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Electronic Supplementary Information for

"One-pot" synthesis of amidoxime via Pd-catalyzed cyanation and amidoximation

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I. General Information

a. Materials

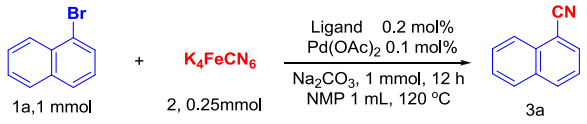
All reactions were carried out in oven-dried Schlenk tubes under an argon or nitrogen atmosphere (purity ≥99.999%).The following chemicals were purchased and used as received: LiO^tBu , Na_2CO_3, K_2CO_3(99.9%, Alfa-Aesar), KO^tBu, NaO^tBu (99%, Acros), Aryl bromides (Alfa-Aesar or Aldrich), $Pd(OAc)_2$, $Pd_2(dba)_3$, DPPF, $P(Cy)_3$, x-phos, s-phos(Aldrich), $K_4[Fe(CN)_6 \cdot 3H_2O$, $NH_2OH \cdot HCl$ (Alfa-Aesar). Anhydrous DMF (Acros) and anhydrous NMP (Acros) were stored over 4 Å molecular sieves under an argon atmosphere in a septum-capped bottle. All other reagents and solvents mentioned in this text were purchased from commercial sources and used without purification.

b. Analytical Methods

^1H, ^{13}C and ^{19}F-NMR spectra were recorded either on Bruker Avance 400 or Varian Mercury 400 spectrometer at ambient temperature in $CDCl_3$ unless otherwise noted. Data for ^1H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ^{13}C-NMR are reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed either on Thermo Scientific AS 3000 Series GC-MS System or Agilent 6890N gas chromatograph coupled to an Agilent 5973 inert mass selective detector. HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. Elementary Analysis was carried out on Elementar Vario EL III elemental analyzer.

II. Experimental Procedures and Spectral Data

Pd-catalyzed cyanation of 1-Bromonaphthalene（1a）[1]

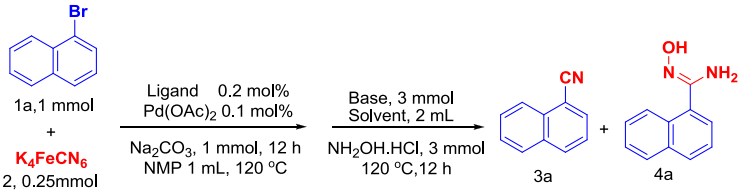


Entry	Catalyst (0.1 mol%)	Ligand (0.2 mol %)	Base	Solvent	Temp. (°C)	Yield (%)[a]
1	$Pd(OAc)_2$	PPh_3	Na_2CO_3	NMP	120	24
2	$Pd(OAc)_2$	PCy_3	Na_2CO_3	NMP	120	61
3	**$Pd(OAc)_2$**	**dppf**	**Na_2CO_3**	**NMP**	**120**	**95**
4	$Pd(OAc)_2$	x-phos	Na_2CO_3	NMP	120	91
5	$Pd(OAc)_2$	s-phos	Na_2CO_3	NMP	120	92
6	$Pd(OAc)_2$	$P(t\text{-}Bu)_3$	Na_2CO_3	NMP	120	45
7	$Pd(OAc)_2$	dppm	Na_2CO_3	NMP	120	13
8	$Pd(OAc)_2$	dppf	Na_2CO_3	^{t}BuOH	120	18

[a] GC yields after 18 hours (average of two runs).

Experimental Procedures for Examples Described in Table 1.

In air, Pd-atalyst (0.001 mmol), Ligand (0.002 mmol), Na_2CO_3 (1 mmol), and $K_4[Fe(CN)_6]$ (0.25 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). NMP (1 mL) and 1-Bromonaphthalene (1 mmol) were added in turn under an argon atmosphere. The reaction mixture was stirred at 120 °C for 12h, then $NH_2OH{\cdot}HCl$ (3 mmol), base (3 mmol), solvent (2 mL) were added to the Schlenk tube. The reaction mixture was stirred at 120 °C for another 12h, then diluted with EtOAc, filtred through silica gel with copious washings (EtOAc), washed with water, concentrated, and purified by column chromatography.



Entry	Cat. (0.1 mol%)	Ligand (0.2 mol%)	Base	Solvent	Yield 3a (%)	Yield 4a (%)[b]
1	$Pd(OAc)_2$	dppf	Na_2CO_3	NMP	94	Trace
2	$Pd(OAc)_2$	dppf	K_2CO_3	NMP	92	Trace
3	$Pd(OAc)_2$	dppf	Cs_2CO_3	NMP	91	Trace
4	$Pd(OAc)_2$	dppf	KO^tBu	NMP	85	Trace
5	$Pd(OAc)_2$	dppf	NaO^tBu	NMP	88	Trace

6	$Pd(OAc)_2$	dppf	LiO^tBu	NMP	90	Trace
7	$Pd(OAc)_2$	dppf	Na_2CO_3	DMF	91	Trace
8	$Pd(OAc)_2$	dppf	Na_2CO_3	DMSO	89	Trace
9	$Pd(OAc)_2$	dppf	Na_2CO_3	Dioxane	93	Trace
10	$Pd(OAc)_2$	dppf	Na_2CO_3	PhMe	92	Trace
11	$Pd(OAc)_2$	dppf	Na_2CO_3	^{t}BuOH	76	21
12	$Pd(OAc)_2$	dppf	Na_2CO_3	EtOH	54	45
13	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH	12	74
14	**$Pd(OAc)_2$**	**dppf**	**Na_2CO_3**	**MeOH: H_2O(9:1)**	**5**	**83**
15	$Pd_2(dba)_3$	dppf	Na_2CO_3	MeOH: H_2O(9:1)	6	79
16	$Pd(OAc)_2$	x-phos	Na_2CO_3	MeOH: H_2O(9:1)	10	73
17	$Pd(OAc)_2$	s-phos	Na_2CO_3	MeOH: H_2O(9:1)	7	81
18[c]	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH: H_2O(9:1)	11	76
19[d]	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH: H_2O(9:1)	4	69
20	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH: H_2O(1:1)	34	47
21	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH: H_2O(3:1)	14	61
22	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH: H_2O(5:1)	8	76
23	$Pd(OAc)_2$	dppf	Na_2CO_3	MeOH: H_2O(20:1)	9	77

[a] Conditions: 1a (1 mmol), 2 (0.25 mmol), Pd catalyst (0.1 mol %), ligand (0.2 mol %), Na_2CO_3 (1 mmol), NMP (1 mL), 120 ℃, 12h; then base (3 mmol), $NH_2OH.HCl$ (3 mmol), solvent (2 mL), 120℃ , 12h.

[b] Isolated yield. [c] 1-Iodonaphthalene was used. [d] 1-Chloronaphthalene was used.

Experimental Procedures for Examples Described in Table 2.

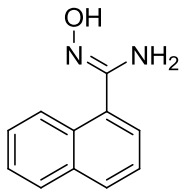
General Procedure A. In air, $Pd(OAc)_2$ (0.001 mmol), dppf (0.002 mmol), Na_2CO_3 (1 mmol), and $K_4[Fe(CN)_6]$ (0.25 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). NMP (1 mL) and aryl bromide (1 mmol) were added in turn under an argon atmosphere (if the aryl bromide is a solid, it was added along with the $Pd(OAc)_2$). The reaction mixture was stirred at 120 ^oC for 12h, then $NH_2OH{\cdot}HCl$ (3 mmol), Na_2CO_3 (3 mmol), MeOH (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk tube. The reaction mixture was stirred at 120 ^oC for another 12h, then diluted with EtOAc, filtred through silica gel with copious washings (EtOAc), washed with water, concentrated, and purified by column chromatography.

General Procedure B. In air, $Pd(OAc)_2$ (0.001 mmol), dppf (0.002 mmol), Na_2CO_3 (1 mmol),

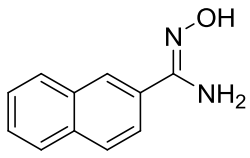
and $K_4[Fe(CN)_6]$ (0.25 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). NMP (1 mL) and aryl bromide (1 mmol) were added in turn under an argon atmosphere (if the aryl bromide is a solid, it was added along with the $Pd(OAc)_2$). The reaction mixture was stirred at 120 °C for 12h, then $NH_2OH{\cdot}HCl$ (2 mmol), Na_2CO_3 (2 mmol), MeOH (0.9 mL) and H_2O (0.1 mL) were added to the Schlenk tube. The reaction mixture was stirred at 120 °C for another 8h, then $NH_2OH{\cdot}HCl$ (2 mmol), Na_2CO_3 (2 mmol), MeOH (0.9 mL) and H_2O (0.1 mL) were added to the Schlenk tube. The resulting mixture was stirred at 120 °C for 8h, then diluted with EtOAc, filtred through silica gel with copious washings (EtOAc), washed with water, concentrated, and purified by column chromatography.

General Procedure C. In air, $Pd(OAc)_2$ (0.002 mmol), dppf (0.004 mmol), Na_2CO_3 (1 mmol), and $K_4[Fe(CN)_6]$ (0.25 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). NMP (1 mL) and heteroaryl bromide (1 mmol) were added in turn under an argon atmosphere. The reaction mixture was stirred at 120 °C for 12h, then $NH_2OH{\cdot}HCl$ (3 mmol), Na_2CO_3 (3 mmol), MeOH (1.8 mL) and H_2O (0.2 mL) were added to the Schlenk tube. The reaction mixture was stirred at 120 °C for another 12h, then diluted with EtOAc, filtred through silica gel with copious washings (EtOAc), washed with water, concentrated, and purified by column chromatography.

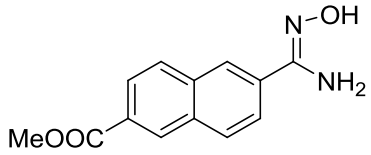
NMR Spectral Data



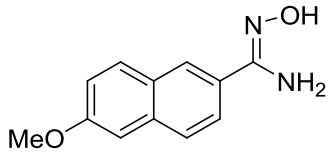
N'-hydroxy-1-naphthimidamide (3a), follow General Procedure A, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.58 (s, 1H), 8.42 – 8.27 (m, 1H), 7.97 – 7.91 (m, 2H), 7.57 – 7.50 (m, 4H), 5.97 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.1, 133.7, 132.7, 131.5, 129.3, 128.5, 127.0, 126.6, 126.4, 125.7 ppm. HRMS calcd for $C_{11}H_{10}N_2O$ (M+):186.0793; found: 187.0860 (M+H).



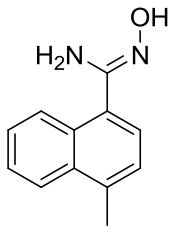
N'-hydroxy-2-naphthimidamide (3b), follow General Procedure A, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 8.22 (s, 1H), 7.94 – 7.84 (m, 4H), 7.56 – 7.50 (m, 2H), 5.95 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.1, 133.6, 133.0, 131.2, 128.6, 128.0, 127.9, 126.9, 126.8, 124.8, 123.8 ppm. HRMS calcd for $C_{11}H_{10}N_2O$ (M+):186.0793; found: 187.0865 (M+H).



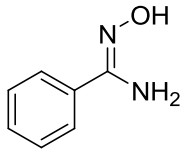
Methyl 6-(N'-hydroxycarbamimidoyl)-2-naphthoate(3c), follow General Procedure A, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (s, 1H), 8.63 (s, 1H), 8.30 (s, 1H), 8.10 (d, J = 8.7 Hz, 1H), 8.05 – 7.98 (m, 2H), 7.97 – 7.92 (m, 1H), 6.01 (s, 2H), 3.92 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.8, 150.8, 135.2, 133.6, 132.6, 130.7, 129.5, 129.3, 127.6, 125.7, 124.8, 124.5, 52.8 ppm. HRMS calcd for $C_{13}H_{12}N_2O_3$ (M+): 244.0848; found: 245.0919 (M+H).



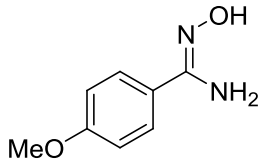
N'-hydroxy-6-methoxy-2-naphthimidamide (3d), follow General Procedure B, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.69 (s, 1H), 8.13 (s, 1H), 7.79 (dt, J = 12.4, 8.9 Hz, 3H), 7.32 (d, J = 2.5 Hz, 1H), 7.18 (dd, J = 8.9, 2.5 Hz, 1H), 5.88 (s, 2H), 3.88 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 158.1, 151.3, 135.0, 130.2, 128.9, 128.3, 126.8, 124.7, 124.3, 119.3, 106.4, 55.7 ppm. HRMS calcd for $C_{12}H_{12}N_2O_2$ (M+):216.0899; found: 217.0970 (M+H).



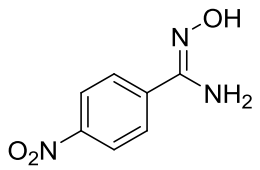
N'-hydroxy-4-methyl-1-naphthimidamide (3e), follow General Procedure B, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.51 (s, 1H), 8.31 (dd, J = 7.1, 2.5 Hz, 1H), 8.04 (dd, J = 7.1, 2.4 Hz, 1H), 7.59 – 7.51 (m, 2H), 7.40 (dd, J = 22.5, 7.2 Hz, 2H), 5.93 (s, 2H), 2.67 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.2, 135.4, 132.6, 131.6, 131.1, 126.9, 126.6, 126.3, 126.3, 126.2, 124.6, 19.65 ppm. HRMS calcd for $C_{12}H_{12}N_2O$ (M+):200.0950; found: 201.1024 (M+H).



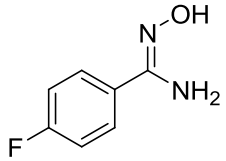
N'-hydroxybenzimidamide (3f), follow General Procedure A, colourless liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.63 (s, 1H), 7.76 – 7.54 (m, 2H), 7.37 (dd, J = 6.7, 3.5 Hz, 3H), 5.81 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.3, 133.8, 129.3, 128.6, 125.8 ppm. HRMS calcd for $C_7H_8N_2O$ (M+):136.0637; found: 137.0709 (M+H).



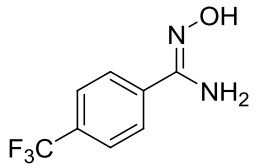
N'-hydroxy-4-methoxybenzimidamide (3g), follow General Procedure B, white solid.^{1}H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H), 7.67 – 7.55 (m, 2H), 6.98 – 6.84 (m, 2H), 5.72 (s, 2H), 3.77 (s, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 160.3, 151.0, 127.2, 126.2, 113.9, 55.6 ppm. HRMS calcd for $C_8H_{10}N_2O_2$ (M+): 166.0742; found: 167.0818 (M+H).



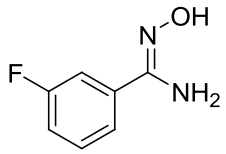
N'-hydroxy-4-nitrobenzimidamide(3h), follow General Procedure C, yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (1 H, s), 8.28 – 8.19 (2 H, m), 7.99 – 7.91 (2 H, m), 6.08 (2 H, s) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.8, 147.9, 140.0, 126.9, 123.8 ppm. HRMS calcd for $C_7H_7N_3O_3$ (M+): 181.0487; found: 182.0556 (M+H).



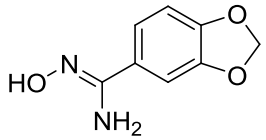
4-fluoro-N'-hydroxybenzimidamide(3i), follow General Procedure A, colourless liquid.^{1}H NMR (400 MHz, DMSO-d_6) δ 9.64 (s, 1H), 7.80 – 7.60 (m, 2H), 7.27 – 7.11 (m, 2H), 5.85 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 162.9 (d, J = 250.5 Hz), 150.5, 130.3 (d, J = 3.1 Hz), 128.0 (d, J = 8.2 Hz), 115.4 (d, J = 21.4 Hz) ppm. HRMS calcd for $C_7H_7N_2OF$ (M+): 154.0542; found: 155.0618 (M+H).



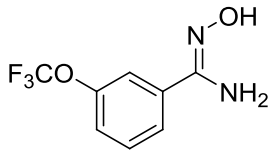
N-hydroxy-4-(trifluoromethyl)benzimidamide(3j), follow General Procedure A, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.94 (s, 1H), 7.90 (d, J = 8.2 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 5.99 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.2, 137.8, 129.5 (q, J = 31.8 Hz), 126.5, 125.5 (q, J = 3.7 Hz), 124.7 (q, J = 272.0 Hz) ppm. HRMS calcd for $C_8H_7F_3N_2O$ (M+):204.0510; found: 205.0585 (M+H).



3-fluoro-N'-hydroxybenzimidamide(3k), follow General Procedure A, colourless liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.79 (s, 1H), 7.54 (d, J = 7.9 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.21 (td, J = 8.4, 2.3 Hz, 1H), 5.90 (s, 2H) ppm.^{13}C NMR (101 MHz, DMSO-d_6) δ 163.2 (d, J = 384.5 Hz), 150.2, 136.2 (d, J = 8.1 Hz), 130.6 (d, J = 8.3 Hz), 121.8 (d, J = 2.5 Hz), 116.0 (d, J = 21.1 Hz), 112.5 (d, J = 23.2 Hz) ppm. HRMS calcd for $C_7H_7N_2OF$ (M+):154.0542; found: 155.0617 (M+H).

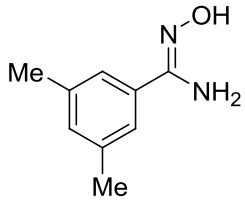


N'-hydroxybenzo[d][1,3]dioxole-5-carboximidamide(3l), follow General Procedure C, faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H), 7.19 (dd, J = 7.2, 1.6 Hz, 2H), 6.95 – 6.83 (m, 1H), 6.03 (s, 2H), 5.73 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.9, 148.2, 147.6, 127.9, 119.7, 108.3, 106.1, 101.6 ppm. HRMS calcd for $C_8H_8N_2O_3$ (M+):180.0535; found: 181.0608 (M+H).

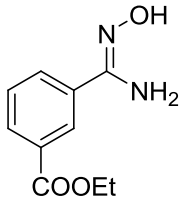


N'-hydroxy-3-(trifluoromethoxy)benzimidamide(3m), follow General Procedure A, colourless liquid.^{1}H NMR (400 MHz, DMSO-d_6) δ 9.86 (s, 1H), 7.72 (d, J = 7.9 Hz, 1H), 7.63 (s, 1H), 7.52 (t, J = 8.0 Hz, 1H), 7.40 – 7.34 (m, 1H), 5.97 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ

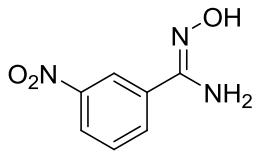
150.0, 148.7, 136.1, 130.7, 124.8, 121.8, 121.7, 118.1, (124.3, 121.8, 119.3, 116.7: CF_3, q, J=256.7Hz) ppm. ^{19}F NMR (376 MHz, DMSO-d_6) δ -56.7 ppm. HRMS calcd for $C_8H_7F_3N_2O_2$ (M+): 220.0460; found: 221.0538 (M+H).



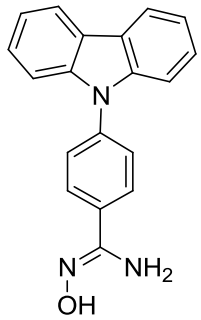
N'-hydroxy-3,5-dimethylbenzimidamide(3n), follow General Procedure B, white solid. ^1H NMR (400 MHz, DMSO-d_6) δ 9.52 (s, 1H), 7.28 (s, 2H), 7.00 (s, 1H), 5.70 (s, 2H), 2.27 (s, 6H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.4, 137.4, 133.7, 130.7, 123.7, 21.4 ppm. HRMS calcd for $C_9H_{12}N_2O$ (M+): 164.0950; found: 165.1020 (M+H).



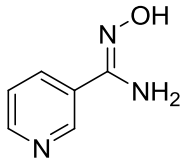
Ethyl 3-(N'-hydroxycarbamimidoyl)benzoate(3o), follow General Procedure A, white solid. ^1H NMR (400 MHz, DMSO-d_6) δ 9.80 (s, 1H), 8.30 (t, J = 1.6 Hz, 1H), 8.02 – 7.81 (m, 2H), 7.54 (t, J = 7.8 Hz, 1H), 5.96 (s, 2H), 4.33 (q, J = 7.1 Hz, 2H), 1.34 (t, J = 7.1 Hz, 3H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 166.0, 150.5, 134.3, 130.4, 130.3, 129.8, 129.1, 126.6, 61.3, 14.6 ppm. HRMS calcd for $C_{10}H_{12}N_2O_3$ (M+): 208.0848; found: 209.0926 (M+H).



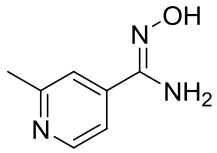
N'-hydroxy-3-nitrobenzimidamide(3p), follow General Procedure C, yellow solid. ^1H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.52 (t, J = 1.9 Hz, 1H), 8.23 (ddd, J = 8.2, 2.3, 0.9 Hz, 1H), 8.13 (dd, J = 7.9, 1.1 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 6.11 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.6, 148.2, 135.4, 132.0, 130.3, 124.0, 120.4 ppm. HRMS calcd for $C_7H_7N_3O_3$ (M+):181.0487; found: 182.0568 (M+H).



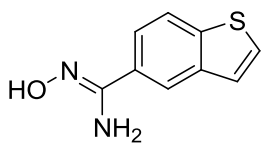
4-(9H-carbazol-9-yl)-N'-hydroxybenzimidamide(3q), follow General Procedure C, faint yellow solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.81 (s, 1H), 8.26 (d, J = 7.8 Hz, 2H), 7.98 (d, J = 8.5 Hz, 2H), 7.65 (d, J = 8.5 Hz, 2H), 7.43 (dd, J = 10.5, 7.6 Hz, 4H), 7.31 (t, J = 7.1 Hz, 2H), 5.98 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.8, 140.4, 137.7, 132.9, 127.6, 126.8, 126.7, 123.3, 121.0, 120.6, 110.1 ppm. HRMS calcd for $C_{19}H_{15}N_3O$ (M+): 301.1215; found: 302.1289 (M+H).



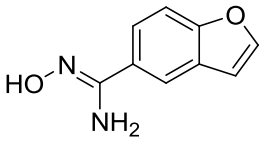
N'-hydroxynicotinimidamide(4a), follow General Procedure C, faint yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.85 (s, 1H), 8.85 (d, J = 1.9 Hz, 1H), 8.56 (dd, J = 4.8, 1.5 Hz, 1H), 8.01 (dt, J = 8.0, 1.9 Hz, 1H), 7.41 (dd, J = 7.9, 4.8 Hz, 1H), 5.99 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 150.2, 149.4, 147.0, 133.3, 129.5, 123.7 ppm. HRMS calcd for $C_6H_7N_3O$ (M+): 137.0589; found: 138.0662 (M+H).



N'-hydroxy-2-methylisonicotinimidamide (4b), follow General Procedure C, faint yellow liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.99 (s, 1H), 8.43 (d, J = 5.2 Hz, 1H), 7.51 (s, 1H), 7.44 (d, J = 5.2 Hz, 1H), 5.96 (s, 2H), 2.48 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 158.4, 149.5, 149.4, 141.3, 119.3, 117.3, 24.6 ppm. HRMS calcd for $C_7H_9N_3O$ (M+): 151.0746; found: 152.0818 (M+H).

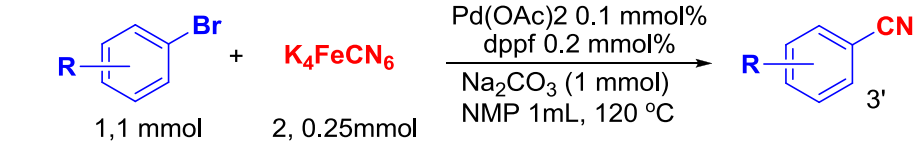


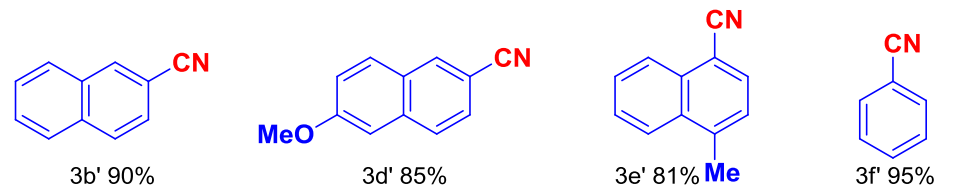
N'-hydroxybenzo[b]thiophene-5-carboximidamide(4c), follow General Procedure C, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.65 (s, 1H), 8.17 (d, J = 1.3 Hz, 1H), 7.98 (d, J = 8.5 Hz, 1H), 7.79 (d, J = 5.4 Hz, 1H), 7.69 (dd, J = 8.5, 1.6 Hz, 1H), 7.48 (d, J = 5.4 Hz, 1H), 5.88 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 151.5, 139.9, 139.7, 130.3, 128.6, 124.7, 122.6, 122.3, 121.0 ppm. HRMS calcd for $C_9H_8N_2OS$ (M+):192.0357; found: 193.0432 (M+H).

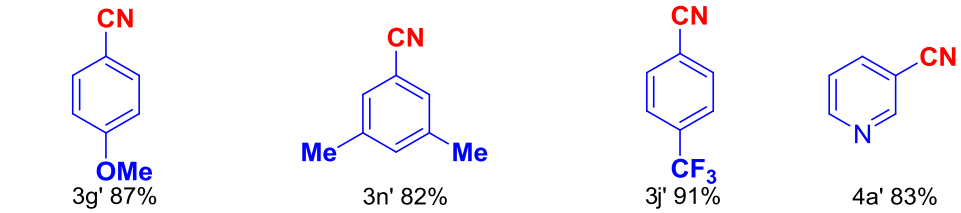


N'-hydroxybenzofuran-5-carboximidamide(4d), follow General Procedure C, white solid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.59 (s, 1H), 8.02 (d, J = 2.2 Hz, 1H), 7.96 (d, J = 1.5 Hz, 1H), 7.66 (dd, J = 8.7, 1.7 Hz, 1H), 7.58 (d, J = 8.7 Hz, 1H), 7.00 (d, J = 1.9 Hz, 1H), 5.85 (s, 2H) ppm. ^{13}C NMR (101 MHz, DMSO-d_6) δ 155.1, 151.6, 147.1, 129.0, 127.4, 122.7, 118.9, 111.3, 107.4 ppm. HRMS calcd for $C_9H_8N_2O_2$ (M+): 176.0586; found: 177.0657 (M+H).

Pd-catalyzed cyanation of aryl bromides







In air, $Pd(OAc)_2$ (0.001 mmol), dppf (0.002 mmol), Na_2CO_3 (1 mmol), and $K_4[Fe(CN)_6]$ (0.25 mmol) were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and filled with argon (three cycles). NMP (1 mL) and aryl bromide (1 mmol) were added in turn under an argon atmosphere (if the aryl bromide is a solid, it was added along with the $Pd(OAc)_2$). The

reaction mixture was stirred at 120 °C for 12h, then diluted with EtOAc, filtred through silica gel with copious washings (EtOAc), washed with water, concentrated, and purified by column chromatography.

Supplementary Fluorescence Spectra

Figure S1. Fluorescence responses of 3a (4.2×10^{-6} M in EtOH solution) toward $[UO_2](NO_3)_2$ (0,1.0, 2.0, 3.0, 4.0, 5.0 equiv) (λexc = 220 nm, slits: 5 nm/5 nm)

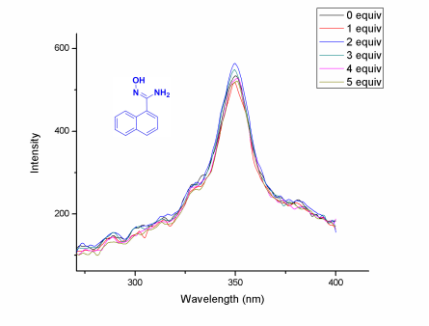
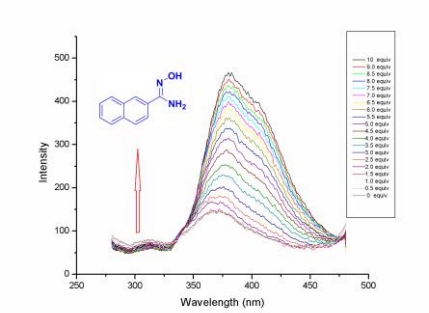
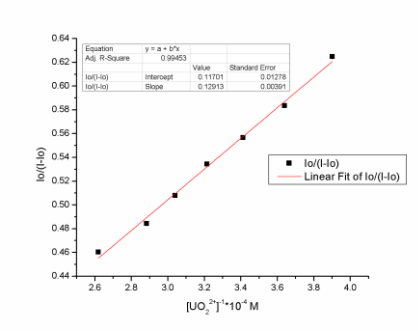


Figure S2. Fluorescence responses of 3b (4.2×10^{-6} M in EtOH solution) toward $[UO_2](NO_3)_2$ (0,0.5,1.0,1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0,10 equiv) (λexc = 250 nm, slits: 5 nm/5 nm)



We calculated the binding constant of 3b with $[UO_2](NO_3)_2$ by using the linear Benesi-Hilderand expression[2]:

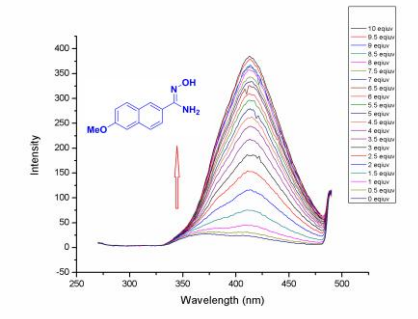
$$\frac{I_0}{I - I_0} = \frac{b}{a - b}\{\frac{1}{K[M]} + 1\}$$



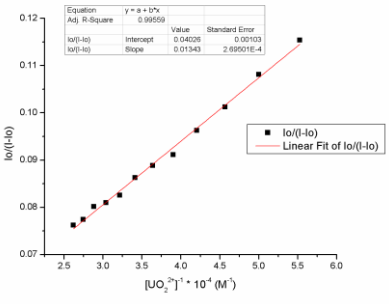
$1/K = 0.012913 \times 10^{-4}/0.11701$

The binding constant of 3b with $[UO_2](NO_3)_2$ is **0.91×10^4**

Figure S3. Fluorescence responses of 3d (4.2×10^{-6} M in EtOH solution) toward $[UO_2](NO_3)_2$ (0,0.5,1.0,1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 7.5, 8.0, 8.5, 9.0, 9.5,10 equiv) (λexc = 250 nm, slits: 5 nm/2.5 nm)



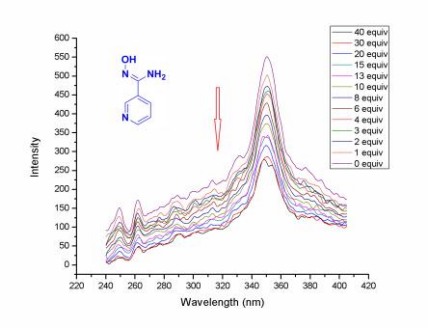
We calculated the binding constant of 3d with $[UO_2](NO_3)_2$ by using the linear Benesi-Hilderand expression.



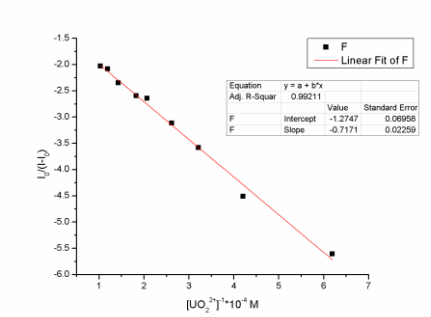
$1/K = 0.01343 \times 10^{-4}/0.04026$

The binding constant of 3b with $[UO_2](NO_3)_2$ is **3×10^4**

Figure S4. Fluorescence responses of 4a (4.2×10^{-6} M in EtOH solution) toward $[UO_2](NO_3)_2$ (0, 1.0, 2.0, 3.0, 4.0, 6.0, 10, 13, 15, 20,30,40 equiv) (λexc = 210 nm, slits: 5 nm/5 nm)



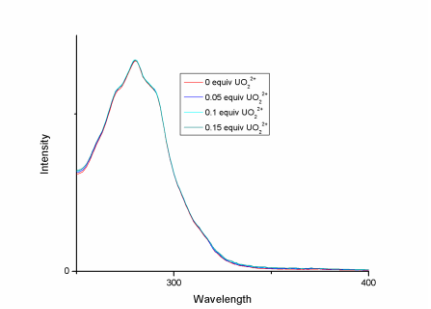
We calculated the binding constant of 4a with $[UO_2](NO_3)_2$ by using the linear Benesi-Hilderand expression.



$$1/K = -0.7171 \times 10^{-4}/-1.2747$$

The binding constant of 3b with $[UO_2](NO_3)_2$ is **1.8×10^4**

Figure S5. UV-Vis responses of 3a (2.1×10^{-4} M in EtOH solution) toward $[UO_2](NO_3)_2$ (0,0.05, 0.10, 0.15 equiv) (pH = 7.4, 25 ^oC)



Supplementary Calculating Data

Thermal correction to enthalpy (TCE), total electronic energy in EtOH (E^{solv}), and the cartesian coordinates of all complexes calculated with B3LYP/(SDD-MWB60:6-311G(d,p)) method.[3]

3a

TCE= 0.20258 hartree

E^{solv}= -610.056191616 hartree

N	2.844586000	0.207036000	-0.660331000
C	1.914378000	-0.207992000	0.129347000
O	4.040335000	-0.534082000	-0.419169000
H	4.642300000	-0.156876000	-1.065797000
N	2.060894000	-1.271486000	0.996632000
H	1.492062000	-1.254803000	1.828681000
H	3.016515000	-1.570878000	1.127435000
C	0.613664000	0.514305000	0.083163000
C	-0.646001000	-0.169127000	0.003125000
C	0.643221000	1.894637000	0.119738000
C	-0.770203000	-1.581334000	-0.118603000
C	-1.847334000	0.614926000	0.000748000
C	-0.542904000	2.656062000	0.104481000
H	1.604627000	2.389729000	0.165587000
C	-2.004394000	-2.179995000	-0.204921000
H	0.125103000	-2.187308000	-0.140833000
C	-3.104156000	-0.040160000	-0.080666000
C	-1.762161000	2.029290000	0.058667000
H	-0.482500000	3.737799000	0.139663000
C	-3.185772000	-1.406404000	-0.177648000
H	-2.072023000	-3.257960000	-0.301047000
H	-4.004375000	0.565614000	-0.074139000
H	-2.680666000	2.606853000	0.057924000
H	-4.152104000	-1.893625000	-0.242819000

3b

TCE= 0.202069 hartree

E^{solv}= -610.053312327 hartree

N	3.299924000	0.682303000	-0.315732000
C	2.460823000	-0.238560000	0.016981000
O	4.638300000	0.299704000	-0.227338000
H	4.680351000	-0.413216000	0.436821000
N	2.895923000	-1.515795000	0.403908000
H	2.180248000	-2.122140000	0.772788000
H	3.476078000	-1.983133000	-0.283331000
C	1.021447000	0.100339000	0.034177000
C	0.047275000	-0.875001000	-0.046240000
C	0.626464000	1.466474000	0.118647000
C	-1.332768000	-0.549141000	-0.038661000
H	0.317438000	-1.921081000	-0.148912000
C	-0.697714000	1.810855000	0.122104000
H	1.400736000	2.219490000	0.179091000
C	-2.344005000	-1.541303000	-0.121094000

C	-1.71822300	0.82429200	0.04809000
H	-0.98552500	2.85482600	0.18921900
C	-3.67314600	-1.19293500	-0.11352500
H	-2.05115300	-2.58394800	-0.19101000
C	-3.09735700	1.15014600	0.05586700
C	-4.05370500	0.16566600	-0.02328900
H	-4.43652100	-1.96008300	-0.17696600
H	-3.38790300	2.19328800	0.12368300
H	-5.10562400	0.42781900	-0.01825700

HNO3

TCE= 0.030925 hartree

E^{solv}= -280.972144891 hartree

O	1.15174100	-0.51585800	-0.00022700
O	-0.21231200	1.24031600	-0.00007700
O	-1.02097200	-0.78683600	0.00009800
N	-0.15246600	0.03243700	0.00000600
H	1.71960600	0.27196000	0.00161000

3a-U

TCE= 0.309364 hartree

E^{solv}= -1672.71807337 hartree

U	1.53080700	-0.17394400	-0.13711700
O	1.78958500	0.25583500	-1.84729500
O	3.96977400	-0.75442200	-0.15168400
O	1.50973900	-0.61821800	1.58640800
O	0.58198500	2.06110800	0.32875300
O	2.73602200	1.93042800	0.49009100
O	1.73754100	3.83700400	0.85672000
N	1.68721000	2.67055800	0.57364600
O	0.23810600	-1.93925400	-0.70775000
N	-0.68869100	-0.93621500	-0.52954400
C	-1.93304800	-1.24206200	-0.71525800
N	-2.29353300	-2.52976200	-0.99781200
H	-3.16044000	-2.68094500	-1.48736400
H	-1.51925300	-3.14248000	-1.21596800
H	4.42245300	-0.40694100	-0.92999300
C	-2.95487000	-0.17117300	-0.62703100
C	-4.19146200	-0.34388600	0.08267400
C	-2.68824500	1.02419600	-1.26764800
C	-4.51353600	-1.50200800	0.84319500
C	-5.13865100	0.73279100	0.06345100
C	-3.62007000	2.08082200	-1.26384600
H	-1.74780000	1.14172200	-1.79028800

C	-5.71154100	-1.60276800	1.50986200
H	-3.79970100	-2.31223300	0.90152300
C	-6.36921800	0.58788800	0.75573700
C	-4.82444700	1.93242200	-0.62471500
H	-3.37817100	3.00421600	-1.77639000
C	-6.65591500	-0.55429800	1.46000400
H	-5.92980600	-2.49381300	2.08777800
H	-7.07853500	1.40826400	0.72613000
H	-5.55252700	2.73668900	-0.62701400
H	-7.59775200	-0.64990300	1.98812100
C	4.86152200	-0.69407000	1.00263500
C	6.13165400	-1.48380800	0.75337700
H	4.27508900	-1.11106400	1.81972000
H	5.06359900	0.35647300	1.22444600
H	6.76452500	-1.45610000	1.64443400
H	5.90474200	-2.52691300	0.52324200
H	6.70936400	-1.06033700	-0.07420000

3b-U

TCE= 0.309397 hartree

E^{solv}= -1672.72386787 hartree

U	1.69576000	-0.19023900	-0.10925900
O	1.86285100	-0.07478900	-1.87882500
O	4.18798800	-0.43790100	-0.10957300
O	1.77186300	-0.28747900	1.66653100
O	0.44305200	1.94153900	-0.05972900
O	2.59428900	2.14794300	0.03823500
O	1.33602700	3.93195400	0.03793100
N	1.45318800	2.73716100	0.00717000
O	0.62571900	-2.17155100	-0.28200000
N	-0.42108500	-1.28309400	-0.21616800
C	-1.61893500	-1.77676200	-0.27392900
N	-1.80628200	-3.13155600	-0.32706300
H	-2.62816900	-3.46448600	-0.80500400
H	-0.95438800	-3.65421300	-0.48153500
H	4.59135600	-0.21435900	-0.95730800
C	5.07698000	-0.04341800	0.97969000
C	6.41498300	-0.74837000	0.87702000
H	4.53595700	-0.32154900	1.88256300
H	5.17869300	1.04418000	0.96063700
H	7.04657000	-0.46460100	1.72307000
H	6.28777830	-1.83277200	0.88975000
H	6.94550700	-0.46897500	-0.03859800
C	-2.78618400	-0.87595700	-0.21723700

C	-4.01637700	-1.35382500	0.19284600
C	-2.65287500	0.49650000	-0.57006600
C	-5.15155800	-0.50893600	0.25790700
H	-4.12442100	-2.38534800	0.50954000
C	-3.73357500	1.33498200	-0.51102300
H	-1.68965400	0.87676800	-0.88104700
C	-6.42146000	-0.98256200	0.68009200
C	-5.01118400	0.86724200	-0.10282900
H	-3.61887700	2.37939100	-0.78015000
C	-7.50250500	-0.13697900	0.73666600
H	-6.52513100	-2.02600000	0.95932000
C	-6.14665800	1.71299500	-0.03408800
C	-7.36390300	1.22349500	0.37564400
H	-8.46781500	-0.50941000	1.06032800
H	-6.03816500	2.75698700	-0.30829200
H	-8.22468300	1.88063600	0.42622300

Note:

a) The relative energy of each species correspond to the addition of E^{solv} with TCE.

b) In calculation, all species are calculated at the reference state of 1 mol/L, 298 K. A correction of 2.8 kcal/mol has been used in our study, because the concentration of HNO_3 will be far lower than 1mol/L (with the hypothesis of 0.01 mol/L HNO_3).

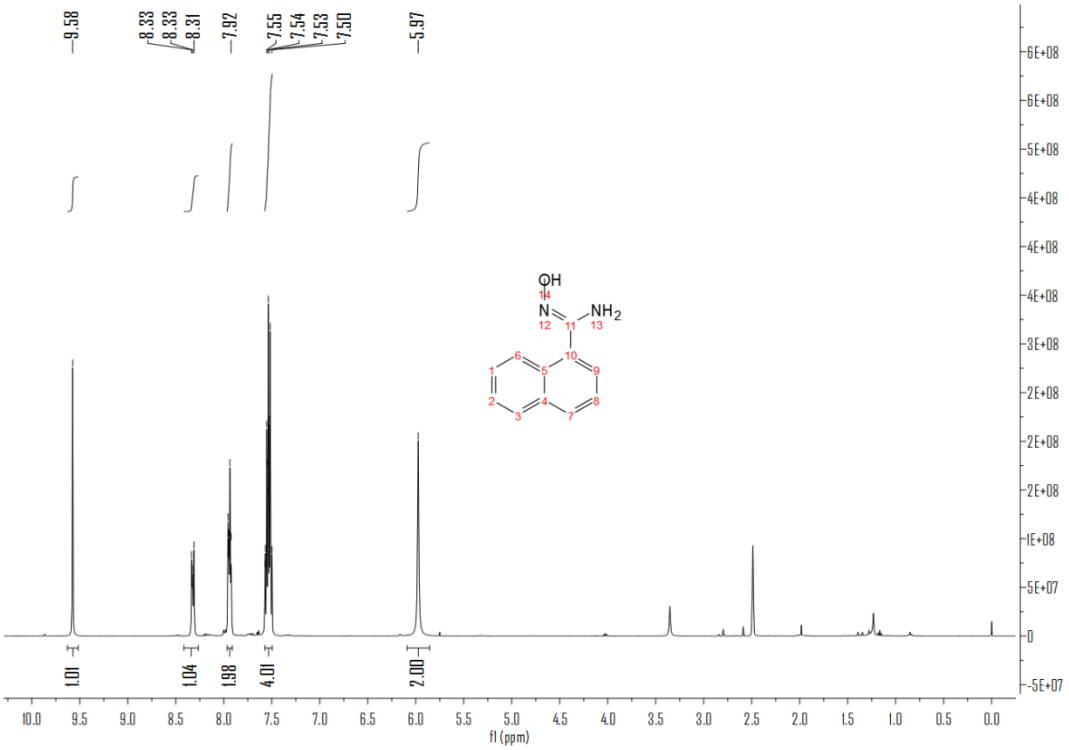
III. References

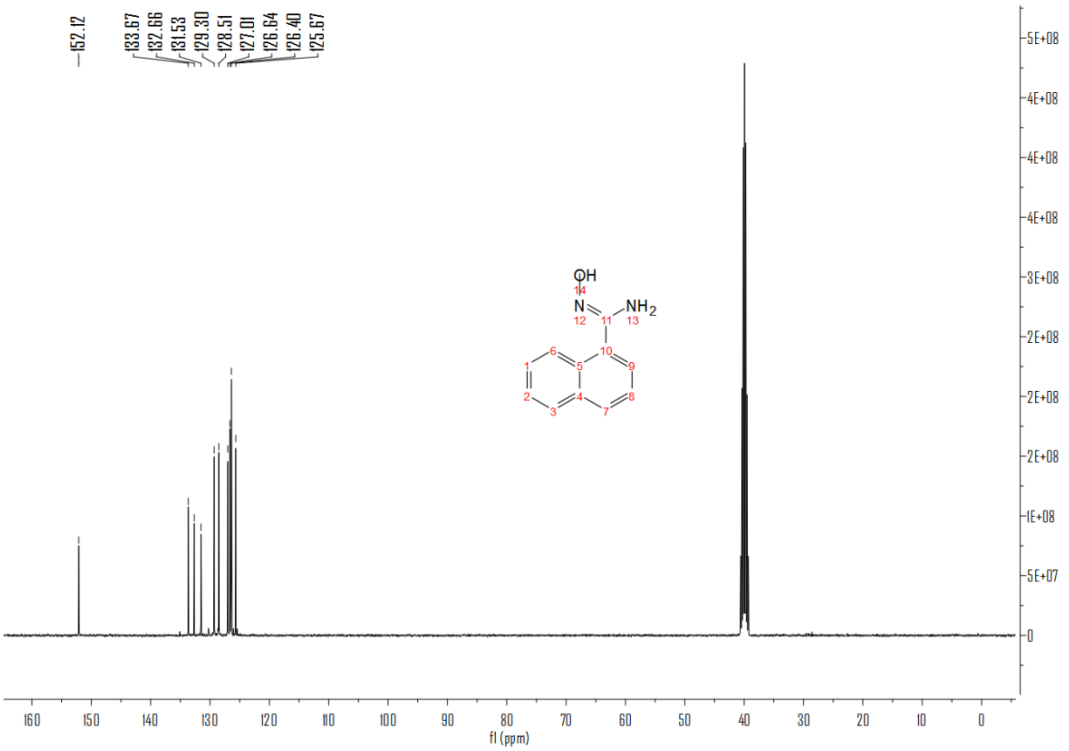
1 (a) T. Schareina, A. Zapf and M. Beller, *Chem. Commun.*, 2004,1388; (b) T. Schareina, A. Zapf and M. Beller, *J. Organomet. Chem.*, 2004, **689**, 4576; (c) O. Grossman and D. Gelman, *Org. Lett.*, 2006, **8**, 1189; (d) T. Schareina, R. Jackstell, T. Schulz, A. Zapf, A. Cotté, M. Gotta and M. Beller, *Adv. Synth. Catal.*, 2009, **351**, 643; (e) P. Y. Yeung, C. M. So, C. P. Lau and F. Y. Kwong, *Angew. Chem., Int. Ed.*, 2010, **49**, 8918; (f) P. Y. Yeung, C. M. So, C. P. Lau and F. Y. Kwong, *Org. Lett.*, 2011,**13**, 648; (g) T. D. Senecal, W. Shu and S. L. Buchwald, *Angew. Chem. Int. Ed.*, 2013, 52, 10035.

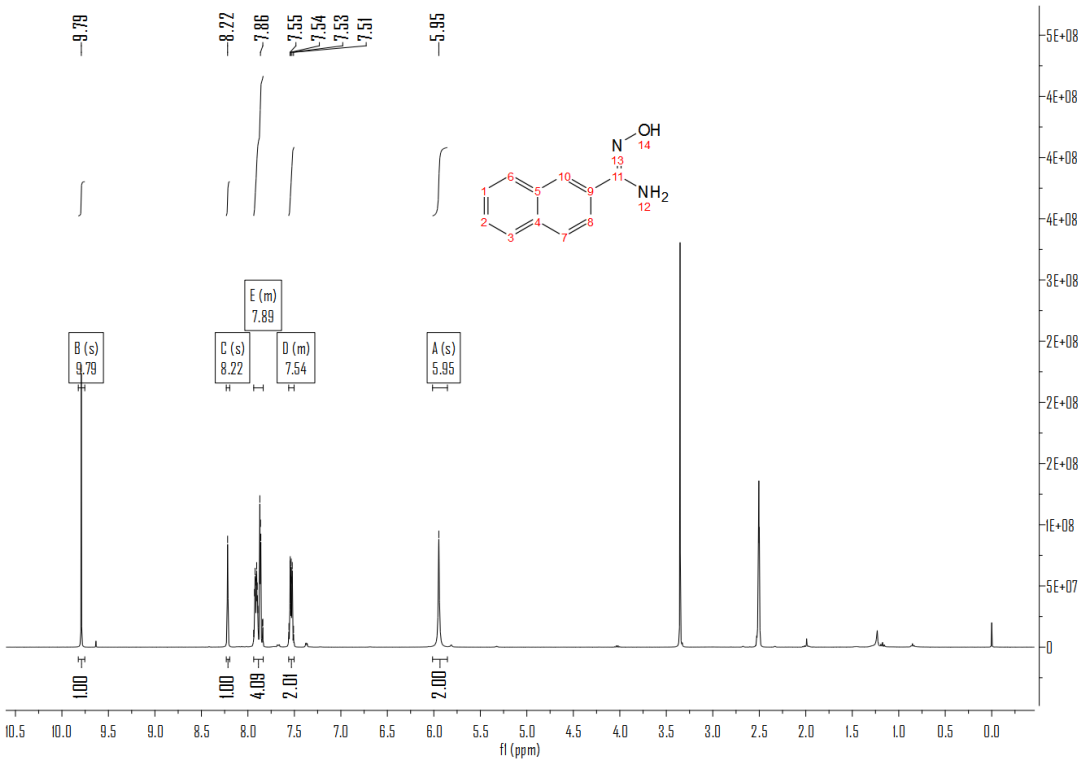
2 (a) H. Benesi and J. Hildebrand, *J. Am. Chem. Soc*.1949, 71, 2703; (b) Z. Huang, J. Du, J. Zhang, X.-Q. Yu and L. Pu, *Chem. Commun.*, 2012,**48**, 3412.

3 CYLview, 1.0b; C. Y. Legault, Université de Sherbrooke, 2009.

IV. NMR Spectra



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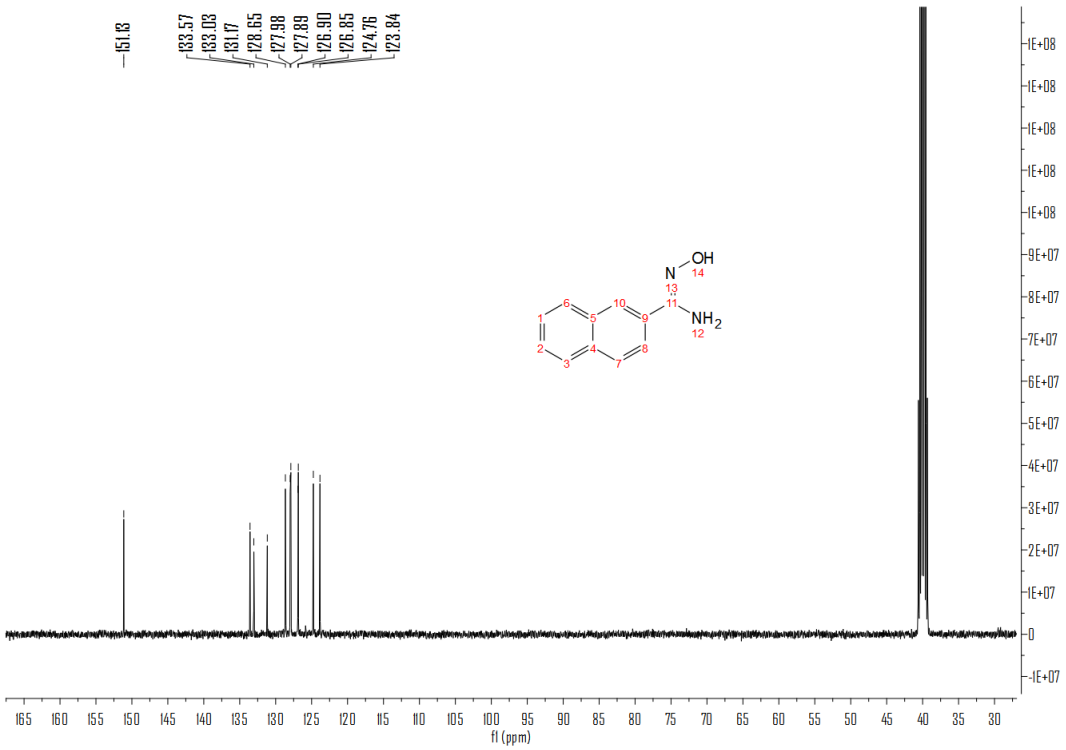
8.22
7.86
7.55
7.54
7.53
7.51
5.95
B (s) 9.79
C (s) 8.22
E (m) 7.89
D (m) 7.54
A (s) 5.95
1.00
1.00
4.09
2.01
2.00
f1 (ppm)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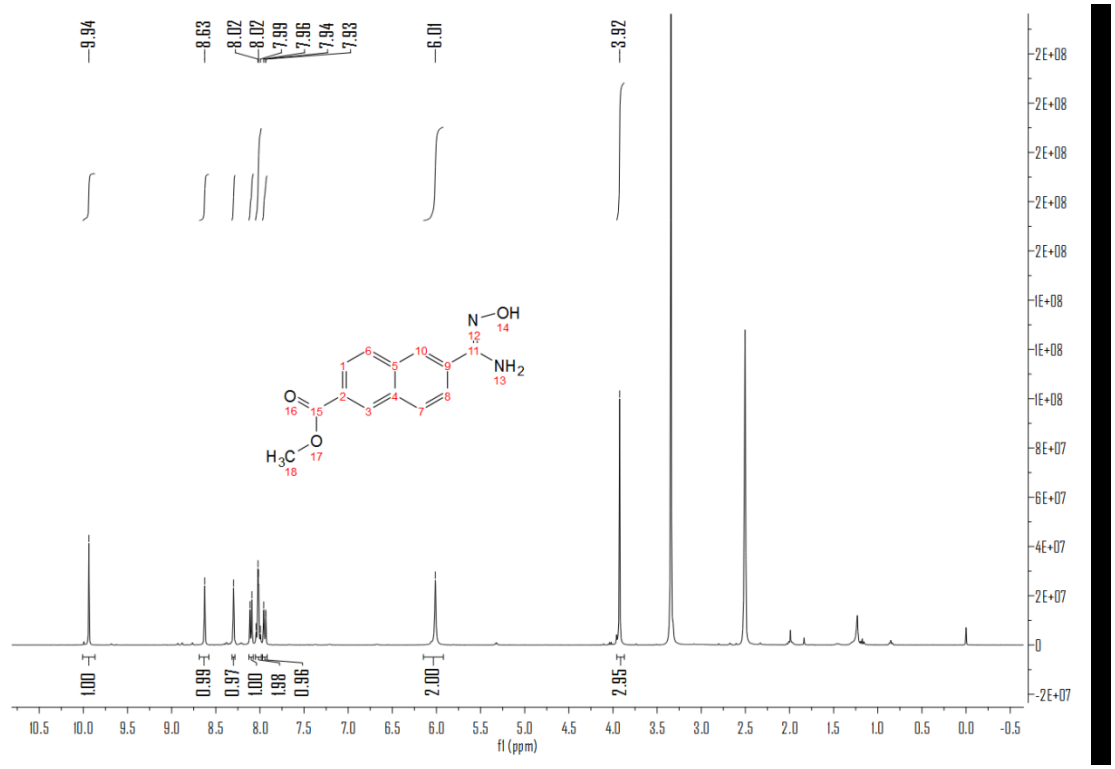
133.03
131.17
128.65
127.98
127.89
126.90
126.85
124.76
123.84
f1 (ppm)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8.63
8.02
8.02
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7.96
7.94
7.93
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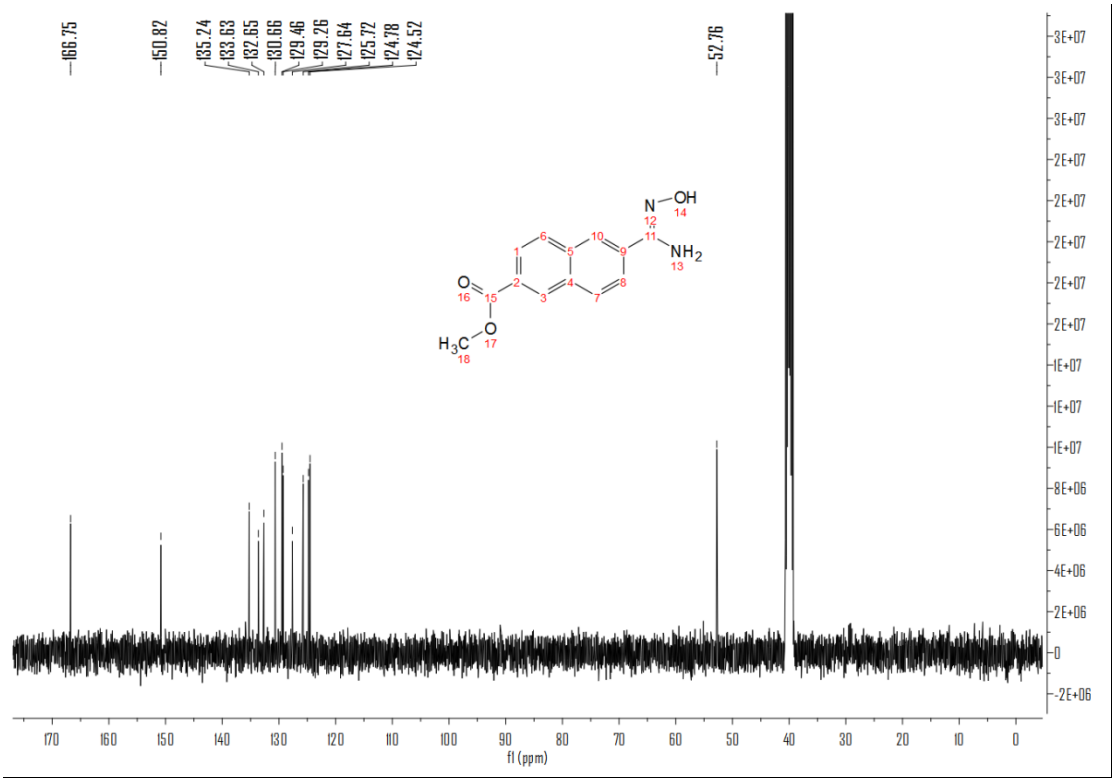
0.97
1.00
1.98
0.96
2.00
2.95
f1 (ppm)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150.82
135.24
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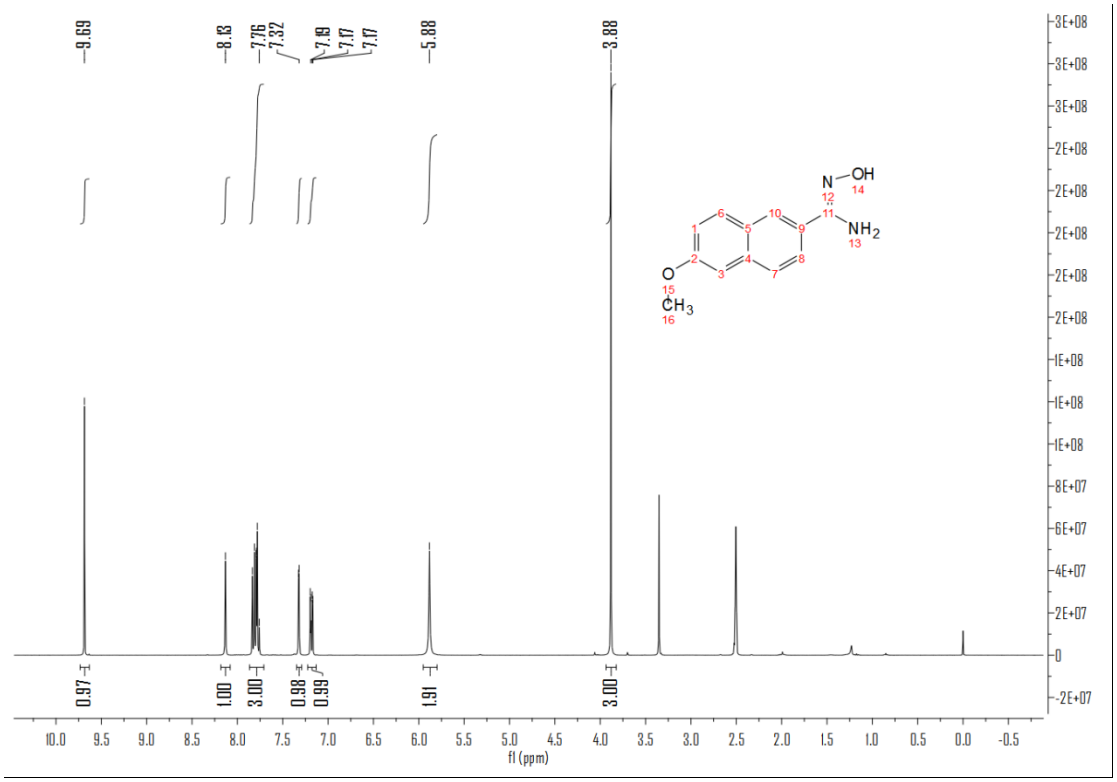
132.65
130.66
129.46
129.26
127.64
125.72
124.78
124.52
52.76
f1 (ppm)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8.13
7.76
7.32
7.19
7.17
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0.97
1.00
3.00
0.98
0.99
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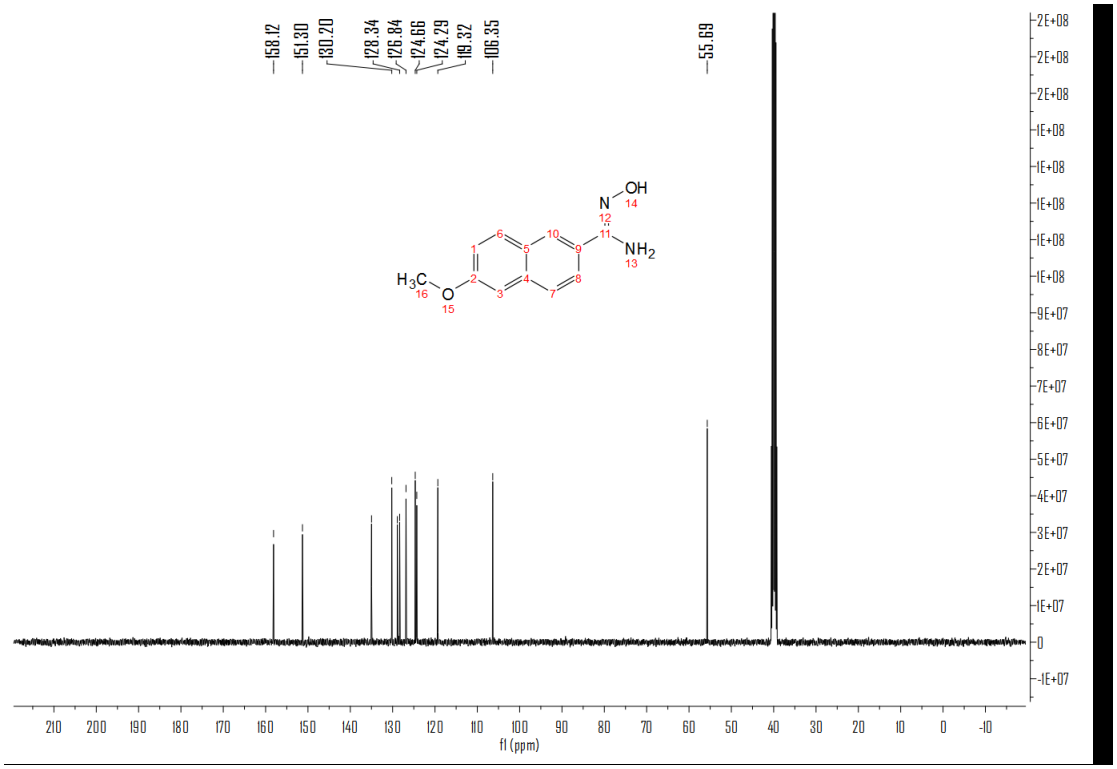
3.00
f1 (ppm)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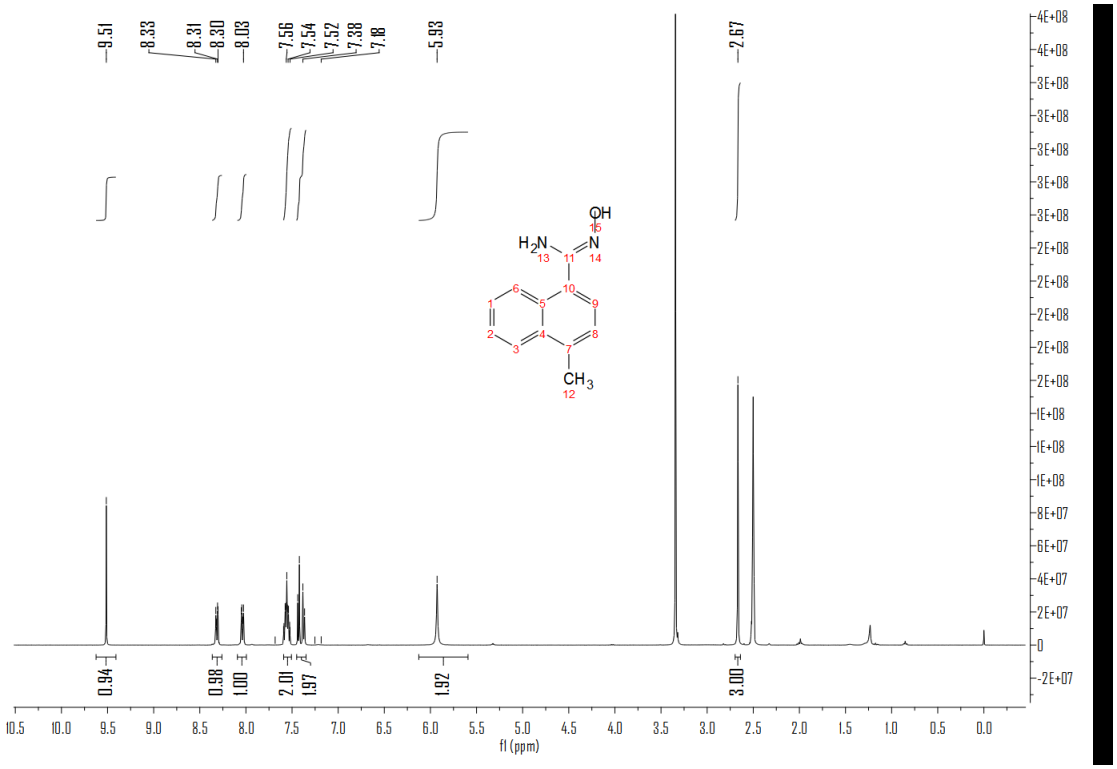
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OH
15
H2N
13
N
14
11
10
9
1
6
5
2
3
4
7
8
CH3
12
0.94
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1.00
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1.97
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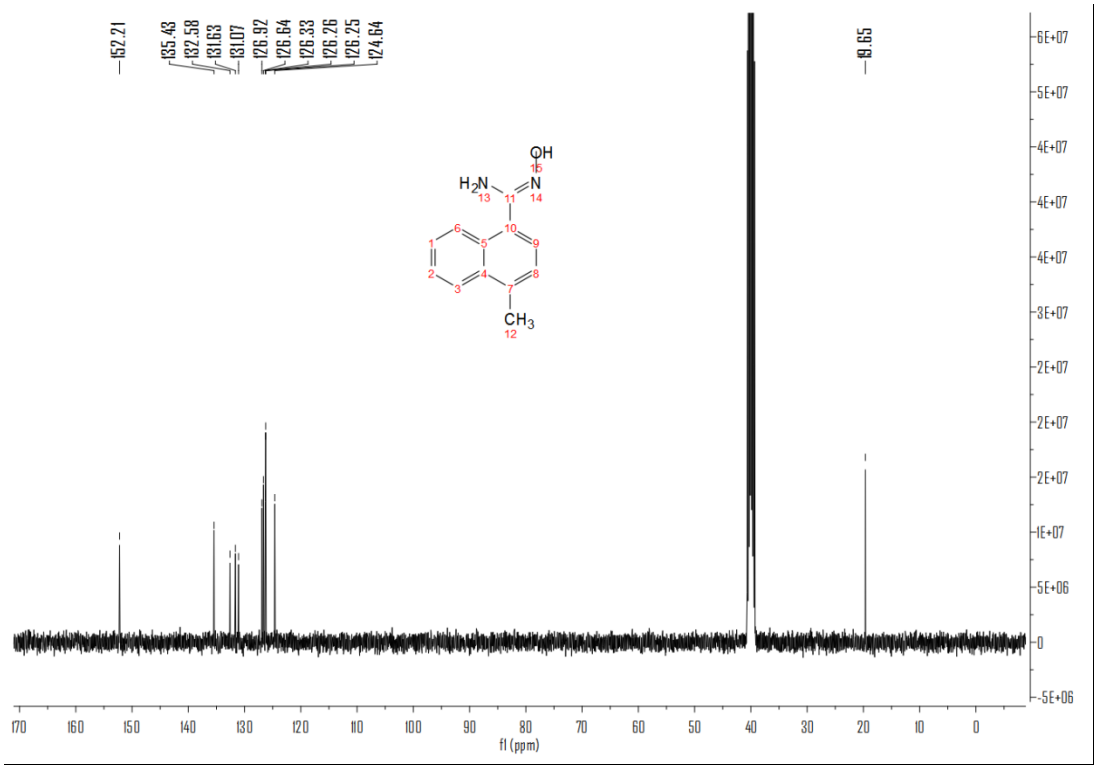
3.00
f1 (ppm)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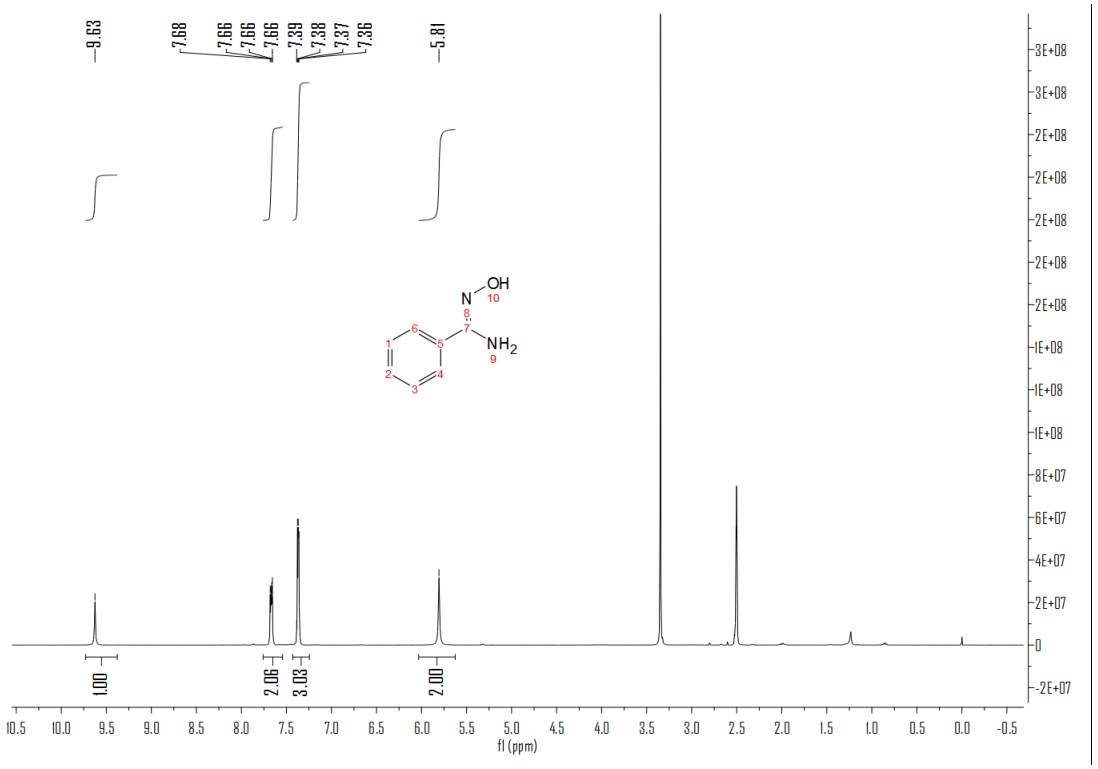
2
3
4
7
8
CH3
12
f1 (ppm)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4
5
6
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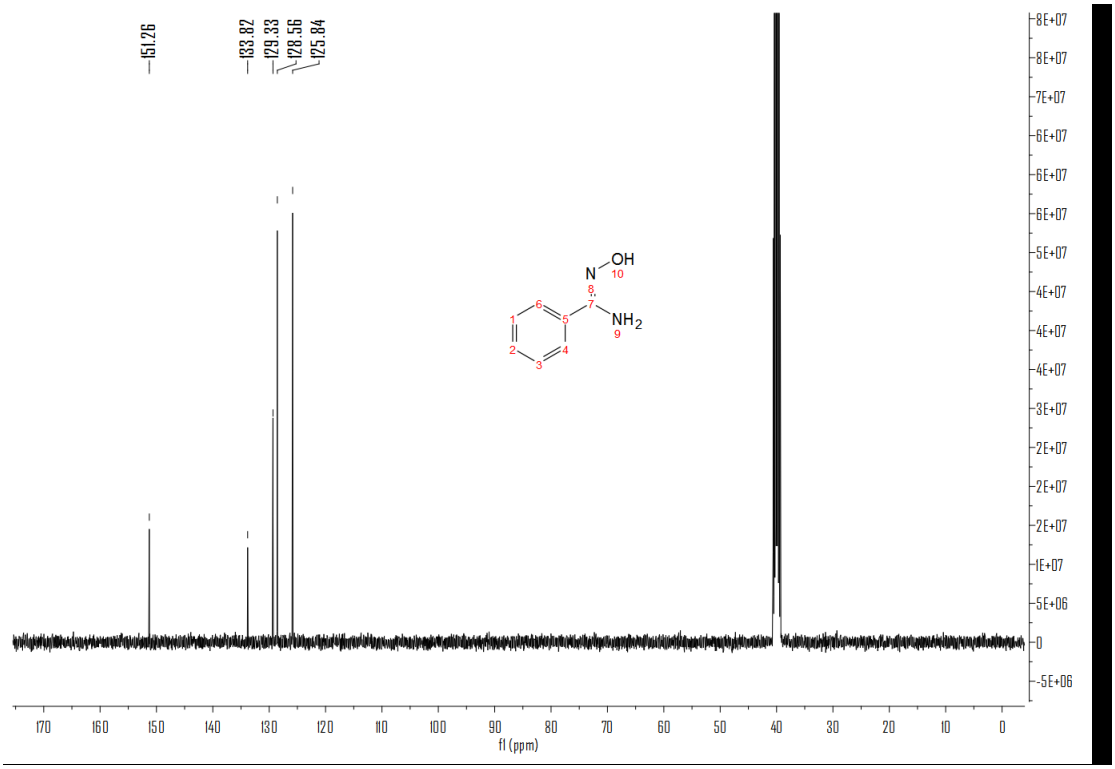
3.03
2.00
f1 (ppm)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NH2
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2
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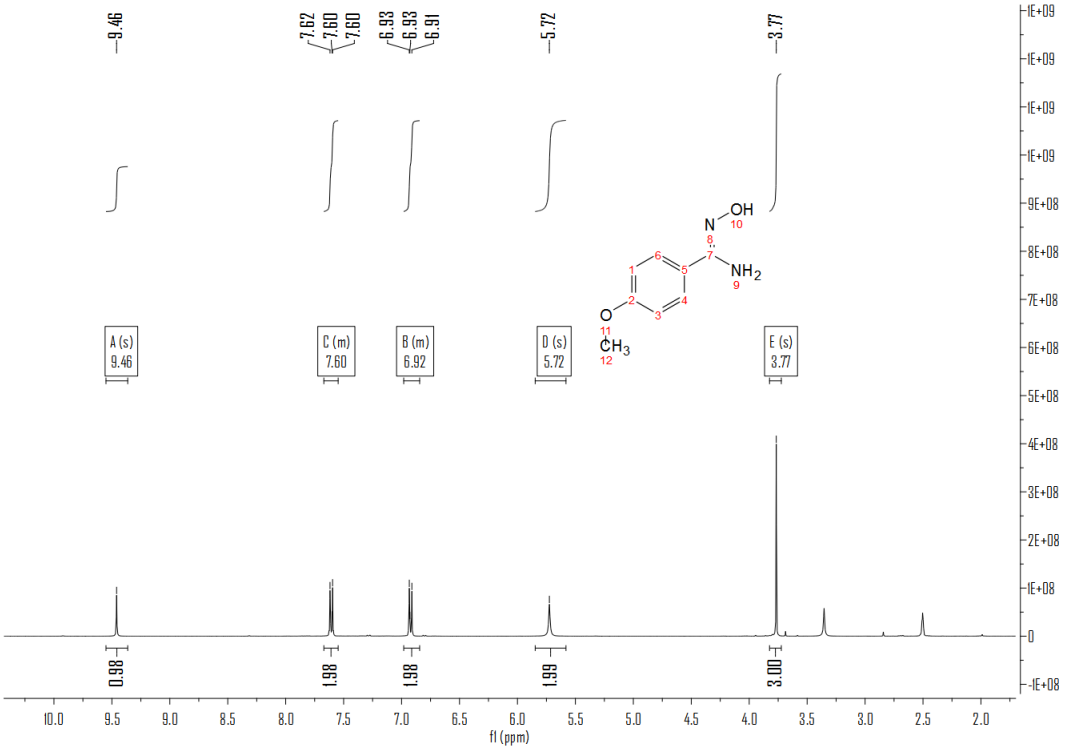
5
6
f1 (ppm)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9.46
C (m)
7.60
B (m)
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E (s)
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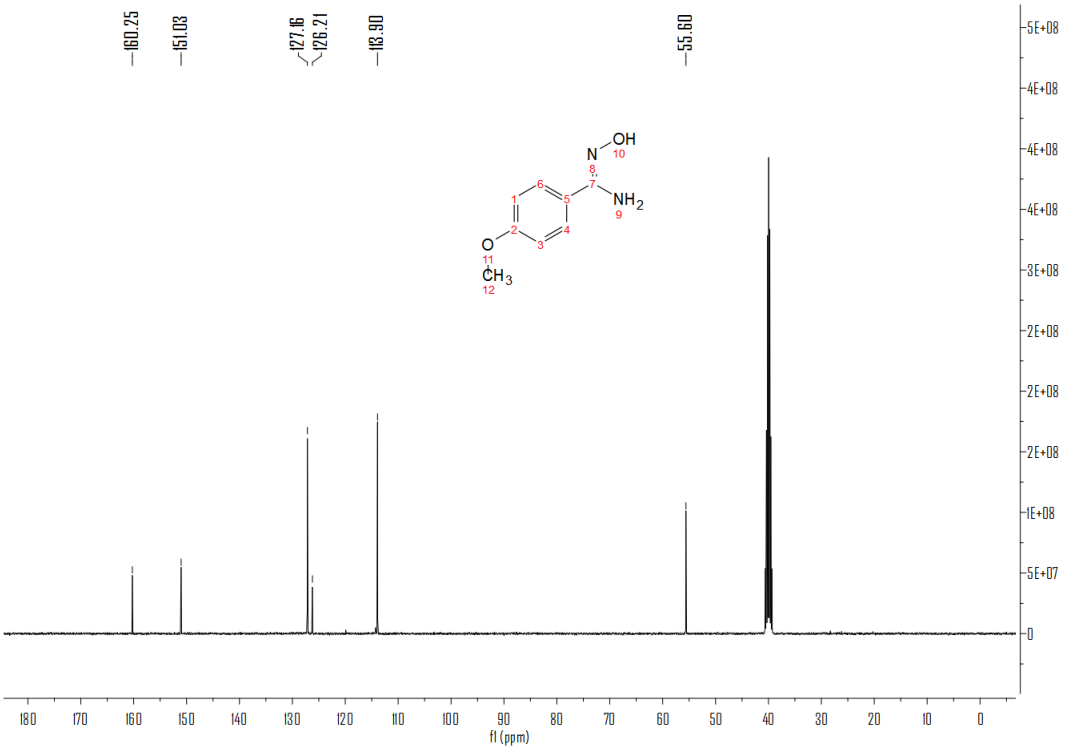
3.00
f1 (ppm)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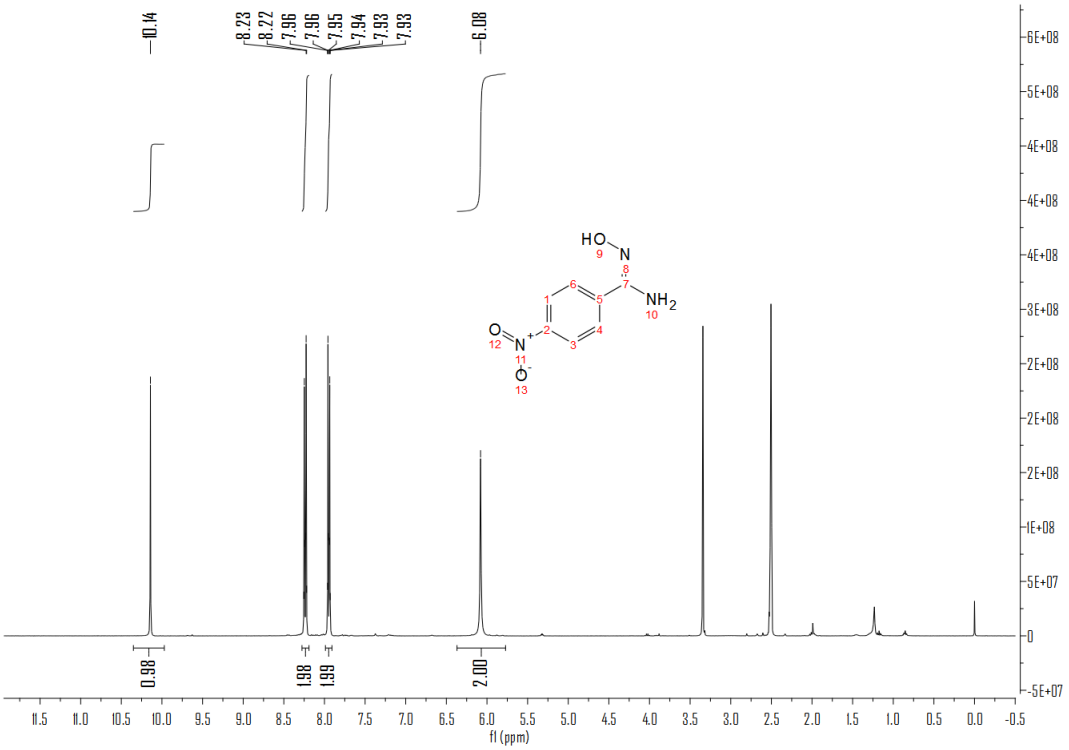
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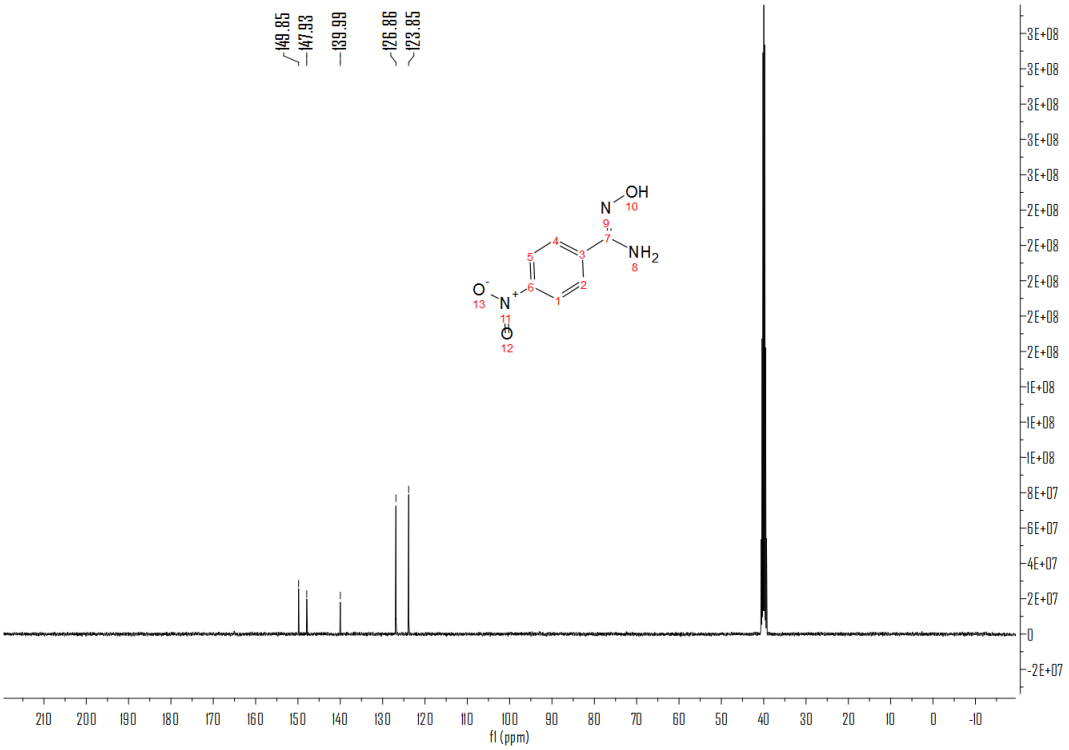
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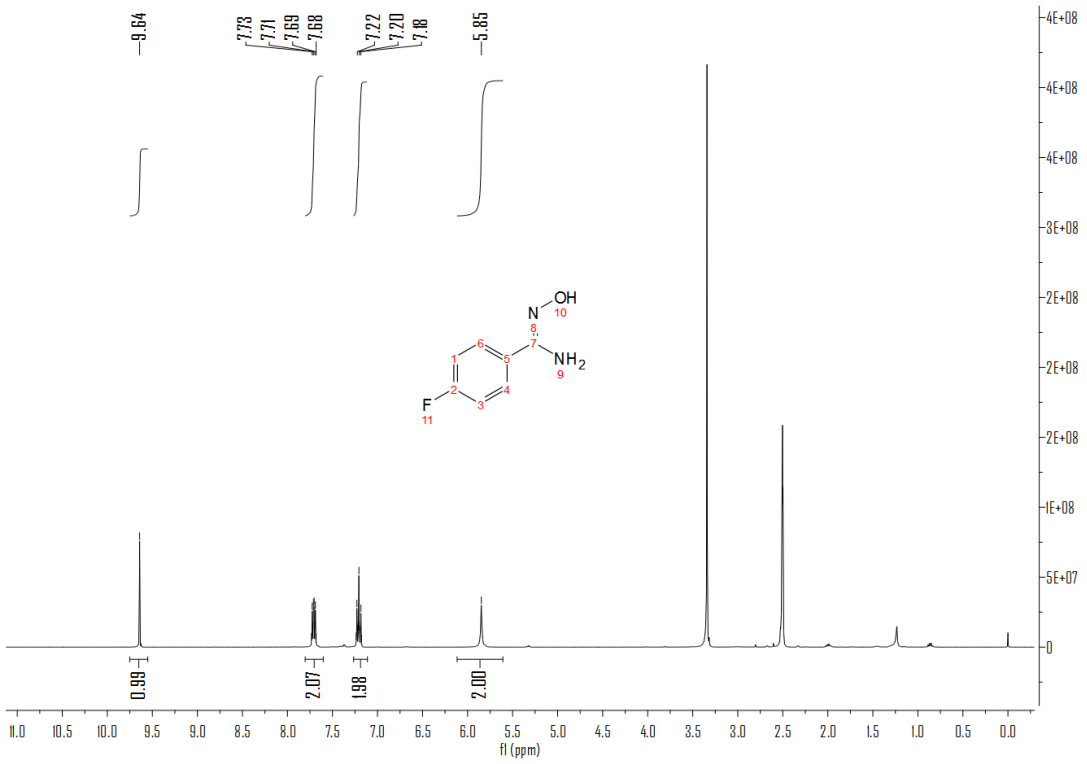
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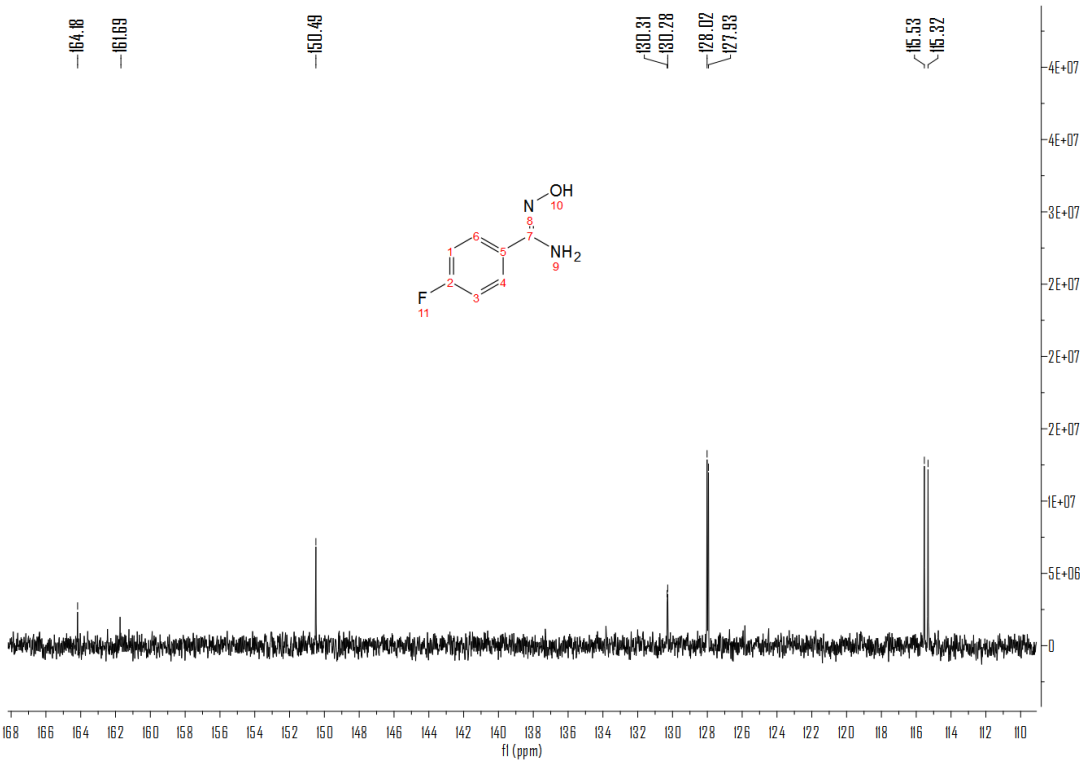
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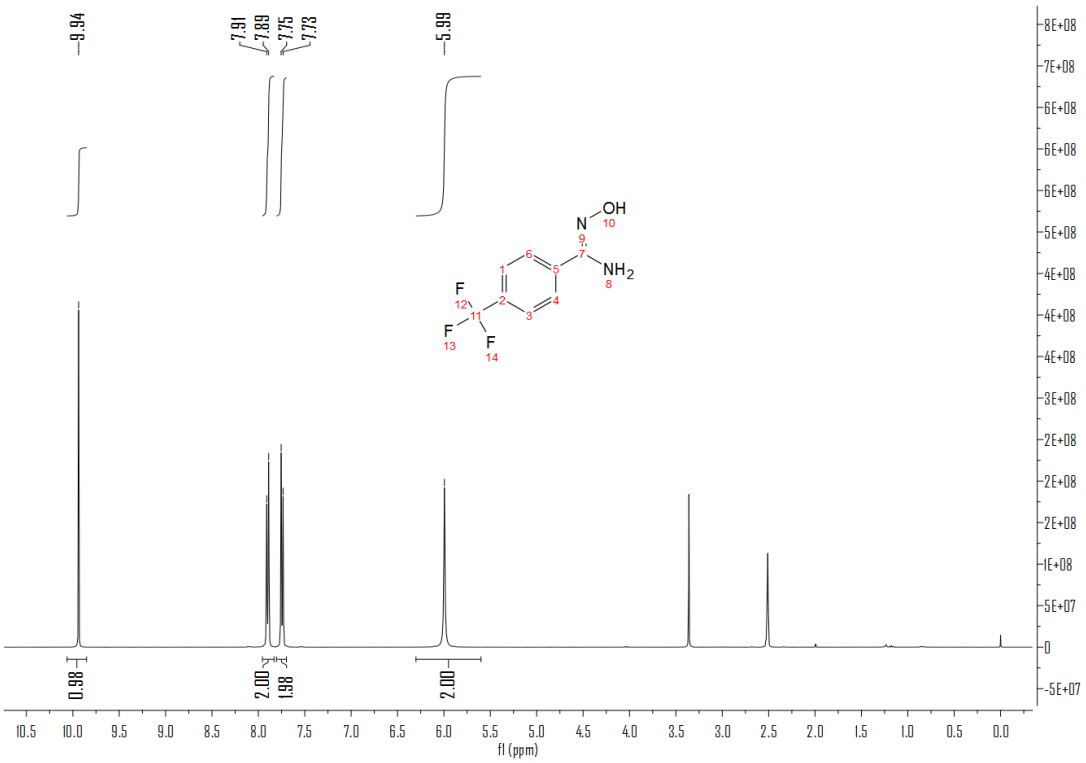
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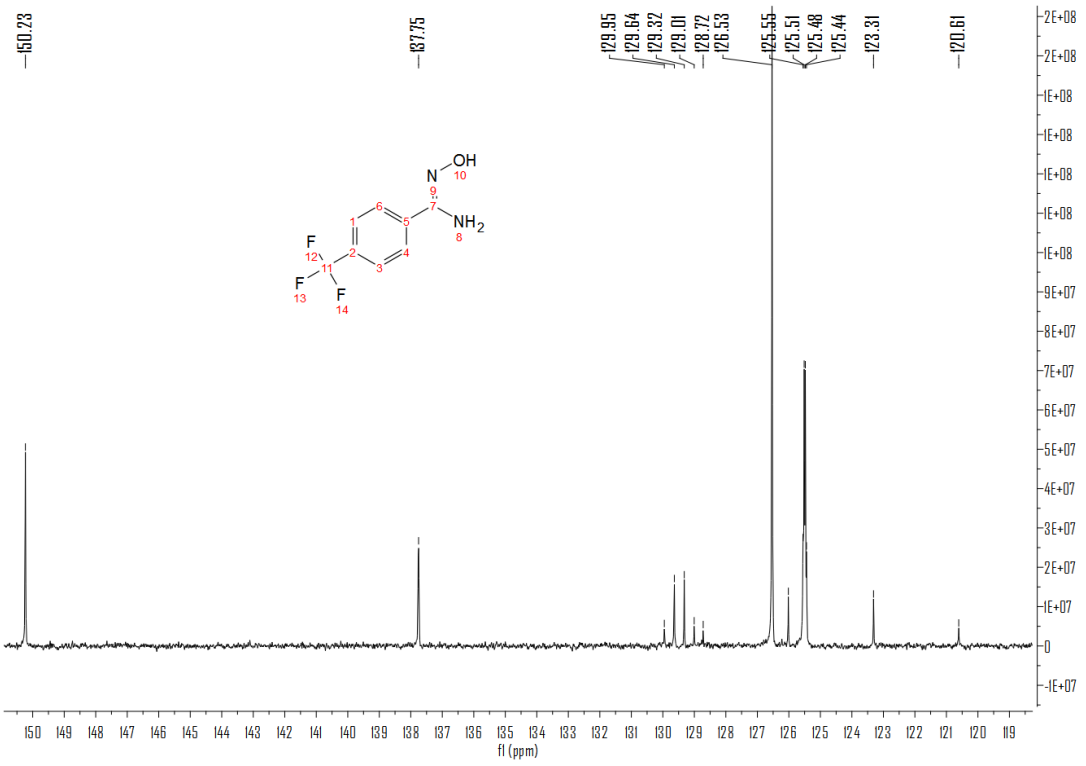
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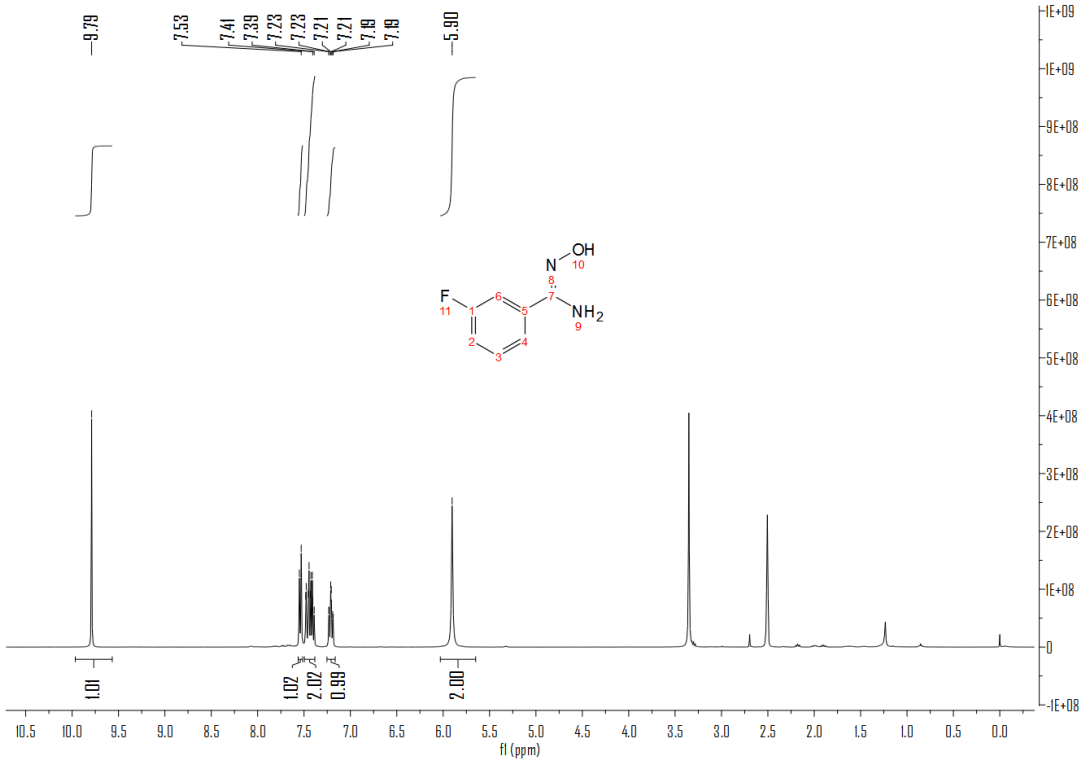
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8
F
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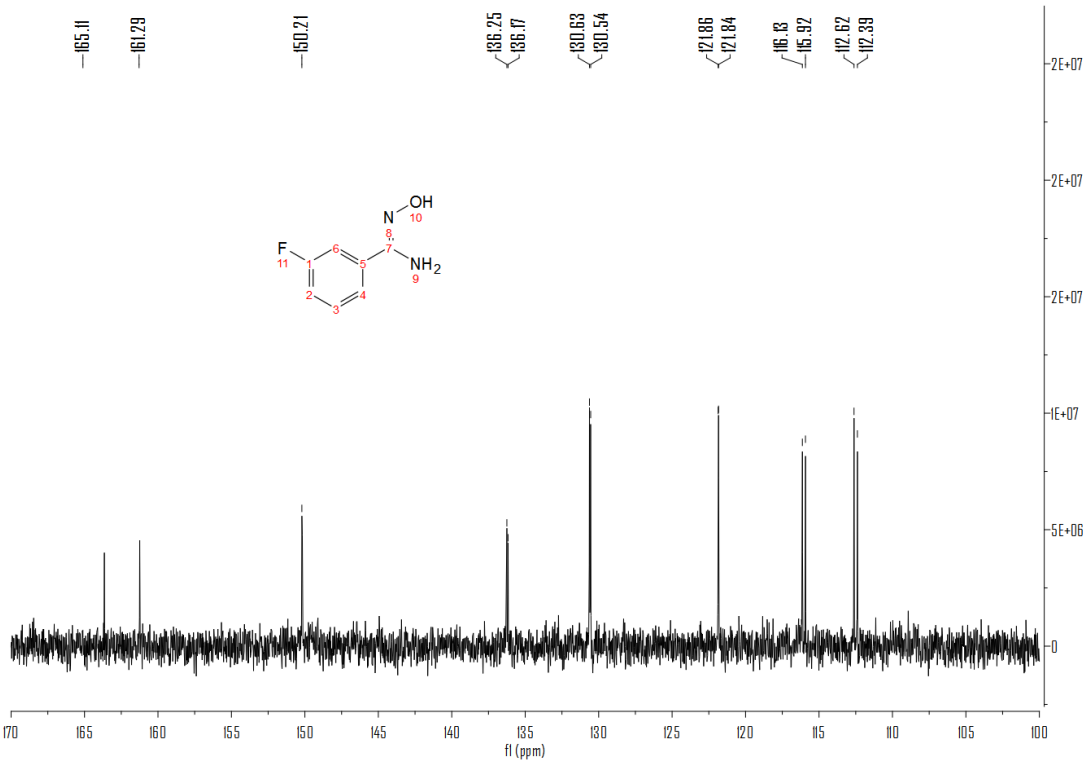
f1 (ppm)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7
5
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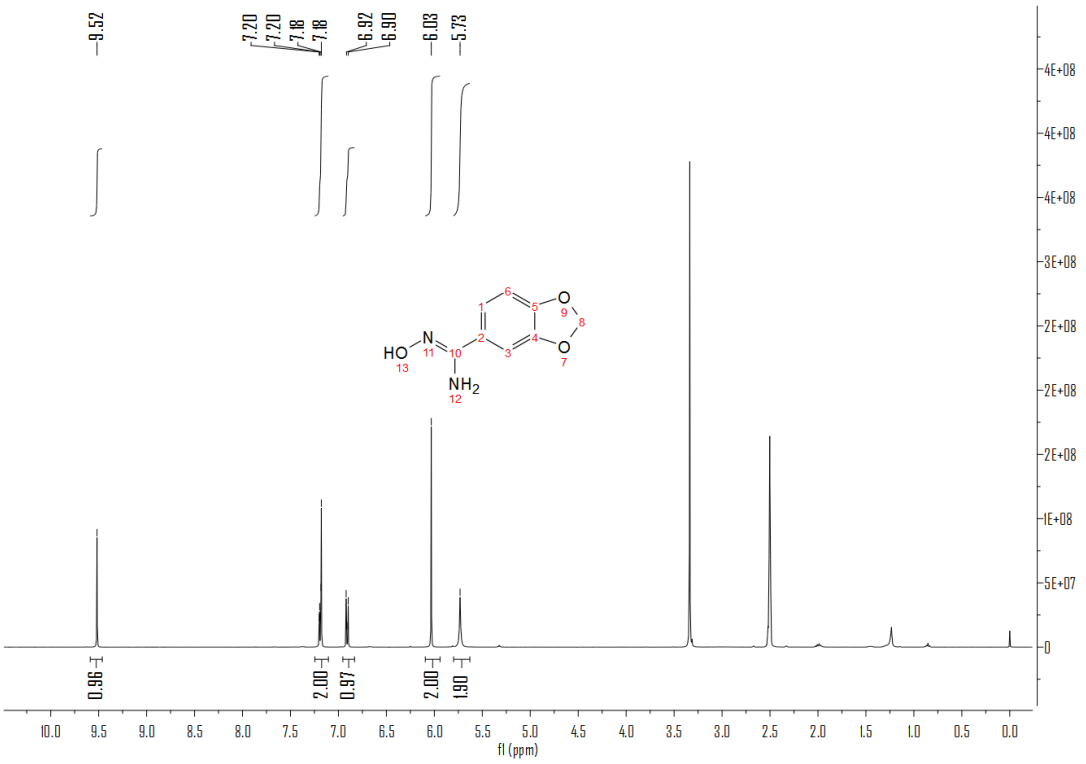
3
f1 (ppm)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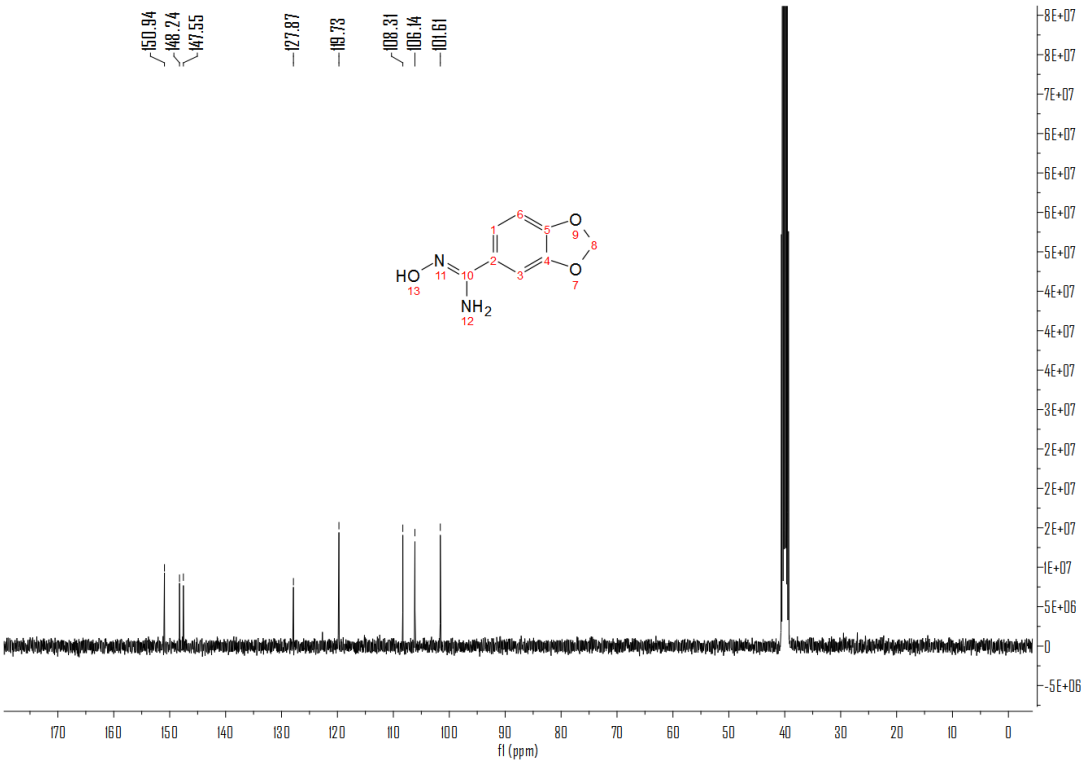
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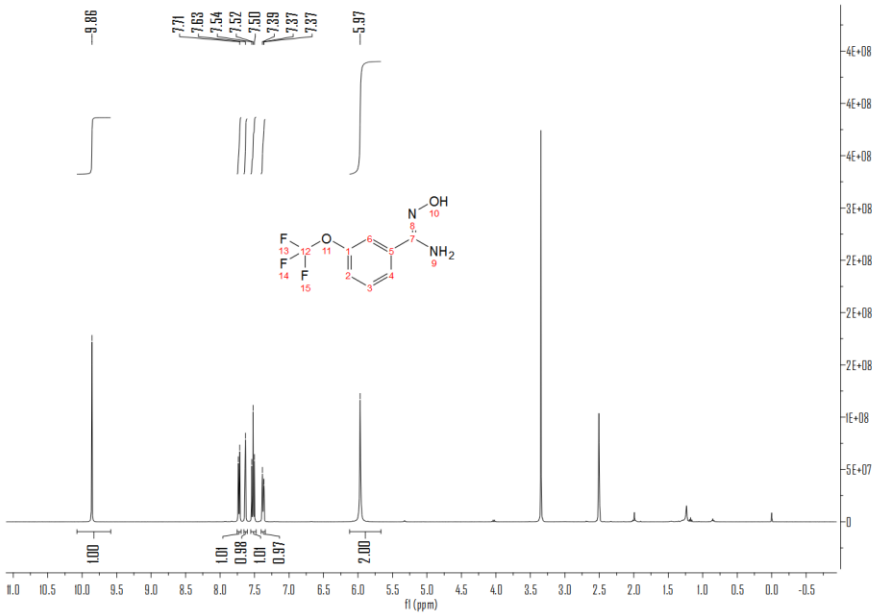
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NH2
9
F
13
12
O
11
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6
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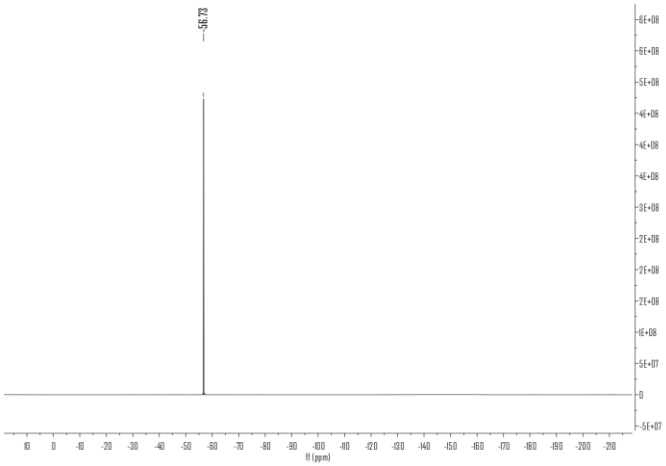
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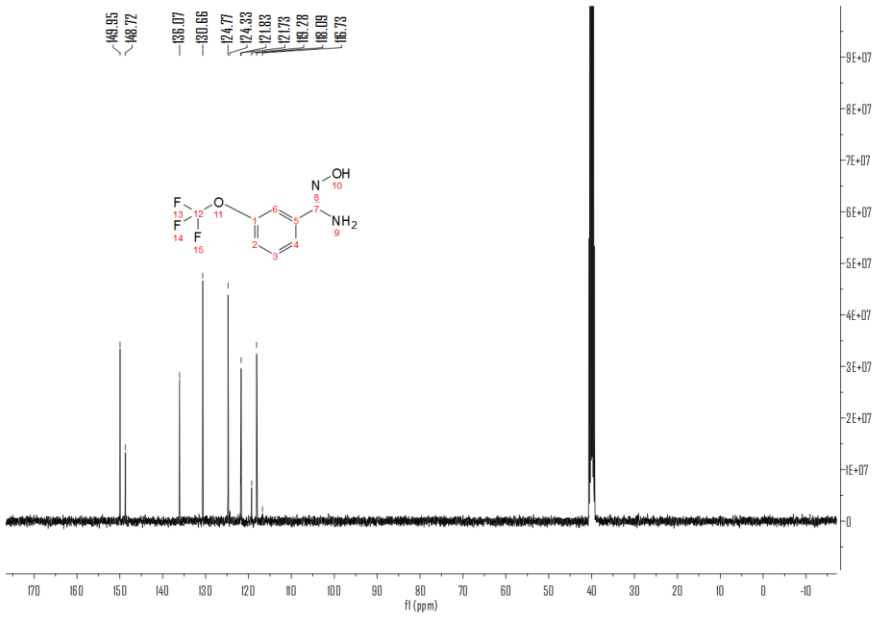
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F
14
F
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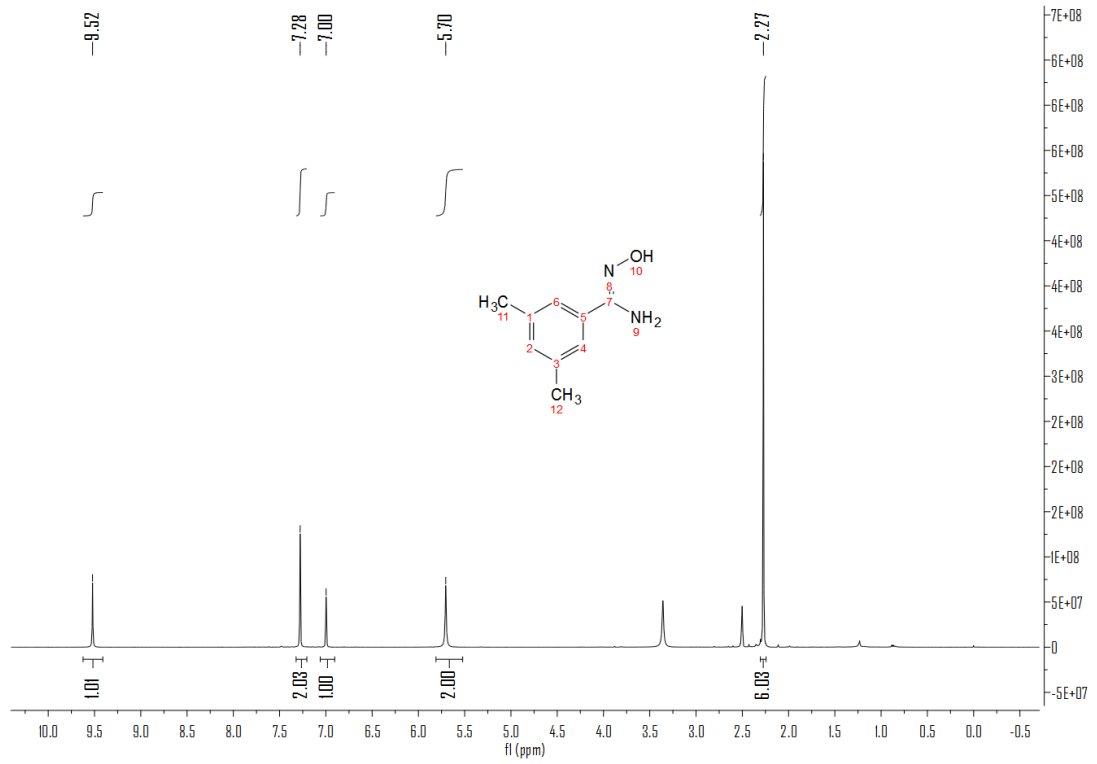
2
3
4
f1 (ppm)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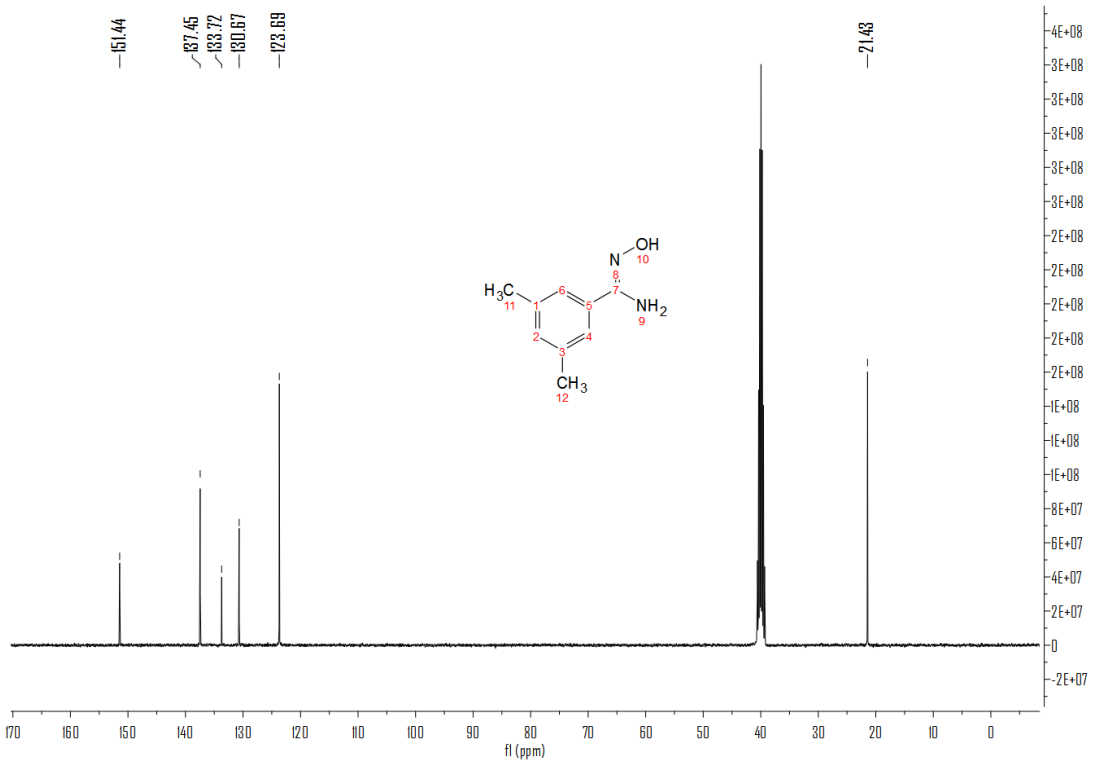
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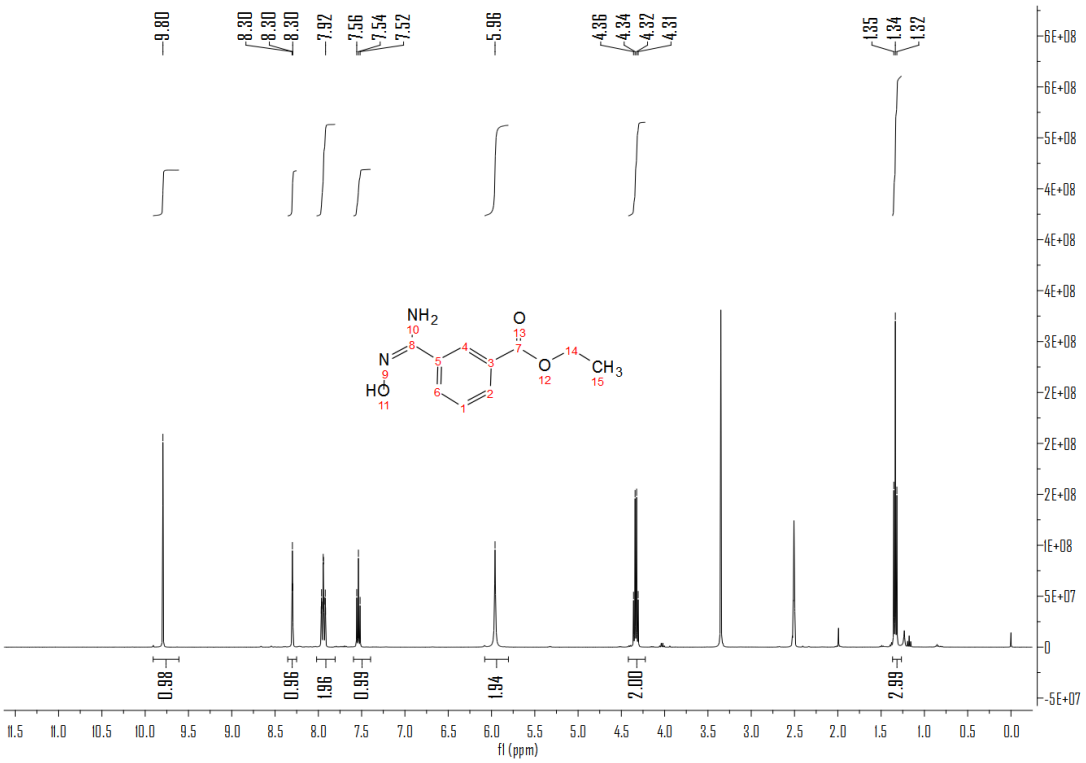
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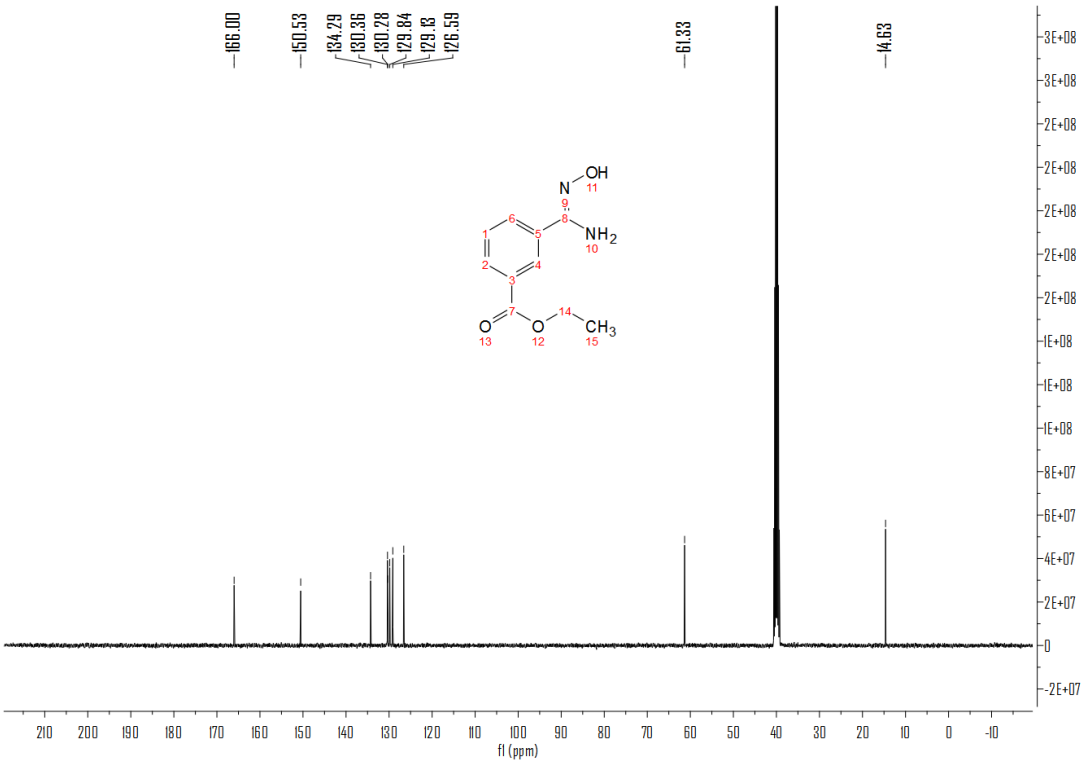
f1 (ppm)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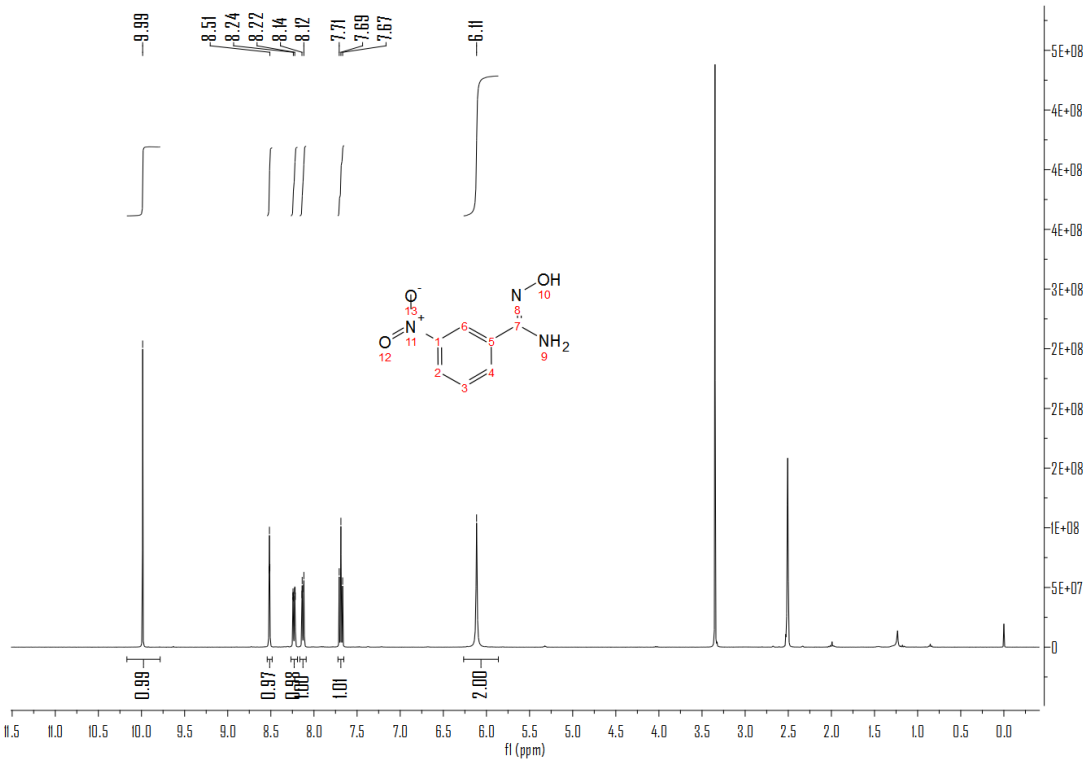
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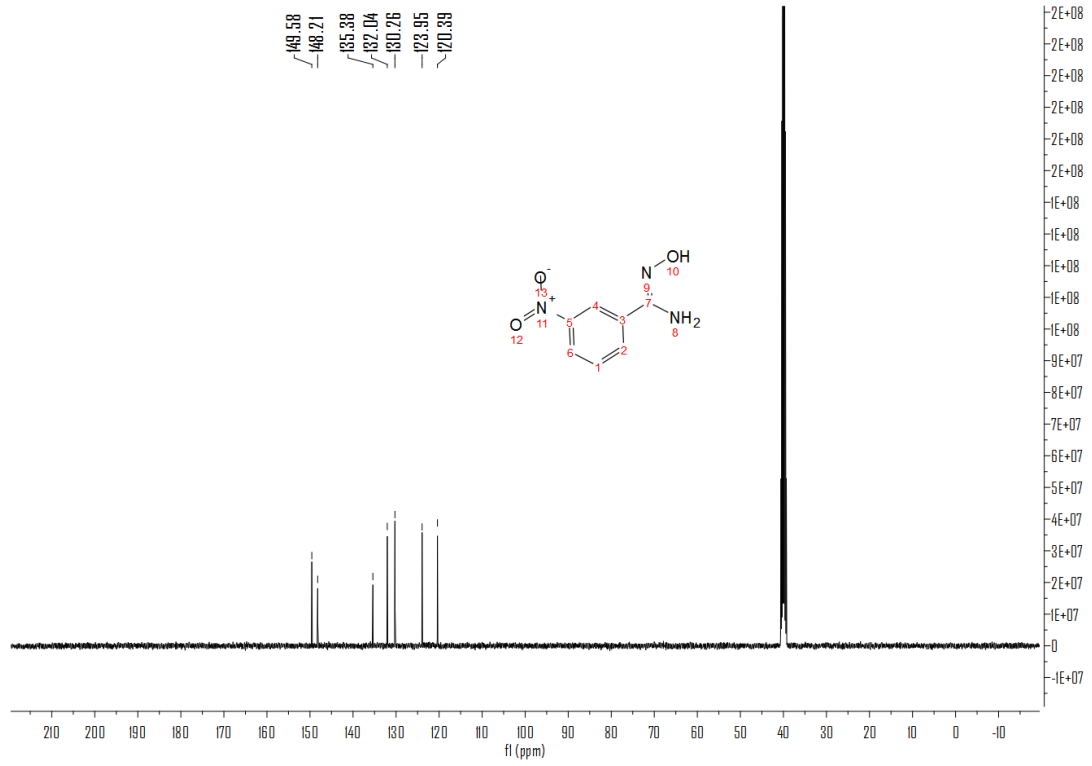
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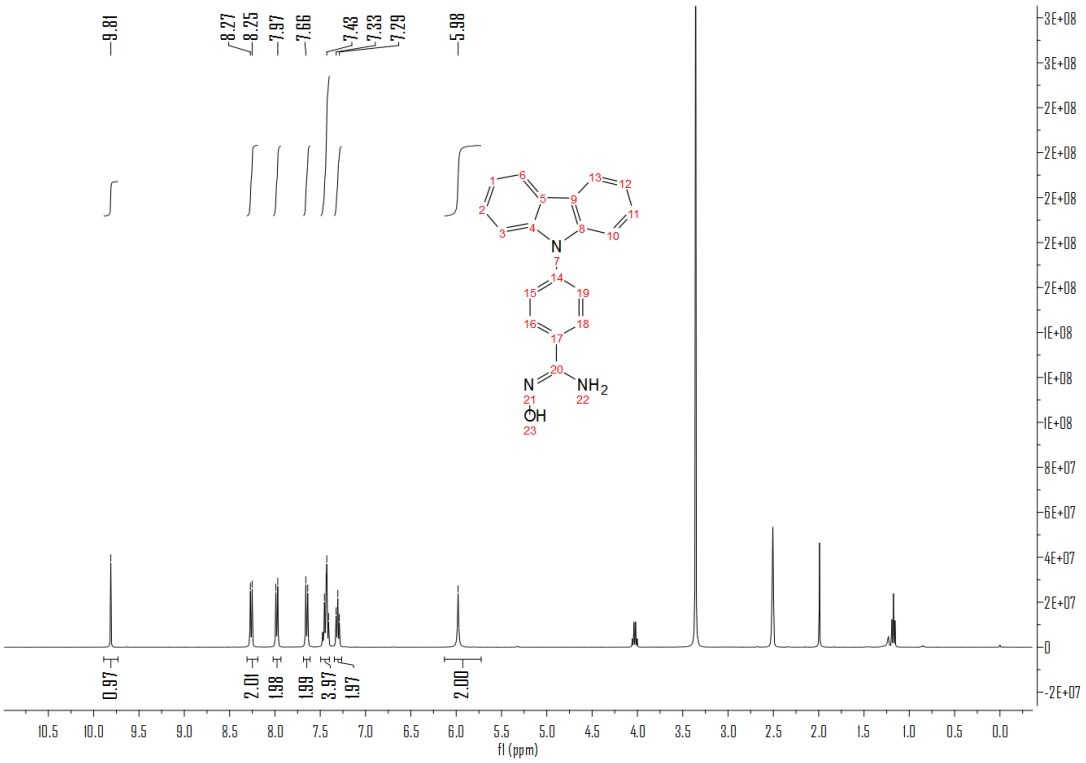
f1 (ppm)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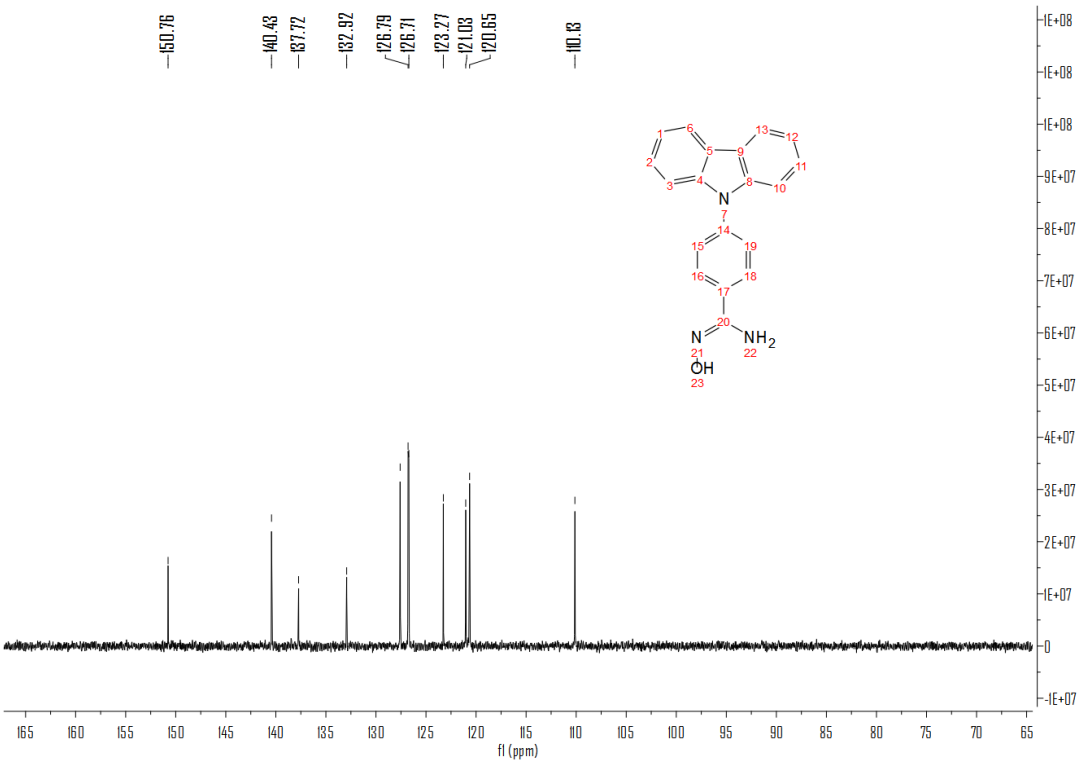
8.27
8.25
7.97
7.66
7.43
7.33
7.29
5.98
0.97
2.01
1.98
1.99
3.97
1.97
2.00
f1 (ppm)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126.79
126.71
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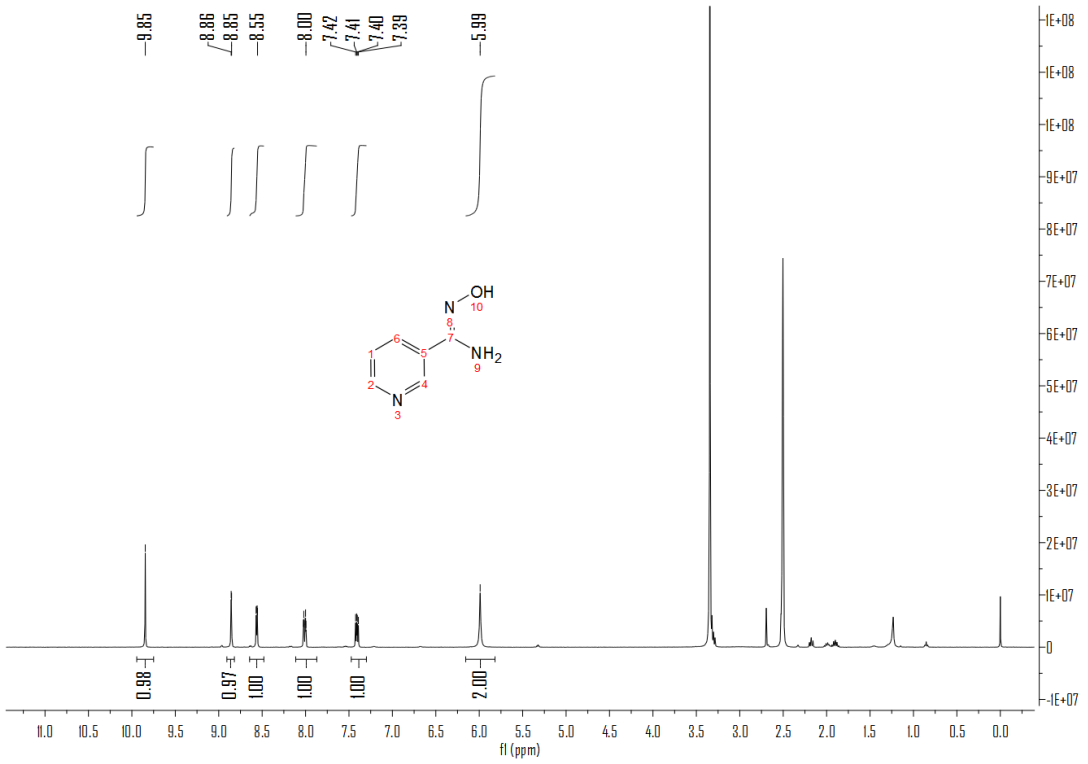
f1 (ppm)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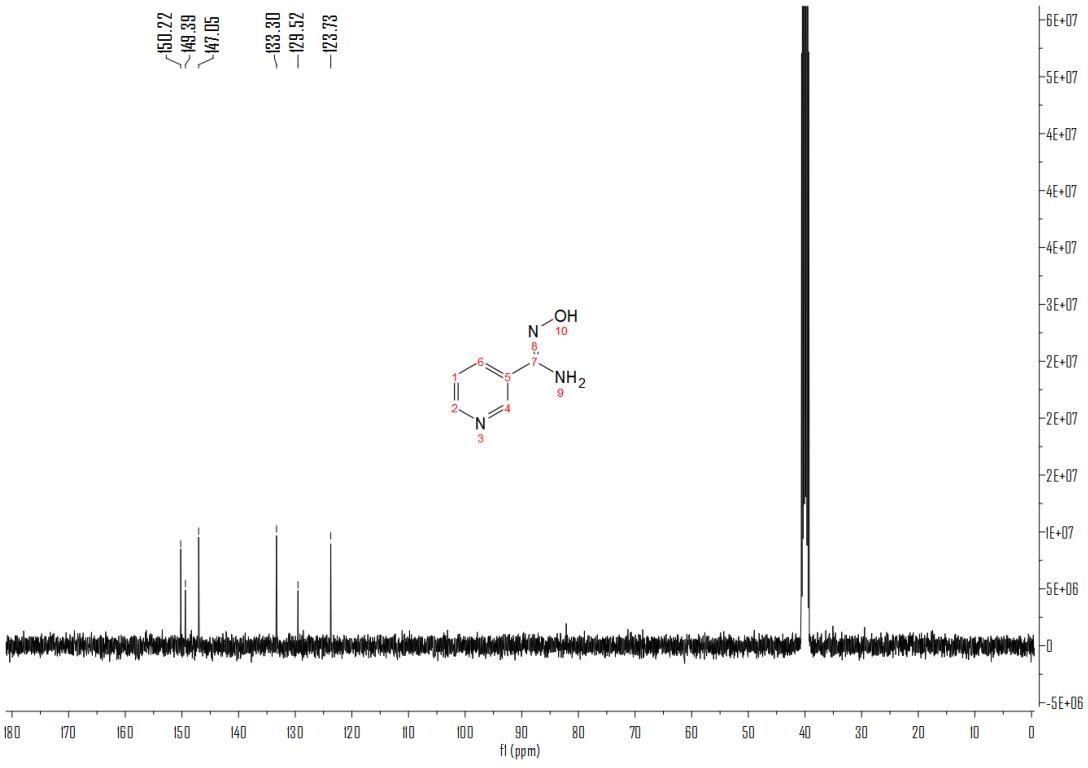
7.42
7.41
7.40
7.39
5.99
OH
N
10
8
7
NH2
9
6
5
1
2
4
N
3
0.98
0.97
1.00
1.00
1.00
2.00
f1 (ppm)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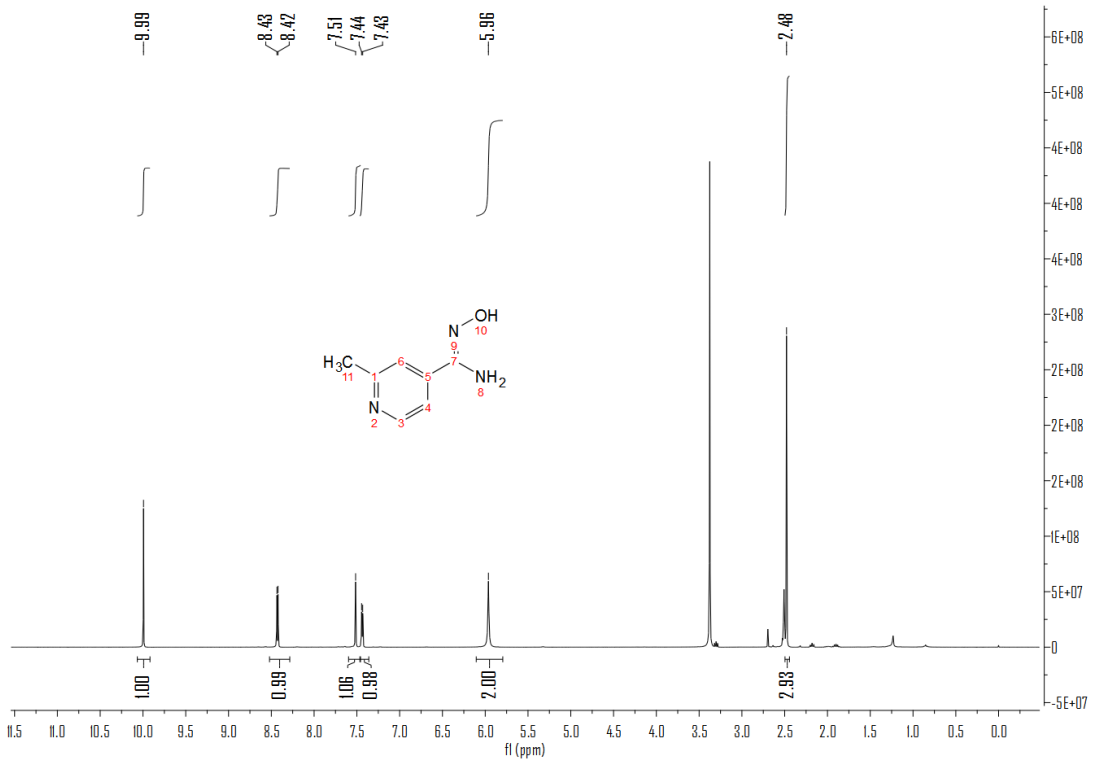
NH2
9
6
5
1
2
4
N
3
f1 (ppm)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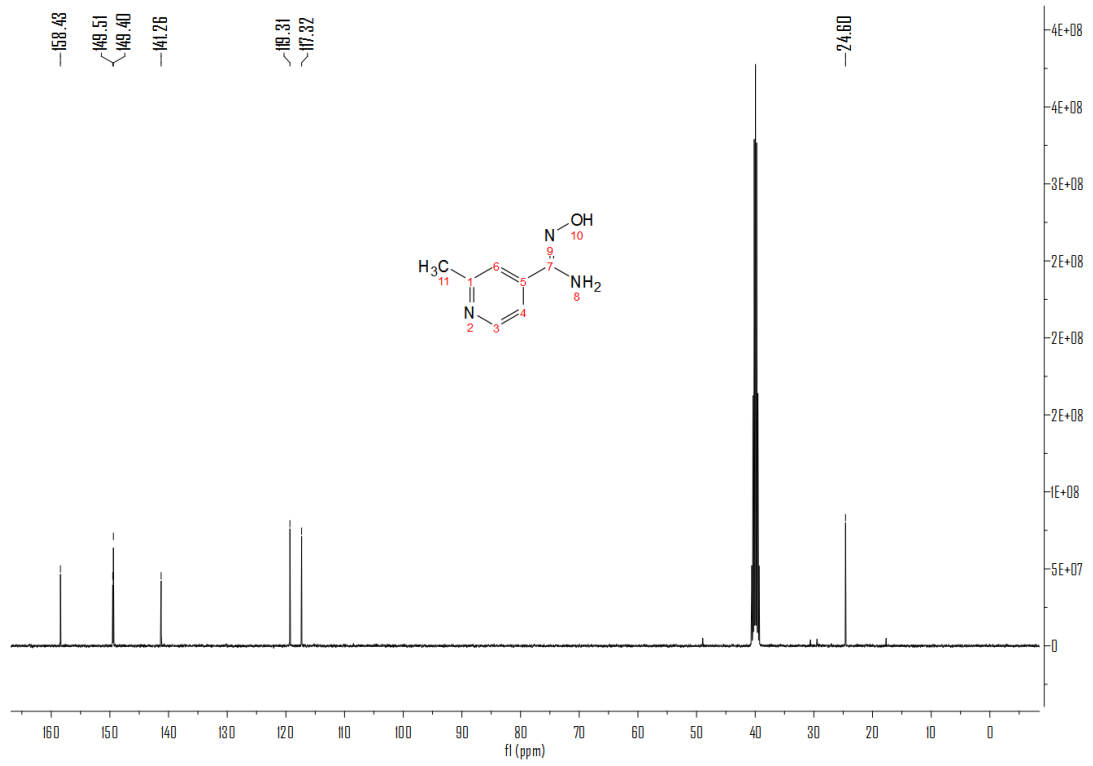
0.99
1.06
0.98
2.00
2.93
f1 (ppm)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117.32
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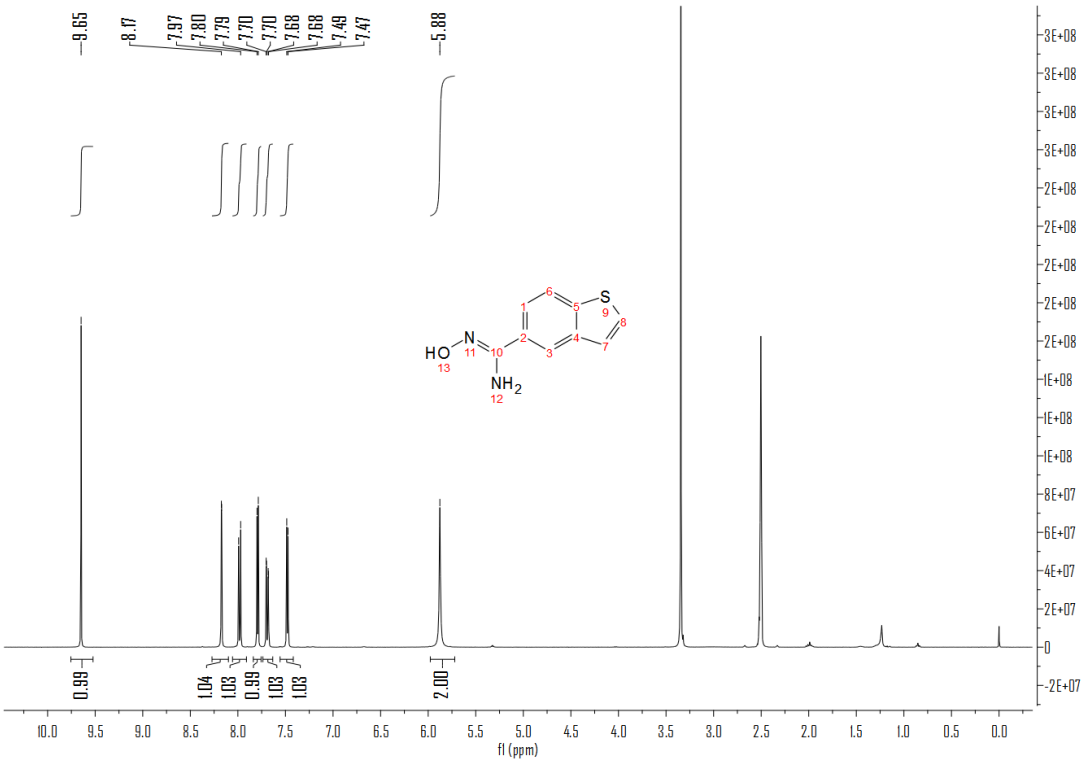
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7.70
7.70
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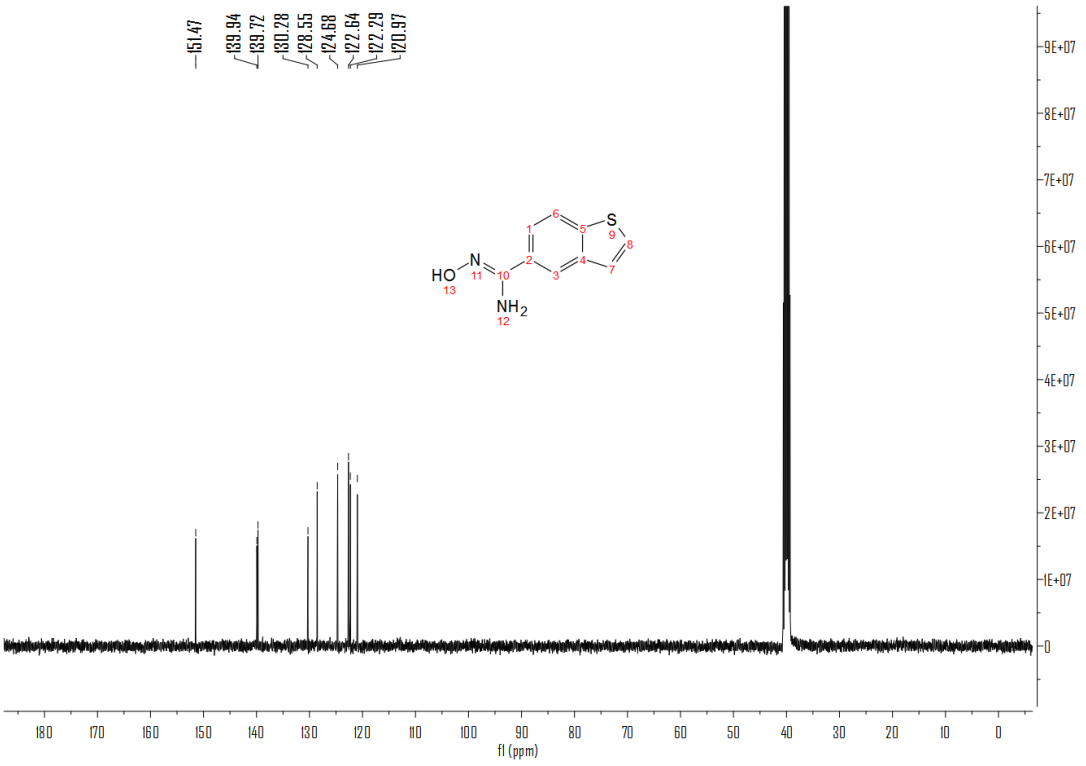
1.03
0.99
1.03
1.03
2.00
f1 (ppm)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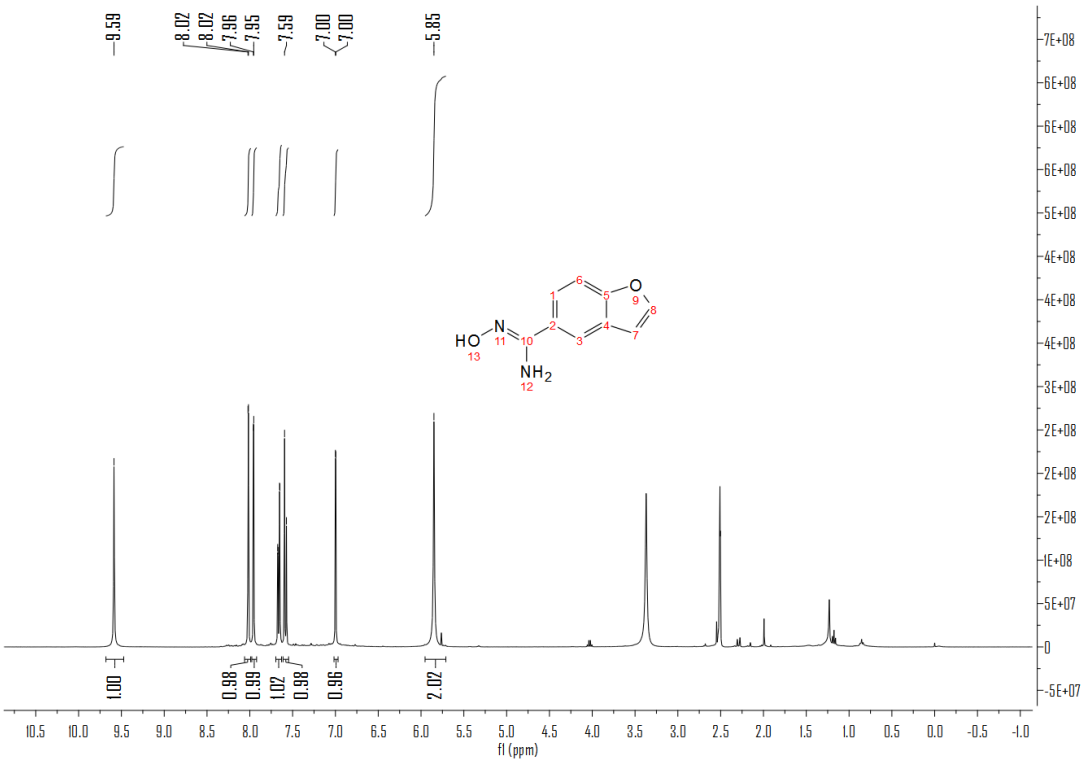
122.29
120.97
f1 (ppm)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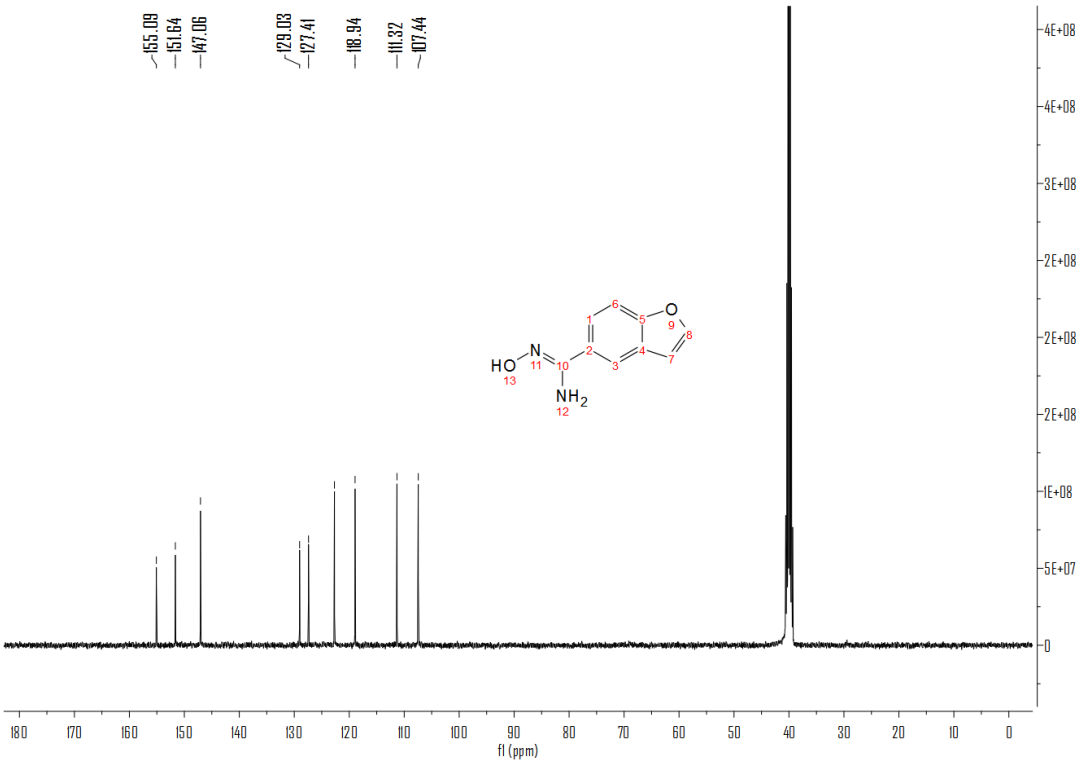
8.02
8.02
7.96
7.95
7.59
7.00
7.00
5.85
1.00
0.98
0.99
1.02
0.98
0.96
2.02
f1 (ppm)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147.06
129.03
127.41
118.94
111.32
107.44
f1 (ppm)

V. Crystallographic data

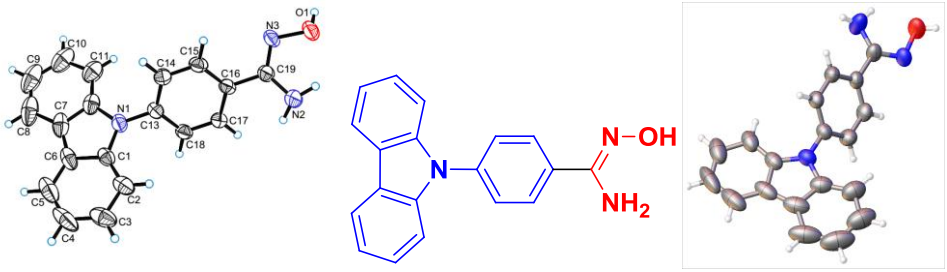

Table 1 Crystal data and structure refinement for ZZQ0923-1.

Identification code	ZZQ0923-1
Empirical formula	$C_{19}H_{15}N_3O$
Formula weight	301.34
Temperature/K	290(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	8.778(5)
b/Å	27.635(5)
c/Å	7.797(5)
α/°	90
β/°	105.261(5)
γ/°	90
Volume/Å^3	1824.7(16)
Z	4
ρ_{calc}g/cm^3	1.090
μ/mm^{-1}	0.070
F(000)	624.0
Crystal size/mm^3	0.45 × 0.41 × 0.32
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/ °	6.398 to 58.204
Index ranges	$-9 \le h \le 11$, $-36 \le k \le 22$, $-10 \le l \le 10$
Reflections collected	12029
Independent reflections	4254 [R_{int} = 0.0216, R_{sigma} = 0.0272]
Data/restraints/parameters	4254/3/215
Goodness-of-fit on F^2	1.085
Final R indexes [I>=2σ (I)]	R_1 = 0.0729, wR_2 = 0.1903
Final R indexes [all data]	R_1 = 0.0952, wR_2 = 0.1987
Largest diff. peak/hole / e Å^{-3}	0.32/-0.25

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic

Displacement Parameters ($Å^2 \times 10^3$) for ZZQ0923-1. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	6859(3)	-43.5(9)	-4170(3)	75.6(7)
N1	3576(3)	1446.0(9)	2466(3)	57.6(6)
N2	8040(4)	108.8(16)	-880(4)	96.8(12)
N3	5925(3)	249.9(9)	-3338(3)	56.4(6)
C13	4328(3)	1161.7(9)	1411(3)	49.8(6)
C14	4098(4)	1259.1(11)	-375(4)	57.9(7)
C16	5848(3)	611.9(10)	-603(3)	48.7(6)
C18	5337(3)	792.4(10)	2188(3)	52.0(7)
C6	3208(5)	1939.6(11)	4643(5)	74.1(10)
C9	-1066(7)	1843(2)	1889(10)	127(2)
C19	6638(3)	311.7(11)	-1685(4)	56.0(7)
C17	6085(3)	523.7(10)	1192(3)	52.1(7)
C1	4346(4)	1681.4(10)	4024(4)	57.2(7)
C2	5925(5)	1699.5(11)	4875(4)	70.6(9)
C12	1947(4)	1548.0(11)	2083(5)	67.0(8)
C3	6390(6)	1976.9(13)	6396(5)	93.7(14)
C15	4831(3)	984.4(11)	-1374(4)	55.9(7)
C8	131(7)	2006.3(17)	3280(8)	112.3(18)
C11	724(4)	1376.8(15)	713(6)	85.9(11)
C7	1710(5)	1854.6(12)	3403(5)	78.9(11)
C5	3711(8)	2216.5(14)	6173(6)	101.8(16)
C10	-761(5)	1529.4(19)	640(8)	111.1(16)
C4	5286(9)	2233.4(14)	7029(6)	112.8(19)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for ZZQ0923-1. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	56.3(13)	114.4(19)	60.2(13)	-29.5(12)	22.5(10)	5.3(12)
N1	64.6(15)	57.3(14)	55.9(14)	-3.1(11)	24.4(12)	6.8(11)
N2	57.6(18)	163(3)	63.6(18)	-30(2)	4.1(14)	31.9(19)
N3	50.7(13)	76.5(16)	46.7(13)	-14.1(11)	20.9(10)	-2.0(11)
C13	59.0(16)	47.4(14)	45.1(14)	-2.9(11)	17.4(12)	-1.2(12)
C14	66.8(19)	58.9(17)	48.0(15)	7.4(12)	15.5(13)	9.4(14)
C16	47.4(15)	57.4(16)	41.5(13)	-7.5(11)	11.8(11)	-6.5(12)

C18	62.9(17)	54.2(16)	38.3(13)	0.0(11)	12.2(12)	1.2(13)
C6	128(3)	44.3(16)	67(2)	6.0(14)	56(2)	10.8(18)
C9	88(3)	125(4)	186(6)	62(4)	71(4)	35(3)
C19	41.7(14)	76.2(19)	50.9(16)	-10.7(13)	13.7(12)	-2.9(13)
C17	55.5(16)	55.2(16)	43.2(14)	-1.7(11)	8.7(12)	4.5(12)
C1	85(2)	44.9(15)	47.6(15)	1.8(12)	27.7(15)	0.9(14)
C2	109(3)	51.8(17)	50.3(17)	-2.0(13)	19.9(17)	-7.3(17)
C12	70(2)	59.6(18)	81(2)	16.5(16)	36.1(18)	11.4(15)
C3	151(4)	61(2)	60(2)	-4.3(17)	12(2)	-24(2)
C15	62.0(18)	67.2(18)	38.5(14)	3.5(12)	13.4(12)	-0.4(14)
C8	127(4)	87(3)	158(5)	40(3)	98(4)	40(3)
C11	64(2)	91(3)	103(3)	17(2)	23(2)	4.8(19)
C7	101(3)	60.2(19)	98(3)	21.7(18)	64(2)	19.9(19)
C5	183(5)	58(2)	82(3)	-3(2)	67(3)	14(3)
C10	69(3)	121(4)	145(4)	43(3)	30(3)	14(3)
C4	223(6)	58(2)	62(2)	-18.2(19)	46(3)	-9(3)

Table 4 Bond Lengths for ZZQ0923-1.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	N3	1.425(3)	C6	C1	1.412(4)
N1	C13	1.419(3)	C6	C7	1.432(6)
N1	C1	1.386(4)	C6	C5	1.388(5)
N1	C12	1.411(4)	C9	C8	1.372(8)
N2	C19	1.348(4)	C9	C10	1.382(8)
N3	C19	1.287(3)	C1	C2	1.371(5)
C13	C14	1.380(4)	C2	C3	1.380(4)
C13	C18	1.382(4)	C12	C11	1.383(5)
C14	C15	1.364(4)	C12	C7	1.391(5)
C16	C19	1.480(4)	C3	C4	1.392(7)
C16	C17	1.381(4)	C8	C7	1.428(6)
C16	C15	1.391(4)	C11	C10	1.357(6)
C18	C17	1.362(4)	C5	C4	1.369(7)

Table 5 Bond Angles for ZZQ0923-1.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°

C1	N1	C13	125.0(3)	C18	C17	C16	121.0(3)
C1	N1	C12	109.0(2)	N1	C1	C6	108.2(3)
C12	N1	C13	126.0(3)	C2	C1	N1	129.7(3)
C19	N3	O1	110.2(2)	C2	C1	C6	122.1(3)
C14	C13	N1	120.7(3)	C1	C2	C3	118.0(4)
C14	C13	C18	119.5(2)	C11	C12	N1	129.3(3)
C18	C13	N1	119.8(2)	C11	C12	C7	122.9(4)
C15	C14	C13	120.1(3)	C7	C12	N1	107.8(3)
C17	C16	C19	120.7(3)	C2	C3	C4	120.7(5)
C17	C16	C15	118.5(2)	C14	C15	C16	120.7(3)
C15	C16	C19	120.8(2)	C9	C8	C7	119.0(5)
C17	C18	C13	120.1(2)	C10	C11	C12	117.9(5)
C1	C6	C7	107.0(3)	C12	C7	C6	108.1(3)
C5	C6	C1	118.7(4)	C12	C7	C8	117.4(5)
C5	C6	C7	134.3(4)	C8	C7	C6	134.4(4)
C8	C9	C10	120.9(5)	C4	C5	C6	119.3(4)
N2	C19	C16	118.4(3)	C11	C10	C9	121.9(5)
N3	C19	N2	123.7(3)	C5	C4	C3	121.2(4)
N3	C19	C16	117.9(3)				

Table 6 Hydrogen Bonds for ZZQ0923-1.

D	H	A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/ °
O1	H1	N3[1]	0.79	2.05	2.752(3)	146.9
N2	H2A	O1	0.899(5)	2.03(4)	2.536(4)	115(4)

[1]1-X,-Y,-1-Z

Table 7 Torsion Angles for ZZQ0923-1.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	N3	C19	N2	-2.2(5)	C1	N1	C12	C11	-177.1(3)
O1	N3	C19	C16	179.5(2)	C1	N1	C12	C7	0.8(3)
N1	C13	C14	C15	179.8(3)	C1	C6	C7	C12	0.6(3)
N1	C13	C18	C17	-178.8(3)	C1	C6	C7	C8	179.6(4)
N1	C1	C2	C3	177.9(3)	C1	C6	C5	C4	0.3(5)
N1	C12	C11	C10	179.6(3)	C1	C2	C3	C4	-0.6(5)

N1	C12	C7	C6	-0.9(3)	C2	C3	C4	C5	0.4(6)
N1	C12	C7	C8	180.0(3)	C12	N1	C13	C14	52.5(4)
C13	N1	C1	C6	177.8(2)	C12	N1	C13	C18	-129.4(3)
C13	N1	C1	C2	0.4(5)	C12	N1	C1	C6	-0.4(3)
C13	N1	C12	C11	4.8(5)	C12	N1	C1	C2	-177.8(3)
C13	N1	C12	C7	-177.4(3)	C12	C11	C10	C9	-0.4(6)
C13	C14	C15	C16	-1.7(5)	C15	C16	C19	N2	152.3(3)
C13	C18	C17	C16	-0.3(4)	C15	C16	C19	N3	-29.3(4)
C14	C13	C18	C17	-0.7(4)	C15	C16	C17	C18	0.3(4)
C18	C13	C14	C15	1.7(4)	C8	C9	C10	C11	-1.3(8)
C6	C1	C2	C3	0.8(4)	C11	C12	C7	C6	177.1(3)
C6	C5	C4	C3	-0.2(6)	C11	C12	C7	C8	-2.0(5)
C9	C8	C7	C6	-178.5(4)	C7	C6	C1	N1	-0.2(3)
C9	C8	C7	C12	0.3(6)	C7	C6	C1	C2	177.5(3)
C19	C16	C17	C18	-178.7(3)	C7	C6	C5	C4	-177.2(4)
C19	C16	C15	C14	179.7(3)	C7	C12	C11	C10	2.0(5)
C17	C16	C19	N2	-28.7(4)	C5	C6	C1	N1	-178.2(3)
C17	C16	C19	N3	149.7(3)	C5	C6	C1	C2	-0.6(5)
C17	C16	C15	C14	0.7(4)	C5	C6	C7	C12	178.3(4)
C1	N1	C13	C14	-125.4(3)	C5	C6	C7	C8	-2.8(7)
C1	N1	C13	C18	52.7(4)	C10	C9	C8	C7	1.3(7)

Table 8 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for ZZQ0923-1.

Atom	***x***	***y***	***z***	**U(eq)**
H1	6306	-178	-5004	113
H14	3442	1512	-899	69
H18	5505	727	3394	62
H9	-2096	1945	1786	152
H17	6765	277	1728	63
H2	6660	1530	4441	85
H3	7453	1993	7004	112
H15	4649	1047	-2584	67
H8	-84	2213	4130	135
H11	914	1164	-132	103
H5	2985	2389	6612	122
H10	-1598	1420	-275	133
H4	5625	2420	8052	135

H2B	8280(40)	20(15)	266(19)	135
H2A	8420(50)	-27(16)	-1730(50)	135

Table 9 Solvent masks information for ZZQ0923-1.

Number	X	Y	Z	Volume	Electron count	Content
1	0.257	0.603	1.002	209	25	

Experimental

A suitable crystal was selected on a diffractometer. The crystal was kept at 290(2) K during data collection. Using Olex2 [1], the structure was solved with the ShelXS [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.
3. Sheldrick, G.M. (2008). Acta Cryst. A64, 112-122.

Crystal structure determination of [ZZQ0923-1]

Crystal Data for $C_{19}H_{15}N_3O$ (M =301.34 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 8.778(5) Å, b = 27.635(5) Å, c = 7.797(5) Å, β = 105.261(5) °, V = 1824.7(16) Å^3, Z = 4, T = 290(2) K, μ(MoKα) = 0.070 mm^{-1}, *Dcalc* = 1.090 g/cm^3, 12029 reflections measured (6.398° ≤ 2Θ ≤ 58.204°), 4254 unique (R_{int} = 0.0216, R_{sigma} = 0.0272) which were used in all calculations. The final R_1 was 0.0729 (I > 2σ(I)) and wR_2 was 0.1987 (all data).

Refinement model description

Number of restraints - 3, number of constraints - unknown.

Details:

1. Others

Fixed Uiso: H1(0.113) H14(0.069) H18(0.062) H9(0.152) H17(0.063) H2(0.085) H3(0.112) H15(0.067) H8(0.135) H11(0.103) H5(0.122) H10(0.133) H4(0.135) H2B(0.135) H2A(0.135)

Fixed X: H1(0.6306) H14(0.3442) H18(0.5505) H9(-0.2096) H17(0.6765) H2(0.666) H3(0.7453) H15(0.4649) H8(-0.0084) H11(0.0914) H5(0.2985) H10(-0.1598) H4(0.5625)

Fixed Y: H1(-0.0178) H14(0.1512) H18(0.0727) H9(0.1945) H17(0.0277) H2(0.153) H3(0.1993) H15(0.1047) H8(0.2213) H11(0.1164) H5(0.2389) H10(0.142) H4(0.242)

Fixed Z: H1(-0.5004) H14(-0.0899) H18(0.3394) H9(0.1786) H17(0.1728) H2(0.4441) H3(0.7004) H15(-0.2584) H8(0.413) H11(-0.0132) H5(0.6612) H10(-0.0275) H4(0.8052)

This report has been created with Olex2, compiled on 2014.07.22 svn.r2960 for OlexSys.