Electronic Supplementary Material (ESI) for Green Chemistry.
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Supporting Information

Visible-Light-Promoted Oxidative Halogenation of (Hetero)Arenes

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I. General Information

NMR Spectrum:

^{1}H and ^{13}C spectra were collected on 400 MHz NMR spectrometers (Bruker AVANCE). Chemical shifts for protons are reported in parts per million (ppm) downfield and are referenced to residual protium in the NMR solvent ($CHCl_3$ = δ 7.26, DMSO = δ 2.50). Chemical for carbon are reported in parts per million downfield and are referenced to coupling of carbon nucleus on deuterium ($CHCl_3$ = δ 77.0, DMSO = δ 39.52). Date are represented as follows: chemical shift, multiplicity (br = broad, s = singlet, d = double, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz), integration.

Mass Spectroscopy:

Mass spectra were recorded on a Shimadzu GCMS-QP2010 Ultra.

Chromatography:

Column chromatography was performed with silica gel (300 - 400 mesh ASTM).

IR:

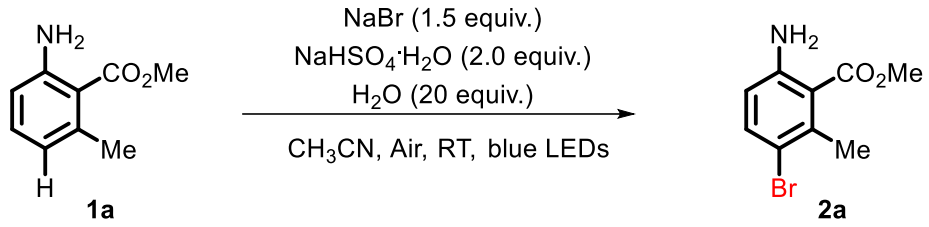
SHIMADZU IR Tracer-100 Spectrometers.

Solvent:

CH_3CN was dried with CaH_2 and distilled using standard methods. Distilled water was bought and used without further purification.

II. Conditions Optimization

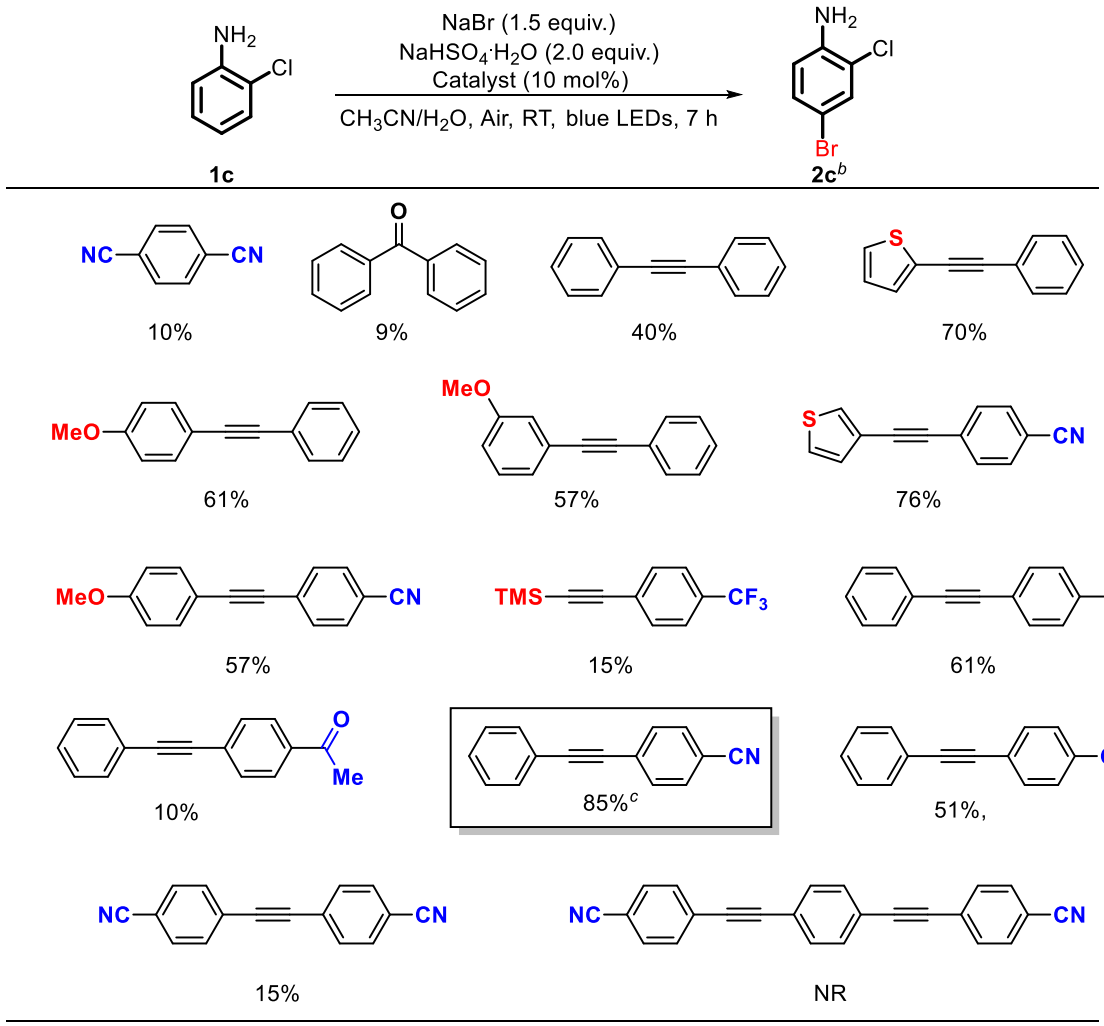
Table S1: Condition optimization of oxybromination.[a]



Entry	Variation from standard conditions	Yield (%)[b]
1	none	89
2	none[c]	81
3	N_2 instead of air	Trace
4	O_2 instead of air	88
5	no light	NR
6[d]	no light, 70 °C	NR
7[d]	no light, 100 °C	NR
8	no NaBr	NR
9	no $NaHSO_4·H_2O$	NR
10	no H_2O	80

[a]The reaction condictions: **1a** (0.2 mmol), H_2O (4.0 mmol), NaBr (0.3 mmol), $NaHSO_4·H_2O$ (0.4 mmol), CH_3CN (2.0 mL), room temperature, air, 2*3 W blue LEDs, 15 h.[b] NMR yields with CH_2Br_2 as internal standard. [c]the schlenk tube (25 mL) were sealed.

Table S2: Condition optimization of oxybromination.[a]



[a] The reaction condictions: **1c** (0.2 mmol), H_2O (4.0 mmol), NaBr (0.3 mmol), $NaHSO_4{\cdot}H_2O$ (0.4 mmol), Catalyst (0.02 mmol, 10 mol%), CH_3CN (2.0 mL), room temperature, air, 2*3 W blue LEDs, 7 h, NMR yields with CH_2Br_2 as internal standard. [b]10% yield without catalyst.[c] isolated yield.

III. Mechanistic Studies

1) Ultraviolet-visible Absorption Experiments

Ultraviolet-visible absorption experiments were performed using a Shimadzu UV-2700 UV-visible spectrophotometer. In each experiment, the varying samples were combined in CH_3CN in screw-top 1.0 cm quartz cuvettes.

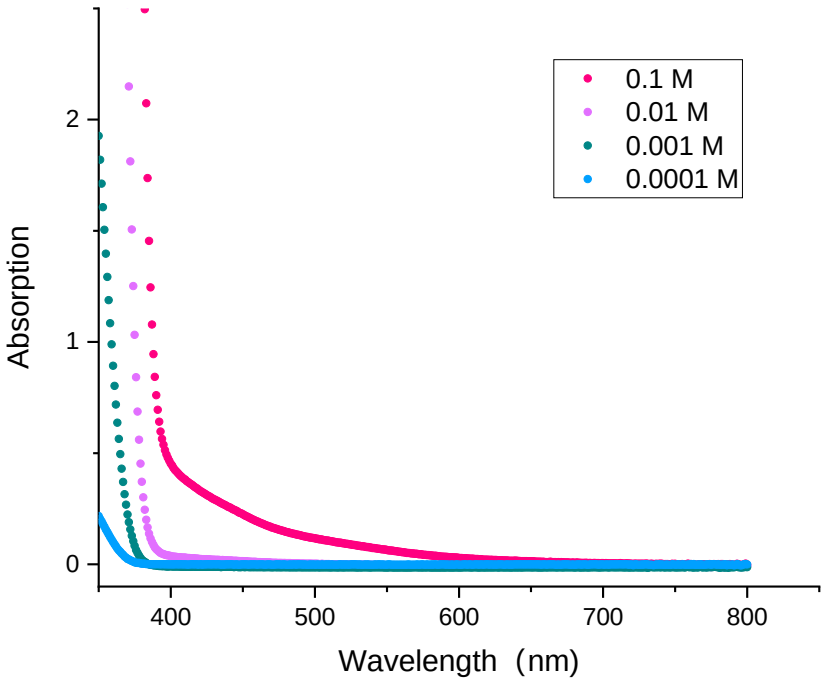
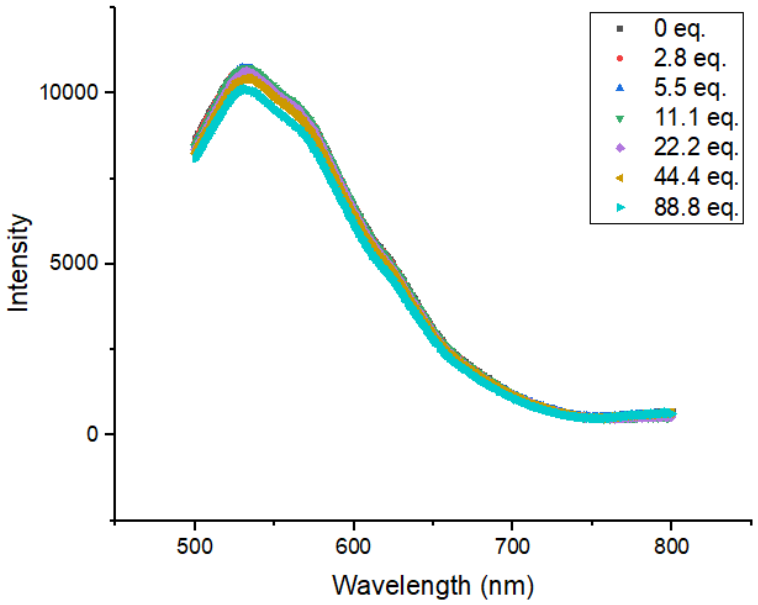


Figure S1: Ultraviolet-visible Absorption of **1a**.

2) Stern-Volmer Fluorescent Quenching Experiments

Fluorescence quenching studies were performed using a Shimadzu RF-6000 Fluorescence Spectrophotometer. In each experiment, the **1a** and varying concentrations of quencher were combined in CH_3CN in screw-top 1.0 cm quartz cuvettes. For the emission quenching of **1a** (0.01 M), the solution was irradiated at 455 nm, and the emission intensity was observed at 531 nm.



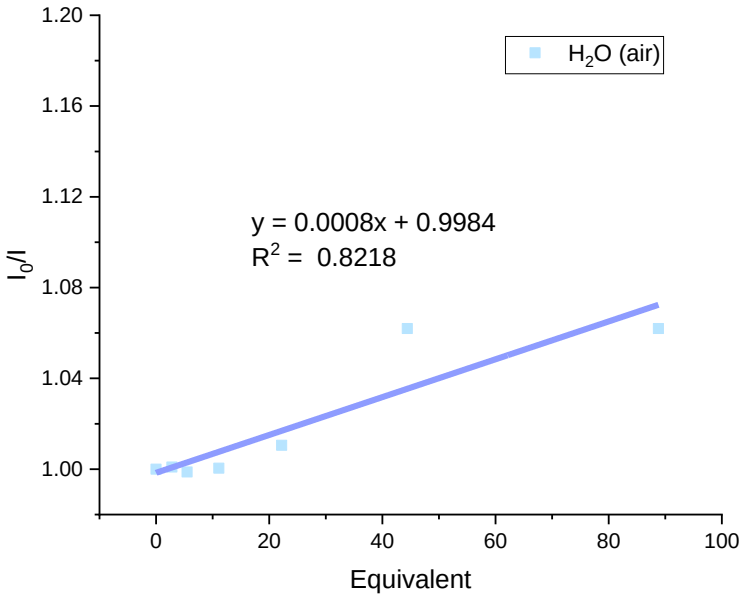
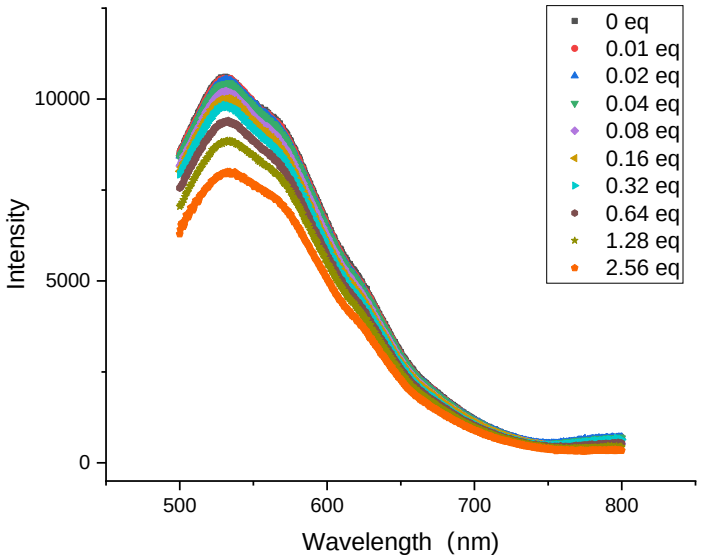


Figure S2: Quenching experiments of **1a** with H_2O.



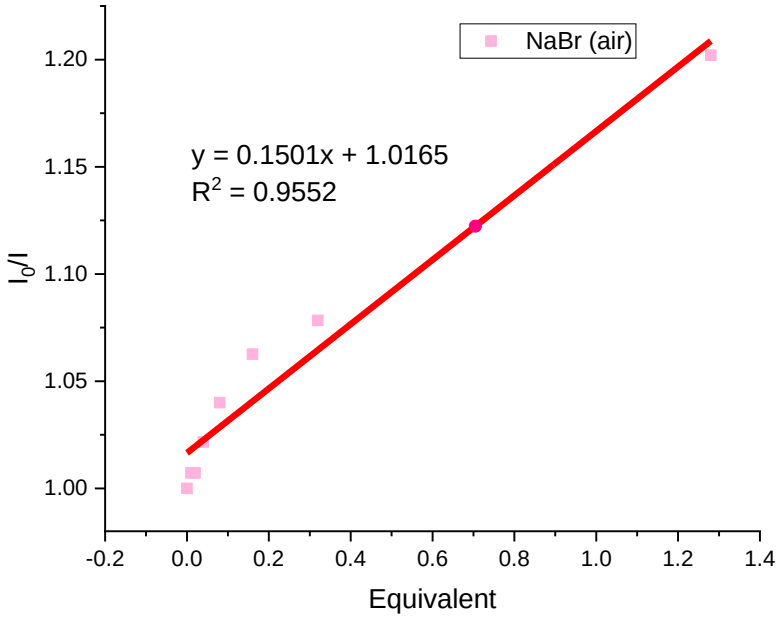
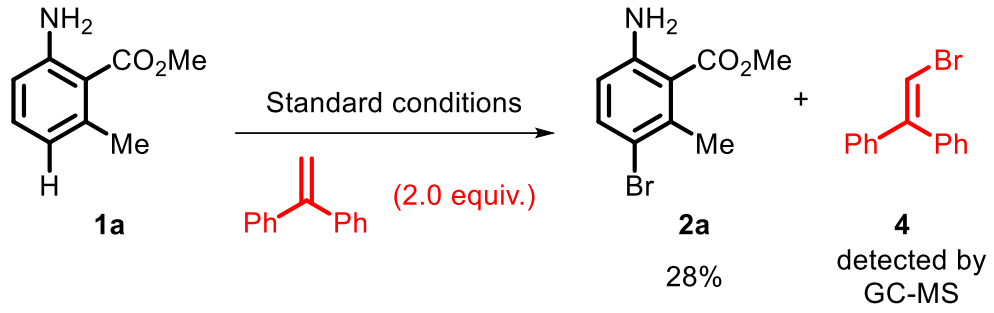


Figure S3: Quenching experiments of **1a** with sat. NaBr (aq).

3) Radical Trapping Experiments with 1,1-diphenylethylene

All reactions were operated under standard conditions with extra 1,1-diphenylethylene (2.0 equiv.). The yields of **2a** were determined with NMR.



The products were analyzed by GC-MS under the conditions:

GC

Column:

Name rtx Thickness 0.25 μm

Length 29.0 m Diameter 0.25 mm

Column temperature:

Heating rate (℃/min)	Temperature (℃)	Hold time (min)
--	50	2
15	200	15
10	250	5

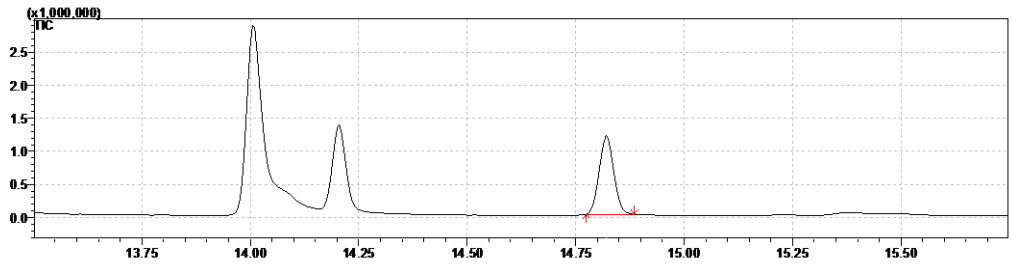
Split ratio: 30:1

Injection temperature: 200 ℃

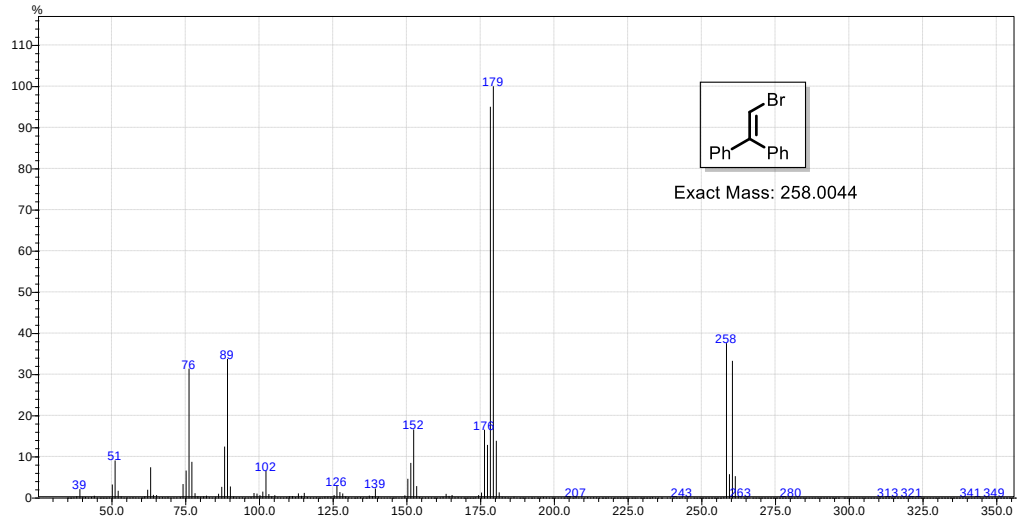
MS

Ion source temperature: 200 ℃ Interface temperature: 250 ℃

Detector voltage: 0.1 kV



Retention time: 14.821 min



4) Electron Paramagnetic Resonance Experiments

EPR measurements were performed on a Bruker E500 CW-EPR spectrometer operating in X-band**.** The reaction systems containing corresponding materials were stirred at room temperature under 2*3 W blue LEDs with paralleled reactors. After 4 hours, DMPO[a] (5 μL) was added to the reaction systems. After 10 mins, melting-point capillaries were used to suck certain amount of sample, then, both ends were melted by fire. This samples were submitted for the EPR experiments. While the group of experiments without DMPO, melting-point tubes were directly used to suck certain amounts of samples and both ends were melted by fire for EPR experiments.

[a]DMPO = 5,5-dimethyl-1-pyrroline-1-oxide.

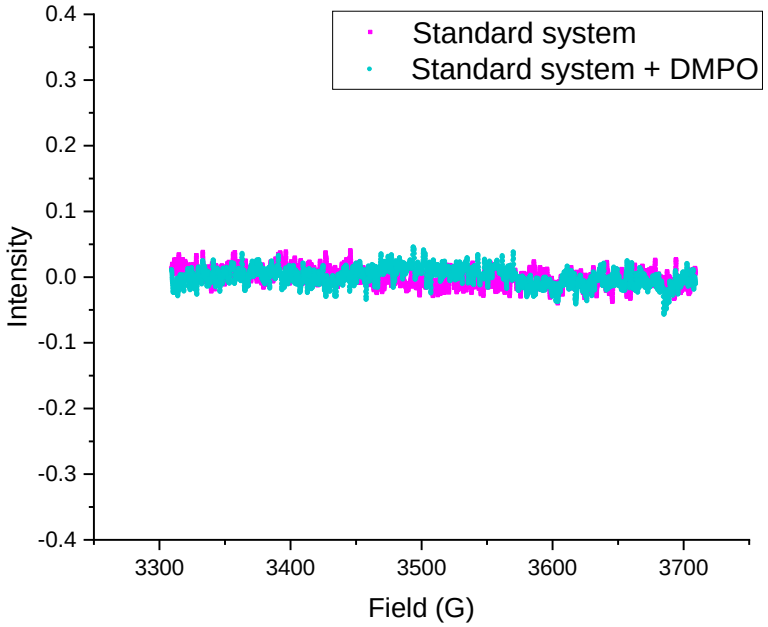


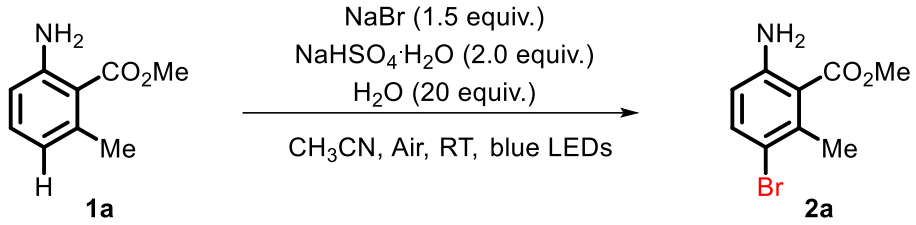
Figure S4: EPR spectrums.

No obvious HO• and $O_2^{-\bullet}$ in standard system.

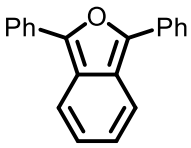
5) Control Experiments

All the reactions were conducted under standard conditions with certain amounts of additives. The corresponding yields were calculated by NMR with CH_2Br_2 as internal standard.

Table S3: Control Experiments.



1a **2a**

Entries	Additives (1 equiv.)	Functions	Yields (%)
1	NaN_3	$^1O_2$ inhibitor	66
2		$^1O_2$ inhibitor $O_2^{\bullet-}$ inhibitor	86
3	^{t}BuOH	$HO^\bullet$ inhibitor	85

6) Studies on Hydrogen Peroxide

The amount of H_2O_2 was determined by titration with iodide ion, as described previously in the literature[1] in which the reflux procedures was instead by stirring at room temperature. In an iodometric titration, the formation of I_3^- and the consumption of H_2O_2 follows a one-to-one ratio as eqs S1-3. The concentration H_2O_2 can be derived from the concentration of I_3(Abs@361 nm = $\varepsilon b[I_3^-]$). All iodometric titrations are conducted anaerobically to avoid the oxidation of I^- to I_3^- by O_2.

$$2\,H_2O_2 + 2\,I^- \longrightarrow H_2O + 1/2\,O_2 + I_2 \quad \text{(eq S1)}$$

$$I_2 + I^- \longrightarrow I_3^- \quad \text{(eq S2)}$$

$$H_2O_2 + 2\,I^- \longrightarrow H_2O + 1/2\,O_2 + I_3^- \quad \text{(eq S3)}$$

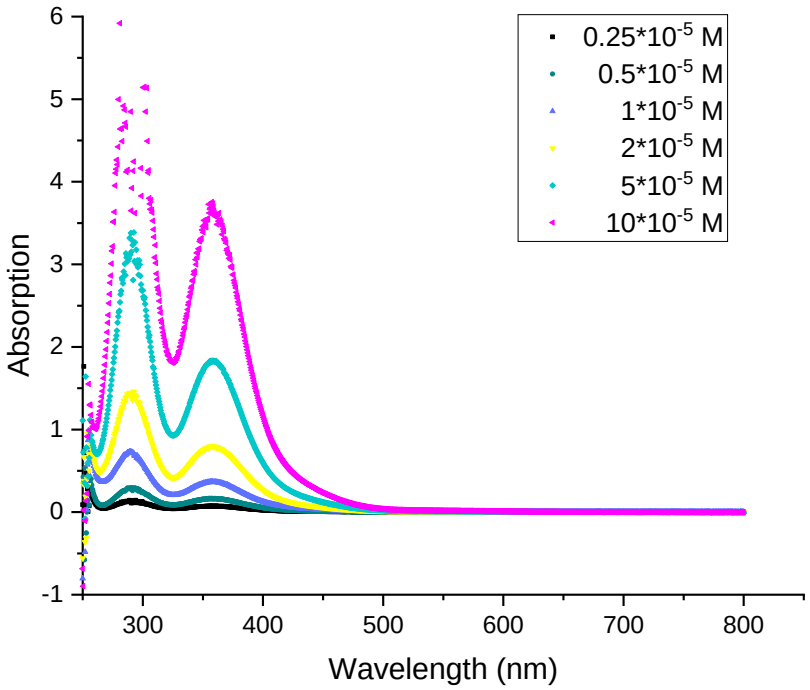


Figure S5: Ultraviolet-visible Absorption of I_3^- Generated by Different Concentration of H_2O_2.

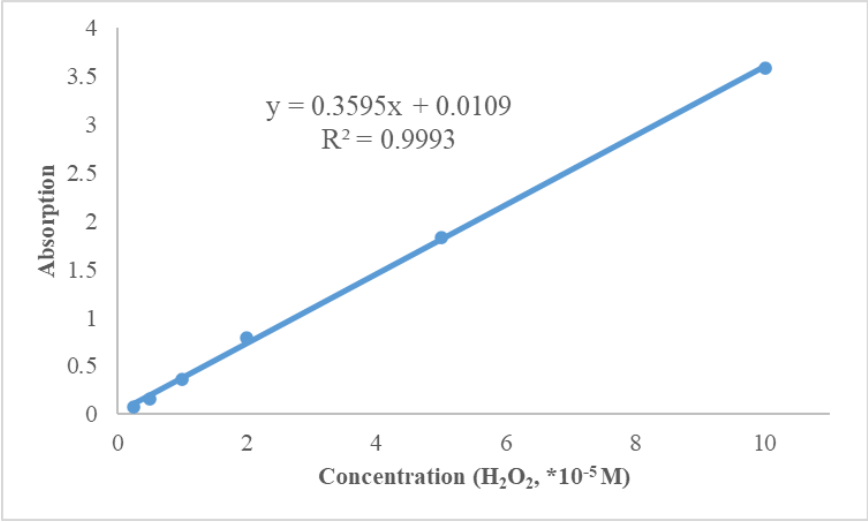


Figure S6 Standard Curve of the Amount of I_3^- for Its Quantitative Studies.

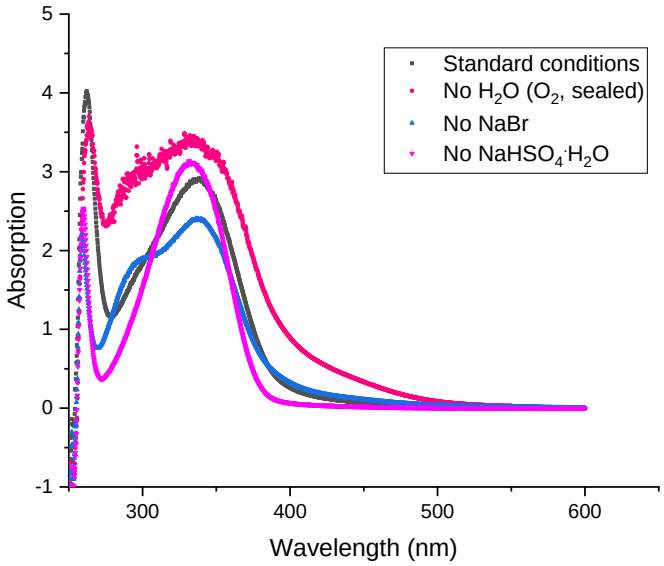
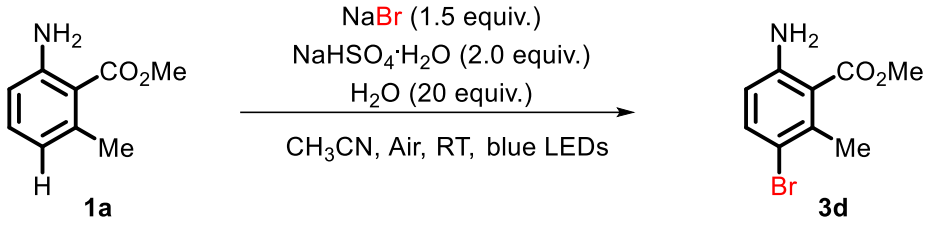


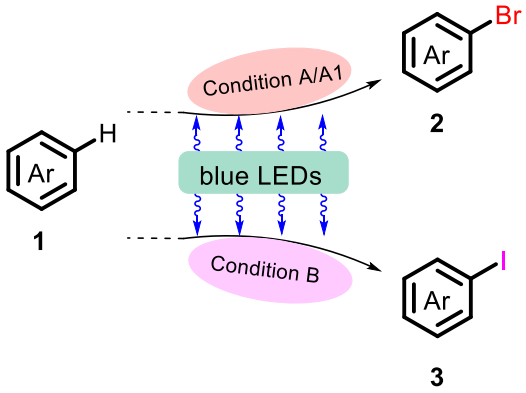
Figure S7: Ultraviolet-visible Absorption of Reaction Systems.

Table S4: Control Experiments Based on the Generation of H_2O_2 under Standard Conditions.



Entries	Conditions	in-situ generated H_2O_2
1	standard conditions	0.0109 mmol
2	No H_2O (O_2, sealed)	0.0154 mmol
3	No NaBr	0.0089 mmol
4	No $NaHSO_4 \cdot H_2O$	0.0084 mmol

IV. The General Procedure



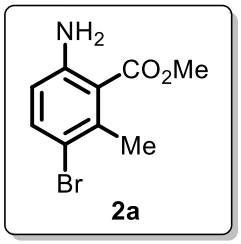
Condition A: In a 25 mL Schlenk tube, **1** (0.2 mmol, 1.0 equiv.), NaBr (0.3 mmol, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (0.4 mmol, 3.5 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), and the reaction mixture was stirred under 2*3 W blue LEDs at room temperature, which is opened to air. After the reaction completed, the reaction mixture was neutralized with saturated sodium bicarbonate and extracted with dichloromethane and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **2**.

Condition A1: In a 25 mL Schlenk tube, **1** (0.2 mmol, 1.0 equiv.), NaBr (0.3 mmol, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (0.4 mmol, 3.5 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), and the reaction mixture was stirred under 2*3 W blue LEDs at room temperature, which is opened to air. After the reaction completed, the reaction mixture was neutralized with saturated sodium bicarbonate and extracted with dichloromethane and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **2**.

Condition B: In a 25 mL Schlenk tube, **1** (0.2 mmol, 1.0 equiv.), NaI (0.6 mmol, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (0.6 mmol, 3.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), and the reaction mixture was stirred under 2*3 W blue LEDs at room temperature, which is opened to air. After the reaction completed, the

reaction mixture was neutralized with saturated sodium bicarbonate and extracted with dichloromethane and organic layers were combined, dried over sodium sulfate. After evaporation of solvent, the residue was purified by column chromatography to give the corresponding products **3**.

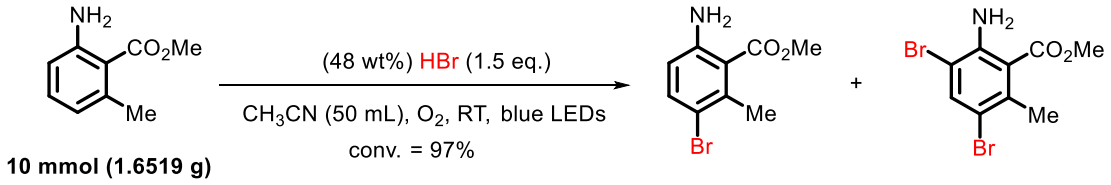
V. The Procedure and Data of Table 2



2a

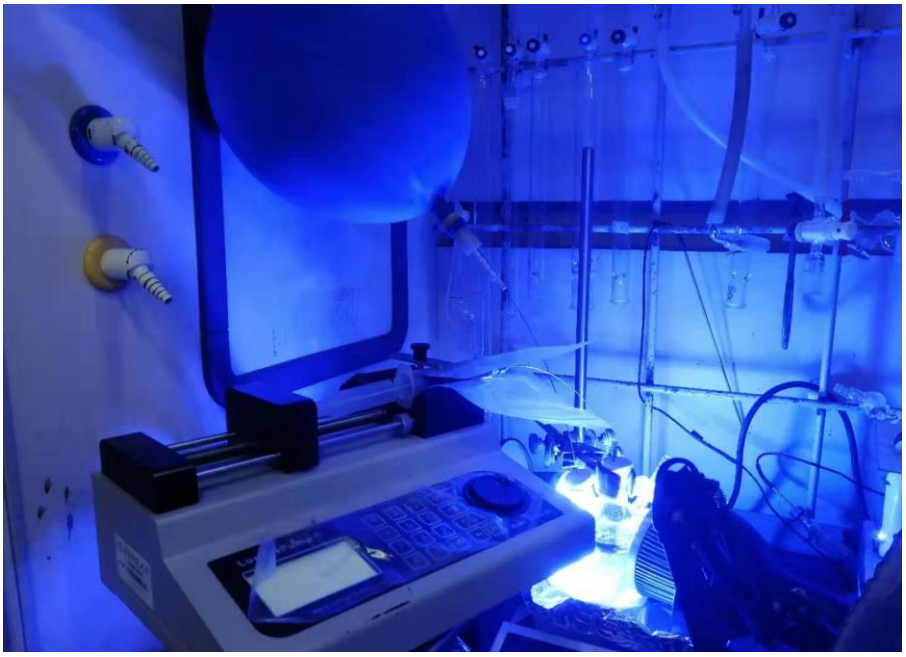
methyl 6-amino-3-bromo-2-methylbenzoate (2a): Prepared under outlined condition A as in general procedure using methyl 2-amino-6-methylbenzoate (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 15 hours affording compound **2a** in 85% (41.3 mg) yield as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 (d, J = 8.7 Hz, 1H), 6.42 (d, J = 8.7 Hz, 1H), 4.58 (s, 2H), 3.90 (s, 3H), 2.42 (br s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 146.5, 137.6, 135.4, 117.4, 115.6, 113.5, 51.9, 22.0. **HRMS** (EI) m/z Calcd for $C_9H_{10}BrNO_2$ 242.9895, Found 242.9897. **IR** (film) 3483, 3383, 2951, 1703, 1606, 1462, 1435, 1282, 1197, 1153, 1109, 1089, 1026, 985, 812, 752, 640 cm^{-1}.

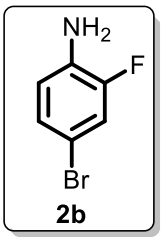
Gram-Scale Reaction



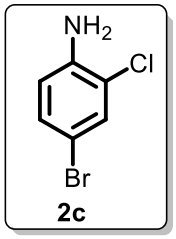
For 10 mmol scale, methyl 2-amino-6-methylbenzoate (10 mmol, 1.6519g) and 30 mL MeCN were stirred at 100 mL round bottom flask under oxygen atmosphere (1 atm, balloon) at room temperature under the irradiation of 2* 18 W blue LEDs. Then the hydrobromic acid (48 wt%, 1.5 equiv.) dissolved 20 mL MeCN was added dropwise by injection pump for 20 h. The system was reacted at room temperature for 97 h with bubbling oxygen using balloon. Subsequently, dichloromethane (DCM) (50 mL) was added and the system was transferred into the separating funnel. The organic phase was washed with $NaHCO_3$ (50 mL) twice. Next, the aqueous phase was extracted with DCM (100 mL*2). The organic phase was combined and dried with $MgSO_4$. After filtration,

distillation, and chromatography, methyl 6-amino-3-bromo-2-methylbenzoate (1.7937 g, 74%) was obtained as brown oil. The apparatus was shown as below:

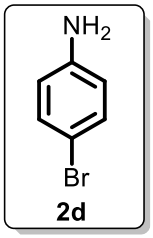




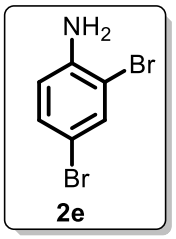
4-bromo-2-fluoroaniline (2b): Prepared under outlined condition A1 as in general procedure using 2-fluoroaniline (22.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4 \cdot H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 24 hours affording compound **2b**[2] in 48% (18 mg) yield as brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 10.5, 2.1 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.65 (t, *J* = 8.9 Hz, 1H), 3.41 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.8 (d, *J* = 244.2 Hz), 133.7 (d, *J* = 12.7 Hz), 127.4 (d, J = 3.6 Hz), 118.6 (d, *J* = 21.9 Hz), 117.7 (d, *J* = 4.0 Hz), 108.9 (d, *J* = 8.6 Hz). **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.34. **MS** (EI) m/z 189. **IR** (film) 3012, 1726, 1618, 1481, 1442, 1365, 1224, 1151, 771, 567 cm^{-1}.



4-bromo-2-chloroaniline (2c): Prepared under outlined condition A1 as in general procedure using 2-chloroaniline (25.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 7 hours affording compound **2c**[3] in 85% (34.8 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 2.2 Hz, 1H), 7.15 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.63 (d, *J* = 8.6 Hz, 1H), 4.02 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.1, 131.6, 130.5, 119.9, 116.8, 109.3. **MS** (EI) m/z 205. **IR** (film) 3483, 3375, 1616, 1485, 1396, 1296, 1253, 1153, 1043, 867, 844, 808, 711, 623 cm^{-1}.

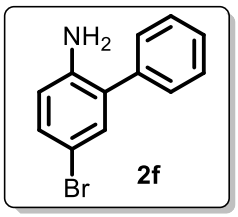


4-bromoaniline (2d): Prepared under outlined condition A1 as in general procedure using aniline (18.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (41.1 mg, 2.0 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 2-(phenylethynyl)thiophene (0.04 mmol, 20 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 12 W blue LEDs at room temperature for 48 hours affording compound **2d**[4] in 44% (15 mg) yield as brown solid. Meanwhile, including 2,4-dibromaniline (10%) as by-product, and aniline was recovered (15%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.26 – 7.20 (m, 1H), 6.60 – 6.51 (m, 1H), 3.64 (s, 1H).. **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.4, 132.0, 116.7, 110.2.

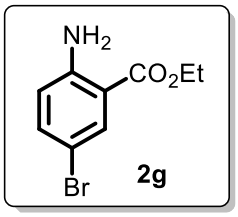


2,4-dibromoaniline (2e): Prepared under outlined condition A1 as in general procedure using 2-bromoaniline (34.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 48 hours affording compound **2e**[3] in 53% (26.4 mg) yield as brown solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ

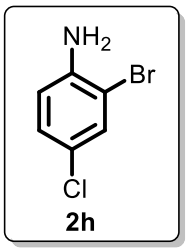
δ 7.53 (d, *J* = 2.2 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.64 (d, *J* = 8.5 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.2, 134.4, 131.1, 116.6, 109.6, 109.5. **MS** (EI) m/z 249. **IR** (film) 3404, 3307, 3192, 2924, 1714, 1625, 1581, 1481, 1392, 1290, 1033, 866, 837, 810, 684, 621 cm^{-1}.



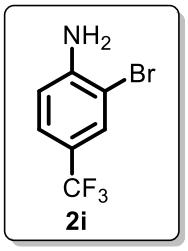
5-bromo-[1,1'-biphenyl]-2-amine (2f): Prepared under outlined condition A1 as in general procedure using [1,1'-biphenyl]-2-amine (33.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 48 hours, then add NaBr (30.8 mg, 1.5equiv.) and $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.) continue to reaction for 24 hours affording compound **2f**[5] in 70% (35 mg) yield as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 – 7.21 (m, 5H), 7.19 – 7.08 (m, 2H), 6.55 (d, *J* = 9.1 Hz, 1H), 3.25 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.6, 138.1, 132.8, 131.0, 129.4, 128.9, 128.9, 127.7, 117.1, 110.2. **MS** (EI) m/z 247. **IR** (film) 3375, 3053, 1664, 1614, 1481, 1400, 1292, 1263, 1149, 1083, 812, 771, 702, 623, 569 cm^{-1}.



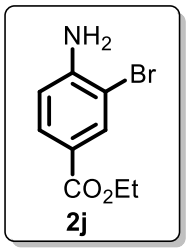
ethyl 2-amino-5-bromobenzoate (2g): Prepared under outlined condition A1 as in general procedure using ethyl 2-aminobenzoate (33.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 34 hours affording compound **2g**[6] in 68% (33 mg) yield as faint yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.4 Hz, 1H), 7.32 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 167.0, 149.2, 136.6, 133.4, 118.4, 112.4, 107.4, 60.7, 14.3. **MS** (EI) m/z 243. **IR** (film) 3466, 3358, 2981, 1681, 1608, 1475, 1365, 1292, 1236, 1165, 1124, 1083, 1020, 825, 786, 704, 630 cm^{-1}.



2-bromo-4-chloroaniline (2h): Prepared under outlined condition A1 as in general procedure using 4-chloroaniline (25.4 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 24 hours affording compound **2h**[3] in 60% (24.6 mg) yield as faint yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 2.3 Hz, 1H), 7.06 (dd, *J* = 8.6, 2.3 Hz, 1H), 6.67 (d, *J* = 8.6 Hz, 1H), 3.97 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.8, 131.8, 128.3, 123.0, 116.2, 109.1. **MS** (EI) m/z 205. **IR** (film) 3473, 3381, 1614, 1479, 1398, 1301, 1151, 1111, 1033, 867, 844, 808, 702, 644 cm^{-1}.

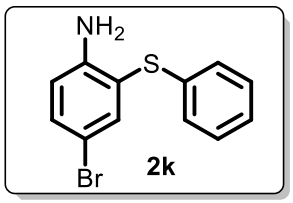


2-bromo-4-(trifluoromethyl)aniline (2i): Prepared under outlined condition A1 as in general procedure using 4-(trifluoromethyl)aniline (32.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 24 hours affording compound **2i**[7] in 80% (38 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 6.76 (dd, *J* = 8.2, 2.0 Hz, 1H), 4.40 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 146.99, 129.95 (q, *J* = 4.0 Hz), 125.59 (q, *J* = 3.7 Hz), 123.85 (q, *J* = 272.0 Hz), 121.05 (q, *J* = 33.3 Hz), 114.73, 108.06. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -61.34. **MS** (EI) m/z 239. **IR** (film) 3493, 3390, 1622, 1517, 1417, 1323, 1263, 1116, 1080, 891, 819, 684, 621 cm^{-1}.



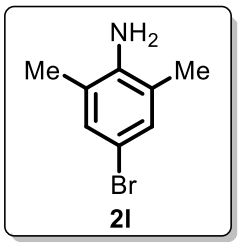
ethyl 4-amino-3-bromobenzoate (2j): Prepared under outlined condition A1 as in general procedure using ethyl 4-aminobenzoate (33.0 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in

CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 10 hours affording compound **2j**[8] in 58% (28.2 mg) yield as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 1.9 Hz, 1H), 7.81 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.75 (d, *J* = 8.4 Hz, 1H), 4.33 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.6, 147.9, 134.4, 130.2, 121.2, 114.3, 107.9, 60.7, 14.4. **MS** (EI) m/z 243. **IR** (film) 3469, 3358, 2980, 1693, 1616, 1506, 1365, 1284, 1244, 1114, 1022, 894, 763, 682, 632 cm^{-1}.



2k

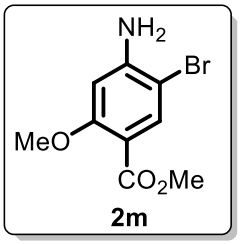
4-bromo-2-(phenylthio)aniline (2k): Prepared under outlined condition A1 as in general procedure using 2-(phenylthio)aniline (33.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 120 hours affording compound **2k**[9] in 71% (35 mg) yield as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 2.3 Hz, 1H), 7.30 (dd, *J* = 8.6, 2.3 Hz, 1H), 7.24 (dd, *J* = 9.7, 5.3 Hz, 2H), 7.15 (d, *J* = 7.2 Hz, 1H), 7.14 – 7.08 (m, 2H), 6.67 (d, *J* = 8.6 Hz, 1H), 3.94 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.6, 138.9, 135.7, 133.7, 129.1, 127.0, 125.9, 116.7, 116.6, 109.3. **MS** (EI) m/z 279. **IR** (film) 3469, 3369, 1606, 1475, 1438, 1390, 1300, 1247, 1153, 1024, 813, 740, 690, 624 cm^{-1}.



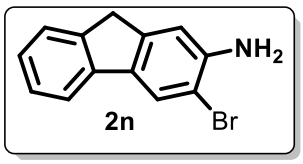
2l

4-bromo-2,6-dimethylaniline (2l): Prepared under outlined condition A1 as in general procedure using 2,6-dimethylaniline (33.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (41.1 mg, 2.0 equiv.), $NaHSO_4{\cdot}H_2O$ (69.0 mg, 2.5 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 72 hours affording compound **2l**[10] in 65% (26 mg) yield as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.06 (s, 2H), 3.47 (s, 2H), 2.15 (br s, 6H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 130.5, 123.6, 109.5, 17.4 (d, *J* = 2.0 Hz). **MS** (EI) m/z 199.

IR (film) 3483, 3396, 2908, 1618, 1475, 1444, 1377, 1284, 1230, 999, 862, 725 cm^{-1}.

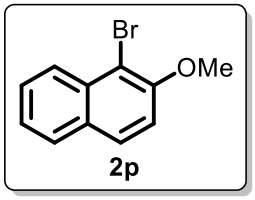


methyl 4-amino-5-bromo-2-methoxybenzoate (2m): Prepared under outlined condition A1 as in general procedure using methyl 4-amino-2-methoxybenzoate (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 10 hours affording compound **2m** in 79% (41 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 6.28 (s, 1H), 4.31 (br s, 2H), 3.82 (d, *J* = 1.8 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.0, 160.7, 148.9, 136.5, 110.3, 98.9, 98.1, 56.0 (d, *J* = 3.1 Hz), 51.6 (d, *J* = 3.2 Hz). **HRMS** (EI) m/z Calcd for $C_9H_{10}BrNO_3$ 258.9844, Found 258.9847. **IR** (film) 3458, 3307, 1714, 1699, 1624, 1591, 1429, 1336, 1236, 1178, 1103, 1043, 991, 833, 775, 673 cm^{-1}.



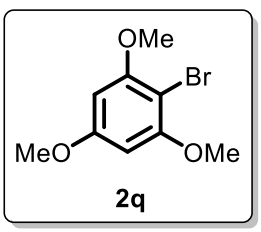
3-bromo-9*H*-fluoren-2-amine (2n): Prepared under outlined condition A as in general procedure using 9H-fluoren-2-amine (36.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (61.7 mg, 3.0 equiv.), $NaHSO_4.H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in acetone (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 48 hours affording compound **2n** in 52% (26.9 mg) yield as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.81 (s, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 6.94 (s, 1H), 4.13 (br s, 2H), 3.77 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 144.1, 142.8, 142.3, 141.1, 134.2, 126.8, 125.7, 124.8, 123.8, 118.8, 112.2, 108.2, 36.5. **HRMS** (EI) m/z Calcd for $C_{13}H_{10}BrN$ 258.9997, Found 258.9993. **IR** (film) 3468, 3365, 1716, 1616, 1566, 1450, 1417, 1355, 1311, 1222, 1139, 1101, 1031, 960, 875, 761, 729 cm^{-1}.

4-(4-bromophenyl)morpholine (2o): Prepared under outlined condition A1 as in general procedure using 4-phenylmorpholine (32.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 48 hours, then add NaBr (20.6 mg, 1.0 equiv.) continue to reaction for 48 hours affording compound **2o**[10] in 50% (24.1 mg) yield as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 – 7.30 (m, 1H), 6.79 (d, *J* = 8.9 Hz, 1H), 3.98 – 3.73 (m, 2H), 3.21 – 3.02 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2, 131.9, 117.3, 112.3, 66.7, 49.2. **MS** (EI) m/z 241. **IR** (film) 2833, 1722, 1589, 1496, 1450, 1379, 1259, 1236, 1118, 1051, 923, 817, 659 cm^{-1}.



2p

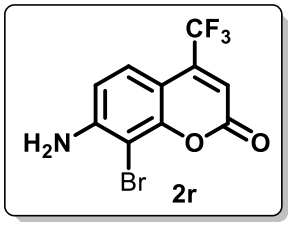
1-bromo-2-methoxynaphthalene (2p): Prepared under outlined condition A1 as in general procedure using 2-methoxynaphthalene (31.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 64 hours affording compound **2p**[10] in 63% (30 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.6 Hz, 1H), 7.78 (dd, *J* = 11.7, 8.6 Hz, 2H), 7.55 (ddd, *J* = 8.3, 6.9, 1.1 Hz, 1H), 7.44 – 7.33 (m, 1H), 7.25 (d, *J* = 8.9 Hz, 1H), 4.01 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 153.7, 133.1, 129.8, 129.0, 128.0, 127.7, 126.1, 124.3, 113.6, 108.6, 57.0 (d, *J* = 2.3 Hz). **MS** (EI) m/z 236. **IR** (film) 3047, 2972, 2843, 1622, 1595, 1500, 1467, 1352, 1271, 1246, 1155, 1062, 893, 804, 763, 746, 648 cm^{-1}.



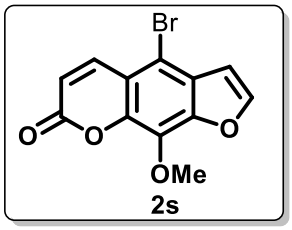
2q

methyl 6-amino-3-bromo-2-methylbenzoate (2q): Prepared under outlined condition A1 as in general procedure using 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (30.8 mg, 1.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), 4-(phenylethynyl)benzonitrile (0.02 mmol, 10 mol%), H_2O (72.0 mg, 20.0 equiv.) were

dissolved in CH_3CN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 48 hours, then add NaBr (30.8 mg, 1.5 equiv.) and $NaHSO_4 \cdot H_2O$ (55.2 mg, 2.0 equiv.) continue to reaction for 48 hours affording compound **2q**[10] in 83% (40.8 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.16 (s, 2H), 3.87 (s, 6H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.5, 157.5, 92.0, 91.7, 56.3 (d, *J* = 3.5 Hz), 55.5 (d, *J* = 3.4 Hz). **MS** (EI) m/z 246. **IR** (film) 2941, 2839, 1587, 1454, 1409, 1342, 1228, 1205, 1161, 1124, 1029, 948, 808, 632 cm^{-1}.

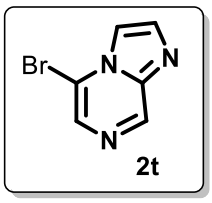


7-amino-8-bromo-4-(trifluoromethyl)-2*H*-chromen-2-one (2r): Prepared under outlined condition A as in general procedure using 7-amino-4-(trifluoromethyl)-2*H*-chromen-2-one (45.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4 \cdot H_2O$ (82.8 mg, 3.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 17 hours affording compound **2r** in 81% (48 mg) yield as yellow solid. **^{1}H NMR** (400 MHz, DMSO) δ 7.46 – 7.31 (m, 1H), 6.85 (d, *J* = 9.0 Hz, 1H), 6.70 (s, 2H), 6.57 (s, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 159.1, 153.2, 151.4, 140.5 (q, *J* = 32.2 Hz), 124.7, 13.85 (d, *J* = 276.7 Hz), 112.6, 109.1 (q, *J* = 5.6 Hz), 103.4, 93.6. **^{19}F NMR** (376 MHz, CDCl3) δ -56.76, -64.30. **HRMS** (EI) m/z Calcd for $C_{10}H_5BrF_3NO_2$ 306.9456, Found 306.9452. **IR** (film) 3367, 1728, 1631, 1595, 1531, 1408, 1280, 1199, 1174, 1145, 862, 675 cm^{-1}.

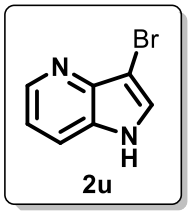


4-bromo-9-methoxy-7*H*-furo[3,2-g]chromen-7-one (2s): Prepared under outlined condition A as in general procedure using 9-methoxy-7*H*-furo[3,2-g]chromen-7-one (43.2 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 96 hours affording compound **2s**[10] in 65% (38.2 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.9 Hz, 1H), 7.72 (d, *J* = 2.1 Hz, 1H), 6.86 (d, *J* = 2.1 Hz, 1H),

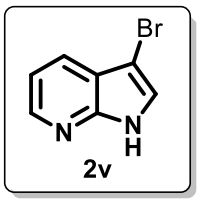
6.43 (d, J = 9.9 Hz, 1H), 4.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 159.7, 146.9, 146.6, 143.7, 142.5, 132.4, 127.9, 115.8, 115.6, 107.4, 105.5, 61.4 (d, J = 2.5 Hz). **MS** (EI) m/z 294. **IR** (film) 2927, 1739, 1724, 1589, 1460, 1415, 1377, 1330, 1155, 1107, 1029, 956, 887, 829, 750 cm^{-1}.



5-bromoimidazo[1,2-*a*]pyrazine (2t): Prepared under outlined condition A as in general procedure using imidazo[1,2-*a*]pyrazine (23.8 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 96 hours affording compound **2t**[10] in 86% (33.8 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.04 (s, 1H), 8.02 (s, 1H), 7.87 (s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 135.6, 131.2, 114.6, 111.6. **MS** (EI) m/z 197. **IR** (film) 3099, 1720, 1485, 1463, 1444, 1365, 1301, 1257, 1203, 1145, 941, 831, 759, 634, 584 cm^{-1}.

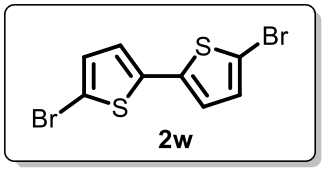


3-bromo-1*H*-pyrrolo[3,2-*b*]pyridine (2u): Prepared under outlined condition A as in general procedure using 1*H*-pyrrolo[3,2-*b*]pyridine (23.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 2.5 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 54 hours affording compound **2u**[11] in 81% (31.7 mg) yield as white solid. **^{1}H NMR** (400 MHz, DMSO) δ 11.70 (s, 1H), 8.40 (d, J = 4.2 Hz, 1H), 8.00 – 7.67 (m, 2H), 7.19 (dd, J = 8.2, 4.5 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 143.7, 142.8, 128.9, 128.6, 119.9, 117.8, 90.0. **MS** (EI) m/z 196. **IR** (film) 3435, 1708, 1651, 1404, 1359, 1226, 1026, 1004, 891, 823, 756, 642, 578 cm^{-1}.

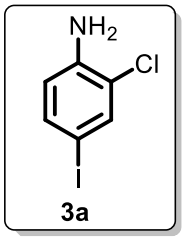


3-bromo-1*H*-pyrrolo[2,3-*b*]pyridine (2v): Prepared under outlined condition A as in general procedure using 1*H*-pyrrolo[2,3-b]pyridine (23.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (51.4 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (110.4 mg, 4.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were

dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 54 hours affording compound **2v**[10] in 81% (31.7 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 11.15 (s, 1H), 8.44 – 8.29 (m, 1H), 7.94 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.41 (s, 1H), 7.19 (dd, *J* = 7.9, 4.8 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 147.4, 143.5, 128.0, 124.4, 120.0, 116.5, 89.4. **MS** (EI) m/z 196. **IR** (film) 3078, 2819, 1720, 1606, 1585, 1411, 1321, 1286, 1222, 979, 786, 767, 646, 592, 569 cm^{-1}.



5,5'-dibromo-2,2'-bithiophene (2w): Prepared under outlined condition A as in general procedure using 2,2'-bithiophene (23.6 mg, 0.2 mmol, 1.0 equiv.), NaBr (61.6 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 96 hours affording compound **2w**[12] in 57% (37 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 3.8 Hz, 2H), 6.85 (d, *J* = 3.8 Hz, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.8, 130.6, 124.1, 111.5. **MS** (EI) m/z 322. **IR** (film) 3496, 3039, 1720, 1504, 1417, 1367, 1224, 1058, 972, 867, 792 cm^{-1}.



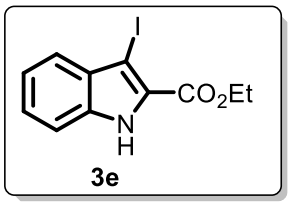
2-chloro-4-iodoaniline (3a): Prepared under outlined condition B as in general procedure using 2-chloroaniline (25.4 mg, 0.2 mmol, 1.0 equiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 90 hours affording compound **3a**[13] in 51% (25.8 mg) yield as yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.31 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 8.4 Hz, 1H), 3.90 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 142.7, 137.1, 136.3, 120.2, 117.4, 77.9. **MS** (EI) m/z 253. **IR** (film) 3475, 3375, 1705, 1614, 1481, 1392, 1307, 1292, 1157, 869, 839, 808, 704, 609 cm^{-1}.

5-iodo-[1,1'-biphenyl]-2-amine (3b): Prepared under outlined condition B as in general procedure using [1,1'-biphenyl]-2-amine (33.8 mg, 0.2 mmol, 1.0 equiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (82.8 mg, 3.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 54 hours affording compound **3b**[14] in 42% (25 mg) yield as brown oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 20.2, 12.9 Hz, 7H), 6.54 (d, J = 8.0 Hz, 1H), 3.44 (br s, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 143.3, 138.6, 138.0, 136.9, 130.0, 128.9, 128.8, 127.6, 117.6, 79.4. **MS** (EI) m/z 295. **IR** (film) 1716, 1612, 1479, 1444, 1392, 1365, 1222, 810, 771, 704, 611, 563 cm^{-1}.

methyl 4-amino-5-iodo-2-methoxybenzoate (3c): Prepared under outlined condition B as in general procedure using methyl 4-amino-2-methoxybenzoate (33.8 mg, 0.2 mmol, 1.0 equiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (82.8 mg, 3.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 51 hours affording compound **3c**[15] in 73% (45 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.16 (s, 1H), 6.27 (s, 1H), 4.45 (br s, 2H), 3.81 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.8, 161.7, 151.6, 142.8, 111.1, 97.2, 71.5, 55.9, 51.6. **MS** (EI) m/z 307. **IR** (film) 3462, 3340, 3001, 2945, 1705, 1616, 1589, 1433, 1408, 1307, 1244, 1220, 1182, 1099, 1039, 983, 831, 777, 657 cm^{-1}.

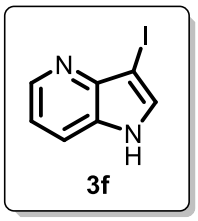
methyl 6-amino-3-iodo-2-methylbenzoate (3d): Prepared under outlined condition B as in general procedure using methyl 2-amino-6-methylbenzoate (33.0 mg, 0.2 mmol, 1.0 equiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (96.6 mg, 3.5 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 96 hours affording compound **3d** in 50% (29.1 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, J = 8.6 Hz, 1H),

6.31 (d, J = 8.6 Hz, 1H), 4.22 (br s, 2H), 3.90 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 169.0, 147.2, 141.7, 140.6, 117.3, 116.1, 87.7, 51.9, 27.6. **HRMS** (EI) m/z Calcd for $C_9H_{10}INO_2$ 290.9756, Found 290.9757. **IR** (film) 3479, 3379, 2949, 1703, 1606, 1460, 1435, 1282, 1201, 1151, 1109, 1083, 979, 812, 750, 626 cm^{-1}.



3e

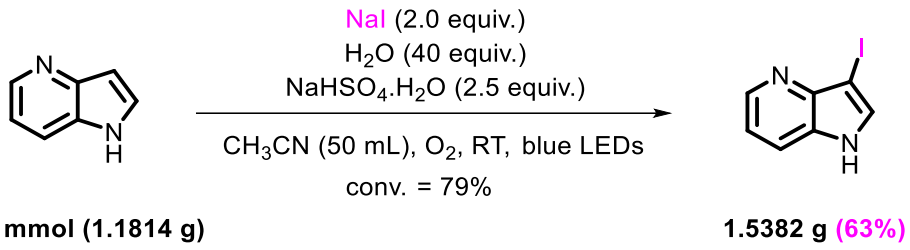
ethyl 3-iodo-1*H*-indole-2-carboxylate (3e): Prepared under outlined condition B as in general procedure using ethyl 1*H*-indole-2-carboxylate (33.0 mg, 0.2 mmol, 1.0 equiv.), NH_4I (58.0 mg, 2.0 equiv.), $NaHSO_4{\cdot}H_2O$ (55.2 mg, 2.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 144 hours affording compound **3e** in 84% (54 mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 7.57 (d, J = 8.2 Hz, 1H), 7.43 – 7.33 (m, 2H), 7.27 – 7.22 (m, 1H), 4.47 (q, J = 7.1 Hz, 2H), 1.48 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.9, 136.1, 131.5, 127.2, 126.6, 123.5, 121.6, 112.0, 66.0, 61.5, 14.3. **MS** (EI) m/z 315. **IR** (film) 3296**,** 2981, 1685, 1508, 1417, 1379, 1330, 1259, 1224, 1195, 1145, 1029, 1010, 773, 756, 742, 686, 599 cm^{-1}.



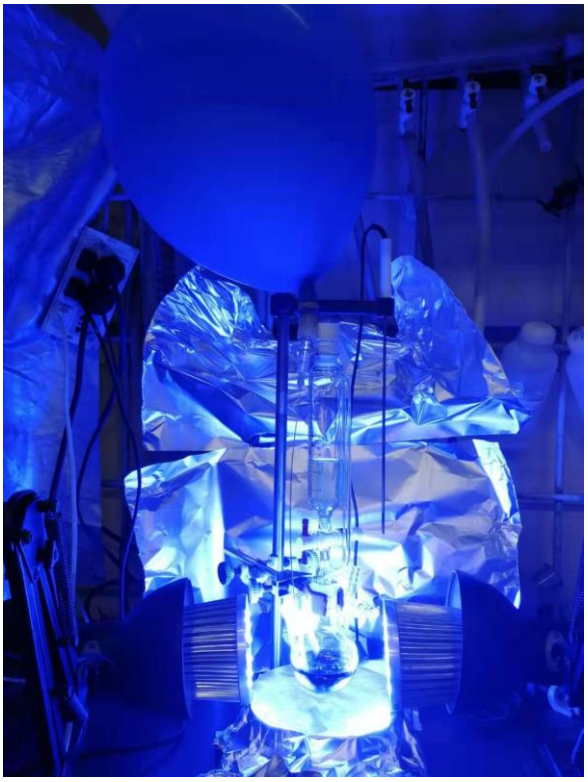
3f

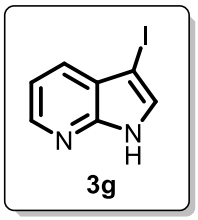
3-iodo-1*H*-pyrrolo[3,2-*b*]pyridine (3f): Prepared under outlined condition B as in general procedure using 1*H*-pyrrolo[3,2-*b*]pyridine (23.6 mg, 0.2 mmol, 1.0 equiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4{\cdot}H_2O$ (82.8 mg, 3.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 44 hours affording compound **3f** in 79% (38.5 mg) yield as white solid. **^{1}H NMR** (400 MHz, DMSO) δ 11.77 (s, 1H), 8.38 (dd, J = 4.5, 1.1 Hz, 1H), 7.84 (d, J = 2.7 Hz, 1H), 7.79 (dd, J = 8.2, 1.2 Hz, 1H), 7.17 (dd, J = 8.2, 4.6 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 145.8, 143.6, 133.5, 128.8, 119.6, 117.8, 58.7. **HRMS** (EI) m/z Calcd for $C_7H_5IN_2$ 243.9497, Found 243.9499. **IR** (film) 3039, 2920, 1720, 1562, 1400, 1319, 1222, 1099, 974, 893, 781, 642, 578 cm^{-1}.

Gram-Scale Reaction



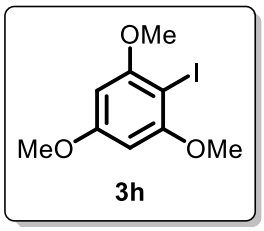
For 10 mmol scale, in a 100 mL round bottom flask, NaI (2.0 eq., 2.9978 g), $NaHSO_4.H_2O$ (2.5 equiv., 3.452 g) and H_2O (40 equiv., 7.2 mL) were dissolved in 30 mL MeCN. The system was stirred at room temperature under the irradiation of 2* 18 W blue LEDs with bubbling oxygen using balloon. Then 1*H*-pyrrolo [3,2-*b*] pyridine (10 mmol, 1.1814 g) dissolved in 25 mL MeCN was added dropwise by constant pressure drip funnel for 7 h. The system was reacted at room temperature for 110 h. Subsequently, dichloromethane (DCM) (50 mL) was added and the system was transferred into the separating funnel. The organic phase was washed with $NaHCO_3$ (50 mL) twice. Next, the aqueous phase was extracted with DCM (100 mL*2). The organic phase was combined and dried with $MgSO_4$. After filtration, distillation, and recrystallization, 3-iodo-1*H*-pyrrolo [3,2-*b*] pyridine (1.5382 g, 63%) was obtained as white solid. The apparatus was shown as below:





3g

3-iodo-1*H*-pyrrolo[2,3-*b*]pyridine (3g): Prepared under outlined condition B as in general procedure using 1*H*-pyrrolo[2,3-*b*]pyridine (23.6 mg, 0.2 mmol, 1.0 eqsuiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (110.5 mg, 4.0 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 94 hours affording compound **3g**[10] in 86% (41 mg) yield as white solid. **^{1}H NMR** (400 MHz, DMSO) δ 12.10 (s, 1H), 8.25 (d, *J* = 3.9 Hz, 1H), 7.85 – 7.58 (m, 2H), 7.15 (dd, *J* = 7.9, 4.7 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 148.4, 144.2, 130.9, 128.5, 122.4, 116.9, 54.7. **MS** (EI) m/z 244. **IR** (film) 3124, 3057, 2920, 1722, 1583, 1411, 1363, 1313, 1286, 1224, 964, 896, 788, 765, 642, 569 cm^{-1}.



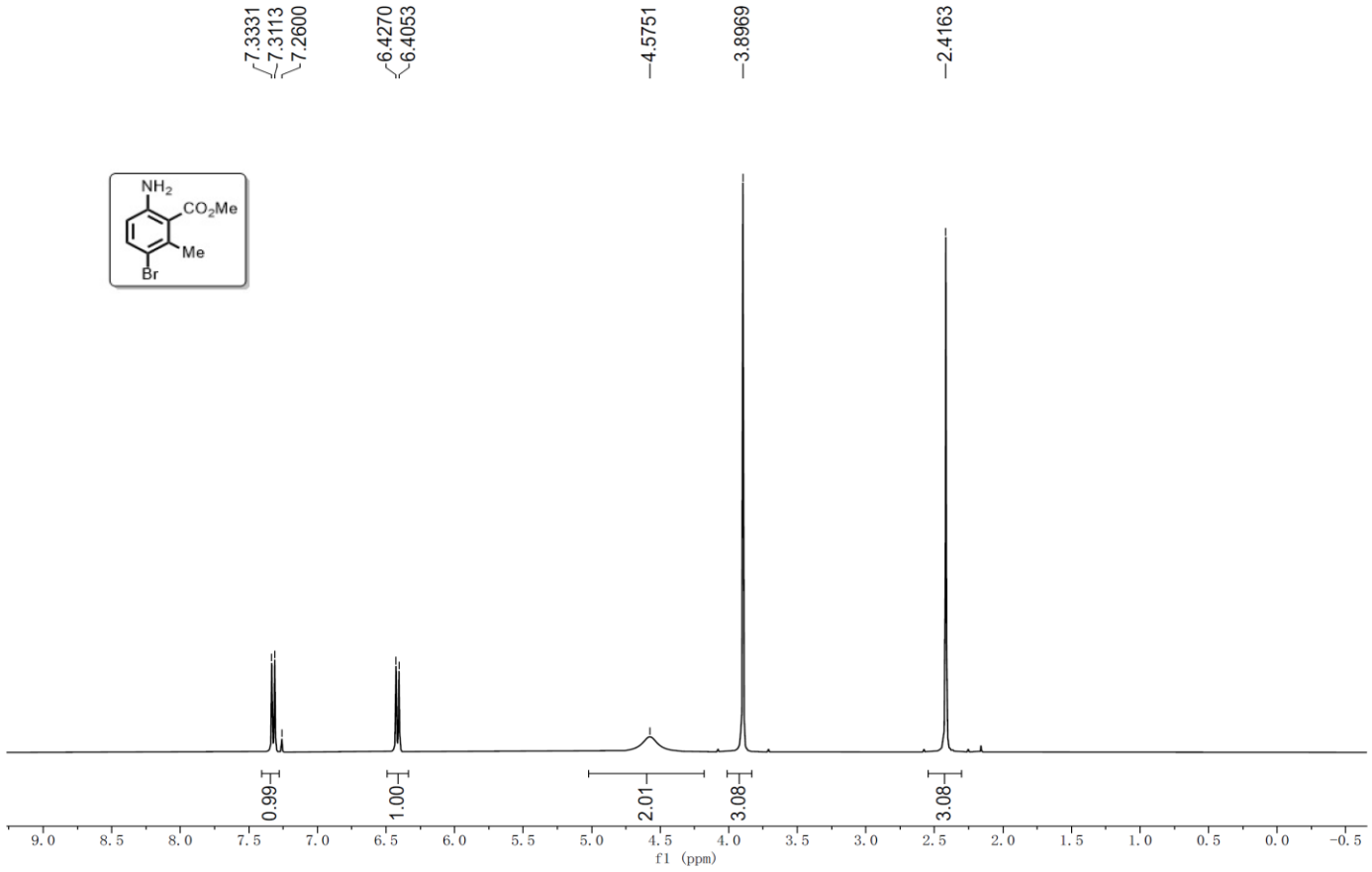
3h

2-iodo-1,3,5-trimethoxybenzene (3h): Prepared under outlined condition B as in general procedure using 1,3,5-trimethoxybenzene (33.6 mg, 0.2 mmol, 1.0 eqsuiv.), NaI (89.9 mg, 3.0 equiv.), $NaHSO_4 \cdot H_2O$ (96.6 mg, 3.5 equiv.), H_2O (72.0 mg, 20.0 equiv.) were dissolved in MeCN (2.0 mL), the reaction was stirred under 2*3 W blue LEDs at room temperature for 65 hours affording compound **3h**[10] in 92% (54.5

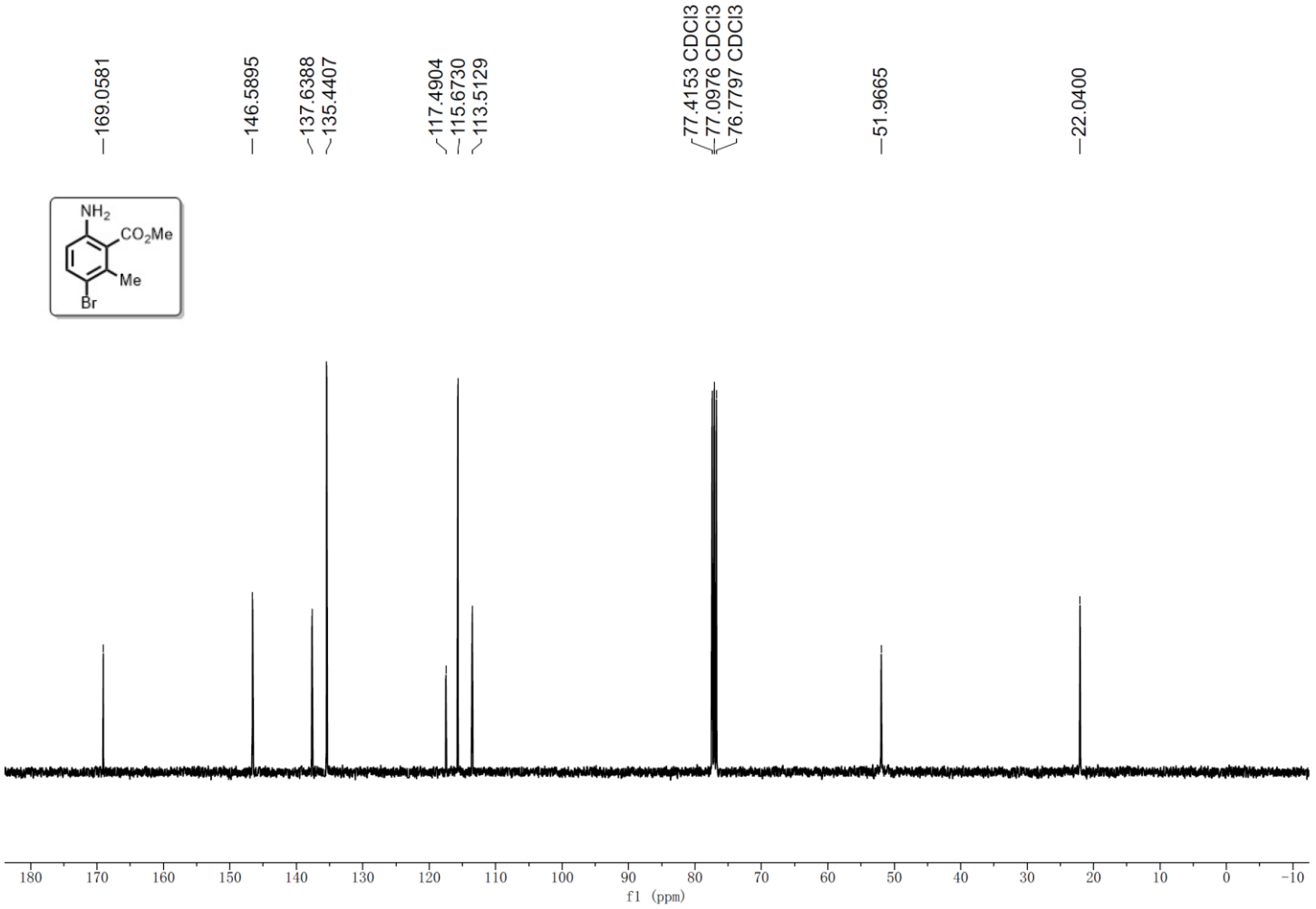
mg) yield as white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.13 (s, 2H), 3.85 (s, 6H), 3.81 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 162.2, 159.8, 91.2, 66.7, 56.4 (d, J = 3.5 Hz), 55.5 (d, J = 3.4 Hz). **MS** (EI) m/z 294. **IR** (film) 2837, 1583, 1465, 1406, 1338, 1226, 1205, 1159, 1120, 1070, 1016, 948, 806, 628 cm^{-1}.

VI. NMR Spectra

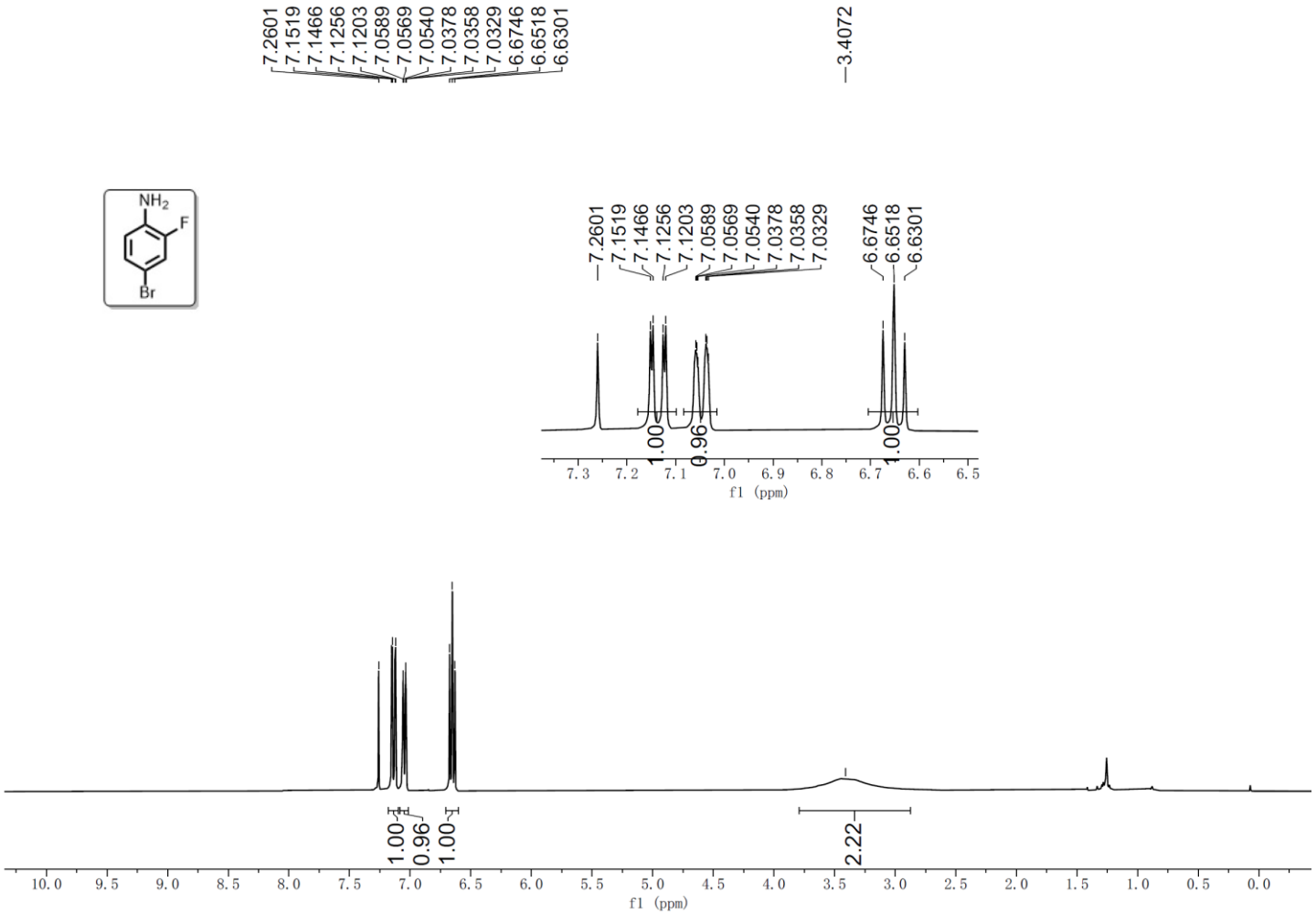
^{1}H NMR of **2a**



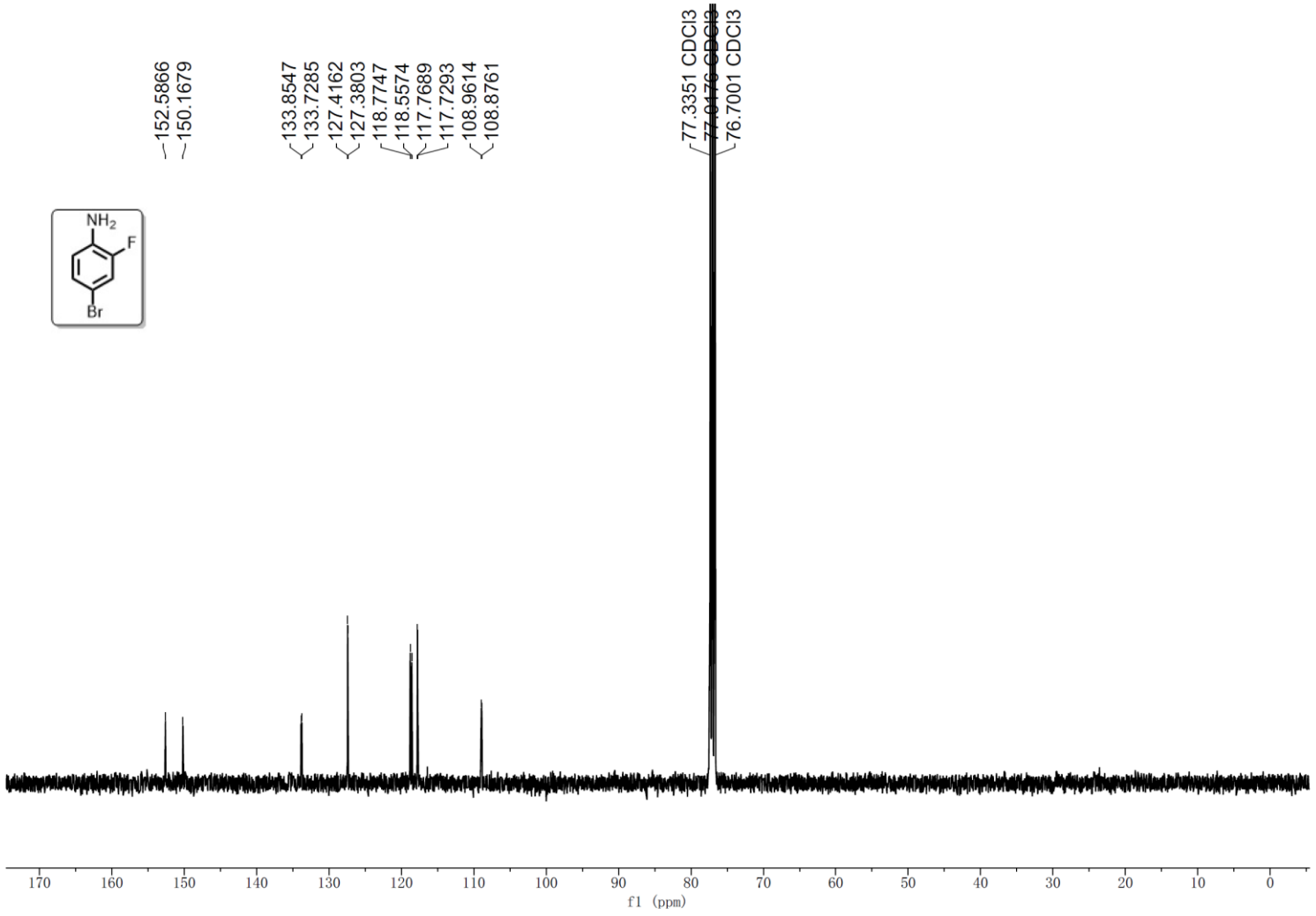
^{13}C NMR of **2a**


169.0581
146.5895
137.6388
135.4407
117.4904
115.6730
113.5129
77.4153 CDCl3
77.0976 CDCl3
76.7797 CDCl3
51.9665
22.0400
NH2
CO2Me
Me
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

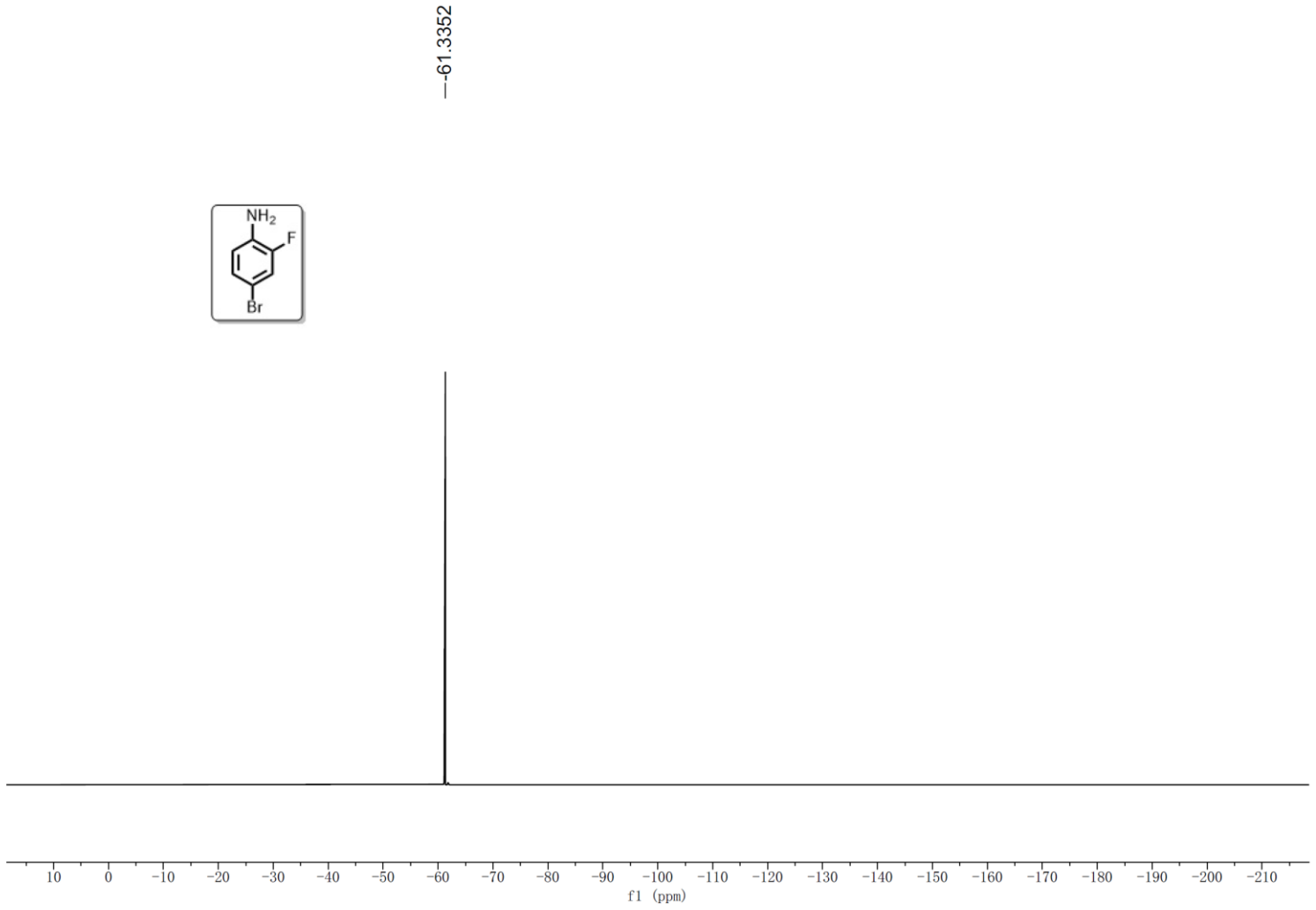
^{1}H NMR of **2b**


7.2601
7.1519
7.1466
7.1256
7.1203
7.0589
7.0569
7.0540
7.0378
7.0358
7.0329
6.6746
6.6518
6.6301
3.4072
NH2
F
Br
1.00
0.96
1.00
2.22
f1 (ppm)

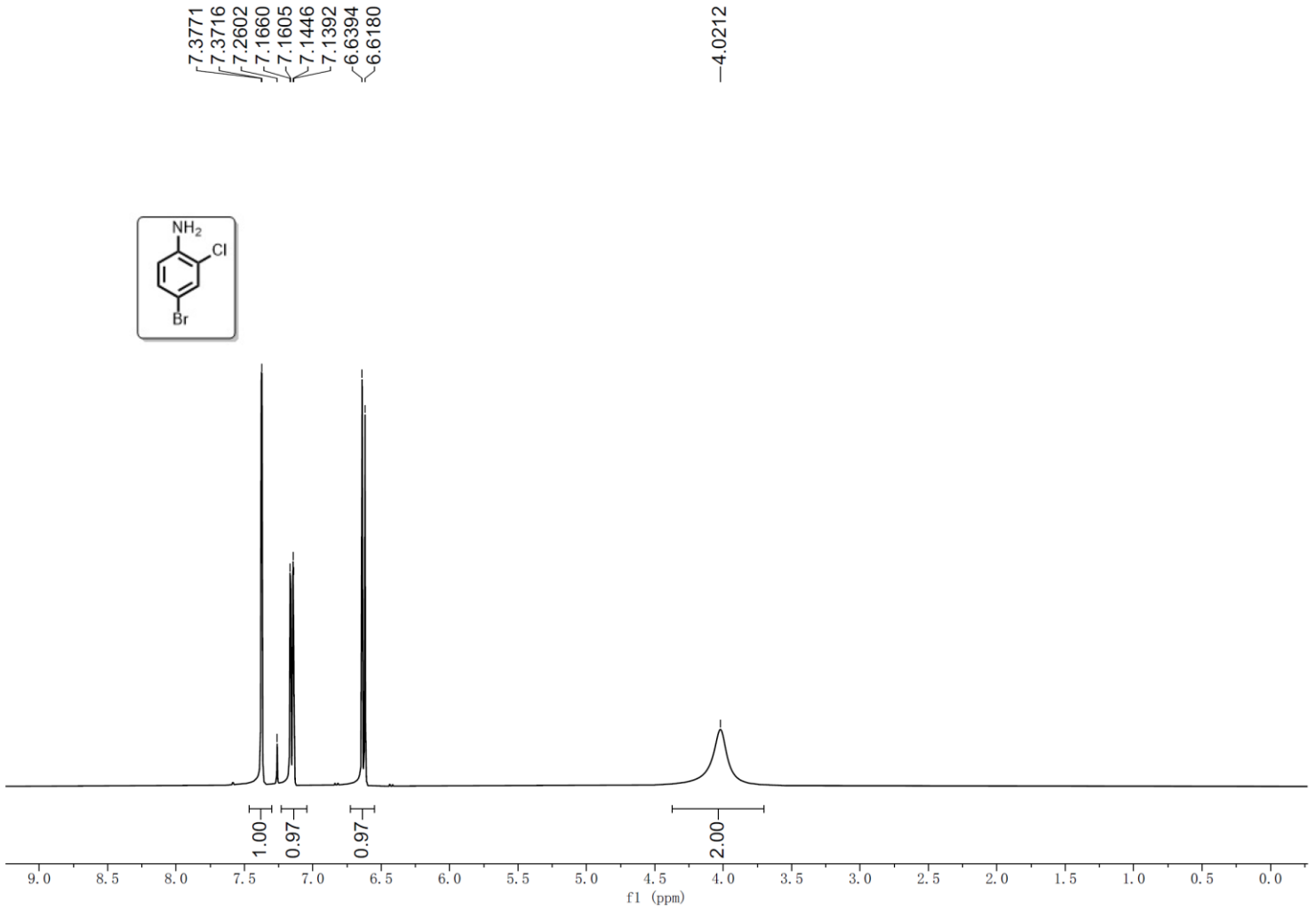
^{13}C NMR of **2b**


152.5866
150.1679
133.8547
133.7285
127.4162
127.3803
118.7747
118.5574
117.7689
117.7293
108.9614
108.8761
77.3351 CDCl3
76.7001 CDCl3
NH2
F
Br
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

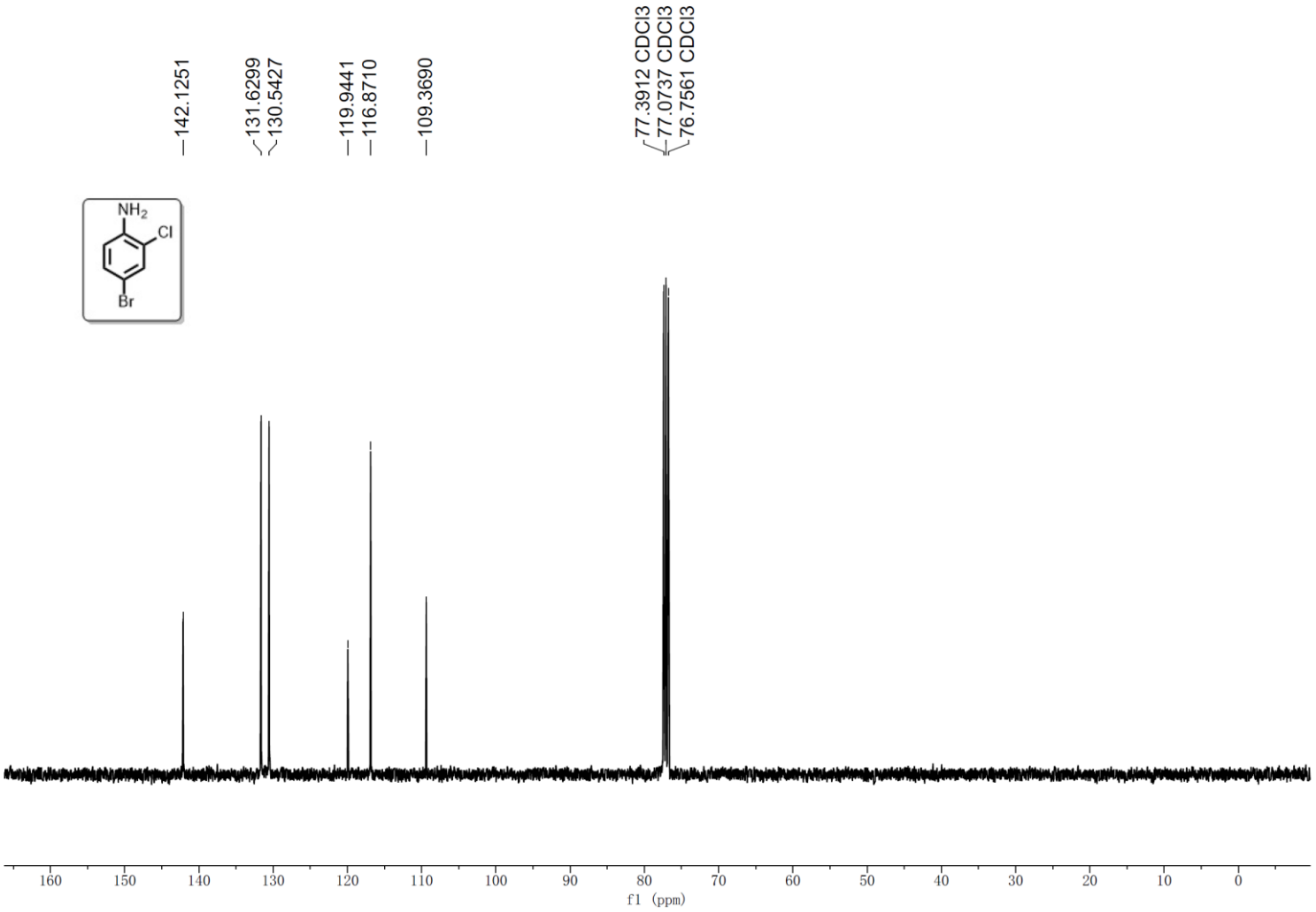
^{19}F NMR of **2b**


-61.3352
NH2
F
Br
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

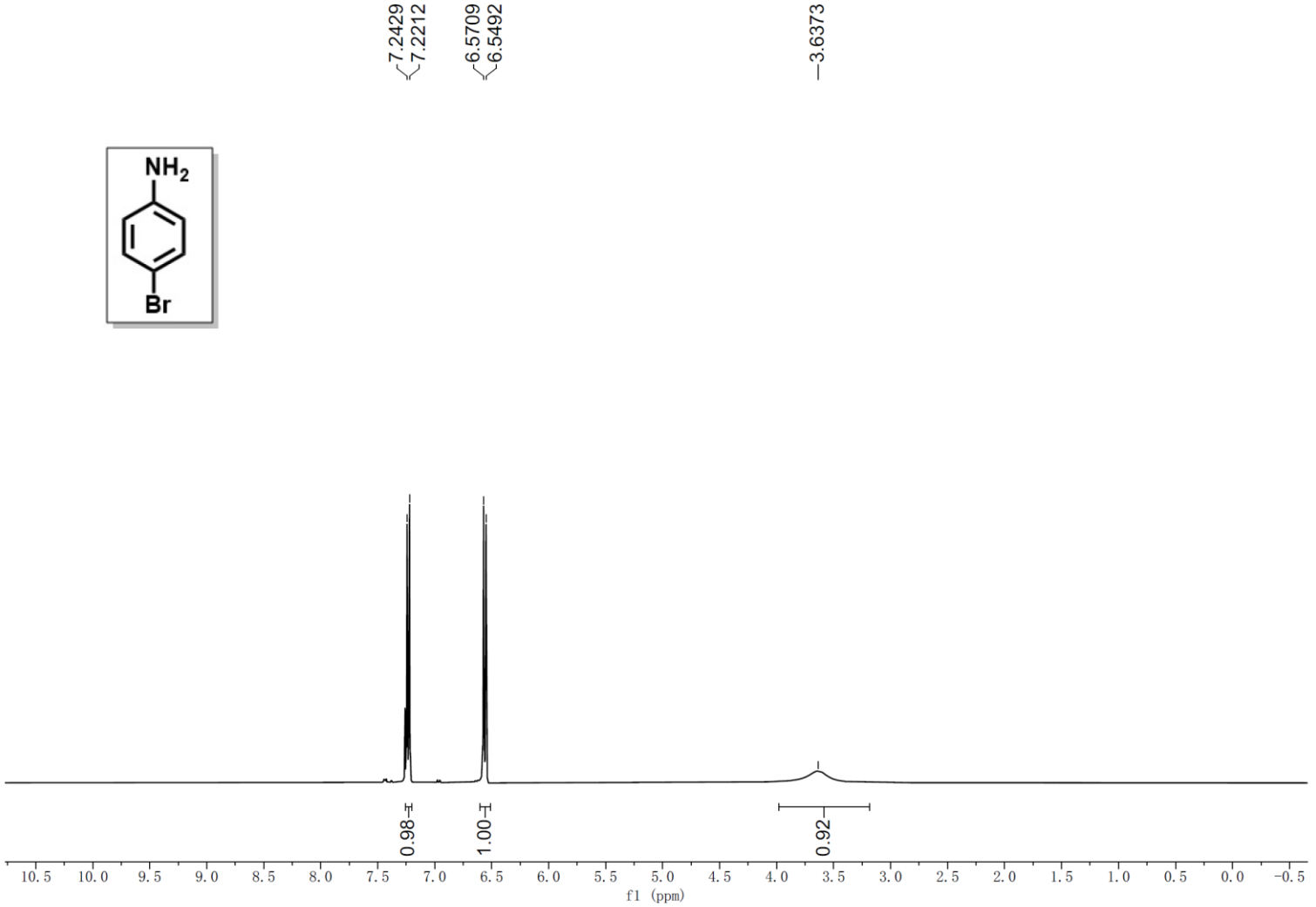
^{1}H NMR of **2c**


7.3771
7.3716
7.2602
7.1660
7.1605
7.1446
7.1392
6.6394
6.6180
4.0212
NH2
Cl
Br
1.00
0.97
0.97
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

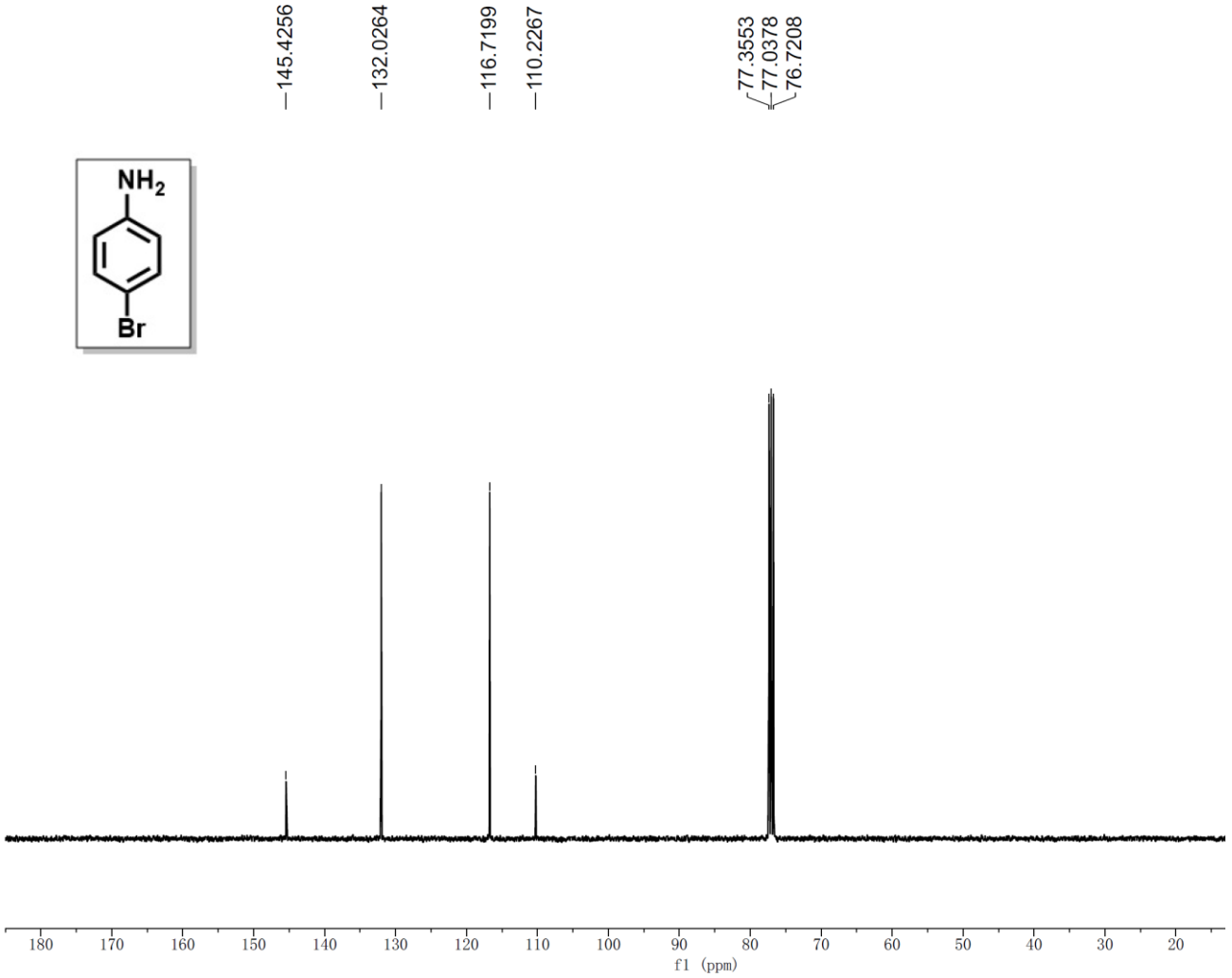
^{13}C NMR of **2c**


142.1251
131.6299
130.5427
119.9441
116.8710
109.3690
77.3912 CDCl3
77.0737 CDCl3
76.7561 CDCl3
NH2
Cl
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

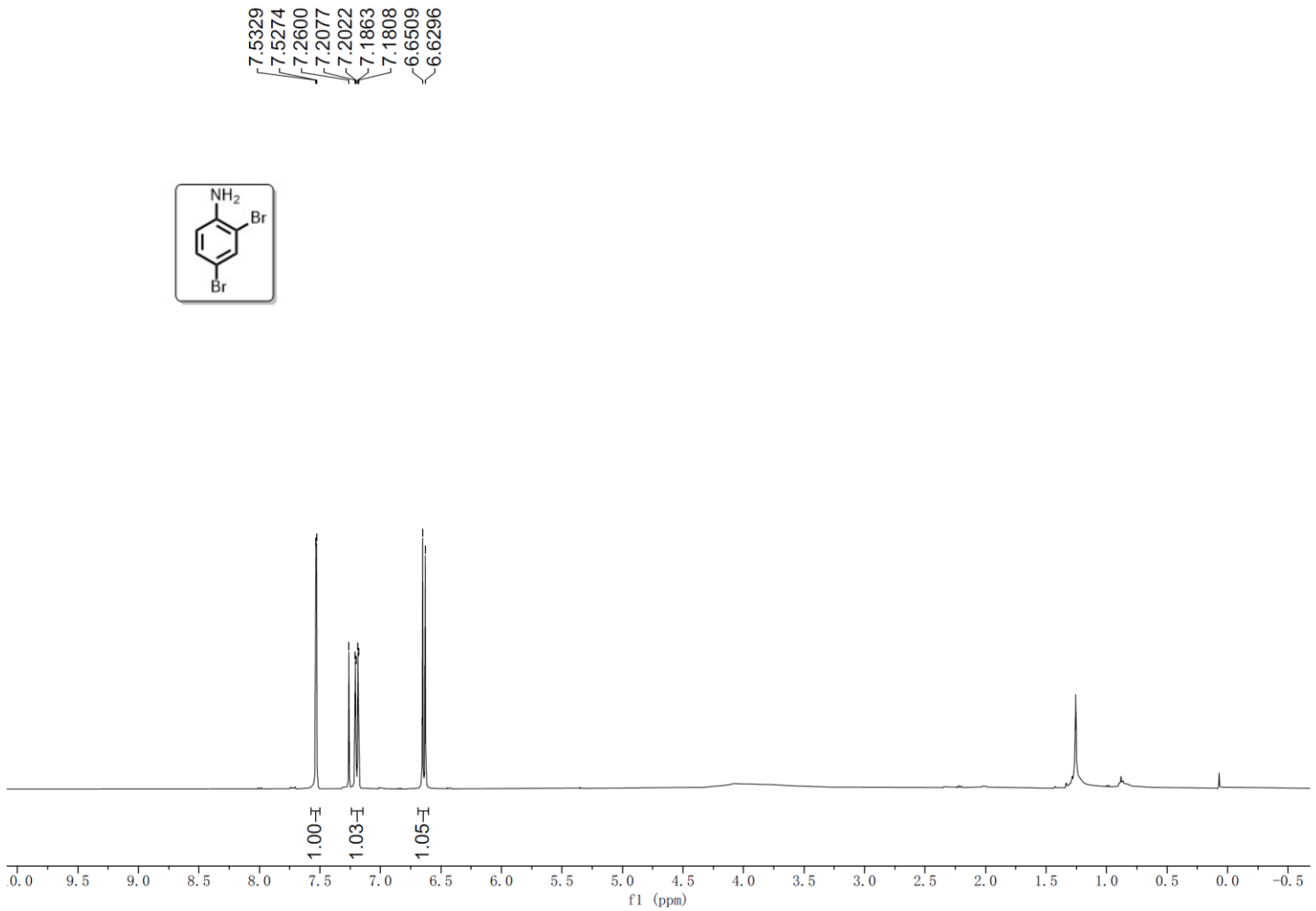
^{1}H NMR of **2d**


7.2429
7.2212
6.5709
6.5492
3.6373
NH2
Br
0.98
1.00
0.92
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

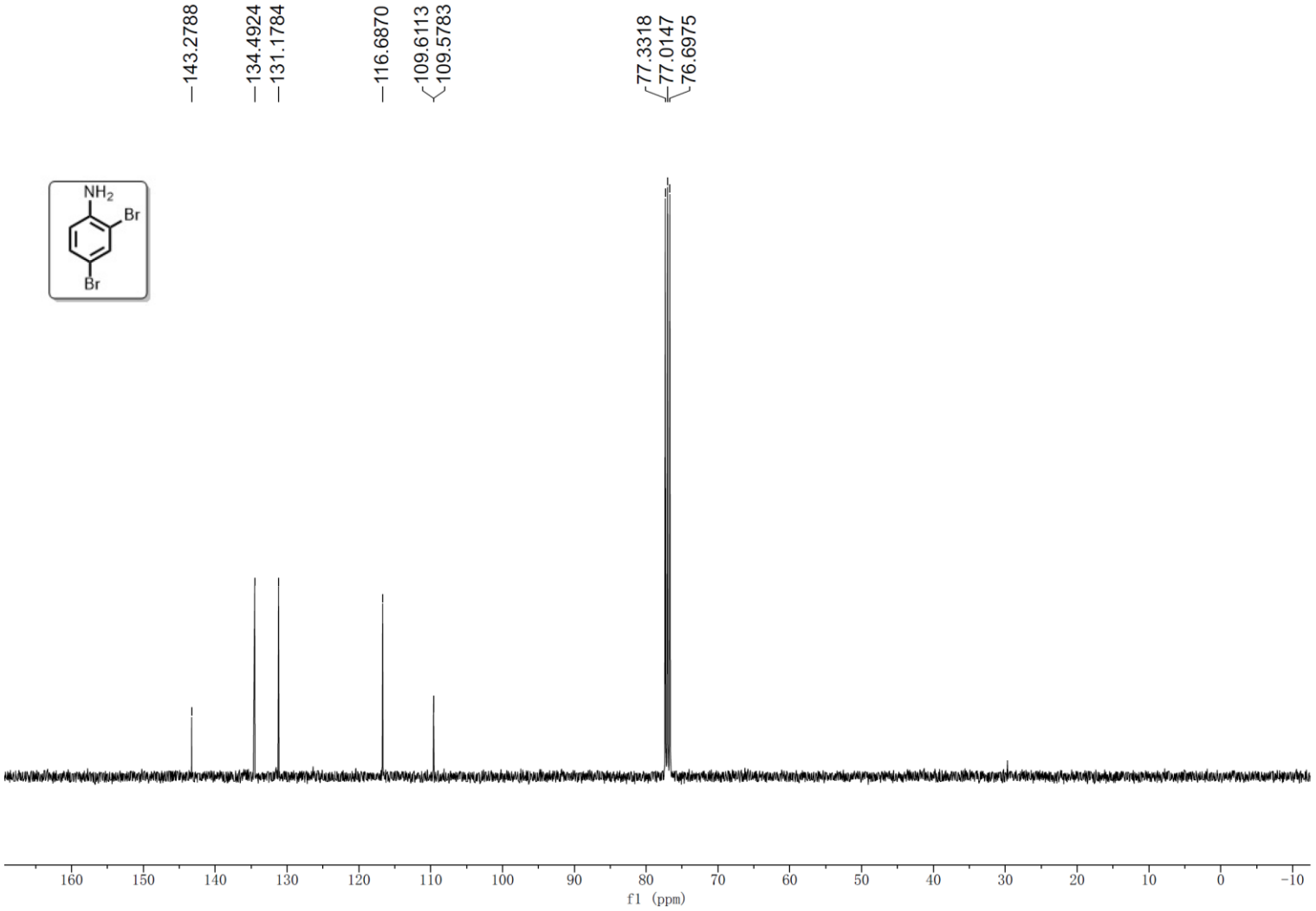
^{13}C NMR of **2d**


145.4256
132.0264
116.7199
110.2267
77.3553
77.0378
76.7208
NH2
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

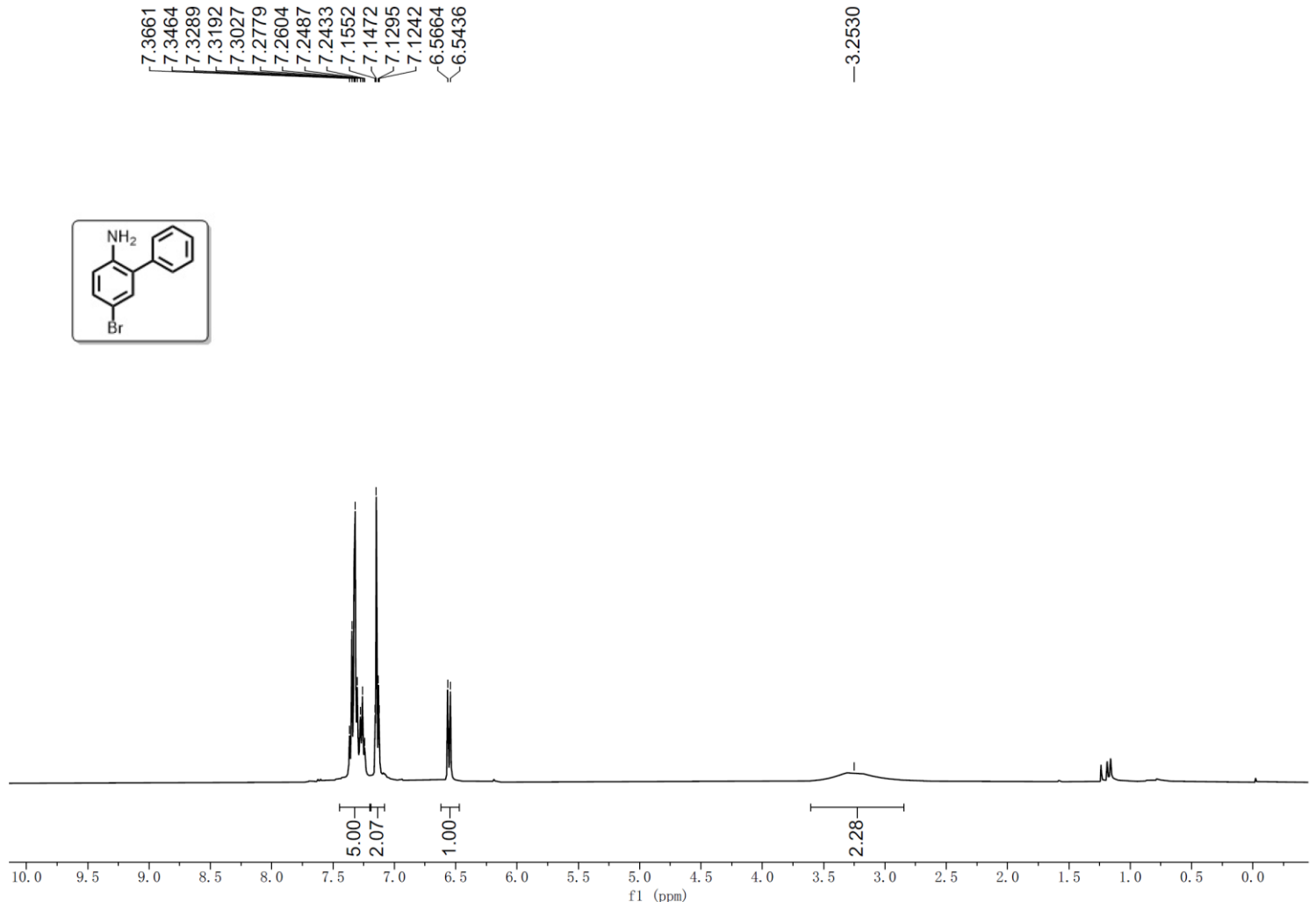
^{1}H NMR of **2e**


7.5329
7.5274
7.2600
7.2077
7.2022
7.1863
7.1808
6.6509
6.6296
NH2
Br
Br
1.00
1.03
1.05
f1 (ppm)

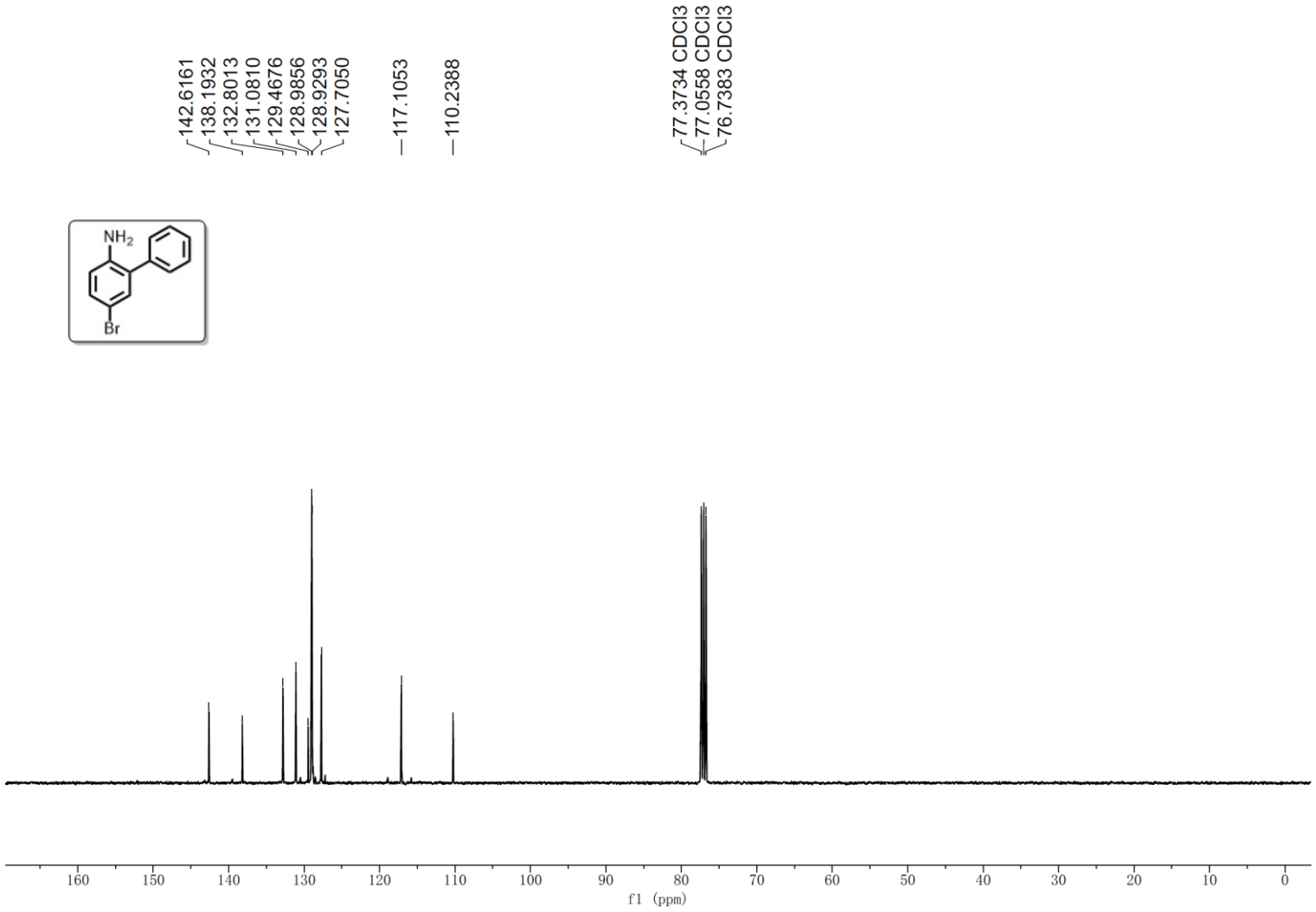
^{13}C NMR of **2e**


143.2788
134.4924
131.1784
116.6870
109.6113
109.5783
77.3318
77.0147
76.6975
NH2
Br
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

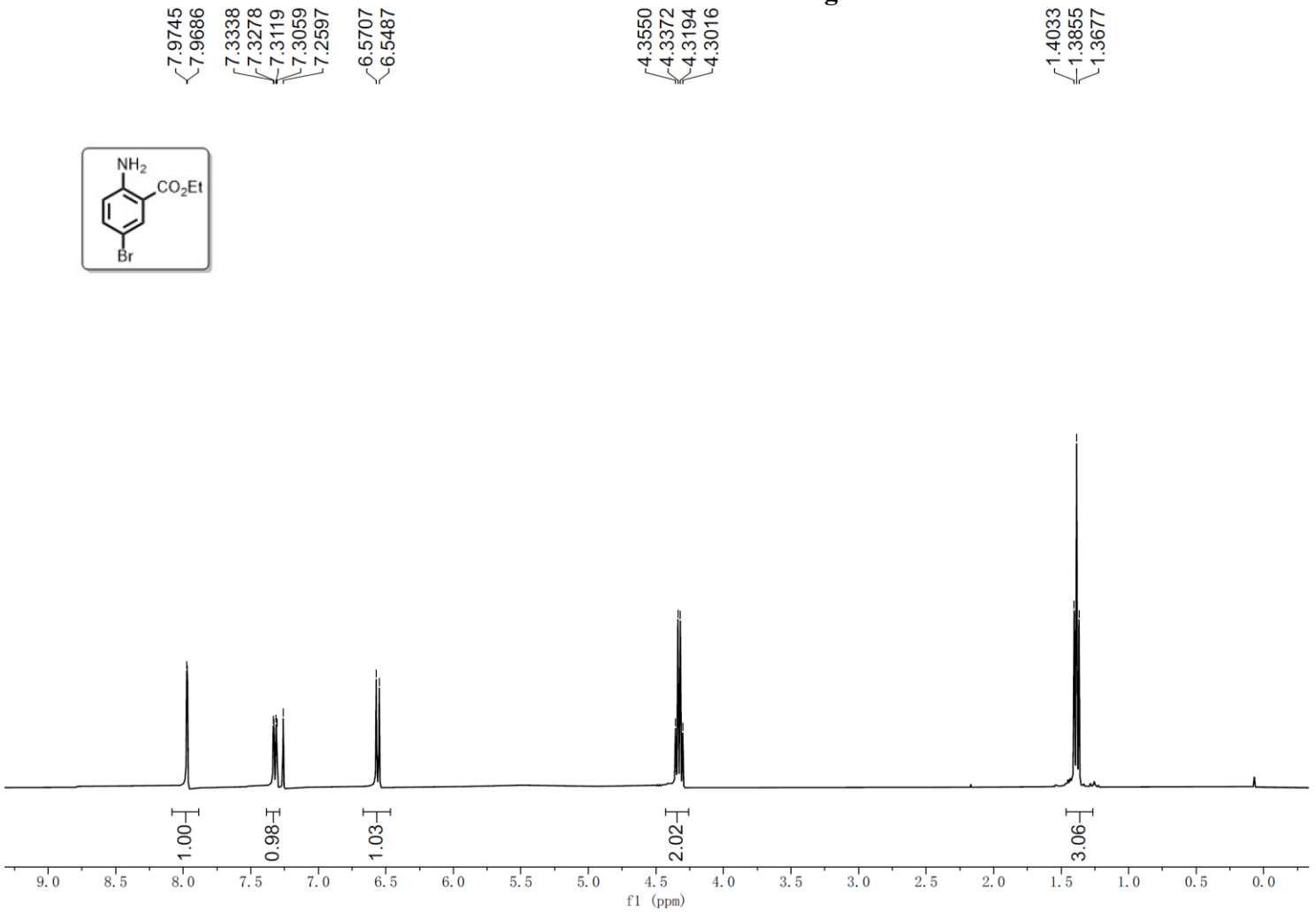
^{1}H NMR of **2f**


7.3661
7.3464
7.3289
7.3192
7.3027
7.2779
7.2604
7.2487
7.2433
7.1552
7.1472
7.1295
7.1242
6.5664
6.5436
3.2530
NH2
Br
5.00
2.07
1.00
2.28
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

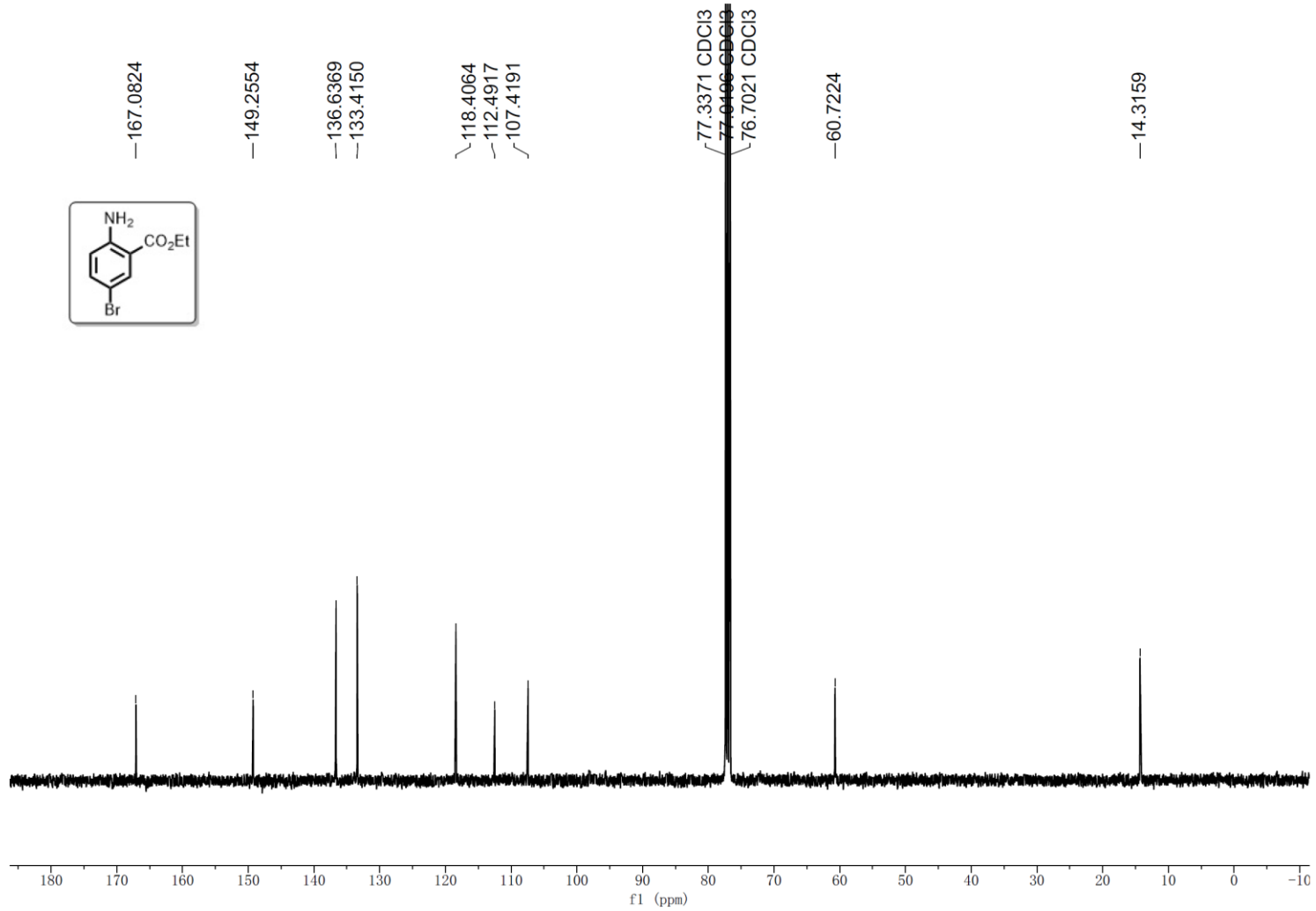
^{13}C NMR of **2f**


142.6161
138.1932
132.8013
131.0810
129.4676
128.9856
128.9293
127.7050
117.1053
110.2388
77.3734 CDCl3
77.0558 CDCl3
76.7383 CDCl3
NH2
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

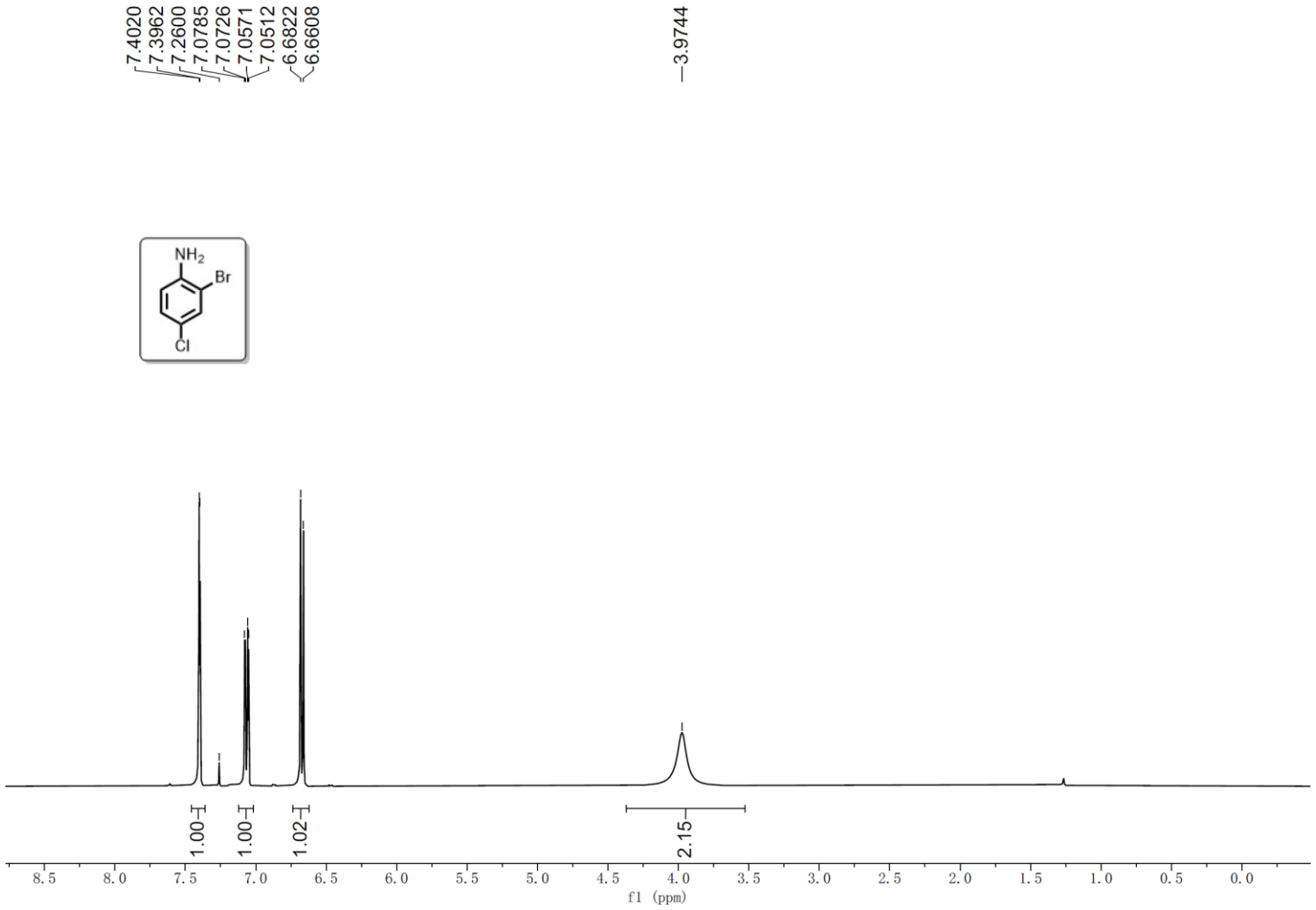
^{1}H NM R of **2g**


7.9745
7.9686
7.3338
7.3278
7.3119
7.3059
7.2597
6.5707
6.5487
4.3550
4.3372
4.3194
4.3016
1.4033
1.3855
1.3677
NH2
CO2Et
Br
1.00
0.98
1.03
2.02
3.06
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

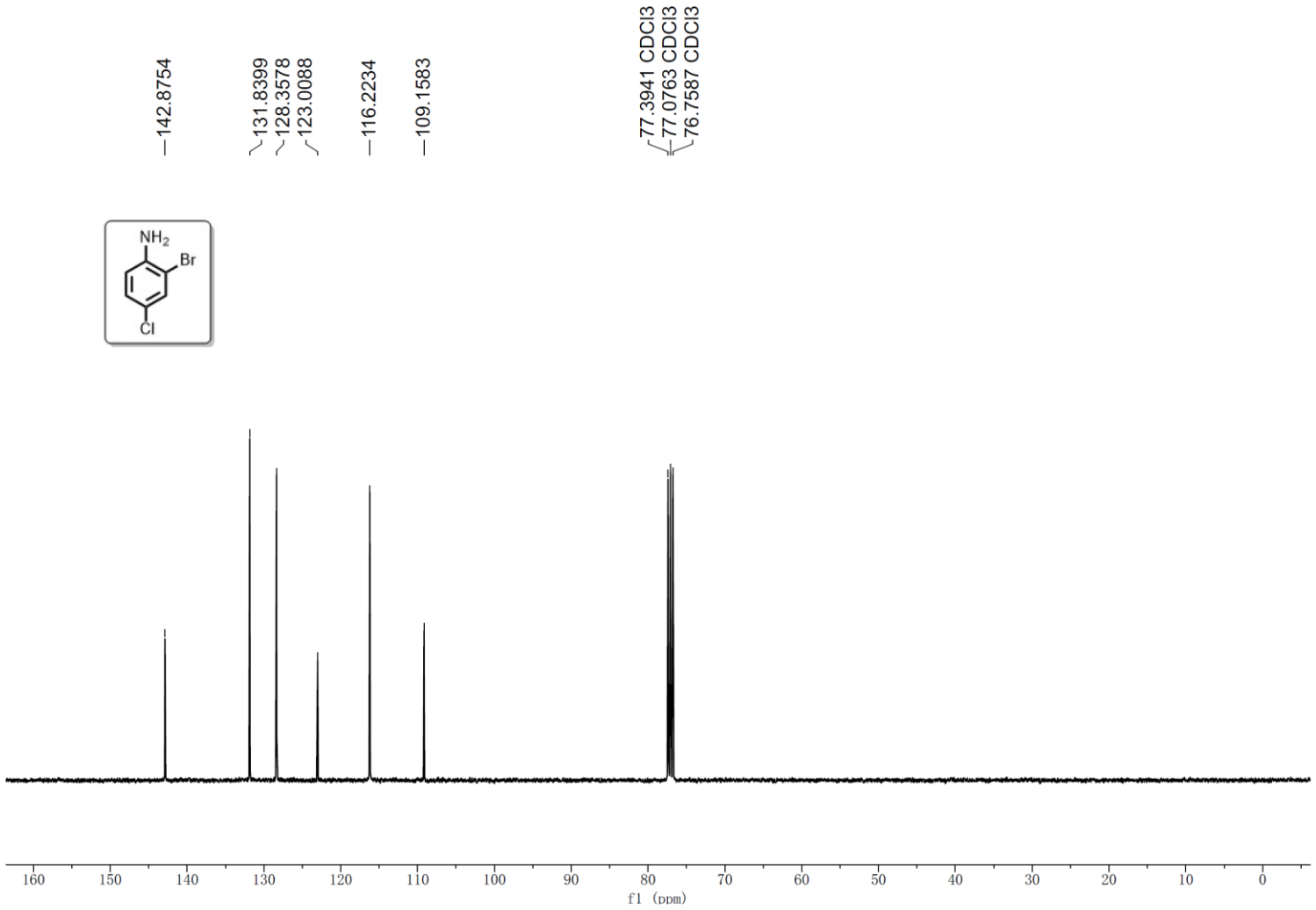
^{13}C NMR of **2g**


167.0824
149.2554
136.6369
133.4150
118.4064
112.4917
107.4191
77.3371 CDCl3
77.0156 CDCl3
76.7021 CDCl3
60.7224
14.3159
NH2
CO2Et
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

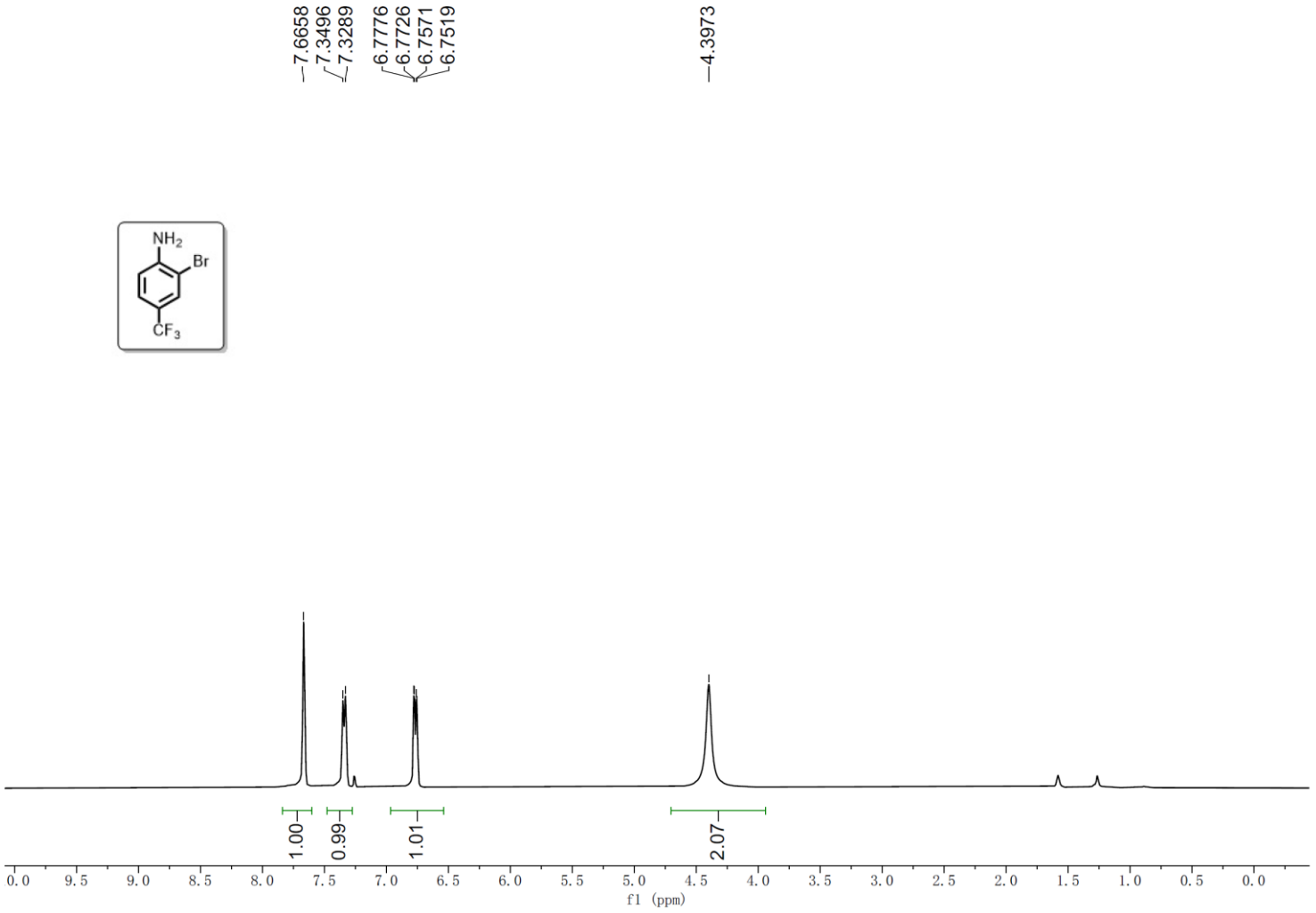
^{1}H NMR of **2h**


7.4020
7.3962
7.2600
7.0785
7.0726
7.0571
7.0512
6.6822
6.6608
3.9744
NH2
Br
Cl
1.00
1.00
1.02
2.15
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

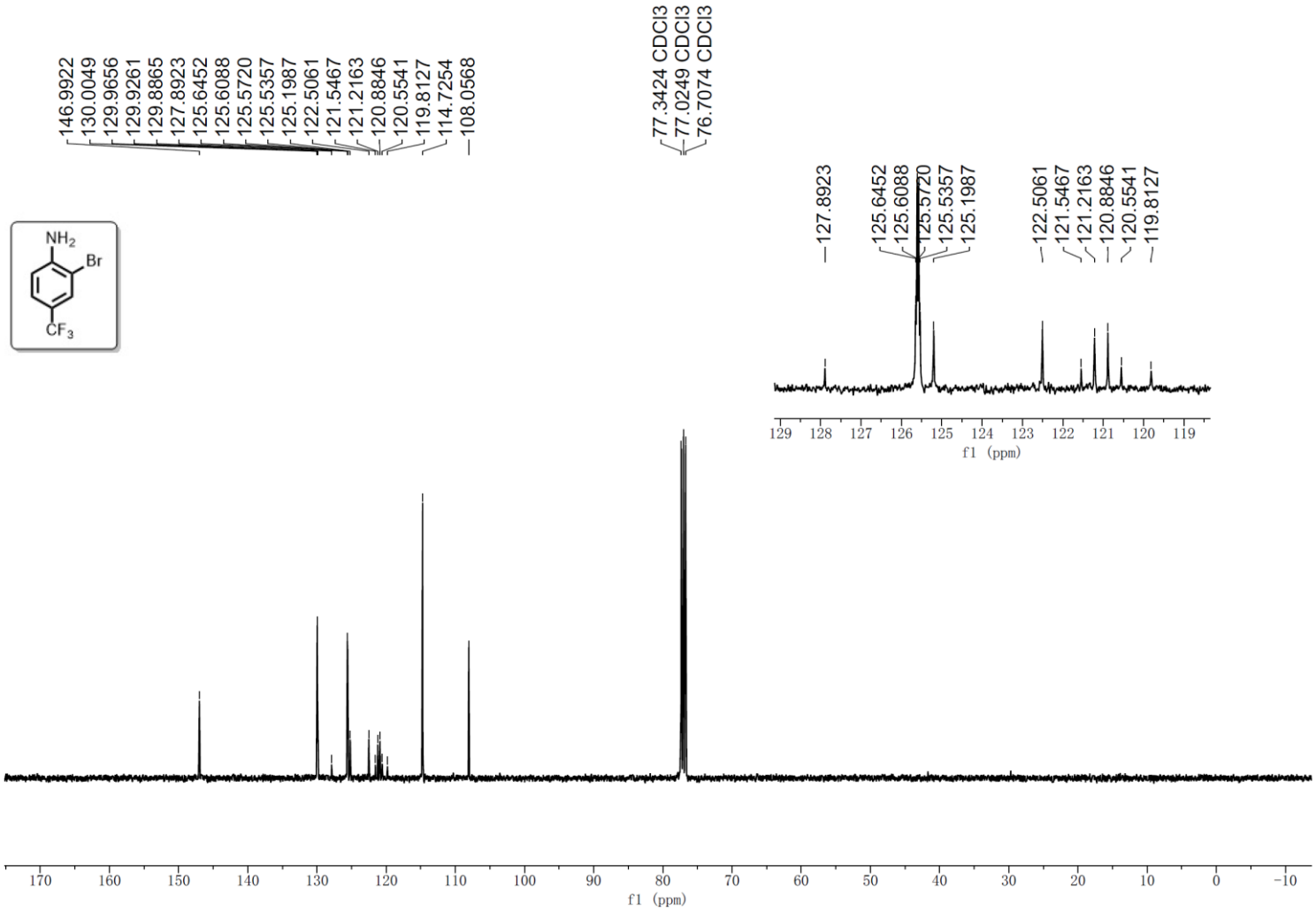
^{13}C NMR of **2h**


142.8754
131.8399
128.3578
123.0088
116.2234
109.1583
77.3941 CDCl3
77.0763 CDCl3
76.7587 CDCl3
NH2
Br
Cl
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

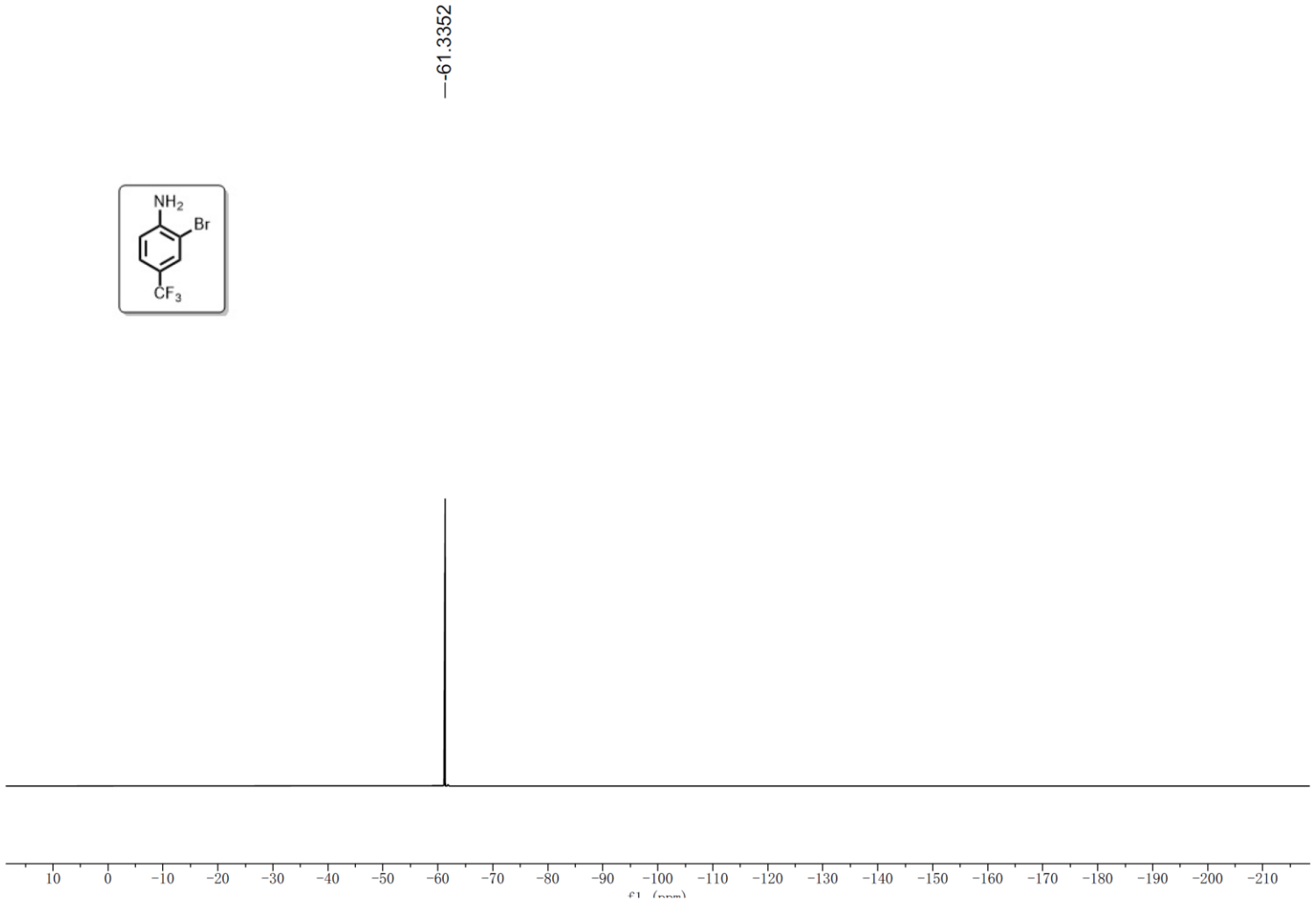
^{1}H NMR of **2i**


7.6658
7.3496
7.3289
6.7776
6.7726
6.7571
6.7519
4.3973
NH2
Br
CF3
1.00
0.99
1.01
2.07
f1 (ppm)

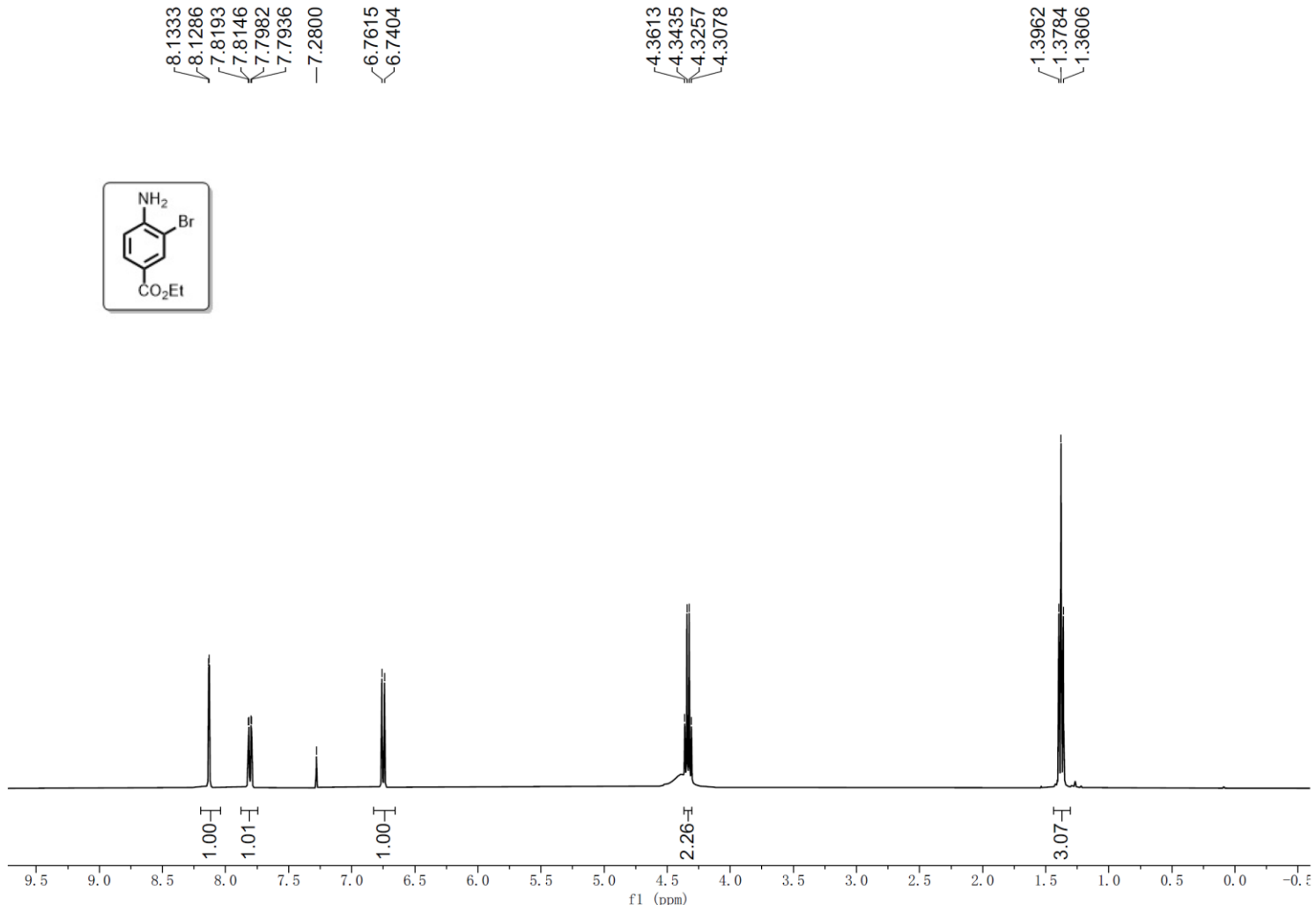
^{13}C NMR of **2i**


146.9922
130.0049
129.9656
129.9261
129.8865
127.8923
125.6452
125.6088
125.5720
125.5357
125.1987
122.5061
121.5467
121.2163
120.8846
120.5541
119.8127
114.7254
108.0568
77.3424 CDCl3
77.0249 CDCl3
76.7074 CDCl3
NH2
Br
CF3
f1 (ppm)

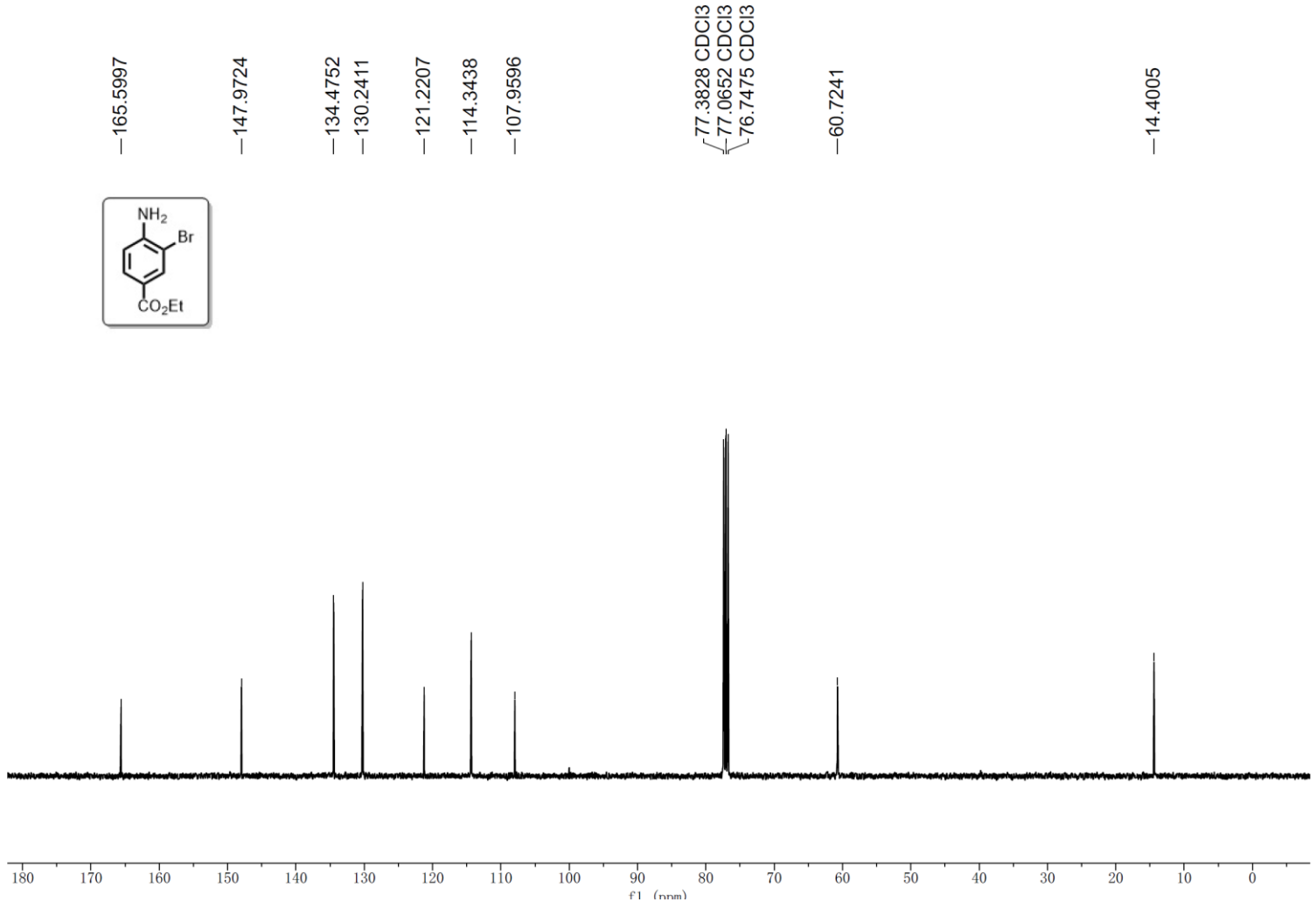
^{19}F NMR of **2i**


-61.3352
NH2
Br
CF3
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210

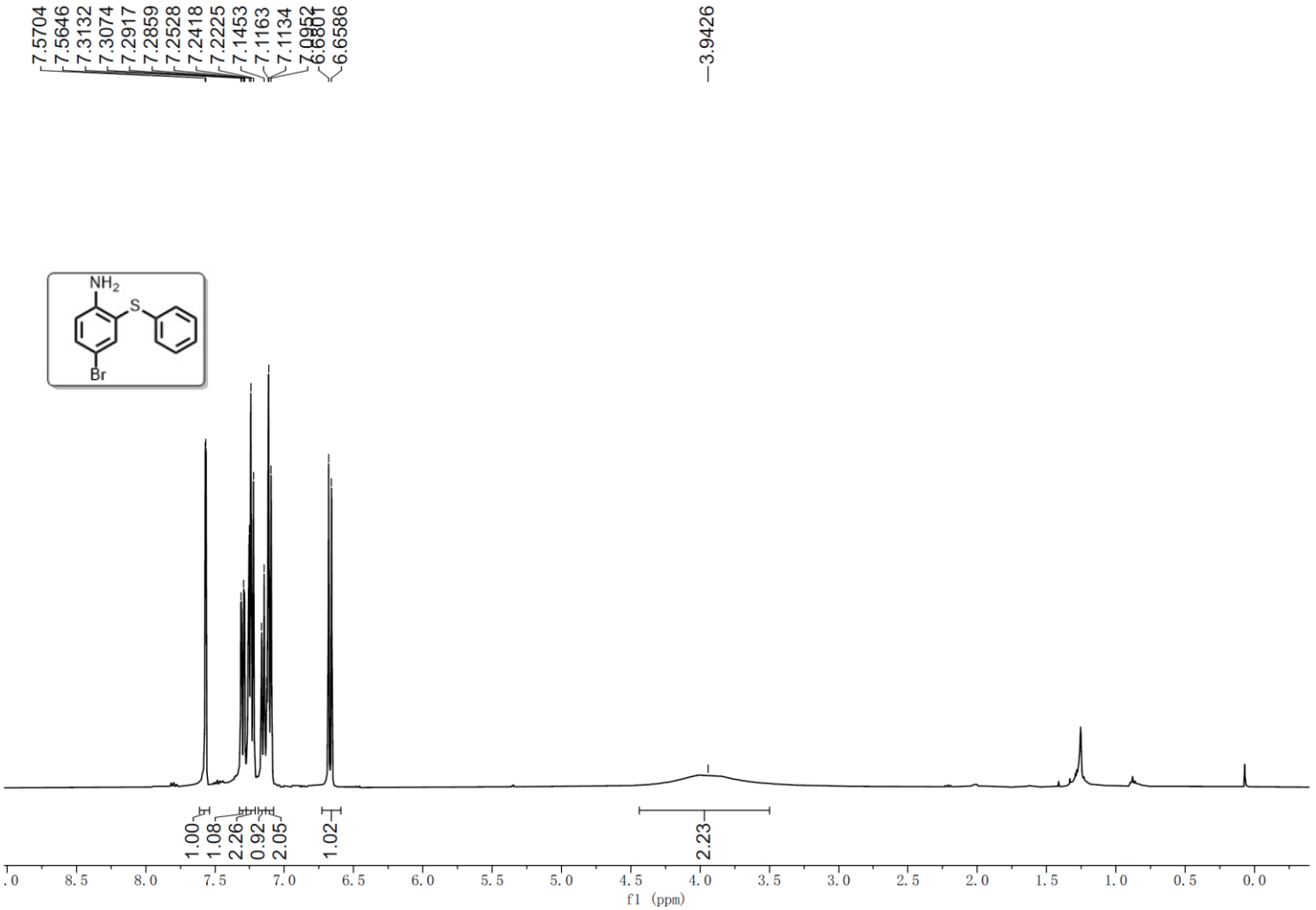
^{1}H NMR of **2j**


8.1333
8.1286
7.8193
7.8146
7.7982
7.7936
7.2800
6.7615
6.7404
4.3613
4.3435
4.3257
4.3078
1.3962
1.3784
1.3606
NH2
Br
CO2Et
1.00
1.01
1.00
2.26
3.07
f1 (ppm)

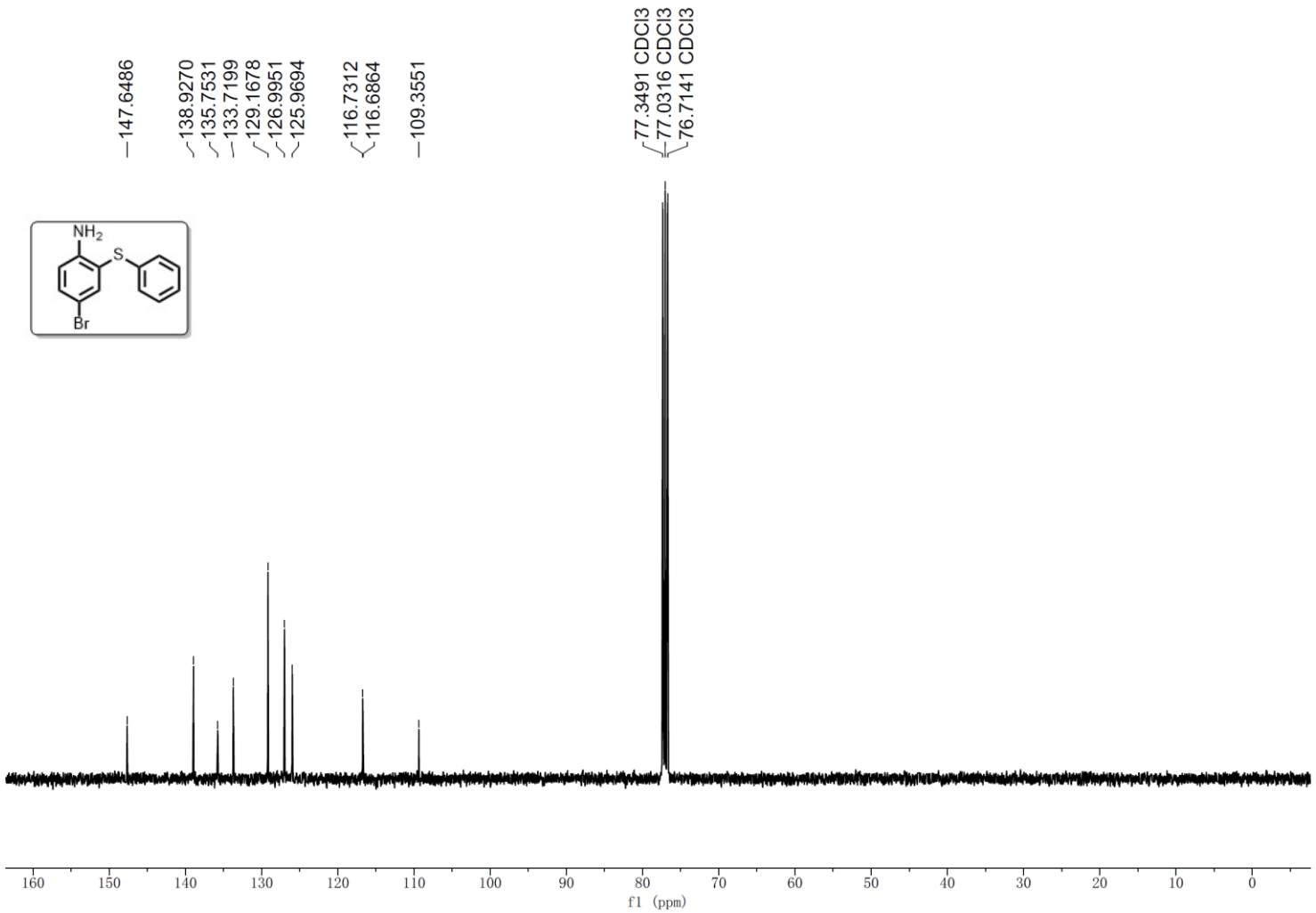
^{13}C NMR of **2j**


165.5997
147.9724
134.4752
130.2411
121.2207
114.3438
107.9596
77.3828 CDCl3
77.0652 CDCl3
76.7475 CDCl3
60.7241
14.4005
NH2
Br
CO2Et
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

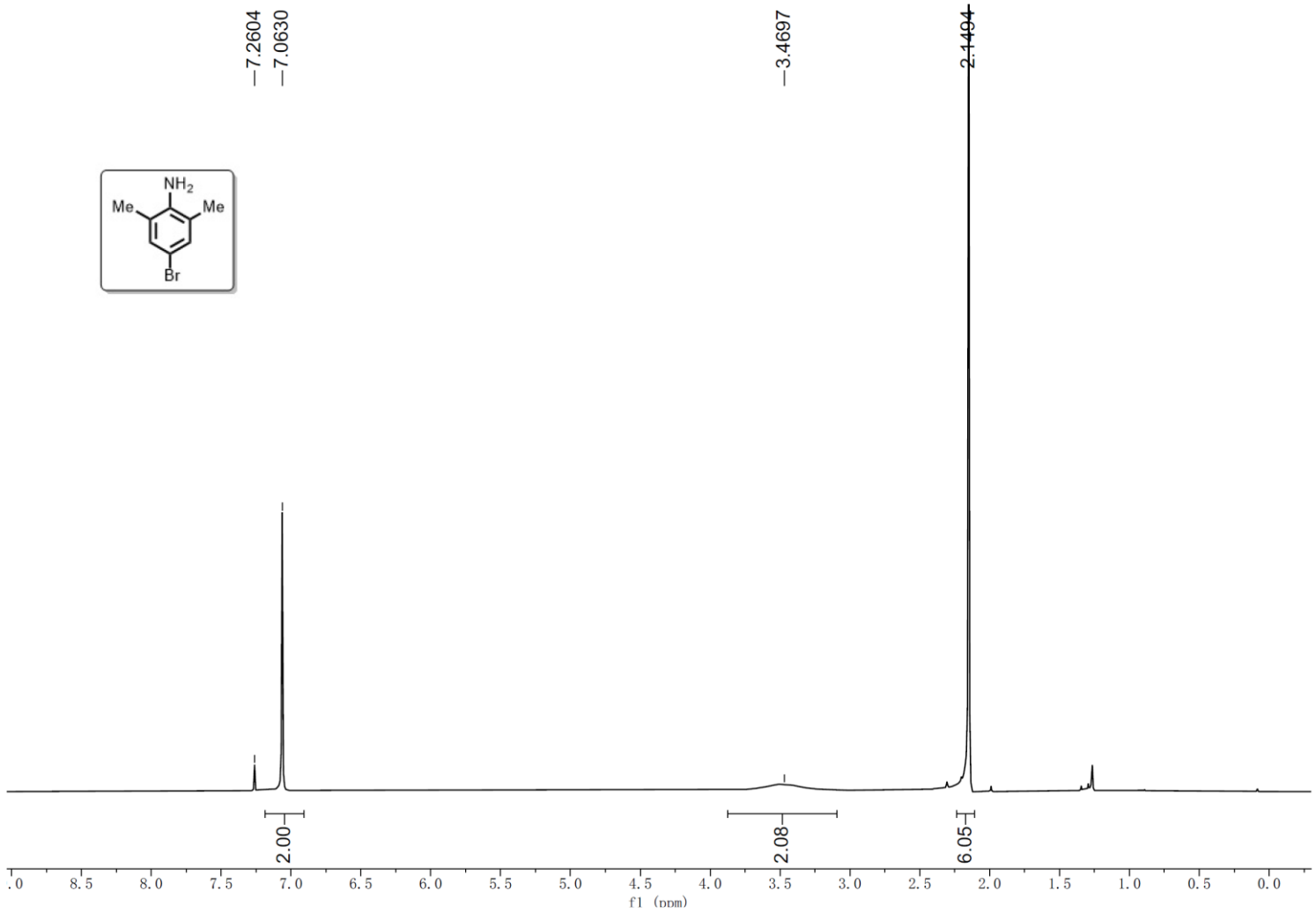
^{1}H NMR of **2k**


7.5704
7.5646
7.3132
7.3074
7.2917
7.2859
7.2528
7.2418
7.2225
7.1453
7.1163
7.1134
7.0952
6.6801
6.6586
3.9426
NH2
S
Br
1.00
1.08
2.26
0.92
2.05
1.02
2.23
f1 (ppm)

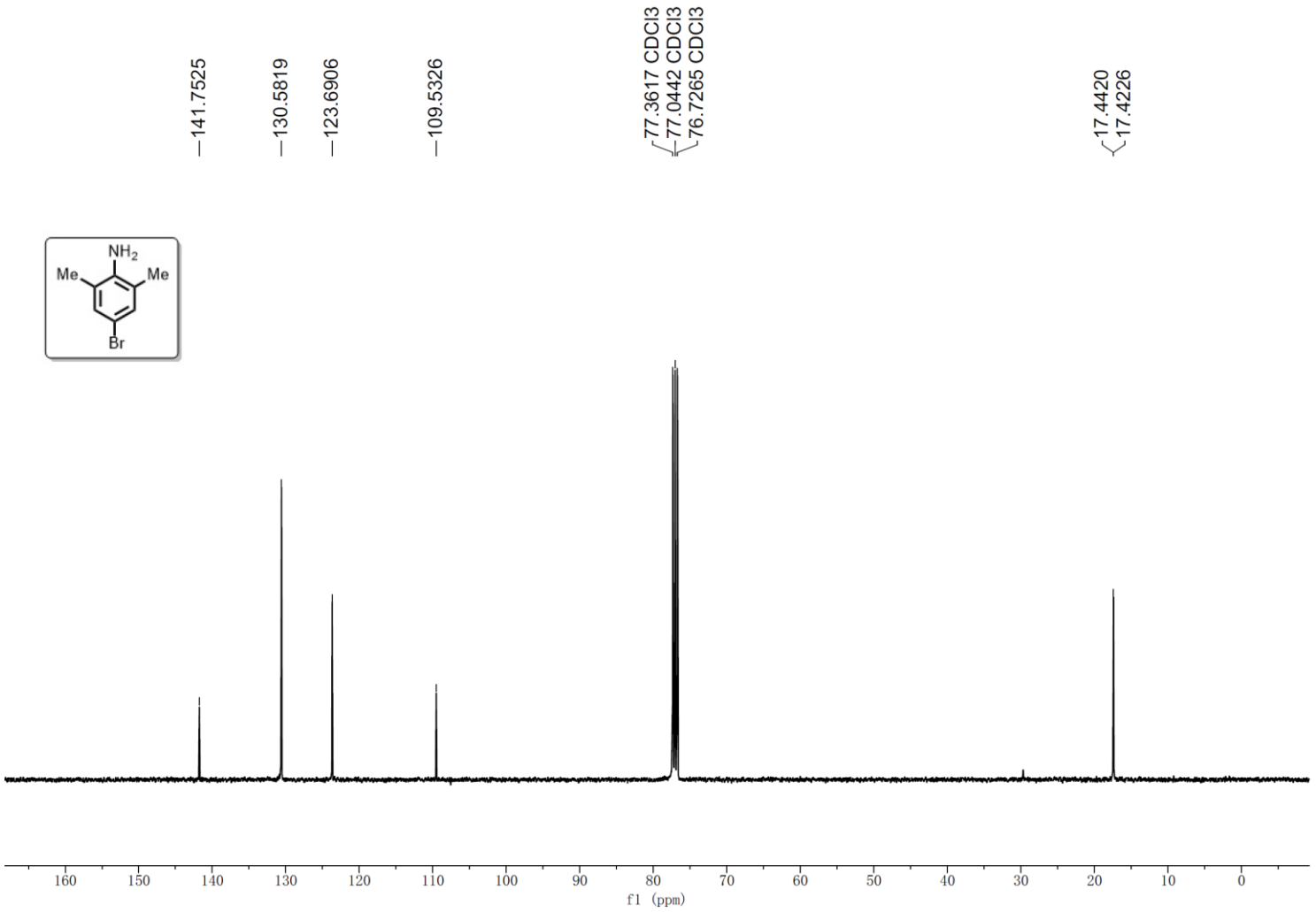
^{13}C NMR of **2k**


147.6486
138.9270
135.7531
133.7199
129.1678
126.9951
125.9694
116.7312
116.6864
109.3551
77.3491 CDCl3
77.0316 CDCl3
76.7141 CDCl3
NH2
S
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

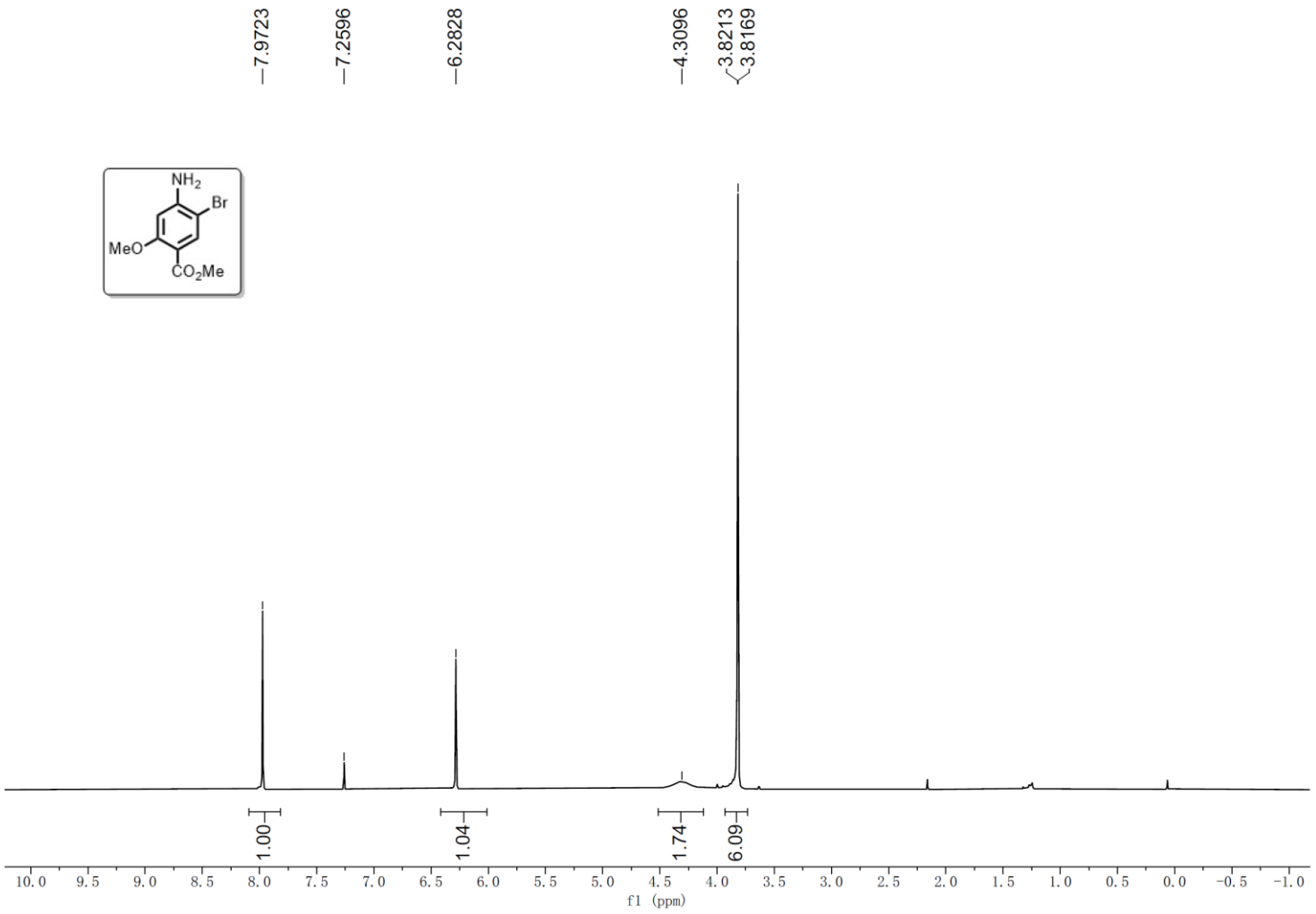
^{1}H NMR of **2l**



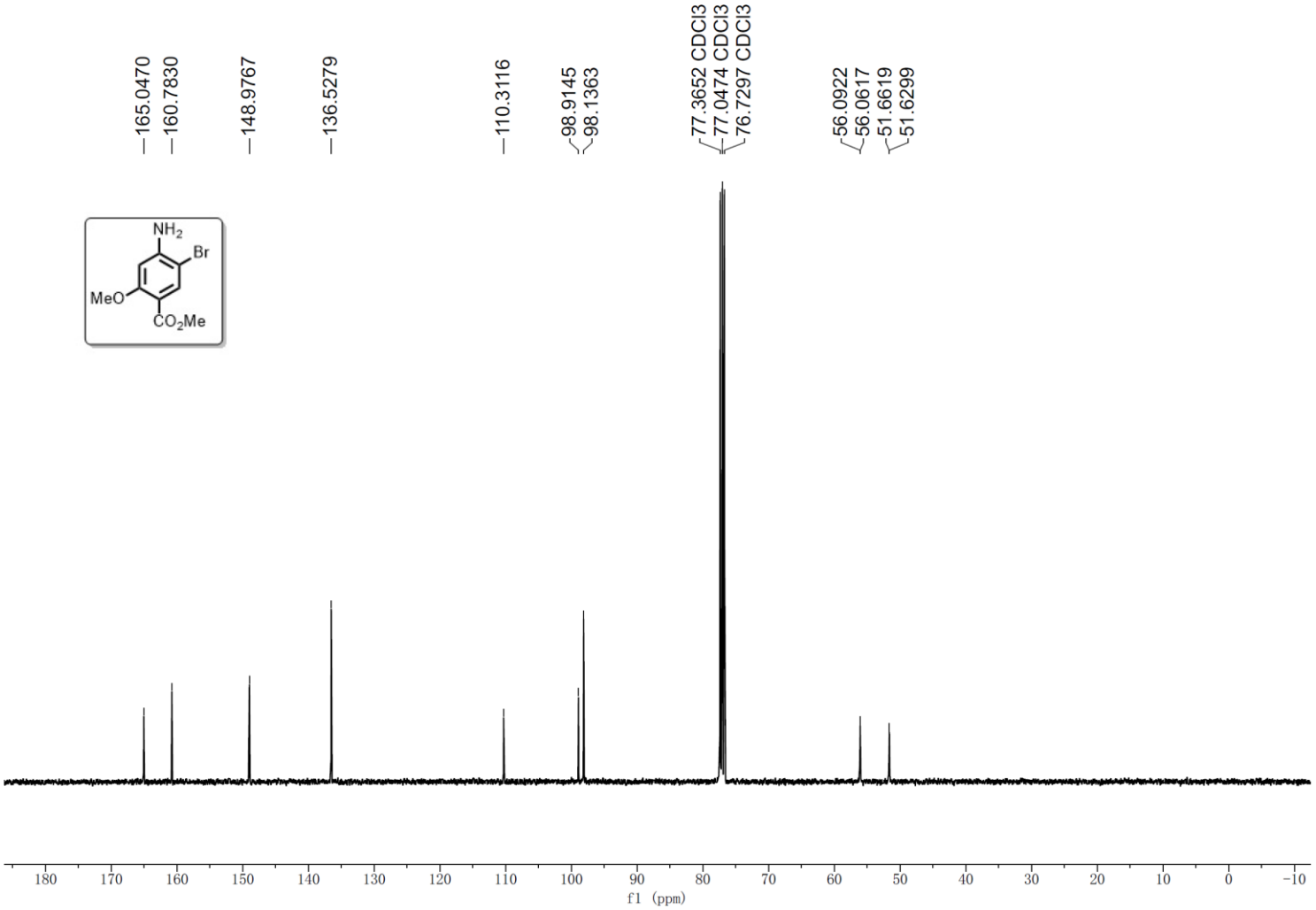
^{13}C NMR of **2l**


141.7525
130.5819
123.6906
109.5326
77.3617 CDCl3
77.0442 CDCl3
76.7265 CDCl3
17.4420
17.4226
NH2
Me
Me
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

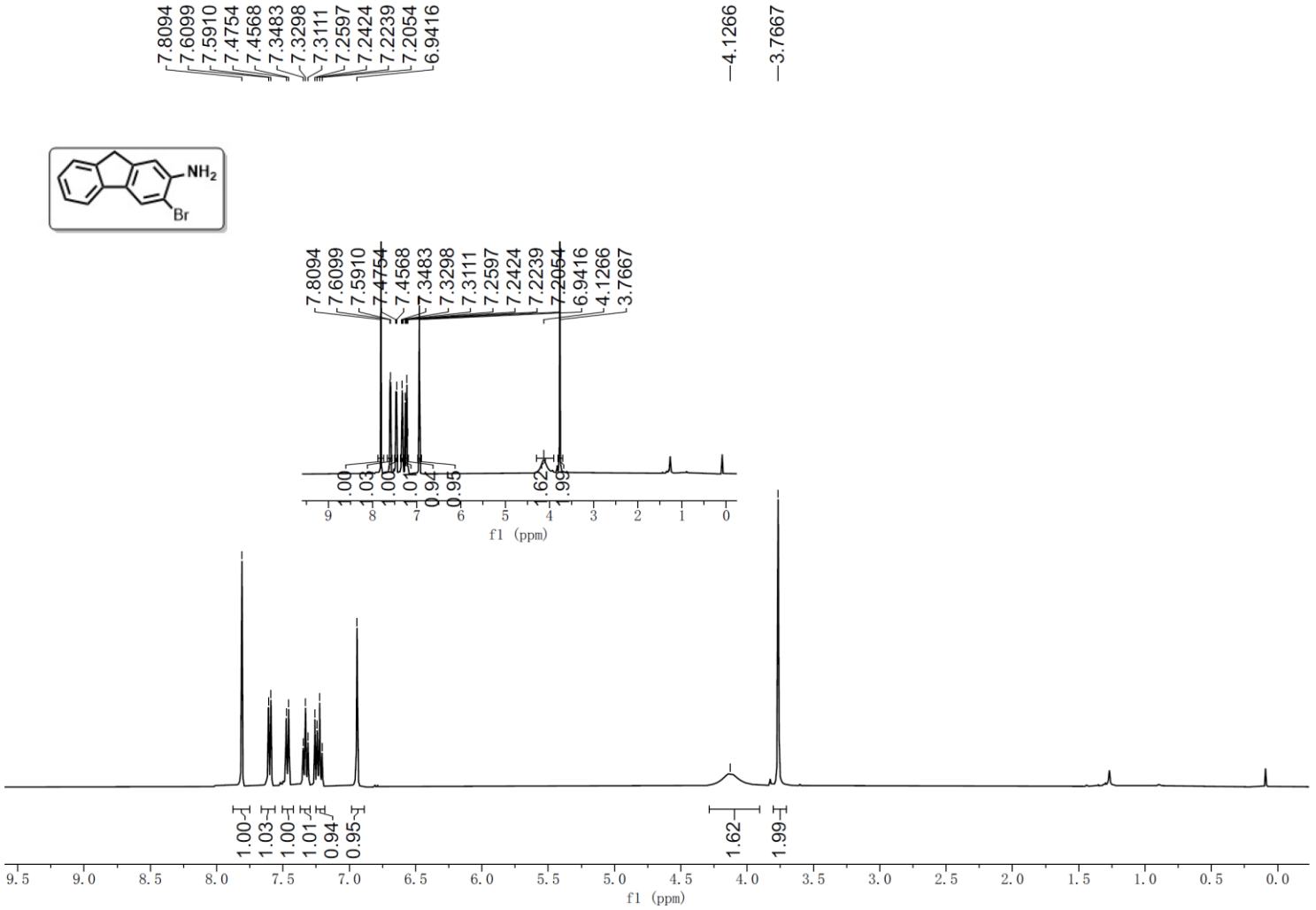
^{1}H NMR of **2m**


7.9723
7.2596
6.2828
4.3096
3.8213
3.8169
NH2
Br
MeO
CO2Me
1.00
1.04
1.74
6.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

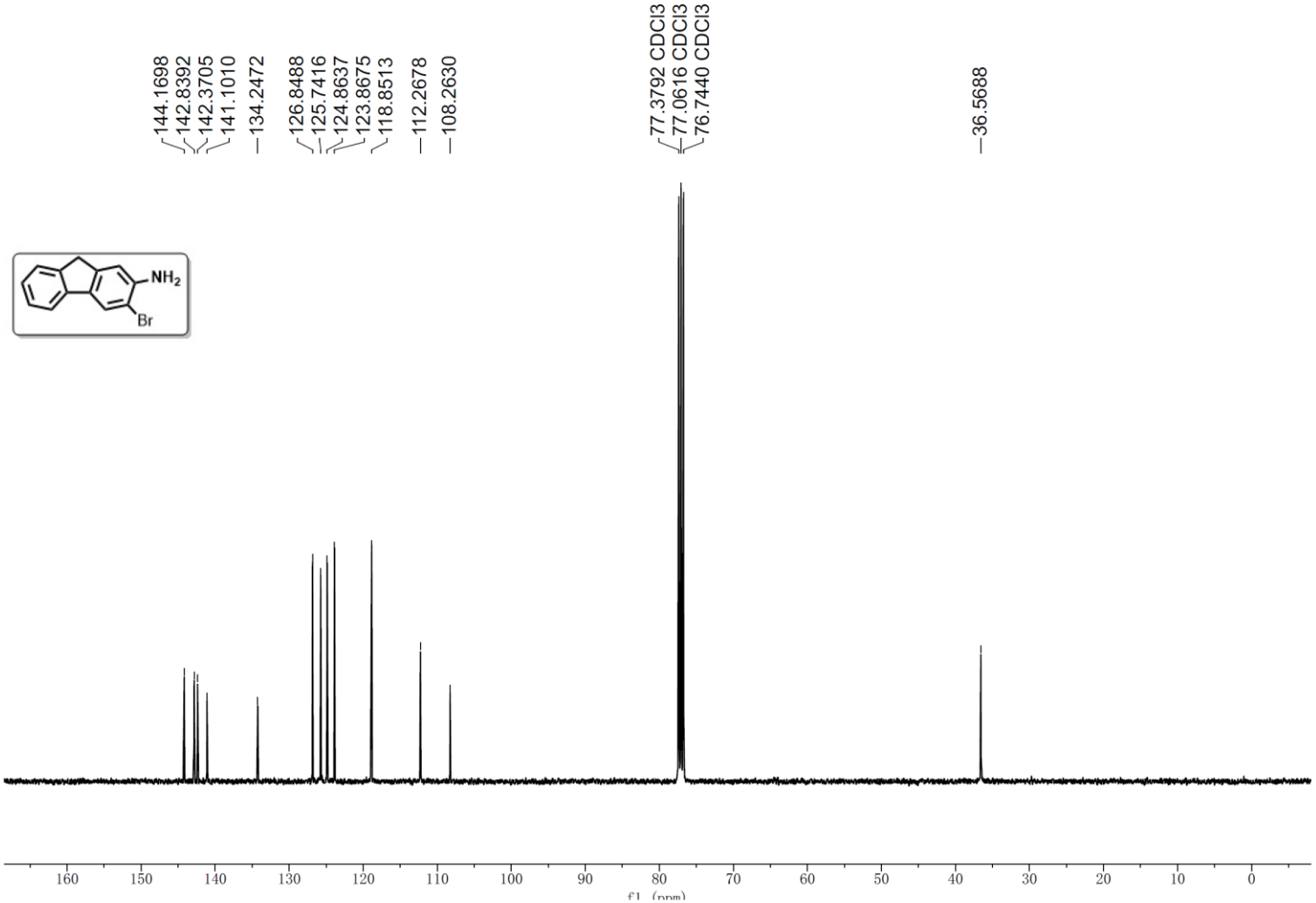
^{13}C NMR of **2m**


165.0470
160.7830
148.9767
136.5279
110.3116
98.9145
98.1363
77.3652 CDCl3
77.0474 CDCl3
76.7297 CDCl3
56.0922
56.0617
51.6619
51.6299
NH2
Br
MeO
CO2Me
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

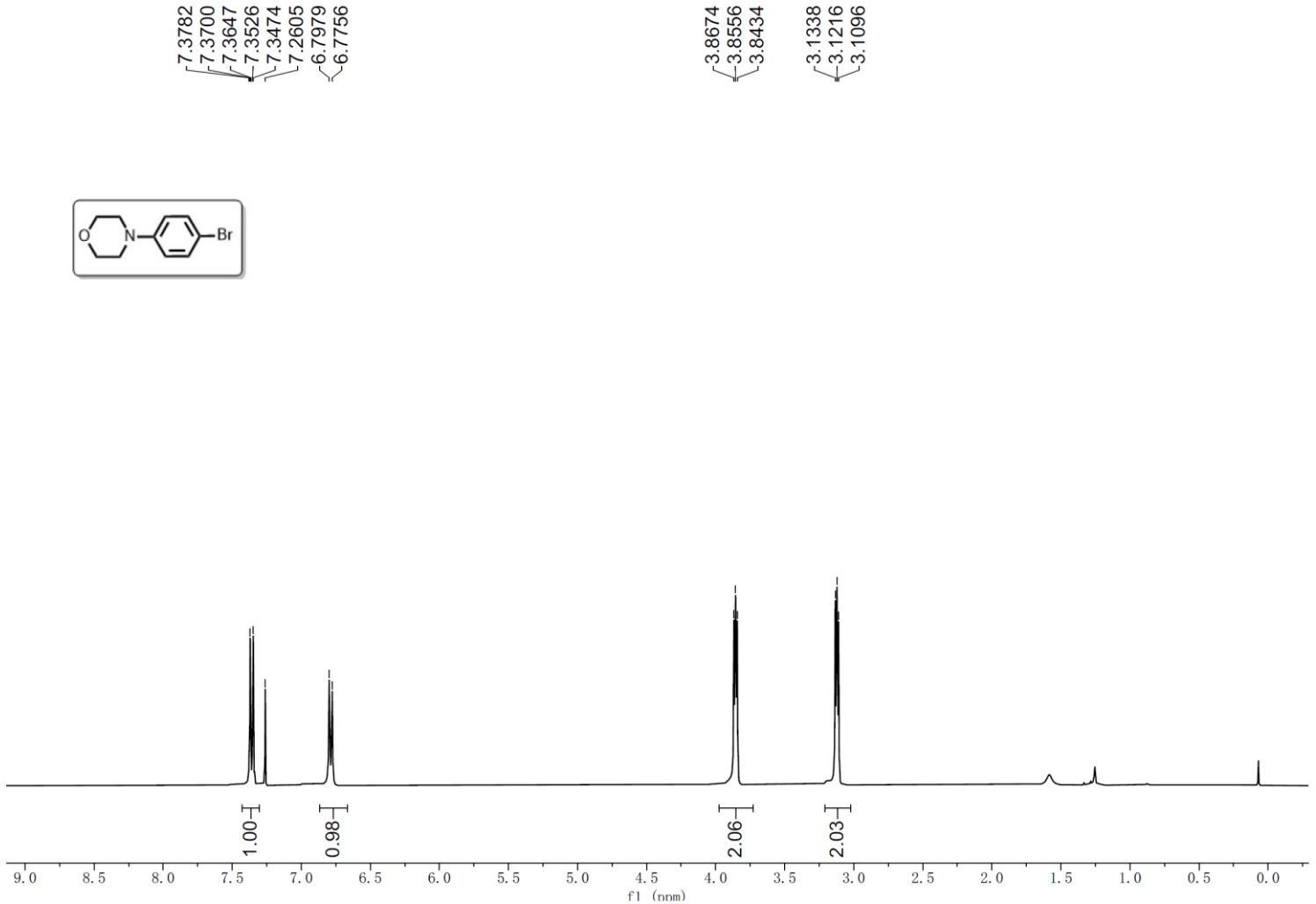
^{1}H NMR of **2n**


7.8094
7.6099
7.5910
7.4754
7.4568
7.3483
7.3298
7.3111
7.2597
7.2424
7.2239
7.2054
6.9416
4.1266
3.7667
NH2
Br
1.00
1.03
1.00
1.01
0.94
0.95
1.62
1.99
f1 (ppm)

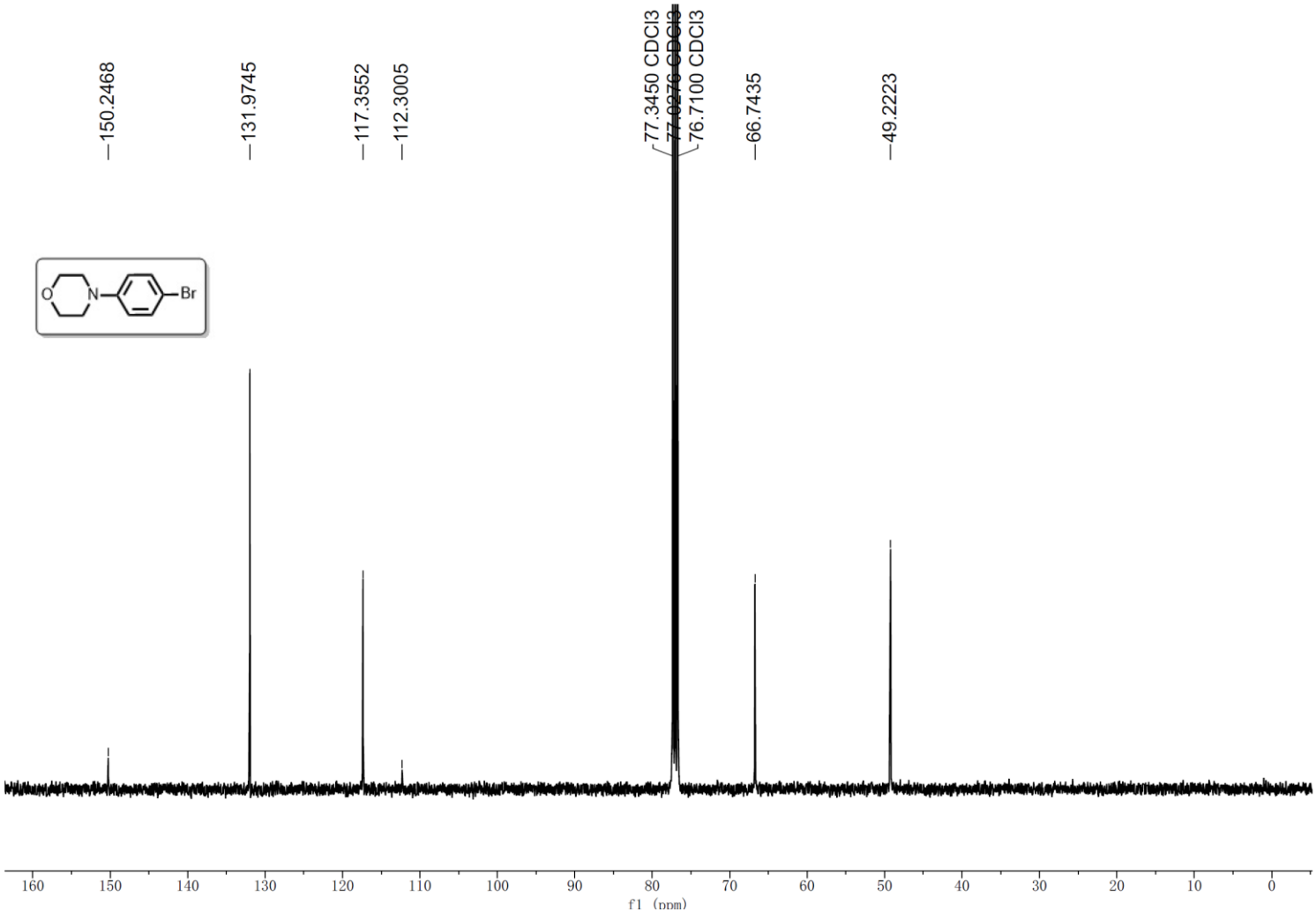
^{13}C NMR of **2n**


144.1698
142.8392
142.3705
141.1010
134.2472
126.8488
125.7416
124.8637
123.8675
118.8513
112.2678
108.2630
77.3792 CDCl3
77.0616 CDCl3
76.7440 CDCl3
36.5688
NH2
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

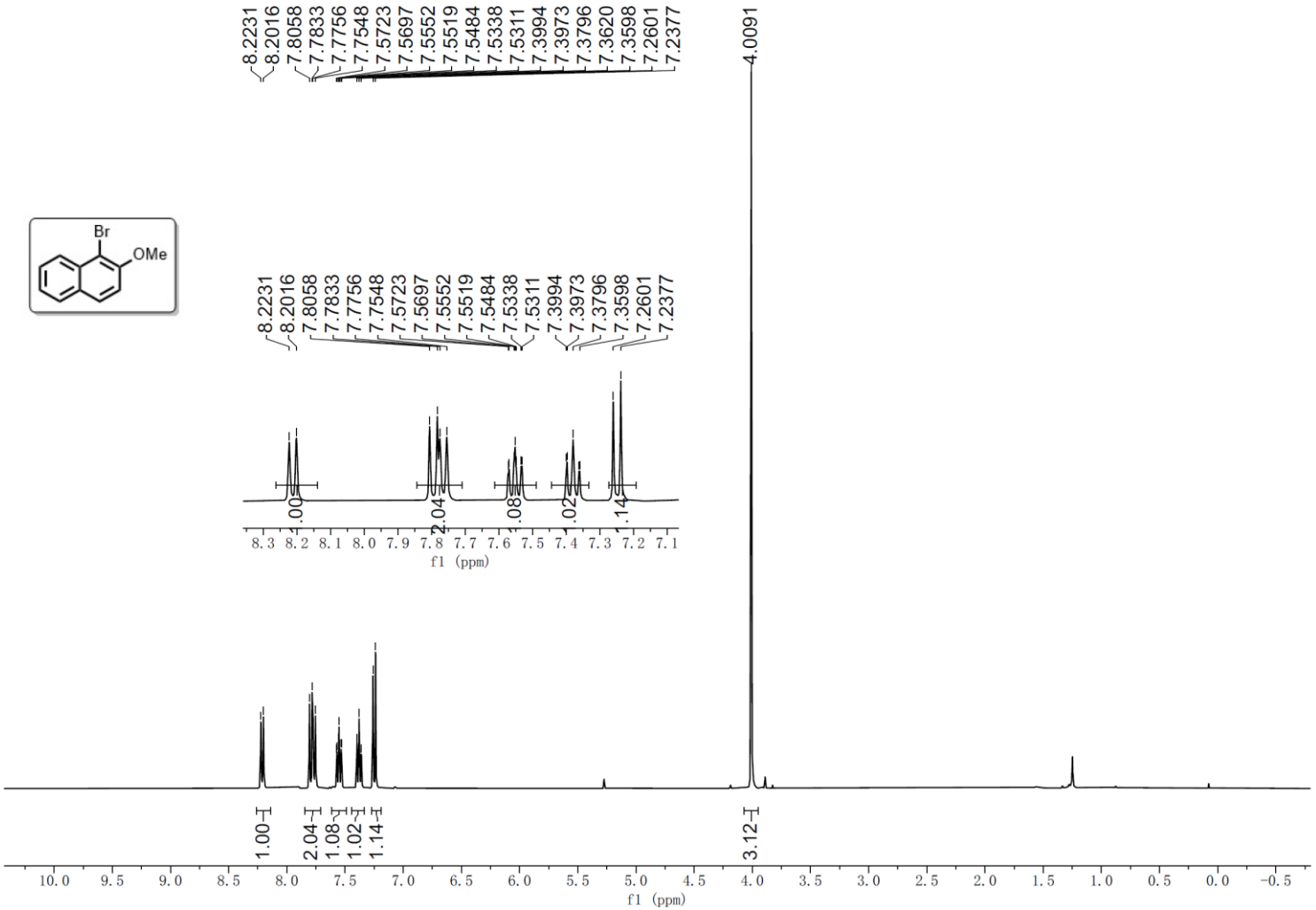
^{1}H NMR of **2o**


7.3782
7.3700
7.3647
7.3526
7.3474
7.2605
6.7979
6.7756
3.8674
3.8556
3.8434
3.1338
3.1216
3.1096
O
N
Br
1.00
0.98
2.06
2.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

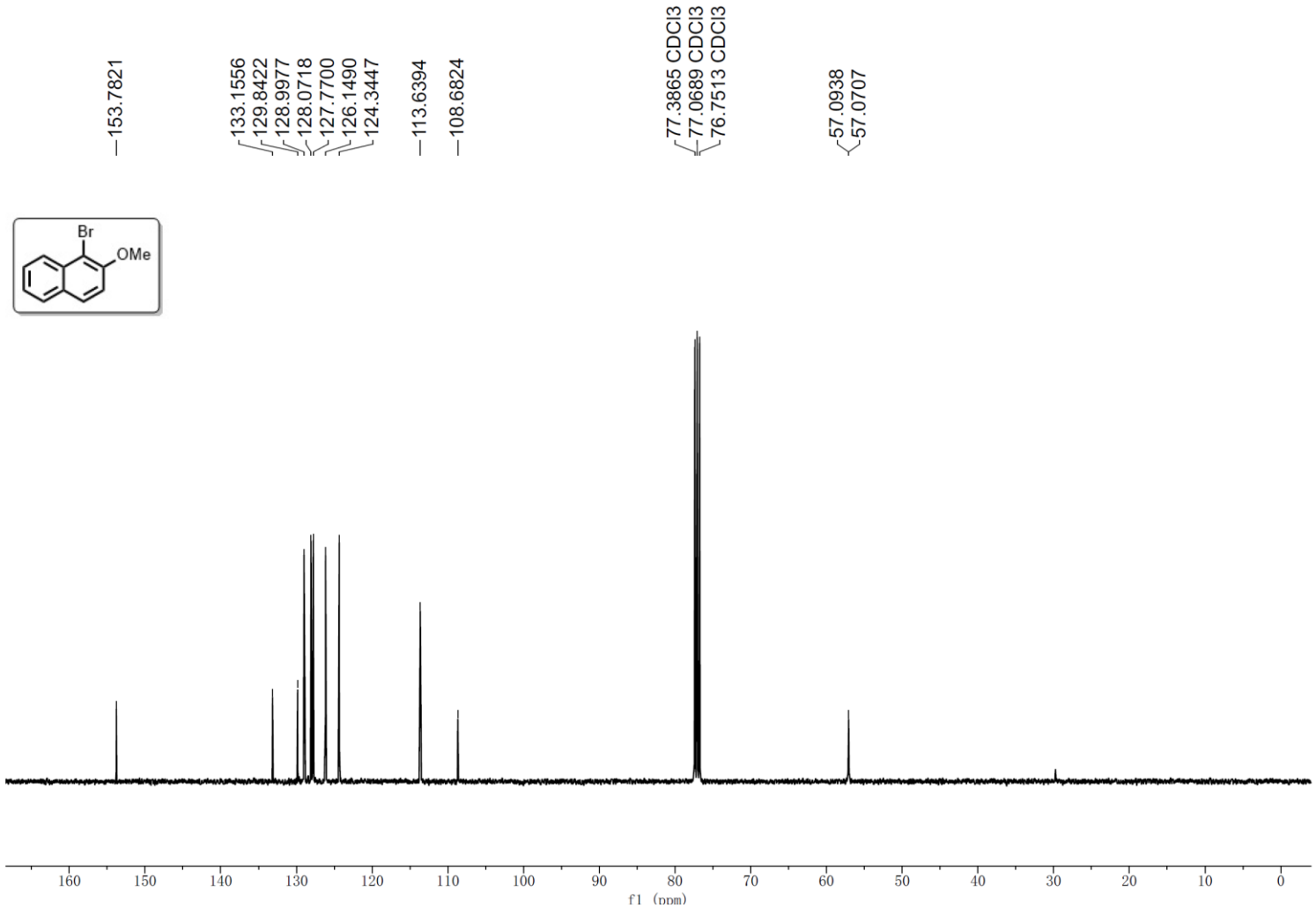
^{13}C NMR of **2o**


150.2468
131.9745
117.3552
112.3005
77.3450 CDCl3
77.0276 CDCl3
76.7100 CDCl3
66.7435
49.2223
O
N
Br
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

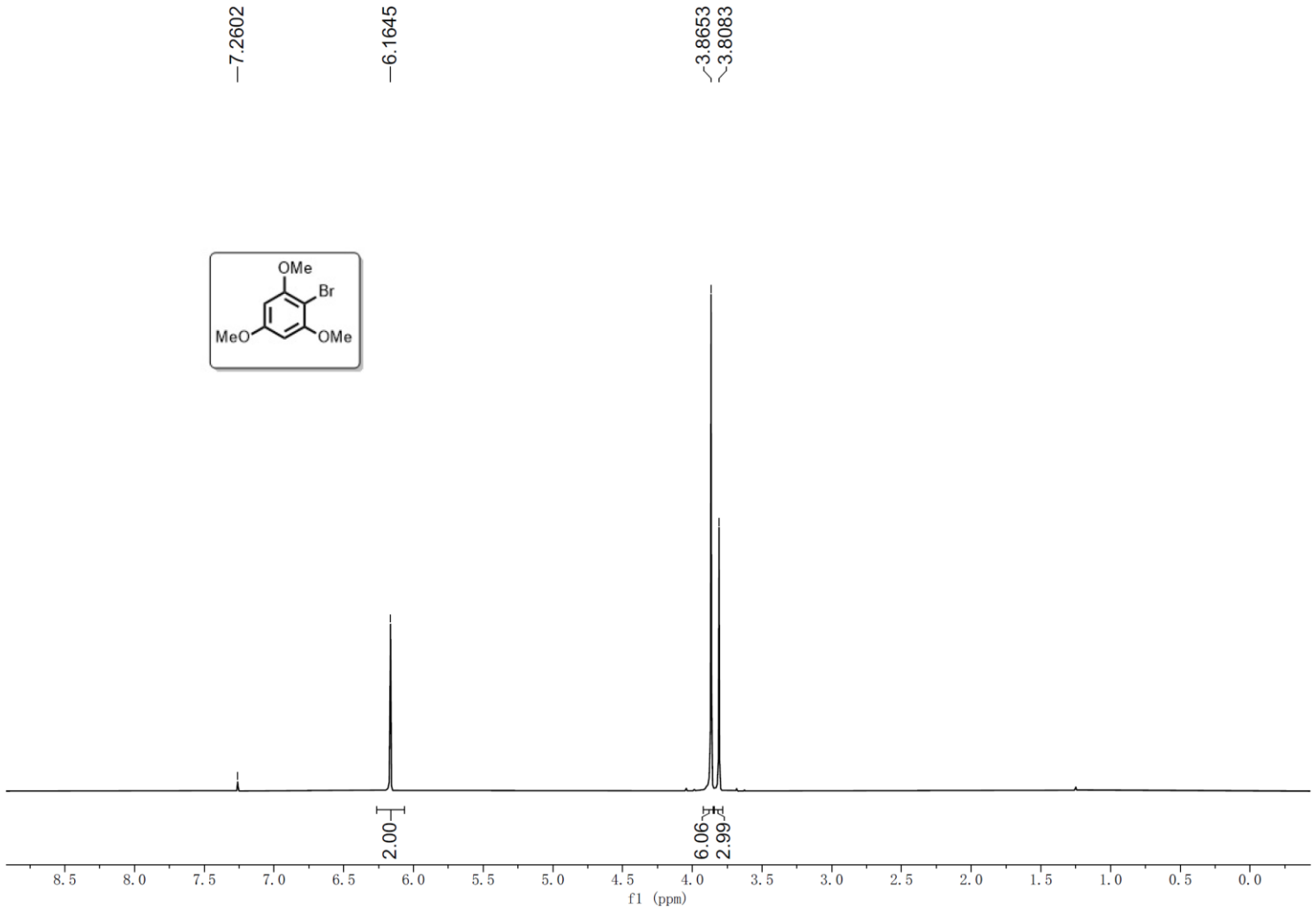
^{1}H NMR of **2p**


Br
OMe
8.2231
8.2016
7.8058
7.7833
7.7756
7.7548
7.5723
7.5697
7.5552
7.5519
7.5484
7.5338
7.5311
7.3994
7.3973
7.3796
7.3620
7.3598
7.2601
7.2377
4.0091
1.00
2.04
1.08
1.02
1.14
3.12
f1 (ppm)

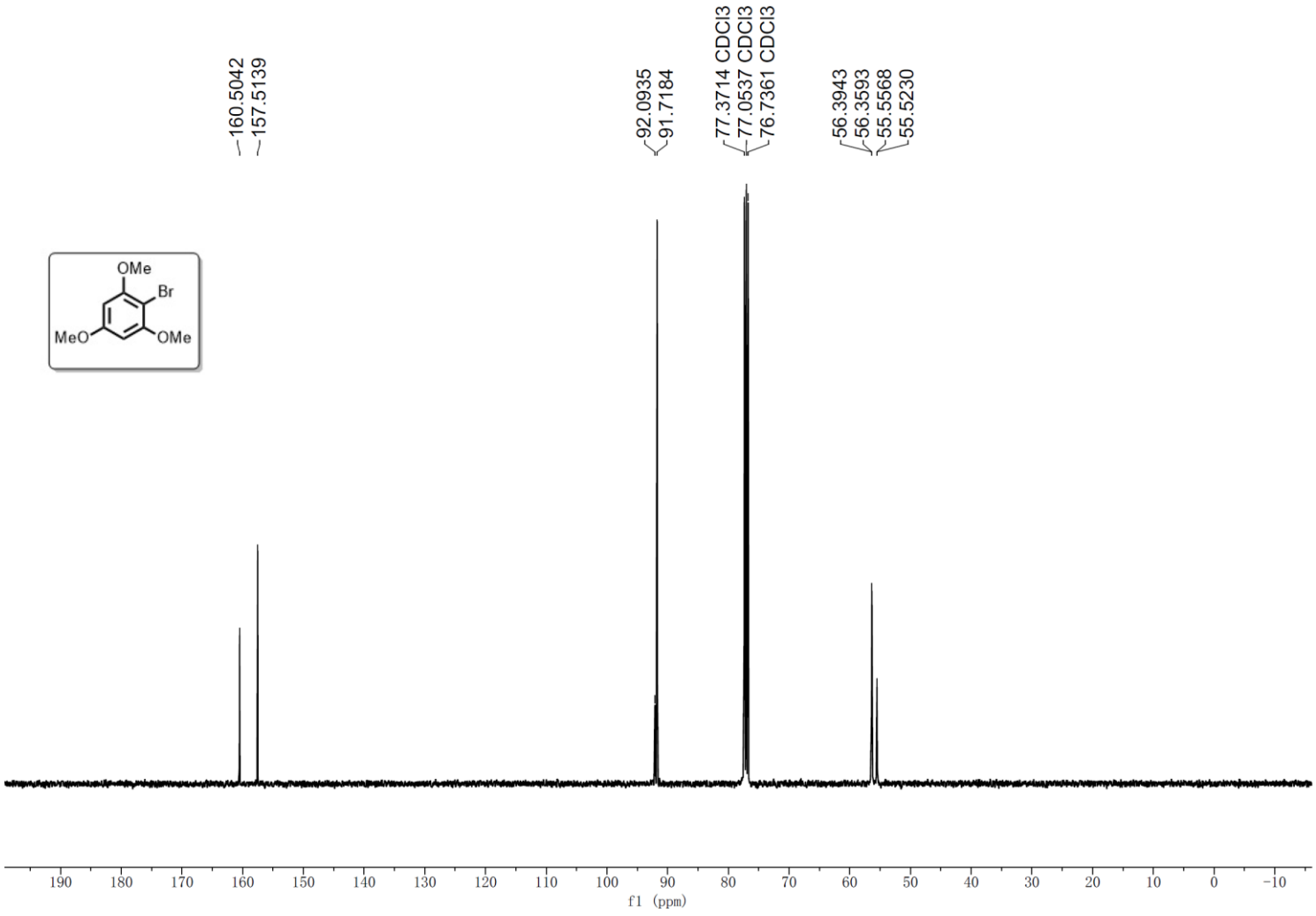
^{13}C NMR of **2p**


153.7821
133.1556
129.8422
128.9977
128.0718
127.7700
126.1490
124.3447
113.6394
108.6824
77.3865 CDCl3
77.0689 CDCl3
76.7513 CDCl3
57.0938
57.0707
Br
OMe
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

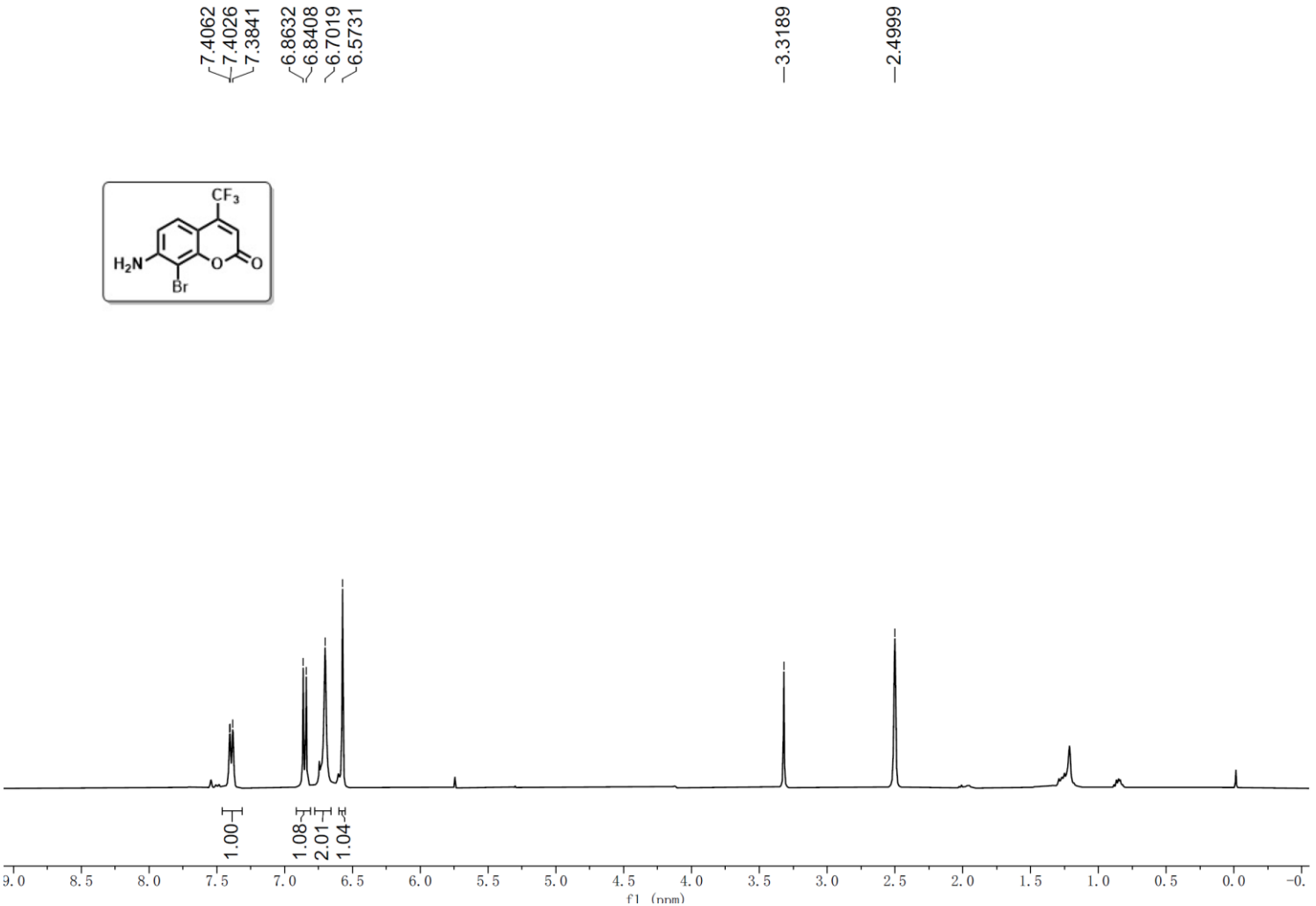
^{1}H NMR of **2q**


7.2602
6.1645
3.8653
3.8083
OMe
Br
MeO
OMe
2.00
6.06
2.99
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

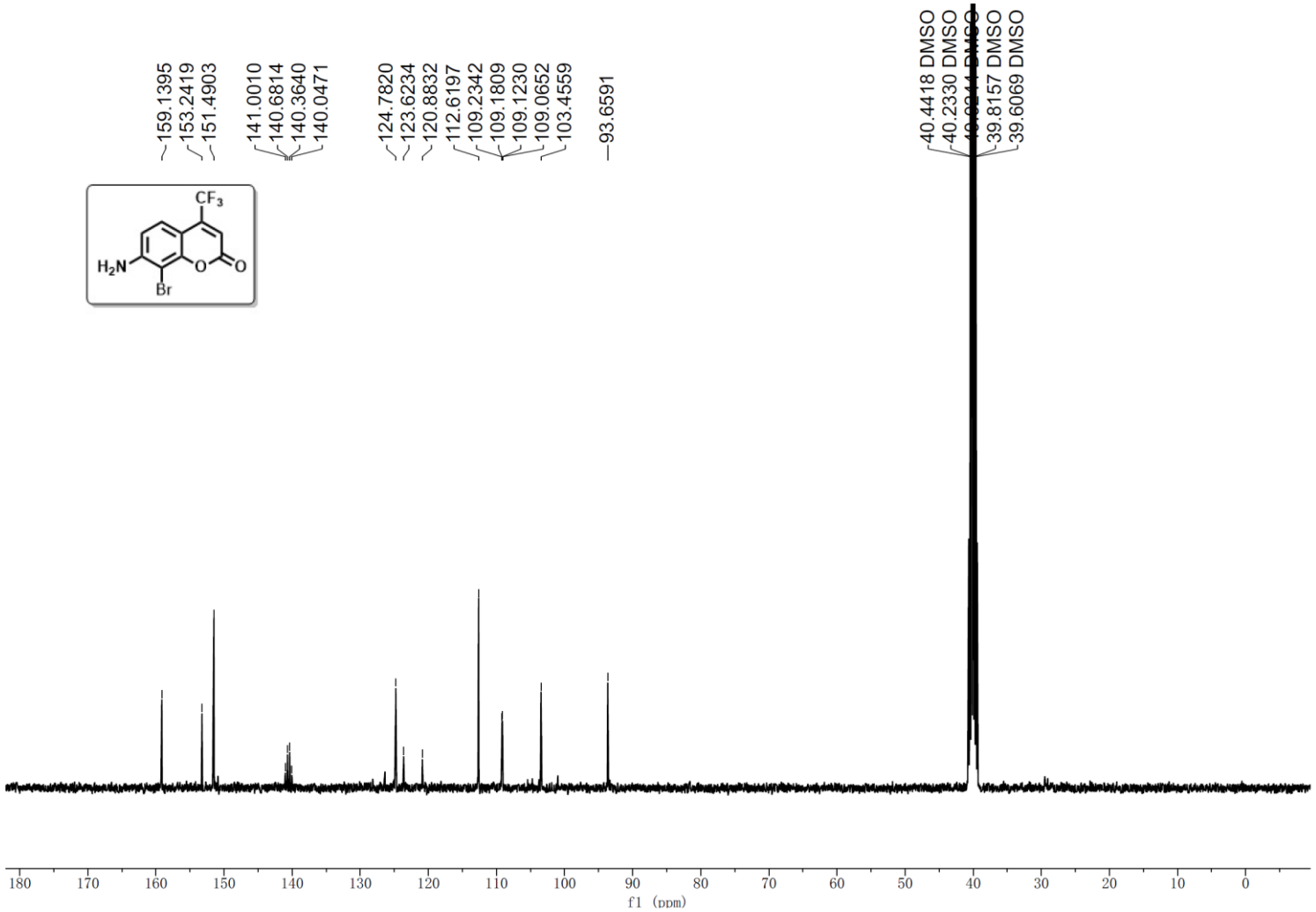
^{13}C NMR of **2q**


160.5042
157.5139
92.0935
91.7184
77.3714 CDCl3
77.0537 CDCl3
76.7361 CDCl3
56.3943
56.3593
55.5568
55.5230
OMe
Br
MeO
OMe
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

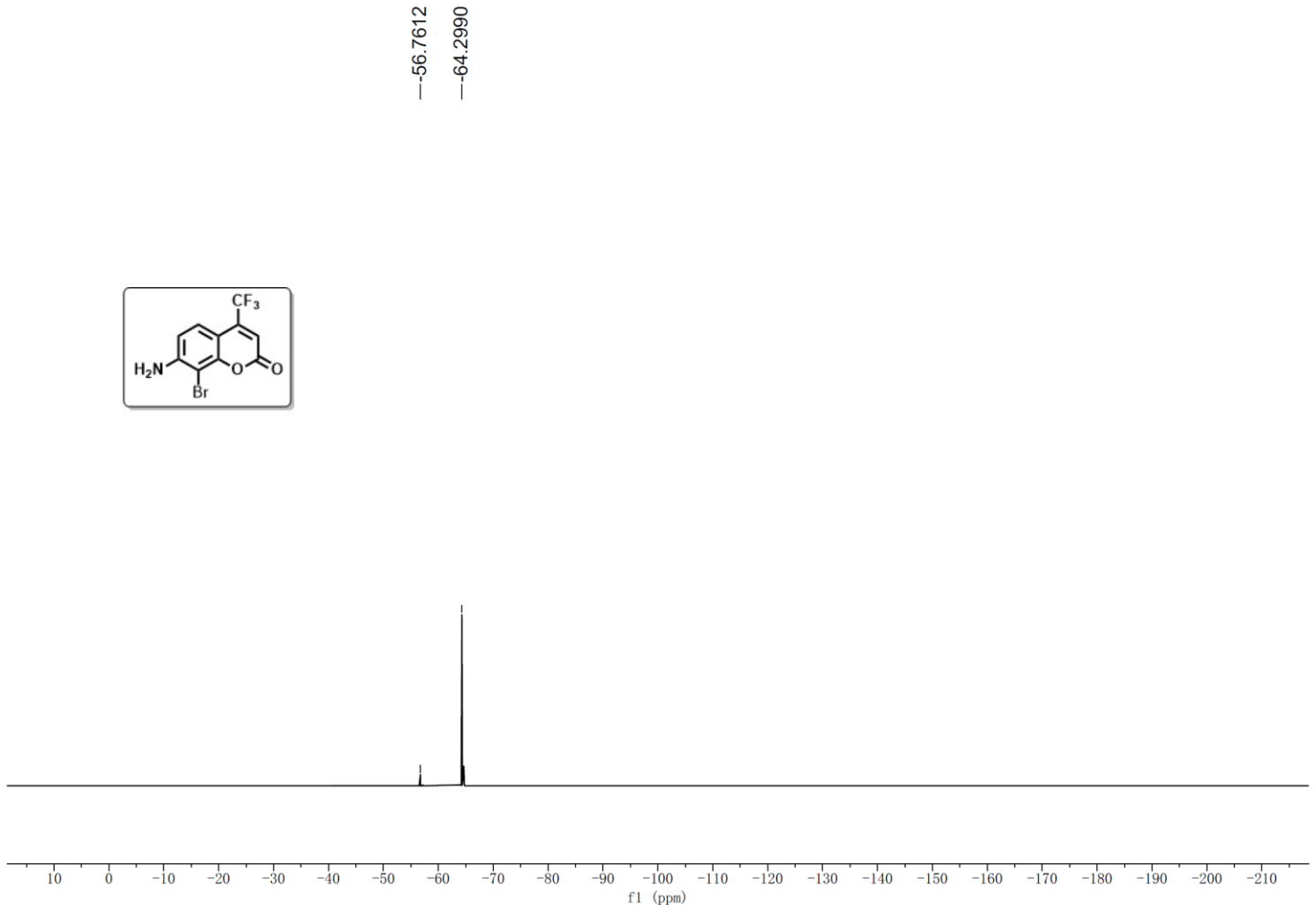
^{1}H NMR of **2r**


7.4062
7.4026
7.3841
6.8632
6.8408
6.7019
6.5731
3.3189
2.4999
CF3
H2N
O
O
Br
1.00
1.08
2.01
1.04
f1 (ppm)

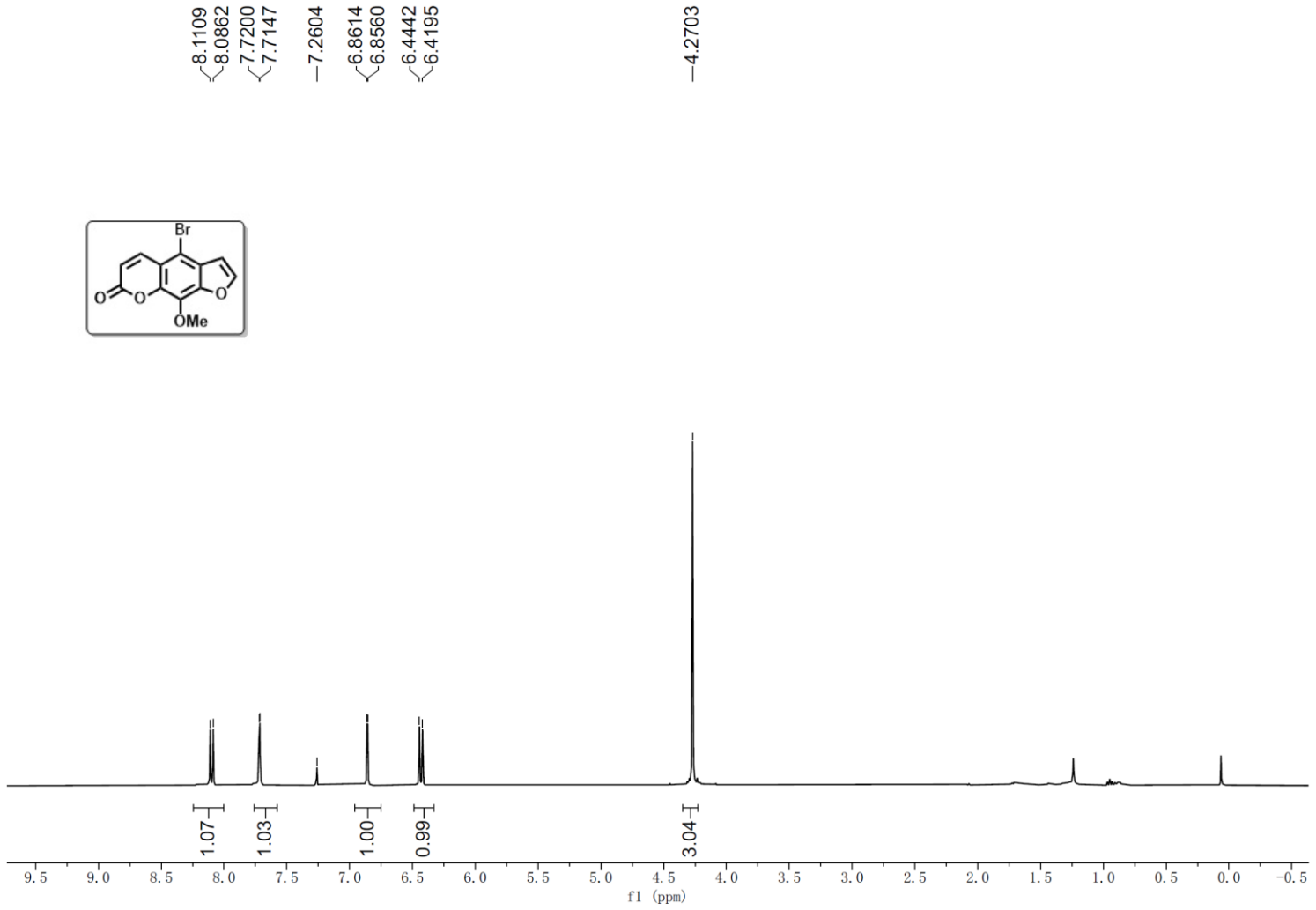
^{13}C NMR of **2r**


159.1395
153.2419
151.4903
141.0010
140.6814
140.3640
140.0471
124.7820
123.6234
120.8832
112.6197
109.2342
109.1809
109.1230
109.0652
103.4559
93.6591
40.4418 DMSO
40.2330 DMSO
39.8157 DMSO
39.6069 DMSO
CF3
H2N
O
O
Br
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

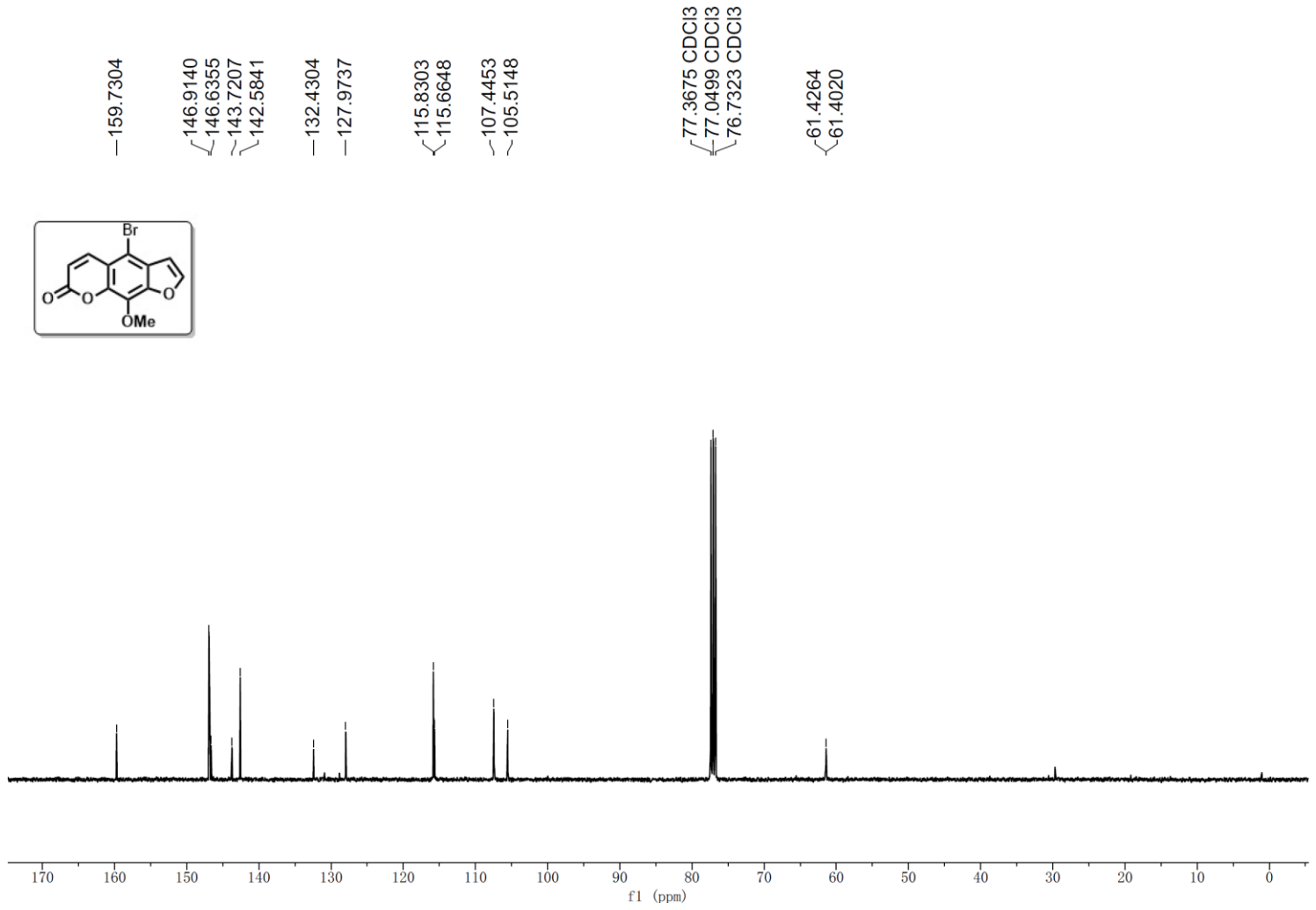
^{19}F NMR of **2r**


-56.7612
-64.2990
CF3
H2N
O
O
Br
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

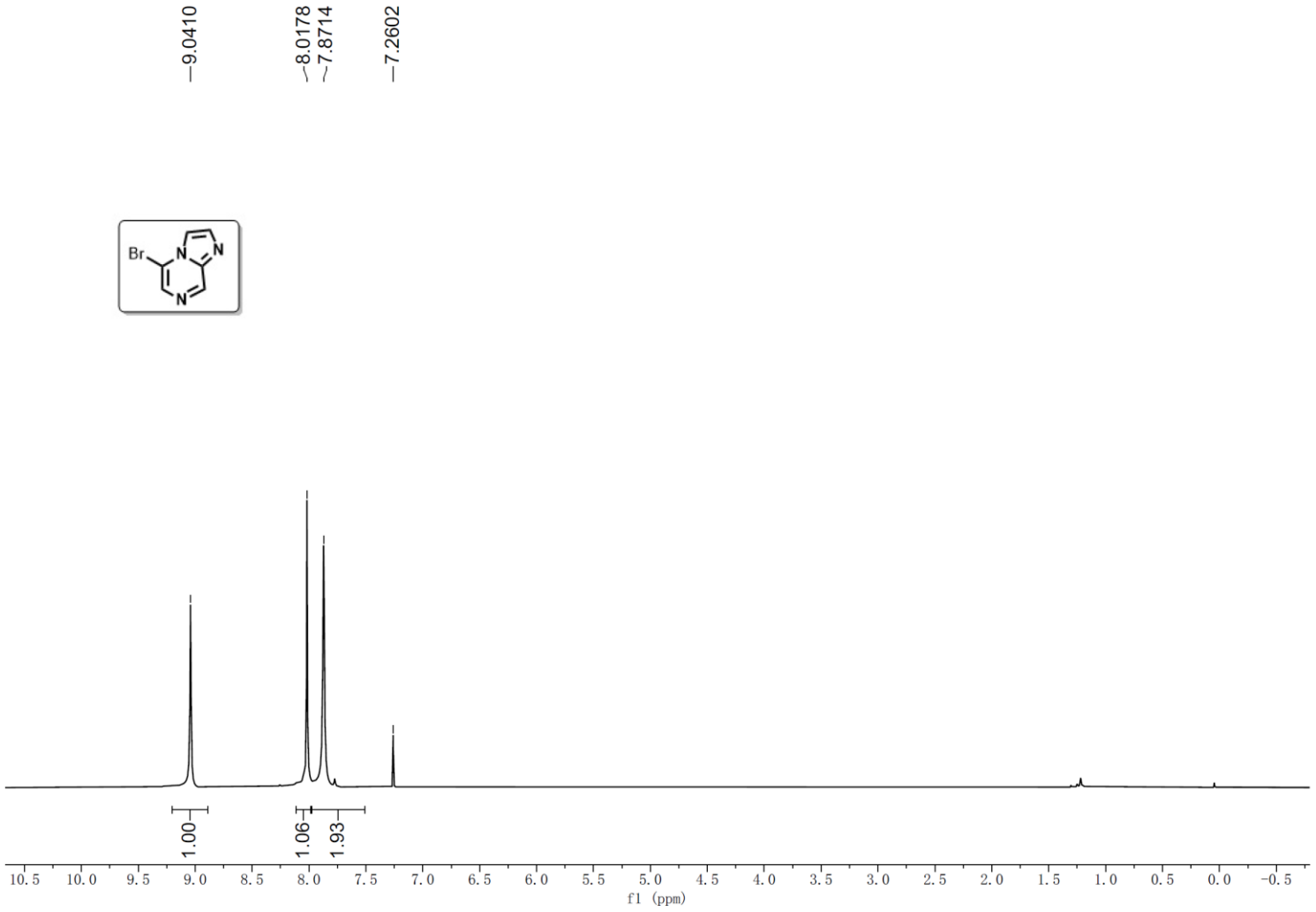
^{1}H NMR of **2s**


8.1109
8.0862
7.7200
7.7147
7.2604
6.8614
6.8560
6.4442
6.4195
4.2703
Br
O
O
O
OMe
1.07
1.03
1.00
0.99
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

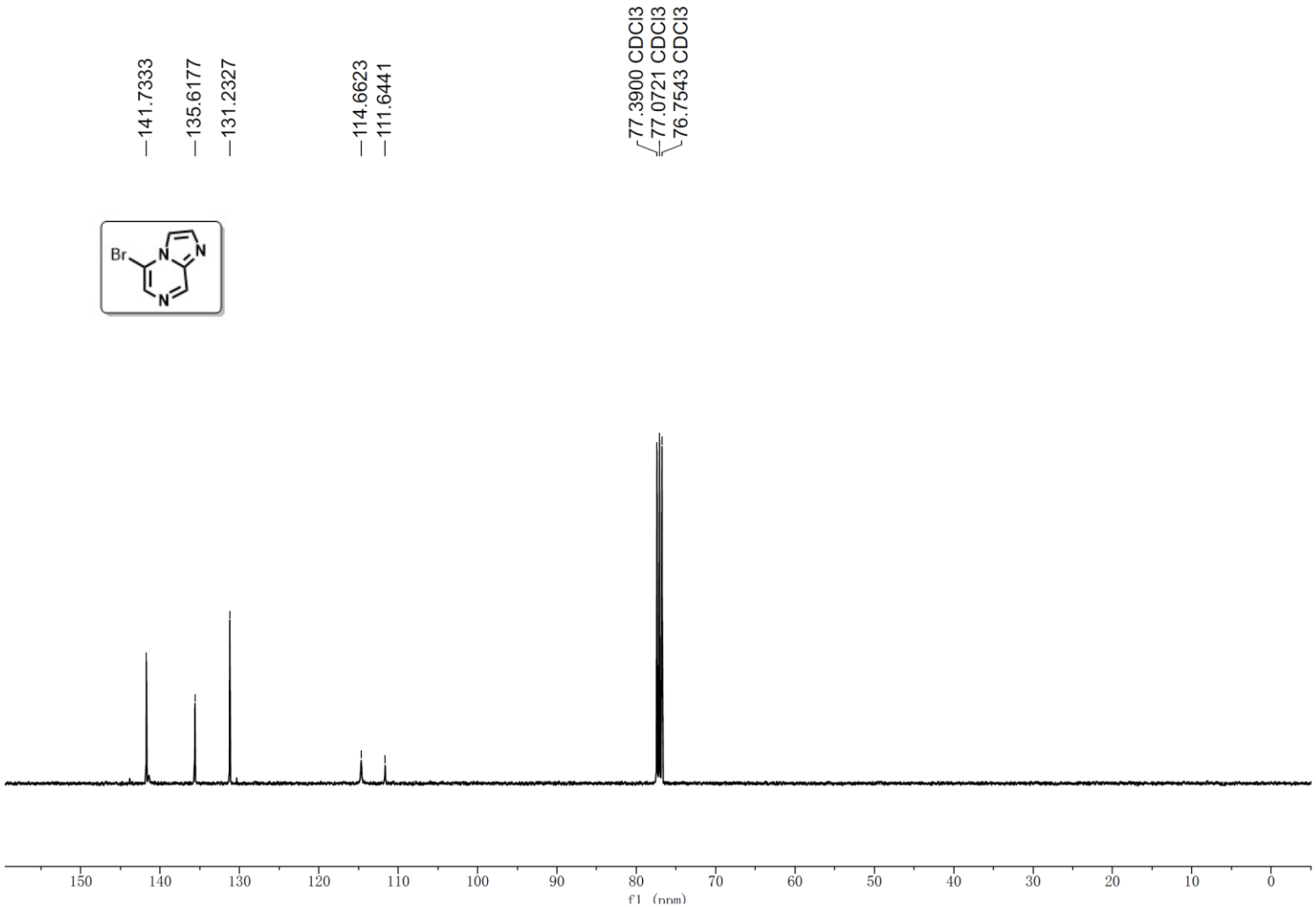
^{13}C NMR of **2s**


159.7304
146.9140
146.6355
143.7207
142.5841
132.4304
127.9737
115.8303
115.6648
107.4453
105.5148
77.3675 CDCl3
77.0499 CDCl3
76.7323 CDCl3
61.4264
61.4020
Br
O
O
O
OMe
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

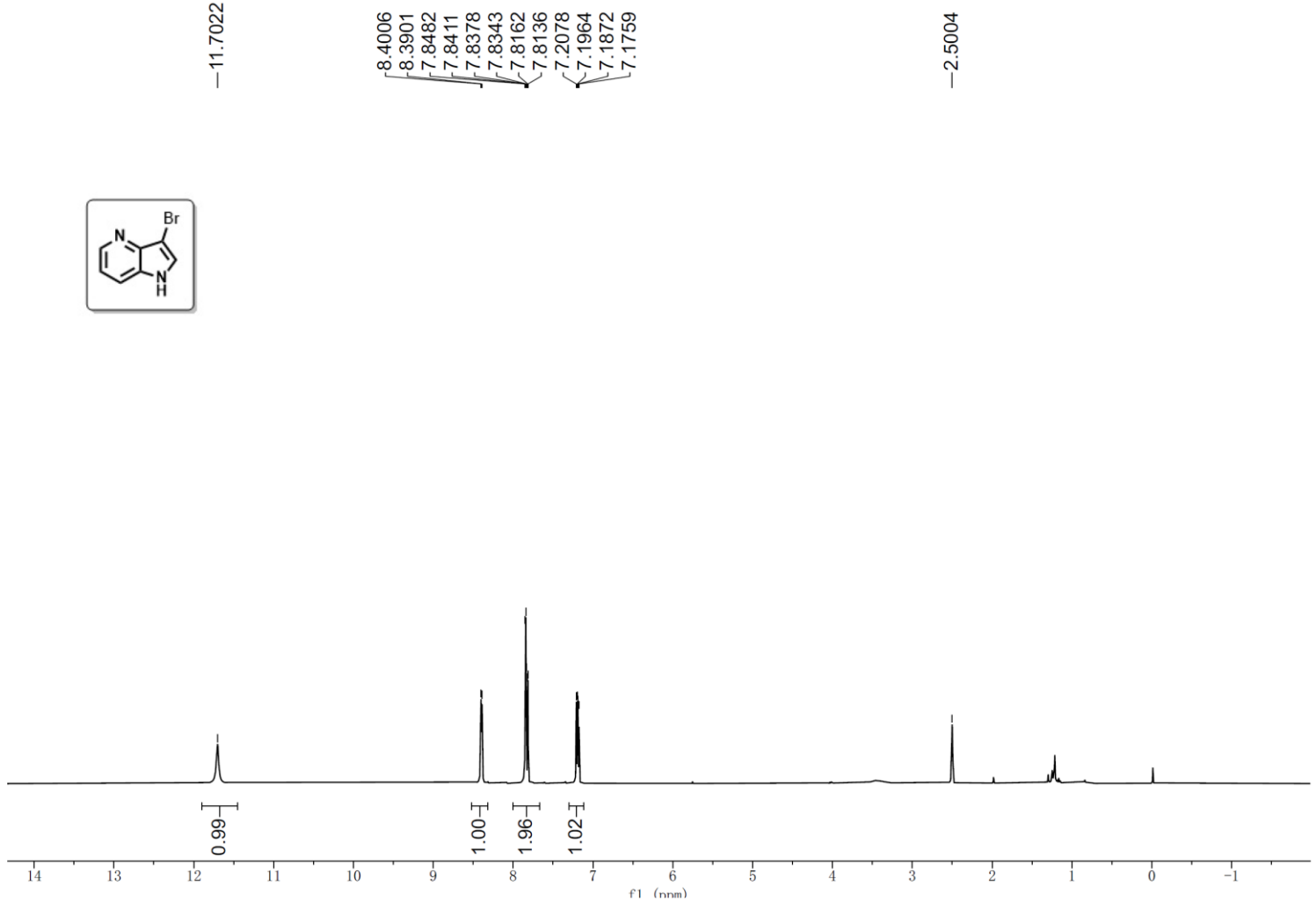
^{1}H NMR of **2t**


9.0410
8.0178
7.8714
7.2602
Br
N
N
N
1.00
1.06
1.93
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

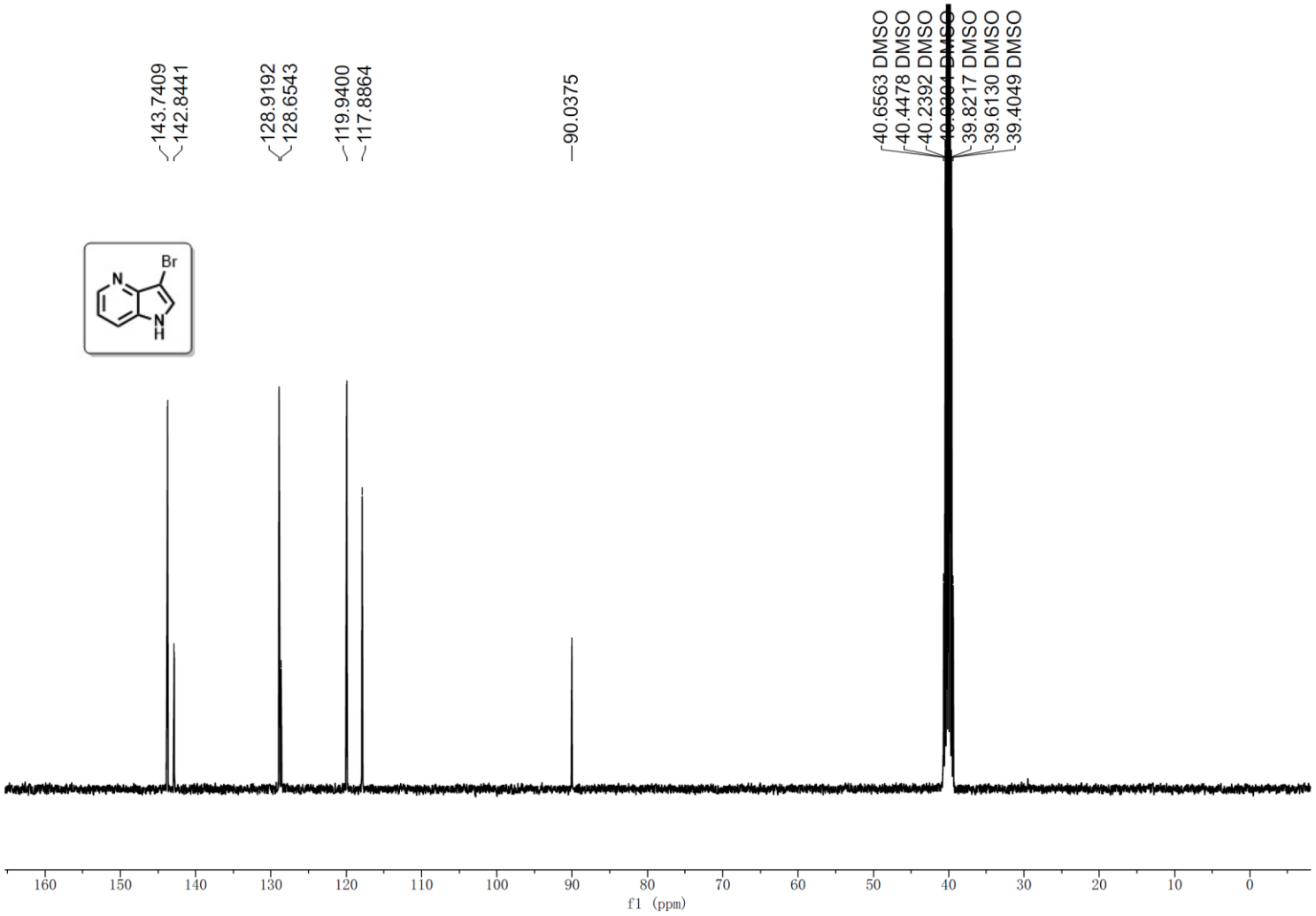
^{13}C NMR of **2t**


141.7333
135.6177
131.2327
114.6623
111.6441
77.3900 CDCl3
77.0721 CDCl3
76.7543 CDCl3
Br
N
N
N
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

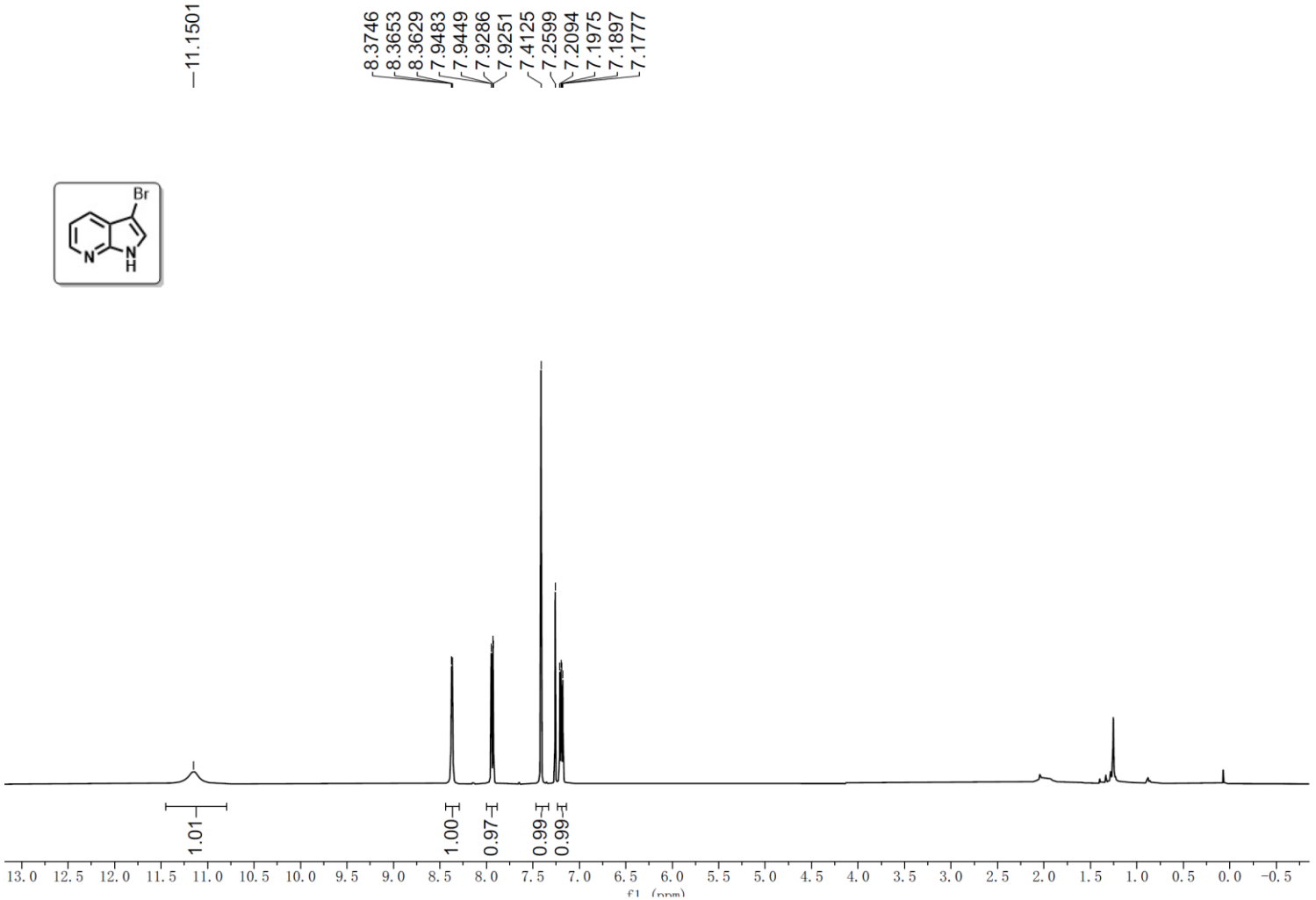
^{1}H NMR of **2u**


11.7022
8.4006
8.3901
7.8482
7.8411
7.8378
7.8343
7.8162
7.8136
7.2078
7.1964
7.1872
7.1759
2.5004
Br
N
N
H
0.99
1.00
1.96
1.02
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
−1
f1 (ppm)

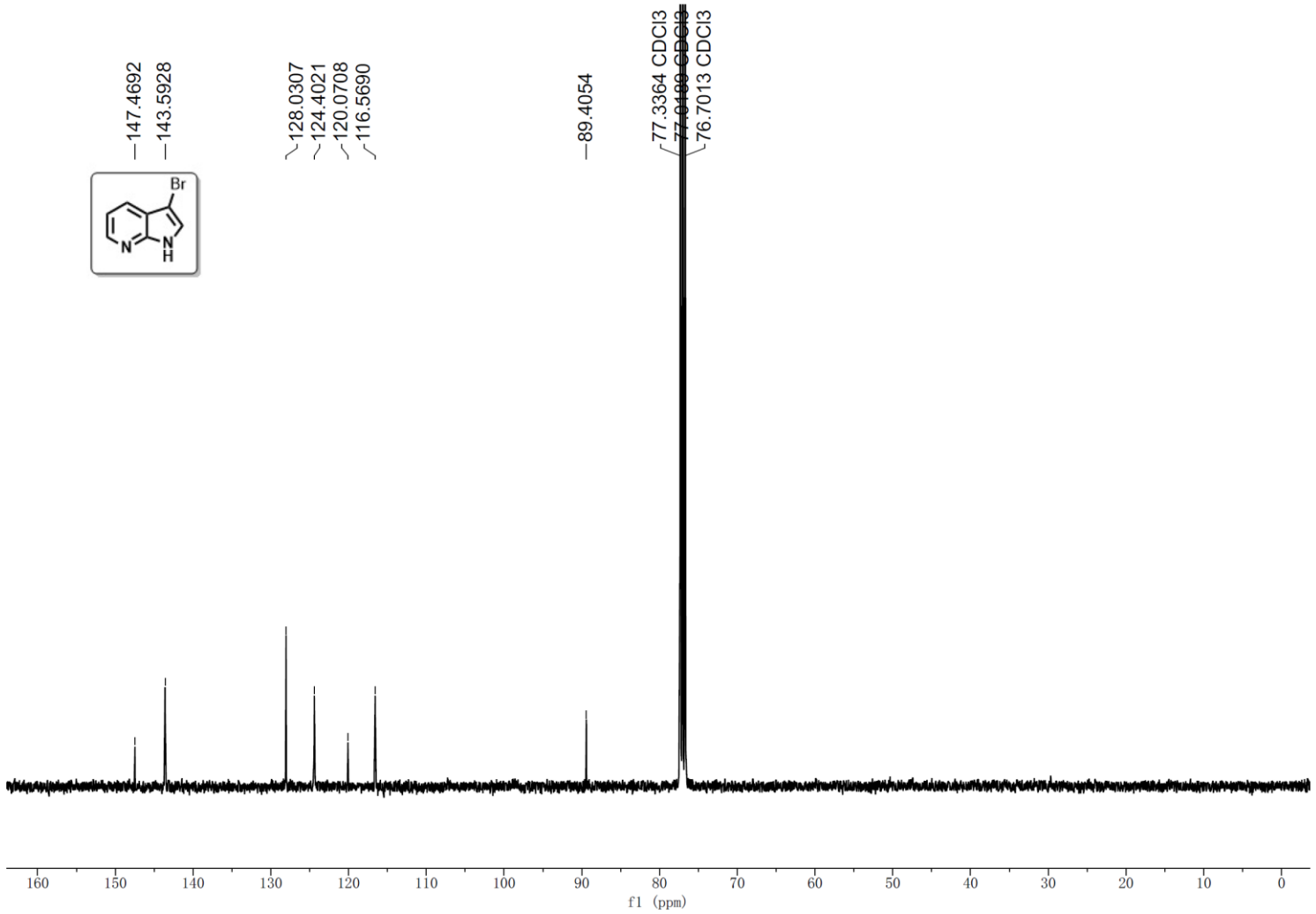
^{13}C NMR of **2u**


143.7409
142.8441
128.9192
128.6543
119.9400
117.8864
90.0375
40.6563 DMSO
40.4478 DMSO
40.2392 DMSO
39.8217 DMSO
39.6130 DMSO
39.4049 DMSO
Br
N
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

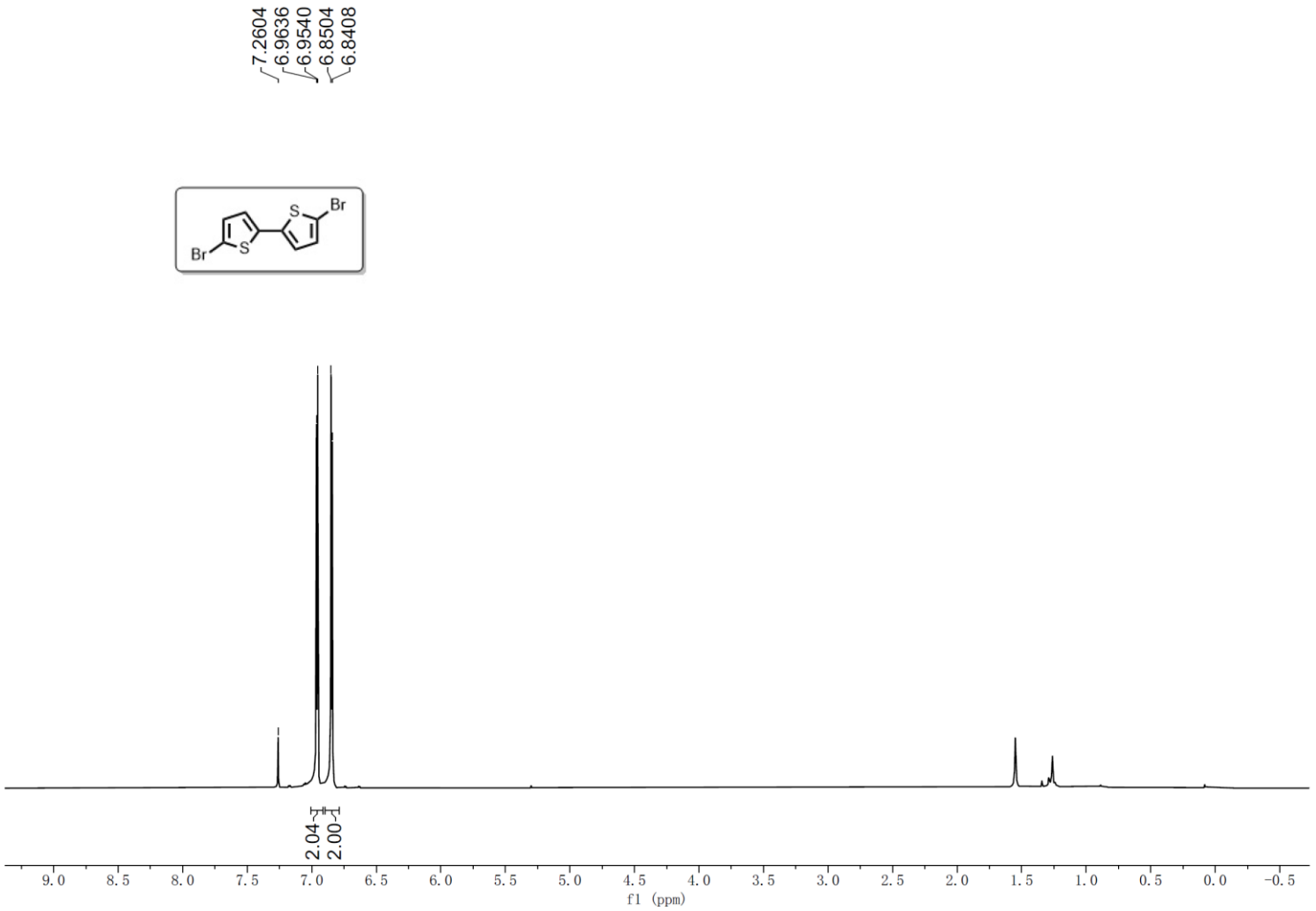
^{1}H NMR of **2v**


11.1501
8.3746
8.3653
8.3629
7.9483
7.9449
7.9286
7.9251
7.4125
7.2599
7.2094
7.1975
7.1897
7.1777
Br
N
H
1.01
1.00
0.97
0.99
0.99
13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

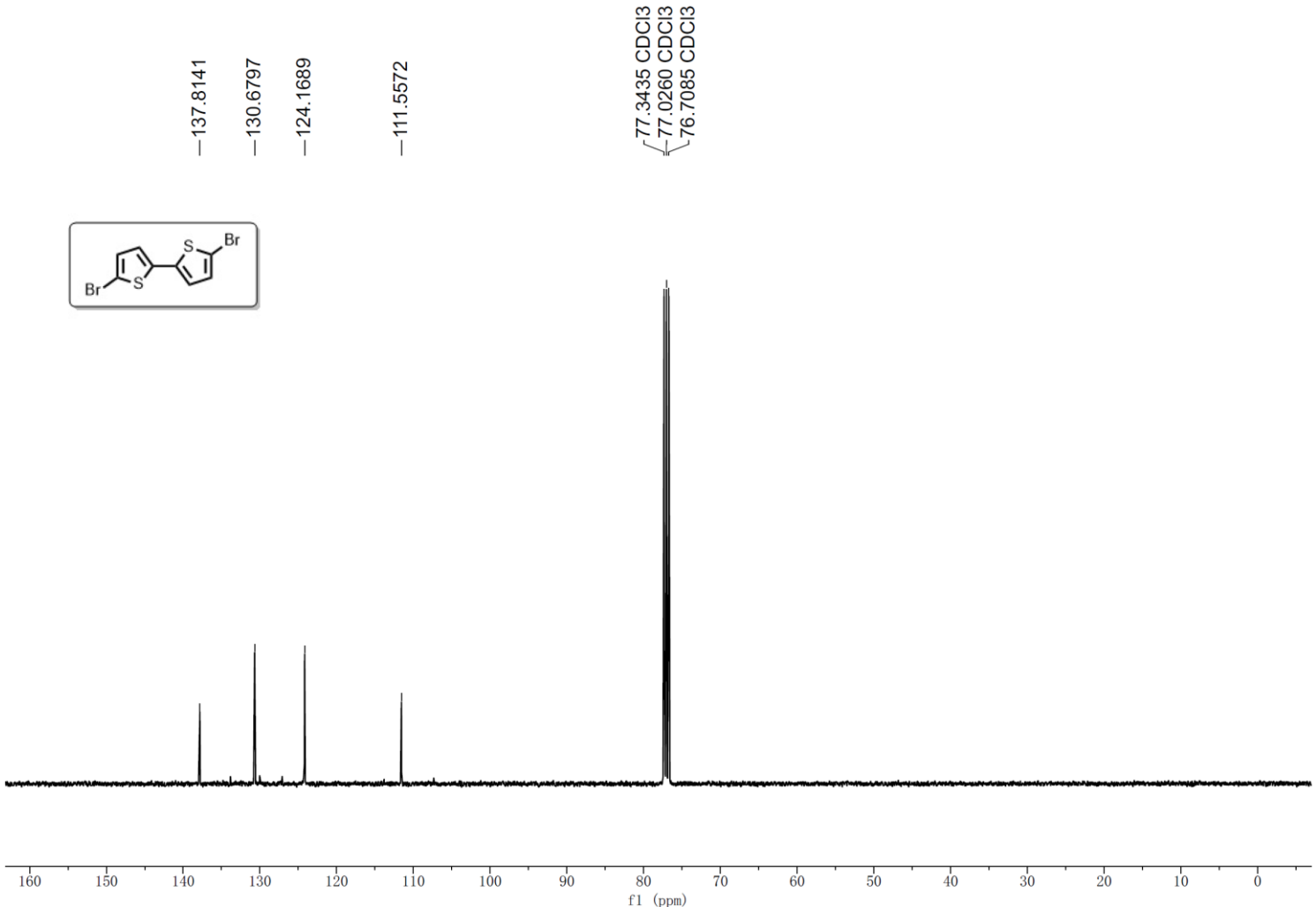
^{13}C NMR of **2v**


147.4692
143.5928
128.0307
124.4021
120.0708
116.5690
89.4054
77.3364 CDCl3
77.0480 CDCl3
76.7013 CDCl3
Br
N
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

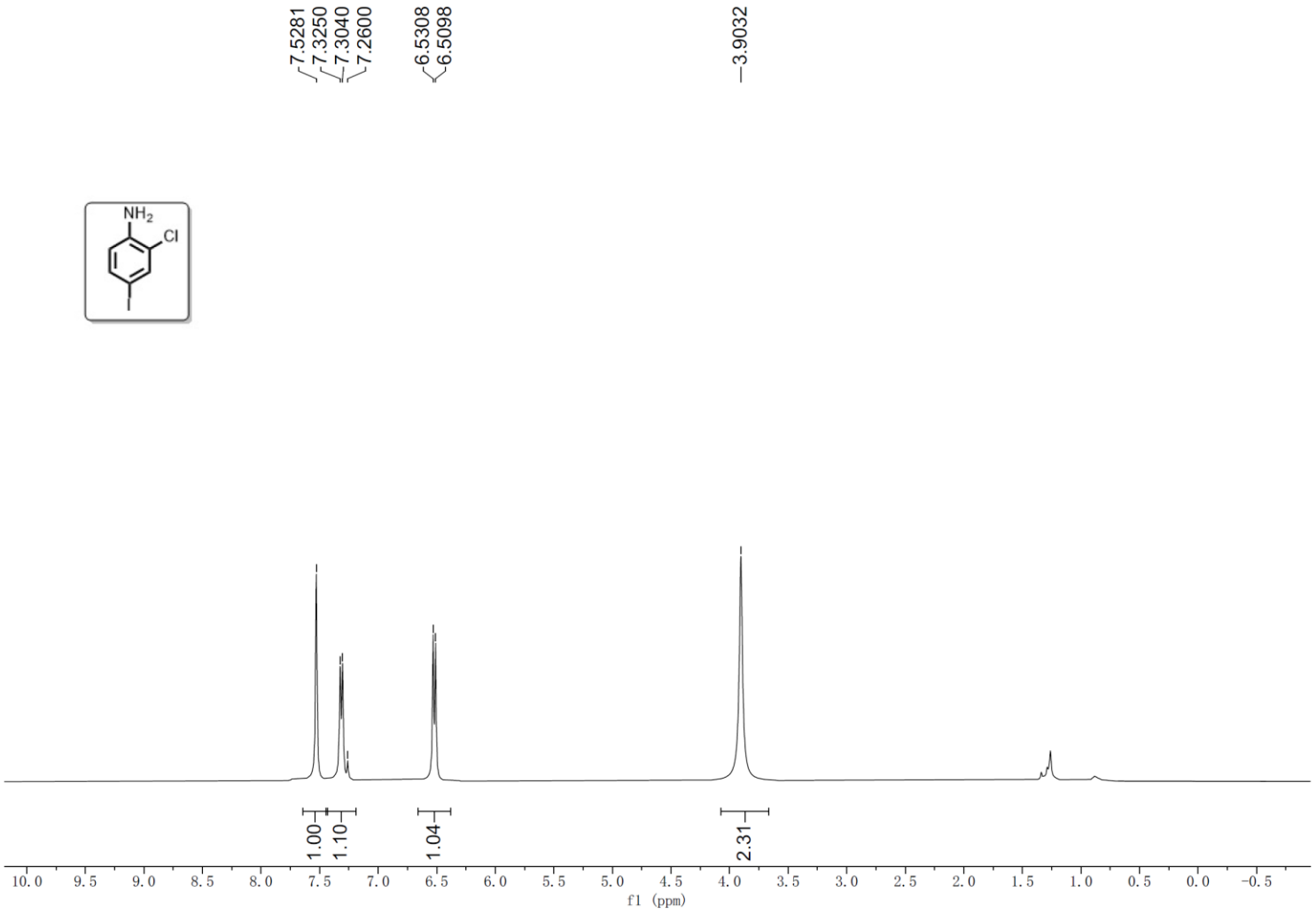
^{1}H NMR of **2w**


7.2604
6.9636
6.9540
6.8504
6.8408
Br
S
S
Br
2.04
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

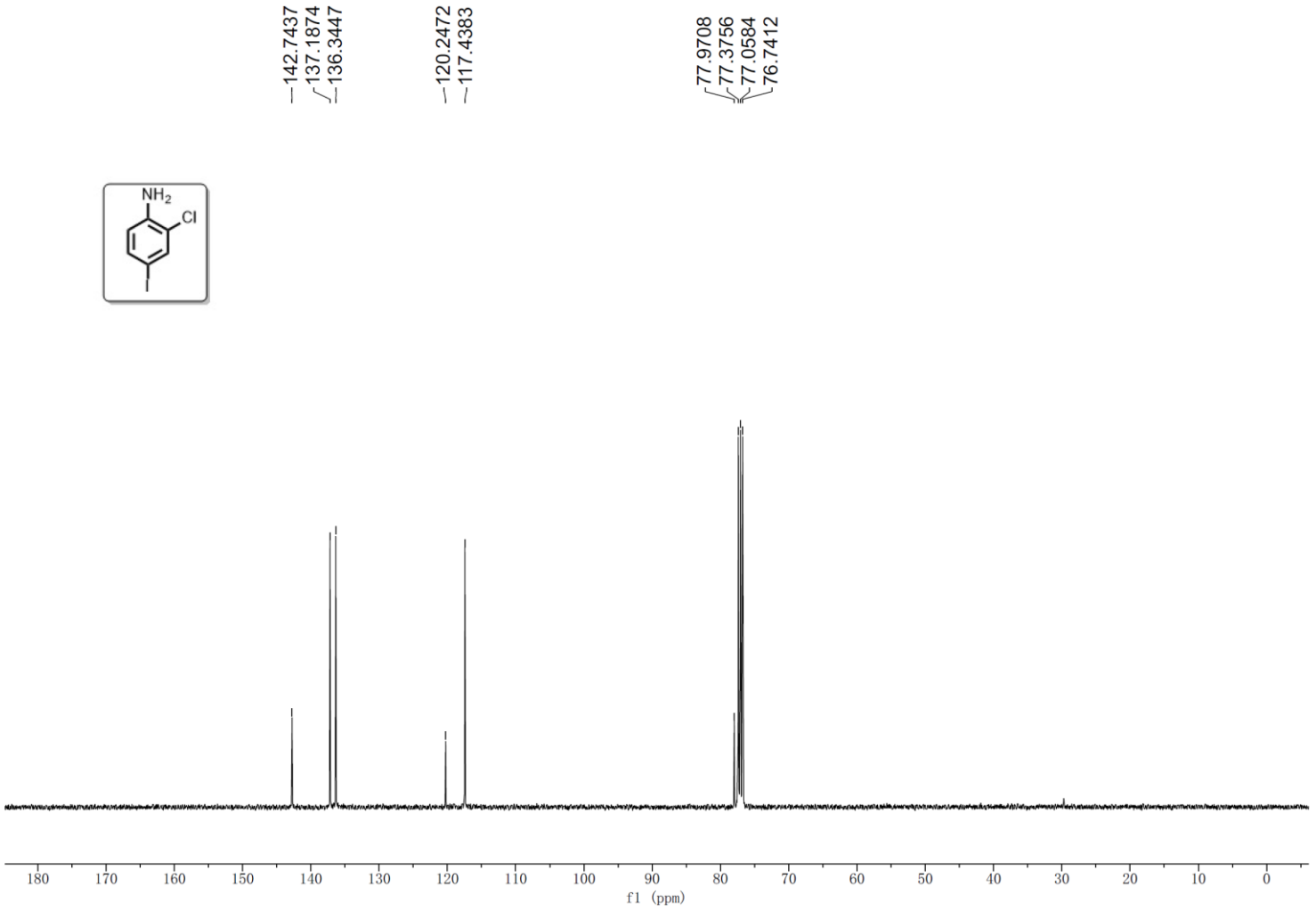
^{13}C NMR of **2w**


137.8141
130.6797
124.1689
111.5572
77.3435 CDCl3
77.0260 CDCl3
76.7085 CDCl3
Br
S
Br
S
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

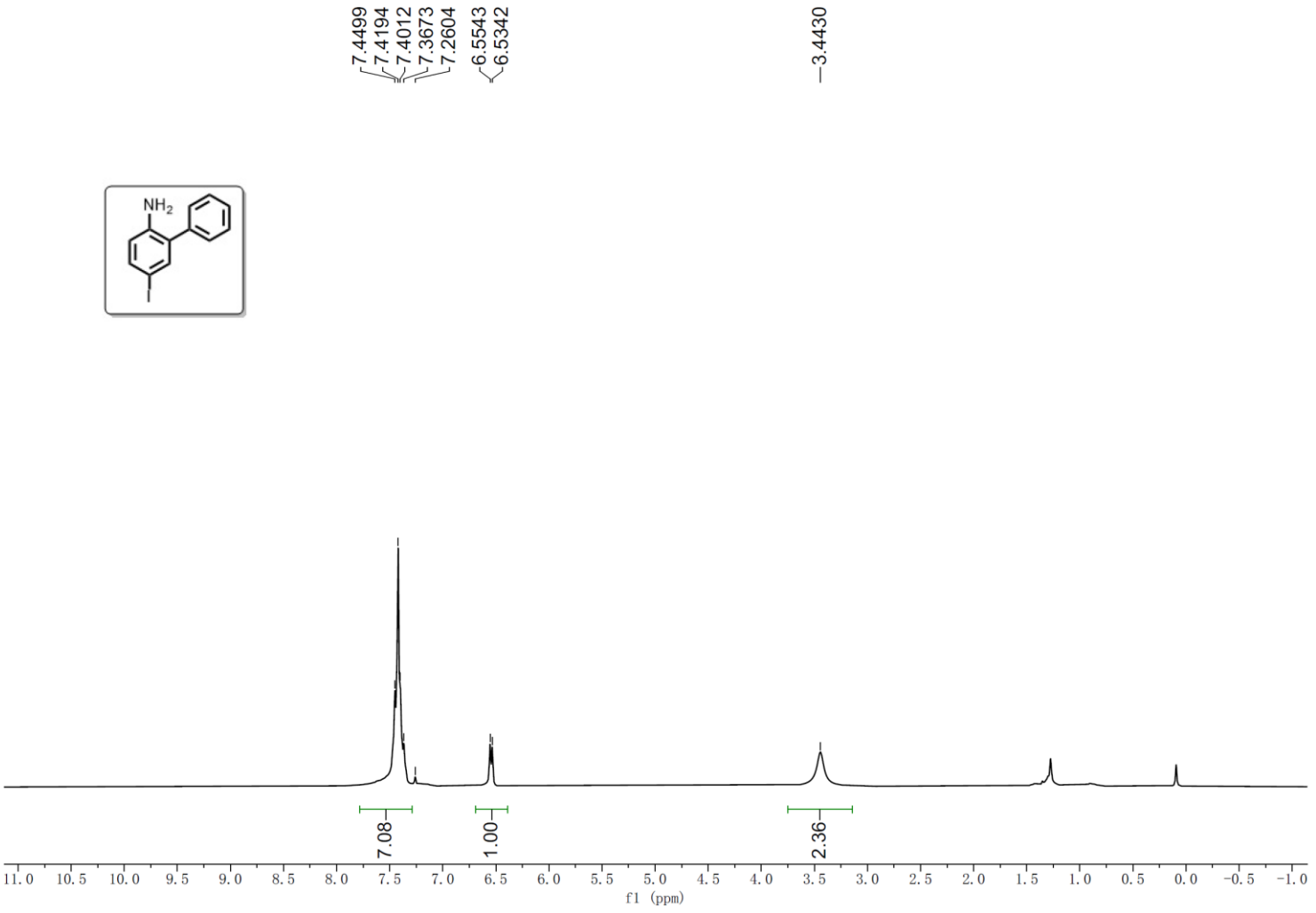
^{1}H NMR of **3a**


7.5281
7.3250
7.3040
7.2600
6.5308
6.5098
3.9032
NH2
Cl
1.00
1.10
1.04
2.31
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

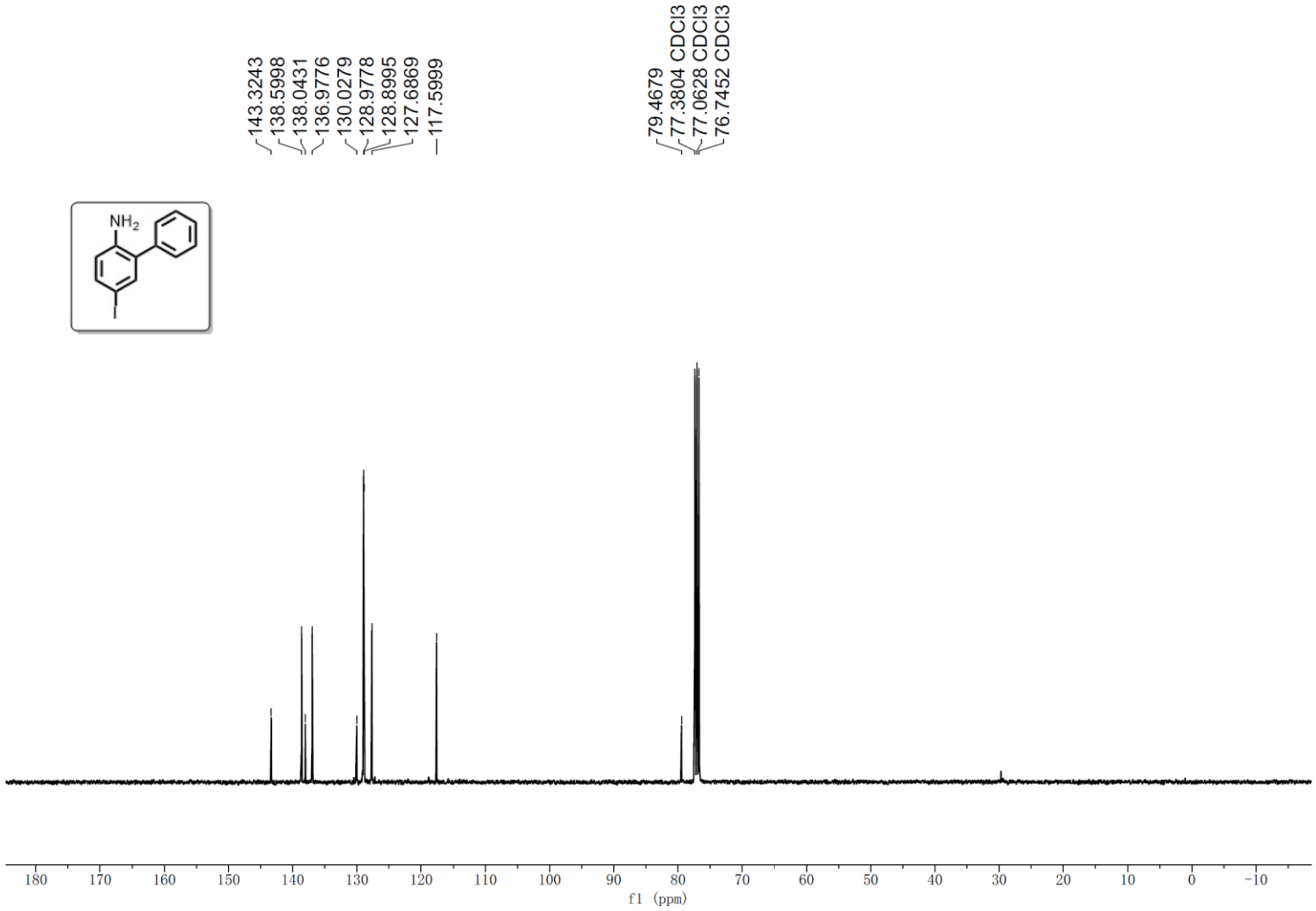
^{13}C NMR of **3a**


142.7437
137.1874
136.3447
120.2472
117.4383
77.9708
77.3756
77.0584
76.7412
NH2
Cl
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

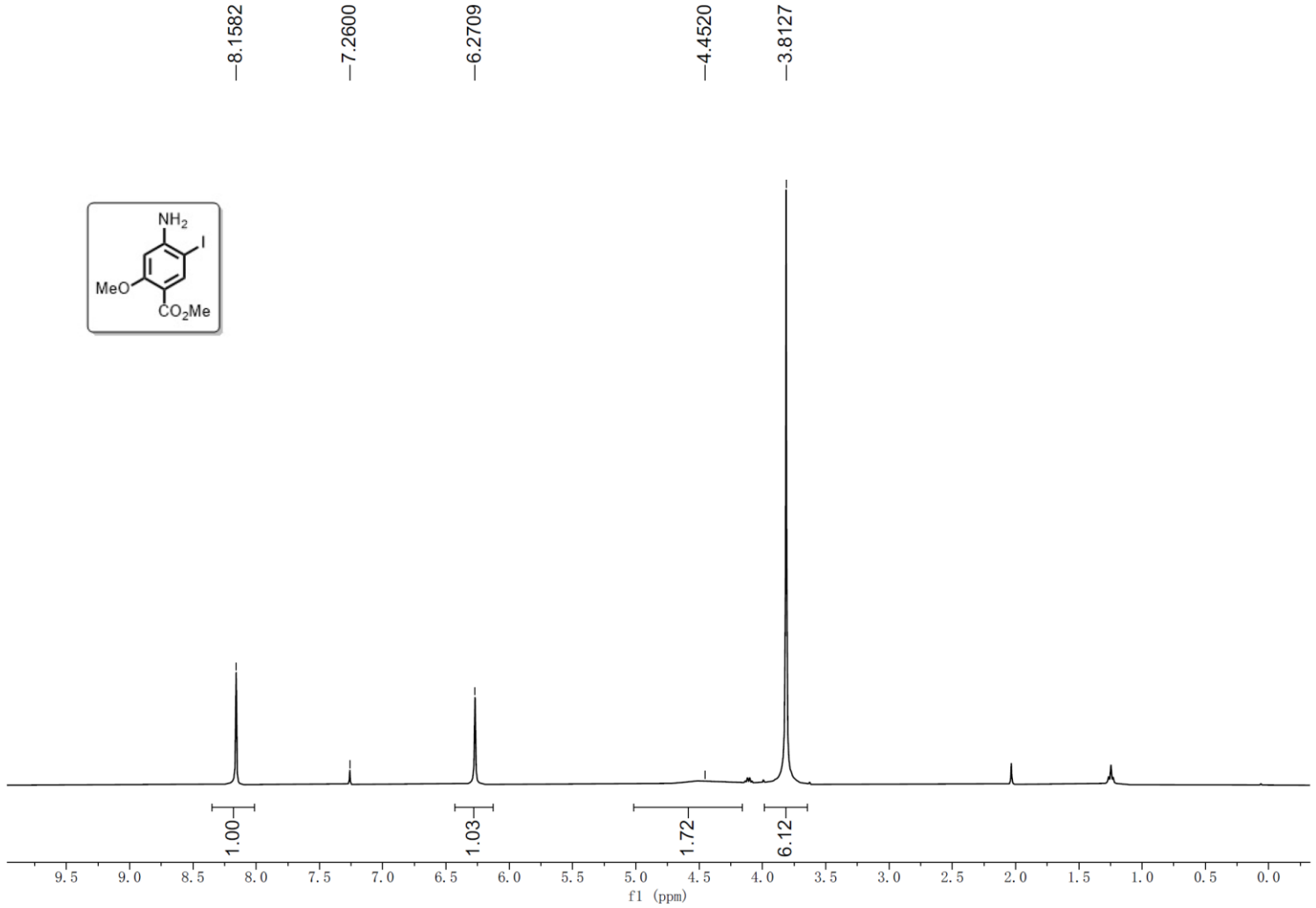
^{1}H NMR of **3b**


7.4499
7.4194
7.4012
7.3673
7.2604
6.5543
6.5342
3.4430
NH2
7.08
1.00
2.36
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

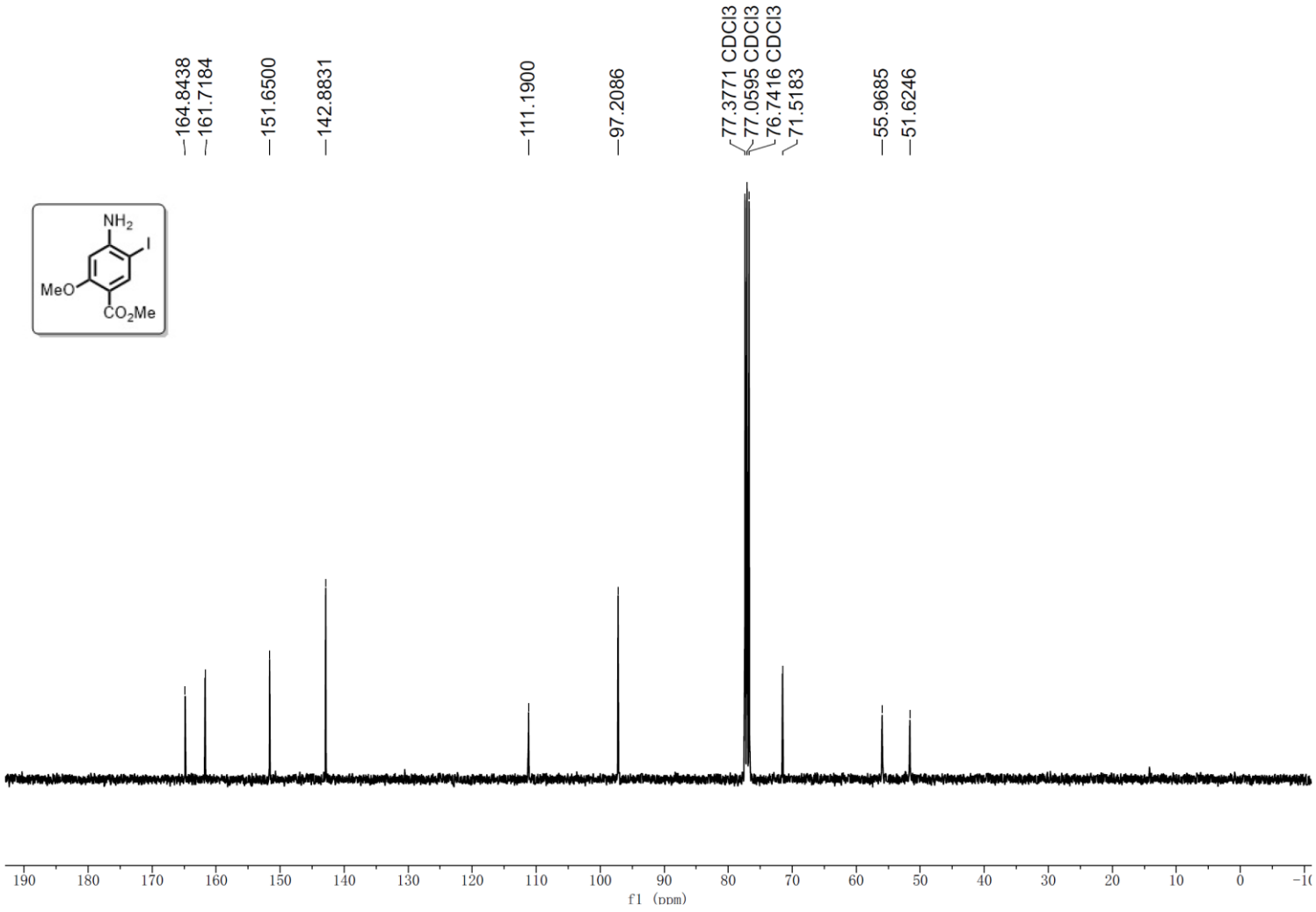
^{13}C NMR of **3b**


143.3243
138.5998
138.0431
136.9776
130.0279
128.9778
128.8995
127.6869
117.5999
79.4679
77.3804 CDCl3
77.0628 CDCl3
76.7452 CDCl3
NH2
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

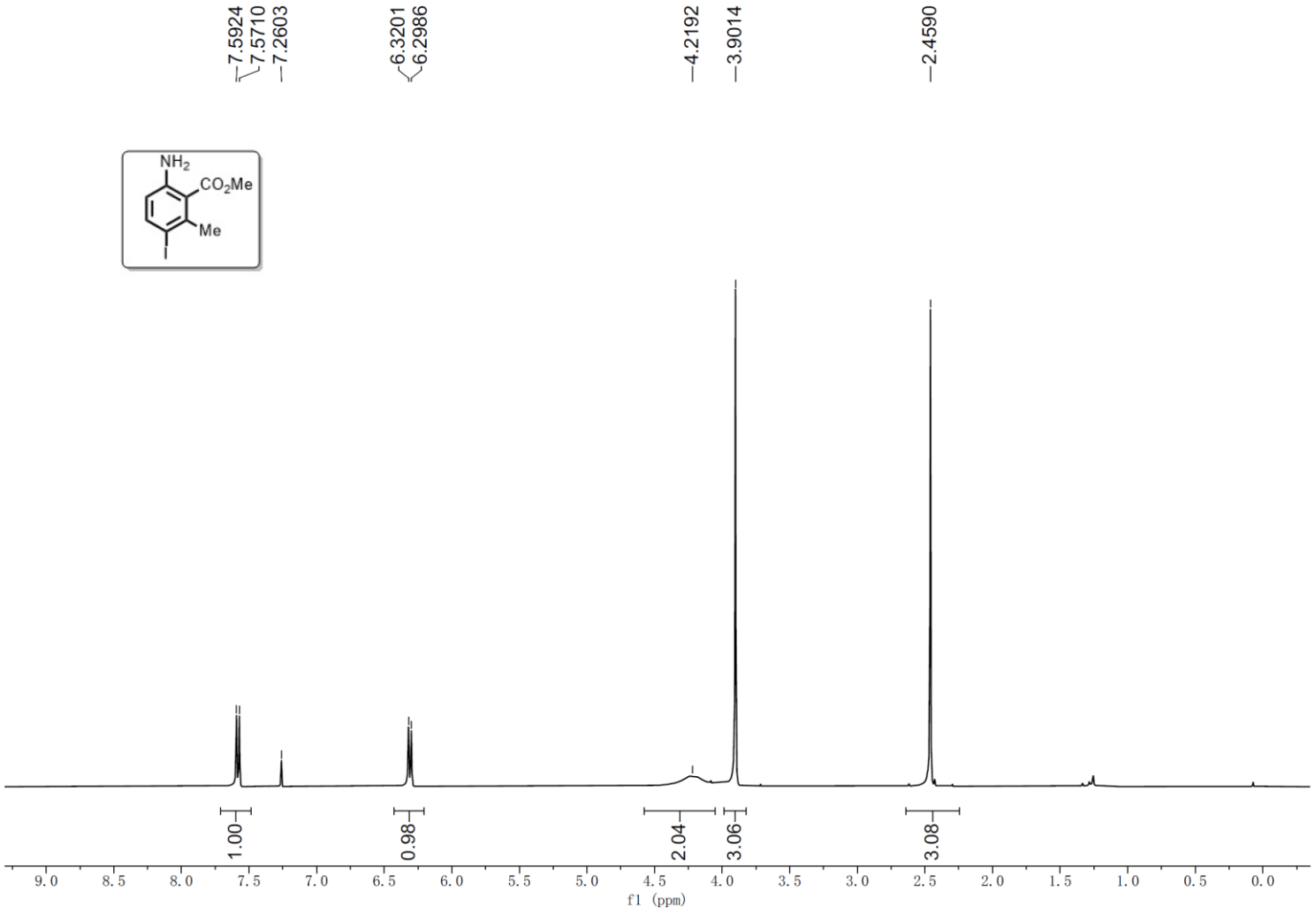
^{1}H NMR of **3c**


8.1582
7.2600
6.2709
4.4520
3.8127
NH2
I
MeO
CO2Me
1.00
1.03
1.72
6.12
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

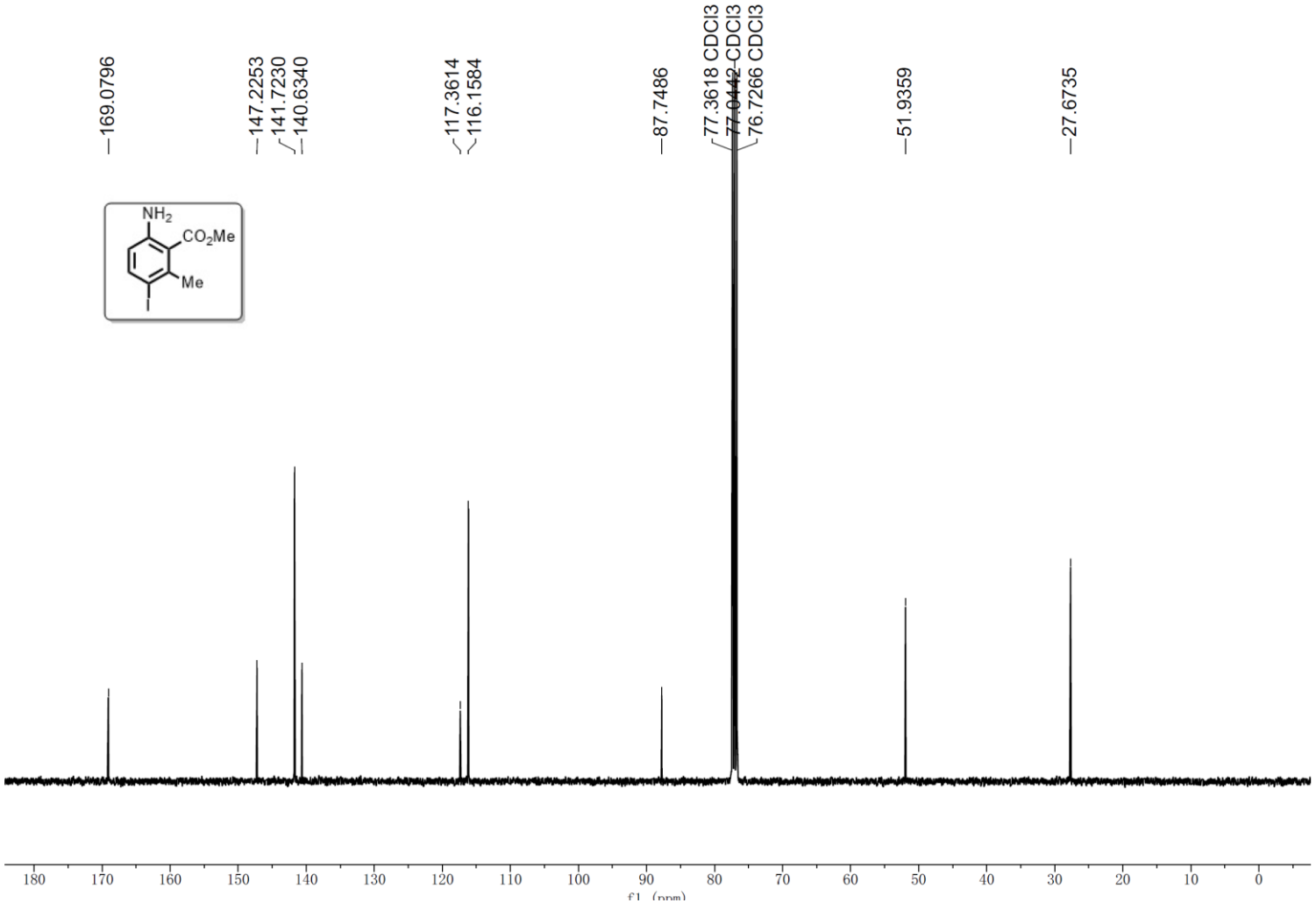
^{13}C NMR of **3c**


164.8438
161.7184
151.6500
142.8831
111.1900
97.2086
77.3771 CDCl3
77.0595 CDCl3
76.7416 CDCl3
71.5183
55.9685
51.6246
NH2
I
MeO
CO2Me
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

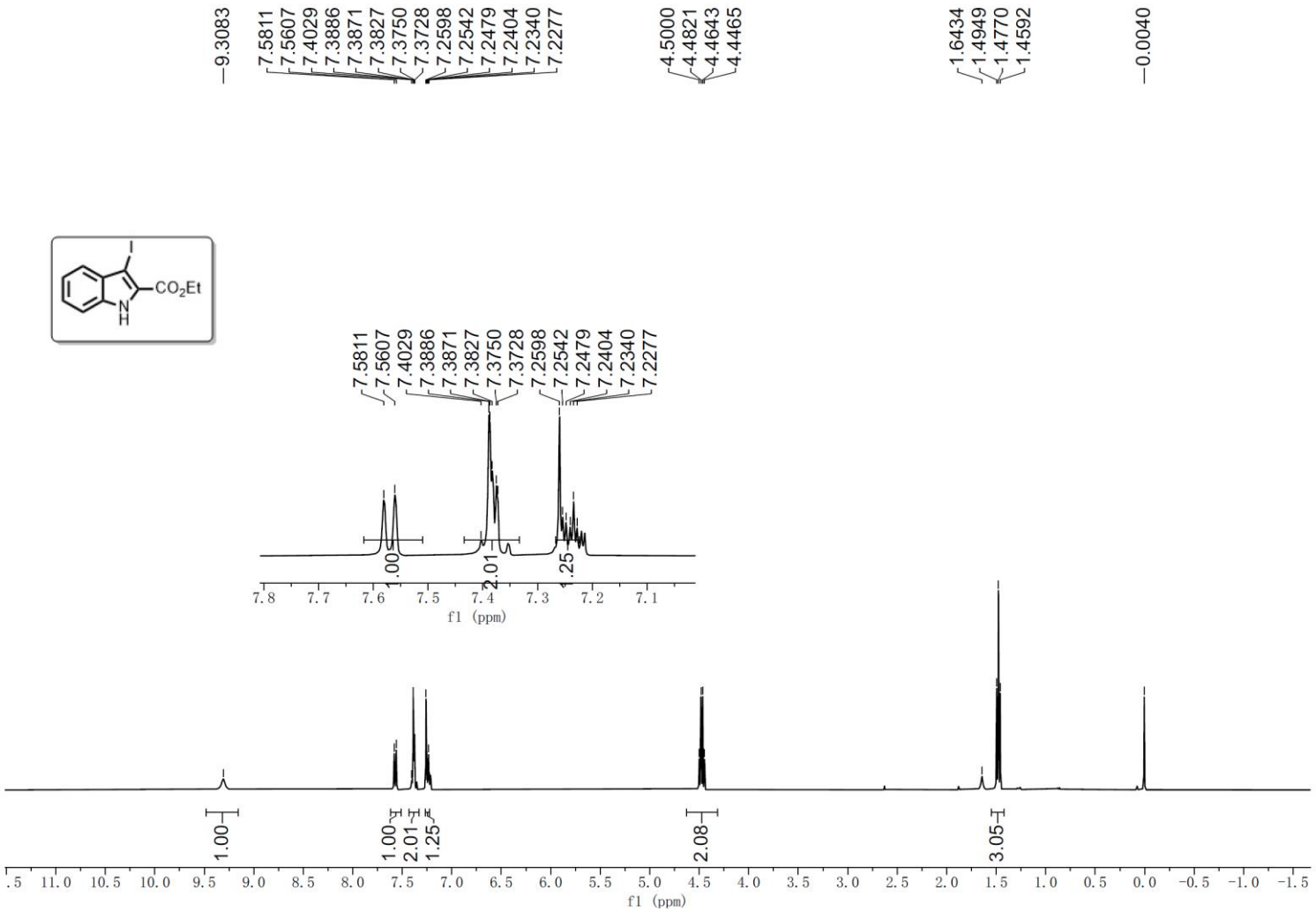
^{1}H NMR of **3d**


7.5924
7.5710
7.2603
6.3201
6.2986
4.2192
3.9014
2.4590
NH2
CO2Me
Me
I
1.00
0.98
2.04
3.06
3.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

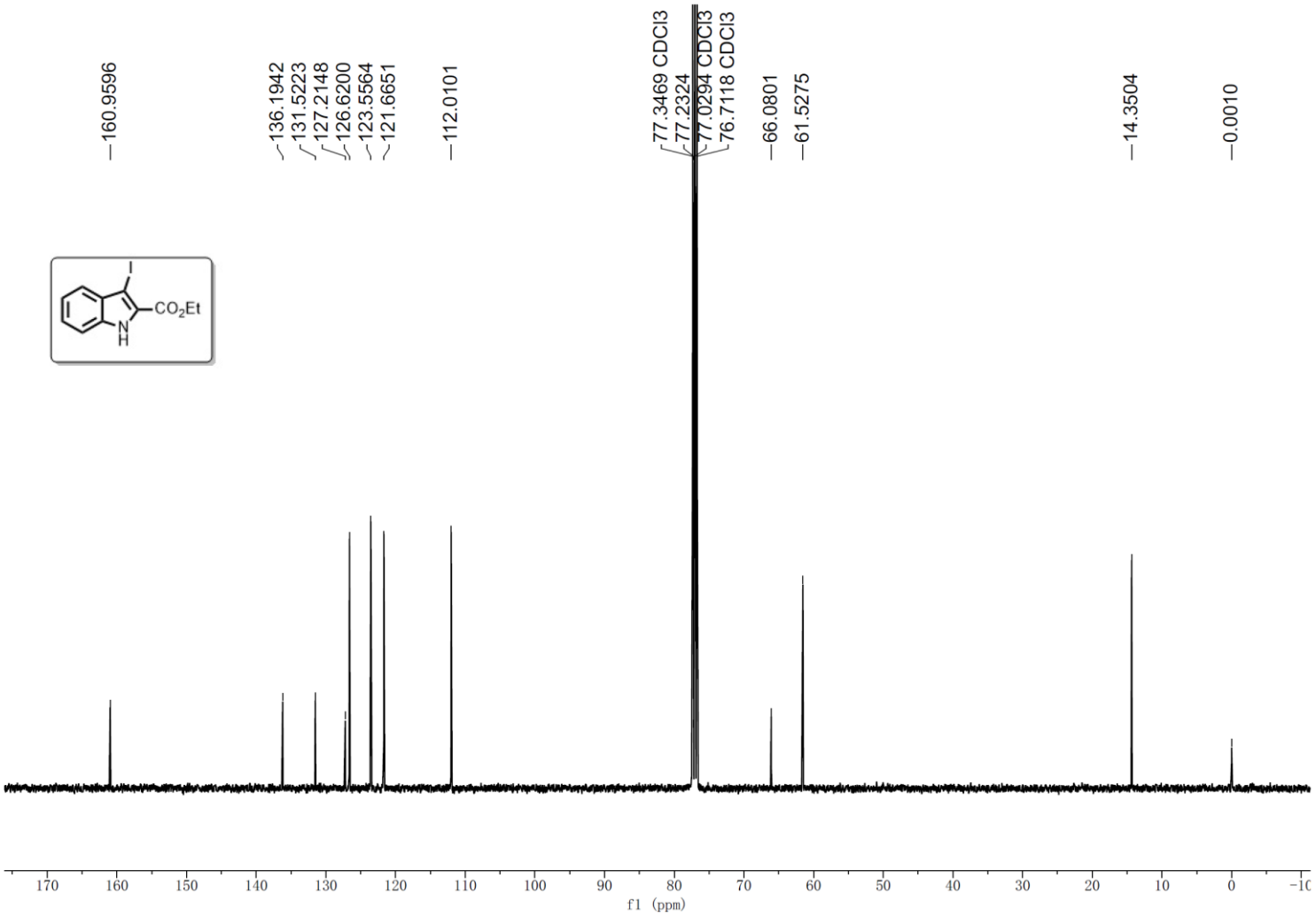
^{13}C NMR of **3d**


169.0796
147.2253
141.7230
140.6340
117.3614
116.1584
87.7486
77.3618 CDCl3
77.0442 CDCl3
76.7266 CDCl3
51.9359
27.6735
NH2
CO2Me
Me
I
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

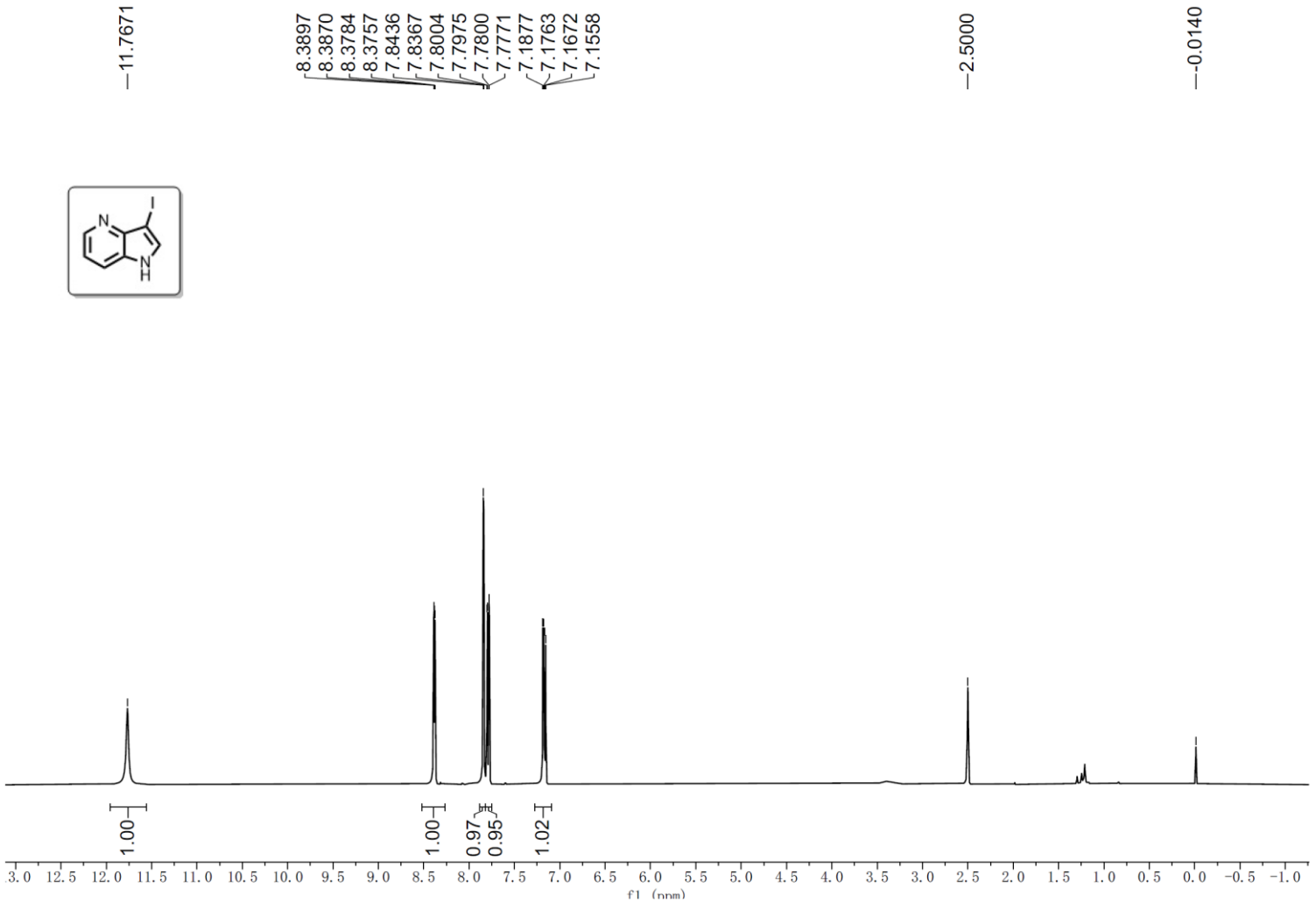
^{1}H NMR of **3e**


9.3083
7.5811
7.5607
7.4029
7.3886
7.3871
7.3827
7.3750
7.3728
7.2598
7.2542
7.2479
7.2404
7.2340
7.2277
4.5000
4.4821
4.4643
4.4465
1.6434
1.4949
1.4770
1.4592
0.0040
I
CO2Et
N
H
1.00
2.01
1.25
2.08
3.05
f1 (ppm)

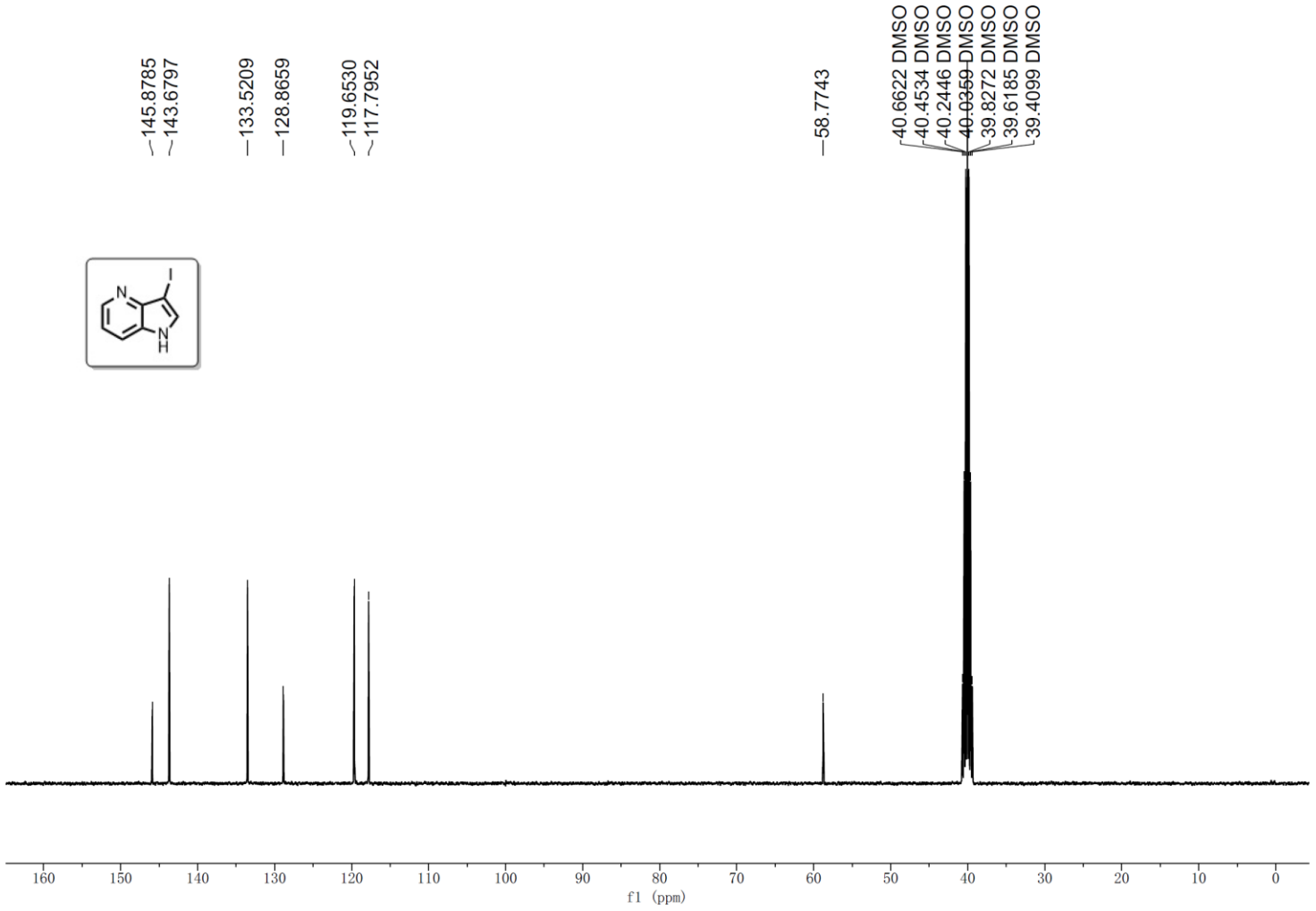
^{13}C NMR of **3e**


160.9596
136.1942
131.5223
127.2148
126.6200
123.5564
121.6651
112.0101
77.3469 CDCl3
77.2324
77.0294 CDCl3
76.7118 CDCl3
66.0801
61.5275
14.3504
0.0010
I
CO2Et
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

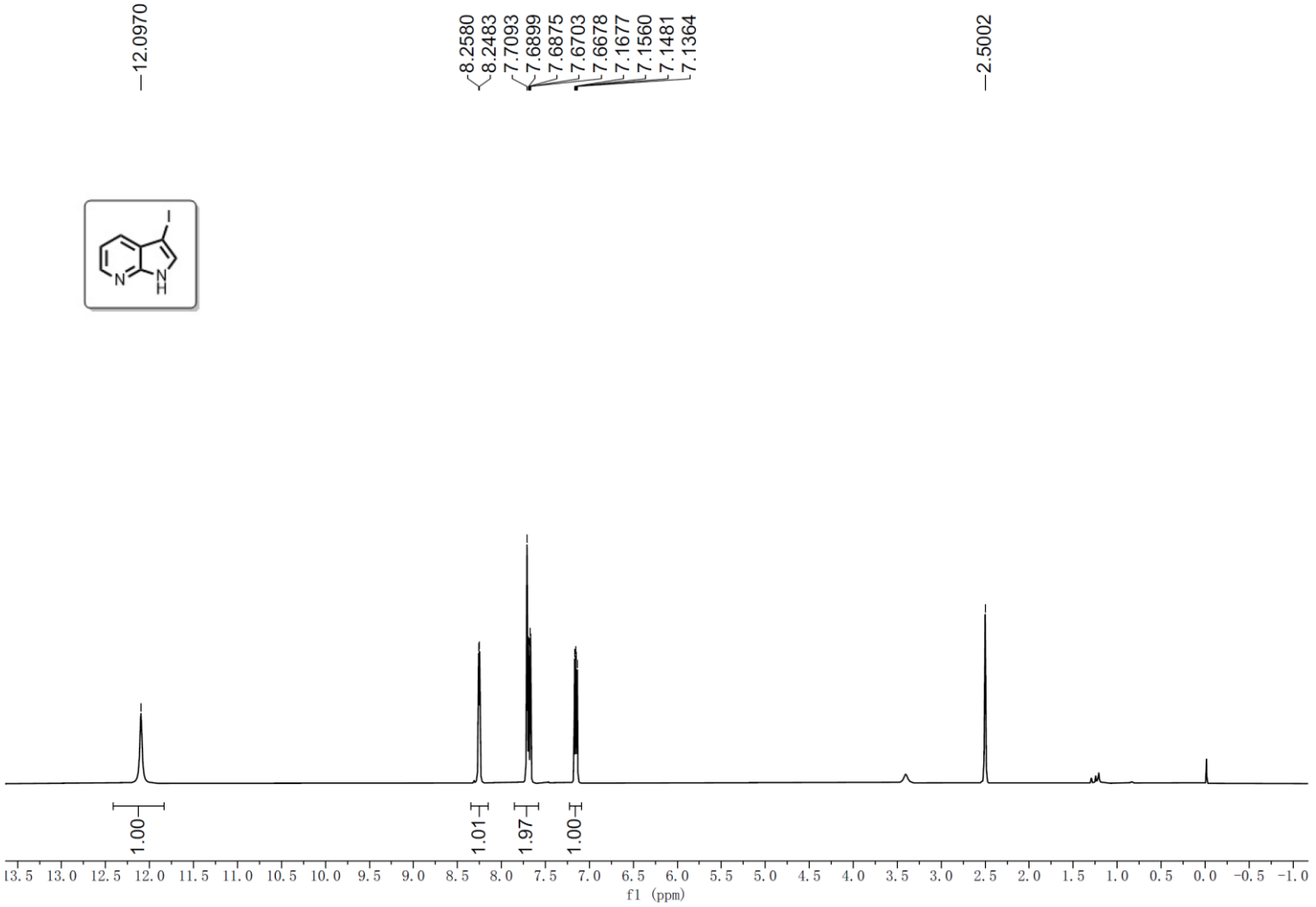
^{1}H NMR of **3f**


11.7671
8.3897
8.3870
8.3784
8.3757
7.8436
7.8367
7.8004
7.7975
7.7800
7.7771
7.1877
7.1763
7.1672
7.1558
2.5000
0.0140
N
I
H
1.00
1.00
0.97
0.95
1.02
f1 (ppm)

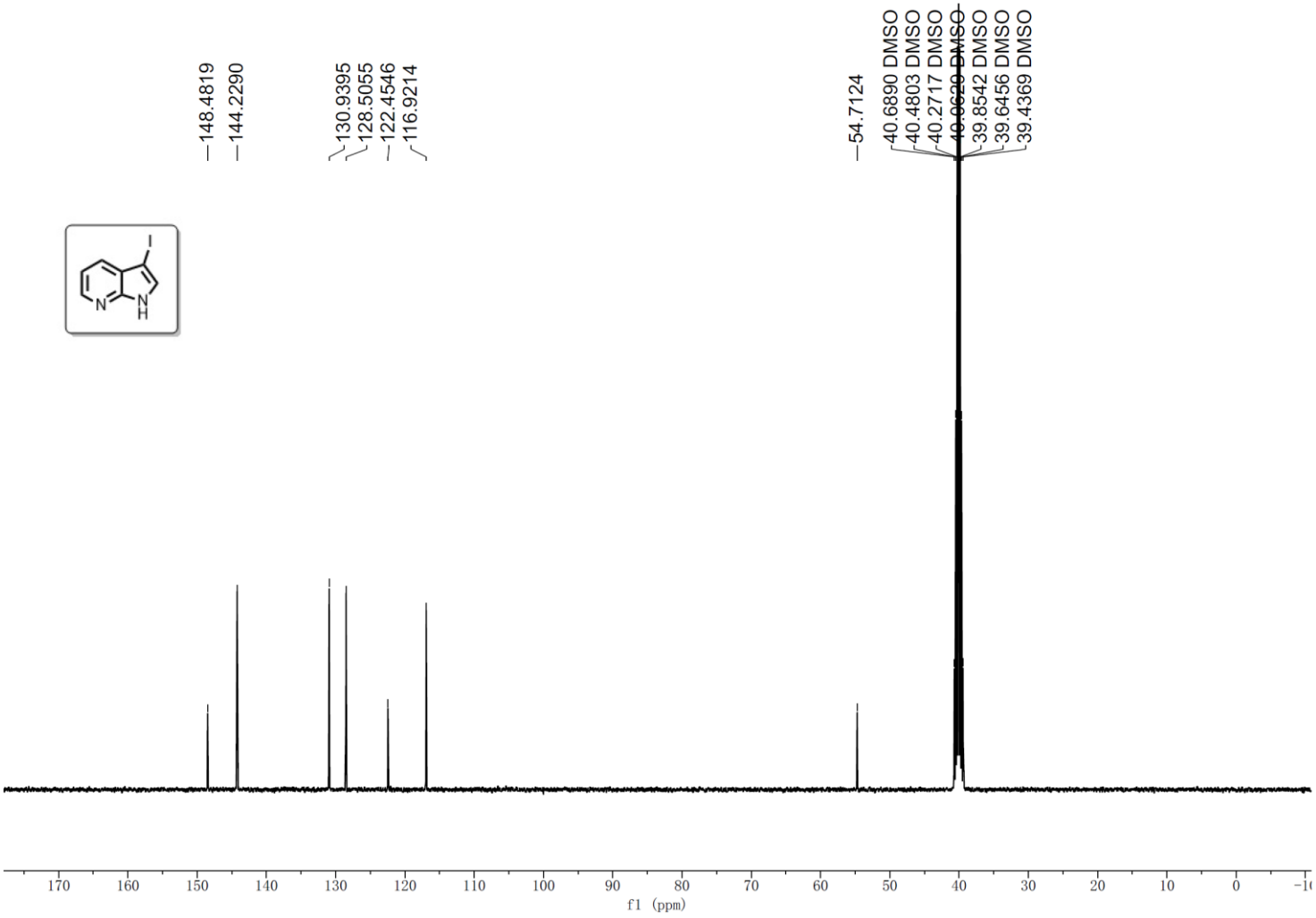
^{13}C NMR of **3f**


145.8785
143.6797
133.5209
128.8659
119.6530
117.7952
58.7743
40.6622 DMSO
40.4534 DMSO
40.2446 DMSO
40.0359 DMSO
39.8272 DMSO
39.6185 DMSO
39.4099 DMSO
N
I
H
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

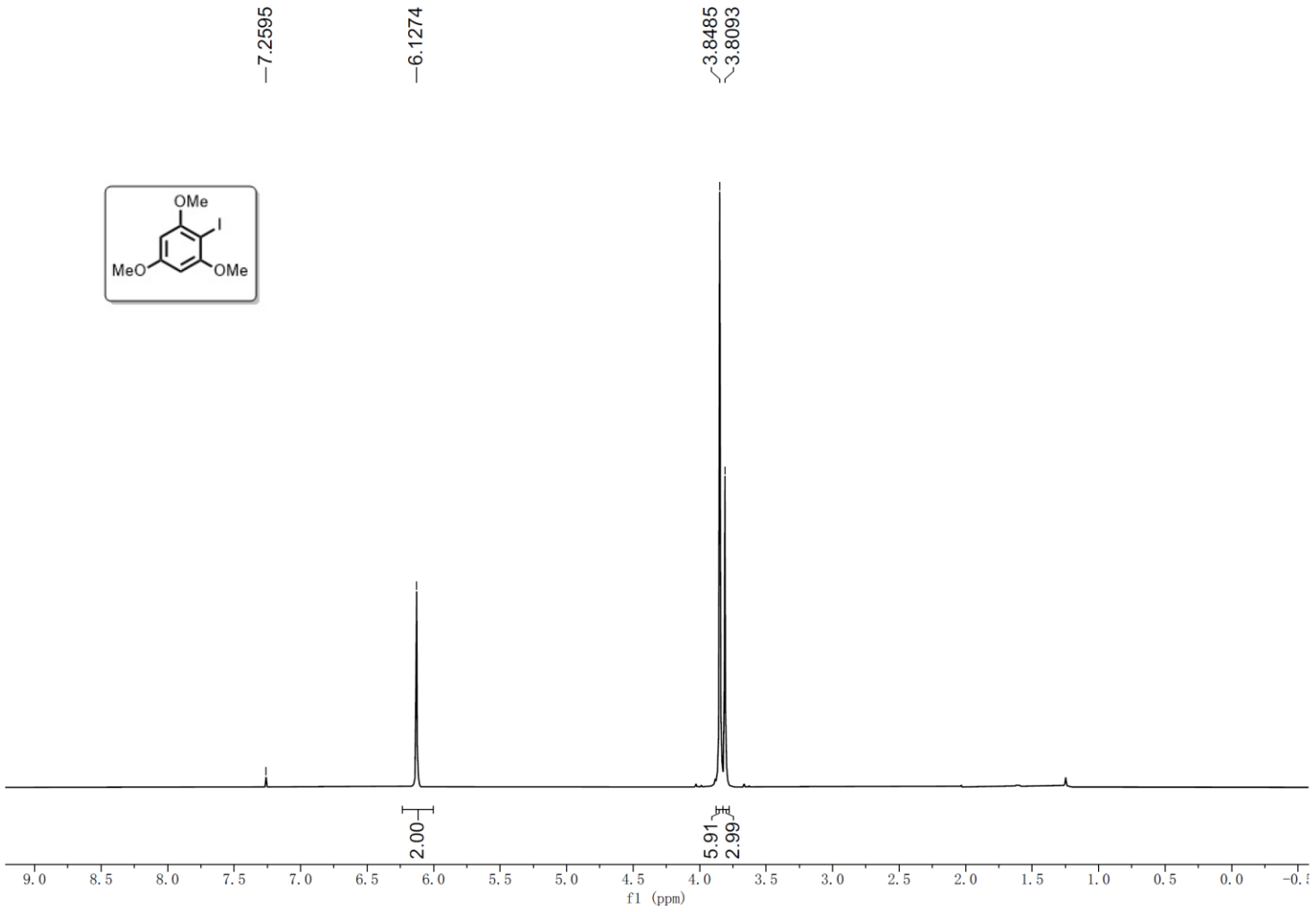
^{1}H NMR of **3g**


12.0970
8.2580
8.2483
7.7093
7.6899
7.6875
7.6703
7.6678
7.1677
7.1560
7.1481
7.1364
2.5002
I
N
H
1.00
1.01
1.97
1.00
f1 (ppm)

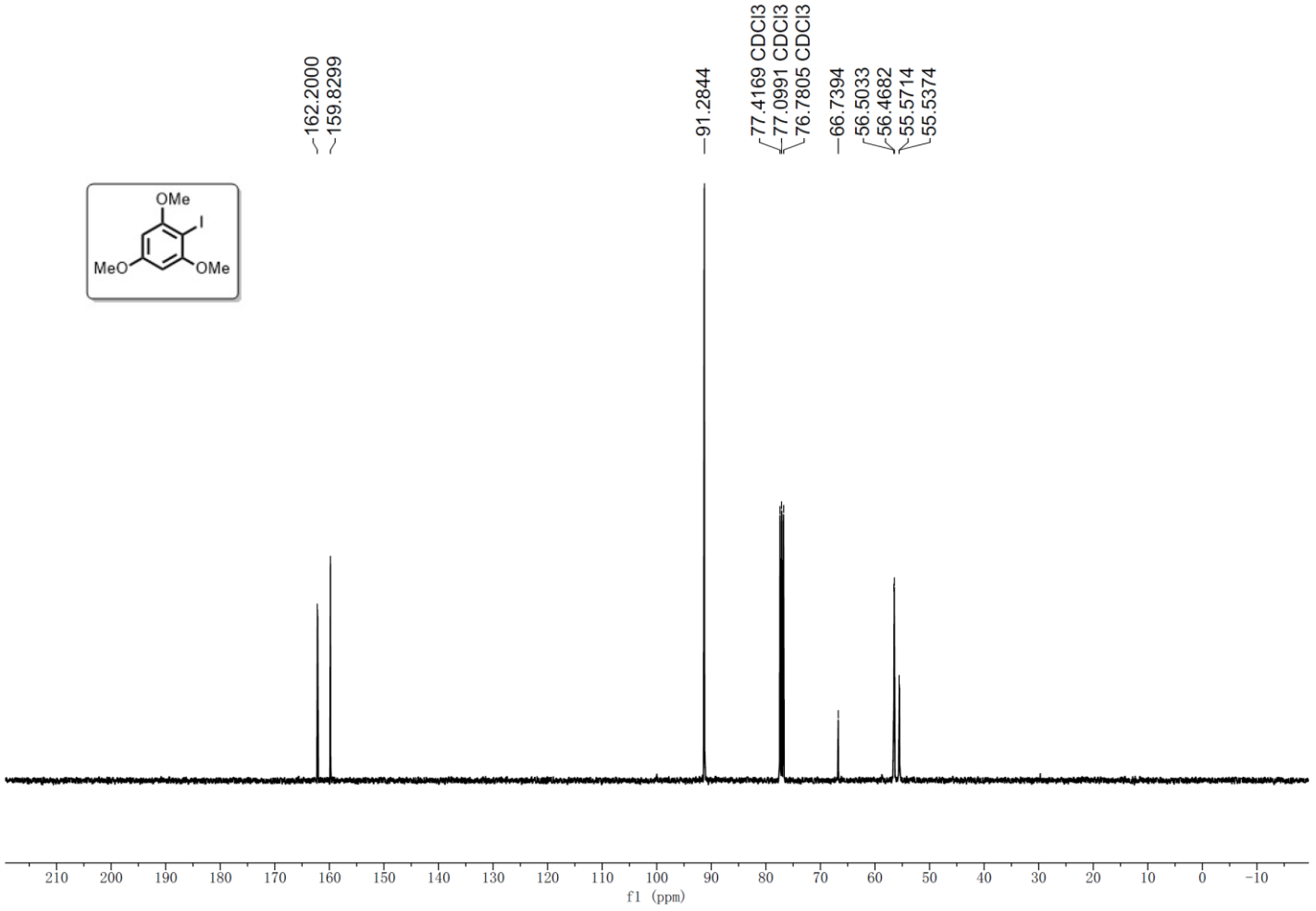
^{13}C NMR of **3g**


148.4819
144.2290
130.9395
128.5055
122.4546
116.9214
54.7124
40.6890 DMSO
40.4803 DMSO
40.2717 DMSO
40.0620 DMSO
39.8542 DMSO
39.6456 DMSO
39.4369 DMSO
I
N
H
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

^{1}H NMR of **3h**


7.2595
6.1274
3.8485
3.8093
OMe
I
MeO
OMe
2.00
5.91
2.99
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

^{13}C NMR of **3h**


162.2000
159.8299
91.2844
77.4169 CDCl3
77.0991 CDCl3
76.7805 CDCl3
66.7394
56.5033
56.4682
55.5714
55.5374
OMe
I
MeO
OMe
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

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