Supporting Materials

Concise Synthesis of Semicarbazides and Formylhydrazines *via* Direct Addition Reaction between Aromatic Azoarenes and *N*-Substituted Formamides

*Defu Liu[1], Jincheng Mao,[1,2]*Guangwei Rong[1], Hong Yan[1], Yang Zheng[1], Jie Chen[1]*

[1]Key Laboratory of Organic Synthesis of Jiangsu Province College of Chemistry, Chemical Engineering and Materials Science, Soochow University, Suzhou 215123, P. R. Chin

[b]State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, P. R. China

jcmao@suda.edu.cn

Content

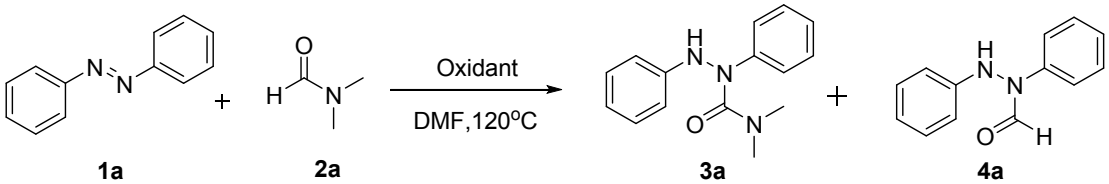
Experimental Section

General Information:

All reactions were carried out under an air atmosphere condition. Azobenzene was purchased from Sinophorm Chemical Reagent Co., Ltd, other Aromatic azo compounds were prepared using literature procedure[1-3]. Various Formamides and various Oxidants and other chemicals were purchased from Aldrich, Acros or Alfa. Column chromatography was generally performed on silica gel (100-200 mesh) and reactions were monitored by thin layer chromatography (TLC) using UV light (254 nm) to visualize the course of the reactions. The ^{1}H (400 MHz) and ^{13}C NMR (100 MHz) data were recorded on Varian 400 M spectrometers using $CDCl_3$ as solvent. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. ^{1}H NMR spectra was recorded with tetramethylsilane (δ = 0.00 ppm) as internal reference; ^{13}C NMR spectra was recorded with $CDCl_3$ (δ = 77.500 ppm) as internal reference. ESI-MS and HRMS were performed by the State-authorized Analytical Center in Soochow University.

Optimization

Optimization of reaction conditions for the reaction of azobenzene with DMF[a]



1a **2a** **3a** **4a**

Entry	Oxidant		Additive (equiv)	Yield of **3a** [%][b]	Yield of **4a** [%][b]
1[c]	DTBP(2eq)	–	–	19	NR
2	DTBP	–	–	25	NR
3[d]	DTBP(6eq)	–	–	24	NR
4	DTBP	PhCOCl	–	31	17
5	DCP	PhCOCl	–	trace	60
6	TBHP	PhCOCl	–	10	14
7	BQ	PhCOCl	–	trace	trace

8	DCP	$PhCH_2COCl$	−	25	30
9	DCP	$PhCH_2Cl$	−	30	22
10	DCP	$POBr_3$	−	13	40
11	DTBP	PhCOCl	I_2 (0.2)	47	trace
12	DTBP	PhCOCl	NaI (02)	57	trace
13	DTBP	PhCOCl	KI (0.2)	51	trace
14	DTBP	PhCOCl	TBAI (0.2)	51	trace
15	DTBP	$PhCH_2COCl$	NaI (02)	40	trace
16	DTBP	$PhCH_2Cl$	NaI (02)	38	trace
17	DTBP	$POBr_3$	NaI (02)	52	trace
18	DTBP	$SOCl_2$	NaI (02)	27	trace
19[e]	DTBP	PhCOCl	NaI (0.2)	65	trace
20[f]	DTBP	PhCOCl	NaI (0.2)	42	trace
21	DCP	PhCOCl	imidazole (1.0)	10	68
22	DCP	PhCOCl	2-methylimidazole (1.0)	<10	55
23	DCP	PhCOCl	4-methylimidazole (1.0)	<10	43
24	DCP	PhCOCl(40%)	imidazole (1.0)	15	30
25	DCP	PhCOCl(10%)	imidazole (1.0)	14	44

[a] Catalytic conditions: azobenzene (0.5 mmol), oxidant (2 mmol, 4 eq), PhCOCl (20 mol%), DMF (2 mL), 120 ^oC, 24 h, air. [b] Yield of isolated product. [c] DTBP 2eq. [d]DTBP 6eq [e]PhCOCl (40 mol%). [f]PhCOCl (10 mol%).

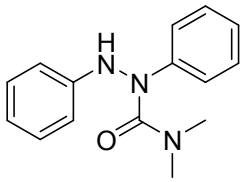
General Procedure for preparation of semicarbazides through the addition Reaction between aromatic azoarenes and *N*-substituted formamides: To a reaction tube equipped with a magnetic stir bar was added under air, azoarene (0.5 mmol), NaI (20 mol%), DTBP (4 equiv) and PhCOCl (40 mol%) in DMF (2 mL). The resulting reaction mixture was kept stirring at 120 ^oC for 24 h. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

General Procedure for Preparation of formylhydrzaines through the addition Reaction between aromatic azoarenes and *N*-substituted formamides: To a reaction tube equipped with a magnetic stir bar was added under air, azoarene (0.5

mmol), imidazole (1 equiv), DCP (4 equiv) and PhCOCl (20 mol%) in DMF (2 mL). The resulting reaction mixture was kept stirring at 120 ^{o}C for 24 h. At the end of the reaction, the reaction mixture was cooled to room temperature. After removal of the solvent, the residue was subjected to column chromatography on silica gel using ethyl acetate and petroleum ether mixtures to afford the desired product in high purity.

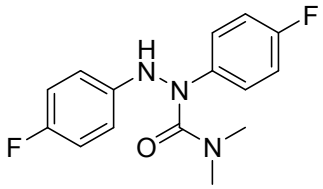
Characterization of the corresponding products:

_N_,_N_-Dimethyl-1,2-diphenylhydrazinecarboxamide



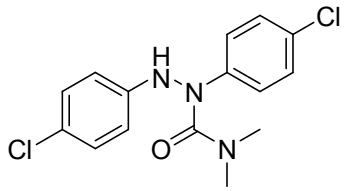
White Solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.29 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 2H), 7.10 – 7.07 (m, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.6 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 2.84 (s, 6H). ^{13}C NMR (100 MHz, DMSO) δ 164.7, 153.5, 150.2, 134.2, 133.9, 128.4, 125.3, 124.0, 117.1, 42.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{18}N_3O$ requires 256.1450，found 256.1448.

1,2-Bis(4-fluorophenyl)-*N*,*N*-dimethylhydrazinecarboxamide



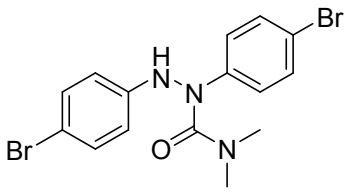
Yellow oil liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11(m, 2H), 7.05(d, *J* = 8.0 Hz, 2H), 7.00 (m, 2H), 6.94 (m, 3H), 2.91 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.0, 160.5, 159.1, 158.5, 156.8, 144.8 (d, *J* = 2.2 Hz, 2C), 142.4 (d, *J* = 3.0 Hz, 2C), 122.8 (d, *J* = 8.2 Hz, 2C), 116.2, 116.0 (d, *J* = 1.5 Hz, 2C), 115.7, 115.0 (d, *J*=7.7, 2C), 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{16}F_2N_3O$ requires 292.1261, found 292.1264.

1,2-bis(4-chlorophenyl)-*N*,*N*-dimethylhydrazinecarboxamide



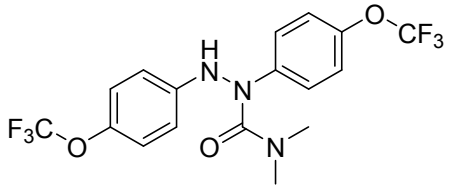
Yellow and oily liquid ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.8 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.26(s, 1H), 7.16 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.8 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 147.0, 144.4, 129.6, 129.3,129.17, 125.8, 121.7, 114.8, 37.4. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{16}Cl_2N_3O$ requires 324.0670, found 324.0661.

1,2-Bis(4-bromophenyl)-*N*,*N*-dimethylhydrazinecarboxamide



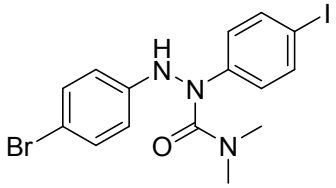
Yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.8 Hz, 1H), 6.97 (s, 2H), 6.94 (s, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 2.90 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 147.5, 144.9, 132.2, 132.1, 122.0, 117.2, 115.2, 113.1, 37.5. MS ESI (m/z): $[M+H]^+$ calcd for $C_{15}H_{15}Br_2N_3O$ requires 411.9655, found 411.9662. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{16}Br_2N_3O$ requires 411.9660, found 411.9653.

_N_,_N_-Dimethyl-1,2-bis(4-(trifluoromethoxy)phenyl)hydrazinecarboxamide



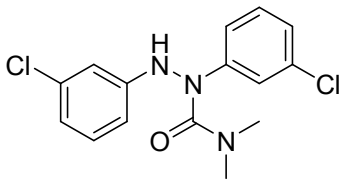
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, *J* = 9.2 Hz, 2H), 7.12-7.10 (m, 5H), 6.92 (m, 2H), 2.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.9, 147.2, 145.6 (d, *J* = 2.0 Hz, 2C), 144.6, 143.3 (d, *J* = 2.0 Hz, 2C), 122.5, 122.1, 121.9, 121.7, 121.6, 119.3, 119.2, 114.3, 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{15}F_6N_3O_3$ requires 424.1096, found 424.1092.

2-(4-Bromophenyl)-1-(4-iodophenyl)-_N_,_N_-dimethylhydrazinecarboxamide



Tan oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (m, 1H), 7.52 (d, *J* = 8.8 Hz, 1H), 7.42 (m, 1H), 7.34 (d, *J* = 8.8Hz, 1H), 6.95 (m, 2H), 6.83 (m, 2H), 6.70 (d, *J* = 8.4 Hz, 1H), 2.90 (d, *J* = 1.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 159.7, 148.3, 147.6, 145.7, 145.0, 138.3, 138.1, 132.2, 132.2, 128.4, 122.3, 122.0, 117.3, 115.8, 115.3, 113.2, 87.8, 82.9, 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{16}BrIN_3O$ requires 459.9540, found 459.9522.

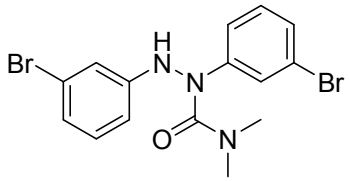
1,2-Bis(3-chlorophenyl)-_N_,_N_-dimethylhydrazinecarboxamide



Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (m, 1H), 7.18 (d, *J* = 8.0

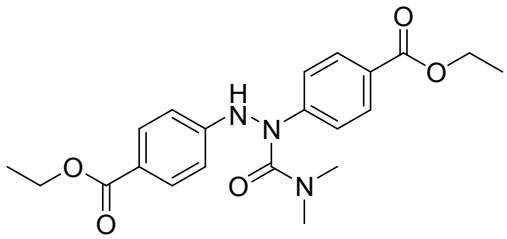
Hz, 1H), 7.12 (m, 3H), 6.96 (m, 1H), 6.94 (t, *J* = 2.0 Hz, 1H), 6.90 (m, 1H), 6.80 (m, 1H), 2.95 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 149.7, 147.0, 135.2, 135.0, 130.5, 130.2, 124.5, 121.2, 120.5, 118.1, 113.5, 111.9, 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{16}Cl_2N_3O$ requires 324.0670, found 324.0681.

1,2-Bis(3-bromophenyl)-*N*,*N*-dimethylhydrazinecarboxamide



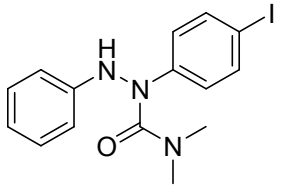
Tan oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 7.24 (m, 1H), 7.17 (m, 2H), 7.10 (m, 2H), 7.00 (m, 2H), 6.83 (m, 1H), 2.93 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 149.8, 147.1, 130.8, 130.5, 127.4, 124.1, 123.4,123.3, 123.0, 118.5, 116.4, 112.3, 37.6. TOF MS CI$^+$ (m/z): [M+H]+ calcd for $C_{15}H_{16}Br_2N_3O$ requires 411.9660, found 411.9664.

Diethyl 4,4'-(1-(dimethylcarbamoyl)hydrazine-1,2-diyl)dibenzoate



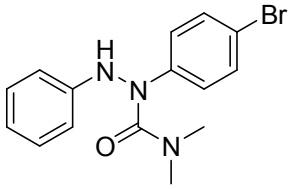
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.93(d, *J* = 8.4Hz, 2H), 7.34 (s, 1H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.4 Hz, 2H), 4.32 (m, 4H), 2.94 (s, 6H), 1.35 (q, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 166.0, 159.2, 152.1, 149.2, 131.5, 131.0, 126.0, 123.0, 118.8, 112.4, 60.9, 60.5, 37.6, 14.4, 14.4. TOF MS CI$^+$ (m/z): [M+H]+ calcd for $C_{21}H_{26}N_3O_5$ requires 400.1872, found 400.1870.

1-(4-Iodophenyl)-*N*,*N*-dimethyl-2-phenylhydrazinecarboxamide



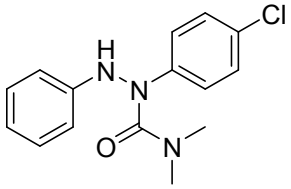
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 2H),, 7.32 (t, *J* = 8.0 Hz, 2H), 7.25 (m, 1H), 7.10 (m, 2H), 6.90 (m, 2H), 6.74 (d, *J* = 8.8 Hz, 1H), 2.90 (d, *J* = 7.6Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.8, 148.7, 148.4, 145.9, 138.0, 129.4, 124.7, 122.2, 121.3, 120.8, 115.9 , 113.6, 82.7, 37.5, 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{17}IN_3O$ requires 382.0416, found 382.0408.

1-(4-Bromophenyl)-*N*,*N*-dimethyl-2-phenylhydrazinecarboxamide



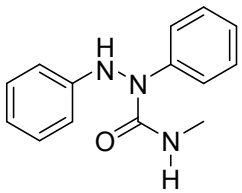
Tan oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (m, 1H), 7.35 (m , 2H), 7.28 (m, 1H), 7.13 (m, 2H), 7.02 (m, 1H), 6.95 (m, 2H), 6.88 (m, 1H), 2.93 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 159.9, 148.4, 148.0, 146.0, 145.3, 132.2,132.1, 129.4, 124.7, 121.9, 121.3, 120.8, 116.9, 115.4, 113.6, 112.9, 37.6, 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{17}BrN_3O$ requires 334.0555, found 334.0555.

1-(4-Chlorophenyl)-*N*,*N*-dimethyl-2-phenylhydrazinecarboxamide



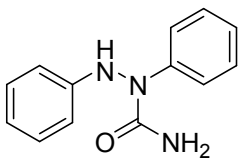
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (m, 1H), 7.29 (m, 2H), 7.22 (d, J = 8.8 Hz, 1H), 7.12 (m, 4H), 6.93 (m, 2H), 2.93 (d, J = 4.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 160.1, 148.4, 147.5, 146.0, 144.8, 133.1, 130.1, 129.3, 129.2, 128.4, 125.6, 124.7, 121.7, 121.2, 120.8, 114.9, 113.5, 37.6, 37.5. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{15}H_{17}ClN_3O$ requires 290.1060, found 290.1062.

***N*-Methyl-1,2-diphenylhydrazinecarboxamide**



Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.0 Hz, 2H), 7.23 (dd, J = 16.0, 8.0 Hz, 4H), 7.06 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.83 (d, J = 8.0 Hz, 2H), 6.53 (d, J = 7.2 Hz, 1H), 6.26 (s, 1H), 2.83 (d, J = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 145.7, 141.5, 129.4, 128.6, 124.6, 122.2, 121.3, 113.4, 26.9. TOF MS CI$^+$ (m/z): $[M+H]^+$ calcd for $C_{14}H_{16}N_3O$ requires 242.1293, found 242.1288.

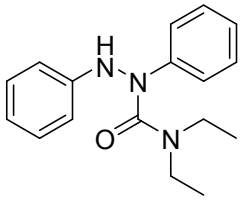
1,2-Diphenylhydrazinecarboxamide



Yellow and oily liquid; ^{1}H NMR (400 MHz, DMSO) δ 8.73 (s, 1H), 7.52 (d, J = 8.0 Hz, 2H), 7.23 (t, J = 8.0Hz, 2H), 7.14 (t, J = 8.0 Hz, 2H), 6.99 (t, J = 7.2 Hz, 1H),

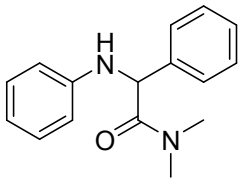
6.72 (d, *J* = 7.6 Hz, 3H), 6.59 (s, 2H). ^{13}C NMR (100 MHz, DMSO) δ 163.0, 151.8, 147.1, 134.1, 133.1, 128.6, 127.4, 124.4, 117.7. TOF MS CI$^+$ (m/z): [M+H]$^+$ calcd for $C_{13}H_{14}N_3O$ requires 228.1137, found 228.1145.

***N*,*N*-Diethyl-1,2-diphenylhydrazinecarboxamide**



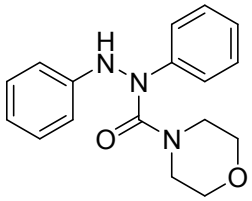
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 8.0 Hz, 2H), 7.17 (d, *J* = 7.6 Hz, 2H), 7.12 (t, *J* = 7.2 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.95 (s, 1H), 6.90 (t, *J* = 7.2 Hz, 1H), 3.34 (d, *J* = 6.8 Hz, 4H), 1.07 (t, *J* =7.2 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.2, 148.9, 147.0, 129.3, 129.2, 124.6, 121.1, 121.0, 113.9, 41.6, 13.0. TOF MS CI$^+$ (m/z): [M+H]$^+$ calcd for $C_{17}H_{22}N_3O$ requires 284.1763, found 284.1759.

***N*,*N*-Dimethyl-2-phenyl-2-(phenylamino)acetamide**



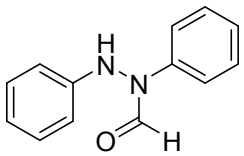
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 2H), 7.28 (s, 1H), 7.26 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 2H), 6.66 (m, 3H), 5.27 (s, 1H), 3.03 (s, 3H), 2.97 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.9, 146.2, 138.1, 129.2, 128.9, 128.1, 127.9, 117.9, 113.7 , 58.2, 37.0, 36.3. TOF MS CI$^+$ (m/z): [M+H]$^+$ calcd for $C_{16}H_{19}N_2O$ requires 255.1497, found 255.1496.

***N*,*N*'-Diphenylmorpholine-4-carbohydrazide**



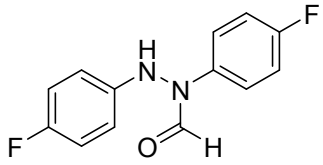
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.34 (t, *J* = 7.9 Hz, 2H), 7.27 (t, *J* = 8.0 Hz, 2H), 7.19 (d, *J* = 7.8 Hz, 2H), 7.14 (t, *J*=7.3, 1H), 6.94 (t, *J* = 7.6 Hz, 3H), 3.60 (m, 4H), 3.60 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 148.7, 145.9, 129.4, 129.4, 124.8, 121.2, 120.9, 113.4, 66.4, 45.8. TOF MS CI$^+$ (m/z): [M+H]$^+$ calcd for $C_{17}H_{20}N_3O_2$ requires 298.1555, found 298.1556.

***N*, *N*'-Diphenylformohydrazide**



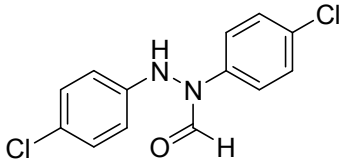
White Solid; ^{1}H NMR (400 MHz, DMSO) δ 9.19 (s, 1H), 8.98 (s, 1H), 8.79 (s, 1H), 8.54 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.38 (m, 4H), 7.18 (m, 6H), 6.75 (m, 6H). ^{13}C NMR (100 MHz, DMSO) δ 170.2, 165.9, 152.4, 152.2, 146.9, 144.6, 134.5, 134.4, 134.1, 133.9, 130.5, 126.2, 125.1, 124.5, 124.2, 117.5, 117.4, 114.5. TOF MS CI^{+} (m/z): [M+H]$^{+}$ calcd for $C_{13}H_{13}N_2O$ requires 213.1034, found 213.1028.

***N*,*N*'-Bis(4-fluorophenyl)formohydrazide**



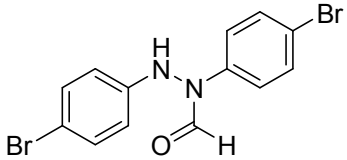
Yellow and oily liquid; ^{1}H NMR (400 MHz, DMSO) δ 9.13 (s, 1H), 8.87 (s, 1H), 8.77 (s, 1H), 8.50 (s, 1H), 7.65 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.53 (dd, *J* = 8.8, 4.8 Hz, 2H), 7.24 (m, 4H), 7.01 (q, *J* = 9.1 Hz, 4H), 6.74 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.96, 162.18, 161.53, 160.25, 159.73, 159.65, 157.26, 142.39, 142.37, 141.95, 136.86, 122.85, 122.77, 121.43, 121.35, 116.79, 116.47, 116.24, 116.06, 115.96, 115.88, 115.83, 114.41, 114.34. TOF MS CI^{+} (m/z): [M+H]$^{+}$ calcd for $C_{13}H_{11}F_2N_2O$ requires 249.0839，found 249.0842.

***N*,*N*'-Bis(4-chlorophenyl)formohydrazide**



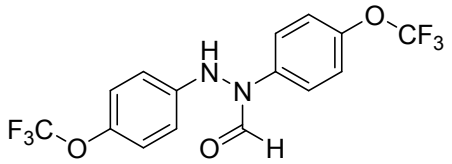
Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.60 (d, *J* = 24.2 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 7.39 (q, *J* = 9.0 Hz, 6H), 7.30 (m, 1H), 7.20 (dd, *J* = 12.0, 8.8 Hz, 4H), 6.96 (s, 1H), 6.80 (s, 1H), 6.73 (dd, *J* = 9.2, 2.5 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 160.0, 144.9, 144.4, 139.3, 137.9, 131.9, 131.2, 129.9, 129.7, 129.3, 129.2, 127.0, 121.7, 120.3, 115.4, 114.0. TOF MS CI^{+} (m/z): [M+H]$^{+}$ calcd for $C_{13}H_{11}Cl_2N_2O$ requires 281.0248, found 281.0239.

***N*,*N*'-Bis(4-bromophenyl)formohydrazide**



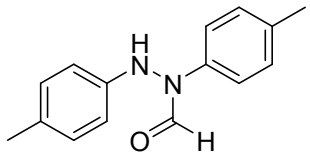
Yellow and oily liquid; ^{1}H NMR (400 MHz, DMSO) δ 9.35 (s, 1H), 8.98 (d, *J* = 8.4 Hz, 2H), 8.51 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 2H), 7.47 (m, 6H), 7.20 (m, 4H), 6.74 (dd, *J* = 15.2, 8.7 Hz, 4H). ^{13}C NMR (101 MHz, DMSO) δ 165.47, 161.17, 146.52, 146.13, 140.97, 138.61, 129.90, 129.78, 129.62, 129.26, 129.23, 124.12, 123.41, 122.97, 121.79, 120.99, 114.53, 114.35. TOF MS CI^{+} (m/z): [M+H]$^{+}$ calcd for $C_{13}H_{11}Br_2N_2O$ requires 368.9238，found 368.9231.

***N*,*N*'-Bis(4-(trifluoromethoxy)phenyl)formohydrazide**



Yellow and oily liquid; ^{1}H NMR (400 MHz, DMSO) δ 9.46 (s, 1H), 9.08 (s, 1H), 9.00(s, 1H), 8.53 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 3H), 7.42 (t, *J* = 7.6 Hz, 5H), 7.18 (dd, *J* = 12.4, 8.8 Hz, 4H), 6.81 (dd, *J* = 15.3, 8.8 Hz, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 160.2, 158.9, 147.2, 146.5, 144.9, 144.5, 143.9, 143.6, 139.3, 137.9, 136.8, 124.1, 122.9, 122.6, 122.4, 121.7, 121.6, 120.4, 119.2, 119.1, 114.9, 113.4. TOF MS CI^{+} (m/z): [M+H]$^{+}$ calcd for $C_{15}H_{11}F_6N_2O_3$ requires 381.0674, found 381.0670.

***N*,*N*'-Dip-tolylformohydrazide**

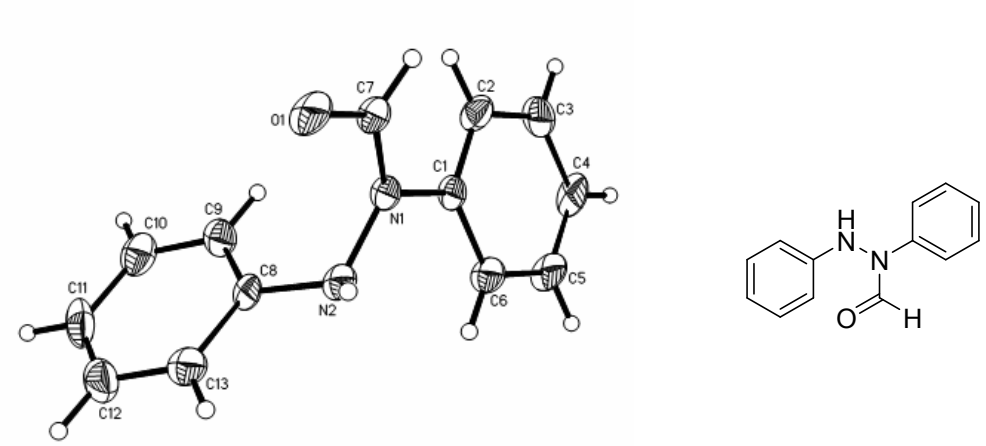


Yellow and oily liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 2H), 8.59 (s, 1H), 7.49 (d, *J* = 8.4 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 3H), 7.21 (d, *J* = 8.4 Hz, 3H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 4H), 6.73 (t, *J* = 8.0 Hz, 5H), 2.33 (d, 6H), 2.25 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 160.3, 144.2, 143.9, 138.6, 137.0, 136.1, 135.7, 131.3, 131.0, 130.2, 130.1, 129.8, 129.6, 120.9, 119.5, 114.4, 113.2, 20.9, 20.9, 20.6, 20.5. TOF MS CI^{+} (m/z): [M+H]$^{+}$ calcd for $C_{15}H_{17}N_2O$ requires 241.1341, found 241.1341.

References

1. C. Zhang, N. Jiao, *Angew. Chem. Int. Ed.***2010**, *49*, 6174 –6177;
2. H. Ma, W. Li, J. Wang, Y. Gong, Z. Lei, *Tetrahedron*, **2012**, *68*, 8358-8366;
3. B. Priewisch, R.-U. K. Braun, *J. Org. Chem.***2005**,*70*, 2350-2352

X-ray crystallographic data for compound 4a (CCDC 1040947):



Summary of Crystallographlic Data for $C_{13}H_{12}N_2O$:

Chemical formula	$C_{13}H_{12}N_2O$
Formula weight	212.25
Crystal Color	Colorless
Crystal System	Orthorhombic
Space Group	P 21 21 21
Cell Volume	1083.22(12)
Crystal Size	0.50×0.40×0.20
Cell formula units Z	4
Cell length a	6.3920(4)
Cell length b	8.4041(5)
Cell length c	20.1646(12)
Cell angle alpha	90.00
Cell angle beta	90.00
Cell angle gamma	90.00
Temp, K/ λ, Å	293(2)
Crystal_F_000	448
R factor all	0.1075
Radiation type	MoK\a

Selected Bond Distances:

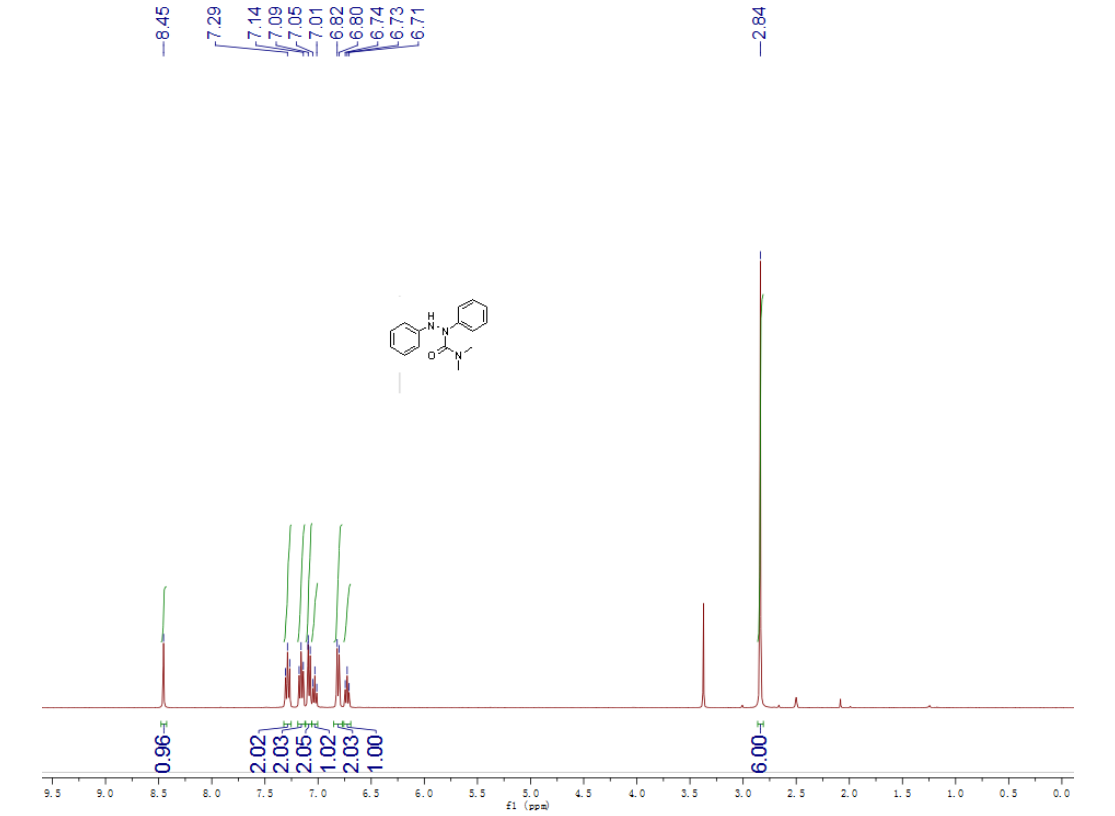
Bond	Length (Å)	Bond	Length (Å)
O1 C7	1.235(5)	C5 H5	0.9300
N1 C7	1.343(5)	C6 H6	0.9300
N1 N2	1.407(4)	C7 H7	0.9300
N1 C1	1.435(5)	C8 C13	1.382(5)
N2 C8	1.420(5)	C8 C9	1.382(6)

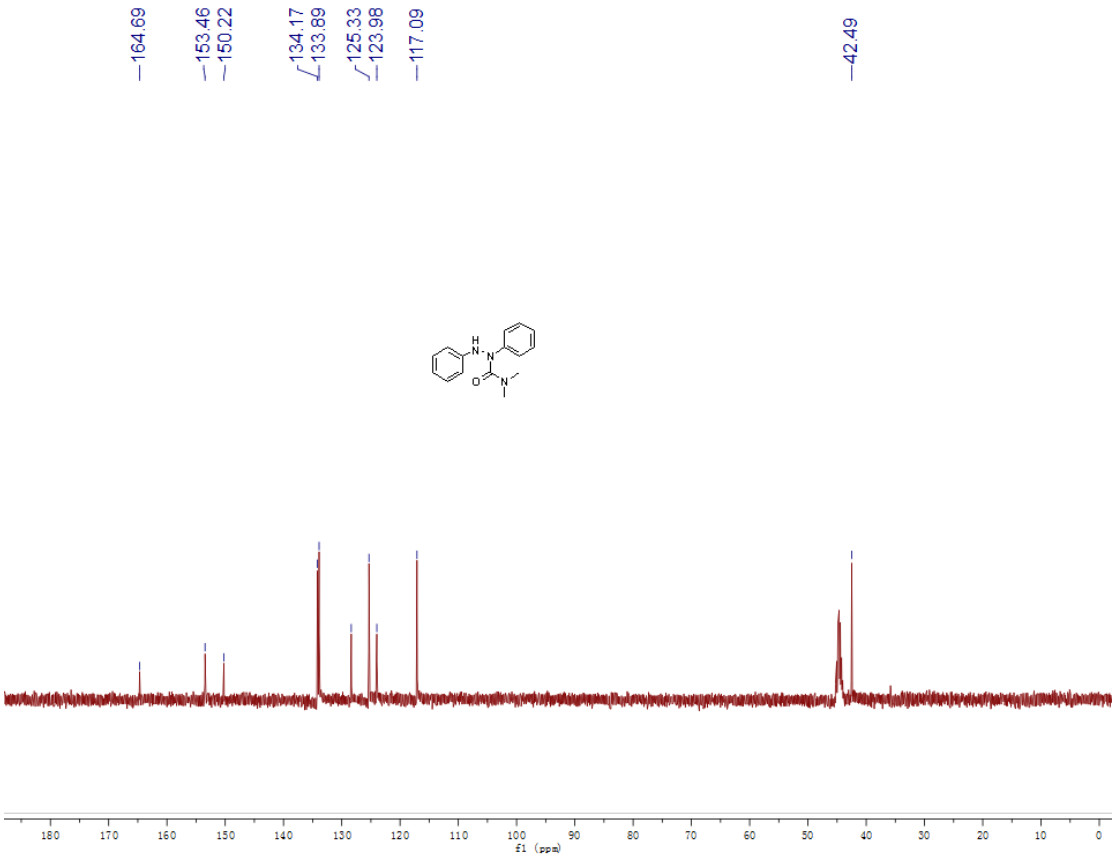
N2 H2A	0.83(5)	C9 C10	1.380(5)
C1 C2	1.374(6)	C9 H9	0.9300
C1 C6	1.396(5)	C10 C11	1.381(7)
C2 C3	1.398(6)	C10 H10	0.9300
C2 H2	0.9300	C11 C12	1.366(7)
C3 C4	1.379(7)	C11 H11	0.9300
C3 H3	0.9300	C12 C13	1.385(6)
C4 C5	1.370(7)	C12 H12	0.9300
C4 H4	0.9300	C13 H13	0.9300
C5 C6	1.390(6)		

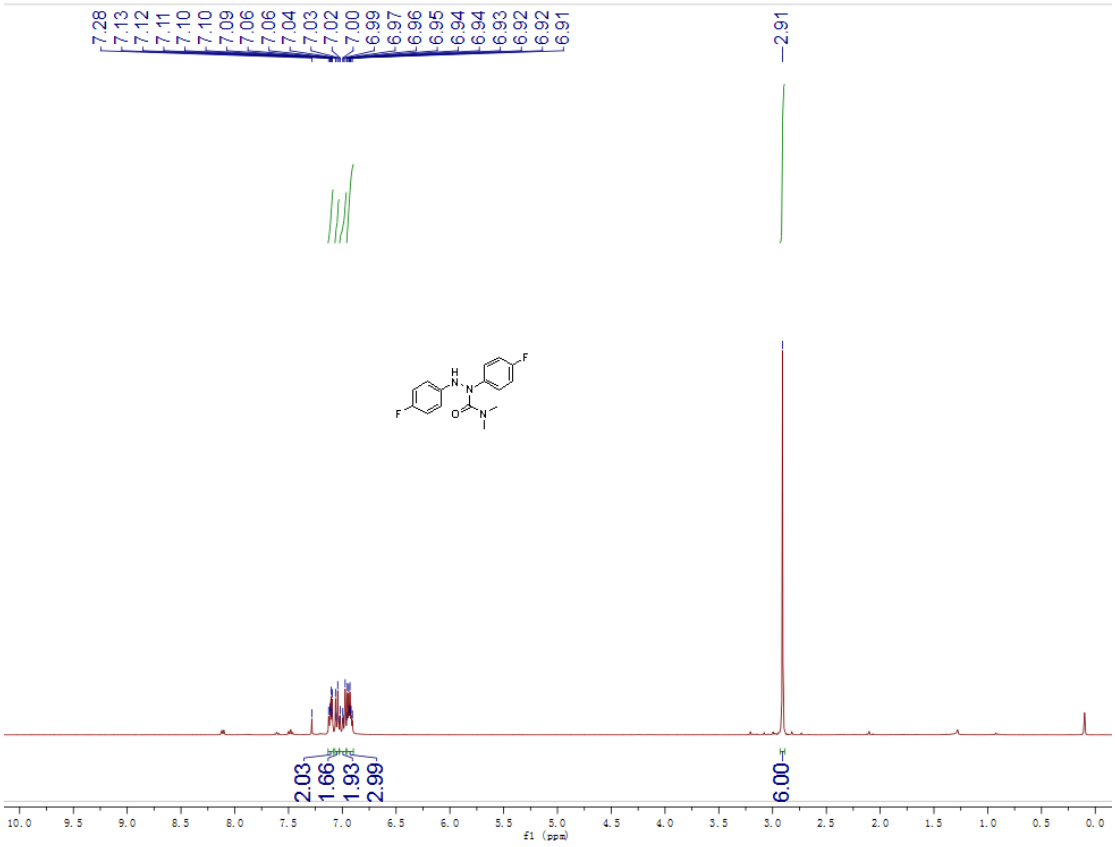
Selected Bond angles:

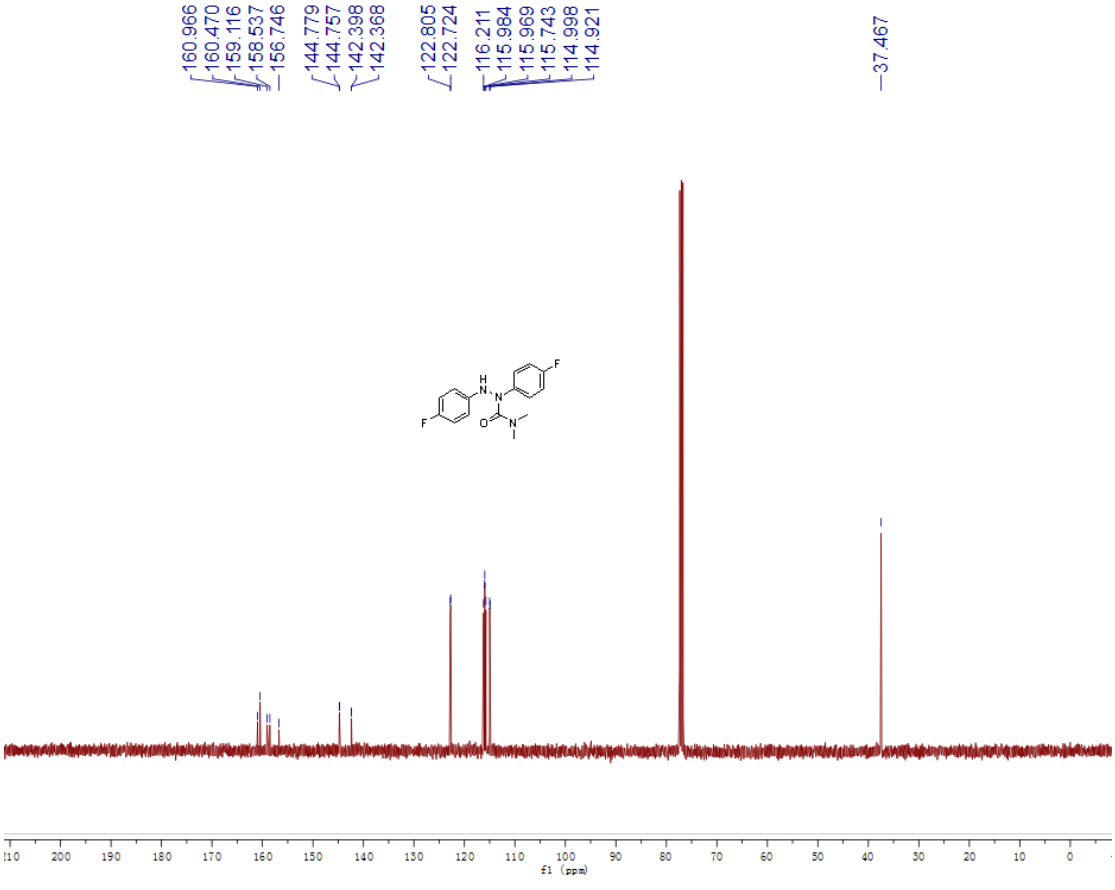
Bond	Angle (deg)	Bond	Angle (deg)
C7 N1 N2	119.1(3)	C1 C6 H6	120.3
C7 N1 C1	122.6(3)	O1 C7 N1	122.5(4)
N2 N1 C1	117.5(3)	O1 C7 H7	118.8
N1 N2 C8	115.8(3)	N1 C7 H7	118.8
N1 N2 H2A	103(3)	C13 C8 C9	119.6(3)
C8 N2 H2A	120(4)	C13 C8 N2	117.2(3)
C2 C1 C6	120.0(4)	C9 C8 N2	123.2(3)
C2 C1 N1	121.0(4)	C10 C9 C8	119.6(4)
C6 C1 N1	119.0(3)	C10 C9 H9	120.2
C1 C2 C3	119.9(4)	C8 C9 H9	120.2
C1 C2 H2	120.0	C9 C10 C11	120.7(4)
C3 C2 H2	120.0	C9 C10 H10	119.7
C4 C3 C2	119.8(5)	C11 C10 H10	119.7
C4 C3 H3	120.1	C12 C11 C10	119.9(4)
C2 C3 H3	120.1	C12 C11 H11	120.1
C5 C4 C3	120.3(4)	C10 C11 H11	120.1
C5 C4 H4	119.8	C11 C12 C13	119.9(4)
C3 C4 H4	119.8	C11 C12 H12	120.0
C4 C5 C6	120.4(4)	C13 C12 H12	120.0
C4 C5 H5	119.8	C8 C13 C12	120.4(4)
C6 C4 H4	119.8	C8 C13 H13	119.8
C5 C6 C1	119.4(4)	C12 C13 H13	119.8
C5 C6 H6	120.3		

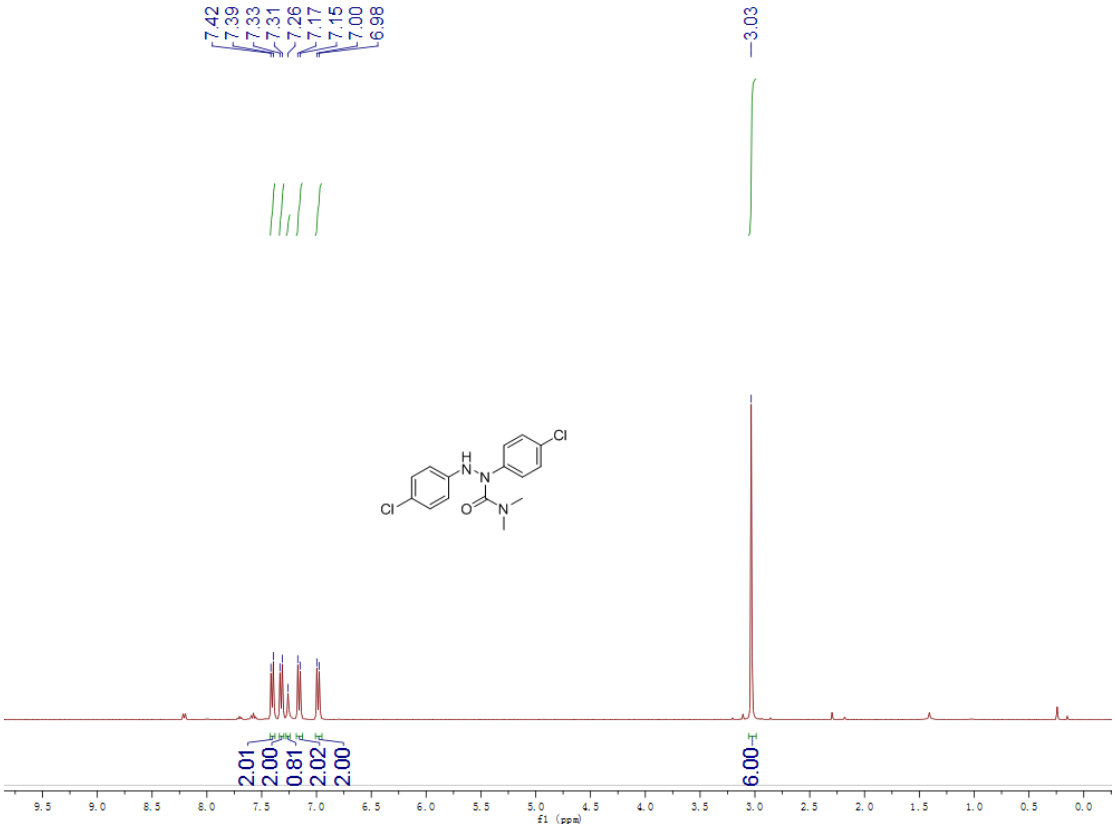
Copy of ^{1}H and ^{13}C NMR Spectra for Corresponding Products:

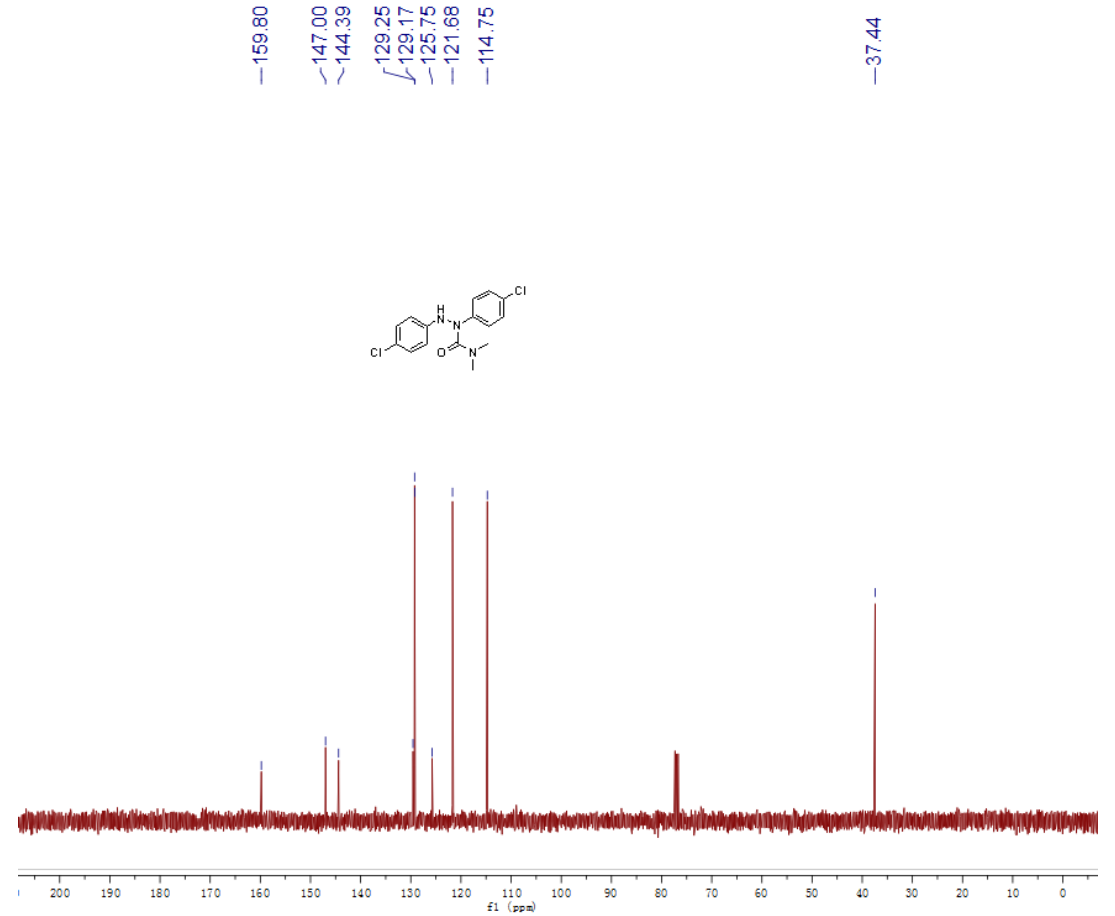


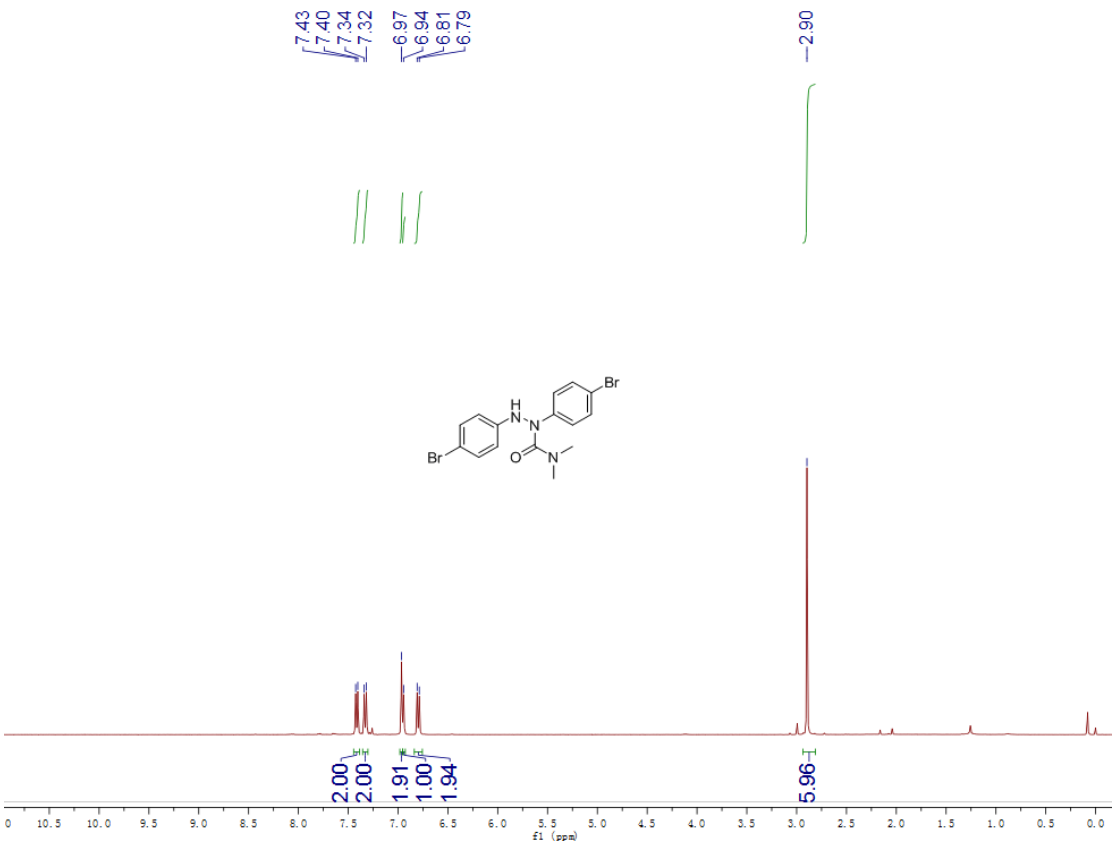


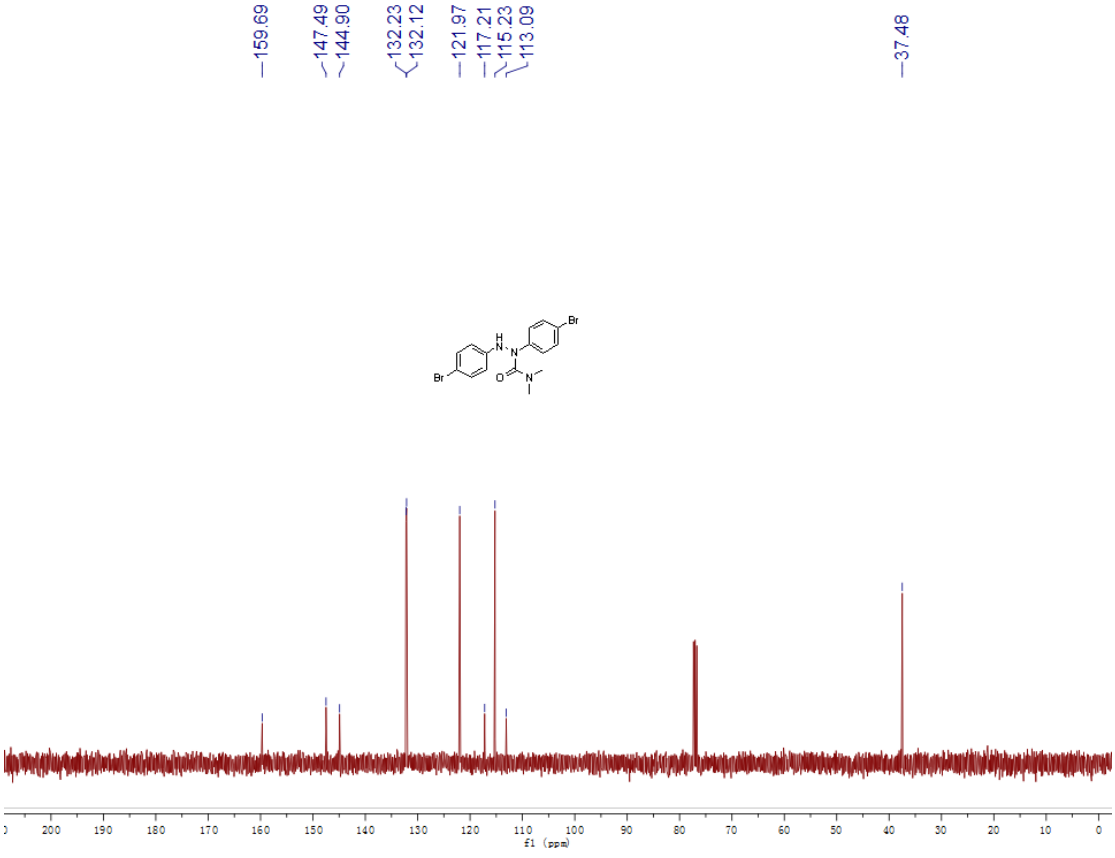

7.28
7.13
7.12
7.11
7.10
7.10
7.09
7.06
7.06
7.04
7.03
7.02
7.00
6.99
6.97
6.96
6.95
6.94
6.94
6.93
6.92
6.92
6.91
2.91
2.03
1.66
1.93
2.99
6.00
f1 (ppm)

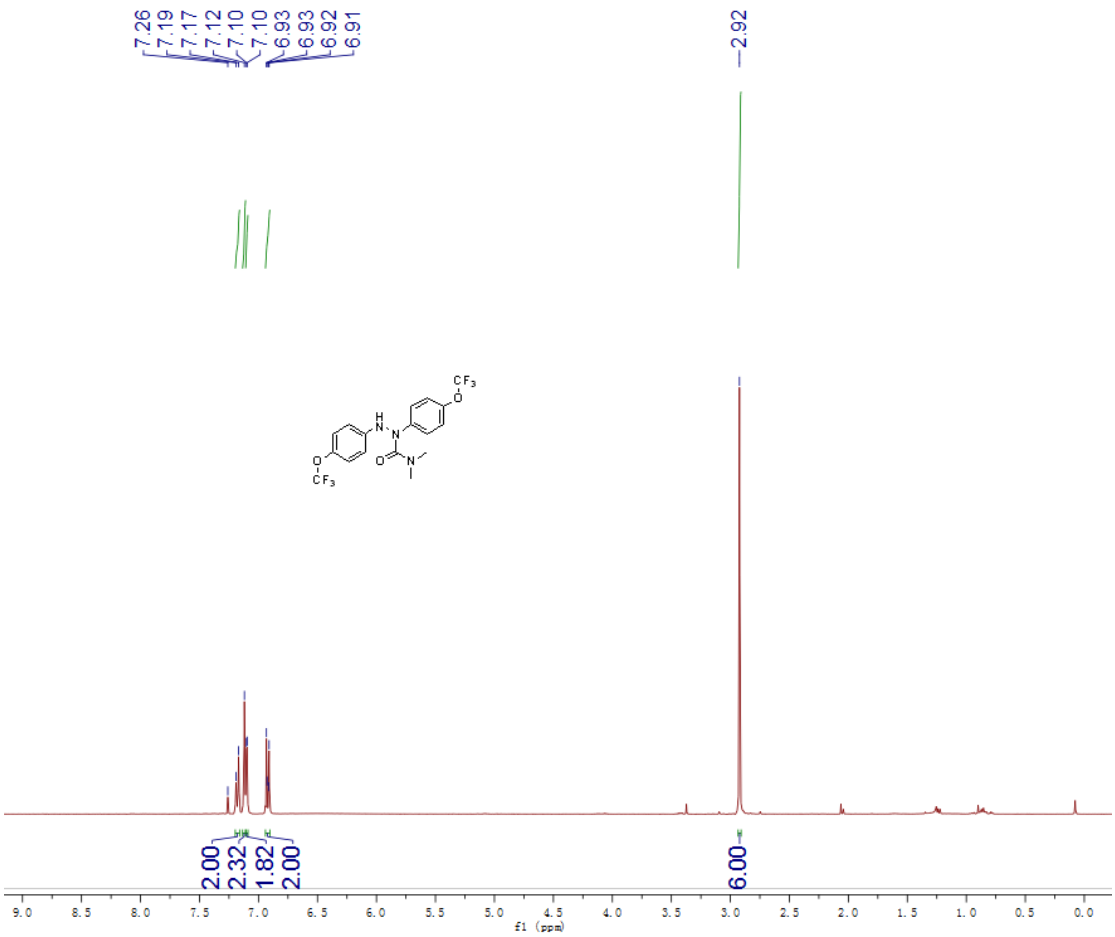

160.966
160.470
159.116
158.537
156.746
144.779
144.757
142.398
142.368
122.805
122.724
116.211
115.984
115.969
115.743
114.998
114.921
37.467
f1 (ppm)

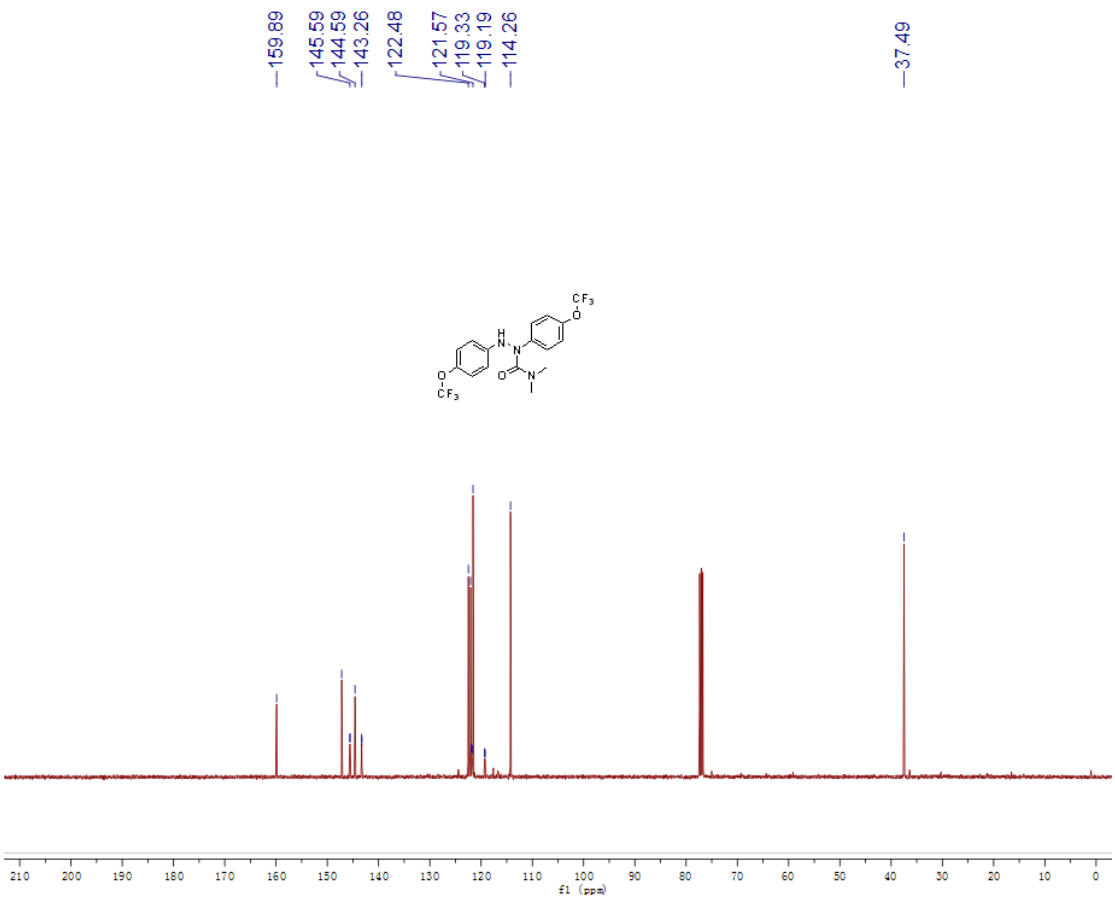

7.42
7.39
7.33
7.31
7.26
7.17
7.15
7.00
6.98
3.03
Cl
Cl
2.01
2.00
0.81
2.02
2.00
6.00
f1 (ppm)

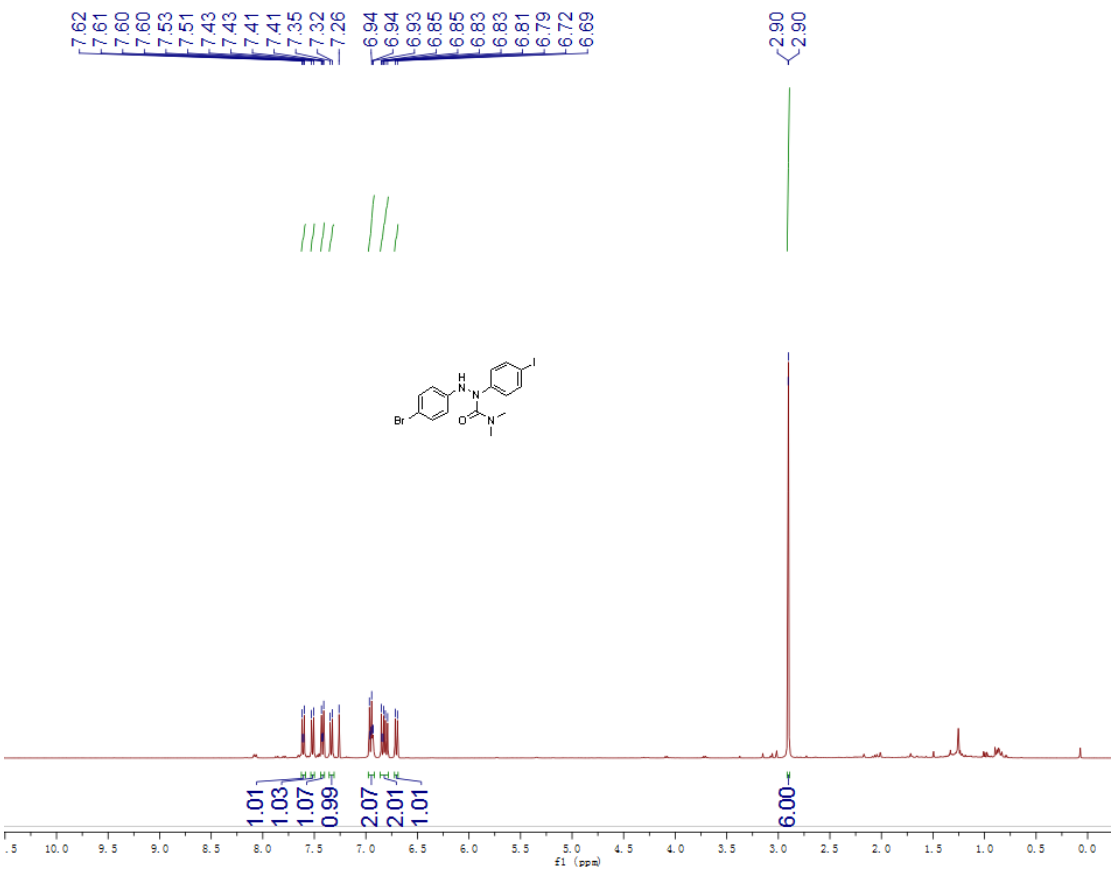

159.80
147.00
144.39
129.25
129.17
125.75
121.68
114.75
37.44
Cl
Cl
f1 (ppm)

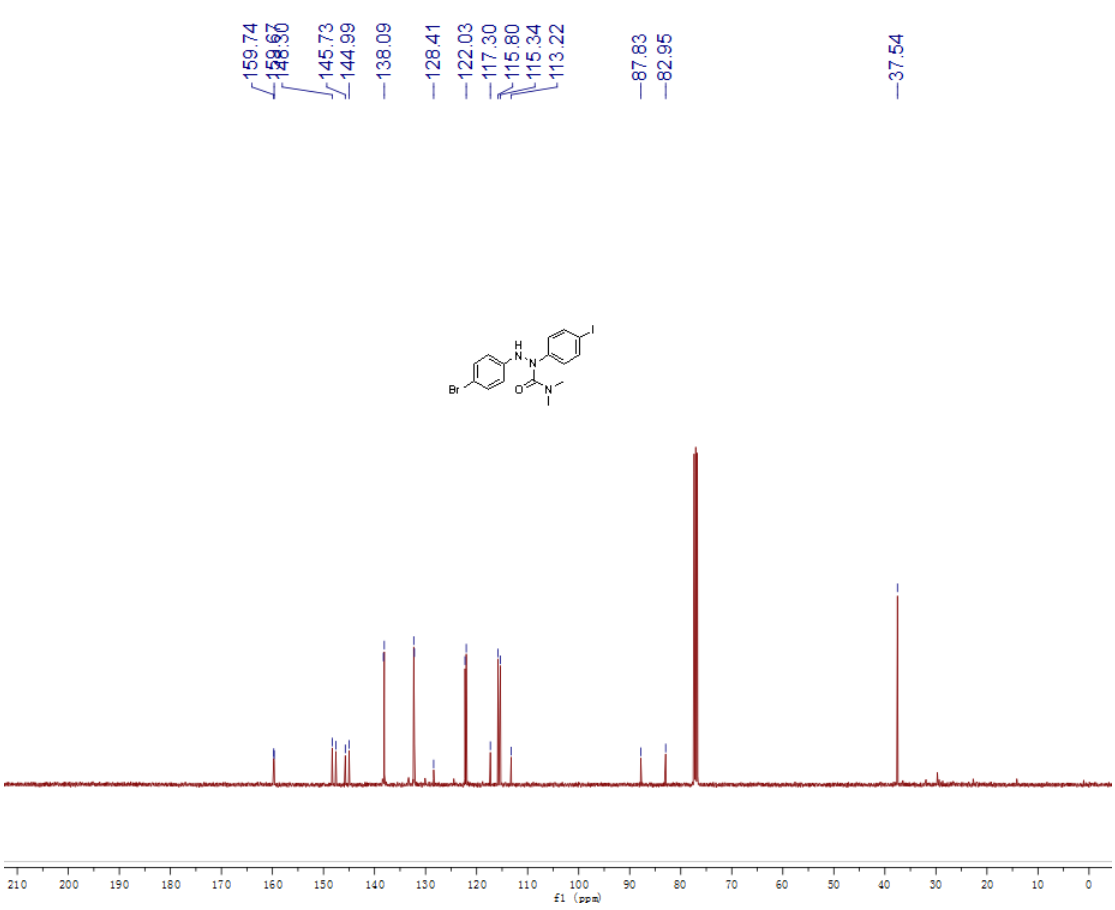

7.43
7.40
7.34
7.32
6.97
6.94
6.81
6.79
2.90
Br
Br
2.00
2.00
1.91
1.00
1.94
5.96
f1 (ppm)

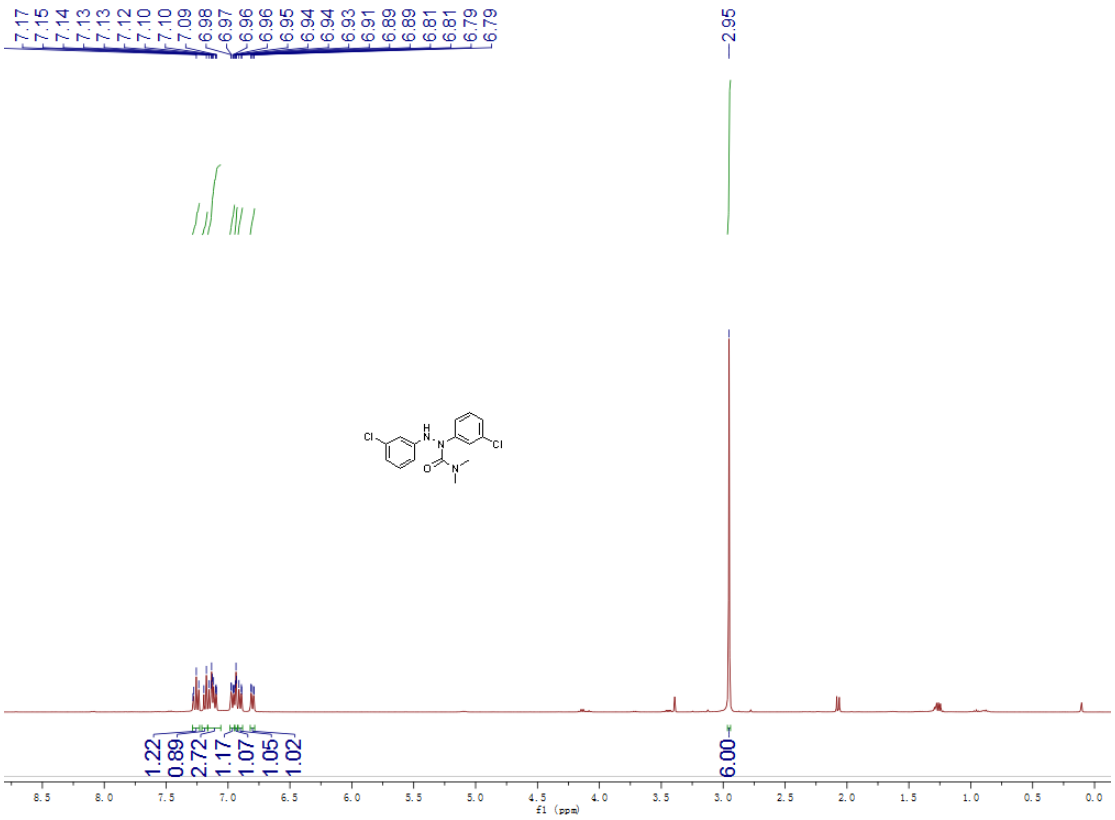

159.69
147.49
144.90
132.23
132.12
121.97
117.21
115.23
113.09
37.48
Br
Br
f1 (ppm)

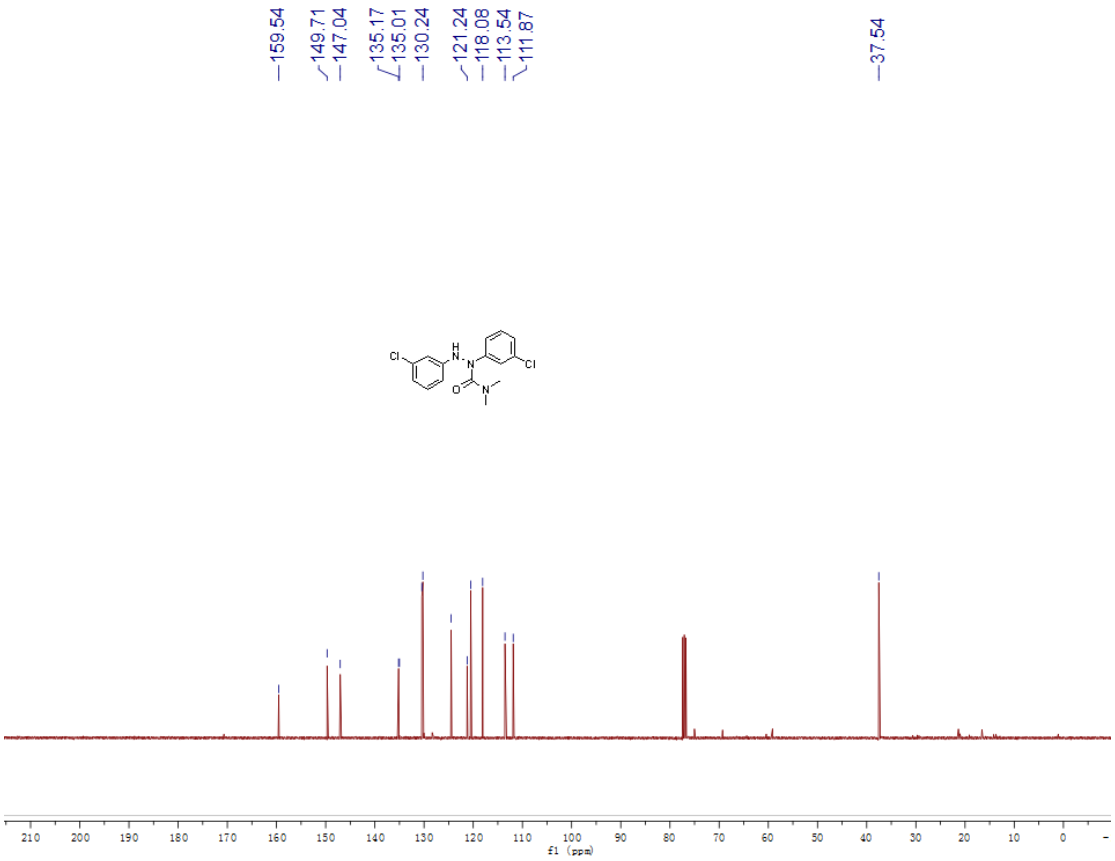

7.26
7.19
7.17
7.12
7.10
7.10
6.93
6.93
6.92
6.91
2.92
2.00
2.32
1.82
2.00
6.00
f1 (ppm)

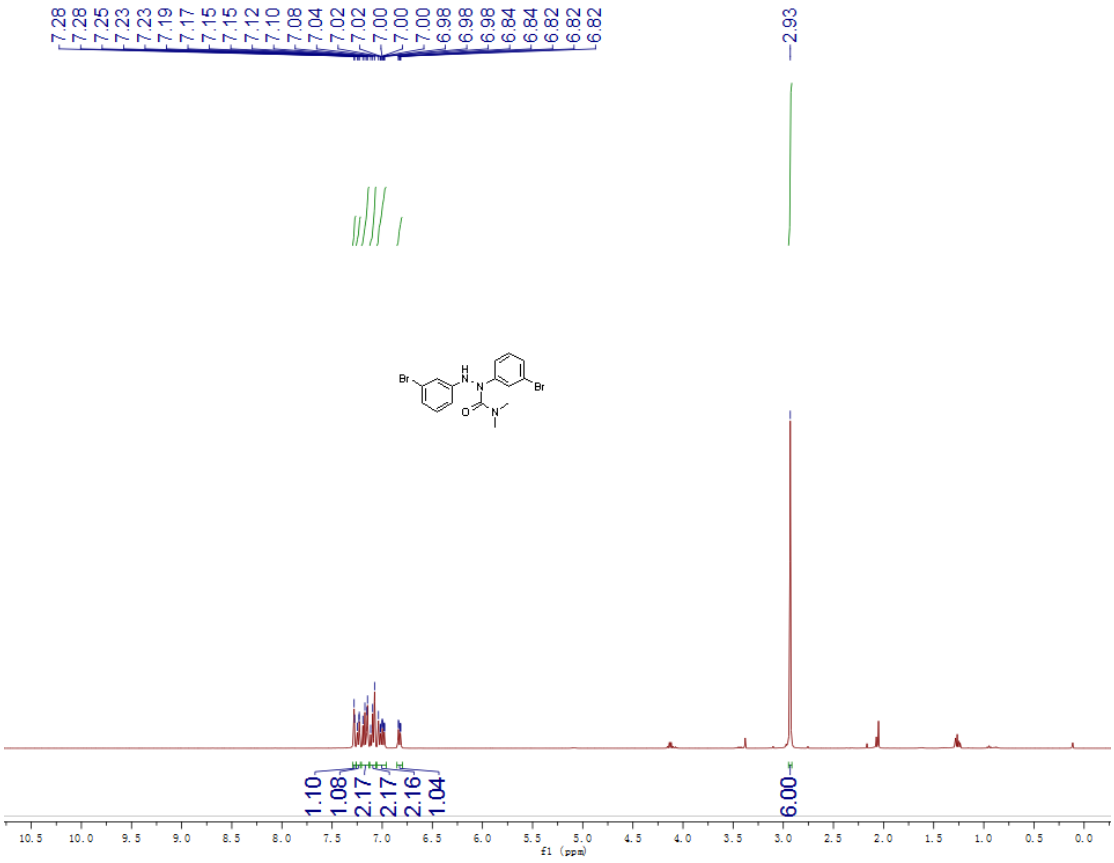

159.89
145.59
144.59
143.26
122.48
121.57
119.33
119.19
114.26
37.49
f1 (ppm)

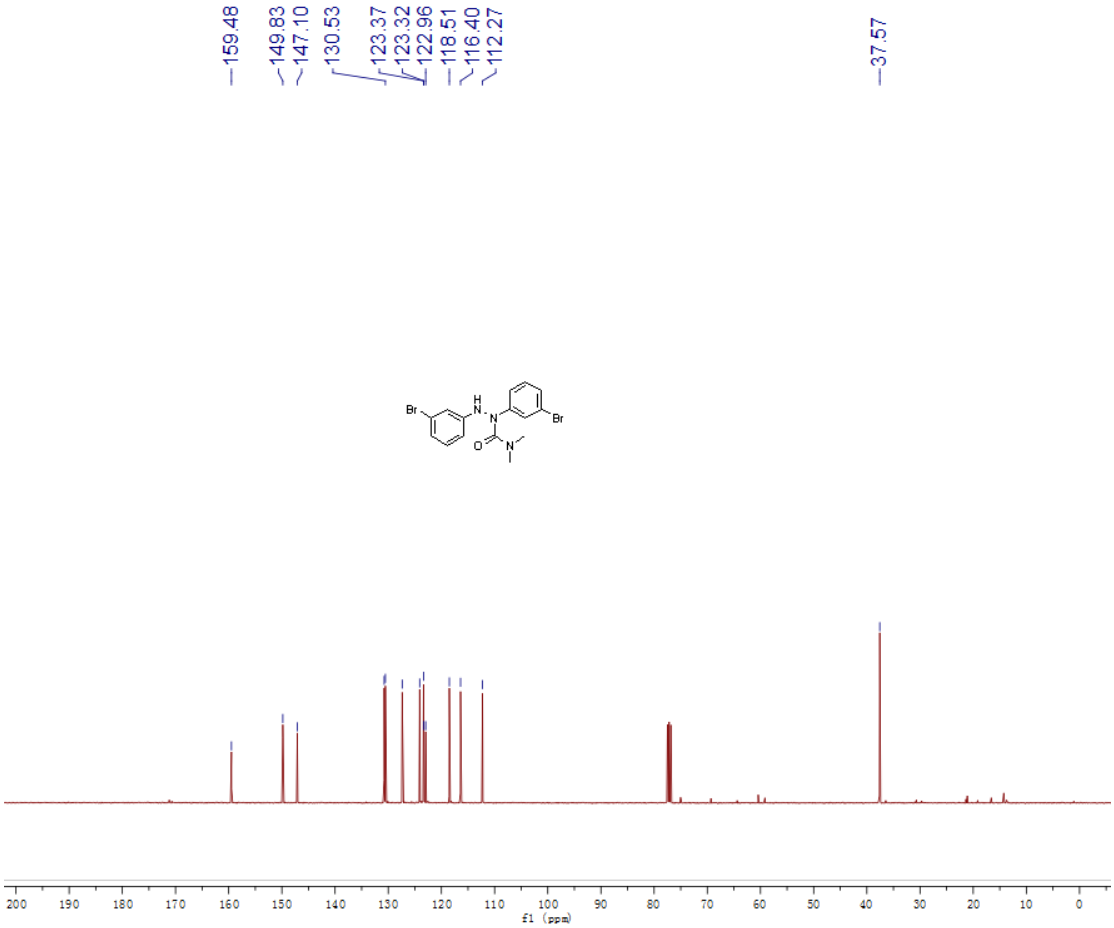

7.62
7.61
7.60
7.60
7.53
7.51
7.43
7.43
7.41
7.41
7.35
7.32
7.26
6.94
6.94
6.93
6.85
6.85
6.83
6.83
6.81
6.79
6.72
6.69
2.90
2.90
1.01
1.03
1.07
0.99
2.07
2.01
1.01
6.00
f1 (ppm)

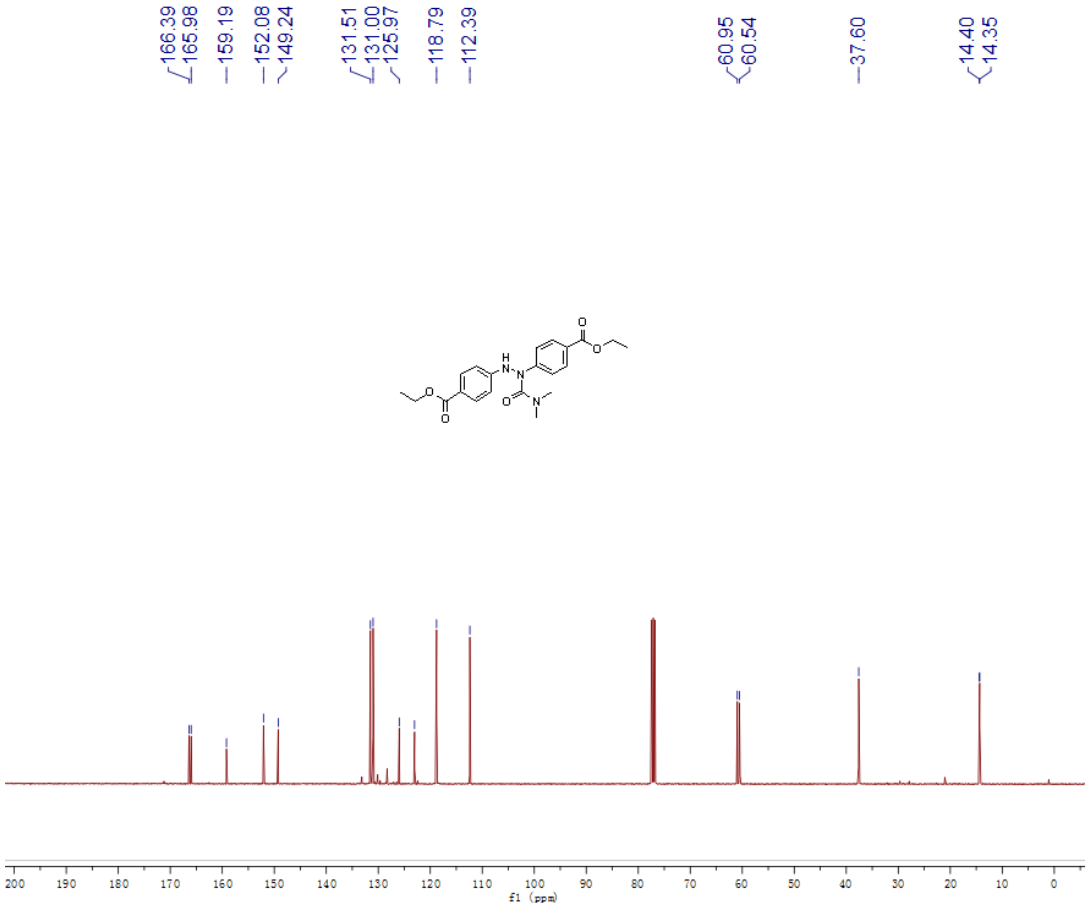

159.74
145.73
144.99
138.09
128.41
122.03
117.30
115.80
115.34
113.22
87.83
82.95
37.54
f1 (ppm)

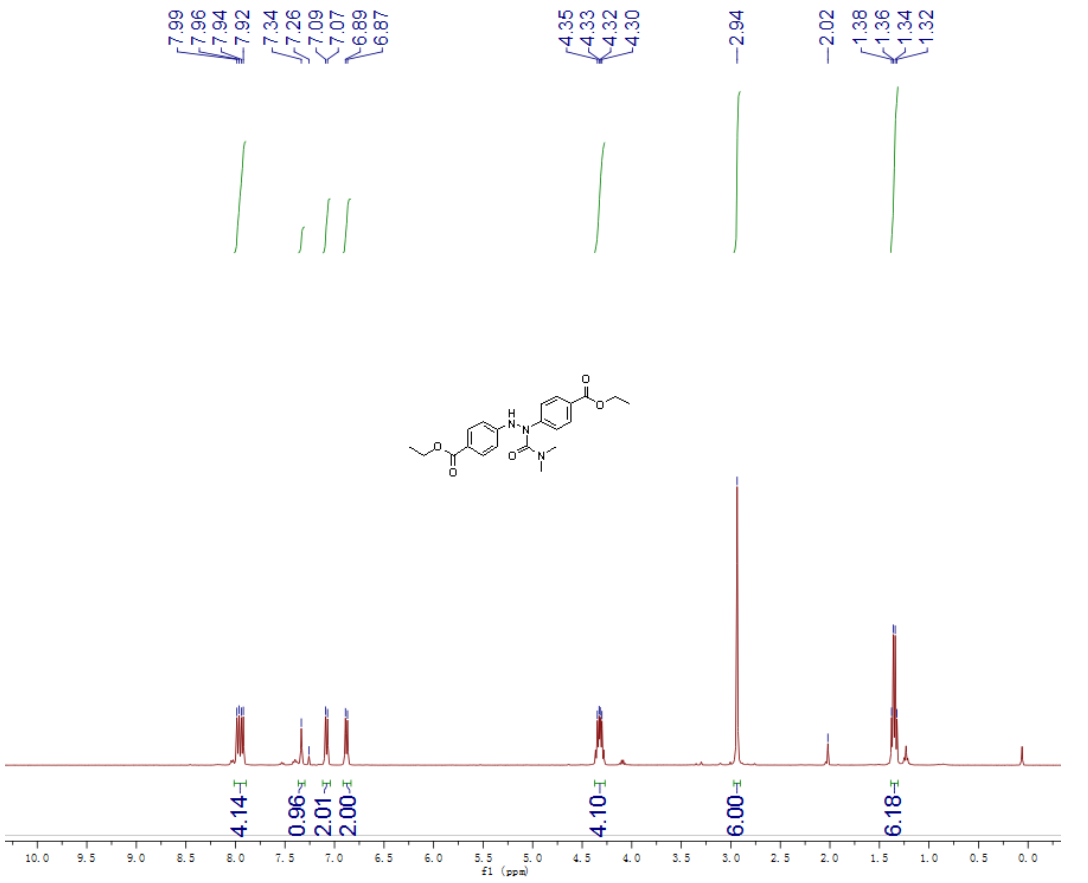

7.17
7.15
7.14
7.13
7.13
7.12
7.10
7.10
7.09
6.98
6.97
6.96
6.96
6.95
6.94
6.94
6.93
6.91
6.89
6.89
6.81
6.81
6.79
6.79
2.95
1.22
0.89
2.72
1.17
1.07
1.05
1.02
6.00
f1 (ppm)

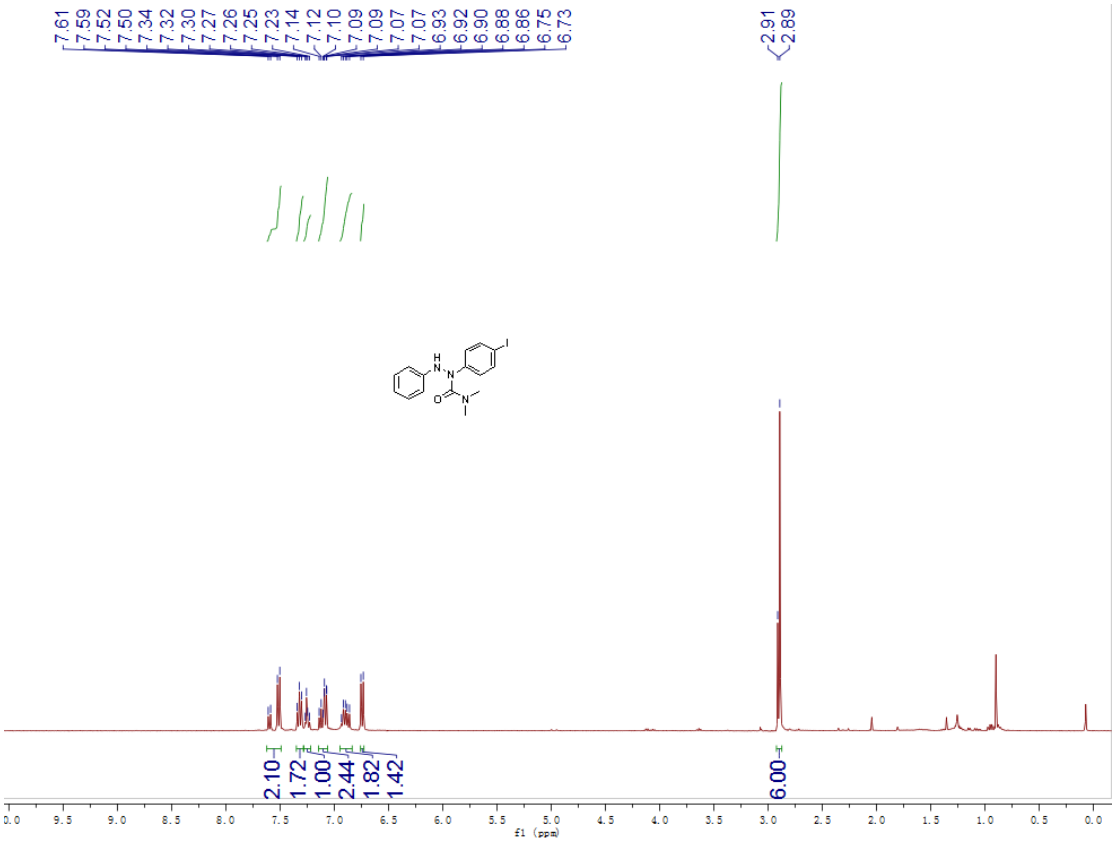

159.54
149.71
147.04
135.17
135.01
130.24
121.24
118.08
113.54
111.87
37.54
f1 (ppm)

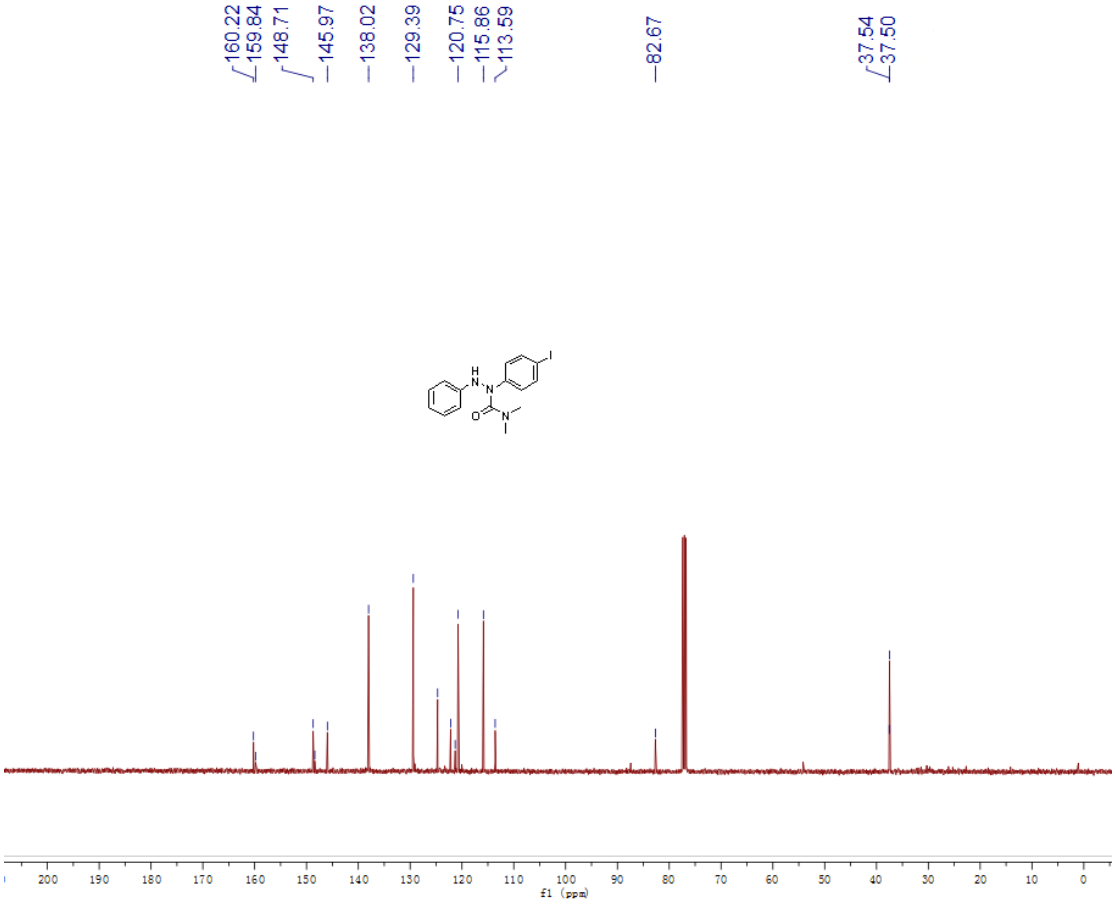

7.28
7.28
7.25
7.23
7.23
7.19
7.17
7.15
7.15
7.12
7.10
7.08
7.04
7.02
7.02
7.00
7.00
7.00
6.98
6.98
6.84
6.84
6.82
6.82
6.82
2.93
Br
Br
1.10
1.08
2.17
2.17
2.16
1.04
6.00
f1 (ppm)

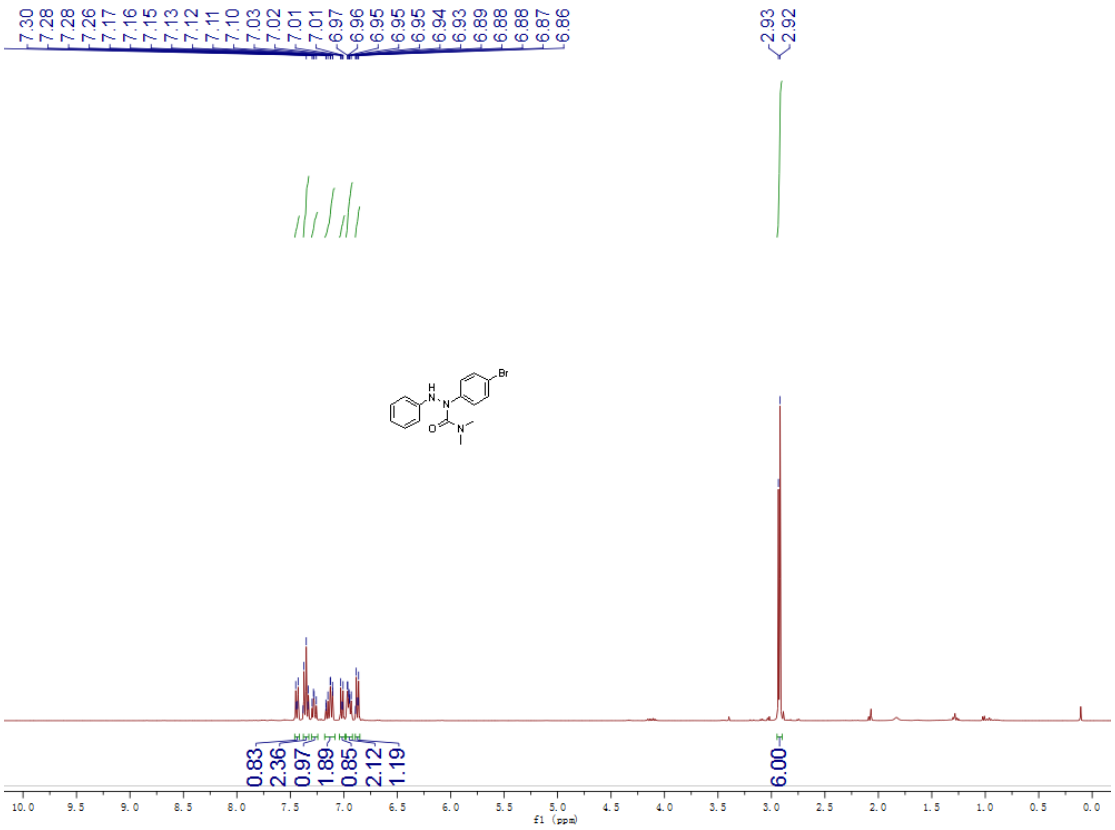

159.48
149.83
147.10
130.53
123.37
123.32
122.96
118.51
116.40
112.27
37.57
Br
Br
f1 (ppm)

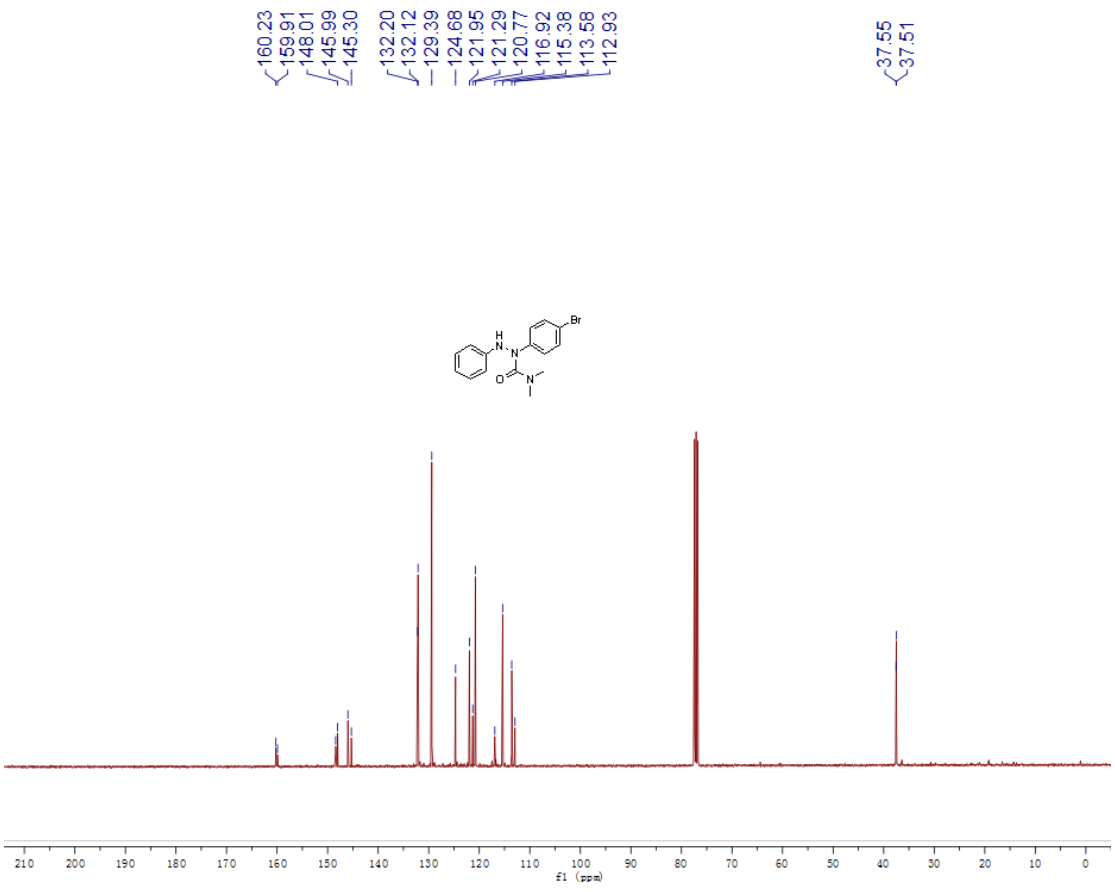

166.39
165.98
159.19
152.08
149.24
131.51
131.00
125.97
118.79
112.39
60.95
60.54
37.60
14.40
14.35
f1 (ppm)

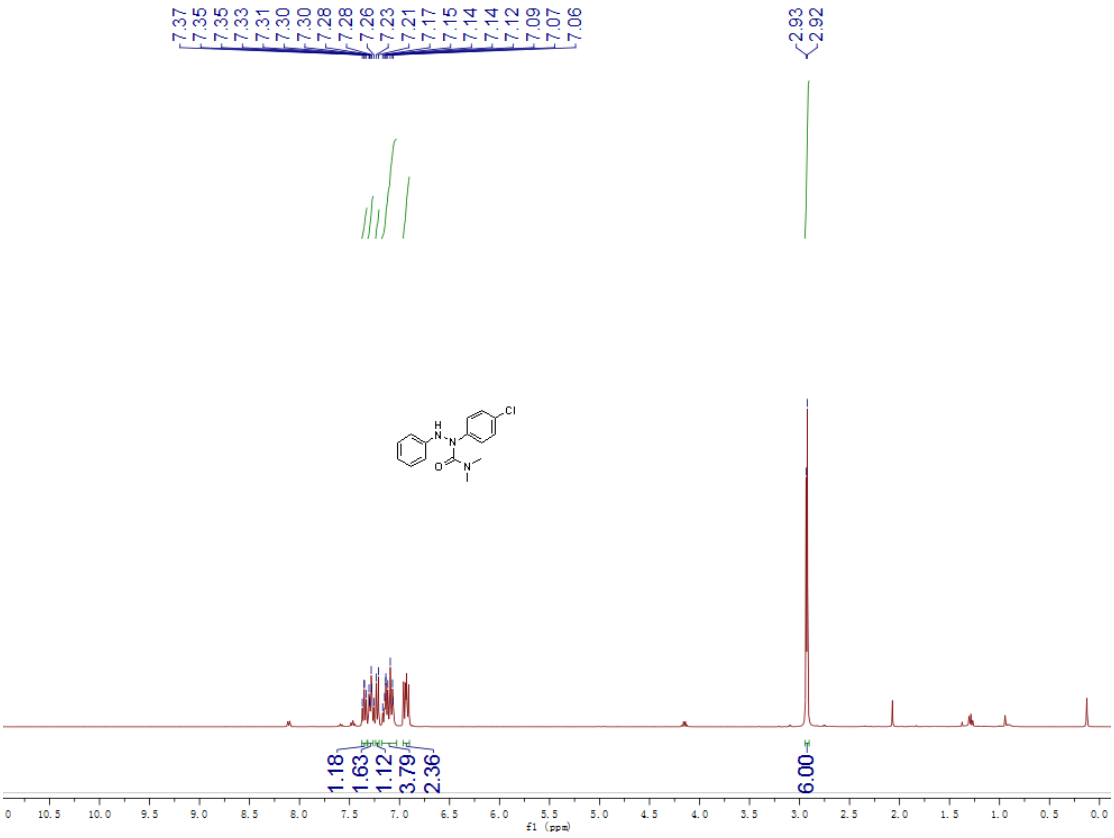

7.99
7.96
7.94
7.92
7.34
7.26
7.09
7.07
6.89
6.87
4.35
4.33
4.32
4.30
2.94
2.02
1.38
1.36
1.34
1.32
4.14
0.96
2.01
2.00
4.10
6.00
6.18
f1 (ppm)

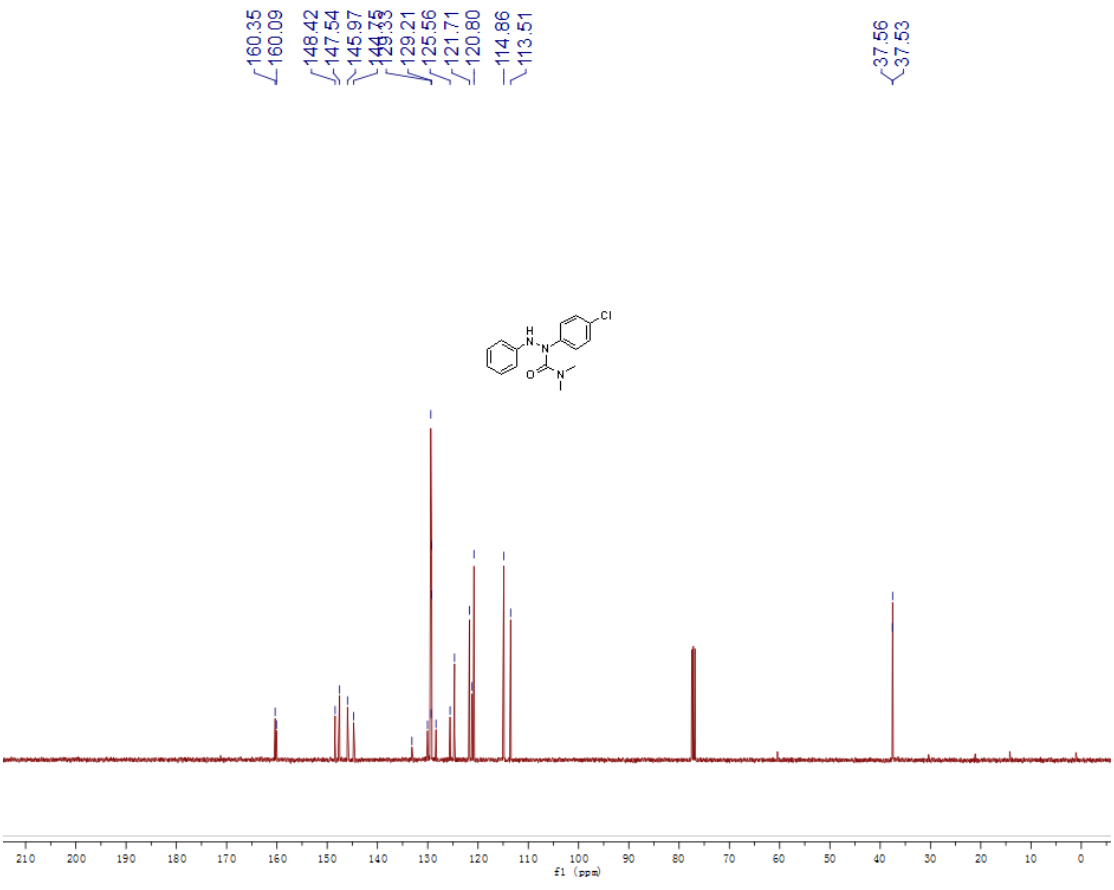

7.61
7.59
7.52
7.50
7.34
7.32
7.30
7.27
7.26
7.25
7.23
7.14
7.12
7.10
7.09
7.09
7.07
7.07
6.93
6.92
6.90
6.88
6.86
6.75
6.73
2.91
2.89
2.10
1.72
1.00
2.44
1.82
1.42
6.00
f1 (ppm)

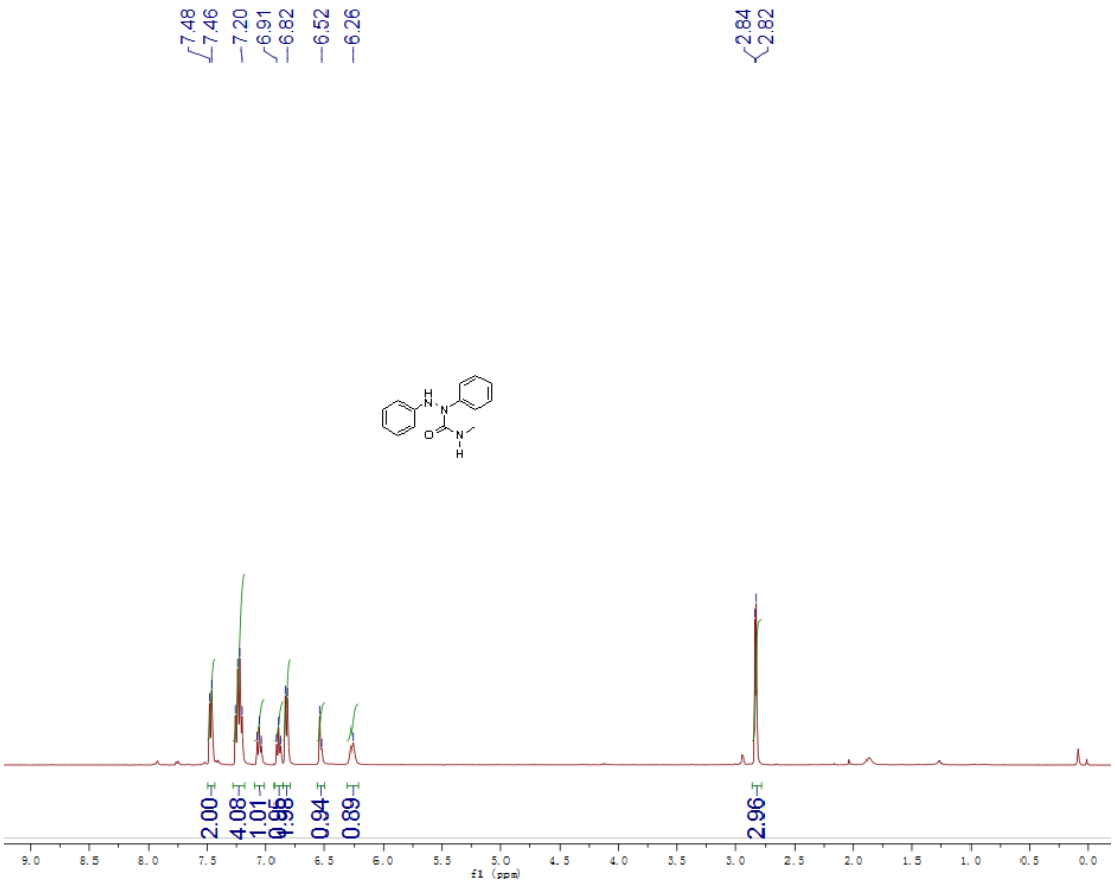

160.22
159.84
148.71
145.97
138.02
129.39
120.75
115.86
113.59
82.67
37.54
37.50
f1 (ppm)

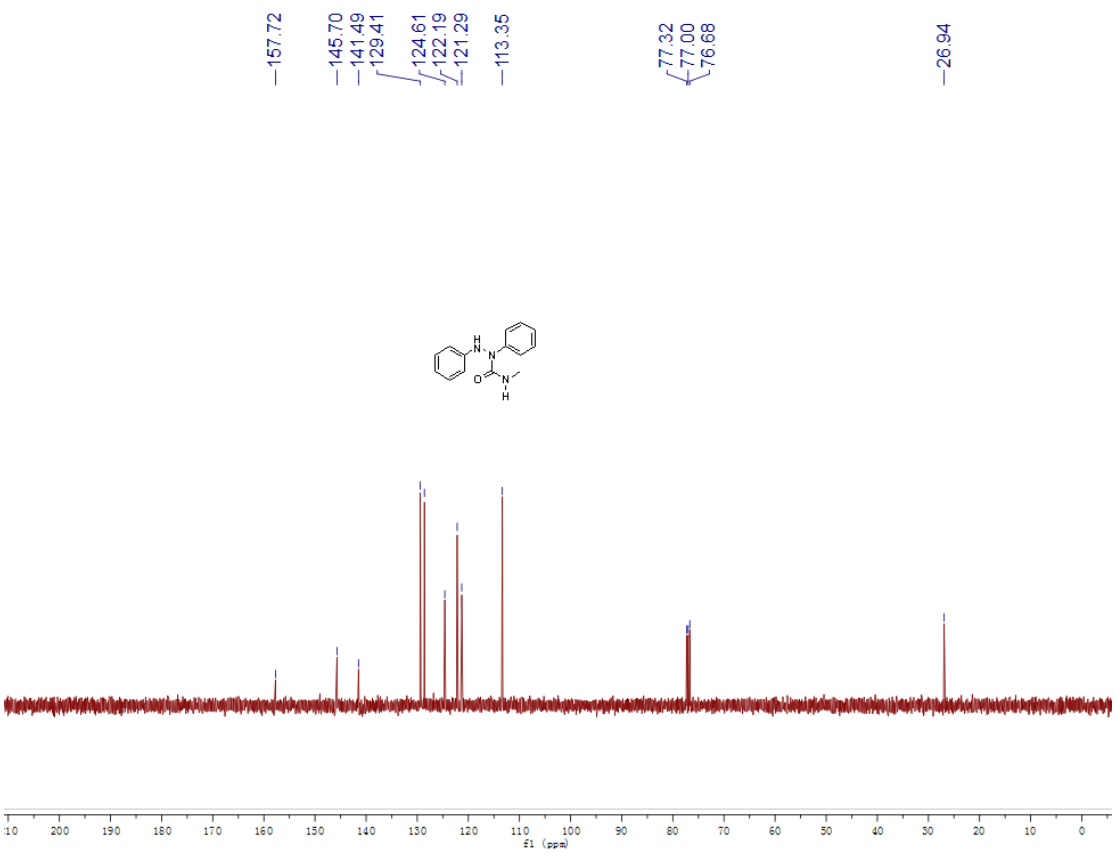

7.30
7.28
7.28
7.26
7.17
7.16
7.15
7.13
7.12
7.11
7.10
7.03
7.02
7.01
7.01
6.97
6.96
6.95
6.95
6.95
6.94
6.93
6.89
6.88
6.88
6.87
6.86
2.93
2.92
Br
0.83
2.36
0.97
1.89
0.85
2.12
1.19
6.00
f1 (ppm)

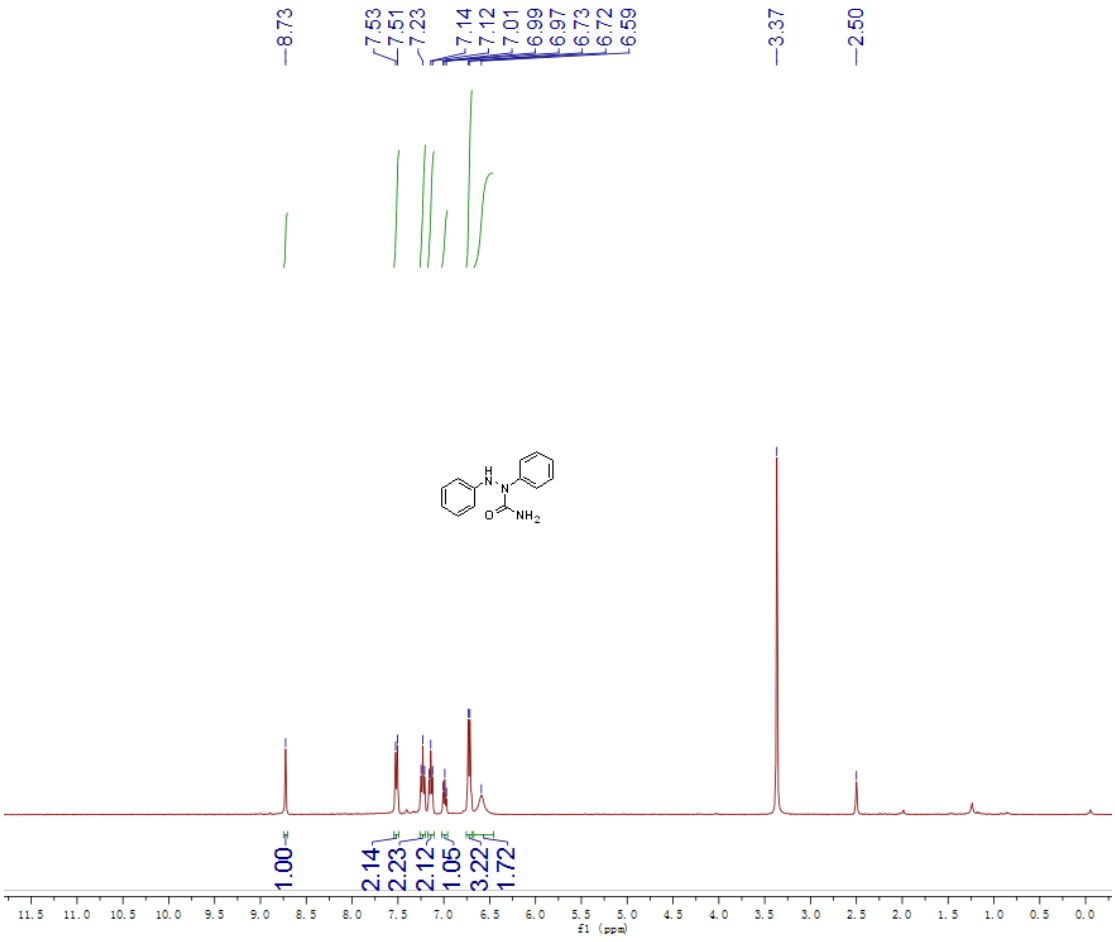

160.23
159.91
148.01
145.99
145.30
132.20
132.12
129.39
124.68
121.95
121.29
120.77
116.92
115.38
113.58
112.93
37.55
37.51
Br
f1 (ppm)

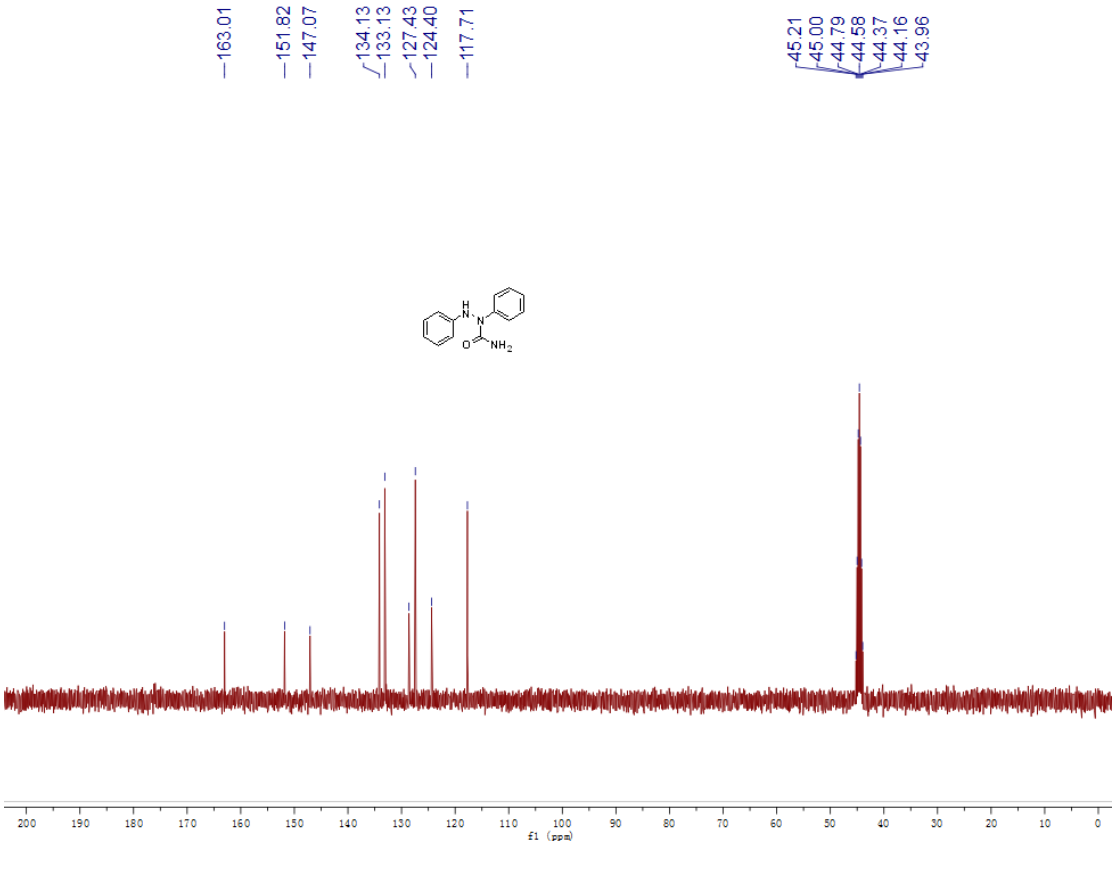

7.37
7.35
7.35
7.33
7.31
7.30
7.30
7.28
7.28
7.26
7.23
7.21
7.17
7.15
7.14
7.14
7.12
7.09
7.07
7.06
2.93
2.92
Cl
1.18
1.63
1.12
3.79
2.36
6.00
f1 (ppm)

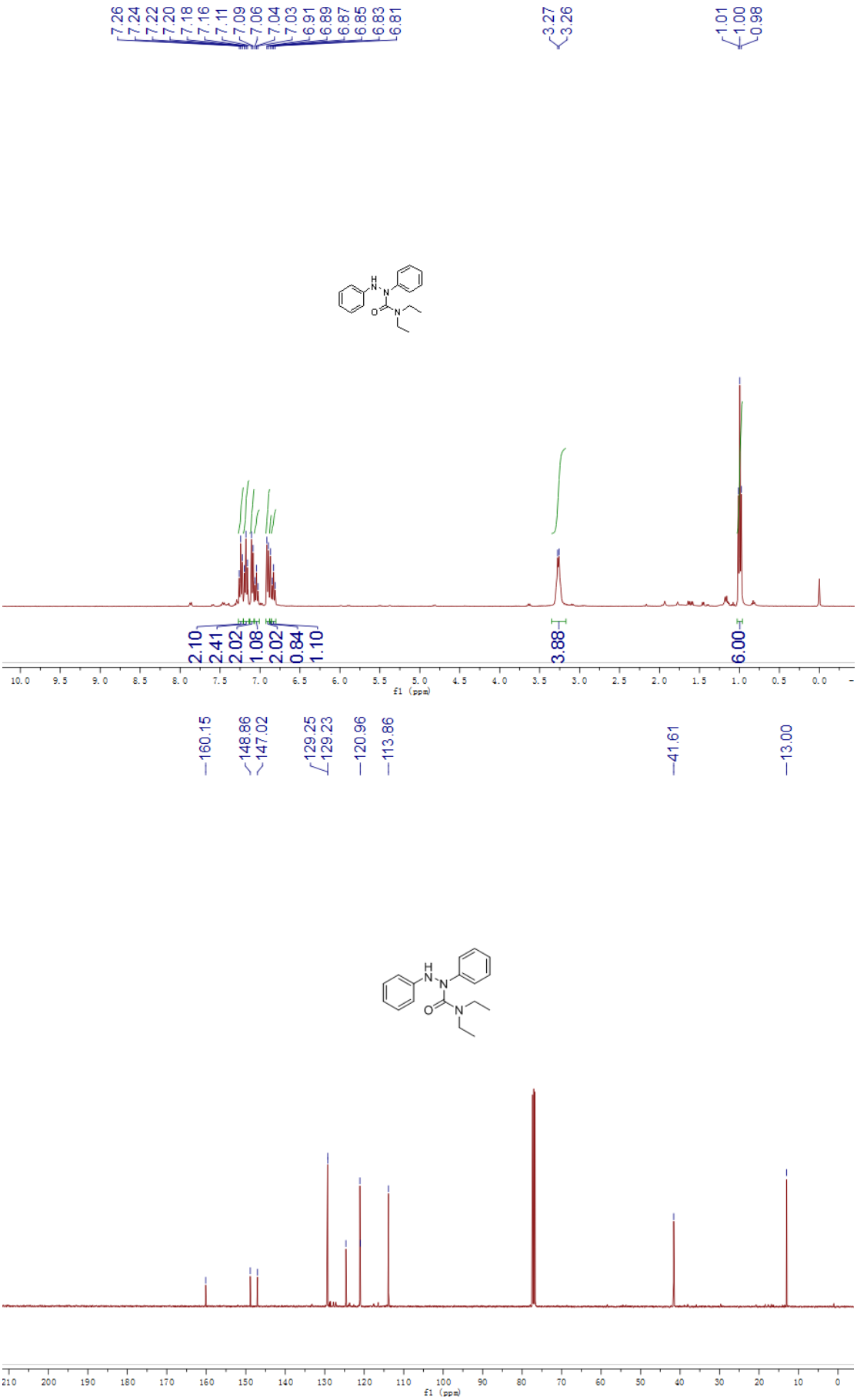

160.35
160.09
148.42
147.54
145.97
129.21
125.56
121.71
120.80
114.86
113.51
37.56
37.53
Cl
f1 (ppm)

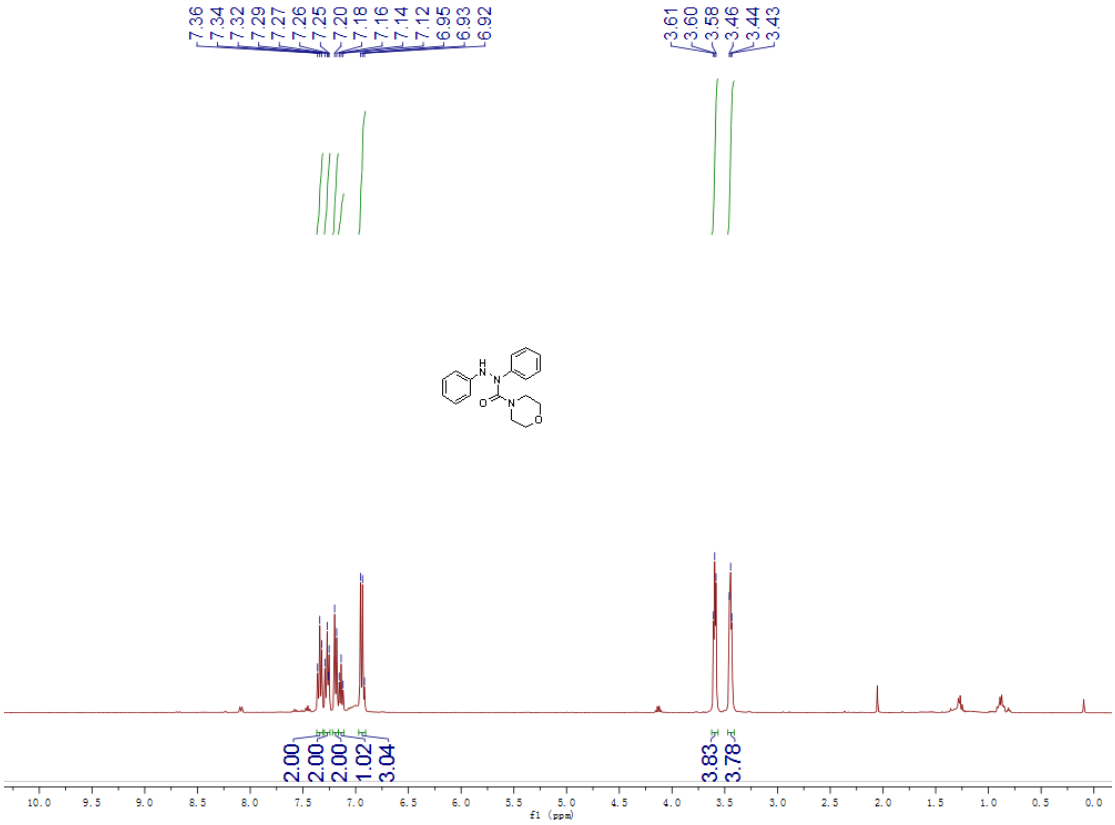

7.48
7.46
7.20
6.91
6.82
6.52
6.26
2.84
2.82
2.00
4.08
1.01
0.94
0.89
2.96
f1 (ppm)

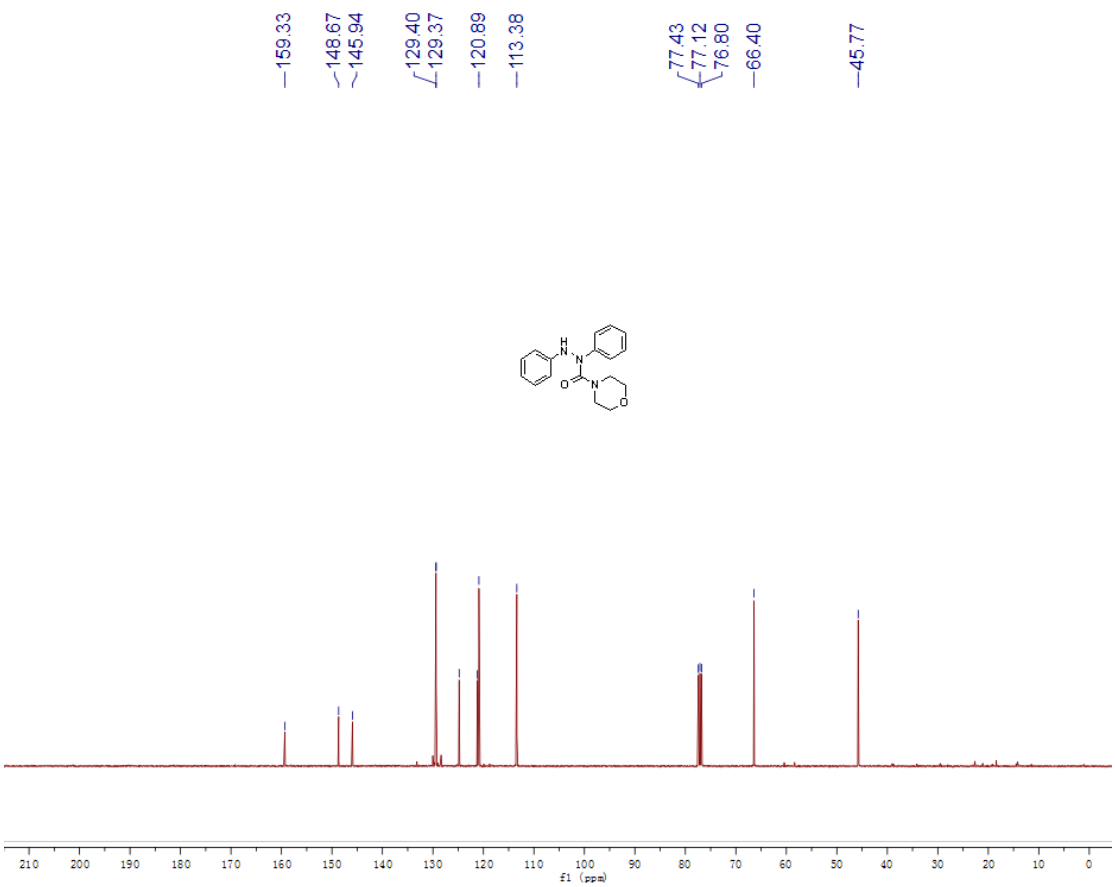

157.72
145.70
141.49
129.41
124.61
122.19
121.29
113.35
77.32
77.00
76.68
26.94
f1 (ppm)

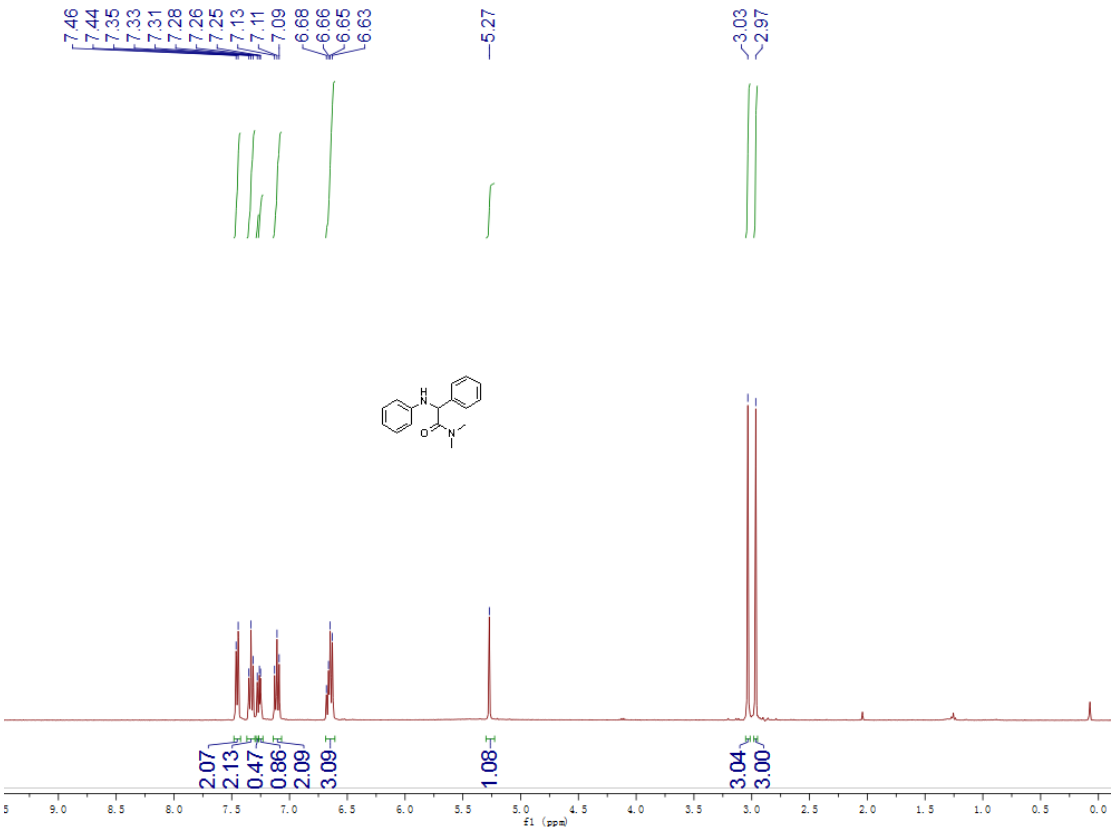

8.73
7.53
7.51
7.23
7.14
7.12
7.01
6.99
6.97
6.73
6.72
6.59
3.37
2.50
1.00
2.14
2.23
2.12
1.05
3.22
1.72
f1 (ppm)

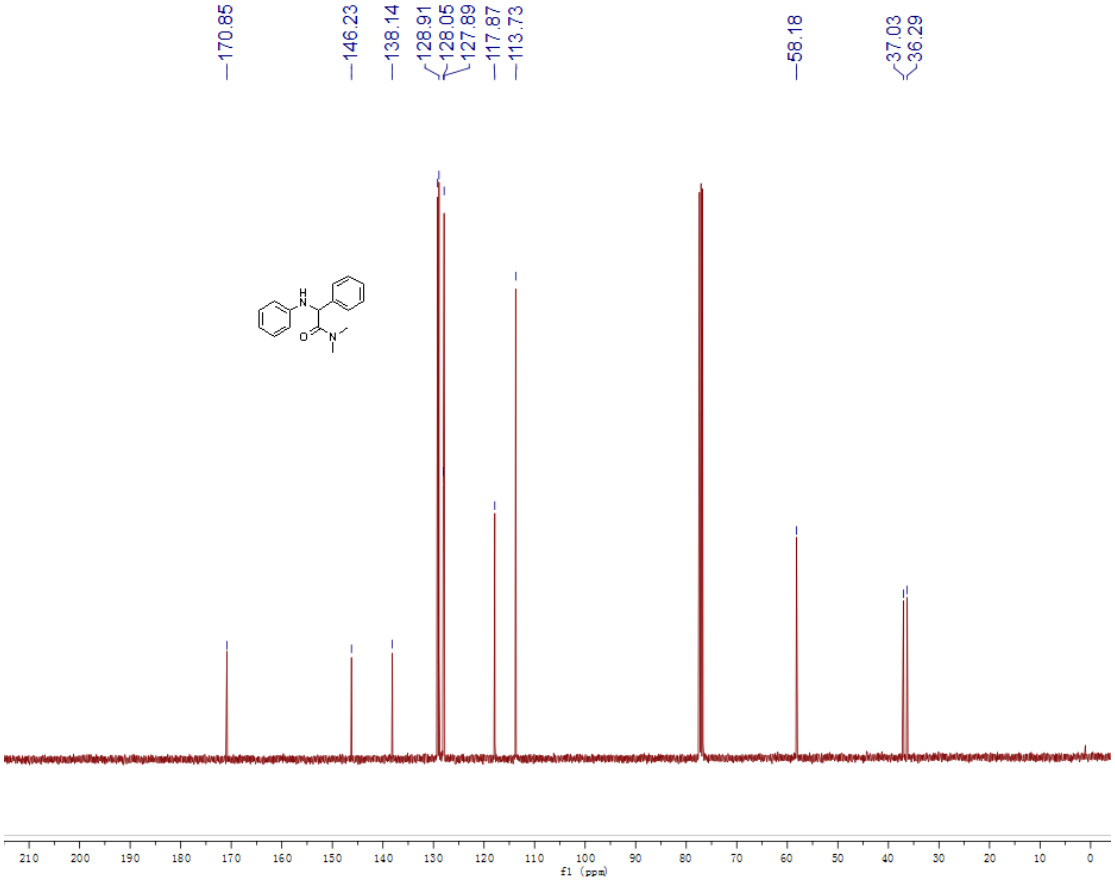

163.01
151.82
147.07
134.13
133.13
127.43
124.40
117.71
45.21
45.00
44.79
44.58
44.37
44.16
43.96
f1 (ppm)

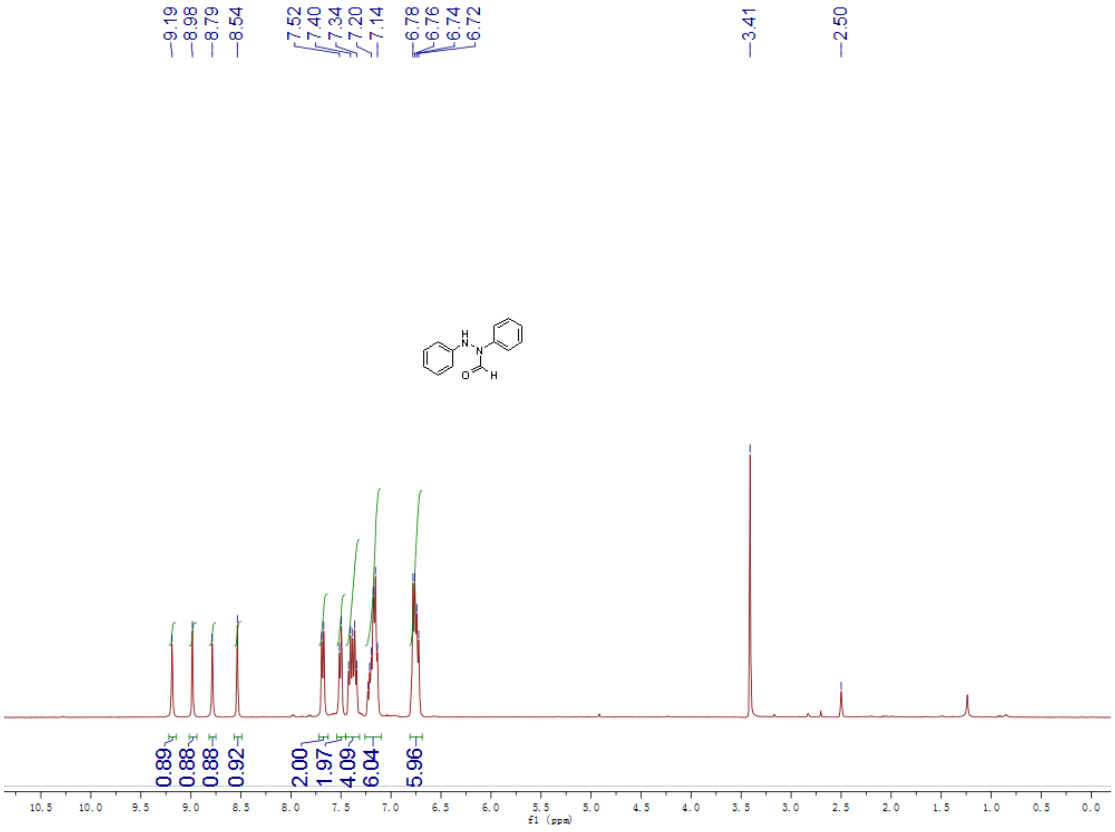

7.26
7.24
7.22
7.20
7.18
7.16
7.11
7.09
7.06
7.04
7.03
6.91
6.89
6.87
6.85
6.83
6.81
3.27
3.26
1.01
1.00
0.98
2.10
2.41
2.02
1.08
2.02
0.84
1.10
3.88
6.00
f1 (ppm)
160.15
148.86
147.02
129.25
129.23
120.96
113.86
41.61
13.00
f1 (ppm)

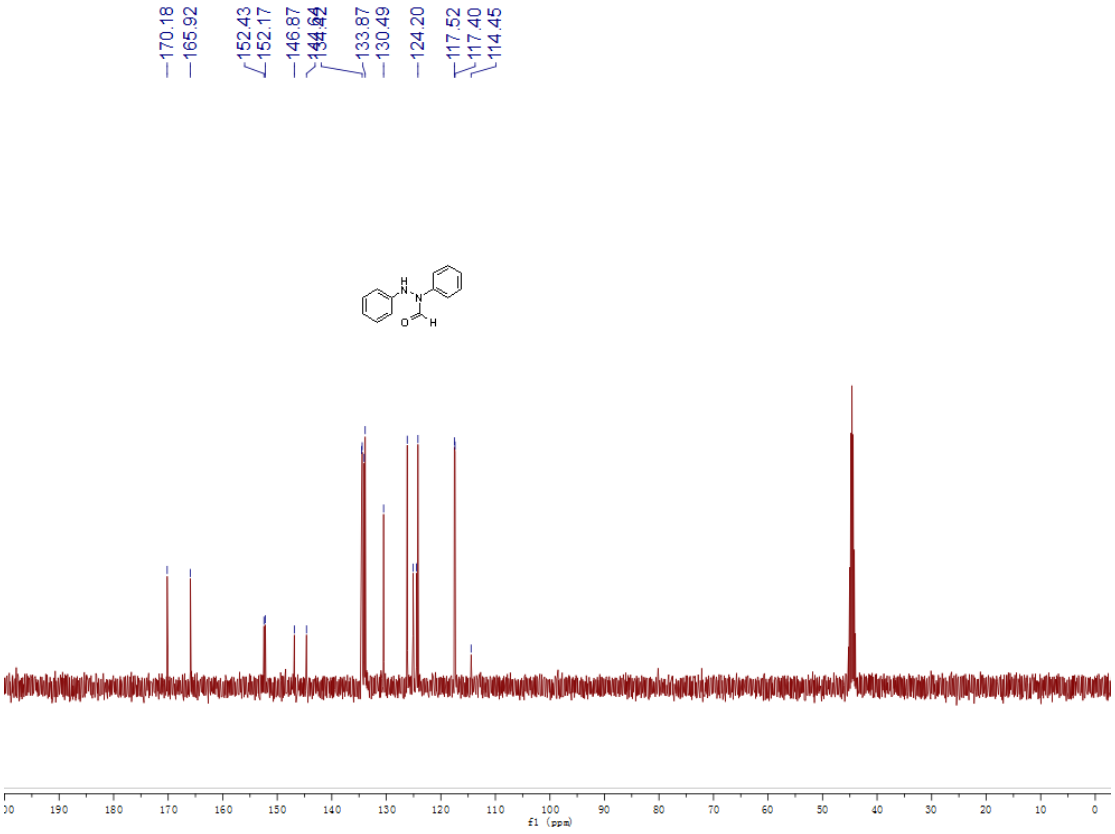

7.36
7.34
7.32
7.29
7.27
7.26
7.25
7.20
7.18
7.16
7.14
7.12
6.95
6.93
6.92
3.61
3.60
3.58
3.46
3.44
3.43
2.00
2.00
2.00
1.02
3.04
3.83
3.78
f1 (ppm)

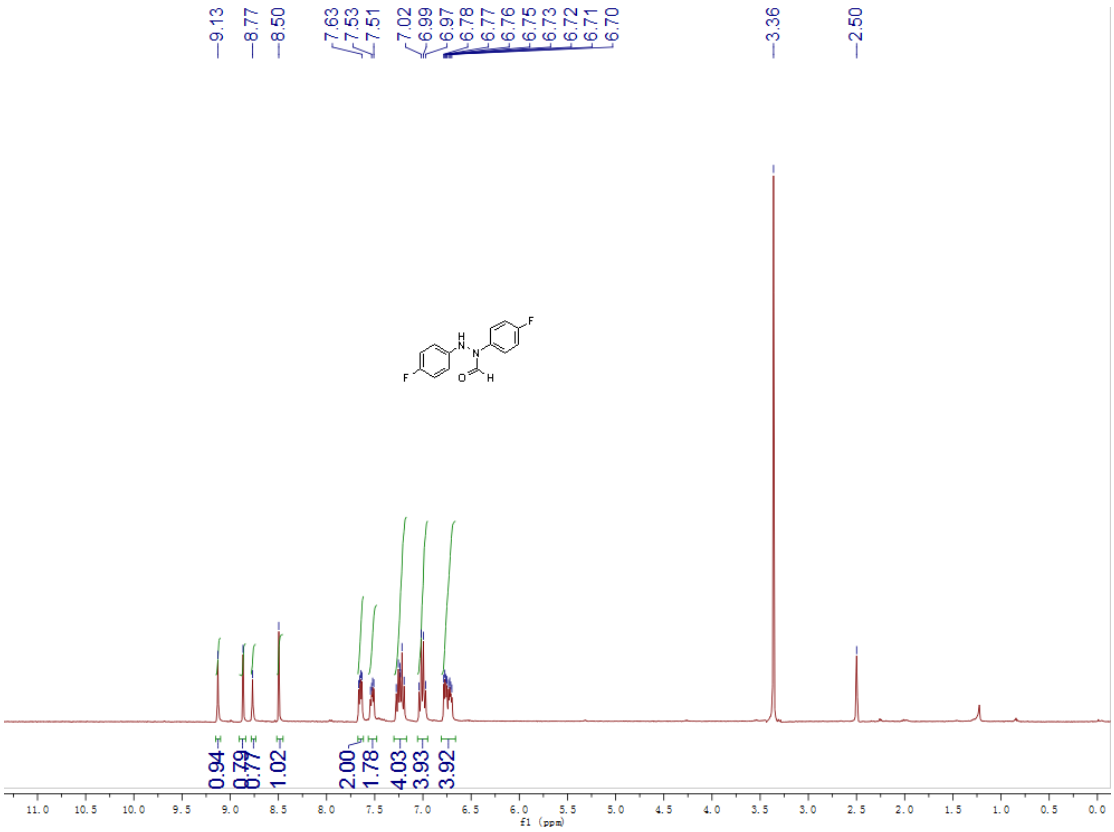

159.33
148.67
145.94
129.40
129.37
120.89
113.38
77.43
77.12
76.80
66.40
45.77
f1 (ppm)

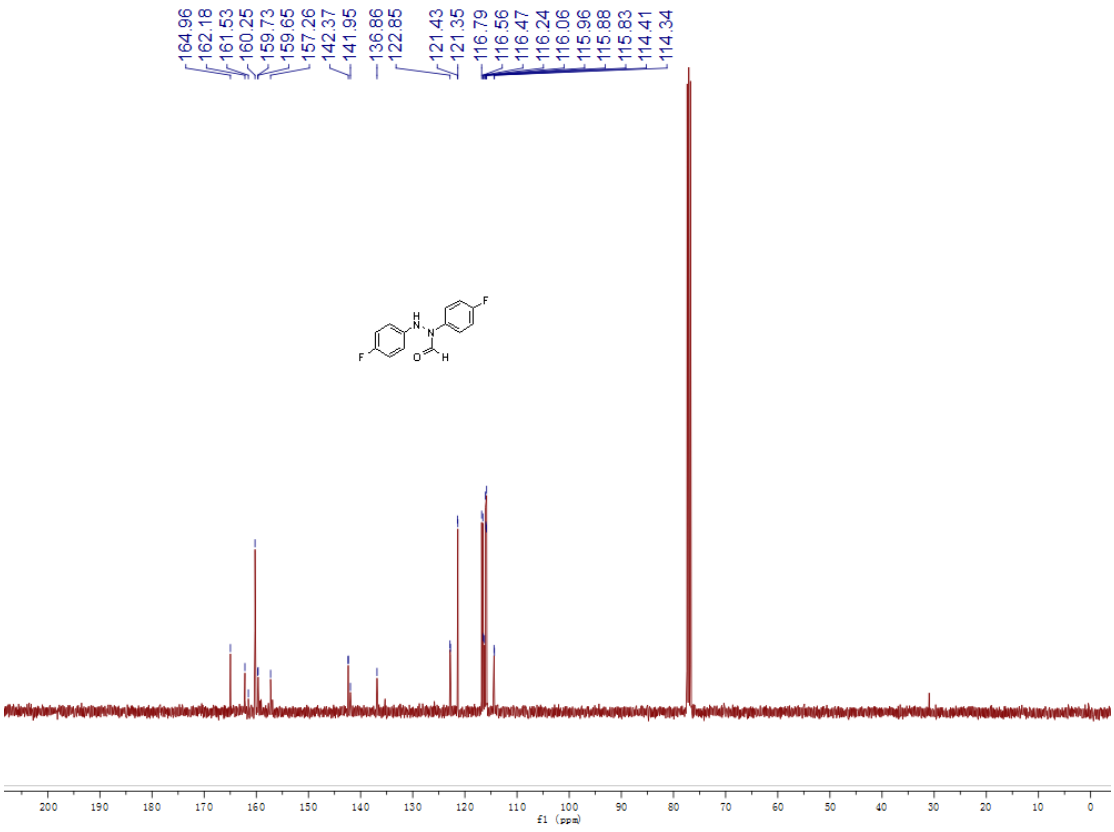

7.46
7.44
7.35
7.33
7.31
7.28
7.26
7.25
7.13
7.11
7.09
6.68
6.66
6.65
6.63
5.27
3.03
2.97
2.07
2.13
0.47
0.86
2.09
3.09
1.08
3.04
3.00
f1 (ppm)

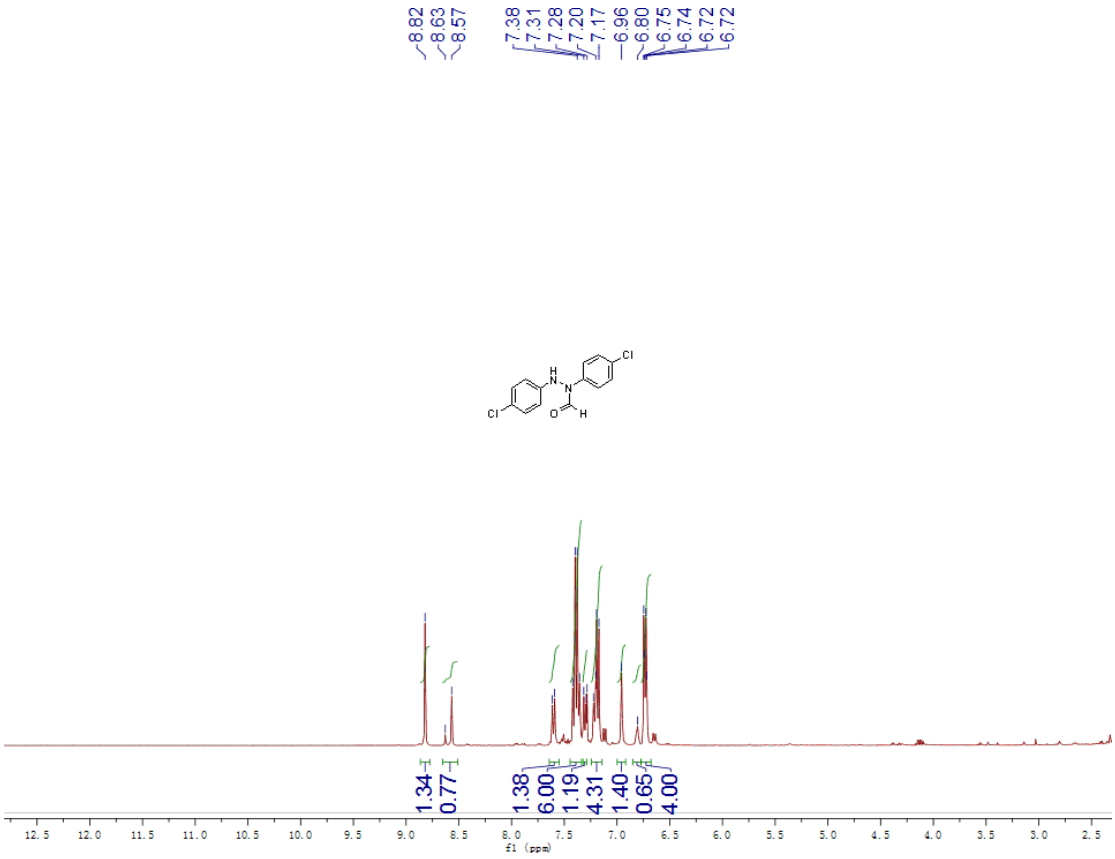

170.85
146.23
138.14
128.91
128.05
127.89
117.87
113.73
58.18
37.03
36.29
f1 (ppm)

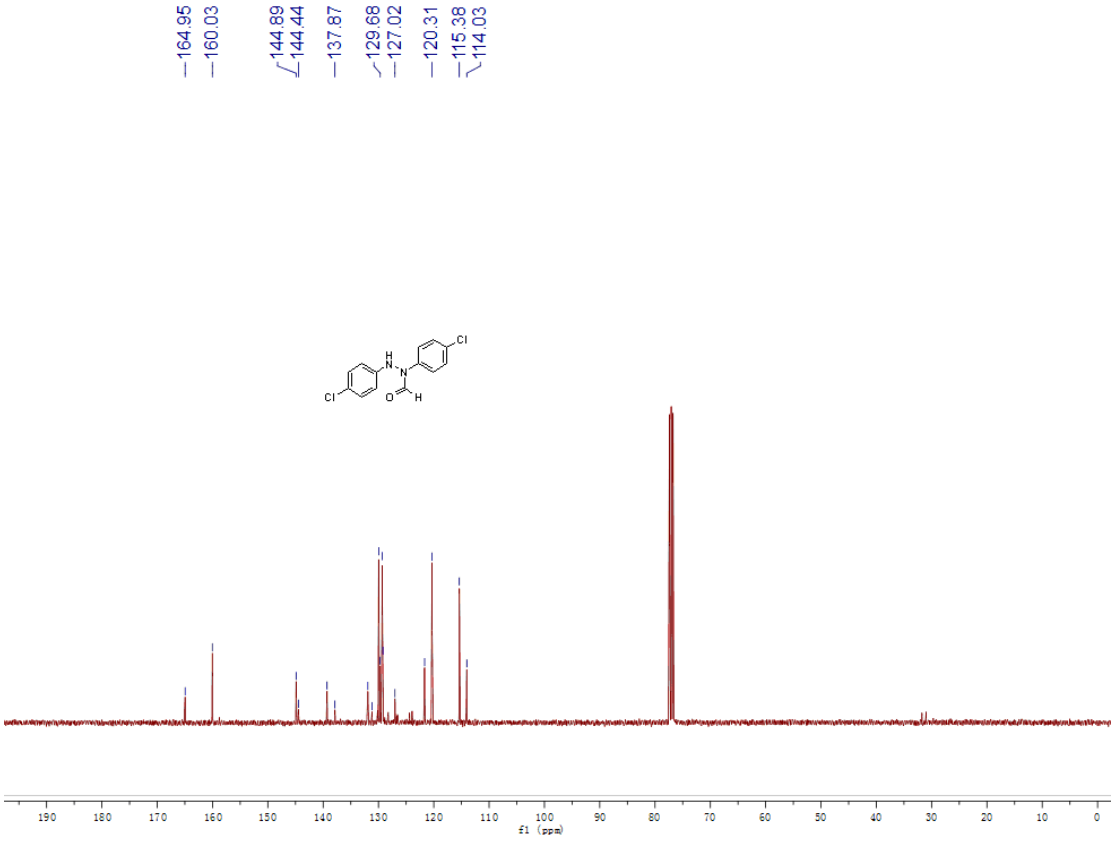

9.19
8.98
8.79
8.54
7.52
7.40
7.34
7.20
7.14
6.78
6.76
6.74
6.72
3.41
2.50
0.89
0.88
0.88
0.92
2.00
1.97
4.09
6.04
5.96
f1 (ppm)

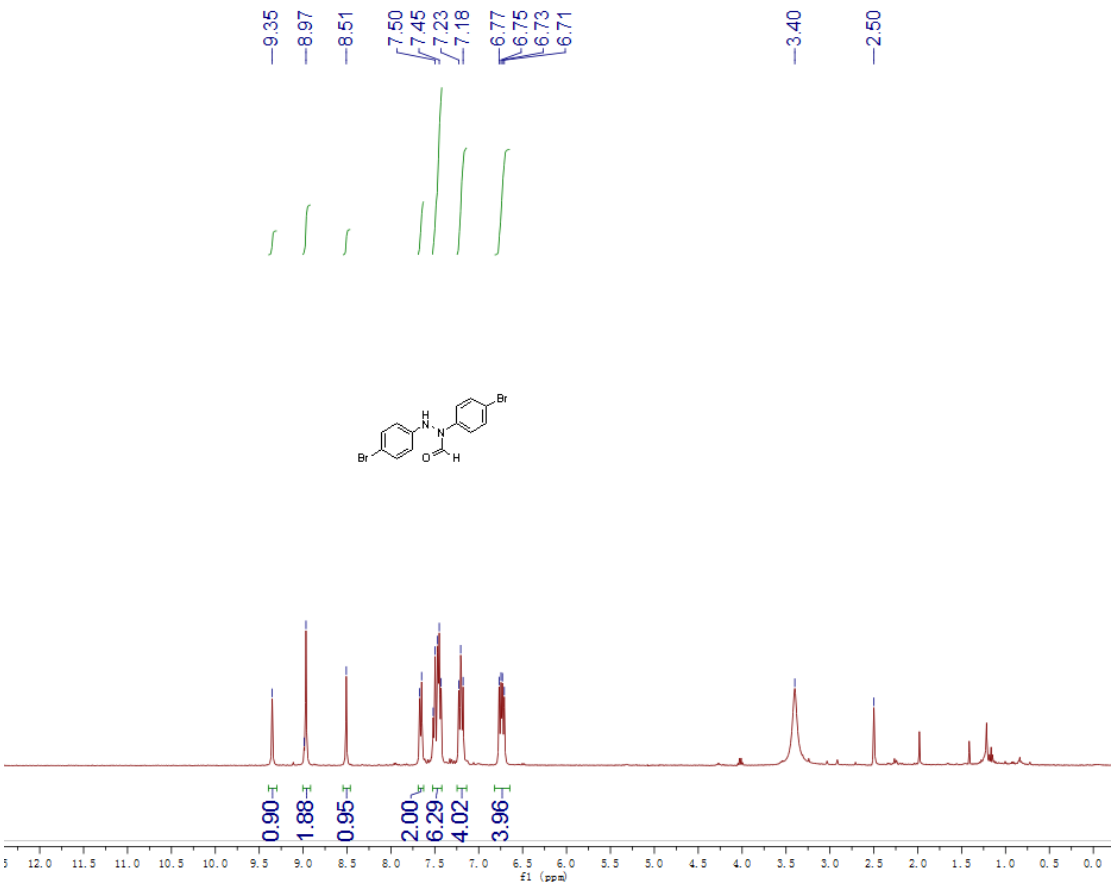

170.18
165.92
152.43
152.17
146.87
133.87
130.49
124.20
117.52
117.40
114.45
f1 (ppm)

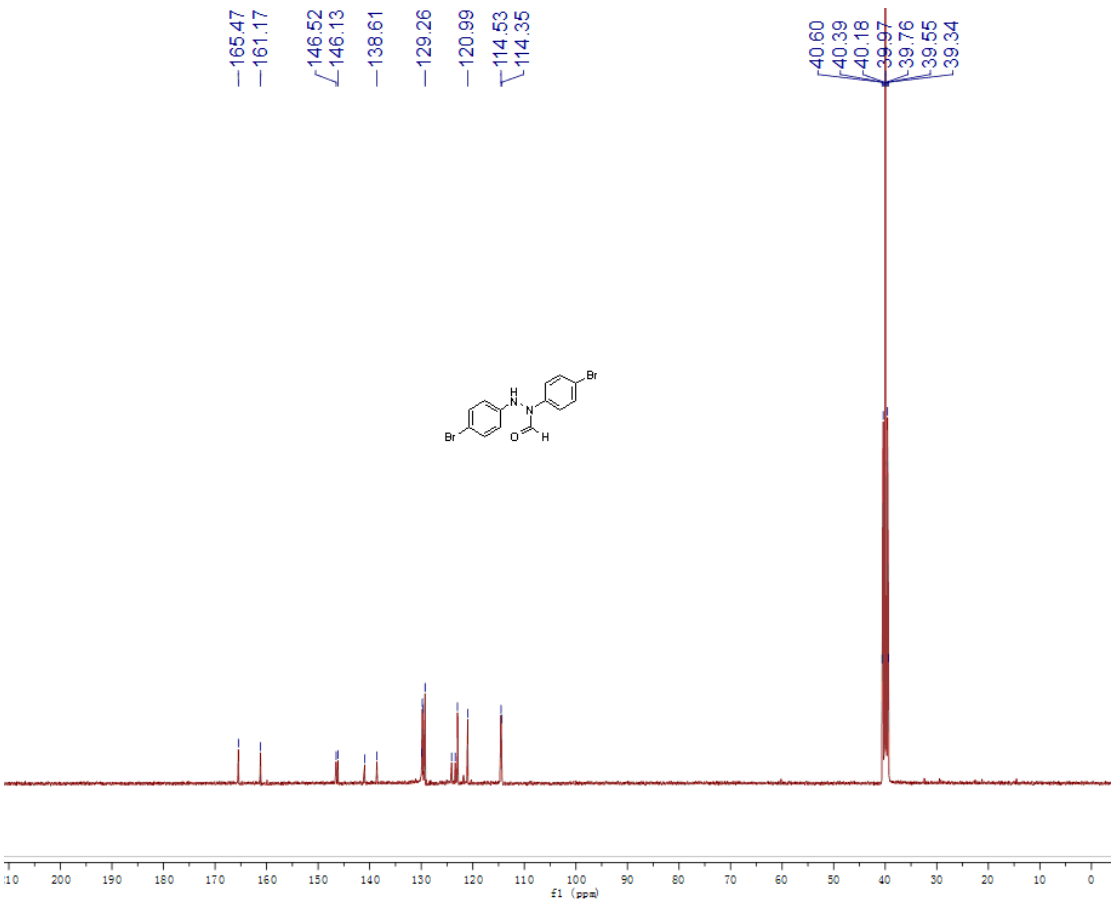

9.13
8.77
8.50
7.63
7.53
7.51
7.02
6.99
6.97
6.78
6.77
6.76
6.75
6.73
6.72
6.71
6.70
3.36
2.50
0.94
0.79
0.77
1.02
2.00
1.78
4.03
3.93
3.92
f1 (ppm)

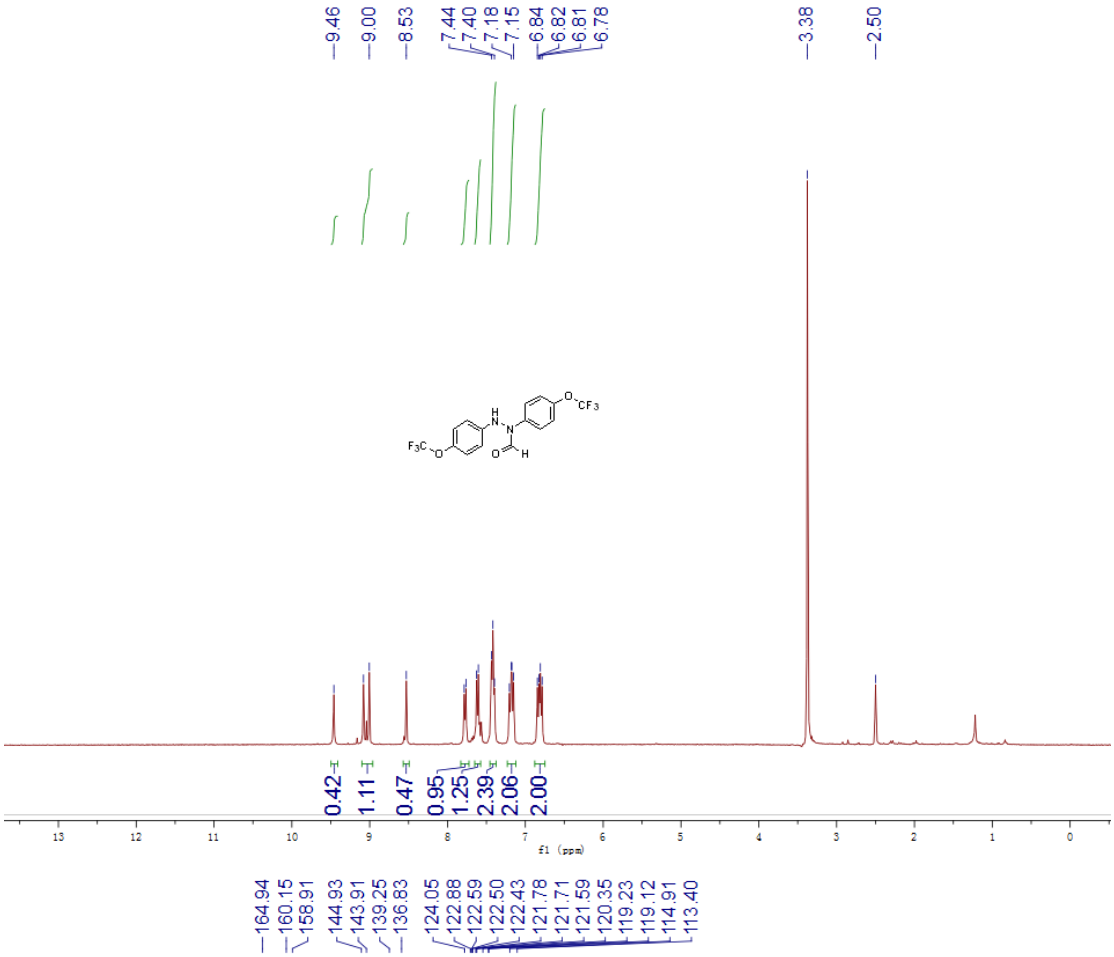

164.96
162.18
161.53
160.25
159.73
159.65
157.26
142.37
141.95
136.86
122.85
121.43
121.35
116.79
116.56
116.47
116.24
116.06
115.96
115.88
115.83
114.41
114.34
f1 (ppm)

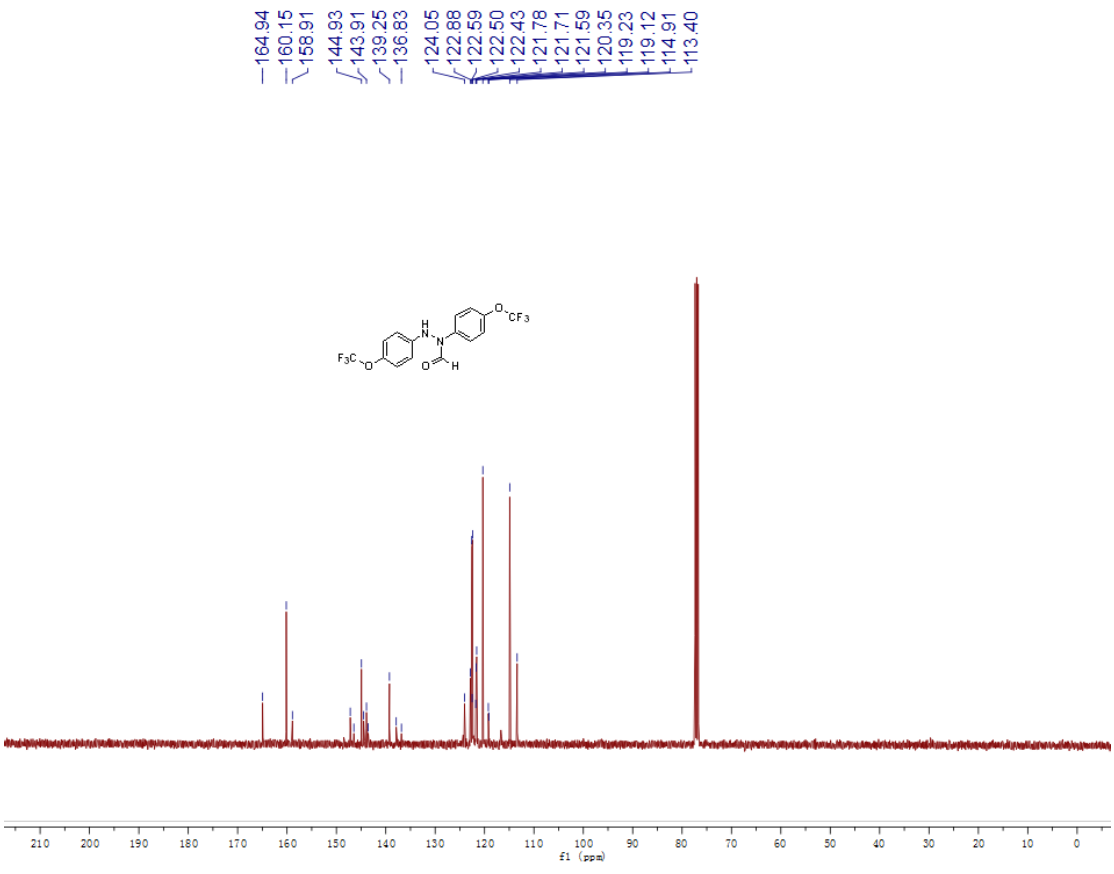

8.82
8.63
8.57
7.38
7.31
7.28
7.20
7.17
6.96
6.80
6.75
6.74
6.72
6.72
Cl
Cl
H
N
N
O
H
1.34
0.77
1.38
6.00
1.19
4.31
1.40
0.65
4.00
f1 (ppm)

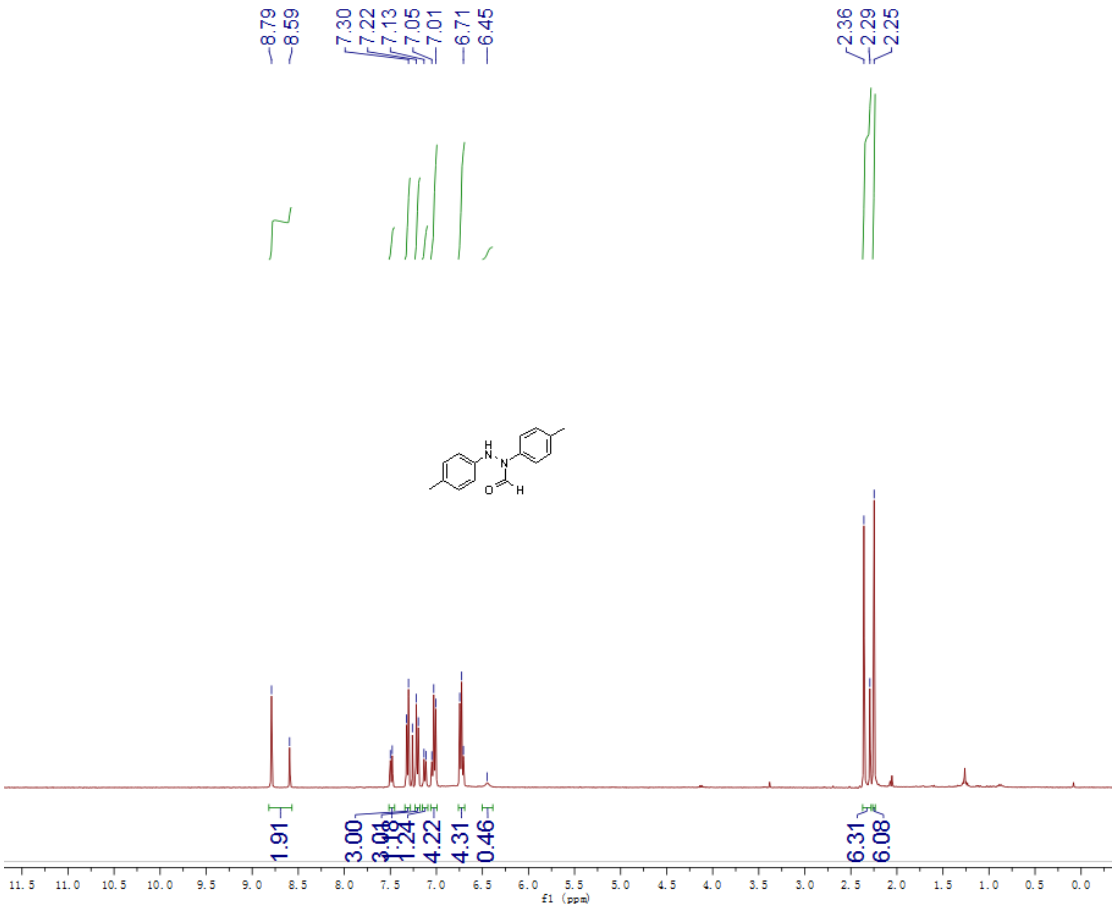

164.95
160.03
144.89
144.44
137.87
129.68
127.02
120.31
115.38
114.03
Cl
Cl
H
N
N
O
H
f1 (ppm)

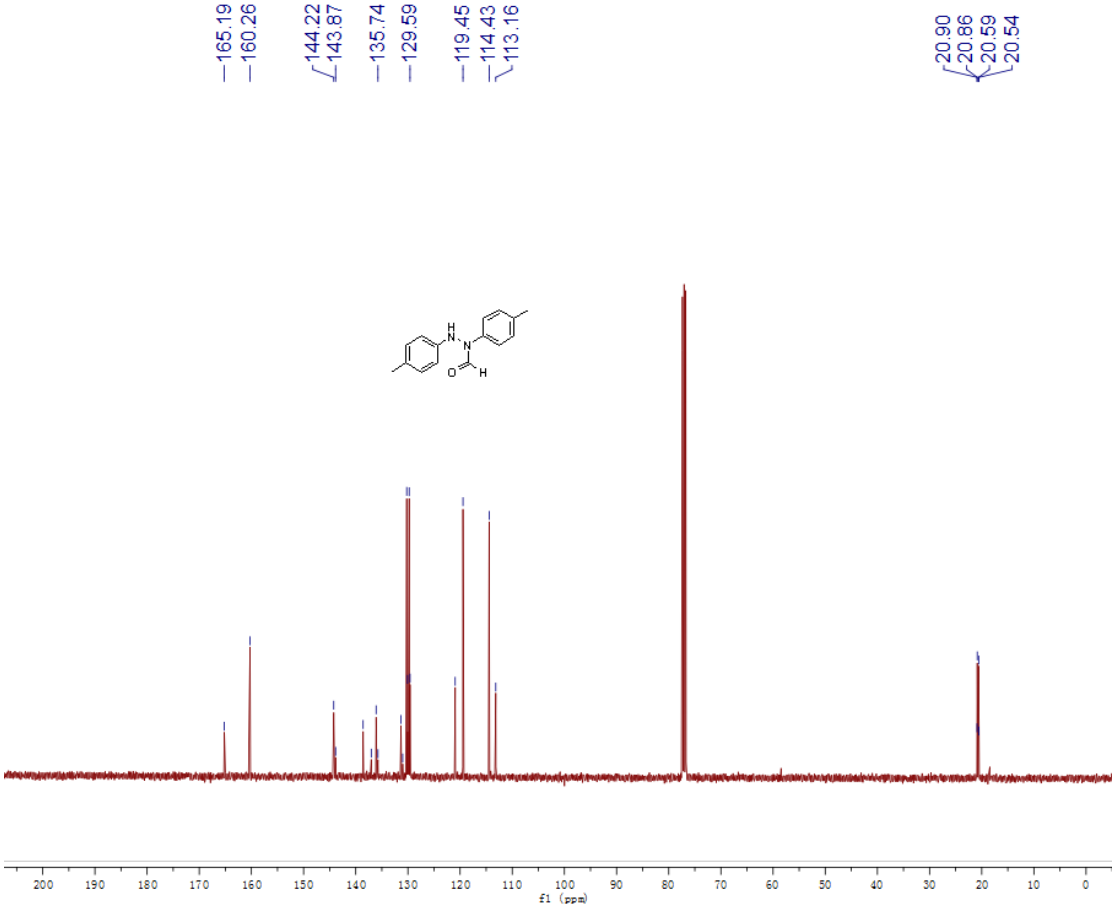

9.35
8.97
8.51
7.50
7.45
7.23
7.18
6.77
6.75
6.73
6.71
3.40
2.50
Br
Br
0.90
1.88
0.95
2.00
6.29
4.02
3.96
f1 (ppm)


165.47
161.17
146.52
146.13
138.61
129.26
120.99
114.53
114.35
40.60
40.39
40.18
39.97
39.76
39.55
39.34
Br
Br
f1 (ppm)


9.46
9.00
8.53
7.44
7.40
7.18
7.15
6.84
6.82
6.81
6.78
3.38
2.50
0.42
1.11
0.47
0.95
1.25
2.39
2.06
2.00
f1 (ppm)


164.94
160.15
158.91
144.93
143.91
139.25
136.83
124.05
122.88
122.59
122.50
122.43
121.78
121.71
121.59
120.35
119.23
119.12
114.91
113.40
f1 (ppm)


8.79
8.59
7.30
7.22
7.13
7.05
7.01
6.71
6.45
2.36
2.29
2.25
1.91
3.00
3.01
1.24
4.22
4.31
0.46
6.31
6.08
f1 (ppm)


165.19
160.26
144.22
143.87
135.74
129.59
119.45
114.43
113.16
20.90
20.86
20.59
20.54
f1 (ppm)