Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information for

Catalyst-free Oxidative N–N Coupling for the Synthesis of 1, 2, 3-Triazole Compounds with *t*BuONO

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1. General Information

All reagents and solvents were purchased from TCI, Sigma-Aldrich, Alfa Aesar, Acros and Meryer. All reactions were conducted using standard Schlenk techniques. Column chromatography was performed using EM silica gel 60 (300-400 mesh). ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were measured on a 500 MHz (or 400M) spectrometer, using DMSO-d_6, $CDCl_3$ or CD_3COD as the solvent with tetramethylsilane (TMS) as the internal standard at room temperature. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), DMSO-d_6 (2.50 ppm) or CD_3COD (3.34 ppm), and ^{13}C-NMR spectra were referenced to $CDCl_3$ (77.0 ppm) or DMSO-d_6 (39.5 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet. Chemical shifts are given in δ relative to TMS, the coupling constants J are given in Hz. Analysis of crude reaction mixture was done on the Varian 4000 GC/MS and Agilent 7890A/5975C. High-resolution mass spectra were recorded on a micrOTOF-Q II 10410 mass spectrometer.

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. The 2-Amino benzamide,[1] 2-aminothiophenol[2] and pyridin-2-ylmethanamine[3] were prepared according to corresponding literature procedures.

Reference:

(1) Abhijeet, D, R.; Arunachalam, S.; Raja, Roy. *J. Org. Chem.*, 2006, **71**, 382-385.

(2) Durga, P, H.; Thea, H.; Burkhard, K. *Org. Lett.*, 2012, **20**, 5334-5337.

(3) Rana, S.; Dey, A.; Maiti, D. *Chemical Communications (Cambridge, United Kingdom),* 2015, **51**, 14469-14472.

2. Optimization of the reaction conditions

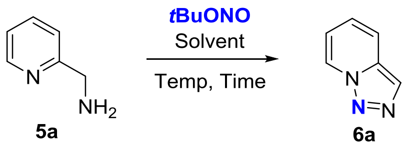


Table S1: Optimization of the reaction conditions

Entry	Solvent	Temp. (^oC)	Time (h)	Yield (%)
1	CH_3CN	r.t.	24	20
2	dioxane	r.t.	24	54
3	DMF	r.t.	24	trace
4	THF	r.t.	24	trace
5	DMSO	r.t.	24	trace
6	DCM	r.t.	24	trace
7	DCE	r.t.	24	trace
8	toluene	r.t.	24	trace
9	NMP	r.t.	24	trace
10	H_2O	r.t.	24	10
11	^{i}PrOH	r.t.	24	trace
12	C_2H_5OH	r.t.	24	trace
13	CH_3OH	r.t.	24	trace
14	benzyl alcohol	r.t.	24	80
15[b]	benzyl alcohol	r.t.	28	79
16[c]	benzyl alcohol	r.t.	24	72
17	benzyl alcohol	60	3	75

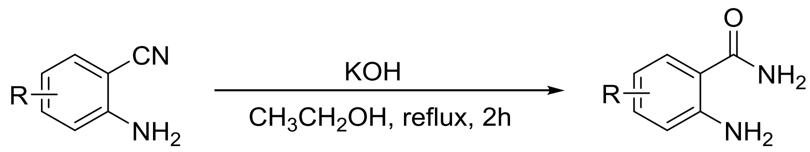
[a]Reaction condition: **5a** (1 mmol), *t*BuONO (2 mmol), solvent (4 mL), temp., time, N_2. [b]1.5 equiv. of *t*BuONO was used. [c]Under air atmosphere.

We began our investigation by combining a 1:2 mixture of pyridin-2-ylmethanamine (substrate **5a**) and tertbutyl nitrite at room temperature in CH_3CN under N_2 atmosphere. To our delight, the desirable product 6a was isolated in 20% yield. We tested the effect of aprotic solvents on the yield. It was found that an improved yield was observed with dioxane (Table S1, entry 2), whereas only trace product was obtained with other aprotic solvents (Table S1, entries 3-9). Further screening of protic solvents showed that *i*PrOH, C_2H_5OH and CH_3OH resulted in insignificant amounts of the desired product **6a** (Table S1, entries 11-13). Notably, the use of water as solvent provided only 10% yield product **6a**, along with a large amount of unwanted hydrolysate (pyridin-2-ylmethanol) (Table S1, entry 10).

Remarkably, the reaction employing benzyl alcohol as solvent delivered product in 80 % yield with complete conversion (Table S1, entry 14). Moreover, the attempt to use a smaller amount of *t*BuONO (1.5 eq) was successful, though slightly prolonging the reaction time was required (Table S1, entry 15). When the reaction was conducted under air atmosphere, a slight decrease in yield was observed (Table S1, entry 16). Raising the reaction temperature to 60 ^{o}C didn't improve the yield (Table S1, entry 17).

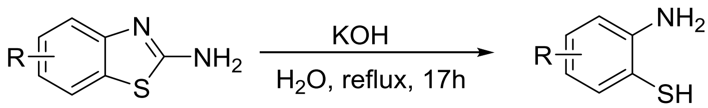
3. General procedure for preparation of material

General procedure for preparation of 2-Amino benzamides



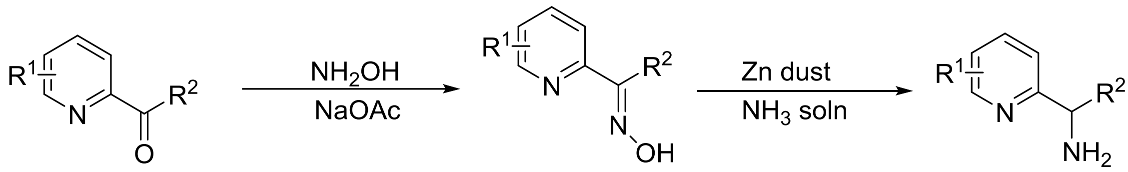
2-Amino benzonitrile (1.04 g, 8.50 mmol) and potassium hydroxide (2.40 g, 42.5 mmol) were dissolved in hot ethanol (25 mL) and the reaction mixture refluxed for two hours. The resulting yellowish brown solution was allowed to cool to room temperature and the ethanol was removed in vacuo. The resulting brown solid was washed with water, saturated solution of $NaHCO_3$, and brine and extracted with ethyl acetate (50 mL x 3). The organic layer was evaporated in vacuo and the analytically pure product was obtained by recrystallization from ethanol.

General procedure for preparation of 2-aminothiophenols



To the stirred solution of KOH (6 g) in 24 mL of water, benzothioazole (3 mmol) was added and refluxed for 17 h. The reaction mixture was then cooled to room temperature, and neutralized with 37.8 wt% hydrochloric acid. The reaction mixture was extracted with ethyl acetate, dried over Na_2SO_4, filtered and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petrol ether/ethyl acetate as eluent.

General procedure for preparation of pyridin-2-ylmethanamines

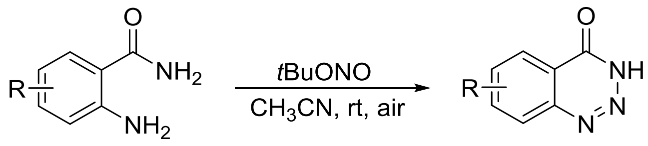


Hydroxylamine hydrochloride (750.5 mg, 10.8mmol) and sodium acetate (NaOAc) (886mg, 10.8 mmol) were heated at 60 ℃ in H_2O (10 mL) for 1 hour. To the above, ketone or aldehyde (1g, 5.43 mmol) in 2 mL MeOH was then added. The resulting mixture was stirred at 60 ℃ overnight. The oxime solidified upon cooling the reaction mixture to room temperature. The product oxime was washed with MeOH and the solvent was dried under vacuum. The crude oxime, was used in the next step without further purification.

The above prepared oxime (1 g, 5 mmol), NH_4OAc (655 mg, 8.5 mmol), NH_3 (25% aqueous, 15 ml), EtOH (20 mL) and H_2O (10 ml) were mixed and heated at 80 ℃. Activated Zn dust (1.47 g, 22.5 mmol) was then added to the reaction mixture in small amounts for over 30 mins. The resulting mixture was refluxed for 3 hour and then stirred at 25 ℃ overnight. The mixture was filtered and the residue was washed with MeOH and water. The filtrate was concentrated and the resulting aqueous solution was made strongly alkaline with 10 (M) NaOH solution. The amine was then extracted with ethyl acetate and the organic phase was then washed with brine, dried over Na_2SO_4 and concentrated under vacuum to afford product.

4. General experimental procedures

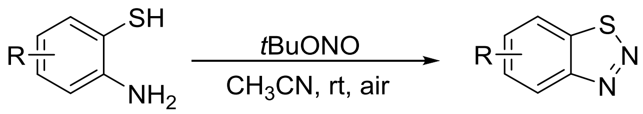
General procedure for synthesis of 1,2,3-benzotriazine-4(3*H*)-ones



1 **2**

To a stirred solution of the corresponding **1** (0.3 mmol) in CH_3CN (2 mL) was added dropwise *t*BuONO (0.45 mmol, 1.5 equiv.). After completion of addition, the mixture was stirred at room temperature until **1** disappeared, which was judged by TLC. The reaction solution was concentrated in vacuum, and the residue was chromatographed with petroleum and ethyl acetate as eluent to provide the corresponding product.

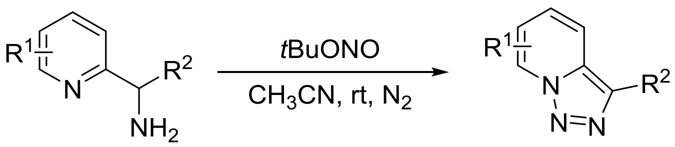
General procedure for synthesis of 1,2,3-benzothiadiazoles



3 **4**

To a stirred solution of the corresponding **3** (0.3 mmol) in CH_3CN (2 mL) was added dropwise *t*BuONO (0.45 mmol, 1.5 equiv.). After completion of addition, the mixture was stirred at room temperature until **3** disappeared, which was judged by TLC. The reaction solution was concentrated in vacuum, and the residue was chromatographed with petroleum and ethyl acetate as eluent to provide the corresponding product.

General procedure for synthesis of triazolopyridines

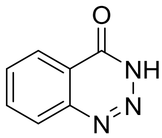


5 **6**

A Schlenk tube equipped with a stir bar was fitted with a rubber septum, and then it was evacuated and refilled with nitrogen three times. Under nitrogen, **5** (0.3 mmol, 1 equiv.), phenylmethanol (2 ml), *t*BuONO (0.45 mmol, 1.5 equiv.) were added in turn to the Schlenk tube through the rubber septum using syringes, and then the septum was replaced by a Teflon screwcap under nitrogen flow. The reaction mixture was stirred at room temperature until **5** disappeared, which was judged by TLC. The reaction solution was concentrated in vacuum, and the residue was chromatographed with petroleum and ethyl acetate as eluent to provide the corresponding product.

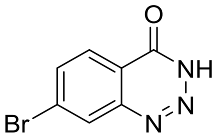
5. Characterization of products in details

Benzo[*d*][1,2,3]triazin-4(*3H*)-one (2a) (**CAS Number: 90-16-4**)



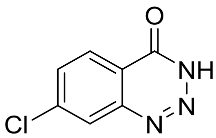
White solid (42 mg, 95% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.95 (s, 0.8H), 8.13-8.20 (m, 2H), 8.03-8.07 (td, *J* = 7.1, 1.4 Hz, 1H), 7.86-7.90 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.5, 144.1, 135.4, 132.5, 127.8, 124.2, 120.1; LRMS (EI 70 ev) m/z (%): 147 (M^+ , 100), 92 (87), 76 (72), 64 (52).

7-bromobenzo[*d*][1,2,3]triazin-4(*3H*)-one (2b) (CAS Number: 1802389-79-2)[1]



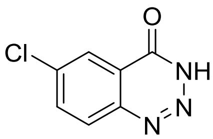
White solid (59 mg, 87% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.08 (s, 1H), 8.39-8.40 (m, 1H), 8.09-8.12 (m, 1H), 8.03-8.05 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.1, 144.9, 135.4, 130.1, 128.7, 126.5, 119.3.

7-chlorobenzo[*d*][1,2,3]triazin-4(*3H*)-one (2c) (CAS Number: 36772-63-1)[1]



White solid (47 mg, 86% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.10 (s, 1H), 8.27 (d, *J* = 1.8 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.92 (dd, *J* = 8.5, 1.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.9, 144.9, 139.8, 132.6, 127.0, 126.5, 119.0.

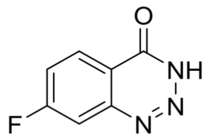
6-chlorobenzo[*d*][1,2,3]triazin-4(*3H*)-one (2d) (CAS Number: 37429-97-3)



White solid (45 mg, 83% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.09 (s, 1H), 8.19 (d, *J* = 8.7 Hz, 1H), 8.15 (s, 1H), 8.09 (d, *J* = 8.7Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.5, 142.7, 136.9, 135.5, 130.1, 123.4, 121.6; LRMS (EI 70 ev) m/z

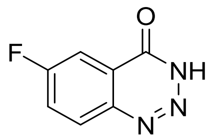
(%): 181 (M^+ , 88), 138 (84), 110 (86), 75 (100).

7-fluorobenzo[*d*][1,2,3]triazin-4(*3H*)-one (2e) (CAS Number: 1436850-60-0)[1]



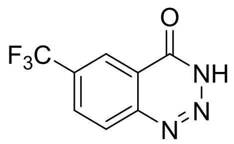
White solid (42 mg, 85% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.04 (s, 1H), 7.75-8.28 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 165.5 (d, J = 251.3 Hz), 154.8, 145.9 (d, J = 11.7 Hz), 127. 7 (d, J = 10.2 Hz), 121.0 (d, J = 23.7 Hz), 117.3 (d, J = 2.1 Hz), 113.0 (d, J = 22.6 Hz); ^{19}F NMR (470 MHz, DMSO-d_6) δ -101.7 (s, 1F).

6-fluorobenzo[*d*][1,2,3]triazin-4(*3H*)-one (2f) (CAS Number: 1008742-31-1)



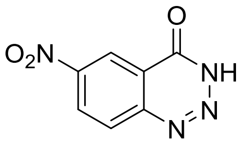
White solid (39 mg, 79% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 15.04 (s, 1H), 8.26-8.29 (dd, J = 8.9, 4.9 Hz, 1H), 7.88-7.97 (m, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 163.1 (d, J = 252.0 Hz), 154.9 (d, J = 3.1 Hz), 141.4 (d, J = 2.1 Hz), 131.5 (d, J = 9.3 Hz), 123.9 (d, J = 24.2 Hz), 122.3 (d, J = 9.5 Hz), 109.4 (d, J = 23.9 Hz). ^{19}F NMR (470 MHz, DMSO-d_6) δ -104.0 (s, 1F); LRMS (EI 70 ev) m/z (%): 165(M^+ , 61), 122 (65), 94 (100), 82 (51).

6-(trifluoromethyl)benzo[*d*][1,2,3]triazin-4(*3H*)-one (2g) (CAS Number: 1802389-77-0)[2]



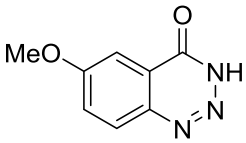
Yellow solid (58.7 mg, 91% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.28 (s, 1H), 8.41 (s, 1H), 8.36 (s, 2H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.7 145.6, 131.5 (q, J = 32.9 Hz), 131.4, 129.4, 123.0 (q, J = 271.2 Hz), 121.8 (q, J = 3.9 Hz), 120.7; ^{19}F NMR (470 MHz, DMSO-d_6) δ -61.6 (s, 3F).

6-nitrobenzo[*d*][1,2,3]triazin-4(*3H*)-one (2h) (CAS Number: 91532-29-5)[2]



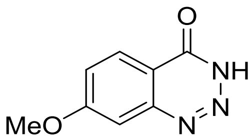
Yellow solid (46.7 mg, 81% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 15.43 (s, 0.9H), 8.81 (d, *J* = 2.4 Hz, 1H), 8.77 (dd, *J* = 8.9, 2.5 Hz, 1H), 8.42 (d, *J* = 8.9 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.7, 148.4, 146.3, 130.1, 129.2, 121.0, 120.2.

6-methoxybenzo[*d*][1,2,3]triazin-4(*3H*)-one (2i)



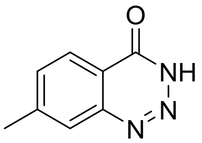
White solid (38.8 mg, 73% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 14.75 (s, 1H), 8.09 (d, *J* = 8.9 Hz, 1H), 7.59 (dd, *J* = 8.9, 1.2 Hz, 1H), 7.53 (s, 1H), 3.95 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 161.8, 155.5, 139.2, 130.0, 124.3, 121.9, 104.1, 56.1.

7-methoxybenzo[*d*][1,2,3]triazin-4(*3H*)-one (2j) (CAS Number: 41994-97-2)[2]



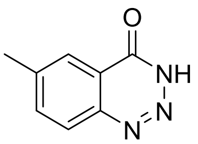
White solid (40.9 mg, 77% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 14.82 (s, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 7.58 (s, 1H), 7.44 (dd, *J* = 8.8, 1.5 Hz, 1H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 164.3, 155.1, 146.3, 126.0, 121.7, 113.5, 108.6, 56.1.

7-methylbenzo[*d*][1,2,3]triazin-4(*3H*)-one (2k) (CAS Number: 176260-30-3)[2]



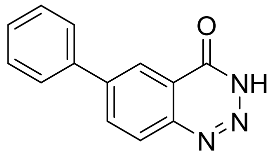
White solid (40.5 mg, 84% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 14.86 (s, 1H), 8.07 (d, *J* = 6.4 H, 1H), 7.94 (s, 1H), 7.69 (d, *J* = 6.3 Hz, 1H), 2.53 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.4, 146.3, 144.3, 133.7, 127.2, 124.0, 117.7, 21.3.

6-methylbenzo[*d*][1,2,3]triazin-4(*3H*)-one (2l) (CAS Number: 91532-23-9)[1]



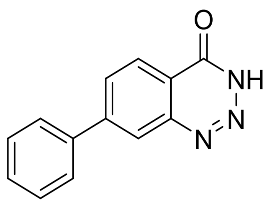
White solid (39.6 mg, 82% yield). ^{1}H NMR (400 MHz, CD_3OD) δ 8.11 (s, 1H), 8.08 (d, J = 8.4 Hz, 1H), 7.92 (dd, J = 8.4, 1.7 Hz, 1H), 2.62 (s, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.4, 143.1, 142.4, 136.4, 127.6, 123.4, 129.9, 21.1.

6-phenylbenzo[*d*][1,2,3]triazin-4(*3H*)-one (2m) (CAS Number: 2230125-77-4)[3]



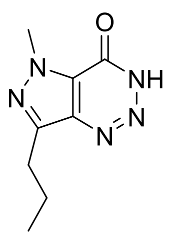
White solid (52.2 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 14.99 (s, 1H), 8.37-8.39 (m, 2H), 8.24-8.26 (m, 1H), 7.84-7.86 (d, J = 7.6 Hz, 2H), 7.47-7.56 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.6, 143.7, 143.3, 137.8, 133.7, 129.3, 128.9, 128.6, 127.3, 121.3, 120.7.

7-phenylbenzo[*d*][1,2,3]triazin-4(*3H*)-one (2n) (CAS Number: 2247157-26-0)[2]



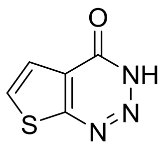
White solid (55.5 mg, 83% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 14.95 (s, 1H), 8.41 (s, 1H), 8.19-8.27 (m, 2H), 7.88 (d, J = 7.6 Hz, 2H), 7.48-7.57 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 155.3, 146.8, 144.7, 137.8, 130.8, 129.2, 129.0, 127.3, 125.1, 125.0, 118.9.

5-methyl-7-propyl-3,5-dihydro-4H-pyrazolo[4,3-*d*][1,2,3]triazin-4-one (2o) (CAS Number: 1357091-38-3)



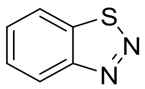
White solid (56.2 mg, 97% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 14.83 (s, 1H), 4.15-4.17 (m, 3H), 2.90-2.93 (m, 2H), 1.76-1.83 (m, 2H), 0.93-0.96 (m, 3H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 150.5, 146.5, 135.4, 124.9, 38.2, 27.2, 21.5, 13.6; LRMS (EI 70 ev) m/z (%): 193 (M^+ , 46), 165 (60), 121 (59), 81 (100).

Thieno[2,3-*d*][1,2,3]triazin-4(*3H*)-one (2p) (CAS Number: 38371-44-7)[4]



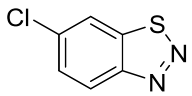
Yellow solid (35.8 mg, 78% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 15.22 (s, 1H), 8.38 (d, *J* = 5.3 Hz, 1H), 7.84 (d, *J* = 5.3 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 154.1, 153.6, 136.6, 126.2, 124.6.

Benzo[*d*][1,2,3]thiadiazole (4a) (CAS Number: 273-77-8)[5]



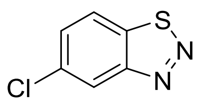
Yellow solid (39.2 mg, 96% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.69 (d, *J* = 8.3Hz, 1H), 8.41 (d, *J* = 8.2Hz, 1H), 7.78-7.81(m, 1H), 7.72-7.75 (m, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 157.7, 140.3, 129.4, 127.3, 123.3, 120.3.

6-chlorobenzo[*d*][1,2,3]thiadiazole (4b) (CAS Number: 23644-01-1)[6]



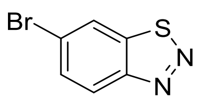
Yellow solid (44.4 mg, 87% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.70 (d, *J* = 8.9 Hz, 1H), 8.55 (d, *J* = 1.9 Hz, 1H), 7.77 (dd, *J* = 8.9, 1.8 Hz, 1H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 156.4, 141.9, 135.0, 128.1, 124.5, 120.1.

5-chlorobenzo[*d*][1,2,3]thiadiazole (4c) (CAS Number: 29241-15-4)



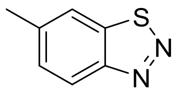
White solid (46.4 mg, 91% yield). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.84 (d, *J* = 1.5 Hz, 1H), 8.44 (d, *J* = 8.7 Hz, 1H), 7.85 (dd, *J* = 8.7, 1.7 Hz, 1H);^{13}C NMR (125 MHz, DMSO-d_6) δ 158.4, 139.3, 132.2, 129.7, 122.5, 122.0; LRMS (EI 70 ev) m/z (%): 170 (M^+ , 40), 142 (100), 107 (57), 69 (38).

6-bromobenzo[*d*][1,2,3]thiadiazole (4d) (CAS Number: 31860-02-3)



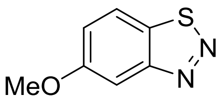
White solid (71 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 8.9 Hz, 1H), 8.24 (s, 1H), 7.71 (dd, *J* = 8.8, 0.8 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 142.5, 130.6, 124.9, 124.7,121.7; LRMS (EI 70 ev) m/z (%): 216/214 (M^+ , 48), 188/186 (66), 107 (100), 63 (66).

6-methylbenzo[*d*][1,2,3]thiadiazole (4e) (CAS Number: 53034-68-7)[5]



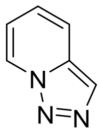
White solid (37.8 mg, 84% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 8.5 Hz, 1H), 7.85 (s, 1H), 7.43 (d, *J* = 8.4Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.1, 141.5, 140.1, 128.8, 123.3, 118.3, 21.7.

5-methoxybenzo[*d*][1,2,3]thiadiazole (4f) (CAS Number: 31860-05-6)



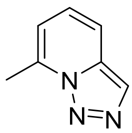
Yellow solid (40.3 mg, 81% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.43 (d, *J* = 9.2 Hz, 1H), 7.40 (d, *J* = 1.9 Hz, 1H), 7.20 (dd, *J* = 9.1, 1.9 Hz, 1H), 3.92 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.9, 153.8, 143.4, 124.3, 118.2, 99.5, 56.0; LRMS (EI 70 ev) m/z (%): 166 (M^+ , 52), 123 (100), 95 (39), 69 (29).

[1,2,3]triazolo[1,5-*a*]pyridine (6a) (CAS Number: 274-59-9)[7]



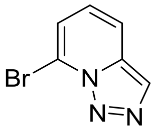
Orange oil (28.6 mg, 80% yield). ^{1}H NMR (500 MHz, DMSO) δ 9.07 (d, *J* = 7Hz, 1H), 8.20 (s, 1H), 7.95 (d, 8.9 Hz, 1H), 7.37-7.40 (m, 1H), 7.14-7.17 (m, 1H); ^{13}C NMR (125 MHz, DMSO) δ 133.3, 125.7, 125.4, 125.3, 118.0, 115.7.

7-methyl-[1,2,3]triazolo[1,5-*a*]pyridine (6b) (CAS Number: 78539-91-0)[8]



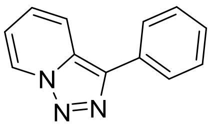
Yellow solid (23.9 mg, 60% yield). ^{1}H NMR (500 MHz, DMSO) δ 8.24 (s, 1H), 7.85 (d, *J* = 10Hz, 1H), 7.33-7.36 (m, 1H), 7.03-7.04 (m, 1H), 2.81 (s, 3H); ^{13}C NMR (125 MHz, DMSO) δ 135.1, 133.6, 125.8, 125.6, 115.5, 114.3, 16.8.

7-bromo-[1,2,3]triazolo[1,5-*a*]pyridine (6c) (CAS Number: 107465-26-9)[9]



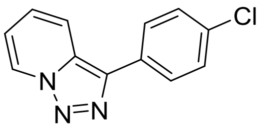
White solid (34.3 mg, 58% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (s, 1H), 7.78 (d, J = 8.7Hz, 1H), 7.27 (d, J = 6.9Hz, 1H), 7.17-7.21 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.2, 127.2, 125.8, 119.4, 116.9, 115.2.

3-phenyl-[1,2,3]triazolo[1,5-*a*]pyridine (6e) (CAS Number: 832-81-5)



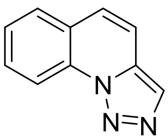
White solid (24.6 mg, 42% yield). ^{1}H NMR (400 MHz, DMSO) δ 9.12 (d, J = 7.0Hz, 1H), 8.27 (d, J = 9.0 Hz, 1H), 7.99-8.02 (m, 2H), 7.48-7.55 (m, 3H), 7.38-7.42 (m, 1H), 7.21-7.25 (m, 1H) ; ^{13}C NMR (125 MHz, DMSO) δ 136.3, 131.1, 129.8, 129.0, 127.6, 126.8, 126.0, 126.0, 118.2, 116.0. HRMS (ESI): calculated for $C_{12}H_9N_3Na$ $[M+Na]^+$ 218.0694, found 218.0721.

3-(4-chlorophenyl)-[1,2,3]triazolo[1,5-*a*]pyridine (6f) (CAS Number: 78539-93-2)



Yellow solid (17.2 mg, 25% yield). ^{1}H NMR (500 MHz, DMSO) δ 9.13 (d, J = 6.8Hz, 1H), 8.25-8.27 (m, 1H), 8.02-8.03 (m, 2H), 7.50-7.58 (m, 3H), 7.23-7.25 (m, 1H) ; ^{13}C NMR (125 MHz, DMSO) δ 135.2, 132.1, 130.0, 129.8, 129.0, 127.6, 127.1, 126.1, 118.1, 116.2. HRMS (ESI): calculated for $C_{12}H_8ClN_3Na$ $[M+Na]^+$ 252.0304, found 252.0313.

[1,2,3]triazolo[1,5-*a*]quinoline (6g) (CAS Number: 235-21-2)[8]



White solid (23.3 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 7.83-7.85 (m, 1H), 7.74-7.78 (m, 1H), 7.50-7.62 (m, 3H); ^{13}C NMR

(125 MHz, $CDCl_3$) δ 131.9, 131.7, 130.0, 128.5, 127.5, 127.1, 126.6, 123.9, 116.3 114.7.

Reference:

(1) Gaolei, W.; Xiulei, C.; Yayun, D.; Zhong, Li.; Xiaoyong X. *J. Agric. Food Chem*. 2015, **63**, 6883-6889

(2) Yao, Z.; Ya, W.; Yixian, L.; Qiuling, S. *Org. Lett.*, 2018, **20**, 6494-6497.

(3) Yasser A, Selim.; Mohamed, A.; Ahmed F, E. *J. Heterocyclic Chem*., 2018, **55**, 1756-1764.

(4) Kasina, S.; Gokaraju, R.; Golakoti, T.; Somepalli, V.; Krishanu, S.; Bhupathiraju, K. PCT Int. Appl., 2010029577, 2010.

(5) Michael, K.; Carl F., N.; Maarten, S.; Kerstin, K.; Stefan, B. *Org. Biomol. Chem.*, 2005, **3**, 1835-1837.

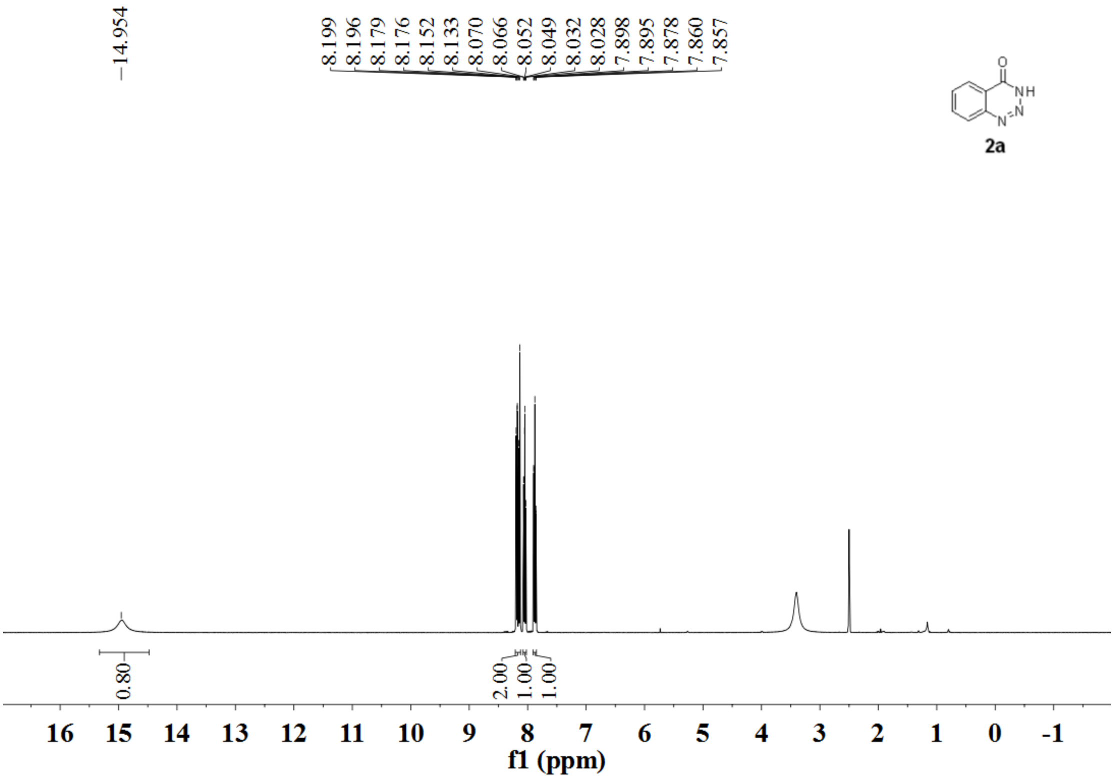
(6) Wilkins, J.; Bradley, A. *Science of Synthesis*, 2004, **13**, 253-275.

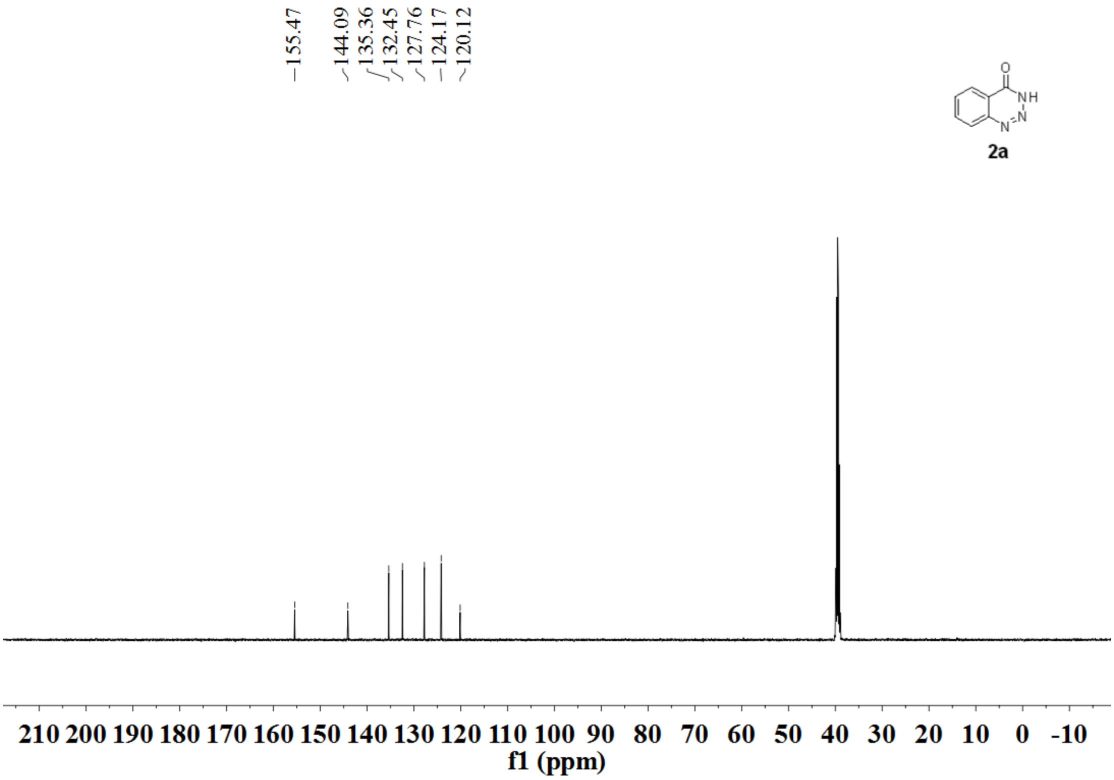
(7) Satyajit, R.; Sandip, D.; Buddhadeb, C. *Angew. Chem. Int. Ed.* 2018, **57**, 2238 -2243.

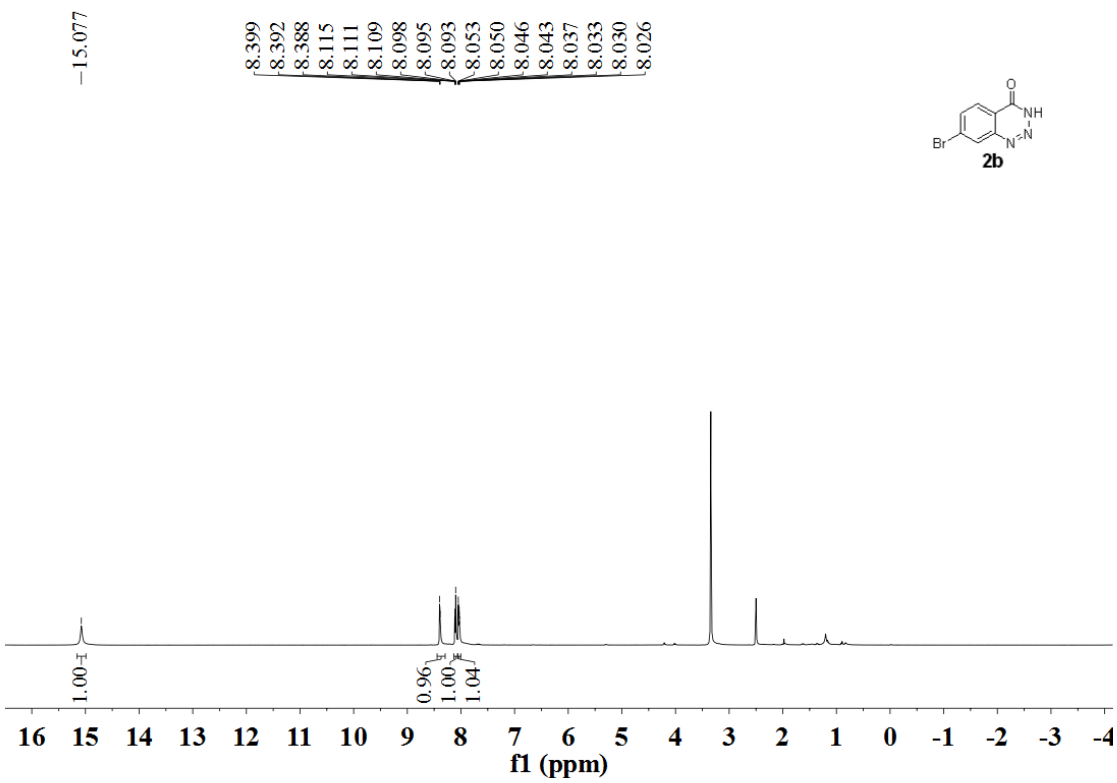
(8) Sreekumar, P.; ZhiGuang, C.; Rakesh, G.; Teck, L. *Chem. Commun.*, 2015, **51**, 5929-5931.

(9) Belen, A.; Rafael, B.; Gurnos, J.; Fatemeh, M. *Tetrahedron Letters*, 1986, **30**, 3543-3546.

6. NMR spectra



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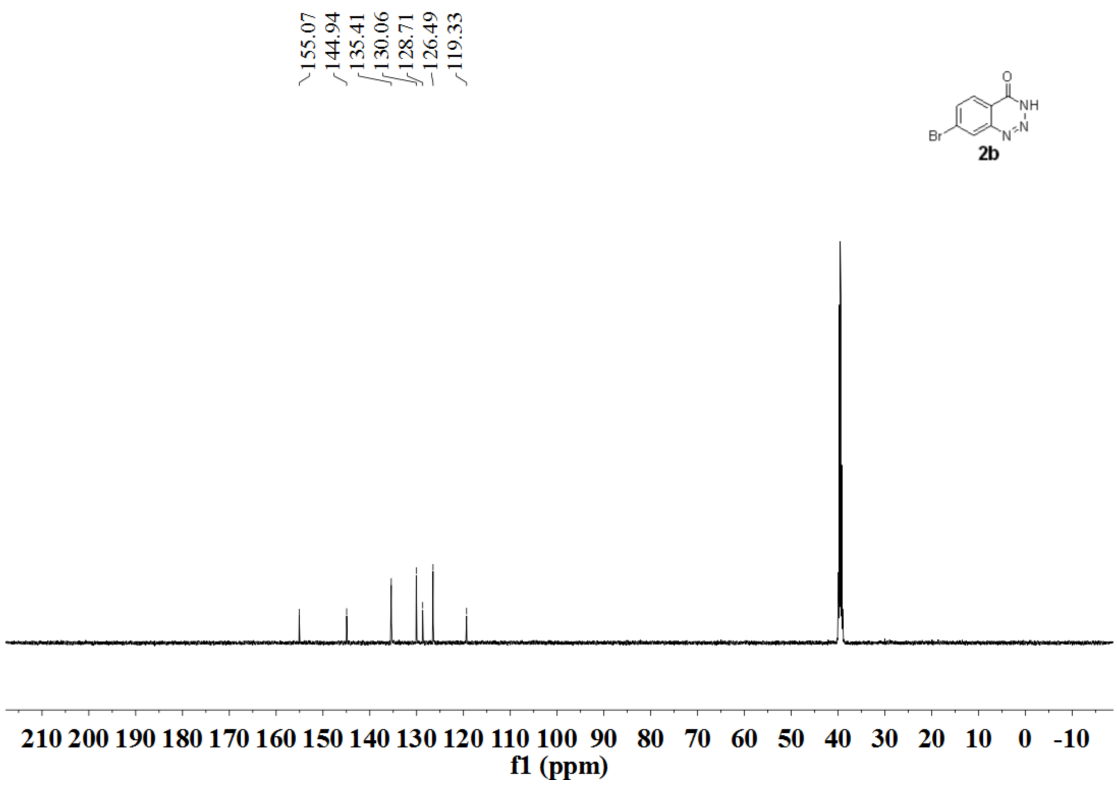
8.388
8.115
8.111
8.109
8.098
8.095
8.093
8.053
8.050
8.046
8.043
8.037
8.033
8.030
8.026
NH
N
N
Br
2b
1.00
0.96
1.00
1.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4
f1 (ppm)


155.07
144.94
135.41
130.06
128.71
126.49
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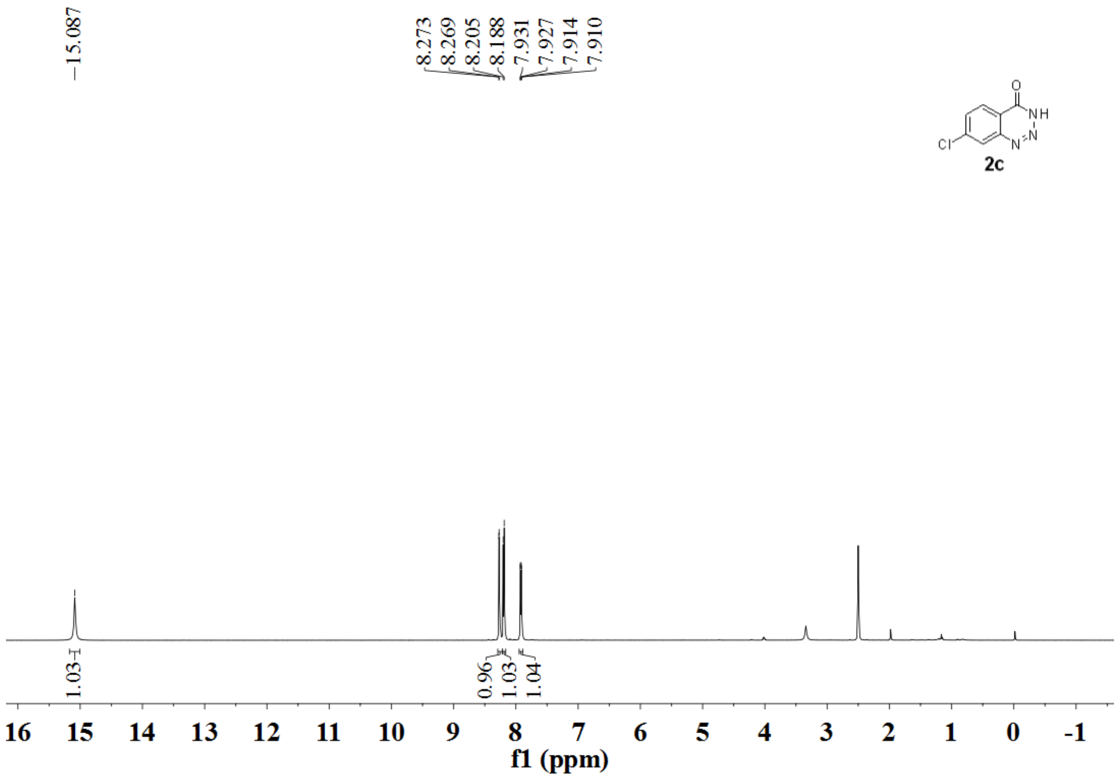
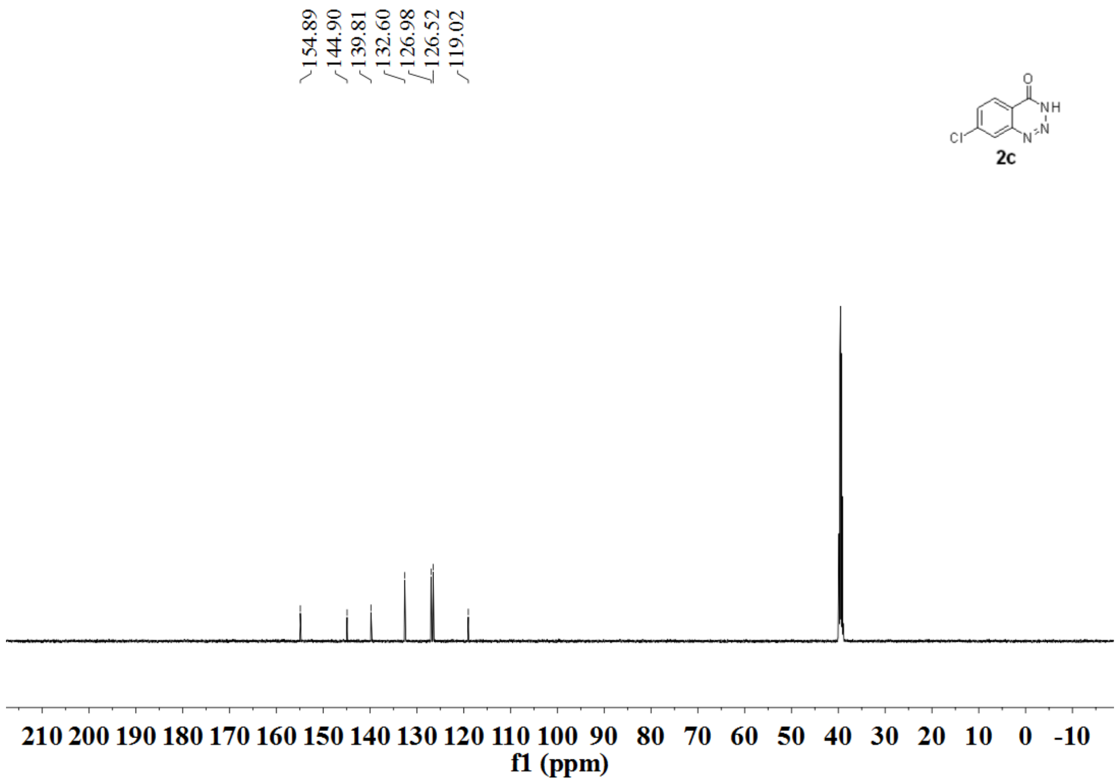
NH
N
N
Br
2b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



15.087
8.273
8.269
8.205
8.188
7.931
7.927
7.914
7.910
2c
1.03
0.96
1.03
1.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



154.89
144.90
139.81
132.60
126.98
126.52
119.02
2c
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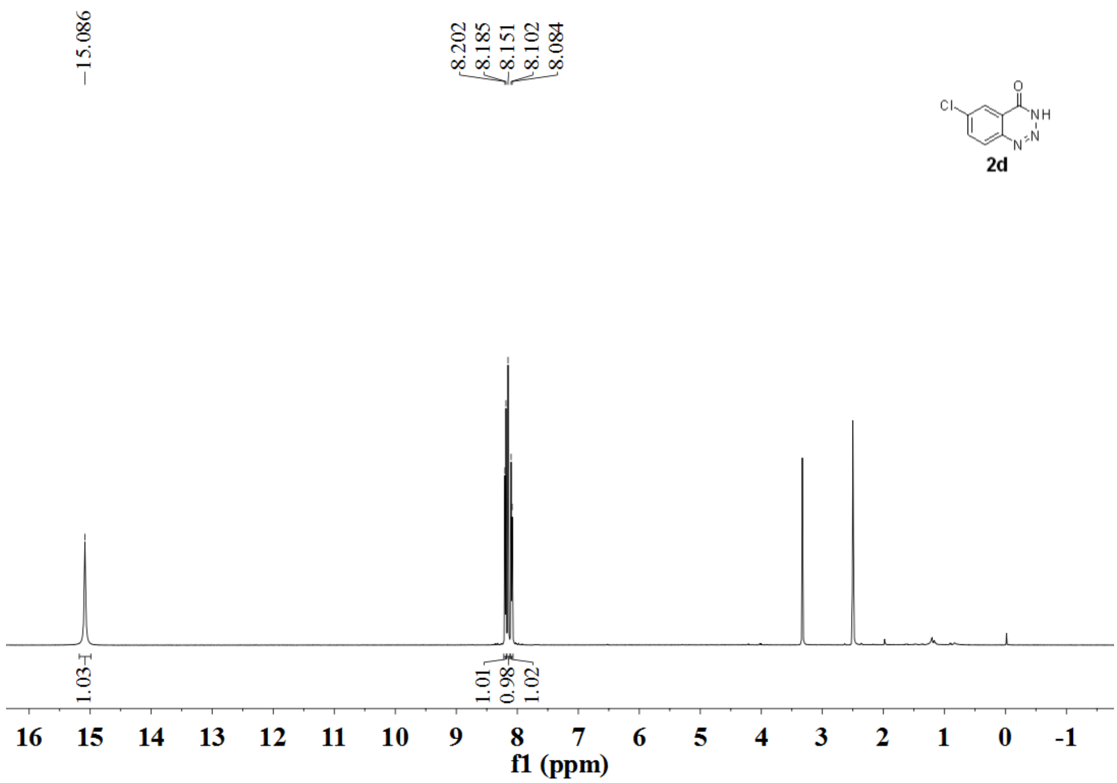
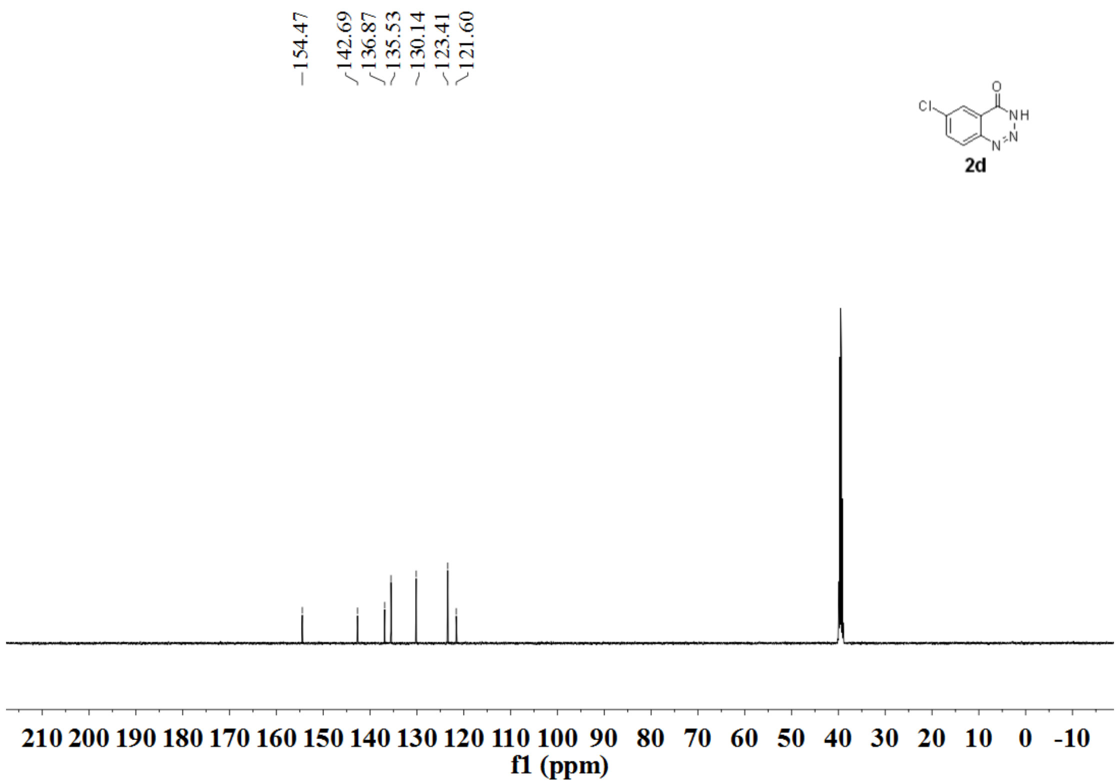
f1 (ppm)


15.086
8.202
8.185
8.151
8.102
8.084
2d
1.03
1.01
0.98
1.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


154.47
142.69
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2d
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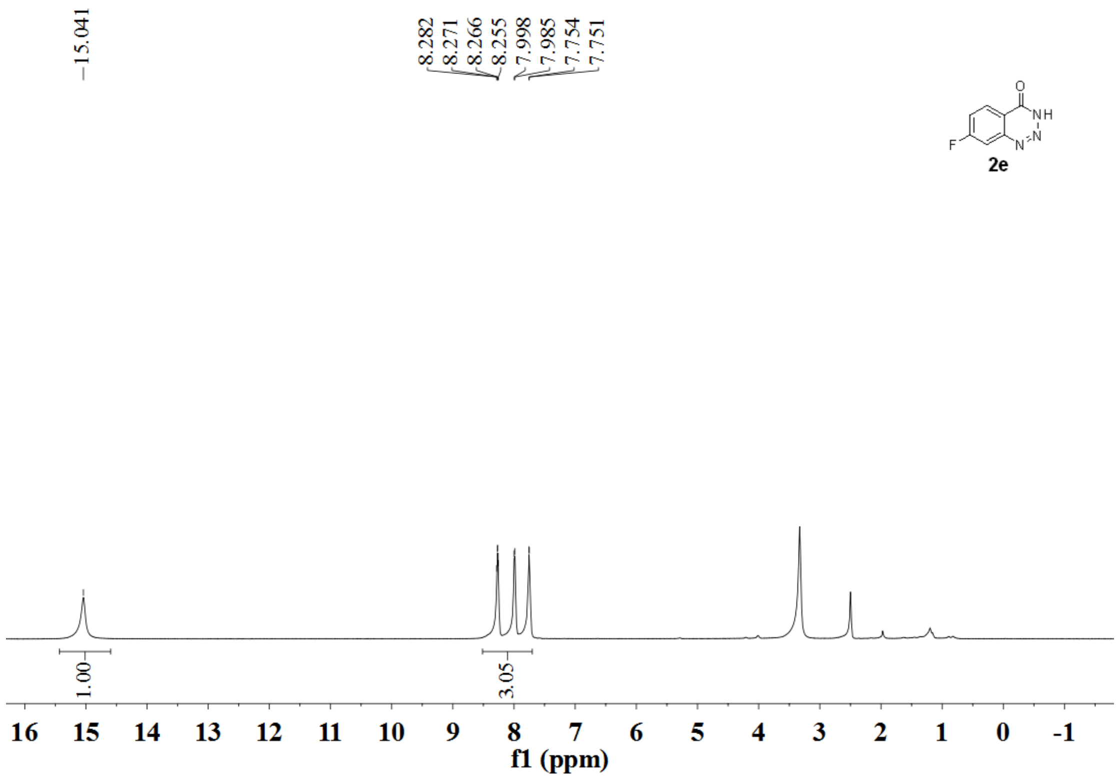
f1 (ppm)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8.255
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7.985
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7.751
2e
1.00
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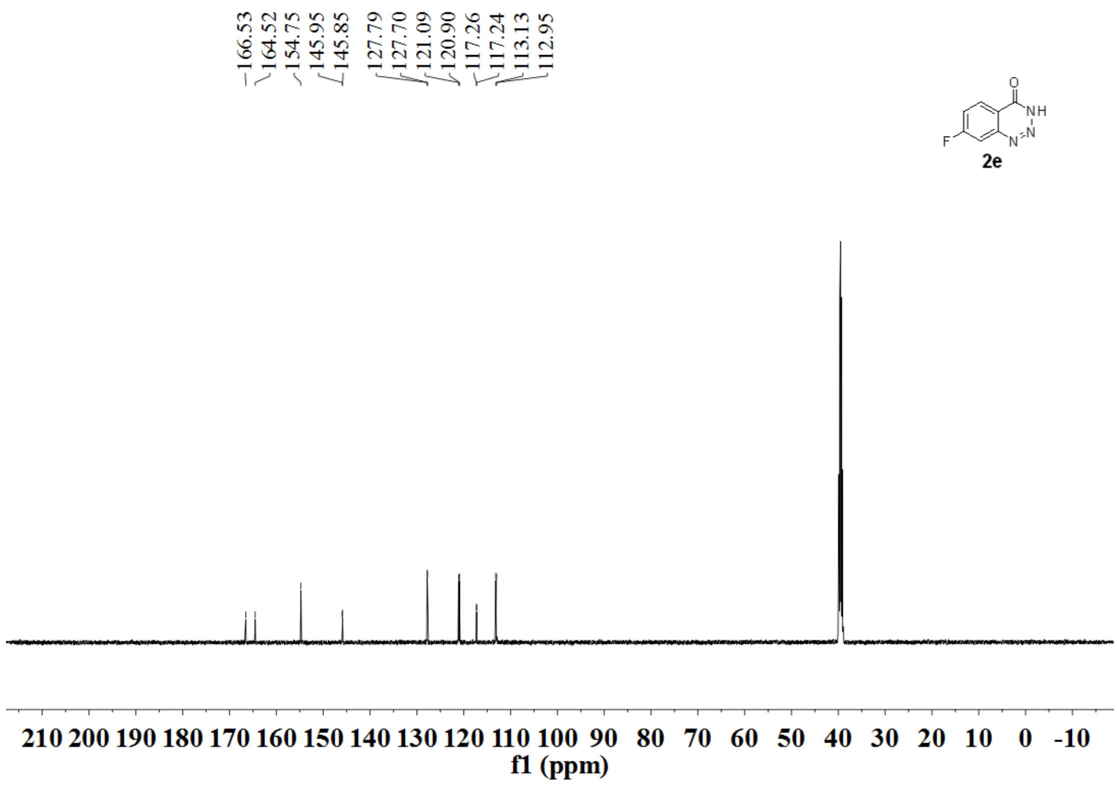
f1 (ppm)


166.53
164.52
154.75
145.95
145.85
127.79
127.70
121.09
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117.26
117.24
113.13
112.95
2e
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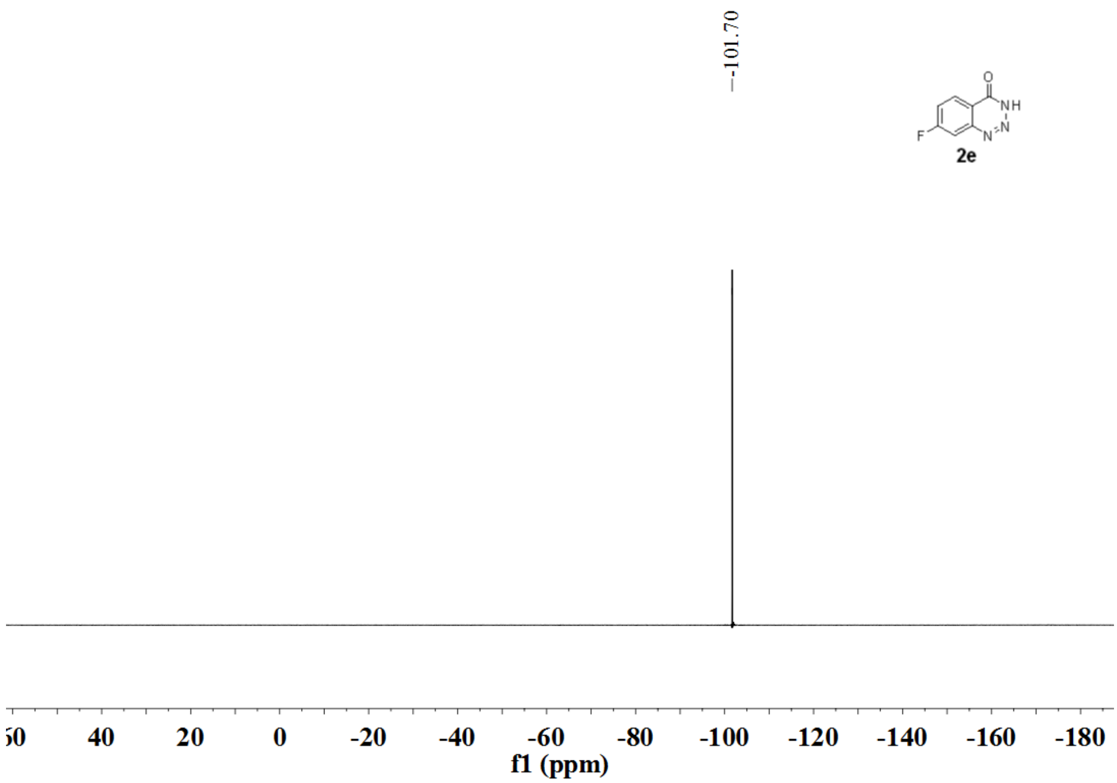
f1 (ppm)



-101.70
O
NH
N
N
F
2e
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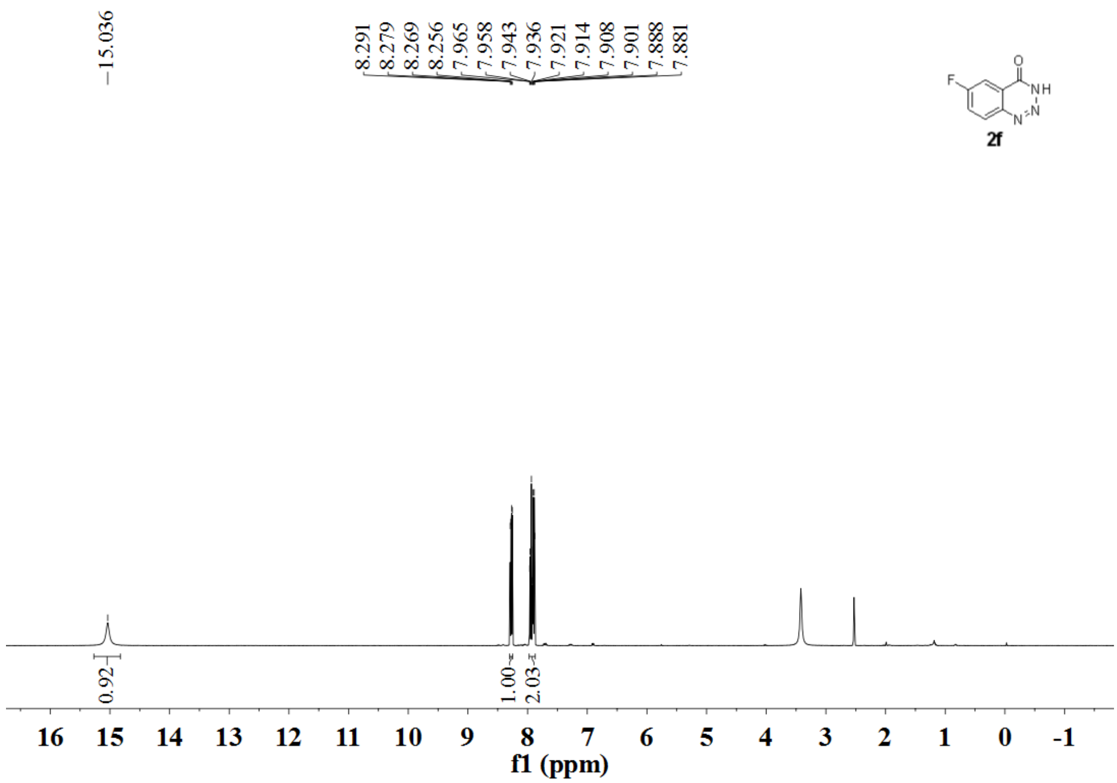
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)



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8.279
8.269
8.256
7.965
7.958
7.943
7.936
7.921
7.914
7.908
7.901
7.888
7.881
2f
0.92
1.00
2.03
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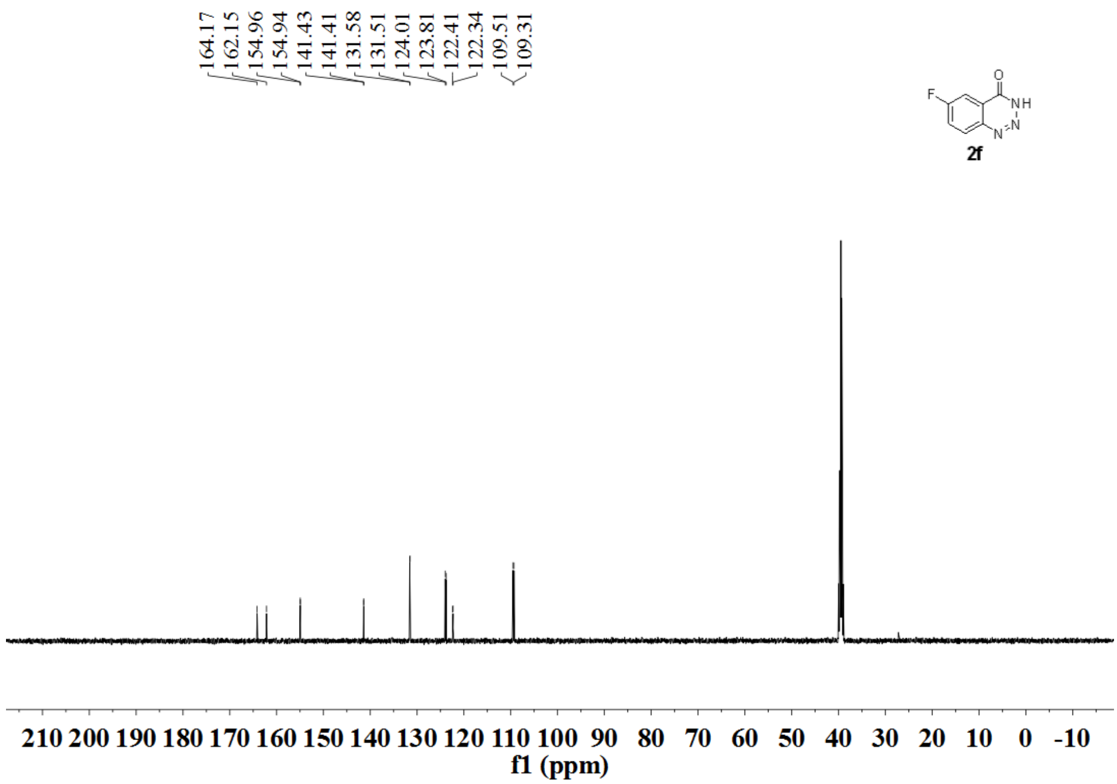
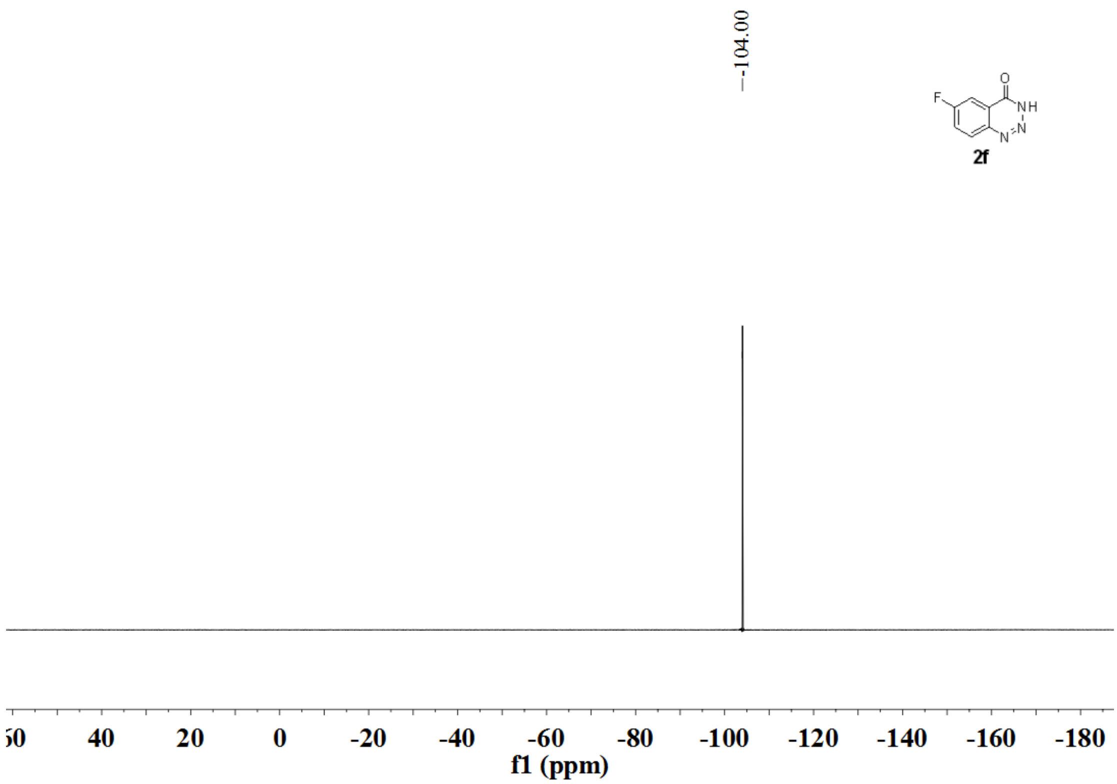
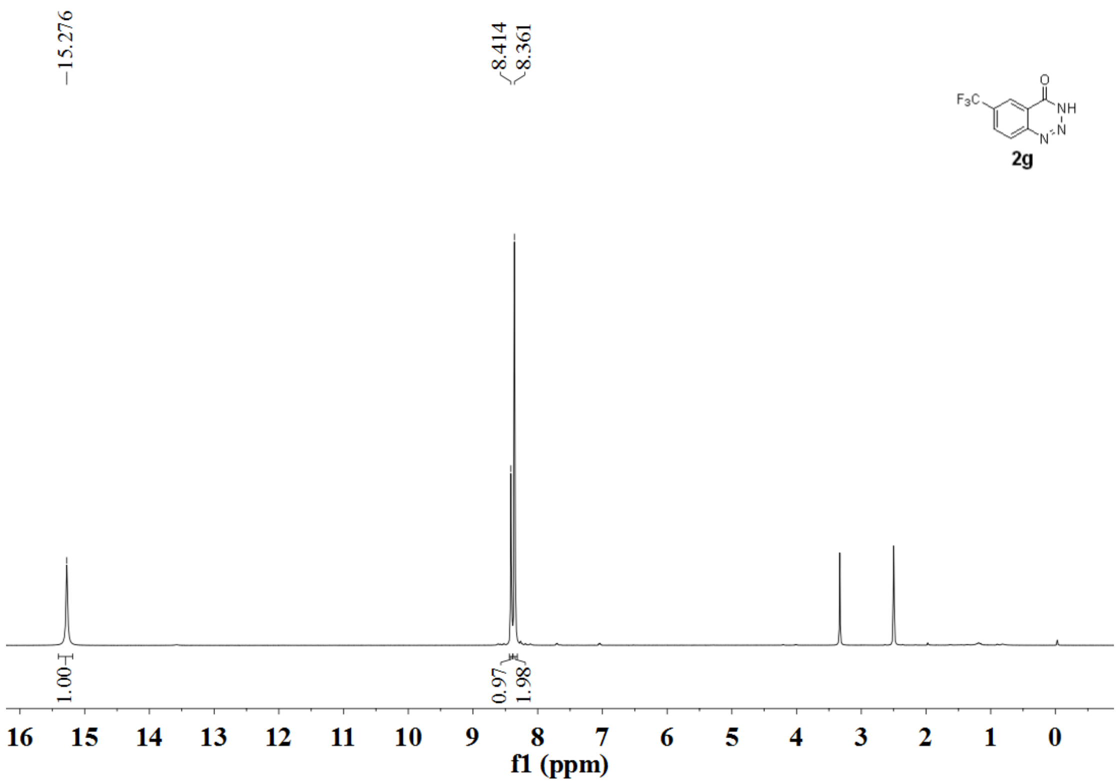
f1 (ppm)



164.17
162.15
154.96
154.94
141.43
141.41
131.58
131.51
124.01
123.81
122.41
122.34
109.51
109.31
2f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



2f



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8.361
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N
N
2g
1.00
0.97
1.98
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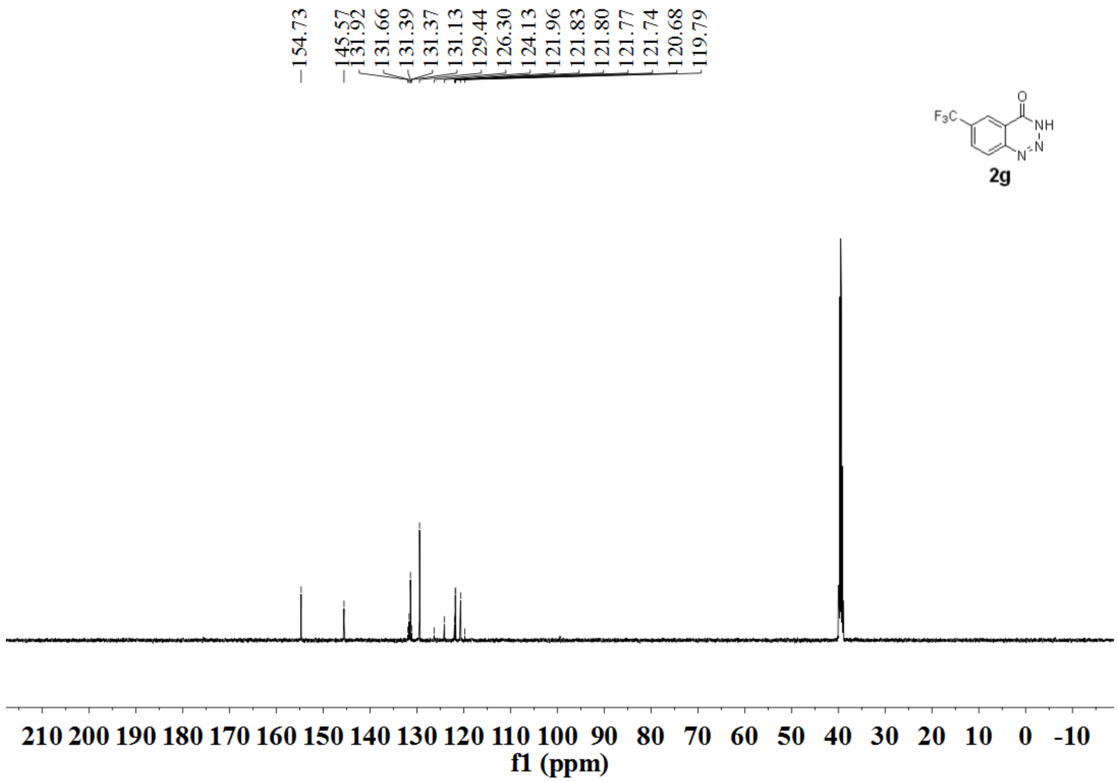
f1 (ppm)



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145.57
131.92
131.66
131.39
131.37
131.13
129.44
126.30
124.13
121.96
121.83
121.80
121.77
121.74
120.68
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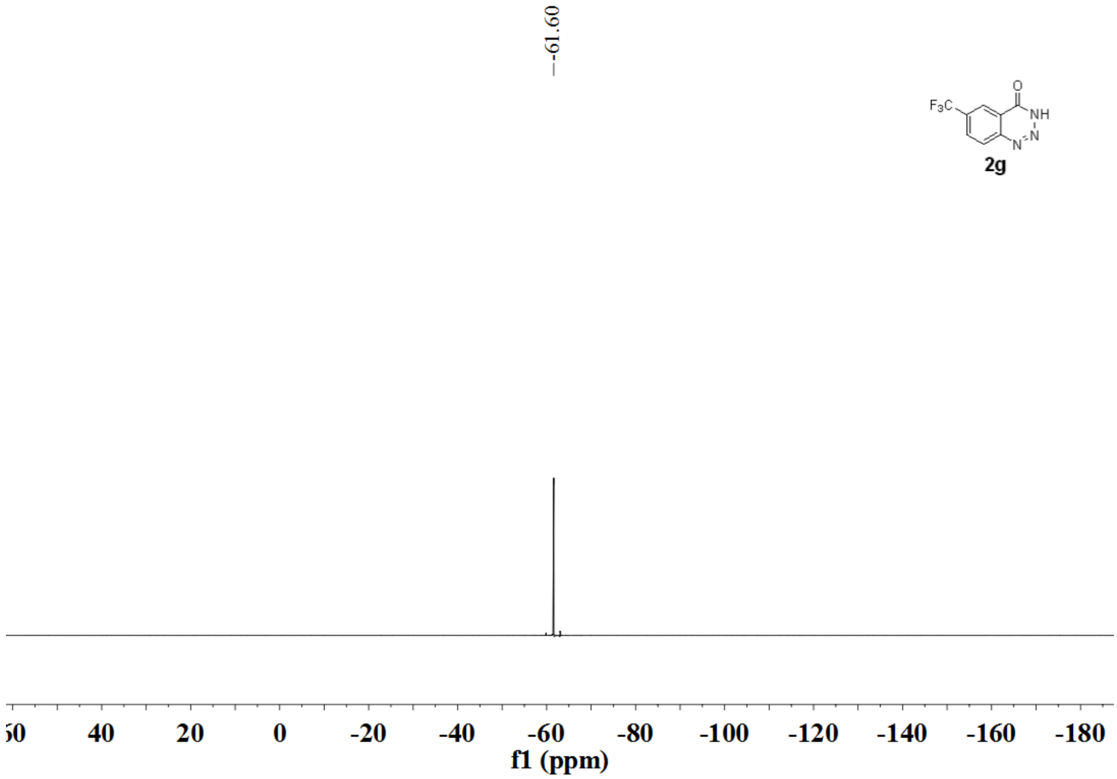
O
NH
N
N
2g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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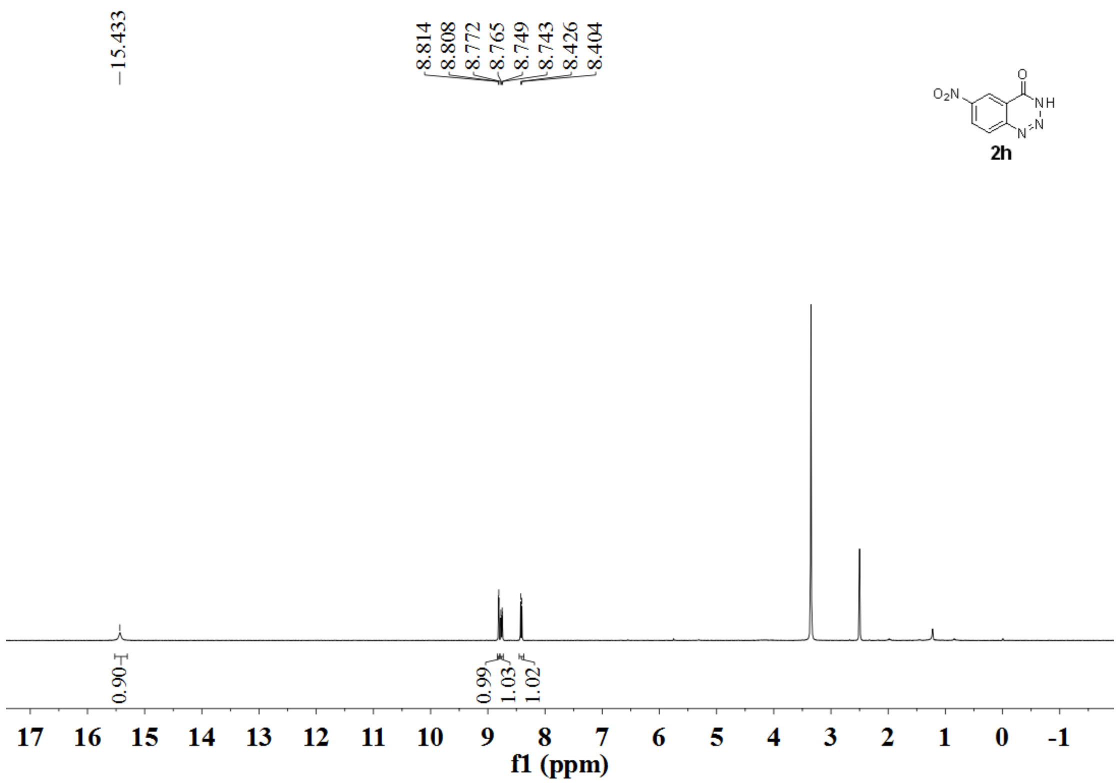
-180
f1 (ppm)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8.772
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O_2N
O
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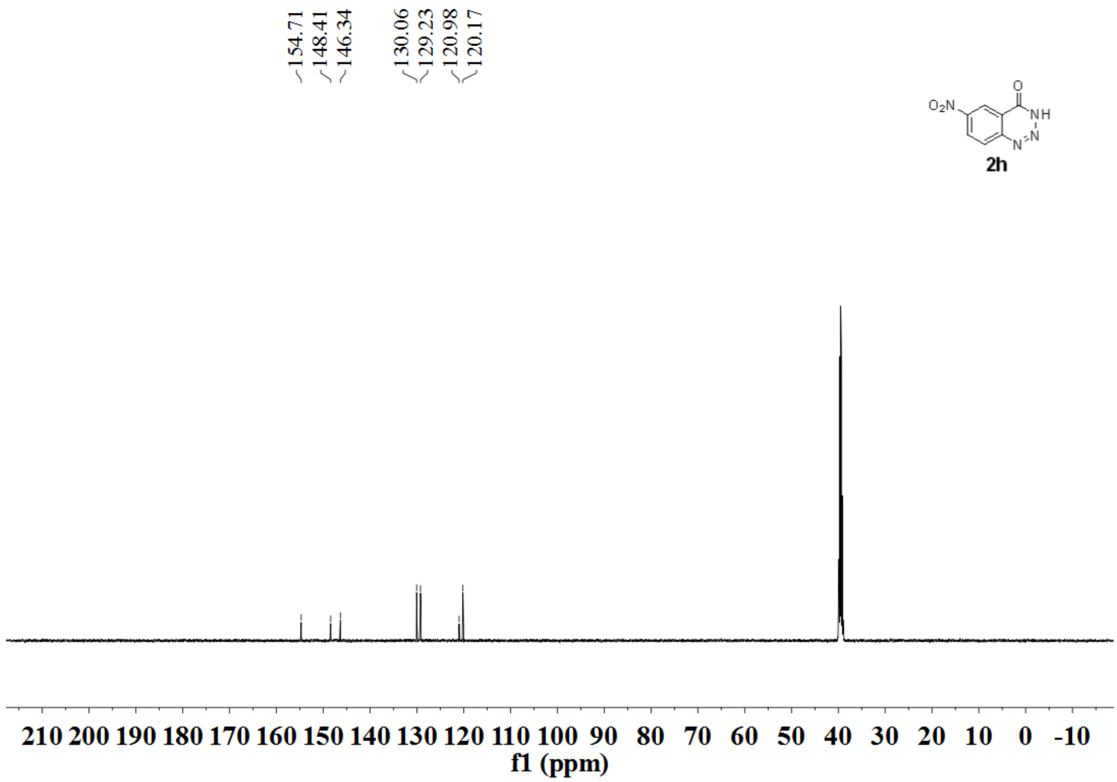
2h
0.90
0.99
1.03
1.02
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)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120.98
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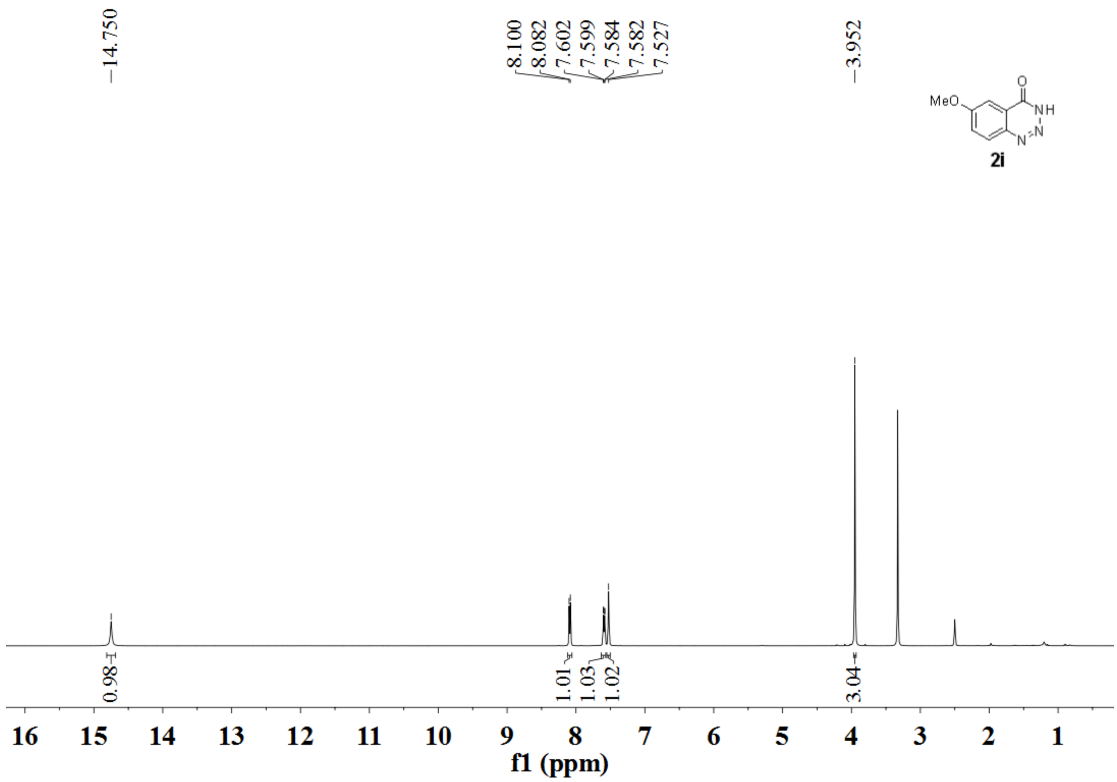
f1 (ppm)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MeO
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1.01
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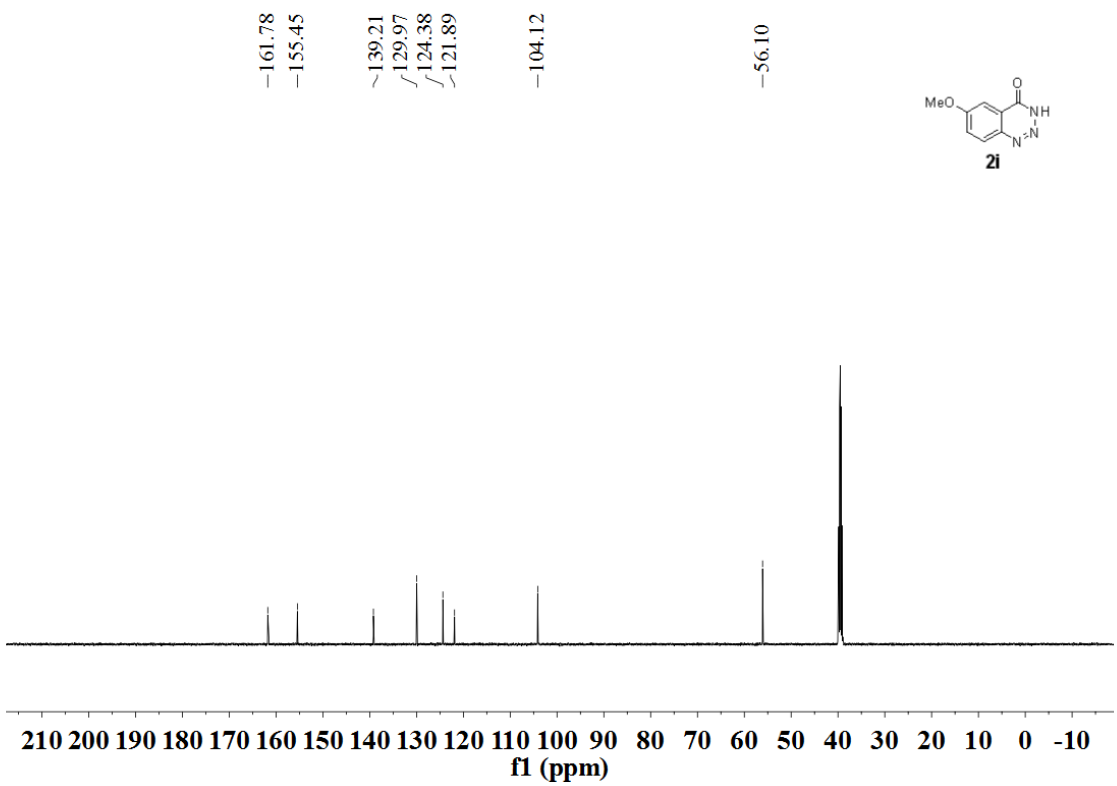
1.02
3.04
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1
f1 (ppm)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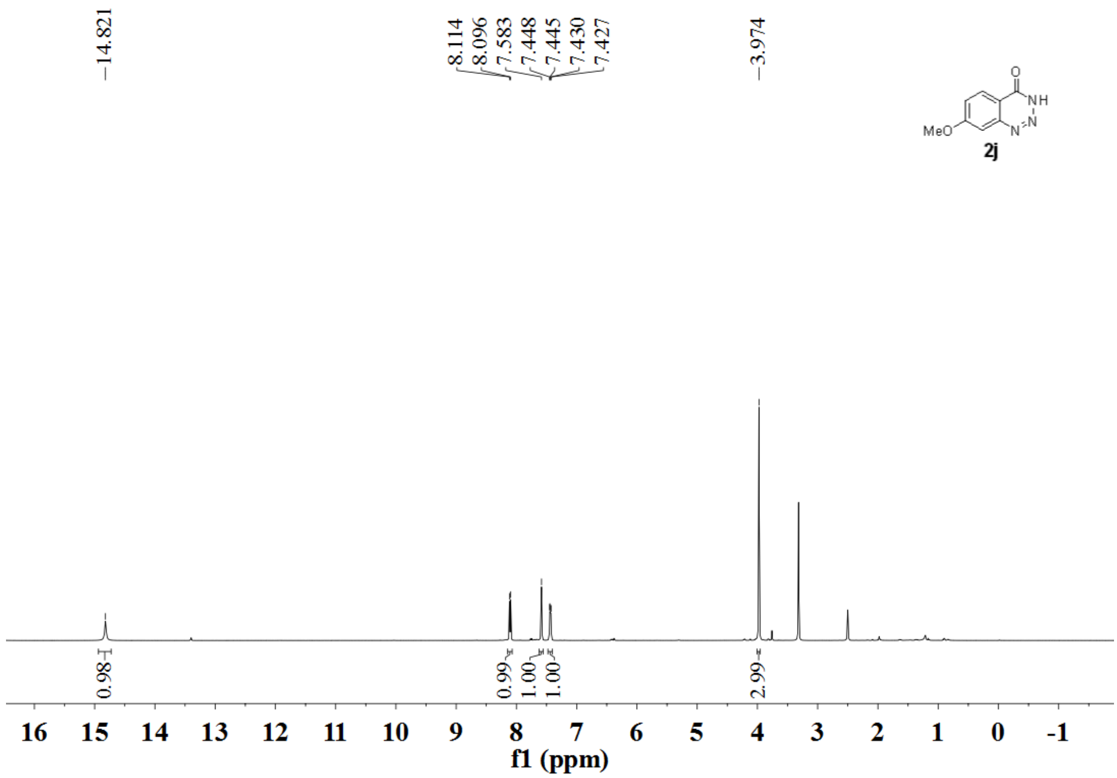
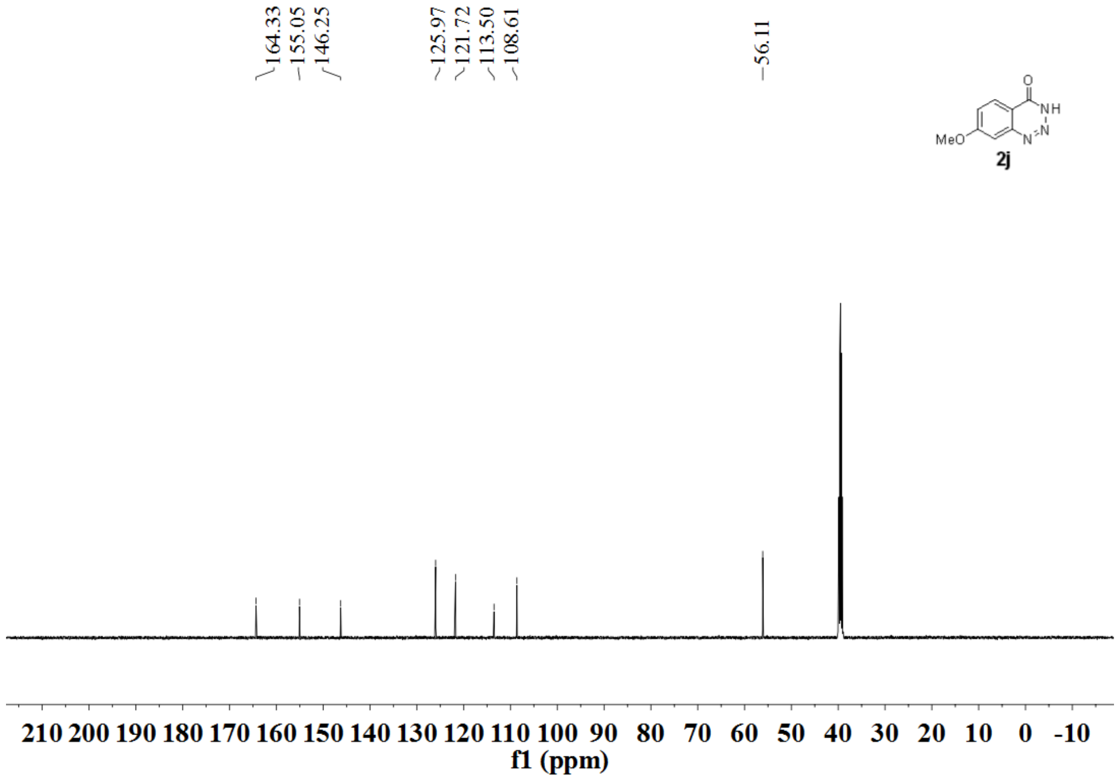
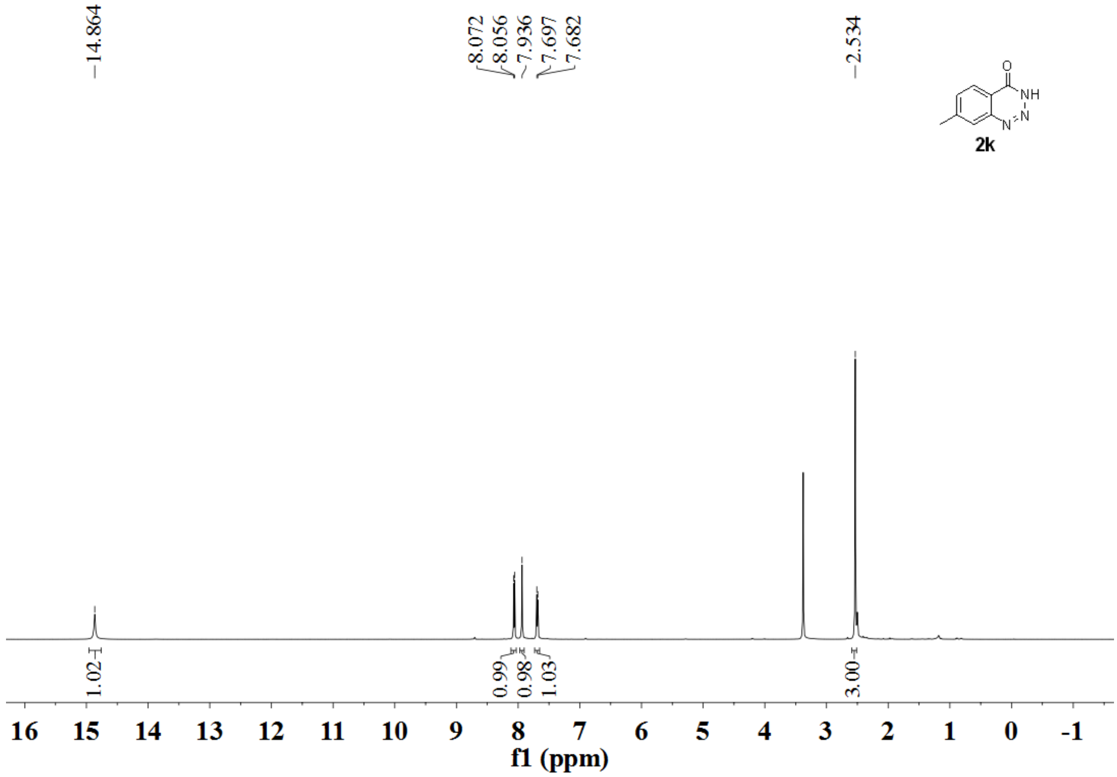
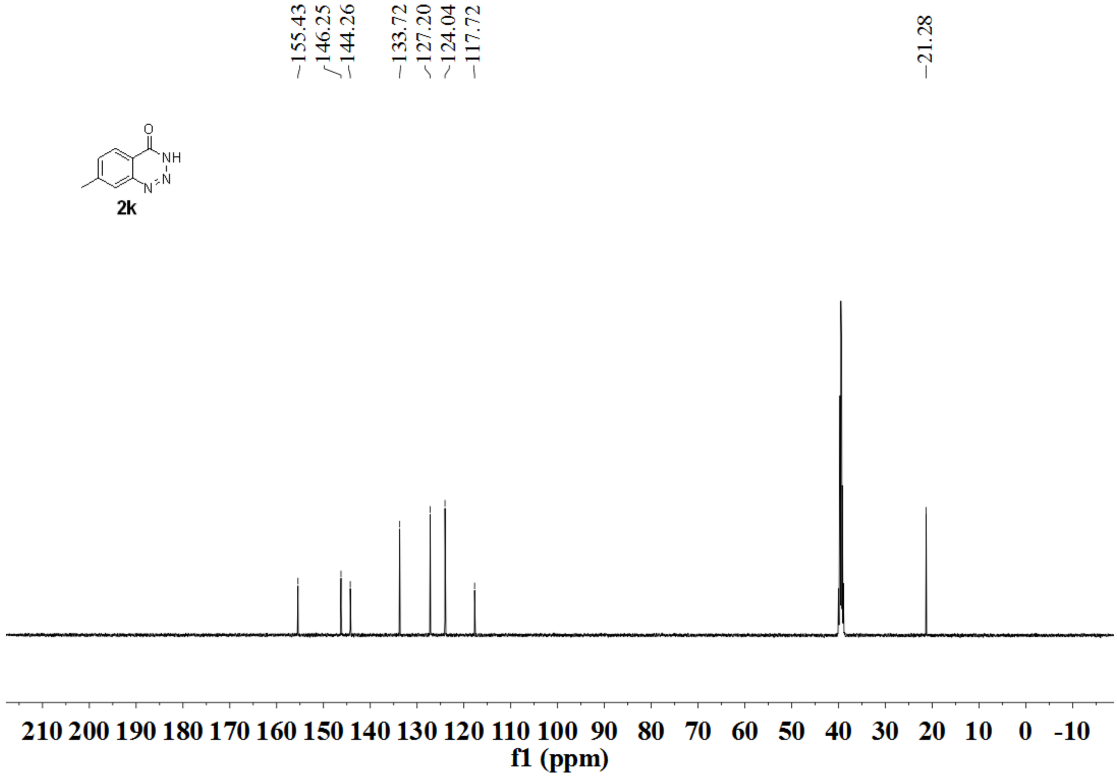
f1 (ppm)



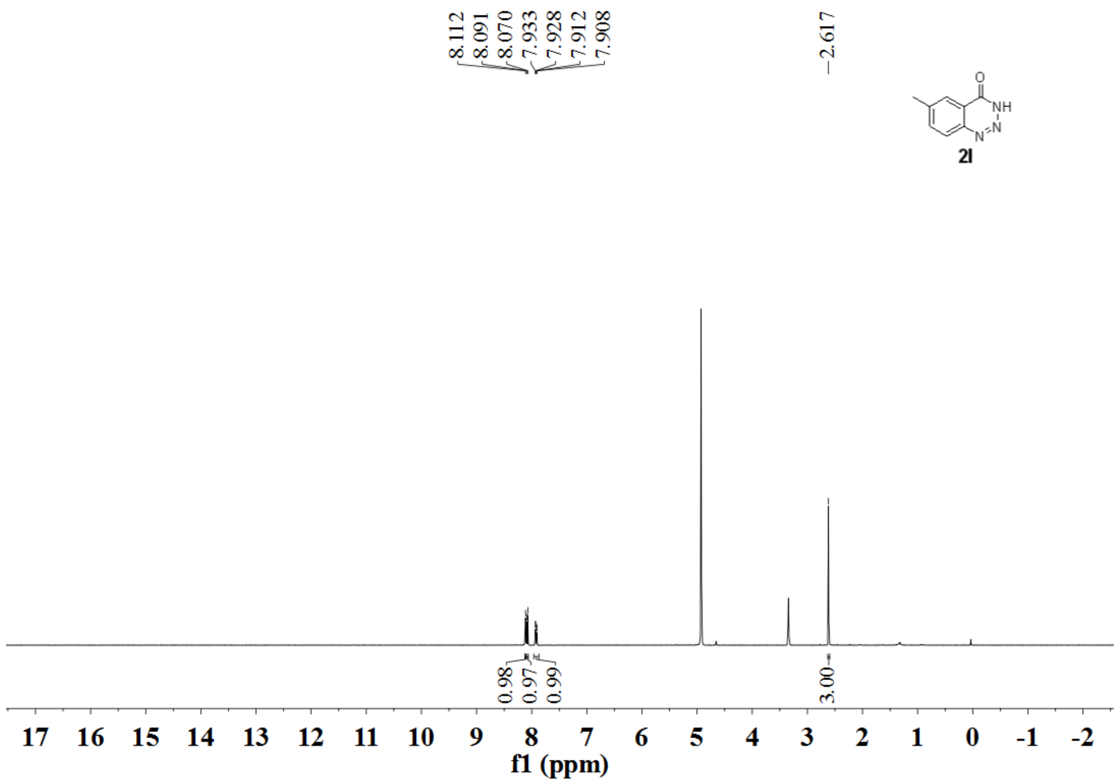




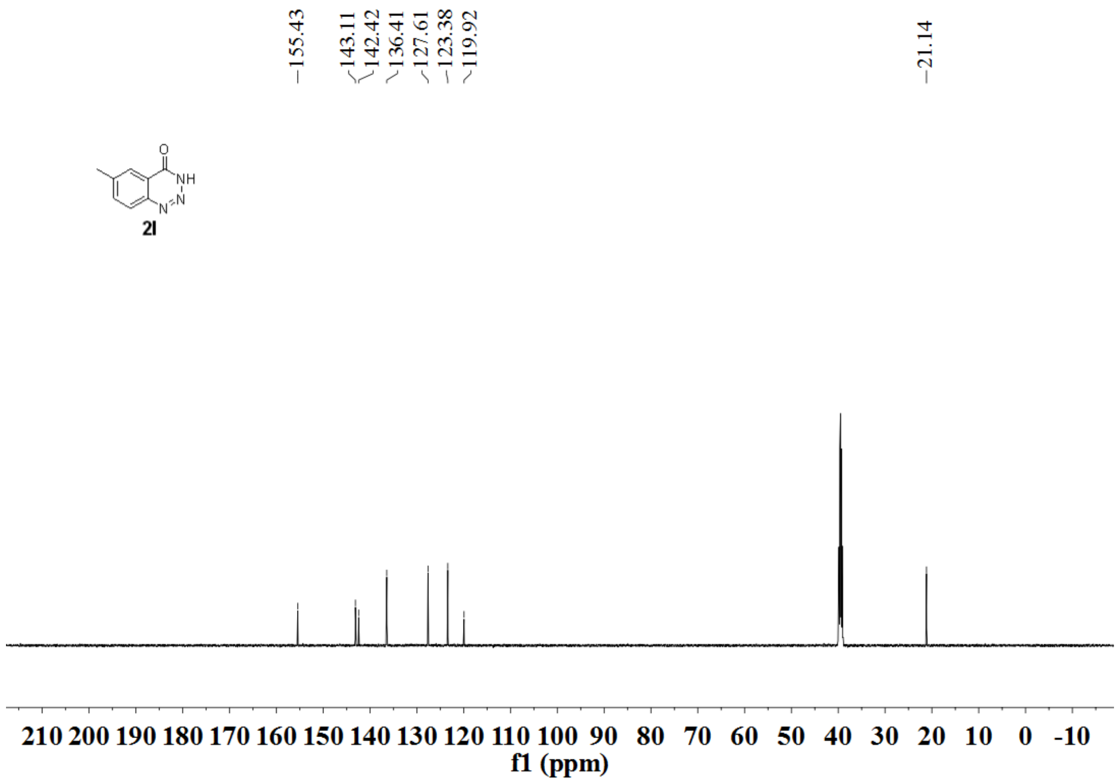
14.864
8.072
8.056
7.936
7.697
7.682
2.534
O
NH
N
N
2k
1.02
0.99
0.98
1.03
3.00
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)



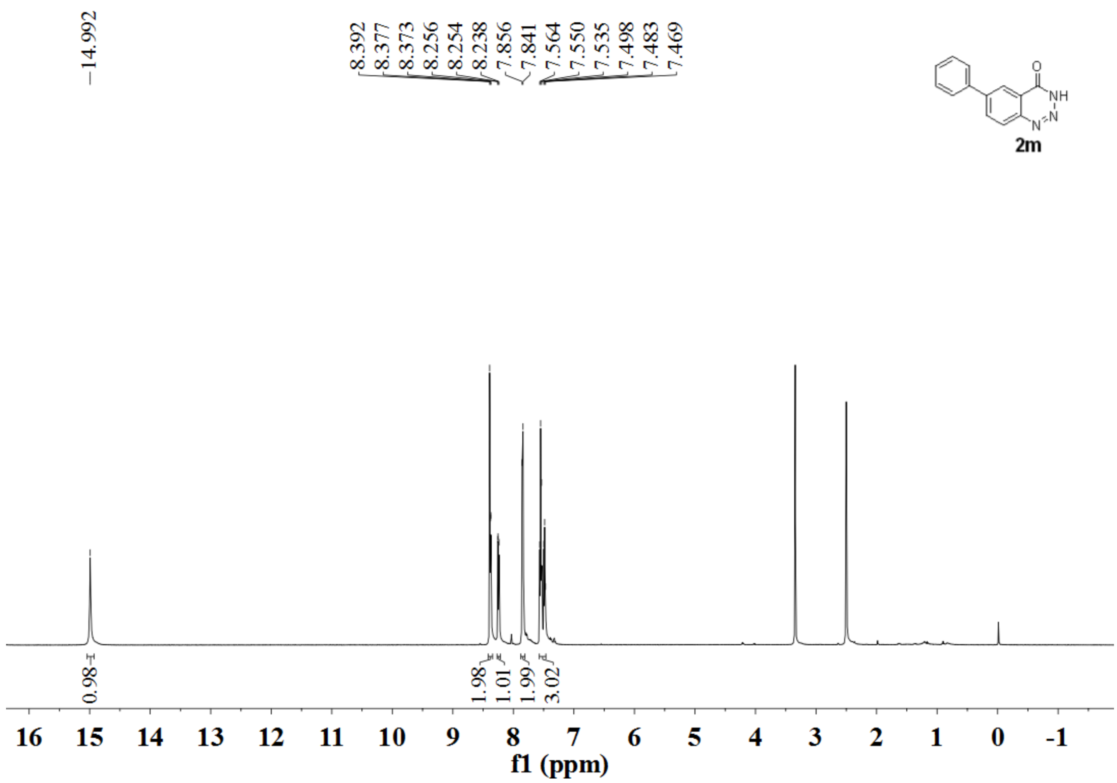
155.43
146.25
144.26
133.72
127.20
124.04
117.72
21.28
O
NH
N
N
2k
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



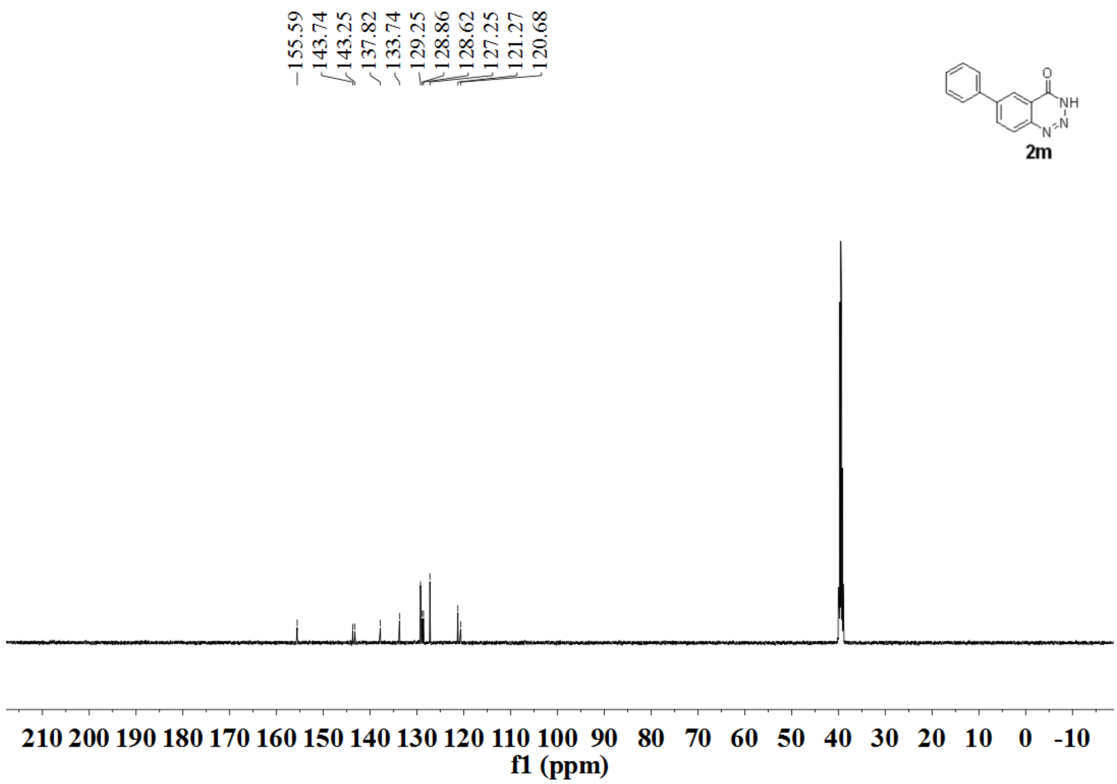
8.112
8.091
8.070
7.933
7.928
7.912
7.908
2.617
O
NH
N
N
2l
0.98
0.97
0.99
3.00
17 16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2
f1 (ppm)



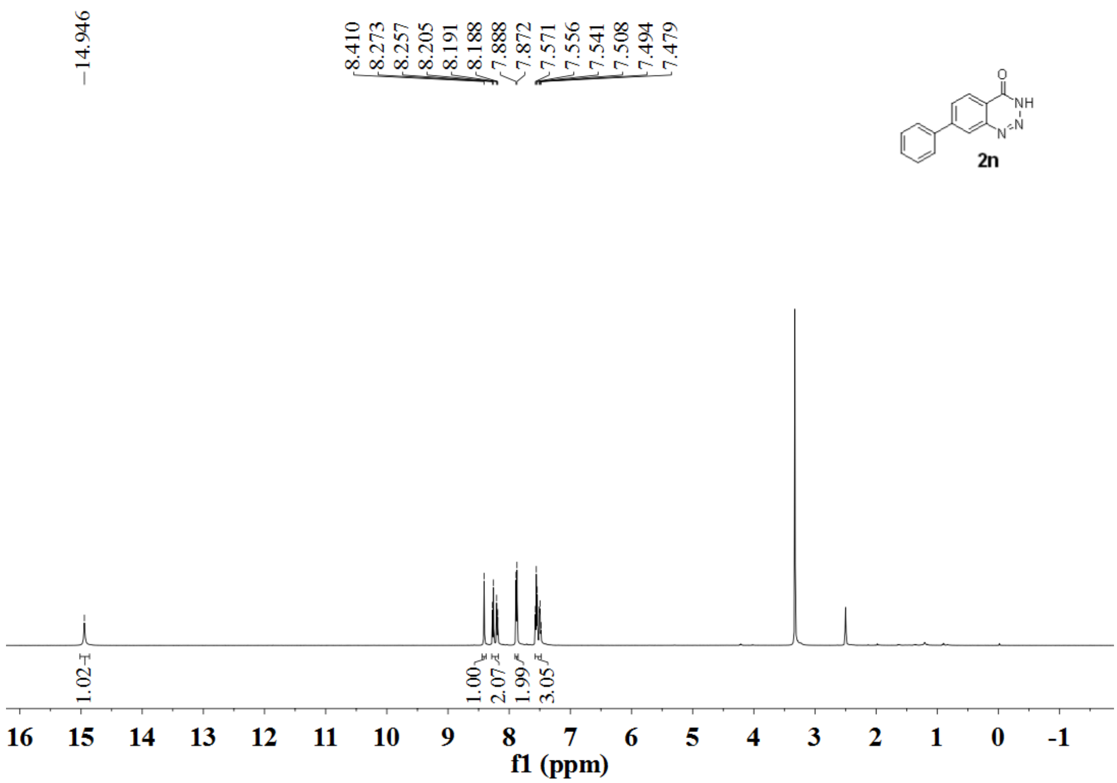
155.43
143.11
142.42
136.41
127.61
123.38
119.92
21.14
O
NH
N
N
2l
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

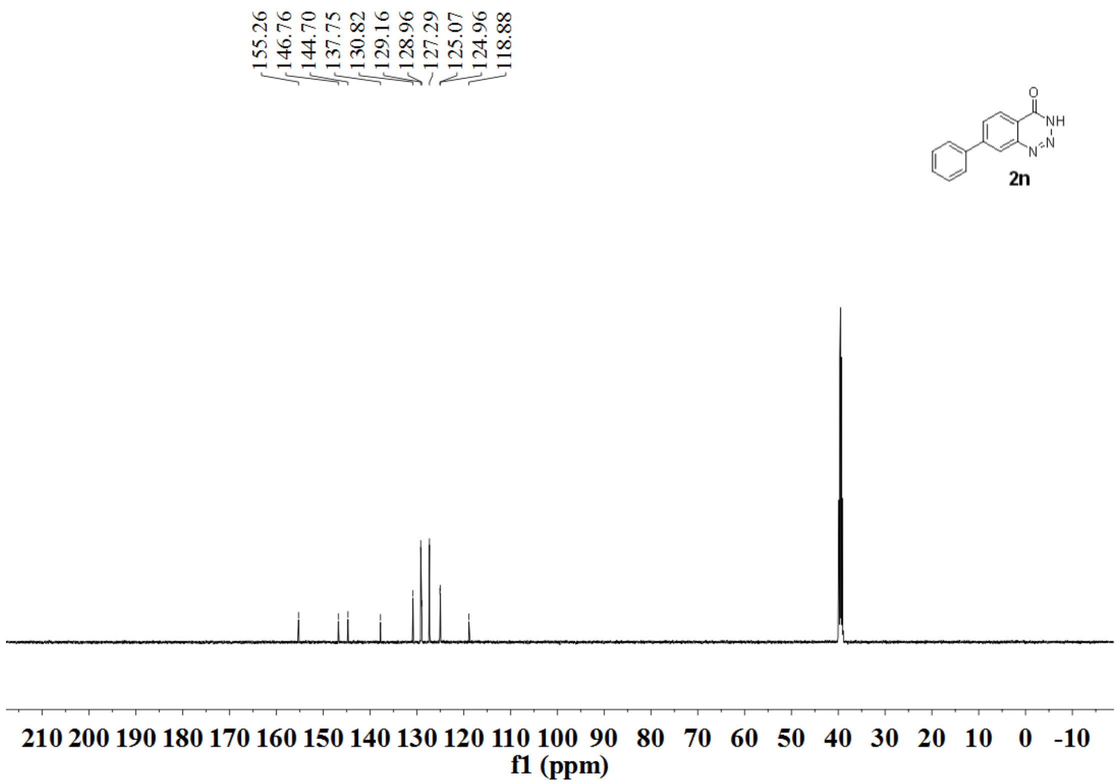


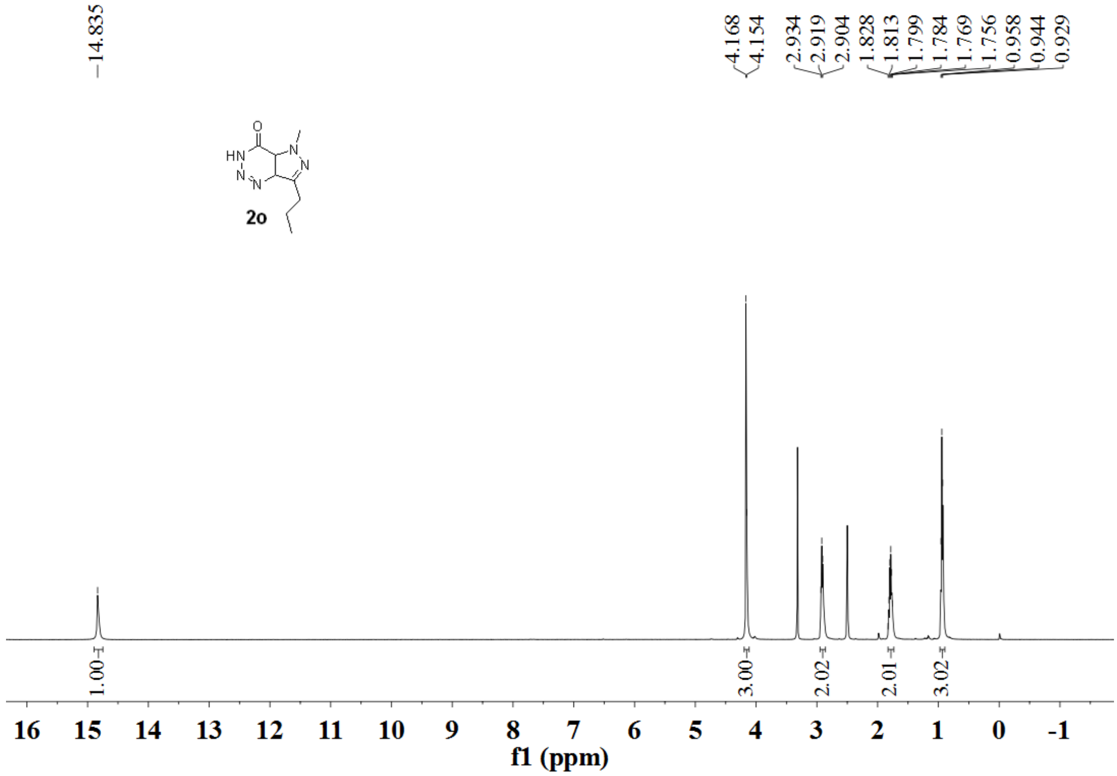
14.992
8.392
8.377
8.373
8.256
8.254
8.238
7.856
7.841
7.564
7.550
7.535
7.498
7.483
7.469
2m
0.98
1.98
1.01
1.99
3.02
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

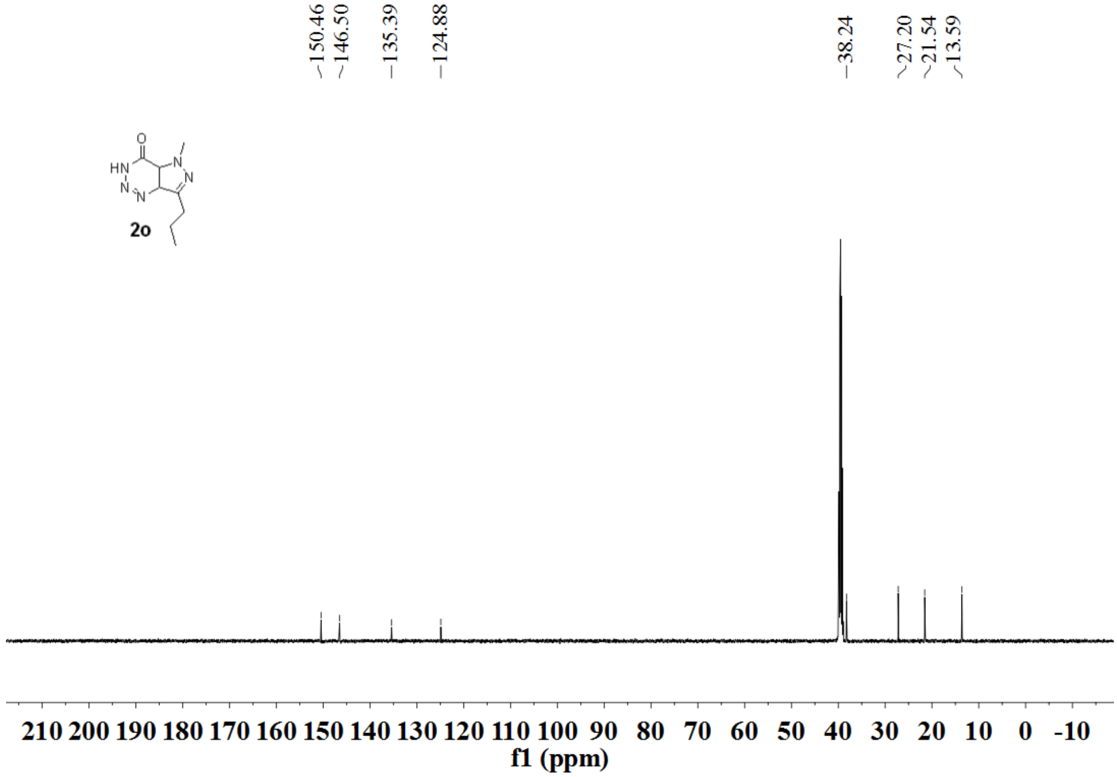


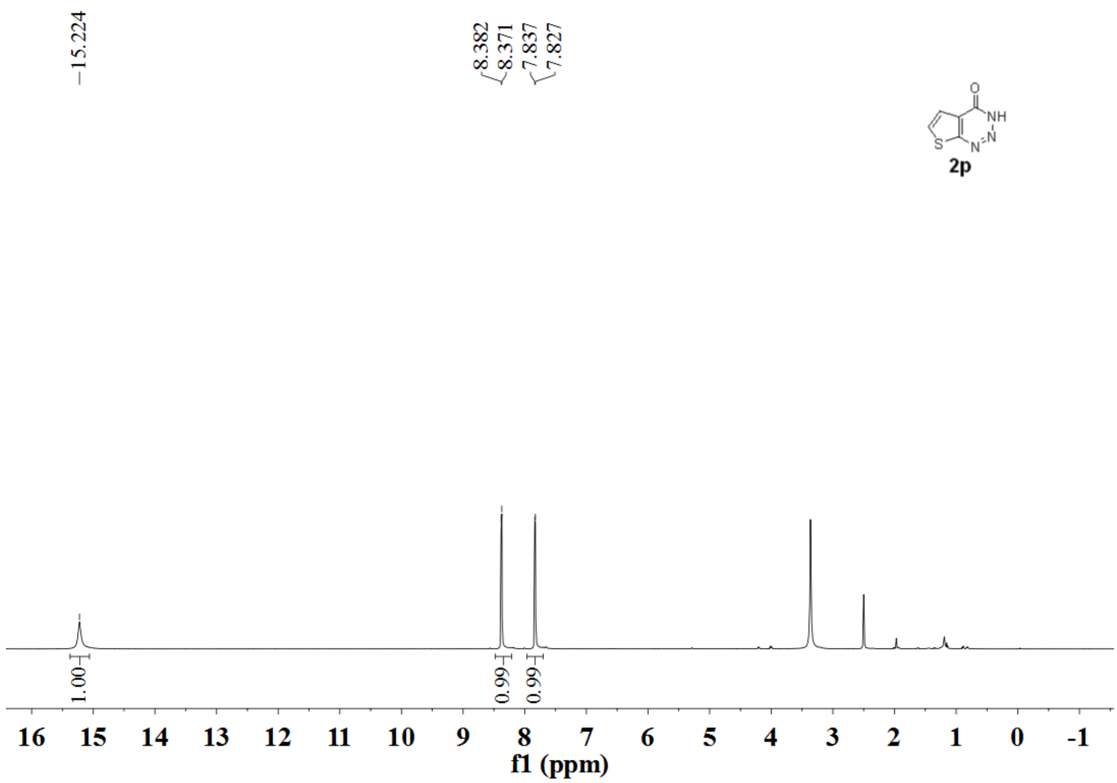
155.59
143.74
143.25
137.82
133.74
129.25
128.86
128.62
127.25
121.27
120.68
2m
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


14.946
8.410
8.273
8.257
8.205
8.191
8.188
7.888
7.872
7.571
7.556
7.541
7.508
7.494
7.479
2n
1.02
1.00
2.07
1.99
3.05
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

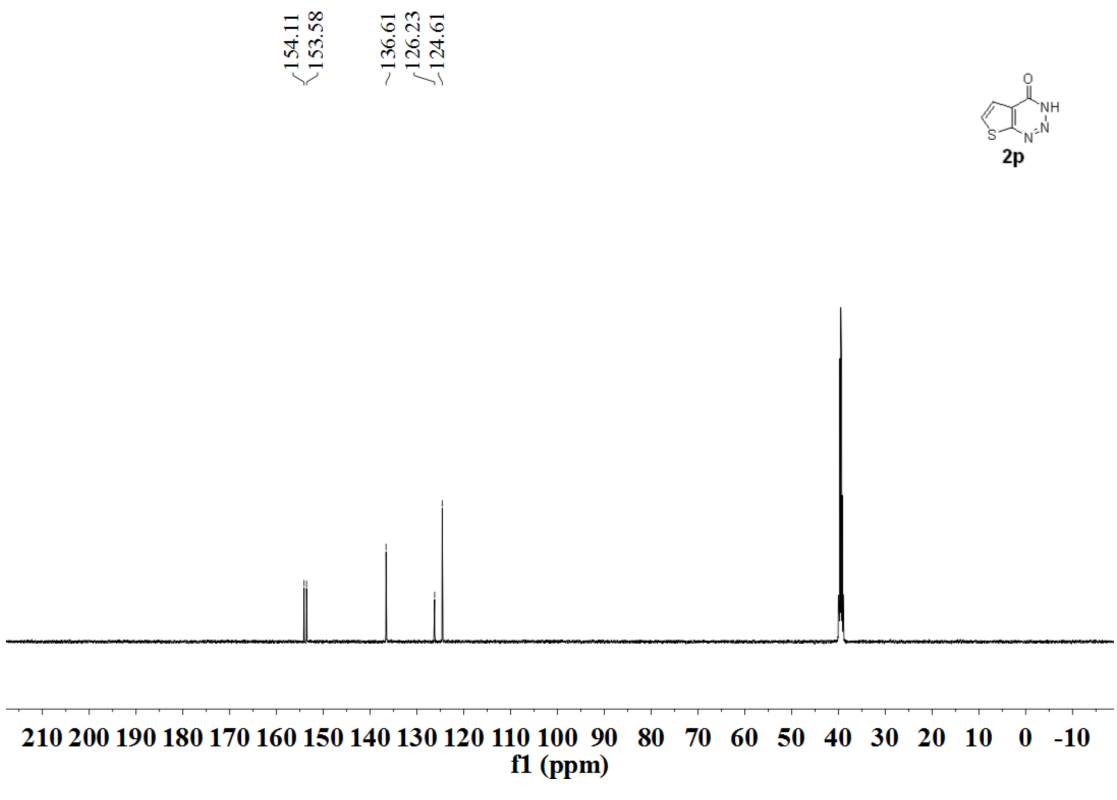

155.26
146.76
144.70
137.75
130.82
129.16
128.96
127.29
125.07
124.96
118.88
2n
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



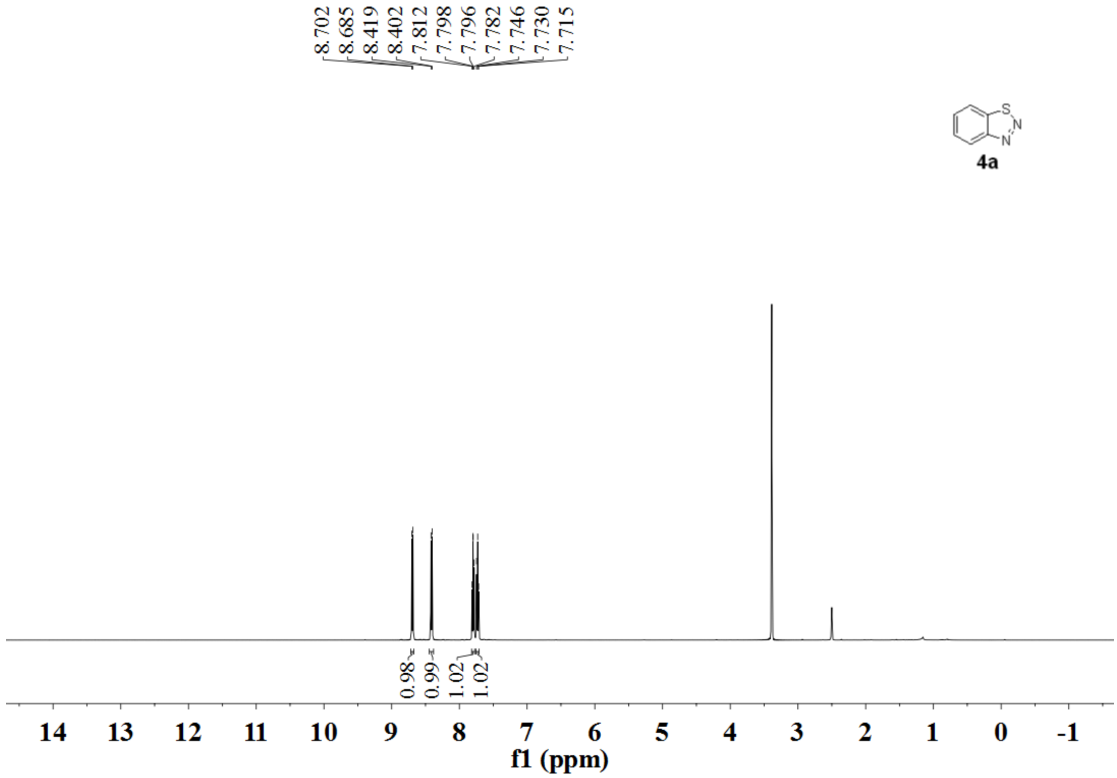


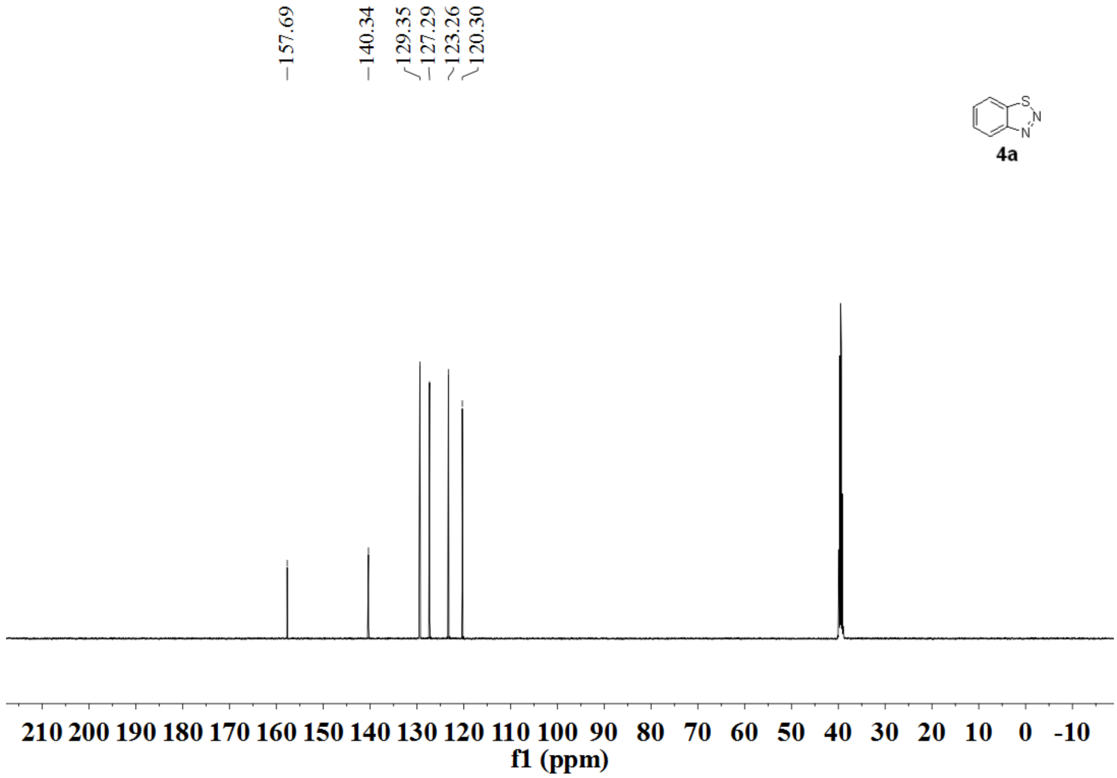


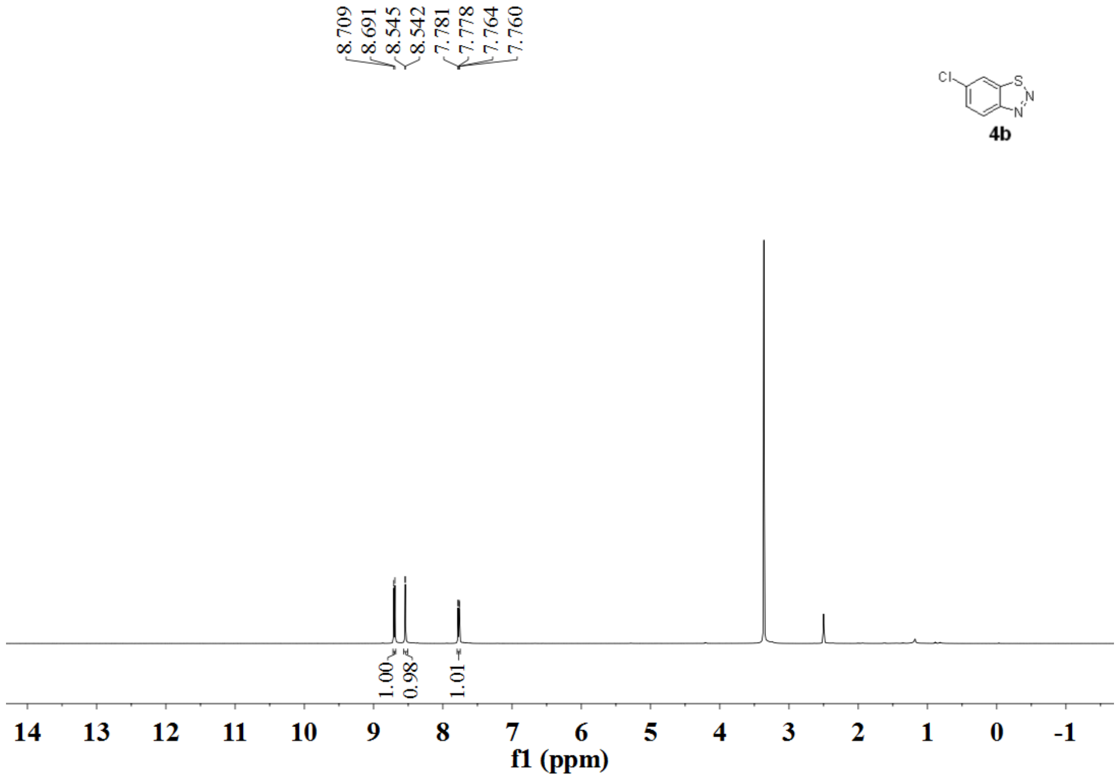
15.224
8.382
8.371
7.837
7.827
O
NH
S
N
N
2p
1.00
0.99
0.99
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

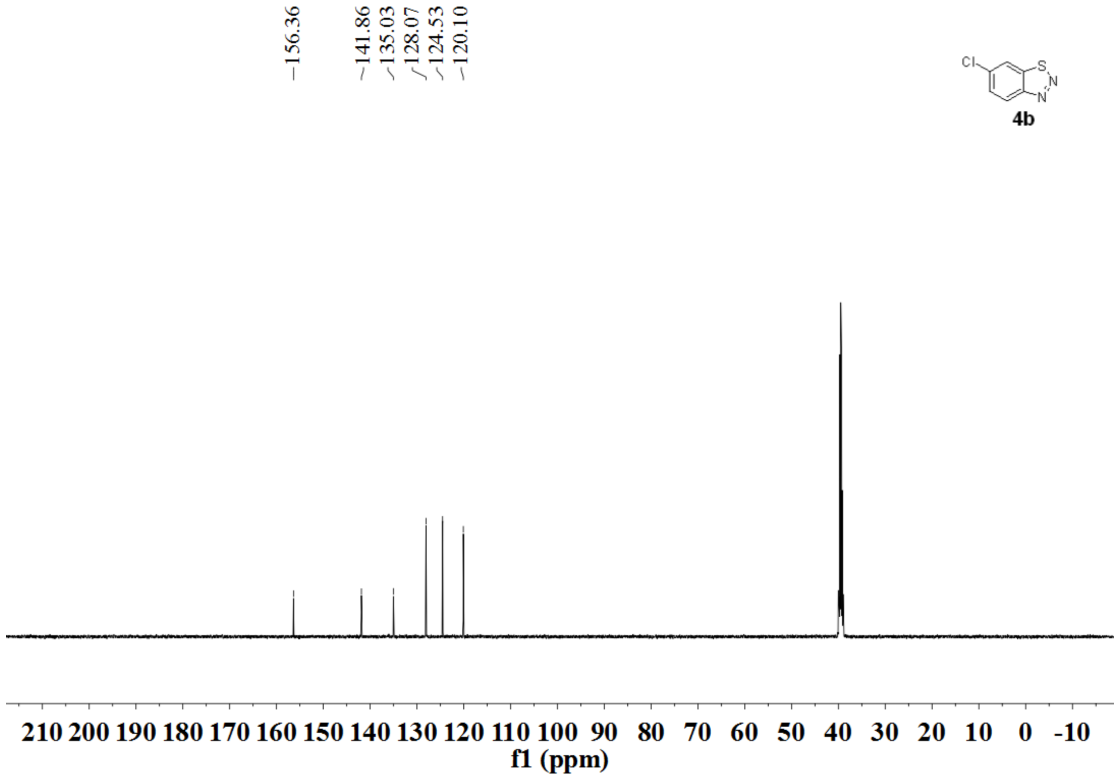


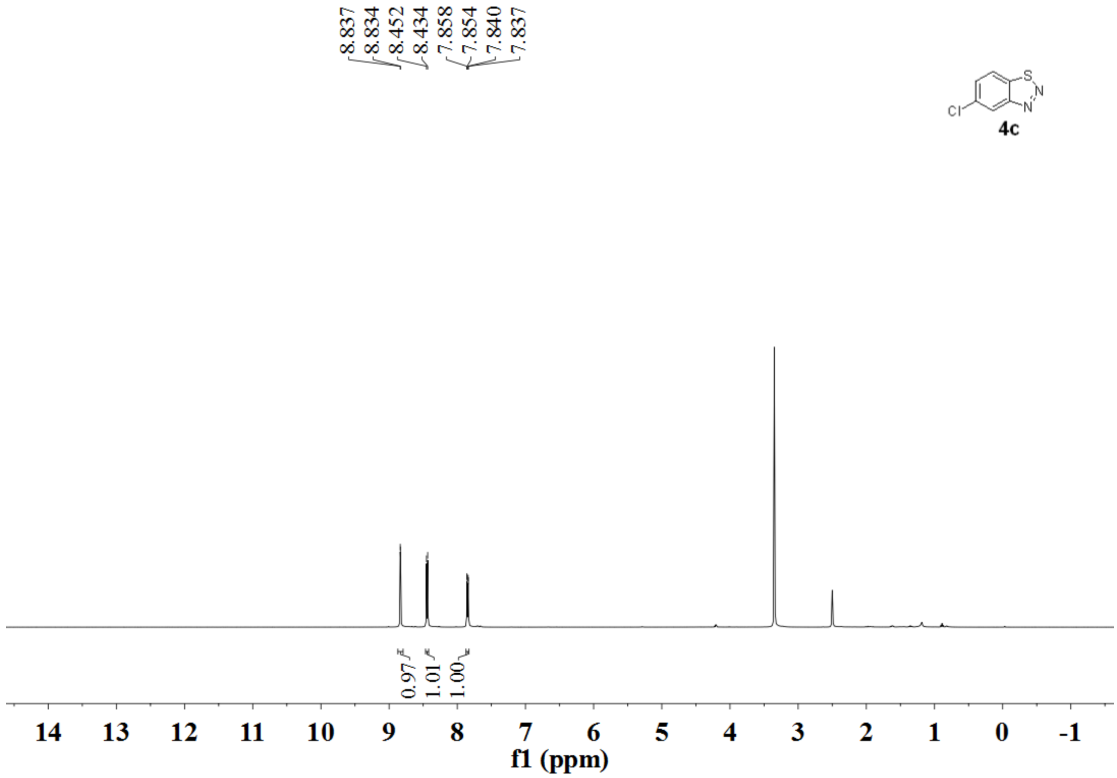
154.11
153.58
136.61
126.23
124.61
O
NH
S
N
N
2p
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

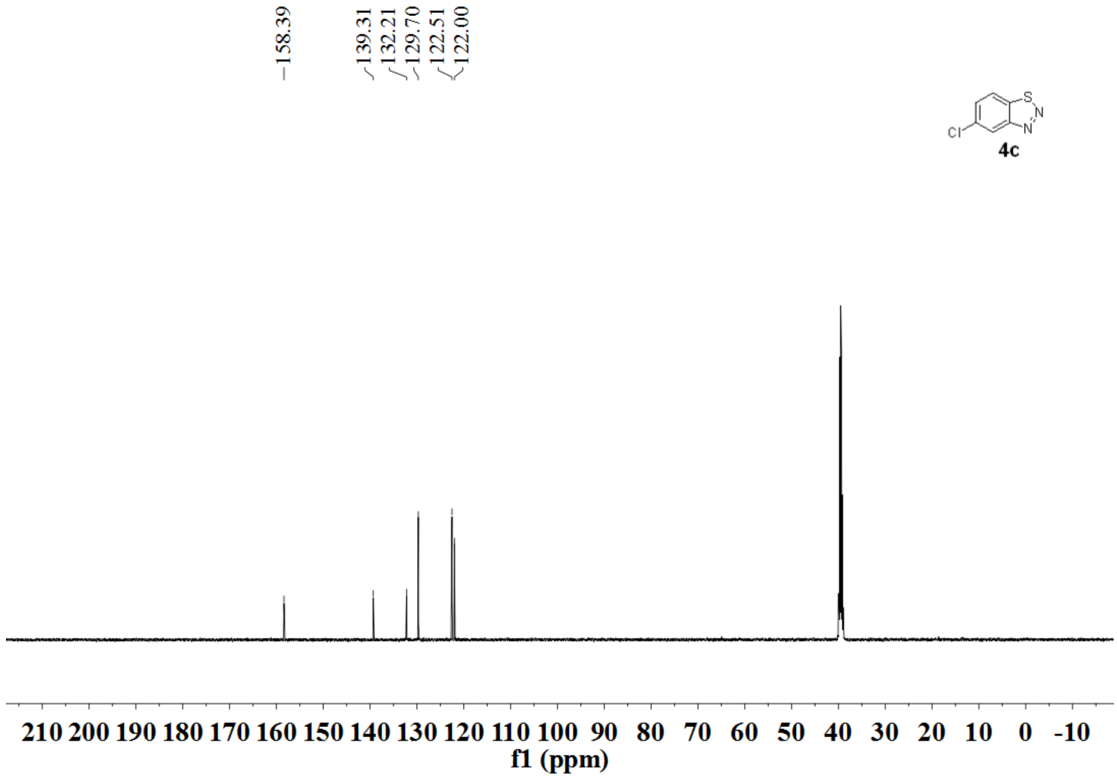

8.702
8.685
8.419
8.402
7.812
7.798
7.796
7.782
7.746
7.730
7.715
4a
0.98
0.99
1.02
1.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

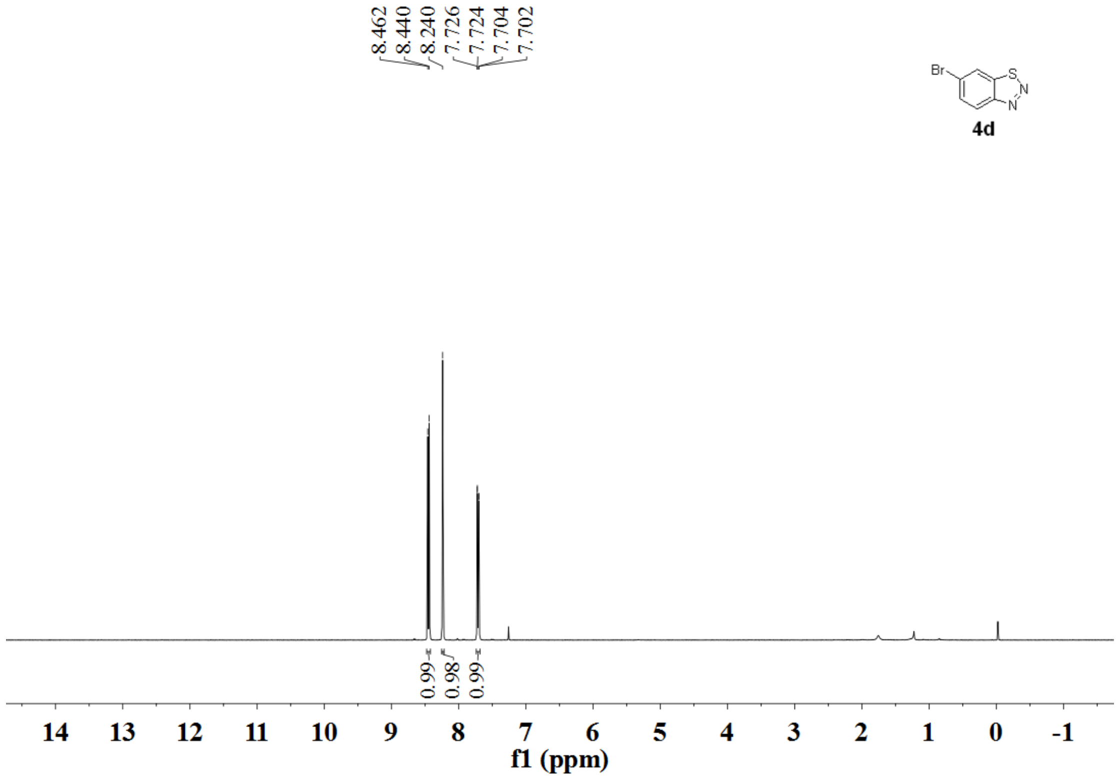

157.69
140.34
129.35
127.29
123.26
120.30
4a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

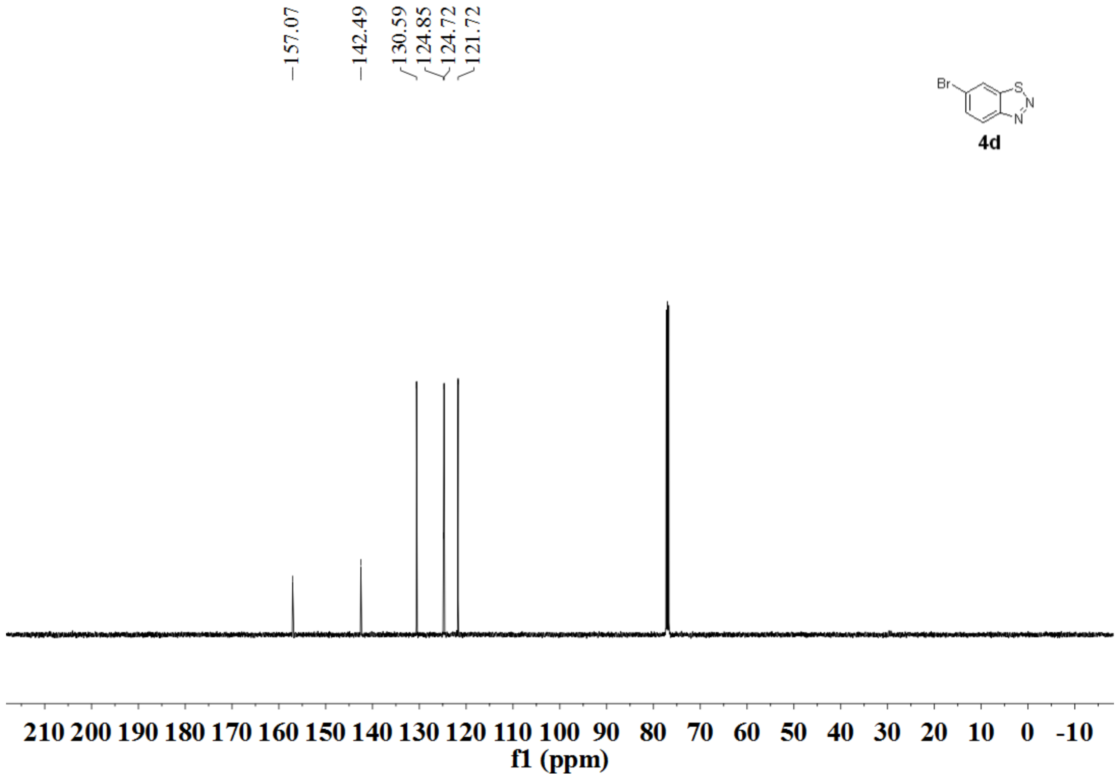

8.709
8.691
8.545
8.542
7.781
7.778
7.764
7.760
Cl
S
N
N
4b
1.00
0.98
1.01
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

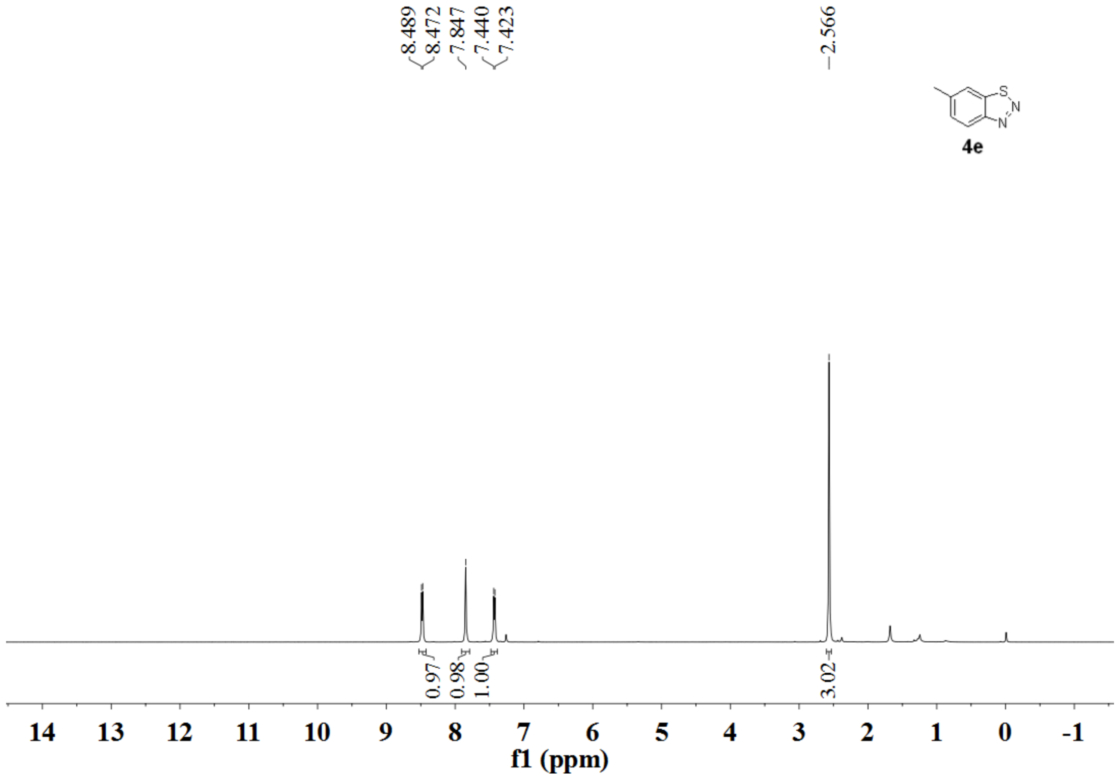

156.36
141.86
135.03
128.07
124.53
120.10
Cl
S
N
N
4b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

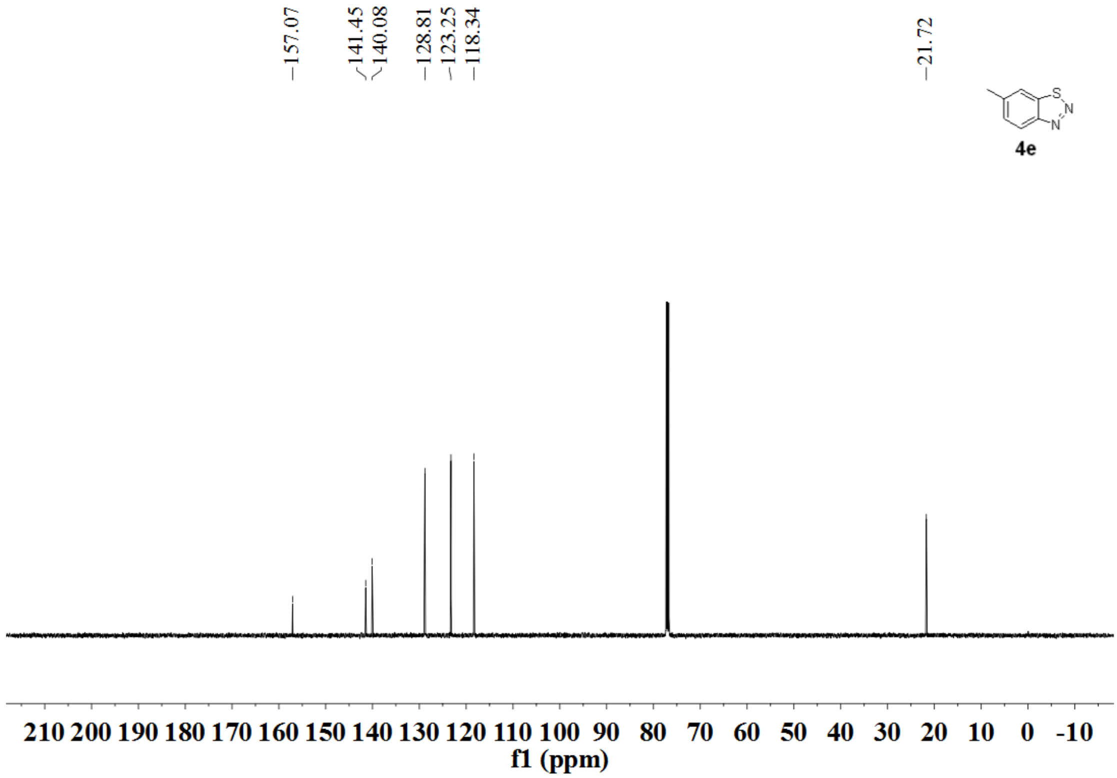

8.837
8.834
8.452
8.434
7.858
7.854
7.840
7.837
Cl
S
N
N
4c
0.97
1.01
1.00
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

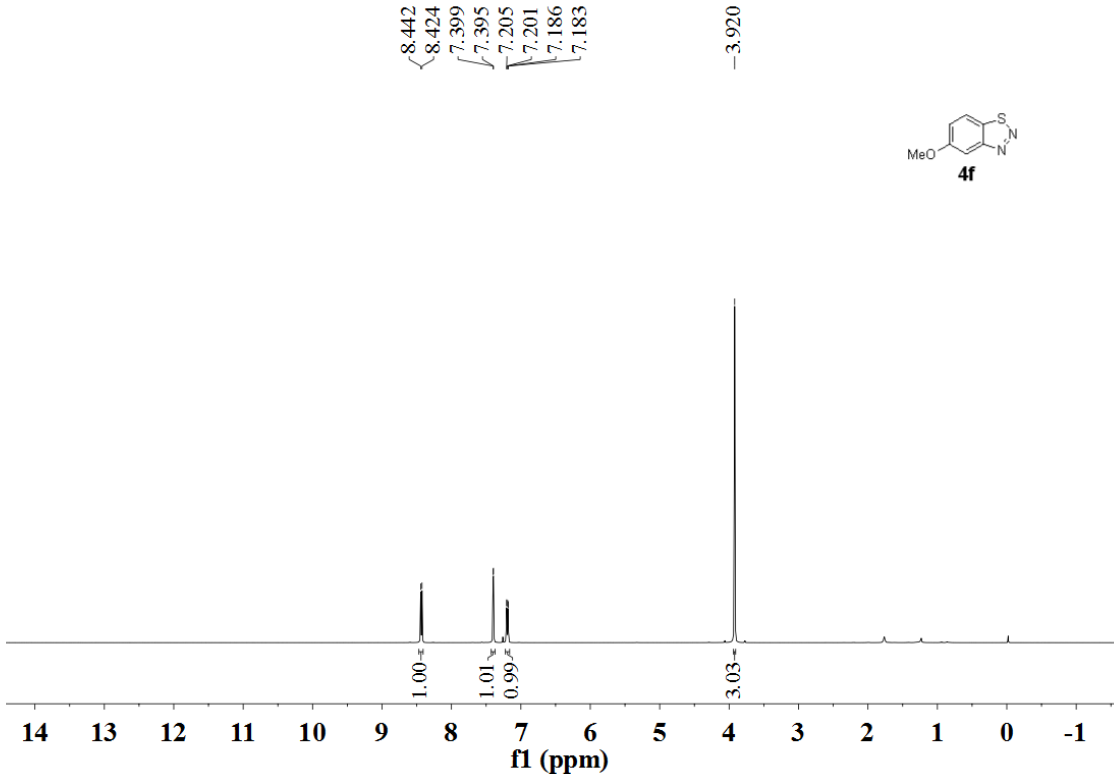

158.39
139.31
132.21
129.70
122.51
122.00
Cl
S
N
N
4c
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

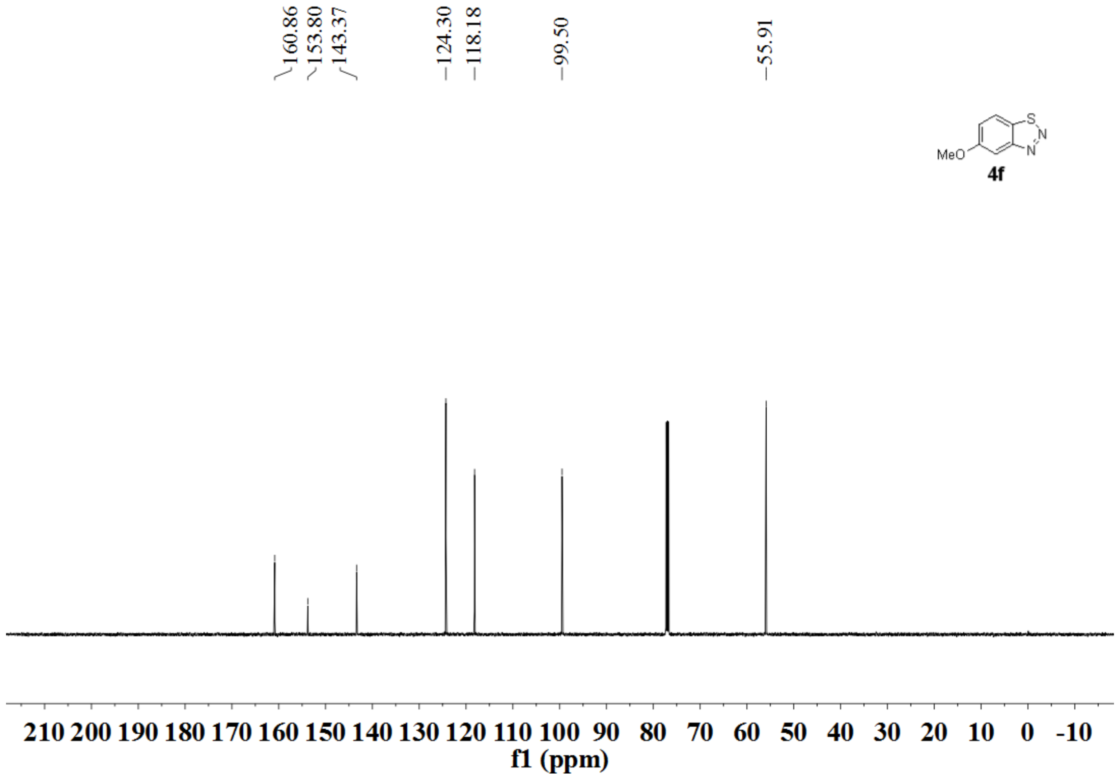

8.462
8.440
8.240
7.726
7.724
7.704
7.702
Br
S
N
N
4d
0.99
0.98
0.99
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

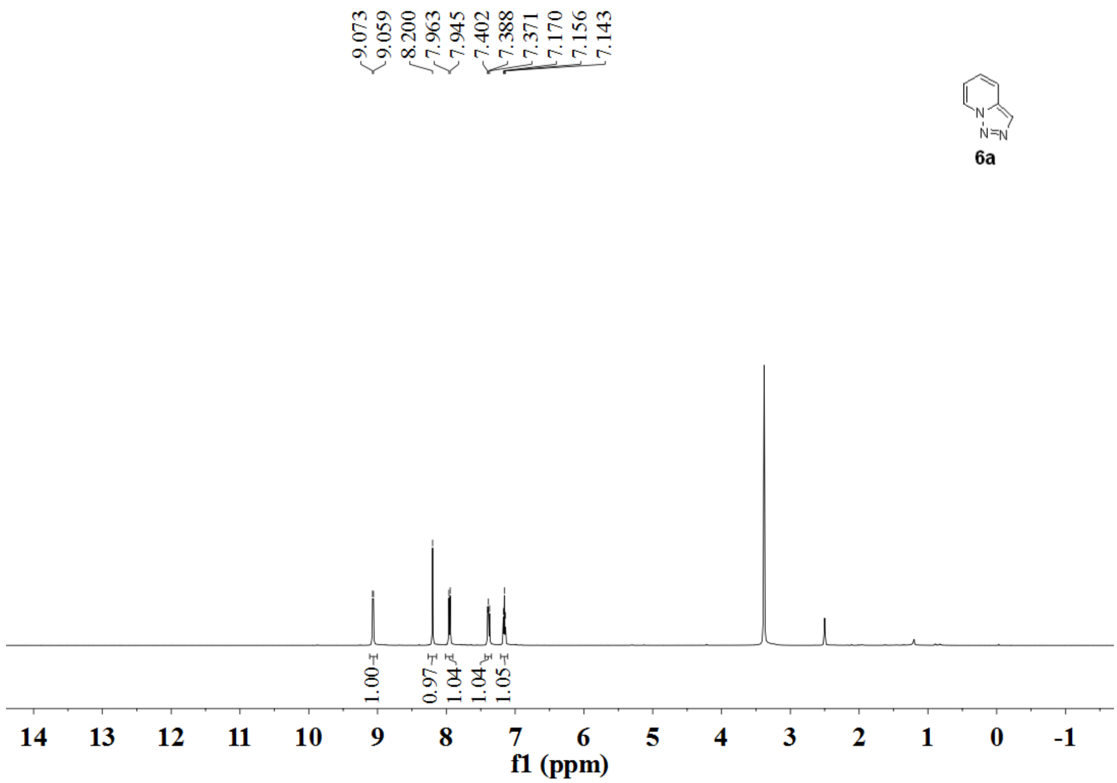

157.07
142.49
130.59
124.85
124.72
121.72
Br
S
N
N
4d
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

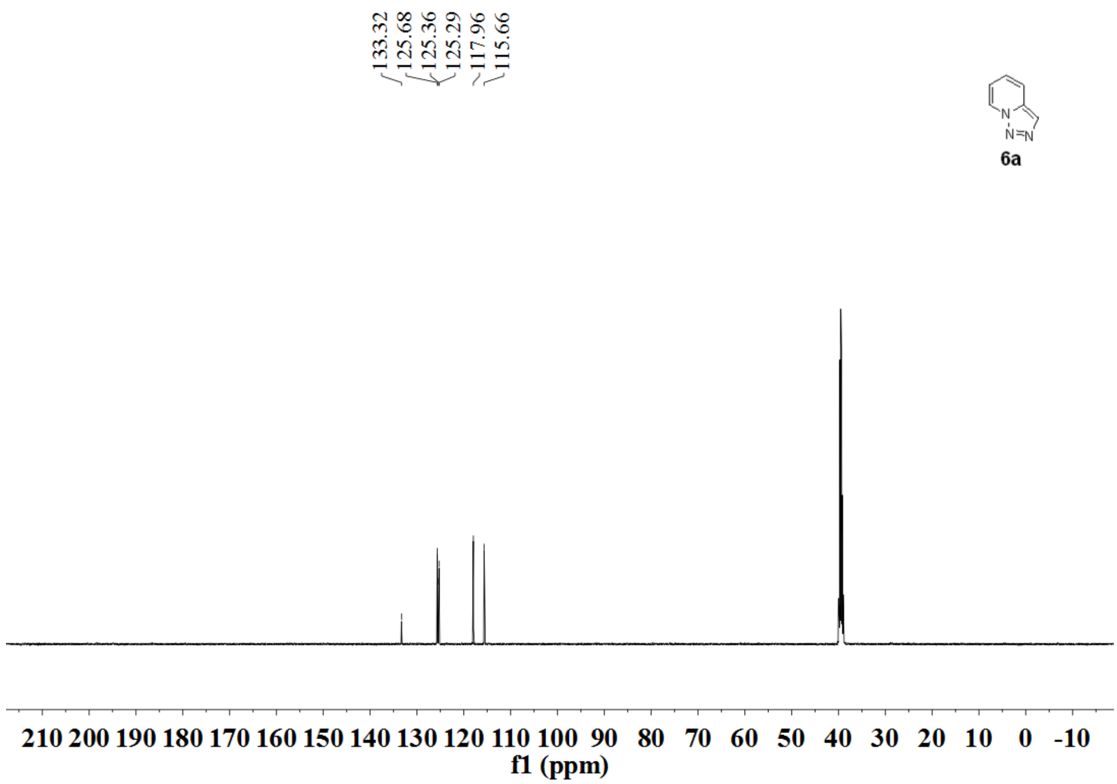

8.489
8.472
7.847
7.440
7.423
2.566
4e
0.97
0.98
1.00
3.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

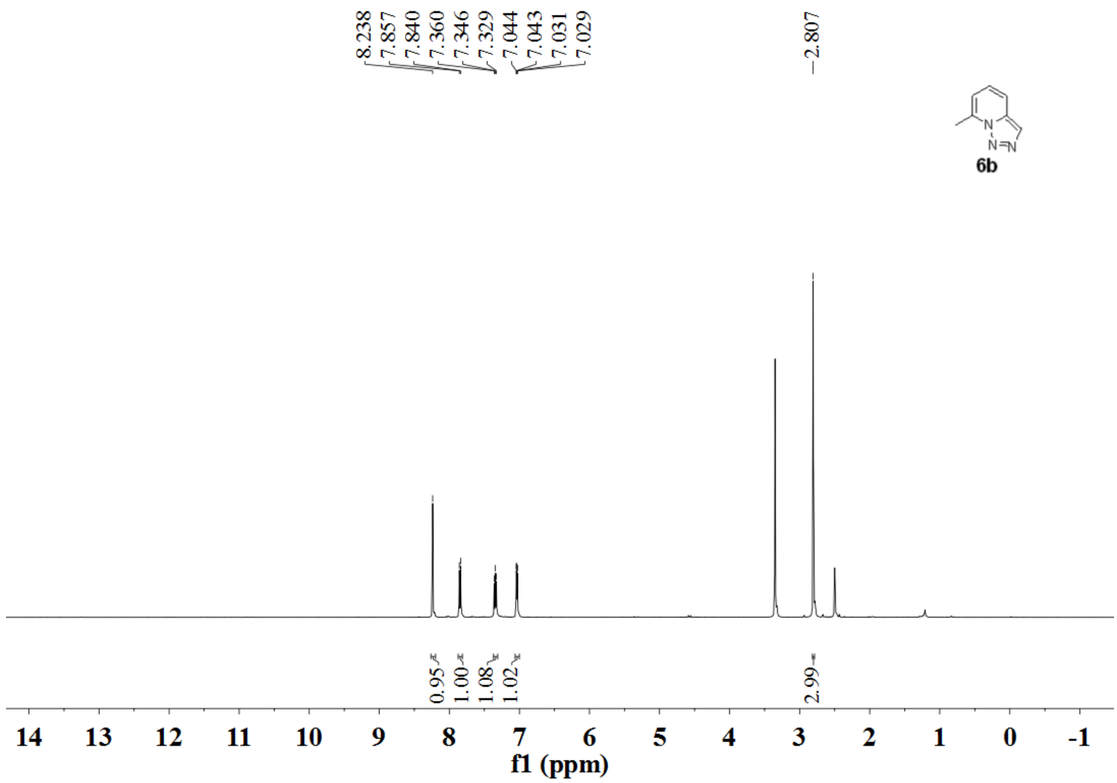

157.07
141.45
140.08
128.81
123.25
118.34
21.72
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

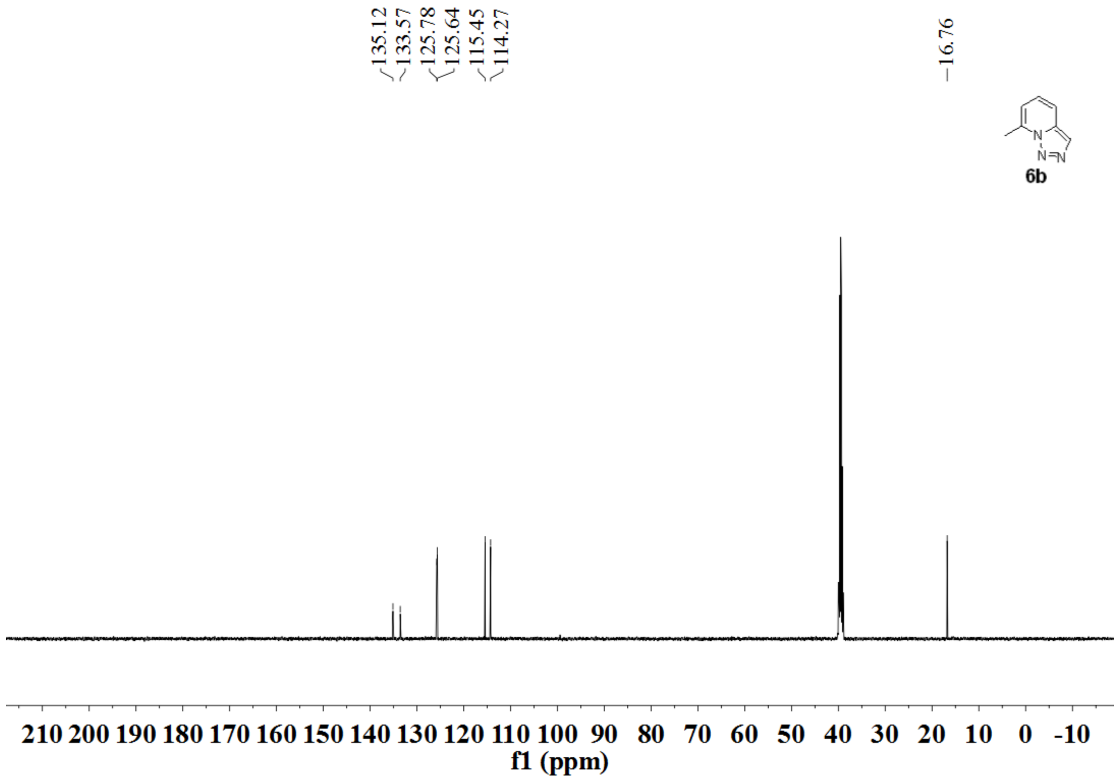

8.442
8.424
7.399
7.395
7.205
7.201
7.186
7.183
3.920
MeO
S
N
N
4f
1.00
1.01
0.99
3.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

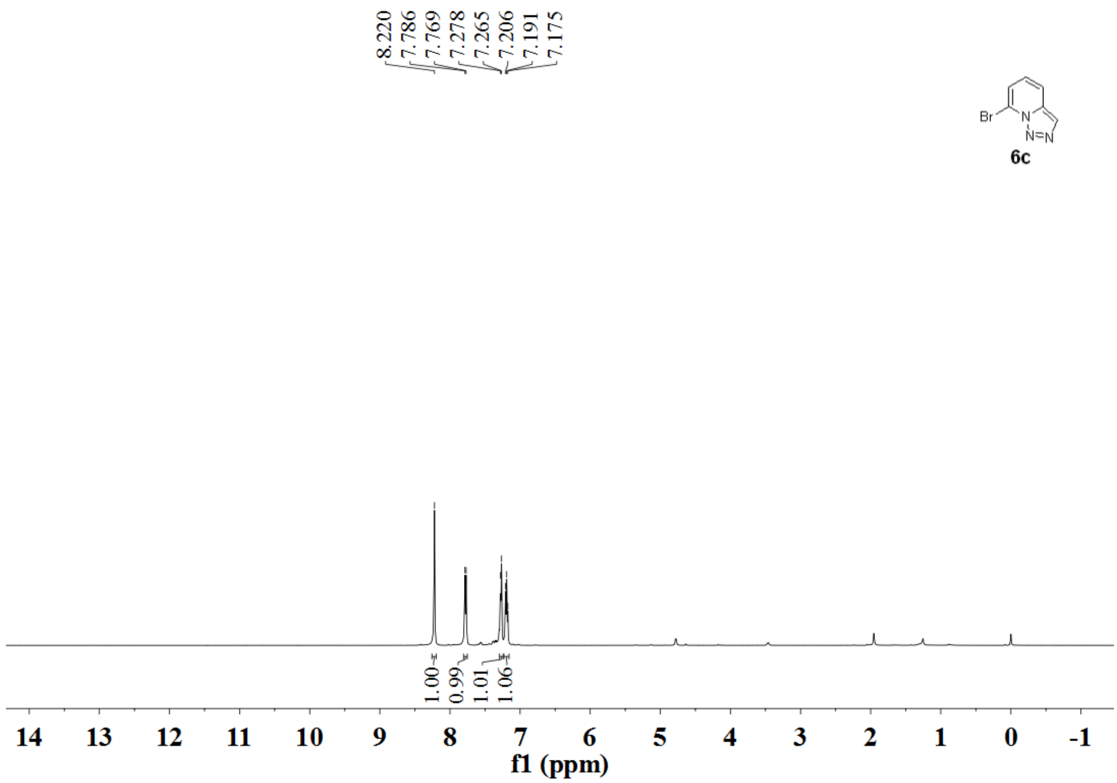

160.86
153.80
143.37
124.30
118.18
99.50
55.91
MeO
S
N
N
4f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.073
9.059
8.200
7.963
7.945
7.402
7.388
7.371
7.170
7.156
7.143
6a
1.00
0.97
1.04
1.04
1.05
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

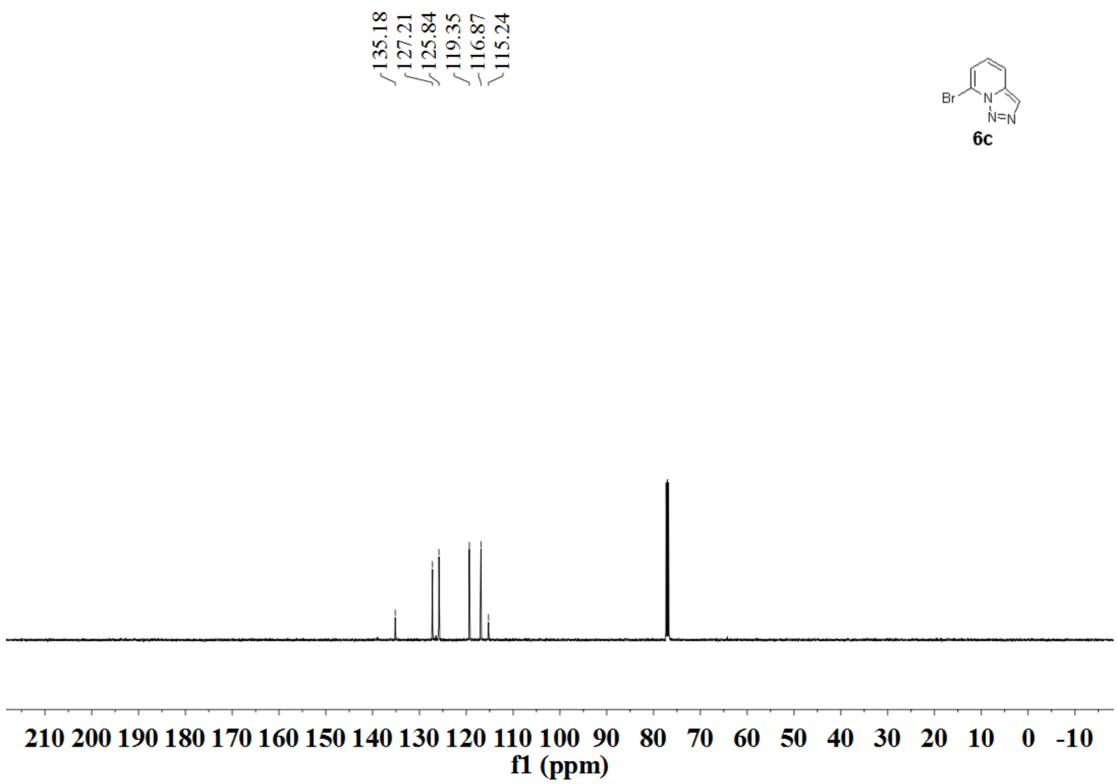

133.32
125.68
125.36
125.29
117.96
115.66
6a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.238
7.857
7.840
7.360
7.346
7.329
7.044
7.043
7.031
7.029
2.807
6b
0.95
1.00
1.08
1.02
2.99
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


135.12
133.57
125.78
125.64
115.45
114.27
16.76
6b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.220
7.786
7.769
7.278
7.265
7.206
7.191
7.175
Br
N
N=N
1.00
0.99
1.01
1.06
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)

6c


135.18
127.21
125.84
119.35
116.87
115.24
Br
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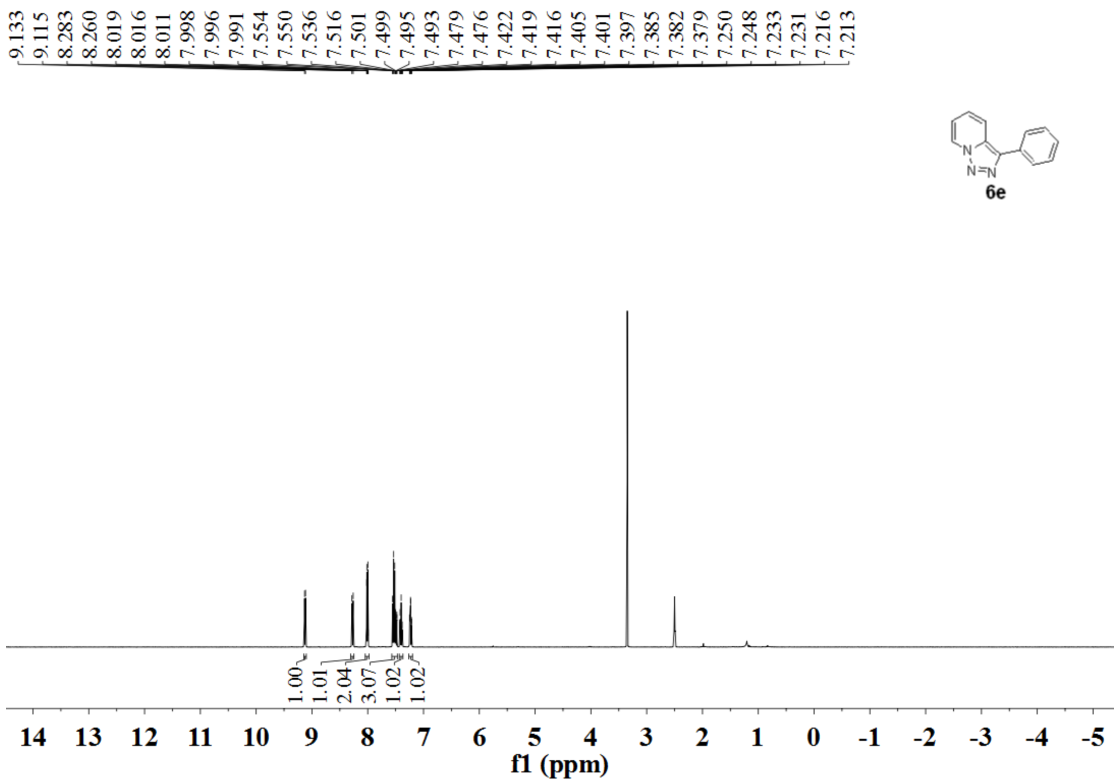
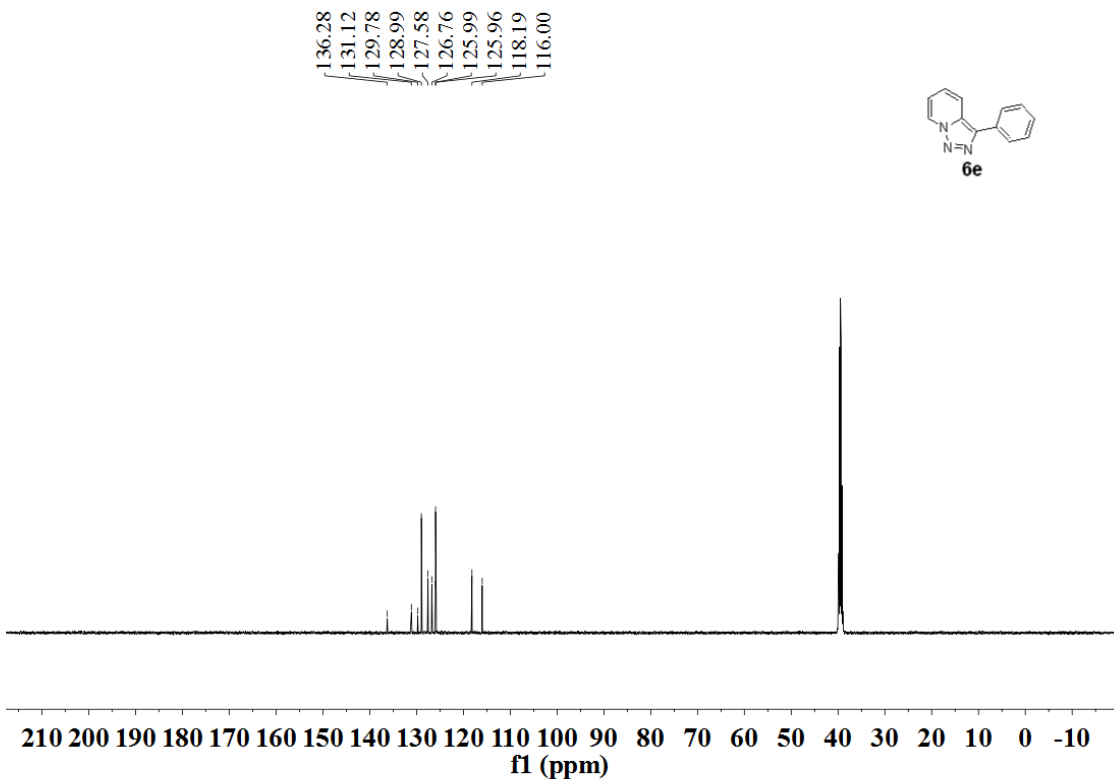
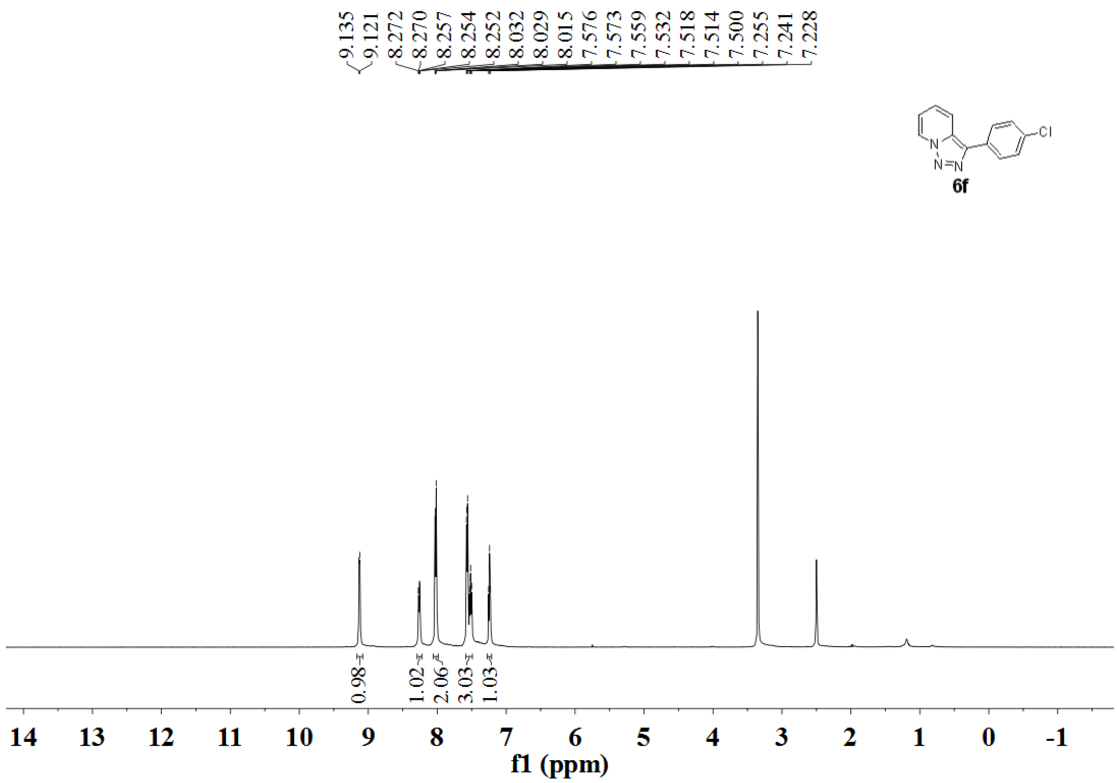
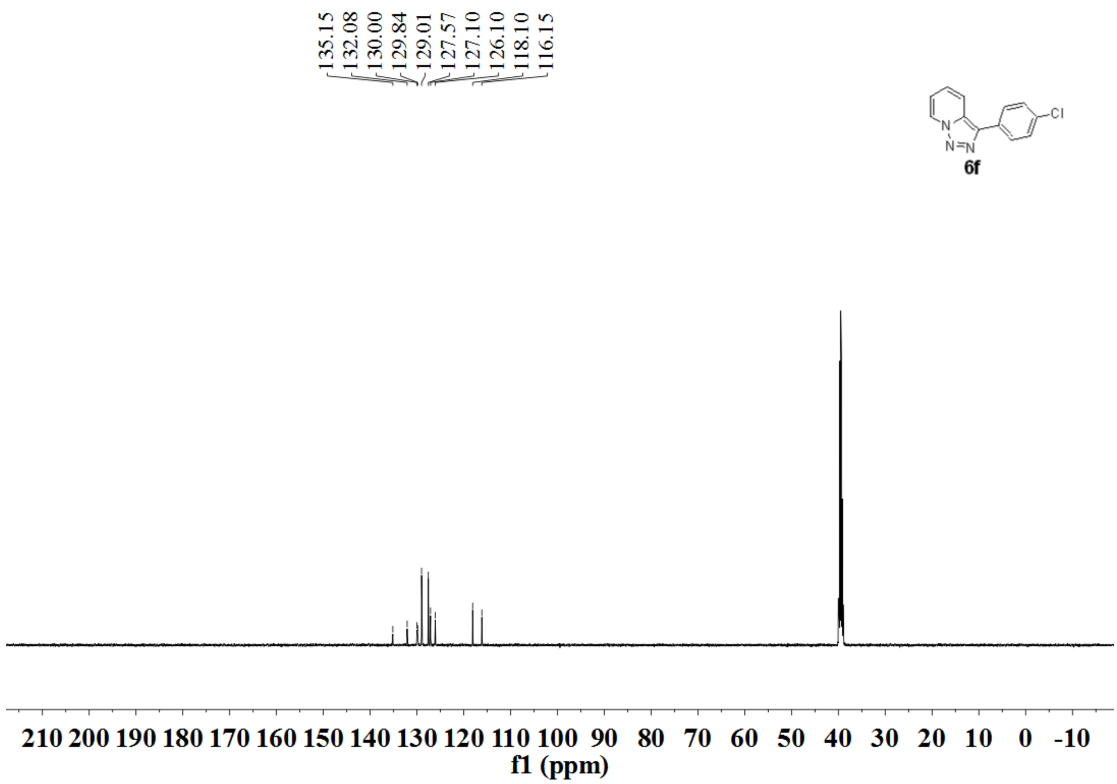
N=N
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

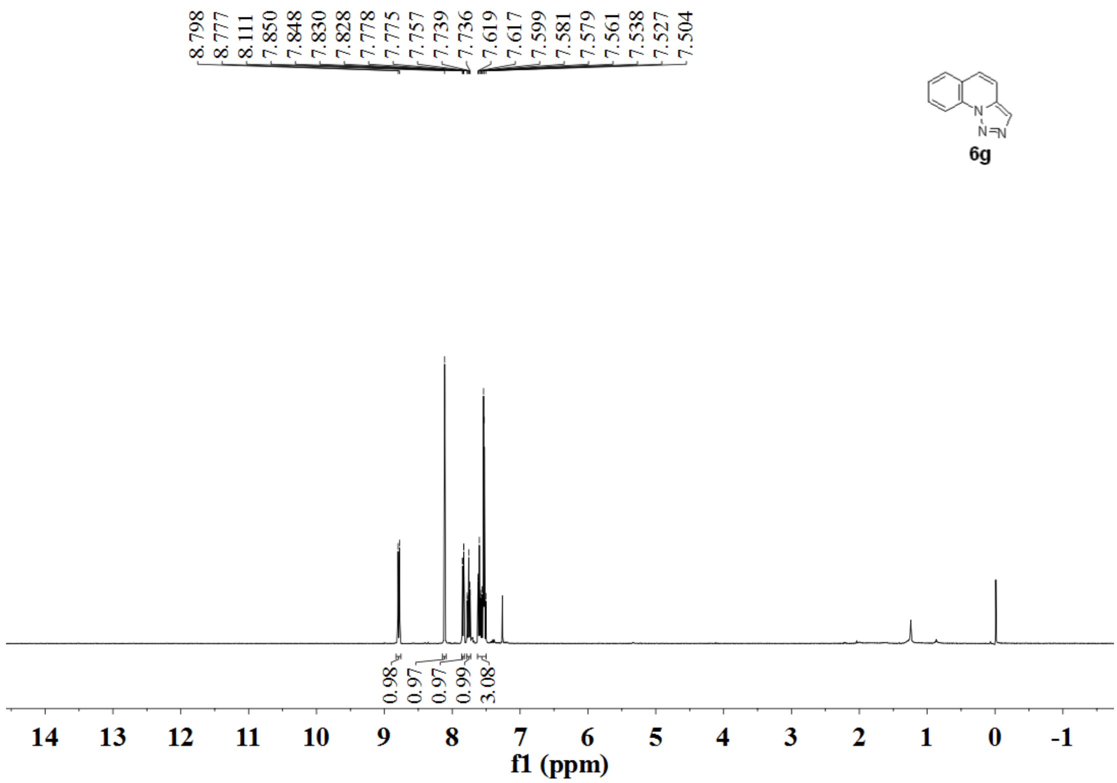
6c

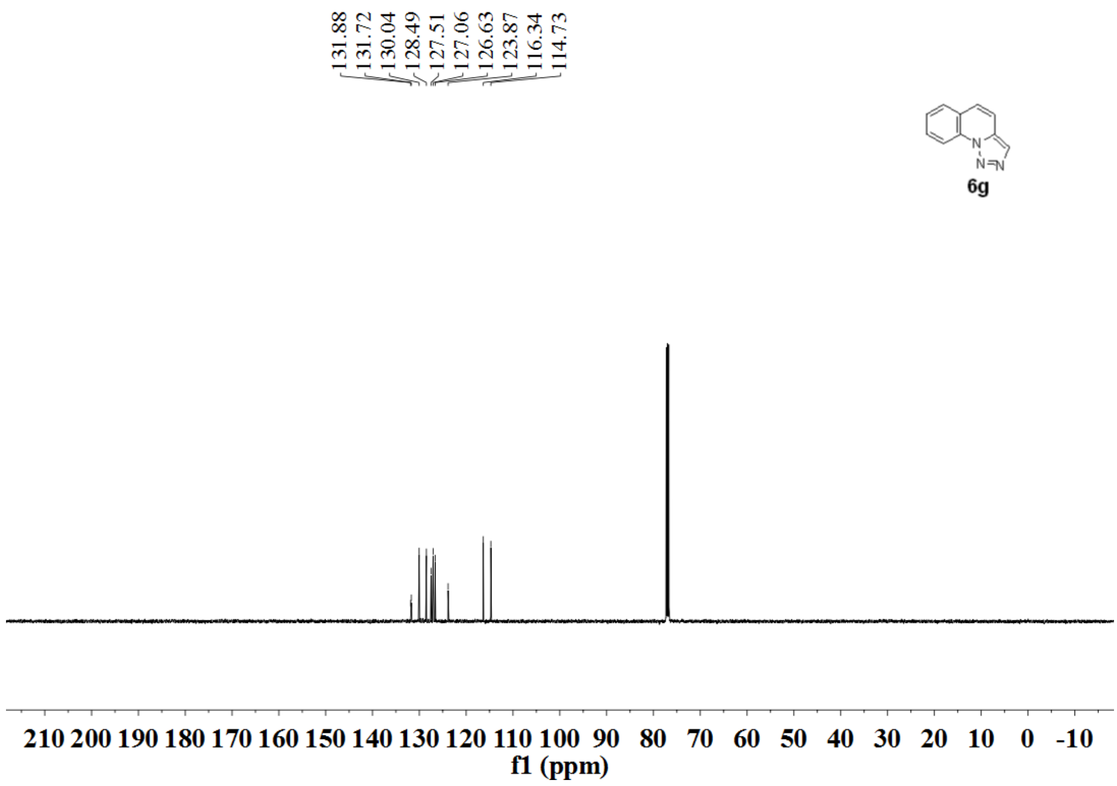

9.133
9.115
8.283
8.260
8.019
8.016
8.011
7.998
7.996
7.991
7.554
7.550
7.536
7.516
7.501
7.499
7.495
7.493
7.479
7.476
7.422
7.419
7.416
7.405
7.401
7.397
7.385
7.382
7.379
7.250
7.248
7.233
7.231
7.216
7.213
6e
1.00
1.01
2.04
3.07
1.02
1.02
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1 -2 -3 -4 -5
f1 (ppm)


136.28
131.12
129.78
128.99
127.58
126.76
125.99
125.96
118.19
116.00
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.135
9.121
8.272
8.270
8.257
8.254
8.252
8.032
8.029
8.015
7.576
7.573
7.559
7.532
7.518
7.514
7.500
7.255
7.241
7.228
Cl
N
N
N
6f
0.98
1.02
2.06
3.03
1.03
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


135.15
132.08
130.00
129.84
129.01
127.57
127.10
126.10
118.10
116.15
Cl
N
N
N
6f
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.798
8.777
8.111
7.850
7.848
7.830
7.828
7.778
7.775
7.757
7.739
7.736
7.619
7.617
7.599
7.581
7.579
7.561
7.538
7.527
7.504
N
N=N
6g
0.98
0.97
0.97
0.99
3.08
14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 -1
f1 (ppm)


131.88
131.72
130.04
128.49
127.51
127.06
126.63
123.87
116.34
114.73
N
N=N
6g
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)