Electronic Supplementary Information

Aryne [3+2] Cycloaddition with *N*-Sulfonylpyridinium Imides and *in situ* Generated *N*-Sulfonylisoquinolinium Imides: A Potential Route to Pyrido[1,2-*b*]indazoles and Indazolo[3,2-*a*]isoquinolines

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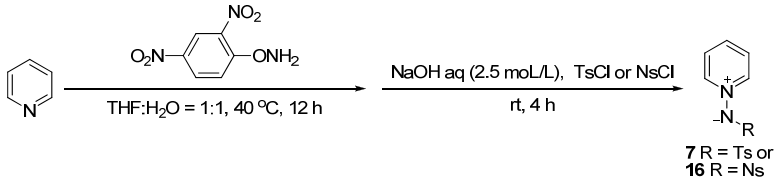
General Information:

All reagents purchased from commercial sources were used as received.[1] The solvents THF and MeCN were distilled from Na/benzophenone and CaH_2, respectively. The silica gel for column chromatography was supplied as 300-400 mesh from Haiyang Chemicals (Qingdao, China).[2] Powered CsF was used as received and stored in a desiccator.

All melting points were measured on an X-6 microscopic melting point apparatus and are uncorrected. The ^1H and ^{13}C NMR spectra were recorded on a Bruker AVANCE spectrometer and are referenced to the residual solvent signals (7.26 ppm for ^1H and 77.0 ppm for ^{13}C in $CDCl_3$, 25.3 ppm for ^{13}C in THF-d_8). The HRMS spectra were recorded on a Bruker APEX IV spectrometer.

All aryne cycloaddition reactions were carried out in oven-dried glassware and were magnetically stirred. Microwave reactions were carried out on a CEM Discovery microwave reactor.

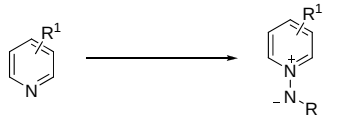
Preparation of the *N*-Sulfonylpyridinium Imides:[3]



To a mixture of H_2O and THF (0.5 mL each) was added pyridine (0.100 mL, 1.24 mmol), followed by *O*-(2,4-Dinitrophenyl)hydroxylamine (272 mg, 1.36 mmol). The reaction flask was sealed, and the resultant suspension was stirred at 40 °C for 12 h, during which time the reaction mixture turned dark-red. Upon completion, the reaction mixture was cooled to room temperature and was sequentially treated with an NaOH solution (2.5 *N*, 6 mL), followed by a *p*-toluenesulfonyl chloride solution (355 mg, 1.86 mmol, in 2 mL of THF) dropwise. After another 4 h, the reaction was diluted with H_2O and extracted three times with CH_2Cl_2. The combined organic phases were washed once with 2.5 *N* NaOH, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2/MeOH 9:1) to afford **7a** as a yellow solid (281 mg, 91%), mp 213 °C (lit[4] 215 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (d, J = 1.4 Hz, 1 H), 8.44 (d, J = 1.2 Hz, 1 H), 7.99 (t, J = 7.8 Hz, 1 H), 7.64-7.57 (m, 4 H), 7.16 (d, J = 8.0 Hz, 2 H), 2.35 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 145.2, 141.6, 138.6, 138.5, 129.2, 127.0, 126.7, 21.4.

Following the above procedure, all *N*-sulfonylpyridinium imides were prepared. Compounds **7a**-**7g**, **7k**-**7n**, **11a** and **13a** have been reported before in our earlier communication.[5] Other compounds are listed in Table ESI1:

Table ESI1. Preparation and characterization of *N*-sulfonylpyridinium imides

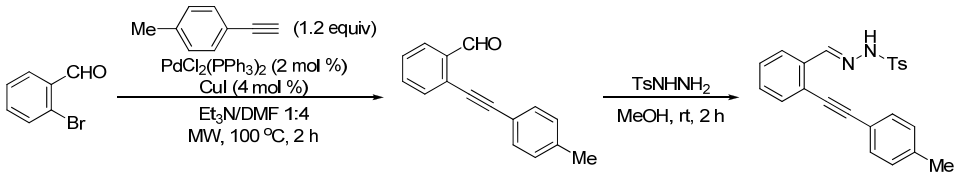


7 R = Ts or
16 R = Ns

entry	compound **7**/**16**	yield (%)	mp (ºC)	characterization
1	**7h** R^1 = 2,6-Me_2 R = Ts	85	167-168	^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 7.8 Hz, 1 H), 7.66 (d, *J* = 8.2 Hz, 2 H), 7.37 (d, *J* = 7.8 Hz, 2 H), 7.19 (d, *J* = 7.9 Hz, 2 H), 2.58 (s, 6 H), 2.38 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2, 142.9, 140.9, 137.7, 129.2, 126.0, 125.7, 21.34, 21.26; HRMS (ESI) calcd for $C_{14}H_{17}N_2O_2S$ (M+H) 277.1005, found 277.1000.
2	**7i** R^1 = 2,4-Me_2 R = Ts	33	238-239	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, *J* = 6.6 Hz, 1 H), 7.60-7.55 (m, 2 H), 7.25 (s, 1 H), 7.22-7.18 (m, 1 H), 7.16 (d, *J* = 8.0 Hz, 2 H), 2.47 (s, 3 H), 2.39 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.3, 152.1, 145.6, 141.3, 140.6, 129.3, 128.6, 126.0, 125.4, 20.9, 20.6, 18.8； HRMS (ESI) calcd for $C_{14}H_{17}N_2O_2S$ (M+H) 277.1005, found 277.1005.
3	**7j** R^1 = 2,3,5-Me_3 R = Ts	26	150	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (s, 1 H), 7.61-7.53 (m, 2 H), 7.50 (s, 1 H), 7.16 (d, *J* = 7.9 Hz, 2 H), 2.37 (s, 6 H), 2.32 (s, 3 H), 2.28 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.9, 143.6, 141.1, 141.0, 140.6, 136.2, 133.3, 129.2, 126.0, 20.9, 19.1, 17.1, 15.2; HRMS (ESI) calcd for $C_{15}H_{19}N_2O_2S$ (M+H) 291.1162, found 291.1162.
4	**7o** R^1 = 3-morpholino R = Ts	60	193-194	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (s, 1 H), 7.76-7.72 (m, 1 H), 7.63 (d, *J* = 8.2 Hz, 2 H), 7.34-7.30 (m, 2 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 3.84 (t, *J* = 4.9 Hz, 4 H), 3.17 (t, *J* = 5.0 Hz, 4 H), 2.36 (s, 3 H); HRMS (ESI) calcd for $C_{16}H_{20}N_3O_3S$ (M+H) 334.1220, found 334.1221.
5	**7p** R^1 = 3-Br-5-OMe R = Ts	74	199-200	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (t, *J* = 1.4 Hz, 1 H), 8.17 (dd, *J* = 2.2, 1.4 Hz, 1 H), 7.68 (d, *J* = 8.2 Hz, 2 H), 7.53 (dd, *J* = 2.2, 1.6 Hz, 1 H), 7.21 (d, *J* = 8.0 Hz, 2 H), 3.86 (s, 3 H), 2.38 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.5, 141.3, 138.7, 137.5, 132.4, 129.3, 127.4, 126.8, 120.7, 57.5, 20.9; HRMS (ESI) calcd for $C_{13}H_{14}BrN_2O_3S$ (M+H) 356.9903, found 356.9906.
6	**16a** R^1 = 2,6-Me_2 R = Ns	48	191-192	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1 H), 7.79 (t, *J* = 7.8 Hz, 1 H), 7.62 (t, *J* = 7.6 Hz, 1 H), 7.54 (t, *J* = 7.6 Hz, 1 H), 7.47 (d, *J* = 7.8 Hz, 1 H), 7.43 (d, *J* = 7.8 Hz, 2 H), 2.65 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.6, 147.2, 139.5, 138.2, 132.3, 132.1, 129.0, 126.4, 123.4, 20.4; HRMS (ESI) calcd for $C_{13}H_{14}N_3O_4S$ (M+H) 308.0700, found 308.0696.

7	**16b** R^1 = 3-Br-5-OMe R = Ns	46	154-155	^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1 H), 8.20-8.17 (m, 2 H), 7.70 (m, 1 H), 7.65 (t, *J* = 7.6 Hz, 1 H), 7.57 (t, *J* = 7.6 Hz, 1 H), 7.45 (d, *J* = 7.8 Hz, 1 H), 3.94 (s, 3 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 157.8, 148.0, 138.5, 133.9, 133.4, 132.8, 132.0, 130.2, 128.6, 123.2, 121.0, 57.7; HRMS (ESI) calcd for $C_{12}H_{11}BrN_3O_5S$ (M+H) 387.9597, found 387.9597.
8	**16c** R^1 = 3-Br R = Ns	42	189-190	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (s, 1 H), 8.53 (d, *J* = 6.3 Hz, 1 H), 8.22-8.18 (m, 2 H), 7.65 (dt, *J* = 1.0, 8.9 Hz, 1 H), 7.60-7.54 (m, 2 H), 7.44 (d, *J* = 7.8 Hz, 1 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.9, 146.4, 144.7, 143.7, 134.1, 132.8, 132.0, 130.1, 128.4, 123.2, 121.0; HRMS (ESI) calcd for $C_{11}H_9N_3O_4S$ (M+H) 357.9492, found 357.9494.
9	**16d** R^1 = 3-CO_2Me R = Ns	35	137-138	^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (dd, *J* = 1.5, 1.1 Hz, 1 H), 8.70 (dt, *J* = 6.3, 1.4 Hz, 1 H), 8.65 (dt, *J* = 8.1, 1.4 Hz, 1 H), 8.20 (dd, *J* = 7.9, 1.4 Hz, 1 H), 7.80 (ddd, *J* = 8.0，6.3，0.4 Hz, 1 H), 7.65 (td, *J* = 7.7, 1.3 Hz, 1 H), 7.55 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.41 (dd, *J* = 7.9, 1.2 Hz, 1 H), 3.99 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.8, 148.5, 147.9, 146.1, 140.0, 135.5, 132.1, 131.8, 130.6, 130.0, 127.1, 123.0, 53.5; HRMS (ESI) calcd for $C_{13}H_{12}N_3O_6S$ (M+H) 338.0441, found 338.0440.
10	**16e** R^1 = 3,5-Me_2 R = Ns	54	205-206	^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (dd, *J* = 7.9, 1.4 Hz, 1 H), 8.11 (s, 2 H), 7.67 (s, 1 H), 7.61 (td, *J* = 7.7, 1.4 Hz, 1 H), 7.53 (td, *J* = 7.6, 1.5 Hz, 1 H), 7.41 (dd, *J* = 7.8, 1.3 Hz, 1 H), 2.40 (s, 6 H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 147.9, 142.3 (two carbons), 137.4, 134.5, 132.5, 131.6, 130.0, 123.2, 17.5; HRMS (ESI) calcd for $C_{13}H_{14}N_3O_4S$ (M+H) 308.0700, found 308.0697.

Preparation of the *N'*-(2-Alkynylbenzylidene)tosylhydrazides:

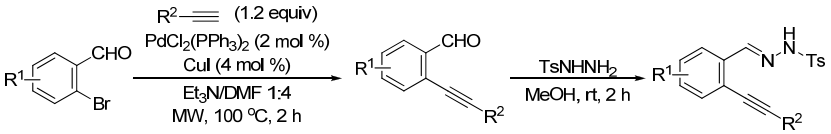


To an oven-dried 10 mL microwave-adaptive vial equipped with a stir bar was charged with 925 mg of 2-bromobenzaldehyde (5 mmol), followed by 696 mg of 4-ethynyltoluene (6 mmol, 1.2 equiv). Et_3N (1 mL) and DMF (4 mL) were added, followed by $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol, 2 mol %) and CuI (38 mg, 0.2 mmol, 4 mol %). The vial was sealed and irradiated with microwave at 100 ºC for 2 h. The mixture was cooled to room temperature, poured into 50 mL of EtOAc, and washed three times with brine. The organic layer was dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (15:1 petroleum ether/EtOAc) to afford 850 mg of 2-(*p*-tolylethynyl)benzaldehyde (77% yield) as a brown solid.[6]

To an oven-dried 25 mL round-bottom flask containing 409 mg of *p*-toluenesulfonyl hydrazide (2.2 mmol, 1.1 equiv) and 5 mL of absolute MeOH was added 2-(*p*-tolylethynyl)benzaldehyde (2 mmol) obtained from the above step. The mixture was stirred at room temperature for 2 h and the volatiles were evaporated *in vacuo*. The residue was recrystallized from minimum amount of MeOH to afford 640 mg of *N'*-(2-alkynylbenzylidene)tosylhydrazides (82% yield) as white crystals.[7]

Following the above procedure, the following *N'*-(2-alkynylbenzylidene)tosylhydrazides were prepared (Table ESI2):

Table ESI2. Preparation and characterization of *N'*-(2-alkynylbenzylidene)tosylhydrazides



entry	compound **3** (R^1, R^2)	yield (%) (step 1)	yield (%) (step 2)	mp (ºC)	^{1}H NMR (300 MHz, $CDCl_3$)
1	**3a** R^1 = H R^2 = 4-MeC_6H_4	77	82	159-161	8.35 (s, 1 H), 7.97 (s, 1 H), 7.95-7.93 (m, 1 H), 7.89 (d, *J* = 8.3 Hz, 2 H), 7.52-7.46 (m, 1 H), 7.41 (d, *J* = 8.1 Hz, 2 H), 7.35-7.30 (m, 4 H), 7.17 (d, *J* = 7.9 Hz, 2 H), 2.40 (s, 3 H), 2.38 (s, 3 H)[a]
2	**3b** R^1 = 4-F R^2 = Ph	80	67	155-156	8.31 (s, 1 H), 8.15 (s, 1 H), 7.95-7.90 (m, 1 H), 7.89-7.87 (m, 2 H), 7.53-7.50 (m, 2 H), 7.39-7.34 (m, 3 H), 7.31 (d, *J* = 8.1 Hz, 2 H), 7.18 (dd, *J* = 9.0, 2.6 Hz, 1 H), 7.03 (td, *J* = 8.4, 2.6 Hz, 1 H), 2.41 (s, 3 H)
3	**3c** R^1 = 4-Me R^2 = Ph	70	72	161-162	8.32 (s, 1 H), 7.89-7.87 (m, 2 H), 7.86-7.81 (m, 2 H), 7.53-7.50 (m, 2 H), 7.39-7.34 (m, 3 H), 7.32 (s, 1 H), 7.30 (d, *J* = 8.0 Hz, 2 H), 7.14 (d, *J* = 8.1 Hz, 1 H), 2.40 (s, 3 H), 2.35 (s, 3 H)

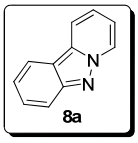
4	**3d** R^1 = 5-Cl R^2 = Ph	78	63	163-165	8.28 (s, 1 H), 8.05 (s, 1 H), 7.91-7.87 (m, 3 H), 7.54-7.48 (m, 2 H), 7.43 (d, *J* = 8.3 Hz, 1 H), 7.38-7.36 (m, 2 H), 7.34-7.31 (m, 3 H), 7.28 (dd, *J* = 9.2, 2.2 Hz, 1 H), 2.42 (s, 3 H)
5	**3e** R^1 = 5-OMe R^2 = Ph	62	86	148-149	8.32 (s, 1 H), 7.93 (s, 1 H), 7.88 (d, *J* = 8.3 Hz, 2 H), 7.53-7.47 (m, 2 H), 7.44 (s, 1 H), 7.42 (d, *J* = 5.6 Hz, 1 H), 7.37-7.29 (m, 5 H), 6.91 (dd, *J* = 8.6 Hz, 1 H), 3.86 (s, 3 H), 2.40 (s, 3 H)
6	**3f** R^1 = H R^2 = Ph	72	62	152-153 (lit[8] 158-161)	8.36 (s, 1 H), 8.07 (s, 1 H), 7.97-7.92 (m, 1 H), 7.92-7.85 (m, 2 H), 7.56-7.47 (m, 3 H), 7.39-7.27 (m, 7 H), 2.40 (s, 3 H)
7	**3g** R^1 = H R^2 = 3-ClC_6H_4	74	70	152-153	8.30 (s, 1 H), 7.96-7.93 (m, 1 H), 7.89-7.86 (m, 2 H), 7.51-7.48 (m, 2 H), 7.40-7.37 (m, 1 H), 7.36-7.27 (m, 7 H), 2.40 (s, 3 H)
8	**3h** R^1 = H R^2 = 3-$(MeO)C_6H_4$	68	74	147-148	8.35 (s, 1 H), 8.03 (s, 1 H), 7.98-7.92 (m, 1 H), 7.89-7.87 (m, 2 H), 7.54-7.47 (m, 1 H), 7.38-7.22 (m, 5 H), 7.11 (dt, *J* = 7.6, 1.2 Hz, 1 H), 7.04 (dd, *J* = 2.5, 1.4 Hz, 1 H), 6.92 (ddd, *J* = 8.3, 2.6, 0.9 Hz, 1 H), 3.83 (s, 3 H), 2.40 (s, 3 H)
9	**3i** R^1 = H R^2 = 3-thiophenyl	54	54	139-140	8.33 (s, 1 H), 7.96–7.91 (m, 2 H), 7.88 (d, *J* = 8.3 Hz, 2 H), 7.55 (dd, *J* = 2.9, 1.0 Hz, 1 H), 7.51–7.45 (m, 1 H), 7.35–7.28 (m, 5 H), 7.19 (dd, *J* = 5.0, 0.9 Hz, 1 H), 2.41 (s, 3 H)
10	**3j** R^1 = H R^2 = 2-pyridyl	58	78	128-130	10.49 (s, 1 H), 8.66 (ddd, *J* = 4.9, 1.7, 0.9 Hz, 1 H), 8.42 (s, 1 H), 7.89 (d, *J* = 8.3 Hz, 2 H), 7.77 (d, *J* = 7.2 Hz, 1 H), 7.58 (dt, *J* = 7.7, 1.8 Hz, 1 H), 7.33-7.27 (m, 3 H), 7.21 (d, *J* = 7.8 Hz, 1 H), 7.14 (t, *J* = 7.3 Hz, 1 H), 7.03 (td, *J* = 7.6, 1.3 Hz, 1 H), 6.77 (d, *J* = 7.6 Hz, 1 H), 2.38 (s, 3 H)
11	**3k** R^1 = H R^2 = pentyl	55	36	117-118	8.24 (s, 1 H), 7.89-7.87 (m, 3 H), 7.81 (s, 1 H), 7.38-7.26 (m, 5 H), 2.44-2.39 (m, 2 H), 2.41 (s, 3 H), 1.68-1.53 (m, 2 H), 1.46-1.30 (m, 4 H), 0.92 (t, *J* = 6.9 Hz, 3 H)
12	**3l** R^1 = H R^2 = $(CH_2)_2OTHP$	26	72	116-117	8.60 (s, 1 H), 8.37 (s, 1 H), 7.95-7.81 (m, 3 H), 7.35-7.23 (m, 5 H), 4.70 (dd, *J* = 4.9, 2.7 Hz, 1 H), 4.09-3.99 (m, 1 H), 3.93 (ddd, *J* = 9.5, 7.8, 5.6 Hz, 1 H), 3.70 (dt, *J* = 9.6, 5.7 Hz, 1 H), 3.61-3.49 (m, 1 H), 2.86-2.60 (m, 2 H), 2.40 (s, 3 H), 1.90-1.49 (m, 6 H)
13	**3m** R^1 = H R^2 = TMS	84	87	149-150	8.24 (s, 1 H), 7.97 (s, 1 H), 7.93-7.85 (m, 3 H), 7.46-7.40 (m, 1 H), 7.36-7.27 (m, 4 H), 2.41 (s, 3 H), 0.25 (s, 9 H)

[a] 400 MHz spectrum.

Reaction Procedures and Characterization of the Products:

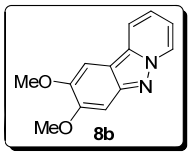
Pyrido[1,2-*b*]indazoles and Analogues:[5]

General procedure: To a 10 mL round-bottom flask equipped with a stirr bar was added *N*-sulfonylpyridinium imide **7** (0.3 mmol), followed by aryne precursor **10** (0.36 mmol). THF (4 mL) was added and the mixture was briefly stirred before addition of CsF (ca. 0.9 mmol). The flask was fitted with a refluxing condenser and sealed with a septum. A balloon was added on top, and the mixture was stirred in a 70 ºC oil bath for 24 h. Upon judged completion by TLC, the mixture was diluted with EtOAc and water. Layers were separated and the aqueous layer was extracted with EtOAc twice. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the desired product.



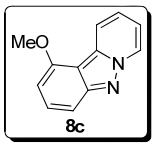
8a

Pyrido[1,2-*b*]indazole (**8a**): yield 43 mg (85%); light yellow solid; mp 85 ºC (lit[9] 83-84 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.80 (dt, *J* = 6.9, 1.0 Hz, 1 H), 8.17-8.06 (m, 2 H), 7.85 (dt, *J* = 8.7, 0.8 Hz, 1 H), 7.62-7.53 (m, 1 H), 7.41-7.32 (m, 1 H), 7.25-7.15 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.6, 135.4, 128.4, 127.9, 121.9, 119.8, 119.7, 117.9, 116.2, 115.5, 115.2; IR (KBr) 1644, 1604, 1510, 1430, 1360, 1213, 1141, 741, 718 cm^{-1}; HRMS (ESI) calcd for $C_{11}H_9N_2$ (M+H) 169.0760, found 169.0760.



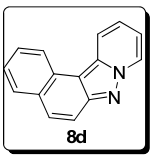
8b

2,3-Dimethoxypyrido[1,2-*b*]indazole (**8b**): yield 60 mg (88%); white solid; mp 132 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, *J* = 7.0 Hz, 1 H), 7.94 (d, *J* = 8.7 Hz, 1 H), 7.31 (s, 1 H), 7.27-7.22 (m, 1 H), 7.16 (s, 1 H), 7.02 (td, *J* = 6.9, 1.2 Hz, 1 H), 4.02 (s, 3 H), 4.01 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.4, 146.0, 134.7, 127.70, 127.67, 121.1, 116.9, 114.0, 108.0, 98.0, 94.8, 56.0, 55.8; HRMS (ESI) calcd for $C_{13}H_{13}N_2O_2$ (M+H) 229.0972, found 229.0968.



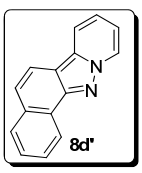
8c

1-Methoxypyrido[1,2-*b*]indazole (**8c**): yield 46 mg (77%); off-white solid; mp 100 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (dt, *J* = 6.9, 0.9 Hz, 1 H), 8.34 (dt, *J* = 8.4, 1.3 Hz, 1 H), 7.48 (dd, *J* = 8.6, 7.3 Hz, 1 H), 7.43-7.33 (m, 2 H), 7.16 (td, *J* = 6.9, 1.5 Hz, 1 H), 6.53 (d, *J* = 7.3 Hz, 1 H), 4.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 151.2, 135.1, 129.2, 127.5, 122.3, 120.1, 115.6, 107.8, 107.0, 97.8, 55.4; HRMS (ESI) calcd for $C_{12}H_{11}N_2O$ (M+H) 199.0866, found 199.0861.



8d

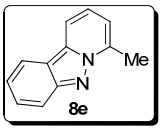
and



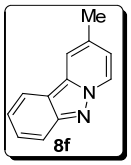
8d'

Benzo[*e*]pyrido[1,2-*b*]indazole (**8d**) and **Benzo[*g*]pyrido[1,2-*b*]indazole** (**8d'**): due to the limited

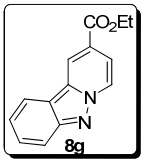
quantity of the two regioisomers separated and poor regioselectivity, we did not attempt to assign the regioisomers. Isomer A: beige solid; mp 140-141 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (d, *J* = 7.0 Hz, 1 H), 8.81-8.72 (m, 1 H), 8.08 (d, *J* = 8.7 Hz, 1 H), 8.01-7.90 (m, 2 H), 7.70-7.60 (m, 2 H), 7.53 (d, *J* = 8.8 Hz, 1 H), 7.43-7.32 (m, 1 H), 7.12 (td, *J* = 6.9, 1.3 Hz, 1 H); HRMS (ESI) calcd for $C_{15}H_{11}N_2$ (M+H) 219.0917, found 219.0916. Isomer B: beige solid; mp 145 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.85 (d, *J* = 7.0 Hz, 1 H), 8.47 (t, *J* = 8.1 Hz, 2 H), 7.97 (d, *J* = 8.0 Hz, 1 H), 7.90-7.82 (m, 2 H), 7.74-7.66 (m, 1 H), 7.54-7.44 (m, 2 H), 7.15 (td, *J* = 6.9, 1.2 Hz, 1 H); HRMS (ESI) calcd for $C_{15}H_{11}N_2$ (M+H) 219.0917, found 219.0916.



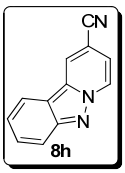
7-Methylpyrido[1,2-*b*]indazole (**8e**): yield 51 mg (93%); beige solid; mp 70 ºC (lit[10] 63-64 ºC); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.2 Hz, 1 H), 8.07 (d, *J* = 8.6 Hz, 1 H), 7.93 (d, *J* = 8.4 Hz, 1 H), 7.58 (t, *J* = 7.6 Hz, 1 H), 7.35 (t, *J* = 7.6 Hz, 1 H), 7.23 (t, *J* = 7.5 Hz, 1 H), 7.10 (d, *J* = 7.0 Hz, 1 H), 2.96 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.4, 137.6, 135.7, 128.3, 121.9, 119.9, 119.5, 115.73, 115.67, 115.6, 115.4, 18.6; HRMS (ESI) calcd for $C_{12}H_{11}N_2$ (M+H) 183.0917, found 183.0912.



9-Methylpyrido[1,2-*b*]indazole (**8f**): yield 49 mg (90%); beige solid; mp 133 ºC (lit[10] 116-121 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (d, *J* = 7.1 Hz, 1 H), 8.04 (dt, *J* = 8.2, 1.0 Hz, 1 H), 7.90 (dt, *J* = 1.8, 0.9 Hz, 1 H), 7.79 (d, *J* = 8.7 Hz, 1 H), 7.54 (ddd, *J* = 8.6, 6.7, 1.1 Hz, 1 H), 7.18 (ddd, *J* = 8.1, 6.8, 0.8 Hz, 1 H), 7.02 (dd, *J* = 7.1, 1.9 Hz, 1 H), 2.55 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 150.0, 135.4, 133.0, 128.3, 127.2, 119.8, 119.1, 118.5, 116.8, 115.3, 114.5, 21.2; IR (KBr) 1648, 1608, 1356, 804, 747 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_{11}N_2$ (M+H) 183.0917, found 183.0912.

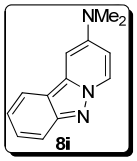


Ethyl pyrido[1,2-*b*]indazole-9-carboxylate (**8g**): yield 65 mg (90%); slightly yellow solid; mp 98 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 – 8.82 (m, 1 H), 8.76 (d, *J* = 7.2 Hz, 1 H), 8.16 (dd, *J* = 8.3, 0.9 Hz, 1 H), 7.91 (dd, *J* = 8.7, 0.7 Hz, 1 H), 7.77 (dd, *J* = 7.2, 1.9 Hz, 1 H), 7.66-7.58 (m, 1 H), 7.38-7.30 (m, 1 H), 4.46 (q, *J* = 7.1 Hz, 2 H), 1.46 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (75 MHz, CDCl3) δ 164.9, 150.1, 134.3, 128.8, 127.3, 123.3, 121.4, 120.1, 119.7, 116.9, 116.4, 115.5, 61.6, 14.3; IR (KBr) 1605, 1278, 759, 714 cm^{-1}; HRMS (ESI) calcd for $C_{14}H_{13}N_2O_2$ (M+H) 241.0972, found 241.0968.



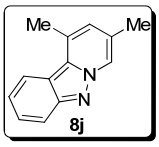
Pyrido[1,2-*b*]indazole-9-carbonitrile (**8h**): yield 38 mg (66%); yellowish green solid; mp 65 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 7.2, 0.9 Hz, 1 H), 8.51 (dd, *J* = 1.9, 0.9 Hz, 1 H), 8.14 (dt, *J* =

8.3, 1.0 Hz, 1 H), 7.95 (d, *J* = 8.7 Hz, 1 H), 7.68 (ddd, *J* = 8.6, 6.8, 1.1 Hz, 1 H), 7.41 (ddd, *J* = 8.2, 6.8, 0.8 Hz, 1 H), 7.33 (dd, *J* = 7.2, 1.9 Hz, 1 H); ^{13}C NMR(100MHz, $CDCl_3$) δ 150.2, 133.9, 129.5, 128.3, 123.4, 122.5, 119.5, 117.6, 116.7, 116.4, 116.3, 103.9; IR (KBr) 2225, 1523, 1451, 1361, 1284, 803, 753, 728, 718 cm^{-1}; HRMS (ESI) calcd for $C_{12}H_8N_3$ (M+H) 194.0713, found 194.0709.



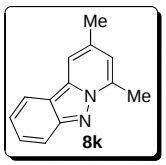
8i

***N*,*N*-Dimethylpyrido[1,2-*b*]indazol-9-amine** (**8i**): yield 25 mg (40%); yellowish green solid; mp 170-171 ºC ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.7 Hz, 1 H), 7.94 (d, *J* = 8.2 Hz, 1 H), 7.65 (d, *J* = 8.6 Hz, 1 H), 7.54-7.42 (m, 1 H), 7.03 (t, *J* = 7.4 Hz, 1 H), 6.98 (d, *J* = 2.5 Hz, 1 H), 6.73 (dd, *J* = 7.7, 2.8 Hz, 1 H), 3.09 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 146.5, 137.3, 128.7, 128.2, 120.3, 117.5, 114.3, 114.0, 105.9, 95.0, 40.3; HRMS (ESI) calcd for $C_{13}H_{14}N_3$ (M+H) 212.1182, found 212.1176.



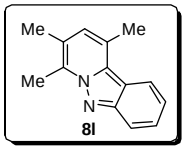
8j

8,10-Dimethylpyrido[1,2-*b*]indazole (**8j**): yield 43 mg (73%); slightly yellow solid; mp 116 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.47 (s, 1 H), 8.12 (d, *J* = 8.3 Hz, 1 H), 7.83 (d, *J* = 8.6 Hz, 1 H), 7.59-7.49 (m, 1 H), 7.25-7.17 (m, 1 H), 6.97 (s, 1 H), 2.82 (s, 3 H), 2.43 (s, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.4, 133.1, 129.7, 127.4, 126.1, 125.4, 125.3, 124.0, 121.30, 119.4, 115.3, 19.1, 18.4; HRMS (ESI) calcd for $C_{13}H_{13}N_2$ (M+H) 197.1073, found 197.1069.



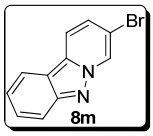
8k

7,9-Dimethylpyrido[1,2-*b*]indazole (**8k**): yield 32 mg (54%); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1 H), 7.86 (d, *J* = 8.7 Hz, 1 H), 7.79 (s, 1 H), 7.57-7.50 (m, 1 H), 7.20-7.14 (m, 1 H), 6.89 (s, 1 H), 2.89 (s, 3 H), 2.50 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.7, 136.8, 135.8, 133.0, 128.2, 120.0, 118.9, 118.1, 115.4, 115.0, 114.5, 21.1, 18.4; HRMS (ESI) calcd for $C_{13}H_{13}N_2$ (M+H) 197.1073, found 197.1073.

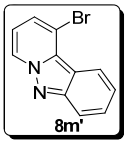


8l

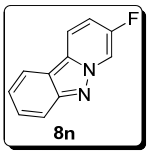
7,8,10-Trimethylpyrido[1,2-*b*]indazole (**8l**): yield 47 mg (75%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dt, *J* = 8.3, 1.0 Hz, 1 H), 7.91 (dt, *J* = 8.7, 0.9 Hz, 1 H), 7.54 (ddd, *J* = 8.6, 5.6, 1.1 Hz, 1 H), 7.20 (ddd, *J* = 8.2, 6.8, 0.9 Hz, 1 H), 7.02 (s, 1 H), 2.89 (s, 3 H), 2.85 (s, 3 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 133.6, 132.5, 127.3, 126.6, 126.0, 123.0, 121.4, 119.1, 116.4, 115.4, 18.9, 18.4, 14.5; HRMS (ESI) calcd for $C_{14}H_{15}N_2$ (M+H) 211.1230, found 211.1230.



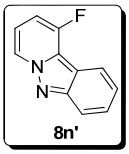
8-Bromopyrido[1,2-*b*]indazole (**8m**): yield 31 mg (29%); off-white solid; mp 103 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (s, 1 H), 8.05 (d, *J* = 8.3 Hz, 1 H), 8.00 (d, *J* = 9.1 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.63-7.56 (m, 1 H), 7.44 (dd, *J* = 9.1, 1.6 Hz, 1 H), 7.30-7.25 (m, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.7, 133.9, 128.7, 128.2, 125.1, 120.6, 119.5, 118.1, 115.9, 115.2, 110.9; HRMS (ESI) calcd for $C_{11}H_8BrN_2$ (M+H) 246.9865, found 246.9861.



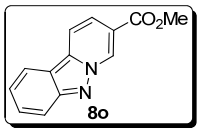
10-Bromopyrido[1,2-*b*]indazole (**8m'**): yield 49 mg (62%); off-white solid; mp 141 ºC; ^{1}H NMR (300 MHz, $CDCL_3$) δ 8.78 (dd, *J* = 6.9, 0.8 Hz, 1 H), 8.63 (dt, *J* = 8.5, 1.0 Hz, 1 H), 7.87 (d, *J* = 8.7 Hz, 1 H), 7.61 (ddd, *J* = 8.7, 6.8, 1.1 Hz, 1 H), 7.55 (dd, *J* = 7.5, 0.7 Hz, 1 H), 7.31 (ddd, *J* = 8.4, 6.8, 0.9 Hz, 1 H), 7.05 (t, *J* = 7.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.9, 133.2, 128.7, 126.9, 125.3, 122.1, 120.4, 116.0, 115.7, 113.8; HRMS (ESI) calcd for $C_{11}H_8BrN_2$ (M+H) 246.9865, found 246.9868.



8-Fluoropyrido[1,2-*b*]indazole (**8n**): yield 13 mg (24%); white solid; mp 91-92 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 (dd, *J* = 4.3, 2.0 Hz, 1 H), 8.14-8.04 (m, 2 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.61-7.54 (m, 1 H), 7.30-7.24 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5 ($^{1}J_{CF}$ = 241.3 Hz), 150.1 ($^{4}J_{CF}$ = 2.1 Hz), 132.9, 128.1, 120.5, 119.3, 117.9 ($^{3}J_{CF}$ = 9.4 Hz), 115.8, 115.6, 115.5 ($^{2}J_{CF}$ = 26.3 Hz), 113.1 ($^{2}J_{CF}$ = 24.3 Hz); HRMS (ESI) calcd for $C_{11}H_8FN_2$ (M+H) 187.0666, found 187.0664.

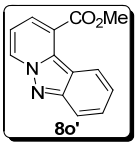


10-Fluoropyrido[1,2-*b*]indazole (**8n'**): yield 25 mg (45%); white solid; mp 95-96 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, *J* = 6.7 Hz, 1 H), 8.22 (d, *J* = 8.3 Hz, 1 H), 7.87 (d, *J* = 8.7 Hz, 1 H), 7.65-7.55 (m, 1 H), 7.33-7.28 (m, 1H), 7.18-7.01 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7 ($^{1}J_{CF}$ = 251.8 Hz), 149.3, 128.6, 127.2 ($^{2}J_{CF}$ = 34.0 Hz), 124.2 ($^{4}J_{CF}$ = 3.9 Hz), 121.3 ($^{4}J_{CF}$ = 3.4 Hz), 120.9, 115.6, 115.1 ($^{3}J_{CF}$ = 7.8 Hz), 113.8 ($^{3}J_{CF}$ = 4.5 Hz), 105.9 ($^{2}J_{CF}$ = 17.6 Hz); HRMS (ESI) calcd for $C_{11}H_8FN_2$ (M+H) 187.0660, found 187.0664.



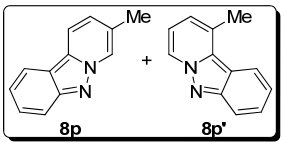
Methyl pyrido[1,2-*b*]indazole-8-carboxylate (**8o**): yield 36 mg (52%); yellow solid; mp 172 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.46 (s, 1 H), 8.12 (d, *J* = 9.0 Hz, 1 H), 8.07 (d, *J* = 8.3 Hz, 1 H), 7.89 (d, *J* =

10.3 Hz, 1 H), 7.86 (d, *J* = 8.9 Hz, 1 H), 7.60 (t, *J* = 7.4 Hz, 1 H), 7.28-7.24 (m, 1 H), 4.01 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 151.2, 136.5, 131.2, 129.4, 121.4, 120.8, 120.1, 119.7, 117.3, 116.0, 115.0, 52.7; HRMS (ESI) calcd for $C_{13}H_{11}N_2O_2$ (M+H) 227.0815, found 227.0813.



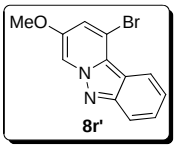
8o'

Methyl pyrido[1,2-*b*]indazole-10-carboxylate (**8o'**): yield 33 mg (47%); yellow solid; mp 128 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (d, *J* = 6.8 Hz, 1 H), 8.79 (d, *J* = 8.6 Hz, 1 H), 8.04 (d, *J* = 7.2 Hz, 1 H), 7.85 (d, *J* = 8.7 Hz, 1 H), 7.59 (t, *J* = 7.3 Hz, 1 H), 7.28-7.24 (m, 1 H), 7.20 (t, *J* = 7.1 Hz, 1 H), 4.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 150.7, 133.2, 131.7, 129.0, 126.4, 124.5, 123.6, 120.5, 115.6, 114.7, 114.5, 52.7; IR (KBr) 1720, 1647, 1302, 1089, 740 cm^{-1}; HRMS (ESI) calcd for $C_{13}H_{11}N_2O_2$ (M+H) 227.0815, found 227.0811



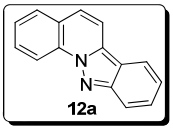
8p **8p'**

10-Methylpyrido[1,2-*b*]indazole (**8p**) and **8-methylpyrido[1,2-*b*]indazole** (**8p'**): yield 64 mg (88% combined); yellow solid; major isomer (**8p'**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 6.3 Hz, 1 H), 8.18 (d, *J* = 8.4 Hz, 1 H), 7.86 (d, *J* = 8.6 Hz, 1 H), 7.57 (t, *J* = 7.7 Hz, 1 H), 7.54 (t, *J* =7.7 Hz, 1 H), 7.17-7.07 (m, 2 H), 2.90 (s, 3 H); minor isomer (**8p**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 8.01 (d, *J* = 8.8 Hz, 1 H), 7.82 (d, *J* = 8.6 Hz, 1 H), 7.25-7.18 (m, 3 H), 2.49 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 130.7, 128.0, 127.8, 126.6, 126.2, 125.7, 124.9, 122.5, 121.6, 119.7, 119.5, 119.5, 117.1, 116, 115.8, 115.4, 115.3, 115.1, 19.3, 18.6; HRMS (ESI) calcd for $C_{12}H_{11}N_2$ (M+H) 183.0917, found 183.0915.



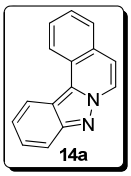
8r'

10-bromo-8-methoxypyrido[1,2-*b*]indazole (**8r'**): yield 34%, beige solid, mp 174-175 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.2 Hz, 1 H), 8.24 (d, *J* = 8.3 Hz, 1 H), 7.82 (d, *J* = 8.7 Hz, 1 H), 7.58-7.52 (m, 1 H), 7.28-7.24 (m, 1 H) 6.78 (d, *J* = 1.1 Hz, 1 H), 4.13 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 149.1, 128.1, 127.0, 121.7, 121.5, 120.8, 115.43, 115.35, 110.6, 104.4, 56.3; HRMS (ESI) calcd for $C_{12}H_{10}BrN_2O$ (M+H) 276.9971, found 276.9970.

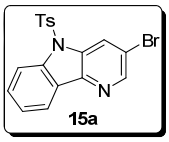


12a

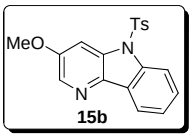
Indazolo[2,3-*a*]quinoline (**12a**): yield 60 mg (92%); beige solid; mp 98 ºC (lit[10] 107-109 ºC); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.95 (d, *J* = 8.5 Hz, 1 H), 8.09 (d, *J* = 8.3 Hz, 1 H), 7.99 (dd, *J* = 8.9, 4.8 Hz, 2 H), 7.92 (d, *J* = 8.0 Hz, 1 H), 7.84-7.76 (m, 1 H), 7.68-7.63 (m, 1 H), 7.64-7.53 (m, 2 H), 7.30-7.24 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.1, 134.0, 132.23, 129.3, 128.3, 127.9, 125.9, 125.1, 123.0, 120.6, 119.6, 117.0, 116.6, 116.5, 115.4; HRMS (ESI) calcd for $C_{15}H_{11}N_2$ (M+H) 219.0917, found 219.0913.



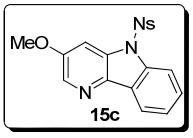
Indazolo[3,2-*a*]isoquinoline (**14a**): yield 57 mg (87%); light-brown solid; mp 90-92 ºC (lit[10] 90-91 ºC); ^{1}H NMR (300 MHz, $CDCL_3$) δ 8.67 (d, *J* = 8.2 Hz, 1 H), 8.59 (d, *J* = 7.4 Hz, 1 H), 8.45 (d, *J* = 8.5 Hz, 1 H), 7.95 (d, *J* = 8.7 Hz, 1 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.81-7.71 (m, 1 H), 7.66-7.59 (m, 1 H), 7.56 (dd, *J* = 4.9, 3.8 Hz, 1 H), 7.40 (d, *J* = 7.4 Hz, 1 H), 7.35 (ddd, *J* = 8.4, 6.7, 0.9 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.2, 130.5, 128.4, 128.2, 127.5, 127.4, 127.2, 126.4, 126.1, 122.9, 121.3, 121.1, 116.9, 116.4, 116.2; HRMS (ESI) calcd for $C_{15}H_{11}N_2$ (M+H) 219.0917, found 219.0912.



3-Bromo-5-tosyl-5*H*-pyrido[3,2-*b*]indole (**15a**): yield 63 mg (52%); light-brown solid; mp 231-232 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 2.0 Hz, 1 H), 8.67 (d, *J* = 2.0 Hz, 1 H), 8.30 (d, *J* = 8.5 Hz, 1 H), 8.18 (d, *J* = 7.2 Hz, 1 H), 7.71 (d, *J* = 8.4 Hz, 2 H), 7.63 (ddd, *J* = 8.5, 7.3, 1.3 Hz, 1 H), 7.45 (td, *J* = 7.5, 0.8 Hz, 1 H), 7.17 (d, *J* = 8.0 Hz, 2 H), 2.32 (d, *J* = 8.5 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 145.7, 143.2, 139.2, 134.3, 132.7, 130.0, 129.7, 126.54, 124.9, 124.74, 124.72, 120.8, 118.0, 114.8, 21.6; HRMS (ESI) calcd for $C_{18}H_{14}BrN_2O_2S$ (M+H) 400.9954, found 400.99529.



3-Bromo-5-tosyl-5*H*-pyrido[3,2-*b*]indole (**15b**): yield 43 mg (41%); light-brown solid; mp 167 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, *J* = 2.2 Hz, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 8.12 (d, *J* = 2.3 Hz, 1 H), 8.10 (d, *J* = 7.8 Hz, 1 H), 7.67 (d, *J* = 8.2 Hz, 2 H), 7.50 (t, *J* = 7.7 Hz, 1 H), 7.40 (t, *J* = 7.5 Hz, 1 H), 7.12 (d, *J* = 8.1 Hz, 2 H), 4.00 (s, 3 H), 2.27 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 145.4, 139.0, 138.1, 135.8, 134.6, 133.3, 129.8, 127.9, 126.5, 125.8, 124.5, 119.9, 114.9, 106.7, 56.2, 21.5; HRMS (ESI) calcd for $C_{19}H_{17}N_2O_3S$ (M+H) 353.0954, found 353.0952.

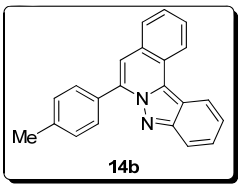


3-Methoxy-5-(2-nitrophenylsulfonyl)-5*H*-pyrido[3,2-*b*]indole (**15c**): yield 25 mg (22%); yellow solid, mp 224 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.43 (d, *J* = 2.5 Hz, 1 H), 8.22-8.17 (m, 1 H), 8.08-8.03 (m, 1 H), 7.93 (d, *J* = 2.5 Hz, 1 H), 7.75–7.64 (m, 2 H), 7.52–7.44 (m, 4 H), 3.98 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.3, 148.0, 138.7, 137.1, 137.0, 134.9, 133.5, 132.3, 131.8, 128.8, 128.1, 125.5, 125.1, 124.9, 120.2, 114.5, 106.4, 56.1; HRMS (ESI) calcd for $C_{18}H_{14}N_3O_5S$ (M+H) 384.0649, found 384.0649.

Indazolo[3,2-*a*]isoquinolines:

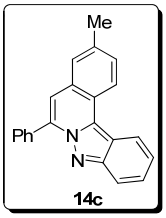
General procedure for AgOTf-catalyzed cyclization/cycloaddition: to an oven-dried 10 mL round-bottom flask equipped with a stir bar was added 0.3 mmol of

N'-(2-alkynylbenzylidene)tosylhydrazides. CH_3CN (4 mL) was added, followed by 0.03 mmol of AgOTf (10 mol %). The reaction mixture was stirred at 80 ºC for 6 h. After being cooled to ambient temperature, 0.36 mmol of aryne precursor (1.2 equiv) was added followed by 0.9 mmol of CsF (3 equiv). The reaction mixture was again stirred at 80 ºC for 12 h and cooled to room temperature. It was poured into brine and extracted three times with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the indazolo[3,2-*a*]isoquinolines.



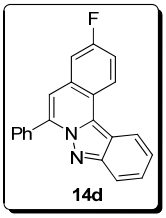
14b

6-*p*-Tolylindazolo[3,2-*a*]isoquinoline (**14b**): yield 87%; yellow solid, mp 178-179 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1 H), 8.52 (d, *J* = 8.5 Hz, 1 H), 7.97 (dt, *J* = 8.7, 0.9 Hz, 1 H), 7.94-7.87 (m, 3 H), 7.76 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1 H), 7.67-7.60 (m, 1 H), 7.54 (ddd, *J* = 8.7, 6.7, 1.0 Hz, 1 H), 7.44 (s, 1 H), 7.42-7.37 (m, 2 H), 7.37-7.32 (m, 1 H), 2.48 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 139.5, 138.5, 131.3, 131.1, 129.5, 129.1, 128.6, 128.0, 127.5, 127.1, 127.0, 125.5, 122.6, 121.3, 121.1, 117.7, 116.7, 116.4, 21.5; IR (KBr) 1619, 1511, 1363, 1233, 809, 752, 724 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}N_2$ (M+H) 309.1386, found 309.1380.



14c

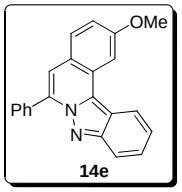
3-Methyl-6-phenylindazolo[3,2-*a*]isoquinoline (**14c**): yield 83%; glassy yellow solid, mp 171-172 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.3, 1 H), 8.49 (d, *J* = 8.5 Hz, 1 H), 8.03-7.99 (m, 2 H), 7.95 (d, *J* = 8.7 Hz, 1 H), 7.68 (s, 1 H), 7.64-7.49 (m, 5 H), 7.38 (s, 1 H), 7.37-7.29 (m, 1 H), 2.58 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 138.3, 137.2, 134.1, 131.6, 129.8, 129.7, 129.4, 128.8, 128.4, 127.14, 127.05, 123.5, 122.5, 121.1, 121.0, 117.5, 116.6, 116.4, 21.6; IR (KBr) 1610, 1526, 1486, 1355, 1233, 801, 768, 735, 691 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}N_2$ (M+H) 309.1386, found 309.1384.



14d

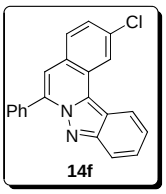
3-Fluoro-6-phenylindazolo[3,2-*a*]isoquinoline (**14d**): yield 82%; glassy yellow solid, mp 167-168 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 8.9, 5.3 Hz, 1 H), 8.44 (d, *J* = 8.5 Hz, 1 H), 8.03-7.98 (m, 2 H), 7.96 (dt, *J* = 8.7, 0.8 Hz, 1 H), 7.66-7.46 (m, 6 H), 7.39 (s, 1 H), 7.35 (ddd, *J* = 8.4, 6.7, 0.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 ($^1J_{CF}$ = 248.4 Hz), 148.9, 139.4, 133.6, 131.2, 130.2 ($^3J_{CF}$ = 9.1 Hz), 129.74, 129.66, 128.5, 127.3, 124.8 ($^3J_{CF}$ = 8.8 Hz), 122.4 ($^4J_{CF}$ = 1.9 Hz), 121.5, 120.8, 117.7, 117.1 ($^2J_{CF}$ = 24.0 Hz), 116.2, 115.9 ($^4J_{CF}$ = 3.8 Hz), 112.2 ($^2J_{CF}$ = 21.7 Hz); IR (KBr) 1615, 1561, 1486, 1234, 1226, 879, 760, 732, 690 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{14}FN_2$ (M+H) 313.1136, found

313.1133.



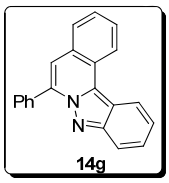
14e

2-Methoxy-6-phenylindazolo[3,2-*a*]isoquinoline (**14e**): yield 88%; glassy yellow solid, mp 100-101 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.5 Hz, 1 H), 8.08 (d, *J* = 2.4 Hz, 1 H), 8.05-7.92 (m, 3 H), 7.82 (d, *J* = 8.8 Hz, 1 H), 7.63-7.48 (m, 4 H), 7.41 (s, 1 H), 7.35 (ddd, *J* = 8.3, 6.8, 0.7 Hz, 1 H), 7.25 (dd, *J* = 8.7, 2.5 Hz, 1 H), 4.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 148.7, 136.2, 134.1, 130.9, 129.6, 129.2, 129.1, 128.4, 126.9, 126.8, 122.9, 121.2, 120.8, 117.6, 117.2, 116.7, 116.6, 103.8, 55.6; IR (KBr) 1620, 1498, 1358, 1267, 1031, 864, 748, 696 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ (M+H) 325.1335, found 325.1330.



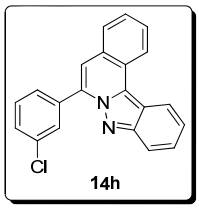
14f

2-Chloro-6-phenylindazolo[3,2-*a*]isoquinoline (**14f**): yield 86%; glassy yellow solid, mp 202-203 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.67 (d, *J* = 1.9 Hz, 1 H), 8.46 (d, *J* = 8.5 Hz, 1 H), 8.01-7.96 (m, 3 H), 7.83 (d, *J* = 8.5 Hz, 1 H), 7.63-7.52 (m, 5 H), 7.41 (s, 1 H); 7.39 (ddd, *J* = 8.3, 6.7, 0.9 Hz, 1 H); ^{13}C NMR (100 MHz, THF-d_8) δ 149.8, 139.7, 134.9, 130.80, 130.78, 130.7, 130.3, 130.1, 128.8, 128.3, 128.0 (overlapped signal), 127.4, 122.7, 122.5, 121.7, 118.4, 117.6, 116.8; IR (KBr) 1619, 1482, 1359, 1235, 860, 735, 691 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ (M+H) 329.0840, found 329.0836.



14g

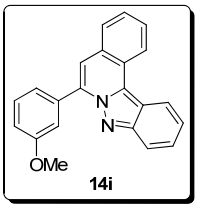
6-Phenylindazolo[3,2-*a*]isoquinoline (**14g**): yield 85%; yellow solid, mp 134-135 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.2 Hz, 1 H), 8.50 (d, *J* = 8.5 Hz, 1 H), 8.05-8.00 (m, 2 H), 7.98 (d, *J* = 8.7 Hz, 1 H), 7.88 (d, *J* = 7.9 Hz, 1 H), 7.76-7.73 (m, 1 H), 7.64-7.51 (m, 5 H), 7.44 (s, 1 H), 7.38-7.34 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$), δ 148.8, 138.4, 134.0, 131.4, 129.7, 129.5, 128.5, 128.4, 128.1, 127.6, 127.13, 127.11, 125.6, 122.6, 121.4, 121.1, 117.7, 116.8, 116.7; IR (KBr) 1618, 1525, 1484, 1233, 752, 735, 685 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{15}N_2$ (M+H) 295.1230, found 295.1226.



14h

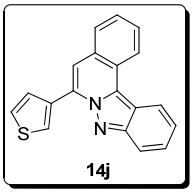
6-(3-Chlorophenyl)indazolo[3,2-*a*]isoquinoline (**14h**): yield 81%; yellow solid, mp 208-209 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.2 Hz, 1 H), 8.52 (d, *J* = 8.5 Hz, 1 H), 8.02-8.00 (m, 1 H), 7.99-7.90 (m, 3 H), 7.80 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1 H), 7.69-7.62 (m, 1 H), 7.59-7,55 (m, 1 H), 7.53-7.51 (m, 2 H), 7.47 (s, 1 H), 7.38-7.35 (m, 1 H); ^{13}C NMR (100 MHz, THF-d_8) δ 149.8, 137.7, 137.1, 134.6, 132.0, 130.7, 130.4, 129.9, 129.4 (overlapped signal), 129.2, 128.8, 128.0, 127.9, 126.7,

123.5, 122.2, 122.0, 118.3, 118.0, 117.5; IR (KBr) 1619, 1595, 1524, 1481, 1365, 1315, 1236, 870, 776, 747, 730, 695 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{14}ClN_2$ (M+H) 329.0840, found 329.0839.



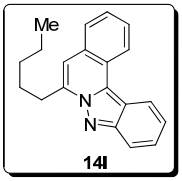
14i

6-(3-Methoxyphenyl)indazolo[3,2-*a*]isoquinoline (**14i**): yield 81%; yellow solid, mp 133-134 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.2 Hz, 1 H), 8.49 (d, *J* = 8.5 Hz, 1 H), 7.99 (d, *J* = 8.7 Hz, 1 H), 7.87 (d, *J* = 7.9 Hz, 1 H), 7.75-7.71 (m, 1 H), 7.63-7.48 (m, 5 H), 7.44 (s, 1 H), 7.39-7.32 (m, 1 H), 7.12-7.09 (m, 1 H), 3.91 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 148.8, 138.1, 135.1, 131.4, 129.5, 128.4, 128.1, 127.6, 127.1, 127.0, 125.6, 122.6, 122.1, 121.4, 121.0, 117.7, 116.8, 116.6, 115.3, 115.2, 55.4; IR (KBr) 1621, 1597, 1471,1359, 1259, 1047, 782, 749, 736, 698 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{17}N_2O$ (M+H) 325.1335, found 325.1329.



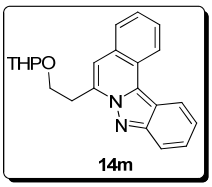
14j

6-(Thiophen-3-yl)indazolo[3,2-*a*]isoquinoline (**14j**): yield 89%; yellow solid, mp 154-155 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.2 Hz, 1 H), 8.61-8.59 (m, 1 H), 8.54-8.51 (m, 1 H), 8.02 (dt, *J* = 8.7, 0.9 Hz, 1 H), 7.95-7.88 (m, 2 H), 7.76 (ddd, *J* = 8.3, 7.2, 1.3 Hz, 1 H), 7.67 (s, 1 H), 7.66-7,54 (m, 2 H), 7.54-7.51(m, 1 H), 7.37 (ddd, *J* = 8.4, 6.7, 0.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 133.7, 133.4, 131.6, 128.3, 128.2, 128.0, 127.5, 127.4, 127.2, 127.1, 125.3, 125.2, 122.5, 121.4, 121.1, 117.5, 116.5, 115.5; IR (KBr) 1600, 1520, 1348, 1296, 1200, 795, 735, 693 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{13}N_2S$ (M+H) 301.1794, found 301.1791.



14l

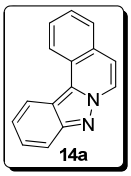
6-Pentylindazolo[3,2-*a*]isoquinoline (**14l**): yield 76%; yellow solid, mp 92-93 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.1 Hz, 1 H), 8.49 (d, *J* = 8.5 Hz, 1 H), 8.02 (d, *J* = 8.7 Hz, 1 H), 7.85 (d, *J* = 7.9 Hz, 1 H), 7.76-7.66 (m, 1 H), 7.65-7.51 (m, 2 H), 7.34 (ddd, *J* = 8.3, 6.7, 0.8 Hz, 1 H), 7.27 (s, 1 H), 3.40 (t, *J* = 7.5 Hz, 2 H), 2.07-1.97 (m, 2 H), 1.59-1.39 (m, 4 H), 0.96 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.8, 139.6, 130.9, 128.4, 127.3, 127.1, 126.9 (overlapped signal), 125.0, 122.6, 121.3, 121.1, 117.2, 116.8, 113.5, 31.6, 31.2, 26.3, 22.6, 14.0; IR (KBr) 2952, 2930, 1620, 1524, 1366, 1351, 1229, 744 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{21}N_2$ (M+H) 289.1699, found 289.1696.



14m

6-((Tetrahydro-2*H*-pyran-2-yloxy)methyl)indazolo[3,2-*a*]isoquinoline (**14m**): yield 60%; yellow

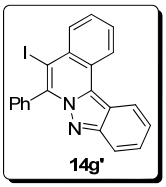
solid, mp 88-89 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.1 Hz, 1 H), 8.42 (d, *J* = 8.5 Hz, 1 H), 7.99 (d, *J* = 8.7 Hz, 1 H), 7.80 (d, *J* = 7.9 Hz, 1 H), 7.72-7.61 (m, 1 H), 7.58-7.53 (m, 2 H), 7.34 (s, 1 H), 7.31 (d, *J* = 7.5 Hz, 1 H), 4.70-4.68 (m, 1 H), 4.36 and 4.15 (t of ABq, ^{3}J = 6.4 Hz, J_{AB} = 9.9 Hz, 2 H), 3.87-3.80 (m, 1 H, left part of an m of ABq), 3.69 (t, *J* = 6.4 Hz, 2 H), 3.52-3.45 (m, 1 H, right part of an m of ABq), 1.84-1.48 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$), δ 148.6, 136.3, 130.8, 128.3, 127.5, 127.1, 127.0, 126.9, 125.1, 122.5, 121.2, 121.1, 117.2, 116.8, 115.0, 98.9, 64.2, 62.3, 32.0, 30.6, 25.4, 19.5; IR (KBr) 2954, 2921, 1622, 1525, 1236, 1136, 1120, 1032, 979, 752 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{23}N_2O_2$ (M+H) 347.1754, found 347.1752.



14a

Indazolo[3,2-a]isoquinoline (**14a**) from **17m**: here this compound was obtained in a modified procedure. Thus, the first step was carried out using 30 mol % of AgOTf for 5 d, and the second step was carried out with additional 0.4 mL of MeOH and 4.0 equiv. of CsF. Yield 40%; light brown solid, mp 88-89 ºC (lit[10] 90-91 ºC); spectroscopic data match those for **14a**.

General procedure for iodocyclization/cycloaddition: to an oven-dried 10 mL round-bottom flask equipped with a stir bar was added 0.3 mmol of *N'*-(2-alkynylbenzylidene)tosylhydrazides. CH_3CN (4 mL) was added, followed by 0.6 mmol of I_2 (2 equiv). The reaction mixture was stirred at 80 ºC for 6 h. After being cooled to ambient temperature, 0.36 mmol of aryne precursor (1.2 equiv) was added followed by 0.9 mmol of CsF (3 equiv). The reaction mixture was again stirred at 80 ºC for 12 h and cooled to room temperature. It was poured into sat. aq. $Na_2S_2O_3$ and extracted three times with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the product **14g'**.



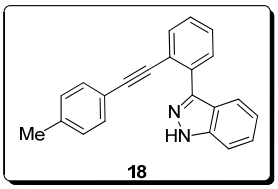
14g'

5-Iodo-6-phenylindazolo[3,2-a]isoquinoline (**14g'**): yield 45%; slightly yellow solid, mp 196-197 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.72 (dd, *J* = 8.2, 0.7 Hz, 1 H), 8.48 (d, *J* = 8.6 Hz, 1 H), 8.35 (dd, *J* = 8.3, 0.8 Hz, 1 H), 7.88 (dt, *J* = 8.8, 0.8 Hz, 1 H), 7.82 (ddd, *J* = 8.2, 7.2, 1.2 Hz, 1 H), 7.76-7.60 (m, 4 H), 7.57-7.46 (m, 3 H), 7.35 (ddd, *J* = 8.4, 6.7, 0.9 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 141.3, 138.4, 133.5, 130.7, 130.2, 129.7, 129.6, 129.0, 128.9, 128.1, 127.4, 125.4, 122.9, 122.0, 121.0, 118.0, 116.3, 92.7; IR (KBr) 1624, 1519, 1348, 1246, 752, 694 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{14}IN_2$ (M+H) 421.0196, found 421.0197.

General procedure for cycloaddition/AgOTf-catalyzed cyclization: to an oven-dried 25 mL round-bottom flask equipped with a stir bar was added 0.4 mmol of *N'*-(2-alkynylbenzylidene)tosylhydrazides, followed by 0.48 mmol of the aryne precursor (1.2 equiv). THF (10 mL) was added, followed by 0.1 mmol of TEBAC (0.25 equiv) and 1.2 mmol of CsF (3 equiv). The reaction mixture was stirred at 70 ºC for 24 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The

residue was purified by column chromatography (petroleum ether/EtOAc) to afford the intermediate.

To an oven-dried 10 mL round-bottom flask equipped with a stir bar was added 0.3 mmol of the intermediate. THF (4 mL) was added, followed by 0.03 mmol of AgOTf (10 mol %). The reaction mixture was stirred at 70 ºC for 10 h, cooled to room temperature, poured into brine and extracted with EtOAc. The combined extracts were dried over $MgSO_4$, filtered, and evaporated. The residue was purified by column chromatography (petroleum ether/EtOAc) to afford the product **14**.



18

Intermediate **18**: yield 77%; white solid, mp 120-121 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.9 (brs, 1 H), 7.94 (d, *J* = 8.2 Hz, 1 H), 7.79-7.71 (m, 2 H), 7.47 (dd, *J* = 5.3, 3.6 Hz, 2 H), 7.33 (t, *J* = 7.6 Hz, 1 H), 7.26-7.22 (m, 1 H), 7.15 (t, *J* = 7.7 Hz, 1 H), 6.96-6.87 (m, 4 H), 2.23 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.8, 140.6, 137.6, 134.9, 132.4, 130.7, 130.0, 128.3, 127.8, 127.7, 126.0, 122.7, 121.6, 121.4, 120.2, 119. 6, 109.7, 92.7, 88.2, 20.9; HRMS (ESI) calcd for $C_{22}H_{17}N_2$ (M+H) 309.1386, found 309.1384.

Product **14b** can be obtained in quant yield from the reaction of **18**, with spectroscopic data matching those for **14b** obtained earlier.

References and Notes:

1. The petroleum ether we used for column chromatography contains a small quantity of long-chain paraffins. Although we pre-distilled all petroleum ether before use, we still observed small, but visible contamination of the products by such paraffins at ~0.87 ppm and ~1.25 ppm in some of the ^{1}H NMR spectra. The products obtained are pure otherwise.
2. This silica gel exhibits significant difference from the silica gels typically supplied in the US market. The same compound is retarded much less on this silica gel.
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4. S. L. Jain, V. B. Sharma, B. Sain, *Tetrahedron Lett.*, 2003, **44**, 4385.
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6. This procedure was taken from Liang's method with modifications, see: Shu, X-Z.; Zhao, S-C.; Ji, K-G.; Zheng, Z-J.; Liu, X-Y.; Liang, Y-M. *Eur. J. Org. Chem.*, 2009, 117.
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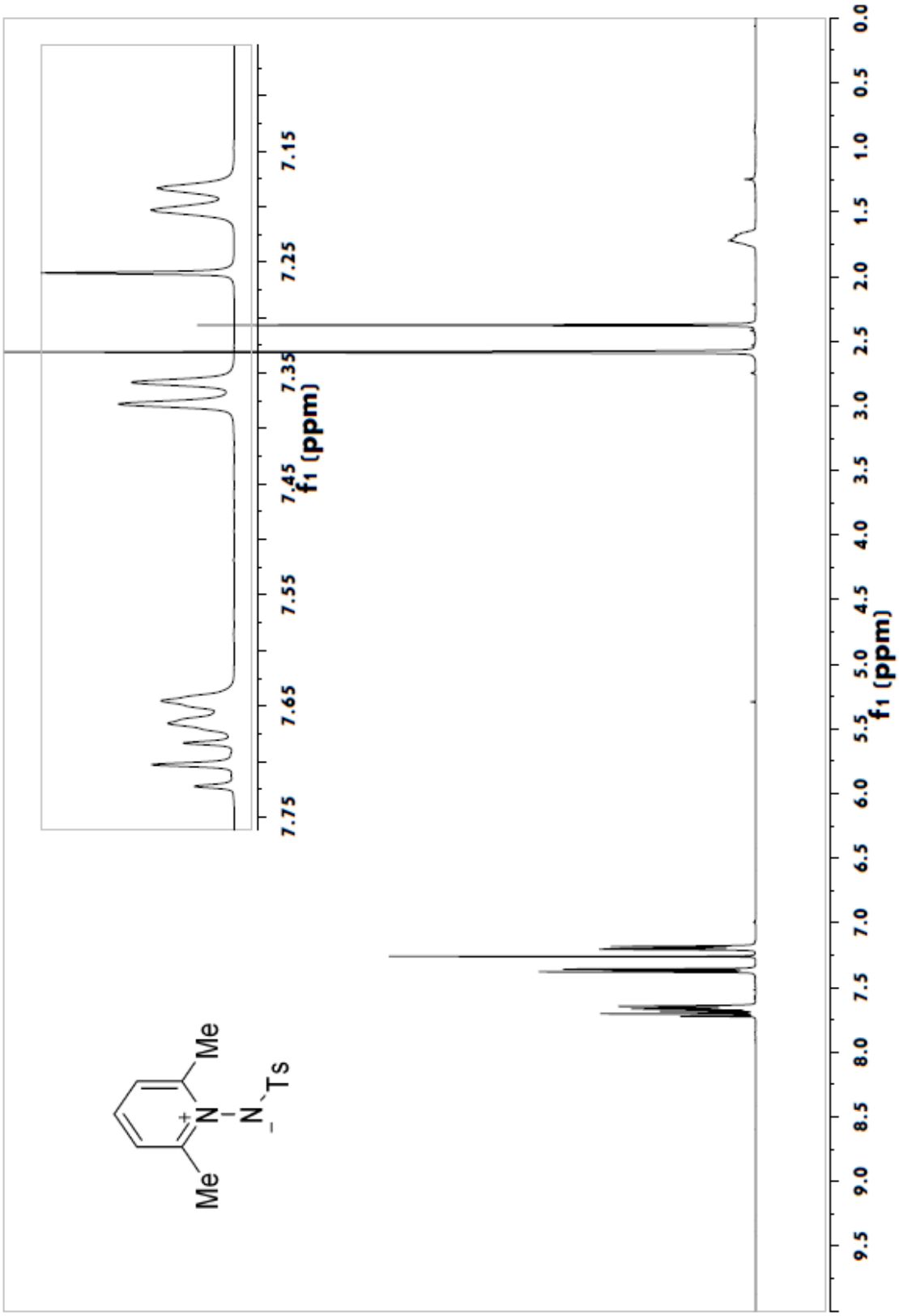
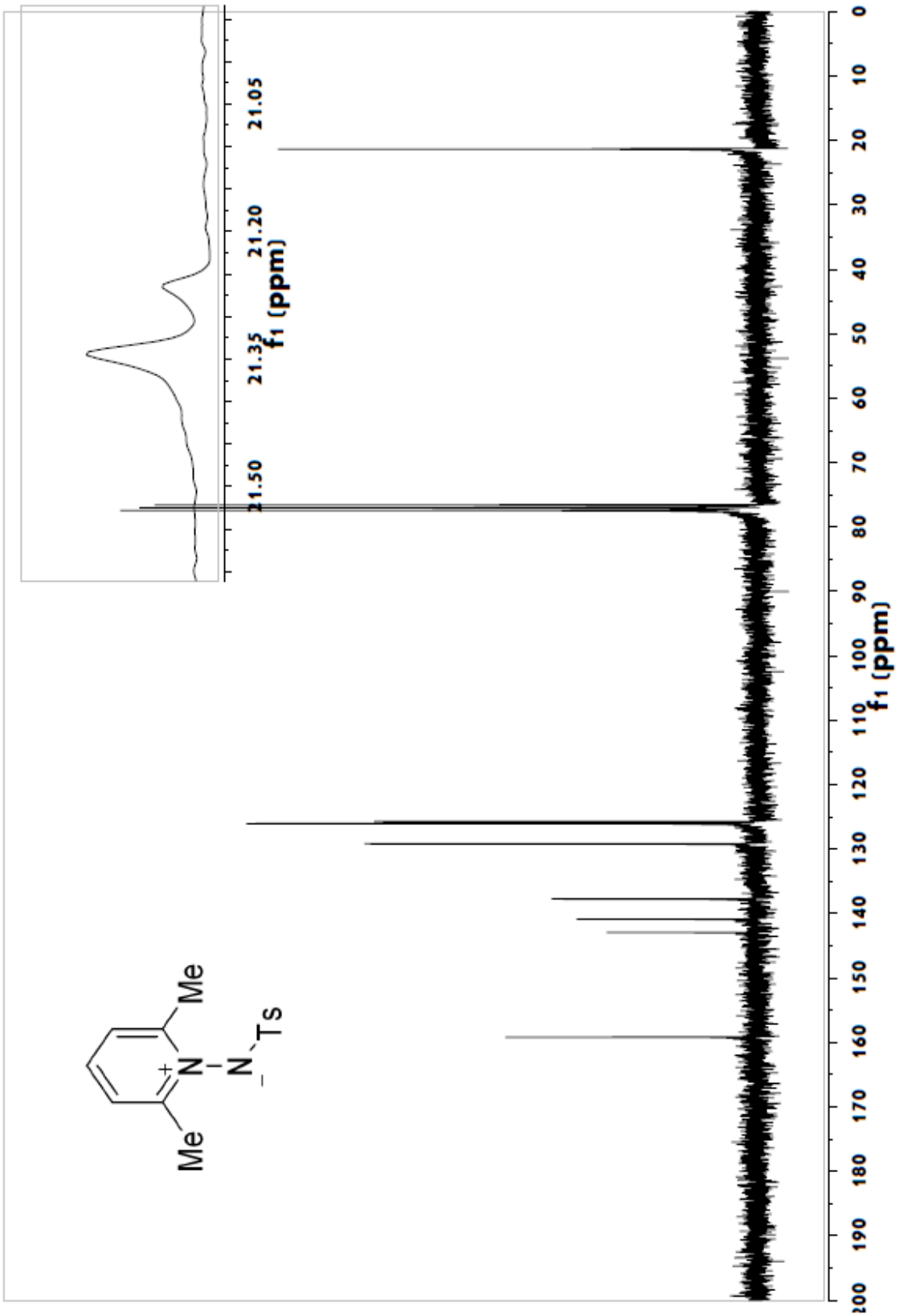
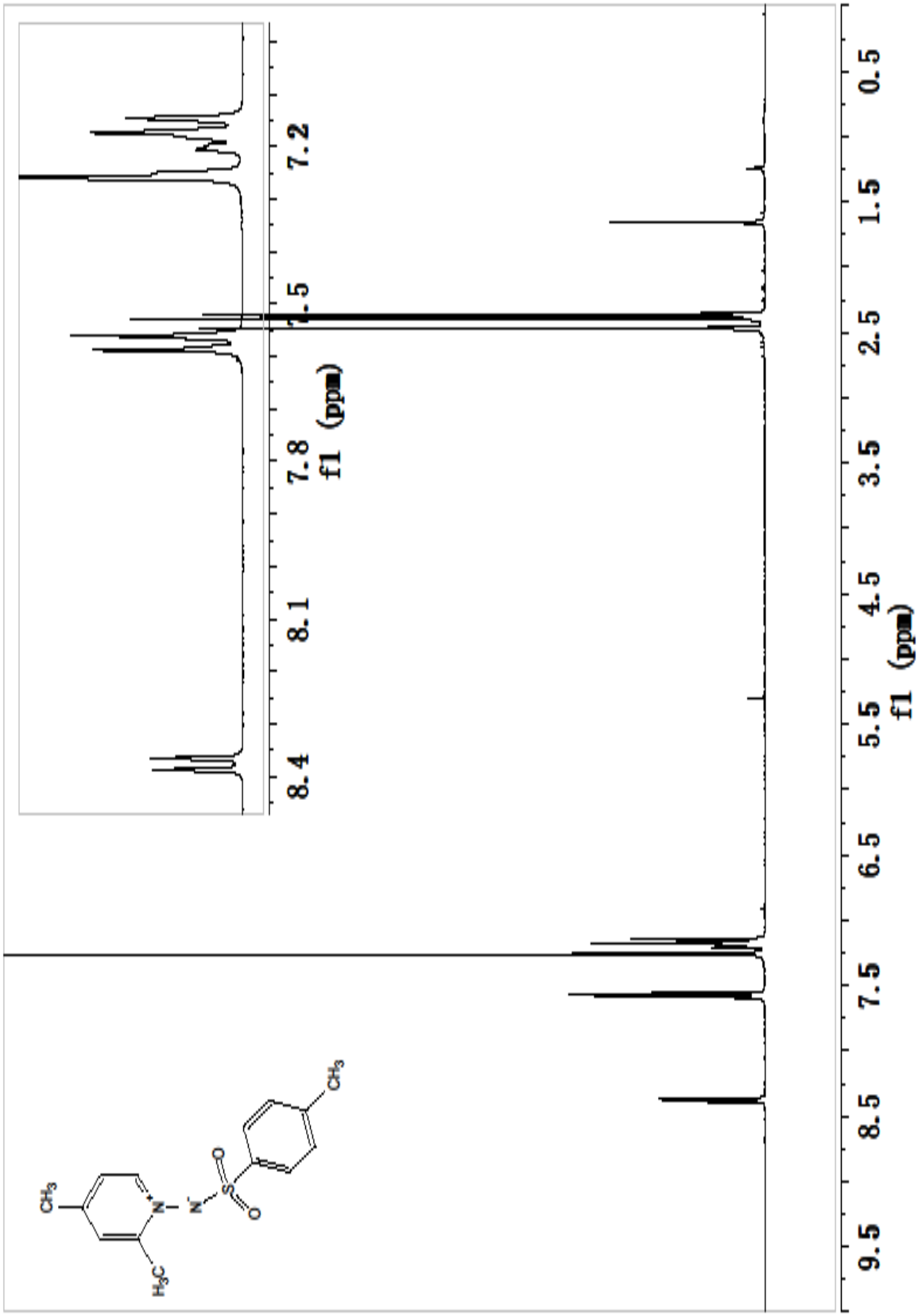
10. Yamashita, Y.; Hayashi, T.; Masumura, M. *Chem. Lett.*, 1980, 1133.

Copies of ^{1}H and ^{13}C NMR Spectra:



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6.5
5.5
4.5
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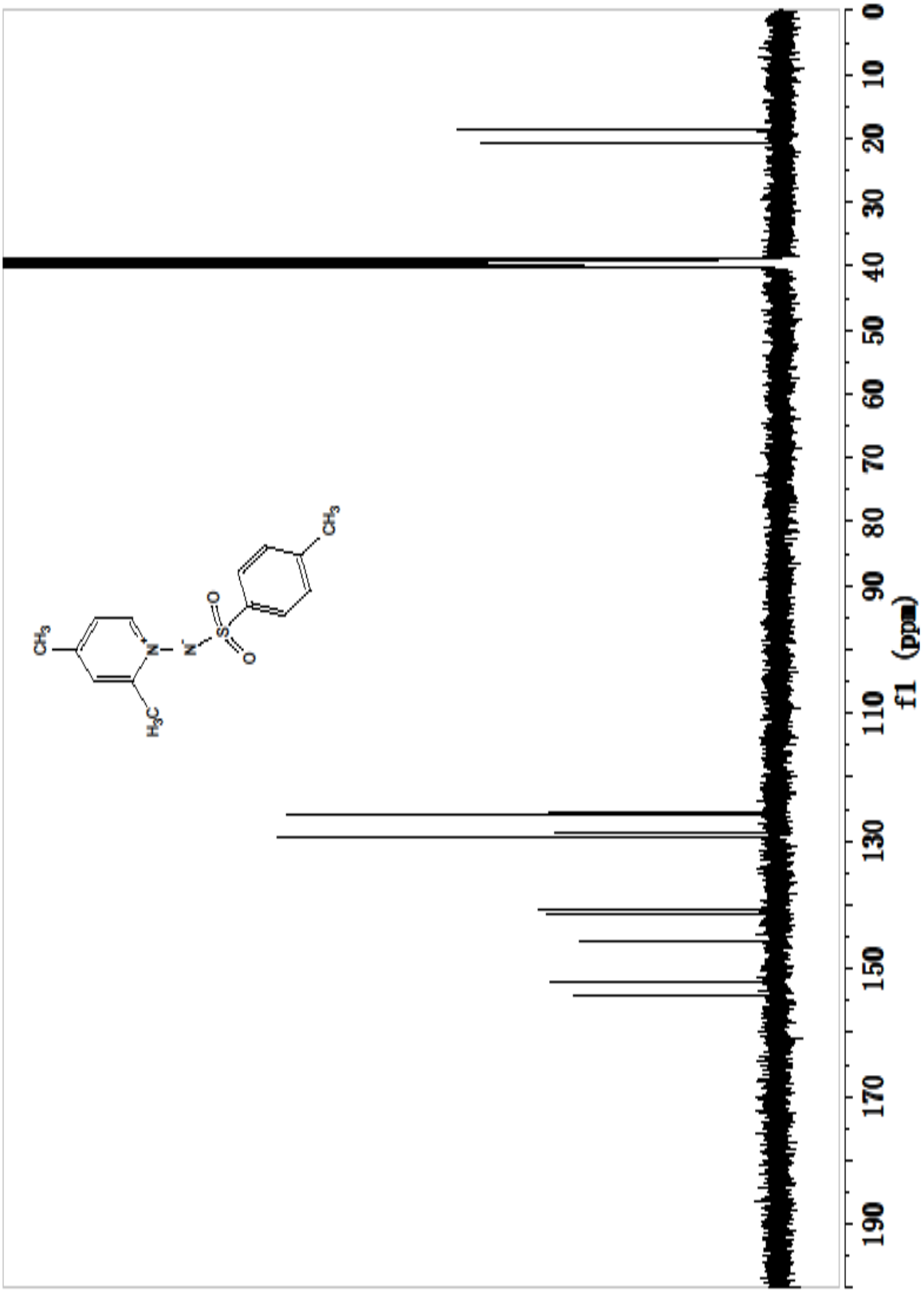
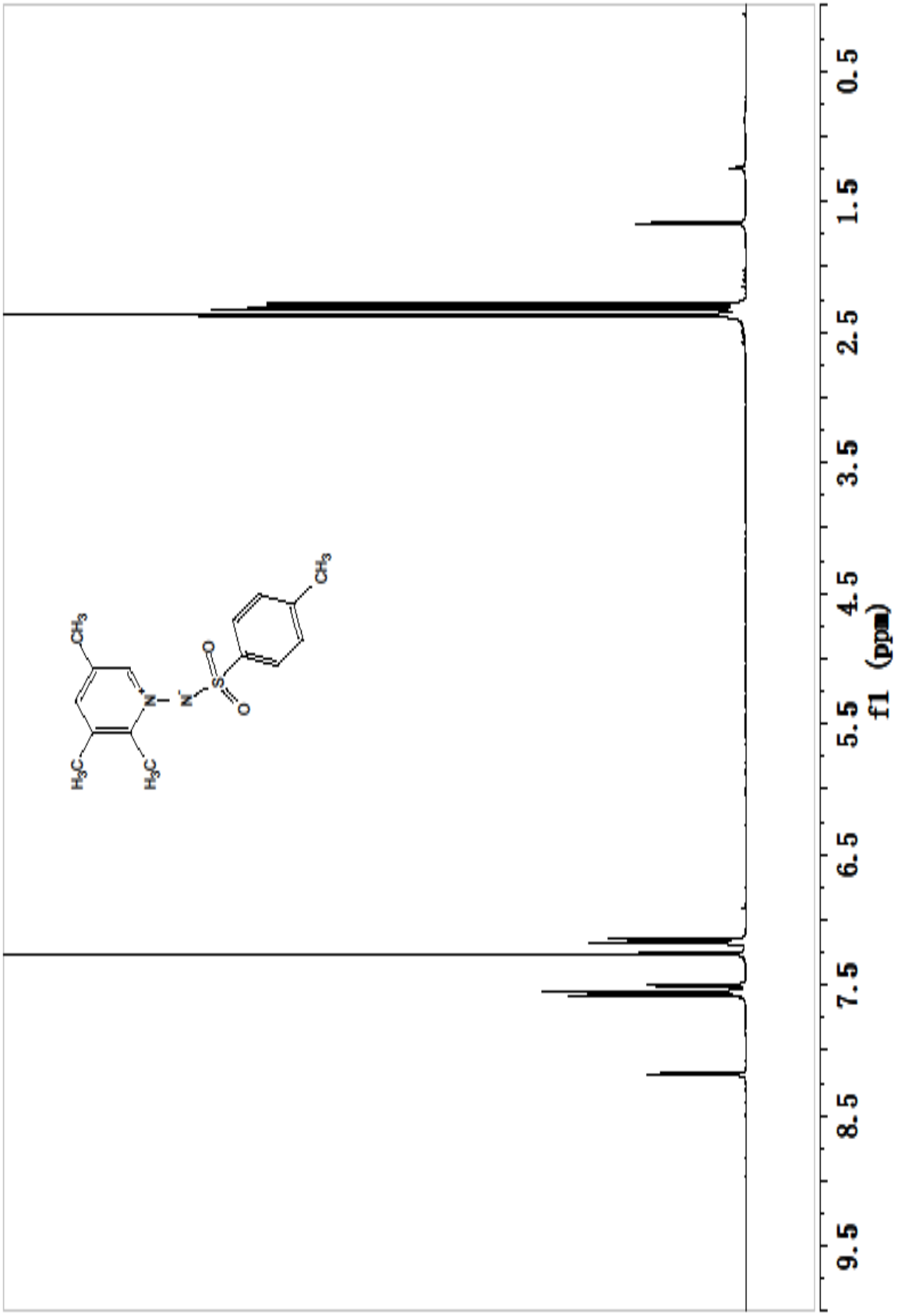
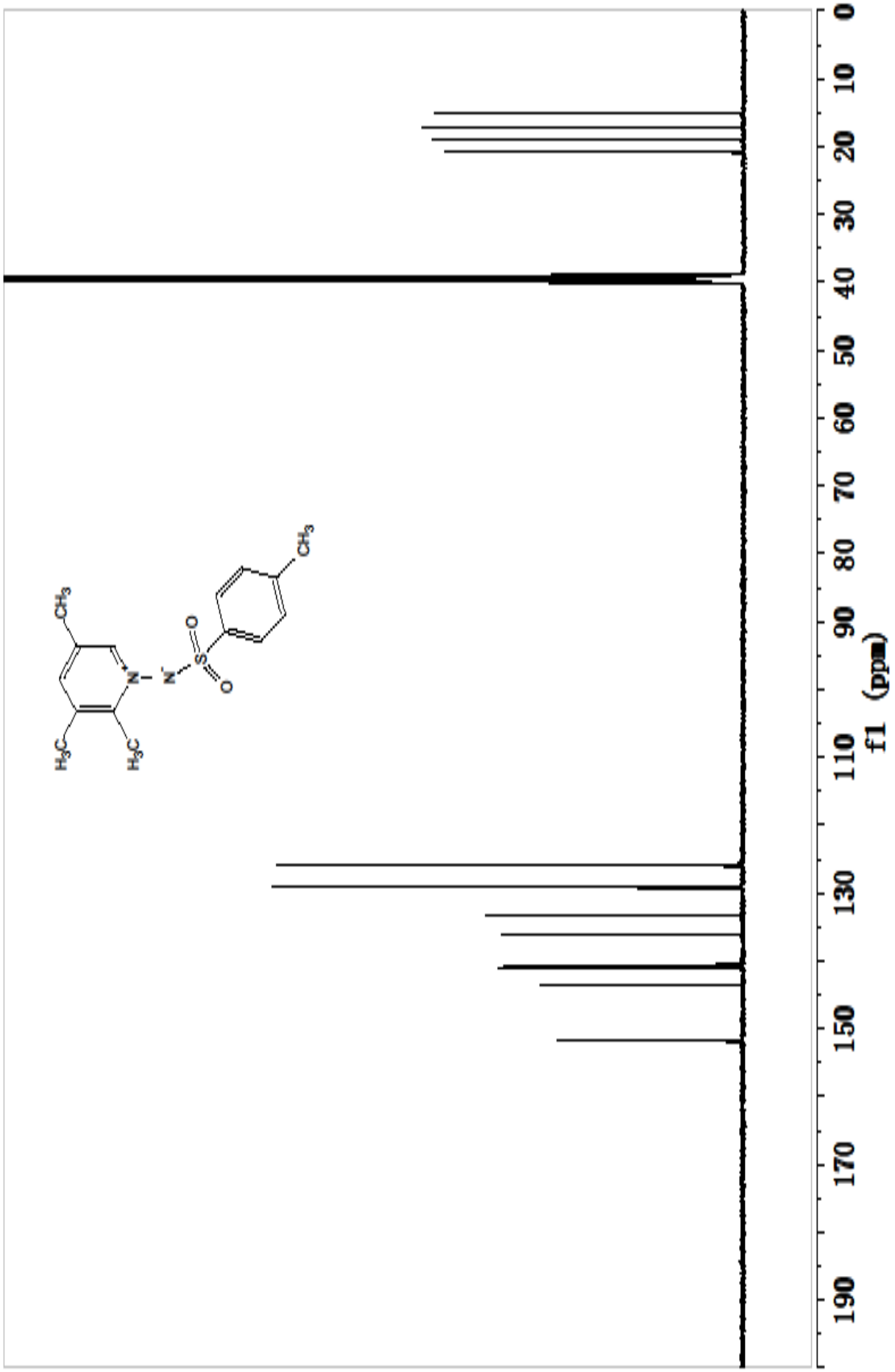
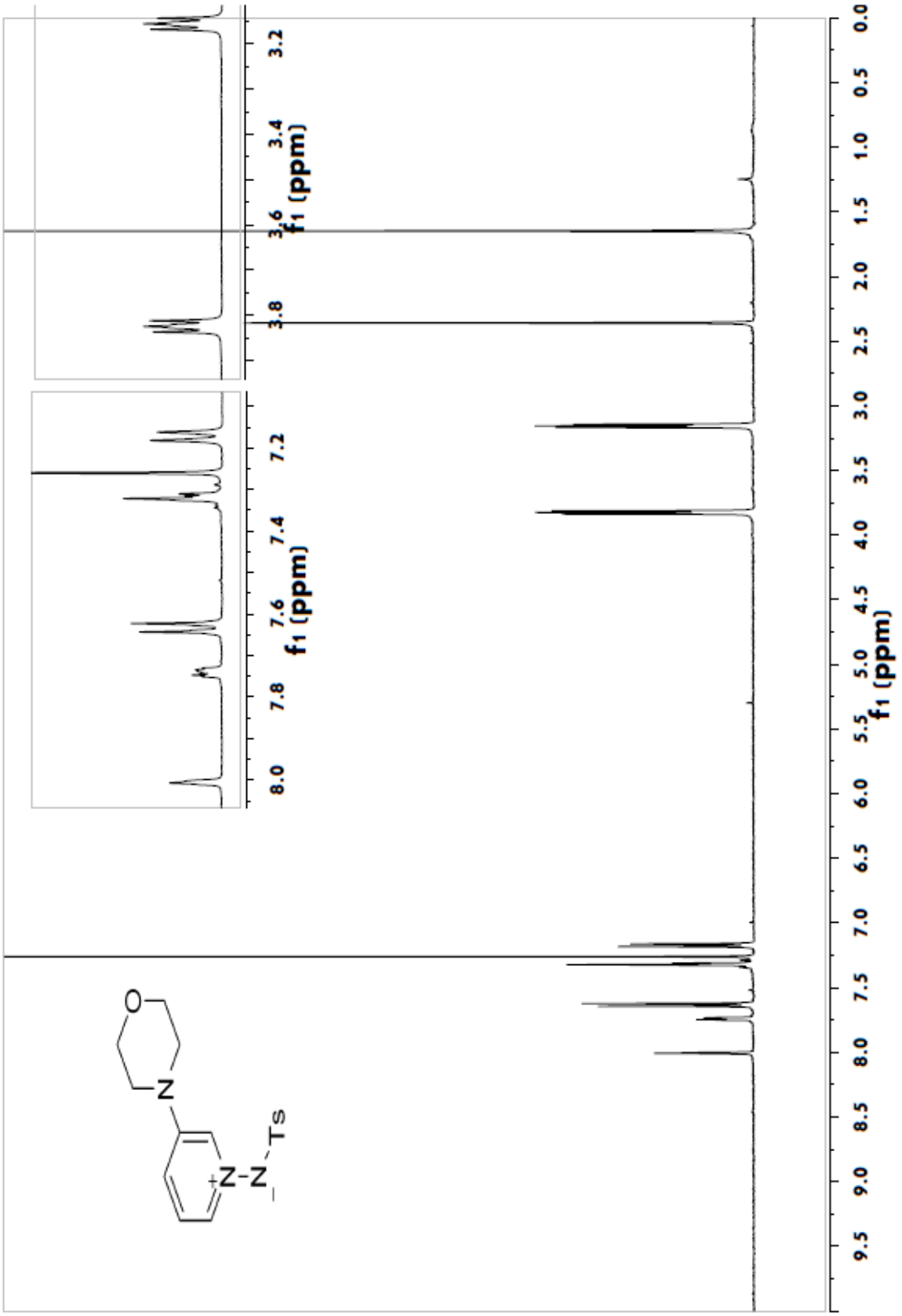
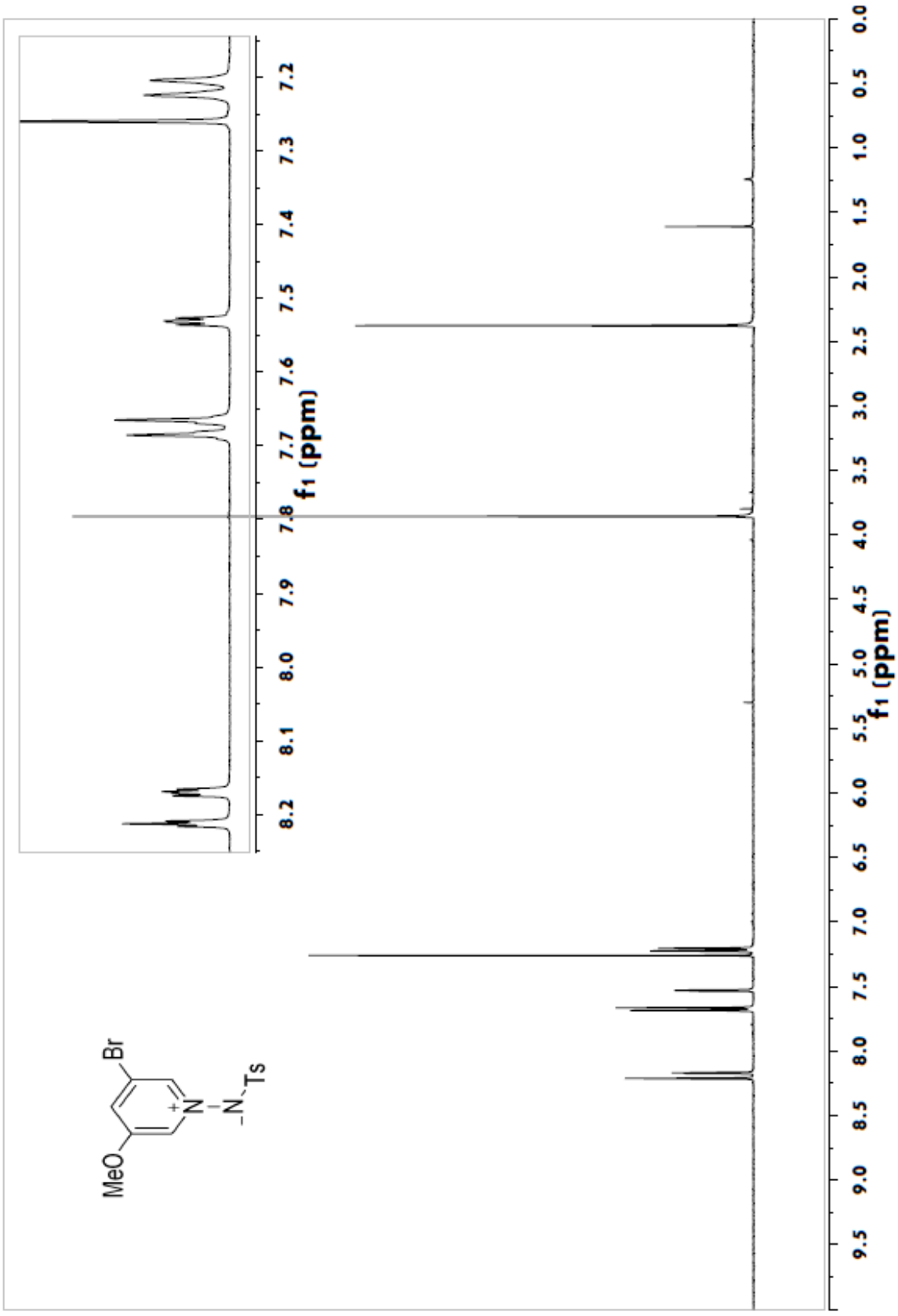
0.5
8.4
8.1
7.8
7.5
7.2
CH3
H3C
N
O
S

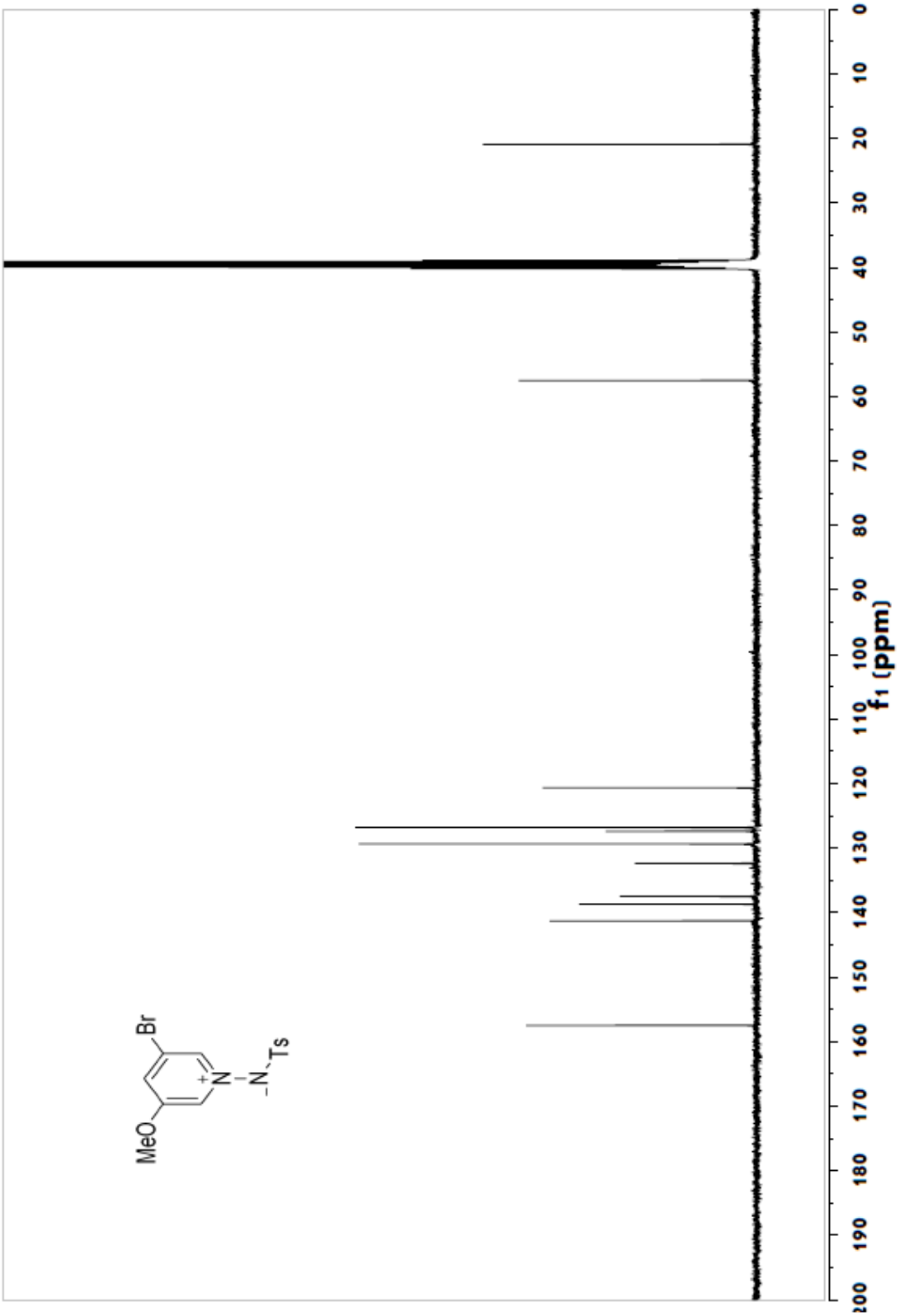


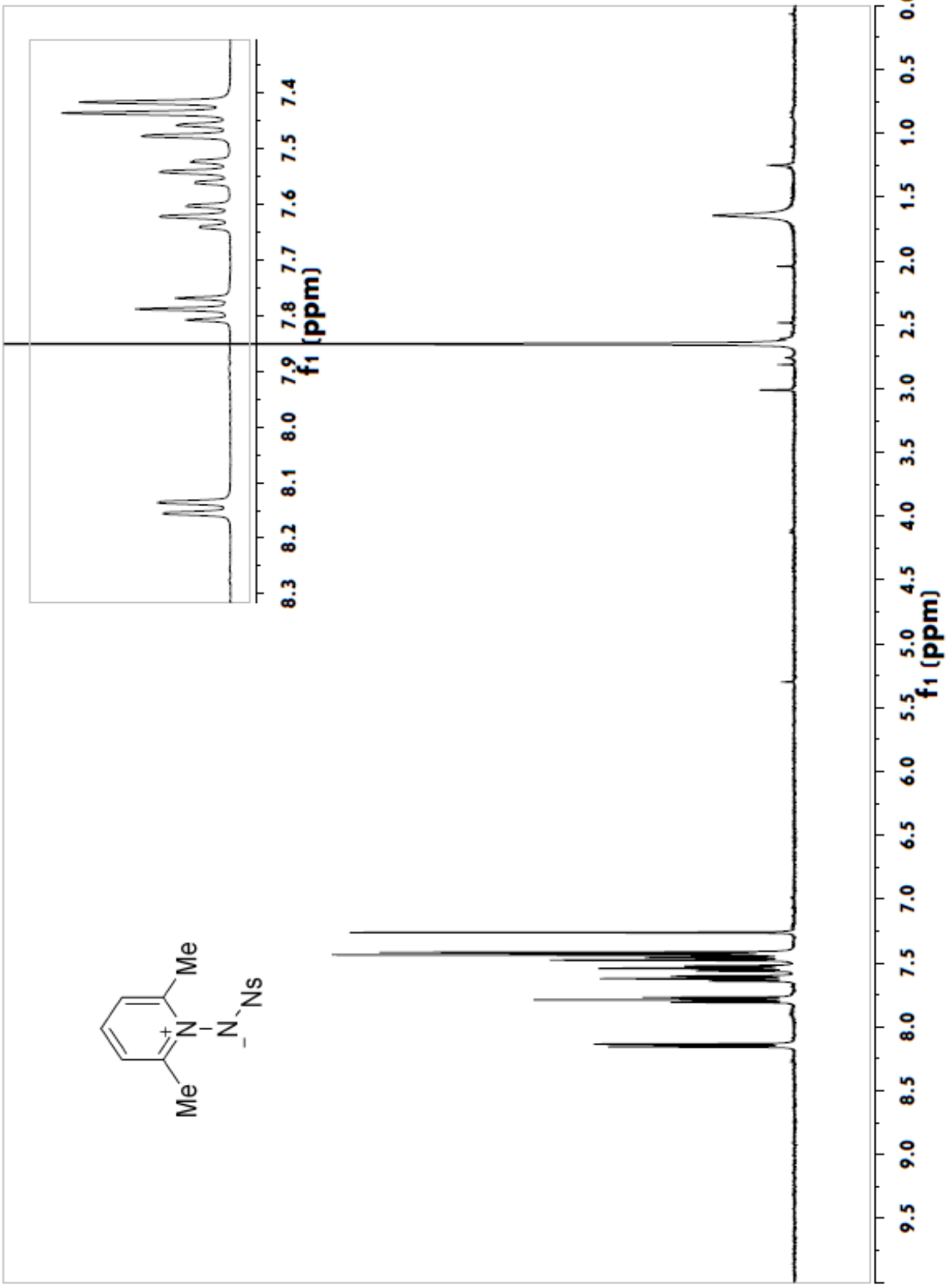


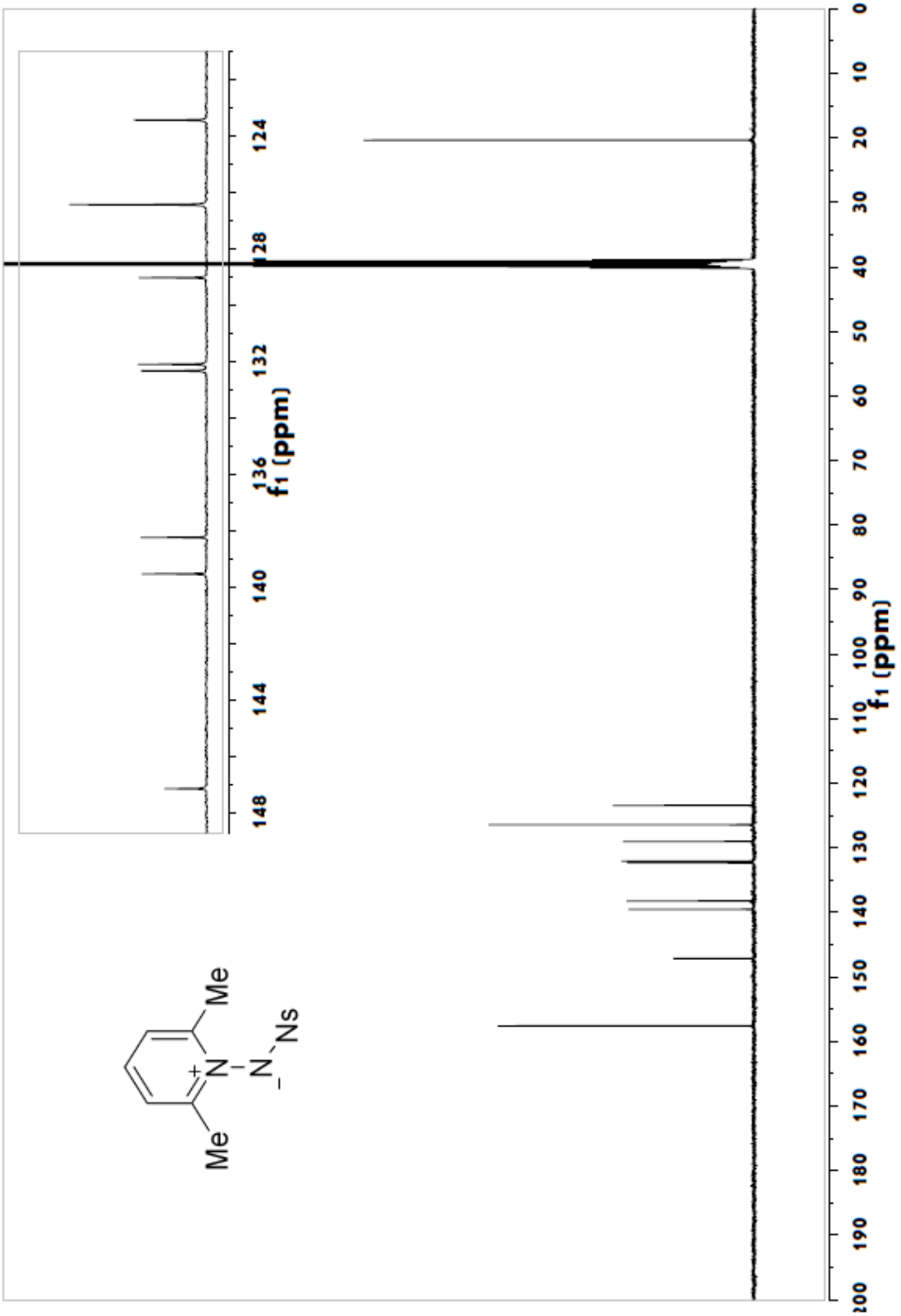


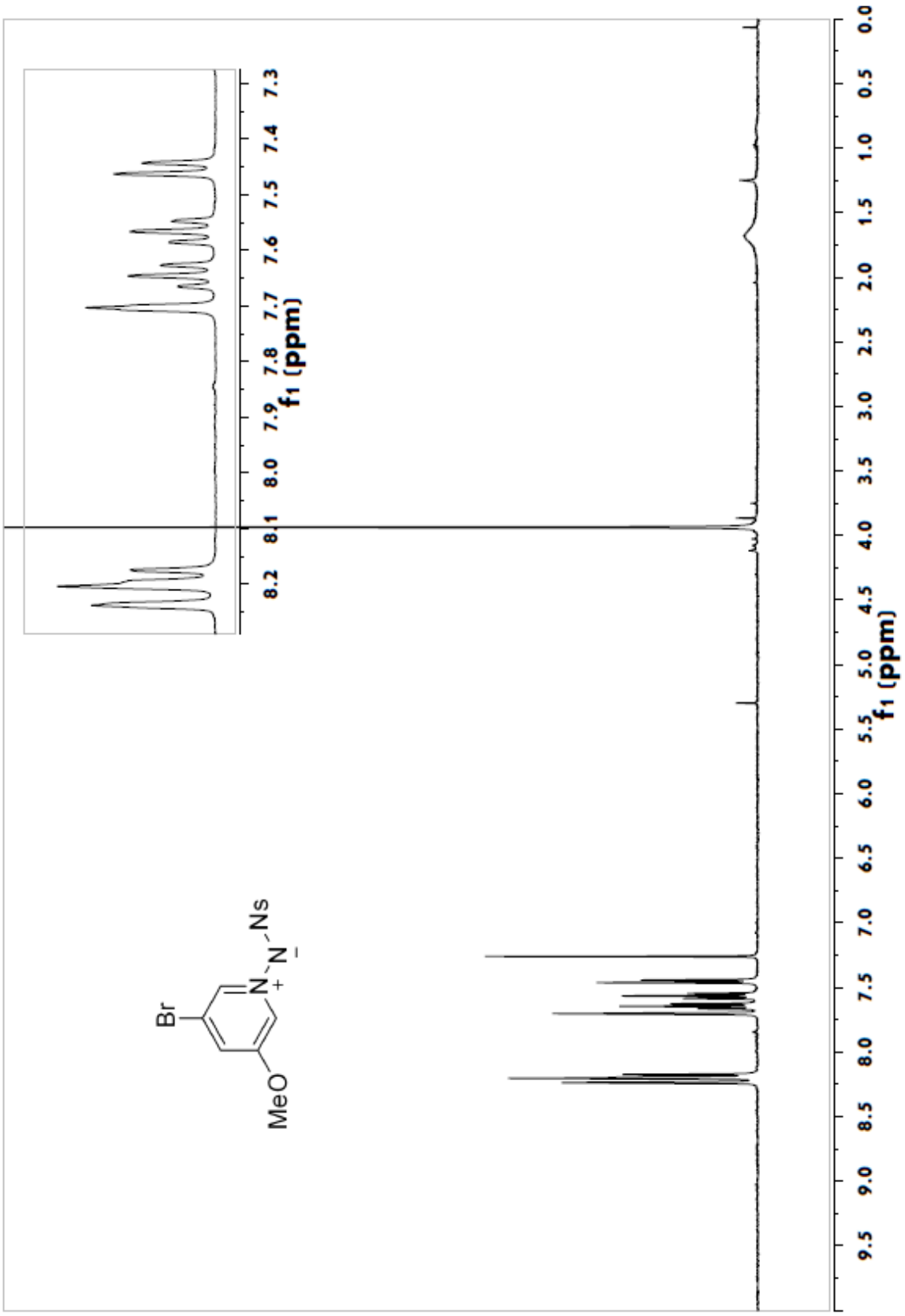


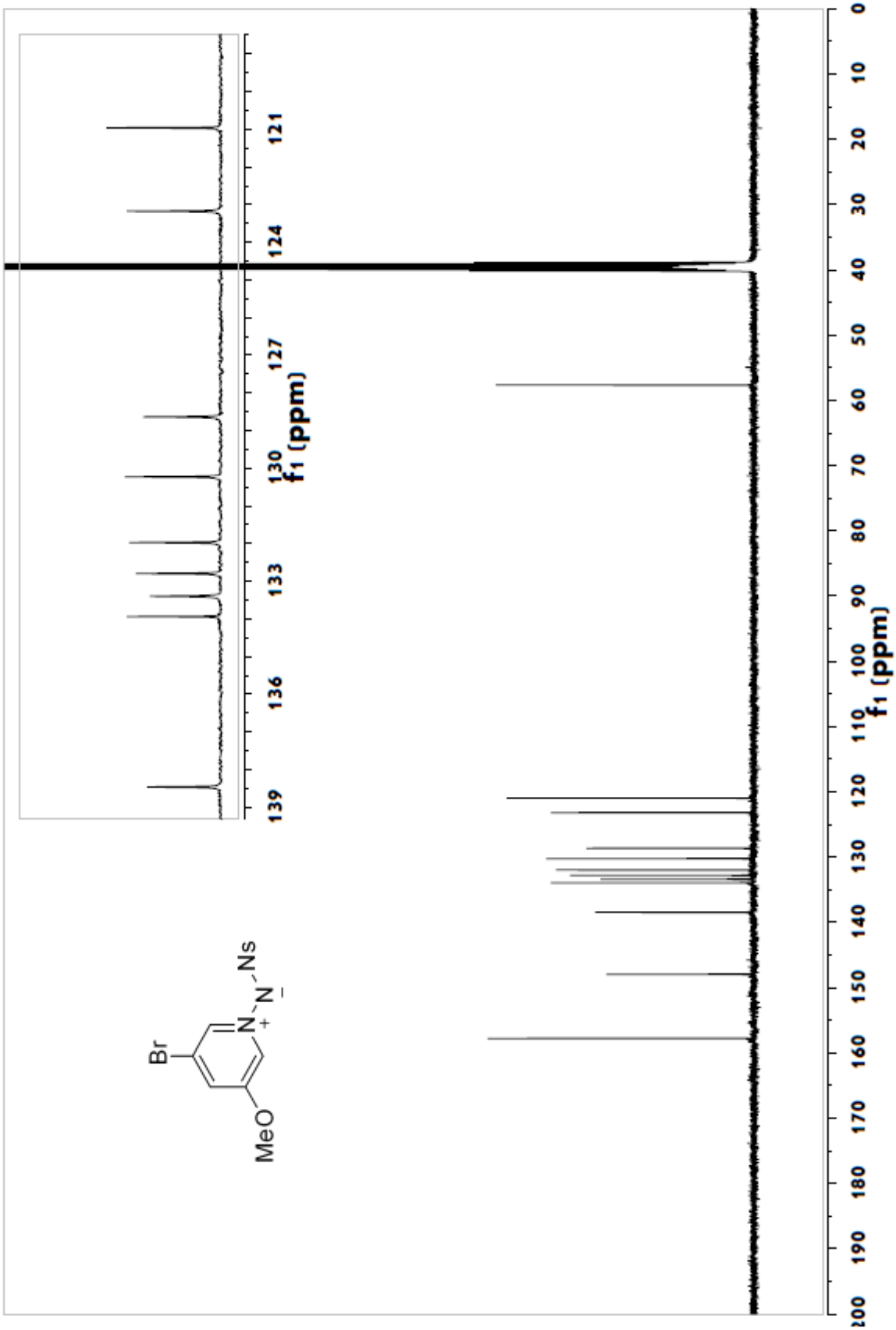


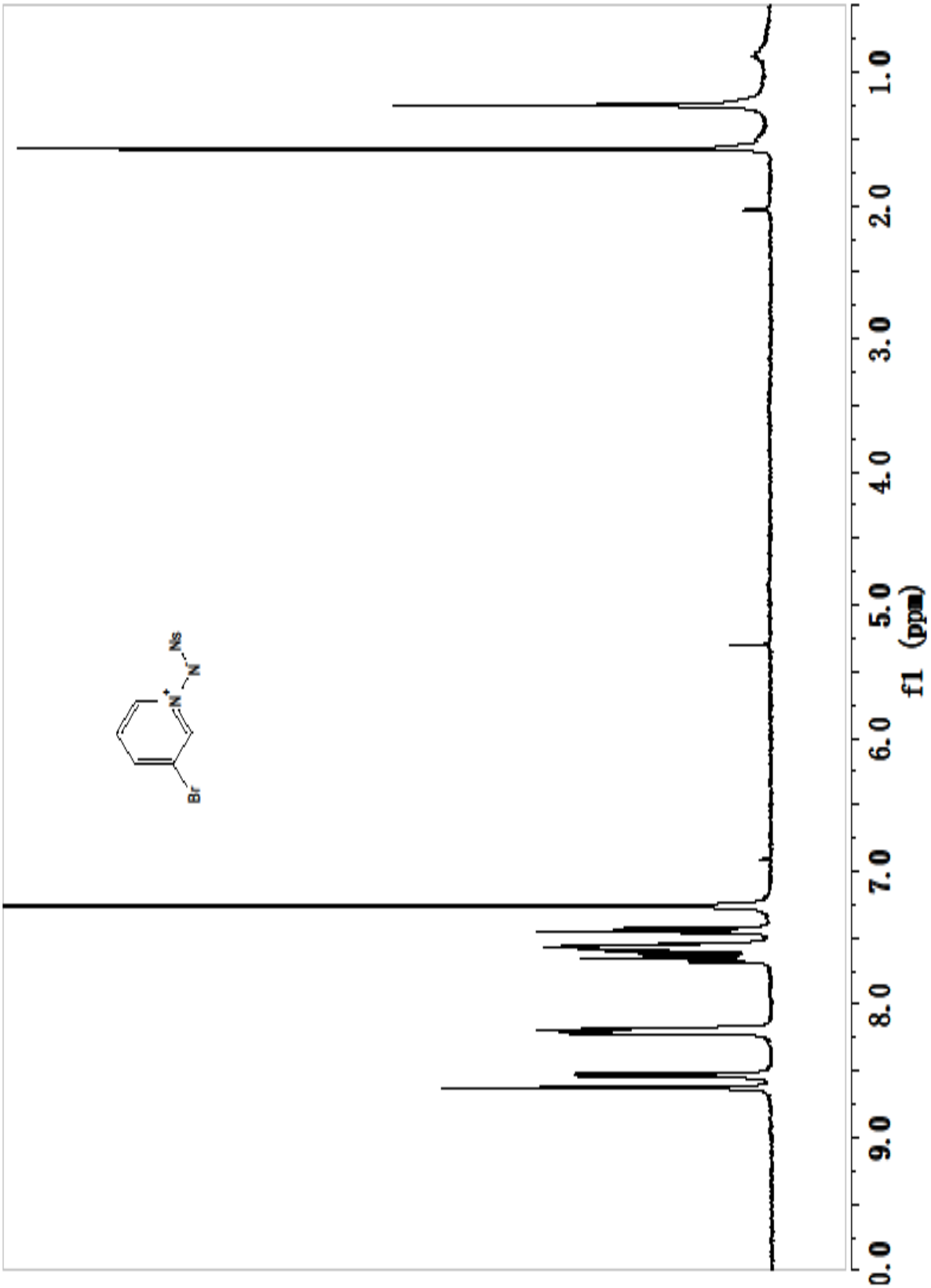


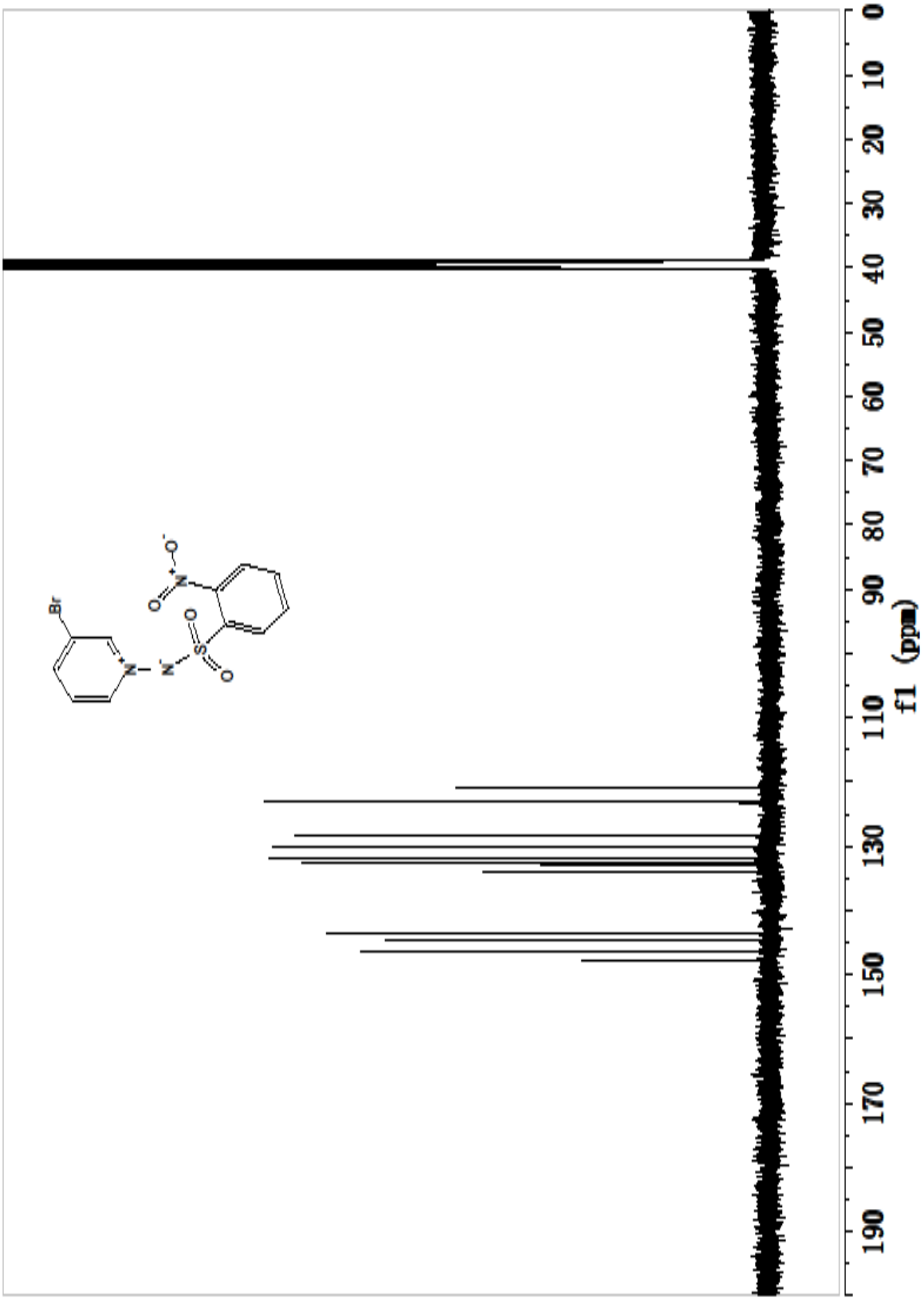








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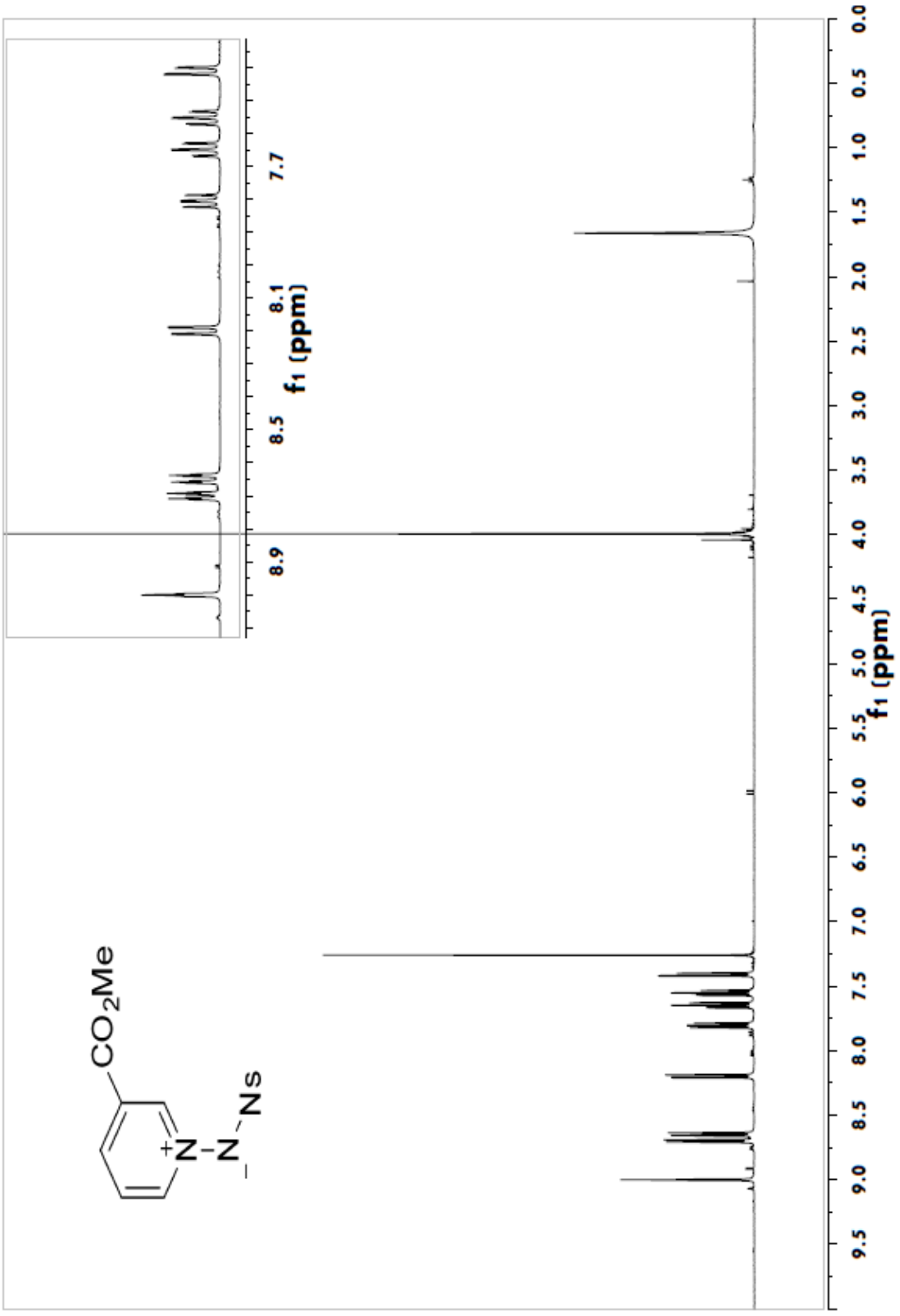
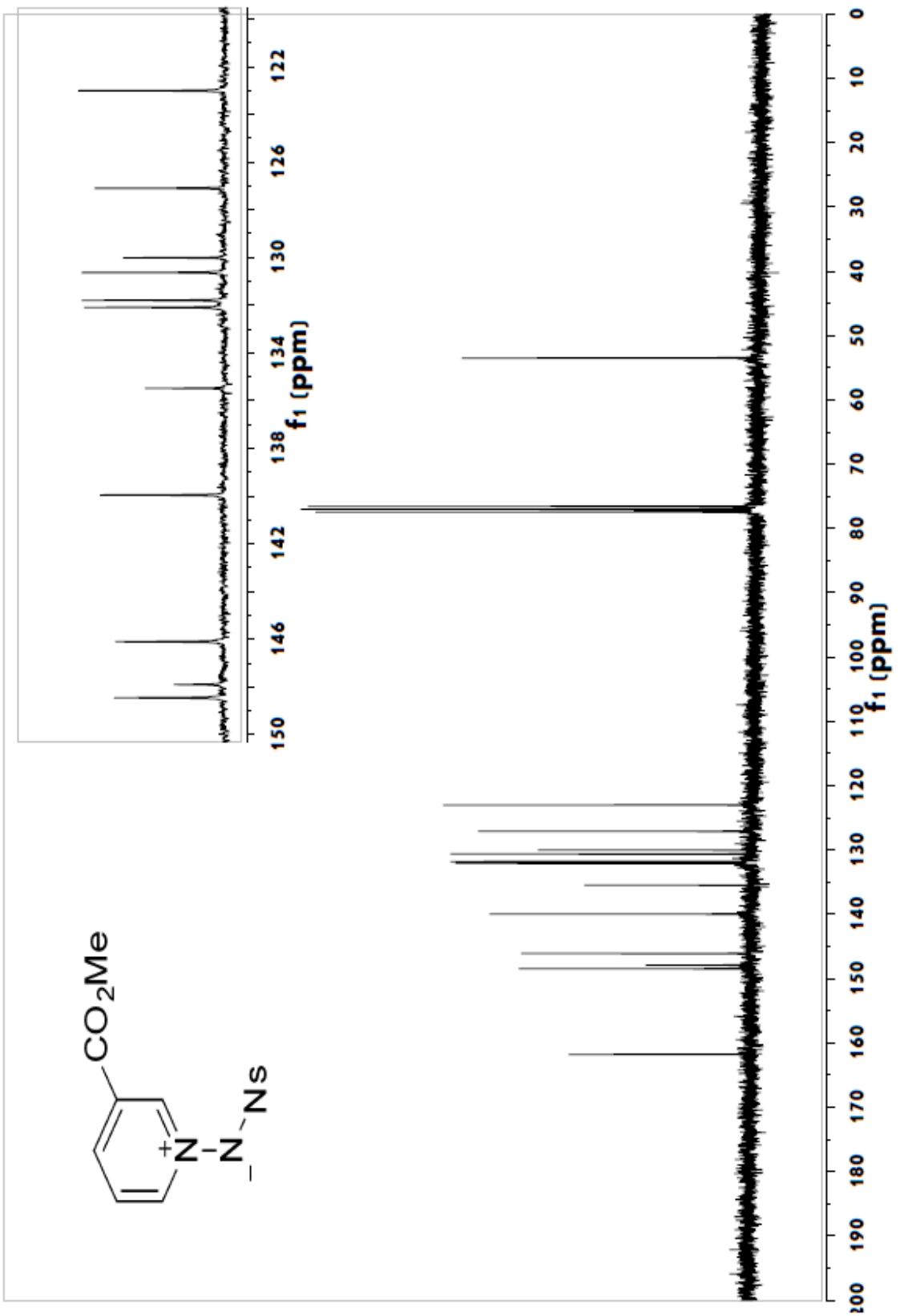
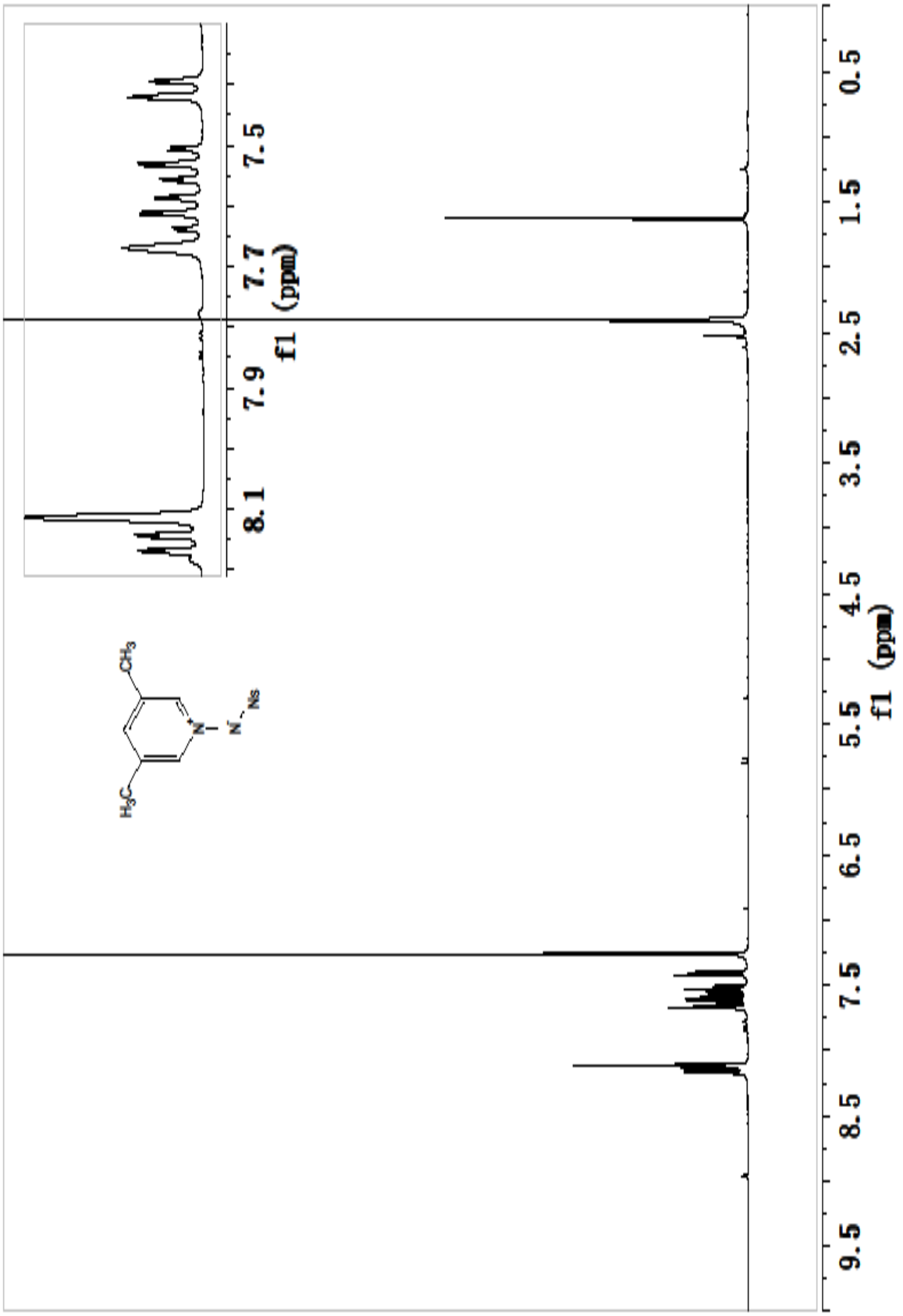
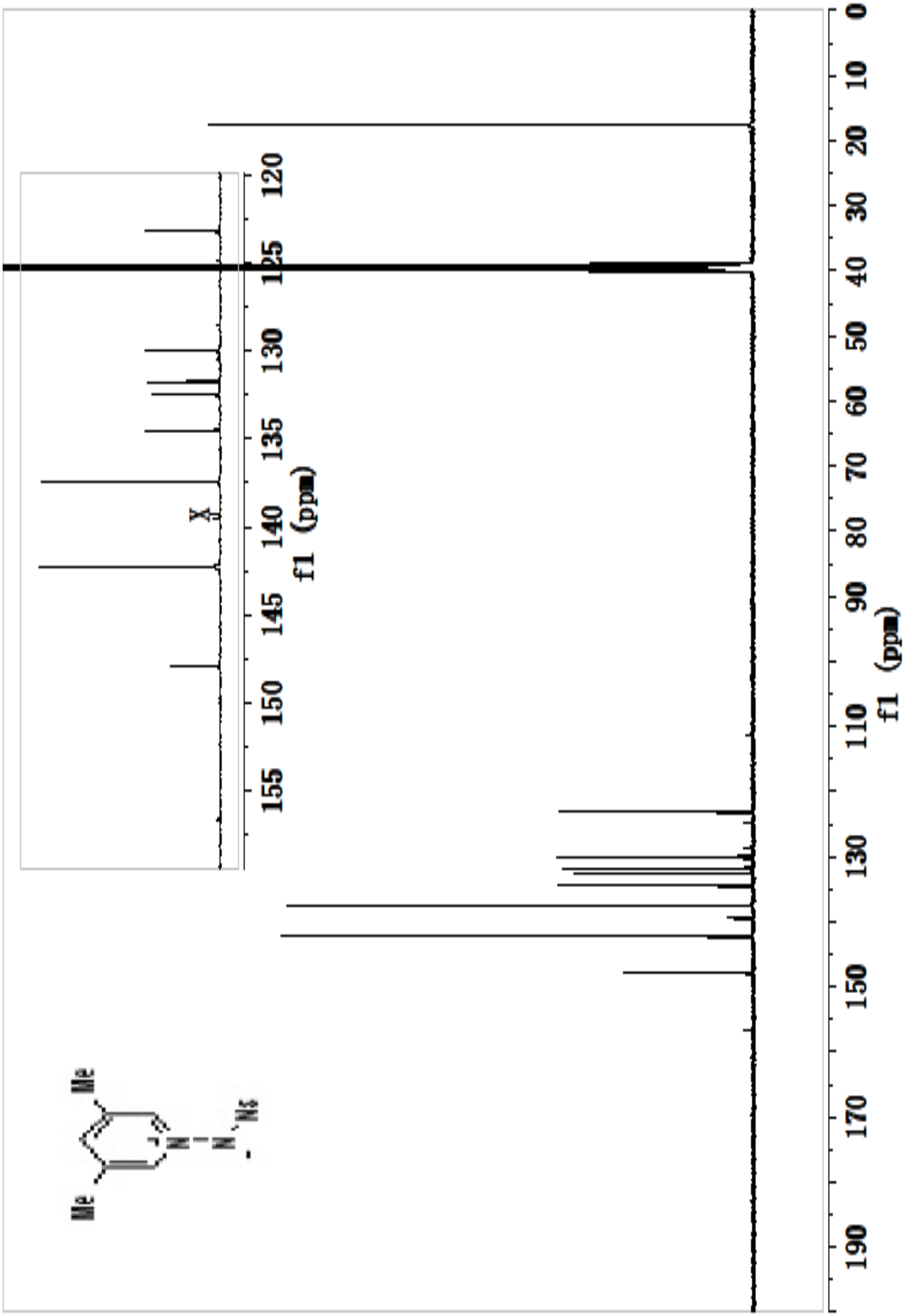
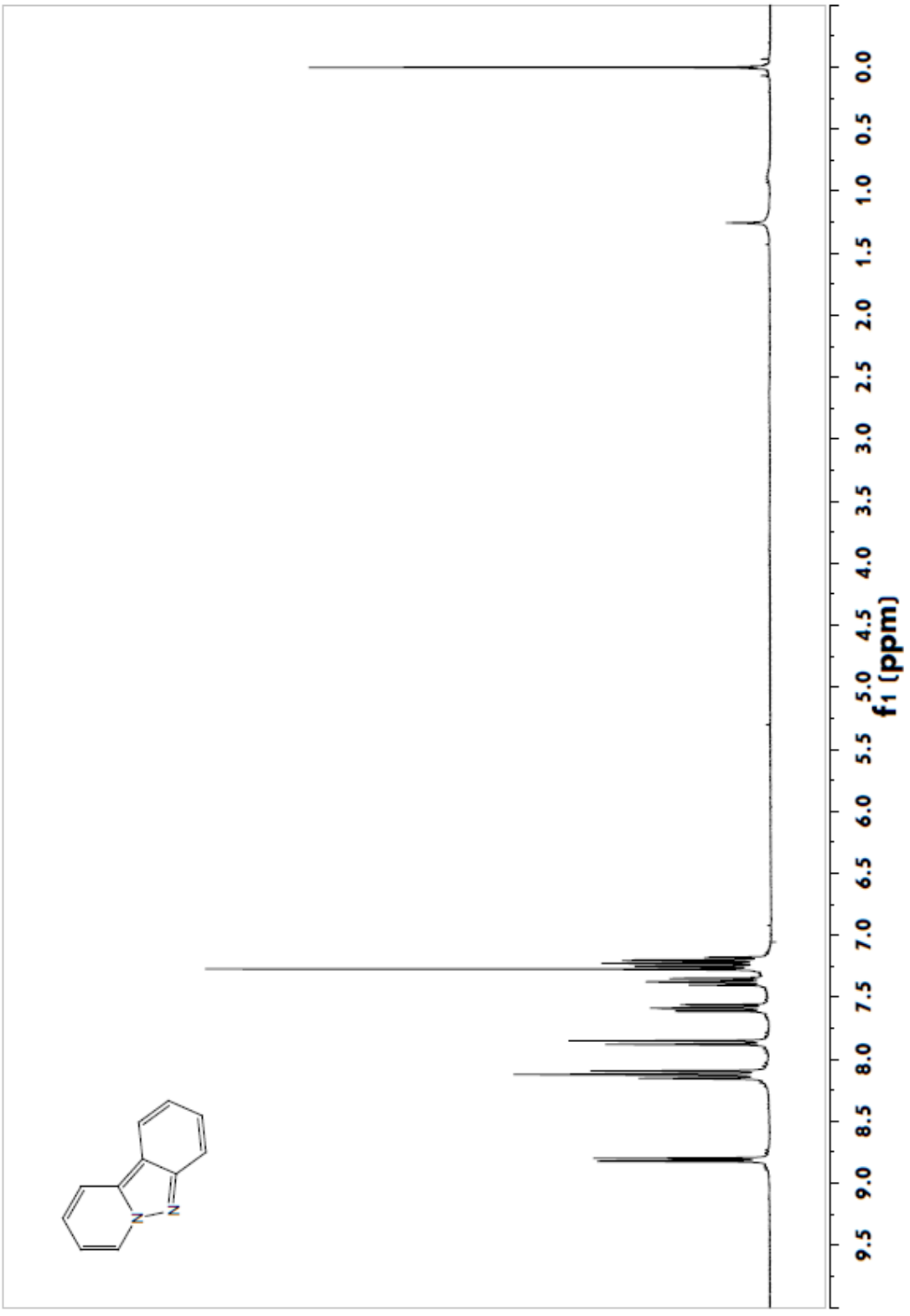
f1 (ppm)

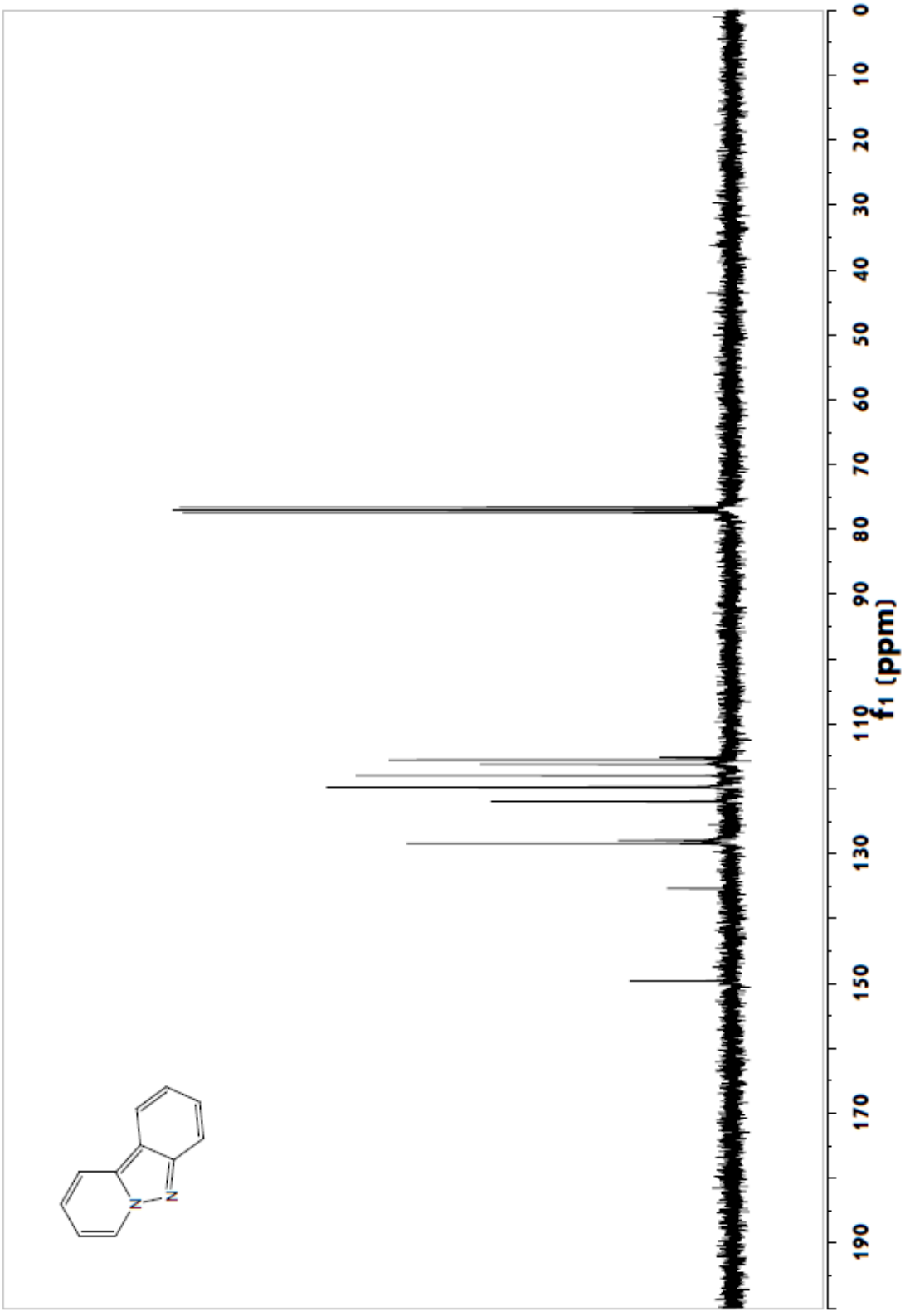


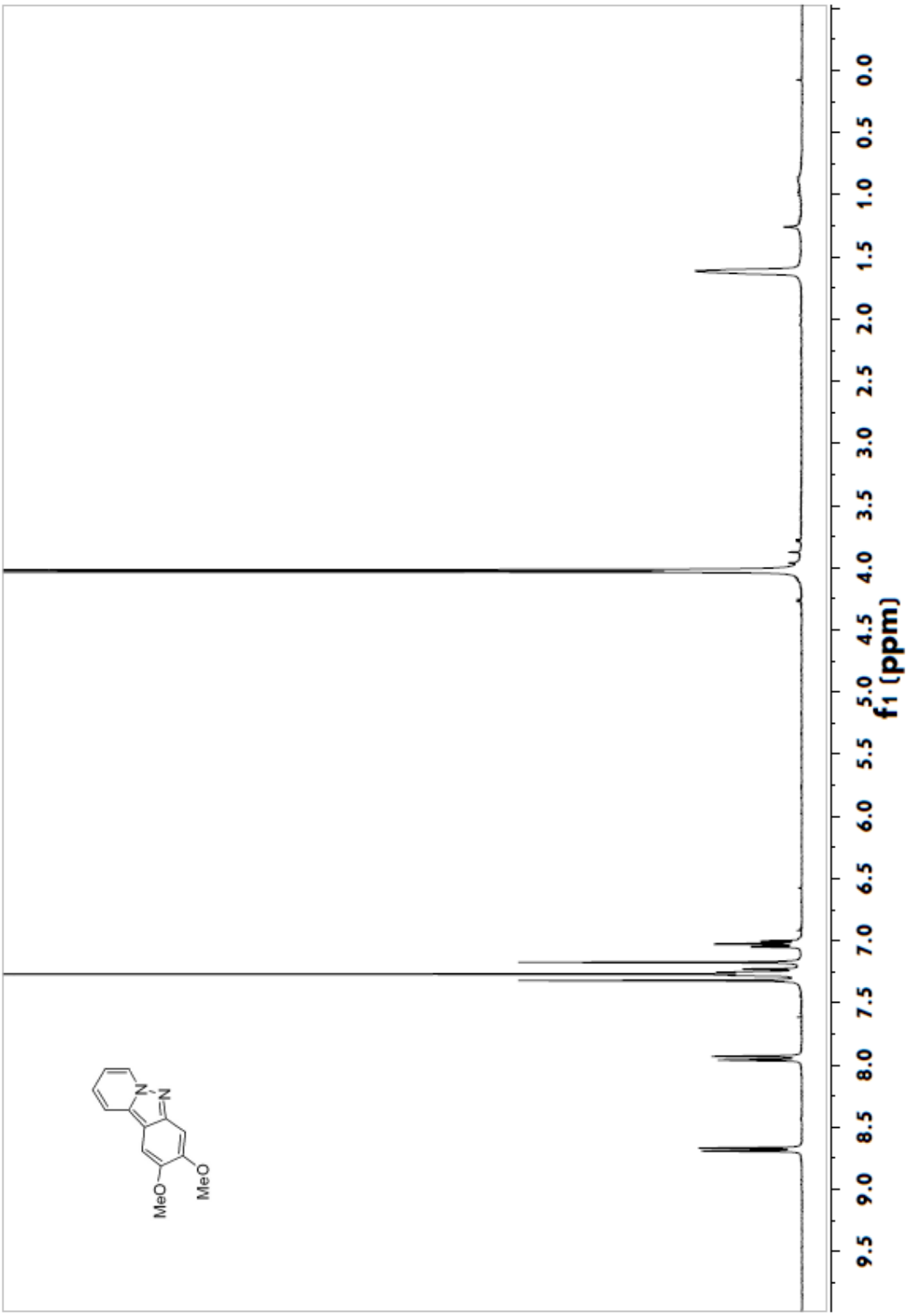


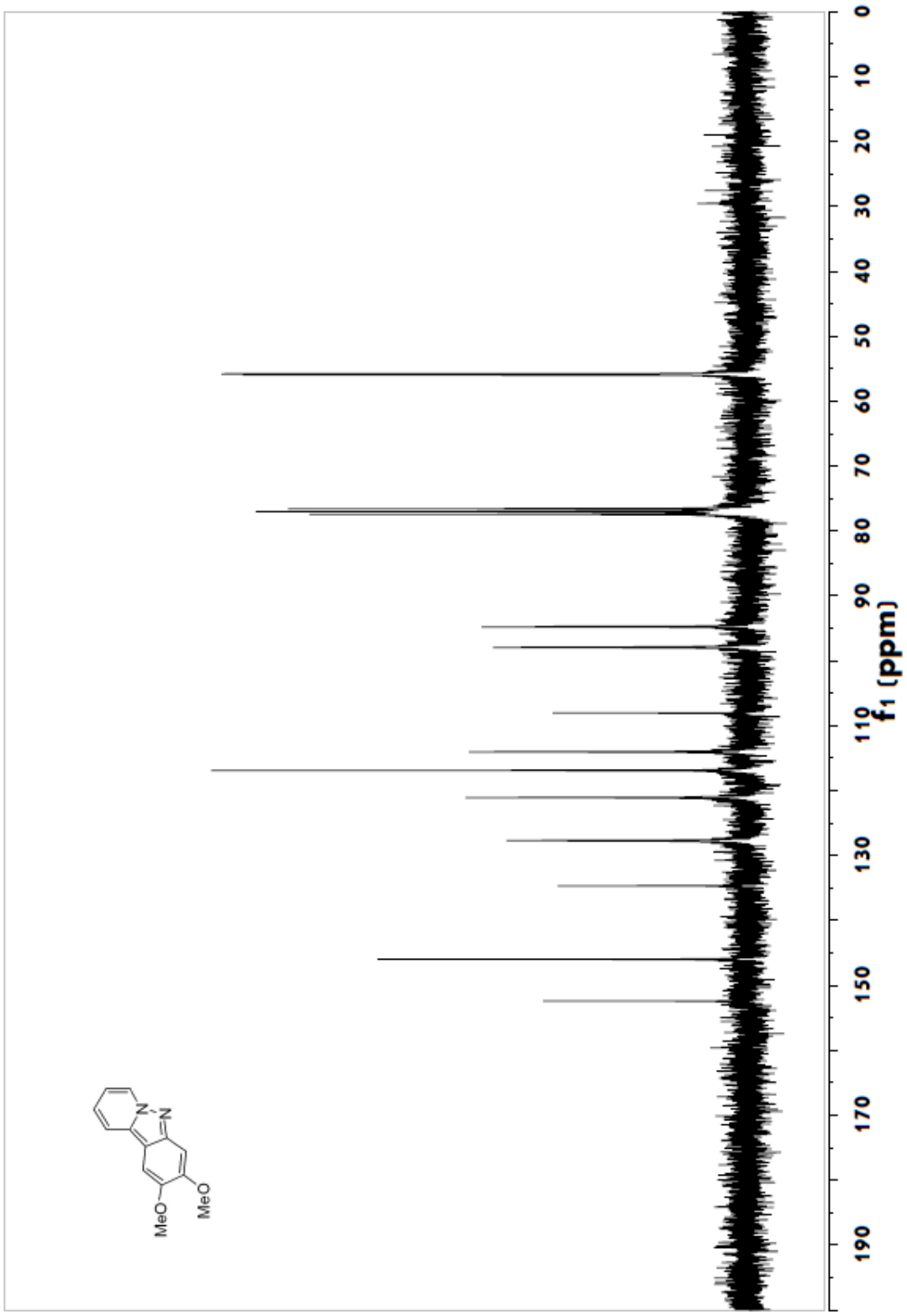


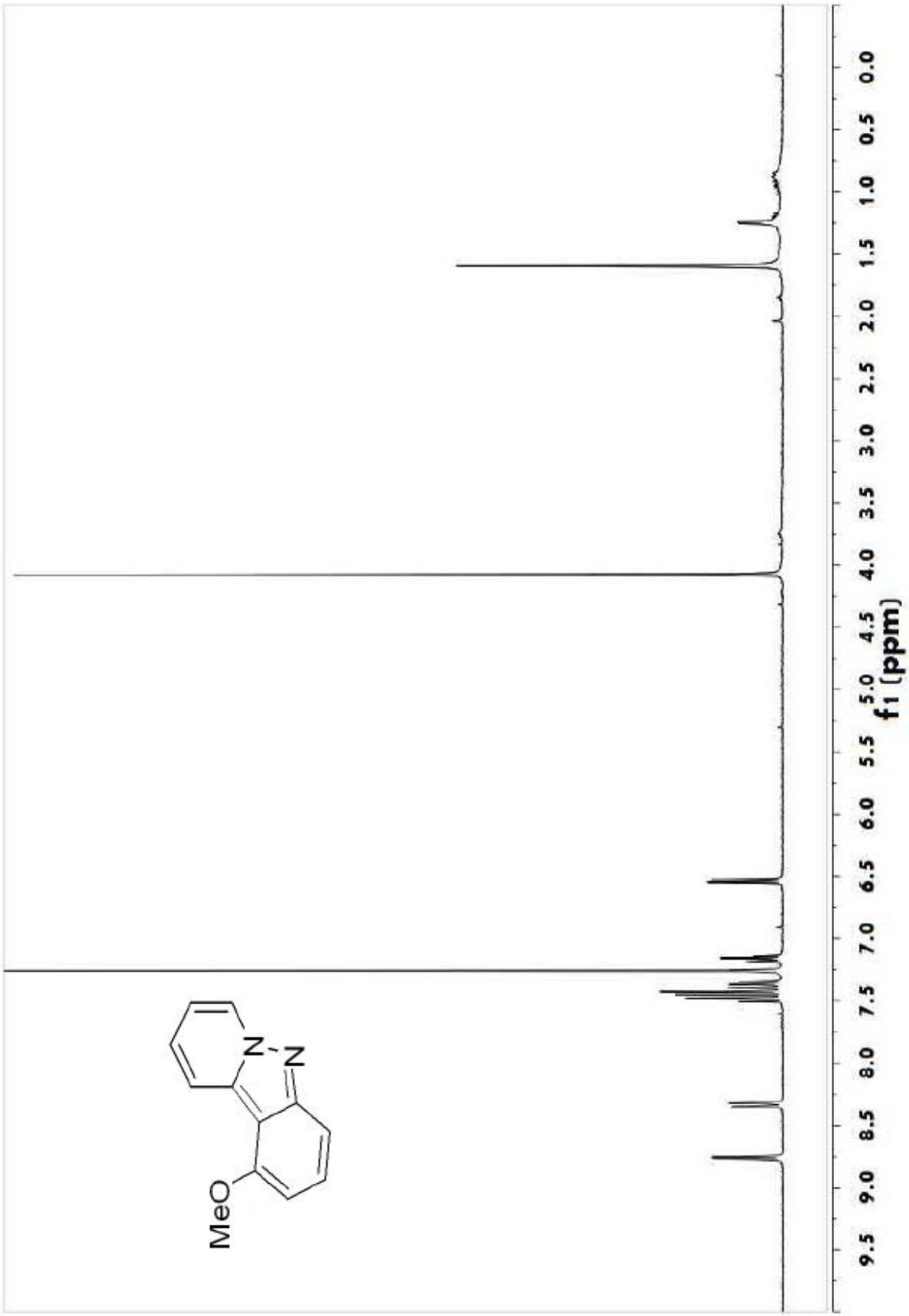


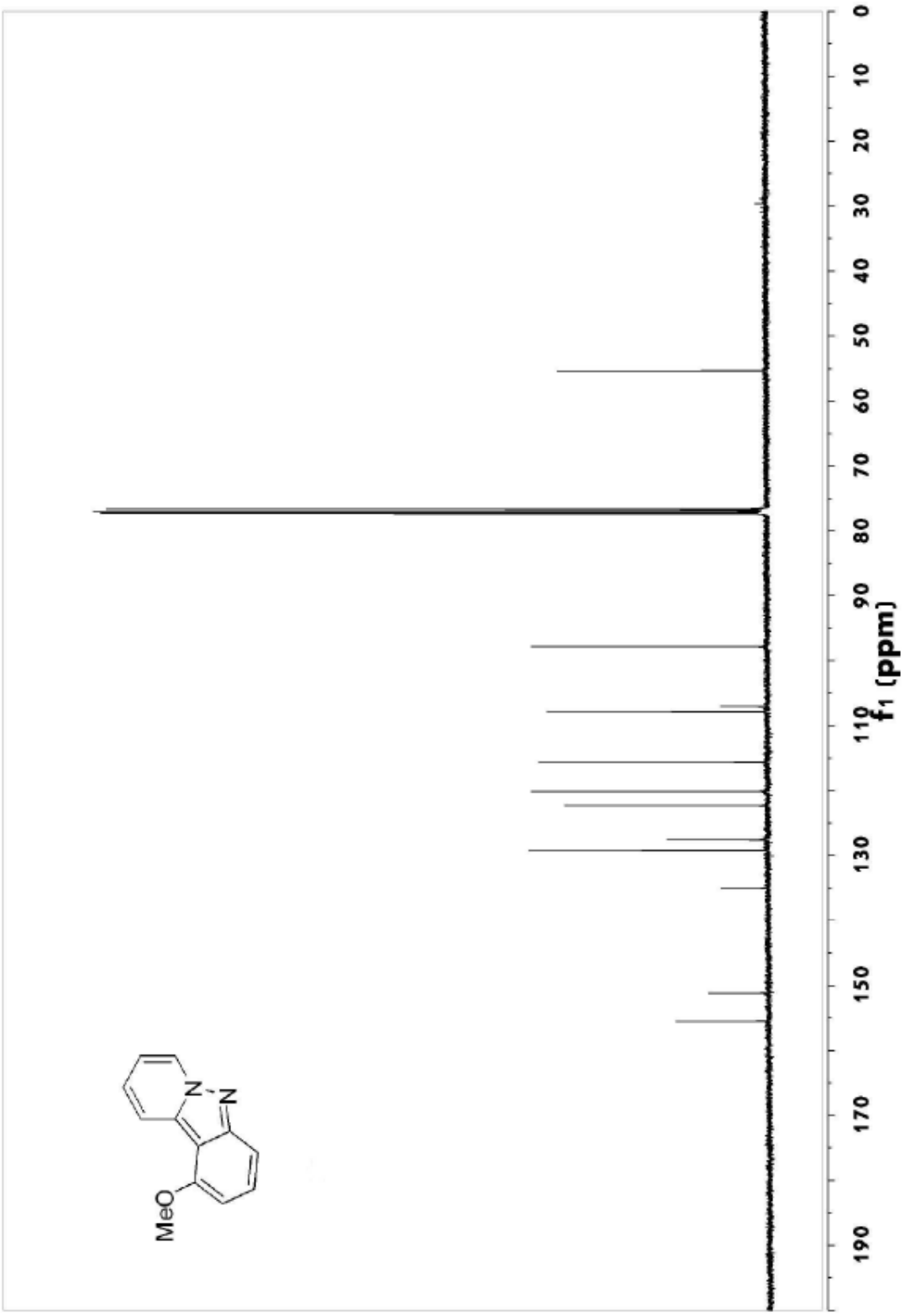






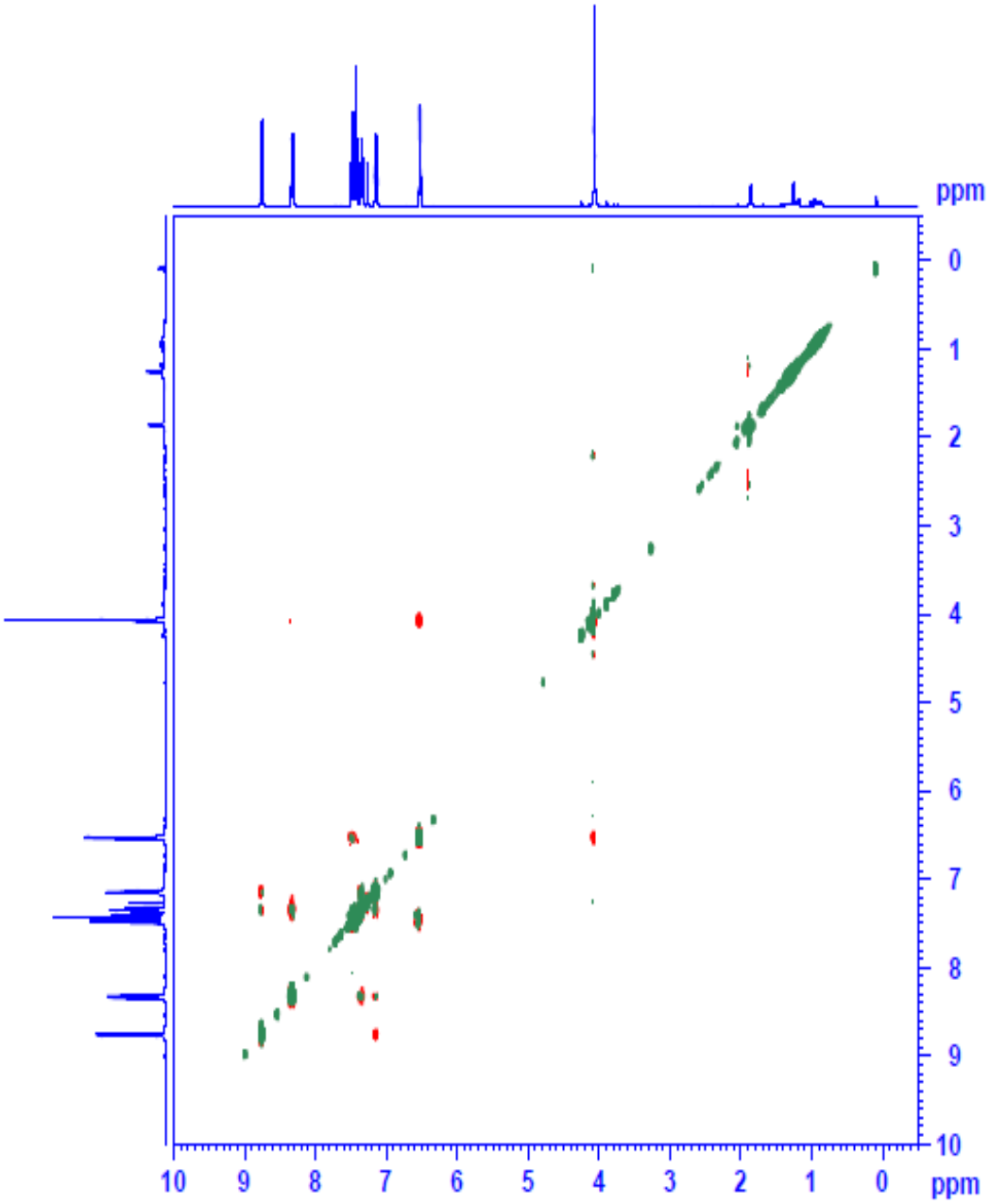


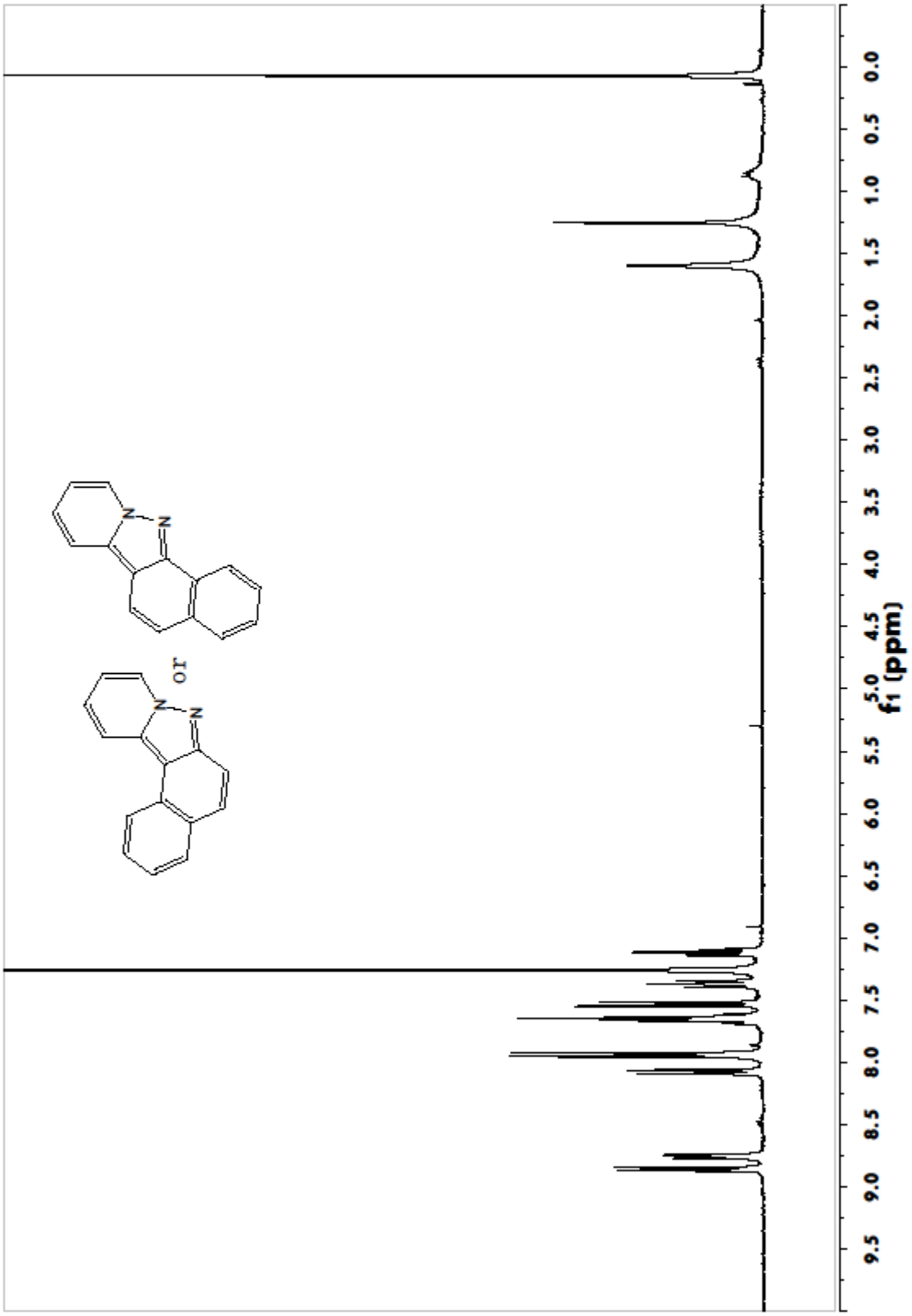


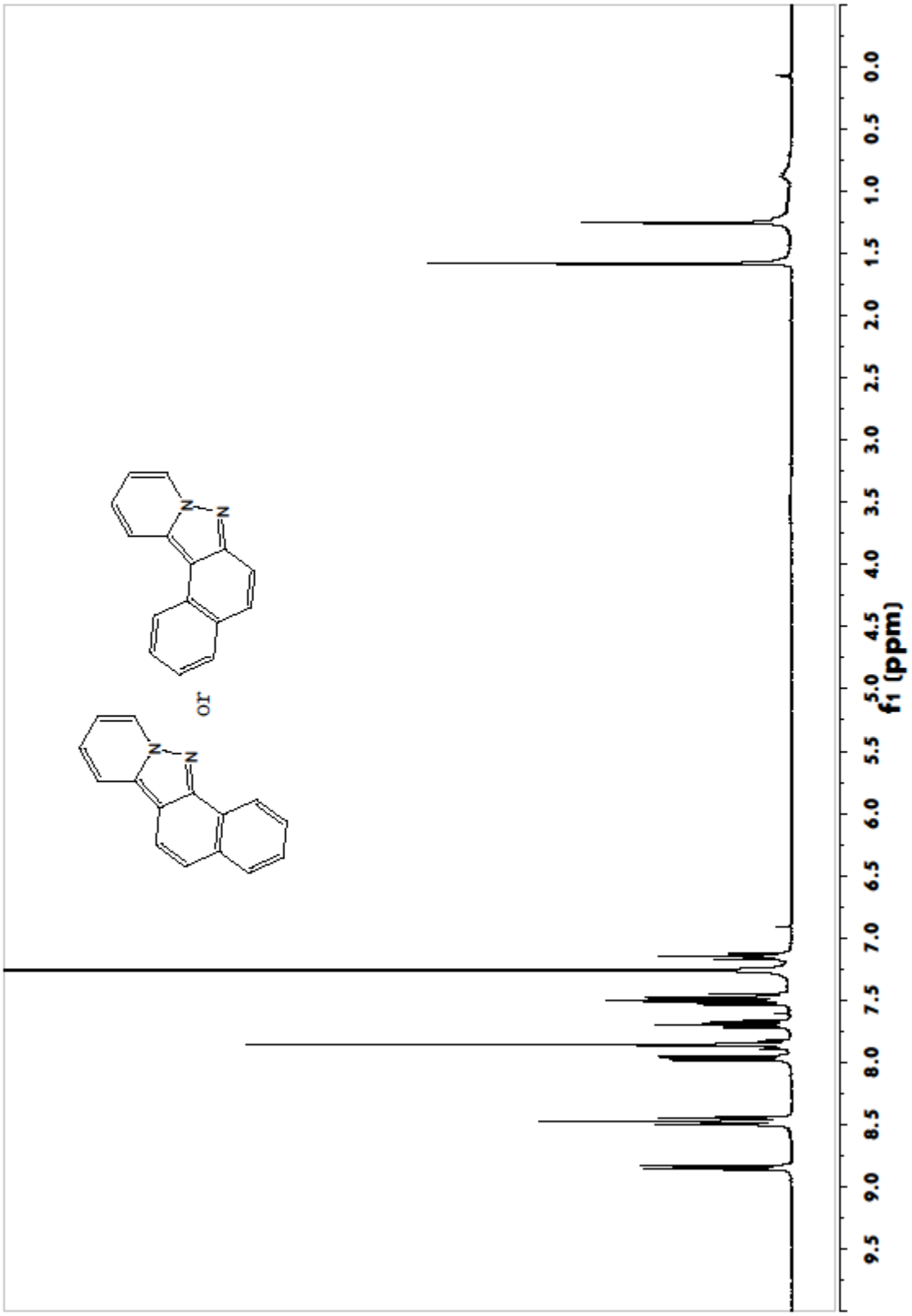


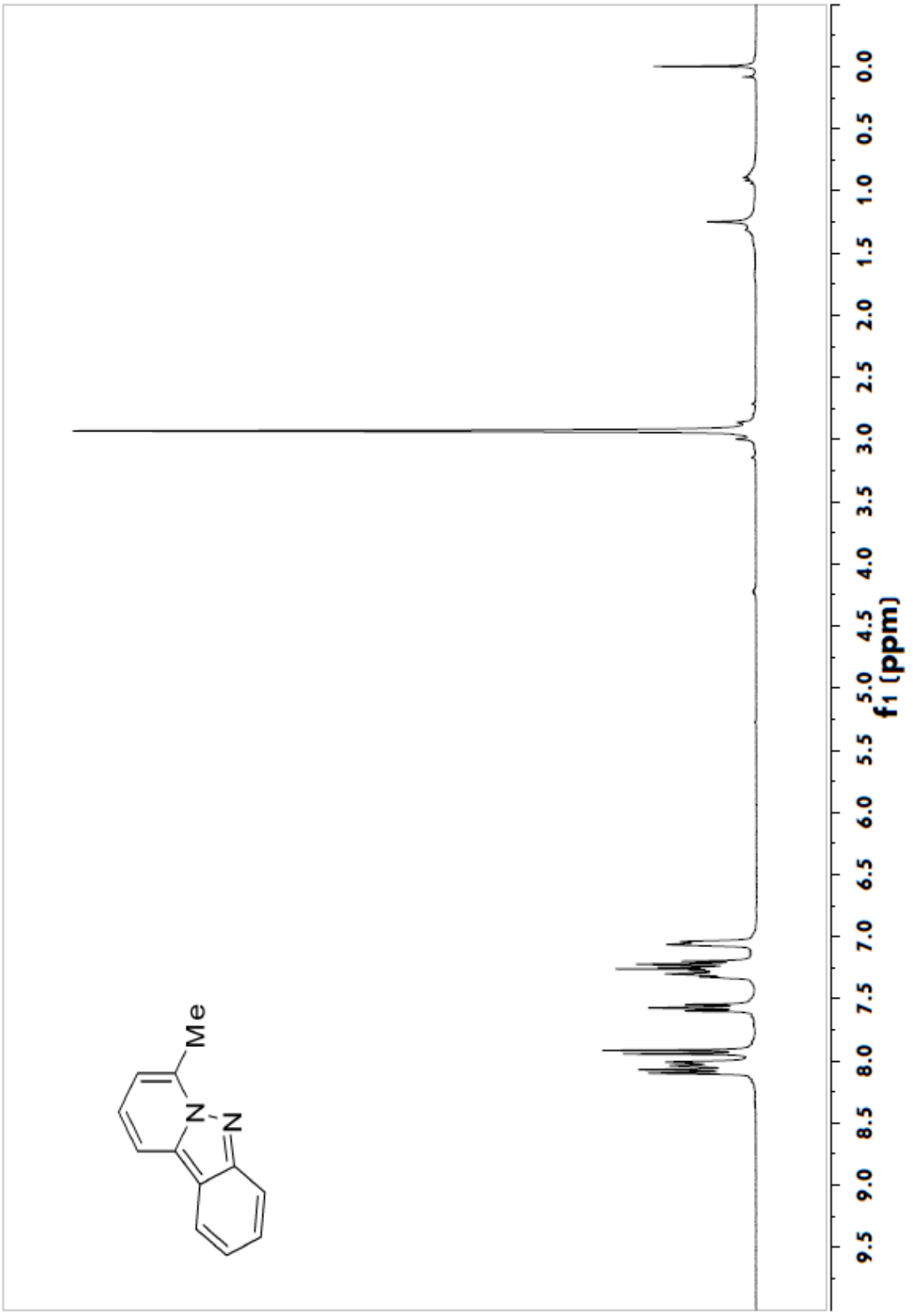
2D NMR Spectra for Compound **8c**:

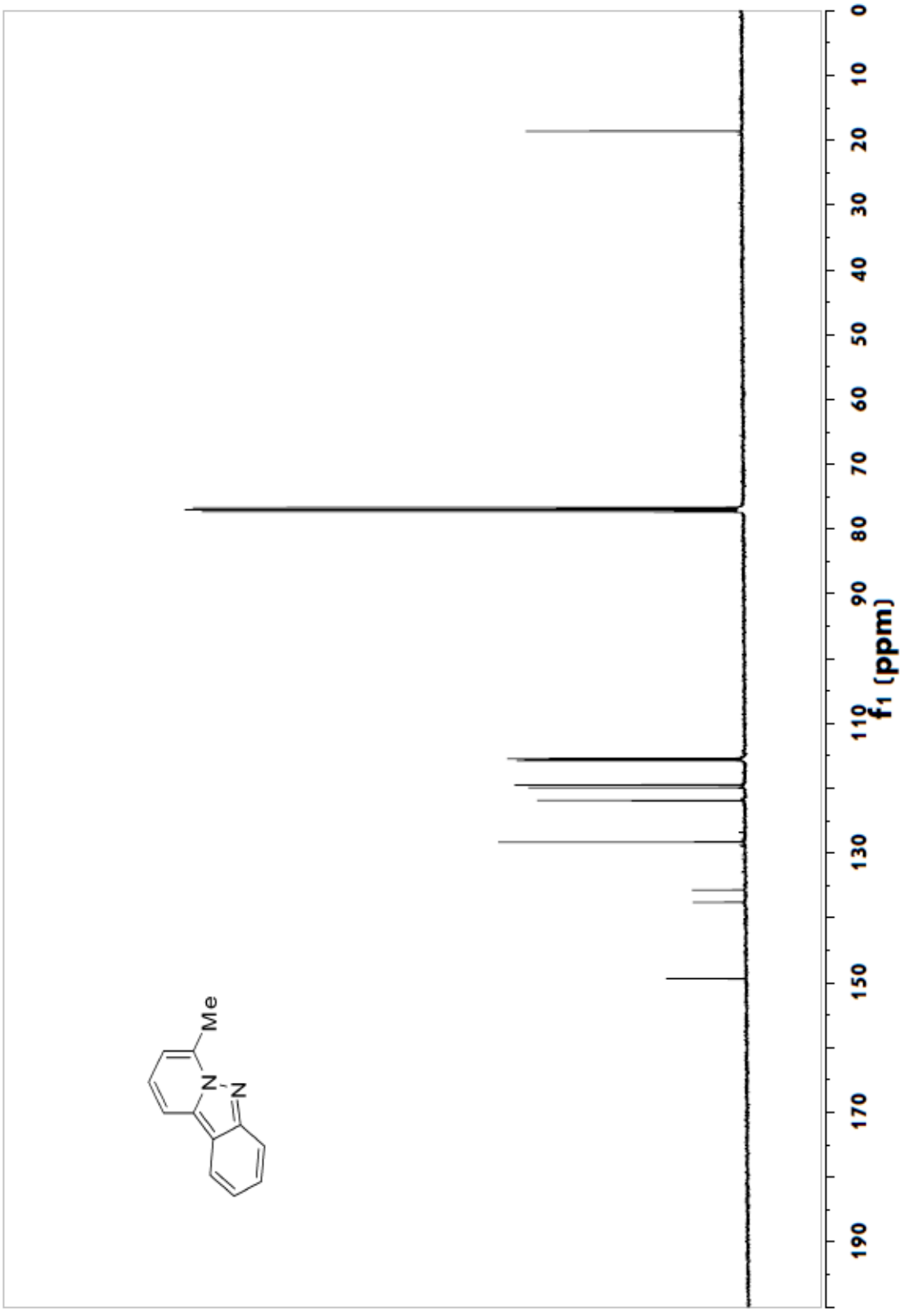
NOESY, showing OMe close to the H at 8.32 ppm.

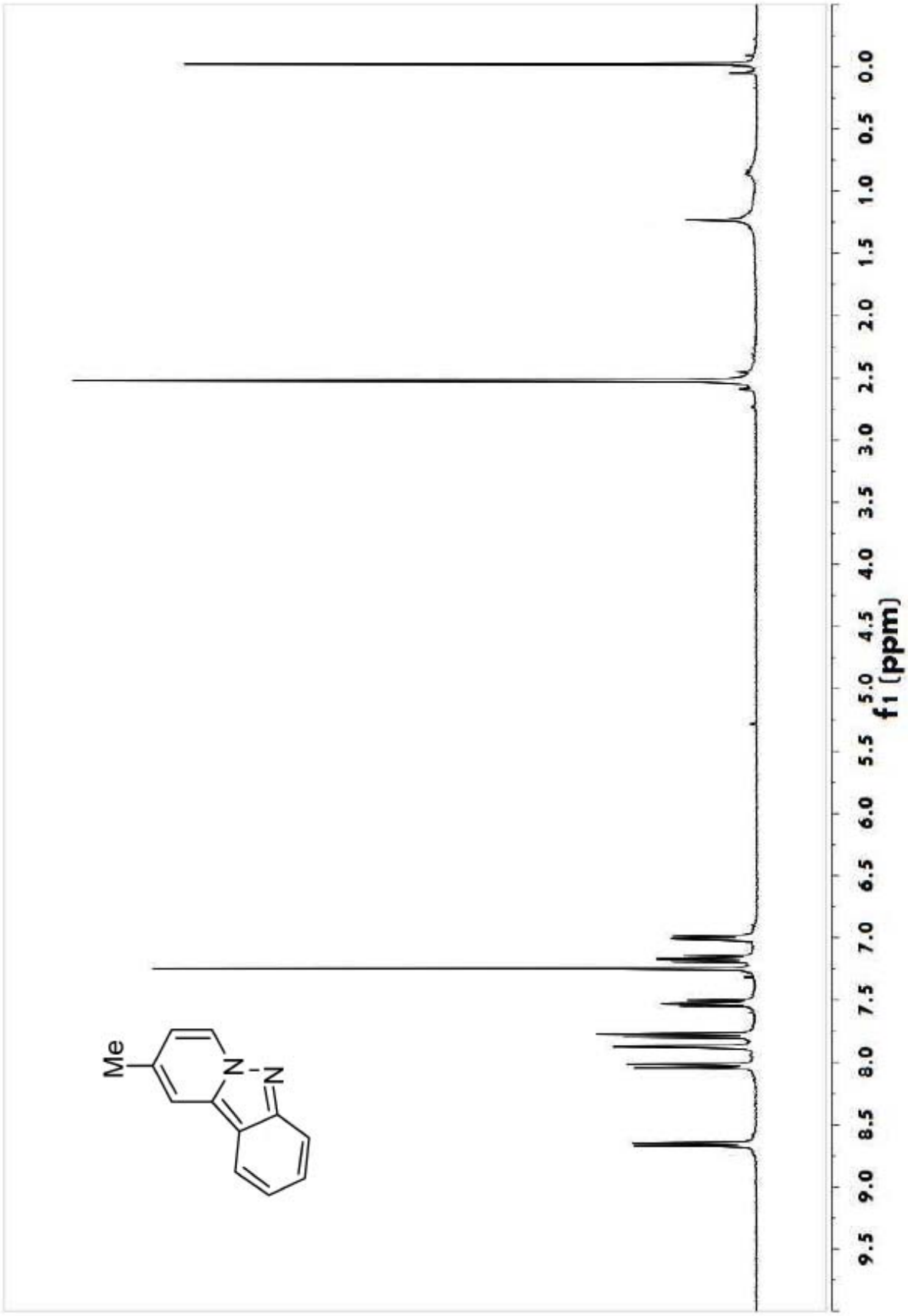


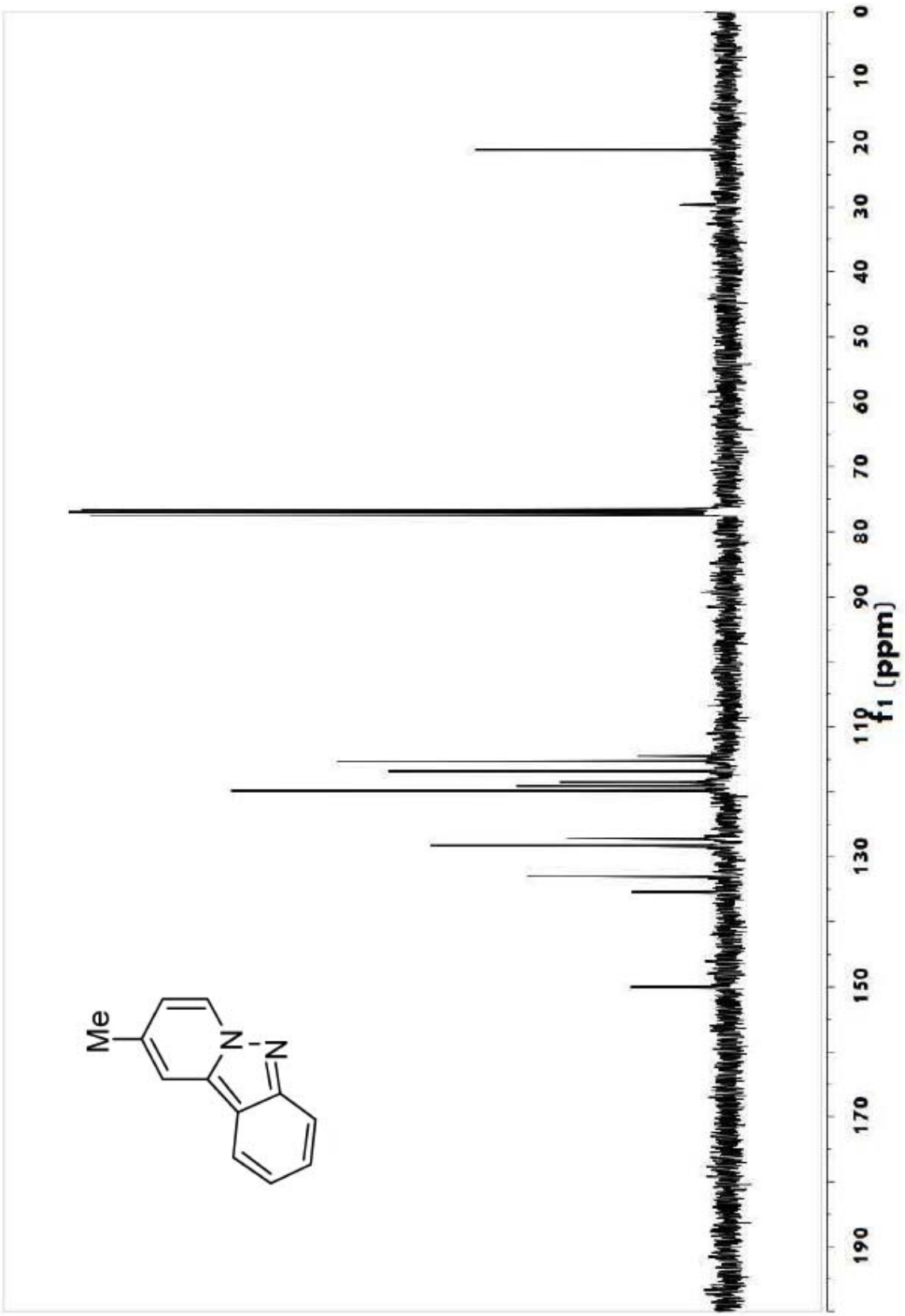


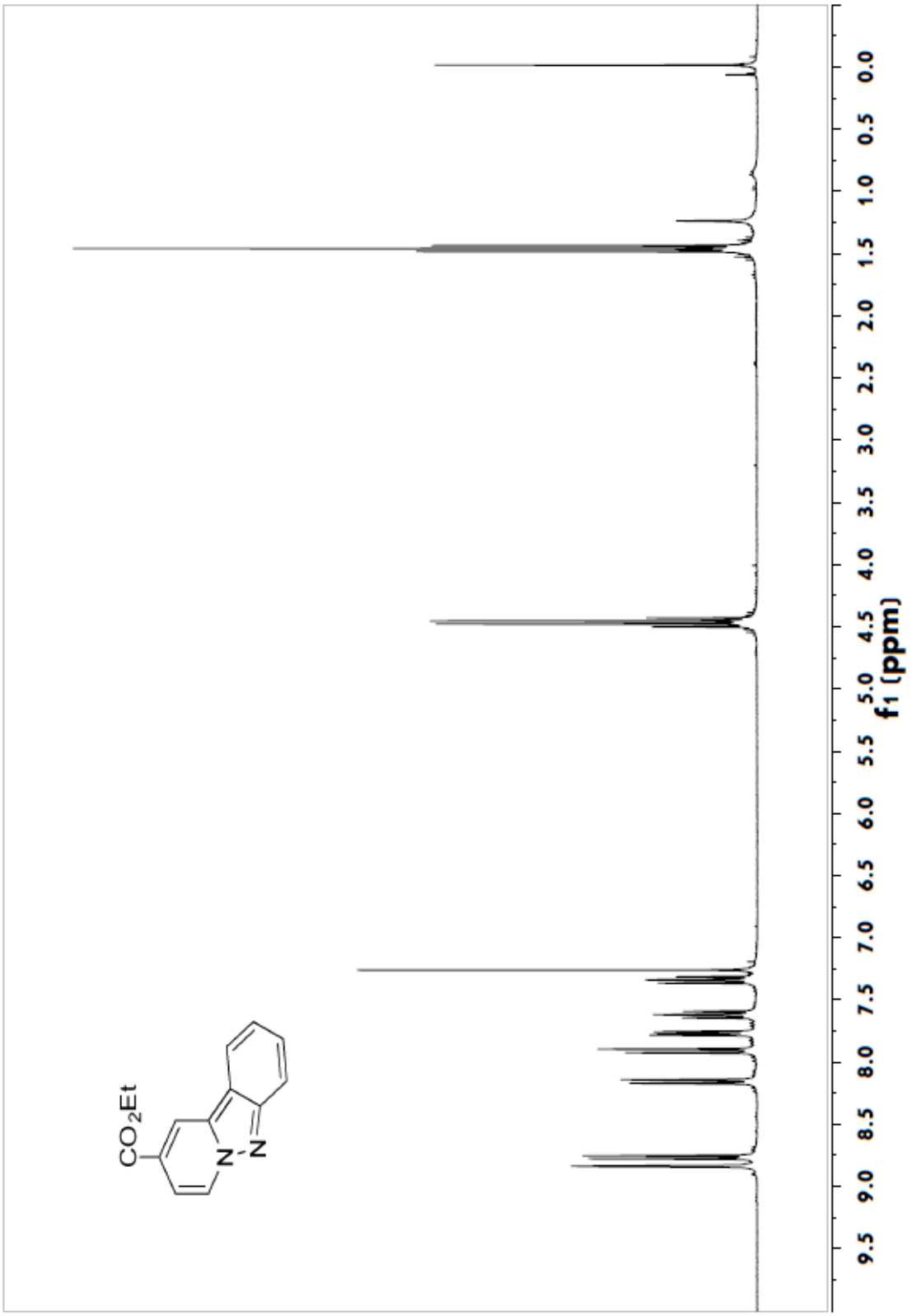


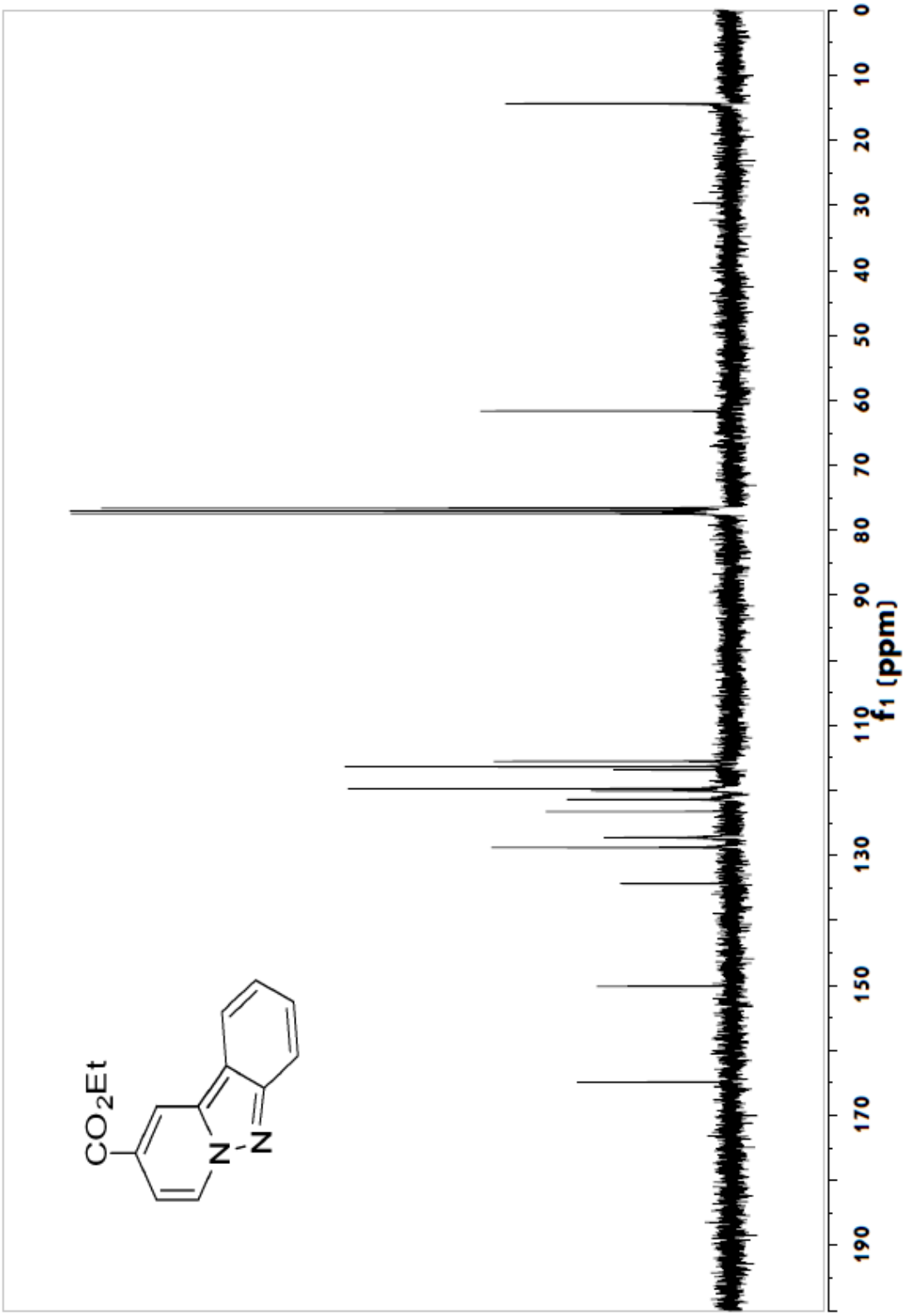


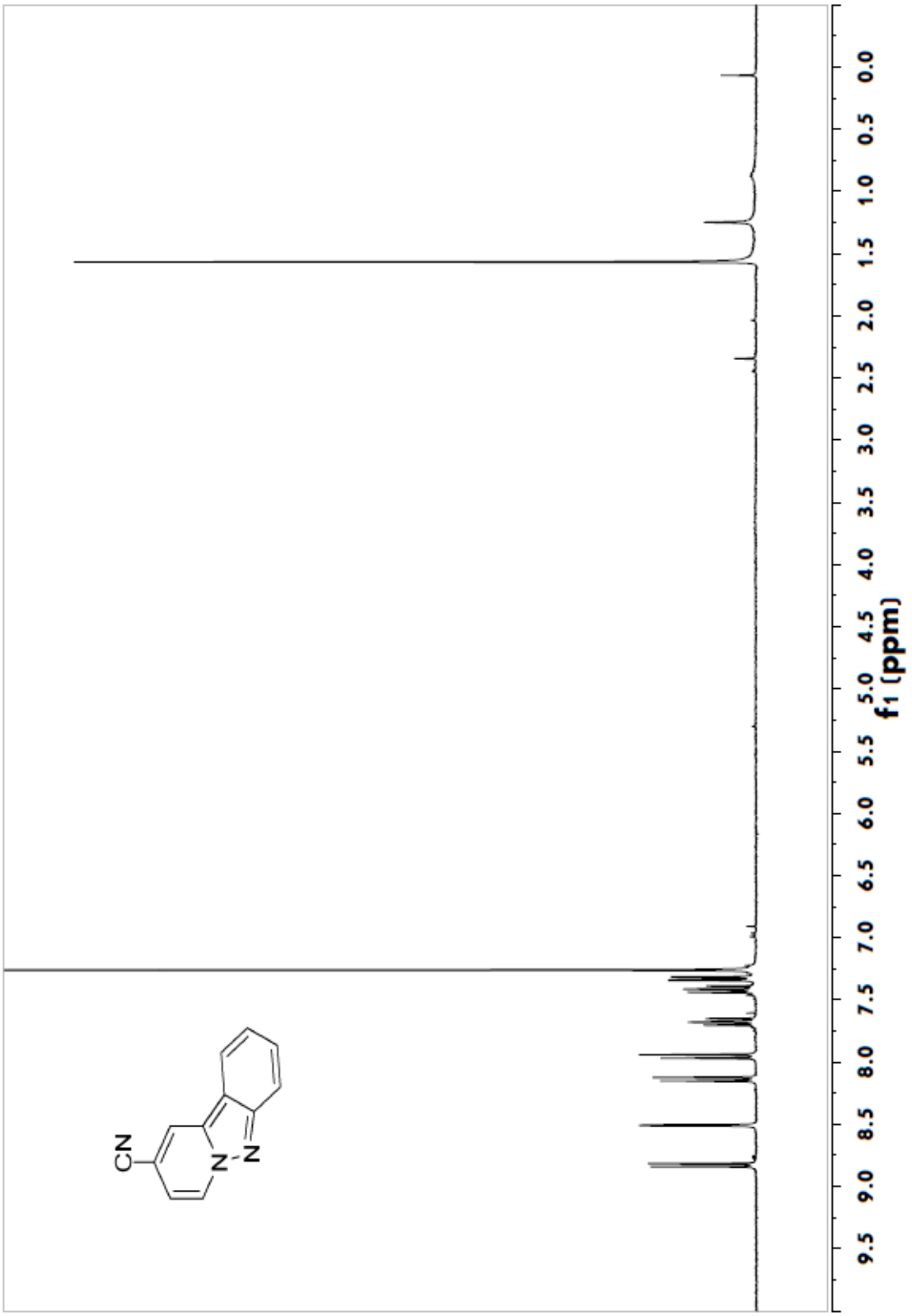


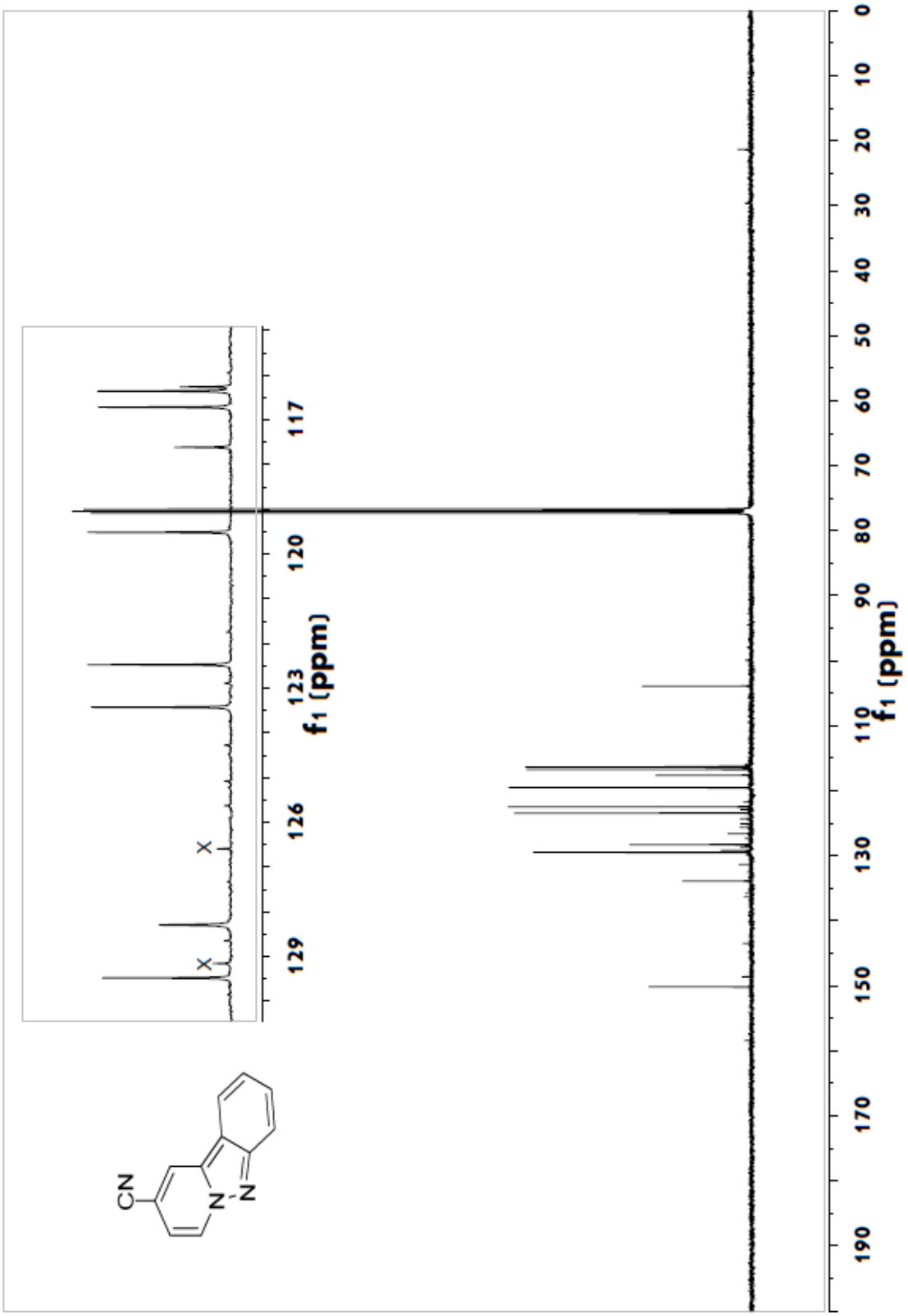


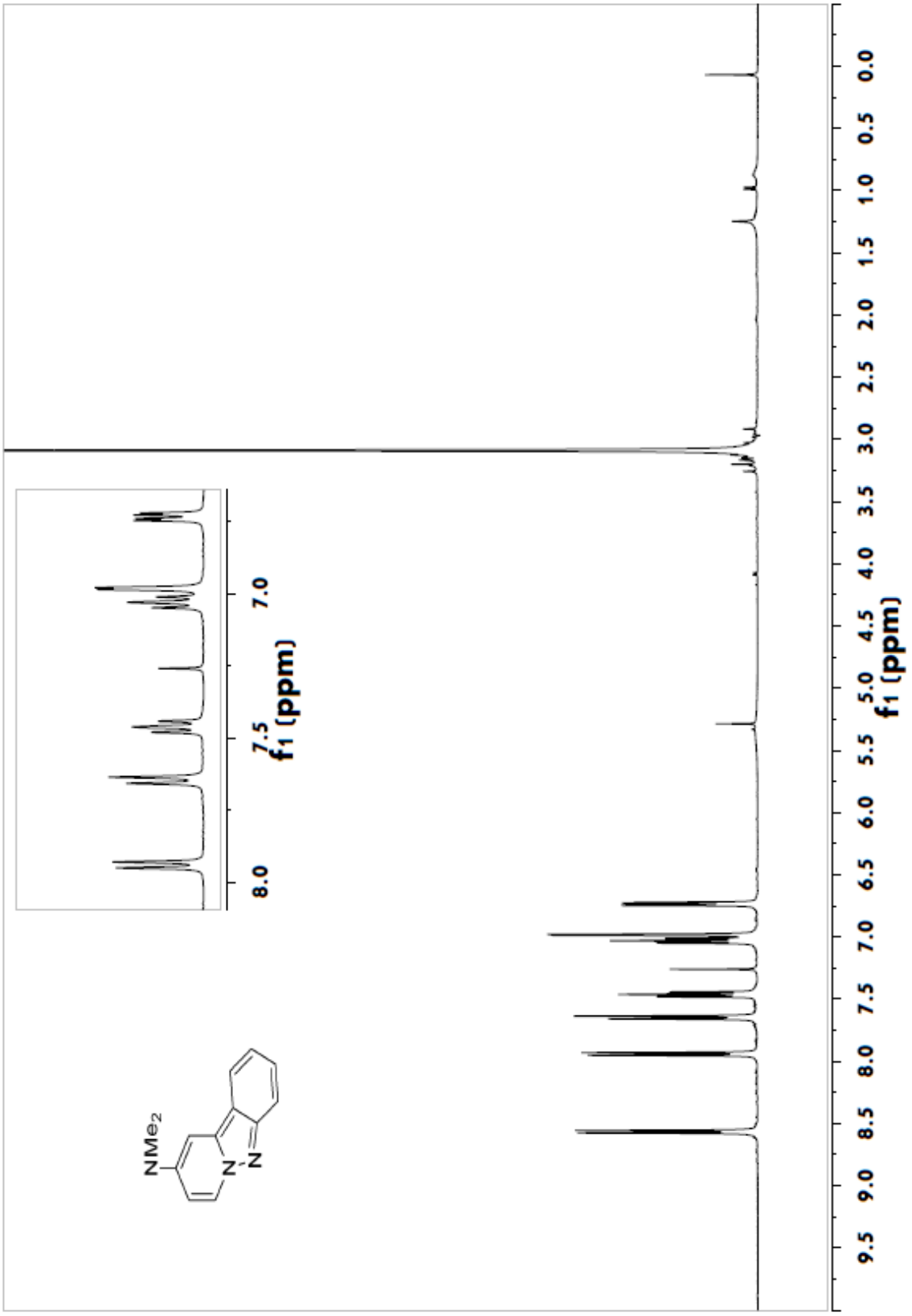


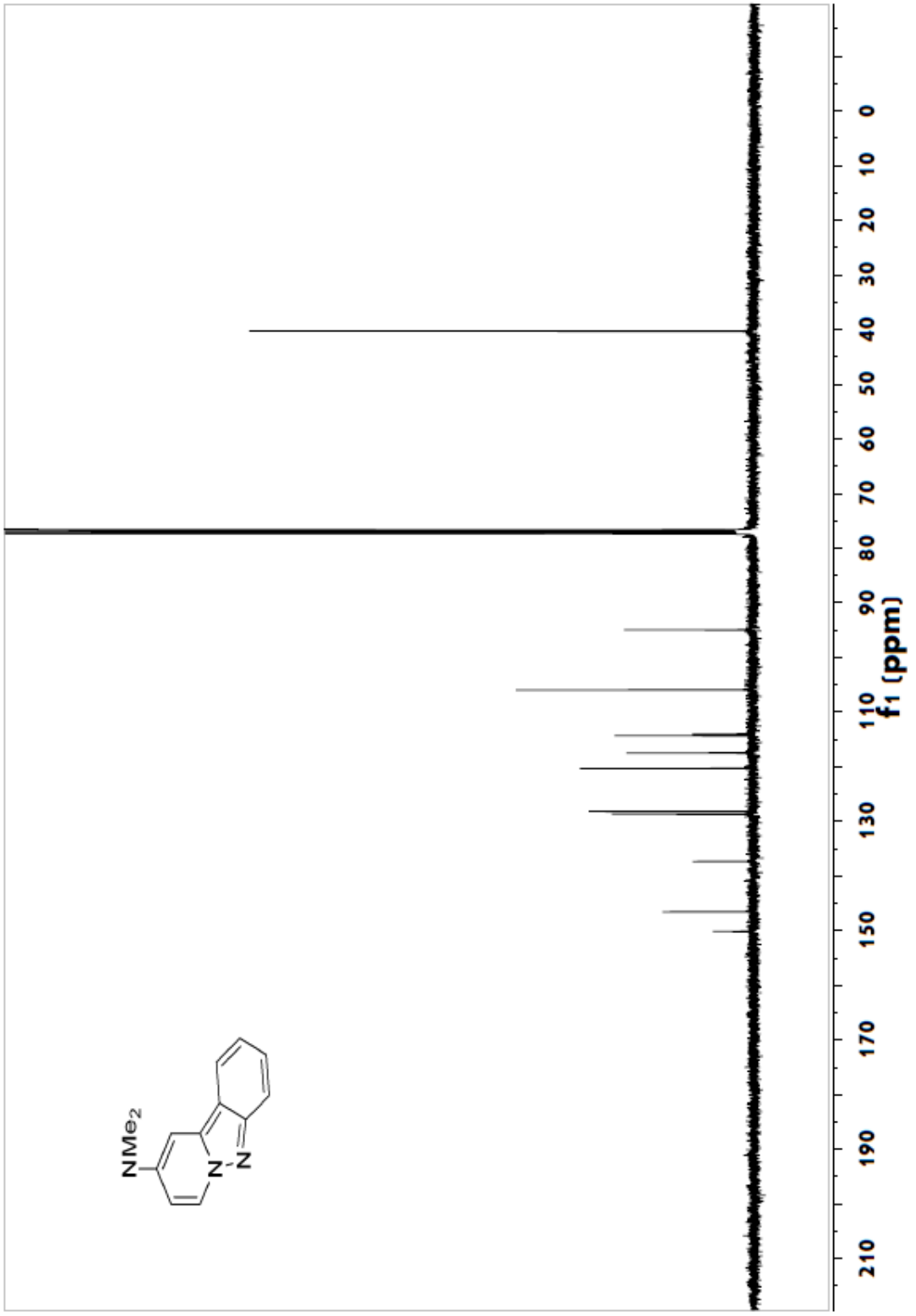


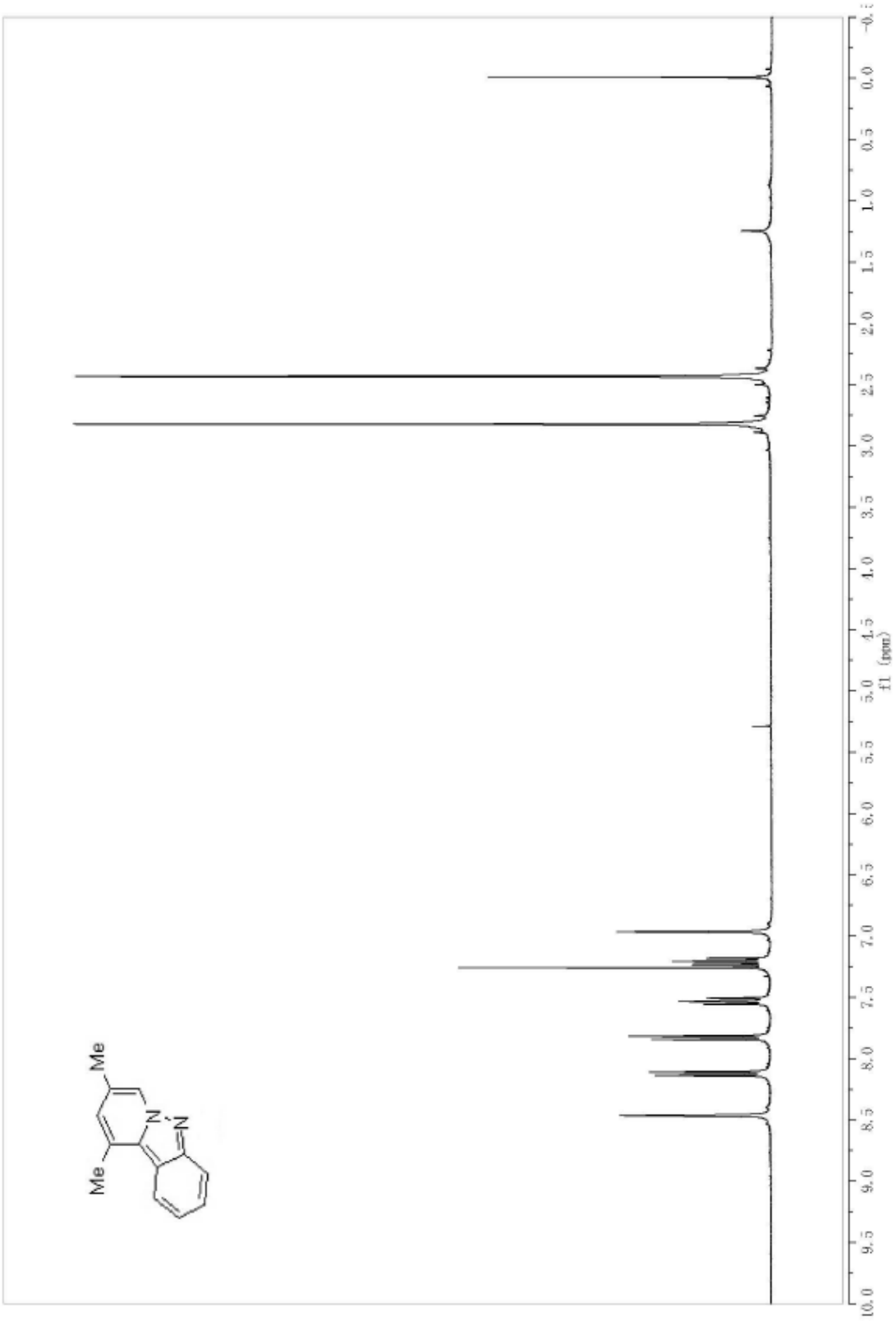


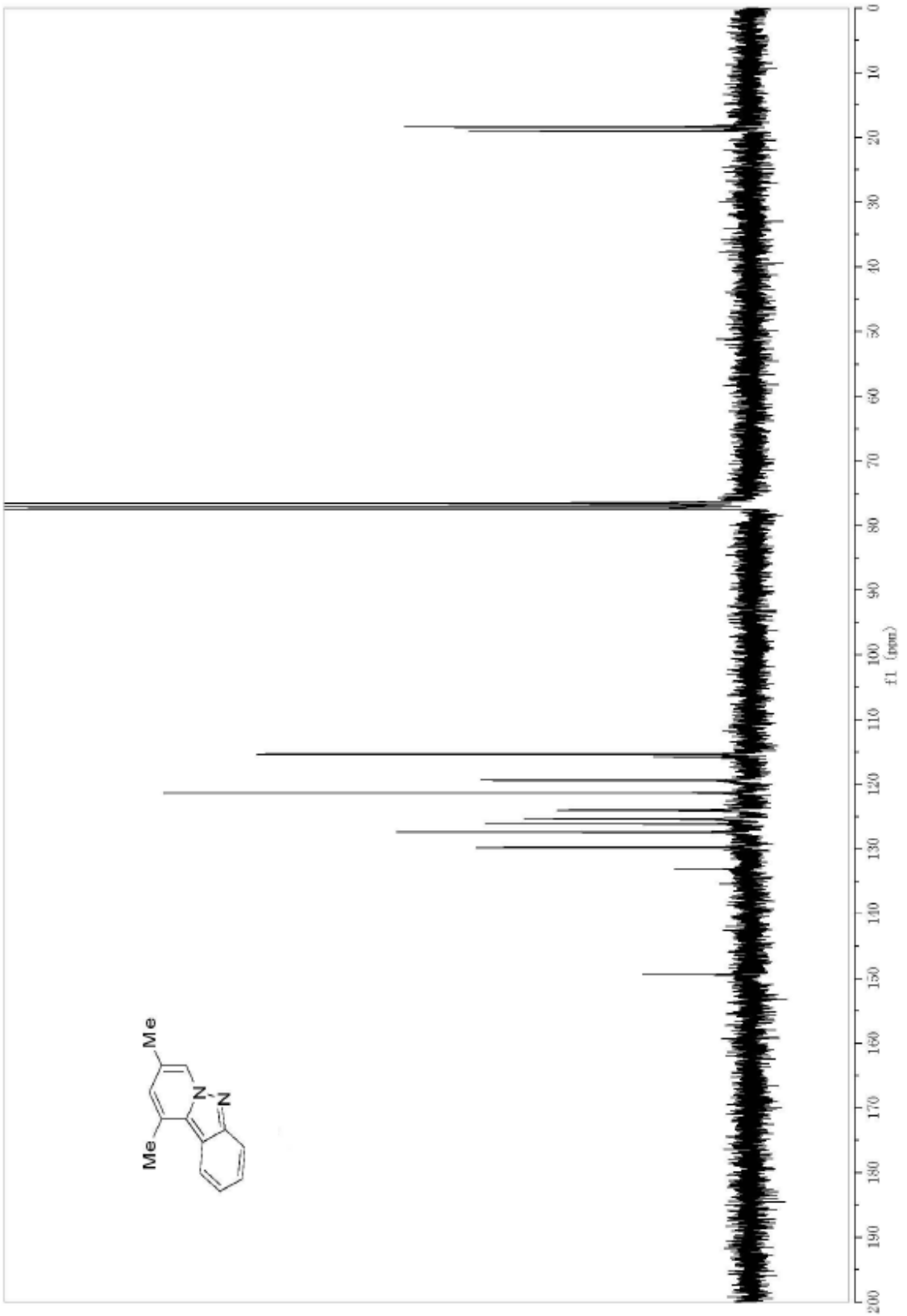


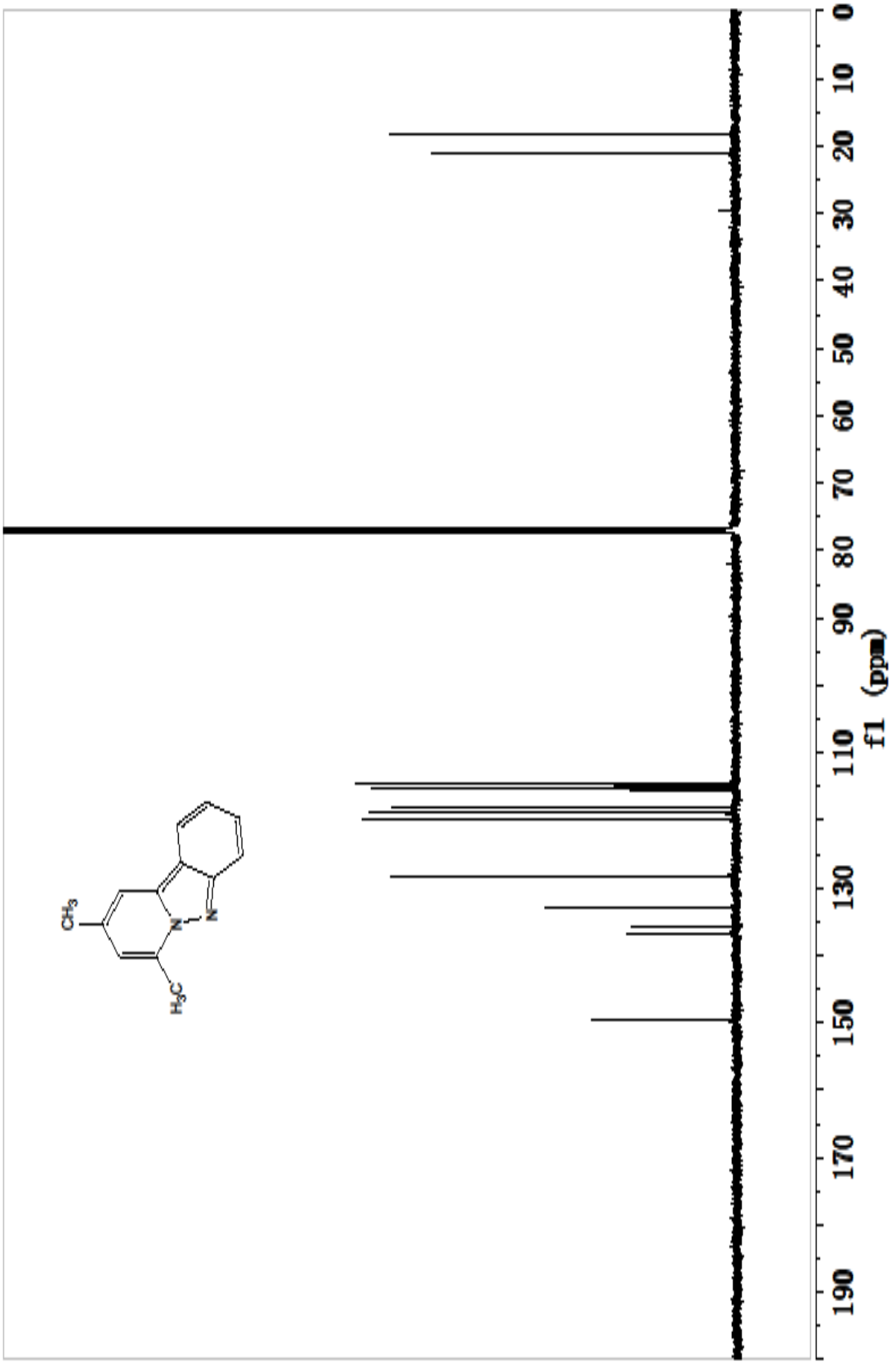


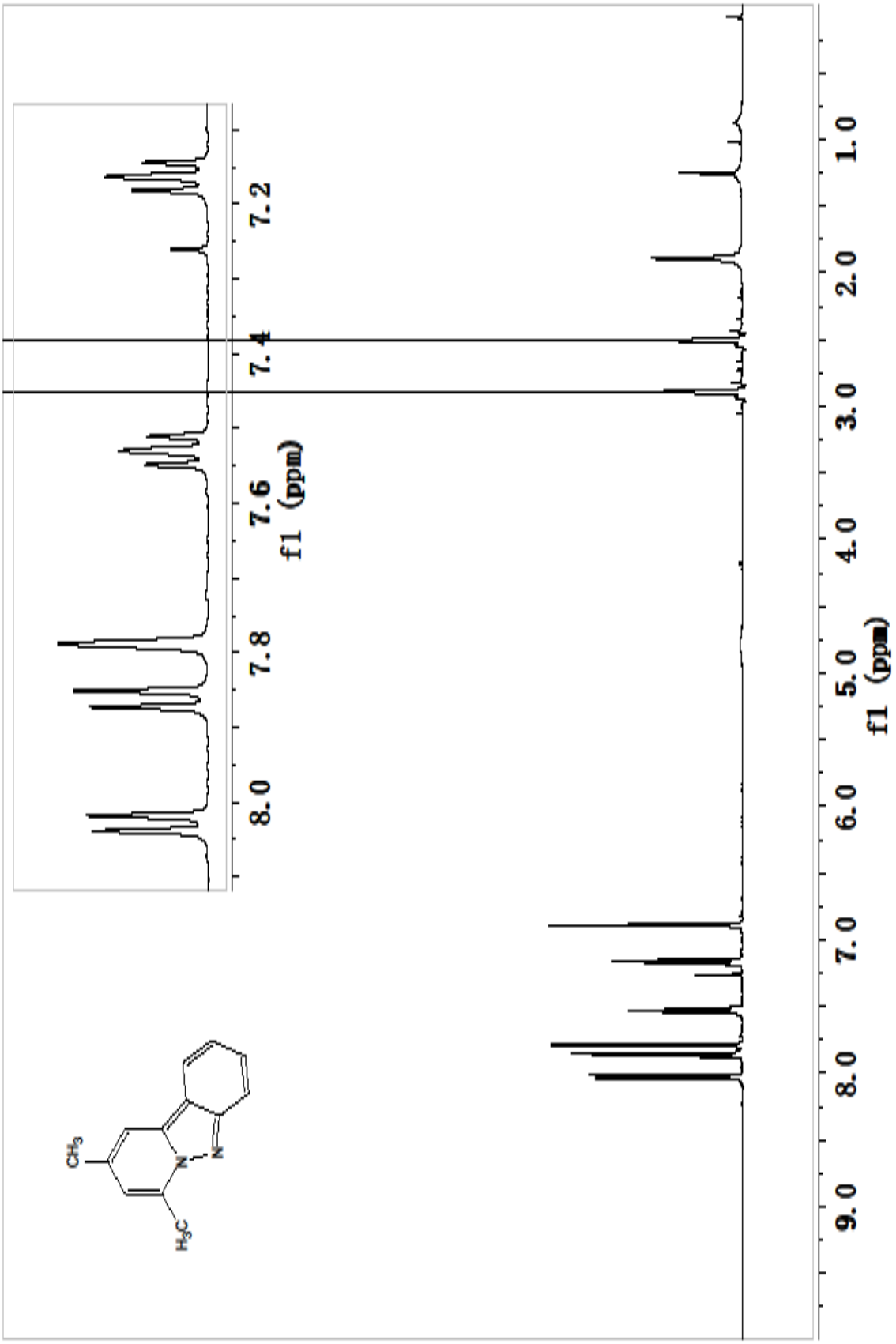


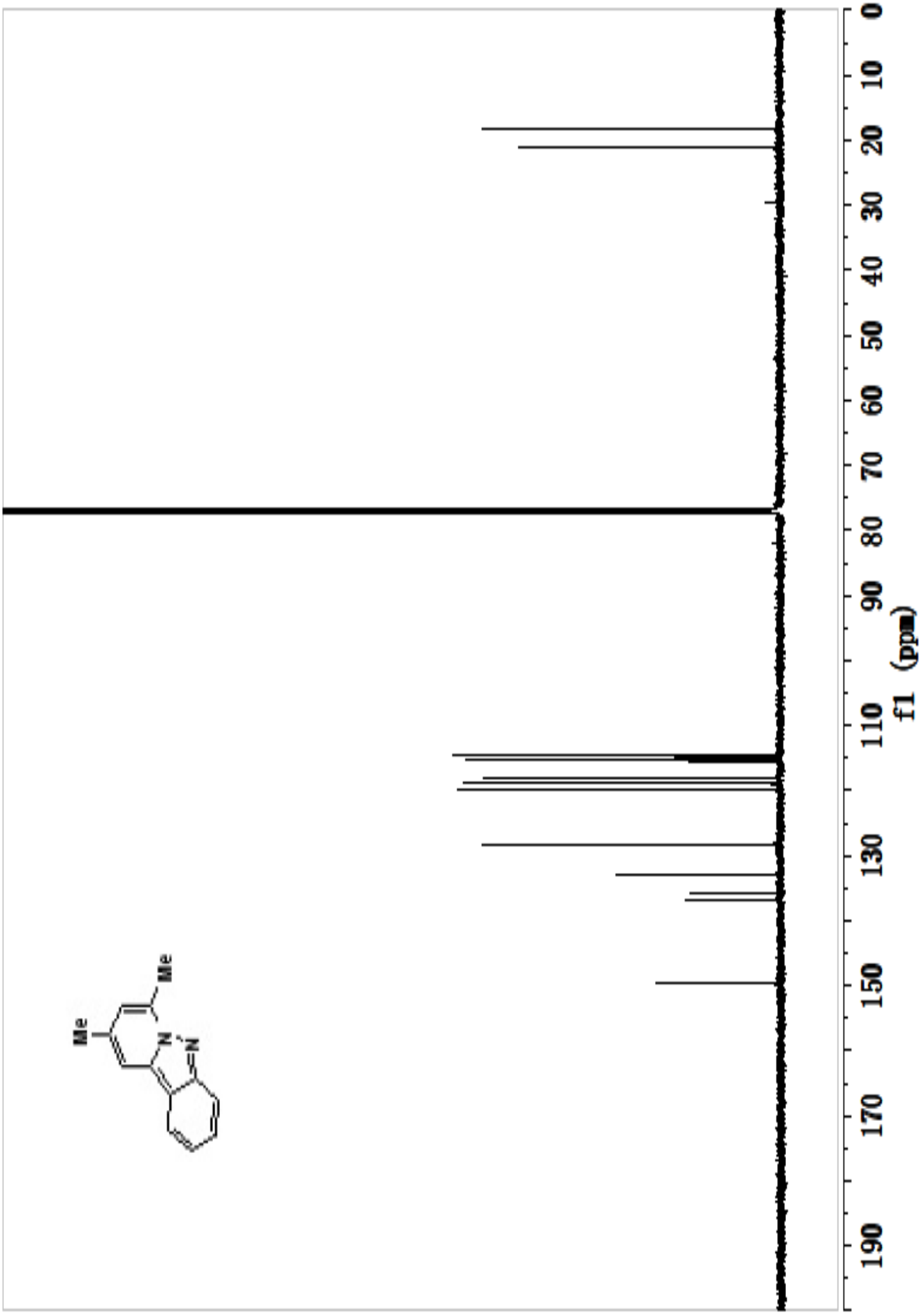


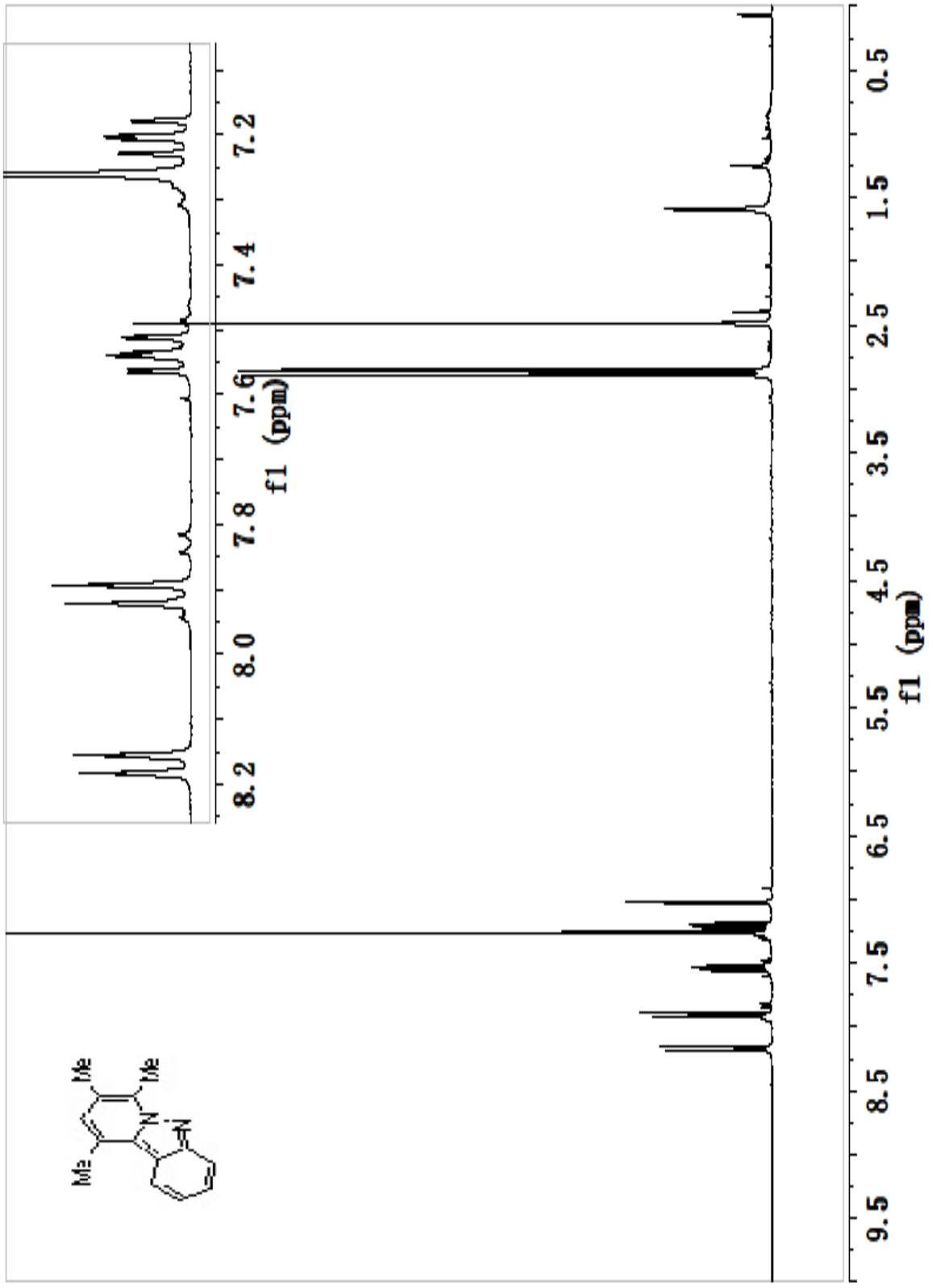


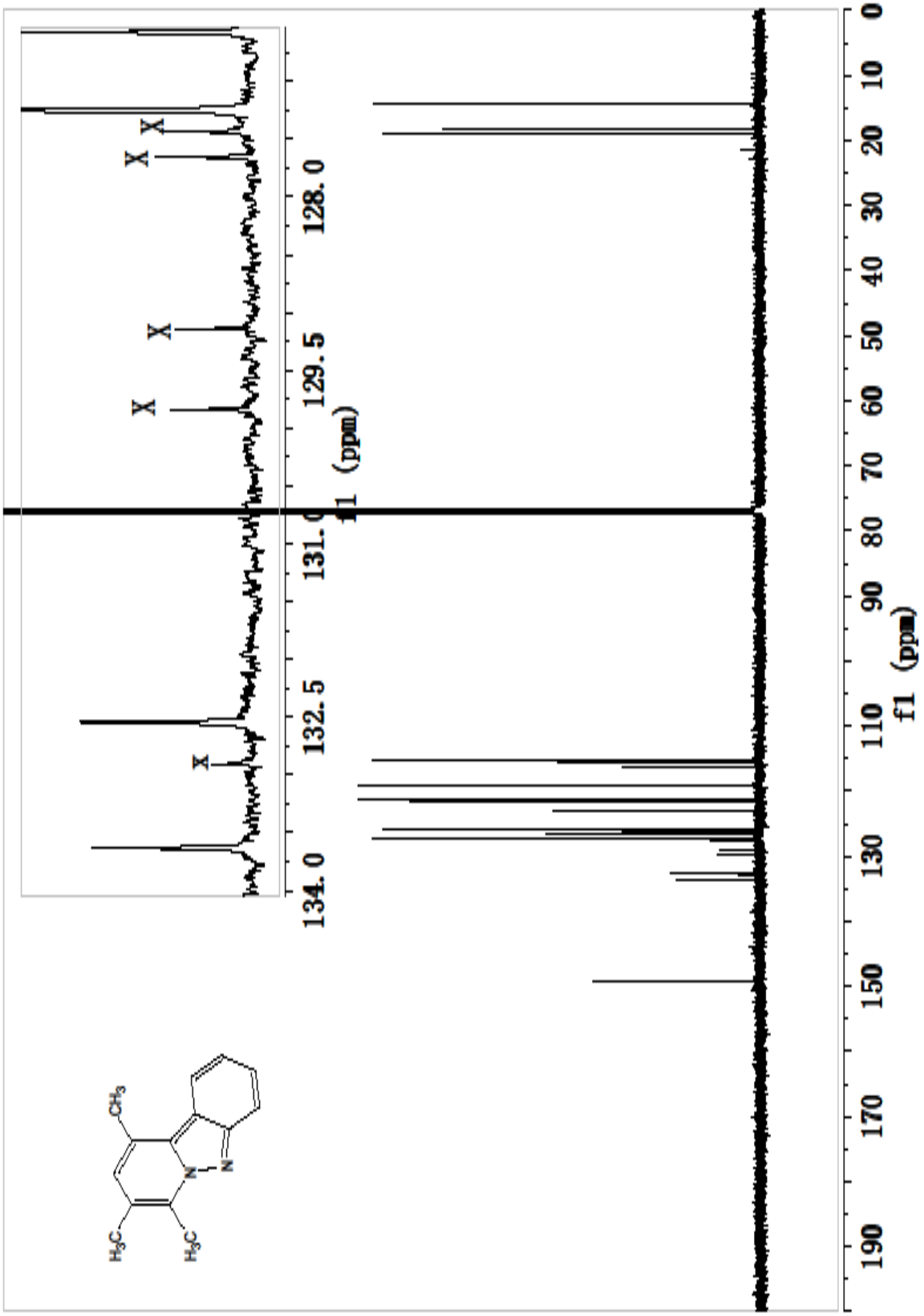


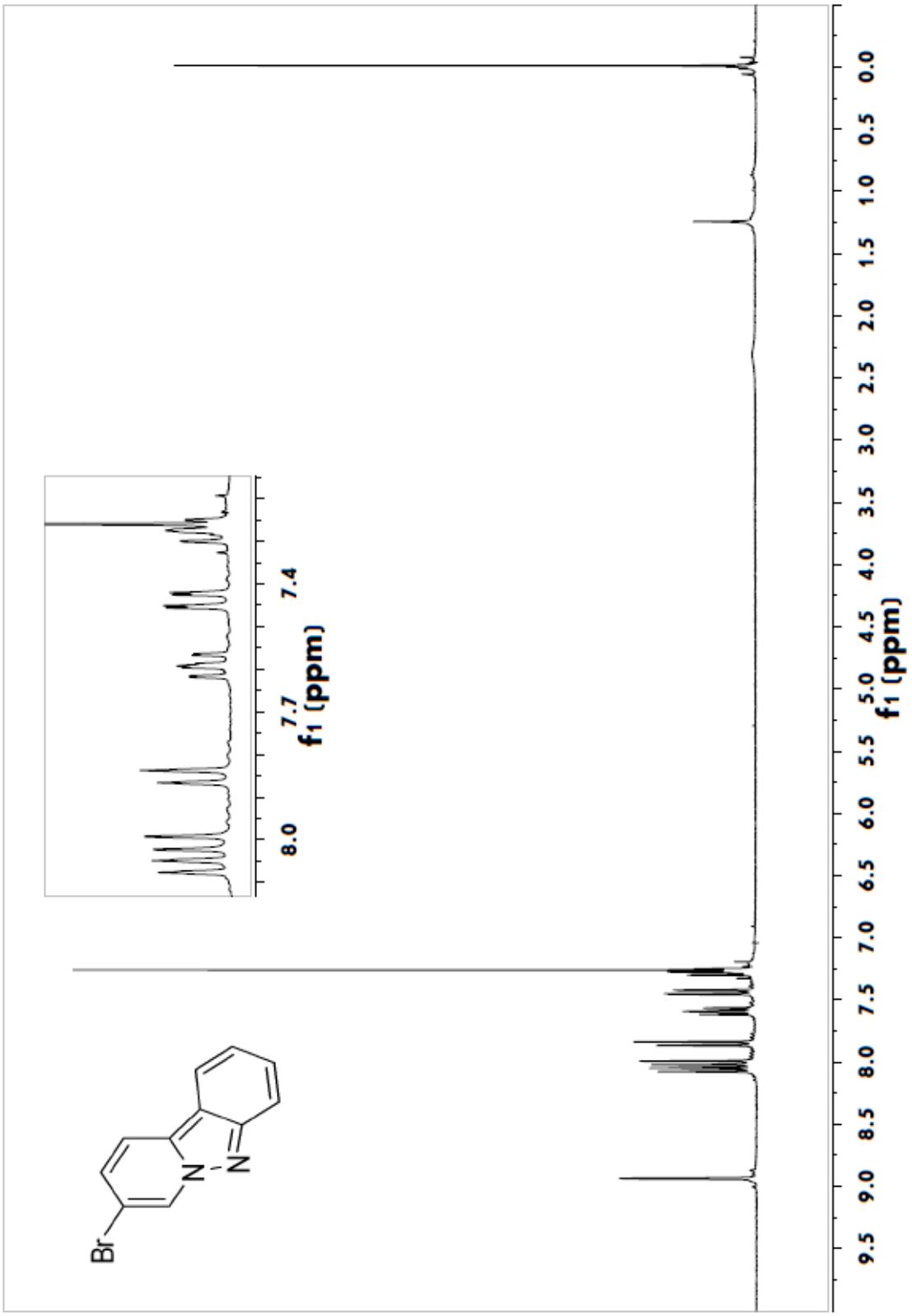


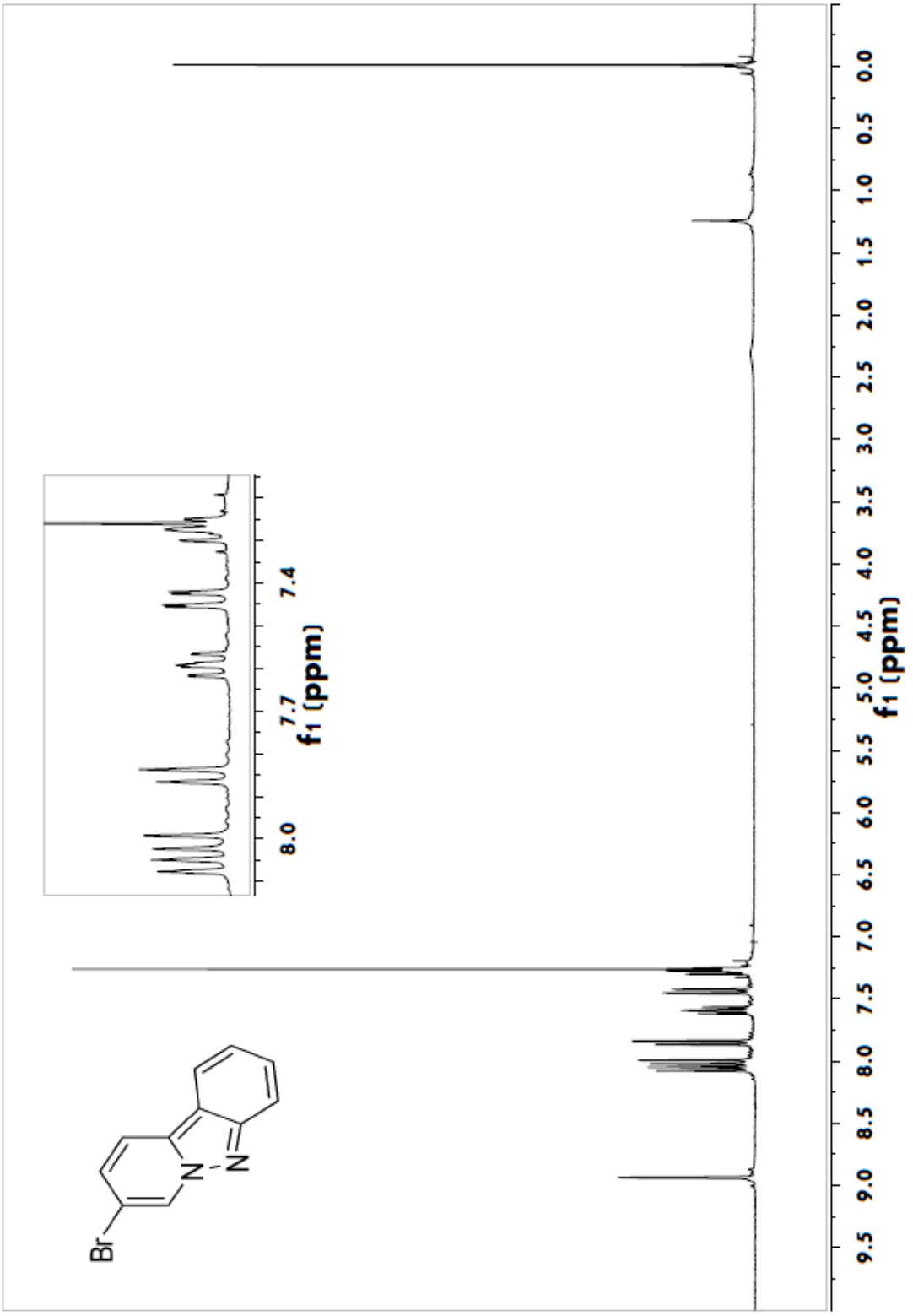


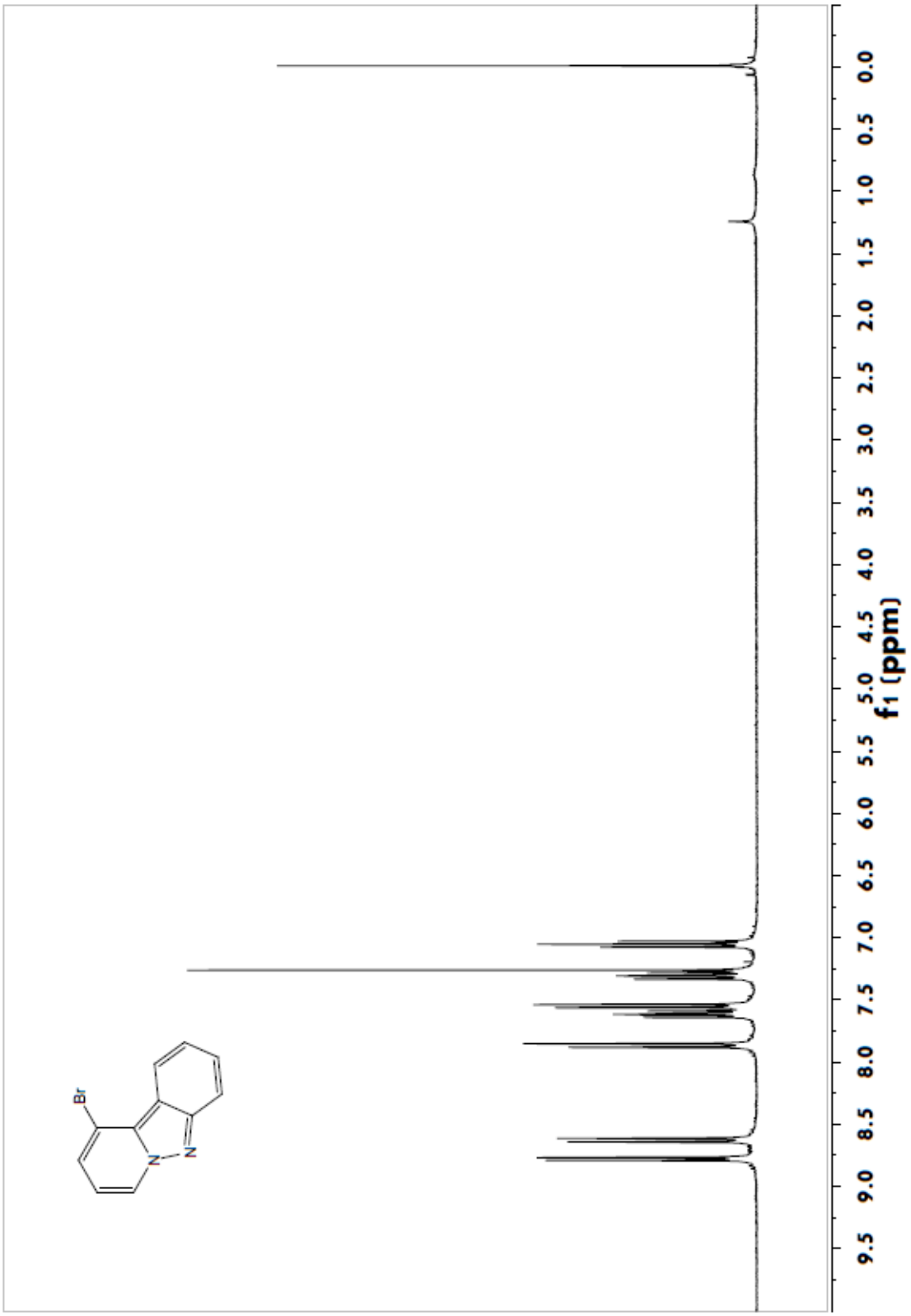


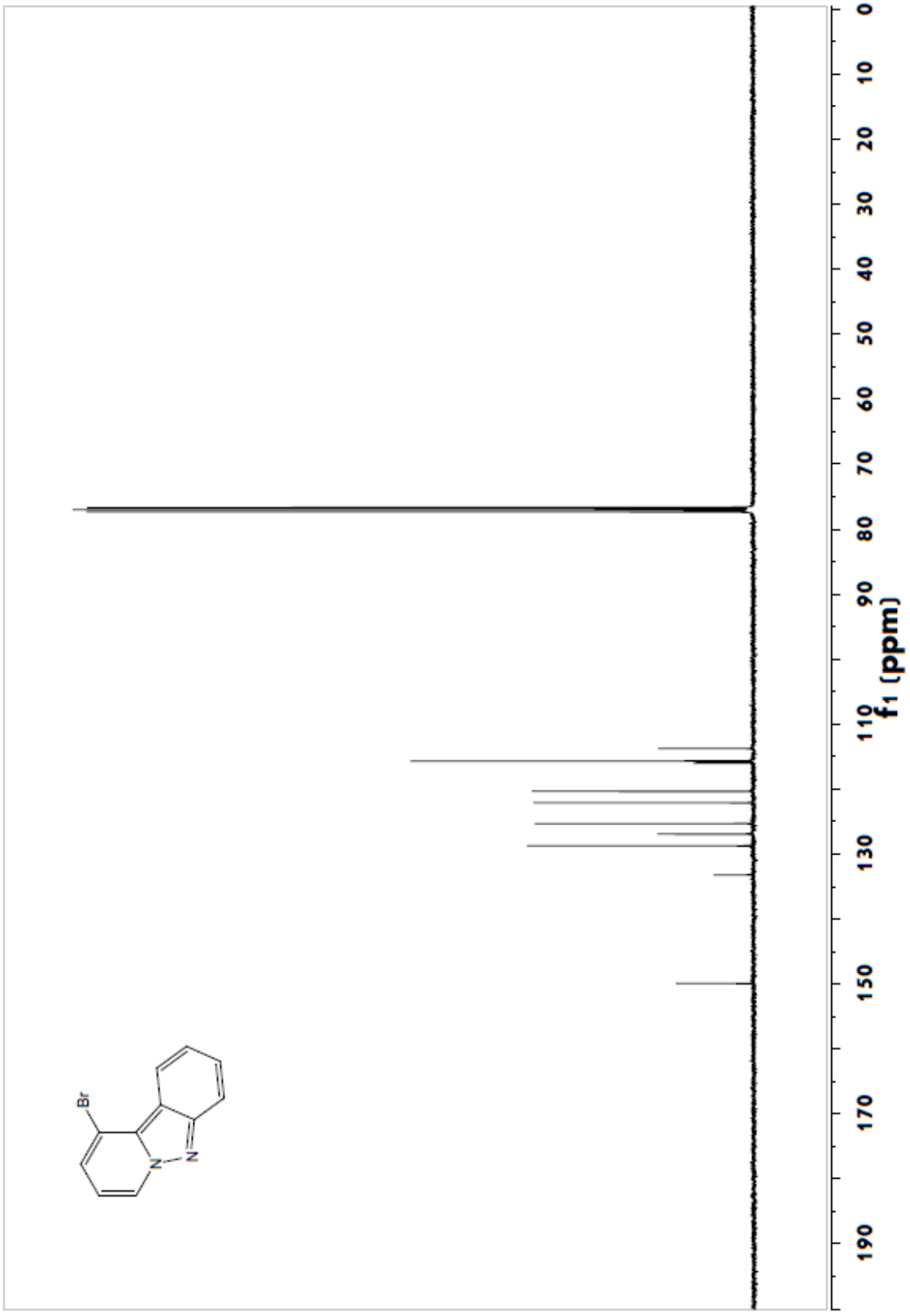


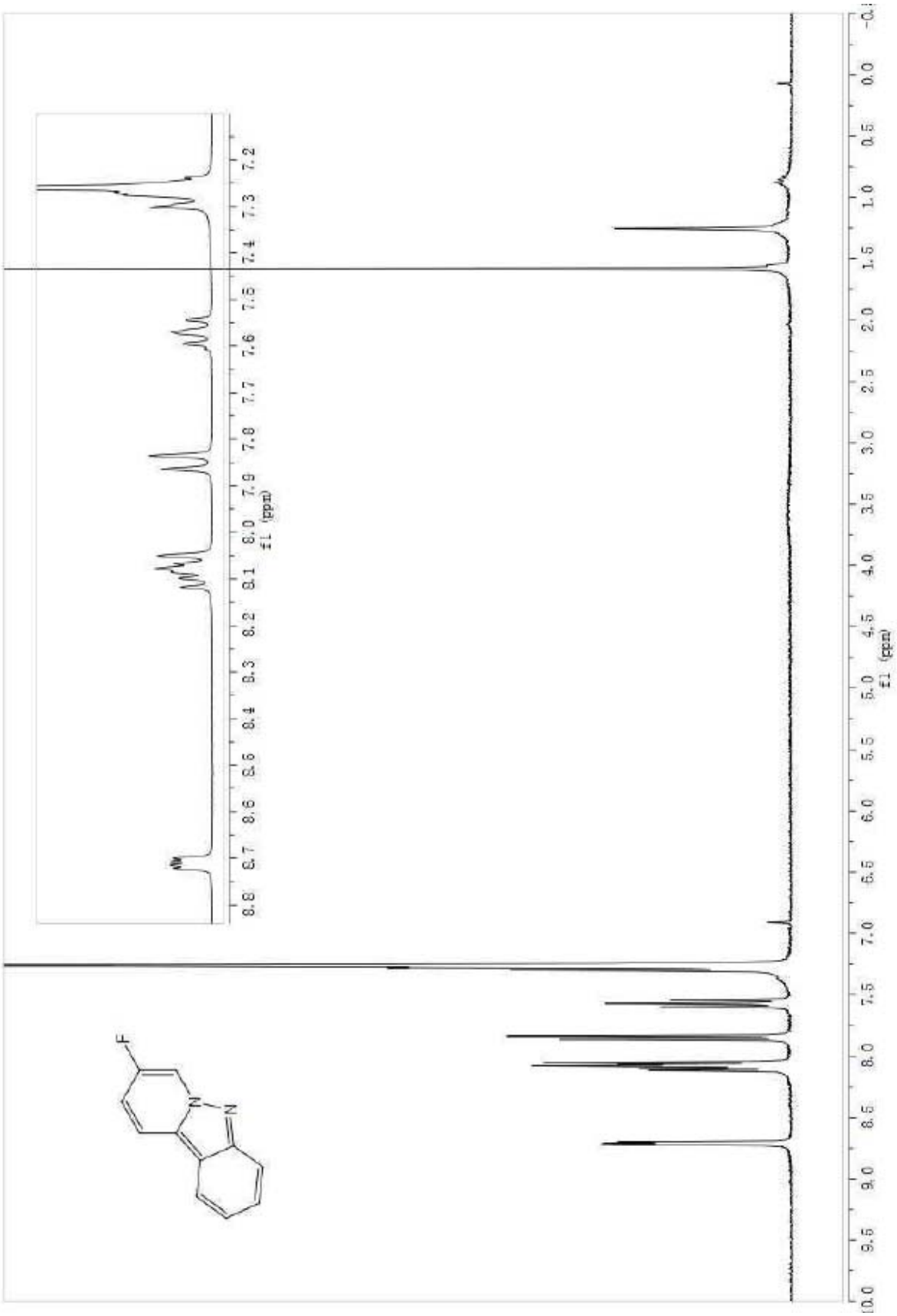


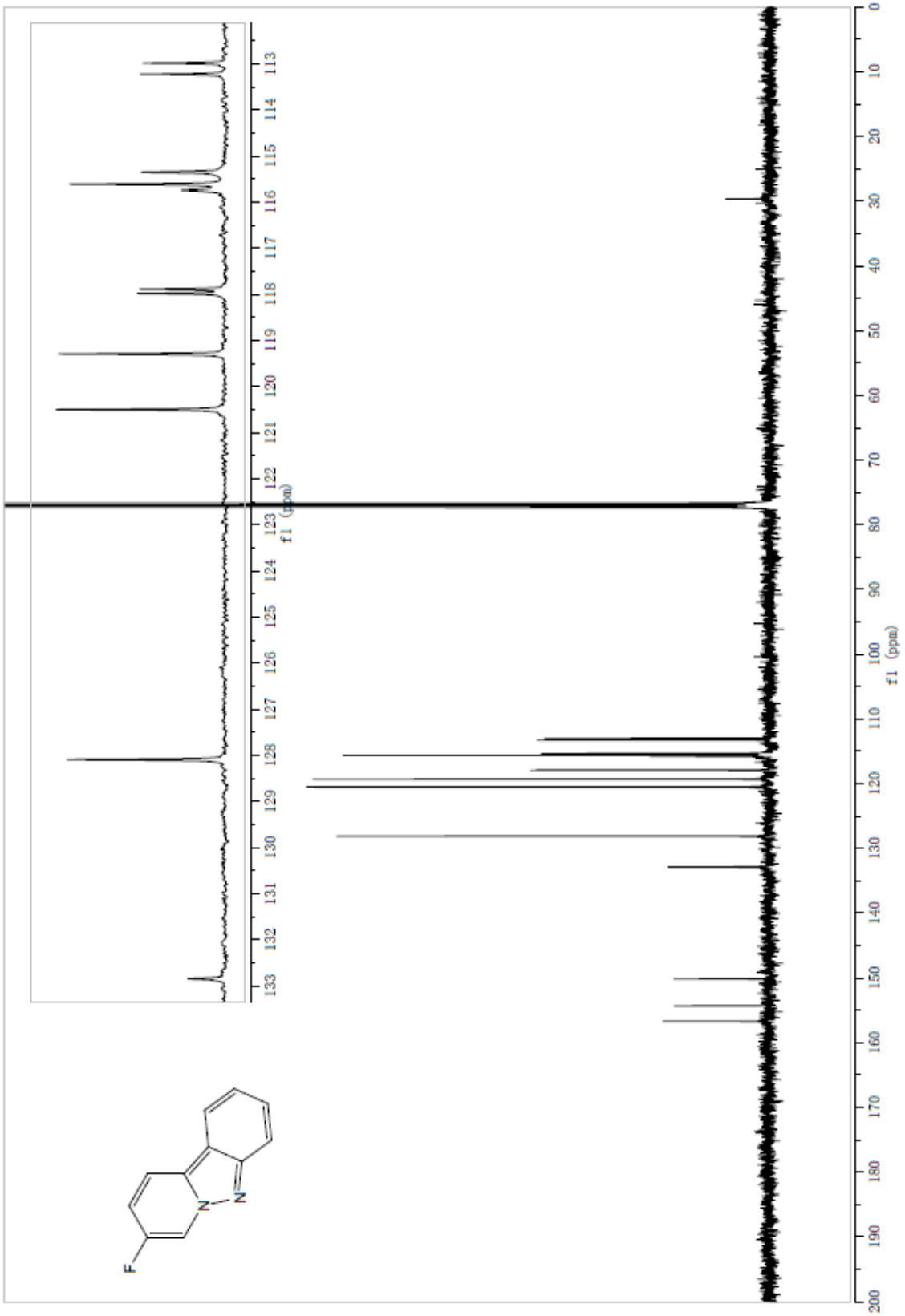


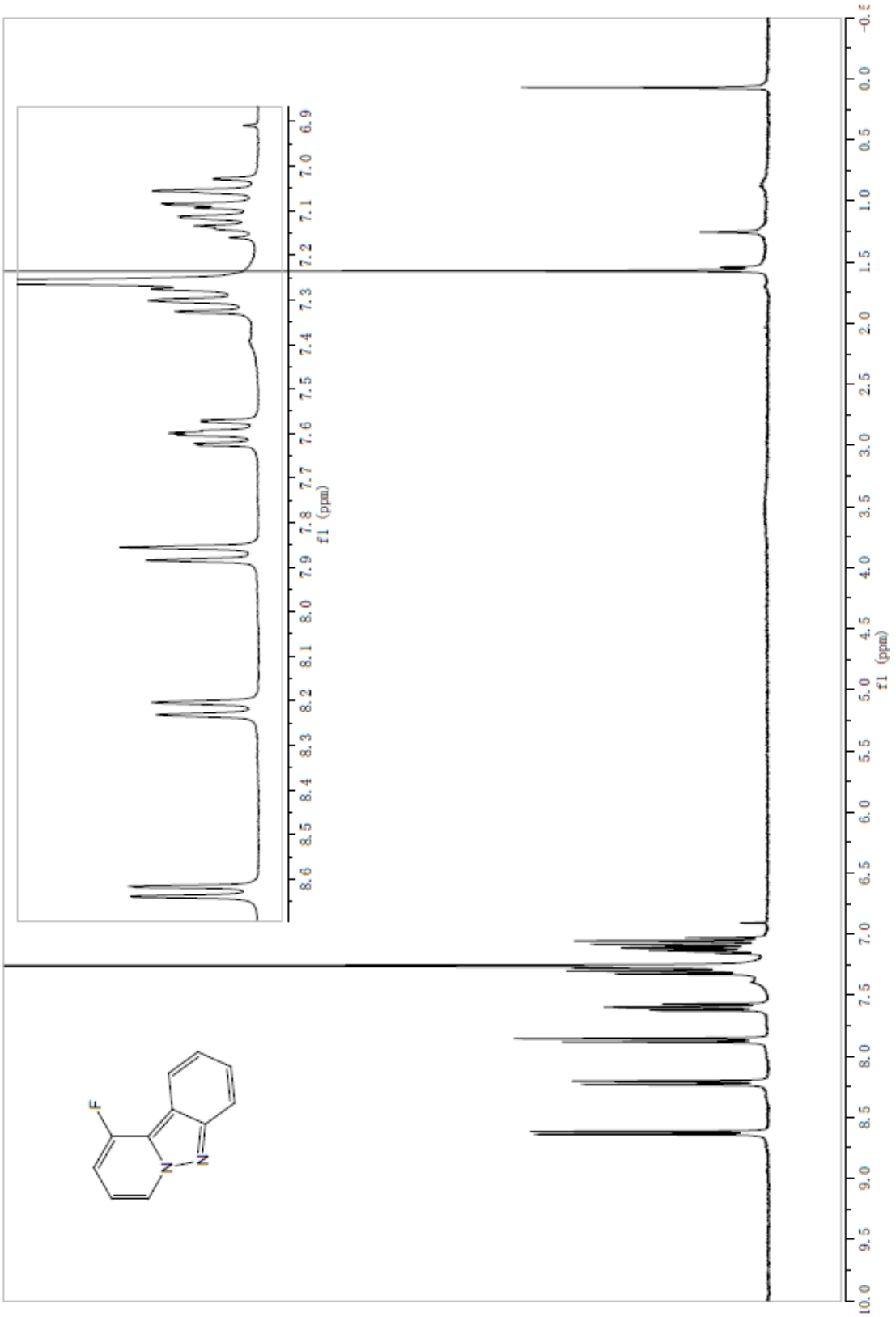


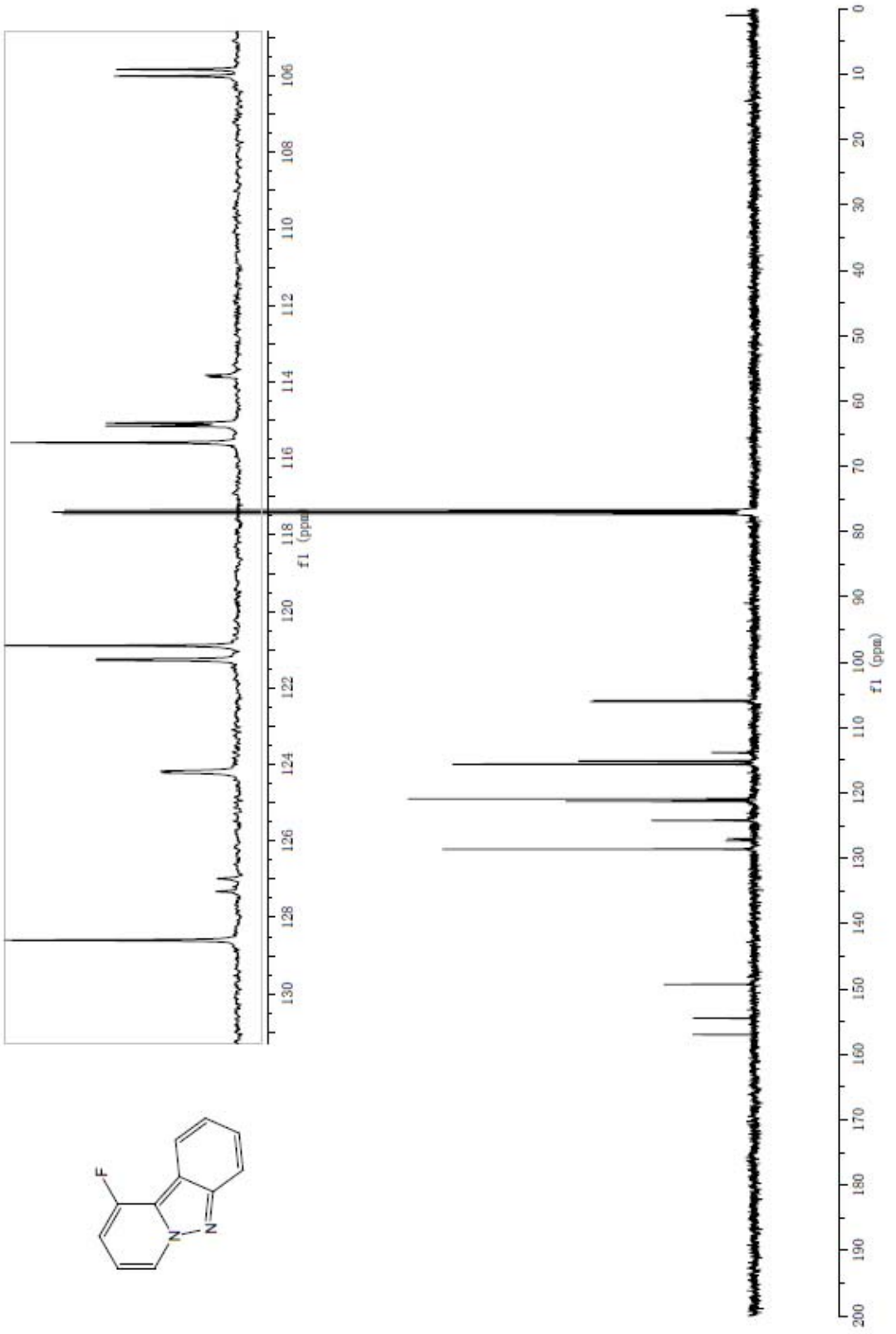


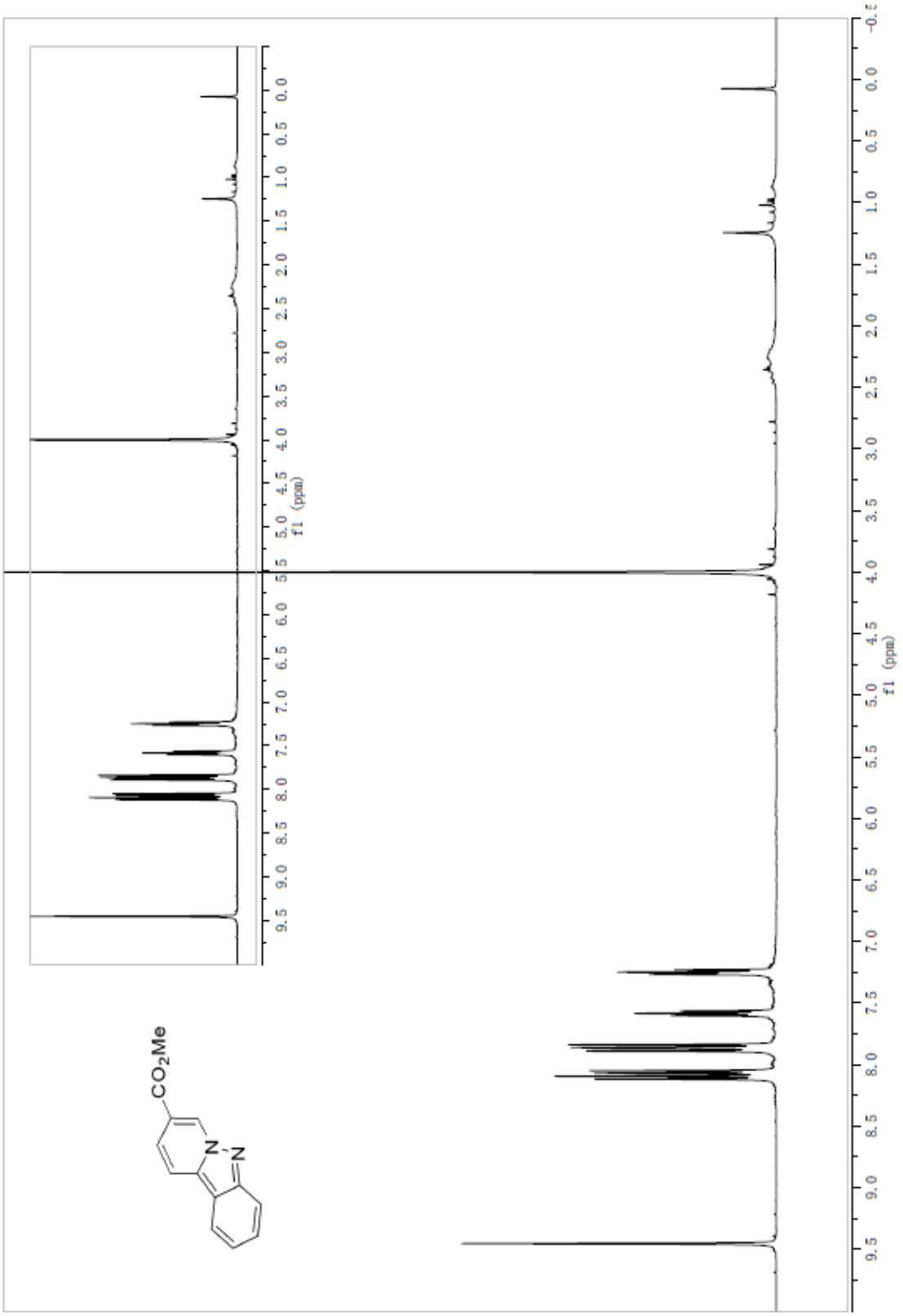


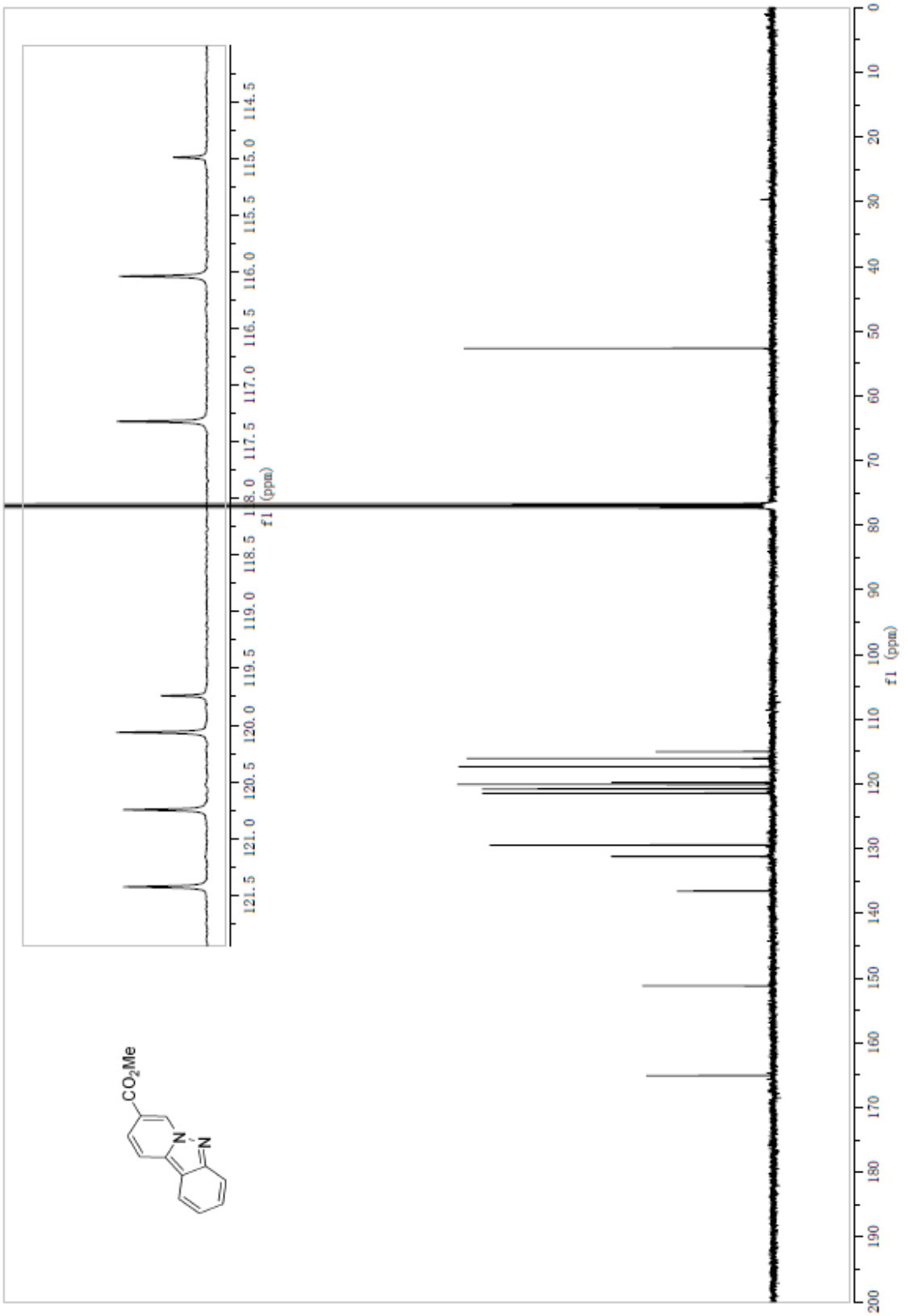


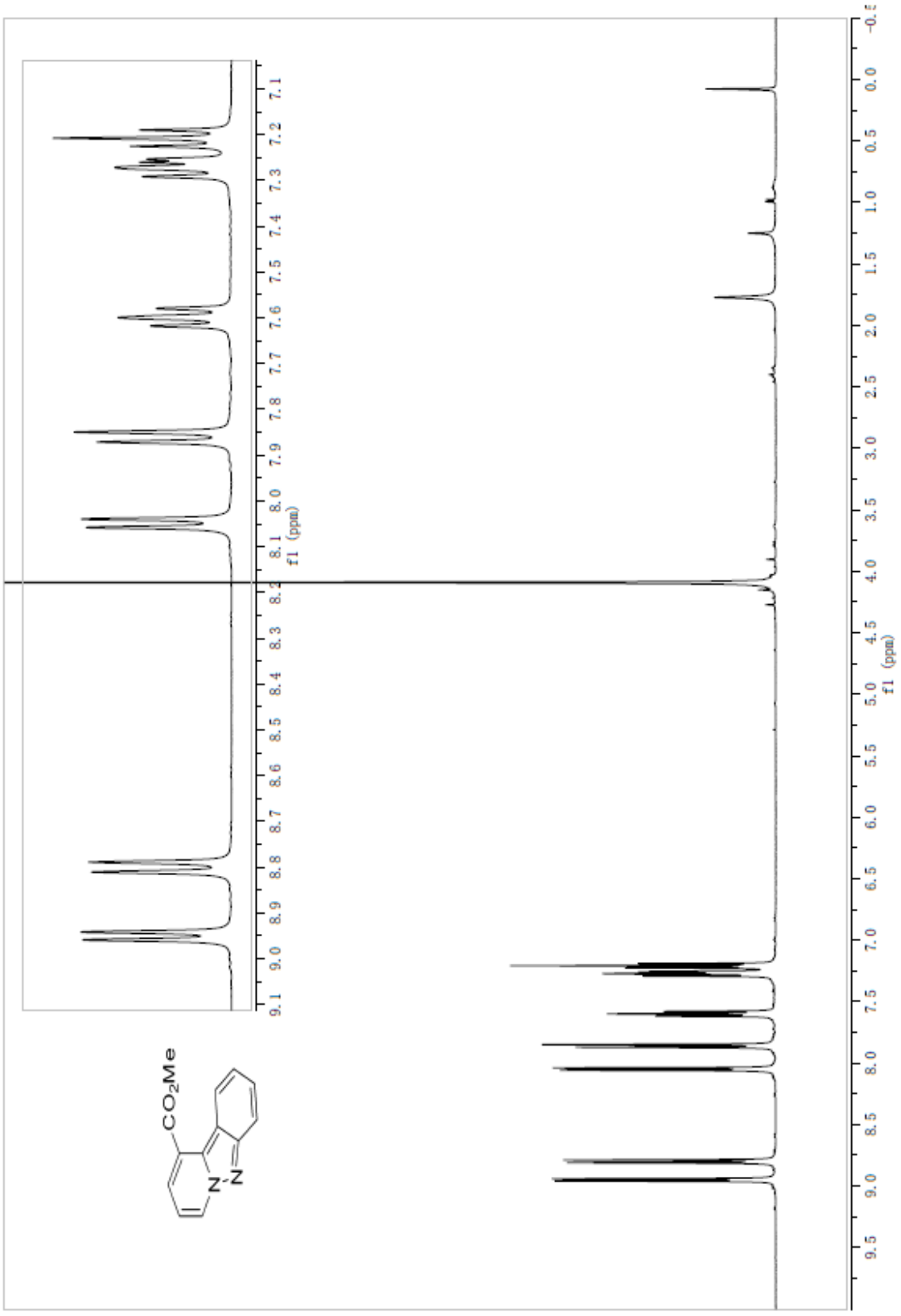


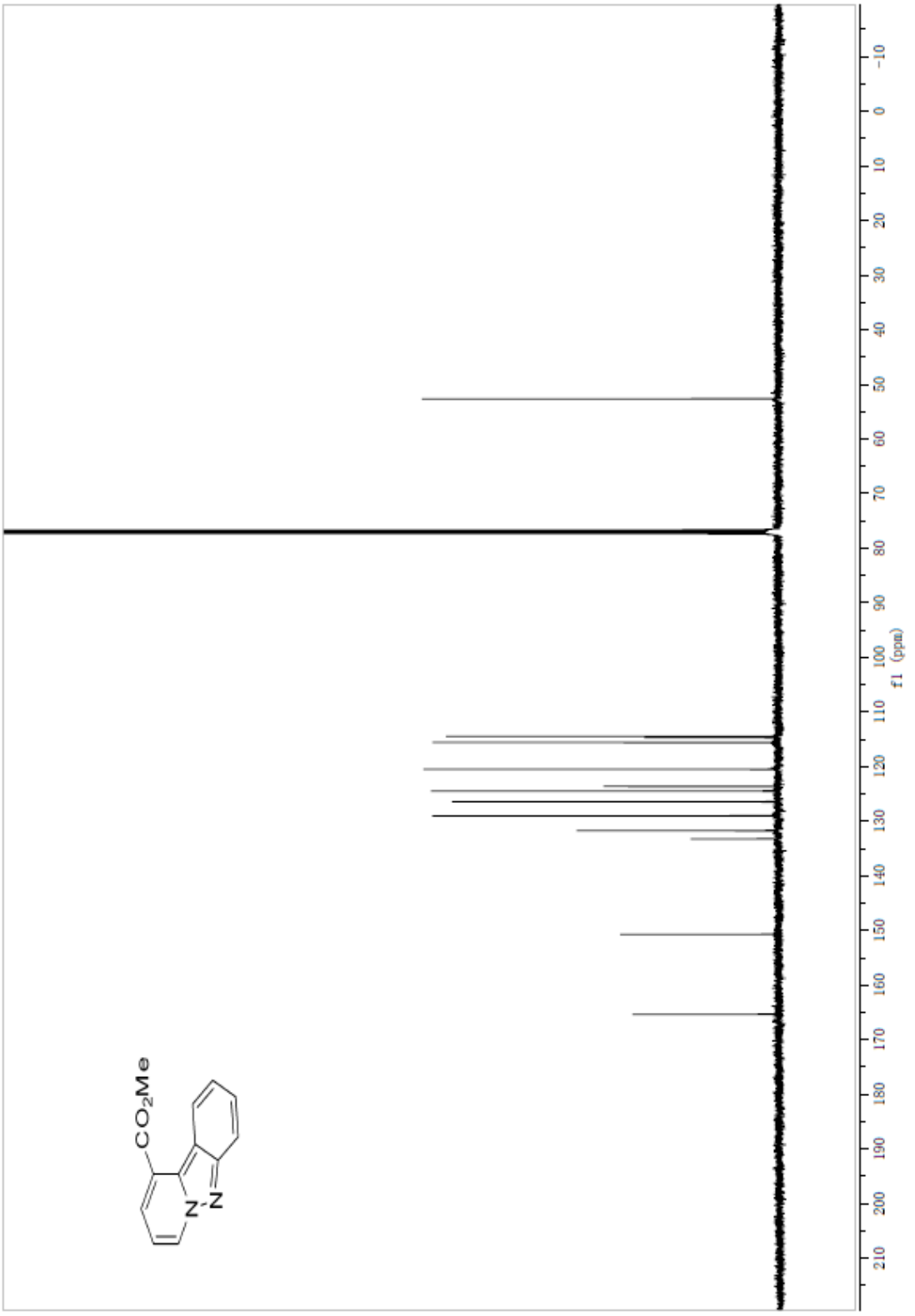


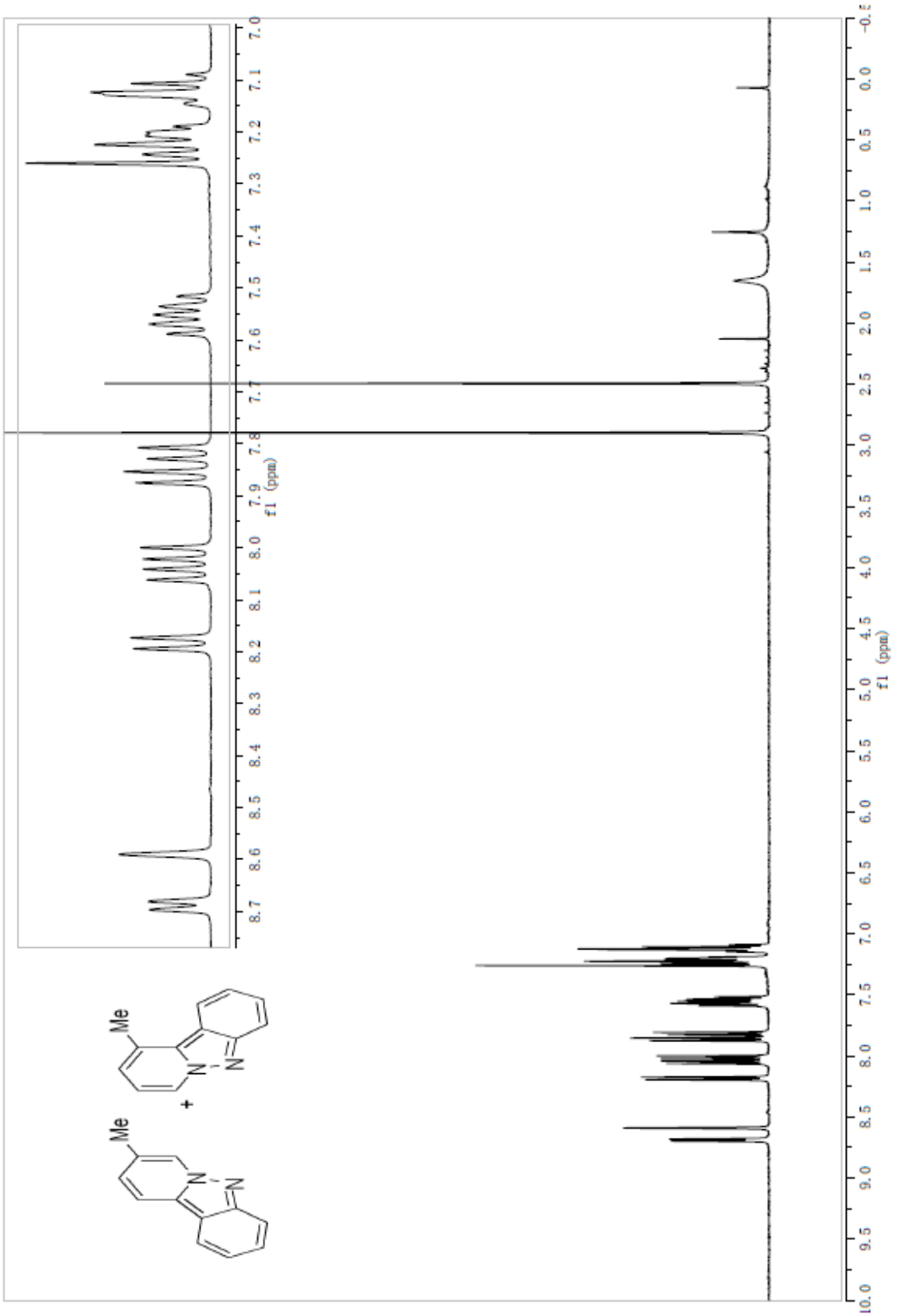


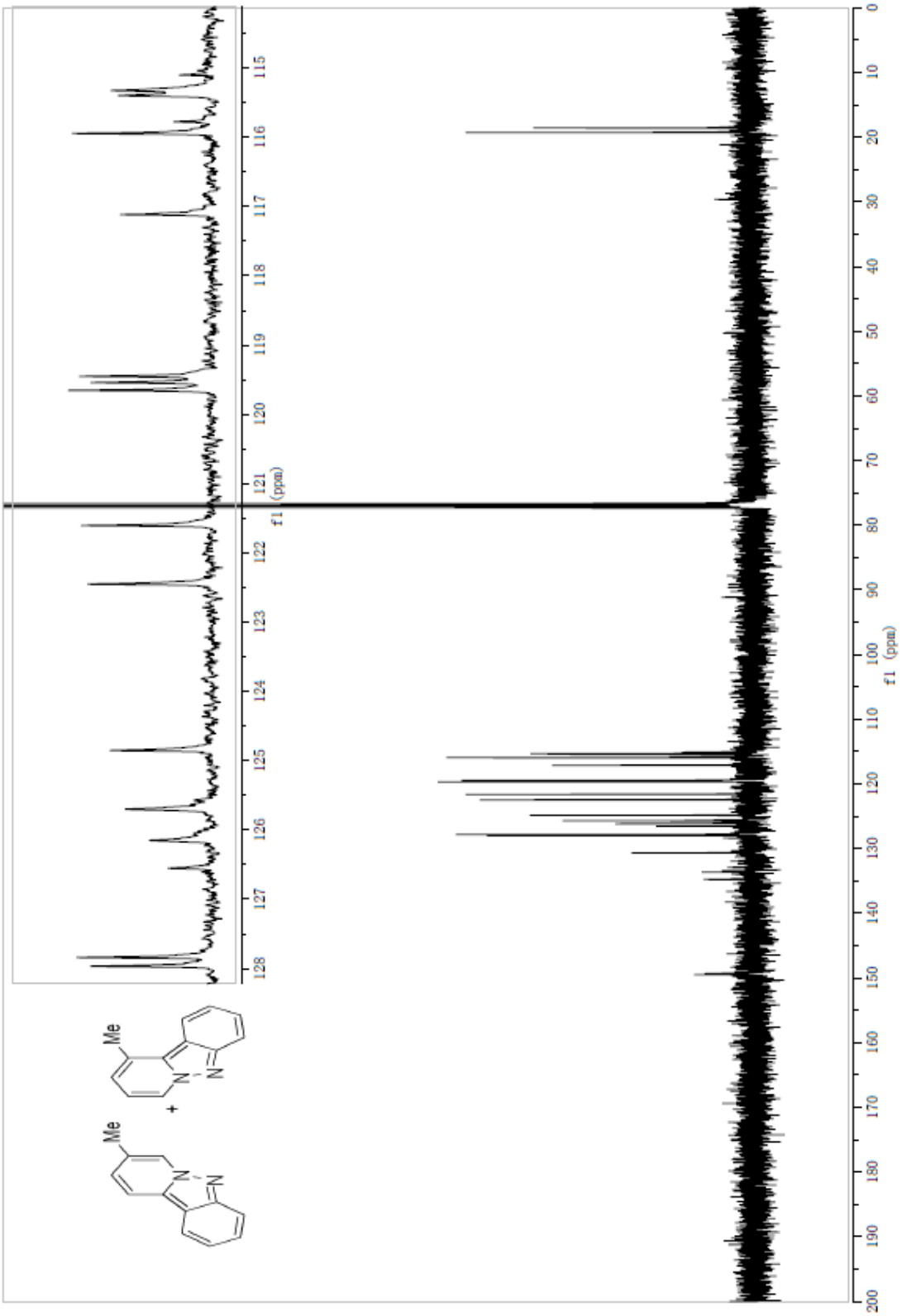


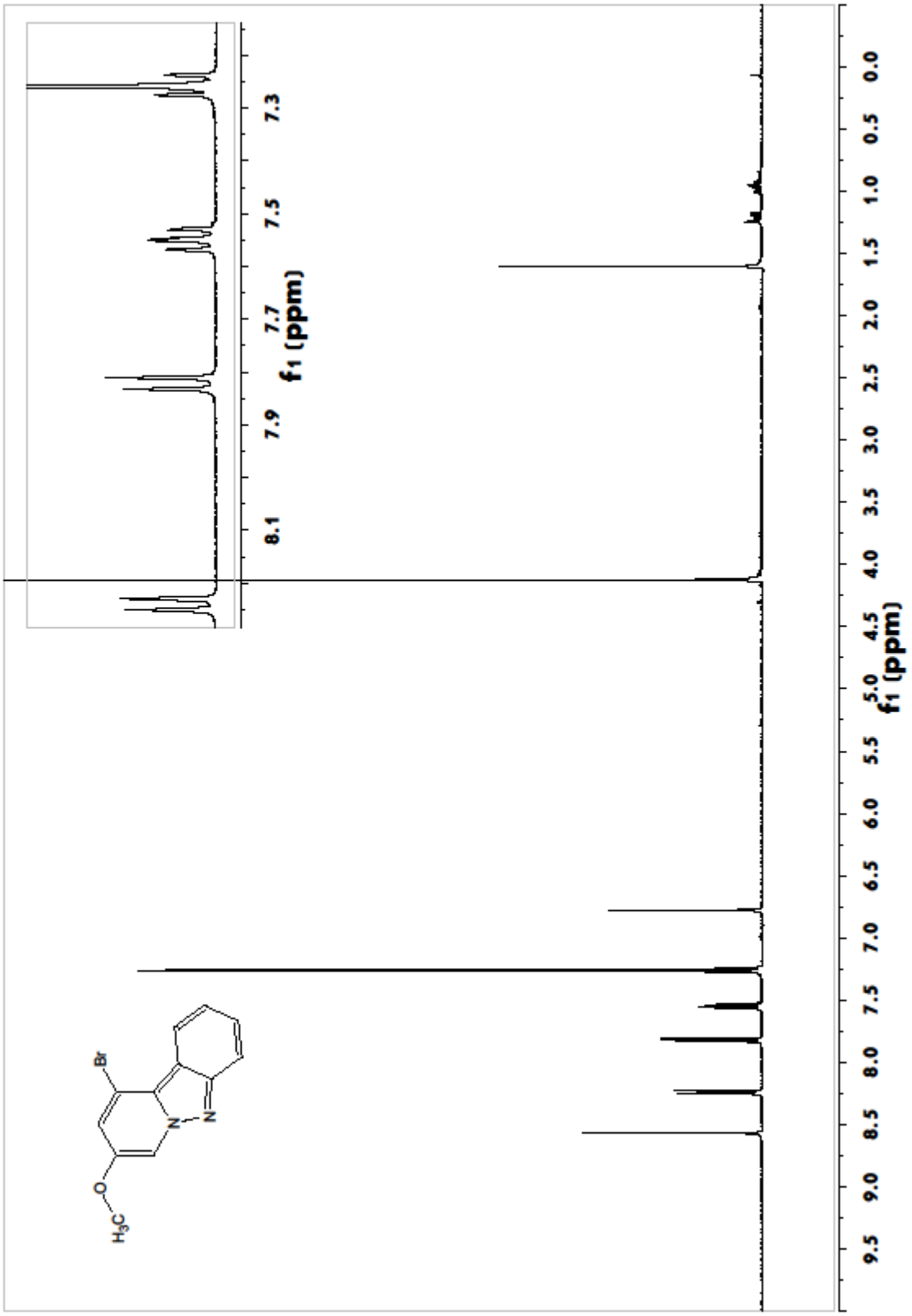


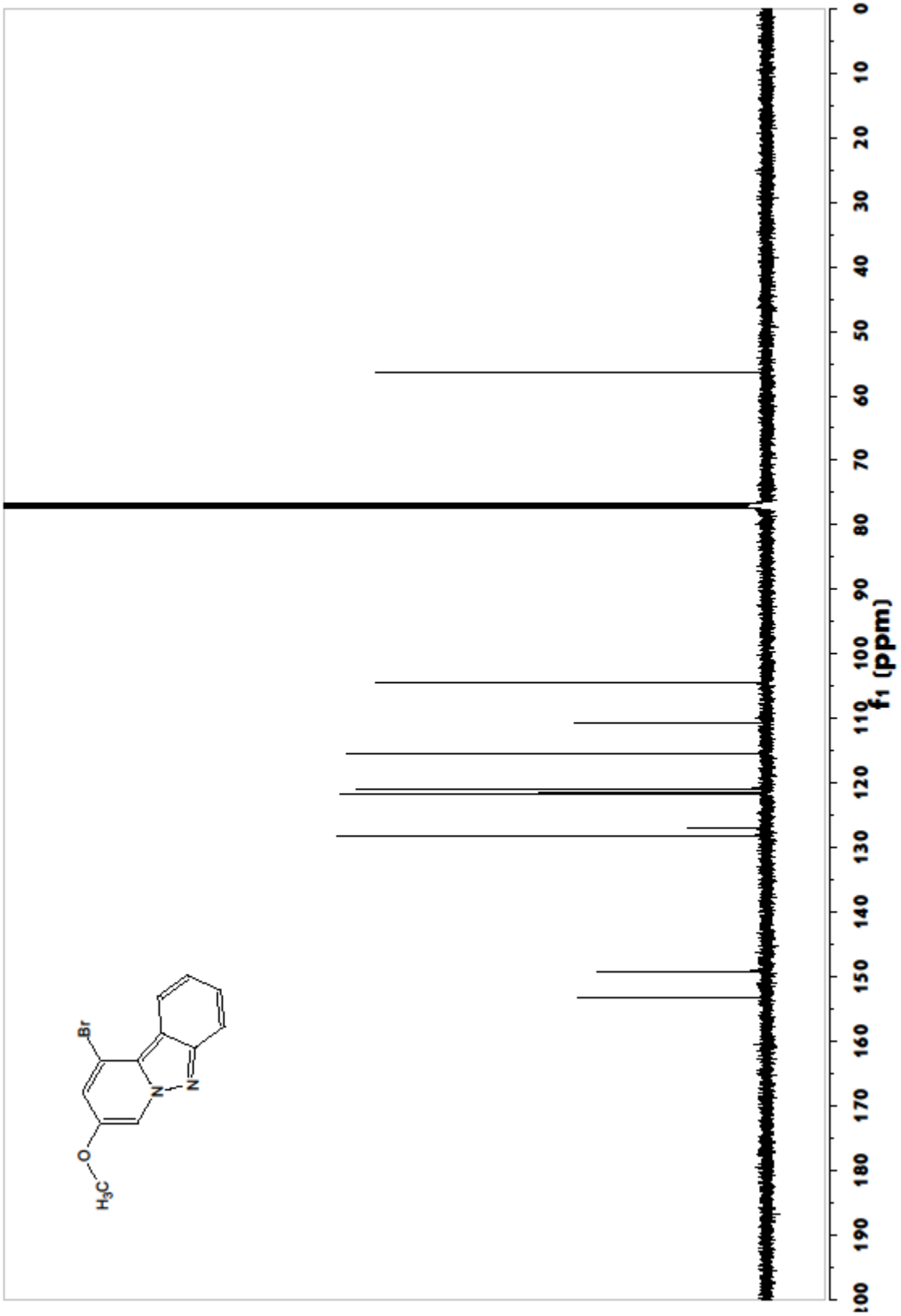




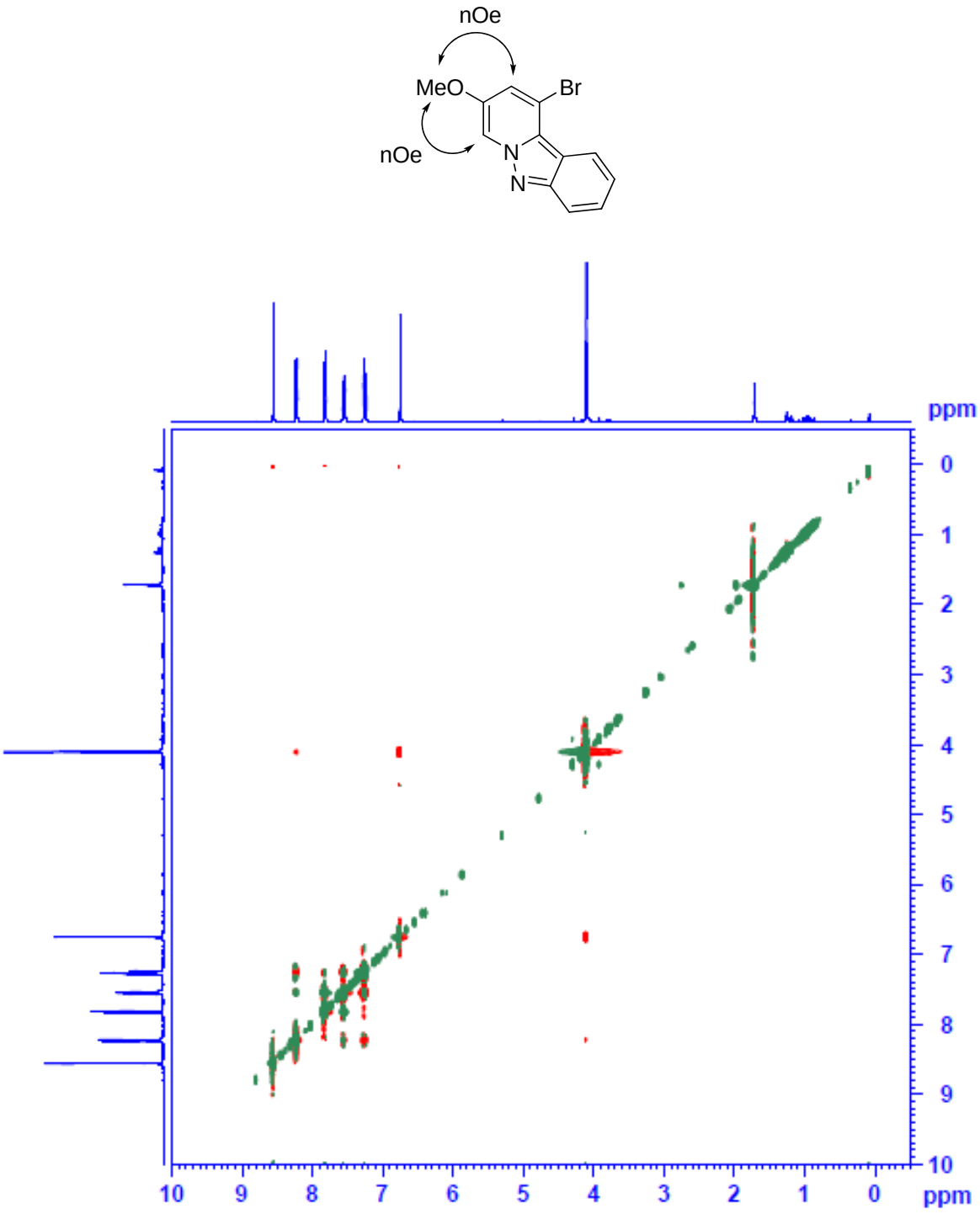


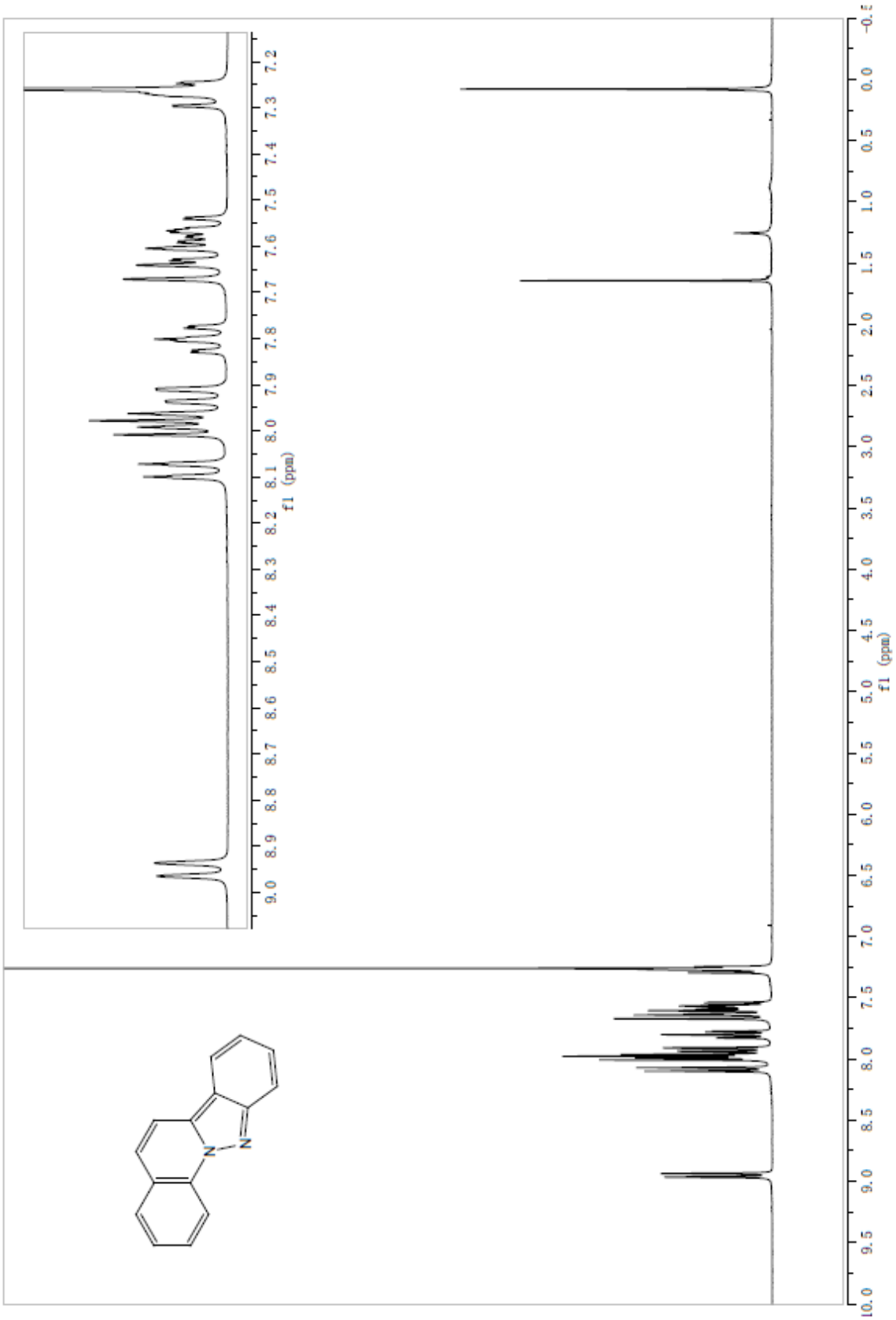


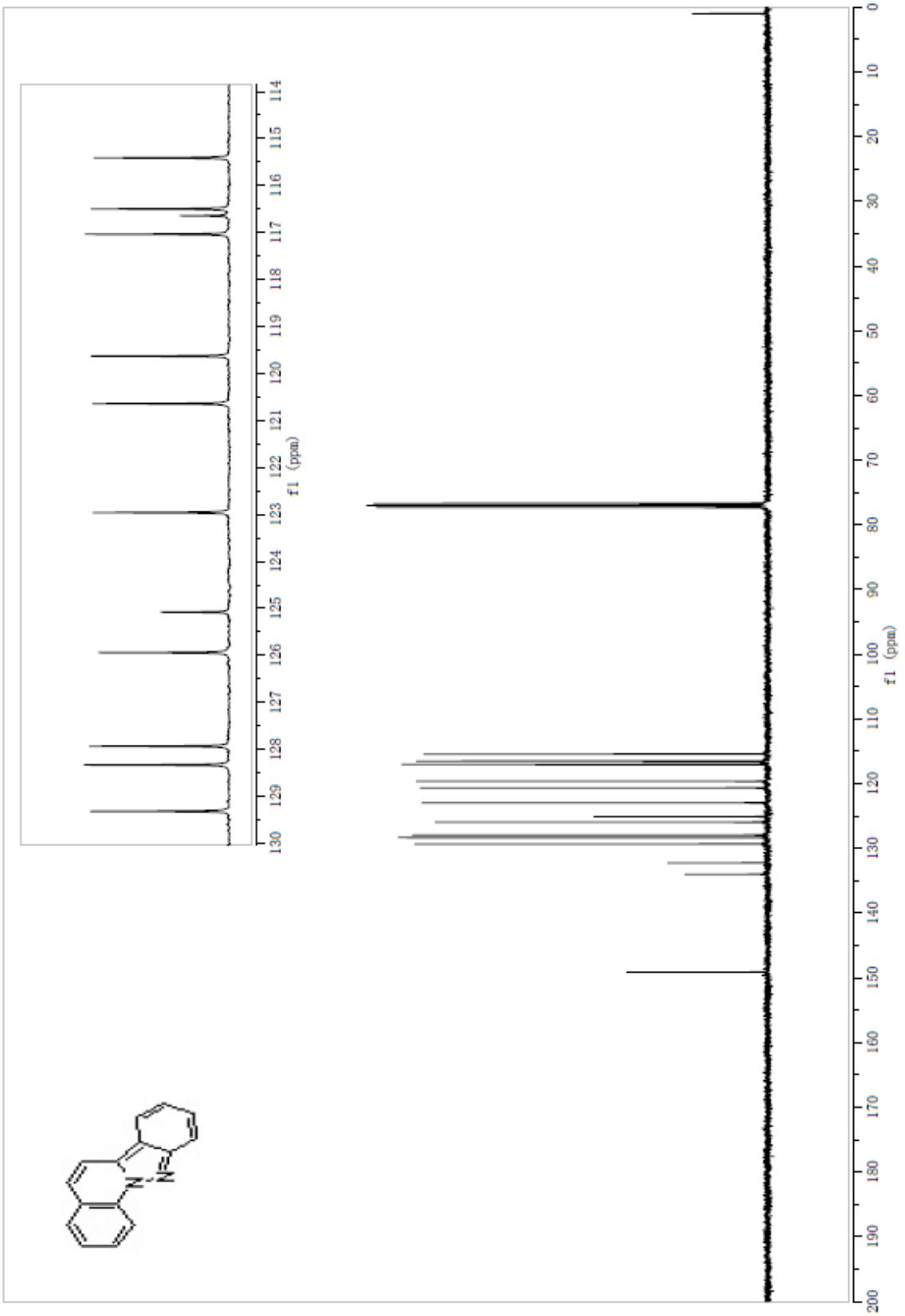


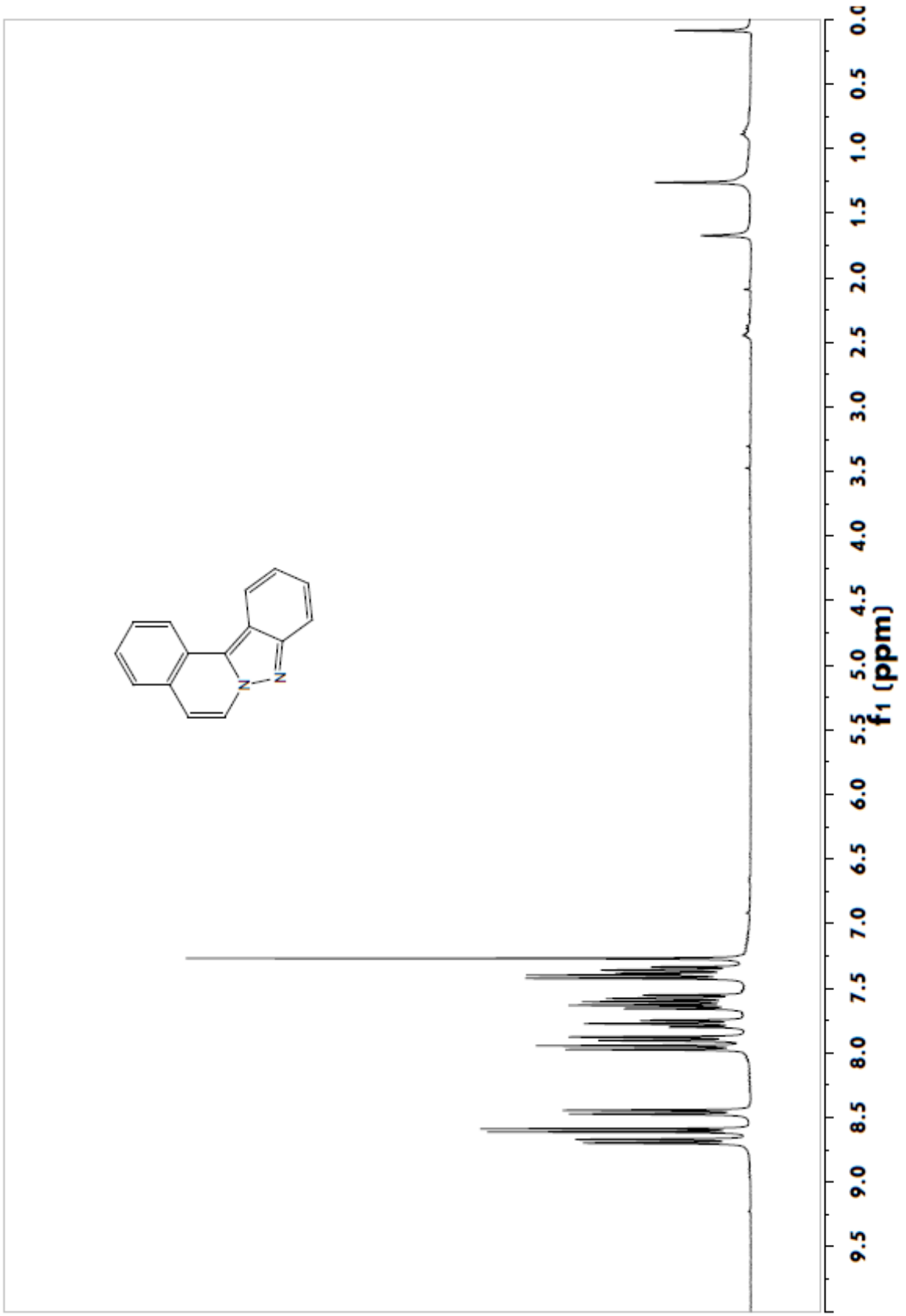


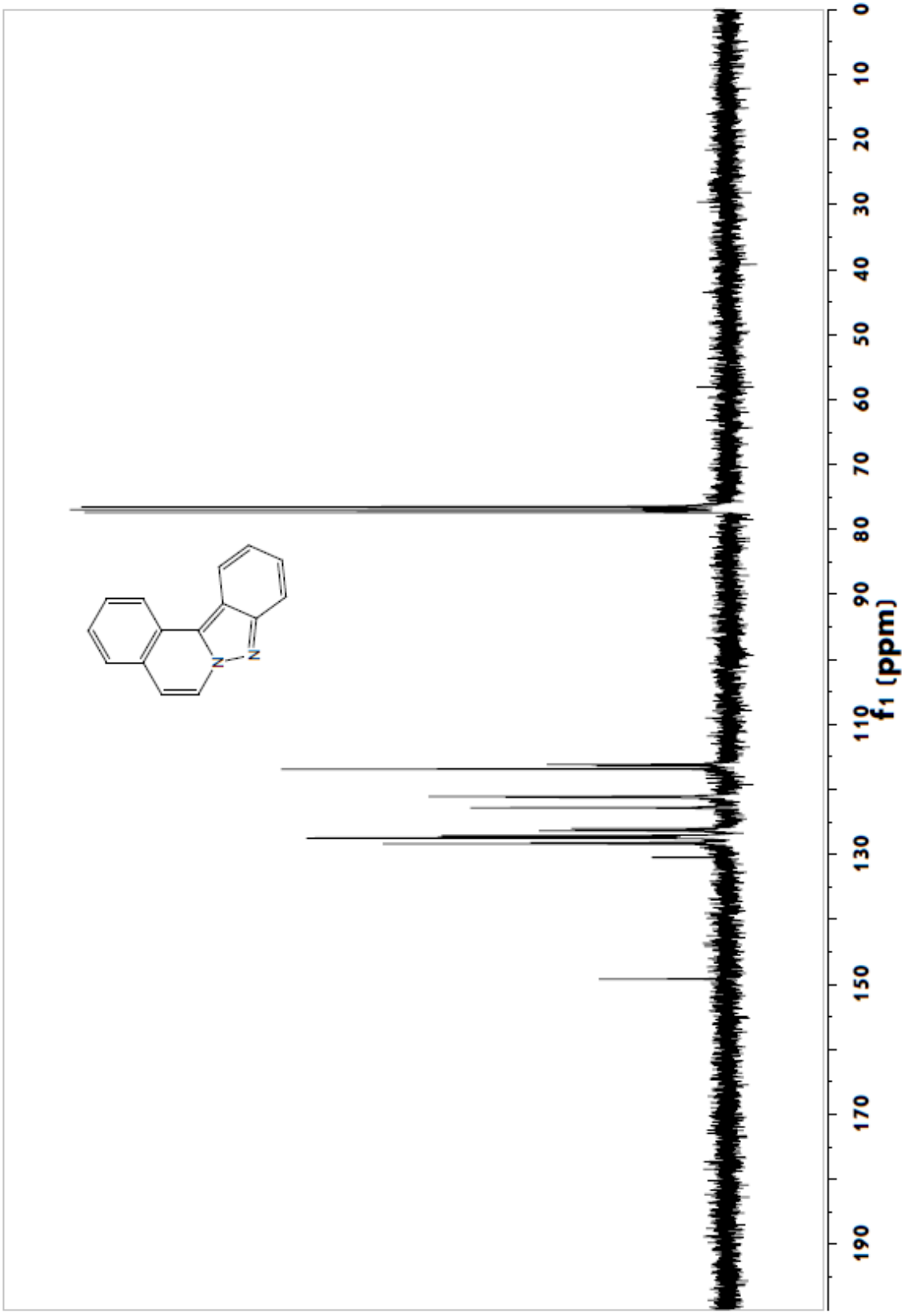
2D-NOESY for Compound **8p'**:

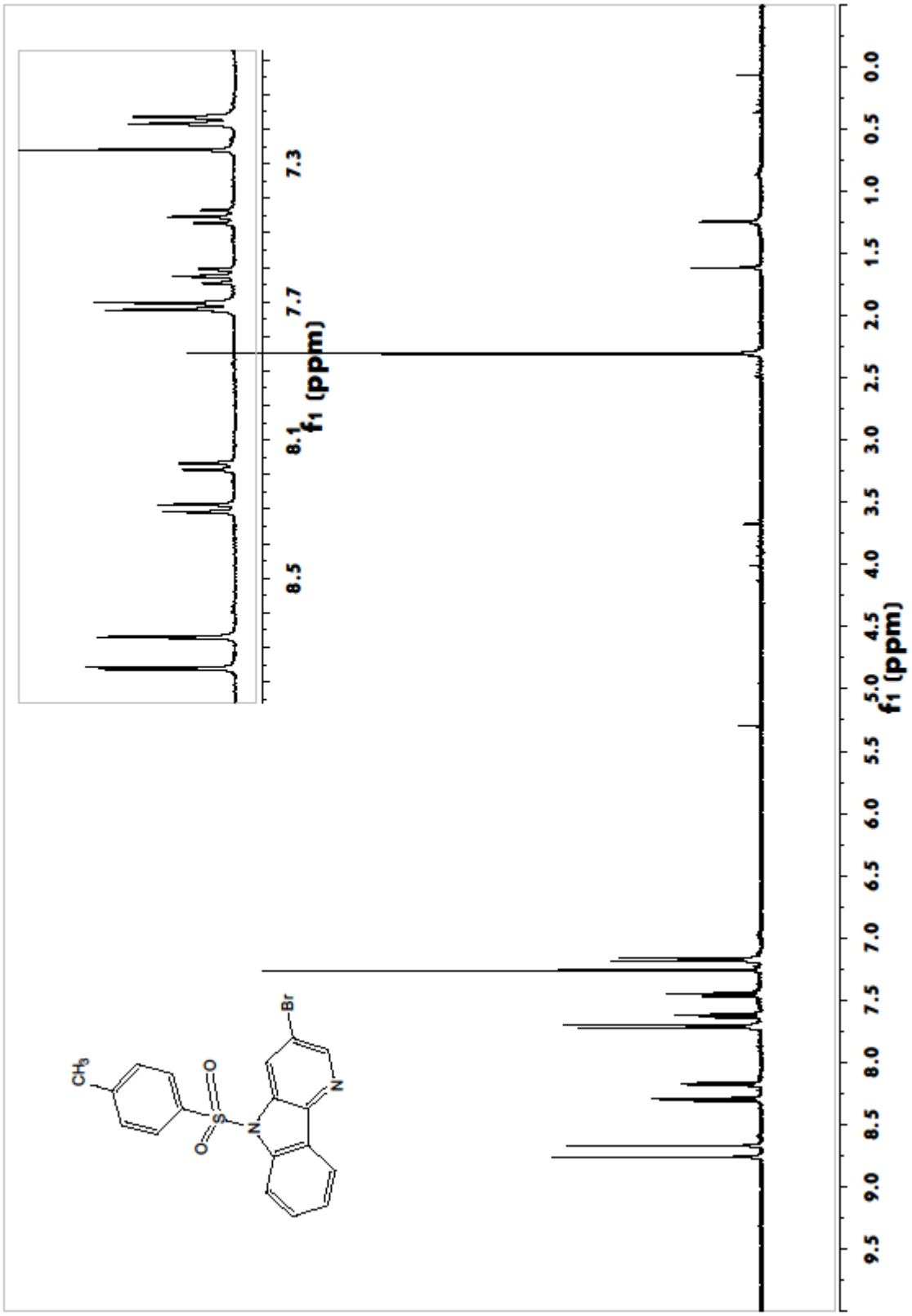


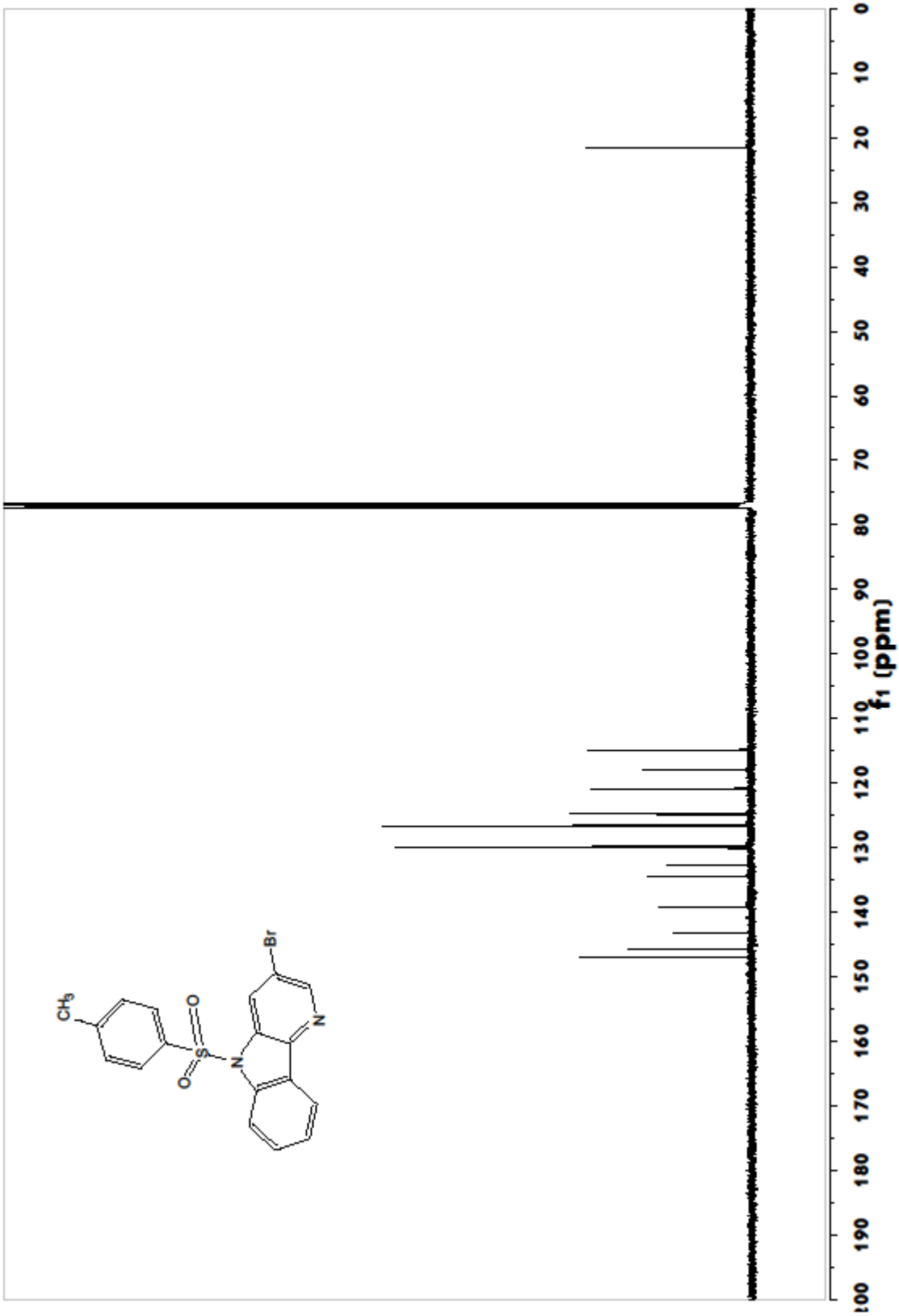


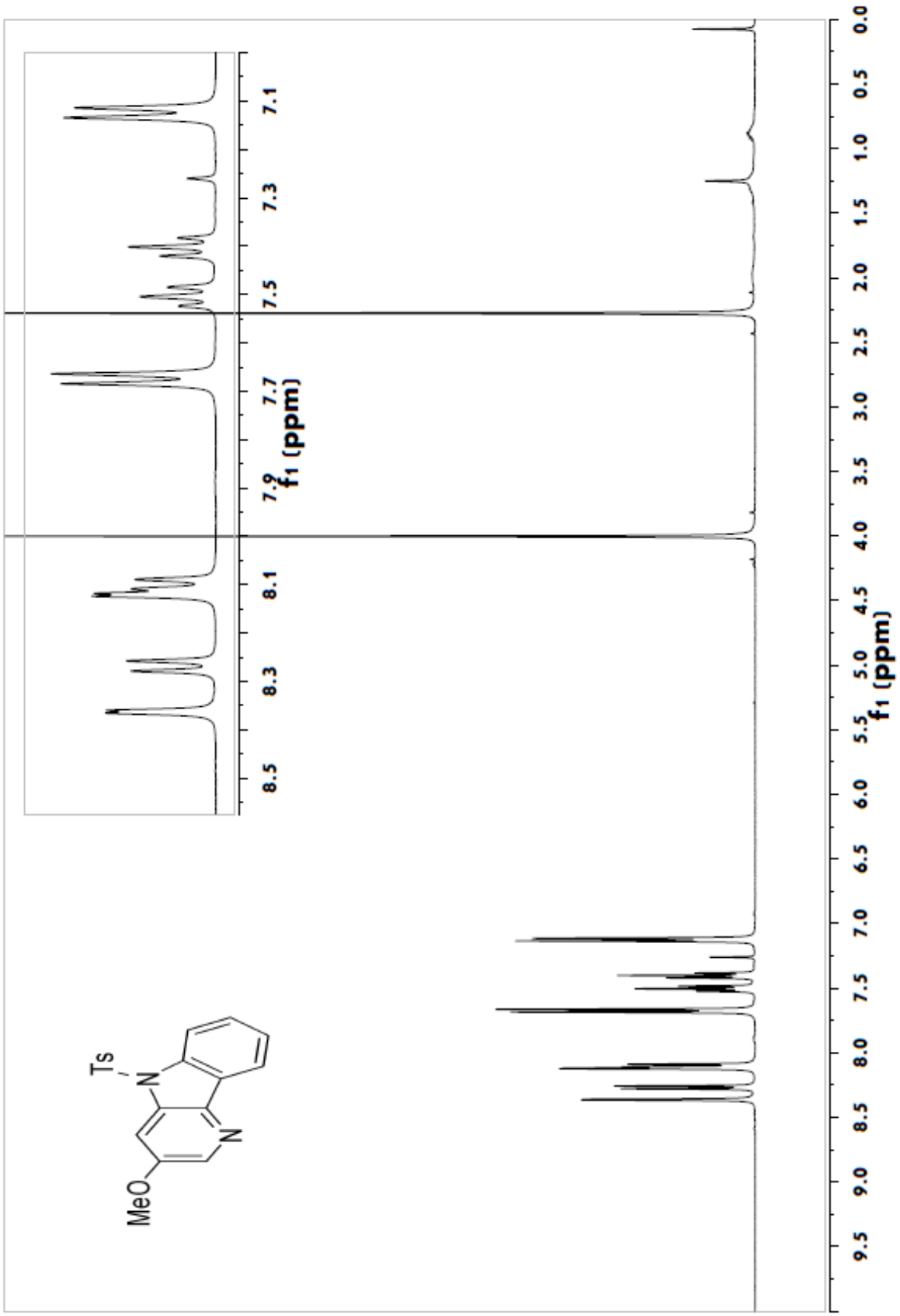


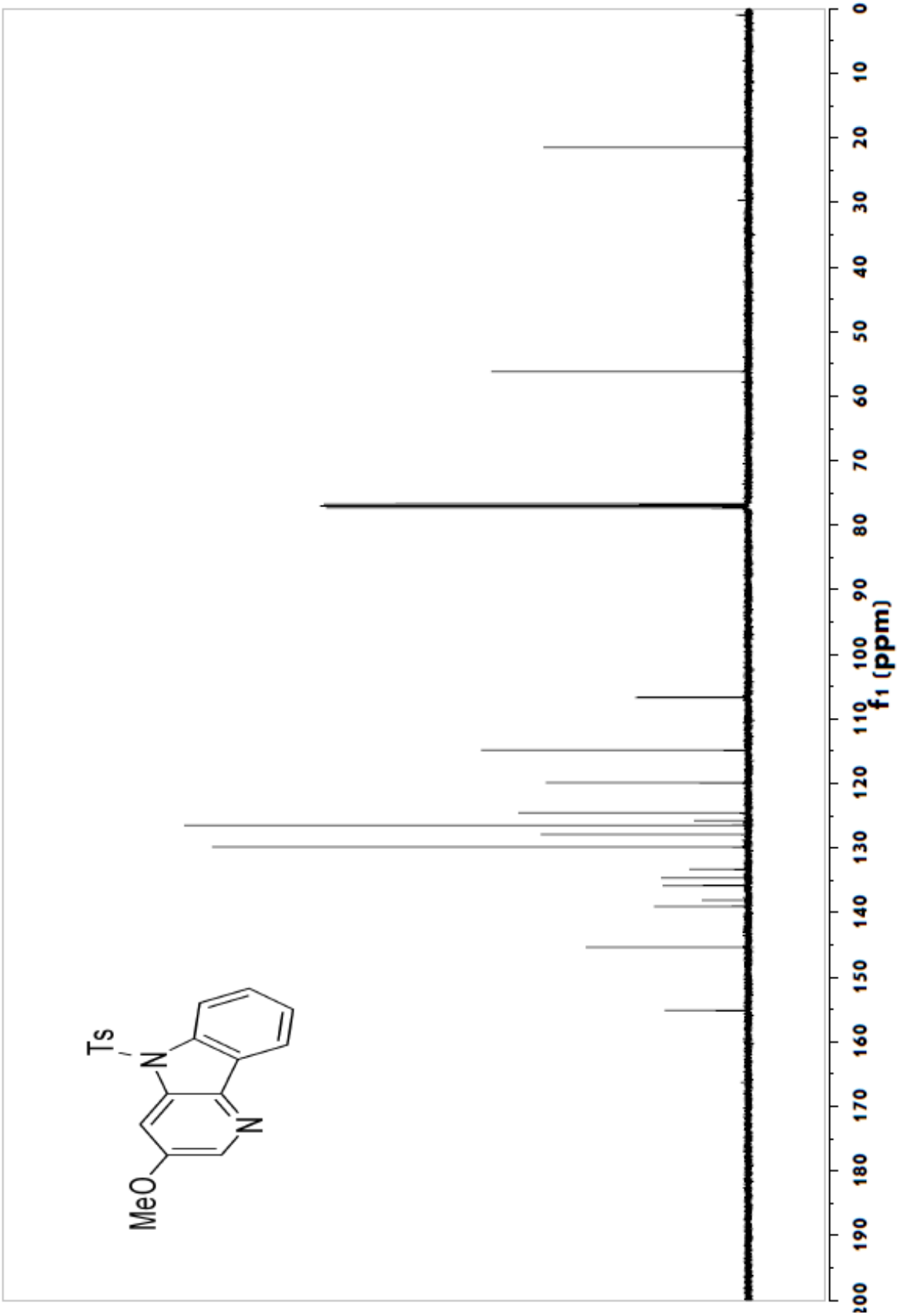






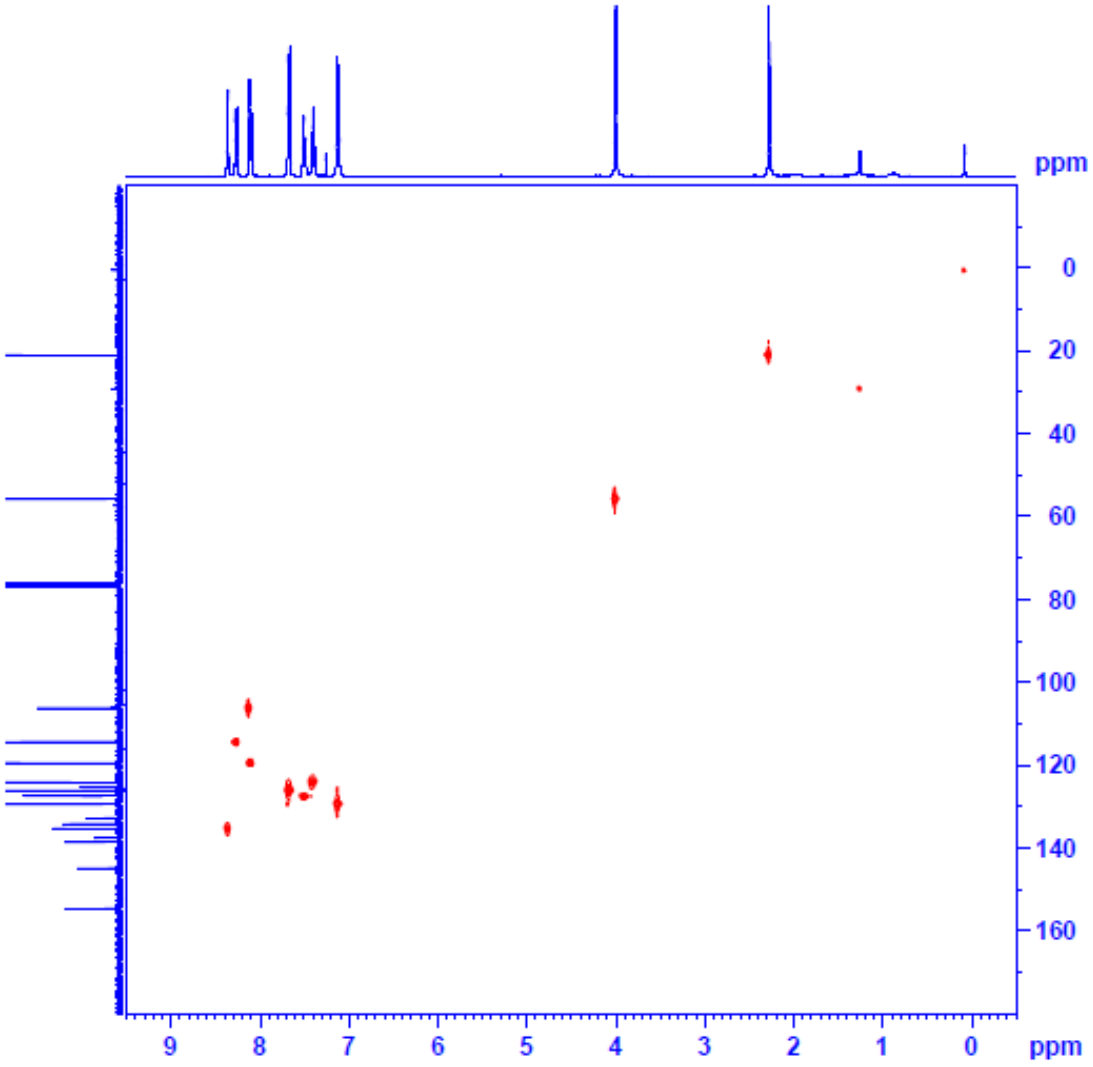




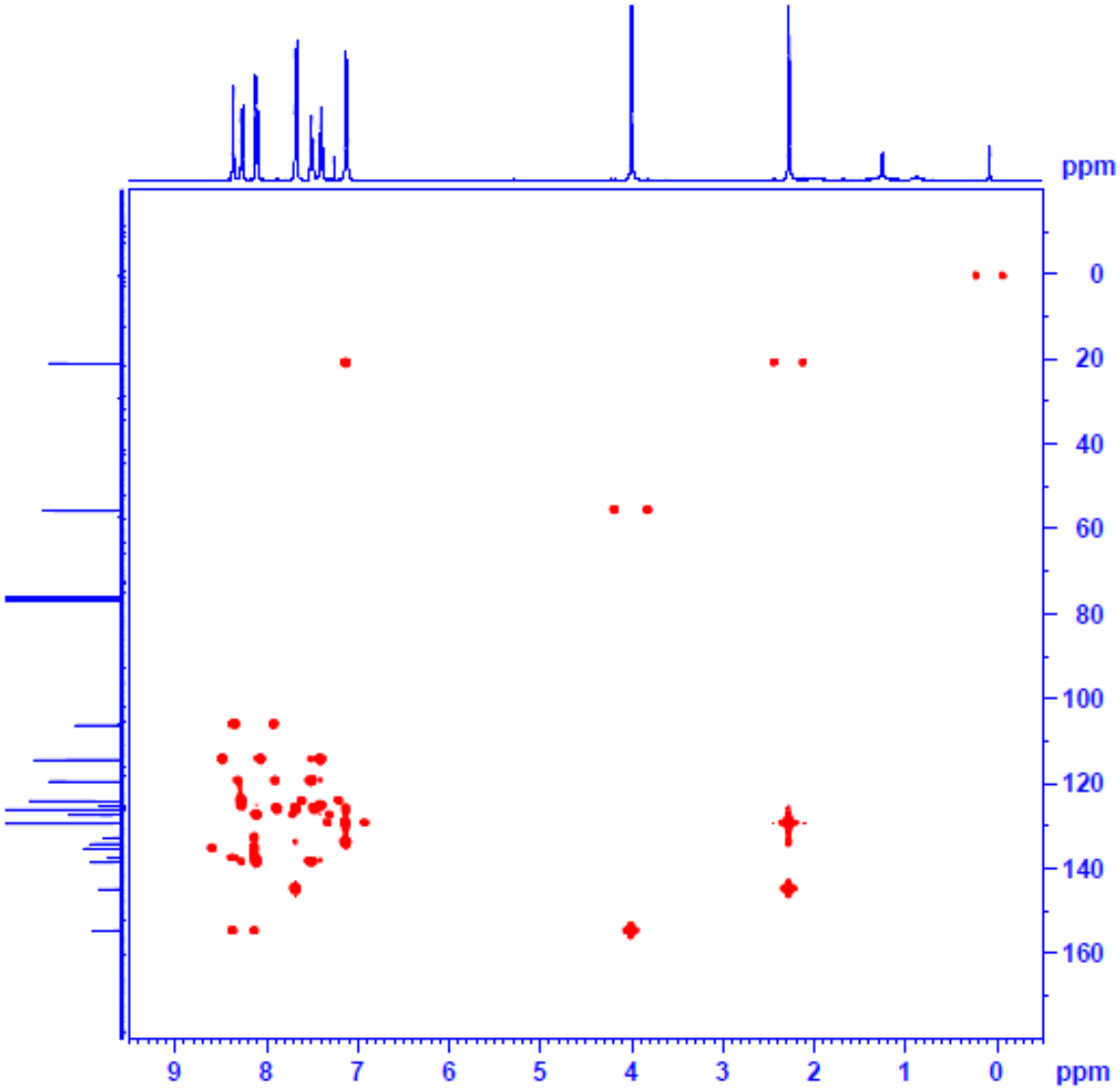


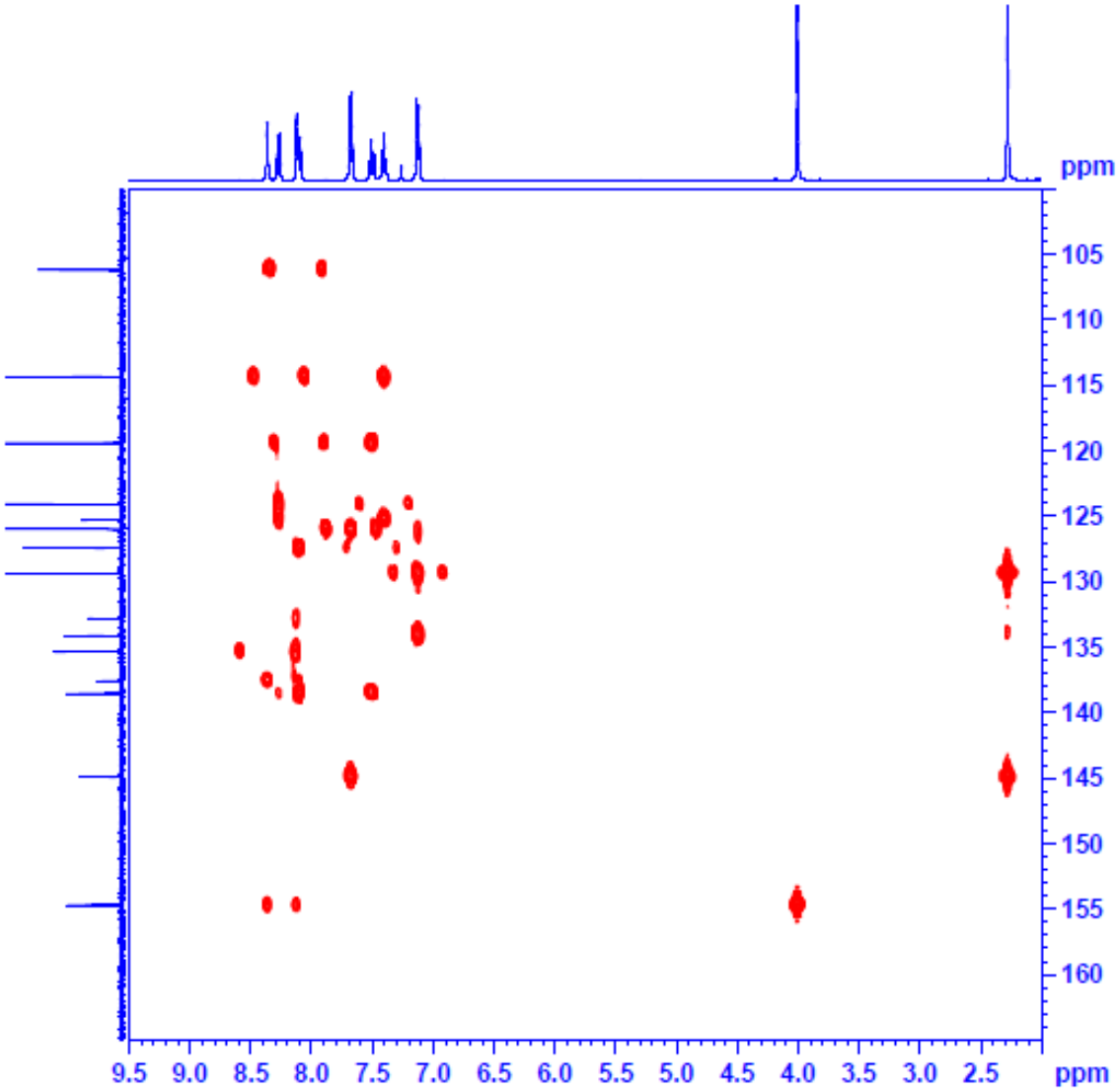
2D-HSQC Spectrum for Compound **15b**

Note: all carbons are labeled from a to q from higher chemical shift to lower. All hydrogen atoms are labeled according to the carbon atoms they attach to (i.e. Ha means the H attached to Ca).

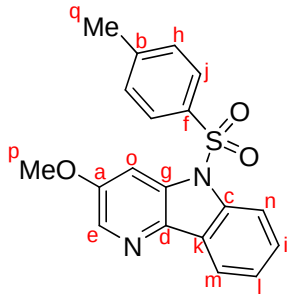


2D-HMBC Spectrum for Compound **15b**





Compound **15b**:



HMBC correlations (Ts part not shown):

He	Ca, Cd
Ho	Ca, Cd, Cg
Hn	Cc, Cl, Ck
Hi	Cc, Cm
Hl	Ck, Cn
Hm	Cc, Cd, Ci

Comparison of calculated vs observed ^{13}C NMR chemical shifts:

C	calculated[a]	observed
Ce	127	135
Ca	148	155
Co	100	106
Cg	130	133
Cd	143	138
Ck	127	125
Cc	147	139
Cn	115	114
Ci	129	127
Cl	117	124
Cm	124	119
[a] ACDLabs, version 6.00		

The other candidate has a 4-bond correlation in HMBC (Hm-Cd). Although less likely, it is not completely impossible and cannot be ruled out.