Contents

1.General Information

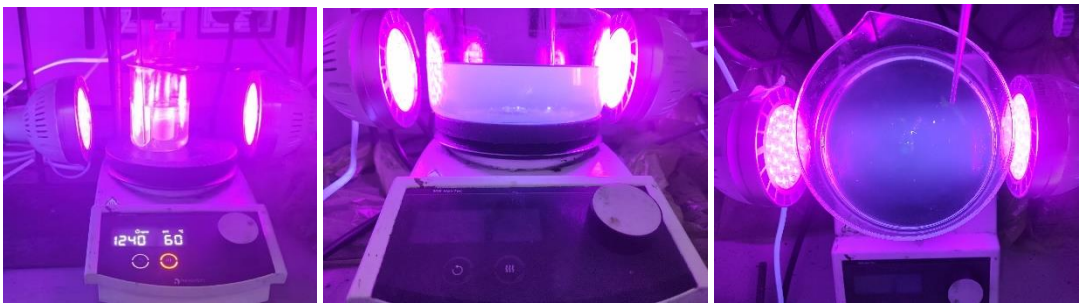
Melting points were determined using a Büchi B-540 capillary melting point apparatus. 1H NMR (400/600 MHz), and 13C NMR (101/151 MHz) spectra were recorded with $CDCl_3$ or DMSO-d_6. Chemical shifts are reported downfield from TMS (=0) for 1H NMR. For 13C{1H} NMR, chemical shifts are reported in the scale relative to $CDCl_3$ (= 77.0). High resolution mass spectrometry (HRMS) analysis was performed on an Agilent 1290–6540 UHPLC Q-Tof HR-MS System ESI spectrometer.

All reagents were obtained from commercial sources and used without further purification unless otherwise indicated. The starting materials were purchased from Aladdin (https://www.aladdin-e.com/). Silica gel for column chromatography was purchased from Qingdao Haiyang Chemical Co., Ltd. Reactions were stirred using Teflon-coated magnetic stir bars. Thin-layer chromatography (TLC) was used to monitor the reaction. Melting points were determined using a Büchi B-540 capillary melting point apparatus. Data are reported as follows: Chemical shift (number of protons, multiplicity, coupling constants). Coupling constants were quoted to the nearest 0.1 Hz and multiplicity reported according to the following convention: s = singlet, d = doublet, t = triplet, q = quartet, hept = heptet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, ddd = doublet of doublet of doublets, br s = broad singlet. HRMS spectra were recorded on a Bruker Impact II UHR-QTOF spectrometer using ESI on a TOF mass analyze.

2. Experiment Section

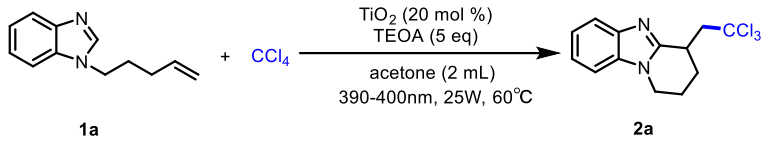
2.1. Details of Visible-Light Source

The experiments under 390-400 nm light irradiation were performed using two 25 W JG LED lamps from Xuzhou Ai Jia Electronic Technology Co., Ltd. The distance from the light source to the irradiation vessel was approximate 5-6 cm, and no filter was used in our study.



2.2. Optimization of reaction condition

Table S1 Optimization of the reaction conditions [a]

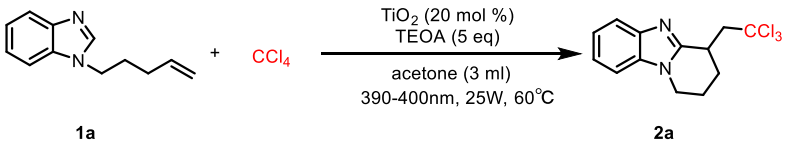


1a 2a

Entry	Light	photocatalyst	additive	base	solvent	Yield[b](%)
1	520-425nm	TiO_2	TEOA	-	acetone	trace
2	With light	TiO_2	TEOA	-	acetone	60
3	450-465nm	TiO_2	TEOA	-	acetone	76
4	390-400nm	TiO_2	MeOH	-	acetone	44
5	390-400nm	TiO_2	^{i}PrOH	-	acetone	54
6	390-400nm	TiO_2	Benzyl alcohol	-	acetone	50
7	390-400nm	TiO_2	TEOA	KOAc	acetone	63
8	390-400nm	TiO_2	TEOA	Na_2CO_3	acetone	73
9	390-400nm	TiO_2	TEOA	K_3PO_4	acetone	76
10	390-400nm	TiO_2	TEOA	$KHCO_3$	acetone	73
11[c]	390-400nm	TiO_2	TEOA	-	acetone	55
12	390-400nm	TiO_2	TEOA	-	CCl_4	37
13	390-400nm	TiO_2	TEOA	-	DMSO	trace
14	390-400nm	TiO_2	TEOA	-	toluene	trace
15	390-400nm	TiO_2	TEOA	-	DMF	trace

[a] Reaction conditions: 1a (0.3 mmol), CCl_4 (1 ml), TiO_2 (20 mol %), TEOA (1.5 mmol), solvent (2 mL), 25 W LED lamp (390-400 nm), 60 ℃, N_2, 48 h. [b] Isolated yield. [c]TiO_2 (10 mol%)

2.3. The Light on/off Experiments



1a 2a

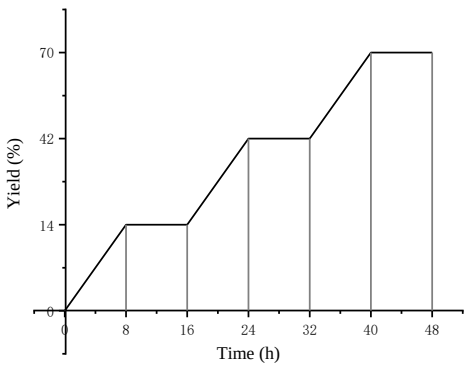


Figure S1 Light–dark cycle experiment.

2.4. Quantum yield measurements[1,2]

According to the procedure of Yoon, the photon flux of the LED (λmax = 400 nm) was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (0.737 g) in H_2SO_4 (10 mL of 0.05 M solution). A buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (5.0 mg) and sodium acetate (1.13 g) in H_2SO_4 (5.0 mL of 0.5 M solution). Both solutions were stored in the dark. To determine the photon flux of the LED, the ferrioxalate solution (3.0 mL) was placed in a cuvette and irradiated for 90 seconds at λmax = 400 nm. After irradiation, the phenanthroline solution (0.525 mL) was added to the cuvette and the mixture was allowed to stir in the dark for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A nonirradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

	No-irrad	Irrad 1	Irrad 2	Irrad 3
A_{510nm}	2.87	3.85	3.69	3.69
Average $A_{510\ nm}$ of irradiation samples		3.74		

$$\textbf{mol } Fe^{2+} = (V \times \Delta A)/ (l \times \varepsilon) \quad (1)$$

$$\textbf{mol } Fe^{2+} = [3.525\times10\text{-}3\ L \times (3.74\text{-}2.87)] / (1\ cm \times 11100\ L\ mol\text{-}1cm\text{-}1) = 2.86\times 10^{-7}$$

V is the total volume (3.525×10^{-3} L) of the solution after addition of phenanthroline; **ΔA** is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions; **l** is the path length (1.00 cm), and **ε** is the molar absorptivity of the ferrioxalate actinometer at 510 nm (11100 L $mol^{-1}cm^{-1}$)[3]. The photon flux can be calculated using eq 2.

$$\textbf{photo flux} = \textbf{mol } Fe^{2+}/ (\Phi \times t \times f) \quad (2)$$

$$\textbf{photo flux} = 2.86\times10^{-7} / (1.13 \times 90 \times 0.9998) = 2.81 \times 10^{-8}\ \textbf{einstein}\ s^{-1}$$

Where **Φ** is the quantum yield for the ferrioxalate actinometer (1.13 for a 0.15 M solution at λ = 400 nm), **t** is the time (90.0 s), and **f** (0.9998) is the fraction of light absorbed at 405 nm by the ferrioxalate actinometer. This value is calculated using eq 3 where A405nm (3.7569) is the absorbance of the ferrioxalate solution at 400 nm. The photon flux was calculated (average of three experiments) to be 9.213×10^{-9} einstein s^{-1}.

$$f = 1 - 10^{-A405\ nm} \quad (3)$$

$$\mathbf{f = 1 - 10^{-3.7569} = 0.9998}$$

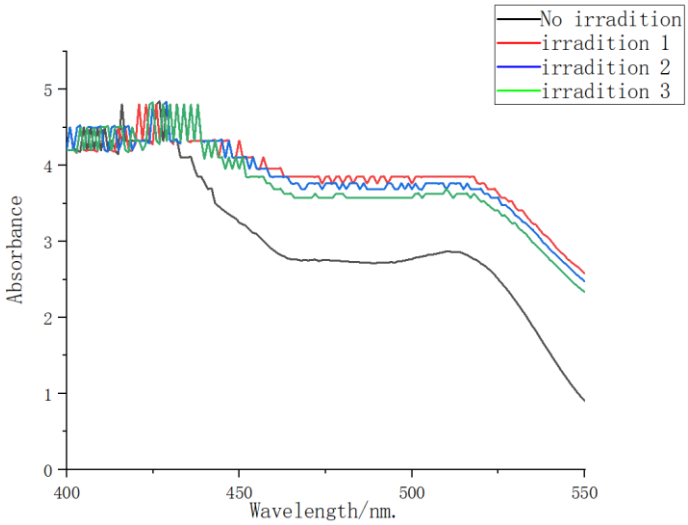
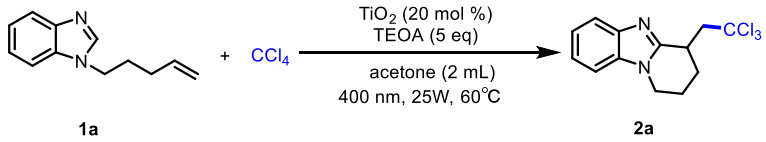


Figure S2. Absorption spectra of three irradiation experiments and non-irradiation experiment

Determination of the reaction quantum yield



1a **2a**

The reaction mixture was stirred and irradiated by blue LED (λmax = 400 nm) for 36000 s. The yield of product was determined by ^{1}H NMR analysis using CH_2Br_2 as an internal standard. The yield of **2a** was determined to be 54% (5.4×10^{-4} mol of **2a**). The reaction quantum yield (Φ) was determined using eq 4 where the photon flux is 2.81×10^{-8} einsteins s^{-1} (determined by actinometry as described above), **t** is the reaction time (36000 s) and **f** is the fraction of incident light absorbed by the catalyst, determined using eq 3.

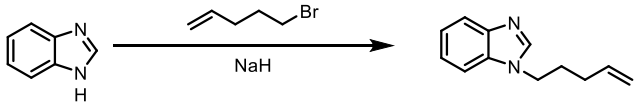
$$\textbf{Quantum Yield = moles of product formed/ (flux × f × t)} \qquad (4)$$

$$=5.4 \times 10^{-4} / (2.81 \times 10^{-8} \times 0.9998 \times 36000)$$

$$=0.544$$

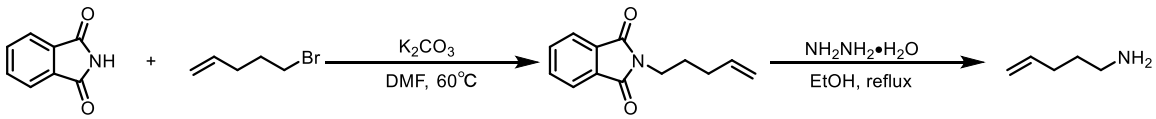
3. Preparation of Substrates

3.1. Preparation of N-substituted benzoimidazole



To a 25 mL Schlenk tube equipped with a magnetic stirring bar were added benzimidazole (590 mg, 5 mmol) and anhydrous tetrahydrofuran (10 mL) under nitrogen atmosphere at room temperature. After cooling to 0 ºC, NaH (240 mg, 10 mmol) was added and stirring was continued for 15 min at room temperature. Subsequently, bromo alkene (6 mmol) was added and stirring was further continued for 2 h at 80 ºC to confirm completion of the reaction by TLC analysis. Water was added to quench the reaction and the organic layer was separated. The aqueous layer was extracted with DCM twice. The combined organic layers were dried over anhydrous sodium sulfate for several hours and concentrated under reduced pressure to leave a crude solid. Flash column chromatography on silica gel using ethyl acetate as an eluent afforded the corresponding N-substituted benzimidazole.

3.2 Preparation of Single substitution N-substituted benzoimidazole

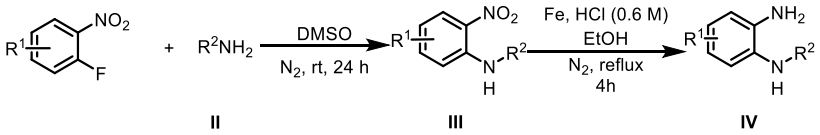


I II

A solution of 5-bromopent-1-ene (16.7 g, 112.08 mmol), potassium carbonate (15.4 g, 111.59 mmol) and phthalimide (15.0 g, 102.04 mmol) in DMF (100 mL) were stirred overnight at 60℃. The solution was diluted with water (100 mL), and extracted with DCM (80 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo to give **I** as a crude product, which was used for the next step without further purification.

A mixture of **I** and hydrazine monohydrate (4.2 mL, 85 mmol) was refluxed in ethanol (200 mL) for 24 h. Concentrated HCl (30 mL) was added dropwise at 0 °C. The mixture was filtered

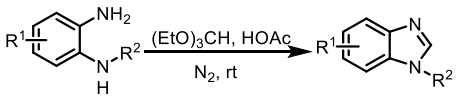
and the filtrate was concentrated in vacuo. The residue was diluted by water (80 mL) and washed by ethyl acetate (40 mL × 2). The aqueous layer was separated and basified with 3 M NaOH to pH 10 at 0°C. The solution was extracted with ethyl ether (50 mL × 3). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo (below 20 °C) to give **II** as a yellow oil, which was used for the next step without further purification.



II III IV

To an oven dried round flask equipped with a magnetic stir bar was added 1-fluoro-4-methyl-2-nitro benzene or its derivatives (3 mmol, 1 equiv.) in DMSO (5 mL). Subsequently, amine (6 mmol, 2 equiv.) was added to this solution. After stirring for 24 hours at room temperature, the solution was poured into water (100 mL) and the resulting mixture was extracted with EtOAc (3 × 50 mL). The combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to obtain crude product **III**. The crude product **III** was used in the next step without further purification.

Aquous HCl (0.6 M, 6.5 mL) was added to a suspension of **III** and iron powder (1.68 g, 30 mmol, 10 equiv.) in ethanol (25 mL). The resulting mixture was stirred for 3 hours at 95 ℃. Upon completion, the reaction was cooled to room temperature and filtered through a pad of celite. The filtrate was diluted with EtOAc (100 mL) and washed with saturated $NaHCO_3$ solution (25 mL) and saturated NaCl solution (25 mL). The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to obtain crude product **III**. The crude product **IV** was used in the next step without further purification.



IV

To a flame-dried 200 mL round bottom flask equipped with a stir bar was added **IV** in HOAc (10 mL). Then $(EtO)_3CH$ (444.6 mg, 3 mmol) was added and the resulting solution was stirred at room temperature until the reaction was complete (monitored by thin layer chromatography). The solution was diluted with DCM, washed with saturated $NaHCO_3$ (2 × 50 mL) and extracted with

DCM (2 × 30 mL). The organic layers were combined, dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The crude products were purified by column chromatography on silica gel eluting with PE/EtOAc to give the desired product.

4. References

(1) M. A. Cismesia, T. P. Yoon, *Chem. Sci.*, 2015, **6**, 5426–5434

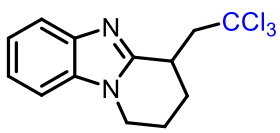
(2) B. Sun, L. Ling, X. H. Zhuang, L. L. Yang, J. L. Yin, C. Jin, *Chin. J. Chem.* 2023, **41**, 37–42

(3) N. Shotaro, S. Takashi, S. Atsushi, K. Tohru, Y. Tsuyoshi, M. Atsunori, *Org. Lett.*, 2012, **14**, 2476–2479.

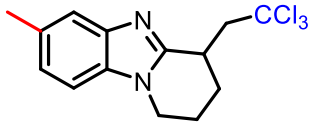
(4) W. Du, Q. S. Gu, Y. Li, Z. Y. Lin, D. Yang, *Org. Lett.*, 2017, **19**, 316–319.

(5) Y. X. Wang, S. L. Qi, Y. X. Luan, X. W. Han, S. Wang, H. Chen, M. C. Ye, *J. Am. Chem. Soc.*, 2018, **140**, 5360–5364.

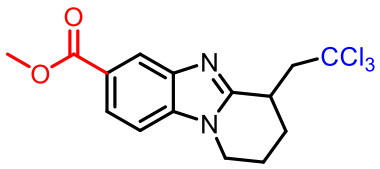
5. Characterization data of compounds 2-6



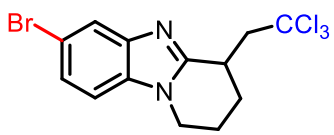
4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (**2a**): white solid (77.0 mg, 85%); mp 83-84 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.96 – 7.64 (m, 1H), 7.40 – 7.14 (m, 3H), 4.28 – 4.19 (m, 1H), 4.18 (dd, *J* = 15.2, 2.4 Hz, 1H), 3.68 – 3.57 (m, 1H), 2.99 (dd, *J* = 15.2, 8.8 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.38 – 2.26 (m, 1H), 2.19 – 2.07 (m, 1H), 1.95 – 1.83 (m, 1H), 1.26 (t, *J* = 7.0 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.7, 142.4, 134.9, 122.4, 122.3, 119.3, 109.0, 98.8, 57.5, 42.4, 35.70, 27.7, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{14}Cl_3N_2^+$ 303.0144, found 303.0140.



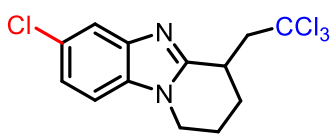
7-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo [1,2-*a*] pyridine (2b): white solid (73.9 mg, 78%) ; mp 150-151 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (s, 1H), 7.21 (d, *J* = 8.1 Hz, 1H), 7.10 (d, *J* = 8.1 Hz, 1H), 4.26 – 4.21 (m, 1H), 4.18 (dd, *J* = 15.3, 2.4 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.68 – 3.59 (m, 1H), 2.99 (dd, *J* = 15.2, 8.8 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.49 (s, 3H), 2.37 – 2.26 (m, 1H), 2.22 – 2.04 (m, 1H), 1.98 – 1.83 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.7, 142.4, 134.9, 122.4, 122.3, 119.3, 109.0, 98.8, 57.5, 42.4, 35.7, 27.7, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{16}Cl_3N_2^+$ 317.0301, found 317.0289.



methyl 4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo [1,2-*a*]pyridine-7-carboxylate (2c): white solid (75.6 mg, 70%); mp 145-146℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.48 (d, J = 1.5 Hz, 1H), 7.99 (dd, J = 8.5, 1.6 Hz, 1H), 7.31 (d, J = 8.7 Hz, 1H), 4.32 – 4.21 (m, 1H), 4.16 (dd, J = 15.2, 2.4 Hz, 1H), 4.08 – 3.96 (m, 1H), 3.94 (s, 3H), 3.67 – 3.55 (m, 1H), 2.98 (dd, J = 15.2, 8.6 Hz, 1H), 2.83 – 2.72 (m, 1H), 2.40 – 2.28 (m, 1H), 2.23 – 2.08 (m, 1H), 1.97 – 1.83 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.6, 154.7, 142.0, 138.2, 124.6, 123.9, 121.6, 108.7, 98.7, 57.4, 52.1, 42.7, 35.8, 27.6, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{15}H_{16}Cl_3N_2O_2^+$ 361.0199, found 361.0071.

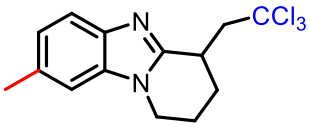


7-bromo-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5]imidazo[1,2-*a*]pyridine (2d): white solid (85.3 mg, 75%); mp 136-137 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 1.7 Hz, 1H), 7.34 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 1H), 4.24 – 4.15 (m, 1H), 4.10 (dd, *J* = 15.2, 2.3 Hz, 1H), 4.02 – 3.91 (m, 1H), 3.72 (q, *J* = 7.0 Hz, 1H), 3.63 – 3.55 (m, 1H), 2.96 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.36 – 2.27 (m, 1H), 2.20 – 2.05 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.9, 143.7, 133.9, 125.3, 122.2, 115.4, 110.2, 98.7, 57.4, 42.5, 35.7, 27.5, 21.7. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{13}Cl_3N_2Br^+$ 380.9249, found 380.9234.

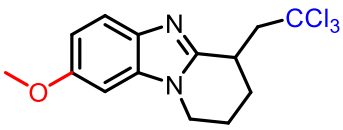


7-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2e): white solid (76.6 mg, 76%); mp 130-131 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 1.4 Hz, 1H), 7.22 (d, *J* = 1.7 Hz, 2H), 4.27 – 4.16 (m, 1H), 4.12 (dd, *J* = 15.2, 2.3 Hz, 1H), 4.05 – 3.93 (m, 1H), 3.66 – 3.55 (m, 1H), 2.98 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.82 – 2.70 (m,

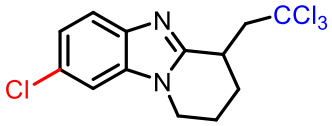
1H), 2.39 – 2.28 (m, 1H), 2.22 – 2.07 (m, 1H), 1.96 – 1.84 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.1, 143.2, 133.5, 127.9, 122.7, 119.1, 109.7, 98.7, 57.4, 42.5, 35.7, 27.5, 21.7. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{13}Cl_4N_2^+$ 336.9755, found 336.9750.



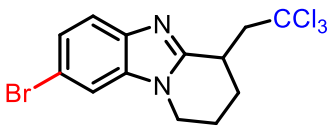
8-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2f) : white solid (74.9 mg, 79%); mp 129-130 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.6 Hz, 1H), 7.18 – 6.97 (m, 2H), 4.23 – 4.12 (m, 2H), 4.02 – 3.90 (m, 1H), 3.65 – 3.57 (m, 1H), 2.98 (dd, *J* = 15.2, 8.8 Hz, 1H), 2.82 – 2.70 (m, 1H), 2.51 (s, 3H), 2.38 – 2.25 (m, 1H), 2.19 – 2.06 (m, 1H), 1.96 – 1.81 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.2, 140.5, 135.1, 132.2, 123.9, 118.7, 109.0, 98.8, 57.5, 42.3, 35.7, 27.7, 21.9, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{16}Cl_3N_2^+$ 317.0301, found 317.0300.



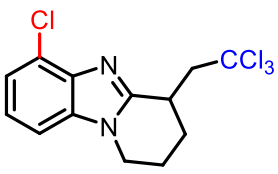
8-methoxy-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2g): white solid (81.7 mg, 82%); mp 132-133 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.8 Hz, 1H), 6.91 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.76 (d, *J* = 2.4 Hz, 1H), 4.20 – 4.10 (m, 2H), 3.99 – 3.87 (m, 1H), 3.87 (s, 3H), 3.64 – 3.53 (m, 1H), 2.97 (dd, *J* = 15.2, 8.8 Hz, 1H), 2.80 – 2.70 (m, 1H), 2.37 – 2.24 (m, 1H), 2.20 – 2.04 (m, 1H), 1.92 – 1.81 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.3, 151.9, 136.8, 135.4, 119.6, 111.3, 98.8, 92.9, 57.5, 55.9, 42.4, 35.7, 27.7, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{16}Cl_3N_2O^+$ 333.0250, found 333.0248.



8-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2h): white solid (73.6 mg, 73%); mp 136-137 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.67 (d, *J* = 8.5 Hz, 1H), 7.33 – 7.22 (m, 2H), 4.25 – 4.15 (m, 1H), 4.14 (dd, *J* = 15.2, 2.4 Hz, 1H), 4.04 – 3.92 (m, 1H), 3.67 – 3.55 (m, 1H), 2.99 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.85 – 2.71 (m, 1H), 2.40 – 2.27 (m, 1H), 2.21 – 2.08 (m, 1H), 1.97 – 1.82 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.7, 141.0, 135.5, 128.0, 123.0, 120.1 , 109.2, 98.7, 57.4, 42.6, 35.7, 27.6, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{13}Cl_4N_2^+$ 336.9755, found 336.9752.

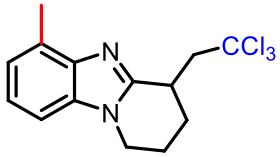


8-bromo-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo [1,2-*a*]pyridine (2i): white solid (82.1 mg, 72%); mp 151-152 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 1.8 Hz, 1H), 7.36 (dd, *J* = 8.5, 1.9 Hz, 1H), 4.21 – 4.15 (m, 1H), 4.12 (dd, *J* = 15.2, 2.4 Hz, 1H), 4.01 – 3.89 (m, 1H), 3.64 – 3.52 (m, 1H), 2.97 (dd, *J* = 15.2, 8.6 Hz, 1H), 2.81 – 2.70 (m, 1H), 2.39 – 2.26 (m, 1H), 2.21 – 2.05 (m, 1H), 1.95 – 1.80 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.6, 141.4, 136.0, 125.6, 120.5, 115.4, 112.2, 98.7, 57.4, 42.5, 35.7, 27.6, 21.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{13}Cl_3N_2Br^+$ 380.9249, found 380.9245.

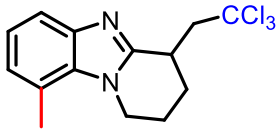


6-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5]imidazo [1,2-*a*]pyridine (2j): white solid (76.6 mg, 76%); mp 139-140 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (dd, J = 7.2, 1.5 Hz, 1H), 7.27 – 7.10 (m, 2H), 4.23 (dd, J = 15.5, 2.4 Hz, 2H), 4.14 – 3.91 (m, 1H), 3.80 –

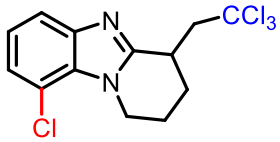
3.62 (m, 1H), 3.00 (dd, J = 15.3, 9.5 Hz, 1H), 2.81 – 2.64 (m, 1H), 2.48 – 2.27 (m, 1H), 2.22 – 2.07 (m, 1H), 2.06 – 1.87 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.4, 139.8, 136.0, 124.1, 122.8, 122.5, 107.8, 98.5, 56.9, 42.8, 35.8, 26.9, 21.6. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{13}Cl_4N_2^+$ 336.9755, found 336.9751.



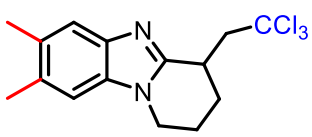
6-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo [1,2-*a*]pyridine (2k): white solid (77.8 mg, 82%); mp 136-137 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.22 – 7.13 (m, 2H), 7.11 – 7.06 (m, 1H), 4.27 – 4.18 (m, 2H), 4.04 – 3.95 (m, 1H), 3.74 – 3.63 (m, 1H), 3.00 (dd, *J* = 15.2, 9.4 Hz, 1H), 2.77 – 2.71 (m, 1H), 2.69 (s, 3H), 2.39 – 2.26 (m, 1H), 2.21 – 2.05 (m, 1H), 1.98 – 1.87 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.7, 141.8, 134.6, 129.4, 122.8, 122.1, 106.4, 98.8, 57.3, 42.5, 35.7, 27.2, 21.7, 16.7. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{16}Cl_3N_2^+$ 317.0301, found 317.0302.



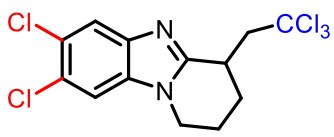
9-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2l): white solid (79.6 mg, 84%); mp 155-156 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.1 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 4.70 – 4.64 (m, 1H), 4.41 – 4.29 (m, 1H), 4.19 (dd, *J* = 15.2, 2.5 Hz, 1H), 3.69 – 3.56 (m, 1H), 2.98 (dd, *J* = 15.2, 8.9 Hz, 1H), 2.73 (s, 4H), 2.38 – 2.23 (m, 1H), 2.21 – 2.00 (m, 1H), 1.98 – 1.80 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.5, 142.5, 133.7, 124.8, 122.3, 121.2, 117.2, 98.8, 57.5, 45.4, 36.0, 27.0, 22.4, 18.8. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{16}Cl_3N_2^+$ 317.0301, found 317.0303.



9-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2m): white solid (73.6 mg, 73%); mp 135-136 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.65 (dd, *J* = 7.6, 1.5 Hz, 1H), 7.22 – 7.14 (m, 2H), 4.96 – 4.86 (m, 1H), 4.39 (m, *J* = 12.5, 11.0, 5.1 Hz, 1H), 4.16 (dd, *J* = 15.2, 2.4 Hz, 1H), 3.69 – 3.57 (m, 1H), 3.00 (dd, *J* = 15.2, 8.7 Hz, 1H), 2.77 – 2.67 (m, 1H), 2.38 – 2.25 (m, 1H), 2.19 – 2.06 (m, 1H), 1.96 – 1.81 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.9, 144.4, 131.2, 123.7, 122.9, 118.1, 116.2, 98.7, 57.6, 45.6, 36.1, 27.0, 22.3. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{13}Cl_4N_2^+$ 336.9755, found 335.9753.

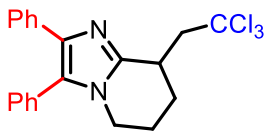


7,8-dimethyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2n): white solid (75.2 mg, 76%); mp 156-157 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (s, 1H), 7.08 (s, 1H), 4.33 – 4.07 (m, 2H), 4.01 – 3.89 (m, 1H), 3.67 – 3.56 (m, 1H), 2.98 (dd, *J* = 15.2, 8.9 Hz, 1H), 2.79 – 2.69 (m, 1H), 2.40 (s, 3H), 2.38 (s, 3H), 2.37 – 2.22 (m, 1H), 2.20 – 2.03 (m, 1H), 1.95 – 1.81 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.7, 140.9, 133.4, 131.4, 131.2, 119.3, 109.3, 98.8, 57.5, 42.3, 35.6, 27.6, 21.9, 20.5, 20.4. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{15}H_{18}Cl_3N_2^+$ 331.0457, found 331.0452.

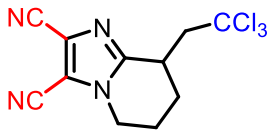


7,8-dichloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (2o): white solid (75.2 mg, 73%); mp 167-168 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.81 (s, 1H), 7.38 (s,

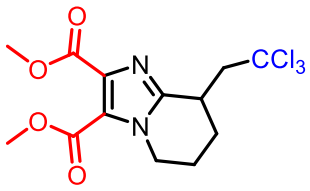
1H), 4.23 – 4.13 (m, 1H), 4.10 (dd, *J* = 15.2, 2.4 Hz, 1H), 3.96 (dd, *J* = 17.2, 5.7 Hz, 1H), 3.65 – 3.53 (m, 1H), 2.98 (dd, *J* = 15.2, 8.5 Hz, 1H), 2.82 – 2.71 (m, 1H), 2.40 – 2.28 (m, 1H), 2.21 – 2.08 (m, 1H), 1.97 – 1.82 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.9, 141.8, 134.2, 126.3, 126.2, 120.5, 110.4, 98.6, 57.3, 42.7, 35.7, 27.5, 21.7. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{12}Cl_5N_2^+$ 370.9365, found 370.9361.



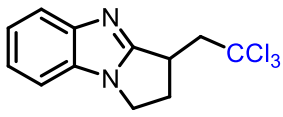
2,3-diphenyl-8-(2,2,2-trichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (2p): white solid (107.9 mg, 89%); mp 168-169 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 – 7.51 (m, 2H), 7.49 – 7.43 (m, 3H), 7.39 – 7.33 (m, 2H), 7.23 (dd, *J* = 8.3, 6.5 Hz, 2H), 7.19 – 7.12 (m, 1H), 4.22 (dd, *J* = 15.2, 2.5 Hz, 1H), 3.83 – 3.64 (m, 2H), 3.64 – 3.54 (m, 1H), 3.01 (dd, *J* = 15.2, 9.2 Hz, 1H), 2.73 – 2.64 (m, 1H), 2.20 – 2.09 (m, 1H), 2.04 – 1.81 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 145.5, 136.8, 134.5, 130.8, 130.7, 129.0, 128.5, 128.2, 128.0, 126.9, 126.3, 99.0, 57.8, 43.9, 35.3, 27.4, 22.2. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{21}H_{20}Cl_3N_2^+$ 405.0614, found 405.0611.



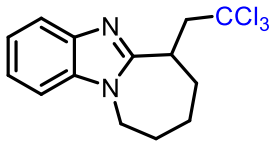
8-(2,2,2-trichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-2,3-dicarbonitrile (2q): white solid (41.7 mg, 46%); mp 180-181 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.33 – 4.22 (m, 1H), 4.11 – 4.00 (m, 1H), 3.87 (dd, *J* = 15.1, 2.5 Hz, 1H), 3.50 – 3.40 (m, 1H), 2.91 (dd, *J* = 15.1, 8.2 Hz, 1H), 2.81 – 2.69 (m, 1H), 2.40 – 2.28 (m, 1H), 2.20 – 2.06 (m, 1H), 1.92 – 1.81 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 151.8, 121.8, 111.7, 111.7, 107.9, 97.8, 56.9, 45.3, 35.2, 27.0, 21.3. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{11}H_{10}Cl_3N_4^+$ 302,9893, found 302.9890.



dimethyl 8-(2,2,2-trichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-2,3-dicarboxylate (2r): white solid (48.6 mg, 44%); mp 173-174 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.44 – 4.34 (m, 1H), 4.13 – 4.01 (m, 1H), 4.00 (dd, *J* = 15.2, 2.6 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 3.51 (dd, *J* = 6.4, 3.0 Hz, 1H), 2.90 (dd, *J* = 15.2, 9.5 Hz, 1H), 2.72 – 2.55 (m, 1H), 2.29 – 2.17 (m, 1H), 2.07 – 1.91 (m, 1H), 1.68 (s, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.4, 160.4, 148.9, 136.3, 124.3, 98.2, 57.0, 52.5, 52.4, 45.5, 35.3, 26.3, 21.7. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{16}Cl_3N_2O_4^+$ 369.0097, found 369.0090.

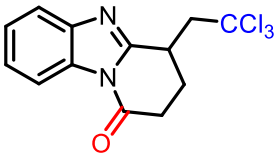


3-(2,2,2-trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-*a*]imidazole (2s): white solid (36.3 mg, 42%); mp 137-138 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.74 (m, 1H), 7.41 – 7.34 (m, 1H), 7.34 – 7.25 (m, 2H), 4.32 – 4.22 (m, 1H), 4.16 – 4.05 (m, 1H), 3.97 – 3.84 (m, 2H), 3.34 – 3.20 (m, 1H), 3.01 (dd, *J* = 15.3, 10.3 Hz, 1H), 2.81 – 2.66 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 160.8, 147.6, 132.2, 122.6, 122.4, 109.8, 98.2, 57.8, 42.5, 35.1, 35.0. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{12}H_{11}Cl_3N_2^+$ 288.9988, found 288.9984.

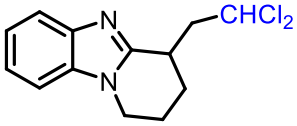


6-(2,2,2-trichloroethyl)-7,8,9,10-tetrahydro-6H-benzo[4,5]imidazo[1,2-*a*]azepine (2t): white solid (35.1 mg, 37%); mp 136-137 °C, **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.69 (m, 1H), 7.38 – 7.18 (m, 3H), 4.56 – 4.32 (m, 2H), 4.14 – 3.99 (m, 1H), 3.56 – 3.42 (m, 1H), 3.03 (dd, *J* = 15.2,

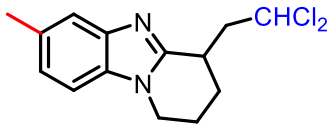
5.4 Hz, 1H), 2.36 (dt, *J* = 13.9, 3.0 Hz, 1H), 2.22 – 2.12 (m, 1H), 2.12 – 2.01 (m, 1H), 2.00 – 1.89 (m, 1H), 1.78 – 1.55 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 157.6, 141.7, 135.9, 122.4, 121.8, 119.5, 108.8, 99.6, 56.3, 43.9, 38.3, 33., 29.2, 28.1. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{16}Cl_3N_2^+$ 317.0301, found 317.0300.



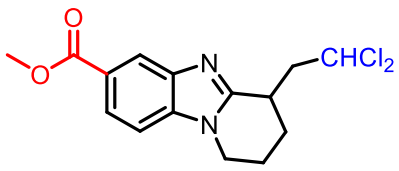
4-(2,2,2-trichloroethyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridin-1(2*H*)-one(2w): white solid (51.2 mg, 54%) ; mp129-130 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.30 – 8.22 (m, 1H), 7.78 – 7.71 (m, 1H), 7.43 – 7.37 (m, 2H), 4.26 (dd, J = 15.2, 2.5 Hz, 1H), 3.69 – 3.58 (m, 1H), 3.06 – 2.92 (m, 3H), 2.90 – 2.82 (m, 1H), 2.21 – 2.10 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 168.2, 155.0, 142.1, 131.7, 125.5, 125.4, 119.6, 115.4, 98.3, 55.8, 35.3, 33.4, 27.5**. HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{12}Cl_3N_2^+$315.9937, found 315.9901.



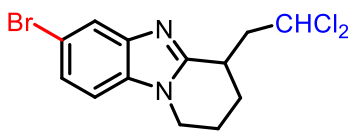
4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (3a): white solid (60.3 mg, 75%) ; mp127-128 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.78 – 7.71 (m, 1H), 7.36 – 7.24 (m, 3H), 6.72 (dd, J = 8.2, 5.2 Hz, 1H), 4.26 – 4.16 (m, 1H), 4.05 – 3.95 (m, 1H), 3.47 – 3.35 (m, 1H), 3.05 – 2.93 (m, 1H), 2.53 – 2.41 (m, 1H), 2.35 – 2.21 (m, 2H), 2.19 – 2.07 (m, 1H), 1.81 – 1.70 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.1, 142.6, 134.4, 122.3, 122.2, 119.3, 108.9, 72.4, 48.1, 42.3, 33.8, 27.3, 21.6. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{15}Cl_2N_2^+$ 269.0534, found 269.0530.



4-(2,2-dichloroethyl)-7-methyl-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3b) : white solid (58.4 mg, 69%); mp 132-133 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.58 – 7.51 (m, 1H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.10 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.70 (dd, *J* = 8.1, 5.3 Hz, 1H), 4.27 – 4.11 (m, 1H), 4.04 – 3.92 (m, 1H), 3.46 – 3.34 (m, 1H), 3.04 – 2.92 (m, 1H), 2.50 (s, 3H), 2.51 – 2.40 (m, 1H), 2.32 – 2.23 (m, 2H), 2.18 – 2.04 (m, 1H), 1.80 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.9, 142.9, 132.5, 131.9, 123.6, 119.1, 108.5, 72.5, 48.1, 42.3, 33.7, 27.2, 21.6, 21.6. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{17}Cl_2N_2^+$ 283.0691, found 283.0689.

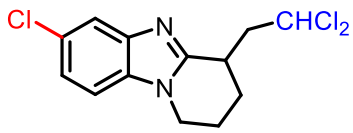


methyl 4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5]imidazo[1,2-*a*]pyridine-7-carboxylate (3c) : white solid (51.8 mg, 53%) ; mp 140-141 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.44 (d, *J* = 1.5 Hz, 1H), 7.98 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 6.72 (dd, *J* = 8.3, 5.0 Hz, 1H), 4.26 – 4.17 (m, 1H), 4.06 – 3.95 (m, 1H), 3.95 (s, 3H), 3.44 – 3.33 (m, 1H), 2.99 – 2.88 (m, 1H), 2.52 – 2.40 (m, 1H), 2.37 – 2.22 (m, 2H), 2.21 – 2.04 (m, 1H), 1.81 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 167.7, 155.0, 142.2, 137.7, 124.5, 123.9, 121.6, 108.7, 72.3, 52.1, 48.0, 42.6, 33.9, 27.1, 21.6. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{15}H_{17}Cl_2N_2O_2^+$ 327.0589, found 327.0582.

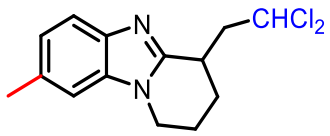


7-bromo-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3d) : white solid (65.4 mg, 63%); mp 98-99 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m,

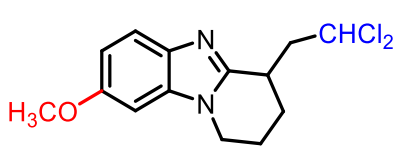
1H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.15 – 7.08 (m, 1H), 6.68 (dd, *J* = 8.2, 5.2 Hz, 1H), 4.17 – 4.09 (m, 1H), 3.99 – 3.87 (m, 1H), 3.40 – 3.28 (m, 1H), 2.97 – 2.84 (m, 1H), 2.48 – 2.36 (m, 1H), 2.31 – 2.21 (m, 2H), 2.18 – 2.04 (m, 1H), 1.75 – 1.66 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 125.7, 125.2, 122.1, 120.5, 115.4, 112.2, 110.2, 72.2, 48.0, 42.5, 33.8, 27.1, 21.5. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{14}Cl_2N_2Br^+$ 346.9639, found 346.9634.



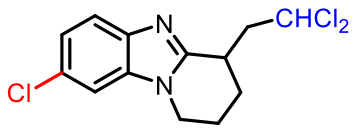
7-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3e) : white solid (58.9 mg, 65%); mp 105-106 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.71 (s, 1H), 7.22 (d, *J* = 1.6 Hz, 2H), 6.69 (dd, *J* = 8.2, 5.1 Hz, 1H), 4.23 – 4.13 (m, 1H), 4.04 – 3.92 (m, 1H), 3.44 – 3.32 (m, 1H), 3.00 – 2.88 (m, 1H), 2.52 – 2.40 (m, 1H), 2.36 – 2.22 (m, 2H), 2.20 – 2.05 (m, 1H), 1.82 – 1.67 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.4, 143.3, 133.0, 127.9, 122.6, 119.1, 109.7, 72.3, 48.0, 42.5, 33.8, 27.1, 21.5. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{13}H_{14}Cl_3N_2^+$ 303.0144, found 303.0140.



4-(2,2-dichloroethyl)-8-methyl-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3f) : white solid (66.0 mg, 78%); mp 143-144 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.6 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.70 (dd, *J* = 8.1, 5.2 Hz, 1H), 4.24 – 4.10 (m, 1H), 4.02 – 3.91 (m, 1H), 3.45 – 3.33 (m, 1H), 3.04 – 2.92 (m, 1H), 2.51 (s, 3H), 2.52 – 2.42 (m, 1H), 2.32 – 2.23 (m, 2H), 2.18 – 2.06 (m, 1H), 1.80 – 1.69 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.5, 140.1, 134.5, 132.3, 124.0, 118.6, 109.0, 72.4, 48.0, 42.3, 33.7, 27.2, 21.8, 21.5. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{17}Cl_2N_2^+$ 283.0691, found 283.0687.

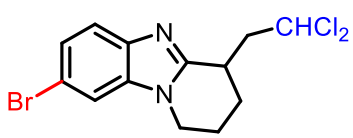


4-(2,2-dichloroethyl)-8-methoxy-1,2,3,4-tetrahydrobenzo [4,5]imidazo[1,2-*a*]pyridine (3g) : white solid (65.3 mg, 73%); mp 158-159 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.8 Hz, 1H), 6.90 (dd, *J* = 8.8, 2.5 Hz, 1H), 6.75 (d, *J* = 2.5 Hz, 1H), 6.69 (dd, *J* = 8.2, 5.2 Hz, 1H), 4.16 – 4.05 (m, 1H), 3.97 – 3.88 (m, 1H), 3.87 (s, 3H), 3.41 – 3.28 (m, 1H), 3.02 – 2.88 (m, 1H), 2.50 – 2.37 (m, 1H), 2.30 – 2.19 (m, 2H), 2.16 – 2.02 (m, 1H), 1.78 – 1.63 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 156.2, 152.2, 136.9, 135.0, 119.6, 111.2, 92.9, 72.5, 55.9, 48.1, 42.3, 33.8, 27.3, 21.6. HRMS (ESI) *m/z*: [M + H]$^+$ calcd for $C_{13}H_{15}Cl_2N_2^+$ 268.0534, found 268.0530. **HRMS** (ESI) *m/z*: [M + H] $^+$ calcd for $C_{14}H_{17}Cl_2N_2O^+$ 299.0640, found 299.0638.

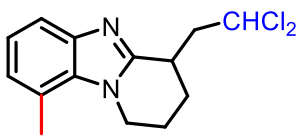


8-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3h) : white solid (58.9 mg, 65%); mp 155-156 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 8.6 Hz, 1H), 7.34 – 7.20 (m, 2H), 6.70 (dd, *J* = 8.2, 5.1 Hz, 1H), 4.22 – 4.10 (m, 1H), 4.00 – 3.92 (m, 1H), 3.45 – 3.33 (m, 1H), 3.02 – 2.90 (m, 1H), 2.53 – 2.41 (m, 1H), 2.37 – 2.22 (m, 2H), 2.21 – 2.06 (m, 1H), 1.80 – 1.69 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.0, 141.1, 135.0, 128.0, 123.0, 120.1, 109.2, 72.3, 48.0, 42.5, 33.8, 27.1, 21.6. **HRMS** (ESI) *m/z*: [M + H]

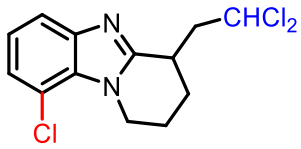
$^{+}$ calcd for $C_{13}H_{14}Cl_3N_2^{+}$ 303.0144, found 303.0140.



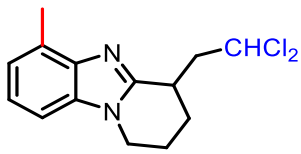
8-bromo-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3i) : white solid (65.4 mg, 63%); mp 181-182 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.5 Hz, 1H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.37 (dd, *J* = 8.5, 1.9 Hz, 1H), 6.70 (dd, *J* = 8.2, 5.1 Hz, 1H), 4.21 – 4.11 (m, 1H), 4.01 – 3.90 (m, 1H), 3.44 – 3.32 (m, 1H), 3.01 – 2.89 (m, 1H), 2.52 – 2.40 (m, 1H), 2.36 – 2.22 (m, 2H), 1.82 – 1.67 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 153.9, 141.5, 135.5, 125.6, 120.5, 115.4, 112.2, 72.3, 48.0, 42.5, 33.8, 27.1, 21.6. **HRMS** (ESI) *m/z*: [M + H] $^{+}$ calcd for $C_{13}H_{14}Cl_2N_2Br^{+}$ 346.9639, found 346.9639.



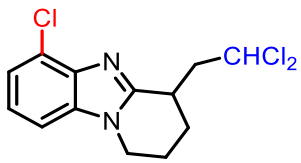
4-(2,2-dichloroethyl)-9-methyl-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3j) : white solid (55.0 mg, 65%); mp 152-152 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.13 (t, *J* = 7.7 Hz, 1H), 6.97 (d, *J* = 7.3 Hz, 1H), 6.67 (dd, *J* = 7.9, 5.4 Hz, 1H), 4.67 – 4.56 (m, 1H), 4.40 – 4.28 (m, 1H), 3.45 – 3.33 (m, 1H), 3.07 – 2.95 (m, 1H), 2.72 (s, 3H), 2.51 – 2.39 (m, 1H), 2.32 – 2.17 (m, 2H), 2.18 – 2.02 (m, 1H), 1.79 – 1.64 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.9, 142.4, 133.2, 124.8, 122.4, 121.2, 117.1, 72.4, 48.2, 45.4, 34.0, 26.6, 22.2, 18.8. **HRMS** (ESI) *m/z*: $[M + H]^{+}$ calcd for $C_{14}H_{17}Cl_2N_2^{+}$ 283.0691, found 283.0690.



9-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3k) : white solid (58.0 mg, 64%); mp 99-100 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.61 (dd, *J* = 7.4, 1.6 Hz, 1H), 7.20 – 7.13 (m, 2H), 6.69 (dd, *J* = 8.2, 5.2 Hz, 1H), 4.89 – 4.77 (m, 1H), 4.44 – 4.32 (m, 1H), 3.45 – 3.33 (m, 1H), 3.03 – 2.91 (m, 1H), 2.52 – 2.40 (m, 1H), 2.32 – 2.20 (m, 2H), 2.18 – 2.01 (m, 1H), 1.76 – 1.65 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 154.2, 144.5, 130.8, 123.6, 122.8, 118.1, 116.2, 72.3, 48.2, 45.5, 34.2, 26.6, 22.1. **HRMS** (ESI) *m/z*: $[M + H]^{+}$ calcd for $C_{13}H_{14}Cl_3N_2^{+}$ 303.0144, found 303.0143.

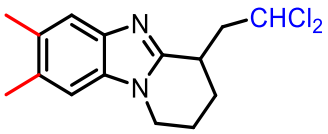


4-(2,2-dichloroethyl)-6-methyl-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3l) : white solid (44.0 mg, 52%); mp 124-125 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.22 – 7.11 (m, 2H), 7.12 – 7.05 (m, 1H), 6.87 (dd, *J* = 8.5, 4.8 Hz, 1H), 4.23 – 4.13 (m, 1H), 4.03 – 3.92 (m, 1H), 3.47 – 3.35 (m, 1H), 3.00 – 2.88 (m, 1H), 2.68 (s, 3H), 2.55 – 2.41 (m, 1H), 2.33 – 2.22 (m, 2H), 2.18 – 2.06 (m, 1H), 1.81 – 1.67 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.2, 141.9, 134.0, 129.3, 122.7, 122.1, 106.4, 72.7, 48.4, 42.4, 33.7, 27.4, 21.6, 16.6. **HRMS** (ESI) *m/z*: [M + H] $^{+}$ calcd for $C_{14}H_{17}Cl_2N_2^{+}$ 283.0691, found 283.0689.

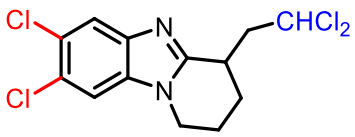


6-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3m) : white solid (58.9 mg, 65%); mp 112-113 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.29 (dd, *J* = 6.7, 4.9 Hz, 1H), 7.26 – 7.13 (m, 2H), 6.68 (dd, *J* = 7.8, 5.5 Hz, 1H), 4.24 – 4.14 (m, 1H), 4.05 – 3.93 (m, 1H), 3.48 – 3.36 (m, 1H), 3.11 – 2.97 (m, 1H), 2.54 – 2.40 (m, 1H), 2.36 – 2.22 (m, *J* = 5.8 Hz, 2H), 2.20 – 2.05 (m, 1H), 1.79 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ

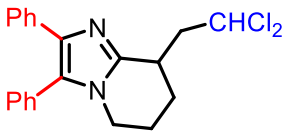
153.8, 139.8, 135.5, 124.1, 122.7, 122.4, 107.7, 72.3, 47.8, 42.7, 33.9, 26.9, 21.5. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{14}Cl_3N_2^+$ 303.0144, found 303.0143.



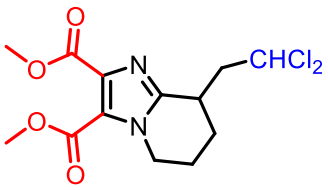
4-(2,2-dichloroethyl)-7,8-dimethyl-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3n) : white solid (65.7 mg, 74%); mp 136-137 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.51 (s, 1H), 7.08 (s, 1H), 6.68 (dd, *J* = 8.1, 5.3 Hz, 1H), 4.20 – 4.11 (m, 1H), 4.02 – 3.90 (m, 1H), 3.45 – 3.34 (m, 1H), 3.04 – 2.93 (m, 1H), 2.52 – 2.42 (m, 1H), 2.40 (s, 3H), 2.39 (s, 3H), 2.29 – 2.23 (m, 2H), 2.16 – 2.05 (m, 1H), 1.79 – 1.69 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.0, 132.8, 131.5, 131.4, 119.1, 109.3, 72.4, 48.0, 42.3, 33.6, 27.2, 21.5, 20.5, 20.3. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{15}H_{19}Cl_2N_2^+$ 297.0847, found 297.0844.



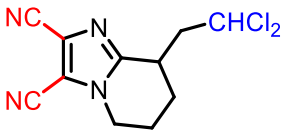
7,8-dichloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo [4,5] imidazo[1,2-*a*]pyridine (3o) : white solid (78.6 mg, 78%); mp 177-178 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.79 (s, 1H), 7.39 (s, 1H), 6.69 (dd, *J* = 8.4, 5.0 Hz, 1H), 4.23 – 4.10 (m, 1H), 4.01 – 3.88 (m, 1H), 3.43 – 3.31 (m, 1H), 3.00 – 2.86 (m, 1H), 2.52 – 2.39 (m, 1H), 2.34 – 2.23 (m, *J* = 5.6, 4.4 Hz, 3H), 2.21 – 2.05 (m, 1H), 1.82 – 1.67 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.2, 141.9, 133.7, 126.3, 126.1, 120.5, 110.4, 72.2, 47.9, 42.6, 33.9, 27.0, 21.5. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{13}Cl_4N_2^+$ 336.9755, found 336.9750.



8-(2,2-dichloroethyl)-2,3-diphenyl-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine (3p) : white solid (91.0 mg, 82%); mp 132-133 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.47 (p, *J* = 4.4, 3.9 Hz, 3H), 7.36 (dd, *J* = 6.9, 2.8 Hz, 2H), 7.29 – 7.16 (m, 3H), 6.93 (dd, *J* = 8.8, 4.5 Hz, 1H), 3.80 – 3.62 (m, 2H), 3.42 (s, 1H), 2.99 (d, *J* = 11.7 Hz, 1H), 2.57 – 2.45 (m, 1H), 2.26 – 2.16 (m, 1H), 2.15 – 2.06 (m, 1H), 2.04 – 1.92 (m, 1H), 1.77 (d, *J* = 11.6 Hz, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 146.1, 136.5, 134.5, 131.0, 130.7, 129.0, 128.5, 128.1, 126.7, 126.3, 73.0, 48.8, 43.8, 33.3, 27.5, 22.2. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{21}H_{21}Cl_2N_2^+$ 371.1004, found 371.1000.

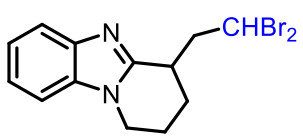


dimethyl 8-(2,2-dichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-*a*]pyridine-2,3-dicarboxylate (3q) : white solid (48.1 mg, 48%); mp 99-100 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.41 (dd, *J* = 7.5, 6.0 Hz, 1H), 4.36 (dd, *J* = 13.8, 4.7 Hz, 1H), 4.11 – 3.99 (m, 1H), 3.92 (s, 3H), 3.90 (s, 3H), 3.29 – 3.17 (m, 1H), 2.99 – 2.88 (m, 1H), 2.41 – 2.32 (m, 1H), 2.19 (dd, *J* = 11.7, 6.1 Hz, 2H), 2.04 – 1.91 (m, 1H), 1.67 – 1.57 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 163.5, 160.4, 149.5, 136.5, 123.7, 71.8, 52.4, 52.3, 47.6, 45.5, 33.4, 26.1, 21.6. **HRMS** (ESI) *m/z*: $[M + H]^+$ calcd for $C_{13}H_{17}Cl_2N_2O_4^+$ 335.0487, found 335.0485.

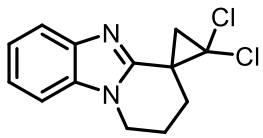


8-(2,2-dichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-2,3-dicarbonitrile (3r) : white solid (36.2 mg, 45%); mp 127-128 °C; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.48 (dd, *J* = 8.7, 4.7 Hz, 1H), 4.30 – 4.19 (m, 1H), 4.08 – 3.98 (m, 1H), 3.31 – 3.18 (m, 1H), 2.82 – 2.70 (m,

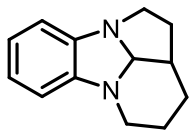
1H), 2.48 – 2.36 (m, 1H), 2.37 – 2.23 (m, 2H), 2.17 – 2.04 (m, 1H), 1.76 – 1.60 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.3, 121.7, 111.8, 111.4, 108.0, 71.3, 47.4, 45.3, 33.5, 26.4, 21.2. **HRMS** (ESI) *m/z*: [M + H] $^{+}$ calcd for $C_{11}H_{11}Cl_2N_4^+$ 269.0283, found 269.0280.



4-(2,2-dibromoethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine(4): white solid (50.2 mg, 47%); mp 128-129 ℃; **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.80 – 7.71 (m, 1H), 7.36 – 7.28 (m, 1H), 7.29 (q, *J* = 4.0, 3.1 Hz, 2H), 6.61 (dd, *J* = 8.3, 5.6 Hz, 1H), 4.25 – 4.16 (m, 1H), 4.07 – 3.95 (m, 1H), 3.44 – 3.34 (m, 1H), 3.24 – 3.14 (m, 1H), 2.72 – 2.60 (m, 1H), 2.36 – 2.23 (m, 2H), 2.21 – 2.07 (m, 1H), 1.81 – 1.68 (m, 1H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 152.8, 134.3, 122.4, 122.3, 119.3, 109.0, 49.9, 45.0, 42.3, 35.4, 26.9, 21.6. **HRMS** (ESI) *m/z*: [M + H]$^{+}$ calcd for $C_{13}H_{15}Br_2N_2^+$ 356.9524, found 356.9520.



2',2'-dichloro-2,3-dihydro-1H-spiro[benzo[4,5]imidazo[1,2-*a*]pyridine-4,1'-cyclopropane] (5): yellow oil (45.5 mg, 57%);**^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.58 – 7.52 (m, 1H), 7.48 (dd, *J* = 7.0, 1.0 Hz, 1H), 7.39 (m, *J* = 8.1, 7.1, 1.0 Hz, 1H), 7.32 – 7.26 (m, 1H), 4.29 – 4.00 (m, 1H), 2.13 – 2.04 (m, 1H), 1.41 – 1.14 (m, 3H), 1.09 (t, *J* = 7.0 Hz, 1H), 0.92 – 0.84 (m, 2H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 147.1, 144.3, 142.2, 123.0, 121.2, 120.1, 110.4, 73.7, 60.3, 42.6, 35.0, 28.4, 18.2. **HRMS** (ESI) *m/z*: [M + H] $^{+}$ calcd for $C_{13}H_{13}Cl_2N_2^+$ 267.0378, found267.0375.

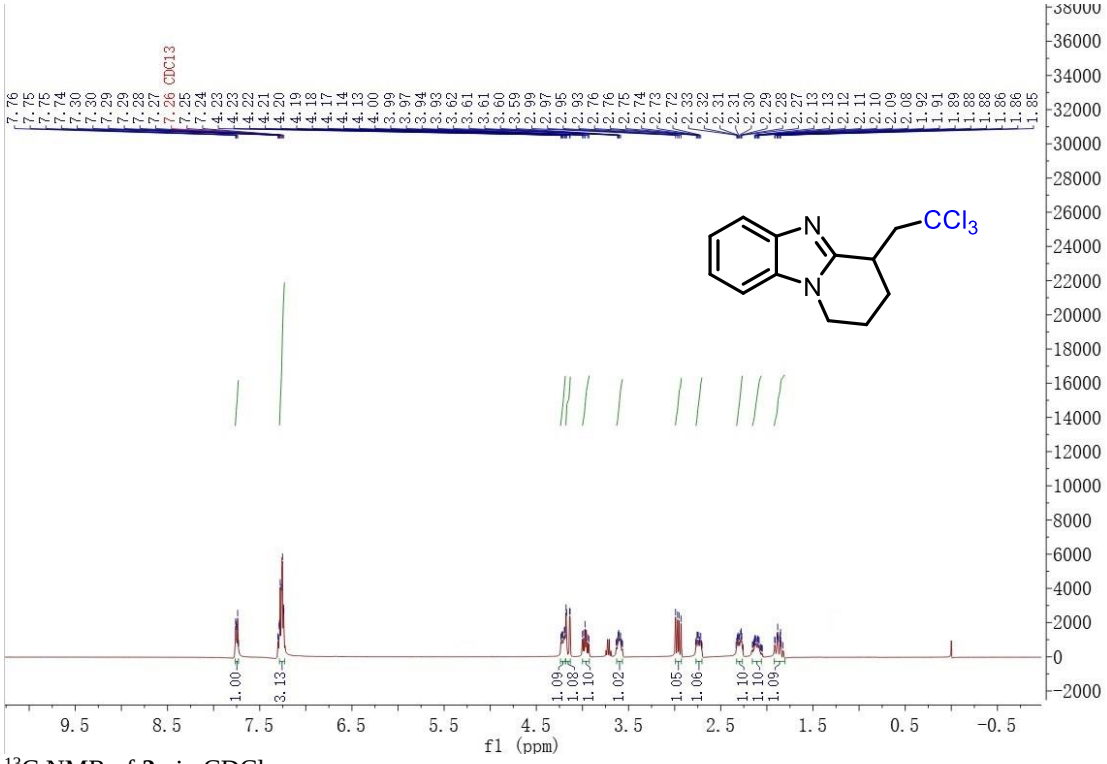


1,2,2a,2a1,4,5-hexahydro-3H-5a,9b-diazacyclopenta[jk]fluorene(6): yellow oil (33.0 mg, 55%);**^{1}H NMR** (600 MHz, Chloroform-*d*) δ 6.78 (td, *J* = 7.6, 1.2 Hz, 1H), 6.67 (dd, *J* = 7.5, 1.2 Hz, 1H), 6.55 (td, *J* = 7.5, 1.1 Hz, 1H), 6.28 (dd, *J* = 7.6, 1.1 Hz, 1H), 5.20 (d, *J* = 6.2 Hz, 1H), 3.53 – 3.47 (m, 1H), 3.32 – 3.21 (m, 2H), 3.15 – 3.06 (m, 1H), 1.96 – 1.88 (m, 1H), 1.81 – 1.73 (m, 1H), 1.69 – 1.64 (m, 1H), 1.59 – 1.40 (m, 4H). **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 144.7, 143.9, 122.0, 116.6, 112.2, 103.9, 83.2, 57.2, 43.2, 38.4, 28.5, 24.3, 19.4. **HRMS** (ESI) *m/z*: [M + H] $^{+}$ calcd for $C_{13}H_{17}N_2^+$ 201.1313, found 201.1310.

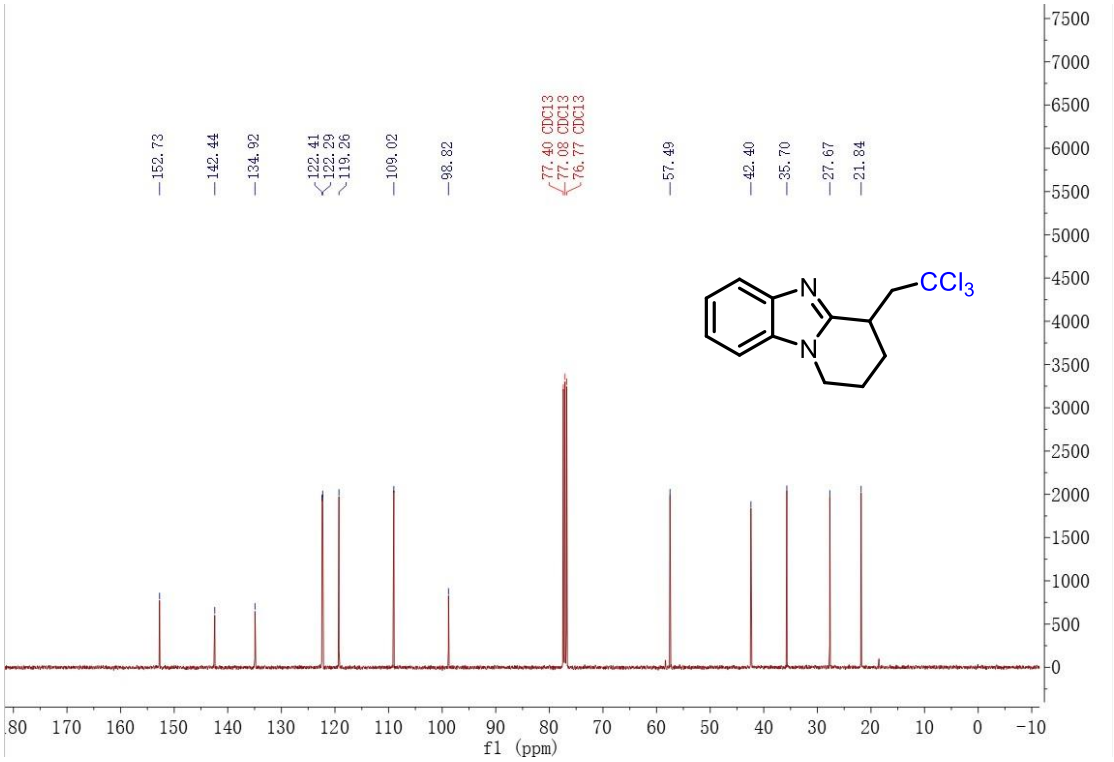
6. Spectra

4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2a)

^{1}H NMR of **2a** in $CDCl_3$

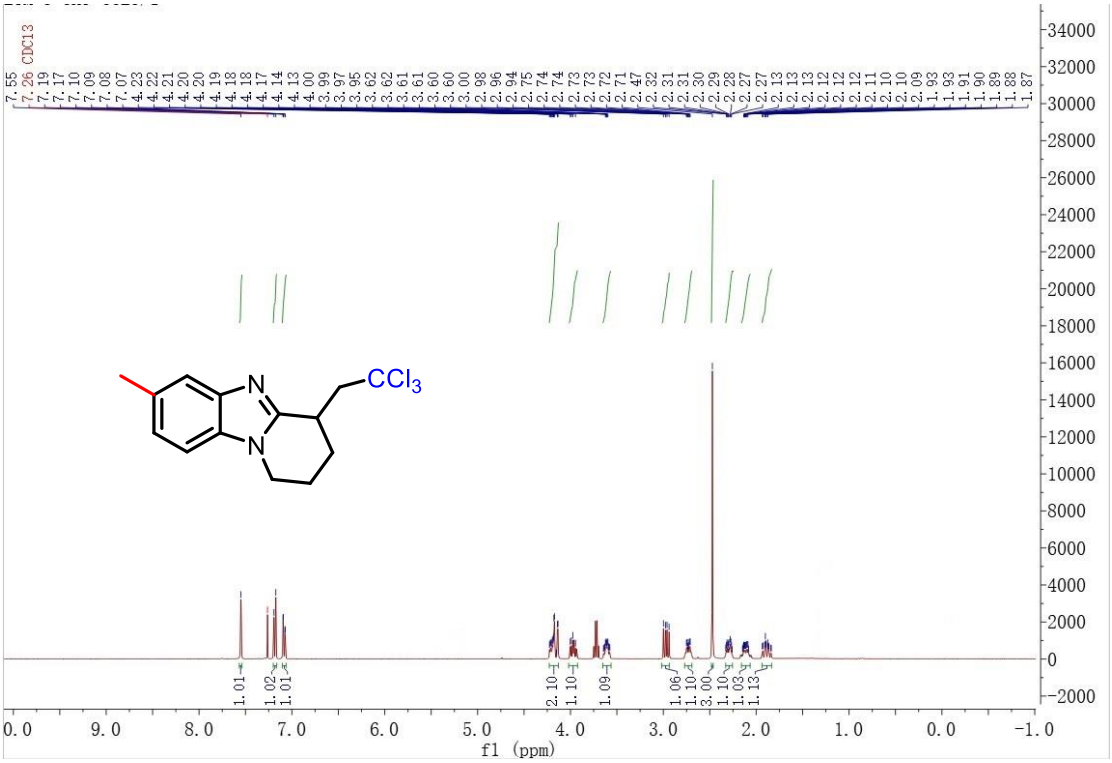


^{13}C NMR of **2a** in $CDCl_3$

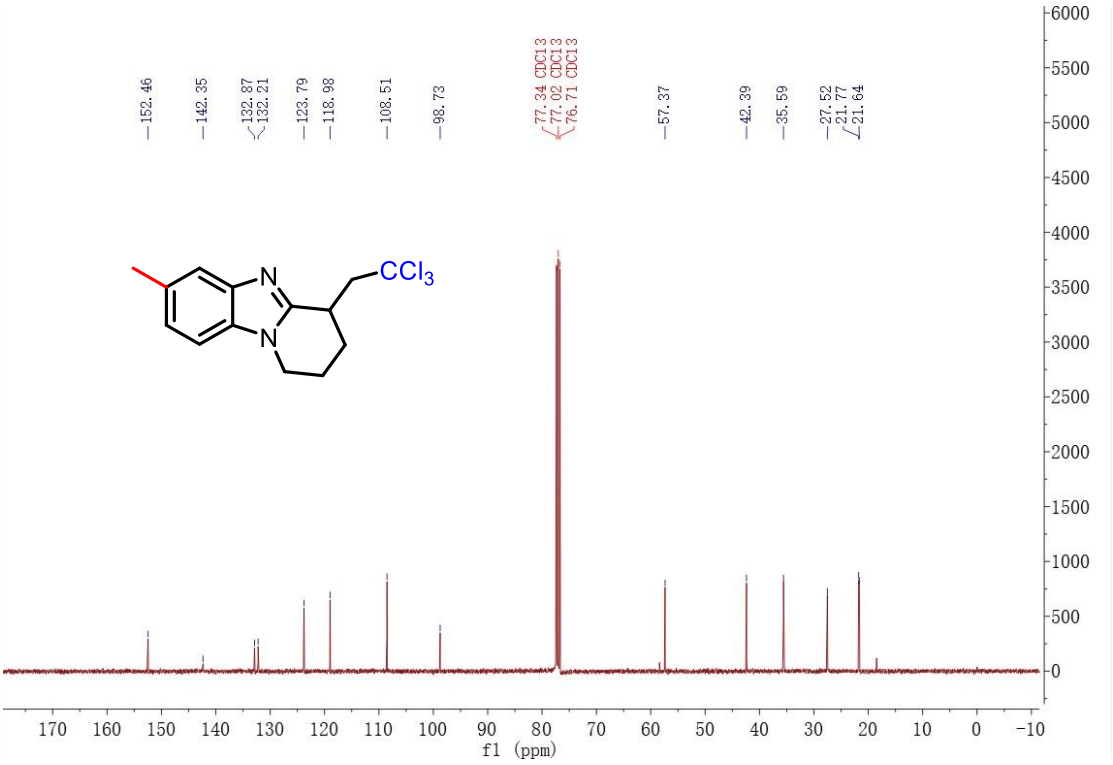


7-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-*a*]pyridine (2b)

^{1}H NMR of **2b** in $CDCl_3$

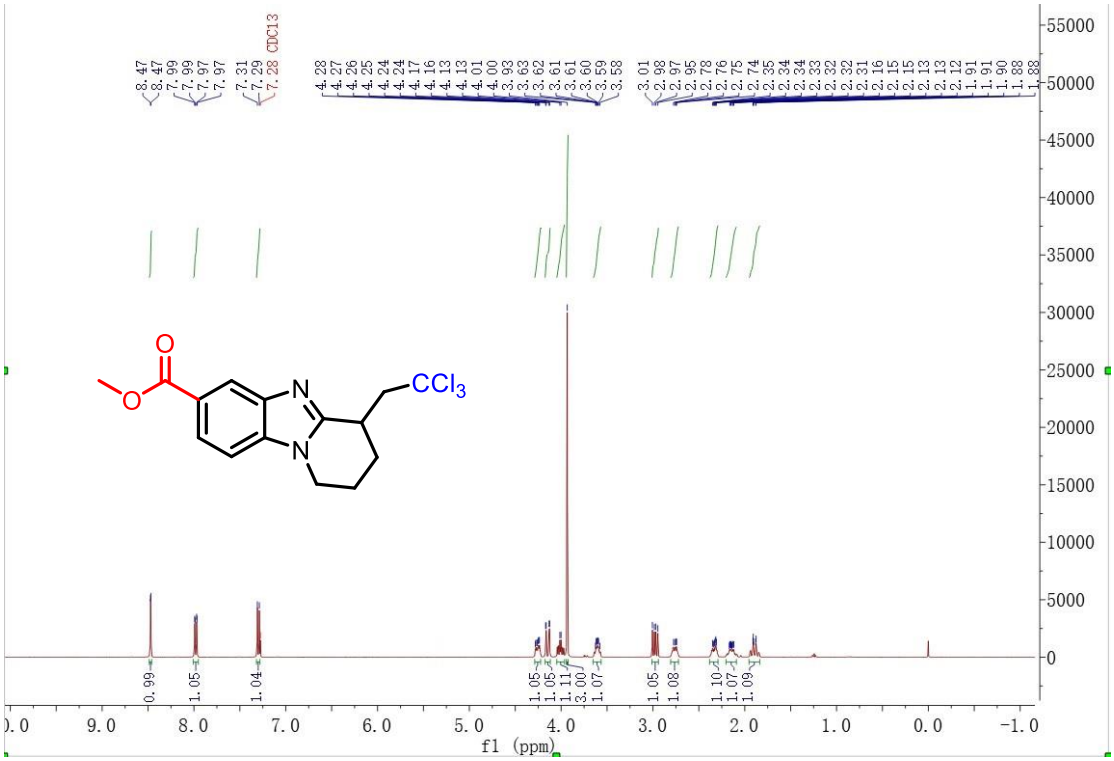


^{13}C NMR of **2b** in $CDCl_3$

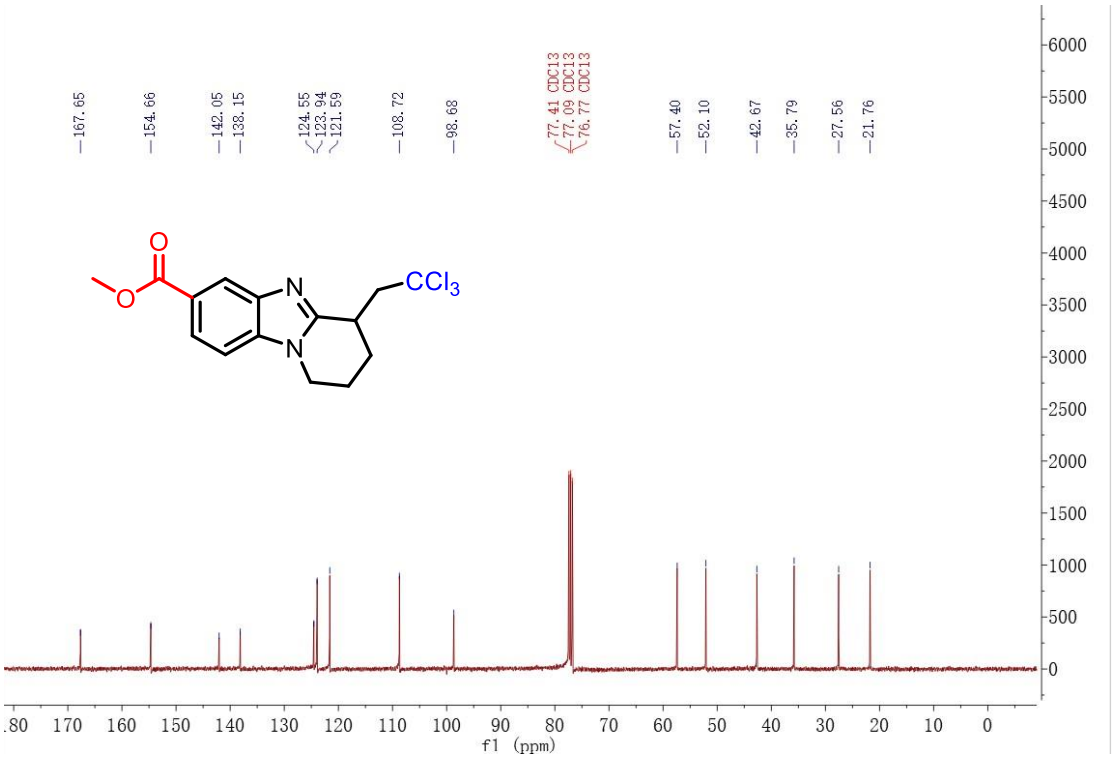


methyl 4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobeno[4,5]imidazo[1,2-a]pyridine-7-carboxylate (2c)

^{1}H NMR of **2c** in $CDCl_3$

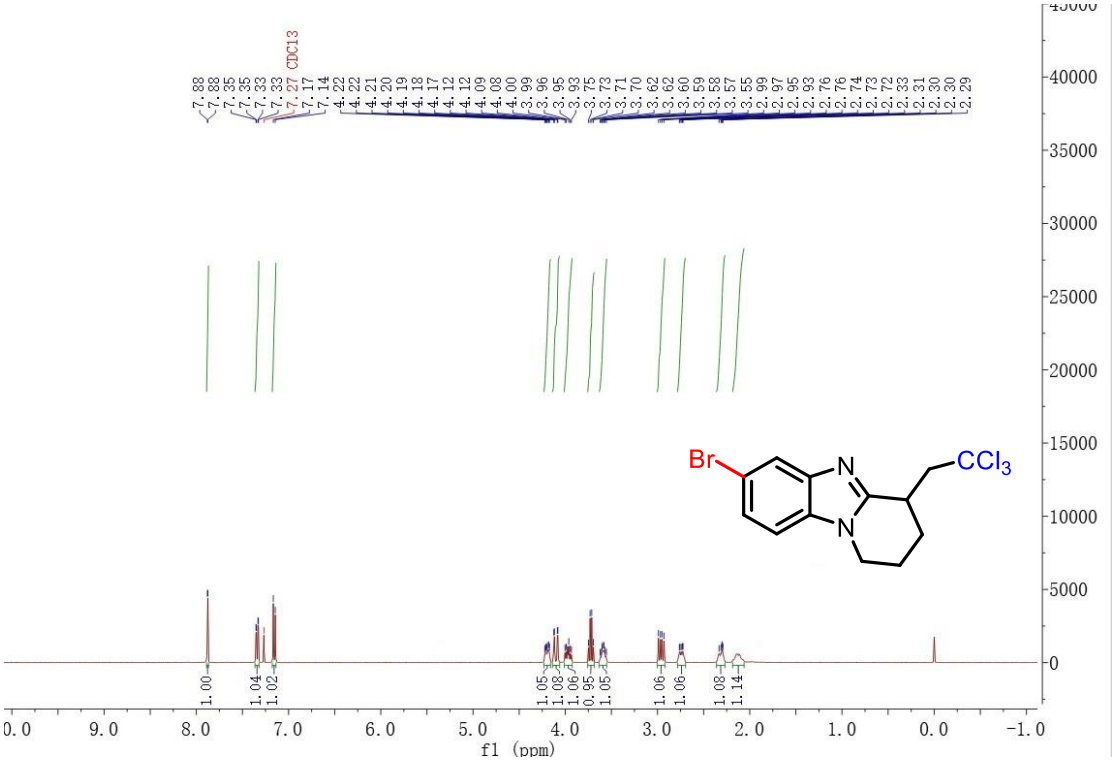


^{13}C NMR of **2c** in $CDCl_3$

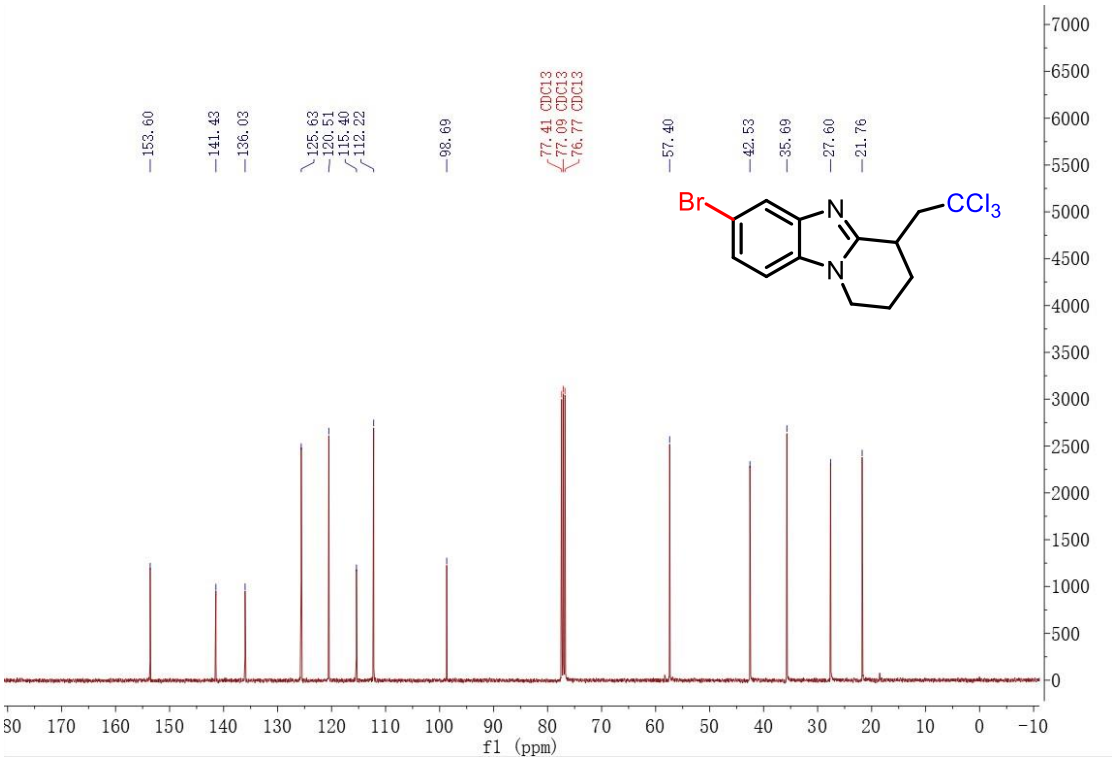


7-bromo-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2d)

^{1}H NMR of **2d** in $CDCl_3$

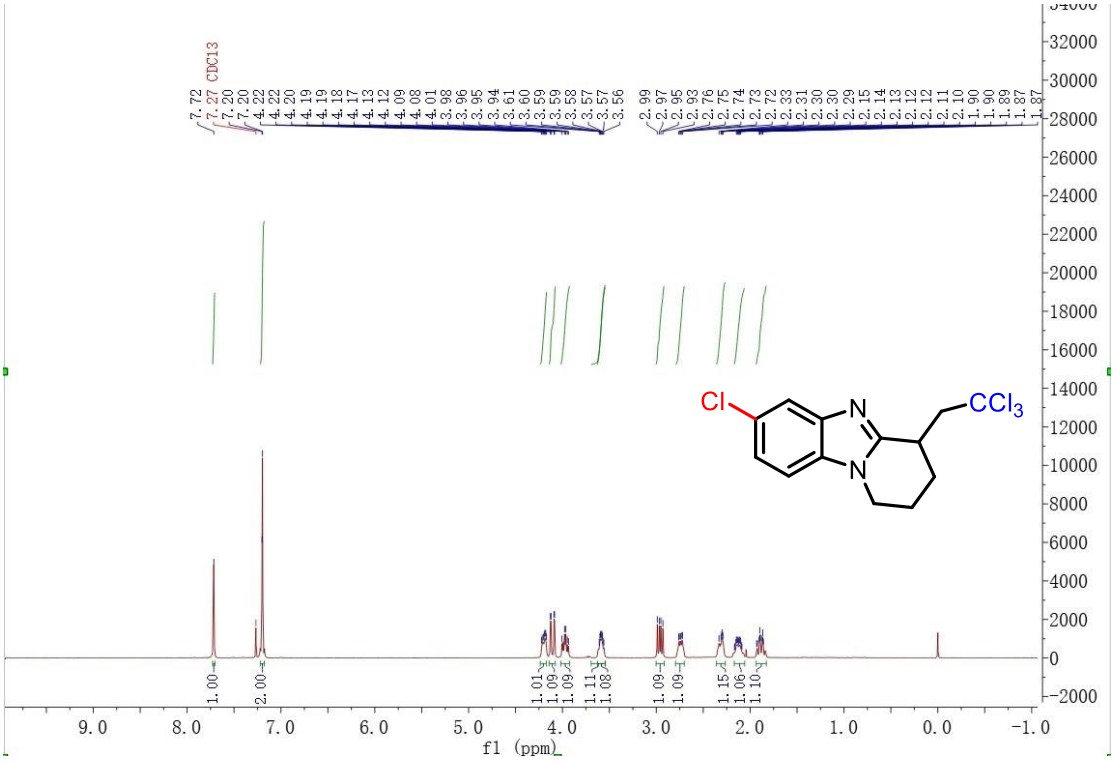


^{13}C NMR of **2d** in $CDCl_3$

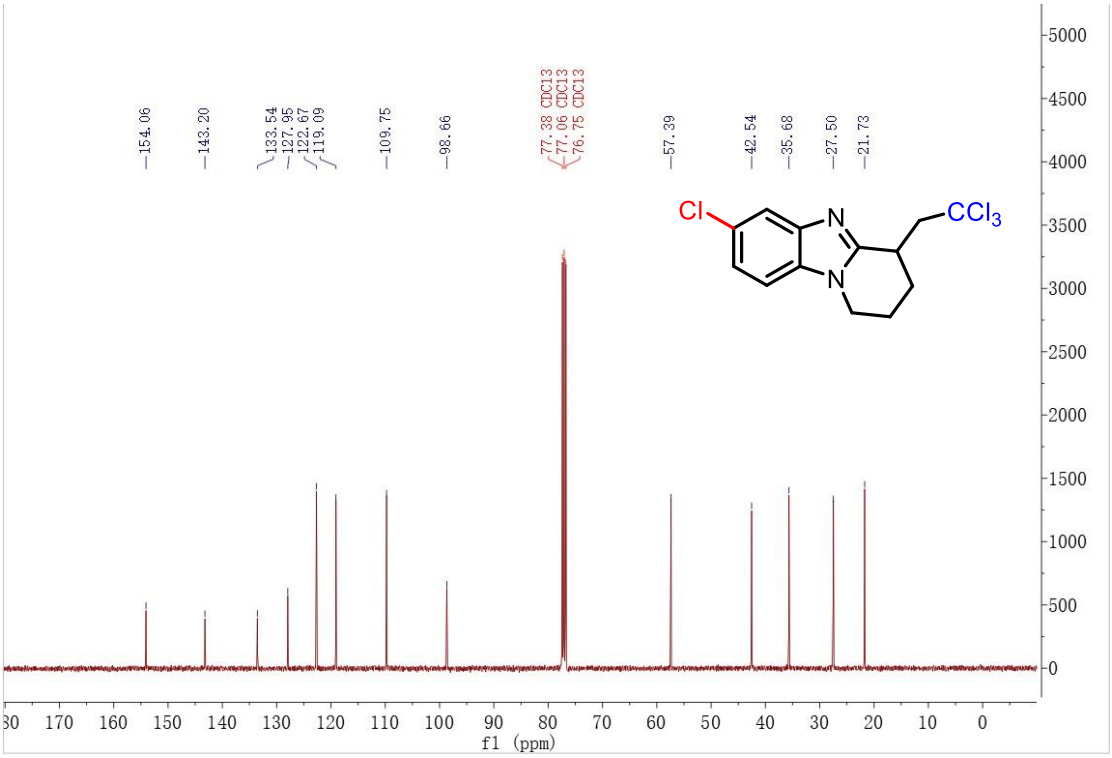


7-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2e)

^{1}H NMR of **2e** in $CDCl_3$

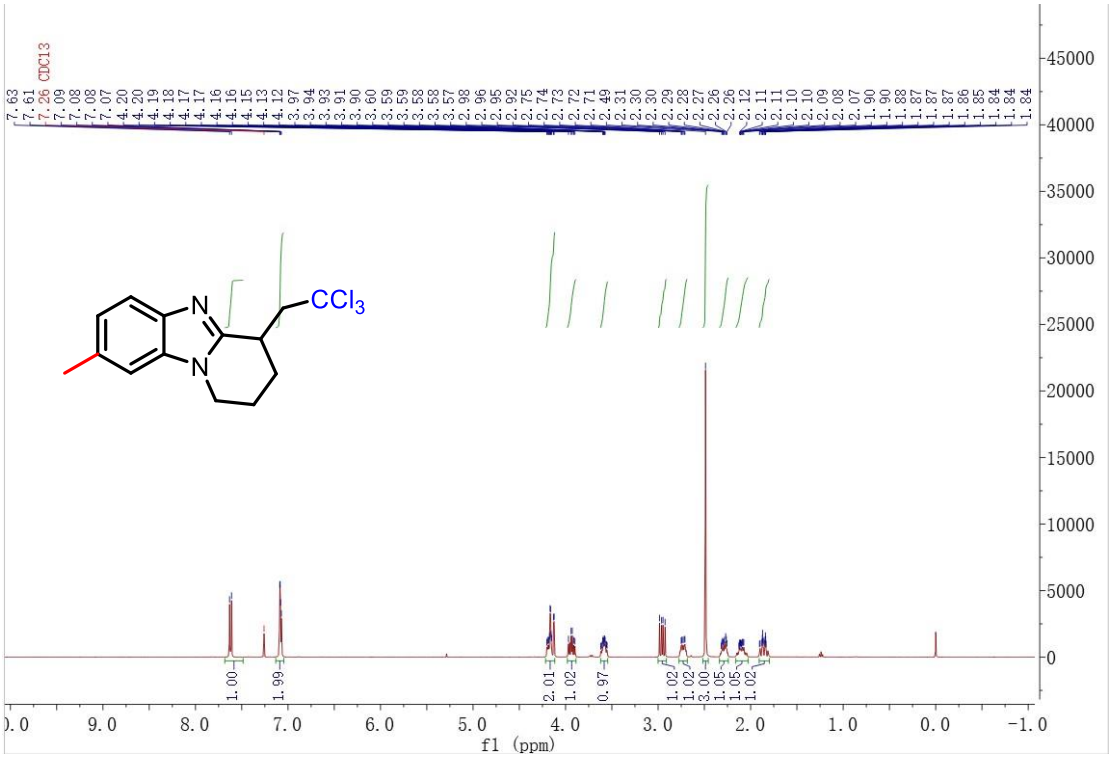


^{13}C NMR of **2e** in $CDCl_3$

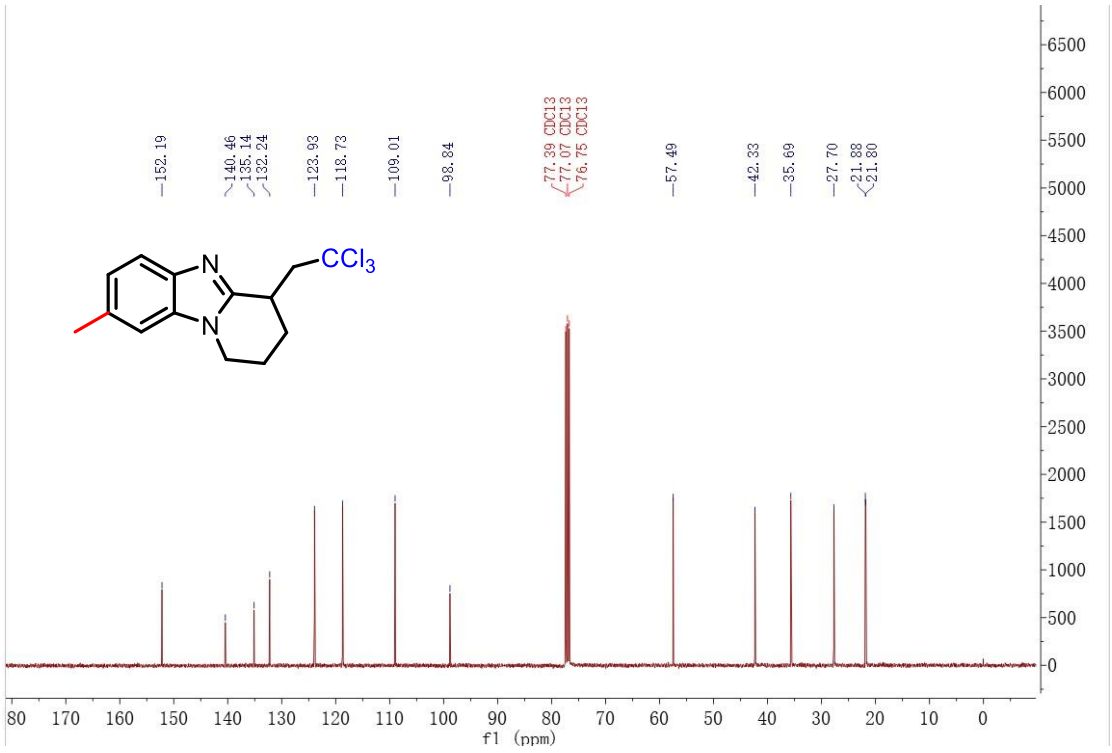


8-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2f)

^{1}H NMR of **2f** in $CDCl_3$

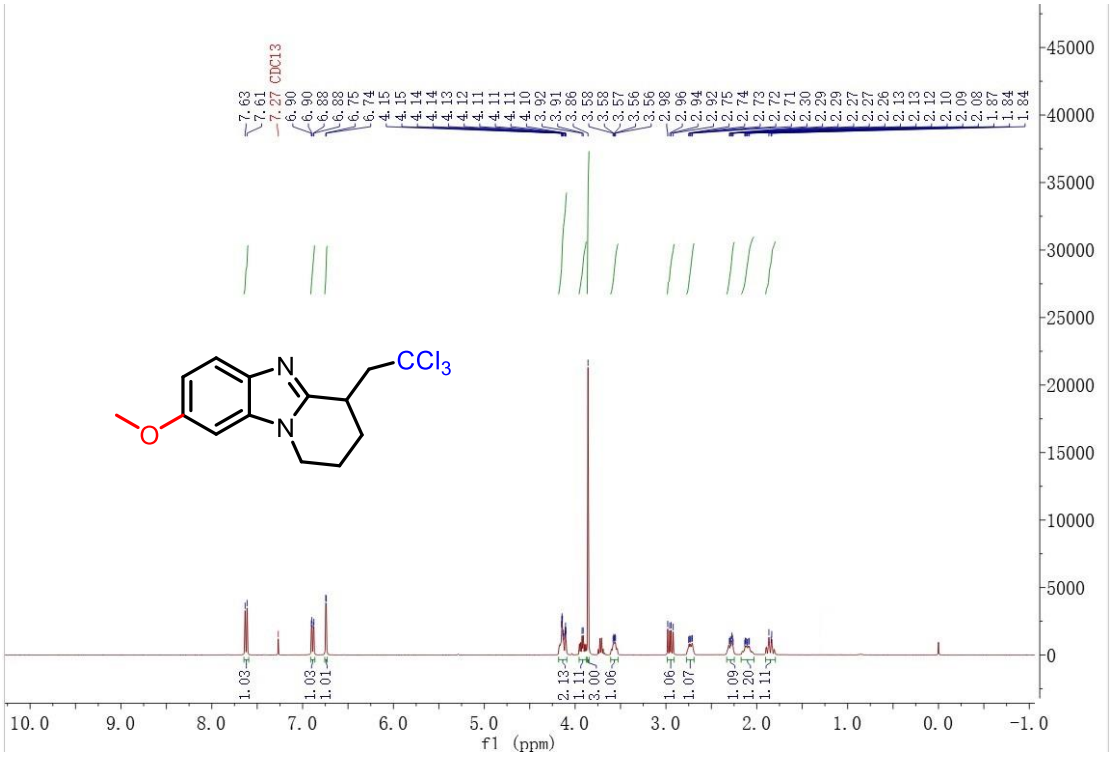


^{13}C NMR of **2f** in $CDCl_3$

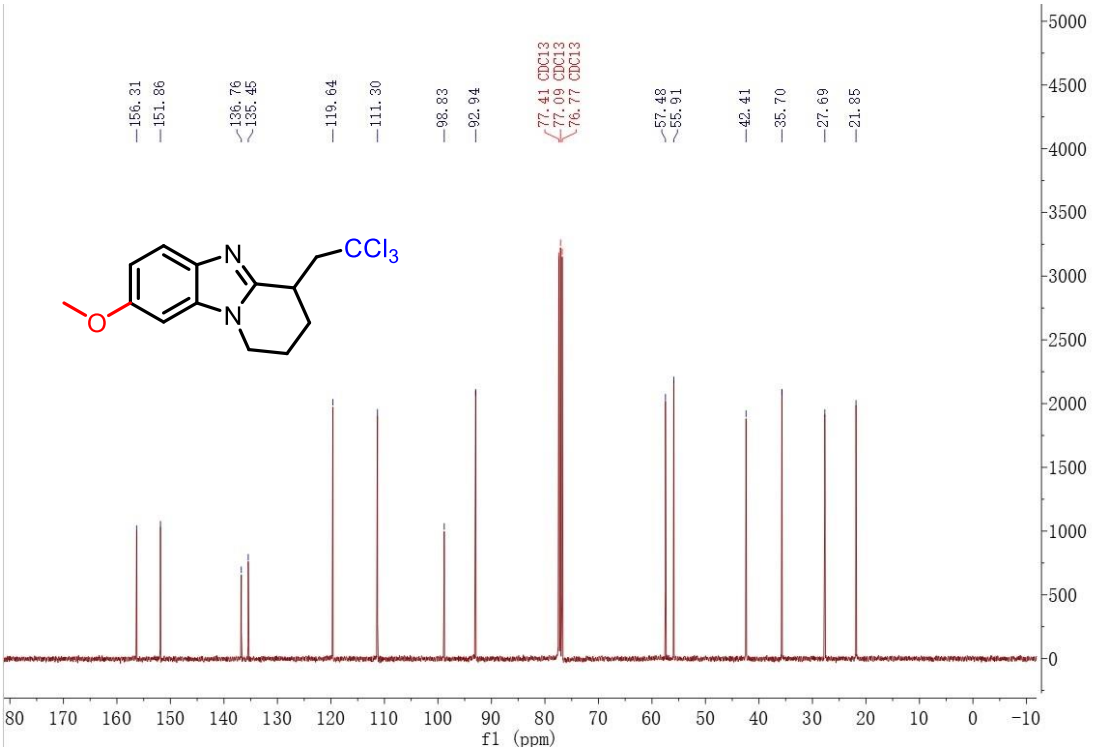


8-methoxy-4-(2,2,2-trichloroethyl)-1,23,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2g)

^{1}H NMR of **2g** in $CDCl_3$

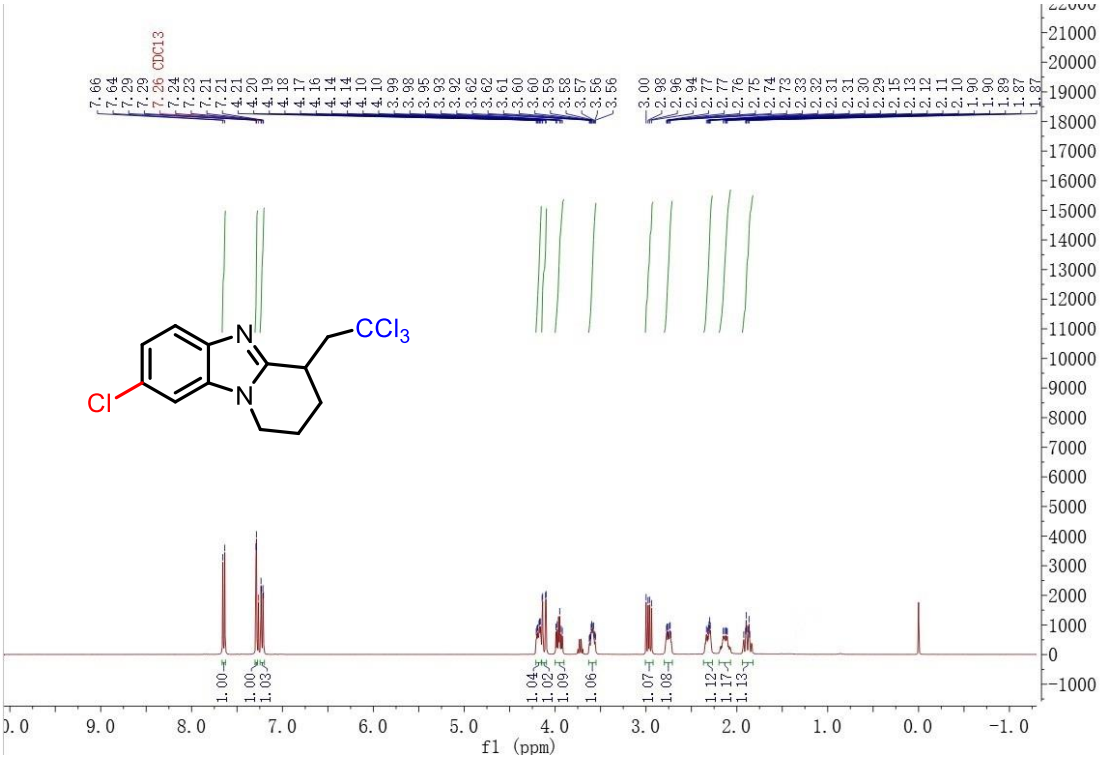


^{13}C NMR of **2g** in $CDCl_3$

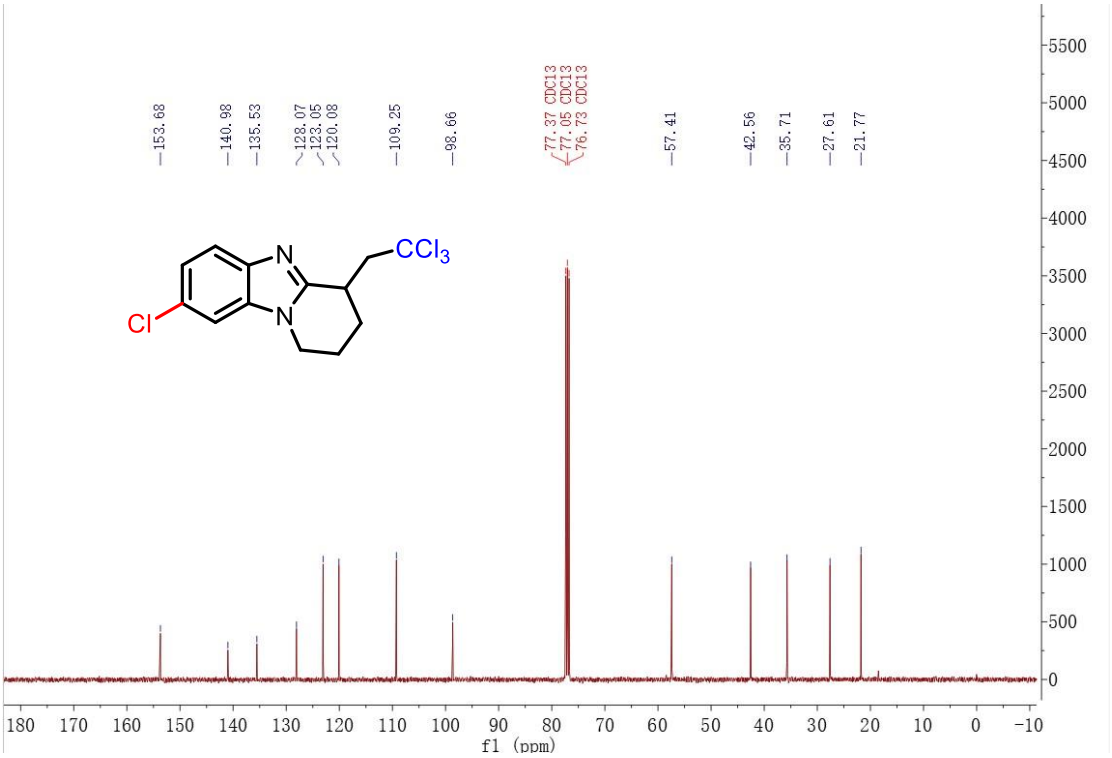


8-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2h)

^{1}H NMR of **2h** in $CDCl_3$

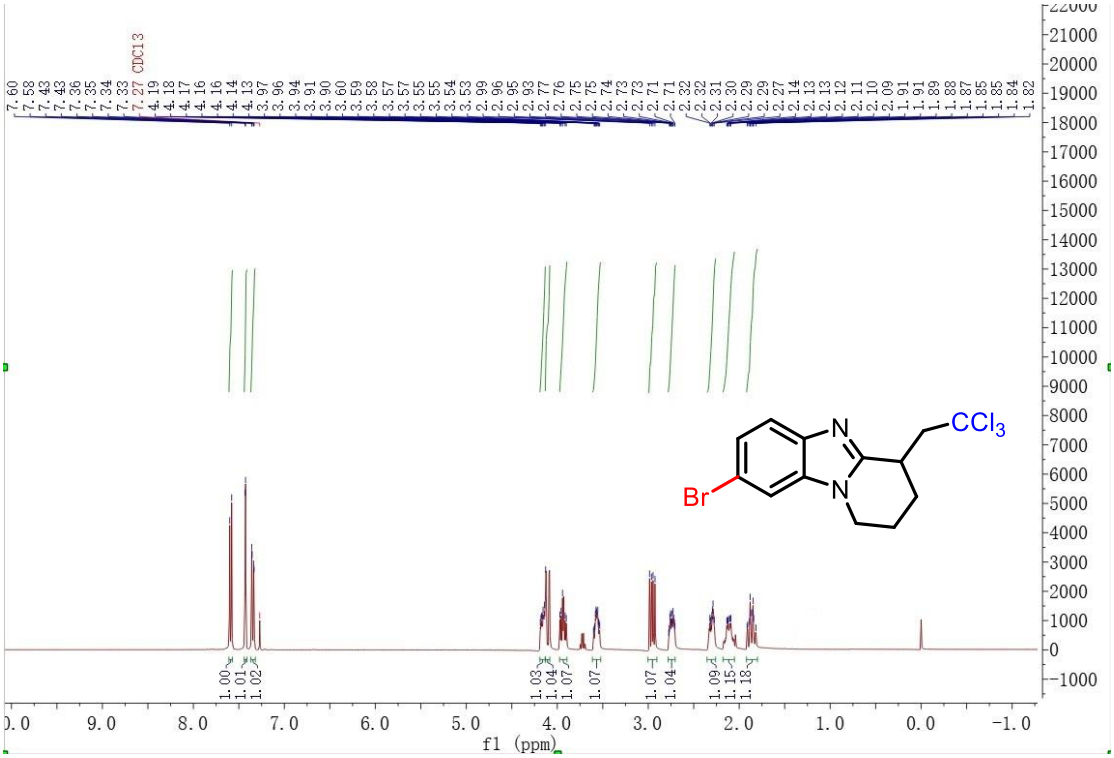


^{13}C NMR of **2h** in $CDCl_3$

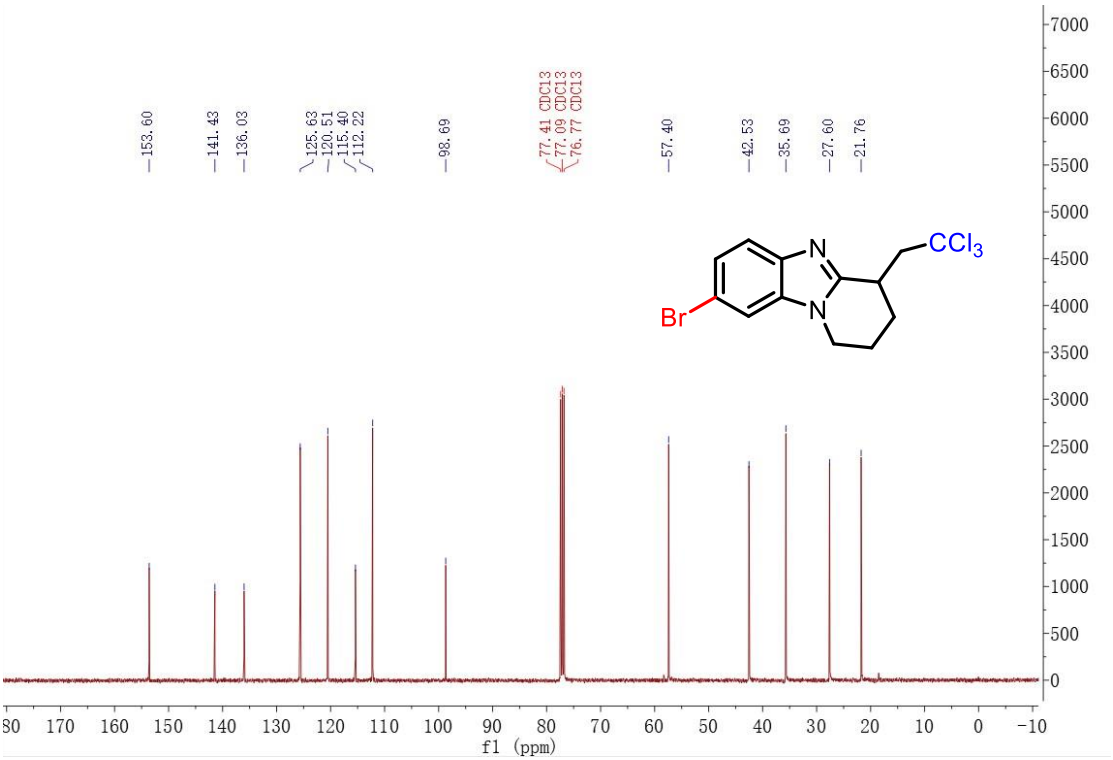


8-bromo-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2i)

^{1}H NMR of **2i** in $CDCl_3$

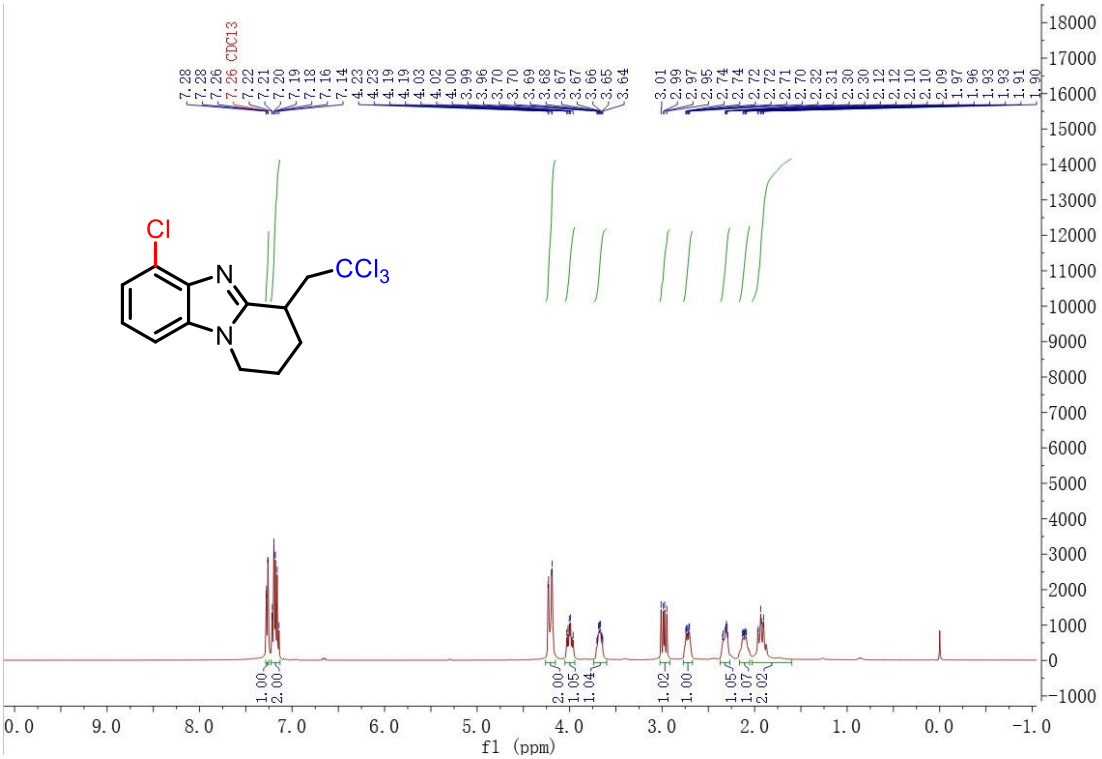


^{13}C NMR of **2i** in $CDCl_3$

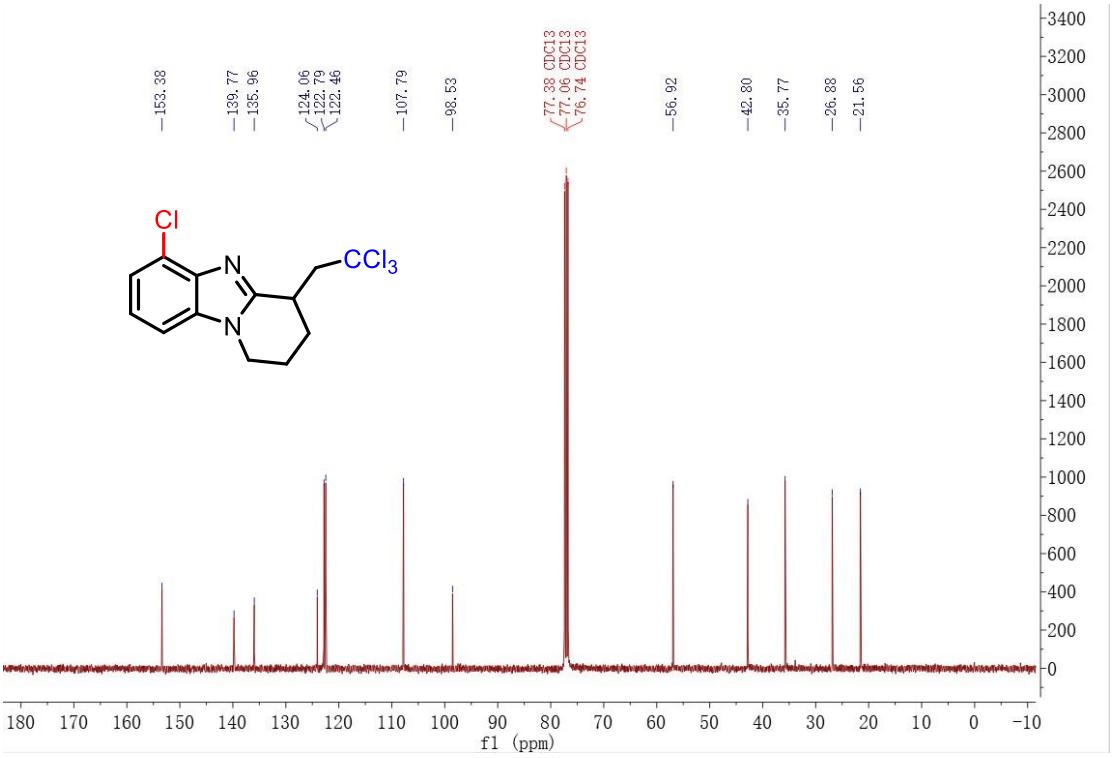


6-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2j)

^{1}H NMR of **2j** in $CDCl_3$

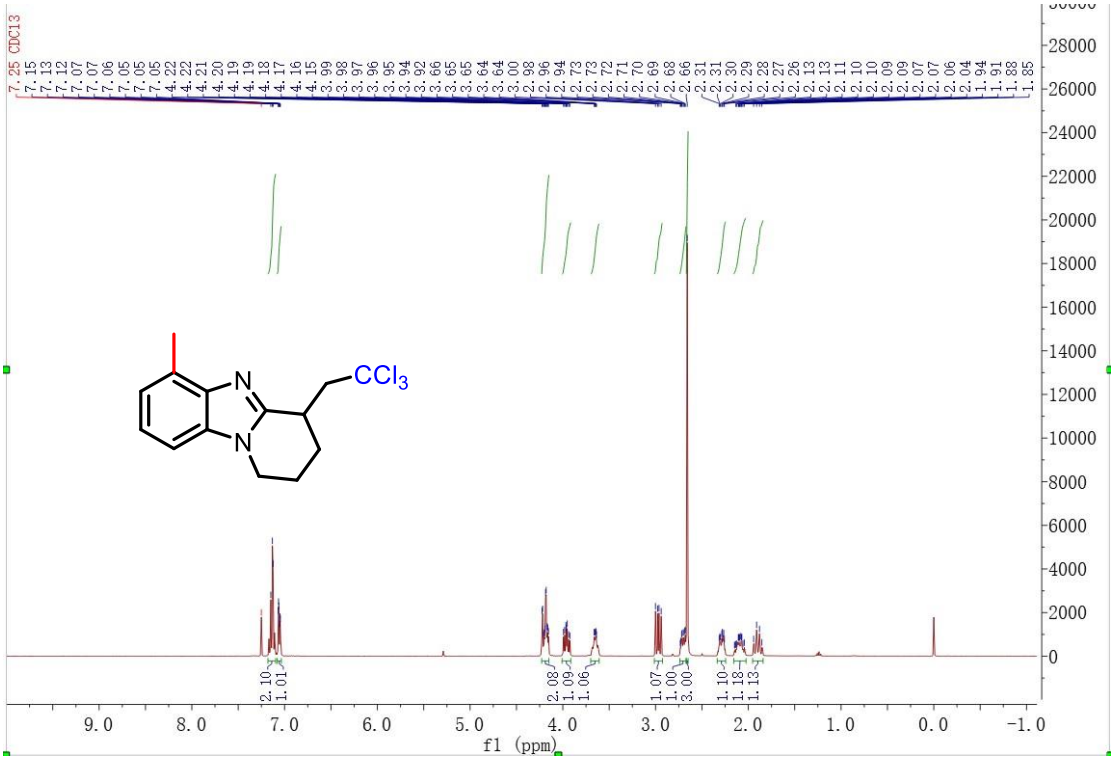


^{13}C NMR of **2j** in $CDCl_3$

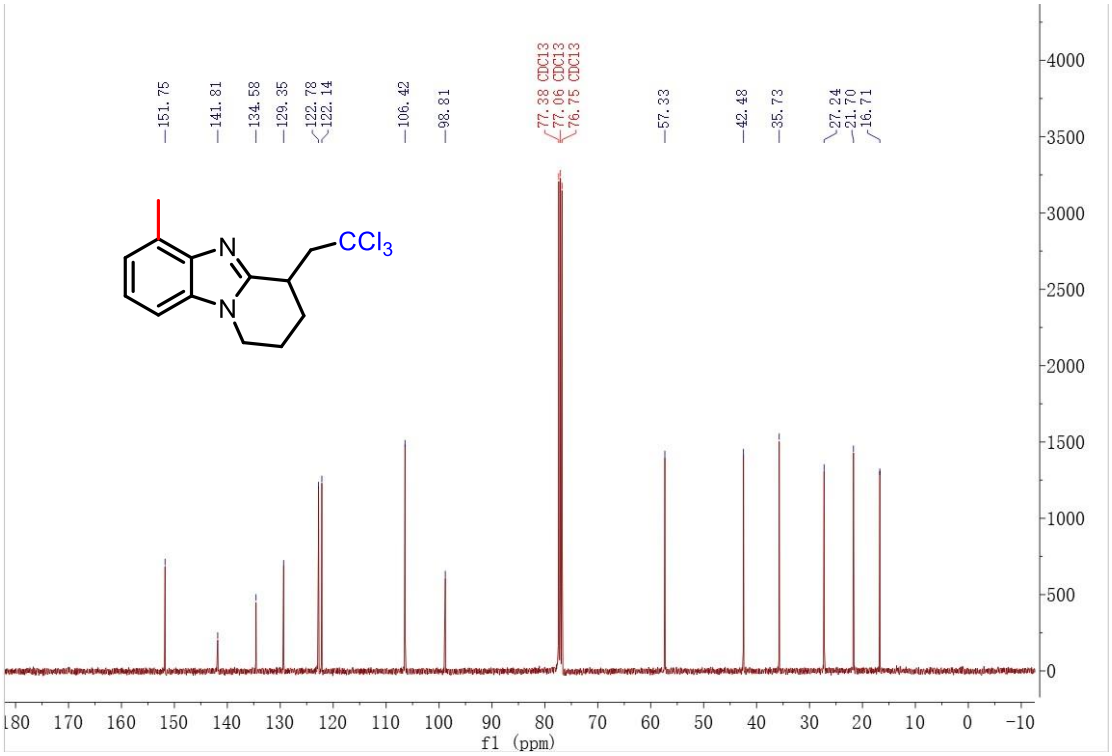


6-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2k)

^{1}H NMR of **2k** in $CDCl_3$

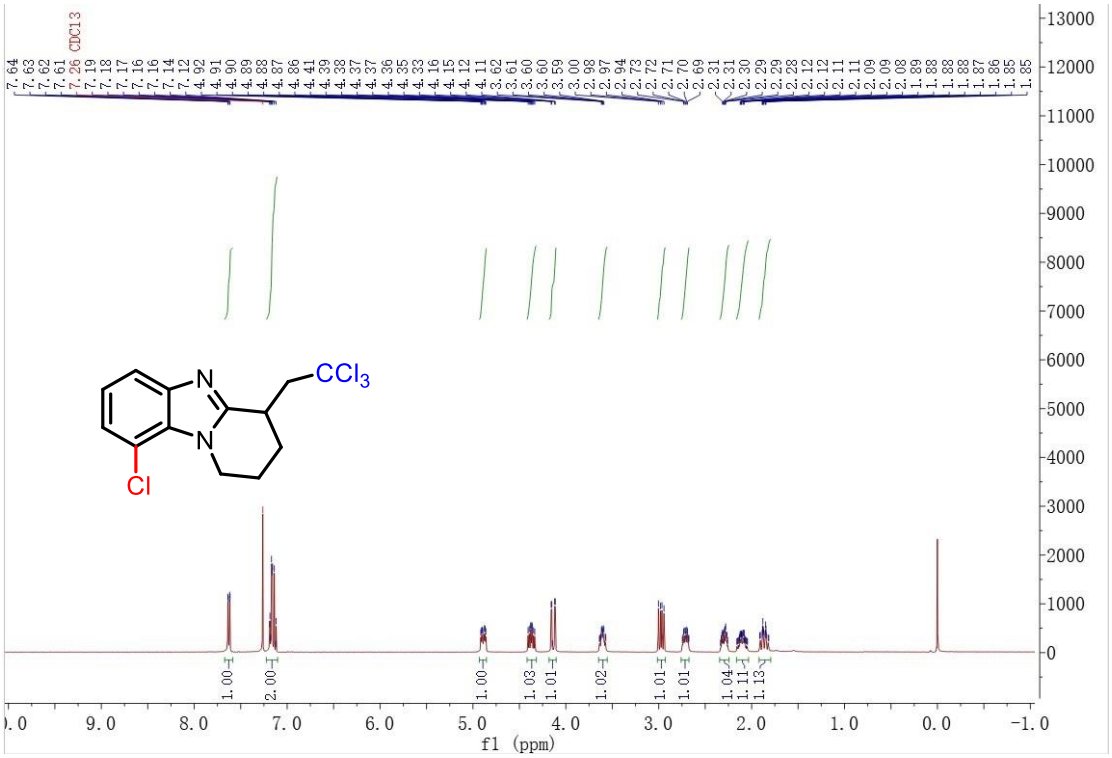


^{13}C NMR of **2k** in $CDCl_3$

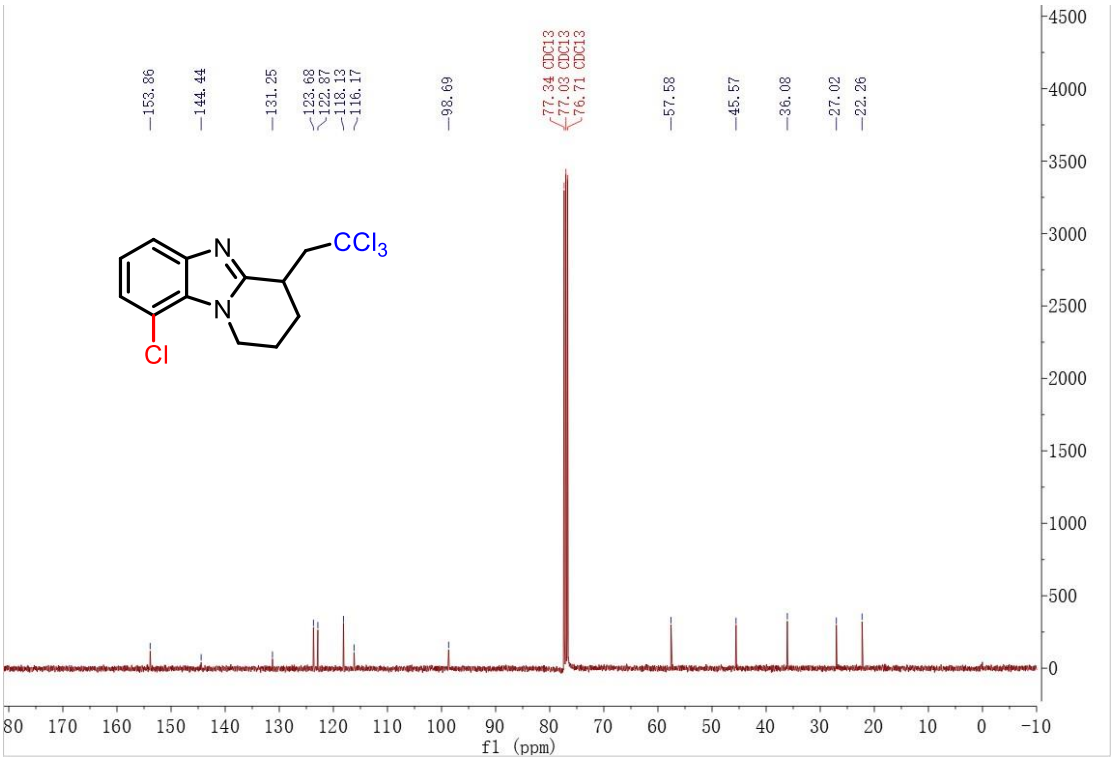


9-chloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2l)

^{1}H NMR of **2l** in $CDCl_3$

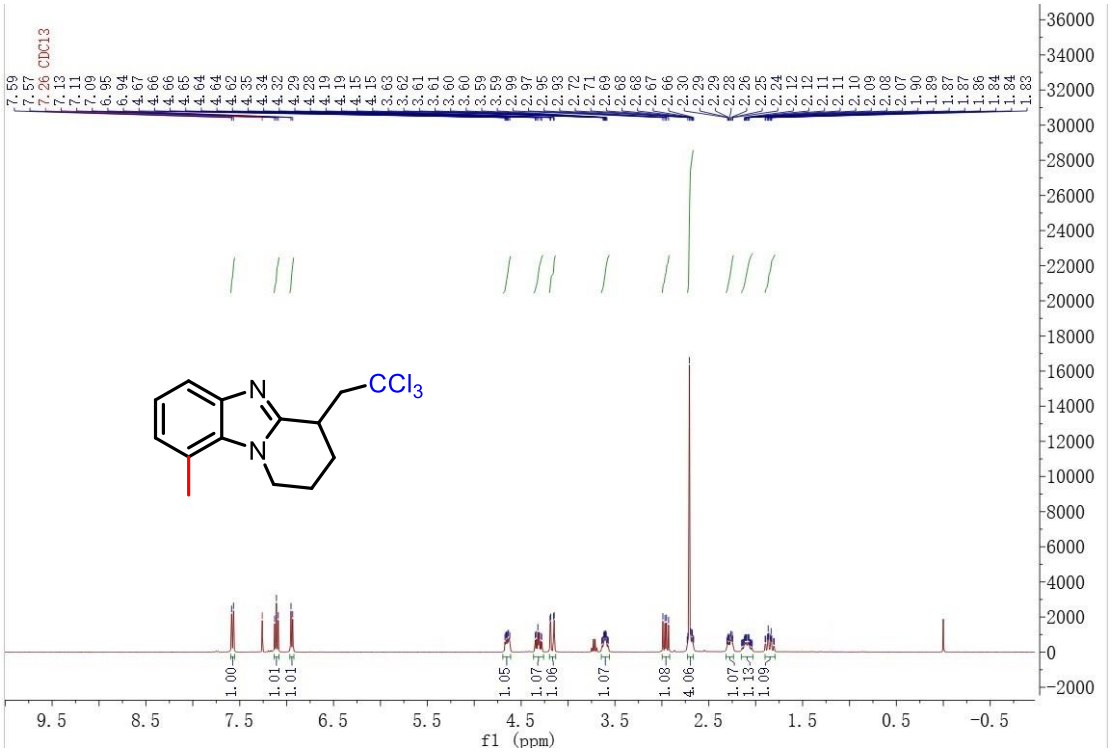


^{13}C NMR of **2l** in $CDCl_3$

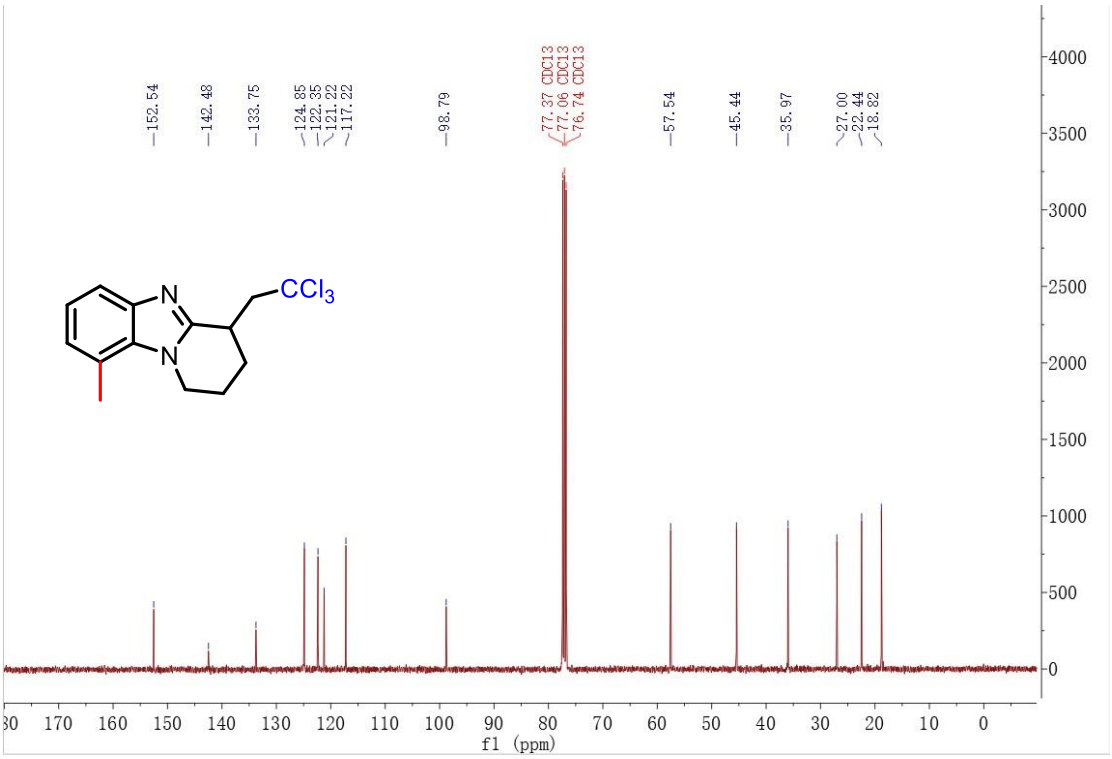


9-methyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2m)

^{1}H NMR of **2m** in $CDCl_3$

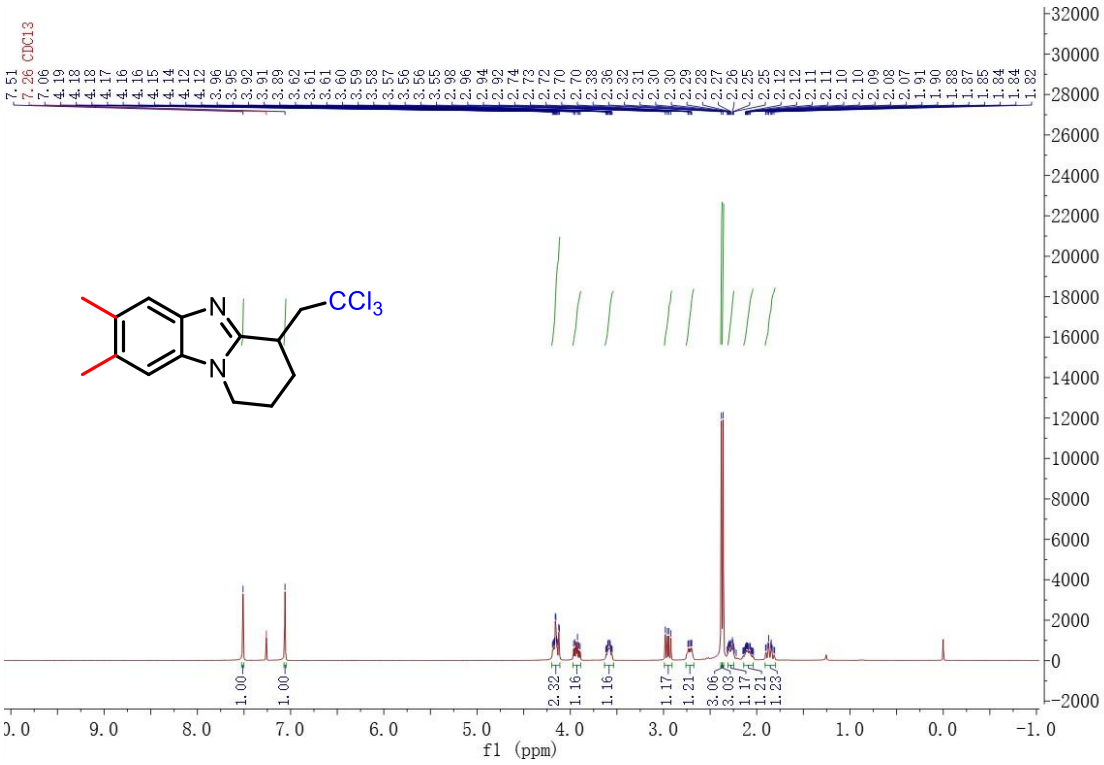


^{13}C NMR of **2m** in $CDCl_3$

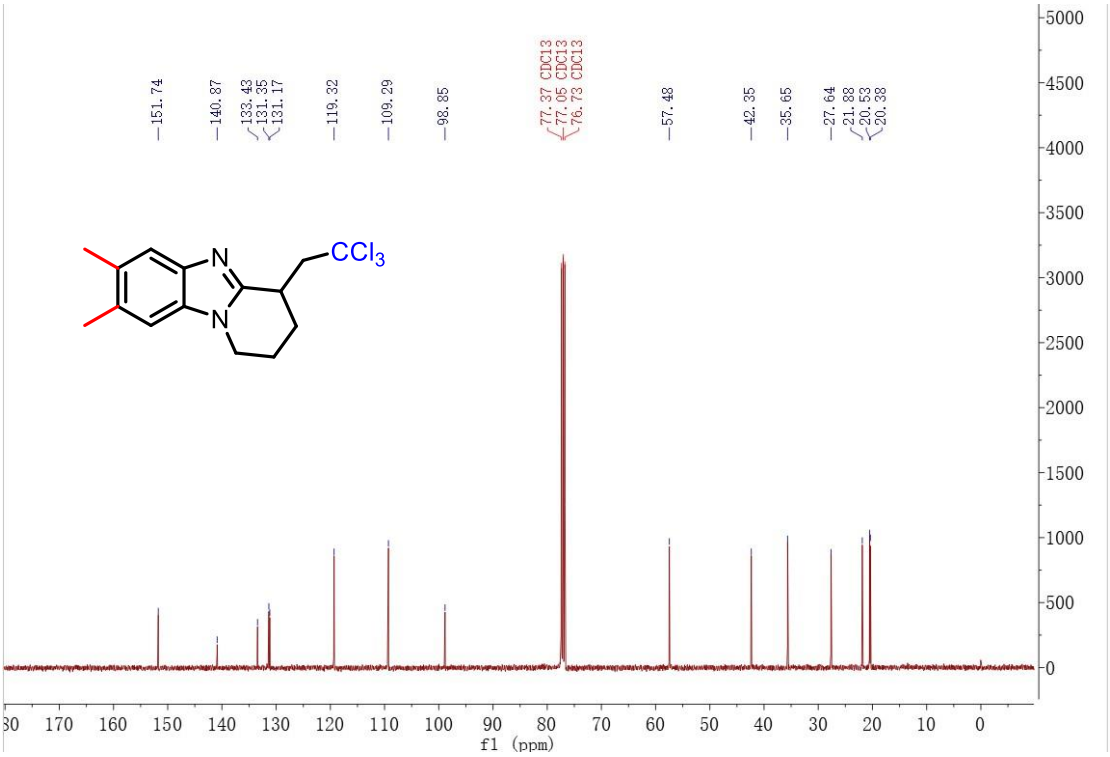


7,8-dimethyl-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2n)

^{1}H NMR of **2n** in $CDCl_3$

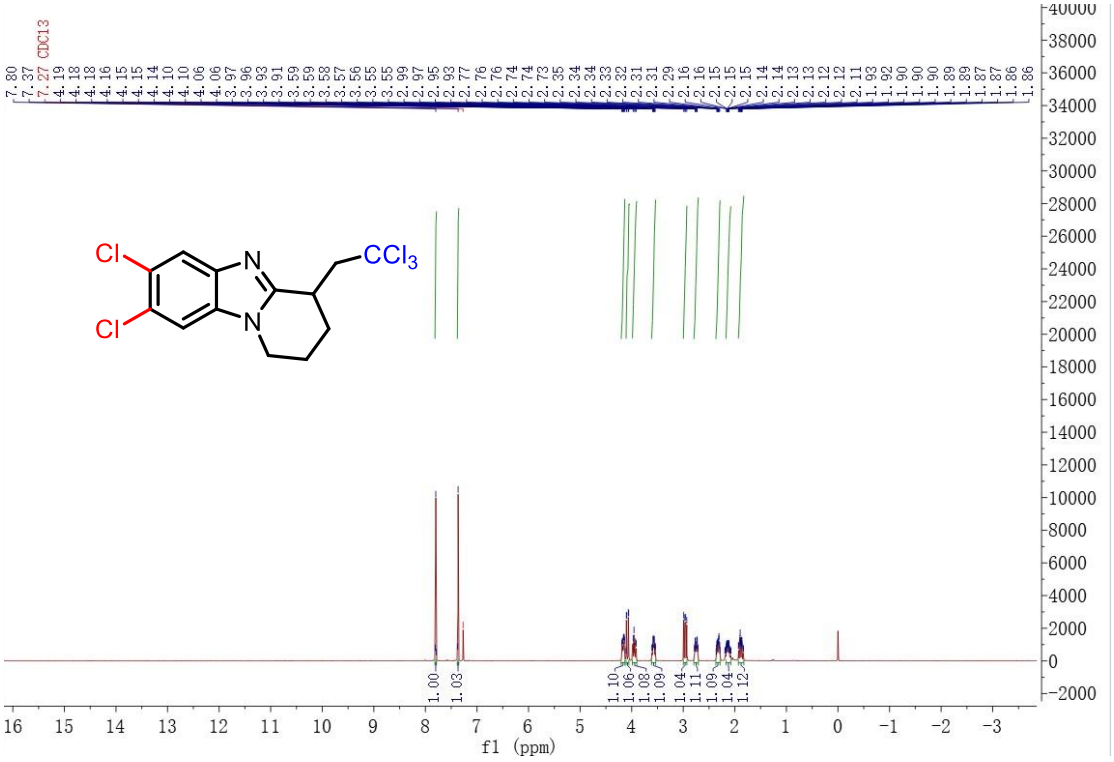


^{13}C NMR of **2n** in $CDCl_3$

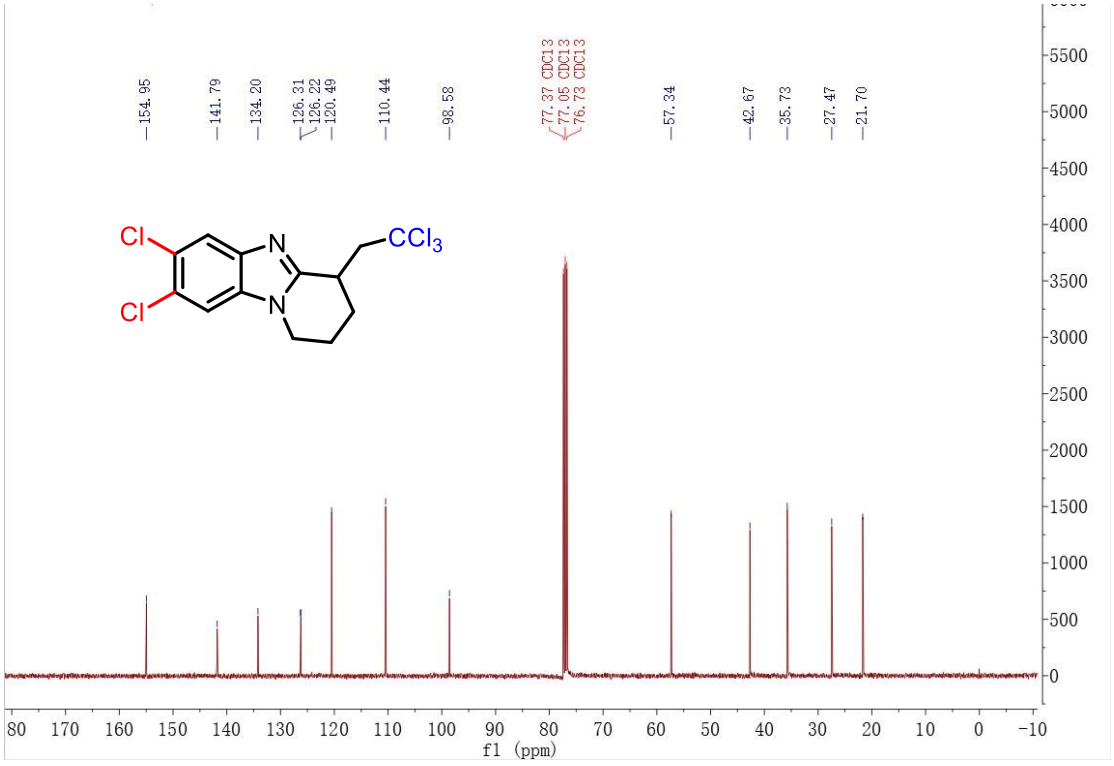


7,8-dichloro-4-(2,2,2-trichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (2o)

^{1}H NMR of **2o** in $CDCl_3$

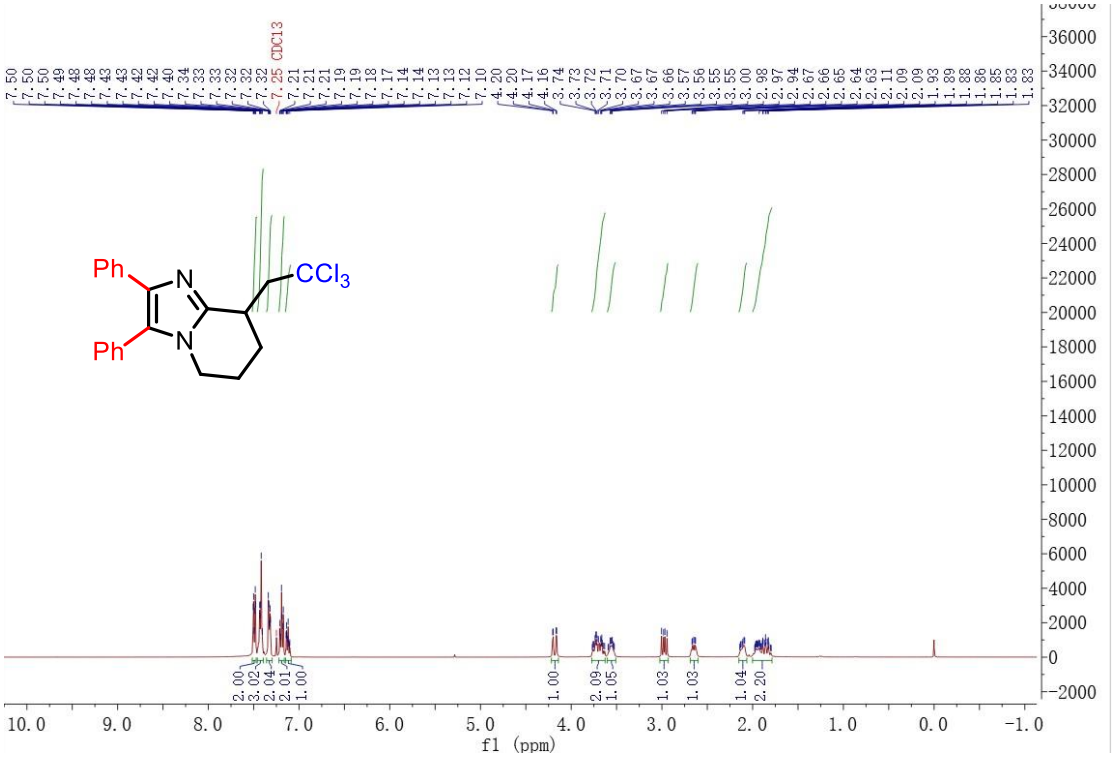


^{13}C NMR of **2o** in $CDCl_3$

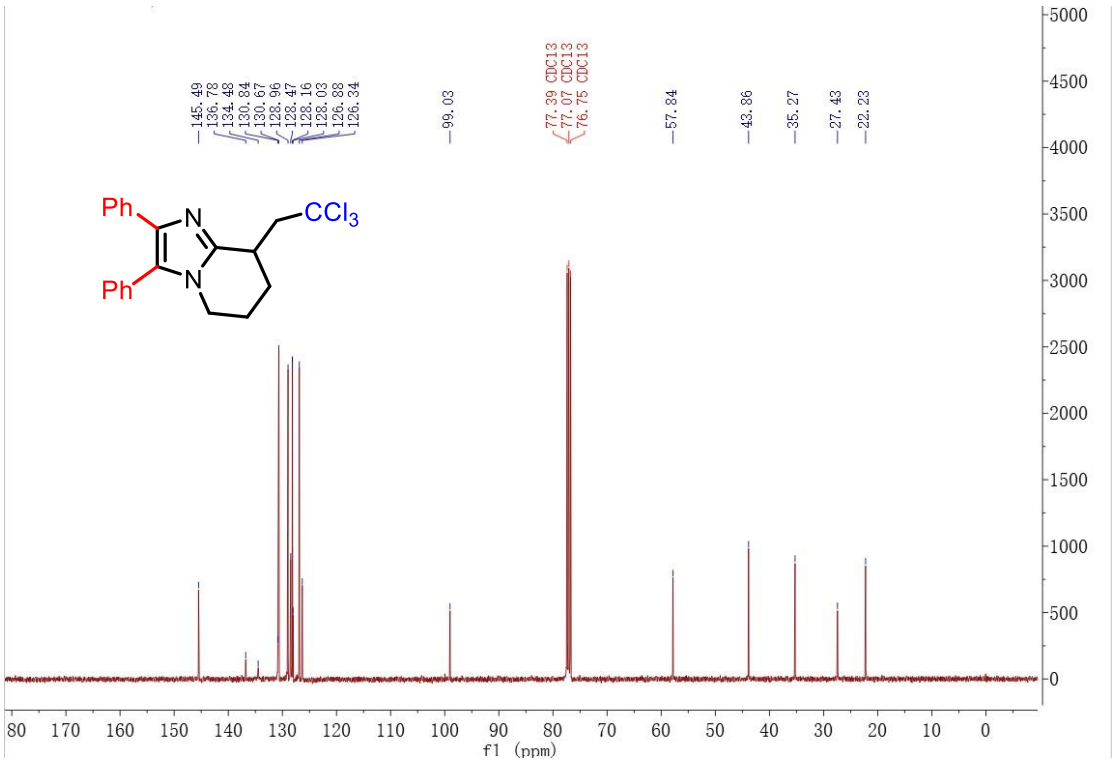


2,3-diphenyl-8-(2,2,2-trichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (2p)

^{1}H NMR of **2p** in $CDCl_3$

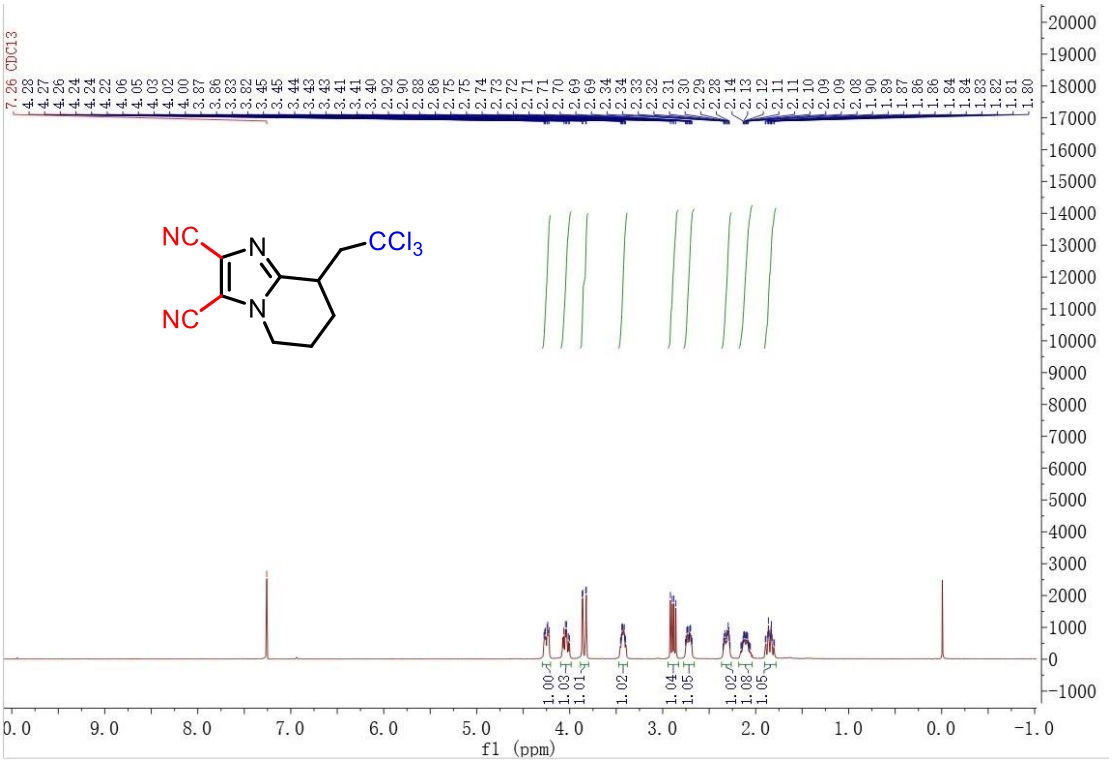


^{13}C NMR of **2p** in $CDCl_3$

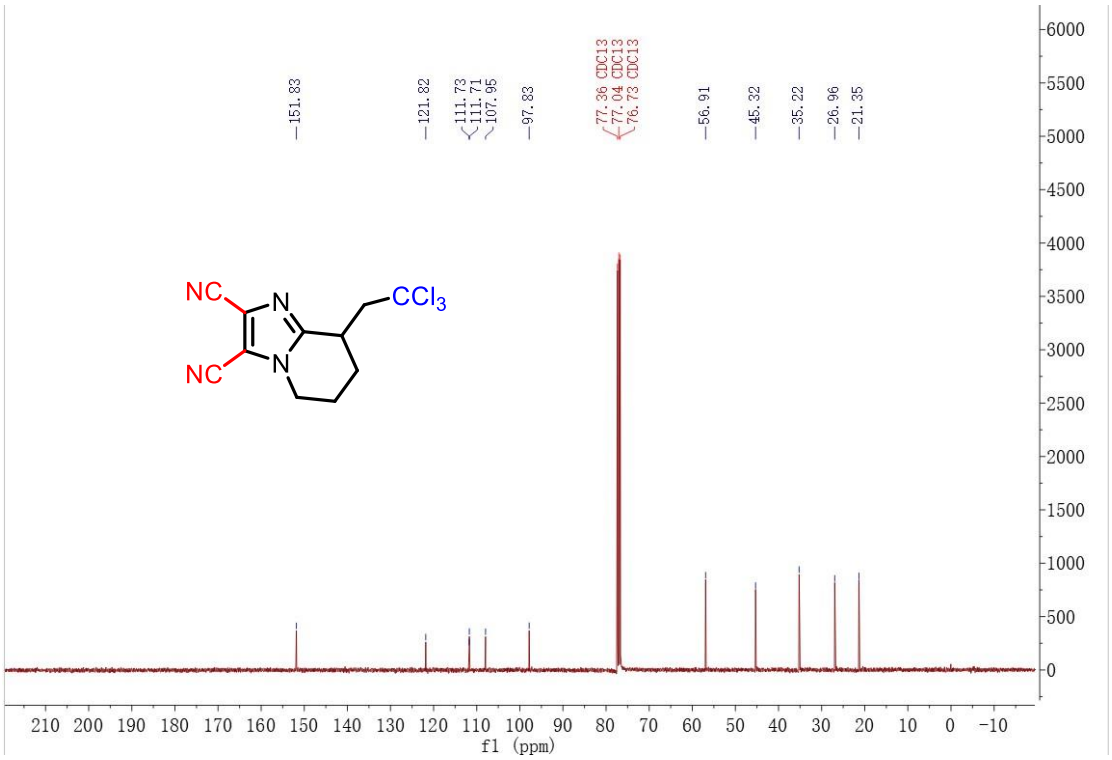


8-(2,2,2-trichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-2,3-dicarbonitrile (2q)

^{1}H NMR of **2q** in $CDCl_3$

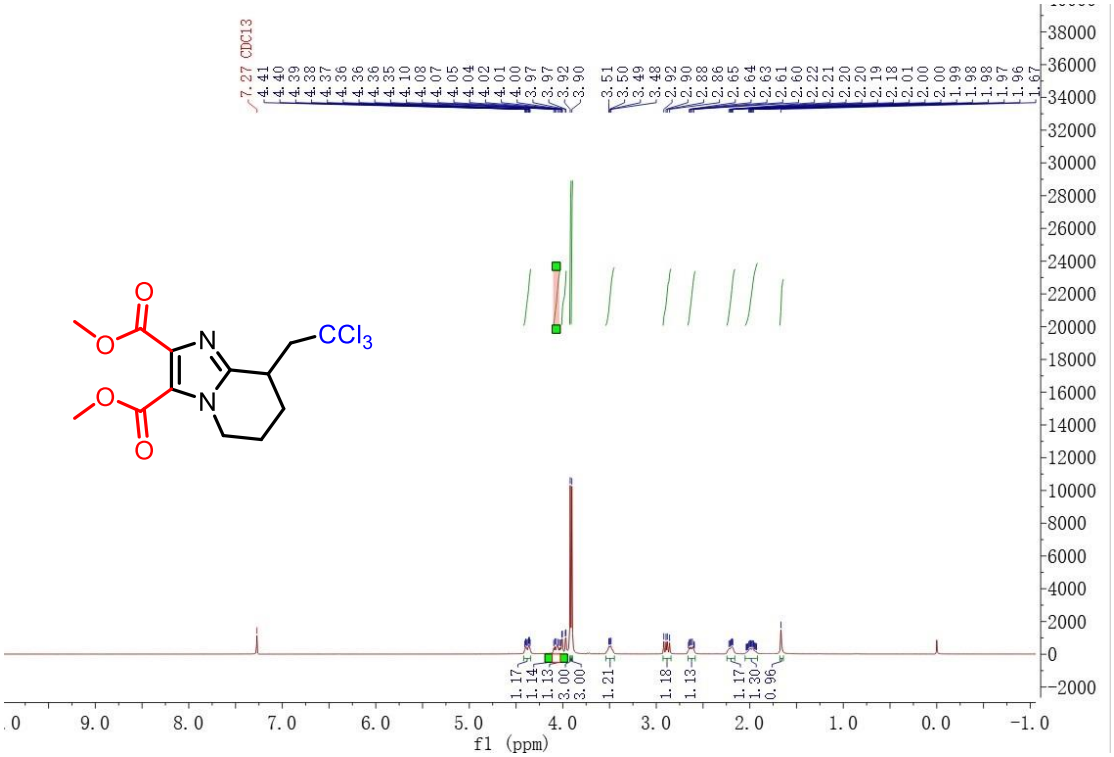


^{13}C NMR of **2q** in $CDCl_3$

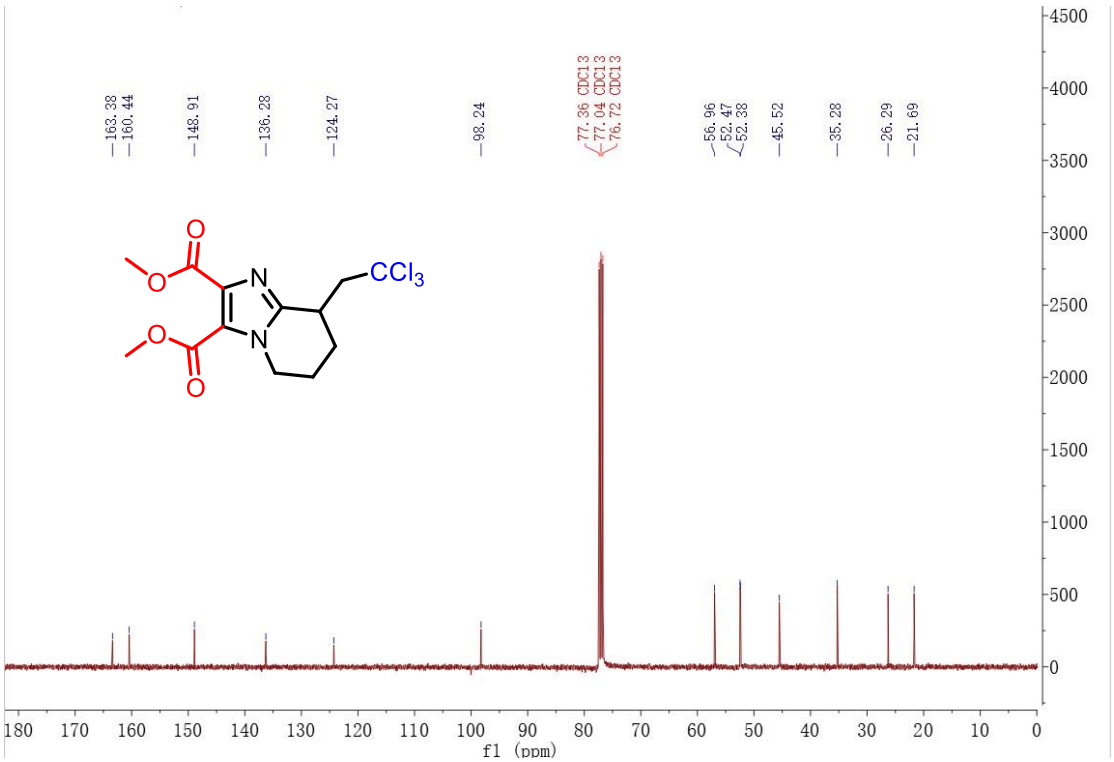


dimethyl 8-(2,2,2-trichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-2,3-dicarboxylate (2r)

^{1}H NMR of **2ra** in $CDCl_3$

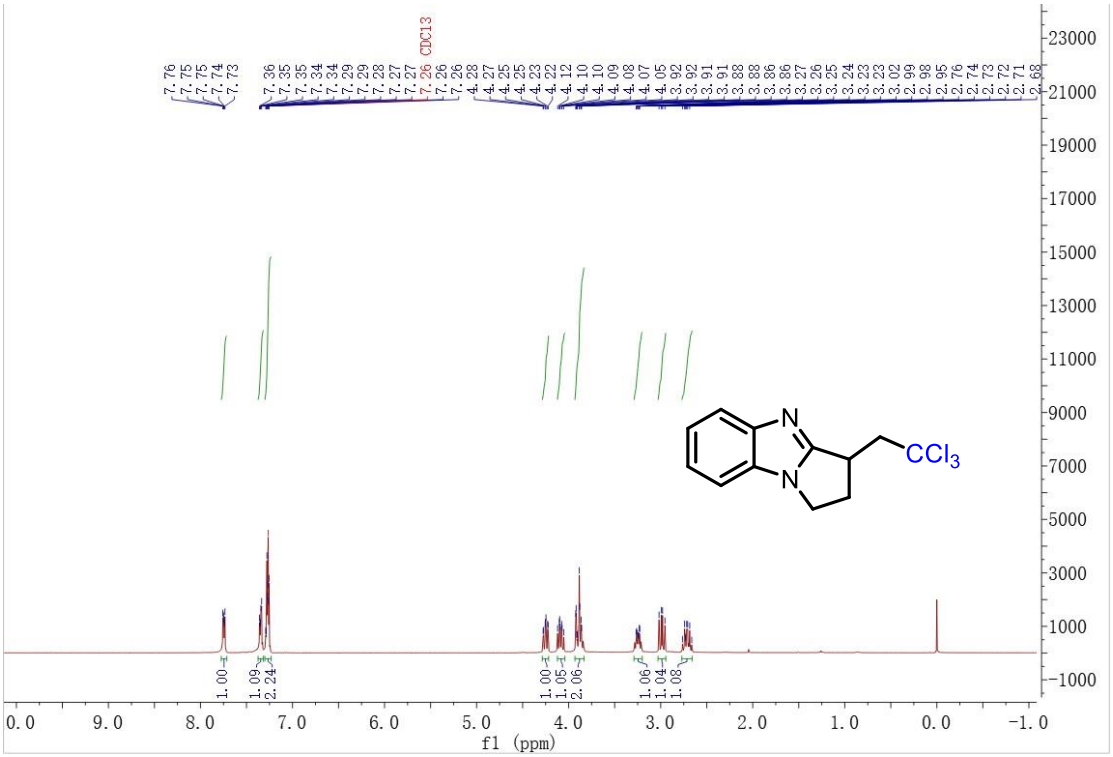


^{13}C NMR of **2r** in $CDCl_3$

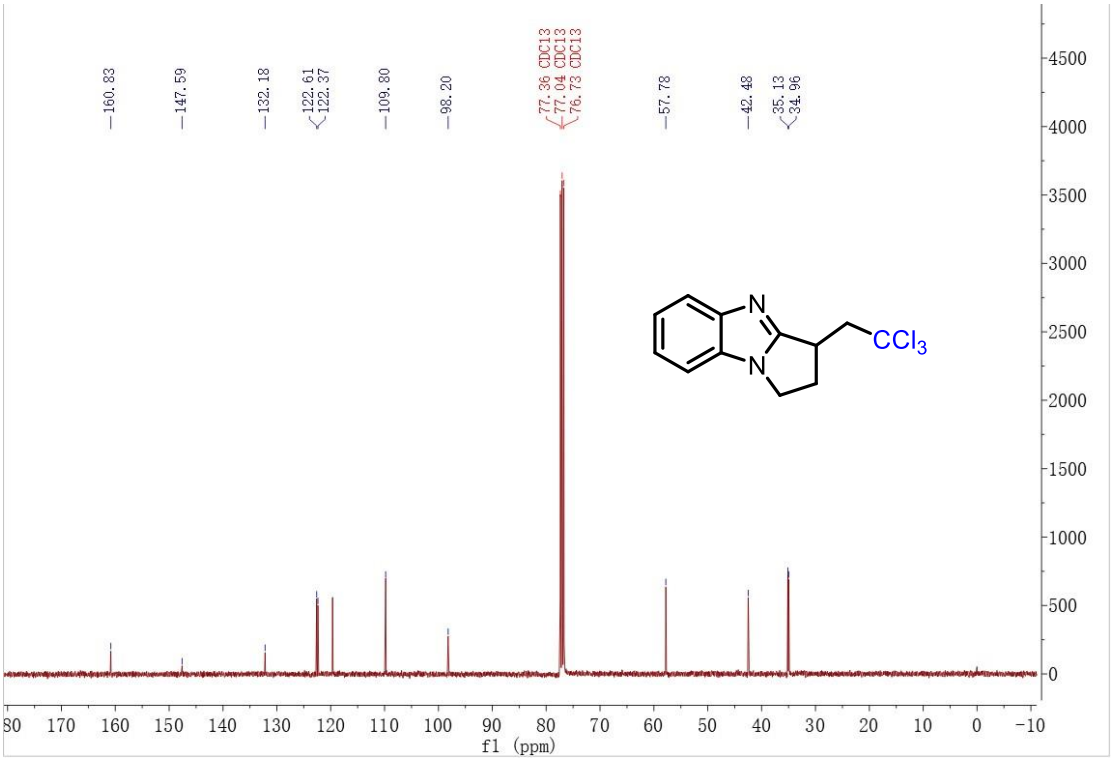


3-(2,2,2-trichloroethyl)-2,3-dihydro-1H-benzo[d]pyrrolo[1,2-a]imidazole (2s)

^{1}H NMR of **2s** in $CDCl_3$

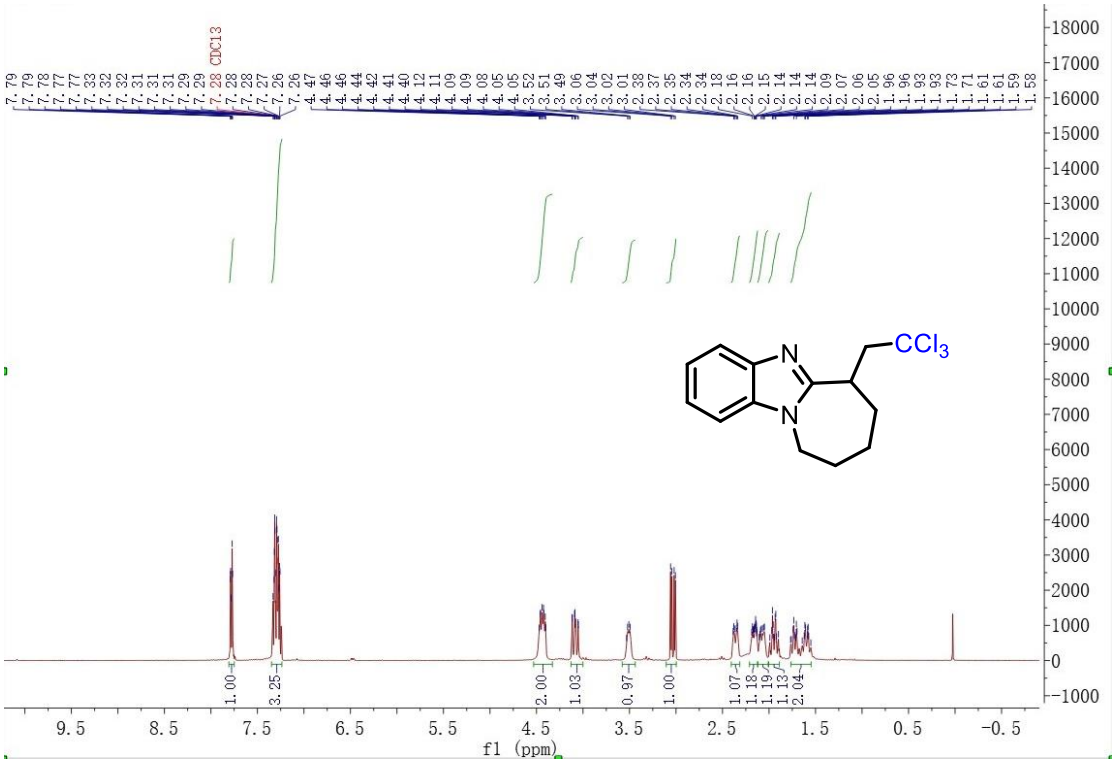


^{13}C NMR of **2s** in $CDCl_3$

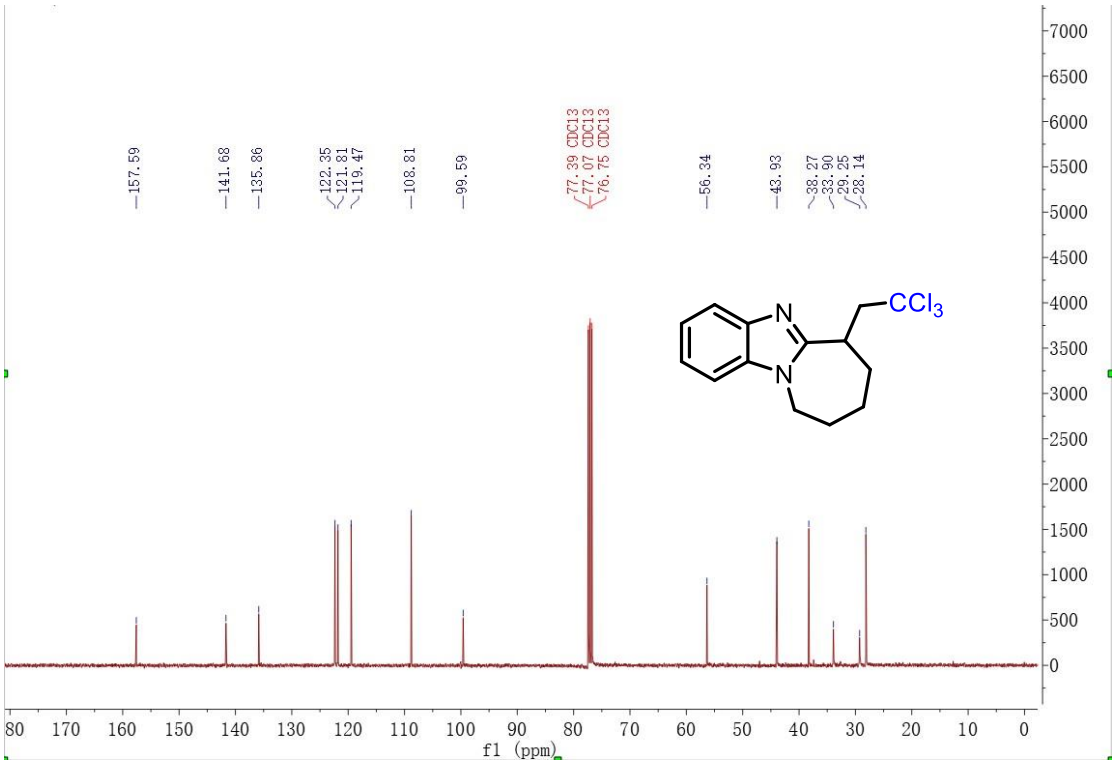


6-(2,2,2-trichloroethyl)-7,8,9,10-tetrahydro-6H-benzo[4,5]imidazo[1,2-a]azepine (2t)

^{1}H NMR of **2t** in $CDCl_3$

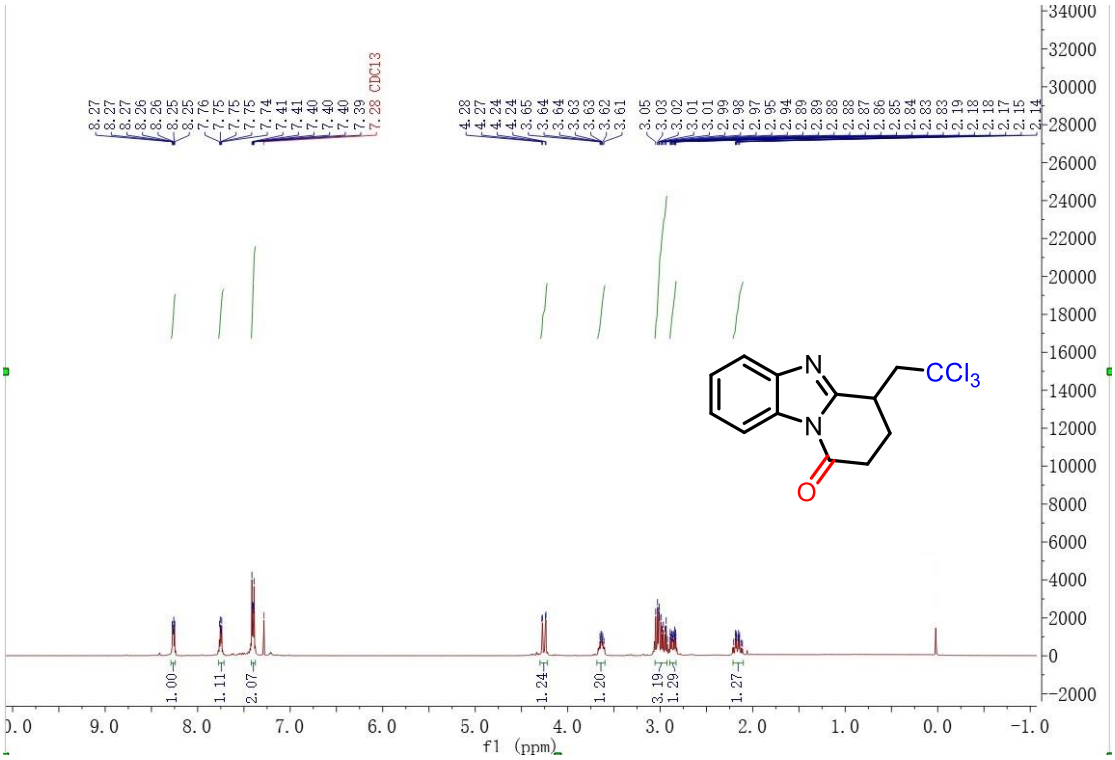


^{13}C NMR of **2t** in $CDCl_3$

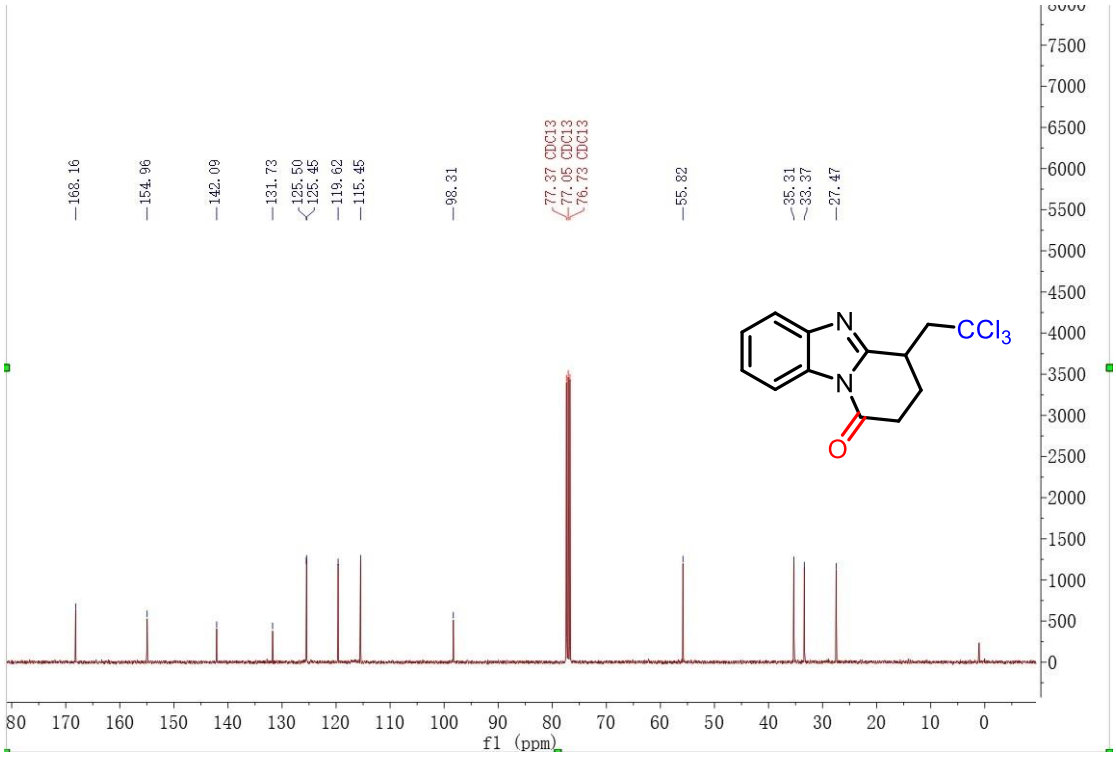


4-(2,2,2-trichloroethyl)-3,4-dihydrobenzo[4,5]imidazo[1,2-*a*]pyridin-1(2*H*)-one(2w)

^{1}H NMR of **2w** in $CDCl_3$

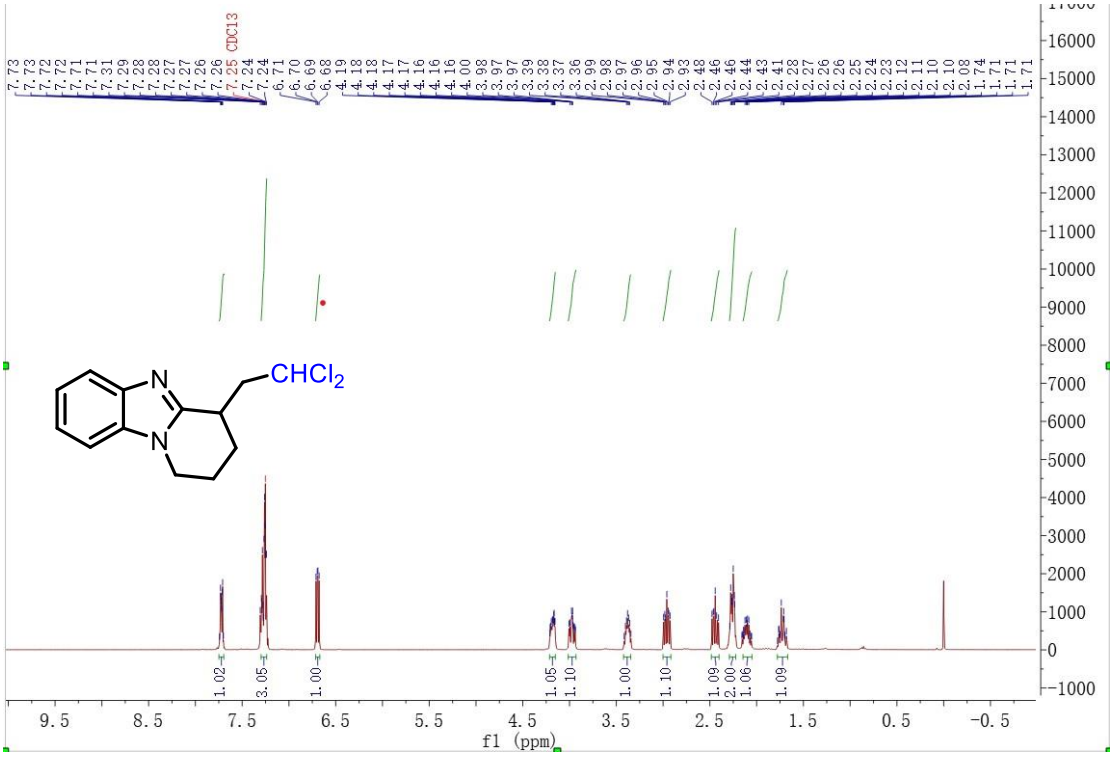


^{13}C NMR of **2w** in $CDCl_3$

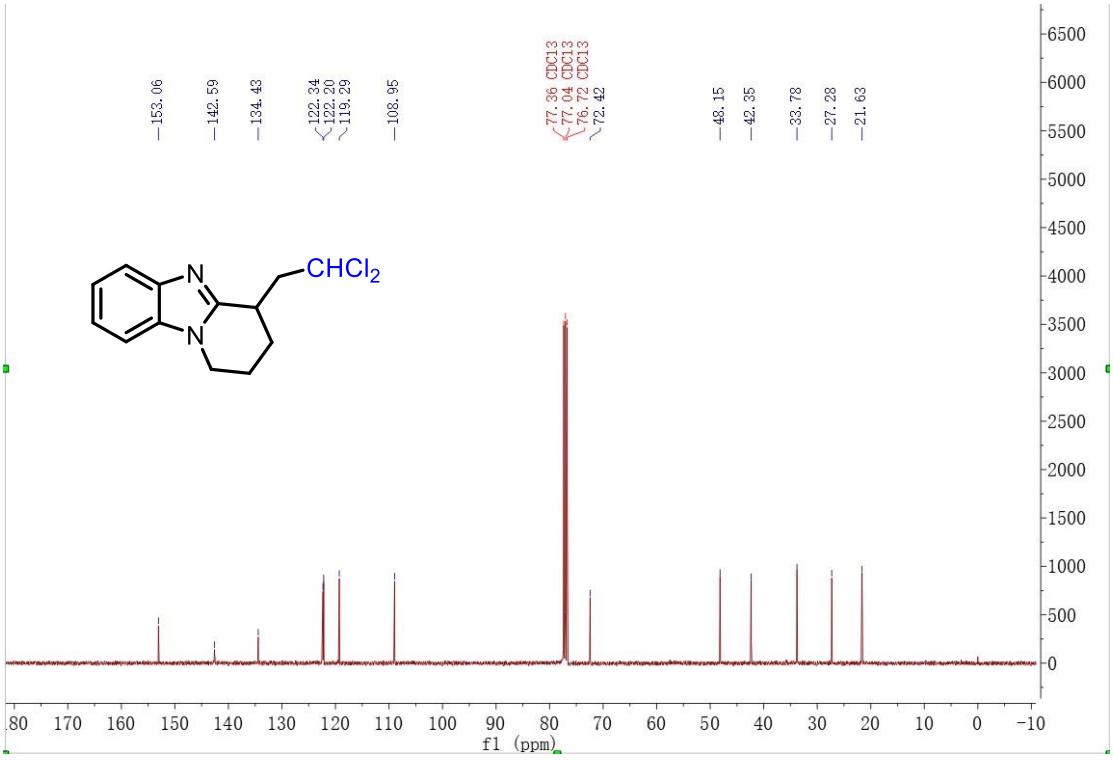


4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3a)

^{1}H NMR of **3a** in $CDCl_3$

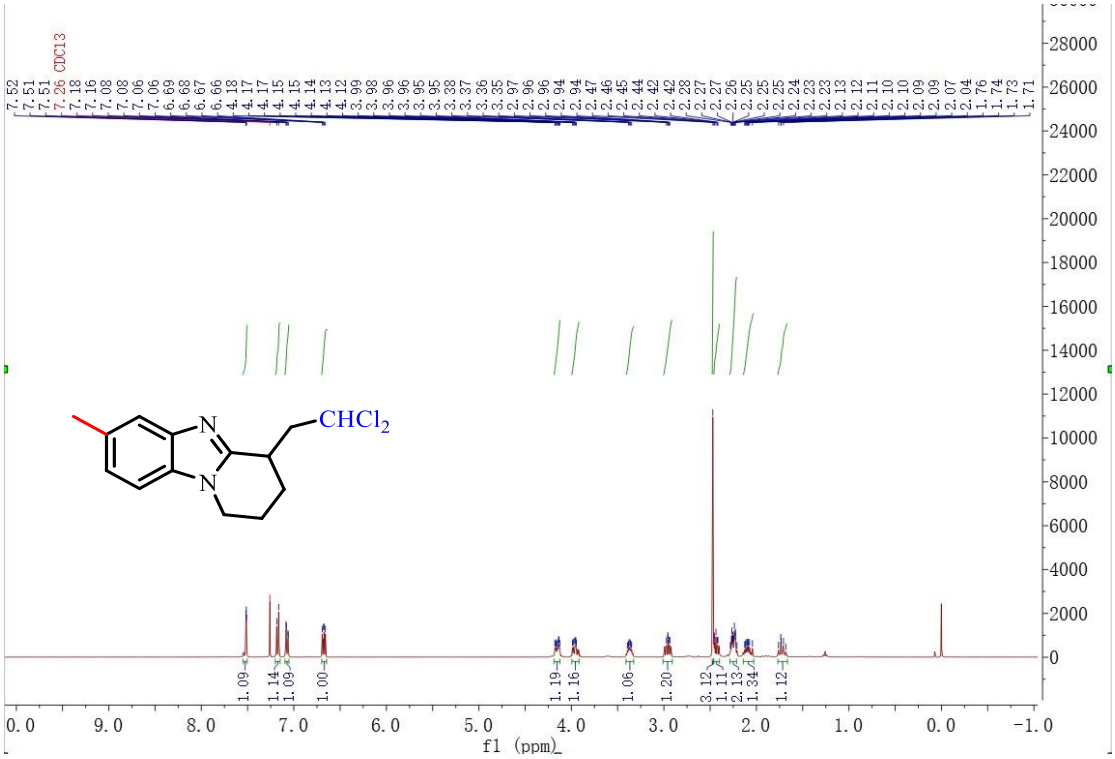


^{13}C NMR of **3a** in $CDCl_3$

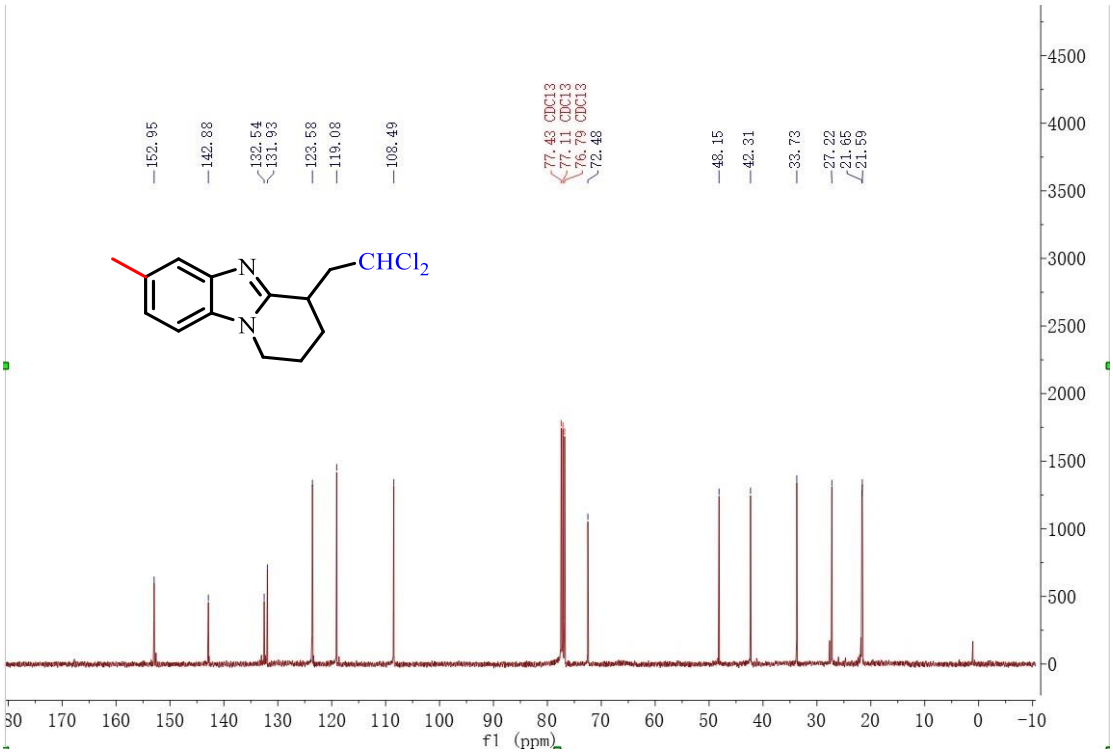


4-(2,2-dichloroethyl)-7-methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3b)

^{1}H NMR of **3b** in $CDCl_3$

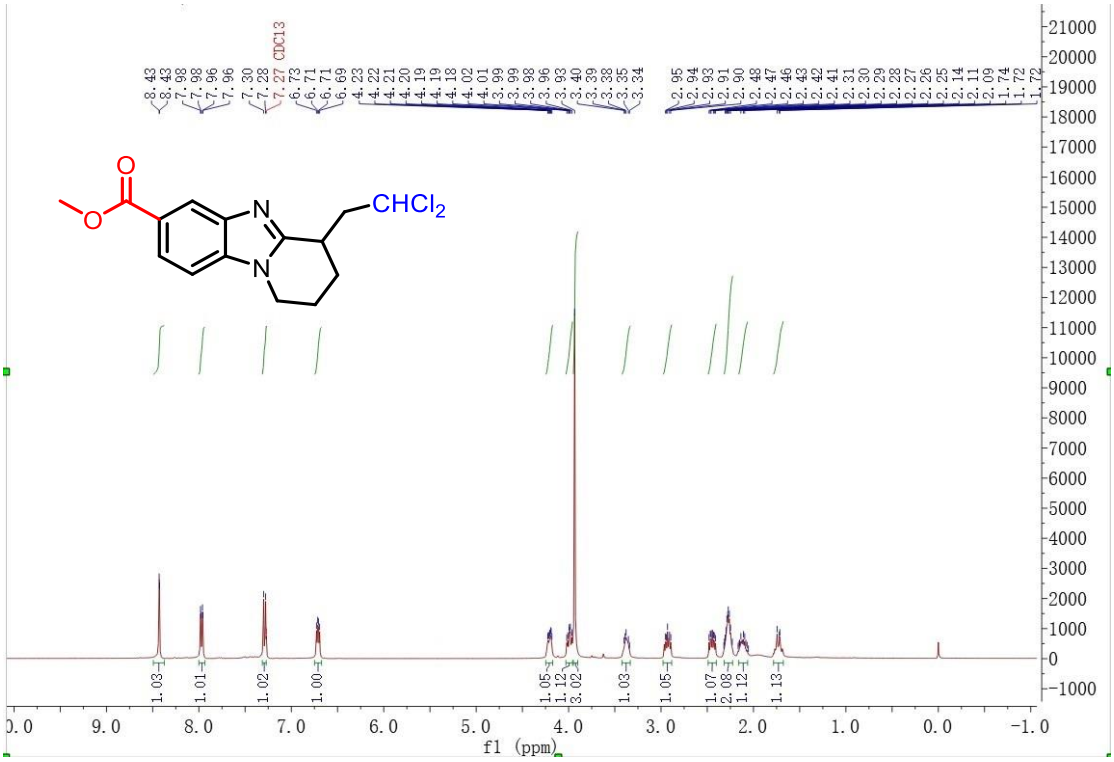


^{13}C NMR of **3b** in $CDCl_3$

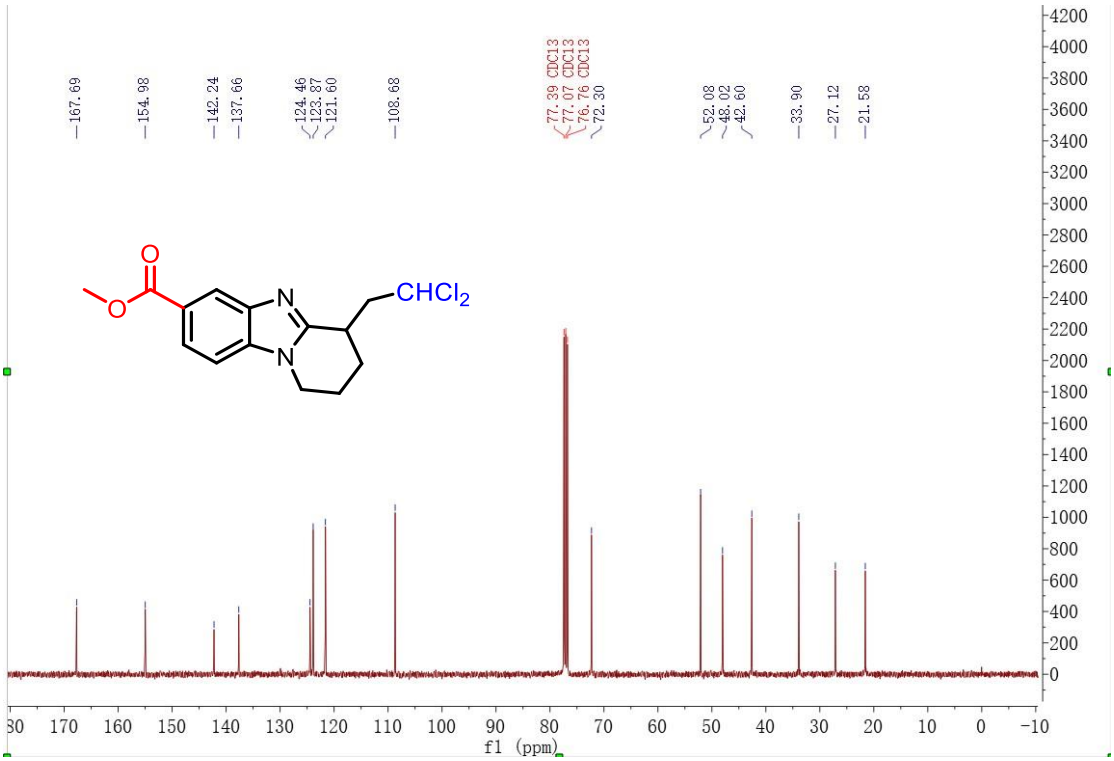


methyl 4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine-7-carboxylate (3c)

^{1}H NMR of **3c** in $CDCl_3$

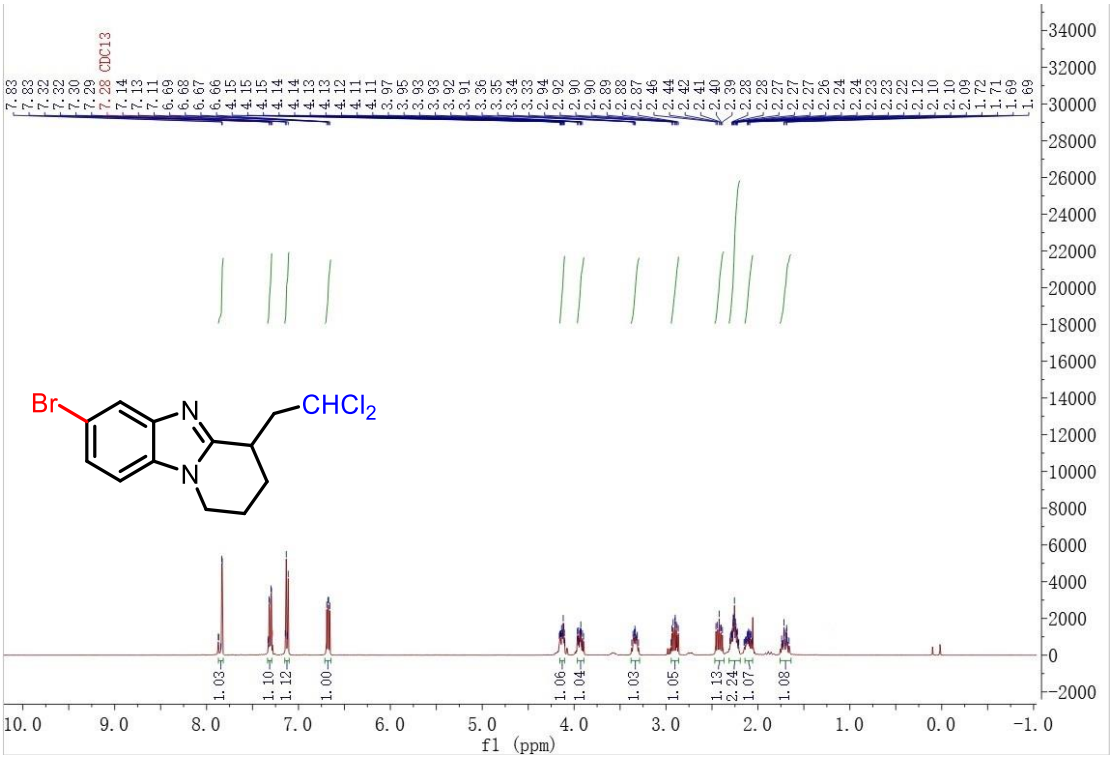


^{13}C NMR of **3c** in $CDCl_3$

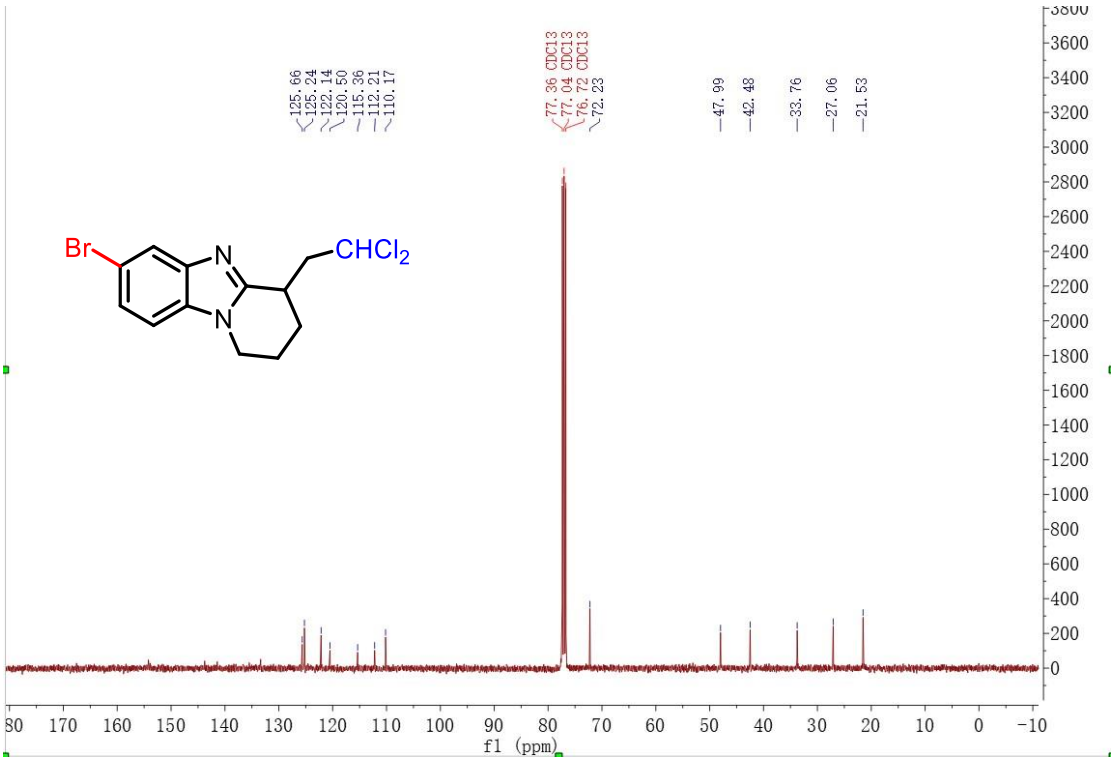


7-bromo-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3d)

^{1}H NMR of **3d** in $CDCl_3$

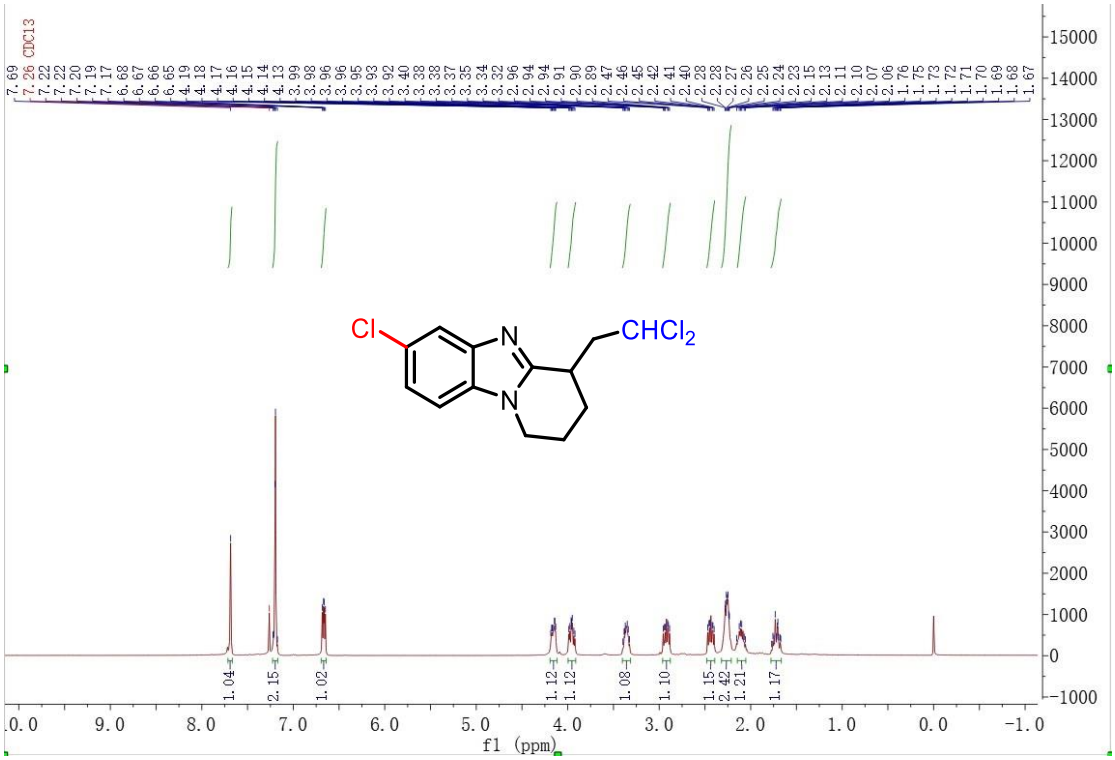


^{13}C NMR of **3d** in $CDCl_3$

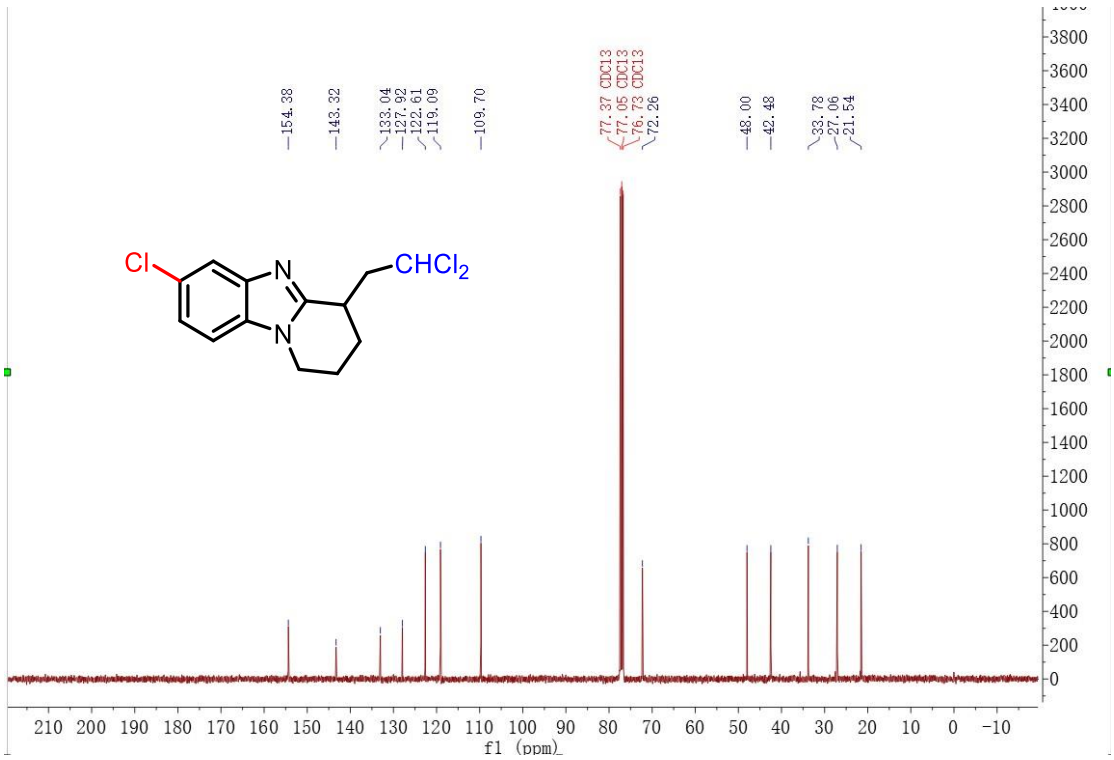


7-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3e)

^{1}H NMR of **3e** in $CDCl_3$

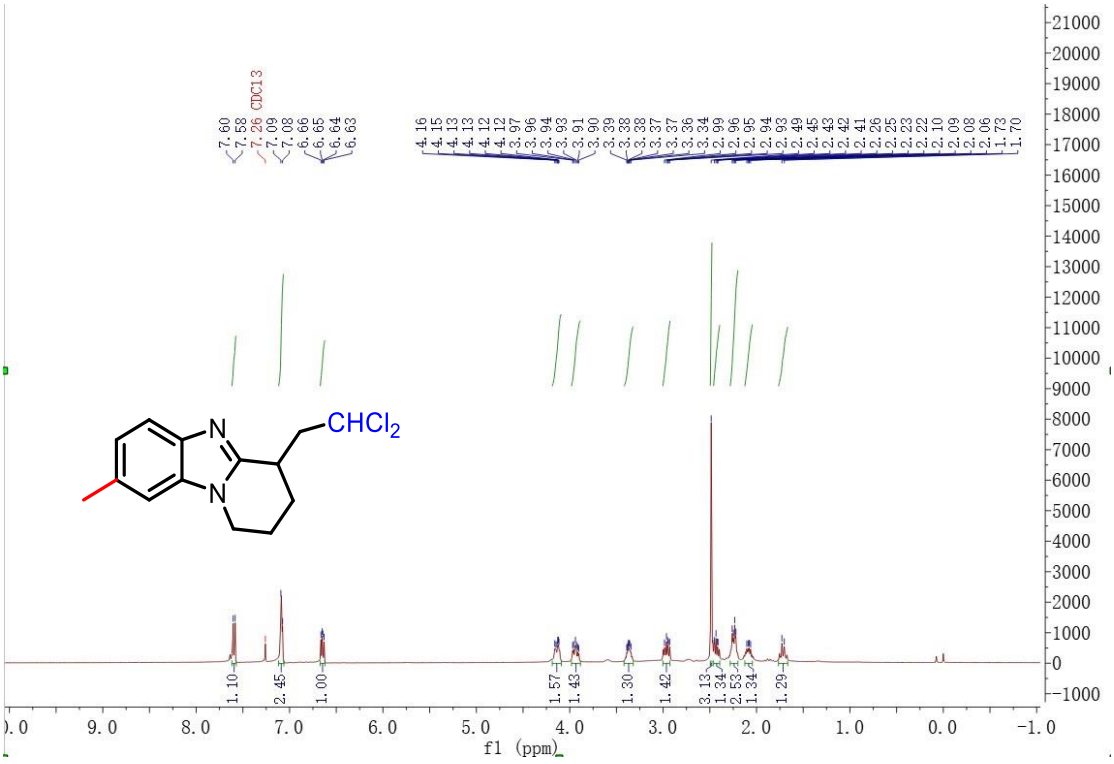


^{13}C NMR of **3e** in $CDCl_3$

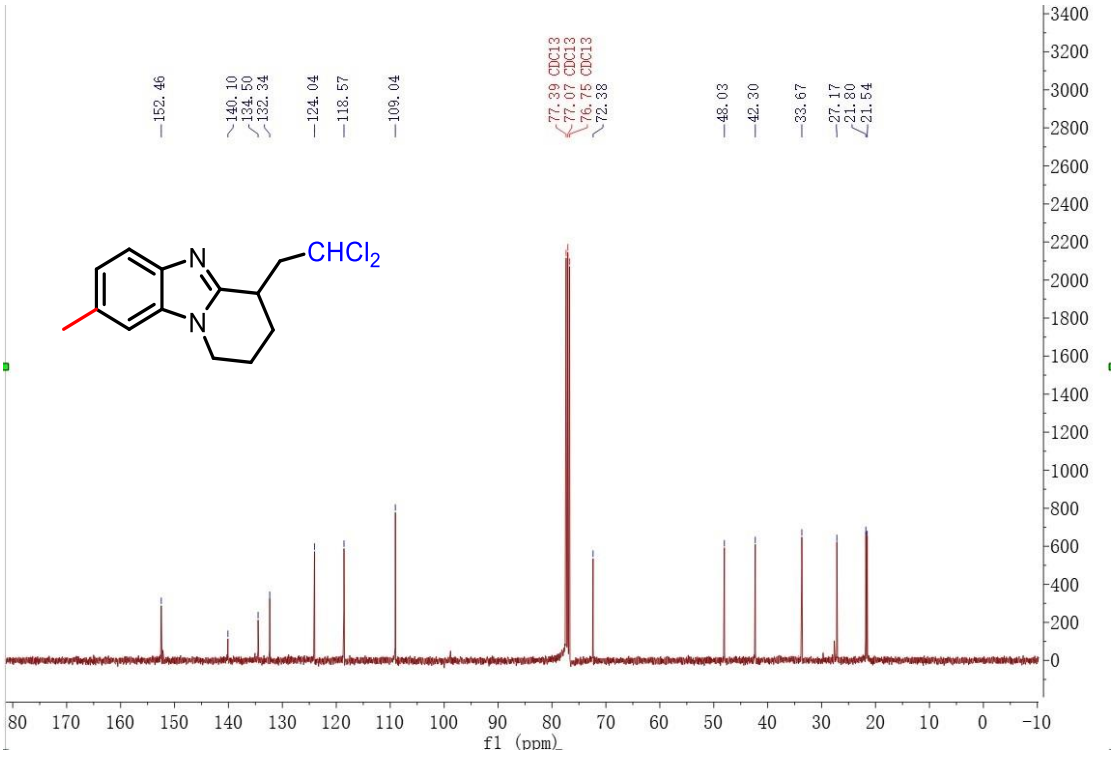


4-(2,2-dichloroethyl)-8-methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3f)

^{1}H NMR of **3f** in $CDCl_3$

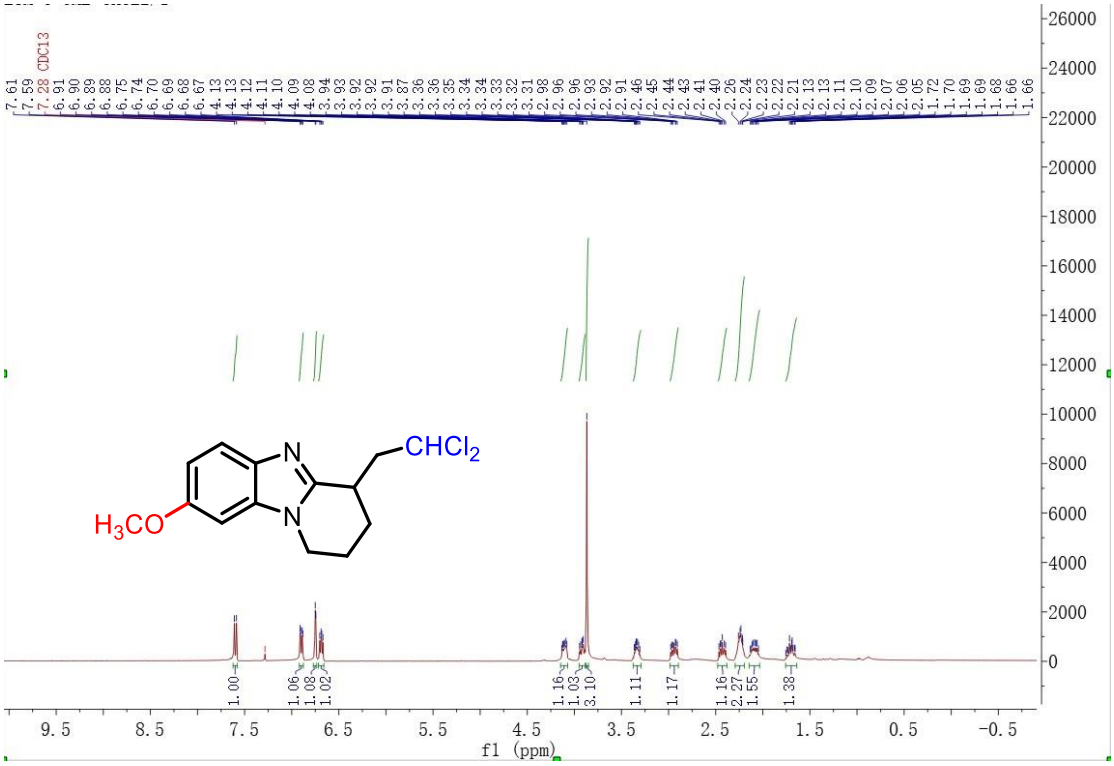


^{13}C NMR of **3f** in $CDCl_3$

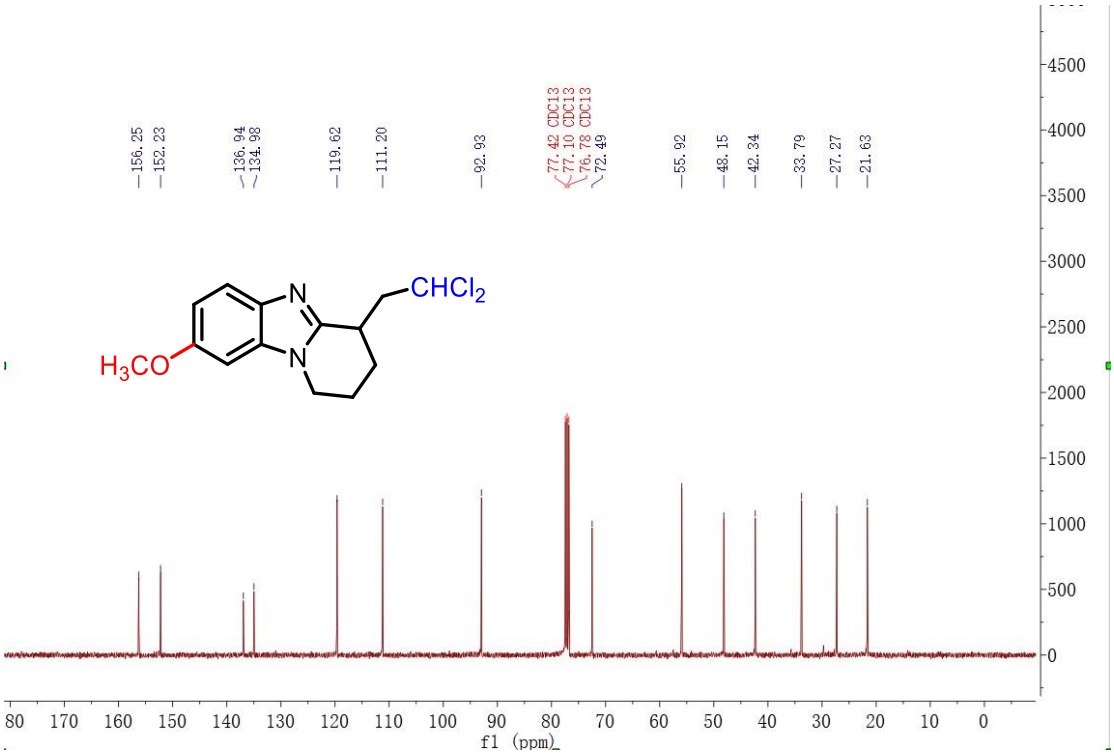


4-(2,2-dichloroethyl)-8-methoxy-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3g)

^{1}H NMR of **3g** in $CDCl_3$

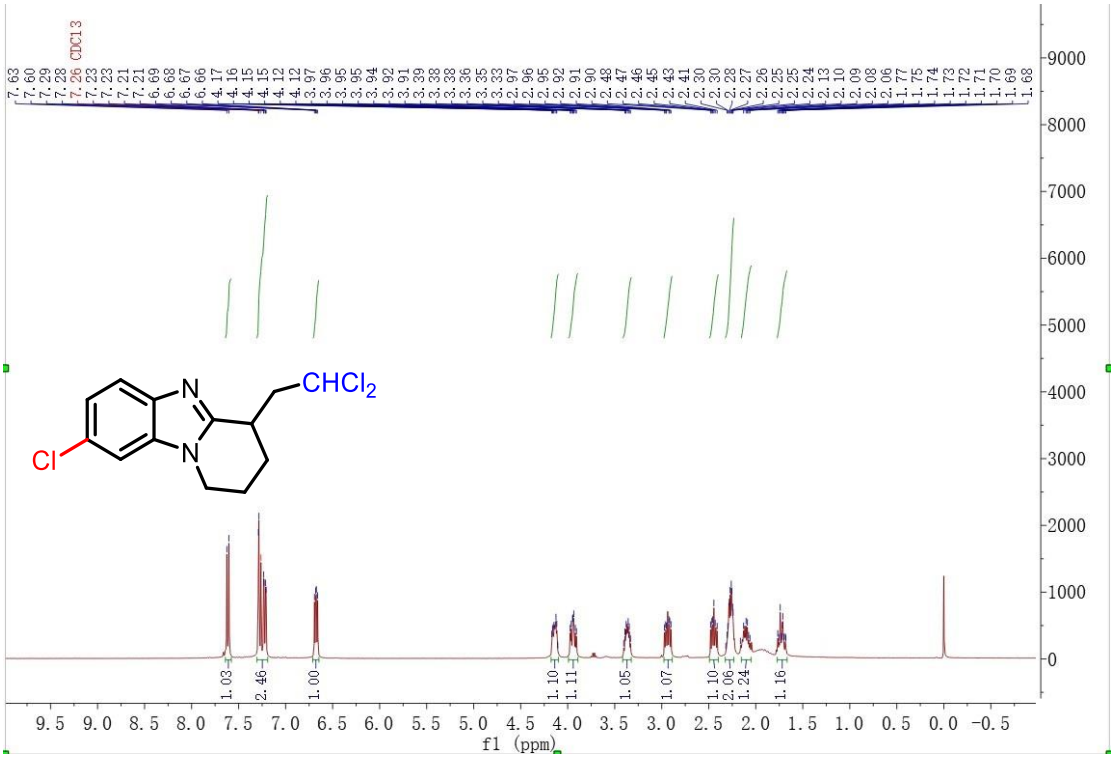


^{13}C NMR of **3g** in $CDCl_3$

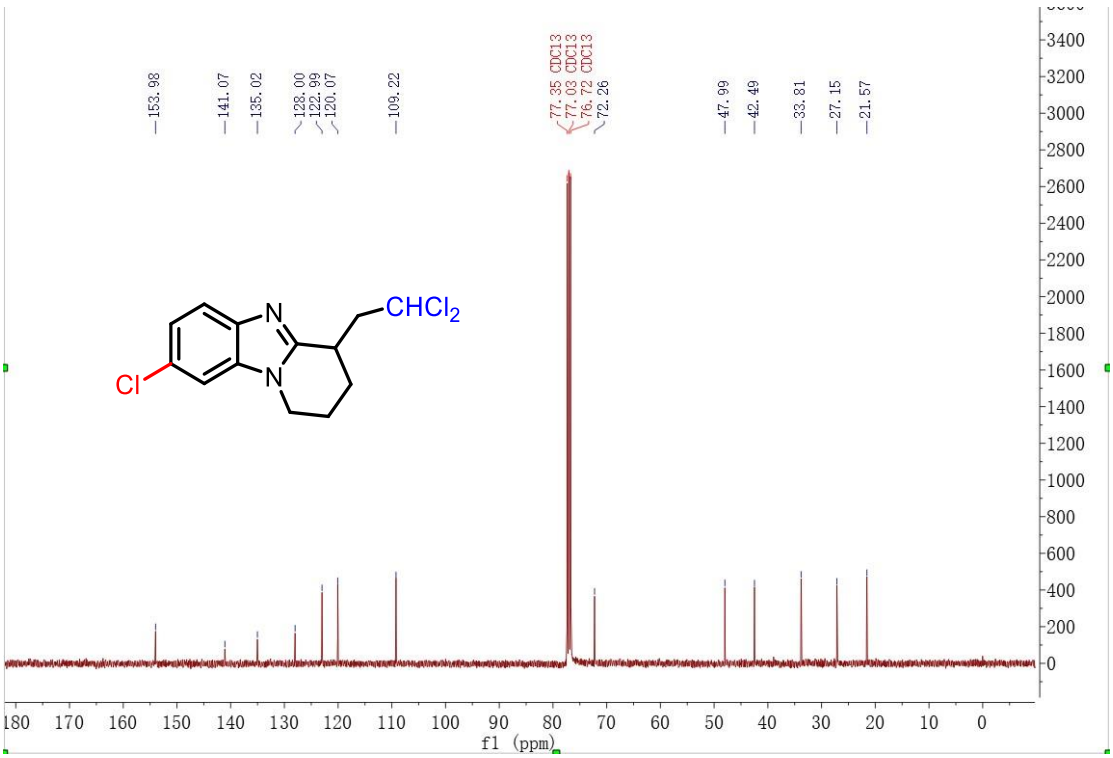


8-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3h)

^{1}H NMR of **3h** in $CDCl_3$

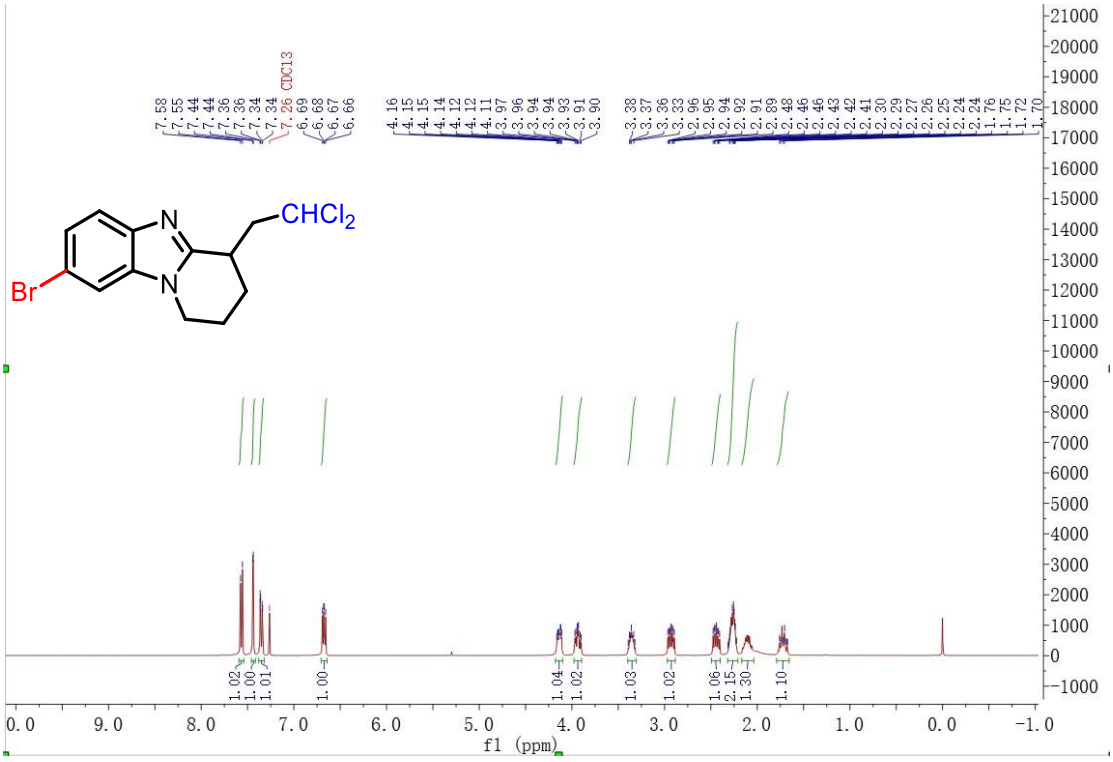


^{13}C NMR of **3h** in $CDCl_3$

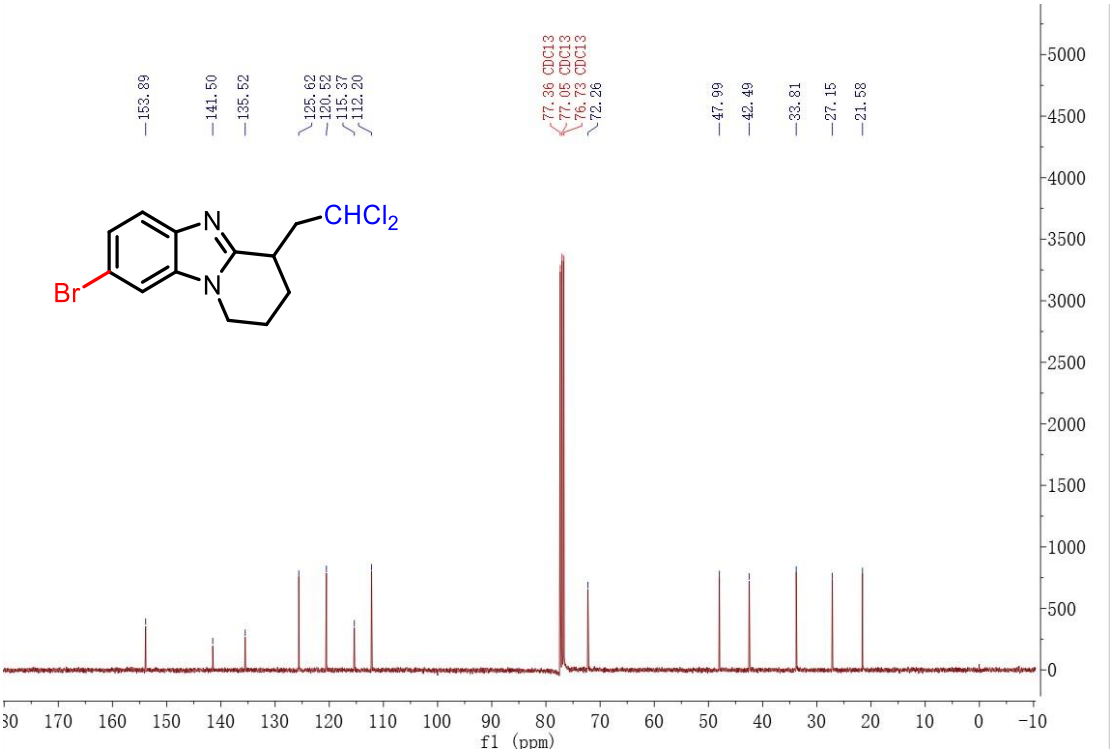


8-bromo-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3i)

^{1}H NMR of **3i** in $CDCl_3$

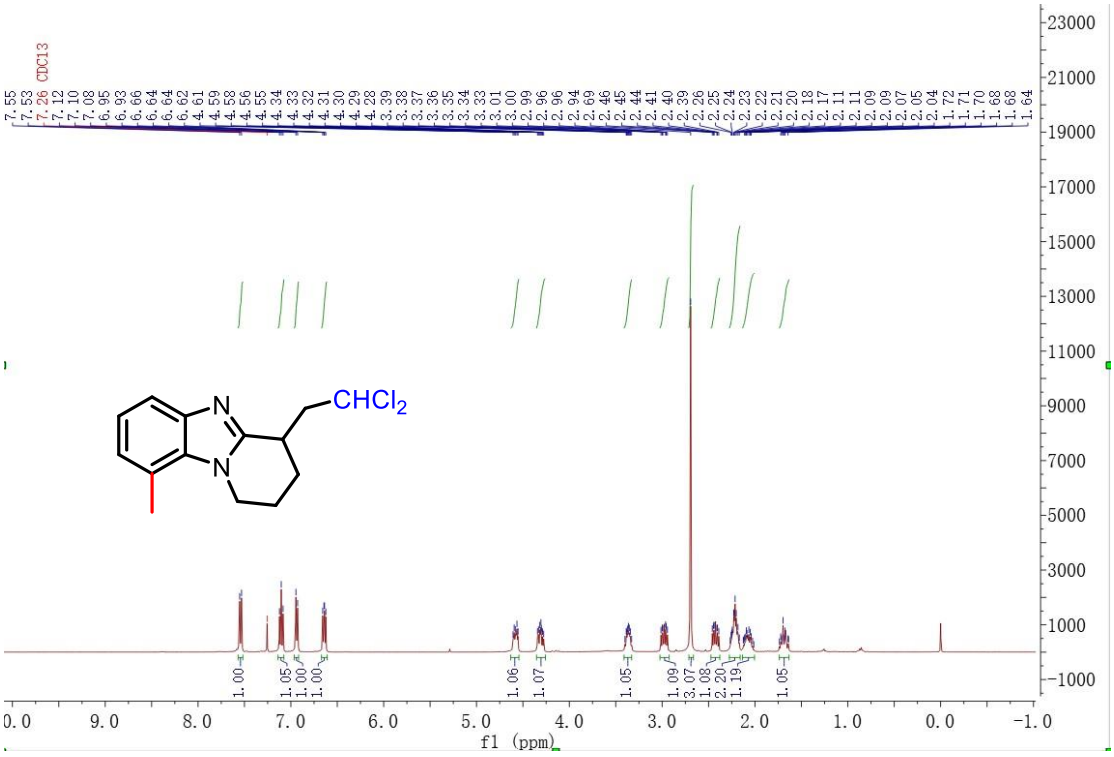


^{13}C NMR of **3i** in $CDCl_3$

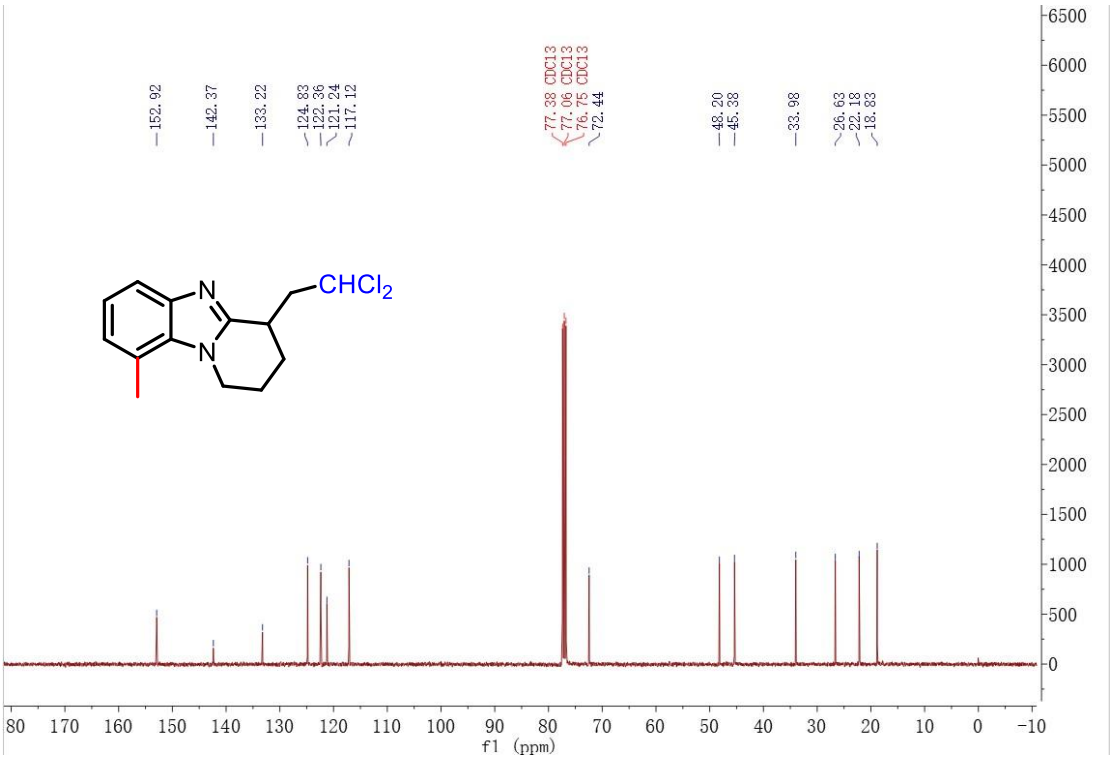


4-(2,2-dichloroethyl)-9-methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3j)

^{1}H NMR of **3j** in $CDCl_3$

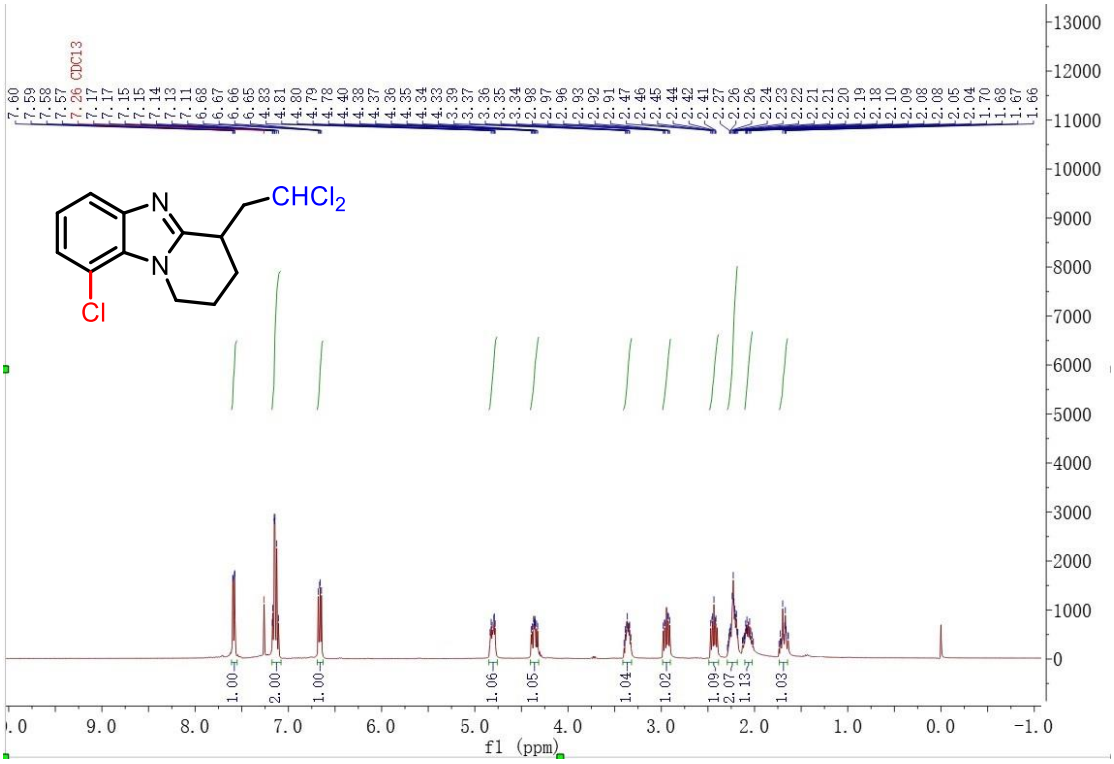


^{13}C NMR of **3j** in $CDCl_3$

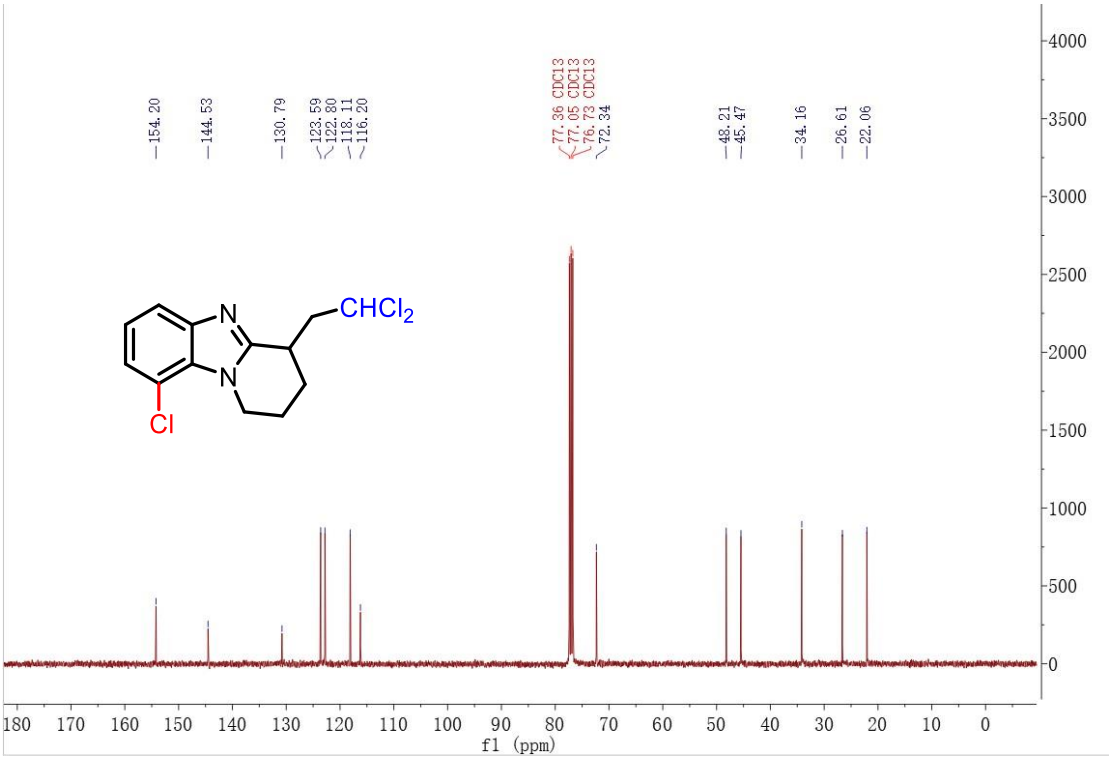


9-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3k)

^{1}H NMR of **3k** in $CDCl_3$

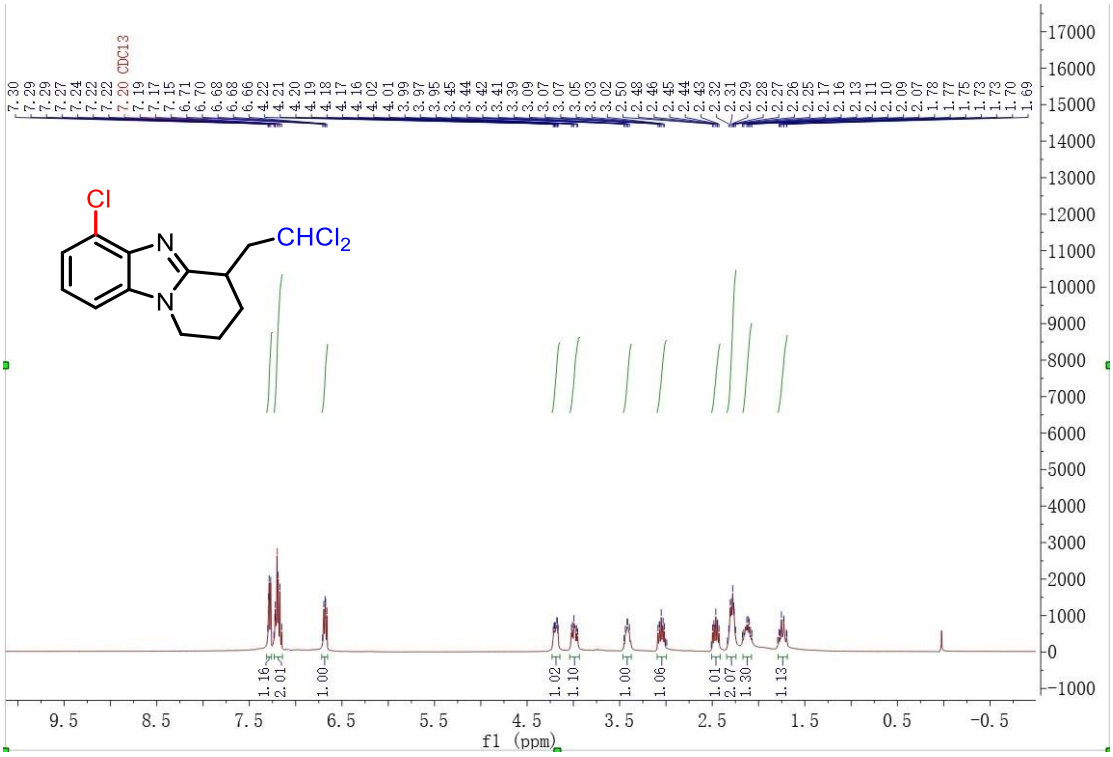


^{13}C NMR of **3k** in $CDCl_3$

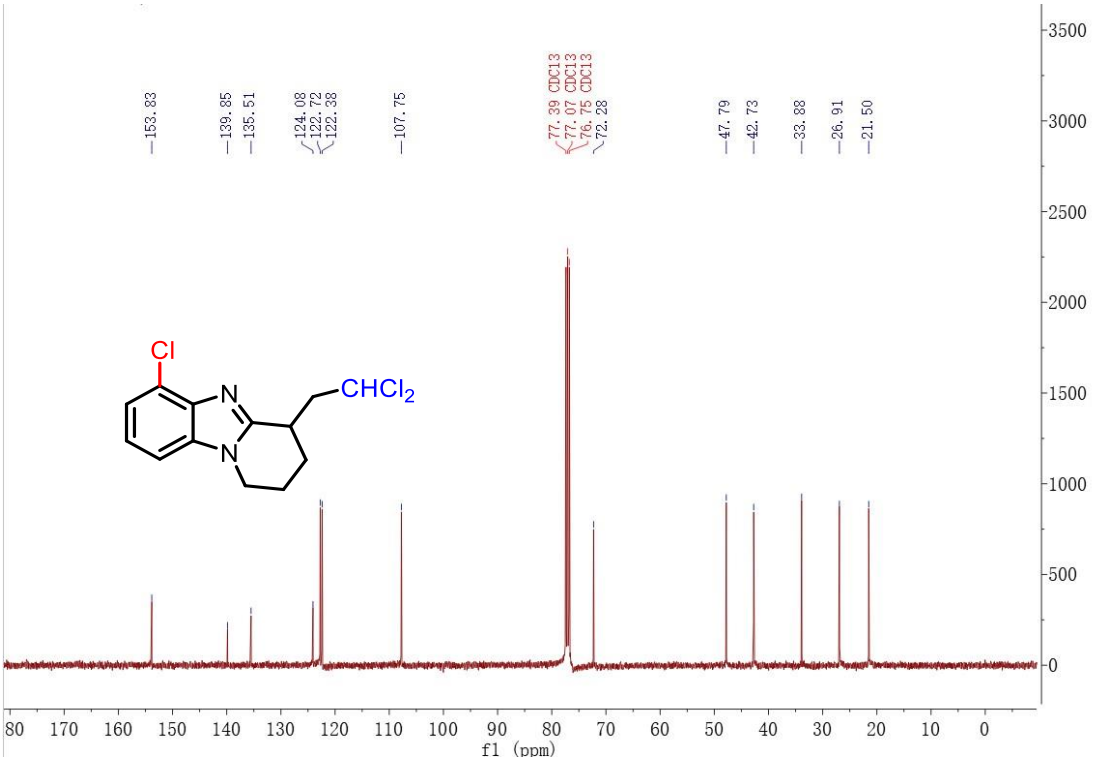


6-chloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3l)

^{1}H NMR of **3l** in $CDCl_3$

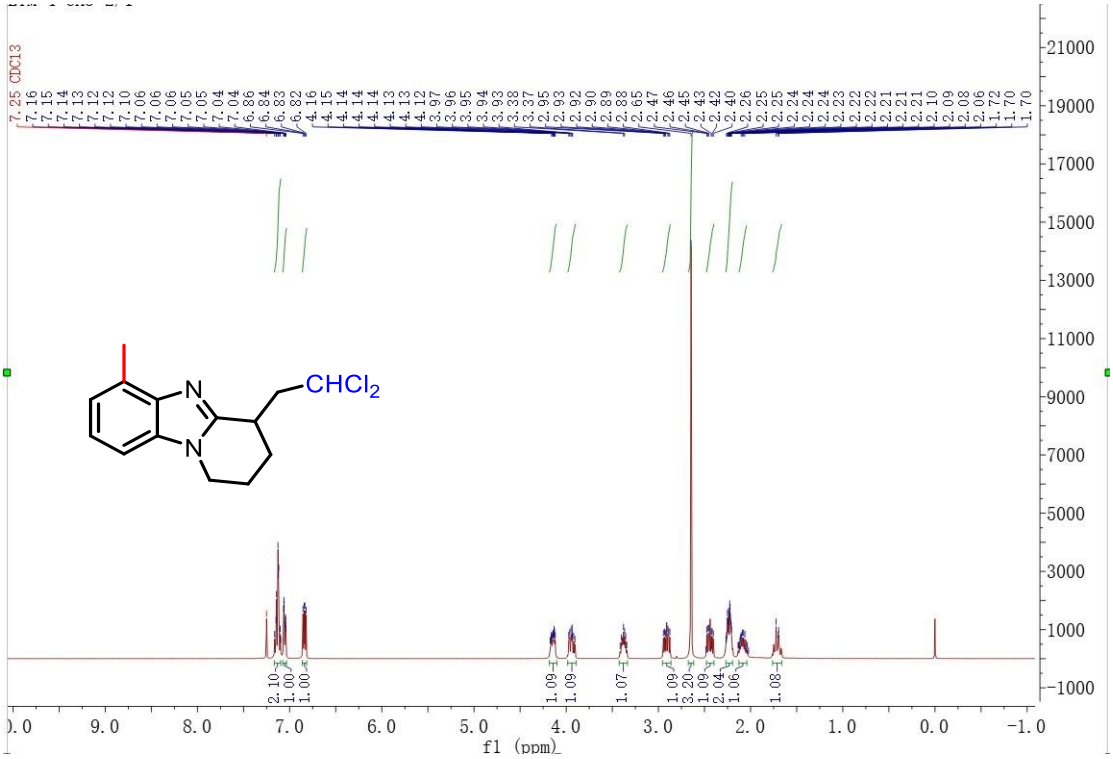


^{13}C NMR of **3l** in $CDCl_3$

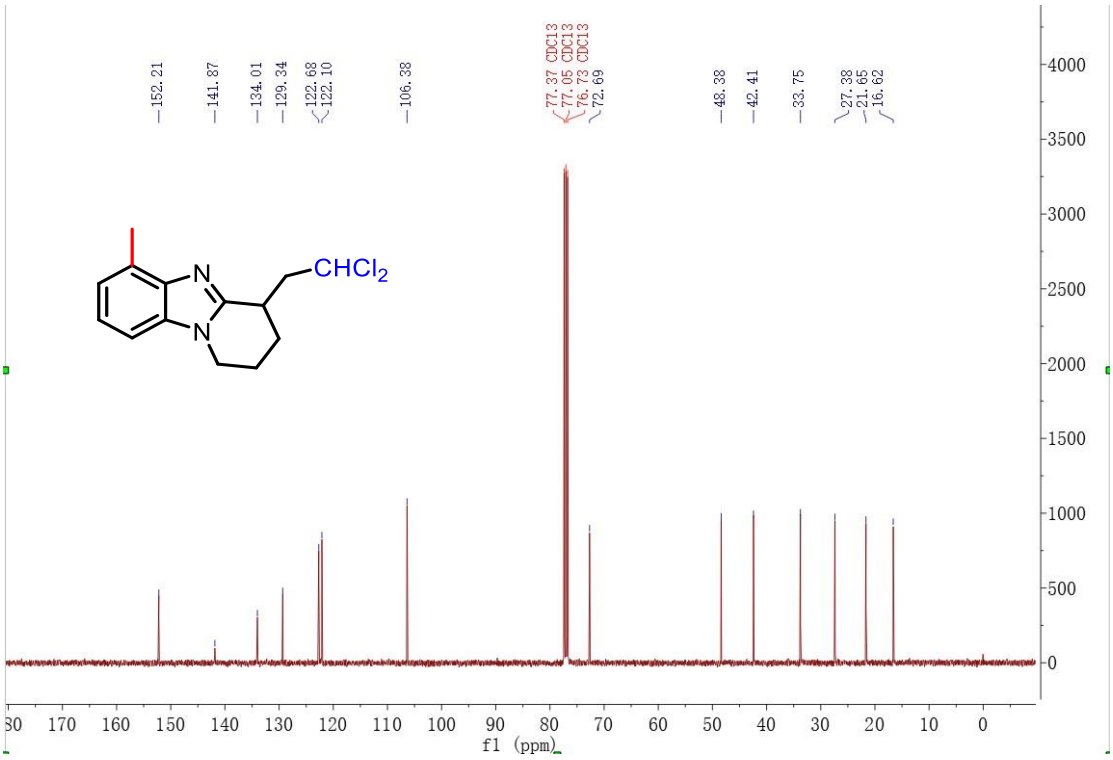


4-(2,2-dichloroethyl)-6-methyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3m)

^{1}H NMR of **3m** in $CDCl_3$

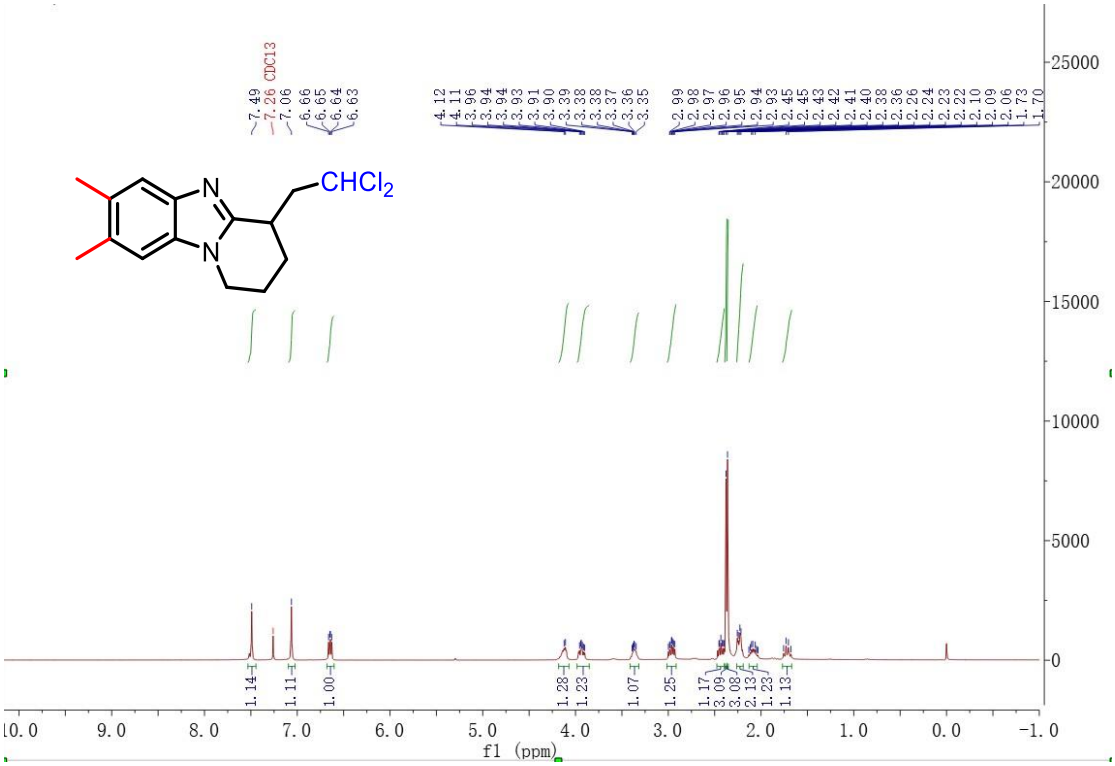


^{13}C NMR of **3m** in $CDCl_3$

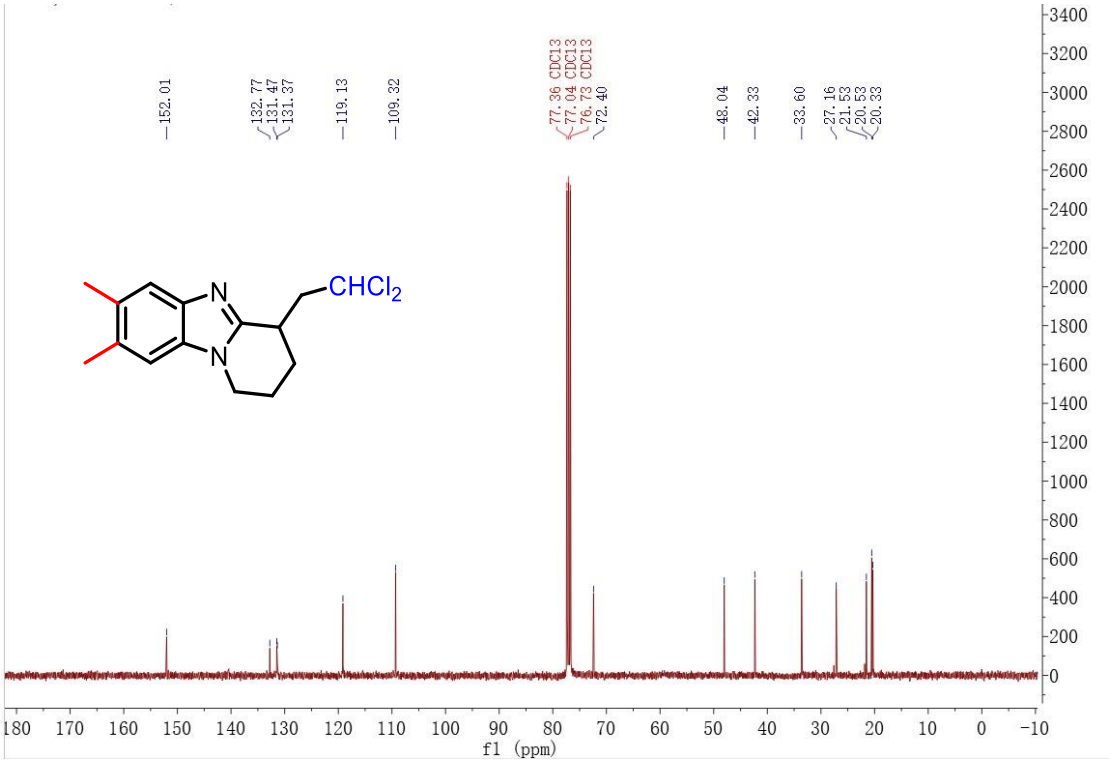


4-(2,2-dichloroethyl)-7,8-dimethyl-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3n)

^{1}H NMR of **3n** in $CDCl_3$

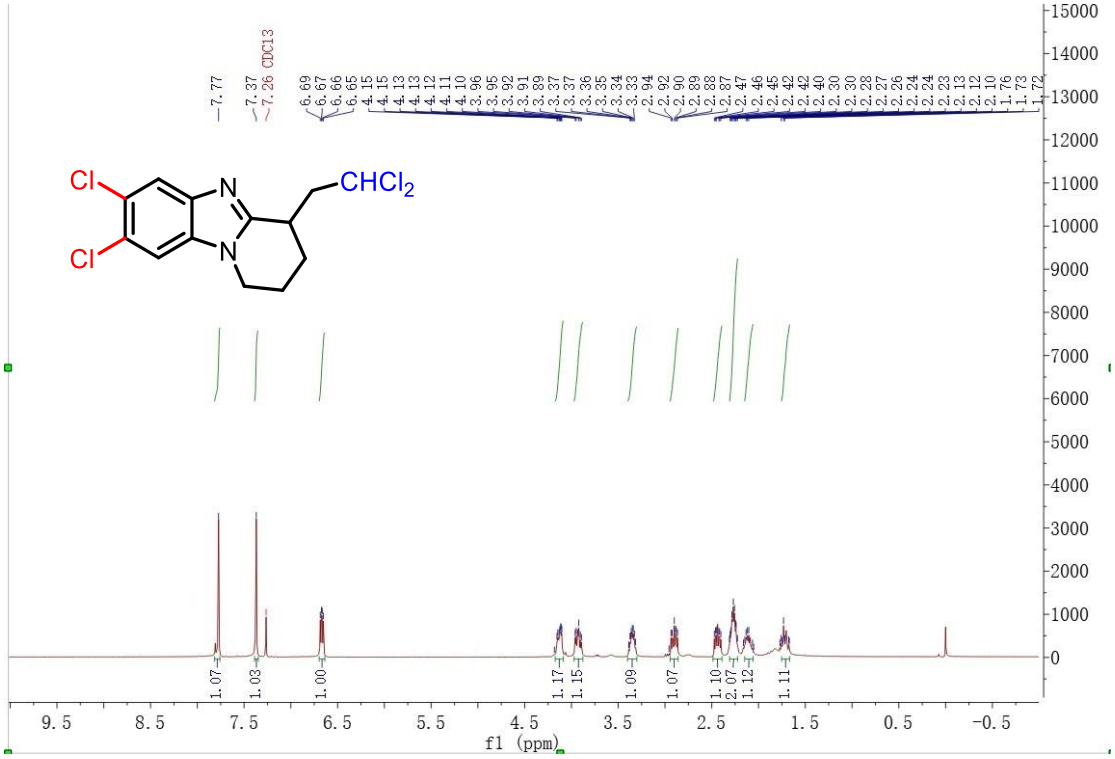


^{13}C NMR of **3n** in $CDCl_3$

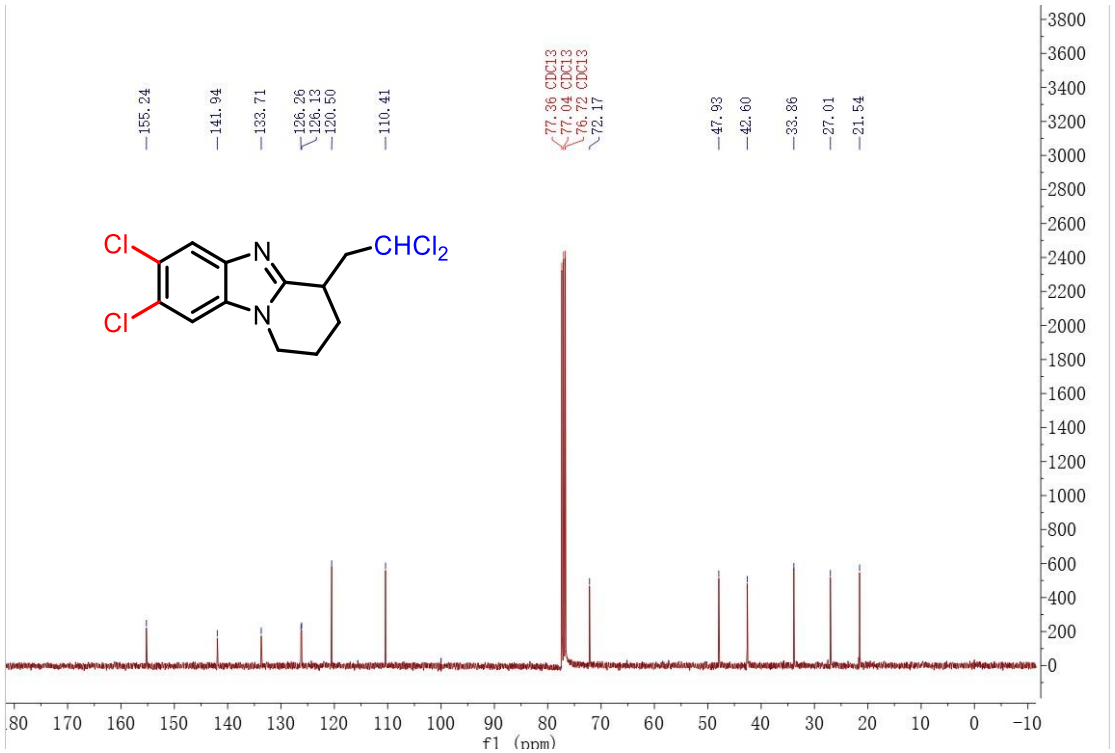


7,8-dichloro-4-(2,2-dichloroethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine (3o)

^{1}H NMR of **3o** in $CDCl_3$

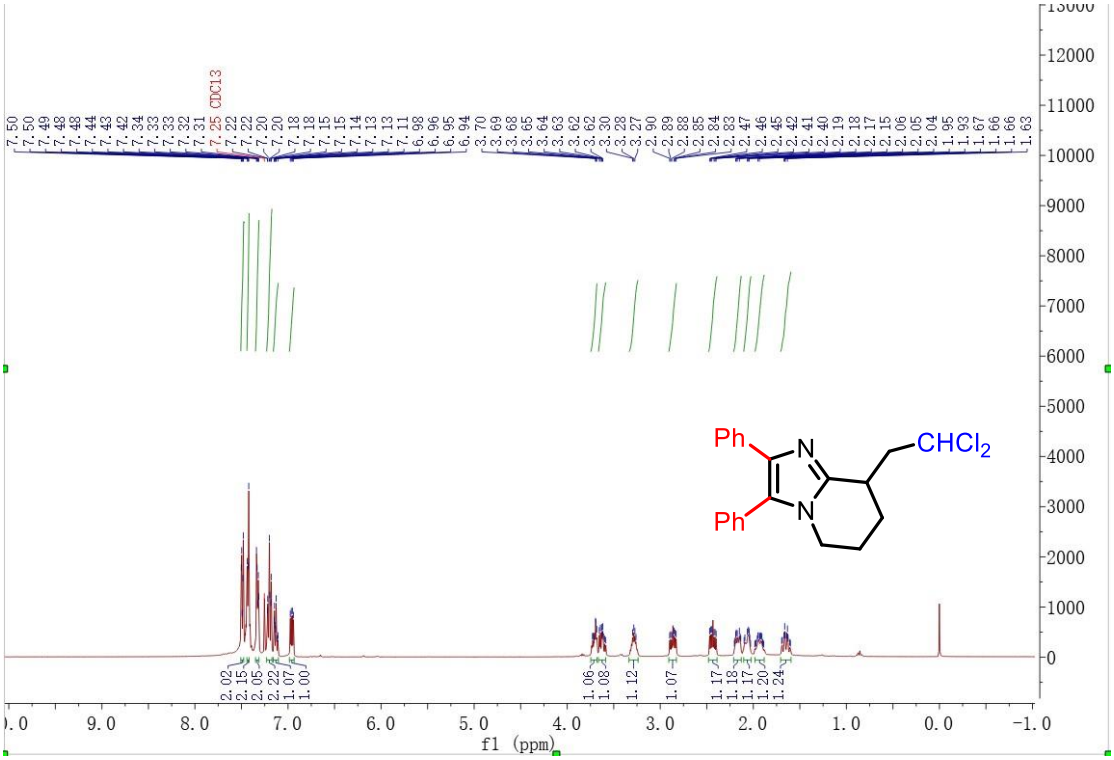


^{13}C NMR of **3o** in $CDCl_3$

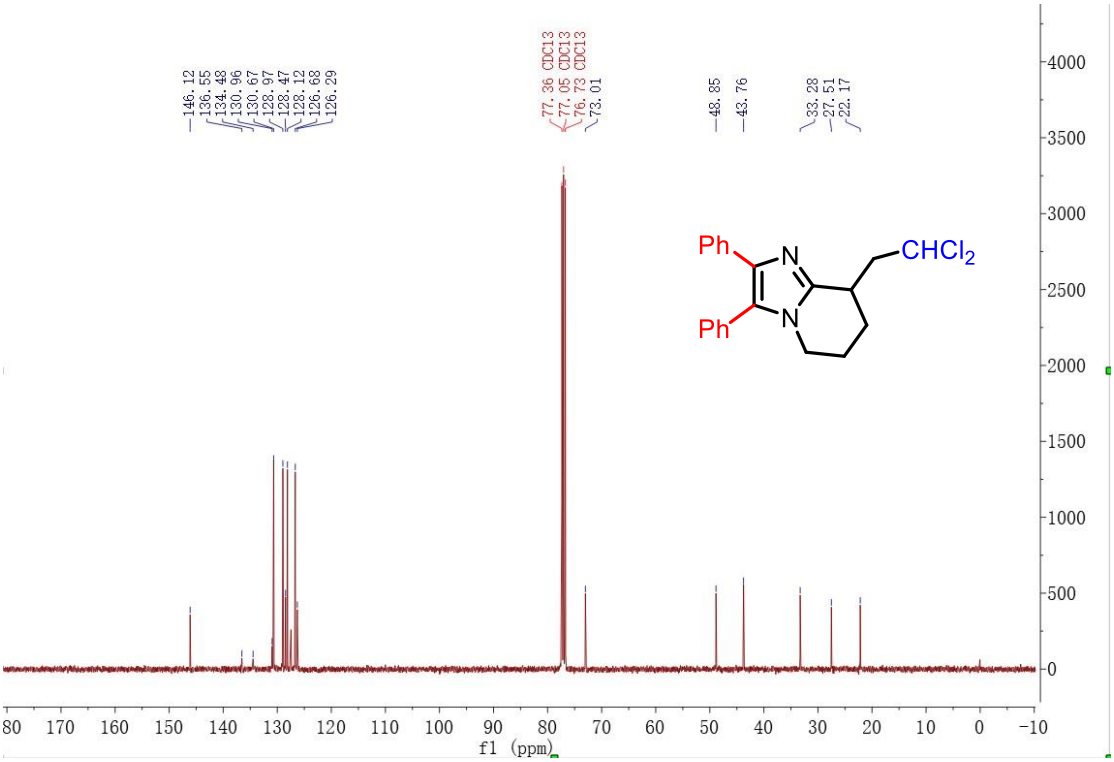


8-(2,2-dichloroethyl)-2,3-diphenyl-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine (3p)

^{1}H NMR of **3p** in $CDCl_3$

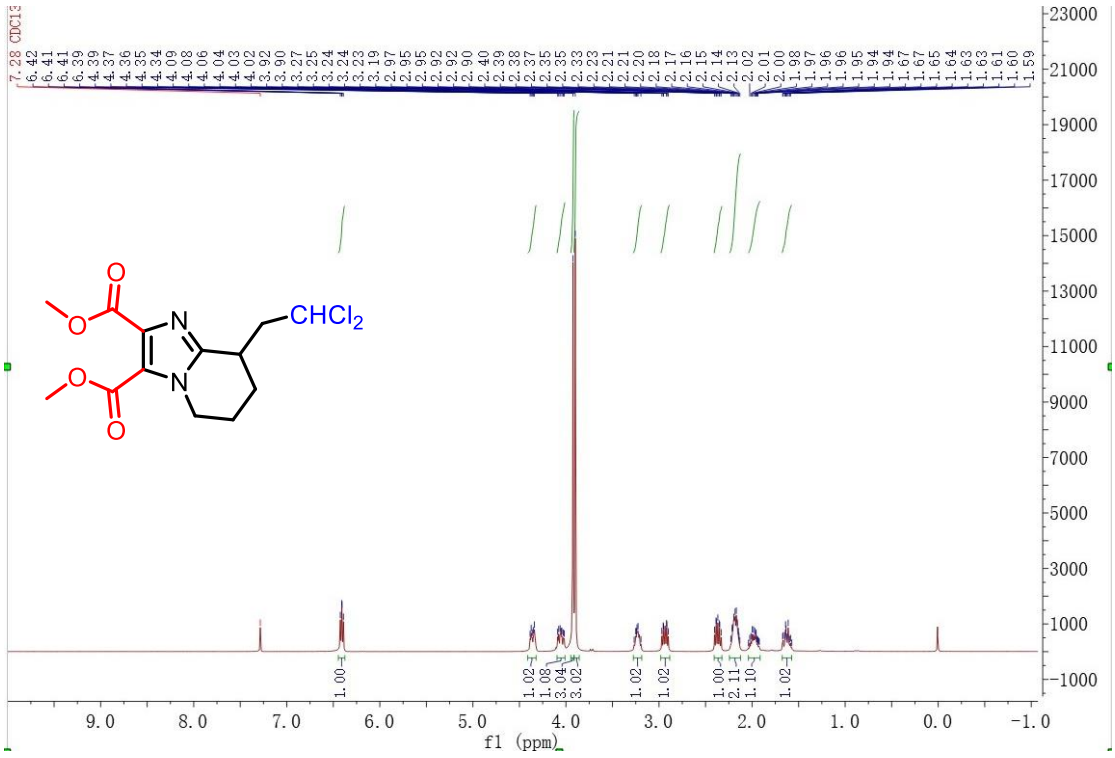


^{13}C NMR of **3p** in $CDCl_3$

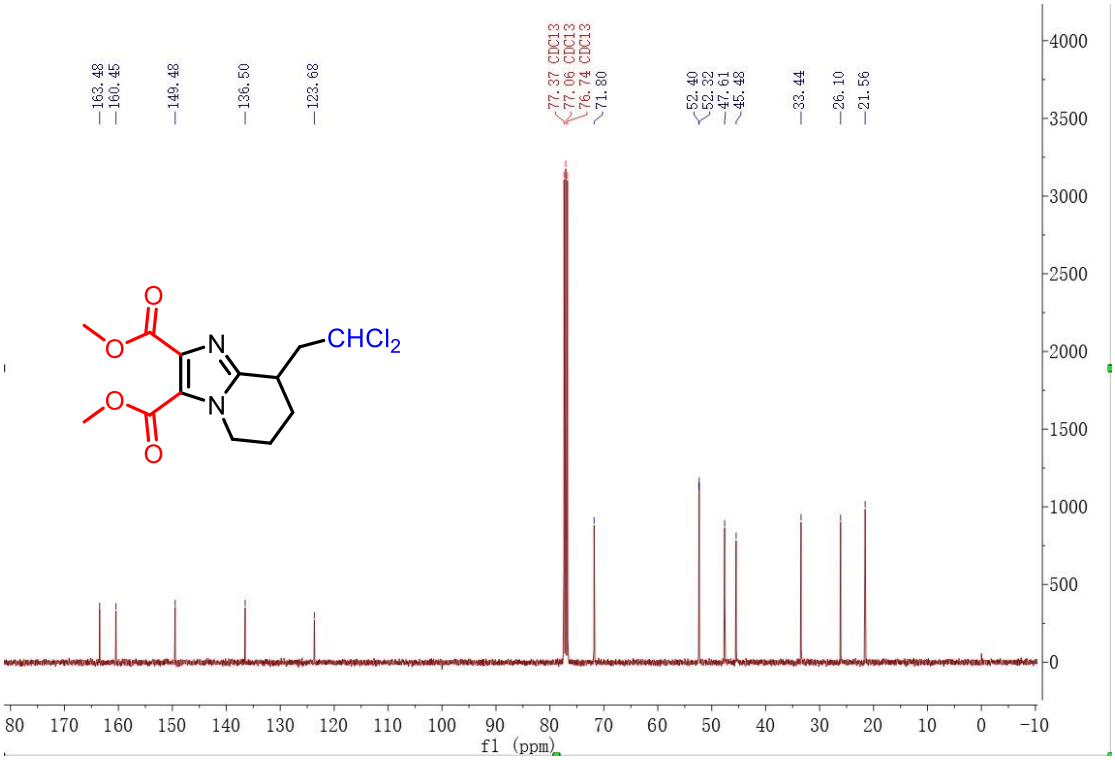


dimethyl 8-(2,2-dichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-2,3-dicarboxylate (3q)

^{1}H NMR of **3q** in $CDCl_3$

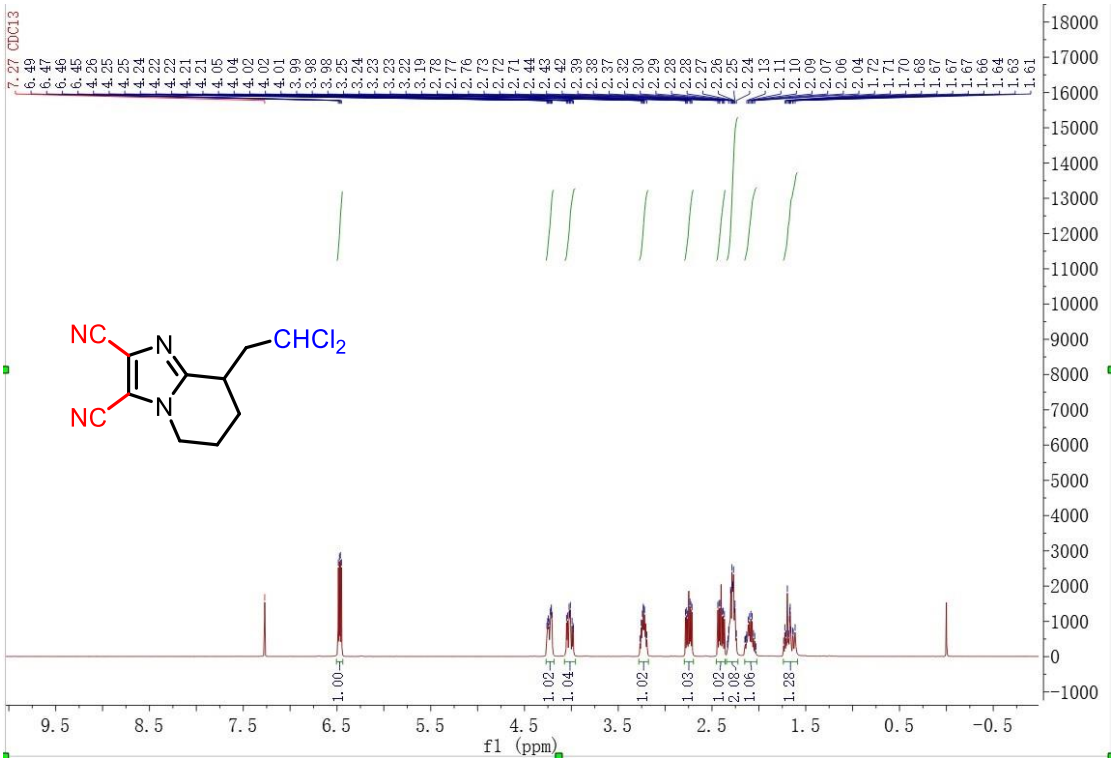


^{13}C NMR of **3q** in $CDCl_3$

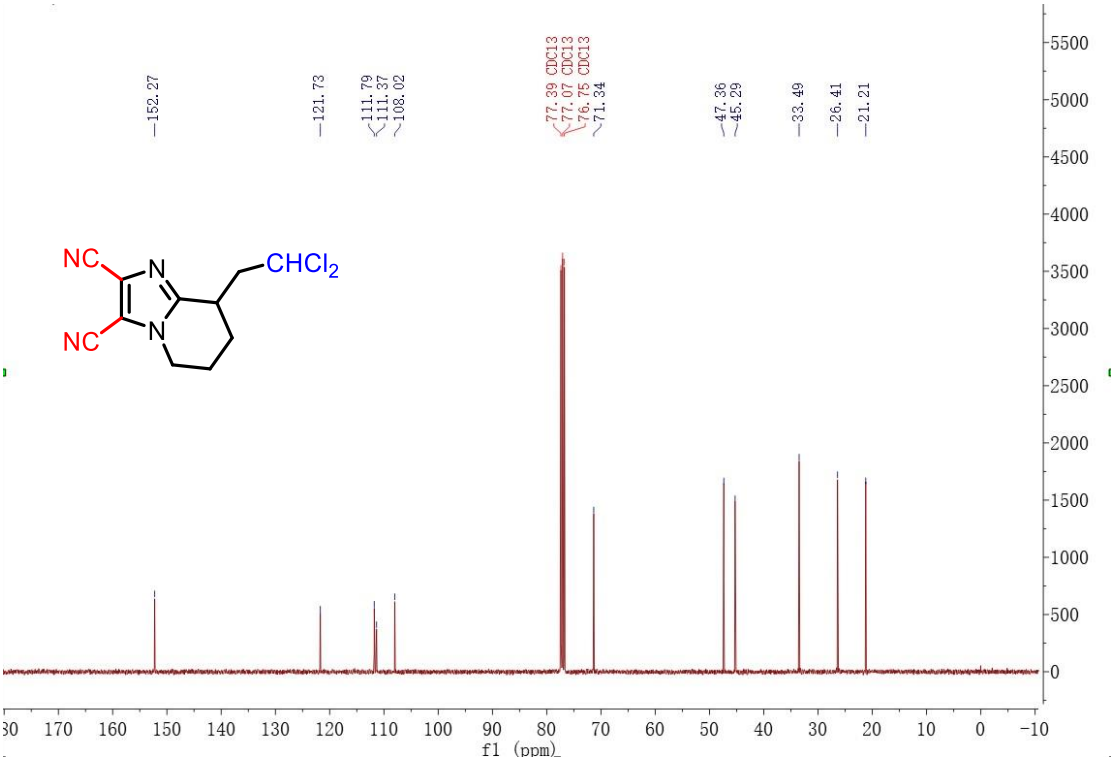


8-(2,2-dichloroethyl)-5,6,7,8-tetrahydroimidazo[1,2-a]pyridine-2,3-dicarbonitrile (3r)

^{1}H NMR of **3r** in $CDCl_3$

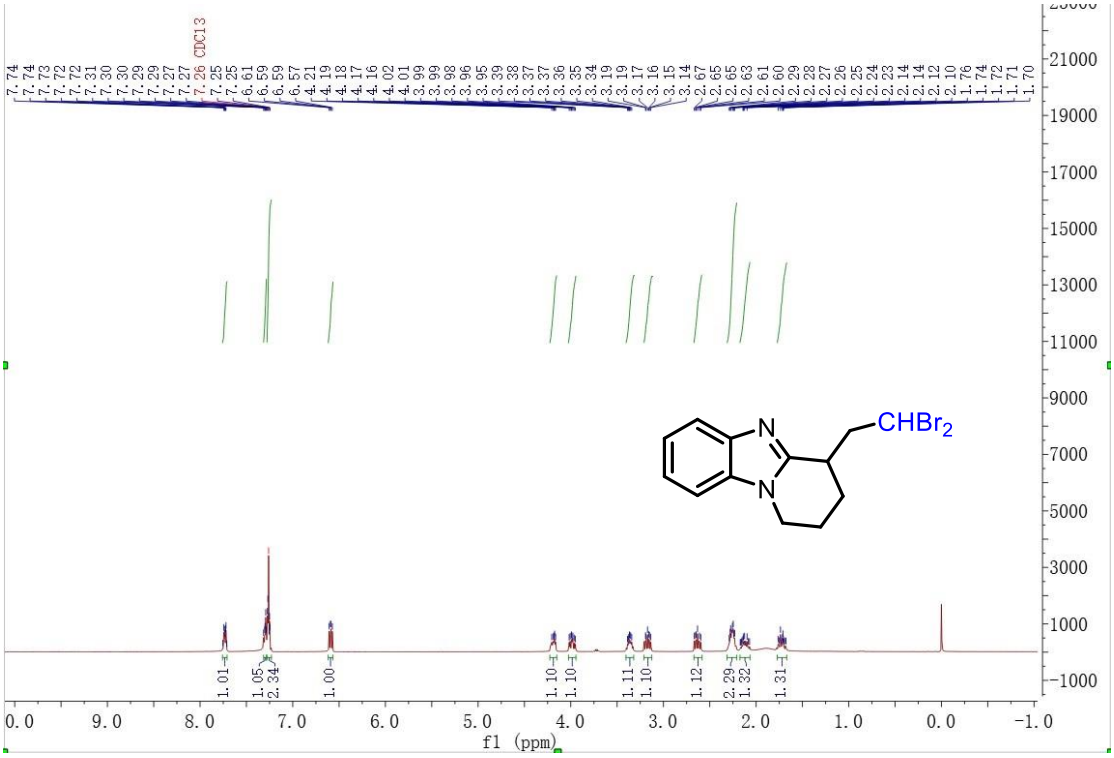


^{13}C NMR of **3r** in $CDCl_3$

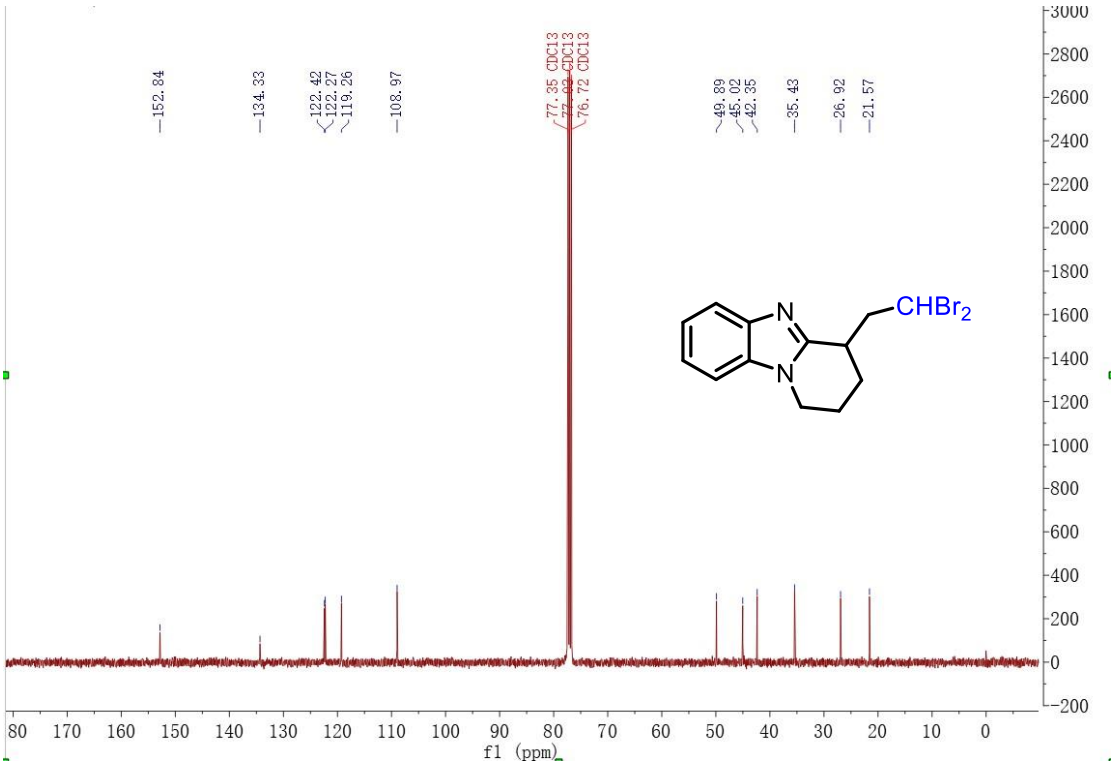


4-(2,2-dibromoethyl)-1,2,3,4-tetrahydrobenzo[4,5]imidazo[1,2-a]pyridine(4)

^{1}H NMR of **4** in $CDCl_3$

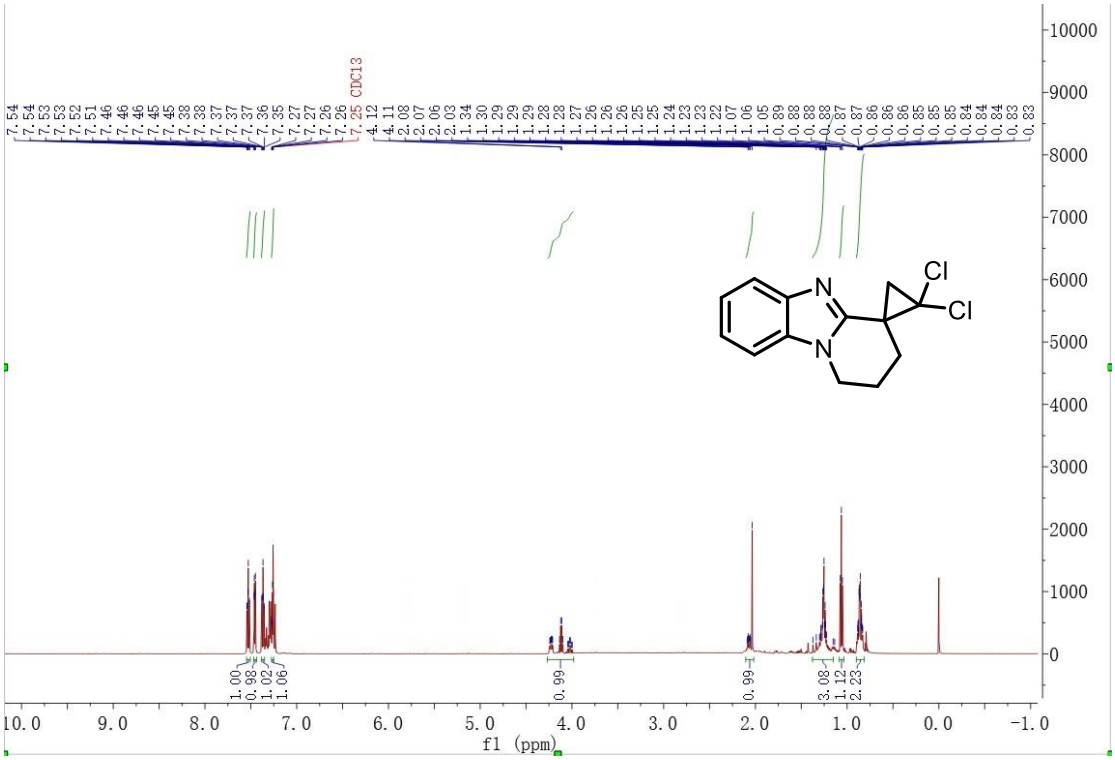


^{13}C NMR of **4** in $CDCl_3$

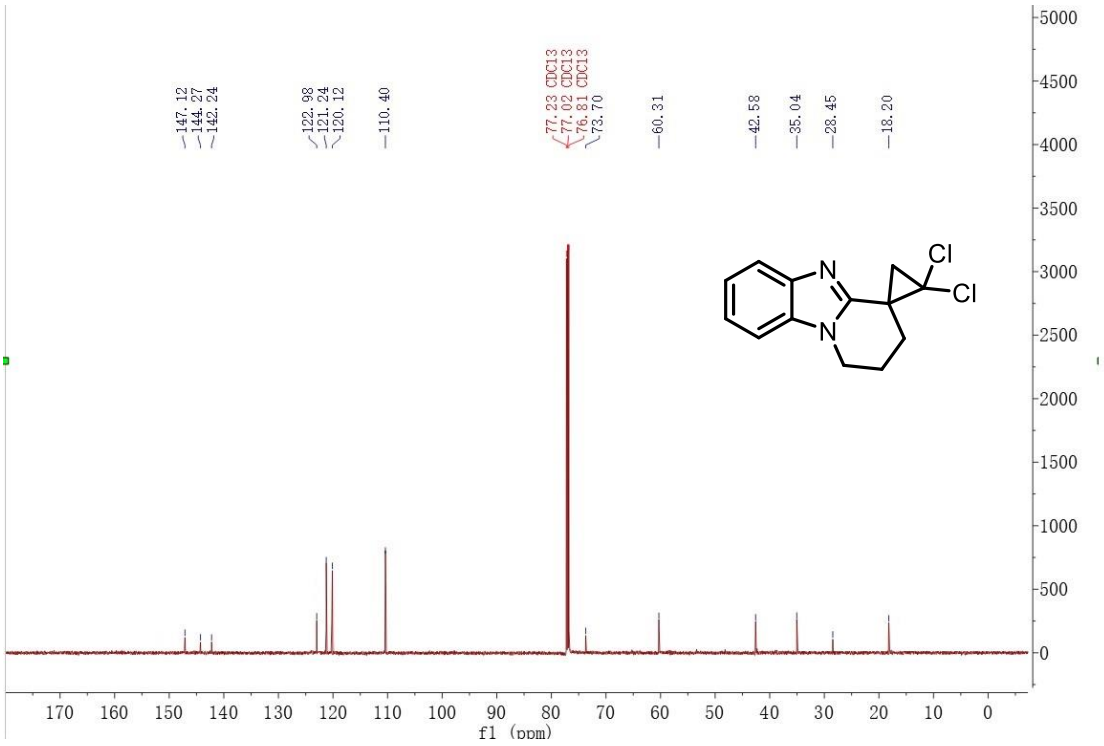


2',2'-dichloro-2,3-dihydro-1H-spiro[benzo[4,5]imidazo[1,2-a]pyridine-4,1'-cyclopropane] (5)

^{1}H NMR of **5** in $CDCl_3$

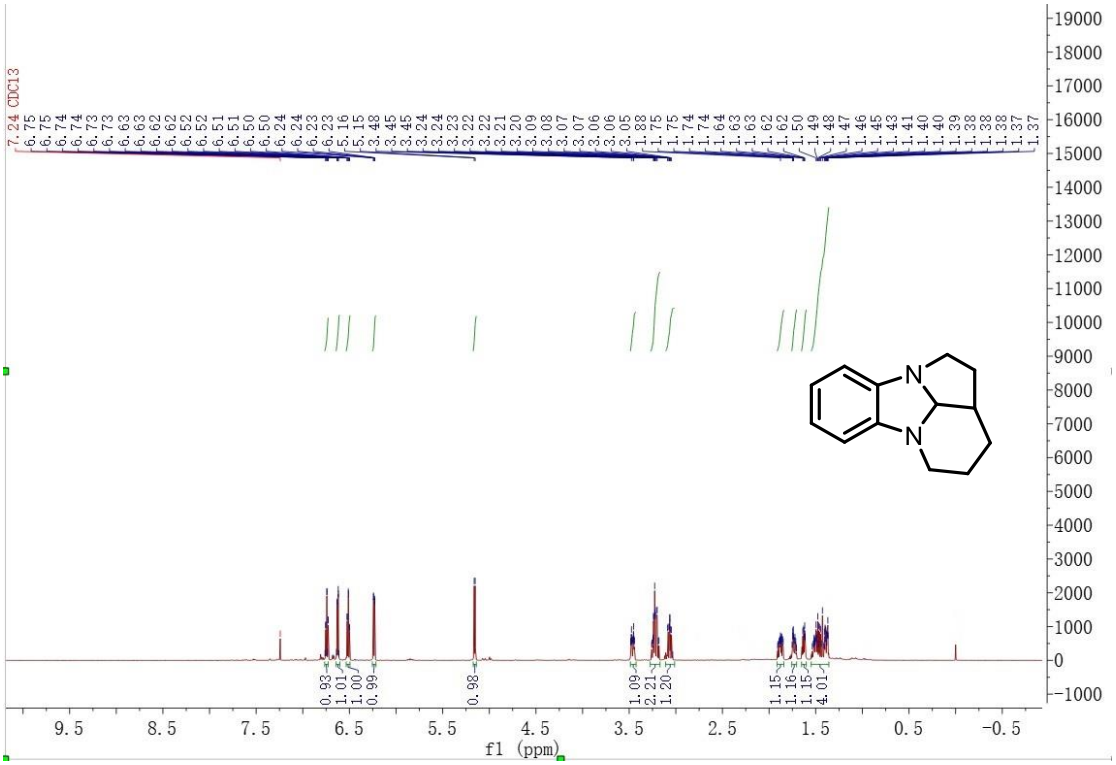


^{13}C NMR of **5** in $CDCl_3$

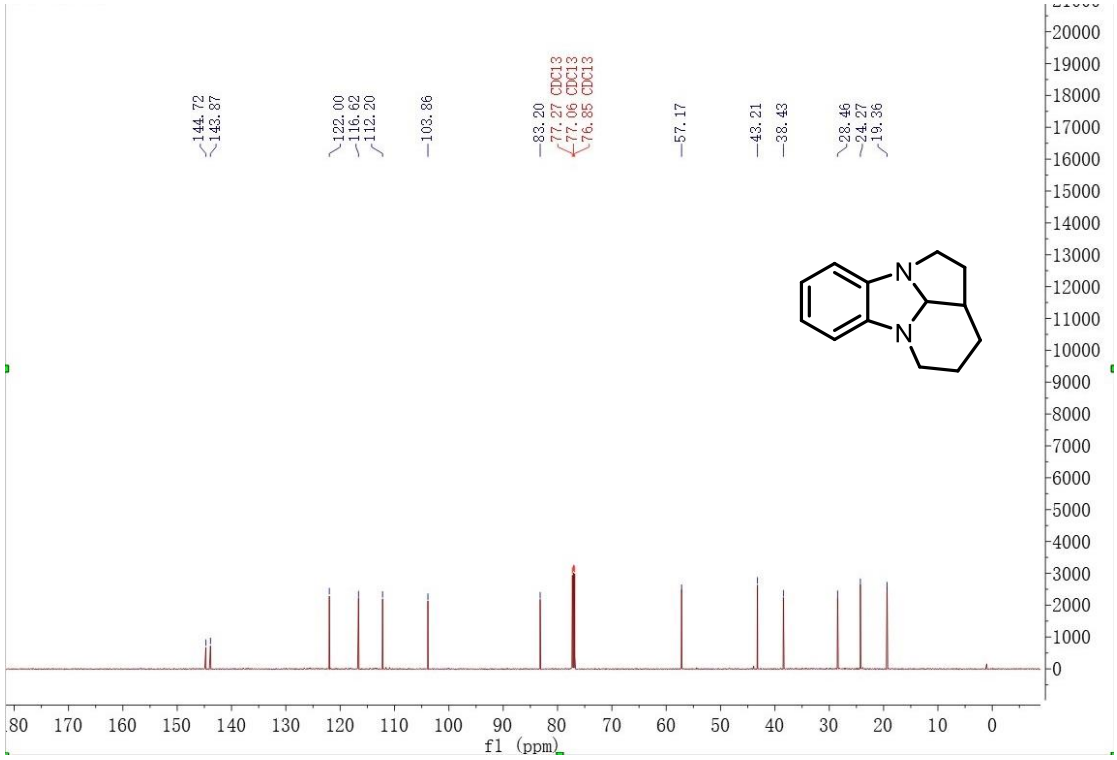


1,2,2a,2a1,4,5-hexahydro-3H-5a,9b-diazacyclopenta[jk]fluorene(6)

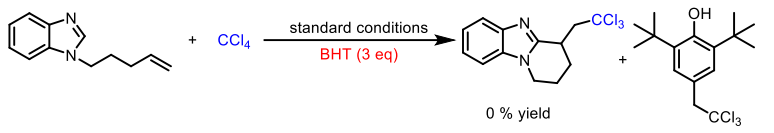
^{1}H NMR of **6** in $CDCl_3$



^{13}C NMR of **6** in $CDCl_3$



7. HRMS data



0 % yield

HRMS found for
$C_{16}H_{23}Cl_3O$: 336.0809

Compound Summary

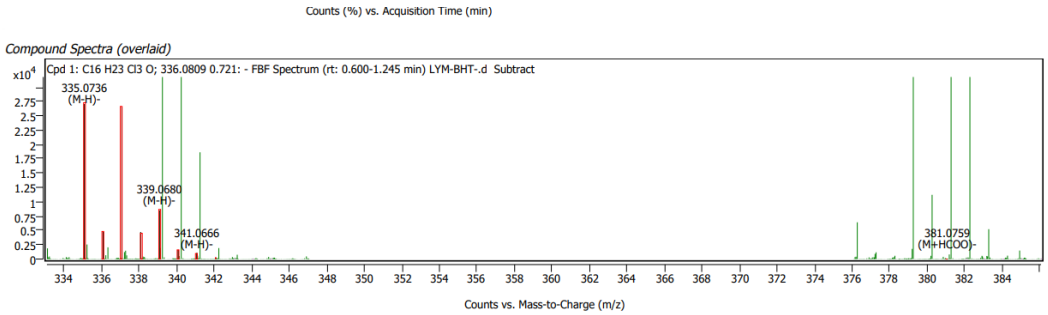
Cpd	Name	Formula	CAS	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Score	Algorithm
1		C16 H23 Cl3 O		0.721	336.0809	336.0814	-1.71	98.87	FBF

Compound Details

Cpd. 1: C16 H23 Cl3 O

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C16 H23 Cl3 O	0.721		336.0809	-1.71		FBF	98.87	FBF

Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
(M-H)- (M+HCOO)-	335.0736 381.0759	98.87				



Compound ID Table

Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (Lib)	Score (Tgt)
	C16 H23 Cl3 O	(M-H)- (M+HCOO)-	0.721		336.0809		FBF	98.87		98.87