Supporting information

Photocatalytic C-N Cross-Couplings Mediated by Heterogeneous Nickel-Coordinated Carbon Nitride

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1. General experimental details

All reagents were commercially available unless otherwise noted. Carbon nitride was prepared according to previous literature.[1] All reactions were carried out under an argon atmosphere by using a blue LED-based photoreactor (λ = 427 nm) as a light source. All solvents were dried and distilled by standard procedures. Solutions were concentrated under reduced pressure by rotary evaporation. Chromatographic purification of desired products was accomplished on silica gel Si 60® (300-400 mesh).

Nuclear magnetic resonance spectra were acquired on a Bruker AMX 400 (400 MHz, and 100 MHz for ^{1}H, and ^{13}C respectively) and a Bruker DRX 600 (600 MHz, and 150 MHz for ^{1}H, and ^{13}C respectively). All ^{1}H NMR spectra are reported in parts per million (ppm) downfield of TMS and were measured relative to the signals at 7.26 ppm ($CDCl_3$). All ^{13}C NMR spectra were obtained with ^{1}H -decoupling and reported in ppm relative to $CDCl_3$ (77.16 ppm). Data for ^{1}H NMR are reported as follow: chemical shift (δ in ppm), multiplicity (s = singlet; brs = broad singlet; vbs = vary broad singlet; d = doublet; t= triplet; q = quartet; m = multiplet), coupling constant (Hz), integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ in ppm), multiplicity, and coupling constant (Hz). High-resolution mass spectra were recorded on a Thermo Scientific Exactive Orbitrap Mass Spectrometer under Electron Spray Ionization conditions preparing sample solution in methanol.

2. Synthesis and characterization of nickel(II) coordinated CN photocatalysts

2.1 Synthesis of carbon nitrides

Graphitic carbon nitride (CN)[1d]: Melamine (1.26 g) and cyanuric acid (1.23 g) were dispersed in 80 mL and 100 mL ultrapure water respectively and stirred for 30 min at 90 °C leading to transparent solutions. Then, the solution of cyanuric acid was poured into a solution of melamine resulting in a milk-white emulsion, which was stirred for 4 h at room temperature. The emulsions were collected by centrifuging, adequately washed with deionized water and ethanol, and dried at 60 °C overnight. Graphitic

carbon nitride (CN) was obtained after being treated at 600 °C using a porcelain crucible with a lid (5 °C min^{-1} ramp rate) for 4 h under nitrogen flow.

Citric acid doped CN (CNC)[1d]: The preparation procedure of CNC was similar to that of CN, except that citric acid (0.38 g) was added to the solution of cyanuric acid with further stirring for 10 min.

Barbituric acid doped CN (CNB)[1c]: Melamine (2.52 g), cyanuric acid (2.58 g), and barbituric acid (0.26 g) were mixed in 100 mL ultrapure water and stirred for 24 h. Then the obtained suspension was centrifuged, extensively washed with deionized water and ethanol, and dried at 60 °C overnight. **CNB** was obtained after annealing at 500 °C using a porcelain crucible with a lid (2.3 °C min^{-1} ramp rate) for 4 h under an air atmosphere.

Oxamide doped crystalline CN (CN-OA-m)[1b]: Urea (20.00 g) and oxamide (1.00 g) were dispersed in 20 mL ultrapure water and the mixture was stirred at 100 °C until fully evaporation of water. The resulting solid was completely ground and heated at 500 °C (5 °C min^{-1} ramp rate) for 1 h under the air atmosphere. Upon the absolute grinding with KCl (6.60 g) and LiCl (5.40 g), the obtained powder was transferred into a porcelain crucible with a lid, and calcined at 550 °C (10 °C min^{-1} ramp rate) for 2 h under a nitrogen atmosphere. The crude product was adequately washed with 100 mL of deionized water for 12 h, isolated by centrifugation, then extensively washed with deionized water and ethanol, and dried at 60 °C overnight.

Mesoporous graphitic carbon nitride (mpg-CN)[1a]: Cyanamide (5.00 g) was dispersed in an aqueous dispersion of SiO_2 nanoparticles (6.50 g, 40 wt.% solids, 22 nm average diameter), and the mixture was stirred at 60 °C until thoroughly evaporation. The solids were fully ground and heated to 550 °C using a porcelain crucible with a lid (2.3 °C min^{-1} ramp rate) for 4 h under an air atmosphere. Next, the powders were suspended in an aqueous solution of NH_4HF_2 (4 M, 180 mL) for 48 h to dislodge SiO_2 nanoparticles. The product mpg-CN was isolated by filtration, extensively washed with deionized water and ethanol, and dried at 60 °C overnight.

2.2 Ni deposition on CN[2]

A general procedure for Ni deposition on CN materials was described as follows: mpg-CN (0.20 g) was dispersed in 20 mL distilled water and a certain amount of $NiCl_2$ (0.0045, 0.0091, 0.0137, 0.0184, and 0.0232 g) were added. The resulted mixture was sonicated for 3 h at room temperature. Then the solution was quickly frozen at -60 °C and desired products of Ni-mpg-CN with different deposited Ni amounts (Ni wt.%, 0.92 wt.%, 2 wt.%, 3 wt.%, 4 wt.%, and 5 wt.%) were isolated by freeze drying without further washing. The nickel loading was determined on the inductively coupled plasma optical emission spectrometer analysis (Table S1). The counterion chloride ion (Cl^-) was present in the Ni-mpg-CN, but the exact role was unknown[3].

Table S1 Metal loading of Ni-CN catalysts.

Entry	Ni-CN catalysts[a]	Ni (wt.%)[b]
1	Ni-mpg-CN (0.92 wt.%)	0.74
2	Ni-mpg-CN (2 wt.%)	1.99
3	Ni-mpg-CN (3 wt.%)	2.82
4	Ni-mpg-CN (4 wt.%)	3.35
5	Ni-mpg-CN (5 wt.%)	5.10
6	Ni-mpg-CN (5 wt.%)[ref4]	1.79
7	Ni-CN (3 wt.%)	3.30
8	Ni-CN-OA-m (3 wt.%)	2.65
9	Ni-CNB (3 wt.%)	2.67
10	Ni-CNC (3 wt.%)	3.23
11	Used Ni-mpg-CN (3 wt.%)	2.87

[a] Theoretical loading was within parentheses. [b] Results tested by ICP-OES.

2.3 Characterization methods

The nickel content in the as-prepared catalysts was measured by an Inductively Coupled Plasma Optical Emission Spectrometer (Varian ICP-OES 720). Transmission electron microscopy (TEM), high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and energy-dispersive spectroscopy (EDS) images were recorded by a JEM 2100F TEM/STEM. Scanning electron microscopy (SEM) images were performed on a Hitachi S-4800 instrument. Powder X-ray diffraction (XRD) patterns were measured on Ultima IV X-ray diffractometer with Cu Kα radiation (λ = 1.541841 Å). Fourier transformed infrared (FT-IR) spectra were obtained using KBr pellets with a VERTEX 80V spectrometer. X-ray photoelectron spectroscopy (XPS) measurements were acquired on a Thermo ESCALAB 250XI with an Al anode (Al-Kα = 1486.6 eV), in which all spectra were calibrated by setting C 1s to 284.6 eV. UV-vis diffuse reflectance spectra (DRS) were examined on a Lambda 950 spectrophotometer with $BaSO_4$ as the reflectance standard.

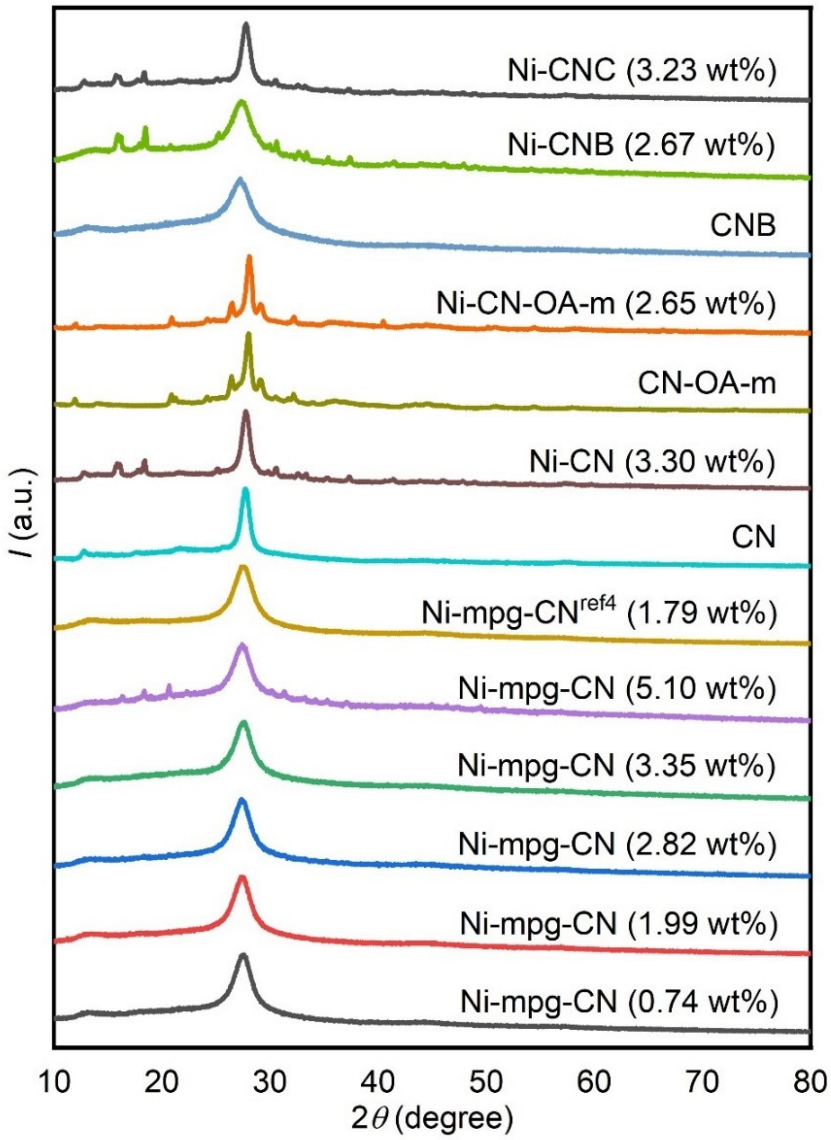


Fig. S1 XRD patterns of Ni-CN catalysts.

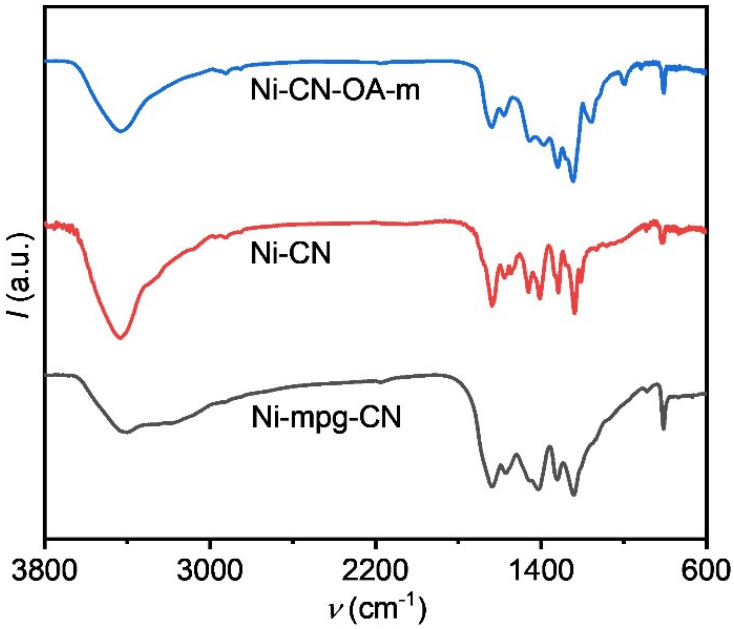


Fig. S2 FT-IR spectra of Ni-mpg-CN (3 wt.%), Ni-CN (3 wt.%), and Ni-CN -OA-m (3 wt.%).

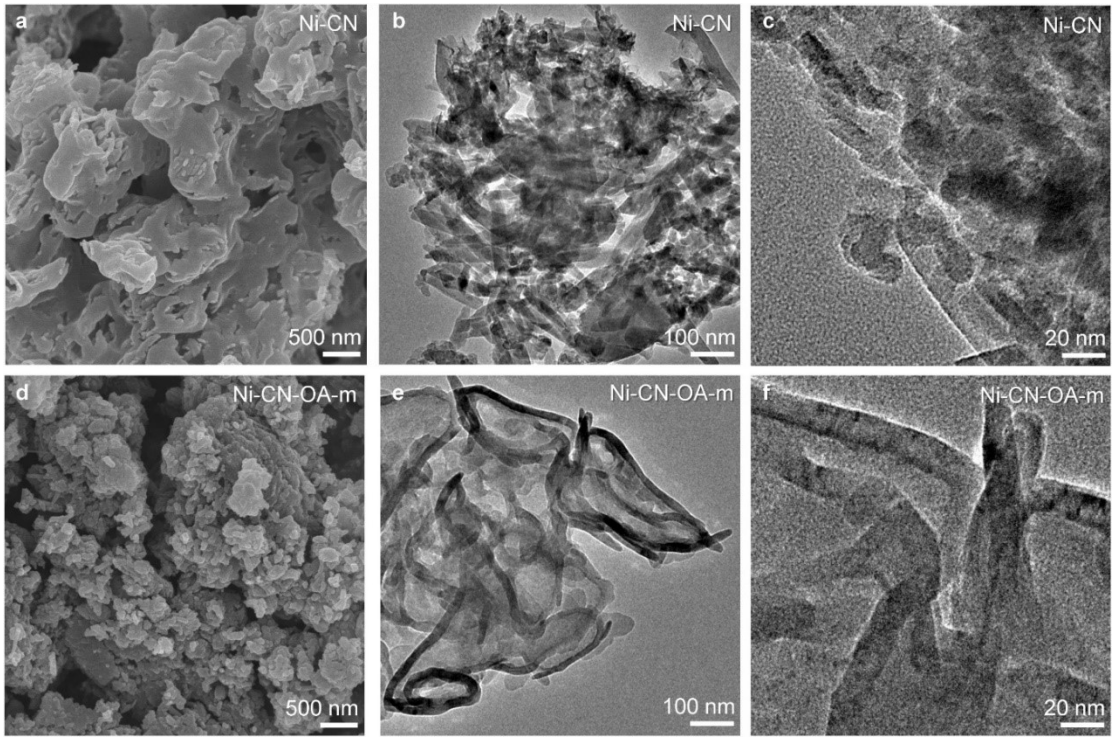


Fig. S3 (a) SEM, (b) TEM, and (c) HR-TEM images of Ni-CN (3 wt.%). (d) SEM, (e) TEM, and (f) HR-TEM images of Ni-CN-OA-m (3 wt.%).

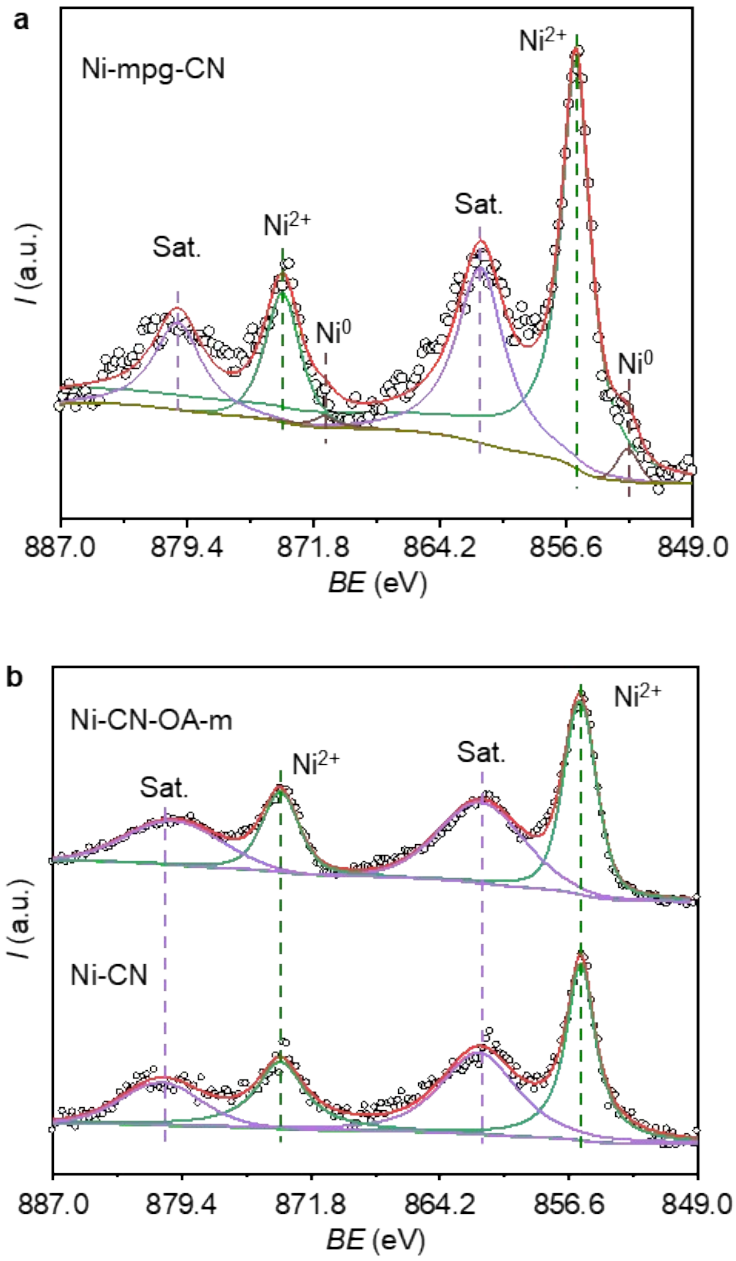


Fig. S4 (a) Ni 2p XPS spectra of Ni-mpg-CN (3 wt.%), (b) Ni 2p XPS spectra of Ni-CN (3 wt.%), and Ni-CN-OA-m (3 wt.%).

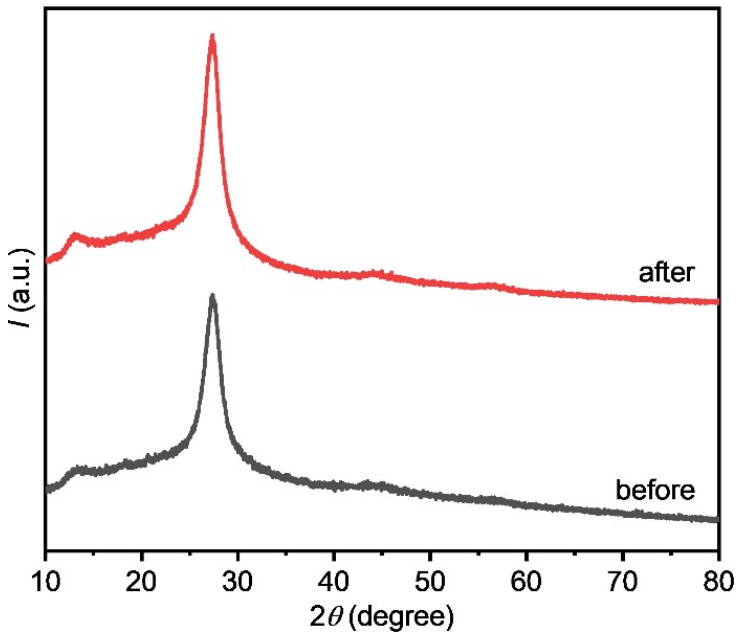


Fig. S5 XRD patterns of Ni-mpg-CN (3 wt.%) before and after three consecutive reaction runs.

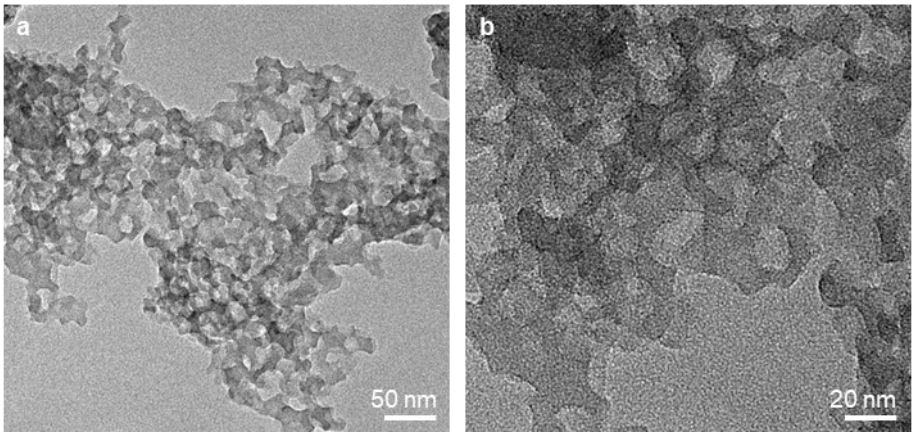


Fig. S6 TEM images of Ni-mpg-CN (3 wt.%) after three consecutive reaction runs.

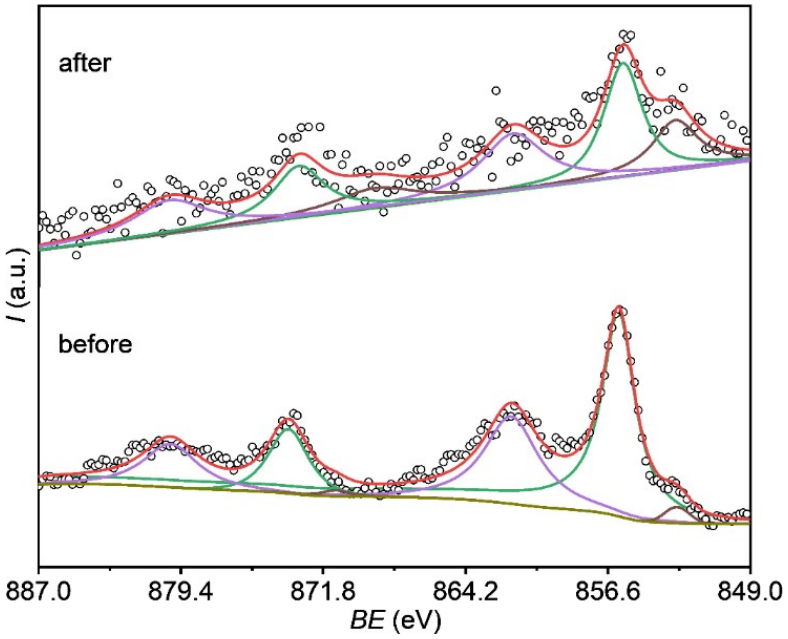


Fig. S7 Normalized Ni 2p XPS spectra of the fresh and used Ni-mpg-CN (3 wt.%) after three consecutive runs.

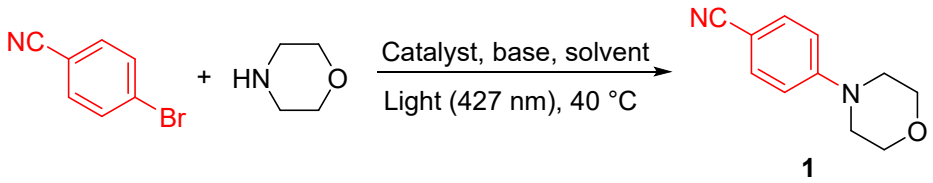
2.4 Photoelectrochemical measurements

Electrochemical measurements were performed on a CHI760E electrochemical workstation (Chenhua Instrument Co. Ltd., Shanghai, China) with a standard three-electrode cell consisting of the prepared electrode as the working electrode, platinum foil as the counter electrode, and Ag/AgCl (saturated KCl) as reference electrode, and an aqueous solution of Na_2SO_4 (0.2 M) was used as the electrolyte. The working electrodes were prepared as follows: catalysts (5 mg) and Nafion solution (0.05 cm^3) were dispersed in ultrapure water (0.45 cm^3) under sonication for 3 h. Then, the above slurry (0.015 cm^3) was dropped onto a π*0.6*0.6 cm^2 fluorine-tin oxide (FTO) glass electrode and dried at 80 °C. The transient photocurrent responses were obtained at a 40 W blue LED (λ = 427 nm) at 0 V (vs. Ag/AgCl). The electrochemical impedance spectroscopies (EIS) were carried out in the frequencies from 10^5 to 10^{-1} Hz with an amplitude of 5 mV at 0 V (vs. Ag/AgCl).

3. General procedure for photocatalytic C-N cross-coupling reactions

To a dried Schenck tube containing a magnetic stirring bar, catalyst (10 mg), aryl bromide (0.4 mmol, 1 equiv.), amine (8 equiv.) were added under an N_2 atmosphere. If the aryl halide is liquid, it was added after the "vacuum and N_2 refill" cycle. The tube was sealed with a septum and purged with N_2 via "vacuum and N_2 refill" cycles three times. Then degassed solvent (DMA, 2 mL) was added via a syringe needle. The reaction mixture was stirred and irradiated with a blue-based photoreactor (λ = 427 nm, 40 W) at 40 °C for 12 h. After being cooled down to room temperature, the reaction mixture was diluted with H_2O and extracted with ethyl acetate three times. The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. The crude product was purified by flash column chromatography to afford an analytically pure sample.

4. Reaction screening and optimization



Scheme S1 C-N cross-coupling of 4-bromobenzonitrile and morpholine.

Table S2 Control experiments

Entry	**Cat.**	Yield/%
1	CN-OA-m+$NiCl_2$ (5 mol%)	83
2	mpg-CN+$NiCl_2$ (5 mol%)	82
3	Ni-mpg-CN (3 wt.%)	90
4	$NiCl_2$ (5 mol%)	0
5	CN-OA-m or mpg-CN	0
6[a]	CN-OA-m+$NiCl_2$ (5 mol%)	0

7[a]	Ni-mpg-CN (3 wt.%)	0
8	-	0

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), catalyst (10 mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield. [a] No irradiation.

Table S3 Screening different catalysts

Entry	**Cat.**	Yield/%
1	Ni-CN-OA-m (3 wt.%)	45
2	Ni-CN (3 wt.%)	87
3	Ni-CNC (3 wt.%)	85
4	Ni-CNB (3 wt.%)	58
5	Ni-mpg-CN (3 wt.%)	90
6	Ni-mpg-CN[ref4] (5 wt.%)	41

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), catalyst (10 mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield.

Table S4 Screening catalyst loading

Entry	Ni-mpg-CN (3 wt.%)/mg	Yield/%
1	10	90
2	5	90
3	3	88
4	2	89

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), Ni-mpg-CN (3 wt.%, XX mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C,

12 h. Isolated yield.

Table S5 Screening different solvents

Entry	Solvent	Yield/%
1	DMA	90
2	DMSO	27
3	DMF	54
4	MeCN	31
5	1,2-Dimethoxyethane	11
6	1,4-Dioxane	11
7	Toluene	7
8	THF	0

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), Ni-mpg-CN (3 wt.%, 10 mg), Solvent (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield.

Table S6 Screening different bases

Entry	Base	Yield/%
1	-	90
2	TEA	89
3	DABCO	82
4	DBU	19
5	KOAc	6

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), Ni-mpg-CN (3 wt.%, 10 mg), base (1.2 equiv.), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield.

Table S7 Screening Ni content of Ni-mpg-CN

Entry	**Cat.**	Yield/%
1	Ni-mpg-CN (0.92 wt.%)	29
2	Ni-mpg-CN (2 wt.%)	81
3	Ni-mpg-CN (3 wt.%)	90
4	Ni-mpg-CN (4 wt.%)	81
5	Ni-mpg-CN (5 wt.%)	78

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), Ni-mpg-CN (XX wt.%, 10 mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield.

Table S8 Screening the wavelength of light

Entry	wavelength/nm	Yield/%
1	427	90
2	390	77
3	440	80

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), Ni-mpg-CN (3 wt.%, 10 mg), DMA (2 mL), irradiation at λ = XX nm, 40 W, 40 °C, 12 h. Isolated yield.

Table S9 Screening equiv. of morpholine and reaction time

Entry	Ni-mpg-CN (3 wt.%)/mg	morpholine/equiv.	T/h	Yield/%
1	10	3	12	90
2	10	5	12	88
3	10	8	12	93
4	10	10	12	93

5	5	8	12	93
6	2	8	12	92
7	10	8	6	93
8	10	8	3	92
9	10	8	1	34

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (XX equiv.), Ni-mpg-CN (3 wt.%, XX mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, XX h. Isolated yield.

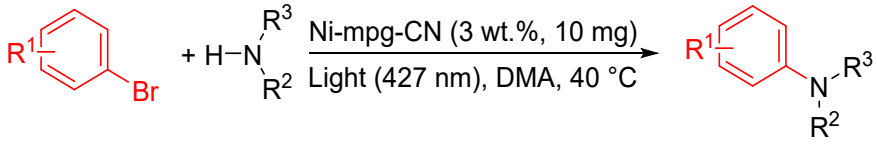
Table S10 Control experiments

Entry	morpholine/equiv.	Additive	Yield/%
1	3	-	90
2	3	2 equiv. $AgNO_3$	0
3	3	2 equiv. triethanolamine	16
4	3	2 equiv. ammonium oxalate	0
5	3	2 equiv. TEMPO	60
6	3	8 equiv. TEMPO	0
7	2	-	59
8	2	3 equiv. TEA	64
9	2	2 equiv. quinuclidine	91
10	1	-	21
11	1	2 equiv. TEA	29
12	3	-	$34^a/34^b$

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (XX equiv.), Ni-mpg-CN (3 wt.%, 10 mg), additive (XX equiv.), DMA (2 mL), irradiation

at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield. [a] 1 h with irradiation. [b] 1 h with irradiation followed by 11 h without irradiation.

5. Recycling experiments and long-time stability test of catalysts



Scheme S2 C-N cross-coupling of aryl bromides and amines catalyzed by Ni-mpg-CN (3 wt.%).

Table S11 Recycling experiments of Ni-mpg-CN (3 wt.%)

Entry	Cycle 1	Cycle 2	Cycle 3
Yield/%	90	90	56

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), morpholine (3 equiv.), Ni-mpg-CN (3 wt.%, 10 mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield.

Method A: When the reaction was accomplished, the reaction mixture was transferred into a centrifuge tube and centrifuged. For the recovered material, we centrifugally wash it with reactive solvent DMA for at least three times. Then recovered catalyst was used for the next run without adding any fresh prepared batch of catalyst.

For the 3th run, the yield decreased from 90% to 56% due to the loss of catalyst during the recovery process.

Table S12 Long-time stability test of Ni-mpg-CN (3 wt.%)

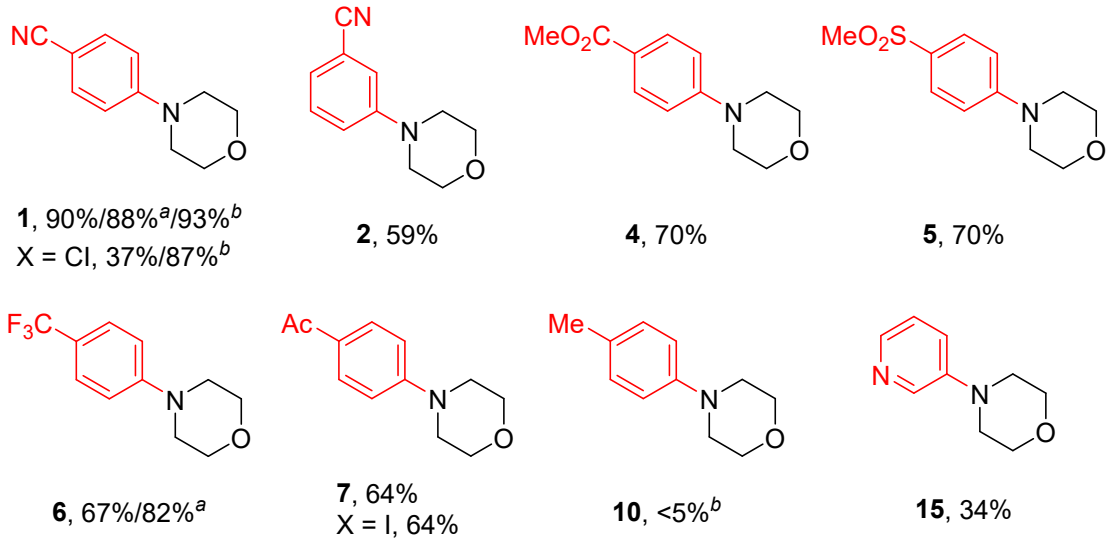
Entry	Cycle 1	Cycle 2	Cycle 3
Conversion/%	100	97	97
Yield/%	93	90	89

Standard condition: 4-bromobenzonitrile (0.4 mmol, 1 equiv.), butylamine (8 equiv.),

Ni-mpg-CN (3 wt.%, 10 mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 3 h. Isolated yield.

Method B: When the reaction was accomplished, new bath of substrates was direct added into the reaction system under an N_2 atmosphere. Then the reaction mixture was irradiated for 3 h. The isolated yield for cycle 2 was the average of the 1st and 2nd runs. The isolated yield for cycle 3 was the average of three runs.

6. Substrate study using 3 equiv. amines



1, 90%/88%[a]/93%[b]
X = Cl, 37%/87%[b]

2, 59%

4, 70%

5, 70%

6, 67%/82%[a]

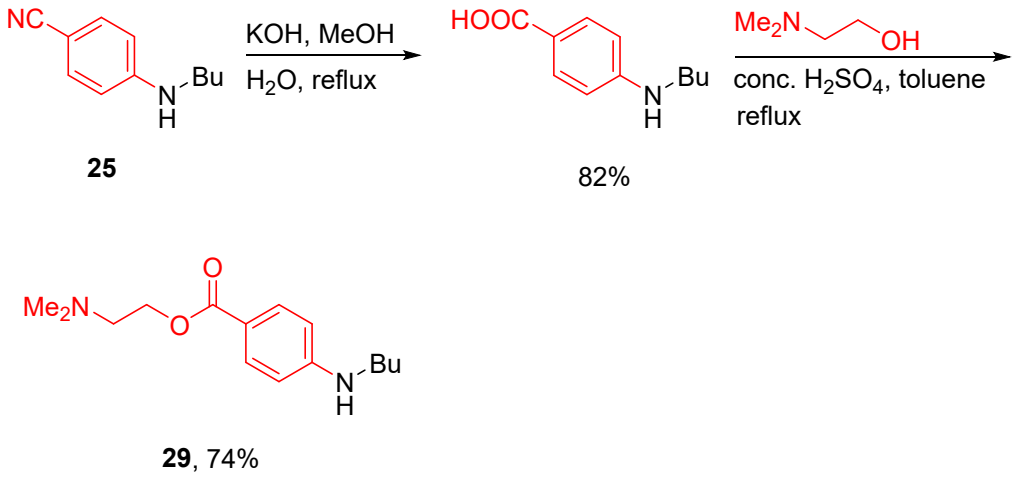
7, 64%
X = I, 64%

10, <5%[b]

15, 34%

Scheme S3 Standard condition: aryl halide (0.4 mmol), amine (3 equiv.), Ni-mpg-CN (3 wt.%, 10 mg), DMA (2 mL), irradiation at λ = 427 nm, 40 W, 40 °C, 12 h. Isolated yield. X = Br unless otherwise indicated. [a] Amine (5 equiv.). [b] Amine (8 equiv.).

7. Synthesis of tetracaine



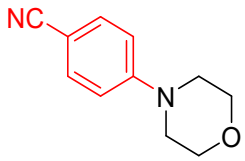
Scheme S4 Synthesis of tetracaine **29** from **25**.

To a Schlenk flask containing a magnetic stirring bar, 4-(butylamino)benzonitrile (**25**, 1.35 mmol, 235 mg), KOH (7.57 g), H_2O (45.0 mL) and MeOH (30.0 mL) were added. The mixture was stirred at 100 °C for 12 h. After cooling to room temperature, the volatiles were removed under vacuum. A solution of hydrochloric acid (2 M) was added dropwise until pH = 3 at 0 °C, and the organic phase was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel to afford carboxylic acid intermediate as a yellow solid (213.1 mg, 82%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.92 (dt, J = 9.7, 2.2 Hz, 2H), 6.55 (dt, J = 9.4, 2.2 Hz, 2H), 3.18 (t, J = 7.1 Hz, 2H), 1.65-1.60 (m, 2H), 1.47-1.41 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 172.29, 152.90, 132.47, 117.22, 111.45, 43.16, 31.54, 20.34, 13.95. The data was the same to previous literature.[5]

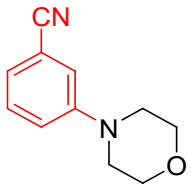
To a Schlenk flask containing a magnetic stirring bar, the carboxylic acid intermediate (1 mmol, 193 mg), toluene (4.4 mL), 2-dimethylaminoethanol (3 equiv., 0.3 mL) and conc. H_2SO_4 (0.25 mL) were added. The mixture was refluxed until the reaction was completed. After cooling to room temperature, 10% aqueous sodium

carbonate solution was added to adjust pH = 10, and the organic phase was extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. The crude product was further purified by column chromatography on silica gel to afford product **29** as a yellow solid (194.7 mg, 74%). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.86 (dt, J = 9.5, 2.2 Hz, 2H), 6.53 (dt, J = 9.7, 2.2 Hz, 2H), 4.37 (t, J = 5.9 Hz, 2H), 4.08 (s, 1H), 3.17-3.14 (m, 2H), 2.69 (t, J = 5.9 Hz, 2H), 2.33 (s, 6H), 1.64-1.59 (m, 2H), 1.46-1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$): δ = 166.91, 152.32, 131.73, 118.12, 111.38, 62.44, 58.11, 45.95, 43.16, 31.51, 20.30, 13.93. The data was the same as in previous literature.[6]

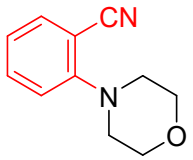
8. Analytic data of products



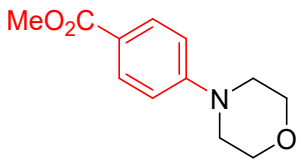
4-Morpholinobenzonitrile (1)[7]: eluent for column chromatography: 25% EtOAc/hexane; yield: 93% (69.8 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.51 (dt, J = 9.7, 2.3 Hz, 2H), 6.86 (dt, J = 9.7, 2.2 Hz, 2H), 3.85 (t, J = 4.9 Hz, 4H), 3.28 (t, J = 5.0 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.63, 133.66, 119.99, 114.21, 101.12, 66.59, 47.44.



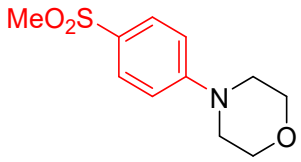
3-Morpholinobenzonitrile (2)[8]: eluent for column chromatography: 25% EtOAc/hexane; yield: 84% (63.2 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.34-7.31 (m, 1H), 7.12-7.09 (m, 3H), 3.85 (t, J = 4.9 Hz, 4H), 3.17 (t, J = 4.9 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.43, 130.04, 123.02, 119.67, 119.35, 118.23, 113.18, 66.67, 48.52.



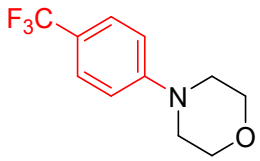
2-Morpholinobenzonitrile (3)[9]: eluent for column chromatography: 25% EtOAc/hexane; yield: 54% (40.3 mg); state of the product: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.56 (dd, J = 7.7, 1.2 Hz, 1H), 7.51-7.48 (m, 1H), 7.04-6.99 (m, 2H), 3.88 (t, J = 4.6 Hz, 4H), 3.19 (t, J = 4.6 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 155.59, 134.53, 133.98, 122.23, 118.64, 118.37, 106.25, 67.02, 51.93.



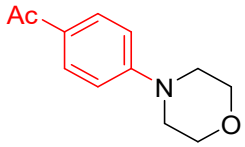
Methyl 4-morpholinobenzoate (4)[10]: eluent for column chromatography: 25% EtOAc/hexane; yield: 85% (75.6 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.93 (dt, J = 9.8, 2.4 Hz, 2H), 6.85 (dt, J = 9.5, 2.3 Hz, 2H), 3.86-3.84 (m, 7H), 3.27 (t, J = 4.9 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.17, 154.32, 131.33, 120.43, 113.59, 66.72, 51.80, 47.82.



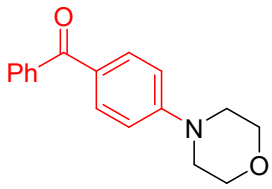
4-(4-(Methylsulfonyl)phenyl)morpholine (5)[11]: eluent for column chromatography: 50-100% EtOAc/hexane; yield: 86% (82.7 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (dt, J = 10.0, 2.4 Hz, 2H), 6.93 (dt, J = 9.9, 2.4 Hz, 2H), 3.85 (t, J = 5.0 Hz, 4H), 3.30 (t, J = 4.9 Hz, 4H), 3.00 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.56, 129.48, 129.22, 113.90, 66.58, 47.55, 45.03.



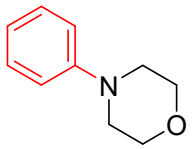
4-(4-Trifluoromethylphenyl)morpholine (6)[7, 10b]: eluent for column chromatography: 10% EtOAc/hexane; yield: 85% (78.4 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.50 (d, J = 7.7 Hz, 2H), 6.92 (d, J = 7.8 Hz, 2H), 3.88-3.86 (m, 4H), 3.25-3.23 (m, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.51, 126.58 (q, J = 3.7 Hz), 124.82 (d, J = 270.9 Hz), 121.17 (d, J = 32.9 Hz), 114.46, 66.78, 48.33.



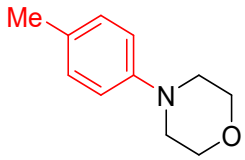
1-(4-Morpholinophenyl)ethan-1-one (7)[7a]: eluent for column chromatography: 25% EtOAc/hexane; yield: 76% (62.3 mg); state of the product: yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ =7.89 (dt, J = 9.9, 2.3 Hz, 2H), 6.86 (dt, J = 9.7, 2.4 Hz, 2H), 3.85 (t, J = 4.9 Hz, 4H), 3.30 (t, J = 4.9 Hz, 4H), 2.52 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 196.67, 154.36, 130.47, 128.29, 113.40, 66.69, 47.66, 26.27.



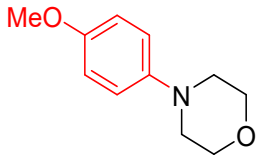
(4-Morpholinophenyl)(phenyl)methanone (8)[12]: eluent for column chromatography: 25% EtOAc/hexane; yield: 71% (76.0 m); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.81 (dt, J = 9.8, 2.3 Hz, 2H), 7.75-7.73 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 6.90 (dt, J = 9.8, 2.5 Hz, 2H), 3.87 (t, J = 4.9 Hz, 4H), 3.33 (t, J = 4.9 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 195.31, 154.16, 138.86, 132.55, 131.64, 129.68, 128.21, 127.94, 113.31, 66.69, 47.71.



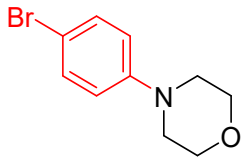
4-Phenylmorpholine (9)[7a]: eluent for column chromatography: 5% EtOAc/hexane; yield: 56% (36.5 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.30-7.27 (m, 2H), 6.94-6.91 (m, 2H), 6.90-6.88 (m, 1H), 3.87 (t, J = 4.8 Hz, 4H), 3.16 (t, J = 4.8 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.44, 129.31, 120.17, 115.85, 67.07, 49.52.



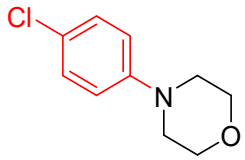
4-(*P*-tolyl)morpholine (10)[7a]: eluent for column chromatography: 5% EtOAc/hexane; yield: 38% (29.3 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.09 (dt, J = 9.5, 2.4 Hz, 2H), 6.84 (dt, J = 9.3, 2.3 Hz, 2H), 3.86 (t, J = 4.8 Hz, 4H), 3.11 (t, J = 4.8 Hz, 4H), 2.28 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 149.32, 129.85, 116.20, 67.11, 50.10, 20.54.



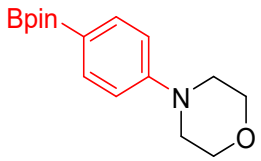
4-(4-Methoxyphenyl)morpholine (11)[7a]: eluent for column chromatography: 5% EtOAc/hexane; yield: 28% (24.2 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.90-6.88 (m, 2H), 6.87-6.84 (m, 2H), 3.86 (t, J = 4.7 Hz, 4H), 3.77 (s, 3H), 3.06 (t, J = 4.7 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 154.16, 145.82, 117.98, 114.69, 67.19, 55.73, 50.99.



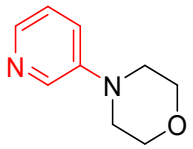
4-(4-Bromophenyl)morpholine (12)[13]: eluent for column chromatography: 10% EtOAc/hexane; yield: 51% (49.6 mg); state of the product: grey powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.36 (dt, J = 10.2, 2.8 Hz, 2H), 6.78 (dt, J = 10.3, 2.8 Hz, 2H), 3.85 (t, J = 4.8 Hz, 4H), 3.12 (t, J = 4.9 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.44, 132.05, 117.39, 112.26, 66.86, 49.26.



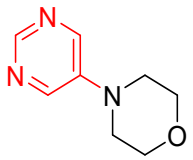
4-(4-Chlorophenyl)morpholine (13)[13]: eluent for column chromatography: 10% EtOAc/hexane; yield: 51% (40.6 mg); state of the product: grey powder; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.22 (dt, J = 10.2, 2.7 Hz, 2H), 6.83 (dt, J = 10.2, 2.7 Hz, 2H), 3.85 (t, J = 4.8 Hz, 4H), 3.12 (t, J = 4.8 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.03, 129.16, 125.02, 117.03, 66.91, 49.45.



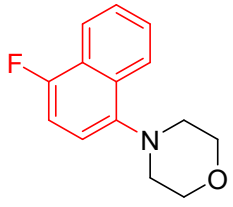
4-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)morpholine (14)[12]: eluent for column chromatography: 12% EtOAc/hexane; yield: 75% (86.7 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.72 (dt, J = 8.9, 2.0 Hz, 2H), 6.88 (dt, J = 8.9, 2.0 Hz, 2H), 3.85 (t, J = 4.8 Hz, 4H), 3.22 (t, J = 4.9 Hz, 4H), 1.33 (s, 12H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.49, 136.28, 114.21, 83.52, 66.90, 48.51, 24.97.



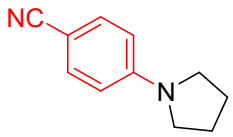
4-(Pyridin-3-yl)morpholine (15)[7a, 14]: eluent for column chromatography: 50-100% EtOAc/hexane; yield: 81% (59.9 mg); state of the product: pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.10 (s, 1H), 7.15 (s, 2H), 3.85 (t, J = 4.5 Hz, 4H), 3.16 (t, J = 4.5 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 147.00, 141.07, 138.27, 123.62, 122.22, 66.73, 48.65.



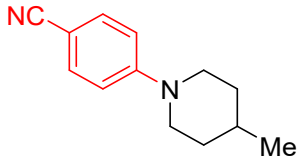
4-(Pyrimidin-5-yl)morpholine (16)[7a, 10b]: eluent for column chromatography: 50-100% EtOAc/hexane; yield: 38% (22.2 mg); state of the product: pale yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.68 (s, 1H), 8.33 (s, 2H), 3.85 (t, J = 4.3 Hz, 4H), 3.19 (t, J = 4.4 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.07, 144.25, 143.42, 66.40, 47.45.


new compound

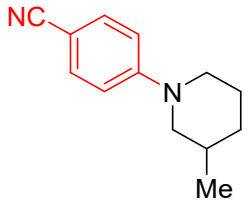
4-(4-Fluoronaphthalen-1-yl)morpholine (17): eluent for column chromatography: 5% EtOAc/hexane; yield: 76% (70.2 mg); state of the product: brown solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.25-8.23 (m, 1H), 8.10-8.09 (m, 1H), 7.57-7.53 (m, 2H), 7.09-7.06 (m, 1H), 7.02-7.01 (m, 1H), 3.98 (t, J = 4.4 Hz, 4H), 3.07 (t, J = 4.1 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 155.64 (d, J = 248.4 Hz), 145.74, 130.18, 126.49 (d, J = 30.6 Hz), 124.79 (d, J = 16.9 Hz), 123.53, 121.18 (d, J = 4.8 Hz), 114.60 (d, J = 8.2 Hz), 109.03 (d, J = 20.6 Hz), 67.61, 53.81; ^{19}F NMR (565 MHz, $CDCl_3$): δ = -128.43--128.46 (m); m.p.: 60.0-63.3 °C; HR-MS (ESI, m/z): calcd for $C_{14}H_{14}FNO$ $[M+H]^+$: 232.1137. Found: 232.1143.



4-(Pyrrolidin-1-yl)benzonitrile (18)[7b, 15]: eluent for column chromatography: 5% EtOAc/hexane; yield: 87% (58.2 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.7 Hz, 2H), 6.49 (d, J = 8.7 Hz, 2H), 3.31 (t, J = 6.5 Hz, 4H), 2.03 (t, J = 6.5 Hz, 4H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.11, 133.52, 121.11, 111.54, 96.59, 47.57, 25.50.

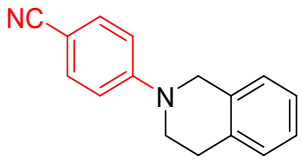


4-(4-Methylpiperidin-1-yl)benzonitrile (19)[7b]: eluent for column chromatography: 25% EtOAc/hexane; yield: 93% (74.5 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.45 (dt, J = 9.8, 2.4 Hz, 2H), 6.84 (dt, J = 9.7, 2.4 Hz, 2H), 3.82 (dt, J = 13.3, 2.7 Hz, 2H), 3.82 (td, J = 18.9, 2.5 Hz, 2H), 1.73 (d, J = 13.4 Hz, 2H), 1.65-1.60 (m, 1H), 1.24 (qd, J = 20.4, 3.9 Hz, 2H), 0.97 (d, J = 6.6 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.58, 133.62, 120.45, 114.24, 99.17, 47.93, 33.62, 30.91, 21.87.

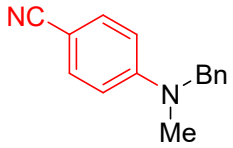


4-(3-Methylpiperidin-1-yl)benzonitrile (20)[7b]: eluent for column chromatography: 25% EtOAc/hexane; yield: 93% (74.7 mg); state of the product: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (dt, J = 9.8, 2.4 Hz, 2H), 6.82 (dt, J = 9.7, 2.3 Hz, 2H), 3.77-3.73 (m, 1H), 3.71-3.68 (m, 1H), 2.79 (td, J = 18.6, 3.0 Hz, 1H), 2.51-2.47 (m, 1H), 1.85-1.81 (m, 1H), 1.76-1.66 (m, 2H), 1.62-1.55 (m, 1H), 1.10 (qd, J = 20.1, 4.0

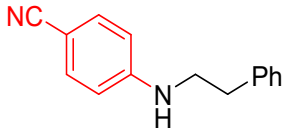
Hz, 1H), 0.94 (d, J = 6.7 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 153.51, 133.58, 120.45, 114.10, 98.88, 55.40, 47.95, 32.94, 30.59, 24.79, 19.35.



4-(3,4-Dihydroisoquinolin-2(1H)-yl)benzonitrile (21)[16]: eluent for column chromatography: 5% EtOAc/hexane; yield: 92% (83.8 mg); state of the product: yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.52 (d, J = 8.8 Hz, 2H), 7.24-7.17 (m, 4H), 6.86 (d, J = 8.8 Hz, 2H), 4.50 (s, 2H), 3.64 (t, J = 5.9 Hz, 2H), 3.00 (t, J = 5.8 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 152.31, 135.02, 133.66, 133.51, 128.29, 127.06, 126.64, 126.58, 120.49, 112.78, 98.83, 48.90, 44.73, 29.05.

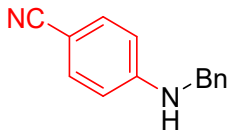


4-(Benzyl(methyl)amino)benzonitrile (22)[7b, 17]: eluent for column chromatography: 5% EtOAc/hexane; yield: 67% (59.4 mg); state of the product: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.44 (dt, J = 9.8, 2.3 Hz, 2H), 7.34 (t, J = 7.5 Hz, 2H), 7.28 (d, J = 7.3 Hz, 1H), 7.16 (d, J = 7.4 Hz, 2H), 6.69 (dt, J = 9.8, 2.4 Hz, 2H), 4.61 (s, 2H), 3.13 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 152.07, 137.28, 133.64, 128.96, 127.46, 126.40, 120.66, 111.74, 97.97, 55.99, 38.86.

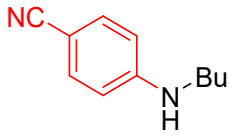


4-(Phenethylamino)benzonitrile (23)[18]: eluent for column chromatography: 25% EtOAc/hexane; yield: 83% (76.2 mg); state of the product: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.42 (dt, J = 9.4, 2.2 Hz, 2H), 7.35-7.32 (m, 2H), 7.27-7.25 (m, 1H),

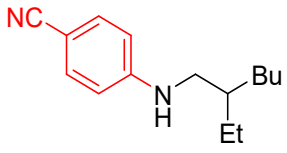
7.22-7.20 (m, 2H), 6.55 (dt, J = 9.3, 2.1 Hz, 2H), 4.21 (s, 1H), 3.44 (q, J = 6.5 Hz, 2H), 2.93 (t, J = 7.0 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.21, 138.55, 133.74, 128.80, 128.75, 126.76, 120.54, 112.33, 98.65, 44.26, 35.17.



4-(Benzylamino)benzonitrile (24)[19]: eluent for column chromatography: 25% EtOAc/hexane; yield: 32% (27.0 mg); state of the product: brown solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (dt, J = 9.3, 2.3 Hz, 2H), 7.38-7.29 (m, 5H), 6.59 (dt, J = 9.3, 2.3 Hz, 2H), 4.65 (s, 1H), 4.38 (d, J = 4.3 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.25, 137.95, 133.82, 128.98, 127.80, 127.42, 120.47, 112.54, 99.21, 47.61.



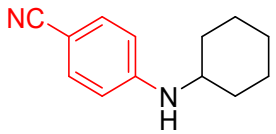
4-(Butylamino)benzonitrile (25)[20]: eluent for column chromatography: 5% EtOAc/hexane; yield: 92% (63.4 mg); state of the product: yellow solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.40 (dt, J = 9.4, 2.1 Hz, 2H), 6.54 (dt, J = 9.3, 2.1 Hz, 2H), 4.18 (s, 1H), 3.14 (d, J = 7.1 Hz, 2H), 1.64-1.59 (m, 2H), 1.46-1.40 (m, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.62, 133.73, 120.72, 112.09, 98.17, 42.96, 31.26, 20.24, 13.87.



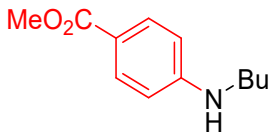
new compound

4-((2-Ethylhexyl)amino)benzonitrile (26): eluent for column chromatography: 5% EtOAc/hexane; yield: 84% (78.0 mg); state of the product: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.41 (dt, J = 9.4, 2.2 Hz, 2H), 6.54 (dt, J = 9.4, 2.1 Hz, 2H), 4.17 (s, 1H), 3.05 (t, J = 5.9 Hz, 2H), 1.59-1.54 (m, 2H), 1.42-1.38 (m, 2H), 1.33-1.28 (m, 5H),

0.91 (q, J = 7.3 Hz, 6H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 151.83, 133.65, 120.75, 112.03, 97.87, 46.32, 38.90, 31.17, 28.92, 24.38, 23.06, 14.09, 10.88; HR-MS (ESI, m/z): Calcd for $C_{15}H_{22}N_2$ $[M+H]^+$: 231.1861. Found: 231.1860.



4-(Cyclohexylamino)benzonitrile (27)[16]: eluent for column chromatography: 5% EtOAc/hexane; yield: 80% (64.3 mg); state of the product: yellow oil; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.38 (d, J = 8.6 Hz, 2H), 6.51 (d, J = 8.6 Hz, 2H), 4.14 (s, 1H), 3,28 (s, 1H), 2.02 (d, J = 9.9 Hz, 2H), 1.78-1.75 (m, 2H), 1.67-1.64 (m, 1H), 1.40-1.34 (m, 2H), 1.26-1.18 (m, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 150.55, 133.82, 120.76, 112.41, 97.95, 51.31, 33.06, 25.74, 24.89.



Methyl 4-(butylamino)benzoate (28)[6a]: eluent for column chromatography: 25% EtOAc/hexane; yield: 86% (70.9 mg); state of the product: white solid; ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.85 (dt, J = 9.5, 2.2 Hz, 2H), 6.54 (dt, J = 9.5, 2.2 Hz, 2H), 3.84 (s, 3H), 3.72 (q, J = 7.0 Hz, 1H), 3.16 (t, J = 7.1 Hz, 2H), 1.46-1.40 (m, 2H), 1.24 (t, J = 7.0 Hz, 2H), 0.96 (t, J = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$): δ = 167.49, 152.30, 131.68, 118.17, 111.44, 51.59, 43.20, 31.55, 20.34, 13.95.

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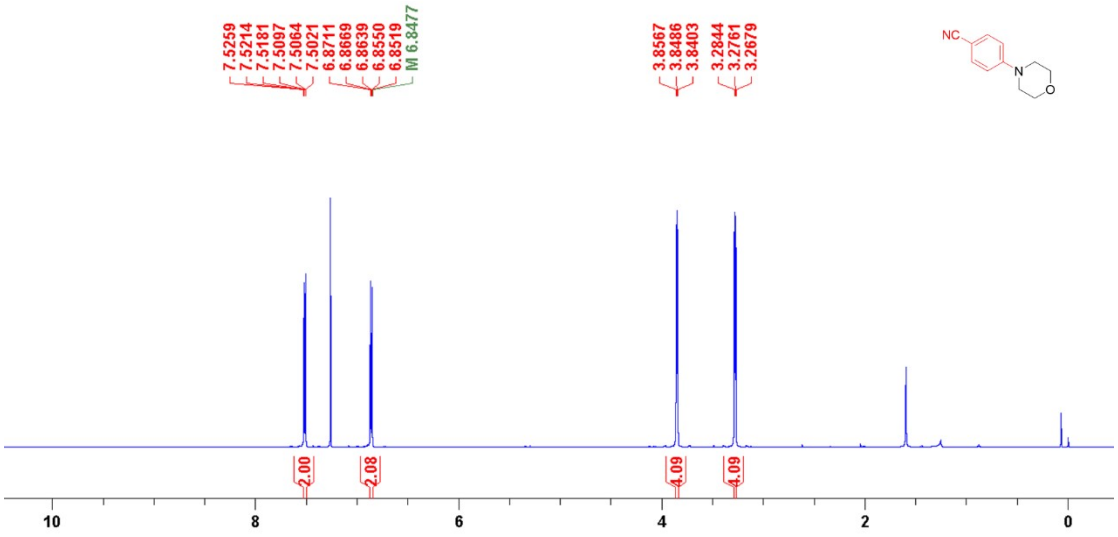
10. NMR and HR-MS (ESI) spectra



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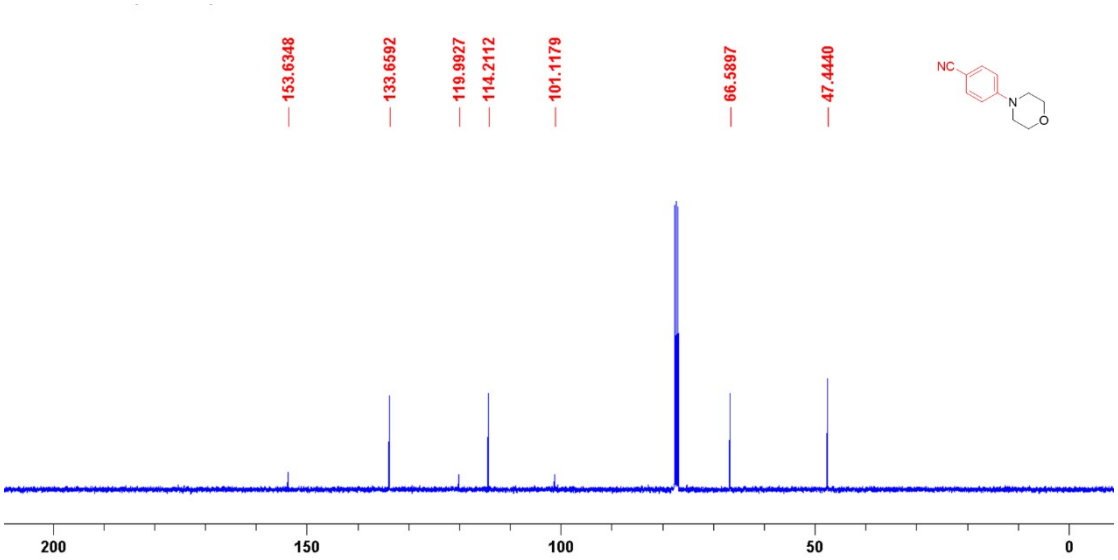

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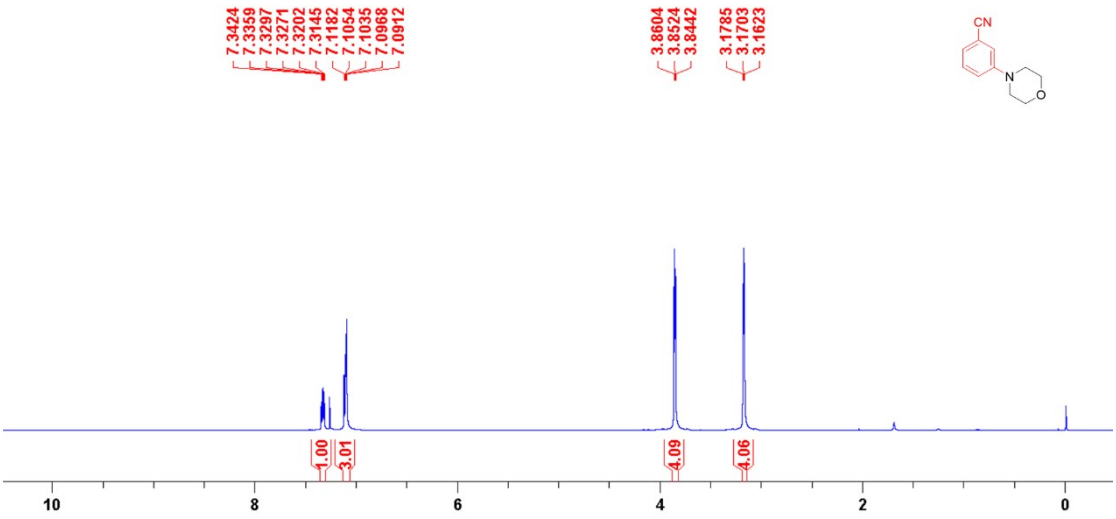

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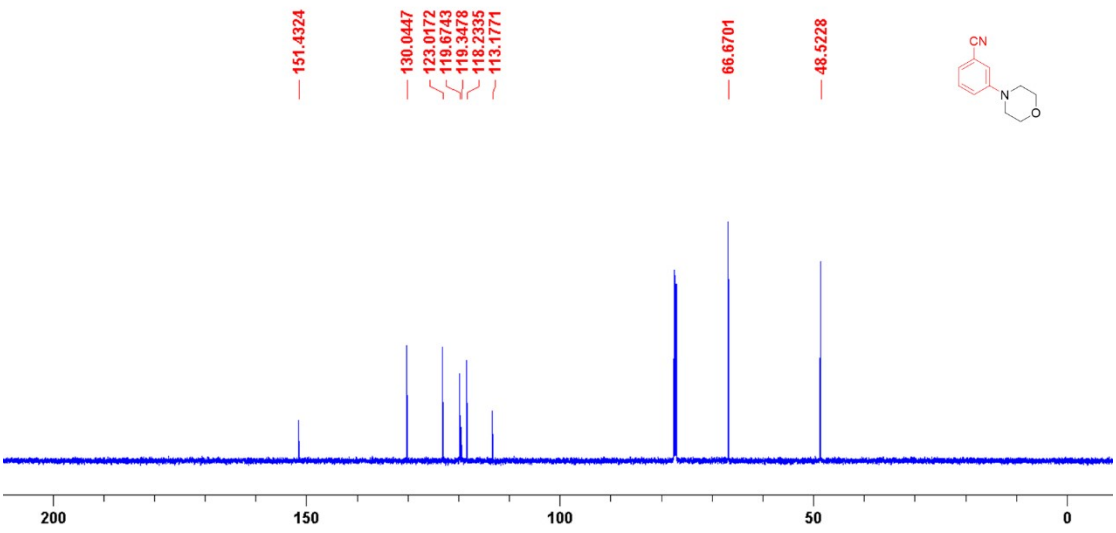

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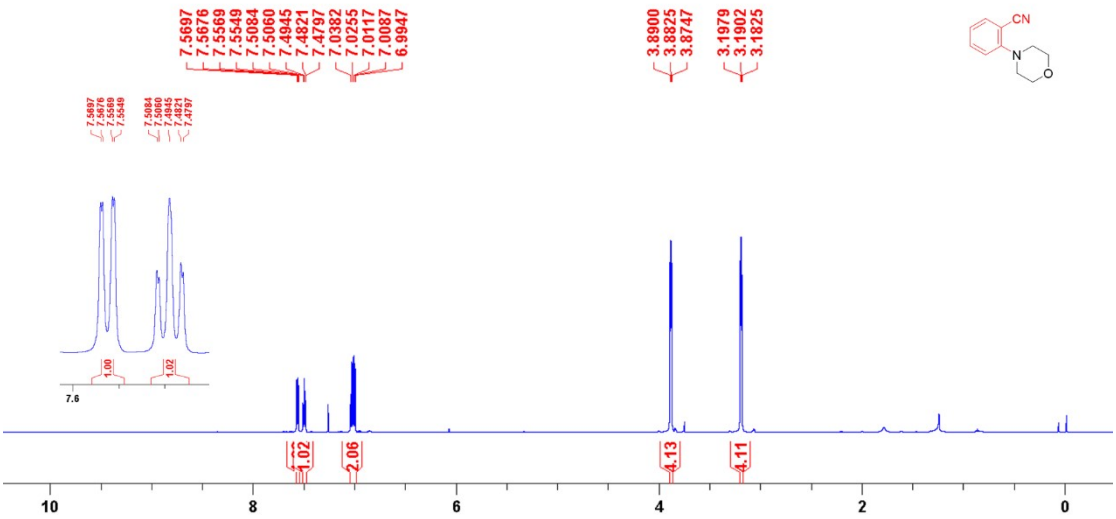

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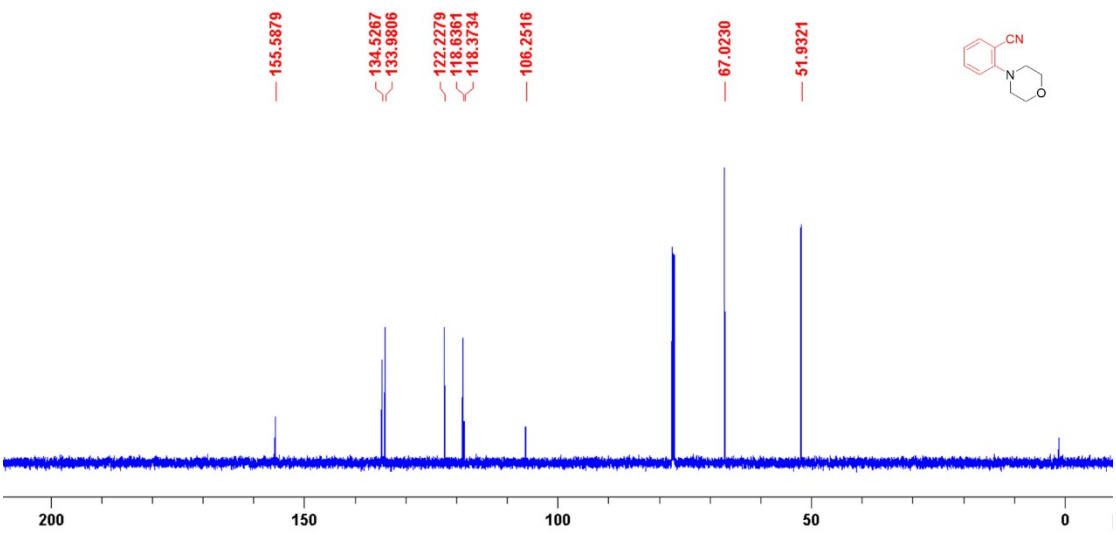

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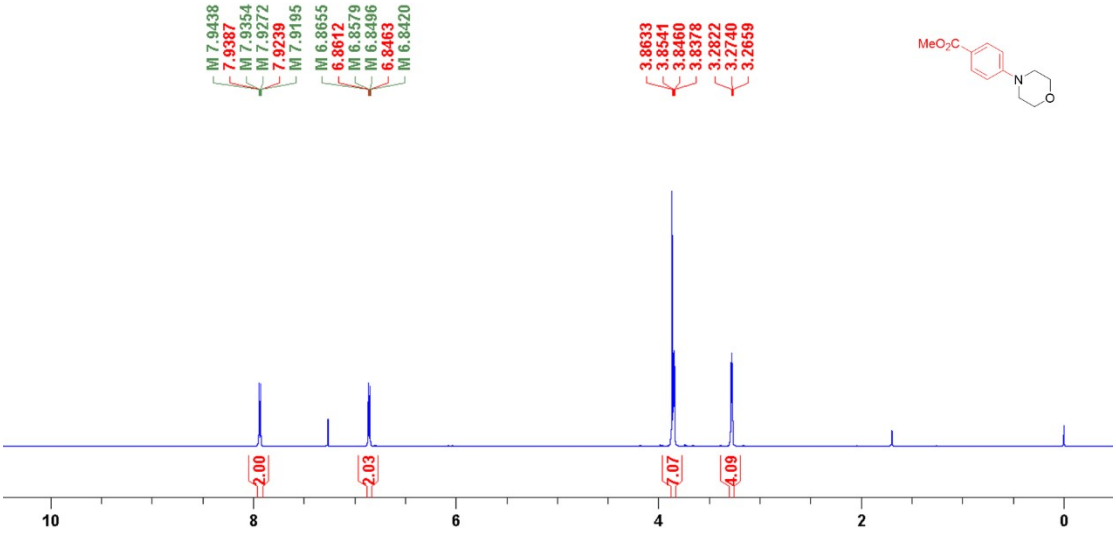

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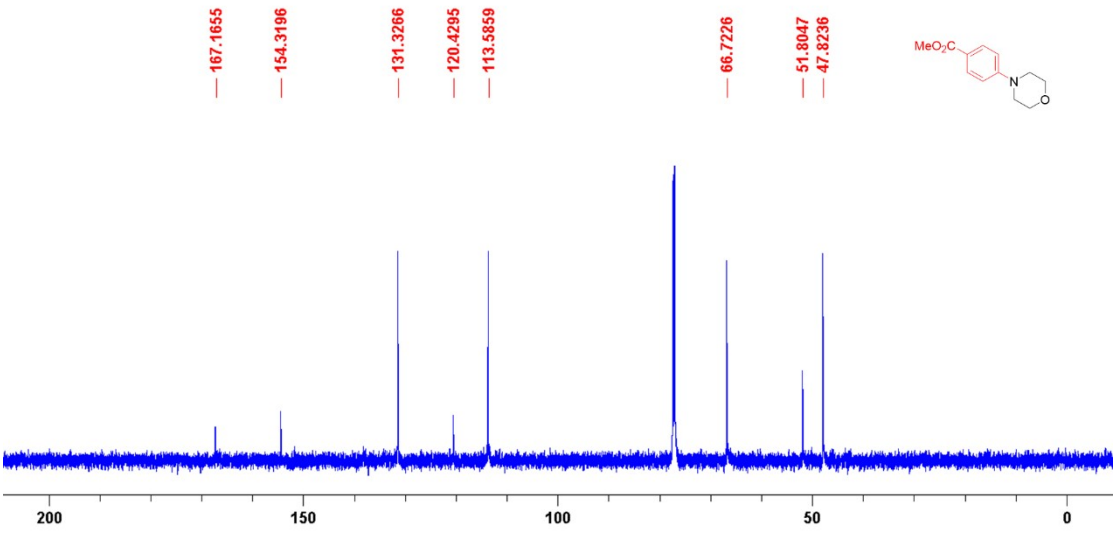

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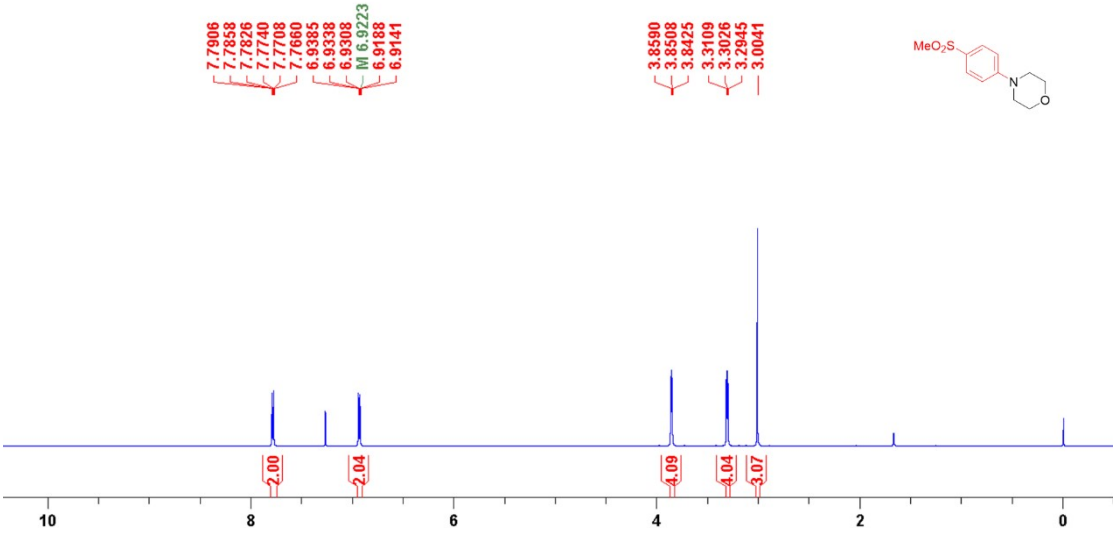

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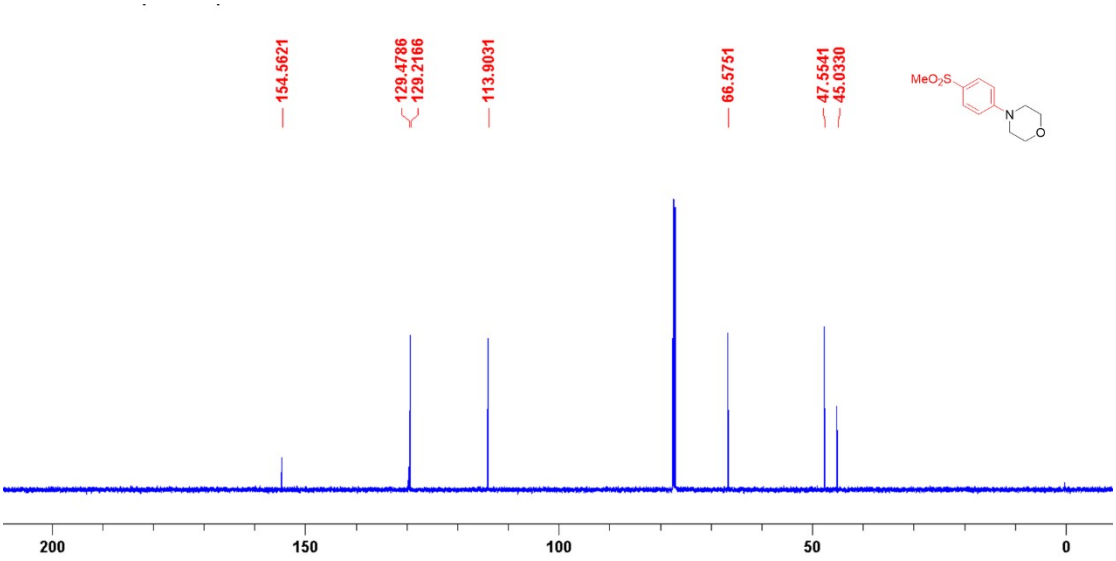

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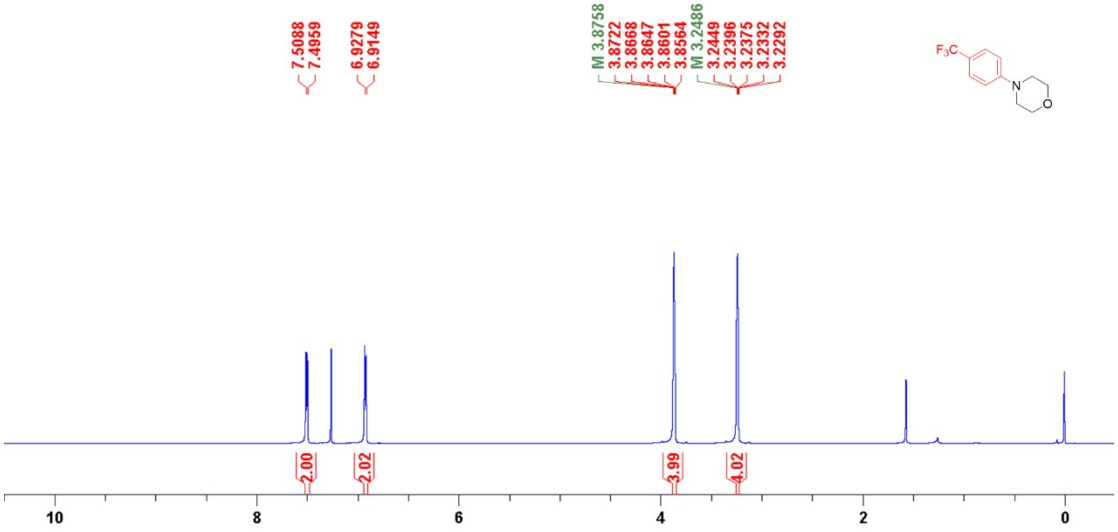

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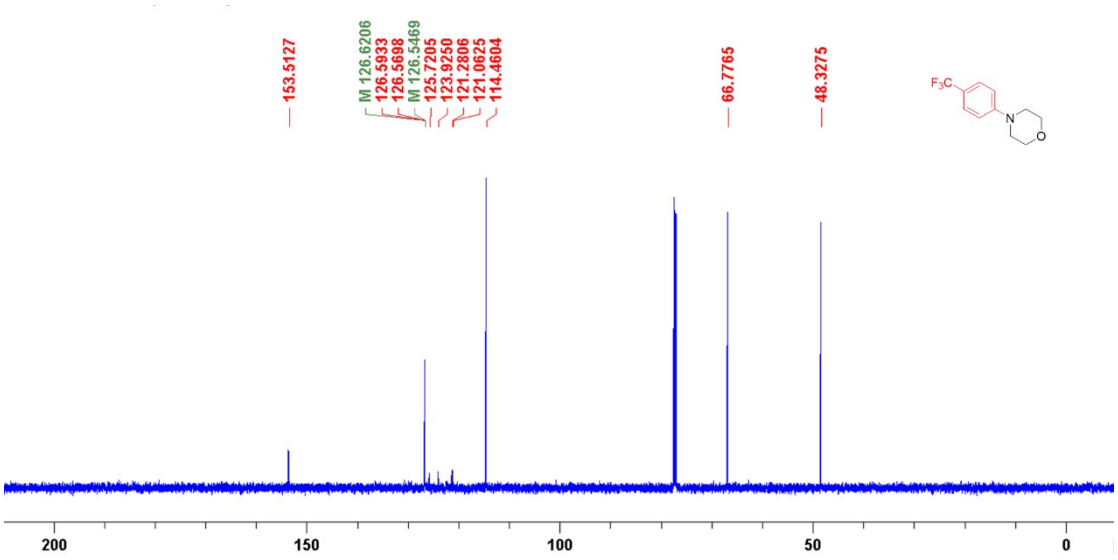

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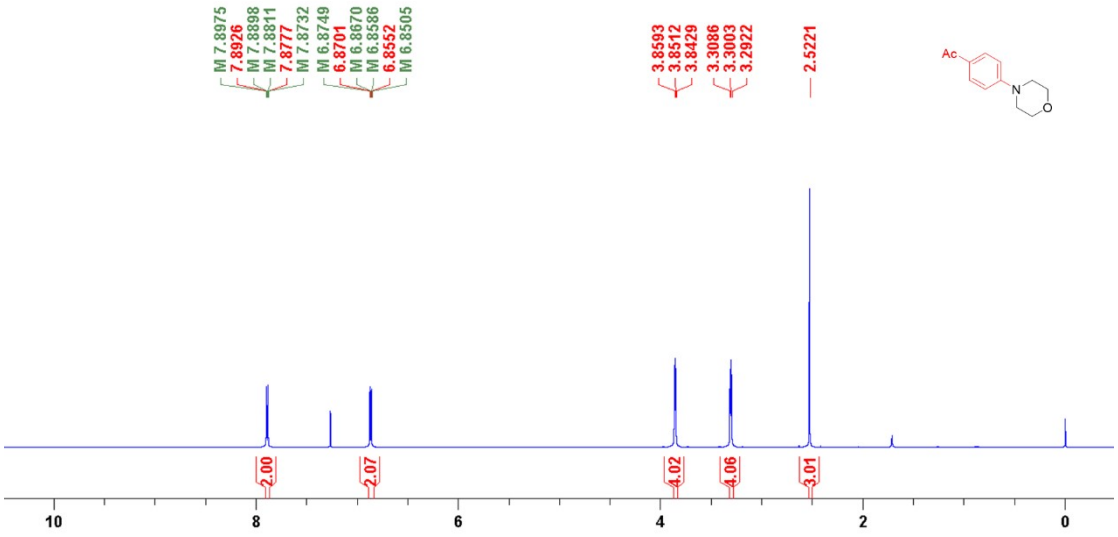

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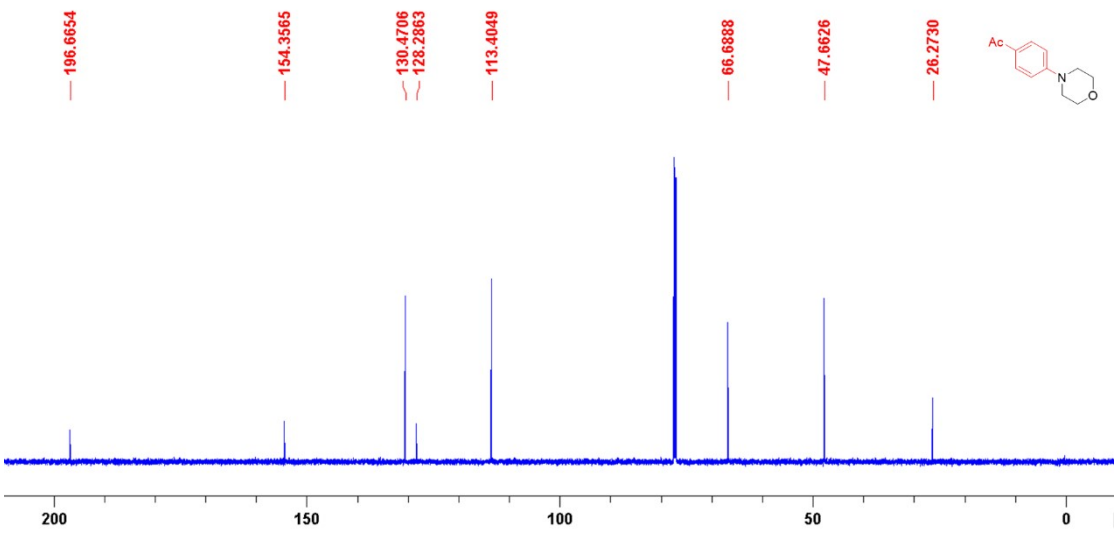

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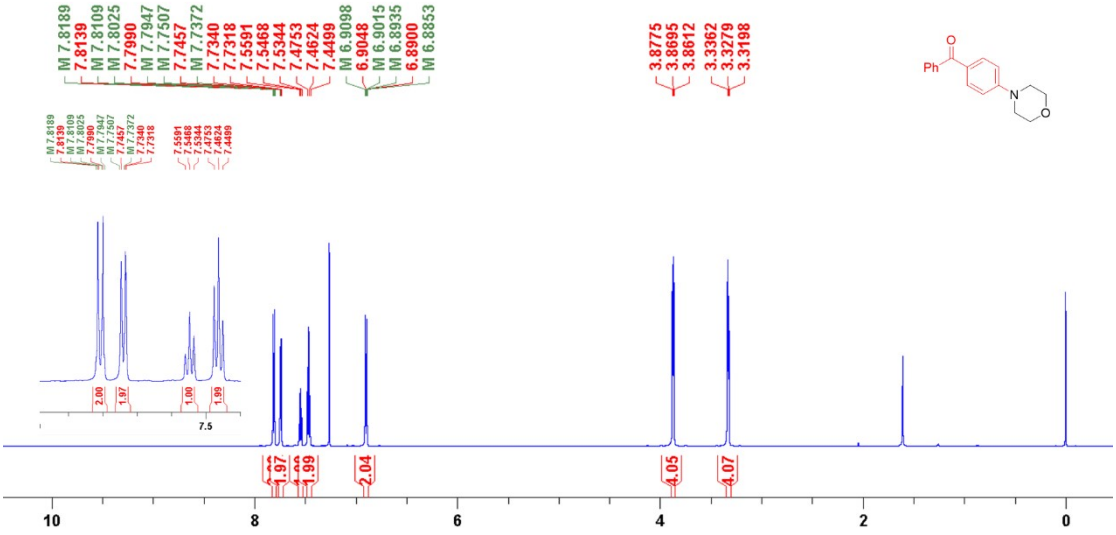

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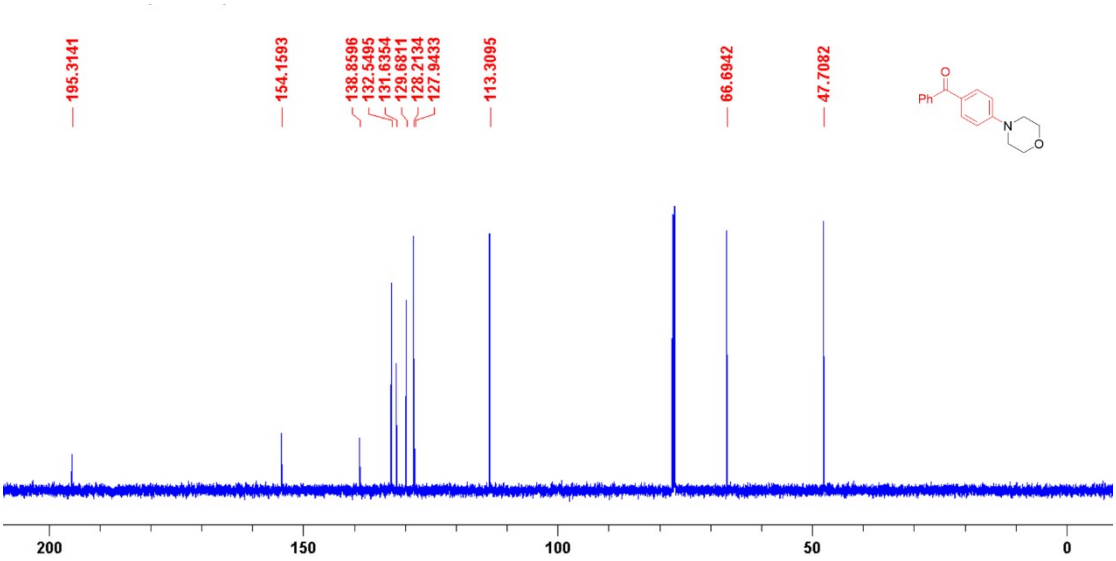

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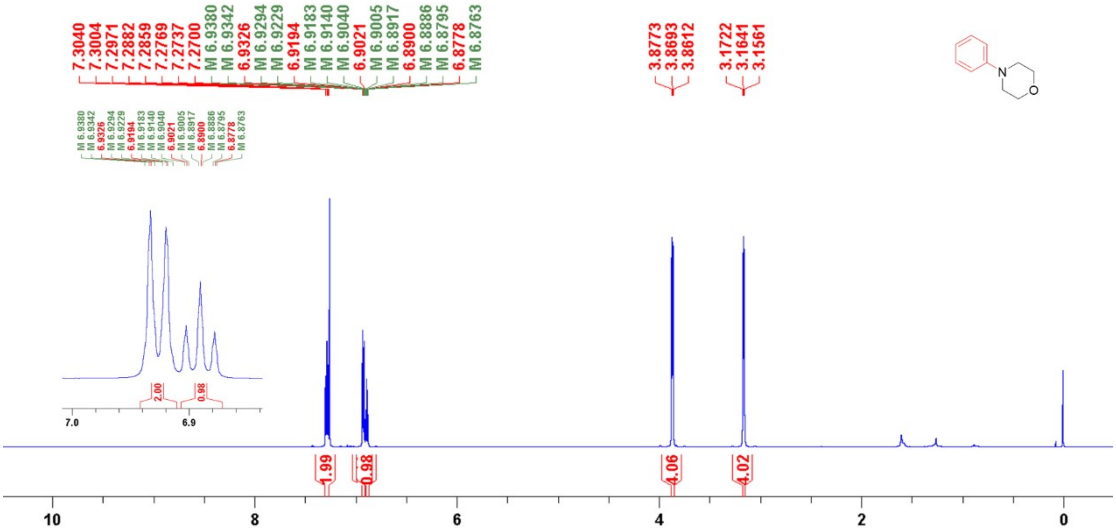

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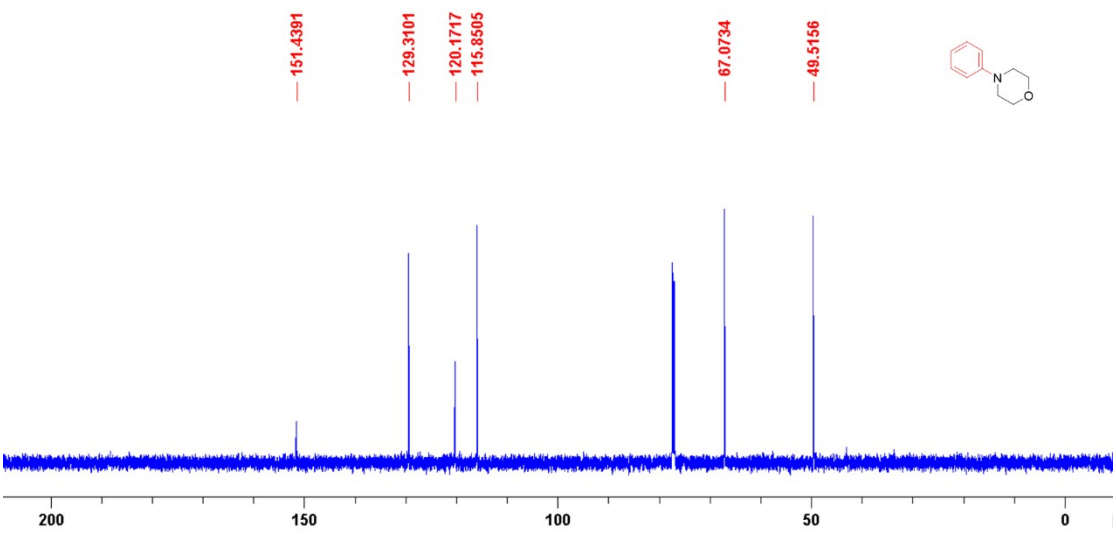

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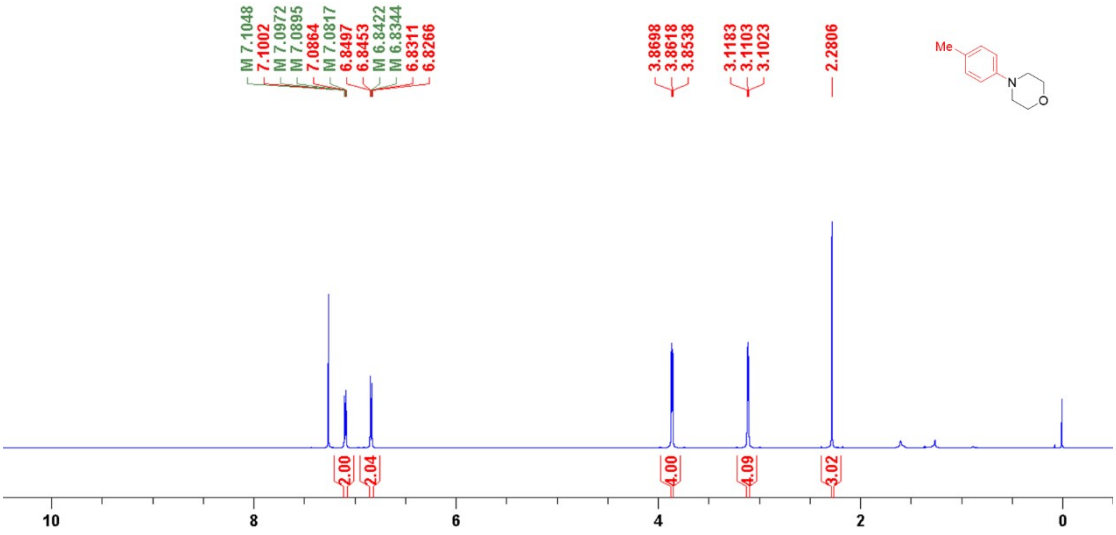

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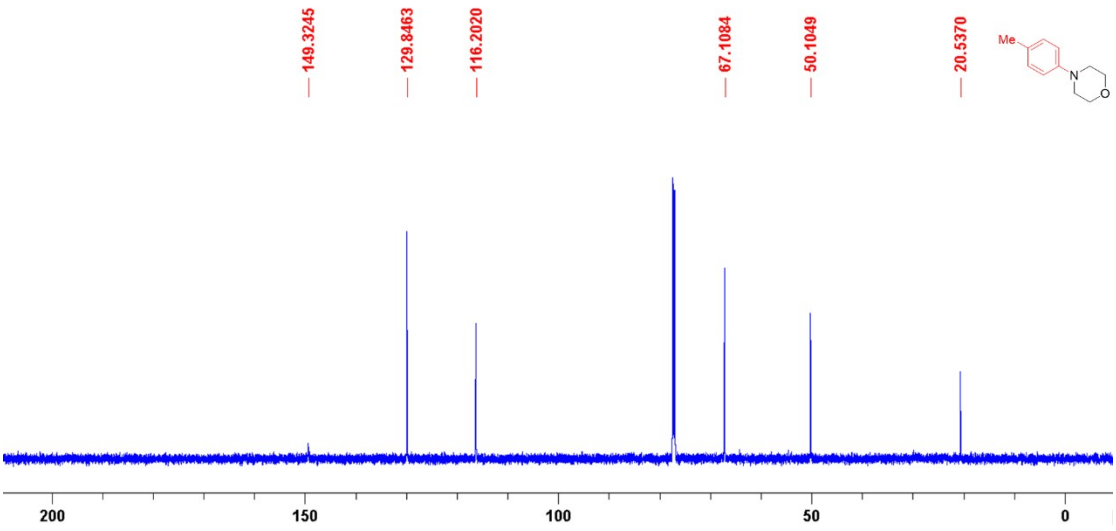

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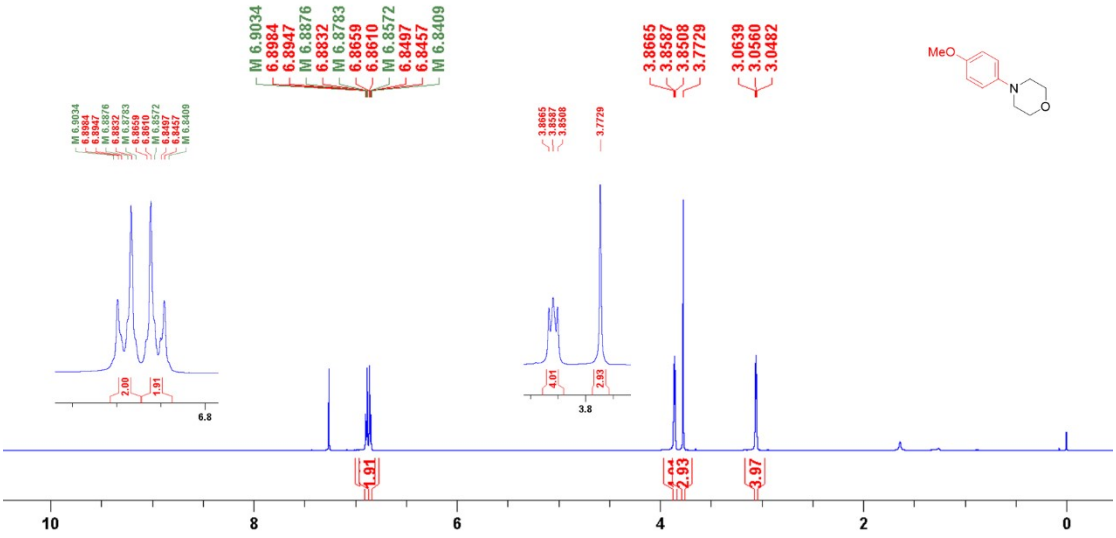

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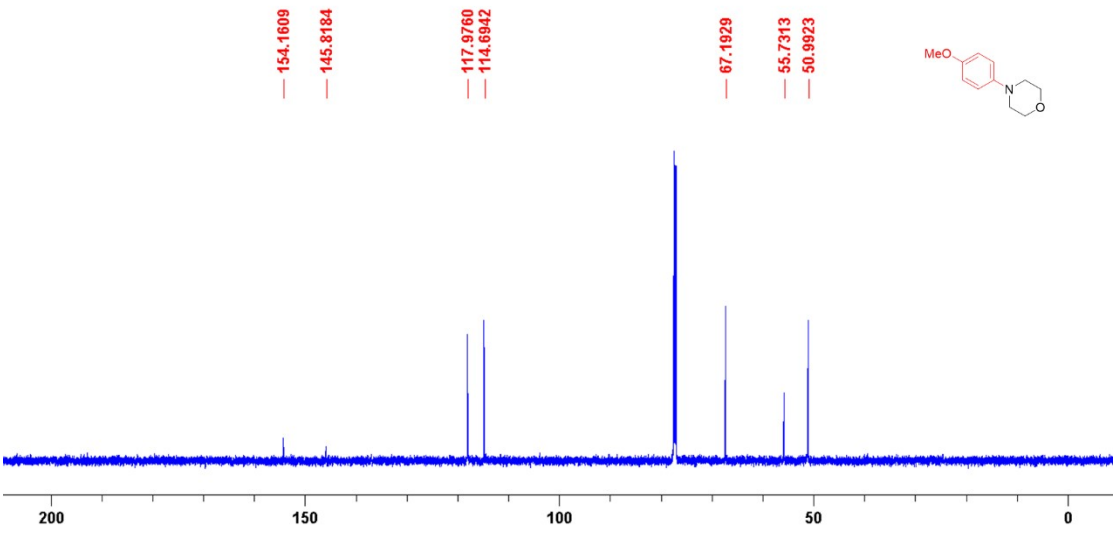

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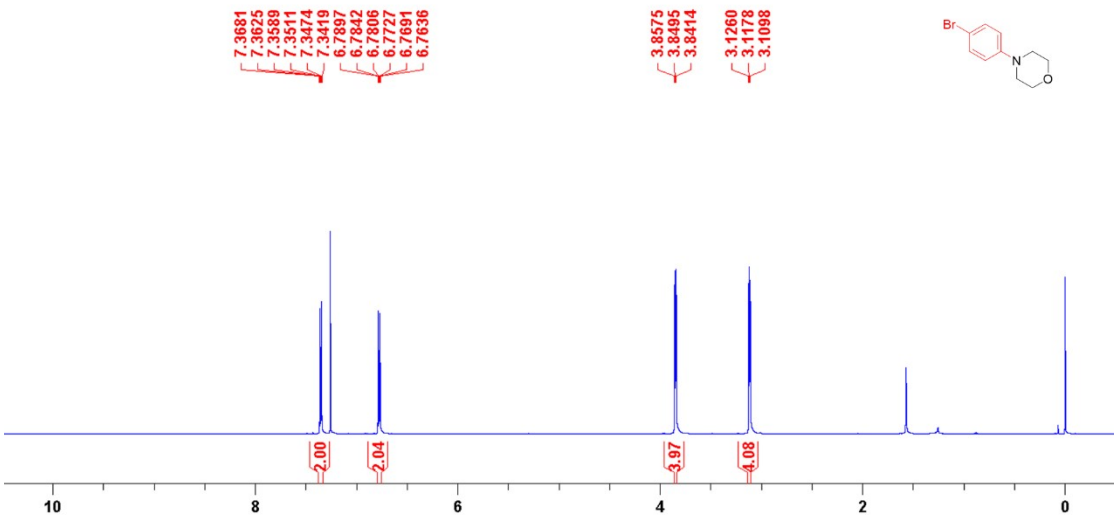

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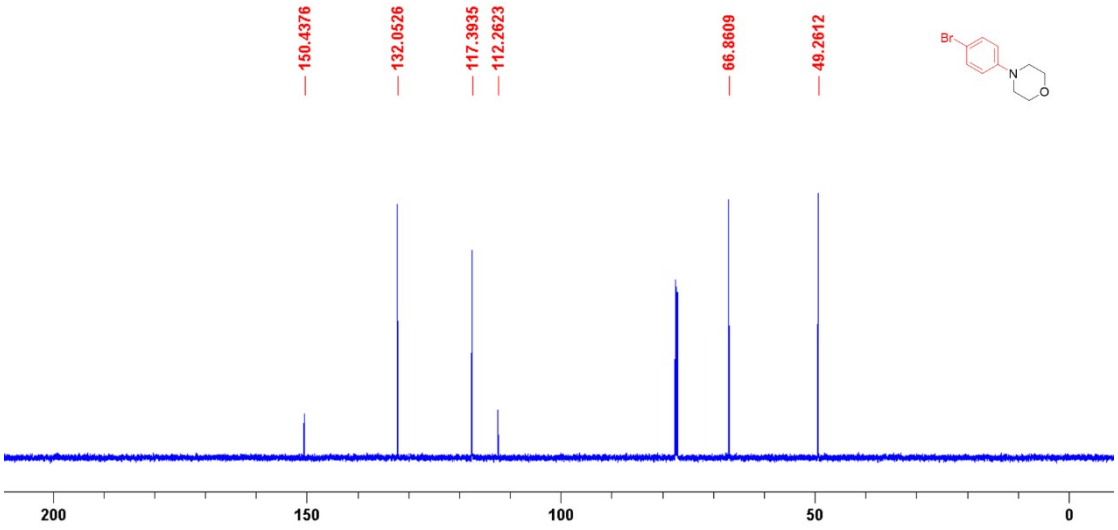

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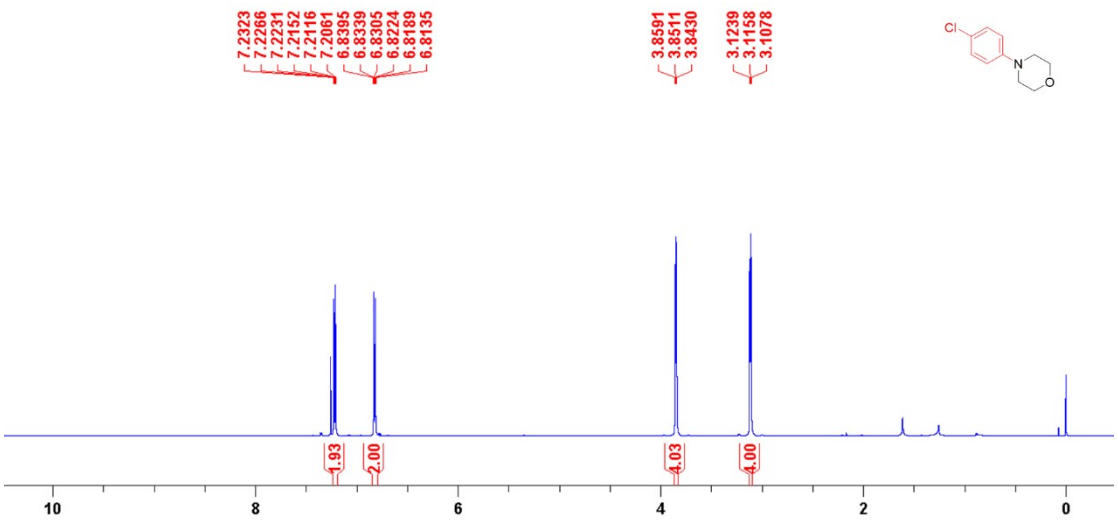

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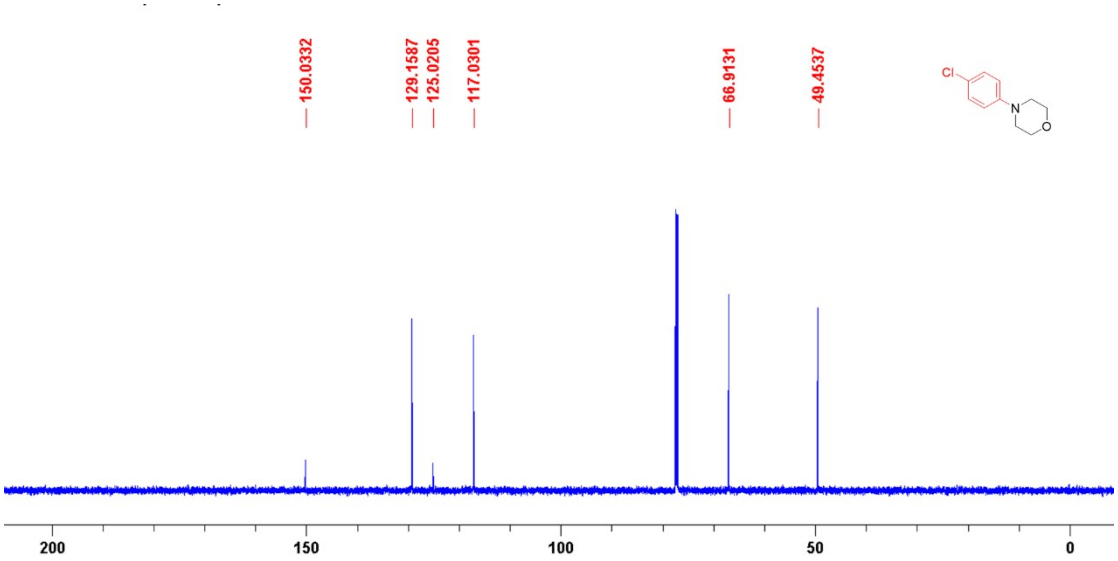

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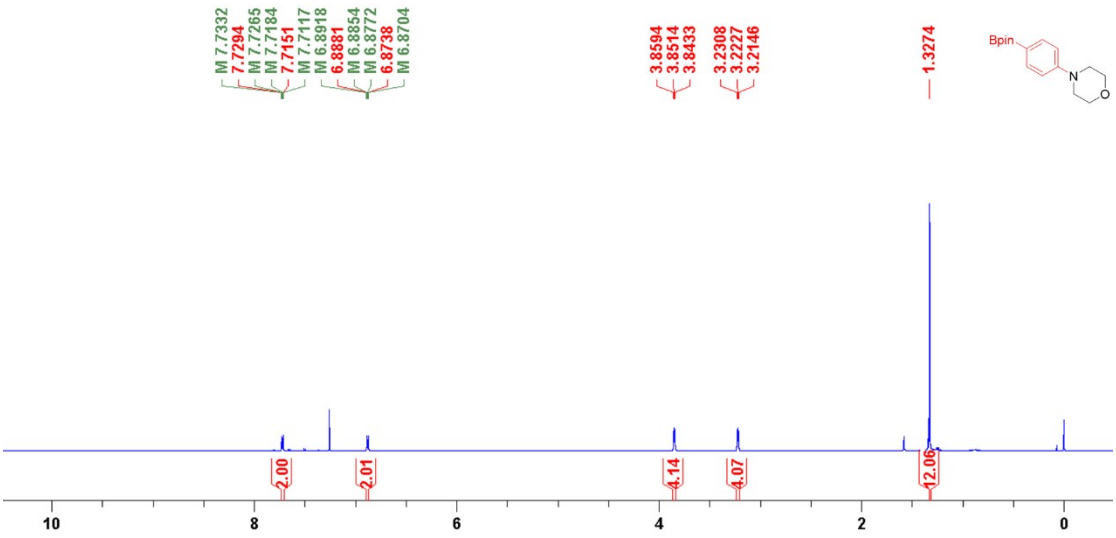
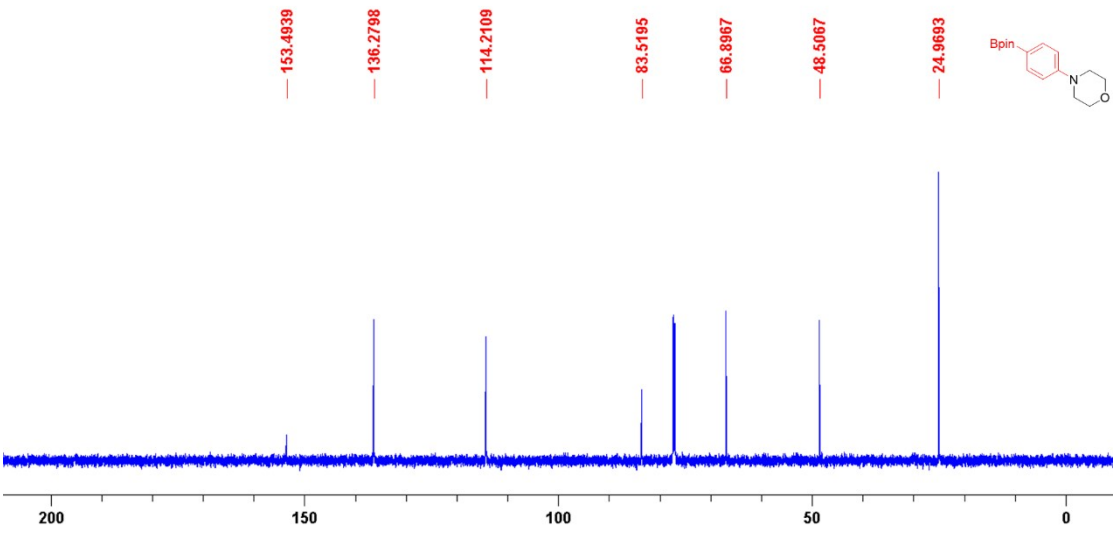
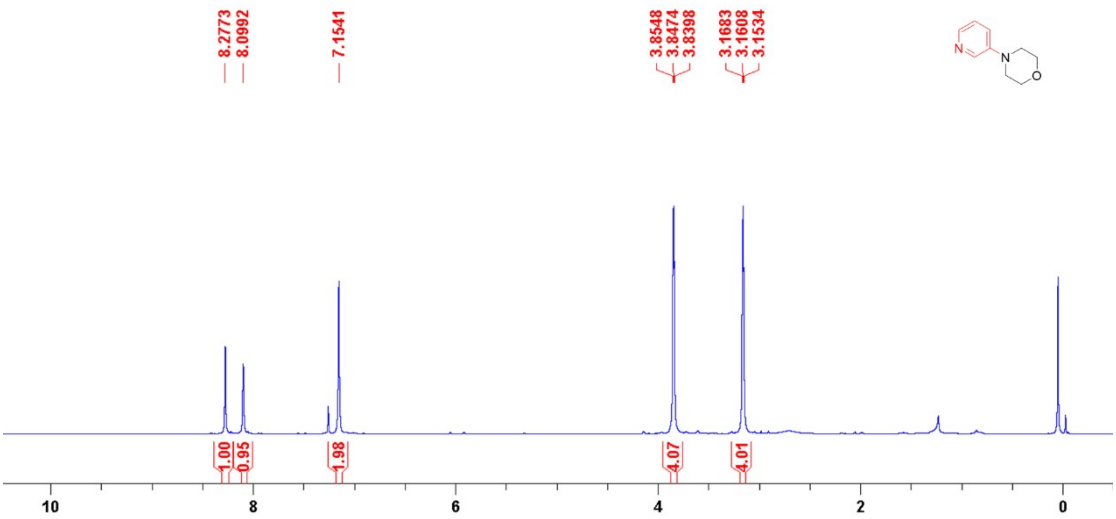


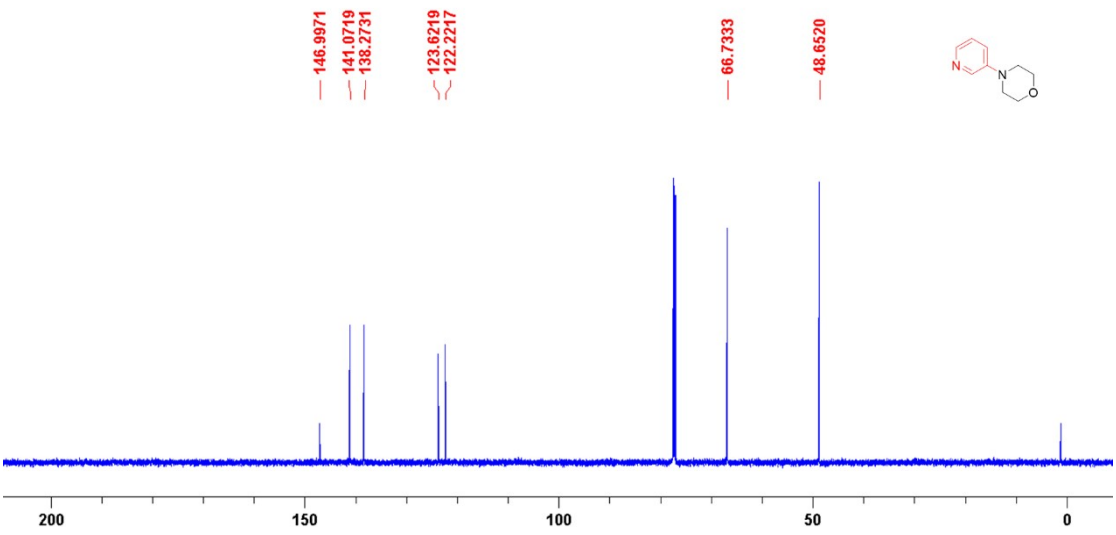
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **14**.



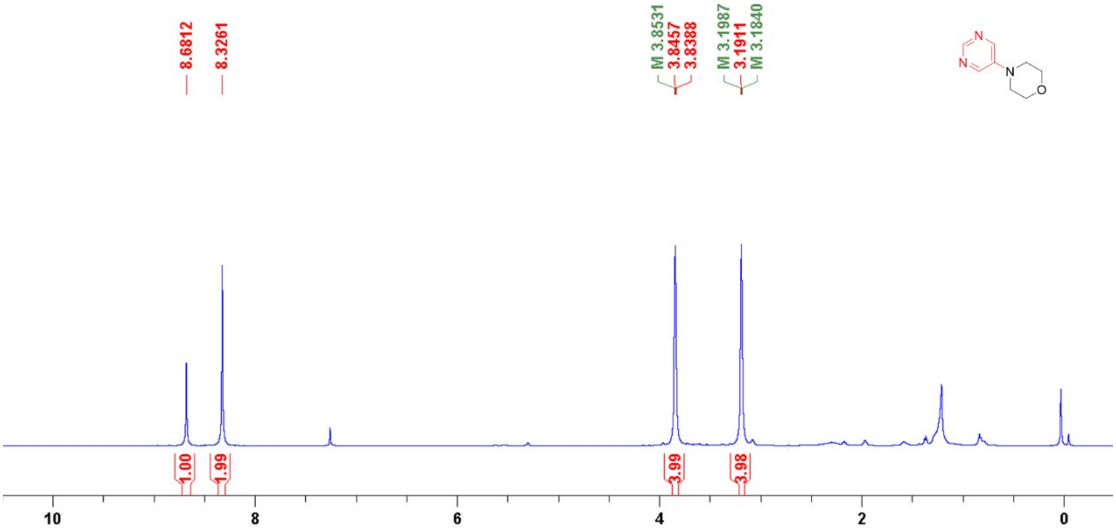
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **14**.



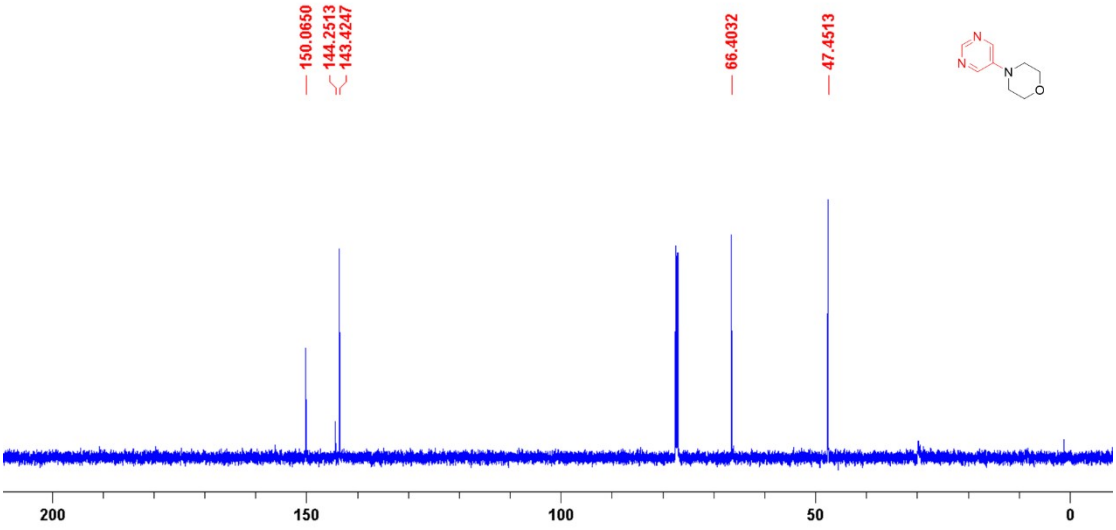
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **15**.



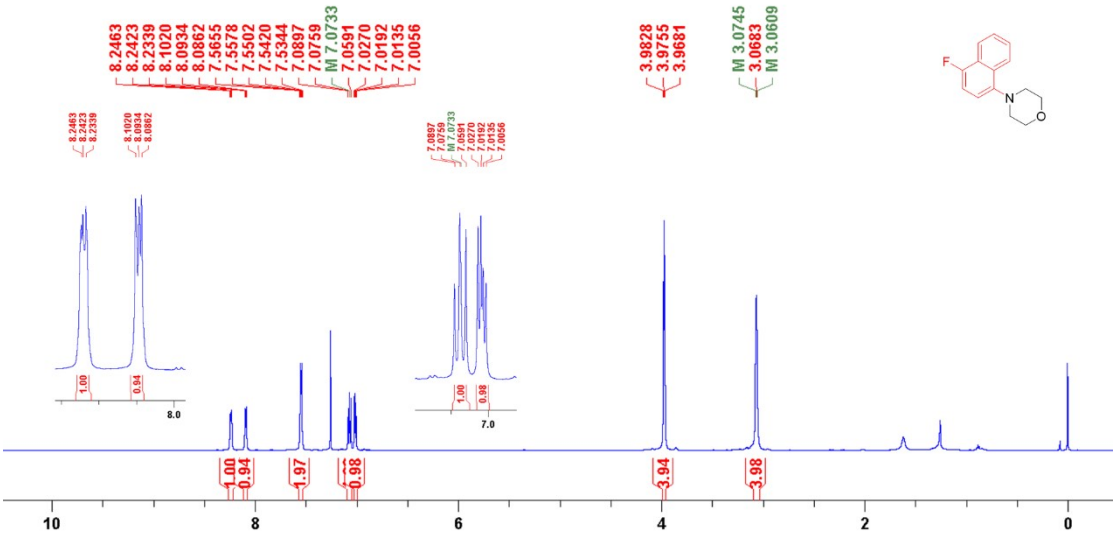
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **15**.



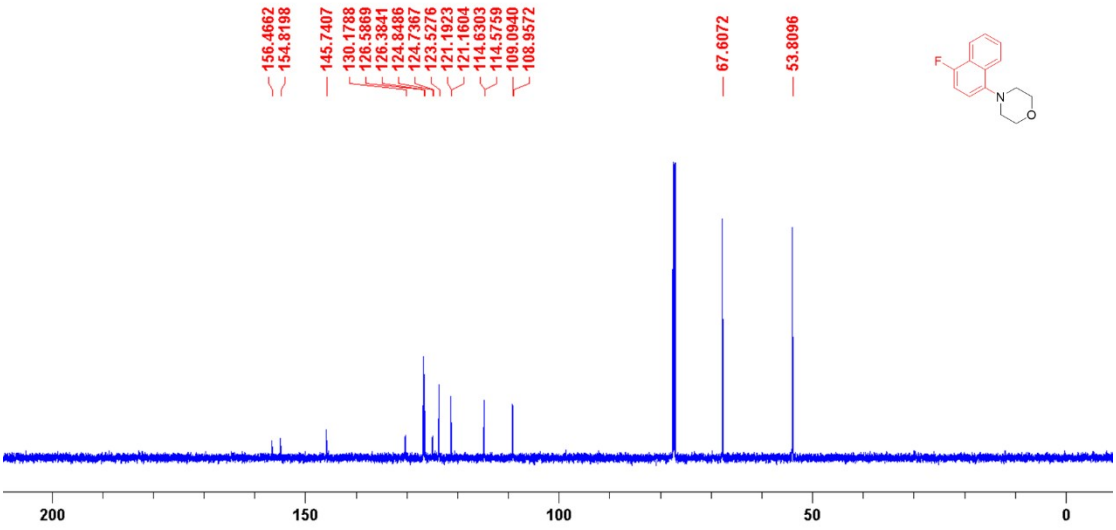
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **16**.



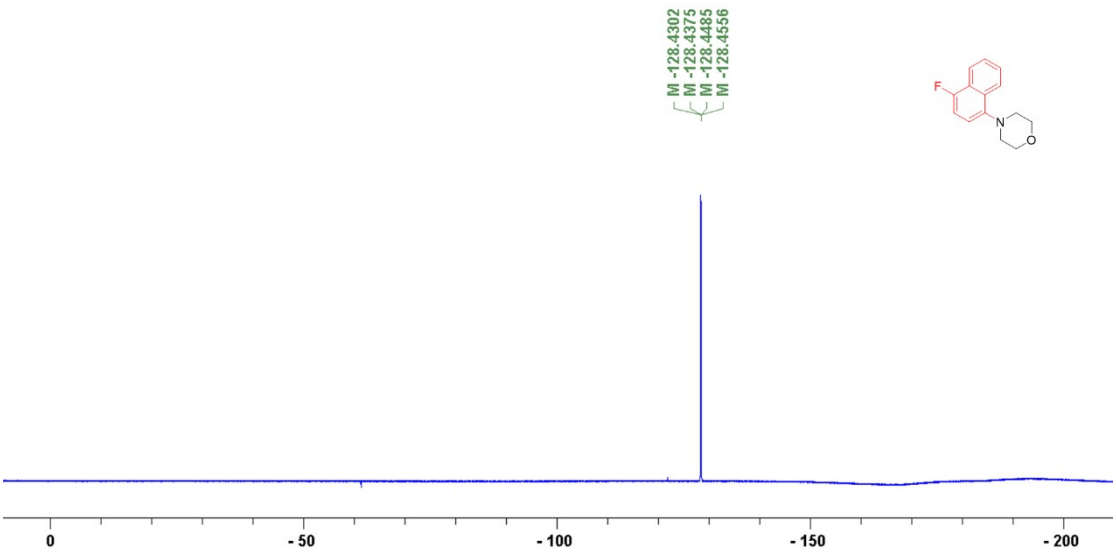
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **16**.



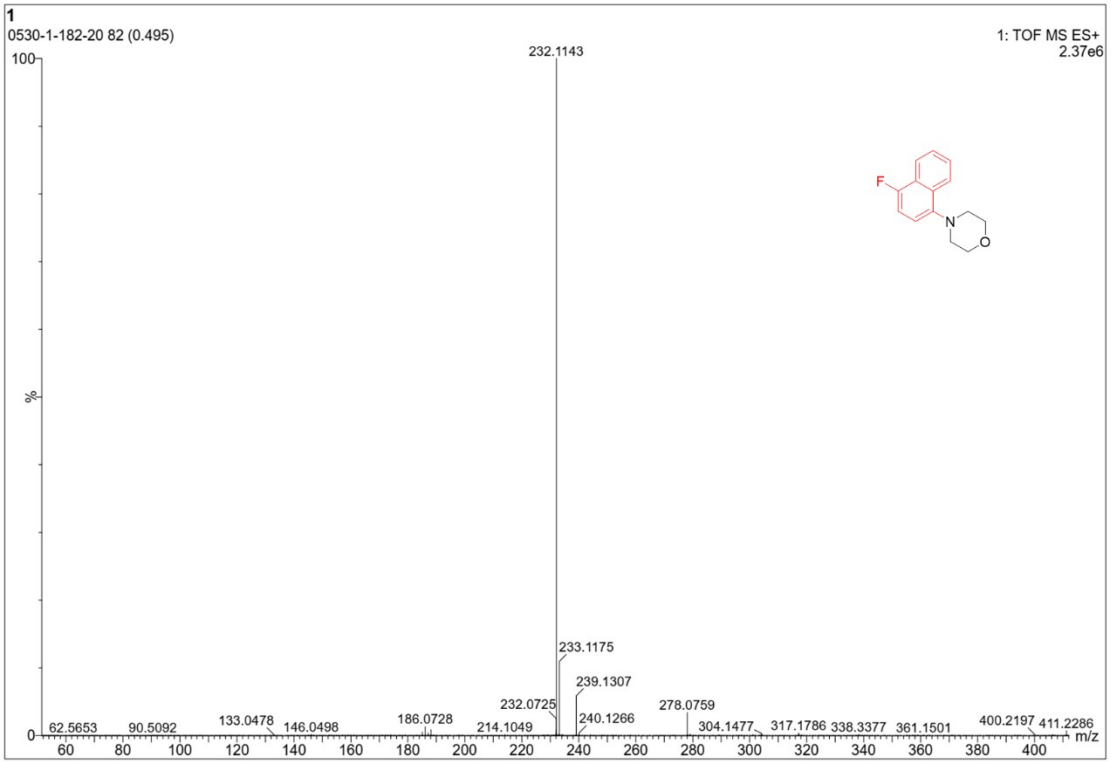
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **17**.



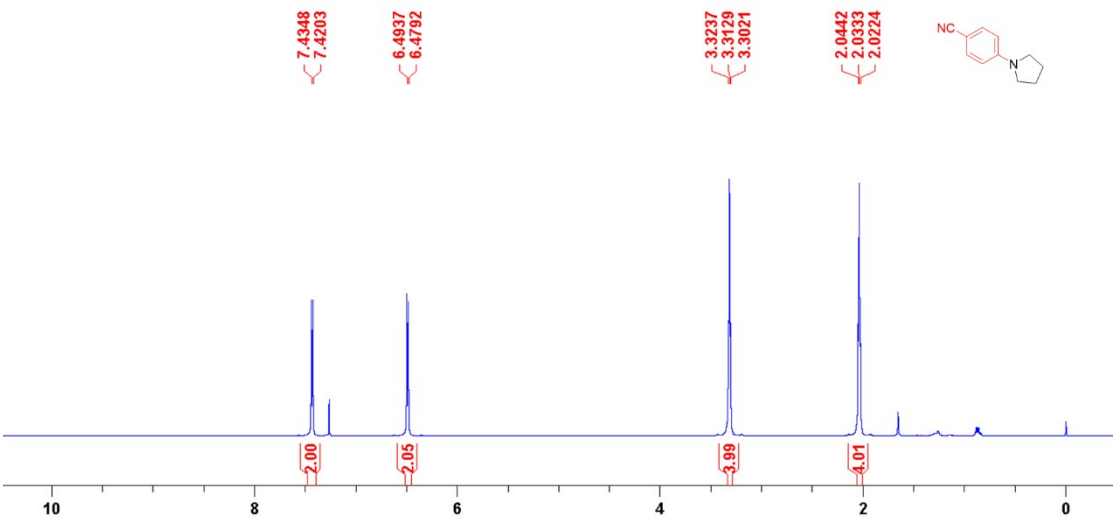
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **17**.



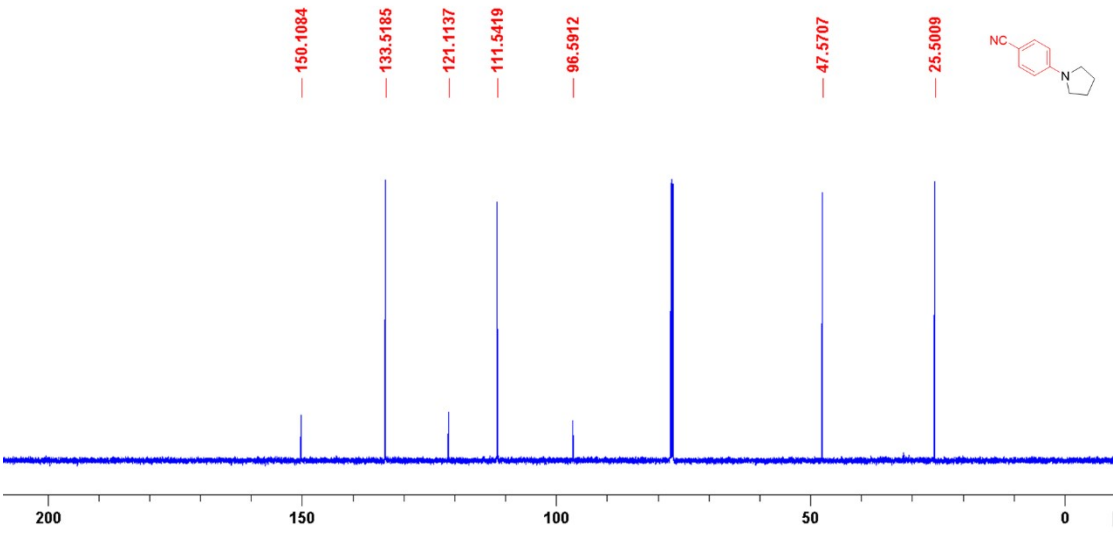
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **17**.



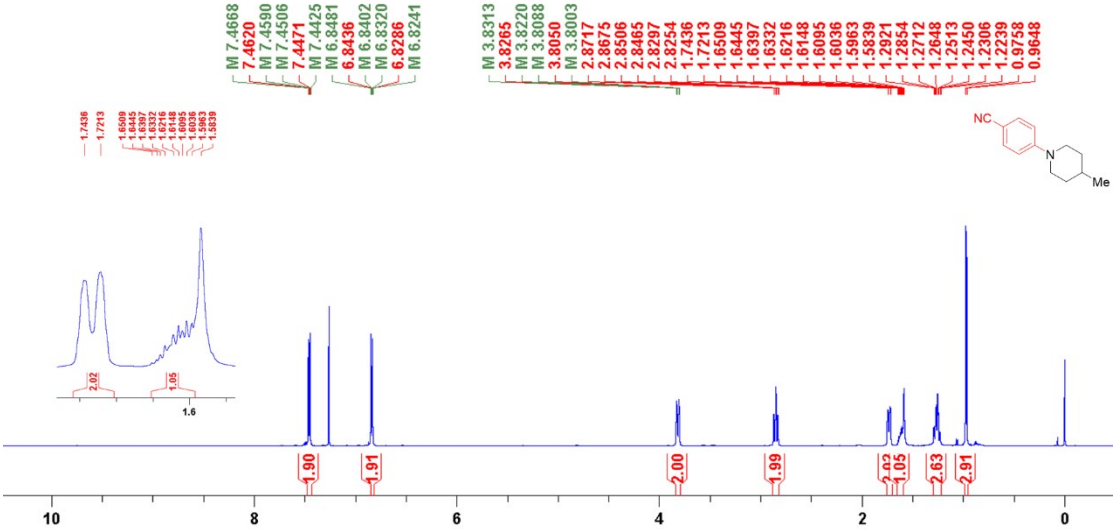
HR-MS (ESI) spectra of **17**.



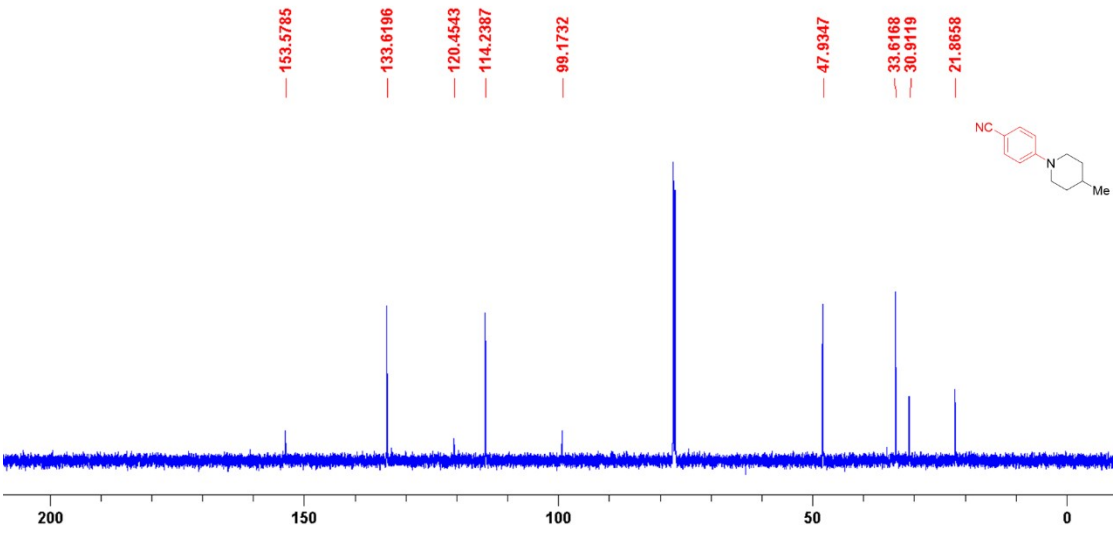
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **18**.



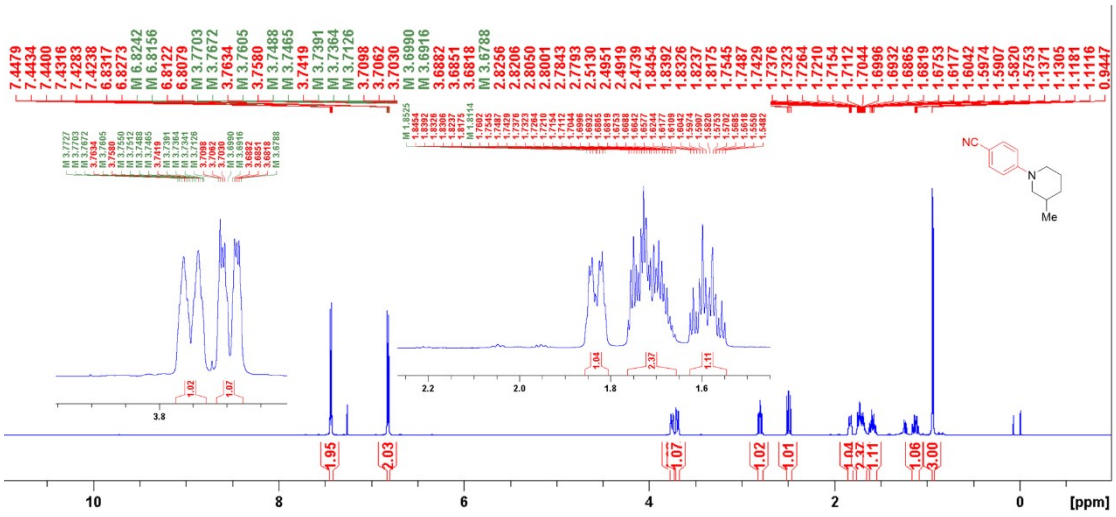
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **18**.



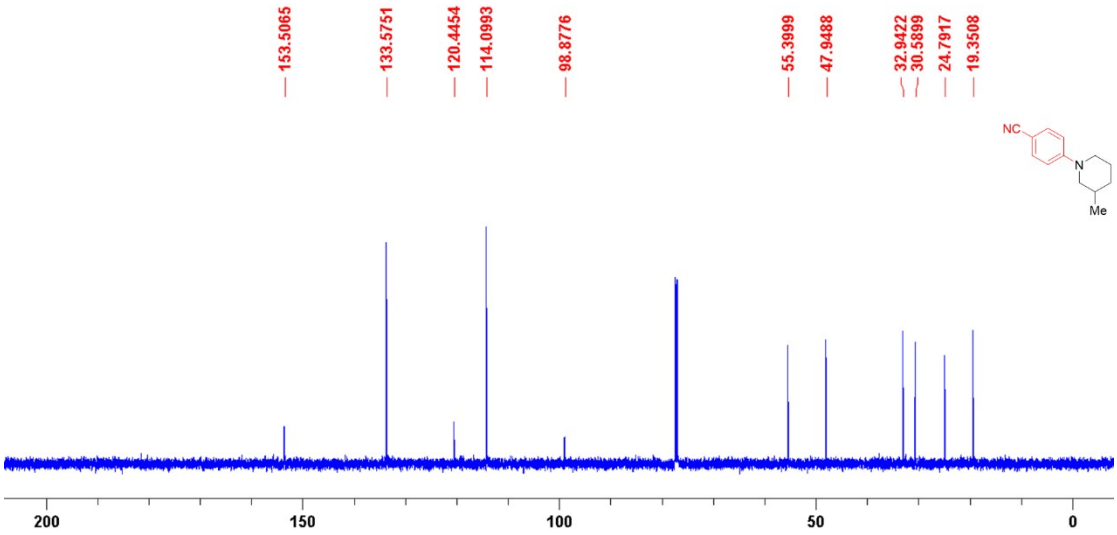
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **19**.



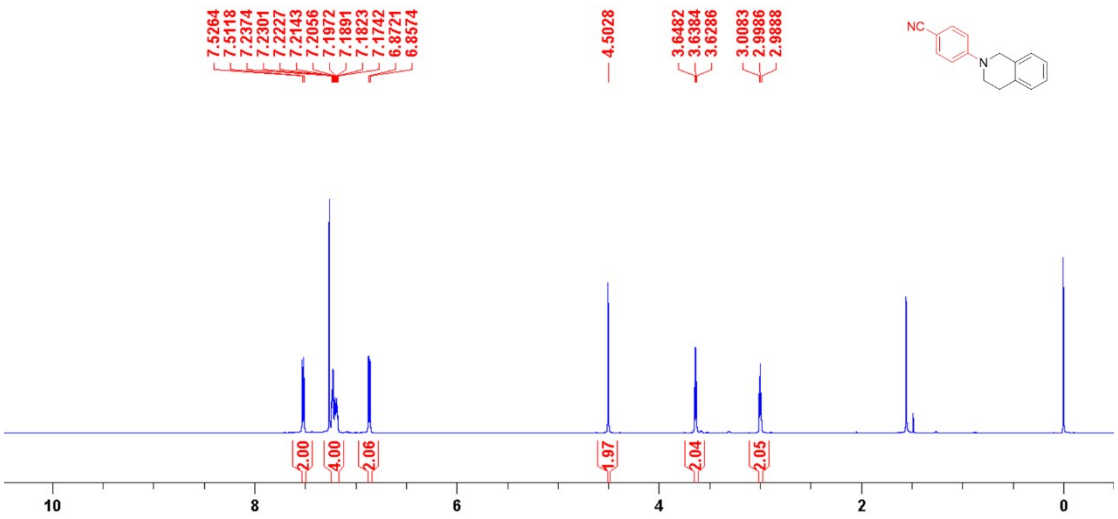
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **19**.



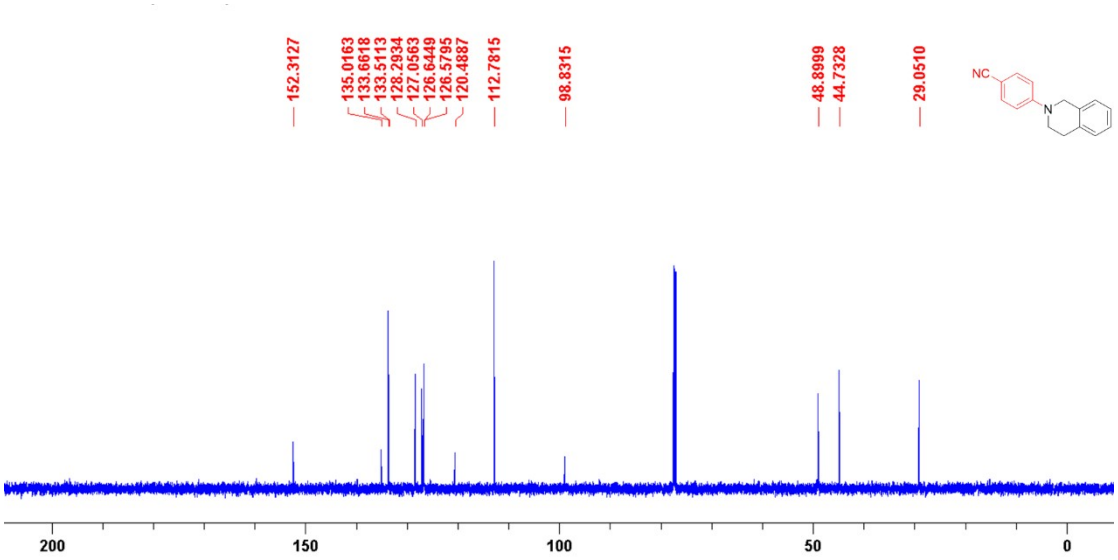
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **20**.



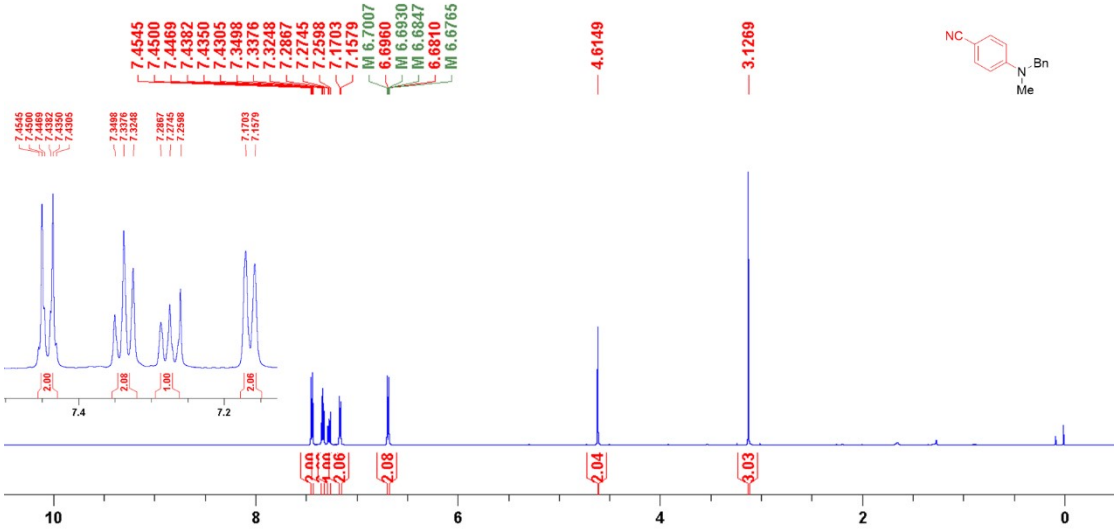
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **20**.



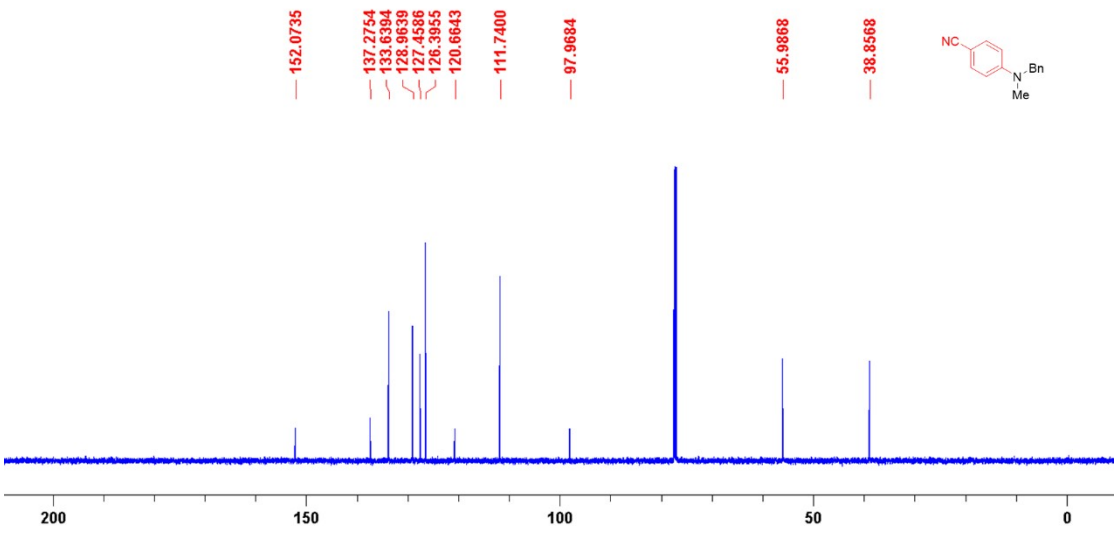
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **21**.



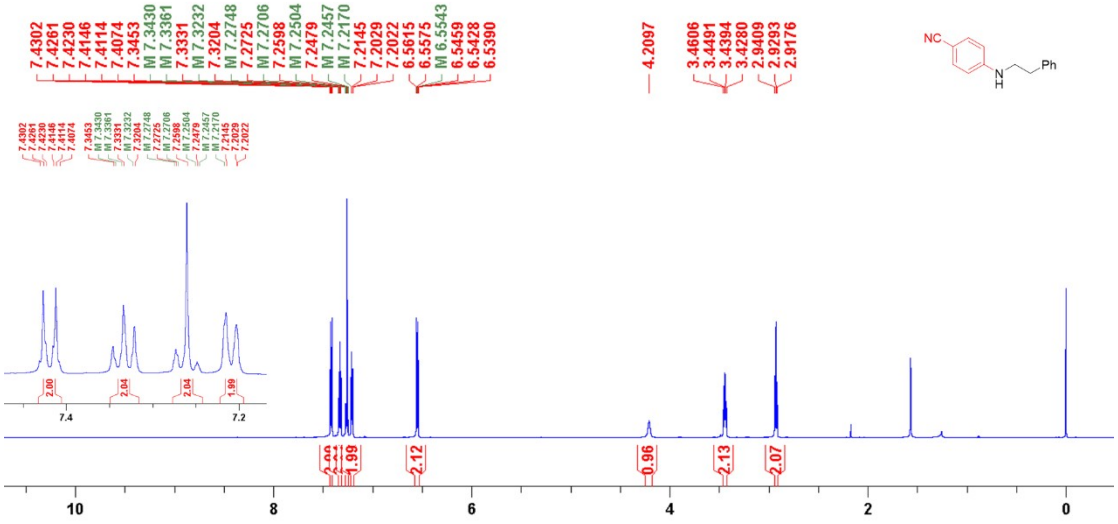
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **21**.



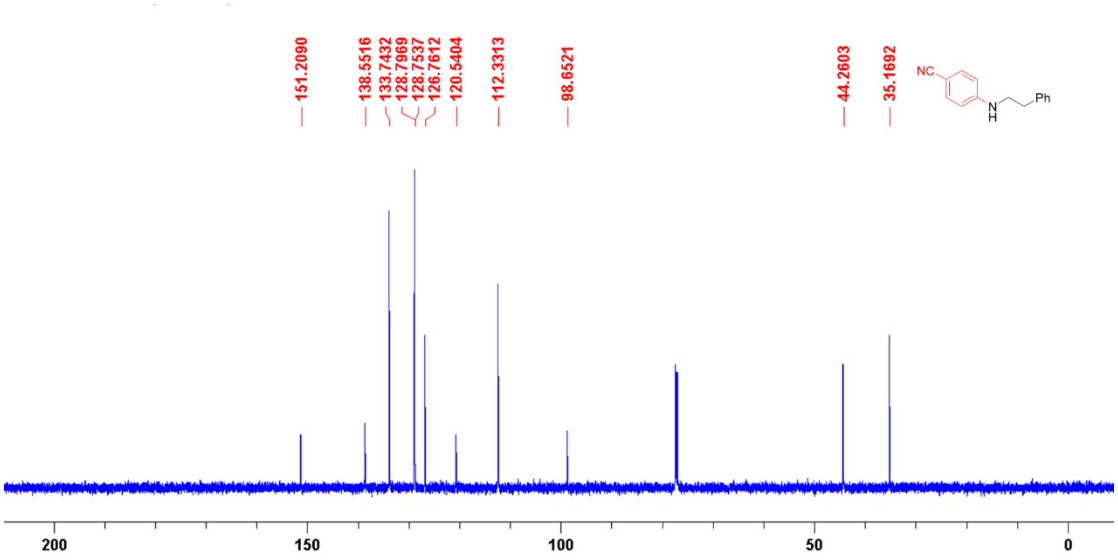
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **22**.



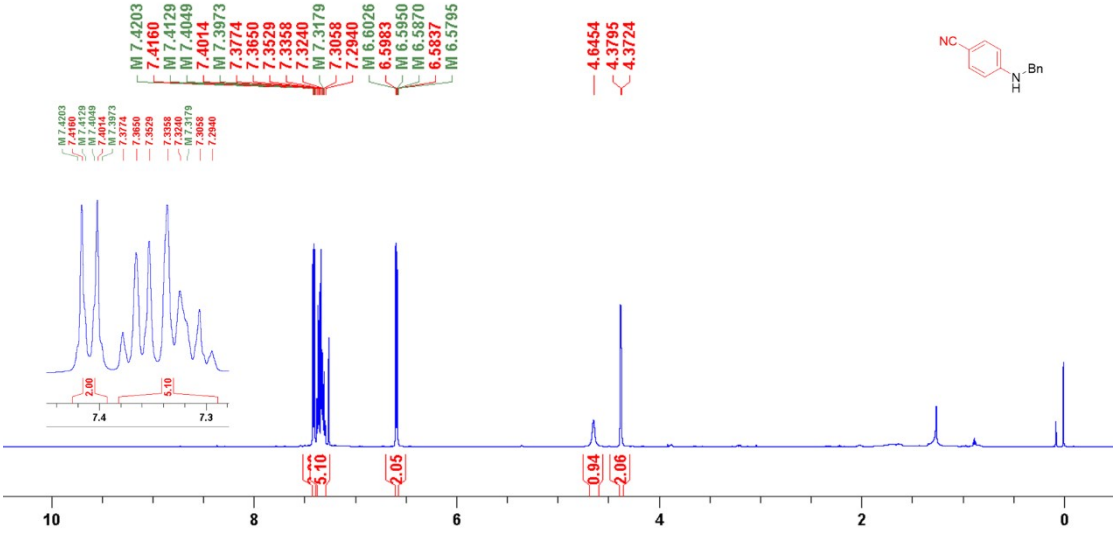
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **22**.



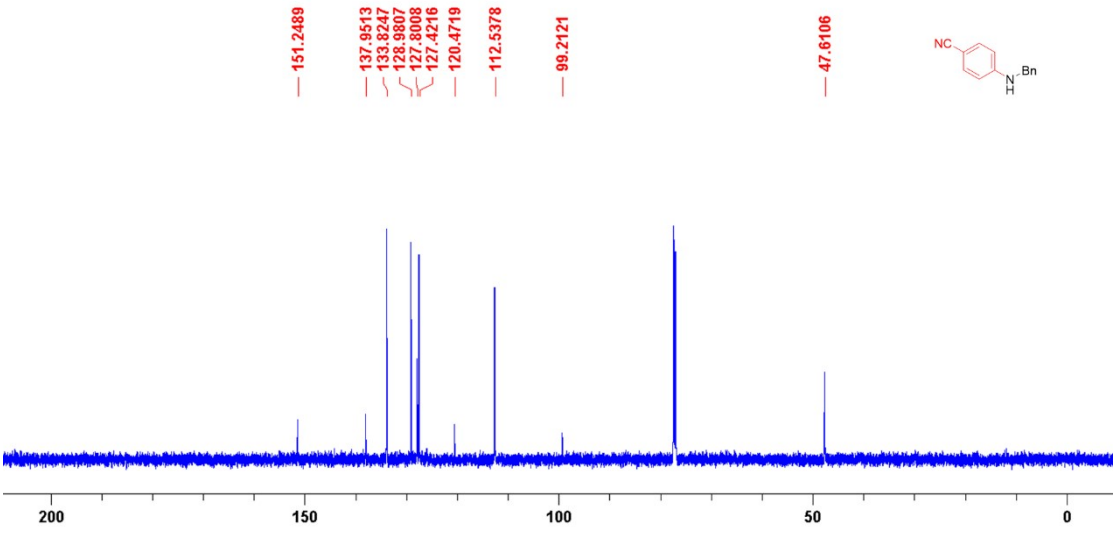
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **23**.



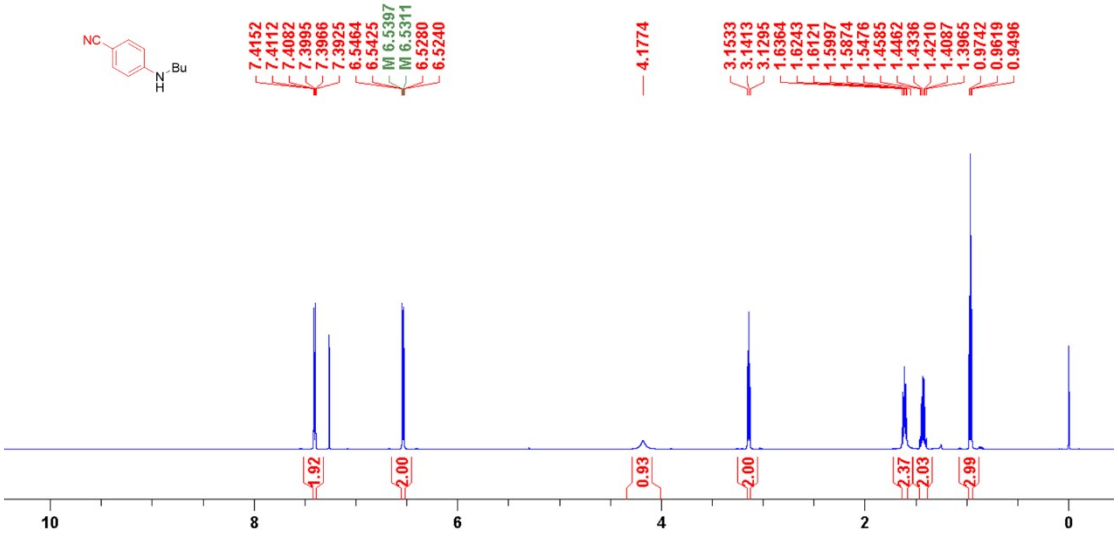
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **23**.



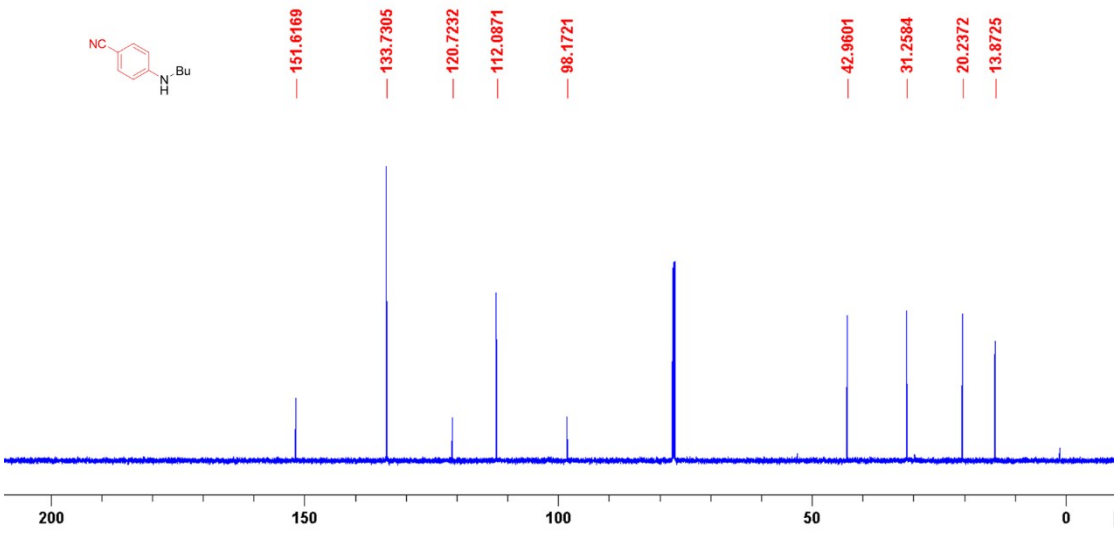
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **24**.



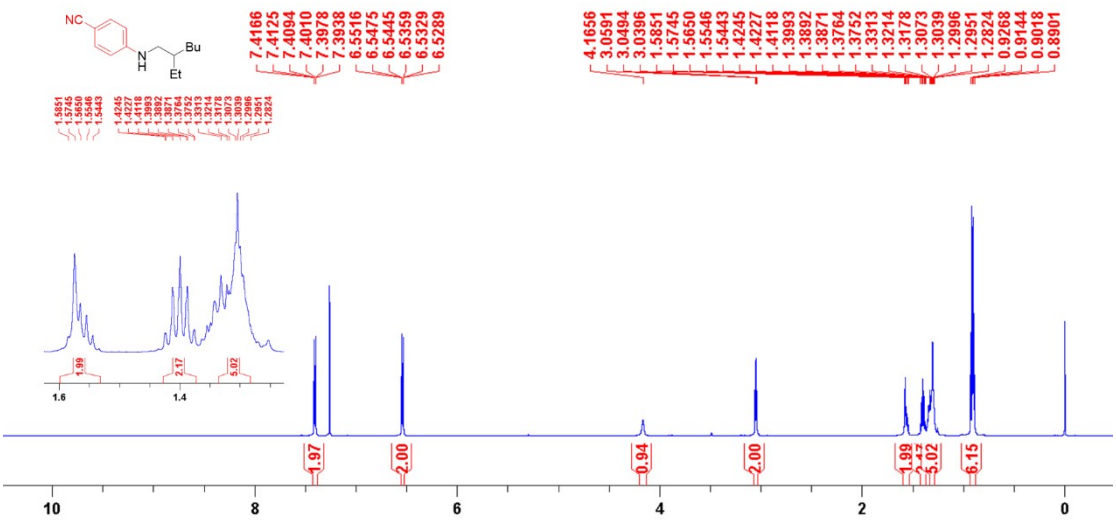
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **24**.



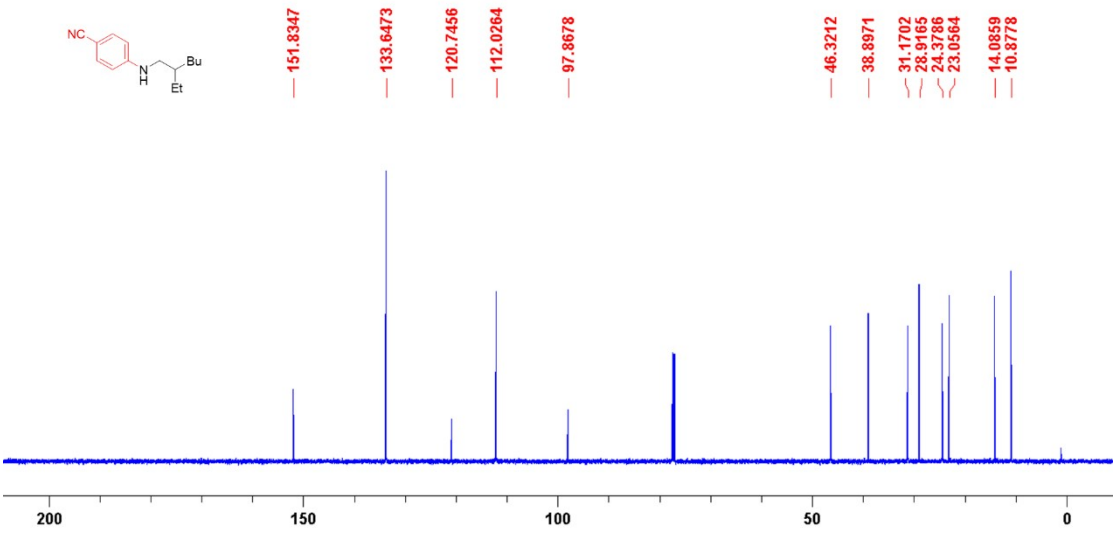
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **25**.



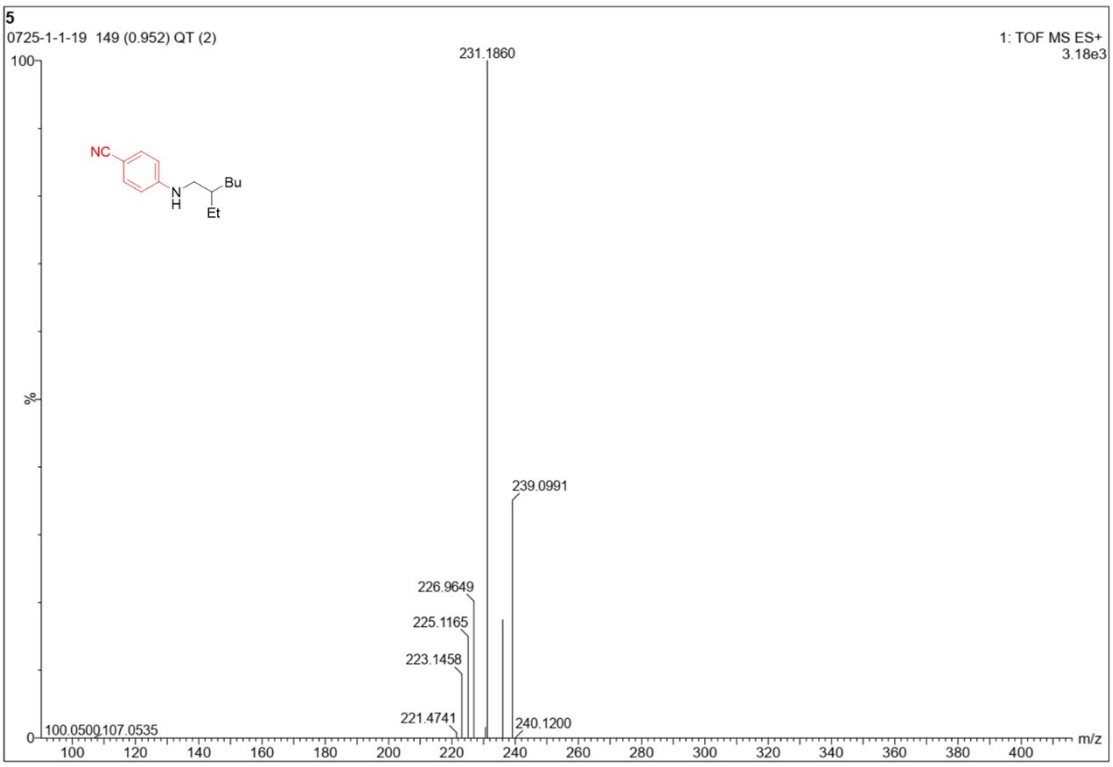
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **25**.



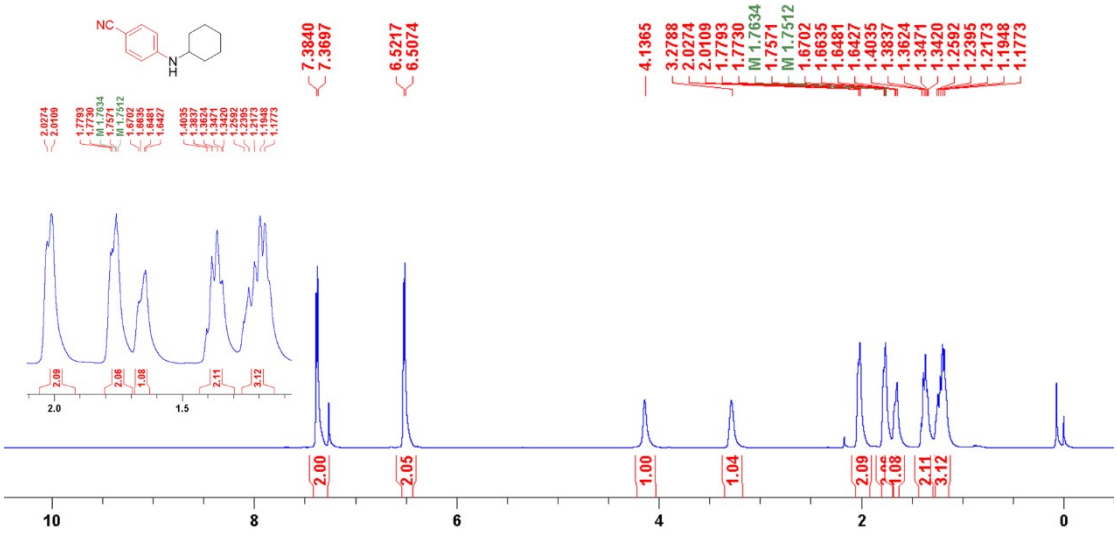
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **26**.



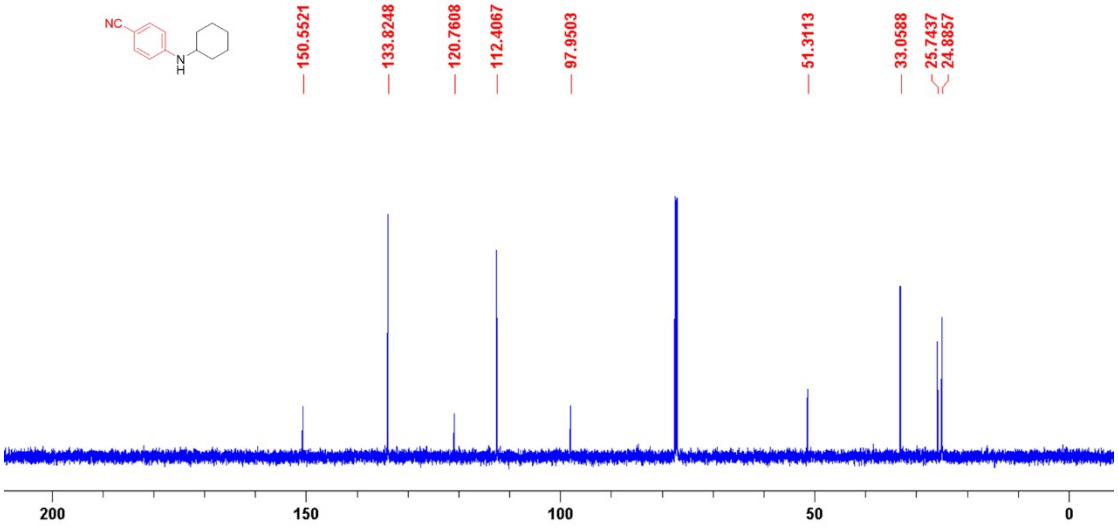
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **26**.



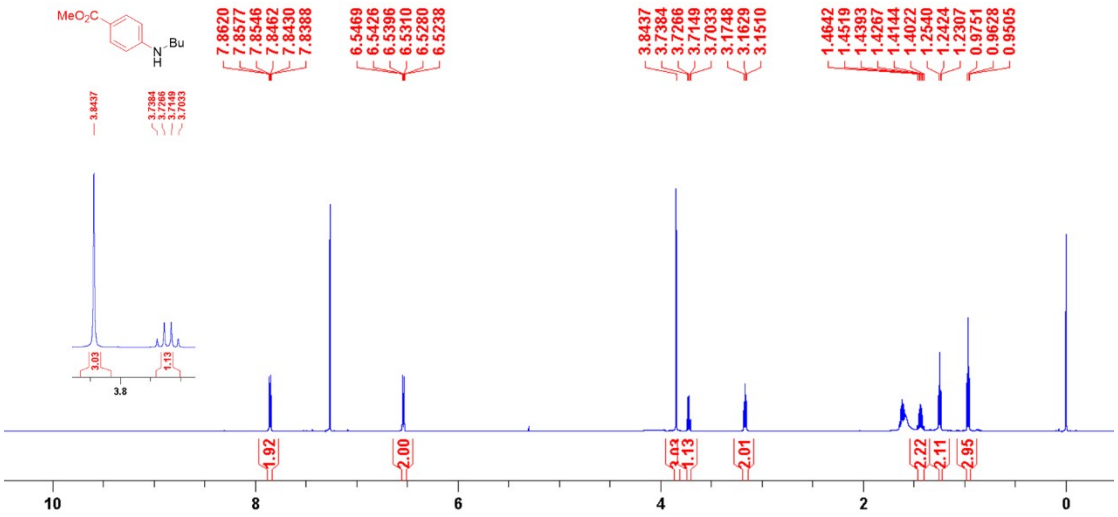
HR-MS (ESI) spectra of **26**.



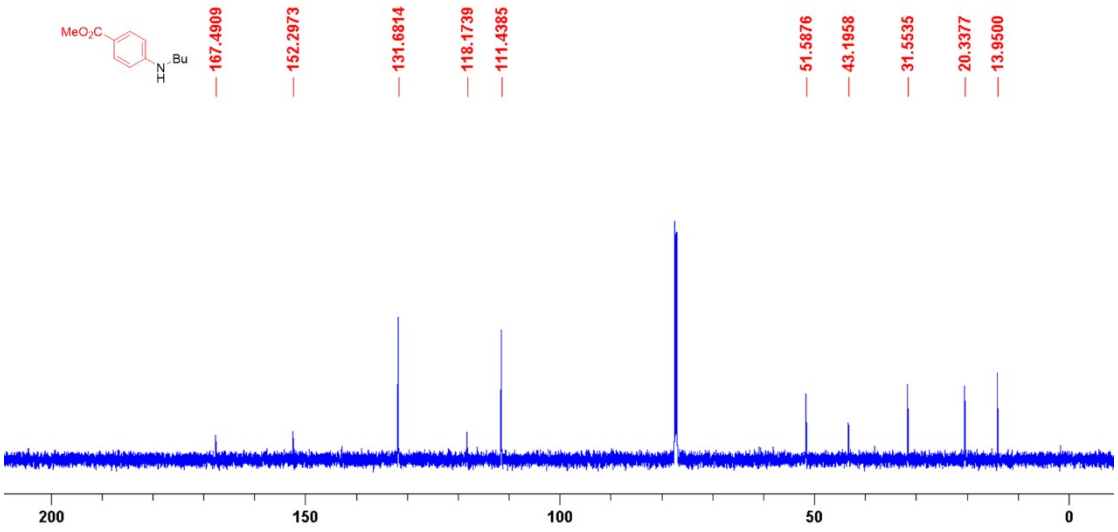
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **27**.



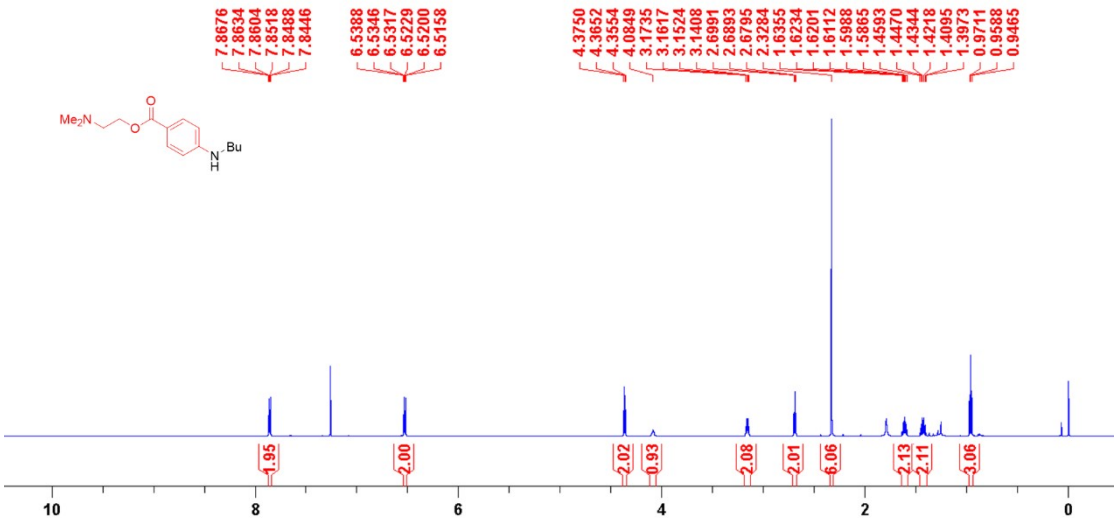
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **27**.



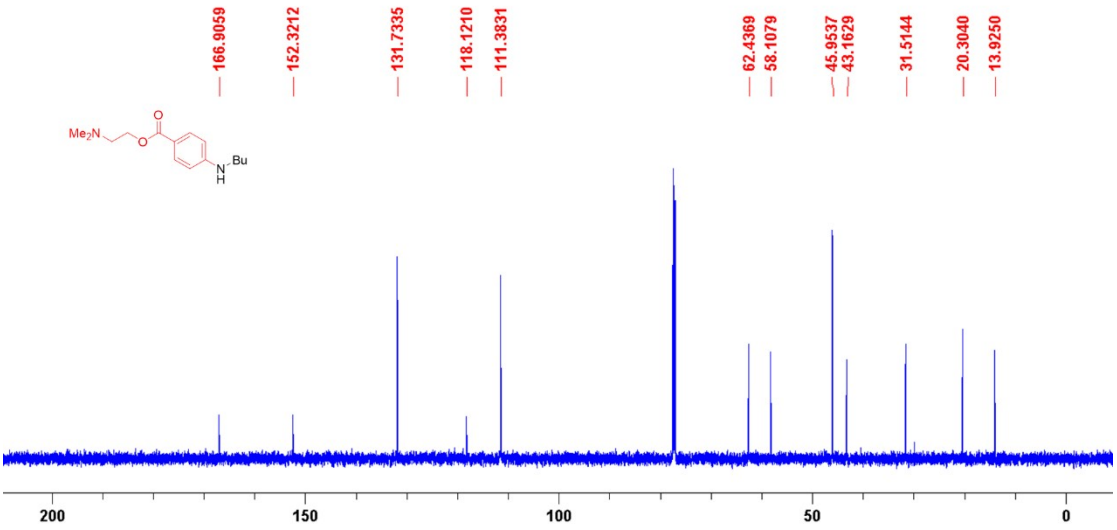
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **28**.



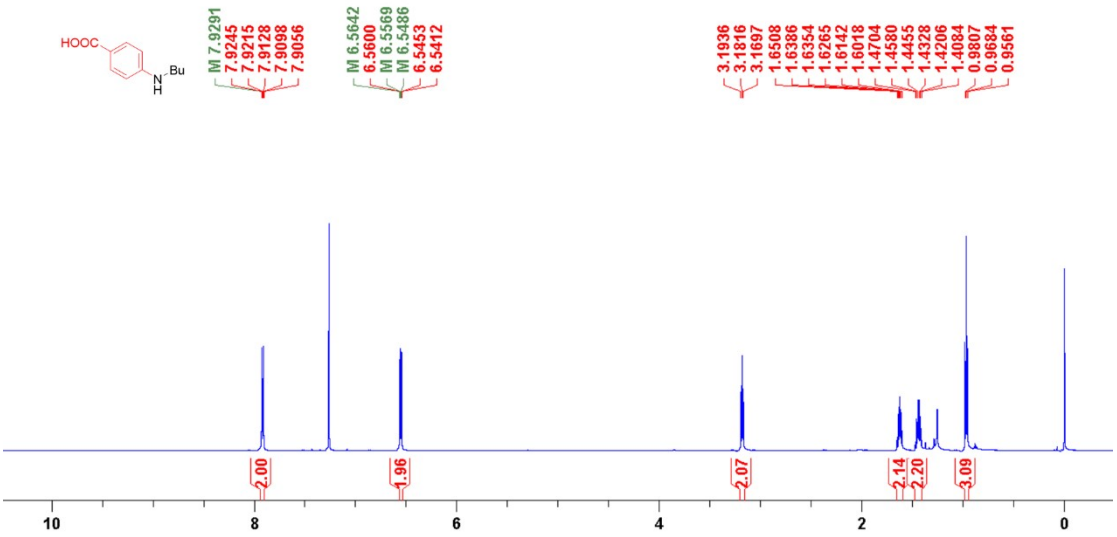
^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **28**.



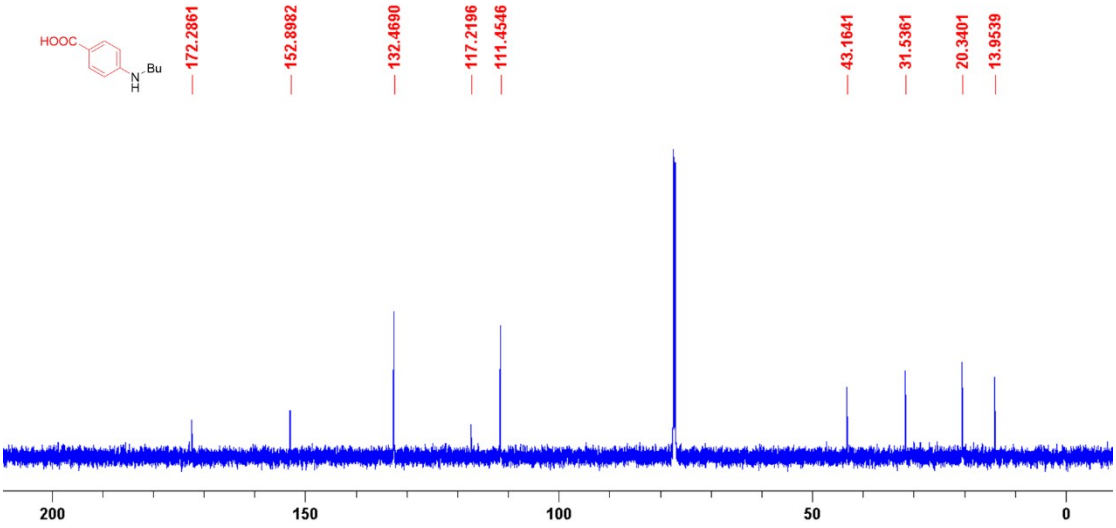
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **29**.



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of **29**.



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of acid intermediate.



^{13}C NMR (151 MHz, $CDCl_3$) spectrum of acid intermediate.