Supporting Information

Preparation of 2-Magnesiated 1,3,5-Triazines via an Iodine-Magnesium Exchange

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CONTENT :

General All reactions were carried out under argon atmosphere in flame-dried glassware. Syringes which were used to transfer anhydrous solvents or reagents were purged with argon prior to use. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Diethyl ether was predried over calcium hydride and dried with the solvent purification system SPS-400-2 from INNOVATIVE TECHNOLOGIES INC (Al_2O_3,1-3 mm, ICN, Eschwege, Germany). Carboxylic acid chlorides and allyl bromides were distilled under argon prior to use. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by ^{1}H NMR (25 °C) and capillary-GC. NMR spectra were recorded on solutions in deuterated chloroform ($CDCl_3$) with residual chloroform (δ 7.25 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, br, broad. Column chromatographical purifications were performed using SiO_2 (0.040 – 0.063 mm, 230 – 400 mesh ASTM) from Merck if not indicated otherwise. Solutions of BuMgCl and *s*BuMgCl in THF are commercially available via ACROS Organics and were titrated prior to use in a dry, argon-flushed Schlenk flask with iodine affording the concentration of active alkylmagnesium reagent.

Preparation of the reagent OctMgBr (1 M in THF)

A 1-L three-necked round-bottom flask equipped with a magnetic stirring bar, reflux condenser, addition funnel, and a thermometer was charged with magnesium turnings (14.2 g, 0.584 mol). The flask was gently heated under argon atmosphere (50 °C), while the magnesium turnings were vigorously stirred for 1 h affording activation of the magnesium surface. After cooling to 25 °C and addition of THF (50 mL), ca. 10 mL of a solution of octyl bromide (96.5 g, 0.50 mol) in THF (400 mL) was added to the suspension while continously stirring. The reaction started after ca. 2-3 min as indicated by a small rise in temperature. Thereafter, the remaining solution of OctBr was added dropwise over a periode of 4 h while keeping the temperature below 30 °C. After stirring the reaction mixture for additional 2 h, the supernatant solution was then cannulated into a new dry, argon-flushed Schlenk flask and titrated with iodine affording the concentration of active octylmagnesium bromide (1.0 M).[1]

Preparation of $ZnCl_2$ solution (1 M in THF)

A dry and argon-flushed 250 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with $ZnCl_2$ (20.45 g, 0.15 mol). The salt was heated to 140 °C under high vacuum for 6 h. After cooling to 25 °C, dry THF (150 mL) was added slowly and stirring was continued until the salt was dissolved (4 h) forming a clear colourless solution, which was kept over molecular sieves (4 Å).

Preparation of $ZnBr_2LiCl$ solution (1 M in THF)

A dry and argon-flushed 250 mL Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with $ZnBr_2$ (33.81 g, 0.15 mol) and LiCl (6.35 g, 0.15 mol). The salts were heated to 140 °C under high vacuum for 6 h. After cooling to 25 °C, dry THF (150 mL) was added slowly and stirring was continued until the salts were dissolved (4 h) forming a clear colourless solution, which was kept over molecular sieves (4 Å).

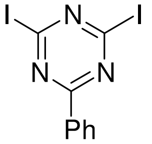
TP1: Typical procedure for the preparation of iodo-1,3,5-triazine derivatives (1a-j)

To a solution of 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 2.0 mmol) and $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol) in THF (20 mL) in a dry and argon-flushed Schlenk-flask was added dropwise a solution of organozinc reagent (1.2 equiv) in THF prepared according to literature procedure[2] at -10 °C followed by continously stirring for 2 h. After stirring for 13 h at 25 °C, the reaction mixture was quenched with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo* and the residue was subjected to flash column chromatography affording the corresponding iodo-1,3,5-triazines **1a-j**.

TP2: Typical procedure for the preparation of 1,3,5-triazin-2-ylmagnesium halides (3a-j)

A dry and argon-flushed Schlenk-flask, equipped with a magnetic stirring bar and a septum, was charged with iodo-1,3,5-triazine derivative (1 mmol) in THF (1 mL) followed by dropwise addition of a solution of alkylmagnesium reagent (1.1 equiv) at -78 °C. The reaction mixture was stirred for 10 min at the same temperature. Complete iodine-magnesium exchange was monitored by GC analysis of reaction aliquots, quenched with brine using tetradecane as internal standard.

Synthesis of 2,4-diiodo-6-phenyl-1,3,5-triazine (6)



A 50 mL round-bottom flask was charged with HI (57w% solution, 20 mL). The solution was cooled to 5 °C and 2,4-dichloro-6-phenyl-1,3,5-triazine (4.52 g, 20 mmol) was added at the same temperature. The reaction mixture was allowed to slowly warm to 25 °C and stirred for 12 h at 25 °C. The mixture was carefully neutralized with K_2CO_3, and decolorized with sat. Na_2SO_3 (aq.) (ca. 5 mL). Water was added until all solid residues dissolved. The aqueous layer was extracted with CH_2Cl_2 (3x 50 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 50:1) afforded 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 5.5 g, 67%) as a white solid.

m. p.: 188.5-190.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.49-8.42 (m, 2H), 7.68-7.48 (m, 3H).

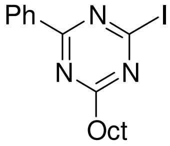
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 170.2, 139.6, 134.4, 132.3, 129.8, 128.9.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3065 (W), 2924 (W), 1469 (S), 1369 (M), 1237 (W), 1205 (M), 1170 (M), 1084 (W), 802 (W), 759 (S), 688 (M), 640 (W).

MS (EI, 70 eV) m/z (%): 408 (M$^+$, 46), 282 (5), 281 (45), 230 (1), 229 (12), 178 (11). 130 (8), 129 (100), 128 (1), 103 (12), 77 (11).

HRMS (EI) calc. $[C_9H_5I_2N_3]^+$: 408.8573; found: 408.8567.

Synthesis of 2-iodo-4-octyl-6-phenyl-1,3,5-triazine (1a)



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with OctZnCl (2.22 mmol, 2.5 mL, 0.89 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 100:1) afforded 2-iodo-4-octyl-6-phenyl-1,3,5-triazine (**1a**, 474 mg, 60%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.52-8.48 (m, 2H), 7.63-7.49 (m, 3H), 2.89 (t, *J* = 7.8 Hz, 2H), 1.93-1.82 (m, 2H), 1.44-1.26 (m, 10H), 0.91 (t, *J* = 7.1 Hz, 3H).

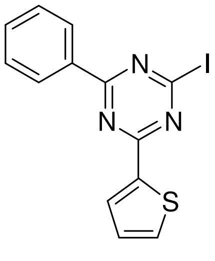
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 180.1, 170.7, 142.2, 134.0, 133.4, 129.3, 128.8, 38.7, 31.8, 29.3, 29.3, 29.2, 27.7, 22.7, 14.1.

IR (Diamond-ATR, neat) ν (cm^{-1}): 2923 (W), 2853 (W), 1600 (VW), 1517 (S), 1483 (VS), 1360 (W), 1236 (M), 1175 (W), 1117 (W), 1026 (W), 908 (W), 800 (M), 767 (M), 689 (S).

MS (EI, 70 eV) m/z (%): 395 (M^+, 0.2), 309 (1), 297 (6), 267 (2), 129 (100), 103 (20), 77 (21).

HRMS (EI) calc. $[C_{17}H_{22}IN_3]^+$: 395.0858; found: 395.0887.

Synthesis of 2-iodo-4-phenyl-6-(thiophen-2-yl)-1,3,5-triazine (1b).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with thiophen-2-ylzinc iodide (2.4 mmol, 3.3 mL, 0.72 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 50:1) afforded **1b** (453 mg, 62%) as a white solid.

m. p.: 122.8-124.3 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.57-8.52 (m, 2H), 8.27 (dd, *J* = 3.8 Hz, 1.3 Hz, 1H), 7.69 (dd, *J* = 4.9 Hz, 1.3 Hz, 1H), 7.67-7.50 (m, 3H), 7.23 (dd, *J* = 4.9 Hz, 3.8 Hz, 1H).

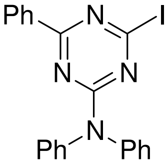
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 170.8, 166.9, 142.2, 139.7, 133.9, 133.8, 133.4, 133.1, 129.3, 128.8, 128.7.

IR (Diamond-ATR, neat) ν (cm^{-1}): 2926 (VW), 2247 (VW), 1509 (S), 1474 (VS), 1426 (M), 1364 (M), 1246 (W), 1209 (W), 1086 (W), 1019 (W), 819 (W), 768 (S), 726 (M), 692 (M), 655 (W).

MS (EI, 70 eV) m/z (%): 364 (M$^+$, 43), 321 (13), 281 (9), 275 (3), 273 (12), 239 (15), 238 (100), 229 (2), 137 (4), 136 (7), 135 (93), 129 (75), 108 (18), 77 (12).

HRMS (EI) calc. [$C_{13}H_8IN_3S$]$^+$: 364.9484; found: 364.9477.

Synthesis of 4-iodo-N,N,6-triphenyl-1,3,5-triazin-2-amine (1c).



To a solution of 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 409 mg, 1 mmol) in THF (20 mL) in a dry and argon-flushed Schlenk-flask was added dropwise a solution of lithium diphenylamide (prepared by addition of BuLi (1.1 mmol, 0.62 mL, 1.8 M in hexane) to a solution of diphenylamine (1.1 mmol) in THF (2 mL) at 0 °C, for 30 min) at -10 °C followed by warming slowly to 25 °C and continously stirring for 12 h. The reaction mixture was quenched with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 50:1) afforded **1c** (358 mg, 80%) as a white solid.

m. p. = 205.3-207.1 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm) 8.18 (d, *J* = 7.1 Hz, 2H), 7.51-7.35 (m, 7H), 7.34-7.27 (m, 6H).

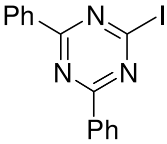
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 170.1, 163.6, 142.5, 141.5, 134.5, 132.7, 129.1, 128.9, 128.4, 127.5, 126.8.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3036 (VW), 1584 (W), 1471 (S), 1436 (S), 1371 (S), 1309 (W), 1225 (M), 1165 (M), 1024 (W), 995 (W), 773 (M), 747 (M), 692 (S), 636 (M).

MS (EI, 70 eV) m/z (%): 451 (17), 450 (M$^+$, 83), 449 (27), 323 (29), 296 (16), 220 (100), 167 (53), 129 (27), 103 (21), 77 (74).

HRMS (EI) calc. $[C_{21}H_{15}IN_4]^+$: 450.0341; found: 450.0333.

Synthesis of 2-iodo-4,6-diphenyl-1,3,5-triazine (1d).



A 50 mL round-bottom flask was charged with HI (57w% solution, 20 mL). The solution was cooled to 5 °C and 2-chloro-4,6-diphenyl-1,3,5-triazine[3] (2.67 g, 10 mmol) was added at the same temperature. The reaction mixture was allowed to slowly warm to 25 °C and stirred for 24 h at 25 °C. The mixture was carefully neutralized with K_2CO_3, and decolorized with sat. Na_2SO_3 (aq.) (ca. 5 mL). Water was added until all solid residues dissolved. The aqueous layer was extracted with CH_2Cl_2 (3x 25 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 100:1) afforded **1d** (2.69 g, 75%) as a white solid.

m. p.: 146.5-147.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.64-8.59 (m, 4H), 7.67-7.53 (m, 6H).

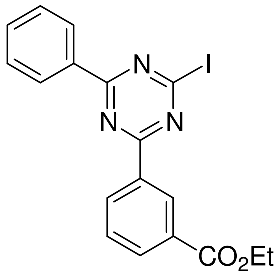
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.1, 142.6, 134.2, 133.4, 129.3, 128.8.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3043 (VW), 2924 (VW), 1587 (W), 1515 (VS), 1480 (VS),1432 (M), 1359 (S), 1314 (W), 1212 (W), 1067 (W),795 (M), 747 (S), 685 (S), 637 (M).

MS (EI, 70 eV) m/z (%): 358 (M$^+$, 2), 232 (36), 207 (10), 130 (10), 129 (100), 127 (1), 126 (1), 103 (22), 77 (35).

HRMS (EI) calc. $[C_{15}H_{10}IN_3]^+$: 358.9919; found: 358.9938.

Synthesis of ethyl 3-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (1e).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with (3-(ethoxycarbonyl)phenyl)zinc iodide (2.4 mmol, 3.2 mL, 0.75 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **1e** (474 mg, 55%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.19 (t, *J* = 1.5 Hz, 1H), 8.75 (dt, *J* = 7.7 Hz, 1.5 Hz, 1H), 8.60-8.57 (m, 2H), 8.28-8.26 (m, 1H), 7.63-7.59 (m, 2H), 7.55-7.51 (m, 2H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H).

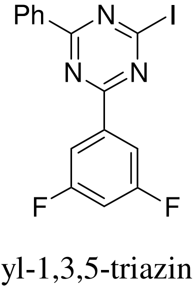
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.1, 170.2, 165.9, 142.7, 134.7, 134.1, 133.9, 133.6, 133.3, 131.3, 130.3, 129.4, 128.9, 128.8, 61.4, 14.4.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3070 (VW), 2981 (VW), 1716 (S), 1511 (VS), 1490 (VS), 1430 (S), 1354 (M), 1260 (S), 1221 (S), 1149 (M), 1070 (M), 906 (S), 799 (M), 728 (VS), 686 (VS), 638 (M).

MS (EI, 70 eV) m/z (%): 431 (M$^+$, 3), 385 (17), 305 (18), 304 (100), 298 (4), 282 (1), 277 (1), 255 (3), 201 (48), 173 (10), 129 (23), 103 (4).

HRMS (EI) calc. $[C_{18}H_{14}IN_3O_2]^+$: 431.0131; found: 431.0117.

Synthesis of 2-(3,5-difluorophenyl)-4-iodo-6-phenyl-1,3,5-triazine (1f).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with

(3,5-difluorophenyl)zinc bromide (2.4 mmol, 3.5 mL, 0.68 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 50:1) afforded **1f** (529 mg, 67%) as a white solid.

m. p.: 150.0-152.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.61-8.56 (m, 2H), 8.17-8.09 (m, 2H), 7.69-7.53 (m, 3H), 7.08 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H).

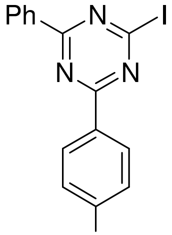
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.3, 168.9 (t, *J* = 3.7 Hz), 163.2 (dd, *J* = 249 Hz, 12.1 Hz), 142.6, 137.7 (t, *J* = 9.7 Hz), 133.8, 133.7, 129.4, 128.9, 112.1 (dd, *J* = 18 Hz, 8.9 Hz), 108.6 (t, *J* = 25.5 Hz).

IR (Diamond-ATR, neat) ν (cm^{-1}): 3078 (VW), 2925 (VW), 1600 (W), 1516 (S), 1491 (VS), 1361 (M), 1235 (M), 1119 (W), 987 (W), 774 (M), 730 (M), 685 (M), 647 (W).

MS (EI, 70 eV) m/z (%): 394 (M^+, 15), 382 (6), 381 (23), 281 (6), 269 (11), 267 (62), 240 (4), 229 (2), 165 (97), 139 (33), 129 (100), 103 (36), 77 (28).

HRMS (EI) calc. $[C_{15}H_8F_2IN_3]^+$: 394.9731; found: 394.9711.

Synthesis of ethyl 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (1g).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with (4-(ethoxycarbonyl)phenyl)zinc iodide (0.72 M in THF, 3.4 mL, 2.4 mmol) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **1g** (440 mg, 51%) as a white solid.

m. p.: 172.3-174.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.68-8.57 (m, 4H), 8.22-8.17 (m, 2H), 7.68-7.51 (m, 3H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.46 (t, *J* = 7.1 Hz, 3H),

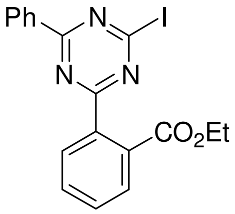
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.2, 170.1, 165.9, 142.7, 138.0, 134.6, 133.9, 133.6, 129.8, 129.4, 129.2, 128.8, 61.4, 14.3.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3054 (VW), 2981 (VW), 1709 (S), 1482 (VS), 1353 (M), 1271 (S), 1221 (S), 1069 (M), 1018 (W), 827 (W), 797 (M), 754 (S), 688 (M), 647 (W).

MS (EI, 70 eV) m/z (%): 432 (100), 322 (6), 217 (13), 145 (1).

HRMS (ESI) calc. [$C_{18}H_{14}IN_3O_2$ + H]$^+$: 432.0209; found: 432.0200 ([$C_{18}H_{14}IN_3O_2$ + H]$^+$).

Synthesis of ethyl 2-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (1h).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with (2-(ethoxycarbonyl)phenyl)zinc iodide (2.4 mmol, 3.4 mL, 0.72 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **1h** (569 mg, 66%) as a white solid.

m. p.: 90.5-92.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.58-8.51 (m, 2H), 8.25-8.18 (m, 1H), 7.78-7.73 (m, 1H), 7.68-7.59 (m, 3H), 7.58-7.50 (m, 2H), 4.30 (q, *J* = 7.1 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 3H).

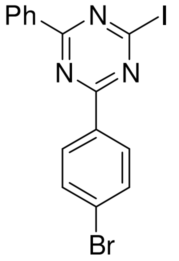
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.9, 170.7, 168.9, 141.8, 134.3, 134.2, 133.8, 133.7, 131.8, 130.7, 130.6, 129.5, 129.2, 128.9, 61.6, 14.1.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3068 (VW), 2976 (VW), 1726 (S), 1509 (VS), 1472 (VS), 1357 (M), 1287 (M), 1237 (M), 1217 (M), 1124 (W), 797 (W), 750 (M), 685 (M).

MS (EI, 70 eV) m/z (%): 431 (M$^+$, 7), 386 (9), 385 (18), 304 (65), 277 (5), 276 (26), 275 (6), 274 (9), 249 (2), 201 (14), 173 (37), 130 (27), 129 (100), 104 (3), 77 (12).

HRMS (EI) calc. [$C_{18}H_{14}IN_3O_2$]$^+$: 431.0131; found: 431.0119.

Synthesis of 2-(4-bromophenyl)-4-iodo-6-phenyl-1,3,5-triazine (1i).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with (4-bromophenyl)zinc iodide (2.4 mmol, 3.5 mL, 0.68 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 100:1) afforded **1i** (417 mg, 47%) as a white solid.

m. p.: 163.5-165.4 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.55 (d, *J* = 7.7 Hz, 2H), 8.44 (d, *J* = 8.5 Hz, 2H), 7.66 (d, *J* = 8.5 Hz, 2H), 7.64-7.50 (m, 3H).

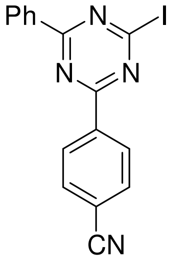
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 171.1, 170.1, 142.6, 133.9, 133.6, 133.1, 132.1, 130.7, 129.3, 128.8, 128.6.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3047 (VW), 1585 (W), 1510 (S), 1480 (VS), 1441 (M), 1354 (M), 1221 (M), 1063 (M),1011 (M), 818 (W), 800 (M), 766 (S), 647 (M), 614 (W).

MS (EI, 70 eV) m/z (%): 436 (M$^+$, 9), 313 (5), 312 (27), 311 (5), 310 (31), 208 (43), 206 (45), 180 (7), 129 (100), 102 (16), 77 (21).

HRMS (EI) calc. $[C_{15}H_9BrIN_3]^+$: 436.9025; found: 436.9009.

Synthesis of 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzonitrile (1j).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with

(4-cyanophenyl)zinc iodide (2.4 mmol, 3.2 mL, 0.74 M in THF) in the presence of $Pd(PPh_3)_2Cl_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **1j** (428 mg, 56%) as a white solid.

m. p.: 176.7-178.5 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.75-8.70 (m, 2H), 8.63-8.58 (m, 2H), 7.88-7.83 (m, 2H), 7.70-7.54 (m, 3H).

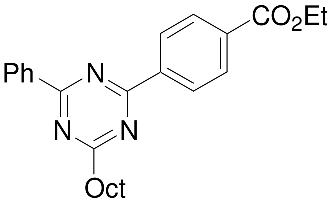
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 171.4, 169.3, 142.7, 138.3, 133.9, 133.7, 132.5, 129.7, 129.5, 128.9, 118.2, 116.5.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3067 (VW), 2918 (VW), 2227 (VW), 1511 (S), 1483 (VS), 1355 (M), 1224 (M), 1068 (W), 800 (W), 773 (M), 690 (W).

MS (EI, 70 eV) m/z (%): 383 (M$^+$, 9), 292 (4), 258 (9), 257 (45), 191 (1), 155 (7), 154 (80), 129 (100), 103 (12), 77 (11).

HRMS (EI) calc. $[C_{16}H_9IN_4]^+$: 383.9872; found: 383.9858.

Synthesis of 4-(4-octyl-6-phenyl-[1, 3, 5]triazin-2-yl)-benzoic acid ethyl ester (5a).



According to **TP2**, 2-iodo-4-octyl-6-phenyl-1,3,5-triazine (**1a**, 395 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3a**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF). After addition of $ZnBr_2 \cdot LiCl$ (1.1 mmol, 1.1 mL, 1 M in THF) at -78 °C and stirring for 10 min, a solution of ethyl 4-iodobenzoate (**4a**, 305 mg, 1.1 mmol), $Pd(dba)_2$ (5 mol%, 28 mg) and $P(2\text{-furyl})_3$ (10 mol%, 23 mg) in THF (1 mL) was added dropwise. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 12 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **5a** (292 mg, 62%) as a pale yellow solid.

m. p.: 54.8 – 56.4 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.73 (d, *J* = 8.8 Hz, 2H), 8.68 (dd, *J* = 8.0 Hz, 1.5 Hz, 2H), 8.22 (d, *J* = 8.8 Hz, 2H), 7.66-7.52 (m, 3H), 4.46 (q, *J* = 7.1 Hz, 2H), 3.08-3.00 (m, 2H), 2.04-1.93 (m, 2H), 1.56-1.22 (m, 10H), 1.47 (t, *J* = 7.2 Hz, 3H), 0.95-0.86 (m, 3H).

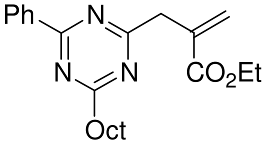
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 180.5, 171.3, 170.3, 166.2, 140.1, 135.9, 133.7, 132.6, 129.7, 128.9, 128.8, 128.7, 61.3, 39.3, 31.9, 29.5, 29.4, 29.3, 27.7, 22.7, 14.4, 14.1.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3583 (W), 2913 (W), 1724 (M), 1529 (S), 1364 (M), 1278 (S), 1101 (M), 1021 (M), 759 (S), 689 (M), 665 (S).

MS (EI, 70 eV) m/z (%): 417 (M$^+$, 7), 388 (2), 372 (3), 332 (12), 320 (18), 319 (100), 176 (10), 104 (16).

HRMS (EI) calc. [$C_{26}H_{31}N_3O_2$]$^+$: 417.2416; found: 417.2408.

Synthesis of 2-(4-octyl-6-phenyl-[1, 3, 5]triazin-2-ylmethyl)-acrylic acid ethyl ester (5b).



According to **TP2**, 2-iodo-4-octyl-6-phenyl-1,3,5-triazine (**1a**, 395 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3a**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF). After addition of CuCN·2LiCl[4] (0.2 mmol, 0.2 mL, 1 M in THF) at -78 °C and stirring for 10 min, ethyl 2-(bromomethyl)acrylate (**4b**, 213 mg, 1.1 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 12 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **5b** (279 mg, 73%) as yellow oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.48 (d, *J* = 8.5 Hz, 2H), 7.57-7.44 (m, 3H), 6.36 (s, 1H), 5.68 (s, 1H), 4.18 (q, *J* = 7.1 Hz, 2H), 3.98 (s, 2H), 2.92-2.85 (m, 2H), 1.89-1.79 (m, 2H), 1.44-1.23 (m, 10H), 1.20 (t, *J* = 7.1 Hz, 3H), 0.87 (t, *J* = 6.7 Hz, 3H)

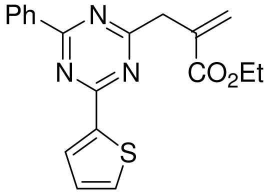
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 179.8, 176.8, 170.8, 166.8, 136.6, 135.7, 132.4, 128.9, 128.6, 127.1, 60.8, 41.7, 39.1, 31.8, 29.4, 29.3, 29.2, 27.8, 22.7, 14.2, 14.1.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3583 (W), 2956 (W), 2927 (M), 2855 (W), 1720 (S), 1534 (VS), 1380 (M), 1148 (M), 1027 (W), 735 (W).

MS (EI, 70 eV) m/z (%): 381 (M$^+$, 19), 380 (3), 352 (9). 336 (8), 308 (12), 296 (25), 284 (16), 283 (100), 237 (20), 211 (18), 104 (29).

HRMS (EI) calc. [$C_{23}H_{31}N_3O_2$]$^+$: 381.2416; found: 381.2412.

Synthesis of ethyl 2-((4-phenyl-6-(thiophen-2-yl)-1,3,5-triazin-2-yl)methyl)acrylate (5c).



According to **TP2**, 2-iodo-4-phenyl-6-(thiophen-2-yl)-1,3,5-triazine (**1b**, 365 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3b**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF). After addition of CuCN·2LiCl[4] (0.2 mmol, 0.2 mL, 1 M in THF) at -78 °C and stirring for 10 min, ethyl 2-(bromomethyl)acrylate (**4b**, 213 mg, 1.1 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 12 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **5c** (213 mg, 59%) as yellow liquid.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.58 (d, *J* = 6.8 Hz, 2H), 8.28-8.23 (m, 1H), 7.65-7.48 (m, 4H), 7.24-7.18 (m, 1H), 6.41 (s, 1H), 5.76 (s, 1H), 4.23 (q, *J* = 7.1 Hz, 2H), 4.06 (s, 2H), 1.24 (t, *J* = 7.1 Hz, 3H).

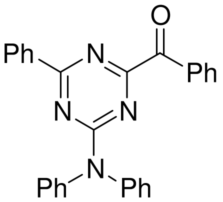
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 177.4, 171.1, 167.6, 166.9, 141.7, 136.6, 135.5, 132.6, 132.3, 131.7, 128.9, 128.6, 128.5, 127.1, 60.8, 41.7, 14.2.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3583 (W), 3066 (W), 2979 (W), 2928 (W), 2253 (W), 1716 (VS), 1519 (VS), 1439 (S), 1375 (S), 1152 (M), 1027 (M), 774 (W), 732 (M), 704 (M), 665 (W).

MS (EI, 70 eV) m/z (%): 351 (M$^+$, 60), 322 (36), 306 (19), 280 (13), 279 (56), 278 (100), 273 (18), 219 (10), 175 (30), 129 (18), 110 (31), 108 (29).

HRMS (EI) calc. [$C_{19}H_{17}N_3O_2S$]$^+$: 351.1041; found: 351.1031.

Synthesis of (4-(diphenylamino)-6-phenyl-1,3,5-triazin-2-yl)(phenyl)methanone (5d).



According to **TP2**, 4-iodo-N,N,6-triphenyl-1,3,5-triazin-2-amine (**1c**, 225 mg, 0.5 mmol) was converted into the corresponding triazinylmagnesium chloride (**3c**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF). After addition of CuCN·2LiCl[4] (0.55 mmol, 0.55 mL, 1 M in THF) at -78 °C and stirring for 10 min, benzoyl chloride (**4c**, 60 mg, 0.55 mmol) was added. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 12 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5d** (154 mg, 71%) as a white solid.

m. p.: 212.6-214.0 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.31 (d, *J* = 7.3 Hz, 2H), 8.09 (d, *J* = 7.3 Hz, 2H), 7.71-7.21 (m, 16H).

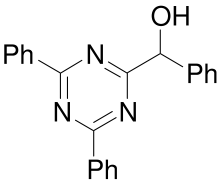
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 190.3, 171.7, 170.5, 165.9, 142.8, 135.5, 134.4, 133.9, 132.6, 130.8, 129.1, 129.0, 128.5, 128.3, 127.6, 126.7.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3583 (W), 3065 (W), 2254 (W), 1969 (W), 1691 (S), 1595 (M), 1537 (S), 1471 (S), 1372 (S), 1221 (M), 908 (S), 733 (M), 638 (W).

MS (EI, 70 eV) m/z (%): 428 (M^+, 100), 323 (53), 296 (45), 220 (12), 193 (5), 180 (8), 167 (7), 105 (20), 77 (21).

HRMS (EI) calc. $[C_{28}H_{20}N_4O]^+$: 428.1637; found: 428.1627.

Synthesis of (4, 6-diphenyl-[1, 3, 5]triazin-2-yl)-phenyl-methanol (5e).



According to **TP2**, 2-iodo-4,6-diphenyl-1,3,5-triazine (**1d**, 359 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3d**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF) followed by addition of benzaldehyde (**4d**, 117 mg, 1.1 mmol). The reaction mixture was allowed to warm to 25 °C and continuously stirred for 1 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5e** (205 mg, 61%) as a white solid.

m. p.: 135.5 – 137.5 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.70-8.64 (m, 4H), 7.75-7,53 (m, 8H), 7.46 - 7.30 (m, 3H), 5.97 (s, 1H), 4.97 (br s, 1H).

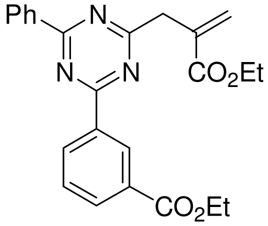
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 178.4, 171.3, 141.2, 135.2, 133.1, 129.1, 128.8, 128.5, 128.1, 126.8, 75.1.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3467 (W), 3064 (W), 2920 (W), 1959 (W), 1539 (S), 1520 (S), 1373 (M), 1372 (M), 1176 (W), 1061(W), 754 (M), 720 (M), 690 (M).

MS (EI, 70 eV) m/z (%): 239(M^+, 100), 323 (11), 322 (23), 262 (39), 234 (12), 233 (53), 130 (30), 105 (14), 103 (60).

HRMS (EI) calc. $[C_{22}H_{17}N_3O]^+$: 339.1372; found: 339.1366.

Synthesis of ethyl 3-(4-(2-(ethoxycarbonyl)allyl)-6-phenyl-1,3,5-triazin-2-yl)benzoate (5f).



According to **TP2**, ethyl 3-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1e**, 431 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3e**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF). After addition of CuCN·2LiCl[4] (0.2 mmol, 0.2 mL, 1 M in THF) at -78 °C and stirring for 10 min, ethyl 2-(bromomethyl)acrylate (**4b**, 213 mg, 1.1 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 12 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5f** (286 mg, 71%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 9.26 (t, *J* = 1.7 Hz, 1H), 8.81-8.79 (m, 1H), 8.65-8.62 (m, 2H), 8.26-8.24 (m, 1H), 7.63-7.57 (m, 2H), 7.55-7.52 (m, 2H), 6.42 (d, *J* = 1.4 Hz, 1H), 5.77-5.76 (m, 1H), 4.46 (q, *J* = 7.2 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 4.11 (s, 2H), 1.46 (t, *J* = 7.2 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H).

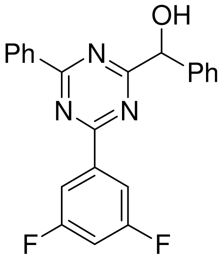
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.7, 171.4, 170.5, 166.9, 166.2, 136.6, 136.3, 135.6, 133.3, 133.1, 132.7, 131.2, 130.0, 129.0, 128.7, 128.6, 127.2, 61.3, 60.8, 41.8, 14.4, 14.2.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3583 (W), 2981 (W), 2256 (W), 1721 (S), 1529 (S), 1366 (M), 1257 (M), 1152 (M), 1026 (W), 752 (M), 690 (W).

MS (EI, 70 eV) m/z (%): 417 (M$^+$, 100), 388 (38), 372 (41), 345 (72), 344 (97), 273 (15), 241 (12), 213 (14), 169 (20), 149 (10), 130 (12), 104 (30).

HRMS (EI) calc. $[C_{24}H_{23}N_3O_4]^+$: 417.1689; found: 417.1688.

Synthesis of (4-(3,5-difluorophenyl)-6-phenyl-1,3,5-triazin-2-yl)(phenyl)methanol (5g).



According to **TP2**, 2-(3,5-difluorophenyl)-4-iodo-6-phenyl-1,3,5-triazine (**1f**, 395 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3f**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF) followed by addition of benzaldehyde (**4d**, 117 mg, 1.1 mmol). The reaction mixture was allowed to warm to 25 °C and continuously stirred for 1 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 20:1) afforded **5g** (202 mg, 54%) as a white solid.

m. p.: 145.2-147.9 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.66-8.61 (m, 2H), 8.17-8.12 (m, 2H), 7.69-7.60 (m, 3H), 7.58-7.54 (m, 2H), 7.41-7.37 (m, 2H), 7.33-7.29 (m, 1H), 7.06-7.02 (m, 1H), 5.94 (d, *J* = 6.1 Hz, 1H), 4.77 (d, *J* = 6.1 Hz, 1H).

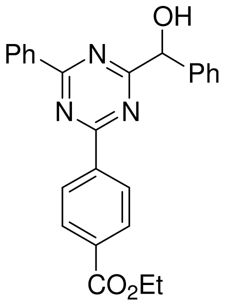
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 178.9, 171.7, 169.4 (t, *J* = 3.5 Hz), 163.2 (dd, *J* = 249 Hz, 12.1 Hz), 140.8, 138.8 (t, *J* = 9.5 Hz), 134.7, 133.4, 129.2, 128.9, 128.5, 128.2, 126.7, 111.9 (dd, *J* = 11.3 Hz, 5.6 Hz), 108.2 (t, *J* = 25.5 Hz), 75.2.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3477 (W), 3080 (VW), 2924 (W), 1522 (VS), 1369 (S), 1177 (W), 1117 (W), 1062 (W), 986 (W), 878 (W), 697 (M).

MS (EI, 70 eV) m/z (%): 375 (M^+, 33), 323 (32), 298 (12), 269 (23), 220 (100), 180 (11), 167 (24), 129 (27), 117 (59), 104 (27), 77 (66).

HRMS (EI) calc. $[C_{22}H_{15}F_2N_3O]^+$: 375.1183; found: 375.1182.

Synthesis of 4-[4-(hydroxy-phenyl-methyl)-6-phenyl-[1,3,5]triazin-2-yl]-benzoic acid ethyl ester (5h).



According to **TP2**, ethyl 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1g**, 431 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3g**, -78 °C, 10 min) using OctMgBr (1.1 mmol, 1.1 mL, 1 M in THF) followed by addition of benzaldehyde (**4d**, 117 mg, 1.1 mmol). The reaction mixture was allowed to warm to 25 °C and continuously stirred for 1 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5h** (309 mg, 75%) as a white solid.

m. p.:144.7-146.3 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.71 (d, *J* = 8.3 Hz, 2H), 8.67 (d, *J* = 7.1 Hz, 2H), 8.22 (d, *J* = 8.3 Hz, 2H), 7.74-7.54 (m, 5H), 7.47-7.25 (m, 3H), 5.97 (s, 1H), 4.46 (q, *J* = 7.1 Hz, 2H), 1.47 (t, *J* = 7.1 Hz, 3H).

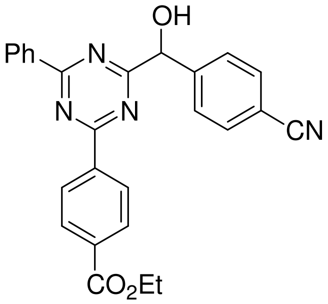
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 178.7, 171.6, 170.6, 166.0, 140.9, 139.1, 134.9, 134.2, 133.3, 129.8, 129.2, 128.9, 128.8, 128.5, 128.1, 126.7, 75.2, 61.4, 14.4.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3467 (M), 3063 (W), 2982 (W), 2929 (W), 1717 (S), 1520 (S), 1372 (S), 1275 (S), 1104 (M), 909 (M), 760 (M), 731 (S), 698 (M).

MS (EI, 70 eV) m/z (%): 411 (M$^+$, 67), 410 (17), 395 (28). 366 (11), 334 (28), 305 (22), 232 (12), 219 (15), 130 (16), 105 (100).

HRMS (EI) calc. $[C_{25}H_{21}N_3O_3]^+$: 411.1583; found: 411.1573.

Synthesis of ethyl 4-{4-[(4-cyanophenyl)(hydroxy)methyl]-6-phenyl-1,3,5-triazin-2-yl} benzoate (5i).



According to **TP2**, ethyl 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1g**, 431 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3g**, -78 °C, 10 min) using OctMgBr (1.1 mmol, 1.1 mL, 1 M in THF) followed by addition of 4-cyanobenzaldehyde (**4e**, 144 mg, 1.1 mmol). The reaction mixture was allowed to warm to 25 °C and continuously stirred for 1 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 9:1) afforded **5i** (275 mg, 75%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.54-8.71 (m, 4H), 8.20 (d, *J* = 8.2 Hz, 2H), 7.83 (d, *J* = 8.2 Hz, 2H), 7.48-7.72 (m, 5H), 5.97 (d, *J* = 3.7 Hz, 1H), 4.99 (d, *J* = 4.5 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.43 (t, *J* = 7.1 Hz, 3H).

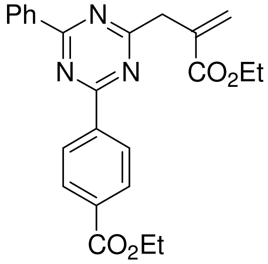
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.5, 171.8, 170.8, 165.9, 146.0, 138.7, 134.6, 134.5, 133.6, 132.2, 129.9, 129.2, 129.0, 128.9, 127.5, 118.7, 112.0, 74.3, 61.5, 14.3.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3454 (VW), 3068 (VW), 2960 (W), 2932 (W), 2872 (VW), 2230 (W), 1716 (S), 1694 (M), 1580 (M), 1514 (VS), 1364 (S), 1270 (VS), 1220 (M), 1102 (S), 1018 (S), 976 (M), 836 (S), 750 (VS), 688 (VS), 650 (S).

MS (EI, 70 eV) m/z (%): 437 (33), 436 (M^+, 100), 434 (34), 420 (29), 419 (31), 334 (34), 305 (20), 130 (50), 129 (25), 104 (39), 103 (38), 102 (28).

HRMS (EI) calc. $[C_{26}H_{20}N_4O_3]^+$: 436.1535; found: 436.1523.

Synthesis of ethyl 4-{4-[2-(ethoxycarbonyl)prop-2-en-1-yl]-6-phenyl-1,3,5-triazin-2-yl} benzoate (5j).



According to **TP2**, ethyl 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1g**, 431 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3g**, -78 °C, 10 min) using OctMgBr (1.1 mmol, 1.1 mL, 1 M in THF). After addition of CuCN·2LiCl[4] (0.2 mmol, 0.2 mL, 1 M in THF) at -78 °C and stirring for 10 min, ethyl 2-(bromomethyl)acrylate (**4b**, 213 mg, 1.1 mmol) was added dropwise. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 4 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 9:1) afforded **5j** (296 mg, 71%) as yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.50-8.74 (m, 4H), 8.17 (d, *J* = 8.4 Hz, 2H), 7.48-7.66 (m, 3H), 6.40 (d, *J* = 1.0 Hz, 1H), 5.75 (d, *J* = 1.0 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 4.33 (q, *J* = 7.2 Hz, 2H), 2.64 (s, 2H), 1.36-1.47 (m, 6H).

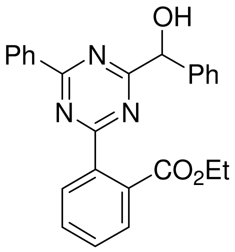
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 177.7, 172.2, 171.7, 170.7, 167.9, 166.1, 141.5, 139.7, 135.5, 134.5, 133.9, 132.9, 129.8, 128.9, 128.7, 61.6, 61.3, 41.8, 15.3, 14.3.

IR (Diamond-ATR, neat) ν (cm^{-1}): 2982 (W), 2938 (W), 1716 (S), 1580 (W), 1516 (VS), 1450 (M), 1362 (S), 1272 (S), 1242 (S), 1160 (M), 1098 (S), 1018 (S), 834 (S), 774 (S), 686 (VS), 650 (S).

MS (EI, 70 eV) m/z (%): 418 (33), 417 (M$^+$, 77), 388 (40), 372 (36), 345 (67), 344 (100), 104 (37), 103 (28), 94 (23), 71 (33), 57 (46), 55 (24), 43 (32).

HRMS (EI) calc. $[C_{24}H_{23}N_3O_4]^+$: 417.1689; found: 417.1690.

Synthesis of ethyl 2-(4-(hydroxy(phenyl)methyl)-6-phenyl-1,3,5-triazin-2-yl)benzoate (5k).



According to **TP2**, ethyl 2-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1h**, 431 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3h**, -78 °C, 10 min) using OctMgBr (1.1 mmol, 1.1 mL, 1 M in THF) followed by addition of benzaldehyde (**4d**, 117 mg, 1.1 mmol). The reaction mixture was allowed to warm to 25 °C and continuously stirred for 1 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5k** (261 mg, 63%) as colorless oil.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.61-8.58 (m, 2H), 8.21-8.16 (m, 1H), 7.77-7.73 (m, 1H), 7.65-7.59 (m, 5H), 7.53 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.32-7.28 (m, 1H), 5.92 (s, 1H), 4.77 (br s, 1H), 4.17-4.06 (m, 2H), 1.02 (t, *J* = 7.2 Hz, 3H).

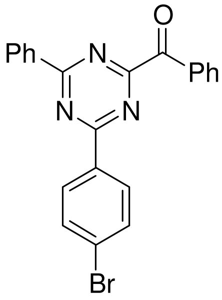
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 178.3, 172.6, 171.2, 169.1, 140.9, 135.5, 134.8, 134.1, 133.3, 131.4, 130.7, 130.4, 129.2, 129.1, 128.8, 128.5, 128.1, 126.7, 75.1, 61.5, 13.8.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3469 (W), 3064 (W), 2918 (W), 2250 (W), 1725 (S), 1536 (S), 1521 (S), 1374 (M), 1287 (M), 1253 (M), 1177 (W), 1121 (W), 1061 (W), 910 (W), 731 (M), 697 (M), 608 (W).

MS (EI, 70 eV) m/z (%): 411 (M$^+$, 100), 410 (25), 409 (82), 394 (11), 366 (13), 364 (32), 349 (23), 335 (15), 288 (24), 276 (20), 259 (20), 234 (38), 173 (23), 130 (71), 105 (86), 77 (46).

HRMS (EI) calc. [$C_{25}H_{21}N_3O_3$]$^+$: 411.1583; found: 411.1580.

Synthesis of (4-(4-bromophenyl)-6-phenyl-1,3,5-triazin-2-yl)(phenyl)methanone (5l).



According to **TP2**, 2-(4-bromophenyl)-4-iodo-6-phenyl-1,3,5-triazine (**1i**, 438 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3i**, -78 °C, 10 min) using OctMgBr (1.1 mmol, 1.1 mL, 1 M in THF). After addition of CuCN·2LiCl[4] (1.1 mmol, 1.1 mL, 1 M in THF) at -78 °C and stirring for 10 min, benzoyl chloride (**4c**, 169 mg, 1.2 mmol) was added. The reaction mixture was allowed to warm to 25 °C and continuously stirred for 12 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5l** (289 mg, 68%) as a white solid.

m. p.: 144.3-146.1 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.69 (d, *J* = 7.1 Hz, 2H), 8.58 (d, *J* = 8.5 Hz, 2H), 8.14 (d, *J* = 7.1 Hz, 2H), 7.75-7.63 (m, 4H), 7.62-7.52 (m, 4H).

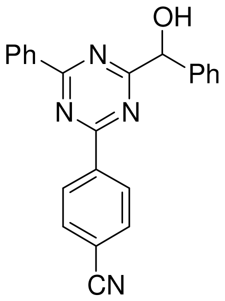
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 190.3, 172.3, 171.5, 170.9, 134.9, 134.4, 134.1, 134.0 133.5, 132.1, 130.9, 130.8, 129.3, 128.9, 128.7, 128.5.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3583 (W), 3064 (W), 2923 (W), 2248 (W), 1686 (S), 1588 (M), 1528 (VS), 1367 (S), 1222 (M), 1176 (W), 1068 (W), 1011 (W), 909 (W), 835 (W), 774 (W), 665 (W), 646 (W).

MS (EI, 70 eV) m/z (%): 416 (22), 415 (M$^+$, 54), 414 (9), 387 (4), 313 (4), 234 (17), 206 (4), 156 (2), 105 (100), 77 (30).

HRMS (EI) calc. $[C_{22}H_{14}BrN_3O]^+$: 415.0320; found: 415.0320.

Synthesis of 4-(4-(hydroxy(phenyl)methyl)-6-phenyl-1,3,5-triazin-2-yl)benzonitrile (5m).



According to **TP2**, 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzonitrile (**1j**, 300 mg, 0.78 mmol) was converted into the corresponding triazinylmagnesium chloride (**3j**, -78 °C, 10 min) using OctMgBr (0.86 mmol, 0.86 mL, 1 M in THF) followed by addition of benzaldehyde (**4d**, 91 mg, 0.86 mmol). The reaction mixture was allowed to warm to 25 °C and continuously stirred for 1 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 10:1) afforded **5m** (186 mg, 64%) as a white solid.

m. p.: 192.0-194.2 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.76 (d, *J* = 8.5 Hz, 2H), 8.70-8.62 (m, 2H), 7.86 (d, *J* = 8.5 Hz, 2H). 7.71-7.54 (m, 5H), 7.45-7.29 (m, 3H), 5.98 (s, 1H), 4.79 (br s, 1H).

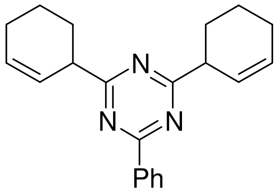
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 179.0, 171.8, 169.9, 140.8, 139.3, 134.7, 133.6, 132.5, 129.5, 129.2, 128.9, 128.6, 128.2, 126.7, 118.3, 116.2, 75.2.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3445 (W), 3062 (W), 2923 (W), 2230 (W), 1575 (W), 1519 (VS), 1371 (S), 1344 (M), 1191 (W), 1020 (W), 910 (W), 821 (W), 695 (W), 665 (W).

MS (EI, 70 eV) m/z (%): 364 (M$^+$, 20), 363 (12), 362 (39). 348 (21), 347 (11), 258 (14), 244 (7), 129 (11), 117 (11), 105 (100).

HRMS (EI) calc. $[C_{23}H_{16}N_4O]^+$: 364.1324; found: 364.1315.

Synthesis of 2,4-di(cyclohex-2-en-1-yl)-6-phenyl-1,3,5-triazine (9).



According to **TP2**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 409 mg, 1 mmol) was converted into the corresponding *di*magnesiated 1,3,5-triazine derivative **7** (-78 °C, 10 min) using *s*BuMgCl (2.2 mmol, 1.25 mL, 1.77 M in THF). After addition of CuCN·2LiCl[4] (2.2 mmol, 2.2 mL, 1 M in THF) at -78 °C and stirring at -40 °C for 30 min, 3-bromocyclohex-1-ene (354 mg, 2.2 mmol) was added dropwise. The reaction mixture was allowed to warm to -10 °C and continuously stirred for 6 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 100:1) afforded **10** (211 mg, 67%) as colorless oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.55 (dd, *J* = 7.7 Hz, 1.7 Hz 2H), 7.60-7.41 (m, 3H), 6.07-5.85 (m, 4H), 3.76-3.61 (m, 2H), 2.28-1.59 (m, 12H).

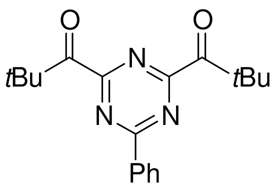
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 181.4, 170.9, 136.2, 132.2, 128.9, 128.7, 128.5, 127.2, 44.5, 27.8, 24.8, 21.4.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3058 (W), 2959 (W), 1674 (M), 1516 (VS), 1378 (W), 1260 (W), 1231 (W), 1025 (M), 776 (M), 699 (M), 650 (W).

MS (EI, 70 eV) m/z (%): 318 (16), 317 (M$^+$, 64), 316 (21), 276 (43), 252 (12), 236 (16), 281 (10), 106 (33), 104 (100), 79 (33), 77 (41).

HRMS (EI) calc. $[C_{21}H_{23}N_3]^+$: 317.1892; found: 317.1893.

Synthesis of 1,1'-(6-phenyl-1,3,5-triazine-2,4-diyl)bis(2,2-dimethylpropan-1-one) (10).



According to **TP2**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 409 mg, 1 mmol) was converted into the corresponding *di*magnesiated 1,3,5-triazine derivative **7** (-78 °C, 10 min) using *s*BuMgCl (2.2 mmol, 1.25 mL, 1.77 M in THF). After addition of CuCN·2LiCl[4] (2.2 mmol, 2.2 mL, 1 M in THF) at -78 °C and stirring at -40 °C for 30 min, pivaloyl chloride (265 mg, 2.2 mmol) was added. The reaction mixture was allowed to warm to -10 °C and continuously stirred for 6 h followed by quenching with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 50:1) afforded **11** (121 mg, 38%) as a white solid.

m. p.: 60.9-62.8 °C.

^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 8.61-8.55 (m, 2H), 7.70-7.52 (m, 3H), 1.43 (s, 18H).

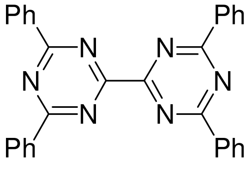
^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm): 204.5, 172.1, 171.0, 134.2, 133.9, 129.4, 128.9, 43.8, 26.7.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3062 (W), 2968 (W), 1710 (S), 1528 (VS), 1477 (M), 1392 (S), 1061 (W), 990 (M), 839 (M), 749 (S), 699 (S), 650 (W).

MS (EI, 70 eV) m/z (%): 325 (M$^+$, 4), 269 (3), 242 (2), 241 (15), 226 (14), 207 (2), 185 (3), 157 (2), 129 (6), 103 (11), 85 (11), 77 (10), 57 (100).

HRMS (EI) calc. $[C_{19}H_{23}N_3O_2]^+$: 325.1790; found: 325.1813.

Synthesis of 4,4',6,6'-tetraphenyl-2,2'-bi(1,3,5-triazine) (11).



According to **TP2**, 2-iodo-4,6-diphenyl-1,3,5-triazine (**1d**, 359 mg, 1 mmol) was converted into the corresponding triazinylmagnesium chloride (**3d**, -78 °C, 10 min) using BuMgCl (1.1 mmol, 0.77 mL, 1.43 M in THF). After addition of $ZnCl_2$ (1.1 mmol, 1.1 mL, 1 M in THF) at -78 °C and stirring for 10 min, a solution of 2-iodo-4,6-diphenyl-1,3,5-triazine (**1d**, 359 mg, 1 mmol) and Pd(PPh$_3$)$_4$ (5 mol%, 58 mg) in THF (2 mL) was added followed by warming slowly to 25 °C and continuously stirring for 24 h. The reaction mixture was quenched with brine (5 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3x 20 mL). The combined organic phases were dried over Na$_2$SO$_4$, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO$_2$, pentane/EtOAc = 10:1) afforded **11** (265 mg, 57%) as a yellow solid.

m. p.: 285.0-287.5 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.92-8.84 (m, 8H), 7.72-7.59 (m, 12H).

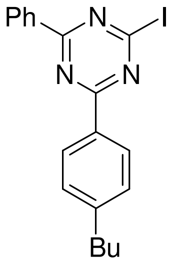
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 172.9, 170.4, 135.6, 133.1, 129.4, 128.8.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3034 (VW), 2924 (VW), 1504 (VS), 1444 (M), 1355 (S), 1245 (W), 1177 (W), 1024 (M), 839 (M), 794 (M), 751 (S), 686 (S), 643 (M).

MS (EI, 70 eV) m/z (%): 465 (100), 445 (3), 305 (12), 259 (8).

HRMS (ESI) calc. [C$_{30}$H$_{20}$N$_6$ + H]$^+$: 465.1828; found: 465.1821 ([C$_{30}$H$_{20}$N$_6$ + H]$^+$).

Synthesis of 2-(4-butylphenyl)-4-iodo-6-phenyl-1,3,5-triazine (15).



According to **TP1**, 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 820 mg, 2 mmol) reacted with (4-butylphenyl)zinc iodide (2.4 mmol, 3.3 mL, 0.72 M in THF) in the presence of Pd(PPh$_3$)$_2$Cl$_2$ (14 mg, 0.02 mmol). Purification by flash column chromatography (SiO$_2$, pentane/EtOAc = 100:1) afforded **15** (515 mg, 62%) as a white solid.

m. p.: 103.3-104.9 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.63-8.58 (m, 2H), 8.51 (d, *J* = 8.3 Hz, 2H), 7.67-7.51 (m, 3H), 7.36 (d, *J* = 8.3 Hz, 2H), 2.77-2.70 (m, 2H), 1.74-1.62 (m, 2H), 1.48-1.34 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

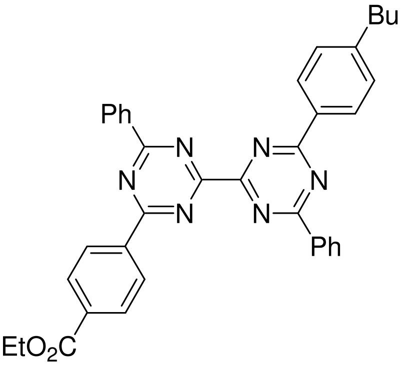
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 171.1, 170.9, 149.3, 142.6, 134.3, 133.3, 131.7, 129.4, 129.3, 128.9, 128.7, 35.8, 33.3, 22.4, 13.9.

IR (Diamond-ATR, neat) ν (cm^{-1}): 2956 (VW), 2928 (VW), 1609 (VW), 1511 (VS), 1479 (S), 1441 (W), 1358 (M), 1221 (M), 1070 (W), 801 (W), 767 (M), 693 (W), 618 (W).

MS (EI, 70 eV) m/z (%): 416 (100), 306 (49), 257 (24), 177 (7).

HRMS (ESI) calc. [$C_{19}H_{18}IN_3$ + H]$^+$: 416.0624; found: 416.0619 ([$C_{19}H_{18}IN_3$ + H]$^+$).

Synthesis of ethyl 4-(4'-(4-butylphenyl)-6,6'-diphenyl-[2,2'-bi(1,3,5-triazin)]-4-yl) benzoate (12).



According to **TP2**, 2-(4-butylphenyl)-4-iodo-6-phenyl-1,3,5-triazine (**15**, 249 mg, 0.6 mmol) was converted into the corresponding triazinylmagnesium chloride using sBuMgCl (0.66 mmol, 0.37 mL, 1.77 M in THF, -78 °C, 10 min). After addition of $ZnCl_2$ (0.66 mmol, 0.66 mL, 1 M in THF) at -78 °C and stirring for 10 min, a solution of ethyl 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1g**, 216 mg, 0.5 mmol) and Pd-PEPPSI-IPr (5 mol %, 17 mg) in THF (2 mL) was added followed by warming slowly to 25 °C and continuously stirring for 24 h. The reaction mixture was quenched with brine (5 mL). The aqueous layer was extracted with CH_2Cl_2 (3x 20 mL). The combined organic phases were dried over Na_2SO_4, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO_2, pentane/EtOAc = 5:1) afforded **12** (154 mg, 52%) as a yellow solid.

m. p.: 164.6-166.5 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.91-8.88 (m, 2H), 8.85-8.81 (m, 4H), 8.73 (d, *J* = 8.2

Hz, 2H), 8.27 (d, J = 8.2 Hz, 2H), 7.68-7.57 (m, 6H), 7.41 (d, J = 7.9 Hz, 2H), 4.45 (q, J = 7.1 Hz, 2H), 2.77-2.73 (m, 2H), 1.72-1.66 (m, 2H), 1.46 (t, J = 7.1 Hz, 3H), 1.44-1.38 (m, 2H), 0.97 (t, J = 7.4 Hz, 3H).

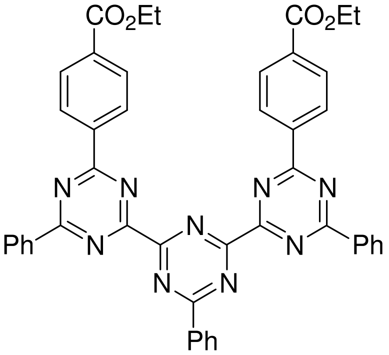
^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 173.0, 172.9, 172.7, 171.9, 170.5, 169.9, 166.1, 148.9, 139.4, 135.6, 135.3, 134.2, 133.3, 133.0, 132.9, 129.9, 129.4, 129.4, 129.3, 129.2, 128.9, 128.8, 128.7, 61.4, 35.8, 33.3, 22.4, 14.3, 13.9.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3065 (W), 2956 (W), 1715 (S), 1504 (VS), 1357 (M), 1271 (S), 1099 (M), 1017 (M), 829 (W), 764 (S), 688 (S), 648 (M).

MS (EI, 70 eV) m/z (%): 592 (M$^+$, 100), 551 (9), 550 (29), 549 (40), 489 (13). 433 (8), 331 (9), 277 (9), 261 (14), 252 (24), 129 (9), 116 (11), 104 (21).

HRMS (EI) calc. $[C_{37}H_{32}N_6O_2]^+$: 592.2587; found: 592.2591.

Synthesis of diethyl 4,4'-(6,6',6''-triphenyl-[2,2':4',2''-ter(1,3,5-triazine)]-4,4''-diyl) dibenzoate (13).



According to **TP2**, ethyl 4-(4-iodo-6-phenyl-1,3,5-triazin-2-yl)benzoate (**1g**, 431 mg, 1 mmol) was converted into the corresponding triazinylmagnesium bromide using OctMgBr (1.1 mmol, 1.53 mL, 0.72 M in THF). After addition of ZnCl$_2$ (1.1 mmol, 1.1 mL, 1 M in THF) at -78 °C and stirring for 10 min, a solution of 2,4-diiodo-6-phenyl-1,3,5-triazine (**6**, 144 mg, 0.35 mmol) and Pd-PEPPSI-IPr (5 mol %, 17 mg) in THF (2 mL) was added followed by warming slowly to 25 °C and continuously stirring for 24 h. The reaction mixture was quenched with brine (5 mL). The aqueous layer was extracted with CH$_2$Cl$_2$ (3x 20 mL). The combined organic phases were dried over Na$_2$SO$_4$, the solvent was removed *in vacuo*. Purification by flash column chromatography (SiO$_2$, pentane/EtOAc = 2:1) afforded **13** (121 mg, 45%) as a yellow solid.

m. p.: 185.0-187.1 °C.

^{1}H NMR (300 MHz, CDCl$_3$) δ (ppm): 8.92 (d, *J* = 7.9 Hz, 6H), 8.86 (d, *J* = 7.4 Hz, 4H), 8.27 (d, *J* = 7.4 Hz, 4H), 7.73-7.59 (m, 9H), 4.45 (q, *J* = 7.1 Hz, 4H), 1.45 (t, *J* = 7.1 Hz, 6H).

^{13}C NMR (75 MHz, CDCl$_3$) δ (ppm): 174.3, 173.2, 172.1, 171.0, 169.9, 166.0, 139.2, 135.1, 134.7, 134.4, 133.9, 133.5, 129.9, 129.9, 129.5, 129.3, 129.0, 128.9, 61.4, 14.3.

IR (Diamond-ATR, neat) ν (cm^{-1}): 3066 (VW), 2927 (VW), 1717 (S), 1504 (VS), 1361 (M), 1270 (S), 1101 (M), 1020 (M), 834 (M), 759 (M), 733 (M), 688 (M), 650 (W).

MS (EI, 70 eV) m/z (%): 763 (M$^+$, 60), 718 (12), 588 (11), 487 (13), 486 (42), 336 (12), 309 (11), 285 (15), 277 (51), 249 (30), 208 (19), 176 (18), 148 (20), 129 (43), 104 (100), 77 (17).

HRMS (EI) calc. [$C_{45}H_{33}N_9O_4$]$^+$: 763.2656; found: 763.2656.

References

[1] Tamborskl, C.; Chen, G. J.; Anderson, D. R.; Jr. Snyder, C. E. Ind. Eng. Chem. Prod. Res. Dev. 1983, 22, 172.

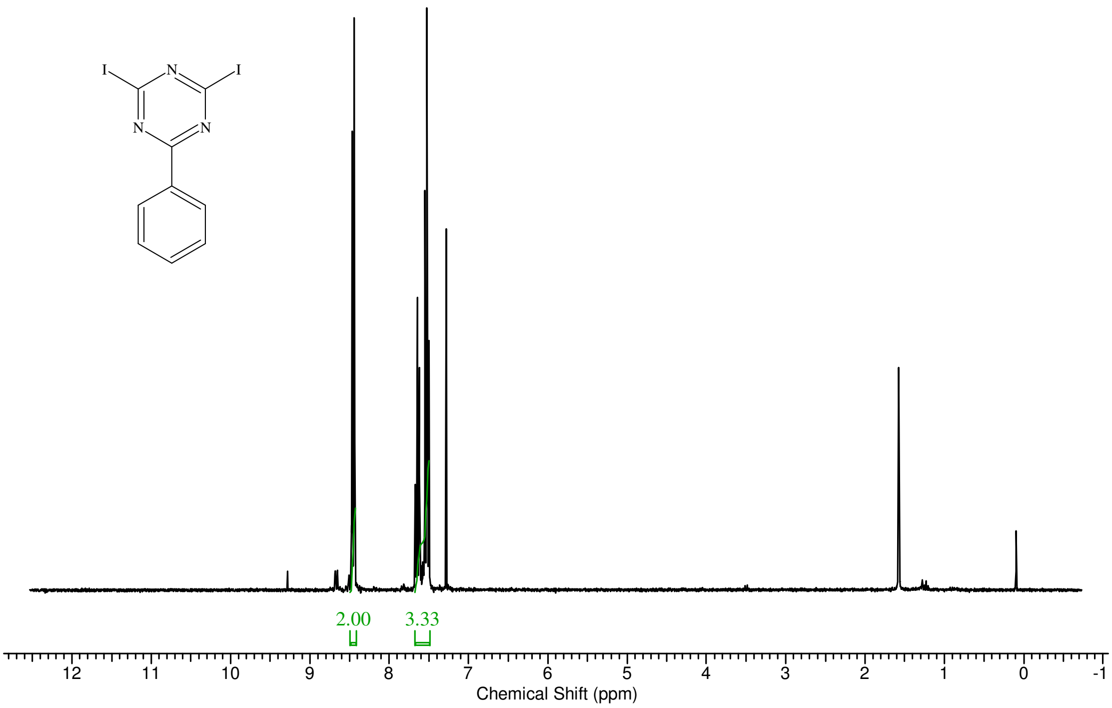
[2] Krasoviskiy, A.; Malakhov, V.; Gavryushin, A.; Knochel, P. Angew. Chem. Int. Ed. 2006, 45, 6040.

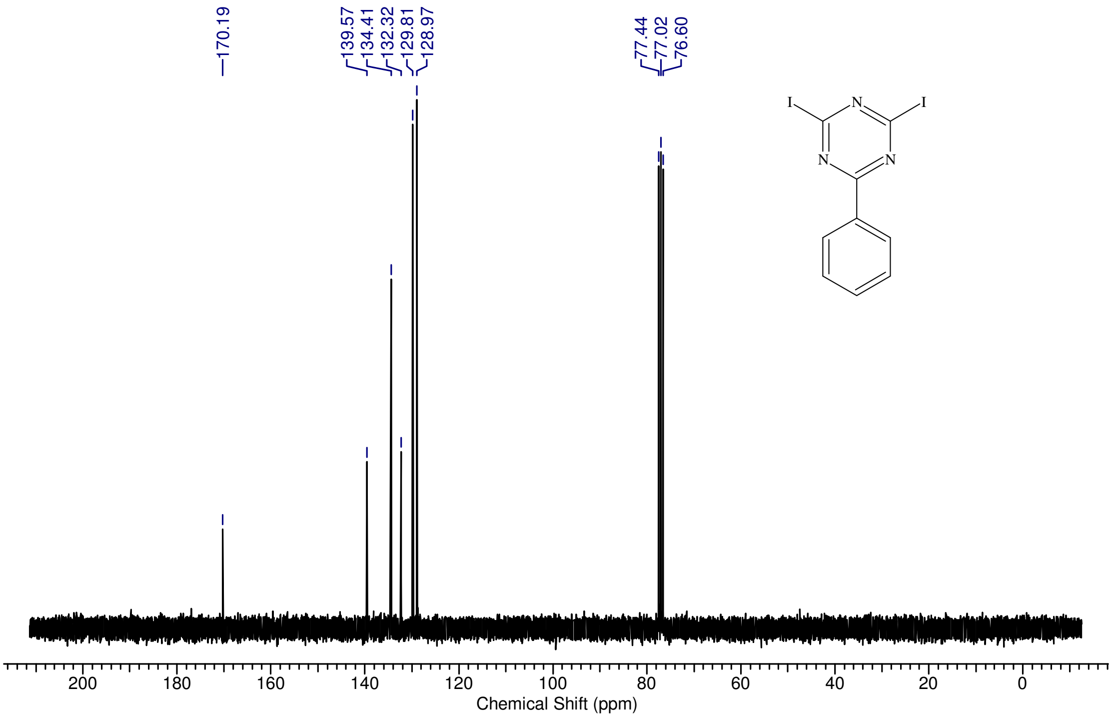
[3] Angerer, S. V. in *Science of Synthesis*, (Ed.: Weinreb, S. M.), **2003**, vol. 17, p 529.

[4] Del Amo, V.; Dubbaka, S. R.; Krasovskiy, A.; Knochel, P. *Angew. Chem. Int. Ed.* **2006**, *45*, 7838-7842.

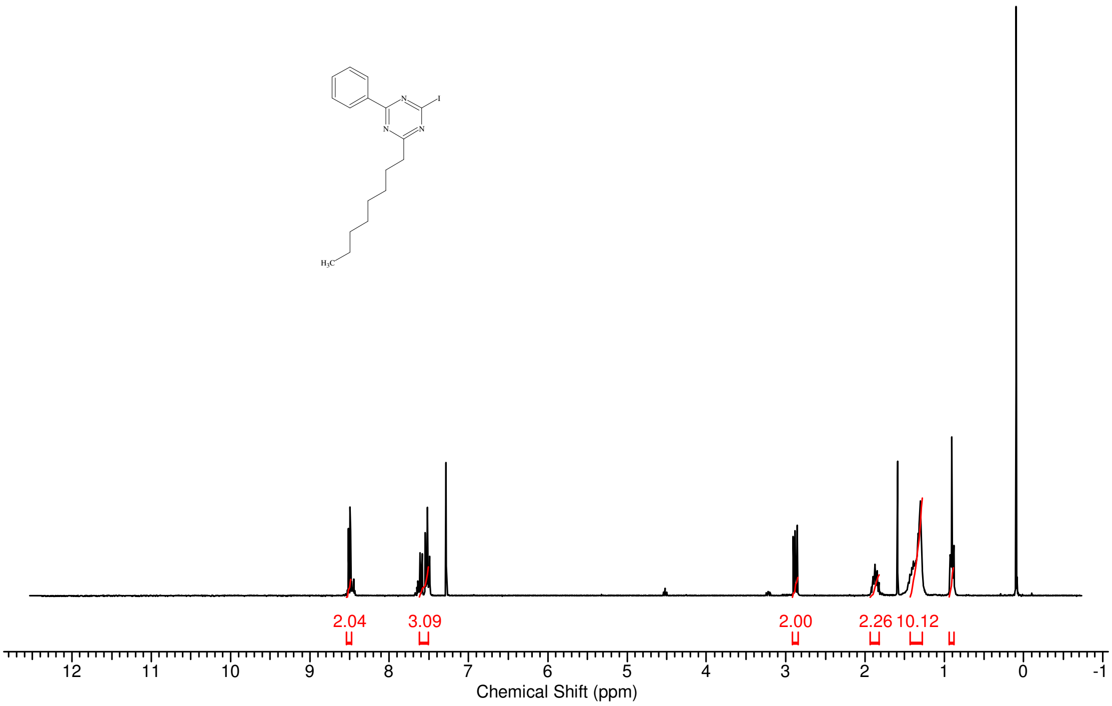
^{1}H NMR and ^{13}C NMR

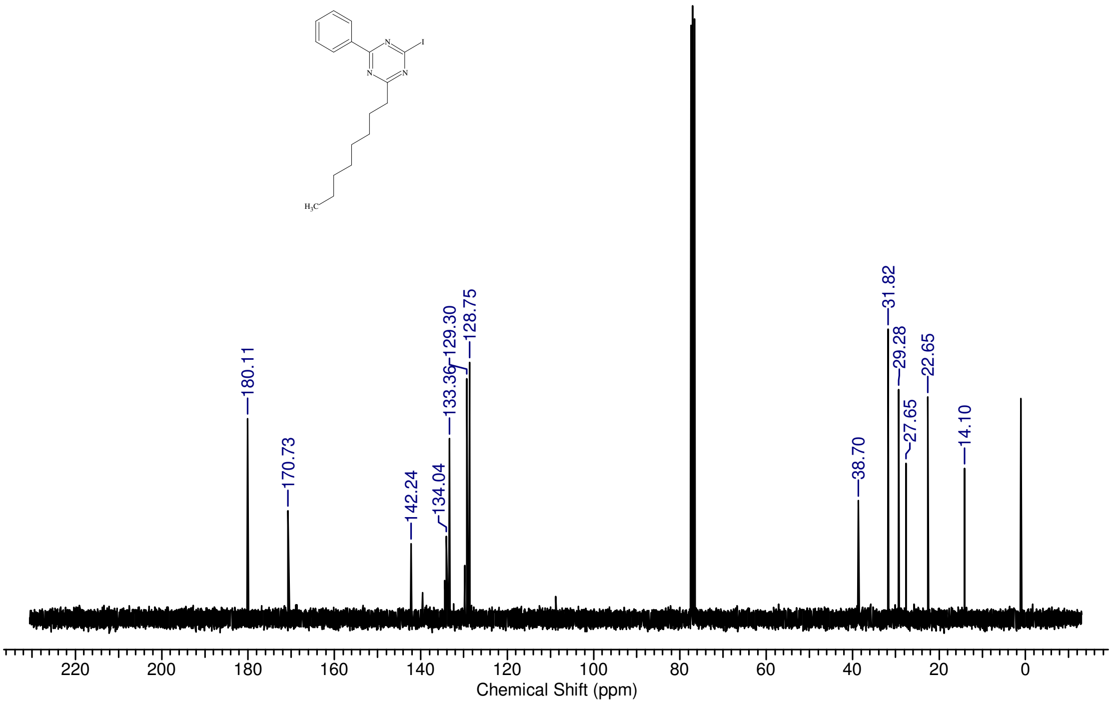
Compound **6**.



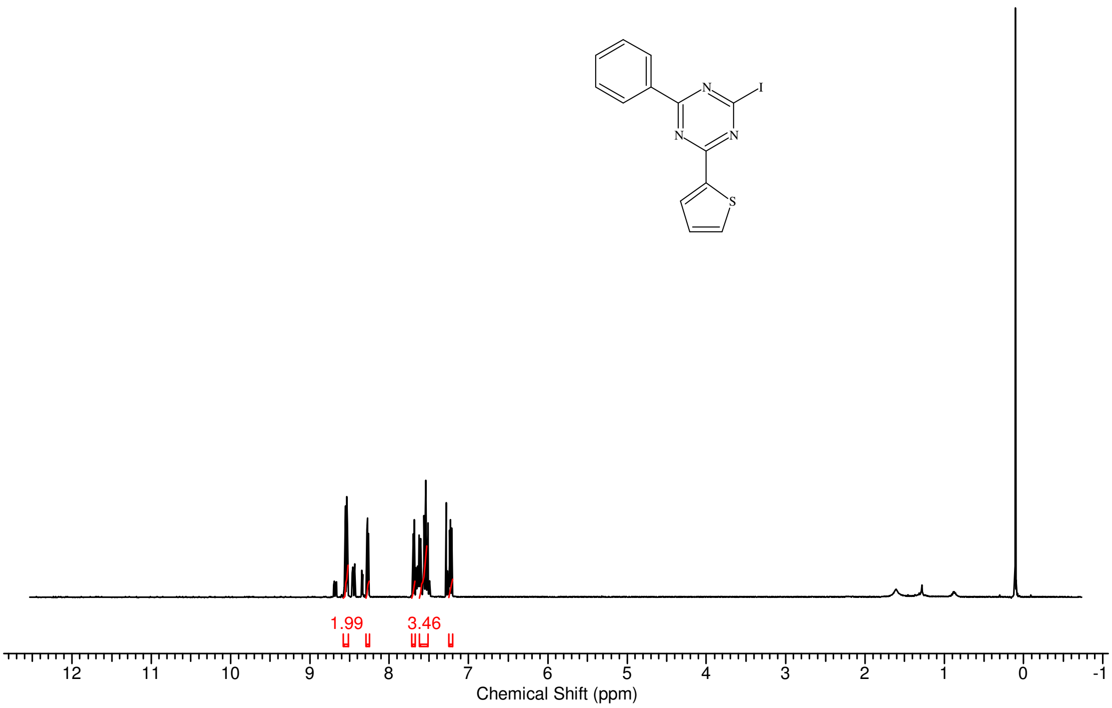


Compound **1a**.

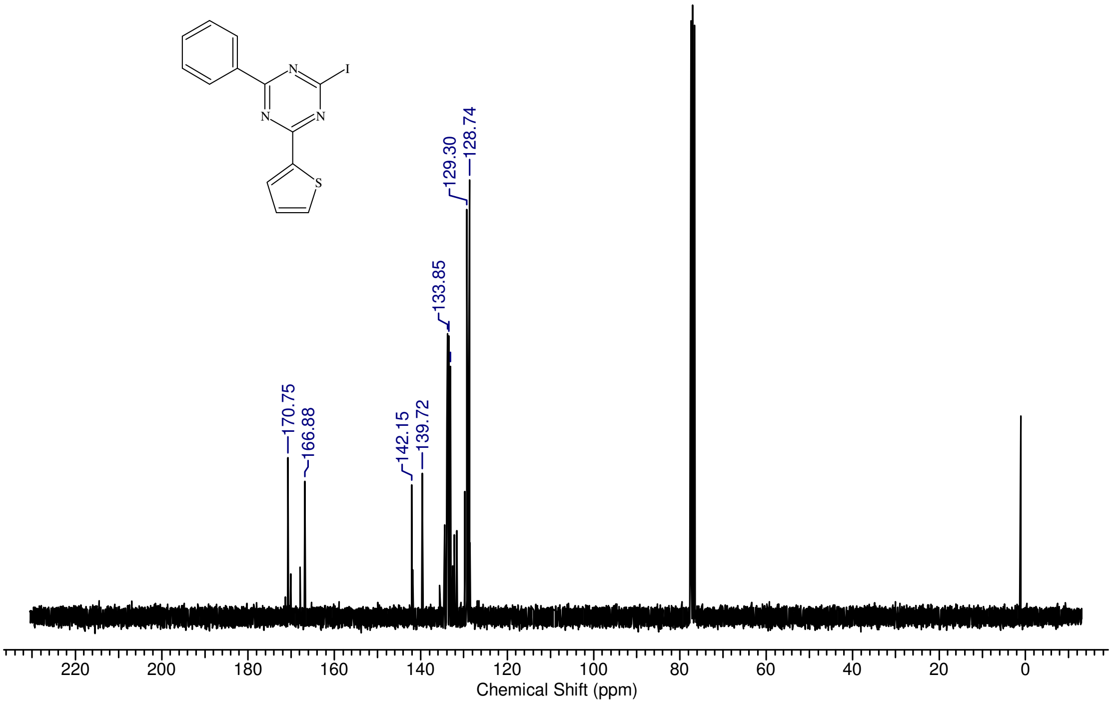

N
N
N
I
H3C
2.04
3.09
2.00
2.26
10.12
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


N
N
N
I
H3C
180.11
170.73
142.24
134.04
133.36
129.30
128.75
38.70
31.82
29.28
27.65
22.65
14.10
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **1b**.

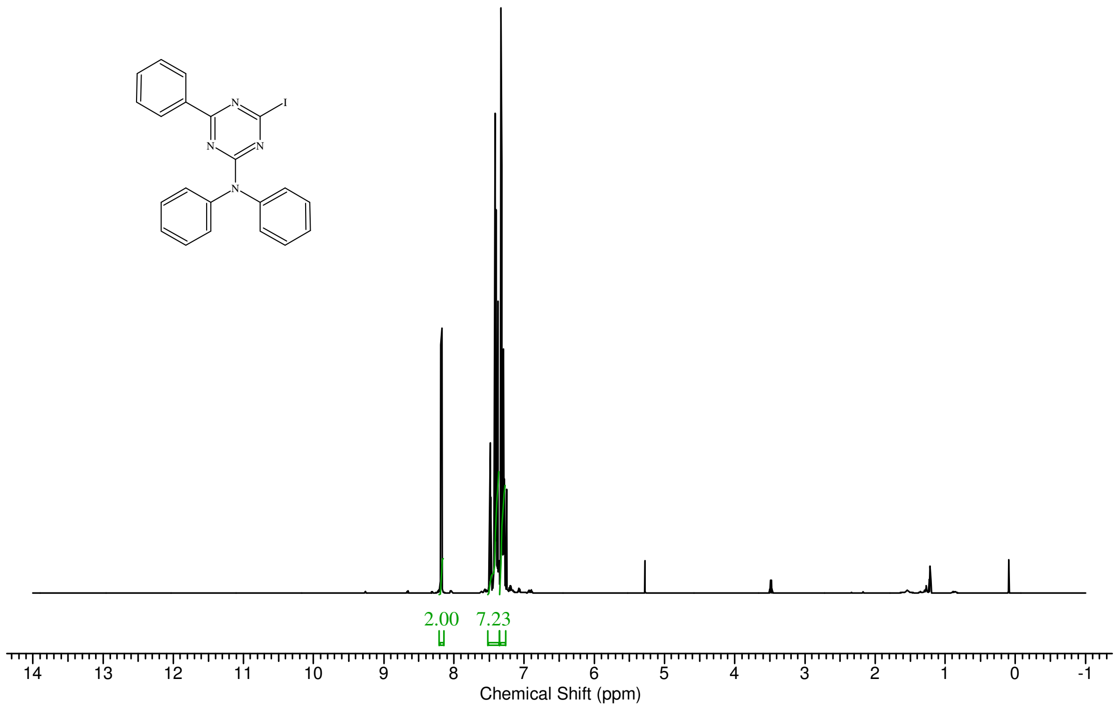


N
N
N
I
S
1.99
3.46
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

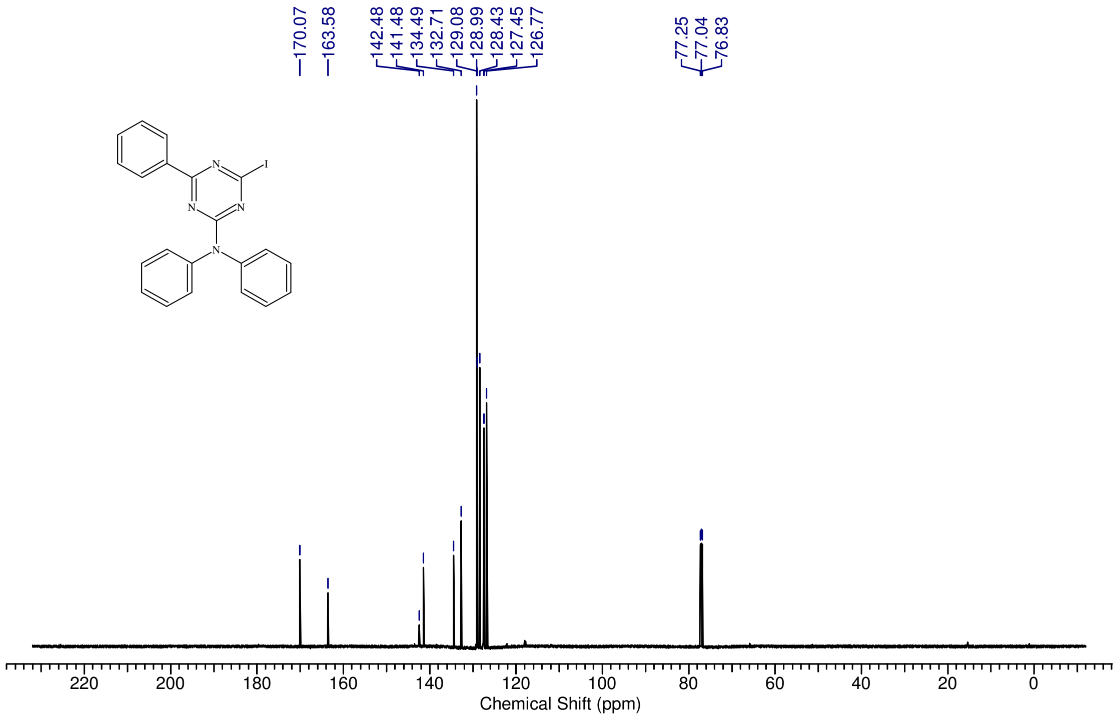


N
N
N
I
S
170.75
166.88
142.15
139.72
133.85
129.30
128.74
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **1c**.

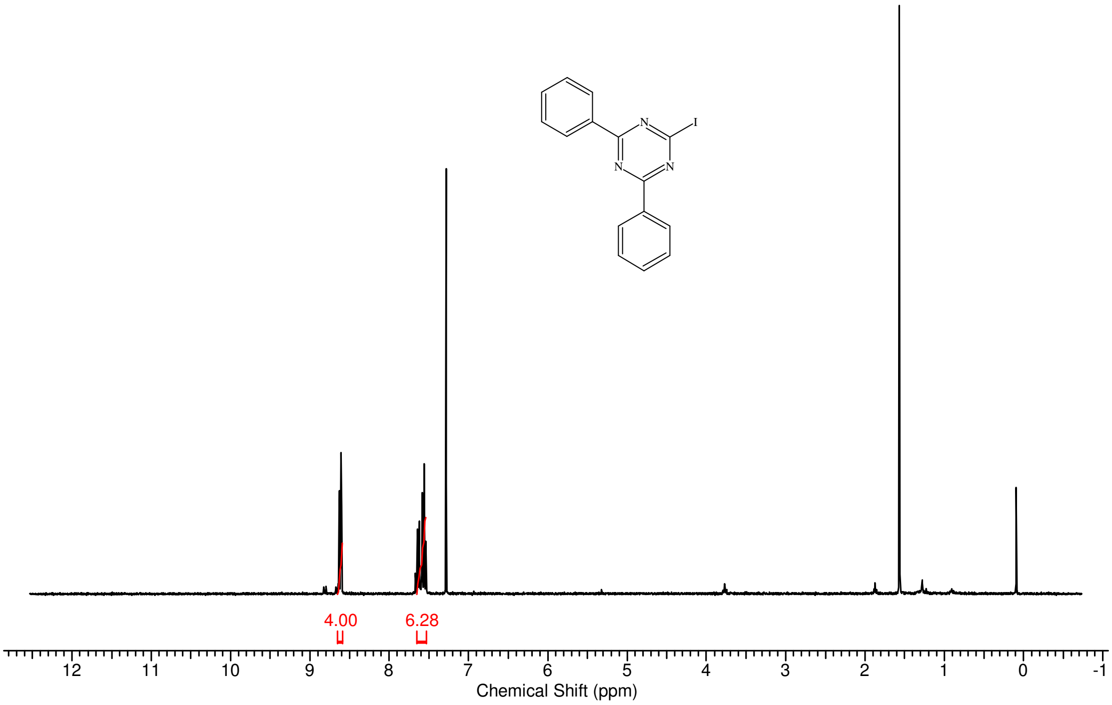


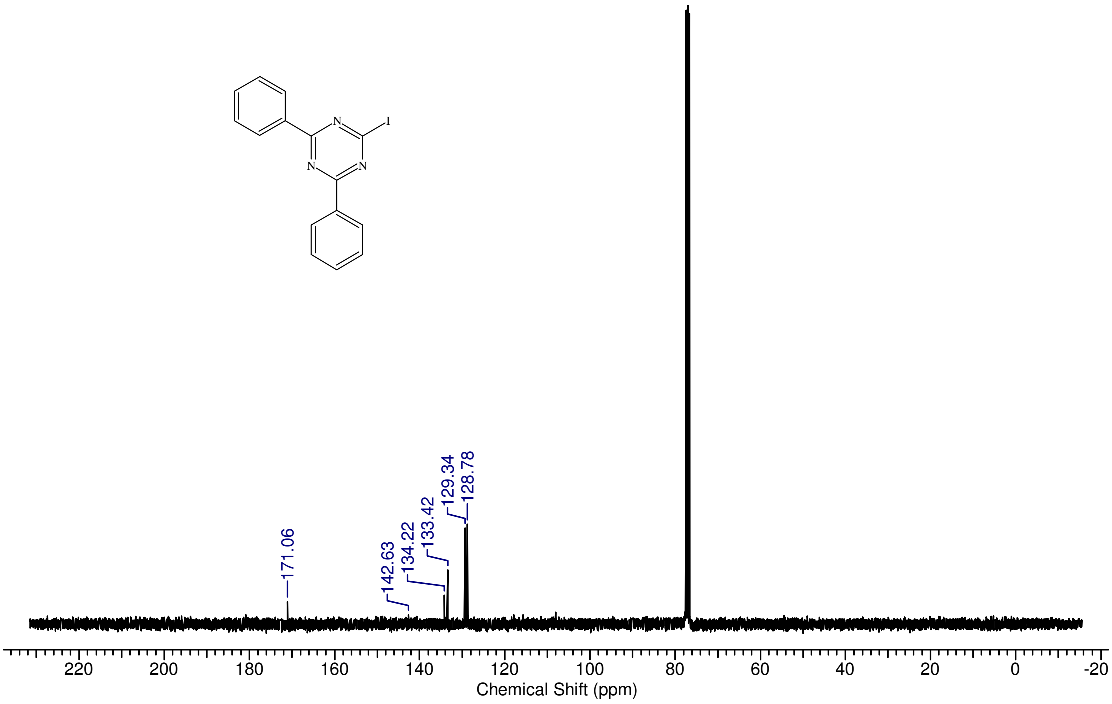
N
N
N
I
N
2.00
7.23
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)



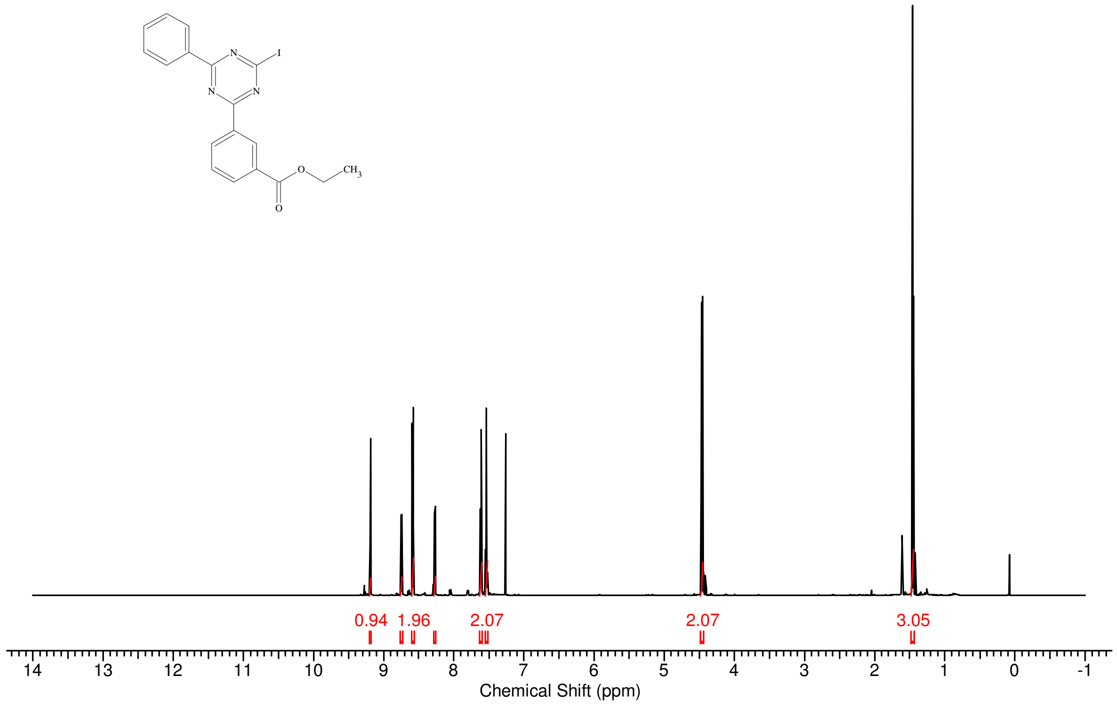
170.07
163.58
142.48
141.48
134.49
132.71
129.08
128.99
128.43
127.45
126.77
77.25
77.04
76.83
N
N
N
I
N
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

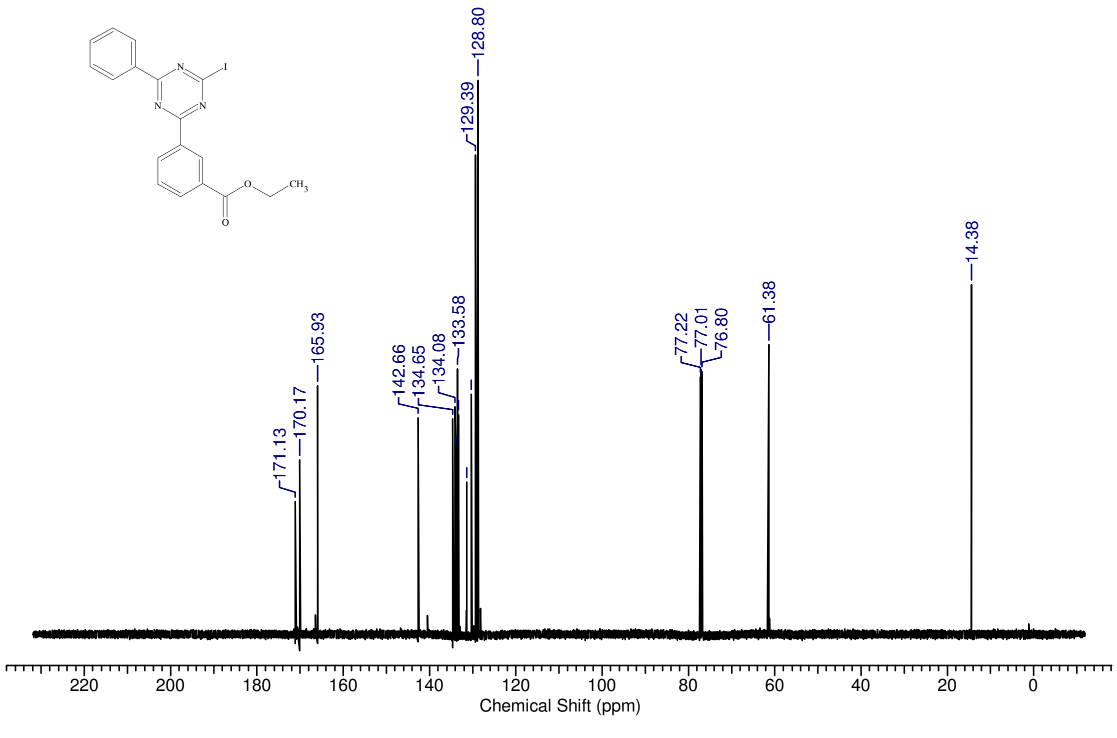
Compound **1d**.


N
N
N
I
4.00
6.28
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

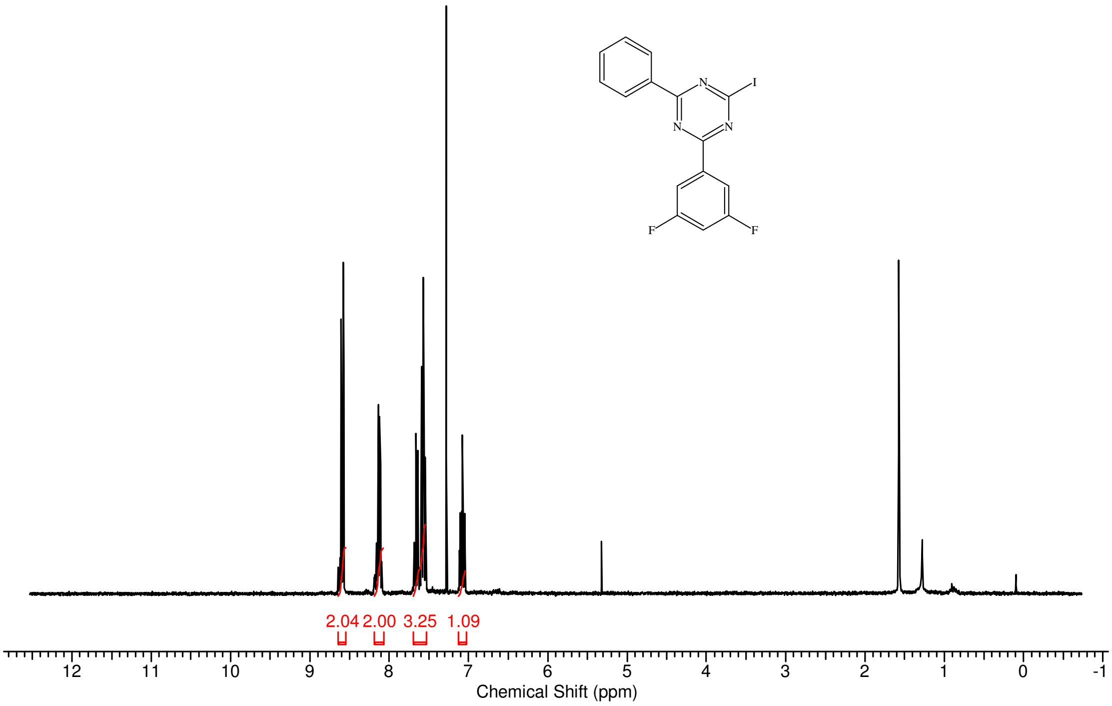

N
N
N
I
171.06
142.63
134.22
133.42
129.34
128.78
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

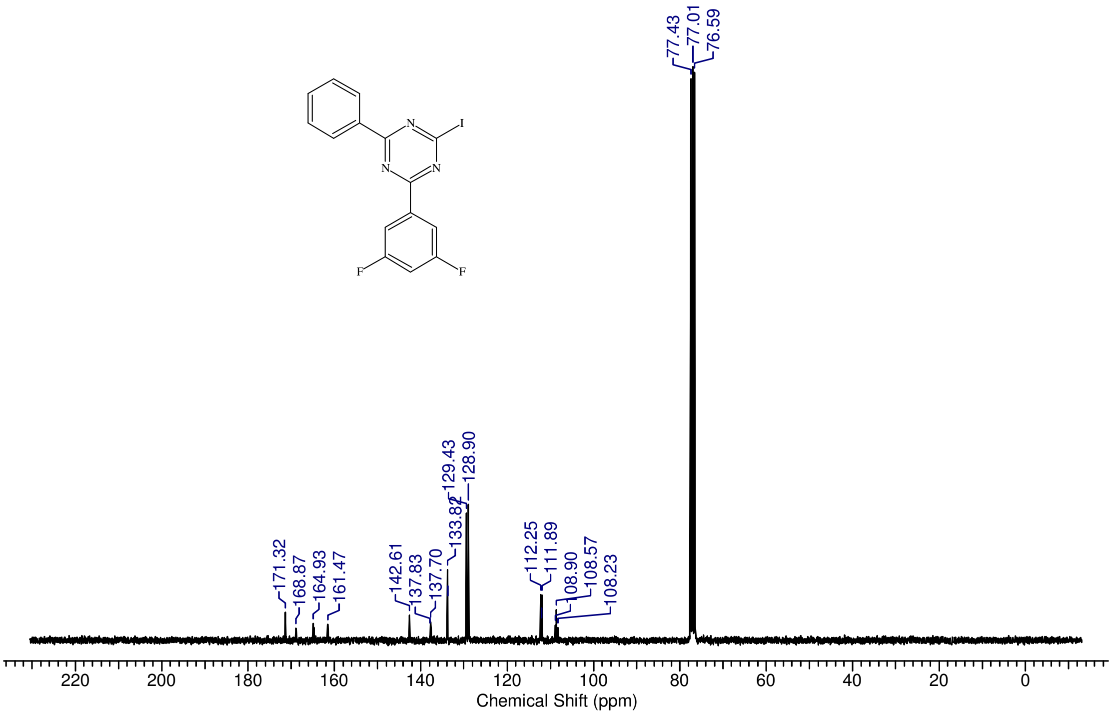
Compound **1e**.


N
N
N
I
O
O
CH3
0.94
1.96
2.07
2.07
3.05
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

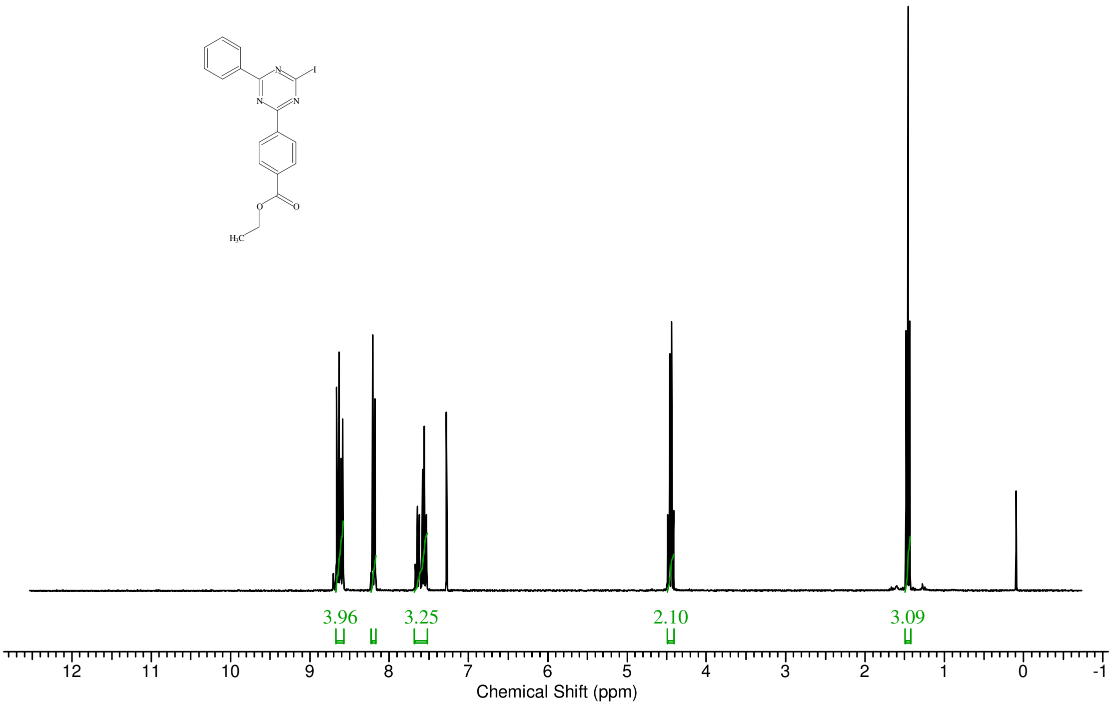

N
N
N
I
O
O
CH3
171.13
170.17
165.93
142.66
134.65
134.08
133.58
129.39
128.80
77.22
77.01
76.80
61.38
14.38
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

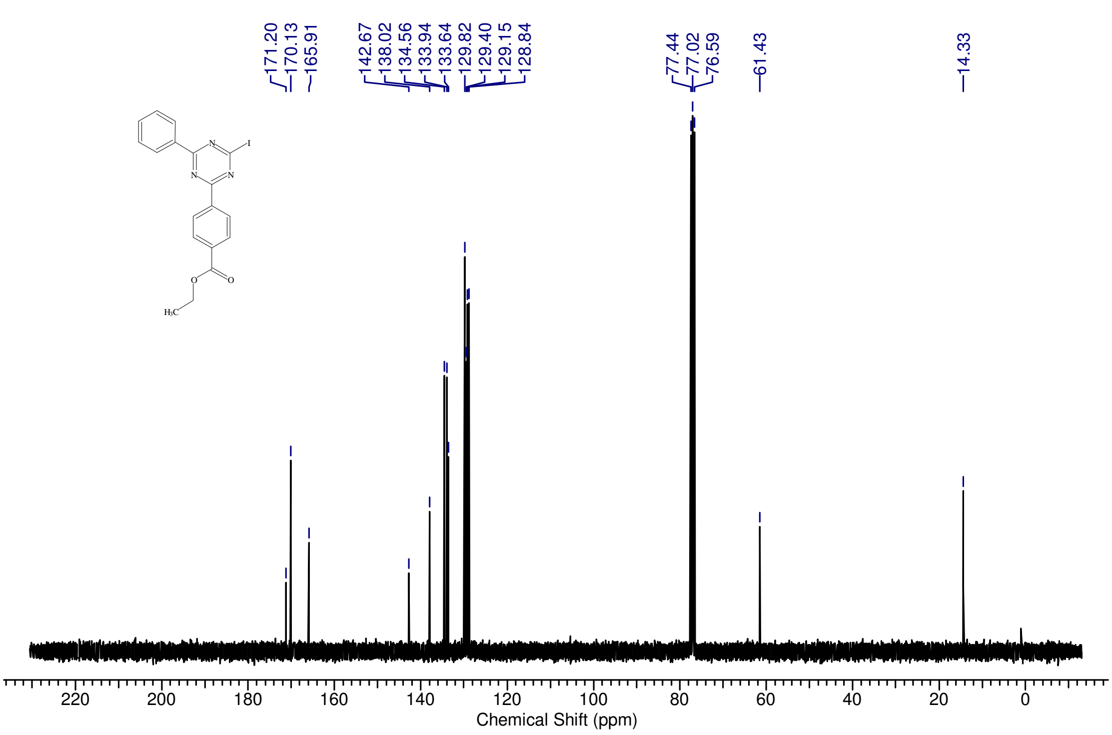
Compound **1f**.


N
N
N
I
F
F
2.04
2.00
3.25
1.09
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

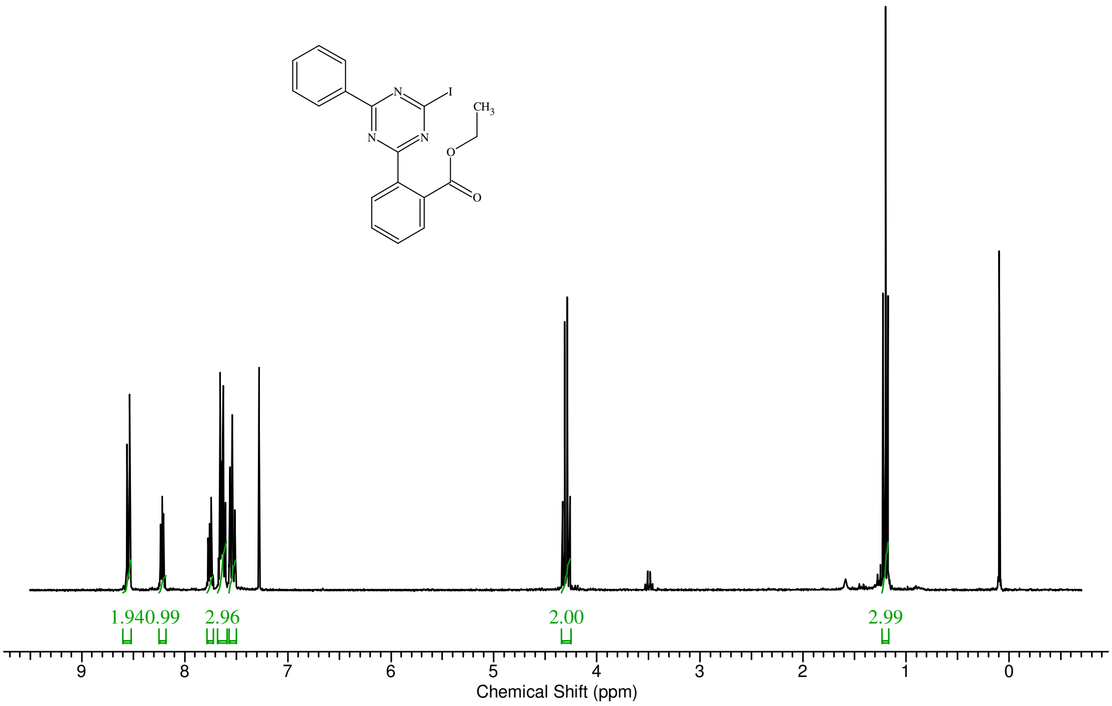

77.43
77.01
76.59
N
N
N
I
F
F
171.32
168.87
164.93
161.47
142.61
137.83
137.70
133.82
129.43
128.90
112.25
111.89
08.90
108.57
108.23
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **1g**.

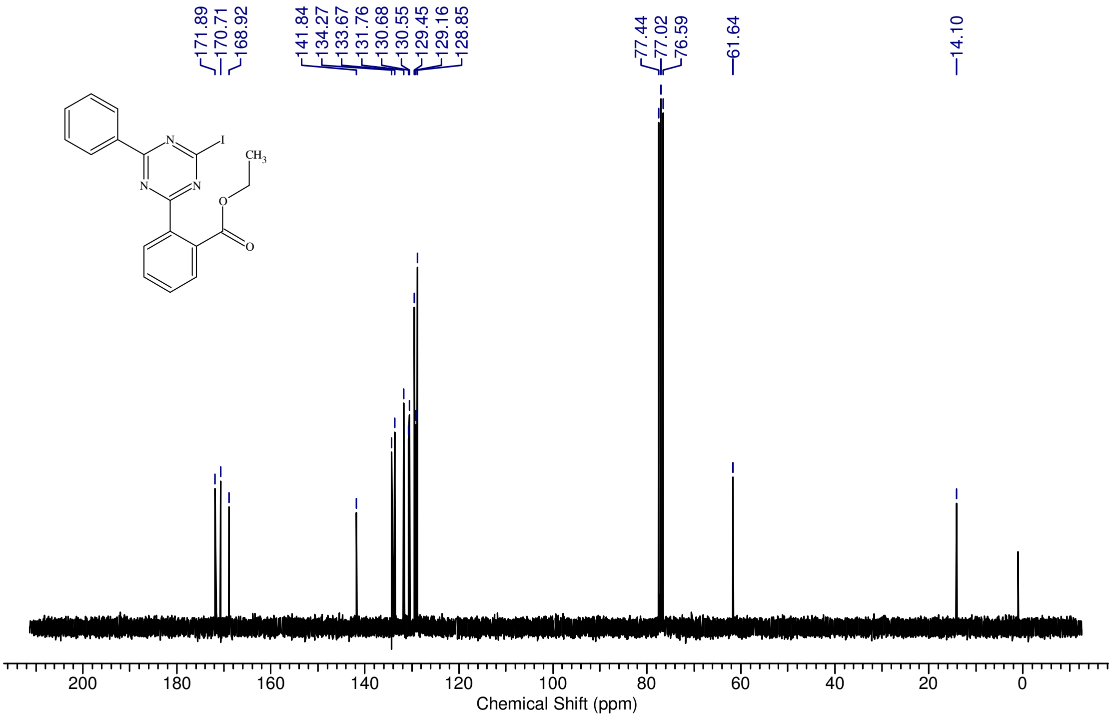

N
N
N
I
O
O
H₃C
3.96
3.25
2.10
3.09
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


171.20
170.13
165.91
142.67
138.02
134.56
133.94
133.64
129.82
129.40
129.15
128.84
77.44
77.02
76.59
61.43
14.33
N
N
N
I
O
O
H₃C
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **1h**.

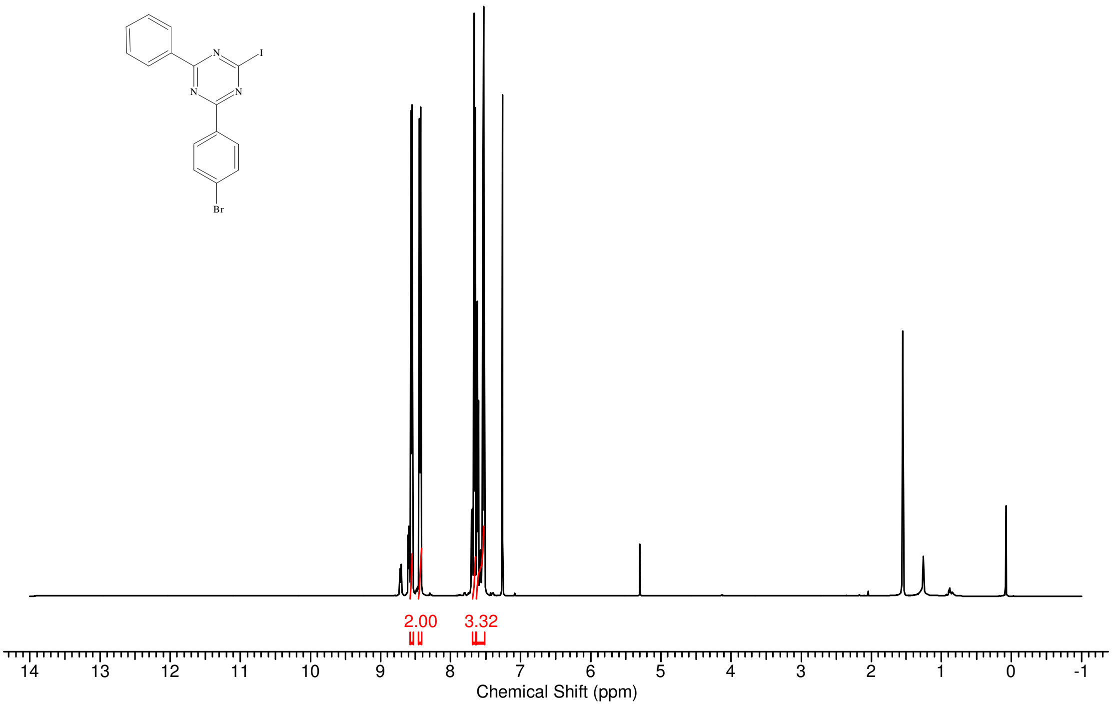


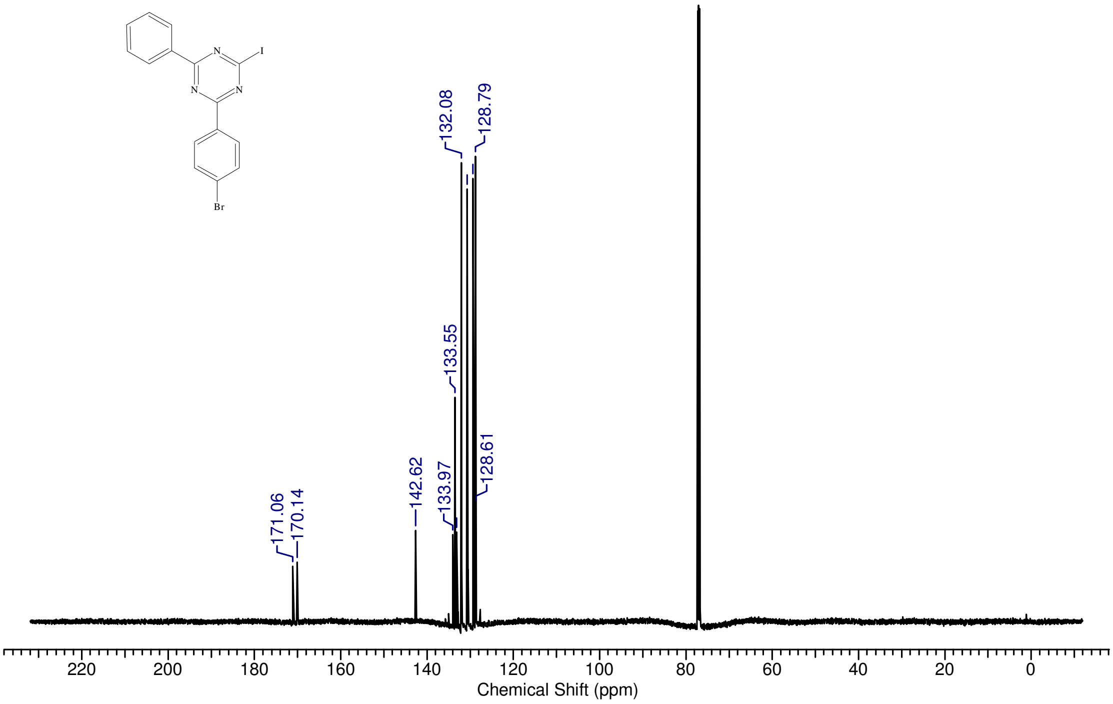
N
N
N
I
CH3
O
O
1.94
0.99
2.96
2.00
2.99
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)



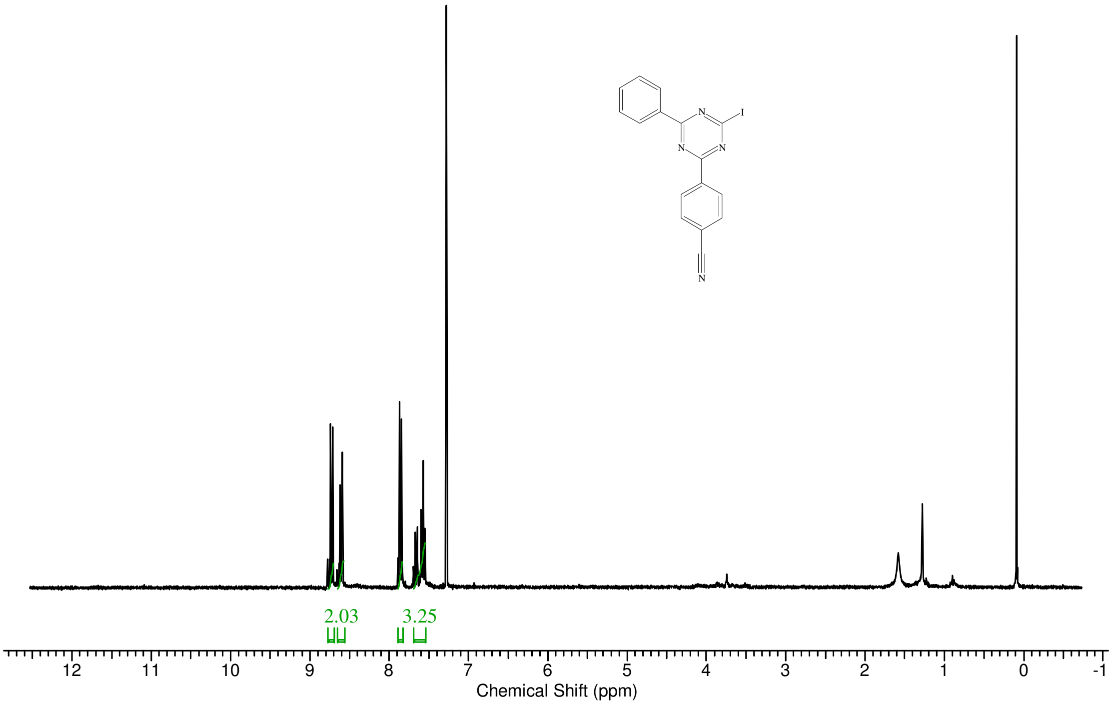
171.89
170.71
168.92
141.84
134.27
133.67
131.76
130.68
130.55
129.45
129.16
128.85
77.44
77.02
76.59
61.64
14.10
N
N
N
I
CH3
O
O
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

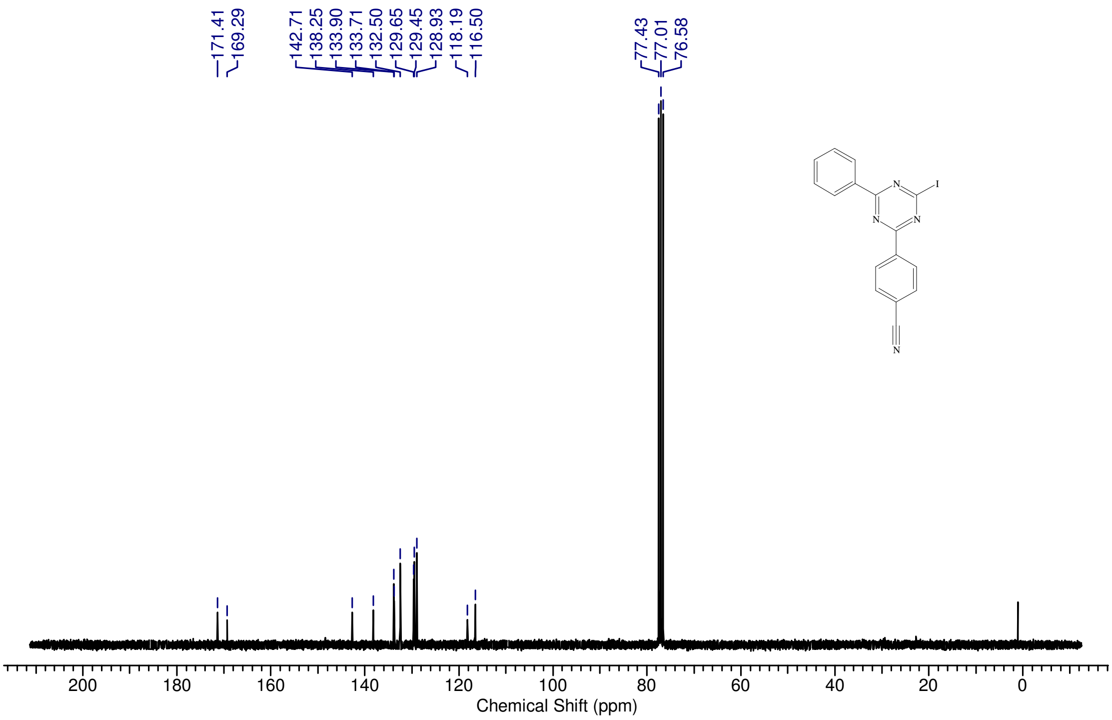
Compound **1i**.


N
N
N
I
Br
2.00
3.32
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

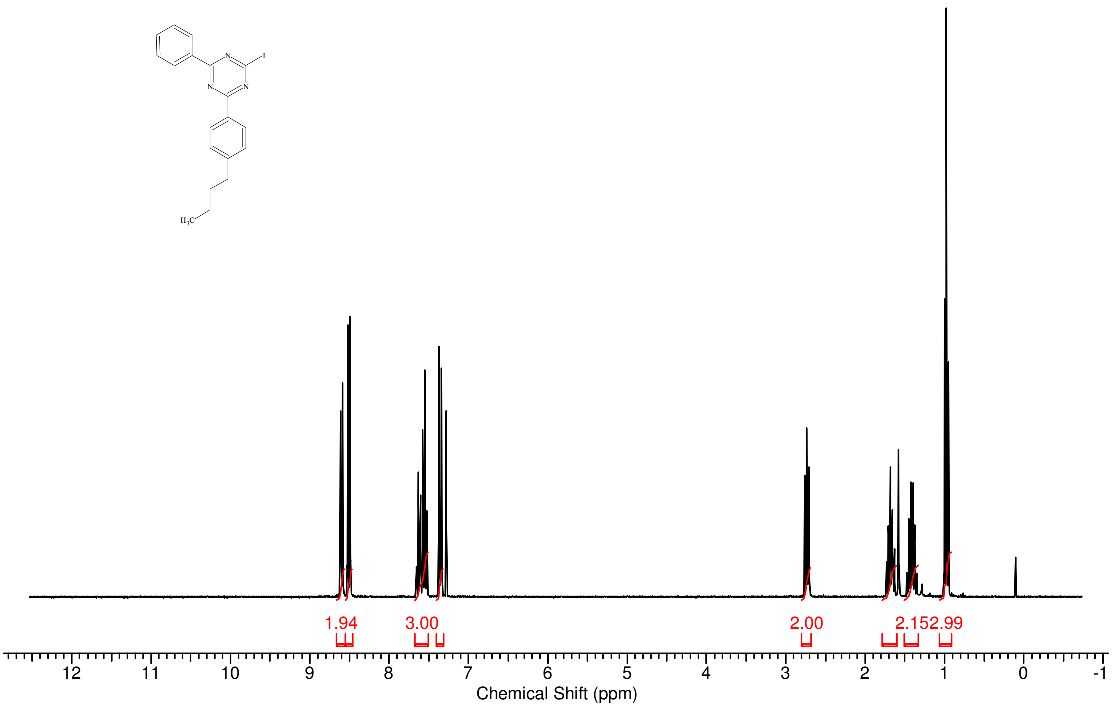

N
N
N
I
Br
132.08
128.79
133.55
128.61
142.62
133.97
171.06
170.14
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

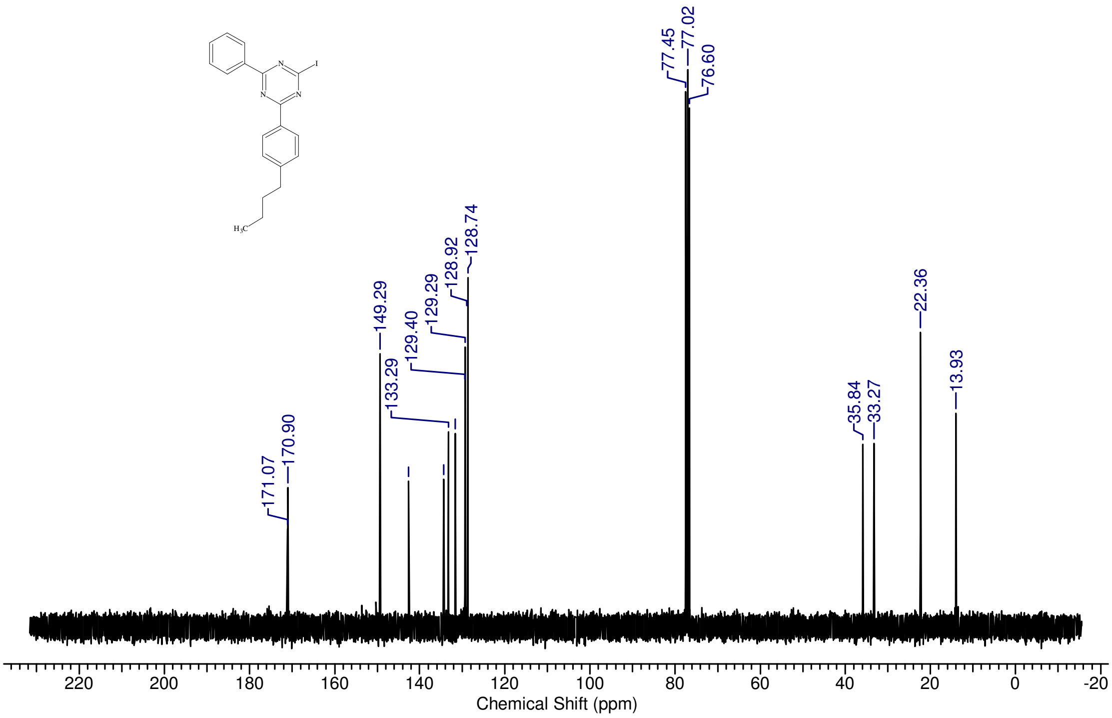
Compound **1j**.


N
N
N
I
N
2.03
3.25
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

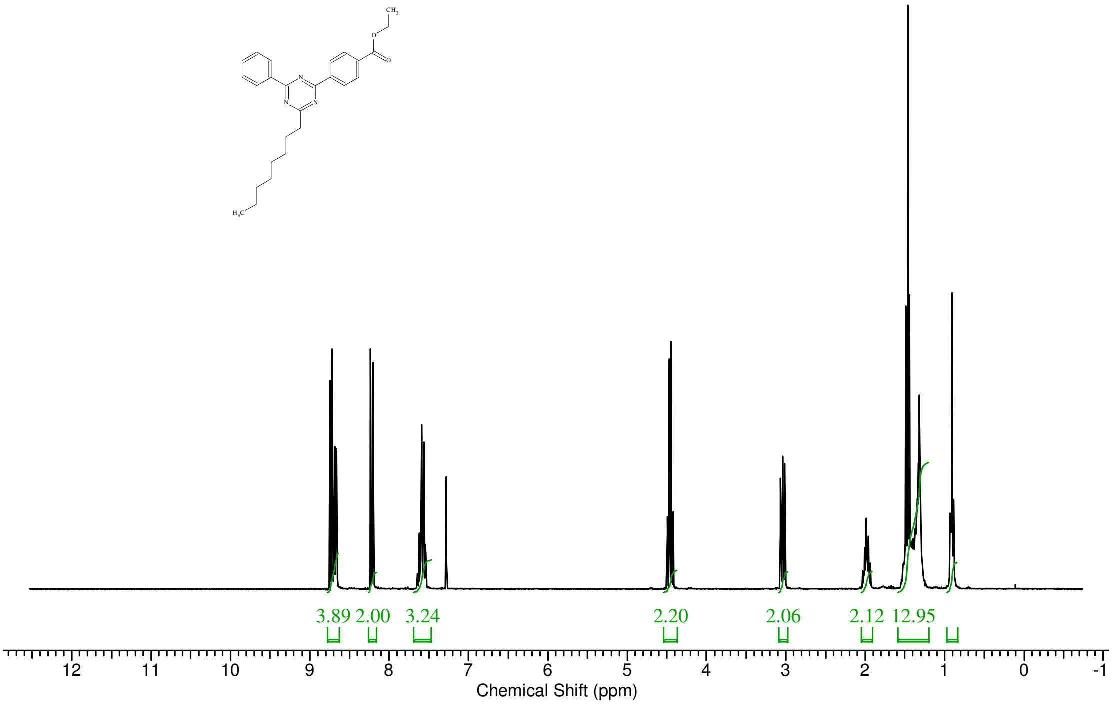

171.41
169.29
142.71
138.25
133.90
133.71
132.50
129.65
129.45
128.93
118.19
116.50
77.43
77.01
76.58
N
N
N
I
N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **15**.

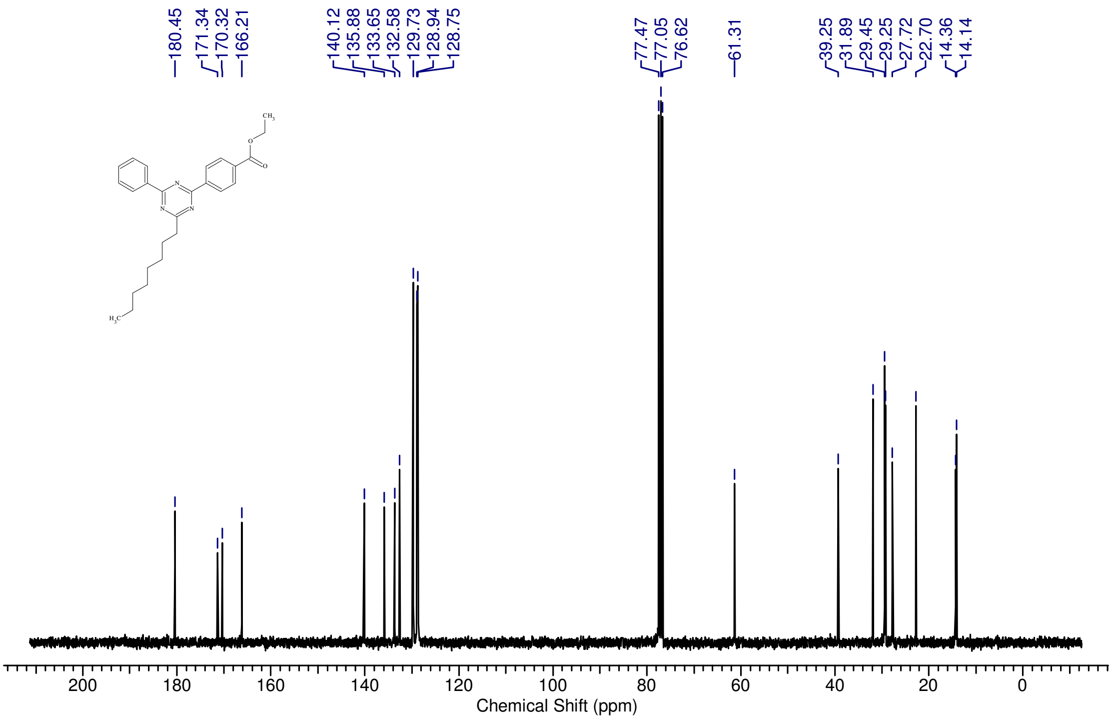

N
N
N
I
H$_3$C
1.94
3.00
2.00
2.15
2.99
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


N
N
N
I
H$_3$C
77.45
77.02
76.60
149.29
133.29
129.40
129.29
128.92
128.74
171.07
170.90
35.84
33.27
22.36
13.93
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound **5a**.

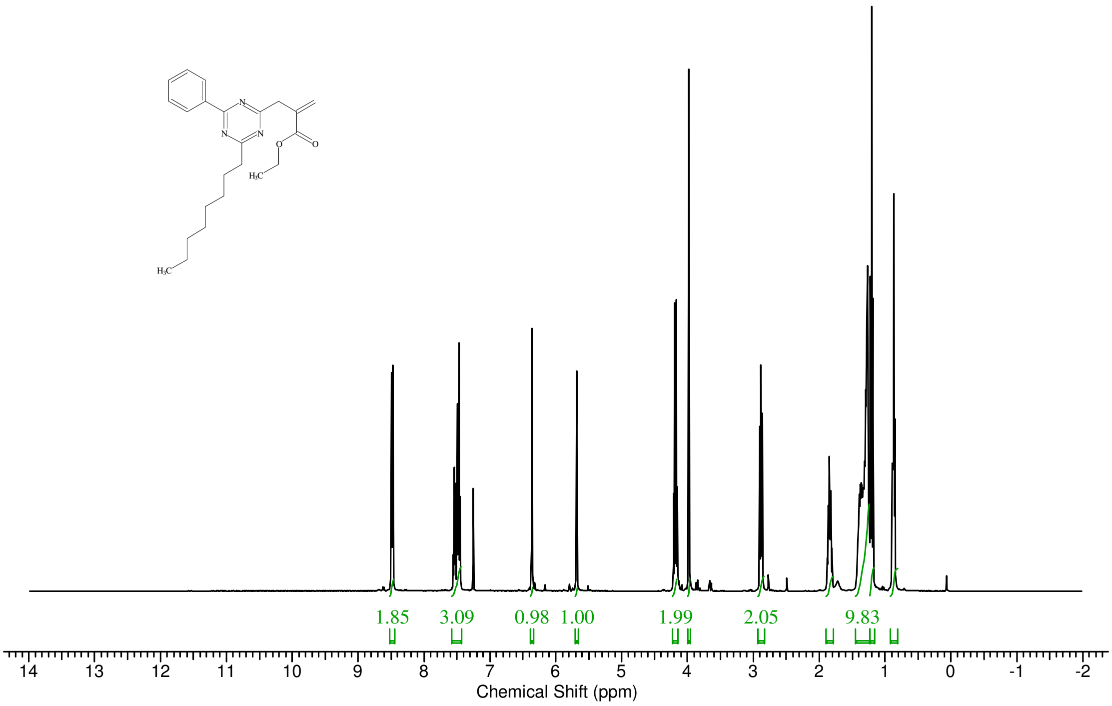


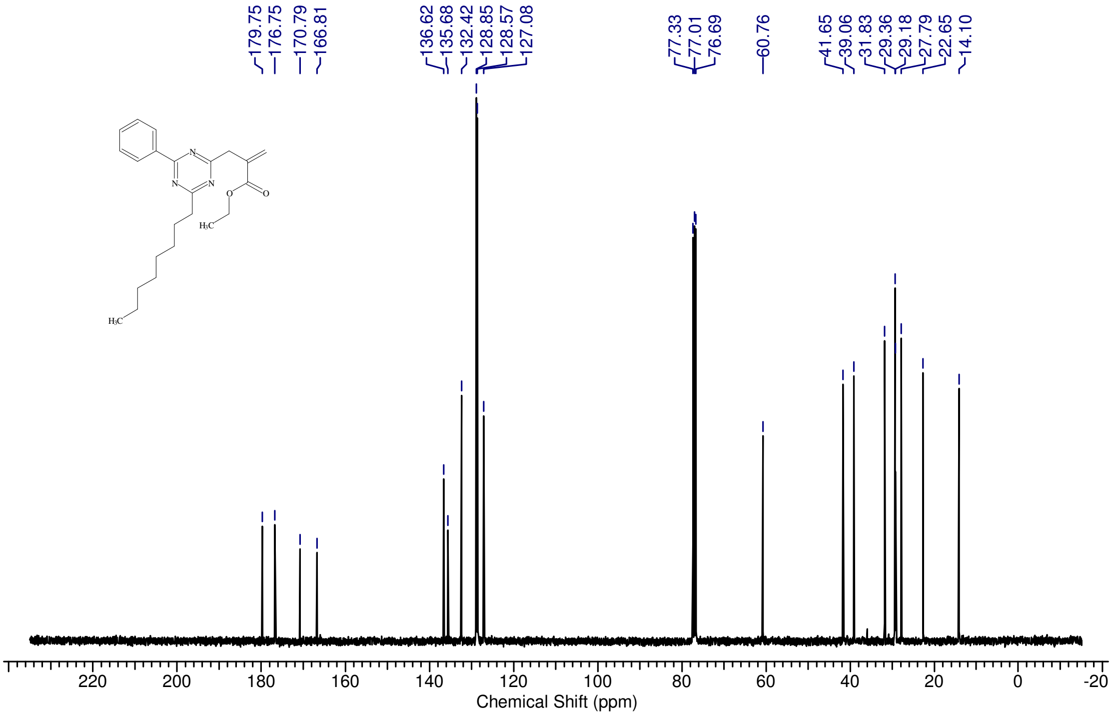
CH3
O
O
N
N
N
H3C
3.89
2.00
3.24
2.20
2.06
2.12
12.95
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)



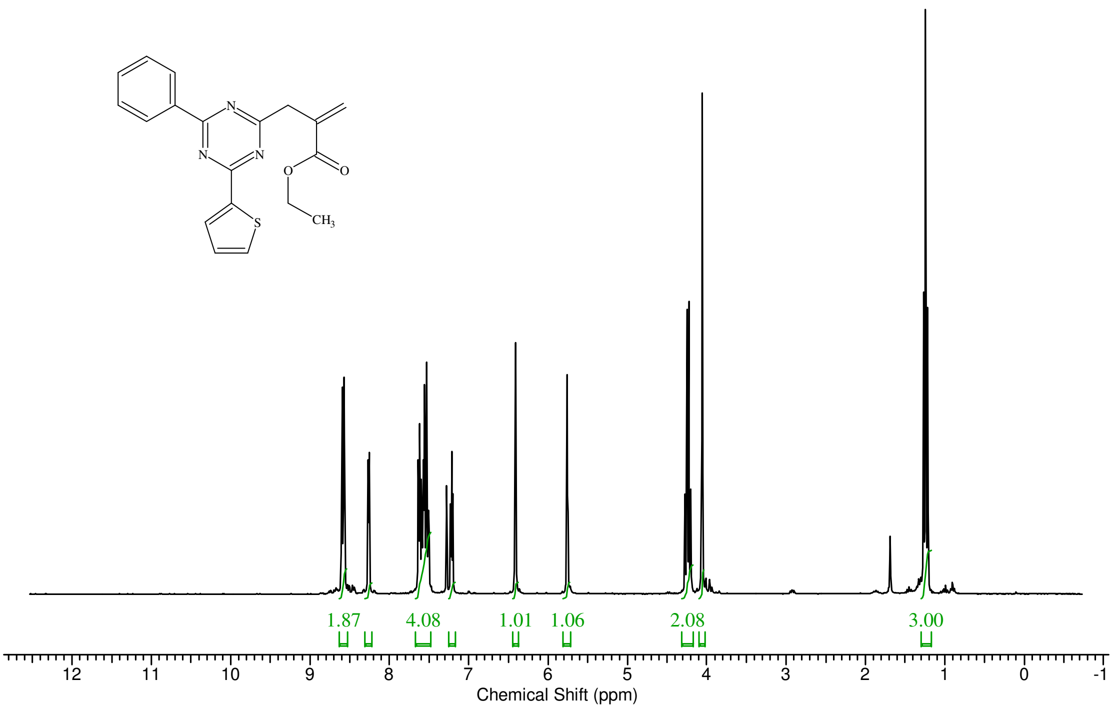
180.45
171.34
170.32
166.21
140.12
135.88
133.65
132.58
129.73
128.94
128.75
77.47
77.05
76.62
61.31
39.25
31.89
29.45
29.25
27.72
22.70
14.36
14.14
CH3
O
O
N
N
N
H3C
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

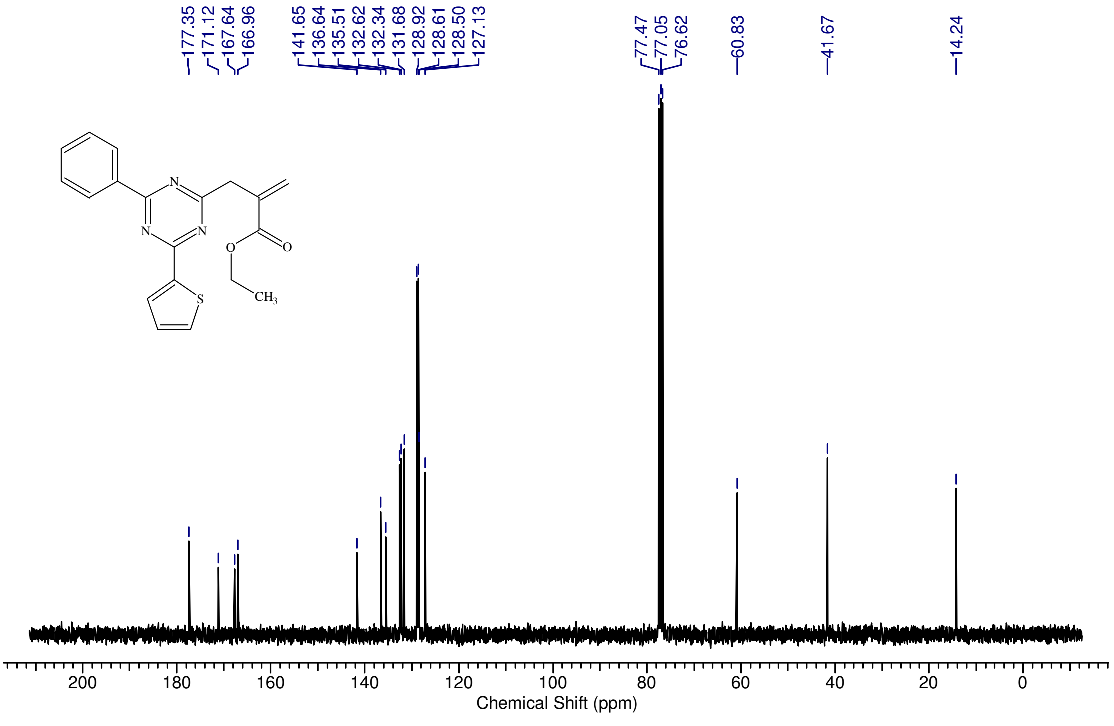
Compound **5b**.


N
N
N
O
O
H3C
H3C
1.85
3.09
0.98
1.00
1.99
2.05
9.83
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
Chemical Shift (ppm)

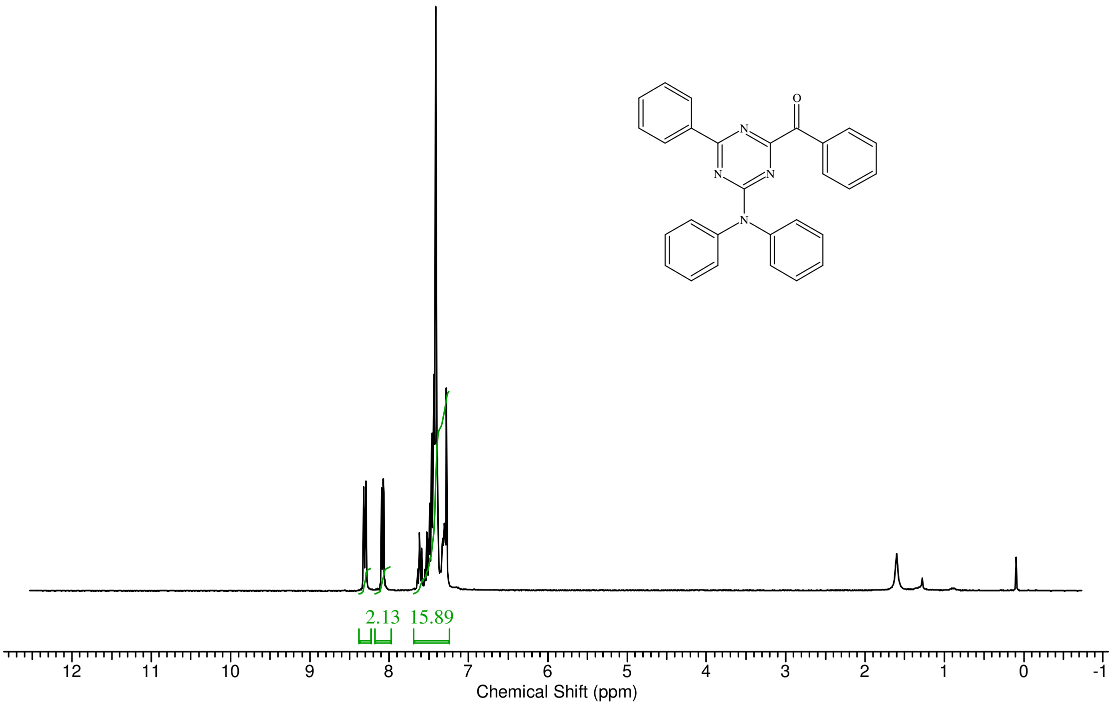

179.75
176.75
170.79
166.81
136.62
135.68
132.42
128.85
128.57
127.08
77.33
77.01
76.69
60.76
41.65
39.06
31.83
29.36
29.18
27.79
22.65
14.10
N
N
N
O
O
H3C
H3C
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

Compound **5c**

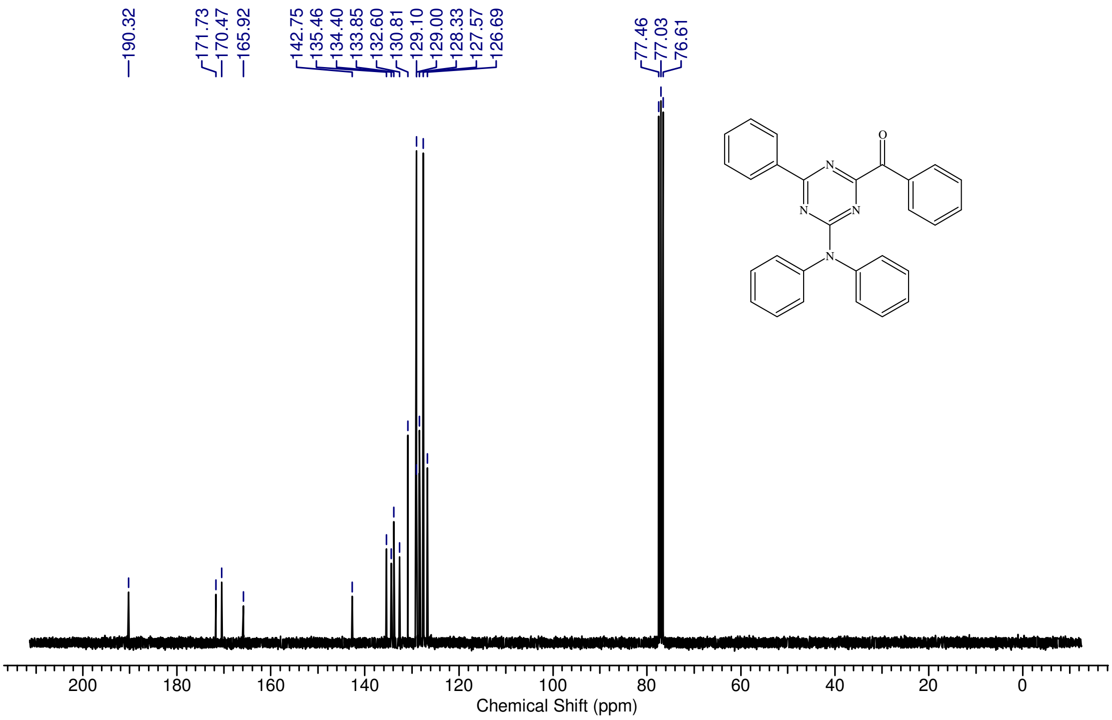

N
N
N
O
O
S
CH3
1.87
4.08
1.01
1.06
2.08
3.00
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


177.35
171.12
167.64
166.96
141.65
136.64
135.51
132.62
132.34
131.68
128.92
128.61
128.50
127.13
77.47
77.05
76.62
60.83
41.67
14.24
N
N
N
O
O
S
CH3
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **5d**.

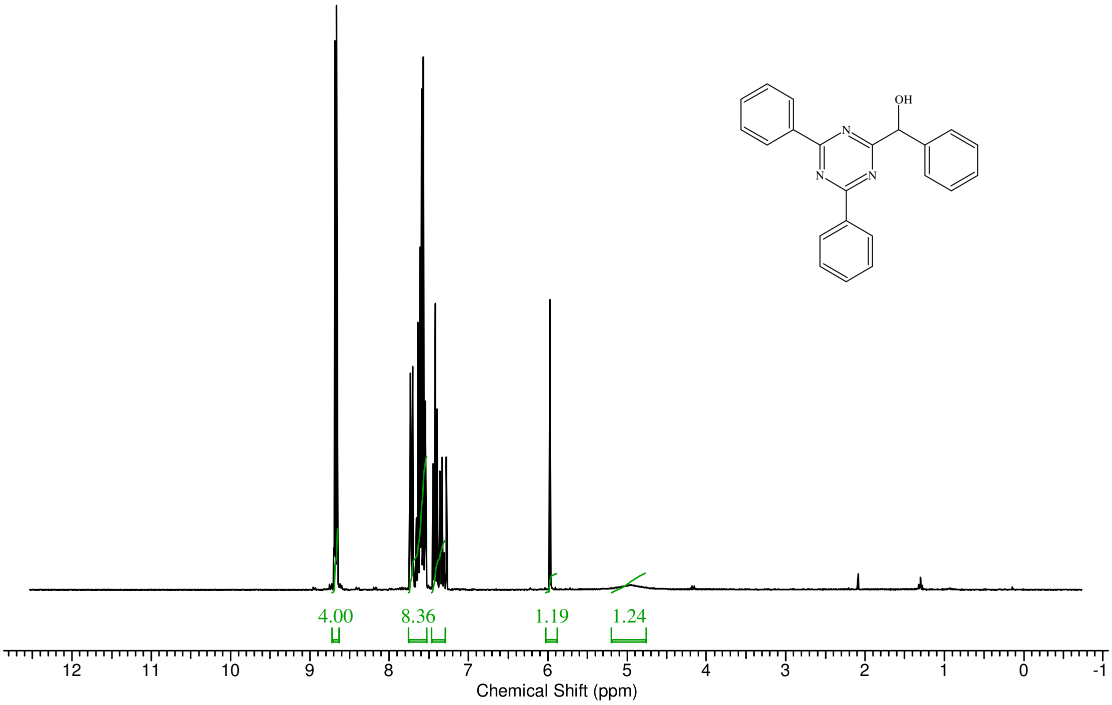


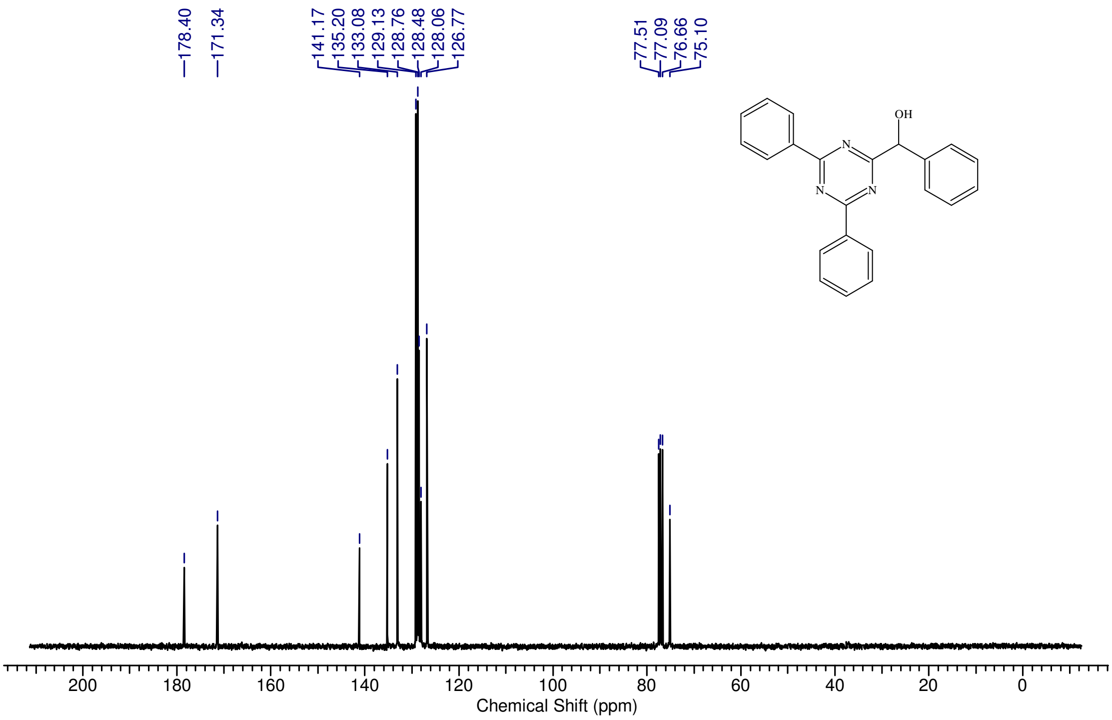
O
N
N
N
N
2.13
15.89
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)



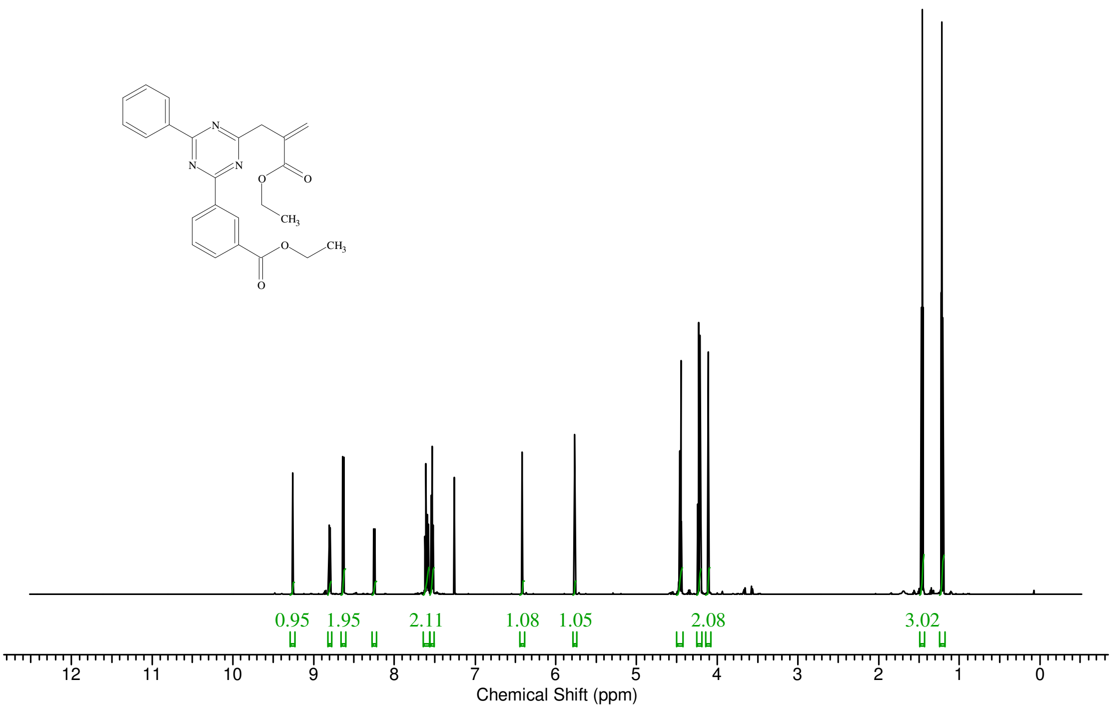
190.32
171.73
170.47
165.92
142.75
135.46
134.40
133.85
132.60
130.81
129.10
129.00
128.33
127.57
126.69
77.46
77.03
76.61
O
N
N
N
N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

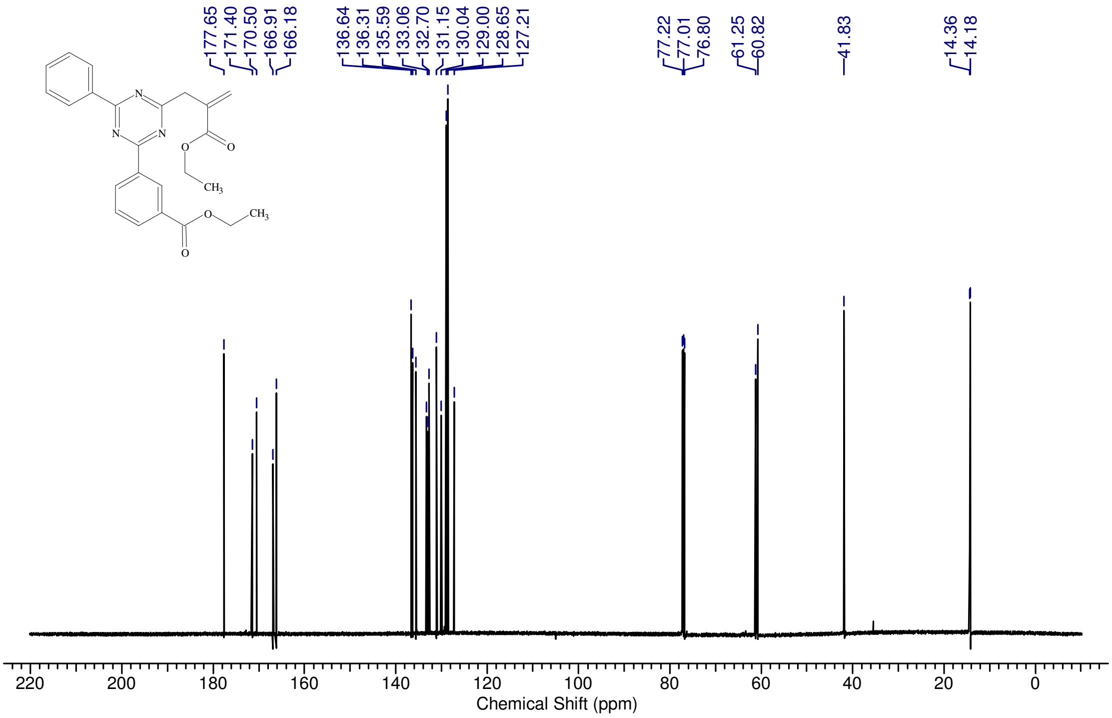
Compound **5e**.


OH
N
N
N
4.00
8.36
1.19
1.24
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

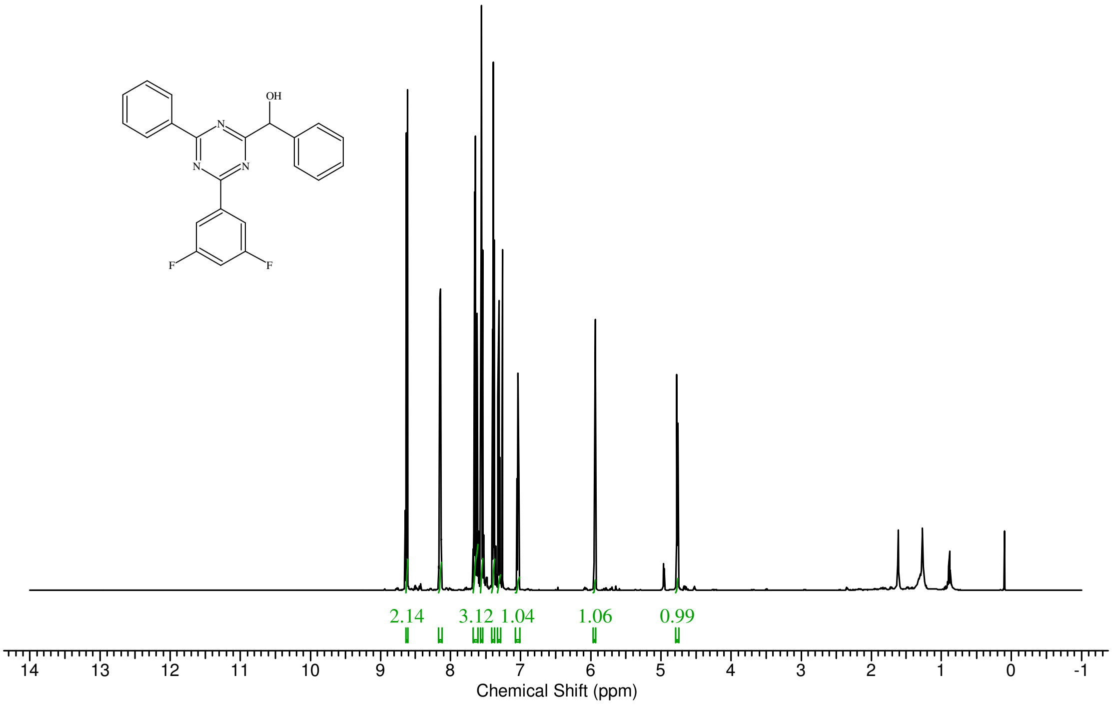

178.40
171.34
141.17
135.20
133.08
129.13
128.76
128.48
128.06
126.77
77.51
77.09
76.66
75.10
OH
N
N
N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

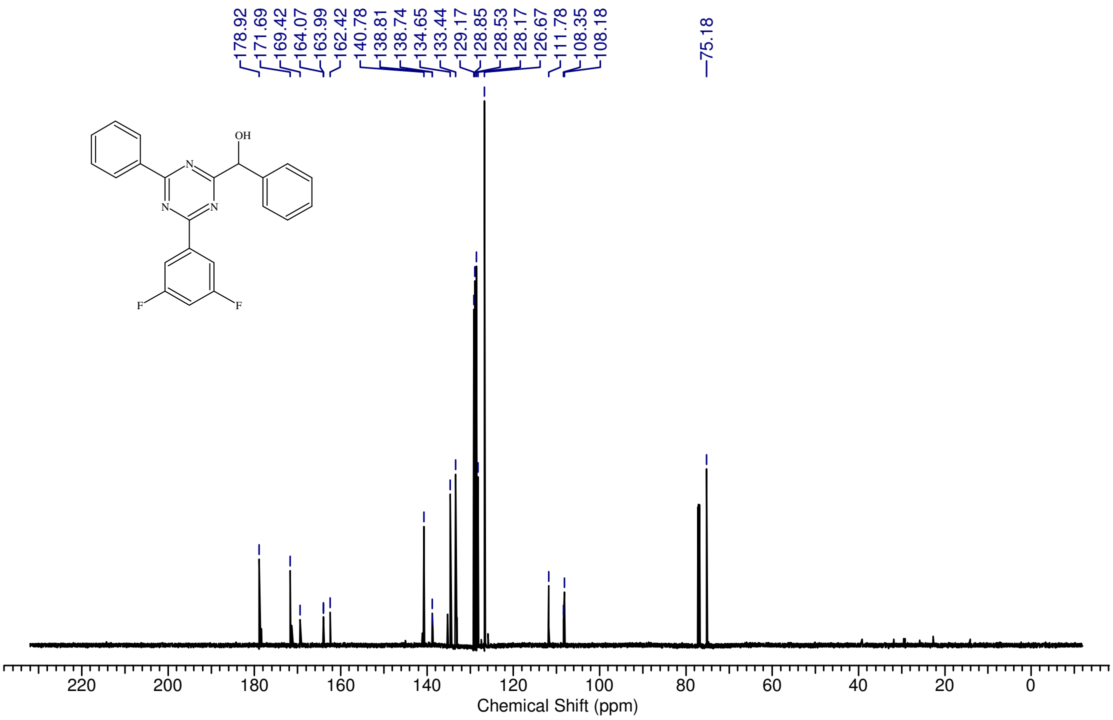
Compound **5f**.


N
N
N
O
O
CH3
O
O
CH3
0.95
1.95
2.11
1.08
1.05
2.08
3.02
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

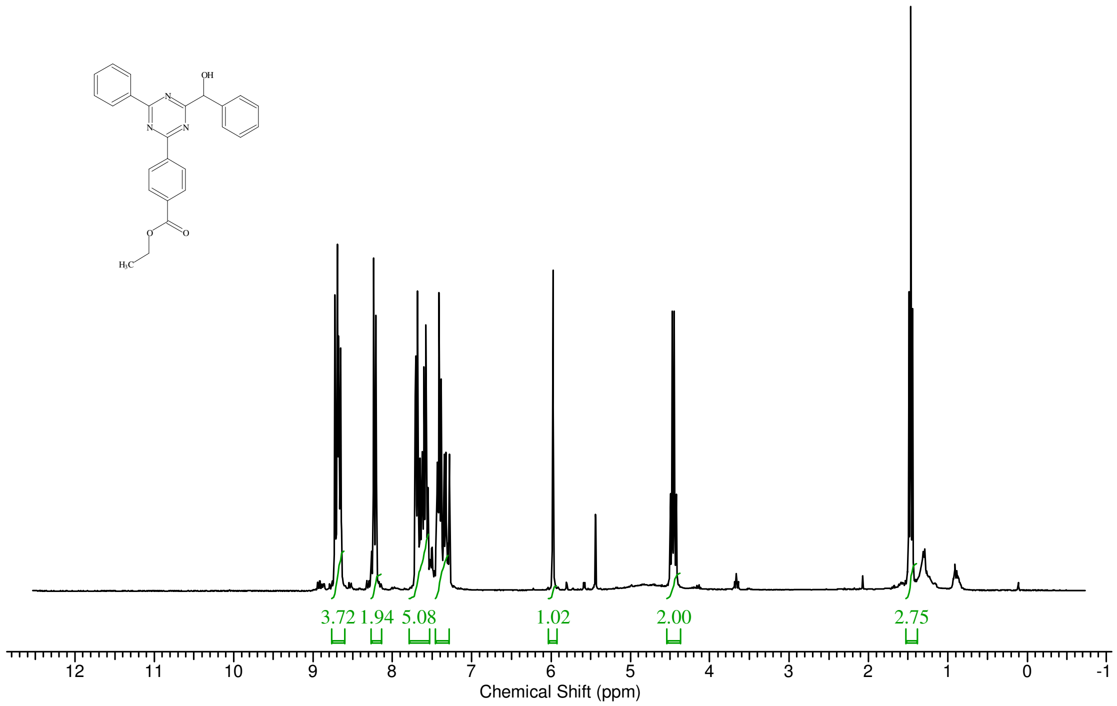

177.65
171.40
170.50
166.91
166.18
136.64
136.31
135.59
133.06
132.70
131.15
130.04
129.00
128.65
127.21
77.22
77.01
76.80
61.25
60.82
41.83
14.36
14.18
N
N
N
O
O
CH3
O
O
CH3
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

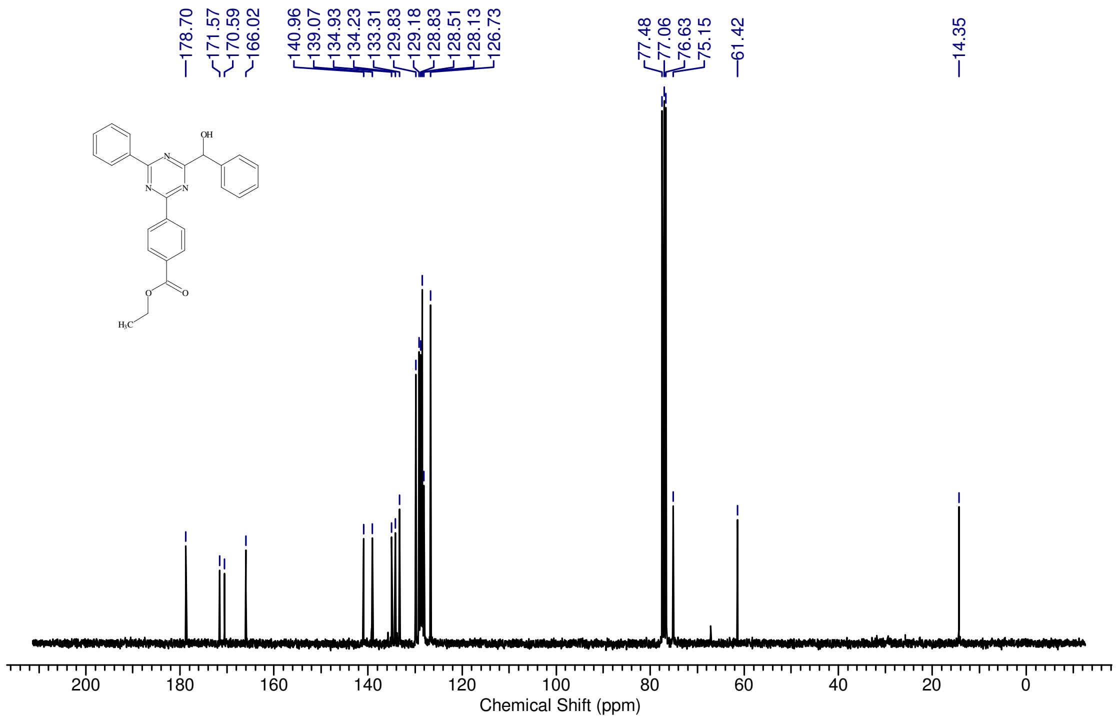
Compound **5g**.


OH
N
N
N
F
F
2.14
3.12
1.04
1.06
0.99
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

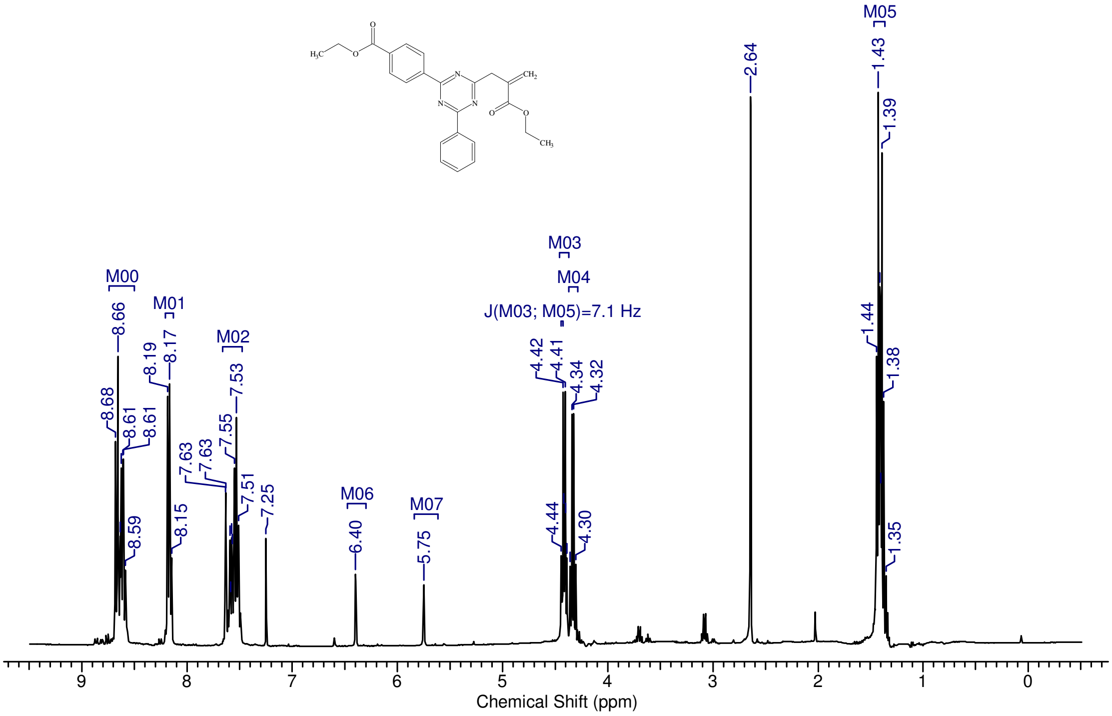

178.92
171.69
169.42
164.07
163.99
162.42
140.78
138.81
138.74
134.65
133.44
129.17
128.85
128.53
128.17
126.67
111.78
108.35
108.18
75.18
OH
N
N
N
F
F
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

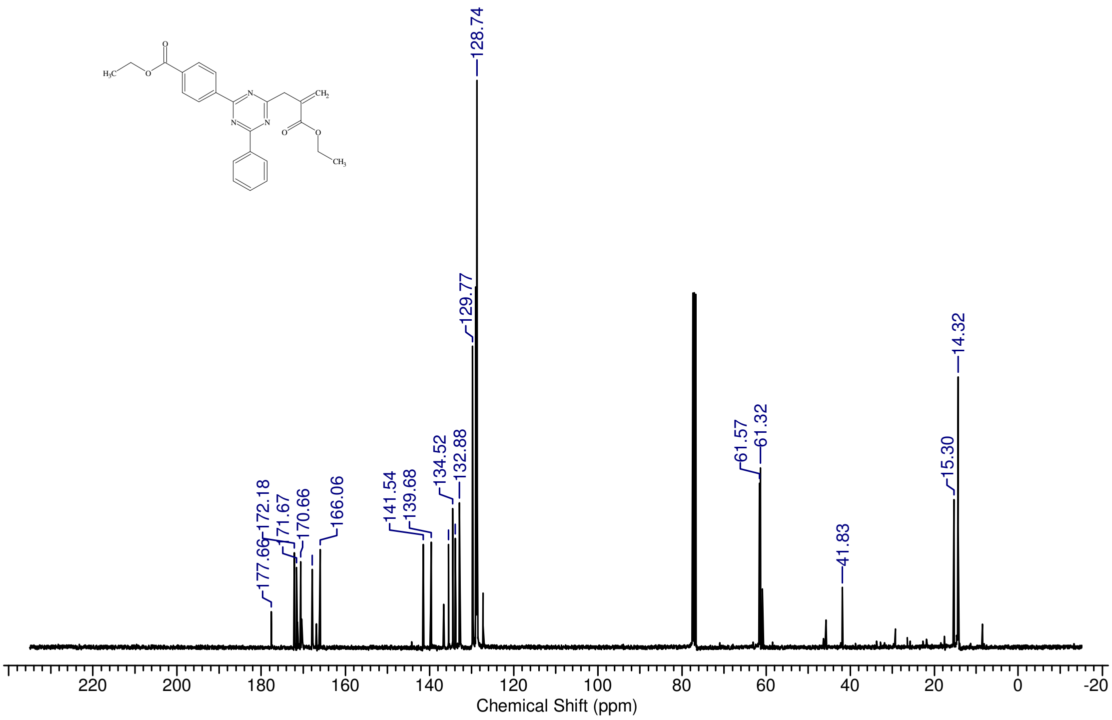
Compound **5h**.


OH
N
N
N
O
O
H₃C
3.72
1.94
5.08
1.02
2.00
2.75
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

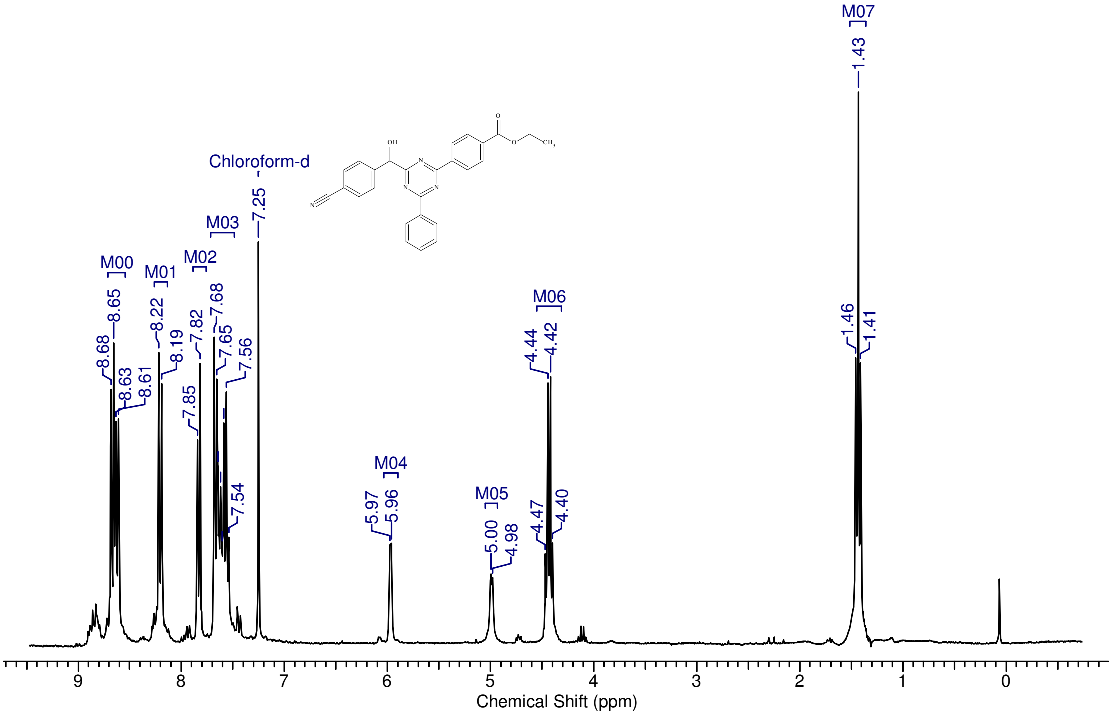

178.70
171.57
170.59
166.02
140.96
139.07
134.93
134.23
133.31
129.83
129.18
128.83
128.51
128.13
126.73
77.48
77.06
76.63
75.15
61.42
14.35
OH
N
N
N
O
O
H₃C
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

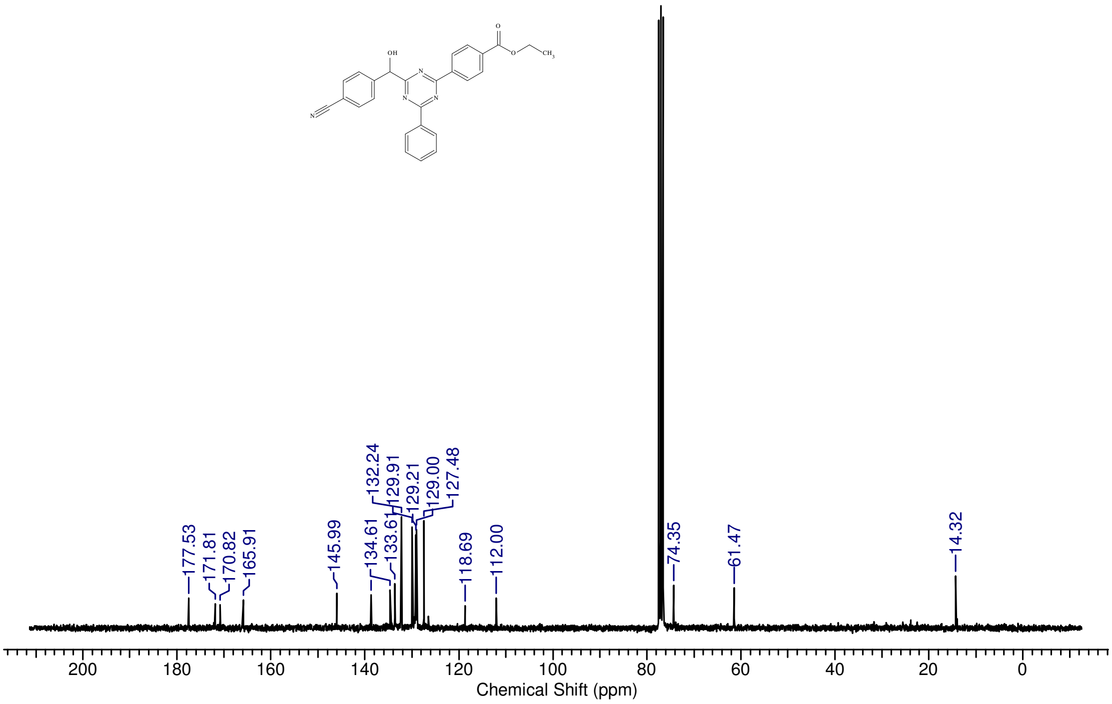
Compound **5i**.


H3C
O
O
N
N
N
CH2
O
O
CH3
M00
8.68
8.66
8.61
8.61
8.59
M01
8.19
8.17
8.15
M02
7.63
7.63
7.55
7.53
7.51
7.25
M06
6.40
M07
5.75
M03
M04
J(M03; M05)=7.1 Hz
4.44
4.42
4.41
4.34
4.32
4.30
2.64
M05
1.44
1.43
1.39
1.38
1.35
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

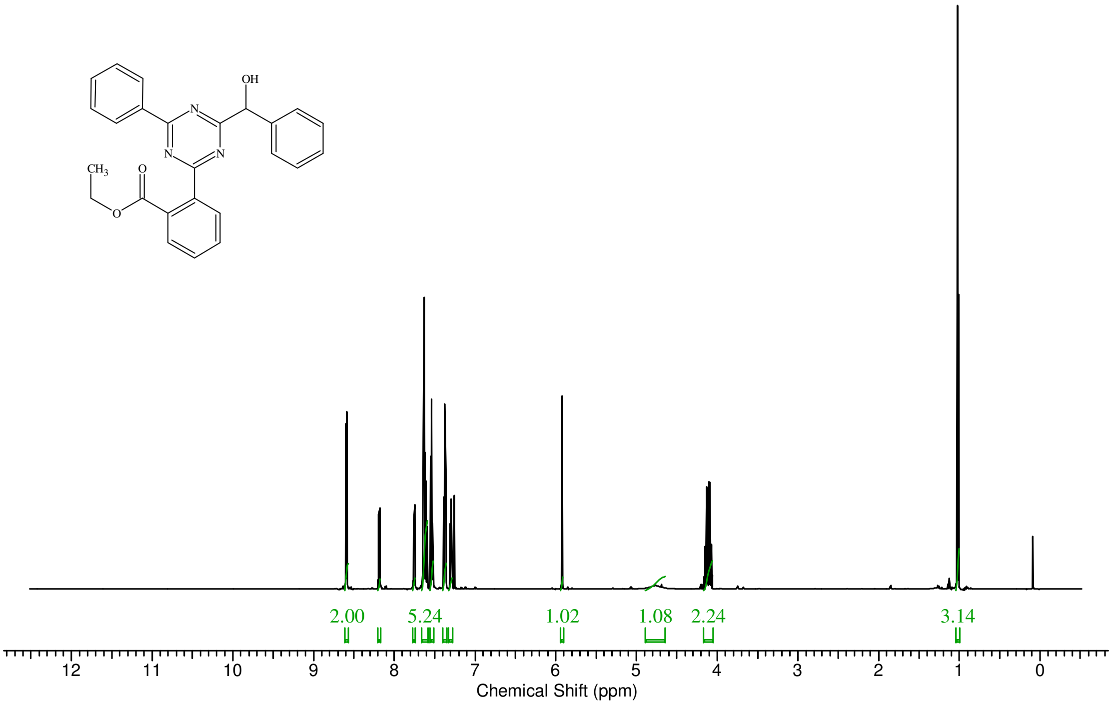

H3C
O
O
N
N
N
CH2
O
O
CH3
177.66
172.18
171.67
170.66
166.06
141.54
139.68
134.52
132.88
129.77
128.74
61.57
61.32
41.83
15.30
14.32
220
200
180
160
140
120
100
80
60
40
20
0
-20
Chemical Shift (ppm)

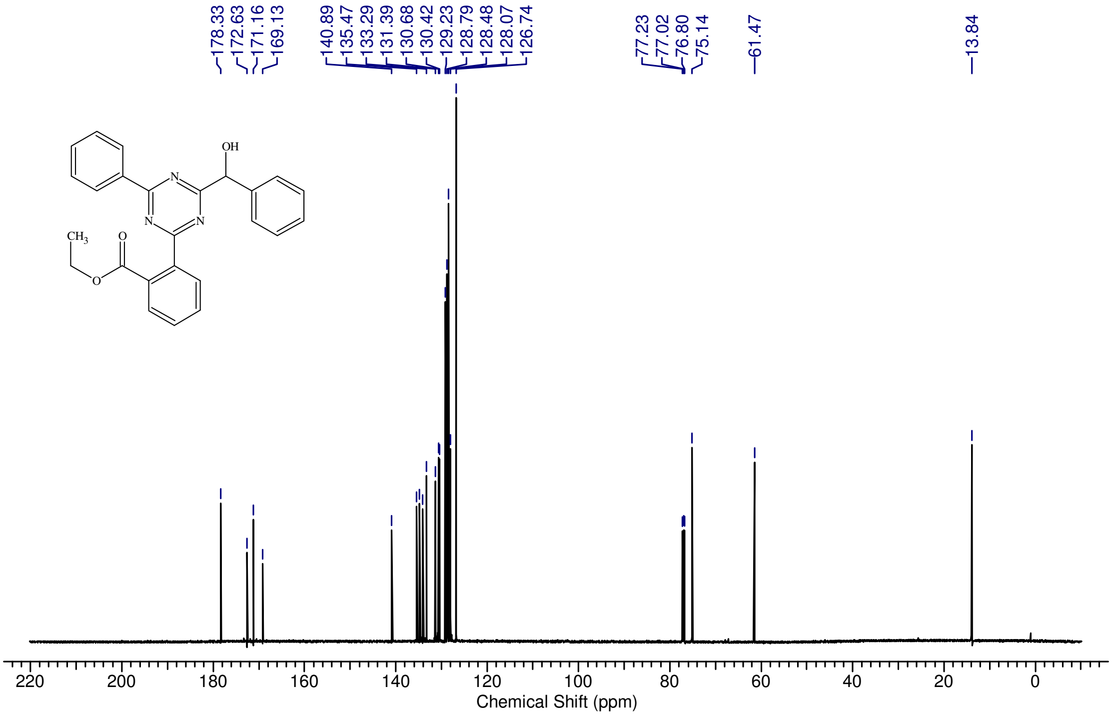
Compound **5j**.


M07
1.43
Chloroform-d
7.25
M00
M01
M02
M03
8.68
8.65
8.63
8.61
8.22
8.19
7.85
7.82
7.68
7.65
7.56
7.54
M04
5.97
5.96
M05
5.00
4.98
M06
4.47
4.44
4.42
4.40
1.46
1.41
OH
N
O
CH3
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

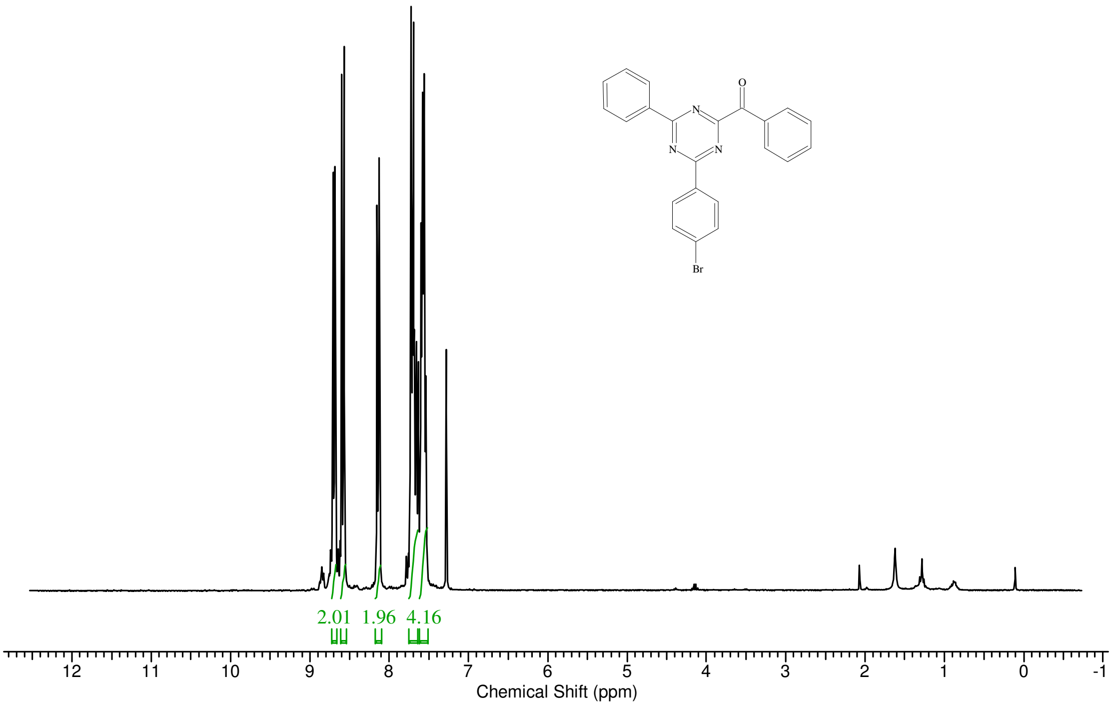

OH
N
O
CH3
177.53
171.81
170.82
165.91
145.99
134.61
133.61
132.24
129.91
129.21
129.00
127.48
118.69
112.00
74.35
61.47
14.32
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

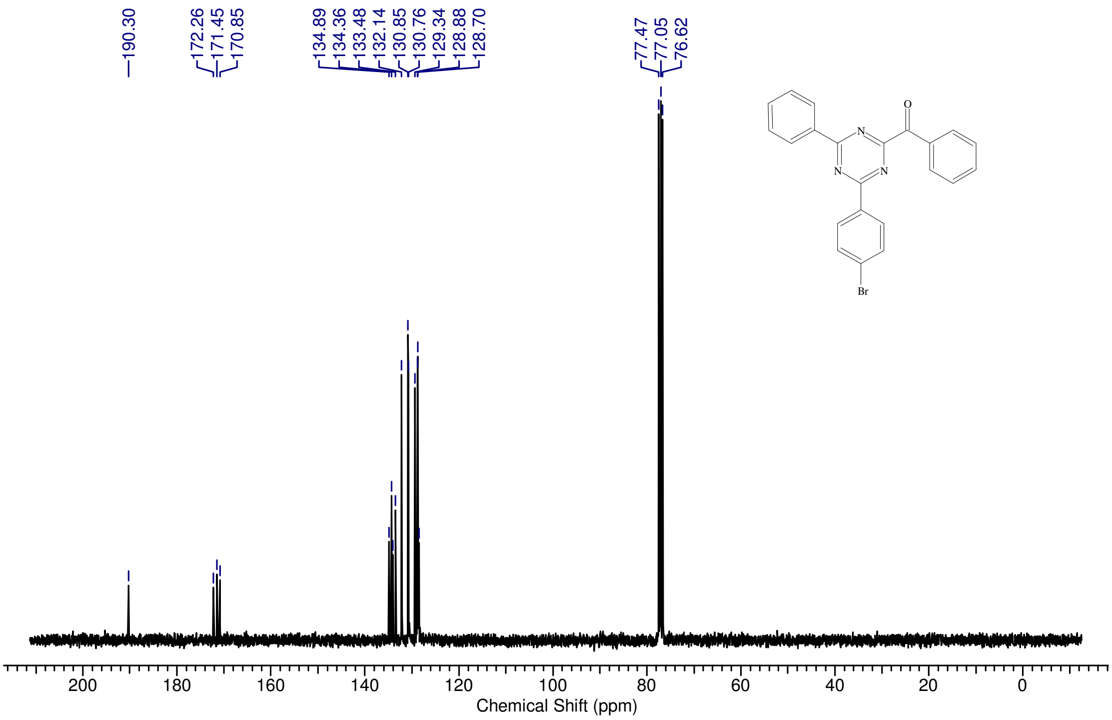
Compound **5k**.


OH
N
N
N
CH3
O
O
2.00
5.24
1.02
1.08
2.24
3.14
12
11
10
9
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)

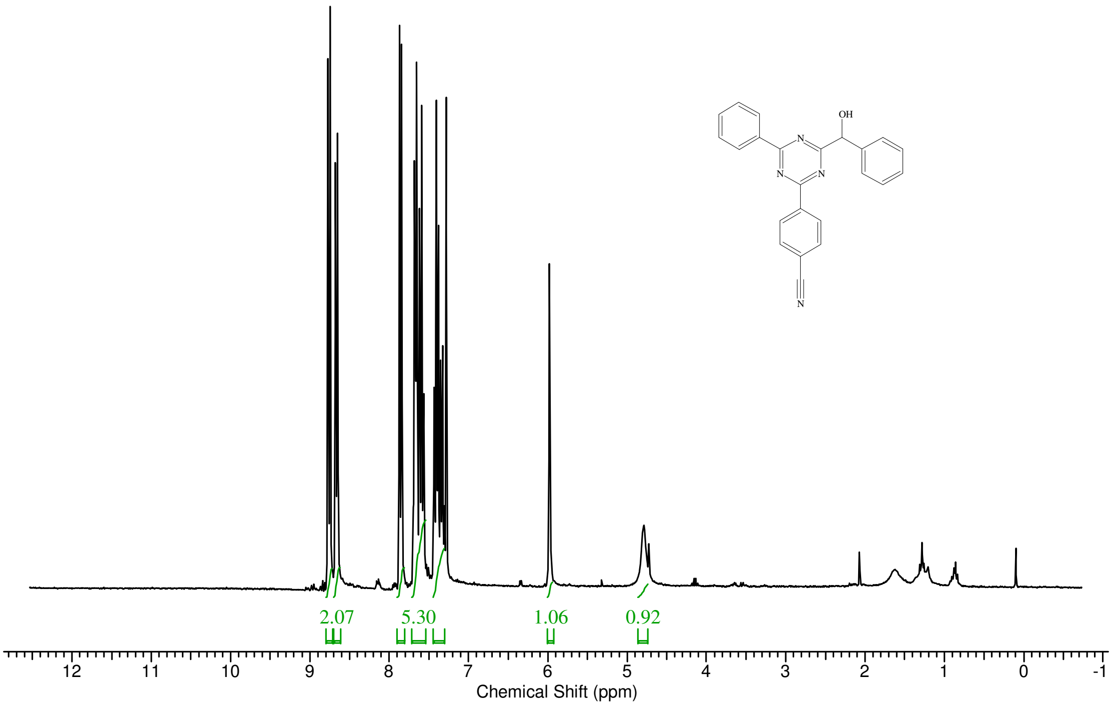

178.33
172.63
171.16
169.13
140.89
135.47
133.29
131.39
130.68
130.42
129.23
128.79
128.48
128.07
126.74
77.23
77.02
76.80
75.14
61.47
13.84
OH
N
N
N
CH3
O
O
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

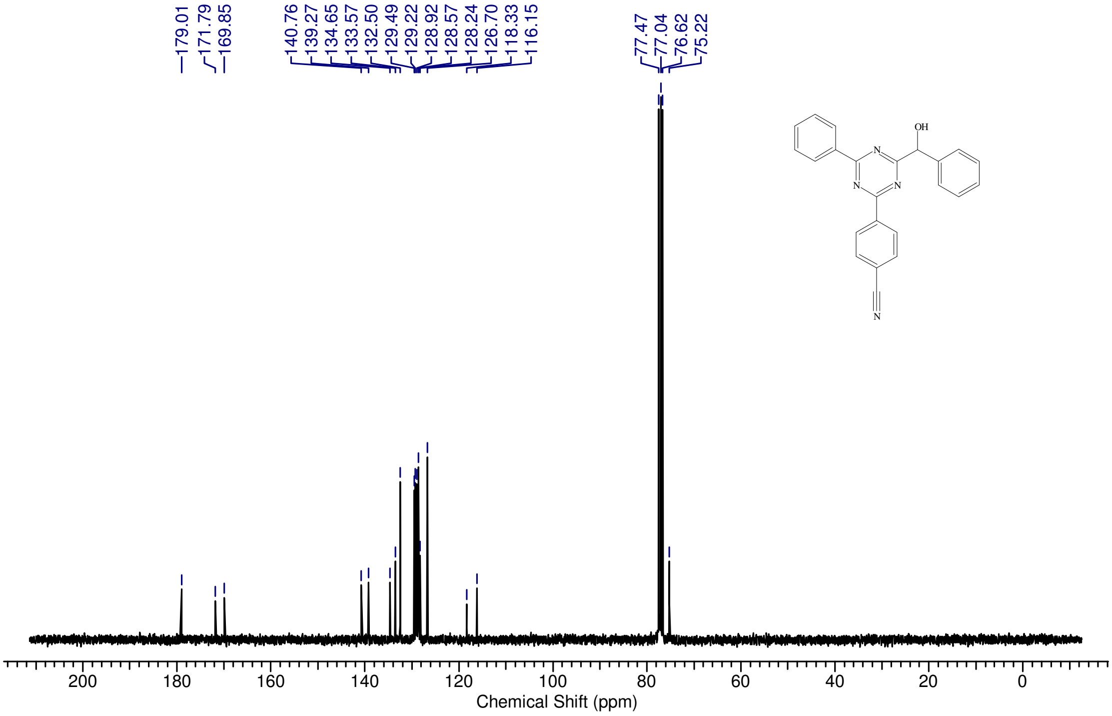
Compound **5l**.


O
N
N
N
Br
2.01
1.96
4.16
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

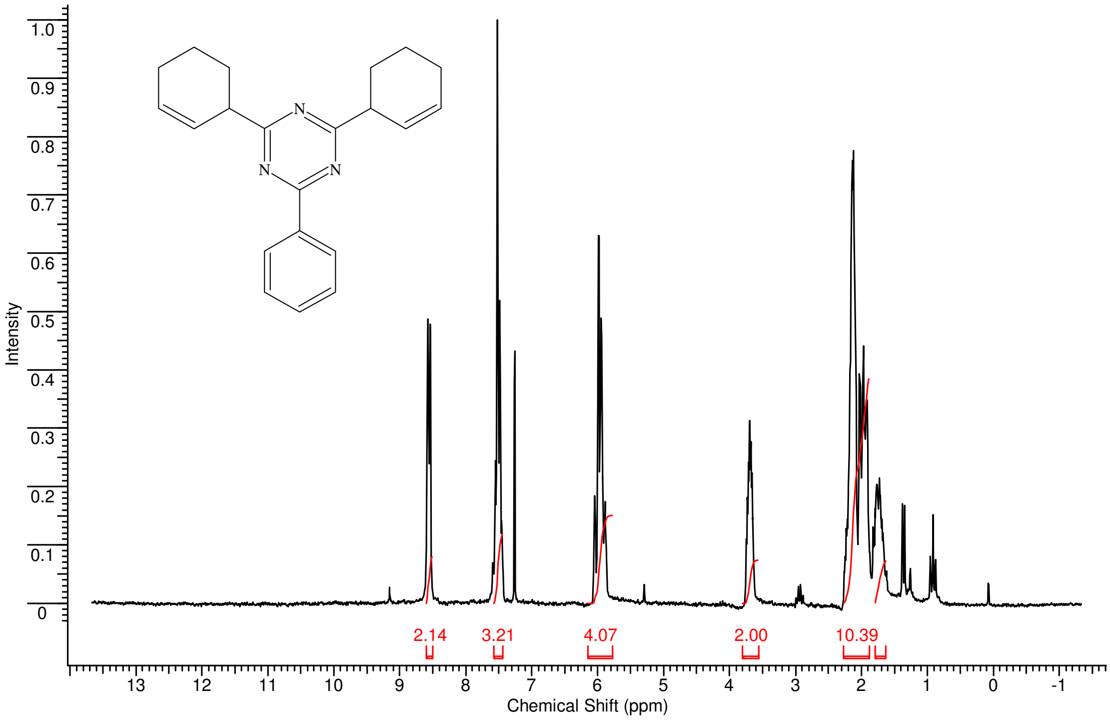

190.30
172.26
171.45
170.85
134.89
134.36
133.48
132.14
130.85
130.76
129.34
128.88
128.70
77.47
77.05
76.62
O
N
N
N
Br
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

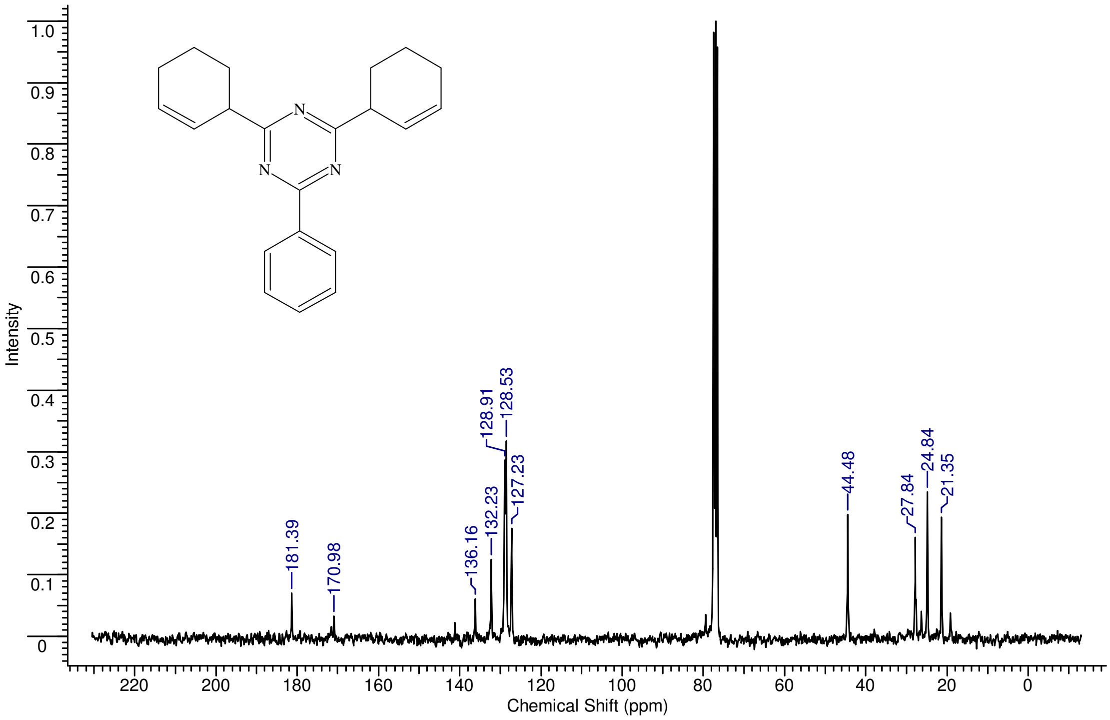
Compound **5m**.


OH
N
N
N
N
2.07
5.30
1.06
0.92
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

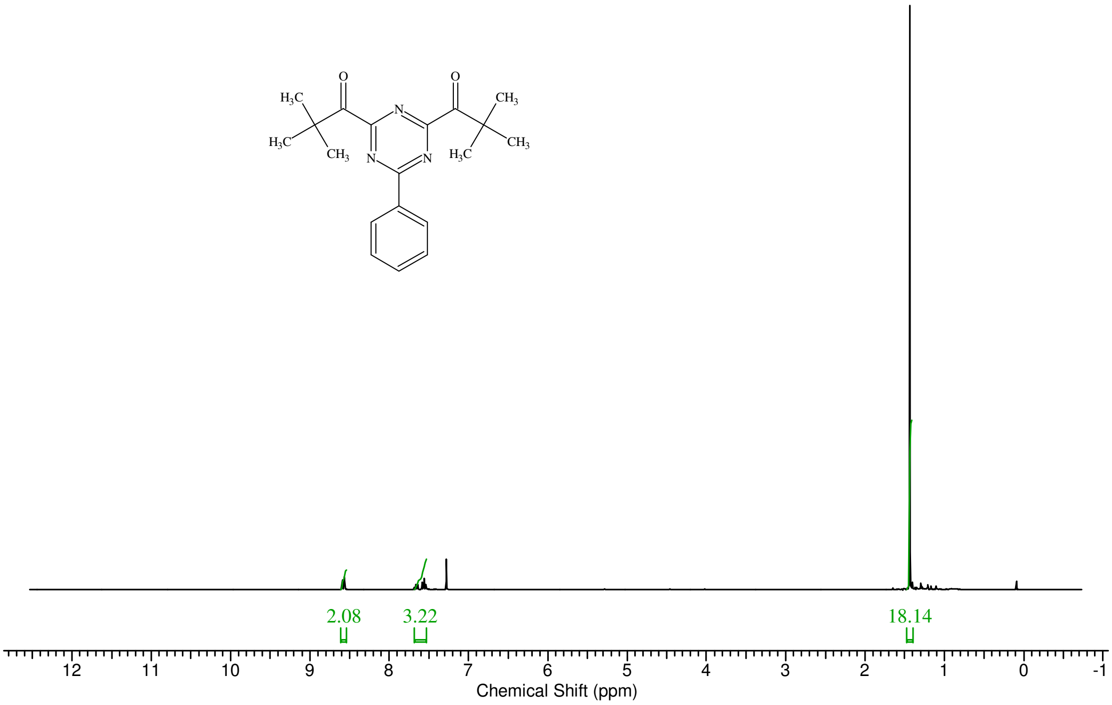

179.01
171.79
169.85
140.76
139.27
134.65
133.57
132.50
129.49
129.22
128.92
128.57
128.24
126.70
118.33
116.15
77.47
77.04
76.62
75.22
OH
N
N
N
N
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

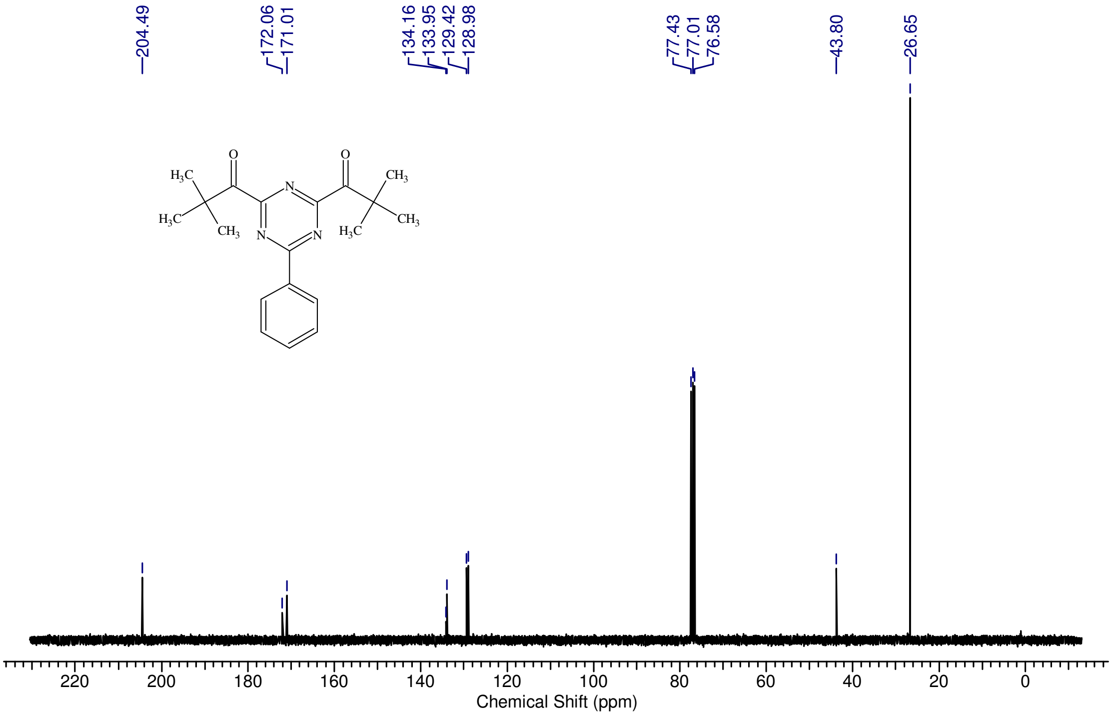
Compound **9**.


N
N
N
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
2.14
3.21
4.07
2.00
10.39
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

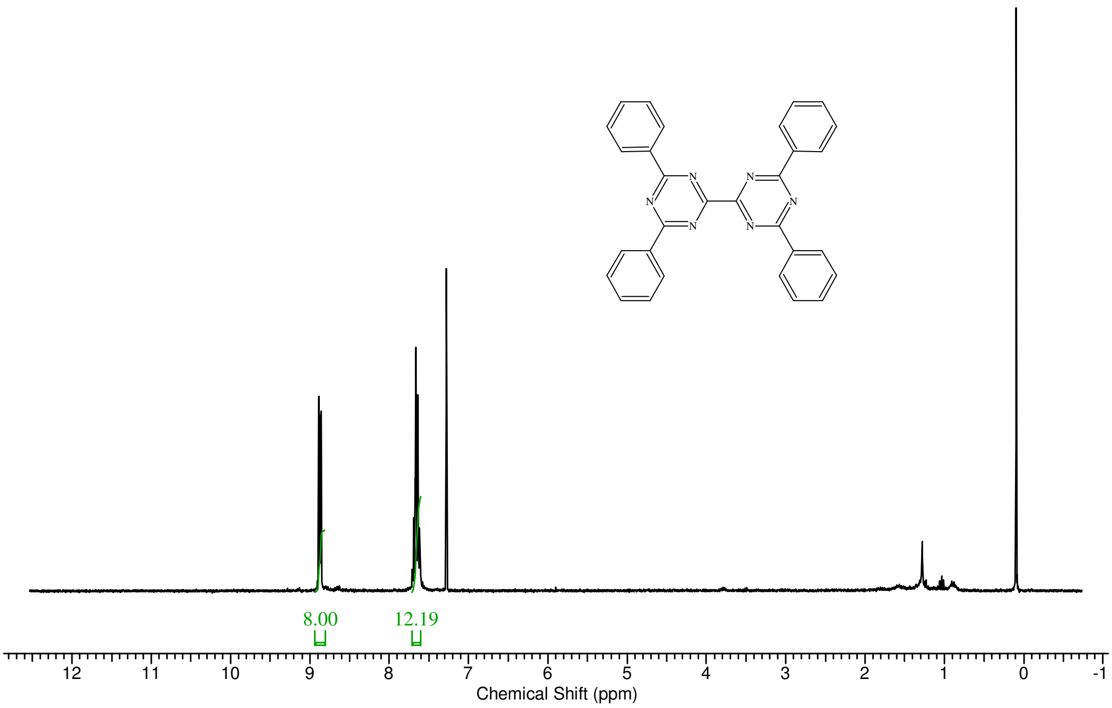

N
N
N
Intensity
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
181.39
170.98
136.16
132.23
128.91
128.53
127.23
44.48
27.84
24.84
21.35
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

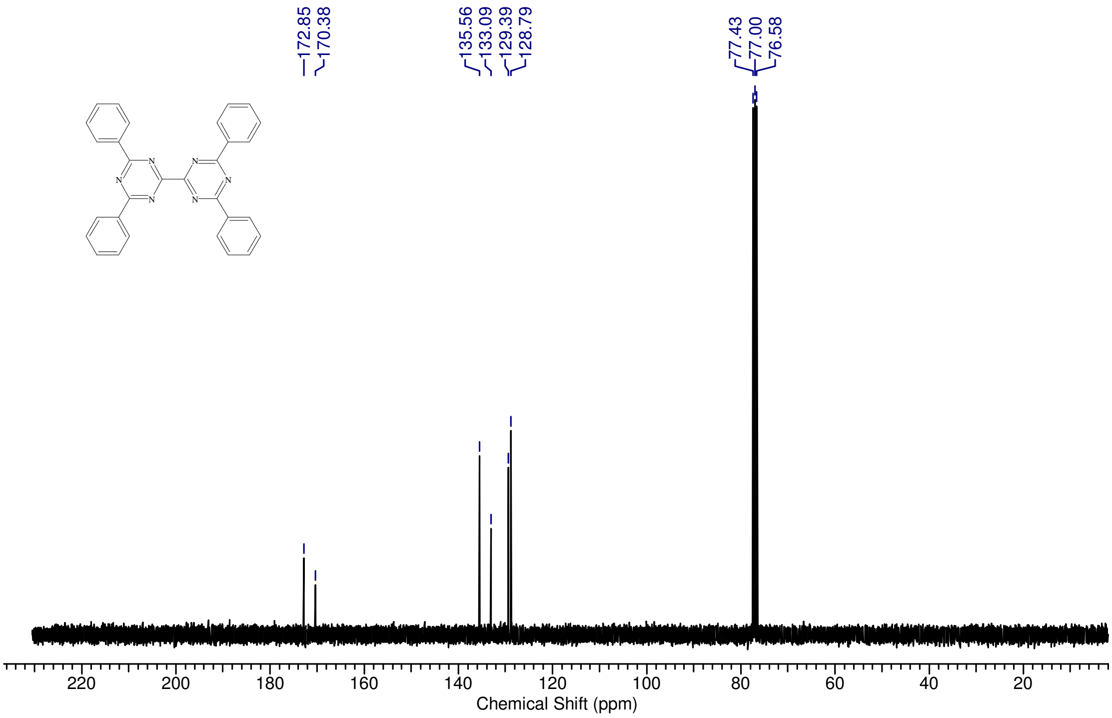
Compound **10**.


O
O
H3C
CH3
H3C
CH3
CH3
H3C
N
N
N
2.08
3.22
18.14
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)

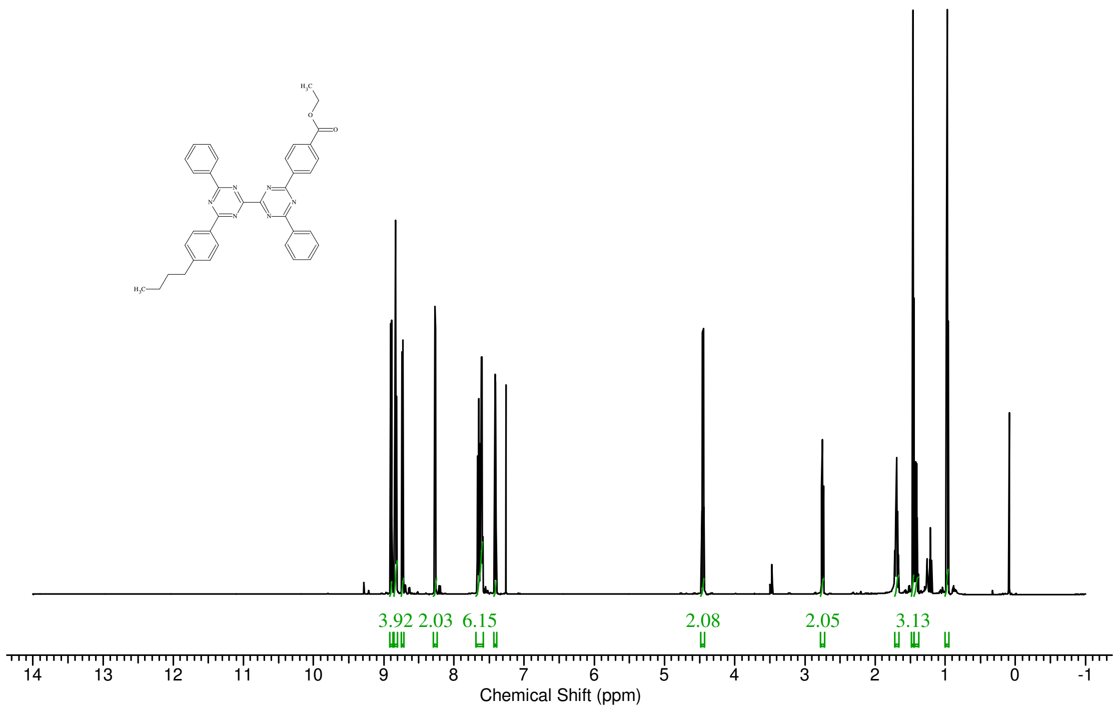

204.49
172.06
171.01
134.16
133.95
129.42
128.98
77.43
77.01
76.58
43.80
26.65
O
O
H3C
CH3
H3C
CH3
CH3
H3C
N
N
N
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

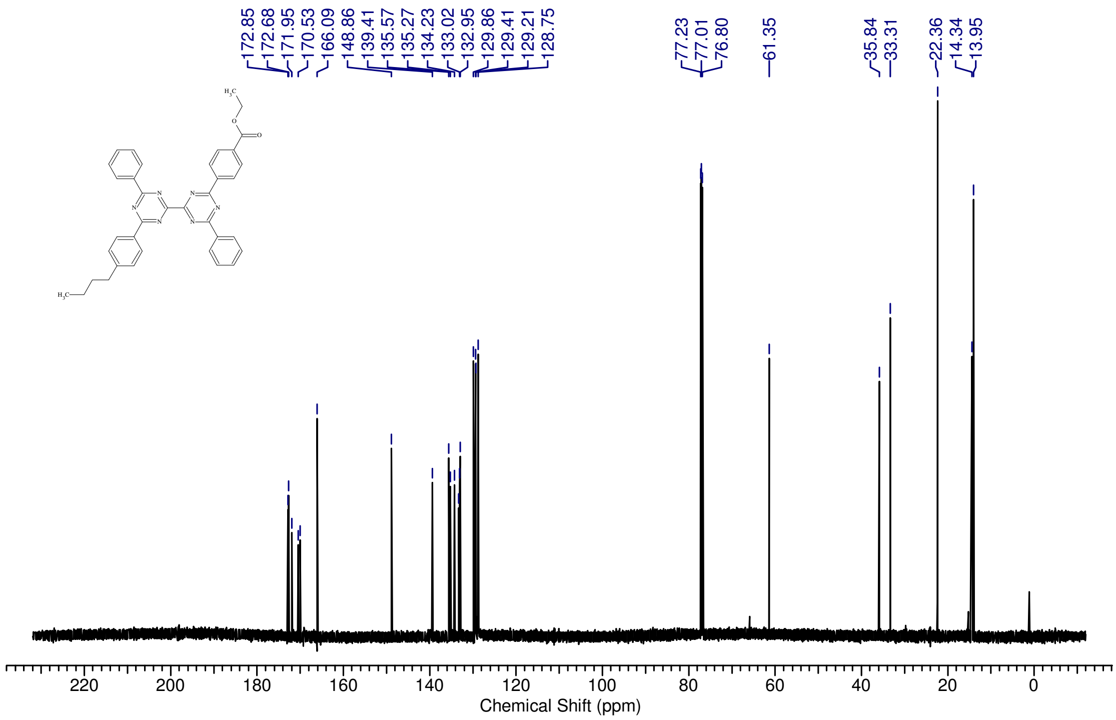
Compound **11**.


8.00
12.19
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)
N
N
N
N
N
N

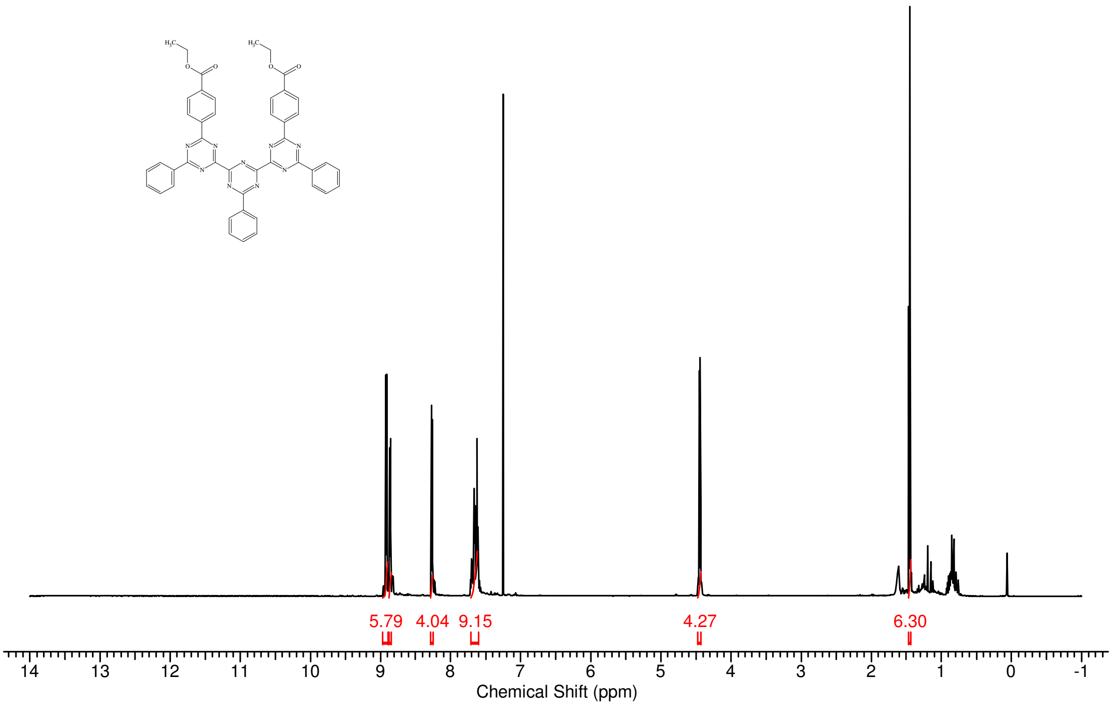

172.85
170.38
135.56
133.09
129.39
128.79
77.43
77.00
76.58
220
200
180
160
140
120
100
80
60
40
20
Chemical Shift (ppm)
N
N
N
N
N
N

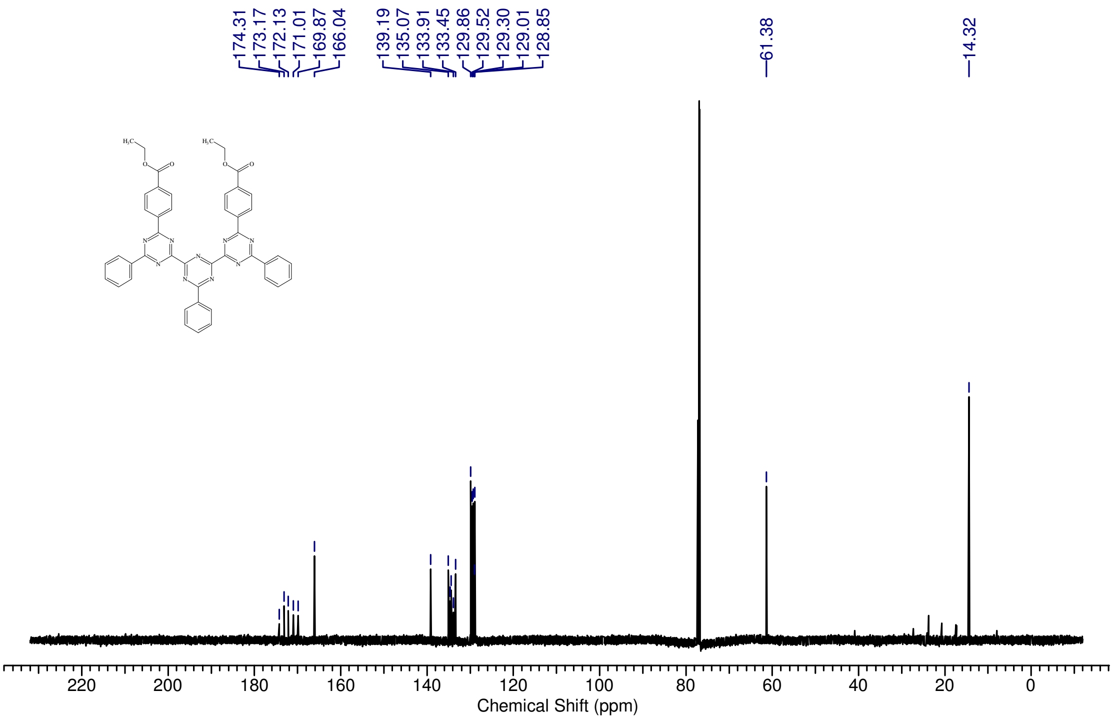
Compound **12**.


H3C
O
O
N
N
N
H3C
3.92
2.03
6.15
2.08
2.05
3.13
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


172.85
172.68
171.95
170.53
166.09
148.86
139.41
135.57
135.27
134.23
133.02
132.95
129.86
129.41
129.21
128.75
77.23
77.01
76.80
61.35
35.84
33.31
22.36
14.34
13.95
H3C
O
O
N
N
N
H3C
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)

Compound **13**.


5.79
4.04
9.15
4.27
6.30
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
Chemical Shift (ppm)


174.31
173.17
172.13
171.01
169.87
166.04
139.19
135.07
133.91
133.45
129.86
129.52
129.30
129.01
128.85
61.38
14.32
220
200
180
160
140
120
100
80
60
40
20
0
Chemical Shift (ppm)