



Supporting Information

Utilizing Nitroarenes and HCHO to Directly Construct Functional N-Heterocycles by Supported Cobalt/Amino Acid Relay Catalysis

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1. General Information

All chemicals were from commercial and used without further purification. Chemicals used in this work were purchased from the following vendors: nitroarenes (Energy Chemical, Bide Pharmatech Ltd., Accela ChemBio Co., Ltd., Macklin); 37 wt% HCHO in H₂O, Cobalt(II) nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99%), Zinc(II) nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%), 2-methylimidazole (>98.0%) were provided by Sinopharm Chemical Reagent Co., Ltd. All solvents were purchased from Greagent (Shanghai Titansci incorporated company) and used without further purification. All reactions were heated by metal sand bath (WATTCAS, LAB-500, <https://www.wattcas.com>). Column chromatography was performed on silica gel (200-300 mesh). Reactions were monitored by using thin layer chromatography (TLC) (Qingdao Jivida silica gel reagent factory GF254).

All the products were characterized by melting points (m.p.), ¹H-NMR, ¹³C-NMR, and mass spectra (MS), the NMR spectra of the known compounds were found to be identical with the ones reported in the literatures. All the new compounds were further characterized by high resolution mass spectra (HRMS). Melting points were measured on an Electrothermal SGW-X4 microscopy digital melting point apparatus and are uncorrected. Proton nuclear magnetic resonance (¹H-NMR) data were acquired on Bruker Avance400 (400 MHz), or Bruker Avance500 (500 MHz). Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; sept, septet; m, multiplet; br, broad; dt, doublet triplet. Proton decoupled Carbon-13 nuclear magnetic resonance (¹³C-NMR) data were acquired at 101 MHz on a Bruker Avance400 spectrometer, or at 125 MHz on a Bruker Avance500. Mass spectra were recorded on Trace DSQ GC/MS, High-resolution mass spectra (HRMS) were recorded on a JEOL JMS-600 spectrometer. TLC was performed using commercially prepared 100-400 mesh silica gel plates (GF254), and visualization was effected at 254 nm.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Thermo Scientific K-Alpha high-performance electron spectrometer using monochromatized Al K α (.6 eV) as the excitation source. The contents of Co in the derived samples were analyzed by an Agilent 5110 inductively coupled plasma atomic emission spectrometer (ICP-AES). Power X-ray diffraction (PXRD) were measured on a D8 ADVANCE diffractometer. Nitrogen sorption measurement was conducted using a Micromeritics ASAP 2460 3.01 system at 77.15 K.

The transmission electron microscopy (TEM) was acquired on Titan G260-300 with an electron acceleration energy of 200 kV. The high resolution TEM, HAADF-STEM images the corresponding Electron energy-loss spectroscopy were recorded by an EM-ARM300F high-resolution transmission electron microscope working at 200 kV and on a JEOL JEM-2100 TEM with a spherical aberration corrector working at 200 kV.

XAFS measurement and data analysis: XAFS spectra at the Co K-edge (7709 eV) were measured at the beamline 1W1B station of the Beijing Synchrotron Radiation Facility, China. The Co K-edge XANES data were recorded in a fluorescence mode. Co foil, CoO were used as references.

All the calculations were carried out by using the Gaussian 16 C.01 program package.^[1] The geometry optimizations were performed using hybrid B3LYP exchange correlation,^[2-4] together with the Grimme D3BJ correction term to the electronic energy.^[5,6] The 6-311G** basis set^[7-9] was used for all atoms. Vibrational frequency calculations were performed to characterize the nature of each stationary point and to make the zero-point energy (ZPE) corrections. The minimum energy path (MEP) was constructed by intrinsic reaction coordinate (IRC) theory for each reaction

channel.^[10] A tight convergence (10^{-12} au) criterion was employed, and the solvent tetrahydrofuran ($\epsilon= 7.43$) was considered using the SMD^[11] continuum solvent model (UFF radii).

2. Procedure for the Preparation of Various Catalysts

2.1. Preparation of Co/N-SiO₂-AC: Initially, a mixture of Co(OAc)₂·4H₂O and 1,10-phenanthroline was added to ethanol, and stirred at 100 °C for 1 hour to *in situ* generate the cobalt complex. Then, Si(OC₂H₅)₄ was added into the above solution and followed by the hydrolysis of TEOS with aq. ammonia to *in situ* form the silica. After refluxing for 2 hours, activated carbon as the support was poured into the solvent and refluxed for another 5 h. After cooling down to room temperature, the solvent of the suspension was removed under vacuum and the remaining solid was dried overnight. Then, the powder sample was pyrolyzed at 800 °C under a constant argon atmosphere for 2 h. Subsequently, the cooled sample was treated with HCl solution to selectively remove the unsupported cobalt particles generated during the pyrolysis process, and the remaining catalyst is named as Co/N-SiO₂-AC.^[12]

2.2. Preparation of Co/N-ZrO₂@C: First, The UiO-66 was synthesized according to the reported literature. A mixture of ZrCl₄ (156 mg) and H₂BDC (1,4-dicarboxybenzene) (108.8 mg) was dissolved in 60 mL DMF containing 7.2 mL HOAc in 100 mL round bottomed flask. Then, the mixture was transferred to a 100 mL Teflon liner and heated at 120 °C for 12 h. After hydrothermal treatment, the as-obtained precipitates were centrifuged at 11000 rpm for 5 min and washed with the methanol and DMF mixture (v/v=1:4) for three times, and then dried under vacuum at 90 °C. Subsequently, Co(OAc)₂·4H₂O (37.4 mg) and 1,10-phenanthroline (54.1 mg) (Co : phenanthroline = 1:2 molar ratio) were added in a 100 mL round bottom flask, and stirred in EtOH (50 mL) at 80 °C for 1 hour. Silica was then introduced into the above solution by *in situ* hydrolysis of the added Si(OC₂H₅)₄ (TEOS) with aqueous ammonia by stirring for 2 hours at 80 °C. After that, the UiO-66 powder (260 mg) was added to the solution and refluxed for 4 hours at 80 °C, and the mixture was then cooled to room temperature. The solvent was evaporated under vacuo and the remained solid was dried at 60 °C for 12 hours. The sample was then grinded to fine particles, which was subsequently pyrolyzed under argon at 800 °C for 3 hours. After the calcined catalyst was cooled down to room temperature, the obtained as black powder was then treated with 2 M NaOH solution for 12 hours at 120 °C to remove the SiO₂ templates, and the Co/N-ZrO₂@C was afforded after filtering, washing and drying.^[13]

2.3. Preparation of Co-ZrO₂/N-C: In a 50 mL round bottomed flask, ZrCl₄ (2.098 g, 9 mmol) and H₂BDC-NH₂ (1.630 g, 9 mmol) were stirred in 60 mL DMF containing 15 mL HOAc at room temperature until dissolved. The mixture of Co(NO₃)₂·6H₂O and ligand DABCO was stirred for 5-10 minutes in 10 mL DMF, which was then added into the above mixture and sonicated for 30 min. After that, the reaction mixture was transferred to a 100 mL Teflon liner and heated at 120 °C for 24 h. Upon a hydrothermal treatment, the product was centrifuged at 11,000 rpm for 5 min and washed with a mixture of methanol and DMF (v/v=1:4) for three times, then dried under vacuum at 90 °C. Subsequently, the powder material was pyrolyzed at the 800 °C for 3 hours under an argon atmosphere, Co-ZrO₂/N-C was obtained as the black powder.^[14]

2.4. Preparation of CoO_x/MSCC: The CoO_x/MSCC nanoparticles were prepared by an *in-situ* hard templates method. (1) **The synthesis of SiO₂ nanospheres:** The SiO₂ nanospheres were synthesized according to the reported work. In brief, 82 mg *L*-arginine was dissolved into the mixture of 62 mL deionized water, then added 4 mL cyclohexane. After the solution was heated to 60 °C, 4.9 mL TEOS was dropwise added to the above mixture and kept stirring at 60 °C for 20 h to make the SiO₂ seeds grew into spherical particle. To control the different cavity size of SiO₂ nanospheres, the secondary growth was necessary. Specifically, 216 mL deionized water and 30 mL cyclohexane

were added to the mother liquor, 21 mL TEOS was dropwise added to the above mixture and kept stirring at 60 °C for 30 h, and finally SiO₂ nanospheres were obtained. (2) **The synthesis of PVP bridged Co-PA/SiO₂**: 1.12 g PVP-k30 (polyvinylpyrrolidone) was dissolved into 40 mL SiO₂ nanosphere solution and stirred for 2 hours to coat on SiO₂. Moreover, Co(OAc)₂·4H₂O (352.0 mg, 1.4 mmol) was stirred in ethanol (100 mL) for 20 min at room temperature until dissolved. Then, 40 mL of SiO₂ nanosphere solution was dropwise added to the above mixture, the whole reaction mixture was stirred at 80 °C for 4 h, then kept stirring at room temperature overnight. After that, 2.62 mL concentrated HCl solution (12 M) and 2.05 mL aniline were poured into the above mixture and kept stirring. Subsequently, 21 mL diluted HCl solution (0.75 M) was dissolved with 5.13 g ammonium persulfate, which was dropwise added to the above solution, and then kept stirring under ice bath for 24 hours. After vaporizing the solvent at 90 °C and grinding the remained bottle-green bulk, the PVP bridged Co-PA/SiO₂ ((PA: polyaniline)) composite powder was obtained. (3) **Pyrolyzing the precursors and removing the SiO₂ template**: Subsequently, the Co-PA/SiO₂ composite was pyrolyzed under argon at 800 °C for 2 h. The SiO₂ templates were removed with 2 M NaOH solution for 12 hours at 120 °C, and after filtering, washing and drying, the CoO_x/MSCC was obtained. Others' MSCC catalysts (**FeO_x/MSCC**, **NiO_x/MSCC**) were prepared via the same procedure.^[15]

2.5. Preparation of Co-N_x/NC-900: At first, Co(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O with a Co²⁺/Zn²⁺ molar ratio of 1 : 20 was dissolved in 80 mL of methanol.^[16] Another solution with 2-methylimidazole (3.70 g) and 80 mL methanol was added into the above solution and stirred at room temperature for 24 h. The total mole of (Zn + Co) was fixed at 5.65 mmol. The purply material was collected by centrifugation and washed with methanol for three times, dried under vacuum at 75 °C overnight. Then, the dried Co₁Zn₂₀-BMOF power (500 mg) was heated to 900 °C for 3 h with a heating rate of 5 °C/min under flowing argon, then cooled to room temperature naturally to afford Co-N_x/NC-900 porous carbon materials. Similarly, the dried Co₁Zn₂₀-BMOF power (500 mg) was calcined at 500 °C, 700 °C and 1100 °C to afford **Co-N_x/NC-500**, **Co-N_x/NC-700** and **Co-N_x/NC-1100**, respectively.

2.6. Preparation of NC-900: At first, Zn(NO₃)₂·6H₂O (1.68 g) dissolved in 80 mL methanol was added to another 80 mL of methanol with 3.70 g of 2-methylimidazole, the mixture was stirred at room temperature for 24 h.^[17] The white power was obtained from solution via centrifugation, washed thoroughly with methanol for three times, and dried under vacuo at 75 °C. Then ZIF-8 power (500 mg) was heated to 900 °C for 3 h with a heating rate of 5 °C/min under flowing argon. After cooling down to room temperature, the NC-900 material was afforded.

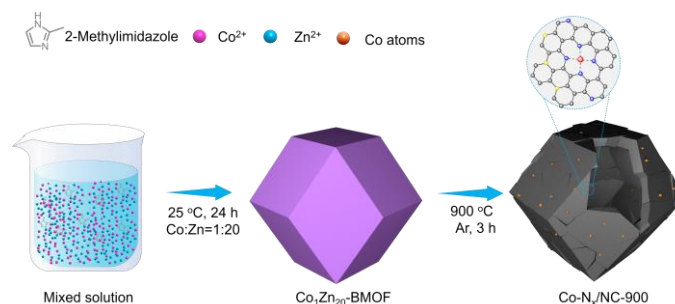
2.7. Preparations of Co_{1/1}-N_x/NC-900, Co_{1/5}-N_x/NC-900, and Co_{1/40}-N_x/NC-900: First, Co(NO₃)₂·6H₂O and Zn(NO₃)₂·6H₂O with a Co²⁺/Zn²⁺ molar ratio of 1 : 1 were dissolved in 80 mL of methanol.^[16] Meanwhile, Co₁Zn₅-BMOF, and Co₁Zn₄₀-BMOF were synthesized by Co²⁺/Zn²⁺ molar ratio of 1:5, and 1:40, respectively. Another solution of 2-methylimidazole (3.70 g) in 80 mL methanol was added into the above solution and stirred at room temperature for 24 h. The total mole of (Zn + Co) was fixed at 5.65 mmol. The purply material was collected by centrifugation and washed with methanol for three times, dried under vacuum at 75 °C overnight. Then, the resulting Co₁Zn₁-BMOF power (500 mg) was heated to 900 °C for 3 h with a heating rate of 5 °C/min under flowing argon, and then cooled to room temperature naturally to afford the Co_{1/1}-N_x/NC-900 porous carbon materials. Other Co-NC catalysts (Co_{1/5}-N_x/NC-900, Co_{1/40}-N_x/NC-900) were prepared through the same procedure.

2.8. Preparation of Co NPs/NC-900: First, a typical procedure was followed to prepare ZIF-67.^[18] 0.45 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 3 mL of distilled water and mixed with a solution of 2-methylimidazole (5.5 g) in 20 mL of water, was then vigorously stirred for 6 h at room temperature (20 °C). The purple products were collected after centrifugation; the product was adequately washed for three times with water and methanol, and dried under vacuum at 75 °C for 12 h. Then, the ZIF-67 powder (500 mg) was heated to 900 °C for 3 h with a heating rate of 5 °C/min under flowing argon, then cooled to room temperature naturally to afford the Co NPs/NC-900 material.

2.9. Preparation of Co-phen/NC: The Co-phen/NC was synthesized similarly to the reported procedure.^[19] Cobalt(II) acetate tetrahydrate (Sigma-Aldrich $\geq 98\%$, 126.8 mg, 0.5 mmol) and 1,10-phenanthroline (phen, Sigma-Aldrich, $\geq 99\%$, 183.5 mg, 1.0 mmol) (Co : phen = 1 : 2 molar ratio) were stirred in ethanol (50 mL) for 30 minutes at room temperature. Then, carbon powder (689.7 mg) (VULCAN® XC72R, Cabot Corporation Prod. Code XVC72R; CAS No. 1333-86-4) was added and the whole reaction mixture was refluxed for 4 hours. The reaction mixture was then cooled to room temperature and the ethanol was removed under vacuo. The solid sample was dried at 60 °C for 12 hours, and then grinded to a fine powder. The grinded powder was transferred into a ceramic crucible and placed in the oven. The oven was heated to 800 °C with a rate of 10 °C/min, and held at 800 °C for 2 hours under argon atmosphere. After cooling down to room temperature, the desired Co-phen/NC was afforded.

2.10. Preparation of Co NPs/C: Cobalt(II) acetate tetrahydrate (126.8 mg, 0.5 mmol) and carbon powder (689.7 mg) (VULCAN® XC72R) were stirred in ethanol (50 mL) for 4 hours at 80 °C. The reaction mixture was cooled to room temperature and the ethanol was removed under vacuo. The solid sample obtained was dried at 60 °C for 12 hours, after which it was grinded to a fine powder. Then, the grinded powder was transferred into a ceramic crucible and placed in the oven. The oven was heated to 800 °C with a rate of 10 °C/min, and held at 800 °C for 2 hours under argon atmosphere. After cooling down to room temperature, the desired Co NPs/C was afforded.

3. Characterization of the Co-N_x/NC-900 Catalyst



Scheme S1. The synthetic process for the synthesis of Co-N_x/NC-900.

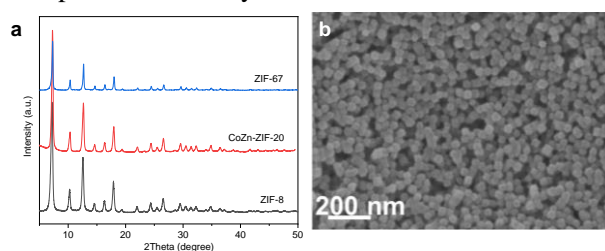


Figure S1. (a) Powder X-ray diffraction (PXRD) patterns for Co₁Zn₂₀-BMOF. (b) Scanning electron microscopy (SEM) for Co₁Zn₂₀-BMOF.

XRD patterns and scanning electron microscopy (SEM) image of the as-synthesized Co₁Zn₂₀-BMOF (Figure S1) matched well with the reported ones.^[16-18]

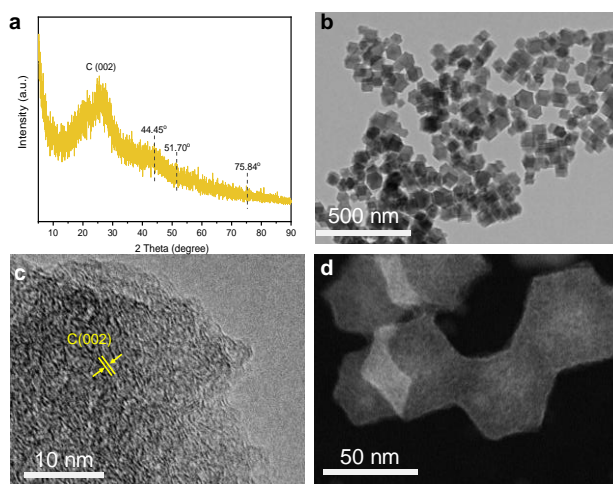


Figure S2. (a) XRD pattern of Co-N_x/NC-900. (b,c) TEM images of Co-N_x/NC-900. (d) HAADF-STEM images of Co-N_x/NC-900.

Transmission electron microscopy (TEM) images of the catalyst revealed that, after pyrolysis, the heterozygous polyhedral morphology of Co₁Zn₂₀-BMOF was preserved integrally (Figure S2b). The TEM image of Co-N_x/NC-900 exhibited clear lattice stripes indexed to the (002) plane of graphitic carbons derived from Co₁Zn₂₀-BMOF, in agreement with a broad peak centered at 25.2° (Figure S2c, Figure S2a). High-angle annular dark-field scanning TEM (HAADF-STEM) and elemental mappings also suggest the cobalt is anchored throughout the Co-N_x/NC-900 with high dispersion (Figure S2d and Figure S6a).

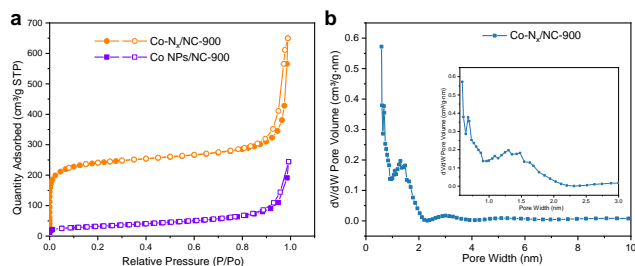


Figure S3. (a) Adsorption-desorption curves and (b) pore diameter distribution of Co-N_x/NC-900.

Co-N_x/NC-900 exhibits a typical type-I N₂ sorption isotherm with a specific surface area of 903 m² g⁻¹ (Figure S3a). The remarkable N₂ uptakes in the low relative pressure range ($P/P_0 < 0.1$) suggest the dominant existence of micropores,^[20,21] as also proved by the pore size distribution (Figure S3b).

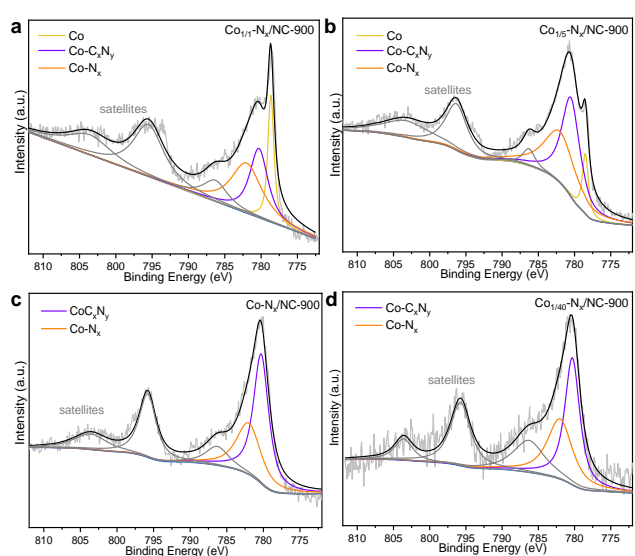


Figure S4. X-ray photoelectron spectroscopy (XPS) spectra of Co 2p. (a) Co_{1/1}-N_x/NC-900. (b) Co_{1/5}-N_x/NC-900. (c) Co-N_x/NC-900. (d) Co_{1/40}-N_x/NC-900.

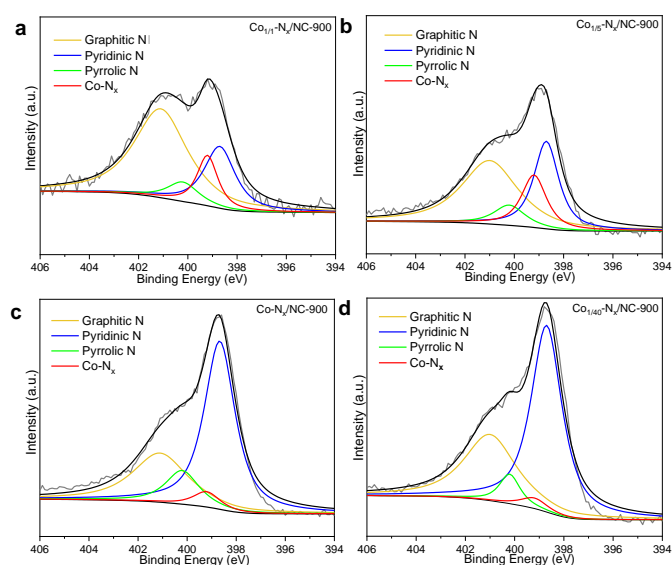


Figure S5. The X-ray photoelectron spectroscopy (XPS) spectra for N 1s of different Co-loading catalysts.

X-ray photoelectron spectroscopy (XPS) analyses show that the high-resolution N 1s spectrum can be deconvoluted into graphitic-N (N1, 401.1 ± 0.3 eV), pyrrolic-N (N2, 400.5 ± 0.3 eV), pyridinic-N (N3, 398.5 ± 0.2 eV) and Co-N_x (N4, 399.2 ± 0.1 eV) (Figure S5, Table S2), and the pyridinic and pyrrolic-N are the major species.

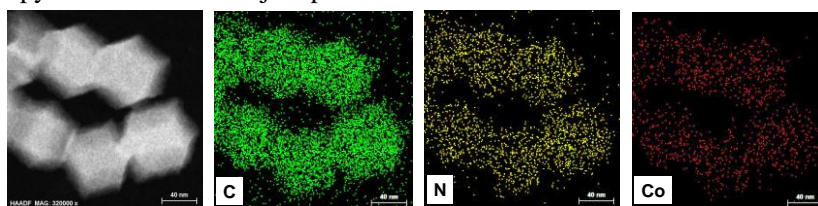


Figure S6. HAADF-STEM image and the corresponding EDX elemental mapping of C (green), N (yellow), and Co (red).

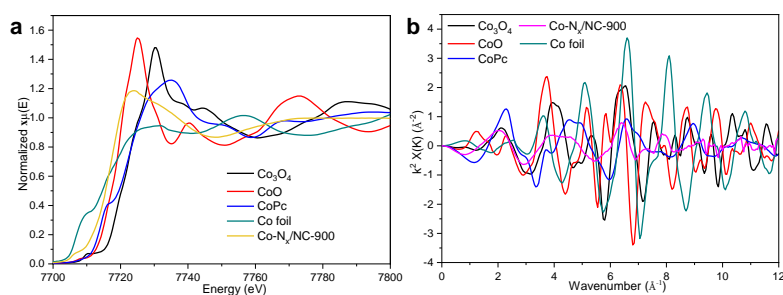


Figure S7. (a) XANES spectra at the Co K-edge of Co₃O₄, CoO, CoPc, Co foil and Co-N_x/NC-900 catalyst. (b) k space EXAFS curves of Co₃O₄, CoO, CoPc, Co foil and Co-N_x/NC-900.

The Co K-edge of Co-N_x/NC-900 is located between that of Co foil and CoPc, suggesting that Co species possess positive charge with the valence number between 0 and +4.

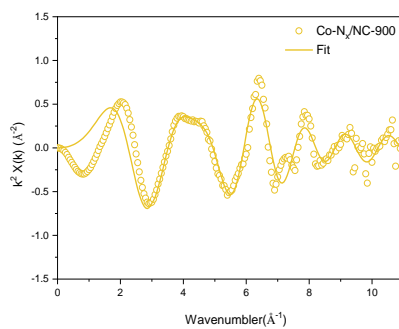


Figure S8. Corresponding Co K-edge EXAFS fitting curve of Co-N_x/NC-900.

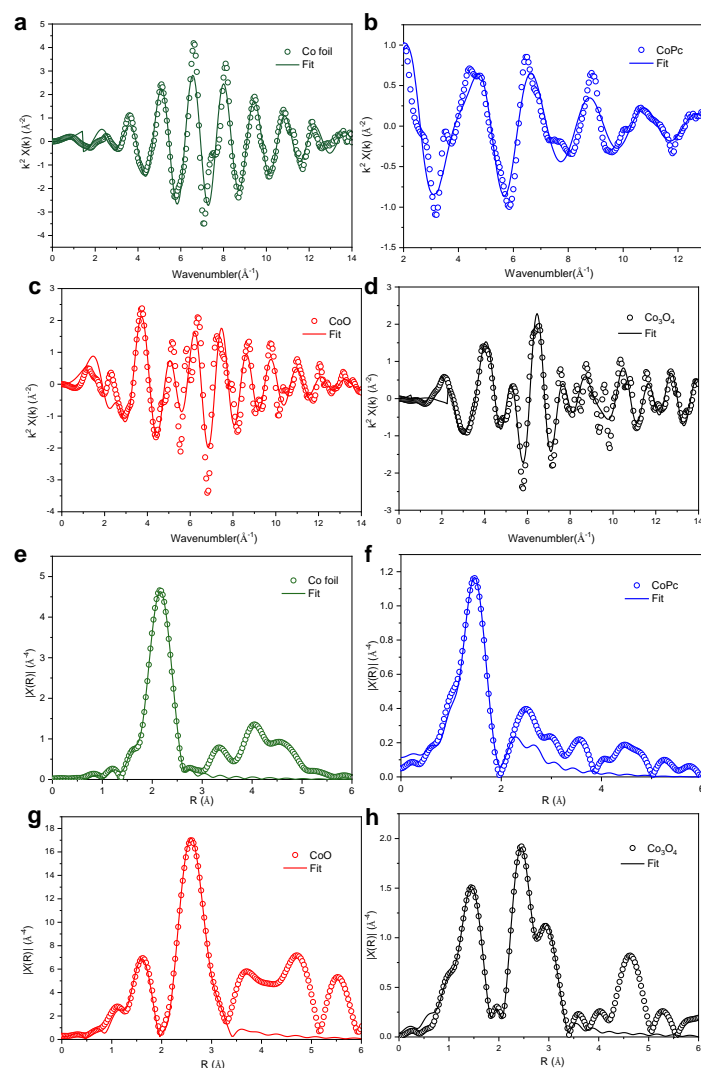


Figure S9. Corresponding Co K-edge EXAFS fitting curves of Co foil, CoPc, CoO, and Co₃O₄.

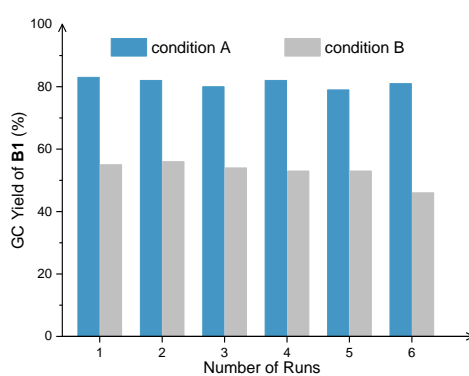


Figure S10. Catalyst recycling experiments at full and half conversions. Reaction condition A: the reaction of **A1** (0.25 mmol), HCHO (0.5 mmol), HCOOH (1.25 mmol), *L*-proline (0.075 mmol), and Co-N_x/NC-900 (20 mg, 3.83 mol%) in THF (2 mL) was performed at 100 °C for 20 h under N₂ protection. Reaction condition B: the same as “A” for 8 h.

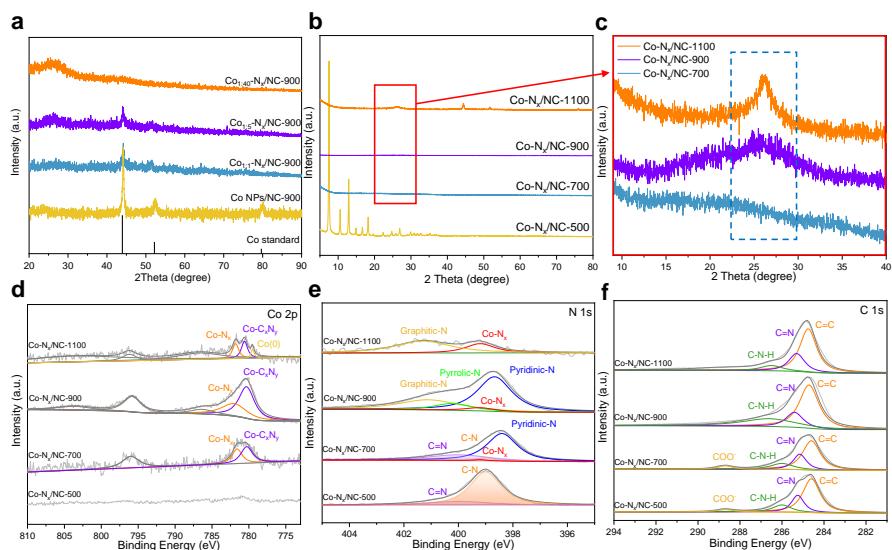


Figure S11. (a) Evolution of PXRD patterns of different Co-loading catalysts. Evolution of (b,c) PXRD patterns, (d) Co 2p XPS, (e) N 1s XPS and (f) C 1s XPS of the pyrolysis of $\text{Co}_1\text{Zn}_{20}$ -BMOF under temperature-dependent measurement.

The results of PXRD and XPS show that the original structure of MOF has been basically retained and there was no Co-N_x species formed during the pyrolysis of $\text{Co}_1\text{Zn}_{20}$ -BMOF at 500 °C (Figures S11b,d-f). The increase of pyrolysis temperature to 700 °C led to gradual collapse of the MOF skeleton, and resulted in small amount of Co-N_x species and pyridinic-N (Figures S11d-f). The material calcined at 900 °C contains abundant pyridinic-N, pyrrolic-N, and Co-N_x species, which exhibits the best catalytic performance. When the temperature was increased to 1100 °C, a set of well-defined Co-nanoparticle signals appeared and no characteristic peaks of pyridinic-N and pyrrolic-N were detected.

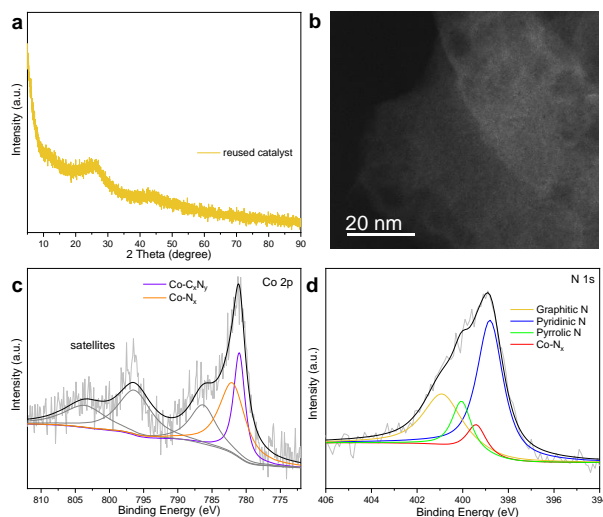


Figure S12. (a) PXRD patterns, (b) HAADF-STEM image and (c,d) XPS spectra of the catalyst after reuse of six runs.

The PXRD, HAADF-STEM and XPS spectra of $\text{Co-N}_x/\text{NC-900}$ after six consecutive runs did not show significant difference as compared with the fresh catalyst, revealing that the structure of cobalt catalyst was maintained very well.

Table S1. EXAFS data fitting results of Co-N_x/NC-900.

Sample	Path	N	ΔE_0 (eV)	100xR(Å)	10 ³ x σ^2 (Å ²)	R-factor
Co foil	Co-Co	12	6.54(0.52)	249.0(0.4)	6.02(0.41)	0.003
CoO	Co-O	6	-6.12(1.94)	211.2(1.3)	8.62(1.61)	0.006
	Co-Co	12	-5.12(1.93)	300.3(1.6)	8.62(2.91)	
Co ₃ O ₄	Co-O1	2	2.57(0.96)	193.3(0.7)	3.69(0.18)	0.002
	Co-O2	4	6.13(1.14)	192.8(0.7)	4.26(0.75)	
	Co-Co1	4	-2.42(0.93)	289.3(1.3)	4.78(0.57)	
	Co-Co2	2	8.61(1.48)	315.3(1.2)	5.46(1.53)	
CoPc	Co-N	4	5.46(1.12)	191.9(2.1)	3.92(0.46)	0.005
Co-N _x /NC-900	Co-N	4.90(0.81)	-4.69(1.91)	197.1(1.6)	8.16(1.23)	0.006
	Co-Co	1.37(0.22)	1.81(0.36)	253.0(1.1)	7.13(2.03)	

N, coordination number; R, distance between absorber and backscatter atoms; σ^2 , the Debye–Waller factor value; ΔE_0 (eV), inner potential correction to account for the difference in the inner potential between the sample and the reference compound.

Table S2. The total-N and relative atomic ratios of different N types based on XPS analyses in series of cobalt catalysts.

	Graphitic-N	Pyridinic-N	Pyrrolic-N	Co-N _x	C=N	C-N	Total-N
Co _{1/1} -N _x /NC-900	56.88%	23.19%	7.31%	12.62%	-	-	7.04%
Co _{1/5} -N _x /NC-900	46.31%	28.39%	8.22%	17.08%	-	-	10.35%
Co-N _x /NC-900	28.53%	55.28%	11.82%	4.38%	-	-	13.77%
Co _{1/40} -N _x /NC-900	33.87%	57.28%	6.04%	2.81%	-	-	17.53%
Co-N _x /NC-500	-	-	-	-	19.73%	80.27%	13.15%
Co-N _x /NC-700	-	67.1%	-	2.07%	27.59%	3.24%	11.21%
Co-N _x /NC-1100	71.26%	-	-	28.74%	-	-	2.94%

4. Experimental Procedure

Table S3. Optimization of reaction conditions for synthesis of **B1** from nitrobenzene **A1**^[a]

Entry	Additive	Hydrogen	Solvent	Yield [%] ^[b]
1	<i>L</i> -proline	HCOOH	THF	81 ^[c]
2	CF ₃ COOH	HCOOH	THF	n.d.
3	Pyridine	HCOOH	THF	18
4	<i>L</i> -Prolinamide	HCOOH	THF	60
5	2-Phenylpyrrolidine	HCOOH	THF	40
6	<i>L</i> -proline	HCOOH	MeCN	24
7	<i>L</i> -proline	HCOOH	toluene	5
8	<i>L</i> -proline	HCOOH	MeOH	47
9	<i>L</i> -proline	HCOOH	tert-amyl alcohol	trace
10	<i>L</i> -proline	HCOOH	1,4-dioxane	34
11	<i>L</i> -proline	HCOOH	H ₂ O	n.d.
12	<i>L</i> -proline	HCOOH	THF	48 ^[d]
13	<i>L</i> -proline	HCOOH	THF	(21, 49) ^[e]

[a] Reaction conditions: nitrobenzene (0.25 mmol), HCHO (2 eq), catalyst (20 mg, 3.83 mol%), *L*-proline (30 mol %), HCOOH (5 eq), and THF (2 mL), 100 °C, 20 h. [b] Determined by gas chromatography (GC) using n-hexadecane as an internal standard. [c] Isolated yield. [d] THF (1 mL) instead of THF (2 mL). [e] Reaction temperatures are with respect to 80 °C and 120 °C, respectively.

Table S4. Control experiments of **B1** from nitrobenzene **A1**^[a]

Entry	Control Experiment	B1 Yield [%] ^[b]
1	standard conditions	81
2	no HCHO	0
3	no HCOOH	0
4	no Co-N _x /NC-900	0
5	cobalt acetate instead of Co-N _x /NC-900	0
6	Co ₁ Zn ₂₀ -BMOF instead of Co-N _x /NC-900	0

[a] Reaction conditions: **A1** (0.25 mmol), HCHO (2 eq.), catalyst (20 mg), *L*-proline (30 mol %), HCOOH (5 eq.), and THF (2 mL), 100 °C, 20 h. [b] Determined by gas chromatography (GC) using n-hexadecane as an internal standard.

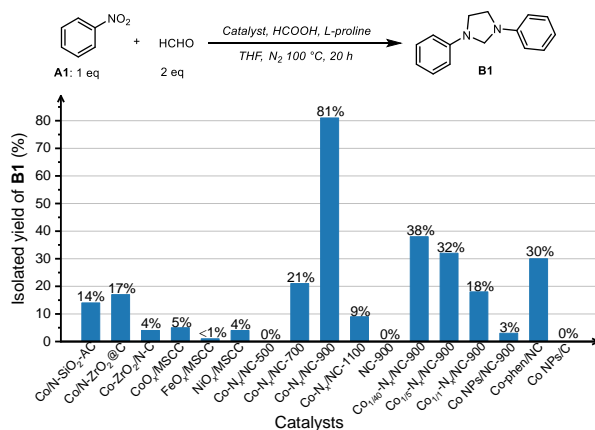
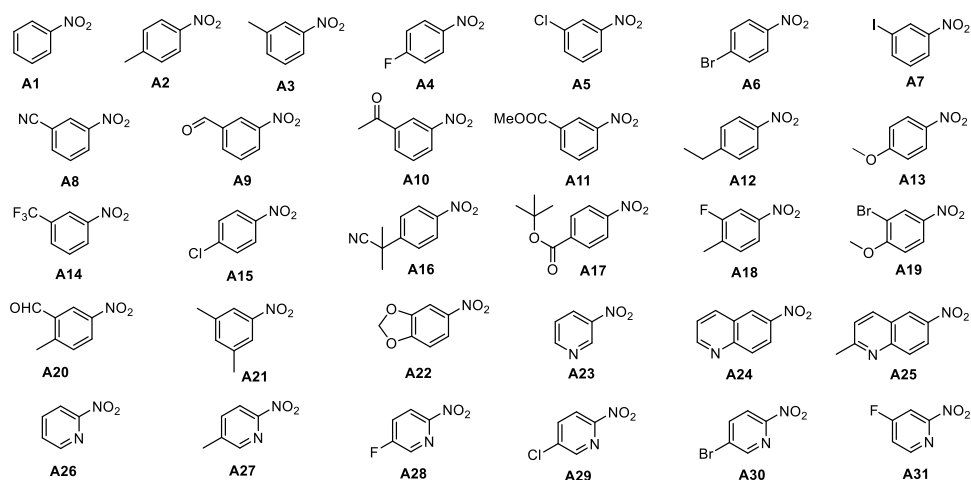


Figure S13. Catalytic performance comparison on the formation of product **B1** from nitrobenzene **A1** and formaldehyde. Reaction conditions: nitrobenzene (0.25 mmol), HCHO (2 eq.), catalyst (Co: 3.83 mol%), *L*-proline (30 mol%), HCOOH (5 eq.), and pure THF (2 mL), 100 °C, N₂, 20 h.

The others heterogeneous base metal catalysts previously employed in transfer hydrogenation reactions^[22-25] were tested to compare with Co-N_x/NC-900, and they resulted in either poor selectivity or no product formation (Figure S13). Meanwhile, the N-doped carbon matrix (NC-900), Co nanoparticles (Co NPs/NC-900, Co-phen/NC and Co NPs/C), and several different Co-loading catalysts (Co_{1/40}-N_x/NC-900, Co_{1/5}-N_x/NC-900 and Co_{1/1}-N_x/NC-900 derived from Co₁Zn₄₀-BMOF, Co₁Zn₅-BMOF and Co₁Zn₁-BMOF, respectively) have also been prepared, and then applied for the model reaction. The NC showed no activity for nitro reduction. Nitrogen-doped Co NPs exhibited low selectivity, and complex aniline by-products (aniline, *N*-methylaniline, *N,N*-dimethylaniline, *N*-formyl aniline) were detected by GC-MS analysis. Similarly, Co NPs/C gave no product formation. The selectivity of **B1** decreased gradually with the increase of Co-loading, revealing that the cobalt loading affects the composition of the active species in the catalysts (Figure S13, Figure S11a). Further, the Co-catalysts pyrolyzed at 500 °C, 700 °C and 1100 °C exhibited lower activity than Co-N_x/NC-900, indicating that the pyrolysis temperatures affect the chemical environments of the Co-species and N-species (Figures S11b-f).



Scheme S2. Nitroarenes employed for the synthesis of imidazolines

4.1. Procedure for Catalyst Recycling

Catalyst recycling experiments at full conversions: under nitrogen atmosphere, Co-N_x/NC-900 (20 mg), *L*-proline (9 mg, 30 mol %), HCOOH (47 μL, 1.25 mmol), nitrobenzene (25.5 μL, 0.25 mmol), 37 wt% HCHO in H₂O (37.2 μL, 0.5 mmol) and fresh THF (2 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 100 °C for 20 h. After cooling down to room temperature, 10 mg *n*-hexadecane was added to the solution and the yield was determined by GC-MS analysis. The catalyst was isolated by centrifugation, washed with methanol for three times, then dried under vacuum at 60 °C for 4 h. Catalyst recycling experiments at half conversions was followed by the same procedure as full conversions for 8 h.

4.2. Poisoning Experiment

Under nitrogen atmosphere, Co-N_x/NC-900 (20 mg), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol), nitrobenzene (25.5 μL, 0.25 mmol), 37 wt% HCHO in H₂O (37.2 μL, 0.5 mmol), KSCN (10.0 mg), and fresh THF (2 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 100 °C for 20 h. After cooling down to room temperature, 10 mg *n*-hexadecane was added to the solution and the yield was determined by GC-MS analysis.

4.3. The Procedure for the Synthesis of Imine int-5

At room temperature, the mixture of aniline (23 μL, 0.25 mmol), 37 wt% HCHO in H₂O (18.6 μL, 0.25 mmol) and MeOH (2 mL) was added successively to a round-bottom flask (50 mL) equipped with a magnetic stirrer bar under air for 1 h. The solvent was evaporated off by rotary evaporator, and the remaining product was put into the reaction directly.

4.4. Formaldehyde-adsorption Experiments

The formaldehyde concentrations in solution were detected by acetylacetone spectrophotometric method. The method is based on the reaction of formaldehyde with the acetylacetone and its read by a spectrophotometer. First, in a 10 mL glass beaker, CH₃COONH₄ (12.5 g) was dissolved in 5 mL distilled water at room temperature. Then, CH₃COOH (1.5 mL) and acetylacetone (0.125 mL) were added into the above solution and diluted to 50 mL to prepare the acetylacetone reagent. Secondly, four identical glass bottles to mark as A, B, C, D. The vial "A" was added 38 μL HCHO (37 wt%) and 2 mL purified water. The vial "B" was added 1 mL acetylacetone and 2 mL purified water. The vial "C" was added 38 μL HCHO (37 wt%), 1 mL acetylacetone and 2 mL purified water to get a yellow liquid. The vial "D" was added 38 μL HCHO (37 wt%), 1 mL acetylacetone, 2 mL purified water and 20 mg catalyst equipped with a magnetic stirrer bar under air for 1 h to get the colorless solution. Finally, the amount of adsorbed formaldehyde was determined by a spectrophotometer at 412 nm wavelength.

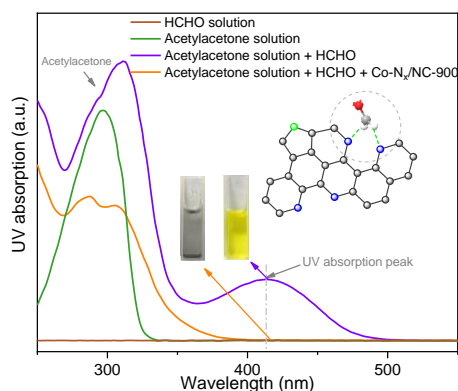


Figure S14. Formaldehyde-adsorption experiments.

4.5. The Crossover Reaction of *N*-hydroxyaniline and 4-cyano aniline

At room temperature, the mixture of *N*-hydroxyaniline (0.25 mmol), 4-cyano aniline (0.5 mmol), HCHO (1.5 mmol) and THF (2 mL) was added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar. Under N_2 atmosphere, $Co-N_x/NC-900$ (20 mg), *L*-proline (0.2 mmol) and HCOOH (1.25 mmol) were then added into the system, successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 100 °C (metal bath temperature) for 10 h. After cooling down to room temperature, 10 mg *n*-hexadecane was added to the solution and the yield was determined by GC-MS analysis.

4.6. pH-comparison Experiments

Under nitrogen atmosphere, $Co-N_x/NC-900$ (20 mg), *L*-proline (9 mg, 30 mol %), hydrogen source (HCOOH / HCOONa in molar ratio, 1.25 mmol), nitrobenzene (25.5 μ L, 0.25 mmol), 37 wt% HCHO in H_2O (37.2 μ L, 0.5 mmol) and fresh THF (2 mL) were added successively to a Schlenk tube (50 mL) equipped with a magnetic stirrer bar, the Schlenk tube was then closed and the resulting reaction mixture was heated at 100 °C for 20 h. After cooling down to room temperature, 10 mg *n*-hexadecane was added to the solution and the yield was determined by GC-MS analysis. The pH of the reaction system was determined using the pH meter.

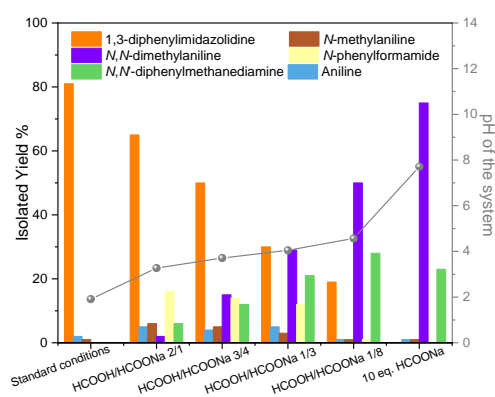
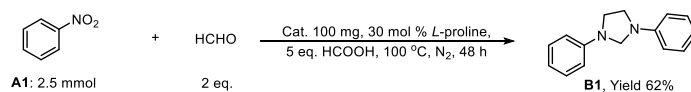


Figure S15. pH-comparison experiments.

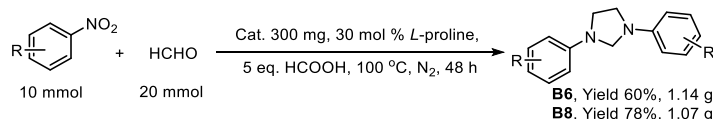
4.7. Synthetic Utility

(1) Amplified synthesis of compound **B1**



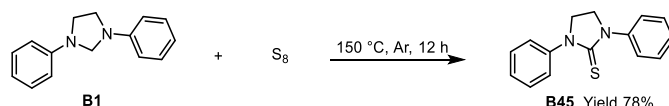
Under N₂ atmosphere, Co-N_x/NC-900 100 mg, *L*-proline (30 mol%), nitrobenzene **A1** (2.5 mmol), HCHO (5 mmol), HCOOH (12.5 mmol), and fresh THF (30 mL) were introduced in a Schlenk tube (200 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 100 °C (metal bath temperature) for 48 h. After cooling down to room temperature, the reaction was quenched with 10% Na₂CO₃ solution, extracted with ethyl acetate (3×15 mL), and dried over anhydrous Na₂SO₄. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (40:1) to give the product **B1**.

(2) Gram-scale synthesis of compound **B6** and **B8**



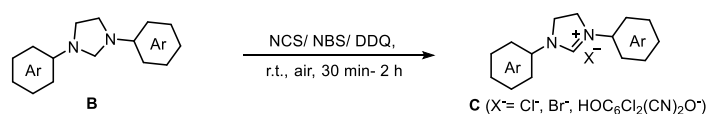
Under N₂ atmosphere, Co-N_x/NC-900 (300 mg), *L*-proline (30 mol%), nitrobenzene **A6** or **A8** (10 mmol), HCHO (20 mmol), HCOOH (50 mmol), and fresh THF (80 mL) were introduced in a Schlenk tube (200 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 100 °C (metal bath temperature) for 48 h. After cooling down to room temperature, the reaction was quenched with 10% Na₂CO₃ solution, extracted with ethyl acetate (3×30 mL), and dried over anhydrous Na₂SO₄. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (40 : 1) or petroleum ether/ethyl acetate (5 : 1) to give the product **B6** and **B8**, respectively.

(3) Preparation of cyclic thiourea **B45** (CAS: 1687-58-7) from **B1**



Under argon atmosphere, sulfur (240.5 mg, 7.5 mmol) and **B1** (336 mg, 1.5 mmol) were introduced in a Schlenk tube (50 mL), sealed and standed at 150 °C (metal bath temperature) for 12 h. After cooling down to room temperature, the reaction was quenched with ethyl acetate (2 mL) and then was filtered through a Buchner funnel. The filtrated mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography on silica gel, eluting with petroleum ether to give the product thioureas **B45** (298 mg, 78% yield).

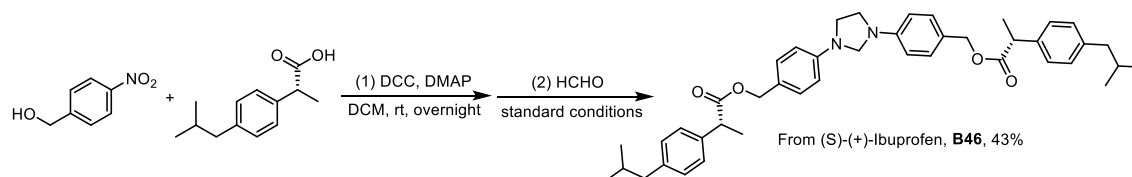
(4) Synthesis of imidazolium salts (**C1-C13**)



To a stirred solution of imidazolines (0.1 mmol) in 1,2-dimethoxyethane (1 mL), the corresponding dehydrogenating agent (0.1-0.5 mmol) was added in two portions at 10 minutes

intervals. Stirring was continued at room temperature for 30 minutes-2 hours. The products were collected, washed with 1,2-dimethoxyethane and recrystallized from anhydrous methanol.

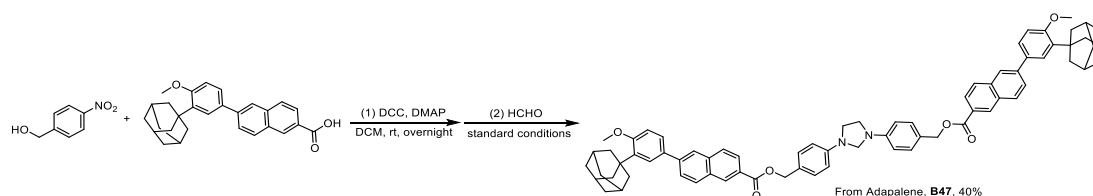
(5) Synthesis of Ibuprofen derivatives **B46**



A flame-dried round-bottom flask was charged with (*R*)-2-(4-isobutylphenyl)propanoic acid (7.0 mmol), DCC (1.90 g, 12.0 mmol), and DMAP (74.0 mg, 0.6 mmol). The contents of the flask were suspended in CH₂Cl₂ (20.0 mL) and allowed to stir for ~5 min before alcohol (612.2 mg, 4.0 mmol) was added. The reaction was stirred for overnight and was then filtered through a cotton plug. The solution was extracted with CH₂Cl₂ (3 x 30.0 mL). The resulting organic layers were combined, dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure to afford the crude material **A46**, which was purified by column chromatography.

Under N₂ atmosphere, Co-N_x/NC-900 (20 mg), *L*-proline (9 mg, 30 mol%), **A46** (85.3 mg, 0.25 mmol), HCHO (38 μL, 0.5 mmol), HCOOH (47 μL, 1.25 mmol), and fresh THF (2 mL) were introduced in a Schlenk tube (50 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 100 °C (metal bath temperature) for 20 h. After cooling down to room temperature, the reaction was quenched with 10% Na₂CO₃ solution, extracted with ethyl acetate (3×15 mL), and dried over anhydrous Na₂SO₄. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5:1) to give the product **B46** (35.5 mg, 43% yield).

(6) Synthesis of Adapalene derivatives **B47**



A flame-dried round-bottom flask was charged with Adapalene (7.0 mmol), DCC (1.90 g, 12.0 mmol), and DMAP (74.0 mg, 0.6 mmol). The contents of the flask were suspended in CH₂Cl₂ (20.0 mL) and allowed to stir for ~5 min before alcohol (612.2 mg, 4.0 mmol) was added. The reaction was stirred for overnight and was then filtered through a cotton plug. The solution was extracted with CH₂Cl₂ (3 x 30.0 mL). The resulting organic layers were combined, dried over sodium sulfate, and filtered. The solvent was removed under reduced pressure to afford the crude material **A47**, which was purified by column chromatography.

Under N₂ atmosphere, Co-N_x/NC-900 (20 mg), *L*-proline (9 mg, 30 mol%), **A47** (137 mg, 0.25 mmol), HCHO (38 μL, 0.5 mmol), HCOOH (47 μL, 1.25 mmol), and fresh THF (2 mL) were introduced in a Schlenk tube (50 mL), successively. Then, the Schlenk tube was closed and the resulting mixture was stirred at 100 °C (metal bath temperature) for 20 h. After cooling down to room temperature, the reaction was quenched with 10% Na₂CO₃ solution, extracted with ethyl

acetate (3×15 mL), and dried over anhydrous Na₂SO₄. The reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography on silica gel, eluting with petroleum ether/ethyl acetate (5:1) to give the product **B47** (53.6 mg, 40% yield).

5. Mechanistic studies

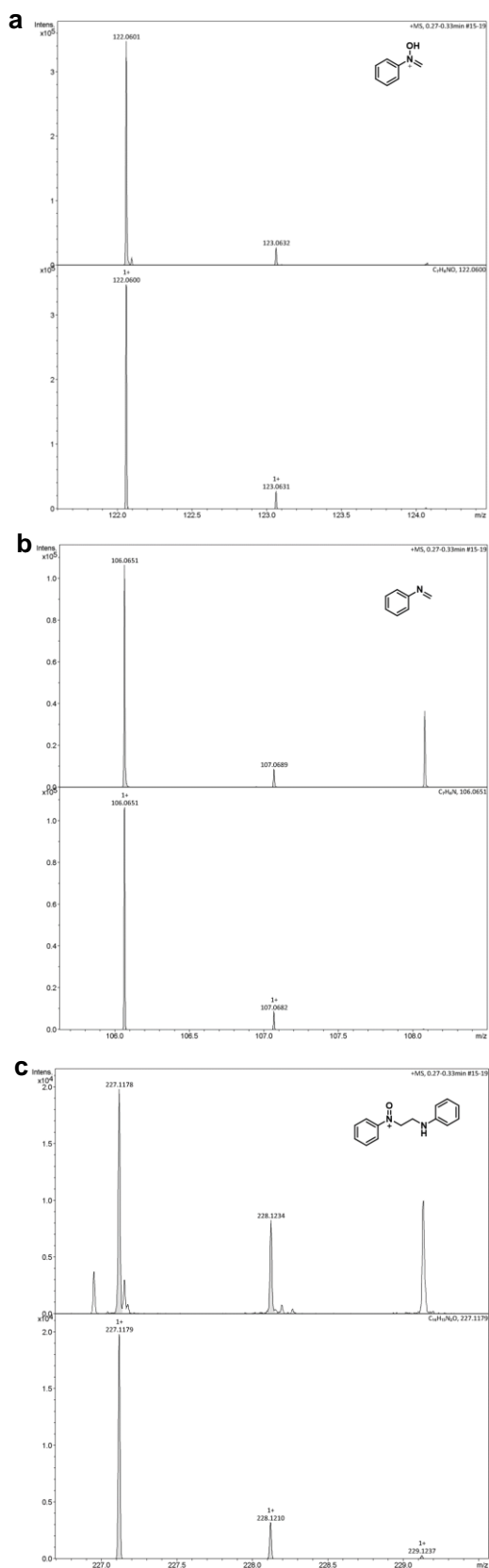


Figure S16. HR-MS of the intermediates by interruption of the model reaction after 20 min: (a) int-3, (b) int-5 and (c) int-6.

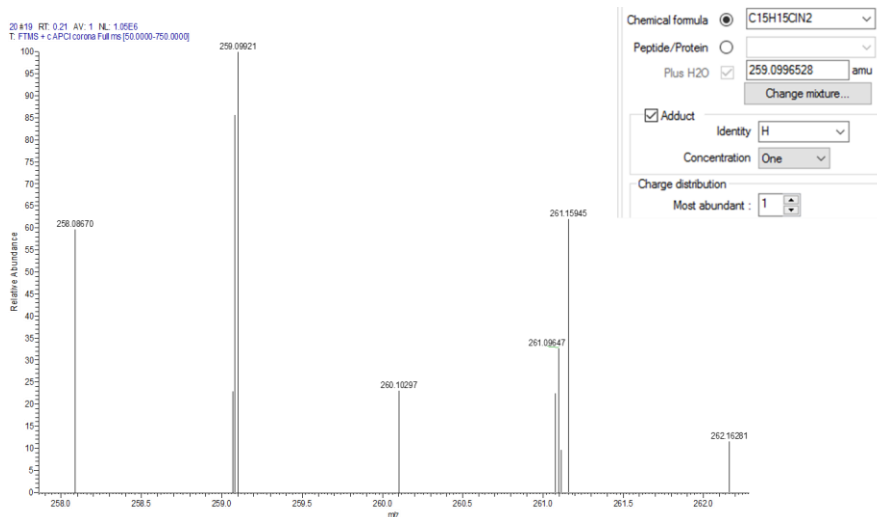


Figure S17. HR-MS of the product **B37** generated from imine **int-5** and *m*-chloronitrobenzene.

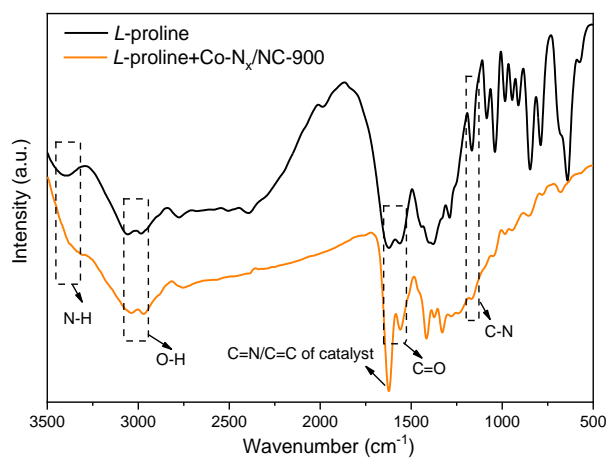


Figure S18. The FT-IR spectra of *L*-proline and the mixture of *L*-proline and Co-N_x/NC-900.

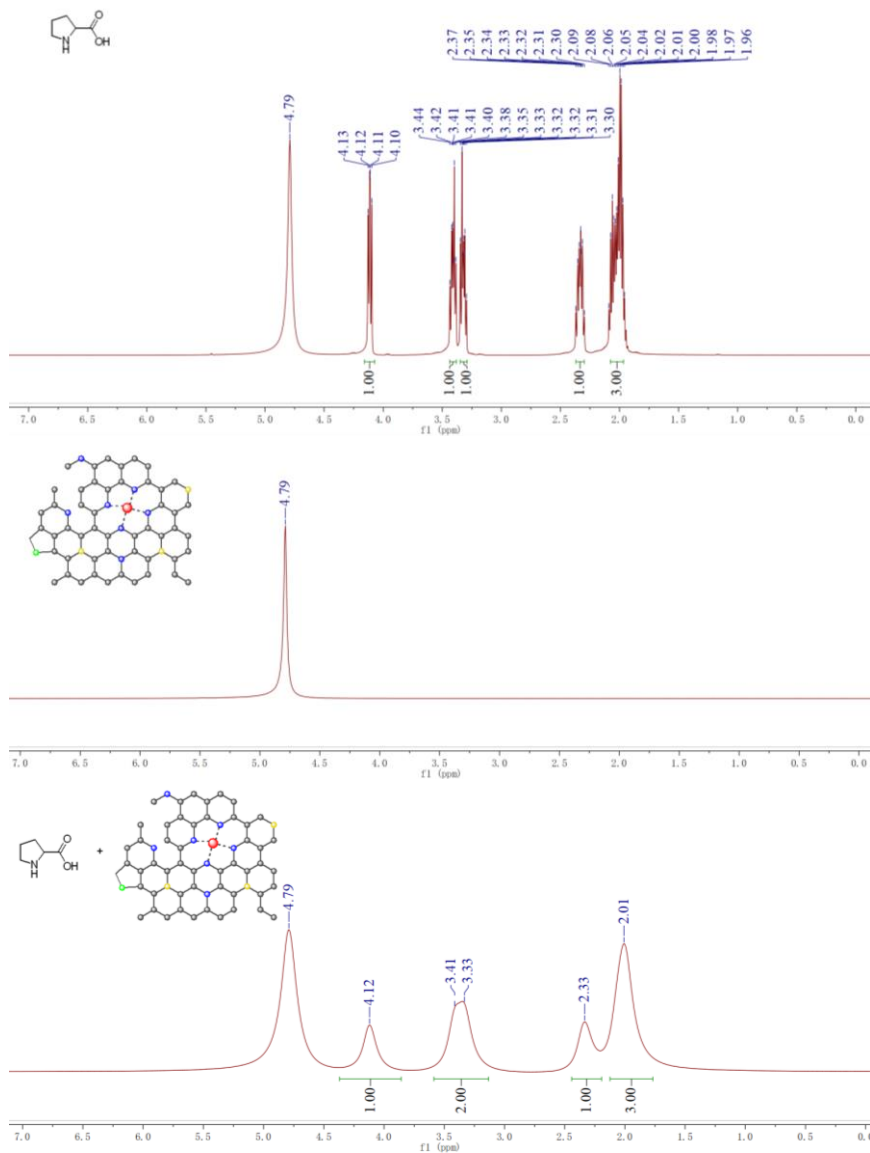


Figure S19. The ¹H NMR (500 MHz, D₂O) spectra of *L*-proline, Co-N_x/NC-900, and the mixture of *L*-proline and Co-N_x/NC-900.

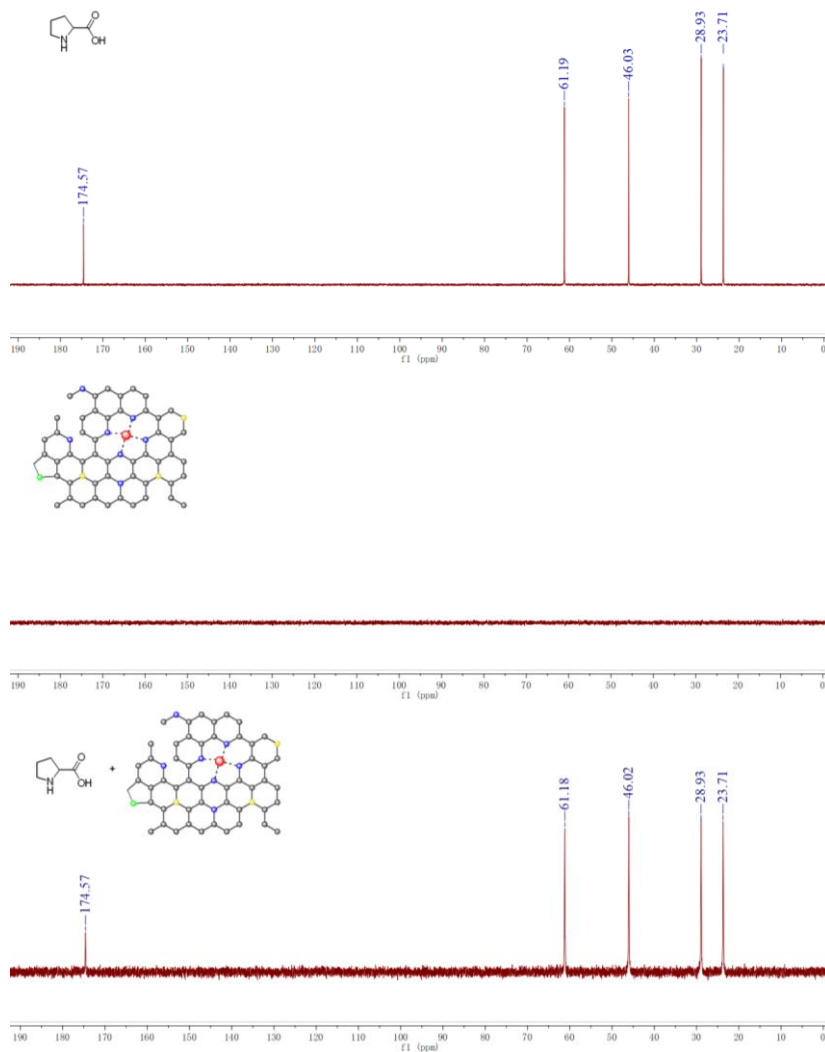


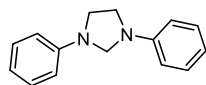
Figure S20. The ^{13}C NMR (500 MHz, D_2O) spectra of *L*-proline, Co- N_x/NC -900, and the mixture of *L*-proline and Co- N_x/NC -900.

6. References

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7. Analytical Data of the Obtained Compounds

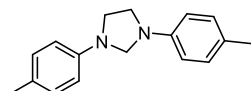
1,3-diphenylimidazolidine (B1)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), nitrobenzene (30.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a yellow solid (23 mg, 81% yield, m.p.: 120.9 – 121.9 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.32 (t, *J* = 7.6 Hz, 4H), 6.83 (t, *J* = 7.0 Hz, 2H), 6.69 (d, *J* = 8.0 Hz, 4H), 4.68 (s, 2H), 3.67 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 146.40, 129.39, 117.65, 112.45, 65.87, 46.48; MS (EI, *m/z*): 224.14 [M]⁺.

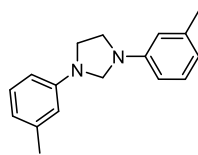
1,3-di-*p*-tolylimidazolidine (B2)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-methyl-4-nitrobenzene (34.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white solid (23 mg, 73% yield, m.p.: 184.2 – 185.2 °C).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.4 Hz, 4H), 6.61 (d, *J* = 8.6 Hz, 4H), 4.62 (s, 2H), 3.62 (s, 4H), 2.30 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 143.44, 128.79, 125.72, 111.48, 65.41, 45.77, 19.34; MS (EI, *m/z*): 252.15 [M]⁺.

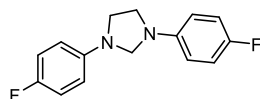
1,3-di-*m*-tolylimidazolidine (B3)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-methyl-3-nitrobenzene (34.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a yellow crystal (19.5 mg, 61% yield, m.p.: 101 – 102 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 8.2 Hz, 2H), 6.65 (d, *J* = 7.4 Hz, 2H), 6.51 (d, *J* = 5.6 Hz, 4H), 4.66 (s, 2H), 3.65 (s, 4H), 2.37 (s, 6H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 146.52, 139.14, 129.21, 118.57, 113.19, 109.67, 65.91, 46.50, 21.82; MS (EI, *m/z*): 252.18 [M]⁺.

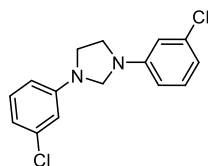
1,3-bis(4-fluorophenyl)imidazolidine (B4)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-fluoro-4-nitrobenzene (35.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 45/1) afforded the title compound as a brown solid (25.1 mg, 77% yield, m.p.: 149.8 – 151 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.01 (t, *J* = 8.8 Hz, 4H), 6.61 – 6.57 (m, 4H), 4.59 (s, 2H), 3.61 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 156.98, 155.11, 143.06, 115.94, 115.76, 113.21, 113.16, 66.88, 47.15; ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -127.70; MS (EI, *m/z*): 260.11 [M]⁺.

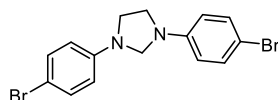
1,3-bis(3-chlorophenyl)imidazolidine (B5)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-chloro-3-nitrobenzene (39.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a yellow solid (22.3 mg, 61% yield, m.p.: 107.9 – 109 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.20 (t, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 8.0 Hz, 2H), 6.63 (s, 2H), 6.53 (d, *J* = 8.4 Hz, 2H), 4.62 (s, 2H), 3.65 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 147.05, 135.23, 130.36, 117.73, 112.41, 110.64, 65.45, 46.30; MS (EI, *m/z*): 292.05 [M]⁺.

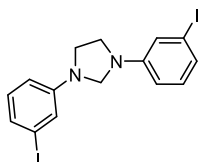
1,3-bis(4-bromophenyl)imidazolidine (B6)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-bromo-4-nitrobenzene (50.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a brown acicular crystal (34.2 mg, 72% yield, m.p.: 199 – 200 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, *J* = 8.8 Hz, 4H), 6.52 (d, *J* = 8.8 Hz, 4H), 4.57 (s, 2H), 3.62 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 144.08, 131.05, 112.99, 108.86, 64.71, 45.47; MS (EI, *m/z*): 379.89 [M]⁺.

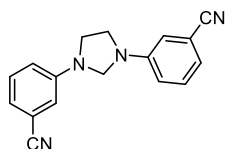
1,3-bis(3-iodophenyl)imidazolidine (B7)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-iodo-3-nitrobenzene (62.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white crystal (28 mg, 47% yield, m.p.: 174.1 – 175 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 7.8 Hz, 2H), 6.99 (dd, *J* = 13.8, 5.4 Hz, 4H), 6.64 – 6.57 (m, 2H), 4.58 (s, 2H), 3.62 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 147.12, 130.76, 126.74, 121.16, 111.73, 95.50, 65.24, 46.21; HRMS (ESI): Calcd. for C₁₅H₁₅I₂N₂ [M+H]⁺: 476.9319; found: 476.9314.

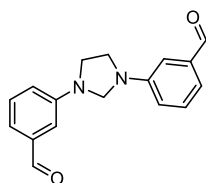
3,3'-(imidazolidine-1,3-diyl)dibenzonitrile (B8)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 3-nitrobenzonitrile (37 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a yellow crystal (28.1 mg, 82% yield, m.p.: 208 – 209 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.38 (t, *J* = 7.8 Hz, 2H), 7.10 (d, *J* = 7.2 Hz, 2H), 6.86 (d, *J* = 8.4 Hz, 4H), 4.68 (s, 2H), 3.72 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 146.30, 130.59, 121.74, 119.60, 116.98, 115.55, 113.67, 65.58, 46.54; HRMS (ESI): Calcd. for C₁₇H₁₅N₄ [M+H]⁺: 275.1291; found: 275.1287.

3,3'-(imidazolidine-1,3-diyl)dibenzaldehyde (B9)

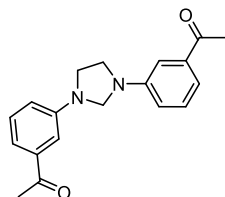


Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 3-nitrobenzaldehyde (37.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a yellow solid (15.4 mg, 44% yield, m.p.: 157 – 158 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 10.00 (s, 2H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.15 (s, 2H), 6.94 (dd, *J* = 8.2, 2.6 Hz, 2H), 4.76 (s, 2H), 3.76 (s, 4H); ¹³C NMR (126 MHz,

Chloroform-*d*) δ 187.52, 141.18, 132.14, 124.71, 115.39, 113.18, 106.04, 60.39, 41.15; HRMS (ESI): Calcd. for $C_{17}H_{17}N_2O_2$ $[M+H]^+$: 281.1284; found: 281.1282.

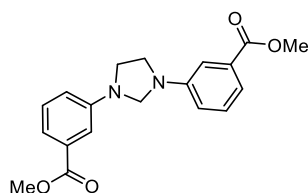
1,1'-(imidazolidine-1,3-diylbis(3,1-phenylene))bis(ethan-1-one) (B10)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-(3-nitrophenyl)ethan-1-one (41.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a brown crystal (21.2 mg, 55% yield, m.p.: 149 – 150 °C).

¹H NMR (400 MHz, Chloroform-*d*) δ 7.38 (dd, J = 4.4, 2.0 Hz, 4H), 7.25 – 7.23 (m, 2H), 6.87 (dt, J = 6.2, 3.0 Hz, 2H), 4.73 (s, 2H), 3.72 (s, 4H), 2.62 (s, 6H); ¹³C NMR (101 MHz, Chloroform-*d*) δ 198.70, 146.33, 138.14, 129.52, 118.34, 117.16, 111.15, 65.74, 46.49, 26.87; HRMS (ESI): Calcd. for $C_{19}H_{21}N_2O_2$ $[M+H]^+$: 309.1597; found: 309.1595.

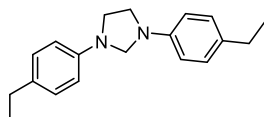
dimethyl 3,3'-(imidazolidine-1,3-diyl)dibenzoate (B11)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), methyl 3-nitrobenzoate (45.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (32.8 mg, 77% yield, m.p.: 157.8 – 159 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.49 (dd, J = 7.8, 1.4 Hz, 2H), 7.38 – 7.32 (m, 4H), 6.86 (dd, J = 8.2, 2.6 Hz, 2H), 4.73 (s, 2H), 3.94 (s, 6H), 3.72 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 167.49, 146.15, 131.15, 129.36, 118.88, 116.78, 113.21, 65.78, 52.17, 46.51; HRMS (ESI): Calcd. for $C_{19}H_{21}N_2O_4$ $[M+H]^+$: 341.1496; found: 341.1495.

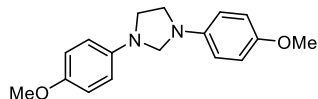
1,3-bis(4-ethylphenyl)imidazolidine (B12)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-ethyl-4-nitrobenzene (37.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a yellow solid (31.2 mg, 89% yield, m.p.: 171.6 – 172.6 °C).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.15 (d, $J = 8.0$ Hz, 4H), 6.64 (d, $J = 8.0$ Hz, 4H), 4.64 (s, 2H), 3.63 (s, 4H), 2.61 (q, $J = 7.6$ Hz, 4H), 1.24 (t, $J = 7.6$ Hz, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.68, 133.42, 128.69, 112.55, 66.39, 46.80, 27.96, 16.02; MS (EI, m/z): 280.16 $[\text{M}]^+$.

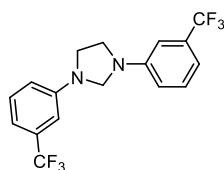
1,3-bis(4-methoxyphenyl)imidazolidine (B13)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-methoxy-4-nitrobenzene (38.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white solid (7.5 mg, 21% yield, m.p.: 143.1 – 144.1 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 6.89 (d, $J = 9.0$ Hz, 4H), 6.63 (d, $J = 9.0$ Hz, 4H), 4.57 (s, 2H), 3.78 (s, 6H), 3.58 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 150.26, 133.78, 126.46, 112.64, 70.16, 40.71, 24.69; MS (EI, m/z): 284.15 $[\text{M}]^+$.

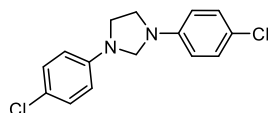
1,3-bis(3-(trifluoromethyl)phenyl)imidazolidine (B14)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-nitro-3-(trifluoromethyl)benzene (47.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white crystal (34.2 mg, 76% yield, m.p.: 158.4 – 159.4 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.40 (t, $J = 8.0$ Hz, 2H), 7.07 (d, $J = 7.8$ Hz, 2H), 6.86 (s, 2H), 6.82 (dd, $J = 8.2, 2.4$ Hz, 2H), 4.71 (s, 2H), 3.72 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.10, 131.88, 131.62, 129.84, 123.24, 115.46, 114.36, 114.33, 114.30, 114.27, 108.79, 108.76, 108.73, 108.70, 65.48, 46.33; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.69; HRMS (ESI): Calcd. for C₁₇H₁₅F₆N₂ $[\text{M}+\text{H}]^+$: 361.1133; found: 361.1132.

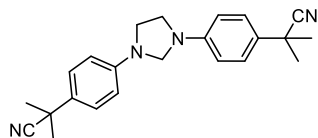
1,3-bis(4-chlorophenyl)imidazolidine (B15)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1-chloro-4-nitrobenzene (39.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white solid (27.1 mg, 74% yield, m.p.: 159 – 160 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.26 – 7.22 (m, 4H), 6.59 – 6.55 (m, 4H), 4.59 (s, 2H), 3.63 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 144.77, 129.22, 122.76, 113.52, 65.93, 46.61; MS (EI, *m/z*): 292.07 [*M*] $^+$.

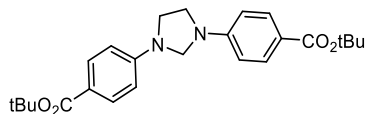
2,2'-(imidazolidine-1,3-diylbis(4,1-phenylene))bis(2-methylpropanenitrile) (B16)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 2-methyl-2-(4-nitrophenyl)propanenitrile (47.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a orange liquid (31.8 mg, 71% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.31 (t, *J* = 8.0 Hz, 2H), 6.88 (d, *J* = 7.8 Hz, 2H), 6.78 (s, 2H), 6.63 (d, *J* = 7.8 Hz, 2H), 4.71 (s, 2H), 3.71 (s, 4H), 1.76 (s, 12H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.55, 142.80, 129.96, 124.76, 114.05, 111.93, 109.21, 65.58, 46.42, 37.48, 29.25; HRMS (ESI): Calcd. for C₂₃H₂₇N₄ [*M*+H] $^+$: 359.2230; found: 359.2226.

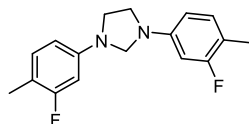
di-*tert*-butyl 4,4'-(imidazolidine-1,3-diyl)dibenzoate (B17)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), *tert*-butyl 4-nitrobenzoate (55.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (44 mg, 83% yield, m.p.: 164.4 – 165.5 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.93 (d, *J* = 8.6 Hz, 4H), 6.60 (d, *J* = 8.8 Hz, 4H), 4.73 (s, 2H), 3.72 (s, 4H), 1.59 (s, 18H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.10, 148.73, 131.32, 121.02, 111.35, 80.17, 64.78, 45.97, 28.35; HRMS (ESI): Calcd. for C₂₅H₃₃N₂O₄ [*M*+H] $^+$: 425.2435; found: 425.2427.

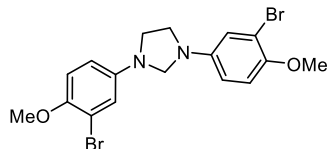
1,3-bis(3-fluoro-4-methylphenyl)imidazolidine (B18)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 2-fluoro-1-methyl-4-nitrobenzene (38.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white crystal (21.3 mg, 59% yield, m.p.: 178 – 179 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.07 (t, J = 8.4 Hz, 2H), 6.35 (s, 2H), 6.33 (dd, J = 4.4, 2.2 Hz, 2H), 4.56 (s, 2H), 3.60 (s, 4H), 2.20 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) 161.99, 160.06, 144.94, 144.86, 130.81, 130.76, 112.35, 112.21, 106.94, 106.91, 98.75, 98.54, 65.03, 45.62, 12.59, 12.56; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -116.28; HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{19}\text{F}_2\text{N}_2$ $[\text{M}+\text{H}]^+$: 289.1511; found: 289.1506.

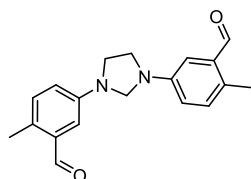
1,3-bis(3-bromo-4-methoxyphenyl)imidazolidine (B19)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 2-bromo-1-methoxy-4-nitrobenzene (57.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a brown solid (10.5 mg, 19% yield, m.p.: 147.1 – 148 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 6.90 – 6.87 (m, 4H), 6.57 (dd, J = 8.8, 3.0 Hz, 2H), 4.53 (s, 2H), 3.85 (s, 6H), 3.57 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 148.57, 141.84, 117.49, 113.94, 112.97, 112.24, 66.79, 57.10, 47.12; HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{19}\text{Br}_2\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 440.9808; found: 440.9802.

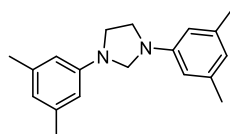
5,5'-(imidazolidine-1,3-diyl)bis(2-methylbenzaldehyde) (B20)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 2-methyl-5-nitrobenzaldehyde (41.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a yellow crystal (17 mg, 44% yield, m.p.: 189.5 – 190 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 10.33 (s, 2H), 7.19 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 2.8 Hz, 2H), 6.83 (dd, J = 8.2, 2.8 Hz, 2H), 4.70 (s, 2H), 3.70 (s, 4H), 2.60 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.63, 144.81, 134.52, 132.71, 129.86, 118.11, 113.60, 66.10, 46.69, 17.94; HRMS (ESI): Calcd. for $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 309.1597; found: 309.1596.

1,3-bis(3,5-dimethylphenyl)imidazolidine (B21)

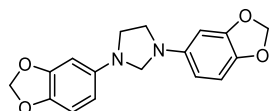


Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 1,3-dimethyl-5-nitrobenzene (37.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-

proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^{\circ}$ C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white solid (21 mg, 60% yield, m.p.: 184.8 – 185 $^{\circ}$ C).

¹H NMR (500 MHz, Chloroform-*d*) δ 6.49 (s, 2H), 6.33 (s, 4H), 4.63 (s, 2H), 3.63 (s, 4H), 2.34 (s, 12H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 145.57, 137.95, 118.57, 109.37, 64.88, 45.46, 20.63; HRMS (ESI): Calcd. for C₁₉H₂₅N₂ [M+H]⁺: 281.2013; found: 281.2012.

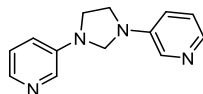
1,3-bis(benzo[d][1,3]dioxol-5-yl)imidazolidine (B22)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 5-nitrobenzo[d][1,3]dioxole (41.8 mg, 0.25 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^{\circ}$ C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 7/1) afforded the title compound as a brown solid (20 mg, 51% yield, m.p.: 314.5 – 315.6 $^{\circ}$ C).

¹H NMR (500 MHz, Chloroform-*d*) δ 6.77 (d, *J* = 8.4 Hz, 2H), 6.30 (d, *J* = 2.4 Hz, 2H), 6.05 (dd, *J* = 8.4, 2.4 Hz, 2H), 5.90 (s, 4H), 4.52 (s, 2H), 3.55 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 148.52, 142.56, 139.77, 108.75, 104.10, 100.75, 95.34, 67.37, 47.35; HRMS (ESI): Calcd. for C₁₇H₁₇N₂O₄ [M+H]⁺: 313.1182; found: 313.1177.

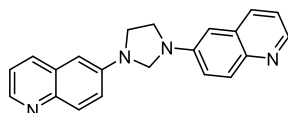
1,3-di(pyridin-3-yl)imidazolidine (B23)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 3-nitropyridine (31 mg, 0.25 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^{\circ}$ C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 2/1) afforded the title compound as a brown oil (24.3 mg, 86% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.10 (q, *J* = 2.8 Hz, 4H), 7.22 (t, *J* = 4.2 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.70 (d, *J* = 2.6 Hz, 2H), 3.71 (s, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 142.08, 139.38, 134.77, 123.85, 119.08, 64.98, 46.07; HRMS (ESI): Calcd. for C₁₃H₁₅N₄ [M+H]⁺: 227.1291; found: 227.1288.

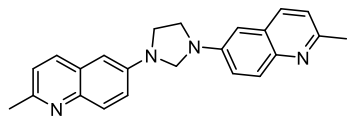
1,3-di(quinolin-6-yl)imidazolidine (B24)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 6-nitroquinoline (43.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μ L, 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^{\circ}$ C, N₂, 20 h. Purification by column chromatography (Eluent: dichloromethane/acetone = 7/1) afforded the title compound as a brown oil (34.7 mg, 85% yield).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.64 (d, J = 4.2 Hz, 2H), 8.02 (d, J = 9.0 Hz, 2H), 7.98 (d, J = 8.4 Hz, 2H), 7.28 (dd, J = 8.2, 4.2 Hz, 2H), 7.24 (dd, J = 7.4, 4.6 Hz, 2H), 6.77 (d, J = 2.8 Hz, 2H), 4.85 (s, 2H), 3.79 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.83, 144.10, 142.83, 134.16, 130.54, 129.81, 121.67, 118.77, 105.40, 65.89, 46.67; HRMS (ESI): Calcd. for $\text{C}_{21}\text{H}_{19}\text{N}_4$ $[\text{M}+\text{H}]^+$: 327.1604; found: 327.1601.

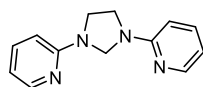
1,3-bis(2-methylquinolin-6-yl)imidazolidine (B25)



Prepared following the general procedure outlined above using Co- N_x/NC -900 (20 mg, 3.83 mol%), 2-methyl-6-nitroquinoline (47.3 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N_2 , 20 h. Purification by column chromatography (Eluent: dichloromethane/acetone = 3/1) afforded the title compound as a brown solid (30.2 mg, 68% yield, m.p.: 196 – 197 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.00 (d, J = 9.2 Hz, 2H), 7.94 (d, J = 8.4 Hz, 2H), 7.28 (d, J = 11.2 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 6.81 (s, 2H), 4.90 (s, 2H), 3.84 (s, 4H), 2.71 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 155.13, 143.66, 142.12, 134.60, 129.52, 127.86, 122.57, 118.61, 105.54, 66.03, 46.71, 24.85; HRMS (ESI): Calcd. for $\text{C}_{23}\text{H}_{23}\text{N}_4$ $[\text{M}+\text{H}]^+$: 355.1917; found: 355.1911.

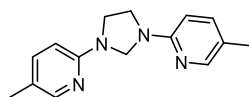
1,3-di(pyridin-2-yl)imidazolidine (B26)



Prepared following the general procedure outlined above using Co- N_x/NC -900 (20 mg, 3.83 mol%), 2-nitropyridine (31 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N_2 , 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (23 mg, 81% yield, m.p.: 97 – 98 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.21 (d, J = 5.0 Hz, 2H), 7.51 (t, J = 7.8 Hz, 2H), 6.66 (t, J = 6.2 Hz, 2H), 6.49 (d, J = 8.4 Hz, 2H), 4.97 (s, 2H), 3.84 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 156.26, 148.30, 137.39, 113.08, 106.89, 63.26, 45.17; HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_4$ $[\text{M}+\text{H}]^+$: 277.1291; found: 277.1288.

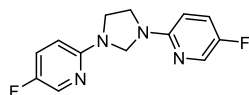
1,3-bis(5-methylpyridin-2-yl)imidazolidine (B27)



Prepared following the general procedure outlined above using Co- N_x/NC -900 (20 mg, 3.83 mol%), 5-methyl-2-nitropyridine (34.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N_2 , 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (29.3 mg, 92% yield, m.p.: 152 – 153 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.02 (s, 2H), 7.33 (d, $J = 10.8$ Hz, 2H), 6.41 (d, $J = 8.6$ Hz, 2H), 4.89 (s, 2H), 3.78 (s, 4H), 2.19 (s, 6H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.78, 147.91, 138.35, 121.78, 106.59, 63.69, 45.44, 17.42; HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{18}\text{N}_4$ $[\text{M}+\text{H}]^+$: 255.1604; found: 255.1600.

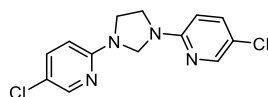
1,3-bis(5-fluoropyridin-2-yl)imidazolidine (B28)



Prepared following the general procedure outlined above using Co- N_x/NC -900 (20 mg, 3.83 mol%), 5-fluoro-2-nitropyridine (35.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N_2 , 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (13.5 mg, 41% yield, m.p.: 148 – 149 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.08 (d, $J = 3.0$ Hz, 2H), 7.31 (td, $J = 8.6, 2.8$ Hz, 2H), 6.43 (dd, $J = 9.2, 3.2$ Hz, 2H), 4.91 (s, 2H), 3.80 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.60, 153.21, 152.67, 135.16, 134.97, 125.28, 125.11, 106.91 (d, $J = 4.0$ Hz), 64.11, 45.83; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -143.39 (dd, $J = 7.6, 3.0$ Hz); HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{12}\text{F}_2\text{N}_4$ $[\text{M}+\text{H}]^+$: 263.1102; found: 263.1101.

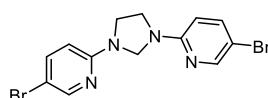
1,3-bis(5-chloropyridin-2-yl)imidazolidine (B29)



Prepared following the general procedure outlined above using Co- N_x/NC -900 (20 mg, 3.83 mol%), 5-chloro-2-nitropyridine (39.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N_2 , 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (22.1 mg, 60% yield, m.p.: 164 – 165 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.14 (s, 2H), 7.48 (d, $J = 8.8$ Hz, 2H), 6.43 (d, $J = 8.8$ Hz, 2H), 4.92 (s, 2H), 3.81 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.46, 146.69, 137.22, 120.45, 107.44, 63.44, 45.37; HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{12}\text{Cl}_2\text{N}_4$ $[\text{M}+\text{H}]^+$: 295.0511; found: 295.0508.

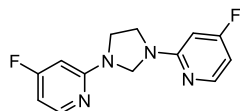
1,3-bis(5-bromopyridin-2-yl)imidazolidine (B30)



Prepared following the general procedure outlined above using Co- N_x/NC -900 (20 mg, 3.83 mol%), 5-bromo-2-nitropyridine (50.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N_2 , 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (32 mg, 67% yield, m.p.: 192 – 193 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.22 (d, $J = 2.4$ Hz, 2H), 7.59 (dd, $J = 9.0, 2.4$ Hz, 2H), 6.39 (d, $J = 8.8$ Hz, 2H), 4.90 (s, 2H), 3.81 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 154.63, 148.93, 139.77, 108.09, 107.92, 63.30, 45.28; HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{12}\text{Br}_2\text{N}_4$ $[\text{M}+\text{H}]^+$: 382.9501; found: 382.9496.

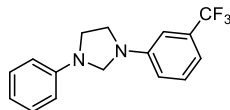
1,3-bis(4-fluoropyridin-2-yl)imidazolidine (B31)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 3.83 mol%), 4-fluoro-2-nitropyridine (35.5 mg, 0.25 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 2 eq.), *L*-proline (9 mg, 30 mol%), HCOOH (47 μL , 1.25 mmol, 5 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a white solid (10.2 mg, 31% yield, m.p.: 139 – 140 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 8.16 (dd, $J = 9.2, 5.8$ Hz, 2H), 6.47 – 6.42 (m, 2H), 6.17 (dd, $J = 11.4, 2.2$ Hz, 2H), 4.96 (s, 2H), 3.84 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 171.05, 169.00, 158.09, 150.65 (d, $J = 9.4$ Hz), 102.06, 101.92, 93.51, 93.34, 63.21, 45.12; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -102.65 (q, $J = 9.8, 9.4$ Hz); HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{12}\text{F}_2\text{N}_4$ $[\text{M}+\text{H}]^+$: 263.1103; found: 263.1101.

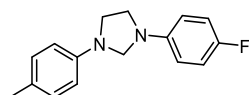
1-phenyl-3-(3-(trifluoromethyl)phenyl)imidazolidine (B32)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), nitrobenzene (15.4 mg, 0.125 mmol, 1 eq.), 1-nitro-3-(trifluoromethyl)benzene (24 mg, 0.125 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL , 1.25 mmol, 10 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a white solid (13.2 mg, 36% yield, m.p.: 92.7 – 93.7 $^\circ\text{C}$).

^1H NMR (500 MHz, Chloroform-*d*) δ 7.38 (t, $J = 8.2$ Hz, 1H), 7.32 (t, $J = 7.8$ Hz, 2H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.86 – 6.83 (m, 2H), 6.80 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.71 (d, $J = 8.2$ Hz, 2H), 4.69 (s, 2H), 3.70 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 146.22, 129.76, 129.42, 118.09, 115.21, 113.88, 112.68, 108.53, 65.70, 46.45, 46.39, 29.71; ^{19}F NMR (471 MHz, Chloroform-*d*) δ -62.71; HRMS (ESI): Calcd. for $\text{C}_{16}\text{H}_{16}\text{F}_3\text{N}_2$ $[\text{M}+\text{H}]^+$: 293.1260; found: 293.1258.

1-(4-fluorophenyl)-3-(*p*-tolyl)imidazolidine (B33)

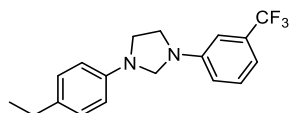


Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 1-methyl-4-nitrobenzene (17.2 mg, 0.125 mmol, 1 eq.), 1-fluoro-4-nitrobenzene (17.7 mg, 0.125 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL , 1.25 mmol, 10 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent:

petroleum ether/ethyl acetate = 40/1) afforded the title compound as a dark yellow solid (16.4 mg, 51% yield, m.p.: 119.7 – 120.4 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.11 (d, *J* = 8.0 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.59 (dd, *J* = 8.4, 5.4 Hz, 4H), 4.60 (s, 2H), 3.62 (hept, *J* = 5.8, 4.8 Hz, 4H), 2.29 (s, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 155.84, 143.33, 142.14, 128.83, 125.95, 114.85, 114.67, 112.09, 112.03, 111.55, 65.63, 46.04, 45.83, 19.34; ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -128.00; HRMS (ESI): Calcd. for C₁₆H₁₈FN₂ [M+H]⁺: 257.1448; found: 257.1446.

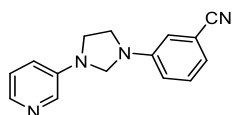
1-(4-ethylphenyl)-3-(3-(trifluoromethyl)phenyl)imidazolidine (B34)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 1-ethyl-4-nitrobenzene (19 mg, 0.125 mmol, 1 eq.), 1-nitro-3-(trifluoromethyl)benzene (24 mg, 0.125 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a grey solid (14 mg, 35% yield, m.p.: 76.7 – 78 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.37 (t, *J* = 8.0 Hz, 1H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.82 (s, 1H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.66 (d, *J* = 8.2 Hz, 2H), 4.67 (s, 2H), 3.70 – 3.64 (m, *J* = 3.8 Hz, 4H), 2.60 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 146.27, 144.43, 134.07, 129.72, 129.61, 129.27, 128.74, 124.80, 115.09, 113.69 (d, *J* = 3.8 Hz), 112.92, 108.38, 65.97, 46.78, 46.42, 27.93, 15.93; ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -62.71; HRMS (ESI): Calcd. for C₁₈H₂₀F₃N₂ [M+H]⁺: 321.1573; found: 321.1568.

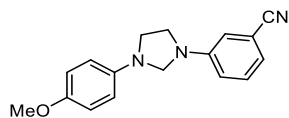
3-(3-(pyridin-3-yl)imidazolidin-1-yl)benzonitrile (B35)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 3-nitropyridine (15.5 mg, 0.125 mmol, 1 eq.), 3-nitrobenzonitrile (18.5 mg, 0.125 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 3/1) afforded the title compound as a brown crystal (11.9 mg, 38% yield, m.p.: 192.7 – 194 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.12 (s, 2H), 7.39 – 7.35 (m, 1H), 7.25 – 7.21 (m, 1H), 7.09 (d, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 10.6 Hz, 2H), 4.69 (d, *J* = 1.8 Hz, 2H), 3.82 – 3.61 (m, *J* = 4.0 Hz, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 145.96, 139.68, 134.96, 130.17, 121.16, 119.13, 116.52, 115.08, 113.24, 65.10, 46.13; HRMS (ESI): Calcd. for C₁₅H₁₅N₄ [M+H]⁺: 251.1291; found: 251.1290.

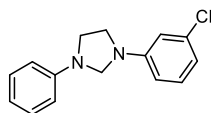
3-(3-(4-methoxyphenyl)imidazolidin-1-yl)benzonitrile (B36)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 1-methoxy-4-nitrobenzene (19.2 mg, 0.125 mmol, 1 eq.), 3-nitrobenzonitrile (18.5 mg, 0.125 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μ L, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 7/1) afforded the title compound as a brown crystal (9.1 mg, 26% yield, m.p.: 206.4 – 207.3 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.34 (t, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 6.80 – 6.78 (m, 1H), 6.68 (d, *J* = 8.6 Hz, 2H), 4.61 (s, 2H), 3.79 (s, 3H), 3.64 (dq, *J* = 10.4, 5.4 Hz, 4H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 152.81, 146.14, 140.89, 130.04, 120.45, 116.09, 115.04, 114.66, 114.22, 113.10, 66.34, 55.79, 47.37, 46.34; HRMS (ESI): Calcd. for C₁₇H₁₈N₃O [M+H]⁺: 280.1444; found: 280.1441.

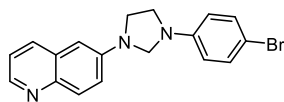
1-(3-chlorophenyl)-3-phenylimidazolidine (B37)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), nitrobenzene (15.4 mg, 0.125 mmol, 1 eq.), 1-chloro-3-nitrobenzene (19.7 mg, 0.125 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μ L, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 40/1) afforded the title compound as a yellow solid (13.9 mg, 43% yield, m.p.: 106.1 – 107 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.33 (t, *J* = 7.8 Hz, 3H), 7.28 (d, *J* = 4.4 Hz, 2H), 6.85 (d, *J* = 6.8 Hz, 1H), 6.70 (d, *J* = 7.2 Hz, 2H), 6.61 (d, *J* = 8.4 Hz, 2H), 4.66 (s, 2H), 3.68 (d, *J* = 5.4 Hz, 2H), 3.66 (d, *J* = 4.8 Hz, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 145.24, 143.90, 128.36, 128.14, 116.85, 112.42, 111.49, 64.88, 45.58, 45.47; HRMS (ESI): Calcd. for C₁₅H₁₆ClN₂ [M+H]⁺: 259.0996; found: 259.0992.

6-(3-(4-bromophenyl)imidazolidin-1-yl)quinoline (B38)

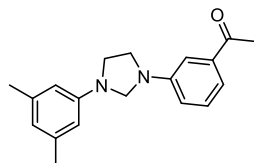


Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 6-nitroquinoline (21.8 mg, 0.125 mmol, 1 eq.), 1-bromo-4-nitrobenzene (25.2 mg, 0.125 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μ L, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: dichloromethane/ acetone = 10/1) afforded the title compound as a brown liquid (12.4 mg, 28% yield).

¹H NMR (500 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 4.0 Hz, 1H), 8.02 (dd, *J* = 18.0, 8.8 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.32 (dd, *J* = 8.2, 4.2 Hz, 1H), 7.26 (d, *J* = 2.8 Hz, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 6.61 – 6.53 (m, 2H), 4.75 (s, 2H), 3.79 (d, *J* = 6.4 Hz, 2H), 3.68 (t, *J* = 6.4 Hz, 2H); ¹³C NMR (126

MHz, Chloroform-*d*) δ 146.69, 145.14, 144.12, 134.23, 132.12, 130.44, 129.82, 121.65, 118.77, 114.12, 110.02, 105.27, 65.83, 46.60 (d, $J = 5.0$ Hz); HRMS (ESI): Calcd. for $C_{18}H_{17}BrN_3$ $[M+H]^+$: 354.0600; found: 354.0597.

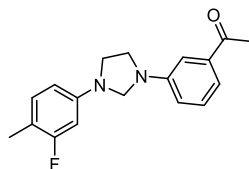
1-(3-(3-(3,5-dimethylphenyl)imidazolidin-1-yl)phenyl)ethan-1-one (B39)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 1,3-dimethyl-5-nitrobenzene (19 mg, 0.125 mmol, 1 eq.), 1-(3-nitrophenyl)ethan-1-one (20.7 mg, 0.125 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μ L, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as an orange-yellow solid (11.1 mg, 30% yield, m.p.: 80.7 – 82 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.37 (d, $J = 6.8$ Hz, 2H), 7.24 – 7.22 (m, 1H), 6.86 (dt, $J = 6.8, 2.4$ Hz, 1H), 6.50 (s, 1H), 6.34 (s, 2H), 4.68 (s, 2H), 3.71 – 3.64 (m, 4H), 2.62 (s, 3H), 2.33 (s, 6H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 198.93, 146.65, 146.57, 139.22, 138.26, 129.56, 120.14, 118.12, 117.07, 111.10, 110.79, 66.04, 46.67, 46.64, 26.97, 21.78; HRMS (ESI): Calcd. for $C_{19}H_{23}N_2O$ $[M+H]^+$: 295.1805; found: 295.1804.

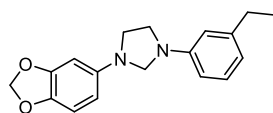
1-(3-(3-(3-fluoro-4-methylphenyl)imidazolidin-1-yl)phenyl)ethan-1-one (B40)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 2-fluoro-1-methyl-4-nitrobenzene (19.4 mg, 0.125 mmol, 1 eq.), 1-(3-nitrophenyl)ethan-1-one (20.7 mg, 0.125 mmol, 1 eq.), HCHO (38 μ L, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μ L, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 5/1) afforded the title compound as a yellow solid (9 mg, 24% yield, m.p.: 152.1 – 153 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.96 – 7.90 (m, 2H), 7.08 (t, $J = 8.4$ Hz, 1H), 6.64 – 6.57 (m, 2H), 6.39 (s, 1H), 6.37 (q, $J = 2.2$ Hz, 1H), 4.68 (s, 2H), 3.75 (dd, $J = 7.4, 5.6$ Hz, 2H), 3.64 (dd, $J = 7.4, 5.6$ Hz, 2H), 2.54 (s, 3H), 2.20 (d, $J = 1.8$ Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 196.54, 162.04 (d, $J = 242.8$ Hz), 149.14, 145.77 (d, $J = 10.4$ Hz), 131.92 (d, $J = 7.0$ Hz), 130.73, 126.80, 114.06 (d, $J = 17.6$ Hz), 111.09, 108.40 (d, $J = 2.8$ Hz), 100.20 (d, $J = 26.6$ Hz), 65.38, 46.64, 46.04, 26.07, 13.62 (d, $J = 3.2$ Hz); ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -116.02; HRMS (ESI): Calcd. for $C_{18}H_{20}FN_2O$ $[M+H]^+$: 299.1554; found: 299.1553.

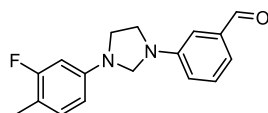
1-(benzo[*d*][1,3]dioxol-5-yl)-3-(4-ethylphenyl)imidazolidine (B41)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 5-nitrobenzo[d][1,3]dioxole (20.9 mg, 0.125 mmol, 1 eq.), 1-ethyl-4-nitrobenzene (18.9 mg, 0.125 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 7/1) afforded the title compound as a light-brown solid (11.5 mg, 31% yield, m.p.: 117.8 – 119 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.61 (d, *J* = 8.2 Hz, 2H), 6.32 (d, *J* = 2.4 Hz, 1H), 6.08 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.90 (s, 2H), 4.58 (s, 2H), 3.63 – 3.55 (m, 4H), 2.59 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.6 Hz, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 148.52, 142.69, 139.75, 133.47, 128.69, 112.49, 108.74, 104.18, 100.72, 95.41, 66.89, 47.37, 46.79, 27.93, 15.97; HRMS (ESI): Calcd. for C₁₈H₂₁N₂O₂ [M+H]⁺: 297.1598; found: 297.1596.

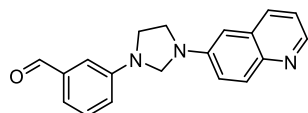
3-(3-(3-fluoro-4-methylphenyl)imidazolidin-1-yl)benzaldehyde (B42)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 2-fluoro-1-methyl-4-nitrobenzene (19.4 mg, 0.125 mmol, 1 eq.), 3-nitrobenzaldehyde (18.9 mg, 0.125 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 10/1) afforded the title compound as a yellow solid (10.7 mg, 30% yield, m.p.: 126.7 – 128.1 °C).

¹H NMR (500 MHz, Chloroform-*d*) δ 9.99 (s, 1H), 7.46 (t, *J* = 7.8 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.12 (t, *J* = 2.0 Hz, 1H), 7.08 (t, *J* = 8.6 Hz, 1H), 6.91 (dd, *J* = 8.2, 2.8 Hz, 1H), 6.39 (s, 1H), 6.37 (dd, *J* = 5.4, 2.2 Hz, 1H), 4.67 (s, 2H), 3.72 (dd, *J* = 7.8, 5.8 Hz, 2H), 3.64 (dd, *J* = 7.8, 5.8 Hz, 2H), 2.20 (s, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 193.02, 161.24, 146.69, 145.96, 137.57, 132.03 (d, *J* = 7.0 Hz), 130.09, 120.58, 118.43, 113.76, 111.29, 108.34 (d, *J* = 2.8 Hz), 100.19, 99.98, 66.05, 46.85, 46.58, 13.75 (d, *J* = 3.2 Hz); ¹⁹F NMR (471 MHz, Chloroform-*d*) δ -116.14; HRMS (ESI): Calcd. for C₁₇H₁₈FN₂O [M+H]⁺: 285.1398; found: 285.1395.

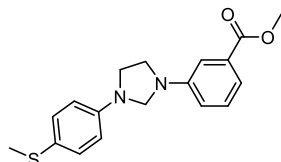
3-(3-(quinolin-6-yl)imidazolidin-1-yl)benzaldehyde (B43)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), 3-nitrobenzaldehyde (18.9 mg, 0.125 mmol, 1 eq.), 6-nitroquinoline (21.8 mg, 0.125 mmol, 1 eq.), HCHO (38 μL, 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL, 1.25 mmol, 10 eq.), and THF (2 mL), 100 °C, N₂, 20 h. Purification by column chromatography (Eluent: dichloromethane/ acetone = 10/1, then petroleum ether/ethyl acetate = 1/1) afforded the title compound as a yellow solid (12.9 mg, 34% yield, m.p.: 353.2 – 354 °C).

^1H NMR (500 MHz, Chloroform-*d*) δ 10.01 (s, 1H), 8.69 (dd, $J = 4.2, 1.6$ Hz, 1H), 8.05 (d, $J = 9.6$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 7.49 (t, $J = 7.8$ Hz, 1H), 7.34 (d, $J = 4.8$ Hz, 1H), 7.32 (d, $J = 5.6$ Hz, 1H), 7.30 (dd, $J = 9.2, 2.8$ Hz, 1H), 7.19 (t, $J = 2.0$ Hz, 1H), 6.97 (dd, $J = 8.2, 2.8$ Hz, 1H), 6.82 (d, $J = 2.8$ Hz, 1H), 4.85 (s, 2H), 3.86 – 3.78 (m, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 192.86, 146.93, 146.55, 144.07, 142.92, 137.47, 134.16, 130.64, 130.01, 129.79, 121.68, 120.82, 118.75, 118.46, 111.15, 105.55, 65.86, 46.65, 46.56; HRMS (ESI): Calcd. for $\text{C}_{19}\text{H}_{18}\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+$: 304.1444; found: 304.1444.

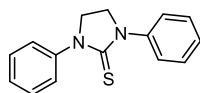
methyl 3-(3-(4-(methylthio)phenyl)imidazolidin-1-yl)benzoate (B44)



Prepared following the general procedure outlined above using Co-N_x/NC-900 (20 mg, 7.66 mol%), methyl(4-nitrophenyl)sulfane (21.2 mg, 0.125 mmol, 1 eq.), methyl 3-nitrobenzoate (22.7 mg, 0.125 mmol, 1 eq.), HCHO (38 μL , 0.5 mmol, 4 eq.), *L*-proline (9 mg, 60 mol%), HCOOH (47 μL , 1.25 mmol, 10 eq.), and THF (2 mL), 100 $^\circ\text{C}$, N₂, 20 h. Purification by column chromatography (Eluent: petroleum ether/ethyl acetate = 20/1) afforded the title compound as a yellow solid (13.2 mg, 32% yield, m.p.: 125.8 – 126.6 $^\circ\text{C}$).

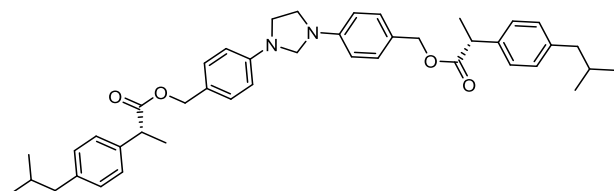
^1H NMR (500 MHz, Chloroform-*d*) δ 7.48 (d, $J = 7.6$ Hz, 1H), 7.34 (dt, $J = 9.2, 7.6$ Hz, 4H), 6.84 (dd, $J = 8.2, 2.8$ Hz, 1H), 6.64 (d, $J = 8.8$ Hz, 2H), 4.68 (s, 2H), 3.93 (s, 3H), 3.71 – 3.66 (m, 4H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.49, 146.19, 144.98, 131.27, 131.14, 129.33, 125.24, 118.76, 116.67, 113.22, 113.14, 65.84, 52.15, 46.53, 18.89; HRMS (ESI): Calcd. for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$: 329.1318; found: 329.1316.

1,3-diphenylimidazolidine-2-thione (B45)



Brown crystal, m.p.: 178.4 – 179 $^\circ\text{C}$; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.85 (d, $J = 7.8$ Hz, 4H), 7.71 (t, $J = 8.0$ Hz, 4H), 7.55 (t, $J = 7.8$ Hz, 2H), 4.43 (s, 4H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 181.32, 140.86, 128.90, 126.66, 125.49, 49.41; MS (EI, m/z): 254.07 $[\text{M}]^+$.

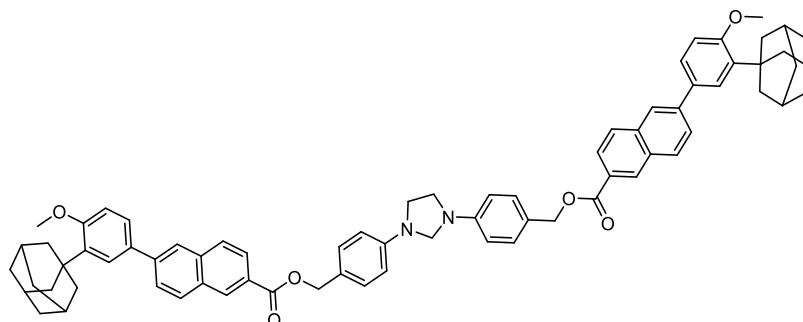
Ibuprofen derivatives (B46)



White solid, ^1H NMR (400 MHz, Chloroform-*d*) δ 7.18 (dt, $J = 4.2, 2.6$ Hz, 8H), 7.08 (d, $J = 8.0$ Hz, 4H), 7.01 (dd, $J = 19.8, 8.6$ Hz, 4H), 5.30 (s, 2H), 5.09 – 4.97 (m, 4H), 3.72 (q, $J = 7.2$ Hz, 4H), 3.42 – 3.34 (m, 2H), 2.44 (d, $J = 7.2$ Hz, 4H), 1.85 (d, $J = 6.8$ Hz, 2H), 1.49 (dd, $J = 7.2, 1.6$ Hz, 6H), 0.90 (d, $J = 6.6$ Hz, 12H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.66 (d, $J = 6.8$ Hz), 148.19,

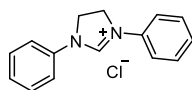
138.78, 137.67 (d, $J = 4.8$ Hz), 129.59, 129.43, 127.33, 115.99, 66.16 (d, $J = 6.8$ Hz), 49.00, 45.16, 45.04, 30.22, 22.42, 18.53.

Adapalene derivatives (B47)



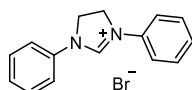
White solid, ^1H NMR (400 MHz, Chloroform- d) δ 8.09 (s, 2H), 7.99 (s, 3H), 7.89 (d, $J = 8.4$ Hz, 6H), 7.82 – 7.72 (m, 3H), 7.67 – 7.50 (m, 9H), 6.98 (d, $J = 8.4$ Hz, 3H), 4.28 – 4.13 (m, 4H), 4.12 (d, $J = 7.2$ Hz, 2H), 3.89 (s, 6H), 3.50 (tdt, $J = 11.0, 7.8, 3.8$ Hz, 4H), 2.17 (s, 18H), 1.80 (d, $J = 3.2$ Hz, 12H); ^{13}C NMR (101 MHz, Chloroform- d) δ 158.86, 154.53, 140.61, 138.98, 133.67, 132.51, 131.32, 129.18, 128.49, 126.92, 126.63, 125.89, 125.67, 124.69, 124.04, 112.11, 55.17, 49.67, 40.59, 37.20, 37.14, 29.12.

1,3-diphenyl-4,5-dihydro-1H-imidazol-3-ium chloride (C1)



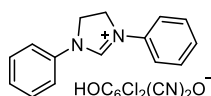
White solid (12.6 mg, 49% yield), ^1H NMR (500 MHz, DMSO- d_6) δ 10.03 (s, 1H), 7.67 (d, $J = 7.8$ Hz, 4H), 7.57 (t, $J = 7.6$ Hz, 4H), 7.39 (t, $J = 7.4$ Hz, 2H), 4.60 (s, 4H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 152.37, 136.60, 130.20, 127.54, 118.99, 48.83; HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{15}\text{N}_2^+$ [$\text{M}-\text{Cl}$] $^+$: 223.1235; found: 223.1227.

1,3-diphenyl-4,5-dihydro-1H-imidazol-3-ium bromide (C2)



White solid (25 mg, 83% yield), ^1H NMR (500 MHz, DMSO- d_6) δ 10.06 (s, 1H), 7.70 (d, $J = 8.2$ Hz, 4H), 7.56 (t, $J = 7.8$ Hz, 4H), 7.38 (t, $J = 7.4$ Hz, 2H), 4.62 (s, 4H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 152.19, 136.58, 130.14, 127.49, 119.03, 48.85; HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{15}\text{N}_2^+$ [$\text{M}-\text{Br}$] $^+$: 223.1235; found: 223.1227.

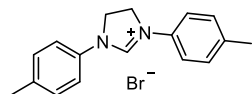
1,3-diphenyl-4,5-dihydro-1H-imidazol-3-ium 2,3-dichloro-5,6-dicyano-4-hydroxyphenolate (C3)



White solid (31.5 mg, 70% yield), ^1H NMR (500 MHz, DMSO- d_6) δ 9.98 (s, 1H), 7.61 (d, $J = 38.6$ Hz, 8H), 7.38 (s, 2H), 4.68 (s, 4H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 153.13, 136.72, 130.46,

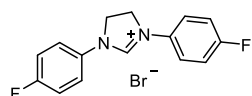
127.89, 119.26, 49.78; HRMS (ESI): Calcd. for $C_{15}H_{15}N_2^+$ [M-HOC₆Cl₂(CN)₂O]⁺: 223.1235; found: 223.1227.

1,3-di-*p*-tolyl-4,5-dihydro-1*H*-imidazol-3-ium bromide (C4)



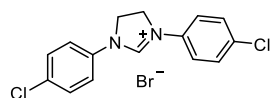
Yellow solid (27 mg, 82% yield), ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.00 (s, 1H), 7.67 (d, *J* = 8.6 Hz, 4H), 7.51 (d, *J* = 8.2 Hz, 4H), 4.70 (s, 4H), 2.65 (s, 6H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 151.61, 137.02, 134.26, 130.51, 118.77, 48.80, 20.92; HRMS (ESI): Calcd. for $C_{17}H_{19}N_2^+$ [M-Br]⁺: 251.1548; found: 225.1540.

1,3-bis(4-fluorophenyl)-4,5-dihydro-1*H*-imidazol-3-ium bromide (C5)



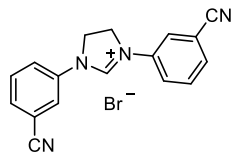
White solid (27 mg, 80% yield), ¹H NMR (500 MHz, DMSO-*d*₆) δ 9.95 (s, 1H), 7.72 (dd, *J* = 9.0, 4.6 Hz, 4H), 7.45 (t, *J* = 8.6 Hz, 4H), 4.60 (s, 4H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 162.00, 160.06, 152.78, 133.12 (d, *J* = 2.8 Hz), 121.35 (d, *J* = 8.6 Hz), 117.08, 116.89, 49.28; HRMS (ESI): Calcd. for $C_{15}H_{13}F_2N_2^+$ [M-Br]⁺: 259.1046; found: 259.1038.

1,3-bis(4-chlorophenyl)-4,5-dihydro-1*H*-imidazol-3-ium bromide (C6)



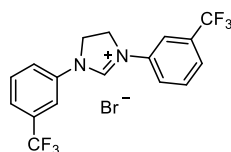
White solid (28.3 mg, 77% yield), ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.00 (s, 1H), 7.67 (s, 8H), 4.59 (s, 4H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 152.87, 135.48, 131.82, 130.09, 120.81, 48.98; HRMS (ESI): Calcd. for $C_{15}H_{13}Cl_2N_2^+$ [M-Br]⁺: 291.0455; found: 291.0445.

1,3-bis(3-cyanophenyl)-4,5-dihydro-1*H*-imidazol-3-ium bromide (C7)



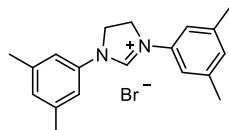
White solid (26.4 mg, 75% yield), ¹H NMR (500 MHz, DMSO-*d*₆) δ 10.17 (s, 1H), 8.22 (s, 2H), 7.98 (d, *J* = 7.8 Hz, 2H), 7.89 (d, *J* = 7.8 Hz, 2H), 7.81 (t, *J* = 8.0 Hz, 2H), 4.66 (s, 4H); ¹³C NMR (126 MHz, DMSO-*d*₆) δ 153.86, 137.18, 131.58, 131.10, 123.72, 122.58, 118.37, 113.04, 48.90; HRMS (ESI): Calcd. for $C_{17}H_{13}N_4^+$ [M-Br]⁺: 273.1140; found: 273.1132.

1,3-bis(3-(trifluoromethyl)phenyl)-4,5-dihydro-1*H*-imidazol-3-ium bromide (C8)



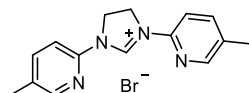
White solid (36.4 mg, 83% yield), ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.23 (s, 1H), 8.13 (s, 2H), 7.95 (d, $J = 10.6$ Hz, 2H), 7.84 (t, $J = 8.0$ Hz, 2H), 7.78 (d, $J = 7.8$ Hz, 2H), 4.71 (s, 4H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 154.02, 137.28, 131.52, 130.97, 130.72, 130.46, 125.25, 124.26 – 123.93 (m), 123.16 (d, $J = 17.7$ Hz), 116.38 – 116.11 (m), 49.07; HRMS (ESI): Calcd. for $\text{C}_{17}\text{H}_{13}\text{F}_6\text{N}_2^+$ [M-Br] $^+$: 359.0983; found: 359.0974.

1,3-bis(3,5-dimethylphenyl)-4,5-dihydro-1H-imidazol-3-ium bromide (C9)



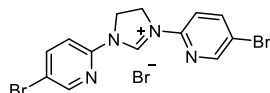
White solid (25.1 mg, 70% yield), ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 9.92 (s, 1H), 7.51 (s, 6H), 4.56 (s, 4H), 2.45 (s, 12H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 152.29, 139.77, 135.23, 125.05, 118.61, 48.79, 23.99; HRMS (ESI): Calcd. for $\text{C}_{19}\text{H}_{23}\text{N}_2^+$ [M-Br] $^+$: 279.1861; found: 279.1851.

1,3-bis(5-methylpyridin-2-yl)-4,5-dihydro-1H-imidazol-3-ium (C10)



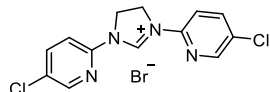
White solid (24.9 mg, 75% yield), ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.28 (s, 1H), 8.38 (s, 2H), 7.91 (d, $J = 8.4$ Hz, 2H), 7.75 (d, $J = 8.6$ Hz, 2H), 4.60 (s, 4H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 152.12, 148.92, 146.54, 140.31, 132.69, 112.59, 47.83, 17.82; HRMS (ESI): Calcd. for $\text{C}_{15}\text{H}_{17}\text{N}_4^+$ [M-Br] $^+$: 253.1448; found: 253.1444.

1,3-bis(5-bromopyridin-2-yl)-4,5-dihydro-1H-imidazol-3-ium bromide (C11)



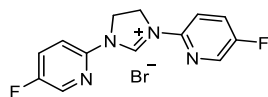
White solid (30.8 mg, 67% yield), ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.34 (s, 1H), 8.57 (s, 2H), 8.09 (s, 1H), 7.83 (d, $J = 8.8$ Hz, 2H), 7.47 (s, 2H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 152.91, 149.22, 140.12, 123.24, 113.17, 47.83; HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{11}\text{Br}_2\text{N}_4^+$ [M-Br] $^+$: 380.9345; found: 380.9339.

1,3-bis(5-chloropyridin-2-yl)-4,5-dihydro-1H-imidazol-3-ium bromide (C12)



White solid (24.6 mg, 66% yield), ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.40 (s, 1H), 8.65 (d, $J = 2.6$ Hz, 2H), 8.28 (dd, $J = 8.8, 2.6$ Hz, 1H), 7.94 (d, $J = 8.8$ Hz, 2H), 4.62 (s, 4H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 162.86, 153.73, 147.59, 139.77, 129.85, 114.76, 48.08; HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{11}\text{Cl}_2\text{N}_4^+$ [M-Br] $^+$: 293.0355; found: 293.0350.

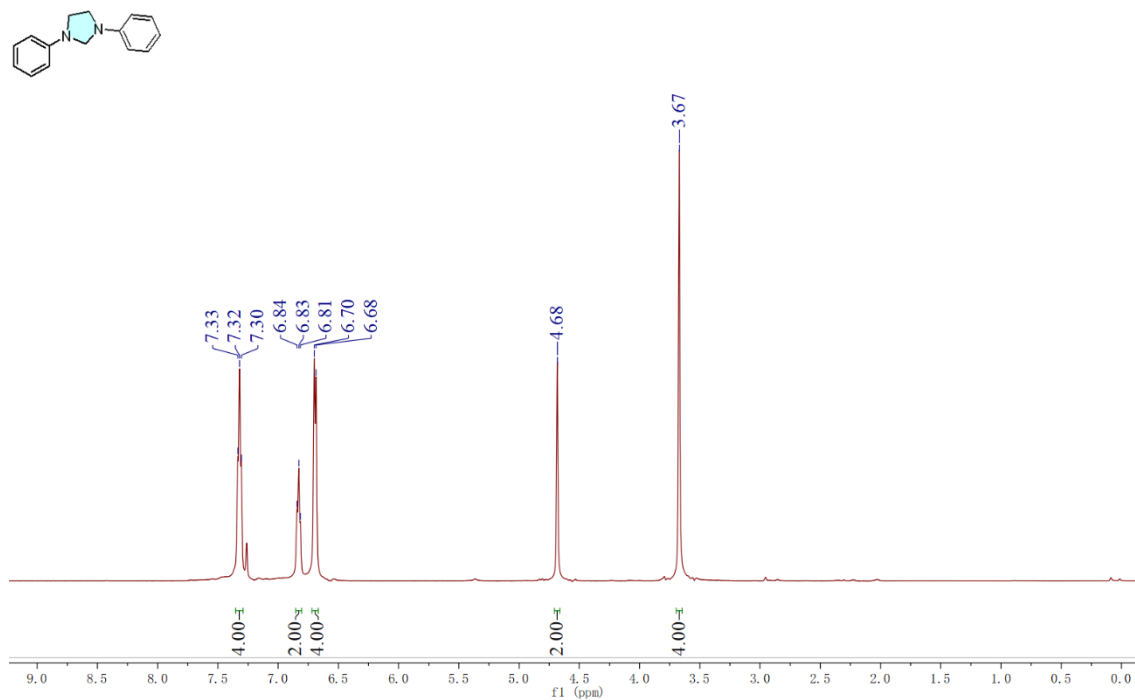
1,3-bis(5-fluoropyridin-2-yl)-4,5-dihydro-1H-imidazol-3-ium bromide (C13)



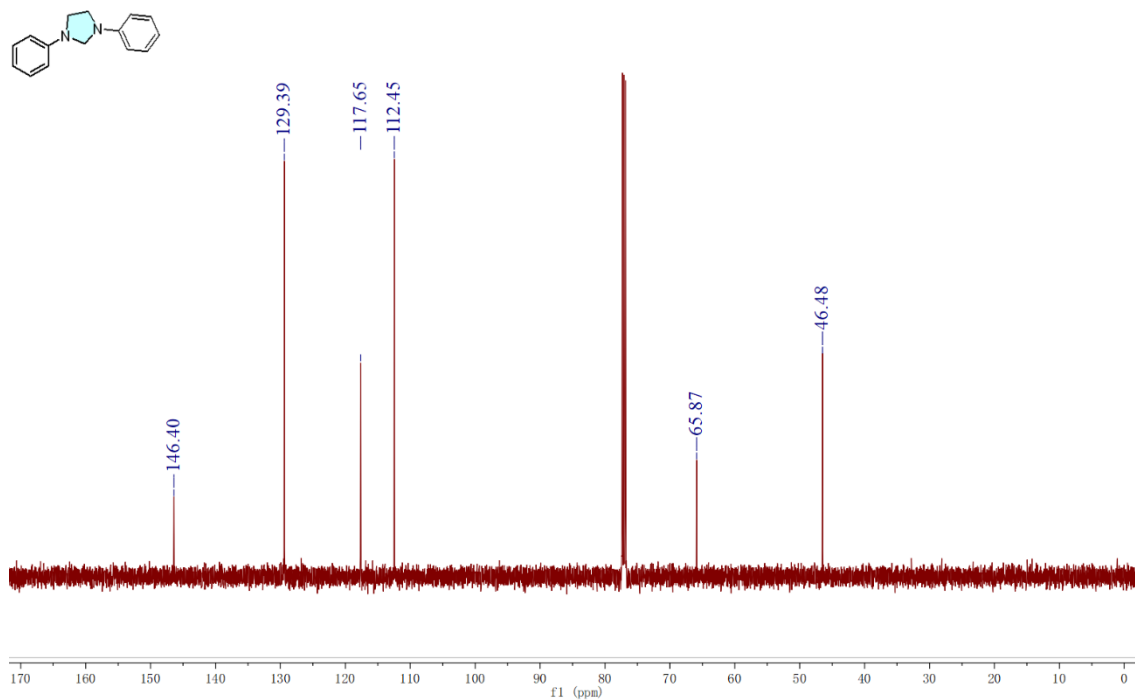
White solid (20.4 mg, 60% yield), ^1H NMR (500 MHz, $\text{DMSO-}d_6$) δ 10.31 (s, 1H), 8.61 (s, 2H), 8.12 (s, 2H), 7.94 (s, 2H), 4.62 (s, 4H); ^{13}C NMR (126 MHz, $\text{DMSO-}d_6$) δ 153.36, 144.97, 136.98, 136.77, 127.44 (d, $J = 21.2$ Hz), 114.87, 48.21; HRMS (ESI): Calcd. for $\text{C}_{13}\text{H}_{11}\text{F}_2\text{N}_4^+$ [M-Br] $^+$: 261.0946; found: 261.0942.

8. NMR Spectra of the Obtained Compounds

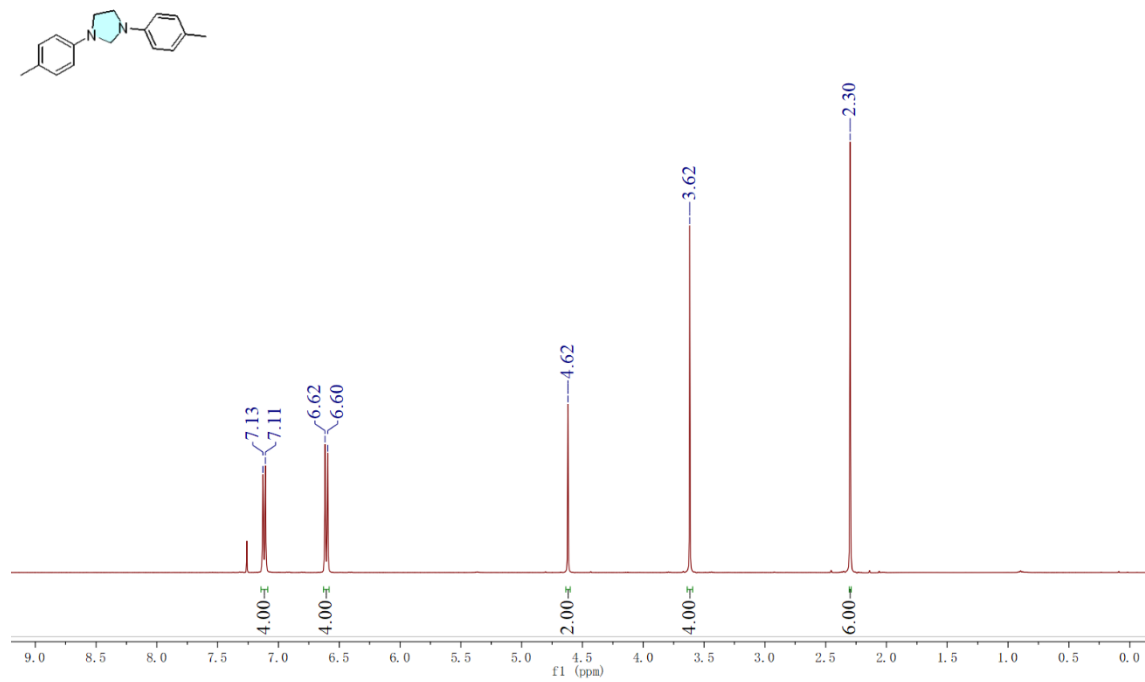
¹H- NMR spectrum of compound B1



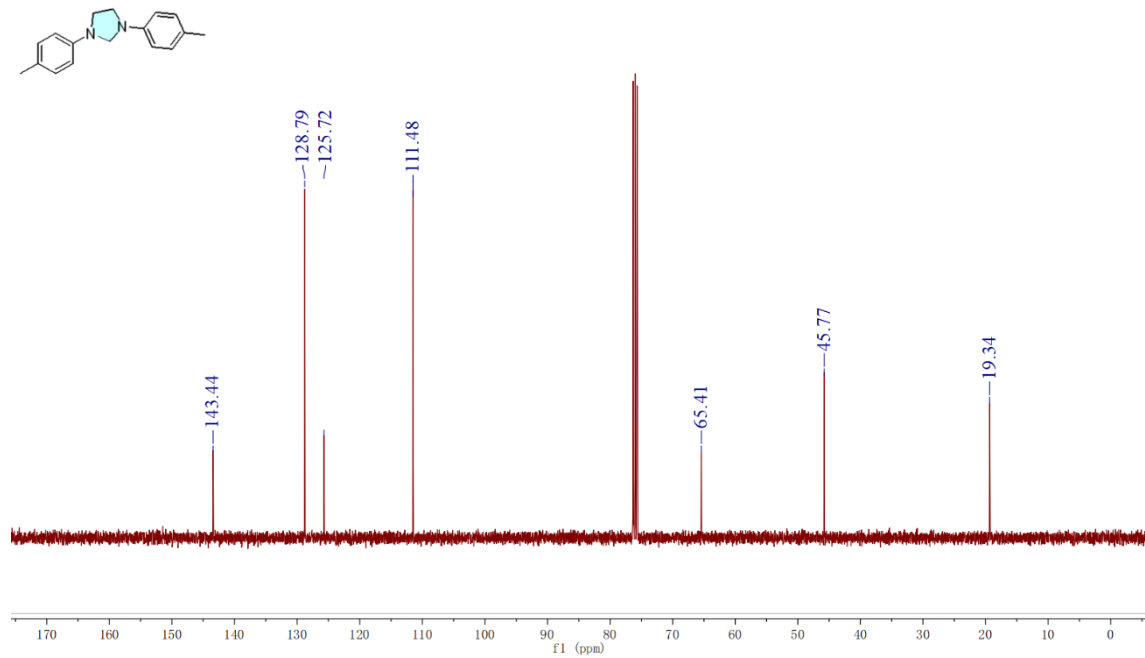
¹³C- NMR spectrum of compound B1



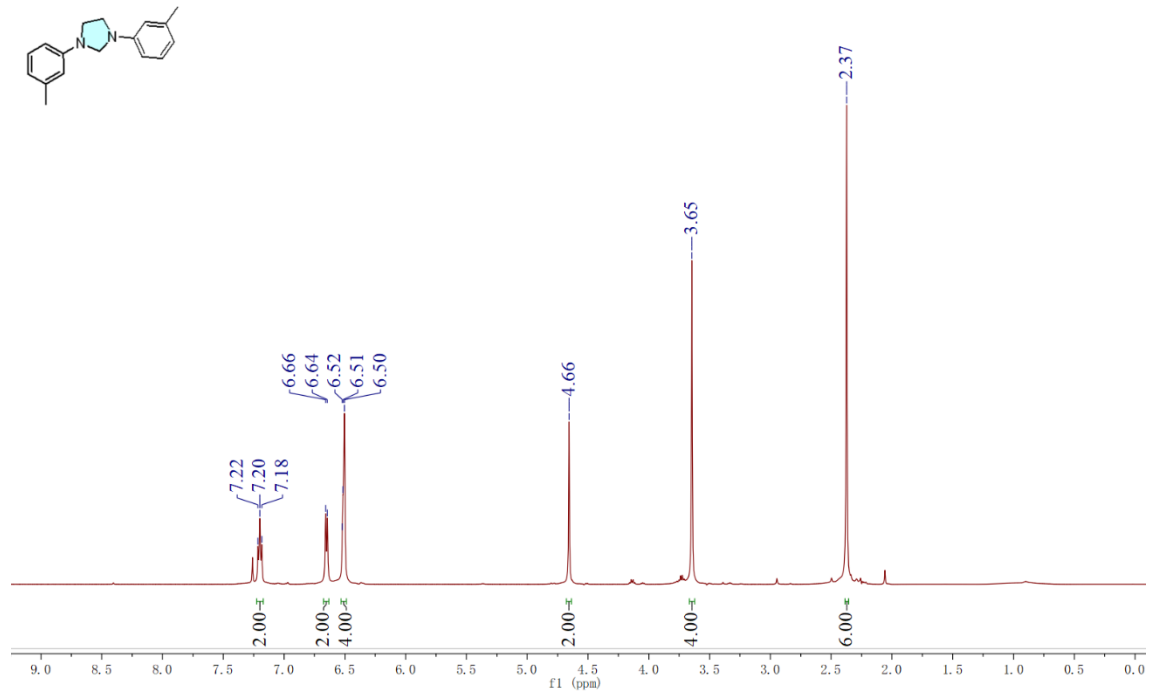
¹H-NMR spectrum of compound B2



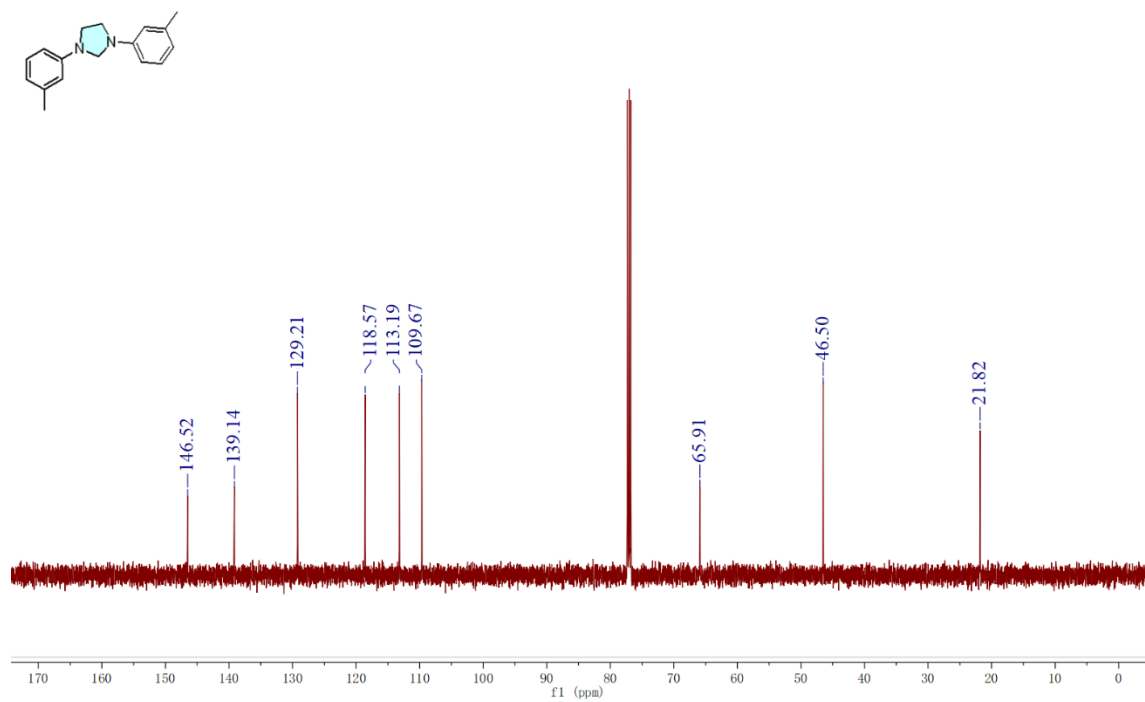
¹³C-NMR spectrum of compound B2



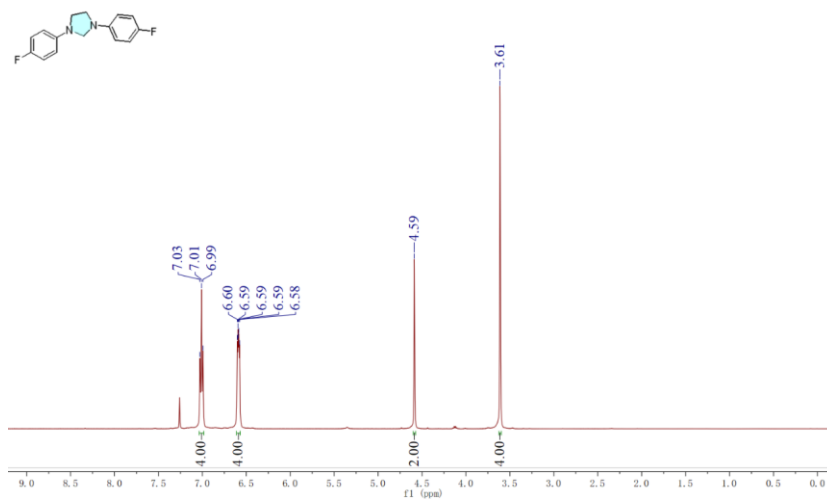
¹H-NMR spectrum of compound B3



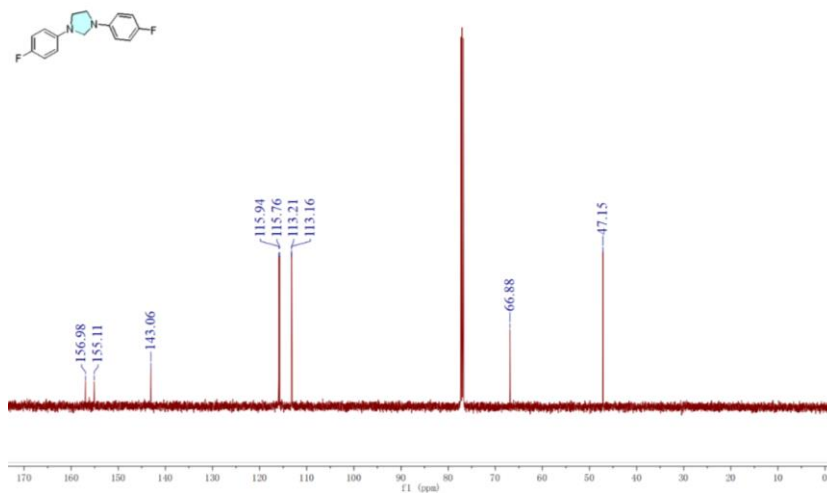
¹³C-NMR spectrum of compound B3



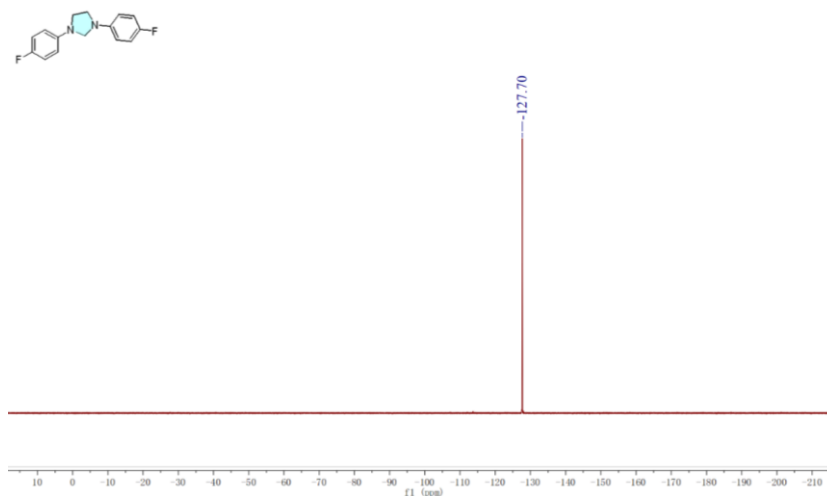
¹H-NMR spectrum of compound B4



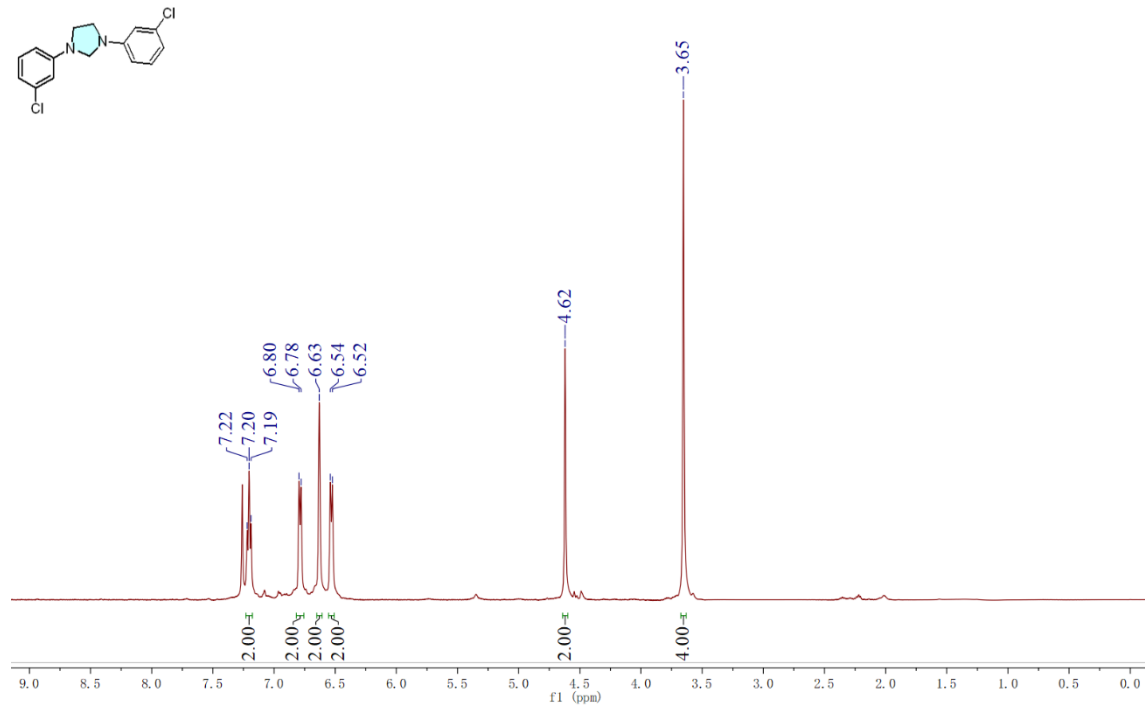
¹³C-NMR spectrum of compound B4



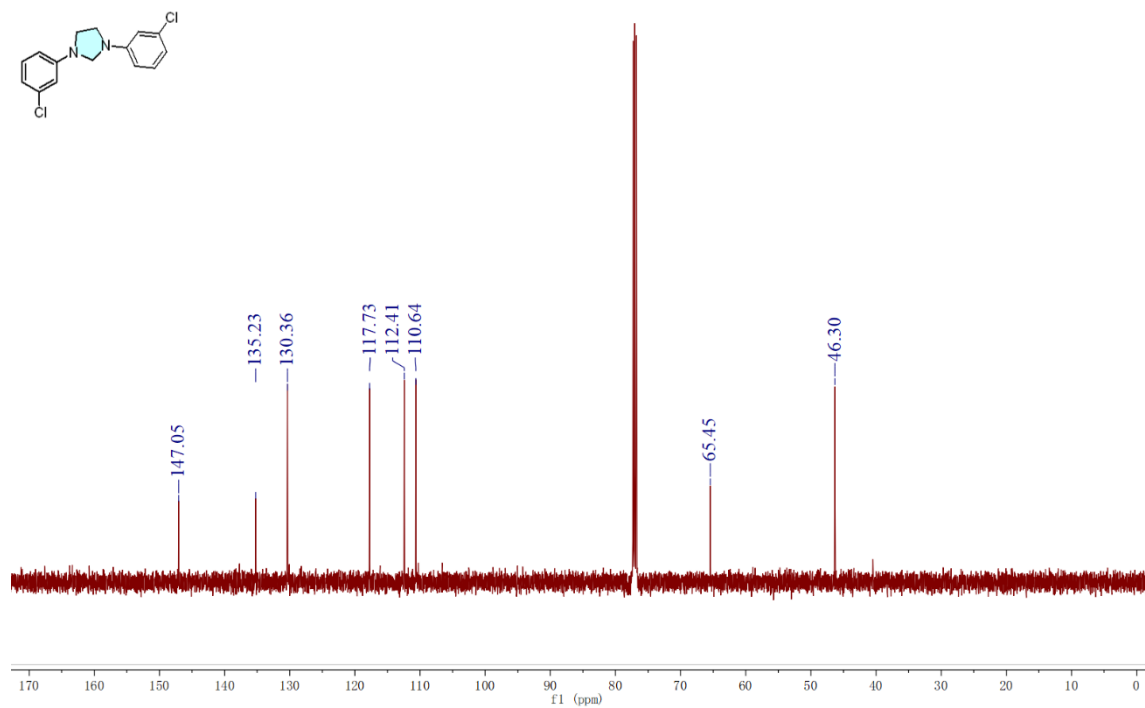
¹⁹F-NMR spectrum of compound B4



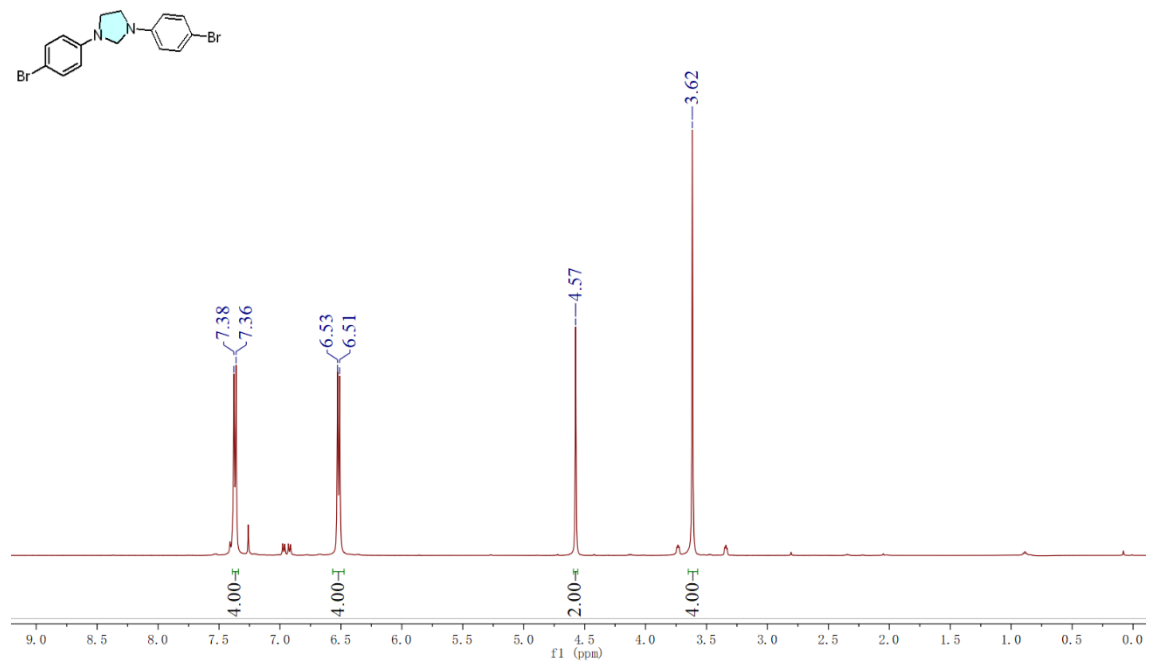
¹H-NMR spectrum of compound B5



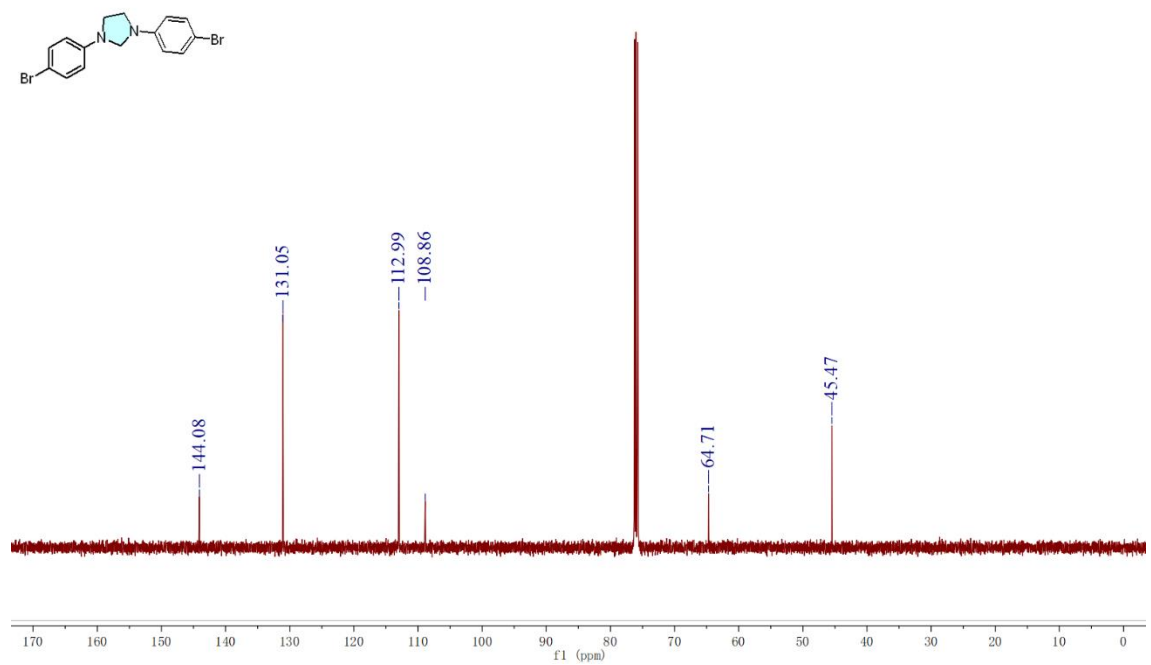
¹³C-NMR spectrum of compound B5



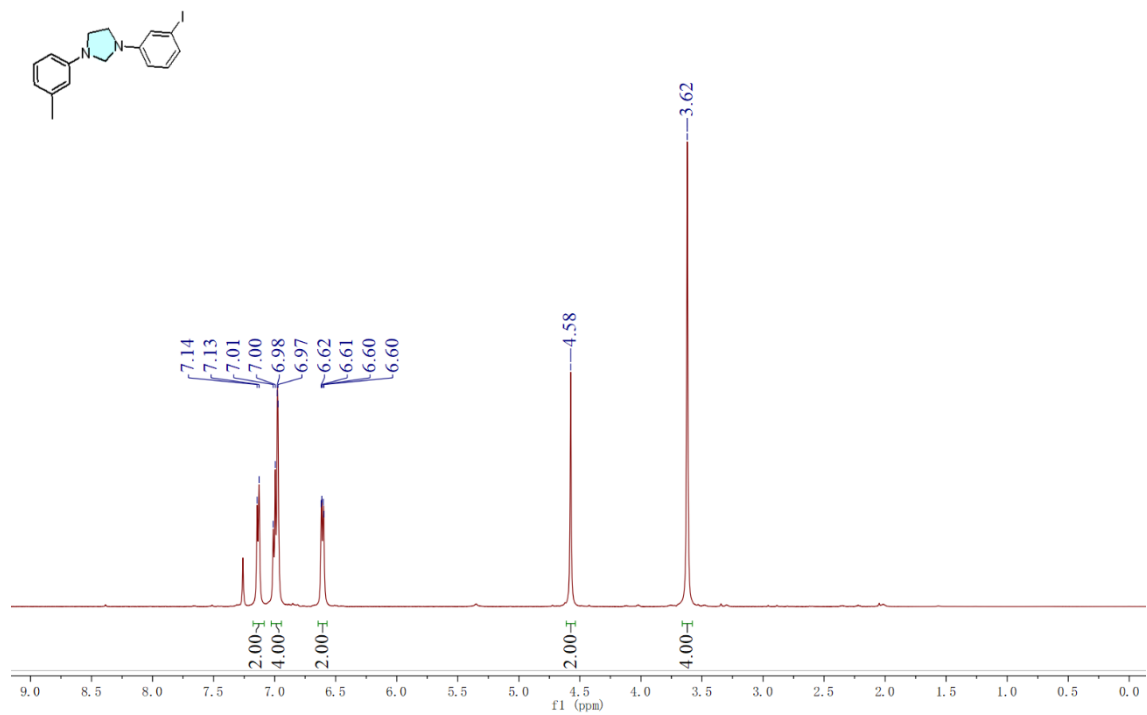
¹H-NMR spectrum of compound B6



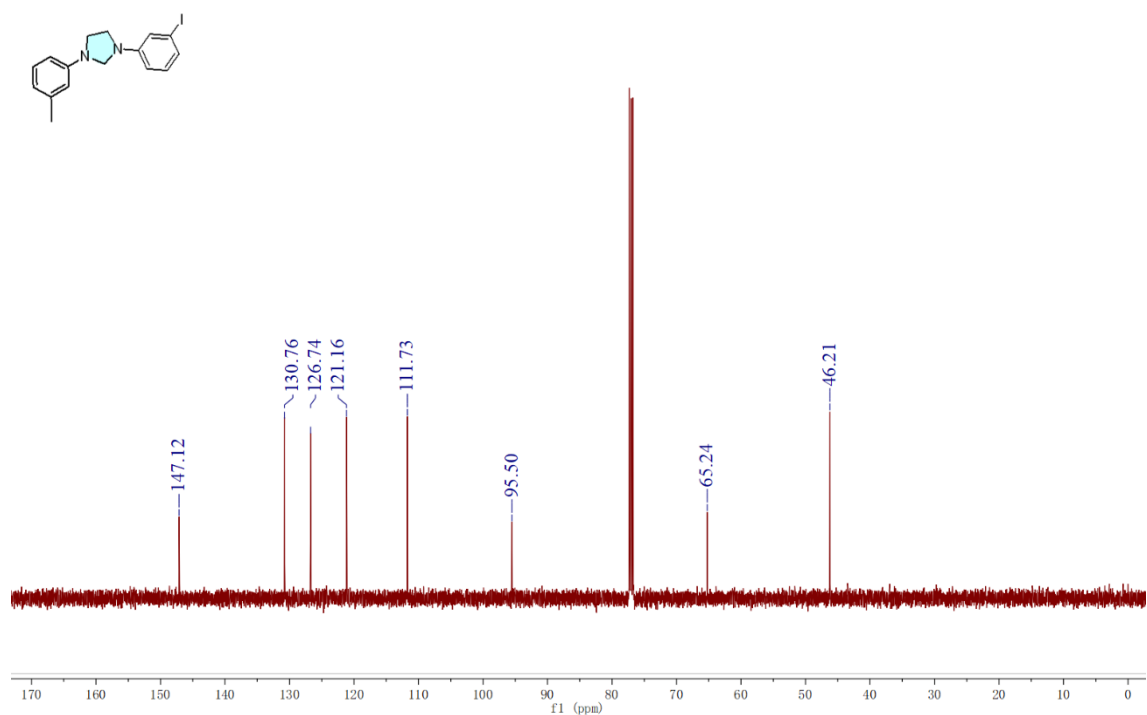
¹³C-NMR spectrum of compound B6



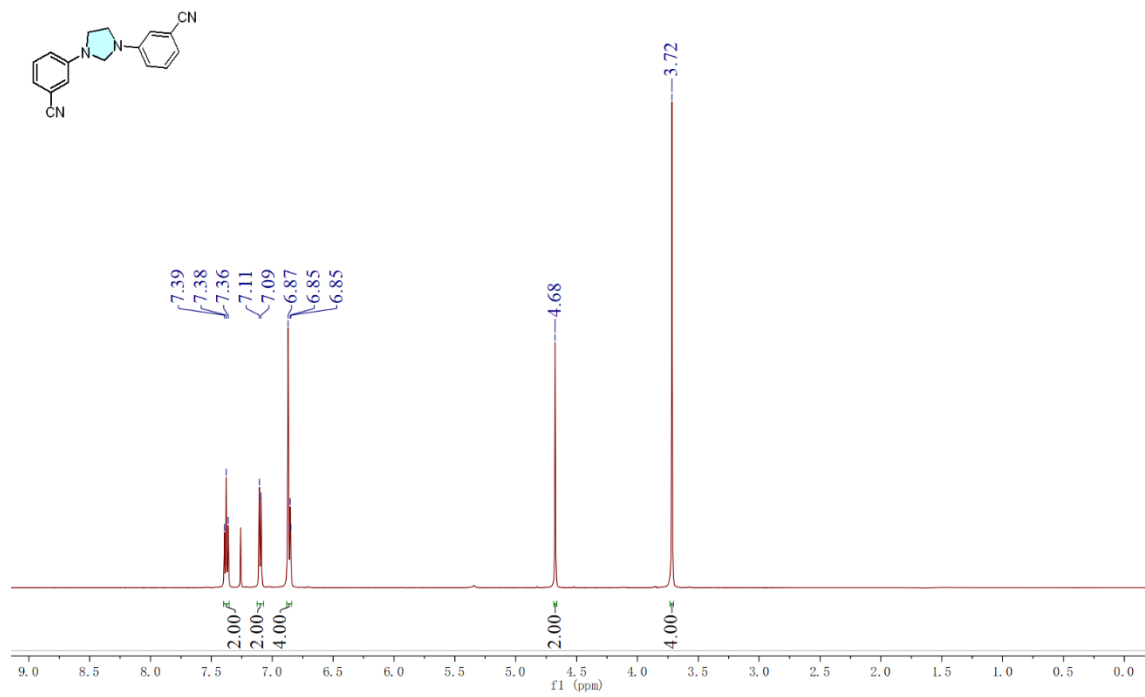
¹H-NMR spectrum of compound B7



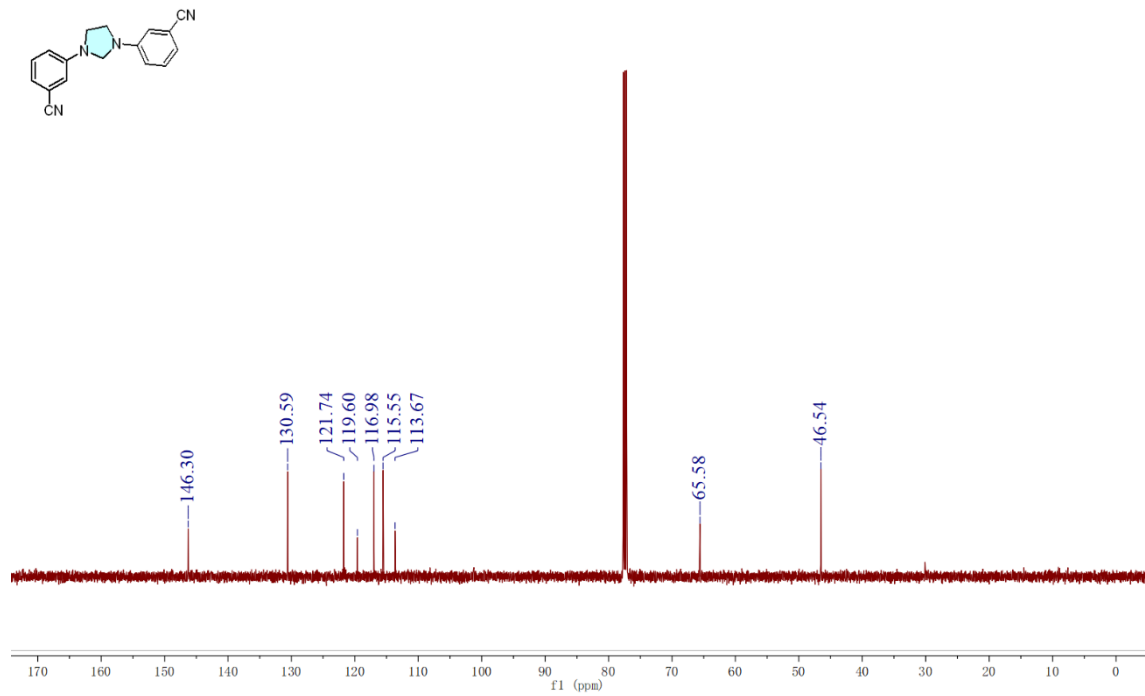
¹³C-NMR spectrum of compound B7



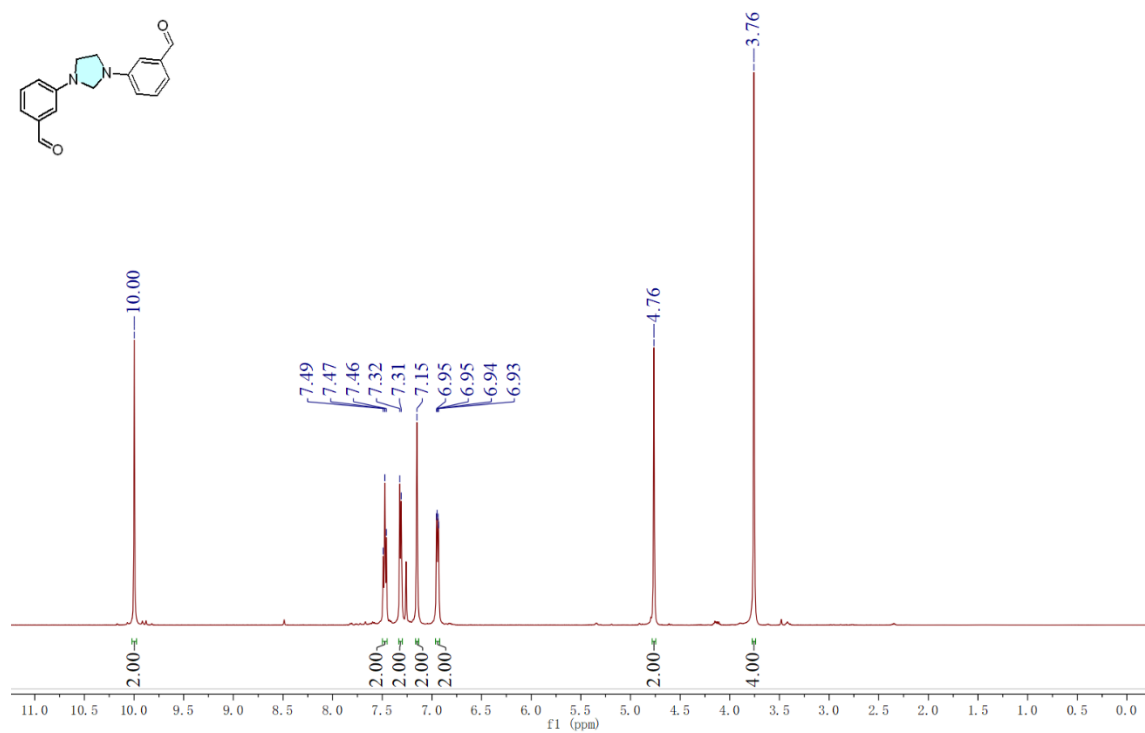
¹H-NMR spectrum of compound B8



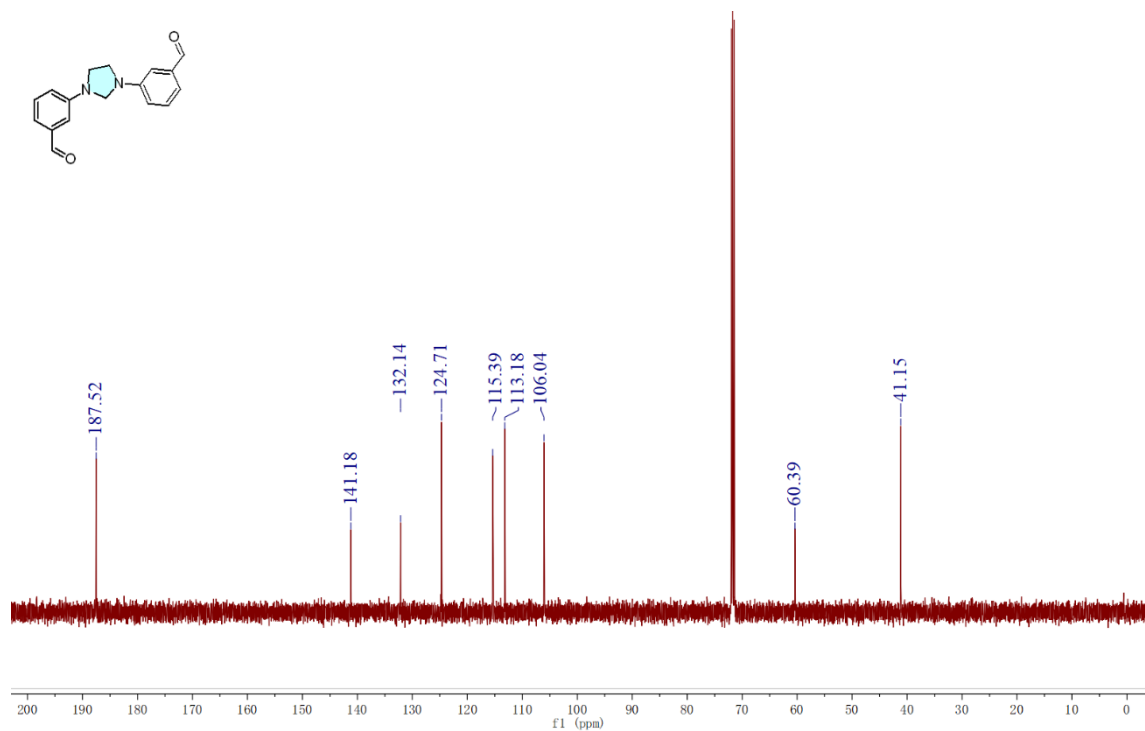
¹³C-NMR spectrum of compound B8



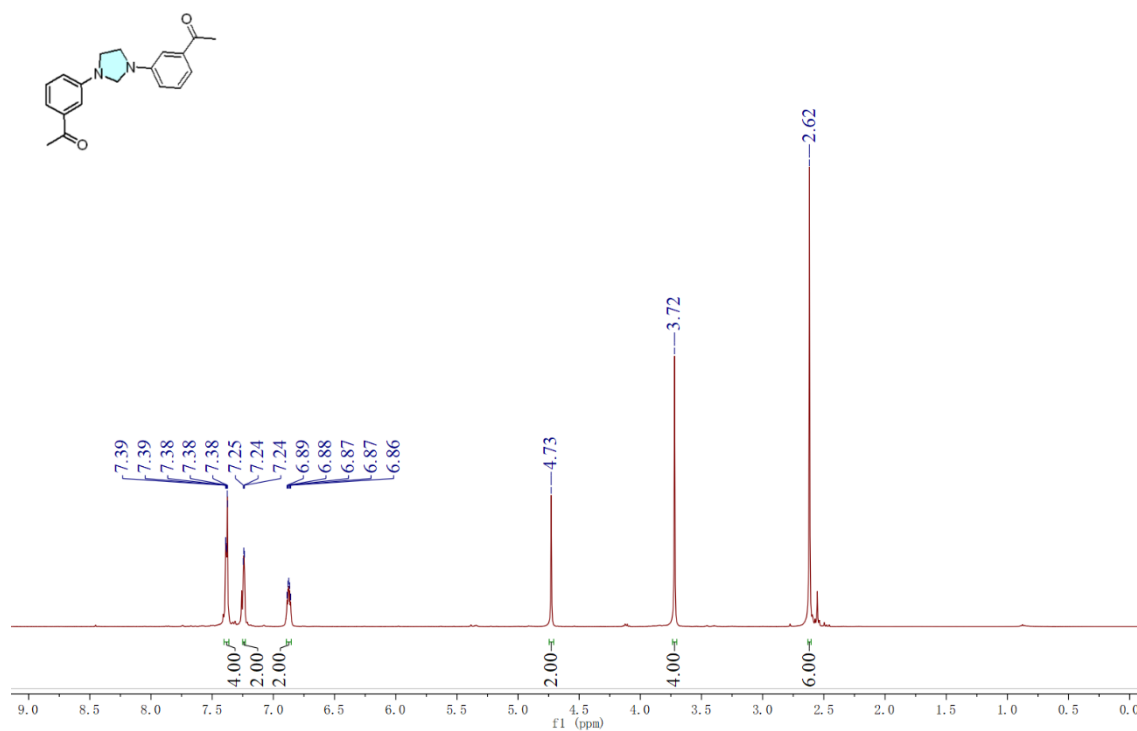
¹H-NMR spectrum of compound B9



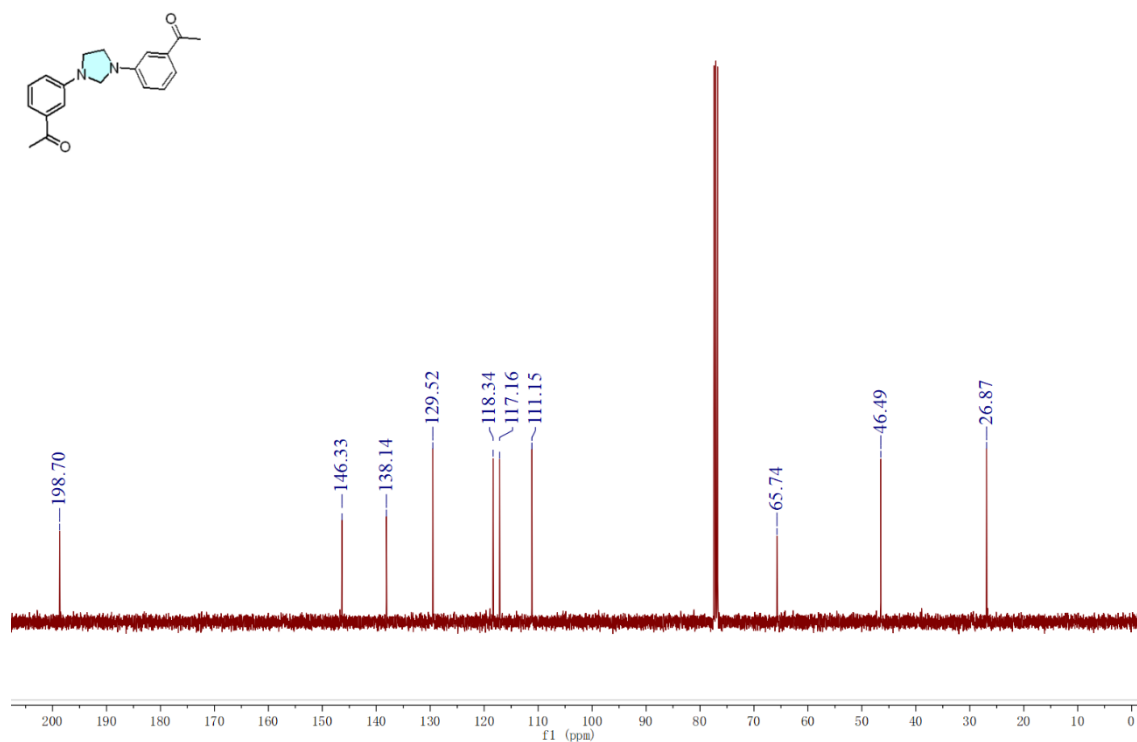
¹³C-NMR spectrum of compound B9



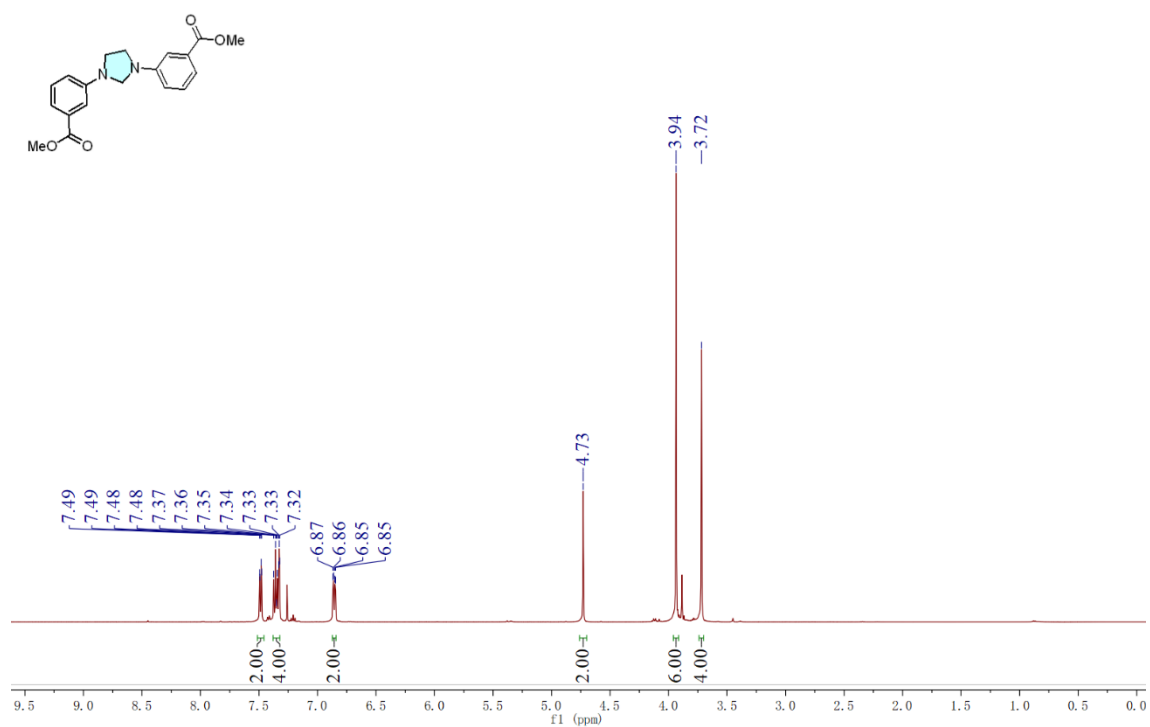
¹H-NMR spectrum of compound B10



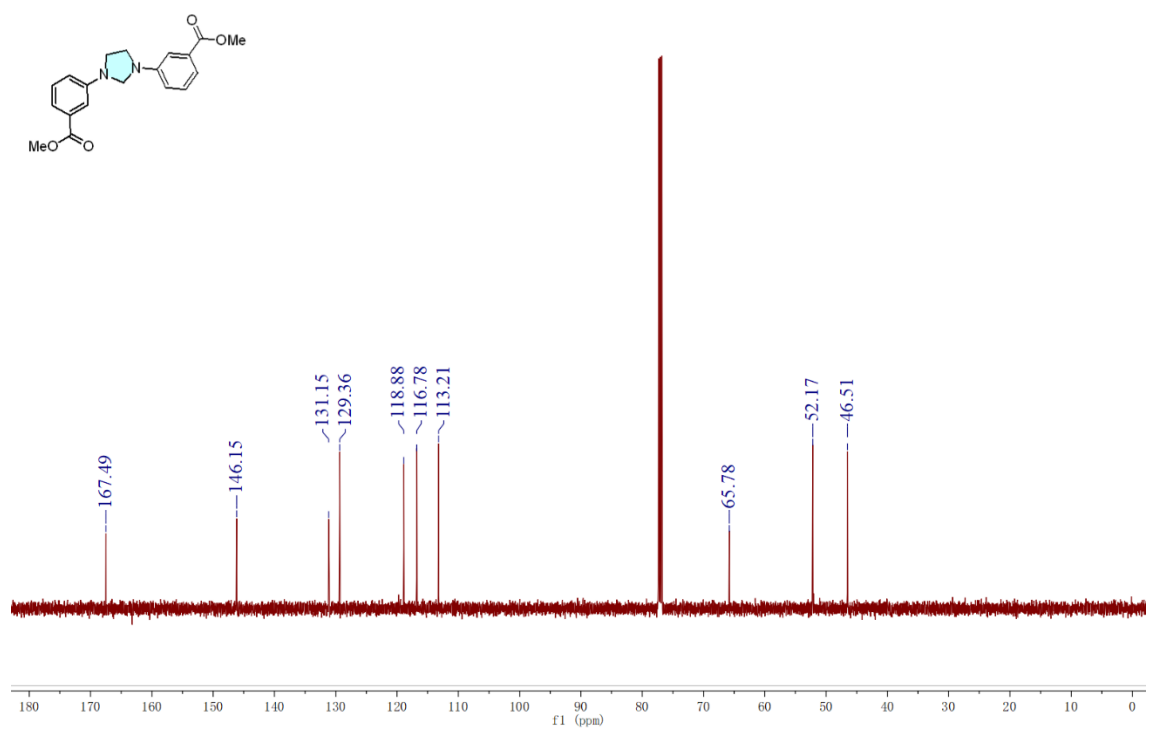
¹³C-NMR spectrum of compound B10



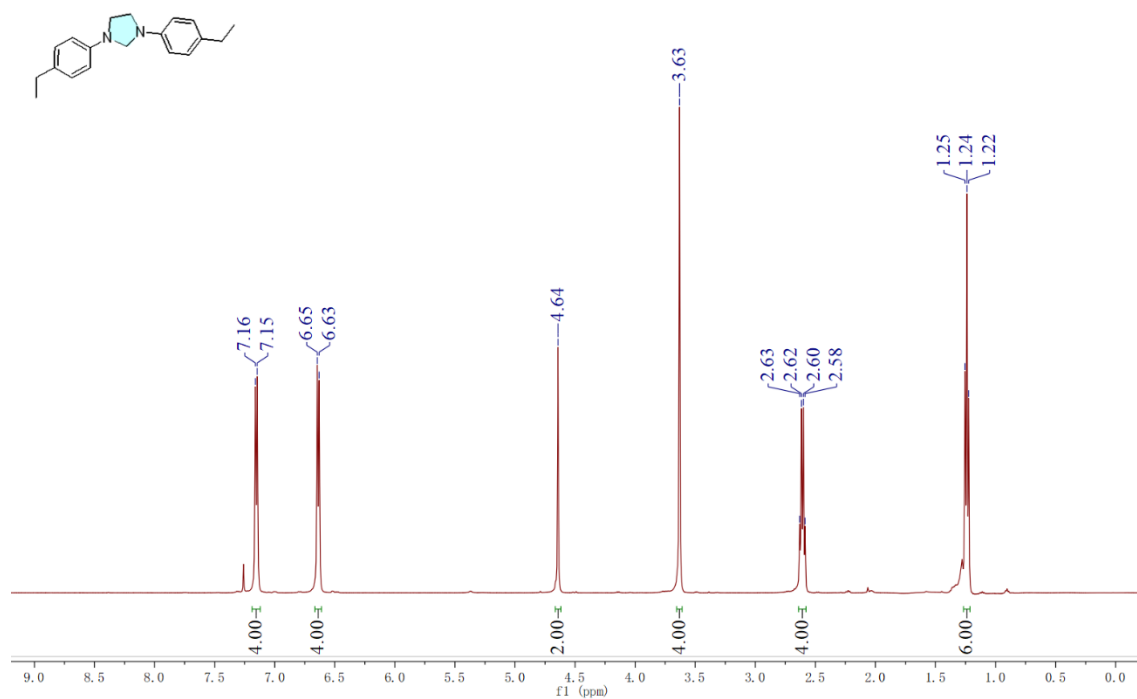
¹H-NMR spectrum of compound B11



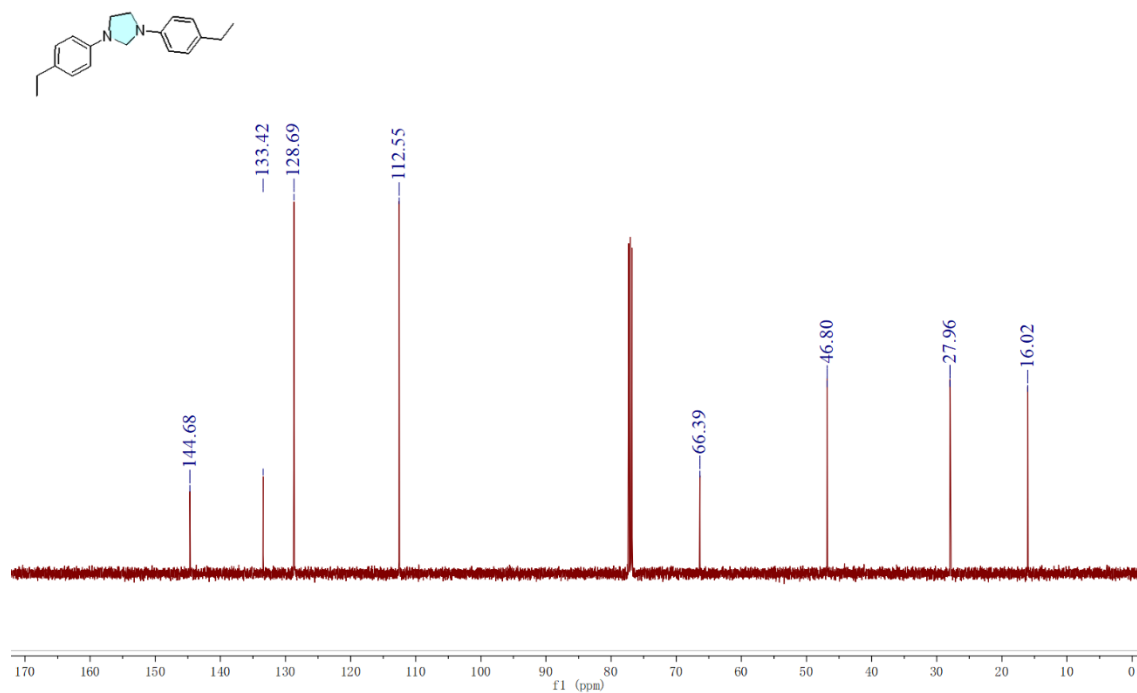
¹³C-NMR spectrum of compound B11



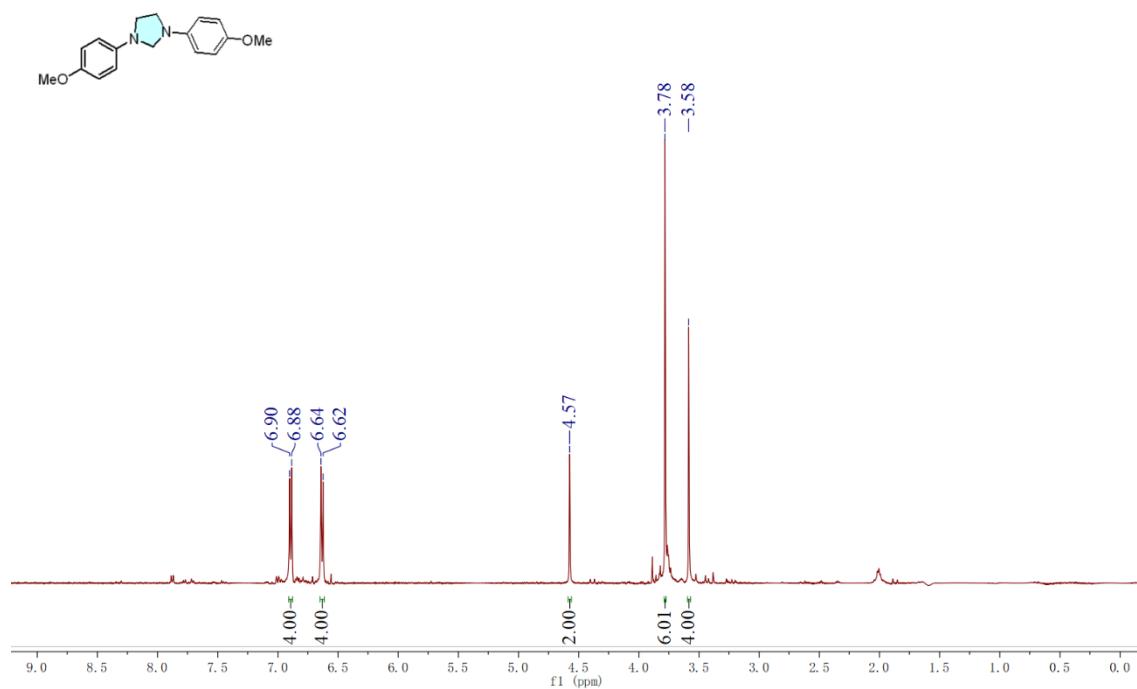
¹H-NMR spectrum of compound B12



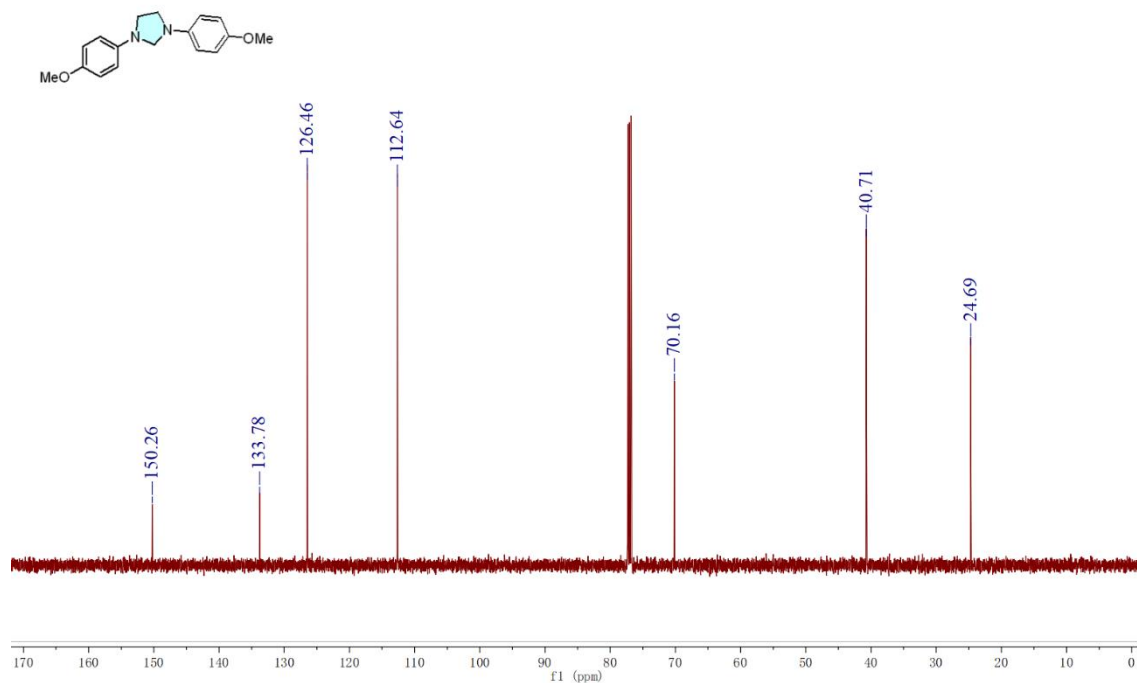
¹³C-NMR spectrum of compound B12



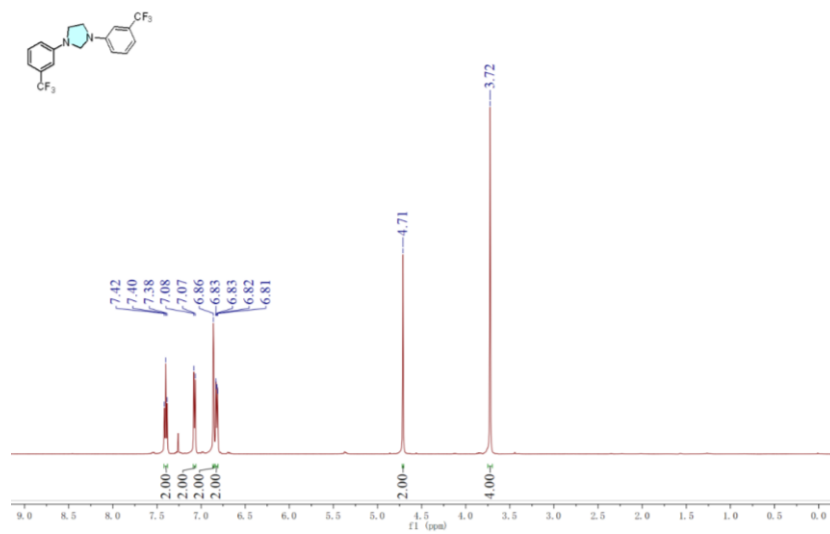
¹H-NMR spectrum of compound B13



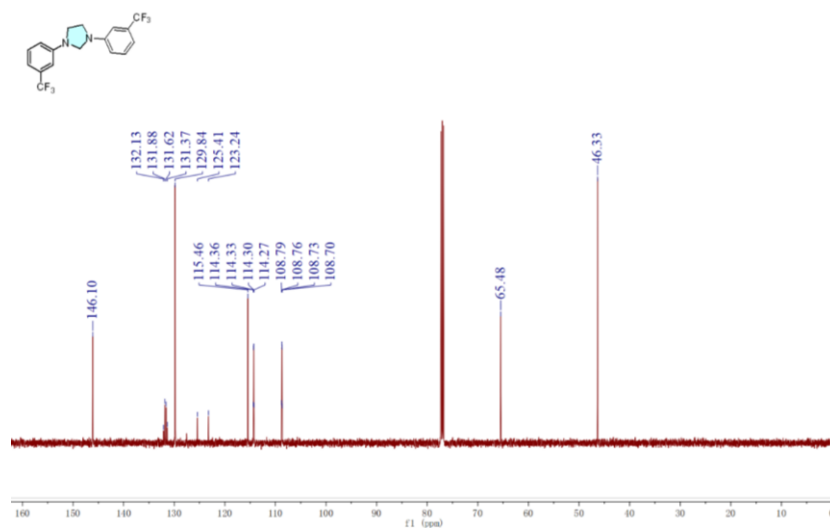
¹³C-NMR spectrum of compound B13



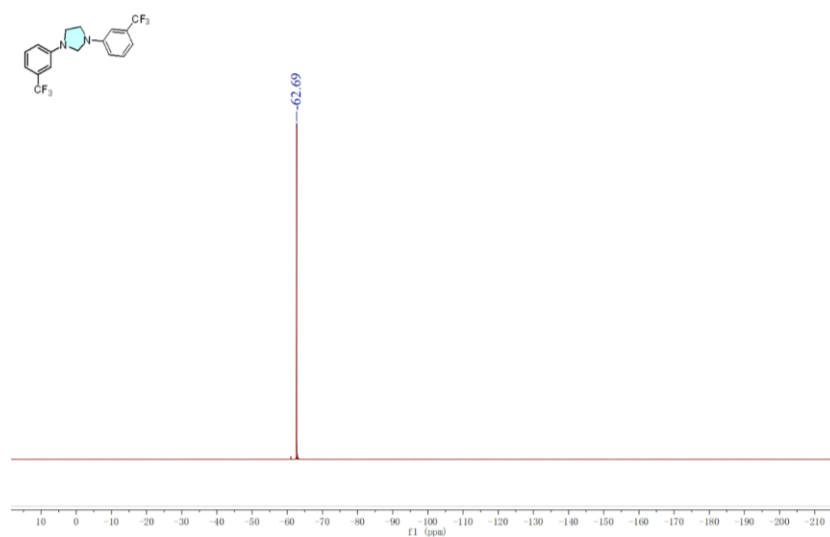
¹H-NMR spectrum of compound B14



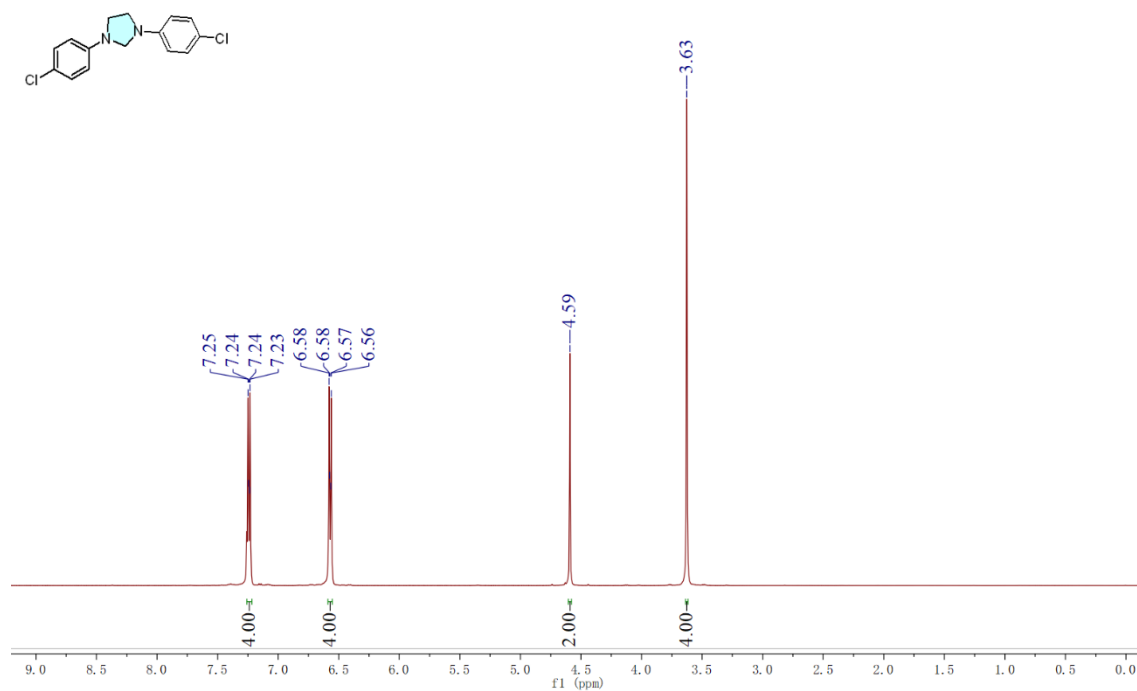
¹³C-NMR spectrum of compound B14



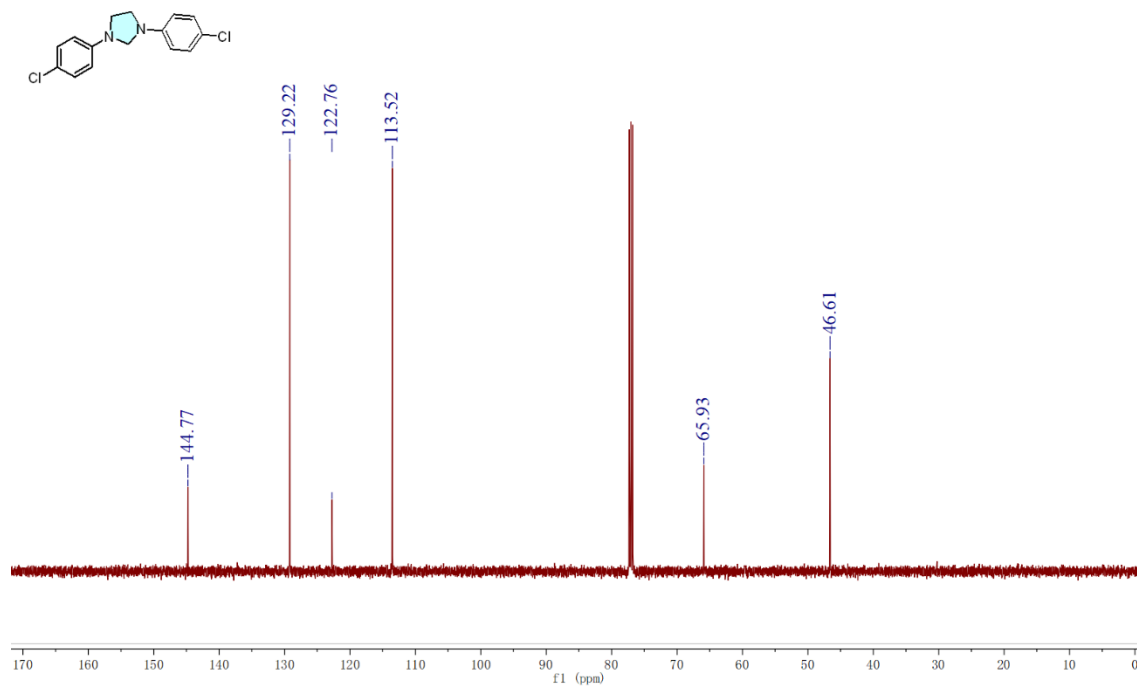
¹⁹F-NMR spectrum of compound B14



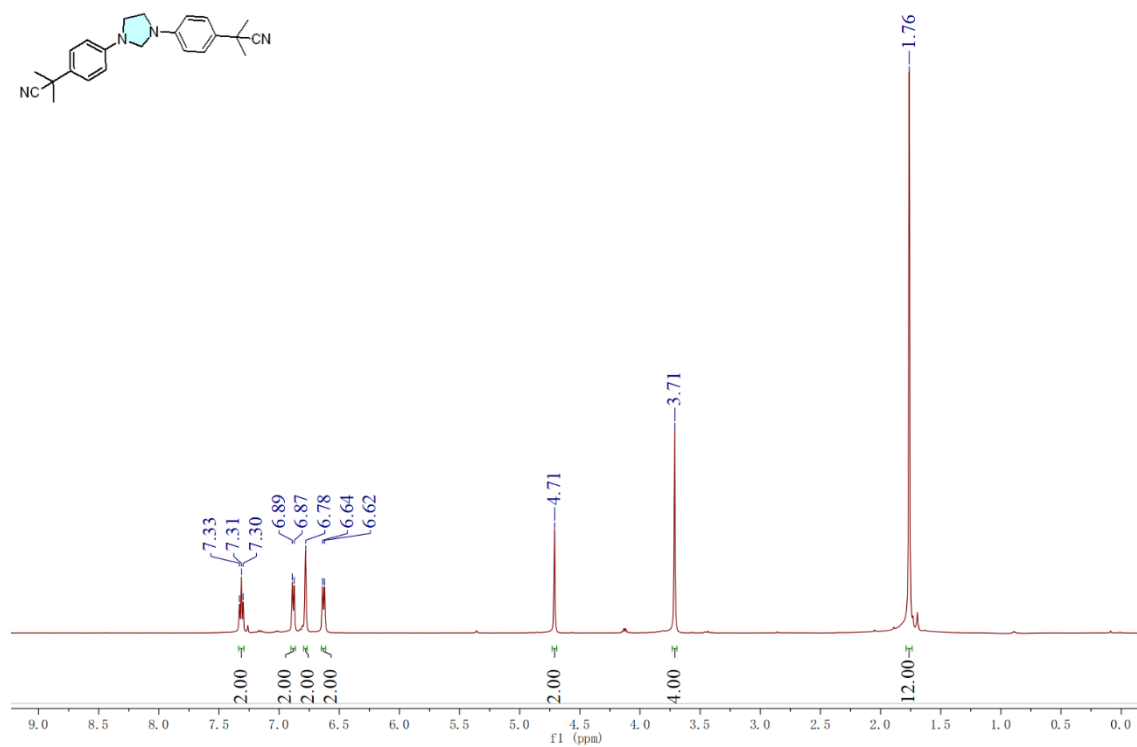
¹H-NMR spectrum of compound B15



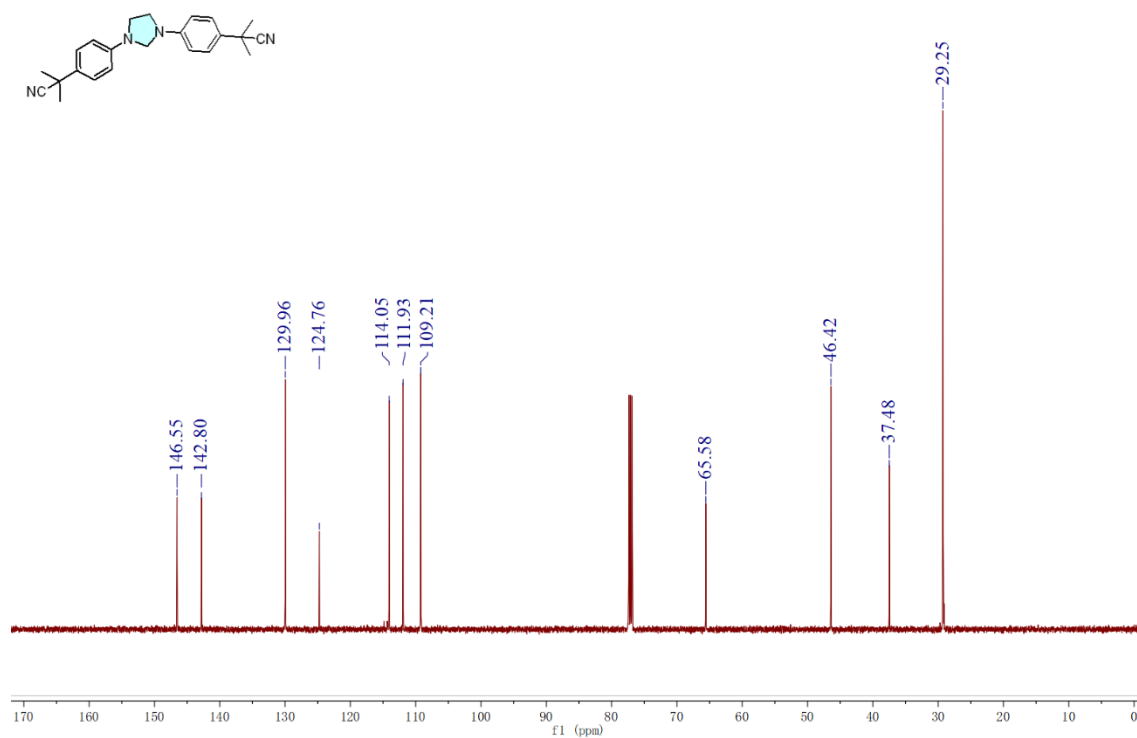
¹³C-NMR spectrum of compound B15



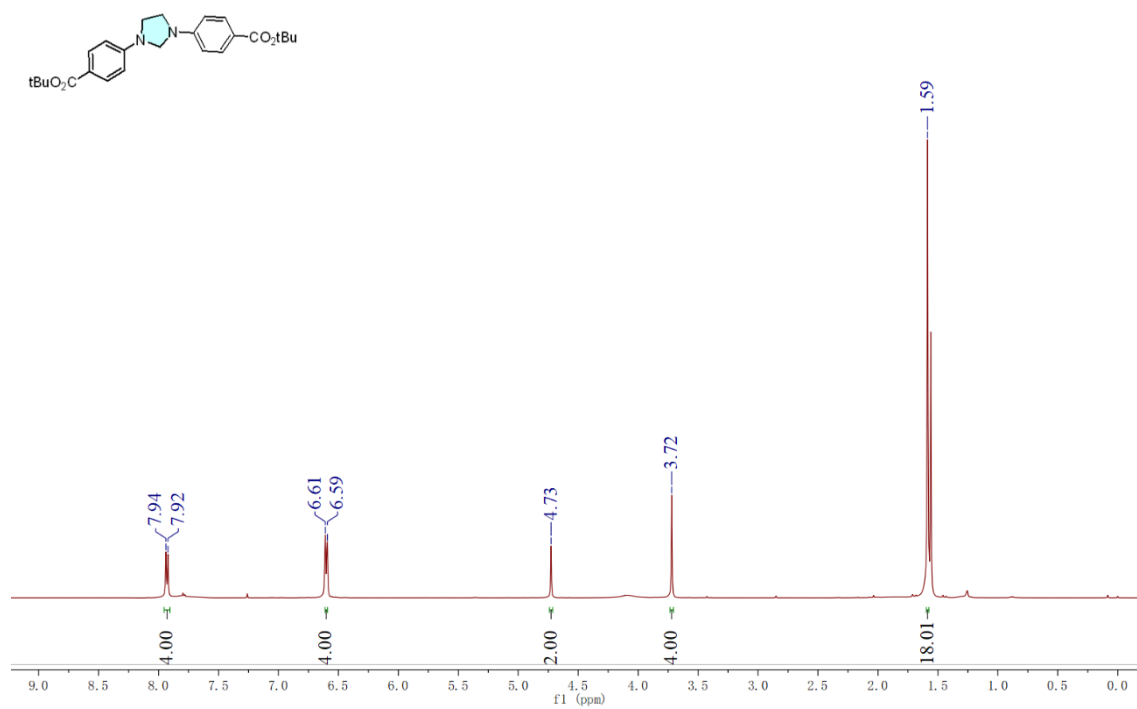
¹H-NMR spectrum of compound B16



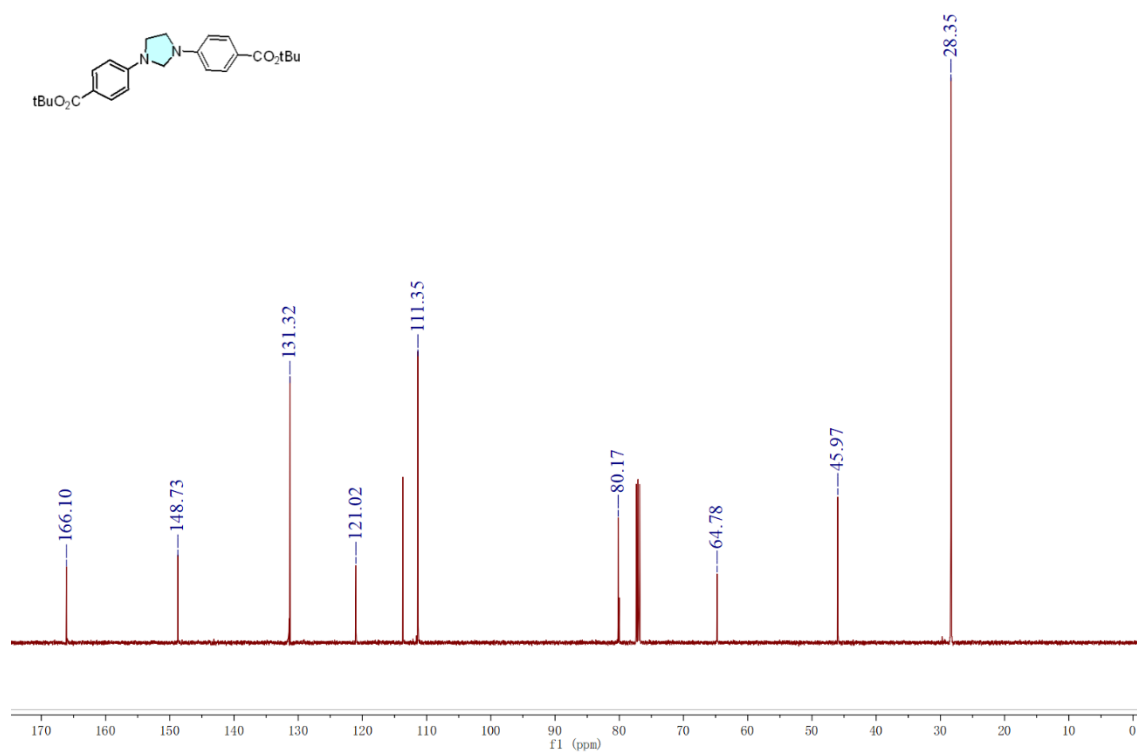
¹³C-NMR spectrum of compound B16



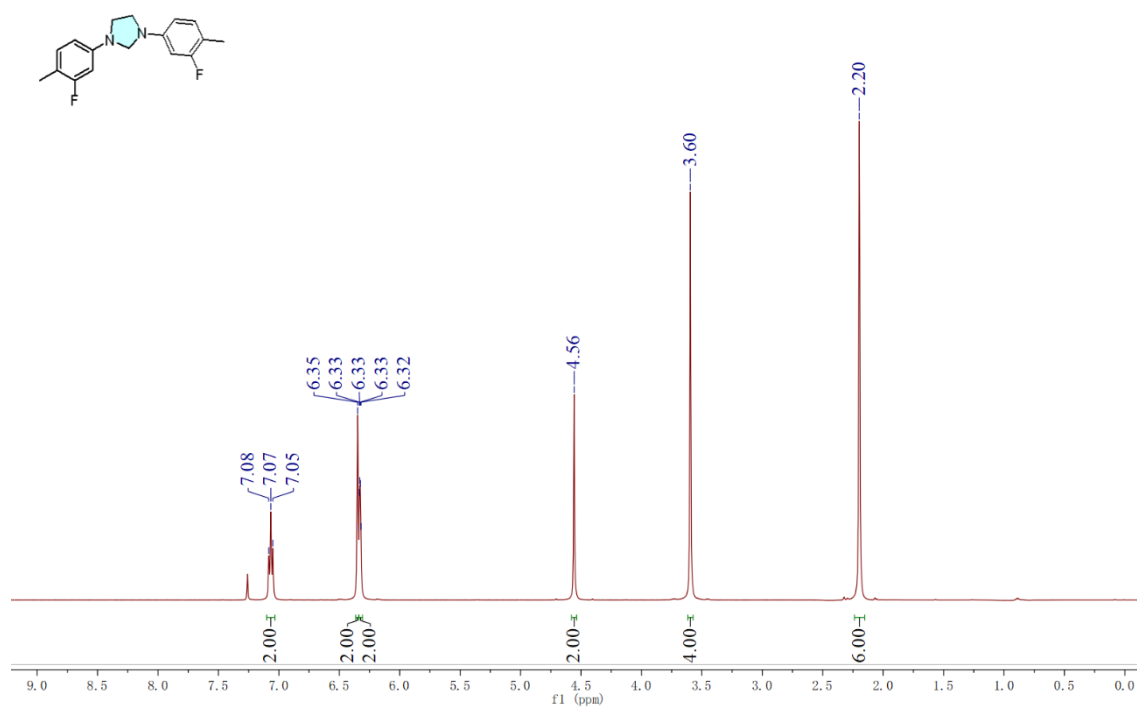
¹H-NMR spectrum of compound B17



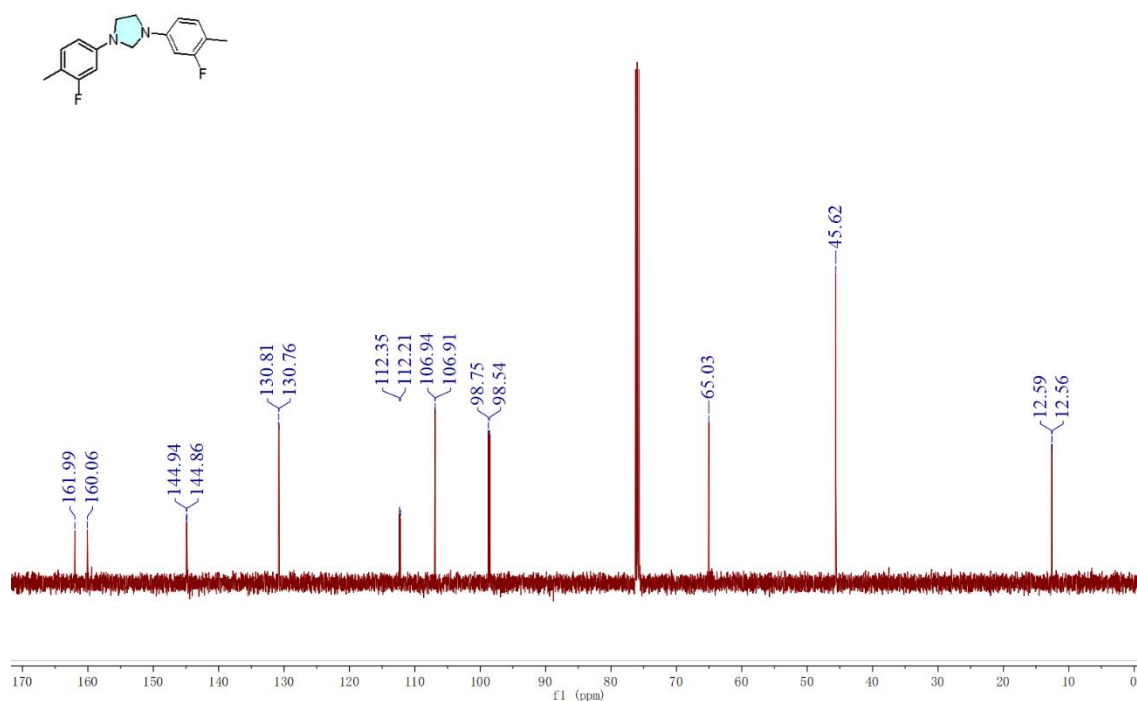
¹³C-NMR spectrum of compound B17



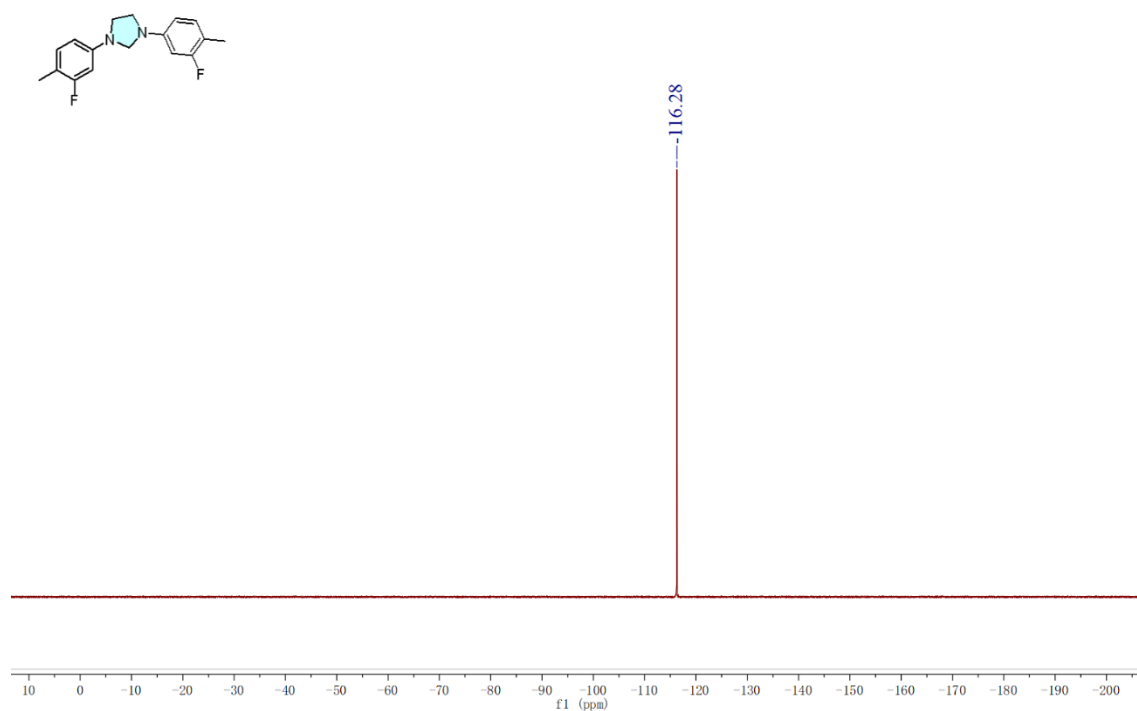
¹H-NMR spectrum of compound B18



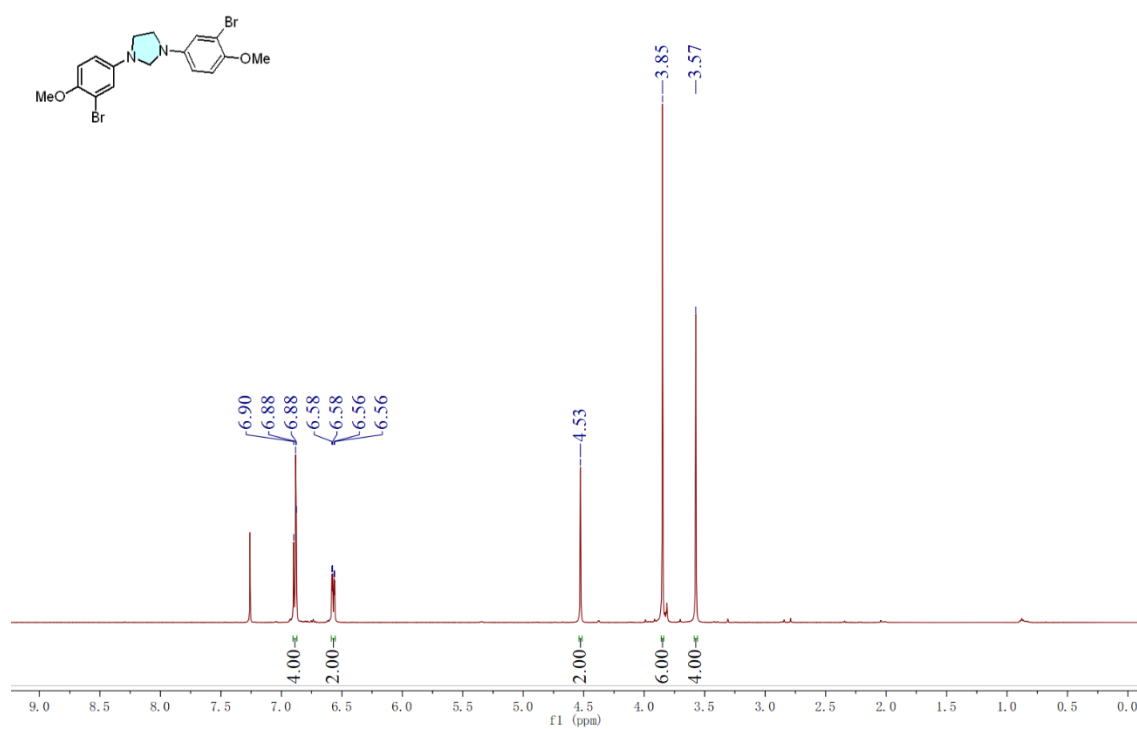
¹³C-NMR spectrum of compound B18



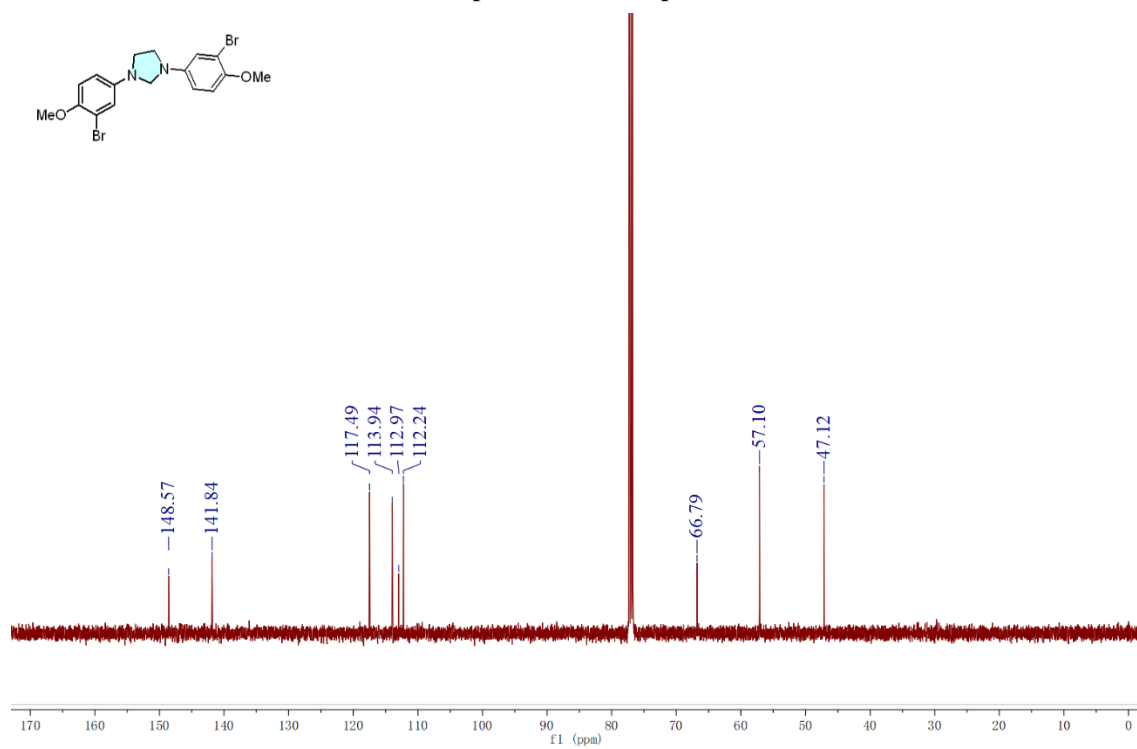
¹⁹F-NMR spectrum of compound B18



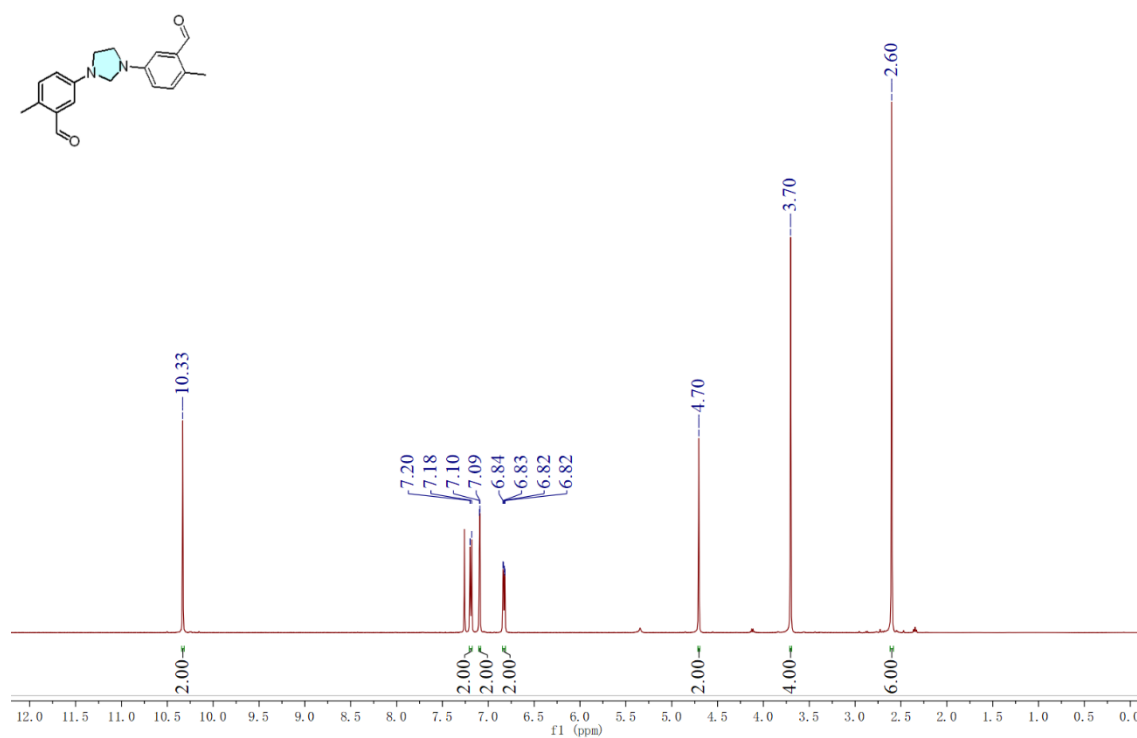
¹H-NMR spectrum of compound B19



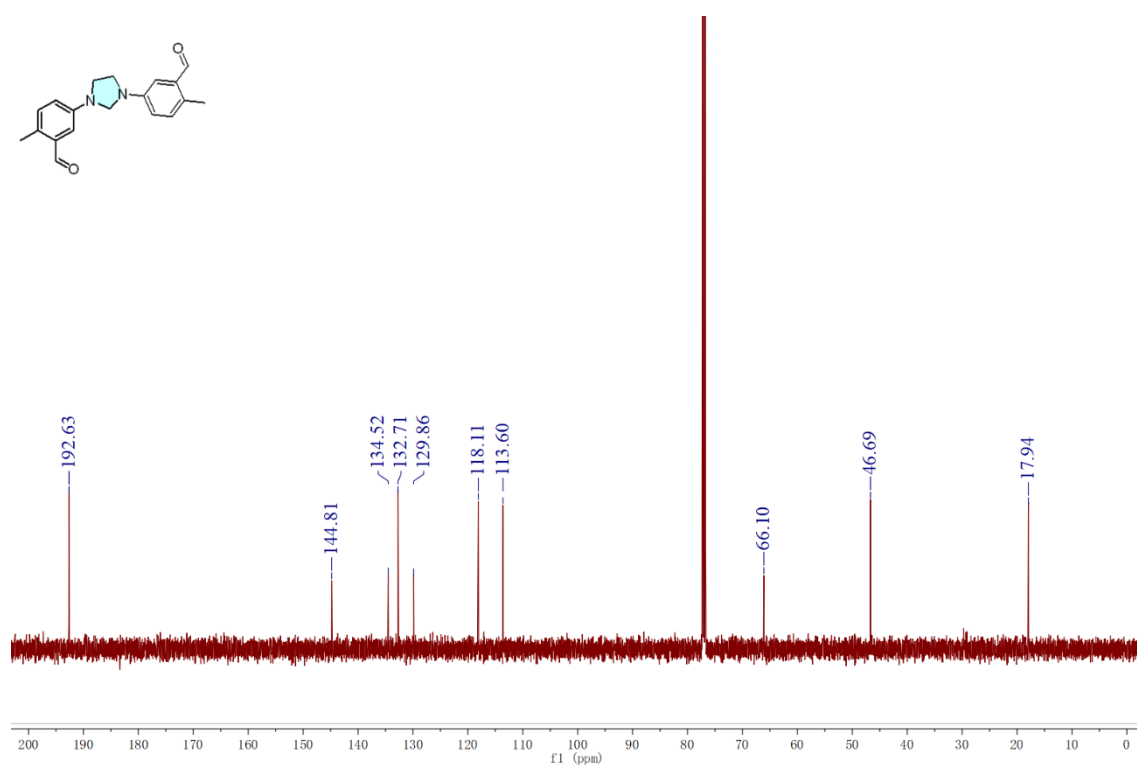
¹³C-NMR spectrum of compound B19



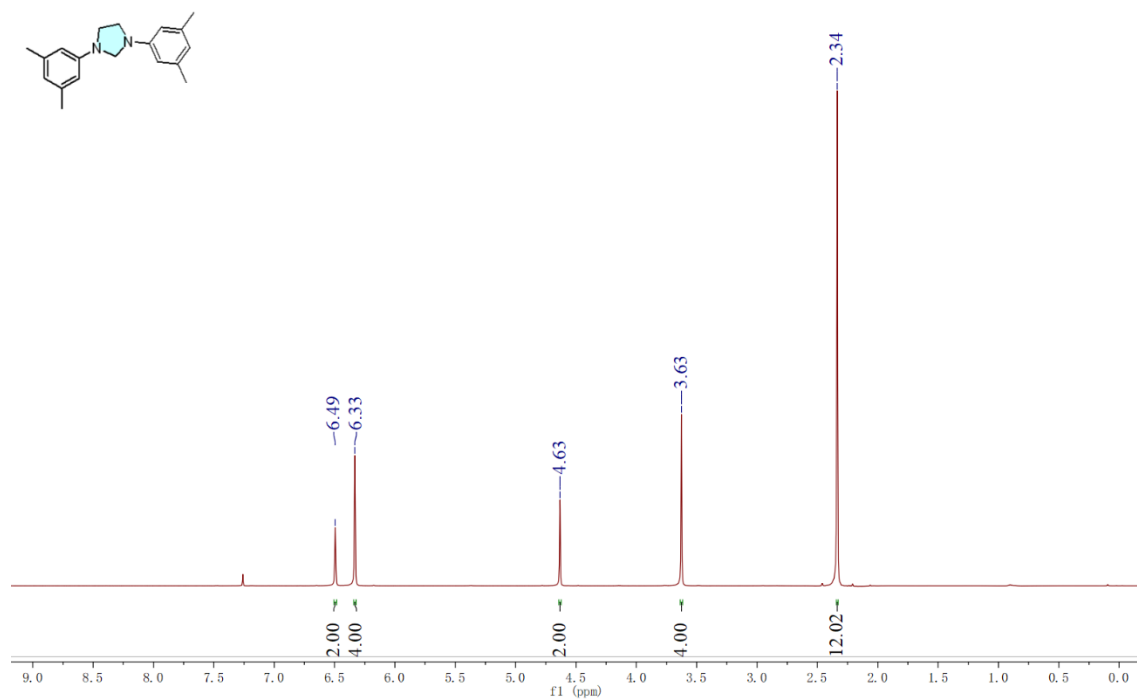
¹H-NMR spectrum of compound B20



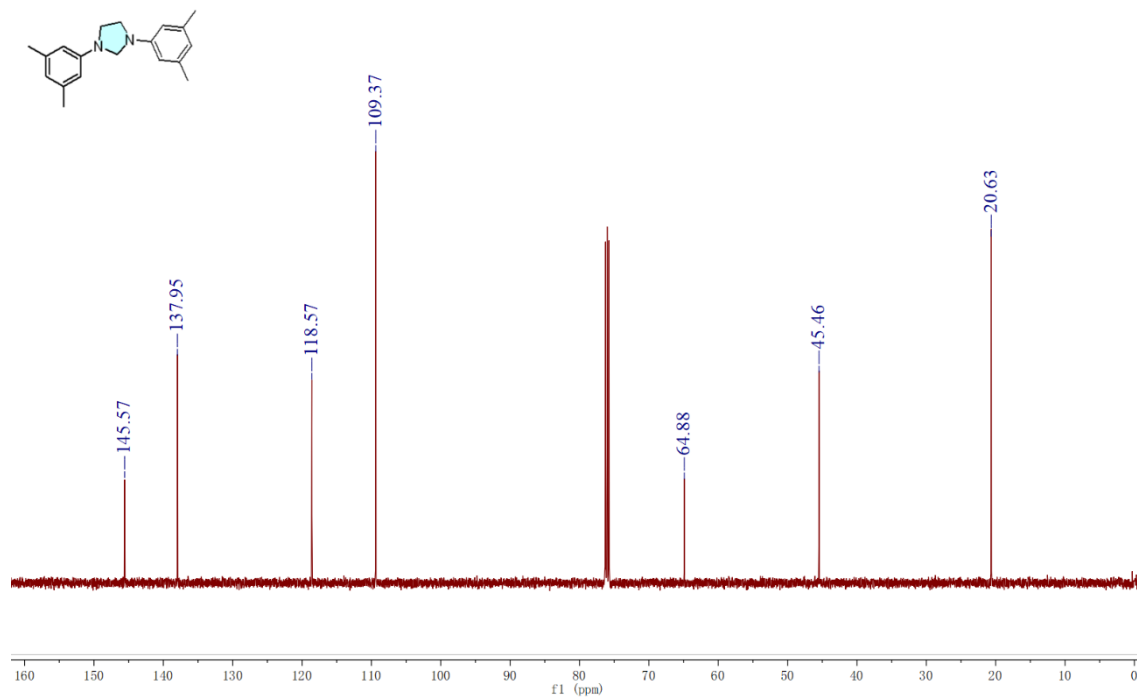
¹³C-NMR spectrum of compound B20



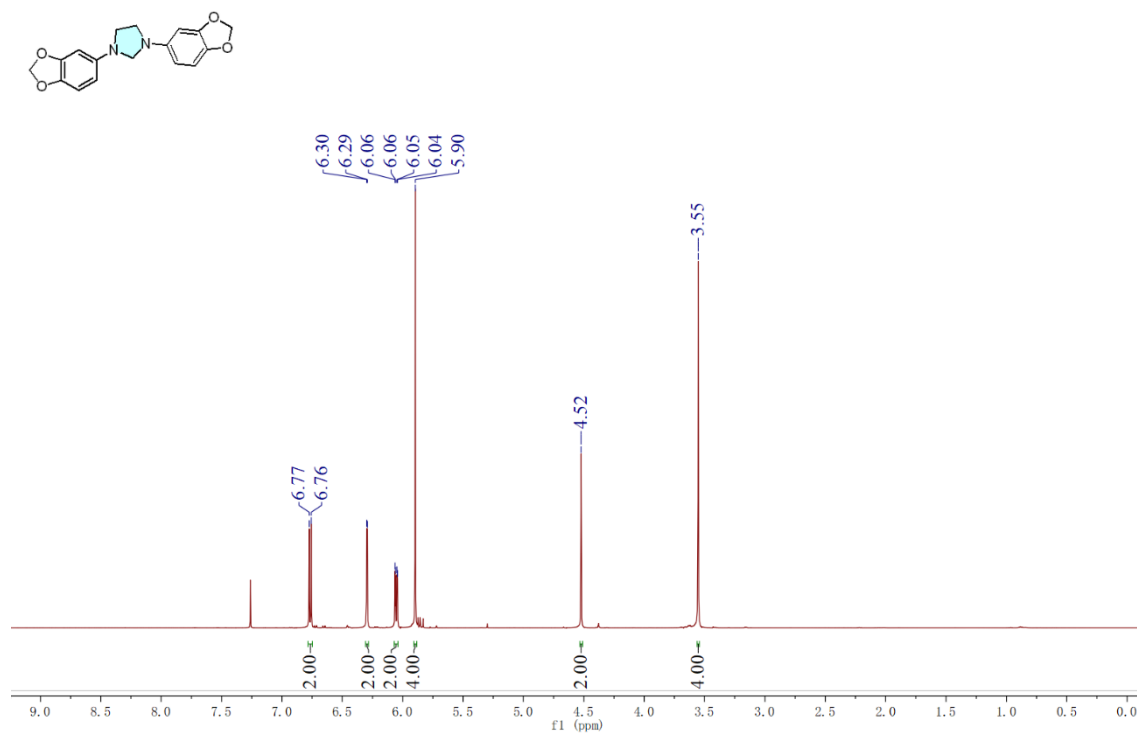
¹H-NMR spectrum of compound B21



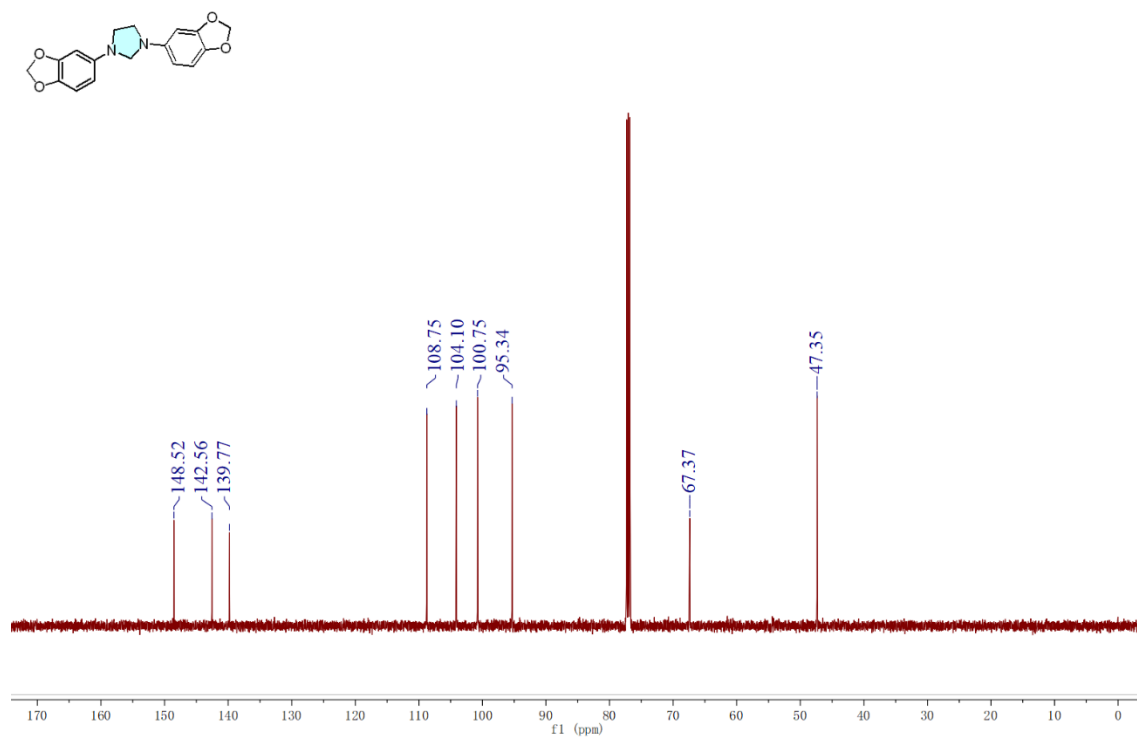
¹³C-NMR spectrum of compound B21



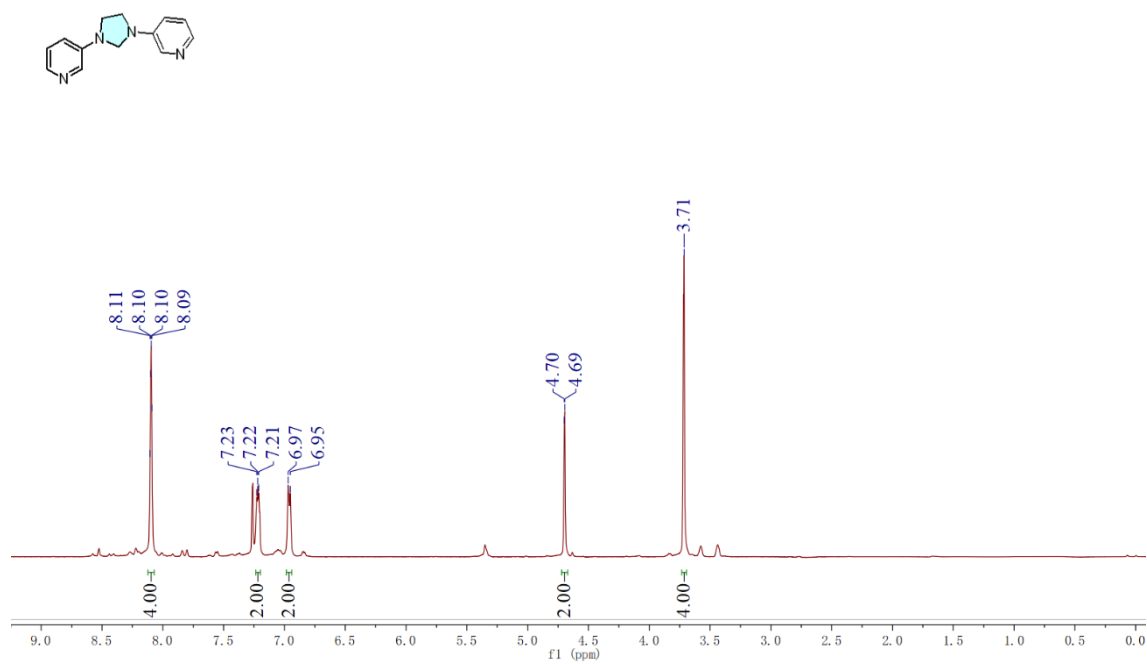
¹H-NMR spectrum of compound B22



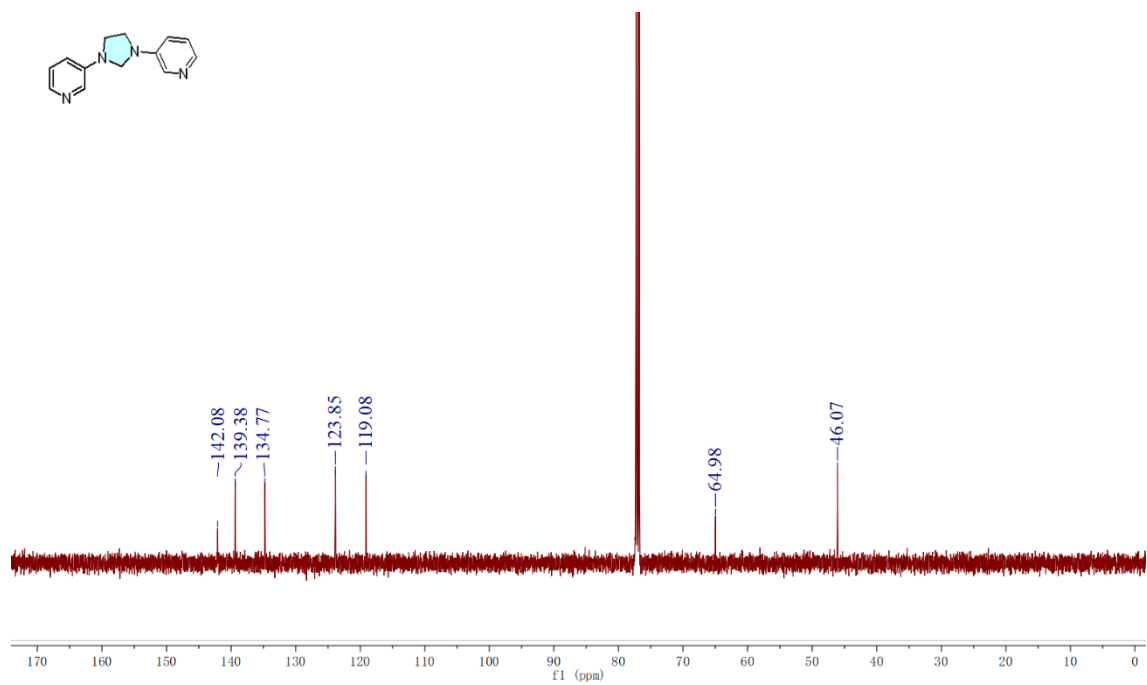
¹³C-NMR spectrum of compound B22



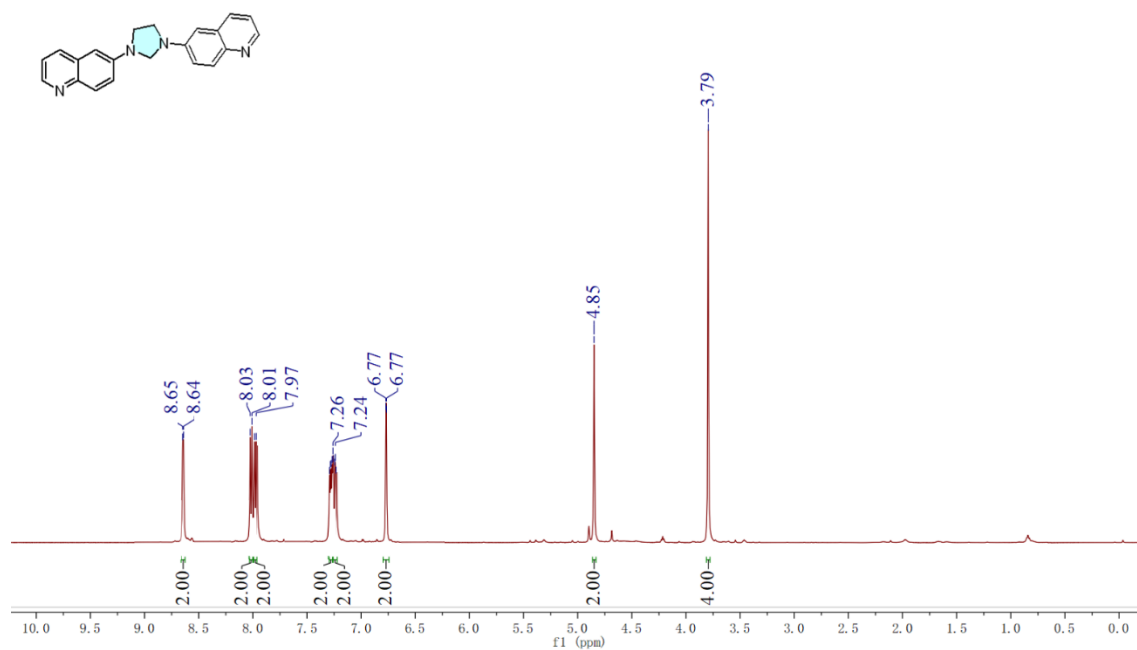
¹H-NMR spectrum of compound B23



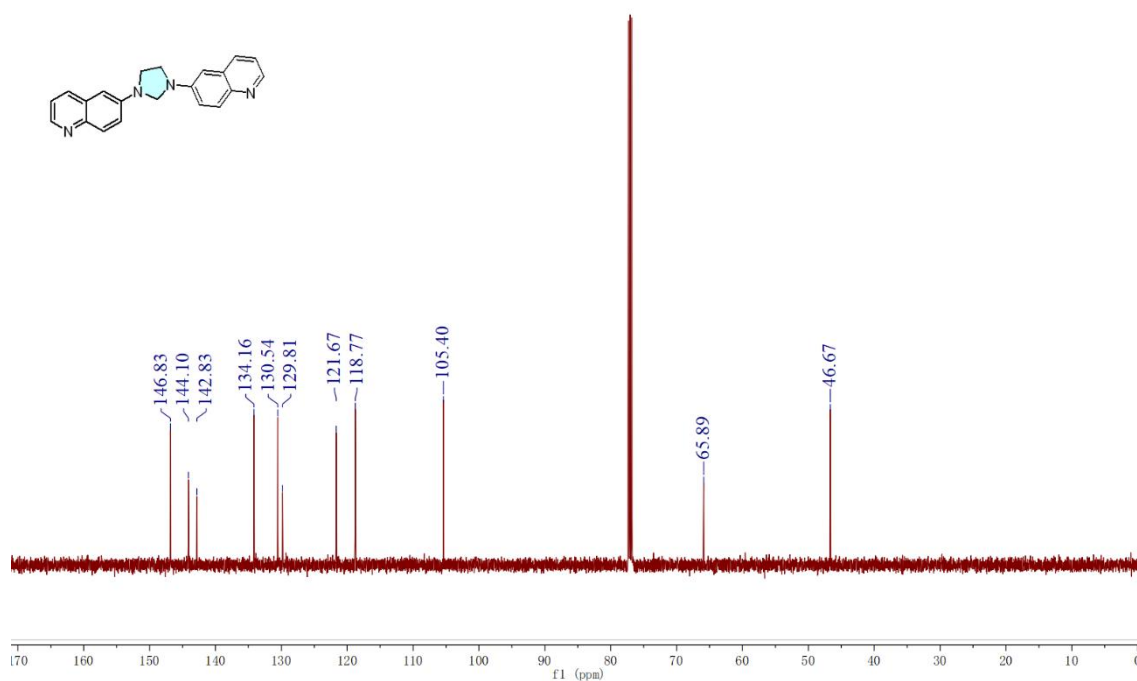
¹³C-NMR spectrum of compound B23



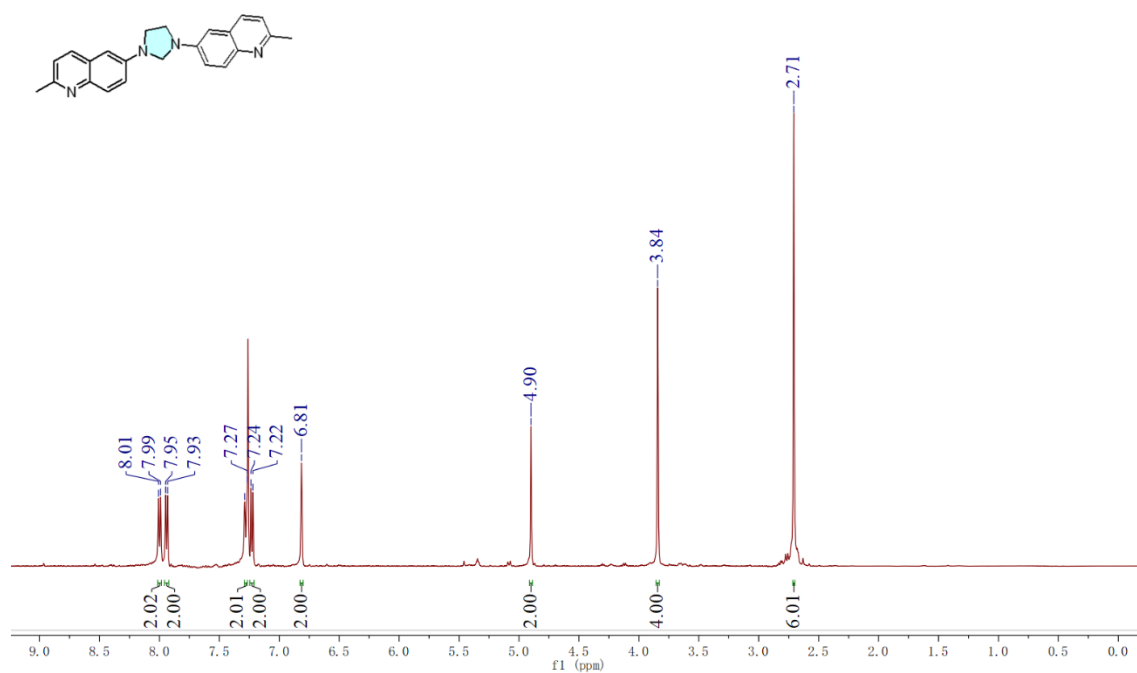
¹H-NMR spectrum of compound B24



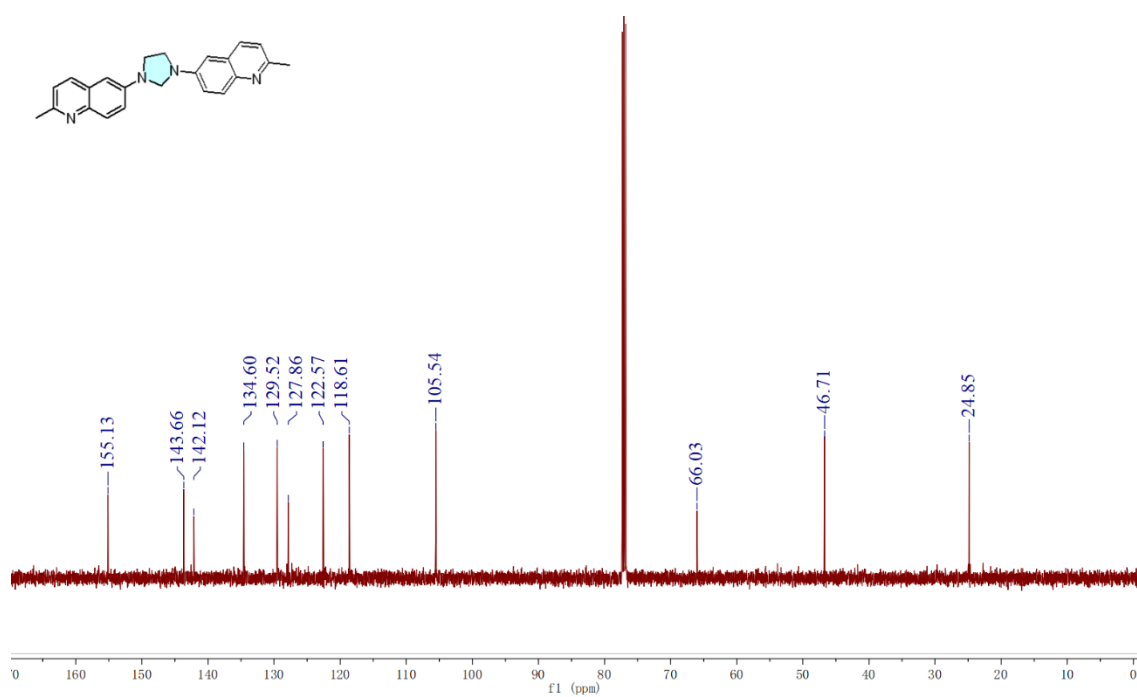
¹³C-NMR spectrum of compound B24



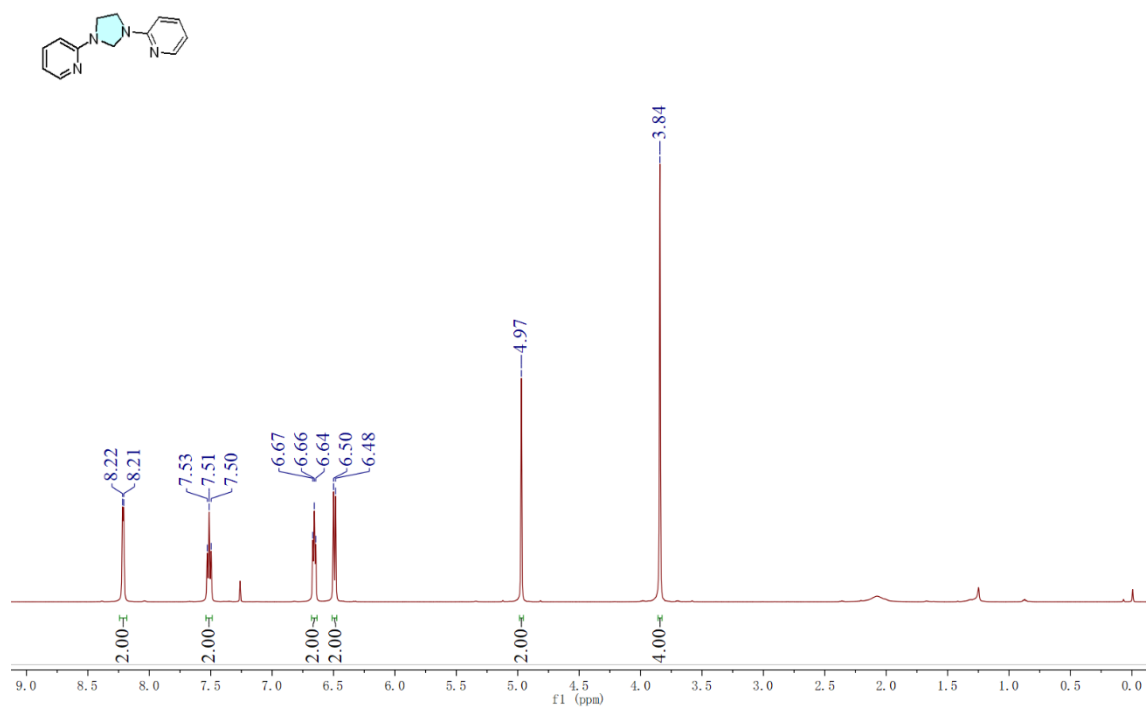
¹H-NMR spectrum of compound B25



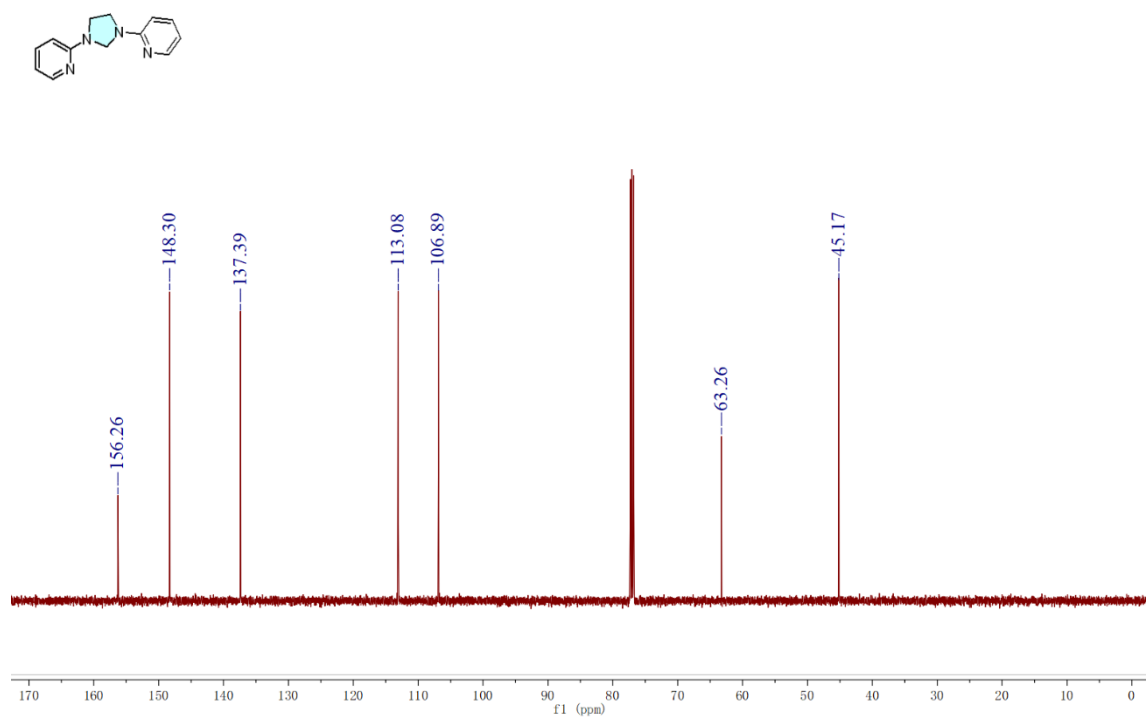
¹³C-NMR spectrum of compound B25



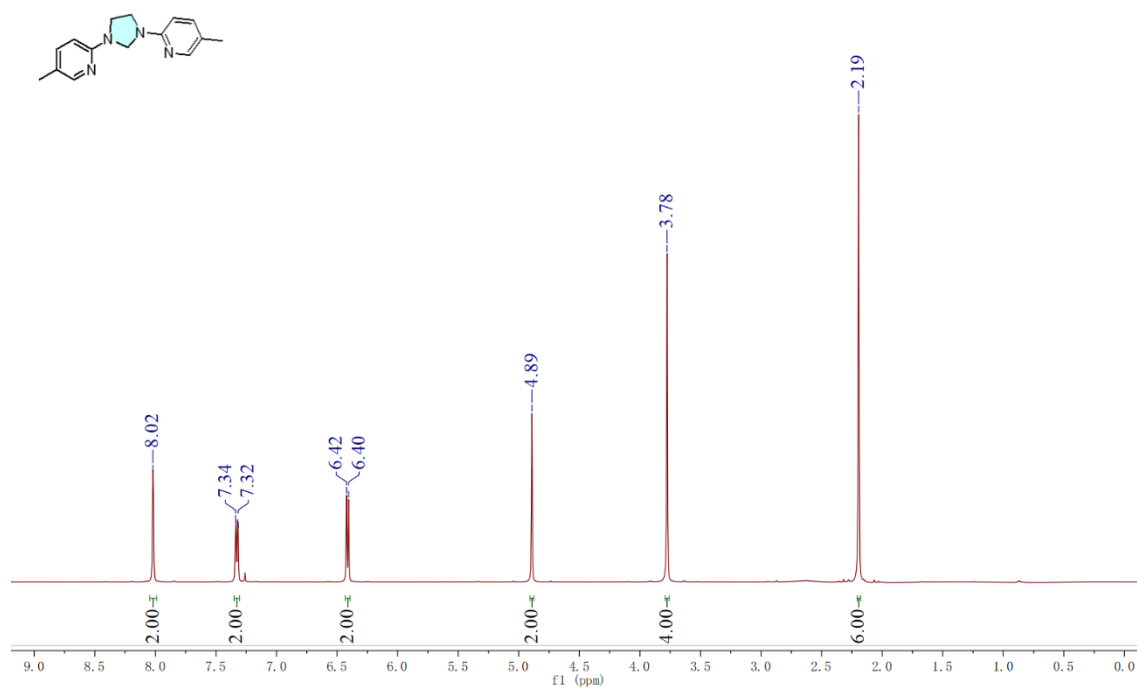
¹H-NMR spectrum of compound B26



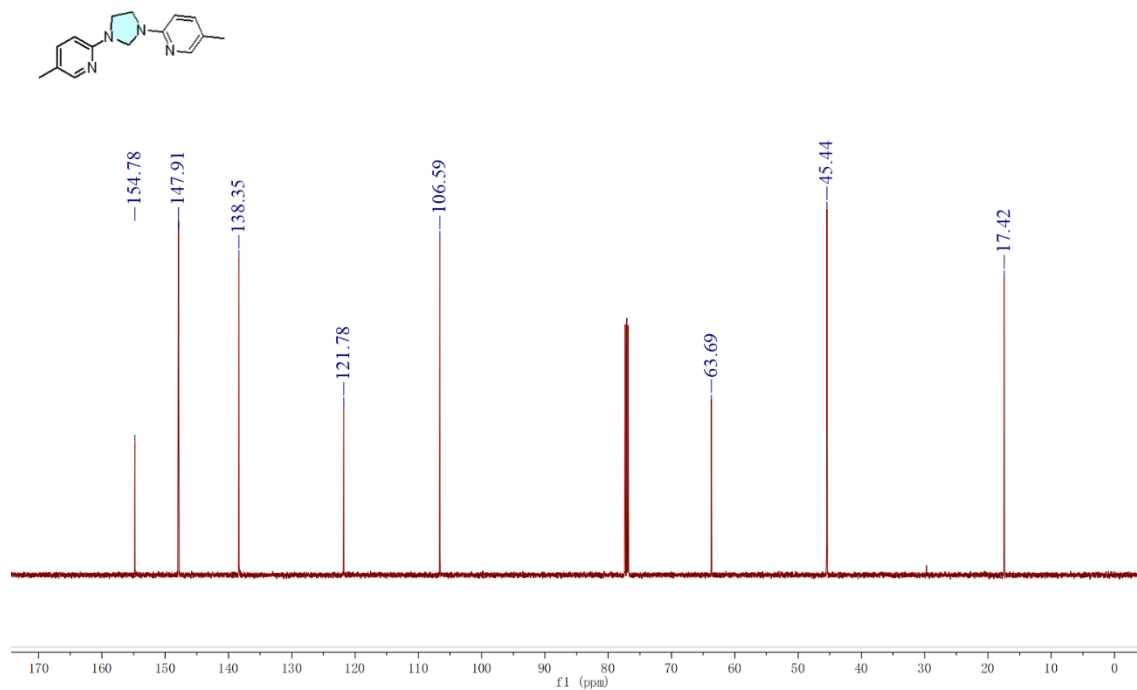
¹³C-NMR spectrum of compound B26



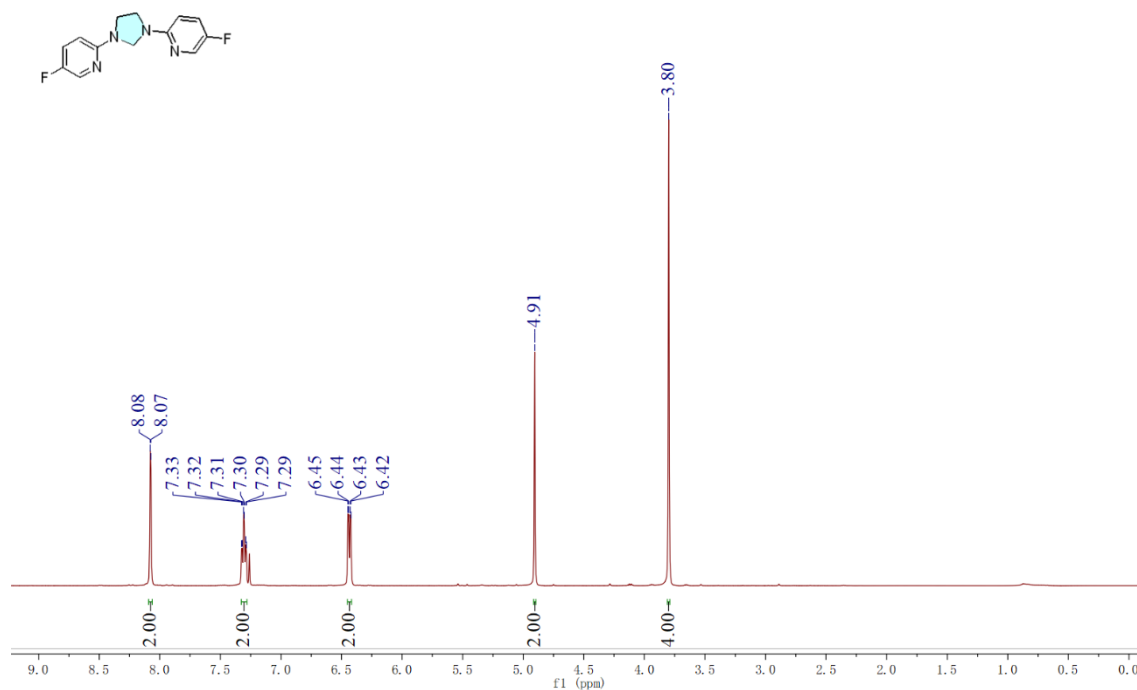
¹H-NMR spectrum of compound B27



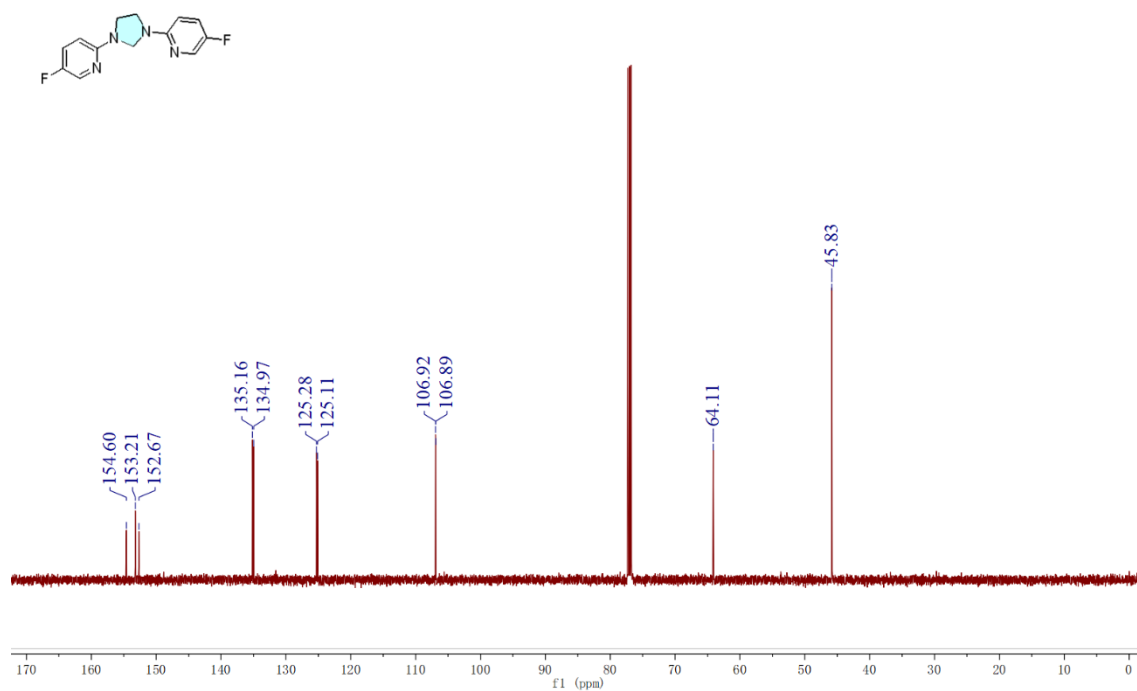
¹³C-NMR spectrum of compound B27



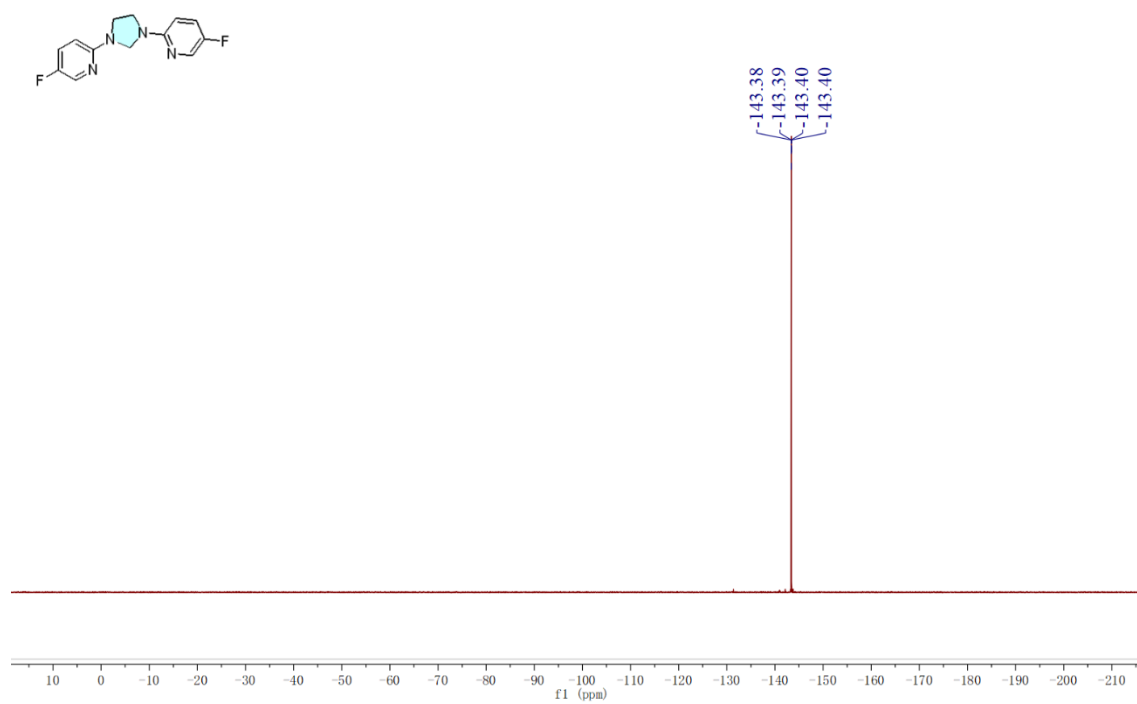
¹H-NMR spectrum of compound B28



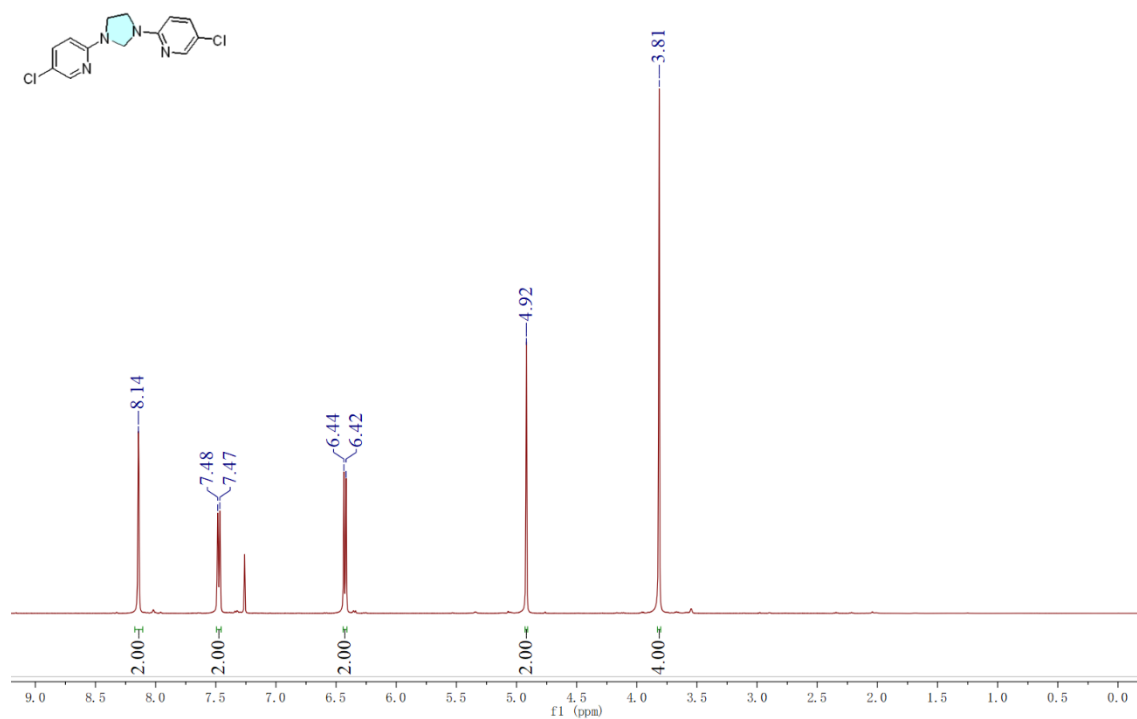
¹³C-NMR spectrum of compound B28



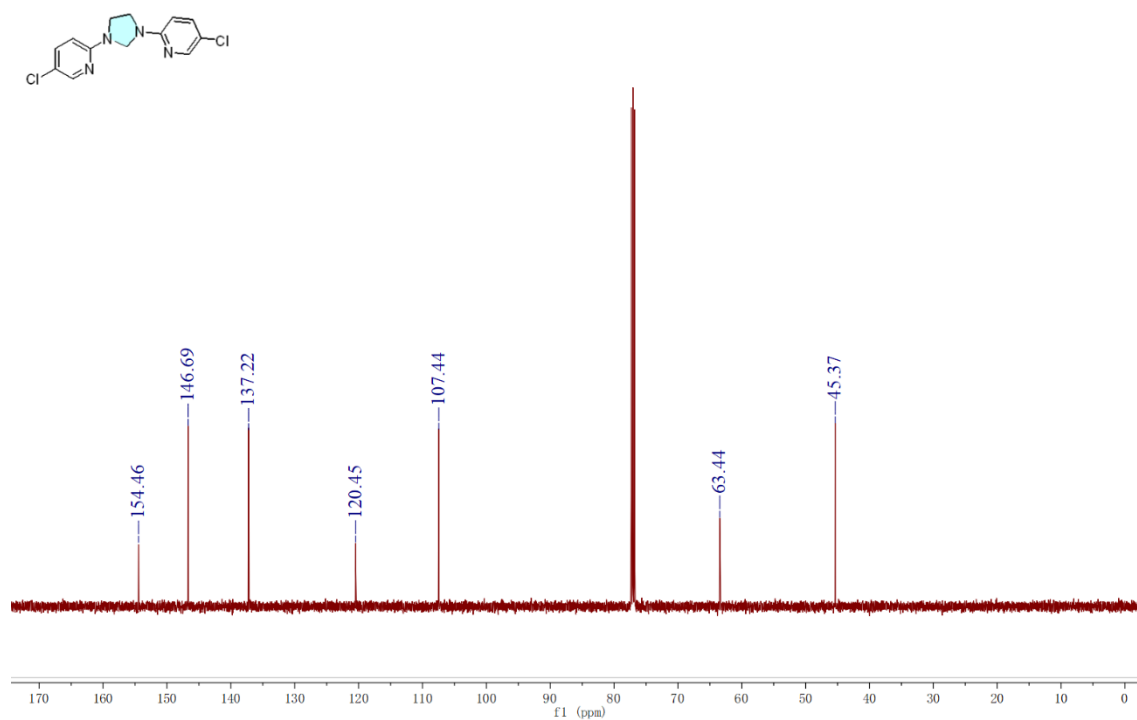
¹⁹F-NMR spectrum of compound B28



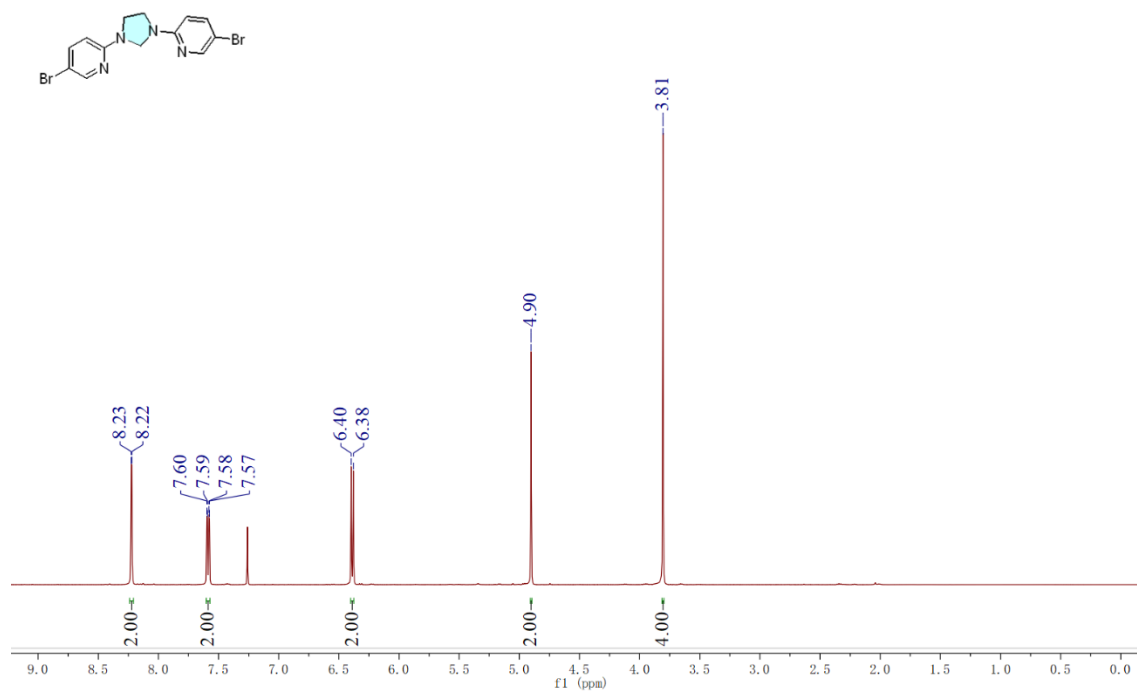
¹H-NMR spectrum of compound B29



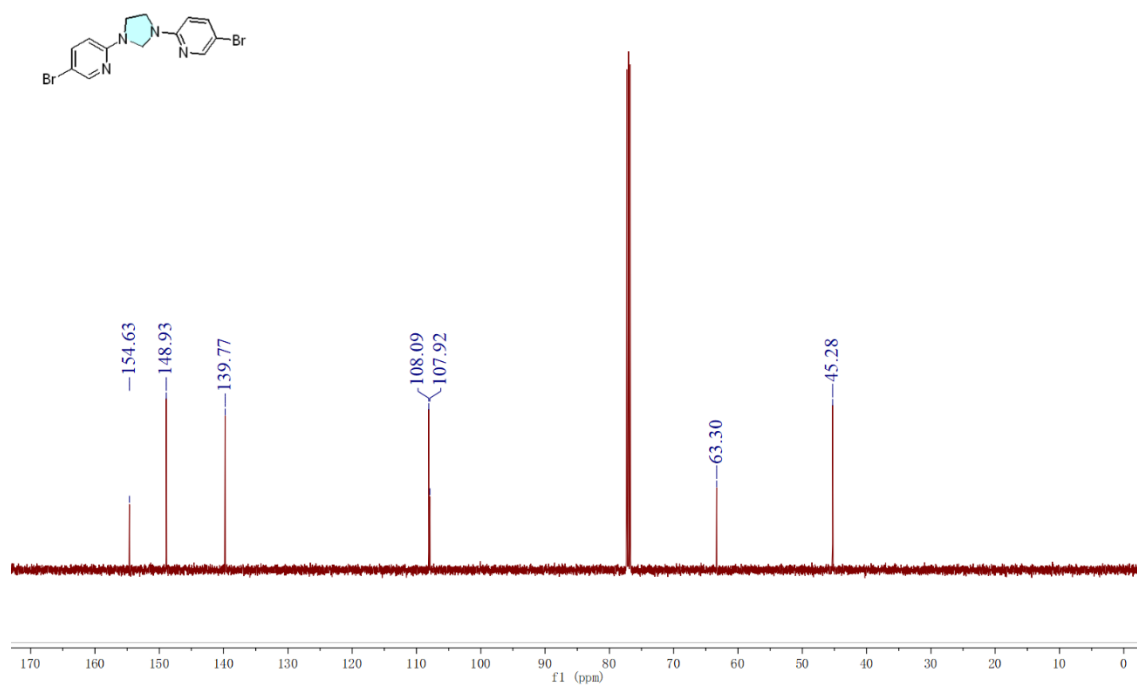
¹³C-NMR spectrum of compound B29



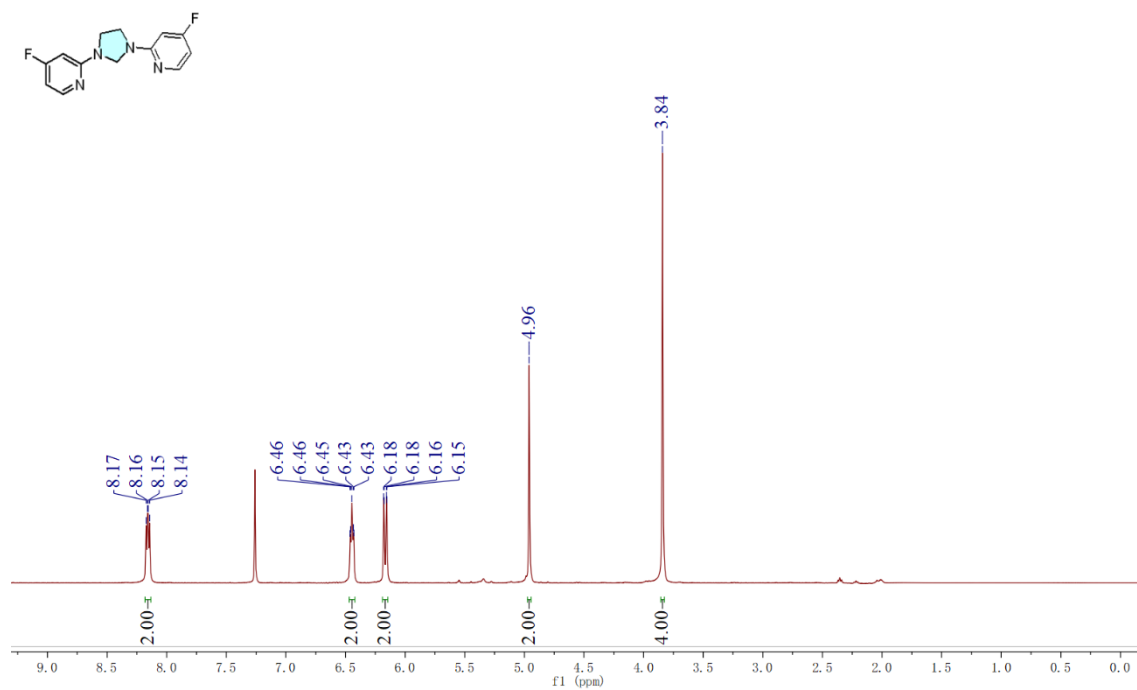
¹H-NMR spectrum of compound B30



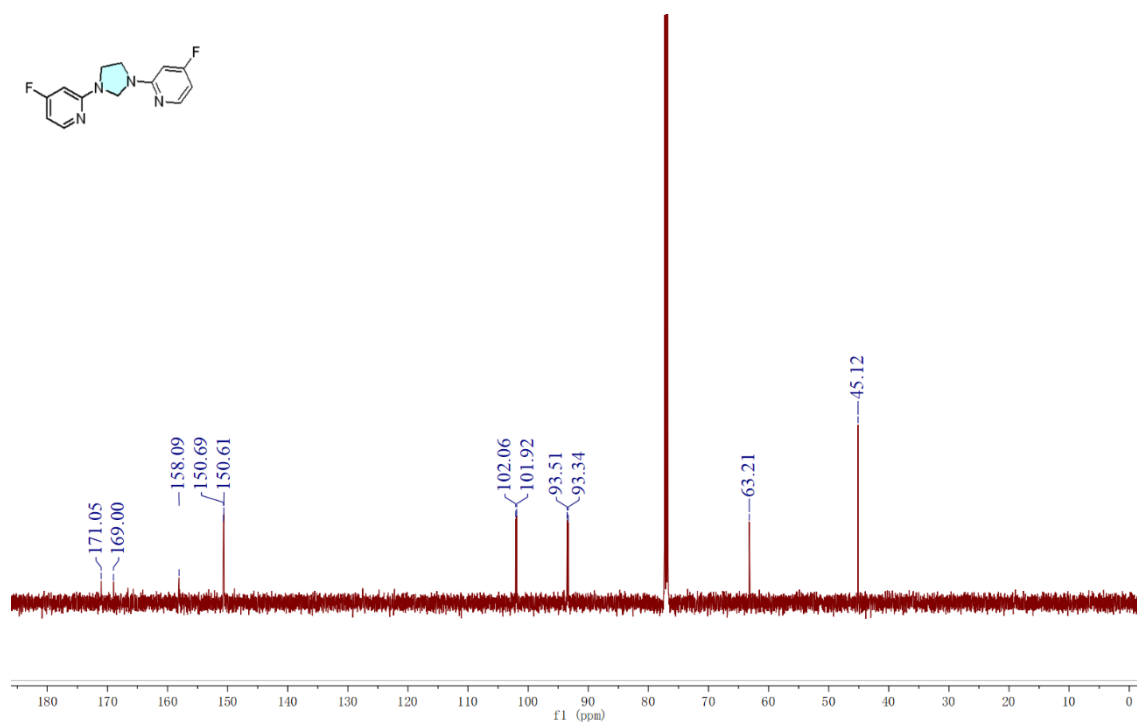
¹³C-NMR spectrum of compound B30



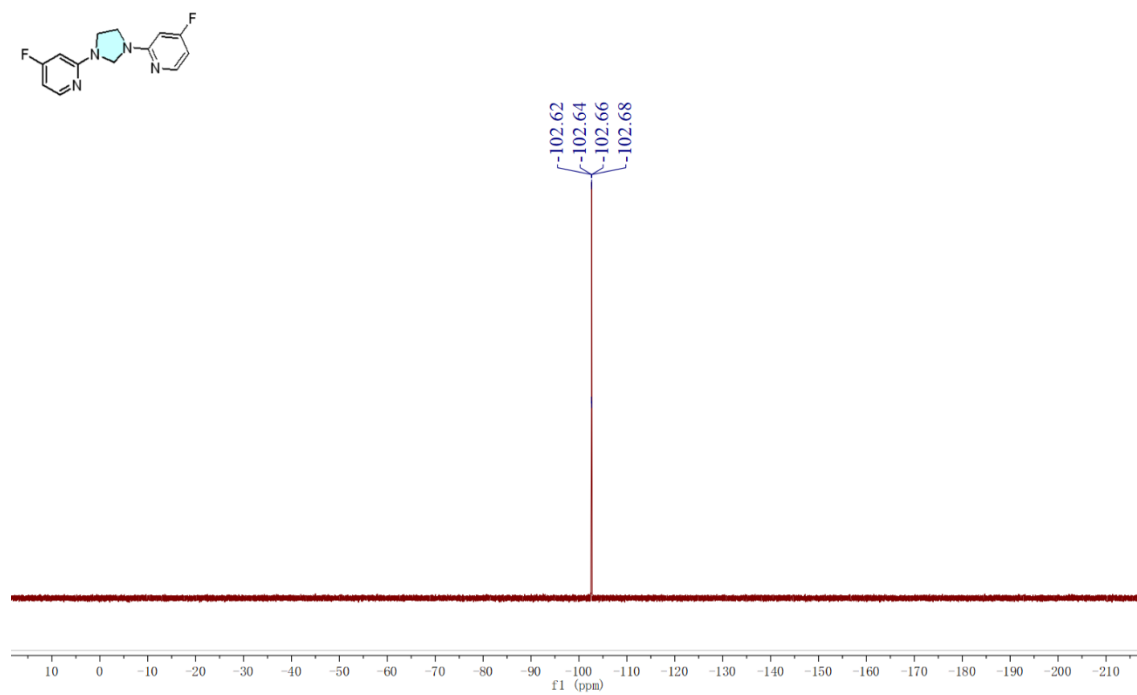
¹H-NMR spectrum of compound B31



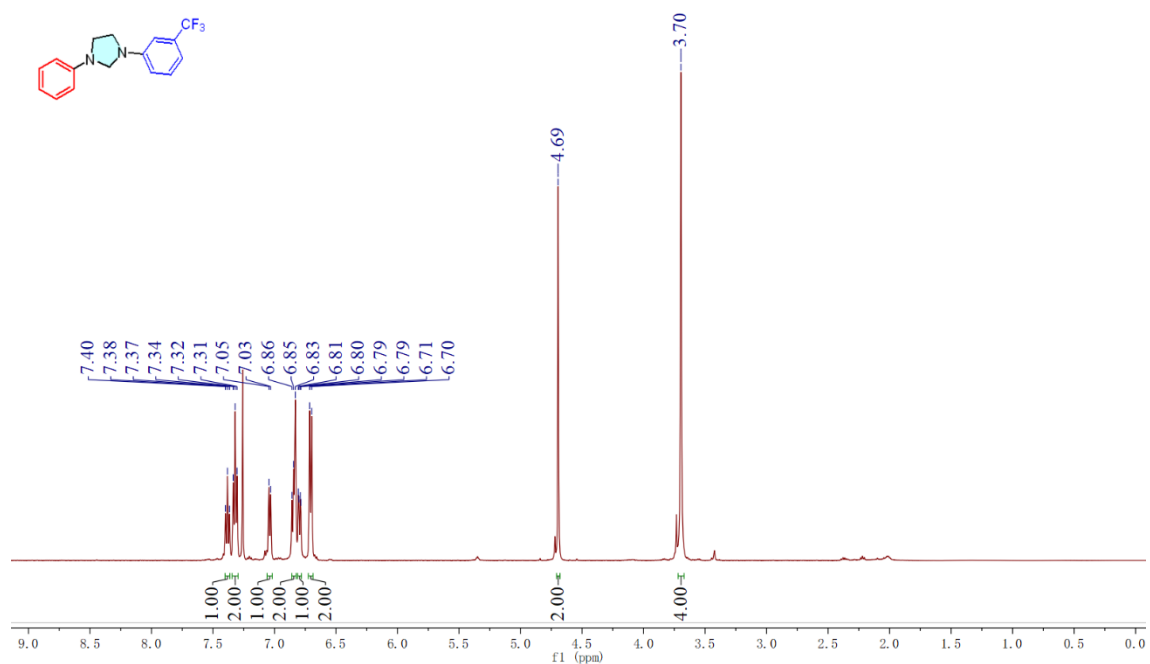
¹³C-NMR spectrum of compound B31



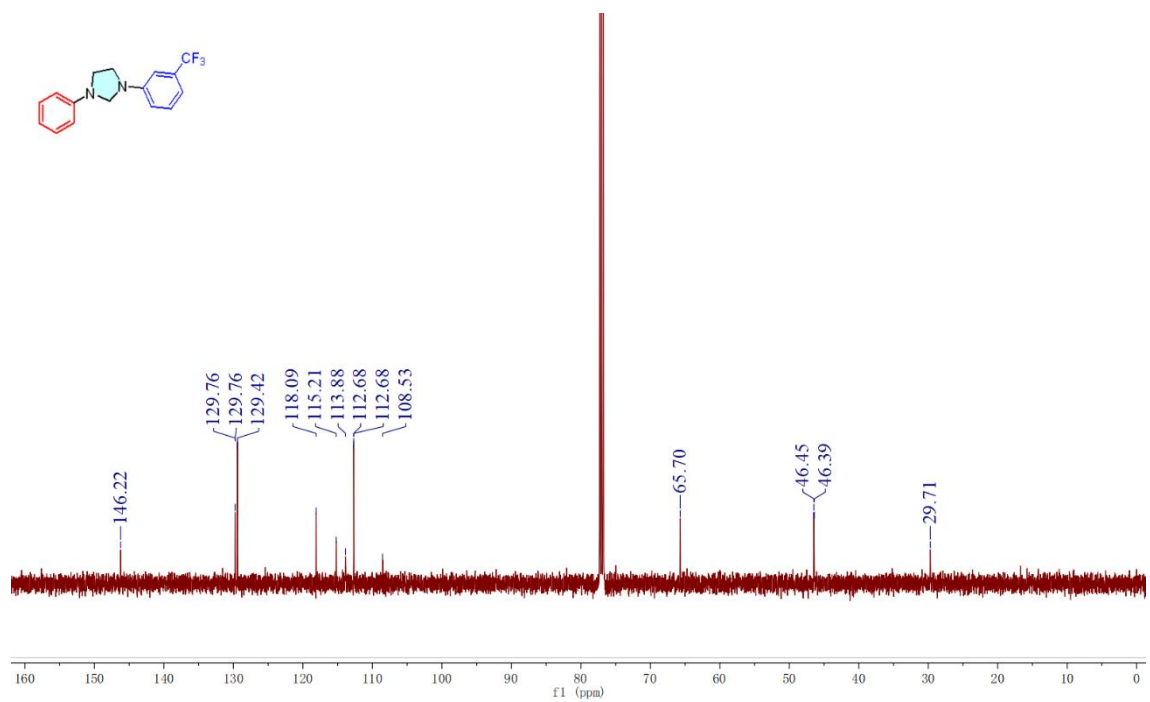
¹⁹F-NMR spectrum of compound B31



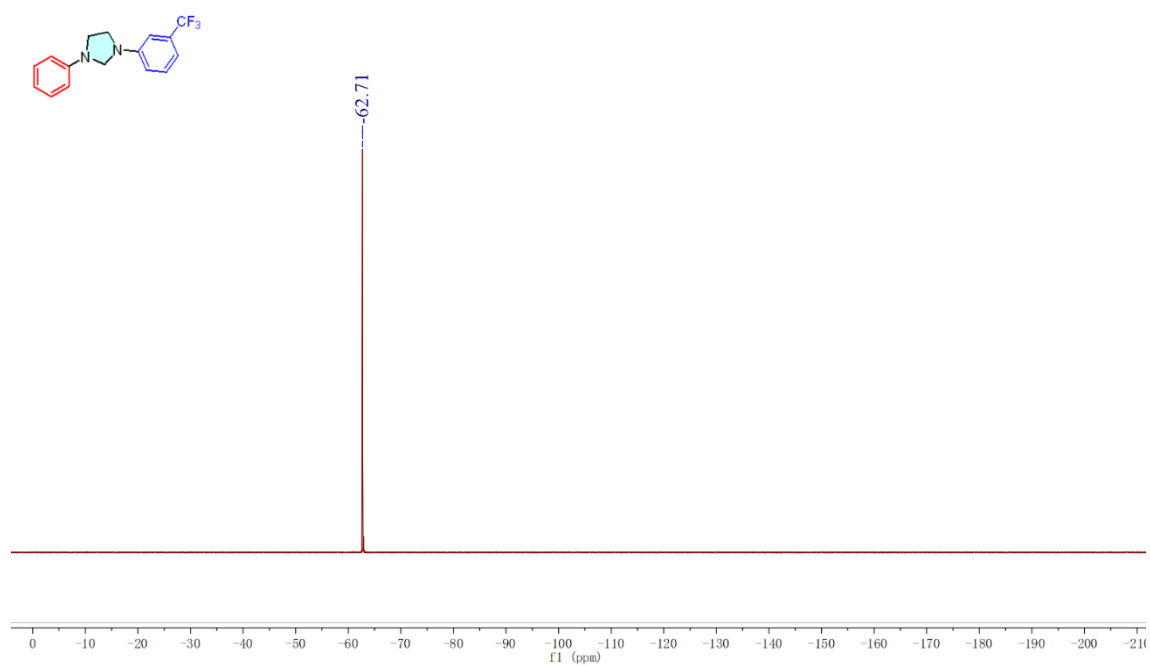
¹H-NMR spectrum of compound B32



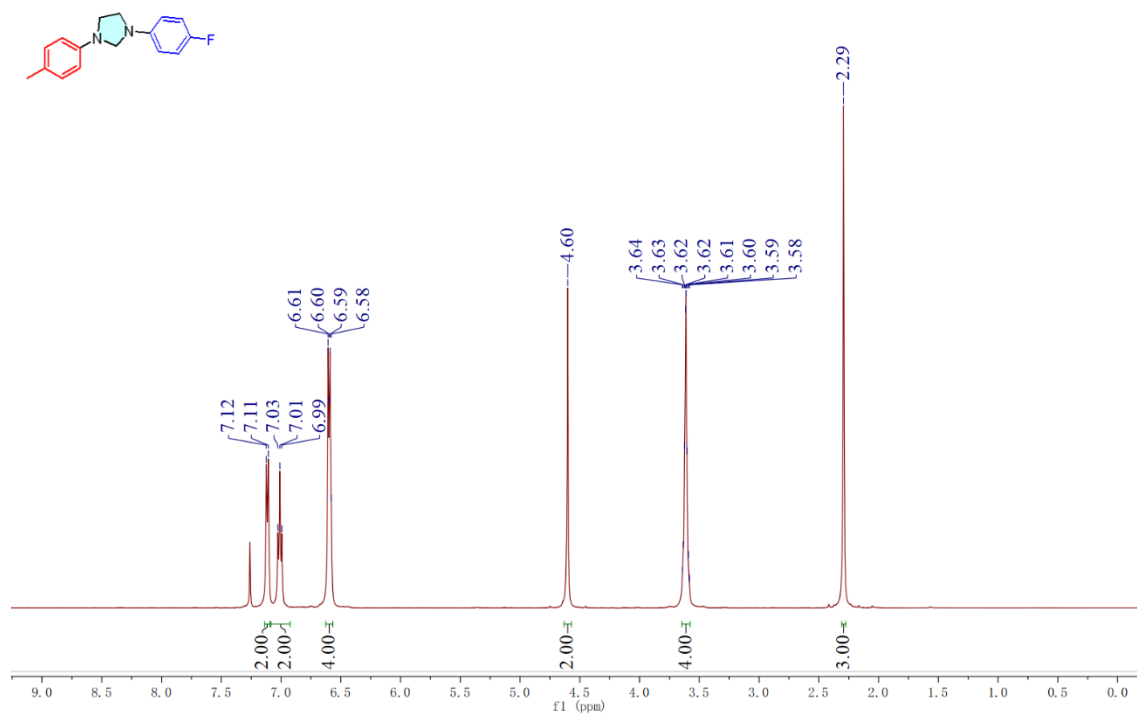
¹³C-NMR spectrum of compound B32



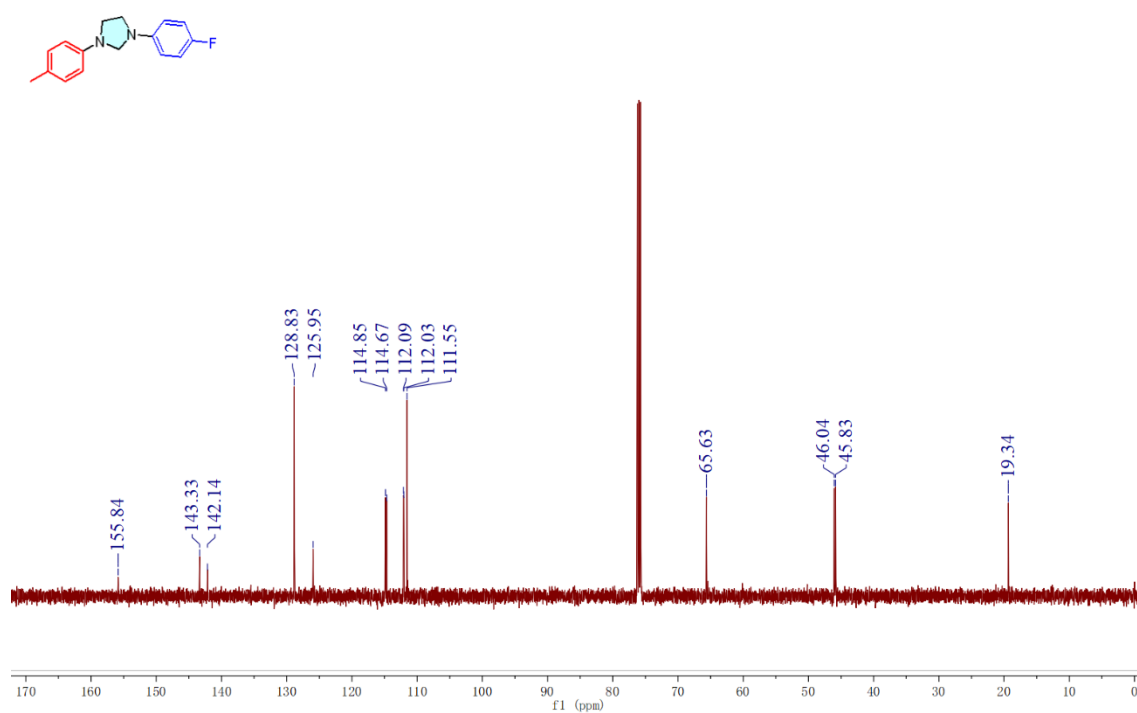
¹⁹F-NMR spectrum of compound B32



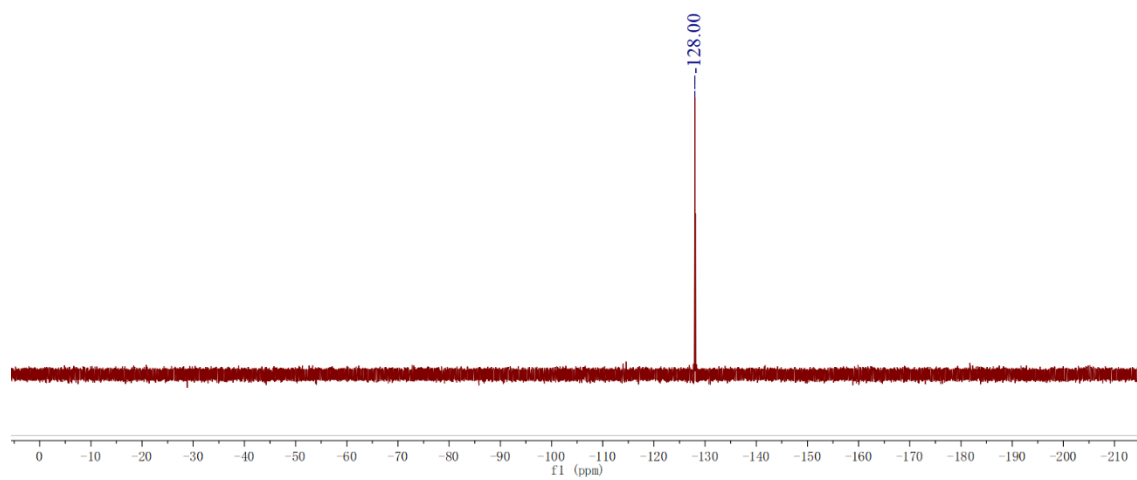
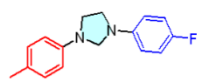
¹H-NMR spectrum of compound B33



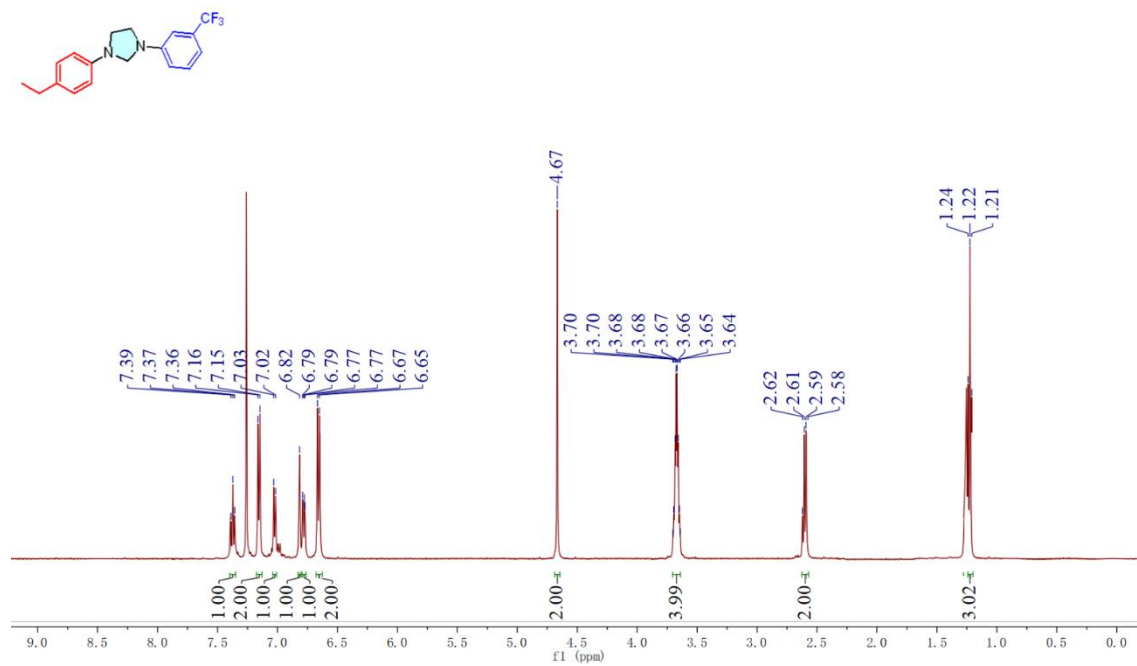
¹³C-NMR spectrum of compound B33



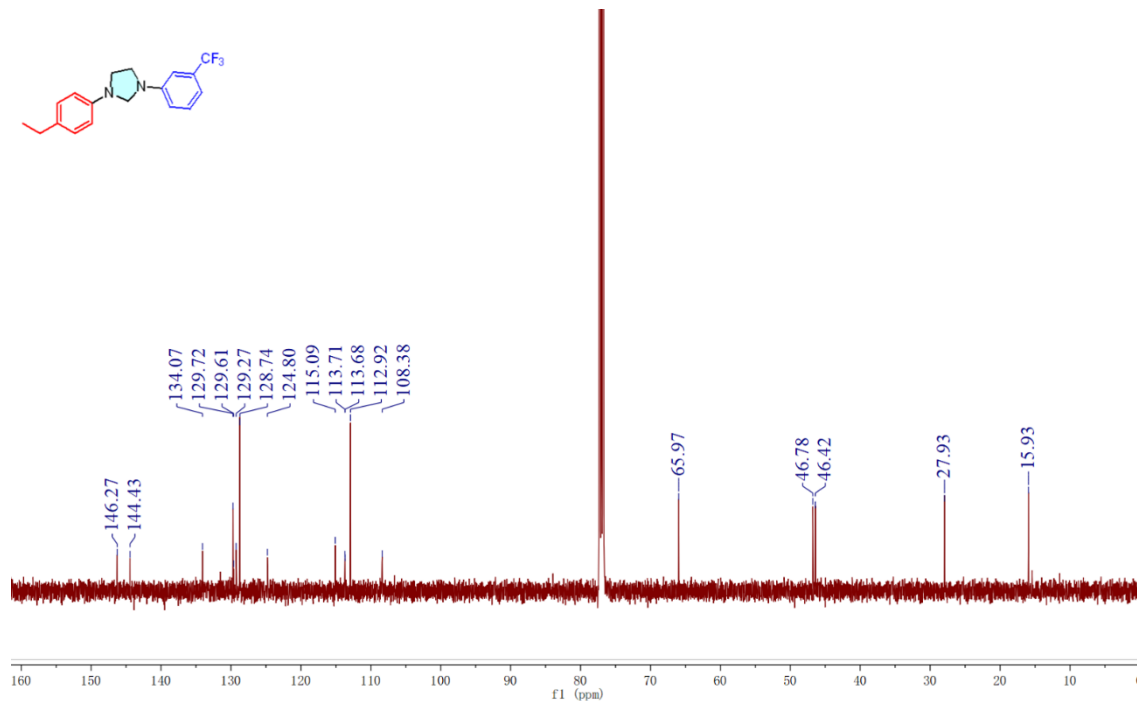
¹⁹F-NMR spectrum of compound B33



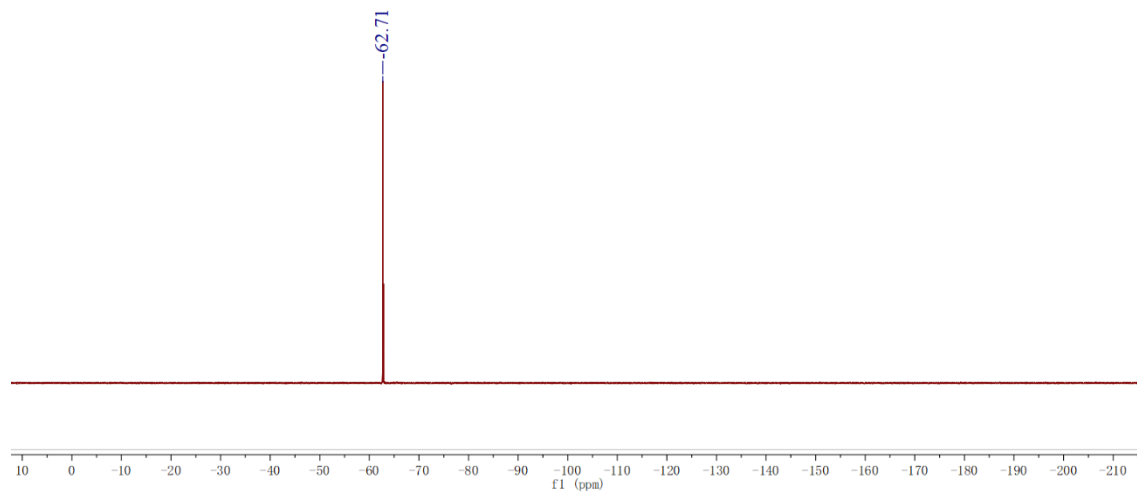
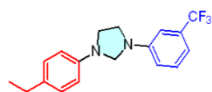
¹H-NMR spectrum of compound B34



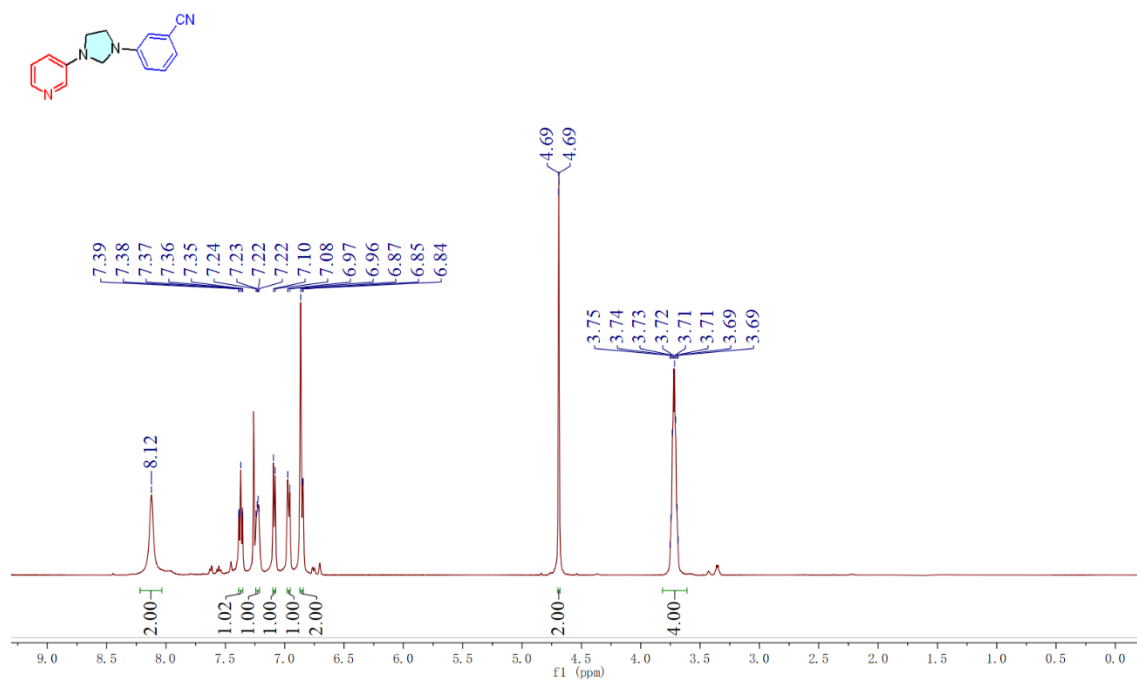
¹³C-NMR spectrum of compound B34



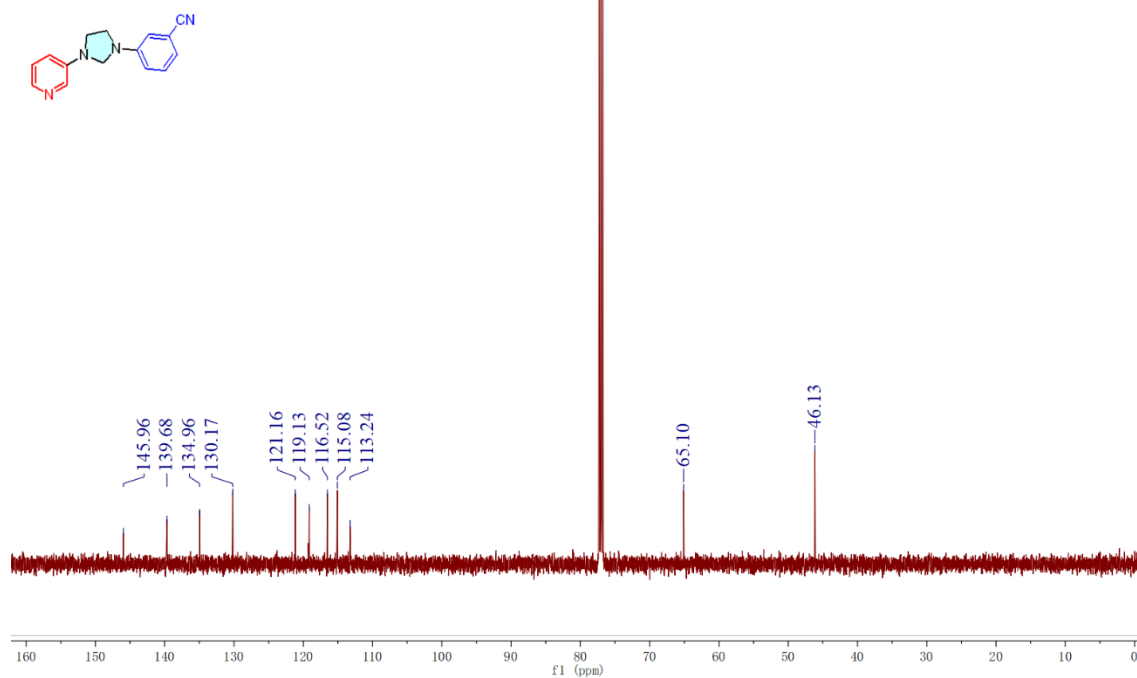
¹⁹F-NMR spectrum of compound B34



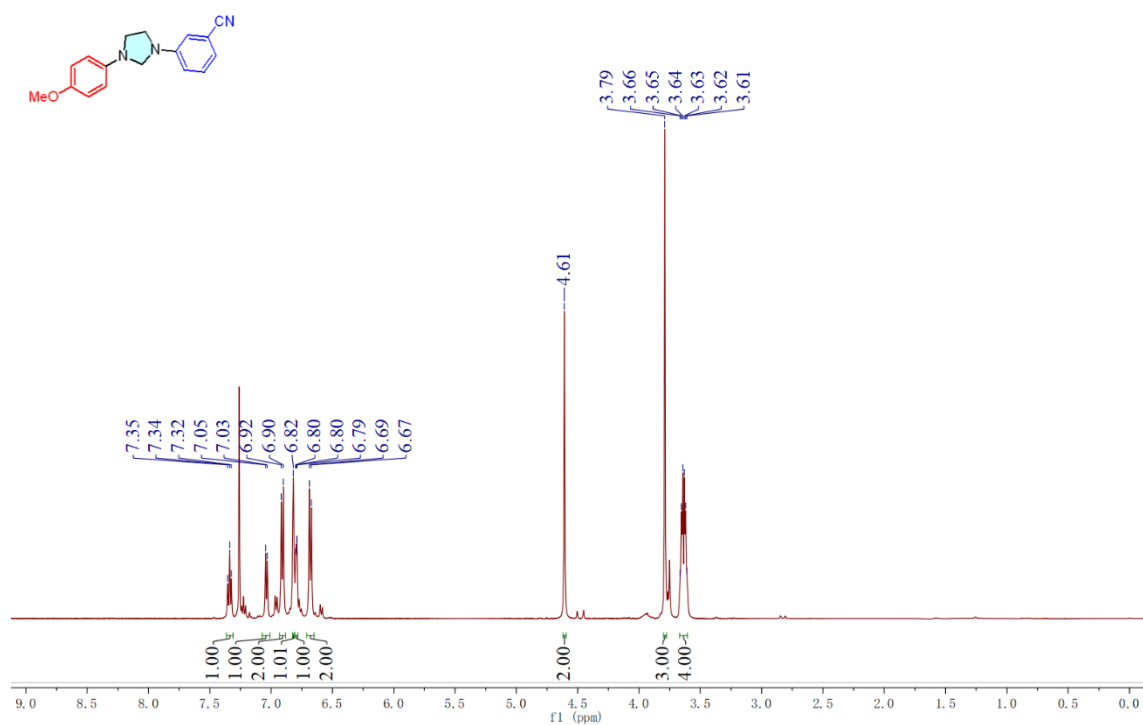
¹H-NMR spectrum of compound B35



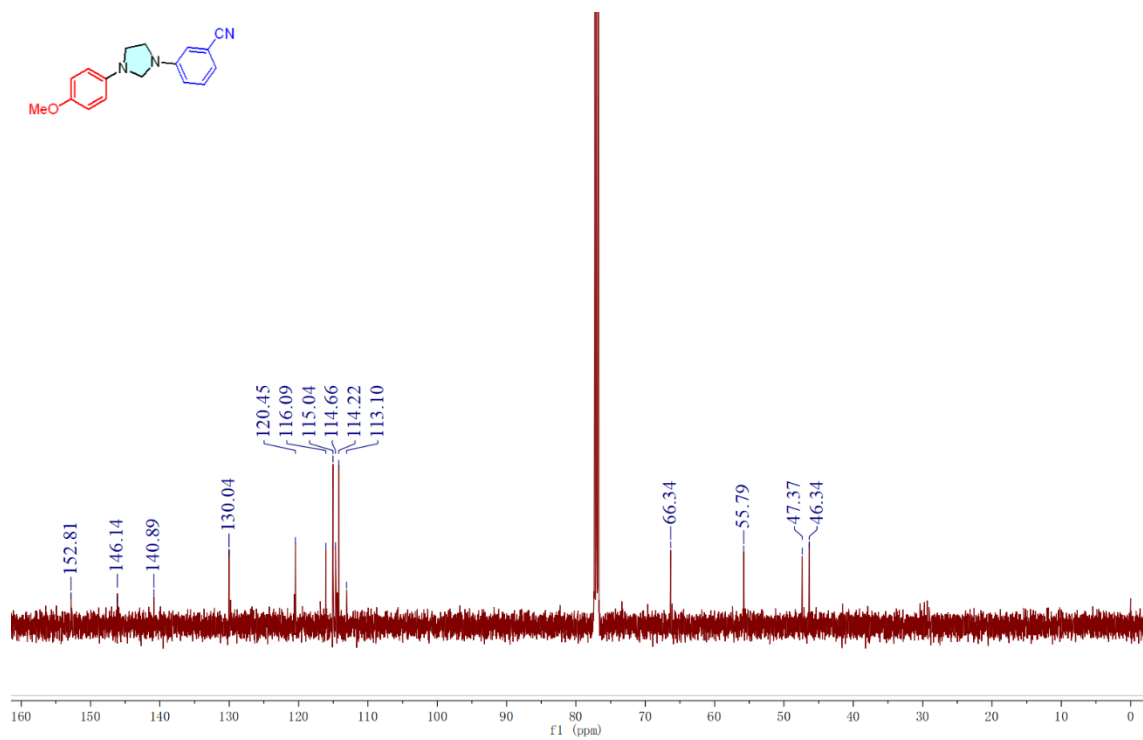
¹³C-NMR spectrum of compound B35



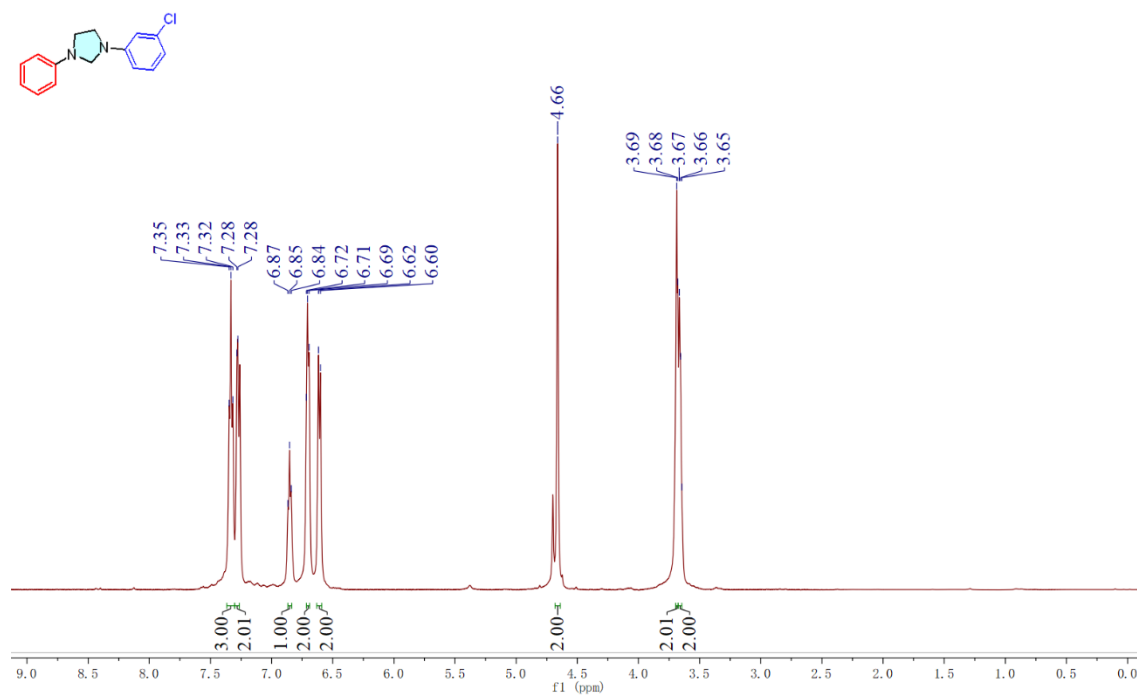
¹H-NMR spectrum of compound B36



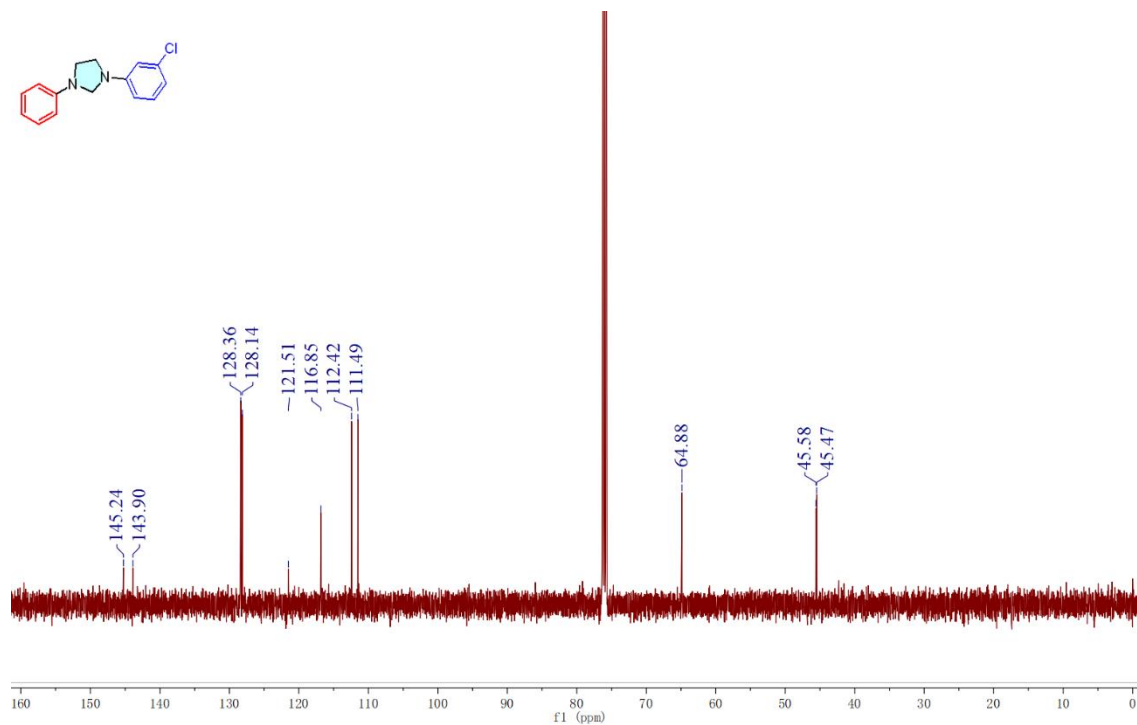
¹³C-NMR spectrum of compound B36



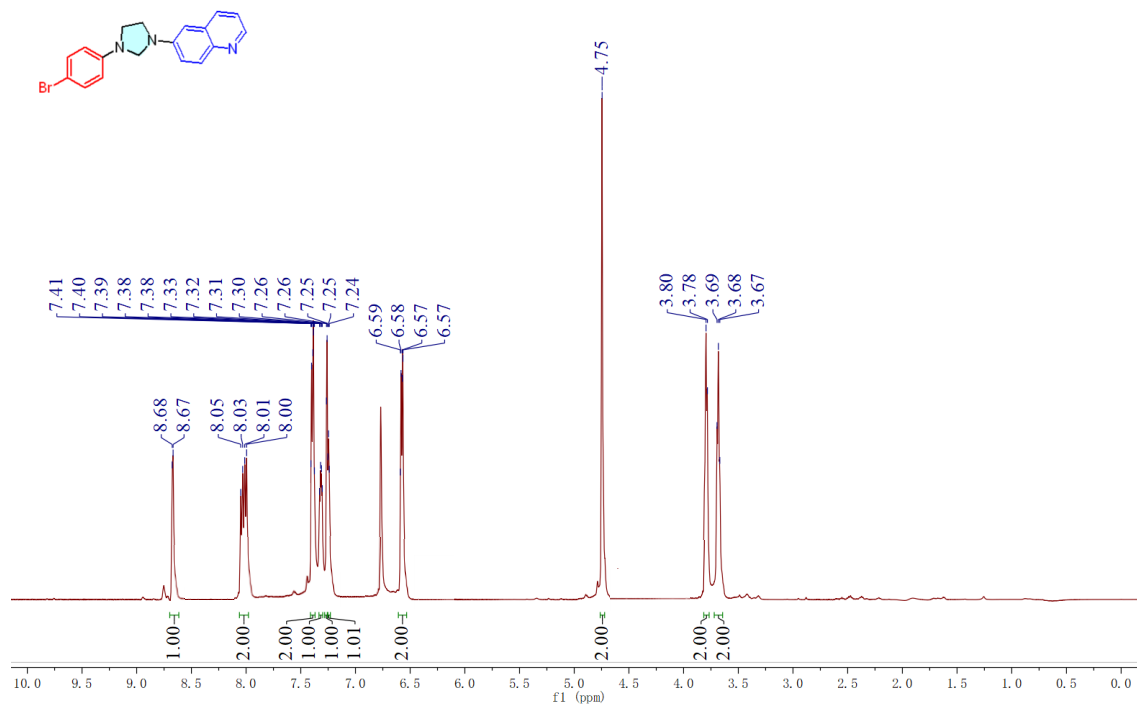
¹H-NMR spectrum of compound B37



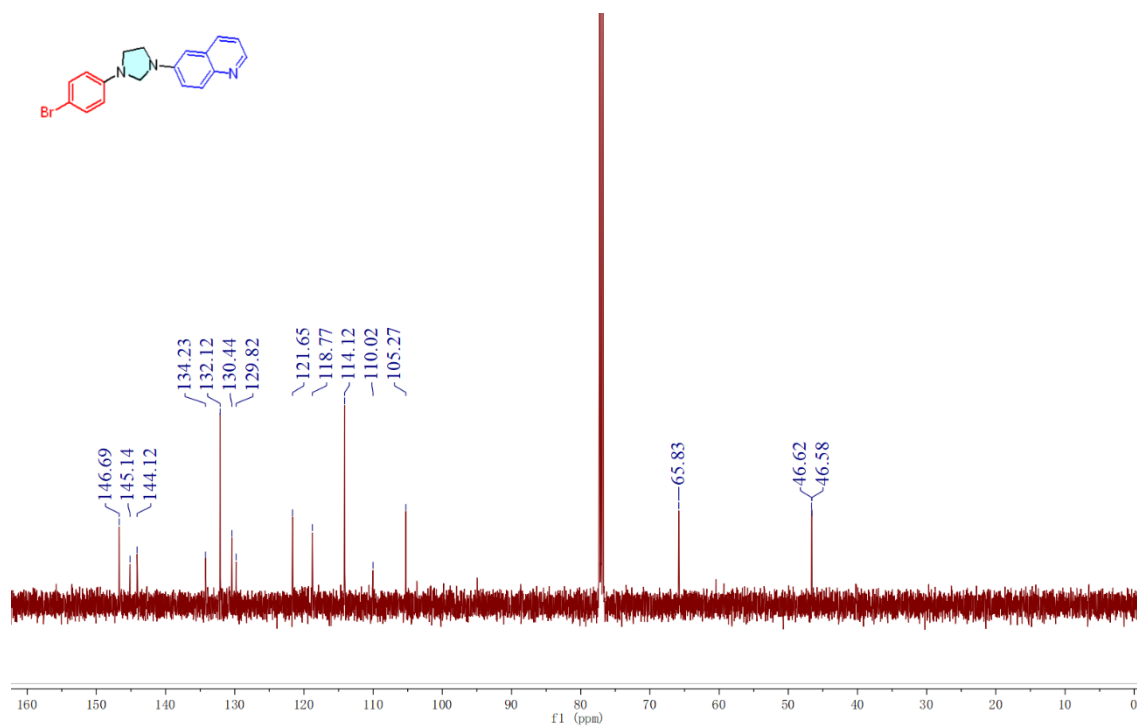
¹³C-NMR spectrum of compound B37



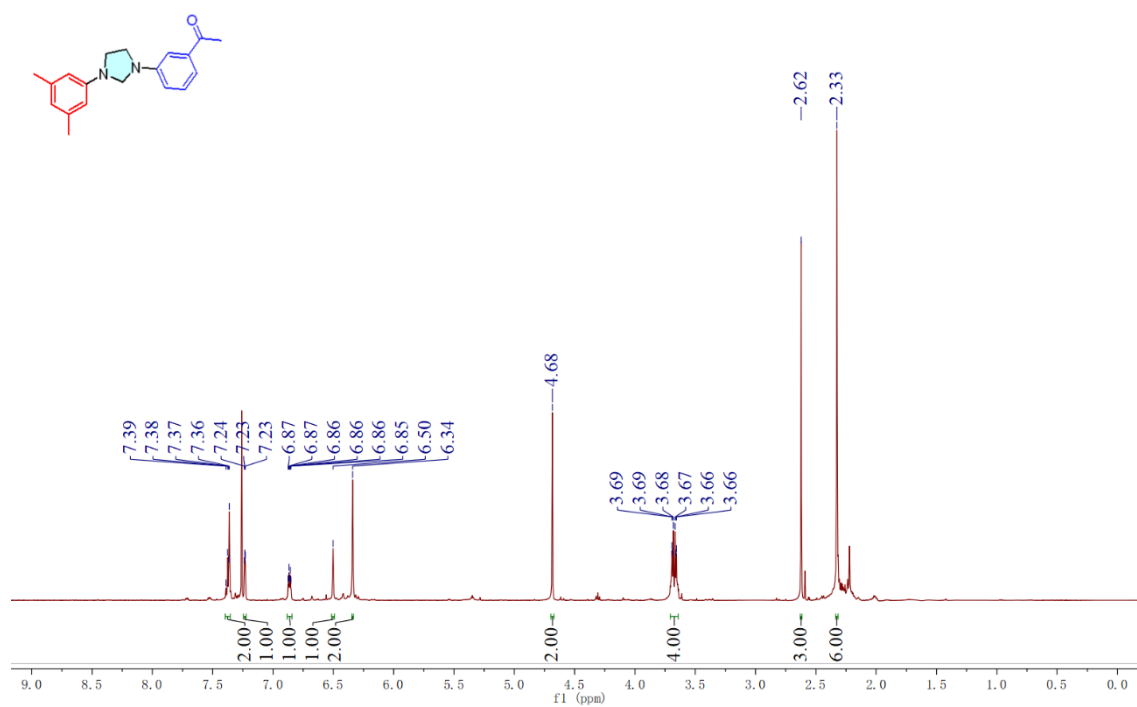
¹H-NMR spectrum of compound B38



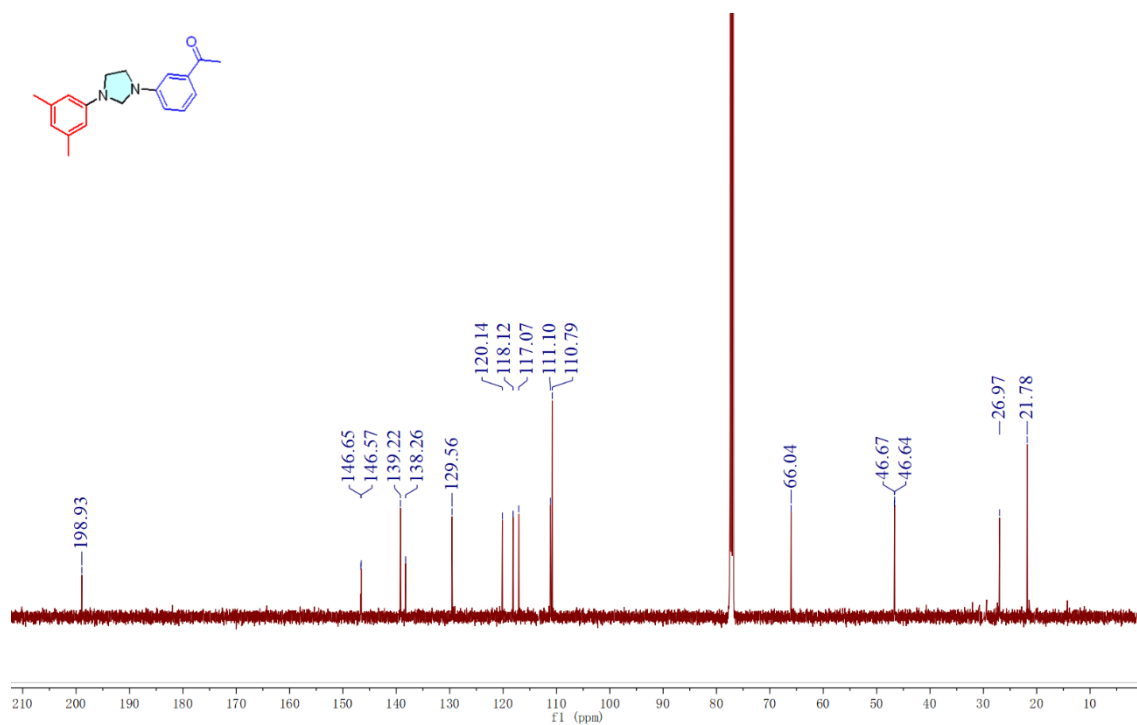
¹³C-NMR spectrum of compound B38



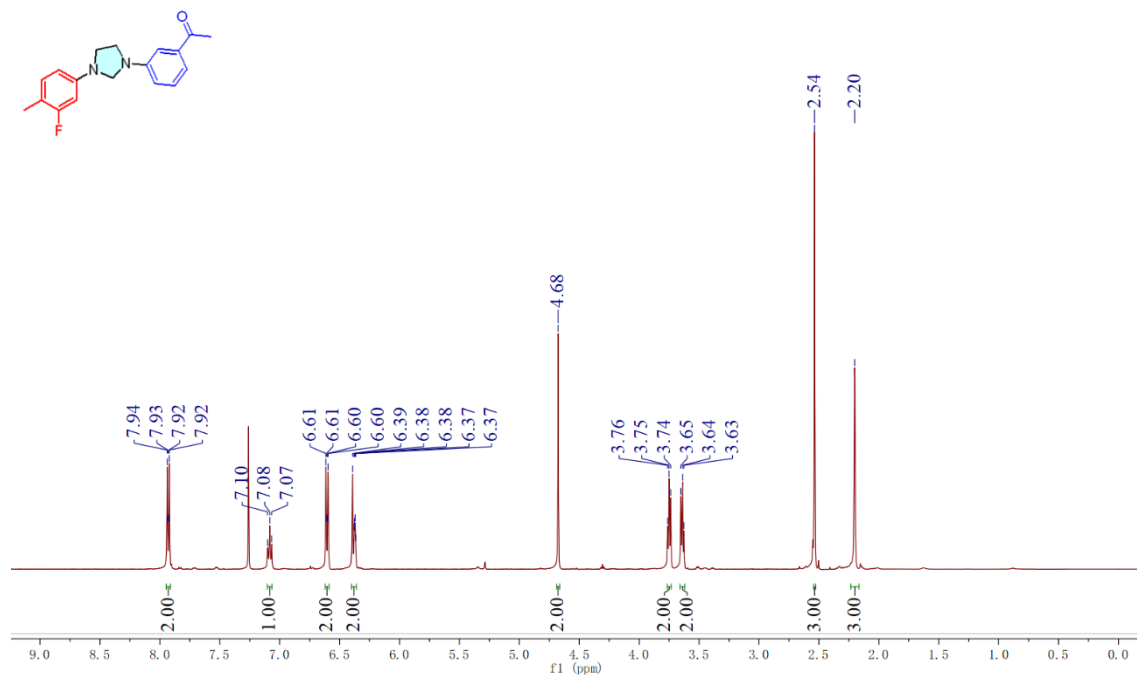
¹H-NMR spectrum of compound B39



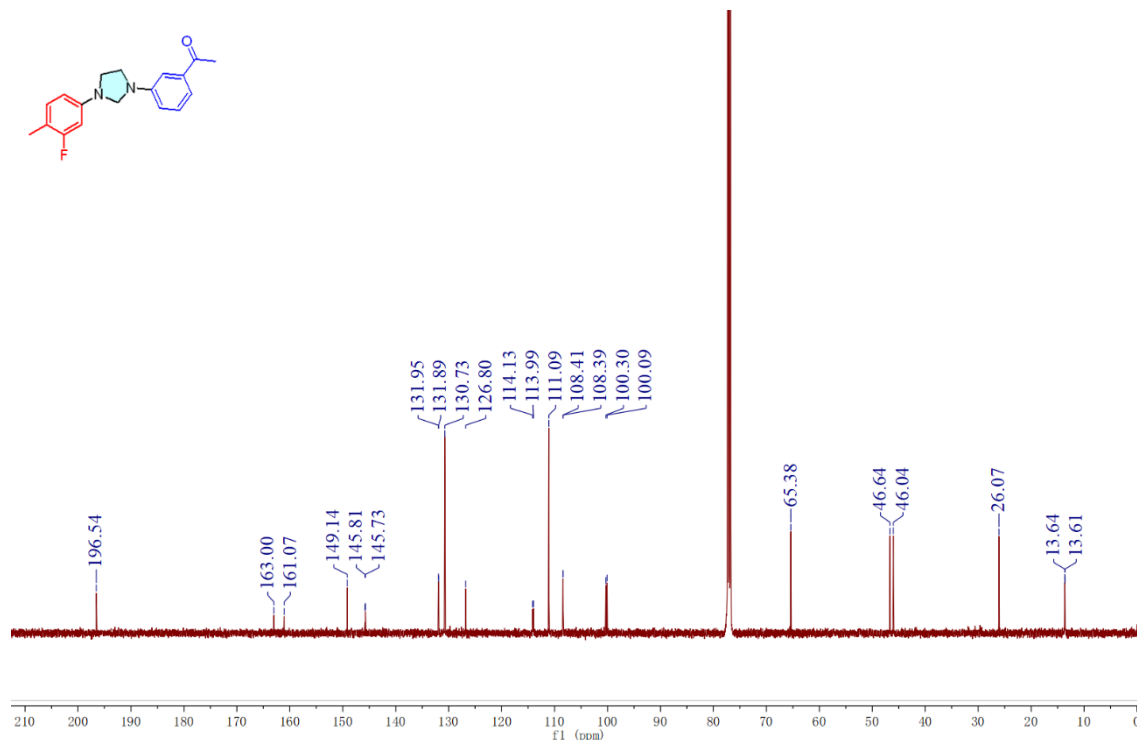
¹³C-NMR spectrum of compound B39



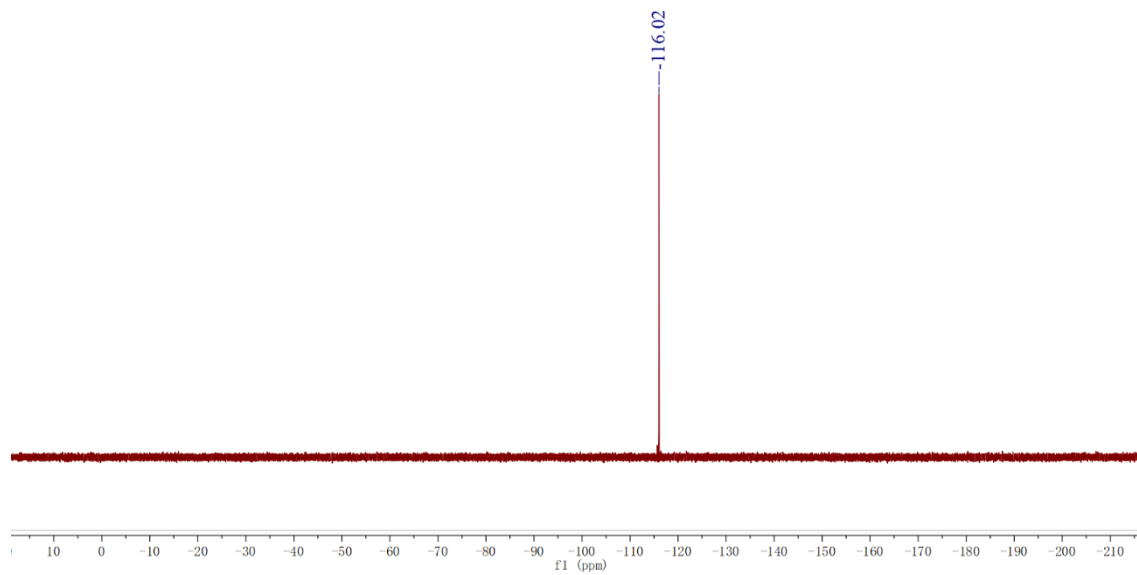
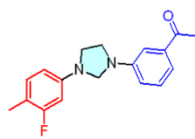
¹H-NMR spectrum of compound B40



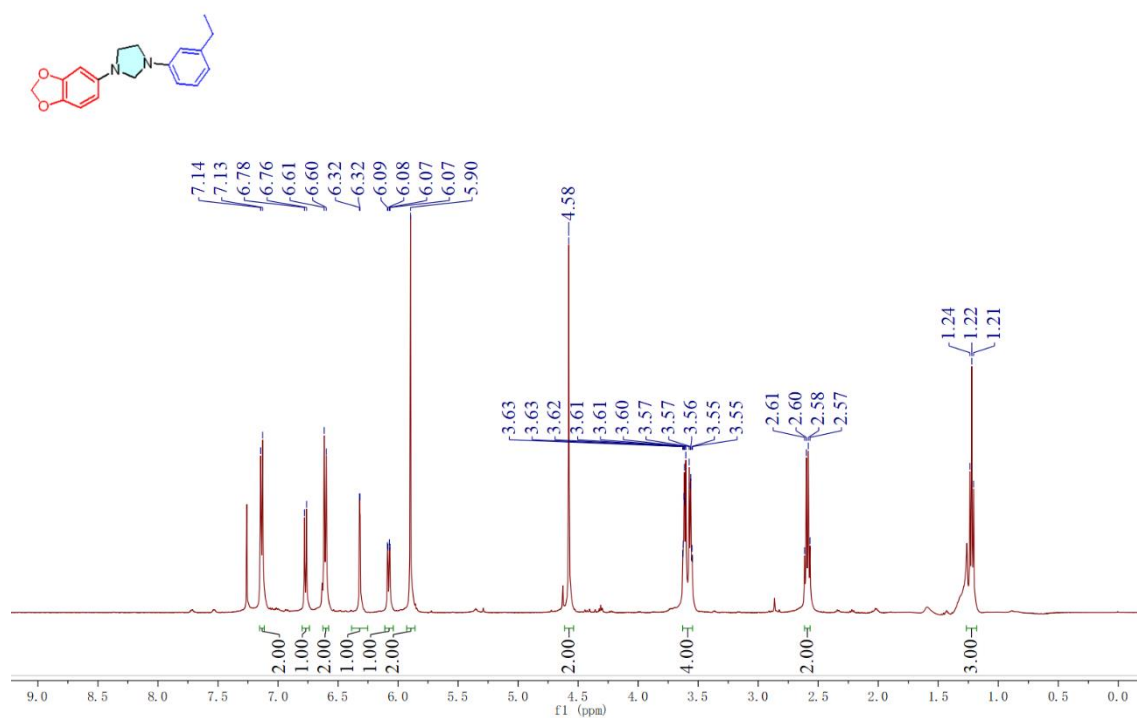
¹³C-NMR spectrum of compound B40



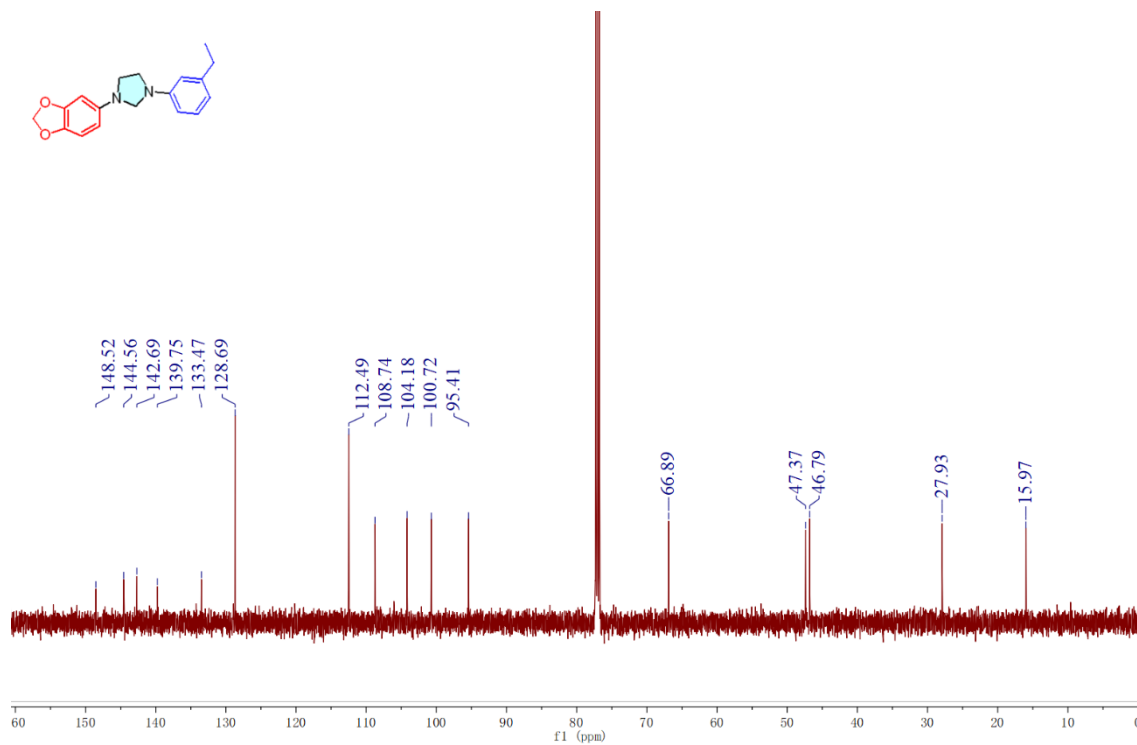
¹⁹F-NMR spectrum of compound B40



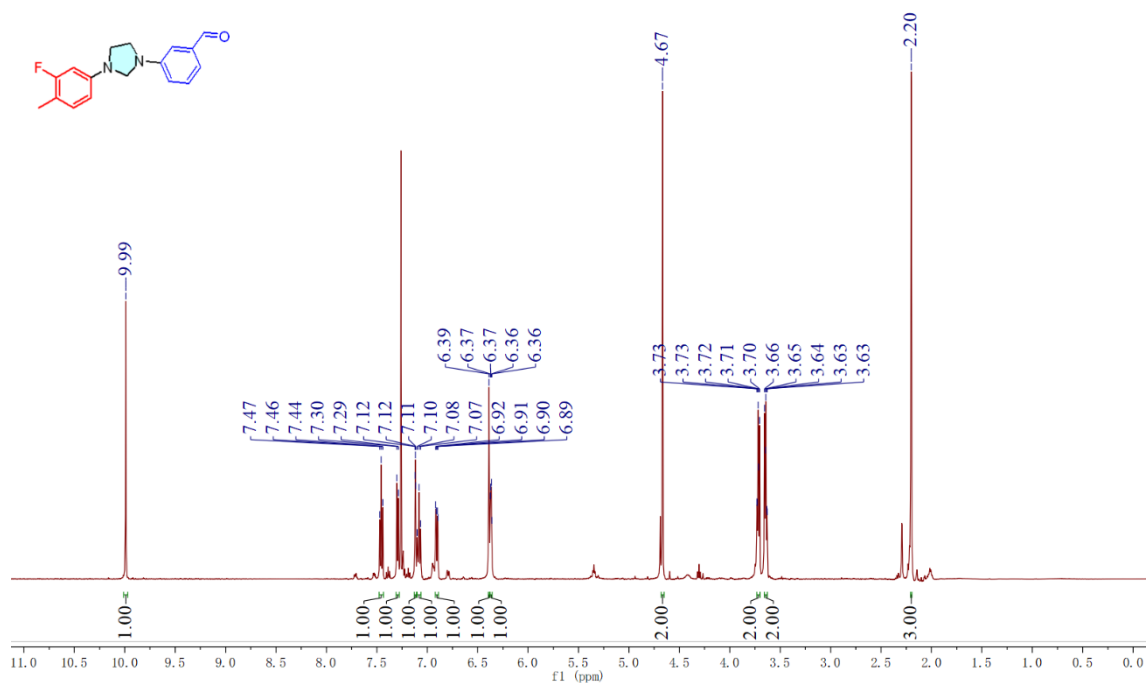
¹H-NMR spectrum of compound B41



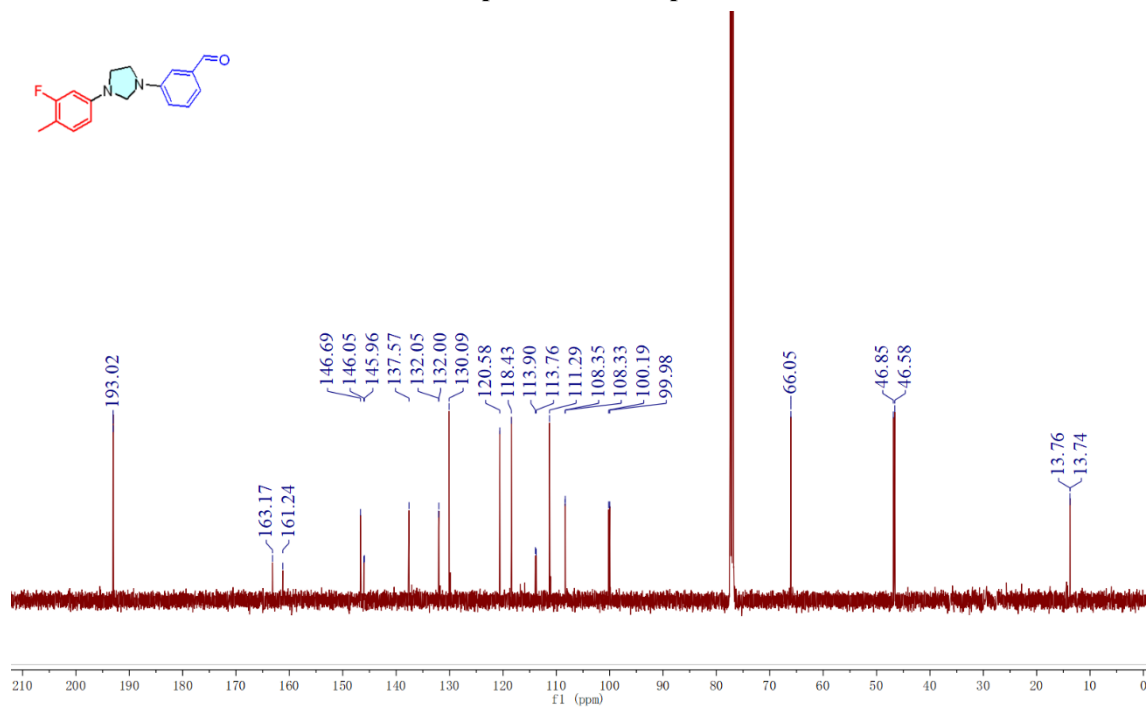
¹³C-NMR spectrum of compound B41



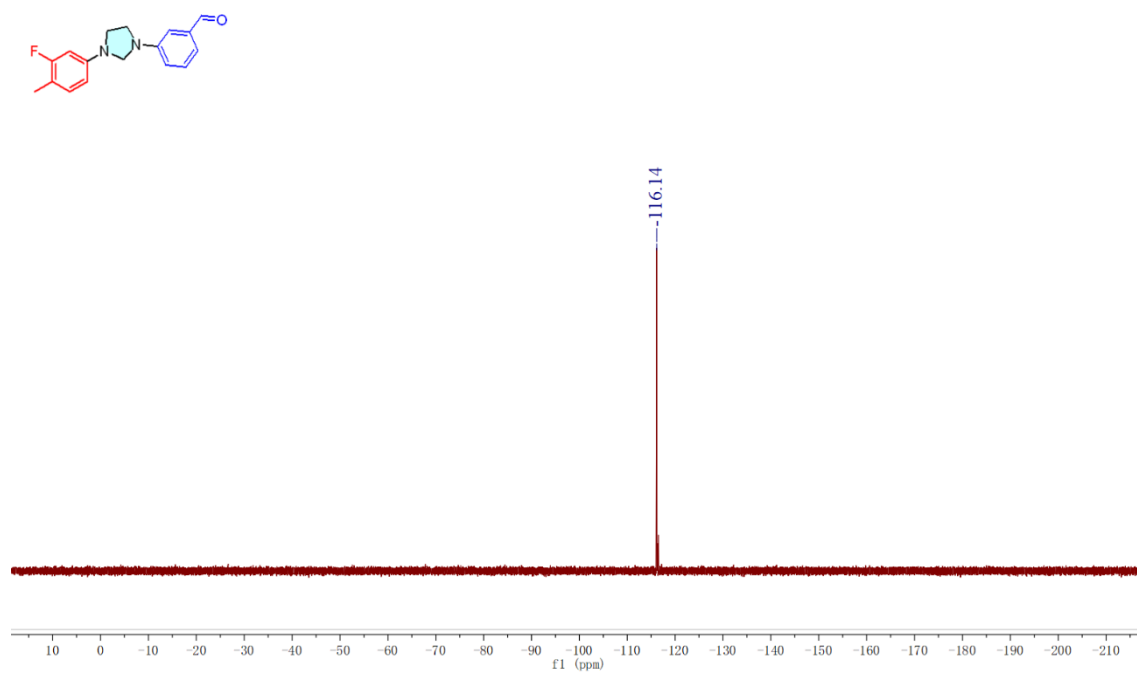
¹H-NMR spectrum of compound B42



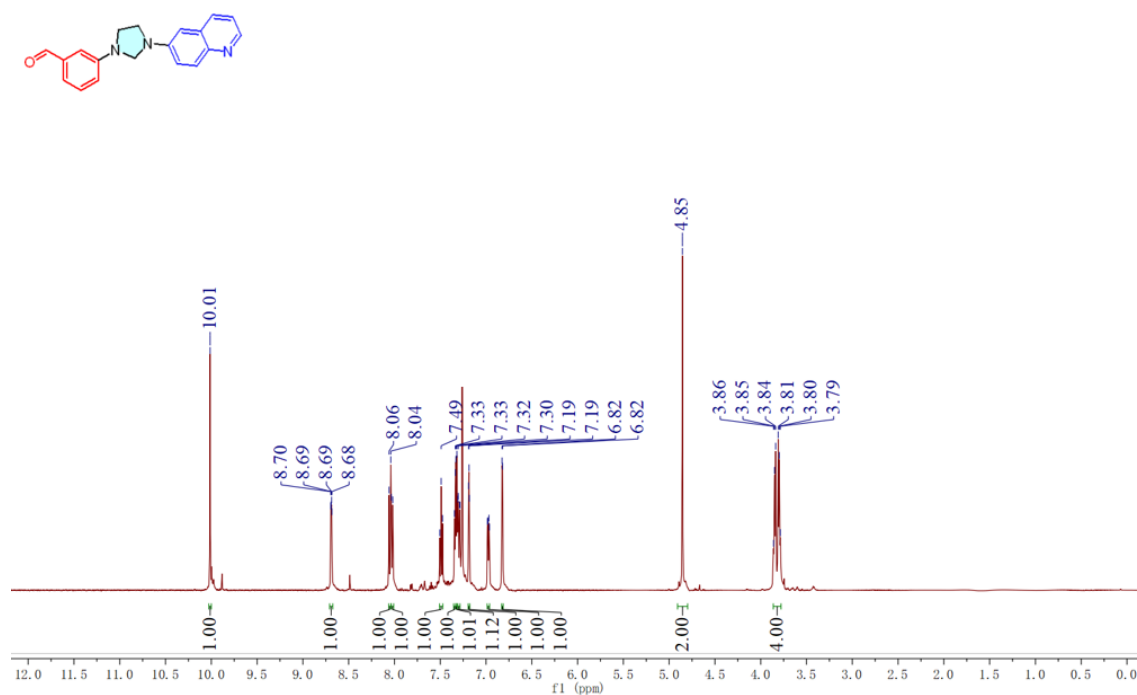
¹³C-NMR spectrum of compound 42



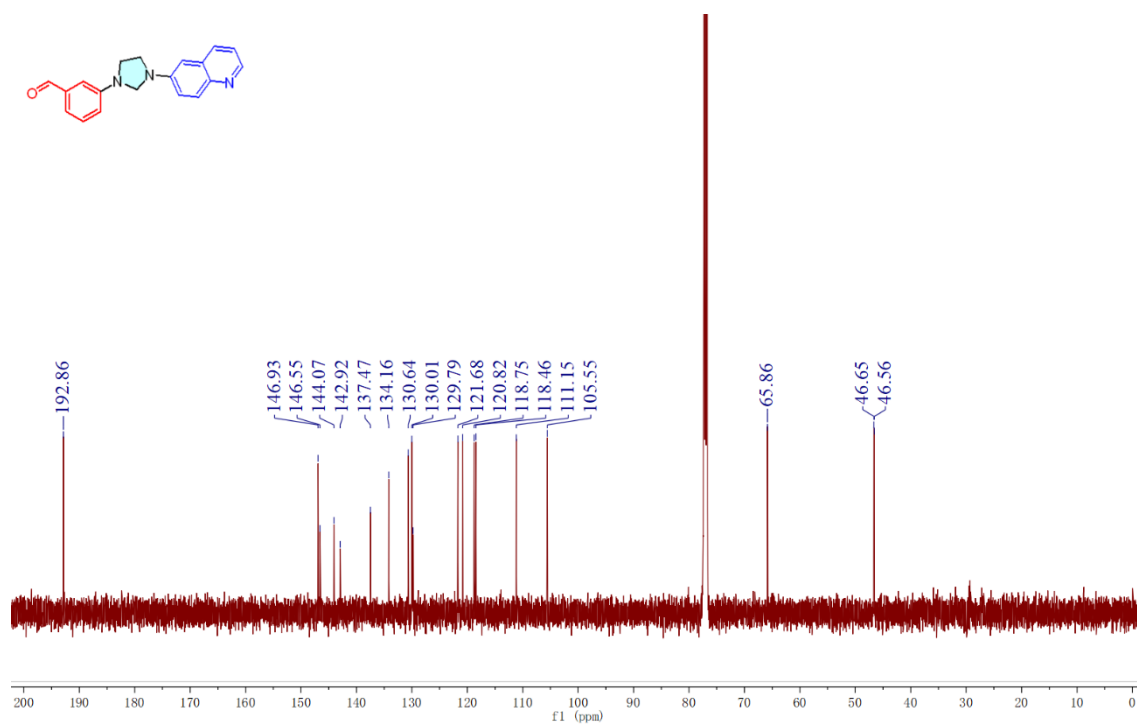
¹⁹F-NMR spectrum of compound B42



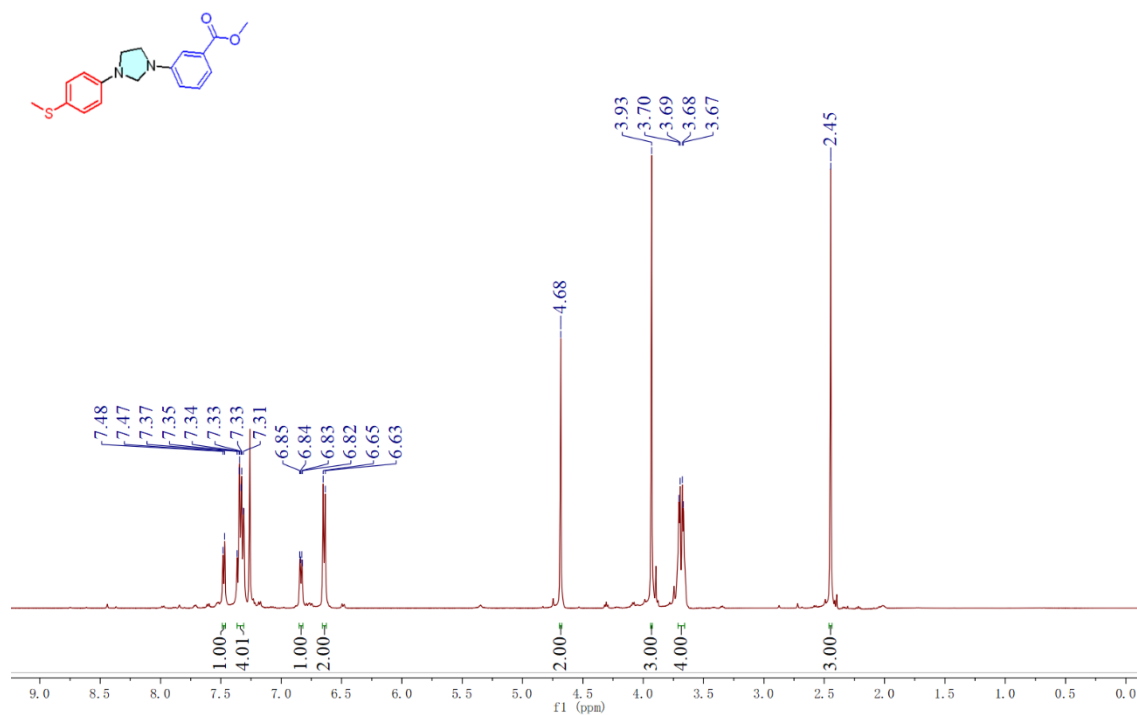
¹H-NMR spectrum of compound B43



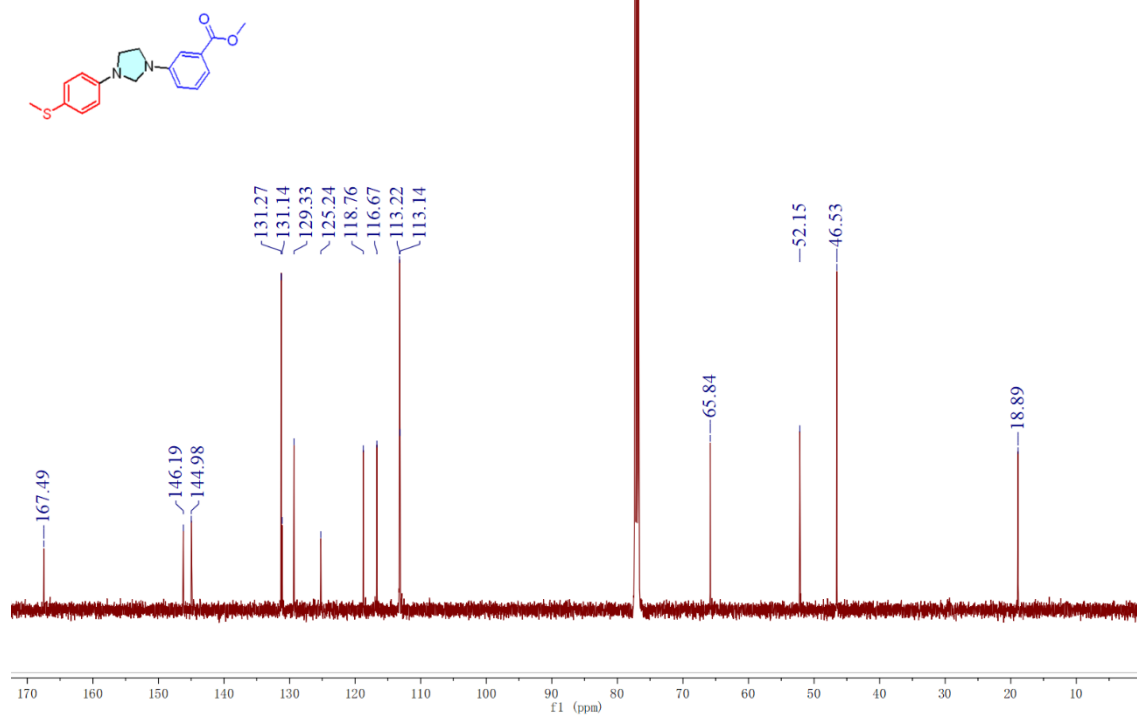
¹³C-NMR spectrum of compound B43



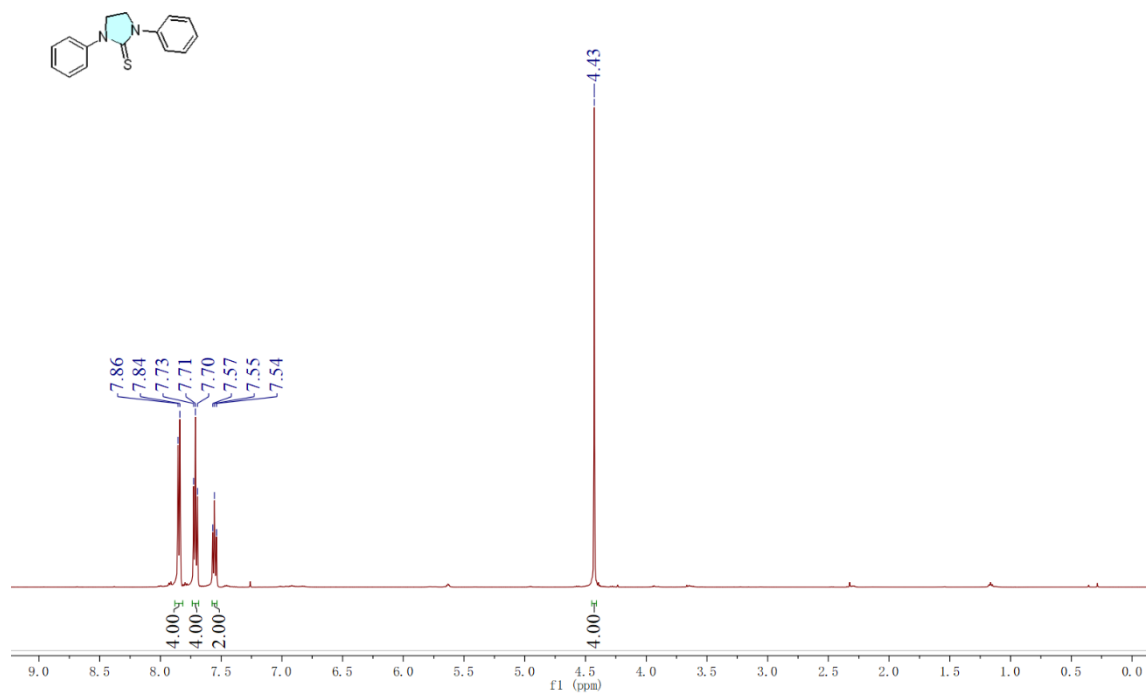
¹H-NMR spectrum of compound B44



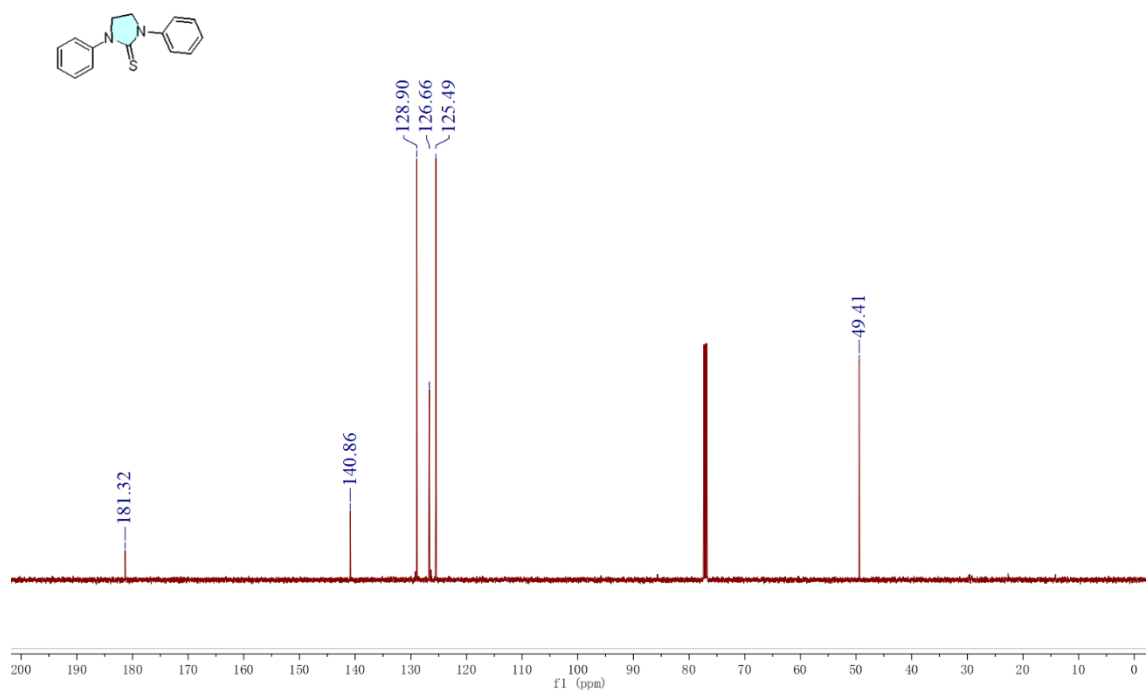
¹³C-NMR spectrum of compound B44



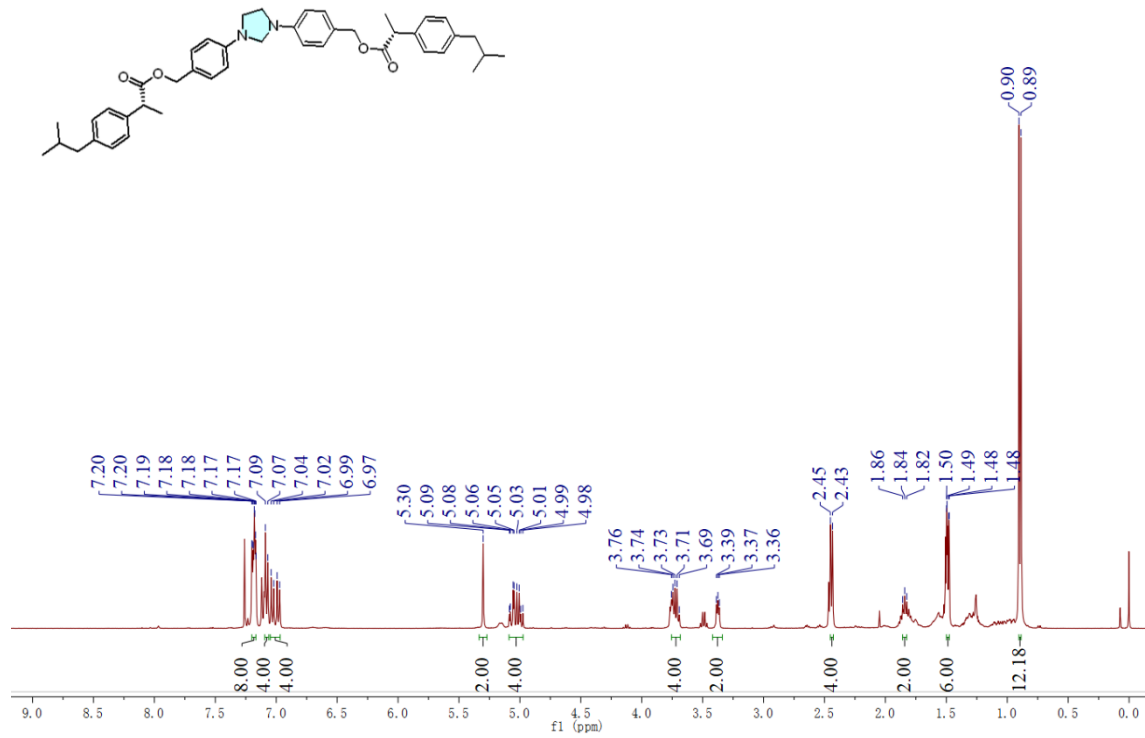
¹H-NMR spectrum of compound B45



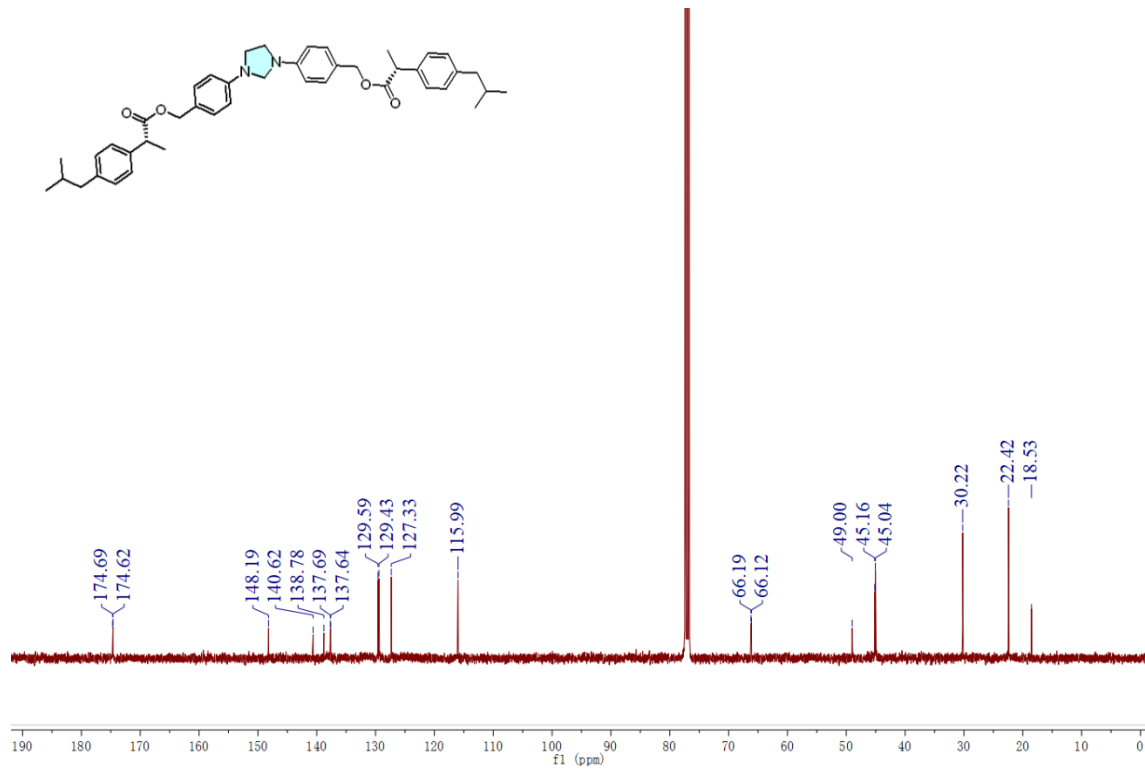
¹³C-NMR spectrum of compound B45



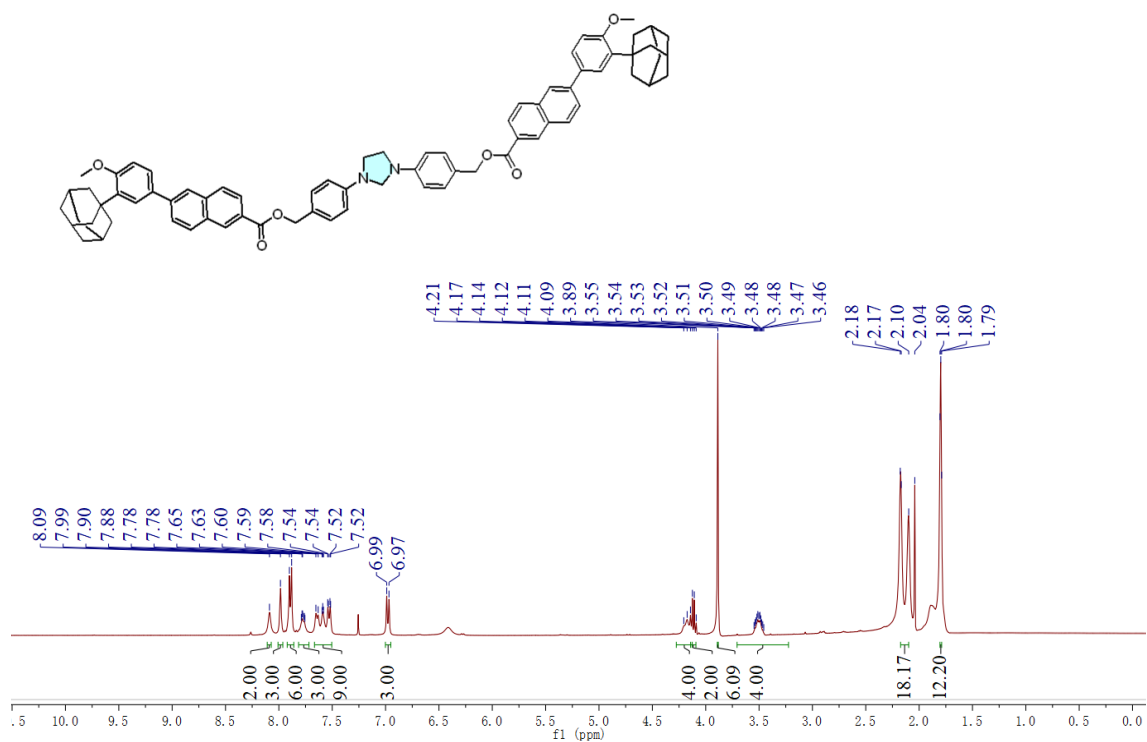
¹H-NMR spectrum of compound B46



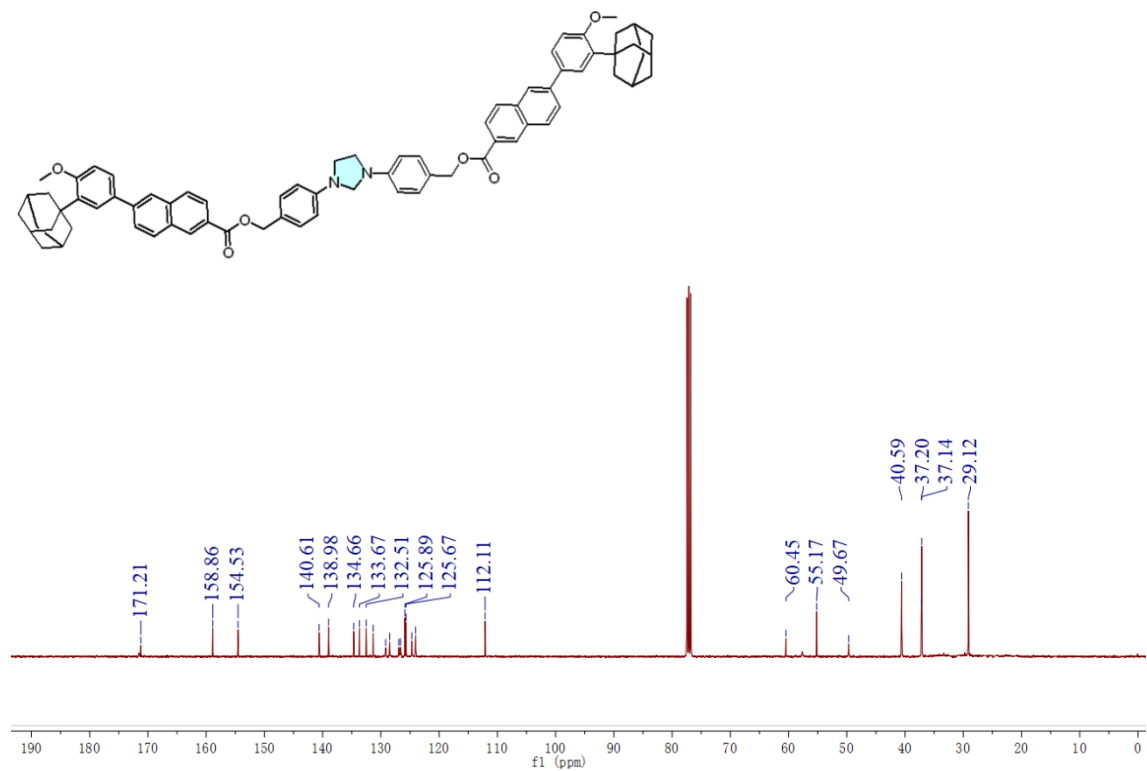
¹³C-NMR spectrum of compound B46



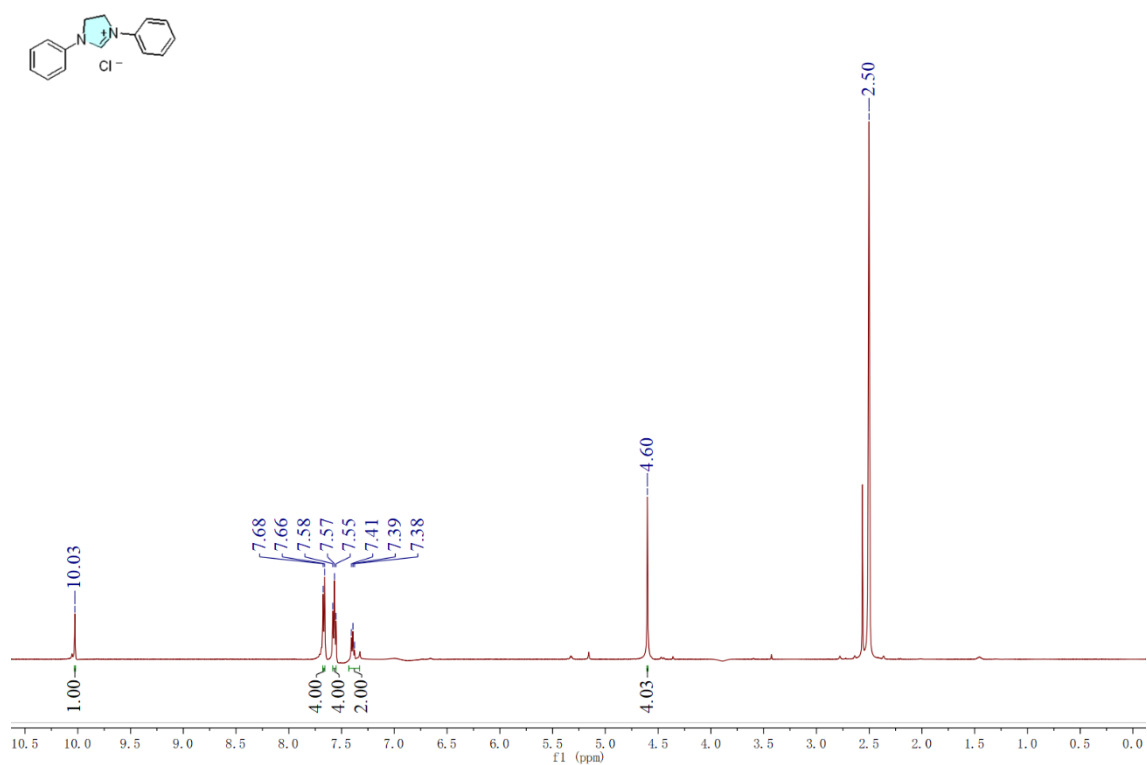
¹H-NMR spectrum of compound B47



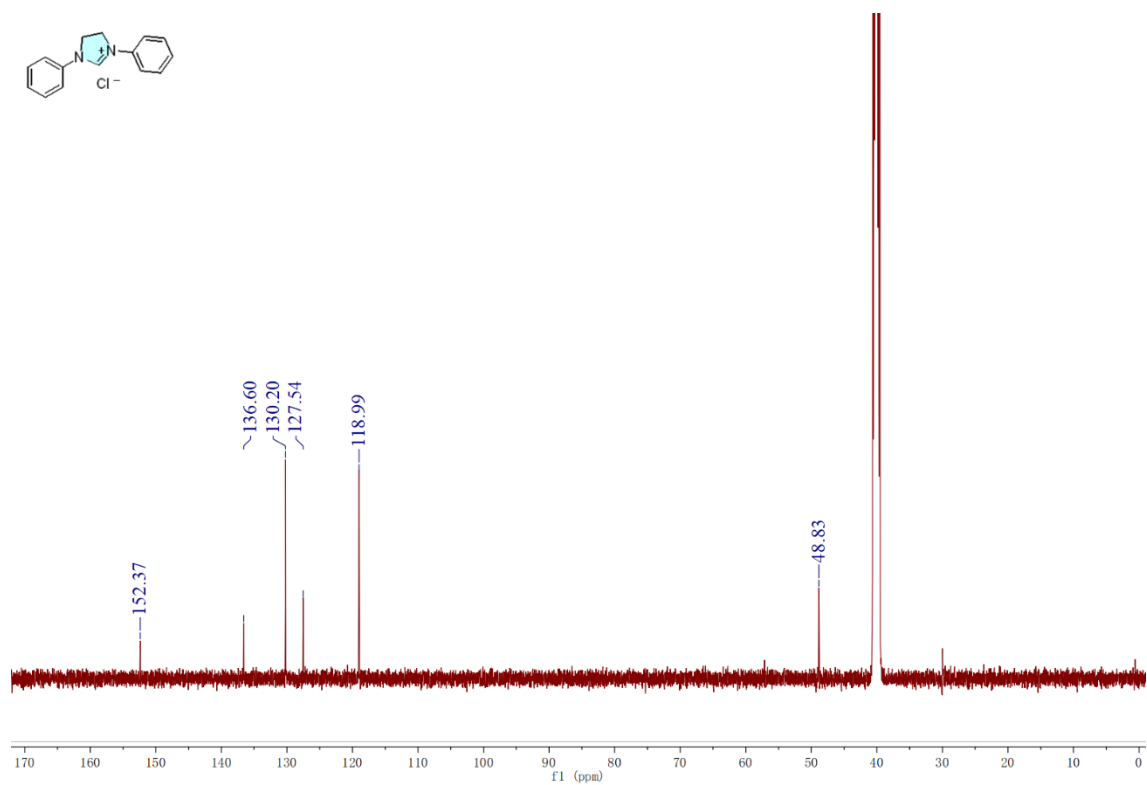
¹³C-NMR spectrum of compound B47



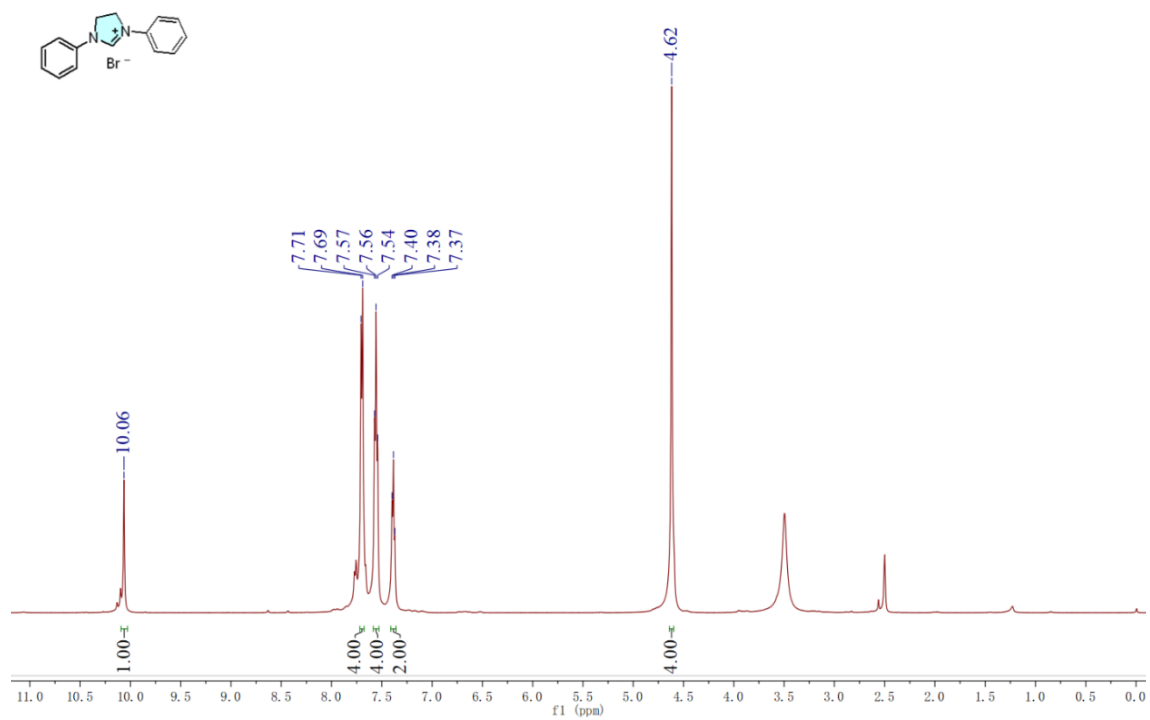
¹H-NMR spectrum of compound C1



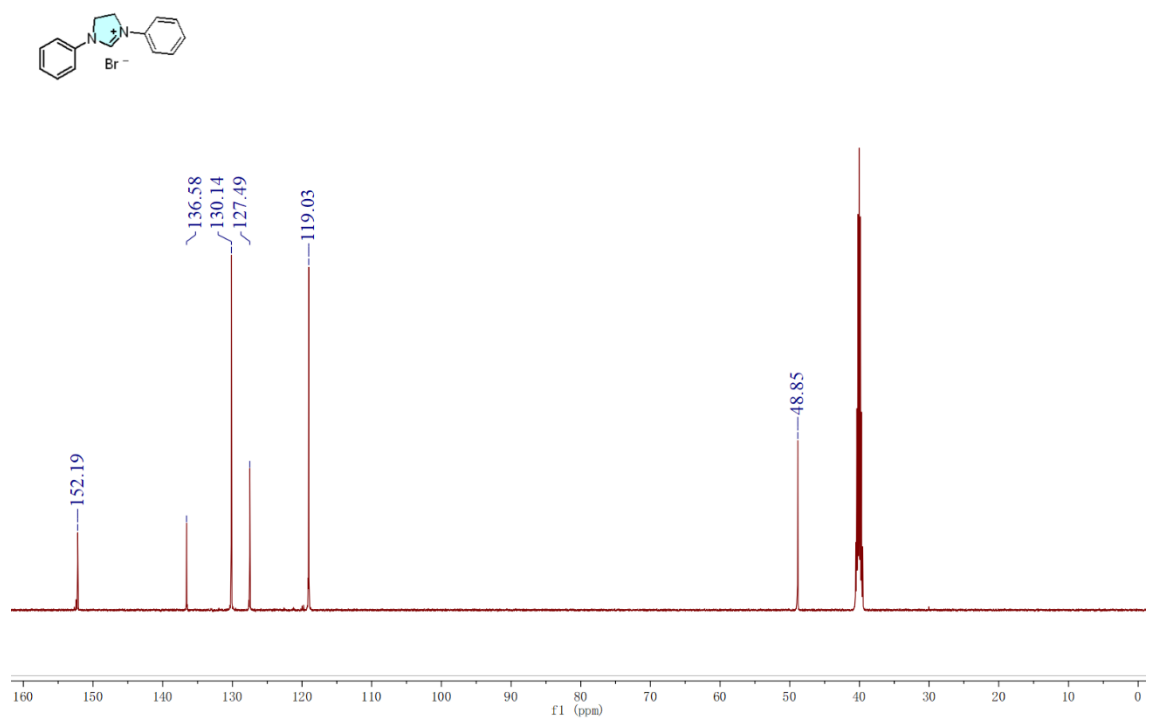
¹³C-NMR spectrum of compound C1



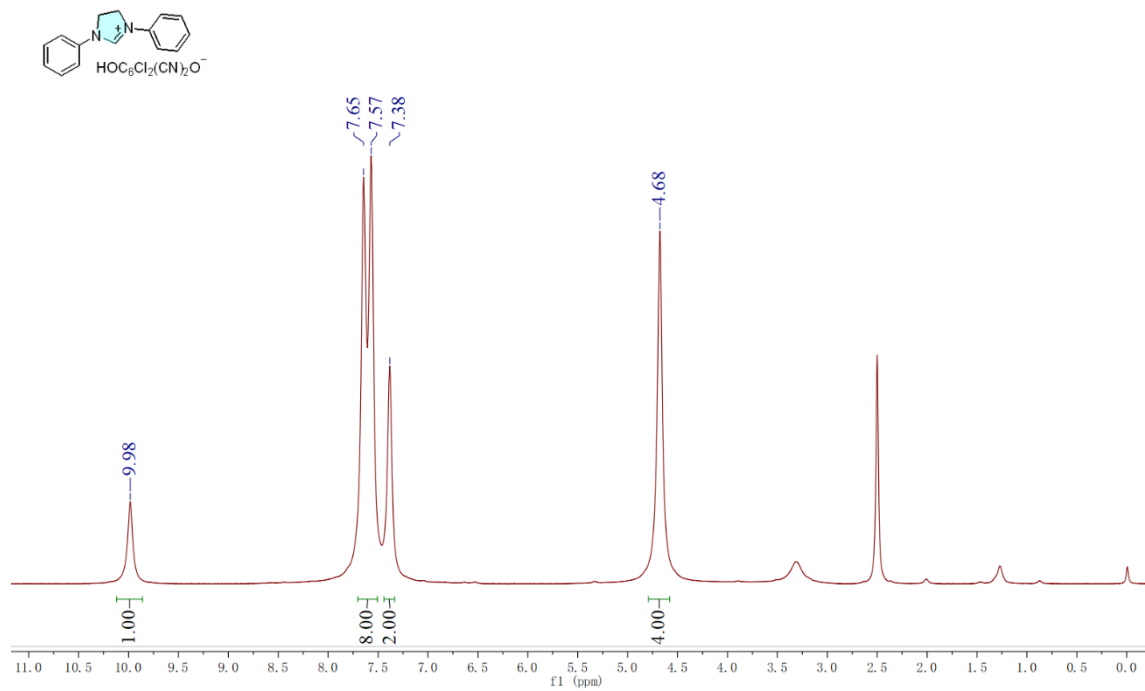
¹H-NMR spectrum of compound C2



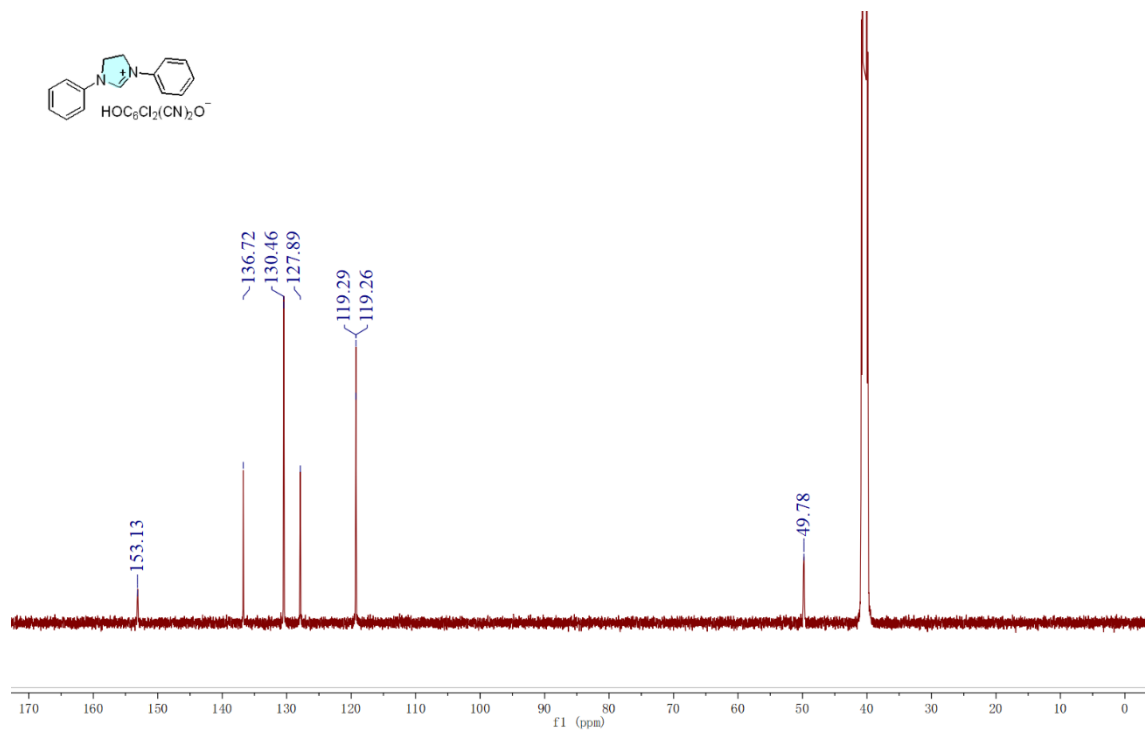
¹³C-NMR spectrum of compound C2



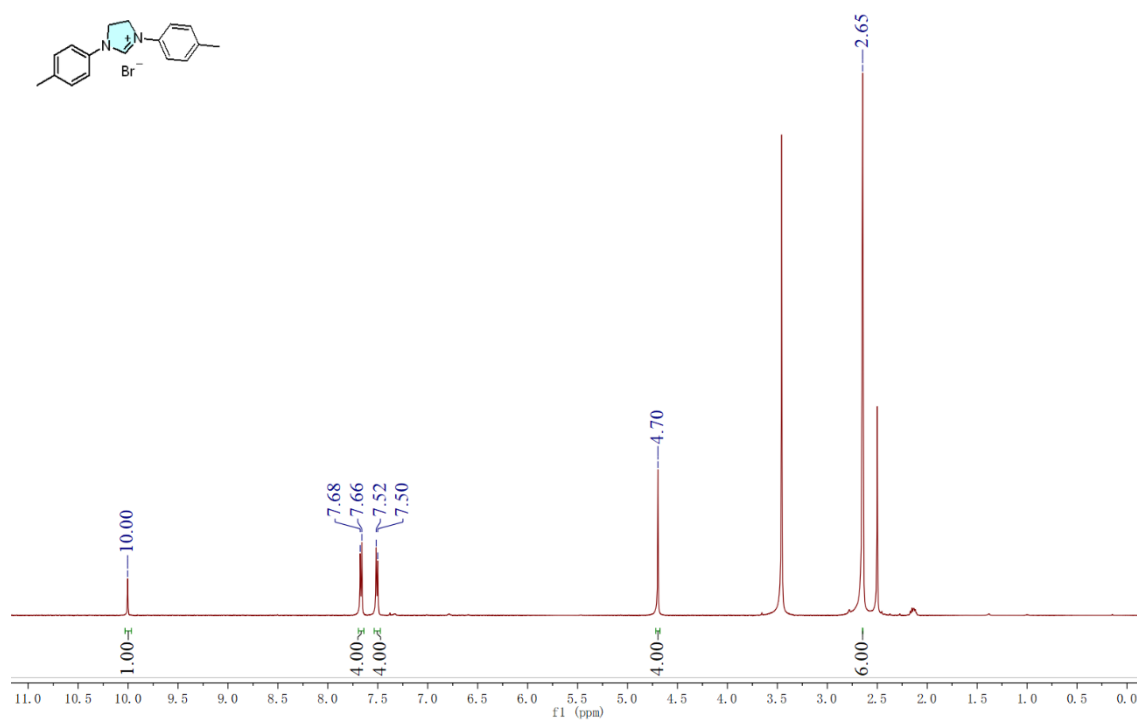
¹H-NMR spectrum of compound C3



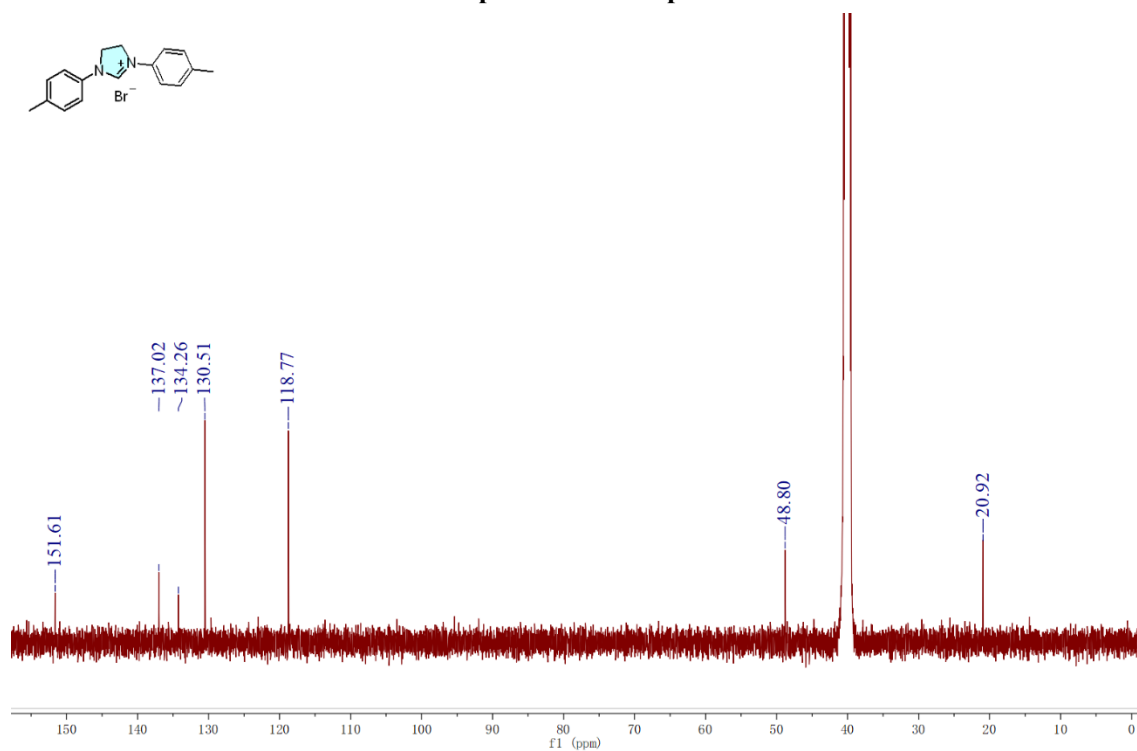
¹³C-NMR spectrum of compound C3



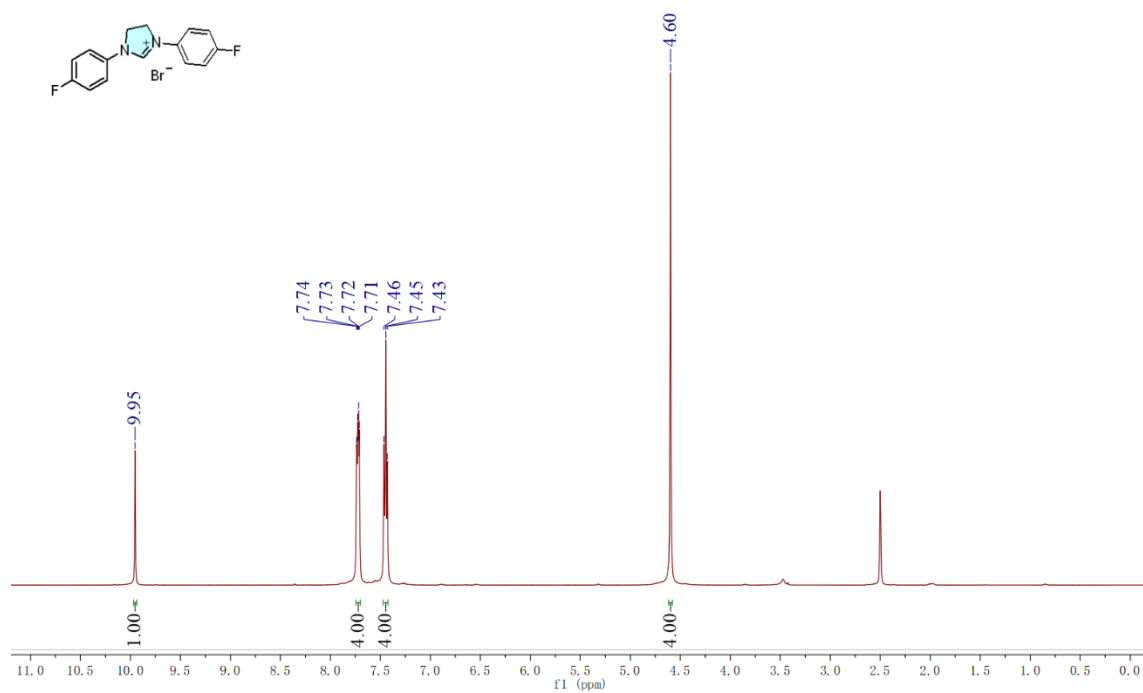
¹H-NMR spectrum of compound C4



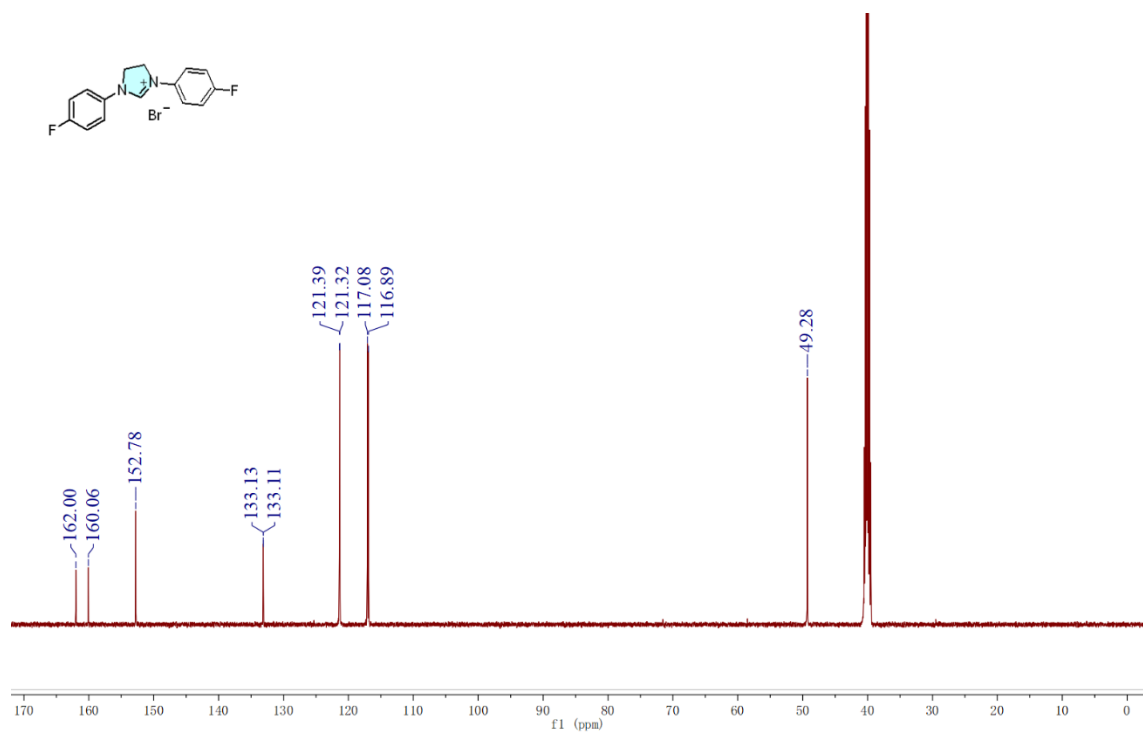
¹³C-NMR spectrum of compound C4



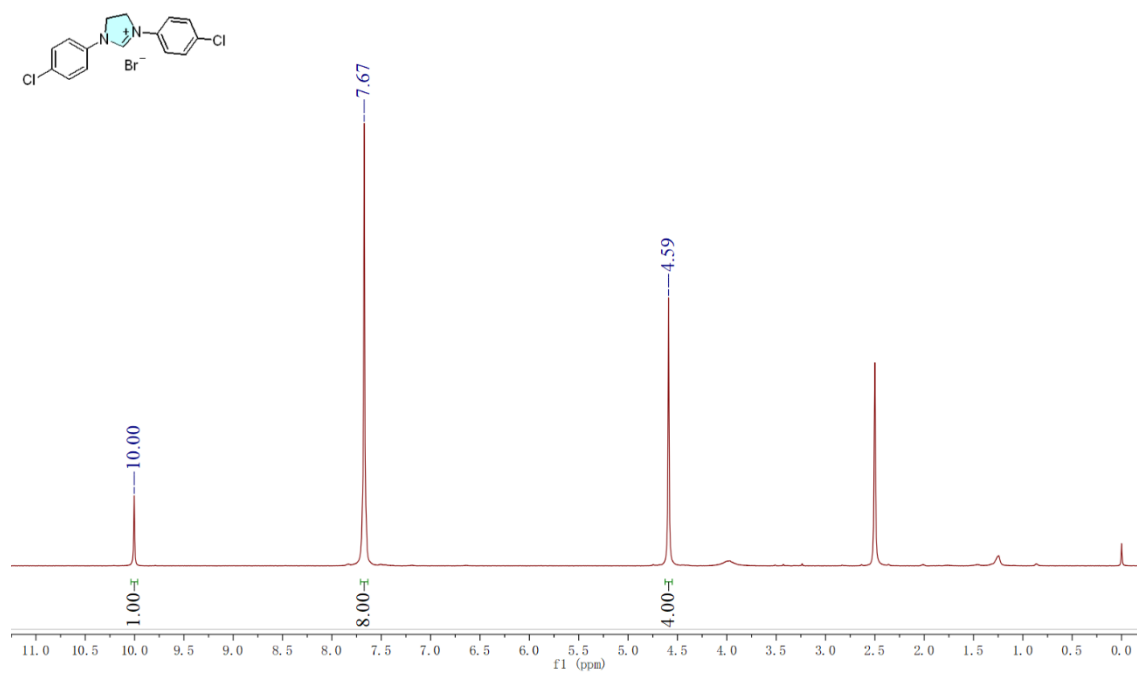
¹H-NMR spectrum of compound C5



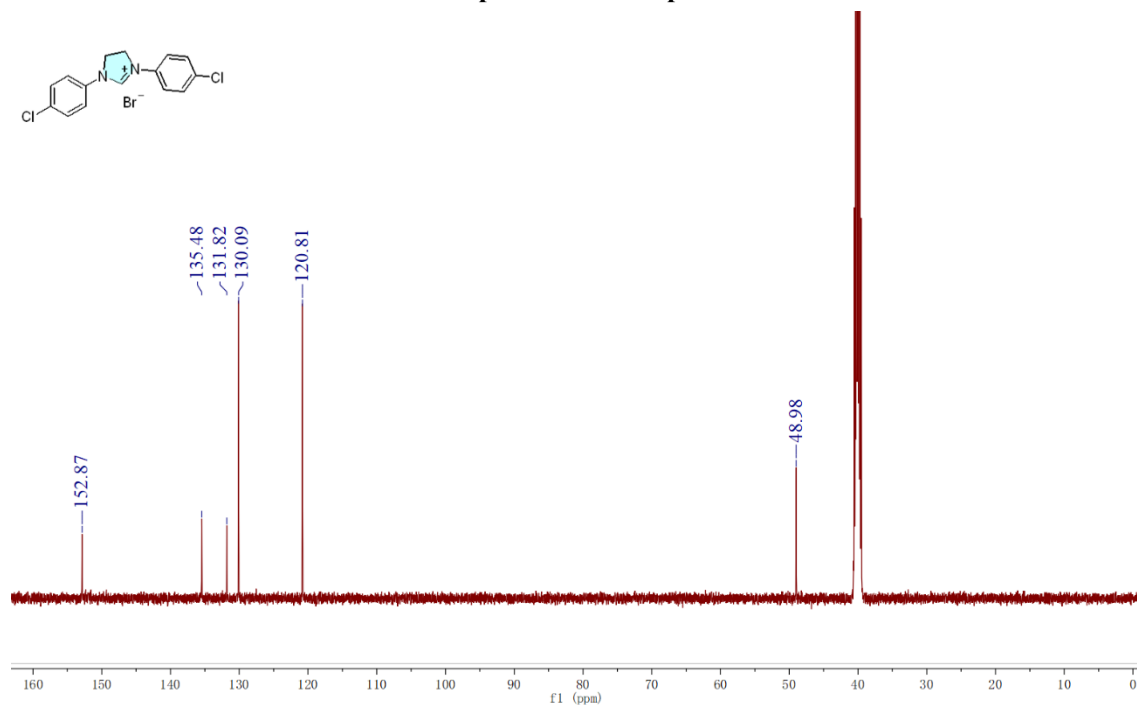
¹³C-NMR spectrum of compound C5



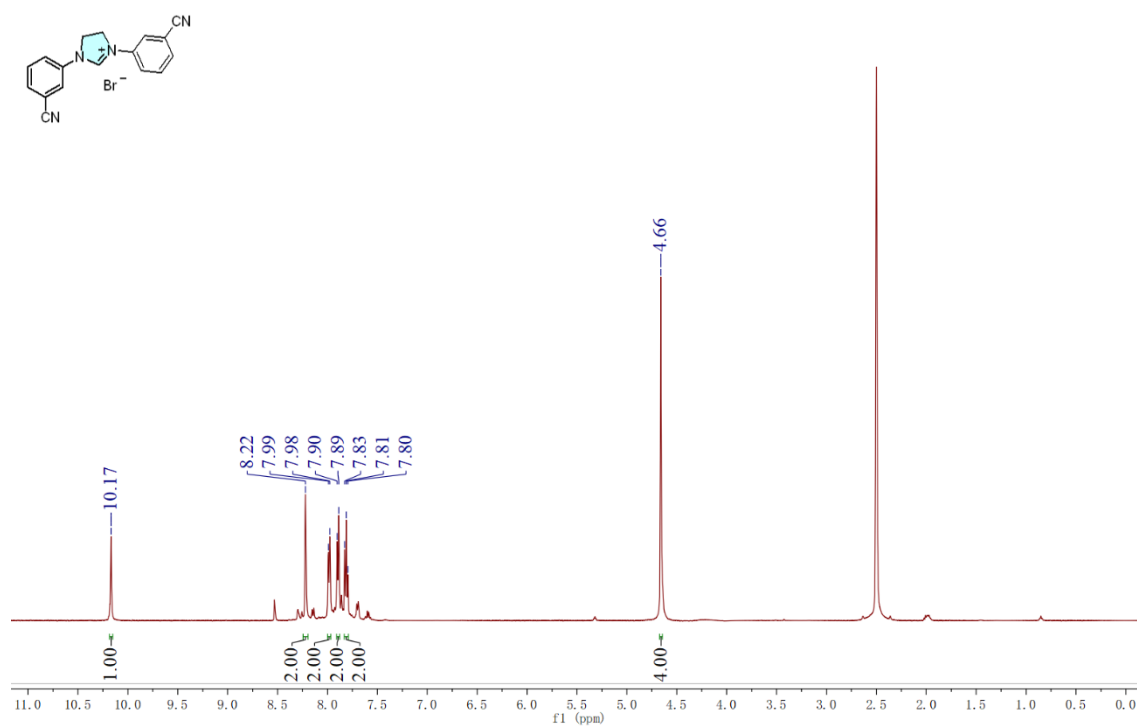
¹H-NMR spectrum of compound C6



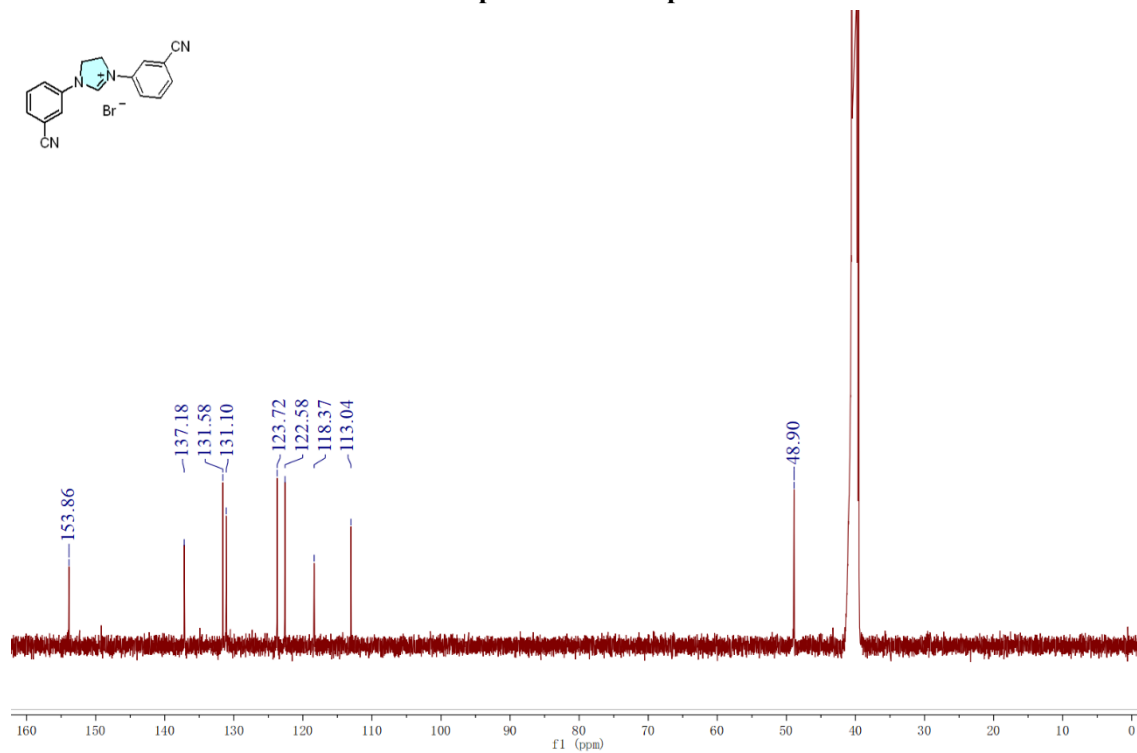
¹³C-NMR spectrum of compound C6



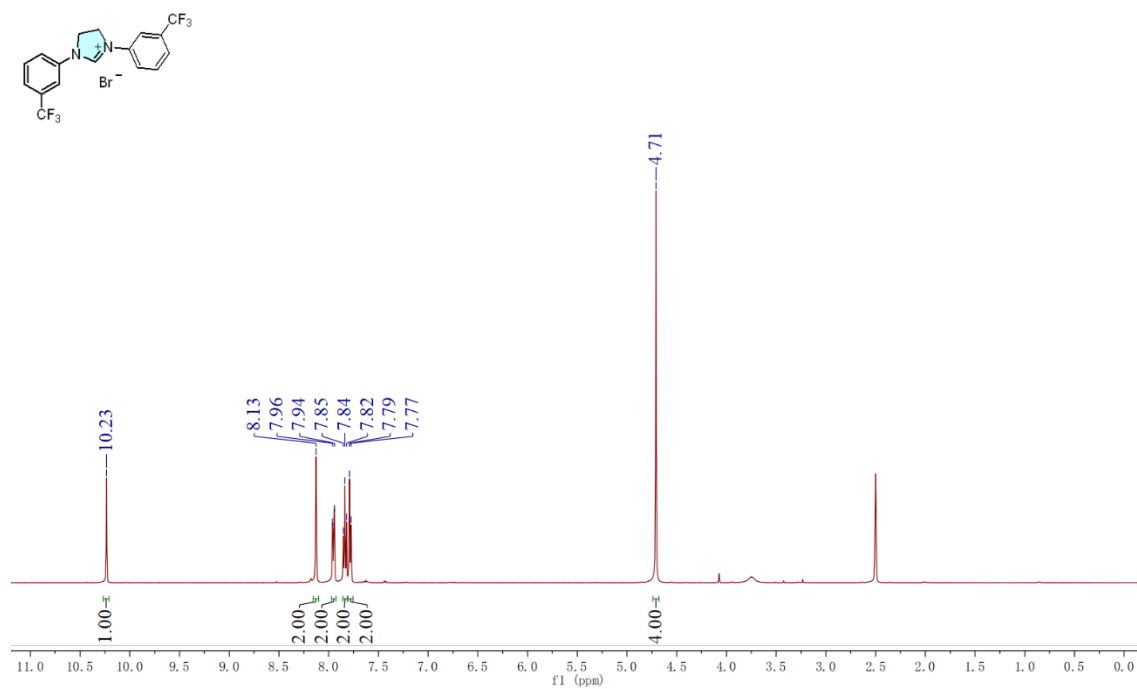
¹H-NMR spectrum of compound C7



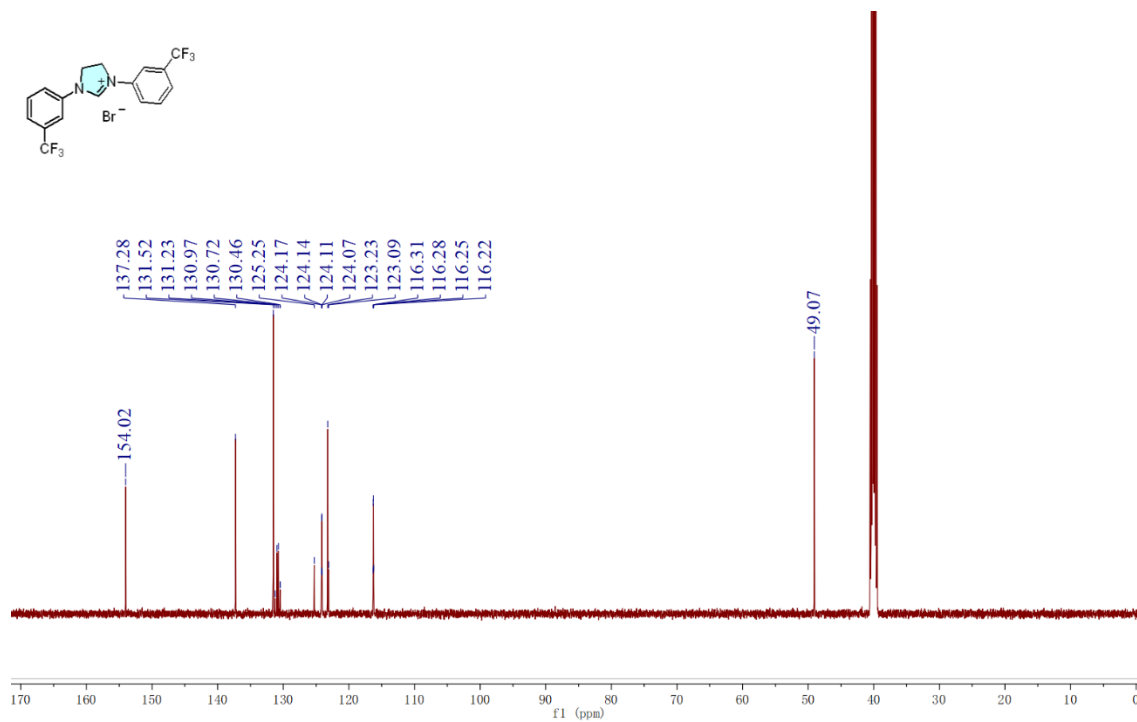
¹³C-NMR spectrum of compound C7



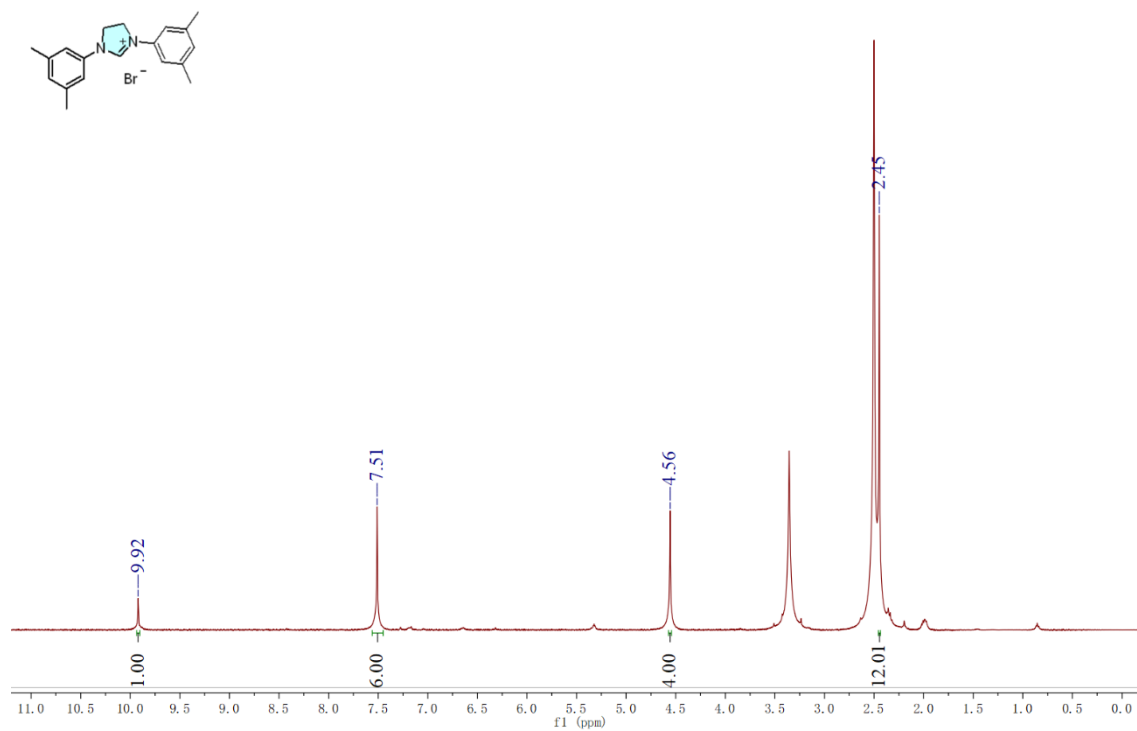
¹H-NMR spectrum of compound C8



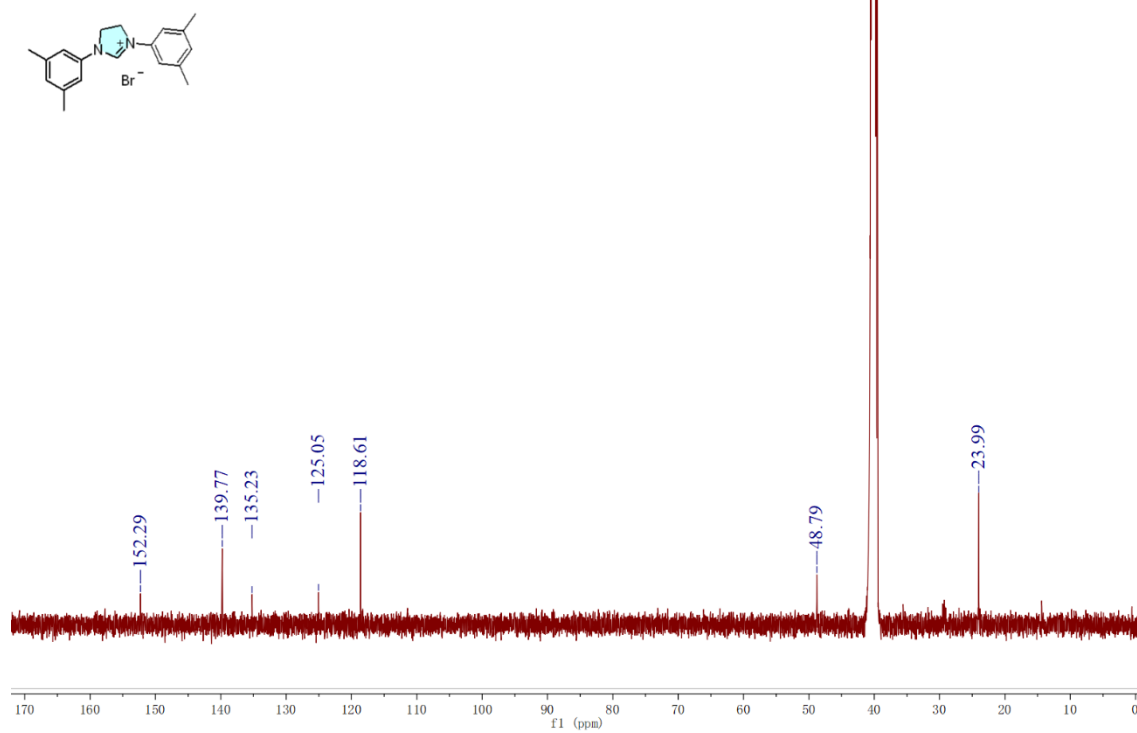
¹³C-NMR spectrum of compound C8



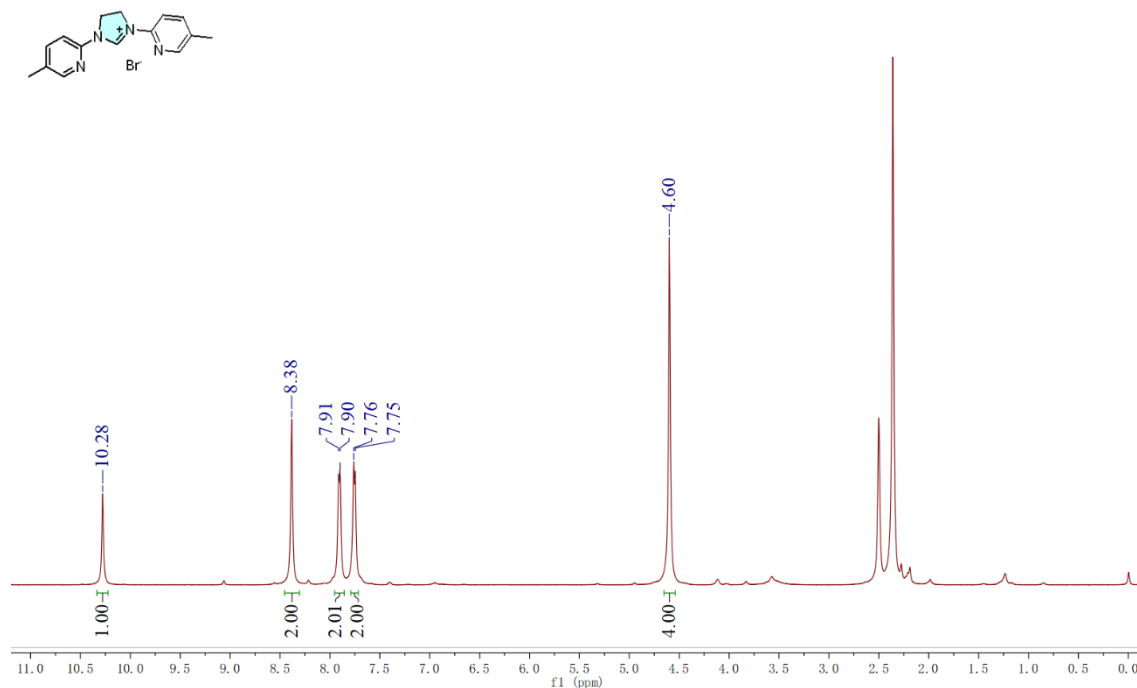
¹H-NMR spectrum of compound C9



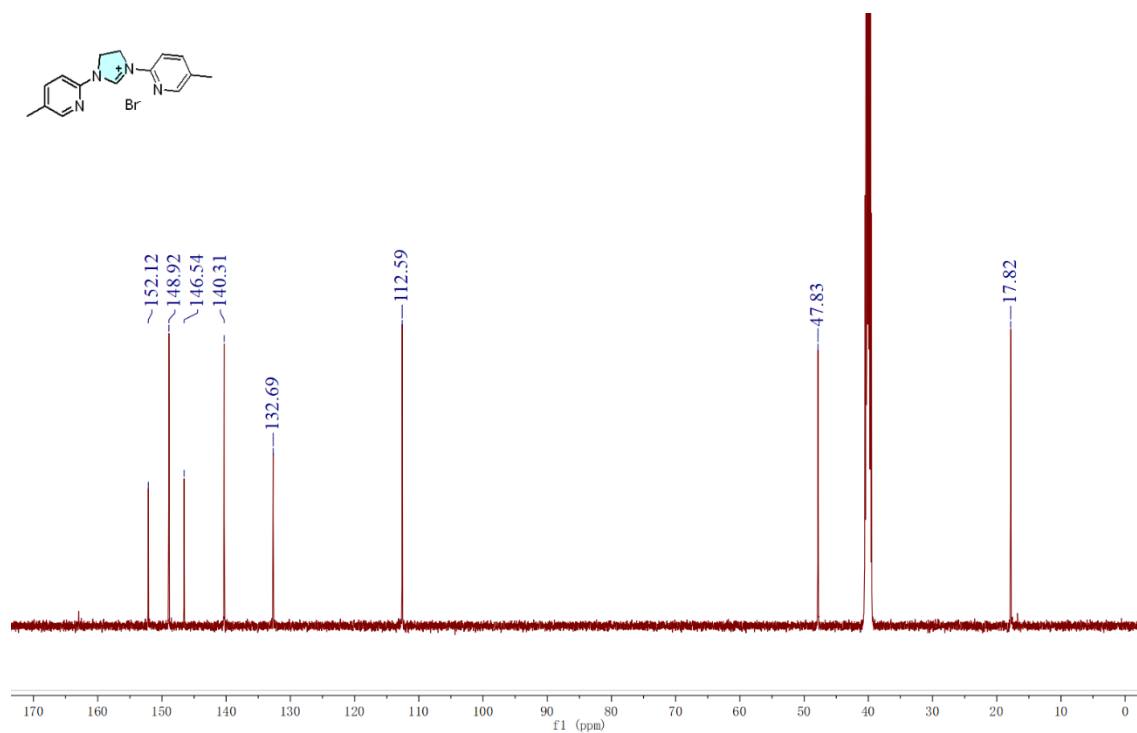
¹³C-NMR spectrum of compound C9



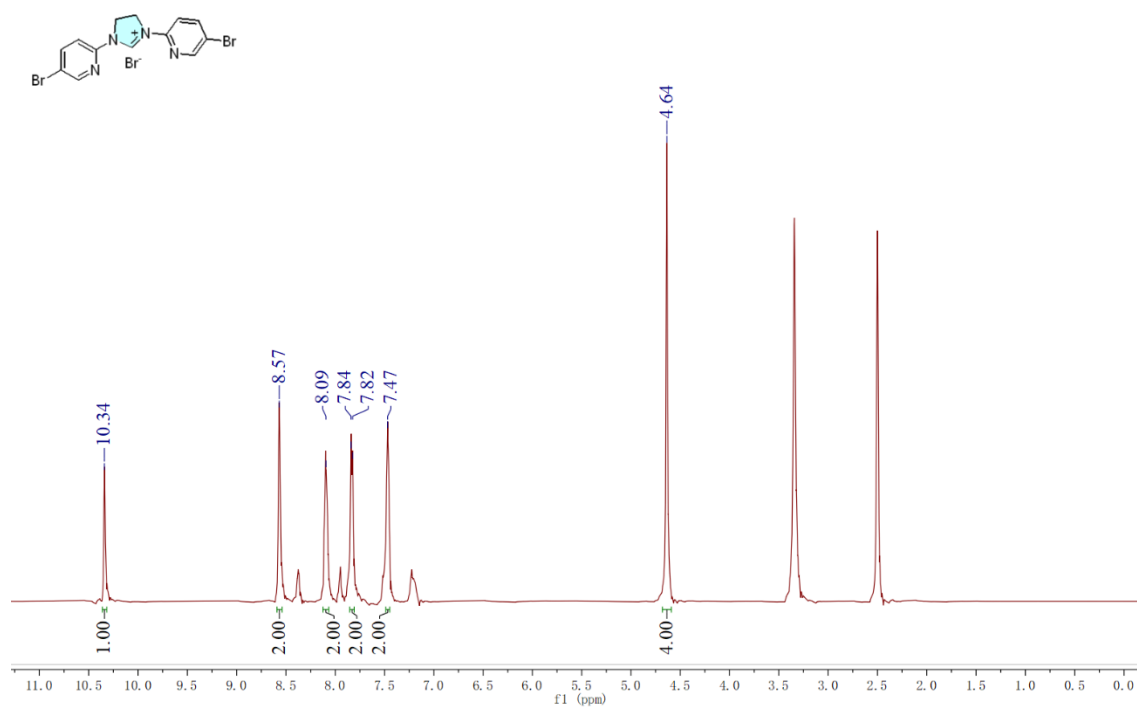
¹H-NMR spectrum of compound C10



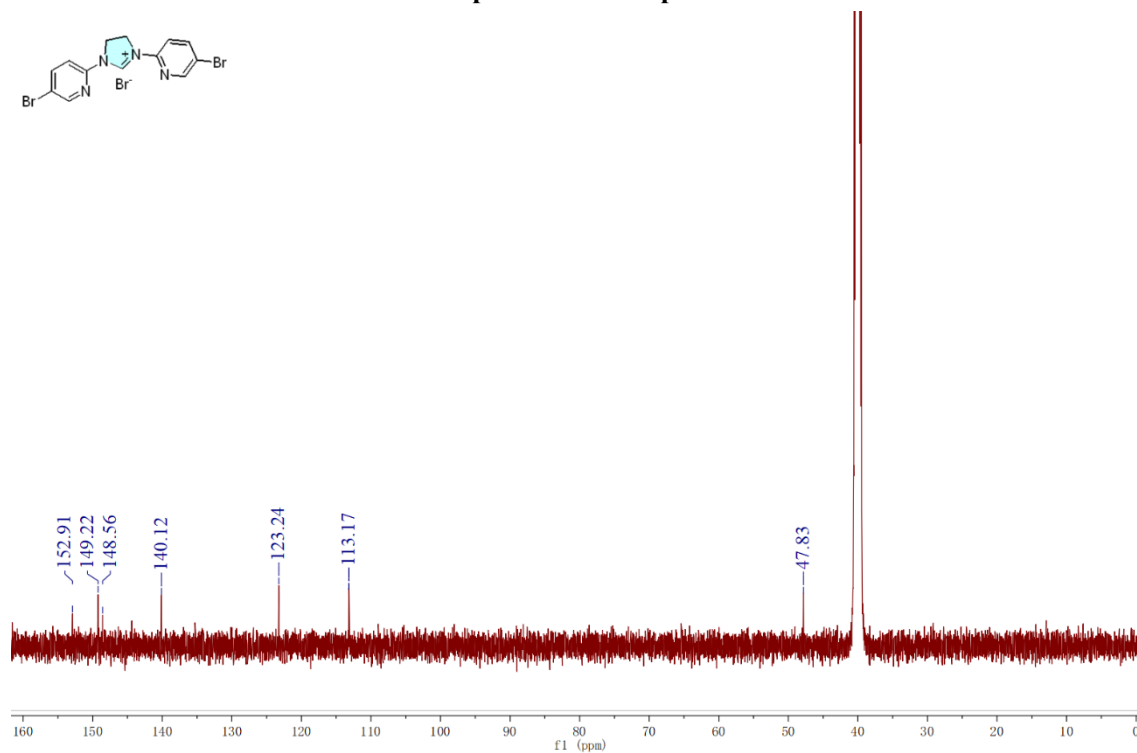
¹³C-NMR spectrum of compound C10



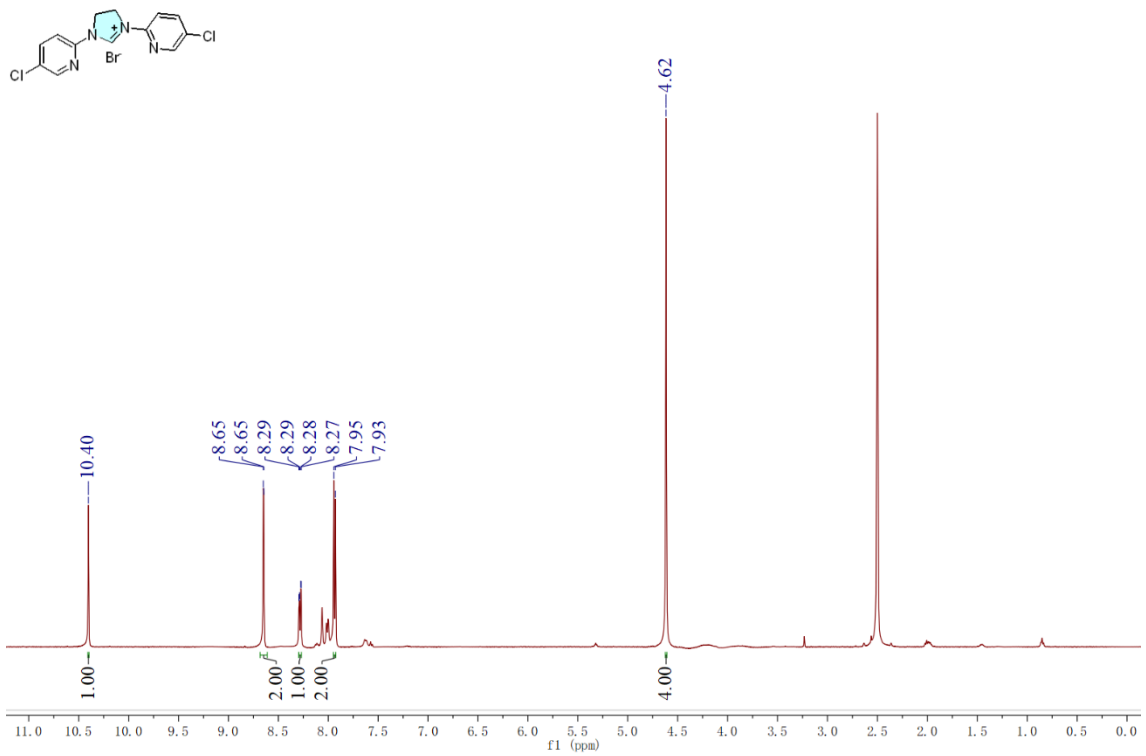
¹H-NMR spectrum of compound C11



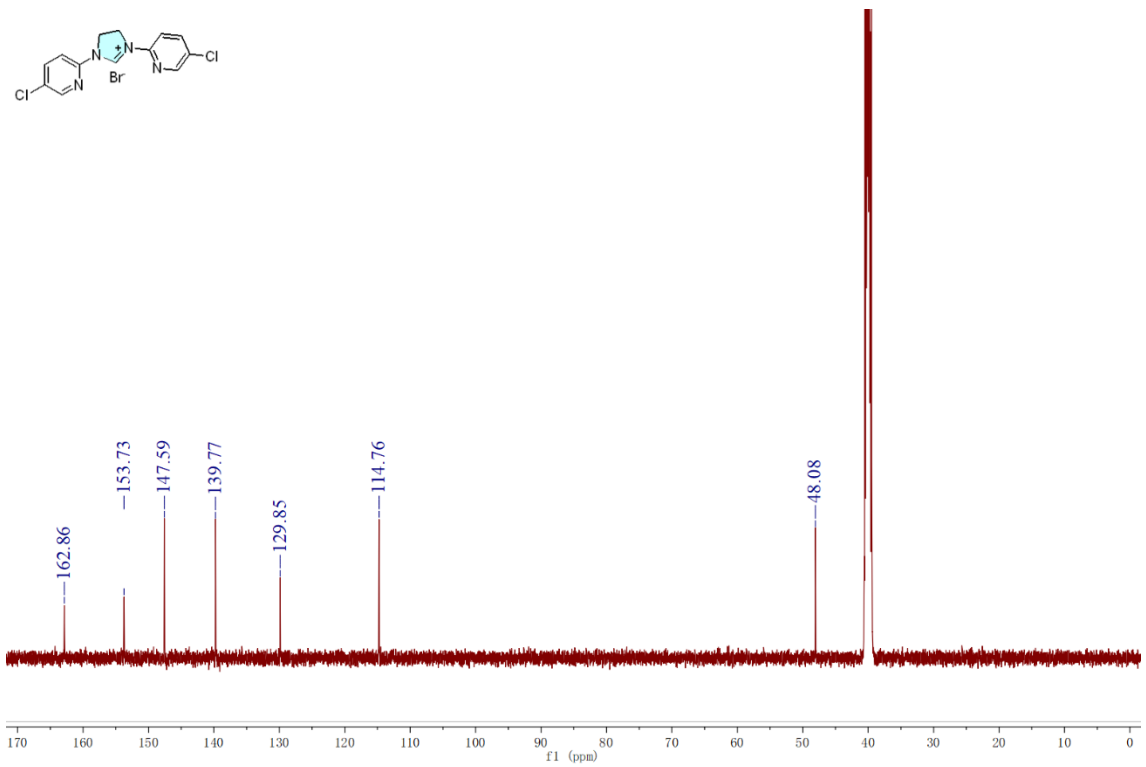
¹³C-NMR spectrum of compound C11



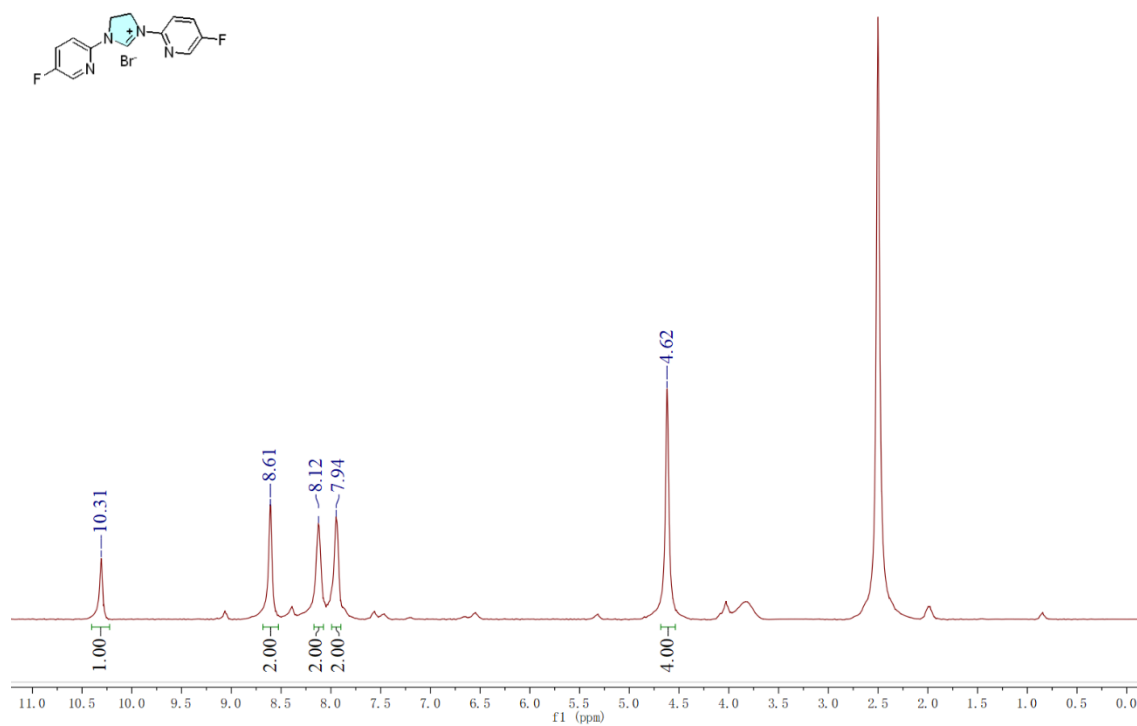
¹H-NMR spectrum of compound C12



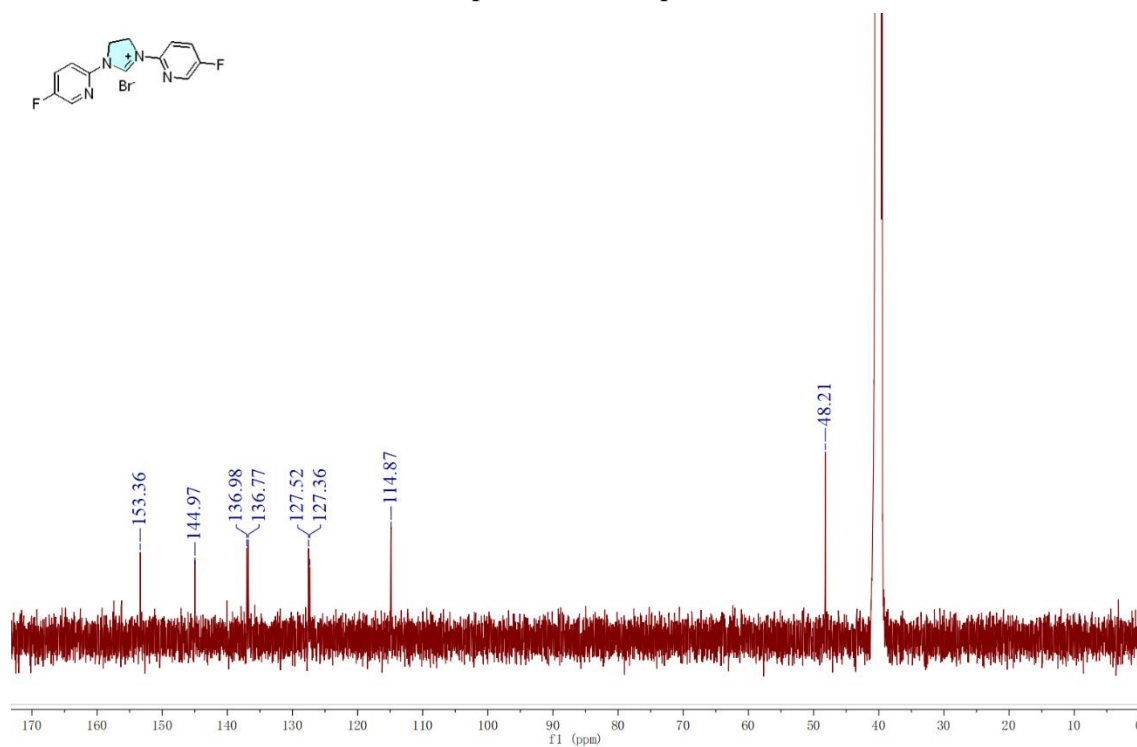
¹³C-NMR spectrum of compound C12



¹H-NMR spectrum of compound C13



¹³C-NMR spectrum of compound C13



9. Cartesian Coordinates and Absolute Energies for All Species

int-3

G+ZPE = -401.19131

C	-4.39961500	0.10690000	0.26433700
C	-3.04646800	-0.11784200	0.51715200
C	-2.09978200	0.83423800	0.16110900
C	-2.54437600	2.00817400	-0.44235500
C	-3.88746900	2.25031100	-0.71844400
C	-4.81787300	1.28497500	-0.35287700
H	-5.12982900	-0.64361100	0.54107900
H	-2.72543700	-1.03473600	0.99497100
H	-1.04745900	0.67808300	0.35468700
H	-4.19090200	3.15296300	-1.23367500
H	-5.86668800	1.44767600	-0.56642900
N	-1.57644900	3.01255000	-0.79361700
C	-1.71785200	4.27532400	-0.64566000
H	-2.59951000	4.62952600	-0.12991000
H	-0.96473600	4.95434300	-1.02813200
O	-0.45394000	2.46215300	-1.36002500
H	0.26188000	3.12002700	-1.27354000

int-4

G+ZPE = -400.783356

C	-4.40751900	0.10862200	0.27437700
C	-3.05184100	-0.12359000	0.50636300
C	-2.10550900	0.82688500	0.13926300
C	-2.53197700	2.01527800	-0.44368700
C	-3.87840900	2.25764900	-0.69604800
C	-4.81670200	1.29462600	-0.33146700
H	-5.14141200	-0.63750600	0.55534100
H	-2.72921900	-1.04758700	0.97134900
H	-1.04701200	0.66522100	0.28846600
H	-4.19034600	3.16789600	-1.19165800
H	-5.86665400	1.47015900	-0.53339900
N	-1.50462400	2.99028900	-0.81293500
C	-1.74507700	4.26574300	-0.68131400
H	-2.68052400	4.59224600	-0.25856700
H	-0.96936300	4.95063100	-0.98909900
O	-0.40219700	2.50446700	-1.23477500

int-5

G+ZPE = -325.599682

C	-4.34095400	0.08623600	0.31094200
C	-2.96163100	-0.08749200	0.43160800

C	-2.08882900	0.89040700	-0.03223700
C	-2.58820200	2.07195400	-0.59341800
C	-3.97315100	2.24001500	-0.72386600
C	-4.84082900	1.24725000	-0.27610900
H	-5.01952700	-0.68408600	0.65840200
H	-2.56505400	-0.99199400	0.87865700
H	-1.01519500	0.76197200	0.04018400
H	-4.36196100	3.13186000	-1.20135300
H	-5.91069000	1.38045100	-0.39135600
N	-1.65679200	3.02963000	-1.05542500
C	-1.87011000	4.26267200	-0.84131000
H	-2.72527300	4.64118300	-0.27043400
H	-1.16570300	4.99454100	-1.23326800

***L*-proline**

G+ZPE = -401.061837

H	-2.75045400	7.14224300	-2.53072100
N	-4.50706300	10.00043200	-0.97048700
C	-3.58430400	11.09536400	-1.30020200
C	-5.00490900	9.43141700	-2.22643700
H	-2.59162500	10.74020300	-1.61651600
H	-3.45318900	11.75650000	-0.44031200
C	-4.30035200	11.76602400	-2.47012000
C	-4.81826300	10.56851100	-3.28483600
H	-6.06020500	9.16268700	-2.13440200
C	-4.31318000	8.17186300	-2.72191700
H	-3.64660700	12.41553300	-3.05455400
H	-5.13617900	12.36213200	-2.09489400
H	-4.07849800	10.27141500	-4.03162200
H	-5.74955300	10.77600200	-3.81084400
O	-3.11824800	7.94857200	-2.13260200
H	-4.07606800	9.29725900	-0.38200100
O	-4.76597200	7.44082900	-3.57007500

***L*-proline⁻**

G+ZPE = -400.590614

N	-4.48847700	10.03660600	-0.91259900
C	-3.59233400	11.13719900	-1.30594300
C	-5.04501600	9.46471000	-2.16656200
H	-2.60307200	10.77628400	-1.63388900
H	-3.43512200	11.83660500	-0.47805400
C	-4.31828000	11.76776700	-2.49328700
C	-4.79910700	10.53062700	-3.26649100
H	-6.12185200	9.29453400	-2.04571500

C	-4.40422100	8.08694100	-2.52941600
H	-3.67911600	12.42885700	-3.08471700
H	-5.17227700	12.35074700	-2.13200400
H	-4.01777900	10.18328700	-3.94844900
H	-5.68891800	10.72279700	-3.86929000
O	-3.55227400	7.64231900	-1.71632600
H	-3.92790000	9.26917600	-0.53760500
O	-4.80994500	7.56805300	-3.59252100

int-5-int-3-L-proline

G+ZPE = -1127.859383

C	-0.10388500	1.94889000	0.40025600
C	1.35678700	2.37077200	0.23525900
N	-0.17465700	0.70936400	-0.42669100
C	1.75374600	1.91283900	-1.19010800
H	1.96223900	1.85900100	0.98520500
H	1.47061100	3.44313800	0.37654500
C	-1.09372000	3.01311800	-0.10441100
H	-0.36115200	1.69698400	1.43067000
C	0.60847100	0.99715500	-1.66190500
H	-1.12993600	0.45205000	-0.66504700
H	1.85810400	2.76210500	-1.86403500
H	2.70140500	1.37639800	-1.17446400
O	-2.38248900	2.74667000	0.10964600
O	-0.74681300	4.02303300	-0.66816200
H	0.95240100	0.06031800	-2.09678700
H	-0.03025200	1.50382600	-2.38869600
H	-2.53803800	1.87466700	0.58520500
N	-2.88521400	0.33710000	1.24643000
C	-2.91326400	0.12547500	2.49954200
C	-3.12387000	-0.71319000	0.32059300
H	-3.16832300	-0.84311500	2.93321200
H	-2.68519900	0.94707000	3.17407400
C	-3.81318500	-0.39771400	-0.85564100
C	-2.61997700	-2.00478500	0.51181100
C	-4.03327400	-1.38170400	-1.81407800
H	-4.18115200	0.61105300	-1.00097800
C	-2.83212400	-2.97765900	-0.45976600
H	-2.03117500	-2.22819800	1.39198700
C	-3.54353800	-2.67255000	-1.61948100
H	-4.58109500	-1.13730800	-2.71646500
H	-2.43178200	-3.97430100	-0.31453800
O	0.45464000	-1.15094400	1.11643800
H	-3.70382200	-3.43372300	-2.37378800

N	1.72679300	-1.11295400	1.55644300
H	0.27407000	-0.35489200	0.39084400
C	1.95497500	-1.19931900	2.81549500
C	2.76057900	-1.05183700	0.54850400
H	1.11187000	-1.19533400	3.49192700
H	2.97682100	-1.28889400	3.15336800
C	2.55044200	-1.72208600	-0.65277600
C	3.91940900	-0.32134100	0.79853700
C	3.54215800	-1.66505500	-1.62542300
H	1.63828700	-2.28005500	-0.81407500
C	4.90079600	-0.27701800	-0.18458200
H	4.04169600	0.22377400	1.72540700
C	4.71329500	-0.94543300	-1.39392200
H	3.39810700	-2.18562500	-2.56388500
H	5.80351500	0.29502500	-0.01067100
H	5.47871900	-0.89995500	-2.15908300

TS1

G+ZPE = -726.757302

C	-6.79838400	3.06892700	-0.22569800
C	-6.33163900	4.25170700	0.34798100
C	-5.01272400	4.64644900	0.17525400
C	-4.15768400	3.84376500	-0.59129200
C	-4.61061000	2.64129200	-1.15324600
C	-5.93370800	2.26753500	-0.97240500
H	-7.82828300	2.76619000	-0.08171800
H	-6.99862000	4.87299300	0.93273600
H	-4.64464800	5.56063700	0.61687500
H	-3.93482000	1.99615700	-1.69784900
H	-6.28648500	1.33807200	-1.40163700
N	-2.81898100	4.24018900	-0.78624900
C	-2.07604200	4.01918600	-1.90115300
H	-1.00284800	4.05357600	-1.73879800
H	-2.43987100	3.23333100	-2.55172400
C	-0.17612600	7.93541100	-1.19849300
C	-0.52004700	6.94189800	-2.14731900
C	0.48774800	6.42347800	-2.99797700
C	1.78438100	6.88932500	-2.88787200
C	2.10819800	7.87167400	-1.94398300
C	1.12465000	8.39369000	-1.10060900
H	-0.95832900	8.32357700	-0.55701200
H	0.25466000	5.67773800	-3.74551600
H	2.55384800	6.49609100	-3.54087100
H	3.12755700	8.23147100	-1.87214300

H	1.37908600	9.15475500	-0.37369500
N	-1.84044800	6.55837600	-2.15070200
C	-2.29105400	5.54191500	-2.91778000
H	-3.37154300	5.52459000	-3.03843200
H	-1.73007500	5.23053400	-3.79905100
O	-2.35886600	5.25442200	-0.01624600
H	-2.23008200	6.03518200	-0.68784800

TS2

G+ZPE = -1127.843606

C	4.48995100	-1.57345900	0.09378100
C	3.90391300	-1.23061400	-1.12448800
C	2.53751300	-1.38837700	-1.31200800
C	1.75977300	-1.90368100	-0.27131100
C	2.33594500	-2.25902300	0.95140400
C	3.70425900	-2.08480500	1.12572900
H	5.55556100	-1.44423600	0.23860700
H	4.51251000	-0.84399900	-1.93268500
H	2.06837400	-1.13679200	-2.25278000
H	1.73392300	-2.63546000	1.76697700
H	4.15488600	-2.34427500	2.07571000
N	0.35070600	-2.01768300	-0.49563100
C	-0.47862500	-2.76071600	0.27085900
H	-1.41306000	-2.98091500	-0.23003100
H	-0.02410900	-3.56215000	0.83704100
C	-3.26412000	0.92570900	-0.10056500
C	-2.83571500	-0.34028600	0.34616100
C	-3.69724700	-1.44011700	0.16264200
C	-4.92604200	-1.27268400	-0.46400600
C	-5.33288700	-0.01516400	-0.90906700
C	-4.49635400	1.08516200	-0.71610100
H	-2.62996400	1.78636600	0.07118900
H	-3.41894700	-2.42640400	0.50905200
H	-5.57336000	-2.13084300	-0.60294400
H	-6.29370000	0.10745500	-1.39440000
H	-4.80868800	2.07001200	-1.04355600
N	-1.57154800	-0.41114900	0.92980200
C	-1.14957800	-1.52984100	1.53668400
H	-0.27029200	-1.39499700	2.16151200
H	-1.87982900	-2.23313500	1.93912000
O	-0.20411000	-1.17736100	-1.28724900
H	-0.94065200	0.98431200	1.42783400
N	0.40055000	1.46878600	-0.86540400
C	1.19944300	2.05208100	-2.01108500

C	1.23710700	1.60137900	0.40926000
H	0.50930800	2.50524800	-2.71887200
H	1.72348600	1.22415500	-2.48497700
C	2.16182100	3.01082400	-1.32630000
C	2.54198300	2.25504800	-0.04852600
H	1.39175700	0.59559400	0.79764300
C	0.46086200	2.41201400	1.46354900
H	1.65725800	3.94911700	-1.08254200
H	3.02059900	3.23597800	-1.95791700
H	2.93223200	2.90498800	0.73108000
H	3.27692300	1.48023200	-0.26922600
O	0.88893100	3.44197100	1.92367200
H	0.15423900	0.46892300	-1.03823900
O	-0.70060600	1.89864600	1.83789100
H	-0.48214300	1.97438900	-0.78315800

TS3

G+ZPE = -1127.841618

C	4.42593400	-1.78937400	-0.13448600
C	3.76641100	-1.30989600	-1.26760600
C	2.38542300	-1.38703100	-1.35669900
C	1.65723400	-1.94945300	-0.29847300
C	2.31176700	-2.44753700	0.83684000
C	3.69552400	-2.35604300	0.90978200
H	5.50520500	-1.72786100	-0.06873200
H	4.33185300	-0.88437100	-2.08739100
H	1.86276900	-1.03439900	-2.23474300
H	1.76225500	-2.87629700	1.66260700
H	4.20475000	-2.72590300	1.79104000
N	0.24680600	-1.97110300	-0.41192800
C	-0.62934500	-2.58962200	0.50628700
H	-1.51668600	-2.91513600	-0.03434200
H	-0.17202700	-3.40461500	1.05609800
C	-3.23010800	0.94711500	-0.36359800
C	-2.83659500	-0.24827000	0.28210800
C	-3.74476400	-1.33040300	0.29990500
C	-4.98233900	-1.21532100	-0.31914800
C	-5.35075800	-0.03405500	-0.96245300
C	-4.46692000	1.04940300	-0.97415400
H	-2.55344800	1.79191200	-0.35853100
H	-3.50236600	-2.24676700	0.82079600
H	-5.66983700	-2.05274500	-0.29169000
H	-6.31976800	0.04772600	-1.43965000
H	-4.75071100	1.97520100	-1.46075100

N	-1.57753500	-0.27828200	0.83567800
C	-1.10433200	-1.41165300	1.51374900
H	-0.24336800	-1.14463000	2.12675500
H	-1.85285400	-1.91282300	2.13314800
O	-0.33717300	-1.11416000	-1.14429700
H	-1.04706400	0.89830300	1.21261300
N	0.50751100	1.59658700	-0.84702100
C	1.36917700	2.18287200	-1.94182100
C	1.32571100	1.59865900	0.44836500
H	0.72437000	2.67727800	-2.66498200
H	1.88973900	1.35290100	-2.41712400
C	2.32512800	3.09024800	-1.18189400
C	2.64797700	2.27239600	0.07419100
H	1.46609700	0.55860600	0.73950300
C	0.51894100	2.29558100	1.56569900
H	1.82634300	4.02558500	-0.91420500
H	3.20800000	3.32830300	-1.77433000
H	2.99761700	2.88322800	0.90335900
H	3.39787900	1.51229200	-0.15074400
O	1.04055400	3.13783200	2.26665800
H	0.18167100	0.64192000	-1.07198500
O	-0.72152600	1.90407000	1.67729900
H	-0.32713800	2.17423600	-0.73067100

TS3'

G+ZPE = -1127.862254

C	3.58241100	-2.52735900	-0.59683000
C	2.89844500	-1.99650200	-1.69465600
C	1.53435100	-1.77676900	-1.62518400
C	0.84883200	-2.10421900	-0.44518400
C	1.52512900	-2.63492400	0.66148400
C	2.89510100	-2.83682300	0.57638700
H	4.64994400	-2.70051800	-0.65766300
H	3.43288200	-1.76212200	-2.60694200
H	0.98631700	-1.37011700	-2.46244900
H	1.00717800	-2.86749000	1.57972400
H	3.42661700	-3.23559000	1.43085100
N	-0.54929100	-1.86955600	-0.41286900
C	-1.39599100	-2.18821700	0.69586600
H	-2.35816100	-2.49502200	0.29128000
H	-0.97317600	-2.94642700	1.34418700
C	-3.57783800	1.59647600	-0.54996100
C	-3.33806100	0.47092500	0.26247100
C	-4.41062600	-0.37404300	0.59905100

C	-5.68801800	-0.08823600	0.13048400
C	-5.92272200	1.02826600	-0.66991200
C	-4.85703100	1.86804900	-1.00564300
H	-2.74741600	2.24294400	-0.81261600
H	-4.25406600	-1.24398300	1.22353500
H	-6.50753500	-0.74579600	0.39622300
H	-6.92191700	1.24350500	-1.02835200
H	-5.02787400	2.73889700	-1.62773000
N	-2.04782800	0.23740100	0.69028600
C	-1.61577500	-0.82400500	1.51049000
H	-0.66987700	-0.54935400	1.97464900
H	-2.34594200	-1.08436400	2.27649800
O	-1.08083800	-1.17212800	-1.28480100
H	-1.31310300	0.86761200	0.37478400
N	2.67924500	1.59483800	-0.99218800
C	3.23353500	2.97477000	-1.11260700
C	2.93543300	1.08672100	0.39107200
H	2.59267400	3.57591700	-1.75735900
H	4.23437800	2.92916300	-1.54840900
C	3.29117300	3.46643500	0.33372700
C	3.70354500	2.20692100	1.10850200
H	3.46526600	0.13650600	0.38265300
C	1.52265600	0.85643300	0.97064800
H	2.30410400	3.80873200	0.65710400
H	3.99292500	4.29134000	0.45666300
H	3.45863300	2.24476700	2.16946000
H	4.77791900	2.03502000	1.01003900
O	1.32864700	0.42684700	2.09239900
H	3.02403300	0.96702300	-1.71119800
O	0.60687500	1.17841000	0.08833800
H	1.36654800	1.49215800	-0.76025400

int-6'-L-proline

G+ZPE = -1127.857426

C	-4.41542500	-1.78862000	0.07579800
C	-3.75919700	-1.44037100	1.25686800
C	-2.37691400	-1.51690000	1.33714700
C	-1.64344000	-1.94673800	0.22273300
C	-2.29488800	-2.31096700	-0.96356700
C	-3.67978500	-2.22284200	-1.02677300
H	-5.49512500	-1.72755200	0.01642700
H	-4.32695500	-1.11764600	2.12098900
H	-1.85731600	-1.26677600	2.25168200
H	-1.73951900	-2.63012500	-1.83410100

H	-4.18598400	-2.48937000	-1.94639000
N	-0.23330200	-1.97445700	0.33541800
C	0.64050600	-2.51918300	-0.62346000
H	1.53606700	-2.87044500	-0.11319900
H	0.18728000	-3.29969100	-1.22544400
C	3.28598200	0.92948300	0.43421500
C	2.85571900	-0.22054000	-0.27168000
C	3.74697100	-1.31690200	-0.36033100
C	4.99165600	-1.26172400	0.25165900
C	5.39056100	-0.12555500	0.95582500
C	4.53015900	0.97383200	1.03621900
H	2.62444600	1.78619100	0.48727900
H	3.48375900	-2.19932500	-0.92768600
H	5.66139700	-2.11025900	0.17254400
H	6.36505700	-0.09118800	1.42772500
H	4.83833100	1.86557900	1.56942900
N	1.59065700	-0.18632900	-0.80619600
C	1.10725700	-1.26644100	-1.55391700
H	0.23349600	-0.96071000	-2.13143000
H	1.84274000	-1.73041500	-2.21737200
O	0.34879700	-1.15596700	1.12492300
H	1.03466600	1.21022500	-1.22800700
N	-0.56118500	1.47633800	0.89598500
C	-1.49564700	2.01583200	1.96093000
C	-1.28416500	1.55059600	-0.45306500
H	-0.90531000	2.55784800	2.69585800
H	-1.97160200	1.15750200	2.43133100
C	-2.49411200	2.85520300	1.17583700
C	-2.68797700	2.04323200	-0.10890400
H	-1.28635300	0.54793600	-0.87884600
C	-0.50112500	2.48120200	-1.39971400
H	-2.07180700	3.83649000	0.94646600
H	-3.41944300	2.99913400	1.73260300
H	-3.09170700	2.63255800	-0.92880100
H	-3.34029200	1.18815000	0.07439000
O	-1.01040300	3.45019300	-1.90888600
H	-0.25883900	0.50154800	1.09034200
O	0.75904500	2.14226500	-1.60562000
H	0.29350000	2.03395800	0.87953100

int-6''-L-proline

G+ZPE = -1127.864741

C	3.58558100	-2.53129100	-0.59765200
C	2.89404800	-2.00917900	-1.69500400

C	1.52889200	-1.79231700	-1.61942400
C	0.85090800	-2.11441400	-0.43421900
C	1.53481600	-2.63458100	0.67140600
C	2.90499300	-2.83426300	0.58074200
H	4.65288300	-2.70415000	-0.66369900
H	3.42257800	-1.78270100	-2.61293800
H	0.97314900	-1.39386400	-2.45576800
H	1.02195100	-2.86186000	1.59342700
H	3.44158700	-3.22643000	1.43516900
N	-0.54992500	-1.89249400	-0.39575000
C	-1.38531300	-2.20639000	0.72005700
H	-2.34921900	-2.52053000	0.32568400
H	-0.95525400	-2.95547600	1.37395000
C	-3.53187300	1.59495100	-0.55983800
C	-3.30556300	0.46869400	0.25692800
C	-4.38997200	-0.36495000	0.58781900
C	-5.66177000	-0.06989500	0.11049400
C	-5.88162900	1.04666100	-0.69431000
C	-4.80596300	1.87621900	-1.02432400
H	-2.69434600	2.23350400	-0.81806200
H	-4.24373400	-1.23467800	1.21510800
H	-6.48868200	-0.71976100	0.37258700
H	-6.87652600	1.26994700	-1.05985600
H	-4.96546800	2.74745800	-1.64906100
N	-2.02241900	0.22258500	0.69168400
C	-1.61071400	-0.83353900	1.52594800
H	-0.66377300	-0.55812600	1.99110800
H	-2.35150600	-1.08910400	2.28327900
O	-1.09271100	-1.20497300	-1.26963500
H	-1.24924600	0.82660400	0.37884100
N	2.74474500	1.61332900	-1.01819300
C	3.32808800	3.00344900	-1.07507600
C	2.85078300	1.09408900	0.40339600
H	2.74875300	3.60319400	-1.77375800
H	4.35398600	2.91370100	-1.43040700
C	3.27570800	3.46863500	0.37682700
C	3.60876500	2.19220900	1.16001000
H	3.36432000	0.13651900	0.39847500
C	1.39870500	0.88313800	0.91083100
H	2.27178900	3.82183900	0.62522700
H	3.97983600	4.27982900	0.56053200
H	3.29299700	2.22414500	2.20131300
H	4.68394800	1.99901100	1.13033200
O	1.27577300	0.43793600	2.05643000

H	3.16585400	0.98294400	-1.69934700
O	0.49402400	1.18677900	0.07130900
H	1.70969000	1.62275900	-1.15881200

int-6

G+ZPE = -726.795126

C	-6.81689100	2.89033900	0.01524800
C	-6.20815100	3.82297900	0.86032600
C	-4.90040700	4.21307100	0.63823100
C	-4.19761400	3.66401500	-0.44765700
C	-4.79810800	2.71936500	-1.29621500
C	-6.11032000	2.34299700	-1.05597200
H	-7.84093200	2.58721200	0.19592800
H	-6.75801000	4.24328400	1.69270900
H	-4.41263700	4.93228400	1.28006100
H	-4.26334000	2.27350300	-2.12120900
H	-6.58176500	1.61581900	-1.70447600
N	-2.86372400	4.09396100	-0.65167500
C	-2.10332100	3.81618700	-1.83715600
H	-1.06276300	3.70389500	-1.54033800
H	-2.46034300	2.94824800	-2.37697400
C	-0.20167400	7.85626900	-1.23358000
C	-0.47126400	6.66457500	-1.93251000
C	0.59999300	5.89124300	-2.41159100
C	1.90719600	6.31085500	-2.19125600
C	2.17158600	7.49160600	-1.50051600
C	1.10654600	8.26122400	-1.02530900
H	-1.02822600	8.44934000	-0.85743800
H	0.42037800	4.97781200	-2.96260500
H	2.72535800	5.70783000	-2.56724900
H	3.19316800	7.81069100	-1.33435100
H	1.29970000	9.18134300	-0.48635600
N	-1.79072000	6.29214000	-2.12040200
C	-2.23464000	5.11279000	-2.75863600
H	-3.27828100	5.22337000	-3.04632800
H	-1.64233600	4.87428500	-3.64340700
O	-2.35879600	4.93954300	0.09417200
H	-2.49477500	6.92494700	-1.76778100

int-6-L-proline

G+ZPE = -1127.866887

C	3.57812500	-2.53414700	-0.59296100
C	2.89715000	-2.00358000	-1.69258200
C	1.53352600	-1.77970200	-1.62493200

C	0.84545500	-2.10799000	-0.44595300
C	1.51858100	-2.64359900	0.66087300
C	2.88848600	-2.84443800	0.57909100
H	4.64561600	-2.70796800	-0.65165800
H	3.43354000	-1.76968700	-2.60368400
H	0.98829400	-1.37070200	-2.46307300
H	0.99747500	-2.88064100	1.57624800
H	3.41826400	-3.24515900	1.43368800
N	-0.55163800	-1.86942700	-0.41292100
C	-1.40030500	-2.18814500	0.69568700
H	-2.36127800	-2.49734000	0.29012000
H	-0.97779600	-2.94558600	1.34494500
C	-3.57884400	1.60132700	-0.55139200
C	-3.34668000	0.47406700	0.26092500
C	-4.42036900	-0.36896000	0.59380700
C	-5.69549500	-0.07905100	0.12304400
C	-5.92431800	1.03908200	-0.67680500
C	-4.85591600	1.87660800	-1.00998700
H	-2.74552100	2.24562800	-0.81105600
H	-4.26472700	-1.23876400	1.21851500
H	-6.51796600	-0.73377400	0.38643300
H	-6.92211100	1.25761200	-1.03708600
H	-5.02355100	2.74820100	-1.63184200
N	-2.05986900	0.23681600	0.69366900
C	-1.62628400	-0.82696400	1.51027200
H	-0.68480500	-0.55156000	1.98160700
H	-2.35719800	-1.09140100	2.27417900
O	-1.08138500	-1.16903900	-1.28381200
H	-1.33521000	0.87984700	0.39223200
N	2.73577200	1.59187600	-1.01358000
C	3.27448200	2.97490000	-1.11355500
C	2.93476100	1.09344900	0.36918700
H	2.63900200	3.58201600	-1.76000700
H	4.28584000	2.96396000	-1.53237000
C	3.30269000	3.46525900	0.33553700
C	3.70073000	2.20382800	1.11213800
H	3.45967100	0.13876200	0.39152100
C	1.54629500	0.85754700	0.97497200
H	2.30864700	3.80438700	0.64236100
H	3.99963800	4.29156100	0.47749000
H	3.44943200	2.23747300	2.17188500
H	4.77412100	2.02328100	1.01895500
O	1.34205300	0.44130400	2.09132300
H	3.14299600	0.96862100	-1.70077600

O	0.56897000	1.16238200	0.11567600
H	1.10824800	1.44225900	-0.70848600

TS4

G+ZPE = -666.996943

C	-0.72719900	-0.98973700	-4.35909800
C	-1.40428400	-1.72195700	-3.38323100
C	-2.16079200	-1.06981900	-2.41617600
C	-2.23651300	0.31986000	-2.45171200
C	-1.55169500	1.07104400	-3.40410500
C	-0.79696700	0.40190600	-4.36387900
H	-0.13602500	-1.50408000	-5.10750000
H	-1.34313200	-2.80351100	-3.37403400
H	-2.68347400	-1.61551400	-1.64282300
H	-1.57887800	2.15221500	-3.35943100
H	-0.25222200	0.97293500	-5.10605800
N	-3.02342600	0.99355300	-1.45131400
C	-3.67592100	2.07601200	-1.67721000
H	-3.77625200	2.43561400	-2.68765800
H	-4.18448100	2.54479600	-0.84876300
O	-2.96566600	0.47491000	-0.20197500
H	-1.26739300	2.78495000	0.55276900
C	-1.67323700	4.55324200	-0.74588700
O	-1.38059600	4.09946700	0.40637700
H	-1.59483300	5.65829600	-0.82482300
O	-2.02511800	3.92315300	-1.75495600
O	-1.13057100	1.69990000	0.74152600
H	-2.04615800	1.03546200	0.29467000
H	-0.29884200	1.42796300	0.33445000

int-6'

G+ZPE = -726.342006

C	-6.65451400	3.63696400	-0.20260200
C	-5.93735300	4.76152500	0.20243700
C	-4.57709900	4.87107300	-0.07088900
C	-3.93039000	3.84420500	-0.76081400
C	-4.63901200	2.70725700	-1.16134100
C	-5.99838700	2.61155300	-0.88347600
H	-7.71310900	3.55677700	0.01460100
H	-6.43910500	5.56380200	0.73144400
H	-4.00834800	5.73841500	0.23216200
H	-4.12764900	1.89892400	-1.66953400
H	-6.54435400	1.72800500	-1.19364100
N	-2.52640100	3.92526400	-1.02503800

C	-2.07664700	3.76868200	-2.39247900
H	-1.01286800	3.53512400	-2.38611100
H	-2.63660200	3.01119600	-2.93472800
C	-0.47667200	7.76280700	-1.01871300
C	-0.68605500	6.70531500	-1.92199300
C	0.40968100	6.23862900	-2.67158700
C	1.66106000	6.82871000	-2.52972900
C	1.85421700	7.87681500	-1.63024200
C	0.77773000	8.33862200	-0.87117400
H	-1.32418500	8.11538300	-0.44291100
H	0.28965300	5.42316900	-3.37307500
H	2.49317900	6.46350300	-3.12144000
H	2.83275600	8.33046200	-1.52369100
H	0.91724400	9.15318300	-0.16940400
N	-1.98721700	6.19233300	-1.97379500
C	-2.30532800	5.21302500	-2.97877900
H	-3.35986200	5.30848800	-3.24363900
H	-1.70122600	5.31762200	-3.88075800
O	-1.89758200	4.96490300	-0.53446000

int-6'-HCOOH

G+ZPE = -916.135795

C	-6.65451400	3.63696400	-0.20260200
C	-5.93735300	4.76152500	0.20243700
C	-4.57709900	4.87107300	-0.07088900
C	-3.93039000	3.84420500	-0.76081400
C	-4.63901200	2.70725700	-1.16134100
C	-5.99838700	2.61155300	-0.88347600
H	-7.71310900	3.55677700	0.01460100
H	-6.43910500	5.56380200	0.73144400
H	-4.00834800	5.73841500	0.23216200
H	-4.12764900	1.89892400	-1.66953400
H	-6.54435400	1.72800500	-1.19364100
N	-2.52640100	3.92526400	-1.02503800
C	-2.07664700	3.76868200	-2.39247900
H	-1.01286800	3.53512400	-2.38611100
H	-2.63660200	3.01119600	-2.93472800
C	-0.47667200	7.76280700	-1.01871300
C	-0.68605500	6.70531500	-1.92199300
C	0.40968100	6.23862900	-2.67158700
C	1.66106000	6.82871000	-2.52972900
C	1.85421700	7.87681500	-1.63024200
C	0.77773000	8.33862200	-0.87117400
H	-1.32418500	8.11538300	-0.44291100

H	0.28965300	5.42316900	-3.37307500
H	2.49317900	6.46350300	-3.12144000
H	2.83275600	8.33046200	-1.52369100
H	0.91724400	9.15318300	-0.16940400
N	-1.98721700	6.19233300	-1.97379500
C	-2.30532800	5.21302500	-2.97877900
H	-3.35986200	5.30848800	-3.24363900
H	-1.70122600	5.31762200	-3.88075800
O	-1.89758200	4.96490300	-0.53446000

int-6-HCOO⁻

G+ZPE = -916.136917

C	-4.29224500	-2.23118100	0.92087600
C	-3.74439700	-1.08231800	1.49431100
C	-2.38652000	-0.82999900	1.39391700
C	-1.57333800	-1.73492000	0.69686800
C	-2.11211300	-2.89619300	0.12371600
C	-3.47375800	-3.13404400	0.24168100
H	-5.35512100	-2.42334100	1.00399600
H	-4.37848500	-0.37377400	2.01222900
H	-1.95331300	0.06094100	1.82142100
H	-1.49036400	-3.61411400	-0.39102800
H	-3.89651300	-4.02943700	-0.19654800
N	-0.18877500	-1.43806300	0.59207100
C	0.66278300	-1.97478000	-0.41807500
H	1.66858500	-2.04100000	-0.01012100
H	0.32086100	-2.92292600	-0.81423200
C	2.34030600	2.23529000	-0.44512000
C	2.22204800	0.89352500	-0.86663600
C	3.38471300	0.10675500	-0.97424200
C	4.62430600	0.65481800	-0.66429900
C	4.73479900	1.98004500	-0.24561000
C	3.58261700	2.76518300	-0.14095400
H	1.44237500	2.83571700	-0.36764600
H	3.32434300	-0.92174600	-1.30655500
H	5.51243100	0.03929100	-0.75177500
H	5.70503900	2.39832600	-0.00611400
H	3.65682400	3.79749900	0.18125000
C	0.67093800	-0.87507000	-1.59673800
H	-0.31823100	-0.88409800	-2.05159600
H	1.40679700	-1.26034500	-2.30483300
O	0.27981000	-0.44295700	1.16980000
N	0.96070200	0.41834400	-1.13714000
C	-1.46001300	2.23215500	0.24002600

O	-2.51870000	2.71768900	0.64543600
H	-0.66008800	2.02909900	1.00169300
O	-1.14087200	1.92663100	-0.95542100
H	0.12212100	1.09652000	-1.04711400