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Supporting Information

Polythene glycol (PEG) as a Reusable Solvent System for The Synthesis of 1,3,5-triazines *via* Aerobic Oxidative Tandem Cyclization of Benzylamines and *N*-substituted Benzylamines with Amidines under Transition Metal-Free Conditions

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General Information

All chemicals and solvents were purchased with high purities and used without further purification. The progress of the reaction was monitored by gas chromatography (GC) Perkin Elmer Clarus 400. GC equipped with a flame ionization detector (FID) with a capillary column (30 m × 0.25 mm × 0.25 µm) and thin layer chromatography (using Merck silica gel 60 F-254 plates. The products were visualized with a 254 nm UV lamp. GC-MS-QP 2010 instrument (Rtx-17, 30 m × 25 mm ID, film thickness (df = 0.25 µm) (column flow 2 mL min^{-1}, 80 °C to 240 °C at 10 °C min^{-1} rise) was used for the mass analysis of the products. HRMS was recorded on a commercial apparatus (ESI Source, ion trap). Products were purified by column chromatography on 100-200 mesh silica gel. The ^{1}H NMR spectras were recorded on 400 MHz spectrometer in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard. The ^{13}C NMR spectras were recorded on 100 MHz in $CDCl_3$. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane as an internal standard. Coupling constant (*J*) values were reported in hertz (Hz). Splitting patterns of proton are described as s (singlet), d (doublet), dd (doublet of doublet), t (triplet) and m (multiplet). The products were confirmed by GCMS, HRMS, ^{1}H and ^{13}C NMR spectroscopic analysis.

General procedure for synthesis of 1,3,5-triazines (3)

To a 25 mL round bottom flask containing 2.5 mL of PEG-600, benzylamine (1, 0.5 mmol), amidine hydrochloride (1.0 mmol) and Cs_2CO_3 (1.0 mmol) were added under aerobic balloon condition, and was stirred at room temperature for 10 min, then heated at 130 ^{o}C for 3 h (with N,N-di substituted benzylamine for 4 h). After completion of the reaction, the mixture was cooled to room temperature. The product was extracted with ether by using (10 x 3 mL), the extract dried and concentrated under reduced pressure and resulting crude product. The product was purified by silica gel column chromatography by using petroleum ether (PE)/ethyl acetate (EA).

Procedure for recyclability of PEG

To a 25 mL round bottom flask containing 2.5 mL of PEG-600, benzylamine (1, 0.5 mmol), amidine hydrochloride (1.0 mmol) and Cs_2CO_3 (1.0 mmol) were added under aerobic balloon condition, and was stirred at room temperature for 10 min, then heated at 130 ^{o}C for 3 h. After completion of the reaction, the mixture was cooled to room temperature. The product was

extracted with ether by using (10 x 3 mL) and the PEG was recovered as it is immiscible with ether. This recovered PEG was then reused for the next cycle. It is important to note that in every cycle fresh base was added.

2,4,6-triphenyl-1,3,5-triazine (3a)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 8.0, 1.5 Hz, 6H), 7.69 – 7.50 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 171.61, 136.19, 132.49, 128.93, 128.61; GCMS (EI, 70 eV): m/z (%): 309 (31, M^+), 103 (89), 76 (14), 32 (100).

2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (3c)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 – 8.62 (m, 6H), 7.64 – 7.49 (m, 6H), 7.04 (d, *J* = 8.9 Hz, 2H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.24, 163.27, 136.36, 132.32, 130.83, 128.96 – 128.45, 113.91, 55.44.

4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (3d)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (d, *J* = 8.7 Hz, 2H), 8.74 (dd, *J* = 8.3, 1.4 Hz, 4H), 7.91 – 7.81 (m, 2H), 7.63 – 7.52 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.97, 169.97, 140.32, 135.64, 132.92, 132.38, 129.31, 129.00, 128.74, 118.54, 115.57; HRMS (ESI-ion trap) m/z calcd [$(M+H)^+$] 335.1297, found 335.1299.

2-(3-nitrophenyl)-4,6-diphenyl-1,3,5-triazine (3f)

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 1H), 9.03 (d, *J* = 7.8 Hz, 1H), 8.71 (d, *J* = 7.1 Hz, 4H), 8.41 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.71 (t, *J* = 7.9 Hz, 1H), 7.59 (m, *J* = 22.9, 7.1 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.91, 169.50, 148.67, 138.04, 135.50, 134.48, 132.93, 129.62, 129.01, 128.72, 126.75, 123.74.

2-(3-chlorophenyl)-4,6-diphenyl-1,3,5-triazine (3g)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.2, 1.5 Hz, 5H), 8.65 (dd, *J* = 7.7, 1.2 Hz, 1H), 7.63 – 7.47 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.75, 170.45, 138.07, 135.89, 134.79, 132.69, 132.38, 129.88, 128.92, 128.88, 128.67, 127.03.

2,4-di-phenyl-6-(pyridin-3-yl)-1,3,5-triazine (3j)

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.91 (s, 1H), 8.96 (d, *J* = 7.9 Hz, 1H), 8.87 – 8.58 (m, 5H), 7.69 – 7.47 (m, 7H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.74, 170.15, 152.84, 150.50, 136.19, 135.73, 132.79, 131.83, 128.97, 128.69, 123.47.

2-phenyl-4,6-di-p-tolyl-1,3,5-triazine (3l)

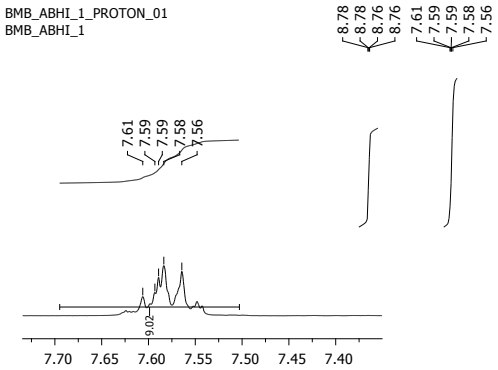
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 8.0, 1.6 Hz, 2H), 8.64 (d, *J* = 8.2 Hz, 4H), 7.60 – 7.52 (m, 3H), 7.35 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.45, 171.35, 142.94, 136.43, 133.61, 132.26, 129.33, 128.90, 128.88, 128.53, 21.71.

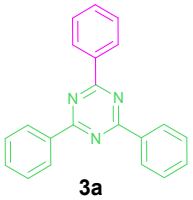
2,4-bis(4-bromophenyl)-6-(4-methoxyphenyl)-1,3,5-triazine (3o)

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 – 8.31 (m, 6H), 7.69 – 7.49 (m, 4H), 7.03 (dd, *J* = 7.8, 4.3 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.39, 165.04, 136.35, 132.32, 131.82, 130.86, 130.35, 128.85, 128.55, 113.94, 55.47.

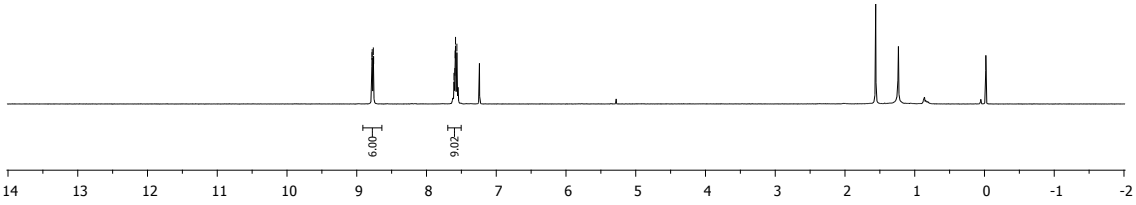
^{1}H NMR and ^{13}C NMR spectra of obtained compounds

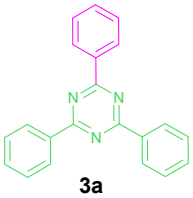
^{1}H NMR and ^{13}C NMR of 2,4,6-triphenyl-1,3,5-triazine (3a)



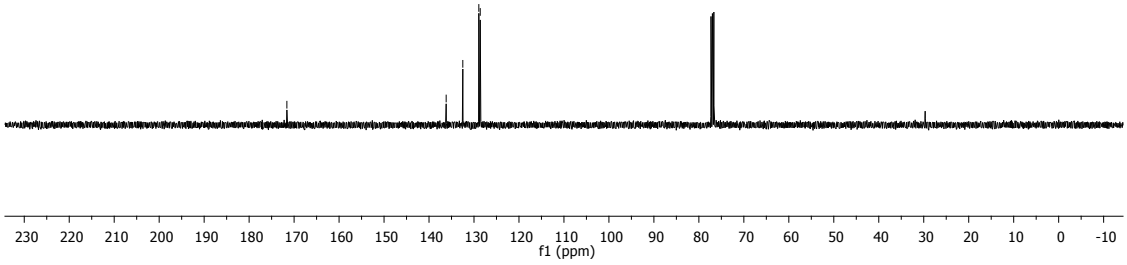


3a

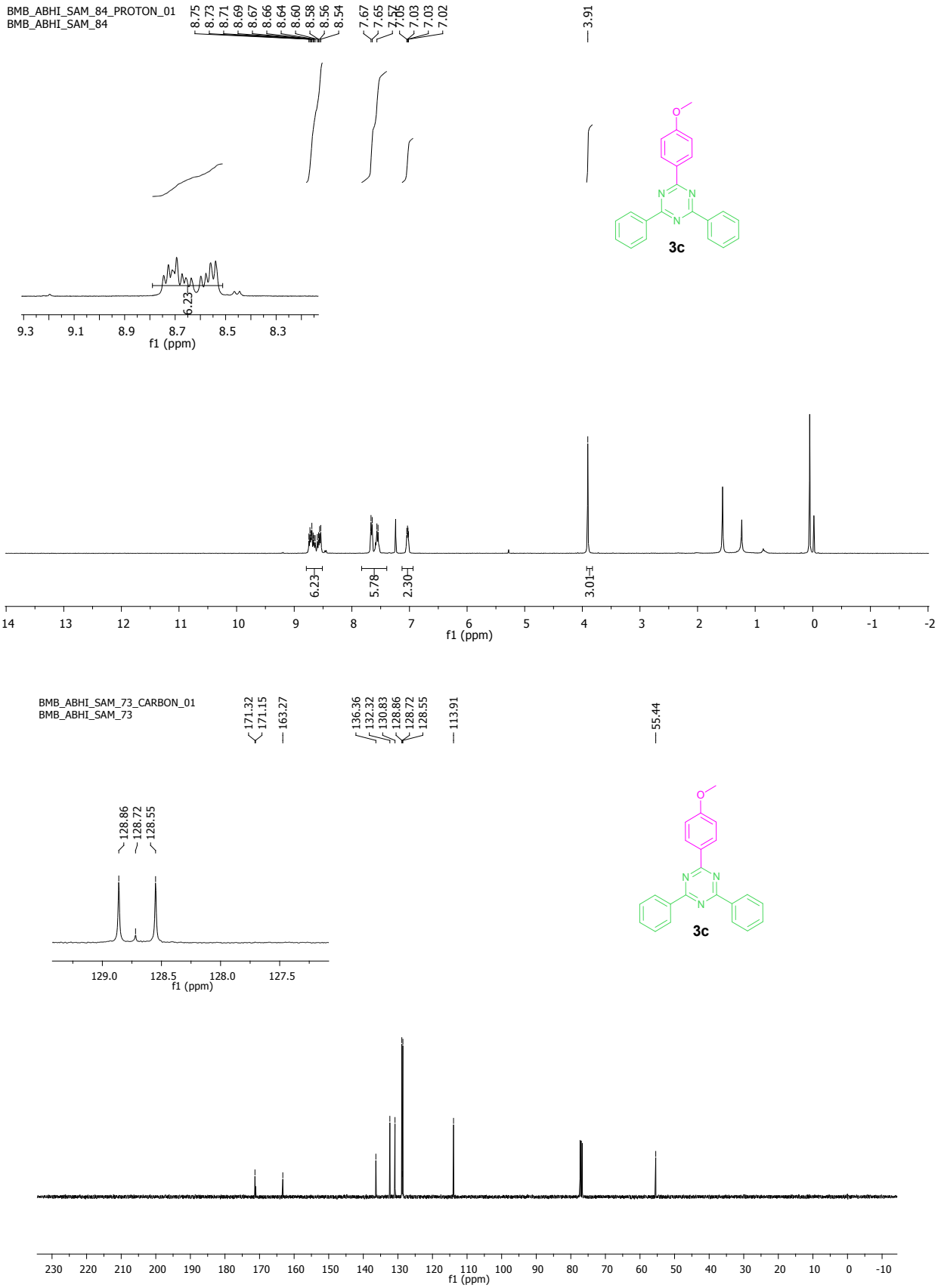




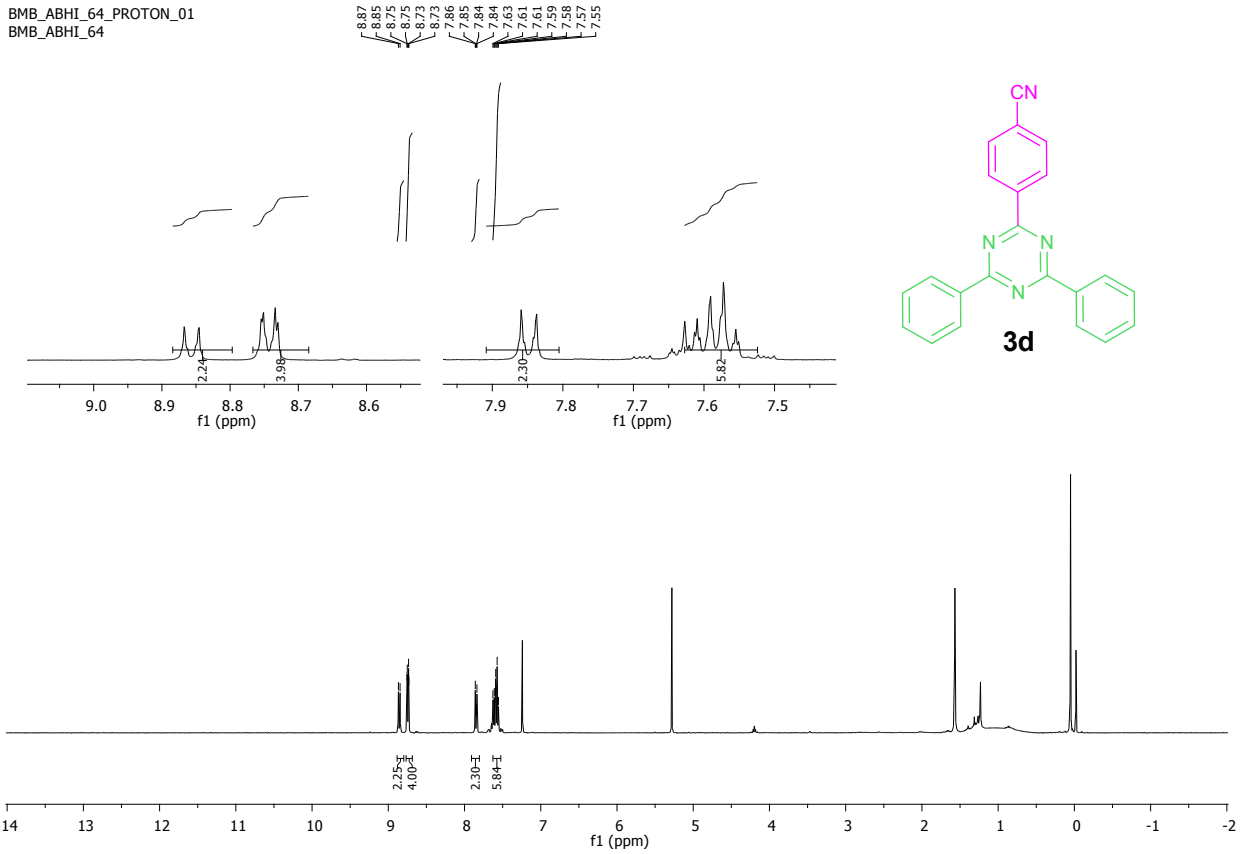
3a

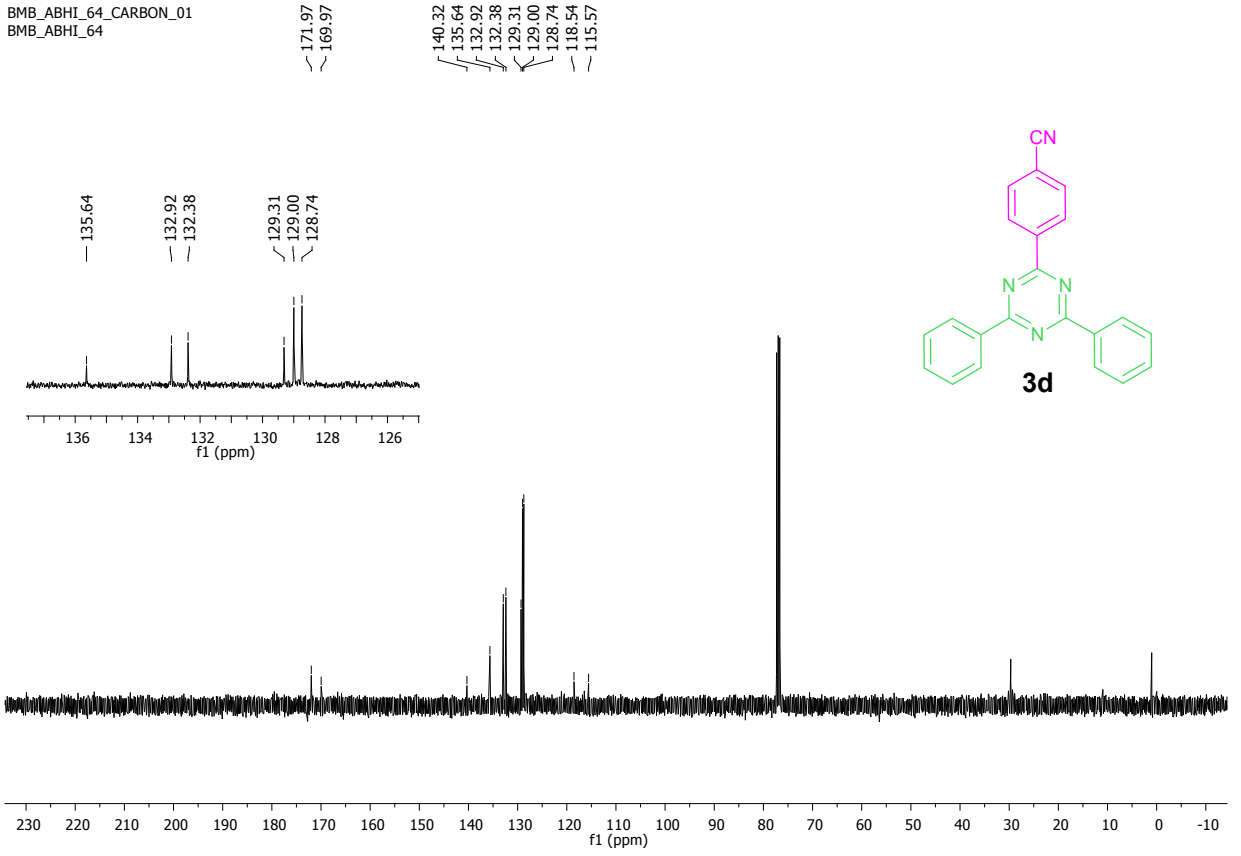


^{1}H NMR and ^{13}C NMR of 2-(4-methoxyphenyl)-4,6-diphenyl-1,3,5-triazine (3c)

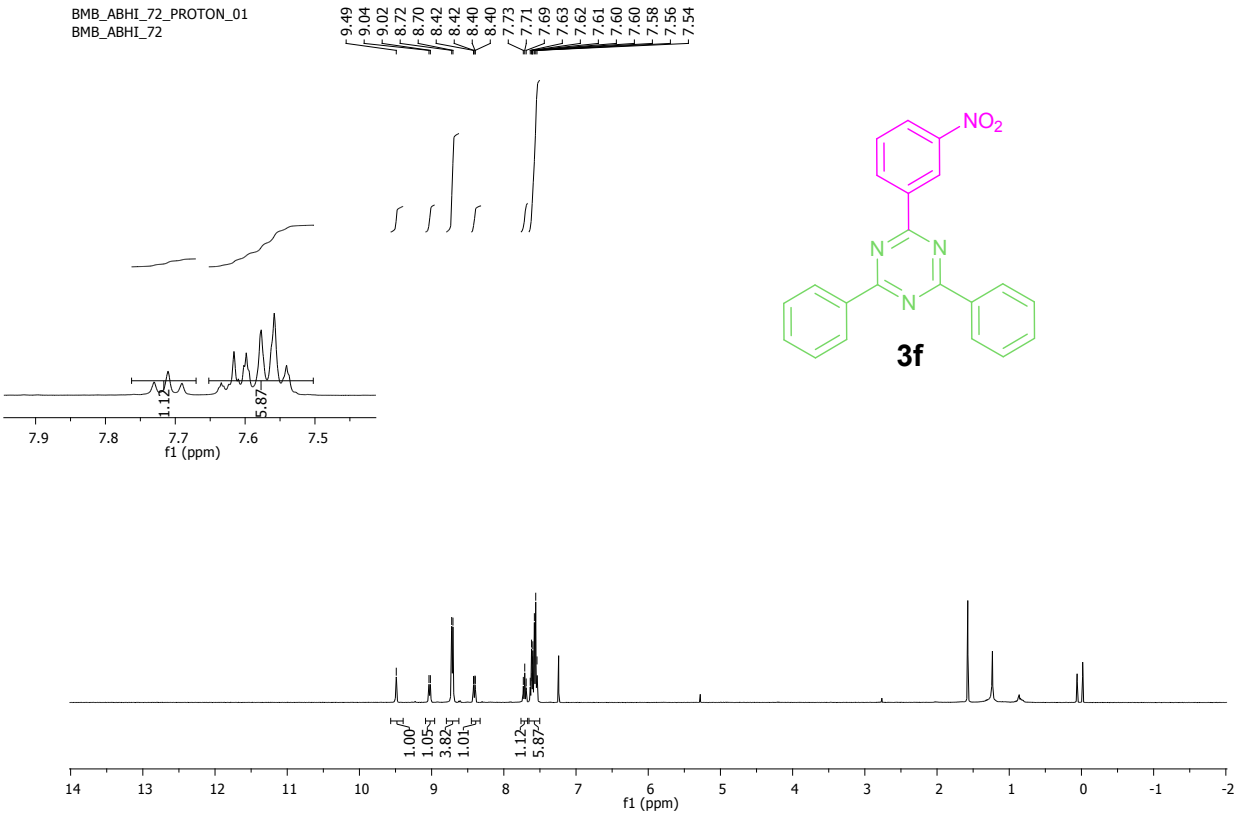


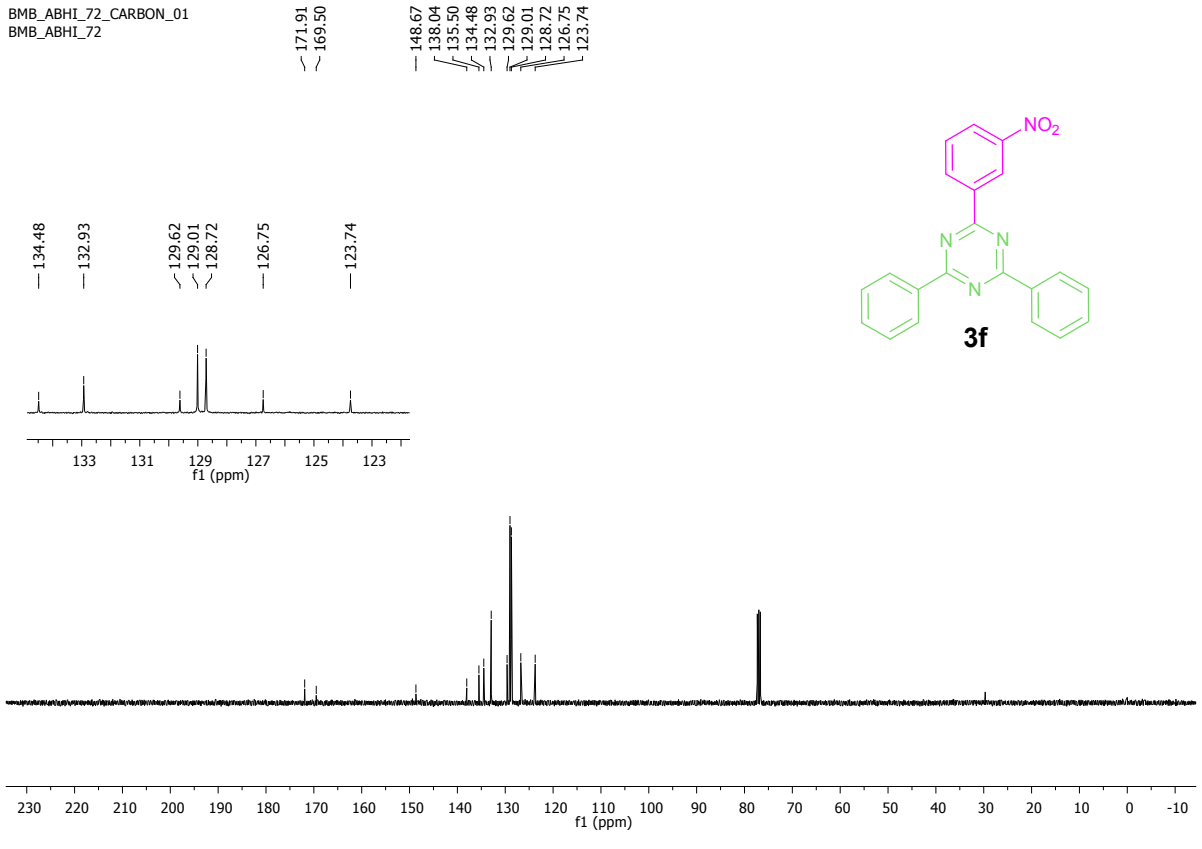
^{1}H NMR and ^{13}C NMR of 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (3d)



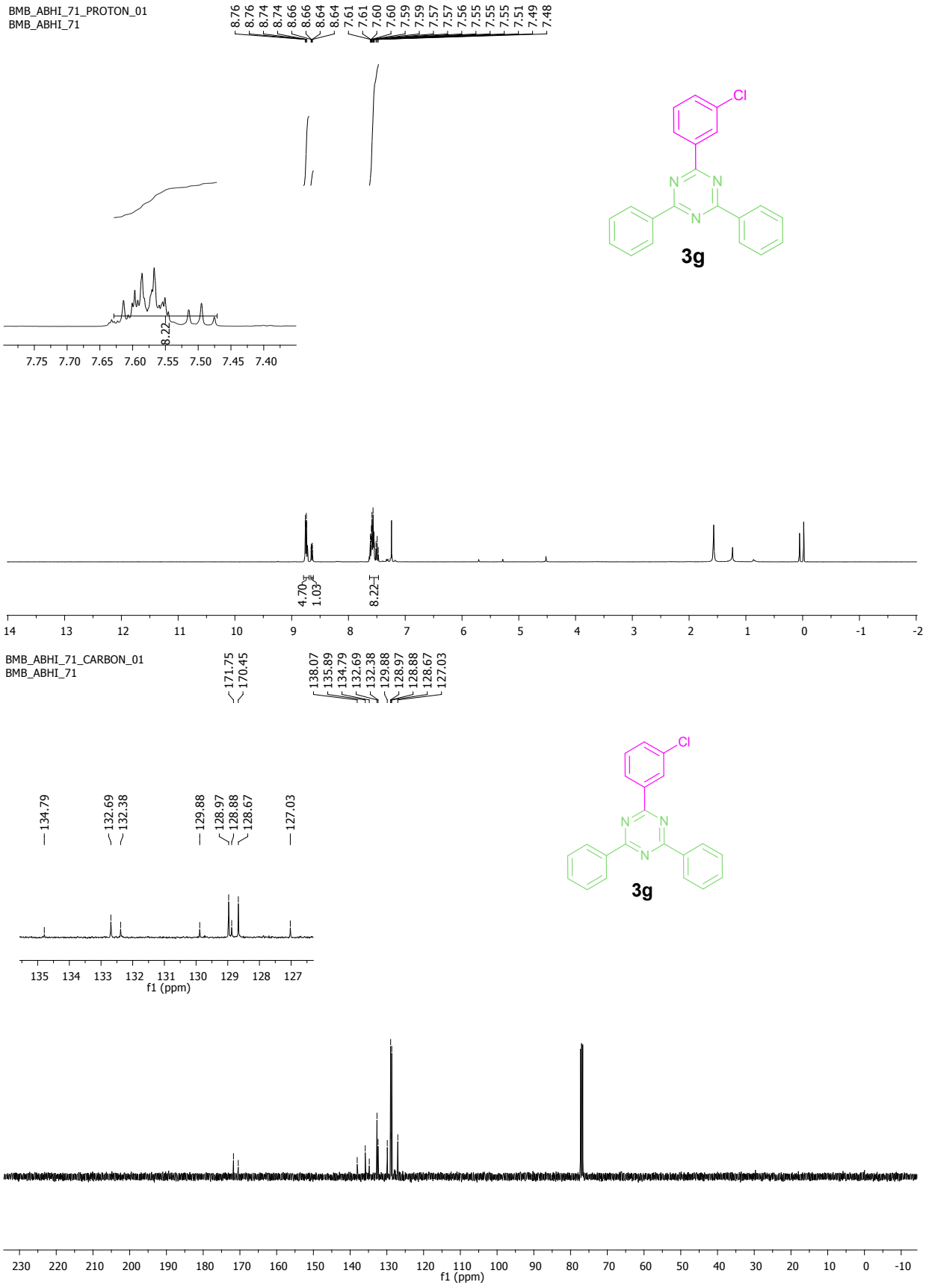


^{1}H NMR and ^{13}C NMR of 2-(3-nitrophenyl)-4,6-diphenyl-1,3,5-triazine (3f)

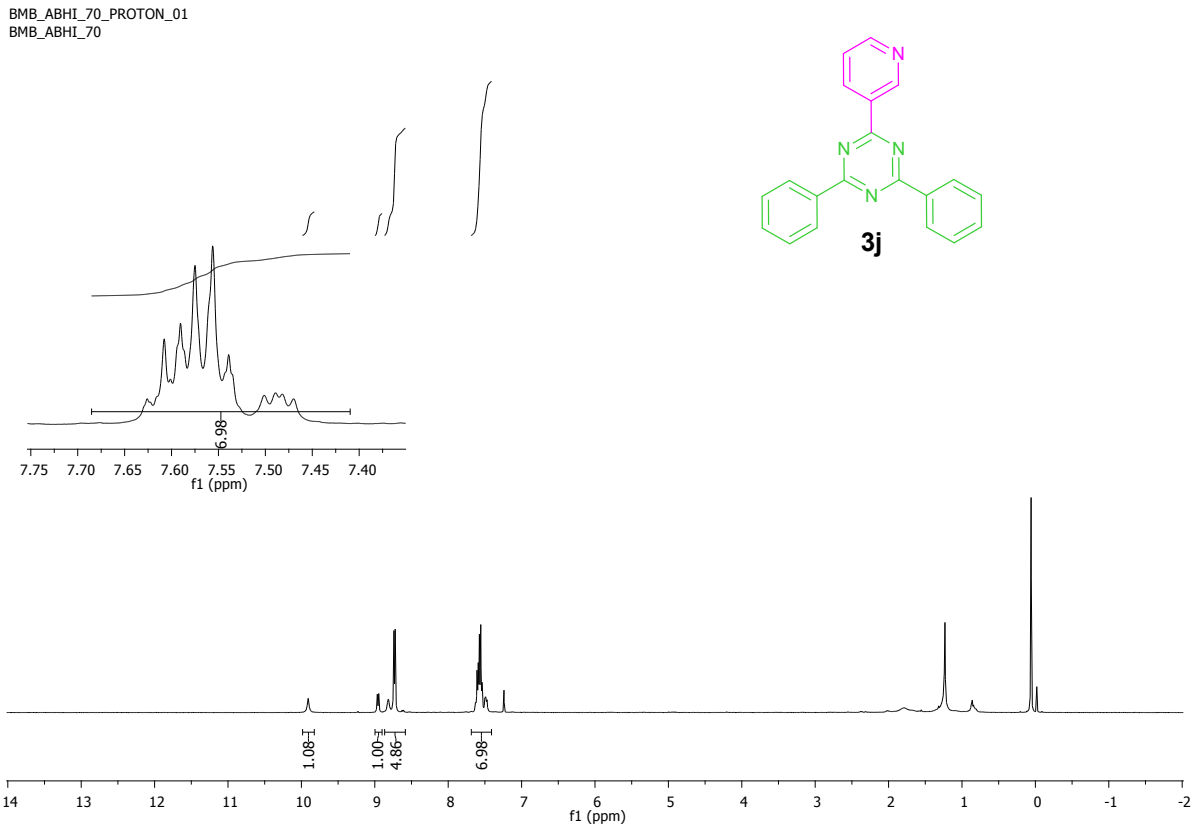


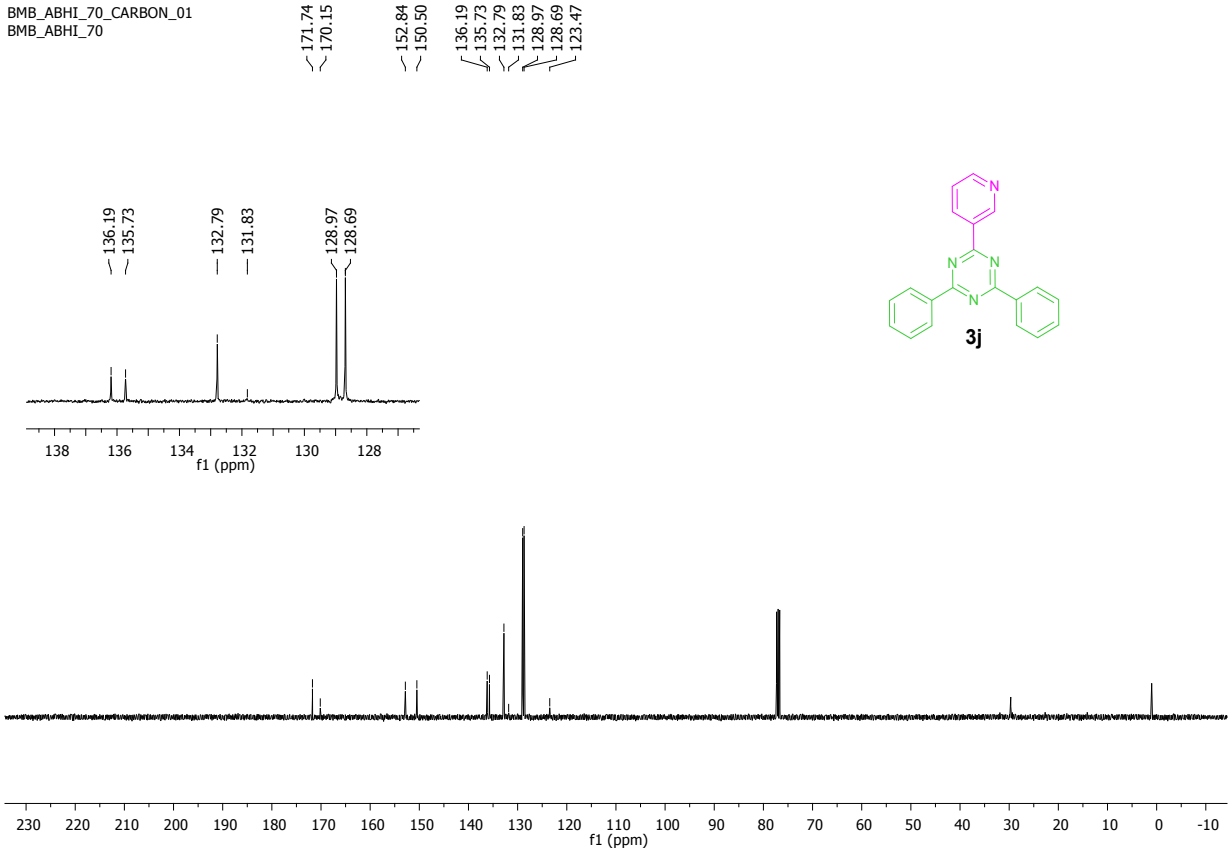


^{1}H NMR and ^{13}C NMR of 2-(3-chlorophenyl)-4,6-diphenyl-1,3,5-triazine (3g)

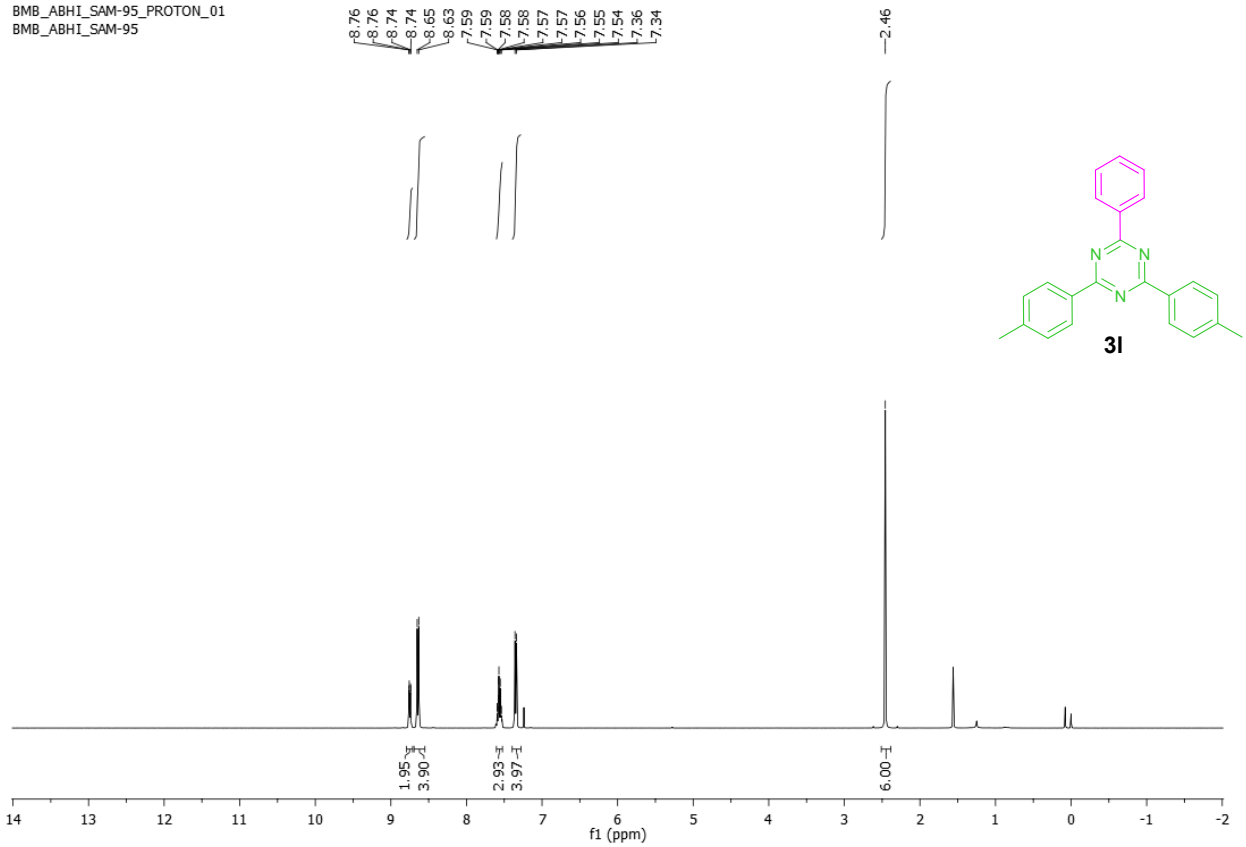


^{1}H NMR and ^{13}C NMR of 2,4-di-phenyl-6-(pyridin-3-yl)-1,3,5-triazine (3j)

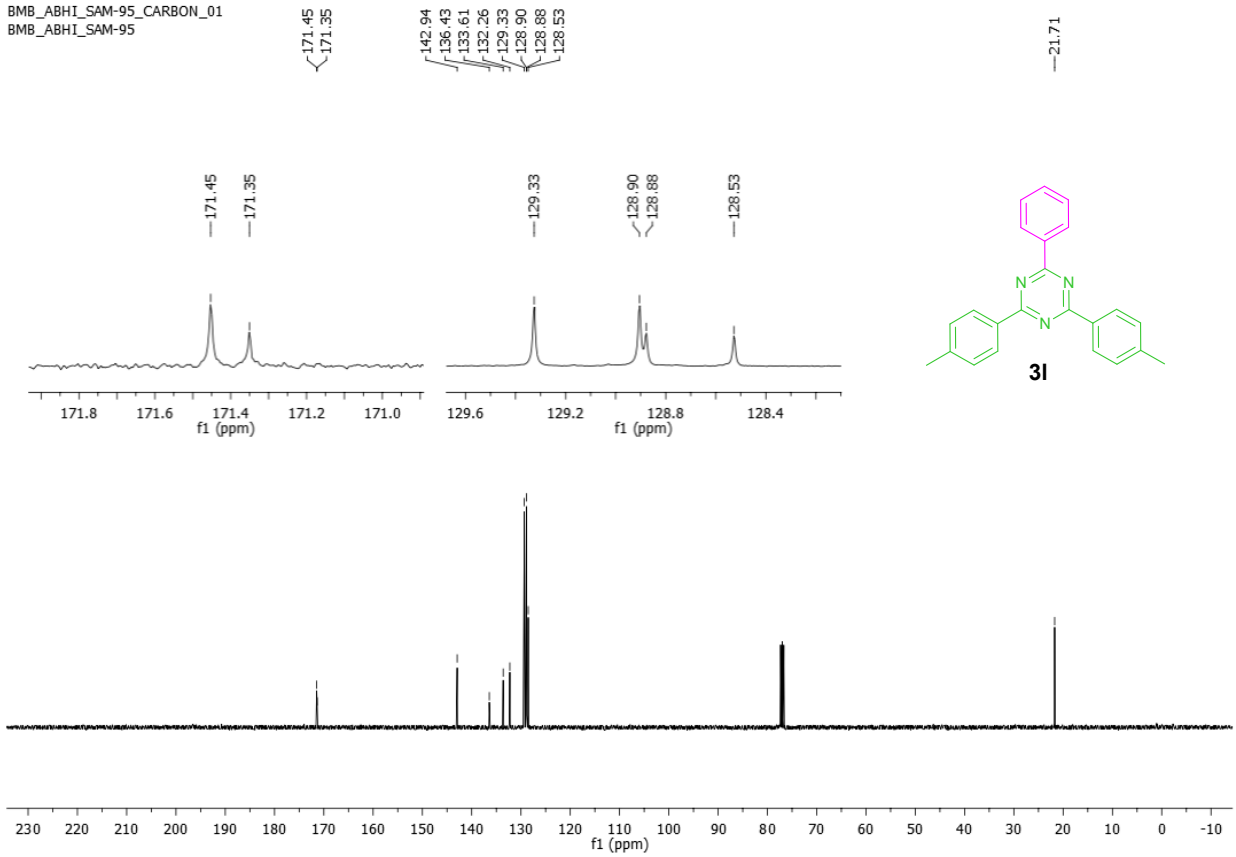




^{1}H NMR and ^{13}C NMR of 2-phenyl-4,6-di-p-tolyl-1,3,5-triazine (3l)

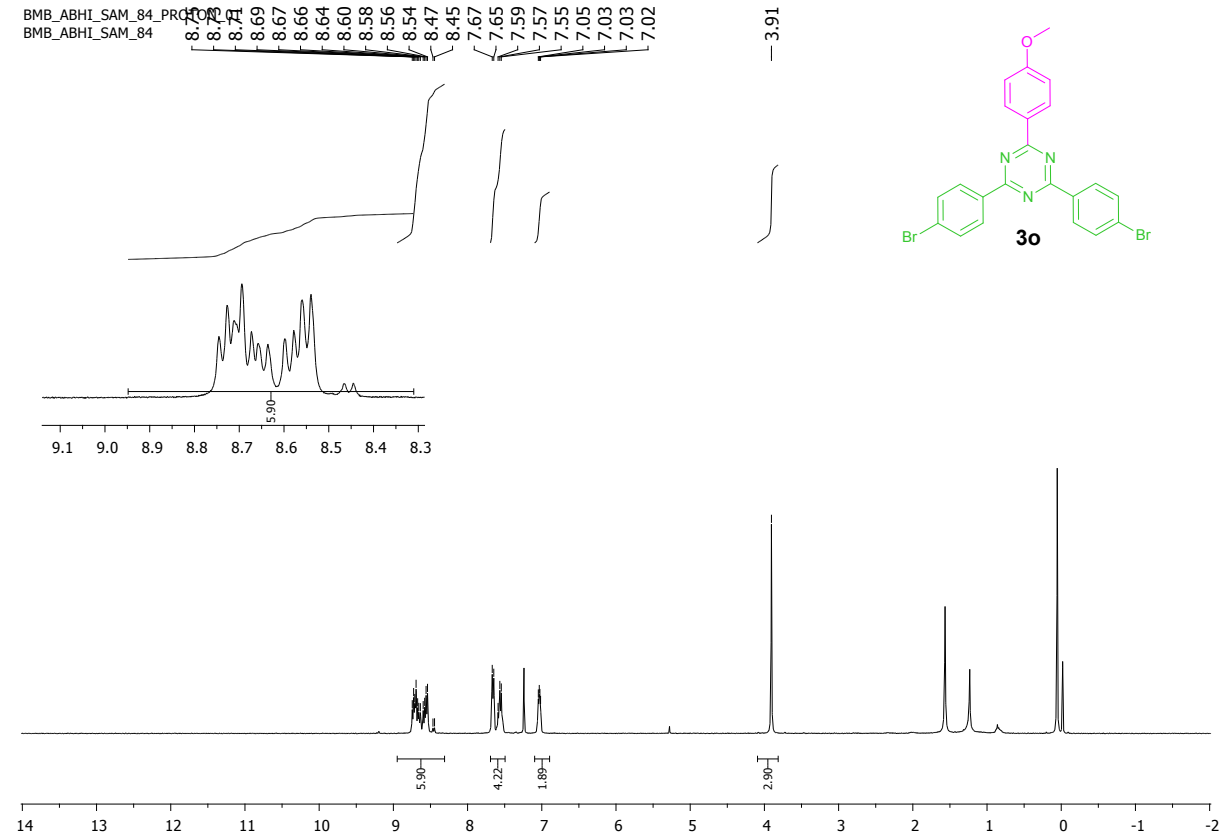


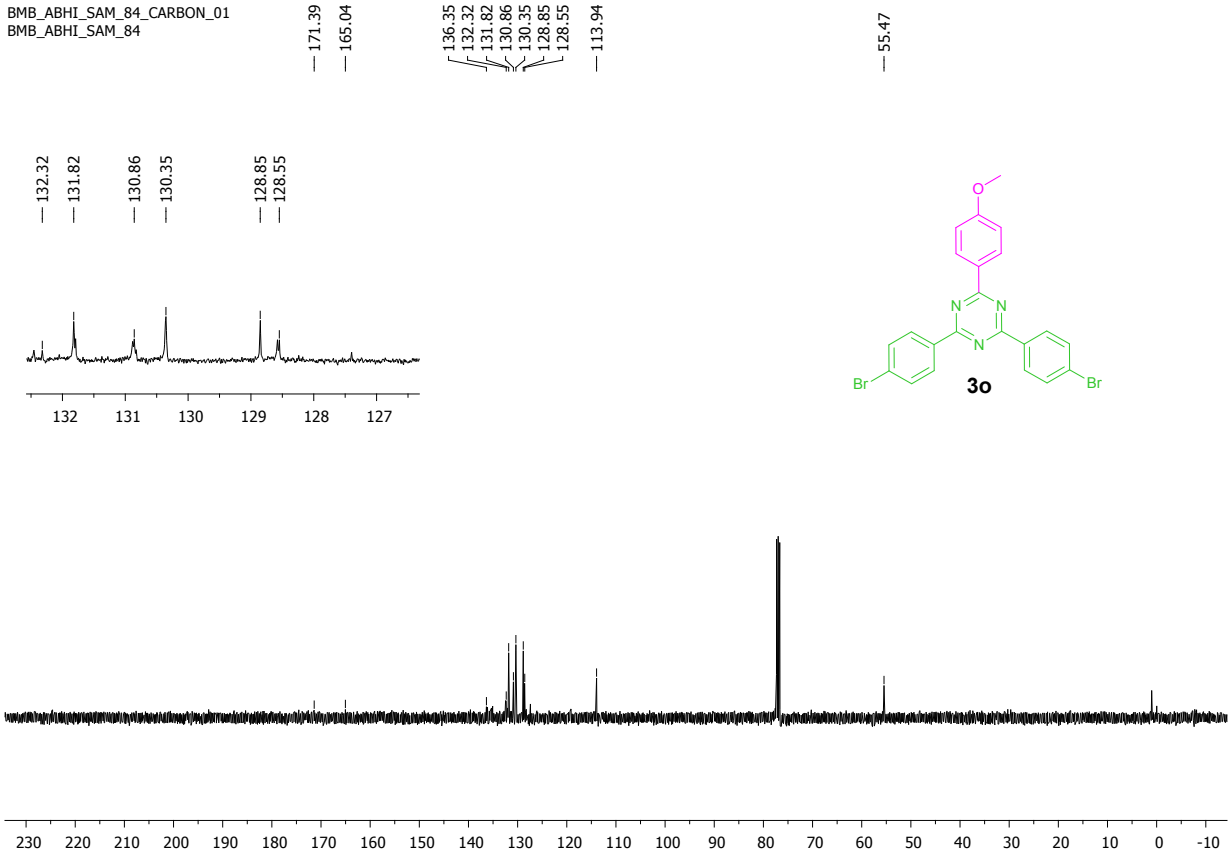
3l



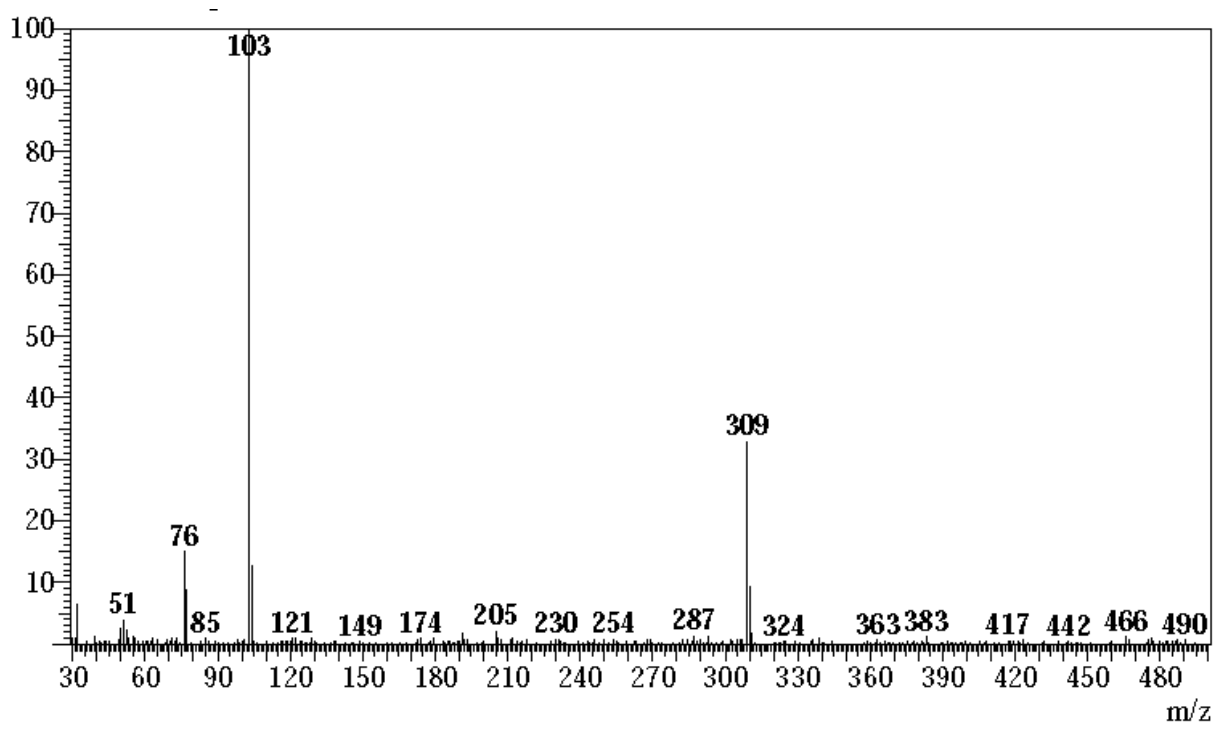
3l

^{1}H NMR and ^{13}C NMR of 2,4-bis(4-bromophenyl)-6-(4-methoxyphenyl)-1,3,5-triazine (3o)





GCMS of 2,4,6-triphenyl-1,3,5-triazine (3a)



HRMS spectra of 4-(4,6-diphenyl-1,3,5-triazin-2-yl)benzonitrile (3d)