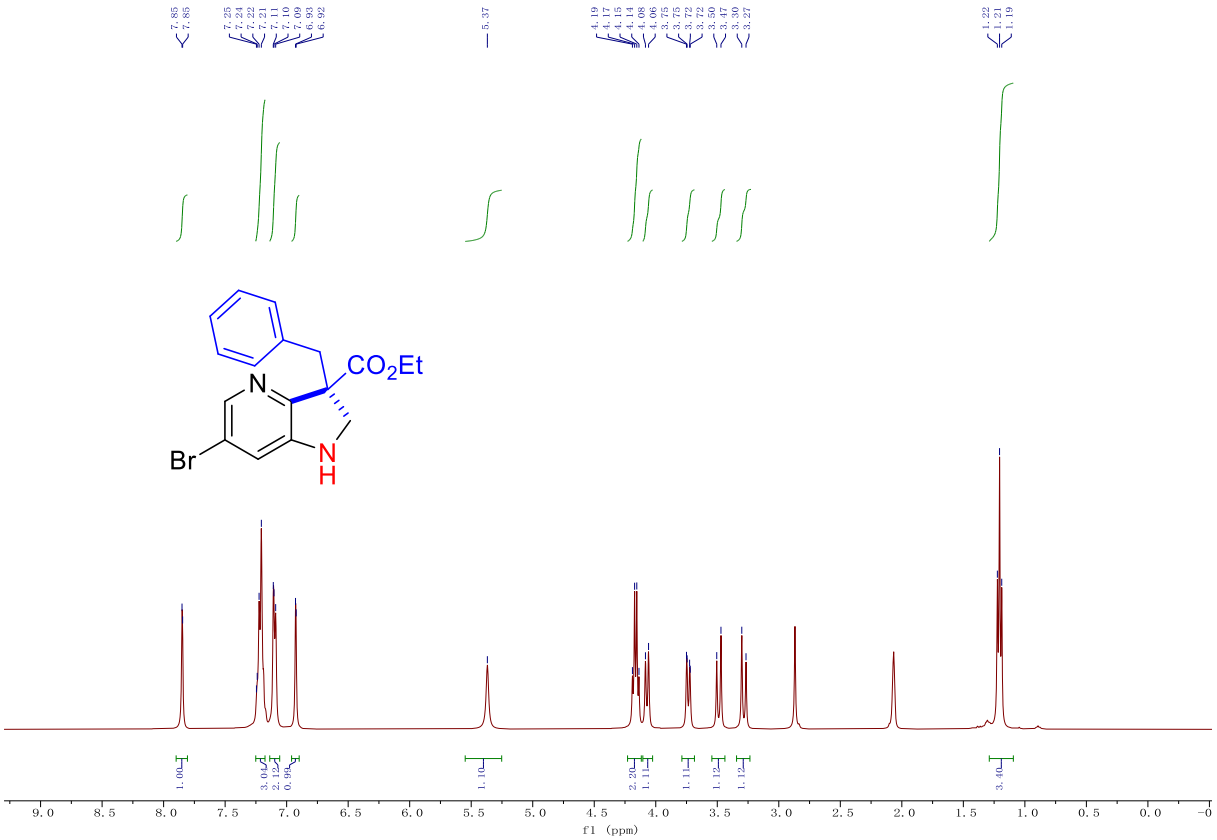
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 4-((6-bromo-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridin-3-yl)sulfonyl)morpholine (4f)

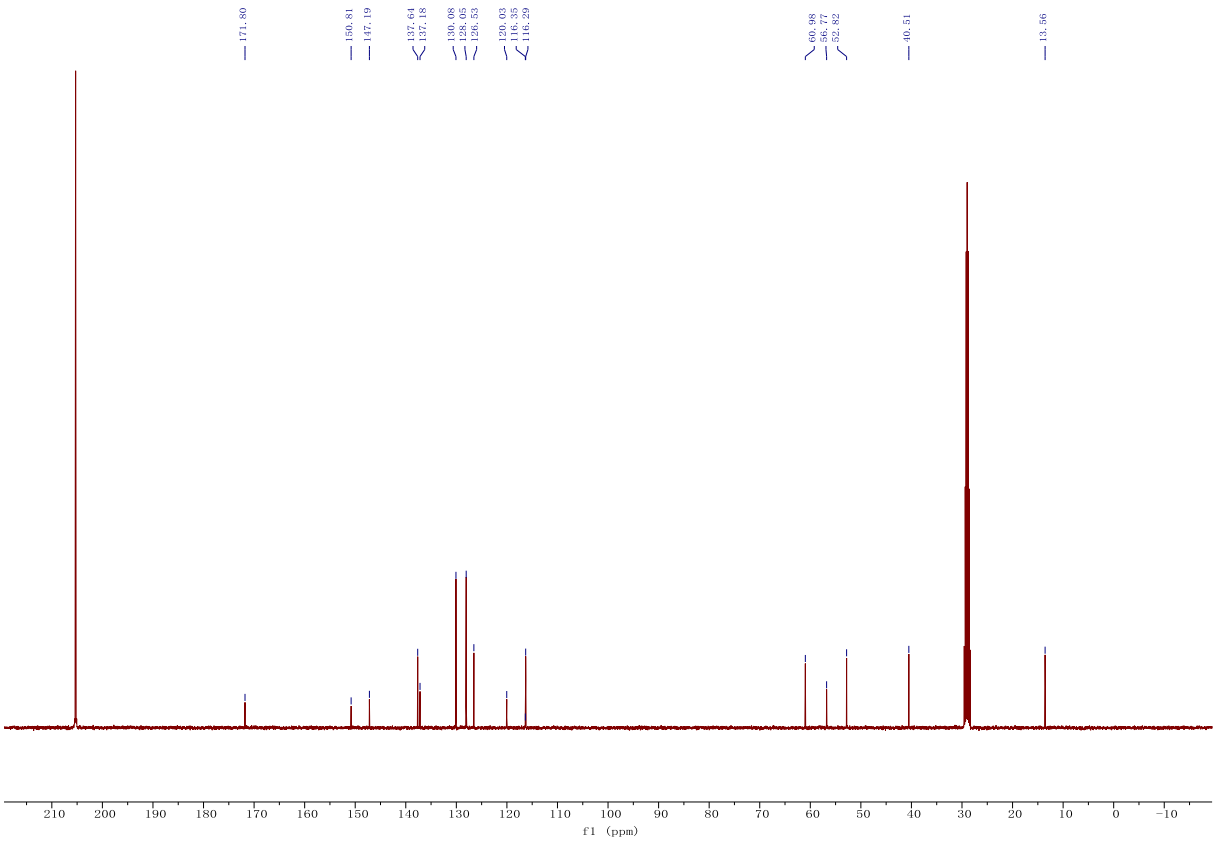


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 6-bromo-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5a)

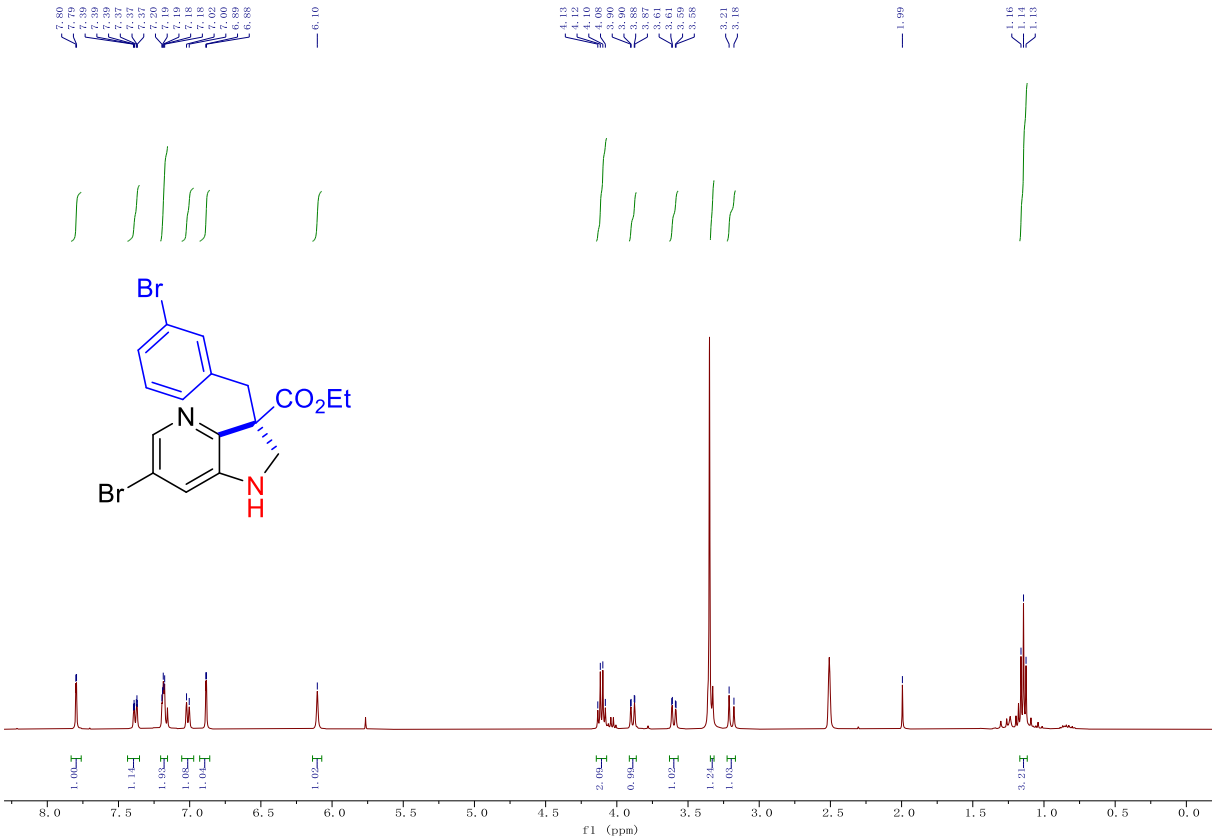


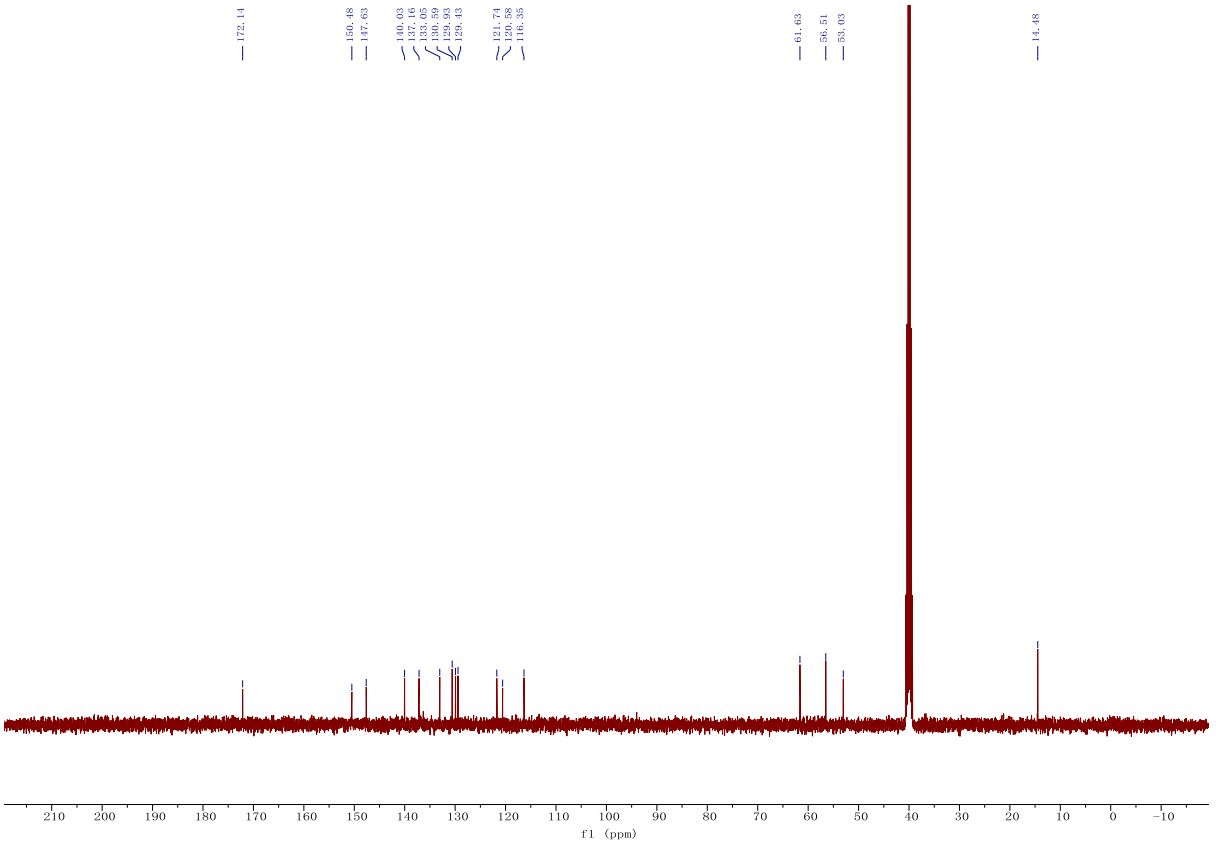
^{1}H NMR (400MHz, Acetone-*d6*) and ^{13}C NMR (101MHz, Acetone-*d6*) spectra of ethyl 3-benzyl-6-bromo-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5b)



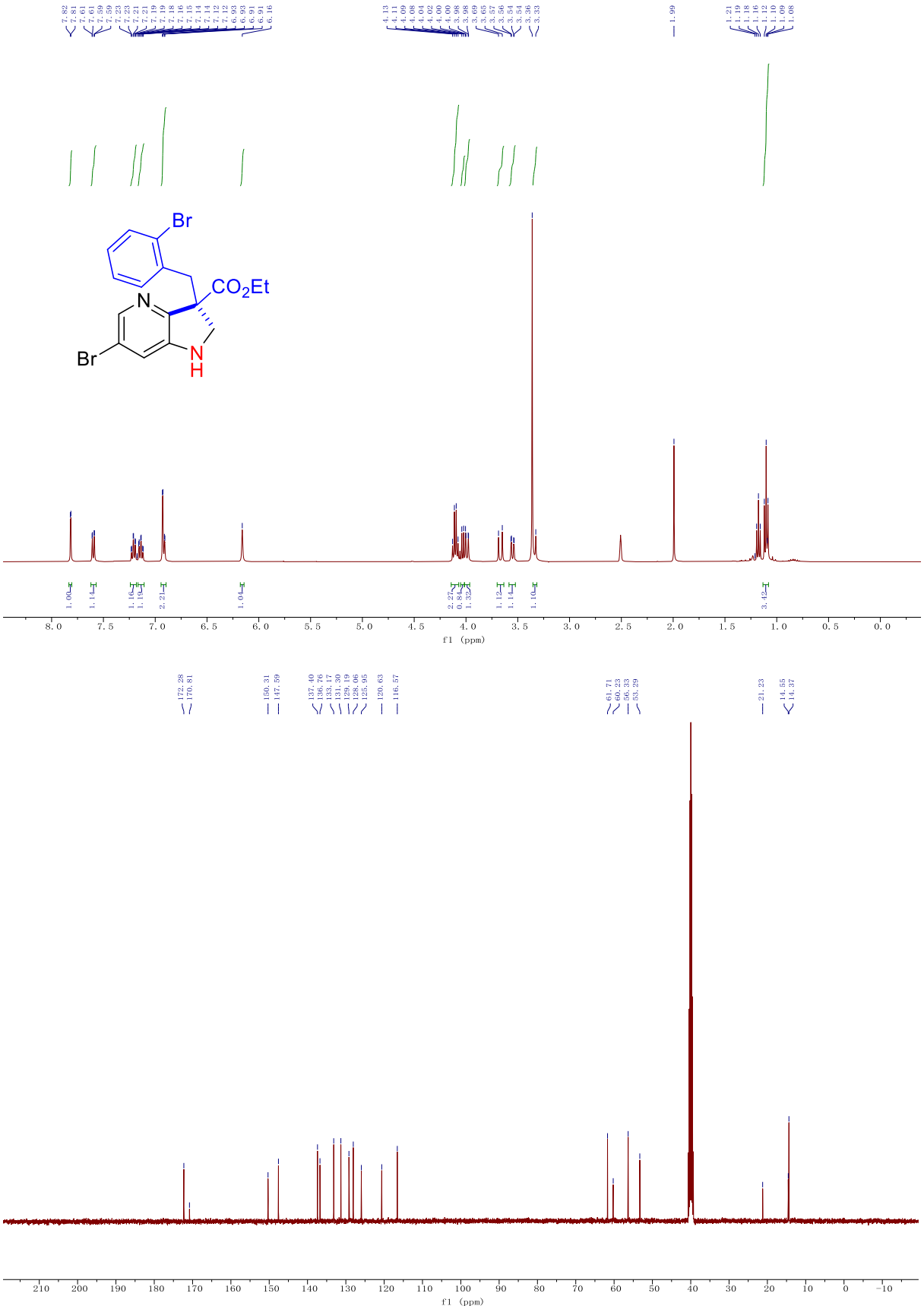


^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of ethyl 6-bromo-3-(3-bromobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5c)

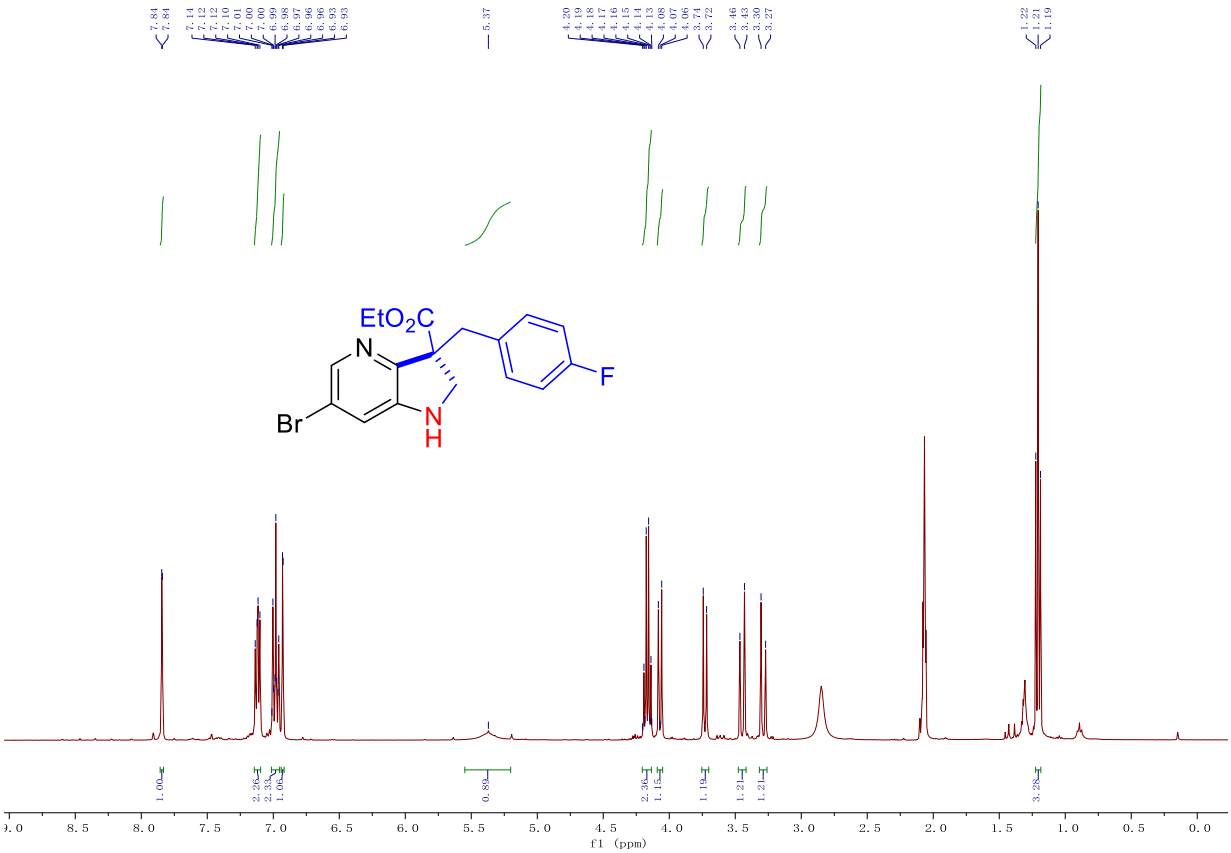


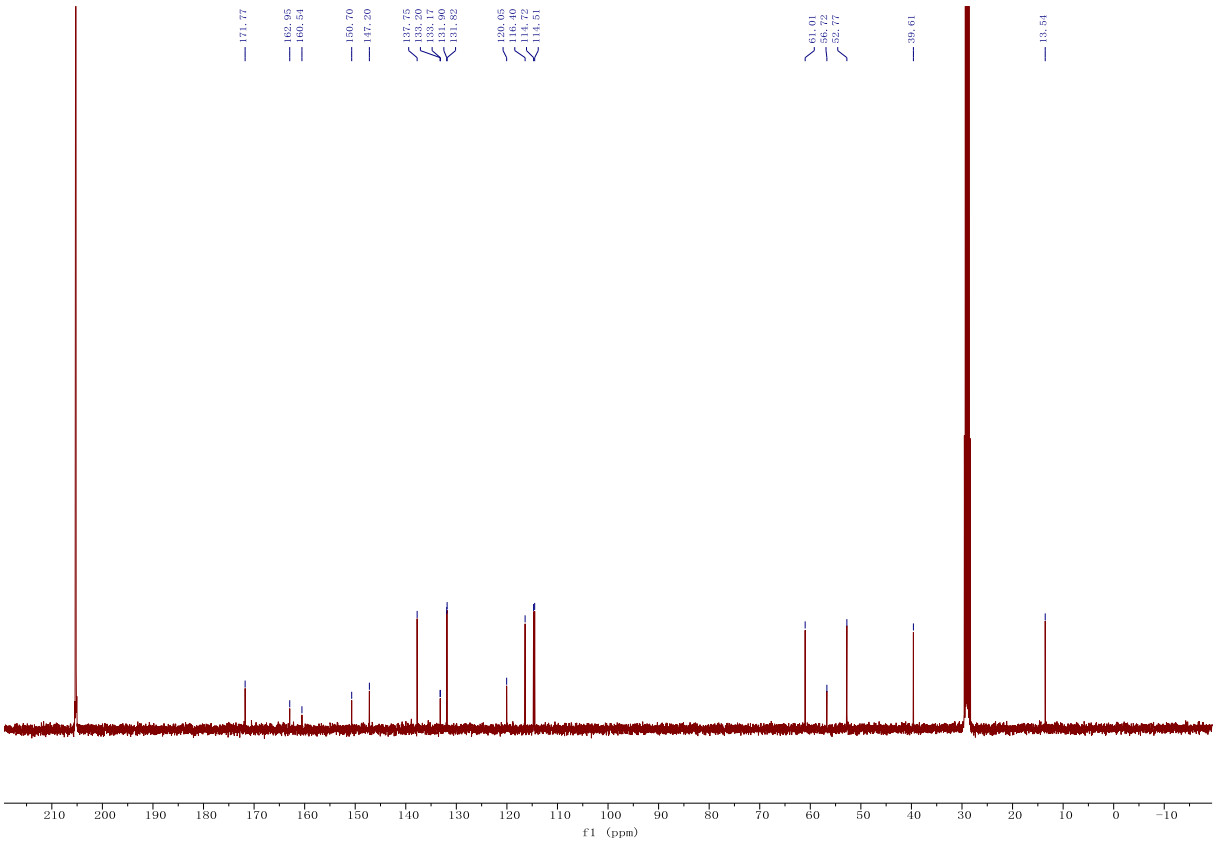


^{1}H NMR (400MHz, Acetone-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of ethyl 6-bromo-3-(2-bromobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5d)

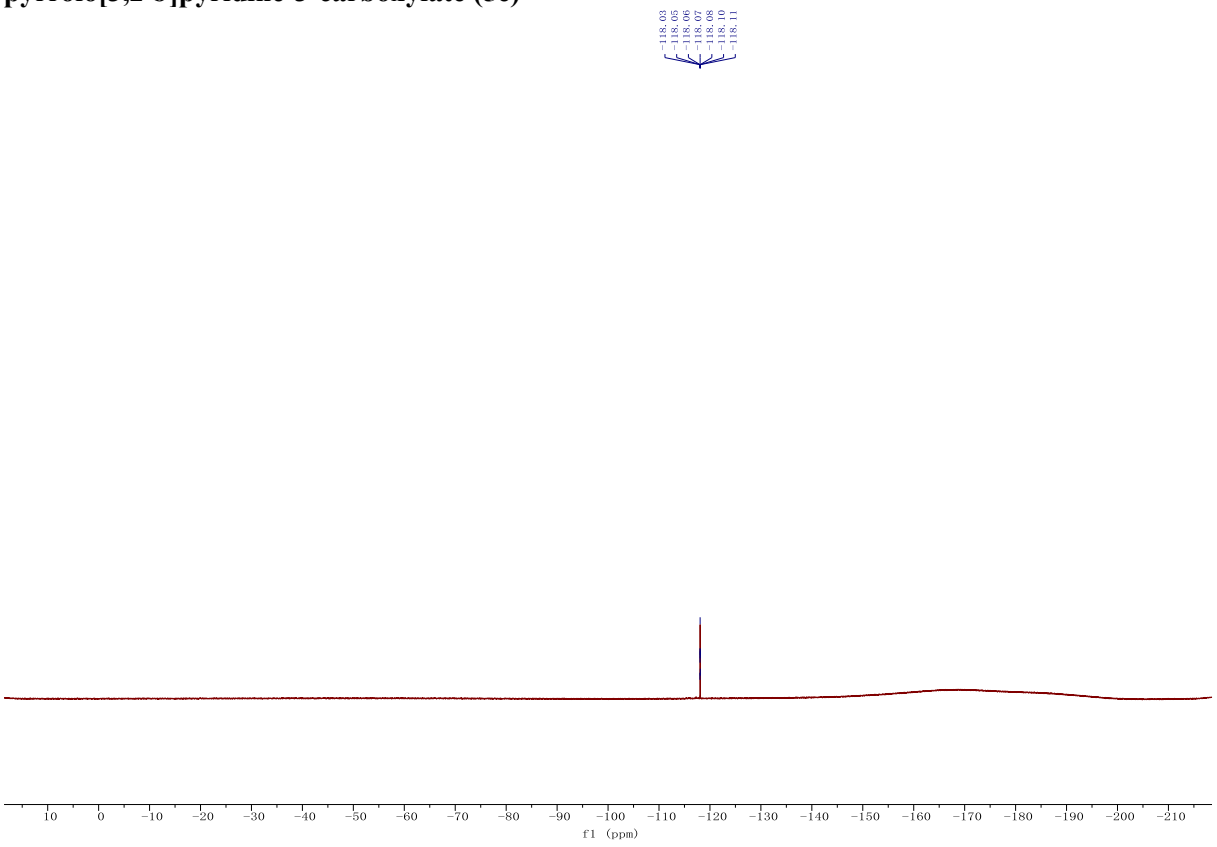


^{1}H NMR (400MHz, Acetone-*d6*), ^{13}C NMR (101MHz, Acetone-*d6*) and ^{19}F NMR (376 MHz, Acetone-*d6*) spectra of Ethyl-6-bromo-3-(4-fluorobenzyl)-2,3-dihydro-1H-pyrrolo[3,2-b]pyridine-3-carboxylate (5e)

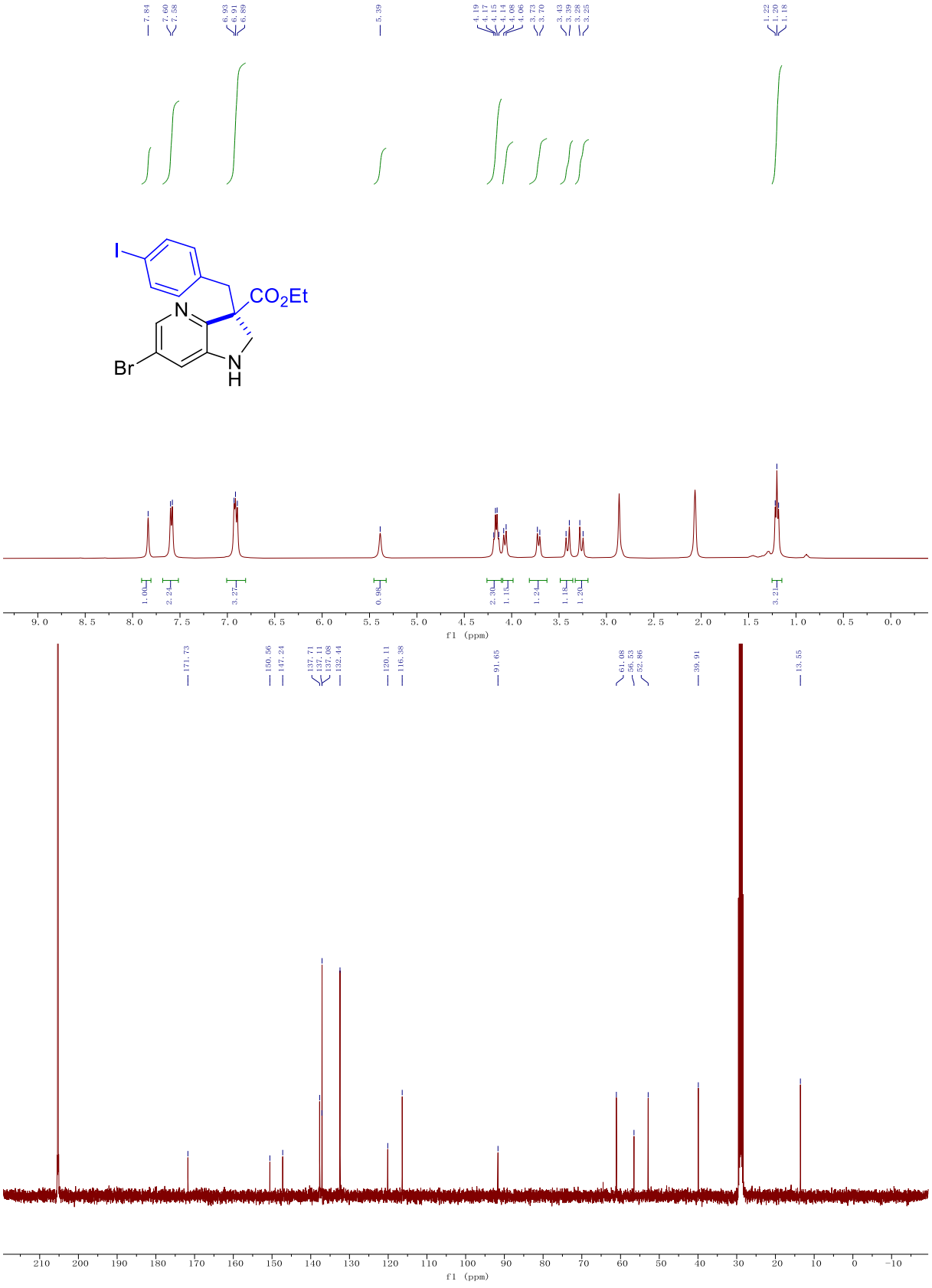




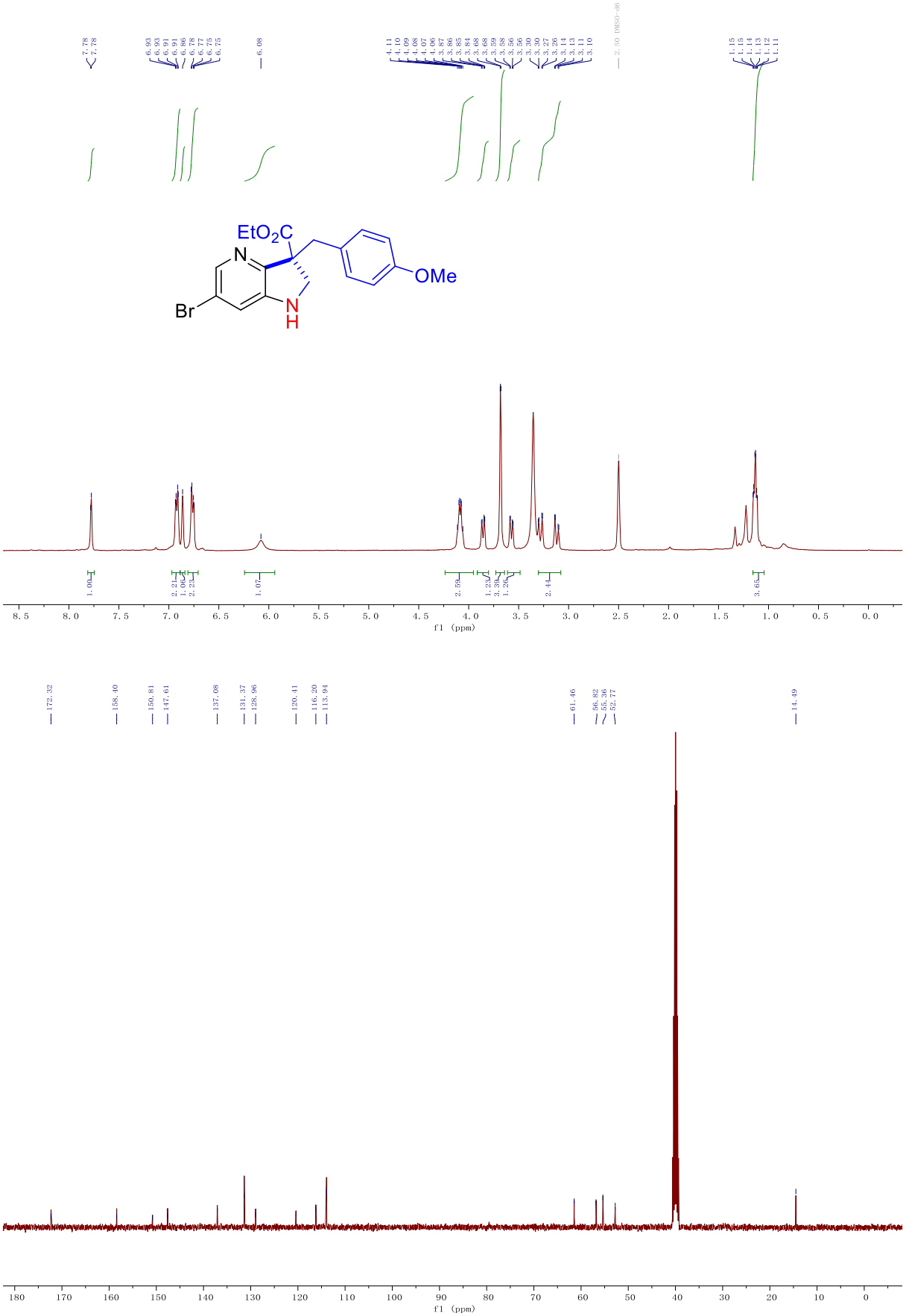
^{19}F NMR (376 MHz, Acetone-*d6*) spectra of ethyl 6-bromo-3-(4-fluorobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5e)



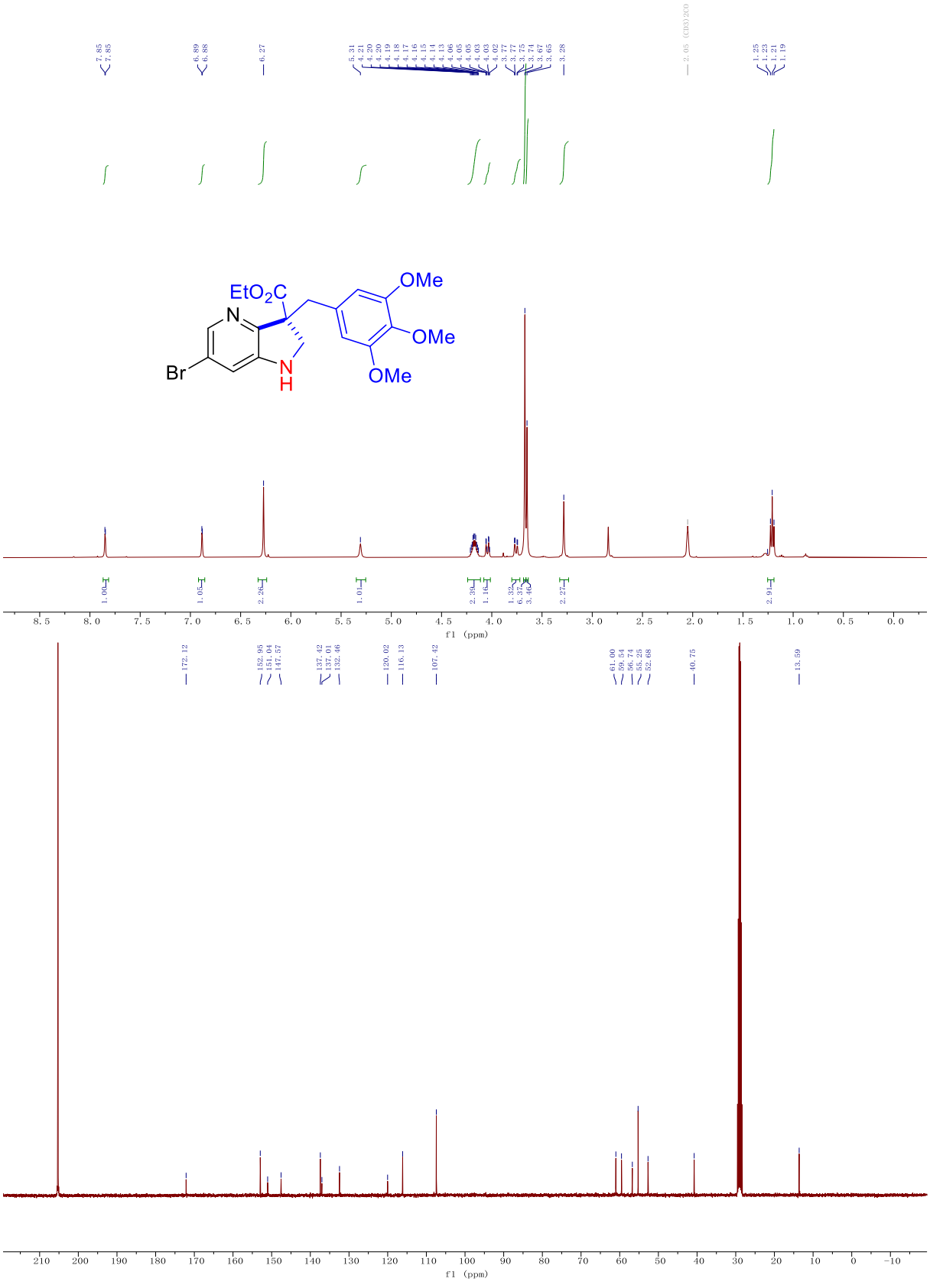
^{1}H NMR (400MHz, Acetone-*d6*) and ^{13}C NMR (101MHz, Acetone-*d6*) spectra of ethyl 6-bromo-3-(4-iodobenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5f)



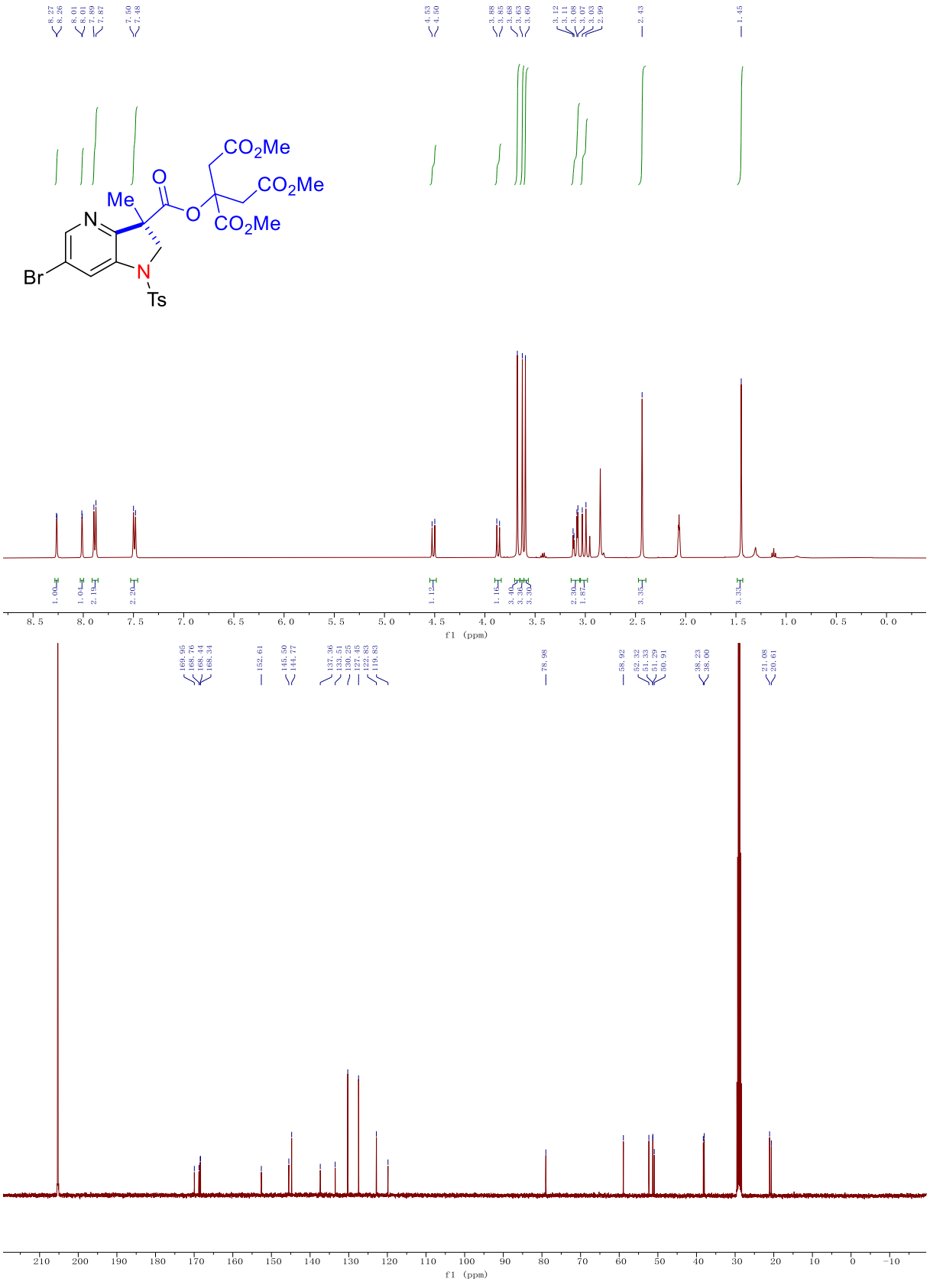
^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of ethyl-6-bromo-3-(4-methoxybenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5g)



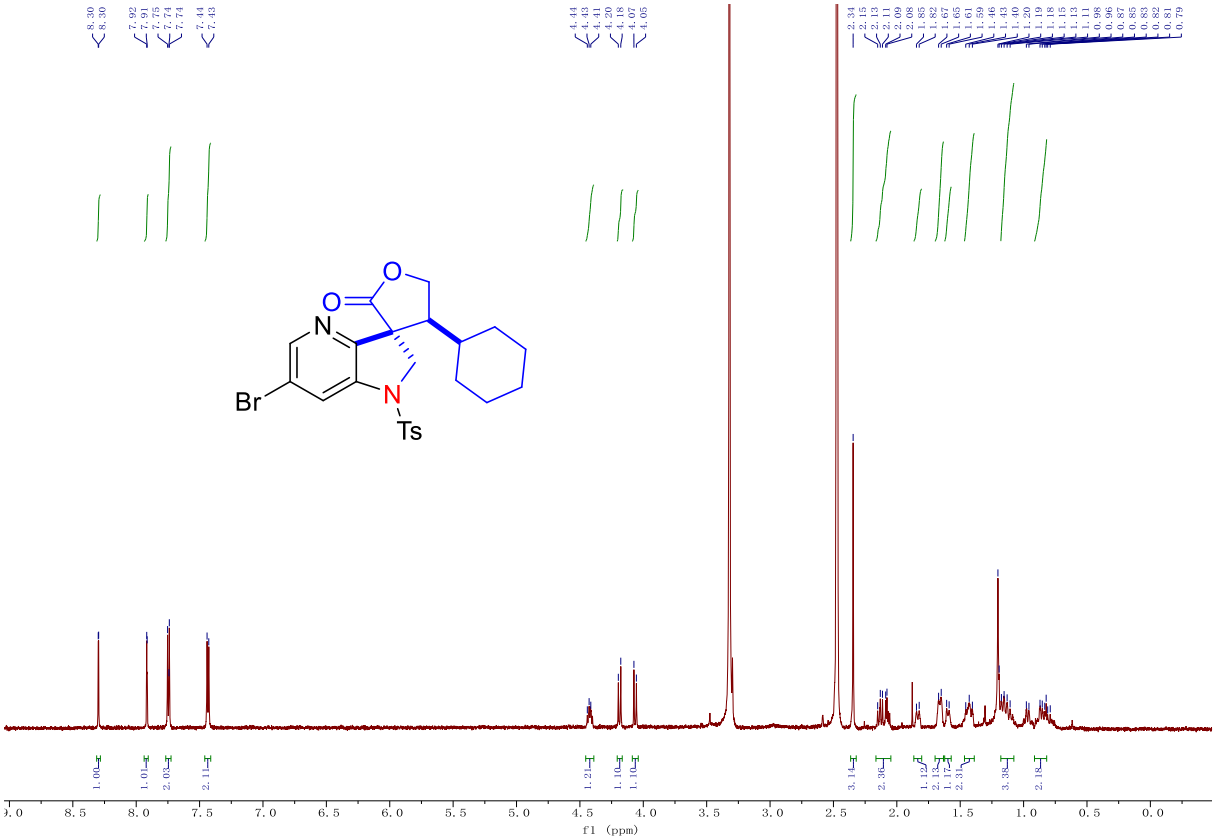
^{1}H NMR (400MHz, Acetone-*d6*) and ^{13}C NMR (101MHz, Acetone-*d6*) spectra of ethyl 6-bromo-3-(3,4,5-trimethoxybenzyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5h)

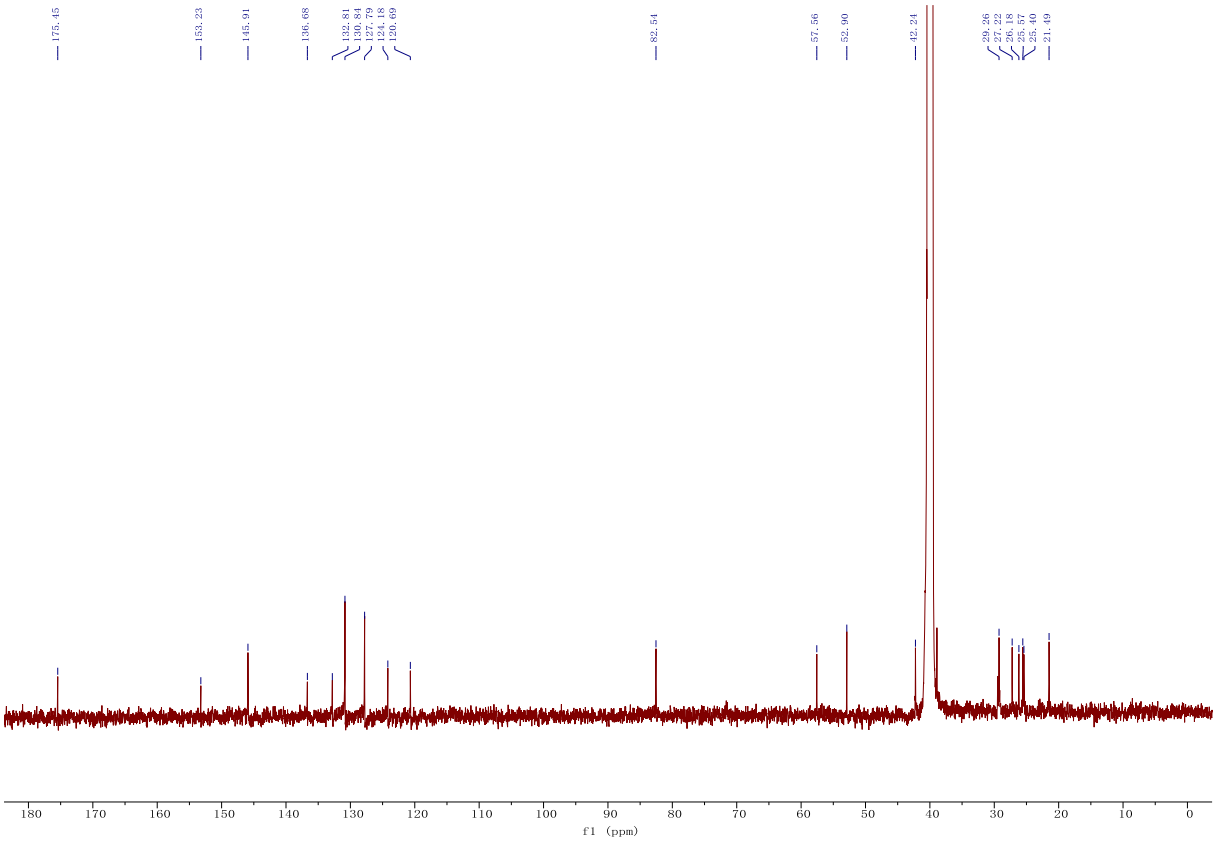


^{1}H NMR (400MHz, Acetone-*d6*) and ^{13}C NMR (101MHz, Acetone-*d6*) spectra of trimethyl 2-((6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonyl)oxy)propane-1,2,3-tricarboxylate (5i)

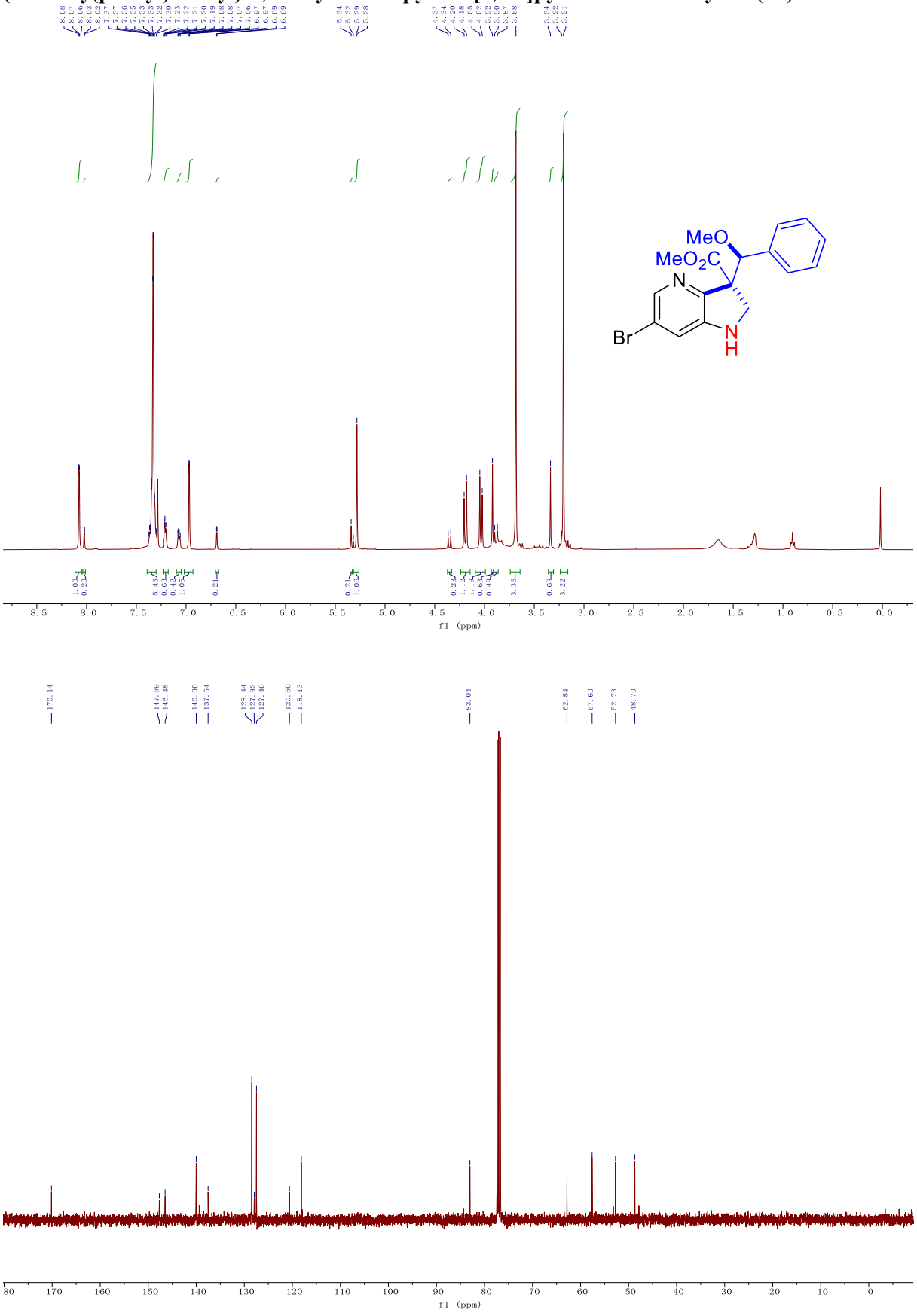


^{1}H NMR (600MHz, DMSO-*d6*) and ^{13}C NMR (151MHz, DMSO-*d6*) spectra of 6'-bromo-4-cyclohexyl-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (5j)

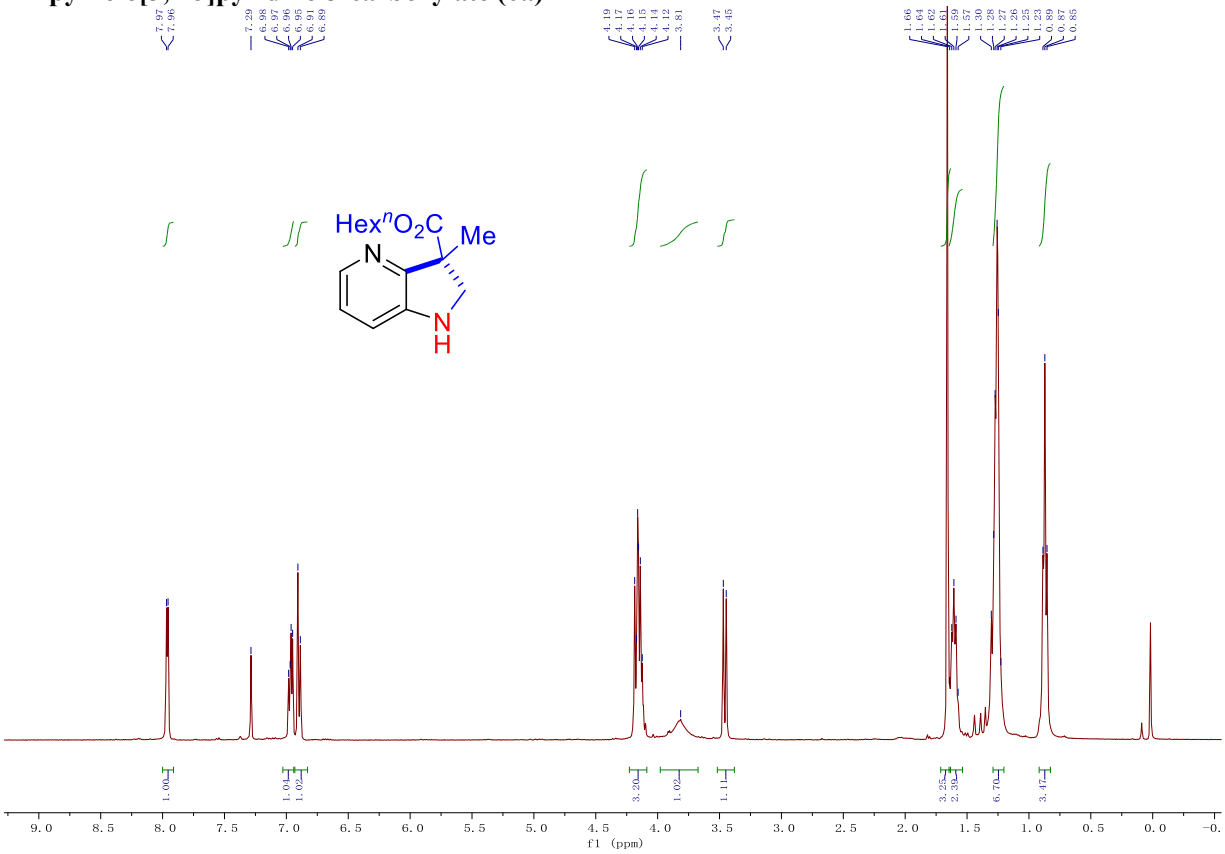


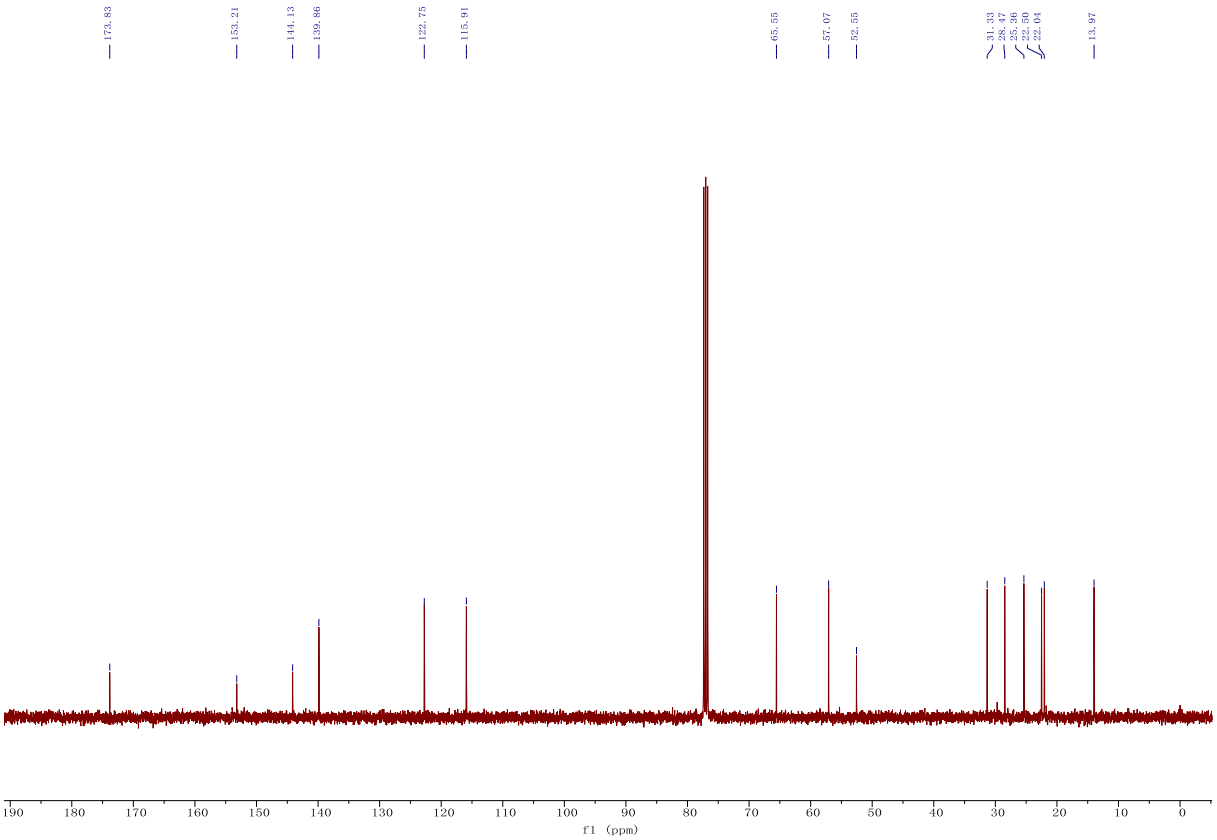


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of methyl 6-bromo-3-(methoxy(phenyl)methyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (5k)

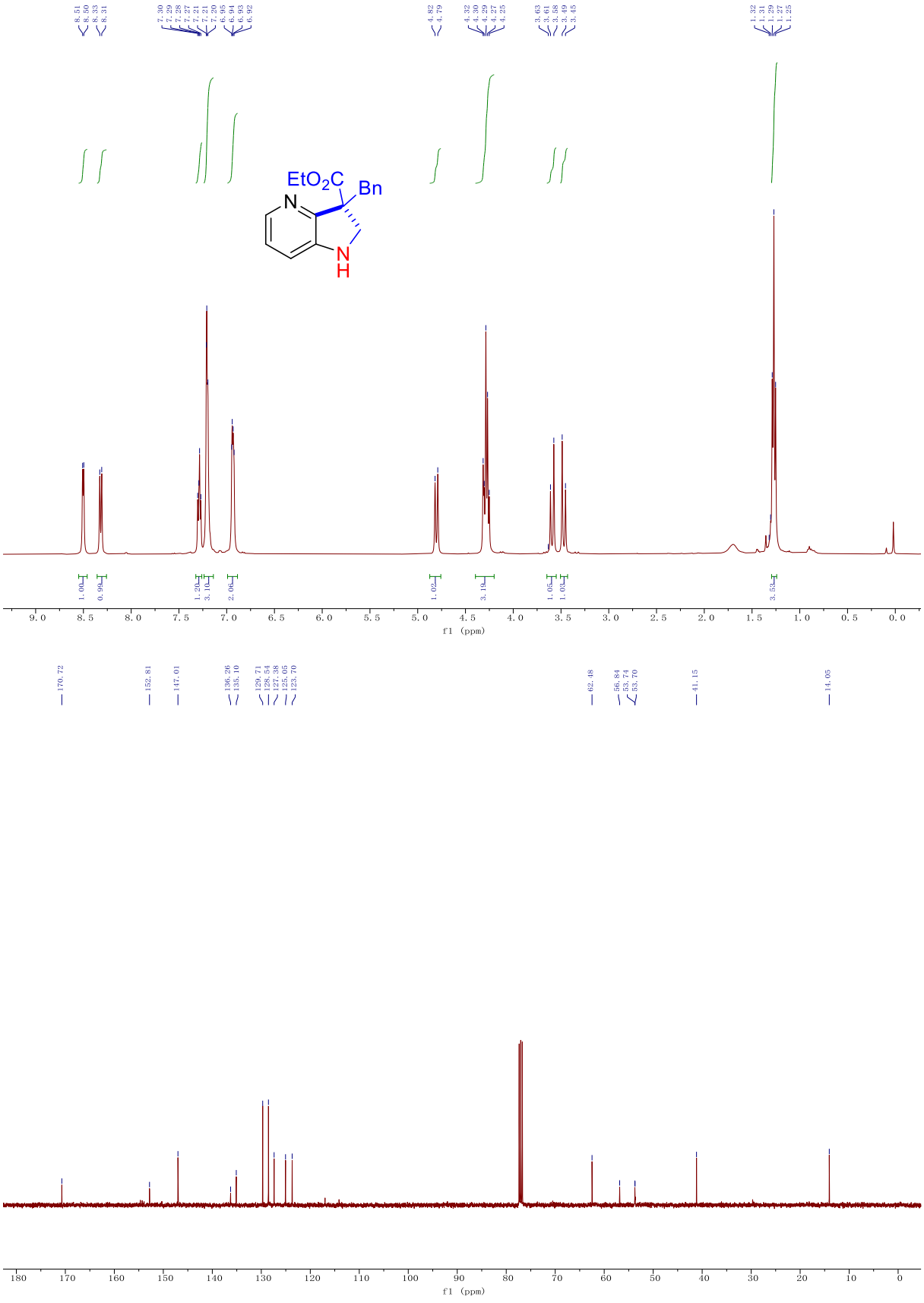


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6a)

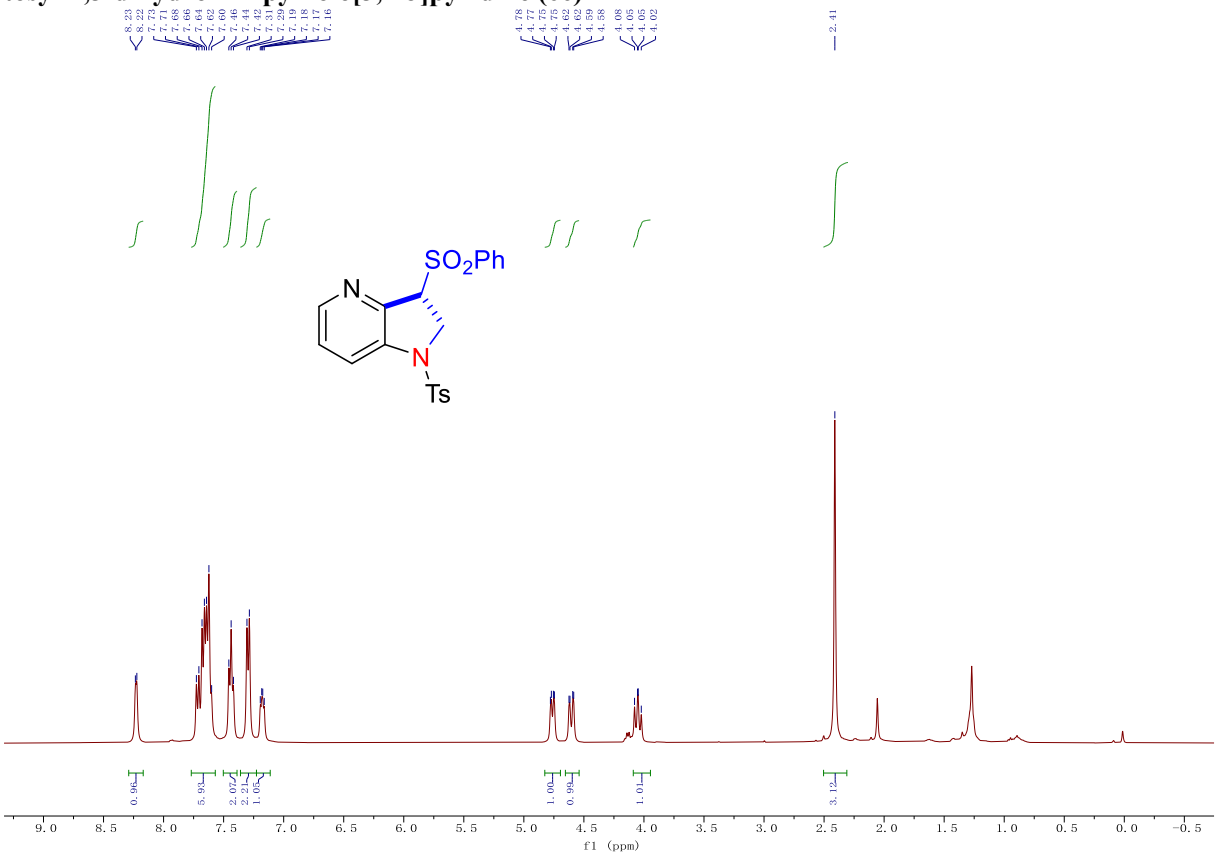


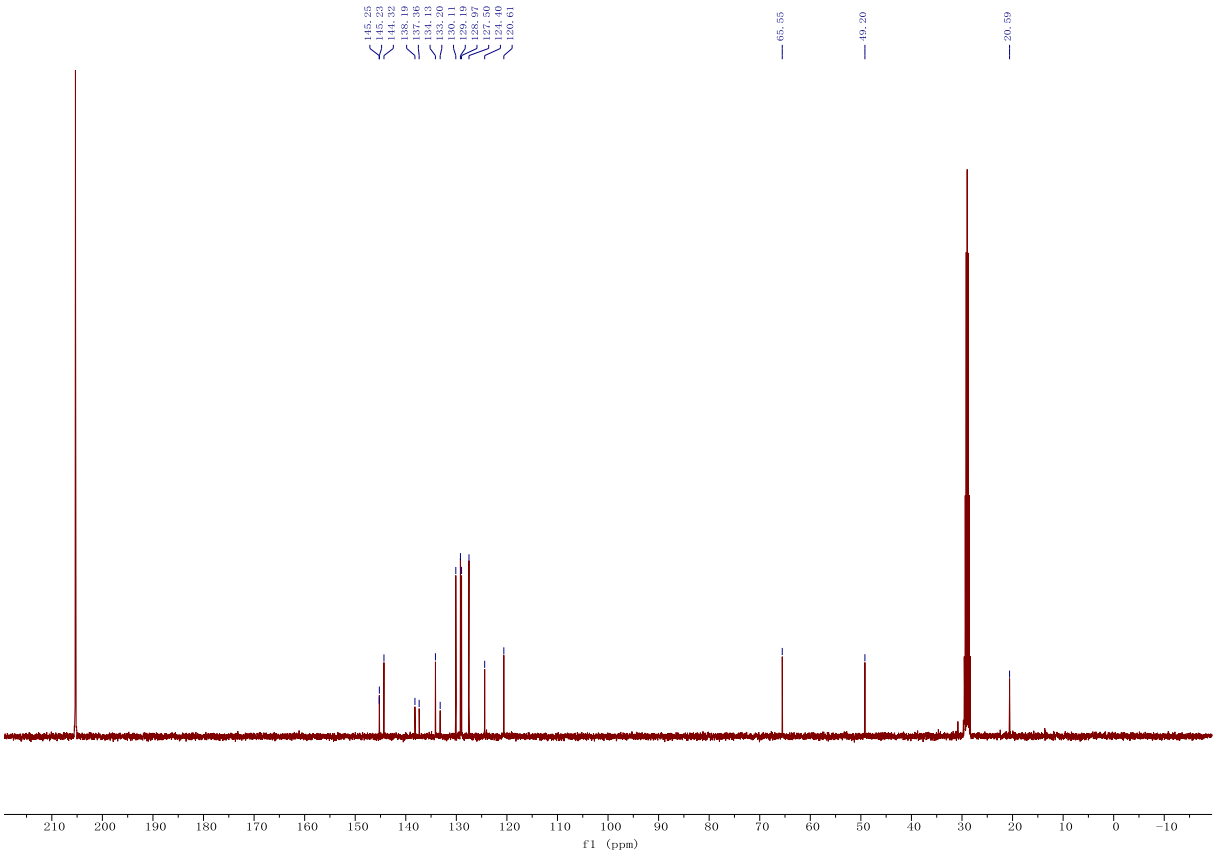


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ethyl 3-benzyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6b)

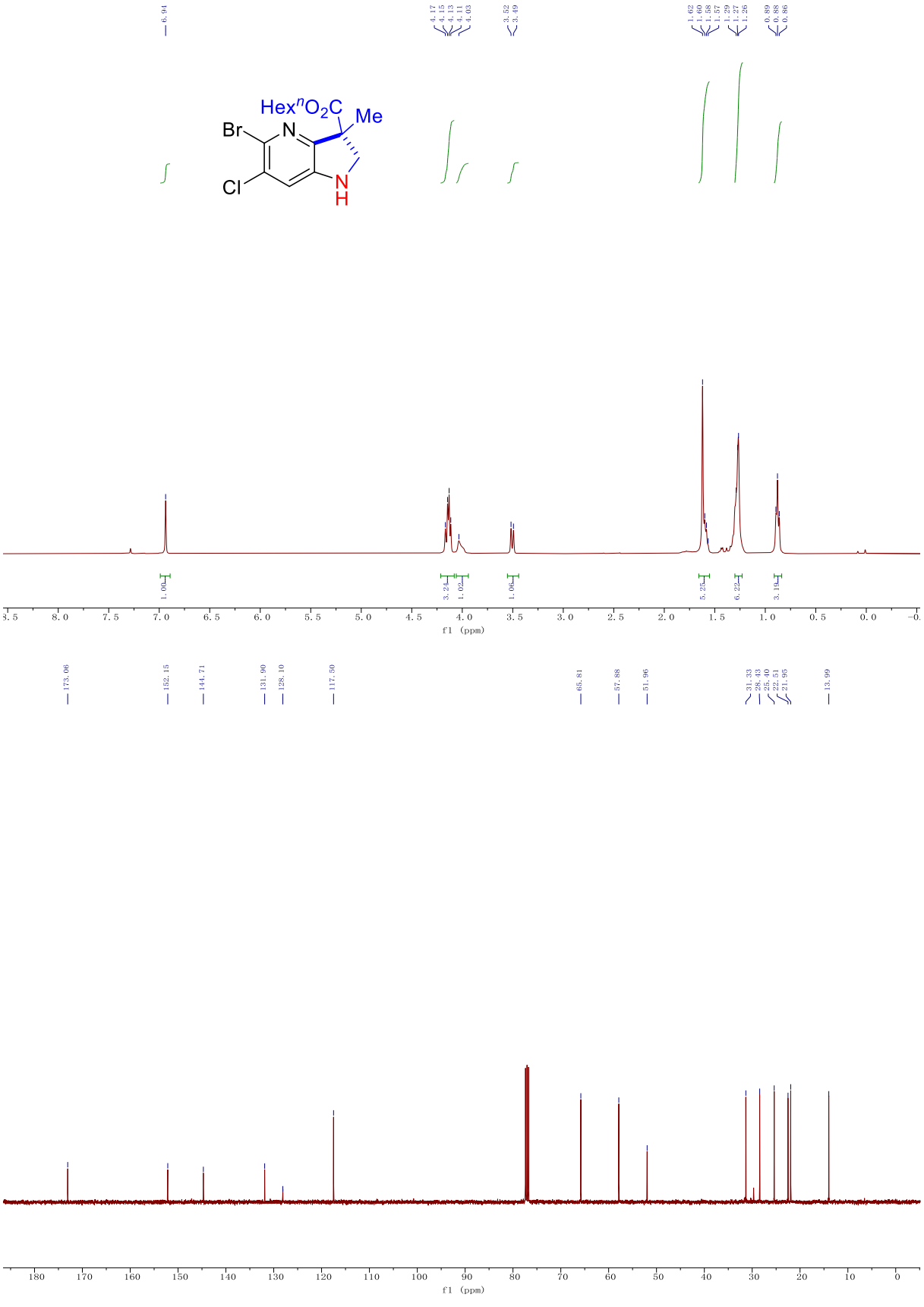


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, Acetone-*d6*) spectra of 3-(phenylsulfonyl)-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (6c)

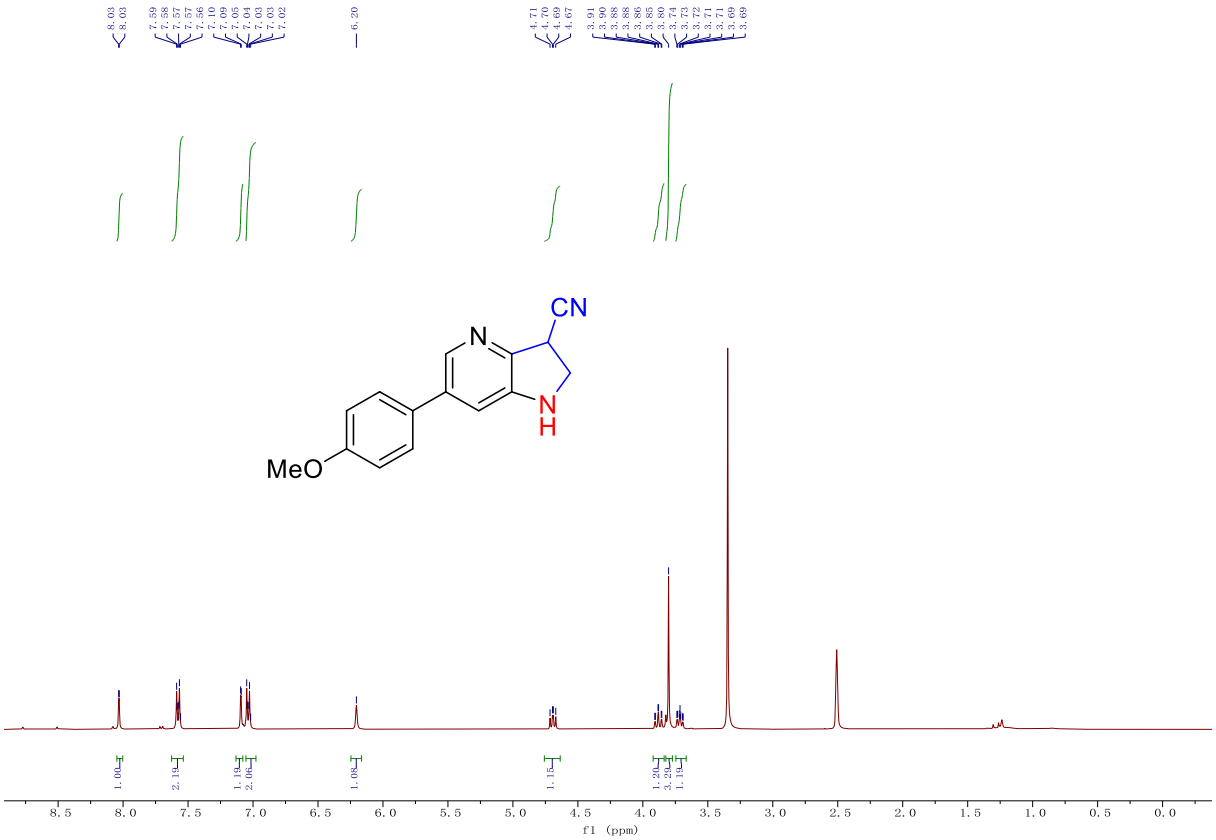


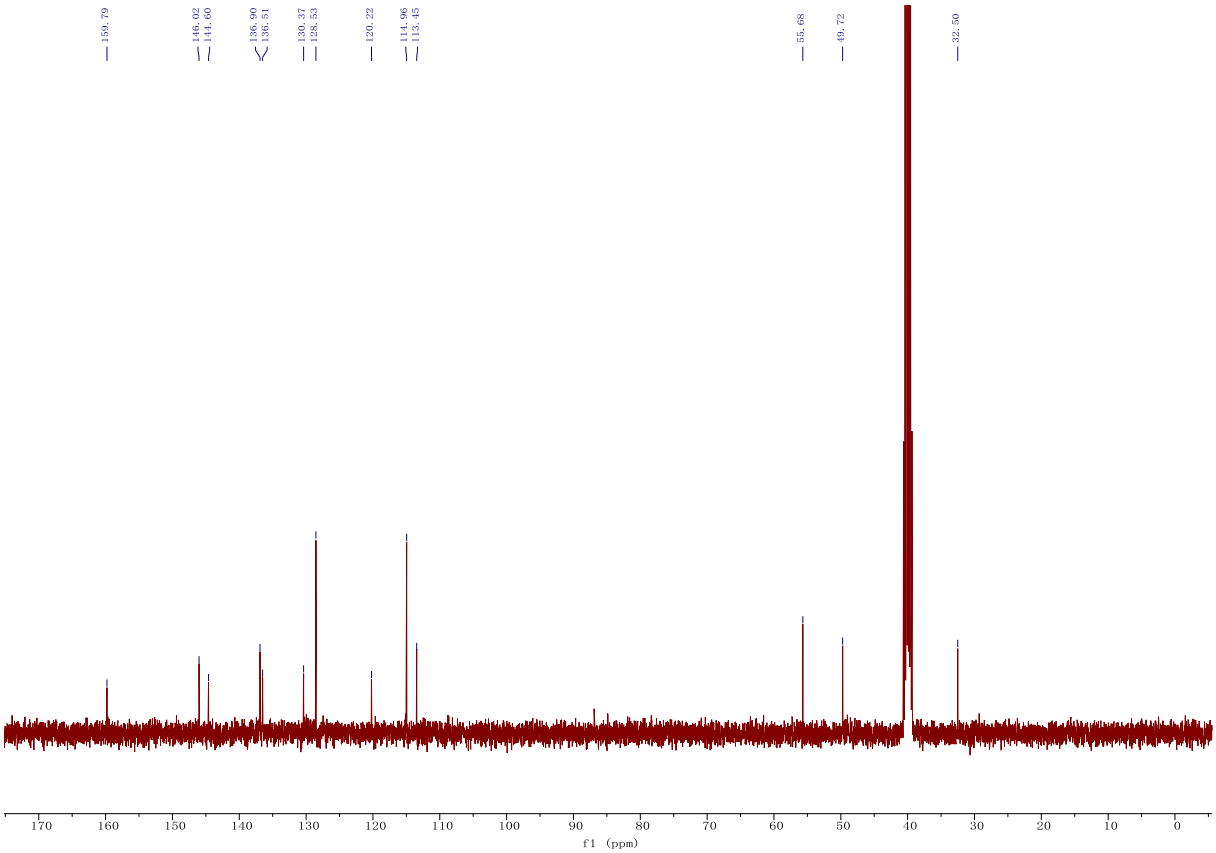


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 5-bromo-6-chloro-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6d)

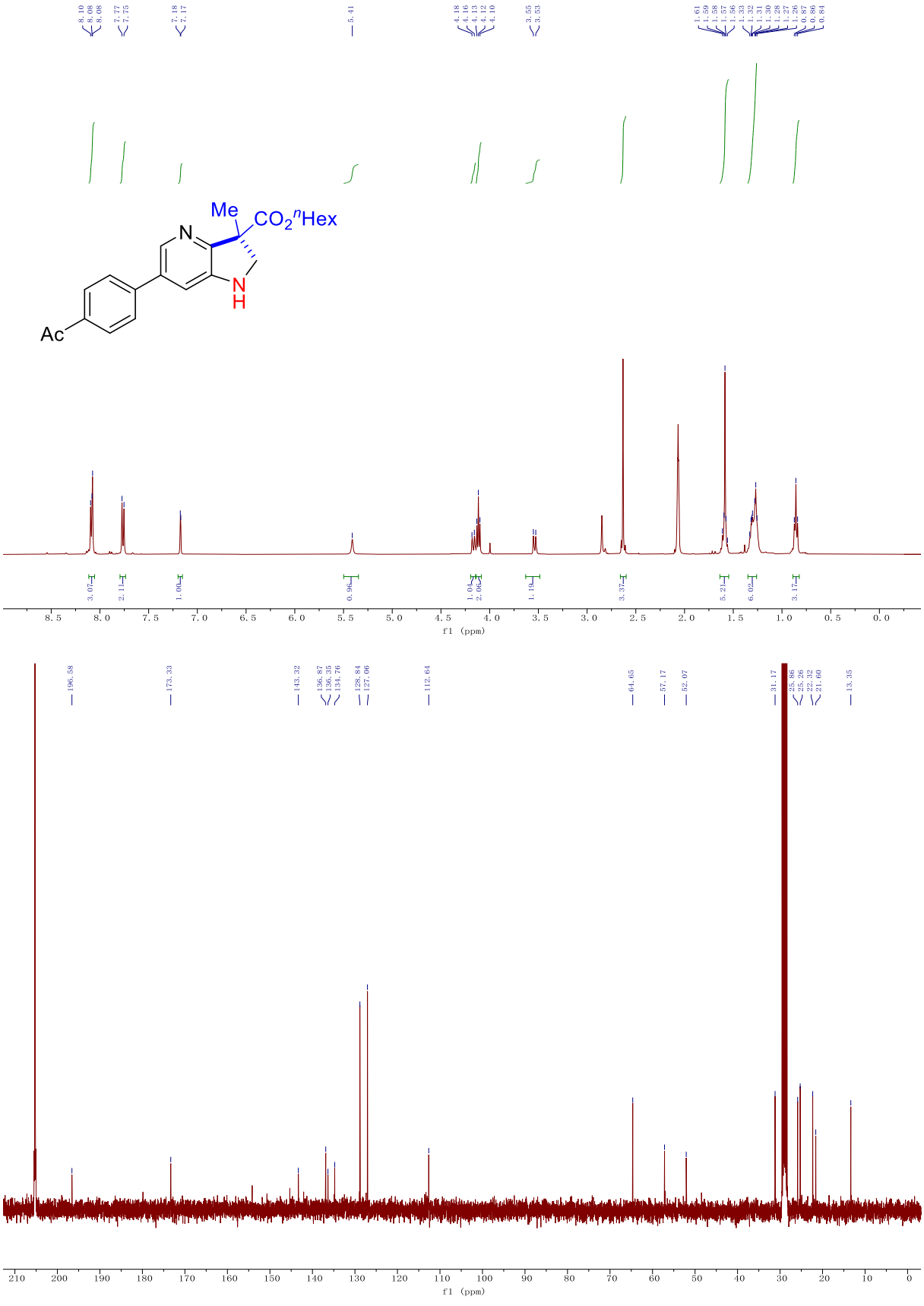


^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of 6-(4-methoxyphenyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (6e)

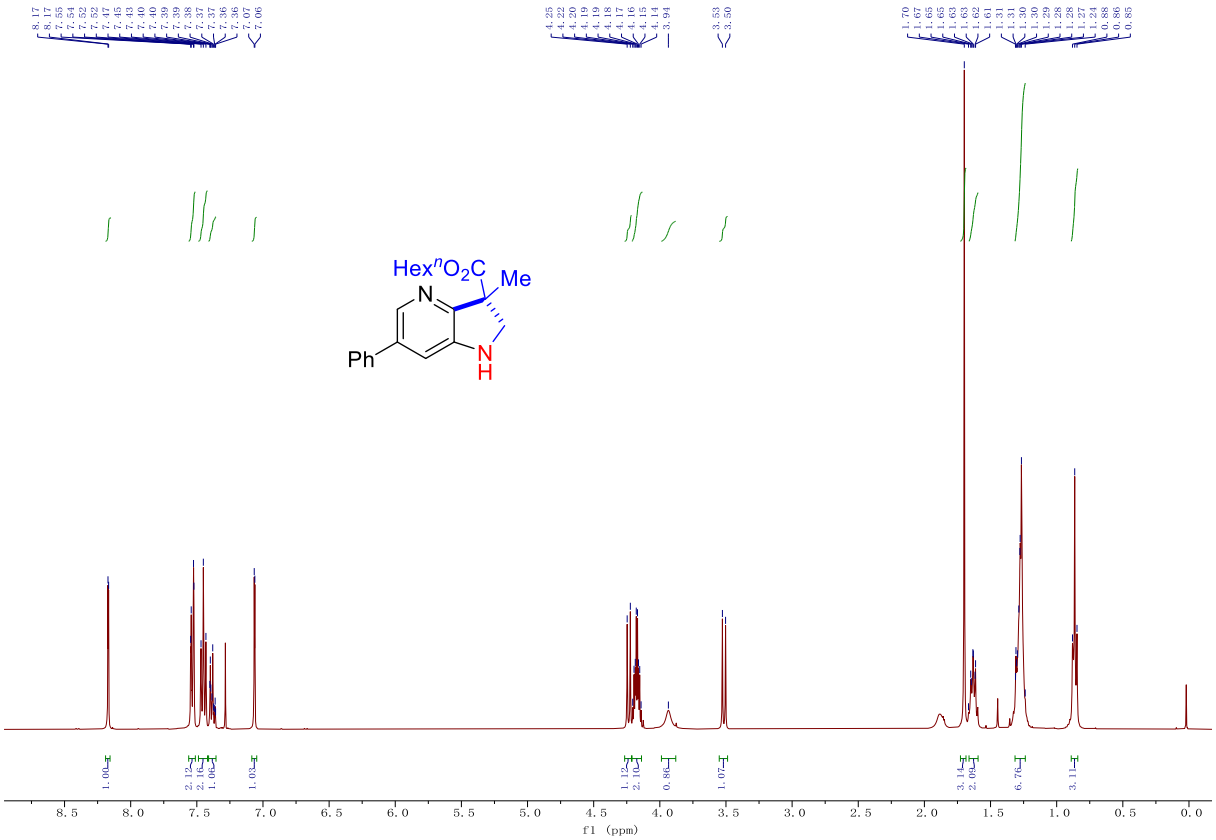


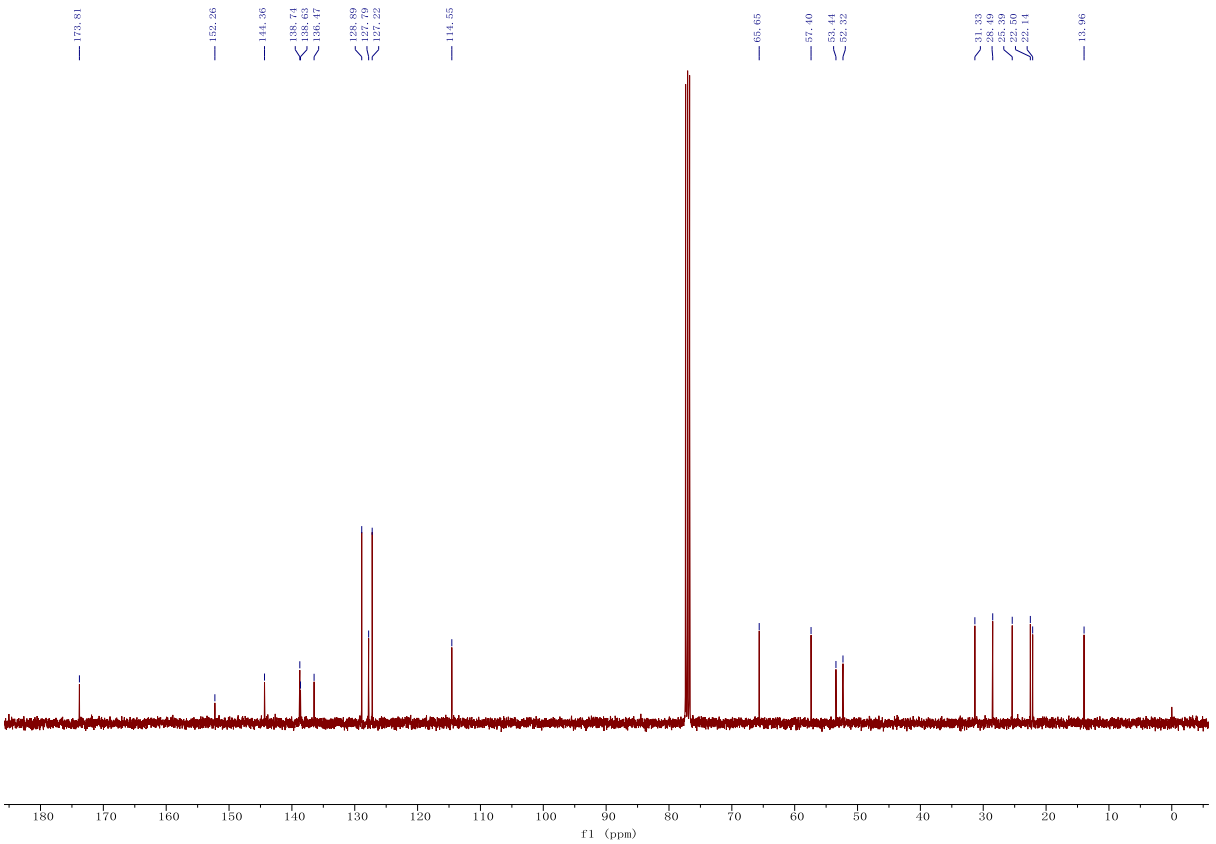


^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of hexyl 6-(4-acetyl-phenyl)-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6f)

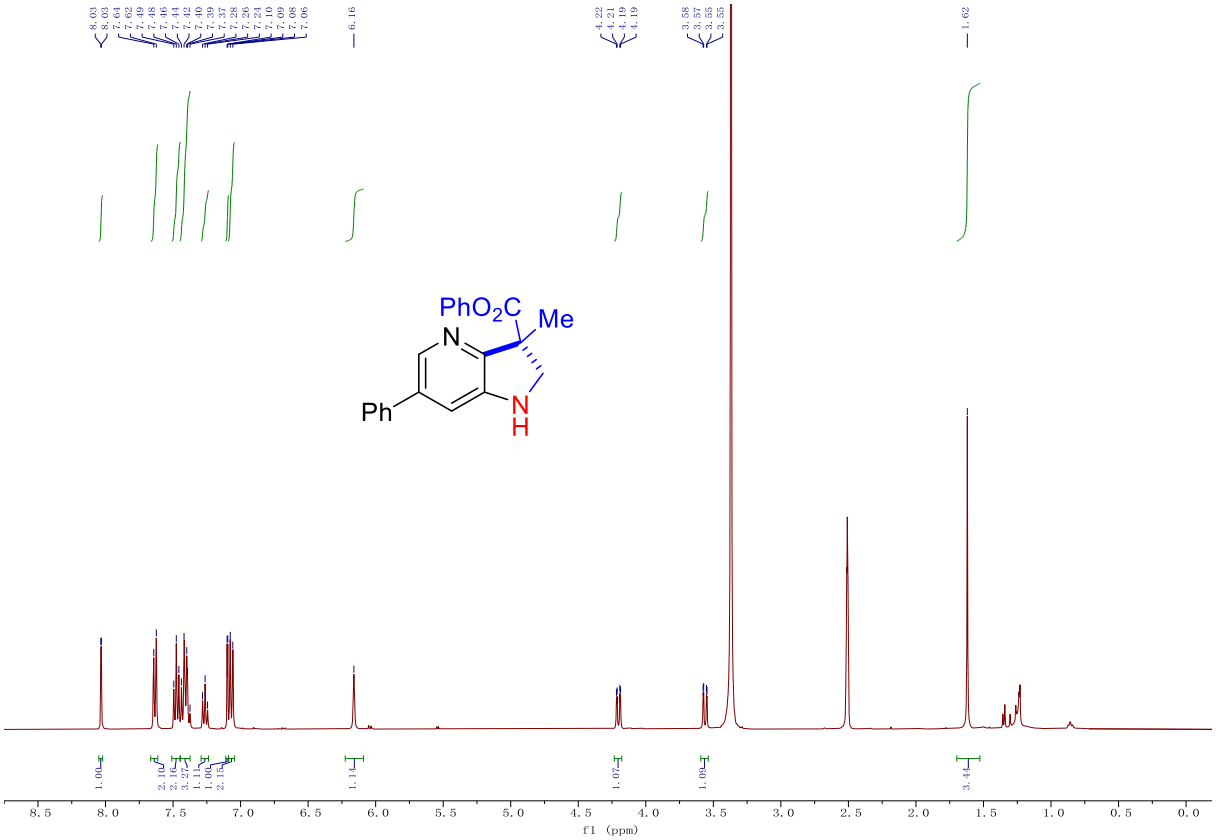


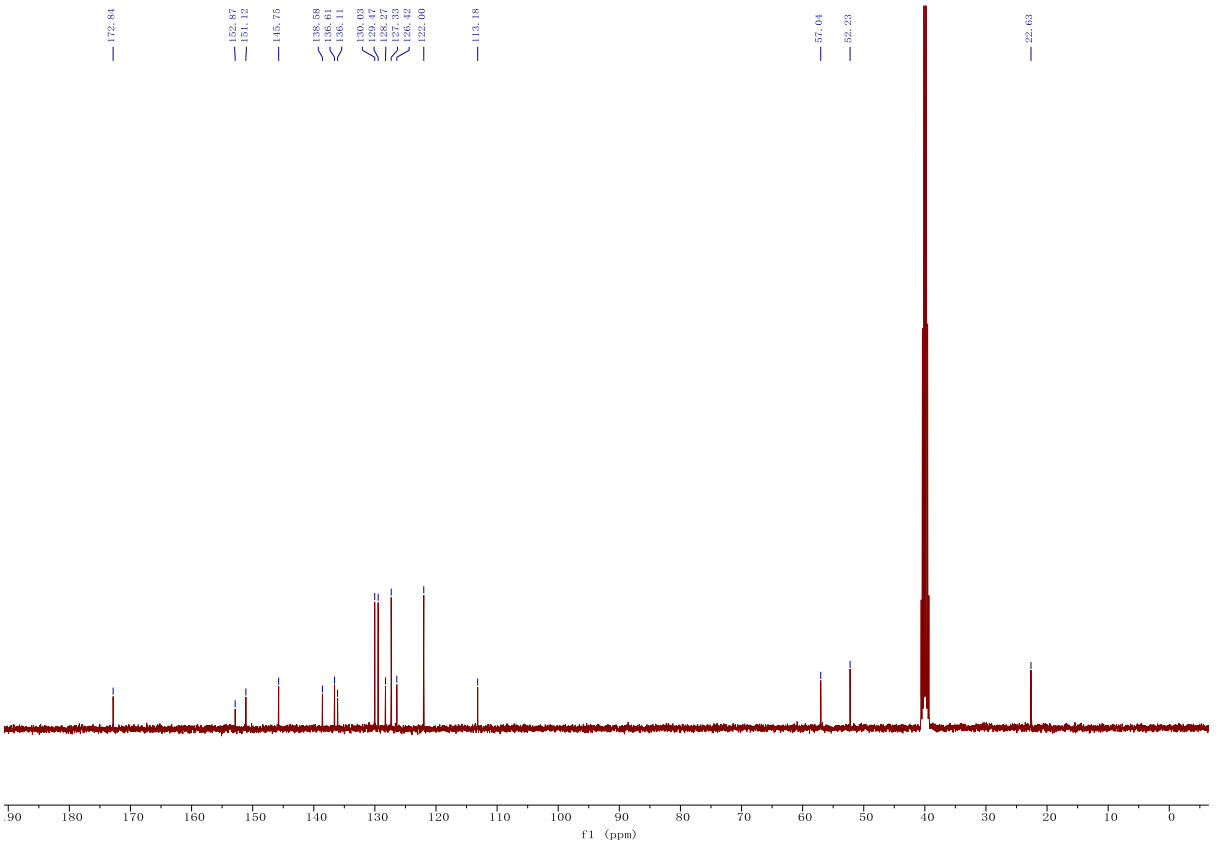
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 3-methyl-6-phenyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6g)



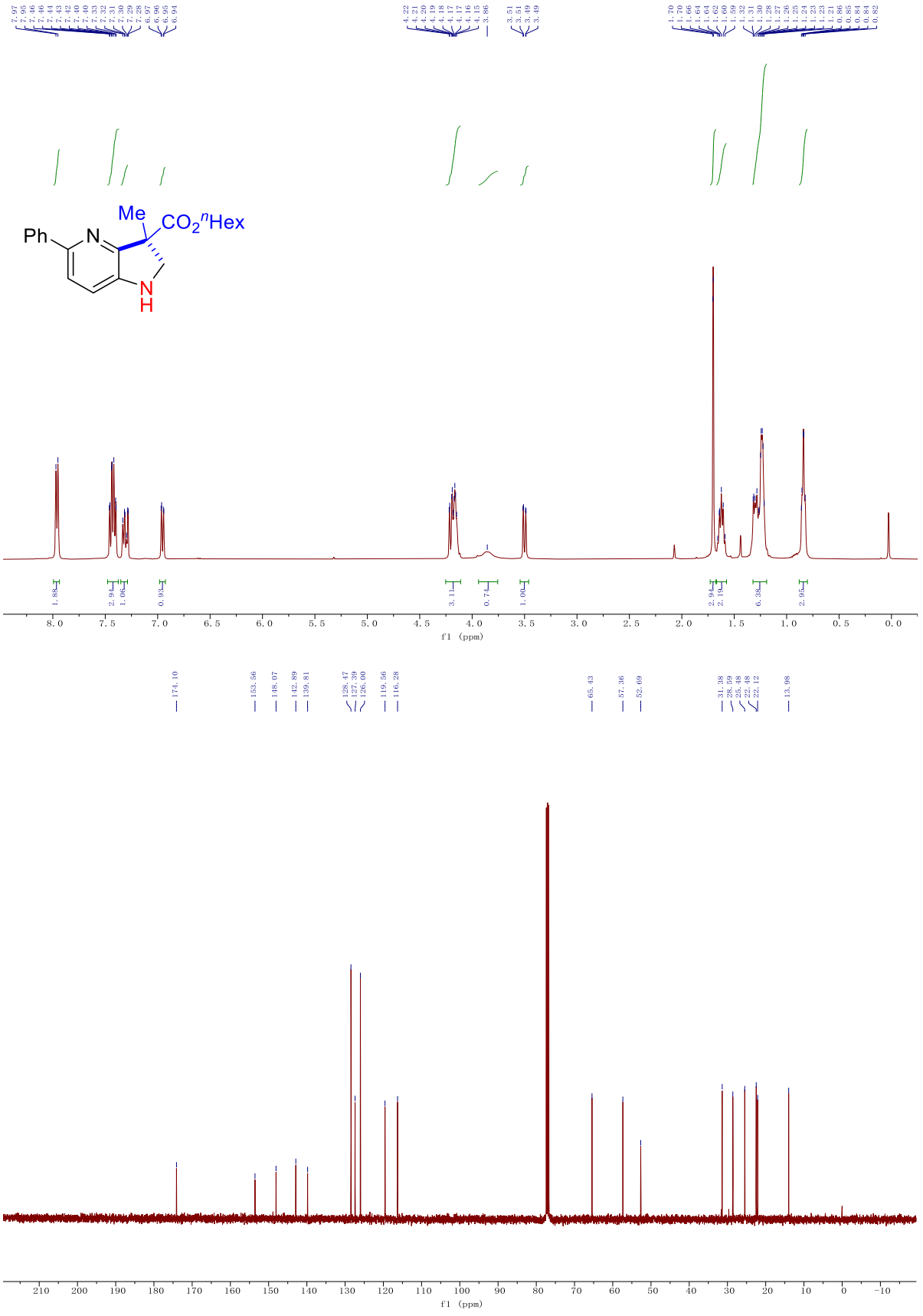


^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of phenyl 3-methyl-6-phenyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6h)

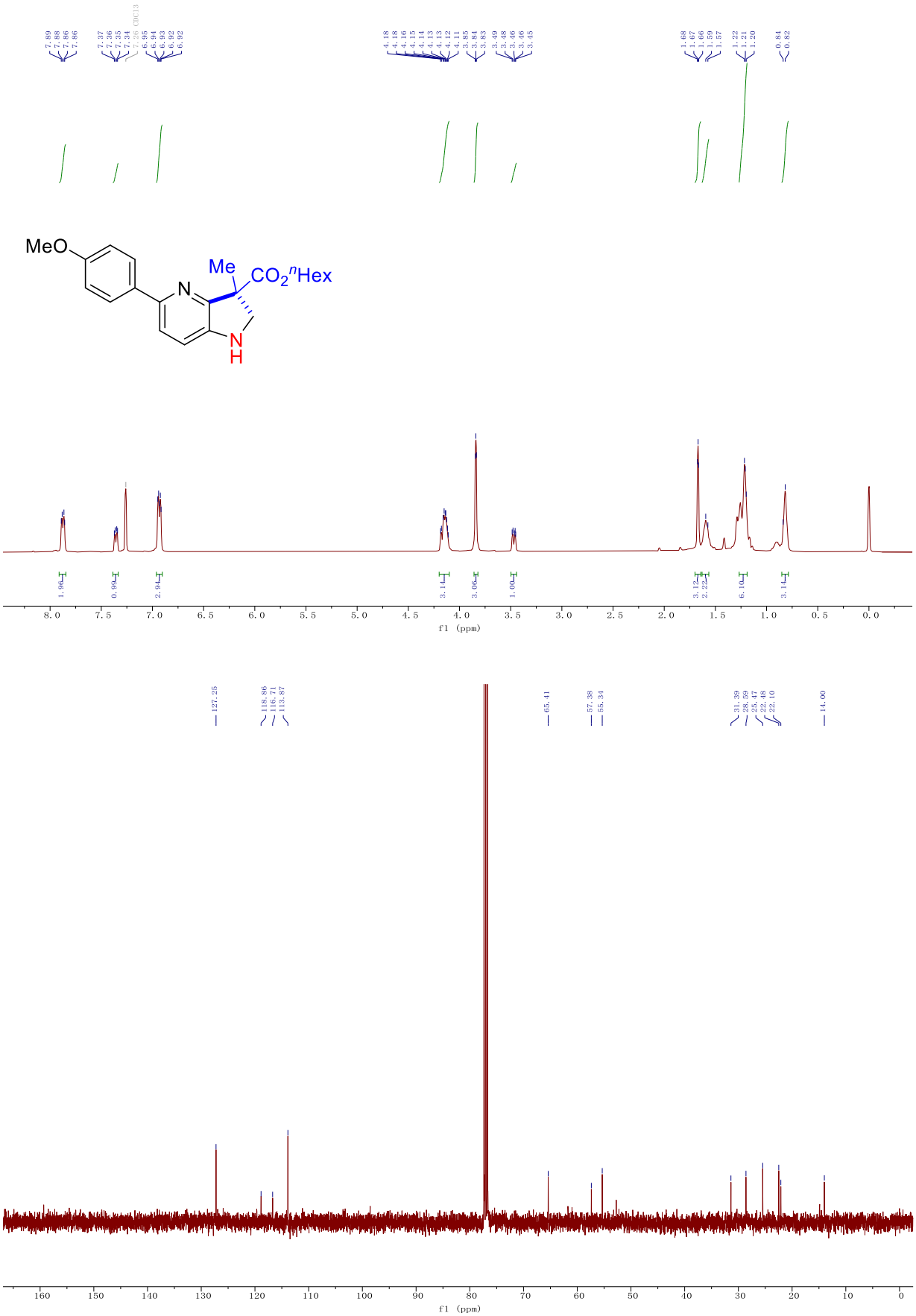




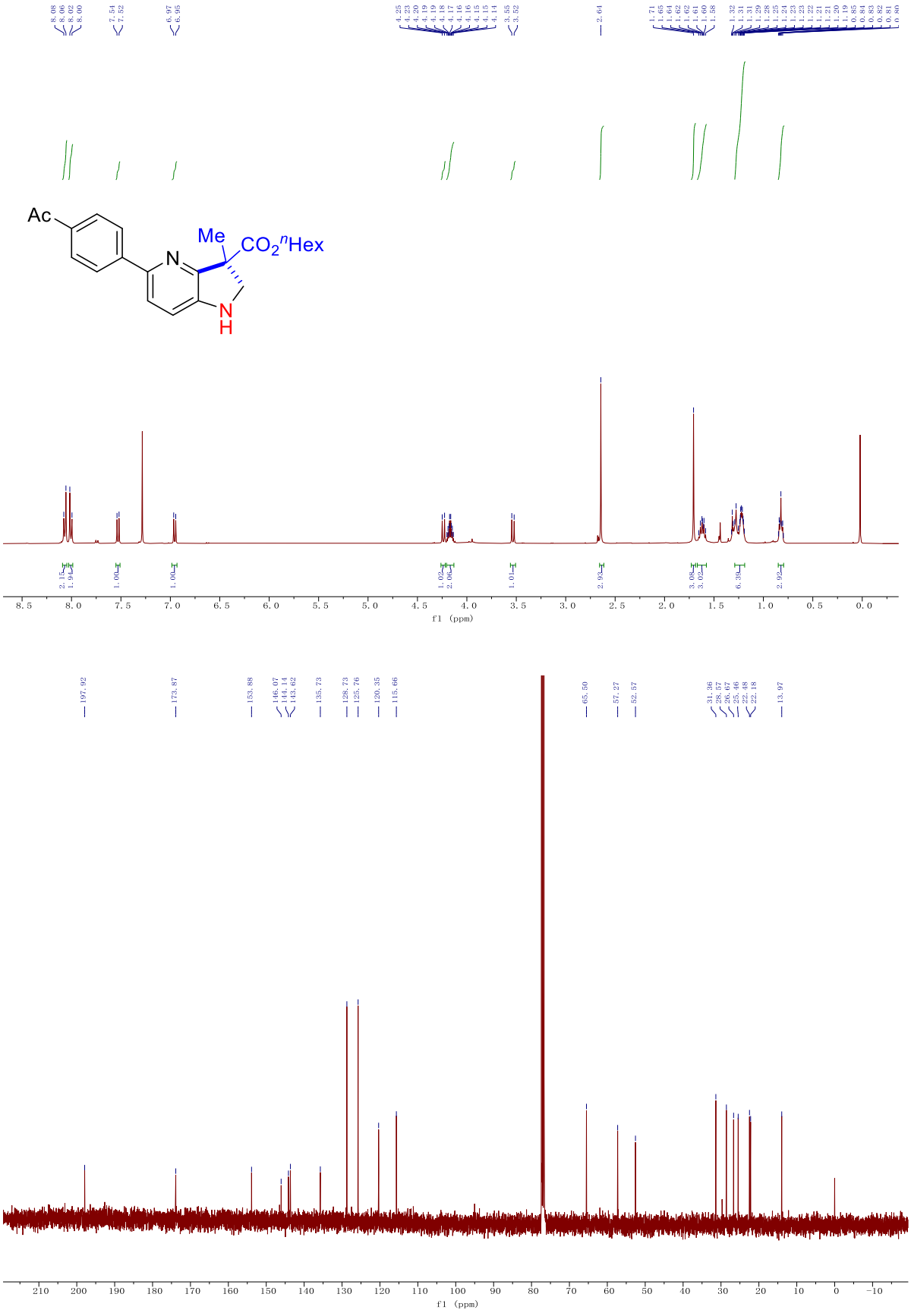
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 3-methyl-5-phenyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6i)



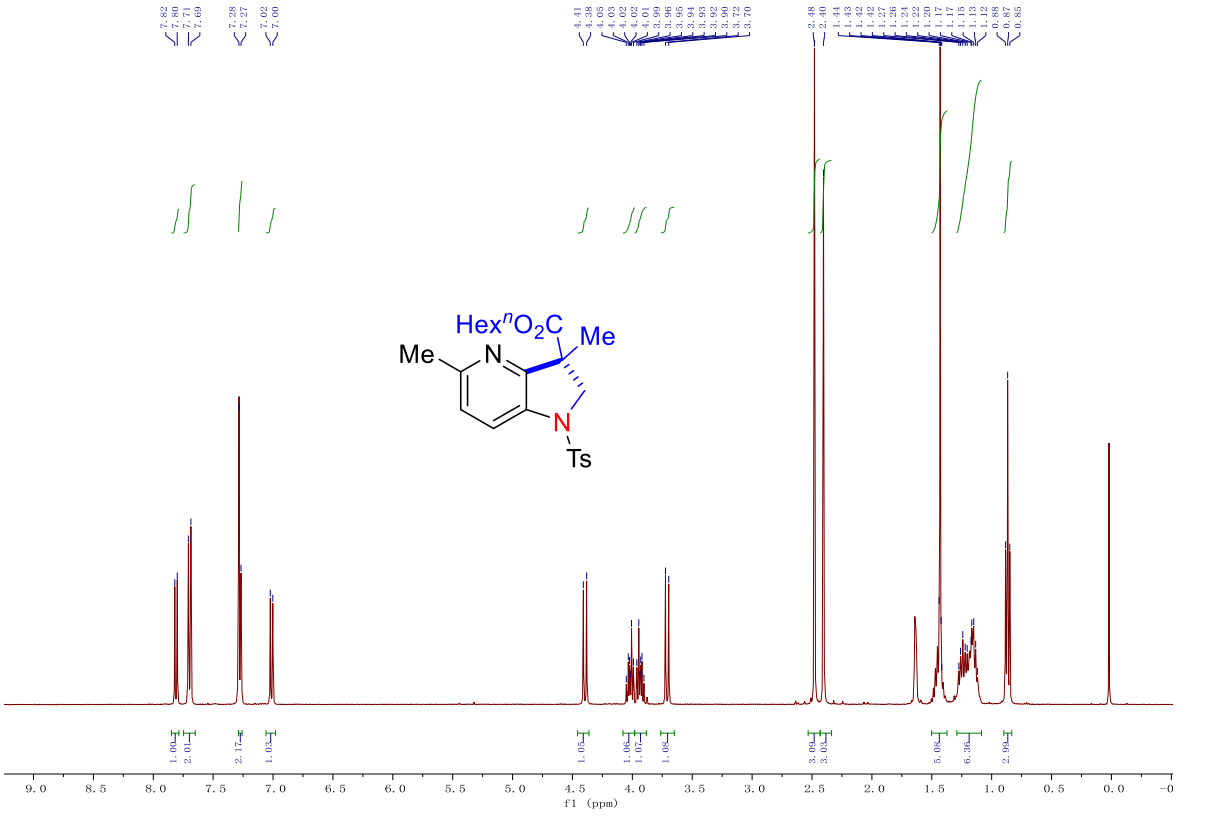
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 5-(4-methoxyphenyl)-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6j)

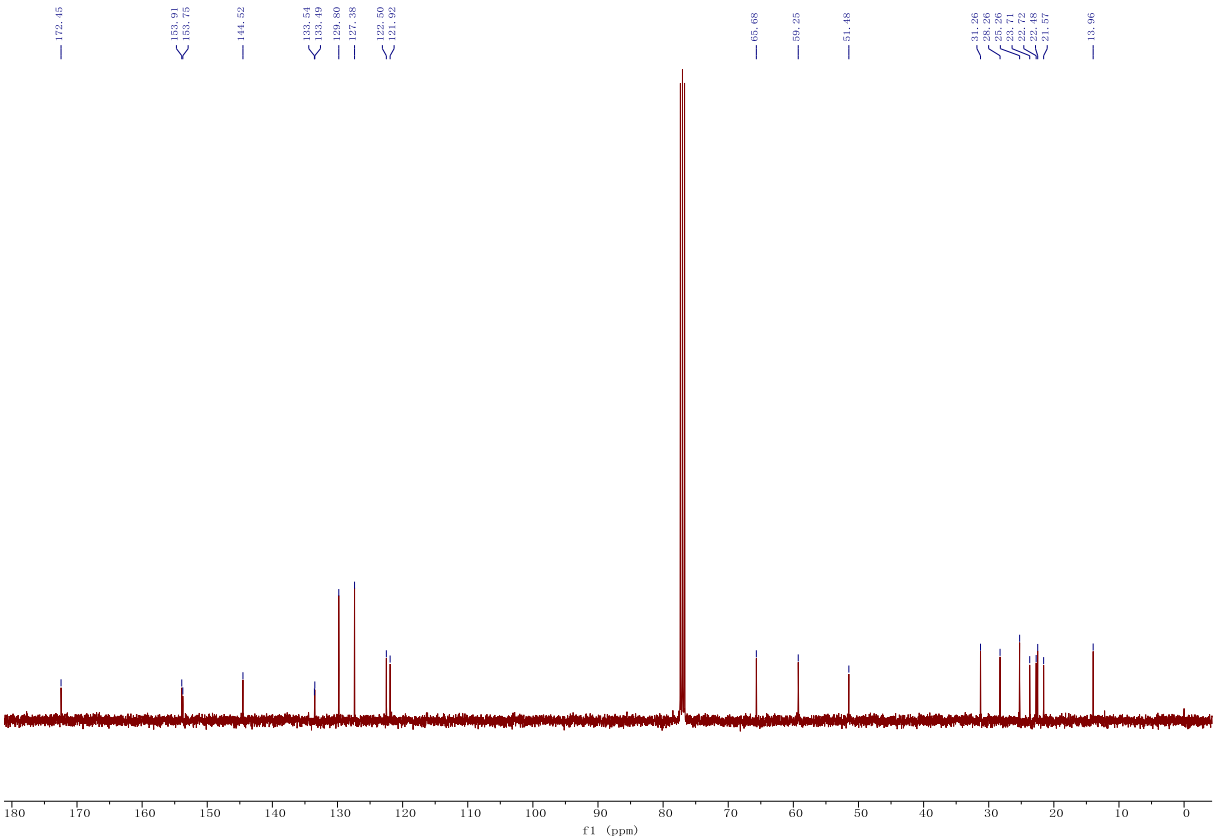


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 5-(4-acetylphenyl)-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6k)

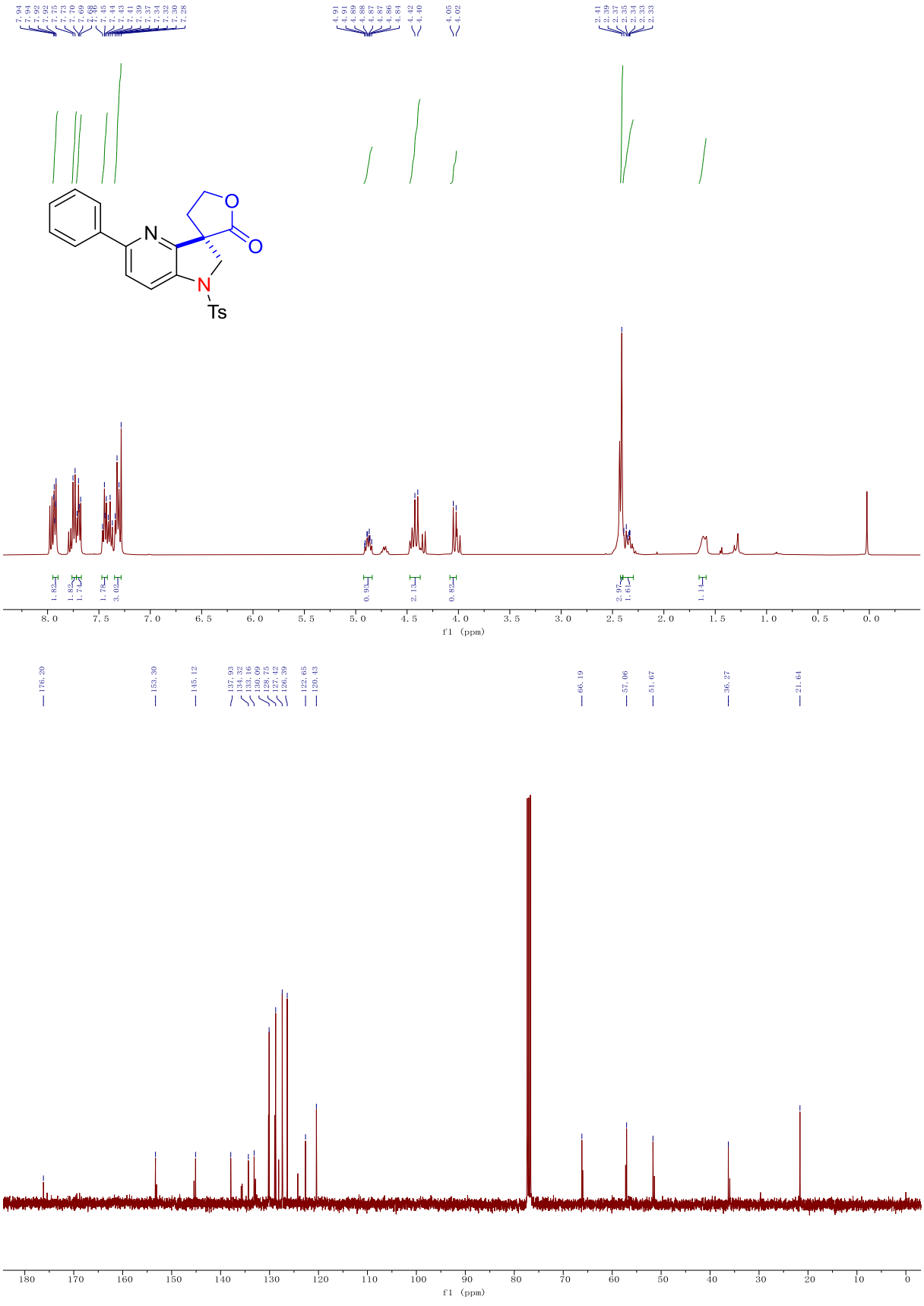


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of phenyl 3,5-dimethyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6l)

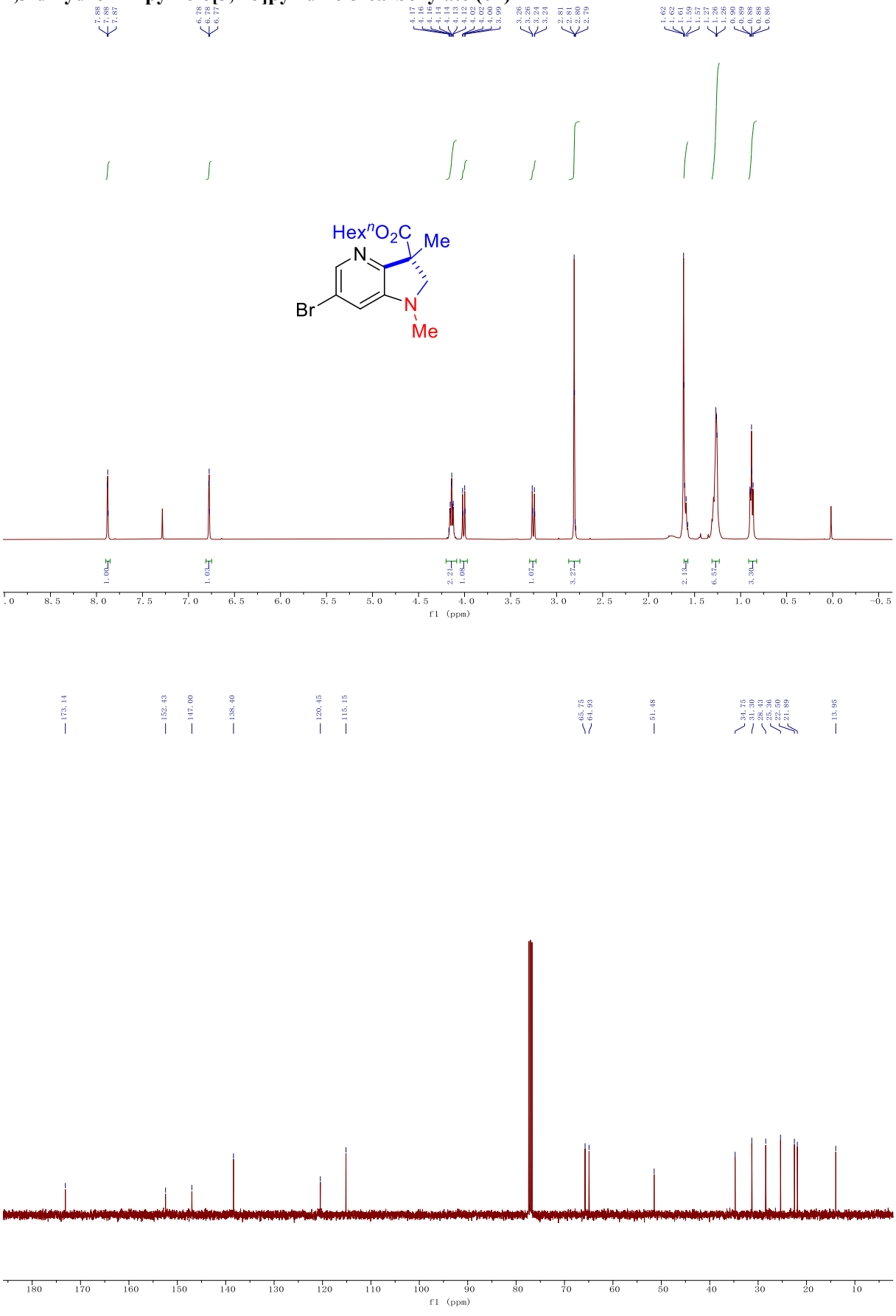




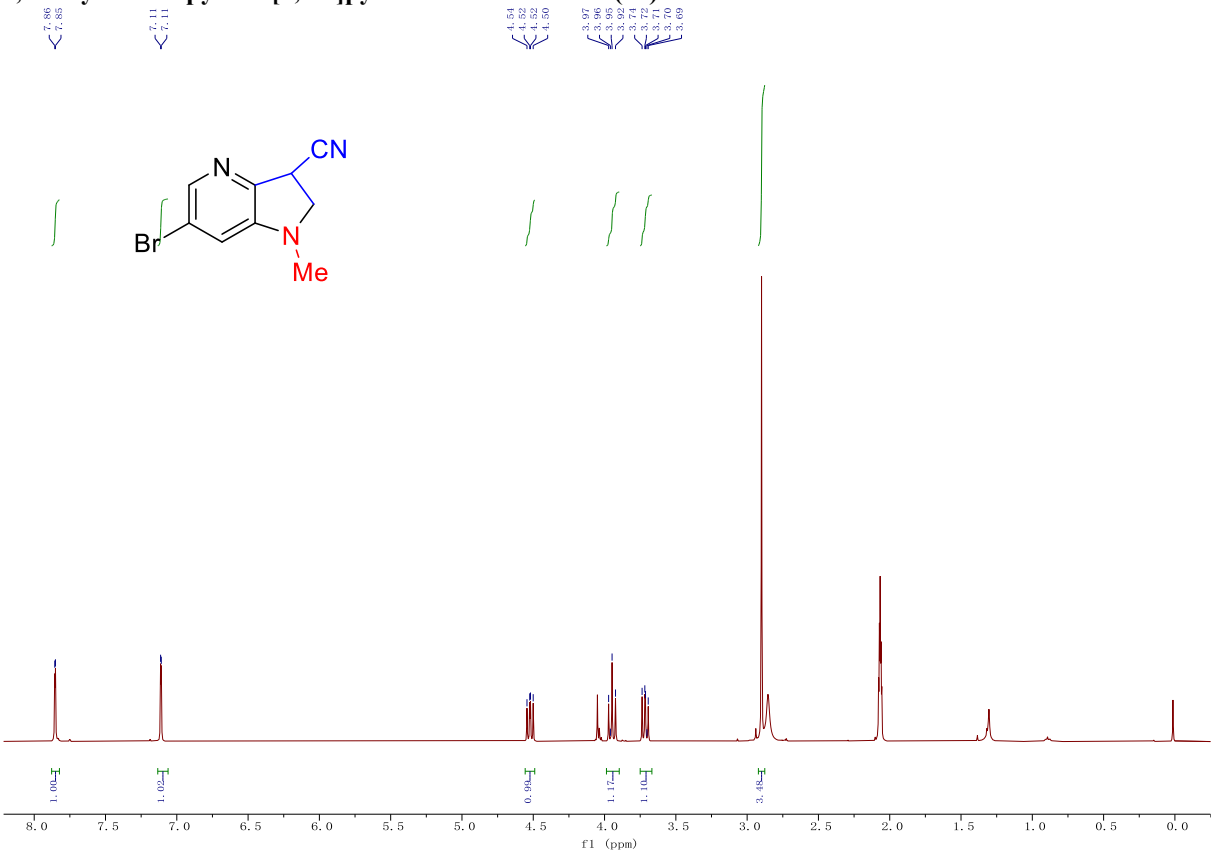
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 5'-phenyl-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (6m)

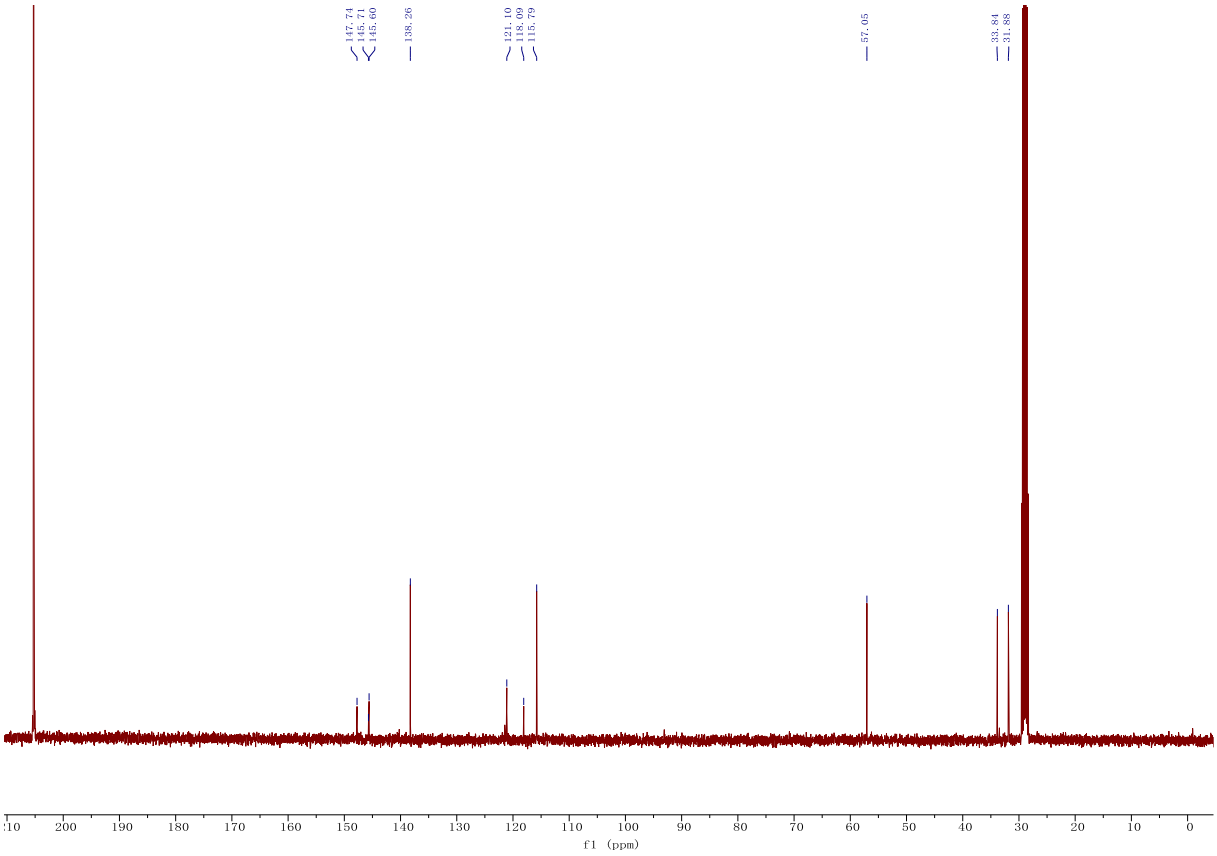


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 6-bromo-1,3-dimethyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6n)

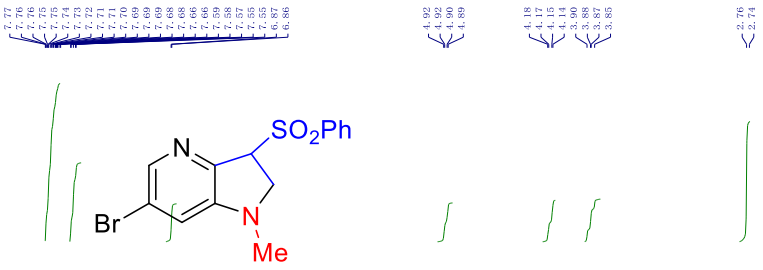


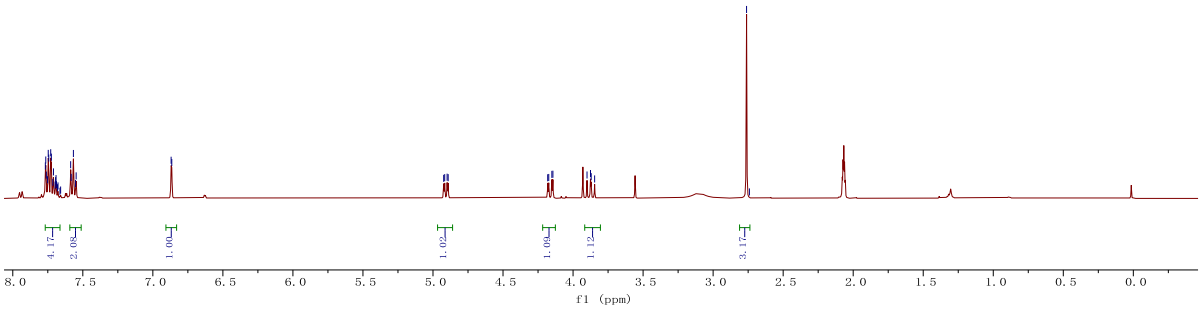
^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of 6-bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (6o)

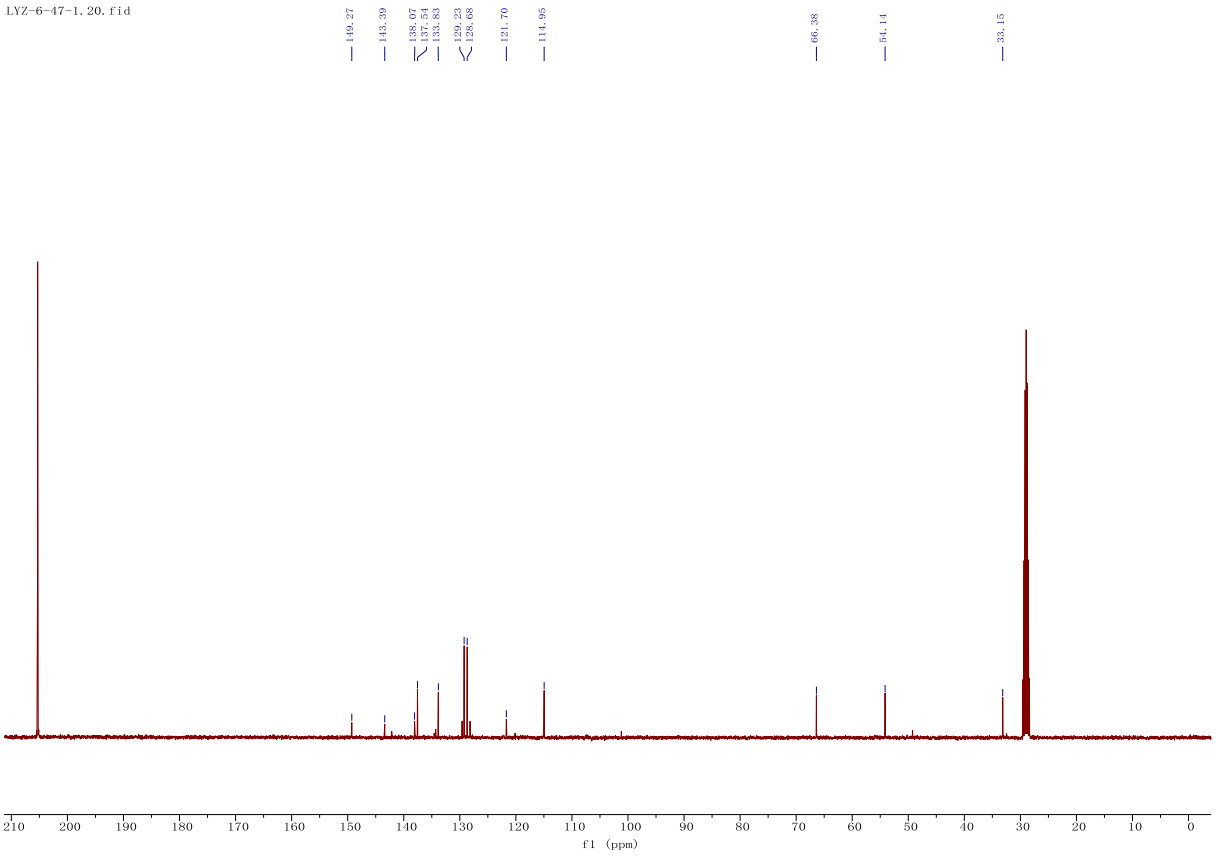




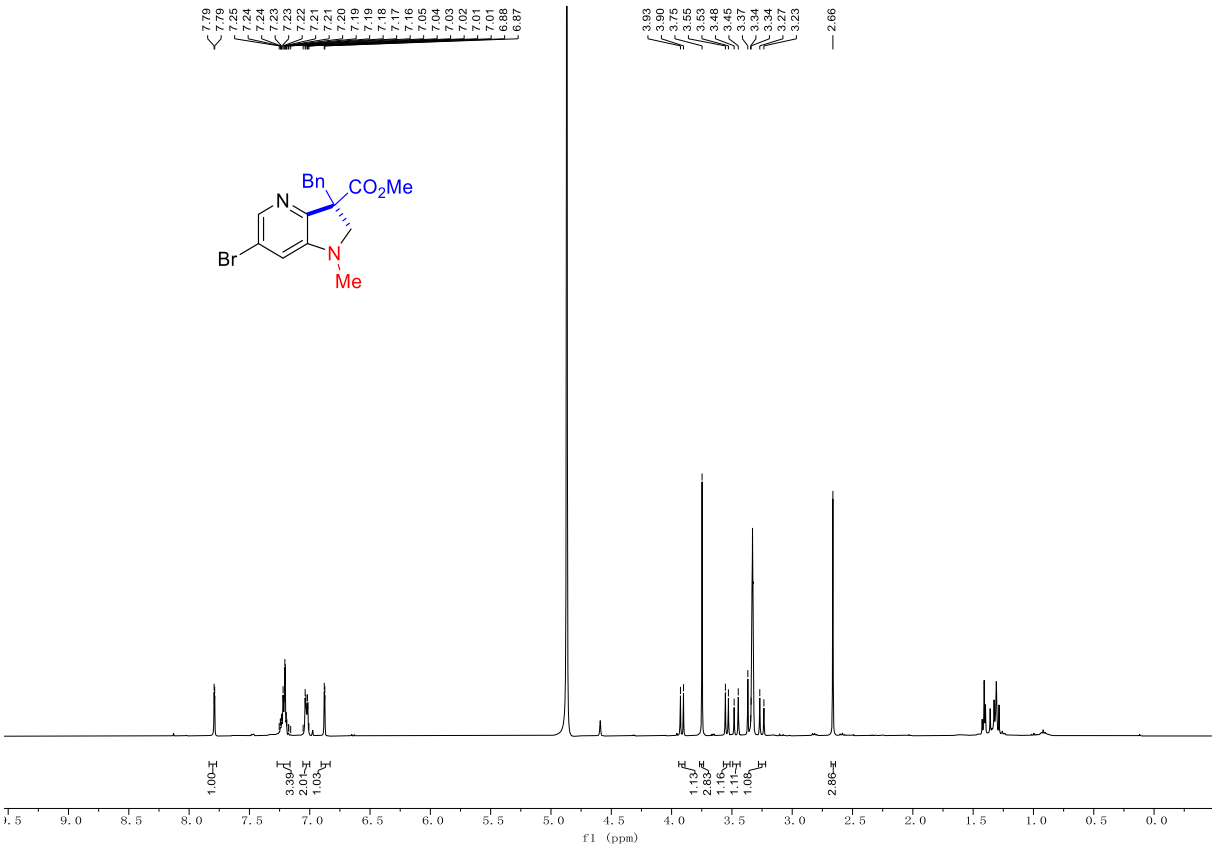
^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of 6-bromo-1-methyl-3-(phenylsulfonyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine (6p)

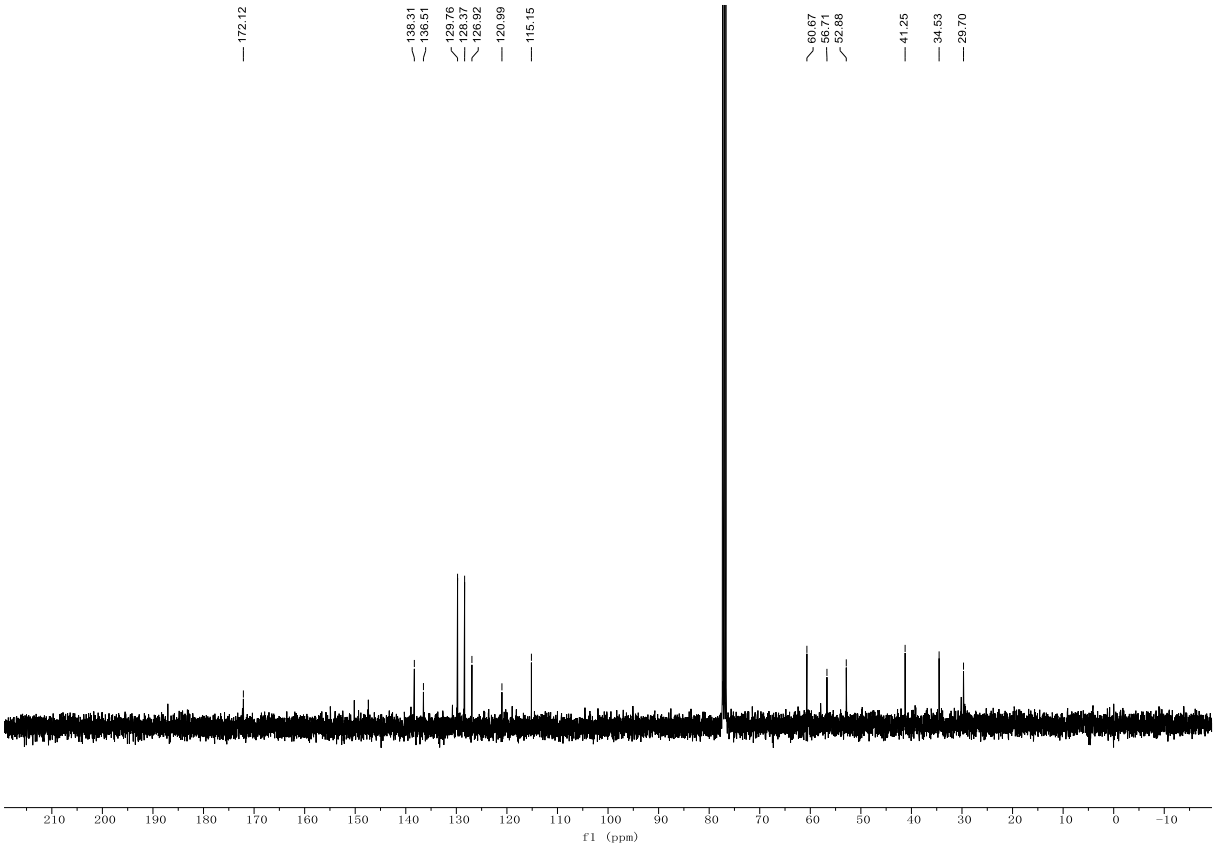




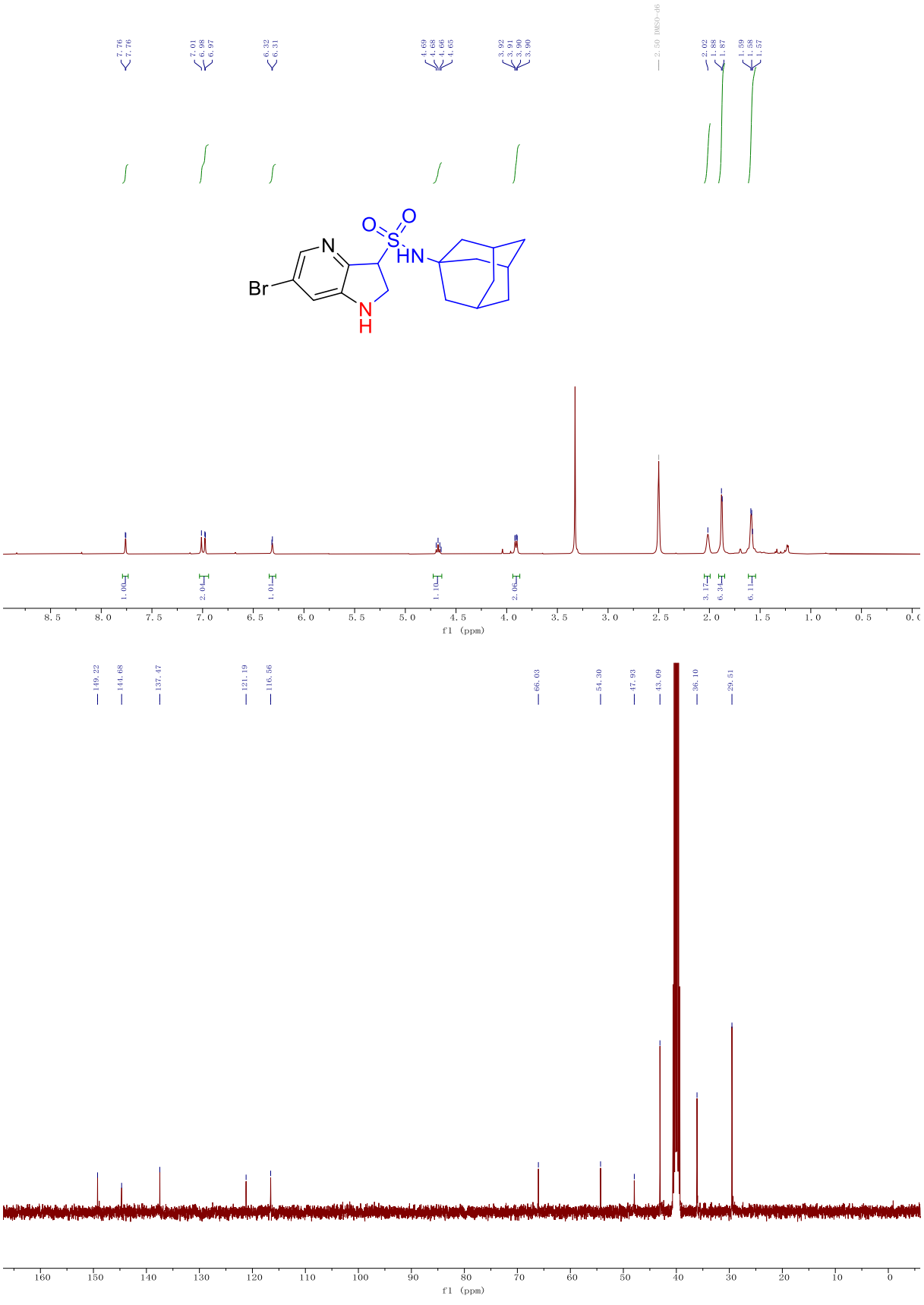


^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of methyl-3-benzyl-6-bromo-1-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (6q)

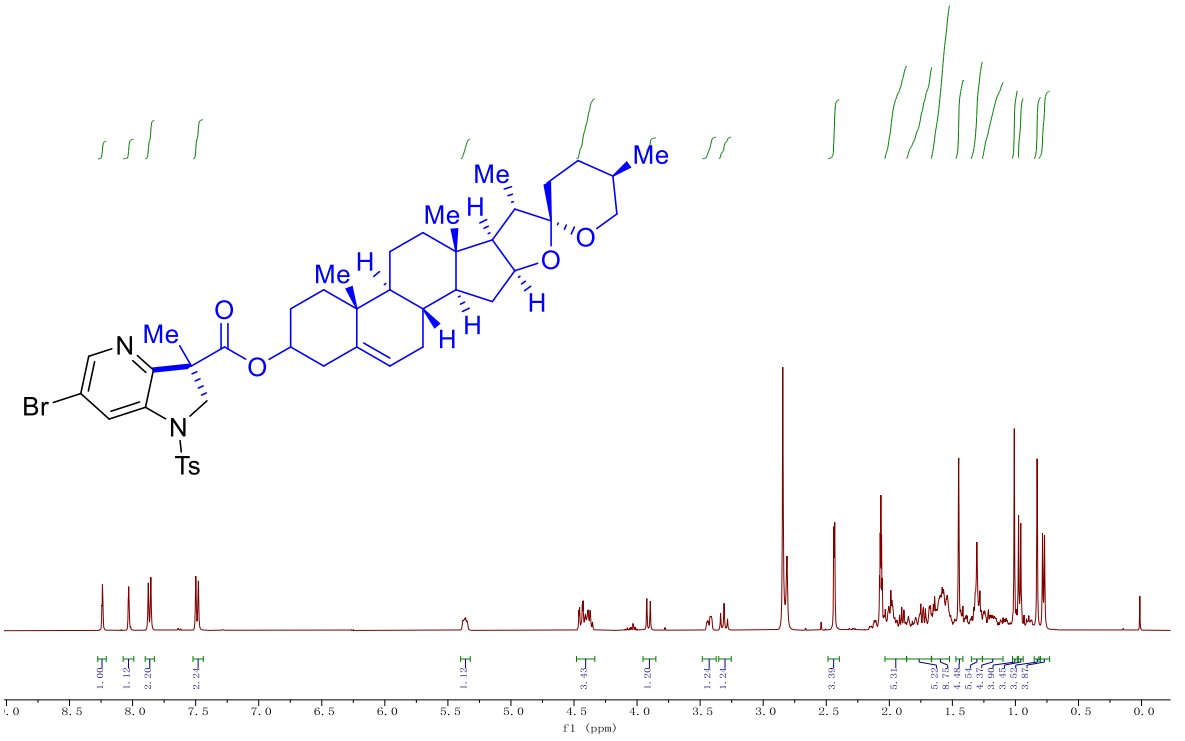


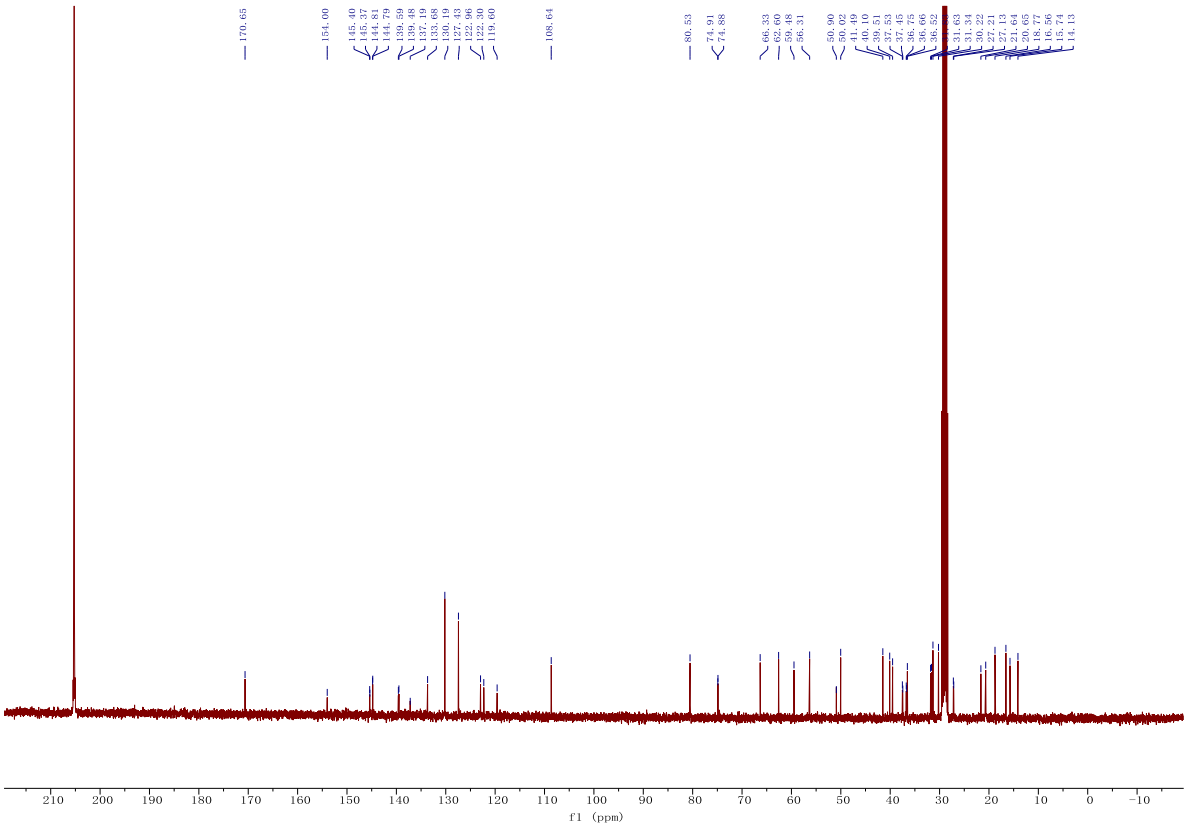


^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of *N*-(Adamantan-1-yl)-6-bromo-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-sulfonamide (7a)

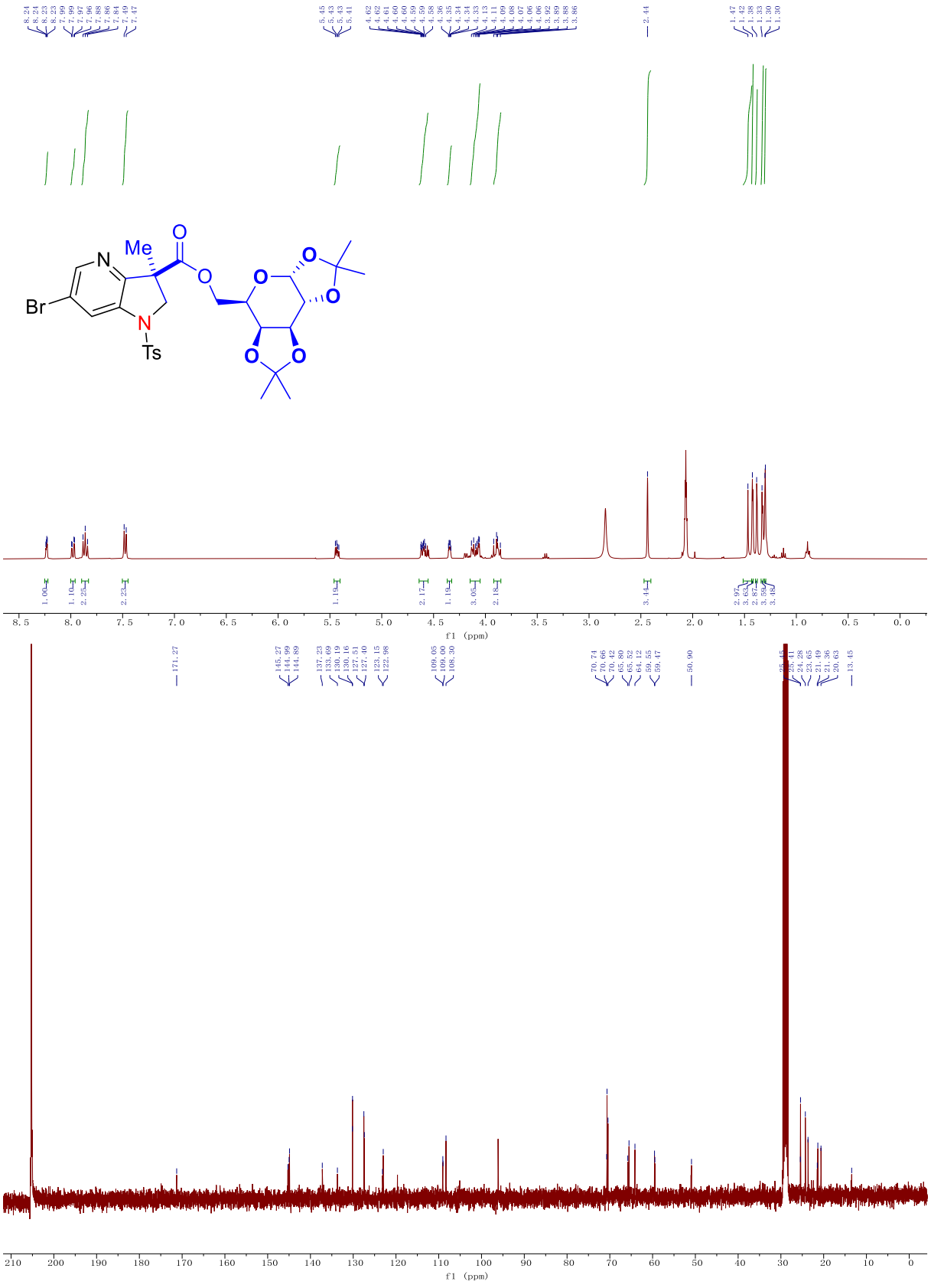


^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of (*5′R,6aR,6bS,8aS,8bR,9S,10R,11aS,12aS,12bS*)-5',6a,8a,9-Tetramethyl-*1,3,3′,4,4′,5,5′,6,6a, 6b,6′,7,8,8a,8b,9,11a,12,12a,12b*-icosahydrospiro[naphtho[2',1':4,5]indeno[2,1-*b*]furan-10,2'-pyran]-*4*-yl 6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (7b)

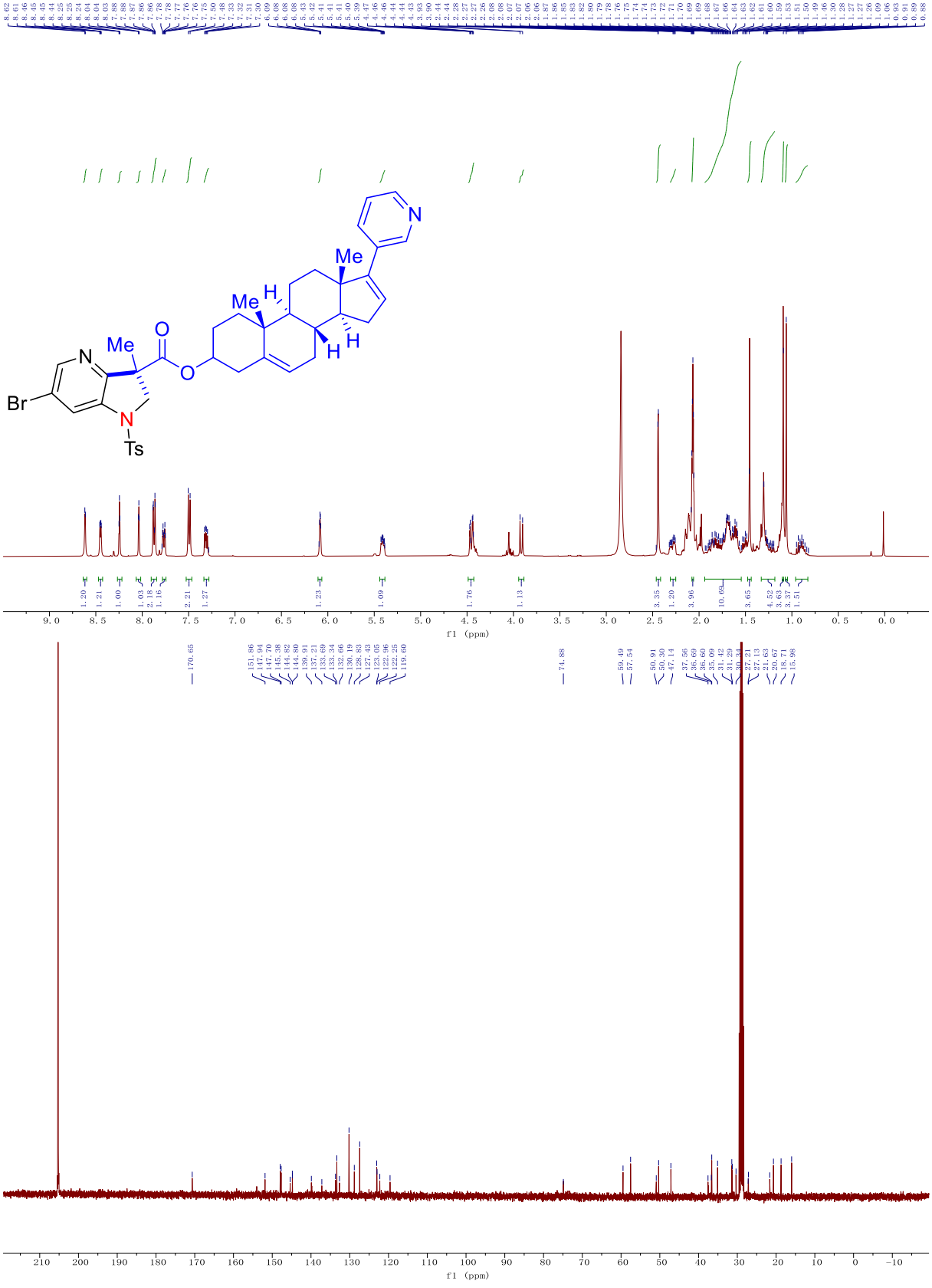




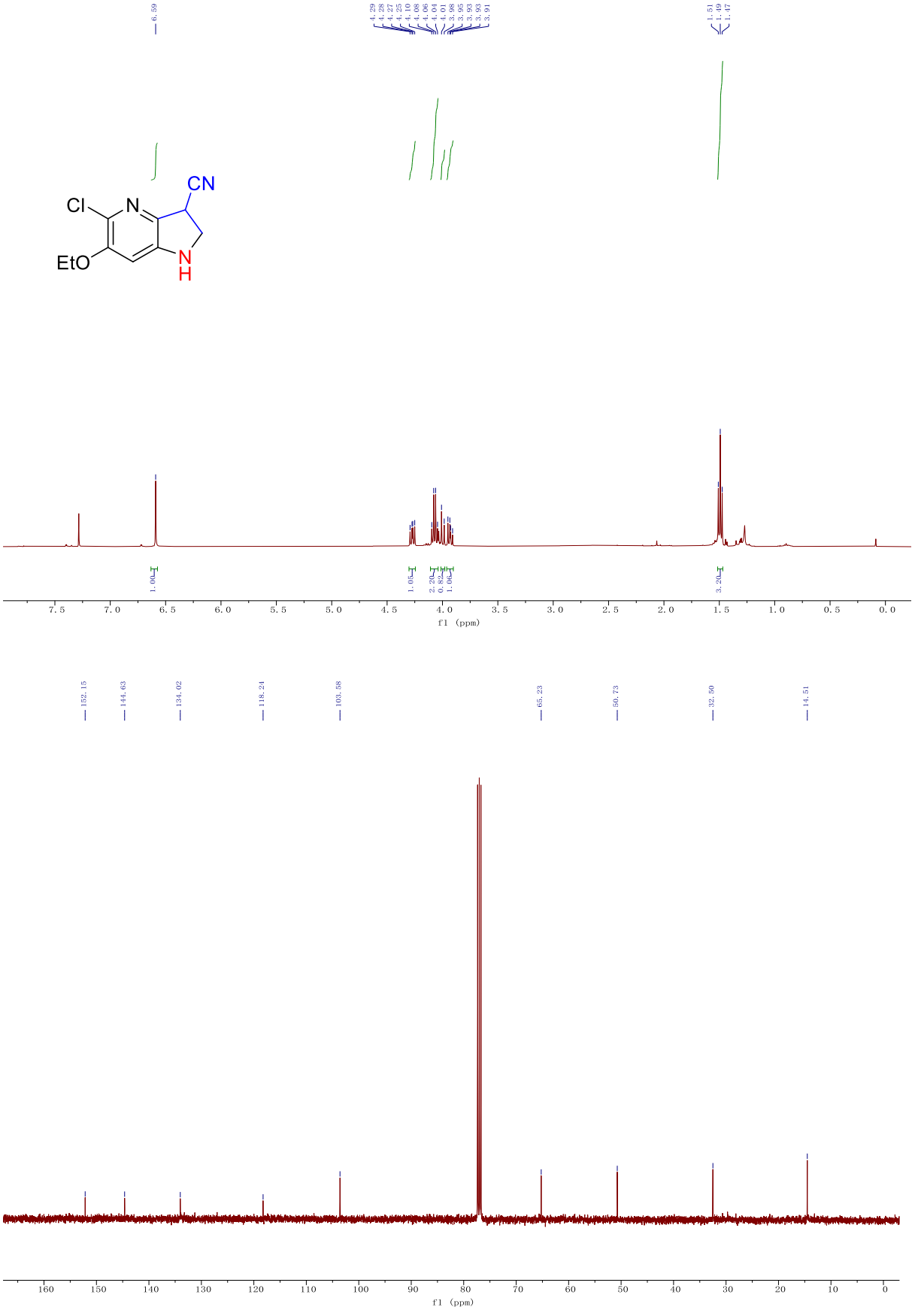
^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of ((*3aR,5R,5aS,8aS,8bR*)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-*d*]pyran-*5*-yl)methyl 6-bromo-3-methyl-1-tosyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (7c)



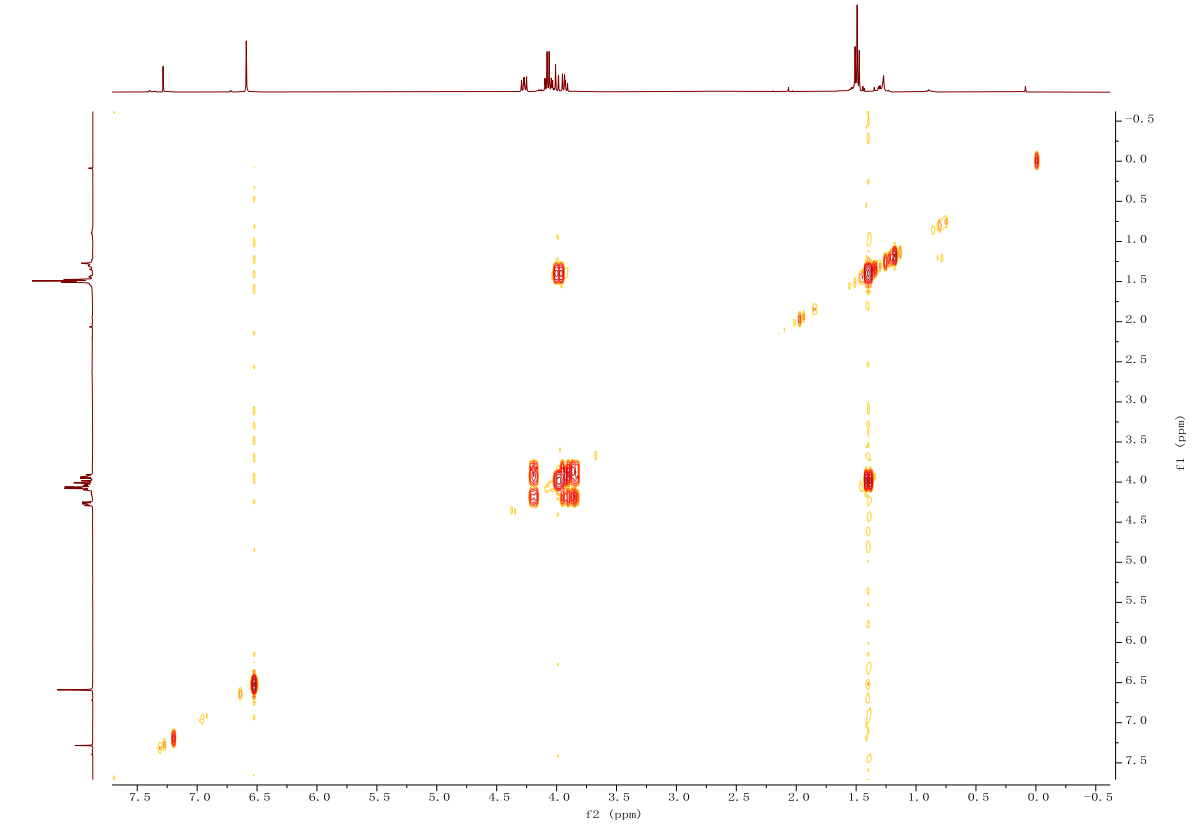
^{1}H NMR (400MHz, acetone-*d6*) and ^{13}C NMR (101MHz, acetone-*d6*) spectra of (*8R,9S,10R,13S,14S*)-*10,13*-Dimethyl-*17*-(pyridin-*3*-yl)-*2,3,4,7,8,9,10,11,12,13,14,15*-dodecahydro-1H-cyclopenta[a]phenanthren-3-yl *6*-bromo-*3*-methyl-1-tosyl-*2,3*-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-*3*-carboxylate (7d)

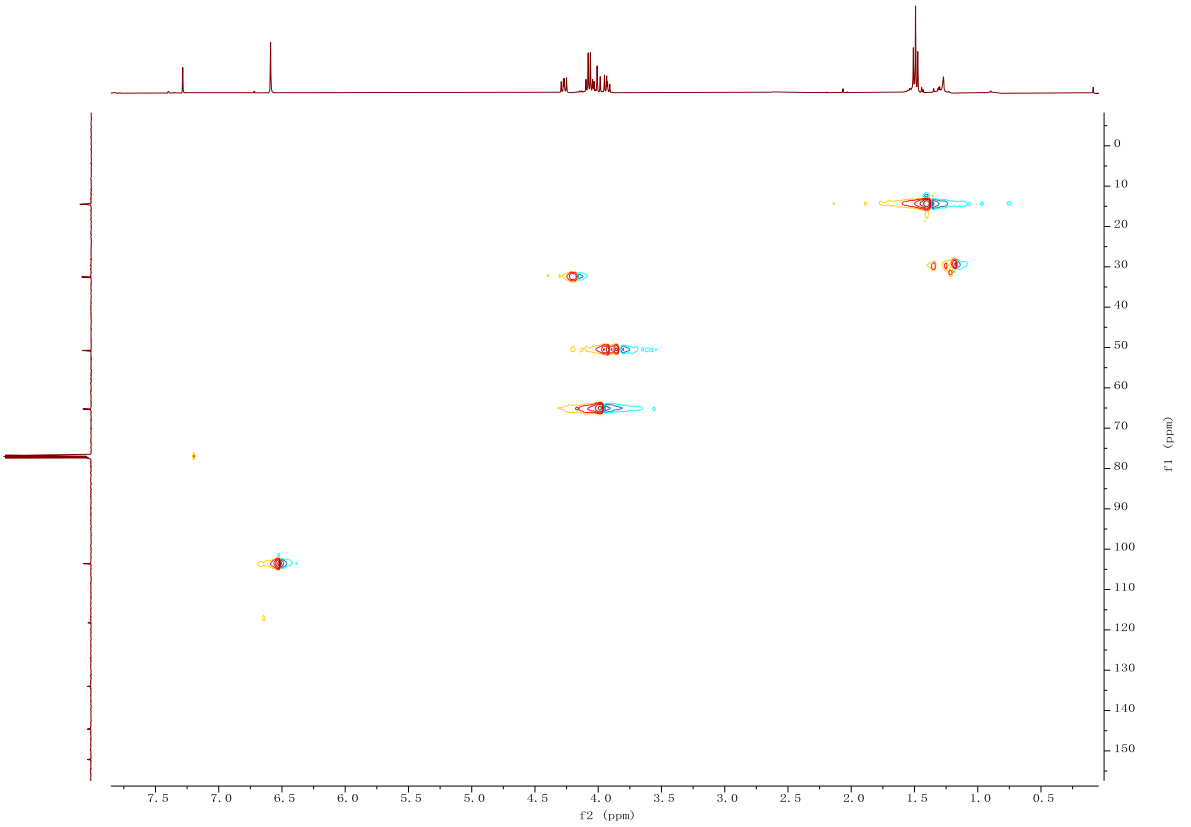


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (9a)

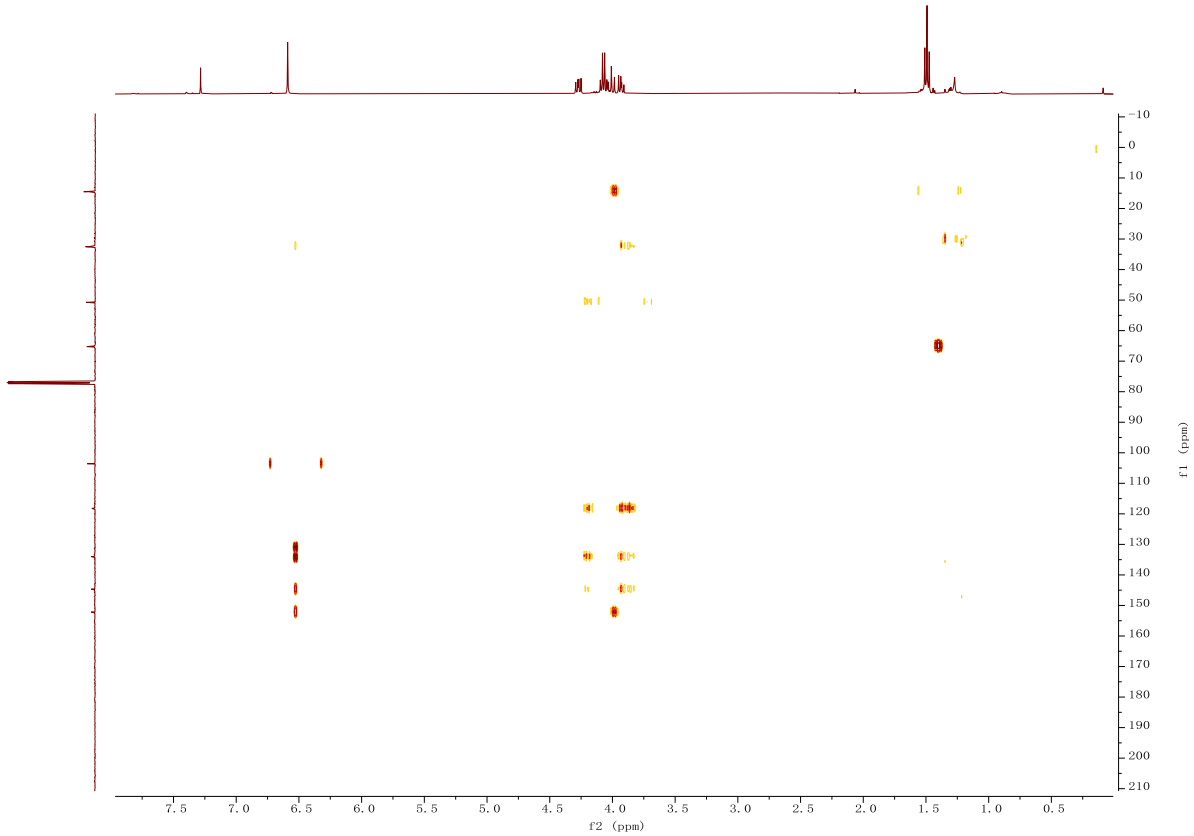


COSY and nOe spectra of 5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (9a)

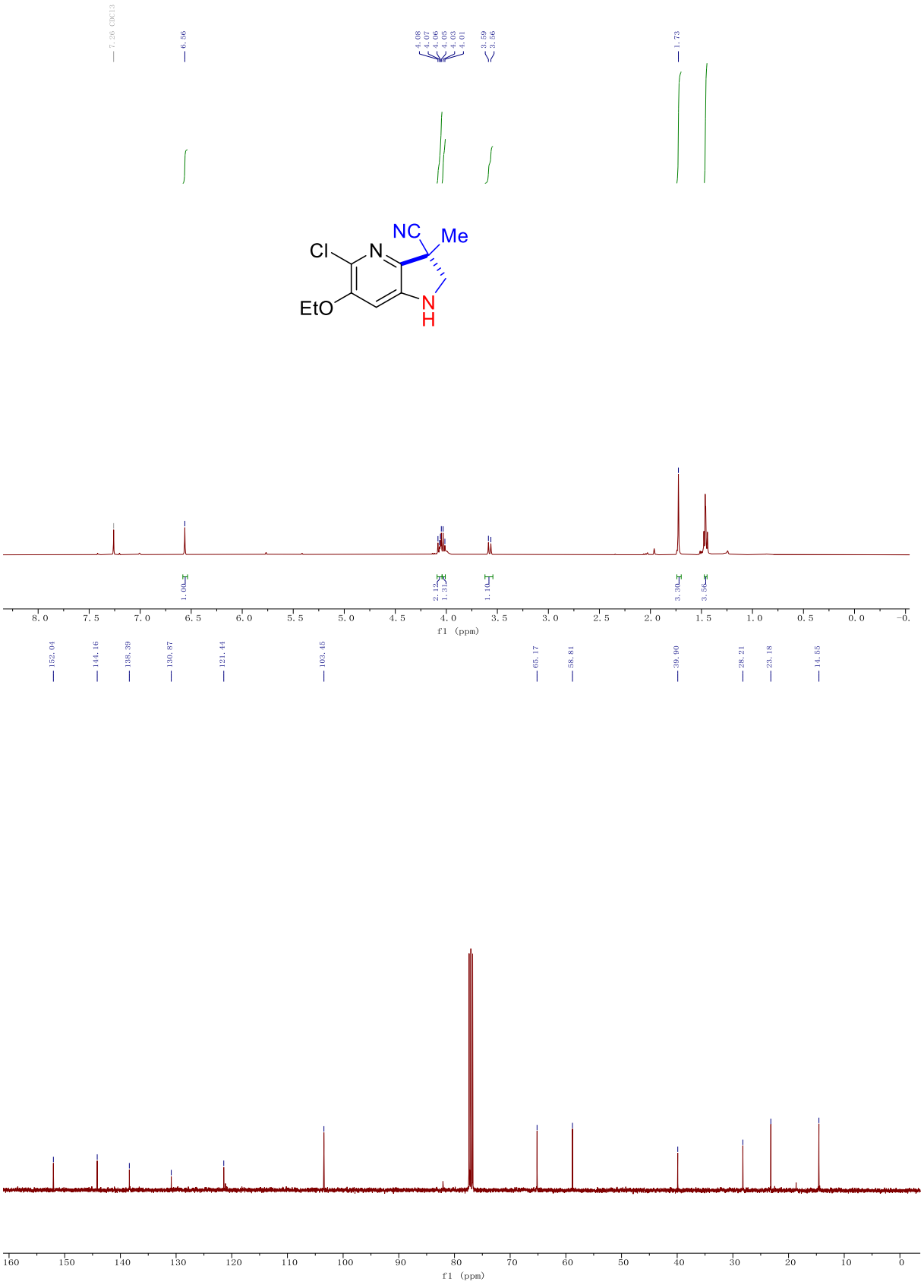




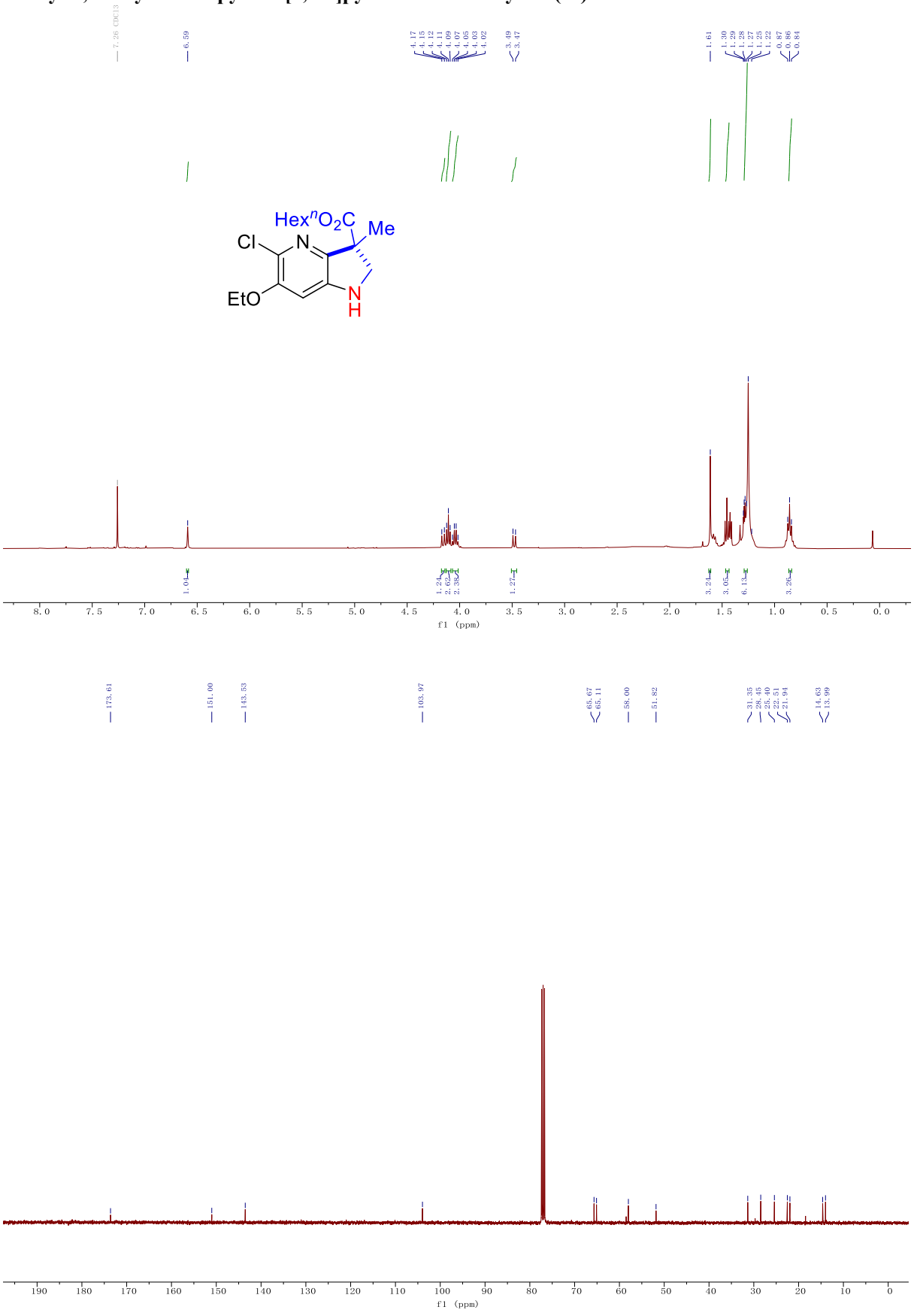
HSQC spectra of 5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (9a)



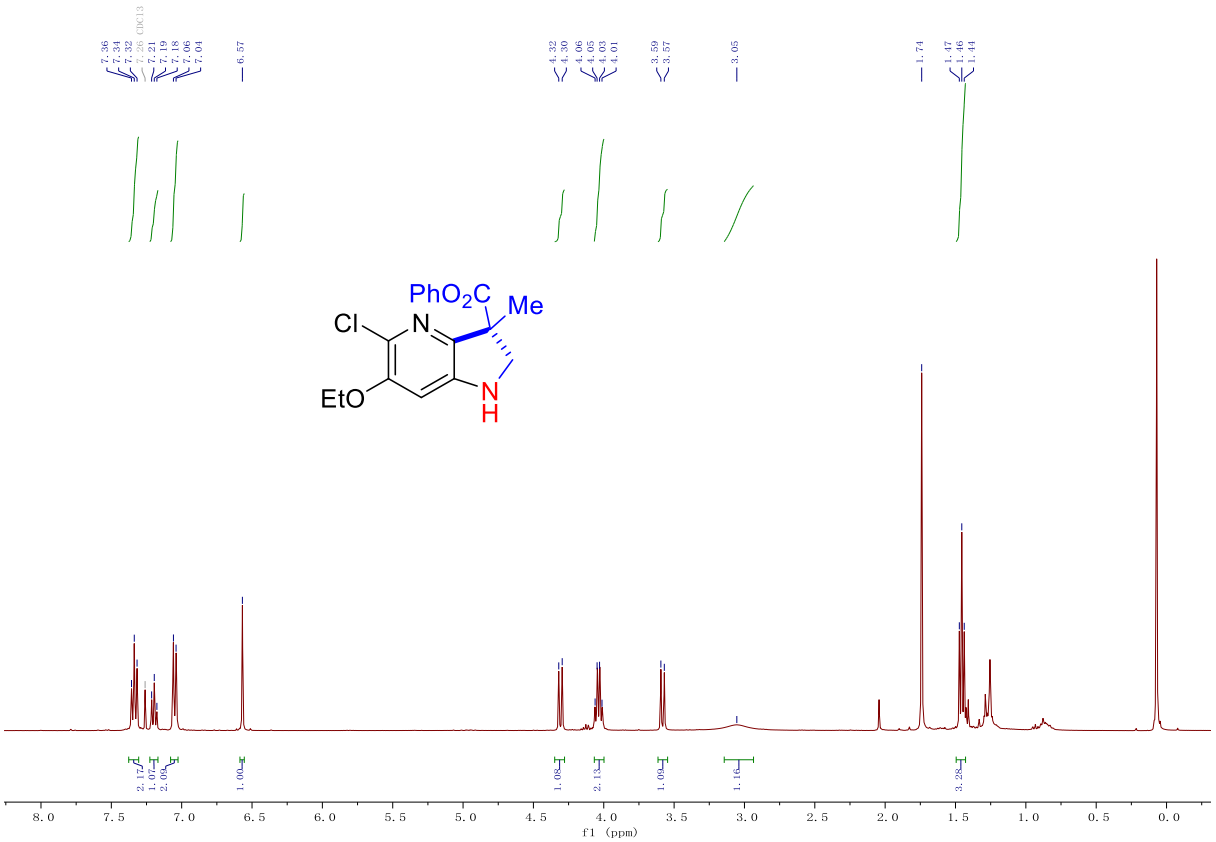
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 5-chloro-6-ethoxy-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carbonitrile (9b)

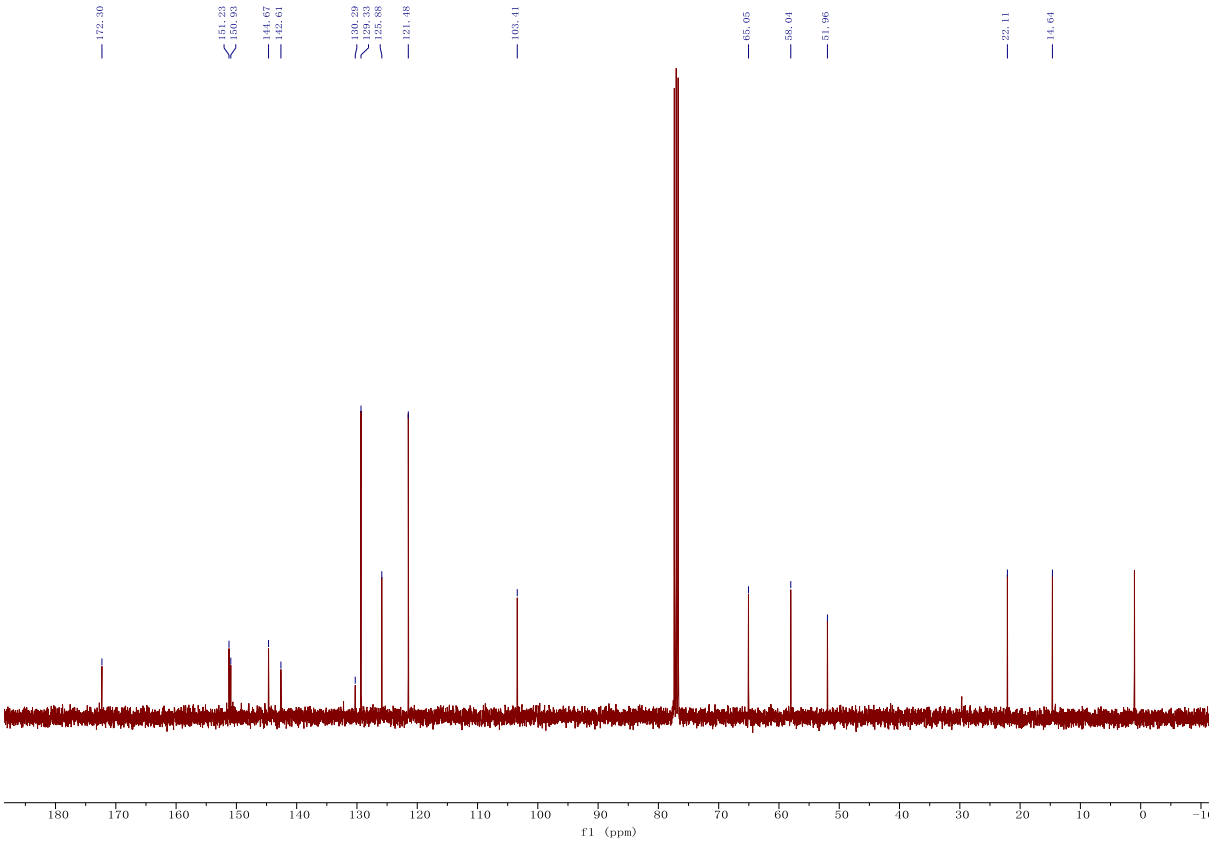


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of hexyl 5-chloro-6-ethoxy-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9c)

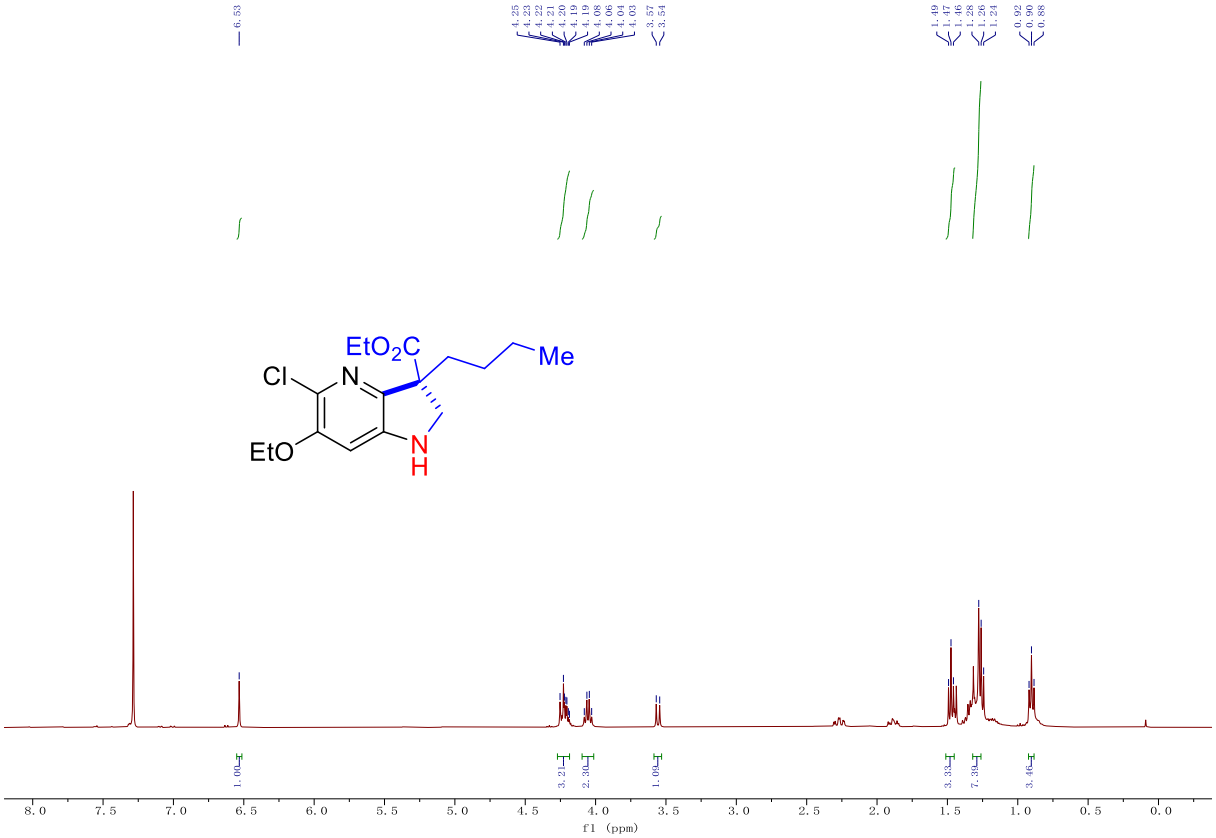


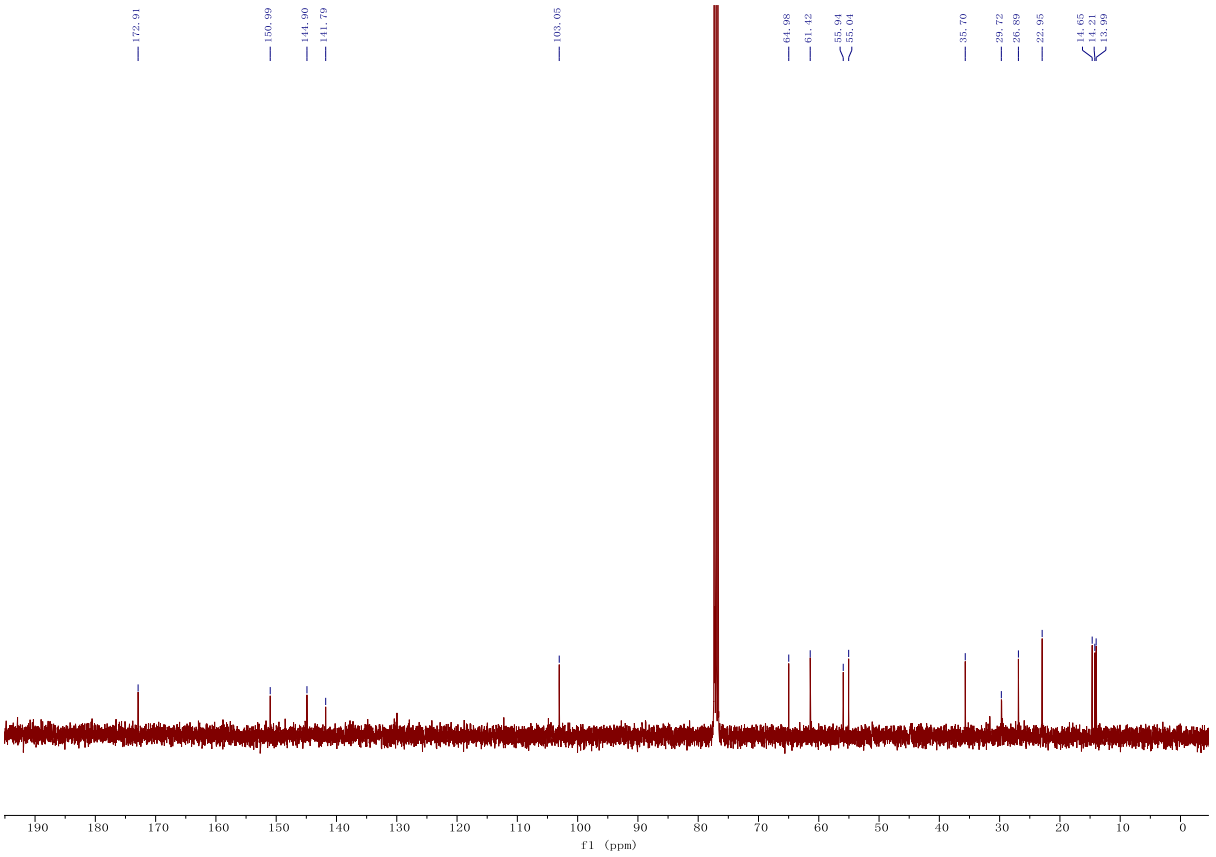
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of phenyl 5-chloro-6-ethoxy-3-methyl-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9d)



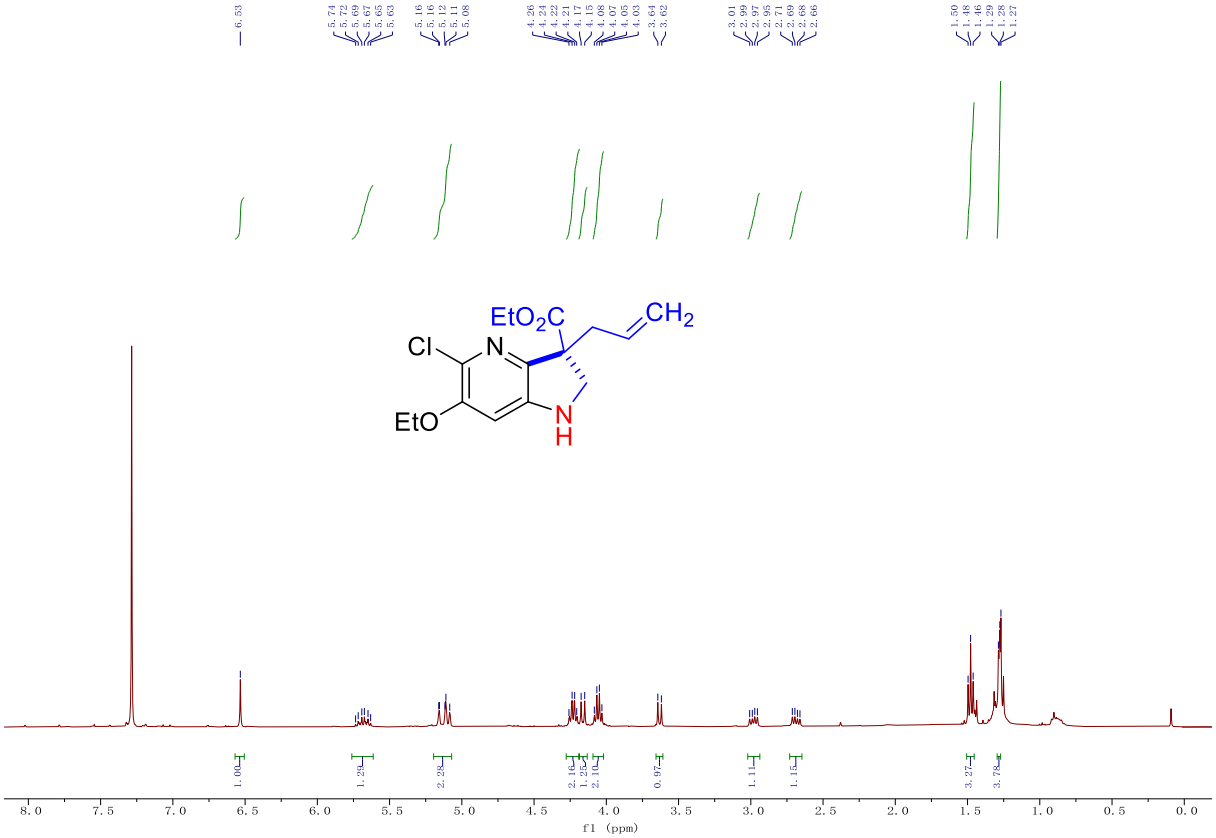


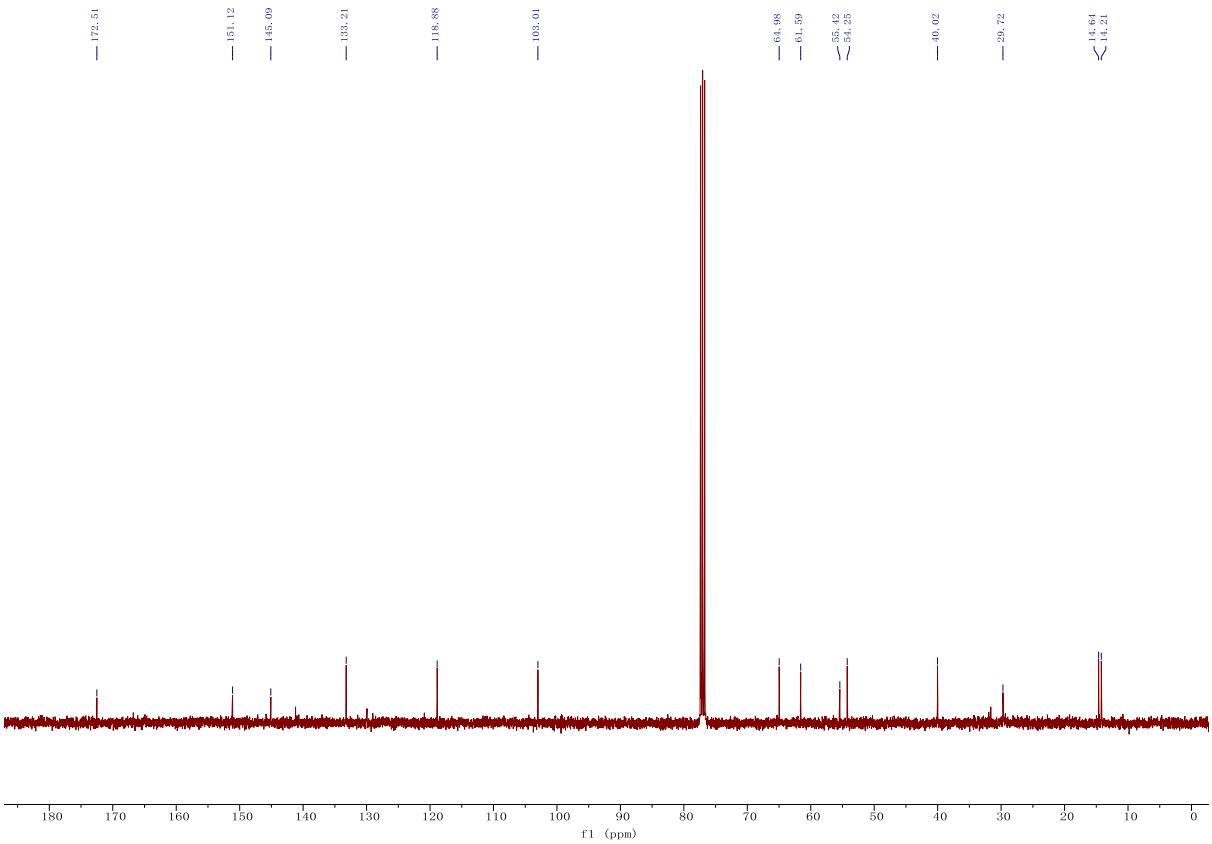
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ethyl 3-butyl-5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9e)



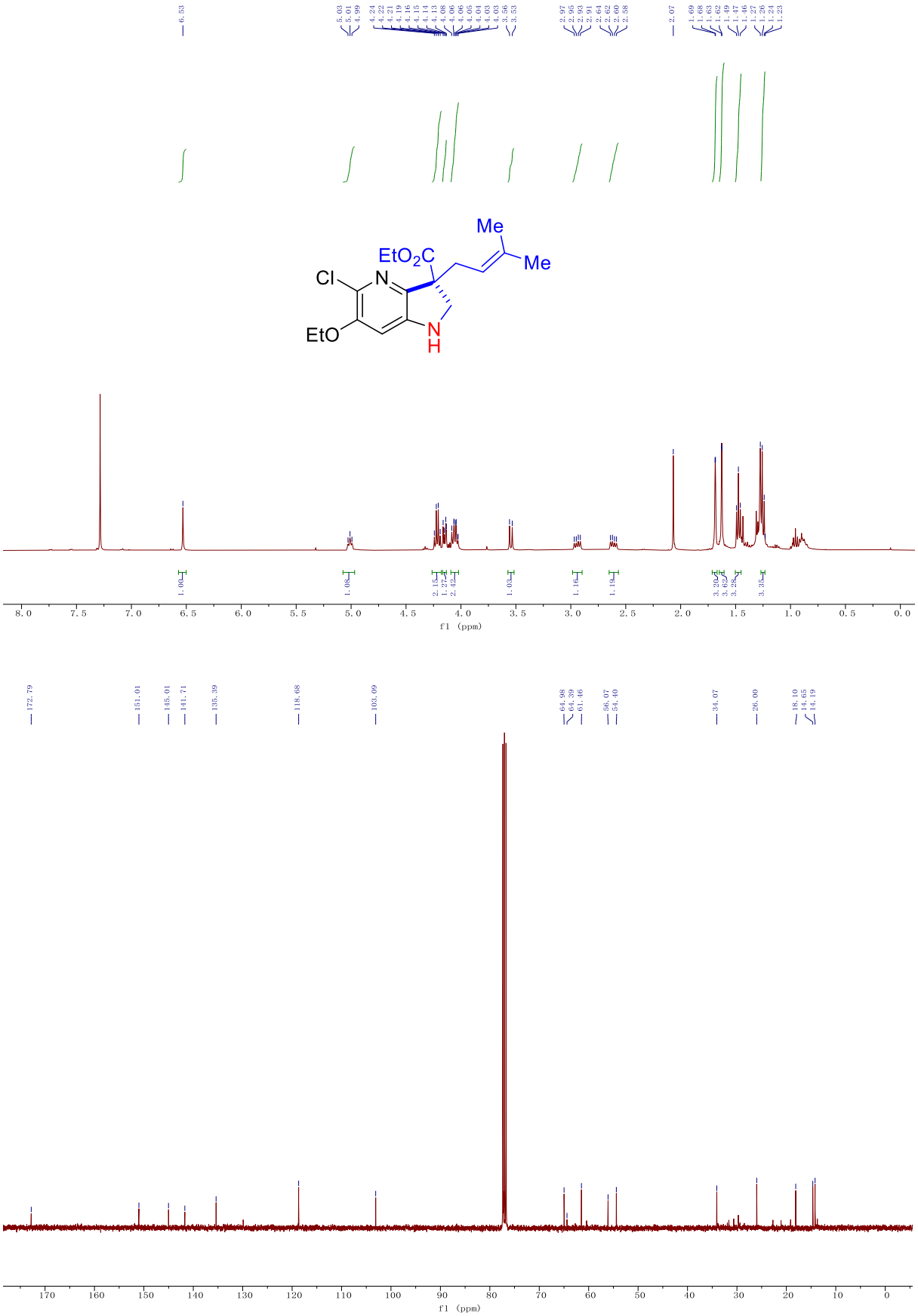


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ethyl 3-allyl-5-chloro-6-ethoxy-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9f)

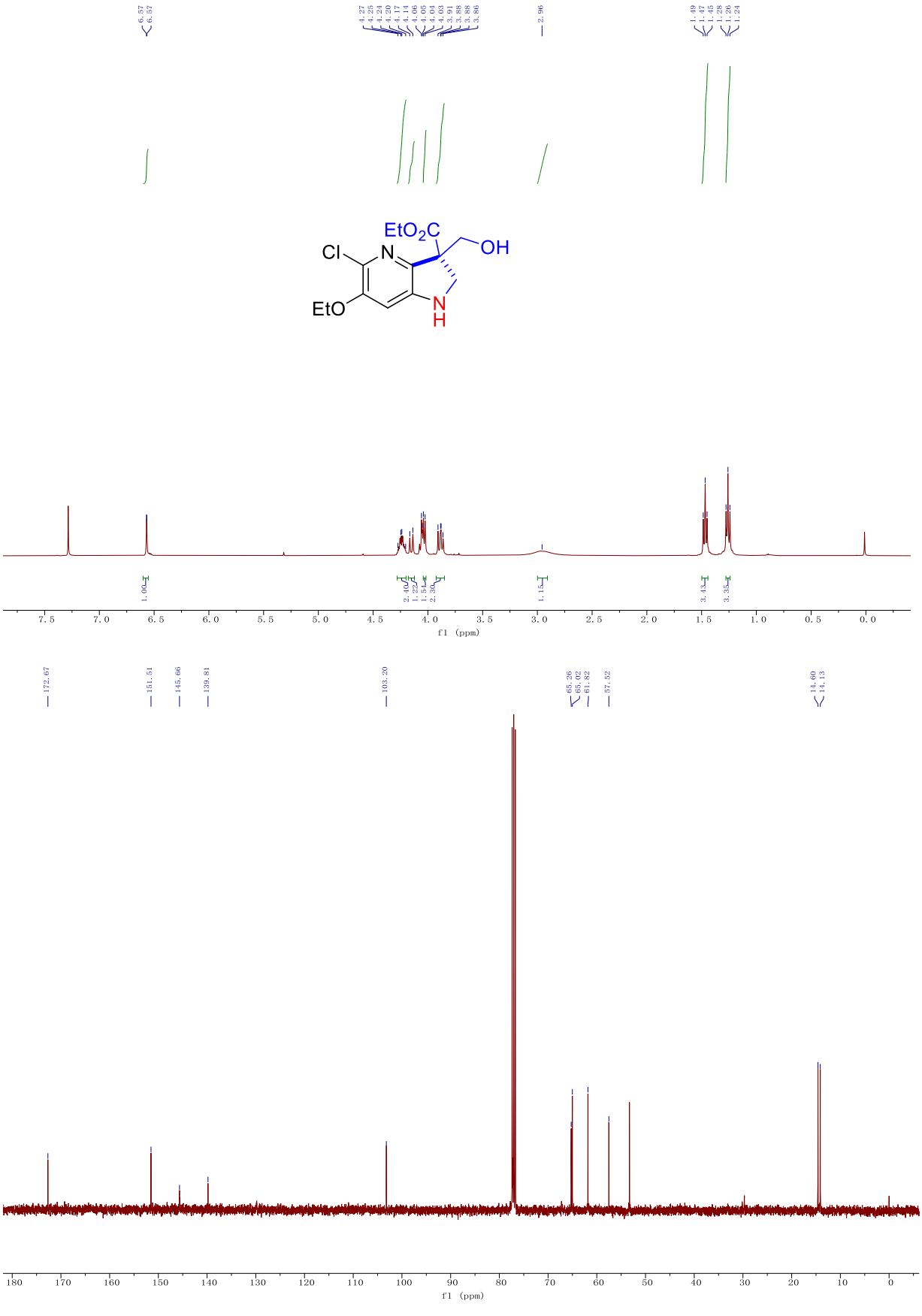




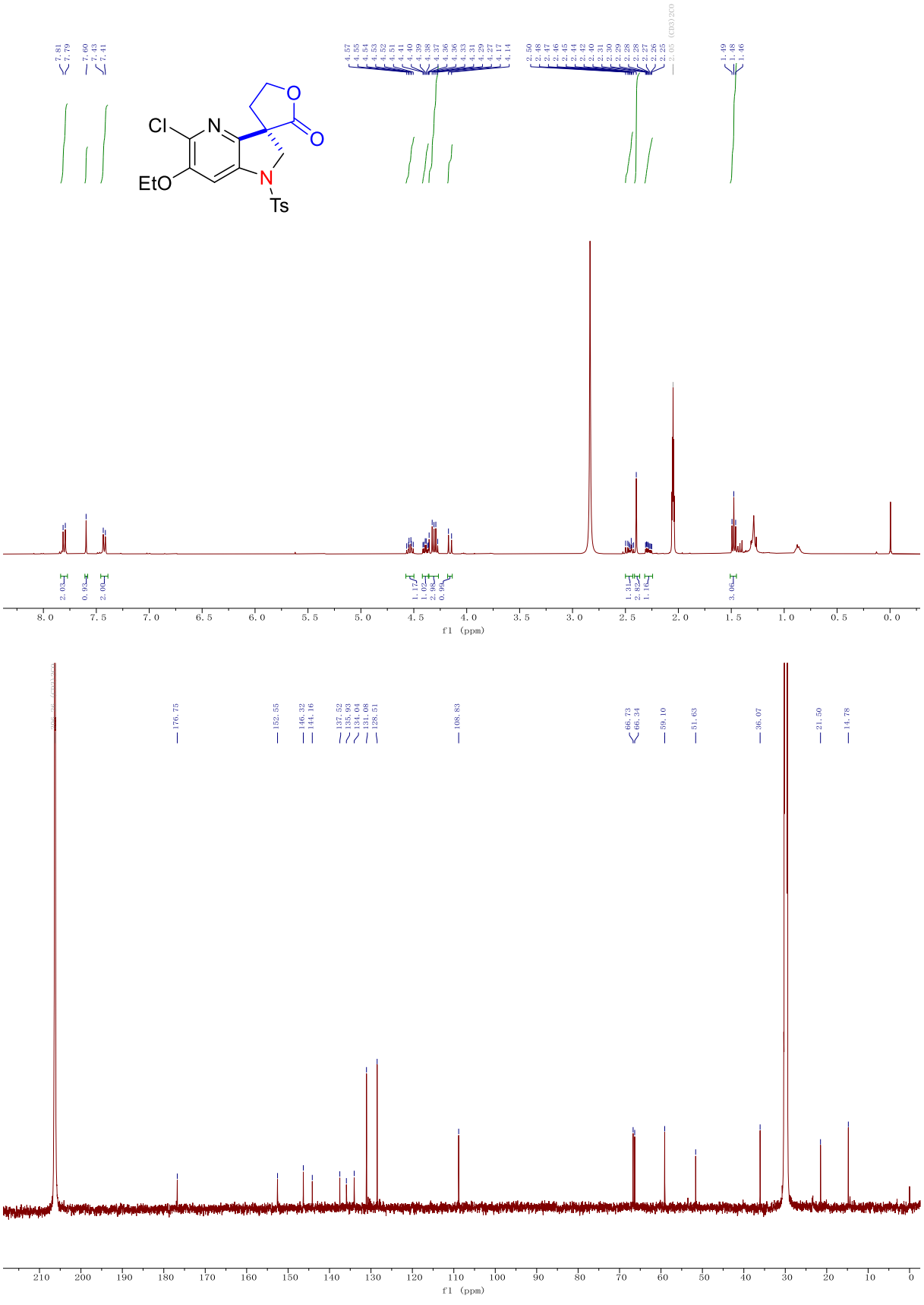
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ethyl 5-chloro-6-ethoxy-3-(3-methylbut-2-en-1-yl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9g)



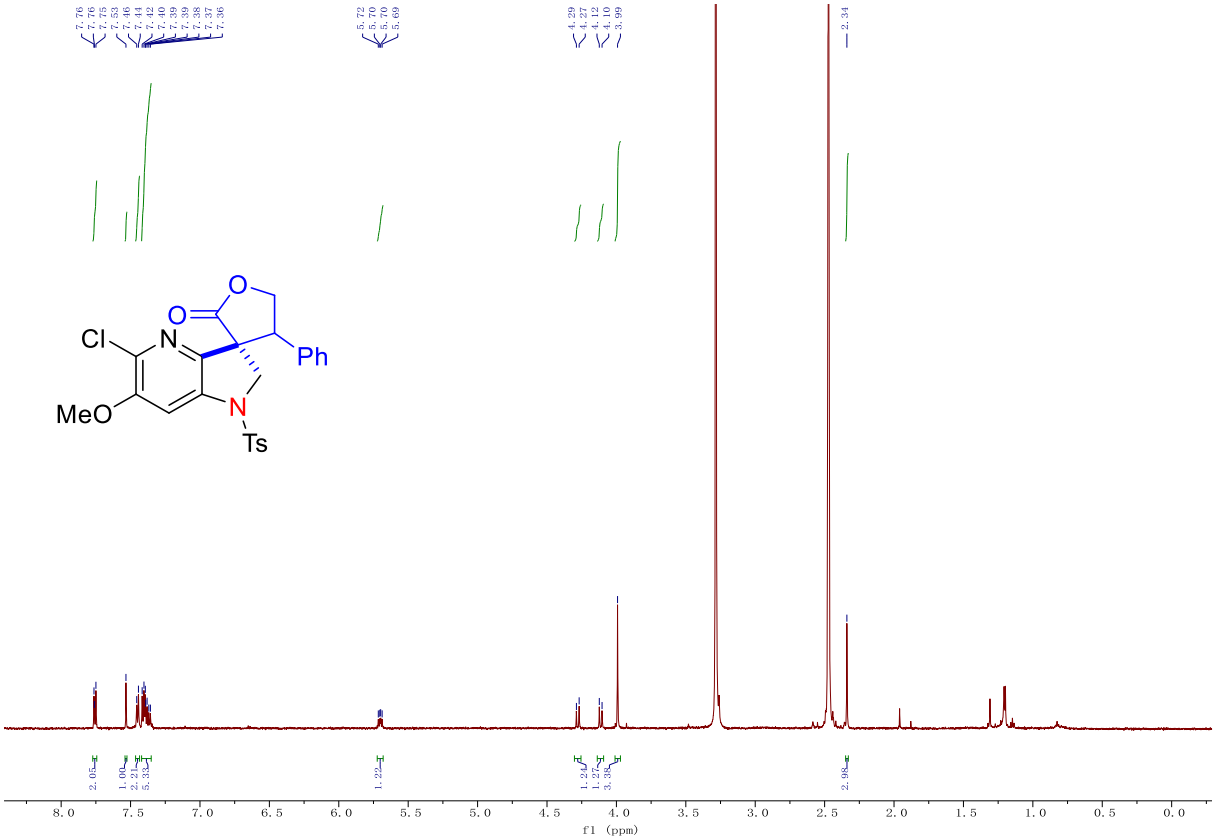
^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of ethyl 6-bromo-3-(hydroxymethyl)-2,3-dihydro-1*H*-pyrrolo[3,2-*b*]pyridine-3-carboxylate (9h)

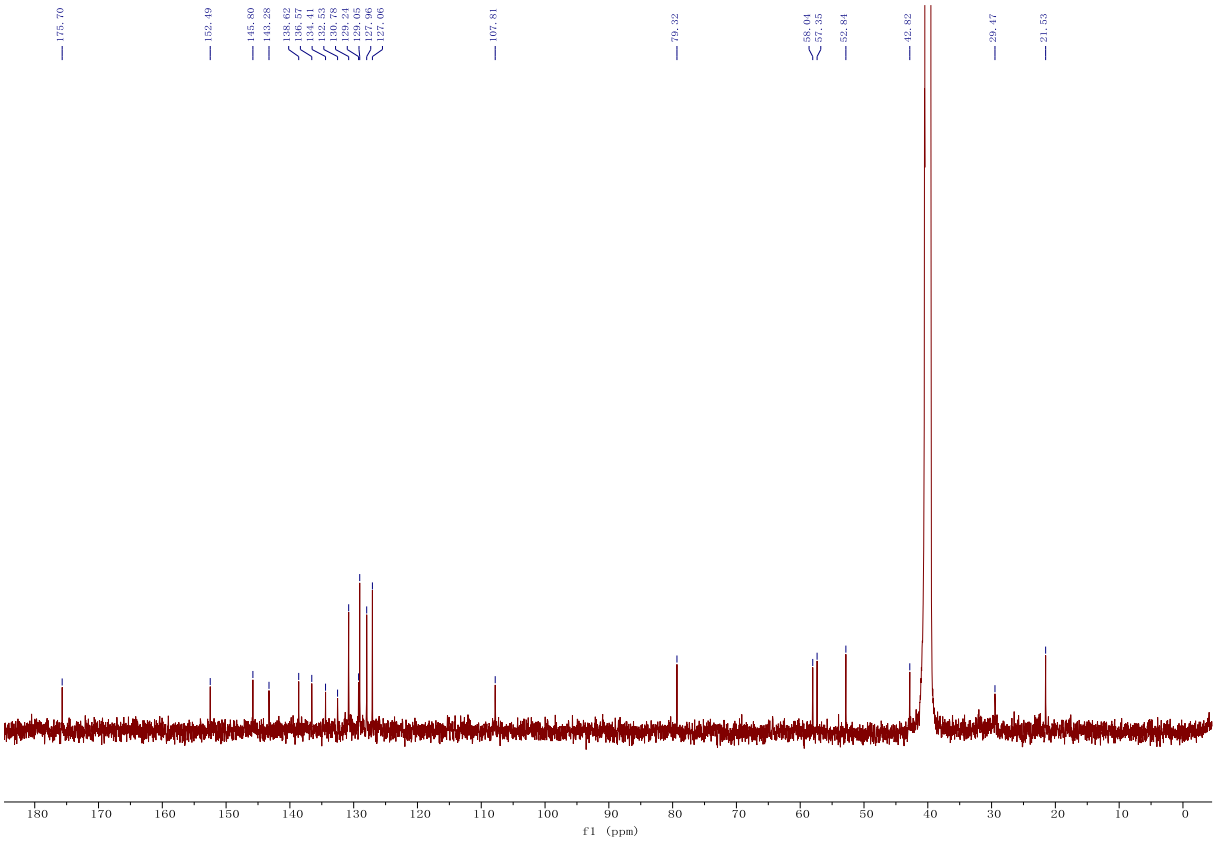


^{1}H NMR (400MHz, $CDCl_3$) and ^{13}C NMR (101MHz, $CDCl_3$) spectra of 5'-chloro-6'-ethoxy-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (9i)

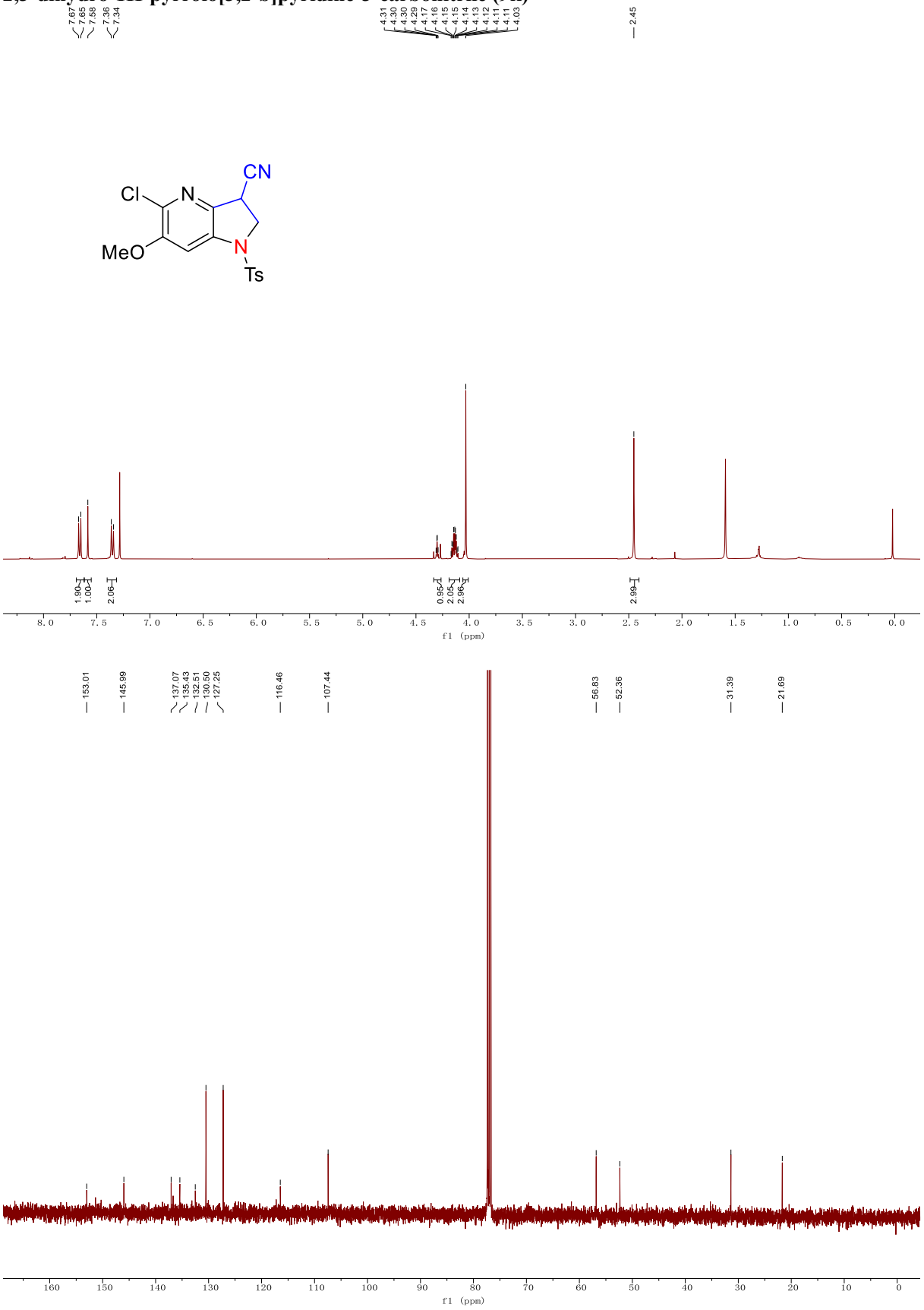


^{1}H NMR (600MHz, $CDCl_3$) and ^{13}C NMR (151MHz, $CDCl_3$) spectra of 6'-bromo-4-phenyl-1'-tosyl-1',2',4,5-tetrahydro-2*H*-spiro[furan-3,3'-pyrrolo[3,2-*b*]pyridin]-2-one (9j)

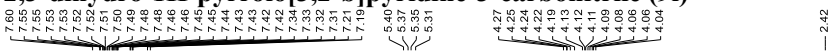


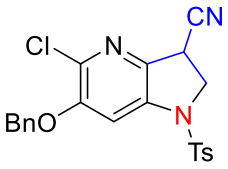


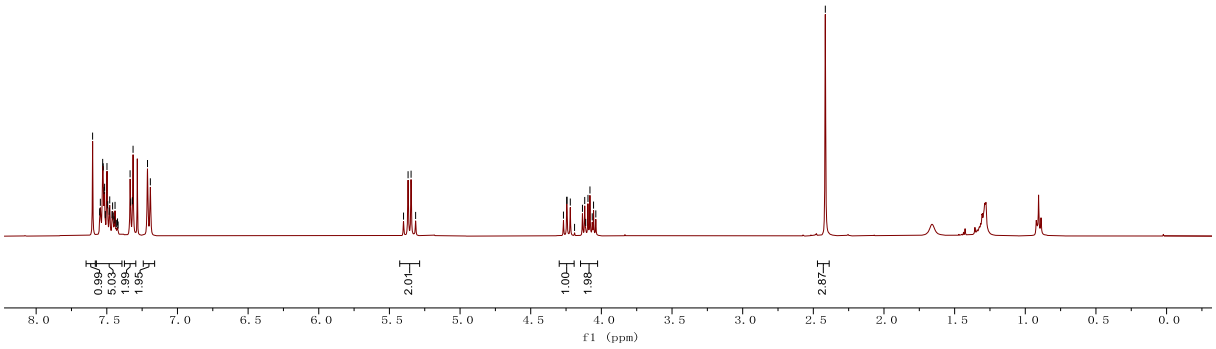
^{1}H NMR (600MHz, $CDCl_3$) and ^{13}C NMR (151MHz, $CDCl_3$) spectra of 5-Chloro-6-methoxy-1-tosyl-2,3-dihydro-1H-pyrrolo[3,2-b]pyridine-3-carbonitrile (9k)

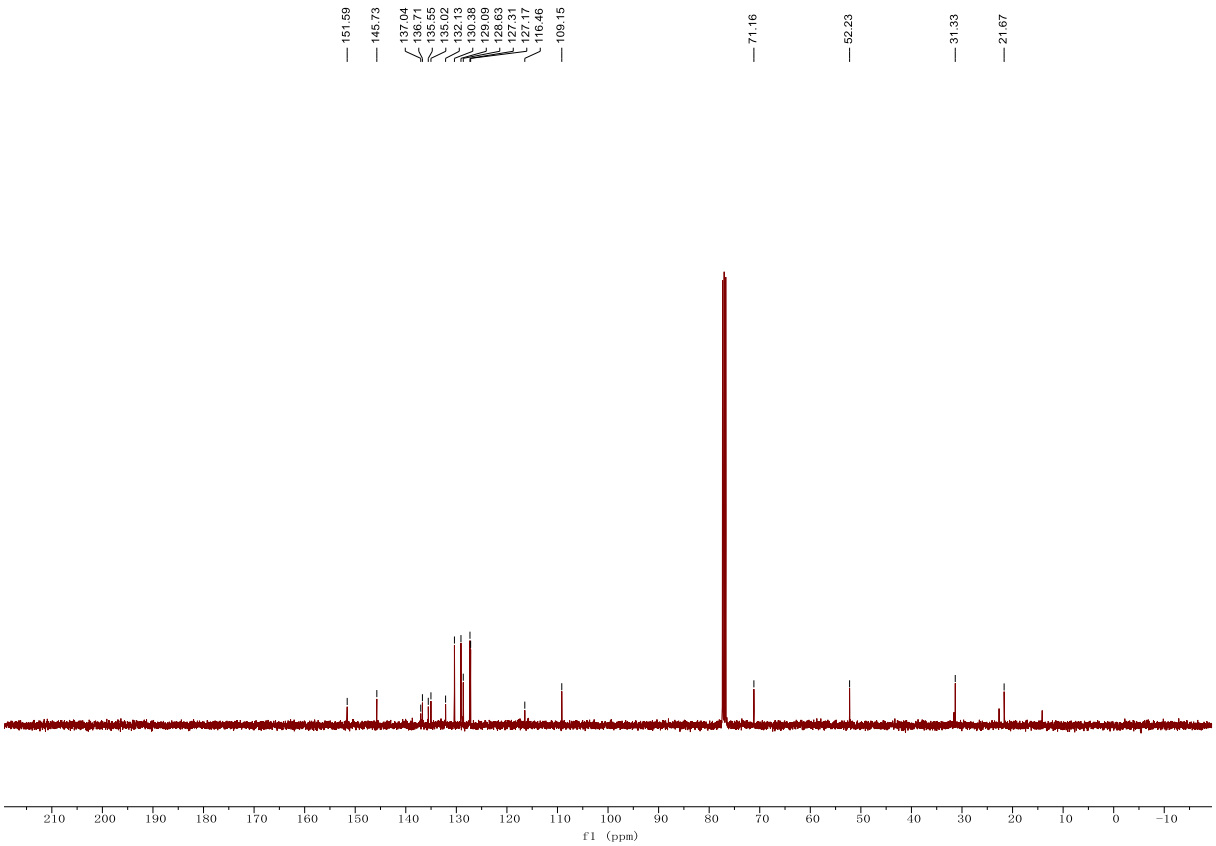


^{1}H NMR (600MHz, $CDCl_3$) and ^{13}C NMR (151MHz, $CDCl_3$) spectra of 6-(Benzyloxy)-5-chloro-1-tosyl-2,3-dihydro-1H-pyrrolo[3,2-b]pyridine-3-carbonitrile (9l)

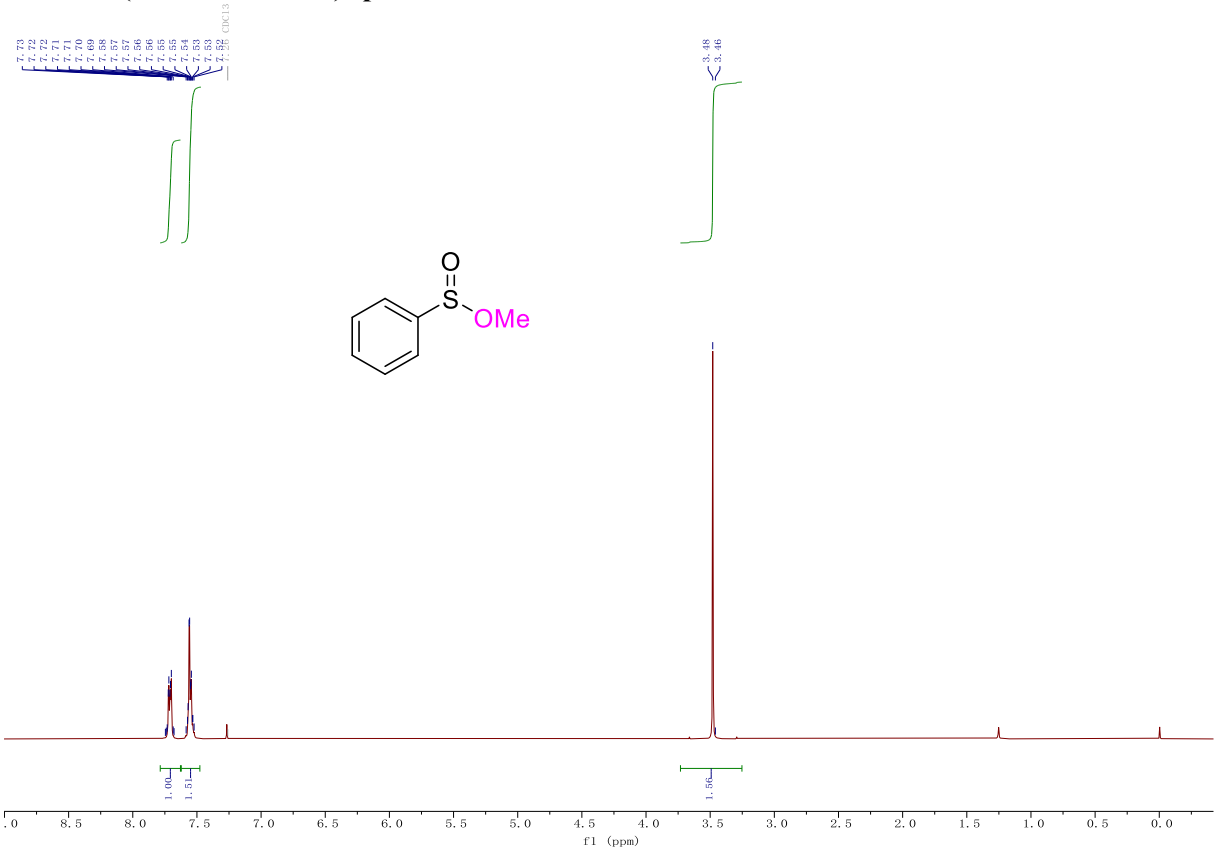




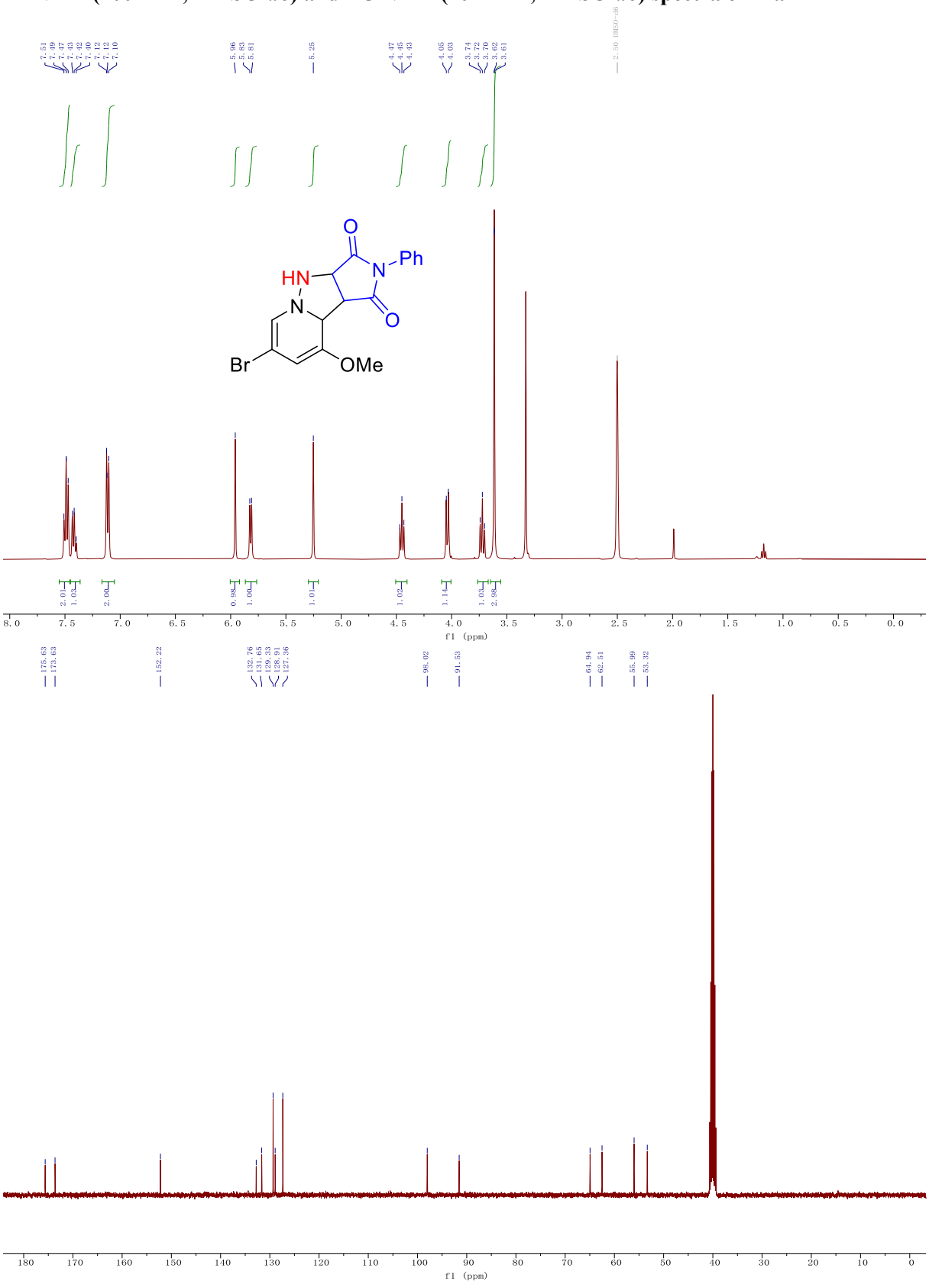




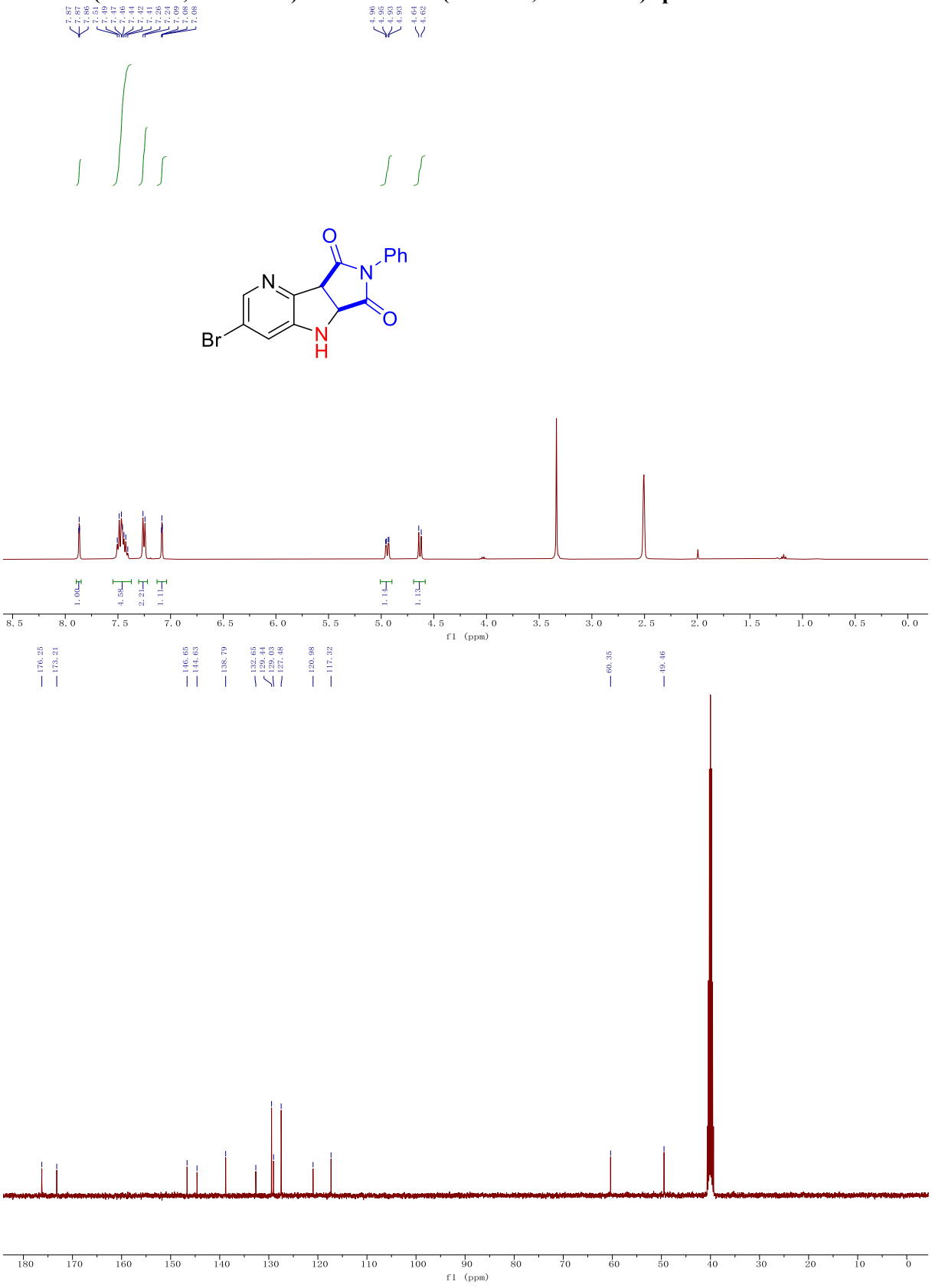
^{1}H NMR (400MHz, $CDCl_3$) spectra of 10a



^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 12a



^{1}H NMR (400MHz, DMSO-*d6*) and ^{13}C NMR (101MHz, DMSO-*d6*) spectra of 12b



Coordiantes

1a

Gsol = -2992.212172 Hartree

C	0.205506	-1.014136	0.021476
C	1.577144	-0.685946	-0.018720
C	1.946668	0.663247	-0.078434
C	-0.329156	1.335312	-0.142345
C	-0.736849	0.002639	-0.028943
H	-0.083613	-2.062725	0.098573
H	2.969679	1.027485	-0.035847
H	-1.025648	2.167653	-0.229407
N	0.987075	1.618567	-0.155496
N	1.433111	2.938713	-0.187910
H	0.647668	3.578647	-0.077503
Br	-2.579470	-0.370720	0.032520
O	2.440878	-1.688427	0.031010
C	3.846135	-1.428760	0.012913
H	4.148533	-0.855394	0.903677
H	4.333625	-2.409387	0.025807
H	4.132063	-0.886786	-0.903039
H	1.912868	3.119742	-1.072216

DBU

Gsol = -462.109846 Hartree

C	-1.993840	1.307525	0.313306
C	-0.899892	1.323354	-0.761926
C	-2.783411	-0.001873	0.371606
C	0.396510	-0.766927	-0.351958
C	-1.942375	-1.264285	0.579660
C	-0.897857	-1.535002	-0.519131
H	-1.523162	1.518005	1.289835
H	-1.303614	0.930037	-1.710992
H	-3.347656	-0.111111	-0.573258
H	-2.625067	-2.128599	0.627354
H	-2.694488	2.136772	0.115474
H	-0.606598	2.362530	-0.971266
H	-3.540236	0.066395	1.171252
H	-1.429398	-1.225307	1.556766
H	-1.342050	-1.335854	-1.510580
H	-0.601658	-2.590938	-0.506142
N	0.317210	0.611634	-0.394140
C	1.470784	1.432515	-0.034605
H	1.937453	1.854311	-0.946406
H	1.120783	2.288877	0.566915
C	2.491223	0.619813	0.749426
H	3.429216	1.188450	0.847500
H	2.110189	0.431541	1.767547
C	2.709168	-0.719413	0.045920
H	3.409807	-1.347153	0.622070
H	3.195959	-0.544180	-0.935003
N	1.469742	-1.449921	-0.143696

DBUH

Gsol = -462.550399 Hartree

C	2.024806	1.274761	-0.470710
C	0.901492	1.462363	0.551625
C	2.858269	0.007466	-0.273340
C	-0.302584	-0.656101	0.295800
C	2.070681	-1.300600	-0.351578
C	0.934696	-1.413797	0.686806
H	1.588923	1.301413	-1.483914
H	1.252664	1.231413	1.569882
H	3.358349	0.061575	0.709980
H	2.756517	-2.144151	-0.182732
H	2.687693	2.150758	-0.394448
H	0.576114	2.509050	0.561238
H	3.662753	-0.015164	-1.024849
H	1.650675	-1.440531	-1.362249
H	1.280023	-1.051316	1.668584
H	0.653765	-2.467023	0.825275
N	-0.312381	0.669816	0.266972
C	-1.515809	1.411268	-0.156902
H	-1.537654	2.353168	0.407181
H	-1.415157	1.667644	-1.225477
C	-2.779353	0.605530	0.105206
H	-2.950470	0.529241	1.190563
H	-3.644594	1.123293	-0.330725
C	-2.644971	-0.787455	-0.490841
H	-2.675436	-0.756796	-1.592761
H	-3.453373	-1.449272	-0.151596
N	-1.371727	-1.362827	-0.057525
H	-1.285395	-2.372823	-0.026481

13

Gsol = -2991.786488 Hartree

C	0.214393	-1.029361	-0.000014
C	1.570206	-0.638424	0.000041
C	1.923726	0.704319	0.000075
C	-0.365464	1.336940	0.000013
C	-0.721250	-0.005312	-0.000026
H	-0.055449	-2.083304	-0.000047
H	2.940756	1.082745	0.000113
H	-1.087522	2.150552	0.000002
N	0.966973	1.707270	0.000066
N	1.393618	2.941721	0.000095
H	0.558815	3.537120	0.000073
Br	-2.578070	-0.420151	-0.000099
O	2.476188	-1.634221	0.000046
C	3.857060	-1.316955	0.000136
H	4.138039	-0.742364	0.899118
H	4.393984	-2.273517	0.000180
H	4.138155	-0.742367	-0.898811

A

Gsol = -345.86429 Hartree

C	0.240705	-0.303869	0.000135
O	0.478961	-1.492662	0.000012
O	1.204753	0.633229	0.000040

C 2.548954 0.156379 -0.000076
H 3.189698 1.046197 -0.000628
H 2.747122 -0.455286 0.893034
H 2.746691 -0.456118 -0.892705
C -1.144960 0.259968 0.000020
C -1.353039 1.585502 -0.000006
H -0.519474 2.289135 0.000047
H -2.367435 1.993600 -0.000080
C -2.242817 -0.766200 -0.000052
H -2.163790 -1.422712 -0.881337
H -2.163932 -1.422679 0.881271
H -3.231649 -0.287351 -0.000140

TS1s

Gsol = -3337.619584 Hartree

C 1.185433 1.203058 -0.297386
C -0.103680 1.112474 -0.812925
C -0.612280 -0.139819 -1.206235
C 1.461238 -1.185904 -0.696223
C 1.955940 0.017958 -0.261810
H 1.609314 2.140996 0.052893
H -1.594967 -0.232378 -1.663002
H 2.000344 -2.129889 -0.675859
N 0.180333 -1.250751 -1.196294
N -0.395388 -2.470774 -1.258085
H -1.191535 -2.372123 -1.892618
Br 3.728091 0.088056 0.416841
O -0.976063 2.128270 -0.918486
C -0.630975 3.386099 -0.362761
H 0.244940 3.822800 -0.871208
H -1.499324 4.038491 -0.513556
H -0.422362 3.297582 0.716338
C -2.907449 -0.607210 0.359159
O -3.598865 -0.960622 -0.591319
O -3.167526 0.548040 1.034161
C -4.203908 1.362563 0.506556
H -4.318661 2.205531 1.200686
H -3.933073 1.737961 -0.493273
H -5.151042 0.808430 0.425757
C -1.724024 -1.282809 0.857640
C -1.429082 -2.562094 0.334922
H -2.255813 -3.108788 -0.126047
H -0.737640 -3.184506 0.908477
C -0.930342 -0.677524 1.986369
H -0.488592 0.302443 1.728201
H -1.560084 -0.501057 2.874893
H -0.104898 -1.343001 2.280854

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c-TS2s

Gsol = -3800.170035 Hartree

C 3.983516 -0.263686 -0.704302
C 3.332104 -1.442503 -0.331330
C 2.650263 -1.495313 0.893942
C 3.314355 0.719956 1.417837
C 3.969892 0.805617 0.208961

H	4.504310	-0.164273	-1.653755
H	2.122244	-2.391125	1.212921
H	3.256997	1.514426	2.157672
N	2.659346	-0.438951	1.746745
N	1.797505	-0.378214	2.785479
H	1.610610	-1.347727	3.053004
Br	4.854267	2.420672	-0.231422
O	3.244968	-2.551408	-1.076103
C	3.799636	-2.549695	-2.385051
H	4.889515	-2.388793	-2.354692
H	3.590213	-3.539223	-2.807223
H	3.327624	-1.775245	-3.011505
C	-0.137421	-1.793106	0.268433
O	-0.324400	-2.706181	1.070701
O	-0.112222	-2.022957	-1.073080
C	-0.149338	-3.385294	-1.484784
H	-0.161887	-3.373377	-2.582072
H	0.743083	-3.921340	-1.128171
H	-1.044346	-3.897084	-1.101499
C	0.057137	-0.391829	0.592345
C	0.089158	-0.035632	1.957786
H	-0.447040	-0.683548	2.656180
H	0.050299	1.028883	2.202384
C	0.349165	0.594381	-0.514398
H	1.283717	0.369730	-1.058623
H	-0.446005	0.595108	-1.279114
H	0.437858	1.615719	-0.114151
C	-5.620934	2.358072	-1.311822
C	-5.966060	1.543283	-0.062191
C	-4.419006	3.291163	-1.148254
C	-3.813874	0.454331	0.379173
C	-3.104811	2.598508	-0.785051
C	-3.154989	1.796886	0.531074
H	-5.464315	1.663559	-2.155136
H	-5.924406	2.174733	0.840103
H	-4.654028	4.035484	-0.366786
H	-2.315562	3.358173	-0.679471
H	-6.505517	2.962552	-1.567716
H	-6.993950	1.167990	-0.132277
H	-4.277106	3.861123	-2.079986
H	-2.780072	1.930408	-1.600590
H	-3.680695	2.373044	1.309382
H	-2.136957	1.620431	0.900217
N	-5.117803	0.353496	0.134856
C	-5.741615	-0.964966	-0.079557
H	-6.772069	-0.907798	0.296067
H	-5.795186	-1.158660	-1.164728
C	-4.972181	-2.065013	0.638843
H	-5.097212	-1.952220	1.727264
H	-5.383538	-3.044572	0.359075
C	-3.495826	-1.989232	0.283463
H	-3.318039	-2.298939	-0.760313
H	-2.875765	-2.630469	0.923059
N	-3.037697	-0.613073	0.457604
H	-2.033364	-0.454506	0.624615

14

Gsol = -3337.650852 Hartree

C	1.362200	1.143504	-0.311950
C	0.044426	1.091252	-0.612783
C	-0.678683	-0.207871	-0.796499
C	1.523167	-1.290322	-0.488720
C	2.100979	-0.104605	-0.193197
H	1.883173	2.085311	-0.149888
H	-1.334436	-0.131828	-1.678374
H	2.024113	-2.254709	-0.413703
N	0.231319	-1.338216	-1.000136
N	-0.498792	-2.514430	-0.730324
H	-1.113388	-2.666882	-1.531229
Br	3.924836	-0.026364	0.356701
O	-0.810267	2.132545	-0.721355
C	-0.311760	3.432563	-0.470887
H	0.486150	3.697507	-1.185815
H	-1.154959	4.123834	-0.592657
H	0.086805	3.513081	0.555352
C	-3.045187	-0.410004	0.026418
O	-3.542056	-0.887689	-0.971278
O	-3.716440	0.384706	0.868431
C	-5.076306	0.667144	0.529615
H	-5.456863	1.326039	1.318811
H	-5.134349	1.166108	-0.448808
H	-5.665983	-0.260359	0.486395
C	-1.602472	-0.649620	0.429434
C	-1.323434	-2.191402	0.446618
H	-2.239121	-2.796287	0.431705
H	-0.757510	-2.436192	1.358782
C	-1.203762	0.012502	1.746550
H	-1.378309	1.095468	1.716327
H	-1.789656	-0.400819	2.580660
H	-0.137542	-0.164351	1.947124

TS2s

Gsol = -3800.172115 Hartree

C	4.098399	0.233370	0.660907
C	3.272938	1.331576	0.483245
C	2.414351	1.388005	-0.647316
C	3.294222	-0.695217	-1.437002
C	4.099602	-0.783735	-0.331090
H	4.753293	0.140481	1.525234
H	1.937657	2.322014	-0.941474
H	3.219607	-1.444509	-2.222309
N	2.504137	0.412683	-1.597646
N	1.389486	0.277546	-2.422306
H	1.165903	1.214879	-2.765777
Br	5.233746	-2.287167	-0.122770
O	3.149716	2.371921	1.318882
C	3.885627	2.362161	2.533357
H	4.971014	2.343176	2.340445
H	3.624858	3.287335	3.060120
H	3.607126	1.493910	3.153605
C	-0.280457	1.948548	-0.234605

O	-0.409264	2.627822	-1.261437
O	-0.535181	2.477899	0.997283
C	-0.749057	3.883489	1.055534
H	-0.889511	4.128287	2.115982
H	0.117958	4.431888	0.656765
H	-1.639872	4.182351	0.482181
C	0.173265	0.593272	-0.201197
C	0.218323	-0.116502	-1.513515
H	-0.655470	0.092339	-2.148752
H	0.296692	-1.204956	-1.371360
C	0.393520	-0.140047	1.099660
H	0.891115	0.504971	1.839496
H	-0.537578	-0.495201	1.583946
H	1.031258	-1.024252	0.944002
C	-5.791845	-2.415409	1.210564
C	-5.837183	-1.832188	-0.204496
C	-4.536958	-3.234729	1.520391
C	-3.719500	-0.598974	-0.242057
C	-3.216241	-2.474202	1.393965
C	-2.964718	-1.876415	-0.004895
H	-5.910835	-1.592238	1.936020
H	-5.513966	-2.579799	-0.947007
H	-4.508895	-4.105504	0.841593
H	-2.384174	-3.159443	1.615727
H	-6.674129	-3.064055	1.328747
H	-6.867233	-1.559378	-0.463185
H	-4.616759	-3.644622	2.539537
H	-3.158942	-1.666486	2.143370
H	-3.232058	-2.605327	-0.786357
H	-1.897290	-1.656354	-0.129159
N	-5.042597	-0.601043	-0.373263
C	-5.783642	0.657072	-0.578709
H	-6.646623	0.429112	-1.218846
H	-6.175224	1.002133	0.393440
C	-4.904703	1.716435	-1.228489
H	-4.695704	1.432894	-2.272095
H	-5.438788	2.676429	-1.247344
C	-3.596491	1.854882	-0.466134
H	-3.752835	2.327550	0.517795
H	-2.860025	2.455521	-1.015788
N	-3.022140	0.525229	-0.272892
H	-2.002767	0.457300	-0.175397

15

Gsol = -3800.175047 Hartree

C	4.409983	0.272742	0.633661
C	3.596905	1.403450	0.496720
C	2.613673	1.419927	-0.508745
C	3.289527	-0.724841	-1.272419
C	4.240713	-0.788361	-0.270680
H	5.169175	0.206187	1.410520
H	1.954464	2.271191	-0.676322
H	3.110502	-1.496928	-2.017455
N	2.505161	0.380109	-1.359538
N	1.439393	0.330981	-2.252351

H	1.166087	1.307334	-2.416944
Br	5.331564	-2.325574	-0.140834
O	3.644165	2.491622	1.266283
C	4.580230	2.549396	2.337458
H	5.614894	2.493892	1.961232
H	4.421826	3.516556	2.827509
H	4.402954	1.737276	3.061373
C	-0.342353	1.742647	-0.272763
O	-0.200152	2.494381	-1.263077
O	-0.710721	2.272763	0.942479
C	-0.724530	3.688447	1.041426
H	-1.109929	3.924165	2.042315
H	0.289889	4.106993	0.933939
H	-1.366018	4.147209	0.273990
C	-0.171677	0.341836	-0.267639
C	0.204411	-0.265214	-1.576983
H	-0.550195	-0.102452	-2.365057
H	0.365967	-1.350410	-1.491421
C	-0.056320	-0.439995	1.023000
H	0.870235	-0.231850	1.592852
H	-0.889887	-0.222261	1.711650
H	-0.070870	-1.525096	0.827794
C	-5.941100	-2.210156	1.367855
C	-6.111274	-1.607746	-0.030148
C	-4.726021	-3.128370	1.518925
C	-3.921620	-0.541219	-0.327460
C	-3.375606	-2.467414	1.238587
C	-3.245648	-1.876089	-0.178483
H	-5.903950	-1.389901	2.105495
H	-5.940824	-2.371908	-0.806066
H	-4.847534	-3.988360	0.835813
H	-2.577178	-3.214962	1.361827
H	-6.851039	-2.789187	1.592073
H	-7.141513	-1.255889	-0.161119
H	-4.715558	-3.546480	2.537978
H	-3.168683	-1.674710	1.977442
H	-3.658598	-2.575767	-0.922470
H	-2.187297	-1.732075	-0.427790
N	-5.251304	-0.441323	-0.294790
C	-5.906971	0.874278	-0.397485
H	-6.864882	0.727823	-0.915042
H	-6.134486	1.241949	0.617924
C	-5.037152	1.866648	-1.157849
H	-4.990622	1.577821	-2.220010
H	-5.488955	2.866888	-1.106498
C	-3.634358	1.886905	-0.570863
H	-3.619950	2.360123	0.424630
H	-2.927749	2.438536	-1.205371
N	-3.146139	0.517059	-0.454690
H	-2.105994	0.380222	-0.428198

TS3s

Gsol = -3800.171052 Hartree

C	4.510686	0.105903	0.534911
C	3.909118	1.364776	0.387769

C	2.839400	1.505184	-0.512517
C	3.018889	-0.763849	-1.166606
C	4.045996	-0.952064	-0.254189
H	5.326885	-0.059399	1.235568
H	2.294341	2.441679	-0.629478
H	2.642943	-1.529842	-1.841060
N	2.441868	0.459137	-1.259183
N	1.395876	0.601314	-2.170757
H	1.213273	1.608997	-2.244152
Br	4.828133	-2.661520	-0.108560
O	4.244036	2.464805	1.055530
C	5.319105	2.421706	1.992148
H	6.262883	2.145827	1.494525
H	5.403180	3.434499	2.401413
H	5.102937	1.713154	2.807508
C	-0.291596	1.963873	-0.197813
O	-0.002015	2.759974	-1.101898
O	-0.597210	2.415793	1.044089
C	-0.552210	3.825843	1.240963
H	-0.811216	3.995862	2.293291
H	0.452593	4.223893	1.032026
H	-1.270352	4.342778	0.586692
C	-0.395322	0.526761	-0.339962
C	0.104321	0.020000	-1.677465
H	-0.587408	0.279839	-2.494782
H	0.191064	-1.076963	-1.675907
C	-0.118819	-0.326885	0.894083
H	0.913373	-0.242535	1.282277
H	-0.790377	-0.048772	1.720180
H	-0.295676	-1.392129	0.674408
C	-5.800599	-2.233806	1.402569
C	-6.088278	-1.547465	0.062528
C	-4.597173	-3.178865	1.382671
C	-3.903736	-0.482453	-0.376794
C	-3.266478	-2.527576	1.002002
C	-3.266582	-1.850546	-0.381316
H	-5.672175	-1.457158	2.176349
H	-6.011883	-2.274985	-0.763089
H	-4.806044	-3.996227	0.668836
H	-2.480620	-3.299295	1.003569
H	-6.696218	-2.810554	1.684987
H	-7.122311	-1.180109	0.052787
H	-4.495480	-3.655138	2.371178
H	-2.967217	-1.784408	1.760591
H	-3.773240	-2.494401	-1.118492
H	-2.236616	-1.718867	-0.732442
N	-5.241641	-0.381742	-0.218494
C	-5.882160	0.938754	-0.172798
H	-6.883539	0.844103	-0.617101
H	-6.019665	1.247788	0.879068
C	-5.058392	1.969883	-0.931690
H	-5.100707	1.752858	-2.011342
H	-5.483463	2.972307	-0.778349
C	-3.613455	1.913033	-0.455898
H	-3.524593	2.303709	0.573427

H -2.959381 2.535302 -1.085523
N -3.111510 0.547969 -0.497390
H -1.826877 0.466804 -0.463945

16
Gsol = -3338.081737 Hartree
C 2.062026 1.186083 0.070609
C 0.853592 1.806048 -0.288211
C -0.192827 1.012477 -0.787281
C 1.145597 -0.938171 -0.655220
C 2.187722 -0.193390 -0.117710
H 2.894201 1.755126 0.481532
H -1.176998 1.421740 -1.014363
H 1.205739 -2.000511 -0.881243
N -0.015819 -0.310586 -0.958996
N -1.033852 -1.073497 -1.536777
H -1.737652 -0.417131 -1.884167
Br 3.796162 -1.073136 0.315383
O 0.583813 3.099749 -0.169899
C 1.567414 3.982657 0.372068
H 2.472063 3.992531 -0.255701
H 1.110440 4.978120 0.372247
H 1.823407 3.693824 1.403797
C -3.522382 -0.396665 0.027398
O -3.320974 0.349578 -0.916961
O -4.602169 -0.326006 0.789760
C -5.561747 0.699965 0.481671
H -6.366394 0.587167 1.215937
H -5.097189 1.692573 0.564679
H -5.946436 0.566034 -0.538648
C -2.558554 -1.472820 0.502940
C -1.704971 -2.038168 -0.650930
H -2.346577 -2.617199 -1.330500
H -0.964417 -2.744280 -0.247857
C -1.750341 -0.955396 1.709434
H -1.192842 -0.035600 1.481769
H -2.424303 -0.734842 2.548833
H -1.033300 -1.721698 2.039818
H -3.176225 -2.309788 0.864078

17
Gsol = -6675.735312 Hartree
C 0.391709 -2.122378 0.260121
C -0.805199 -1.635647 0.662607
C -1.676637 -0.812171 -0.238380
C 0.136451 -1.030790 -1.918356
C 0.842905 -1.831605 -1.091947
H 1.011766 -2.739671 0.906748
H -2.046718 0.059241 0.320356
H 0.422175 -0.794012 -2.942134
N -0.966432 -0.316464 -1.433785
N -1.954098 0.017918 -2.392368
H -2.320187 0.930802 -2.115575
Br 2.510335 -2.558123 -1.659280
O -1.417480 -1.857546 1.839906

C	-0.858310	-2.817393	2.723973
H	0.135220	-2.499814	3.078722
H	-1.542467	-2.892414	3.577623
H	-0.771585	-3.798234	2.227405
C	-4.168758	-1.050415	-0.044709
O	-4.337628	0.116495	0.243058
O	-5.050815	-2.006547	0.242680
C	-6.245037	-1.600022	0.921739
H	-6.837458	-2.510660	1.064410
H	-5.998227	-1.144589	1.891510
H	-6.801104	-0.869187	0.317334
C	-2.949556	-1.562427	-0.797639
C	-2.990860	-1.010933	-2.269720
H	-3.964119	-0.584588	-2.546664
H	-2.772477	-1.843007	-2.956660
C	-2.815504	-3.084956	-0.786261
H	-2.805249	-3.479888	0.237730
H	-3.658847	-3.548070	-1.316560
H	-1.883127	-3.382363	-1.287264
C	3.353289	0.189037	1.181247
C	3.842954	0.445884	-0.112019
C	2.993416	1.061023	-1.042868
C	1.232930	1.164957	0.537397
C	2.043387	0.556900	1.487890
H	3.969881	-0.299911	1.933807
H	3.285102	1.250279	-2.073667
H	0.204735	1.457238	0.724425
N	1.739958	1.400931	-0.696327
N	0.944043	1.972002	-1.704337
H	0.029506	1.506183	-1.660701
Br	1.333363	0.247503	3.205660
O	5.056455	0.137824	-0.552218
C	5.940356	-0.608388	0.283079
H	6.186228	-0.047304	1.198680
H	6.851073	-0.764160	-0.305432
H	5.495702	-1.582762	0.541537
C	-1.364055	3.457536	-0.463797
O	-1.850616	2.793860	-1.359099
O	-1.995409	3.748064	0.665520
C	-3.365452	3.314542	0.787603
H	-3.672214	3.587365	1.803201
H	-3.455932	2.231914	0.627519
H	-3.987562	3.839125	0.048485
C	0.037348	4.049859	-0.511674
C	0.838390	3.434454	-1.667553
H	0.355384	3.701365	-2.618336
H	1.851851	3.862587	-1.689760
C	-0.038358	5.579686	-0.656689
H	-0.592970	6.021450	0.181897
H	-0.542678	5.860015	-1.594458
H	0.973469	6.011379	-0.669509
H	0.518596	3.834983	0.456686

16’

Gsol = -3338.226311 Hartree

C	1.365154	1.270726	-0.041555
C	0.072066	1.477494	-0.571841
C	-0.636717	0.436127	-1.148869
C	1.224650	-1.063952	-0.785428
C	1.917450	-0.033706	-0.215664
H	1.931331	2.048459	0.461187
H	-1.600152	0.579549	-1.629370
H	1.618919	-2.065976	-0.944025
N	-0.078086	-0.849753	-1.201753
N	-0.893553	-1.975606	-1.381991
H	-1.654673	-1.704172	-2.001428
Br	3.720318	-0.338817	0.331615
O	-0.566432	2.675088	-0.558118
C	0.086802	3.791872	0.012248
H	1.035055	4.015908	-0.505286
H	-0.595703	4.643650	-0.103471
H	0.291788	3.637932	1.085585
C	-3.020934	-0.658857	0.271664
O	-3.573449	-0.825904	-0.796385
O	-3.181464	0.437005	1.021253
C	-3.936504	1.515436	0.463247
H	-4.212909	2.164735	1.302768
H	-3.304194	2.073664	-0.243984
H	-4.832114	1.144145	-0.052640
C	-2.091633	-1.674659	0.914033
C	-1.440532	-2.581340	-0.161666
H	-2.181295	-3.307373	-0.526338
H	-0.643416	-3.161485	0.330449
C	-1.102022	-1.076766	1.920862
H	-0.432966	-0.340517	1.457626
H	-1.635107	-0.575818	2.739842
H	-0.482356	-1.877600	2.351846
H	-2.767777	-2.342773	1.480733

14’

Gsol = -3799.564567 Hartree

C	-0.304205	1.524870	1.444232
C	0.846590	0.794078	1.280297
C	1.432085	0.621679	-0.082901
C	-0.093017	2.410720	-0.838016
C	-0.823798	2.255649	0.334412
H	-0.821719	1.575303	2.399796
H	0.916566	-0.288421	-0.557406
H	-0.380657	3.095944	-1.636142
N	1.048309	1.726166	-0.964096
N	2.014491	1.949677	-1.918638
H	1.627341	2.114604	-2.847509
Br	-2.503847	3.091475	0.473388
O	1.479381	0.106218	2.216483
C	1.022929	0.163720	3.568802
H	0.000357	-0.232475	3.650594
H	1.709392	-0.464350	4.146643
H	1.056504	1.200035	3.939110
C	3.450204	-0.896823	-0.078058
O	2.767096	-1.827518	0.270469

O	4.752086	-0.982904	-0.354277
C	5.358827	-2.276685	-0.216202
H	6.414517	-2.144335	-0.476505
H	5.257879	-2.636531	0.817306
H	4.880068	-2.996778	-0.894915
C	2.955041	0.530803	-0.291458
C	3.027060	0.896969	-1.795389
H	2.780948	0.023549	-2.422968
H	4.010058	1.287262	-2.086012
C	3.745560	1.535240	0.562096
H	3.645697	1.302465	1.630093
H	4.809093	1.495457	0.294042
H	3.377604	2.556921	0.389043
C	-3.641405	-2.784215	1.031518
C	-3.237928	-3.214836	-0.382862
C	-2.522775	-2.940215	2.063133
C	-1.135286	-1.967420	-0.815106
C	-1.227843	-2.194107	1.733998
C	-0.548033	-2.613813	0.418054
H	-3.989922	-1.737031	0.992015
H	-2.697342	-4.174643	-0.346511
H	-2.288545	-4.015287	2.165838
H	-0.510386	-2.367632	2.551716
H	-4.505620	-3.391103	1.348333
H	-4.137127	-3.397961	-0.987753
H	-2.890265	-2.612737	3.049842
H	-1.415807	-1.106470	1.707171
H	-0.587049	-3.712077	0.315895
H	0.513939	-2.343926	0.435442
N	-2.445016	-2.221695	-1.107186
C	-3.156938	-1.452058	-2.130409
H	-3.319673	-2.083190	-3.023219
H	-4.152679	-1.190293	-1.736959
C	-2.390051	-0.192383	-2.503787
H	-2.822629	0.251653	-3.412954
H	-2.477163	0.553071	-1.695968
C	-0.920057	-0.557767	-2.695206
H	-0.323539	0.334860	-2.945427
H	-0.816846	-1.241112	-3.560360
N	-0.366156	-1.180316	-1.506531

TS1

Gsol = -3799.563186 Hartree

C	-0.457441	1.657968	1.348489
C	0.703166	0.924456	1.257398
C	1.342732	0.708224	-0.050909
C	-0.156055	2.442654	-0.951867
C	-0.927702	2.351688	0.189577
H	-1.010642	1.748140	2.280489
H	0.739520	-0.358665	-0.551535
H	-0.402409	3.083131	-1.798896
N	0.986825	1.732806	-1.001617
N	2.002267	1.948307	-1.931175
H	1.629156	2.005516	-2.879615
Br	-2.608652	3.209490	0.235161

O	1.293002	0.279728	2.260896
C	0.790144	0.429165	3.586068
H	-0.239605	0.049533	3.661327
H	1.447776	-0.166585	4.228847
H	0.819769	1.486281	3.894144
C	3.357662	-0.839114	0.067281
O	2.694691	-1.743799	0.511499
O	4.647202	-0.954552	-0.263538
C	5.257170	-2.235490	-0.053441
H	6.299210	-2.130880	-0.374894
H	5.207724	-2.512819	1.009037
H	4.745491	-3.006168	-0.647566
C	2.865275	0.576218	-0.212801
C	2.997859	0.890998	-1.723159
H	2.776742	-0.008555	-2.323873
H	3.996399	1.259674	-1.987335
C	3.643353	1.601507	0.633973
H	3.497803	1.407925	1.704445
H	4.716152	1.540849	0.407634
H	3.292139	2.618809	0.408461
C	-3.620687	-3.010673	0.843729
C	-2.891351	-3.503944	-0.408613
C	-2.721847	-2.914659	2.076878
C	-0.917065	-2.025638	-0.583004
C	-1.494311	-2.015139	1.915145
C	-0.511027	-2.439560	0.809054
H	-4.080755	-2.032057	0.621748
H	-2.250923	-4.366217	-0.163373
H	-2.378665	-3.930999	2.341640
H	-0.940082	-2.015905	2.866597
H	-4.448942	-3.705766	1.057081
H	-3.616744	-3.863781	-1.150957
H	-3.318187	-2.560961	2.933593
H	-1.808660	-0.971996	1.738073
H	-0.379755	-3.535385	0.825852
H	0.484747	-2.019554	0.987706
N	-2.092014	-2.474048	-1.081287
C	-2.668461	-1.919258	-2.312993
H	-2.595660	-2.671220	-3.118219
H	-3.740220	-1.738667	-2.135563
C	-1.973652	-0.628953	-2.719502
H	-2.266202	-0.356558	-3.744081
H	-2.278912	0.194137	-2.052636
C	-0.467324	-0.836660	-2.600627
H	0.084779	0.078150	-2.860137
H	-0.133457	-1.612749	-3.313853
N	-0.115158	-1.231719	-1.247304

18

Gsol = -3337.041664 Hartree

C	1.391968	1.118810	0.020717
C	0.002731	1.163435	0.302164
C	-0.675754	0.009200	0.647780
C	1.359879	-1.312639	0.379206
C	2.026190	-0.158305	0.068071

H	1.961203	2.004834	-0.242212
H	1.807686	-2.302921	0.431079
N	0.021369	-1.213335	0.694595
N	-0.852991	-2.322496	0.645343
H	-1.067082	-2.482352	-0.346899
Br	3.897900	-0.254419	-0.286857
O	-0.742679	2.294774	0.239698
C	-0.121371	3.510926	-0.127685
H	0.318061	3.452306	-1.137872
H	-0.909604	4.274361	-0.121555
H	0.665458	3.797485	0.590599
C	-2.920424	-0.074224	-0.413166
O	-3.860280	0.663871	-0.574852
O	-2.427152	-0.860874	-1.393949
C	-3.055202	-0.757908	-2.673522
H	-2.522007	-1.453052	-3.332643
H	-4.118975	-1.030491	-2.609247
H	-2.977174	0.269161	-3.058867
C	-2.141290	-0.262399	0.892384
C	-2.065183	-1.787146	1.268591
H	-2.941361	-2.362806	0.943628
H	-1.976596	-1.866238	2.363054
C	-2.771695	0.582619	1.999929
H	-2.766381	1.643310	1.721364
H	-3.814671	0.277390	2.174024
H	-2.201893	0.458126	2.931982

TS2

Gsol = -3337.024283 Hartree

C	1.605827	1.063637	-0.149827
C	0.230805	1.341196	-0.022671
C	-0.654691	0.289448	0.264038
C	1.126902	-1.283004	0.258676
C	2.027437	-0.267702	0.002572
H	2.331420	1.846942	-0.351775
H	1.418868	-2.329515	0.357068
N	-0.189124	-0.983210	0.375047
N	-1.147625	-1.718490	1.719176
H	-1.588209	-2.422457	1.120765
Br	3.875706	-0.690425	-0.212478
O	-0.291273	2.575124	-0.182087
C	0.563119	3.657011	-0.499297
H	1.088551	3.489784	-1.454765
H	-0.080997	4.540236	-0.592238
H	1.306687	3.833419	0.296558
C	-2.953241	-0.185958	-0.514972
O	-3.535858	0.513127	-1.309633
O	-2.954955	-1.528861	-0.589994
C	-3.647605	-2.104270	-1.700427
H	-3.539645	-3.190389	-1.597498
H	-4.710135	-1.820973	-1.684889
H	-3.206052	-1.764204	-2.648614
C	-2.121070	0.339272	0.661761
C	-2.114238	-0.651317	1.885565
H	-3.127355	-1.055670	2.042648

H -1.846209 -0.051743 2.771149
C -2.669829 1.703501 1.080867
H -2.755296 2.377431 0.223182
H -3.670846 1.569805 1.520045
H -2.017060 2.168082 1.831549

19
Gsol = -3337.058091 Hartree
C 1.662775 0.975779 0.014536
C 0.302521 1.282597 -0.105416
C -0.619432 0.221678 -0.303806
C 1.096219 -1.345110 -0.326965
C 2.053957 -0.359464 -0.098791
H 2.407639 1.750826 0.184512
H 1.378731 -2.396372 -0.430723
N -0.197476 -1.034279 -0.419119
N -2.140072 1.134077 2.023689
H -2.068233 0.111155 2.131946
Br 3.891303 -0.829315 0.054641
O -0.188530 2.535891 -0.053549
C 0.673440 3.612057 0.269786
H 1.455405 3.746718 -0.496673
H 0.044890 4.510096 0.305244
H 1.146869 3.460592 1.254039
C -2.807408 -0.915527 -0.413053
O -3.328706 -1.452970 -1.357576
O -2.802969 -1.449107 0.821863
C -3.343802 -2.765014 0.949483
H -3.267081 -3.025407 2.011689
H -4.393519 -2.789821 0.622857
H -2.764333 -3.473187 0.339173
C -2.125176 0.460203 -0.442077
C -2.688110 1.353182 0.719019
H -3.784916 1.172098 0.767789
H -2.566769 2.409347 0.440252
C -2.428104 1.129827 -1.792828
H -2.118399 0.477132 -2.619575
H -3.507912 1.315906 -1.895282
H -1.894786 2.086597 -1.864912

TS3
Gsol = -3337.028012 Hartree
C -1.490963 0.967215 -0.151778
C -0.109171 1.299731 0.047279
C 0.729093 0.244224 0.594329
C -1.056770 -1.193910 0.862455
C -1.929572 -0.285915 0.233683
H -2.178618 1.694004 -0.581634
H -1.418027 -2.151223 1.246075
N 0.247205 -0.915966 0.982986
N 0.930302 1.123524 -1.633876
H 0.767982 0.148366 -1.917751
Br -3.751495 -0.783730 -0.021026
O 0.269056 2.578982 0.332546
C -0.307177 3.621368 -0.440018

H -1.364378 3.787867 -0.171594
H 0.261892 4.531484 -0.211183
H -0.222739 3.385740 -1.512527
C 2.835293 -0.975695 0.197747
O 3.635045 -1.482264 0.943874
O 2.378327 -1.579532 -0.914398
C 2.808783 -2.923146 -1.132885
H 2.349928 -3.242402 -2.076092
H 3.905109 -2.976351 -1.202915
H 2.474475 -3.569441 -0.307913
C 2.228992 0.420344 0.362199
C 2.249673 1.184952 -1.010362
H 3.007951 0.756286 -1.684523
H 2.509948 2.237410 -0.833218
C 2.936227 1.170187 1.492491
H 2.883118 0.593771 2.426231
H 3.999179 1.321573 1.249565
H 2.458069 2.146946 1.642590

20

Gsol = -3337.061104 Hartree

C -1.289373 0.644556 -0.666968
C 0.072141 1.189566 -0.338356
C 0.781932 0.287055 0.655493
C -1.131212 -0.742611 1.338719
C -1.853792 -0.224483 0.221377
H -1.827857 1.016213 -1.539775
H -1.631660 -1.360130 2.087777
N 0.203015 -0.552927 1.456510
N 0.994595 1.256919 -1.463172
H 0.883019 0.429462 -2.047493
Br -3.655529 -0.817064 -0.010576
O 0.002296 2.468990 0.294273
C -0.529791 3.518250 -0.495818
H -1.621521 3.417099 -0.632391
H -0.330813 4.453961 0.044596
H -0.047293 3.557825 -1.486223
C 2.811983 -1.015119 0.110497
O 3.710048 -1.576510 0.684988
O 2.147399 -1.553587 -0.930807
C 2.534770 -2.872532 -1.324370
H 1.880564 -3.146086 -2.160402
H 3.588147 -2.890446 -1.640519
H 2.403551 -3.576264 -0.489733
C 2.279239 0.380233 0.431446
C 2.332329 1.274075 -0.859534
H 3.084790 0.937163 -1.583875
H 2.582326 2.302166 -0.561873
C 3.014481 0.971742 1.634179
H 2.889844 0.323871 2.512563
H 4.090373 1.064073 1.423864
H 2.602581 1.964824 1.862648

TS4

Gsol = -3337.047161 Hartree

C	-1.330926	0.420562	-0.851068
C	0.033550	0.809857	-0.609691
C	0.733861	0.121856	0.465292
C	-1.168853	-0.863645	1.216741
C	-1.911016	-0.376037	0.118934
H	-1.884776	0.783314	-1.717055
H	-1.653884	-1.479041	1.978085
N	0.162410	-0.638554	1.351192
N	0.966365	1.180859	-1.541538
H	0.706585	1.808323	-2.295020
Br	-3.750921	-0.851232	-0.014757
O	-0.313045	2.341187	0.478369
C	-0.633068	3.425413	-0.312106
H	-1.678485	3.422700	-0.691317
H	-0.506157	4.348667	0.289335
H	0.039388	3.551623	-1.193863
C	3.021644	-0.818867	0.195025
O	3.960130	-1.158636	0.870748
O	2.556799	-1.526200	-0.845119
C	3.221869	-2.759094	-1.130822
H	2.702120	-3.192846	-1.992970
H	4.280795	-2.582512	-1.370882
H	3.163601	-3.437310	-0.267077
C	2.209632	0.465105	0.390335
C	2.271415	1.354398	-0.897141
H	3.079978	1.056495	-1.579795
H	2.436889	2.402541	-0.598398
C	2.672602	1.205947	1.646574
H	2.564116	0.556256	2.525278
H	3.729271	1.497229	1.557305
H	2.046049	2.097756	1.780877

˙OMe

Gsol = -115.096086 Hartree

O	0.788950	0.000030	-0.008049
C	-0.566531	-0.000038	-0.015590
H	-1.020435	-0.916218	-0.450902
H	-0.870969	0.001288	1.061881
H	-1.021010	0.914915	-0.453041

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pro

Gsol = -3221.978999 Hartree

C	-1.440523	-1.005542	0.639762
C	-0.062029	-1.183102	0.502696
C	0.650030	-0.298940	-0.338187
C	-1.217550	0.872840	-0.907440
C	-2.001136	0.051668	-0.090423
H	-2.053598	-1.644739	1.276171
H	-1.668763	1.694322	-1.469592
N	0.108122	0.683050	-1.026328
N	0.785724	-2.126777	1.032992
H	0.537848	-2.605711	1.891057
Br	-3.874279	0.382401	0.035844
C	3.033960	0.481910	-0.200473

O	3.885067	0.827963	-0.982448
O	2.771293	1.132472	0.943392
C	3.531277	2.316537	1.193142
H	3.174778	2.711858	2.151528
H	4.605356	2.085453	1.249687
H	3.370387	3.052688	0.392079
C	2.115125	-0.723620	-0.380507
C	2.178733	-1.702511	0.836206
H	2.564028	-1.182672	1.729216
H	2.829865	-2.562956	0.623170
C	2.420892	-1.427579	-1.707956
H	2.227370	-0.745574	-2.547161
H	3.474231	-1.740707	-1.749921
H	1.777786	-2.313363	-1.815886

MeOH

Gsol = -115.75522 Hartree

O	-0.746336	0.122752	0.000017
C	0.655727	-0.019296	0.000007
H	1.039046	-0.551744	-0.893392
H	1.093703	0.990903	-0.004275
H	1.039772	-0.544505	0.897413
H	-1.136196	-0.760897	0.000075

16'-TS

Gsol = -3338.193442 Hartree

C	1.533376	1.177293	-0.325186
C	0.382341	1.341616	-1.049456
C	-0.387202	0.202133	-1.536820
C	1.367475	-1.244379	-0.617769
C	2.021426	-0.162695	-0.113652
H	2.087325	2.018765	0.084397
H	-0.831450	0.352070	-2.534731
H	1.682897	-2.276919	-0.476846
N	0.234920	-1.077903	-1.380155
N	-0.614217	-2.185907	-1.482432
H	-1.041842	-2.166047	-2.409193
Br	3.638707	-0.403264	0.855724
O	-0.206214	2.516329	-1.342318
C	0.380179	3.709212	-0.852974
H	1.401390	3.843871	-1.248553
H	-0.255397	4.534179	-1.197687
H	0.418026	3.710666	0.249572
C	-2.645314	-0.382779	1.028429
O	-1.924464	-0.636481	1.980999
O	-3.659648	0.518633	1.121542
C	-3.814754	1.153833	2.384308
H	-4.662860	1.842757	2.281409
H	-4.020253	0.417706	3.176832
H	-2.906415	1.710812	2.662843
C	-2.492810	-0.924400	-0.323800
C	-1.656129	-2.184835	-0.419777
H	-2.285742	-3.066541	-0.634399
H	-1.145697	-2.356916	0.537592
C	-3.619369	-0.777893	-1.320116

H -4.443661 -1.485732 -1.114196
H -4.040668 0.236237 -1.309356
H -3.264036 -0.986351 -2.343944
H -1.483989 0.001864 -0.836854

16'-1
Gsol = -3338.202338 Hartree
C 1.385723 1.109980 -0.353931
C 0.193224 1.154016 -0.994110
C -0.442671 -0.078467 -1.578558
C 1.344575 -1.330082 -0.404824
C 2.011276 -0.178316 -0.139004
H 1.860663 2.003061 0.047552
H -0.325191 -0.091306 -2.685639
H 1.728164 -2.326344 -0.185694
N 0.092309 -1.294012 -0.974167
N -0.707462 -2.407799 -0.806496
H -1.235275 -2.587751 -1.660488
Br 3.787493 -0.233947 0.547876
O -0.569356 2.247536 -1.210641
C -0.107752 3.485430 -0.702372
H 0.860133 3.764390 -1.153493
H -0.862415 4.237048 -0.966198
H 0.005862 3.442396 0.394204
C -2.496733 -0.095243 0.898066
O -1.463435 0.242935 1.463499
O -3.538703 0.760678 0.730317
C -3.330231 2.092683 1.184021
H -4.282278 2.619485 1.042670
H -3.037713 2.111623 2.244486
H -2.538860 2.577522 0.592637
C -2.722635 -1.403438 0.318347
C -1.604753 -2.387907 0.391184
H -2.000034 -3.413054 0.474629
H -0.960222 -2.186523 1.256644
C -3.973151 -1.765346 -0.412125
H -4.516513 -2.573991 0.113062
H -4.649215 -0.909628 -0.522342
H -3.744817 -2.161293 -1.419805
H -1.527761 -0.033866 -1.388806

21
Gsol = -2992.368497 Hartree
C 0.210831 -1.031014 -0.033110
C 1.594047 -0.682316 -0.009455
C 1.995110 0.635729 -0.039497
C -0.322869 1.351401 -0.109942
C -0.710486 0.035191 -0.079476
H -0.092856 -2.074974 -0.025014
H 3.022859 0.983677 -0.020591
H -1.013340 2.192374 -0.131150
N 1.037469 1.658770 -0.069547
N 1.489757 2.936262 -0.411784
H 1.094001 3.617416 0.238052
Br -2.579067 -0.355668 -0.086816

O	2.455539	-1.726561	0.047548
C	3.841245	-1.458965	0.065952
H	4.126831	-0.861422	0.950042
H	4.350052	-2.430557	0.107958
H	4.161839	-0.920695	-0.843849
H	1.165253	3.181076	-1.353207