Supplementary Information

Research on catalytic activity of MNPs-[Dop-OH]-$CuBr_2$ nanocomposite: A novel and stable reusable nanocatalyst for synthesis of 1,3,5-Triazine derivatives

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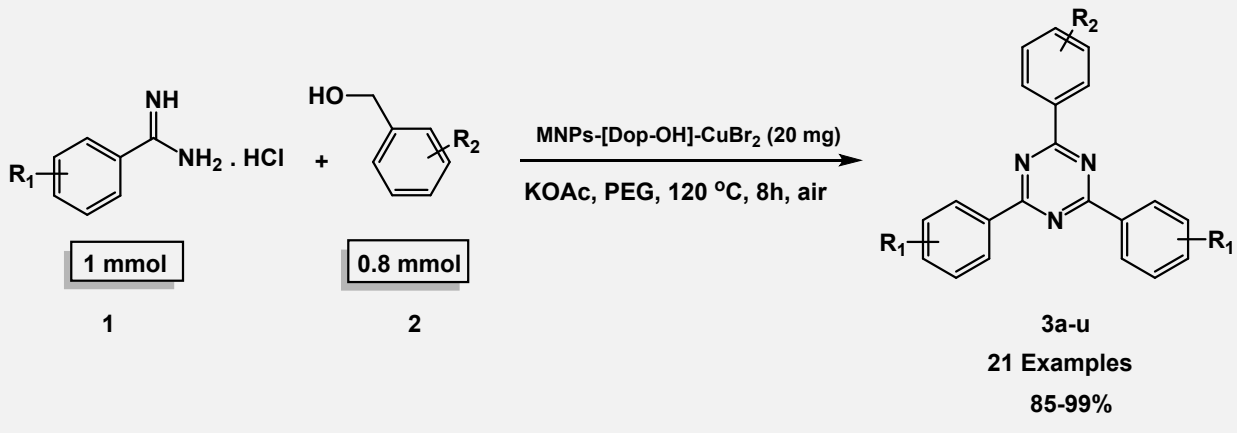
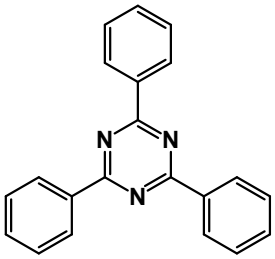
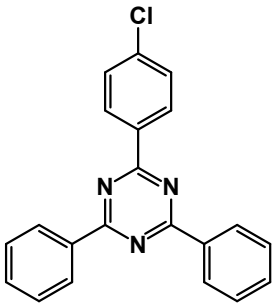
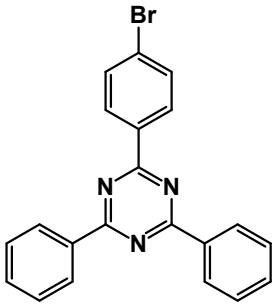
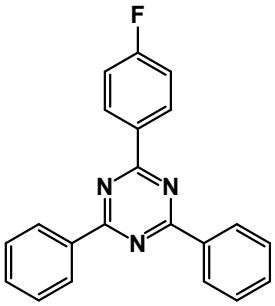
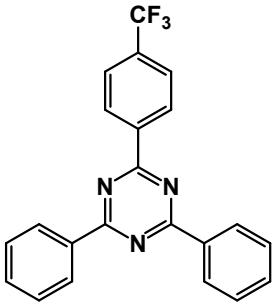
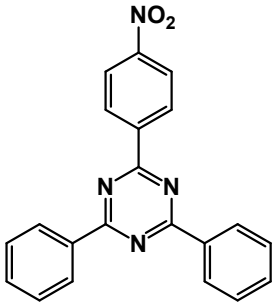
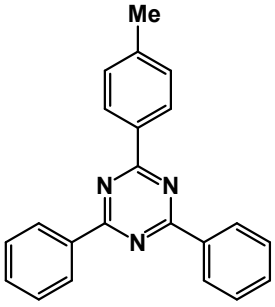
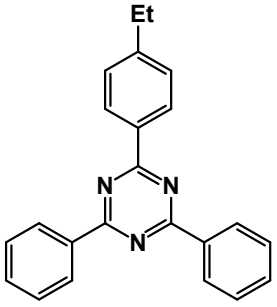
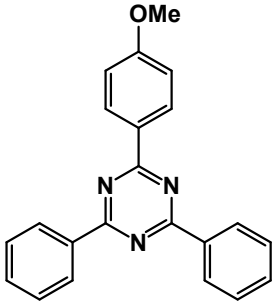
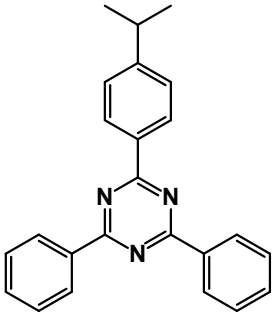
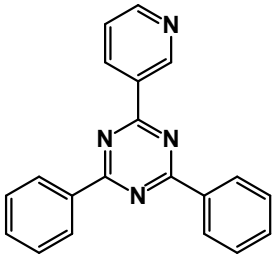
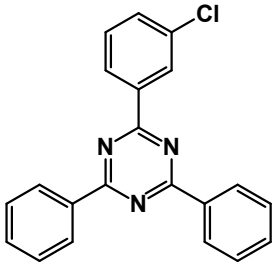
Abstract

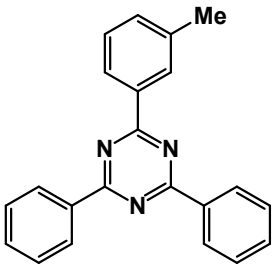
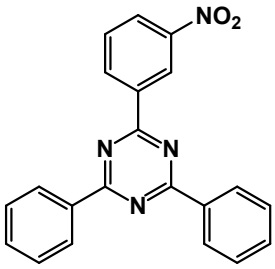
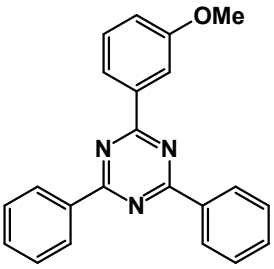
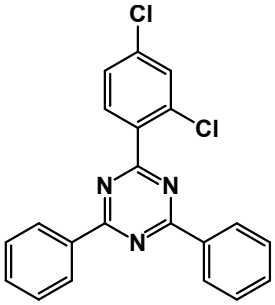
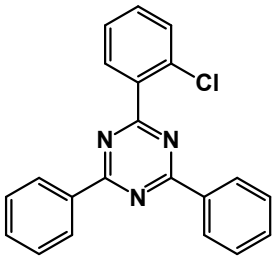
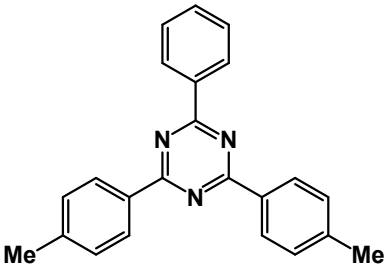
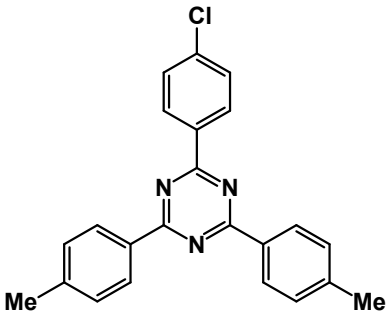
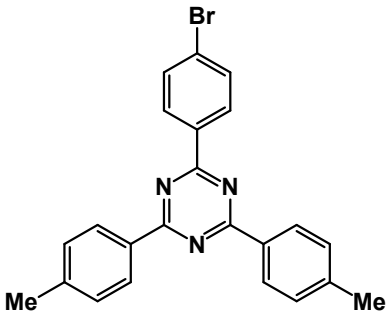
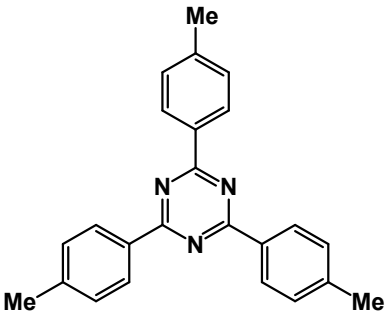
Magnetic nanocatalysts have been one of the best suggestions of chemists in recent years. Among magnetic nanoparticles, Fe_3O_4 nanoparticles are more suitable due to their magnetic properties, chemical stability and less toxicity. These catalysts can be separated after the chemical process through magnetic separation and reused after regeneration. Considering the importance of 1,3,5-triazines derivatives in pharmaceutical and medicinal chemistry, the synthesis of these compounds is always one of the important goals of organic chemists. In this research work, we first successfully synthesized the $CuBr_2$ immobilized on magnetic Fe_3O_4 nanoparticles functionalized with Dop-OH [prepared the reaction of MNPs-Dopamine with 2-phenyloxirane] nanocomposite and then investigated its catalytic application in the synthesis of 1,3,5triazine derivatives through oxidative coupling reaction of amidine hydrochlorides and alcohols in air. Recycling experiments clearly revealed that MNPs-[Dop-OH]-$CuBr_2$ nanocatalyst could be reused for at least 8 runs with reasonable loss of catalytic activity.

Keywords: MNPs-[Dop-OH]-$CuBr_2$ nanocatalyst, 1,3,5-triazines derivatives, Oxidative coupling reaction, High reusability.

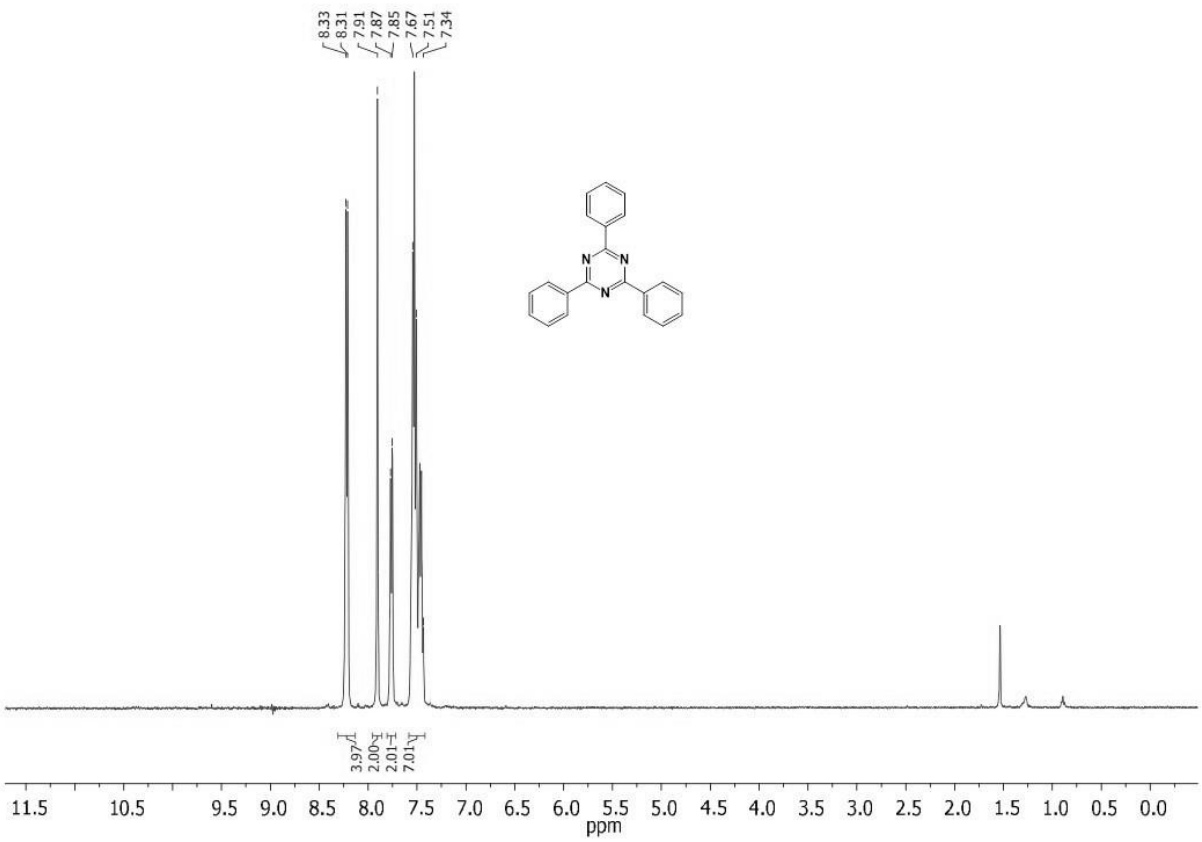
Scope of oxidative coupling reaction of amidine hydrochlorides and alcohols catalyzed by MNPs-[Dop-OH]-$CuBr_2$ nanocomposite under air conditions [a]

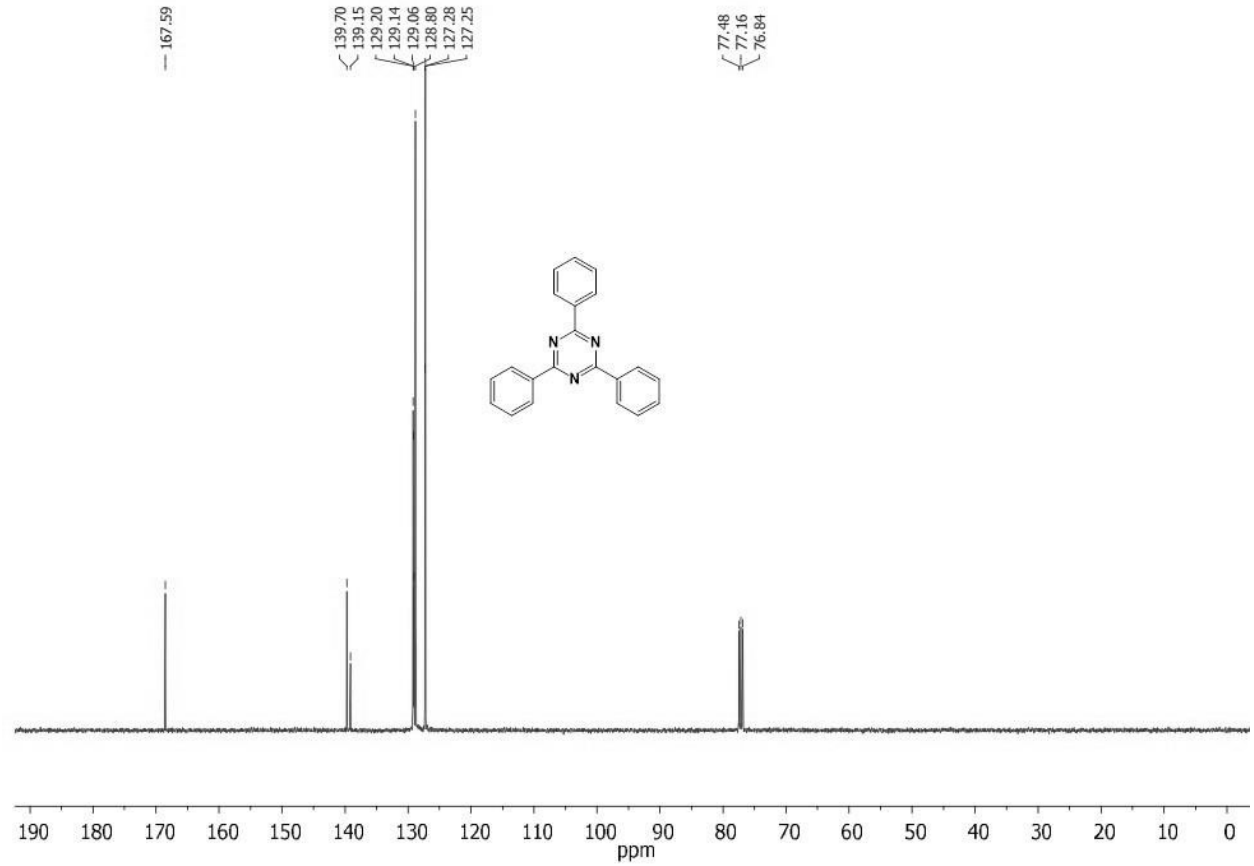


 3a (98%)	 3b (99%)	 3c (99%)
 3d (96%)	 3e (93%)	 3f (97%)
 3g (94%)	 3h (92%)	 3i (93%)
 3j (90%)	 3k (92%)	 3l (92%)

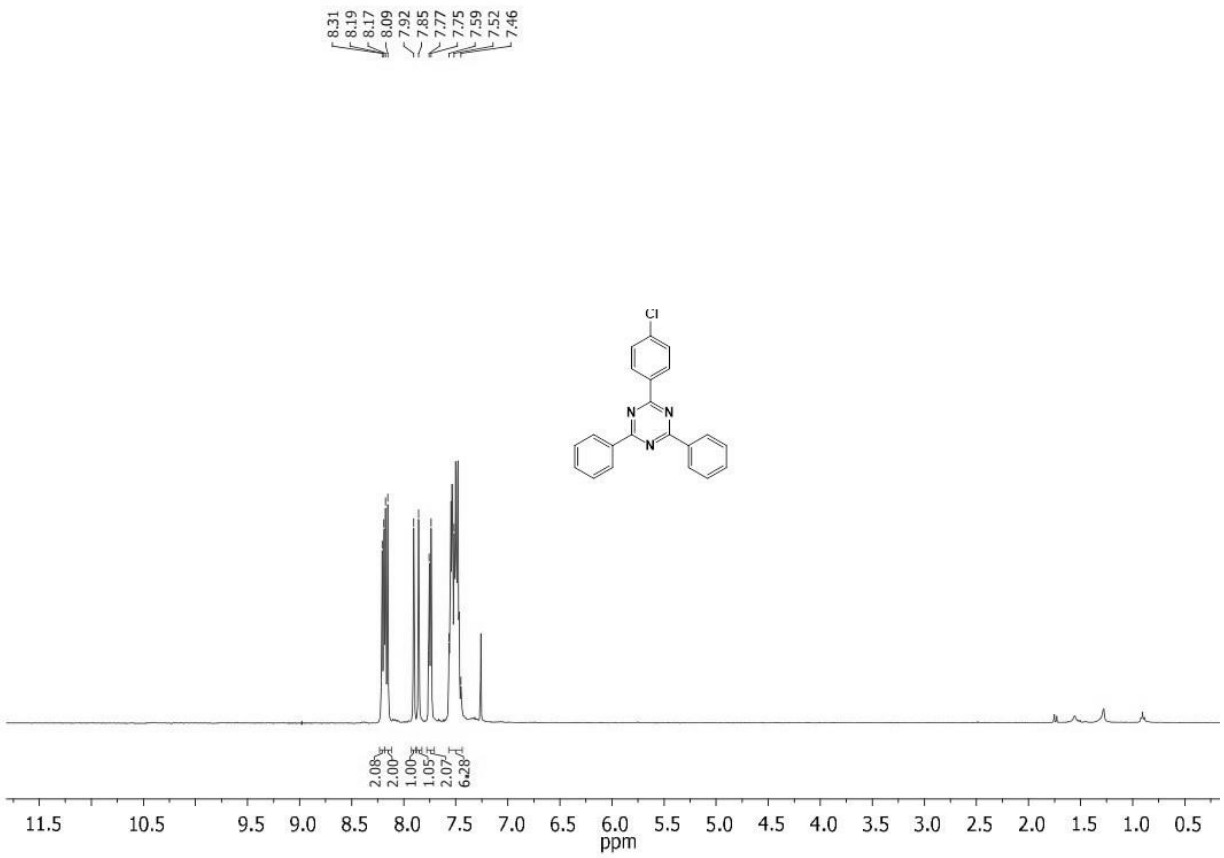
 **3m (88%)**	 **3n (91%)**	 **3o (89%)**
 **3p (94%)**	 **3q (93%)**	 **3r (94%)**
 **3s (92%)**	 **3t (93%)**	 **3u (90%)**

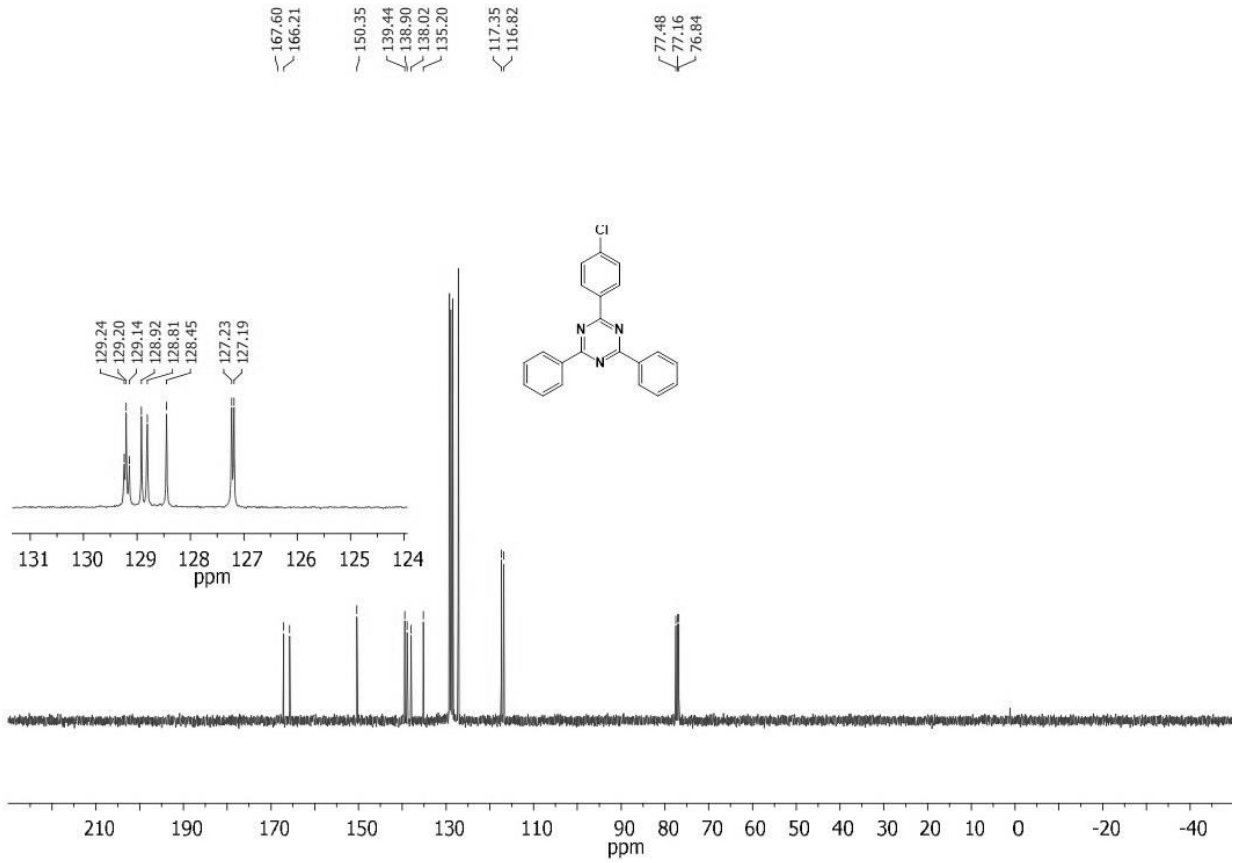
[a] Isolated yield.


8.33
8.31
7.91
7.87
7.85
7.67
7.51
7.34
3.97
2.00
2.01
7.01
11.5
10.5
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
ppm

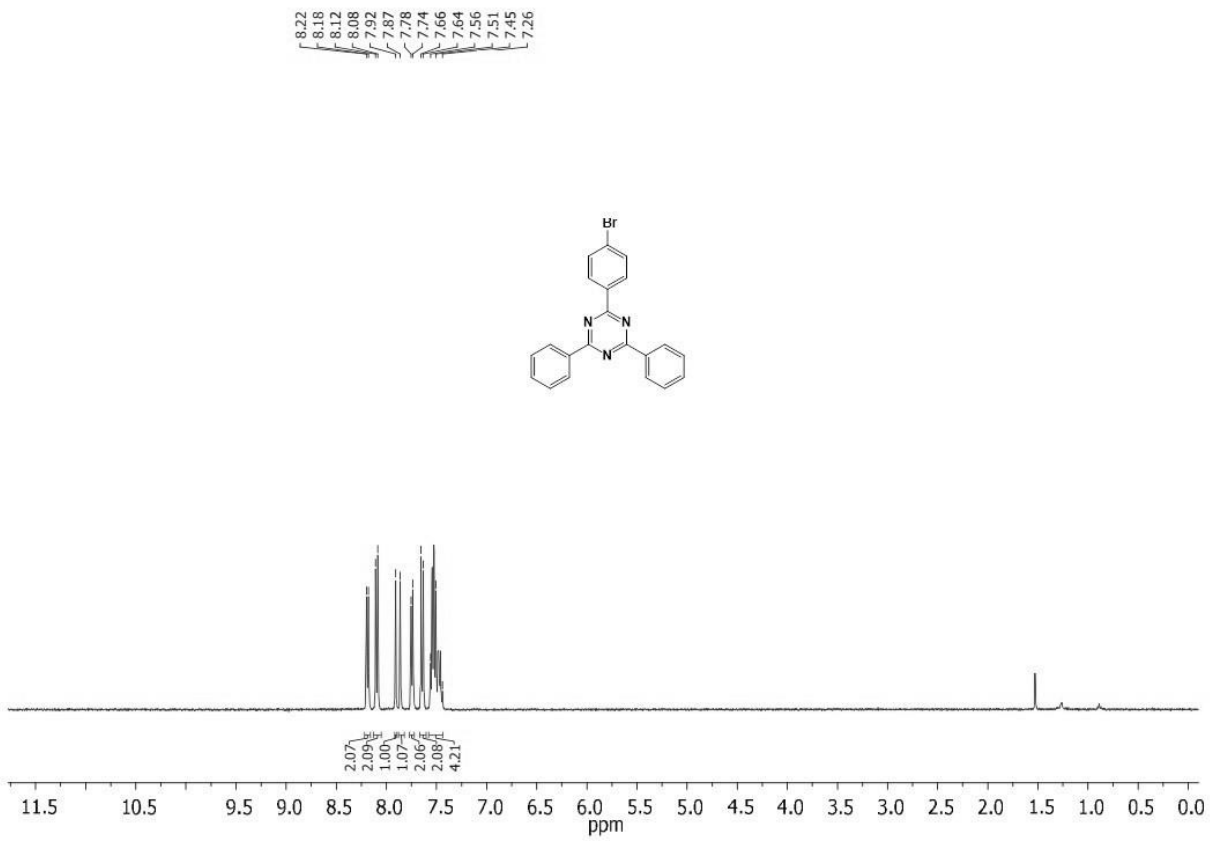


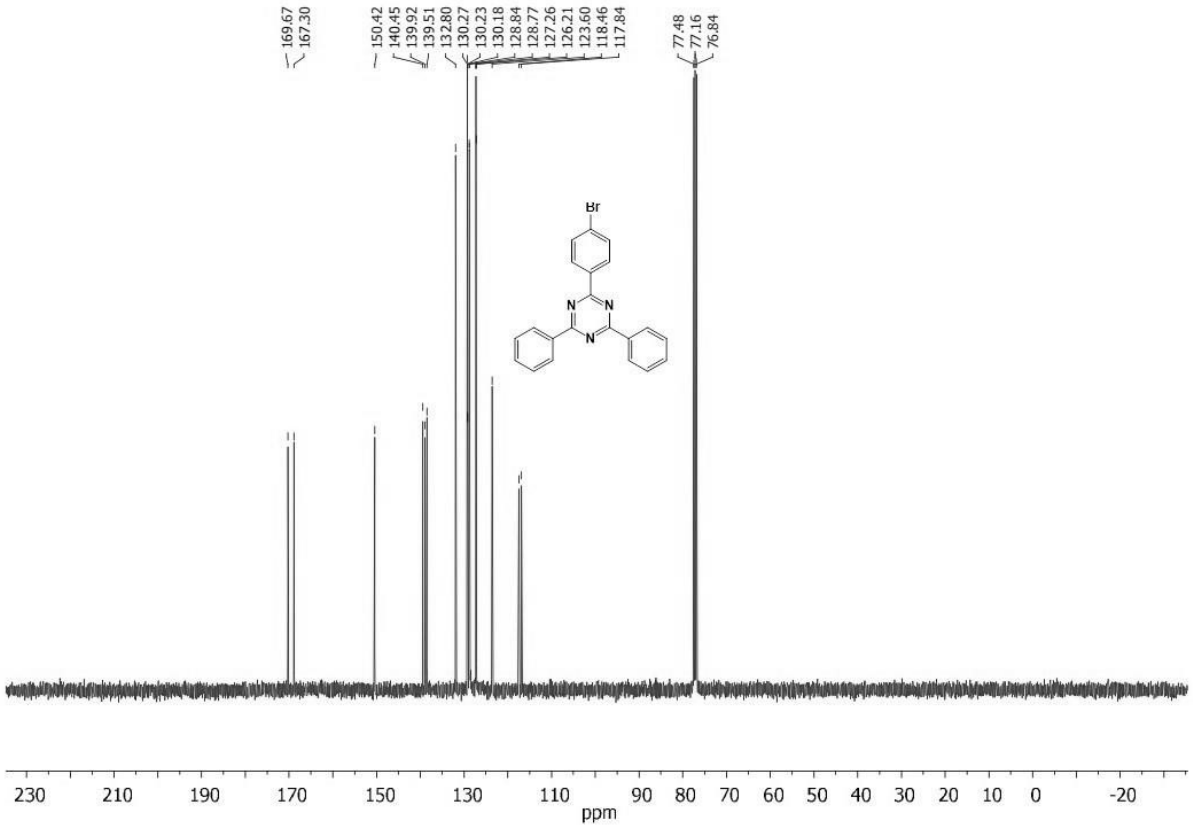
2,4,6-triphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.33-8.31 (d, J = 7.4 Hz, 4H), 7.91 (s, 2H), 7.87-7.85 (d, J = 7.4 Hz, 2H), 7.67-7.34 (m, 7H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 167.6, 139.8, 139.2, 129.3, 129.1, 129.1, 128.8, 127.3, 127.3.


8.31
8.19
8.17
8.09
7.92
7.85
7.77
7.75
7.59
7.52
7.46
Cl
N
N
N
2.08
2.00
1.00
1.05
2.07
6.28
11.5
10.5
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
ppm

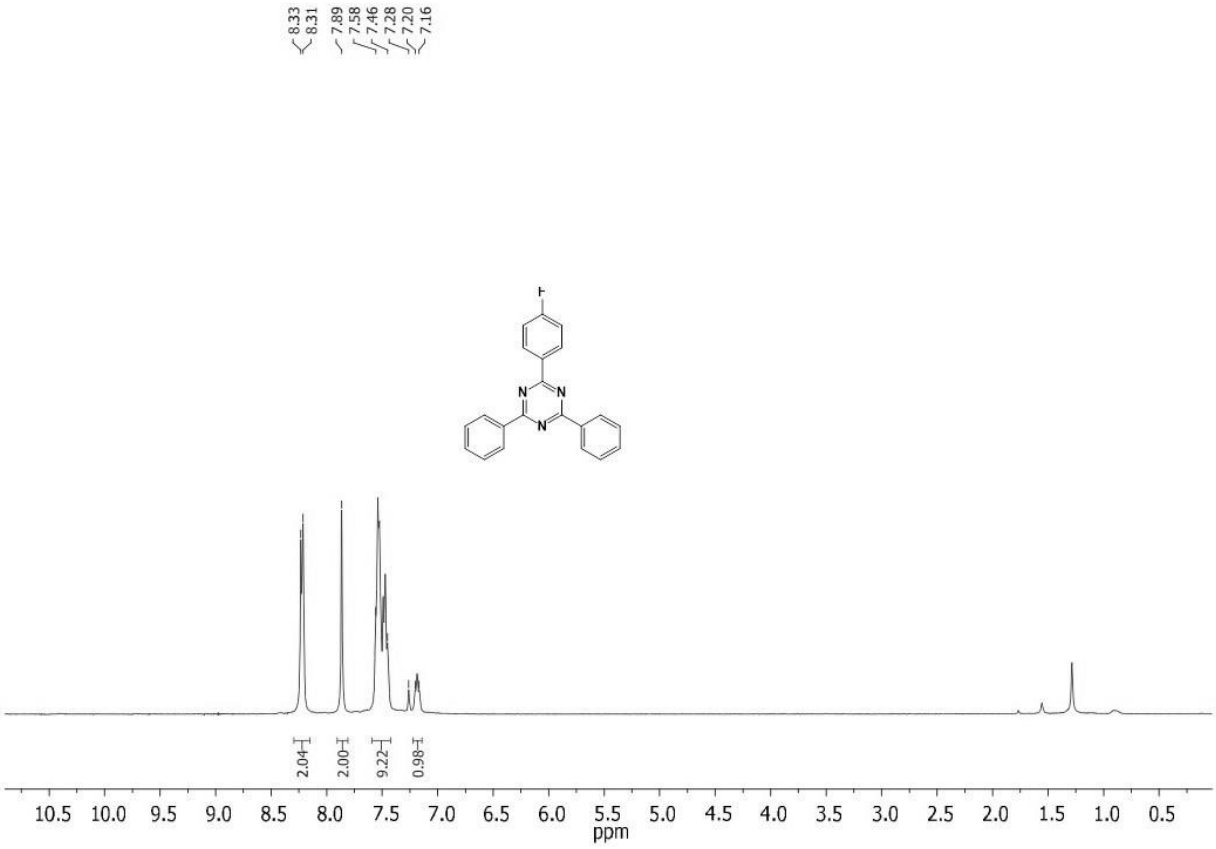


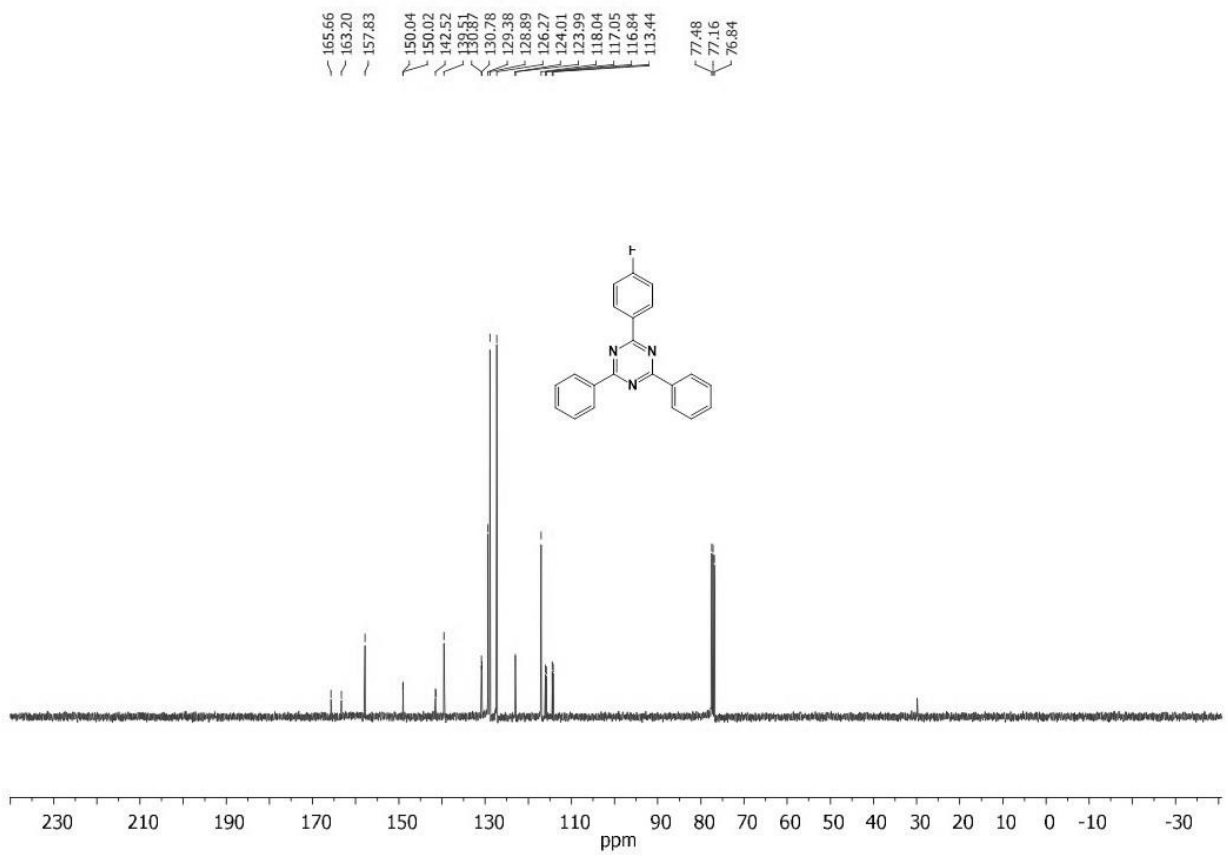
2-(4-chlorophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.31-8.09 (d, J = 7.3 Hz, 4H), 7.92-7.85 (d, J = 8.5 Hz, 2H), 7.77-7.75 (s, 2H), 7.59-7.46 (m, 6H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 167.6, 166.2, 150.4, 139.4, 138.9, 138.0, 135.2, 129.2, 129.2, 129.1, 128.9, 128.8, 128.5, 127.2, 127.2, 117.4, 116.8.


8.22
8.18
8.12
8.08
7.92
7.87
7.78
7.74
7.66
7.64
7.56
7.51
7.45
7.26
Br
N
N
N
2.07
2.09
1.00
1.07
2.06
2.08
4.21
11.5
10.5
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
ppm

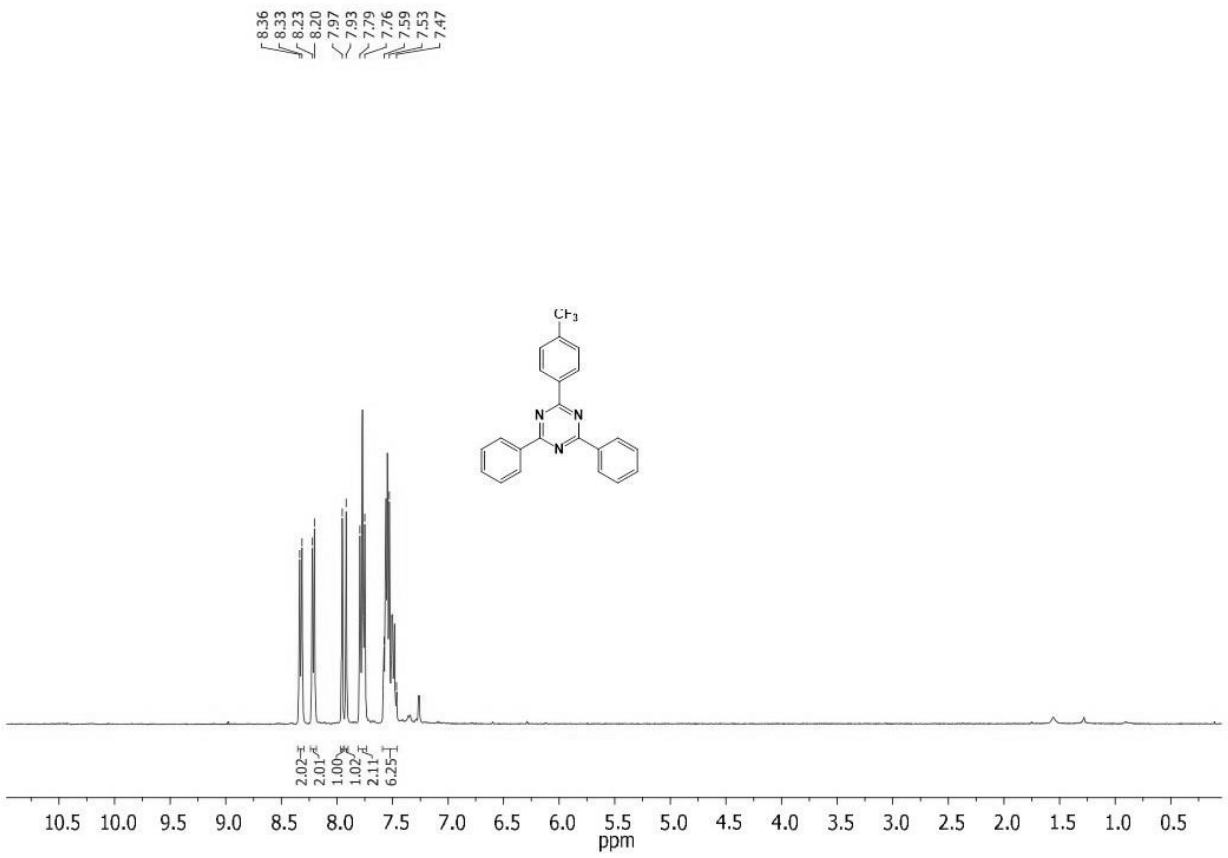

169.67
167.30
150.42
140.45
139.92
139.51
132.80
130.27
130.23
130.18
128.84
128.77
127.26
126.21
123.60
118.46
117.84
77.48
77.16
76.84
Br
N
N
N
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-20
ppm

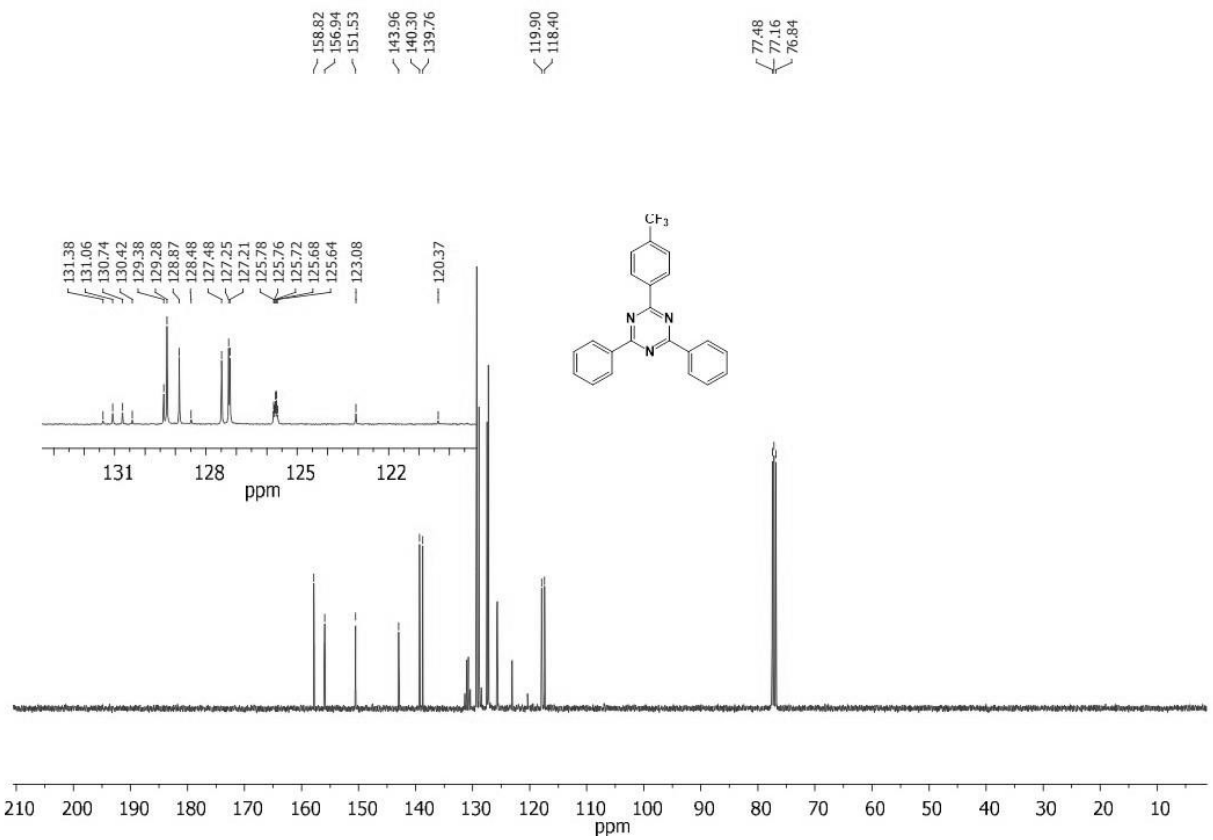
2-(4-bromophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.22 (d, J = 7.1 Hz, 2H), 8.18 (d, J = 8.6 Hz, 2H), 7.92 (s, 1H), 7.87 (s, 1H), 7.78-7.74 (d, J = 6.9 Hz, 2H), 7.66-7.64 (d, J = 8.6 Hz, 2H), 7.56–7.26 (m, 4H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 169.7, 167.3, 150.4, 140.5, 138.9, 139.5, 132.9, 130.3, 130.2, 130.2, 128.8, 128.8, 127.3, 126.2, 123.6, 118.5, 117.8.



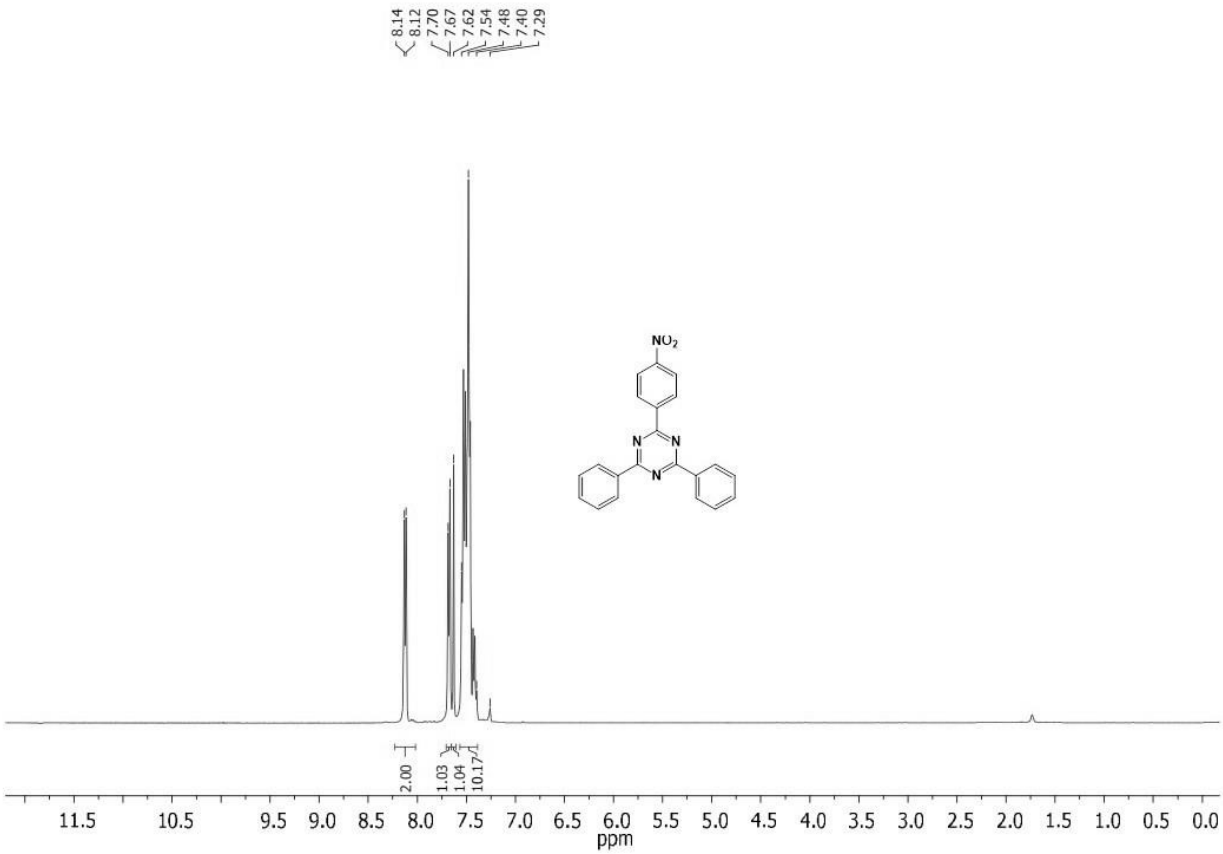


2-(4-fluerophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.33-8.31 (d, J = 7.4 Hz, 2H), 7.89 (s, 2H), 7.58–7.28 (m, 9H), 7.20–7.16 (m, 1H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 165.7, 163.2, 157.8, 150.0, 142.5 (d, J = 7.8 Hz), 140.5, 131.8 (d, J = 8.3 Hz), 130.3, 129.9, 128.3, 126.4, 124.0 (d, J = 2.8 Hz), 118.0, 117.0 (d, J = 21.1 Hz), 116.9, 113.3 (d, J = 22.4 Hz).


8.36
8.33
8.23
8.20
7.97
7.93
7.79
7.76
7.59
7.53
7.47
CF3
N
N
N
2.02
2.01
1.00
1.02
2.11
6.25
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
ppm



2,4-diphenyl-6-(4-(trifluoromethyl)phenyl)-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.36 (d, J = 8.3 Hz, 2H), 8.23 (d, J = 7.0 Hz, 2H), 7.97 (s, 1H), 7.93 (s, 1H), 7.79–7.76 (m, 2H), 7.59–7.47 (m, 6H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 158.8, 156.9, 151.5, 143.0, 140.3, 139.8, 130.9 (q, J = 32.3), 129.4, 129.3, 129.3, 128.9, 127.5, 127.3, 127.2, 125.7 (q, J = 3.8 Hz), 124.4 (q, J = 272.0 Hz), 119.9, 118.4.


8.14
8.12
7.70
7.67
7.62
7.54
7.48
7.40
7.29
NO2
N
N
N
2.00
1.03
1.04
10.17
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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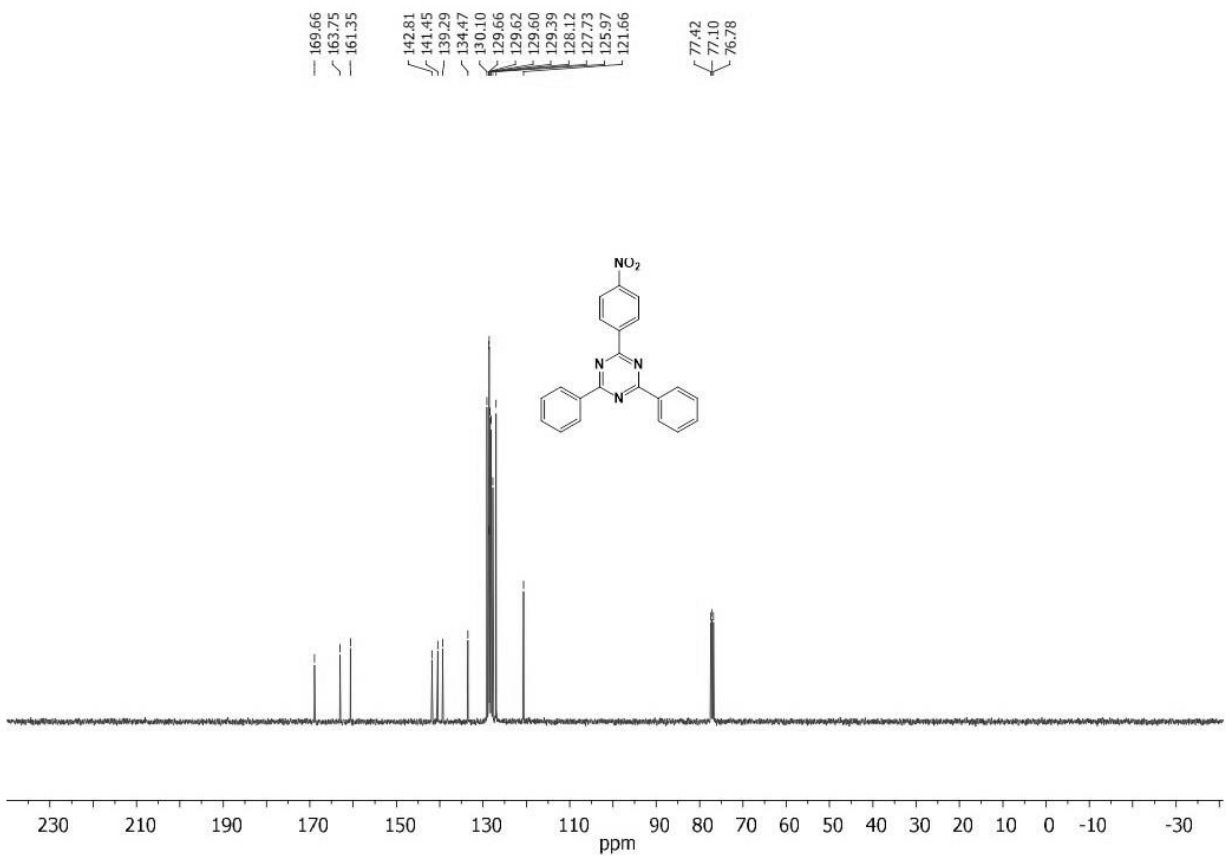
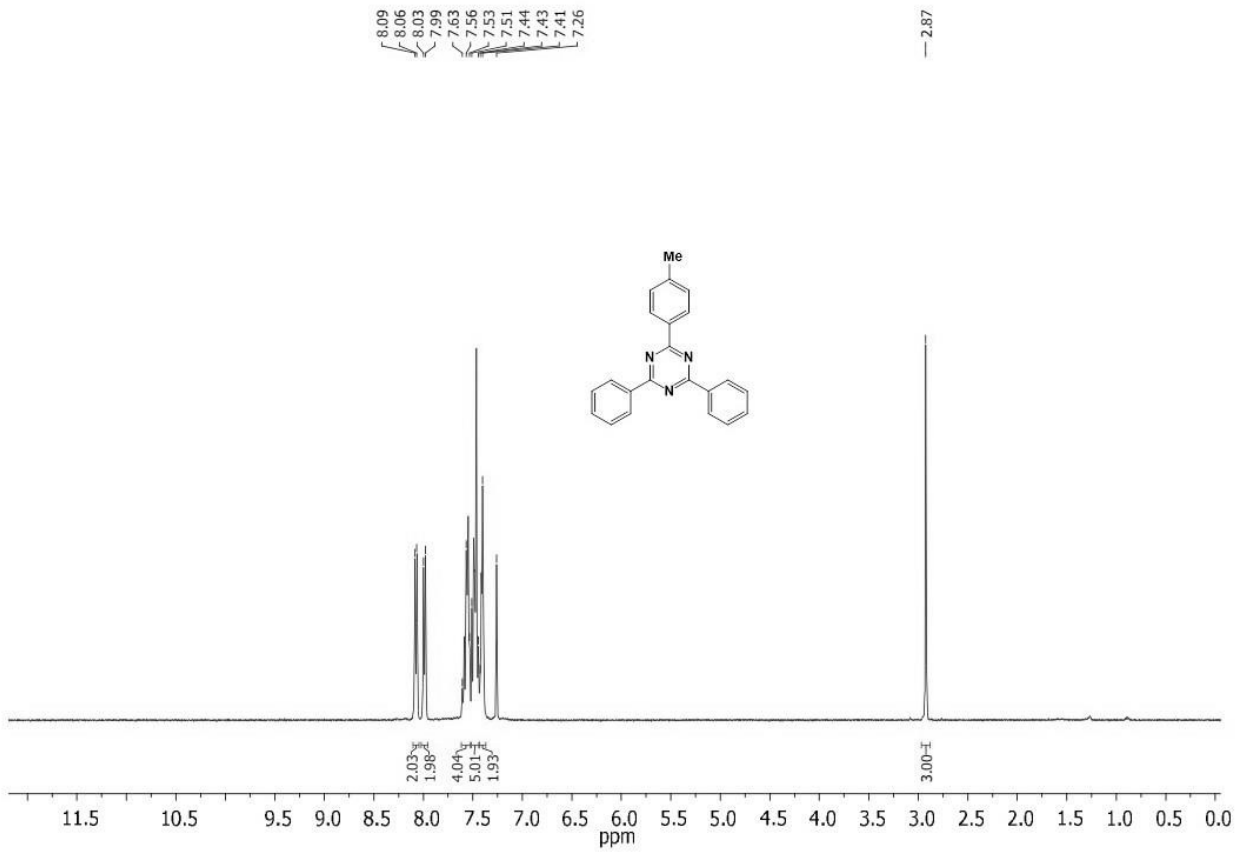
ppm



2-(4-nitrophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.14 (d, J = 7.5 Hz, 2H), 7.70 (d, J = 7.5 Hz, 1H), 7.67 (s, 1H), 7.54–7.29 (m, 10H),13C{1H} NMR (100.6 MHz, CDCl3): δ = 169.7, 163.8, 161.4, 141.8, 141.5, 139.3, 134.5, 130.1, 129.7, 129.6, 129.6, 129.6, 129.4, 128.1, 127.7, 125.0, 121.7.


8.09
8.06
8.03
7.99
7.63
7.56
7.53
7.51
7.44
7.43
7.41
7.26
2.87
Me
N
N
N
2.03
1.98
4.04
5.01
1.93
3.00
11.5
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
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4.0
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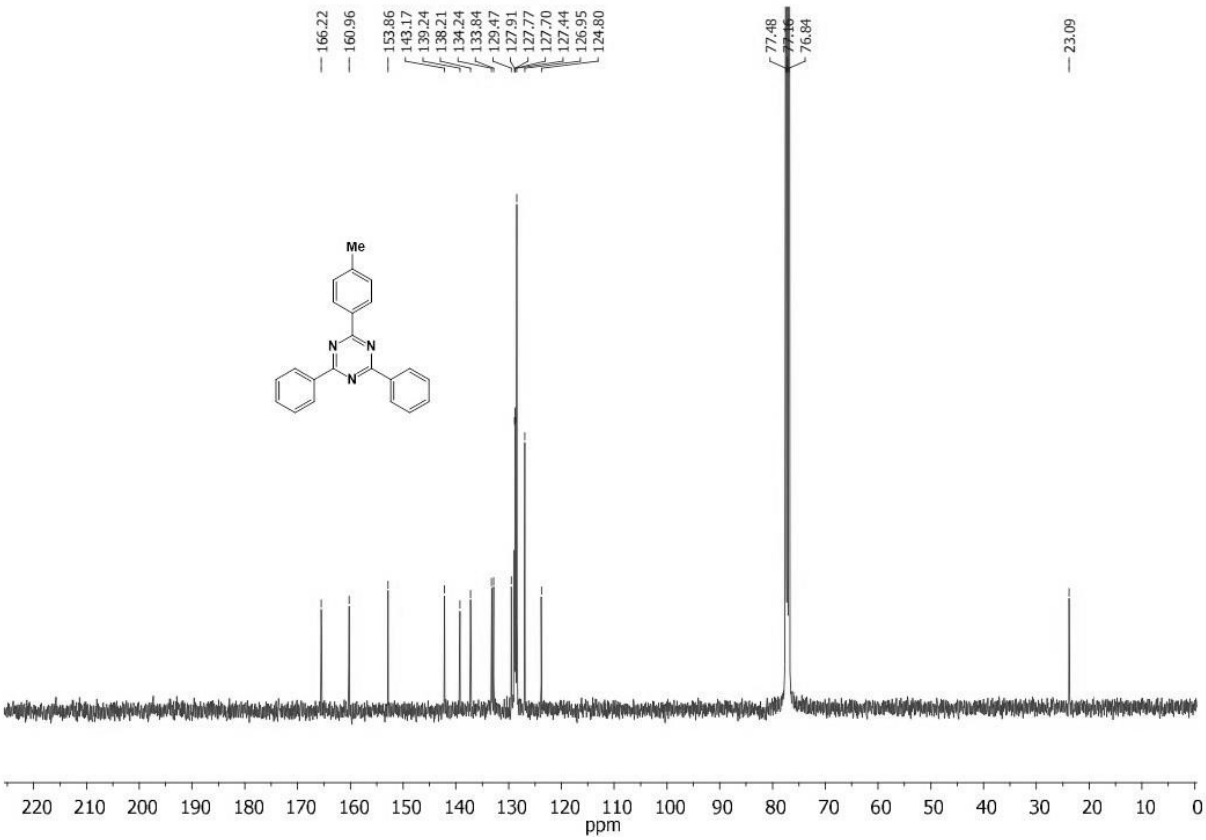
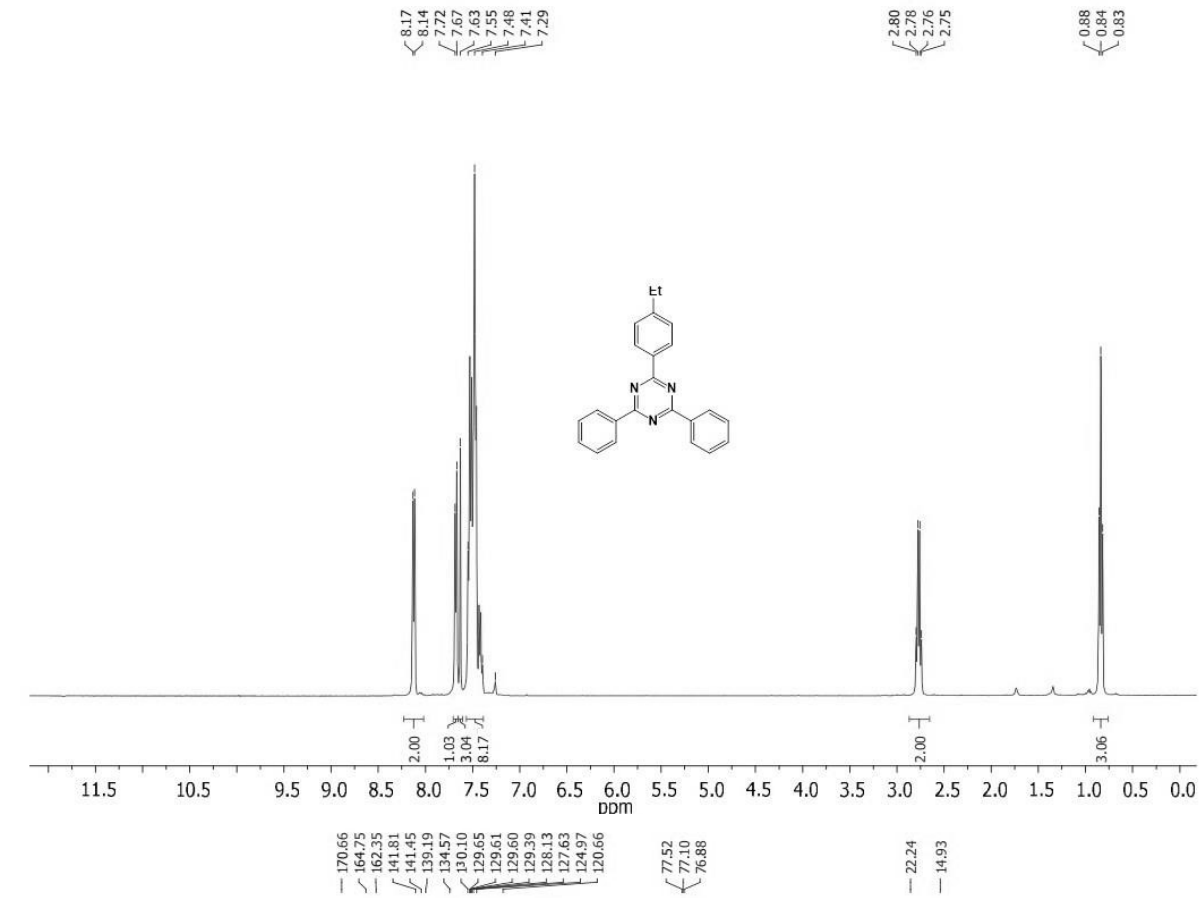
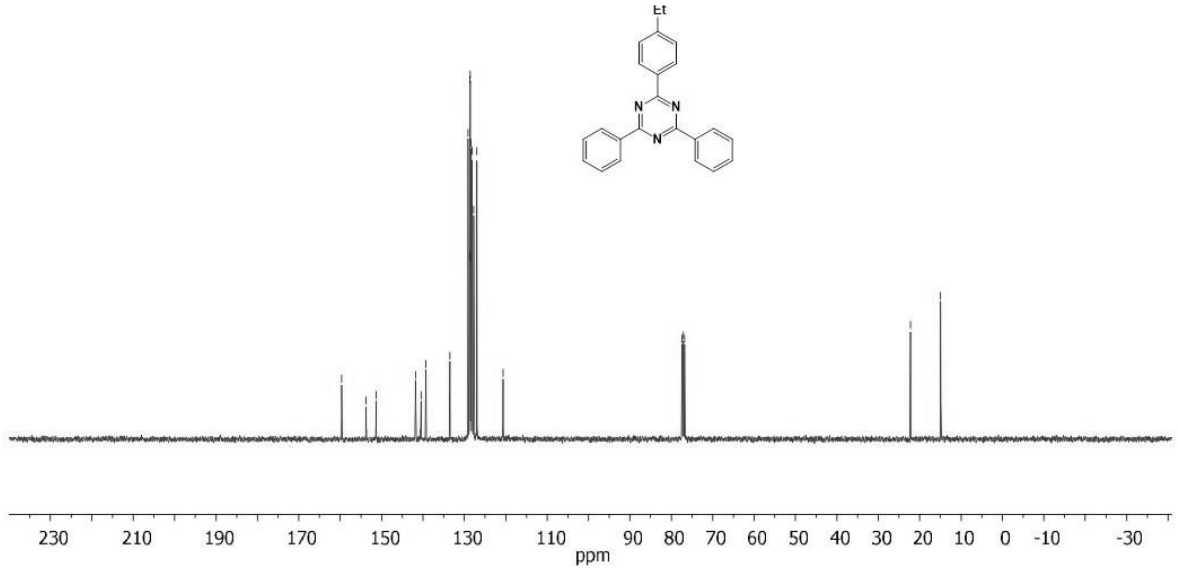
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm



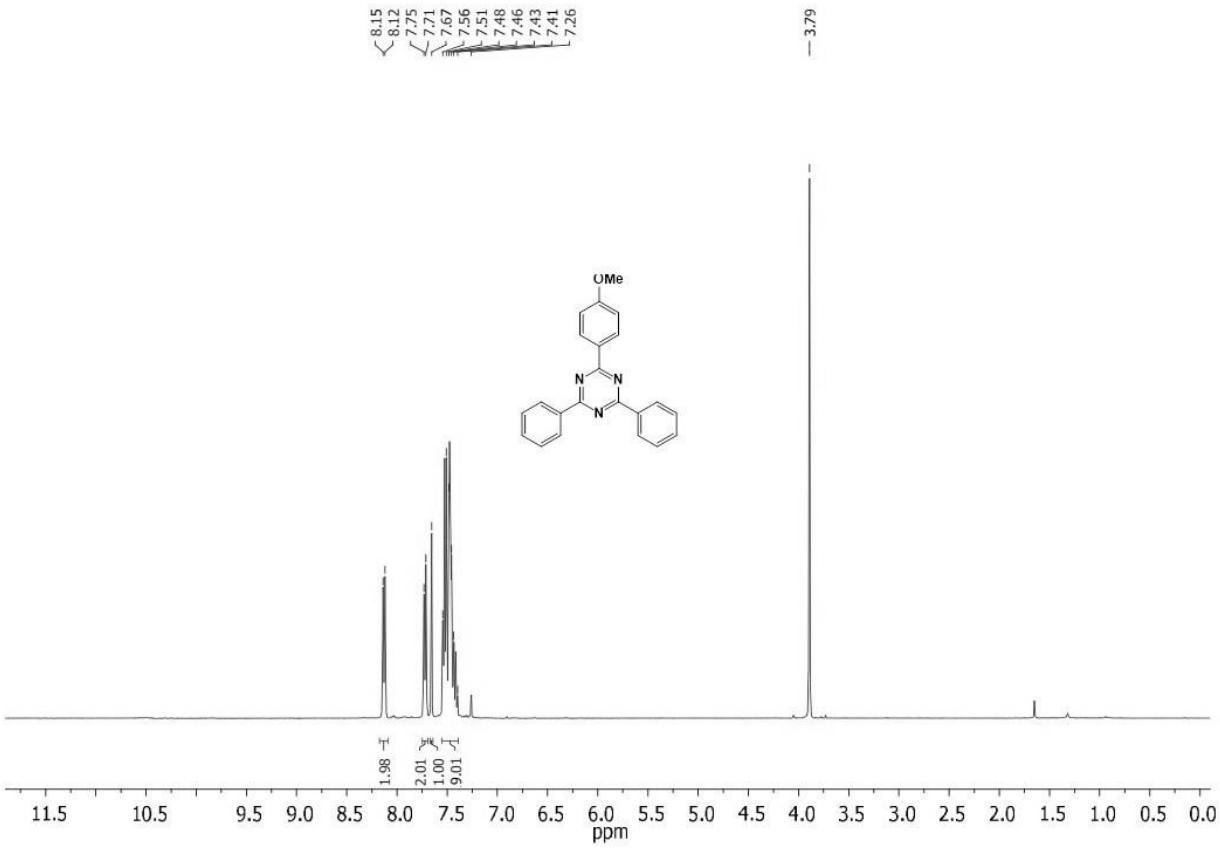
2,4-diphenyl-6-(p-tolyl)-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.09 (d, J = 7.4 Hz, 2H), 8.03 (d, J = 7.4 Hz, 2H), 7.63–7.53 (m, 4H), 7.51–7.43 (m, 5H), 7.41–7.40 (m, 2H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 166.2, 161.0, 153.9, 143.2, 139.2, 138.2, 134.2, 133.8, 129.5, 127.9, 127.8, 127.7, 127.4, 127.4,126.0, 124.8, 23.1.

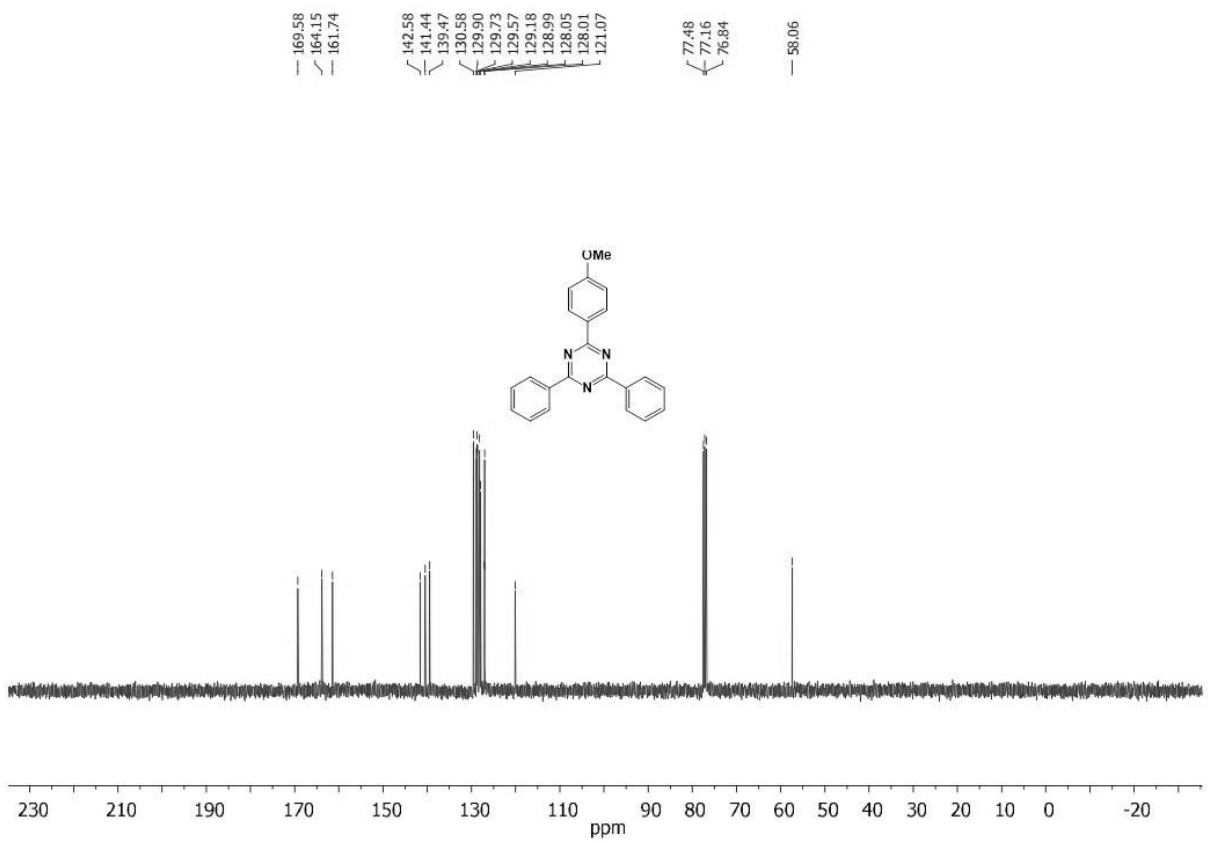




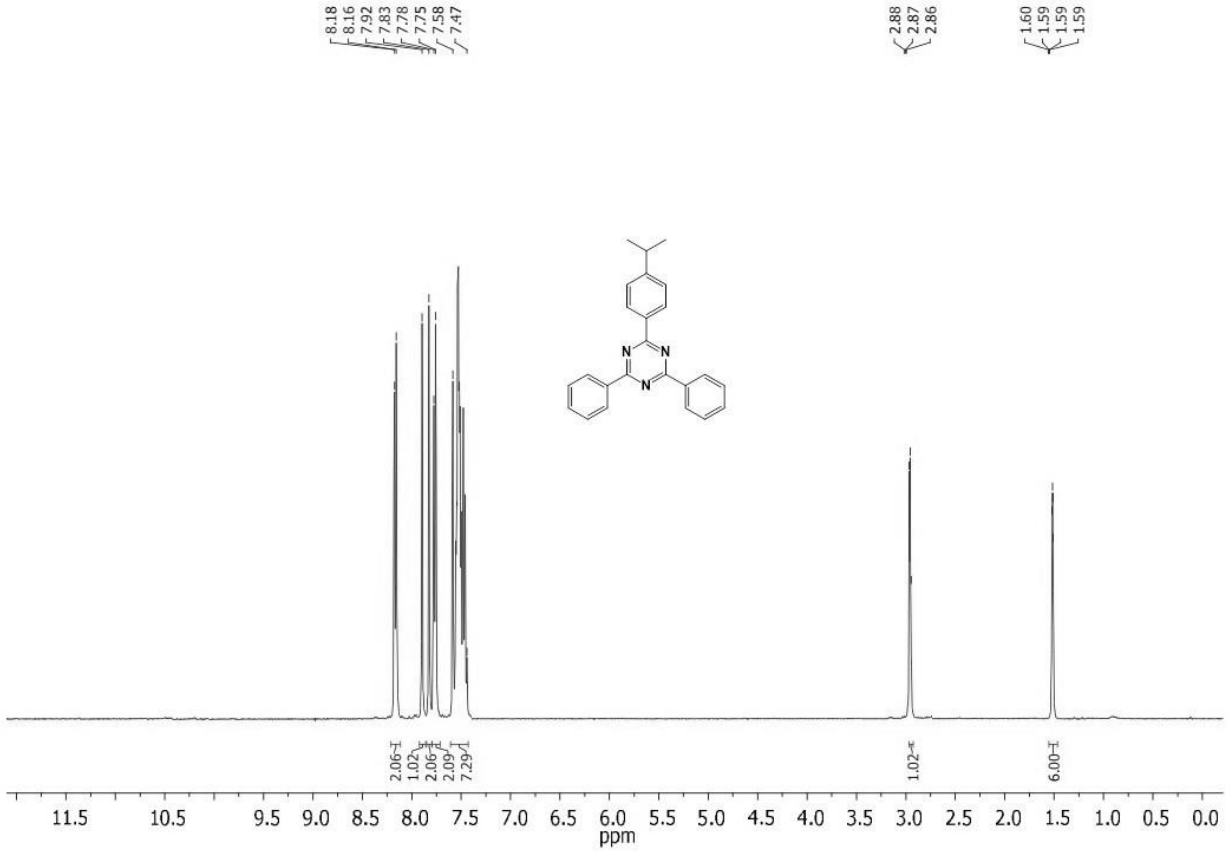
2-(4-ethylphenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.17 (d, J = 7.5 Hz, 2H), 7.72 (d, J = 7.5 Hz, 1H), 7.63 (m, 3H), 7.55–7.41 (m, 8H), 13C{1H} NMR (100.6 MHz, CDCl3): δ

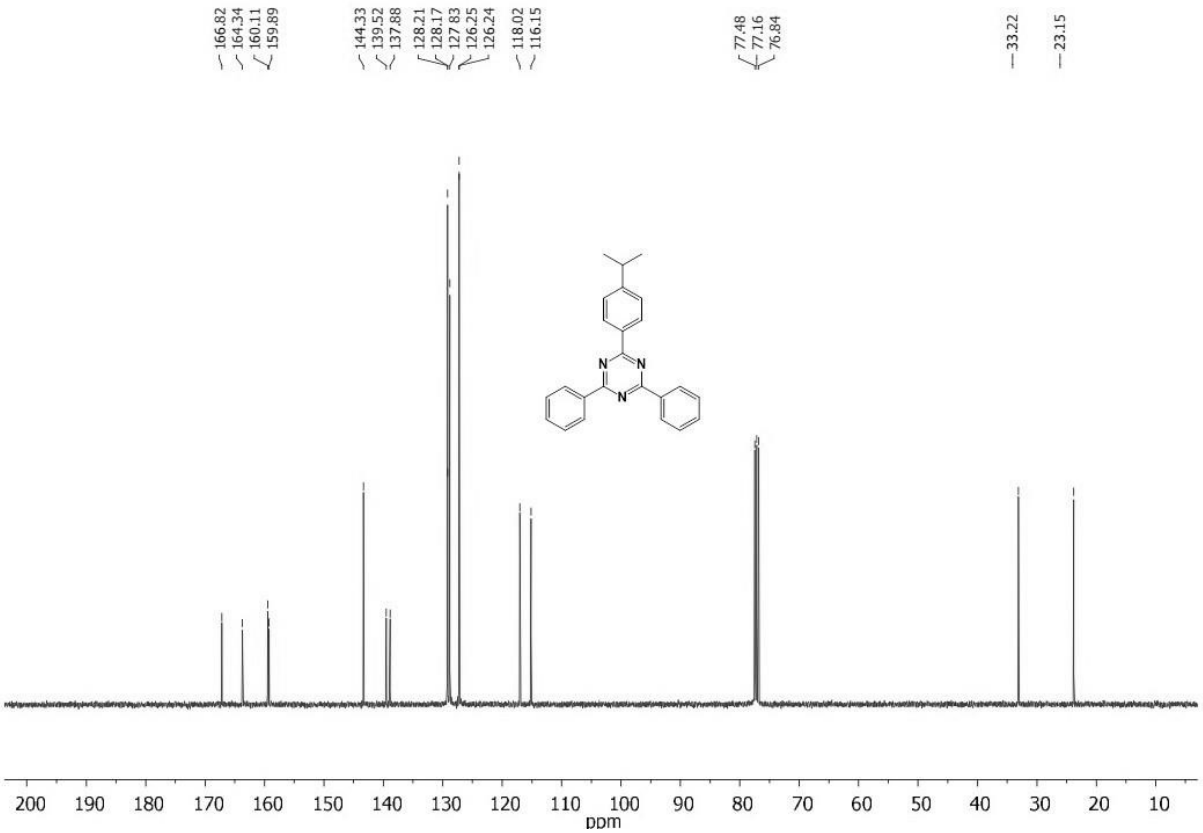
= 170.7, 164.8, 162.4, 141.8, 141.5, 139.3, 134.5, 130.1, 129.7, 129.6, 129.6, 129.6, 129.4, 128.1, 127.7, 124.0, 120.7, 22.4, 14.9.



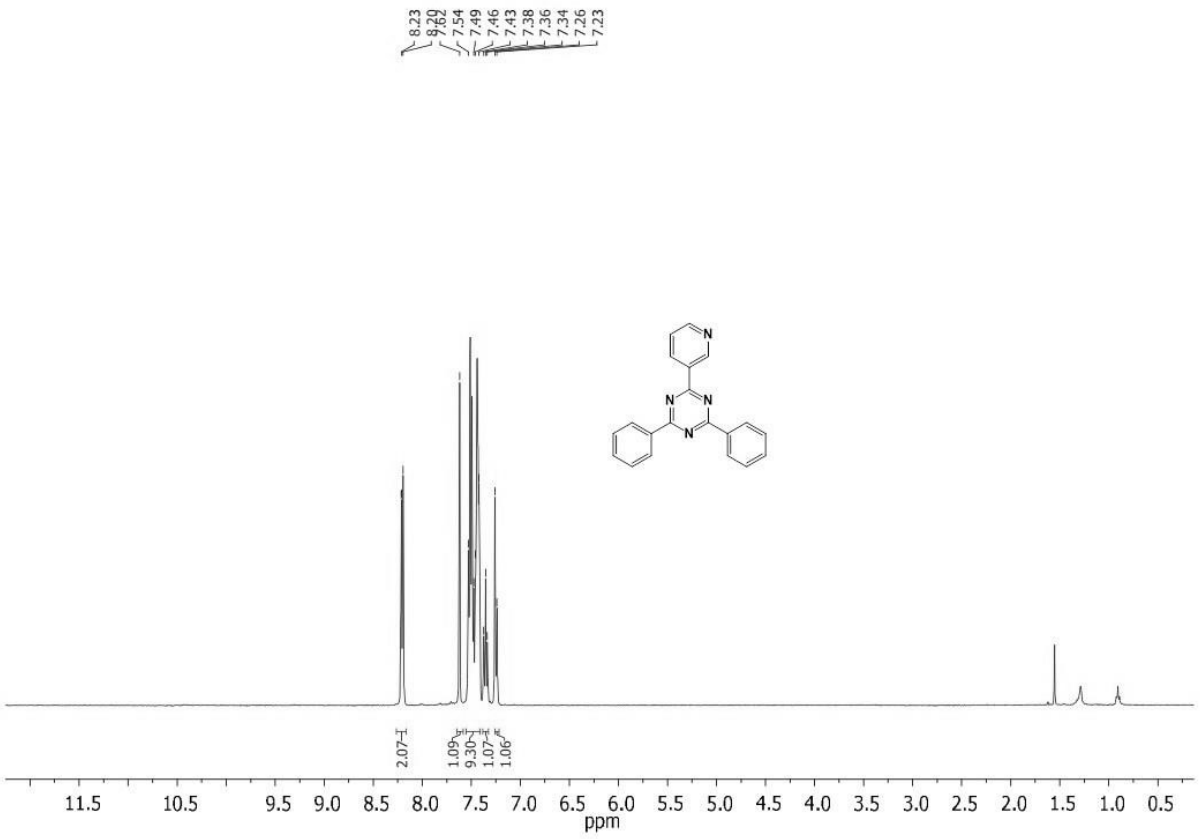


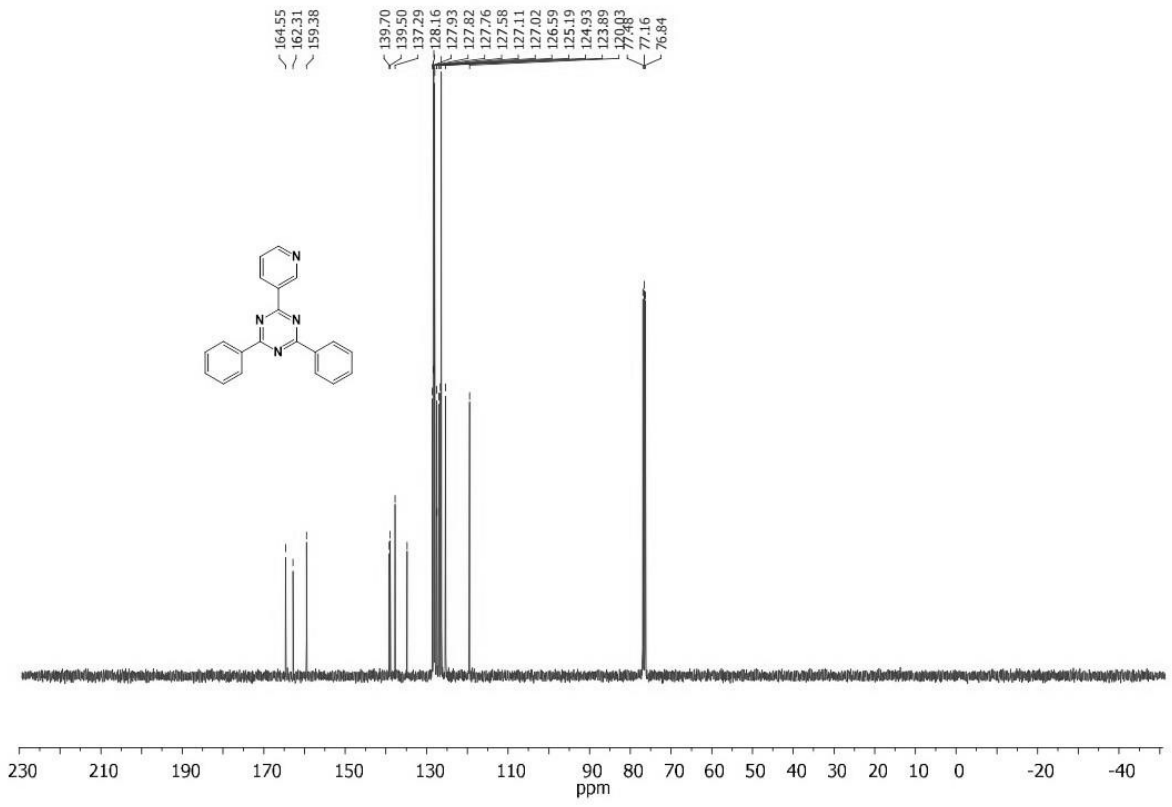
2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.15 (d, J = 7.6 Hz, 2H), 7.75–7.70 (m, 2H), 7.67 (s, 1H), 7.56–7.41 (m, 9H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 169.6, 164.2, 161.7, 142.6, 141.4, 139.5, 130.6, 129.9, 129.7, 129.7, 129.6, 128.2, 128.0, 128.0, 128.1, 12.0, 121.1, 58.1.


8.18
8.16
7.92
7.83
7.78
7.75
7.58
7.47
2.88
2.87
2.86
1.60
1.59
1.59
1.59
N
N
N
2.06
1.02
2.06
2.09
7.29
1.02
6.00
11.5
10.5
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
ppm

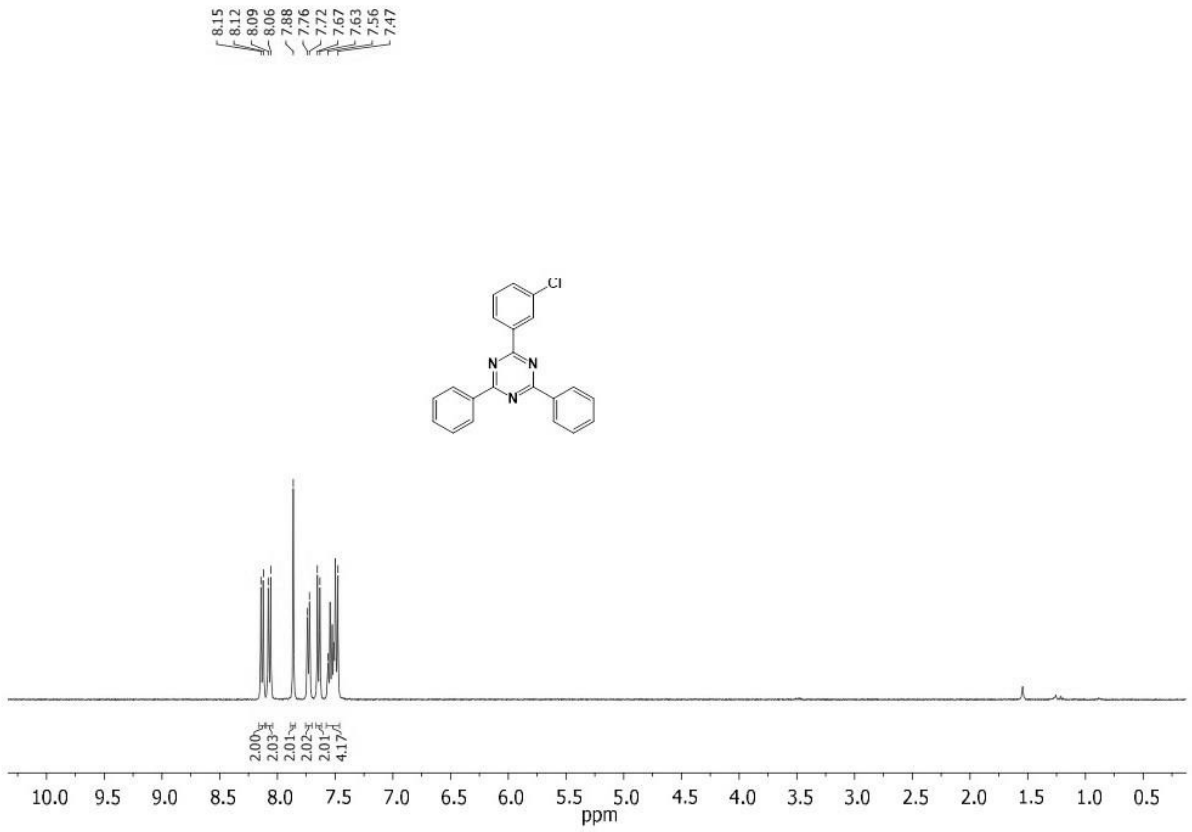


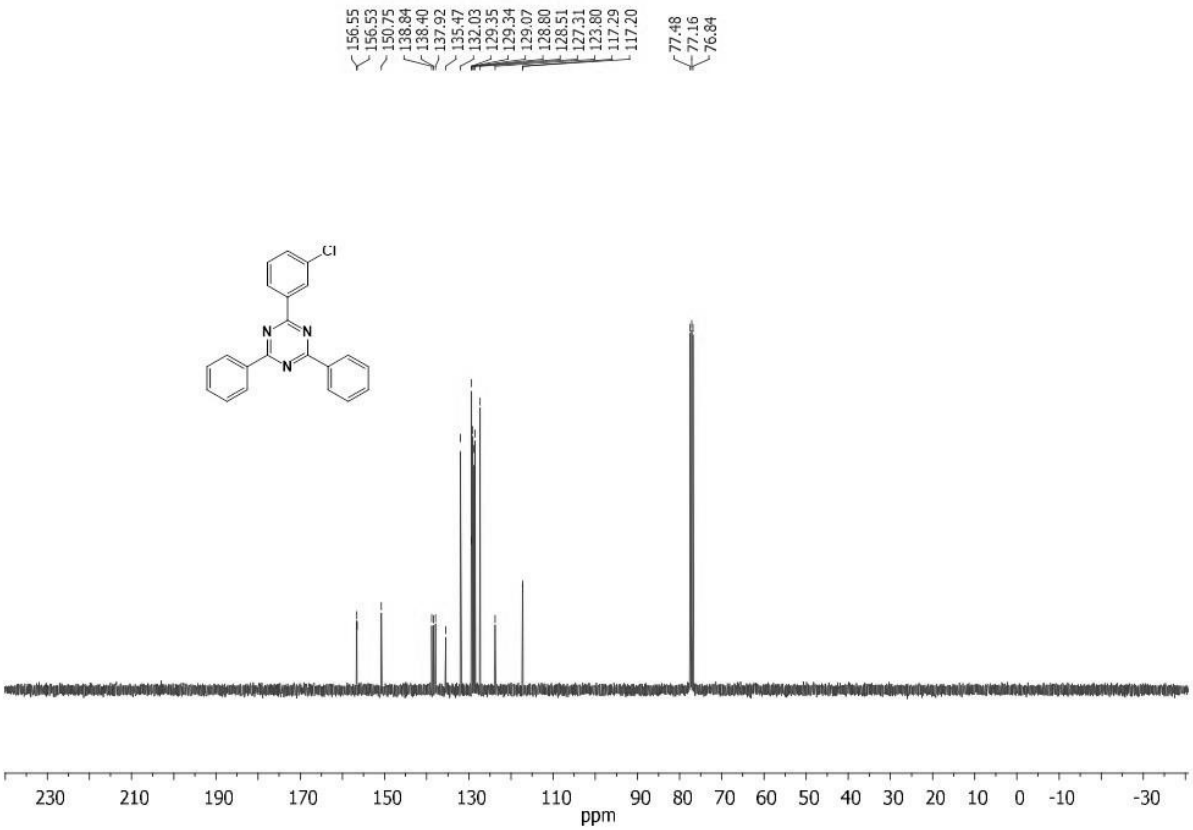
2-(4-isopropylphenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.16 (d, J = 7.2 Hz, 2H), 7.92 (s, 1H), 7.83 (s, 2H), 7.78 (d, J = 7.0 Hz, 2H), 7.58–7.47 (m, 7H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 166.8, 164.3, 160.1, 159.9, 144.3, 139.5, 137.9, 128.2, 128.2, 127.8, 126.3, 126.2, 118.0, 116.2, 33.2, 23.1.


8.23
8.20
7.62
7.54
7.49
7.46
7.43
7.38
7.36
7.34
7.26
7.23
2.07
1.09
9.30
1.07
1.06
11.5 10.5 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
ppm

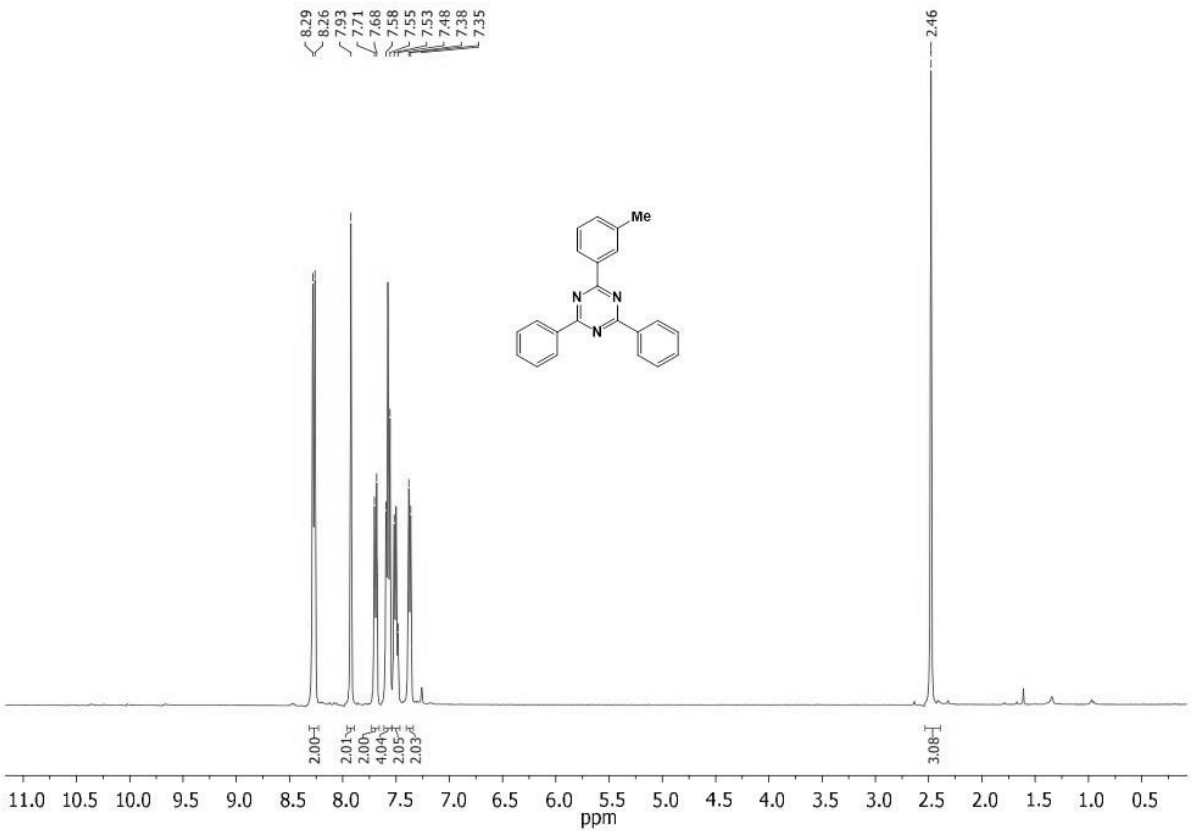

164.55
162.31
159.38
139.70
139.50
137.29
128.16
127.93
127.82
127.76
127.58
127.11
127.02
126.59
125.19
124.93
123.89
120.03
77.16
76.84
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40
ppm

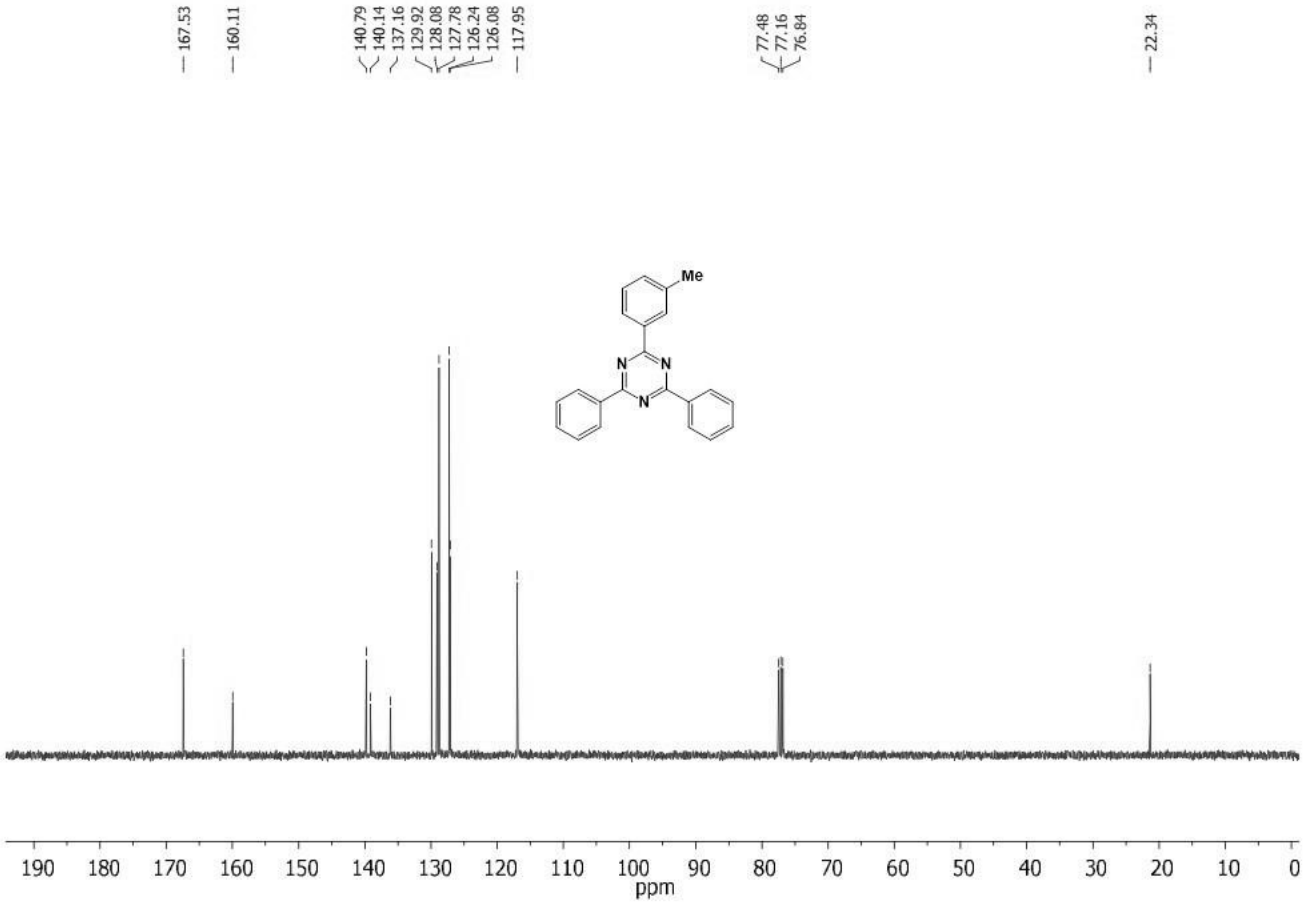
2,4-diphenyl-6-(pyridin-3-yl)-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.23 (d, J = 8.3 Hz, 2H), 7.63 (s, 1H), 7.54–7.43 (m, 9H), 7.36 (t, J = 7.4 Hz, 1H), 7.23 (d, J = 8.5 Hz, 1H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 164.5, 162.3, 159.4, 139.7, 139.5, 137.3, 135.4, 128.2, 127.9, 127.8, 127.8, 127.6, 127.1, 127.0, 126.6, 125.2, 125.9, 123.9, 120.0.



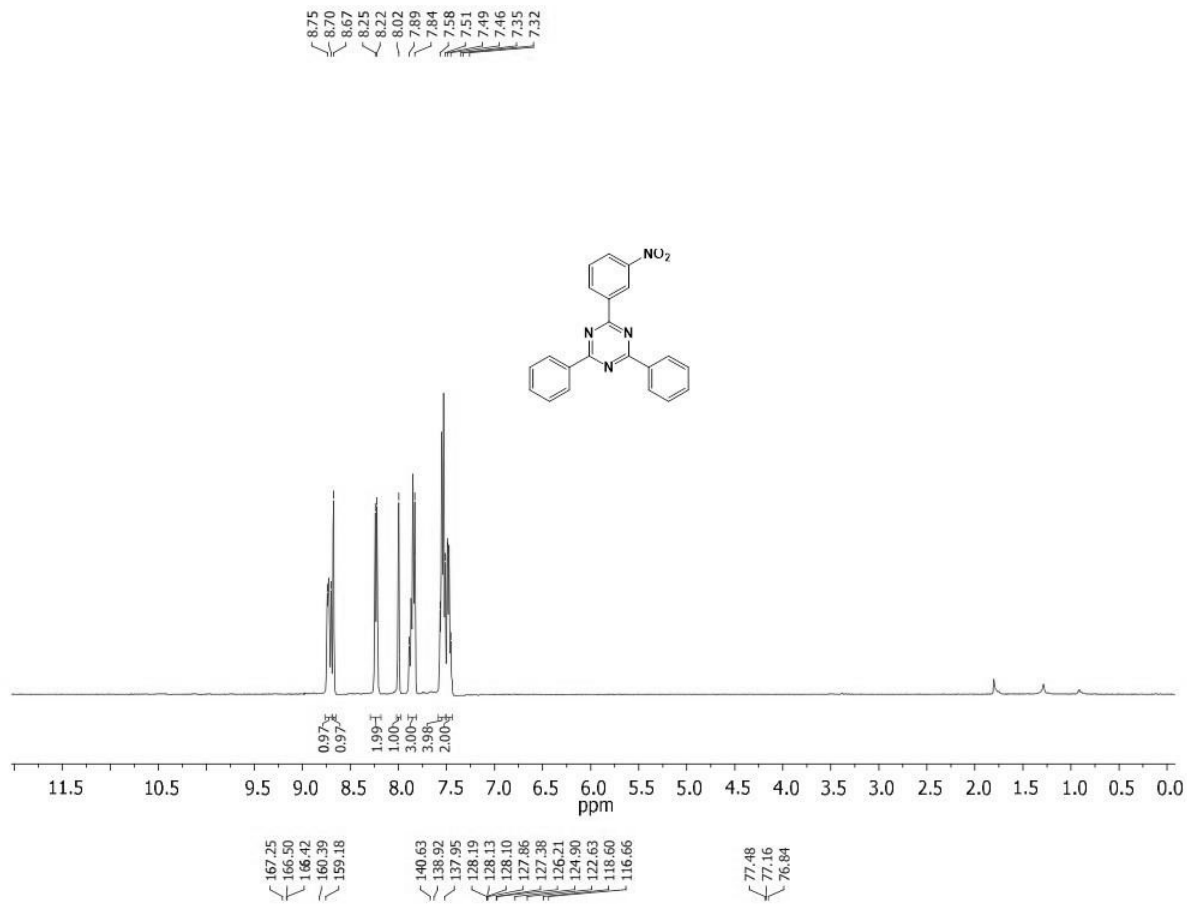


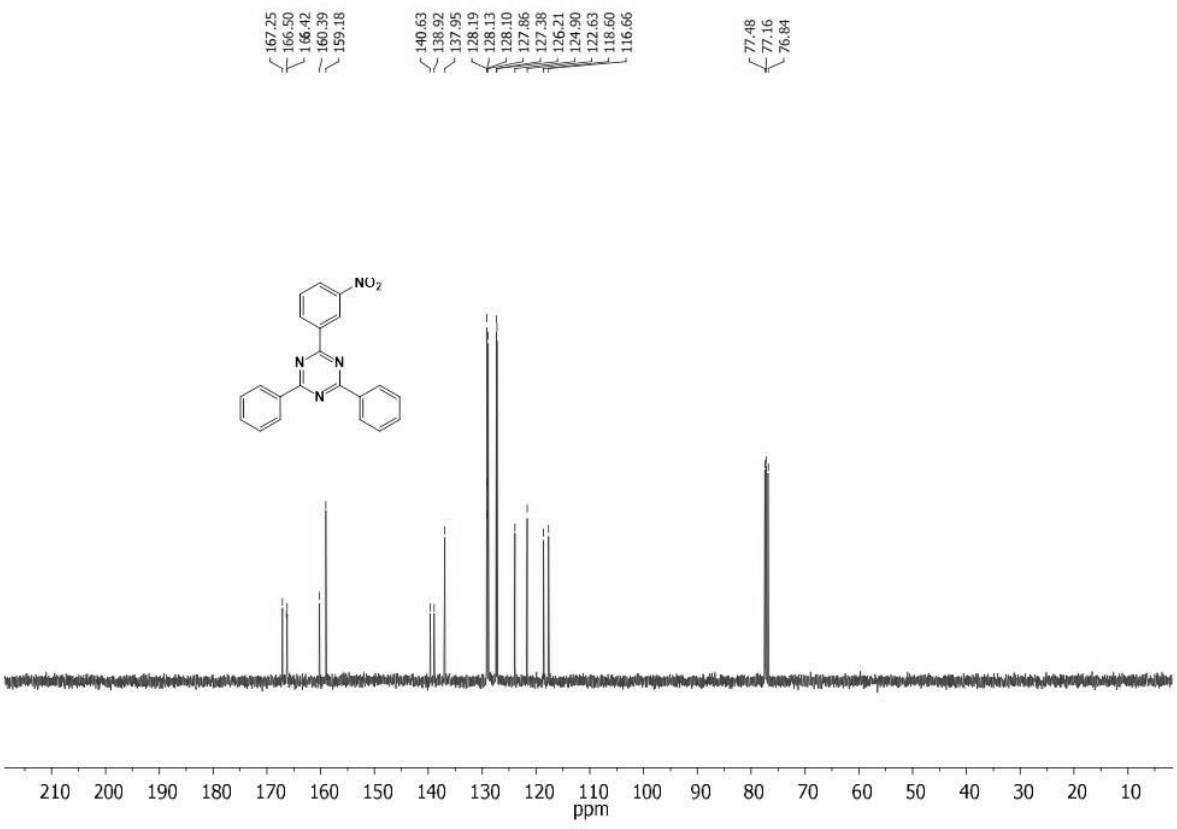
2-(3-chlorophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.15 (d, J = 8.6 Hz, 2H), 8.09 (d, J = 8.6 Hz, 2H), 7.88 (s, 2H), 7.76 (d, J = 6.9 Hz, 2H), 7.67 (d, J = 8.6 Hz, 2H), 7.63–7.47 (m, 4H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 156.6, 156.5, 150.8, 138.8, 138.4, 137.9, 135.5, 132.0, 129.4, 129.3, 129.1, 128.8, 128.5, 127.3, 123.8, 117.3, 117.2.


8.29
8.26
7.93
7.71
7.68
7.58
7.55
7.53
7.48
7.38
7.35
2.46
Me
N
N
N
2.00
2.01
2.00
4.04
2.05
2.03
3.08
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
ppm

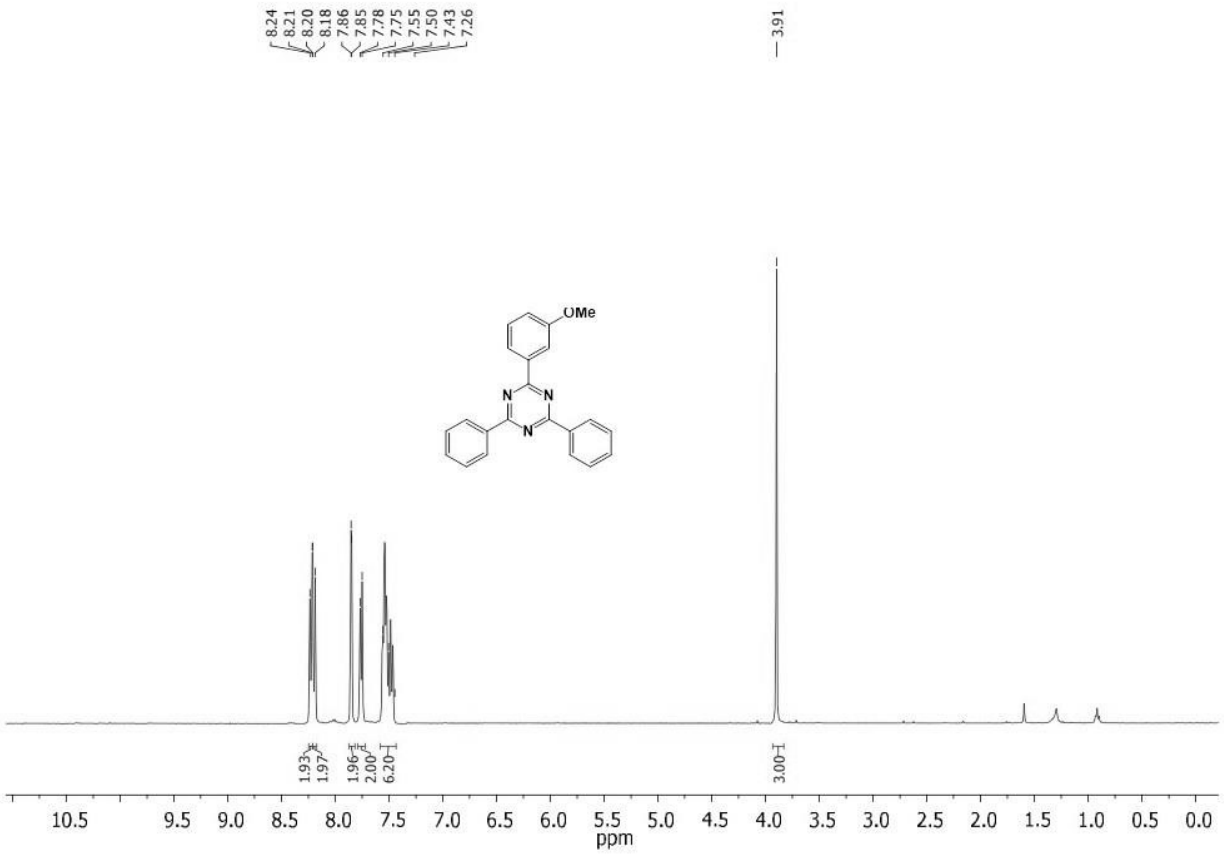


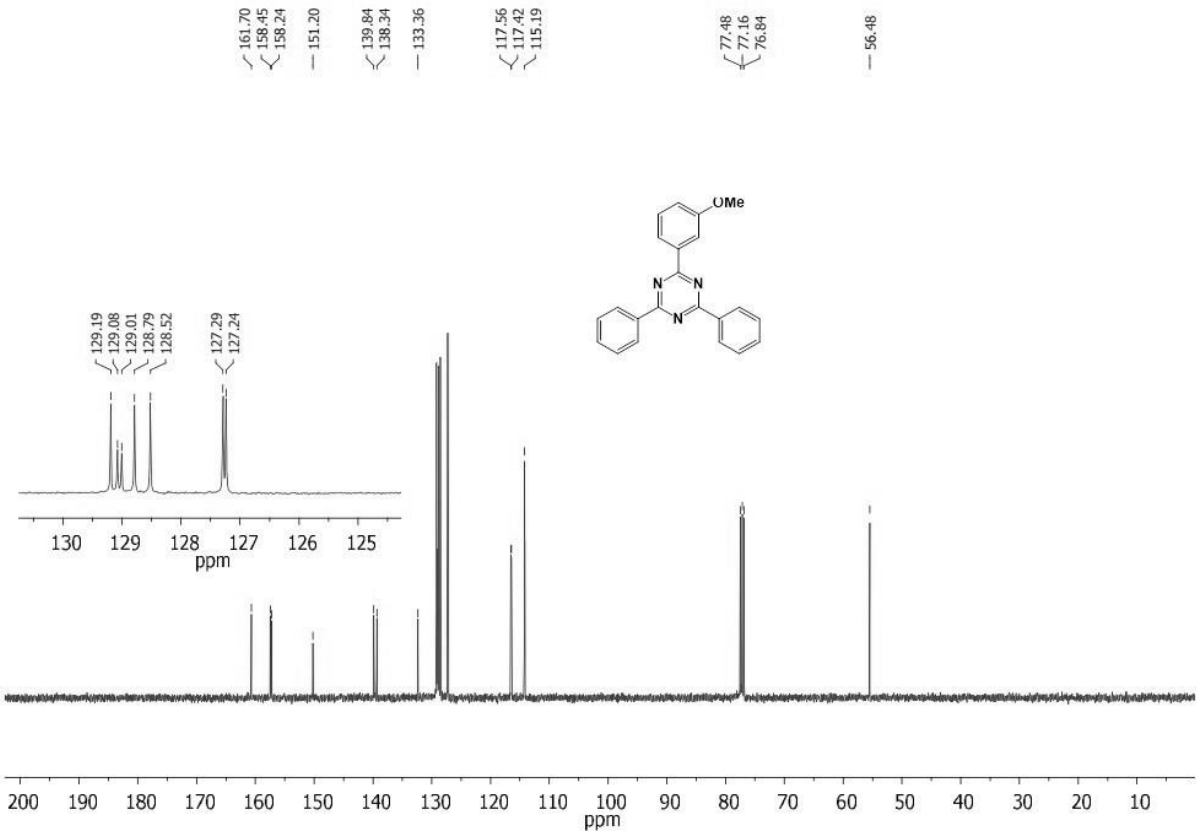
2-(3-methylphenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.29 (d, J = 7.5 Hz, 2H), 7.93 (s, 2H), 7.68 (d, J = 7.7 Hz, 2H), 7.58–7.53 (m, 4H), 7.48 (t, 2H), 7.38 (d, J = 7.7 Hz, 2H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 167.5, 160.1, 140.8, 140.1, 137.2, 129.9, 128.1, 127.8, 126.2, 126.1, 118.0, 22.3.


8.75
8.70
8.67
8.25
8.22
8.02
7.89
7.84
7.58
7.51
7.49
7.46
7.35
7.32
NO2
N
N
N
0.97
0.97
1.99
1.00
3.00
3.96
2.00
11.5
10.5
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
ppm

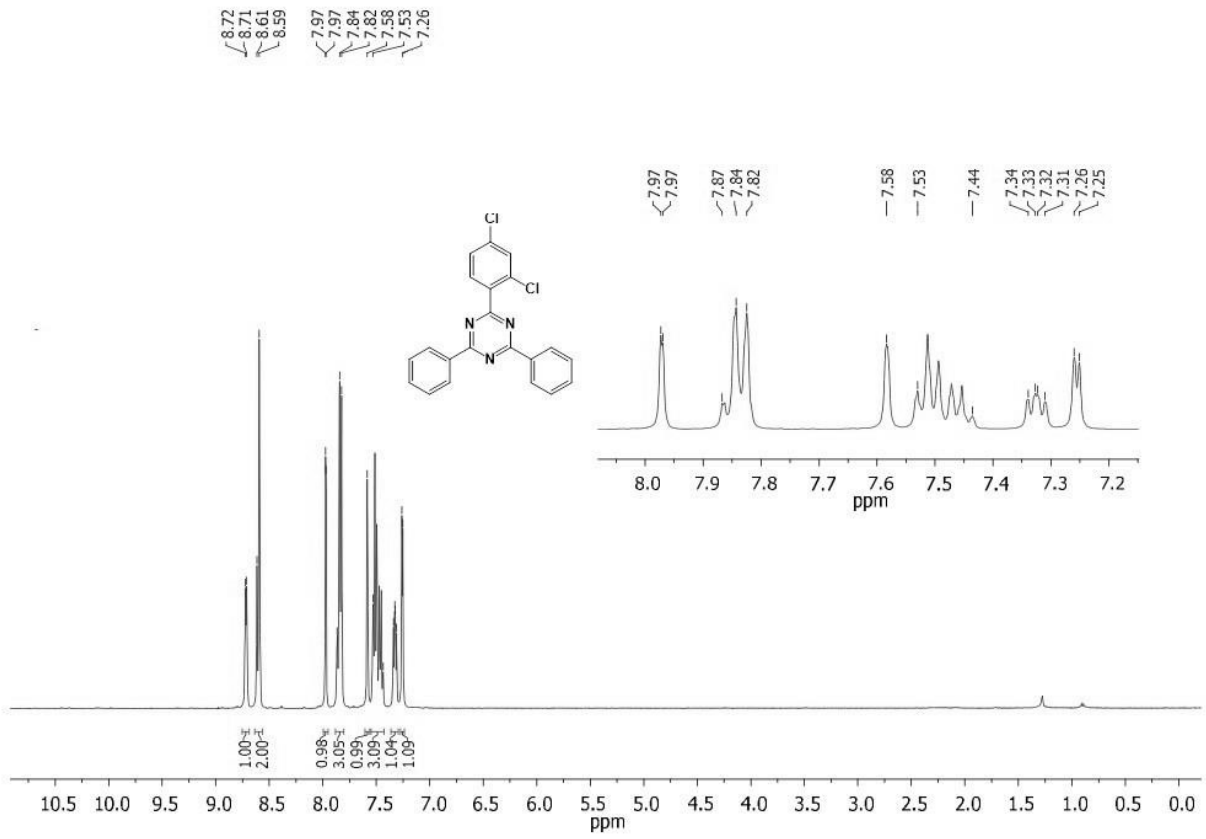

167.25
166.50
166.42
160.39
159.18
140.63
138.92
137.95
128.19
128.13
128.10
127.86
127.38
126.21
124.90
122.63
118.60
116.66
77.48
77.16
76.84
NO2
N
N
N
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

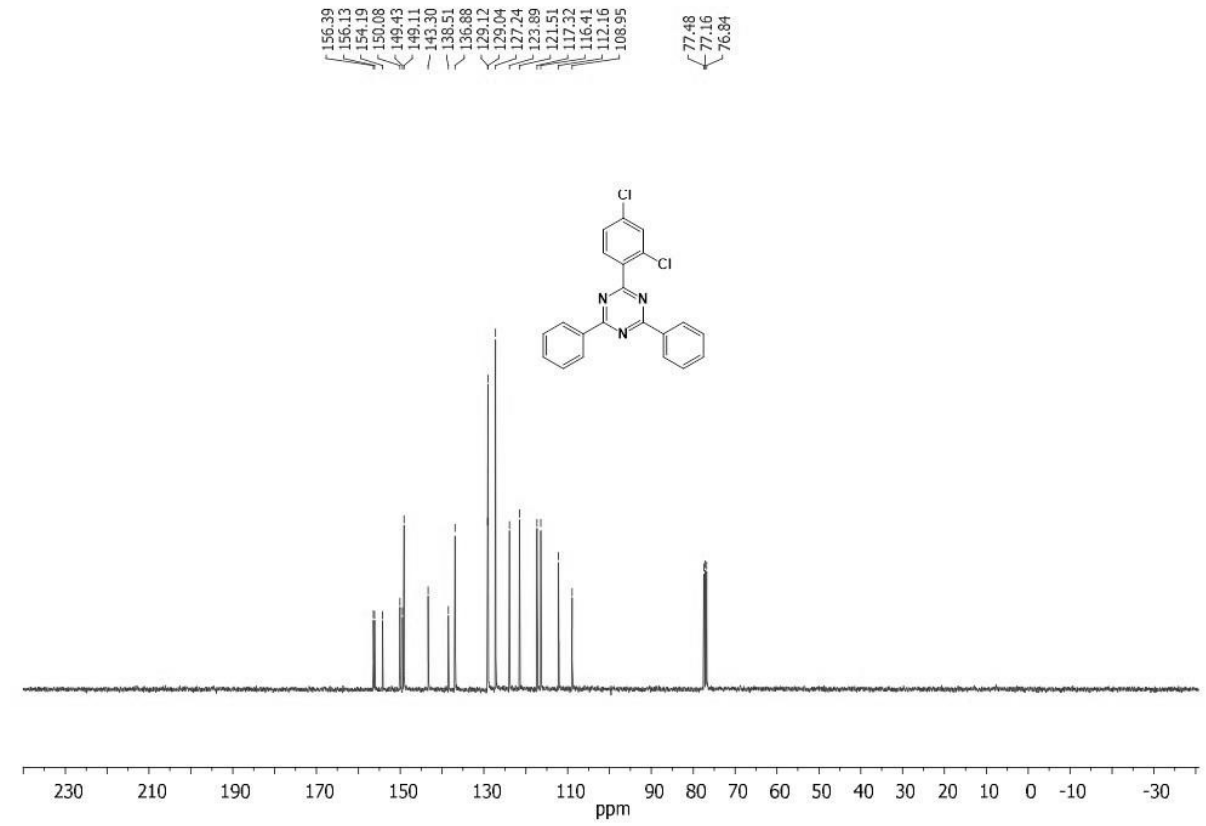
2-(3-nitrophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.75–8.70 (t, 1H), 8.68 (s, 1H), 8.25 (d, J = 7.3 Hz, 2H), 8.02 (s, 1H), 7.89–7.84 (m, 3H), 7.58–7.51 (m, 4H), 7.49–7.46 (m, 2H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 167.3, 166.5, 166.4, 160.4, 140.2, 140.0, 138.9, 137.0, 128.2, 128.1, 128, 127.9, 127.4, 126.2, 124.9, 122.6, 118.6, 116.7.



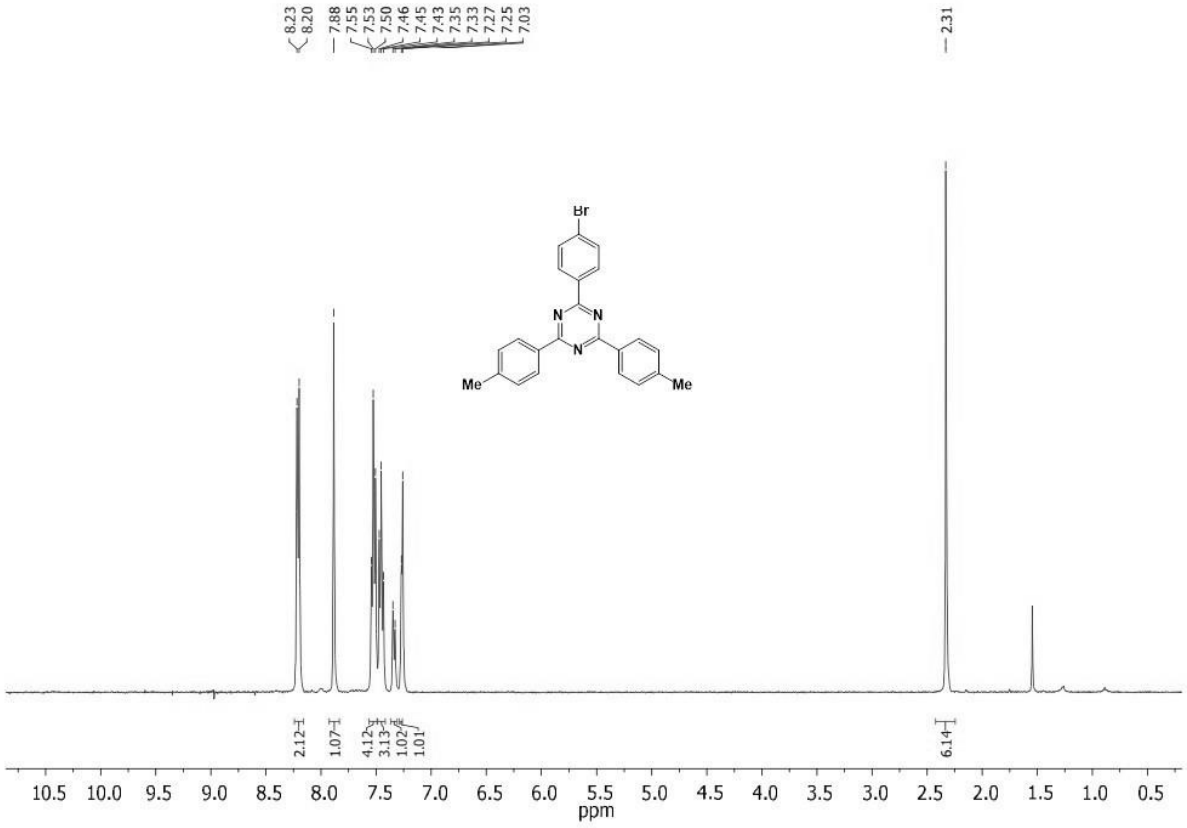


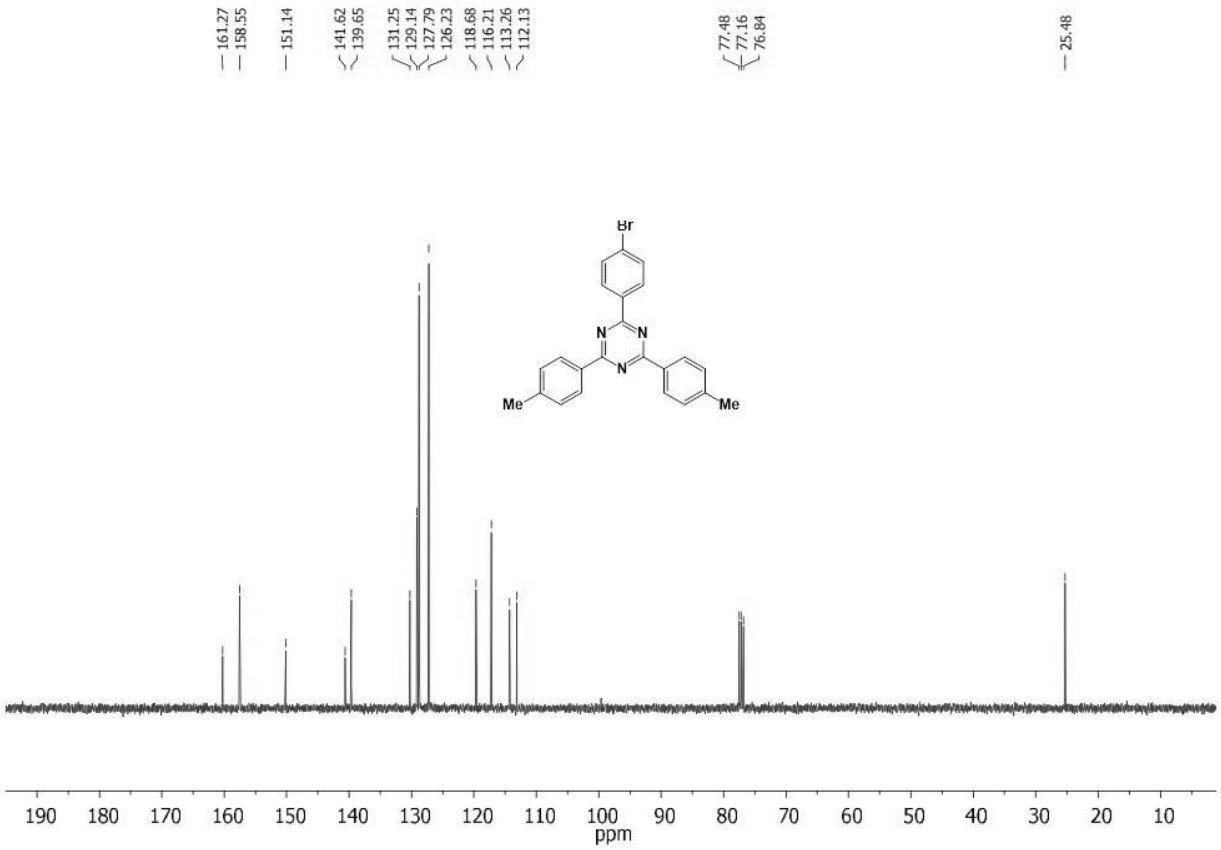
2-(3-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.24 (d, J = 7.8 Hz, 2H), 8.21 (d, J = 8.8 Hz, 2H), 7.86 (s, 1H), 7.85 (s, 1H), 7.78 (d, J = 7.2 Hz, 2H), 7.55–7.43 (m, 6H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 161.7, 158.5, 158.2, 151.2, 139.8, 138.3, 133.4, 129.2, 129.1, 129.0, 128.8, 128.5, 127.3, 127.2, 117.6, 117.4, 115.2, 56.5.


8.72
8.71
8.61
8.59
7.97
7.97
7.84
7.82
7.58
7.53
7.26
Cl
Cl
N
N
N
7.97
7.97
7.87
7.84
7.82
7.58
7.53
7.44
7.34
7.33
7.32
7.31
7.26
7.25
8.0 7.9 7.8 7.7 7.6 7.5 7.4 7.3 7.2
ppm
1.00
2.00
0.98
3.05
0.99
3.09
1.04
1.09
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
ppm

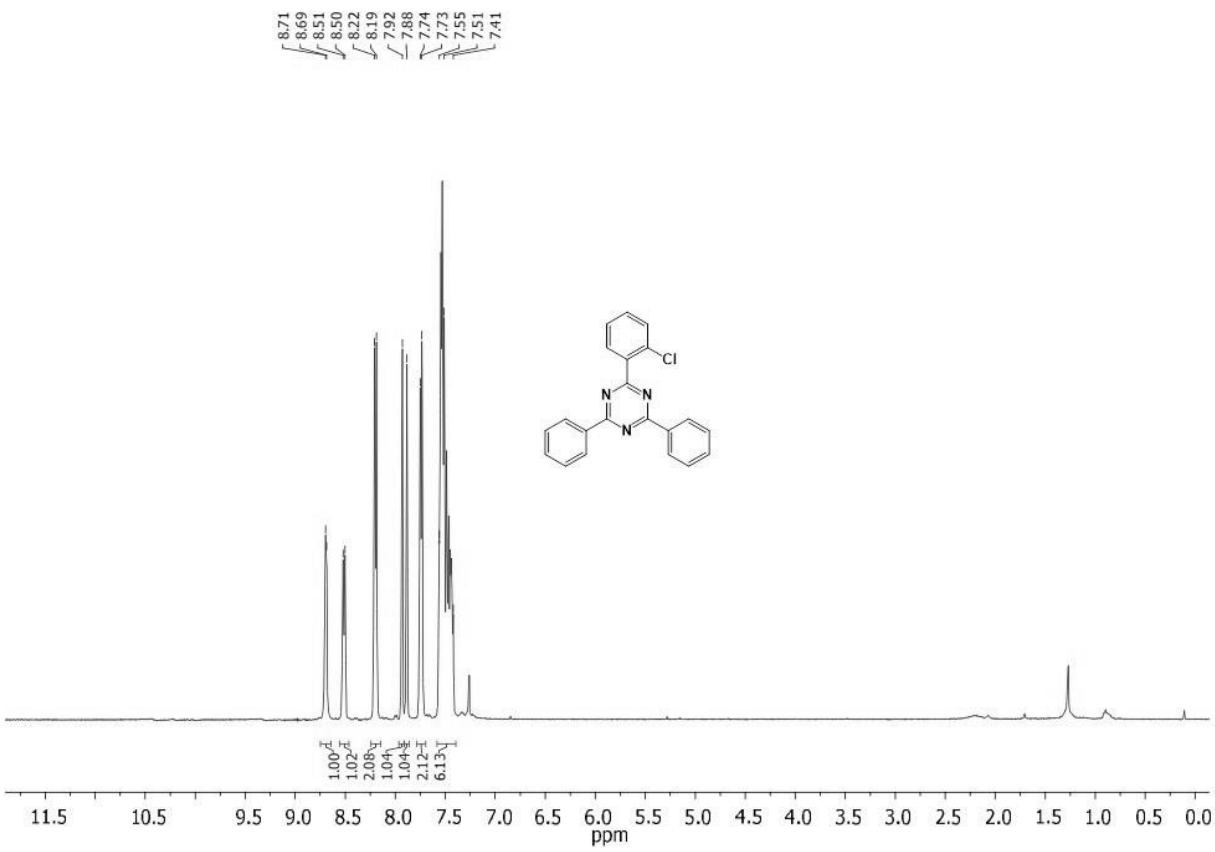

156.39
156.13
154.19
150.08
149.43
149.11
143.30
138.51
136.88
129.12
129.04
127.24
123.89
121.51
117.32
116.41
112.16
108.95
77.48
77.16
76.84
Cl
Cl
N
N
N
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10 -30
ppm

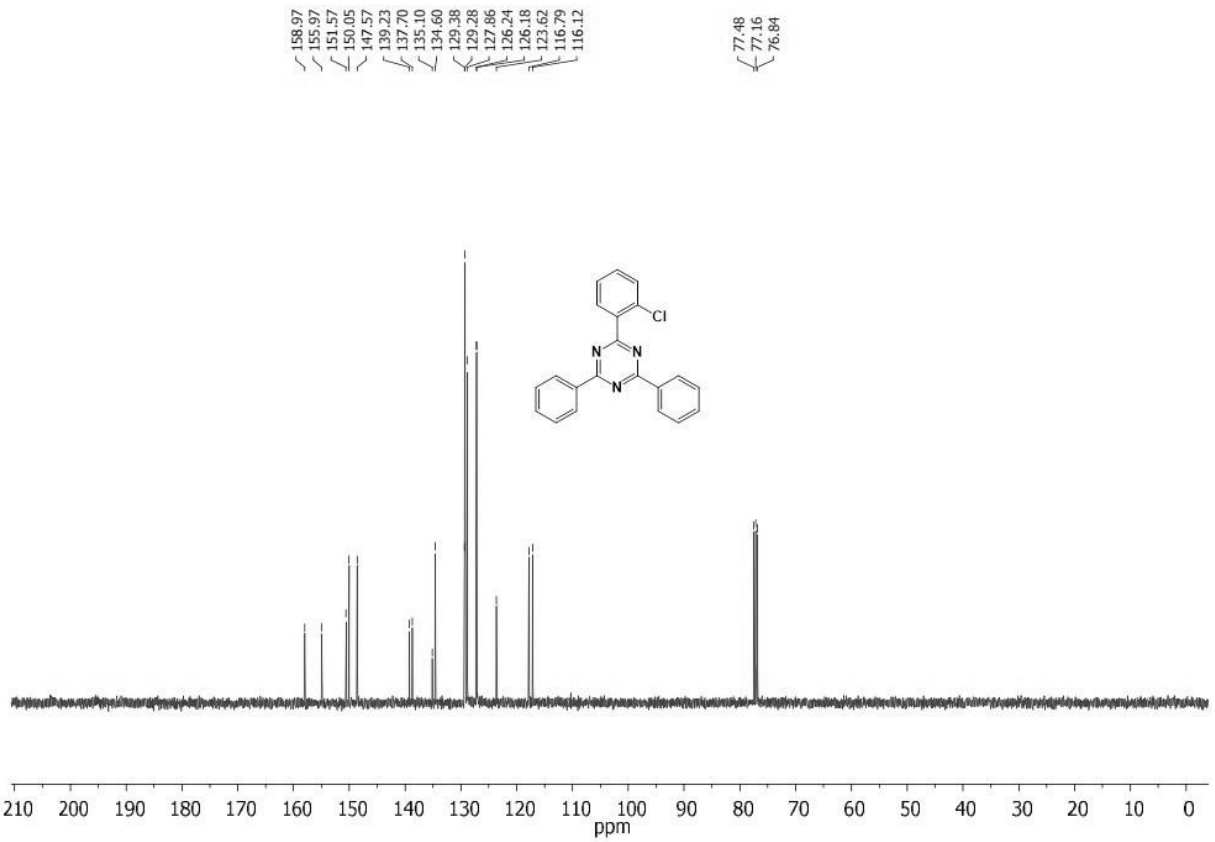
2-(2,4-dichlorophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.71 (d, J = 4.0 Hz, 1H), 8.61–8.58 (m, 2H), 7.97 (t, 1H), 7.87–7.82 (m, 3H), 7.58 (s, 1H), 7.53–7.43 (m, 3H), 7.32 (dd, J = 5.0 Hz, J = 6.5 Hz, 1H), 7.26 (d, J = 3.3 Hz, 1H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 156.4, 156.1, 154.3, 150.1, 149.4, 149.2, 143.3, 138.5, 136.8, 129.1, 129.0, 127.1, 123.9, 121.5, 117.3, 116.4, 112.2, 108.9.





2-(4-bromophenyl)-4,6-di-p-tolyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.22 (d, J = 7.4 Hz, 2H), 7.88 (s, 1H), 7.55–7.50 (m, 4H), 7.46–7.43 (m, 3H), 7.33 (d, J = 7.6 Hz, 1H), 7.27–7.25 (m, 1H), 13C{1H} NMR (100.6 MHz, CDCl3): δ = 161.3, 158.6, 151.1, 141.6, 139.7, 131.3, 129.1, 127.8, 126.2, 118.7, 116.2, 113.3, 112.1, 25.5.


8.71
8.69
8.51
8.50
8.22
8.19
7.92
7.88
7.74
7.73
7.55
7.51
7.41
Cl
N
N
N
1.00
1.02
2.08
1.04
1.04
2.12
6.13
11.5
10.5
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
ppm



2-(2-chlorophenyl)-4,6-diphenyl-1,3,5-triazine: 1H NMR (400.1 MHz, CDCl3): δ = 8.71 (d, J = 3.7 Hz, 1H), 8.51 (d, J = 7.9 Hz, 1H), 8.22 (d, J = 7.2 Hz, 2H), 7.92 (s, 1H), 7.88 (s, 1H), 7.73 (d, J = 6.9 Hz, 2H), 7.55–7.41 (m, 6H). 13C{1H} NMR (100.6 MHz, CDCl3): δ = 159.0, 156.0, 151.6, 150.1, 147.6, 139.2, 137.7, 135.1, 134.6, 129.4, 129.3, 127.9, 126.2, 126.2, 123.6, 116.8, 116.1.