Electronic Supplementary Material (ESI) for RSC Advances.
This journal is © The Royal Society of Chemistry 2016

Supporting Information

Synthesis of 1,2,4-Triazine Derivatives via [4+2] Domino Annulations Reactions in Onepot

Dong Tang,[a] Jing Wang,[a] Ping Wu,[a] Xin Guo,[a] Sen Yang, [a] Ji-Hui Li,[b] and Bao-Hua Chen[a*]

[a]*State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Gansu Lanzhou, 730000, P. R. China*

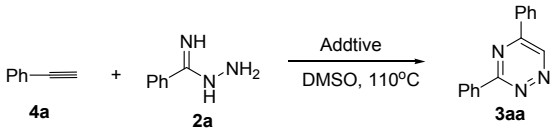
[b] *College of Materials and Chemical Engineering, Hainan University, Haikou, 570228, China*

Email: chbh@lzu.edu.cn

Table of Contents

1. General Remarks

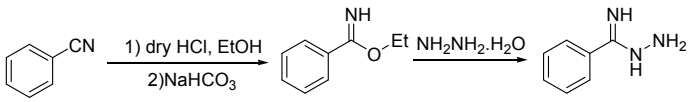
1.1 Table 1 To optimize the reaction conditions of alkynes and amidrazones [a]



Entry	Amidrazone	Alkyne	Addtive	Yield [b]
1	1.0 equiv.	1.0 equiv.	I_2 (1.1 equiv.)	32
2	1.0 equiv.	1.0 equiv.	NIS (1.1 equiv.)	41
3	1.0 equiv.	1.0 equiv.	$PhI(OAc)_2$ (1.1 equiv.)	0
4	1.0 equiv.	1.0 equiv.	$FeCl_3$ (1.1 equiv.)	0
5	1.0 equiv.	1.0 equiv.	NIS (1.2 equiv.)	43
6	1.0 equiv.	1.2equiv.	NIS (1.1 equiv.)	48
7	1.2 equiv.	1.0equiv.	NIS (1.1 equiv.)	38
8	1.0 equiv.	2.0 equiv.	NIS (1.1 equiv.)	50
9	1.0 equiv.	2.0 equiv.	NIS (1.1 equiv.) /K_2CO_3 (1.0 equiv.)	0
10	1.0 equiv.	2.0 equiv.	NIS (1.1 equiv.) /TsOH (0.1 equiv.)	62

[a] Reaction conditions: **4a** (0.2 mmol), **2a** (0.2 mmol), iodine sources (1.1 equiv.), DMSO (2 mL), 110 °C. b Isolated yield based on **2a**.

1.2 Synthesis of aryl-imidohydrazide



The amidrazones is synthesized according a modified method. General procedure for the synthesis of benzimidohydrazide (2a): A mixture of benzonitrile (1 mmol) and ethanol (12 mmol) was added to a 250 ml flask with a stirring bar and cooled to 0 °C. Then, AcCl (8 mmol) was added dropwise into the catalytic system. The reaction allowed stirring overnight at room temperature, and the volatiles were removed under reduced pressure to isolate the crude ethyl benzimidate hydrochloride (white solid). The residual was washed with ethyl acetate, and the pure ethyl benzimidate was dissolved into water. The above aqueous solution was neutralized by sodium bicarbonate, and the mixture was extracted with ethyl acetate. The oil layer was combined to obtain the ethyl benzimidate after removed the ethyl acetate under reduced pressure. Subsequiv.uently, ethyl benzimidate (1mmol) and hydrazine hydrate (1.1 mmol) were stirred in anhydrous EtOH (50 mL) overnight at RT. The volatiles was then removed, and the remaining syrup was crystallized on addition of a little ethyl acetate to give benzimidohydrazide (**2a**) as a pale yellow solid without further purification.

2. ^{1}H and ^{13}C NMR spectra data of the products

3,5-diphenyl-1,2,4-triazine (**3aa**): yellow solid; mp 79−84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 (s, 1H), 8.67 – 8.64 (dd, J = 6.8, 3.0 Hz, 2H), 8.29 – 8.26 (dd, J = 7.5, 2.0 Hz, 2H), 7.62 – 7.52 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 155.0, 144.1, 135.0, 133.6, 132.4, 131.7, 129.3, 128.8, 128.6, 128.3, 127.5. HRMS (ESI) calcd for $C_{15}H_{12}N_3$ $(M + H)^+$ 234.1026, found 234.1022. 0.2 mmol, 37mg.

5-(4-methoxyphenyl)-3-phenyl-1,2,4-triazine (**3ab**): yellow solid; mp 118−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.67 – 8.57 (m, 2H), 8.28 – 8.20 (m, 2H), 7.59 – 7.50 (m, 3H), 7.08 – 6.99 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 163.0, 154.4, 143.6, 135.2, 131.5, 129.3, 128.7, 128.2, 125.8, 114.7, 55.5. HRMS (ESI) calcd for $C_{16}H_{14}N_3O$ $(M + H)^+$ 264.1132, found 264.1129.0.2 mmol, 36mg.

5-(3-methoxyphenyl)-3-phenyl-1,2,4-triazine (**3ac**): yellow solid; mp 122−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.68 – 8.57 (m, 2H), 7.89 – 7.70 (m, 2H), 7.56 – 7.53 (dd, J = 6.4, 3.0 Hz, 3H), 7.49 – 7.44 (t, J = 8.0 Hz, 1H), 7.18 – 7.07 (m, 1H), 3.91 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 160.3, 154.8, 144.1, 135.0, 134.9, 131.6, 130.3, 128.7, 128.3, 119.8, 118.0, 112.7, 55.4. HRMS (ESI) calcd for $C_{16}H_{14}N_3O$ $(M + H)^+$ 264.1132, found 264.1129. 0.2mmol, 41mg.

5-(2-methoxyphenyl)-3-phenyl-1,2,4-triazine (**3ad**): yellow solid; mp 81−84 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.87 (s, 1H), 8.65 (dd, J = 6.7, 2.8 Hz, 2H), 8.31 (d, J = 7.6 Hz, 1H), 7.55 (dd, J = 10.4, 6.9 Hz, 4H), 7.17 (t, J = 7.6 Hz, 1H), 7.06 (d, J = 8.4 Hz, 1H), 3.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 158.5, 154.6, 148.1, 135.3, 133.4, 131.4, 131.3, 128.6, 128.1, 122.8, 121.4, 111.5, 55.6. HRMS (ESI) calcd for $C_{16}H_{14}N_3O$ $(M + H)^+$ 264.1132, found 264.1128. 0.2mmol, 47mg.

3-phenyl-5-(p-tolyl)-1,2,4-triazine (**3ae**): yellow solid; mp 100−102 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.67 – 8.57 (m, 2H), 8.28 – 8.20 (m, 2H), 7.59 – 7.50 (m, 3H), 7.08 – 6.99 (m, 2H), 3.88 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 154.8, 143.9, 143.2, 135.1, 131.5, 130.7, 123.0, 128.7, 128.2, 127.4, 21.5. HRMS (ESI) calcd for $C_{16}H_{14}N_3$ $(M + H)^+$ 248.1182, found 248.1179.0.2mmol, 38mg.

3-phenyl-5-(m-tolyl)-1,2,4-triazine (**3af**): yellow solid; mp 78−80 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.67 – 8.63 (ddd, J = 5.0, 2.3, 1.3 Hz, 2H), 8.07 – 8.02 (d, J = 12.7 Hz, 2H), 7.63 – 7.50 (m, 3H), 7.50 – 7.35 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 155.1, 144.2, 139.1, 135.0), 133.6, 133.2, 131.6, 129.2, 128.7, 128.3, 128.0, 124.7, 21.5. HRMS (ESI) calcd for $C_{16}H_{14}N_3$ $(M + H)^+$ 248.1182, found 248.1179. 0.2mmol, 42mg.

3-phenyl-5-(o-tolyl)-1,2,4-triazine (**3ag**): yellow solid; mp 122−124 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.32 (s, 1H), 8.66 – 8.56 (m, 2H), 7.66 – 7.59 (m, 1H), 7.57 – 7.49 (m, 3H), 7.43 (dd, J = 5.3, 3.3 Hz, 1H), 7.37 (t, J = 5.4 Hz, 2H), 2.59 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.8, 158.4, 147.2, 137.4, 134.9, 133.9, 131.7, 131.6, 130.8, 129.9, 128.7, 128.3, 126.5, 20.7. HRMS (ESI) calcd for $C_{16}H_{14}N_3$ $(M + H)^+$ 248.1182, found 248.1180. 0.2mmol, 36mg.

5-(3,4-dimethoxyphenyl)-3-phenyl-1,2,4-triazine (**3ah**): yellow solid; mp 138−141 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.50 (s, 1H), 8.67 – 8.56 (m, 2H), 7.87 – 1.86 (d, J = 2.1 Hz, 1H), 7.82 – 7.78 (dd, J = 8.4, 2.1 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.01 – 6.98 (dd, J = 8.5, 2.7 Hz, 1H), 4.03 (d, J = 2.1 Hz, 3H), 3.96 (d, J = 2.3 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.9, 154.4, 152.9, 149.6, 143.6, 1351, 131.4, 128.6, 128.1, 126.0, 121.2, 111.1, 109.6, 56.0. HRMS (ESI) calcd for $C_{17}H_{16}N_3O_2$ $(M + H)^+$ 294.1237, found 294.1232. 0.2mmol, 44mg.

5-(4-fluorophenyl)-3-phenyl-1,2,4-triazine (**3ai**): yellow solid; mp 153−156 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.64 – 8.61 (dd, J = 6.6, 3.1 Hz, 2H), 8.32 – 8.27 (dd, J = 8.8, 5.3 Hz, 2H), 7.62 – 7.49 (m, 3H), 7.29 – 7.24 (dd, J = 9.2, 7.9 Hz, 2H). ^{13}C NMR (75 MHz, CDCl3) δ 167.2, 163.8, 163.2, 153.9, 143.8, 134.8, 131.7, 129.9, 129.7, 128.8, 128.3, 116.7, 116.4. HRMS (ESI) calcd for $C_{15}H_{11}FN_3$ $(M + H)^+$ 252.0932, found 252.0928. 0.2mmol, 38mg.

5-(4-chlorophenyl)-3-phenyl-1,2,4-triazine (**3aj**): yellow solid; mp 161−164 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.54 (s, 1H), 8.65 – 8.54 (m, 2H), 8.24 – 8.13 (m, 2H), 7.62 – 7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 153.8, 143.7, 138.9, 134.7, 132.0, 131.8, 129.6, 128.8, 128.7, 128.3. HRMS (ESI) calcd for $C_{15}H_{11}ClN_3$ $(M + H)^+$ 268.0636, found 268.0634. 0.2mmol, 38mg.

5-(3,4-dichlorophenyl)-3-phenyl-1,2,4-triazine (**3ak**): yellow solid; mp 162−165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.65 – 8.58 (m, 2H), 8.39 – 8.38 (d, J = 2.1 Hz, 1H), 8.09 –8.05 (dd, J = 8.4, 2.1 Hz, 1H), 7.67 – 7.64 (d, J = 8.4 Hz, 1H), 7.61 – 7.51 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 152.8, 143.6, 137.0, 134.5, 134.1, 133.6, 132.0, 131.3, 129.3, 128.9, 128.4, 126.4. HRMS (ESI) calcd for $C_{15}H_{10}Cl_2N_3$ $(M + H)^+$ 302.0247, found 302.0245. 0.2mmol, 42mg.

5-(naphthalen-1-yl)-3-phenyl-1,2,4-triazine (**3am**): yellow solid; mp 79−81 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.68 – 8.62 (m, 2H), 8.39 – 8.35 (dd, J = 5.5, 4.2 Hz, 1H), 8.39 – 8.35 (d, J = 8.2 Hz, 1H), 7.99 – 7.92 (m, 1H), 7.84 – 7.81 (dd, J = 7.2, 1.2 Hz, 1H), 7.65 – 7.53 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 158.1, 148.0, 134.9, 134.0, 132.9, 132.1, 131.8, 131.7, 130.4, 129.1, 128.8, 128.4, 127.7, 126.6, 125.2, 124.4. HRMS (ESI) calcd for $C_{19}H_{14}N_3$ $(M + H)^+$ 284.1182, found 284.1179. 0.2mmol, 43mg.

5-([1,1'-biphenyl]-4-yl)-3-phenyl-1,2,4-triazine (**3an**): yellow solid; mp 121−123 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.66 – 8.63 (dd, J = 6.7, 3.0 Hz, 2H), 8.31 – 8.28 (d, J = 8.2 Hz, 2H), 7.77 – 7.74 (d, J = 7.8 Hz, 2H), 7.65 – 7.62 (d, J = 7.4 Hz, 2H), 7.57 – 7.53 (dd, J = 6.5, 3.7 Hz, 3H), 7.51 – 7.34 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.2, 154.5, 145.1, 143.9, 139.5, 135.0, 132.3, 131.6, 128.9, 128.7, 128.3, 128.2, 127.9, 127.8, 127.1. HRMS (ESI) calcd for $C_{21}H_{16}N_3$ $(M + H)^+$ 310.1339, found 310.1337. 0.2mmol, 47mg.

3-(furan-2-yl)-5-phenyl-1,2,4-triazine (**3ao**): yellow solid; mp 89 −93 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.44 – 9.43 (d, J = 1.4 Hz, 1H), 8.64 – 8.52 (m, 2H), 7.72 (s, 1H), 7.64 – 7.47 (m, 5H), 6.6 – 6.65 (dt, J = 3.3, 1.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.1, 149.3, 146.9, 146.8, 142.3, 134.8, 131.6, 128.7, 128.2, 116.0, 113.2. HRMS (ESI) calcd for $C_{13}H_{10}N_3O$ $(M + H)^+$ 224.0818, found 224.0815. 0.2mmol, 35mg.

5-phenyl-3-(p-tolyl)-1,2,4-triazine (**3ba**): yellow solid; mp 94 −99 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.56 – 8.53 (d, J = 8.2 Hz, 2H), 8.28 – 8.25 (dd, J = 7.4, 2.0 Hz, 2H), 7.62 – 7.53 (m, 3H), 7.37 – 7.34 (d, J = 8.1 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 154.9, 143.9, 142.1, 133.8, 132.3, 132.2, 129.5, 129.3, 128.3, 127.5, 21.6. HRMS (ESI) calcd for $C_{16}H_{14}N_3$ $(M + H)^+$ 248.1182, found 248.1179. 0.2mmol, 42mg.

5-phenyl-3-(m-tolyl)-1,2,4-triazine (**3bb**): yellow solid; mp 59−64 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.55 (s, 1H), 8.46 – 8.42 (dd, J = 6.1, 5.3 Hz, 2H), 8.30 – 8.19 (m, 2H), 7.62 – 7.51 (m, 3H), 7.46 – 7.41 (t, J = 7.5 Hz, 1H), 7.39 – 7.31 (m, 1H), 2.47 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.4, 154.9, 144.0, 138.4, 134.9, 133.6, 132.4, 132.2, 129.2, 128.8, 128.6, 127.5, 125.5, 21.4. HRMS (ESI) calcd for $C_{16}H_{14}N_3$ $(M + H)^+$ 248.1182, found 248.1180. 0.2mmol, 39mg.

3-(4-methoxyphenyl)-5-phenyl-1,2,4-triazine (**3bc**): yellow solid; mp 170−173 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.51 (s, 1H), 8.63 – 8.57 (m, 2H), 8.28 – 8.22 (m, 2H), 7.60 – 7.53 (m, 3H), 7.08 – 7.02 (m, 2H), 3.89 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.0, 162.6, 154.8, 143.5, 133.8, 132.2, 130.0, 129.2, 129.0, 127.5, 114.1, 55.3. HRMS (ESI) calcd for $C_{16}H_{14}N_3O$ $(M + H)^+$ 264.1132, found 264.1128. 0.2mmol, 46mg.

3-(4-fluorophenyl)-5-phenyl-1,2,4-triazine (**3bd**): yellow solid; mp 163−165 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.58 (s, 1H), 8.72 – 8.61 (m, 2H), 8.34 – 8.19 (m, 2H), 7.66 – 7.51 (m, 3H), 7.26 – 7.20 (dd, J = 13.9, 5.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 166.9, 163.6, 162.46, 155.06, 144.0, 133.56, 132.56, 131.2, 130.6, 130.5, 129.4, 127.54, 116.0, 115.7. HRMS (ESI) calcd for $C_{15}H_{11}FN_3$ $(M + H)^+$ 252.0932, found 252.0931. 0.2mmol, 38mg.

3-(4-chlorophenyl)-5-phenyl-1,2,4-triazine (**3be**): yellow solid; mp 118−122 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.59 – 9.50 (m, 1H), 8.59 – 8.47 (m, 2H), 8.27 – 8.15 (m, 2H), 7.68 – 7.51 (m, 3H), 7.51 – 7.42 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.3, 154.9, 144.1, 137.9, 133.3,133.3 132.5, 129.5, 129.3, 128.9, 127.4. HRMS (ESI) calcd for $C_{15}H_{11}ClN_3$ $(M + H)^+$ 268.0636, found 268.0633. 0.2mmol, 40mg.

3-(4-bromophenyl)-5-phenyl-1,2,4-triazine (**3bf**): yellow solid; mp 112−114 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.61 – 9.49 (m, 1H), 8.50 – 8.44 (dd, J = 11.8, 5.4 Hz, 2H), 8.24 – 8.20 (t, J = 6.8 Hz, 2H), 7.75 – 7.45 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.4, 154.9, 144.2, 133.82, 133.3, 132.5, 131.9, 129.7, 129.3, 127.5, 126.6. HRMS (ESI) calcd for $C_{15}H_{11}BrN_3$ $(M + H)^+$ 312.0131, found 312.0129. 0.2mmol, 51mg.

5-phenyl-3-(pyridin-2-yl)-1,2,4-triazine (**3bg**): yellow solid; mp 129 −133 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.69 (s, 1H), 8.91 – 8.90 (d, J = 4.1 Hz, 1H), 8.66 – 8.64 (d, J = 7.9 Hz, 1H), 8.29 – 8.26 (dd, J = 7.8, 1.1 Hz, 2H), 7.96 – 7.86 (m, 1H), 7.62 – 7.52 (m, 3H), 7.50 – 7.42 (m, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 162.7, 155.7,

152.9, 150.4, 145.2, 137.0, 133.3, 132.6, 129.3, 127.8, 125.5, 124.1. HRMS (ESI) calcd for $C_{14}H_{11}N_4$ (M + H)+ 235.0978, found 235.0975. 0.2mmol, 27mg.

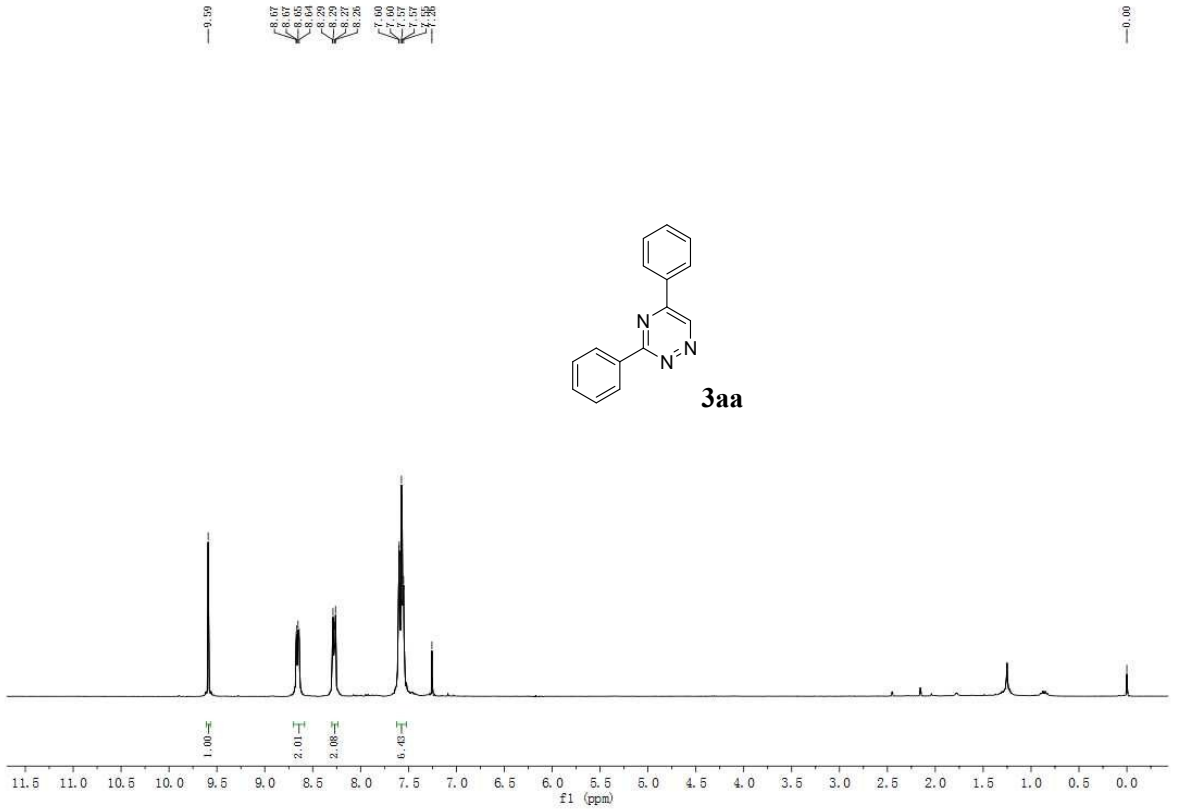
5-(4-bromophenyl)-3-phenyl-1,2,4-triazine (**3ar**): yellow solid; mp 173 −176 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.56 (s, 1H), 8.66 – 8.58 (m, 2H), 8.17 – 8.10 (m, 2H), 7.74 – 7.67 (m, 2H), 7.60 – 7.50 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 163.3, 154.0, 143.7, 134.77, 132.6, 132.5, 131.8, 128.9, 128.8, 128.3, 127.4. HRMS (ESI) calcd for $C_{15}H_{11}BrN_3$ $(M + H)^+$ 312.0131, found 312.0129. 0.2mmol, 36mg;

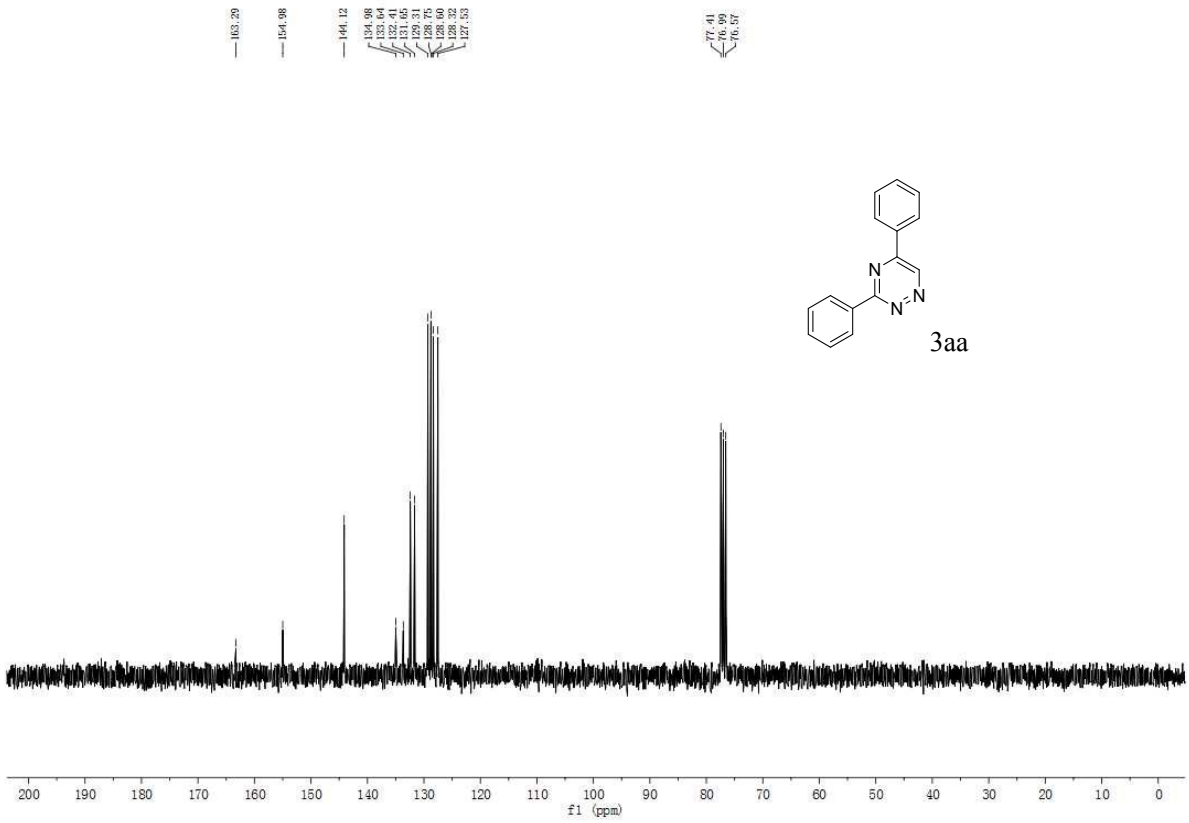
5-(3-fluorophenyl)-3-phenyl-1,2,4-triazine (**3as**): yellow solid; mp 103 −106 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.57 (s, 1H), 8.66 – 8.63 (dd, J = 6.6, 3.1 Hz, 2H), 8.05 – 8.01 (dd, J = 8.1, 5.3 Hz, 2H), 7.62 – 7.53 (m, 4H), 7.34 – 7.28 (td, J = 8.3, 2.5 Hz, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.0, 163.4, 161.7, 153.8, 143.9, 136.0, 135.9, 134.7, 131.8, 131.0, 130.9, 128.8, 128.4, 123.1, 123.0, 119.6, 119.3, 114.7, 114.3. HRMS (ESI) calcd for $C_{15}H_{11}FN_3$ $(M + H)^+$ 252.0932, found 252.0929. 0.2mmol, 26mg.

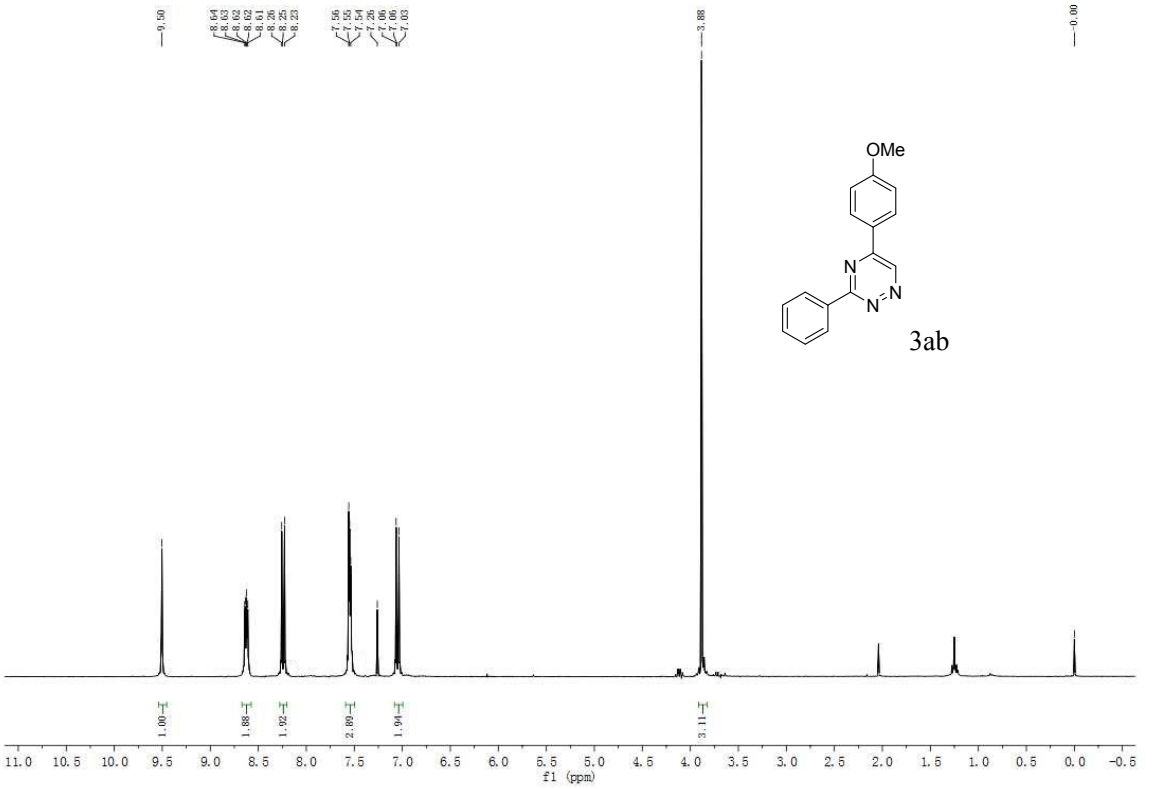
5-(2-chlorophenyl)-3-phenyl-1,2,4-triazine (**3at**): yellow solid; mp 108 −113 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.62 (s, 1H), 8.64 – 8.61 (dd, J = 6.3, 2.4 Hz, 2H), 7.89 – 7.81 (m, 1H), 7.62 – 7.44 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 1637, 155.9, 147.6, 134.8, 133.7, 132.7, 132.1, 132.0, 131.8, 130.7, 128.8, 128.4, 127.6. HRMS (ESI) calcd for $C_{15}H_{11}ClN_3$ $(M + H)^+$ 268.0636, found 268.0633. 0.2mmol, 31 mg.

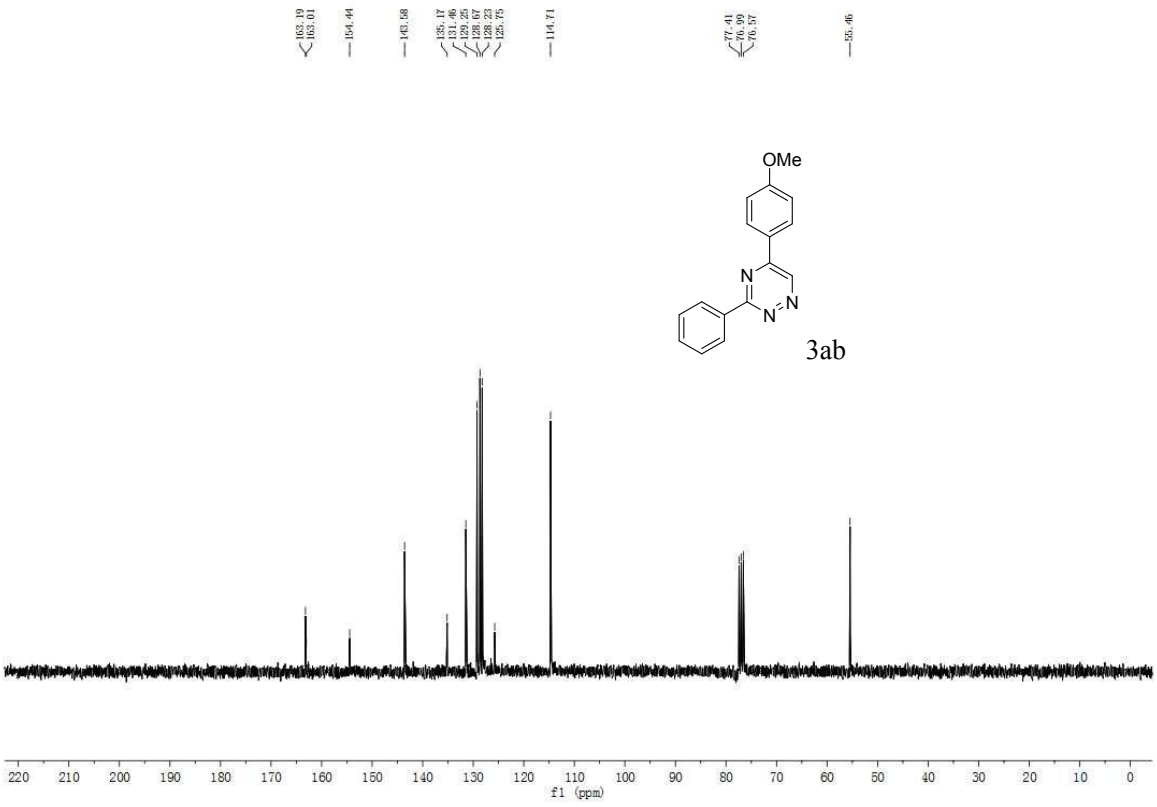
3,5,6-triphenyl-1,2,4-triazine (**8aa**): yellow solid; mp 127 − 131 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.71 – 8.64 (m, 2H), 7.70 – 7.59 (m, 4H), 7.58 – 7.53 (m, 3H), 7.45 – 7.33 (m, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.1, 155.4, 135.8, 135.5, 134.7, 131.5, 130.6, 129.8, 129.5, 129.4, 128.8, 128.5, 128.4, 128.3. HRMS (ESI) calcd for $C_{21}H_{16}N_3$ $(M + H)^+$ 310.1339, found 310.1336. 0.2 mmol, 32 mg.

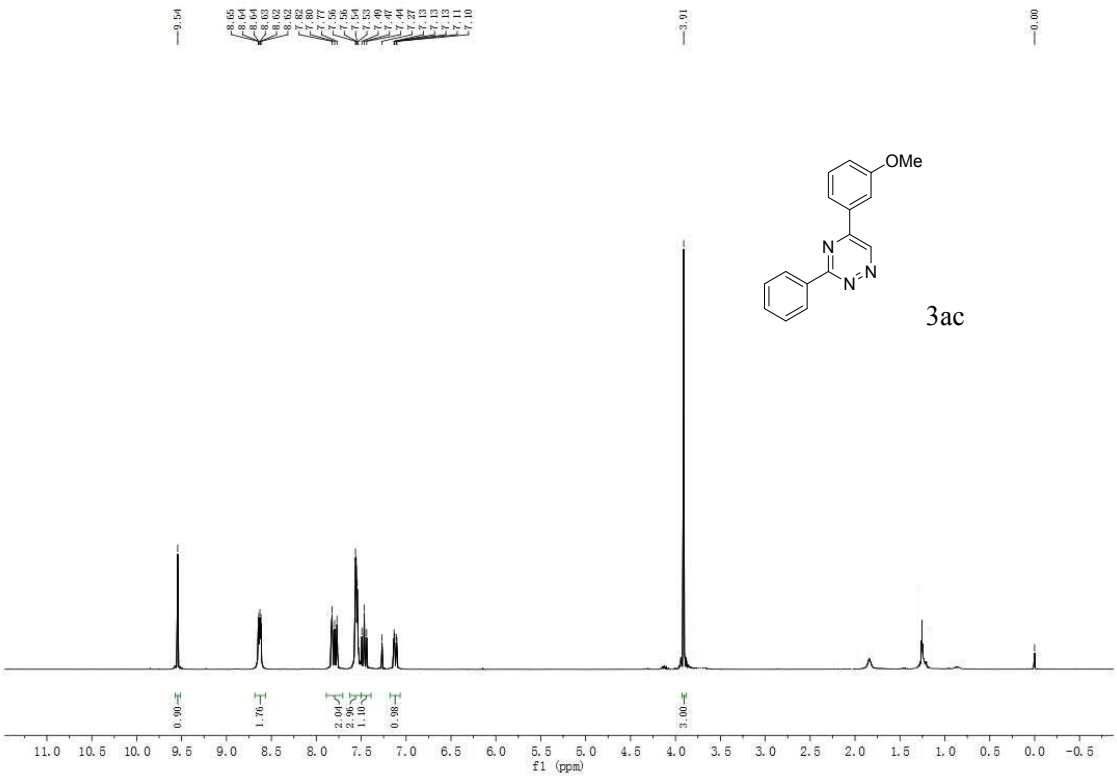
3. ^{1}H and ^{13}C NMR spectra of the products

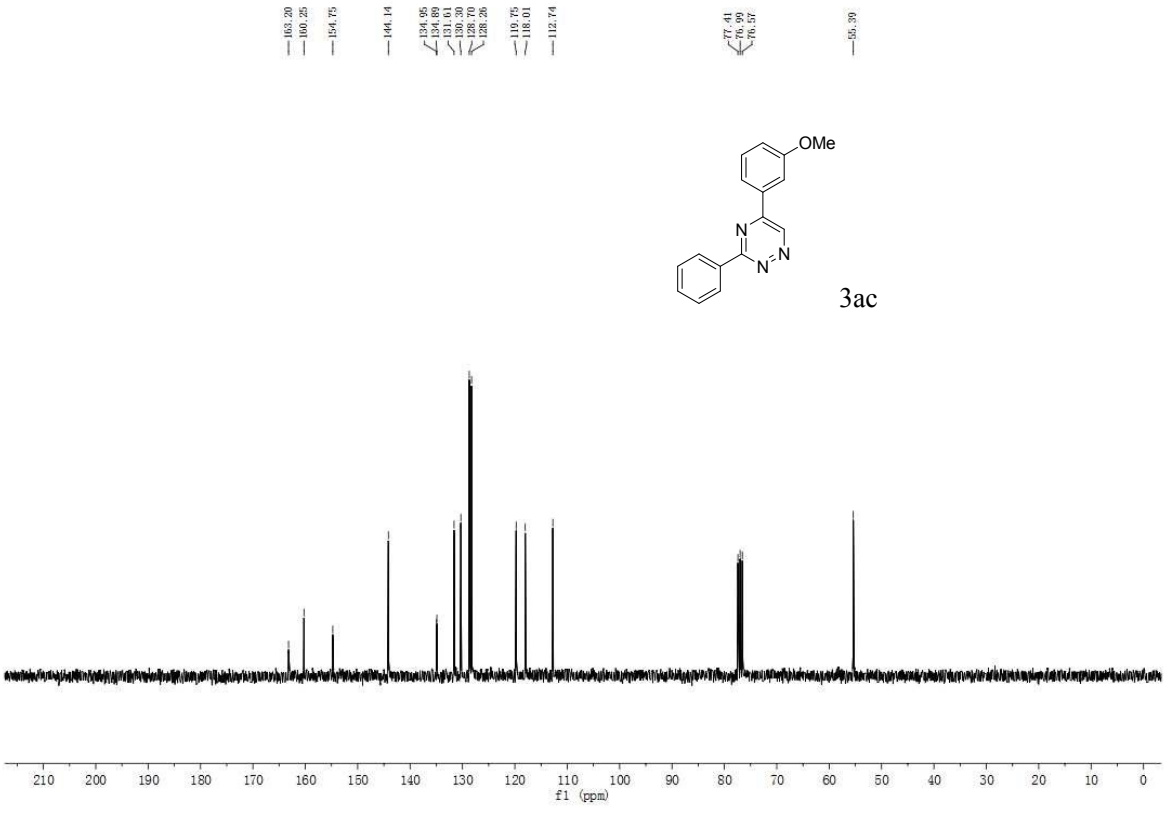


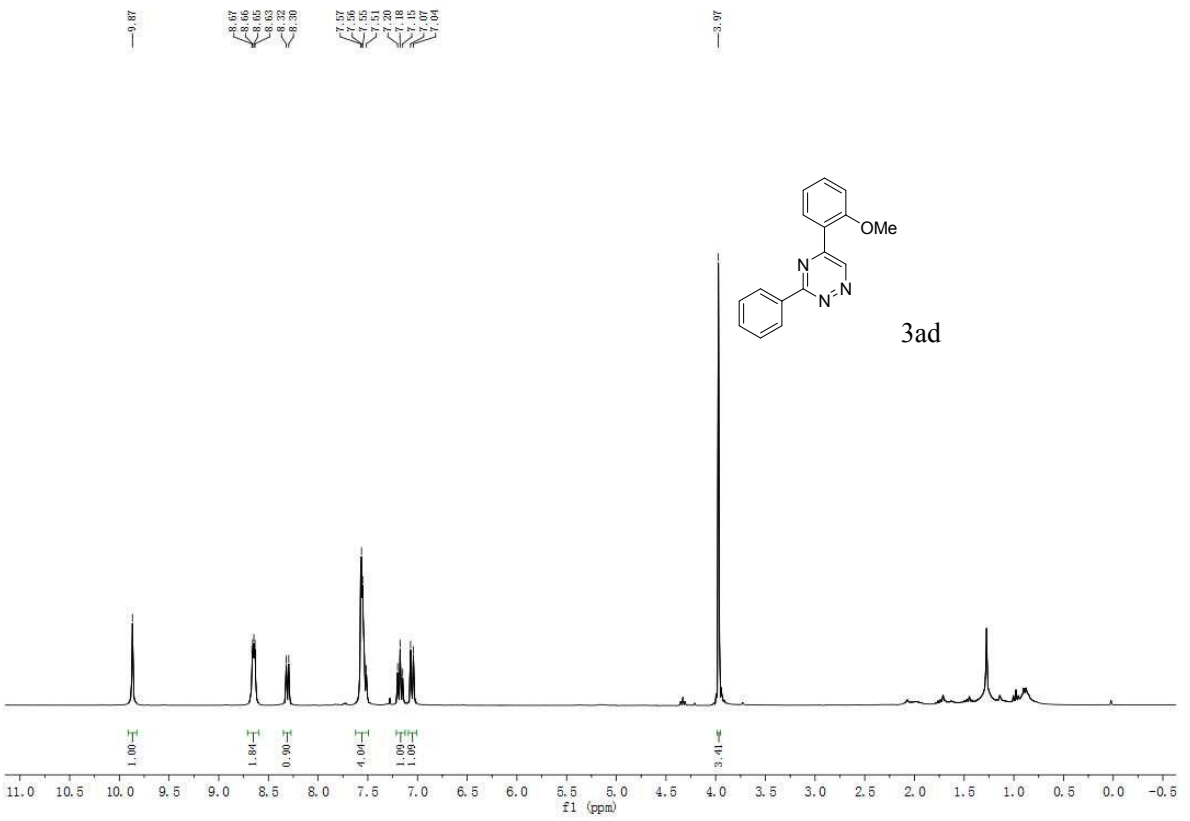


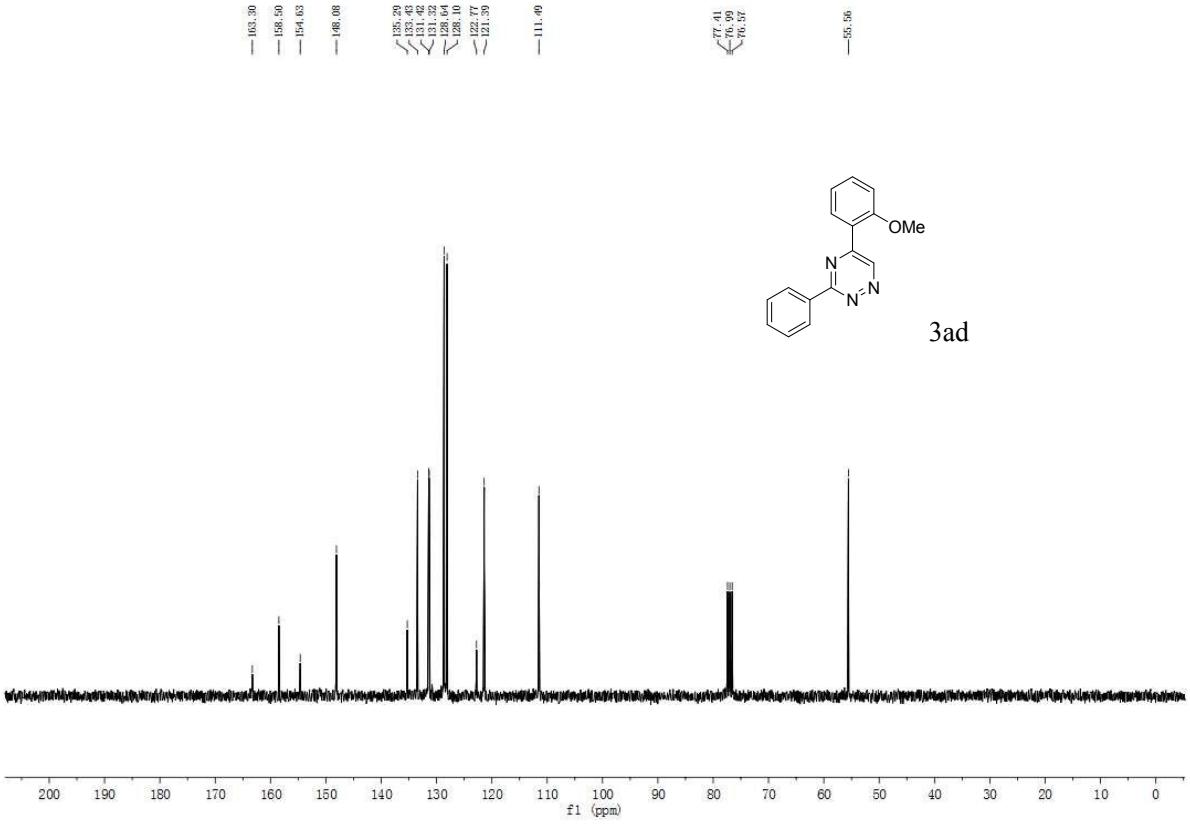

9.50
8.64
8.63
8.62
8.62
8.61
8.26
8.25
8.23
7.56
7.55
7.54
7.36
7.06
7.06
7.03
3.88
0.00
OMe
N
N
N
3ab
1.00
1.88
1.92
2.89
1.94
3.11
f1 (ppm)

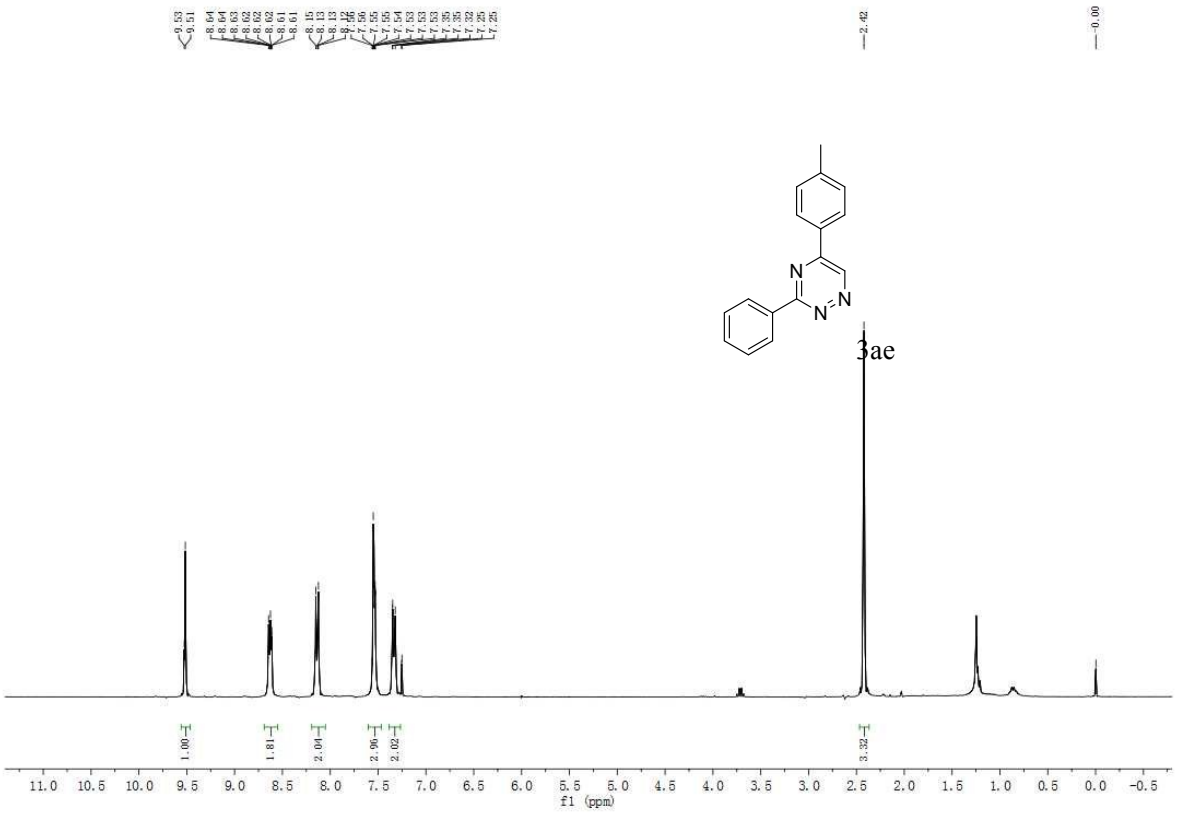

163.19
163.01
154.44
143.58
135.17
131.46
129.25
128.67
128.23
125.75
114.71
77.41
76.99
76.57
55.46
OMe
N
N
N
3ab
f1 (ppm)

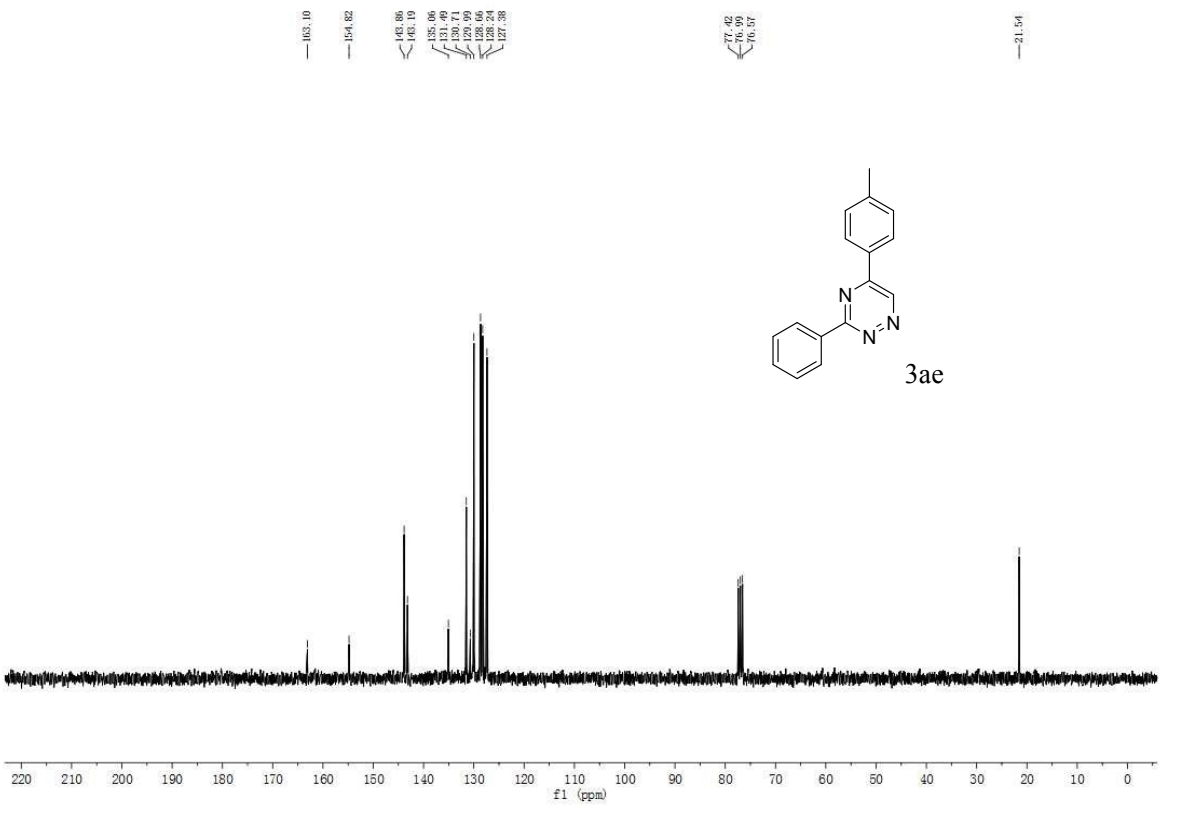

9.54
8.65
8.64
8.64
8.63
8.62
8.62
7.80
7.77
7.56
7.56
7.54
7.53
7.49
7.47
7.27
7.13
7.13
7.11
7.10
3.91
0.00
OMe
N
N
N
3ac
0.90
1.76
2.04
2.96
1.10
0.98
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.20
160.25
154.75
144.14
134.95
134.89
131.61
130.30
128.70
128.26
119.75
118.01
112.74
77.41
76.99
76.57
55.39
OMe
N
N
N
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

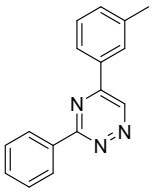

9.87
8.67
8.66
8.65
8.63
8.32
8.30
7.57
7.56
7.55
7.51
7.20
7.18
7.15
7.07
7.04
3.97
OMe
N
N
N
3ad
1.00
1.84
0.90
4.04
1.09
1.09
3.41
f1 (ppm)


163.30
158.50
154.63
148.08
135.29
133.43
131.42
131.32
128.64
128.10
122.77
121.39
111.49
77.41
76.99
76.57
55.56
OMe
N
N
N
3ad
f1 (ppm)

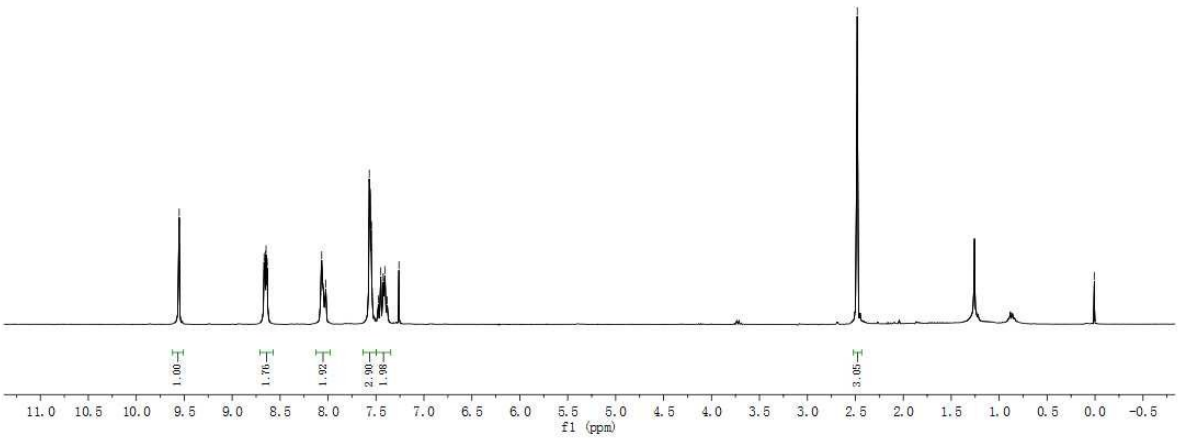

9.53
9.51
8.64
8.64
8.63
8.62
8.62
8.62
8.61
8.61
8.15
8.13
8.13
7.56
7.55
7.55
7.54
7.53
7.53
7.35
7.35
7.32
7.25
7.25
2.42
0.00
3ae
1.00
1.81
2.04
2.96
2.02
3.32
f1 (ppm)


163.10
154.82
145.86
145.19
135.06
131.49
130.71
130.69
129.89
128.56
128.24
127.38
77.42
76.99
76.57
21.54
3ae
f1 (ppm)

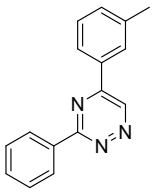

9.55
8.67
8.66
8.66
8.65
8.65
8.64
8.64
8.63
8.07
8.02
7.57
7.57
7.56
7.56
7.55
7.55
7.54
7.47
7.45
7.42
7.41
7.38
7.26
2.48
0.01



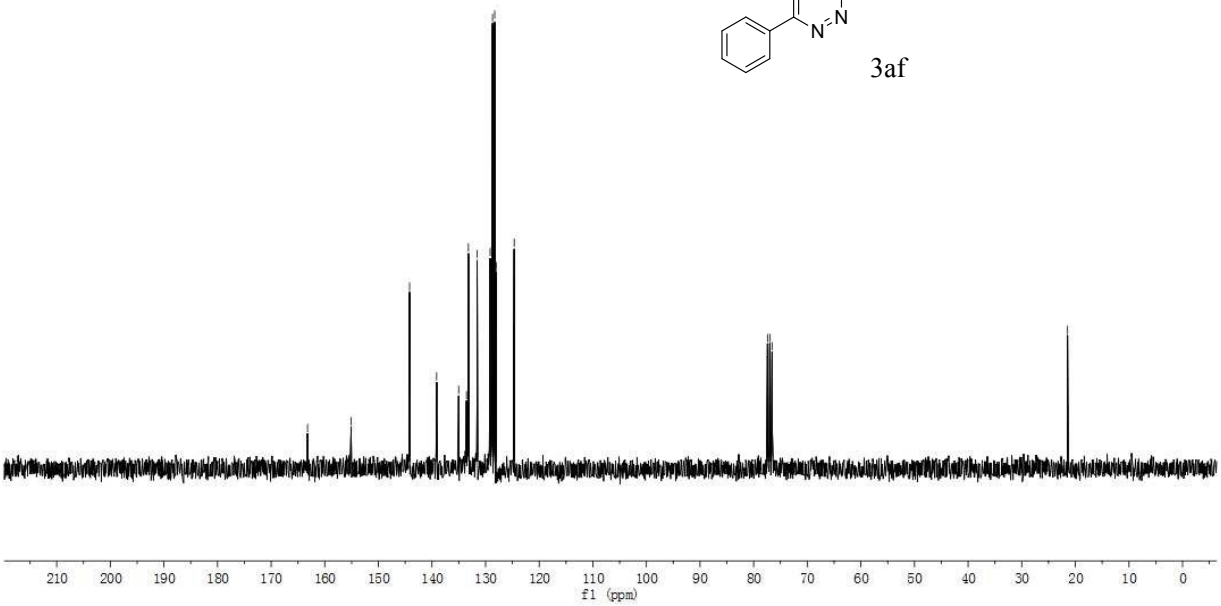
3af

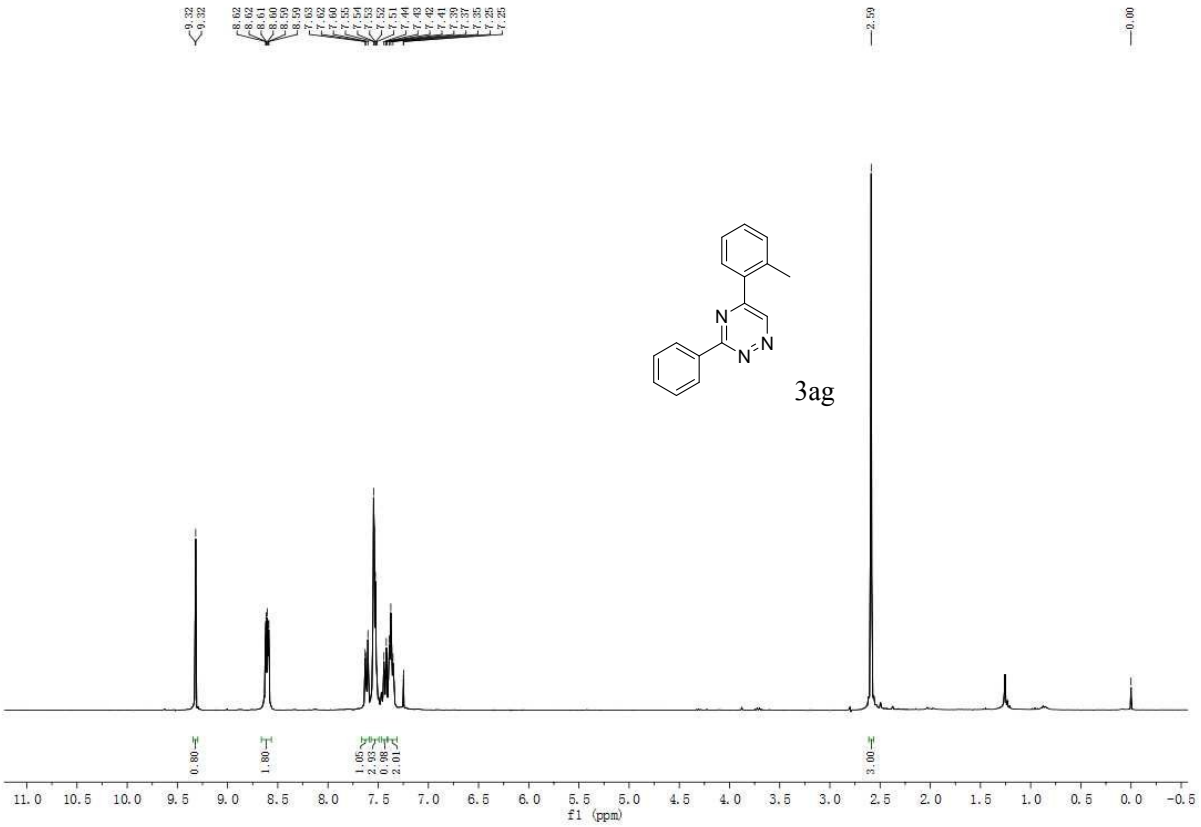

1.00
1.76
1.92
2.90
1.98
3.05
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

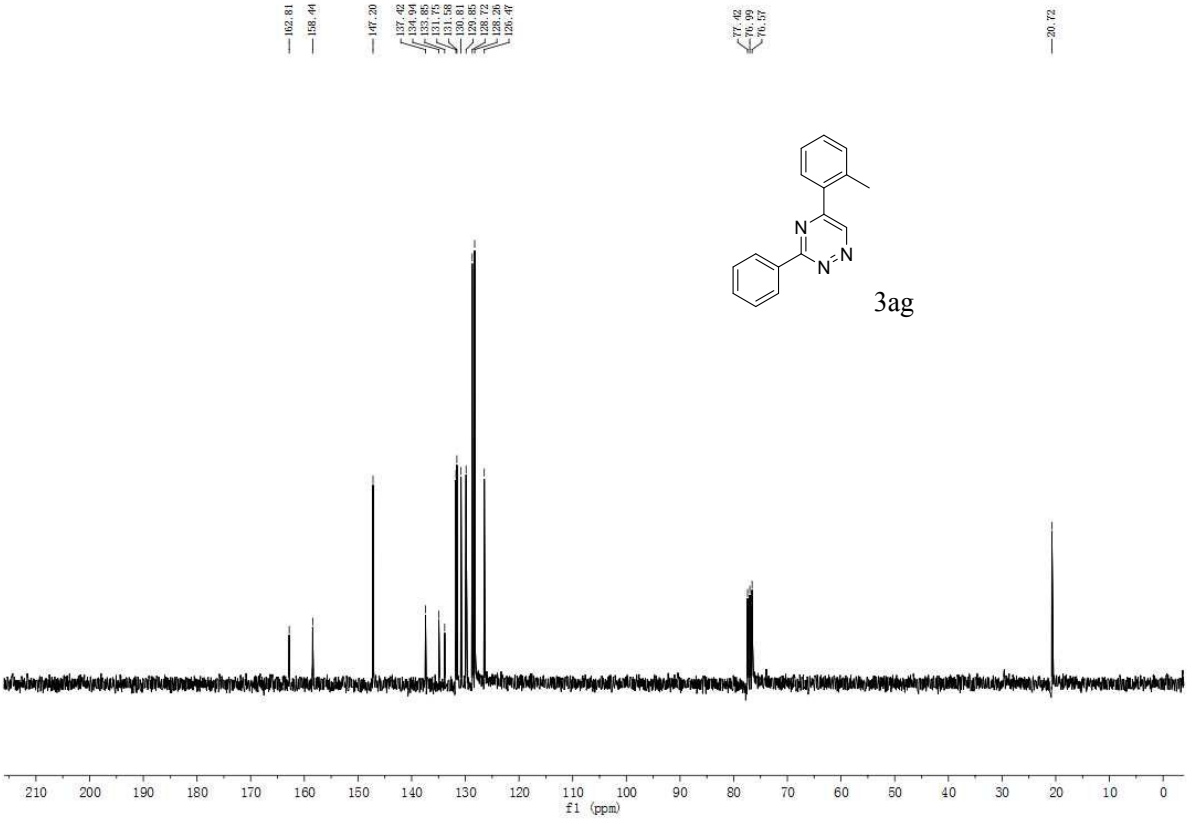

163.22
155.08
144.18
139.13
135.02
133.56
133.20
131.57
129.16
128.70
128.29
128.03
124.67
77.42
76.99
76.57
21.46

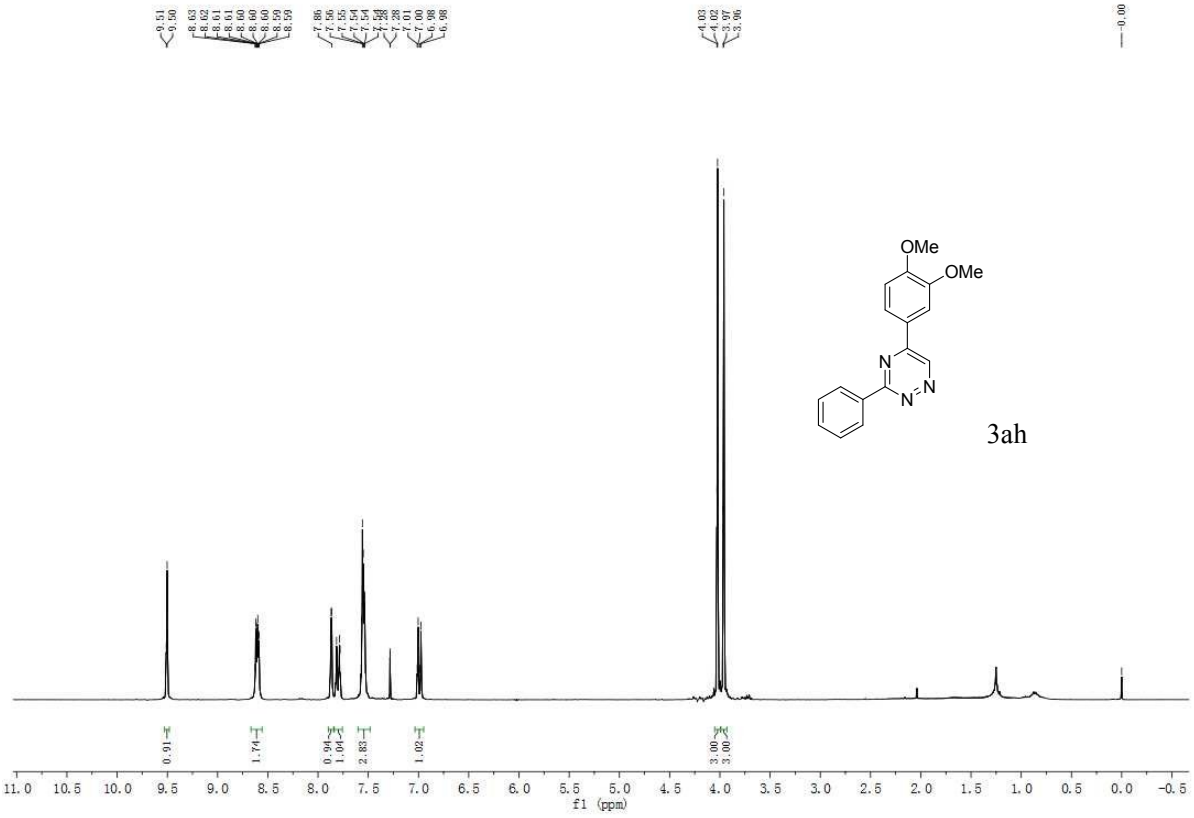


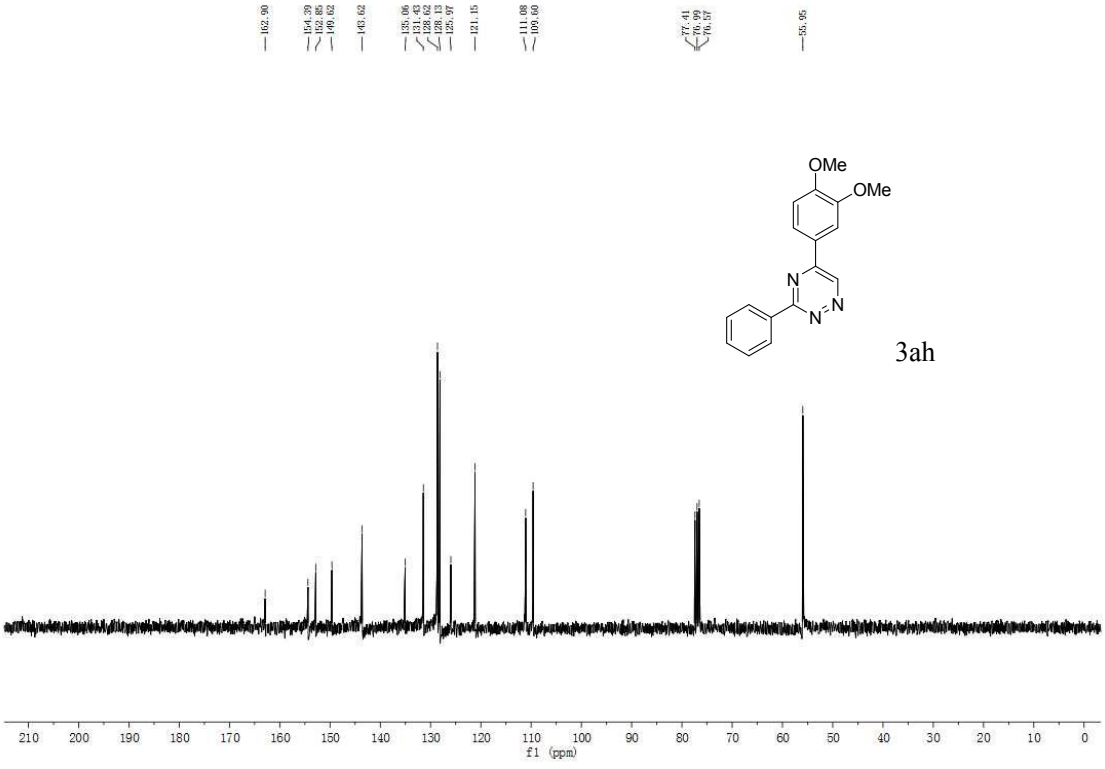
3af

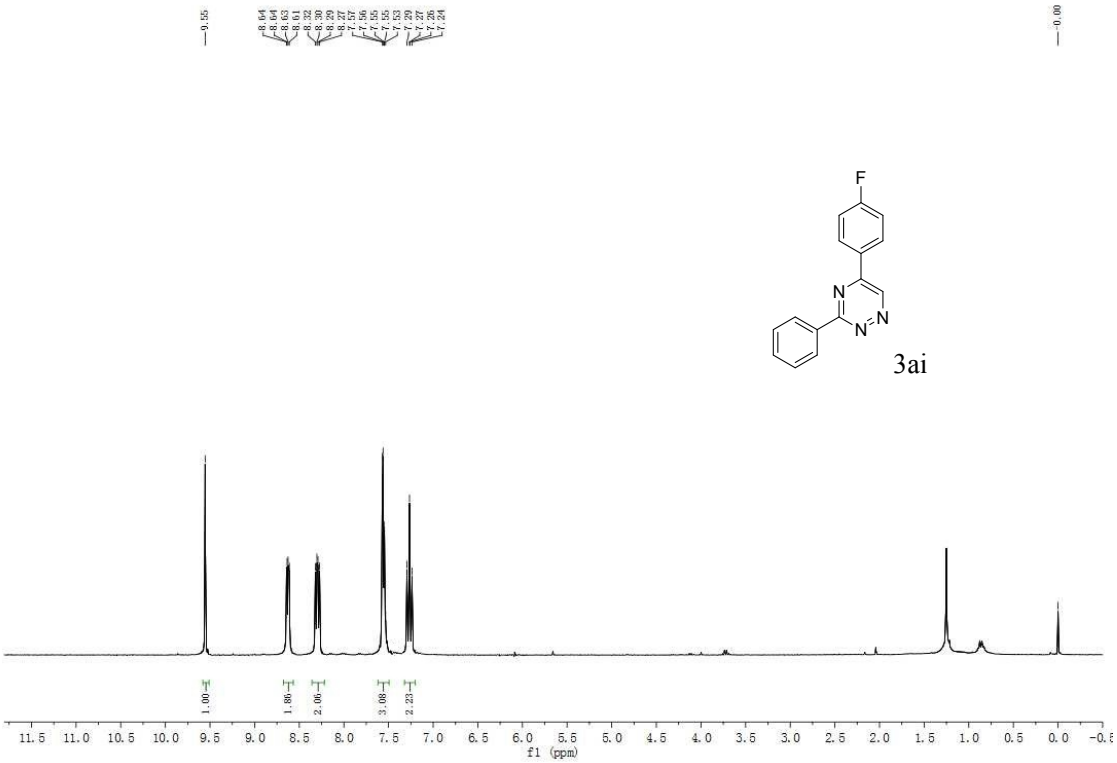

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

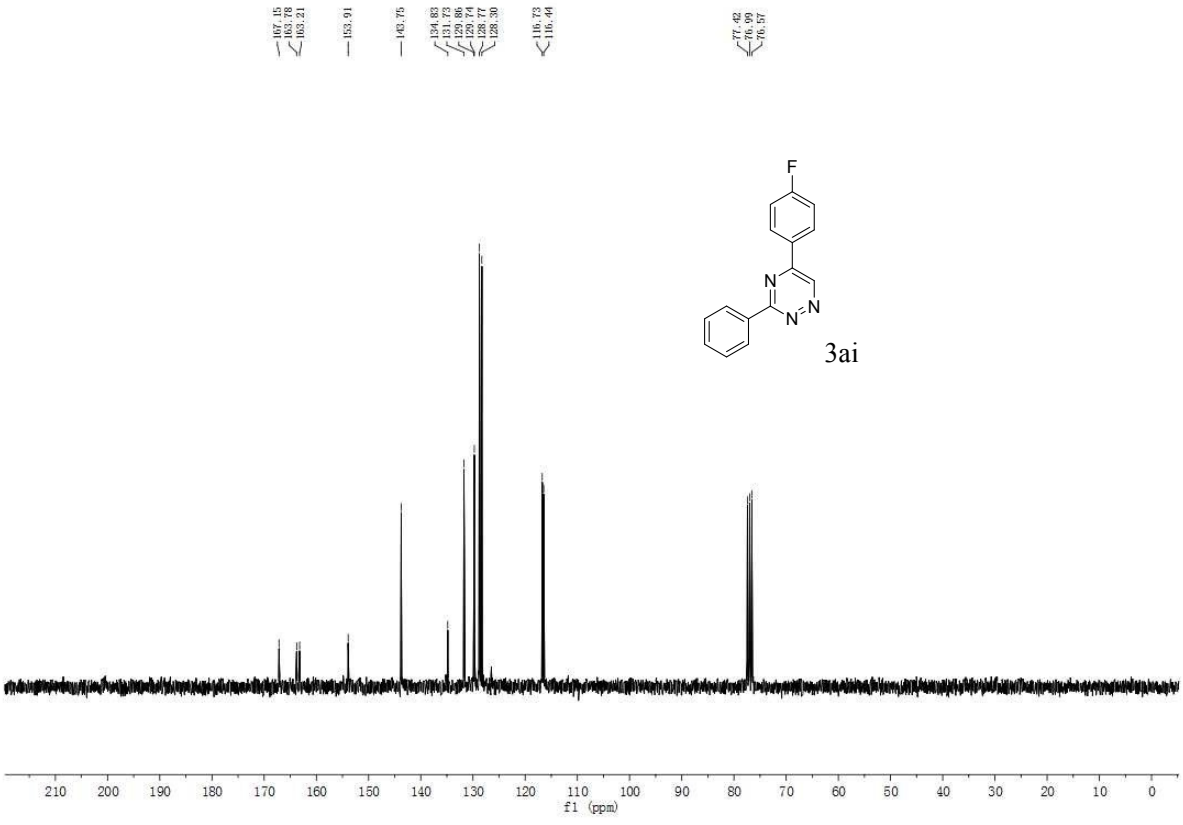

9.32
9.32
8.62
8.62
8.61
8.60
8.59
8.59
7.63
7.62
7.60
7.55
7.54
7.53
7.52
7.51
7.44
7.43
7.42
7.41
7.39
7.37
7.35
7.25
7.25
2.59
0.00
3ag
0.80
1.80
1.05
2.93
0.98
2.01
3.00
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

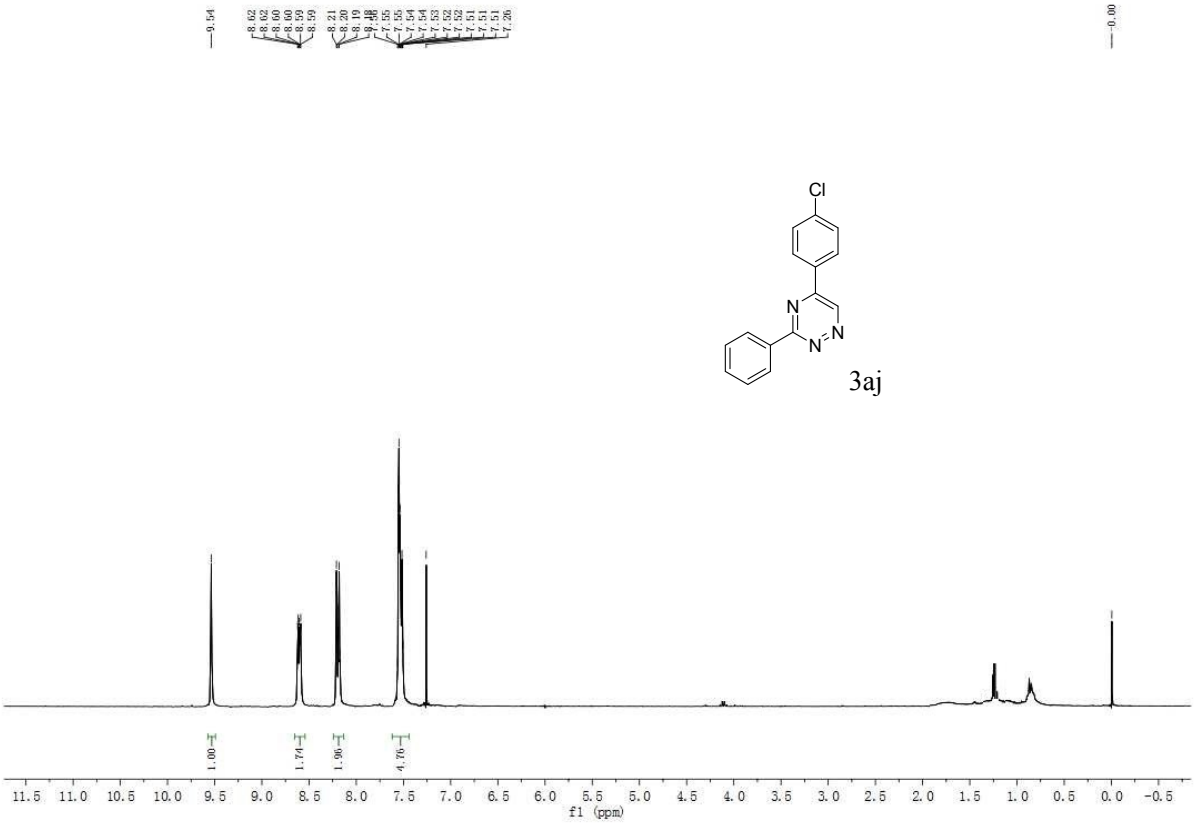

162.81
158.44
147.20
137.42
134.94
133.85
131.75
131.58
130.81
129.85
128.72
128.26
126.47
77.42
76.99
76.57
20.72
3ag
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

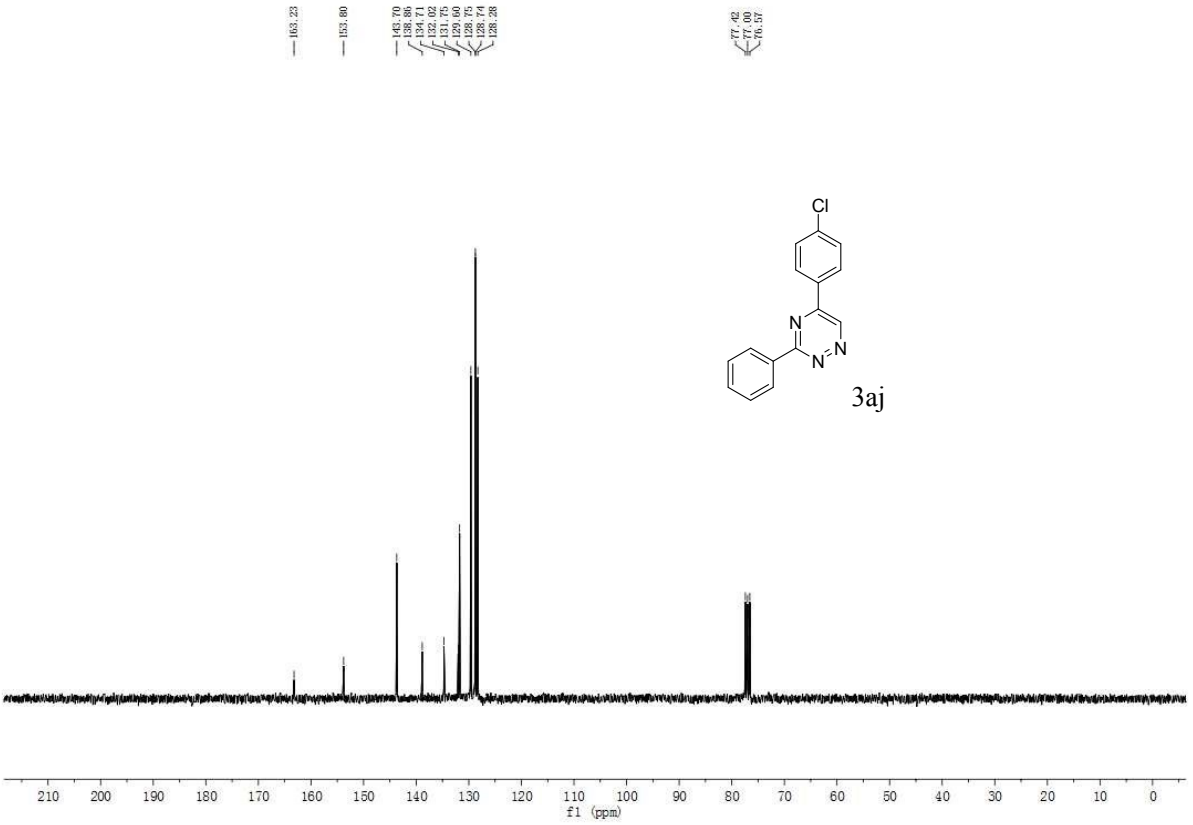

OMe
OMe
N
N
N
3ah
f1 (ppm)


OMe
OMe
N
N
N
3ah
f1 (ppm)

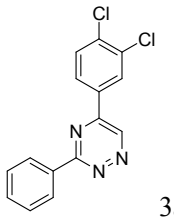

9.55
8.64
8.64
8.63
8.61
8.32
8.30
8.29
8.27
7.97
7.96
7.95
7.93
7.53
7.29
7.27
7.26
7.24
-0.00
F
N
N
N
3ai
1.00
1.86
2.06
3.08
2.23
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.15
163.78
163.21
153.91
143.75
134.83
131.73
129.86
129.74
128.77
128.30
116.73
116.44
77.42
76.99
76.57
F
N
N
N
3ai
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

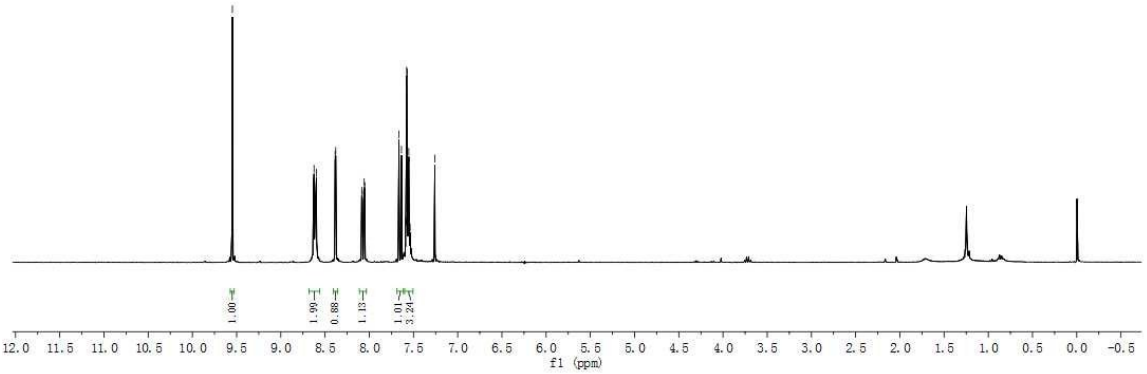

9.54
8.02
8.02
8.00
8.00
8.00
8.00
8.21
8.20
8.19
8.19
7.55
7.55
7.54
7.54
7.53
7.52
7.52
7.51
7.51
7.51
7.51
7.26
0.00
Cl
N
N
N
3aj
1.00
1.74
1.96
4.76
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


163.23
153.80
143.70
138.86
134.71
132.02
131.75
129.60
128.73
128.34
128.28
77.42
77.00
76.57
Cl
N
N
N
3aj
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

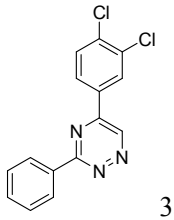

9.55
8.63
8.62
8.61
8.61
8.60
8.39
8.38
8.06
8.05
7.66
7.64
7.58
7.56


Cl
Cl
N
N
N

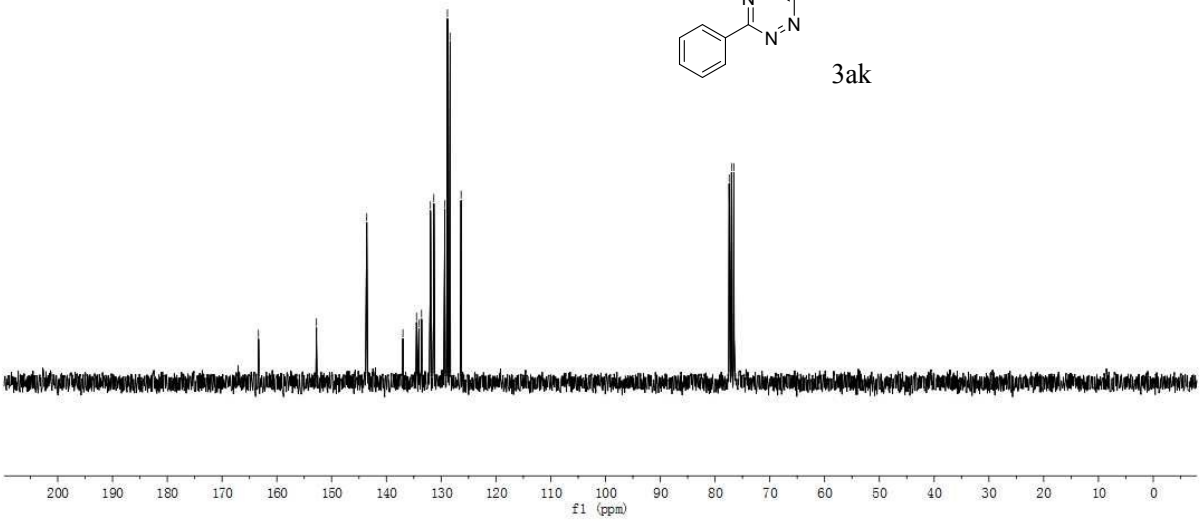
3ak

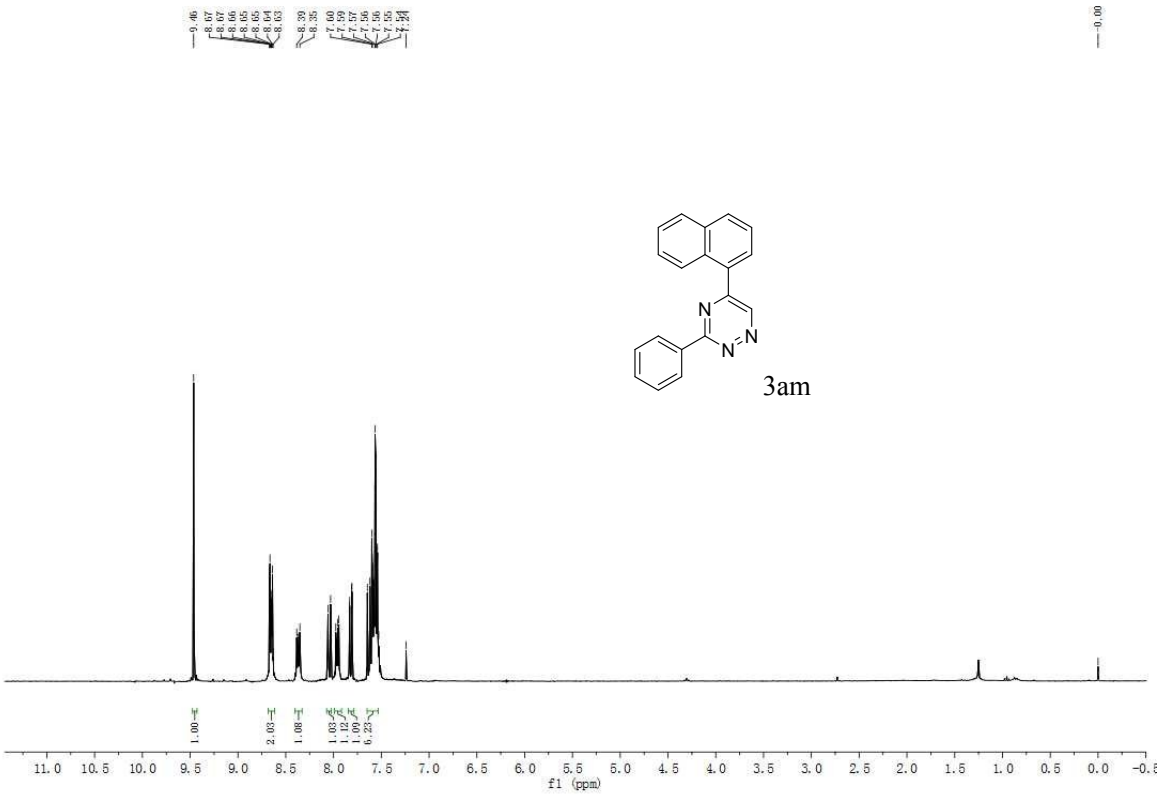

1.00
1.99
0.88
1.13
1.01
3.24
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

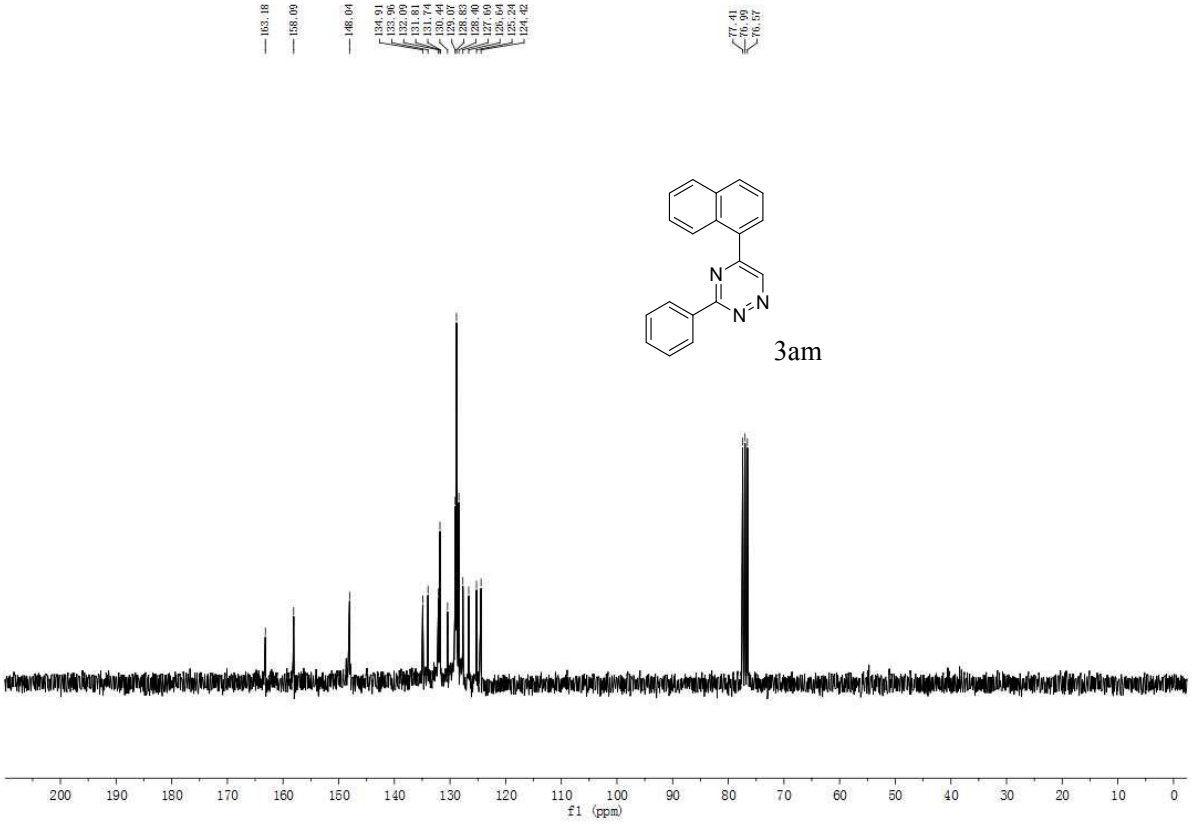

163.35
152.77
143.59
136.97
134.50
134.07
133.58
131.96
131.34
129.33
128.85
128.36
126.36
77.41
76.99
76.56

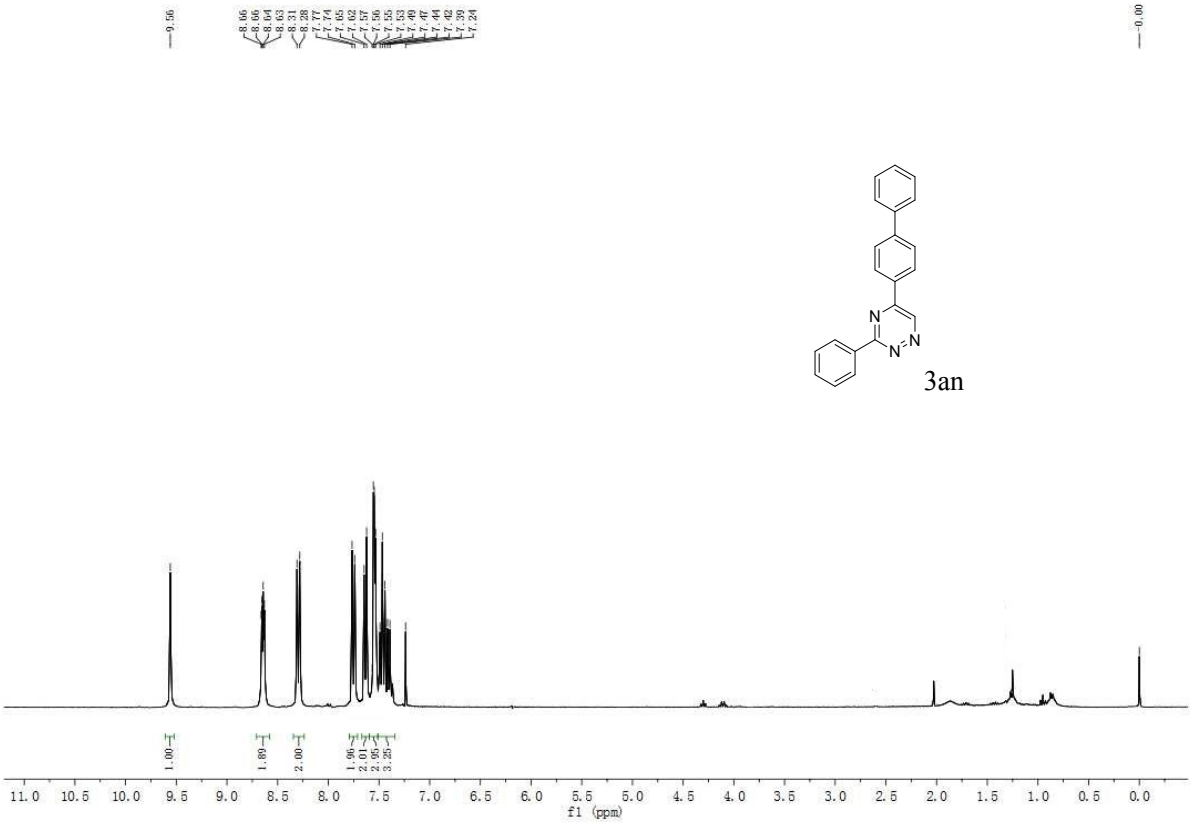

Cl
Cl
N
N
N

3ak

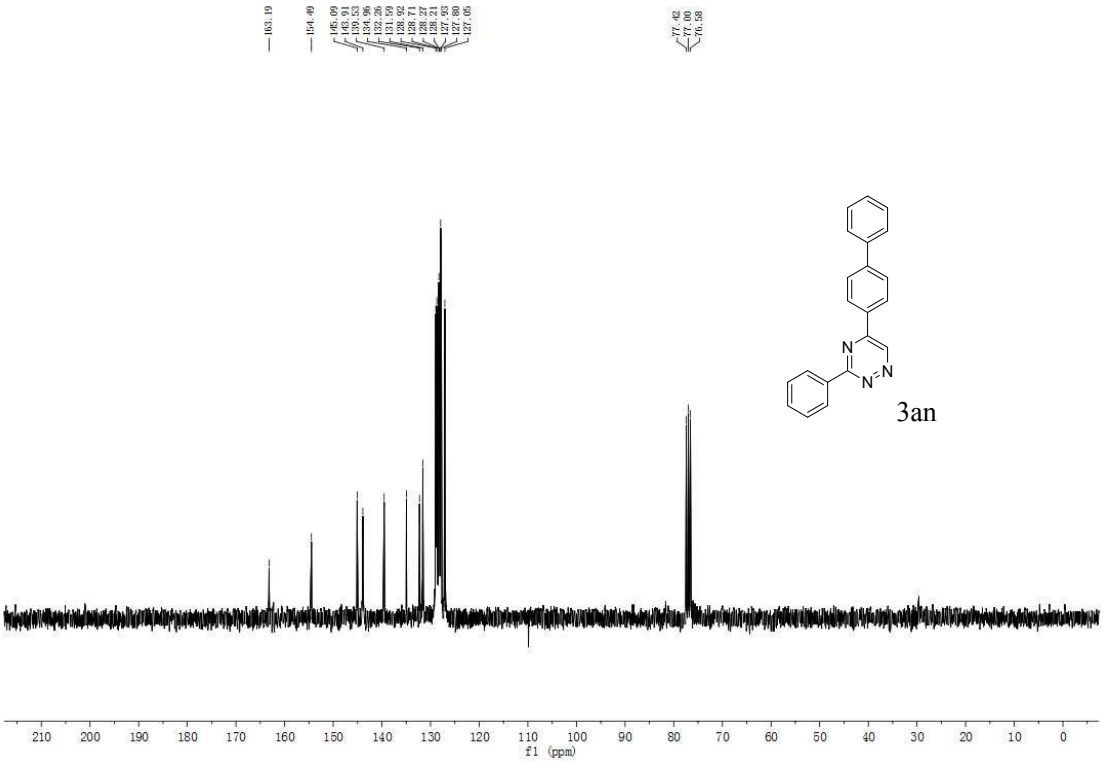

200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


3am
f1 (ppm)

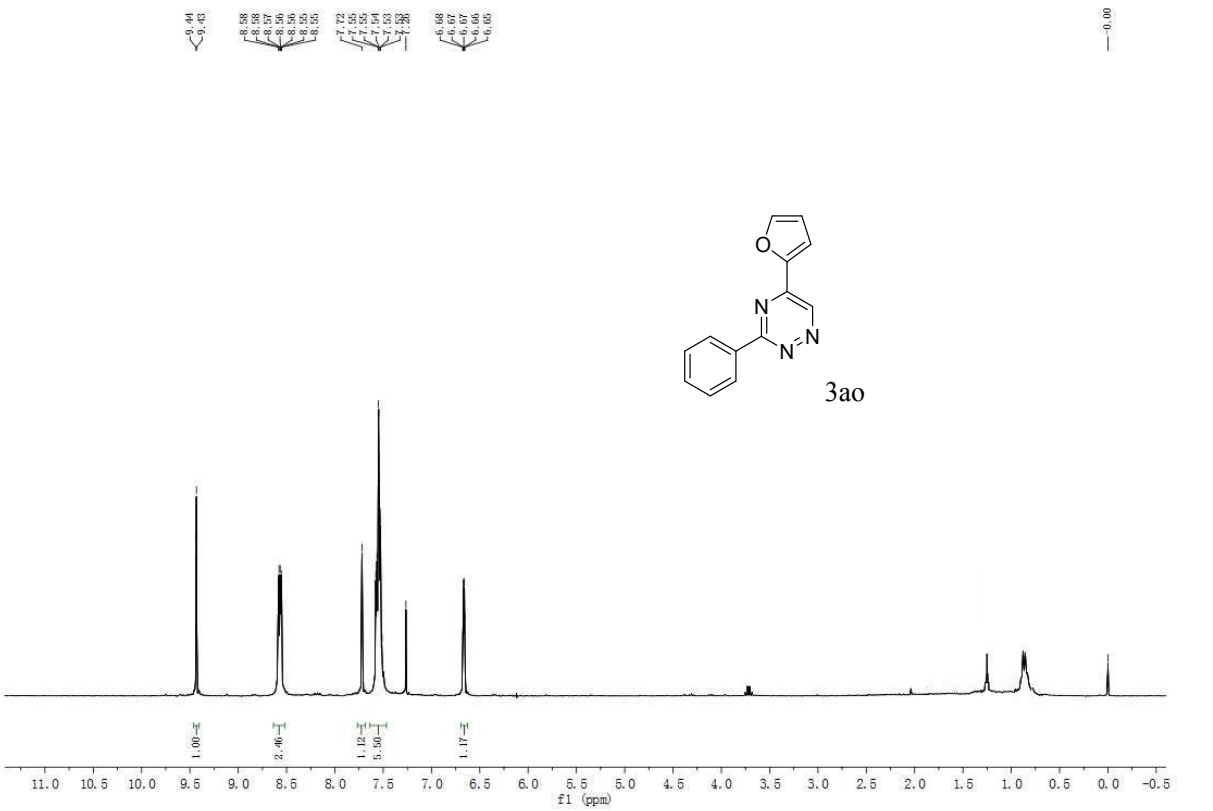

3am
f1 (ppm)

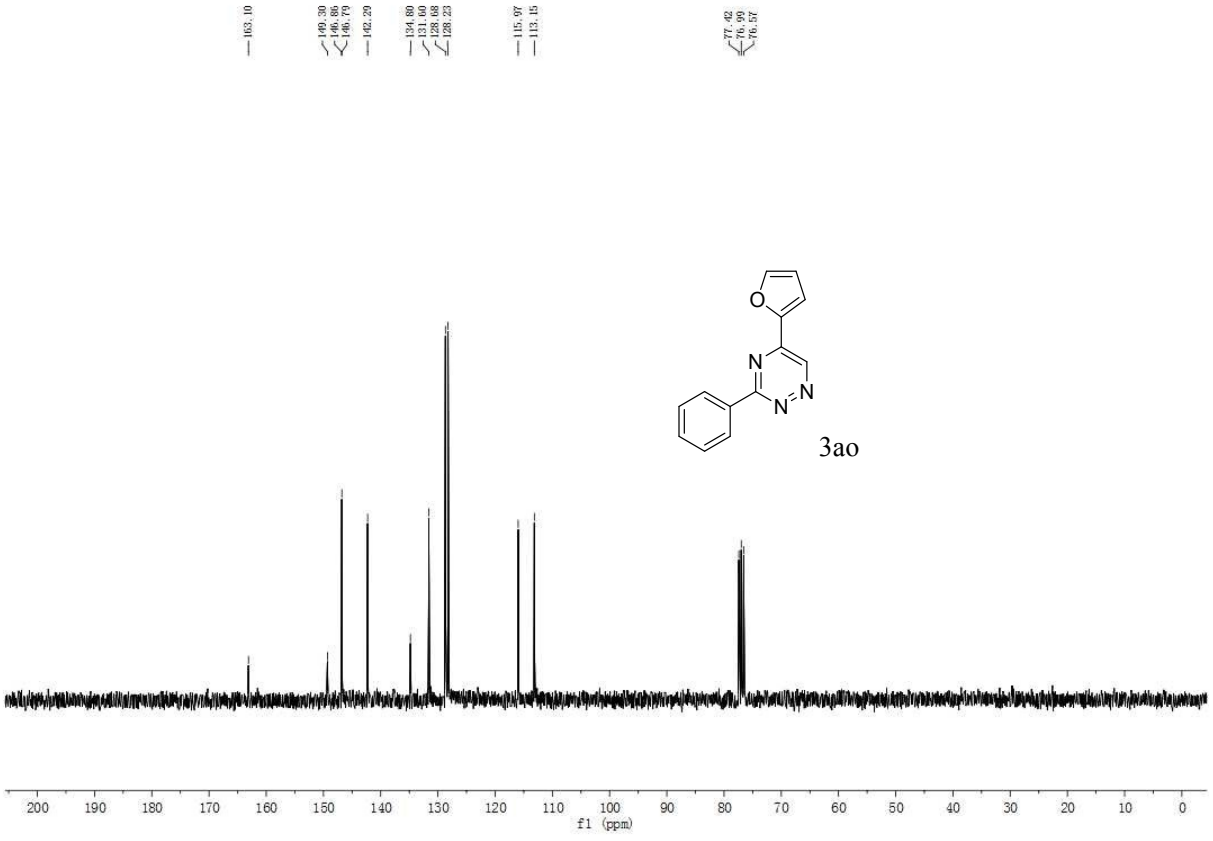

9.56
8.66
8.66
8.64
8.63
8.31
8.28
7.77
7.74
7.65
7.62
7.57
7.56
7.55
7.53
7.49
7.47
7.44
7.42
7.39
7.24
0.00
1.00
1.89
2.00
1.96
2.01
2.95
3.25
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

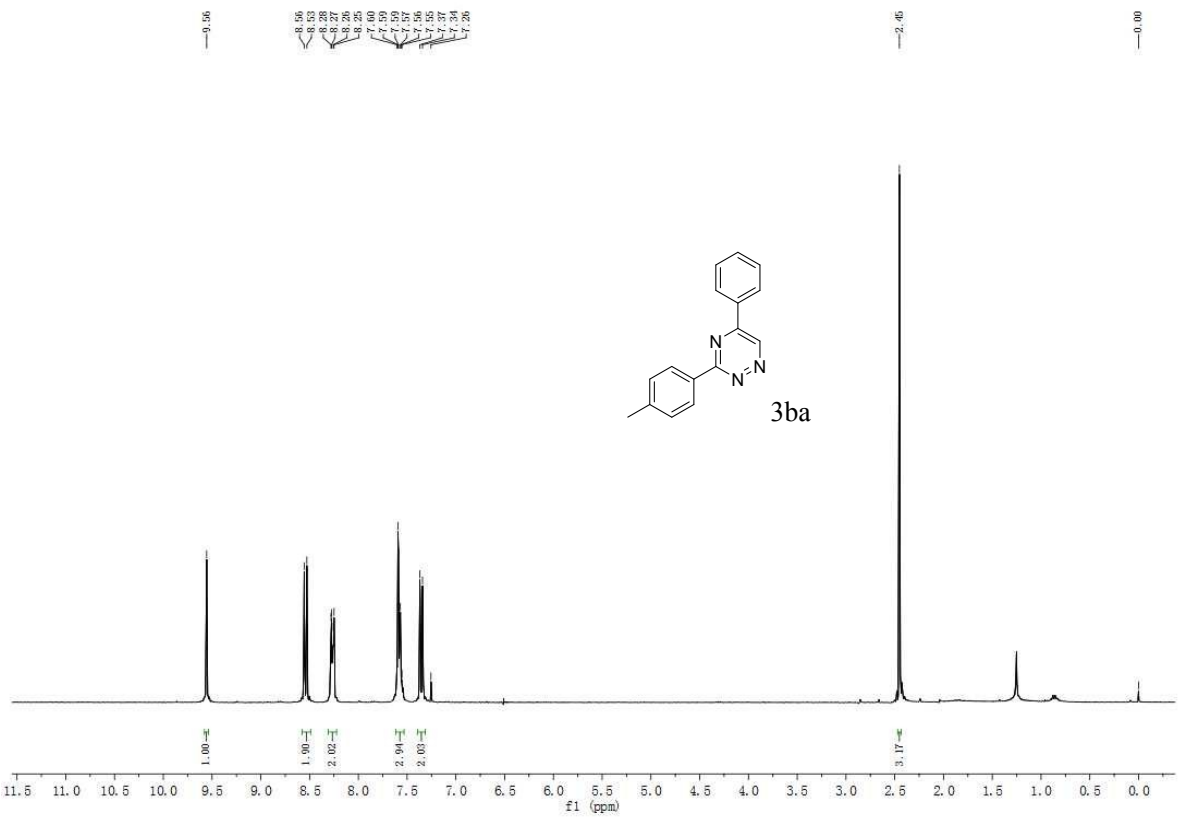
3an

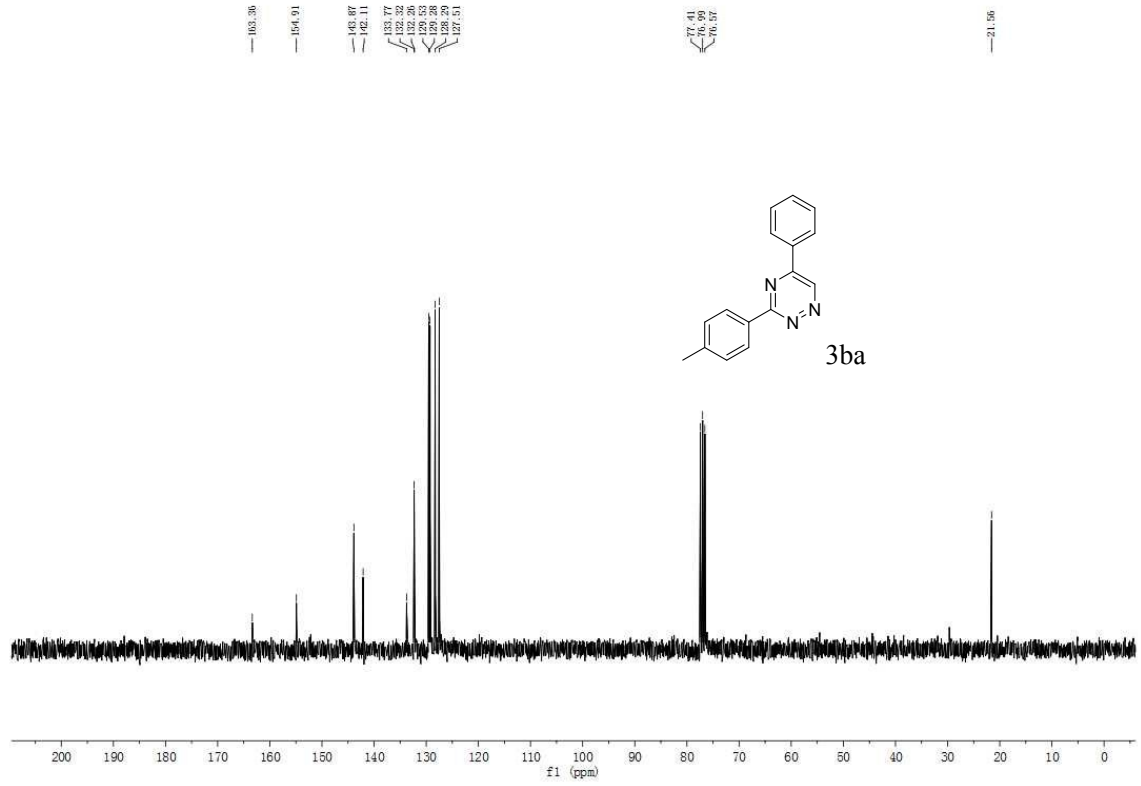

163.19
154.49
146.09
145.91
139.53
134.96
132.26
131.59
128.92
128.77
128.27
128.21
127.93
127.80
127.05
77.42
77.00
76.58
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

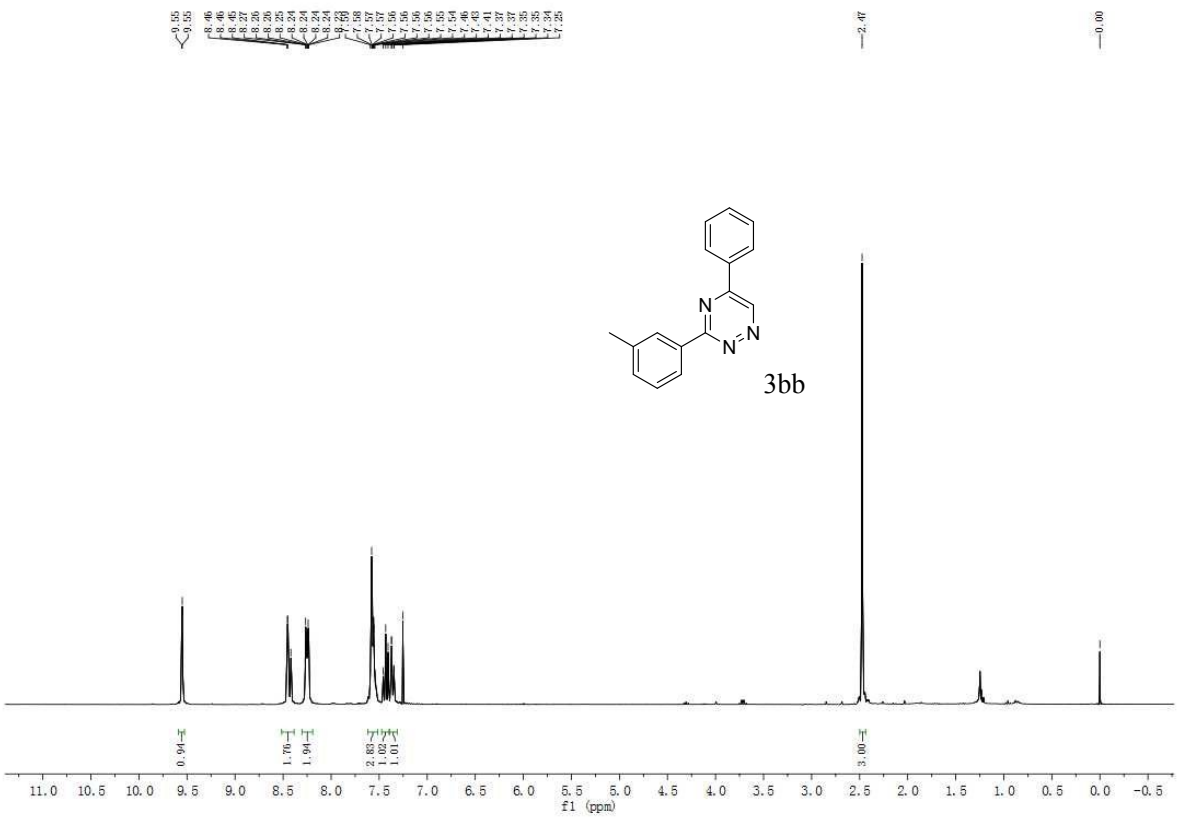
3an

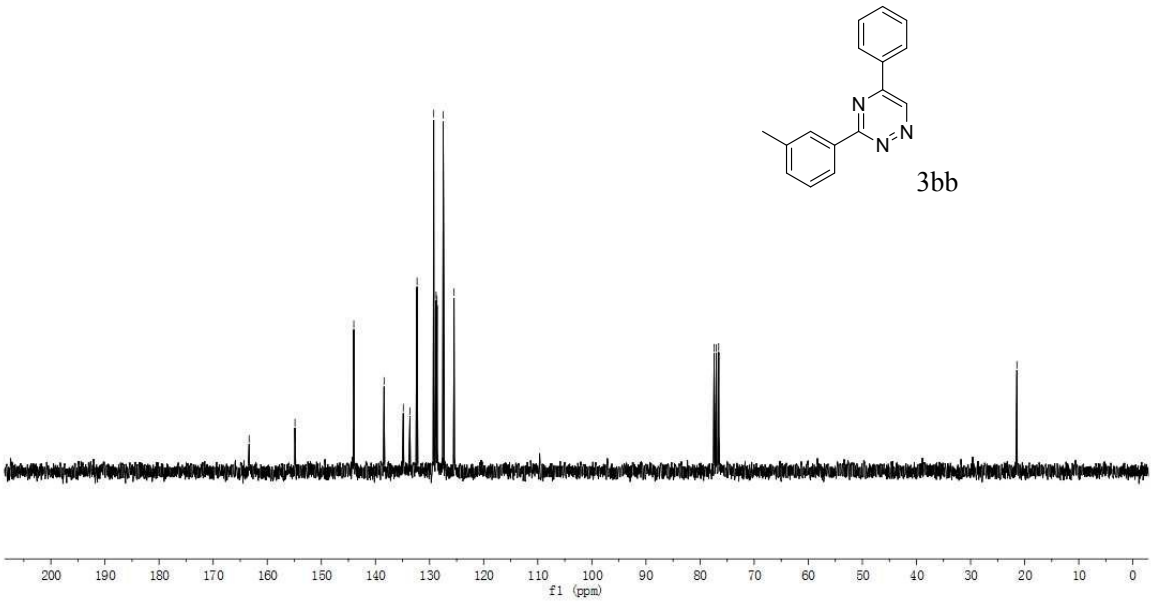

9.44
9.43
8.58
8.58
8.57
8.56
8.56
8.55
8.55
7.72
7.55
7.55
7.54
7.53
7.53
6.68
6.67
6.67
6.66
6.65
0.00
O
N
N
N
3ao
1.00
2.46
1.12
5.50
1.17
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

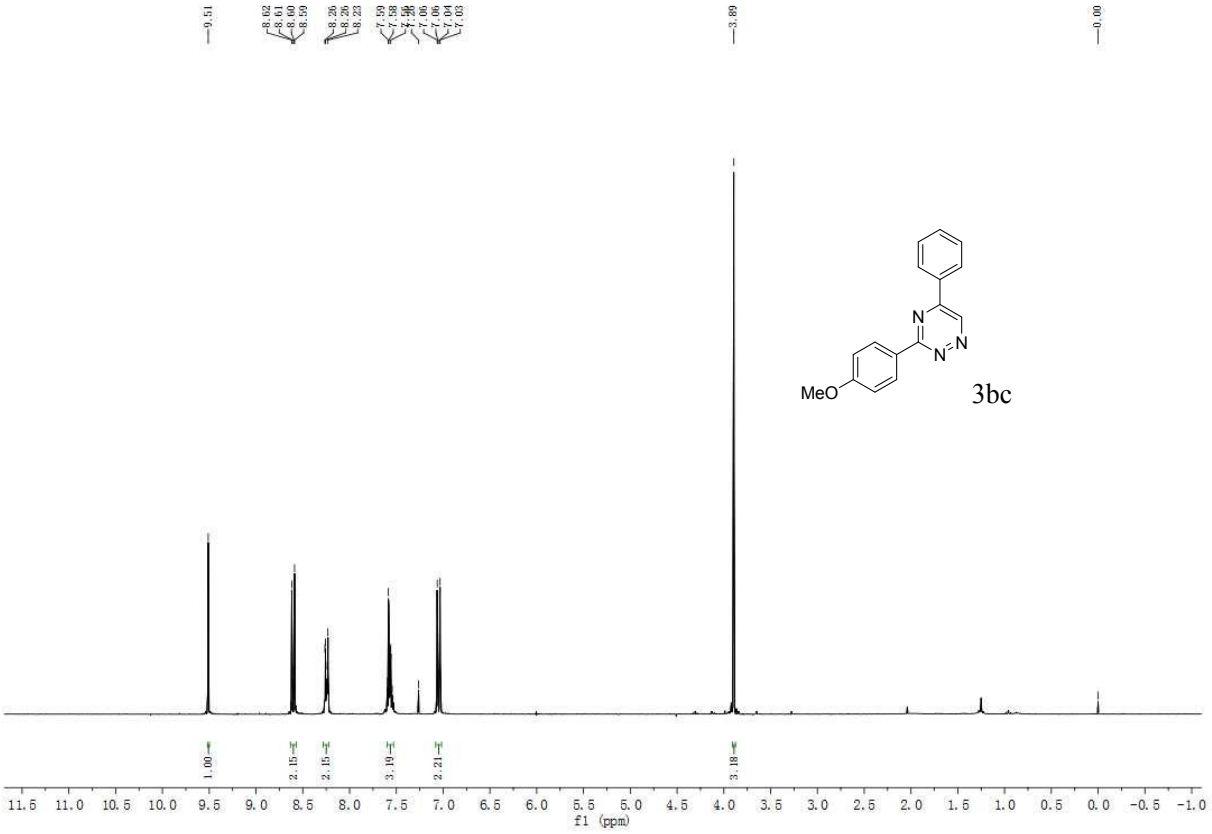

163.10
149.30
146.86
146.79
142.29
134.80
131.60
128.68
128.23
115.97
113.15
77.42
76.99
76.57
O
N
N
N
3ao
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

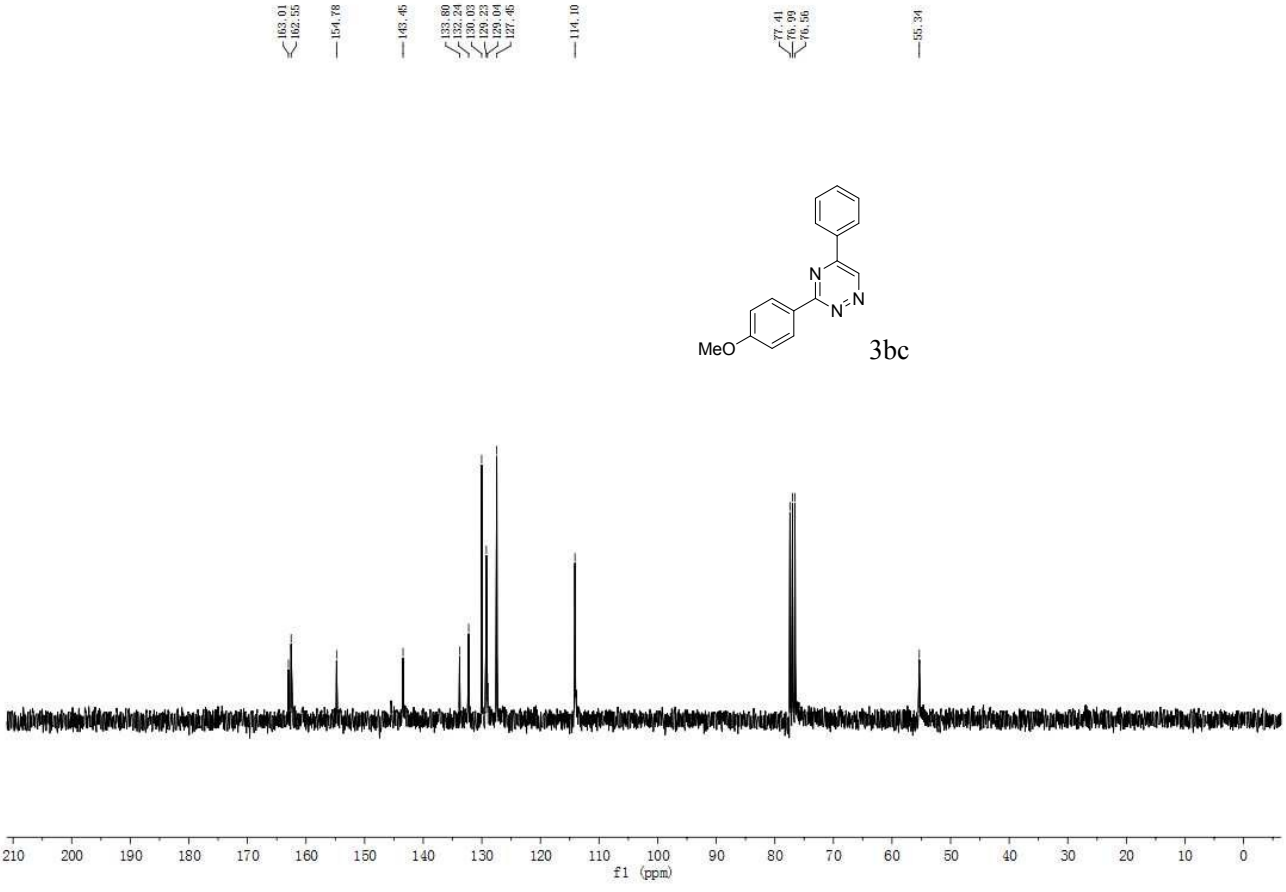

9.56
8.56
8.53
8.28
8.27
8.26
8.25
7.60
7.59
7.59
7.57
7.56
7.55
7.37
7.34
7.26
2.45
0.00
3ba
1.00
1.00
2.02
2.94
2.03
3.17
f1 (ppm)

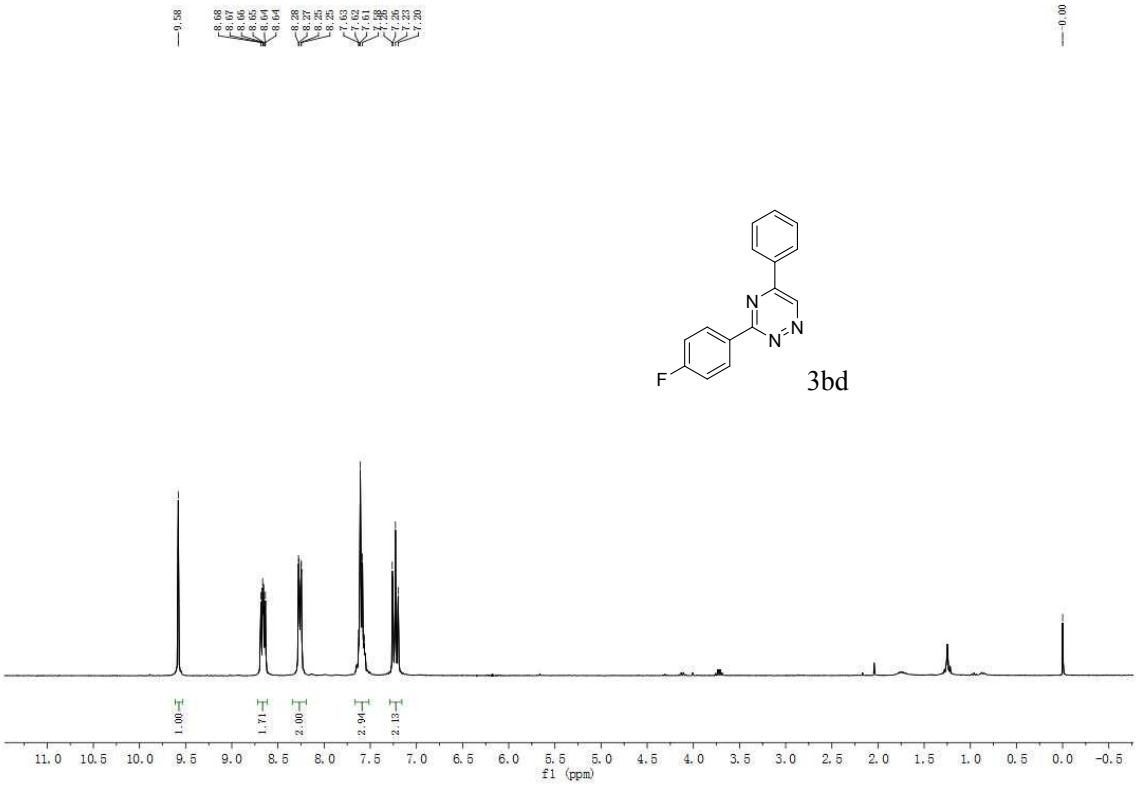

163.36
154.91
143.87
142.11
133.77
132.32
132.26
129.53
129.38
128.20
127.51
77.41
76.99
76.57
21.56
3ba
f1 (ppm)

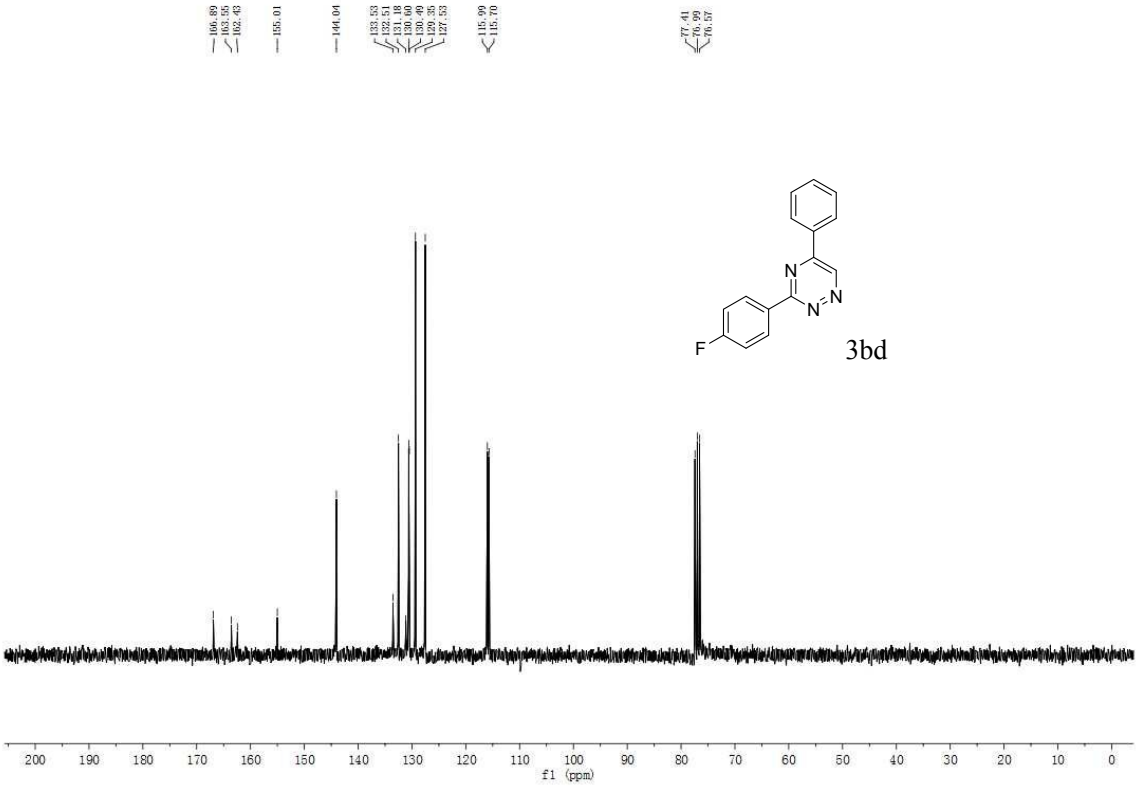

3bb
f1 (ppm)

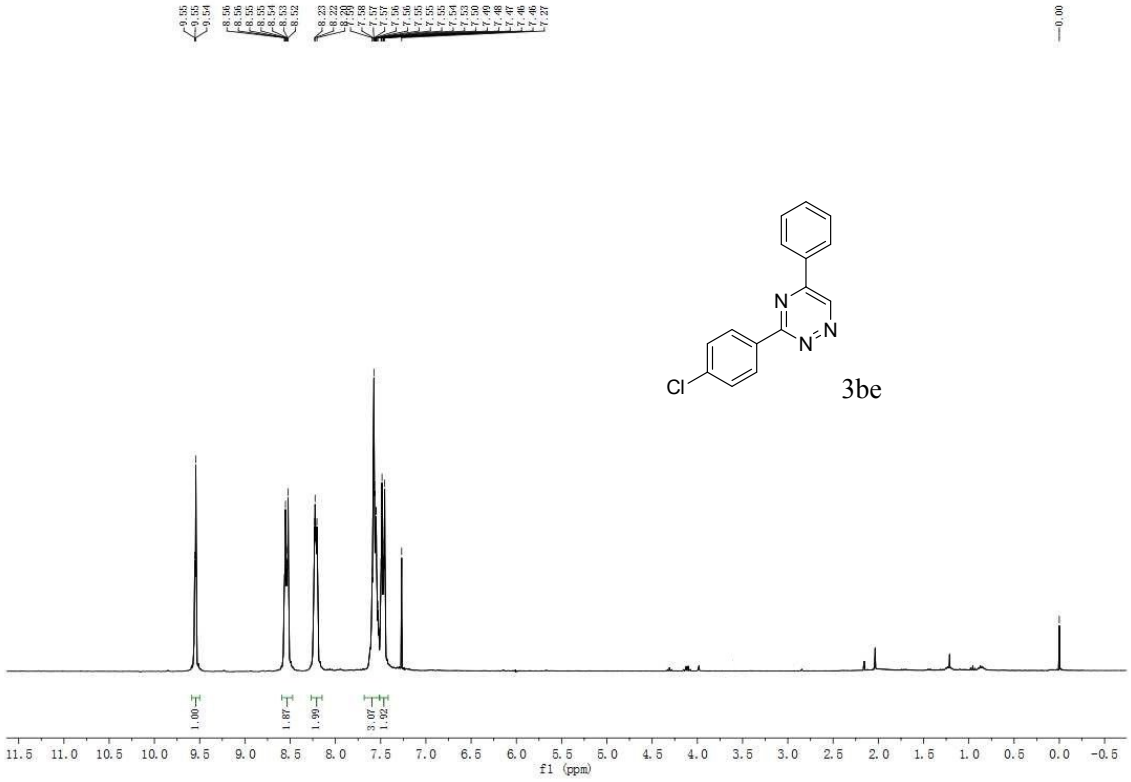

3bb
f1 (ppm)

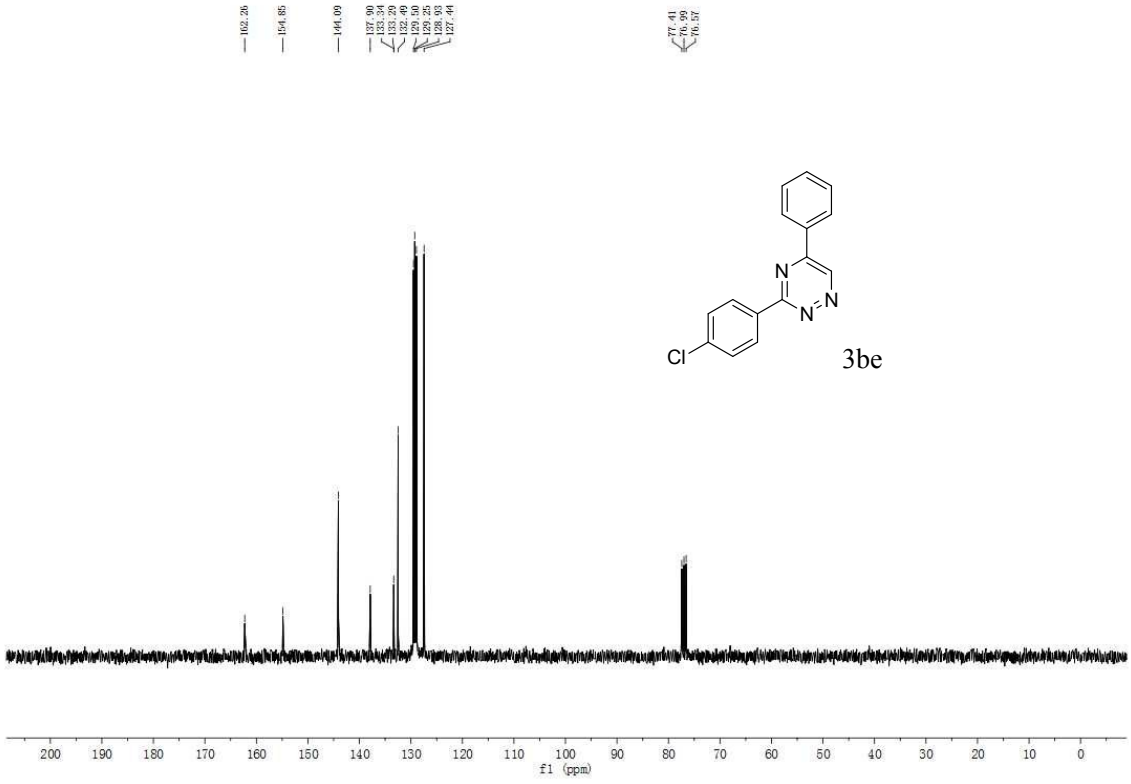

9.51
8.62
8.61
8.60
8.59
8.26
8.26
8.23
7.59
7.58
7.06
7.04
7.03
3.89
0.00
1.00
2.15
2.15
3.19
2.21
3.18
MeO
3bc
f1 (ppm)

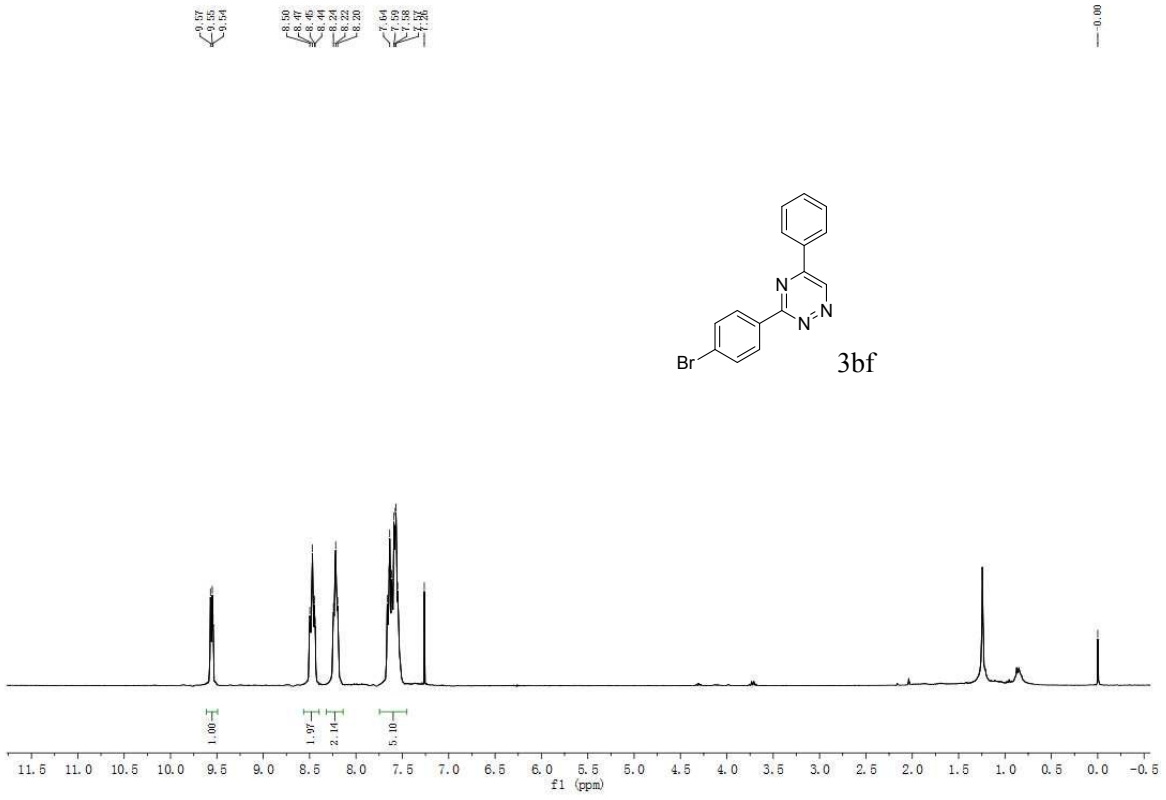

163.01
162.55
154.78
143.45
133.80
132.24
130.03
129.23
129.04
127.45
114.10
77.41
76.99
76.56
55.34
MeO
3bc
f1 (ppm)

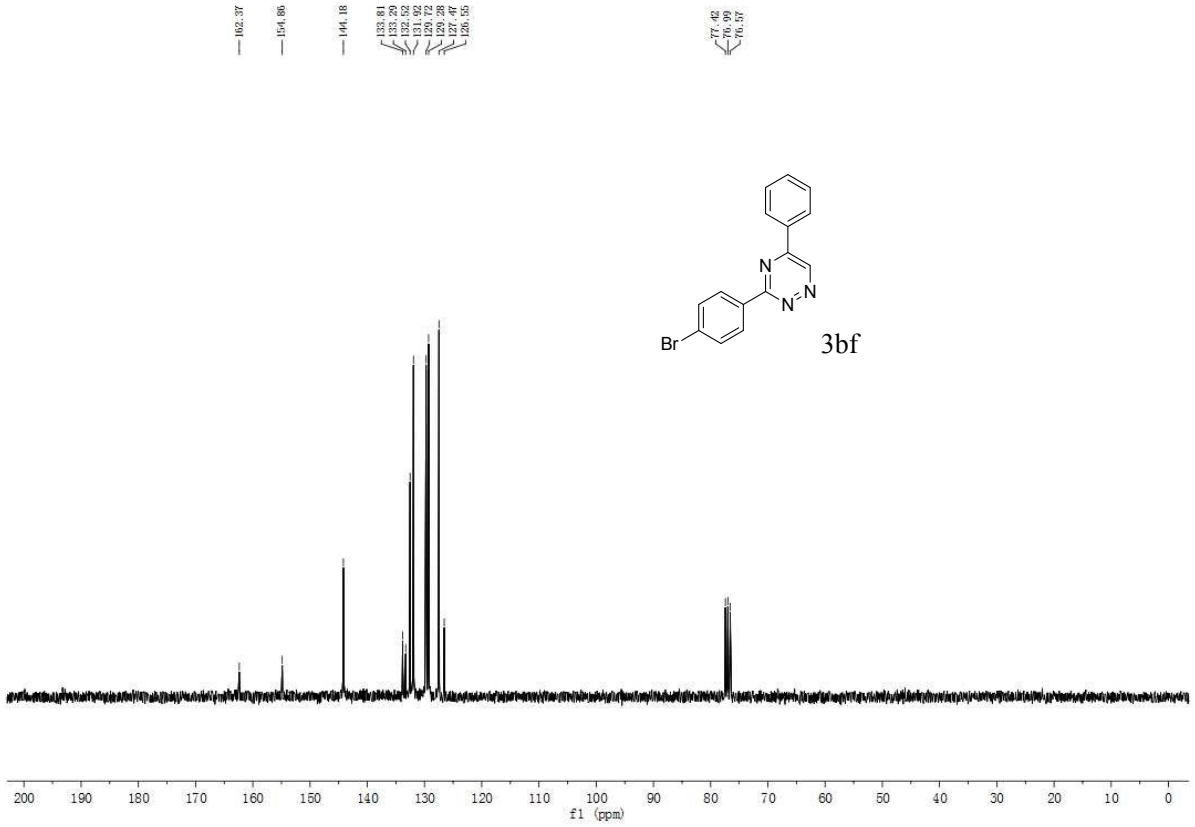

9.58
8.68
8.67
8.66
8.65
8.64
8.64
8.28
8.27
8.25
8.25
7.63
7.62
7.61
7.61
7.26
7.23
7.20
0.00
N
N
N
F
3bd
1.00
1.71
2.00
2.94
2.13
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

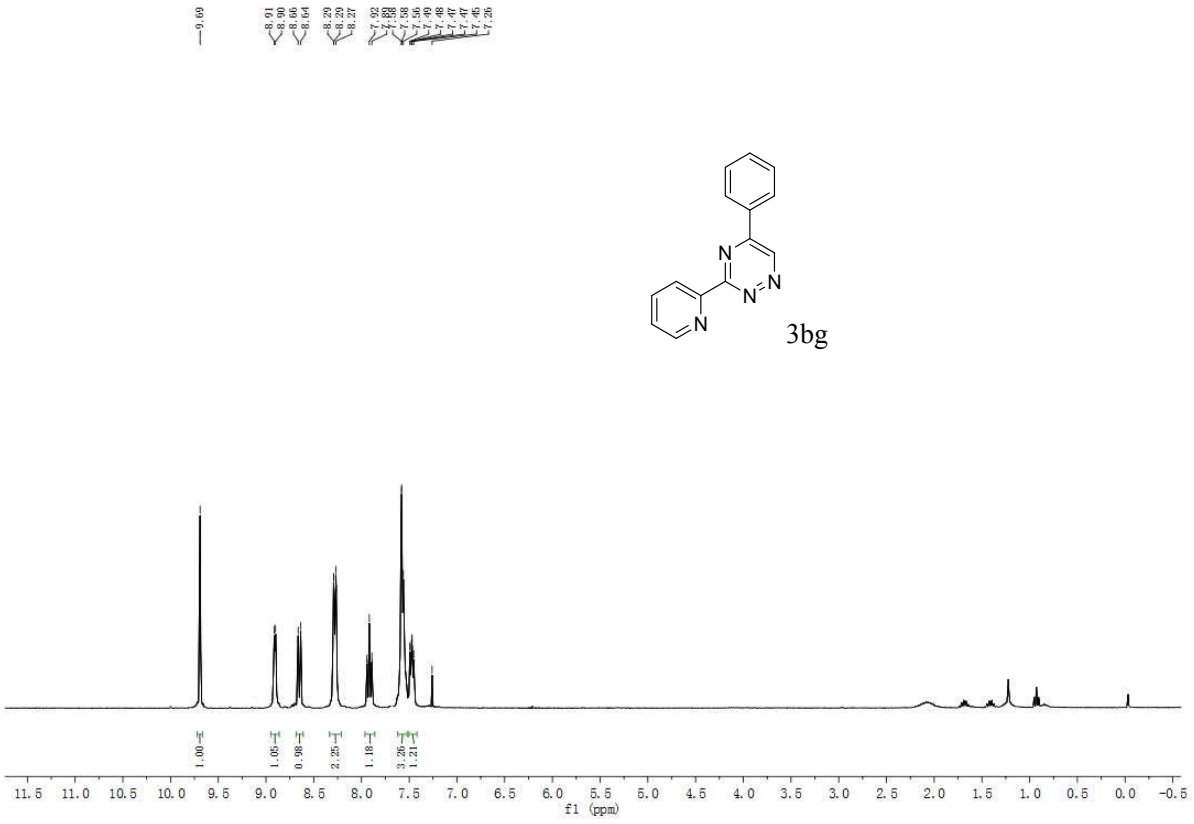

166.89
163.55
162.43
155.01
144.04
133.53
132.51
131.48
130.60
130.49
129.35
127.53
115.99
115.70
77.41
76.99
76.57
N
N
N
F
3bd
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.55
9.55
9.54
8.56
8.56
8.55
8.55
8.54
8.54
8.53
8.52
8.23
8.22
8.20
7.59
7.58
7.57
7.57
7.56
7.56
7.55
7.55
7.55
7.54
7.53
7.50
7.49
7.48
7.48
7.47
7.47
7.46
7.46
7.27
0.00
N
N
N
Cl
3be
1.00
1.87
1.99
3.07
1.92
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

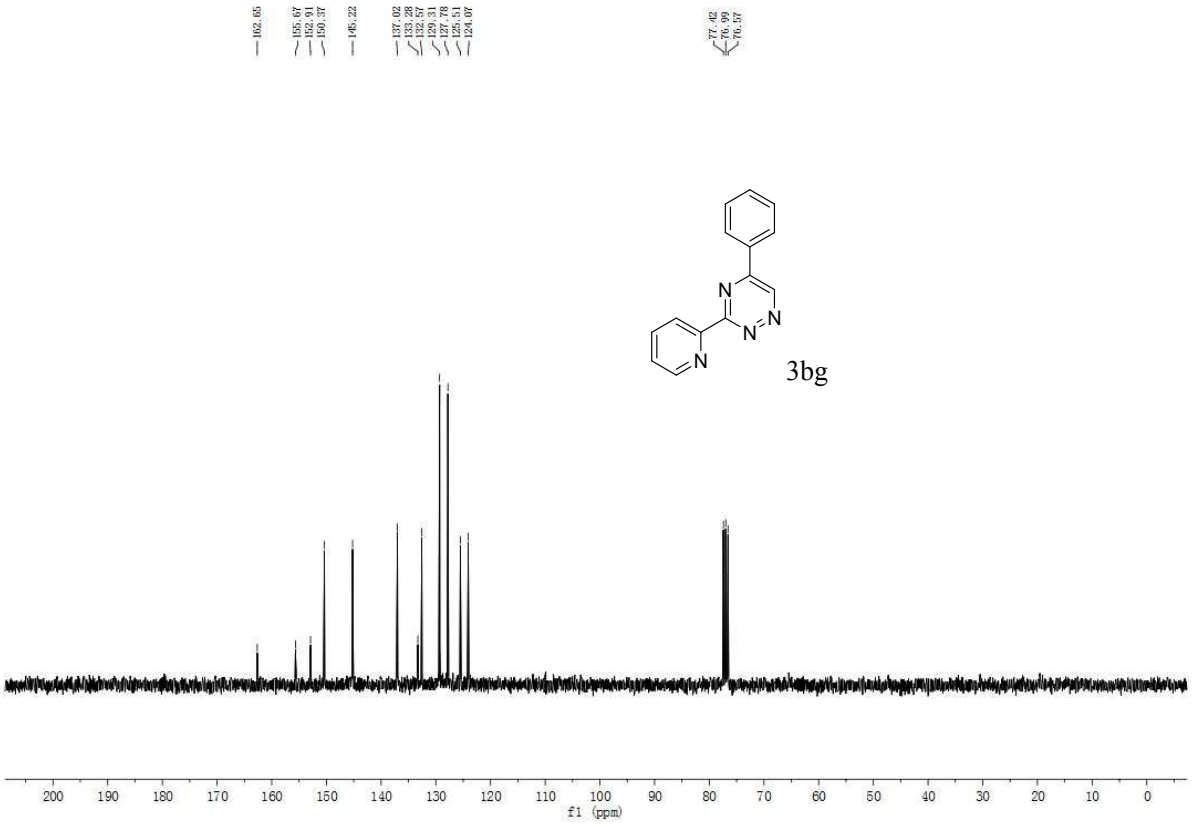

162.26
154.85
144.09
137.90
133.34
133.29
132.49
129.50
129.25
128.93
127.44
77.41
76.99
76.57
N
N
N
Cl
3be
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


9.57
9.55
9.54
8.50
8.47
8.45
8.44
8.24
8.22
8.20
7.64
7.59
7.58
7.57
7.56
0.00
Br
3bf
1.00
1.97
2.14
5.10
f1 (ppm)

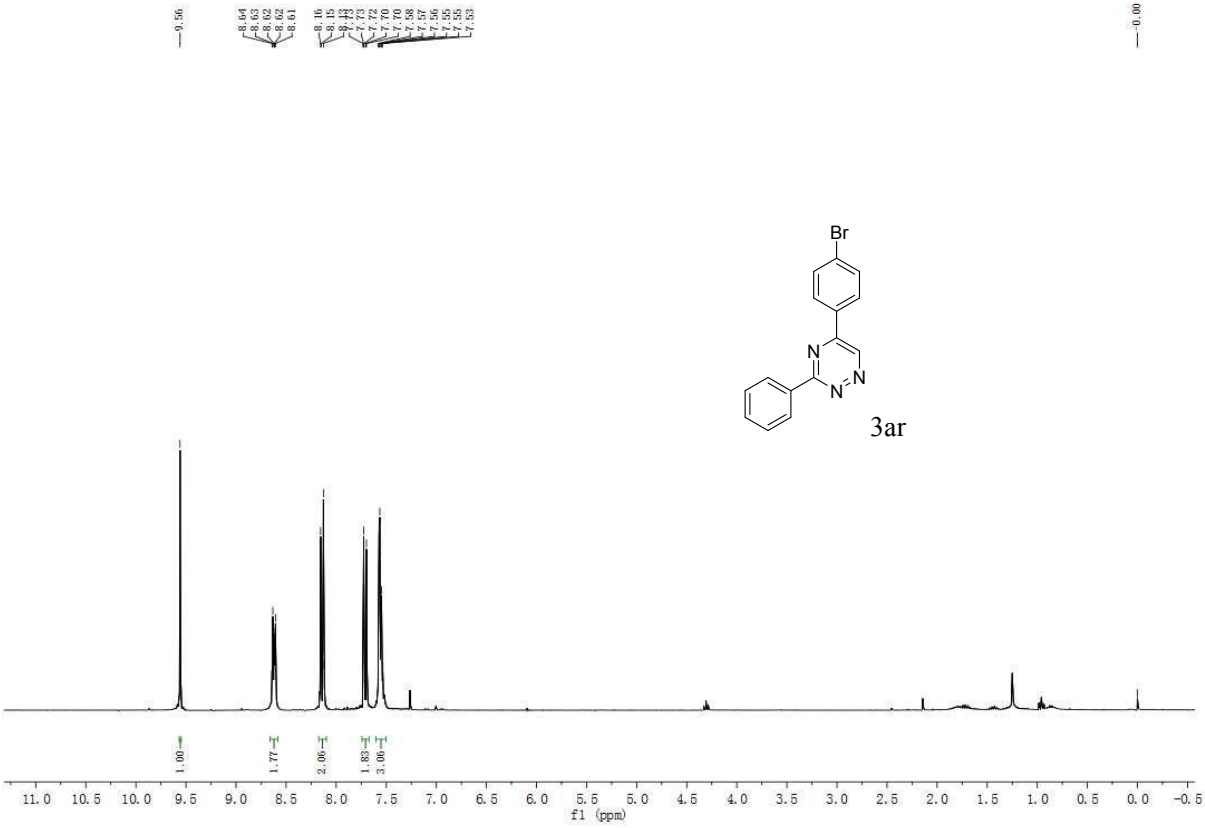

162.37
154.86
144.18
133.81
133.29
132.52
131.52
129.72
129.28
127.47
126.55
77.42
76.99
76.57
Br
3bf
f1 (ppm)

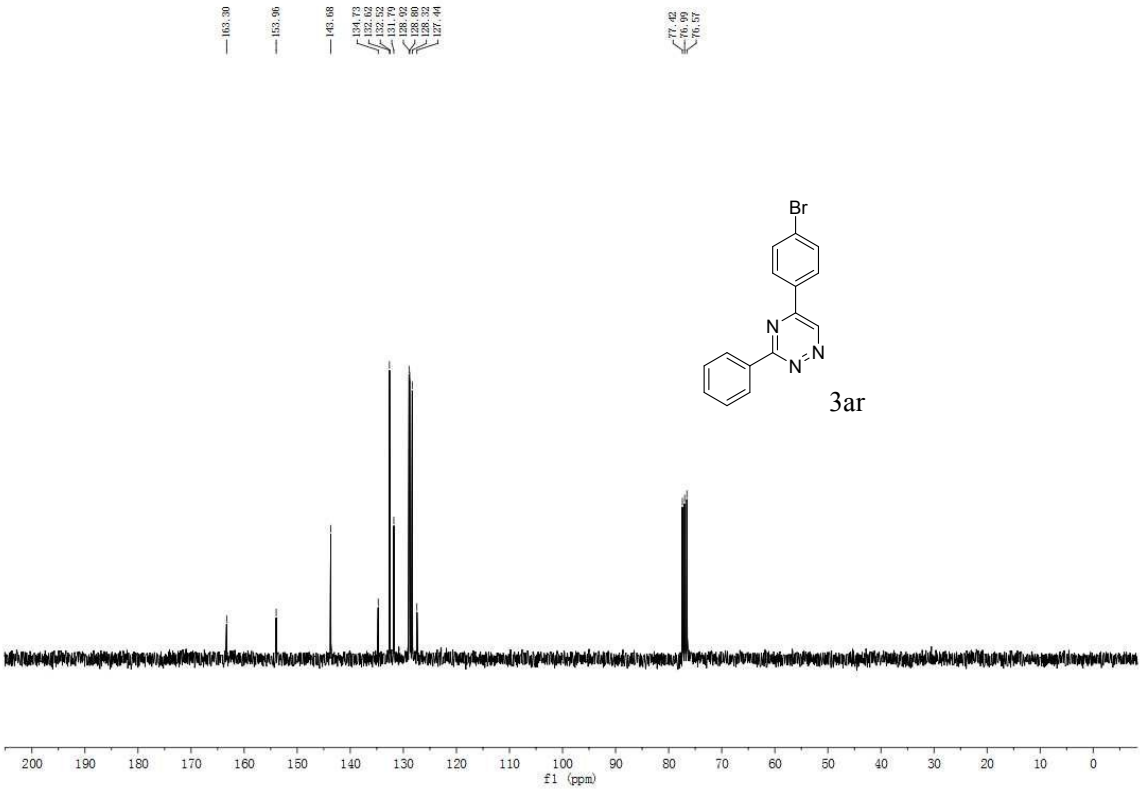

9.69
8.91
8.90
8.66
8.64
8.29
8.29
8.27
7.92
7.88
7.58
7.56
7.49
7.48
7.47
7.47
7.45
7.26
1.00
1.05
0.98
2.25
1.18
3.26
1.21
11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

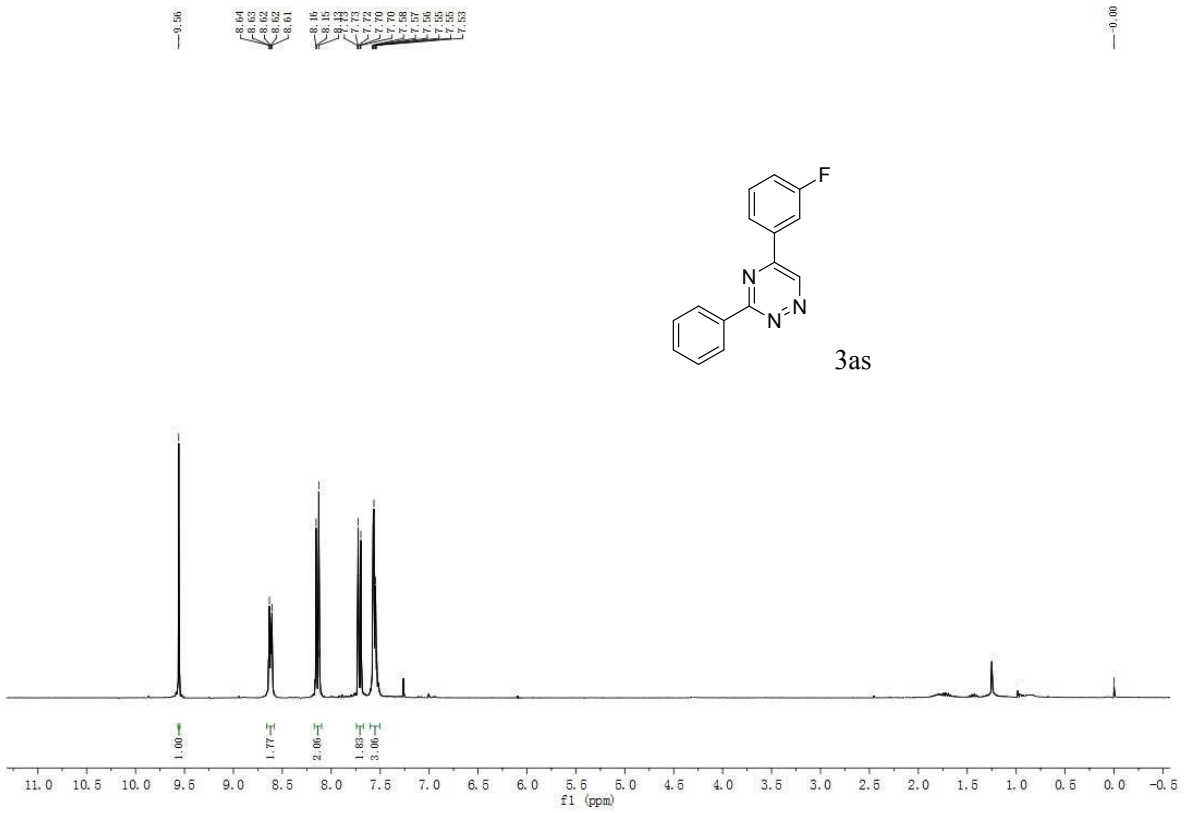
3bg

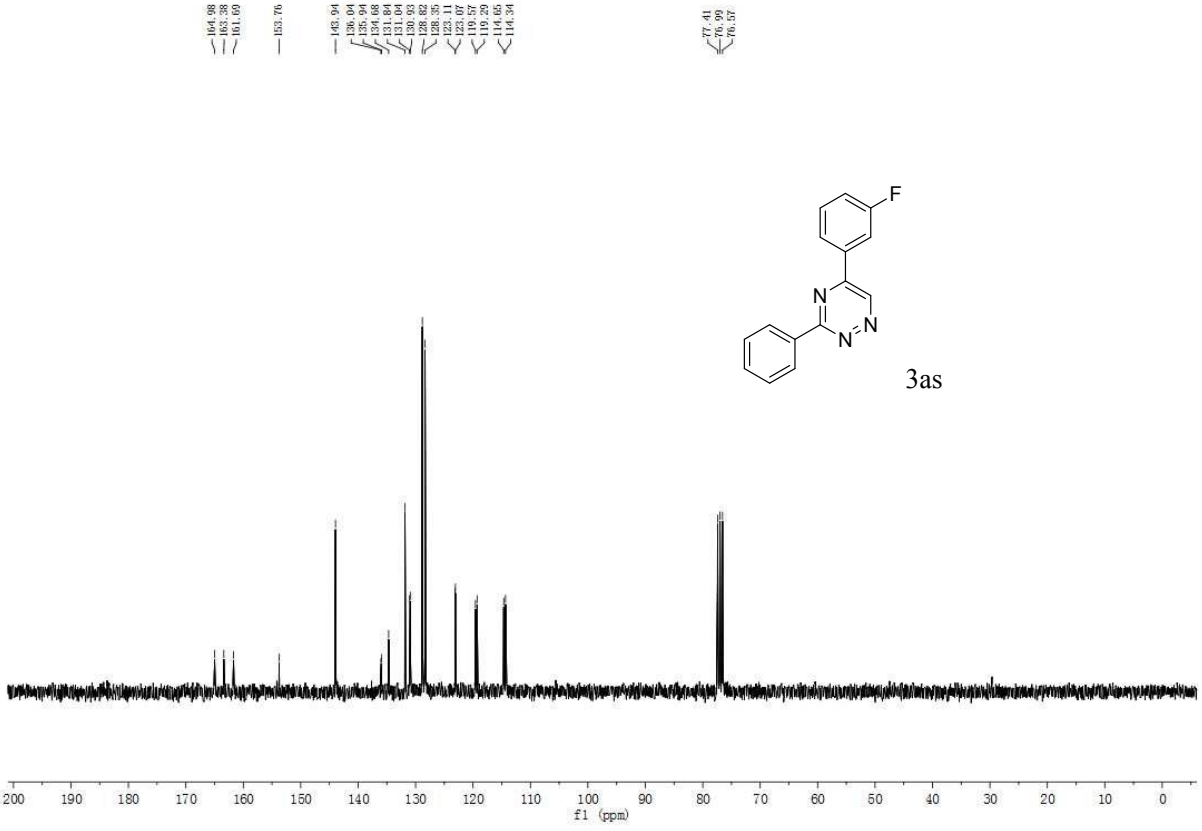

162.65
155.67
152.91
150.37
145.22
137.02
133.28
132.57
129.31
127.78
125.51
124.07
77.42
76.99
76.57
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

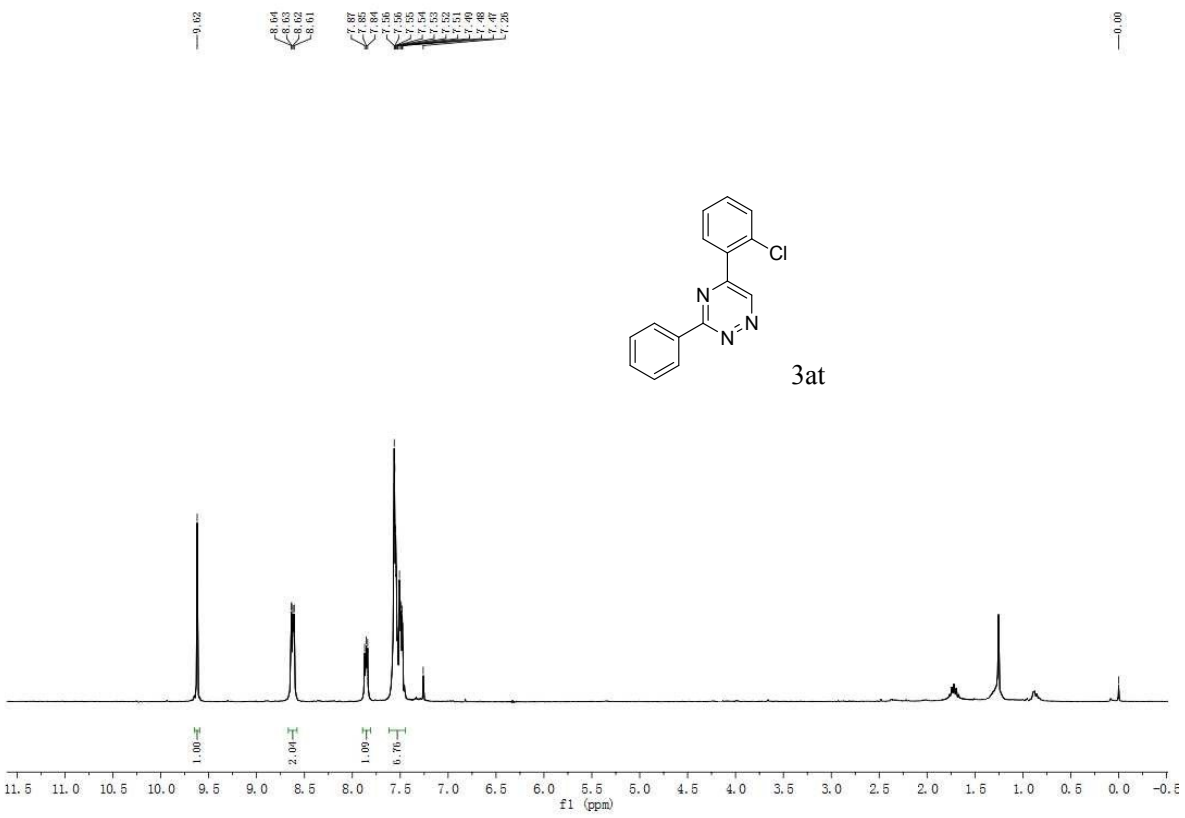
3bg

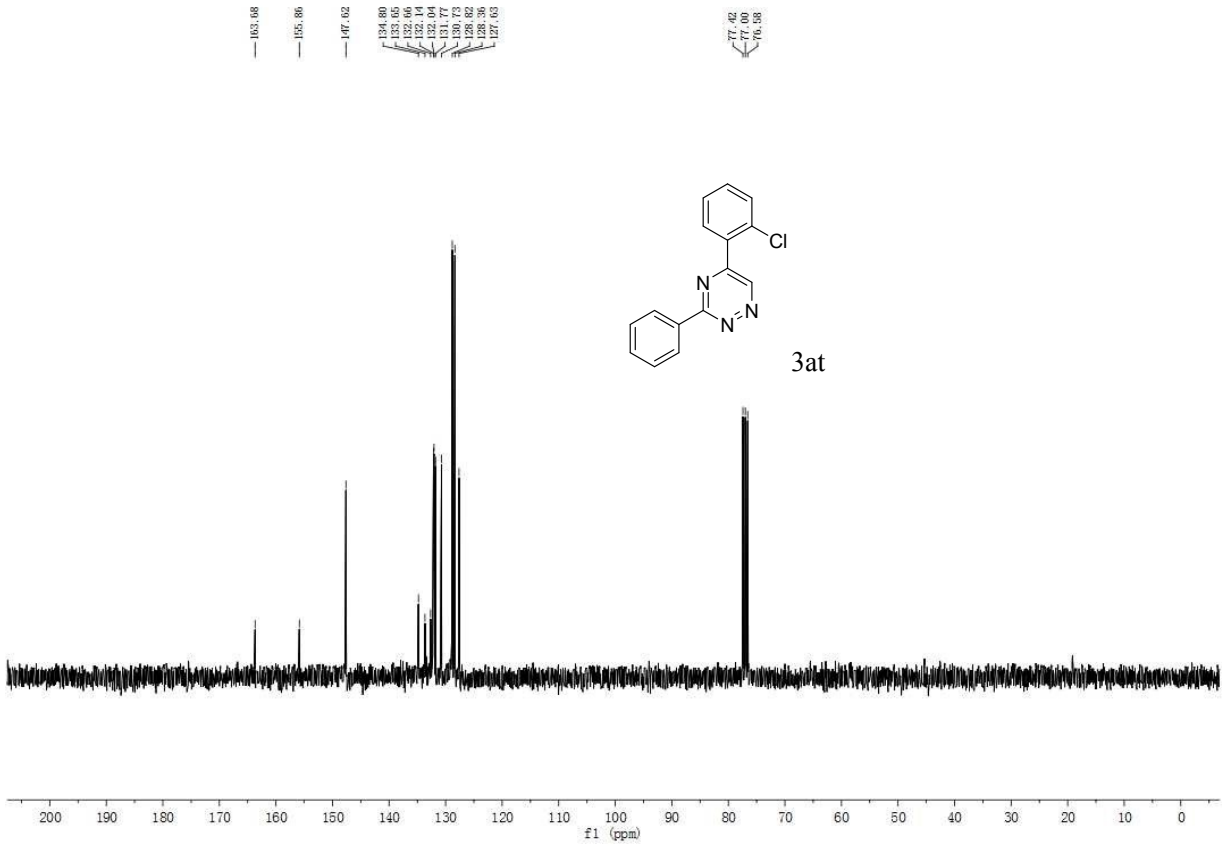

9.56
8.64
8.63
8.62
8.62
8.61
8.16
8.15
7.73
7.72
7.70
7.70
7.58
7.57
7.56
7.55
7.55
7.53
0.00
Br
N
N
N
3ar
1.00
1.77
2.06
1.83
3.06
f1 (ppm)

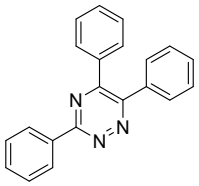

163.30
153.96
145.68
134.73
132.62
132.52
131.79
128.92
128.80
128.32
127.44
77.42
76.99
76.57
Br
N
N
N
3ar
f1 (ppm)


9.56
8.64
8.63
8.62
8.62
8.61
8.16
8.15
8.13
8.13
7.73
7.72
7.70
7.70
7.58
7.57
7.56
7.55
7.55
7.53
0.00
F
N
N
N
3as
1.00
1.77
2.06
1.83
3.06
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

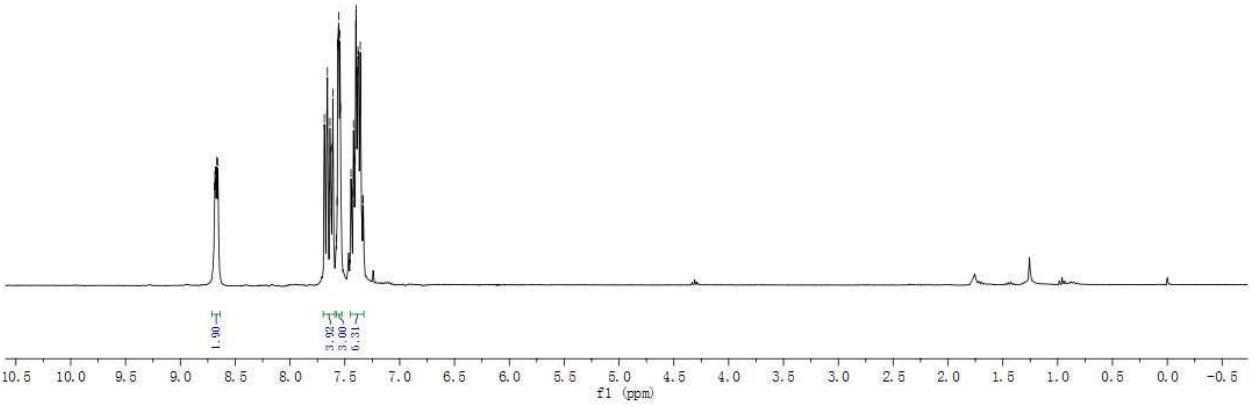

164.98
163.38
161.69
153.76
143.94
136.04
135.94
134.68
131.84
131.84
130.93
128.82
128.35
123.11
123.07
119.57
119.29
114.65
114.34
77.41
76.99
76.57
F
N
N
N
3as
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

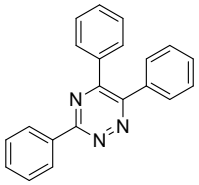

9.62
8.64
8.63
8.62
8.61
7.87
7.85
7.84
7.56
7.55
7.54
7.53
7.52
7.51
7.49
7.48
7.47
7.26
0.00
Cl
N
N
N
3at
1.00
2.04
1.09
6.76
f1 (ppm)


163.68
155.86
147.62
134.80
133.65
132.66
132.14
132.04
131.77
130.73
128.82
128.36
127.63
77.42
77.00
76.58
Cl
N
N
N
3at
f1 (ppm)

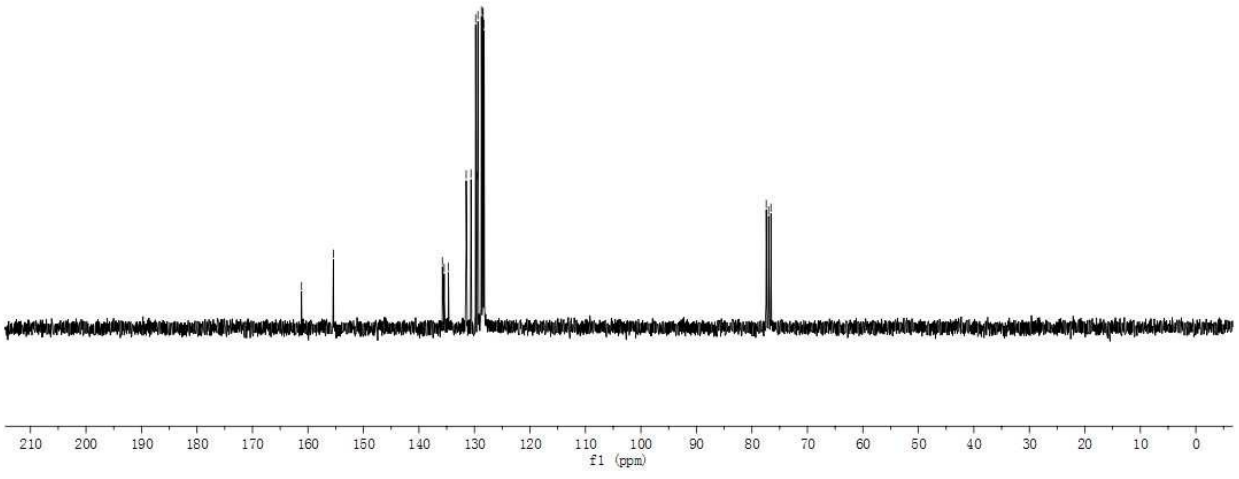


8aa


1.90
3.92
3.00
6.31
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



8aa


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)