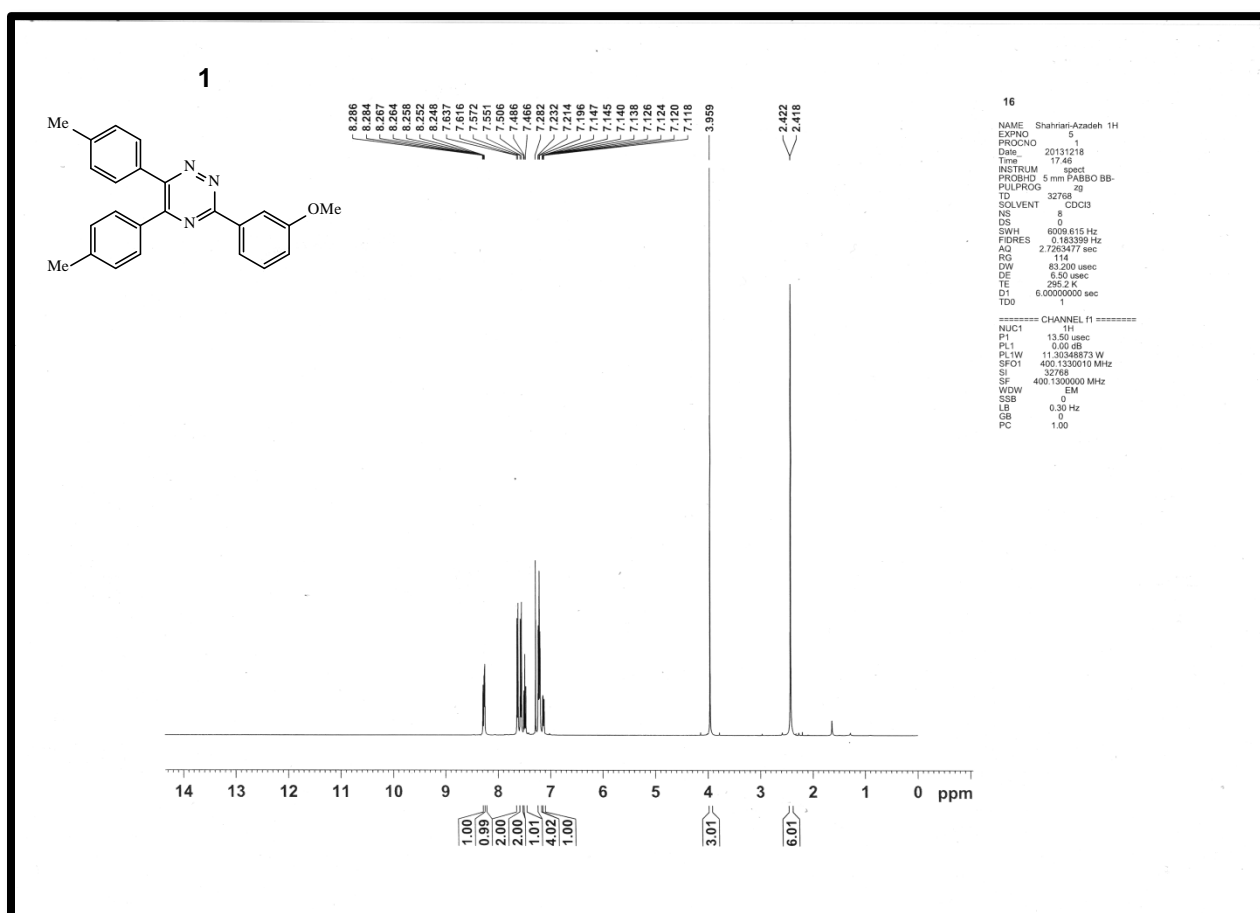
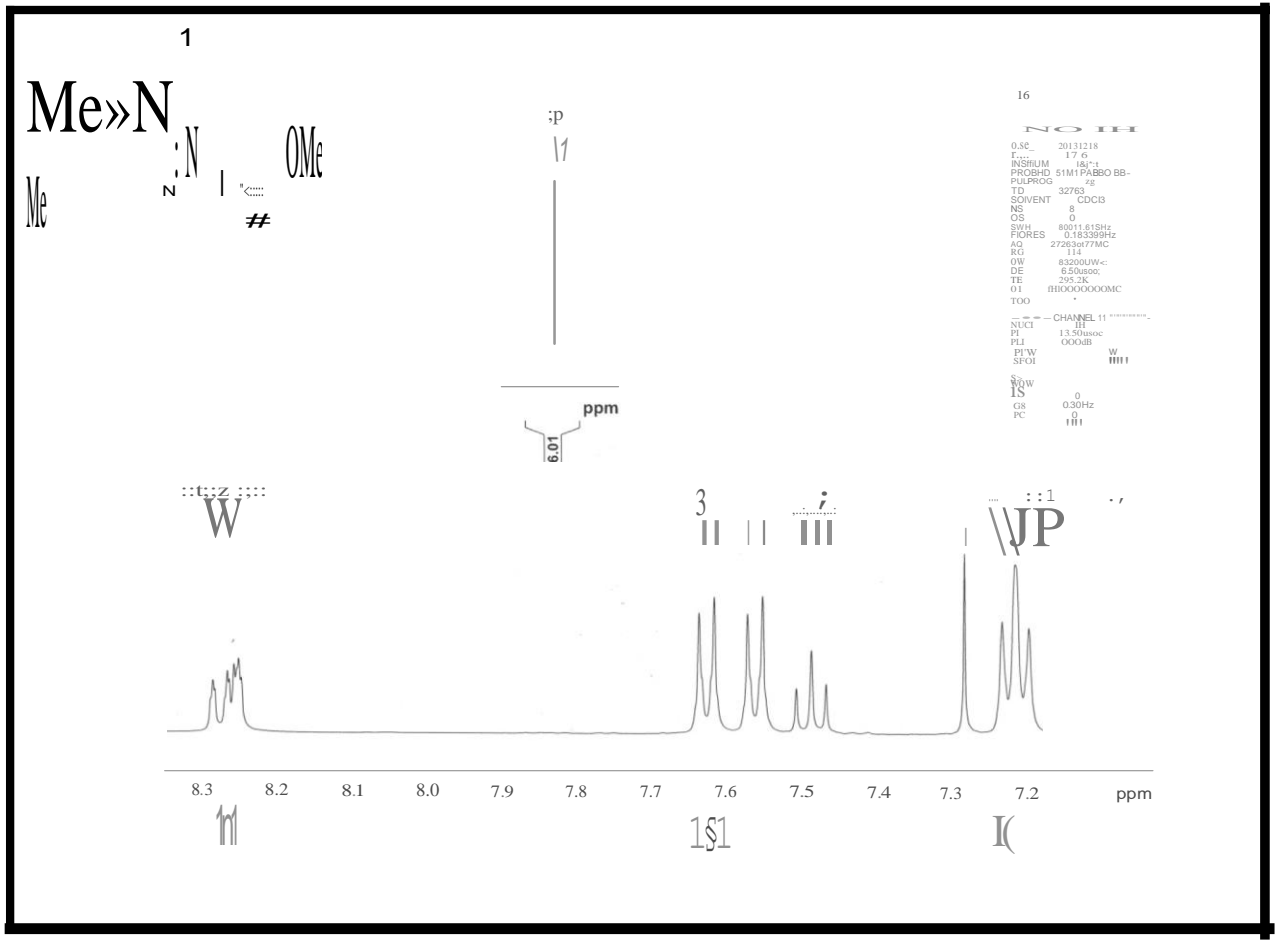


Solvent-free Synthesis of Triazines Using *N*-Halosulfonamides

Ramin Ghorbani-Vaghei^{a,*}, Azadeh Shahriari^a, Zahra Salimi^a, Somayeh Hajinazari^b

1. **3-(3-Methoxyphenyl)-5,6-di(*p*-tolyl)-1,2,4-triazine (Table 2, entry 1):** Yellow powder. Mp: 100-103 °C (99°C)²⁸; ¹H NMR (400 MHz CDCl₃): δ_H (ppm) 2.41 (s, CH₃, 3H), 2.42 (s, CH₃, 3H), 3.95 (s, CH₃, 3H), 7.11-8.28 (m, CH aromatic, 12H). ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) 21.43, 21.52, 55.49, 112.67, 117.93, 120.84, 129.25, 129.30, 129.33, 129.81, 132.80, 133.13, 136.33, 139.67, 141.17, 155.32, 155.41, 160.02, 160.75. MS: *m/z* 367. . Anal. Calcd for C₂₄H₂₁N₃O: C, 78.45; H, 5.76; N, 11.44; Found: C, 77.43; H, 5.83; N, 11.09.





DATE 20 12 91 TIME 14 12 12 OPERATOR ID GHAEMI

RUN 28 ID SH16 WEIGHT 2.584

SIGNALS

CARBON 77.43%
HYDROGEN 5.83%
NITROGEN 11.09%

ZR 1656
NR 3407
CR 31443
HR 36913

BLANKS 82 201 314
KFACTORS 13.971 35.007 5.013

OXFILL COMB BOOST1 BOOST2
0 0 0 0

FILL TIME 10 SECONDS

DATE 20 12 91 TIME 14 16 36 OPERATOR ID GHAEMI

RUN 29 BLANK RUN

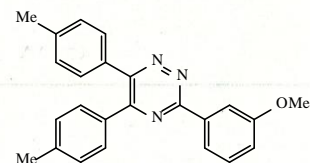
SIGNALS

CARBON 96
HYDROGEN 200
NITROGEN 305

ZR 1657
NR 1962
CR 2058
HR 2258

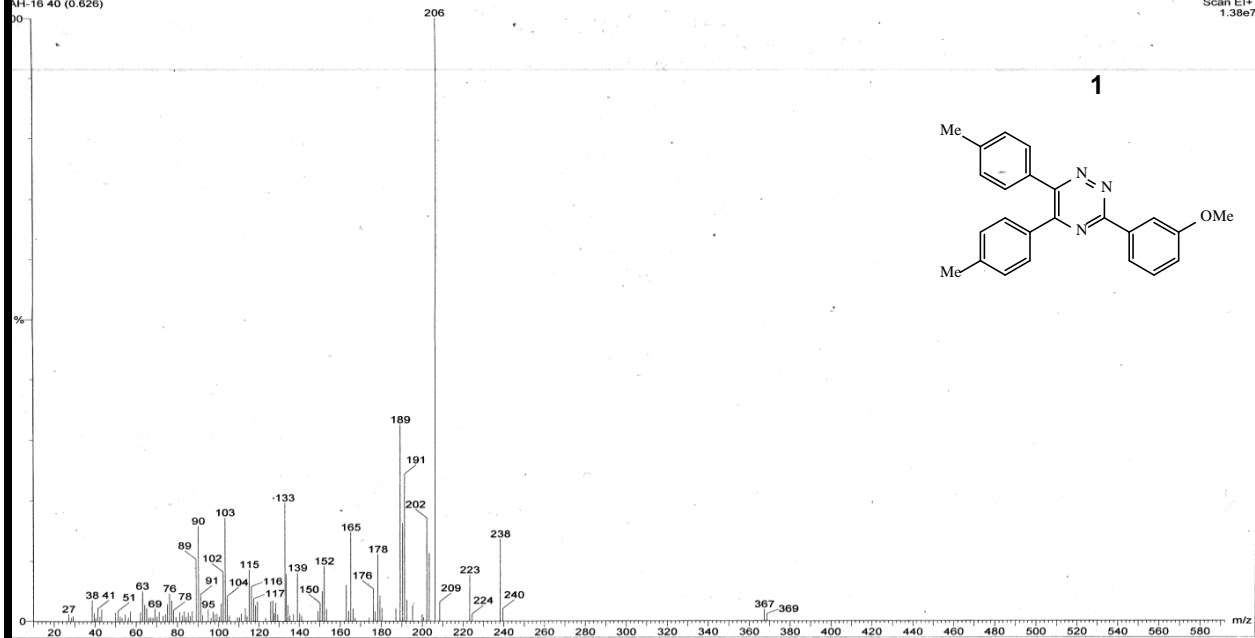
AVERAGE RESULTS

CARBON 89
HYDROGEN 200
NITROGEN 309

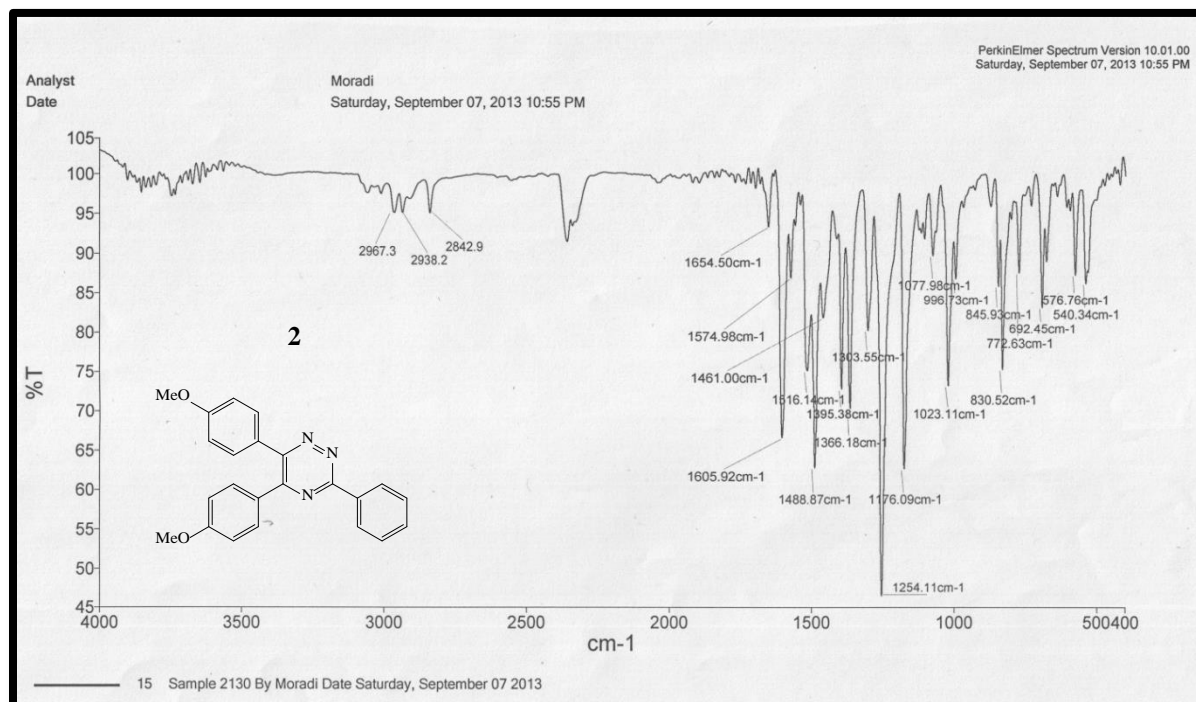


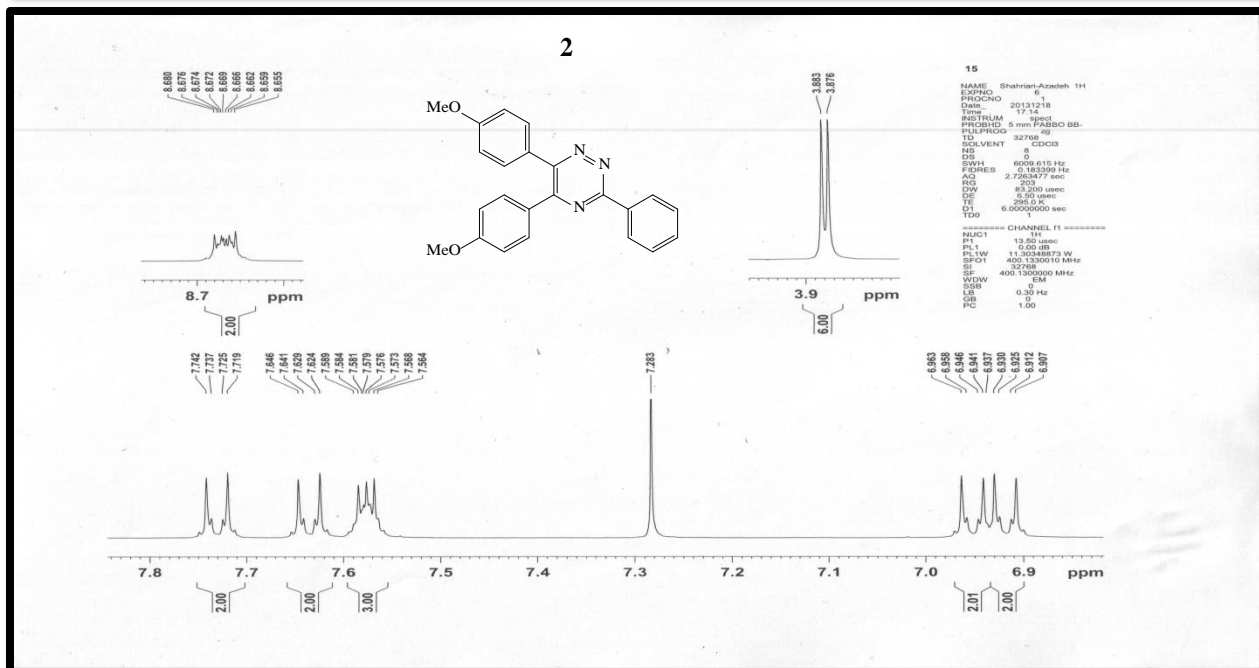
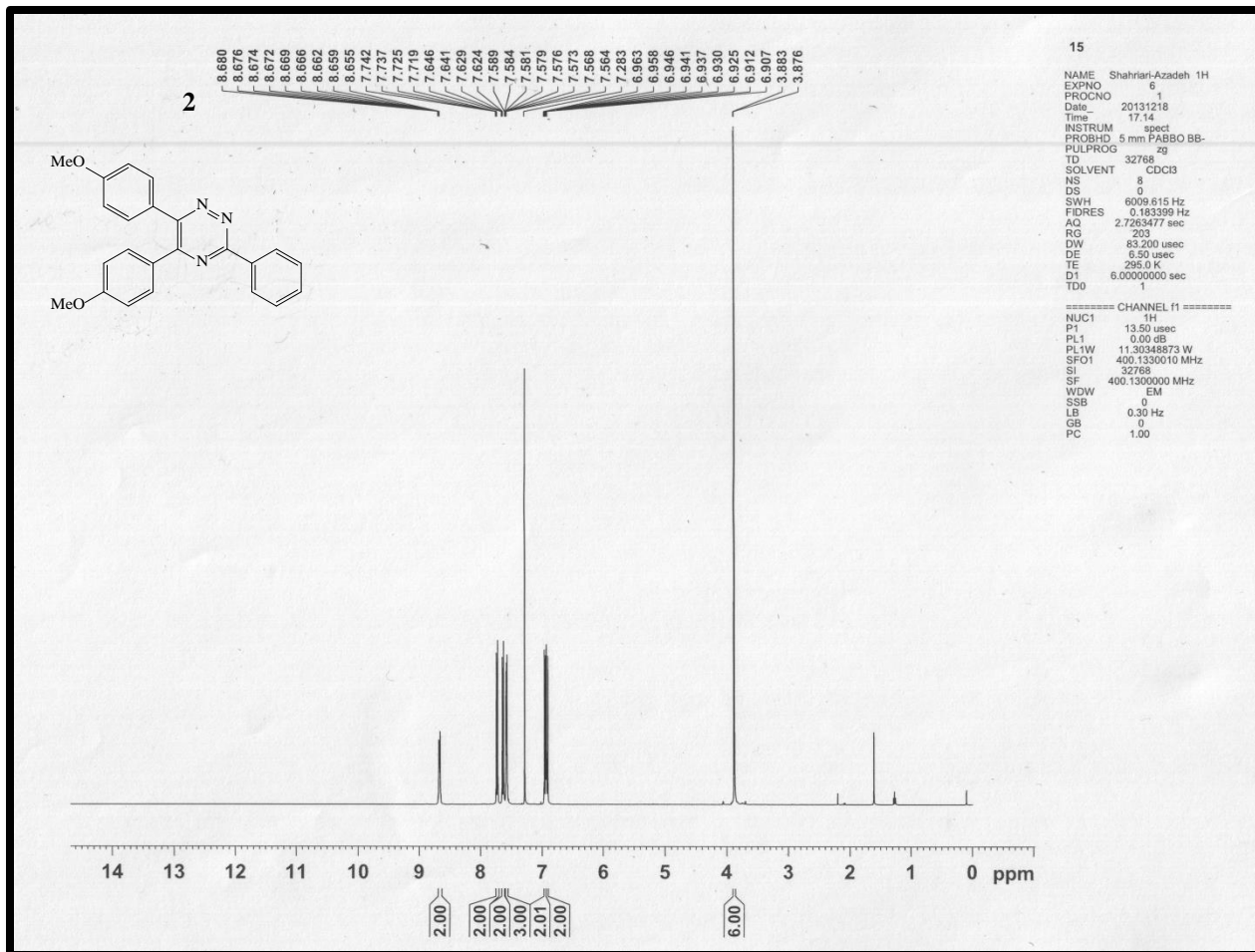
NH-16 40 (0.626)

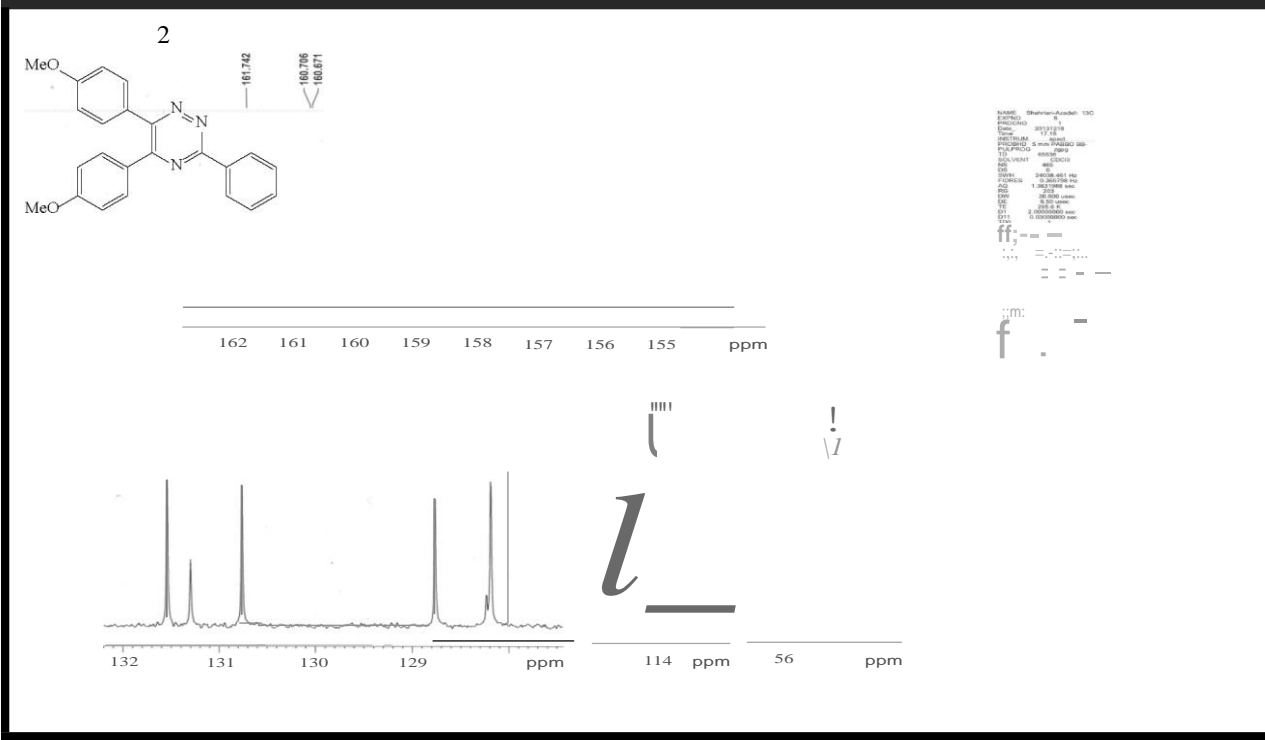
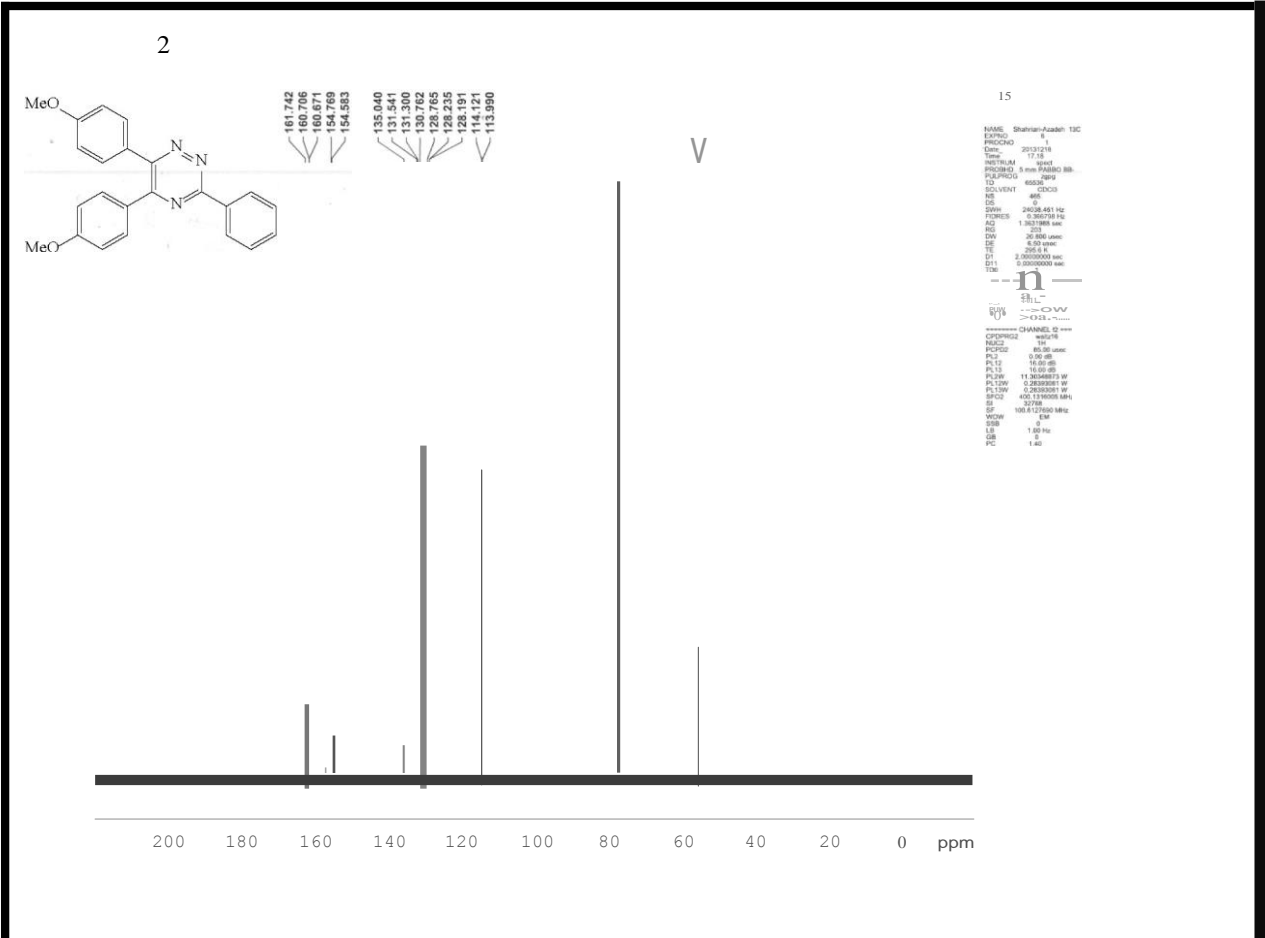
Solid Probe
Scan E1+
1.38e7



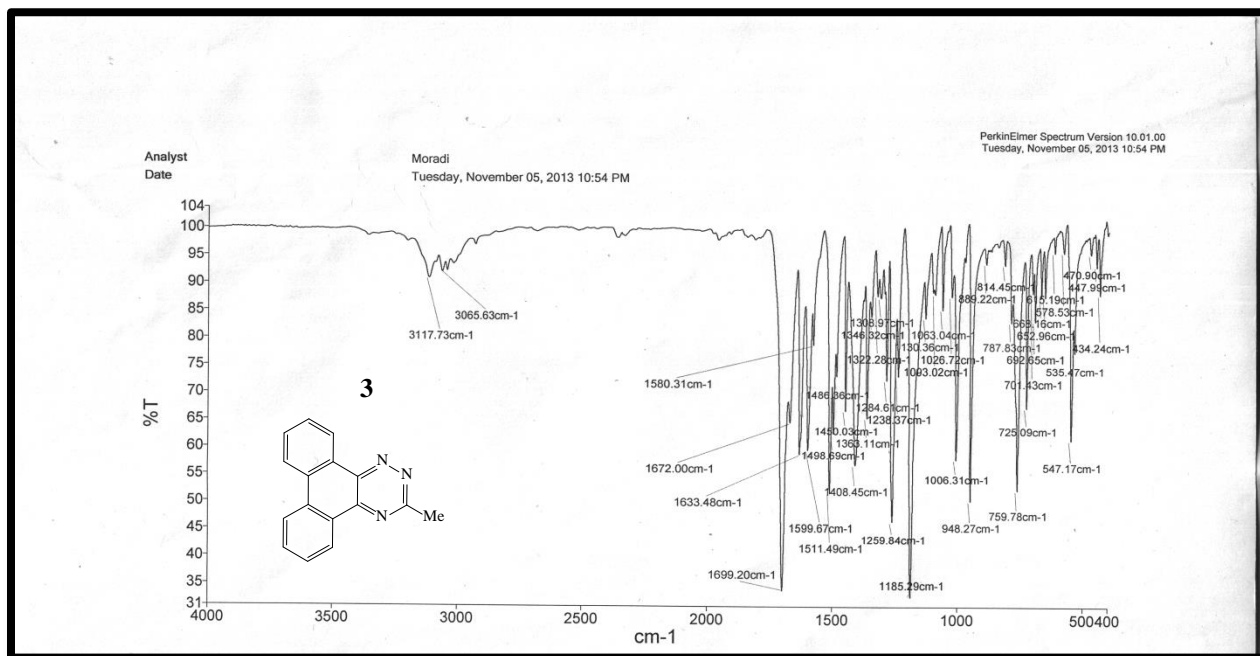
2. **5,6-Bis(4-methoxyphenyl)-3-phenyl-1,2,4-triazine** (Table 2, entry 2): Yellow powder. Mp: 155-158 °C (165 °C)²⁸; IR (KBr): 2967, 2938, 2842, 1605, 1574, 1488, 1254; ¹H NMR (400 MHz CDCl₃): δ_H (ppm) 3.87 (s, OCH₃, 3H), 3.88 (s, OCH₃, 3H), 6.90-8.68 (m, CH aromatic, 13H). ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) 55.34, 55.40, 113.99, 114.12, 128.19, 128.23, 128.76, 130.76, 131.30, 131.54, 135.04, 154.58, 154.76, 160.67, 160.70, 161.74. MS: *m/z* 369. Anal. Calcd for C₂₃H₁₉N₃O₂: C, 74.78; H, 5.18; N, 11.37; Found: C, 74.77; H, 4.87; N, 11.09.

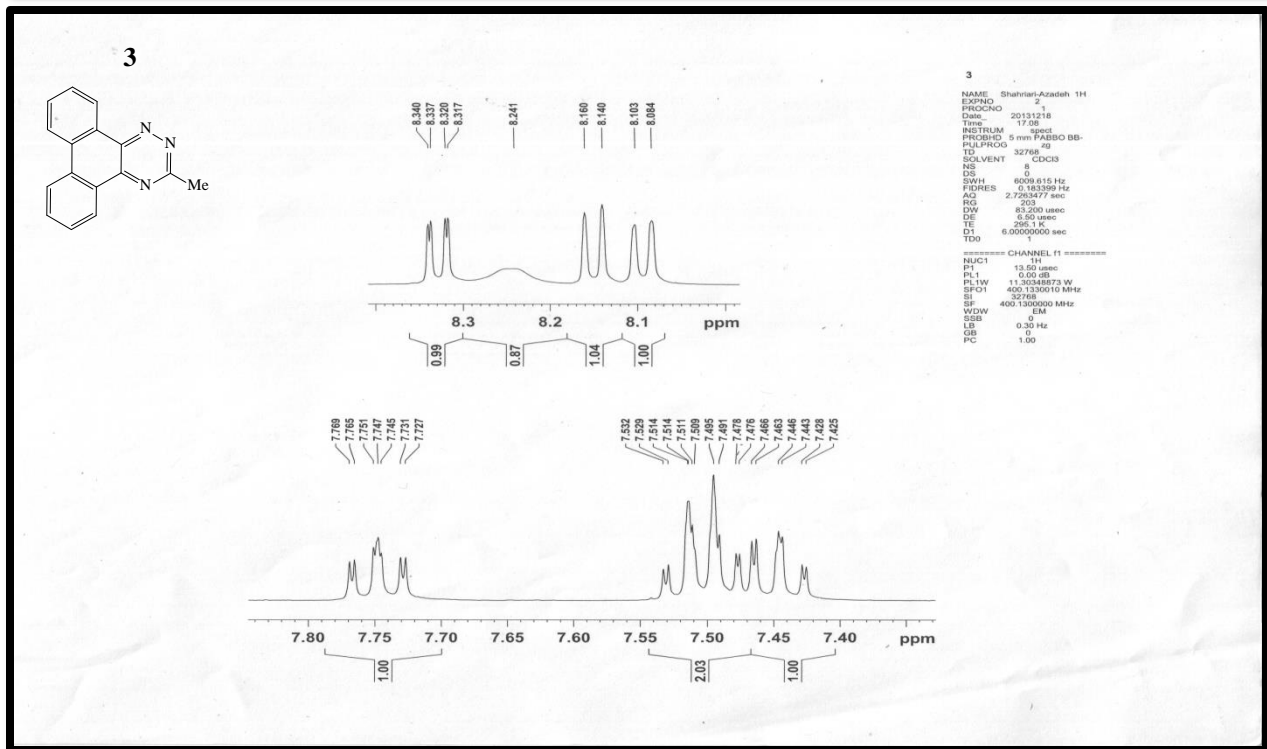
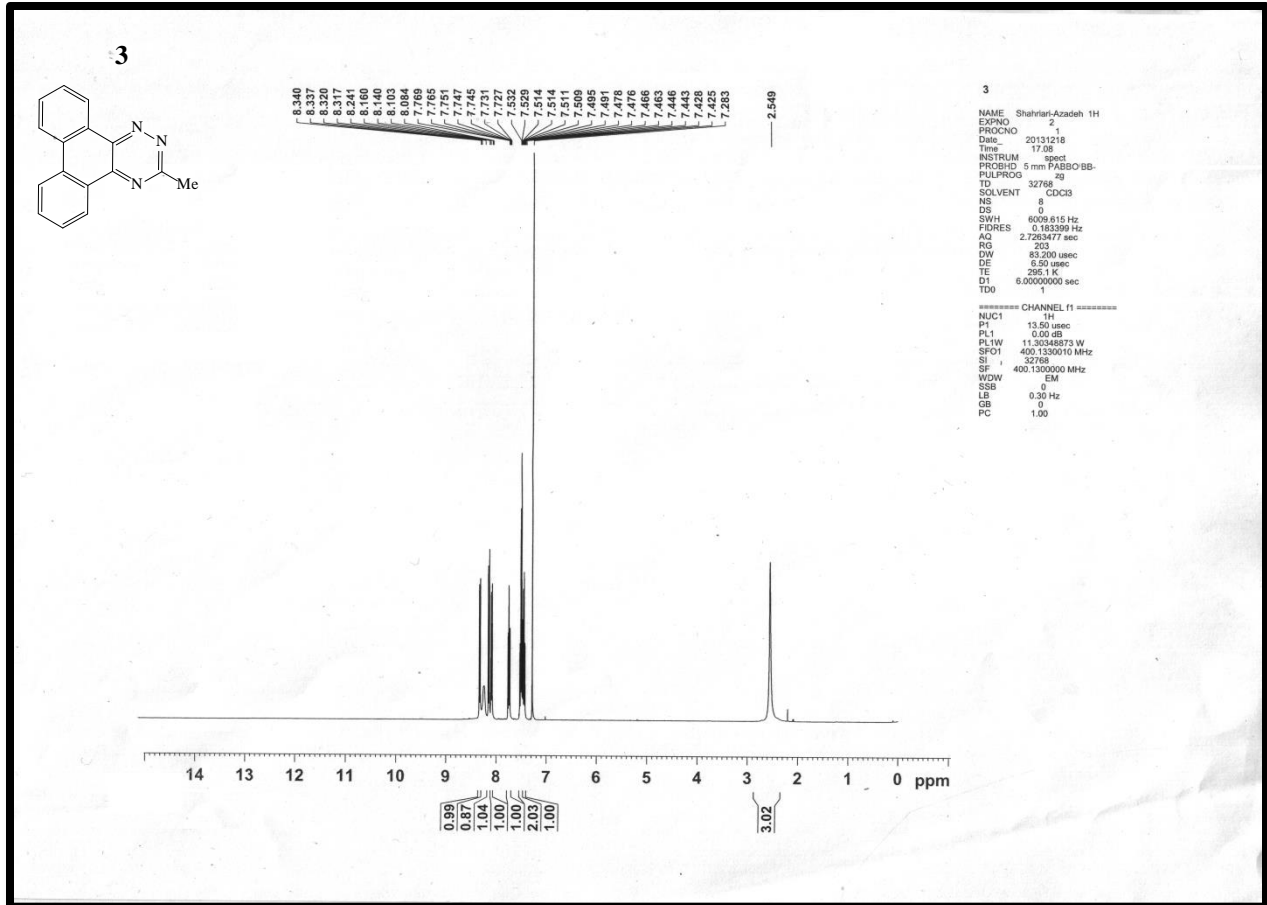


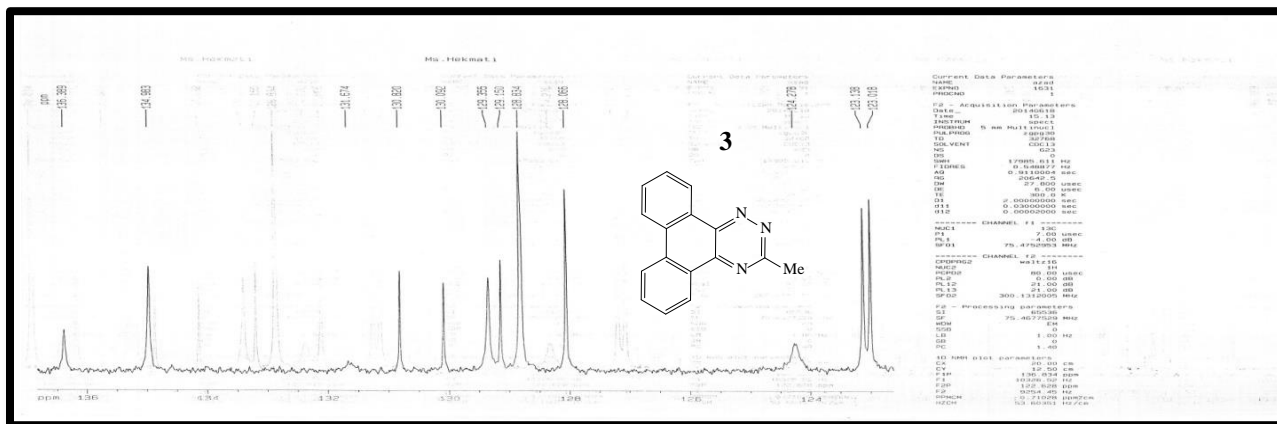
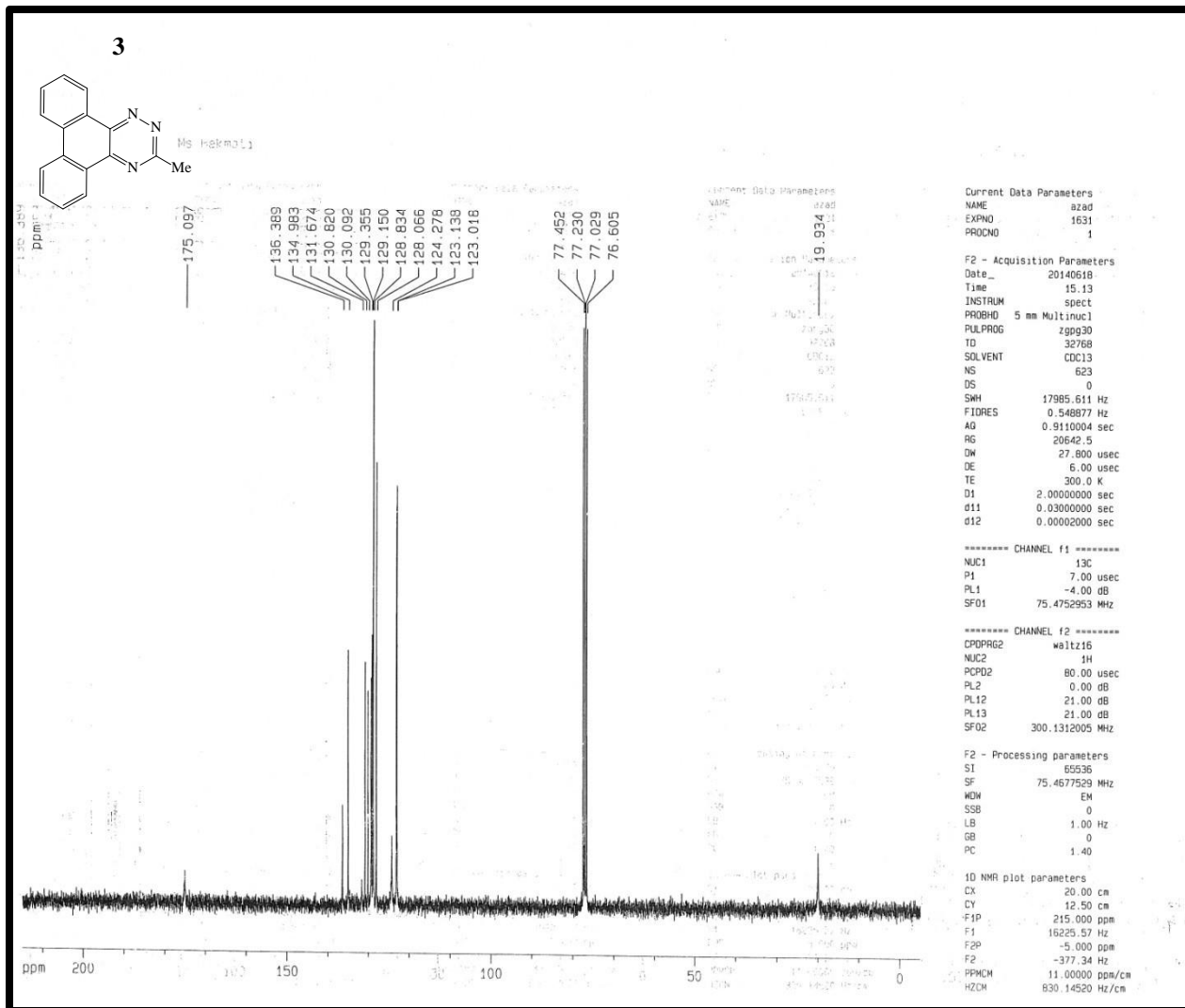


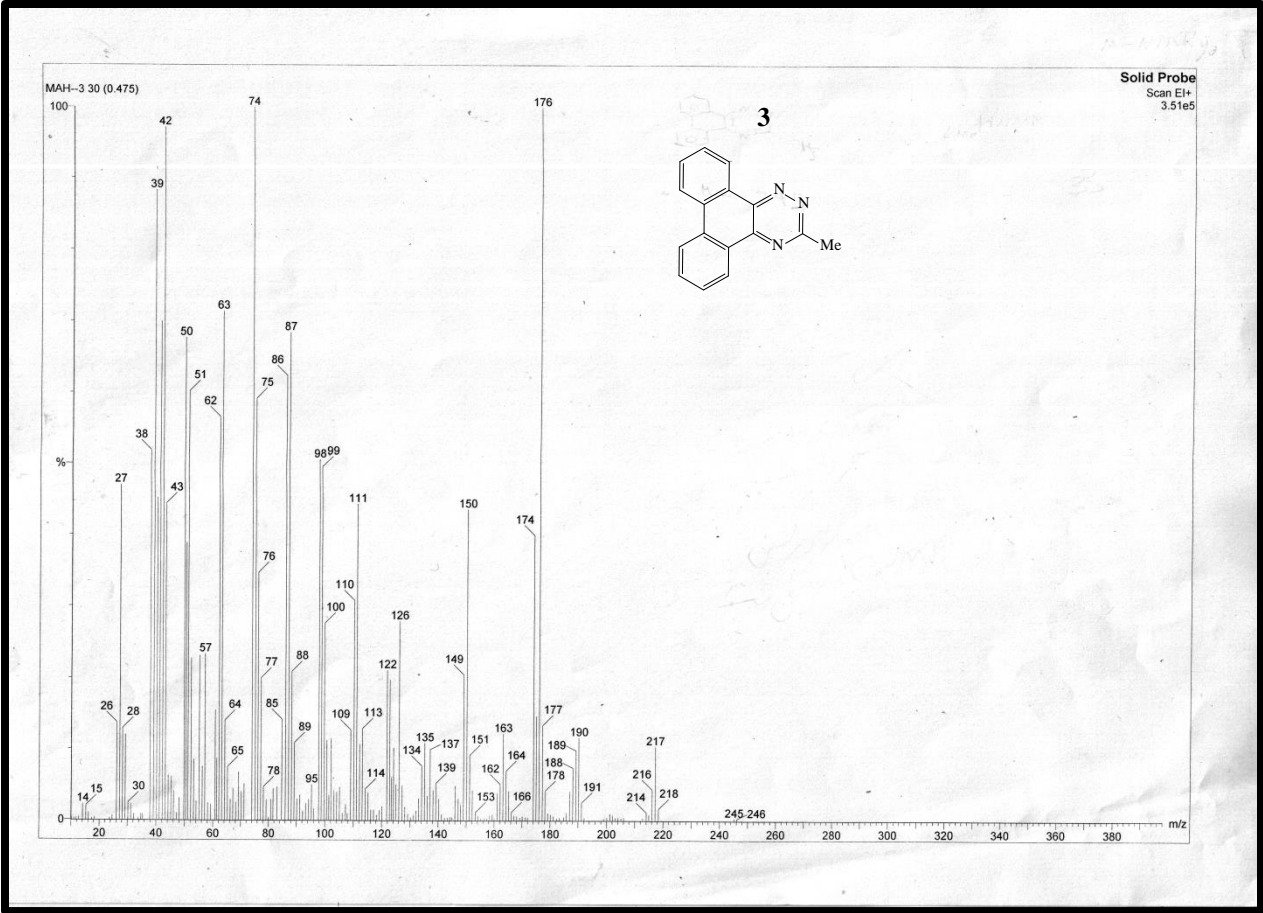


- 3. 3-Methylphenanthro[9,10-e][1,2,4]triazine (Table 2, entry 3):** Yellow powder. Mp: 166-168 °C; IR (KBr): 3117, 3065, 1699, 1672, 1185, 948; ¹H NMR (400 MHz, CDCl₃): δ_H (ppm) 2.54 (s, CH₃, 3H), 7.28-8.34 (m, CH aromatic, 8H) ¹³C NMR (100 MHz, CDCl₃): δ_C(ppm) 19.93, 123.01, 123.13, 124.2, 128.06, 128.83, 129.15, 129.35, 130.09, 130.82, 131.67, 134.98, 136.38, 175.09. MS: *m/z* 245.

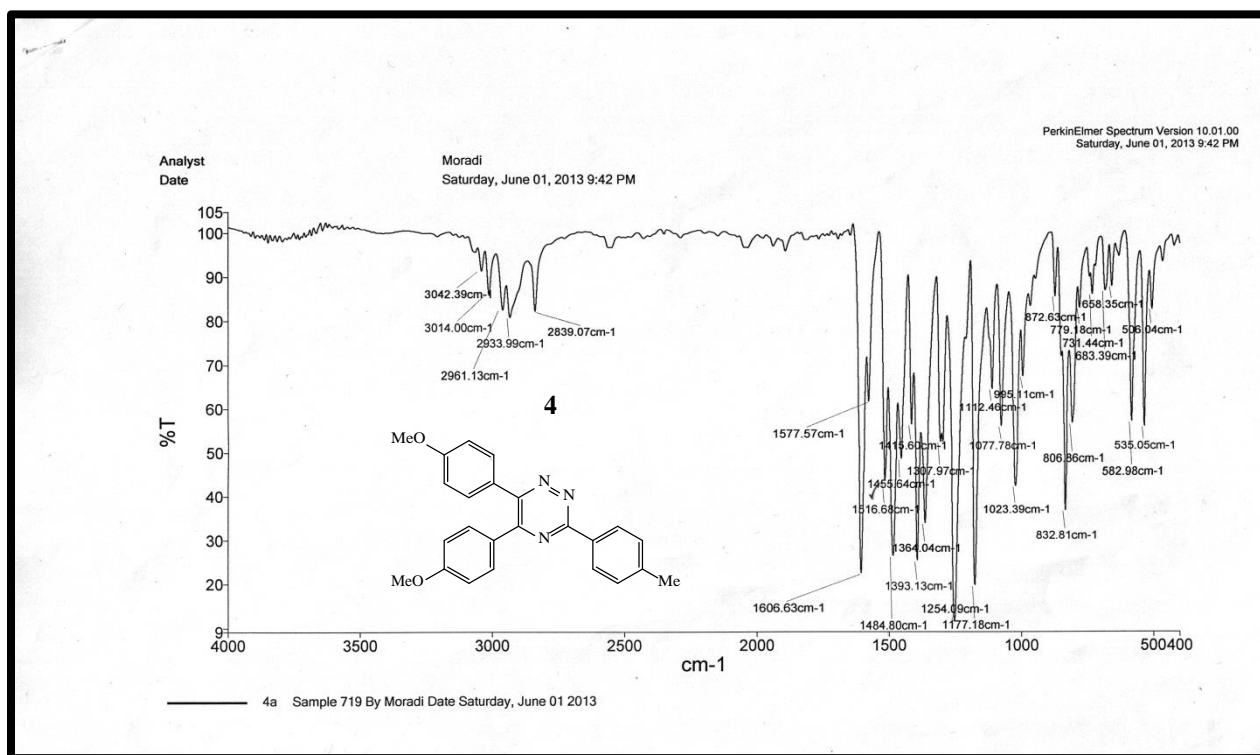


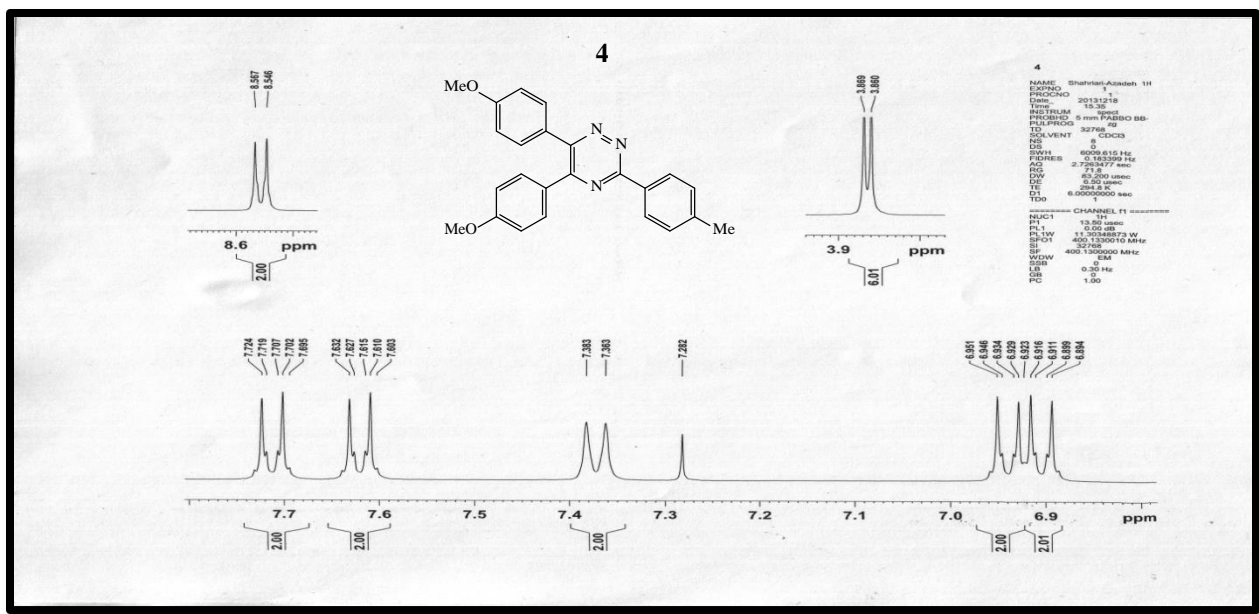
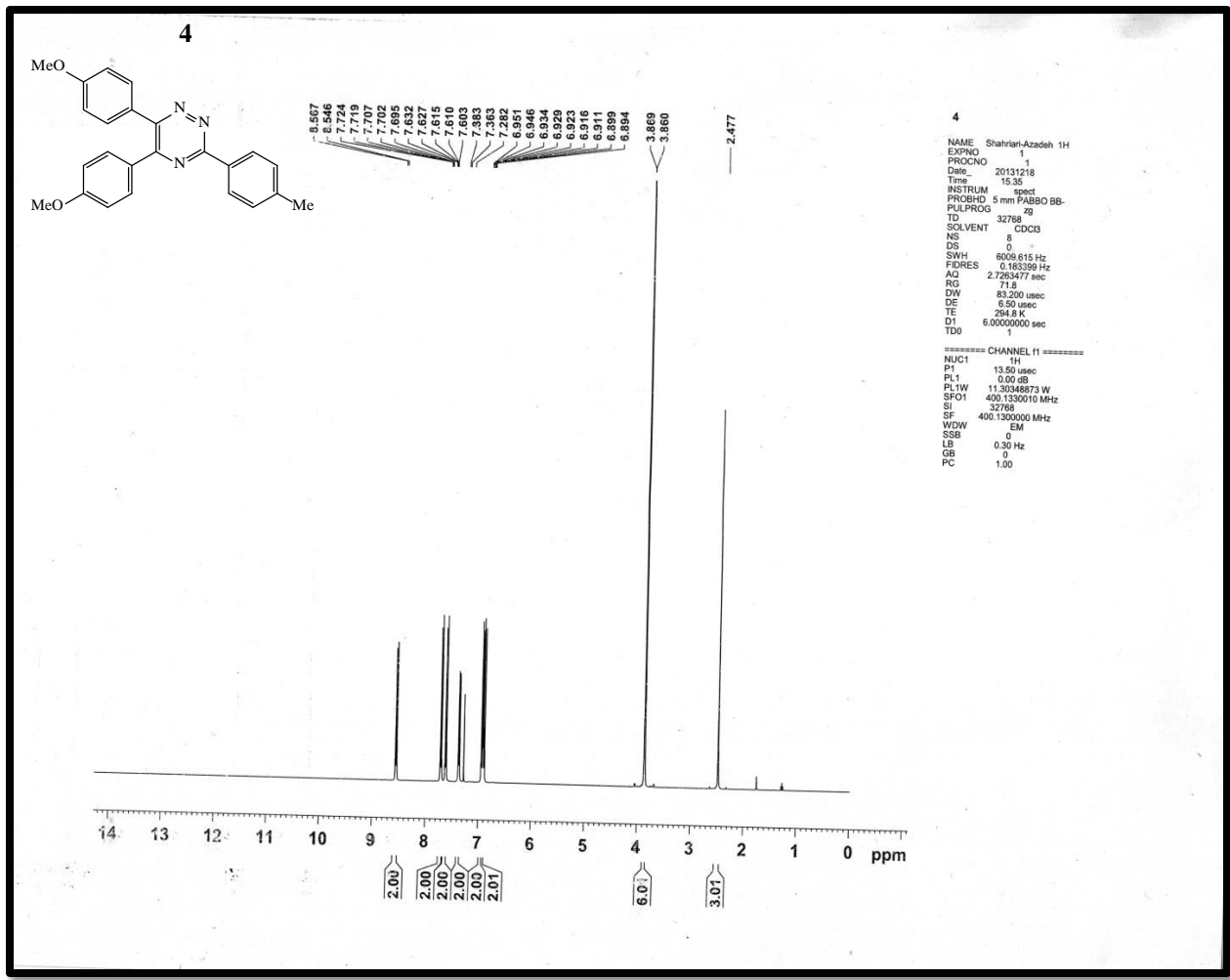


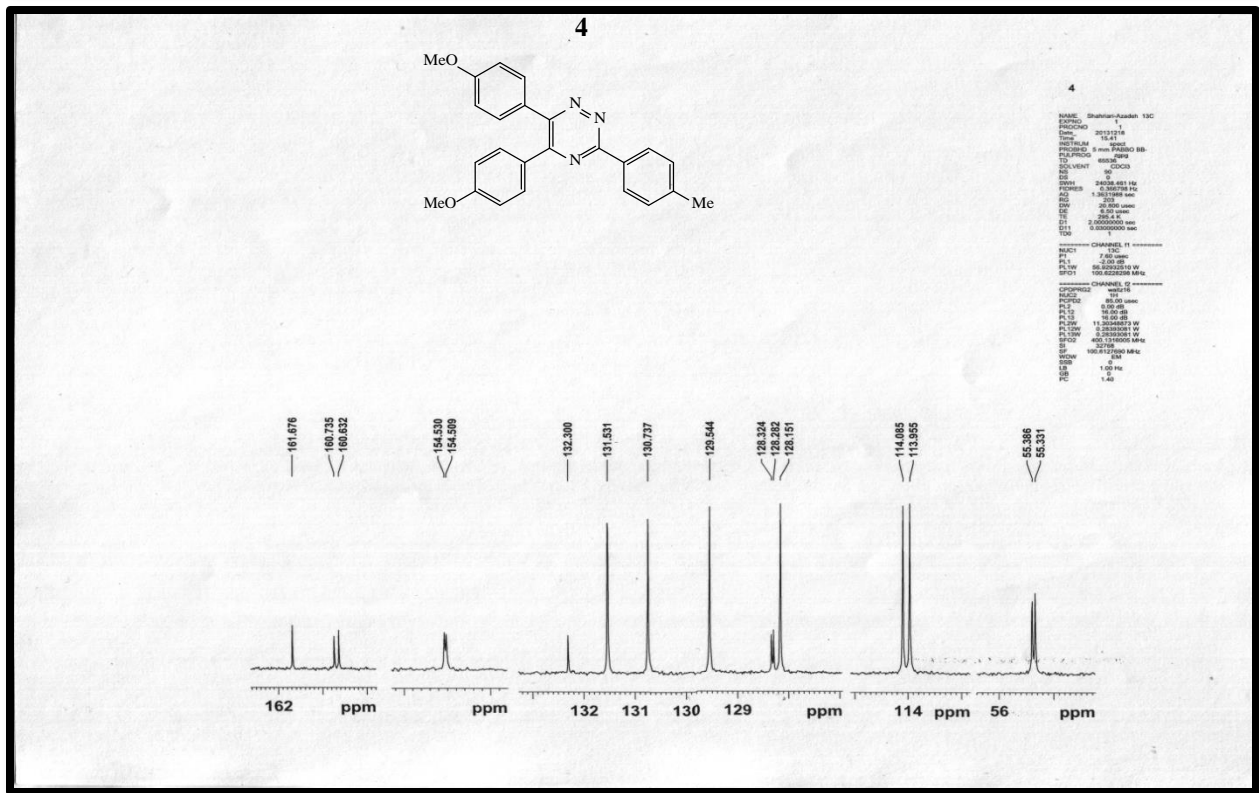
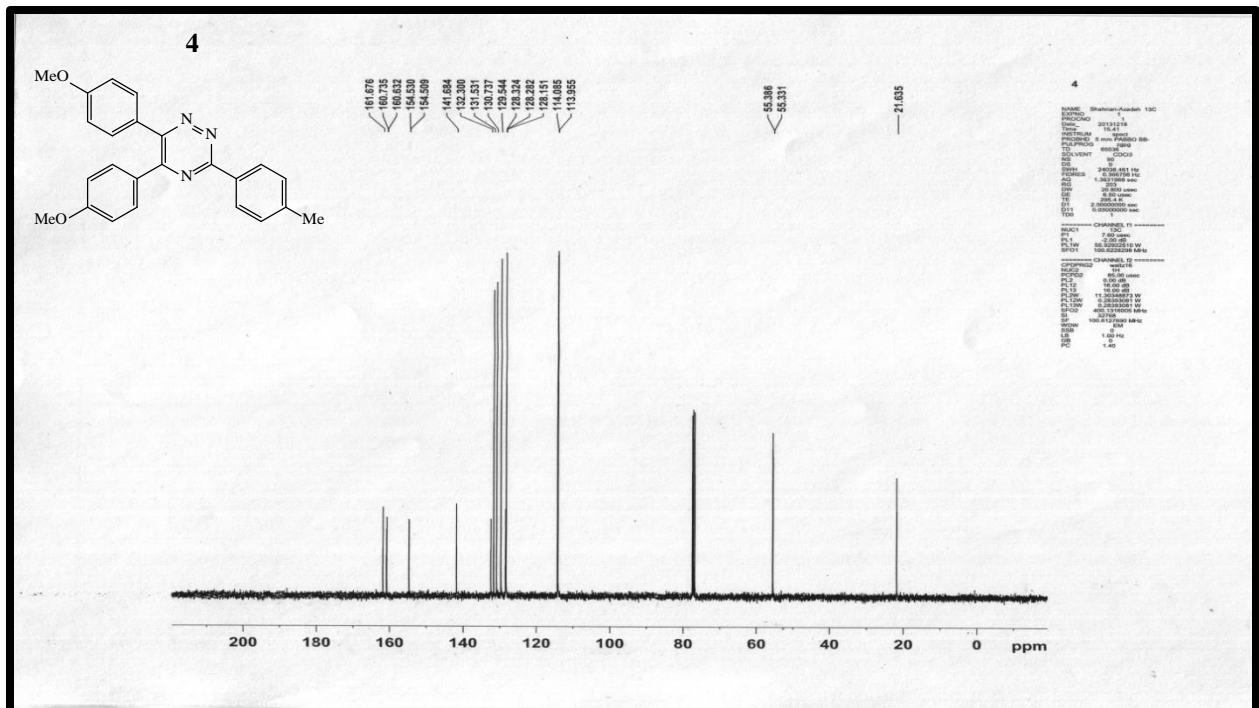


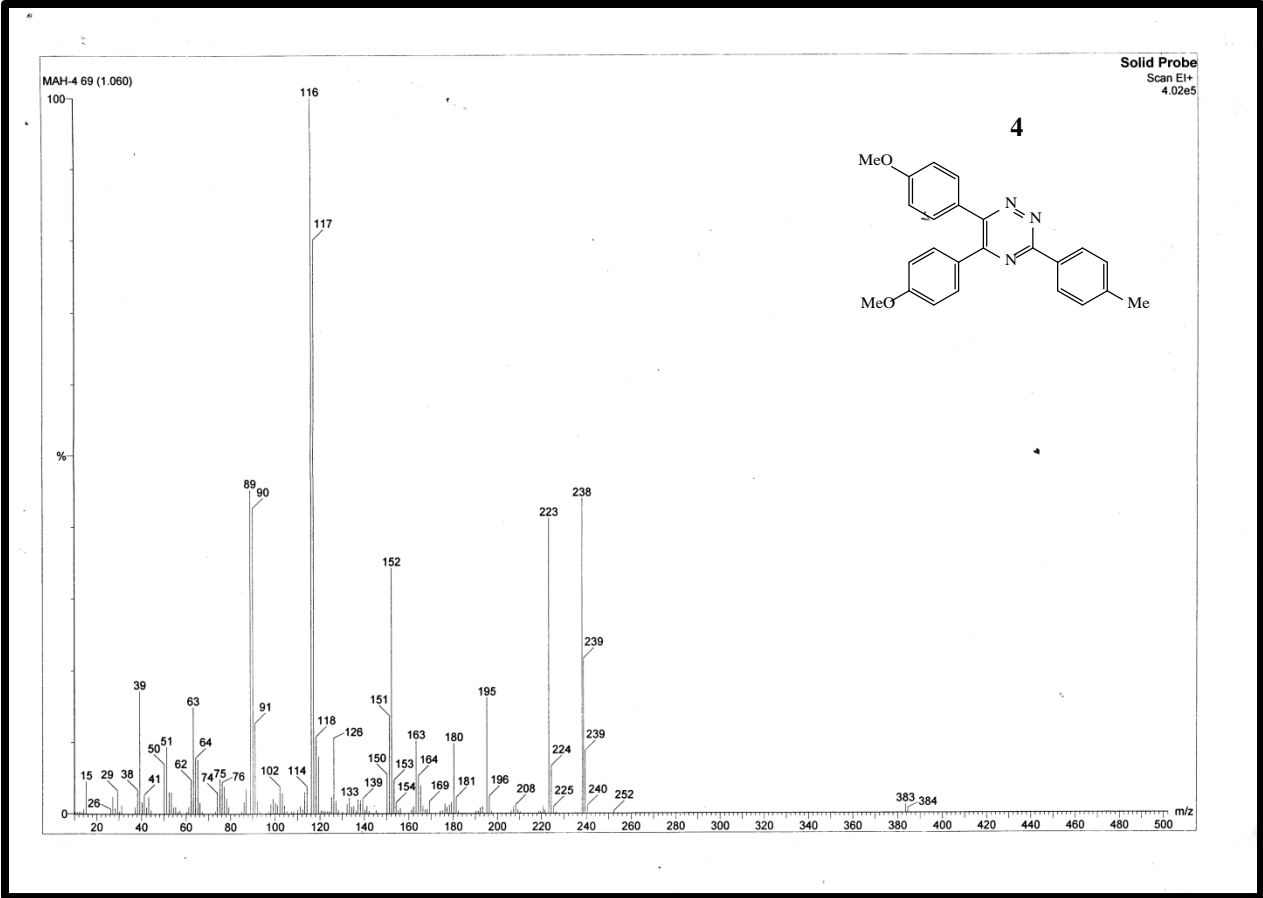


4. **5,6-Bis(4-methoxyphenyl)-3-(*p*-tolyl)-1,2,4-triazine (Table 2, entry 4):** Yellow powder. Mp: 146-148 °C (149°C)²⁸; IR (KBr): 3042, 3014, 2961, 2839, 1606, 1577, 1484, 1177, 832 ; ¹H NMR (400 MHz, CDCl₃): δ_H (ppm) 2.47 (s, CH₃, 3H), 3.86 (s, OCH₃, 3H), 3.86 (s, OCH₃, 3H), 6.89-8.56(m, CH aromatic, 12H). ¹³C NMR (100 MHz, CDCl₃): δ_c (ppm) 55.33, 55.38, 113.95, 114.08, 128.15, 128.28, 128.32, 129.54, 130.73, 131.53, 132.30, 154.50, 154.53, 160.63, 160.73, 161.67. MS: *m/z* 383.

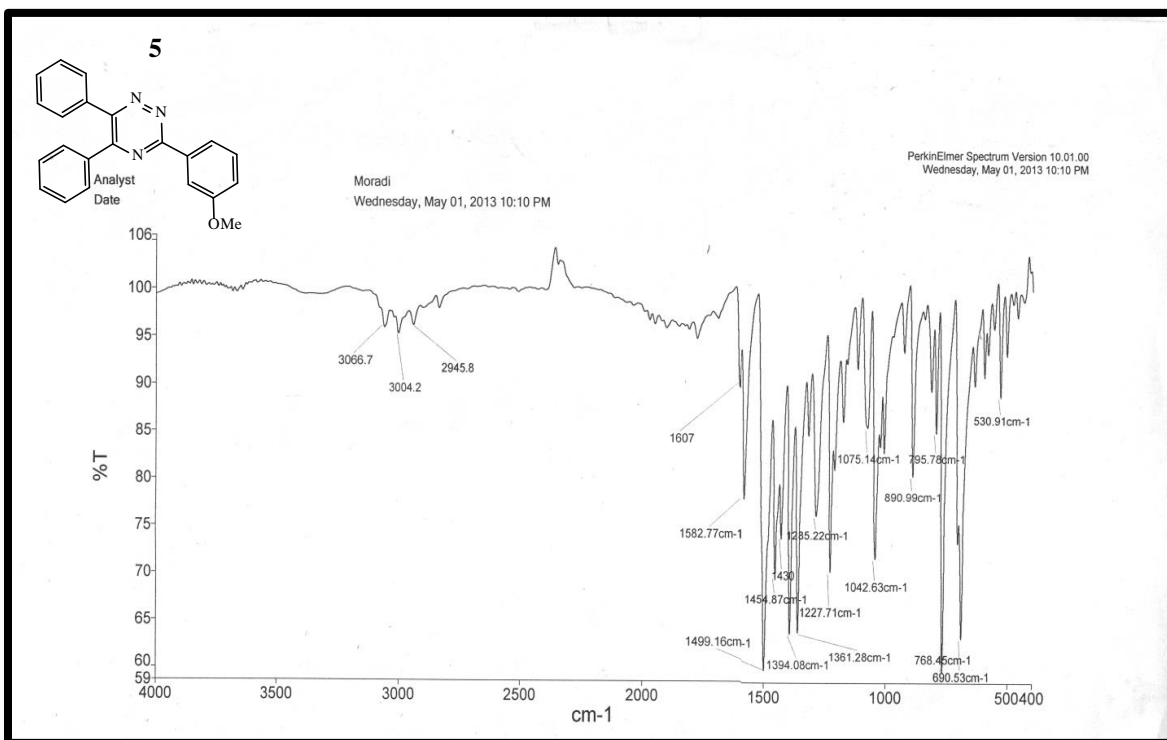


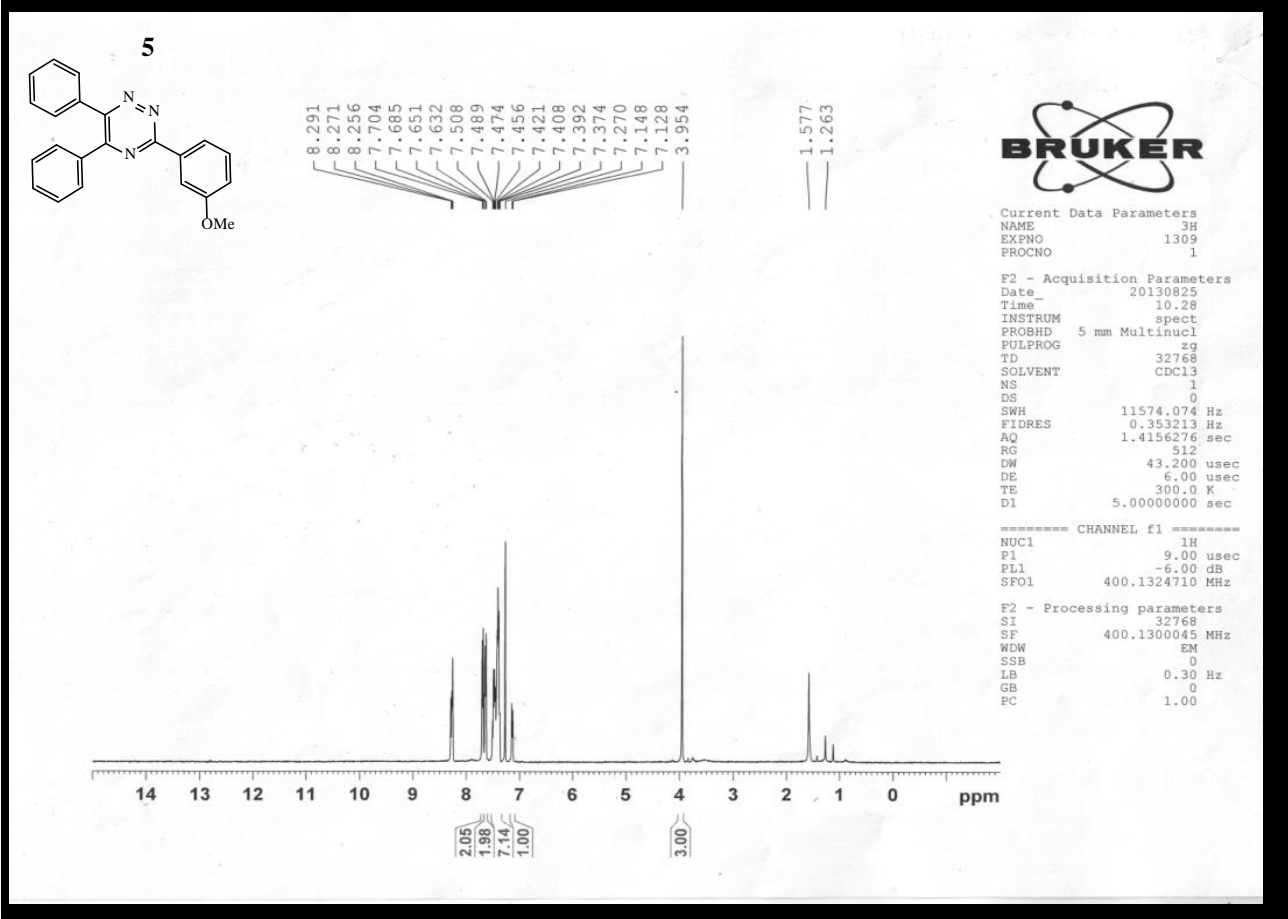


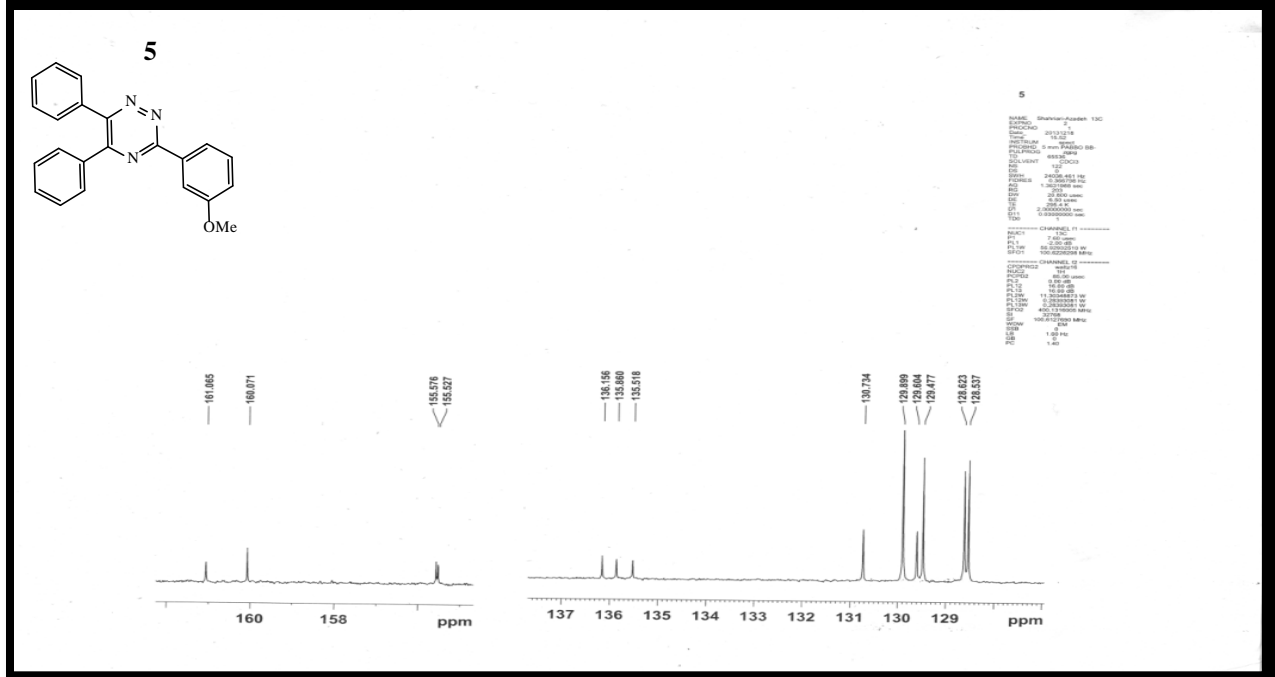
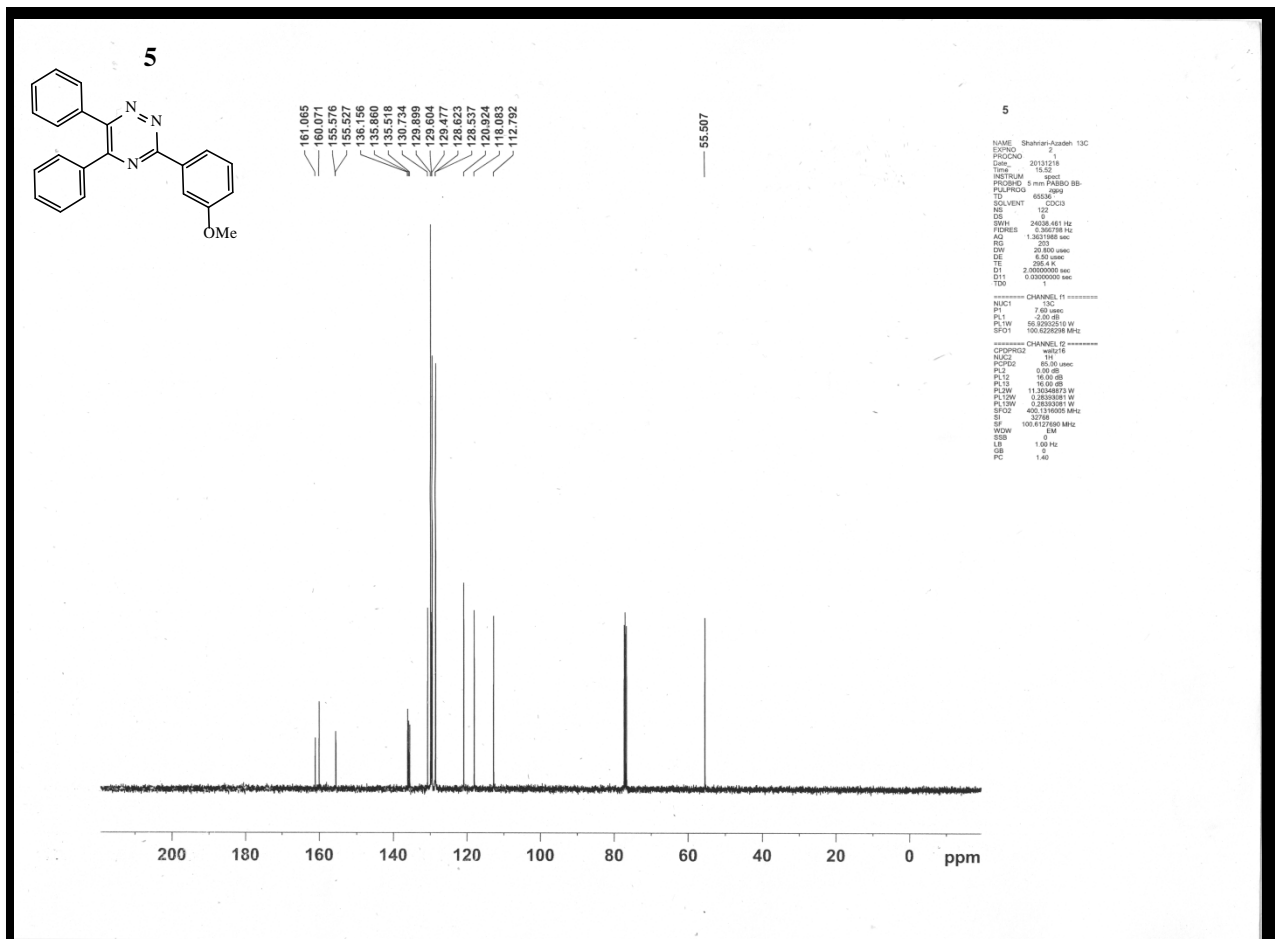


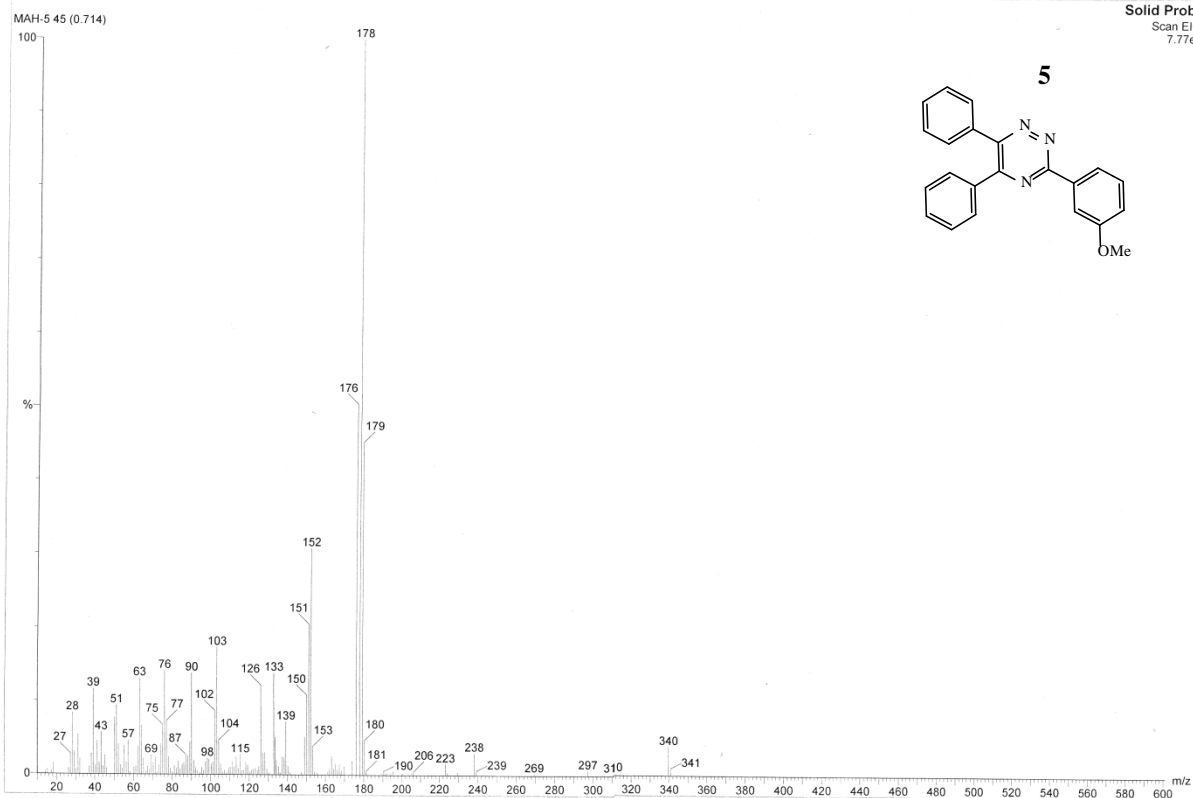


5. 3-(3-Methoxyphenyl)-5,6-diphenyl-1,2,4-triazine (Table 2, entry 5): yellow powder. Mp: 133-135 °C; IR (KBr): 3066, 3004, 2945, 1607, 1582, 1499, 690; ¹H NMR (400 MHz, CDCl₃): δH (ppm) 3.95 (s, OCH₃, 3H), 6.89-8.25 (m, CH aromatic, 14H). ¹³C NMR (100 MHz, CDCl₃): δc (ppm) 55.50, 112.79, 118.08, 120.92, 128.53, 128.62, 129.47, 129.60, 129.89, 130.73, 135.51, 135.86, 136.15, 155.52, 155.57, 160.07, 161.06. MS: m/z 340, Anal. Calcd for C₂₂H₁₇N₃O: C, 77.86; H, 5.05; N, 12.38; Found: C, 78.55; H, 5.18; N, 12.54.









FILL TIME 10 SECONDS

DATE 20 12 91 TIME 16 55 40 OPERATOR ID GHAEMI

RUN 64 ID SHN5 WEIGHT 2.801

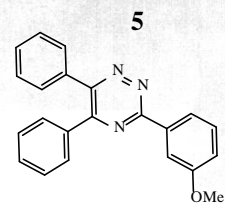
SIGNALS

ZR 1721
NR 3796
CR 35510
HR 40826

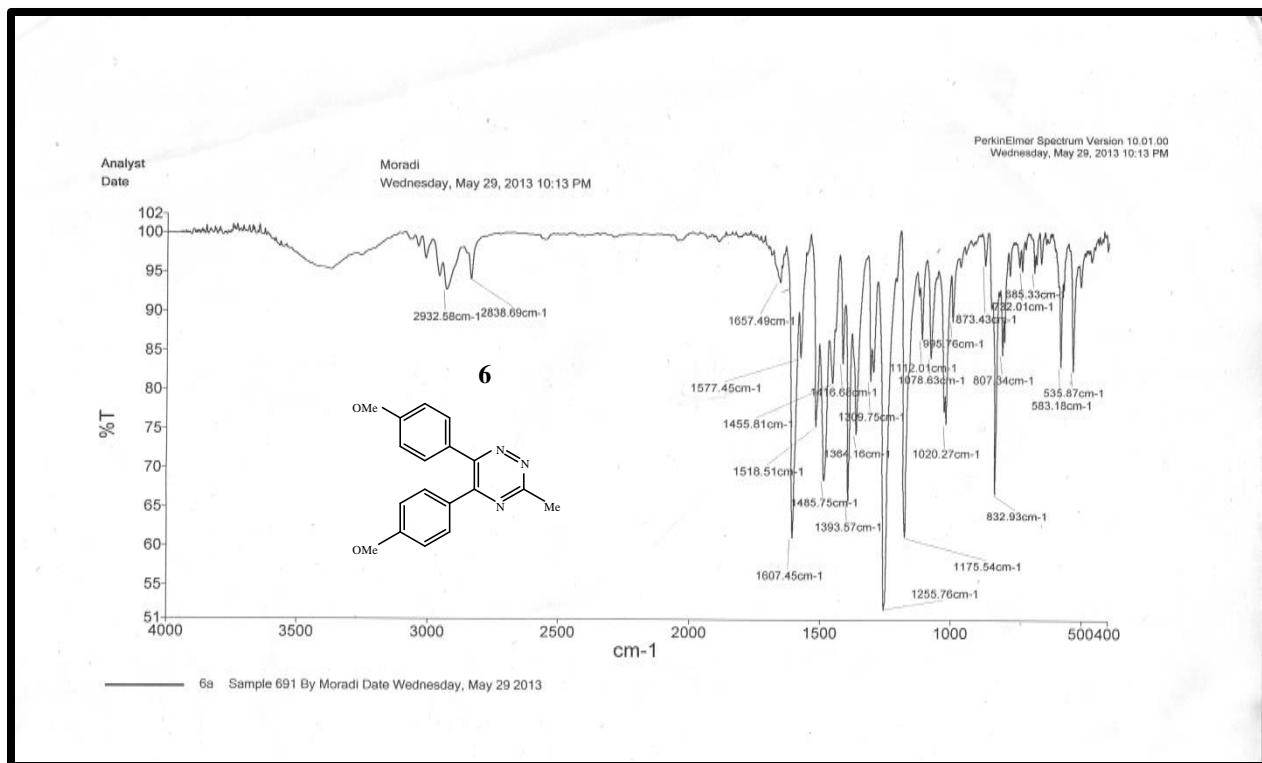
CARBON 78.55%
HYDROGEN 5.18%
NITROGEN 12.54%

BLANKS 62 186 284
KFACTORS 14.387 35.385 5.099

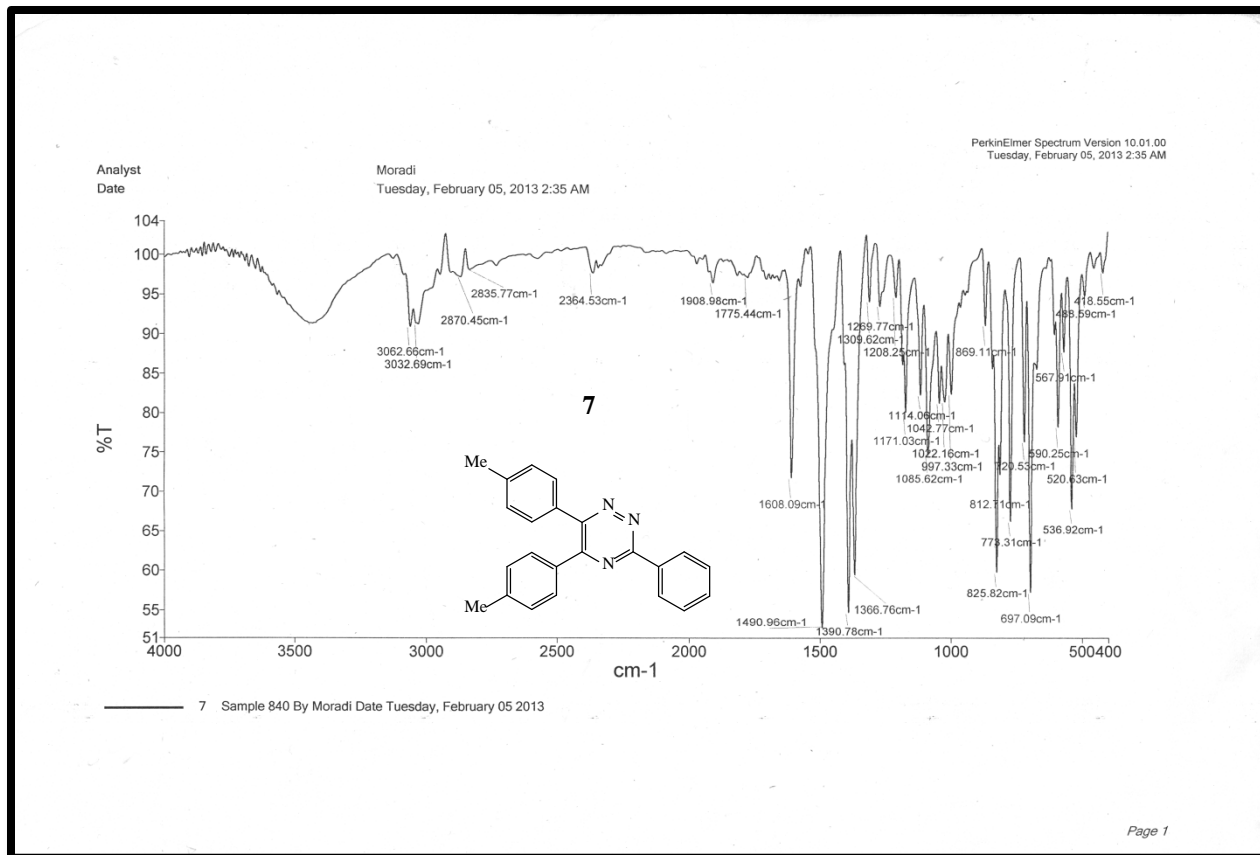
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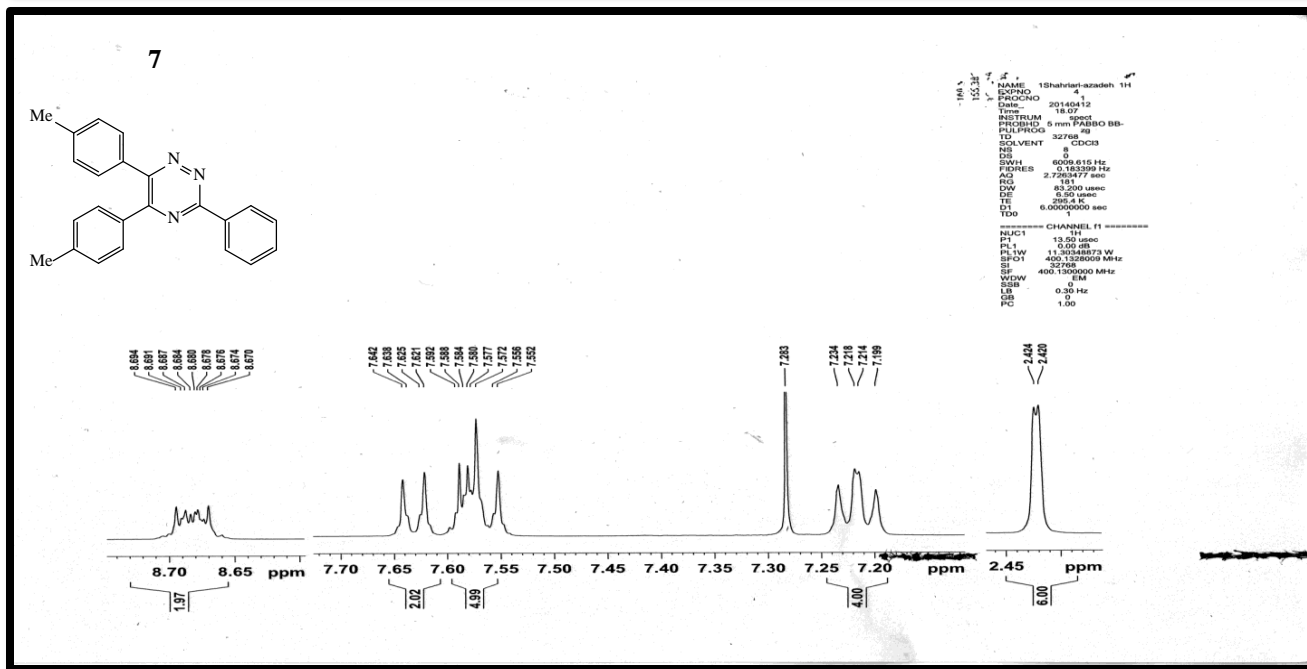


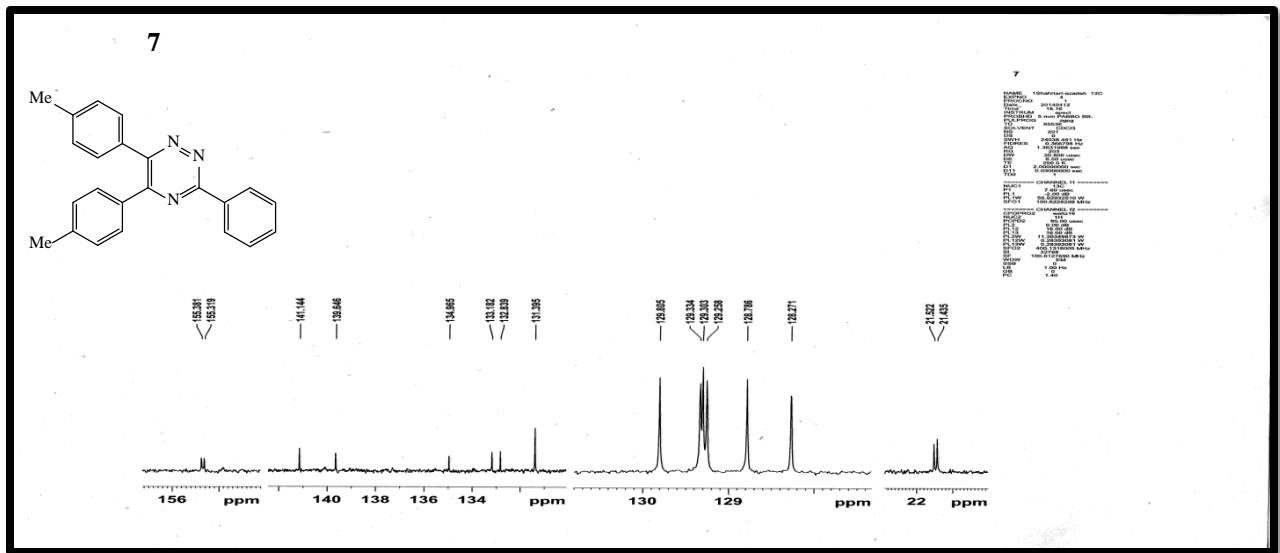
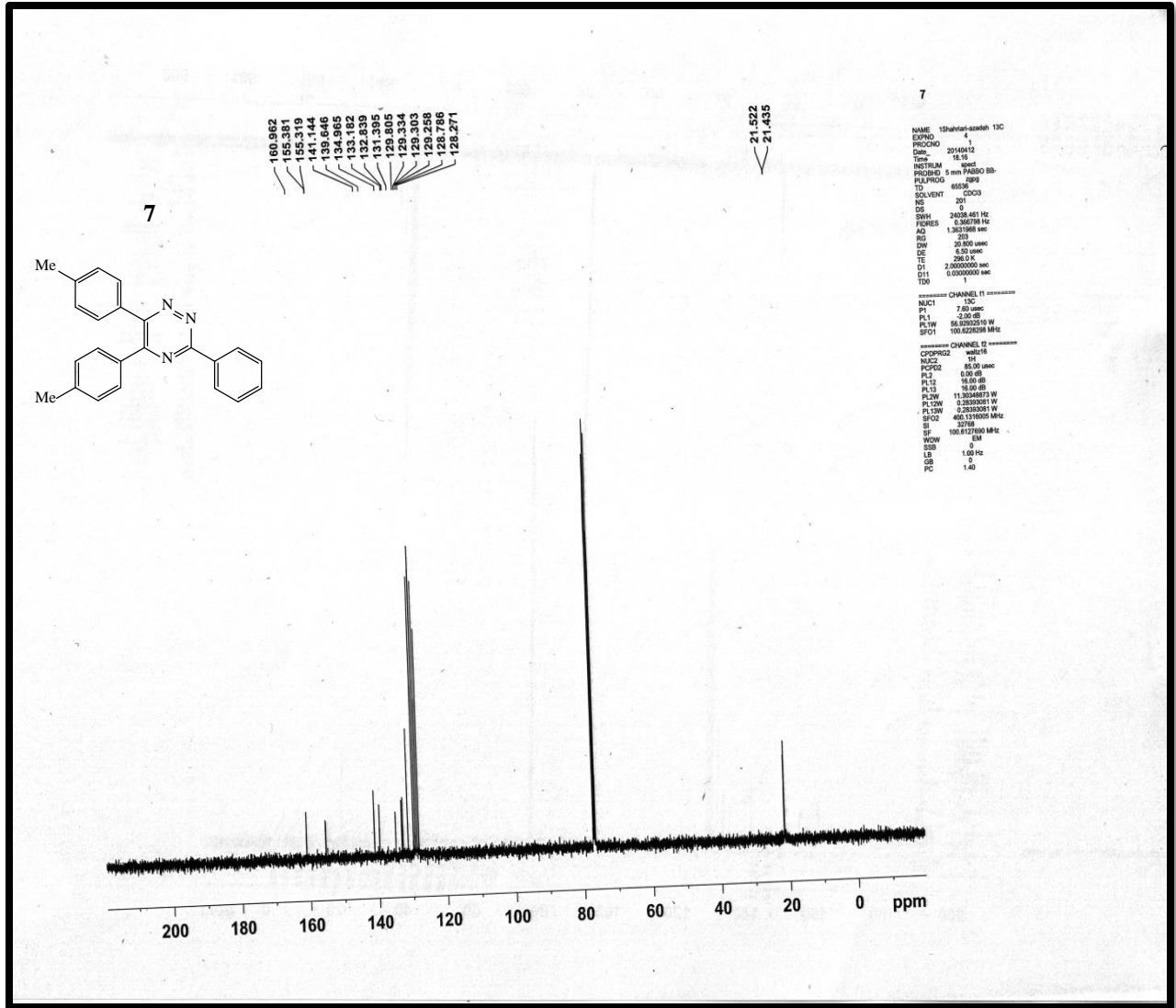
6. 5,6-Bis(4-methoxyphenyl)-3-methyl-1,2,4-triazine (Table 2, entry 6): Yellow powder. Mp: 122-125 °C (109-113 °C)²⁹; IR (KBr): 2932, 2838, 1607, 1577, 1255, 832; ¹H NMR (90 MHz, DMSO-d₆): δH (ppm) 2.81 (s, CH₃, 3H), 3.34 (s, OCH₃, 6H), 6.936-7.450 (m, CH aromatic, 8H). MS: m/z 307.

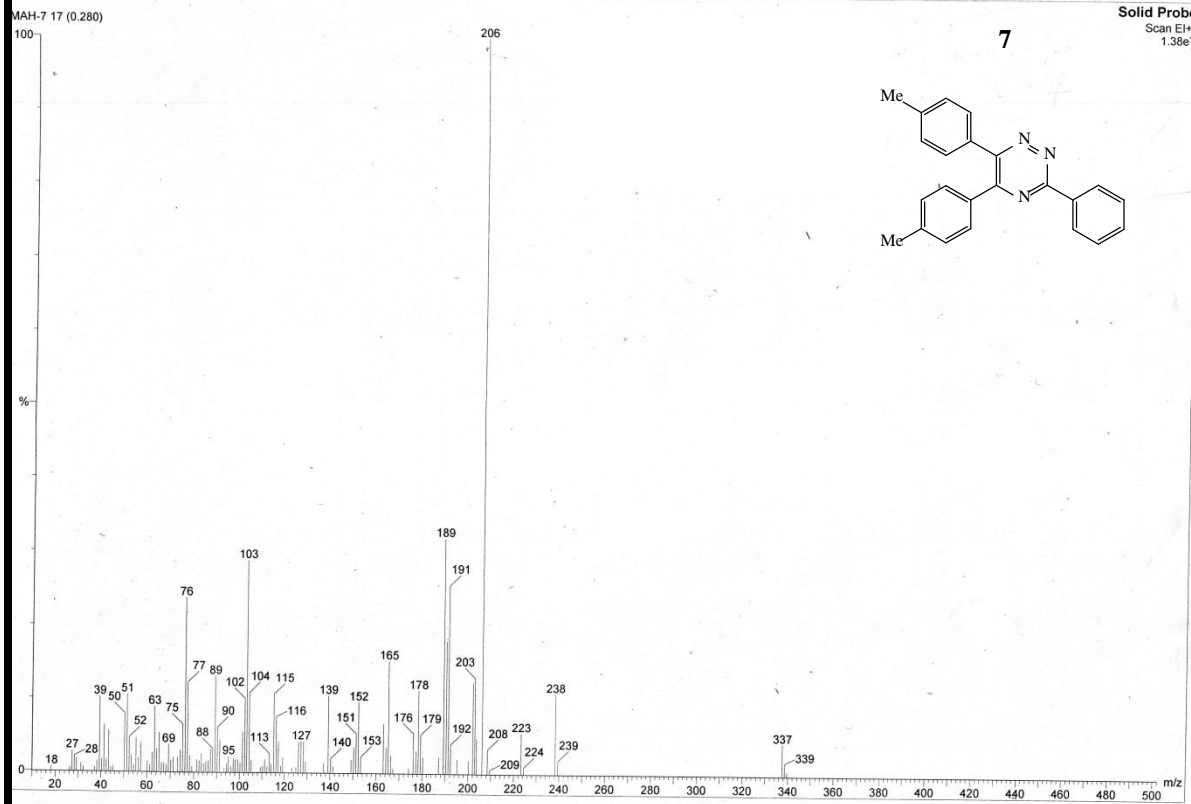


7. **3-Phenyl-5,6-di(*p*-tolyl)-1,2,4-triazine (Table 2, entry 7):** Yellow powder. Mp: 165-166 °C (168 °C)²⁸; IR (KBr): 3062, 3032, 1608, 1490, 1366, 697; ¹H NMR (400 MHz, CDCl₃): δ_H (ppm) 2.42 (s, CH₃, 3H), 2.42 (s, CH₃, 3H), 7.19-8.69 (m, CH aromatic, 13H). ¹³C NMR (100 MHz, CDCl₃): δ_c (ppm) 21.43, 21.52, 128.27, 128.78, 129.25, 129.30, 129.33, 129.80, 131.39, 132.83, 133.182, 134.96, 139.64, 141.14, 155.31, 155.38, 160.96. MS: *m/z* 337. Anal. Calcd for C₂₃H₁₉N₃: C, 81.87; H, 5.68; N, 12.45 Found: C, 83.07; H, 5.78; N, 12.44.









7

OXFILL COMB BOOST1 BOOST2
0 0 0

FILL TIME 11 SECONDS

DATE 20 12 91 TIME 14 07 49 OPERATOR ID GHAEMI

RUN 27 ID SH7 WEIGHT 2.090

SIGNALS

ZR 1654
NR 3271
CR 27609
HR 32040

CARBON 83.07%
HYDROGEN 5.78%
NITROGEN 12.44%

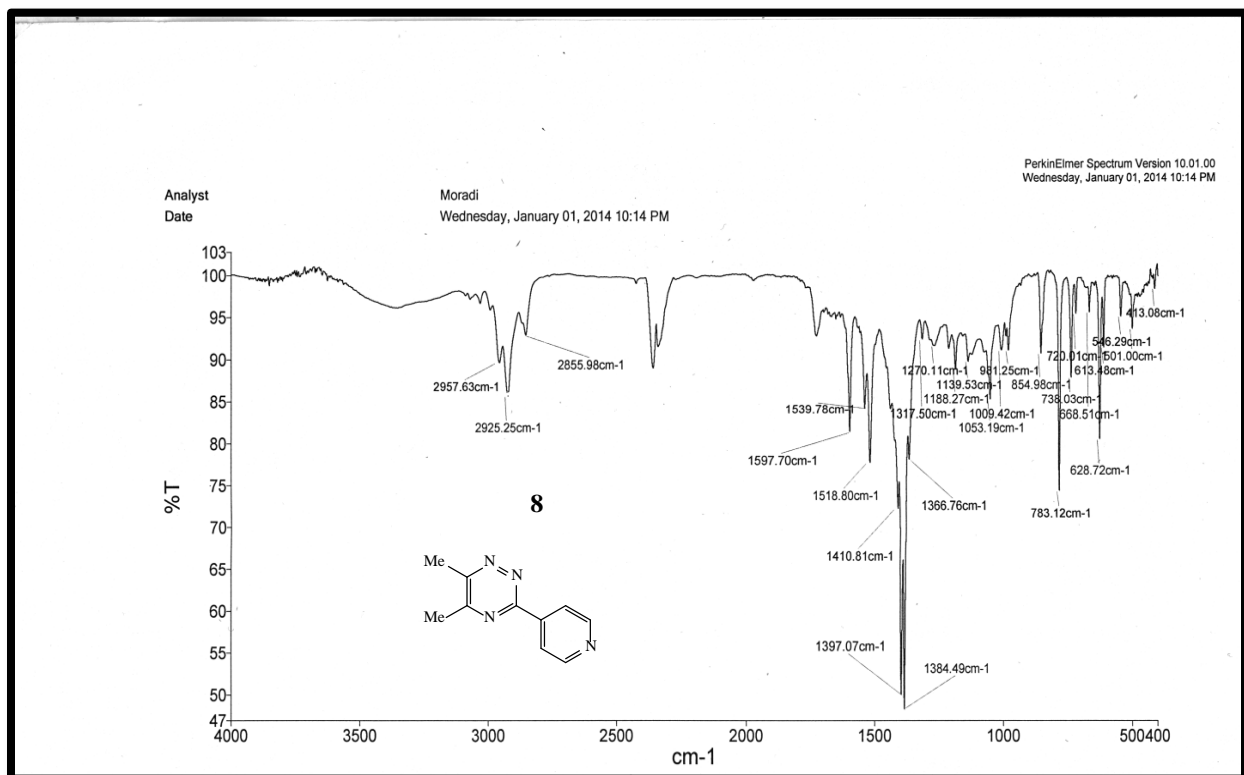
BLANKS 32 201 314
KFACTORS 13.971 35.007 5.013

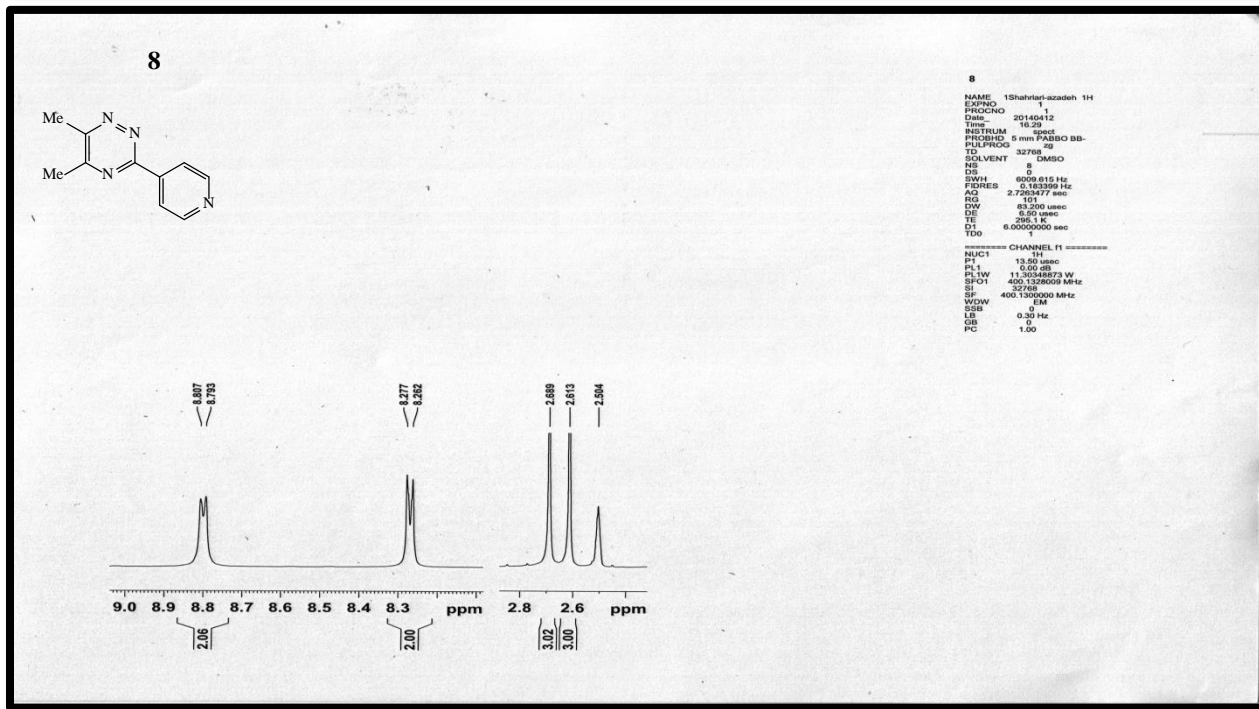
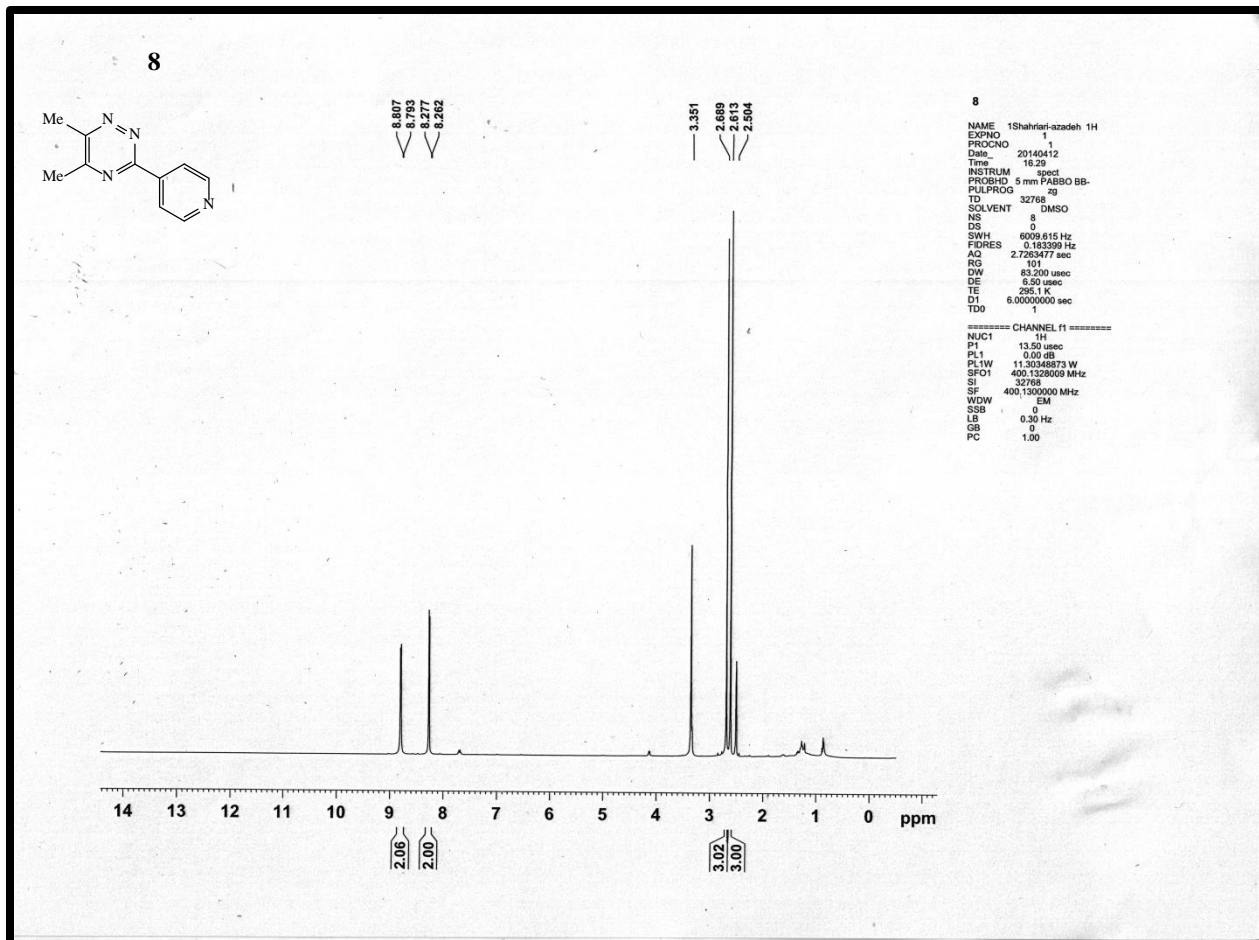
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FILL TIME 10 SECONDS

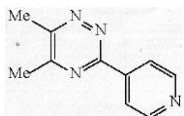
Chemical structure of 7: Cc1ccc(cc1)/C(=N2C(=N3C=CC=C3N2)c4ccc(C)cc4)c5ccc(C)cc5

8. **5,6-Dimethyl-3-(pyridin-4-yl)-1,2,4-triazine (Table 2, entry 8)**: Yellowish powder. Mp: 119-121 °C; IR (KBr): 2957, 2925, 2855, 1597, 1518, 1397, 1384, 783; ¹H NMR (400 MHz, DMSO-d₆): δ_H (ppm) 2.61 (s, CH₃, 3H), 2.68 (s, CH₃, 3H), 8.26-8.80 (m, CH aromatic, 4H). ¹³C NMR (100 MHz, DMSO-d₆): δ_c (ppm) 19.76, 22.24, 121.60, 142.68, 151.12, 158.50, 159.80, 160.686. MS: *m/z* 186.





8

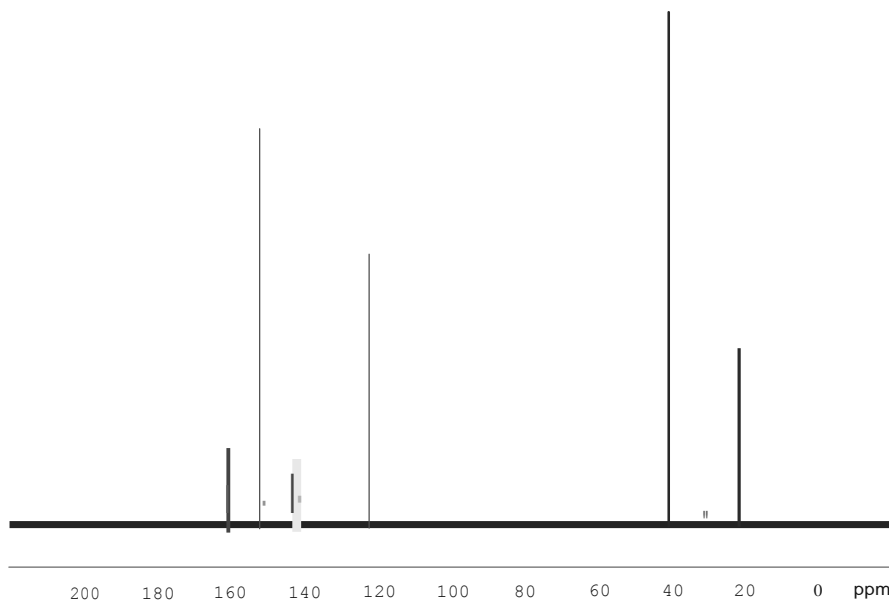


gg N
1/1

ME

;

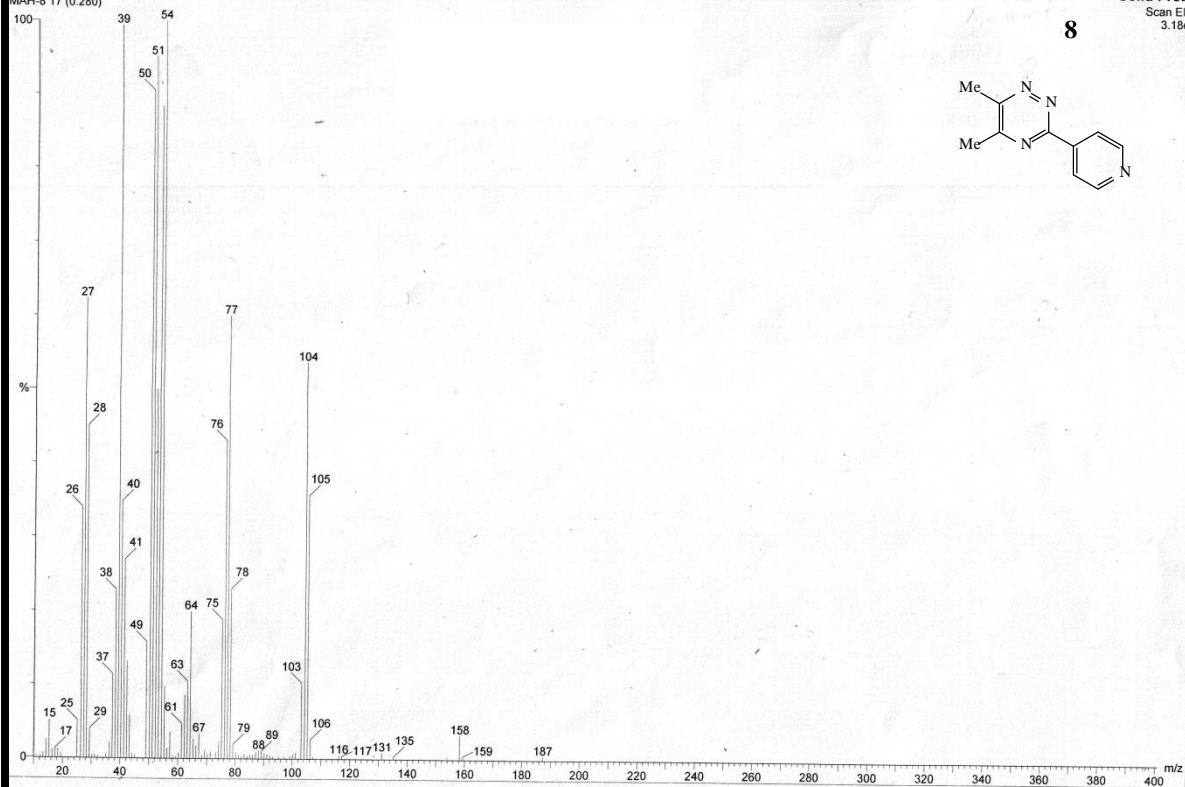
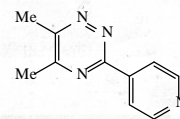
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PROCNO 1
PROC 2016412
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Time 16:41
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TD 65536
SOLVENT DMSO
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SF 240.615 MHz
F2 50.615 MHz
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TD0
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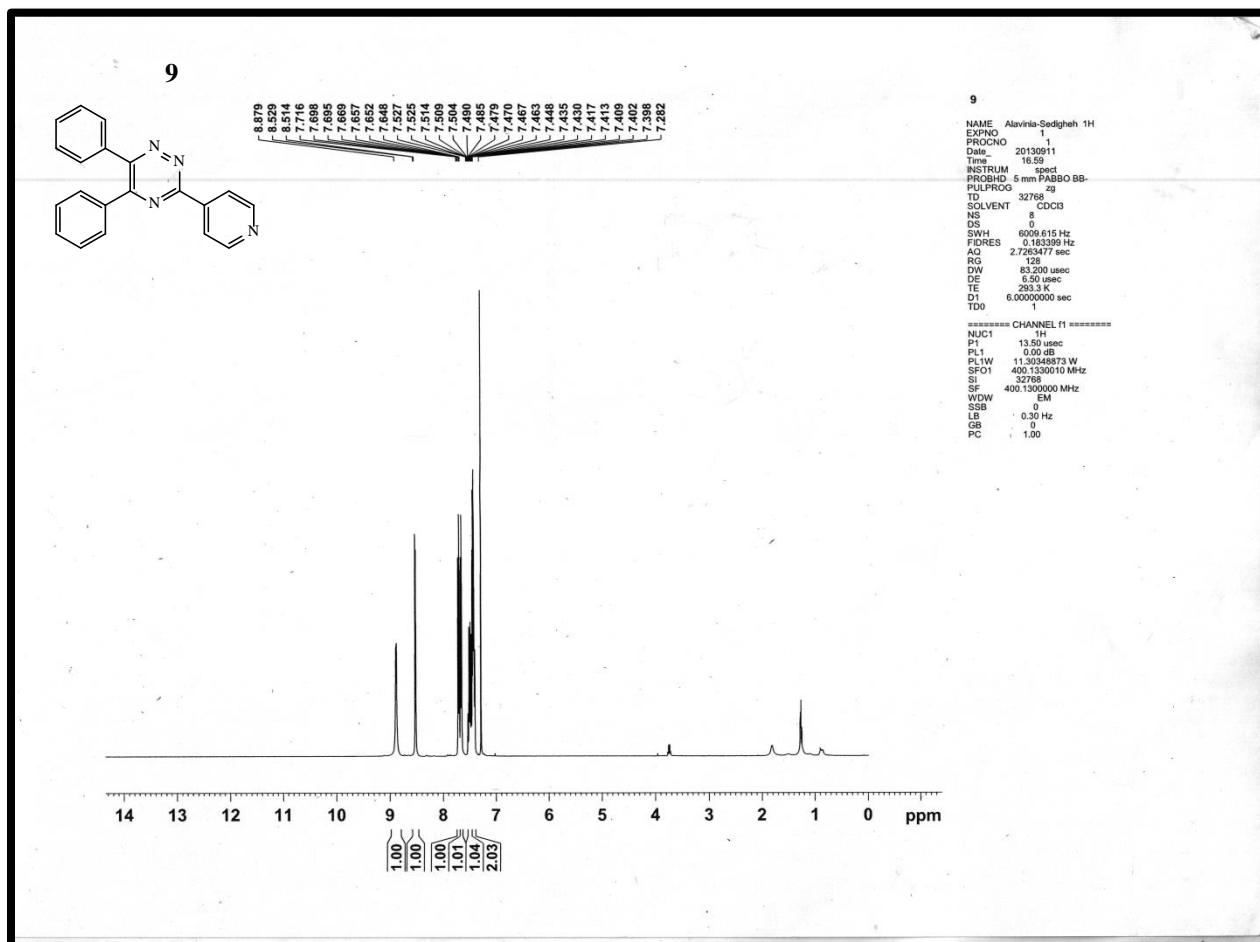
MAH-8 17 (0.280)

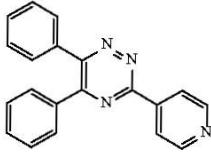
Solid Probe
Scan E1+
3.18e6

8



9. **5,6-Diphenyl-3-(pyridin-4-yl)-1,2,4-triazine (Table 2, entry 9):** Yellow powder. Mp: 163-164 °C; ¹H NMR (400 MHz CDCl₃): δ_H (ppm) 7.28-8.87 (m, CH aromatic, 14H). ¹³C NMR (100 MHz, CDCl₃): δ_c (ppm) 121.87, 128.68, 128.75, 129.52, 129.87, 130.02, 131.11, 135.07, 135.32, 142.19, 150.76, 155.95, 156.74, 159.64. MS: *m/z* 310. Anal. Calcd for C₂₀H₁₄N₄: C, 77.40; H, 4.55; N, 18.05 Found: C, 77.48; H, 4.33; N, 17.71.





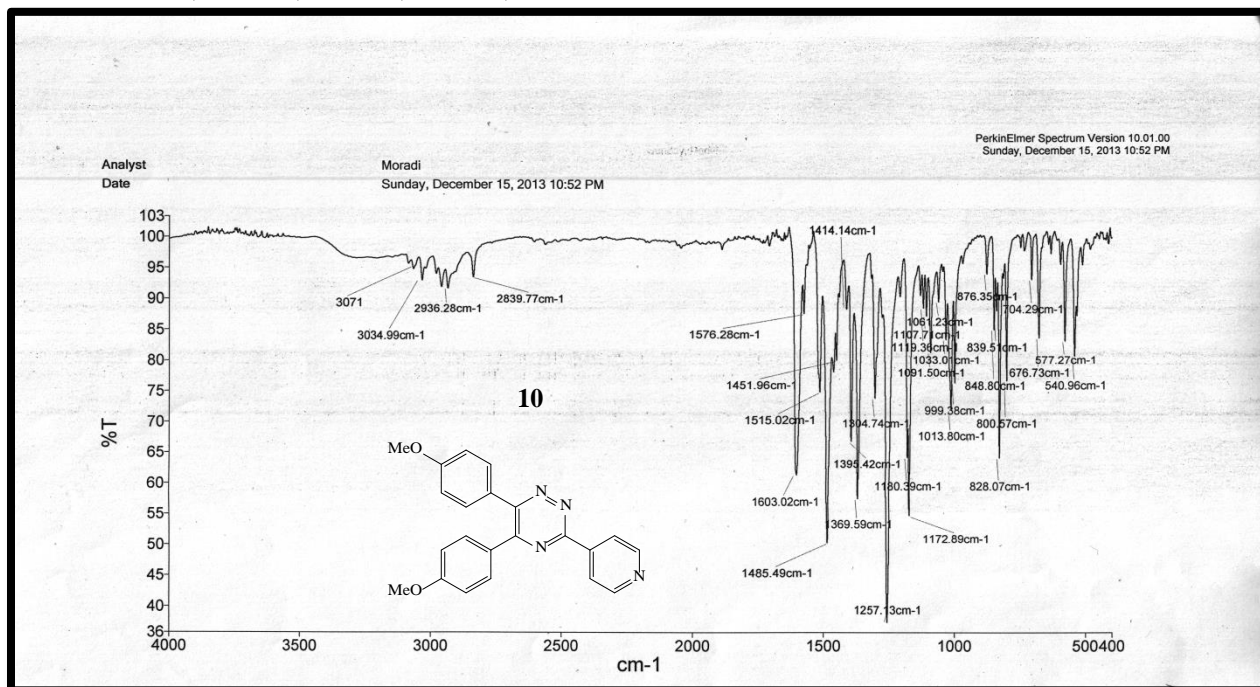
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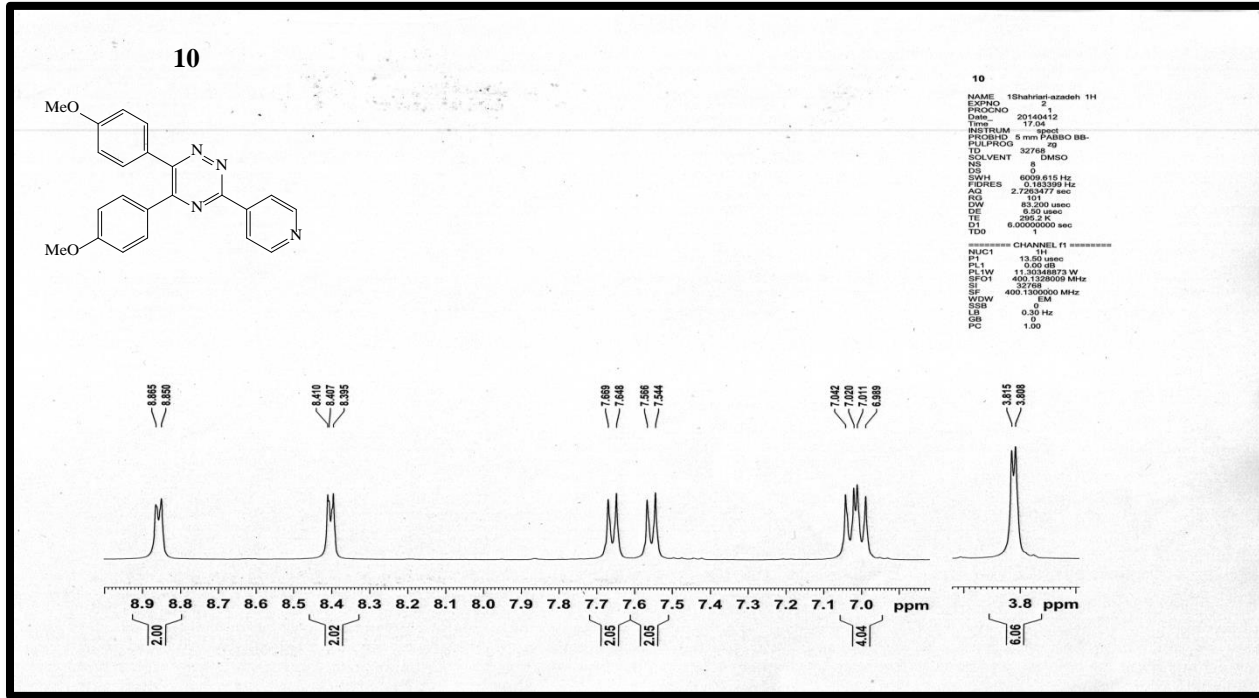
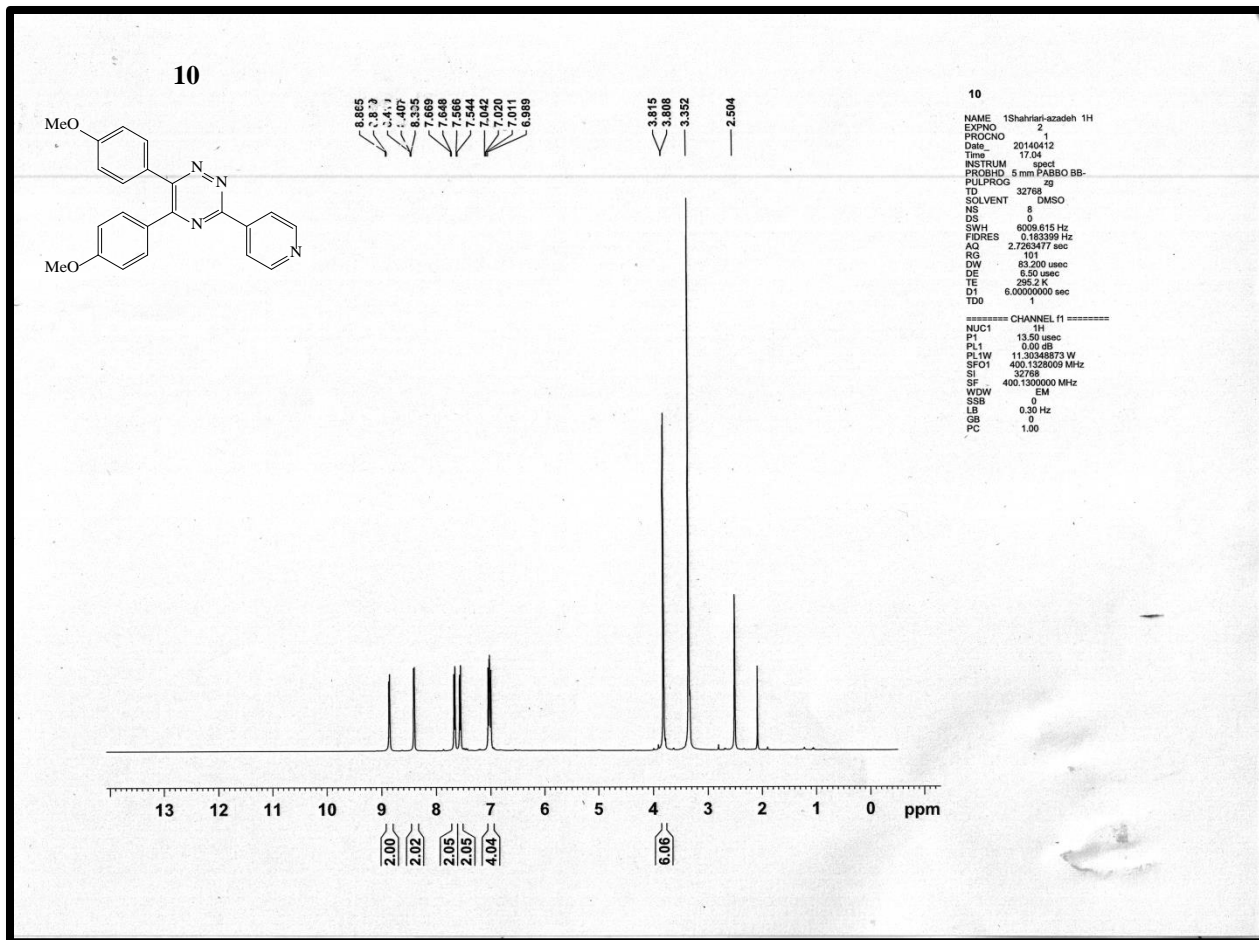
Page : / of

Result Table (ESTD- Shshrysri 9 09_10_2013_10_9_2013 9_00_47 PM_052 - INT7- 1)

	Reten. Time [min]	Response	Weight [mg]	Weight [%]	Peak Type	Element Name	Carbon Response Ratio
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	1.363	23614.050	4.588	77.48	Refer	Carbon	1.000
3	5.537	5885.472	0.256	4.33	Refer	Hydrogen	0.249
	Total		5.922	99.52			

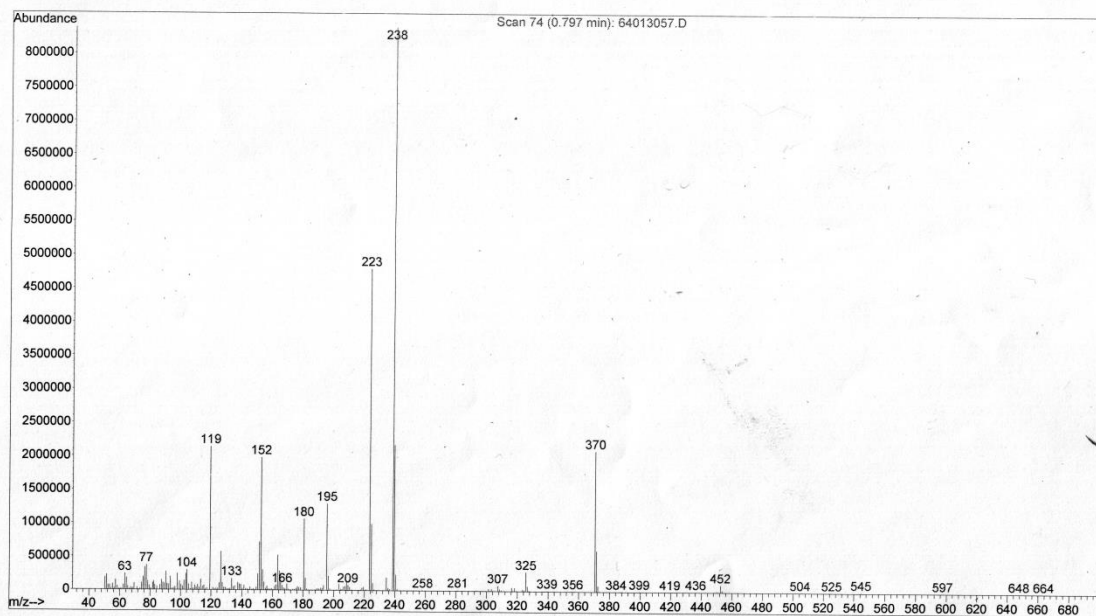
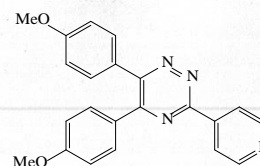
10. **5,6-Bis(4-methoxyphenyl)-3-(pyridin-4-yl)-1,2,4-triazine (Table 2, entry 10)**: Yellow powder. Mp: 155-157 °C; IR (KBr): 3071, 3034, 2936, 2839, 1603, 1576, 1485, 1257, 828; ¹H NMR (400 MHz, DMSO-d₆): δH (ppm) 3.80 (s, OCH₃, 3H), 3.81 (s, OCH₃, 3H), 6.98-8.86 (m, CH aromatic, 12CH). ¹³C NMR (100 MHz, DMSO-d₆): δc (ppm) 55.74, 55.87, 114.54, 114.62, 121.84, 127.75, 128.05, 131.19, 132.00, 142.46, 151.21, 155.37, 156.47, 158.91, 160.92, 161.99. MS: m/z 370.



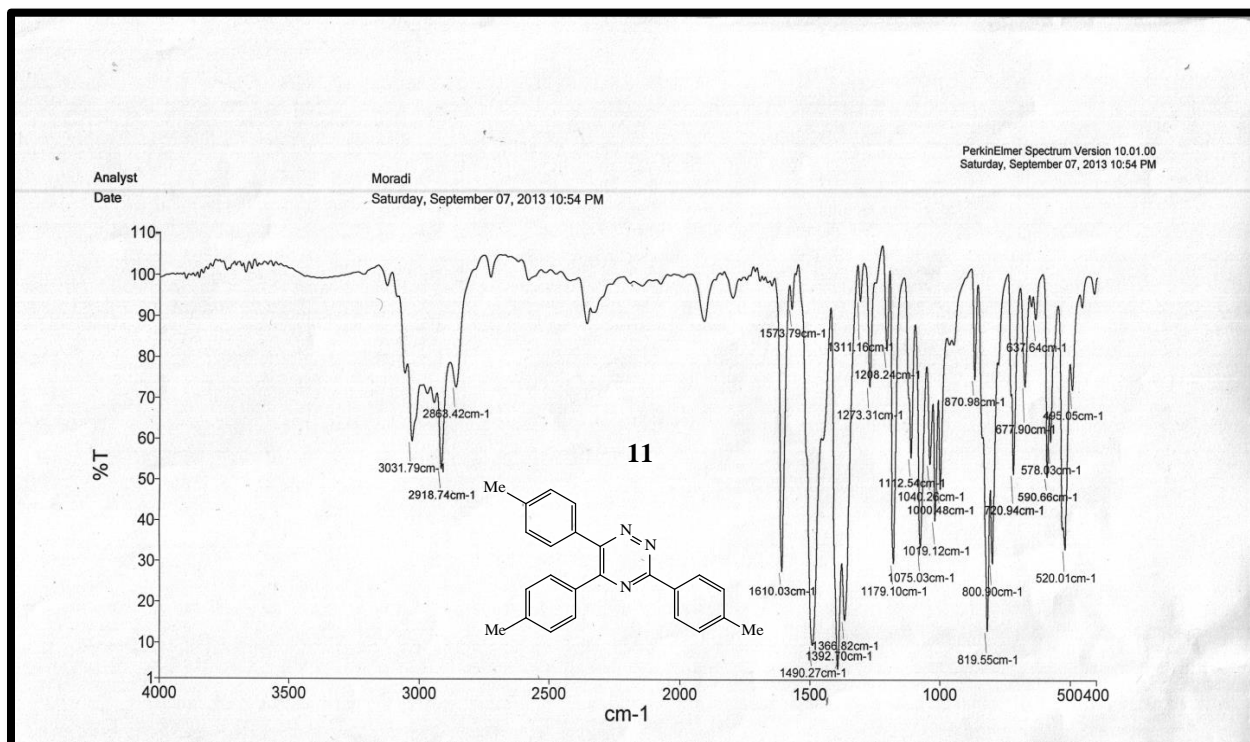


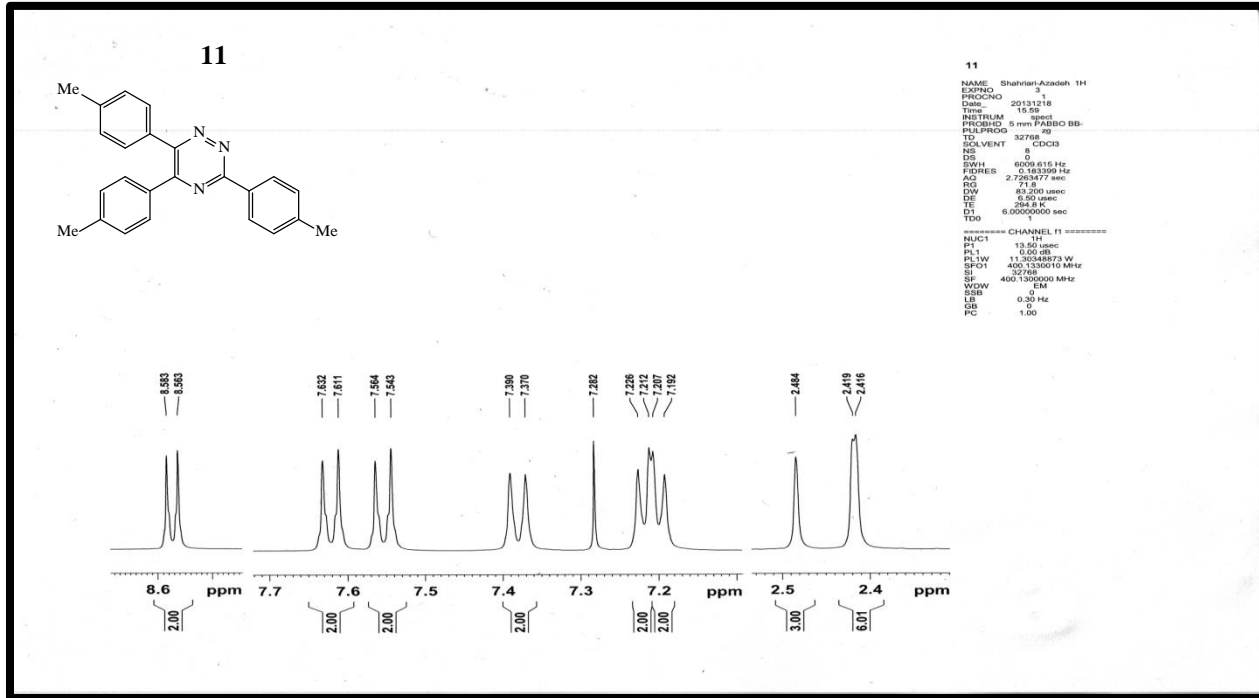
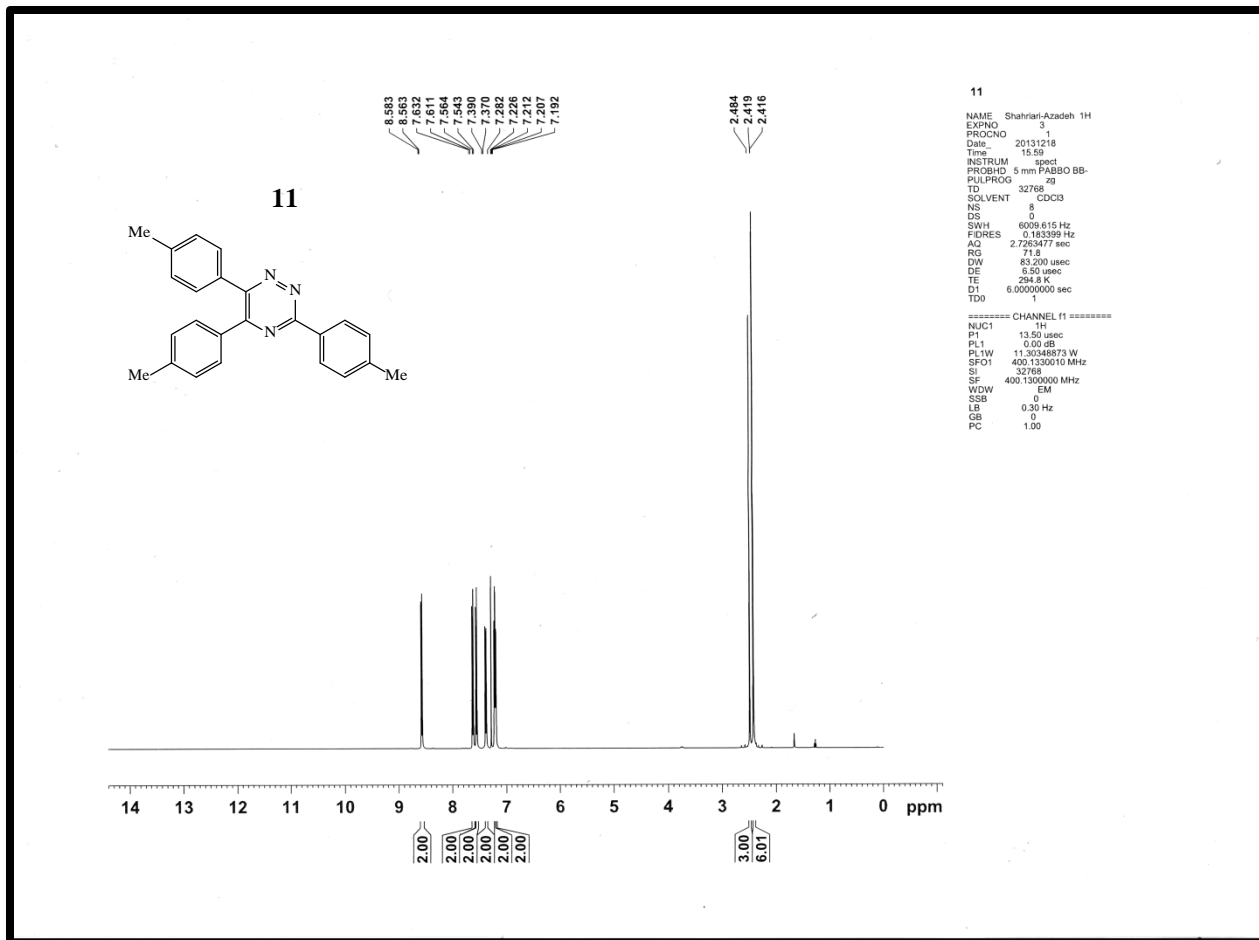
10

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Vial Number: 1

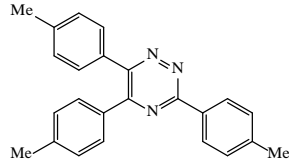


11. **3,5,6-Tri(*p*-tolyl)-1,2,4-triazine (Table 2, entry 11):** Yellow powder. Mp: 166-167 °C (165 °C)²⁸; IR (KBr): 3031, 2918, 2863, 1610, 1490, 819.55; ¹H NMR (400 MHz CDCl₃): δ_H (ppm) 2.41 (s, CH₃, 3H), 2.41 (s, CH₃, 3H), 2.48 (s, CH₃, 3H), 7.19-8.58 (m, CH aromatic, 12H). ¹³C NMR (100 MHz, CDCl₃): δ_c (ppm) 21.43, 21.52, 21.64, 128.23, 129.23, 129.28, 129.30, 129.56, 129.79, 132.22, 132.93, 133.28, 139.52, 141.04, 141.79, 155.13, 155.24, 161.03. MS: *m/z* 351.



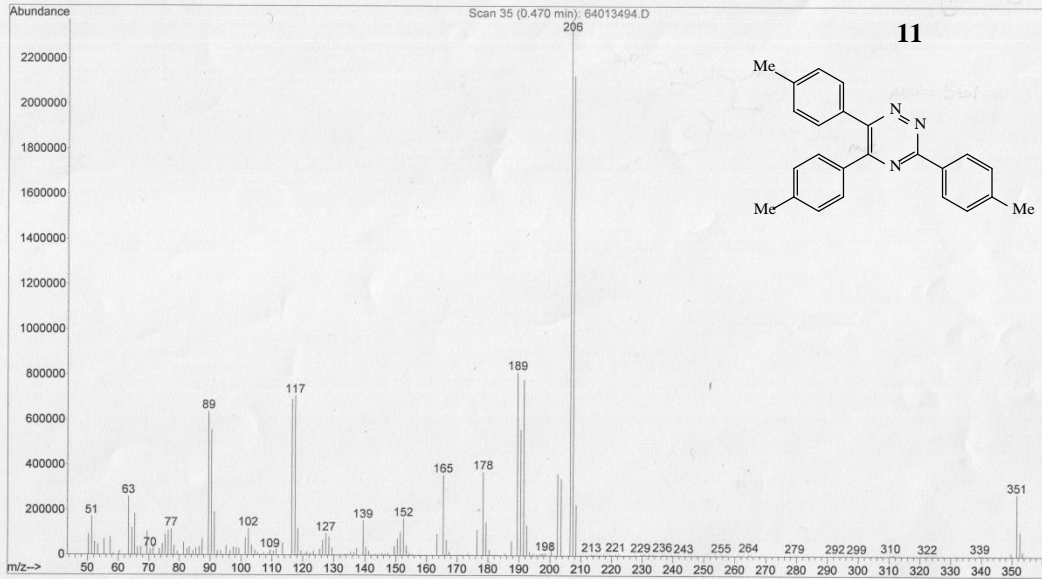


11

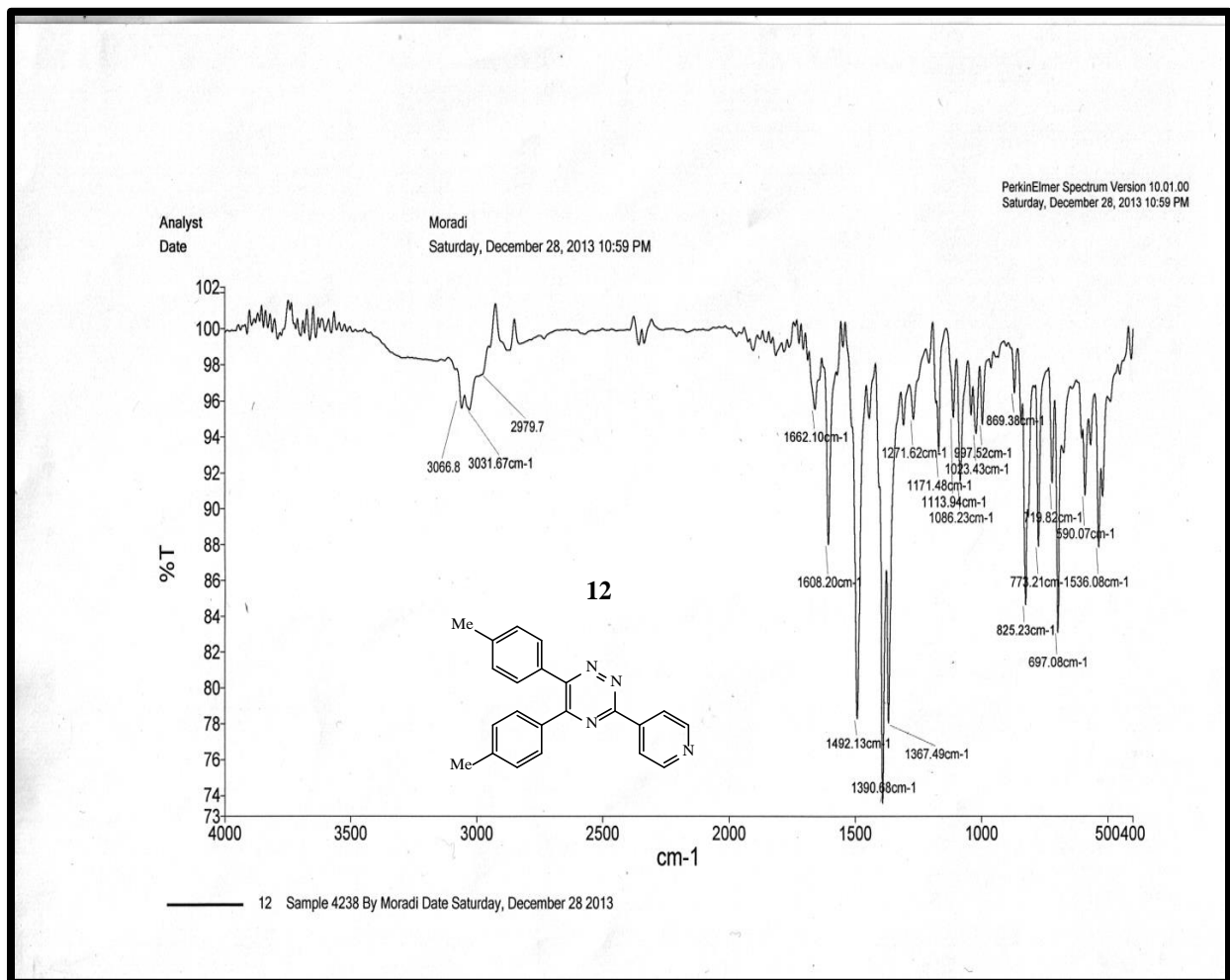


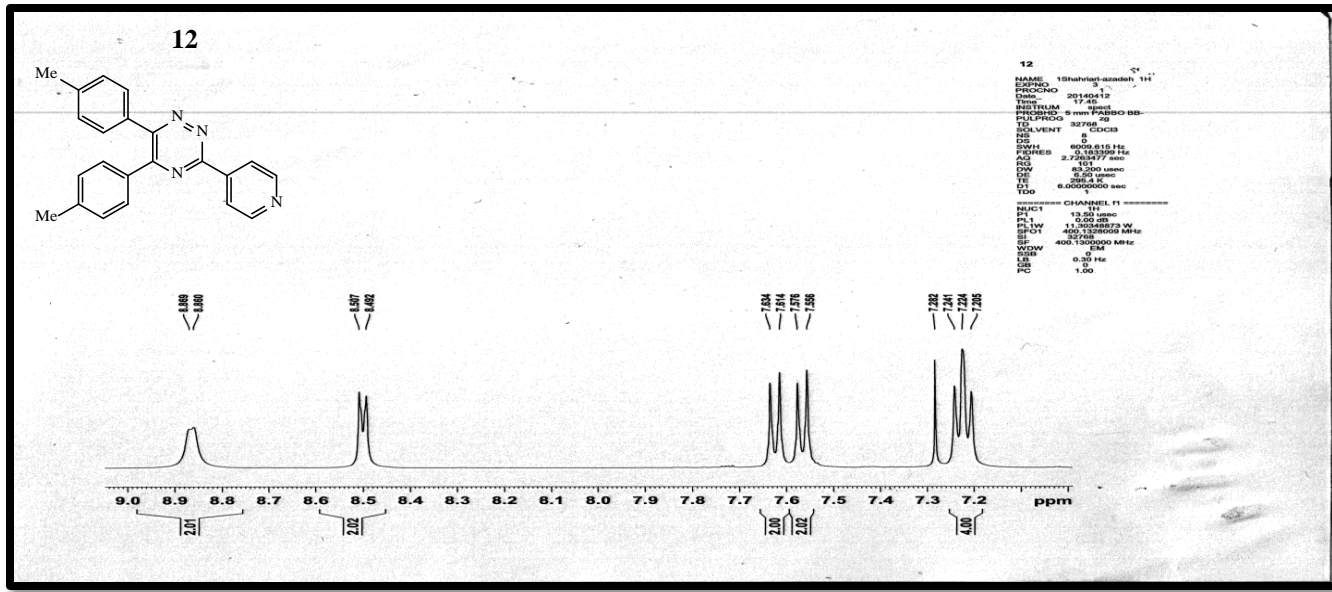
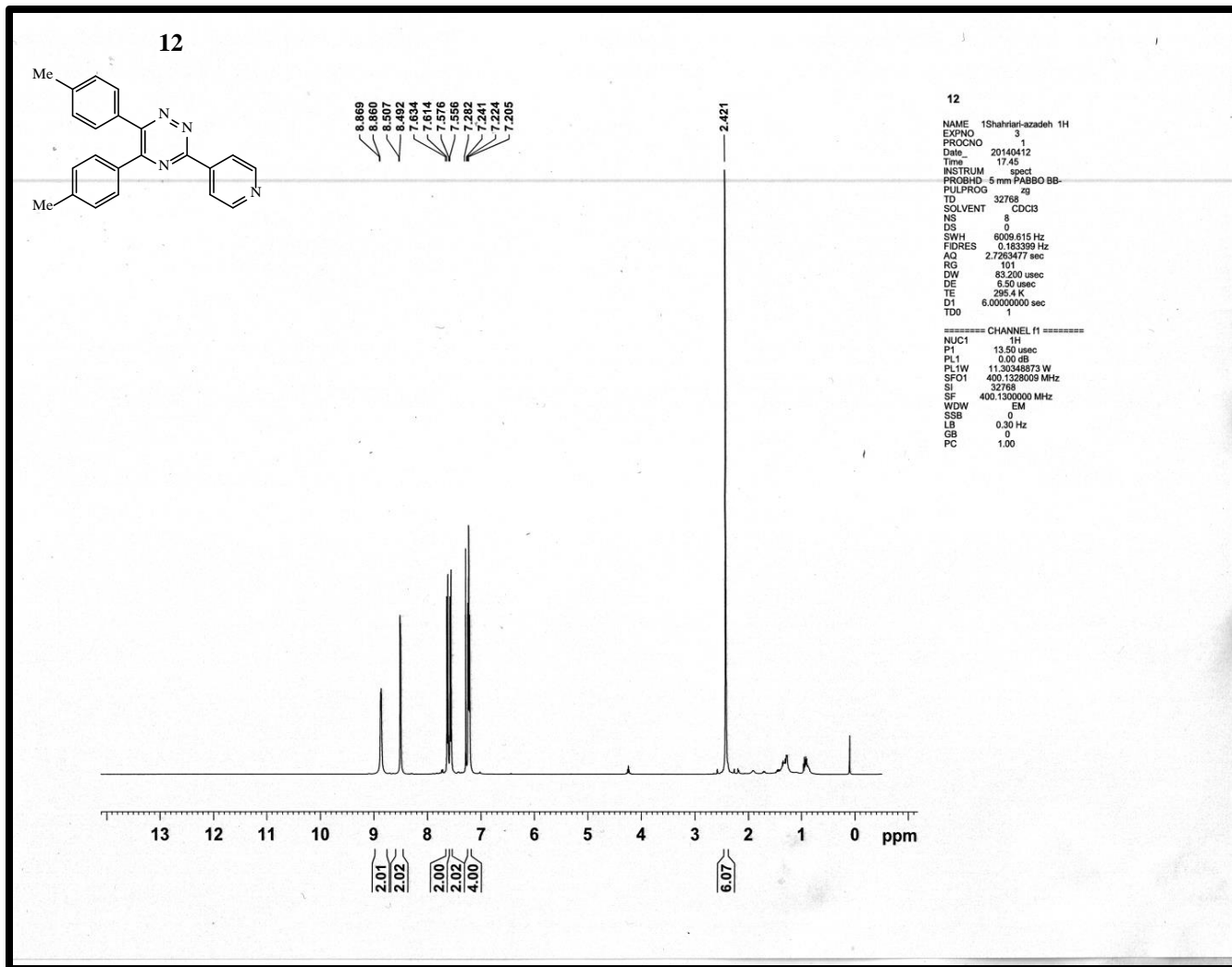
	Reten. Time [min]	Response	Weight [mg]	Weight [%]	Peak Type	Element Name	Carbon Response Ratio
	0.980	1762.871	0.648	11.86	Refer	Nitrogen	0.076
	1.377	23166.181	4.466	81.74	Refer	Carbon	1.000
3	5.833	7156.328	0.324	5.94	Refer	Hydrogen	0.309
	Total		5.464	99.54			

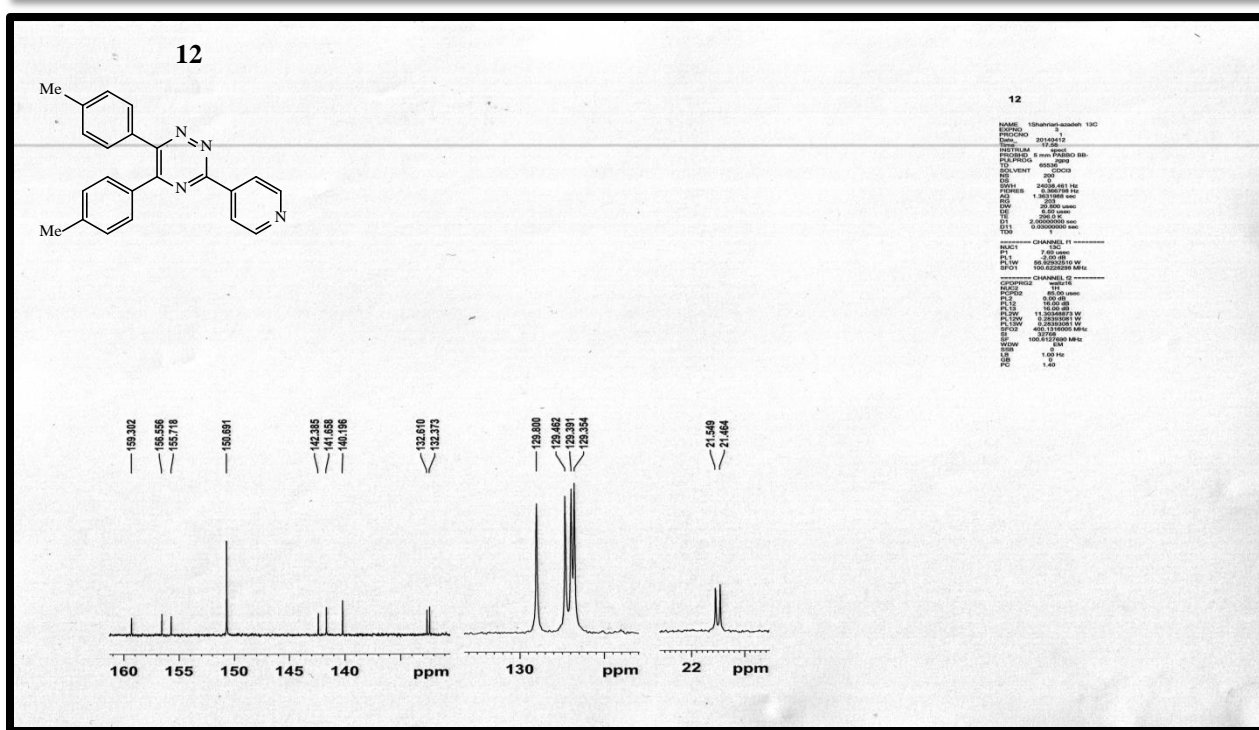
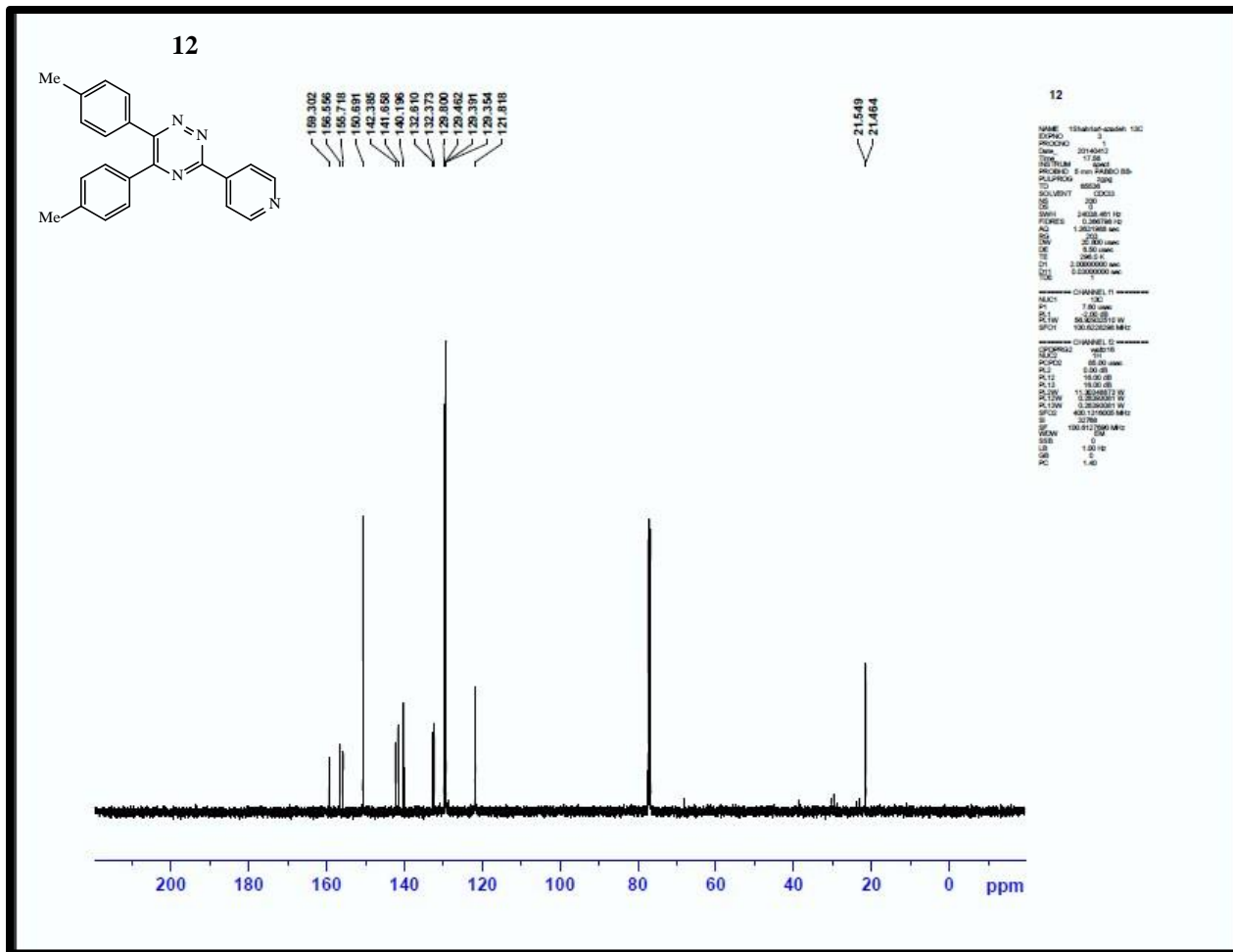
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 Acquired : 4 Jan 1980 1:57 using AcqMethod TEST ARI
 Instrument : Instrumen
 Sample Name: 11
 Misc Info :
 Vial Number: 1

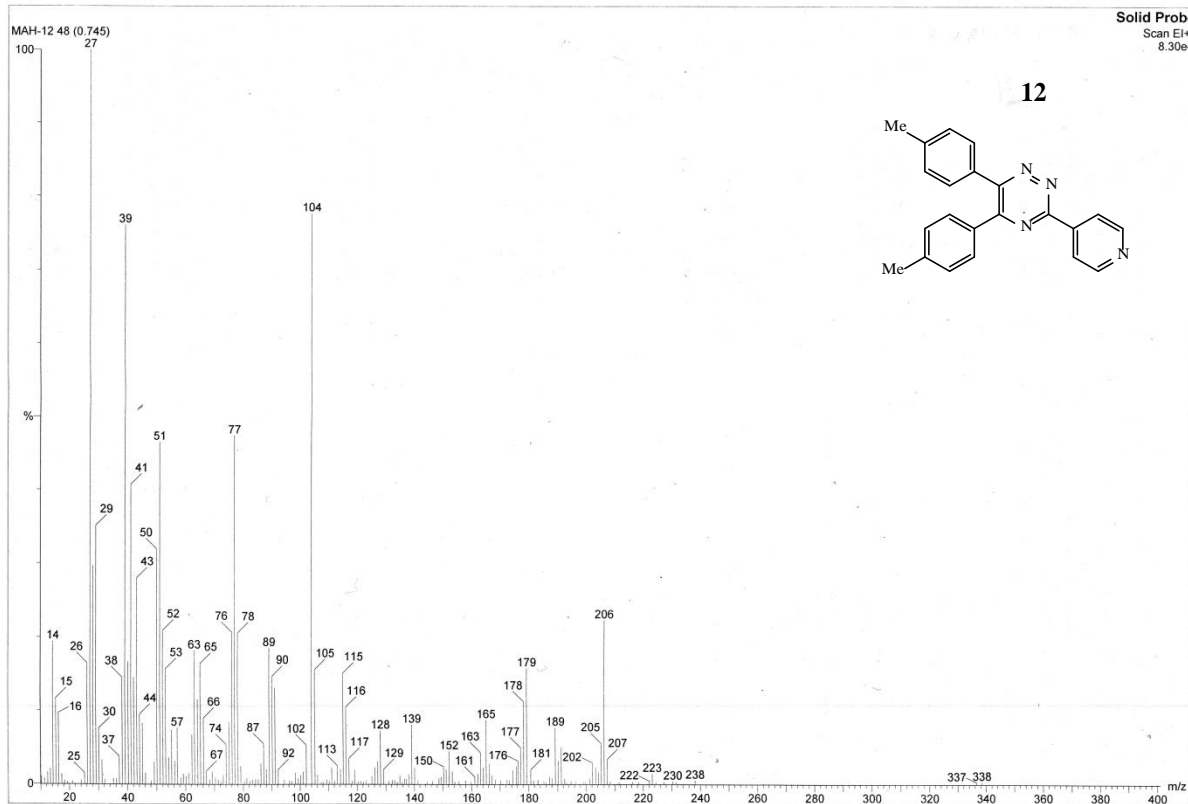


12. **3-(Pyridin-4-yl)-5,6-di(*p*-tolyl)-1,2,4-triazine (Table 2, entry 12):** Yellow powder. Mp: 145-147 °C; IR (KBr): 3066, 3031, 2979, 1608, 1492, 1390, 697; ¹H NMR (400 MHz CDCl₃): δ_H (ppm) 2.42 (s, CH₃, 6H), 7.20-8.86 (m, CH aromatic, 12H). ¹³C NMR (100 MHz, CDCl₃): δ_C (ppm) 21.46, 21.54, 121.81, 129.35, 129.39, 129.46, 129.80, 132.37, 132.61, 140.19, 141.65, 142.38, 150.69, 155.71, 156.55, 159.30. MS: *m/z* 338.

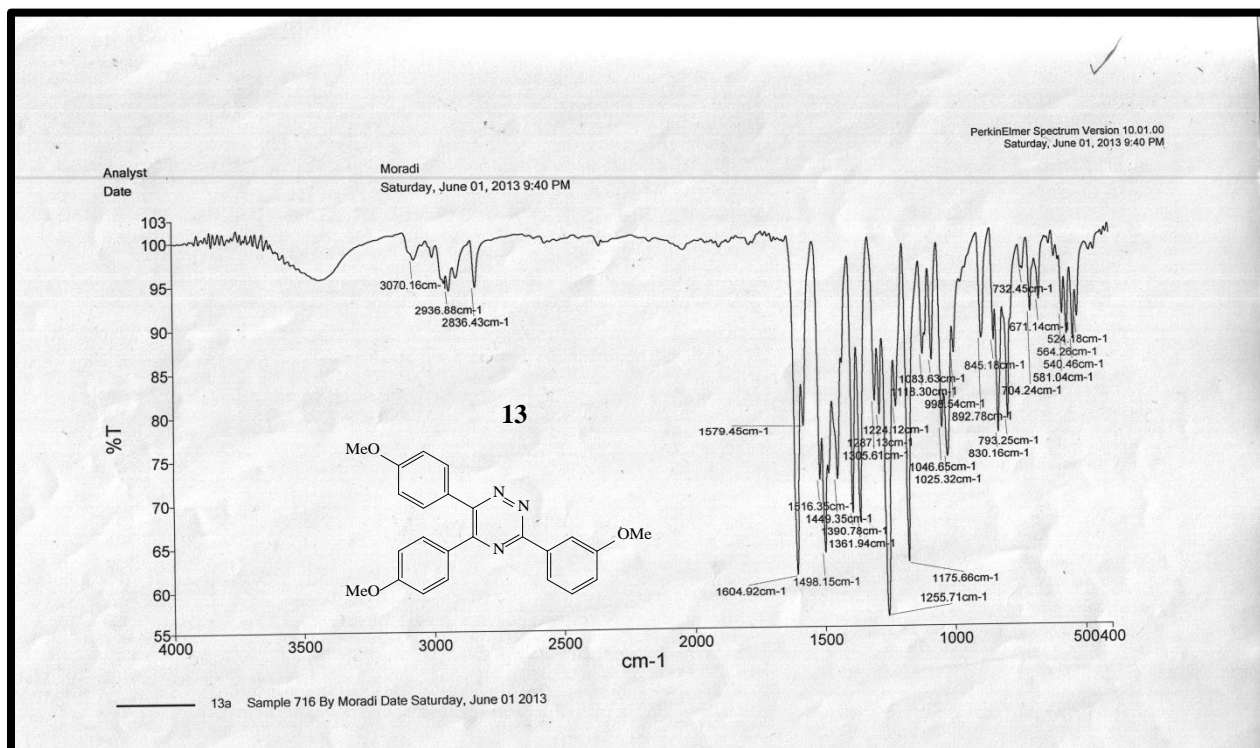


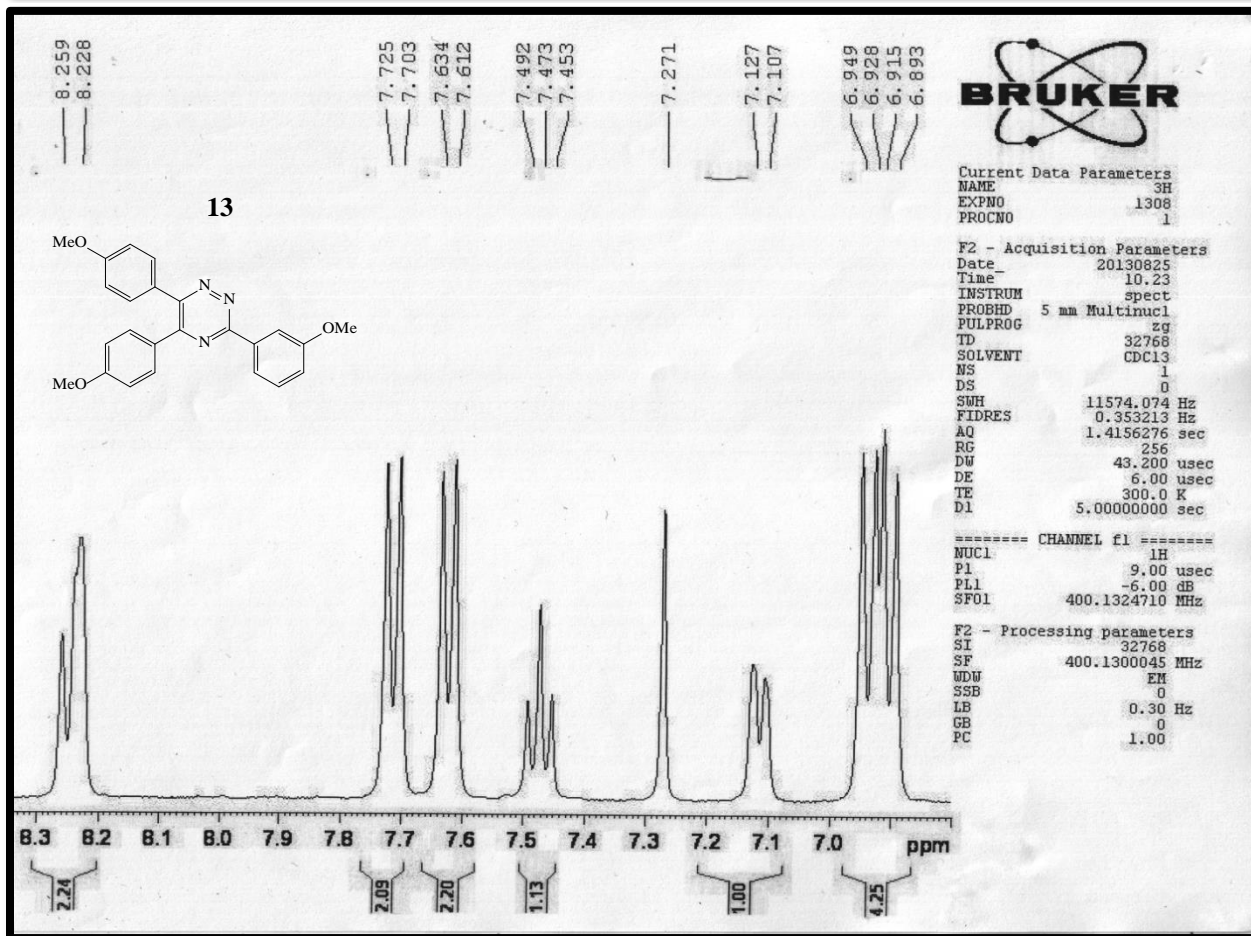
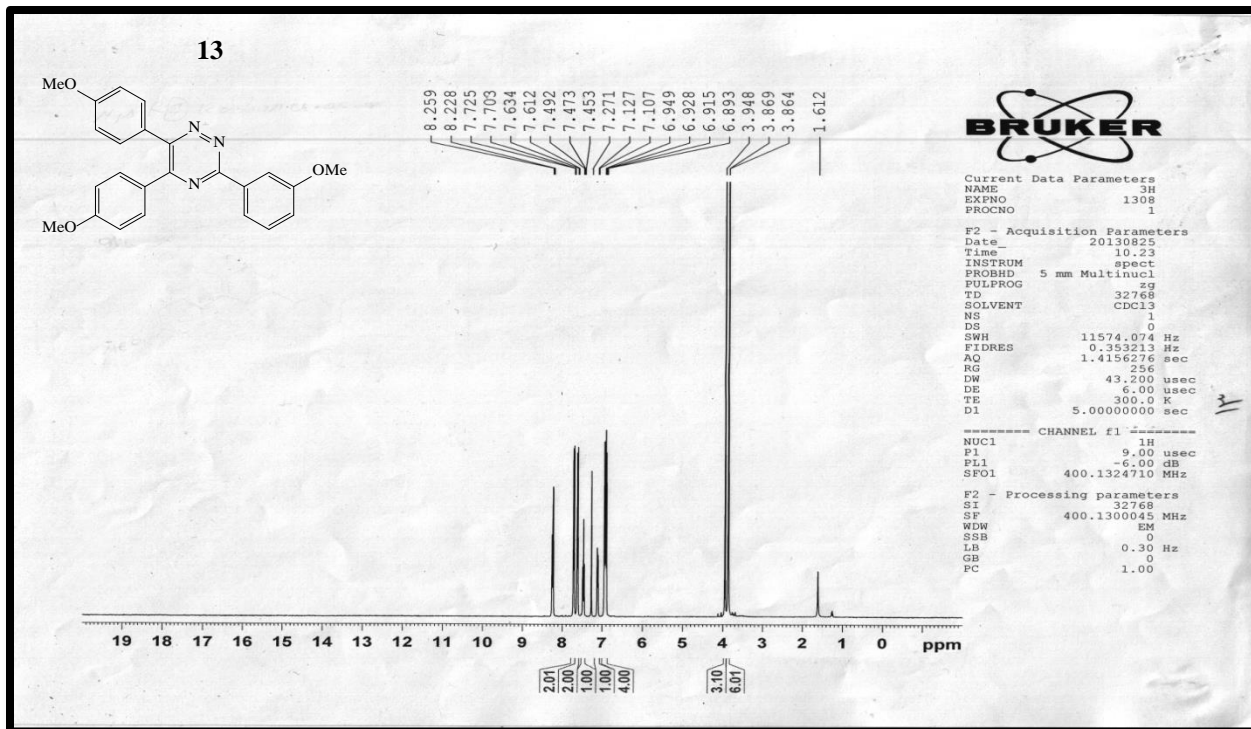


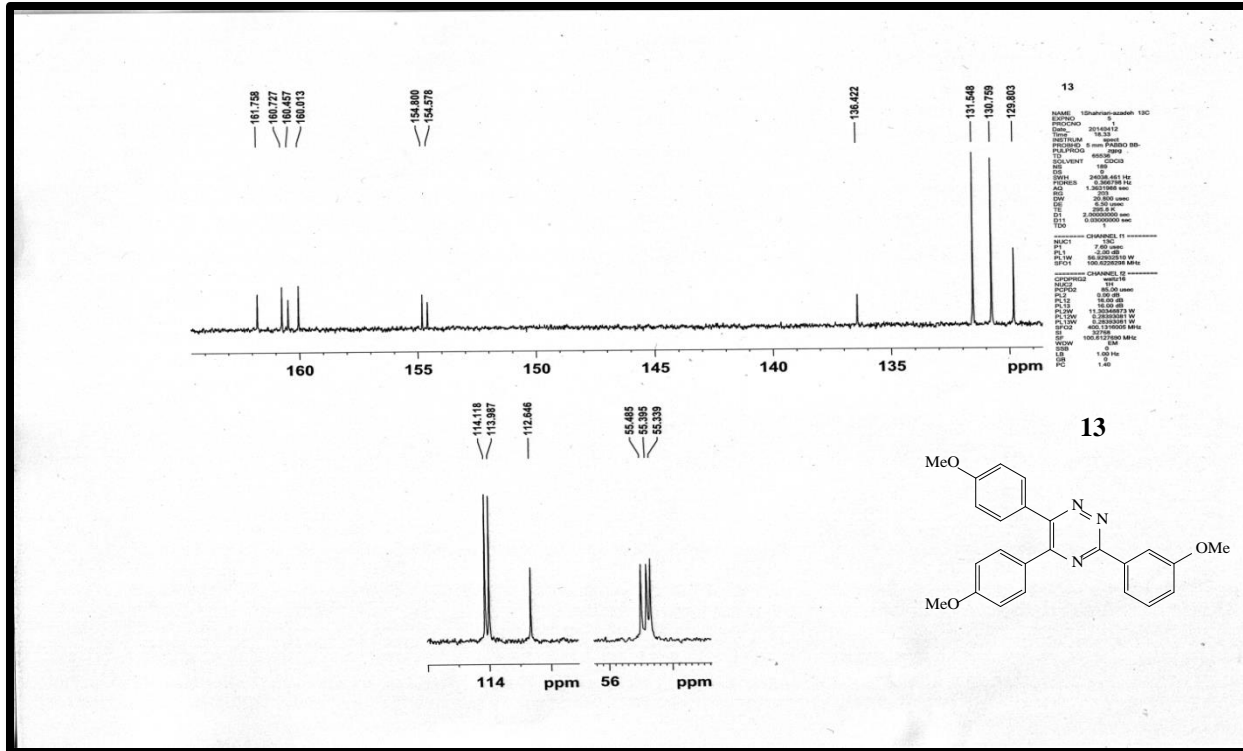
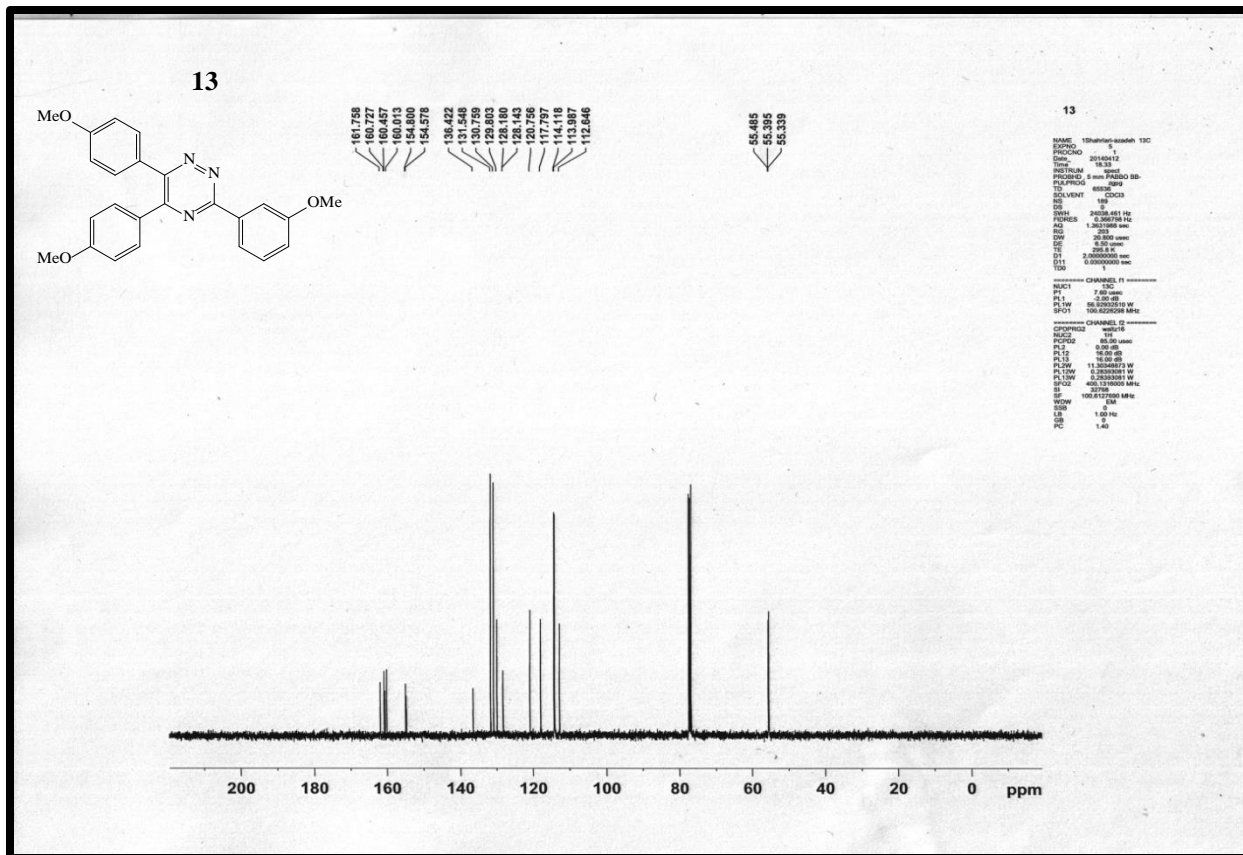


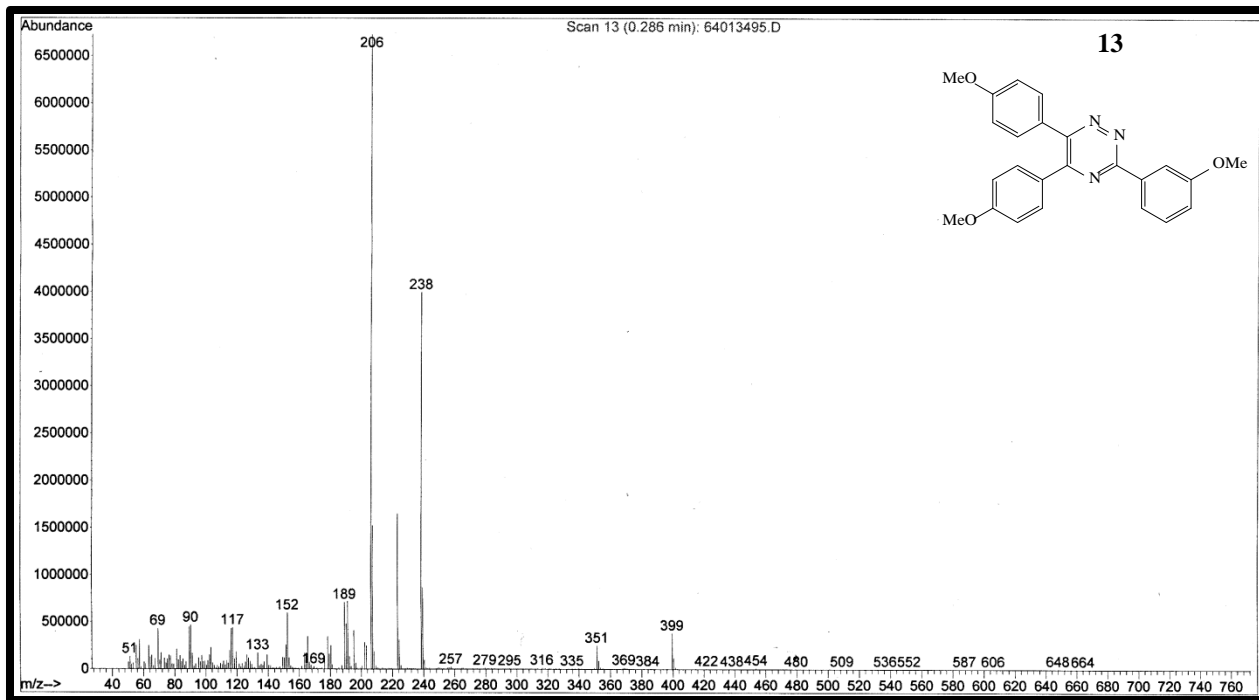


13. **3-(3-Methoxyphenyl)-5,6-bis(4-methoxyphenyl)-1,2,4-triazine (Table 2, entry 13):**
Yellow powder. Mp: 139-140 °C; IR (KBr): 3070, 2936, 2836, 1604, 1579, 1498, 1255, 1175; ¹H NMR (400 MHz CDCl₃): δ_H (ppm) 3.86 (s, OCH₃, 3H), 3.86 (s, OCH₃, 3H), 3.94 (s, OCH₃, 3H), 6.89-8.25 (m, CH aromatic, 12H). ¹³C NMR (100 MHz, CDCl₃): δ_c (ppm) 55.33, 55.39, 55.48, 112.64, 113.98, 114.11, 117.79, 120.75, 128.14, 128.18, 129.80, 130.75, 131.54, 136.42, 154.57, 154.80, 160.01, 160.45, 160.72, 161.75. MS: *m/z* 399.









14. **3,5,6-Triphenyl-1,2,4-triazine (Table 2, entry 14):** Yellow powder. Mp: 145-146 °C; IR (KBr):3058,2923,1600,1577,1504,1391; ¹H NMR (90 MHz DMSO-d₆): δ_H (ppm) 7.10-8.50 (m,CH aromatic,15H)

