Supporting Information

NIS-Catalyzed Oxidative Cyclization of Alcohols with Amidines: A Simple and Efficient, Transition-Metal Free Method For The Synthesis of 1,3,5-triazines

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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.

It is important to note that these compounds could only slightly dissolved in the best chosen solvent $CDCl_3$.We have tested different solvents but these compounds were having very poor solubility. It is unavoidable to show the peaks of water (around 1.6 ppm), petroleum ether around 1.2 and 0.8 ppm in ^{1}H NMR and at around 29 ppm in ^{13}C NMR spectrum. This could be because of the low sample concentration in $CDCl_3$.

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

To a schlenk tube containing mixture of benzyl alcohol 1 (0.5 mmol) and amidine hydrochloride 2 (1 mmol) dissolved in DMSO (2 mL), Cs_2CO_3 (1.0 mmol) was added and stirred at room temperature for 5 min. Then NIS (10 mol%) was added and heated at 100 °C for 16 h. After completion of the reaction, the reaction mixture was cooled to room temperature. The reaction mixture was diluted with 5 mL of water and the product was extracted with ethyl acetate (10 × 3 mL). The product was purified by silica gel column chromatography by using petroleum ether (PE)/ethyl acetate (EA).

2,4-diphenyl-6-(p-tolyl)-1,3,5-triazine (3ba)[2]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.80 – 8.70 (m, 4H), 8.65 (d, *J* = 8.2 Hz, 2H), 7.64 – 7.51 (m, 6H), 7.36 (d, *J* = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.59, 171.48, 143.08, 136.32, 133.50, 132.37, 129.36, 128.93, 128.56, 21.72.

2-(4-nitrophenyl)-4,6-diphenyl-1,3,5-triazine (3ea)[1,2]

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 8.9 Hz, 2H), 8.75 (dd, *J* = 8.2, 1.3 Hz, 3H), 8.63 (d, *J* = 6.9 Hz, 1H), 8.39 (d, *J* = 8.9 Hz, 2H), 7.57 (dd, *J* = 11.5, 4.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.03, 166.70, 141.97, 135.59, 132.96, 132.78, 129.81, 129.02, 128.86, 123.71.

2-(4-chlorophenyl)-4,6-diphenyl-1,3,5-triazine (3ga)[2]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 – 8.59 (m, 6H), 7.62 – 7.42 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.65, 170.66, 138.75, 136.20, 135.99, 134.69, 132.59, 130.24, 128.93, 128.62.

2-(4-fluorophenyl)-4,6-diphenyl-1,3,5-triazine (3ia)[2]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 – 8.65 (m, 4H), 7.64 – 7.51 (m, 4H), 7.23 (dd, *J* = 11.2, 6.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.61, 170.62, 164.50, 136.08, 132.45 (d, *J* = 18.8 Hz), 131.25 (d, *J* = 9.1 Hz), 128.91, 128.61, 115.77, 115.55.

2-(4-chlorophenyl)-4,6-di-p-tolyl-1,3,5-triazine (3gb)[2]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 2H), 8.61 (d, *J* = 8.2 Hz, 4H), 7.50 (d, *J* = 8.6 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.51, 170.42, 143.13, 138.52, 134.90, 133.38, 130.19, 129.36, 128.90, 128.80, 21.73.

2,4-diphenyl-6-(pyridin-2-yl)-1,3,5-triazine (3ja)[1]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, *J* = 7.9 Hz, 1H), 8.82-8.72 (m, 5H), 7.68 – 7.41 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.74, 170.15, 152.84, 150.50, 136.19, 135.73, 132.79, 128.97, 128.69, 123.49.

2-(furan-2-yl)-4,6-diphenyl-1,3,5-triazine (3la)[1]

White solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 – 8.58 (m, 5H), 7.64 – 7.54 (m, 7H), 6.68 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.68, 165.49, 146.60, 135.85, 132.78, 132.58, 128.93, 128.73, 128.60, 112.56; GCMS (EI, 70 eV): m/z (%): 299 (M^+, 64), 103 (60), 95 (100), 44 (34).

2-(5-methylfuran-2-yl)-4,6-diphenyl-1,3,5-triazine (3ma)

White solid. m. p. 128 – 130 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 – 8.61 (m, 4H), 7.84 – 7.32 (m, 8H), 6.25 (dd, *J* = 3.3, 0.8 Hz, 1H), 2.50 (s, 3H). HRMS (ESI-ion trap) m/z calcd 314.1293, obtain 314.1281.

2,4-diphenylpyrimidine (4na)[3]

White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 (dd, *J* = 5.3, 0.7 Hz, 1H), 8.62 – 8.55 (m, 2H), 8.26 – 8.18 (m, 2H), 7.57 (dd, *J* = 5.3, 1.5 Hz, 1H), 7.55 – 7.49 (m, 6H);^{13}C NMR (100 MHz, $CDCl_3$) δ 164.53, 163.82, 157.83, 137.83, 136.90, 130.96, 130.72, 128.93, 128.54, 128.27, 127.19, 114.51.

References

1. F. Xie, M. Chen, X. Wang, H. Jiang, and M. Zhang, *Org. Biomol. Chem.,* 2014, **12**, 2761.

2. Q. You, F. Wang, C. Wu, T. Shi, D. Min, H. Chen, and Wu Zhang, *Org. Biomol. Chem.,* 2015, **13**, 6723.

3. X. Zheng, B. Song and B. Xu, *Eur. J. Org. Chem.*, 2010, **23**, 4376

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

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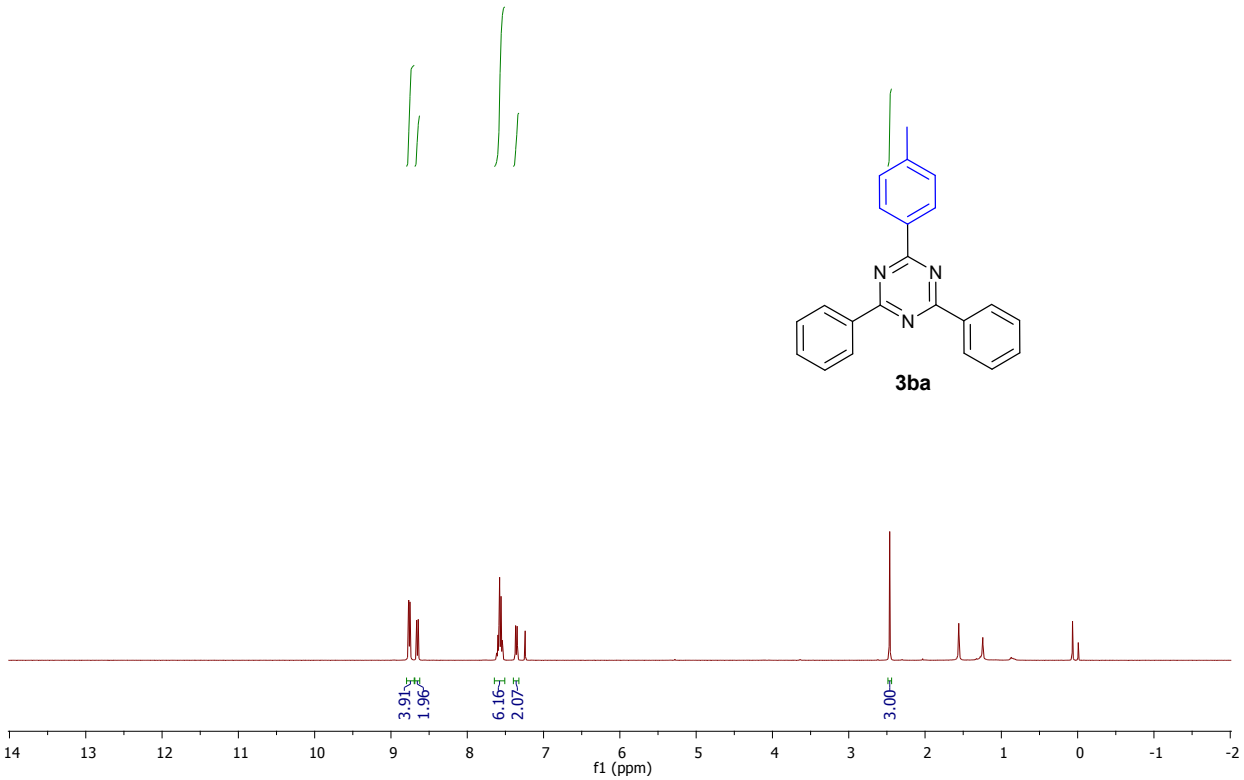

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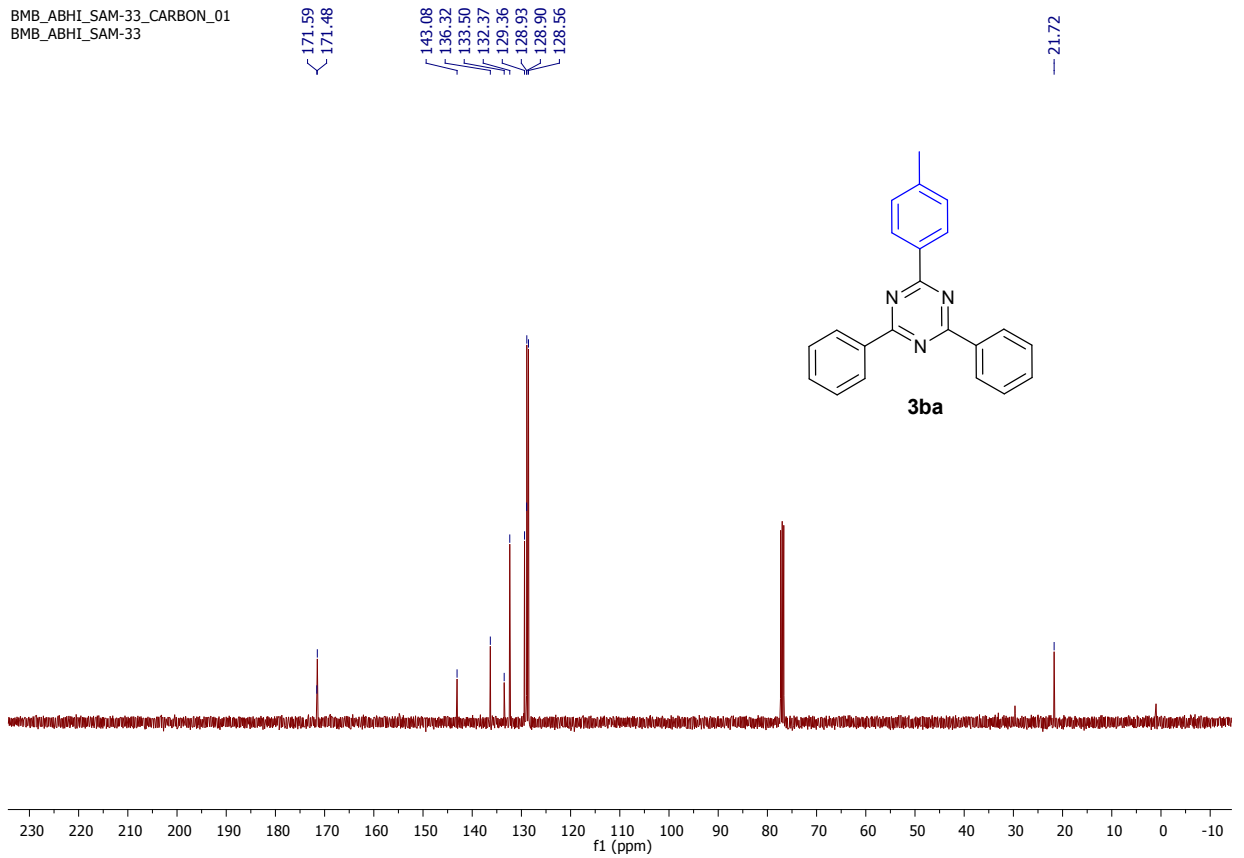

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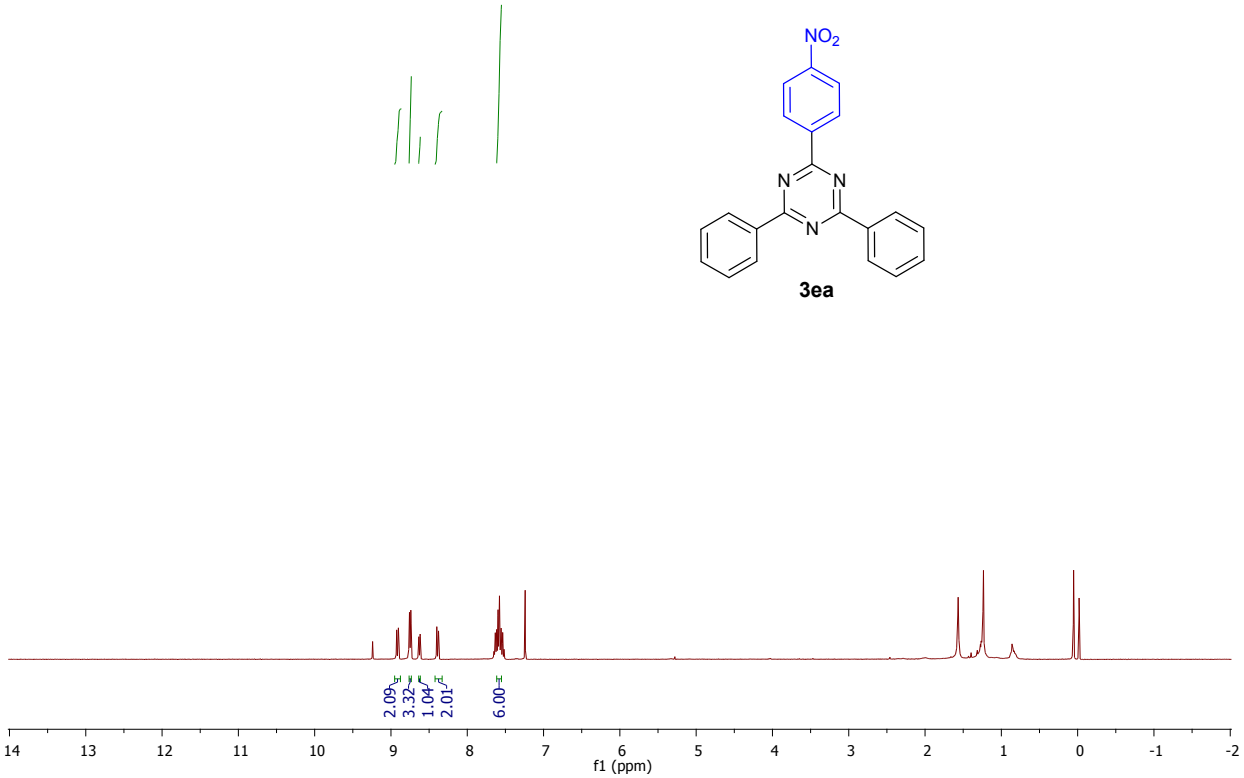

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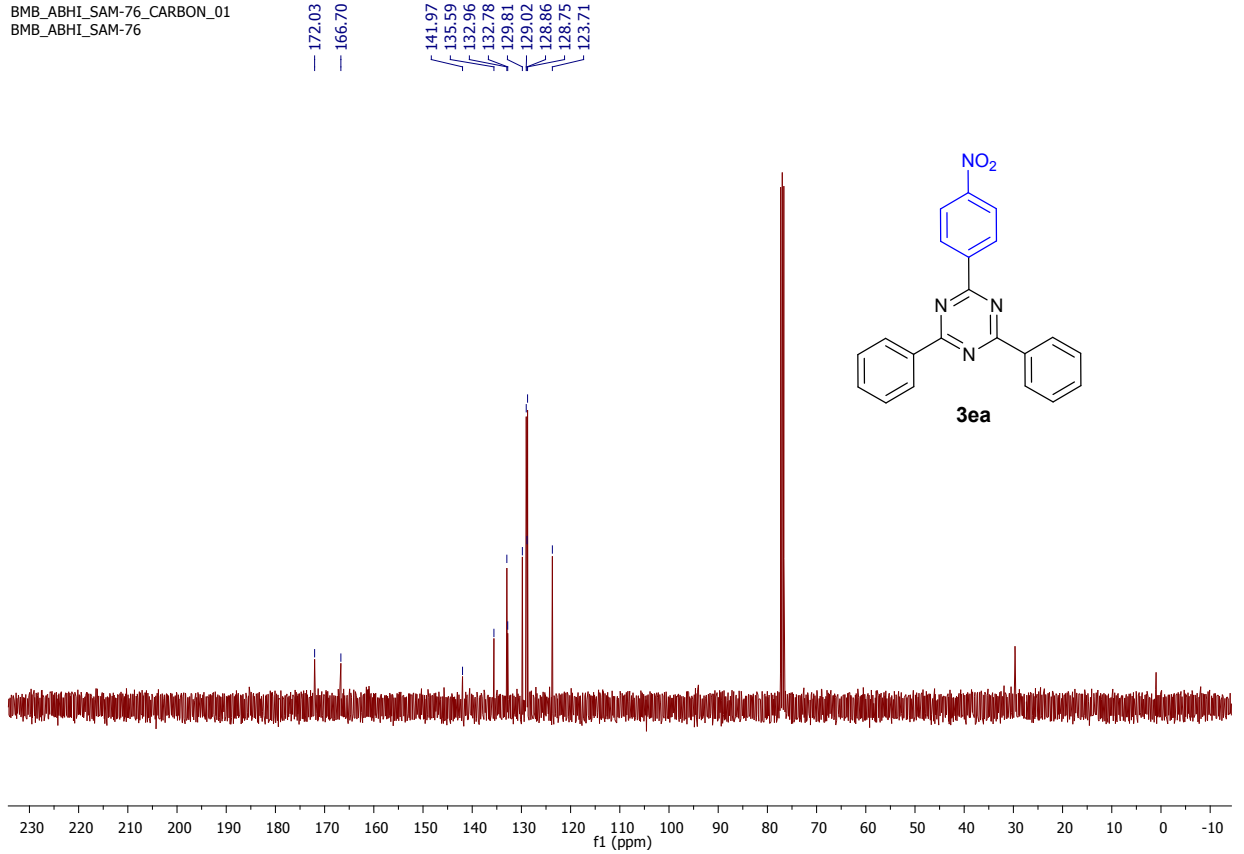

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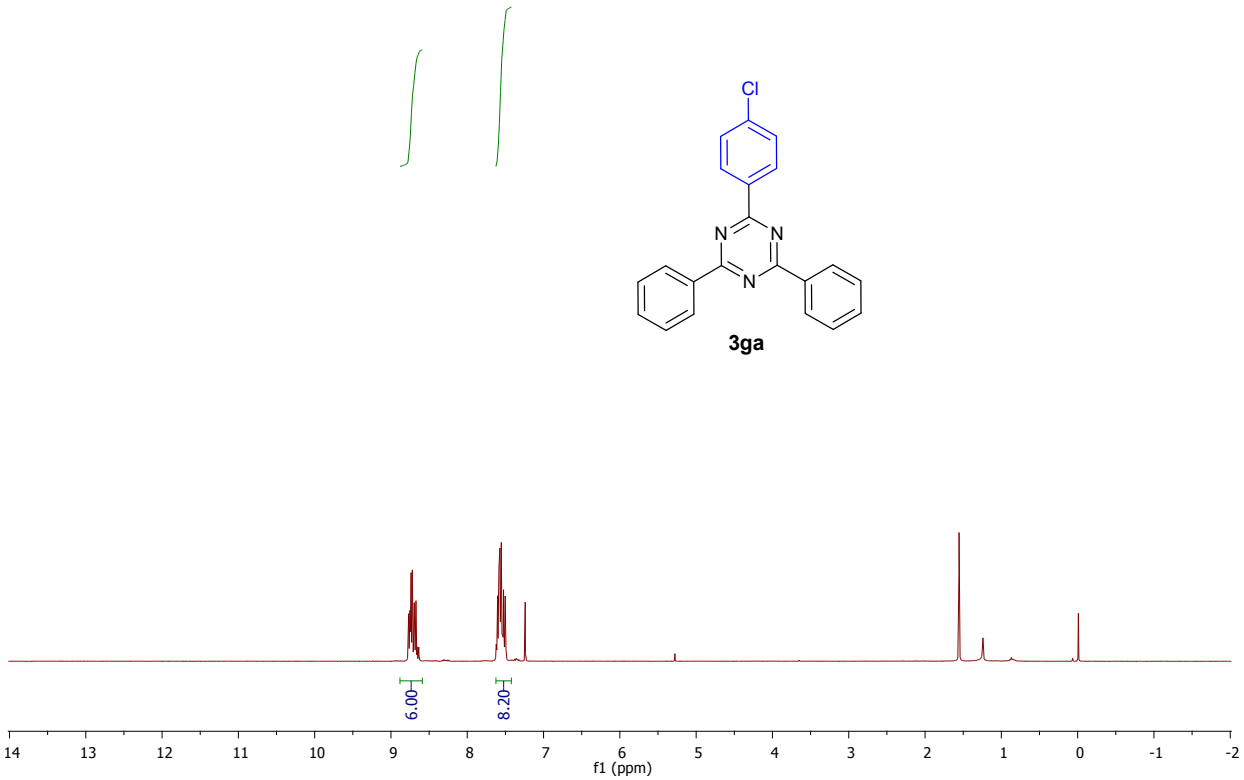

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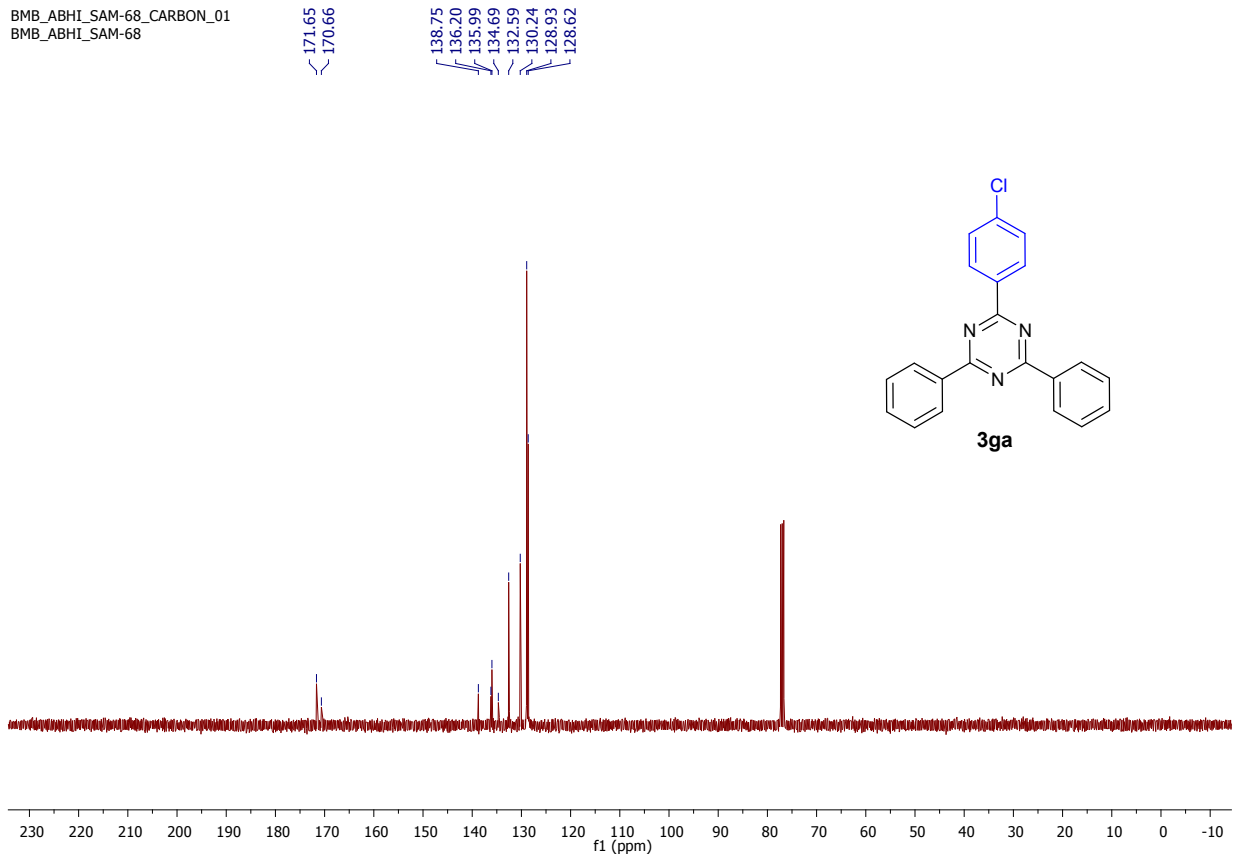

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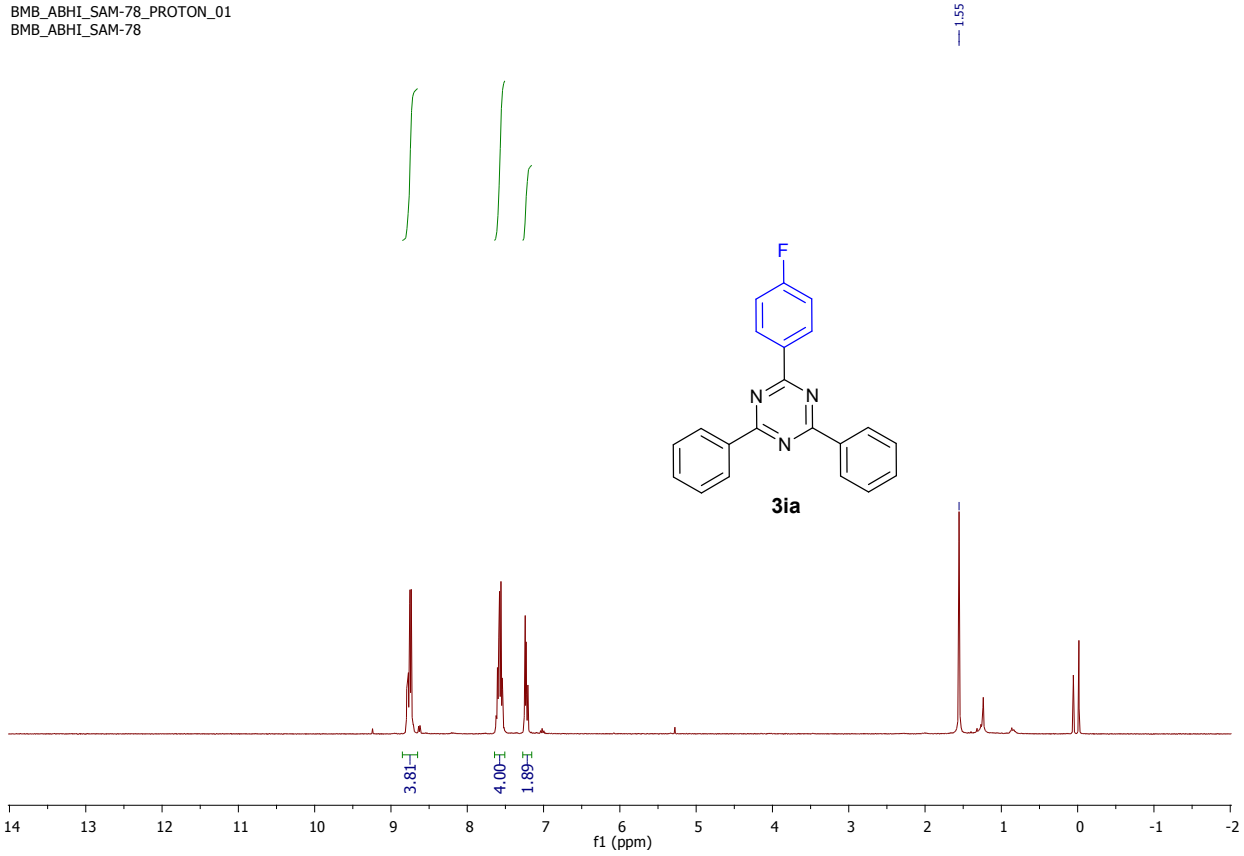
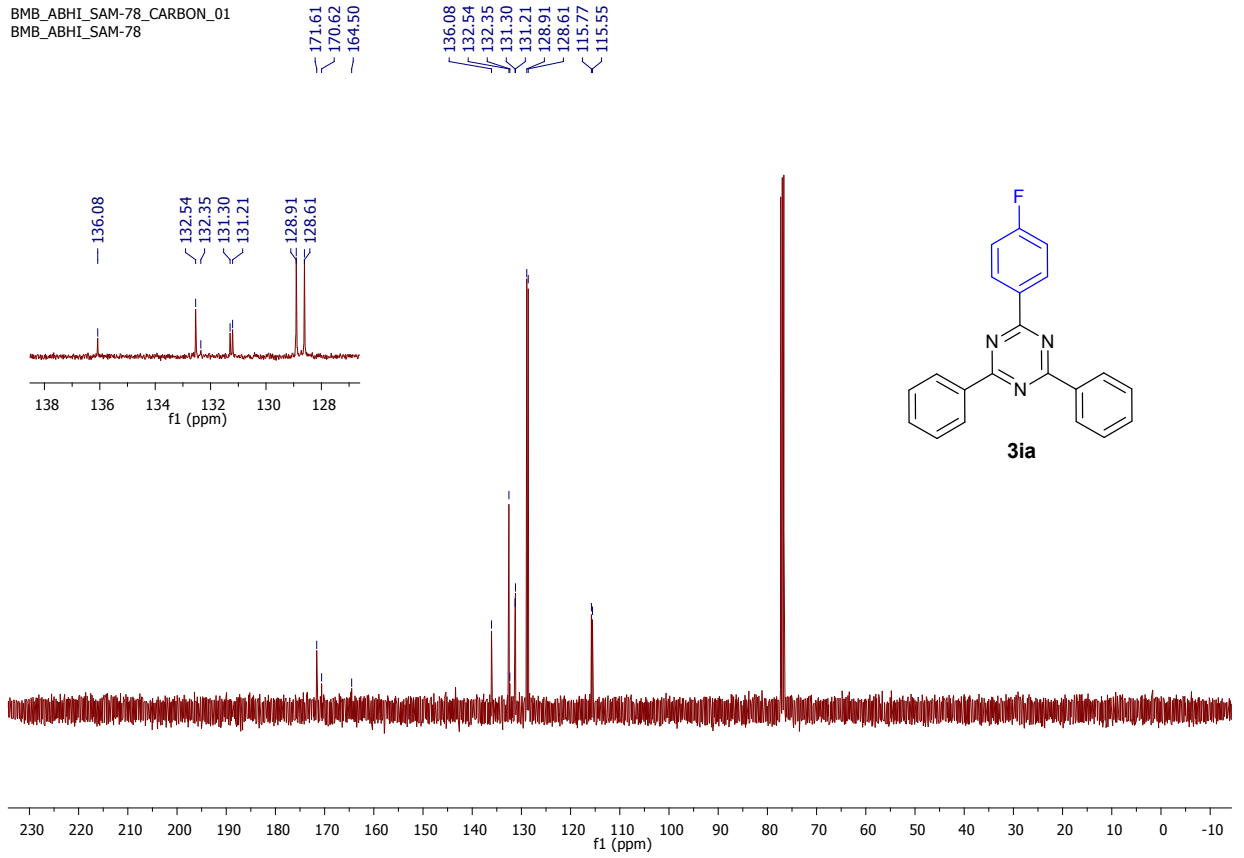
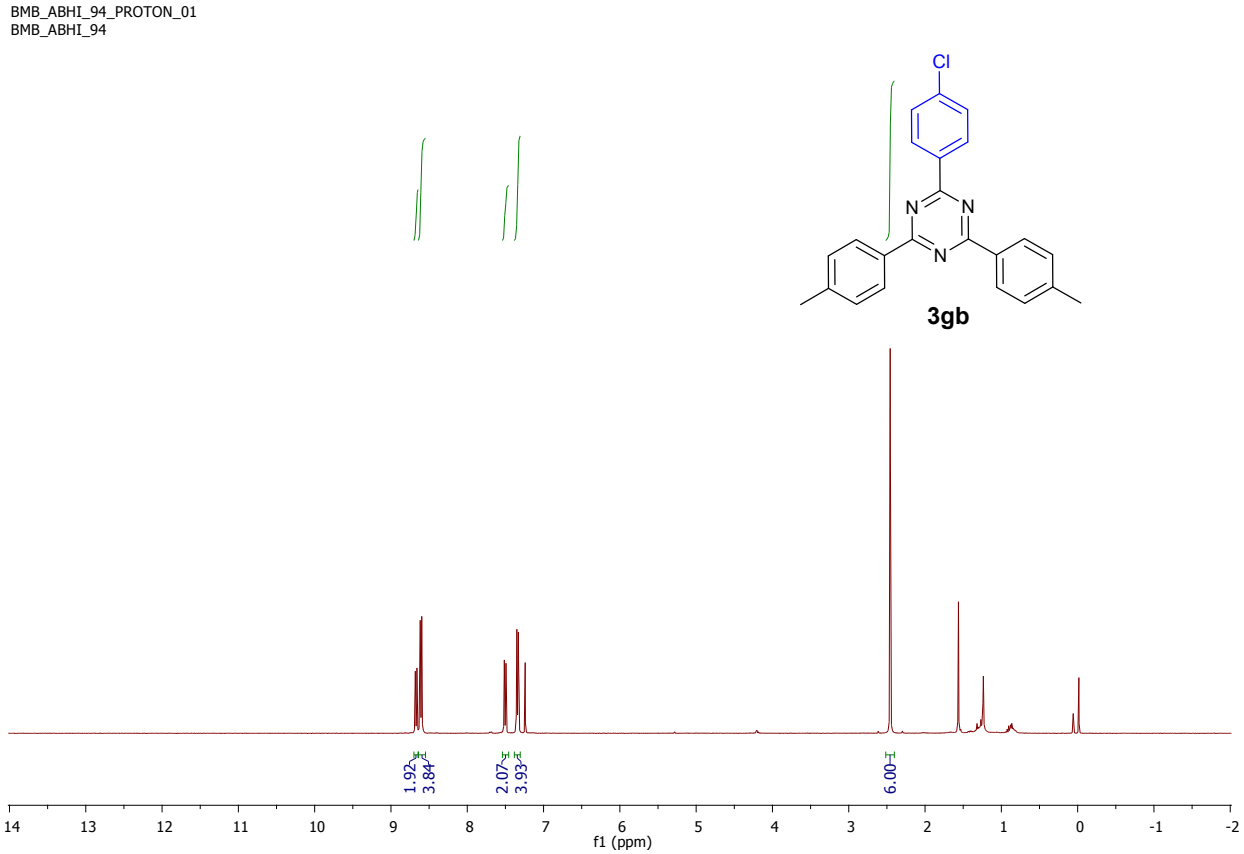
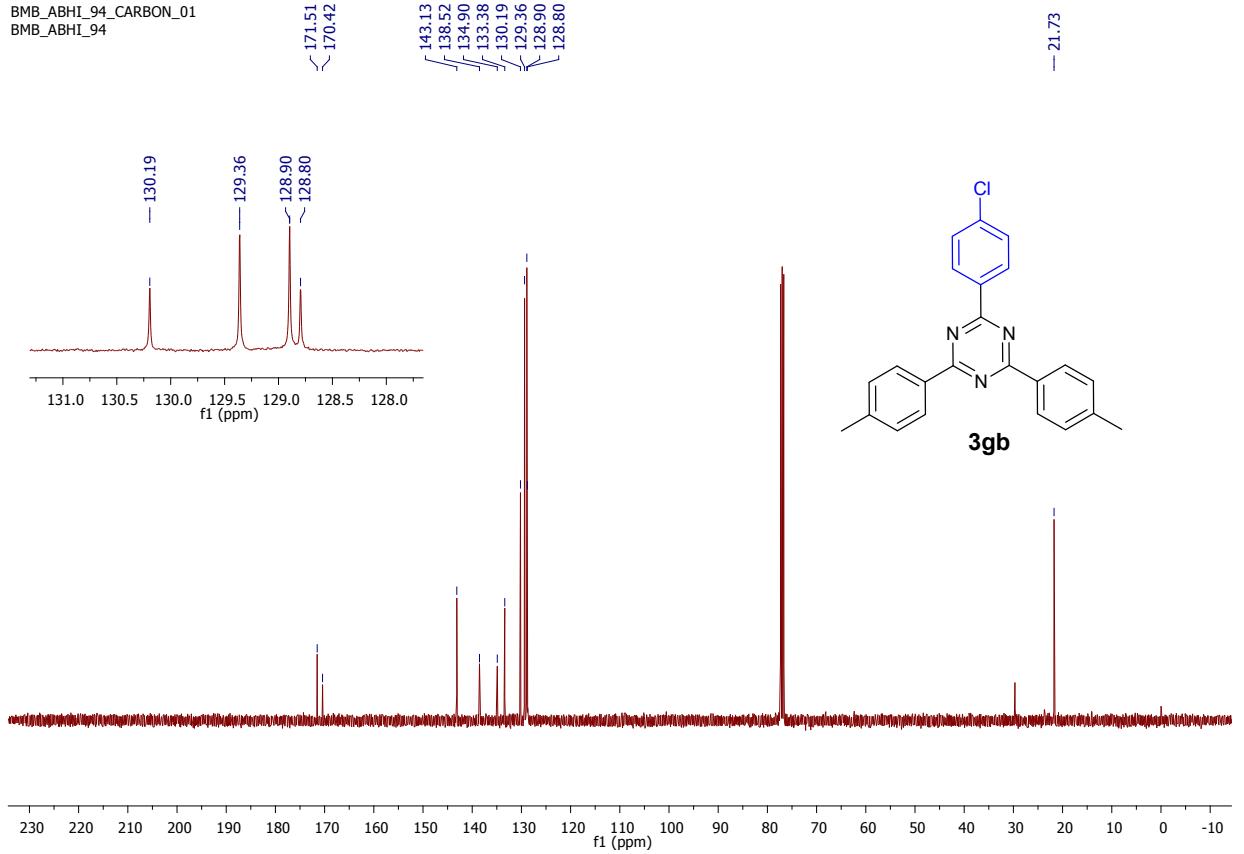




^{1}H NMR and ^{13}C NMR of 2-(4-chlorophenyl)-4,6-di-p-tolyl-1,3,5-triazine (3gb)





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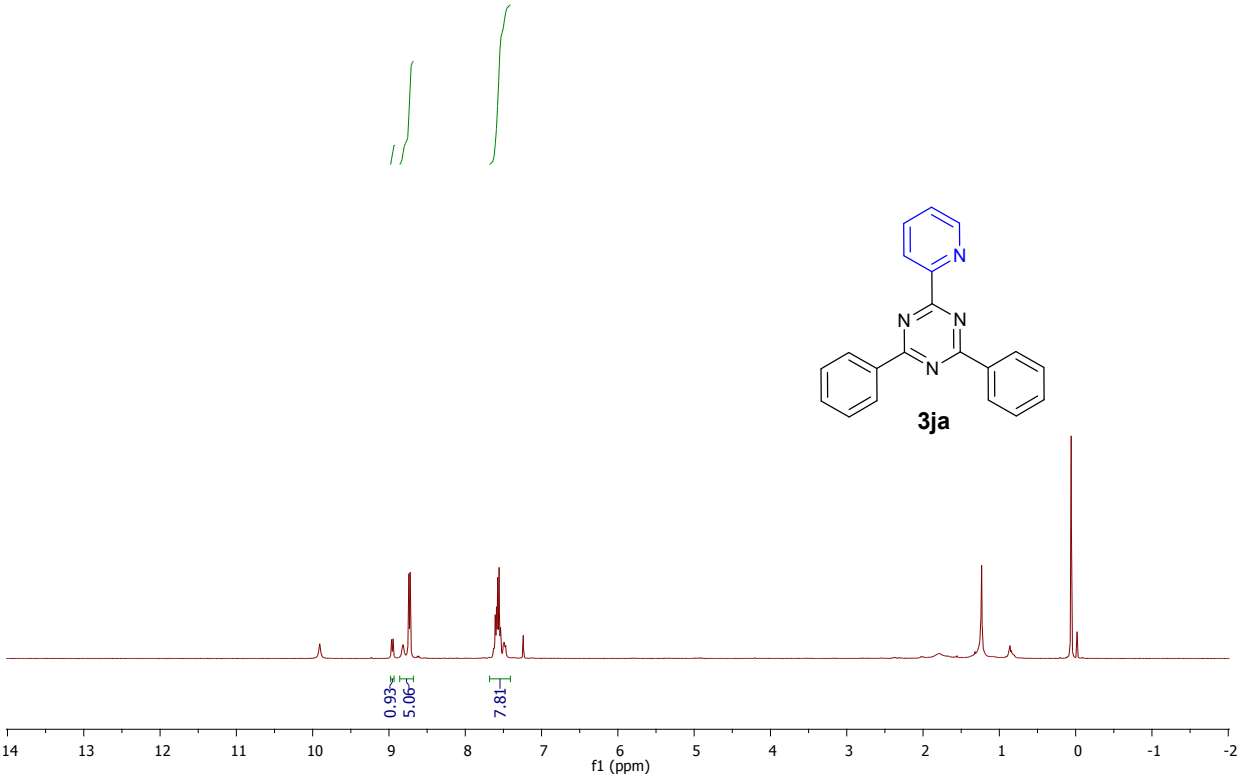

3ja

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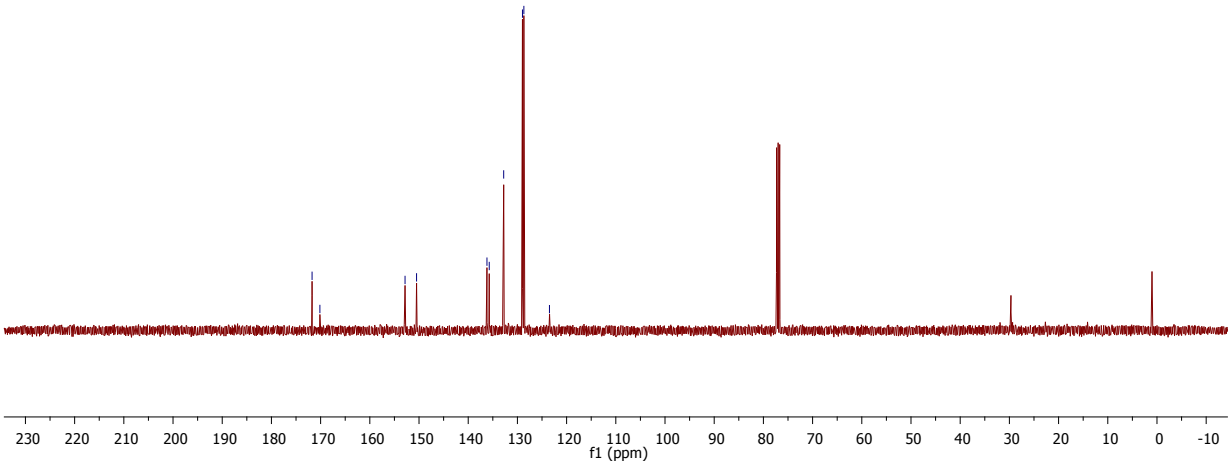
132.79
128.97
128.69
123.49



3ja

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

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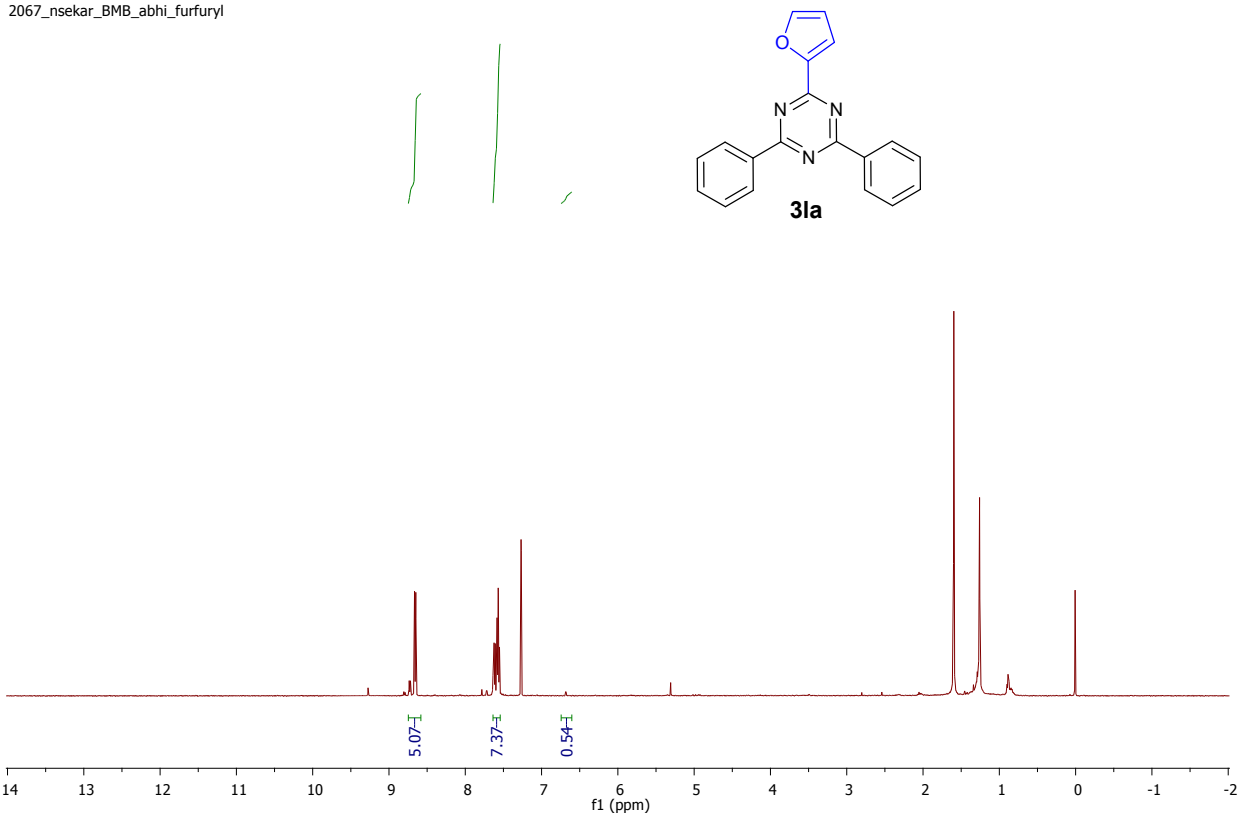

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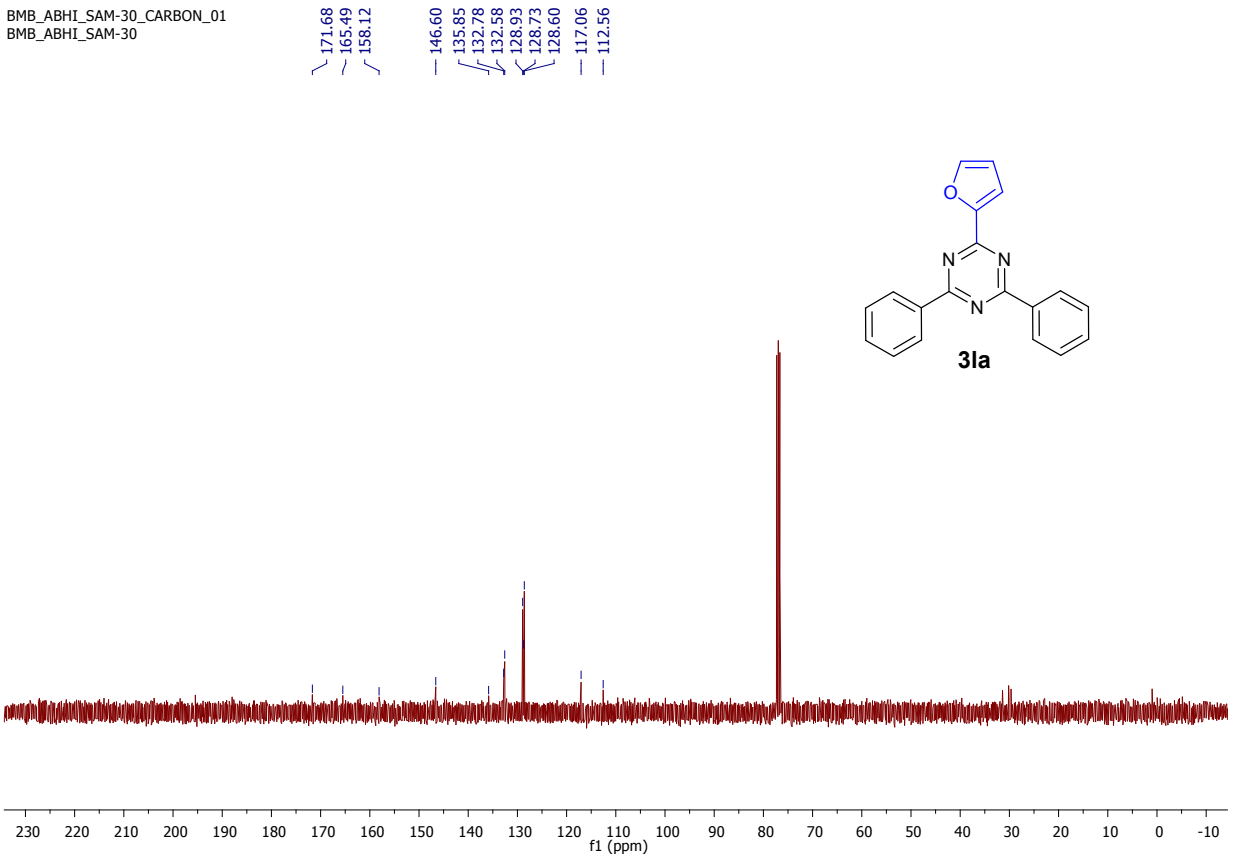

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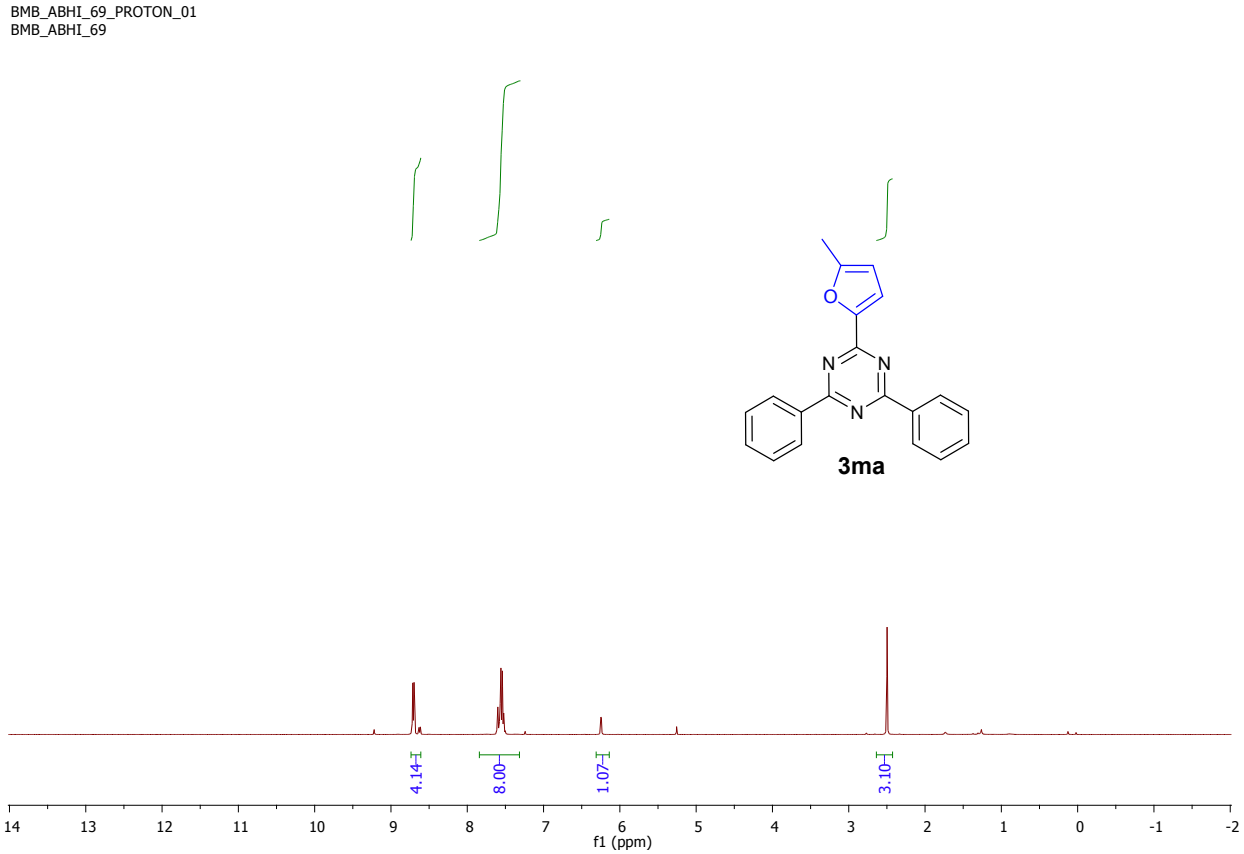
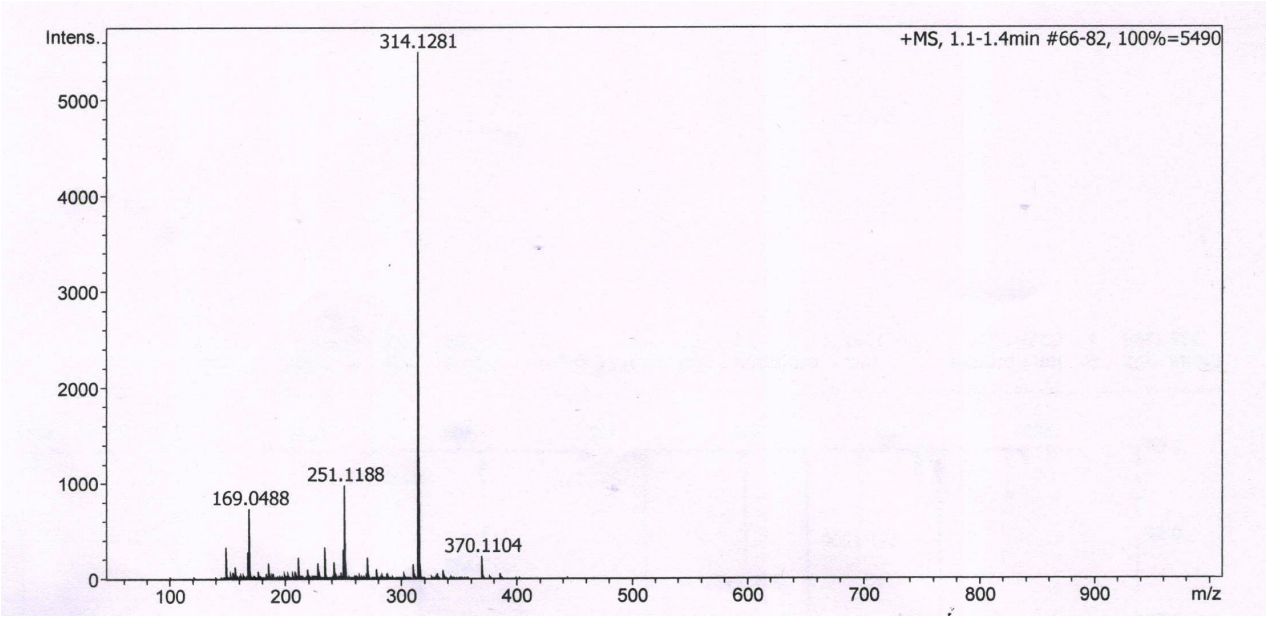


HRMS of 2-(5-methylfuran-2-yl)-4,6-diphenyl-1,3,5-triazine (3ma)



^{1}H NMR and ^{13}C NMR of 2,4-diphenylpyrimidine (4na)