Supporting information

Synthesis of 1,2-dihydro-1,3,5-triazines derivatives via Cu(II)-catalyzed C(SP^3)-H activation of *N,N*-dimethylethanolamine with amidines

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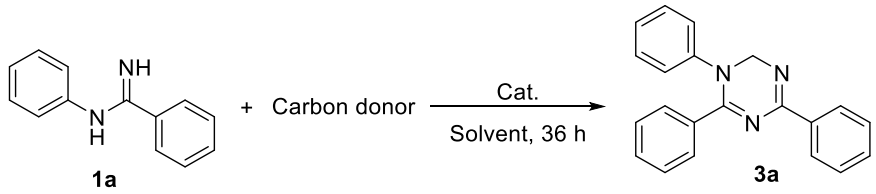
1. General Information

All reagents and solvents were used as supplied without further purification. ^{1}H NMR and ^{13}C NMR were determined in $CDCl_3$ or DMSO-d_6 on a Brucker spectrometer at room temperature, and tetramethylsilane (TMS) served as an internal standard. The chemical shifts are reported in parts per million (ppm), the coupling constants (*J*) are expressed in hertz (Hz). All the reactions were monitored by thin-layer chromatography (TLC). TLC was performed on pre-coated silica gel plates (Qingdao Haiyang Chemical Co., Ltd, China).

2.Optimization of the Reaction Conditions

Table S1 Optimization of the Reaction Conditions[a]



Entry	Carbon source (equiv.)	Solvent	Catalyst (equiv.)	Conversion (%)	Yield (%)[b]
1	DMEA (3.0)	MeCN	$CuBr_2$ (0.1)	61	35
2	DMF (3.0)	MeCN	$CuBr_2$ (0.1)	-	-
3	DMSO (3.0)	MeCN	$CuBr_2$ (0.1)	-	-
4	TMEDA (3.0)	MeCN	$CuBr_2$ (0.1)	57	29
5	DMEA (2.0)	MeCN	$CuBr_2$ (0.1)	36	23
6	DMEA (4.0)	MeCN	$CuBr_2$ (0.1)	63	36
7	DMEA (3.0)	DMSO	$CuBr_2$ (0.1)	45	26
8	DMEA (3.0)	DMF	$CuBr_2$ (0.1)	43	24
9	DMEA (3.0)	1,4-dioxane	$CuBr_2$ (0.1)	63	30
10	DMEA (3.0)	THF	$CuBr_2$ (0.1)	44	15
12	DMEA (3.0)	MeCN	-	-	-
13	DMEA (3.0)	MeCN	$FeSO_4$ (0.1)	-	-
14	DMEA (3.0)	MeCN	$Pd(OAc)_2$ (0.1)	-	-
15	DMEA (3.0)	MeCN	$NiCl_2$ (0.1)	31	14
16	DMEA (3.0)	MeCN	$CoCl_2$ (0.1)	34	15
17	DMEA (3.0)	MeCN	$Cu(OTf)_2$ (0.1)	-	-
18	DMEA (3.0)	MeCN	CuI (0.1)	67	34
19	DMEA (3.0)	MeCN	$Cu(OAc)_2$ (0.1)	53	22
20	DMEA (3.0)	MeCN	$CuCl_2$ (0.1)	50	42
21	DMEA (3.0)	MeCN	$CuCl_2$ (0.15)	59	50

22	DMEA (3.0)	MeCN	$CuCl_2$ (0.2)	61	51
23	DMEA (3.0)	MeCN	$CuCl_2$ (0.3)	64	52
24[c]	DMEA (3.0)	MeCN	$CuCl_2$ (0.15)	77	50
25[d]	DMEA (3.0)	MeCN	$CuCl_2$ (0.15)	75	53
26	**DMEA (10.0)**	-	**$CuCl_2$ (0.15)**	**72**	**65**
27[d]	DMEA (10.0)	-	$CuCl_2$ (0.15)	85	12
28[e]	DMEA (10.0)	-	$CuCl_2$ (0.15)	74	51
29[f]	DMEA (10.0)	-	$CuCl_2$ (0.15)	79	43

[a]All reactions were carried out with *N*-phenylbenzimidamide (**1a**, 0.5 mmol), solvent (0.5 mL) at 80 °C for 36 h unless indicated; [b]Isolated yield; [c]1.0 equiv. of TBHP; [d]1.0 equiv. of $K_2S_2O_8$; [e]reaction at 90 °C; [f]reaction at 100 °C.

The effect of different carbon sources, solvents, catalysts and temperatures on the product yields were investigated (Table S1). It can be shown that the reaction of *N*-phenylbenzimidamide (0.5 mmol) and DMEA (1.5 mmol) in the presence of $CuBr_2$ (0.05 mmol) in acetonitrile (MeCN) under air atmosphere at 80 °C for 36 h performed 61% conversion with 35% isolated yield of the desired product (entry 1). The carbon sources were first screened. Although *N,N*-dimethylformamide (DMF)[1] and DMSO[2] have been reported to be a methylene donor in many cases, they failed to facilitate our reaction (entries 2-3). In contrast, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was successively employed in this reaction as the methylene donor, but both the conversion rate and the isolated yield of **3a** was lower than those of DMEA (entry 4 vs 1). Decreasing the use of DMEA to 2 equiv. significantly reduced the transformation while increasing the amount of DMEA had no marked improvement (entries 5-6 vs 1). Amongst the solvents employed, MeCN was found to be the best solvent for the reaction (entries 1 and 7-10). In the absence of $CuBr_2$, the reaction did not proceed at all (entry 11). In the pursuit of our program directed towards the most suitable catalyst, a series of metal salts were then screened. The results showed that $CuBr_2$ gave the highest yield by compared to other salts such as $FeSO_4$, $Pd(OAc)_2$, $NiCl_2$ and $CoCl_2$ (entry 1 vs 13-16). On the other hand, amongst the copper sources screened, $CuCl_2$ was found to be the best catalyst (entries 17-20). Although $CuBr_2$, CuI and $Cu(OAc)_2$ gave higher conversion rates, the isolated yields of **3a** are lower compared to that of $CuCl_2$. By increasing the amount of the catalyst from 0.1 to 0.15 equiv., the yield of **3a** was improved (entry 21). Further increase of the amount of $CuCl_2$ to 0.3 equiv. did not affect the yield markedly (entries 22-23). Considering that the reaction involves DMEA oxidation, TBHP and $K_2S_2O_8$ at 1 equiv. was supplied respectively. The result shows that although the conversion rates of **1a** were increased, the product yields were similar to that in the absence of the additional oxidants, indicating that the peroxidant might not be essential to this reaction (entries 24-25). Exhilaratingly, the reaction under such initial conditions was carried out in 0.5 mL of DMEA (10 equiv.) without an additional solvent to provide the desired product 3a in an elevated yield (entry 26). Again, the presence of $K_2S_2O_8$ at 1 equiv. elevated the reaction conversion rate but lowered the product yield dramatically, probably due to an over-oxidation of the resulting product (entry 27). By increasing the reaction temperature, diminished product yields were observed (entries 28-29). Based on these results, the optimal conditions were established as described in entry 26.

3.The kinetic studies were carried out under air and O_2

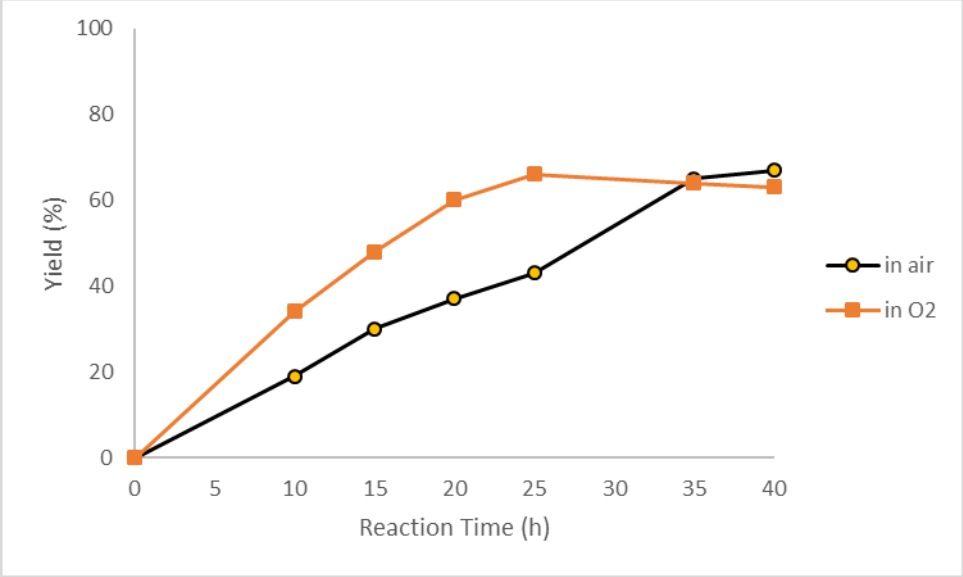
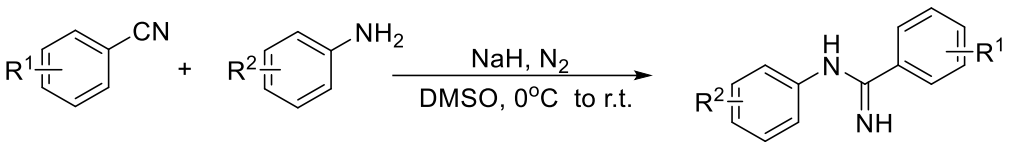


Figure S1 Yield *vs* time curves of the annulation reaction of amidines with DMEA under air and O_2 respectively. Reaction conditions: **1** (0.5 mmol), $CuCl_2$ (0.15 equiv), in DMEA (0.5 mL) at 80 °C.

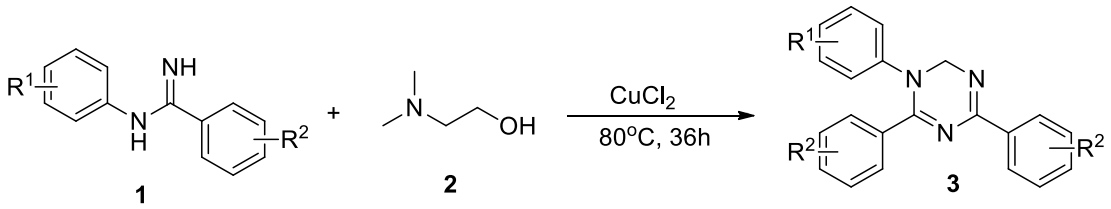
4. General Procedure for Synthesis of substrates



A 50 mL pressure flask equipped with a stir-bar was charged with 5.0 mL of anhydrous DMSO and NaH (15.0 mmol, 60%, 1.5 equiv). Then aniline (12.0 mmol, 1.2 equiv.) and carbonitrile (10.0 mmol, 1.0 equiv.) were added to the flask in portions at 0°C under a nitrogen atmosphere. The reaction mixture was stirred at 0°C for 40-60 min and then stirred at room temperature about 2h. Upon completion the reaction mixture was quenched by ice water (20 ml) and extracted by ethyl acetate (3×20 ml). The combined organic layer was dried over Na_2SO_4, filtered and concentrated in vacuo. Purification by silica-gel chromatography with a mixture eluent of petroleum ether and ethyl acetate. [3]

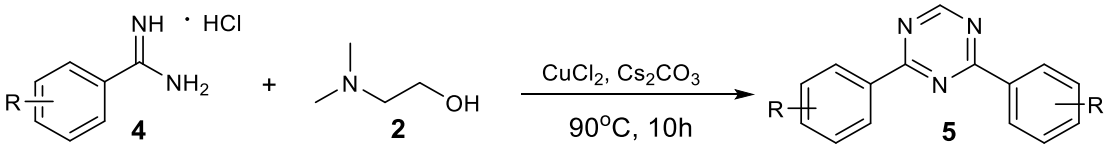
5. General Procedure for Synthesis of products

5.1 General Procedure for 1,4,6-triphenyl-1,2-dihydro-1,3,5-triazines



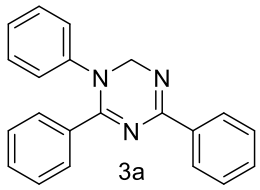
A 25 mL flask equipped with a stir-bar was charged with benzimidamide **1** (0.5 mmol, 1.0 equiv) , $CuCl_2$ (0.075 mmol, 0.15 equiv) and DMEA (0.5 ml). The reaction mixture was stirred at 80°C for 36 h. The reaction was monitored by TLC. Upon completion the reaction mixture was cooled to room temperature. Water (10 ml) was added and the mixture was extracted with ethyl acetate (3×10 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and removal of solvent produced. The residue was purified by column chromatography on silica gel with a mixed eluent of petroleum ether and ethyl to give the corresponding products **3.**

5.2 General Procedure for 2,4-disubstituted-1,3,5-triazines



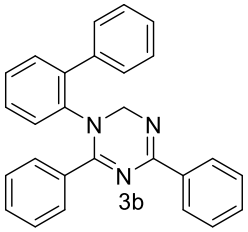
A 25 mL flask equipped with a stir-bar was charged with benzamidine hydrochloride **4** (0.5 mmol, 1.0 equiv) , $CuCl_2$ (0.075 mmol, 0.15 equiv) , Cs_2CO_3 (2 mmol, 1.0 equiv) and DMEA (0.5 ml). The reaction mixture was stirred at 90°C for 10 h. The reaction was monitored by TLC. Upon completion the reaction mixture was cooled to room temperature. Water (10 ml) was added and the mixture was extracted with ethyl acetate (3×10 mL). Combined organic phase were dried over anhydrous Na_2SO_4, and removal of solvent produced. The residue was purified by column chromatography on silica gel with a mixed eluent of petroleum ether and ethyl to give the corresponding products **5.**

6. Spectrum Data



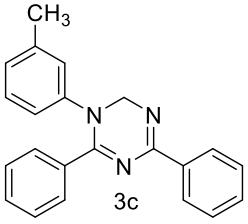
3a

1,4,6-Triphenyl-1,2-dihydro-1,3,5-triazine (3a): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.2 Hz, 2H), 7.53-7.50 (m, 3H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.26 (t, *J* = 7.8 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.6 Hz, 2H), 5.55 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.43, 161.50, 143.27, 136.04, 134.03, 131.27, 130.58, 130.54, 129.00, 128.26, 128.16, 127.98, 125.69, 124.66, 66.76. HRMS (ESI) Calcd for $C_{21}H_{18}N_3$ $[M+H]^+$ 312.1495;found 312.1506.



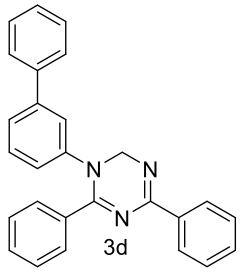
3b

1-([1,1'-Biphenyl]-2-yl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3b): Yellow solid; Mp: 98-99 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.3 Hz, 2H), 7.45-7.42 (m, 3H), 7.39-7.34 (m, 2H), 7.29-7.24 (m, 2H), 7.18-7.13 (m, 4H), 7.08 (t, *J* = 7.7 Hz, 2H), 7.03 (t, *J* = 7.7 Hz, 2H), 6.92 (d, *J* = 7.1 Hz, 2H), 5.42 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.50, 162.39, 141.10, 138.18, 138.02, 136.32, 133.84, 131.25, 130.98, 130.33, 130.14, 128.85, 128.49, 128.40, 128.05, 128.00, 127.61, 127.14, 127.04, 126.55, 67.54. HRMS (ESI) Calcd for $C_{27}H_{22}N_3$ $[M+H]^+$ 388.1808; found 388.1818.

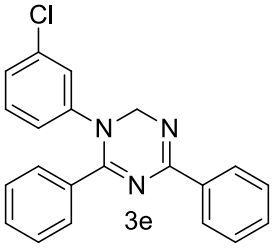


3c

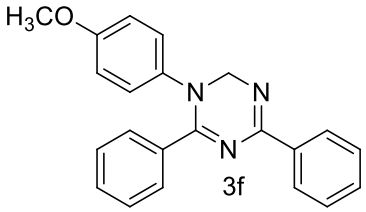
4,6-Diphenyl-1-(m-tolyl)-1,2-dihydro-1,3,5-triazine (3c): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.9 Hz, 2H), 7.72 (d, *J* = 7.1 Hz, 2H), 7.53-7.48 (m, 3H), 7.43 (t, *J* = 7.4 Hz, 1H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 6.85 (s, 1H), 6.77 (d, *J* = 7.9 Hz, 1H), 5.53 (s, 2H), 2.29 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.44, 161.53, 143.26, 139.06, 136.22, 134.18, 131.22, 130.52, 128.70, 128.24, 128.16, 127.97, 126.55, 125.17, 122.05, 66.90, 21.30. HRMS (ESI) Calcd for $C_{22}H_{20}N_3$ $[M+H]^+$ 326.1652; found 326.1648.



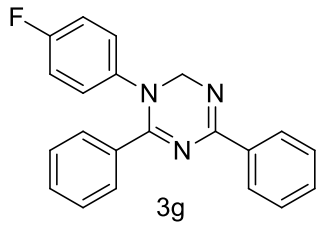
1-([1,1'-Biphenyl]-3-yl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3d): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 7.1 Hz, 2H), 7.49–7.43 (m, 3H), 7.41–7.35 (m, 3H), 7.33 (d, *J* = 8.0 Hz, 6H), 7.29 (d, *J* = 8.4 Hz, 1H), 7.13 (t, *J* = 1.6 Hz, 1H), 6.94 (dt, *J* = 8.4 H, 1.6 Hz, 1H), 5.56 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.40, 161.45, 143.63, 142.14, 139.98, 136.12, 134.10, 131.34, 130.56, 129.36, 128.83, 128.38, 128.18, 127.95, 127.78, 127.06, 124.37, 123.48, 123.09, 66.82. HRMS (ESI) Calcd for $C_{27}H_{22}N_3$ $[M+H]^+$ 388.1808; found 388.1823.



1-(3-Chlorophenyl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3e): Yellow solid; Mp: 70-71 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.2 Hz, 2H), 7.54-7.50 (m, 3H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.16-7.13 (m, 2H), 7.04 (s, 1H), 6.84-6.81 (m, 1H), 5.51 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.12, 161.33, 144.53, 135.85, 134.70, 133.53, 131.67, 130.71, 130.48, 129.82, 128.50, 128.23, 127.93, 125.69, 124.26, 122.95, 66.69. HRMS (ESI) Calcd for $C_{21}H_{17}ClN_3$ $[M+H]^+$ 346.1106; found 346.1112.

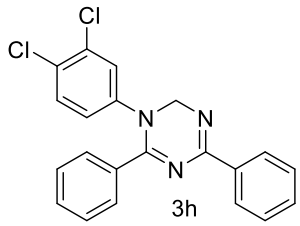


1-(4-Methoxyphenyl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3f): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (d, *J* = 7.6 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.51-7.48 (m, 3H), 7.41 (t, *J* = 7.2 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 6.94 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 5.51 (s, 2H), 3.78 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.30, 161.58, 157.54, 136.34, 134.22, 131.08, 130.54, 130.47, 128.72, 128.24, 128.15, 127.96, 126.11, 114.27, 67.28, 55.42. HRMS (ESI) Calcd for $C_{22}H_{20}N_3O$ $[M+H]^+$ 342.1601; found 342.1609.



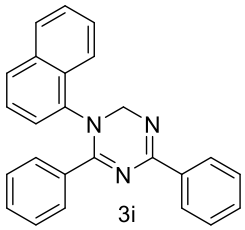
3g

1-(4-Fluorophenyl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3g): Yellow sticky mass;^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, *J* = 7.9 Hz, 2H), 7.68 (d, *J* = 7.2 Hz, 2H), 7.53-7.48 (m, 3H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.02–6.86 (m, 4H), 5.51 (s, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.31, 161.46, 160.33 (d, *J* = 245 Hz), 139.48, 136.05, 133.83, 131.40, 130.64, 130.54, 128.39, 128.21, 127.96, 126.28 (d, *J* = 8.4 Hz), 115.99 (d, *J* = 22.8 Hz), 67.08. HRMS (ESI) Calcd for $C_{21}H_{17}FN_3$ $[M+H]^+$ 330.1401; found 330.1407.



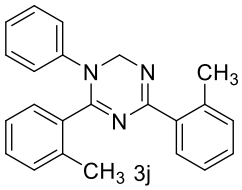
3h

1-(3,4-Dichlorophenyl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3h): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.66 (d, *J* = 7.2 Hz, 2H), 7.50–7.42 (m, 4H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 1H), 7.09 (d, *J* = 2.6 Hz, 1H), 6.72 (dd, *J* = 8.7, 2.6 Hz, 1H), 5.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.85, 161.22, 142.85, 135.71, 133.27, 133.01, 131.15, 130.43, 128.90, 128.65, 128.25, 127.93, 127.02, 125.61, 123.89, 121.13, 66.67. HRMS (ESI) Calcd for $C_{21}H_{16}Cl_2N_3$ $[M+H]^+$ 380.0716; found 380.0710.

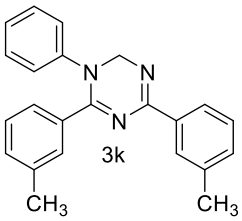


3i

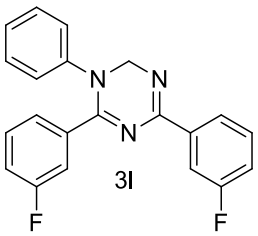
1-(Naphthalen-1-yl)-4,6-diphenyl-1,2-dihydro-1,3,5-triazine (3i): Yellow solid; Mp: 92-93 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (dd, *J* = 8.0, 2.2 Hz, 2H), 8.03 (d, *J* = 8.5 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.72-7.61 (m, 4H), 7.58–7.46 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 1H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.08 (d, *J* = 8.2 Hz, 1H), 5.61 (d, *J* = 11.7 Hz, 1H), 5.47 (d, *J* = 11.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.09, 162.26, 140.09, 136.29, 134.52, 134.20, 131.36, 130.60, 130.07, 129.63, 128.79, 128.19, 128.14, 128.03, 127.88, 127.34, 126.62, 125.71, 125.30, 122.91, 67.80. HRMS (ESI) Calcd for $C_{25}H_{20}N_3$ $[M+H]^+$ 362.1652; found 362.1665.



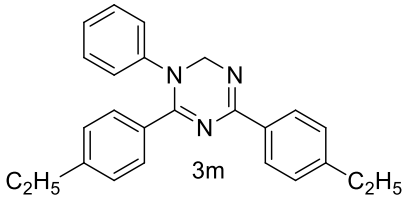
1-Phenyl-4,6-di-o-tolyl-1,2-dihydro-1,3,5-triazine (3j): Yellow solid; Mp: 118-119 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.1 Hz, 1H), 7.46 (d, *J* = 7.5 Hz, 1H), 7.32-7.12 (m, 7H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.4 Hz, 2H), 5.54 (s, 2H), 2.61 (s, 3H), 2.26 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.07, 163.20, 141.89, 137.16, 136.79, 136.33, 134.36, 130.87, 130.55, 130.50, 130.19, 129.25, 128.98, 128.70, 125.86, 125.82, 125.52, 124.21, 65.82, 21.24, 19.95. HRMS (ESI) Calcd for $C_{23}H_{22}N_3$ $[M+H]^+$ 340.1808; found 340.1811.



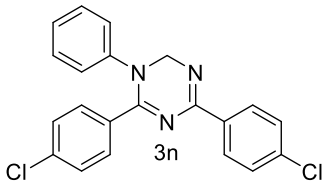
1-Phenyl-4,6-di-m-tolyl-1,2-dihydro-1,3,5-triazine (3k): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.4 Hz, 1H), 8.20 (s, 1H), 7.61 (s, 1H), 7.47-7.34 (m, 3H), 7.27-7.23 (m, 3H), 7.21–7.12 (m, 2H), 7.00 (d, *J* = 7.6 Hz, 2H), 5.54 (s, 2H), 2.49 (s, 3H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.60, 161.68, 143.40, 138.12, 137.79, 136.14, 134.01, 132.05, 131.31, 131.05, 128.94, 128.42, 128.09, 128.04, 127.78, 125.57, 125.23, 124.61, 66.81, 21.48, 21.35. HRMS (ESI) Calcd for $C_{23}H_{22}N_3$ $[M+H]^+$ 340.1808; found 340.1813.



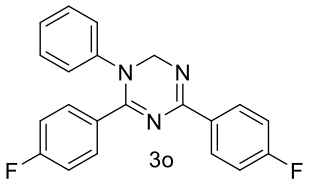
4,6-bis(3-Fluorophenyl)-1-phenyl-1,2-dihydro-1,3,5-triazine (3l): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 7.8 Hz, 1H), 8.06 (dt, *J* = 10.8, 1.6 Hz, 1H), 7.50–7.38 (m, 3H), 7.30-7.26 (m, 3H), 7.24-7.16 (m, 2H), 7.14 (dt, *J* = 8.3, 2.9 Hz, 1H), 7.01 (d, *J* = 7.5 Hz, 2H), 5.56 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.86 (d, *J* = 243 Hz), 162.44 (d, *J* = 245 Hz), 161.32, 160.28 142.82, 138.39 (d, *J* = 6.5 Hz), 136.18 (d, *J* = 7.7 Hz), 129.84 (d, *J* = 7.8 Hz), 129.64 (d, *J* = 8 Hz), 129.22, 126.19, 124.66, 123.55, 123.53, 118.41 (d, *J* = 21.4 Hz), 117.48 (d, *J* = 21.1 Hz), 117.32 (d, *J* = 23.1 Hz), 114.85 (d, *J* = 22.8 Hz), 66.92. HRMS (ESI) Calcd for $C_{21}H_{16}F_2N_3$ $[M+H]^+$ 348.1307; found 348.1312.



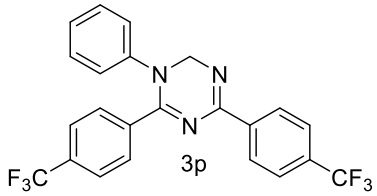
4,6-bis(4-Ethylphenyl)-1-phenyl-1,2-dihydro-1,3,5-triazine (3m): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.3 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 2H), 7.11-7.08 (m, 3H), 6.95 (d, *J* = 7.4 Hz, 2H), 5.46 (s, 2H), 2.72 (q, *J* = 7.5 Hz, 2H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H), 1.19 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.21, 161.62, 147.97, 146.97, 143.56, 133.70, 131.35, 130.60, 128.93, 127.98, 127.81, 127.69, 125.41, 124.59, 66.80, 28.87, 28.79, 15.50, 15.14. HRMS (ESI) Calcd for $C_{25}H_{26}N_3$ $[M+H]^+$ 368.2121; found 368.2125.



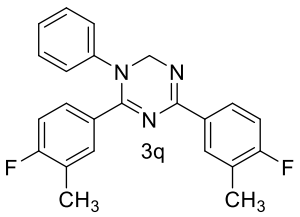
4,6-bis(4-Chlorophenyl)-1-phenyl-1,2-dihydro-1,3,5-triazine (3n): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.22 (t, *J* = 8.0 Hz, 2H), 7.14 (t, *J* = 7.6 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 2H), 5.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.39, 160.39, 142.95, 137.58, 136.70, 134.57, 132.38, 131.74, 129.27, 129.20, 128.64, 128.36, 126.04, 124.67, 66.93. HRMS (ESI) Calcd for $C_{21}H_{16}Cl_2N_3$ $[M+H]^+$:380.0716, found 380.1713.



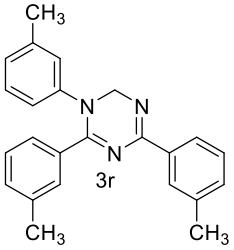
4,6-bis(4-Fluorophenyl)-1-phenyl-1,2-dihydro-1,3,5-triazine (3o): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.9, 5.6 Hz, 2H), 7.65 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.23 (t, *J* = 7.7 Hz, 2H), 7.17–7.07 (m, 3H), 7.01–6.91 (m, 4H), 5.47 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.54 (d, *J* = 248 Hz), 164.49 (d, *J* = 252 Hz), 161.35 160.45, 143.10, 139.30, 132.70 (d, *J* = 8.9 Hz), 132.23 (d, *J* = 3.0 Hz), 130.02 (d, *J* = 8.5 Hz), 129.15, 125.93, 124.69, 115.51 (d, *J* = 21.8 Hz), 115.06 (d, *J* = 21.4 Hz), 66.85. HRMS (ESI) Calcd for $C_{21}H_{16}F_2N_3$ $[M+H]^+$ 348.1307; found 348.1313.



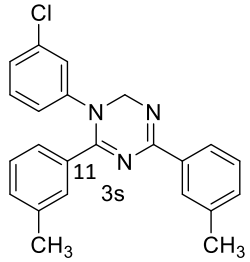
1-Phenyl-4,6-bis(4-(trifluoromethyl)phenyl)-1,2-dihydro-1,3,5-triazine (3p): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.0 Hz, 2H), 7.78 (t, *J* = 8.8 Hz, 4H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 2H), 7.24 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 7.6 Hz, 2H), 5.63 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.64, 160.38, 142.30, 137.24, 133.17 (q, *J* = 32.5 Hz), 132.59 (q, *J* = 29.6 Hz), 130.82, 129.47, 128.62, 128.41, 126.75, 125.37 (q, *J* = 3.4 Hz), 125.92 (q, *J* = 270 Hz), 125.26 (q, *J* = 3.2 Hz), 124.89 (q, *J* = 270 Hz), 124.80, 66.49. HRMS (ESI) Calcd for $C_{23}H_{16}F_6N_3$ $[M+H]^+$ 448.1243; found 448.1246.



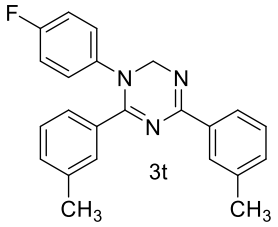
4,6-bis(4-Fluoro-3-methylphenyl)-1-phenyl-1,2-dihydro-1,3,5-triazine (3q): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99-7.94 (m 2H), 7.35 (dd, *J* = 10.4, 1.6 Hz, 1H), 7.25–7.20 (m, 4H), 7.13 (t, *J* = 7.4 Hz, 1H), 7.06 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.6 Hz, 2H), 5.46 (s, 2H), 2.34 (s, 3H), 2.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.43 (d, *J* = 242 Hz), 161.26, 160.88 (d, *J* = 244 Hz), 160.41, 143.12, 135.90 (d, *J* = 4.3 Hz), 133.41 (d, *J* = 7.6 Hz), 131.20 (d, *J* = 13.1 Hz), 131.14 (d, *J* = 13.0 Hz), 129.13, 128.80 (d, *J* = 17.3 Hz), 127.47 (d, *J* = 13.0 Hz), 126.01 (d, *J* = 3.4 Hz), 125.92, 124.62, 123.24 (d, *J* = 3.2 Hz), 116.89 (d, *J* = 24.1 Hz), 114.43 (d, *J* = 23.9 Hz), 66.87, 14.72, 14.69. HRMS (ESI) Calcd for $C_{23}H_{20}F_2N_3$ $[M+H]^+$ 376.1620; found 376.1618.



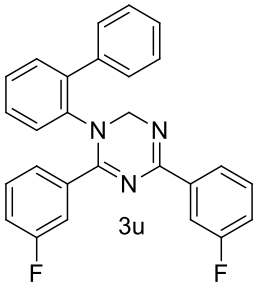
1,4,6-Tri-m-tolyl-1,2-dihydro-1,3,5-triazine (3r): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.9 Hz, 1H), 8.06 (s, 1H), 7.51 (s, 1H), 7.30-7.20 (m, 3H), 7.10 (d, *J* = 7.6 Hz, 1H), 7.04 (t, *J* = 7.6 Hz, 1H), 6.98 (t, *J* = 7.8 Hz, 1H), 6.83 (d, *J* = 7.6 Hz, 1H), 6.72 (s, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 5.39 (s, 2H), 2.36 (s, 3H), 2.24 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.61, 161.71, 143.33, 138.96, 138.06, 137.77, 136.16, 134.08, 132.01, 131.27, 130.98, 128.62, 128.39, 128.08, 127.98, 127.75, 126.45, 125.20, 125.07, 122.04, 66.86, 21.50, 21.39, 21.33. HRMS (ESI) Calcd for $C_{24}H_{24}N_3$ $[M+H]^+$ 354.1965; found 354.1977.



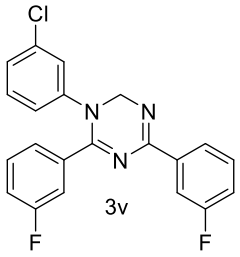
1-(3-Chlorophenyl)-4,6-di-m-tolyl-1,2-dihydro-1,3,5-triazine (3s): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.9 Hz, 1H), 8.12 (s, 1H), 7.57 (s, 1H), 7.37-7.33 (m, 2H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.11-7.05 (m, 2H), 6.99 (s, 1H), 6.77 (dt, *J* = 7.6, 2.4 Hz, 1H), 5.44 (s, 2H), 2.44 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.32, 161.52, 144.65, 138.38, 137.86, 135.83, 134.62, 133.50, 132.46, 131.47, 130.92, 129.76, 128.38, 128.25, 128.14, 127.72, 125.58, 125.21, 124.19, 122.91, 66.66, 21.48, 21.40. HRMS (ESI) Calcd for $C_{23}H_{21}ClN_3$ $[M+H]^+$ 374.1419; found 374.1424.



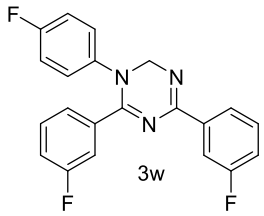
1-(4-Fluorophenyl)-4,6-di-m-tolyl-1,2-dihydro-1,3,5-triazine (3t): Yellow solid; Mp: 92-94 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.4 Hz, 1H), 8.13 (s, 1H), 7.53 (s, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.6 Hz, 1H), 7.15 (t, *J* = 7.6 Hz, 1H), 6.93 (s, 2H), 6.91 (d, *J* = 2.8 Hz, 2H), 5.45 (s, 2H), 2.44 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.53, 161.66, 160.24 (d, J = 245 Hz), 138.26, 137.84, 135.86, 133.89, 133.69, 132.19, 131.44, 131.02, 128.40, 128.14, 128.11, 127.74, 126.20 (d, J = 8.4 Hz), 125.21, 115.91 (d, J = 22.9 Hz) 66.90, 21.47, 21.36. HRMS (ESI) Calcd for $C_{23}H_{21}FN_3$ $[M+H]^+$ 358.1714; found 358.1727.



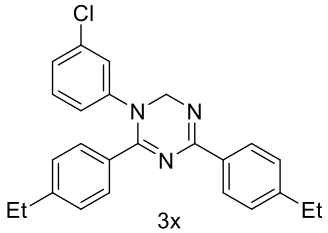
1-([1,1'-Biphenyl]-2-yl)-4,6-bis(3-fluorophenyl)-1,2-dihydro-1,3,5-triazine (3u): Yellow solid; Mp: 107-108 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.8 Hz, 1H), 7.87 (dt, *J* = 10.0, 2.0 Hz, 1H), 7.45–7.36 (m, 3H), 7.30 (dt, *J* = 7.4, 1.6 Hz, 1H), 7.23–7.15 (m, 3H), 7.06–6.95 (m, 4H), 6.88 (t, *J* = 7.0 Hz, 3H), 6.76 (dt, *J* = 9.5, 1.6 Hz, 1H), 5.46 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.75 (d, *J* = 243 Hz), 161.97 (d, *J* = 245 Hz), 161.48, 161.14, 140.63, 138.52 (d, *J* = 7.6 Hz), 138.09, 137.86, 135.95 (d, *J* = 7.7 Hz), 131.32, 129.55 (d, *J* = 8.0 Hz), 129.01 (d, *J* = 7.8 Hz), 128.82, 128.73, 128.44, 127.57, 127.28, 126.36, 125.68 (d, *J* = 2.8 Hz), 123.59 (d, *J* = 2.8 Hz), 118.06 (d, *J* = 21.1 Hz), 117.31 (d, *J* = 21.2 Hz), 116.94 (d, *J* = 23.1 Hz), 114.82 (d, *J* = 22.7 Hz), 67.60. HRMS (ESI) Calcd for $C_{27}H_{20}F_2N_3$ $[M+H]^+$ 424.1620; found 424.1624.



1-(3-Chlorophenyl)-4,6-bis(3-fluorophenyl)-1,2-dihydro-1,3,5-triazine (3v): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.9 Hz, 1H), 8.01 (dt, *J* = 10.3, 1.6 Hz, 1H), 7.43–7.35 (m, 3H), 7.25–7.20 (m, 1H), 7.16 (dt, *J* = 8.1, 2.8 Hz, 1H), 7.11-7.06 (m, 2H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.80 (s, 1H), 6.74 (d, *J* = 7.9 Hz, 1H), 5.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.86 (d, *J* = 243 Hz), 162.40 (d, *J* = 245 Hz), 161.32 (d, *J* = 2.8 Hz), 160.29 (d, *J* = 3.1 Hz), 142.77, 139.33, 138.48 (d, *J* = 7.7 Hz), 136.29 (d, *J* = 7.6 Hz), 129.80 (d, *J* = 8.0 Hz), 129.62 (d, *J* = 8.0 Hz), 128.90, 127.06, 126.20 (d, *J* = 3.0 Hz), 125.15, 123.54 (d, *J* = 2.8 Hz), 122.01, 118.34 (d, *J* = 21.2 Hz), 117.42 (d, *J* = 21.3 Hz), 117.28 (d, *J* = 23.1 Hz), 114.84 (d, *J* = 22.9 Hz), 66.99. HRMS (ESI) Calcd for $C_{21}H_{15}ClF_2N_3$ $[M+H]^+$ 382.0917; found 382.0917.

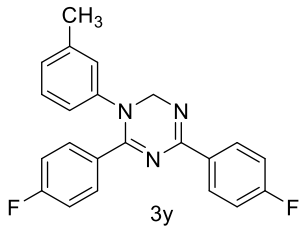


4,6-bis(3-Fluorophenyl)-1-(4-fluorophenyl)-1,2-dihydro-1,3,5-triazine (3w): Yellow solid; Mp: 78-79 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.8 Hz, 1H), 8.05 (dt, *J* = 10.3, 2.0 Hz, 1H), 7.49–7.40 (m, 2H), 7.38 (dt, *J* = 7.6, 1.2, 1H), 7.33-7.27 (m, 1H), 7.22 (td, *J* = 8.3, 2.6 Hz, 1H), 7.15 (td, *J* = 8.0, 2.8 Hz, 1H), 6.99 (d, *J* = 6.3 Hz, 4H), 5.52 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.87 (d, *J* = 244 Hz), 162.48 (d, *J* = 246 Hz), 161.56, 160.70 (d, *J* = 247 Hz), 160.45, 145.02, 140.65, 138.84, 130.05 (d, *J* = 7.9 Hz), 129.80 (d, *J* = 7.7 Hz), 126.39 (d, *J* = 8.4 Hz), 126.28, 123.72, 118.73 (d, *J* = 21.2 Hz), 117.91 (d, *J* = 20.3 Hz), 117.41 (d, *J* = 23.2 Hz), 116.34 (d, *J* = 22.9 Hz), 115.02 (d, *J* = 22.6 Hz), 66.72. HRMS (ESI) Calcd for $C_{21}H_{15}F_3N_3$ $[M+H]^+$ 366.1213; found 366.1217.



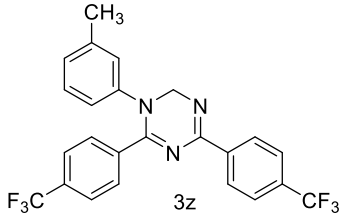
1-(3-Chlorophenyl)-4,6-bis(4-ethylphenyl)-1,2-dihydro-1,3,5-triazine (3x): Yellow solid; Mp: 104-106 ^{o}C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.3 Hz, 2H), 7.10-7.06 (m,

2H), 6.99 (d, *J* = 1.8 Hz, 1H), 6.77 (dt, *J* = 7.1, 2.1 Hz, 1H), 5.42 (s, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.64 (q, *J* = 7.6 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H), 1.21 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.93, 161.44, 148.40, 147.14, 144.85, 134.61, 133.44, 130.88, 130.54, 129.74, 128.01, 127.98, 127.73, 125.42, 124.17, 122.91, 66.68, 28.87, 28.82, 15.48, 15.13. HRMS (ESI) Calcd for $C_{25}H_{25}ClN_3$ $[M+H]^+$ 402.1732; found 402.1745.



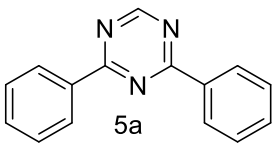
3y

4,6-bis(4-Fluorophenyl)-1-(m-tolyl)-1,2-dihydro-1,3,5-triazine (3y): Yellow sticky mass; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (dd, *J* = 8.9, 5.6 Hz, 2H), 7.66 (dd, *J* = 8.8, 5.2 Hz, 2H), 7.14–7.07 (m, 3H), 7.00–6.93 (m, 3H), 6.79 (s, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.45 (s, 2H), 2.26 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 164.54 (d, *J* = 248 Hz), 164.48 (d, *J* = 251 Hz), 161.38, 160.50, 143.04, 139.26, 132.69 (d, *J* = 8.8 Hz), 132.29 (d, *J* = 2.8 Hz), 130.88 (d, *J* = 2.8 Hz), 130.03 (d, *J* = 8.3 Hz), 128.84, 126.82, 125.19, 122.05, 115.47 (d, *J* = 21.8 Hz), 115.06 (d, *J* = 21.4 Hz), 66.89, 21.31. HRMS (ESI) Calcd for $C_{22}H_{18}F_2N_3$ $[M+H]^+$ 362.1463; found 362.1460.



3z

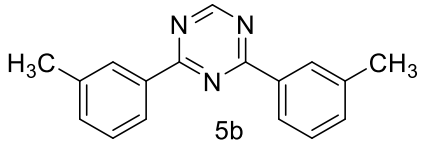
1-(m-Tolyl)-4,6-bis(4-(trifluoromethyl)phenyl)-1,2-dihydro-1,3,5-triazine (3z): Yellow solid; Mp: 101-103 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.71 (d, *J* = 8.2 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.11 (t, *J* = 7.8 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.81 (s, 1H), 6.73 (d, *J* = 7.9 Hz, 1H), 5.54 (s, 2H), 2.27 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.33, 160.15, 142.47, 139.54, 139.35, 137.59, 132.84 (q, *J* = 32.5 Hz), 132.52 (q, *J* = 31.7 Hz), 130.69, 129.04, 128.18, 127.33, 125.26 (q, *J* = 3.7 Hz), 125.20, 125.12 (q, *J* = 3.8 Hz), 124.16 (q, *J* = 271 Hz), 123.61 (q, *J* = 271 Hz), 122.15, 67.09, 21.30. HRMS (ESI) Calcd for $C_{24}H_{18}F_6N_3$ $[M+H]^+$ 462.1399; found 462.1403.



5a

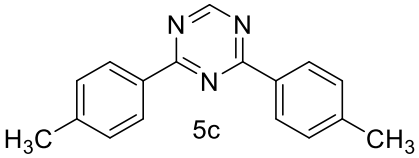
2,4-Diphenyl-1,3,5-triazine (5a)[4]: White solid; Mp: 73-74 ºC; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (s, 1H), 8.65-8.63(m, 4H), 7.64 – 7.59 (m, 2H), 7.58 – 7.53 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.37, 166.77, 135.58, 132.85, 128.92, 128.79. ESI-MS: $[M+H]^+$ 234.



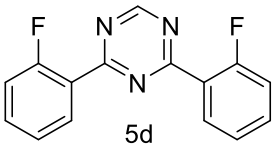
5b

2,4-bis(*m*-Tolyl)-1,3,5-triazine (5b)[4]: White solid; Mp: 85-86 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.25 (s, 1H), 8.45 (d, *J* = 6.5 Hz, 4H), 7.46-7.41 (m, 4H), 2.50 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.50, 166.63, 138.54, 135.55, 133.66, 129.38, 128.71, 126.15, 21.52. ESI-MS: $[M+H]^+$ 262.



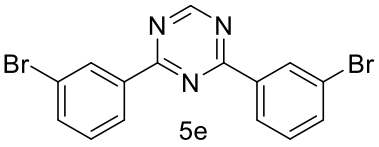
5c

2,4-bis(*p*-Tolyl)-1,3,5-triazine (5c)[4]: White solid; Mp: 160-161 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.19 (s, 1H), 8.52 (d, *J* = 8.2 Hz, 4H), 7.35 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.22, 166.57, 143.44, 132.98, 129.52, 128.89, 21.73. ESI-MS: $[M+H]^+$ 262.



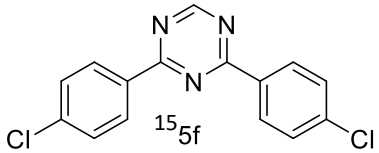
5d

2,4-bis(2-Fluorophenyl)-1,3,5-triazine (5d)[4]: White solid; Mp: 68-69 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 1H), 8.36 (dt, J_1= 7. 7 Hz, J_2 = 1.8 Hz, 2H), 7.57 – 7.50 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.24 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.48 (d, *J* = 5.1 Hz), 166.58, 162.29 (d, *J* = 260.5 Hz), 134.00 (d, *J* = 9.0 Hz), 132.25, 124.40 (d, *J* = 3.0 Hz), 124.05 (d, *J* = 8.0 Hz), 117.32 (d, *J* = 22.2 Hz).ESI-MS: $[M+H]^+$ 270.



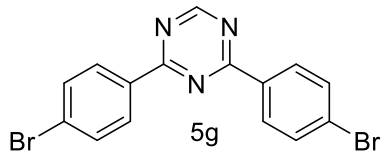
5e

2,4-bis(3-Bromophenyl)-1,3,5-triazine (5e)[4]: White solid; Mp: 178-179 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.28 (s, 1H), 8.77 (t, *J* = 1.7 Hz, 2H), 8.58 (d, *J* = 7.9 Hz, 2H), 7.75 (dq, J_1 = 7.9, J_1 = 1.0 Hz, 2H), 7.45 (t, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.35, 166.93, 137.35, 135.89, 131.87, 130.39, 127.54, 123.11. ESI-MS: $[M+H]^+$ 392.



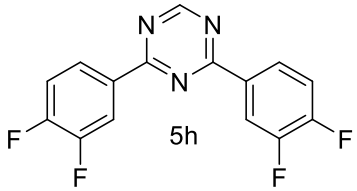
^{15}5f

2,4-bis(4-Chlorophenyl)-1,3,5-triazine (5f)[4]**:** White solid; Mp: 189-190 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.60 – 8.55 (m, 4H), 7.55 – 7.50 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.56, 166.85, 139.38, 133.88, 130.25, 129.14. ESI-MS: $[M+H]^+$ 303.



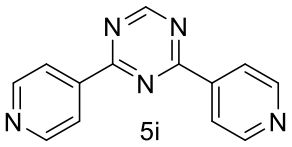
5g

2,4-bis(4-Bromophenyl)-1,3,5-triazine (5g)[4]**:** White solid; Mp: 195-196 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.49 (d, *J* = 8.7 Hz, 4H), 7.69 (d, *J* = 8.7 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.69, 166.86, 134.30, 132.11, 130.40, 128.07. ESI-MS: $[M+H]^+$ 392.



5h

2,4-bis(3,4-Difluorophenyl)-1,3,5-triazine (5h): White solid; Mp: 173-174 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (s, 1H), 8.48 – 8.37 (m, 4H), 7.39 – 7.29 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.71, 166.90, 153.74 (dd, *J* = 255, 12.9 Hz), 150.69 (dd, *J* = 248, 12.9 Hz), 132.39 (dd, *J* = 5.9, 3.4 Hz), 125.70 (dd, *J* = 7.2, 3.5 Hz), 118.08 (dd, *J* = 18.9, 1.3 Hz), 117.75 (d, *J* = 17.7 Hz). HRMS (ESI) Calcd for $C_{15}H_8F_4N_3$ $[M+H]^+$ 306.0649; found 306.0659.



5i

2,4-bis(Pyridin-4-yl)-1,3,5-triazine (5i)[4]**:** White solid; Mp: 182-183 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.44 (s, 1H), 8.90 (d, *J* = 5.9 Hz, 4H), 8.51 – 8.37 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 167.57, 150.97, 142.34, 122.18. ESI-MS: $[M+H]^+$ 235.

7. References

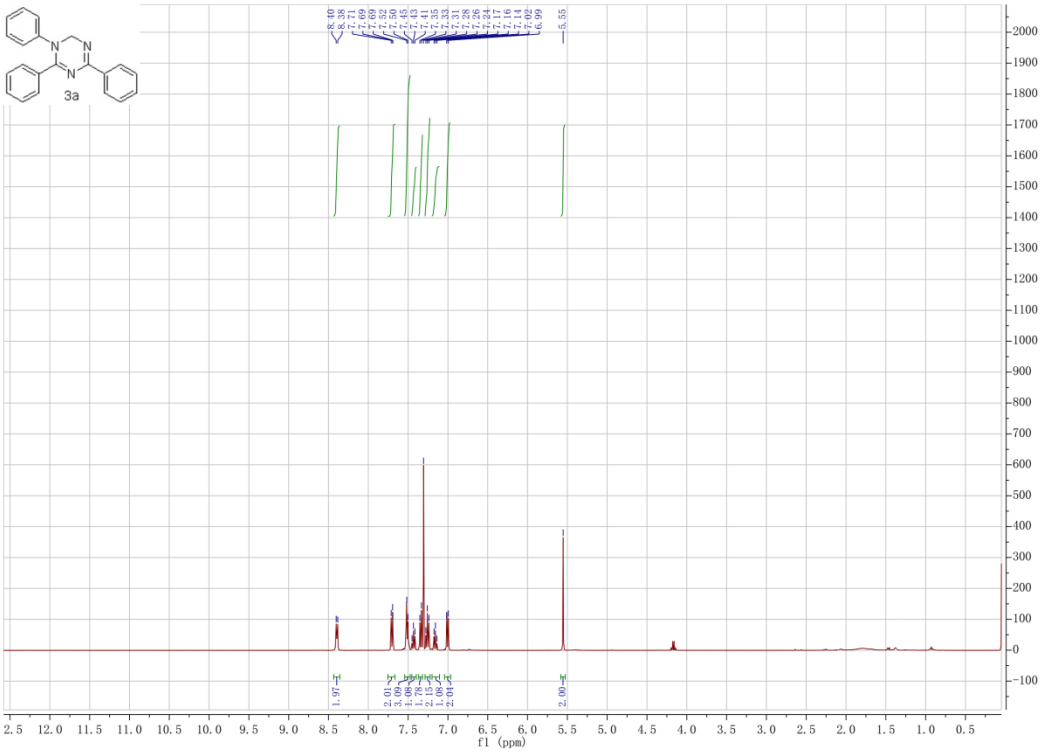
1 (a) Y. Bai, L. Tang, H. Huang and G.-J. Deng, *Org. Biomol. Chem.*, 2015, **13**, 4404-4407. (b) Z. Jia, K. Wang, B. Tan and Y. Gu, *Adv. Synth. Catal.*, 2017, **359**, 78-88. (c) H. Li, Z. He, X. Guo, W. Li, X. Zhao and Z. Li, *Org. Lett.*, 2009, **11**, 4176-4179.

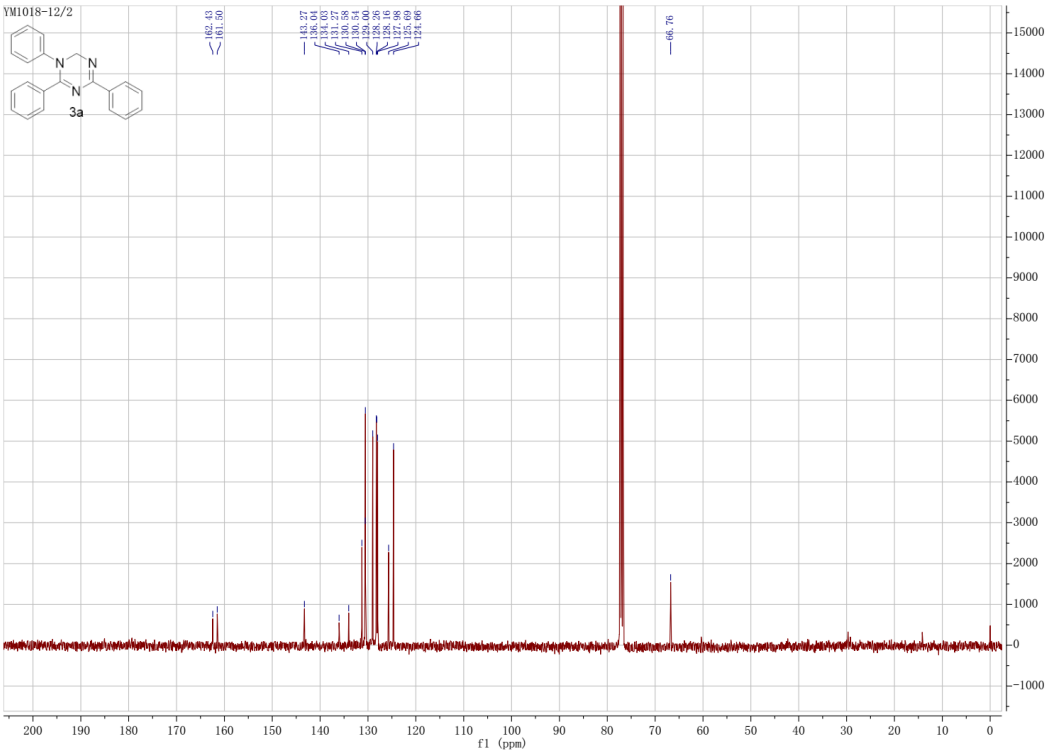
2 X.-F. Wu and K. Natte, *Adv. Synth. Catal.*, 2016, **358**, 336-352.

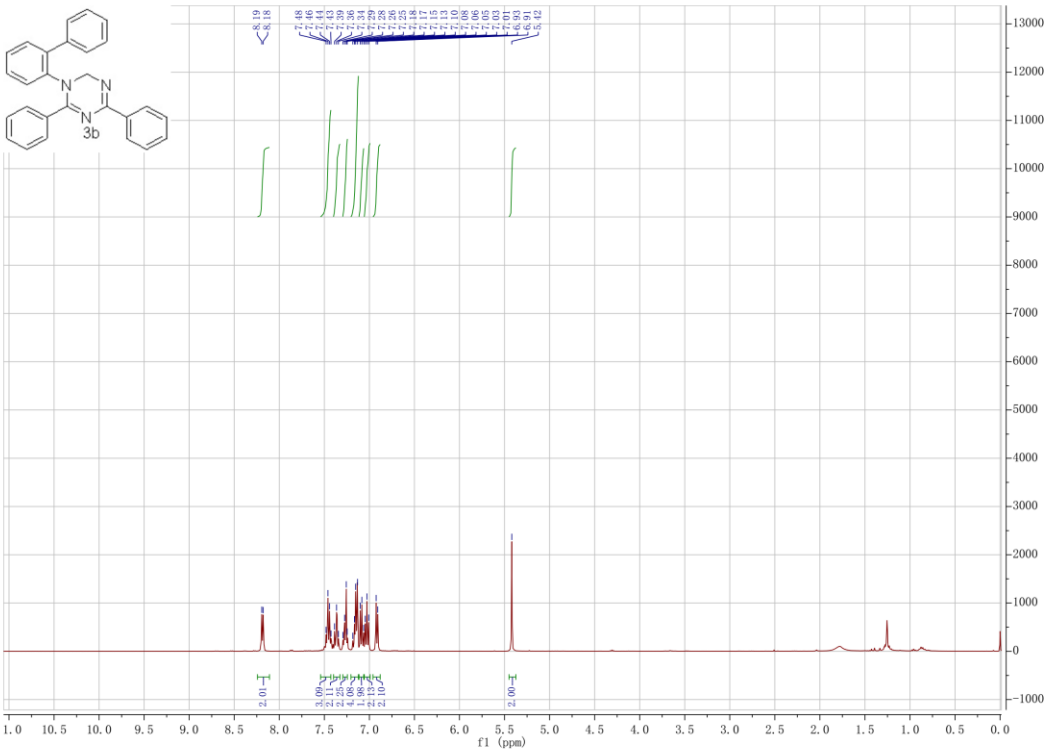
3 (a) B. Singh and J. C. Collins, *Chem. Commun.* 1971, 498-499; (b) Q. Xiao, W.-H. Wang, G. Liu, F.-K. Meng, J.-H.Chen, Z. Yang and Z.-J. Shi, *Chem. Eur. J.* 2009, **15**, 7292-7296.

4 Y.Z. Yan, L. Zheng, H.Y. Li, C. Cui, M.M. Shi and Y.Q. Liu, *Org. Lett.* 2017, **19**, 6228-6231.

8. Copies of NMR Spectra



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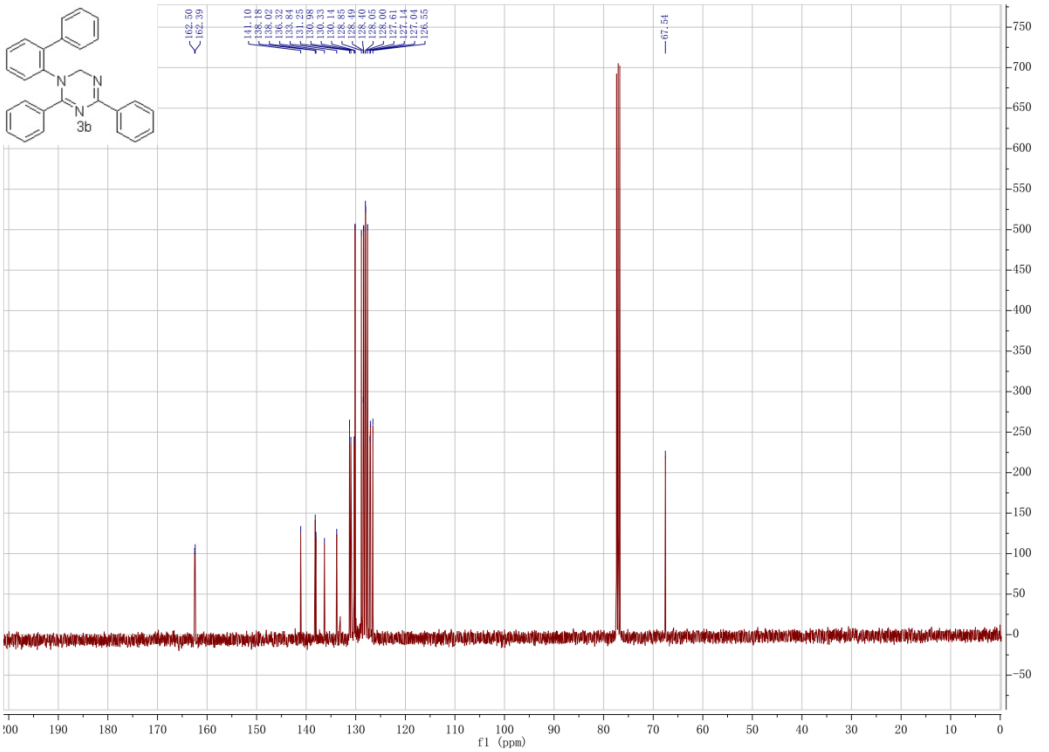
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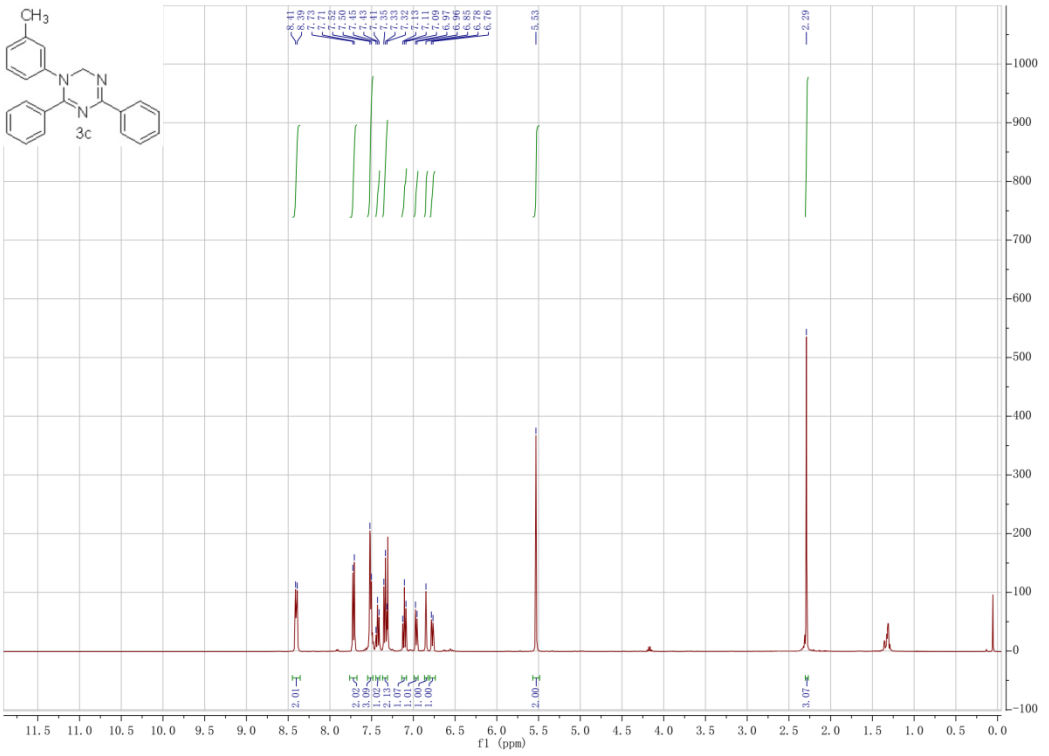
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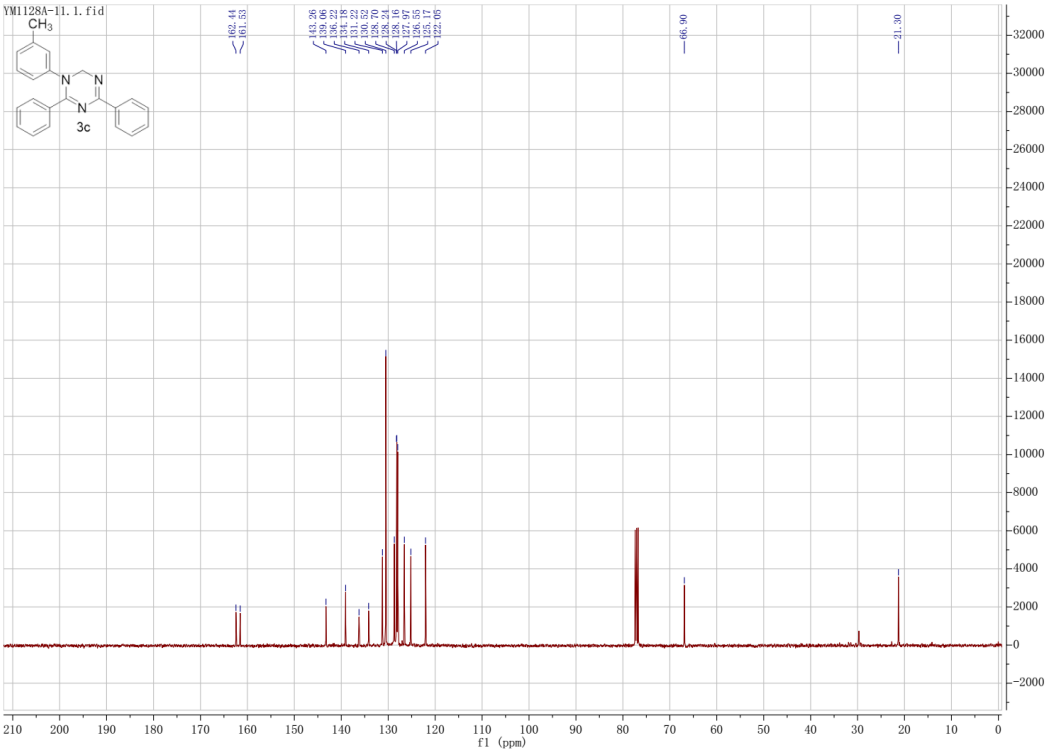
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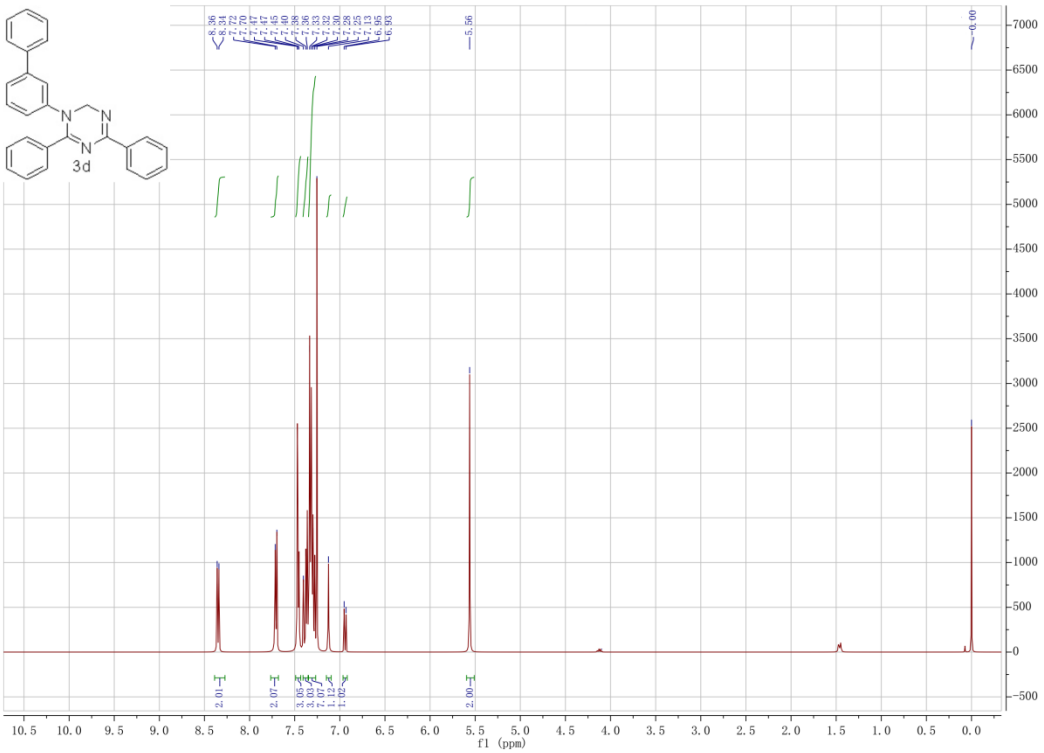
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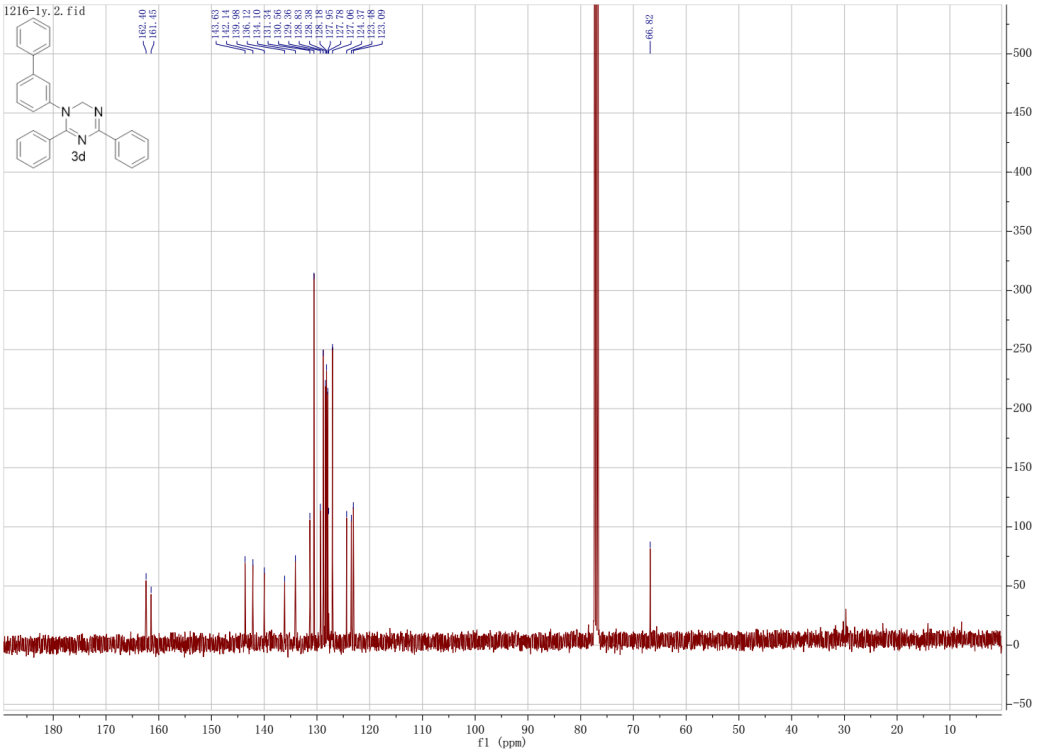
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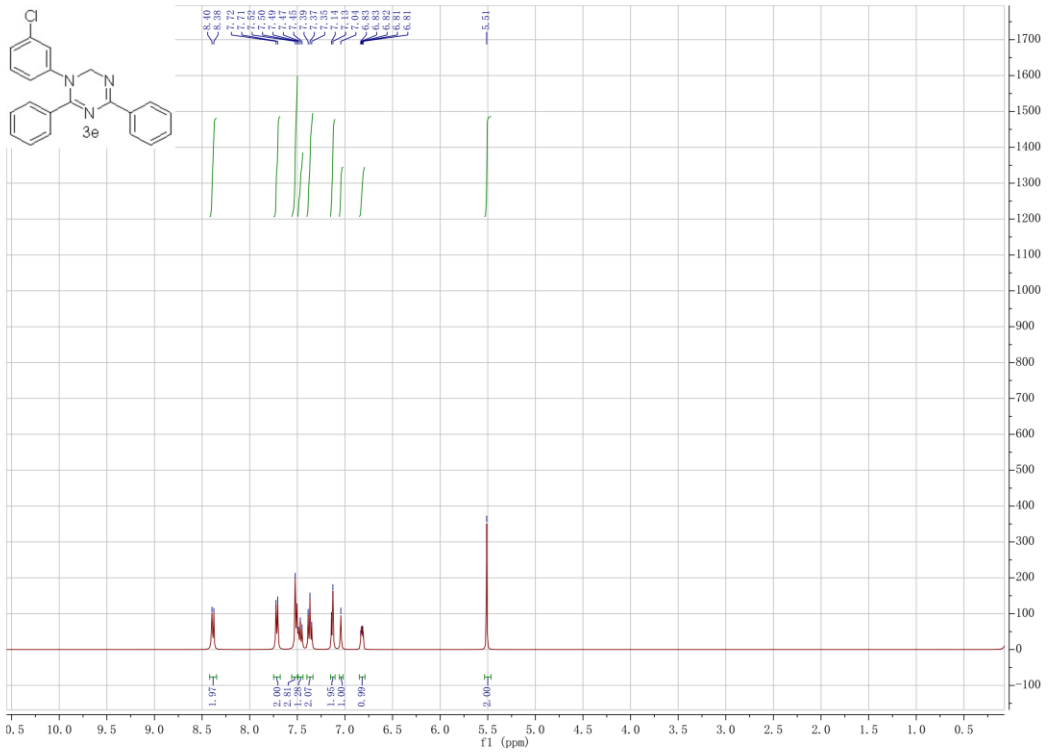
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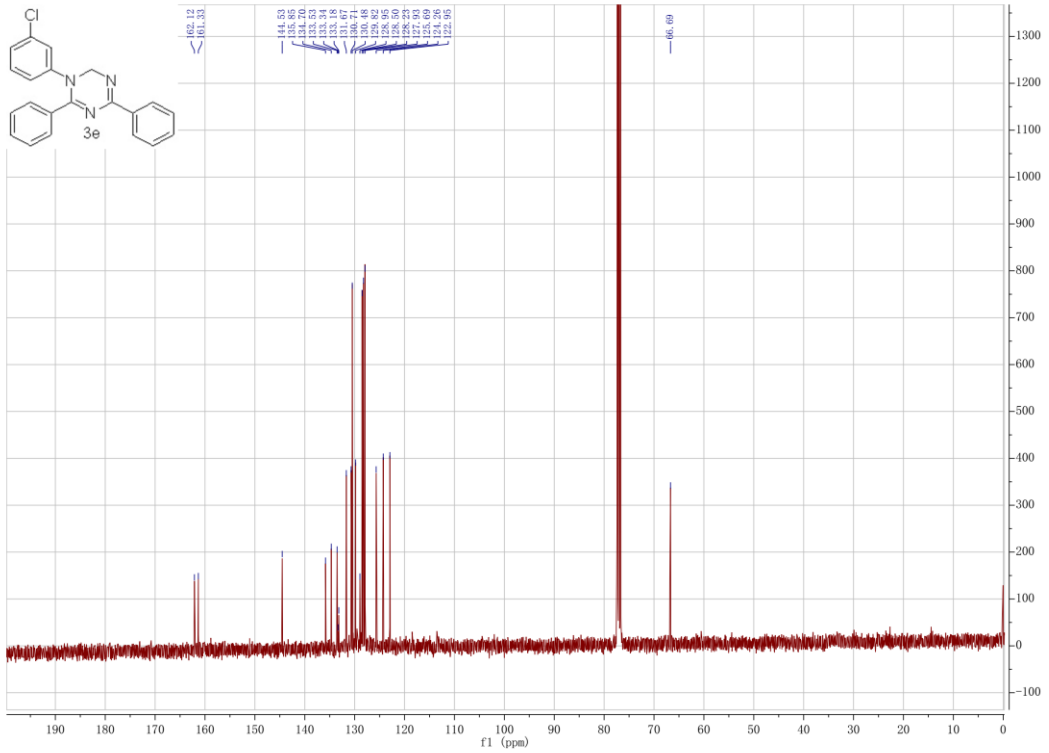
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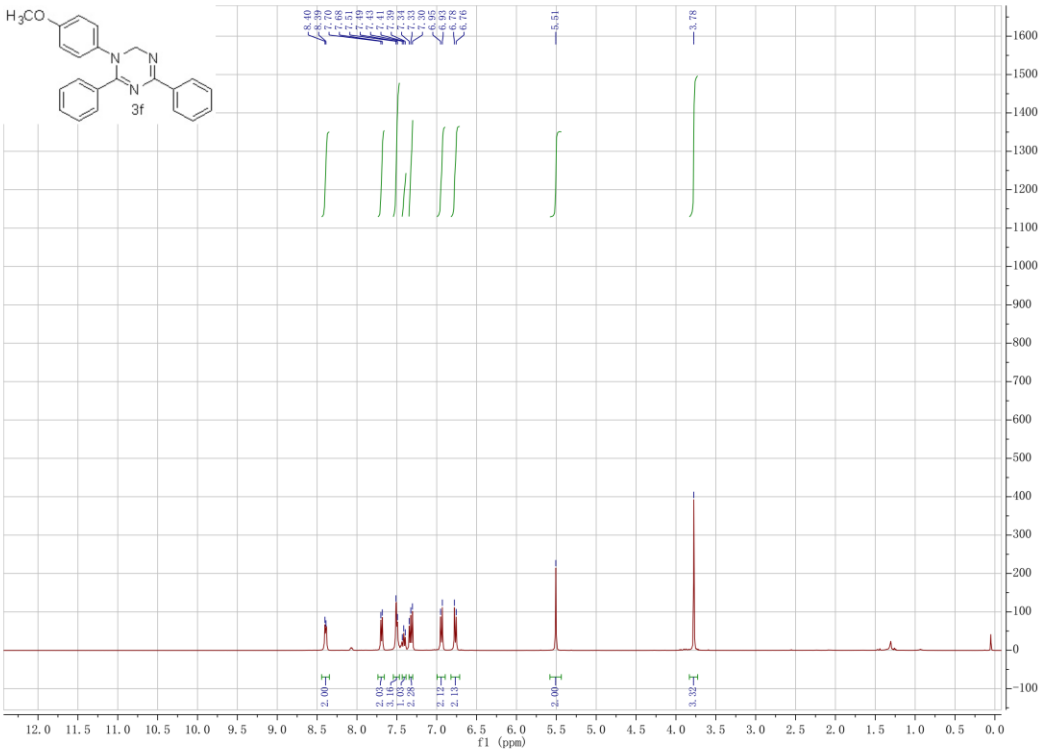
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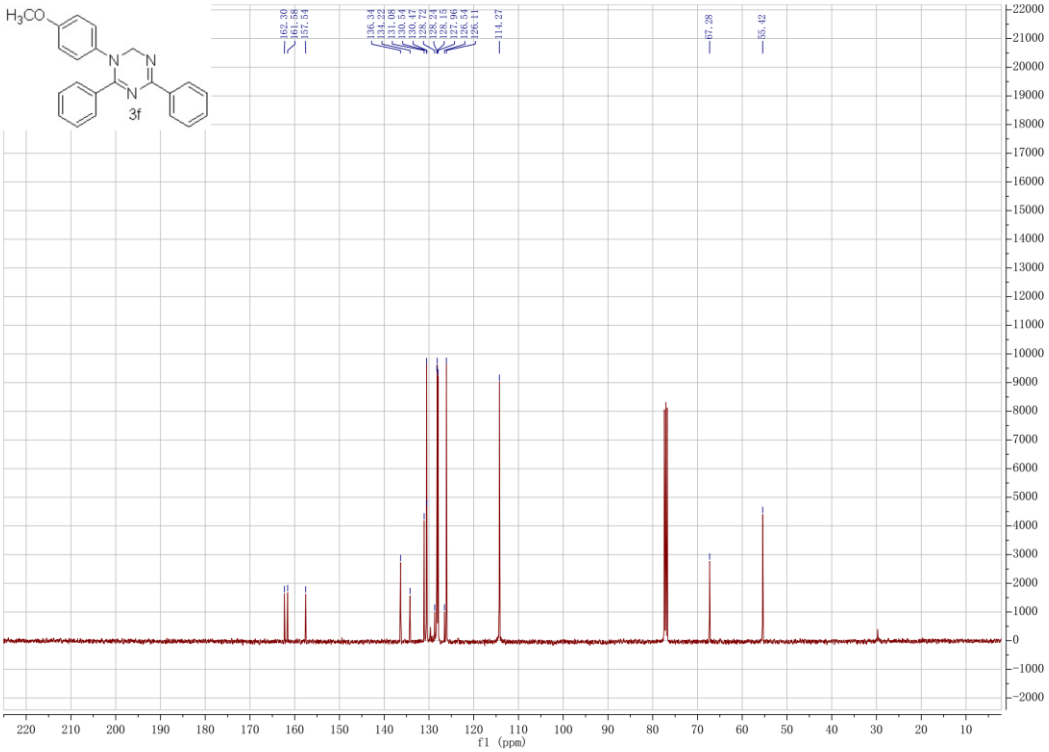
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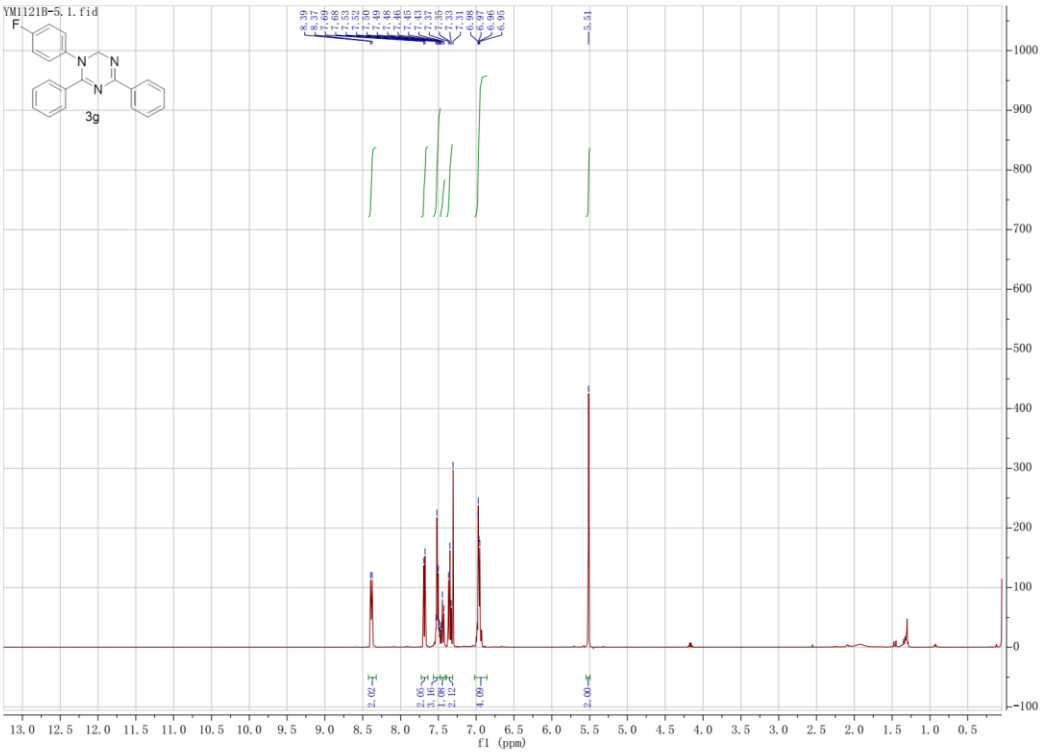
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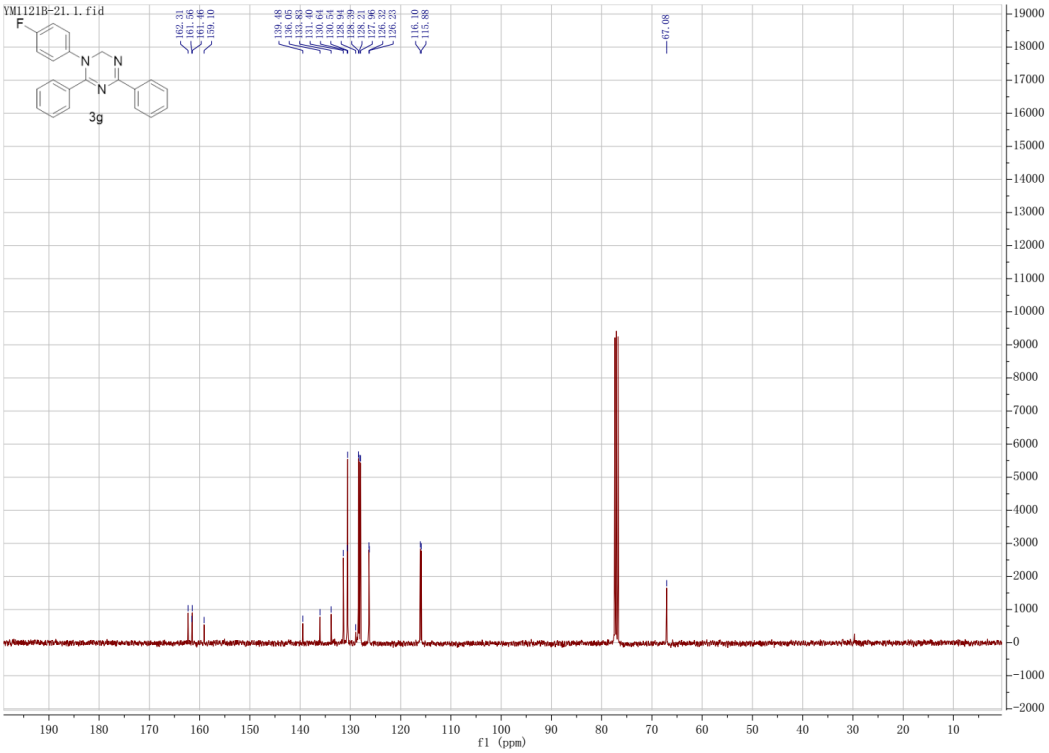
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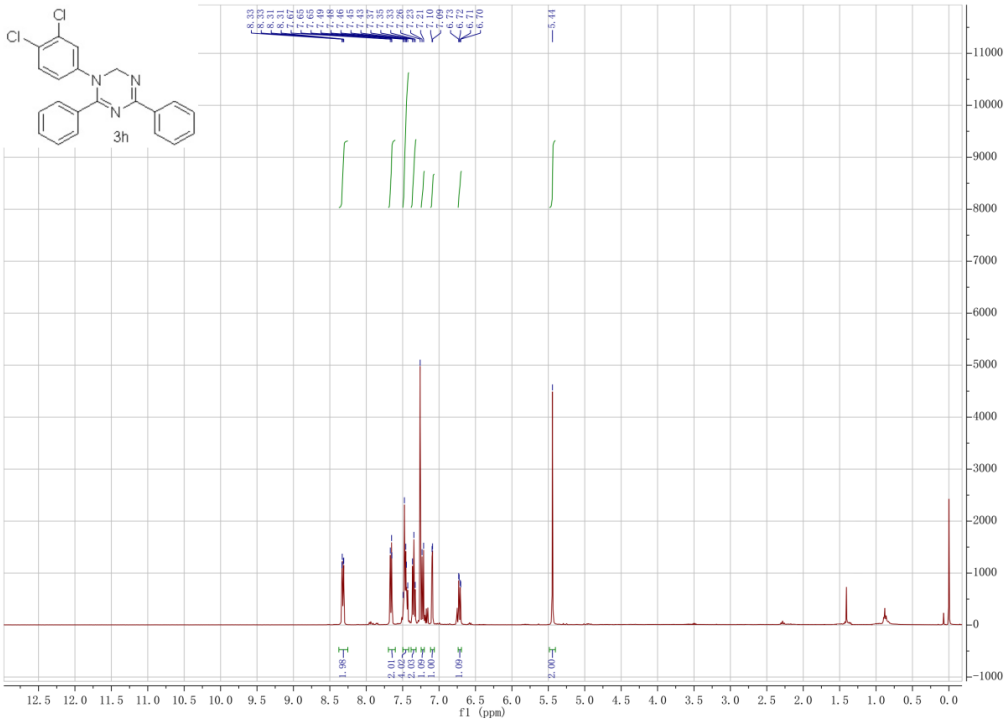
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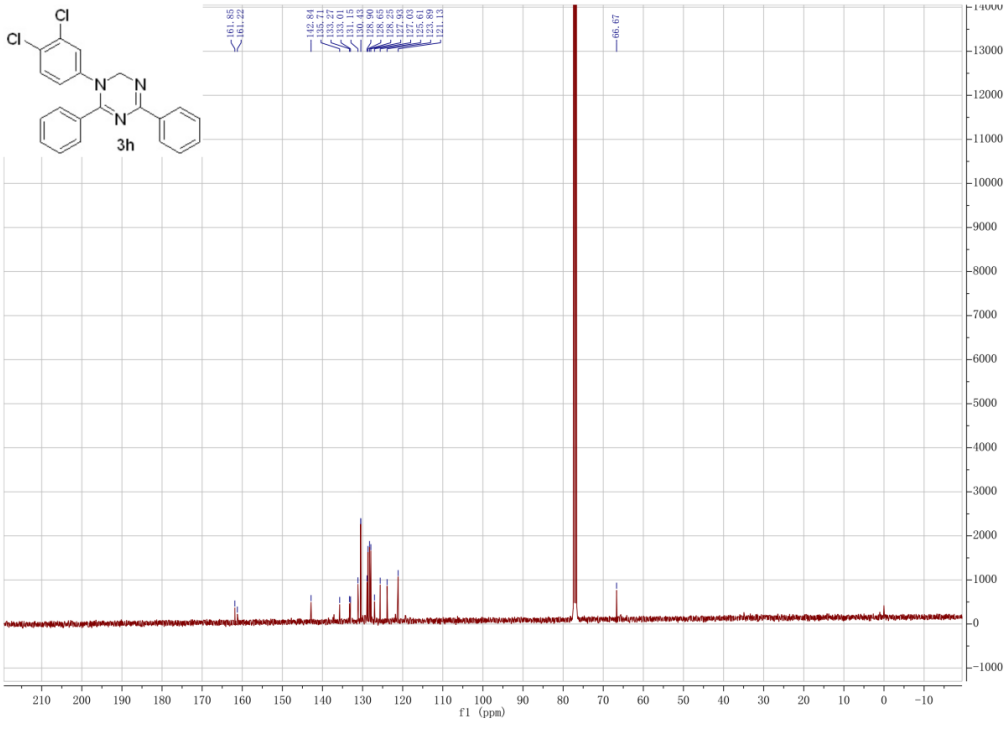
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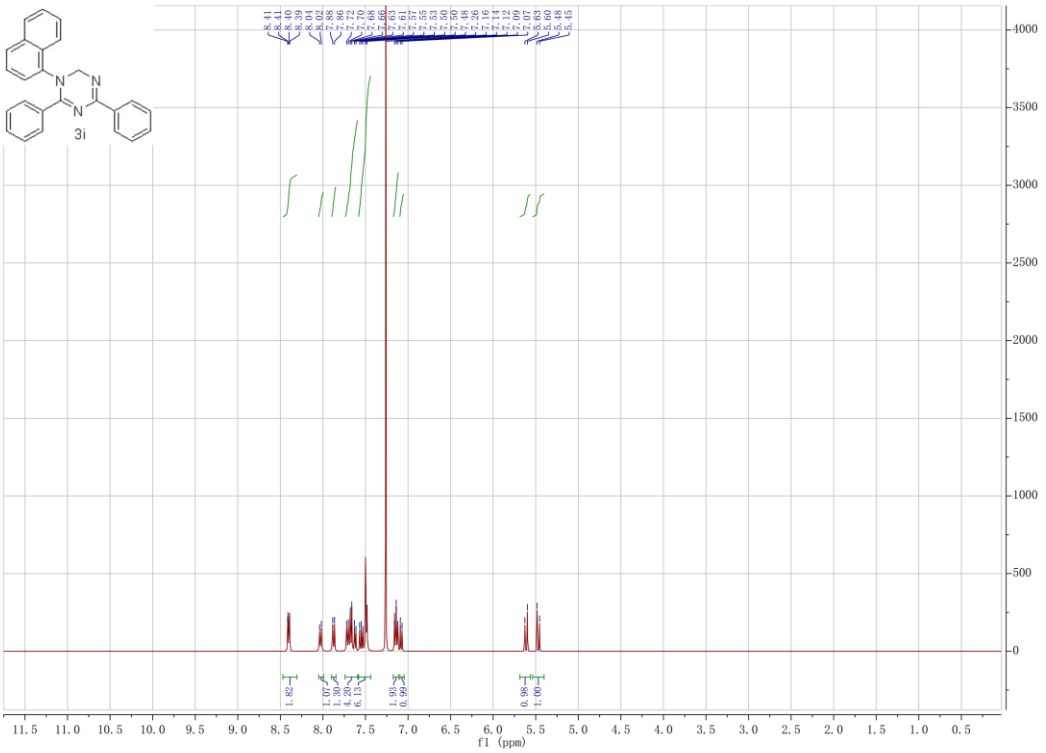
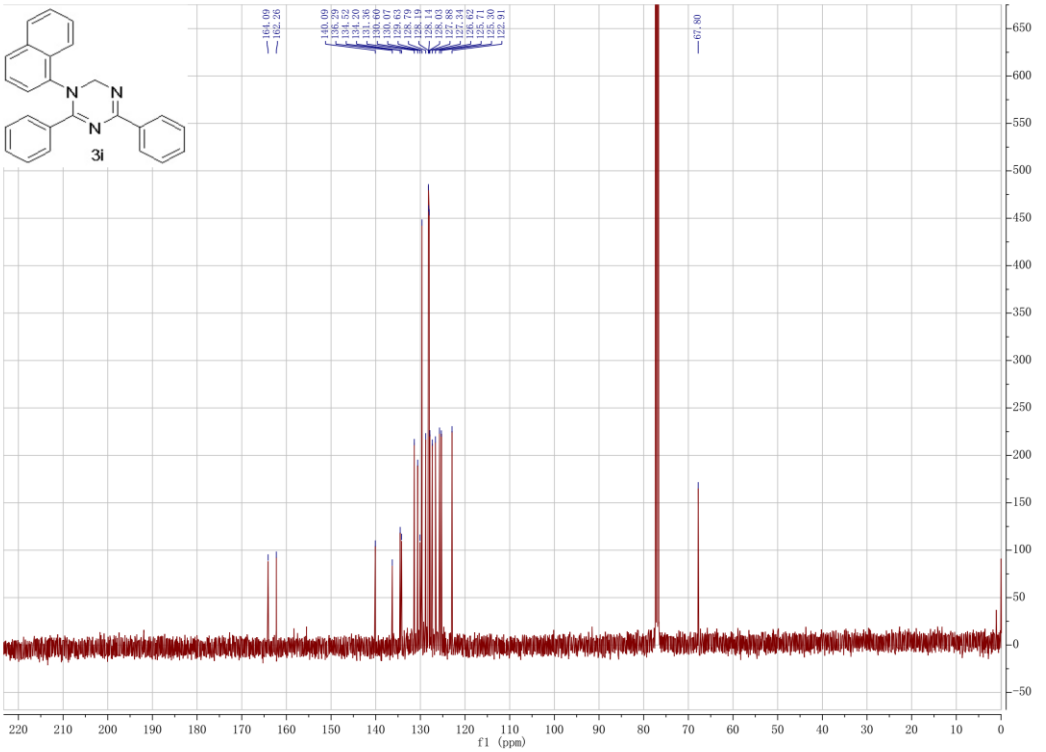
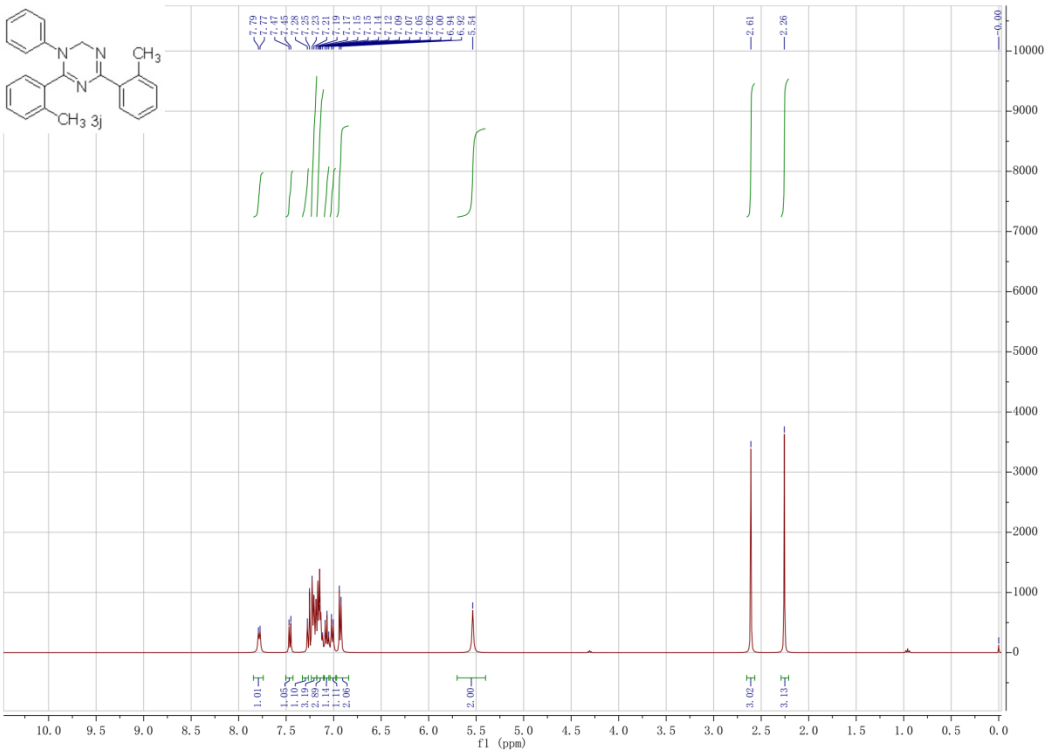
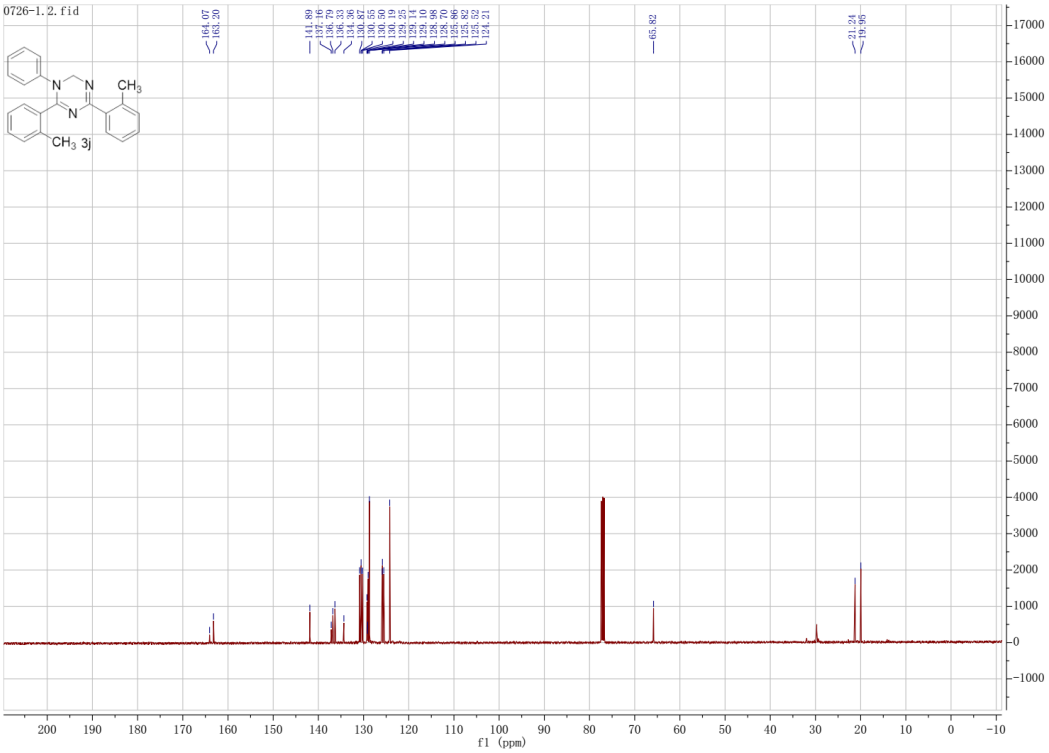
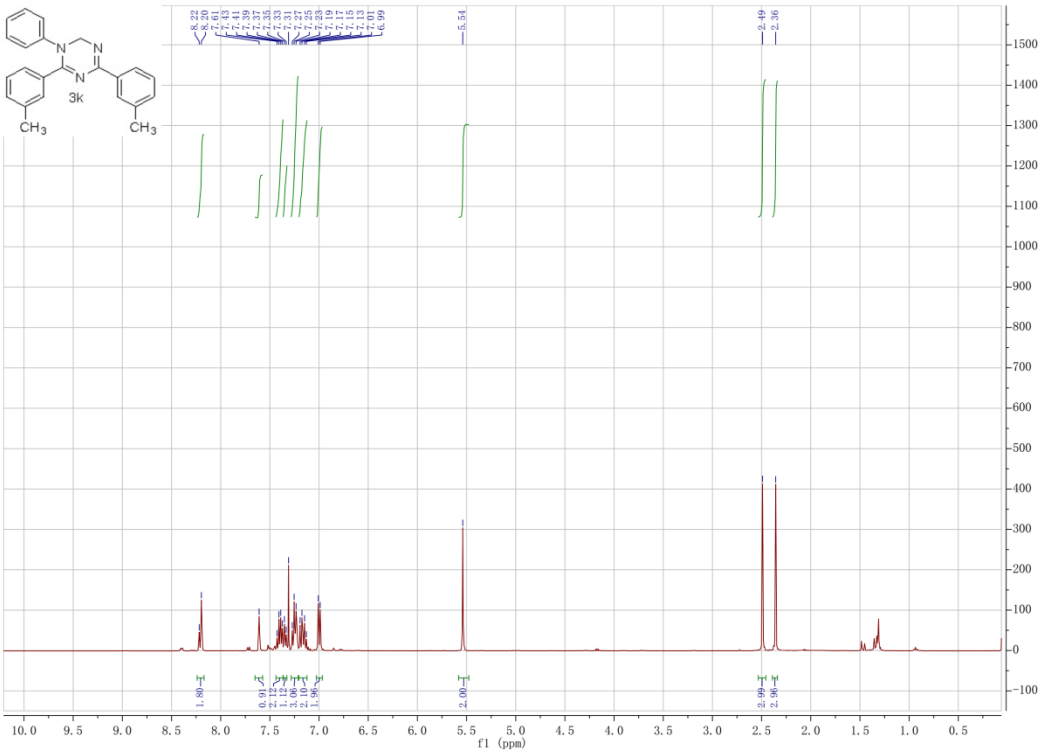
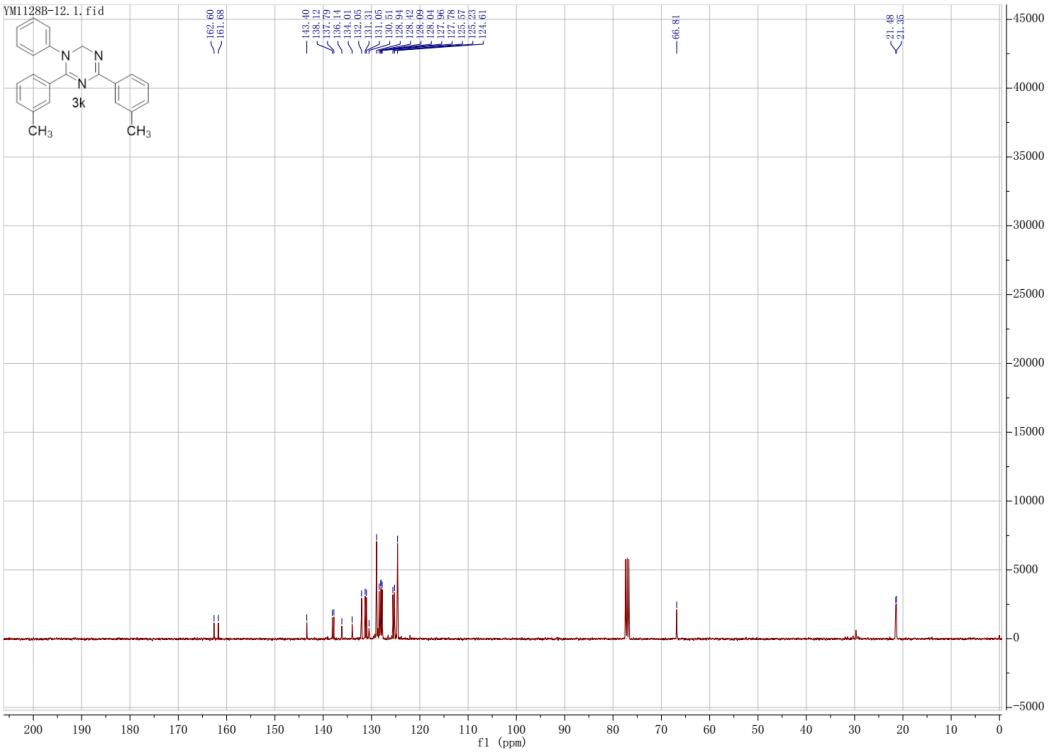

3i
f1 (ppm)

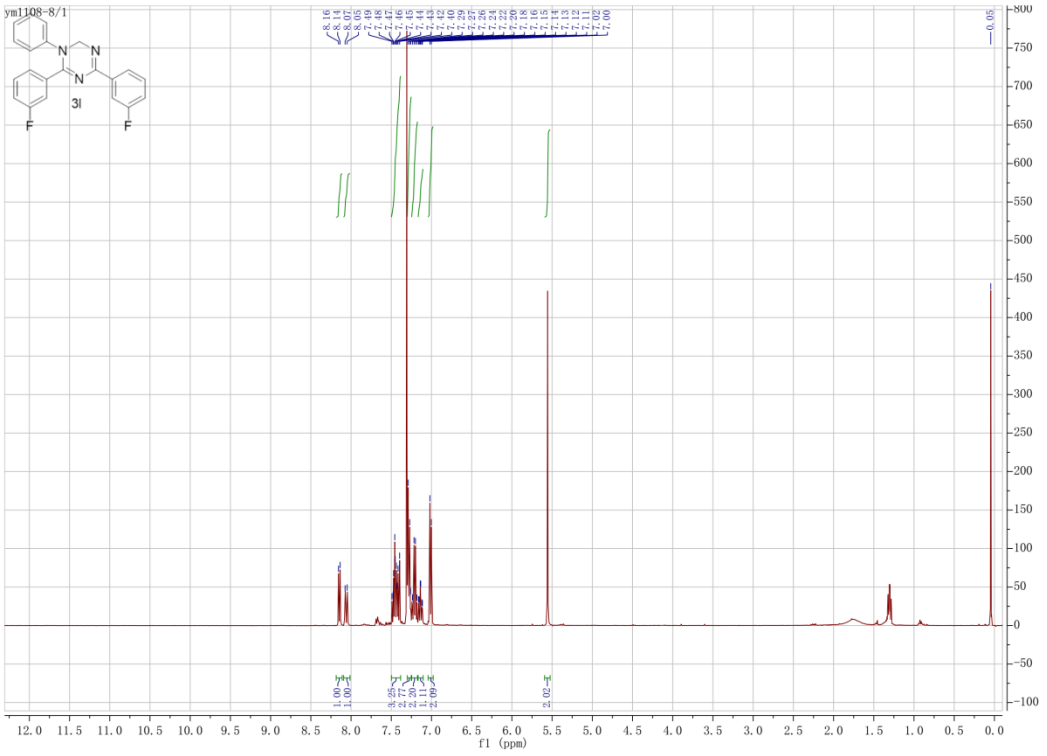

3i
f1 (ppm)

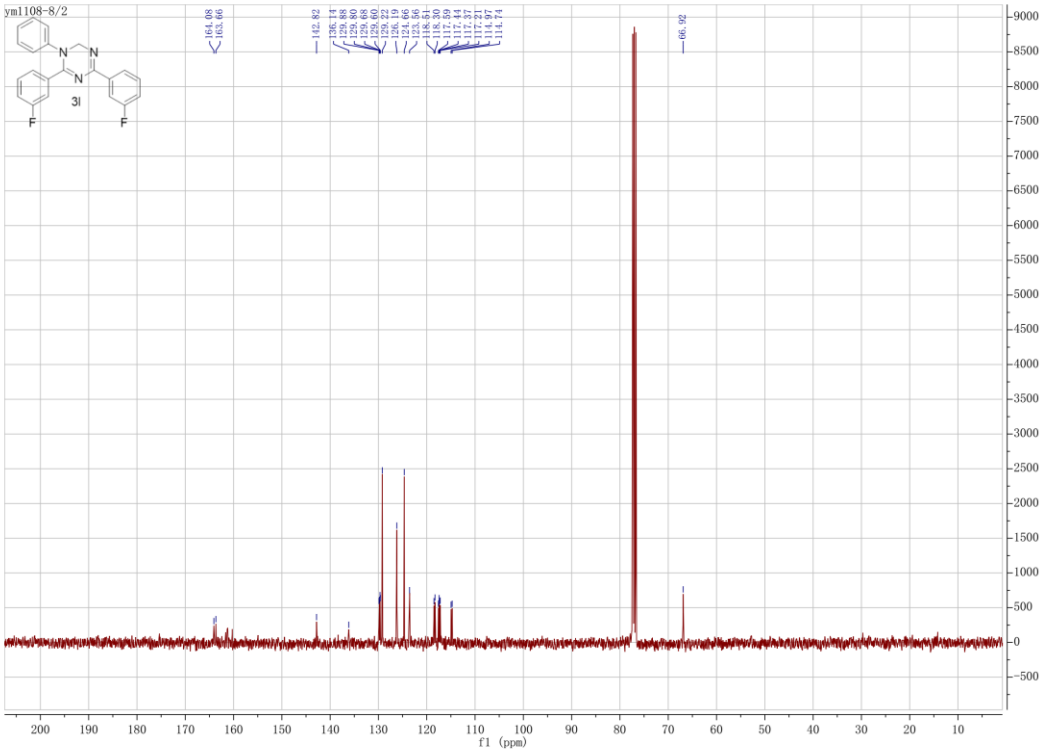

CH3
CH3 3j
7.79
7.77
7.47
7.45
7.28
7.25
7.21
7.19
7.17
7.15
7.14
7.12
7.09
7.07
7.05
7.02
7.00
6.94
6.92
5.84
2.61
2.26
0.00
1.01
1.05
1.10
2.89
1.14
1.11
2.06
2.00
3.02
3.13
f1 (ppm)

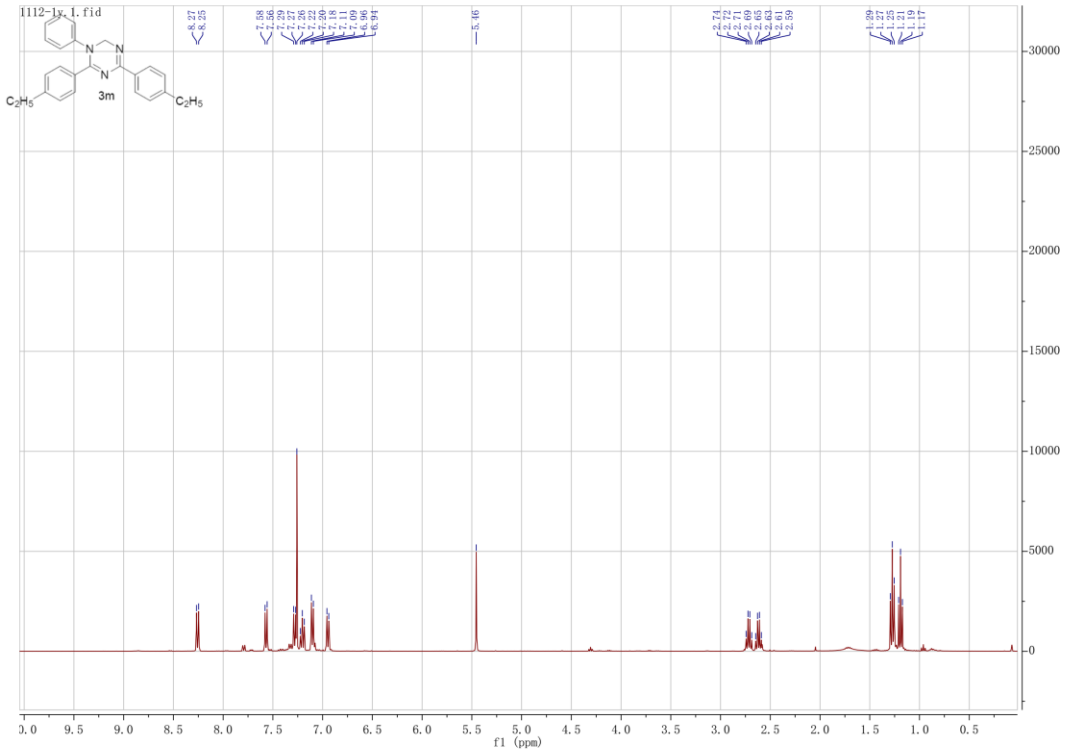

0726-1.2.fid
CH3
CH3 3j
164.07
163.20
141.89
137.46
136.79
136.33
134.36
130.57
130.55
130.50
130.19
129.35
129.14
129.10
128.98
128.70
125.86
125.82
125.52
124.21
65.82
21.04
19.95
f1 (ppm)

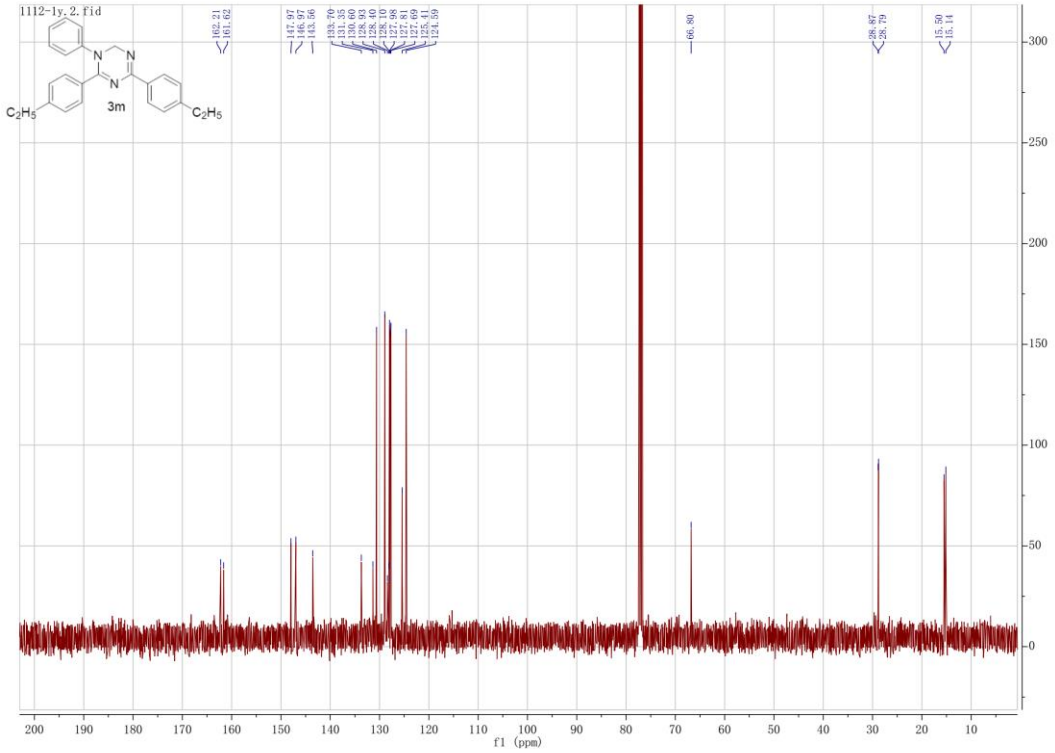

3k
CH3
CH3
8.22
8.20
7.61
7.43
7.41
7.39
7.37
7.35
7.33
7.31
7.27
7.25
7.23
7.19
7.17
7.15
7.13
7.01
6.99
5.54
2.49
2.36
1.80
0.91
2.12
1.12
3.06
2.10
1.96
2.00
2.99
2.96
f1 (ppm)

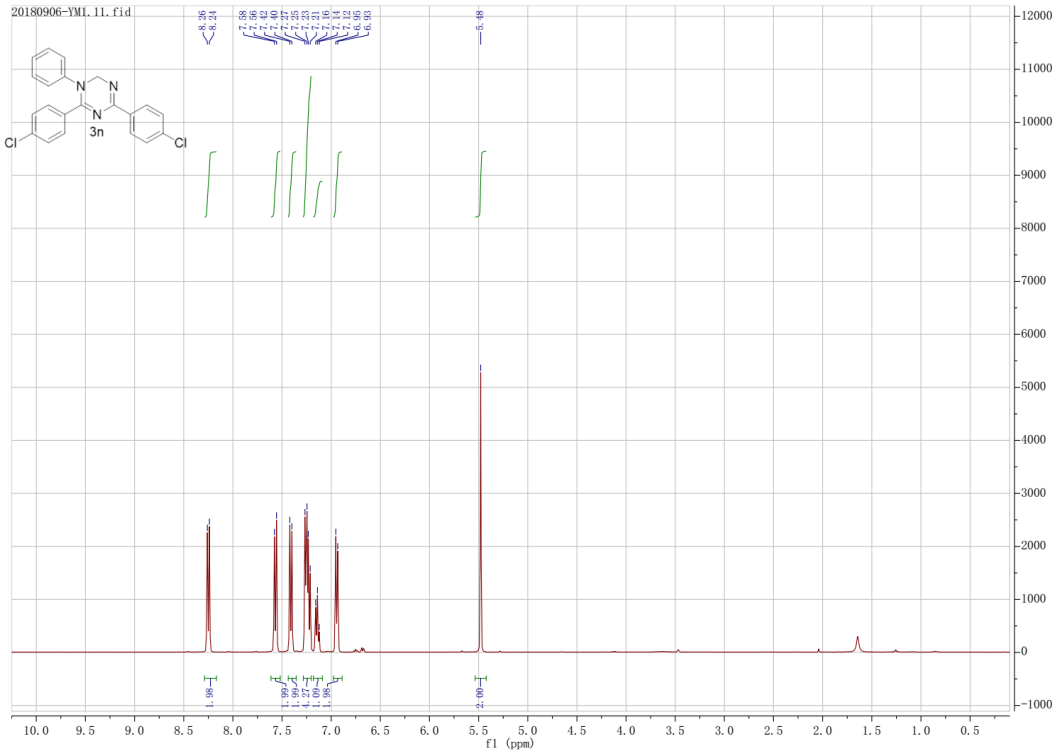

YM1128B-12.1.fid
3k
CH3
CH3
162.69
161.88
143.40
138.12
137.79
136.14
134.01
132.05
131.31
131.05
130.51
128.94
128.42
128.09
128.04
127.96
127.78
125.57
125.23
124.61
66.81
21.48
21.35
f1 (ppm)

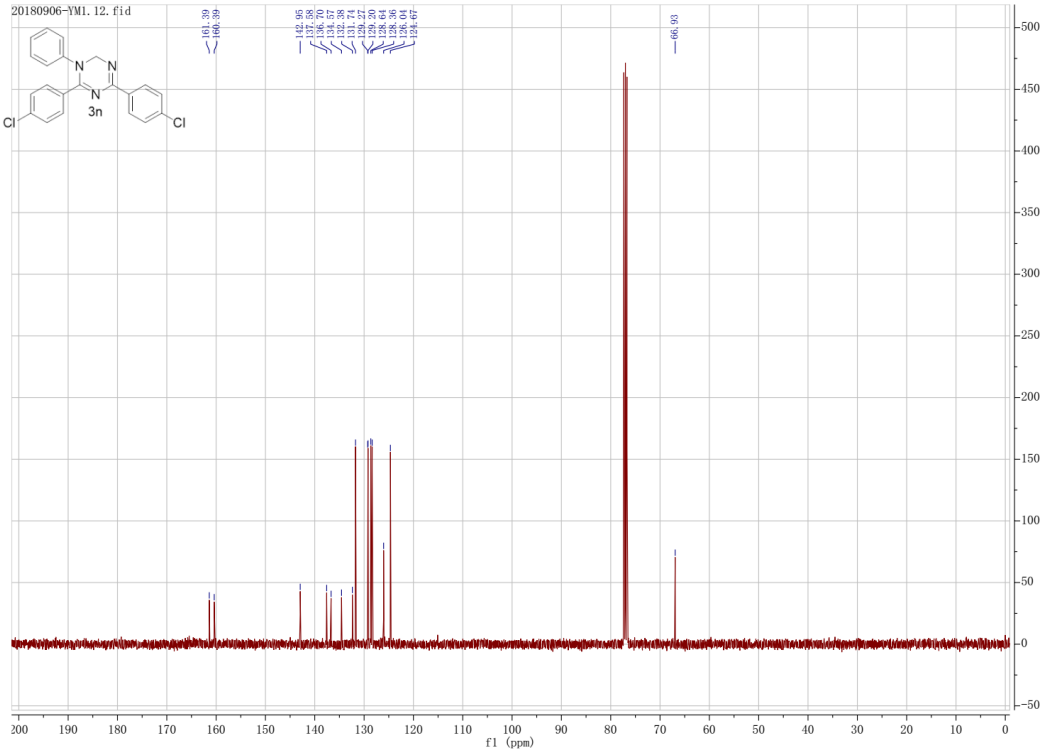

ym1108-8/1
3l
F
F
f1 (ppm)

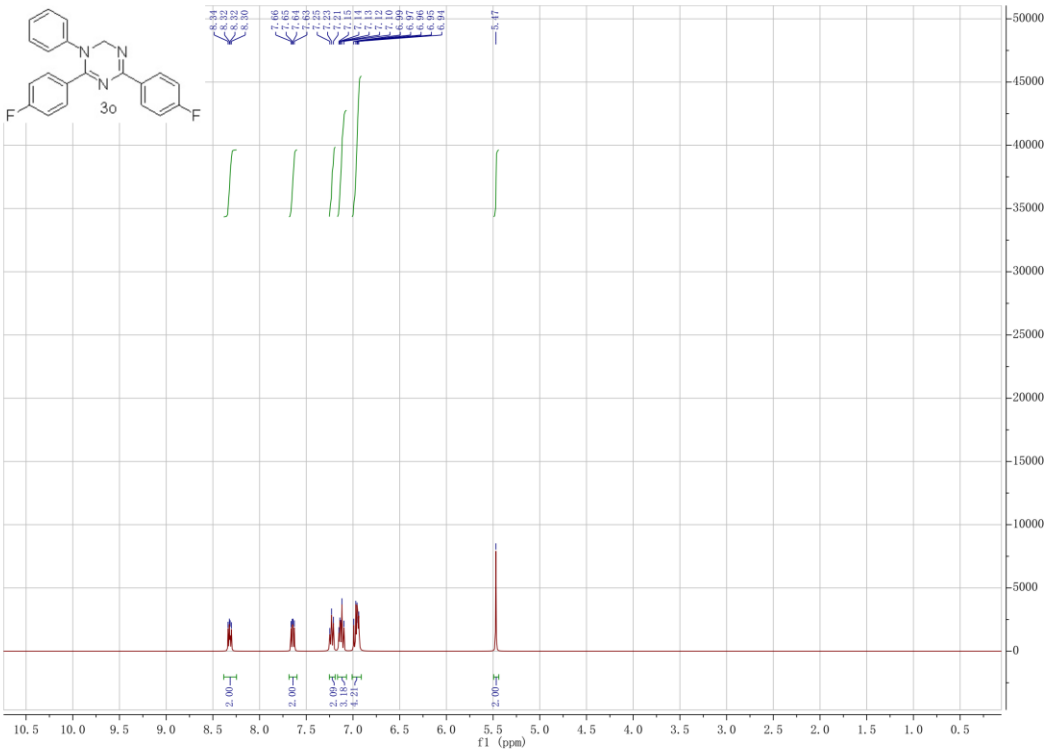

ym1108-8/2
3l
F
F
f1 (ppm)

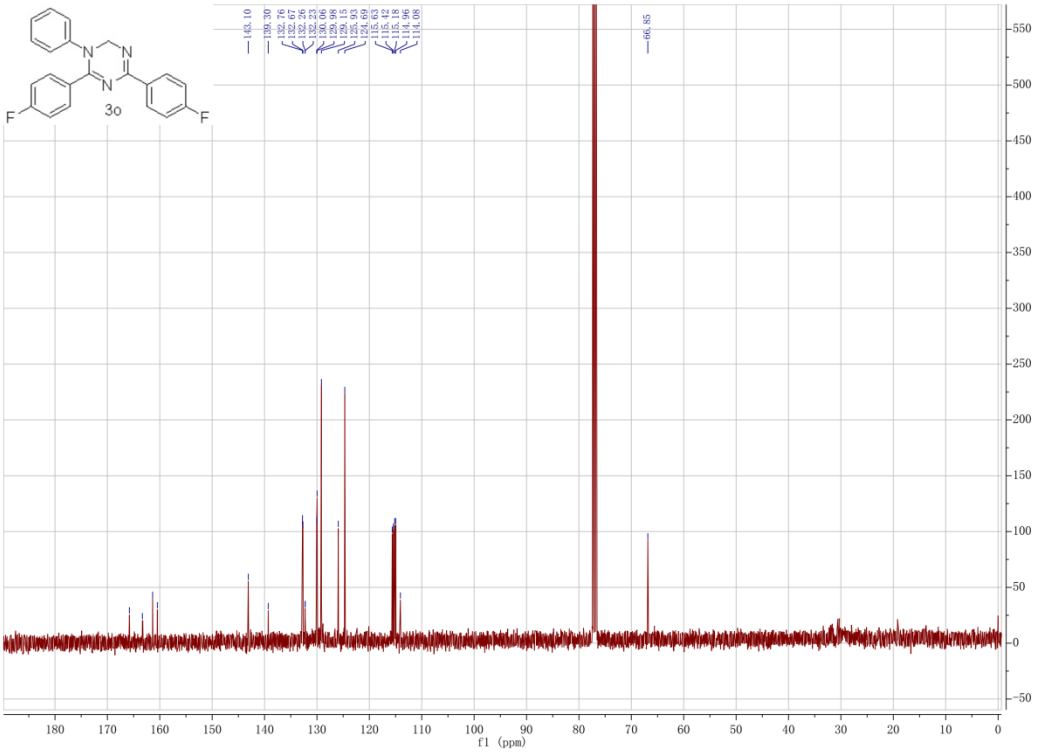

1112-1y.1.fid
3m
f1 (ppm)

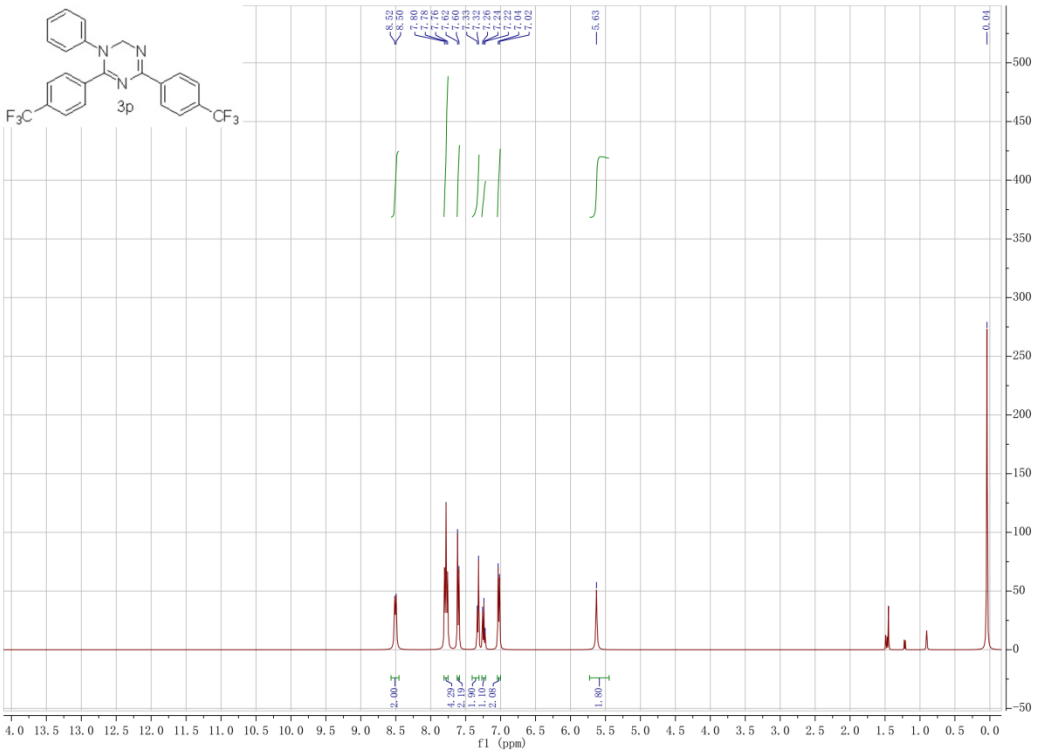

1112-1y.2.fid
3m
f1 (ppm)

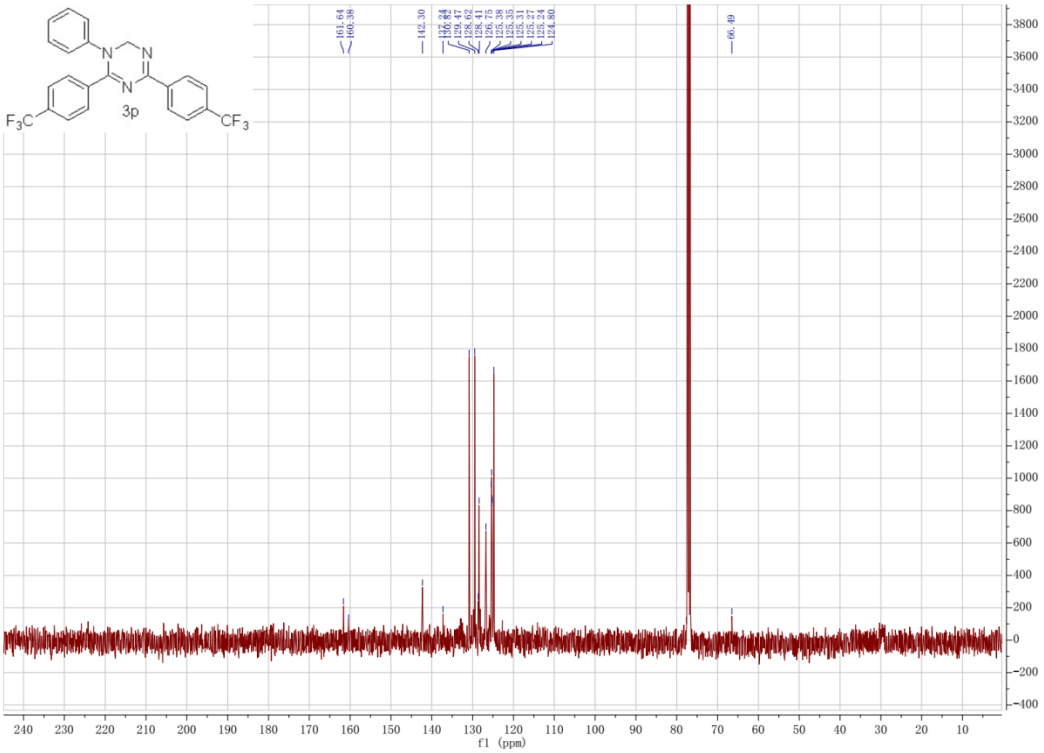

20180906-YM1.11.fid
8.36
8.24
7.98
7.96
7.42
7.40
7.25
7.23
7.21
7.16
7.14
7.12
6.95
6.93
5.48
3n
Cl
Cl
1.98
1.99
1.99
4.27
1.09
1.98
2.00
f1 (ppm)

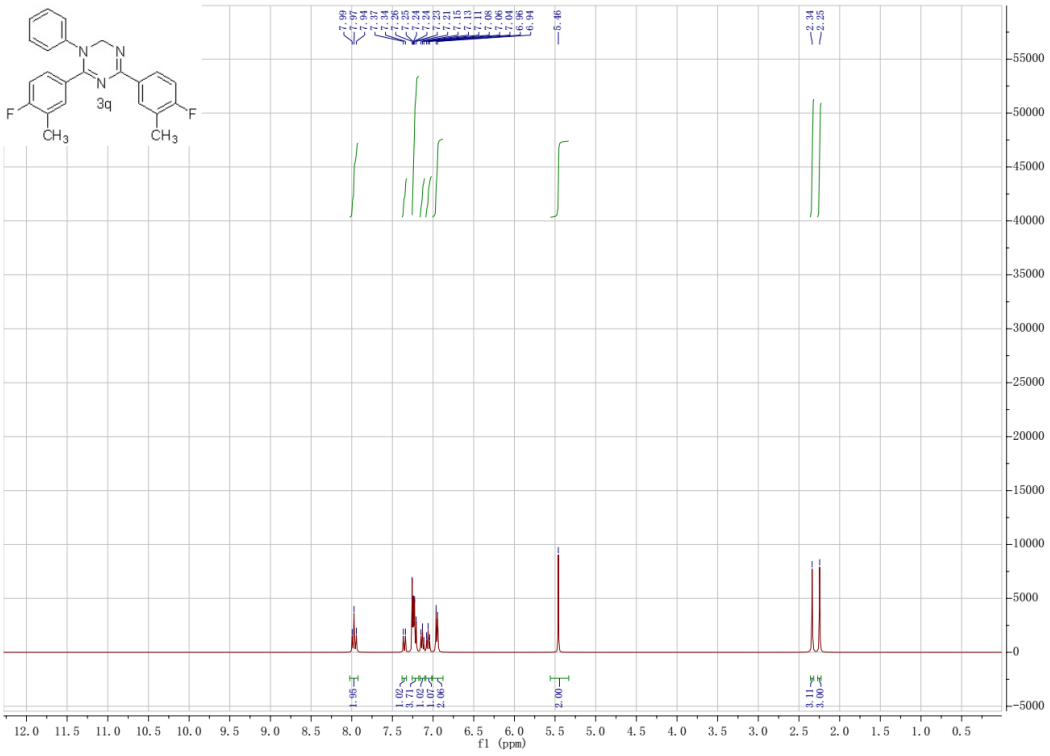

20180906-YM1.12.fid
161.39
160.39
142.95
137.58
136.70
134.57
133.38
131.74
129.27
129.20
128.64
128.36
126.04
124.67
66.93
3n
Cl
Cl
f1 (ppm)

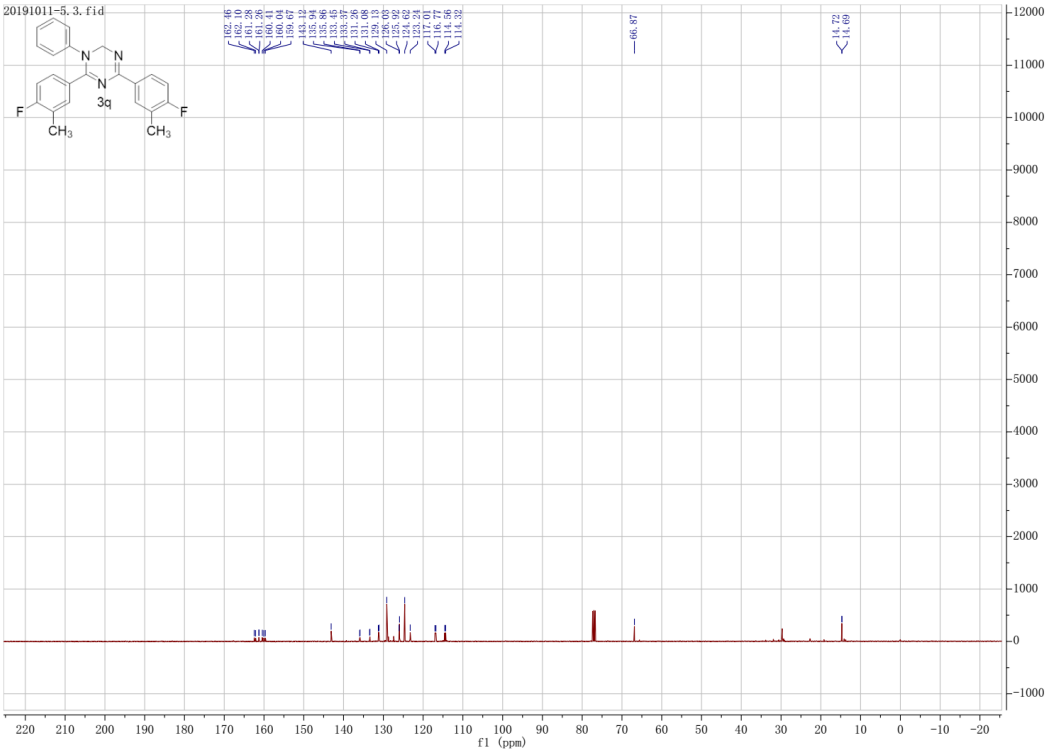

3o
F
F
8.34
8.32
8.32
8.30
7.66
7.65
7.64
7.63
7.25
7.23
7.21
7.15
7.14
7.13
7.12
7.10
6.99
6.97
6.96
6.95
6.94
5.47
2.00
2.00
2.09
3.18
4.21
2.00
f1 (ppm)

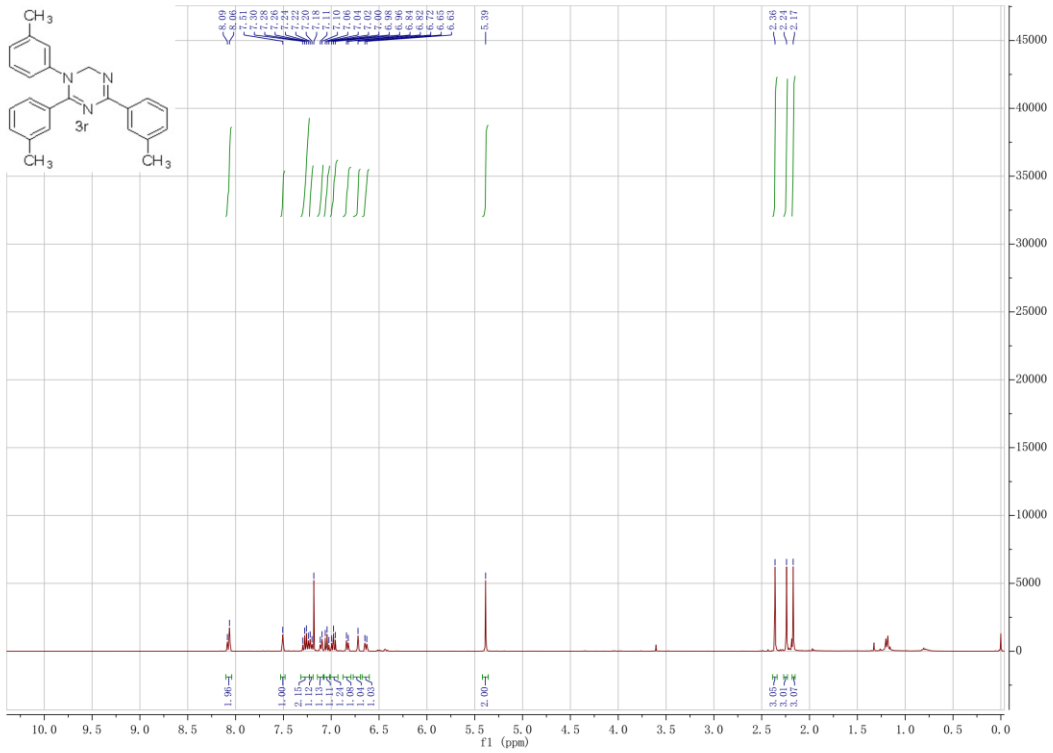

3o
F
F
163.10
159.30
132.76
132.67
132.56
132.23
130.06
129.98
129.15
125.93
124.69
115.63
115.42
115.18
114.96
114.98
66.85
f1 (ppm)

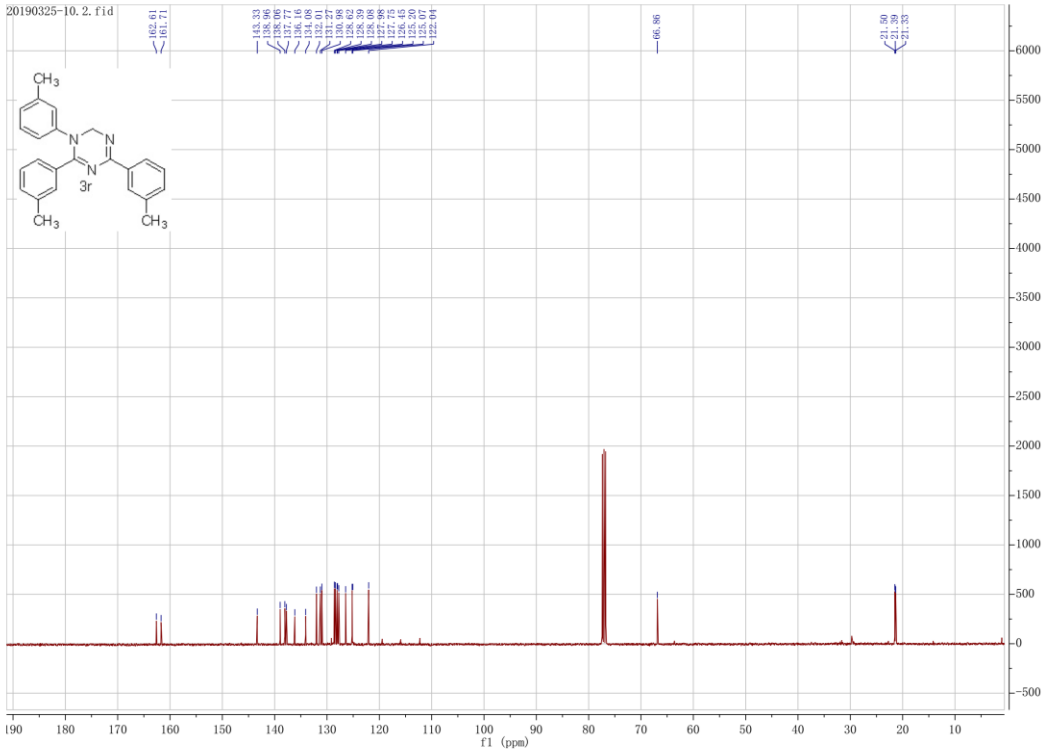

3p
F3C
CF3
8.52
8.50
7.80
7.78
7.76
7.62
7.60
7.33
7.32
7.26
7.24
7.22
7.04
7.02
5.63
0.01
2.00
4.29
2.19
1.80
1.10
2.08
1.80
f1 (ppm)

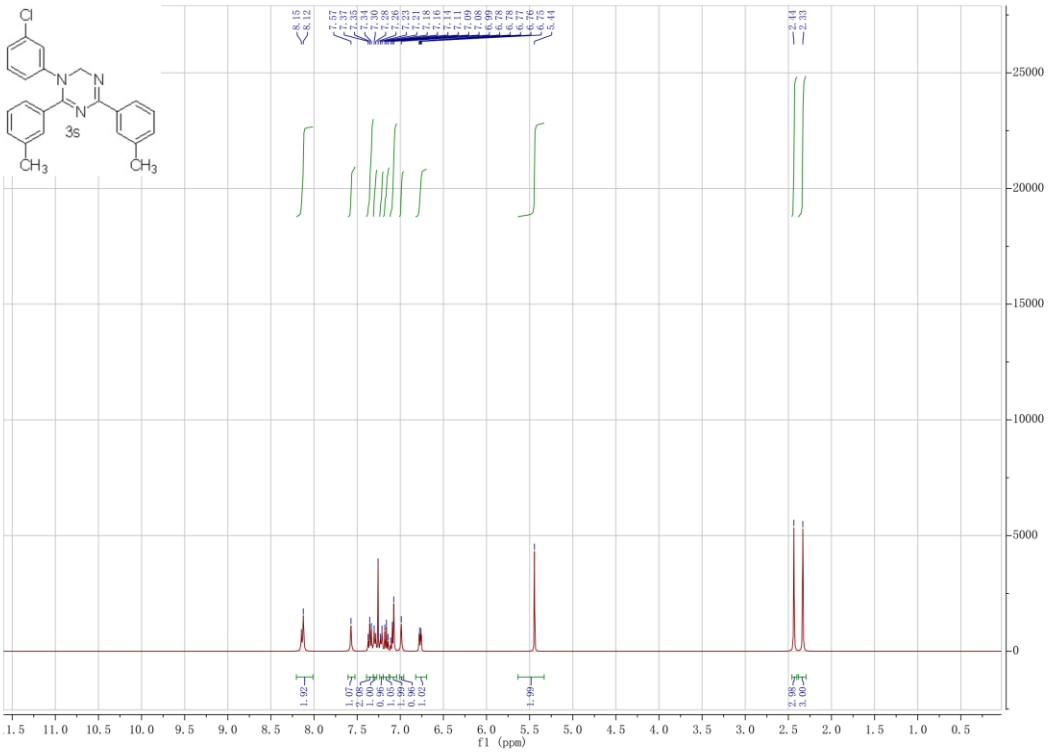

3p
F3C
CF3
161.64
160.38
142.30
137.24
136.42
129.17
128.62
128.41
126.75
125.38
125.31
125.27
125.24
124.80
66.49
f1 (ppm)

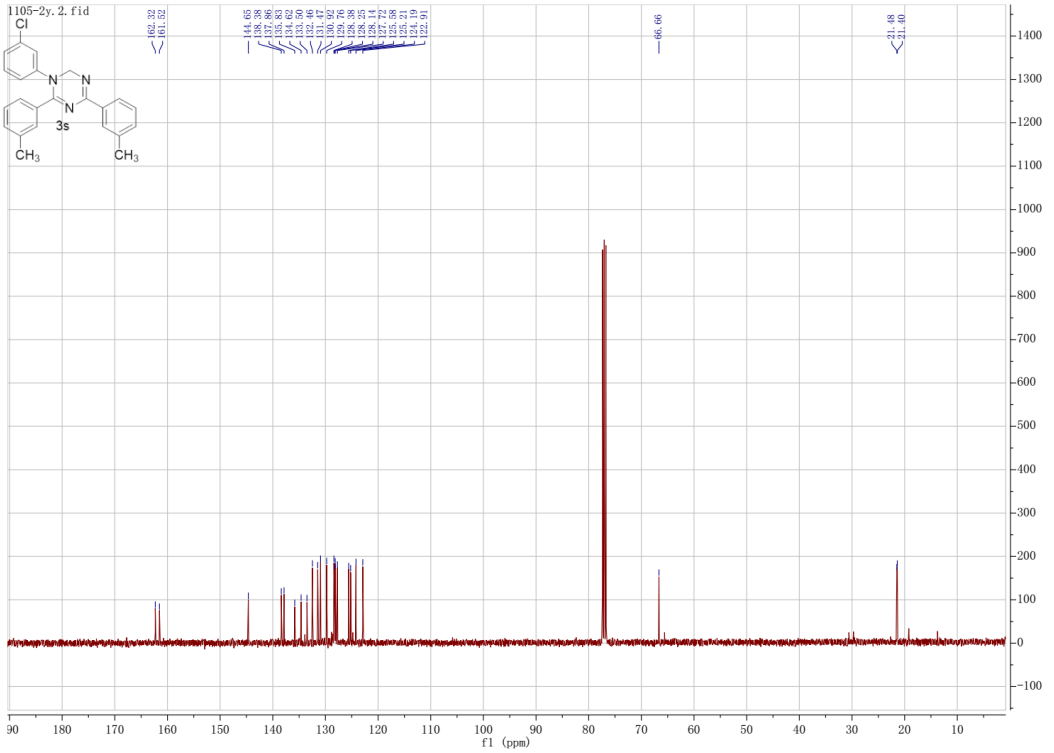

3q
F
F
CH3
CH3
7.99
7.97
7.94
7.77
7.34
7.26
7.25
7.24
7.24
7.23
7.21
7.15
7.13
7.11
7.08
7.06
7.04
6.96
6.94
5.46
2.34
2.25
1.95
1.02
3.71
1.02
1.07
2.06
2.00
3.11
3.00
f1 (ppm)

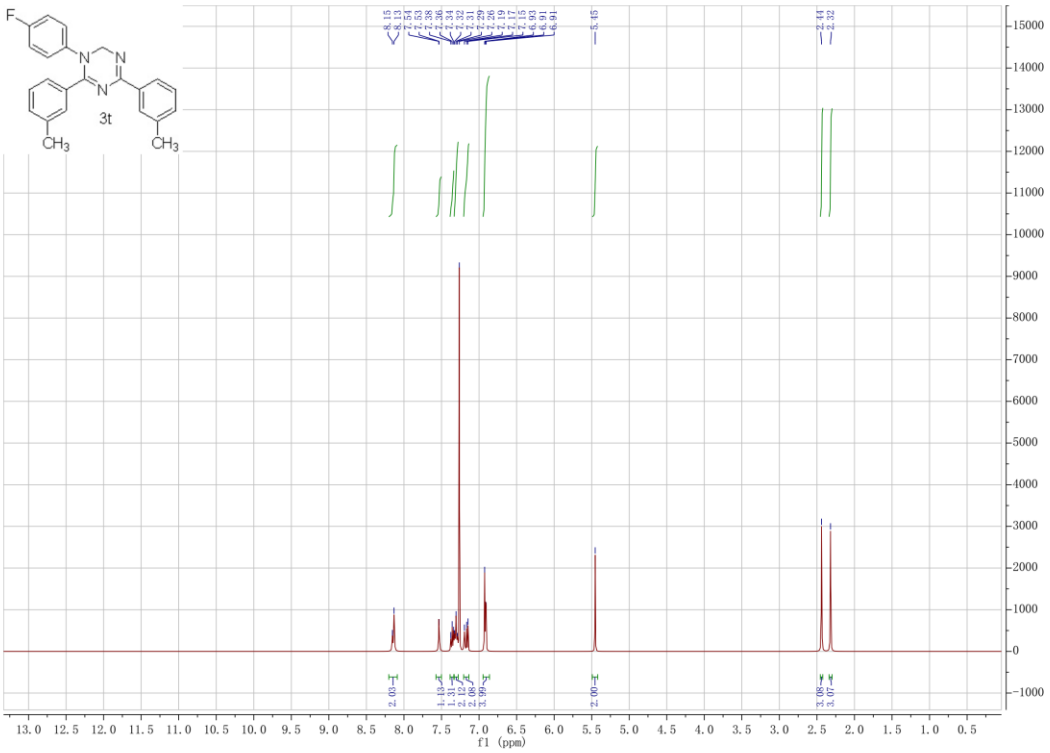

20191011-5.3.fid
3q
F
F
CH3
CH3
162.46
162.10
161.38
161.26
160.41
160.04
159.67
143.12
135.94
135.86
133.45
133.37
131.26
131.08
130.31
128.03
125.92
124.62
123.24
117.01
116.77
114.56
114.32
66.87
14.72
14.69
f1 (ppm)

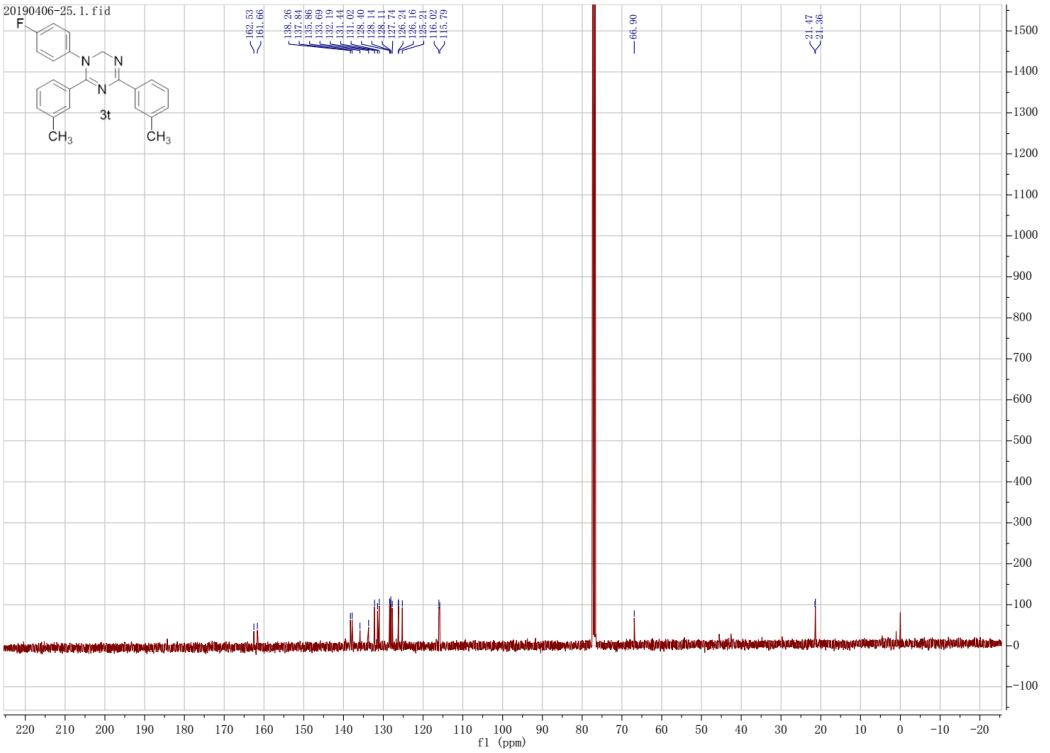

3r
8.09
8.06
7.51
7.39
7.38
7.26
7.24
7.22
7.20
7.18
7.11
7.10
7.06
7.04
7.02
7.00
6.98
6.96
6.84
6.82
6.72
6.65
6.63
5.39
2.36
2.34
2.17
1.96
4.00
2.15
1.13
1.11
1.24
1.04
1.03
2.00
3.05
3.01
3.07
fl (ppm)


20190325-10.2.fid
3r
162.61
161.71
143.33
138.96
138.06
137.77
136.16
134.08
132.01
131.27
130.98
130.62
128.39
128.08
127.98
127.75
126.45
125.20
125.07
122.04
66.86
21.59
21.39
21.33
fl (ppm)

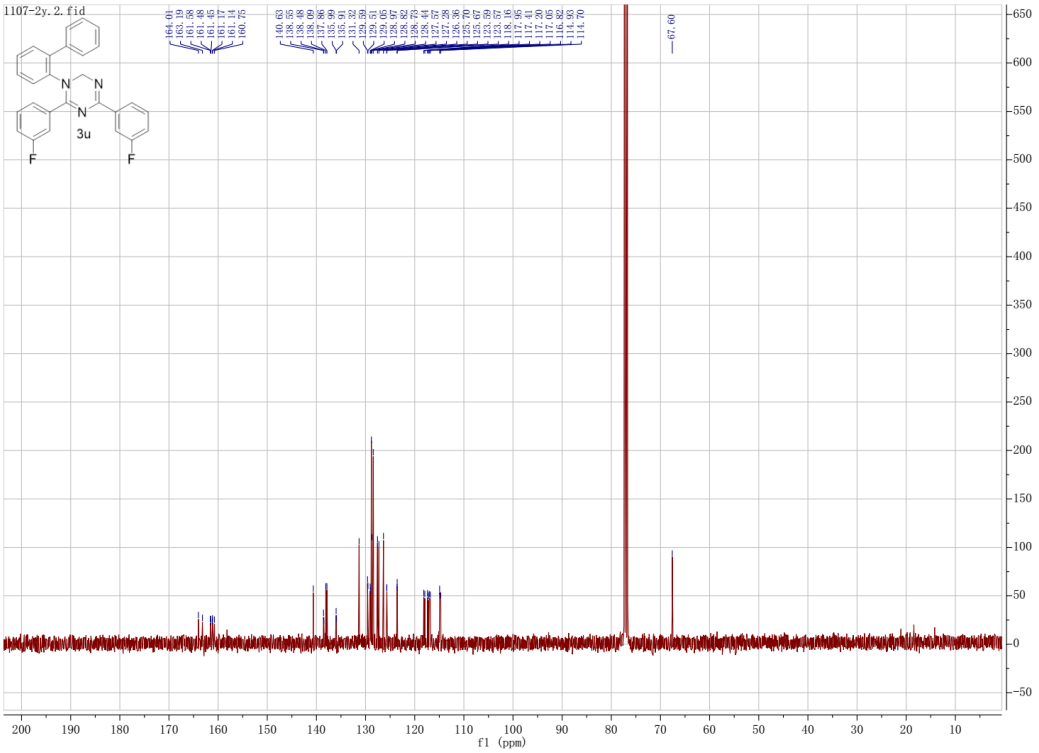

Cl
N
N
N
3s
CH3
CH3
8.15
8.12
7.57
7.37
7.35
7.34
7.30
7.28
7.26
7.23
7.21
7.18
7.16
7.14
7.11
7.09
7.08
6.99
6.98
6.78
6.77
6.76
6.75
5.44
2.44
2.33
25000
20000
15000
10000
5000
0
1.92
1.07
2.05
1.00
0.96
1.05
1.04
0.96
1.02
1.99
2.98
3.00
f1 (ppm)

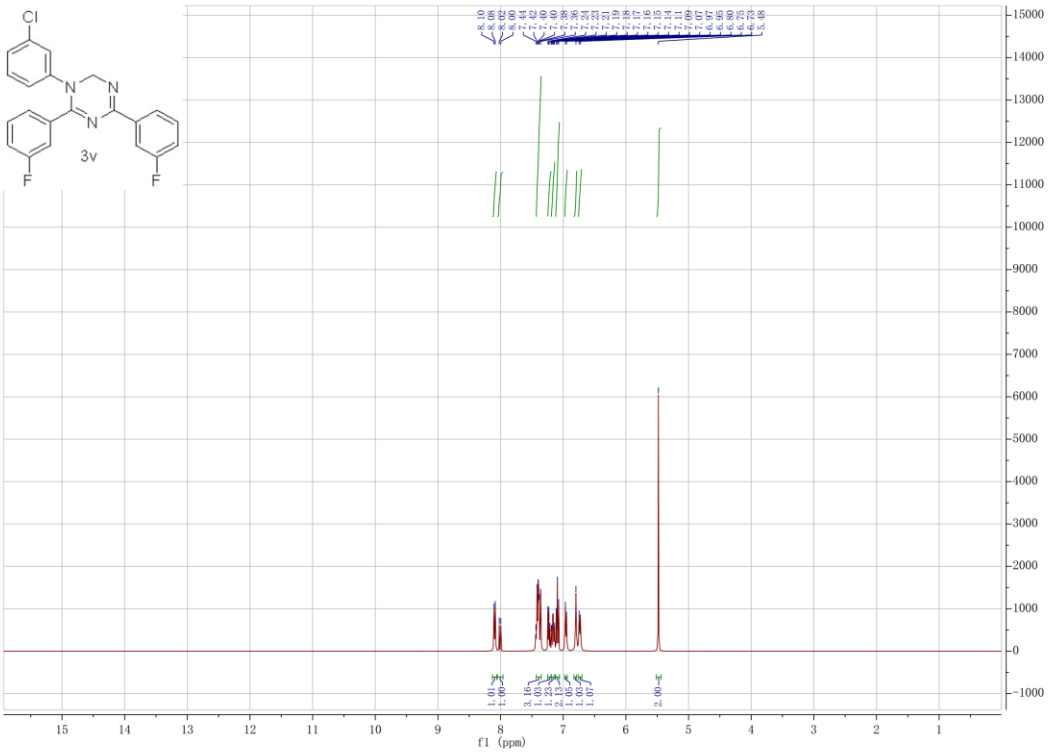

1105-2y.2.fid
Cl
N
N
N
3s
CH3
CH3
162.32
161.52
144.65
138.38
137.86
135.52
134.62
133.59
132.46
131.47
130.92
129.76
129.38
128.25
128.14
127.72
125.58
125.21
124.19
122.91
66.66
21.48
21.40
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
−100
f1 (ppm)

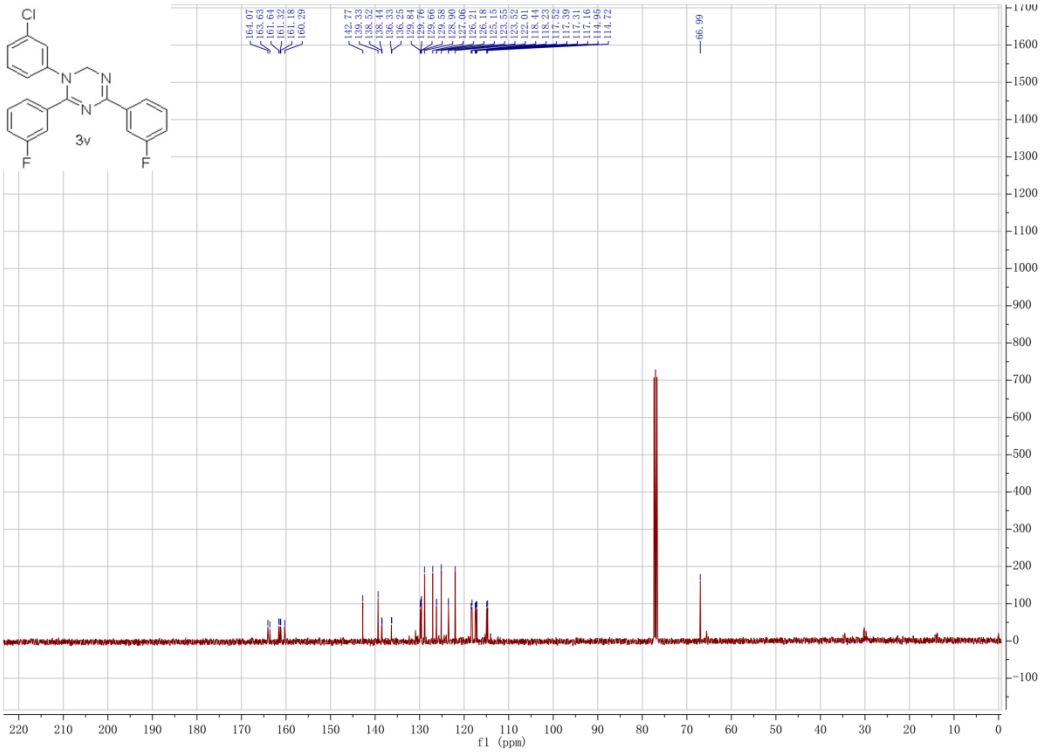

F
3t
CH3
CH3
8.15
8.13
7.54
7.53
7.38
7.36
7.34
7.32
7.31
7.29
7.26
7.19
7.17
7.15
6.93
6.91
6.91
5.45
2.44
2.32
2.03
4.13
1.31
2.12
2.08
2.99
2.00
3.08
3.07
f1 (ppm)

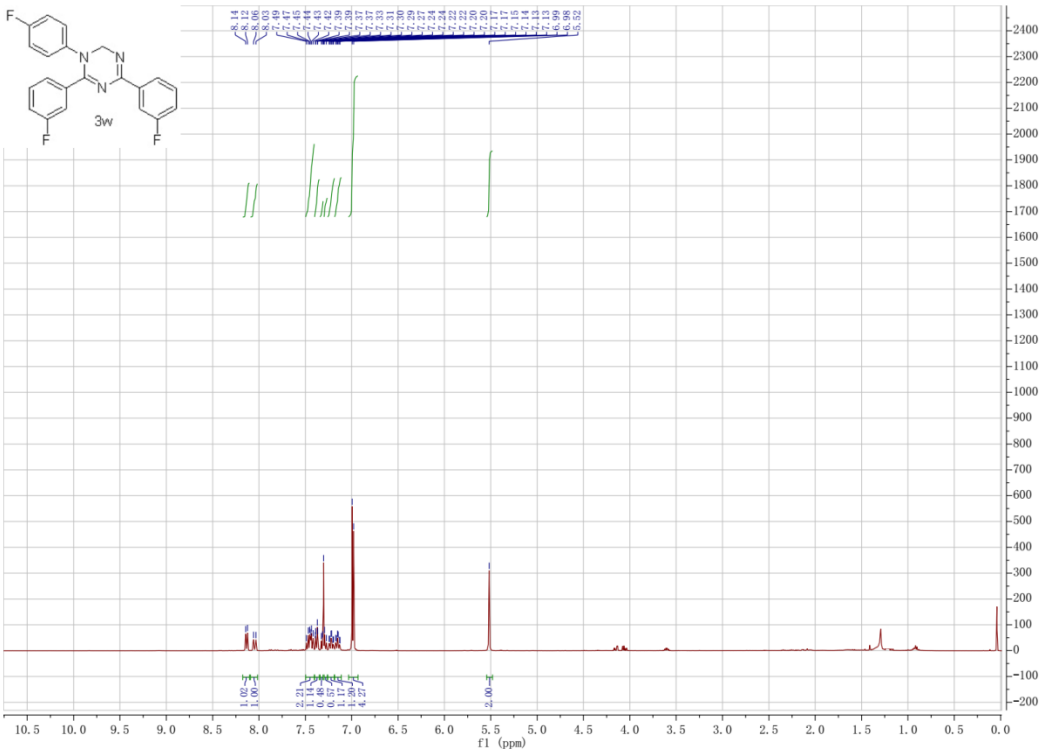

20190406-25.1.fid
F
3t
CH3
CH3
162.53
161.66
138.26
137.84
135.86
133.69
132.19
131.44
131.02
129.40
128.14
127.74
126.24
126.16
125.21
116.02
115.79
66.90
21.47
21.36
f1 (ppm)

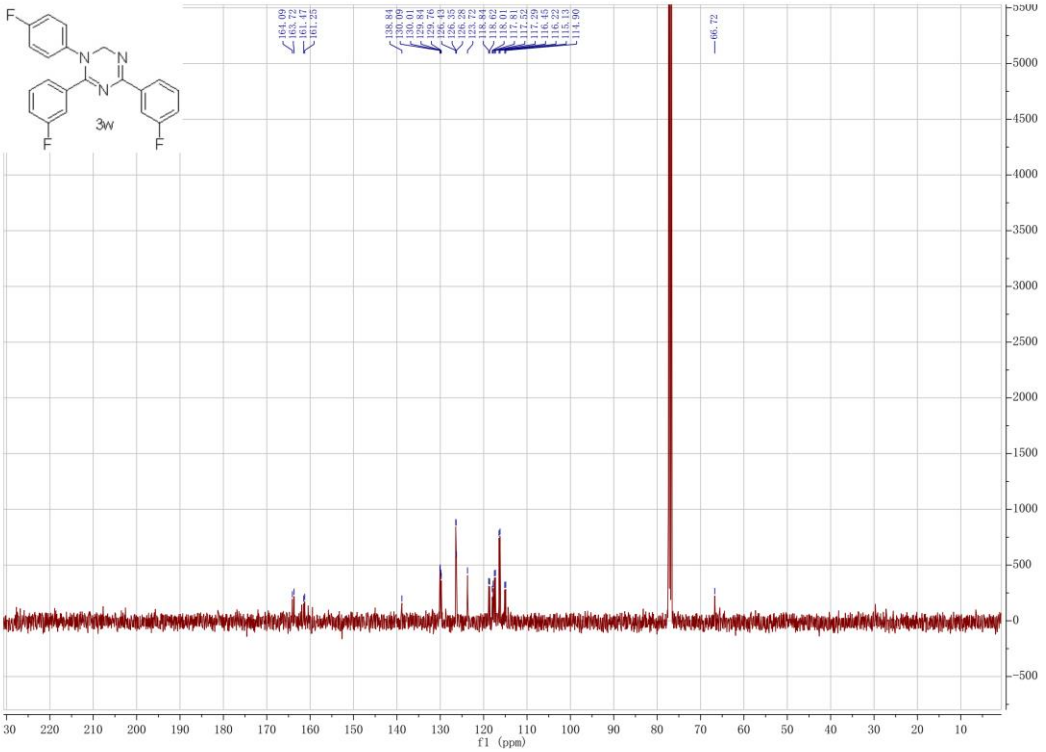

1107-2y.1.fid
3u
F
F
f1 (ppm)

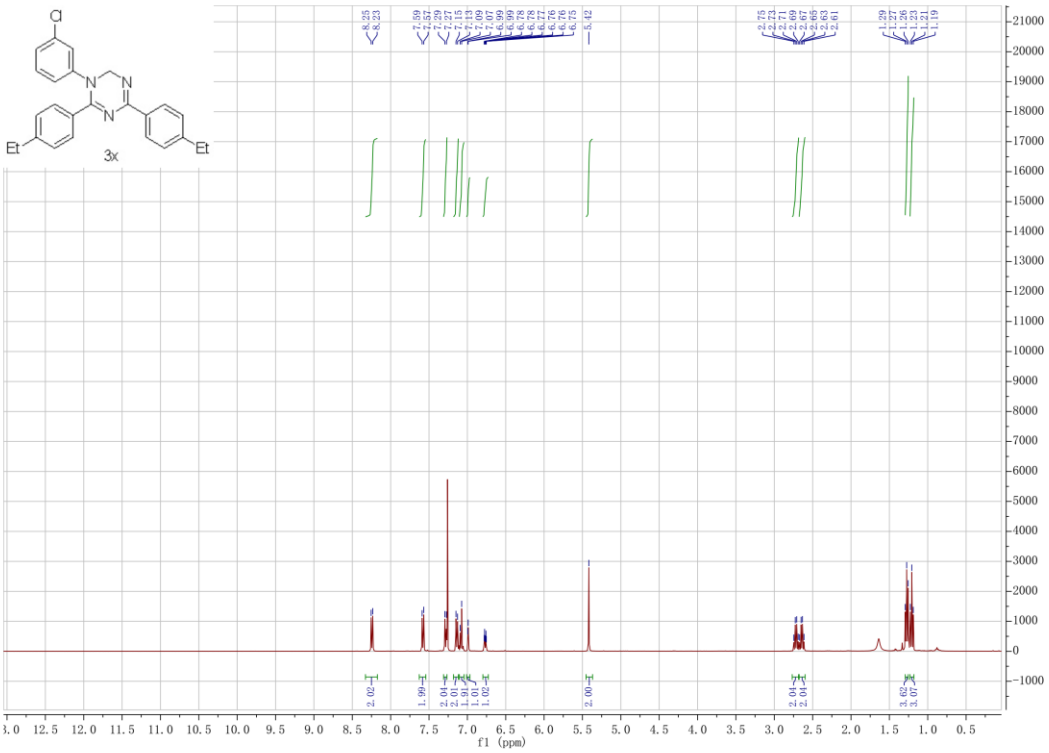

1107-2y.2.fid
3u
F
F
f1 (ppm)

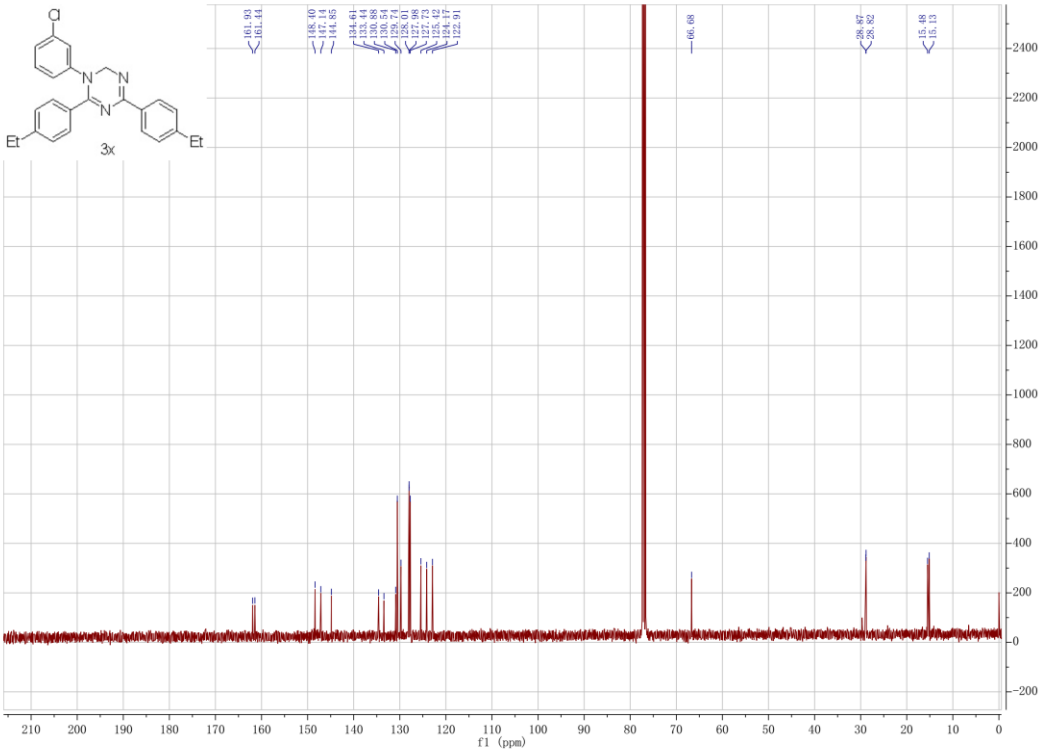

Cl
N
N
N
3v
F
F
f1 (ppm)

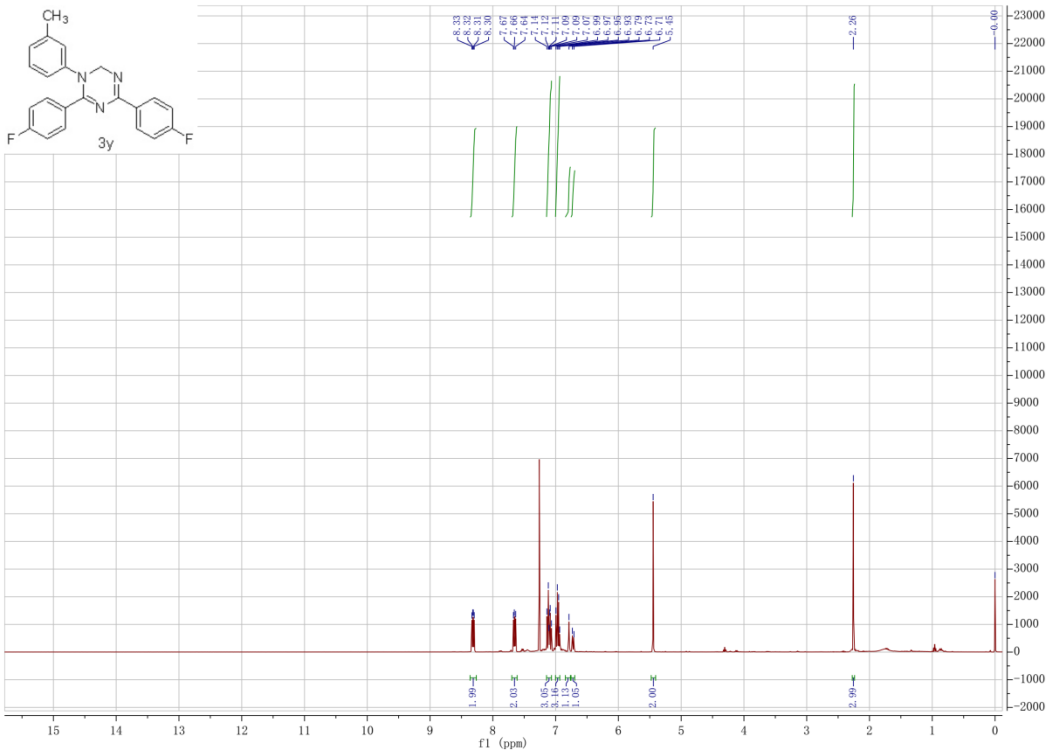

Cl
N
N
N
3v
F
F
f1 (ppm)

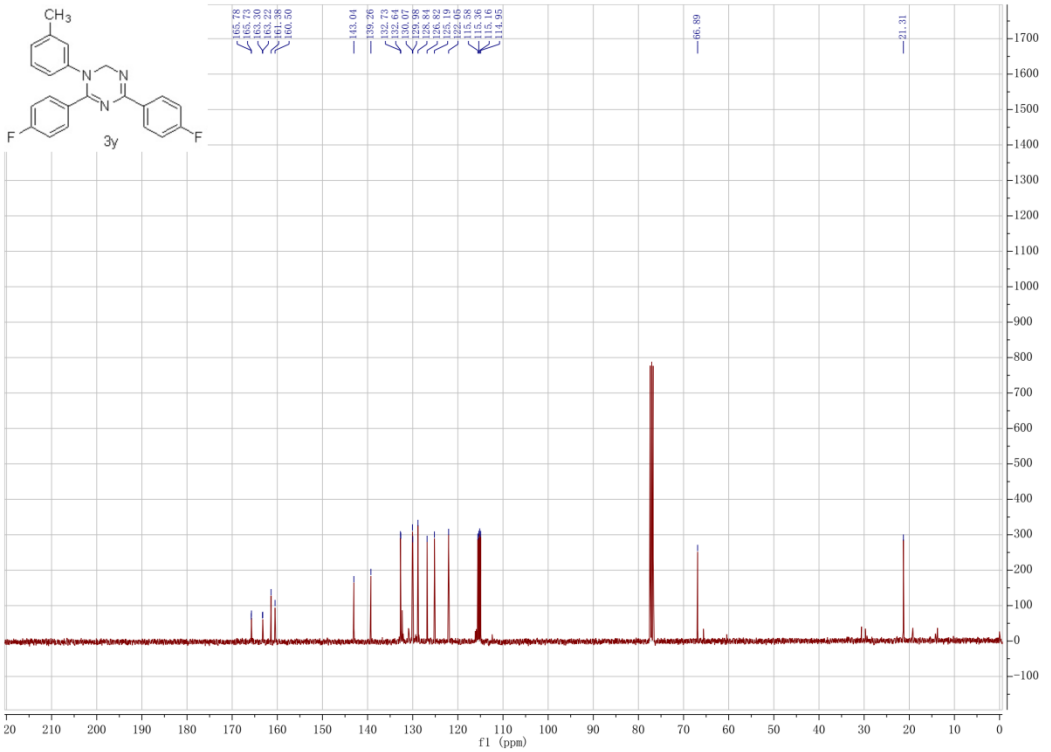

3w
f1 (ppm)

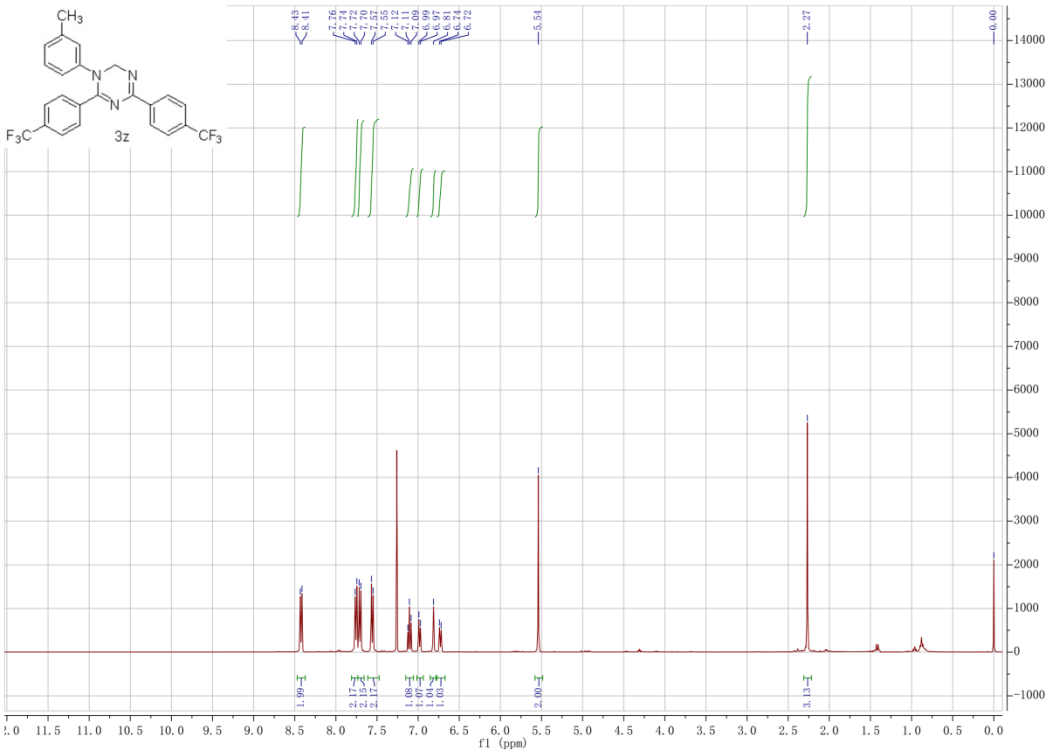

3w
f1 (ppm)

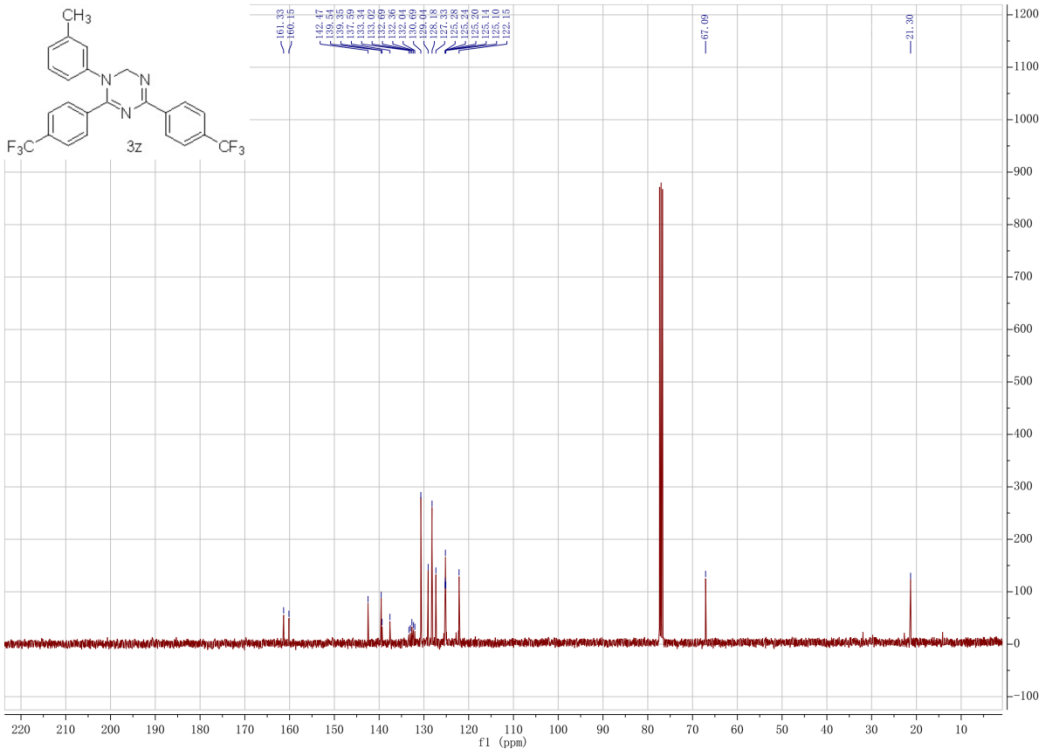

Cl
N
N
N
Et
Et
3x
8.25
8.23
7.59
7.57
7.29
7.27
7.15
7.13
7.09
7.07
6.99
6.99
6.78
6.78
6.77
6.77
6.76
6.76
6.75
5.42
2.75
2.73
2.71
2.69
2.67
2.65
2.63
2.61
1.29
1.27
1.26
1.23
1.21
1.19
2.02
1.99
2.04
2.01
1.91
1.01
1.02
2.00
2.04
2.04
3.62
3.07
f1 (ppm)

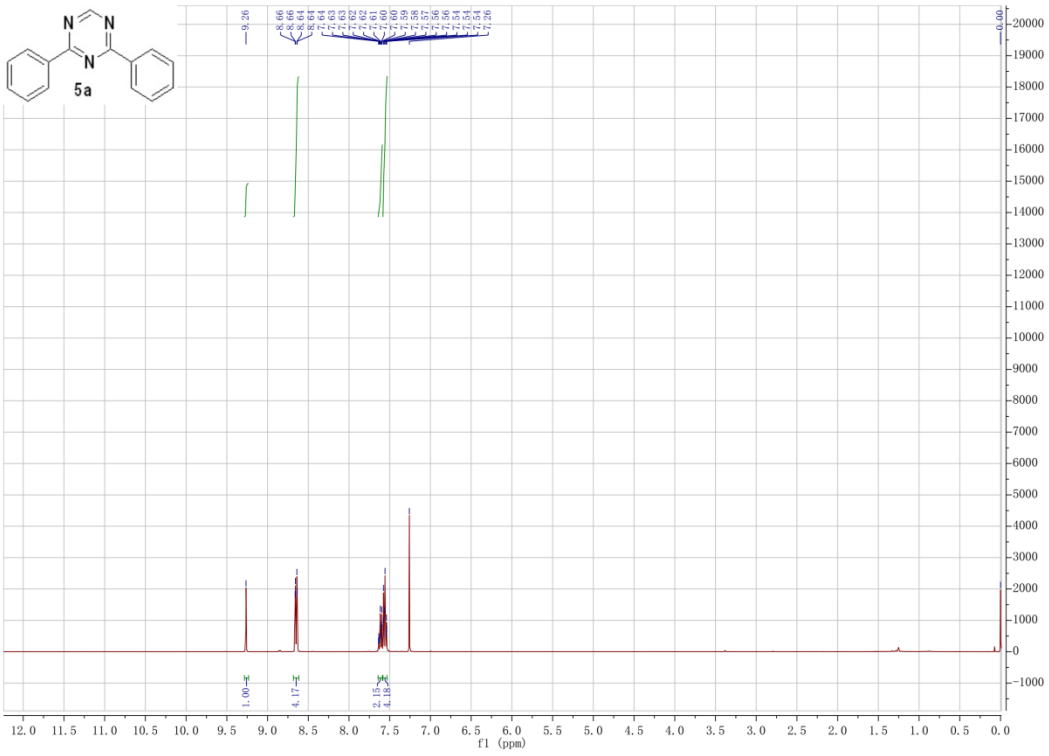

Cl
N
N
N
Et
Et
3x
161.93
161.44
148.40
147.14
144.85
134.61
133.44
130.88
130.54
129.74
128.01
127.98
127.73
125.42
124.17
122.91
66.68
28.87
28.82
15.48
15.13
f1 (ppm)


3y
f1 (ppm)


3y
f1 (ppm)


CH3
F3C
3z
CF3
8.43
8.41
7.76
7.74
7.72
7.70
7.57
7.55
7.12
7.11
7.09
6.99
6.97
6.91
6.84
6.72
5.54
2.27
0.00
1.99
2.17
2.15
2.12
1.08
1.07
1.04
1.03
2.00
3.13
f1 (ppm)


CH3
F3C
3z
CF3
161.33
160.15
142.47
139.54
139.35
137.39
133.34
133.17
133.02
132.69
132.36
132.04
130.69
129.04
128.18
127.53
125.28
125.24
125.20
125.14
125.10
122.15
67.09
21.30
f1 (ppm)


5a
9.26
8.66
8.65
8.64
8.64
7.64
7.63
7.63
7.62
7.62
7.61
7.61
7.60
7.60
7.59
7.58
7.57
7.56
7.56
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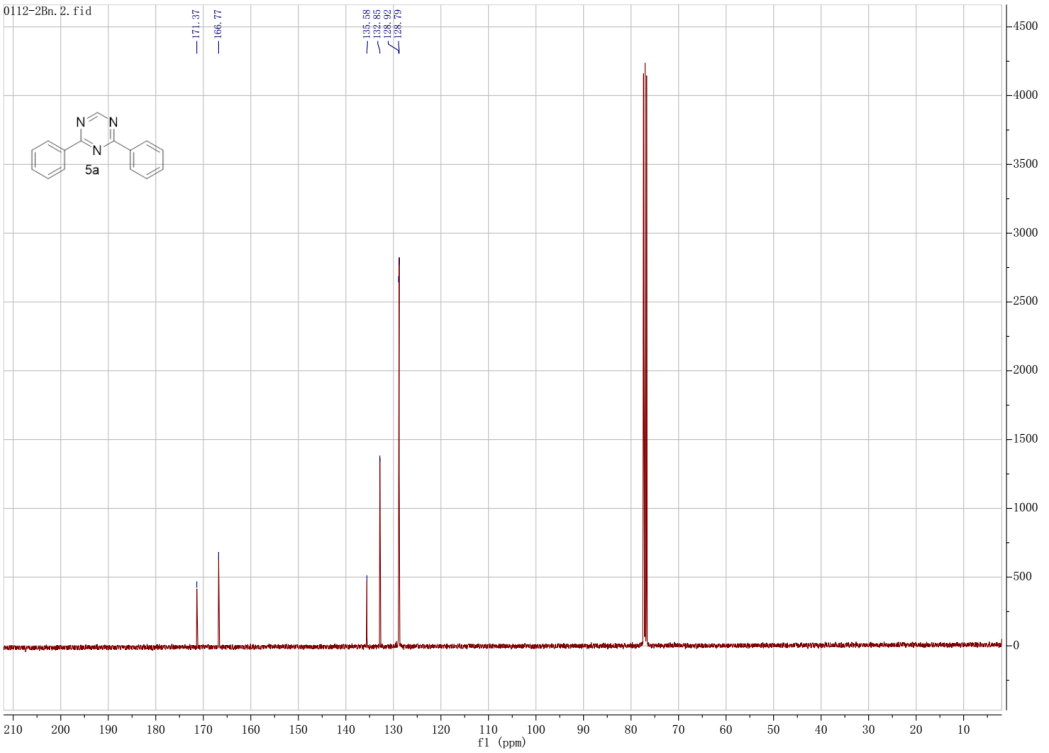
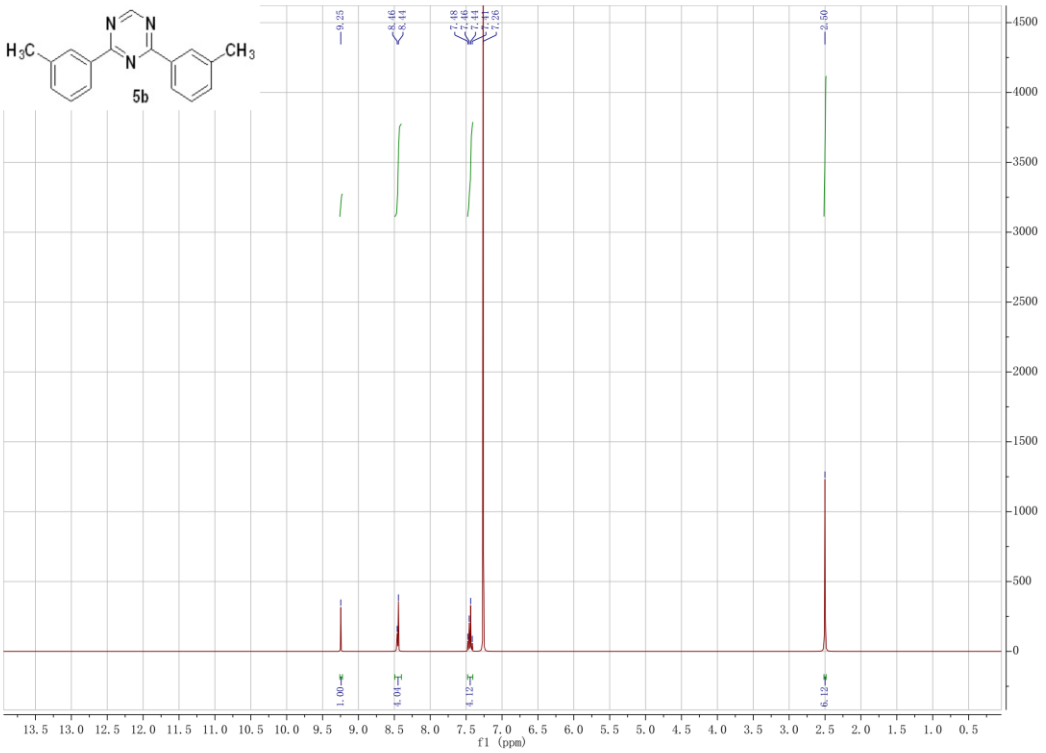
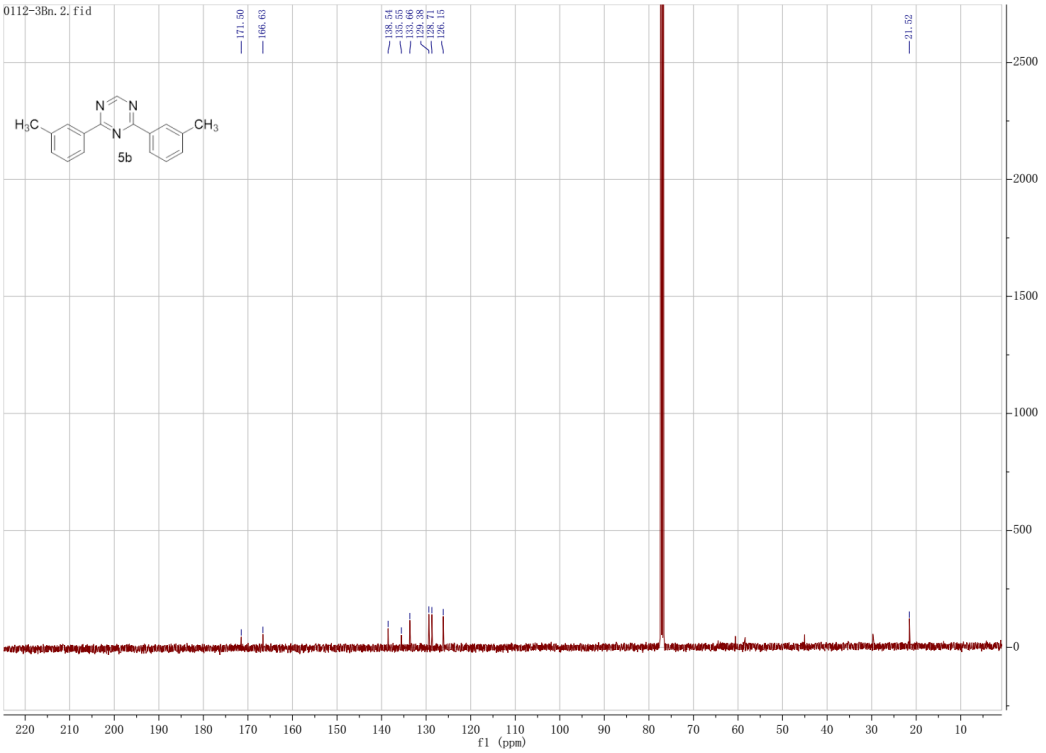
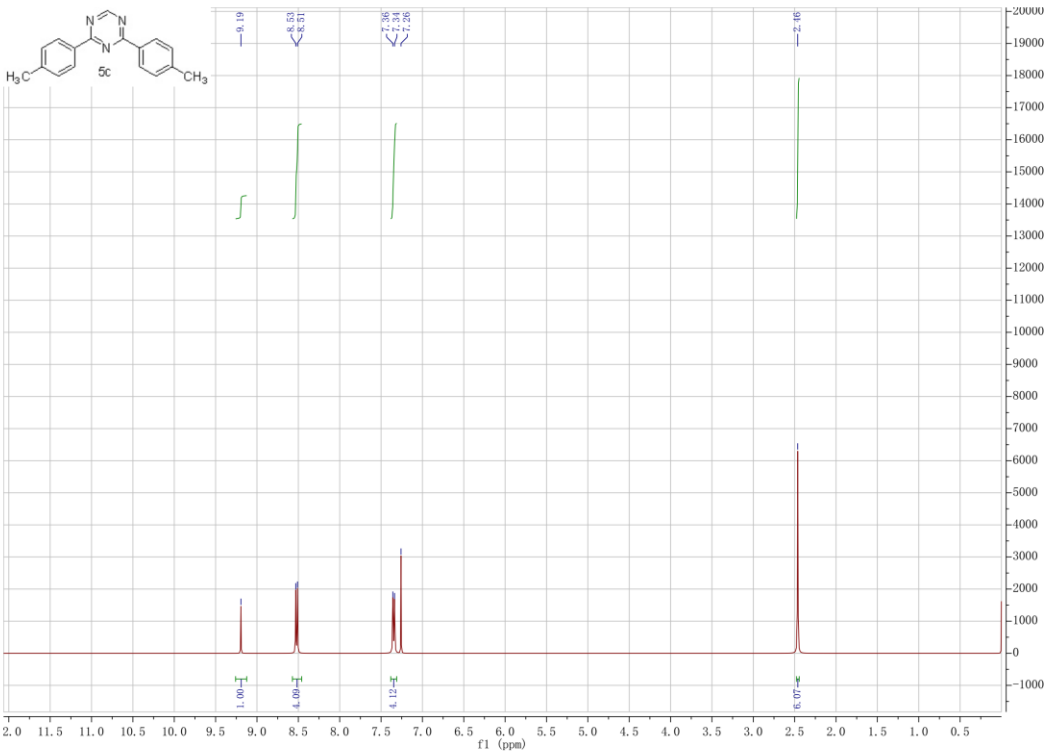
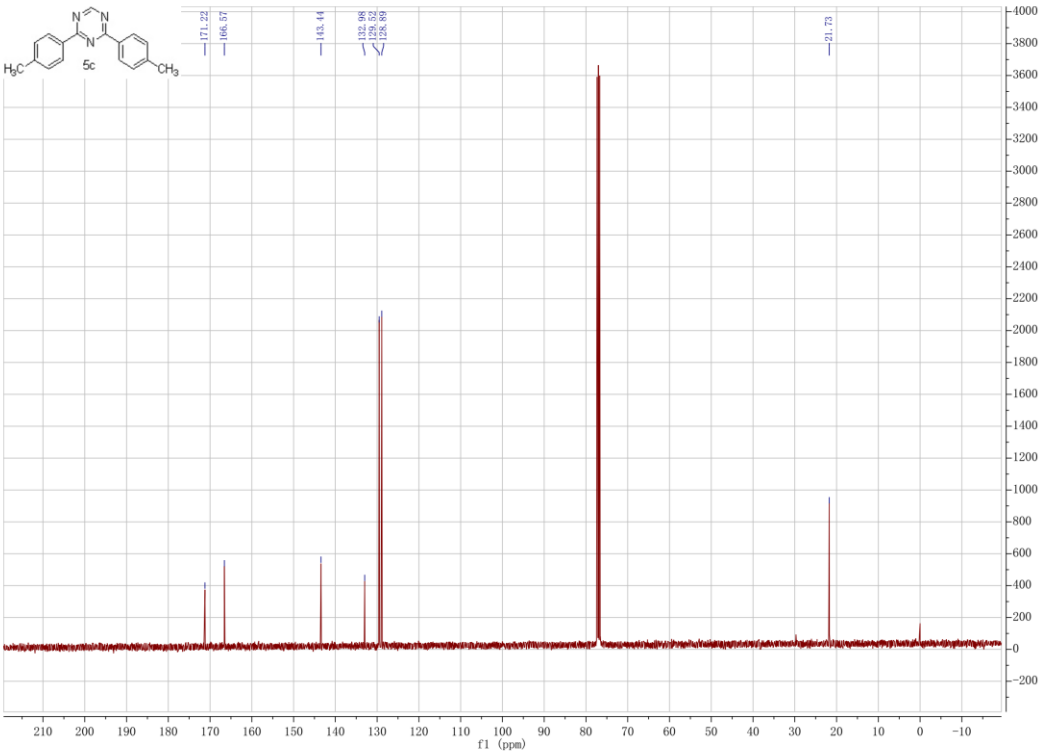
7.54
7.54
7.26
6.00
1.00
4.17
2.15
4.18
f1 (ppm)

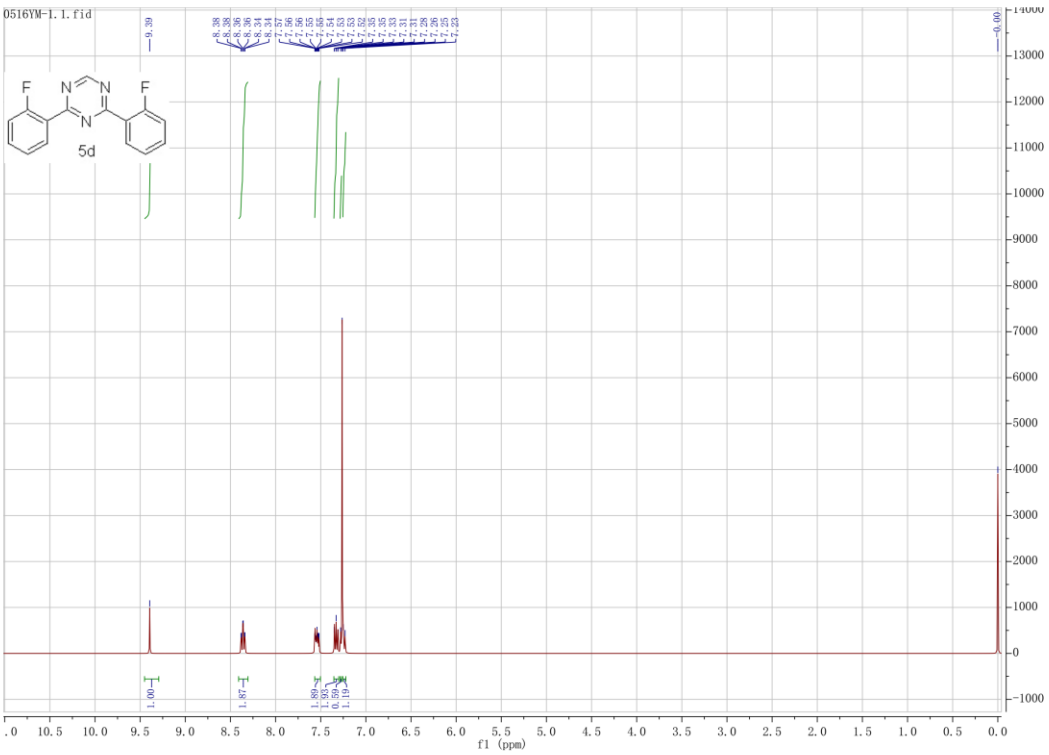

0112-2Bn.2.fid
5a
171.37
166.77
135.58
132.85
128.97
128.79
f1 (ppm)

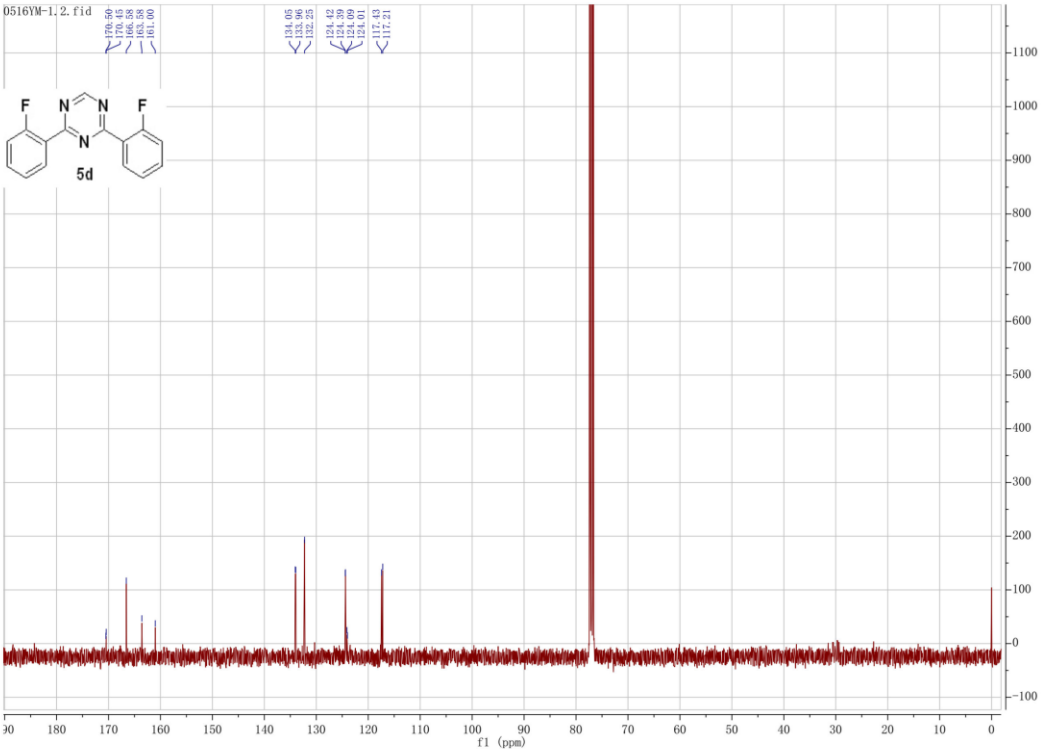

5b
9.25
8.46
8.44
7.48
7.46
7.44
7.41
7.26
2.50
1.00
4.04
4.12
6.12
f1 (ppm)

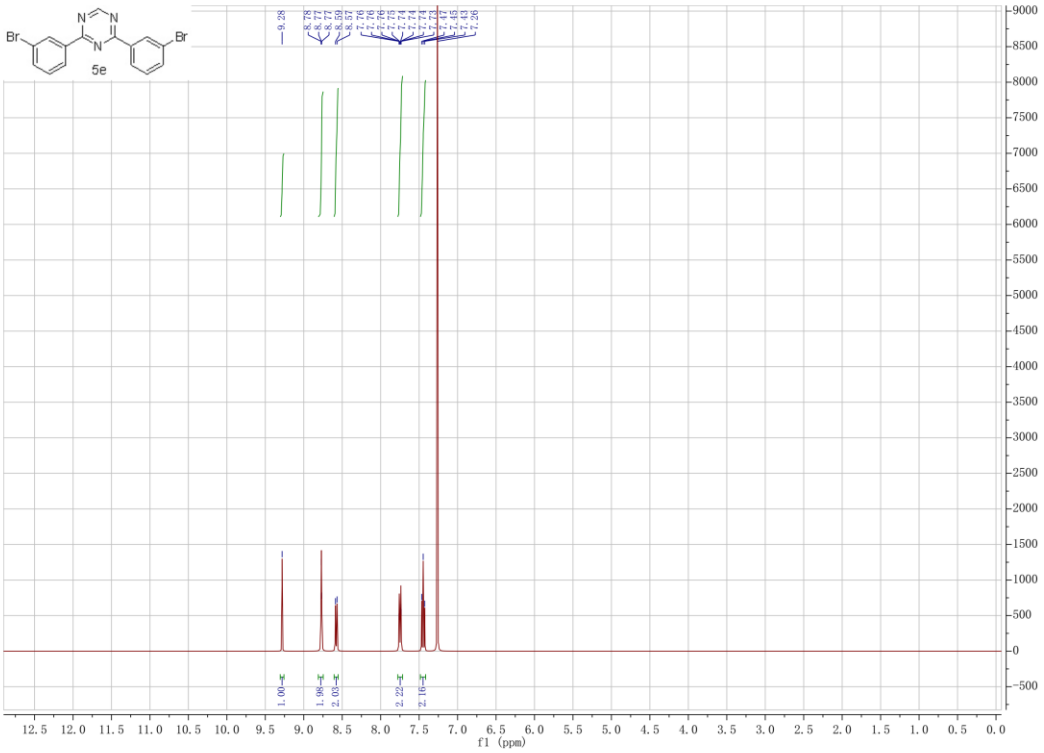

0112-3Bn.2.fid
5b
171.50
166.63
138.54
135.55
133.66
129.38
128.71
126.15
21.52
f1 (ppm)

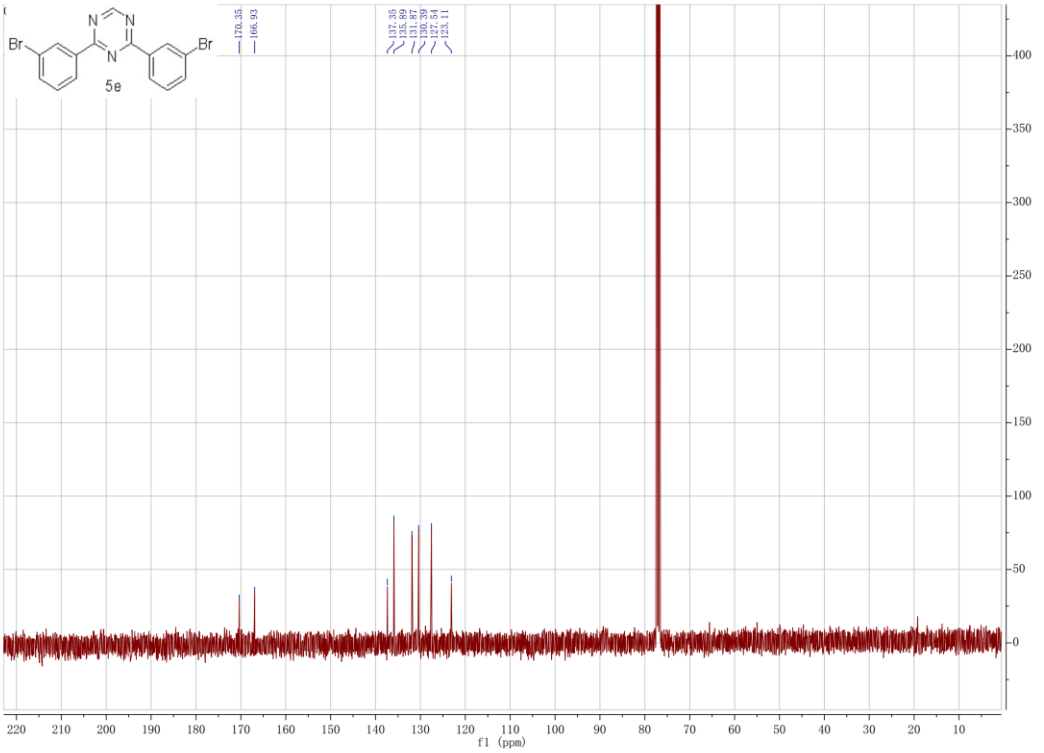

5c
9.19
8.53
8.51
7.36
7.34
7.26
2.46
1.00
4.09
4.12
6.07
f1 (ppm)

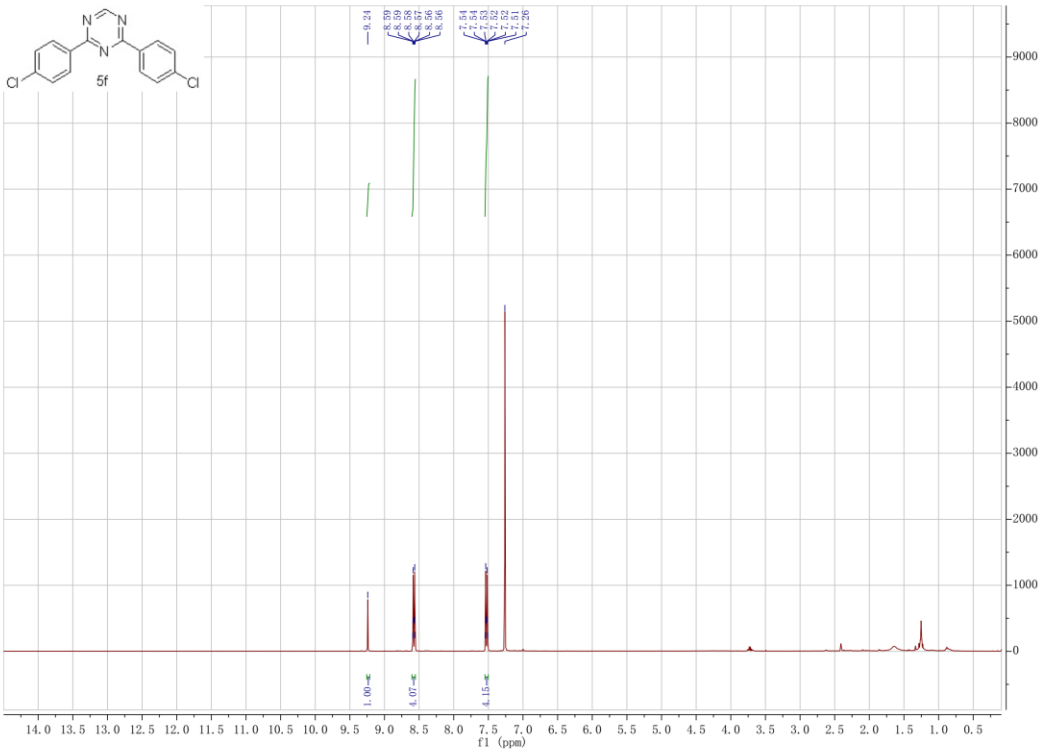

5c
171.22
166.57
143.44
132.98
129.52
128.89
21.73
f1 (ppm)

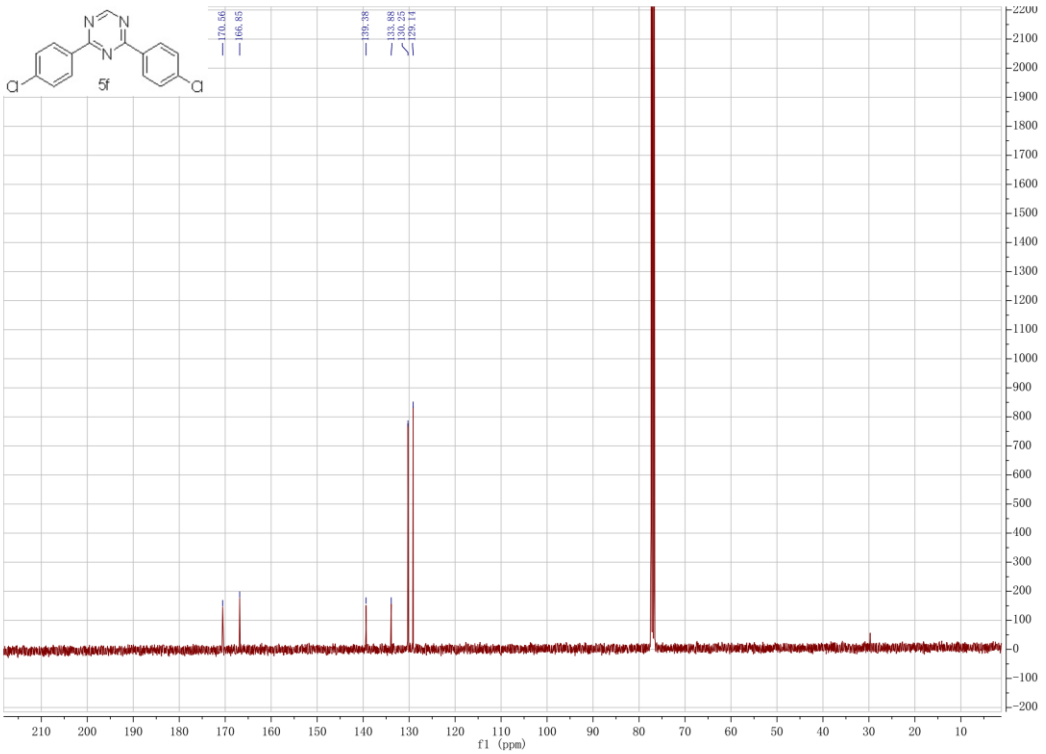

0516YM-1.1.fid
5d
f1 (ppm)

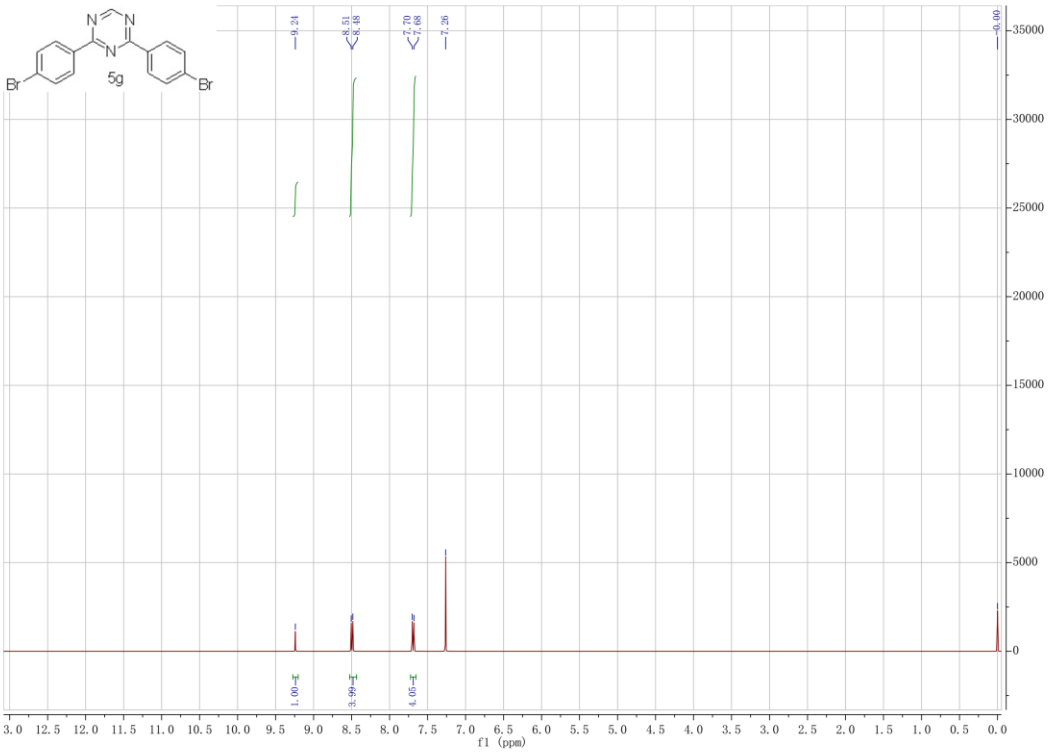

0516YM-1.2.fid
5d
f1 (ppm)

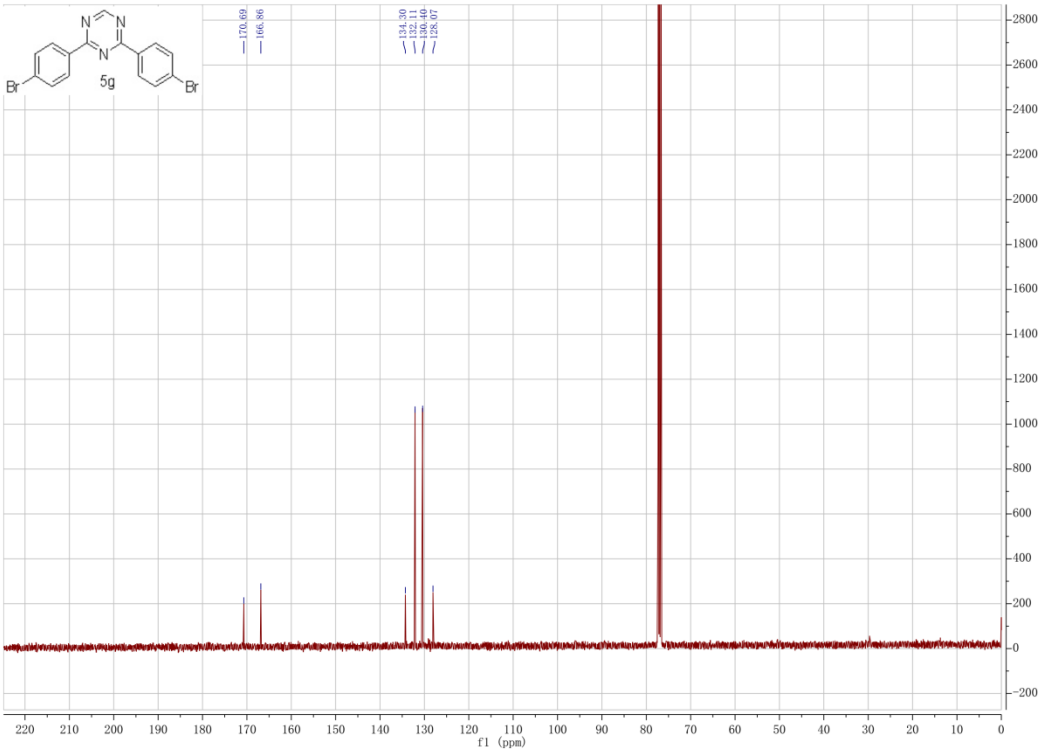

Br
Br
5e
9.28
8.78
8.77
8.77
8.59
8.57
7.76
7.76
7.76
7.75
7.74
7.74
7.74
7.73
7.73
7.47
7.45
7.43
7.26
1.00
1.06
2.03
2.22
2.16
f1 (ppm)

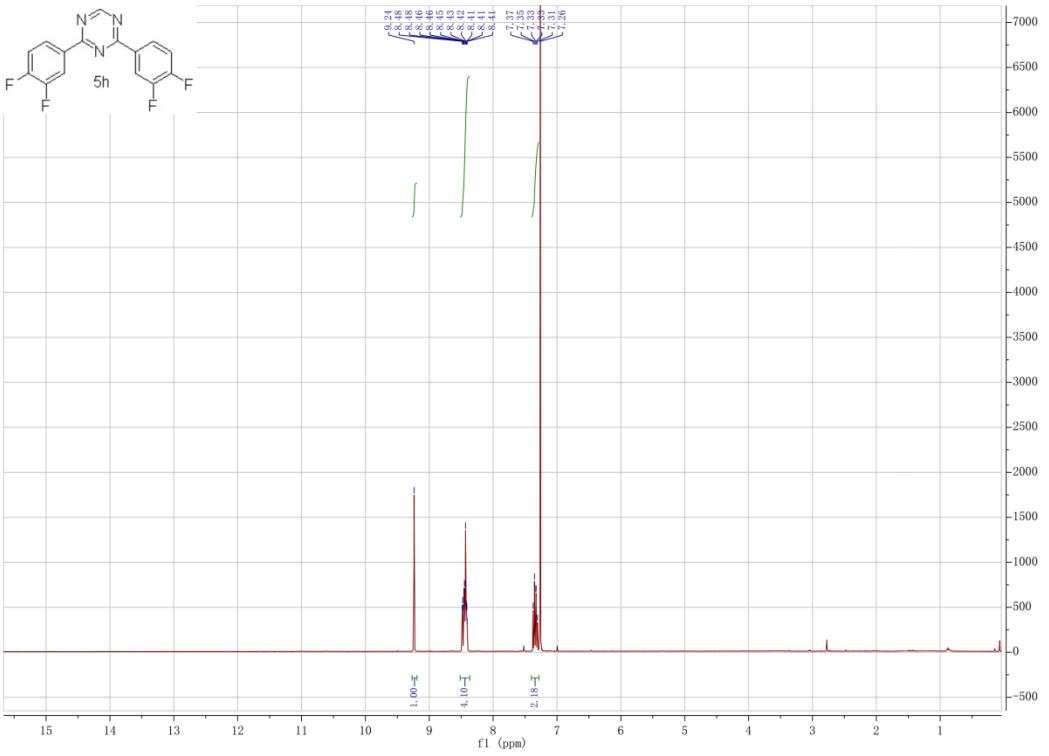

Br
Br
5e
170.35
166.93
137.35
135.69
131.87
130.39
127.54
123.11
f1 (ppm)

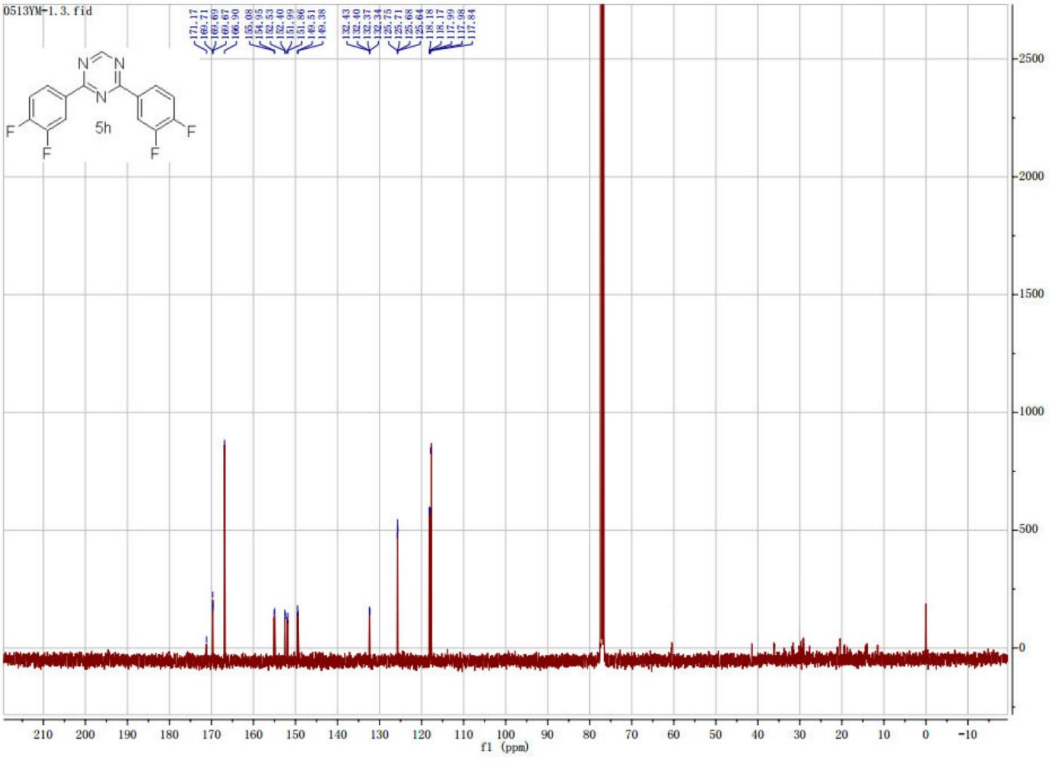

5f
Cl
Cl
9.24
8.59
8.58
8.57
8.56
7.54
7.53
7.52
7.51
7.26
1.00
4.07
4.15
f1 (ppm)

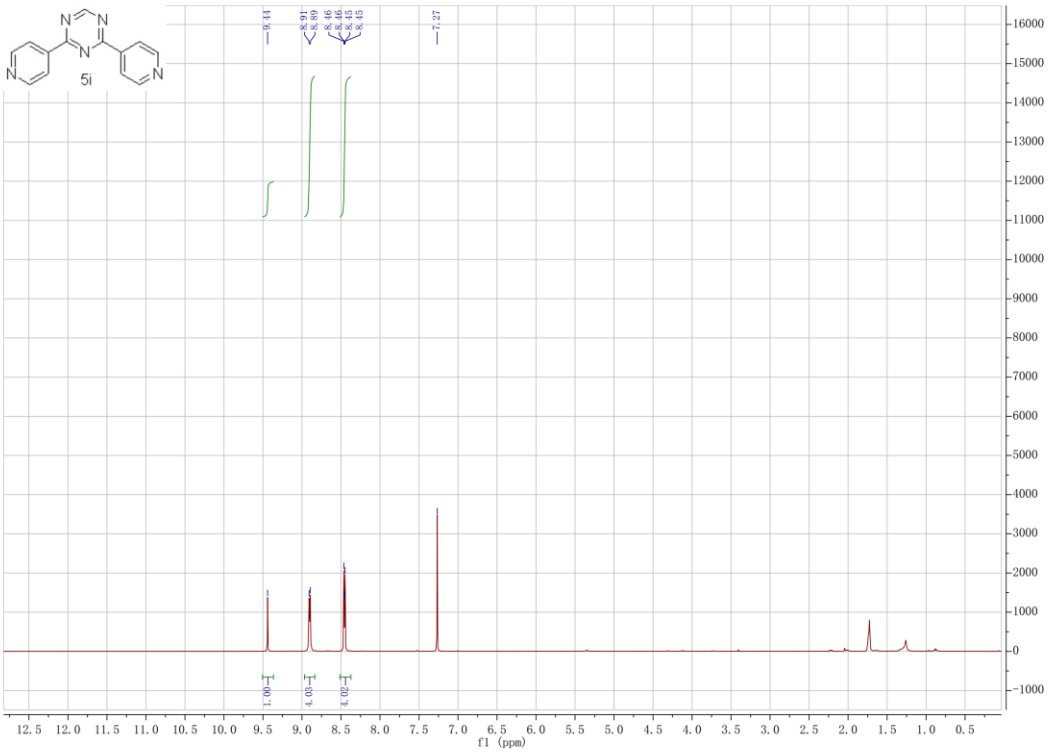

5f
Cl
Cl
170.56
166.85
139.38
133.88
130.35
129.14
f1 (ppm)

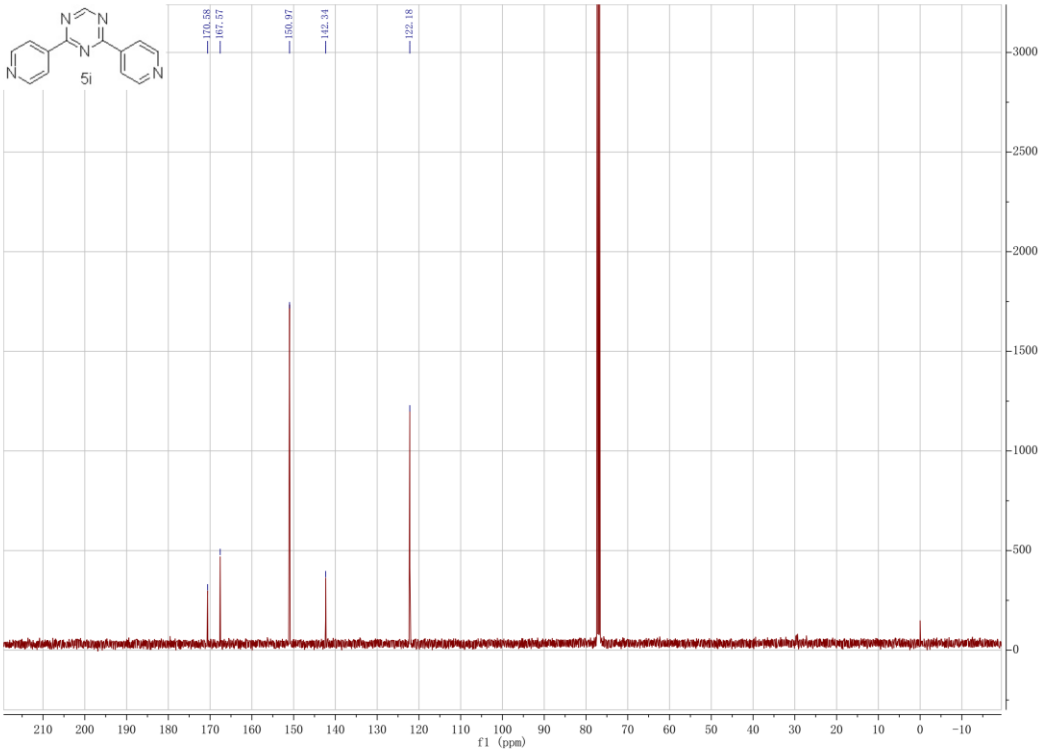

5g
Br
Br
9.24
8.51
8.49
7.70
7.68
7.26
0.00
1.00
3.99
4.05
f1 (ppm)


5g
Br
Br
170.69
166.86
134.30
132.11
130.40
128.07
f1 (ppm)


5h
F
F
F
F
9.24
8.48
8.46
8.45
8.42
8.41
7.37
7.35
7.33
7.31
7.26
1.00
4.10
2.18
f1 (ppm)


0513YM-1.3.fid
5h
F
F
F
F
171.17
169.71
169.69
169.67
166.90
155.08
154.95
152.53
152.40
151.99
151.86
149.51
149.38
132.43
132.40
132.37
132.34
125.75
125.71
125.68
125.64
118.36
118.17
117.99
117.98
117.84
f1 (ppm)


5i
9.44
8.91
8.89
8.46
8.45
8.45
7.27
1.00
4.03
4.02
f1 (ppm)


5i
170.58
167.97
150.97
142.34
122.18
f1 (ppm)