

Electronic Supplementary Information

Transition metal-free C-F/C-Cl/C-C cleavage of $\text{ClCF}_2\text{COONa}$ for the synthesis of heterocycles

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General Information

Unless otherwise indicated, all commercial reagents, including the substrates **1** and **2** were used without additional purification. ¹H-NMR spectra were recorded with a Bruker Ascend™ 600 spectrometer. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl₃ or DMSO-*d*⁶ as an internal standard. ¹³C-NMR spectra were obtained by the same NMR spectrometer and were calibrated with CDCl₃ ($\delta = 77.00$ ppm) or DMSO-*d*⁶ ($\delta = 39.6$ ppm). MS was recorded on an AB SCIEX QTRAP 5500 LC-MS/MS. Melting point was recorded on a Hanon MP430 Auto Melting Point System.

Experimental Procedure

Preparation of 2-Aminobenzamides

2-Aminobenzamides (**4a-4i**) were synthesized from isatoic anhydride and the corresponding amines according to previous methods.⁴ **4a**: 70% yield, white solid, mp 115-117 °C; **4b**: 60% yield, yellowish solid, mp 125-127 °C; **4c**: 49% yield, white solid, mp 140-142 °C; **4d**: 59% yield, white solid, mp 147-148 °C; **4e**: 36% yield, yellowish solid, mp 113-115 °C; **4f**: 81% yield, white solid, mp 123-125 °C; **4g**: 89% yield, white solid, mp 86-88 °C; **4h**: 58% yield, yellowish solid, mp 132-133 °C; **4i**: 59% yield, yellowish solid, mp 187-188 °C.

General Procedure for the Synthesis of Symmetrical 2,4-Disubstituted 1,3,5-Triazines

Amidines **1** (0.4 mmol), ClCF₂COONa (1 equiv), and Cs₂CO₃ (2 equiv) were added to a 10 mL Schlenk tube, followed by addition of CH₃CN (1 mL). The mixture was stirred at 120 °C for 24 h. The solution was then cooled to r.t., quenched by water and extracted with EtOAc (3×10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the symmetrical 2,4-disubstituted 1,3,5-triazines.

General Procedure for the Synthesis of Unsymmetrical 2,4-Disubstituted 1,3,5-Triazines

Amidines **1** (0.2 mmol), amidines **1'** (0.8 mmol), ClCF₂COONa (1 equiv), and Cs₂CO₃ (2 equiv) were added to a 10 mL Schlenk tube, followed by addition of CH₃CN (1 mL). The mixture was stirred at 120 °C for 24 h. The solution was then cooled to r.t., quenched by water and extracted with EtOAc (3×10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the unsymmetrical 2,4-disubstituted 1,3,5-triazines.

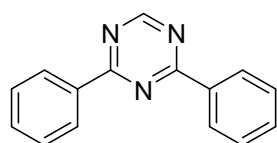
General Procedure for the Synthesis of Quinazolinones

2-Aminobenzamides **4** (0.2 mmol), ClCF₂COONa (2 equiv), and Cs₂CO₃ (2 equiv) were added to a 10 mL Schlenk tube, followed by addition of CH₃CN (1 mL). The mixture was stirred at 120 °C for 24 h. The solution was then cooled to r.t., quenched by water and extracted with EtOAc (3×10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the quinazolinones.

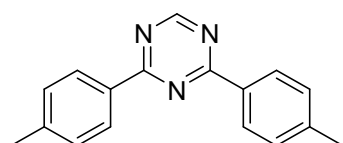
Gram-scale Synthesis of 2,4-Diphenyl-1,3,5-triazine

Benzamidinium hydrochloride (10 mmol), ClCF₂COONa (1 equiv), and Cs₂CO₃ (2 equiv) were added to a 50 mL Schlenk tube, followed by addition of CH₃CN (25 mL). The mixture was stirred at 80 °C for 24 h. After cooling, the solution was evaporated under vacuum to remove the solvent, quenched by water and extracted with EtOAc (3×30 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the 2,4-diphenyl-1,3,5-triazine as a white solid (1.024 g, 88% yield).

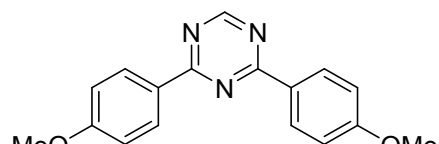
Characterization of Products



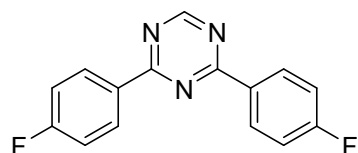
2,4-diphenyl-1,3,5-triazine (**3a**)¹: 44.7 mg (96%); Yellowish solid; Mp: 74-75 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.26 (s, 1H), 8.66-8.63 (m, 4H), 7.63-7.59 (m, 2H), 7.57-7.54 (m, 4H); ¹³C NMR (150 MHz, CDCl₃): δ 171.3, 166.7, 135.5, 132.8, 128.9, 128.7.



2,4-di-*p*-tolyl-1,3,5-triazine (**3b**)¹: 39.7 mg (76%); White solid; Mp: 159-161 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.19 (s, 1H), 8.52 (d, *J* = 8.2 Hz, 4H), 7.34 (d, *J* = 8.0 Hz, 4H), 2.46 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 171.1, 166.3, 143.5, 132.8, 129.5, 128.9, 21.7.

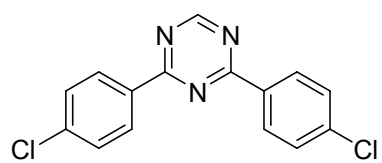


2,4-bis(4-methoxyphenyl)-1,3,5-triazine (**3c**)¹: 36.3 mg (62%); White solid; Mp: 158-160 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.11 (s, 1H), 8.59-8.57 (m, 4H), 7.04-7.02 (m, 4H), 3.91 (s, 6H); ¹³C NMR (150 MHz, CDCl₃): δ 170.5, 166.3, 163.4, 130.7, 128.1, 114.0, 55.4.



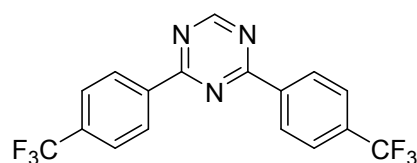
2,4-bis(4-fluorophenyl)-1,3,5-triazine (**3d**)¹: 46.8 mg (87%); White solid; Mp: 154-156 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.18 (s, 1H), 8.64-8.61 (m, 4H), 7.23-7.19 (m,

4H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.3, 166.6, 165.9 (d, $J = 252.6$ Hz), 131.5 (d, $J = 2.7$ Hz), 131.2 (d, $J = 9.2$ Hz), 115.9 (d, $J = 21.8$ Hz).



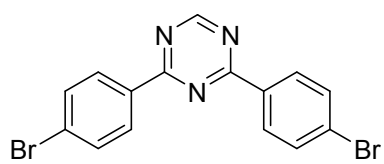
130.2, 129.1.

2,4-bis(4-chlorophenyl)-1,3,5-triazine (**3e**)¹: 56.2 mg (93%); White solid; Mp: 189-191 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.23 (s, 1H), 8.56 (d, $J = 8.1$ Hz, 4H), 7.51 (d, $J = 8.1$ Hz, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.5, 166.8, 139.3, 133.8,



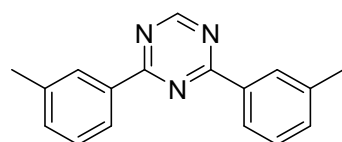
167.1, 138.4, 134.4 (q, $J = 32.6$ Hz), 129.3, 125.8 (q, $J = 3.5$ Hz), 123.8 (q, $J = 270.9$ Hz).

2,4-bis(4-(trifluoromethyl)phenyl)-1,3,5-triazine (**3f**)¹: 63.4 mg (86%); White solid; Mp: 151-153 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.34 (s, 1H), 8.75 (d, $J = 8.2$ Hz, 4H), 7.82 (d, $J = 8.2$ Hz, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.4,



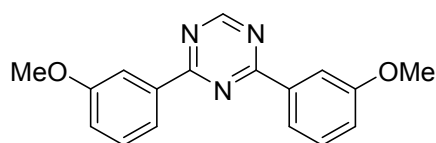
130.4, 128.1.

2,4-bis(4-bromophenyl)-1,3,5-triazine (**3g**)¹: 60.2 mg (77%); White solid; Mp: 195-197 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.23 (s, 1H), 8.48 (d, $J = 8.5$ Hz, 4H), 7.68 (d, $J = 8.5$ Hz, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.6, 166.8, 134.3, 132.1,



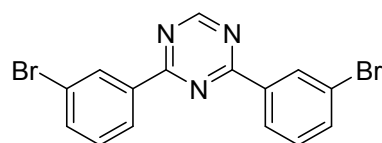
126.1, 21.5.

2,4-di-*m*-tolyl-1,3,5-triazine (**3h**)¹: 46.9 mg (90%); White solid; Mp: 87-89 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.23 (s, 1H), 8.45-8.43 (m, 4H), 7.46-7.40 (m, 4H), 2.49 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 171.4, 166.5, 138.5, 135.4, 133.6, 129.3, 128.7,



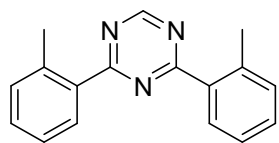
126.1, 21.5.

2,4-bis(3-methoxyphenyl)-1,3,5-triazine (**3i**)¹: 43.9 mg (75%); White solid; Mp: 109-110 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.25 (s, 1H), 8.24 (d, $J = 7.8$ Hz, 2H), 8.16 (s, 2H), 7.46 (t, $J = 7.8$ Hz, 2H), 7.15 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.9$ Hz, 2H), 3.94 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 171.1, 166.6, 159.9, 136.9, 129.8, 121.4, 119.2, 113.3, 55.4.

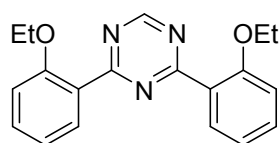


2,4-bis(3-bromophenyl)-1,3,5-triazine (**3j**)¹: 39.1 mg (50%); White solid; Mp: 182-183 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.27 (s, 1H), 8.76 (t, $J = 1.5$ Hz, 2H), 8.56

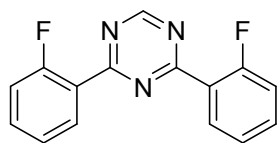
(d, $J = 7.8$ Hz, 2H), 7.74 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.0$ Hz, 2H), 7.44 (t, $J = 7.9$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.3, 166.9, 137.3, 135.9, 131.8, 130.3, 127.5, 123.1.



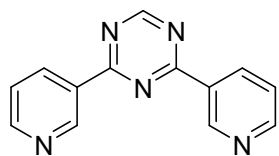
2,4-di-*o*-tolyl-1,3,5-triazine (**3k**)¹: 39.2 mg (75%); Yellowish oil; ^1H NMR (600 MHz, CDCl_3): δ 9.32 (s, 1H), 8.15 (dd, $J_1 = 7.7$ Hz, $J_2 = 0.7$ Hz, 2H), 7.43 (td, $J_1 = 7.4$ Hz, $J_2 = 1.1$ Hz, 2H), 7.36-7.31 (m, 4H), 2.72 (s, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 173.8, 165.6, 138.9, 135.4, 131.8, 131.2, 131.1, 126.1, 22.0.



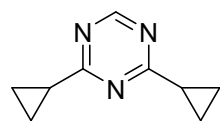
2,4-bis(2-ethoxyphenyl)-1,3,5-triazine (**3l**)¹: 54.0 mg (84%); Colorless oil; ^1H NMR (600 MHz, CDCl_3): δ 9.32 (s, 1H), 7.99 (dd, $J_1 = 7.7$ Hz, $J_2 = 1.8$ Hz, 2H), 7.48-7.44 (m, 2H), 7.07 (td, $J_1 = 7.5$ Hz, $J_2 = 0.8$ Hz, 2H), 7.04 (d, $J = 8.4$ Hz, 2H), 4.16 (q, $J = 7.0$ Hz, 4H), 1.44 (t, $J = 7.0$ Hz, 6H); ^{13}C NMR (150 MHz, CDCl_3): δ 172.6, 165.4, 158.0, 132.5, 132.2, 126.2, 120.5, 113.4, 64.5, 14.7.



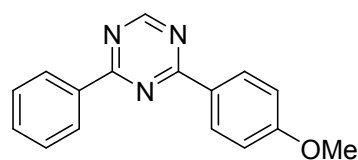
2,4-bis(2-fluorophenyl)-1,3,5-triazine (**3m**)¹: 39.2 mg (73%); White solid; Mp: 63-65 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.39 (s, 1H), 8.36 (td, $J_1 = 7.7$ Hz, $J_2 = 1.7$ Hz, 2H), 7.58-7.54 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.4 (d, $J = 5.1$ Hz), 166.5, 162.2 (d, $J = 258.3$ Hz), 134.0 (d, $J = 9.3$ Hz), 132.2, 124.4 (d, $J = 3.8$ Hz), 124.0 (d, $J = 7.8$ Hz), 117.3 (d, $J = 22.4$ Hz).



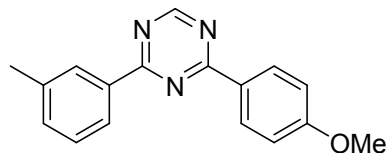
2,4-di(pyridin-3-yl)-1,3,5-triazine (**3n**)¹: 9.9 mg (21%); Yellowish solid; Mp: 181-183 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.83 (s, 2H), 9.34 (s, 1H), 8.89 (d, $J = 7.8$ Hz, 2H), 8.87 (d, $J = 3.3$ Hz, 2H), 7.54-7.51 (dd, $J_1 = 7.4$ Hz, $J_2 = 4.9$ Hz, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 170.0, 167.0, 153.1, 150.1, 136.5, 131.0, 123.8.



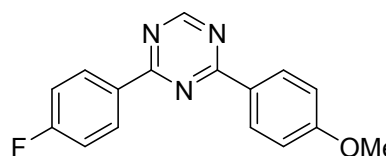
2,4-dicyclopropyl-1,3,5-triazine (**3o**)¹: 16.9 mg (52%); Yellowish oil; ^1H NMR (600 MHz, CDCl_3): δ 8.71 (s, 1H), 2.12-2.07 (m, 2H), 1.23-1.19 (m, 4H), 1.15-1.11 (m, 4H); ^{13}C NMR (150 MHz, CDCl_3): δ 179.6, 164.6, 17.7, 12.0.



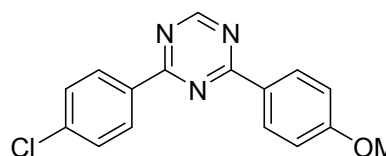
2-(4-methoxyphenyl)-4-phenyl-1,3,5-triazine (**3p**)¹: 31.5 mg (60%); White solid; Mp: 107-109 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.18 (s, 1H), 8.63-8.59 (m, 4H), 7.61-7.58 (m, 1H), 7.56-7.53 (m, 2H), 7.05-7.02 (m, 2H), 3.91 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 171.0, 170.8, 166.5, 163.6, 135.7, 132.7, 130.8, 128.8, 128.7, 127.9, 114.1, 55.5.



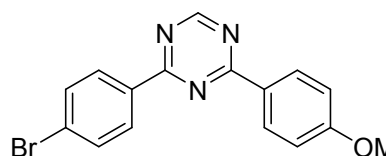
2-(4-methoxyphenyl)-4-(*m*-tolyl)-1,3,5-triazine (**3q**)²: 32.2 mg (58%); White solid; Mp: 111-113 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.17 (s, 1H), 8.62-8.58 (m, 2H), 8.43-8.41 (m, 2H), 7.45-7.39 (m, 2H), 7.06-7.02 (m, 2H), 3.91 (s, 3H), 2.48 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 171.1, 170.7, 166.3, 163.5, 138.4, 135.5, 133.5, 130.9, 129.3, 128.6, 127.9, 126.0, 114.1, 55.4, 21.5.



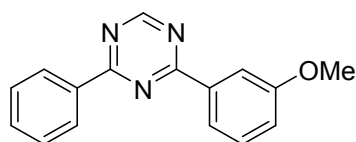
2-(4-fluorophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (**3r**)²: 34.4 mg (61%); White solid; Mp: 152-154 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.15 (s, 1H), 8.65-8.62 (m, 2H), 8.59-8.57 (m, 2H), 7.23-7.19 (m, 2H), 7.05-7.02 (m, 2H), 3.91 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 170.8, 170.0, 166.4, 165.8 (d, *J* = 252.3 Hz), 163.6, 131.9 (d, *J* = 2.9 Hz), 131.2 (d, *J* = 9.2 Hz), 130.8, 127.8, 115.8 (d, *J* = 21.7 Hz), 114.1, 55.5.



2-(4-chlorophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (**3s**)¹: 44 mg (74%); Yellow solid; Mp: 128-130 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.16 (s, 1H), 8.59-8.54 (m, 4H), 7.52-7.49 (m, 2H), 7.05-7.02 (m, 2H), 3.91 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 170.9, 170.1, 166.5, 163.7, 139.0, 134.2, 130.9, 130.1, 129.0, 127.8, 114.1, 55.5.

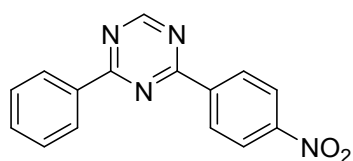


2-(4-bromophenyl)-4-(4-methoxyphenyl)-1,3,5-triazine (**3t**)³: 30.8 mg (45%); White solid; Mp: 170-172 °C; ¹H NMR (600 MHz, CDCl₃): δ 9.17 (s, 1H), 8.60-8.55 (m, 4H), 7.52-7.49 (m, 2H), 7.05-7.02 (m, 2H), 3.92 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 170.9, 170.1, 166.5, 163.7, 139.0, 134.2, 130.9, 130.1, 129.0, 127.7, 114.1, 55.5.

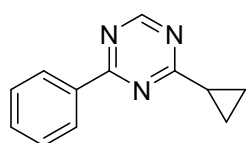


2-(3-methoxyphenyl)-4-phenyl-1,3,5-triazine (**3u**)²: 24.7 mg (47%); White solid; Mp: 85-87°C; ¹H NMR (600 MHz, CDCl₃): δ 9.24 (s, 1H), 8.65-8.61 (m, 2H), 8.24 (d, *J* = 7.7 Hz, 1H), 8.17-8.16 (m, 1H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.54 (t, *J* = 7.5 Hz, 2H), 7.45

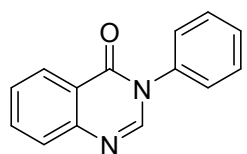
(t, $J = 7.9$ Hz, 1H), 7.16-7.13 (m, 1H), 3.93 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3): δ 171.2, 171.1, 166.6, 159.9, 136.9, 135.4, 132.8, 129.7, 128.9, 128.7, 121.4, 119.1, 113.3, 55.4.



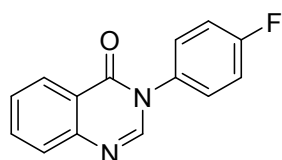
2-(4-nitrophenyl)-4-phenyl-1,3,5-triazine (**3v**)¹: 18.4 mg (33%); White solid; Mp: 171-173 °C; ^1H NMR (600 MHz, CDCl_3): δ 9.31 (s, 1H), 8.81-8.78 (m, 2H), 8.64-8.62 (m, 2H), 8.39-8.36 (m, 2H), 7.66-7.62 (m, 1H), 7.59-7.55 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 171.8, 169.4, 167.0, 150.4, 141.2, 134.9, 133.3, 129.8, 129.0, 128.9, 123.8.



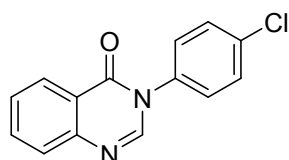
2-cyclopropyl-4-phenyl-1,3,5-triazine (**3w**)¹: 15.8 mg (40%); White solid; Mp: 53-55 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.99 (s, 1H), 8.49 (d, $J = 7.7$ Hz, 2H), 7.57 (t, $J = 7.2$ Hz, 1H), 7.50 (t, $J = 7.6$ Hz, 2H), 2.29-2.24 (m, 1H), 1.37-1.33 (m, 2H), 1.24-1.20 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 180.6, 170.4, 165.4, 135.3, 132.7, 128.8, 128.6, 18.1, 12.4.



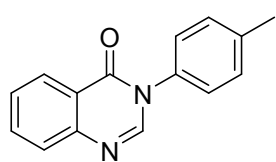
3-phenylquinazolin-4(3H)-one (**5a**)⁴: 25.8 mg (58%); White solid; Mp: 133-135 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.38-8.35 (m, 1H), 8.13 (s, 1H), 7.82-7.75 (m, 2H), 7.57-7.53 (m, 3H), 7.51-7.47 (m, 1H), 7.44-7.41 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 160.7, 147.8, 146.0, 137.4, 134.5, 129.6, 129.1, 127.6, 127.5, 127.1, 126.9, 122.3.



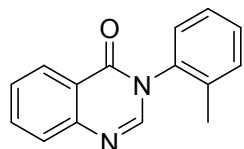
3-(4-fluorophenyl)quinazolin-4(3H)-one (**5b**)⁴: 28.9 mg (60%); White solid; Mp: 180-182 °C; ^1H NMR (600 MHz, CDCl_3): δ 8.36 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.0$ Hz, 1H), 8.11 (s, 1H), 7.84-7.77 (m, 2H), 7.56-7.54 (m, 1H), 7.44-7.40 (m, 2H), 7.26-7.22 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ 162.6 (d, $J = 248.0$ Hz), 160.7, 147.7, 145.8, 134.7, 133.3 (d, $J = 3.1$ Hz), 128.9 (d, $J = 8.8$ Hz), 127.8, 127.6, 127.2, 122.2, 116.7 (d, $J = 22.9$ Hz).



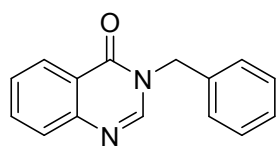
3-(4-chlorophenyl)quinazolin-4(3H)-one (**5c**)⁴: 28.8 mg (56%); White solid; Mp: 200-202 °C; ^1H NMR (600 MHz, $\text{DMSO-}d_6$): δ 8.37 (s, 1H), 8.21 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.2$ Hz, 1H), 7.92-7.88 (m, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.67-7.63 (m, 2H), 7.63-7.59 (m, 3H); ^{13}C NMR (150 MHz, $\text{DMSO-}d_6$): δ 160.0, 147.7, 147.1, 136.5, 134.9, 133.5, 129.6, 129.3, 127.6, 127.3, 126.6, 121.9.



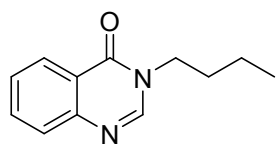
3-(*p*-tolyl)quinazolin-4(*3H*)-one (**5d**)⁴: 28.4 mg (60%); White solid; Mp: 143-144 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.37 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.9 Hz, 1H), 8.14 (s, 1H), 7.81-7.76 (m, 2H), 7.57-7.53 (m, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.32-7.29 (m, 2H), 2.44 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.7, 147.5, 146.3, 139.3, 134.8, 134.5, 130.2, 127.6, 127.3, 127.2, 126.7, 122.3, 21.2.



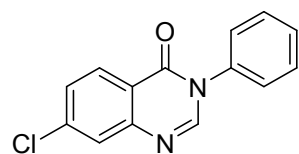
3-(*o*-tolyl)quinazolin-4(*3H*)-one (**5e**)⁴: 28.3 mg (60%); Colorless oil; ¹H NMR (600 MHz, CDCl₃): δ 8.39-8.37 (m, 1H), 8.02 (s, 1H), 7.83-7.79 (m, 2H), 7.58-7.54 (m, 1H), 7.43-7.35 (m, 3H), 7.27-7.25 (m, 1H), 2.21 (s, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.3, 147.8, 146.3, 136.5, 135.8, 134.6, 131.3, 129.7, 127.8, 127.6, 127.4, 127.3, 127.2, 122.3, 17.7.



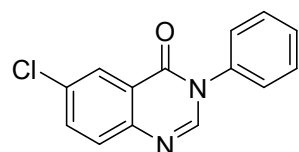
3-benzylquinazolin-4(*3H*)-one (**5f**)⁴: 19.4 mg (41%); White solid; Mp: 115-117 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.33 (dd, *J*₁ = 8.0 Hz, *J*₂ = 1.0 Hz, 1H), 8.15 (s, 1H), 7.78-7.71 (m, 2H), 7.53-7.49 (m, 1H), 7.37-7.30 (m, 5H), 5.21 (s, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 161.0, 147.7, 146.4, 135.6, 134.3, 129.0, 128.3, 128.0, 127.4, 127.3, 126.9, 122.1, 49.6.



3-butylquinazolin-4(*3H*)-one (**5g**)⁴: 13.4 mg (33%); White solid; Mp: 69-70 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.32 (dd, *J*₁ = 8.0 Hz, *J*₂ = 0.8 Hz, 1H), 8.11 (s, 1H), 7.78-7.72 (m, 2H), 7.53-7.50 (m, 1H), 4.03 (t, *J* = 7.4 Hz, 2H), 1.79 (quintet, *J* = 7.5 Hz, 2H), 1.42 (sextet, *J* = 7.5 Hz, 2H), 0.98 (t, *J* = 7.4 Hz, 3H); ¹³C NMR (150 MHz, CDCl₃): δ 160.9, 147.6, 146.7, 134.2, 127.3, 127.1, 126.7, 122.0, 46.9, 31.4, 19.8, 13.6.

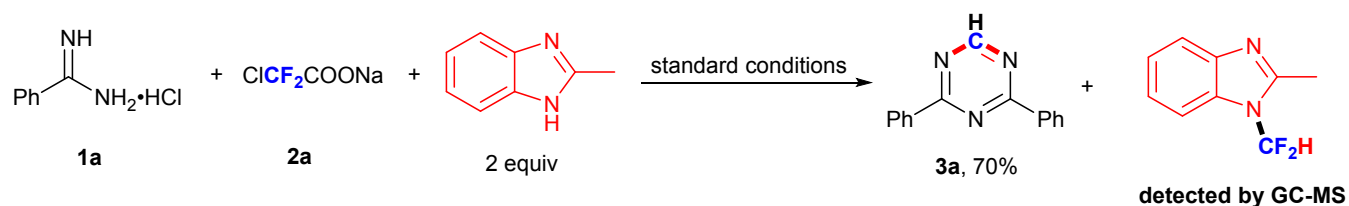


7-chloro-3-phenylquinazolin-4(*3H*)-one (**5h**)⁴: 22.2 mg (43%); White solid; Mp: 145-146 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.29 (d, *J* = 0.8 Hz, 1H), 8.15 (s, 1H), 7.77 (d, *J* = 2.0 Hz, 1H), 7.58-7.54 (m, 2H), 7.52-7.49 (m, 2H), 7.43-7.41 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 160.1, 148.7, 147.3, 140.9, 137.1, 129.7, 129.3, 128.6, 128.3, 127.1, 126.9, 120.8.

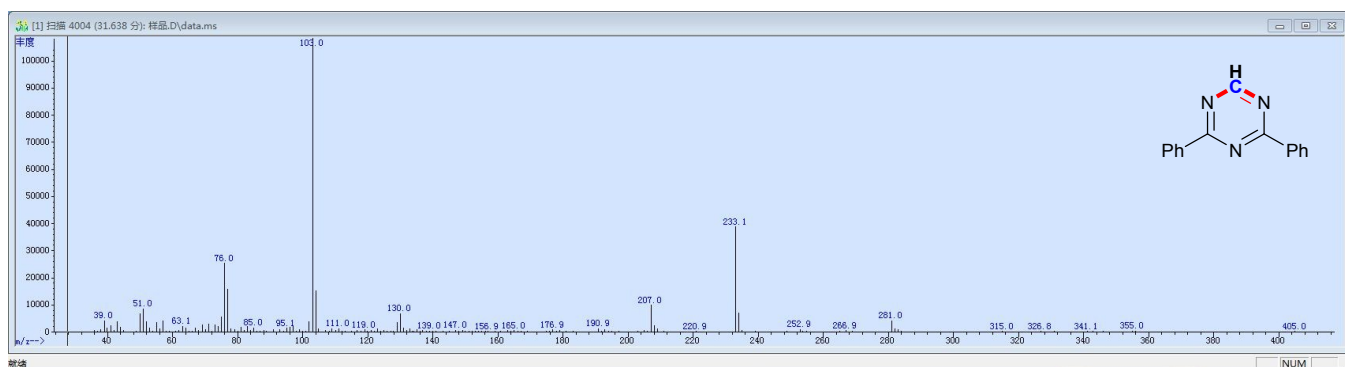
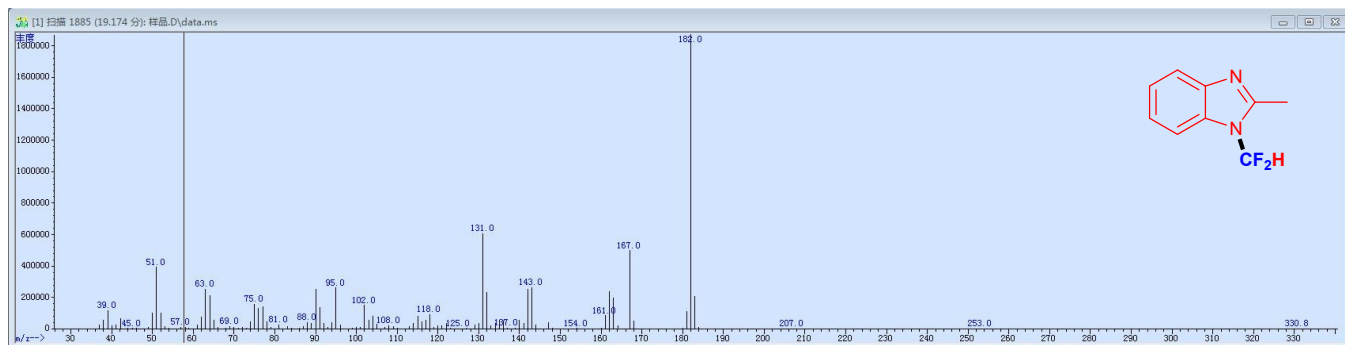
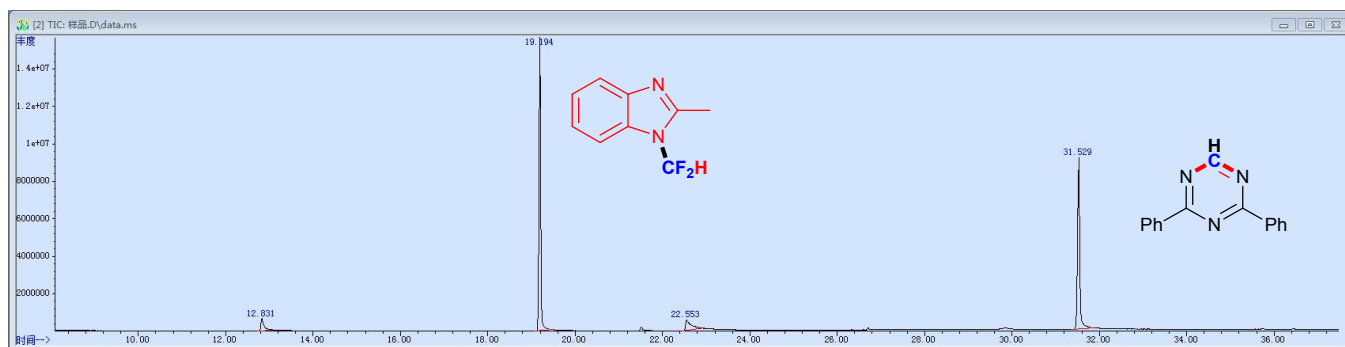


6-chloro-3-phenylquinazolin-4(*3H*)-one (**5i**)⁴: 23.1 mg (45%); White solid; Mp: 178-179 °C; ¹H NMR (600 MHz, CDCl₃): δ 8.32 (d, *J* = 2.2 Hz, 1H), 8.12 (s, 1H), 7.75-7.70 (m, 2H), 7.58-7.51 (m, 2H), 7.51-7.49 (m, 1H), 7.43-7.41 (m, 2H); ¹³C NMR (150 MHz, CDCl₃): δ 159.7, 146.2, 137.1, 135.0, 133.5, 129.7, 129.3, 129.2, 126.9, 126.5, 123.4.

Detection Experiment of CF₂ Carbene



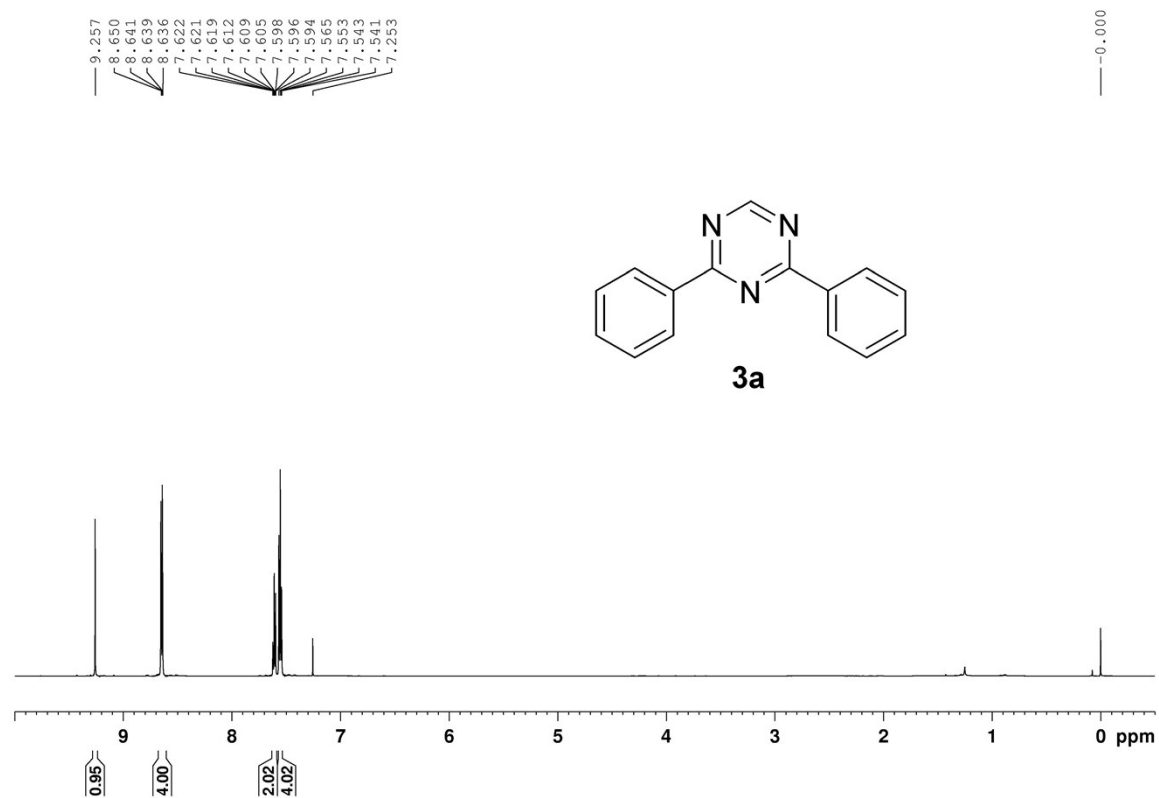
Amidines **1** (0.4 mmol), ClCF₂COONa (1 equiv), 2-methyl-1*H*-benzo[*d*]imidazole (2 equiv) and Cs₂CO₃ (2 equiv) were added to a 10 mL Schlenk tube, followed by addition of CH₃CN (1 mL). The mixture was stirred at 120 °C for 24 h. The solution was then cooled to r.t., quenched by water and extracted with EtOAc (3×10 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford **3a** in 70% yield. Meanwhile, trace amount of residue was dissolved in CH₂Cl₂ and analyzed by GC-MS.

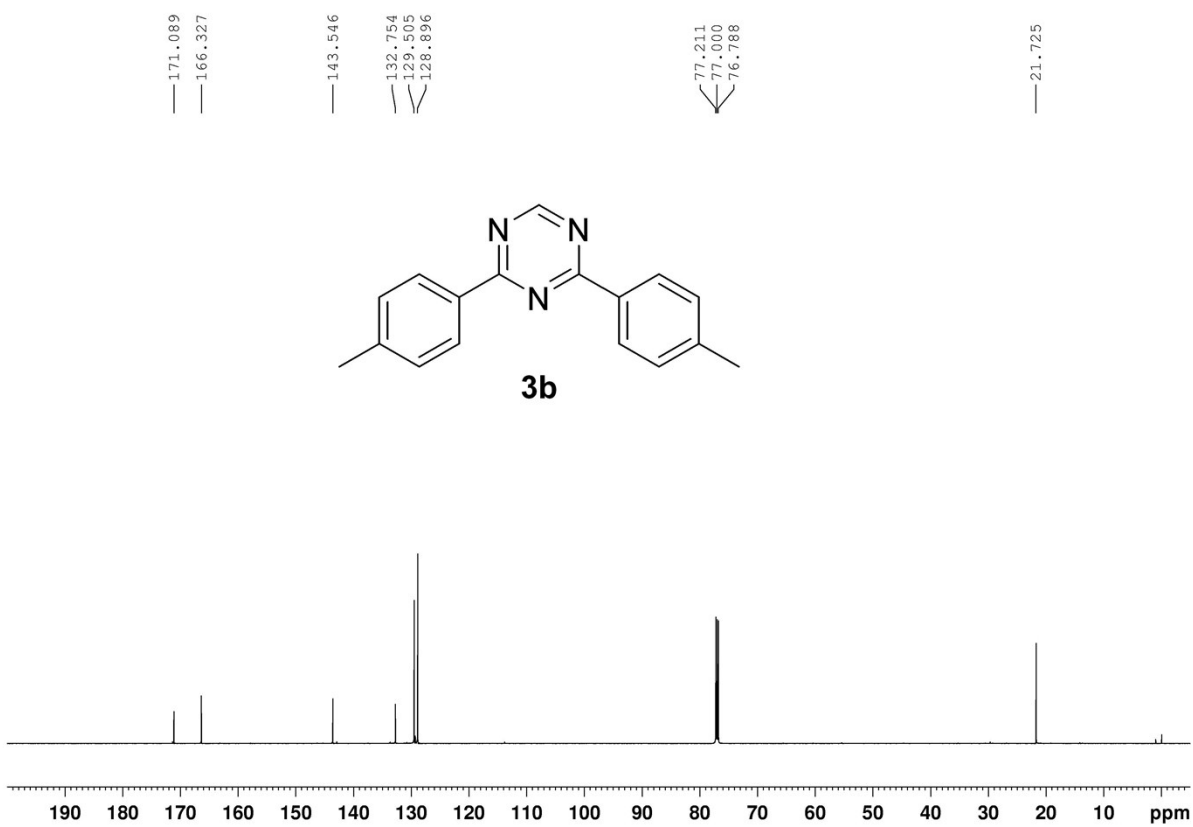
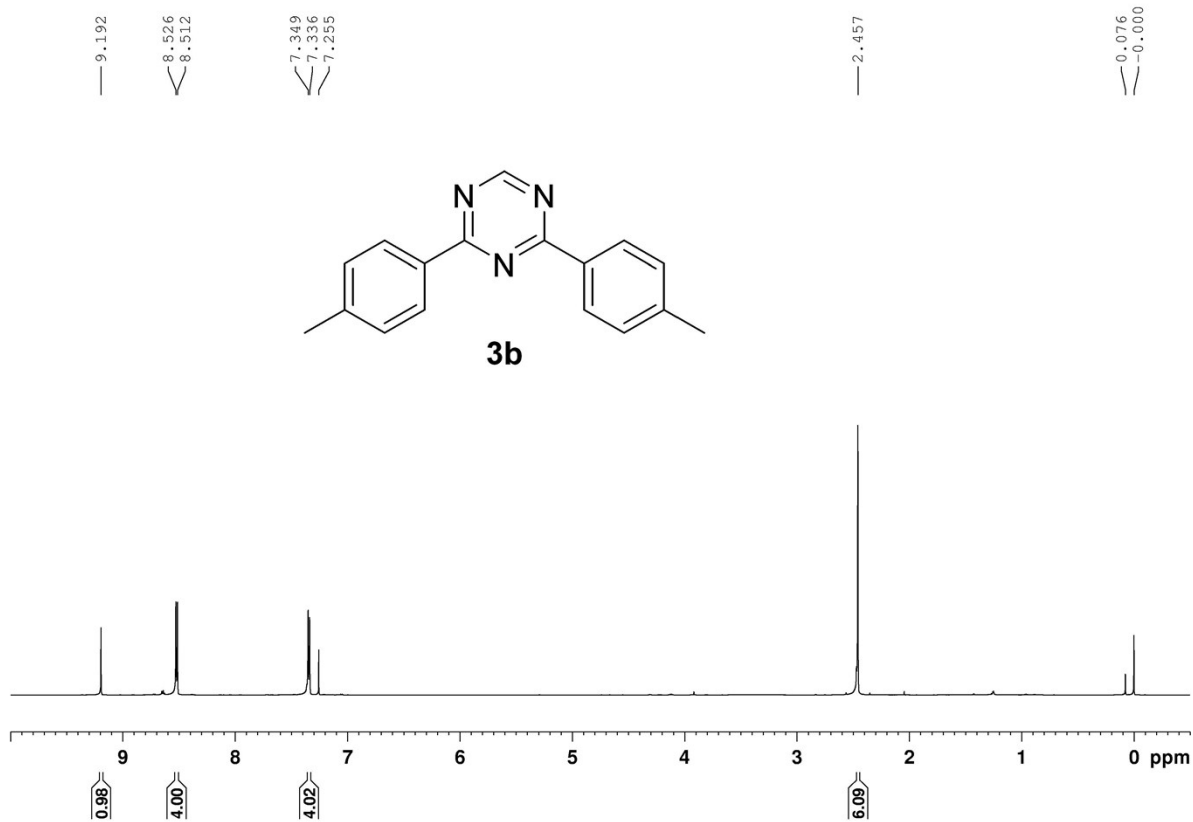


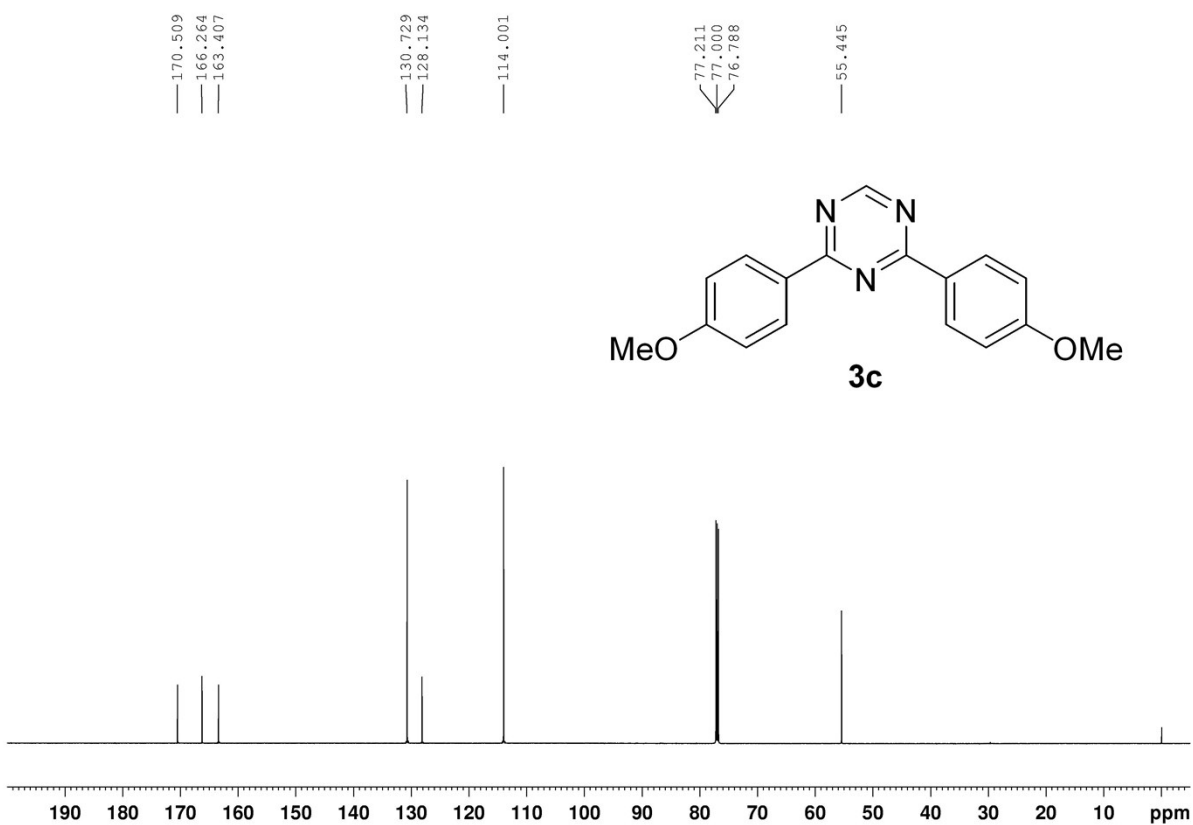
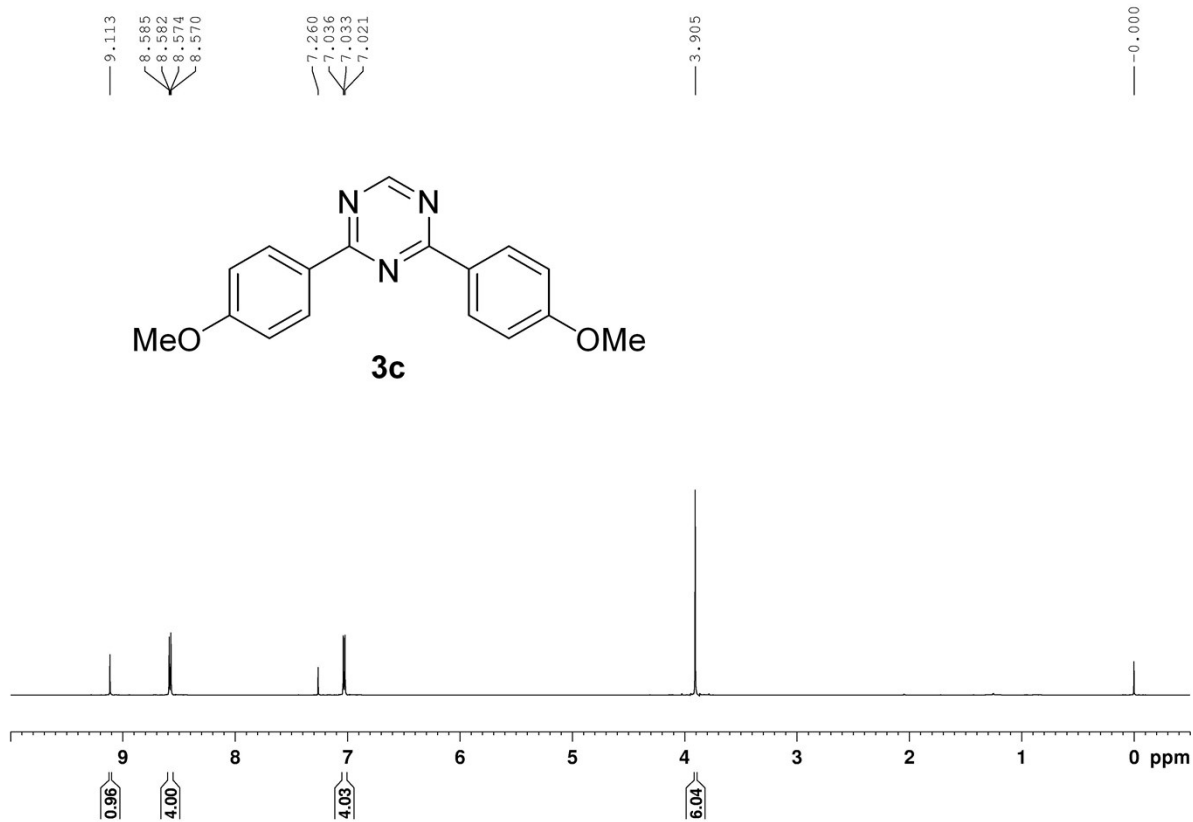
References

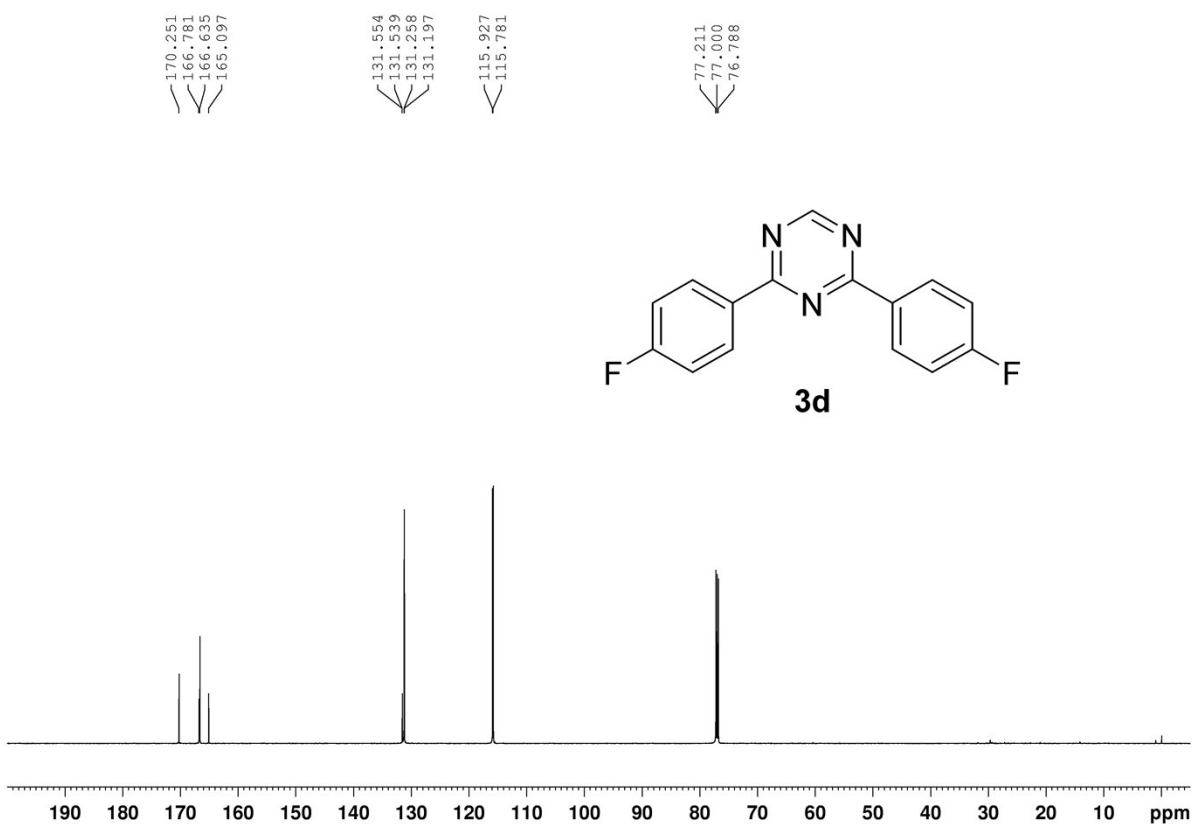
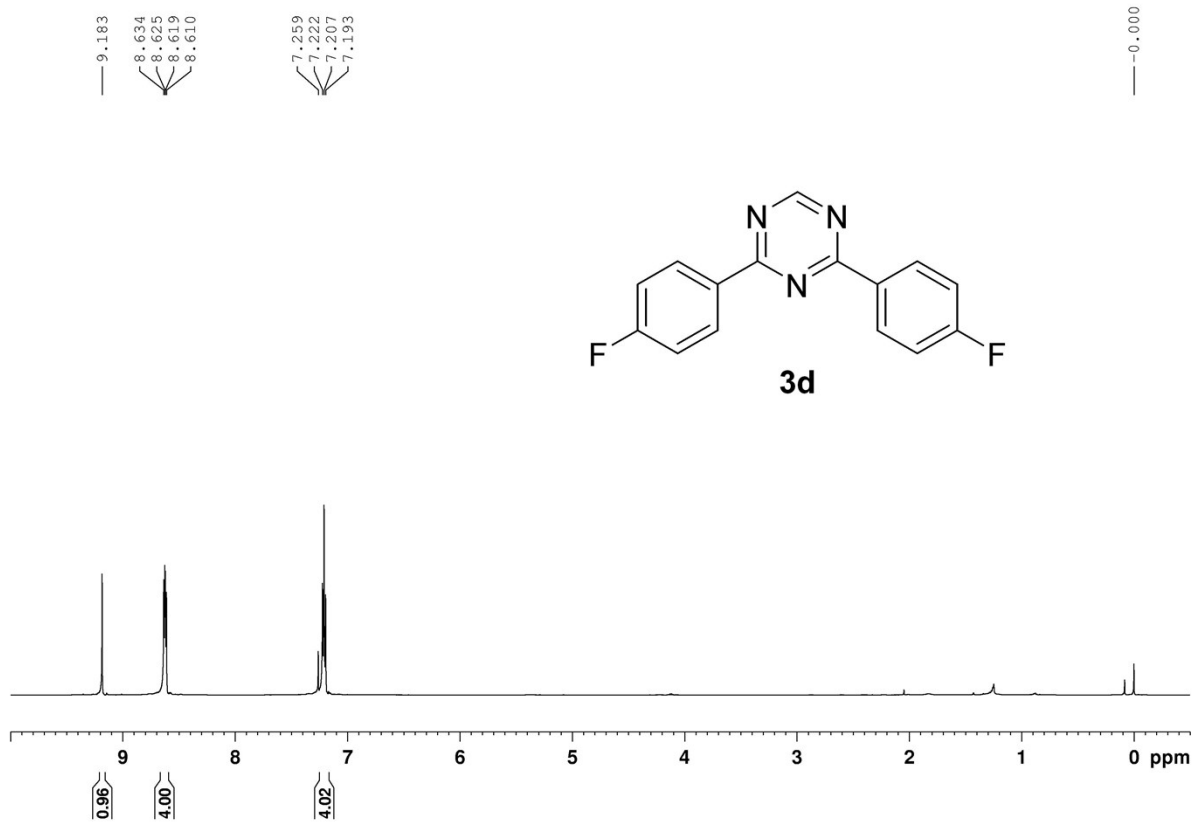
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2. Y. Yan, C. Cui, J. Wang, S. Li, Y. Liu, *Adv. Synth. Catal.* **2019**, *361*, 1166.
3. X. Lu, X. Xin, B. Wan, *Tetrahedron Lett.* **2018**, *59*, 361.
4. Y. Bao, Y. Yan, K. Xu, J. Su, Z. Zha, Z. Wang, *J. Org. Chem.* **2015**, *80*, 47362.

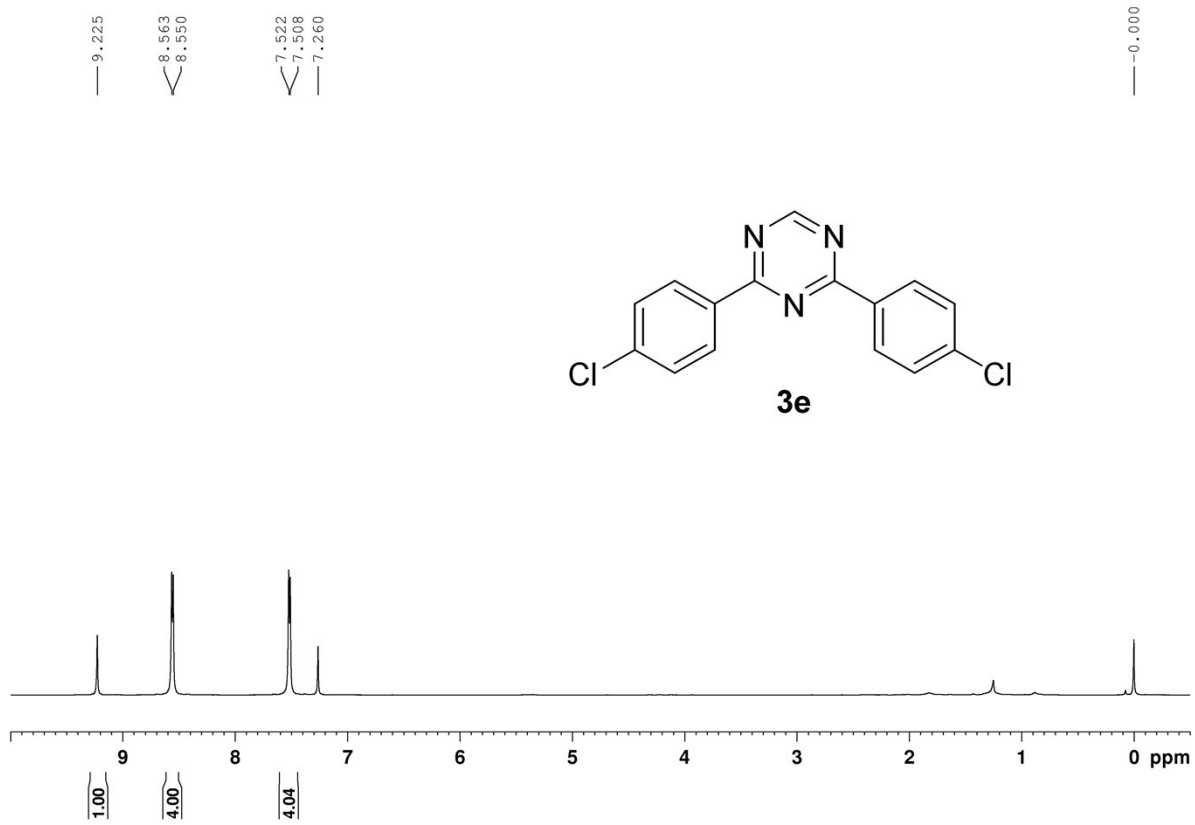
^1H NMR and ^{13}C NMR Spectra

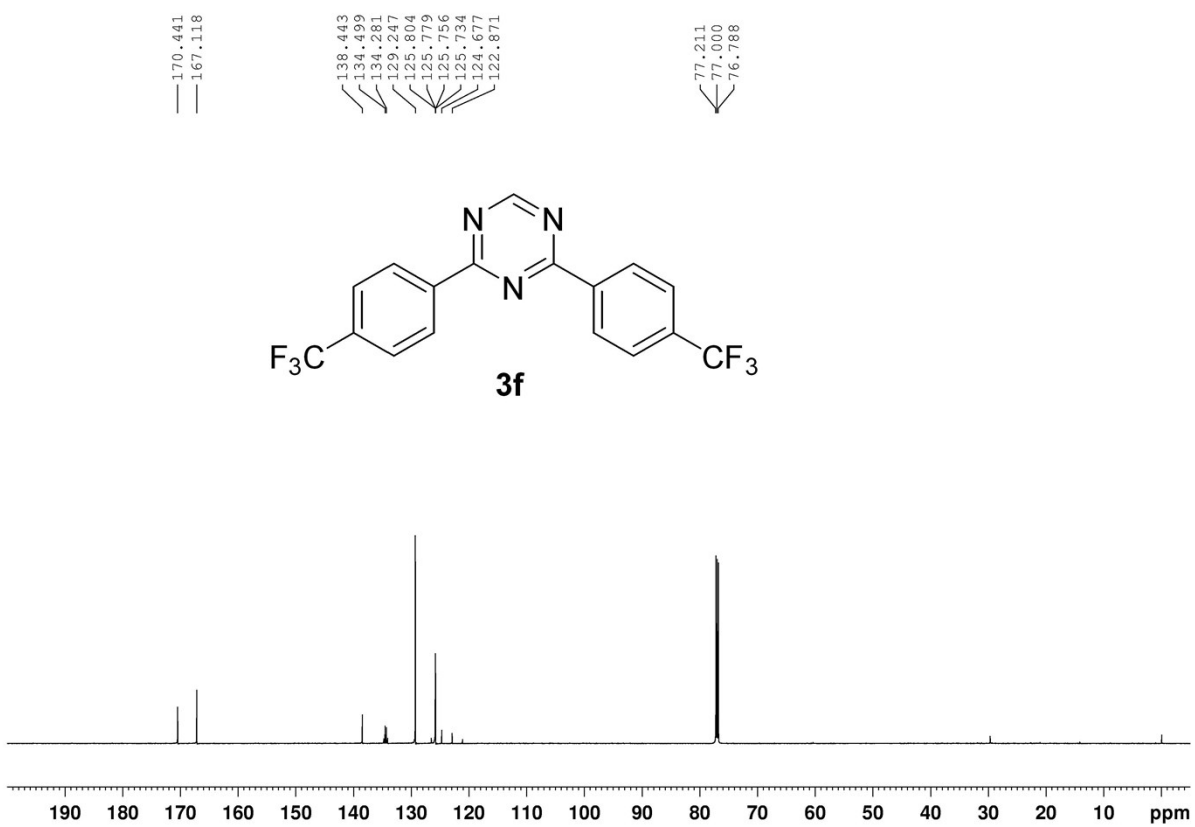
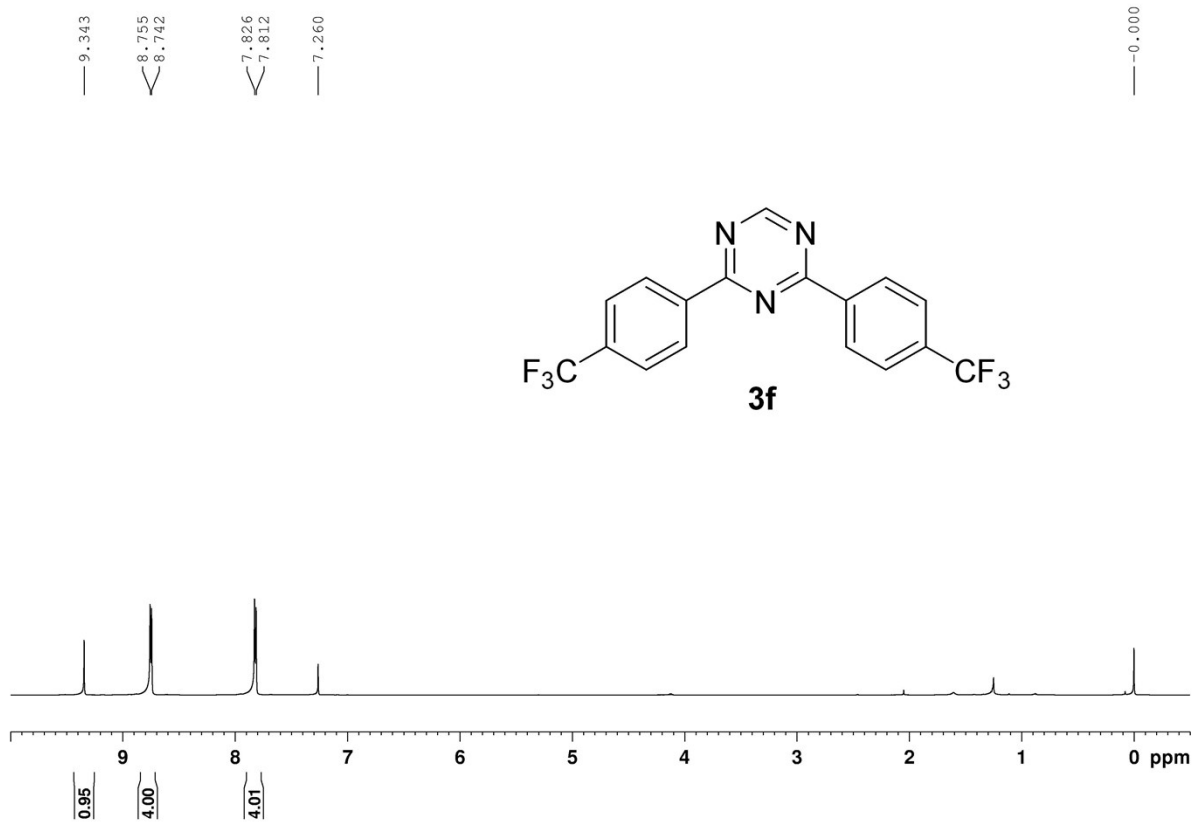


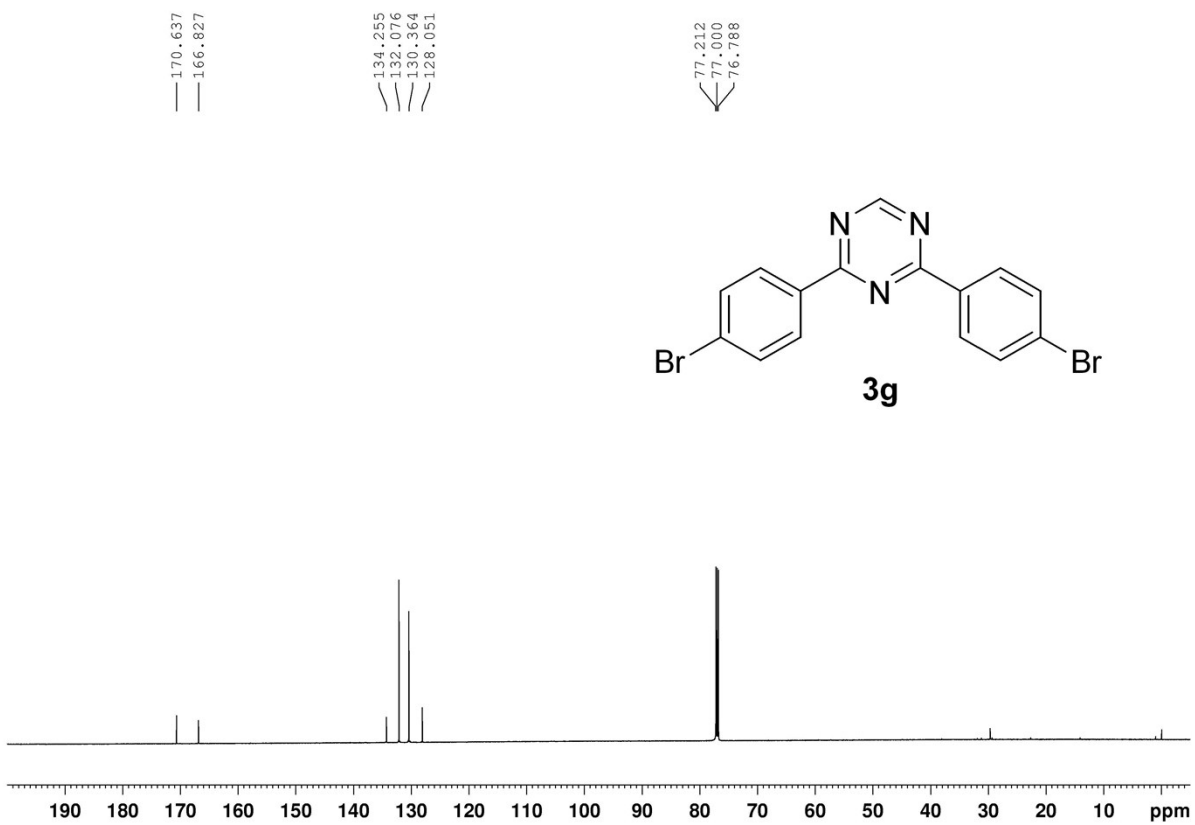
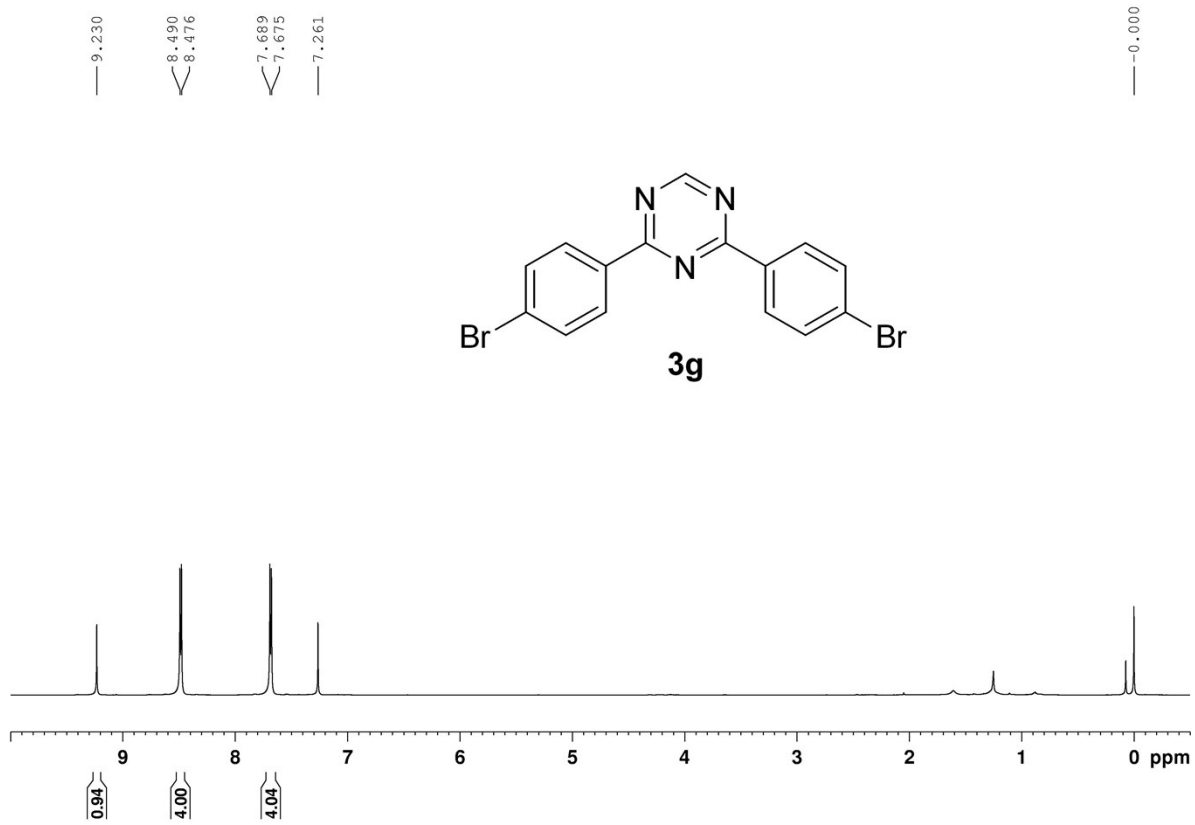


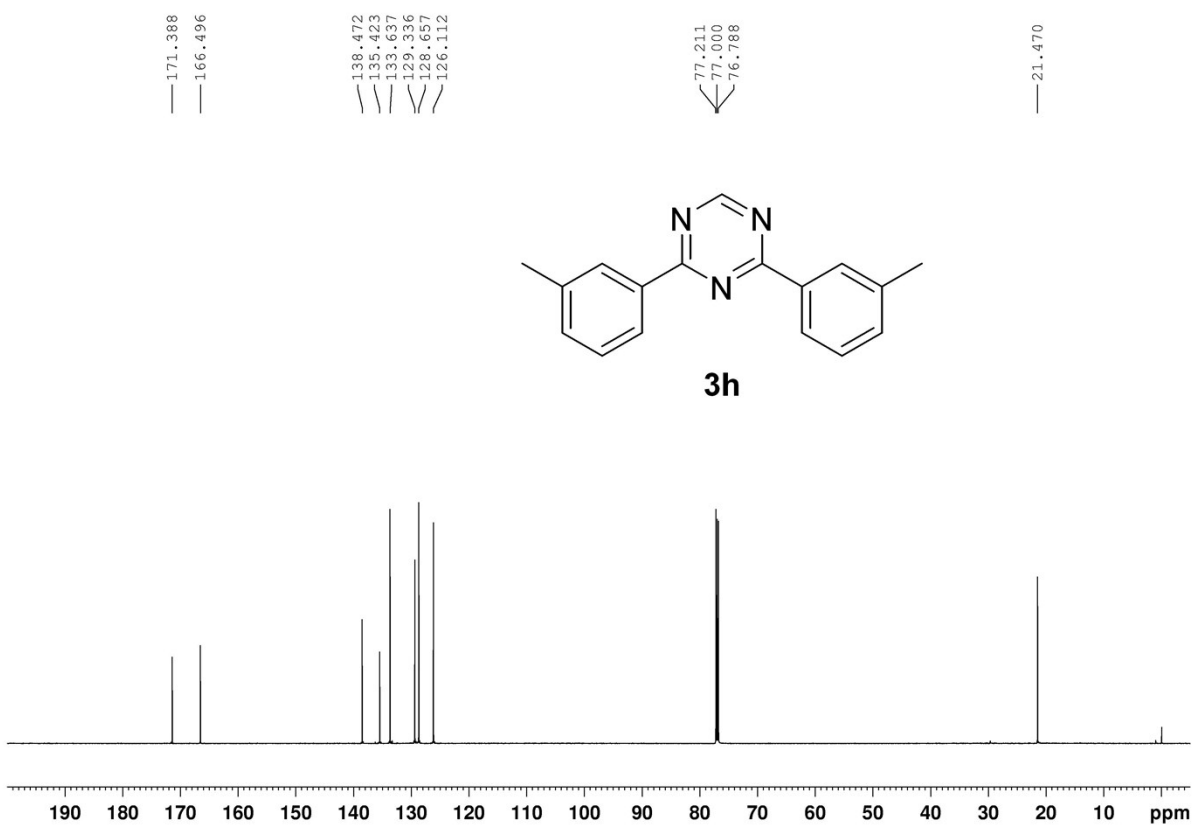
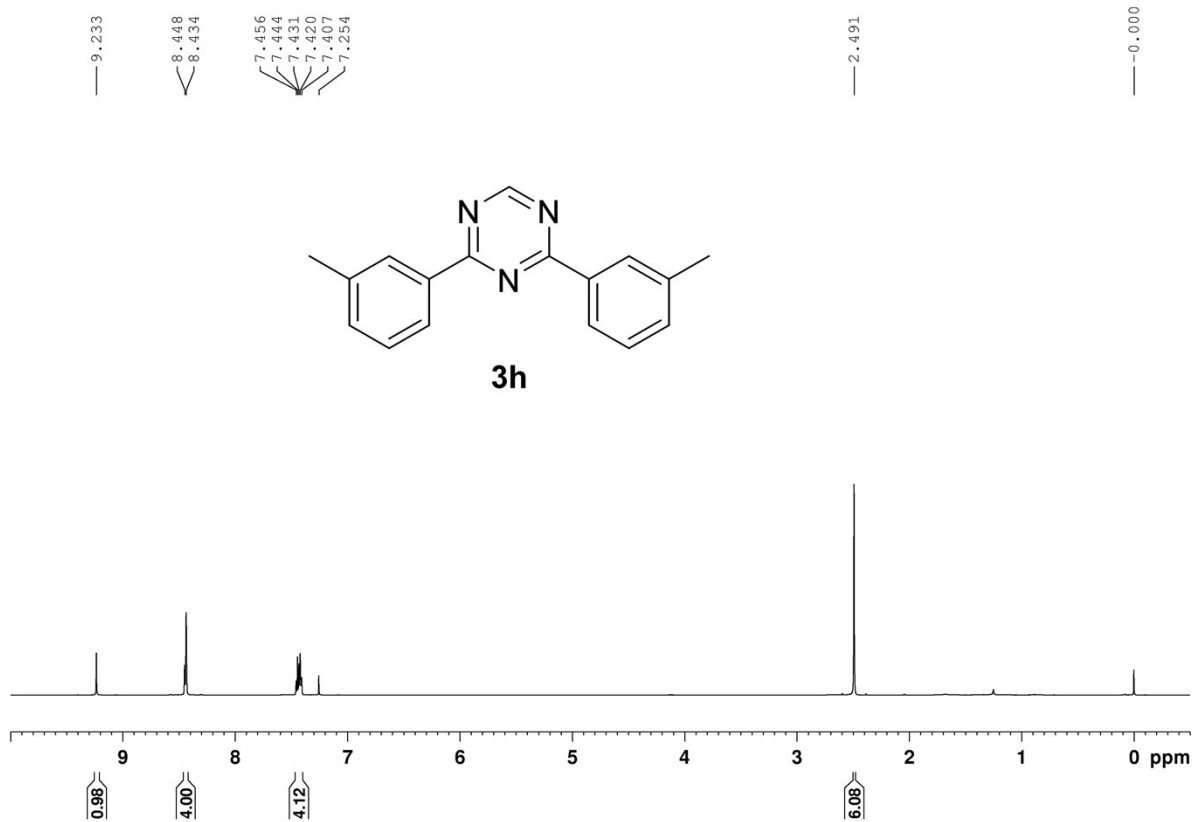


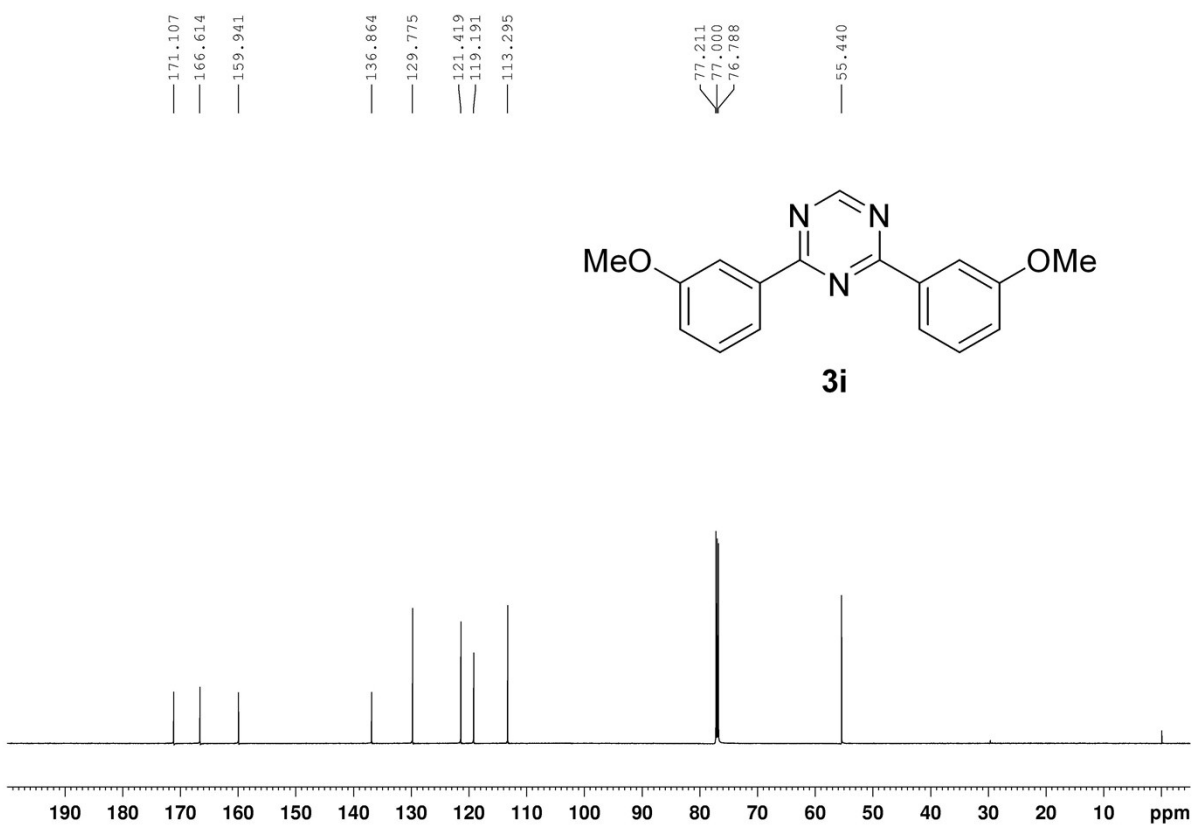
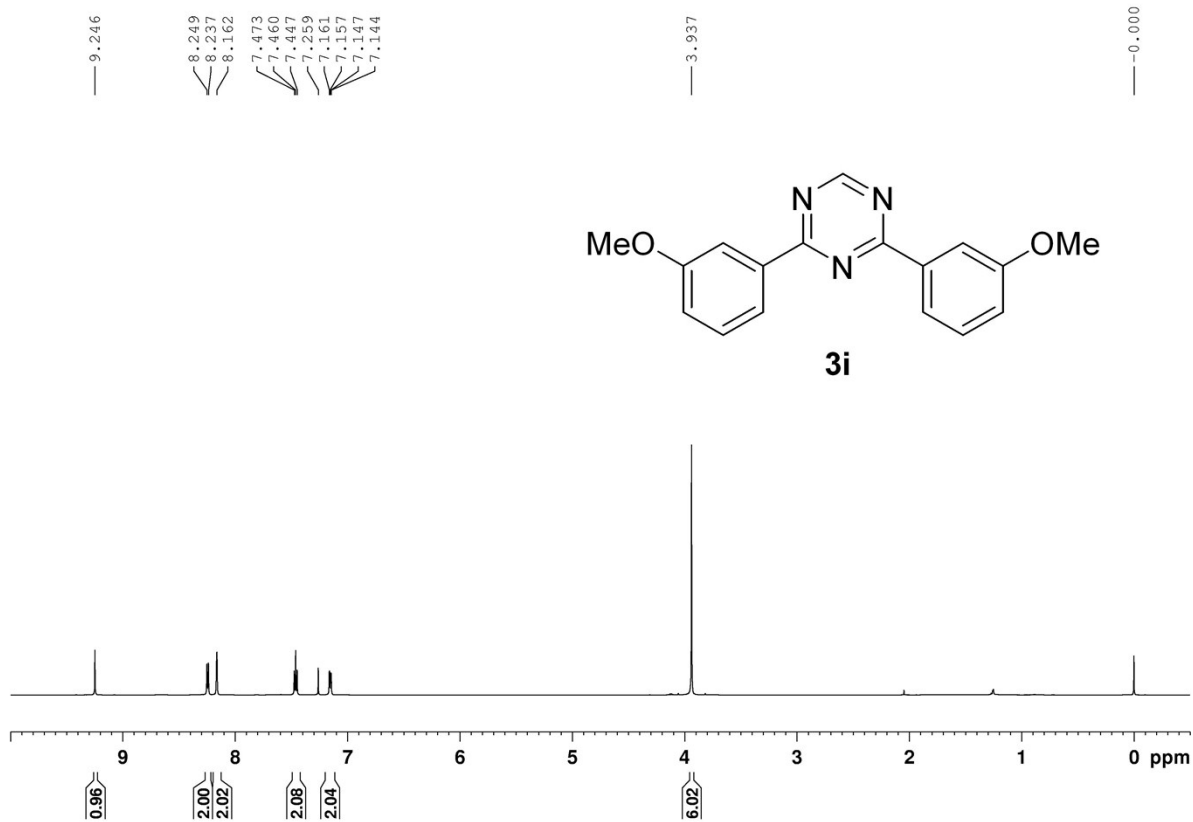


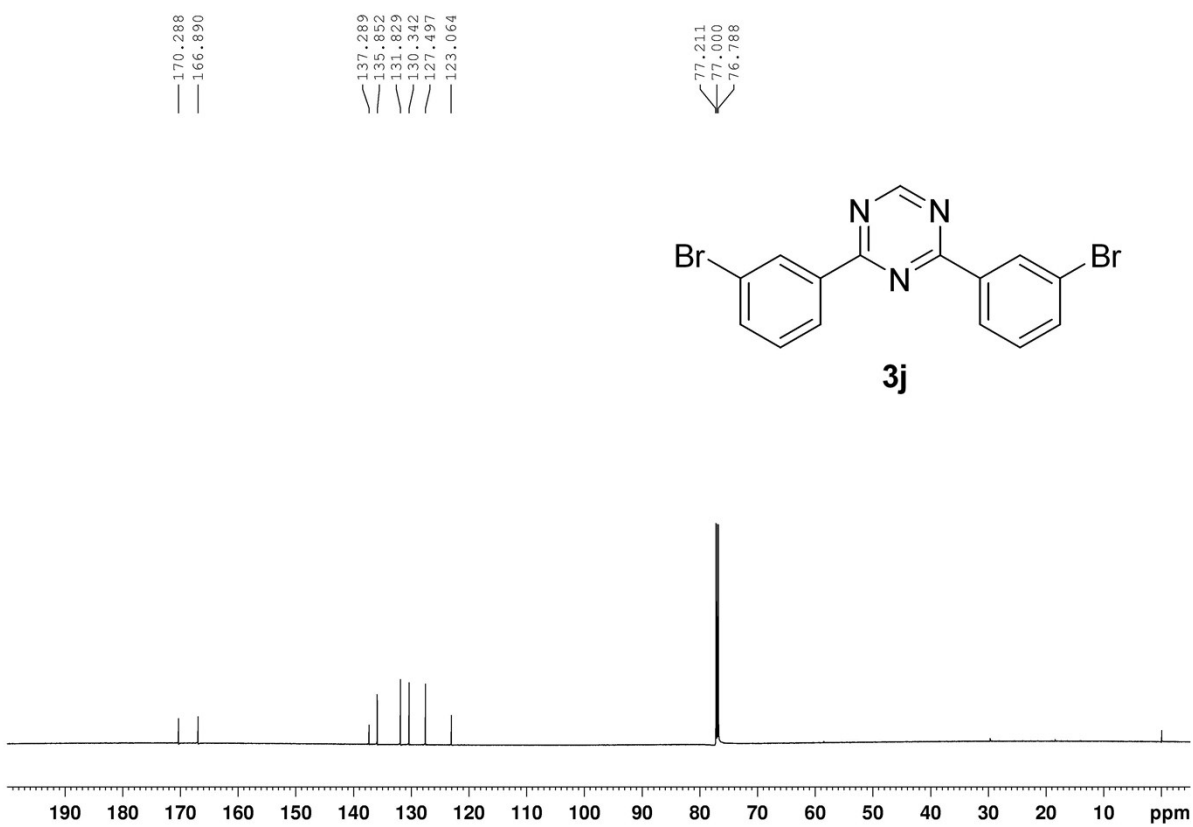
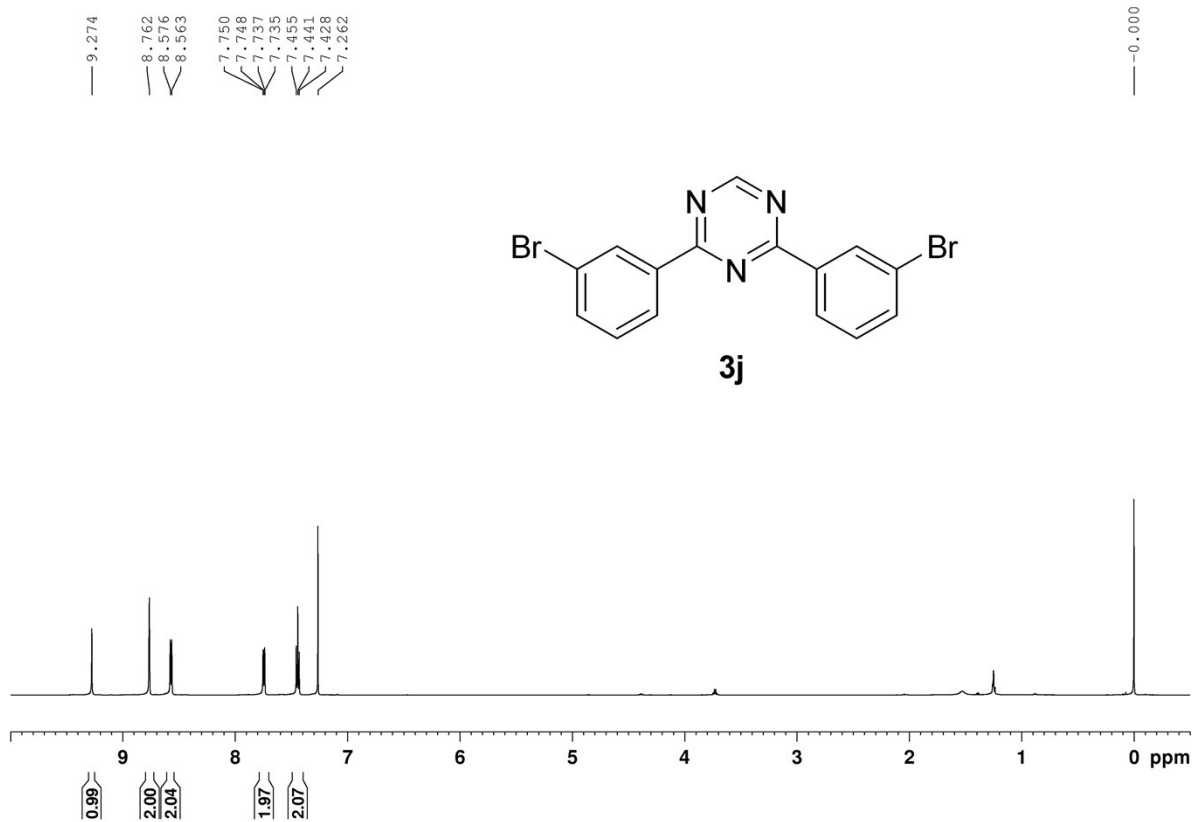


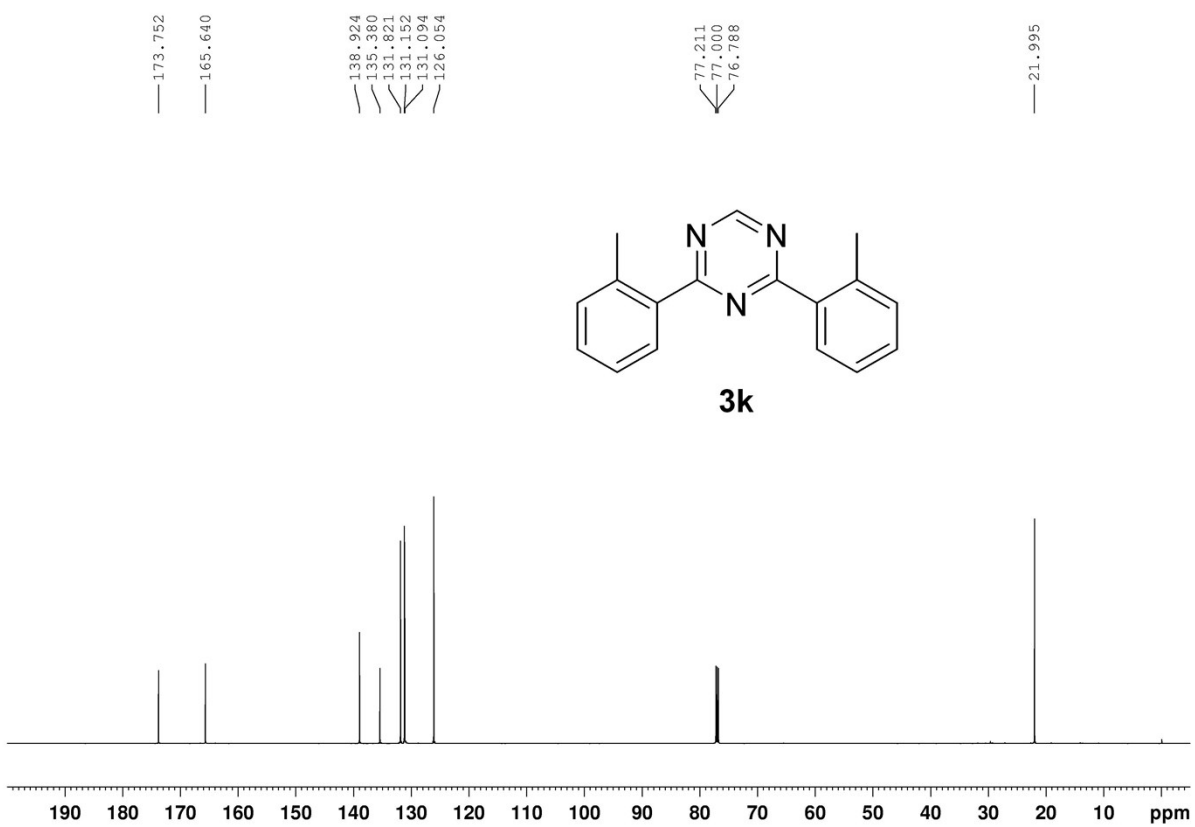
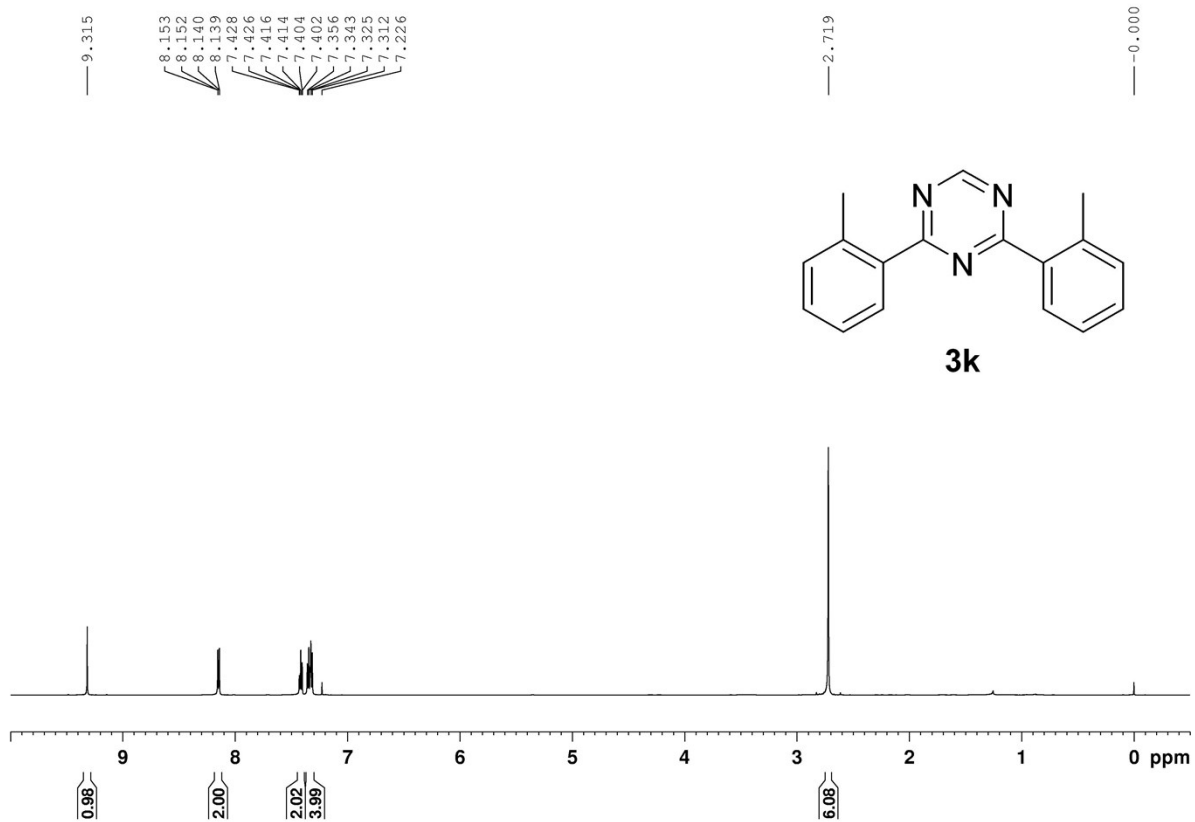


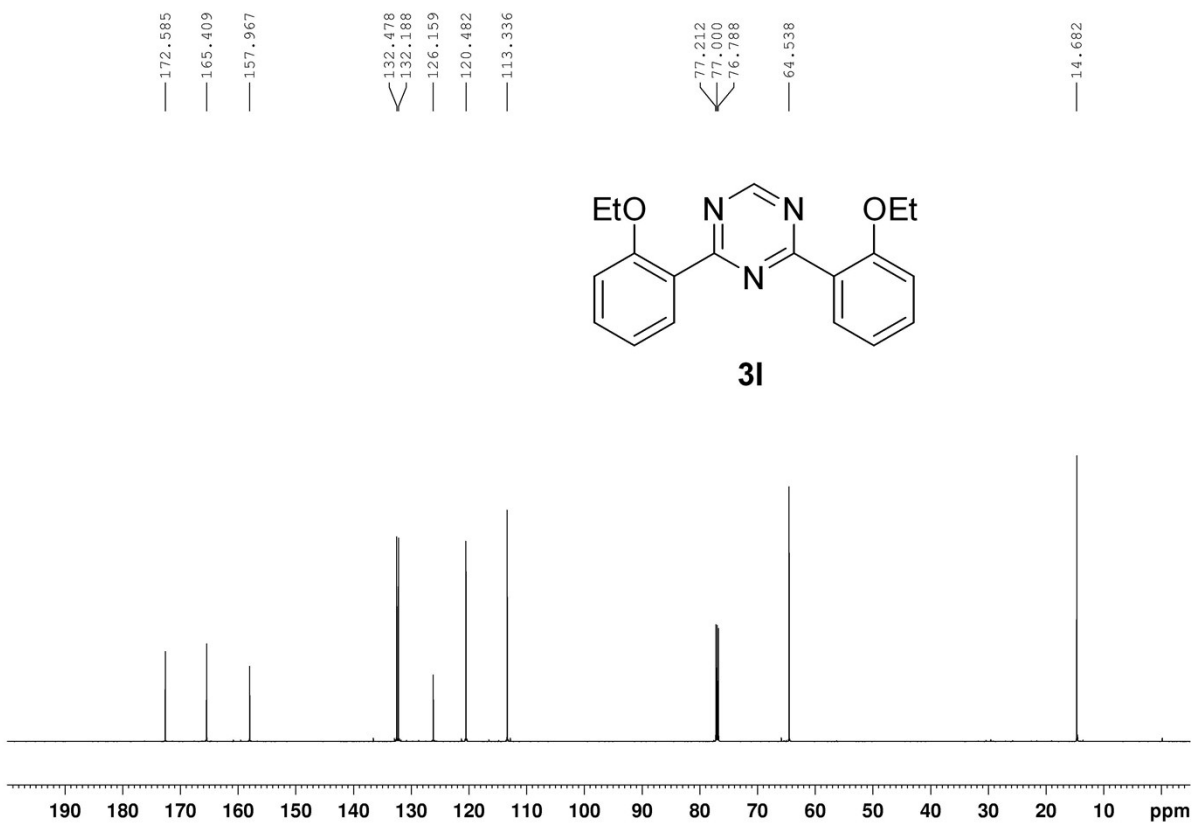
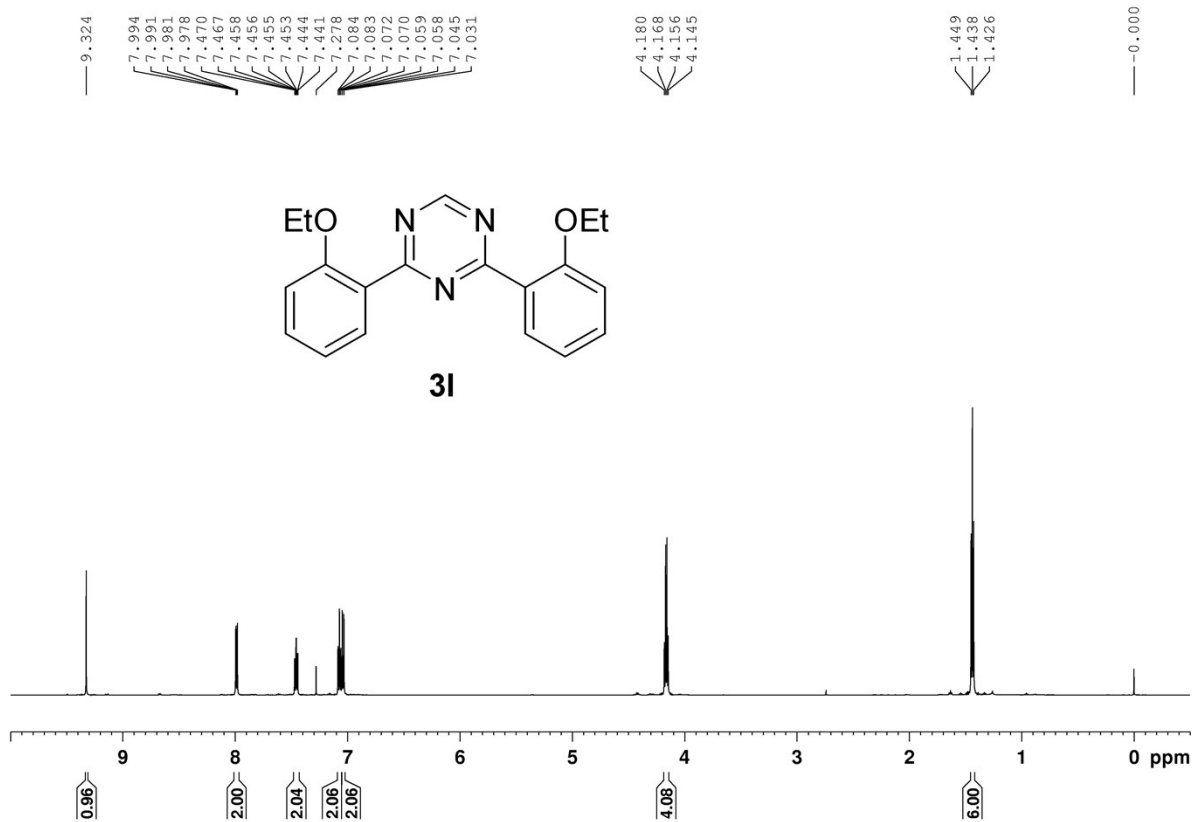


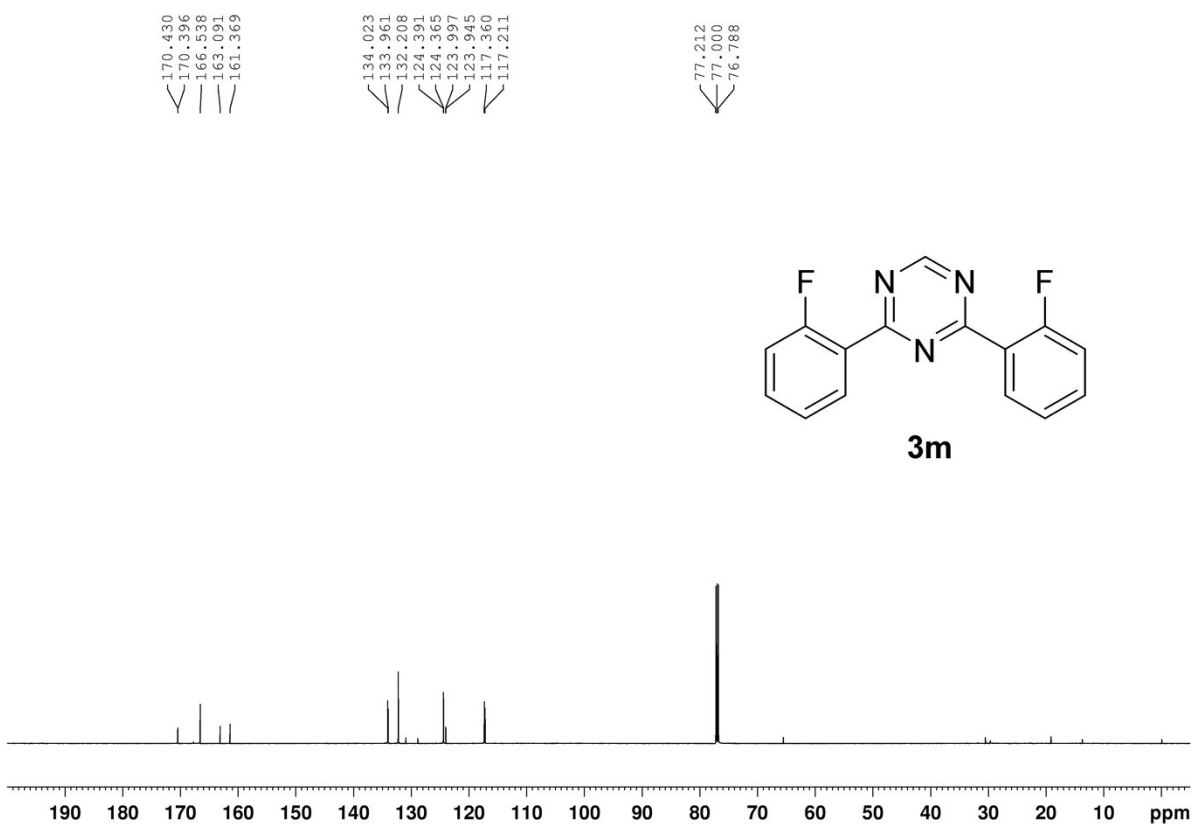
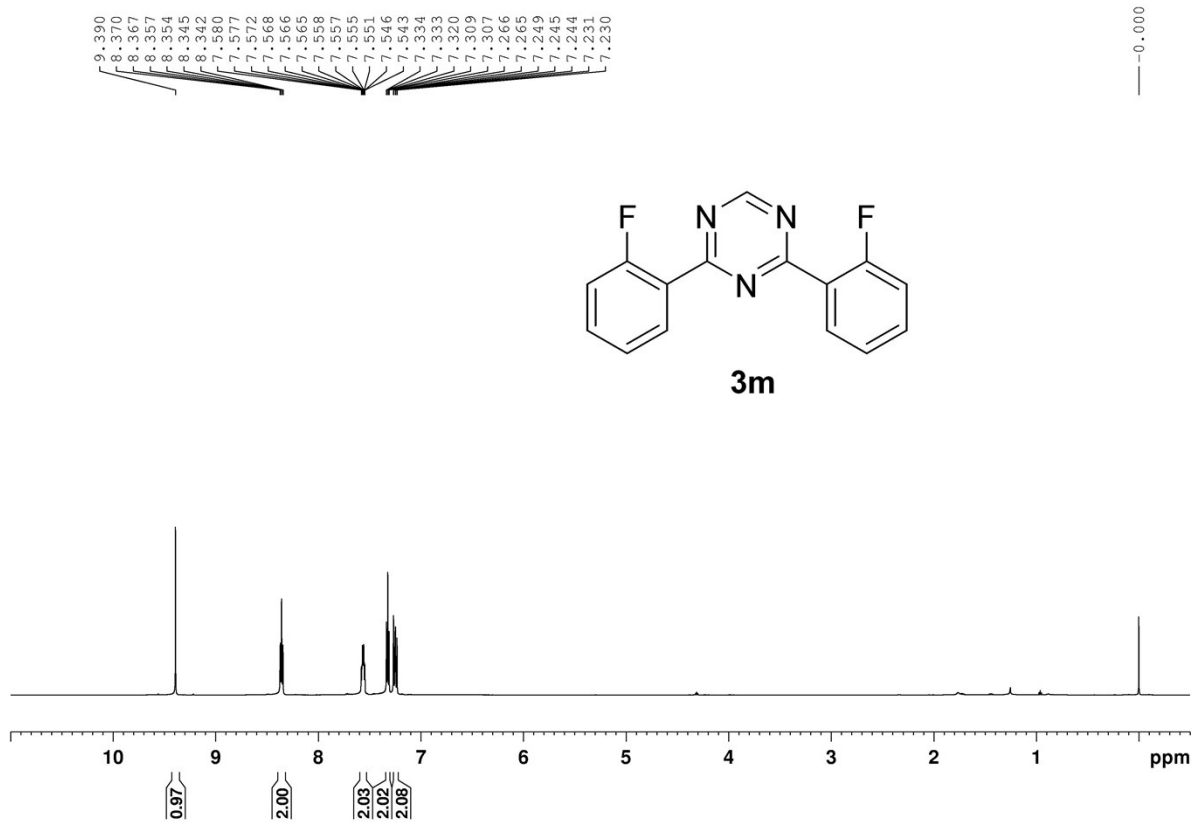


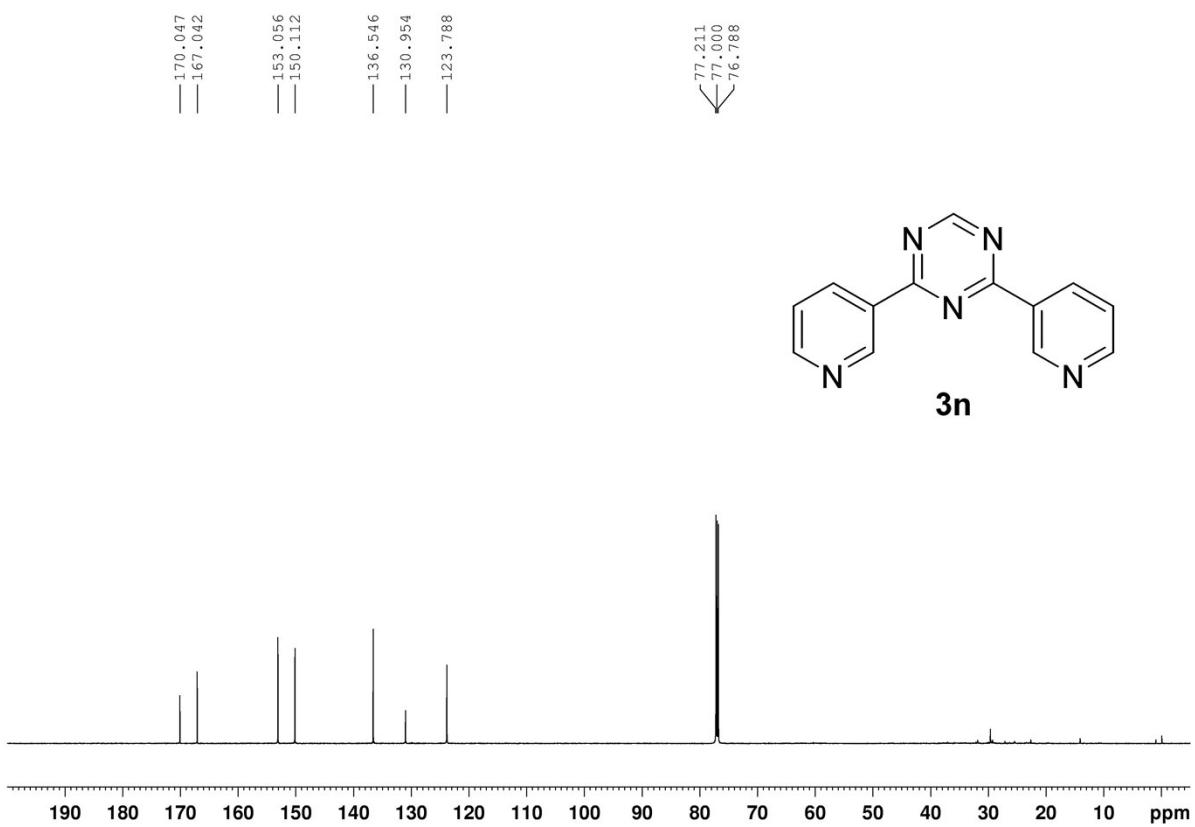
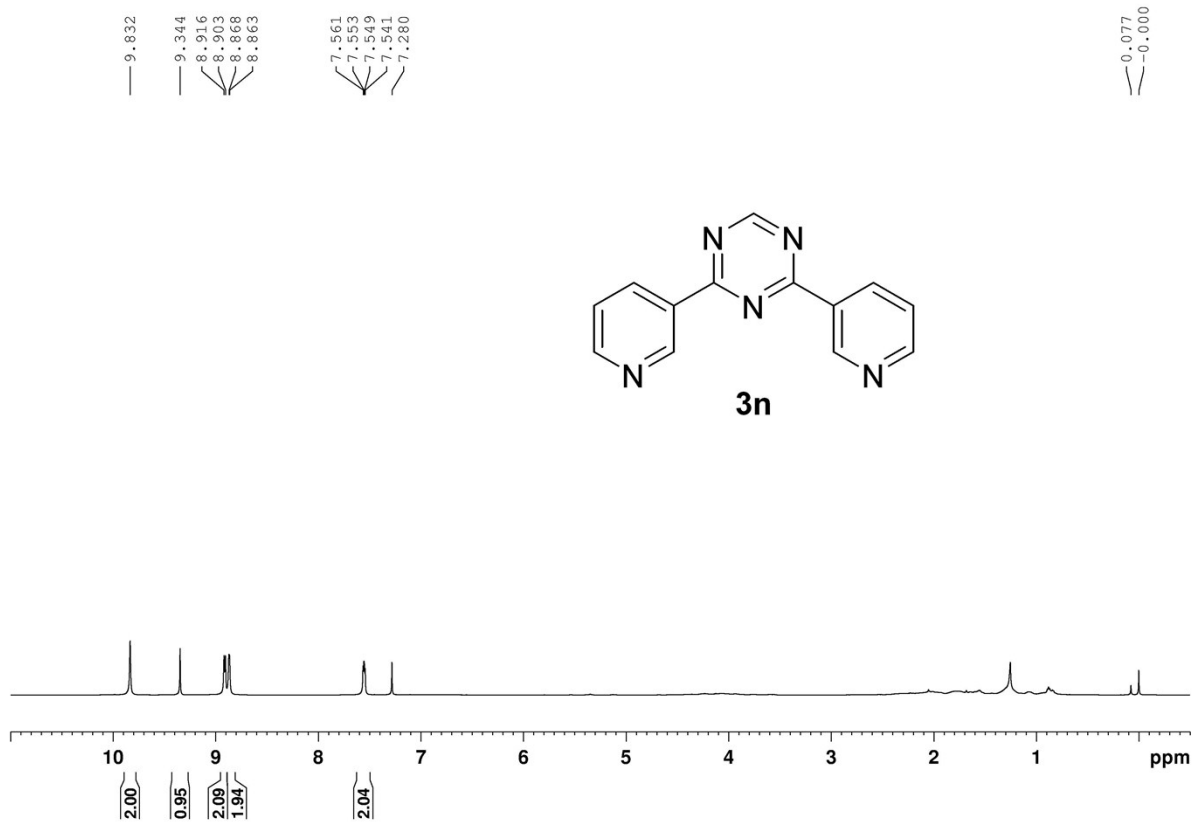


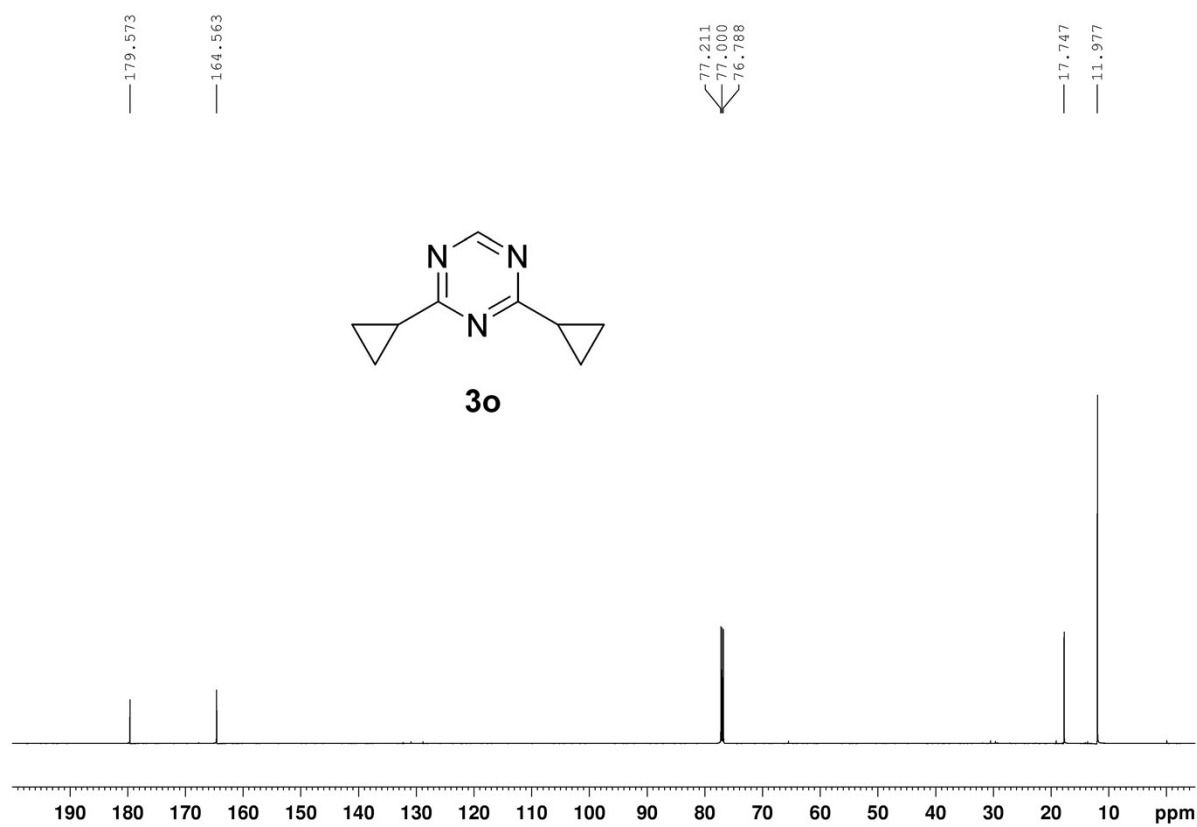
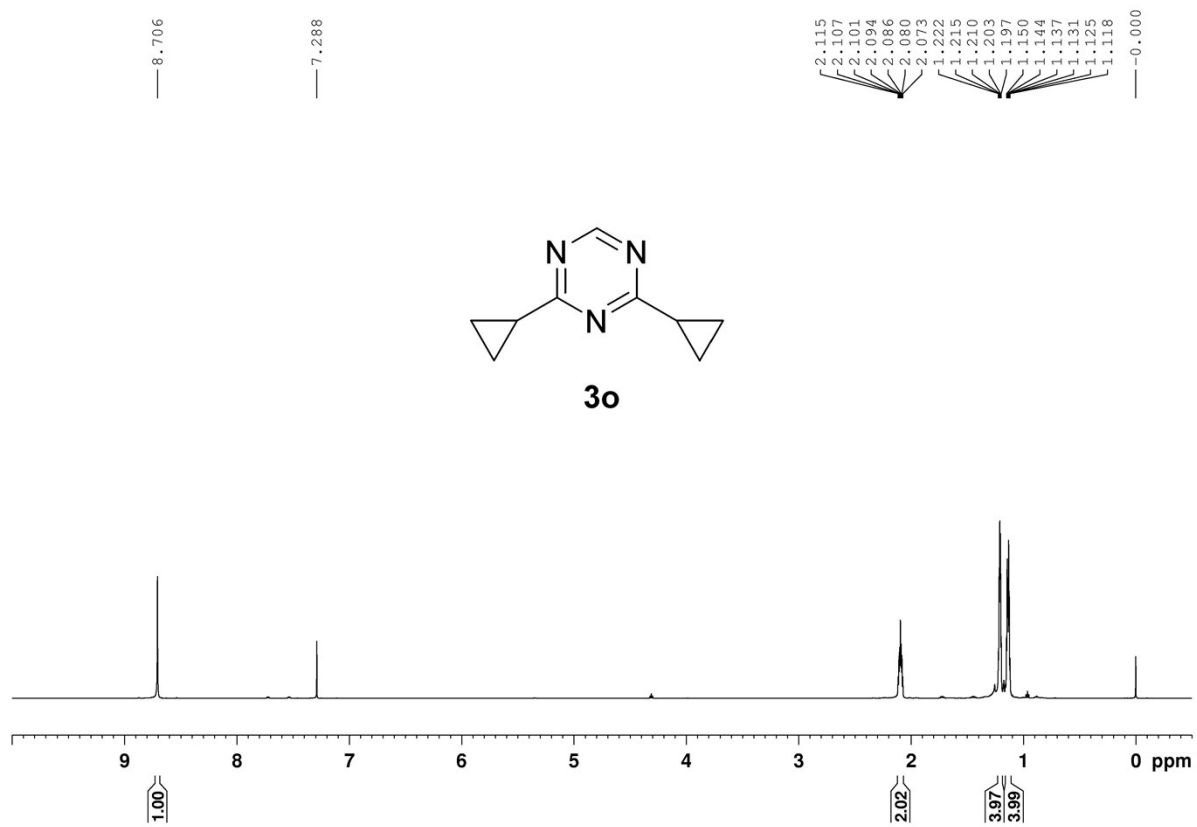


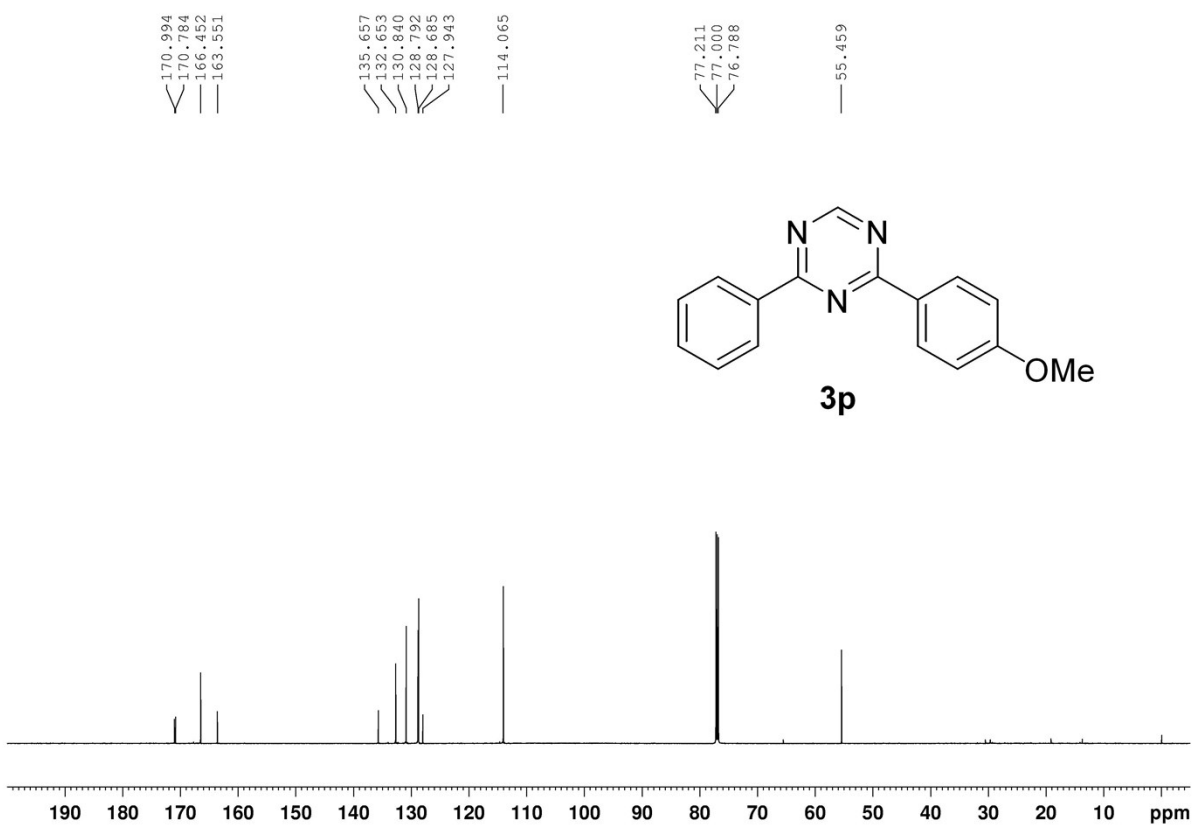
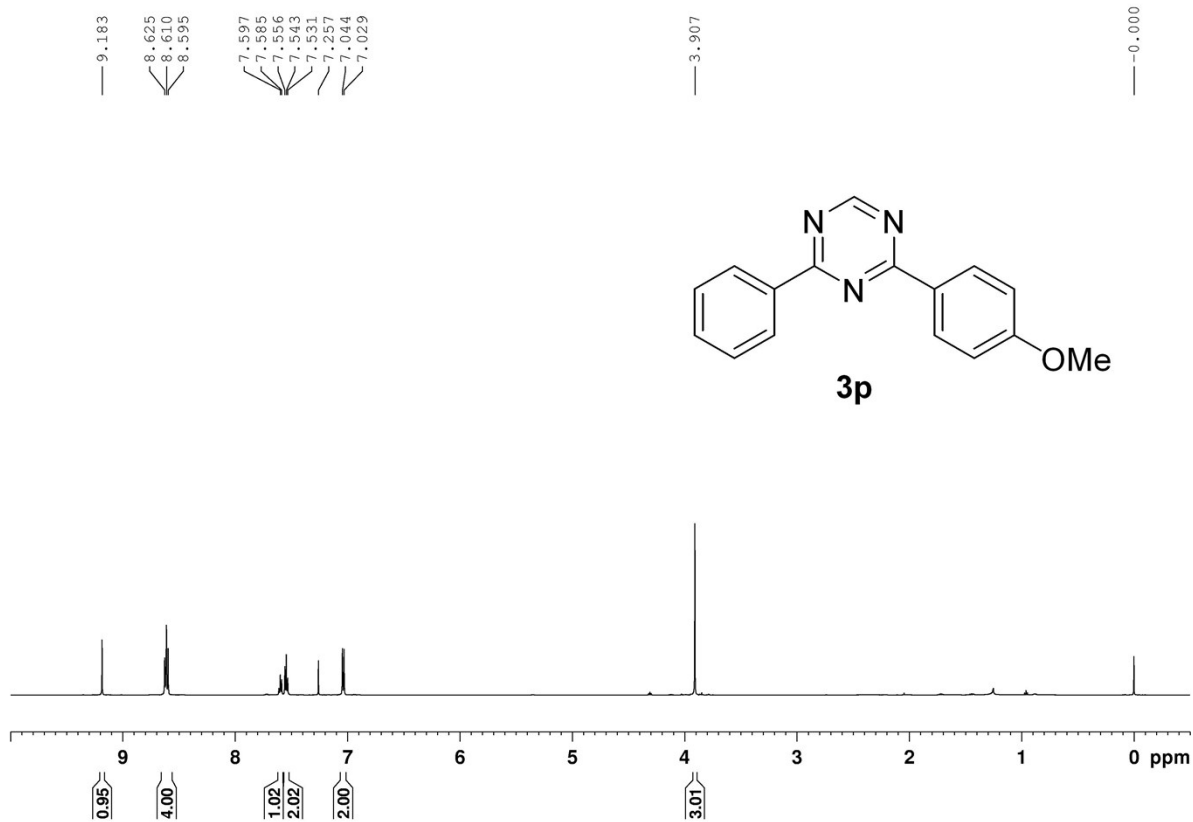


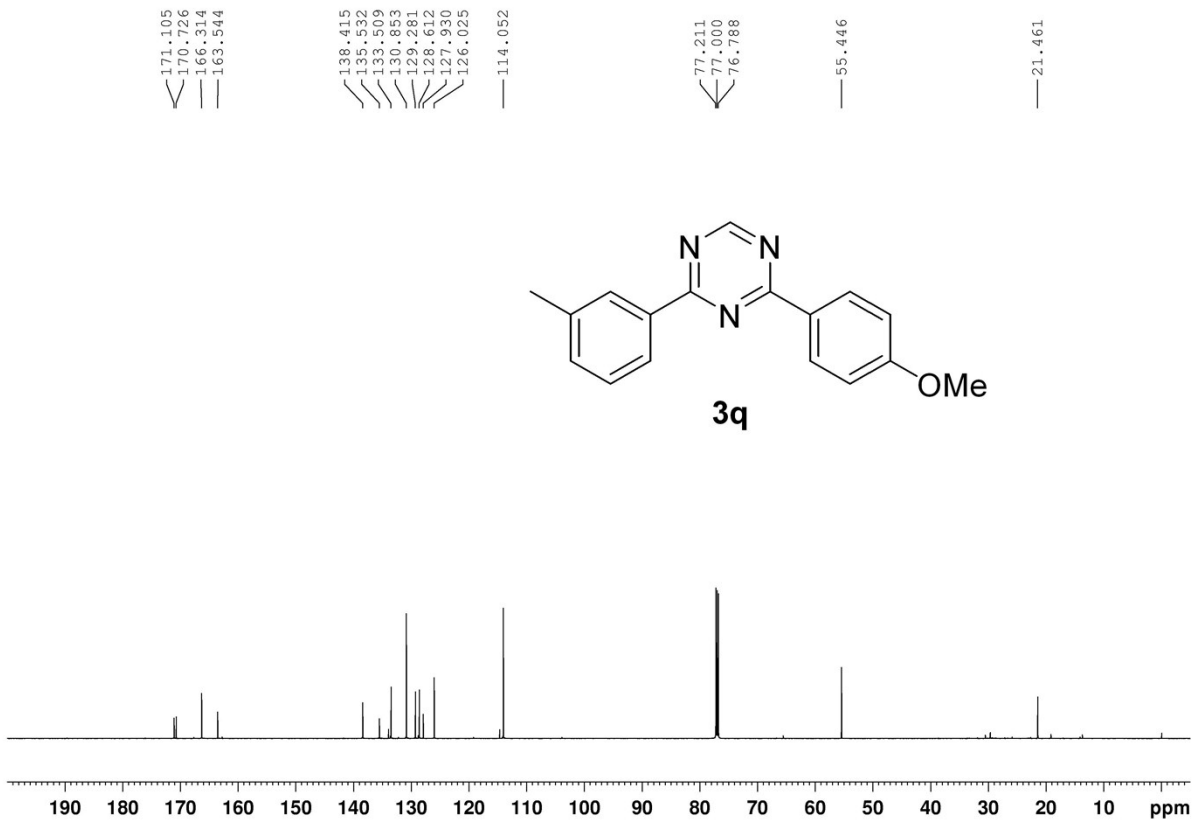
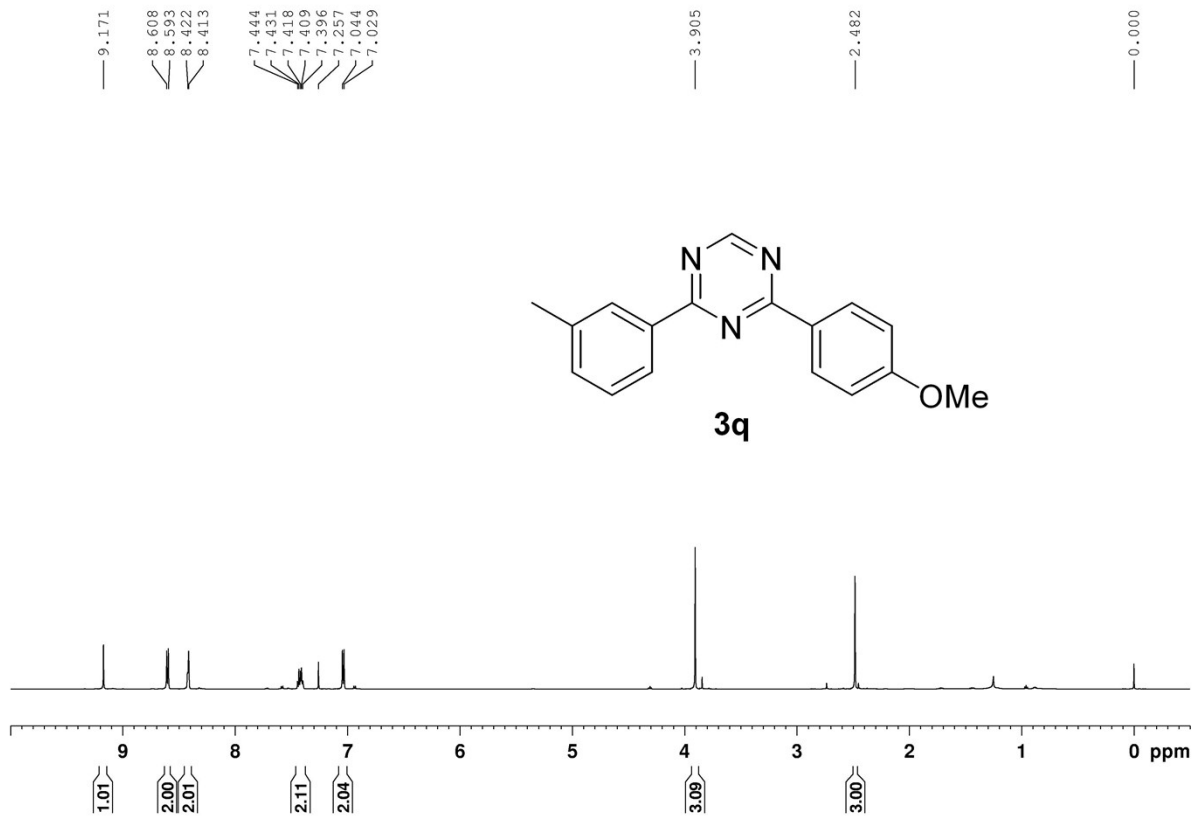


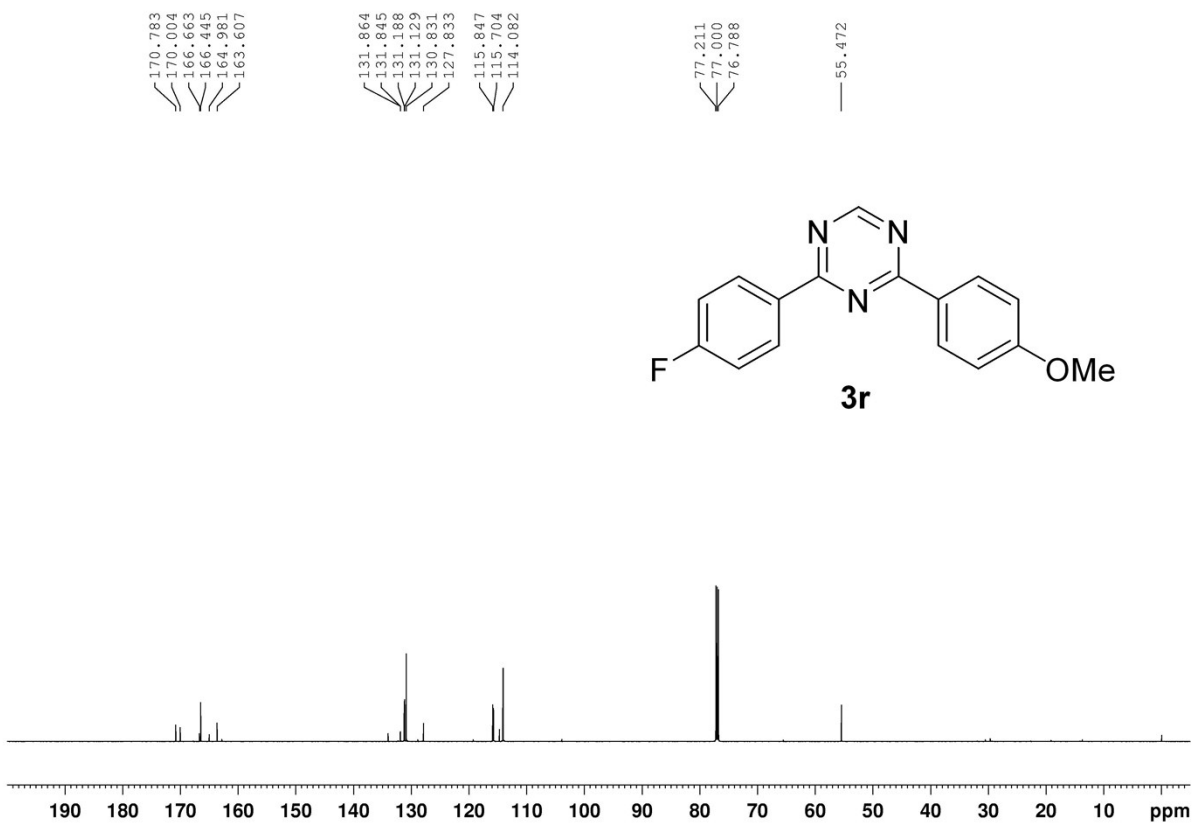
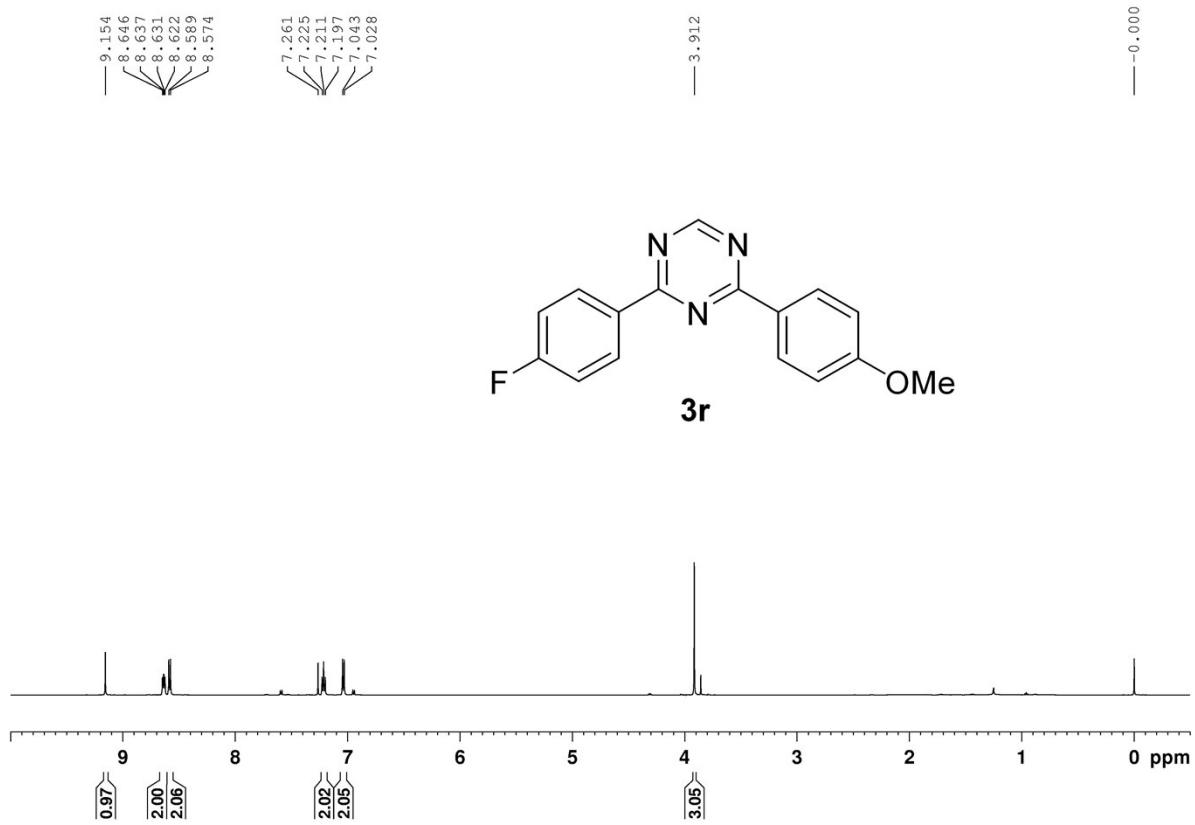


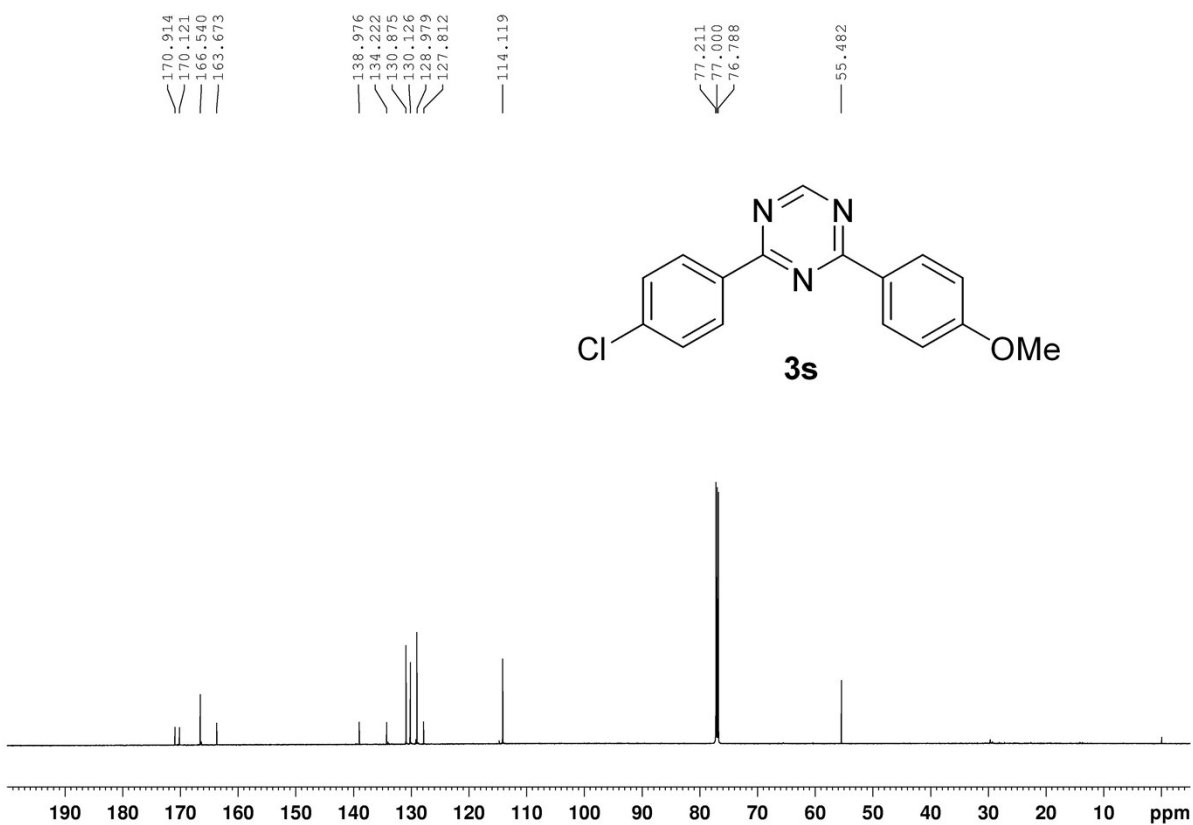
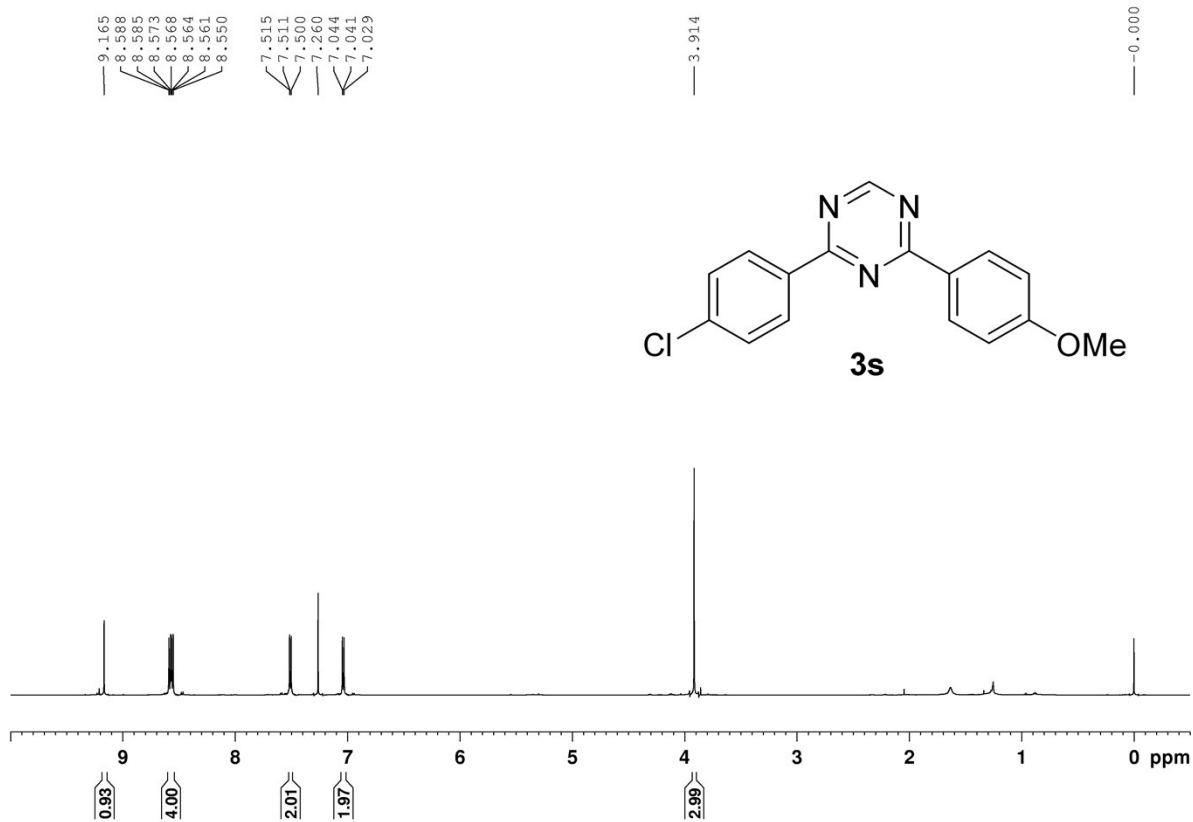


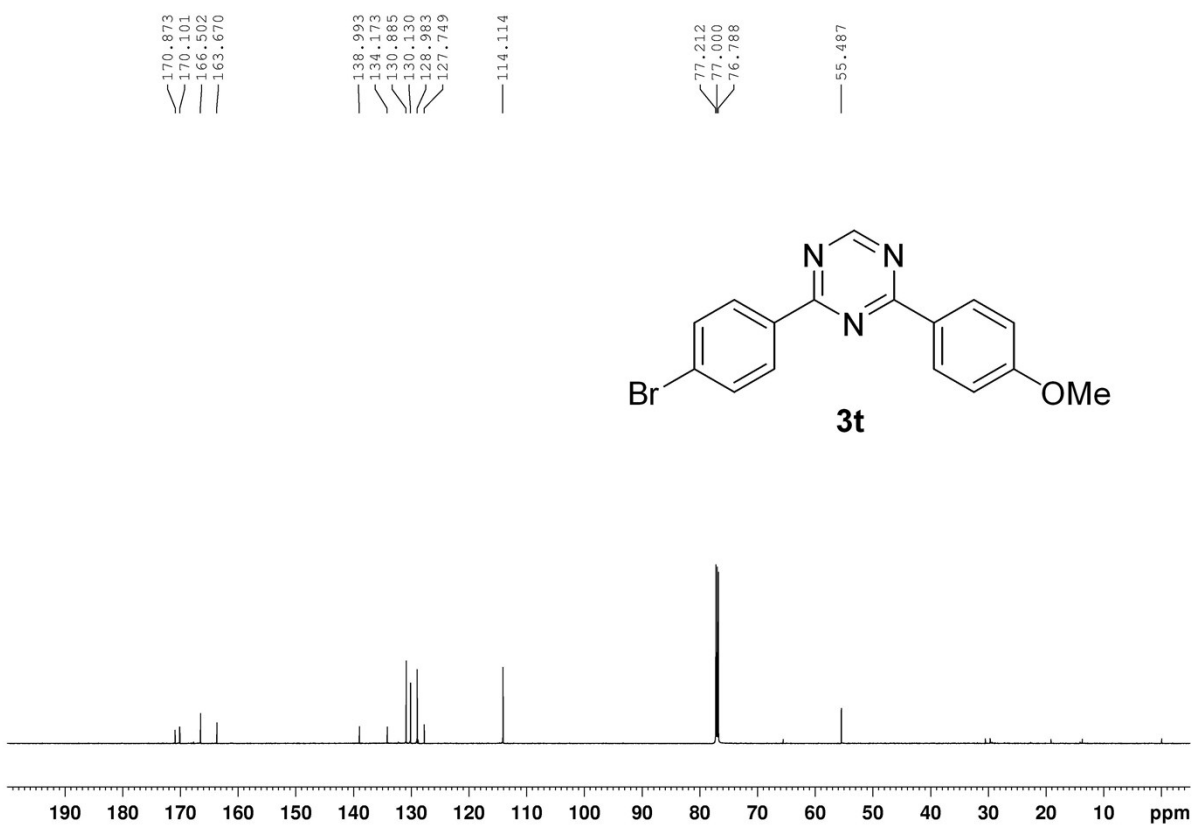
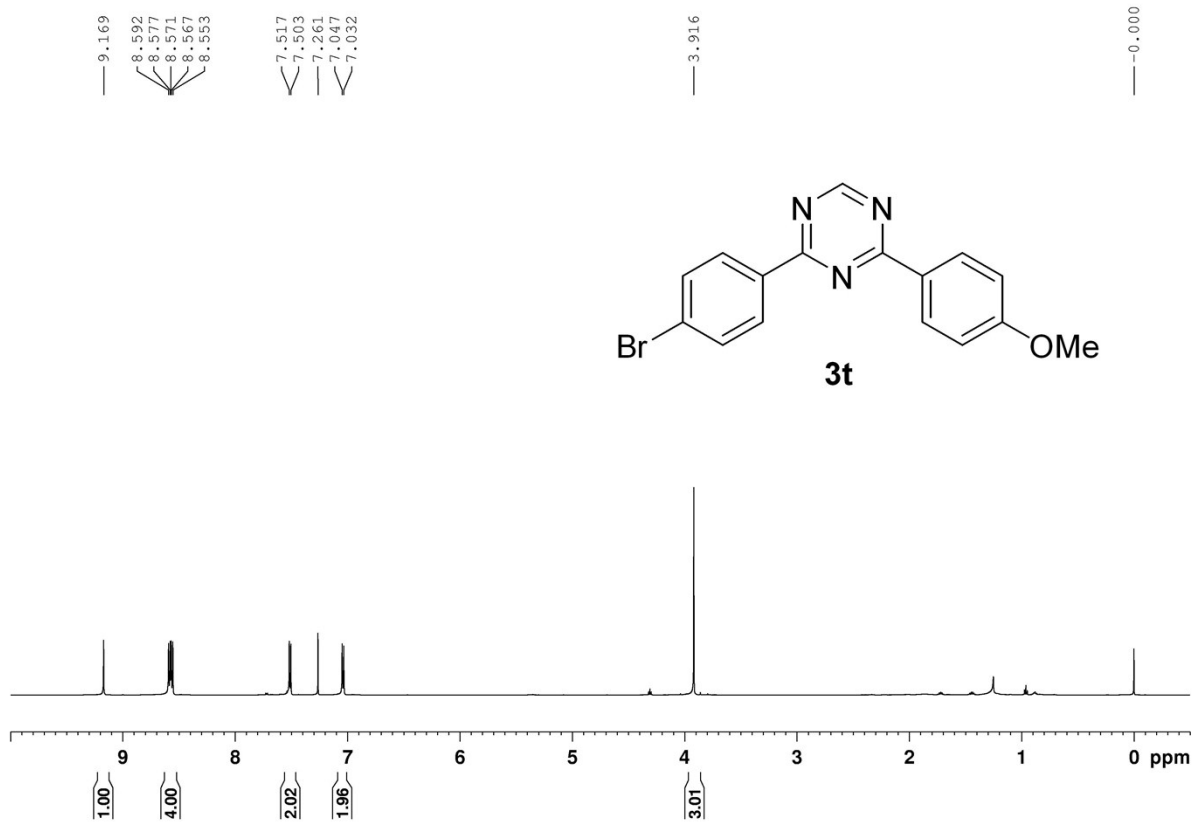


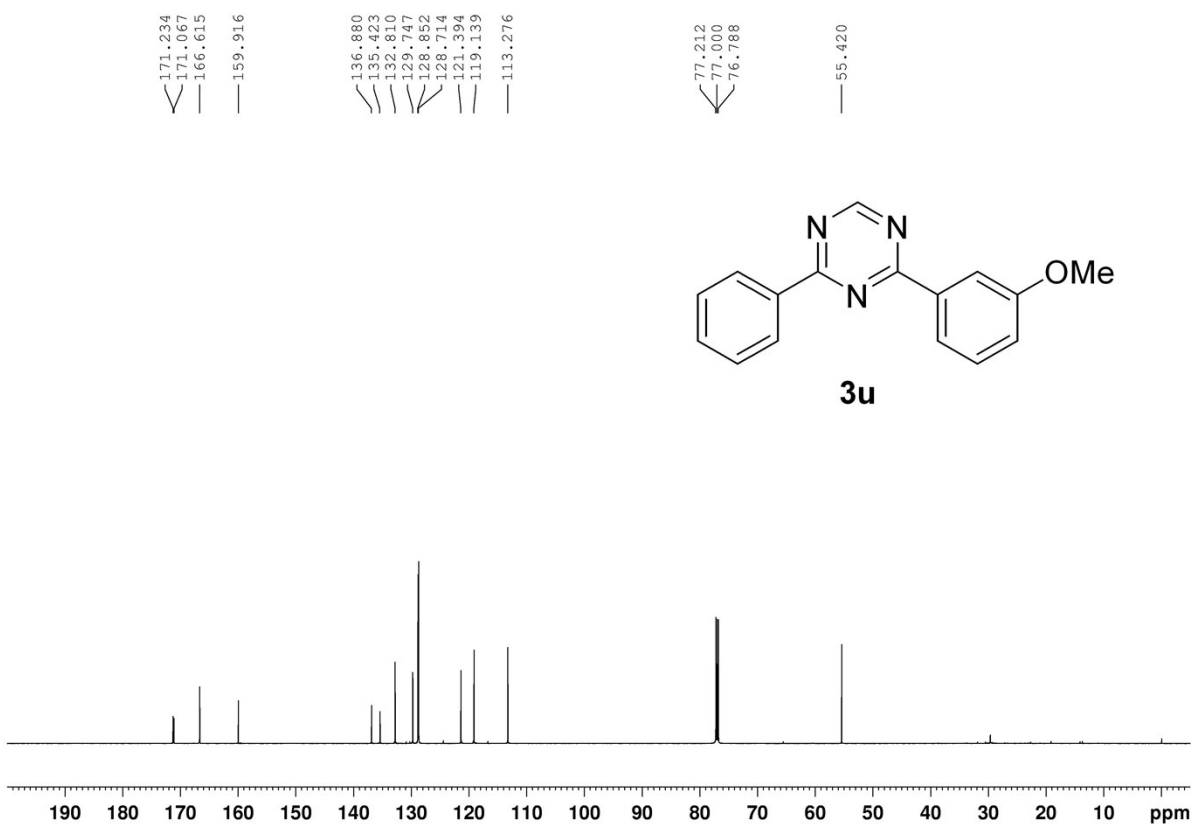
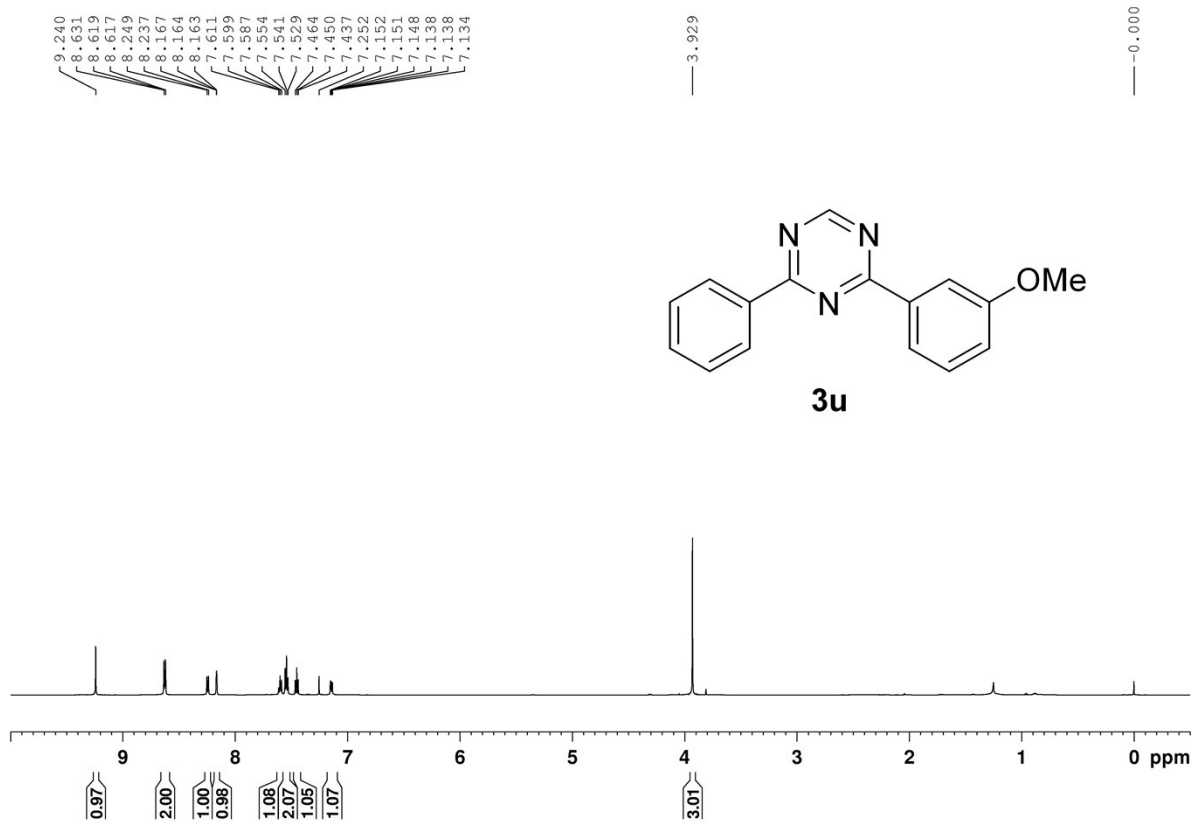


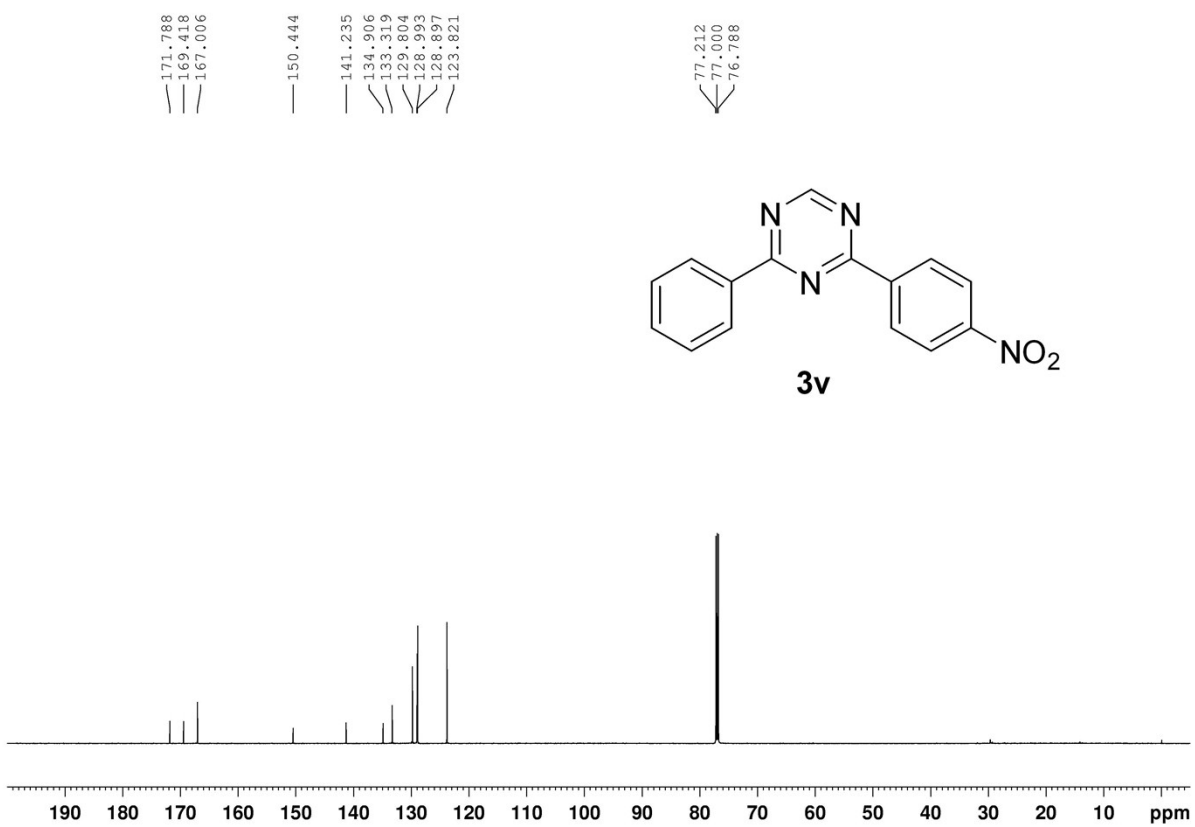
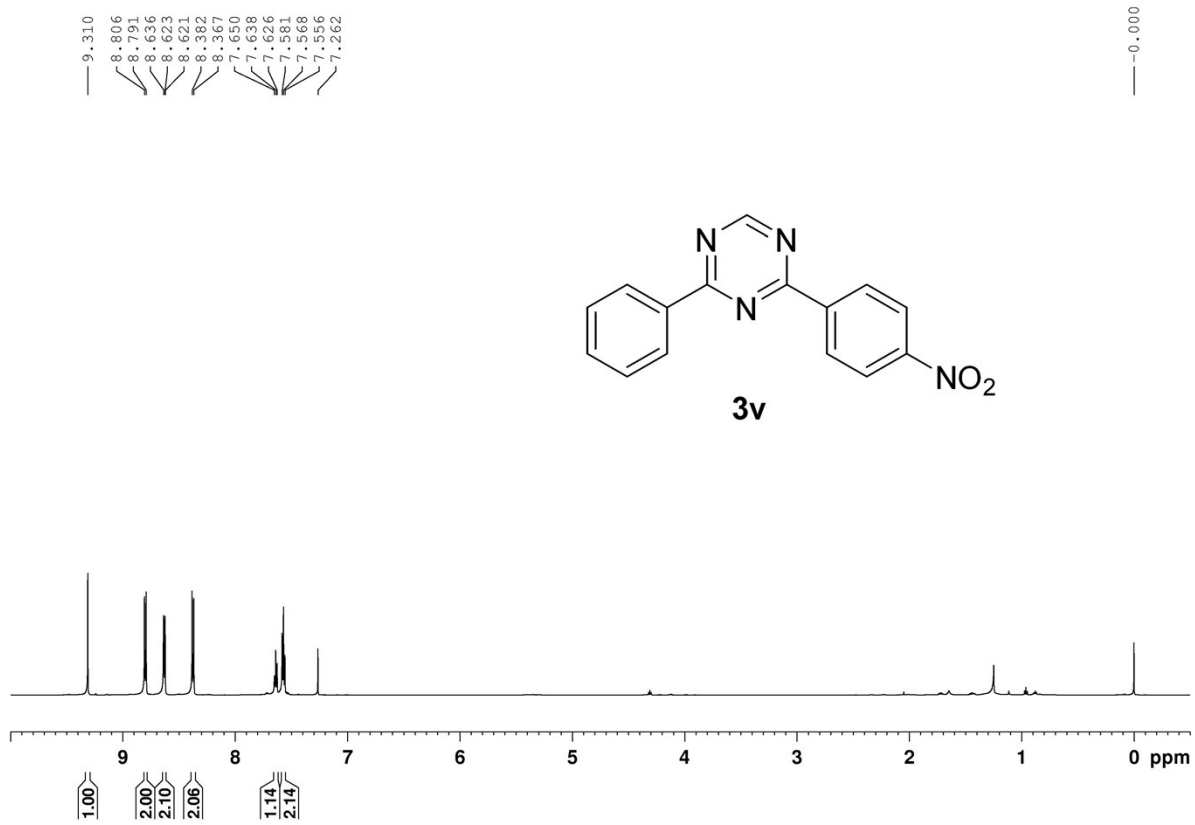


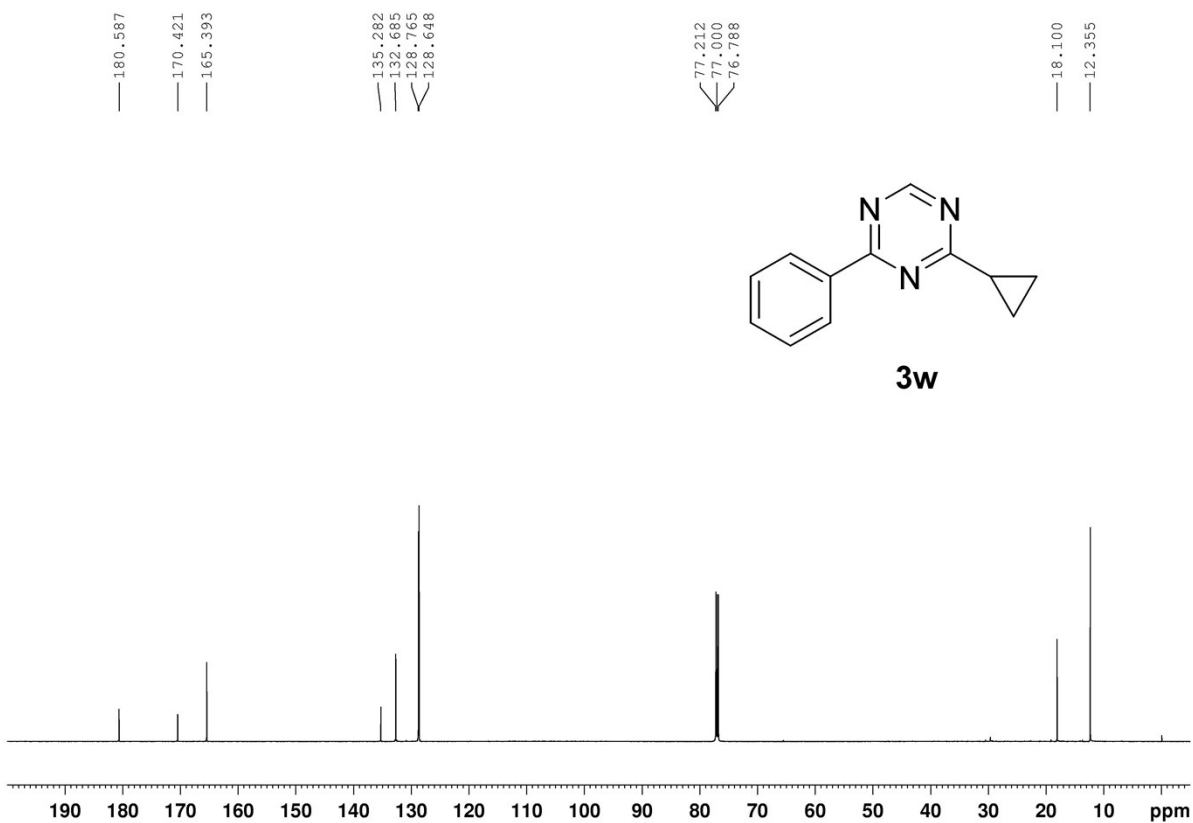
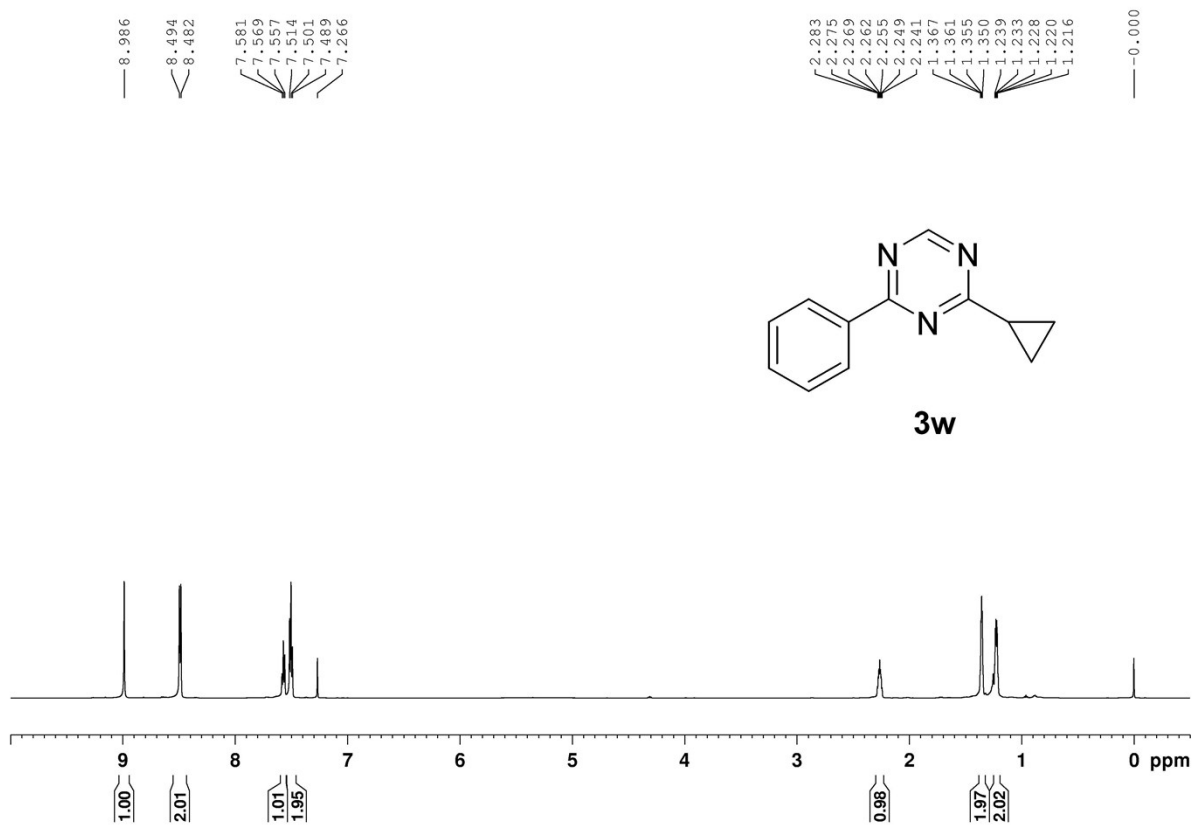




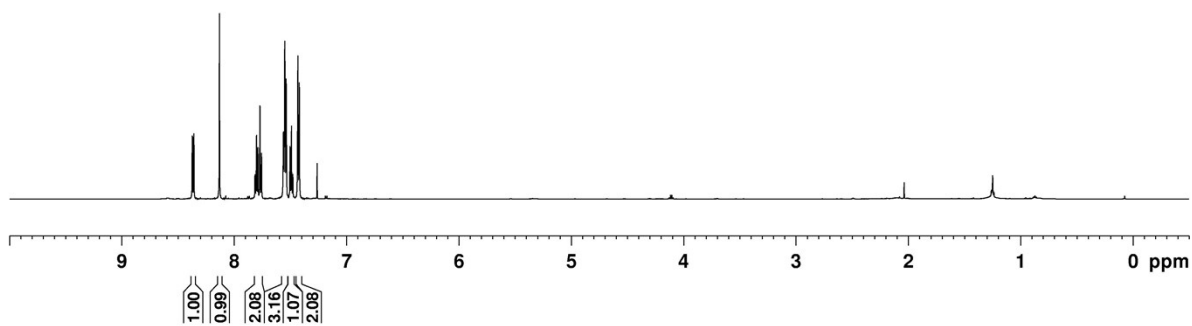
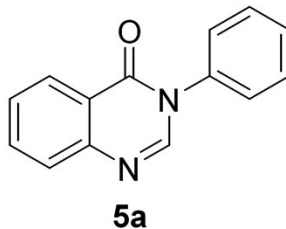








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