

Supplementary Information for
Convenient synthesis of s-triazine based urea derivatives via palladium
catalyzed C-N coupling reaction

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1. Experimental

1.1 Reagents

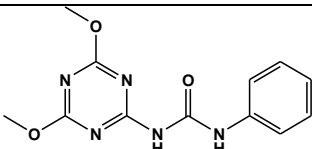
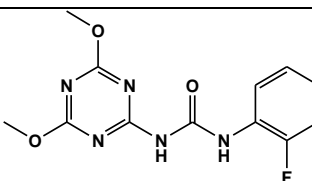
All reactions were carried out under a nitrogen atmosphere. Air- and moisture-sensitive solvents and solutions were transferred via syringe or stainless steel cannula. All chemicals were purchased from sigma Aldrich, merck and fluka. Solvents used were of analytical grade. Anhydrous cesium carbonate was stored in a nitrogen-filled glovebox, ground and was taken out in small quantities and stored in a desiccator. Aryl ureas (1a-13a) were prepared by known methods¹. 1a², 1b³, 1c^{2, 3}, 1d^{2, 4} and 1e were synthesized using literature procedures. All reactions were routinely checked by TLC. TLC was performed on aluminum-backed silica gel plates (silica gel 60 F₂₅₄ grade, Merck DC) with spots visualized by UV light. Column chromatography was performed on silica gel LC 60A (70-200 micron).

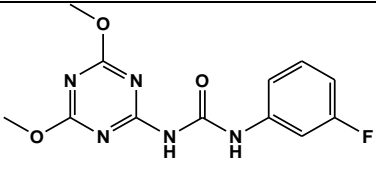
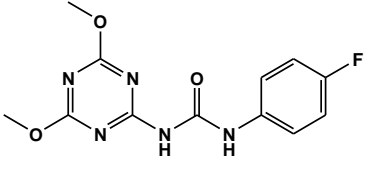
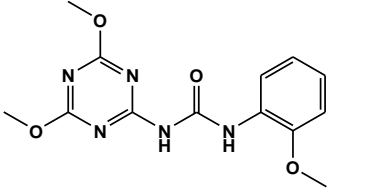
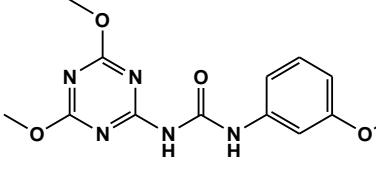
1.2 Instrumental

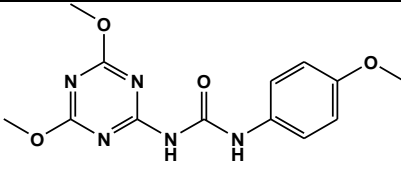
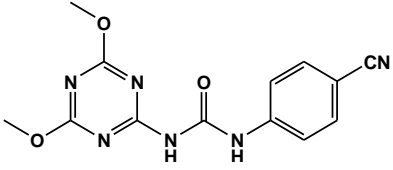
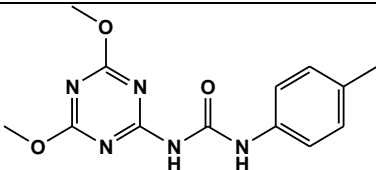
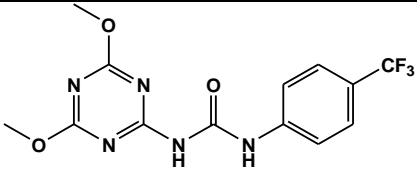
All compounds were characterized by ¹H NMR, ¹³C NMR as well as elemental analysis. Melting points were determined in open capillaries on a Veego electronic apparatus VMP-D (Veego Instrument Corporation, Mumbai, India) and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz model spectrometer using DMSO-*d*₆ as a solvent and TMS as internal standard with ¹H resonant frequency of 400 MHz and ¹³C resonant frequency of 100 MHz. The ¹H NMR, ¹³C NMR chemical shifts were reported as parts per million (ppm) downfield from TMS (Me₄Si). The splitting patterns are designated as follows; s, singlet; d, doublet; t, triplet; m, multiplet. Elemental analyses (C, H, N) were performed using a Heraeus Carlo Erba 1180 CHN analyzer (Hanau, Germany).

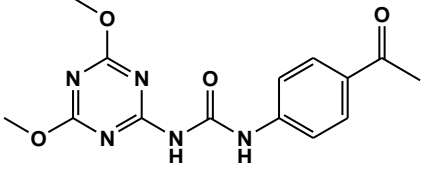
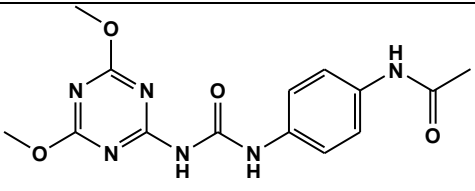
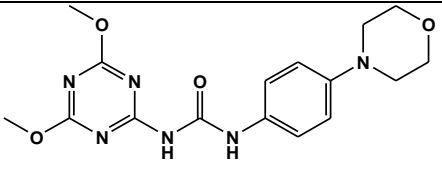
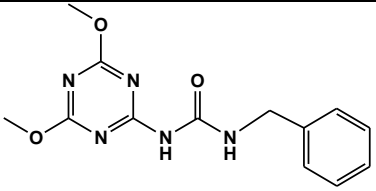
2. General procedure for Pd-catalyzed couplings of 2-Chloro-4,6-disubstituted-s-triazine with various ureas:

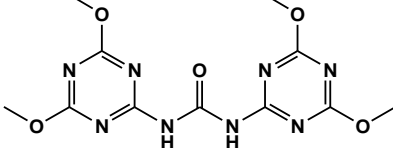
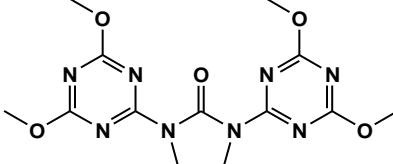
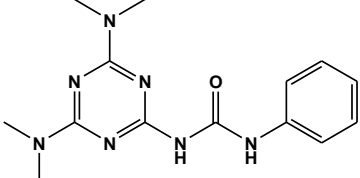
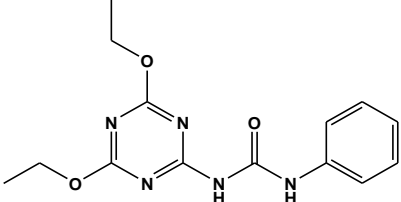
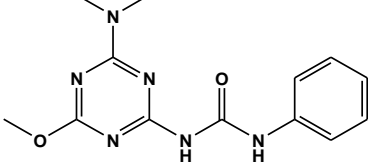
To an oven dried flat-bottomed flask which was equipped with a magnetic stir bar, was charged with ureas (1.0mmol), Cs₂CO₃ (1.4 mmol), Xantphos (5 mol %), Pd₂(dba)₃ (3.3 mol %), and 2-chloro-4, 6-disubstituted-s-triazine (1.0mmol) in 1,4-dioxane (5.0 mL). The reaction was sparged with nitrogen for 15 minutes, stirred and heated to 100 °C for 10 hours. The reaction mixture was cooled to room temperature and filtered through a pad of Celite eluting with ethyl acetate. The filtrate was concentrated and purification of the residue by silica gel column chromatography gave the desired product 3a–3t. Yield: 45-96 %.

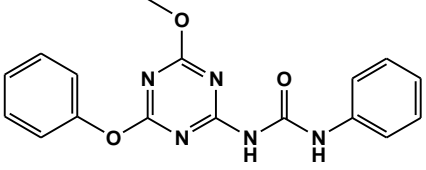
No.	Compounds	Charecterization
3a		¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.72 (s, 1H), 8.95(s, 1H), 7.46 (d, <i>J</i> = 7.6 Hz, 2H), 7.30 (t, <i>J</i> = 7.6 Hz, 2H), 7.01 (t, <i>J</i> = 7.4 Hz, 1H), 3.85 (s, 6H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.45, 168.55, 156.55, 141.08, 129.02, 121.45, 118.19, 56.52. Anal. Calcd. For C ₁₂ H ₁₃ N ₅ O ₃ : C, 52.36; H, 4.76; N, 25.44. Found: C, 52.18; H, 4.87; N, 25.29. mp 137°C.
3b		¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.75 (s, 1H), 9.05 (s, 1H), 8.10(td, <i>J</i> = 8.2, 2.0 Hz, 1H), 7.29 (m, 1H), 7.18 (t, <i>J</i> = 7.6, 1H), 7.07 (m, 1H), 3.86 (s, 6H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.49, 168.69, 155.49- 155.31 (m), 152.97, 130.09 (d, <i>J</i> = 8.4 Hz), 128.99 (d, <i>J</i> = 19.8 Hz), 125.95 (d, <i>J</i> = 2.9 Hz), 122.71 (d, <i>J</i> = 7.6 Hz), 121.86 (d, <i>J</i> = 19.8 Hz), 56.57. Anal. Calcd. For C ₁₂ H ₁₂ N ₅ O ₃ F: C, 49.15; H, 4.12;

		N,6.48. Found: C, 49.25; H, 4.21; N, 6.41. mp 168-170°C.
3c		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm :9.74 (s, 1H), 9.09 (s, 1H), 7.87 (dt, <i>J</i> = 9.0, 2.0 Hz, 1H), 7.38 (td, <i>J</i> = 7.6, 5.8 Hz, 1H), 6.79 (ddt, <i>J</i> = 11.0, 7.8, 2.1 Hz, 2H), 3.86 (s, 6H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.47, 168.75, 164.03, 161.51, 156.35, 140.93 (d, <i>J</i> = 7.6 Hz),130.01(d, <i>J</i> = 7.6 Hz), 116.62 (d, <i>J</i> = 2.9 Hz), 111.48 (d, <i>J</i> = 19.8 Hz), 106.60 (d, <i>J</i> = 19.8 Hz), 56.60. Anal. Calcd. For C ₁₂ H ₁₂ N ₅ O ₃ F: C, 49.15; H, 4.12; N, 6.48. Found: C, 49.28; H, 4.17; N, 6.34. mp 175-176°C.
3d		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.70 (s, 1H), 9.04 (s, 1H), 7.48 (m, 2H), 7.09 (m, 2H), 3.84 (s, 6H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.51, 168.44, 161.51, 158.99, 156.63, 139.74(d, <i>J</i> = 2.9 Hz), 119.60 (d, <i>J</i> = 8.4 Hz), 114.55, 114.34, 56.50. Anal. Calcd. For C ₁₂ H ₁₂ N ₅ O ₃ F: C, 49.15; H, 4.12; N, 6.48. Found: C, 49.11; H, 4.24; N, 6.56. mp 193-194°C.
3e		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.69 (s, 1H),8.97 (s, 1H), 7.21 (dd, <i>J</i> = 7.2, 2.1 Hz, 1H), 7.17-7.11 (m, 2H) 7.00 (dd, <i>J</i> = 7.8, 1.9 Hz, 1H). 3.87 (s, 6H). 3.65 (s, 3H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.37, 168.33, 156.60, 153.07, 129.41, 125.33, 124.19, 120.71, 113.78, 56.63, 57.02. . Anal. Calcd. For C ₁₃ H ₁₅ N ₅ O ₄ : C, 51.14; H, 4.95; N, 22.94. Found: C, 51.16; H, 4.98; N, 22.85. mp 147-149°C.
3f		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.67 (s, 1H), 9.00 (s, 1H), 6.95 (dd, <i>J</i> = 8.0, 2.0 Hz, 1H), 7.22 (t, <i>J</i> = 8.0 Hz, 1H), 6.75 (t, <i>J</i> = 2.0 Hz, 1H), 6.62 (dd, <i>J</i> = 8.0, 2.0 Hz, 1H) 3.86 (s, 6H). 3.68 (s, 3H).). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.39, 168.41, 159.17, 156.58, 141.29, 129.69, 116.33, 113.161, 107.45, 56.57,

		57.14. Anal. Calcd. For C ₁₃ H ₁₅ N ₅ O ₄ : C, 51.14; H, 4.95; N, 22.94. Found: C, 51.10; H, 4.99; N, 22.97. mp 142-143°C.
3g		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.70 (s, 1H), 8.89 (s, 1H), 7.40 (d, <i>J</i> = 7.6 Hz, 2H), 6.79 (d, <i>J</i> = 7.6 Hz, 2H), 3.86 (s, 6H), 3.73 (s, 3H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.44, 168.50, 159.97, 156.68, 137.53, 119.54, 114.36, 56.56, 56.89. Anal. Calcd. For C ₁₃ H ₁₅ N ₅ O ₄ : C, 51.14; H, 4.95; N, 22.94. Found: C, 51.24; H, 4.89; N, 22.90. mp 157°C.
3h		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.77 (s, 1H), 9.11 (s, 1H), 8.20 (d, <i>J</i> = 8.6 Hz, 2H), 7.69 (d, <i>J</i> = 8.6 Hz, 2H), 3.85 (s, 6H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.53, 168.66, 156.71, 142.44, 133.30, 119.13, 119.01, 107.68, 56.22. Anal. Calcd. For C ₁₃ H ₁₂ N ₆ O ₃ : C, 52.00; H, 4.03; N, 27.99. Found: C, 52.09; H, 4.00; N, 27.94. mp 154°C.
3i		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.71 (s, 1H), 8.97 (s, 1H), 7.33 (d, <i>J</i> = 7.8 Hz, 2H), 7.07 (d, <i>J</i> = 7.8, 2H), 3.84 (s, 6H), 2.34 (s, 3H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.41, 168.30, 156.63, 139.91, 137.54, 128.74, 118.98, 56.32, 22.01. Anal. Calcd. For C ₁₃ H ₁₅ N ₅ O ₃ : C, 53.97; H, 5.23; N, 24.21. Found: C, 53.93; H, 5.26; N, 24.16. mp 124-126°C.
3j		¹H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.76 (s, 1H), 9.06 (s, 1H), 7.89 (d, <i>J</i> = 8.8 Hz, 2H), 7.55 (d, <i>J</i> = 8.8 Hz, 2H), 3.85 (s, 6H). ¹³C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.57, 168.80, 156.79, 143.44, 132.49, 132.17, 126.75 (m), 124.00, 119.69 (d, <i>J</i> = 2.2 Hz), 56.47. Anal. Calcd. For C ₁₃ H ₁₂ N ₅ O ₃ F ₃ : C, 45.49; H, 3.52; N, 16.60. Found: C, 45.60; H, 3.46; N,

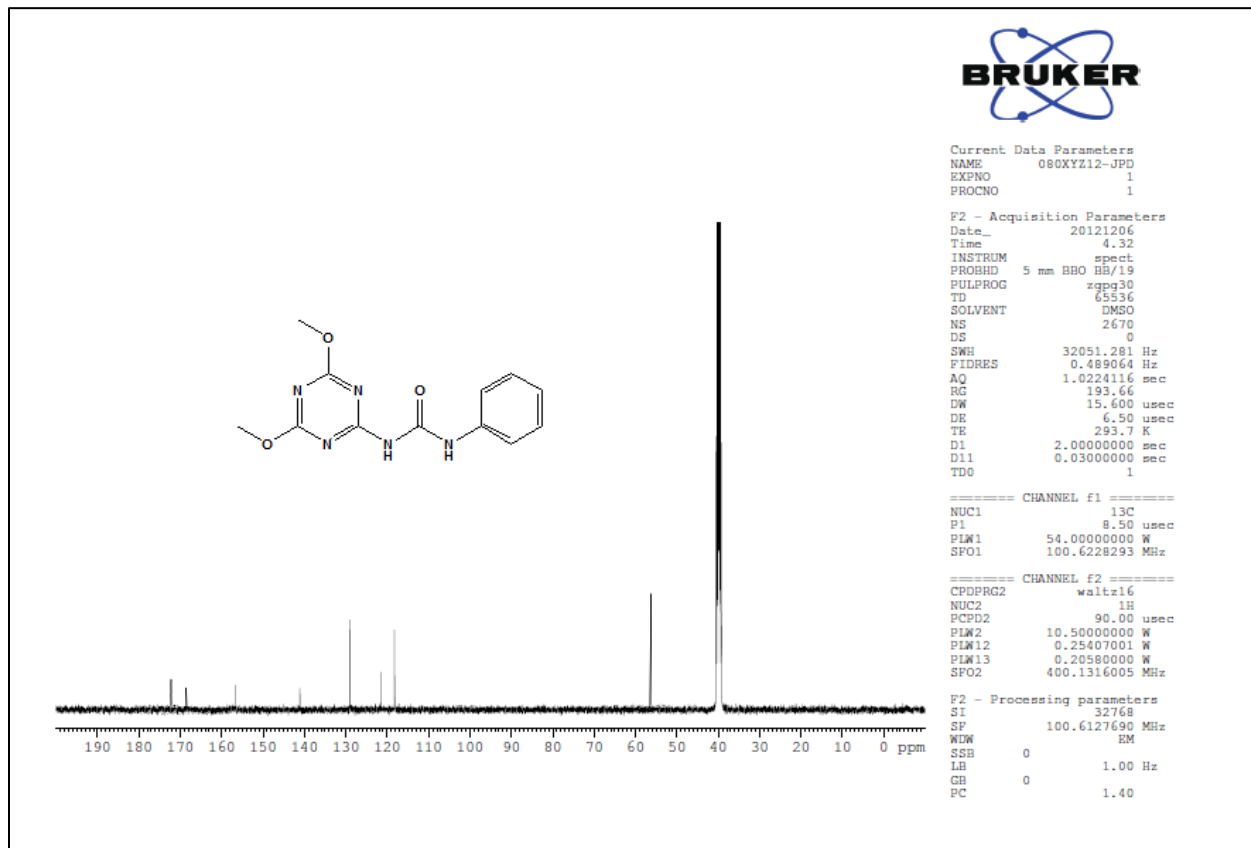
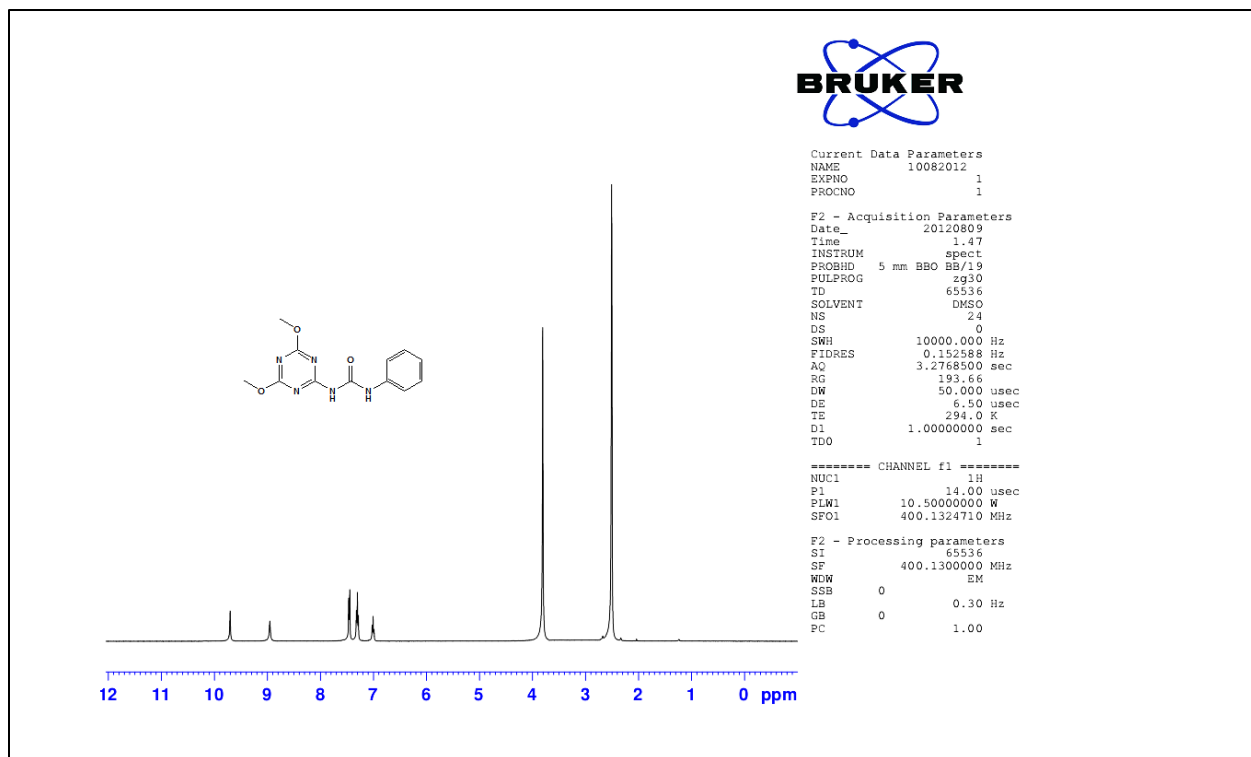
		16.67.mp205°C.
3k		¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm :9.79 (s, 1H), 9.08(s, 1H), 7.94 (d, 8.2 Hz, 2H), 7.85 (d, 8.2 Hz, 2H), 3.88 (s, 6H), 2.60 (s, 3H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 197.93, 172.50, 168.61, 156.70, 141.54, 135.58, 128.76, 118.61, 56.44, 25.75. Anal. Calcd. For C ₁₄ H ₁₅ N ₅ O ₄ : C, 52.99; H, 4.76; N, 22.07. Found: C, 52.95; H, 4.79; N, 22.03. mp 184-186°C.
3l		¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.95(s, 1H), 9.77 (s, 1H), 9.05 (s, 1H), 7.73 (d, <i>J</i> = 7.8 Hz, 2H), 7.58 (d, <i>J</i> = 7.8 Hz, 2H), 3.87 (s, 6H), 2.11 (s, 3H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.40, 170.04, 168.44, 156.50, 139.00, 137.87, 119.13, 119.01, 56.55, 23.51. Anal. Calcd. For C ₁₄ H ₁₆ N ₆ O ₄ : C, 50.60; H, 4.85; N, 25.29. Found: C, 50.67; H, 4.80; N, 25.42.mp 199-201°C.
3m		¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.66 (s, 1H), 8.90 (s, 1H), 7.50 (d, <i>J</i> = 7.6 Hz, 2H), 6.90 (d, <i>J</i> = 7.6 Hz, 2H), 3.84 (s, 6H), 3.72 (t, 4H), 3.24 (t, 4H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.37, 168.27, 156.47, 151.75, 136.00, 120.56, 118.39, 67.01, 56.29, 49.79. Anal. Calcd. For C ₁₆ H ₂₀ N ₆ O ₄ : C, 53.33; H, 5.59; N, 23.32. Found: C, 53.44; H, 5.48; N, 23.43mp 180-182°C.
3n		¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.69 (s, 1H), 7.96 (s, 1H), 7.30-7.16 (m, 5H), 4.33 (s, 2H), 3.74 (s, 6H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 172.26, 163.10, 155.53, 141.17, 128.373, 128.19, 126.72, 45.01, 57.00. Anal. Calcd. For C ₁₃ H ₁₅ N ₅ O ₃ : C, 53.97; H, 5.23; N, 24.21. Found: C, 53.93; H, 5.28; N, 24.29.mp 114-115°C.

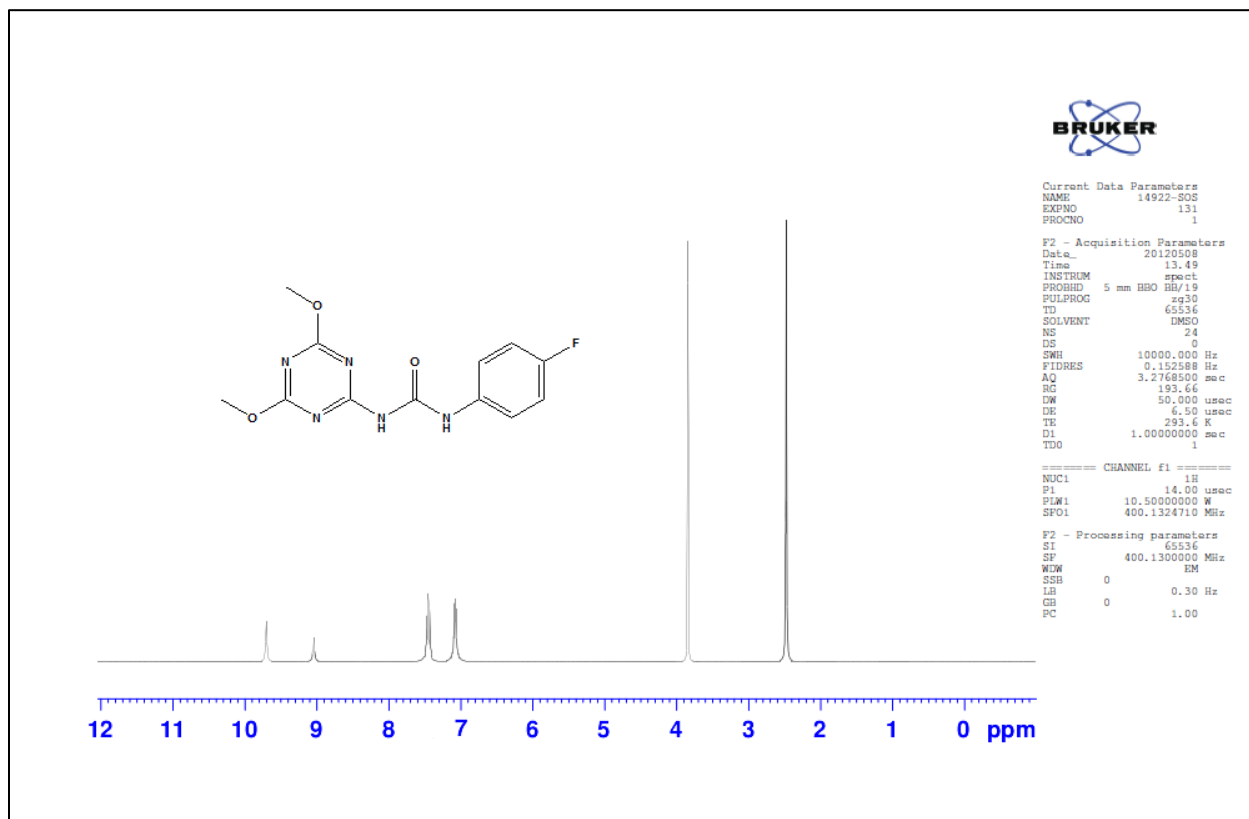
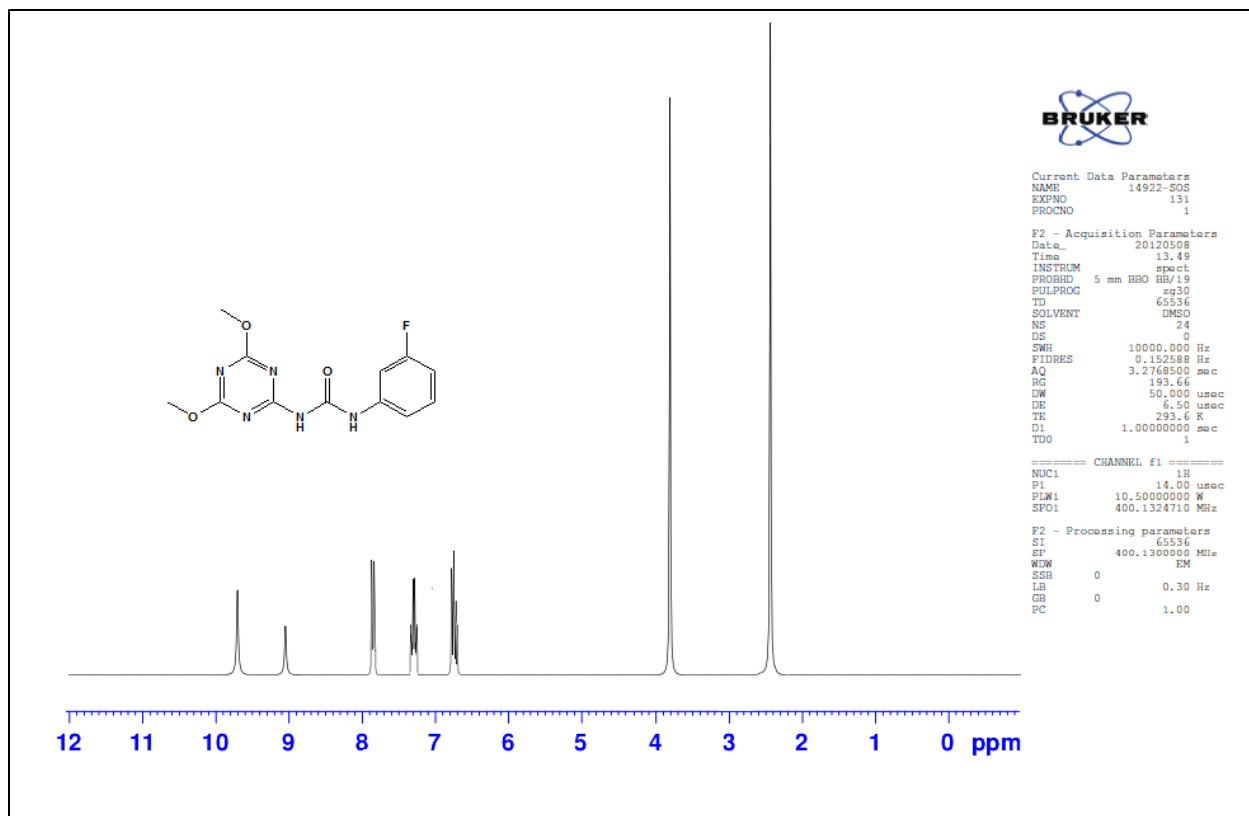
3o		<p>¹H NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 9.85 (s, 2H), 3.90 (s, 12H). ¹³C NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 173.00, 169.06, 156.88, 56.15. Anal. Calcd. For C₁₁H₁₄N₈O₅: C, 39.06; H, 4.17; N, 33.12. Found: C, 39.01; H, 4.20; N, 33.38. mp 230°C.</p>
3p		<p>¹H NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 4.19 (m, 4H), 3.89 (s, 12H). ¹³C NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 173.02, 168.89, 156.82, 56.23, 42.68. Anal. Calcd. For C₁₃H₁₆N₈O₅: C, 42.86; H, 4.43; N, 30.76. Found: C, 42.95; H, 4.42; N, 30.79. mp 216°C.</p>
3q		<p>¹H NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 9.55 (s, 1H), 8.73 (s, 1H), 7.42 (d, <i>J</i> = 7.8 Hz, 2H), 7.25 (t, <i>J</i> = 7.7 Hz, 2H), 7.00 (t, <i>J</i> = 7.3 Hz, 1H), 3.01 (s, 12H). ¹³C NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 166.71, 163.57, 160.07, 139.82, 128.60, 125.17, 120.03, 36.90. Anal. Calcd. For C₁₄H₁₉N₇O: C, 55.80; H, 6.36; N, 32.54. Found: C, 55.68; H, 6.37; N, 32.59. mp 132°C.</p>
3r		<p>¹H NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 9.67 (s, 1H), 8.79 (s, 1H), 7.43 (d, <i>J</i> = 8.0 Hz, 2H), 7.28 (t, <i>J</i> = 8.0 Hz, 2H), 7.01 (t, <i>J</i> = 7.9 Hz, 1H), 4.32 (q, <i>J</i> = 6.0 Hz, 4H), 1.30 (t, <i>J</i> = 6.0 Hz, 6H). ¹³C NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 171.65, 164.59, 160.30, 139.81, 128.76, 125.08, 119.98, 60.49, 15.01. Anal. Calcd. For C₁₄H₁₇N₅O₃: C, 55.44; H, 5.65; N, 23.09. Found: C, 55.37; H, 5.70; N, 23.06. mp 139-140°C.</p>
3s		<p>¹H NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 9.70 (s, 1H), 8.93 (s, 1H), 7.45 (d, <i>J</i> = 7.7 Hz, 2H), 7.30 (t, <i>J</i> = 7.6 Hz, 2H), 7.03 (t, <i>J</i> = 7.3 Hz, 1H), 3.94 (s, 3H), 3.10 (s, 6H). ¹³C NMR (400 MHz, DMSO-<i>d</i>₆) δ ppm : 168.47, 167.42, 162.62, 160.30, 139.89, 128.60, 125.19, 120.04, 55.57, 36.69. Anal. Calcd. For C₁₃H₁₆N₆O₂: C, 54.16; H, 5.59; N, 29.15. Found: C, 54.25; H, 5.63; N,</p>

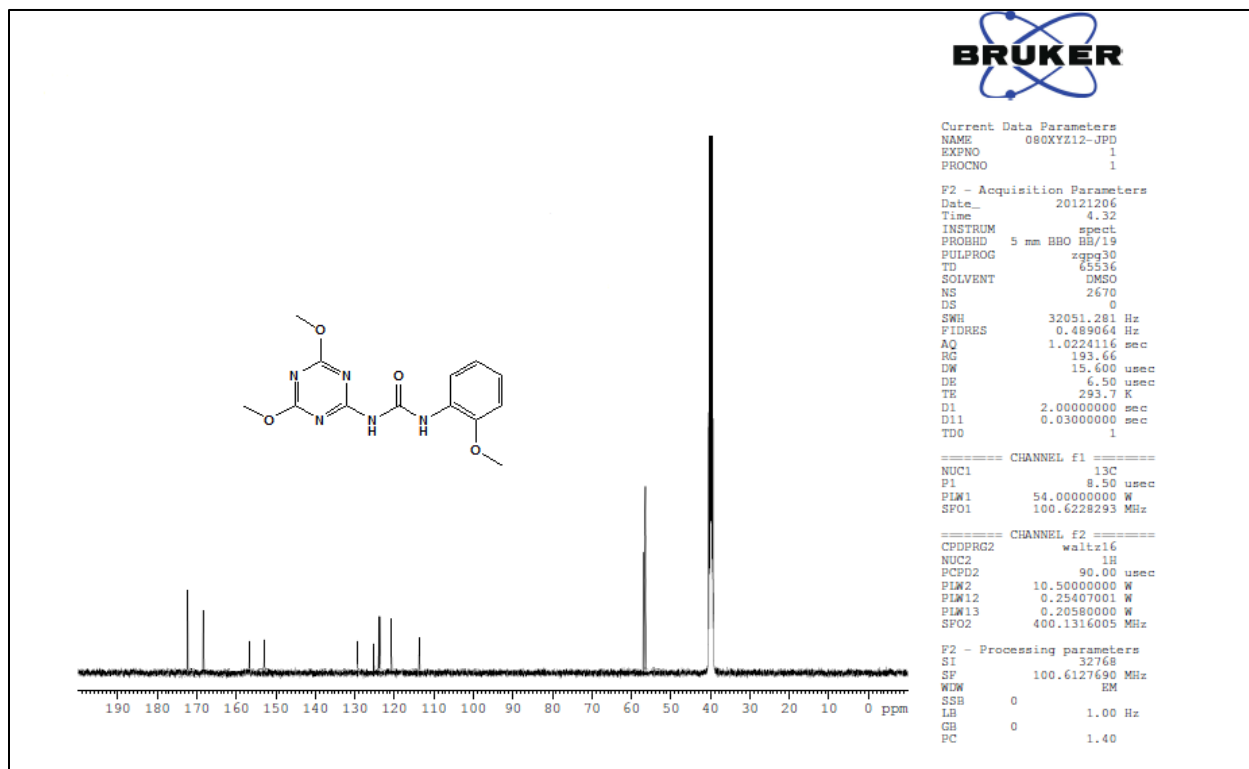
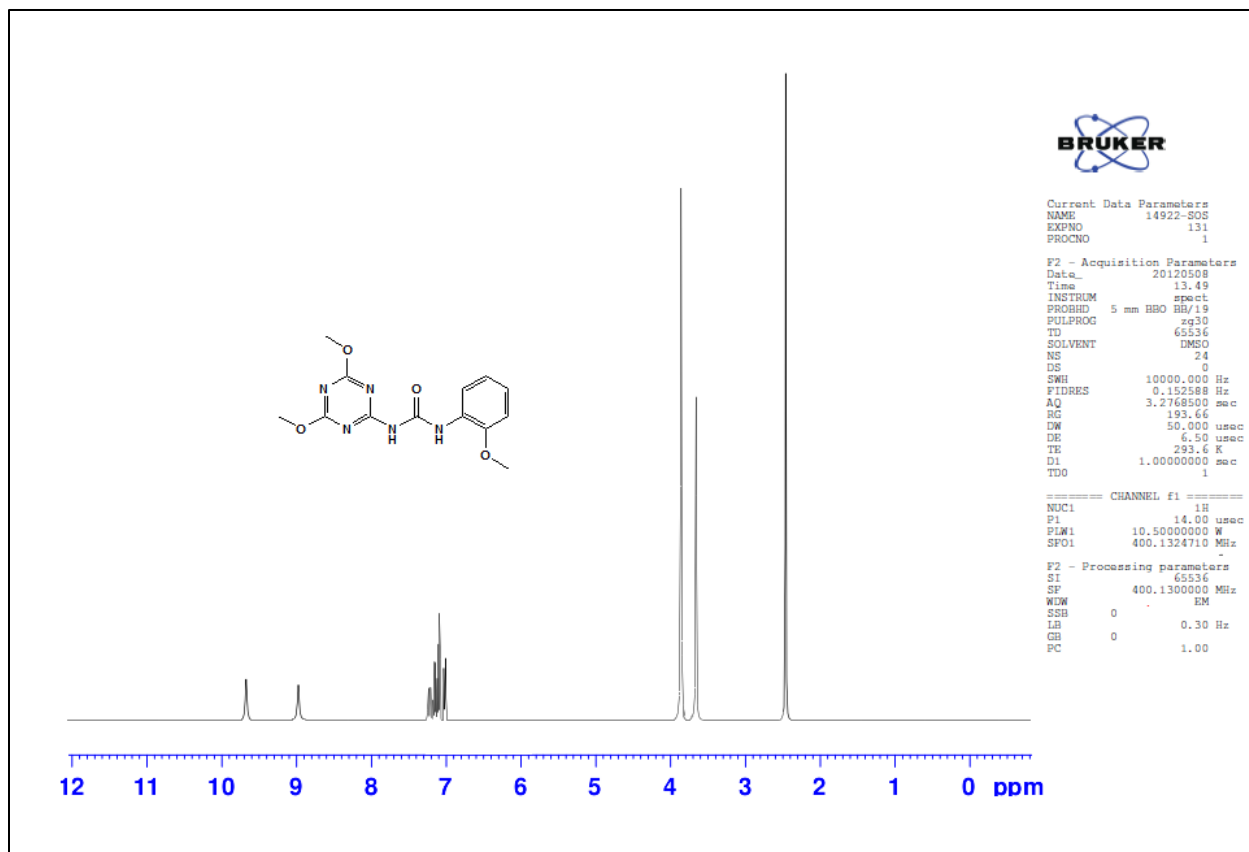
		29.11.mp 149-150°C.
3t	 <chem>COC1=CC=C(OC)N=C2N(C(=O)Nc3ccccc3)N=CN=C12</chem>	¹ H NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 9.48 (s, 1H), 8.75 (s, 1H), 7.48 (dd, <i>J</i> = 7.6, 1.9 Hz, 2H), 7.31 (dt, <i>J</i> = 7.5 Hz, 4H), 7.19 (dd, <i>J</i> = 7.6, 2.0 Hz, 2H), 7.10 (tt, <i>J</i> = 7.6, 2.1 Hz, 1H), 6.89 (tt, <i>J</i> = 7.6, 2.0 Hz, 1H), 3.89 (s, 3H). ¹³ C NMR (400 MHz, DMSO- <i>d</i> ₆) δ ppm : 174.19, 172.60, 163.02, 161.00, 149.97, 139.94, 133.33, 127.06, 128.11, 122.14, 125.25, 120.00, 56.00. Anal. Calcd. For C ₁₇ H ₁₅ N ₅ O ₃ : C, 60.53; H, 4.48; N, 20.76. Found: C, 60.51; H, 4.43; N, 20.80. mp 210°C.

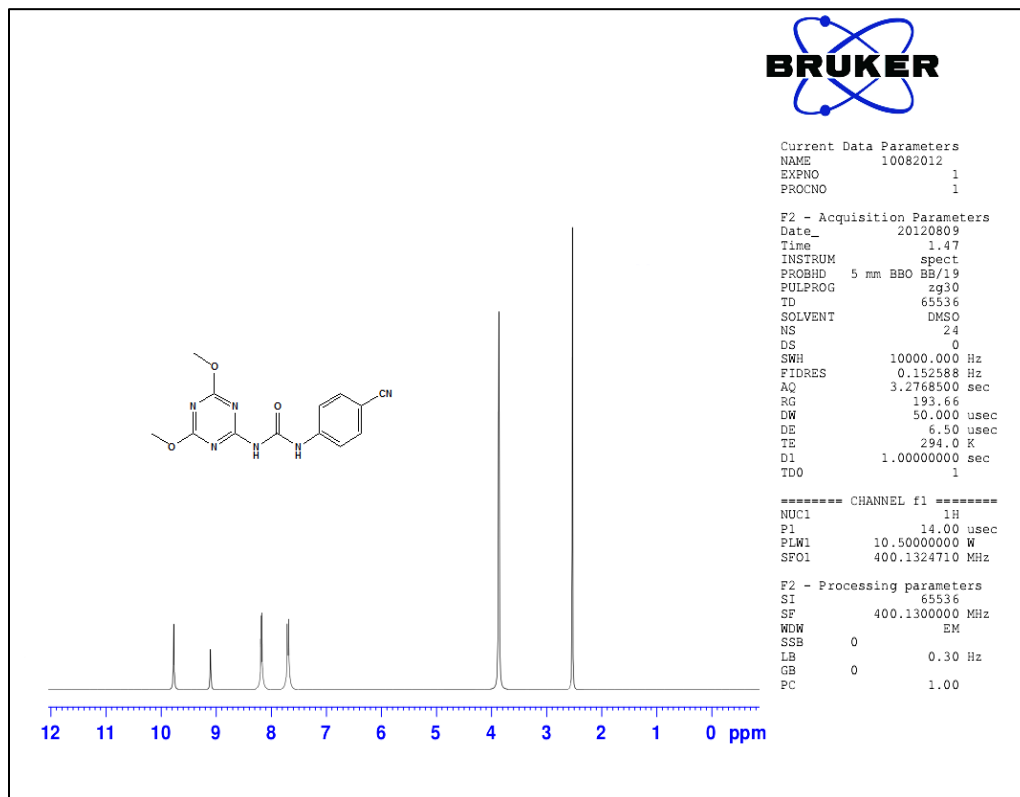
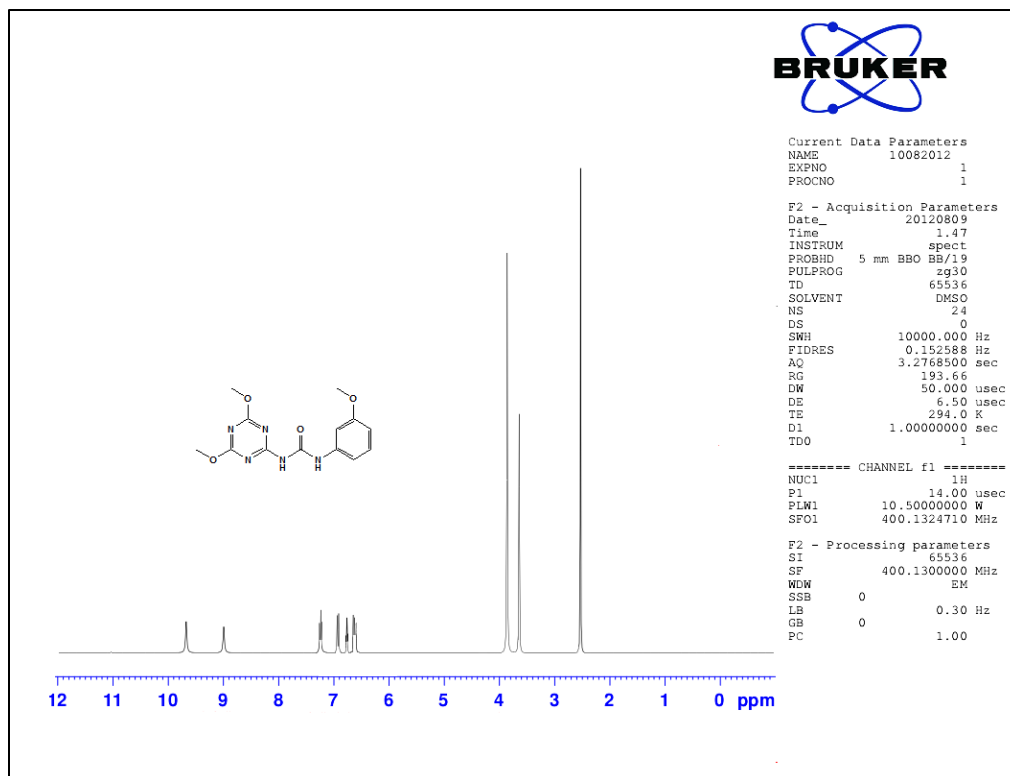
References

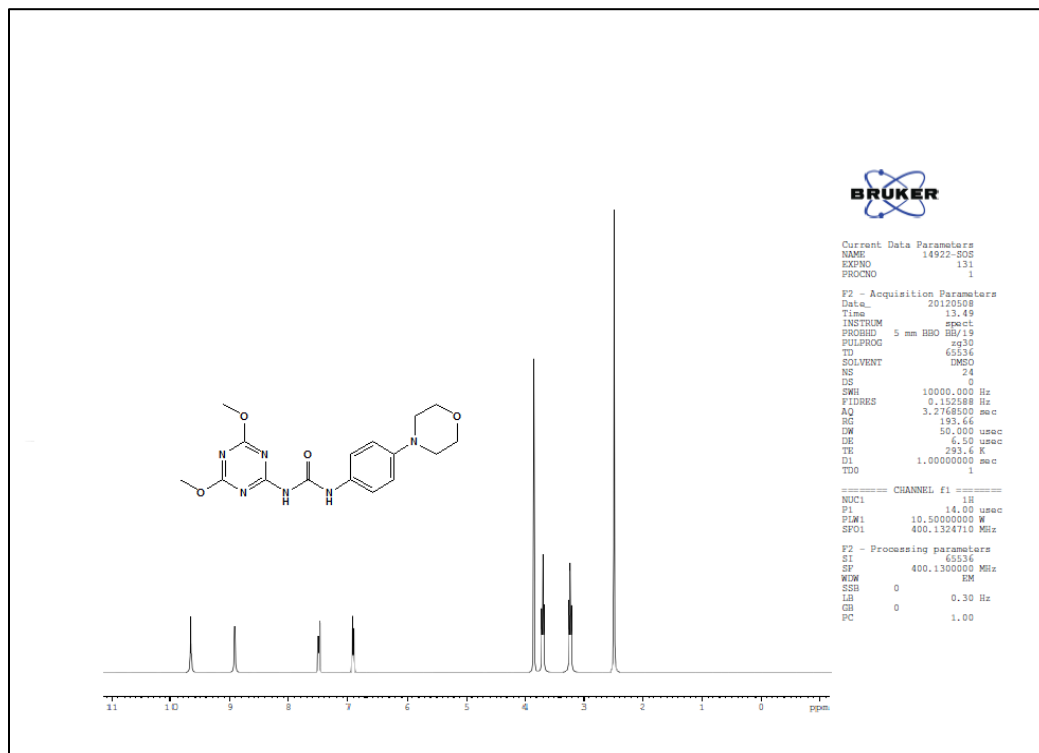
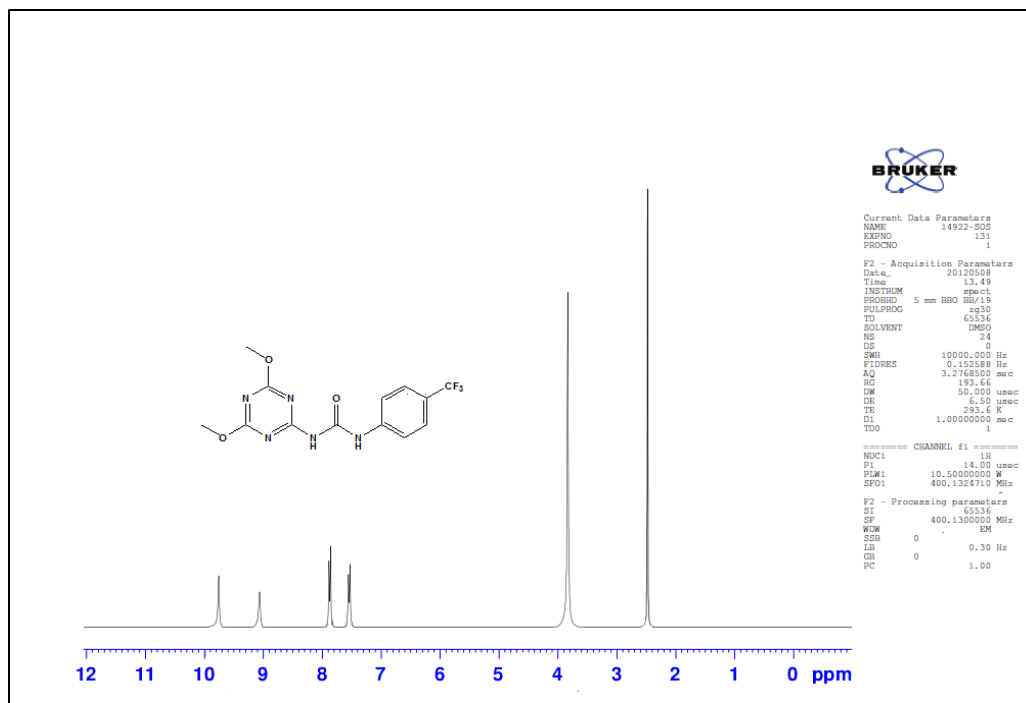
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- [2] J. R. Dudley, J. T. Thurston, F. C. Schaefer, *J. Am. Chem. Soc.* 1950, **73**, 2986-2989.
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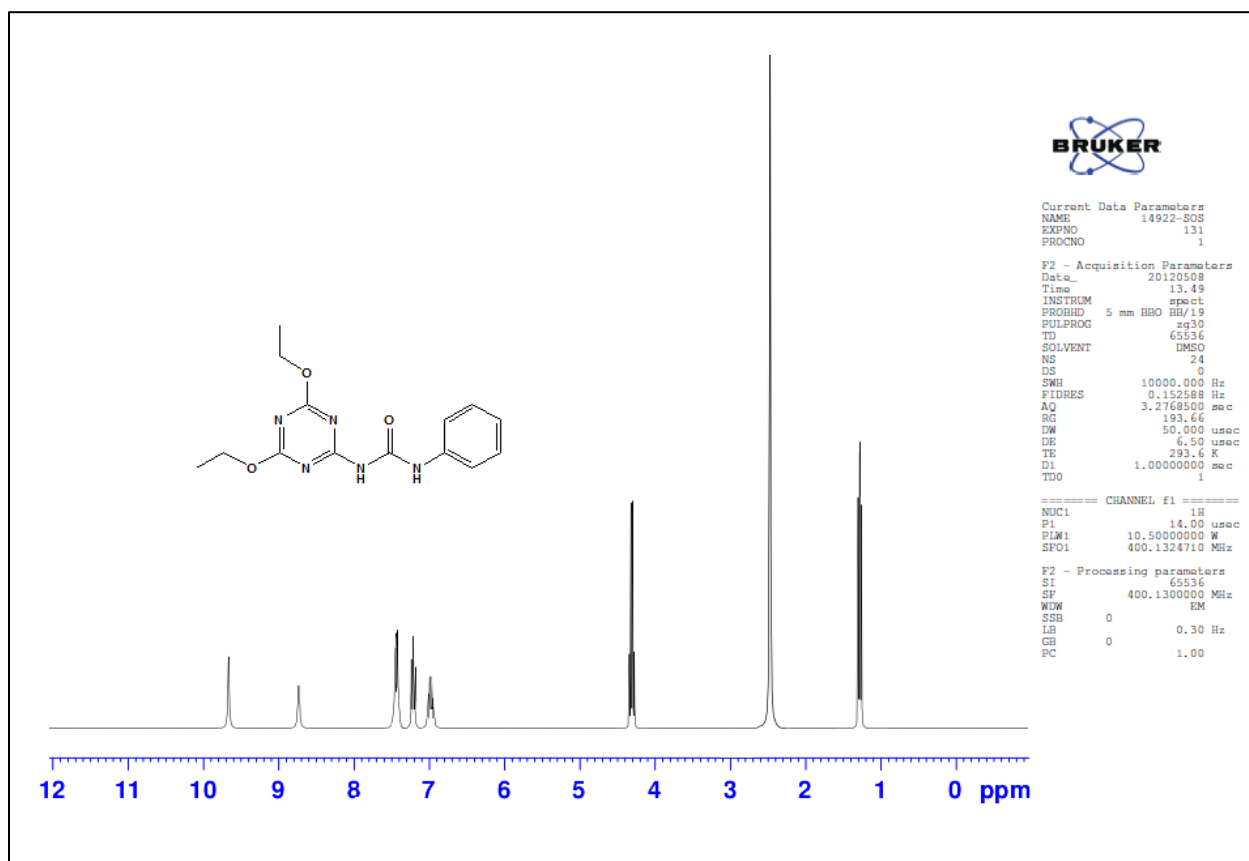
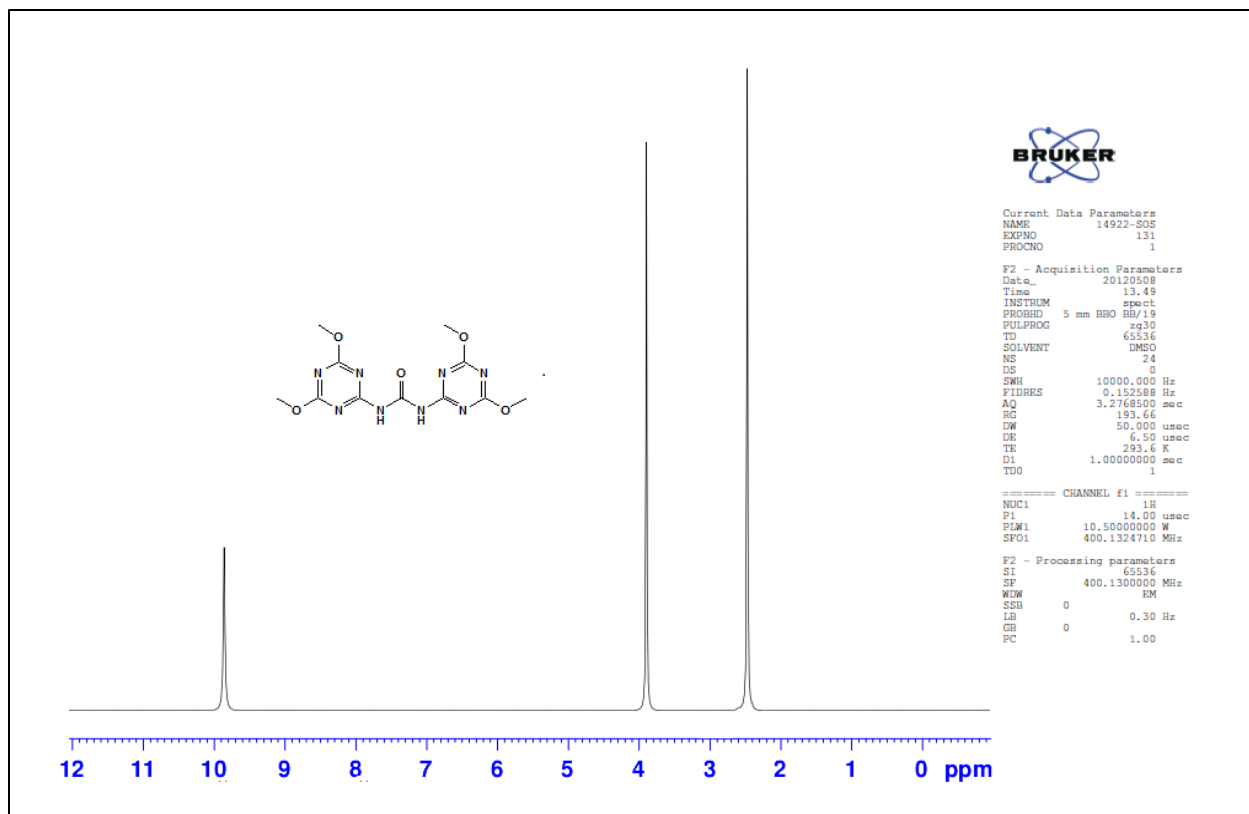


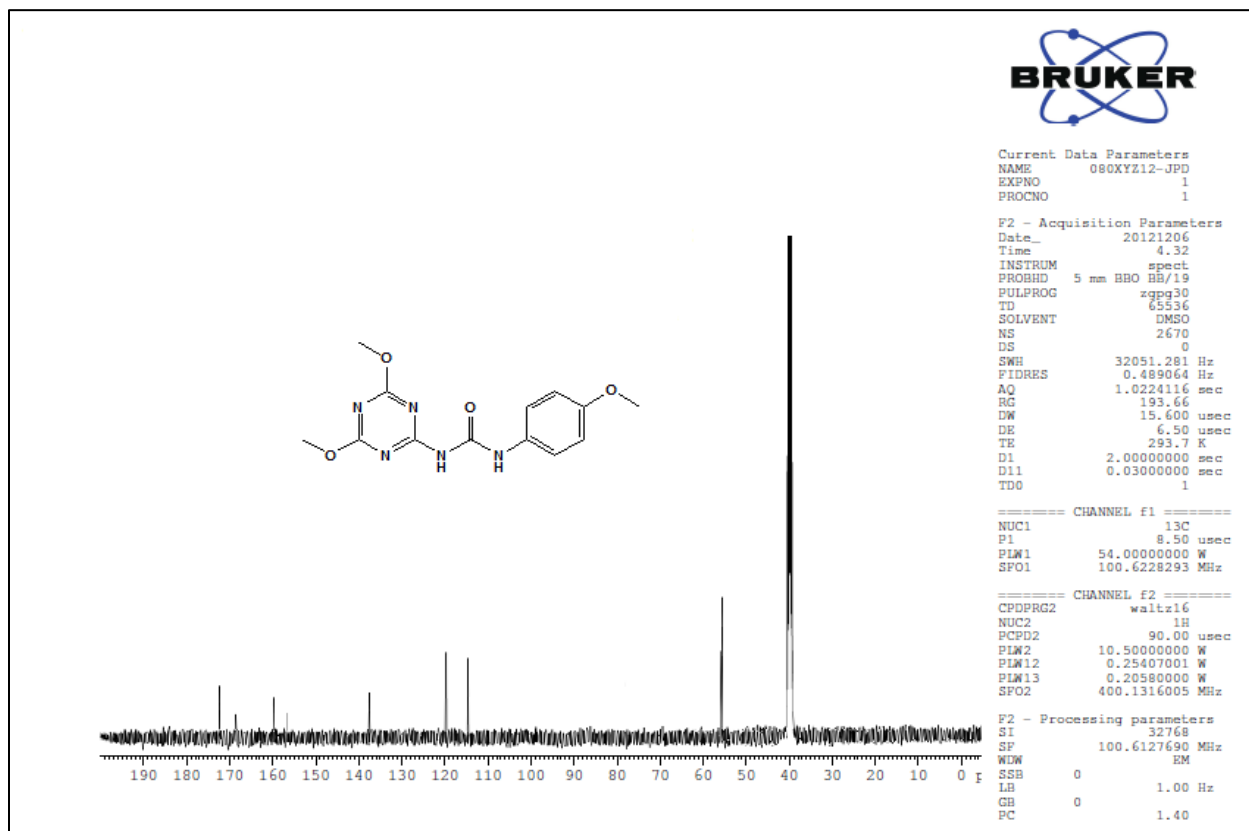
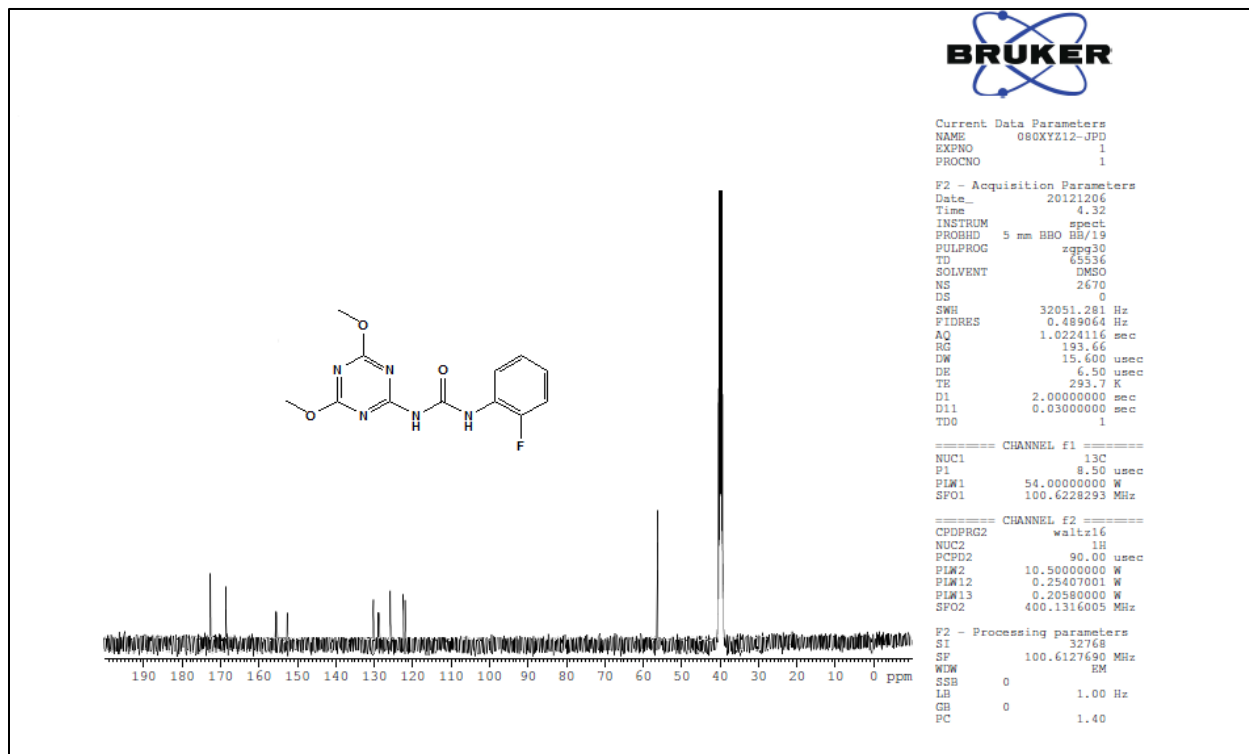


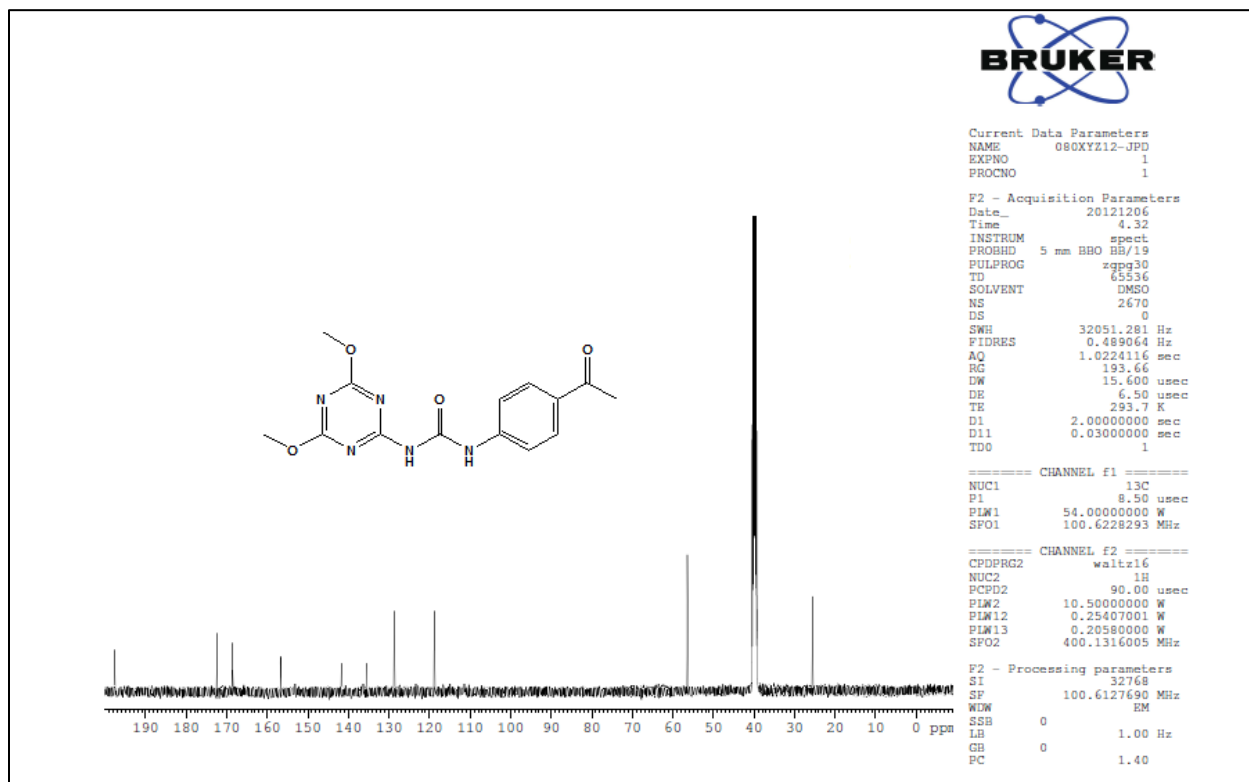
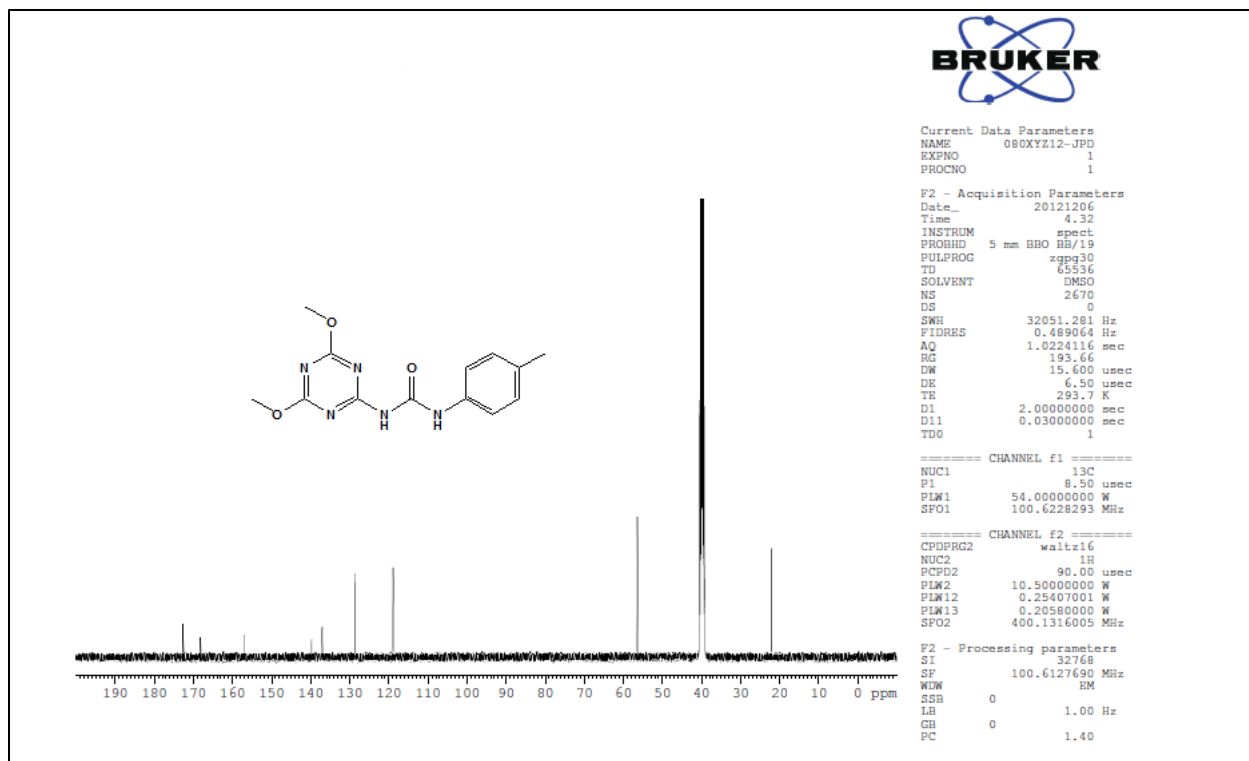


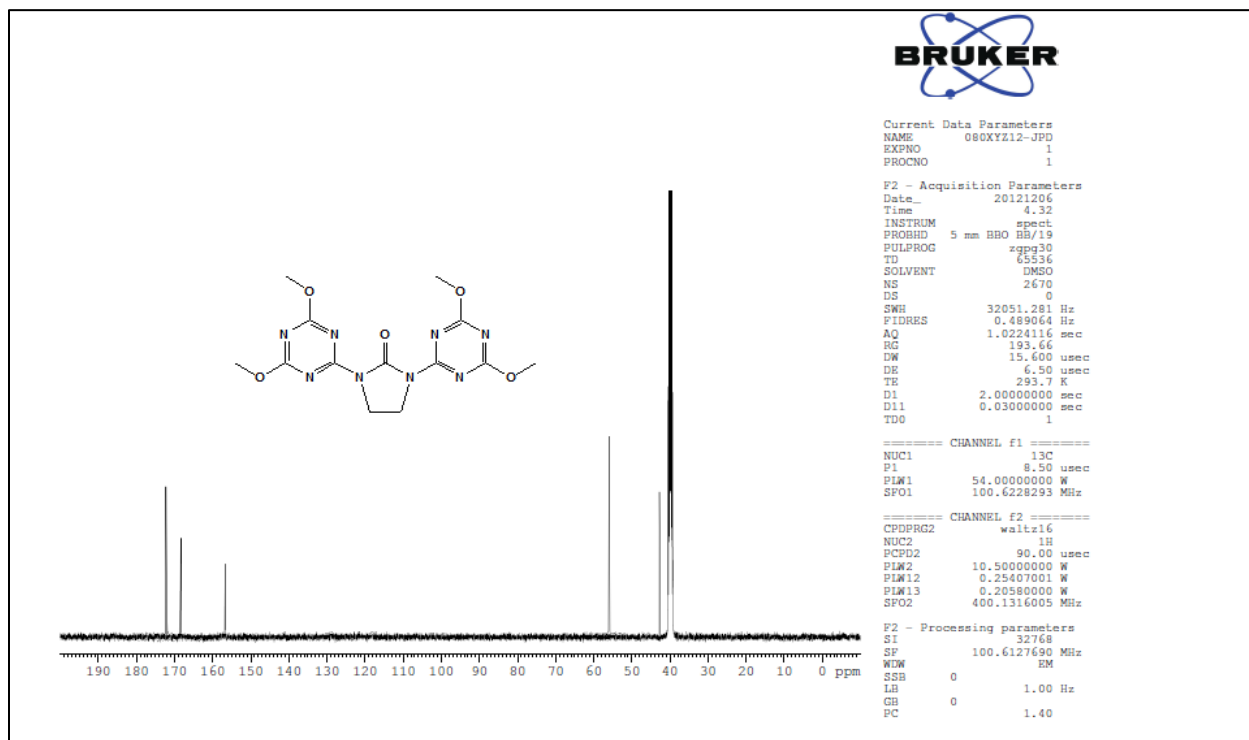
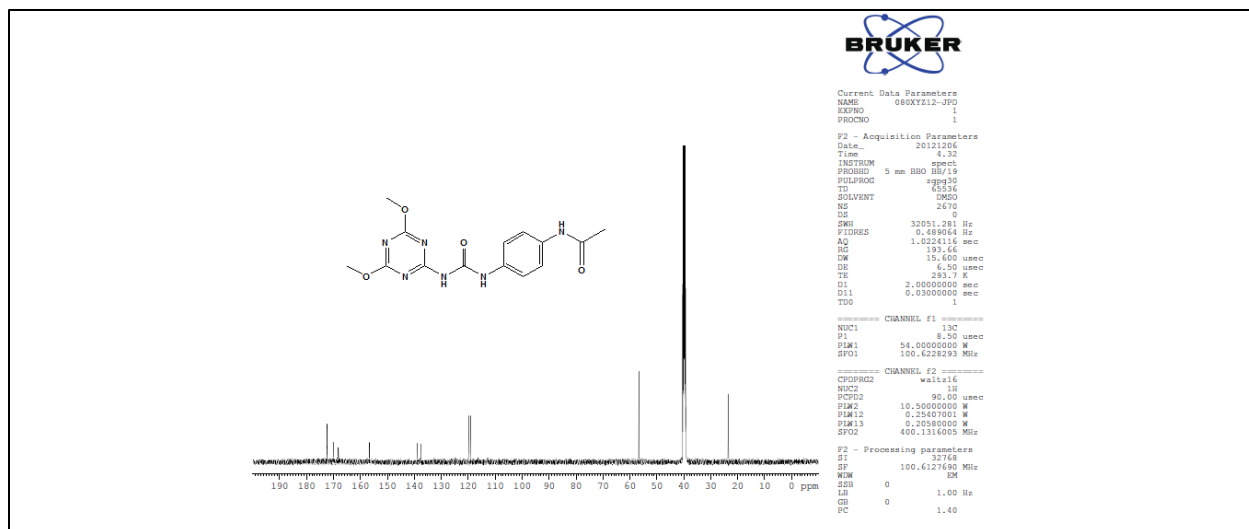


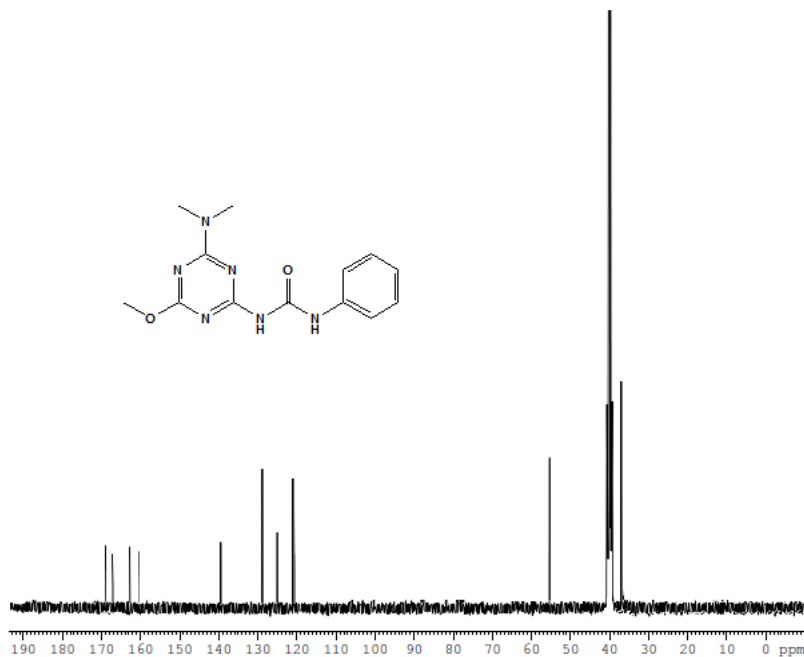
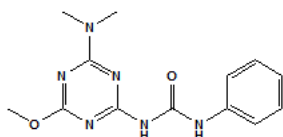












Current Data Parameters
NAME 080XYZ12-JPD
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
Date_ 20121206
Time 4.32
INSTRUM spect
PROBHD 5 mm BBO BB/19
PULPROG zgpg30
TD 65536
SOLVENT DMSO
NS 2670
DS 0
SWH 32051.281 Hz
FIDRES 0.489064 Hz
AQ 1.0224116 sec
RG 193.66
DW 15.600 usec
DE 6.50 usec
TE 293.7 K
D1 2.0000000 sec
D11 0.0300000 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.50 usec
PLW1 54.0000000 W
SFO1 100.6228293 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PLW2 10.50000000 W
PLW12 0.25407001 W
PLW13 0.20580000 W
SFO2 400.1316005 MHz

F2 - Processing parameters
SI 32768
SF 100.6127690 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40