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Electronic supplementary information

***s*-tetrazines functionalized with phenols: synthesis and physico-chemical properties**

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Experimental procedures:

Spectroscopic measurements: UV-visible absorption spectra were recorded on a Uvikon 942 spectrophotometer in 1 cm optical length quartz cuvettes. Corrected emission spectra were obtained on a Jobin-Yvon Horiba Spex FluoroMax-3 spectrofluorometer. Dichloromethane, dimethylsulfoxyde, acetonitrile, toluene and ethanol (Aldrich, spectrometric grade or SDS, spectrometric grade) were employed as solvents for absorption and fluorescence measurements. The fluorescence quantum yields were determined by using rhodamine 6G in ethanol as a standard (Φ_F=0.95).[18] The estimated experimental error is less than 10%. For the emission measurements, a right-angle configuration was used and the absorbance at the excitation wavelength are kept below 0.1 in order to avoid reabsorption artefacts.
Fluorescence decay curves were obtained using an Edinburgh instrument LP920 laser flash photolysis spectrometer, with an NdYAG laser (Surelite II-10 from Continuum) and a doubling or tripling crystal used to reach 532 or 355 nm excitation. The repetition rate is 10Hz, and the pulse width is 4-6ns (fwhm) at 355 nm. The Levenberg-Marquardt algorithm was used for non linear least square fit (tail fit) as implemented in the L900 software (Edinbugh instrument). In order to estimate the quality of the fit, the weighted residuals were calculated. A fit was said appropriate for reduced χ^2 values between 0.8 and 1.2.

Electrochemistry: Solvents (SDS, HPLC grade) and electrolyte (tetrabutylammonium hexafluorophosphate from Fluka, puriss.) were used without further purification. Cyclic voltammetry was performed in a three-electrode cell with a potentiostat (CH instruments 600) driven by a PC. Carbon electrode (1 mm diameter) was used as working electrode, whereas platinium wire and Ag^+ (0.01 M in acetonitrile)/Ag were used, respectively, as the counter and reference electrodes. All the investigated solutions were deaereted by argon-bubbling for at least 2 min before performing the electrochemical measurements.

Synthesis: Reagents were commercially available from Aldrich and used without further purification. Column chromatography was performed with SDS 0.040-0.063 mm silica gel. All compounds were characterized by the usual analytic method: ^{1}H, ^{13}C NMR spectra were recorded with a JEOL ECS (400 MHz) spectrometer. All chemical shifts are referenced to solvent peak (J values are given in Hz). Melting points were measured with a Kofler melting-point apparatus. IR spectra were recorded with a Nicolet Avatar 330 FT-IR spectrometer.

3,6-dichlorotetrazine **4**[1] and 3-chloro-6-methoxytetrazine **5**[2] were prepared according to litterature procedures.

Detailed synthetic procedures

3-chloro-6-phenoxy-*s*-tetrazine 1a: The procedure A was followed during 45 min with 3,6-dichlorotetrazine **4** (300 mg, 1.98 mmol), phenol (187 mg, 1.98 mmol) and 2,4,6-trimethylpyridine (0.26 mL, 1.98 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 260 mg of an orange solid (63%).
m.p.: 130°C;

[1] Y.-H. Gong, F. Miomandre, R. Méallet-Renault, S. Badré, L. Galmiche, J. Tang, P. Audebert and G. Clavier, *Eur. J. Org. Chem.*, 2009, 6121.

[2] P. Audebert, F. Miomandre, G. Clavier, M. C. Vernières, S. Badré and R. Méallet-Renaud, *Chem. Eur. J.*, 2005, **11**, 5667.

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.50 (dd, J=7.4, 8.2 Hz, 2H), 7.37 (t, J=7.4 Hz, 1H), 7.27 (d, J=7.8 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.7, 165.4, 151.9, 130.4, 127.2, 120.9;
IR(cm^{-1}): 3060, 2349, 1585, 775.
MS (ES+) calcd for $C_8H_5N_4OCl$ 208.0152 found 208.0144.

3-methoxy-6-phenoxy-*s*-tetrazine 2a: The procedure C was followed during 3 days with 3-chloro-6-methoxy-*s*-tetrazine **5** (250 mg, 1.7 mmol), phenol (160 mg, 1.7 mmol) and 2,4,6-trimethylpyridine (0.23 mL, 1.7 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/petroleum ether (7/3)) to give 83 mg of a pink oil (24%).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.46 (dd, J=7.3, 8.2 Hz, 2H), 7.30 (t, J=7.3 Hz, 1H), 7.2 (d, J=7,8 Hz, 2H), 4.24 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.1, 166.8, 152.7, 130.1, 126.4, 120.9, 57.0.
MS (ES+) calcd for $C_9H_9N_4O_2$ 205.0720 found 205.0716.

3,6-diphenoxy-*s*-tetrazine 3a: The procedure B was followed during 2 hours at room temperature with 3,6-dichlorotetrazine **4** (300 mg, 1.9 mmol), phenol (373 mg, 3.9 mmol) and 2,4,6-trimethylpyridine (0.52 mL, 3.9 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 403 mg of a pink solid (76%).
m.p.: 173°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.44 (t, J=8.3, 7.8 Hz, 4H), 7.29 (t, J=7.3 Hz, 2H), 7.25 (d, J=7.3 Hz, 4H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.5, 152.5, 130.2, 126.5, 121.0;
IR(cm^{-1}): 3068, 2357, 1589.
MS (ES+) calcd for $C_{14}H_{11}N_4O_2$ 267.0877 found 267.0871.

3-chloro-6-(4-oxophenoxy)-*s*-tetrazine 1b: The procedure A was followed during 1 hour with 3,6-dichlorotetrazine **4** (604 mg, 4 mmol), 4-hydroxybenzaldehyde (488 mg, 4 mmol) and 2,4,6-trimethylpyridine (0.6 mL, 4 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2 until CH_2Cl_2/methanol (99/1)) to give 640 mg of an orange solid (68%).
m.p.: 138°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=10.06 (s, 1H), 8.05 (d, J=8.7 Hz, 2H), 7.45 (d, J=8.7 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=190.6, 167.4, 165.9, 156.1, 135.1, 132.1, 121.7;
IR(cm^{-1}): 2987, 2365, 1703, 1425, 828.
MS (ES+) calcd for $C_9H_5N_4O_2Cl$ 236.0101 found 236.0111.

3-methoxy-6-(4-oxophenoxy)-*s*-tetrazine 2b: The procedure C was followed during 13 hours with 3-chloro-6-methoxy-*s*-tetrazine **5** (400 mg, 3 mmol), 4-hydroxybenzaldehyde (374 mg, 3 mmol) and 2,4,6-trimethylpyridine (0.4 mL, 3 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 399 mg of a pink solid (60%).
m.p.: 106°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=10.34 (s, 1H), 8.33 (d, J=8.7 Hz, 2H), 7.78 (d, J=8.7 Hz, 2H), 4.61 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=190.7, 167.1, 166.7, 157.3, 134.4, 131.9, 121.4, 57.3;
IR(cm^{-1}): 2987, 2357, 1692, 1452, 1368, 827.

3,6-di-(4-oxophenoxy)-*s*-tetrazine 3b: The procedure B was followed during 7 hours at room temperature with 3,6-dichlorotetrazine **4** (604 mg, 4 mmol), 4-hydroxybenzaldehyde (976 mg, 8 mmol) and 2,4,6-trimethylpyridine (1.2 mL, 8 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2 until CH_2Cl_2/AcOEt (95/5)) to give 420 mg of a brilliant pink solid (44%).
m.p.: 207°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=10.04 (s, 2H), 8.02 (d, J=8.6 Hz, 4H), 7.47 (d, J=8.3 Hz, 4H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=190.6, 167.2, 156.8, 134.7, 132.0, 121.6;
IR(cm^{-1}): 2987, 2361, 1690, 1452, 826.

3-methoxy-6-(4-nitrophenoxy)-*s*-tetrazine 2c: The procedure C was followed during 12 hours with 3-chloro-6-methoxy-*s*-tetrazine **5** (500 mg, 3.3 mmol), 4-nitrophenol (1.1 g, 7.6 mmol) and 2,4,6-trimethylpyridine (0.75 mL, 5.7 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 623 mg of a brilliant pink solid (66%).
m.p.: 166°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=8.36 (d, J=9.1 Hz, 2H), 7.46 (d, J=9.1 Hz, 2H), 4.30 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.2, 166.5, 157.3, 145.6, 126.0, 121.5, 57.4;
IR(cm^{-1}): 3109, 2398, 1500, 1444, 1376, 1345, 836.
MS (ES+) calcd for $C_9H_7N_5O_4$ 249.0498 found 249.0514.

3,6-di-(4-nitrophenoxy)-*s*-tetrazine 3c: The procedure B was followed during 4 hours at room temperature with 3,6-dichlorotetrazine **4** (500 mg, 3.3 mmol), 4-nitrophenol (921 mg, 6.6 mmol) and 2,4,6-trimethylpyridine (0.88 mL, 6.6 mmol) to give 740 mg of a pink solid (63%).
m.p.: 270°C;
^{1}H NMR (400 MHz, DMSO): δ (ppm)=8.42 (d, J=9.2 Hz, 4H), 7.69 (d, J=9.2 Hz, 4H);
^{13}C NMR (100 MHz; DMSO): δ (ppm)=166.6, 157.3, 145.1, 126.3, 121.6;
IR(cm^{-1}): 3117, 2434, 1514, 1487, 1339, 850.

3-chloro-6-(4-bromophenoxy)-*s*-tetrazine 1d: The procedure A was followed during 1 hour with 3,6-dichlorotetrazine **4** (250 mg, 1.65 mmol), 4-bromophenol (143 mg, 0.82 mmol) and 2,4,6-trimethylpyridine (0.11 mL, 0.82 mmol). The crude product was purified by a first silica gel column chromatography (CH_2Cl_2/petroleum ether (1/1)) and a second one (CH_2Cl_2) to give 29 mg of an orange solid (12%).
m.p.: 148°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.62 (d, J=9.4 Hz, 2H), 7.18 (d, J=9.2 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.5, 165.7, 150.8, 133.5, 122.7, 120.5;
IR(cm^{-1}): 2974, 2357, 1482, 693.

3-methoxy-6-(4-bromophenoxy)-*s*-tetrazine 2d: The procedure C was followed during 2 days with 3-chloro-6-methoxy-*s*-tetrazine **5** (250 mg, 1.7 mmol), 4-bromophenol (295 mg, 1.7 mmol) and 2,4,6-trimethylpyridine (0.23 mL, 1.7 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 97 mg of a brilliant orange solid (21%).
m.p.: 98°C;

^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.58 (d, J=8.7 Hz, 2H), 7.16 (d, J=8.7 Hz, 2H), 4.27 (s, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.0, 166.9, 151.7, 133.2, 122.8, 119.6, 51.2;
IR(cm^{-1}): 2941, 2357, 1482, 1324, 711.
MS (ES+) calcd for $C_9H_4BrNO_2$ 281.9752 found 281.9744.

3, 6-di-(4-bromophenoxy)-*s*-tetrazine 3d: The procedure B was followed during 4 hours at room temperature with 3,6-dichlorotetrazine **4** (250 mg, 1.65 mmol), 4-bromophenol (429 mg, 2.48 mmol) and 2,4,6-trimethylpyridine (0.33 mL, 2.48 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/petroleum ether (7/3)) to give 424 mg of a brilliant pink solid (59%).
m.p.: 186°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.58 (d, J=6.9 Hz, 4H), 7.17 (d, J=6.7 Hz, 4H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.3, 151.4, 133.3, 122.8, 119.9;
IR(cm^{-1}): 2982, 2357, 1484, 707.

3-chloro-6-(4-chlorophenoxy)-*s*-tetrazine 1e: The procedure A was followed during 1 hour with 3,6-dichlorotetrazine **4** (250 mg, 1.65 mmol), 4-chlorophenol (213 mg, 1.65 mmol) and 2,4,6-trimethylpyridine (0.22 mL, 1.65 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 278 mg of an orange solid (69%).
m.p.: 140°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.47 (d, J=9.6 Hz, 2H), 7.23 (d, J=9.7 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.6, 165.7, 150.2, 132.7, 130.5, 122.4;
IR(cm^{-1}): 3105, 2361, 1485, 703.
MS (APPI) calcd for $C_{14}H_8Cl_2N_4O_2$ 334.0024 found 334.0014.

3-methoxy-6-(4-chlorophenoxy)-*s*-tetrazine 2e: The procedure C was followed during 2 days with 3-chloro-6-methoxy-*s*-tetrazine **5** (250 mg, 1.7 mmol), 4-chlorophenol (218 mg, 1.7 mmol) and 2,4,6-trimethylpyridine (0.22 mL, 1.7 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/petroleum ether (7/3)) to give 87 mg of a pink solid (21%).
m.p.: 98°C;
^{1}H NMR (400 MHz, $CDCl_3$): 7.43 (d, J=6.4 Hz, 2H), 7.21 (d, J=6.4 Hz, 2H), 4.27 (s, 3H);
^{13}C (100 MHz, $CDCl_3$): δ (ppm)=167.0, 166.9, 151.1, 131.9, 130.2 , 122.4, 57.2;
IR(cm^{-1}): 3060, 2349, 1487, 1366, 719.

3,6-di-(4-chlorophenoxy)-*s*-tetrazine 3e: The procedure B was followed during 2 days under reflux with 3,6-dichlorotetrazine **4** (250 mg, 1.65 mmol), 4-chlorophenol (426 mg, 3.3 mmol) and 2,4,6-trimethylpyridine (0.44 mL, 3.3 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 287 mg of a brilliant pink solid (52%).
m.p.: 166°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.43 (d, J=8.8 Hz, 4H), 7.22 (d, J=9.1 Hz, 4H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.4, 150.8, 132.2, 130.3, 122.4;
IR(cm^{-1}): 3088, 2361, 1484, 708.

3-chloro-6-(3-chlorophenoxy)-*s*-tetrazine 1f: The procedure A was followed during 4 hours with 3,6-dichlorotetrazine **4** (150 mg, 0.993 mmol), 3-chlorophenol (127 mg, 0,993 mmol)

and 2,4,6-trimethylpyridine (0.13 mL, 0,993 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give m=137 mg of an orange solid (57%).
m.p.: 77°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.42 (dd, J=8.0, 8.2 Hz, 1H); 7.36 (d, J=8.2 Hz, 1H), 7.31 (s, 1H), 7.18 (d, J=8.4 Hz, 1H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.5, 165.7, 152.1, 135.7, 131.1, 127.6, 121.7, 119.3;
IR (cm^{-1}): 3069, 2358, 1587, 1353, 792.

3-methoxy-6-(3-chlorophenoxy)-*s*-tetrazine 2f: The procedure C was followed during 6 days with 3-chloro-6-methoxy-*s*-tetrazine **5** (80 mg, 0.546 mmol), 3-chlorophenol (84.2 mg, 0.655 mmol) and 2,4,6-trimethylpyridine (0.09 mL, 0.655 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give m=79 mg of an red solid (61%).
m.p.: 62°C.
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.37 (t, J=8.5 Hz, 1H), 7.28-7.24 (m, 2H), 7.13 (d, J=7.9 Hz, 1H), 4.24 (s, 3H).
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=166.9, 166.8, 153.1, 135.4, 130.9, 126.7, 121.6, 119.2, 57.1;
IR (cm^{-1}): 3089, 2360, 1494, 1386, 715.

3,6-di-(3-chlorophenoxy)-*s*-tetrazine 3f: The procedure B was followed during 4 hours at room temperature with 3,6-dichlorotetrazine **4** (150 mg, 0.993 mmol), 3-chlorophenol (240.5 mg, 1.88 mmol) and 2,4,6-trimethylpyridine (0.26 mL, 1.88 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give m=110 mg of an pink solid (33%).
m.p.: 128°C;
^{1}H NMR (400 MHz, CDCl3): δ (ppm)=7.42 (s, 2H), 7.39 (d, J=8.7 Hz, 2H), 7.31 (dd, J=5.5, 8.7 Hz, 2H), 7.18 (d, J=8.7 Hz, 2H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.3, 152.7, 135.6, 131.0, 127.1, 121.7, 119.3;
IR (cm^{-1}): 3093, 2340, 1470, 1375, 798.

3-chloro-6-(4-*tert*butylphenoxy)-*s*-tetrazine 1g: The procedure A was followed during 2 hours with 3,6-dichlorotetrazine **4** (605 mg, 4 mmol), 4-*tert*butylphenol (601 mg, 4 mmol) and 2,4,6-trimethylpyridine (0.6 mL, 4 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2) to give 840 mg of a pink solid (61%).
m.p.: 53°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.49 (J=8.7 Hz, 2H), 7.19 (d, J=9.1 Hz, 2H), 1.36 (s, 9H);
^{13}C (100 MHz, $CDCl_3$): δ (ppm)=167.8, 165.3, 150.2, 149.6, 127.3, 120.2, 34.8, 31.5;
IR(cm^{-1}): 2962, 2361, 1442, 1361, 796.

3-methoxy-6-(4-*tert*butylphenoxy)-*s*-tetrazine 2g: The procedure C was followed during 2 days with 3-chloro-6-methoxy-*s*-tetrazine **5** (400 mg, 3 mmol), 4-*tert*butylphenol (450 mg, 3 mmol) and 2,4,6-trimethylpyridine (0.4 mL, 3 mmol). The crude product was purified by a silica gel column chromatography ($CHCl_3$/petroleum ether (9/1)) to give 554 mg of a brilliant pink solid (71%).
m.p.: 56°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.46 (d, J=8.7 Hz, 2H), 7.17 (d, J=8.7 Hz, 2H), 4.25 (s, 3H), 1.34 (s, 9H);

^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.3, 166.8, 150.4, 149.4, 127.1, 120.3, 57.0, 34.7, 31.6;
IR(cm^{-1}): 2959, 2357, 1441, 1361.
MS (ES+) calcd for $C_{13}H_{16}N_4O_2$ 261.1350 found 261.1352.

3,6-di-(4-*tert*butylphenoxy)-*s*-tetrazine 3g: The procedure B was followed during 4 days in a pressure tube with 3,6-dichlorotetrazine **4** (250 mg, 1.65 mmol), 4-*tert*butylphenol (743 mg, 4.9 mmol) and 2,4,6-trimethylpyridine (0.7 mL, 4.9 mmol). The mixture was heated to reflux to give 403 mg of a pink brilliant solid (93%).
m.p.: 264°C;
^{1}H NMR (400 MHz, DMSO): δ (ppm)=7.45 (d, J=8.7 Hz, 4H), 7.17 (d, J=8.7 Hz, 4H), 1.33 (s, 18H);
^{13}C (100 MHz, DMSO): δ (ppm)=167.5, 150.2, 149.6, 127.1, 120.4, 34.7, 31.5;
IR(cm^{-1}): 2959, 2349, 1450, 1377.

4-decyloxyphenol h: In a three-neck-round-bottom-flask was placed hydroquinone (2 g, 18.1 mmol), potassium carbonate (2.52 g, 18.2 mmol) in DMSO (30 mL) under argon atmosphere. 1-bromodecane (1.89 mL, 9.08 mmol) was added and the mixture was stirred and heated at 70°C during 2 days. Then the mixture was cooled to room temperature and water (20 mL) and hydrochloric acid (1 mol.L-1, 10 mL) were added. The aqueous layer was extracted with CH2Cl2 then the organic layers were combined, washed with water, dried with anhydrous magnesium sulfate, filtered and concentrated under vacuum. The crude product was purified by a silica gel column chromatography (CH2Cl2) to give 650 mg of a white solid (29%).
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=6.78 (m, 4H), 4.80 (s, 1H), 3.89 (t, J=6.4 Hz, 2H), 1.75 (m, 2H), 1.62 (m, 14H), 0.88 (t, J=6.4 Hz, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=153.4, 149.5, 116.1, 115.7, 68.9, 32.0, 29.7, 29.6, 29.5, 29.3, 26.3, 26.2, 22.8, 14.3;
IR(cm^{-1}): 3419, 2916, 1511.

3-chloro-6-(4-decyloxyphenoxy)-*s*-tetrazine 1h: The procedure A was followed during 2 hours with 3,6-dichlorotetrazine **4** (183 mg, 1.21 mmol), 4-decyloxyphenol **h** (300 mg, 1.21 mmol) and 2,4,6-trimethylpyridine (0.16 mL, 1.21 mmol). The crude product was purified by a silica gel column chromatography ($CHCl_3$) to give 328 mg of a pink solid (78%).
m.p.: 82°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.17 (d, J=9.2 Hz, 2H), 6.97 (d, J=9.2 Hz, 2H), 3.97 (t, J=6.4 Hz, 2H), 1.79 (m, 2H), 1.30 (m, 14H), 0.88 (t, J=6.8 Hz, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=168.0, 165.3, 157.8, 145.1, 121.7, 115.8, 68.7, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 22.8, 14.3;
IR(cm^{-1}): 2917, 2357, 1506, 1376, 799.
MS (APPI) calcd for $C_{18}H_{25}ClN_4O_2$ 364.1666 found 364.1665.

3-methoxy-6-(4-decyloxyphenoxy)-*s*-tetrazine 2h: The procedure C was followed during 1 day with 3-chloro-6-methoxy-*s*-tetrazine **5** (85 mg, 0.58 mmol), 4-decyloxyphenol **h** (144 mg, 0.58 mmol) and 2,4,6-trimethylpyridine (0.07 mL, 0.58 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/petroleum ether (7/3)) to give 100 mg of a brilliant pink solid (50%).

m.p.: 49°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.16 (d, J=9.2 Hz, 2H), 6.95 (d, J=9.2 Hz, 2H), 4.25 (s, 3H), 3.96 (t, J=6.4 Hz, 2H), 1.79 (m, 2H), 1.46 (m, 2H), 1.30 (m, 12H), 0.88 (t, J=6.9 Hz, 3H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.5, 166.8, 157.4, 145.9, 121.9, 115.7, 68.6, 57.0, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 22.8, 14.3;
IR(cm^{-1}): 2918, 2361, 1506, 1376.

3,6-di-(4-decyloxyphenoxy)-*s*-tetrazine 3h: The procedure B was followed during 4 days under reflux with 3,6-dichlorotetrazine **4** (46 mg, 0.3 mmol), 4-decyloxyphenol **h** (150 mg, 0.6 mmol) and 2,4,6-trimethylpyridine (0.08 mL, 0.6 mmol). The crude product was purified by a silica gel column chromatography (CH_2Cl_2/petroleum ether (7/3)) to give 111 mg of a pink solid (66%).
m.p.: 106°C;
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm)=7.16 (d, J=9.2 Hz, 4H), 6.93 (d, J=6.9 Hz, 4H), 3.95 (t, J=6.6 Hz, 4H), 1.78 (m, 4H), 1.45 (m, 4H), 1.27 (m, 24H), 0.88 (t, J=6.6 Hz, 6H);
^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm)=167.7, 157.4, 145.8, 121.9, 115.6, 68.6, 32.0, 29.7, 29.6, 29.5, 29.4, 29.3, 26.2, 22.8, 14.3;
IR(cm^{-1}): 2953, 2353, 1470, 1382.

NMR Spectra

Figure 1: ^{1}H NMR of 3-chloro-6-phenoxy-*s*-tetrazine **1a**

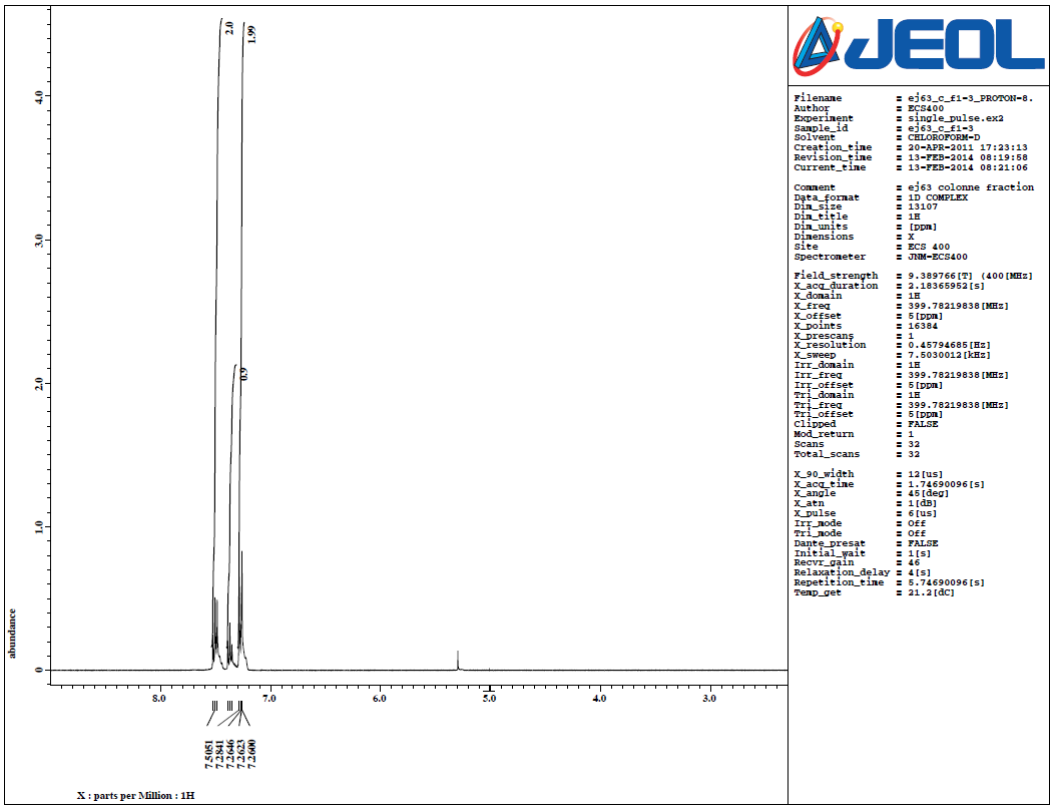


Figure 2: ^{13}C NMR of 3-chloro-6-phenoxy-*s*-tetrazine **1a**

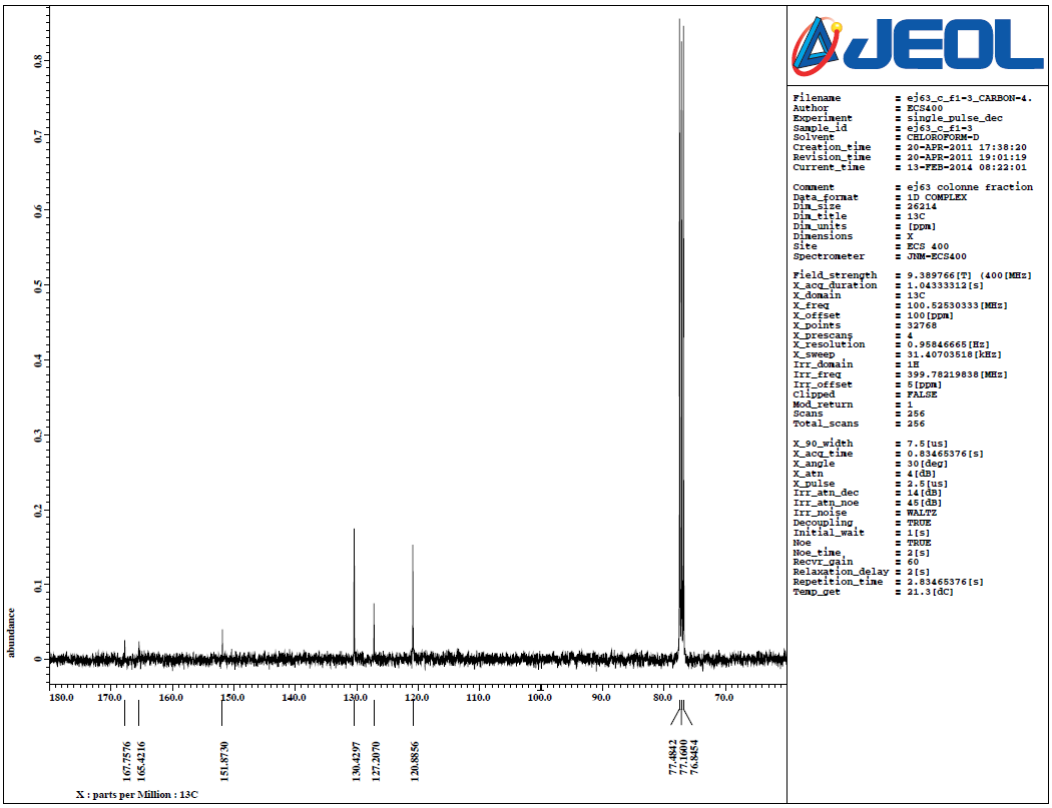


Figure 3: ^{1}H NMR of 3-methoxy-6-phenoxy-*s*-tetrazine **2a**

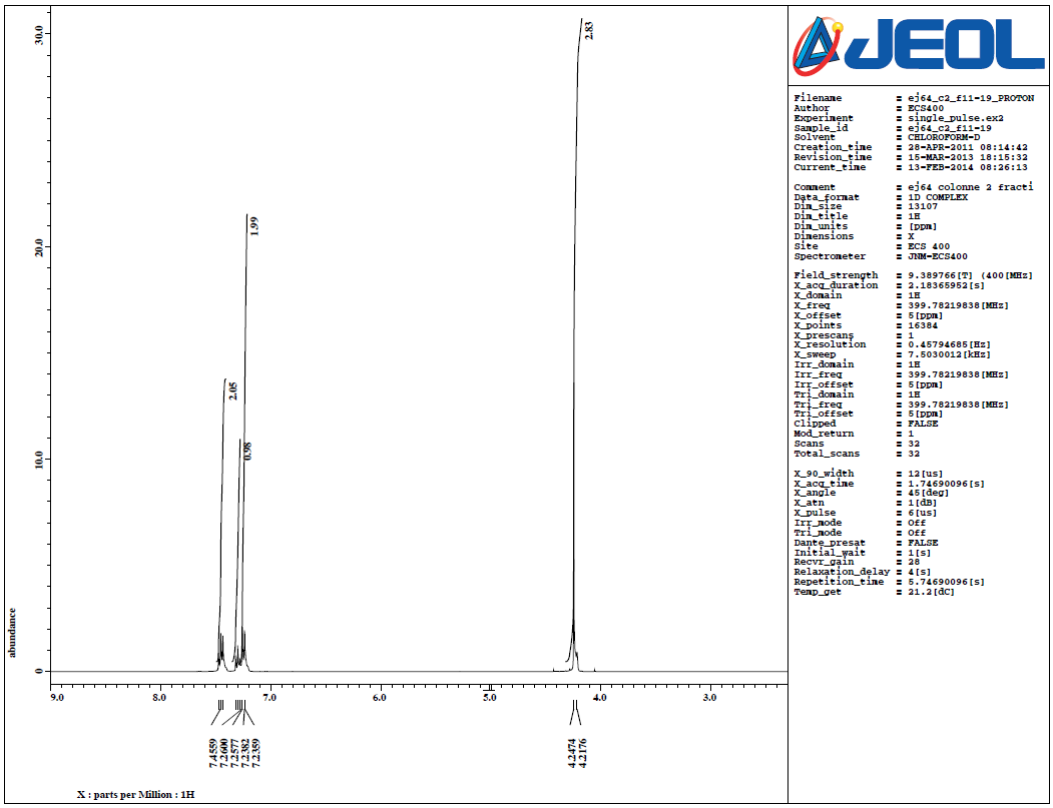


Figure 4: ^{13}C NMR of 3-methoxy-6-phenoxy-*s*-tetrazine **2a**

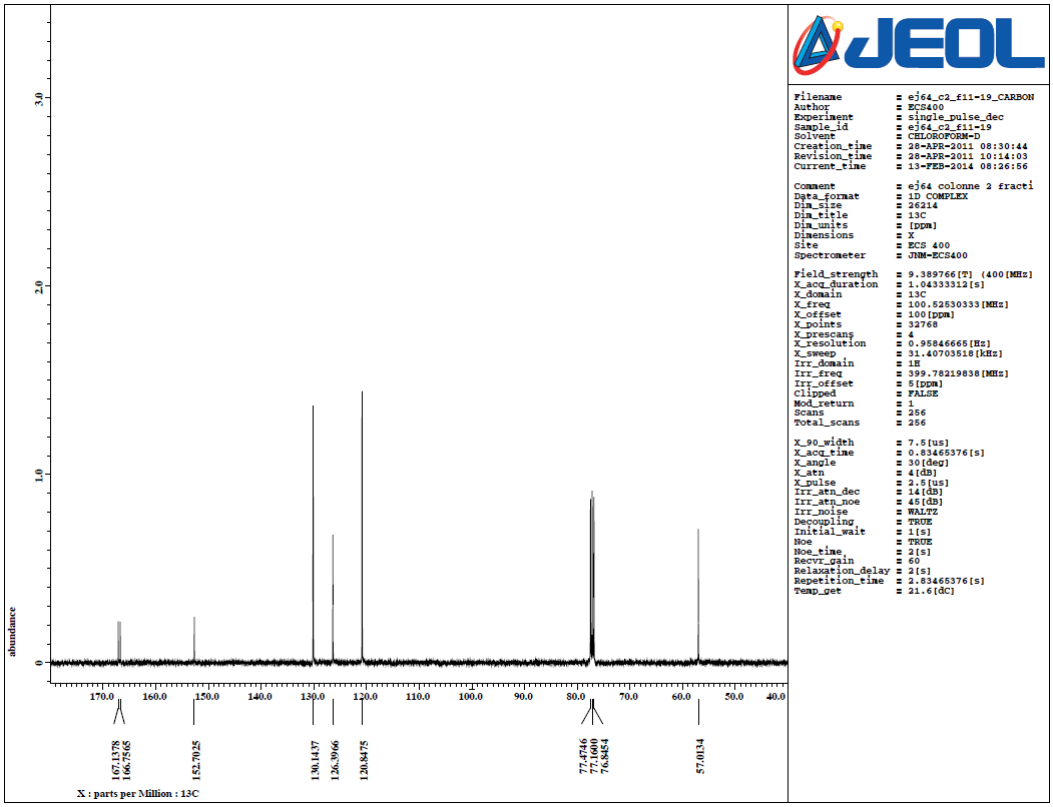


Figure 5: ^{1}H NMR of 3,6-diphenoxy-*s*-tetrazine **3a**

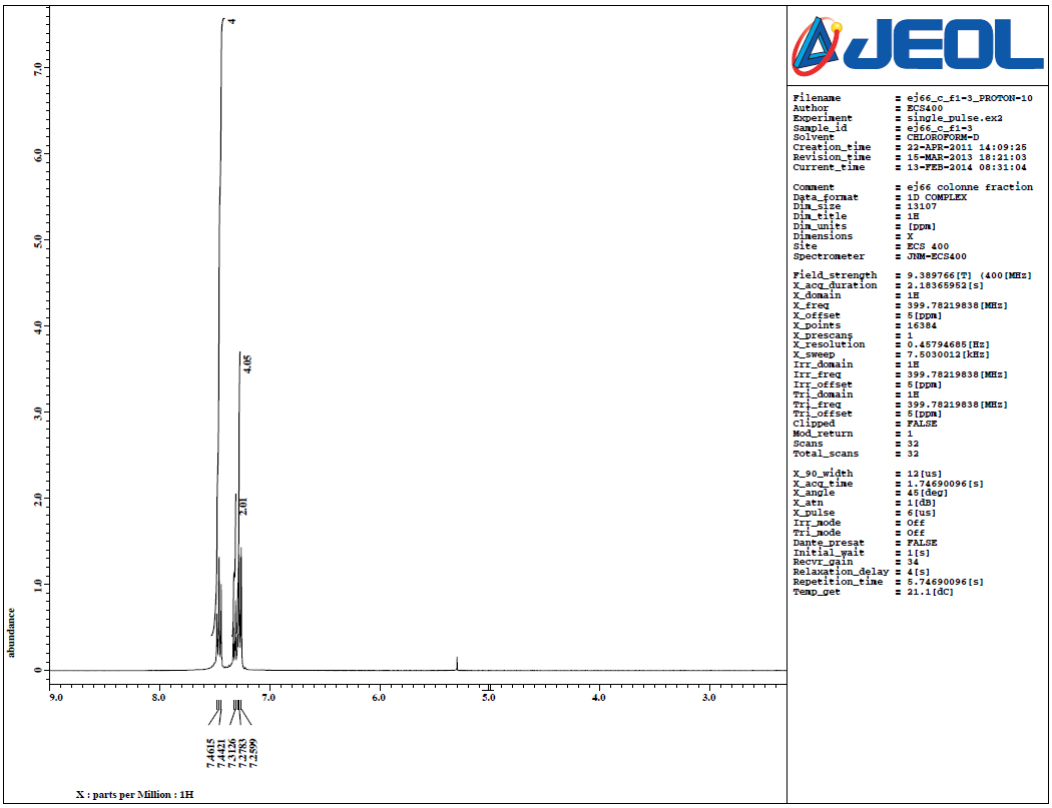


Figure 6: ^{13}C NMR of 3,6-diphenoxy-*s*-tetrazine **3a**

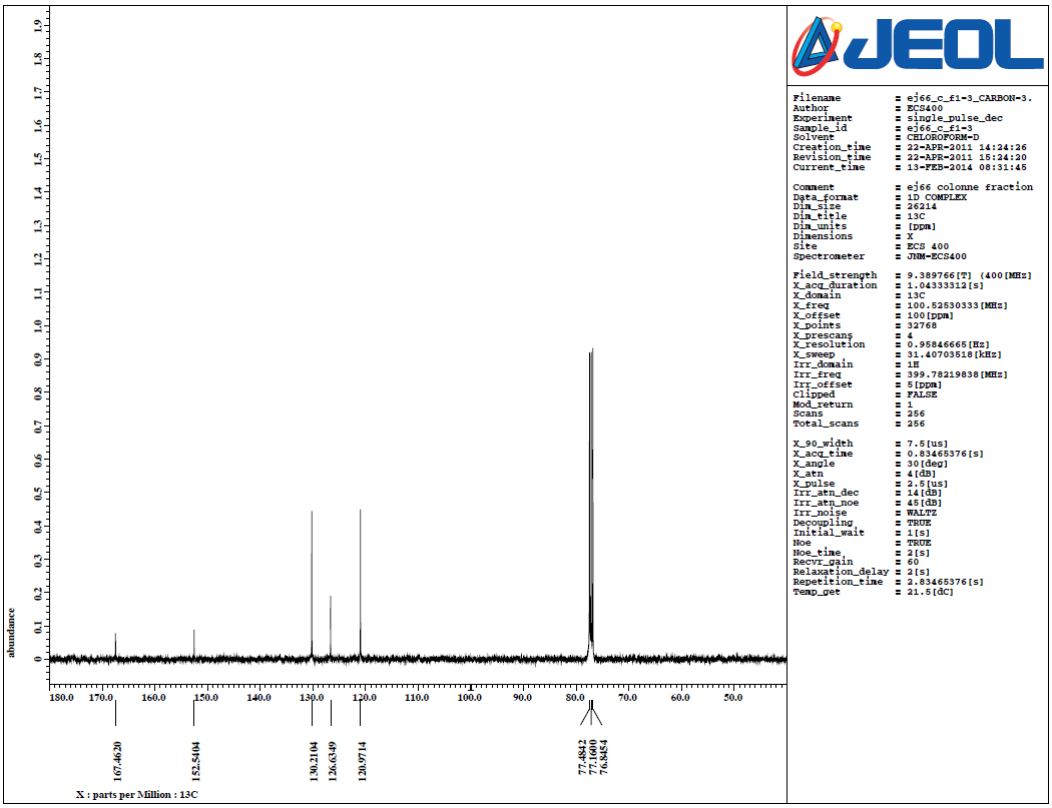


Figure 7: ^{1}H NMR of 3-chloro-6-(4-oxophenoxy)-*s*-tetrazine **1b**

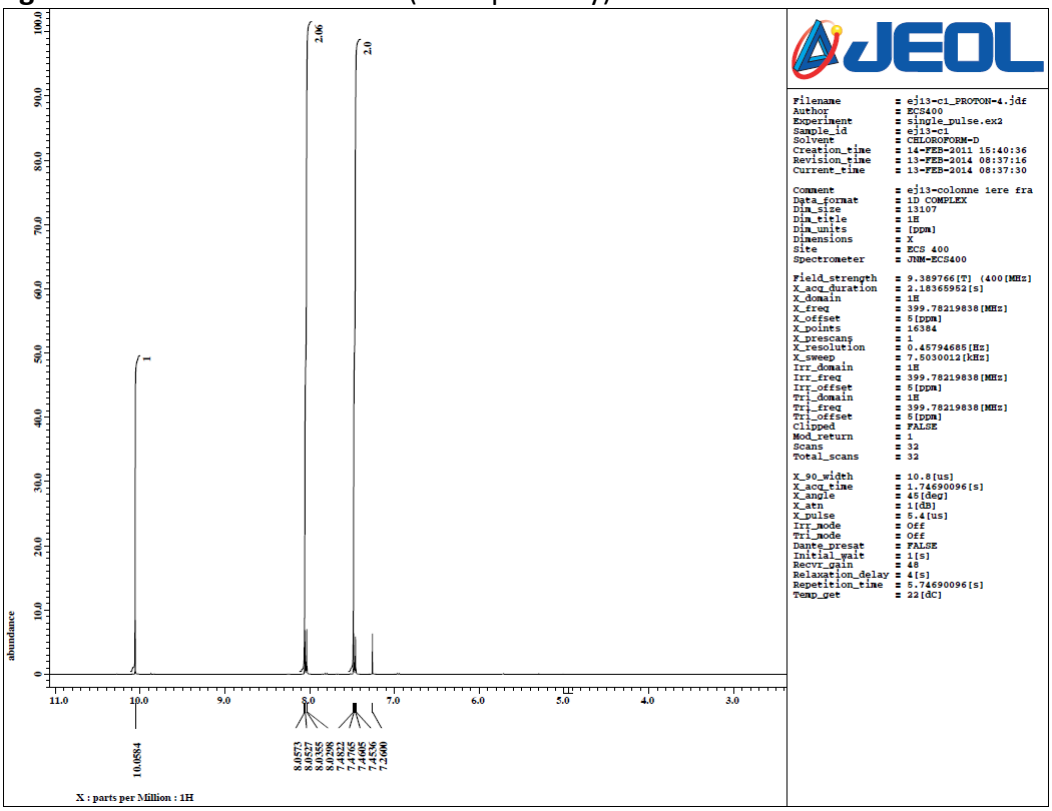


Figure 8: ^{13}C NMR of 3-chloro-6-(4-oxophenoxy)-*s*-tetrazine **1b**

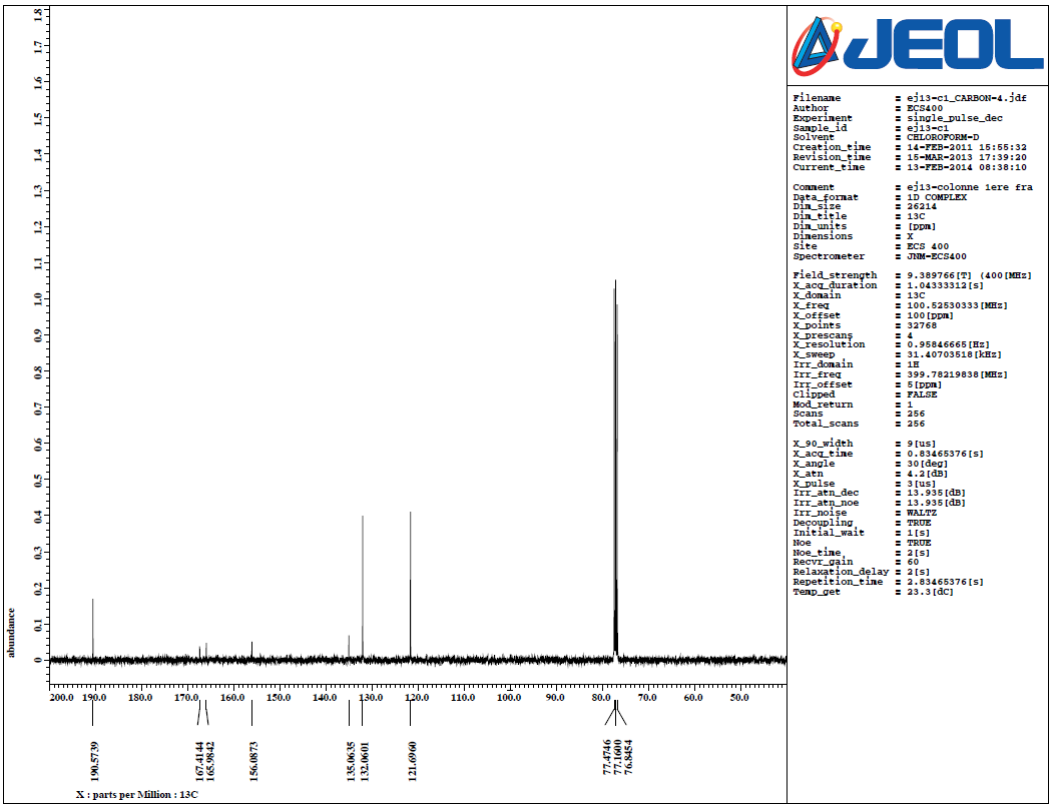


Figure 9: ^{1}H NMR of 3-methoxy-6-(4-oxophenoxy)-*s*-tetrazine **2b**

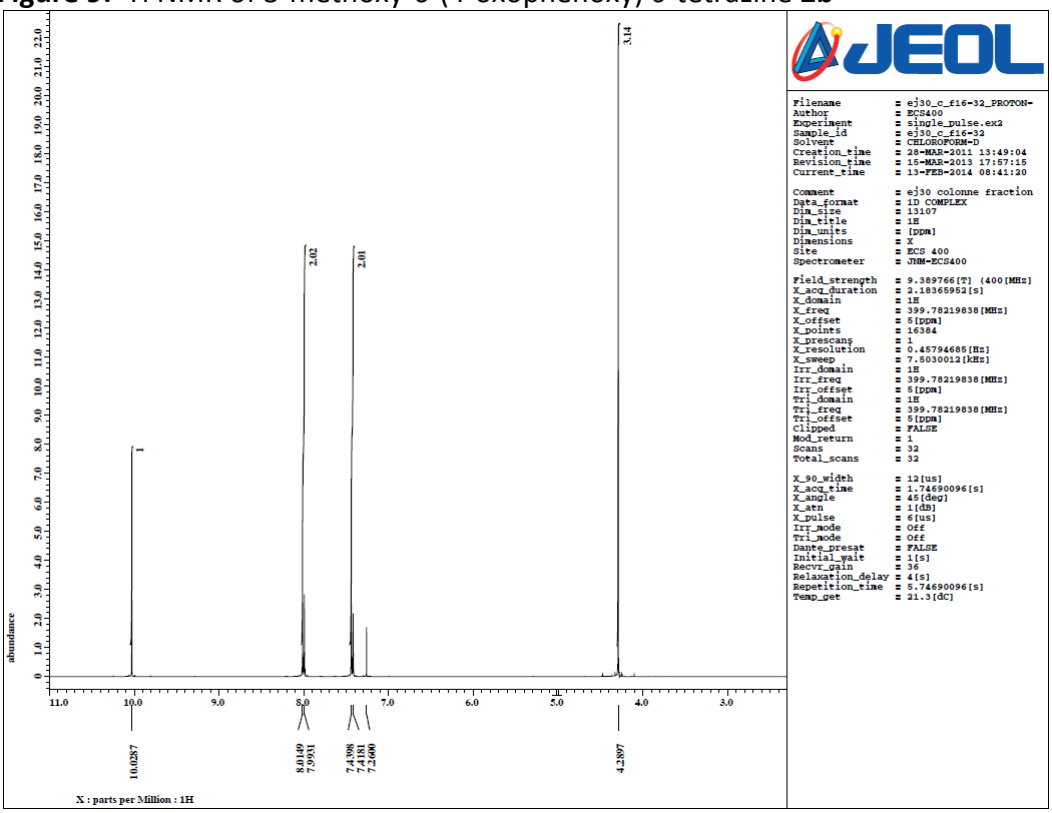


Figure 10: ^{13}C NMR of 3-methoxy-6-(4-oxophenoxy)-*s*-tetrazine **2b**

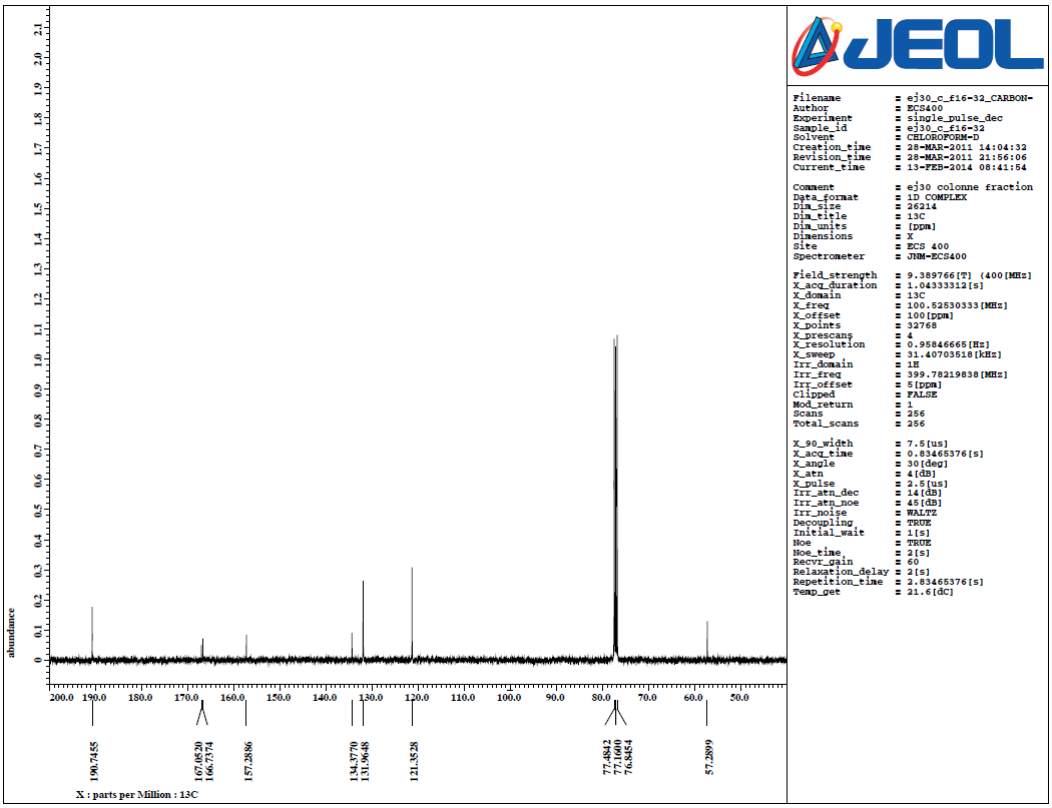


Figure 11: ^{1}H NMR of 3,6-di-(4-oxophenoxy)-*s*-tetrazine **3b**

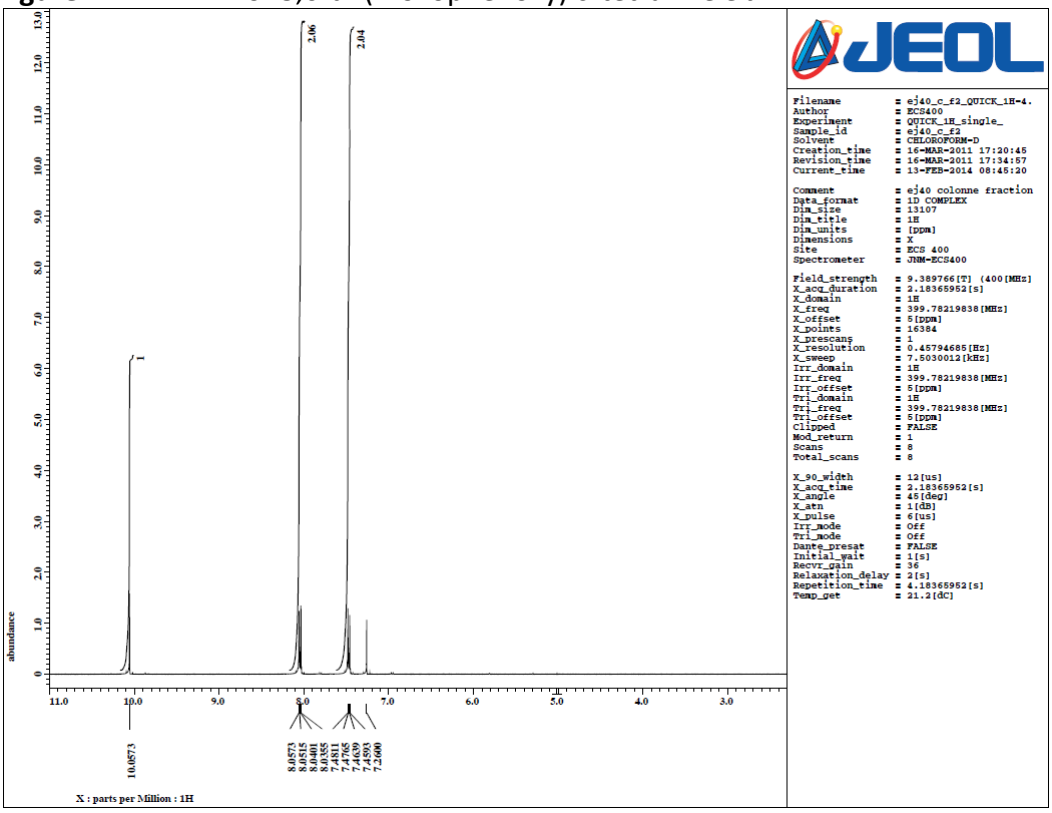


Figure 12: ^{13}C NMR of 3,6-di-(4-oxophenoxy)-*s*-tetrazine **3b**

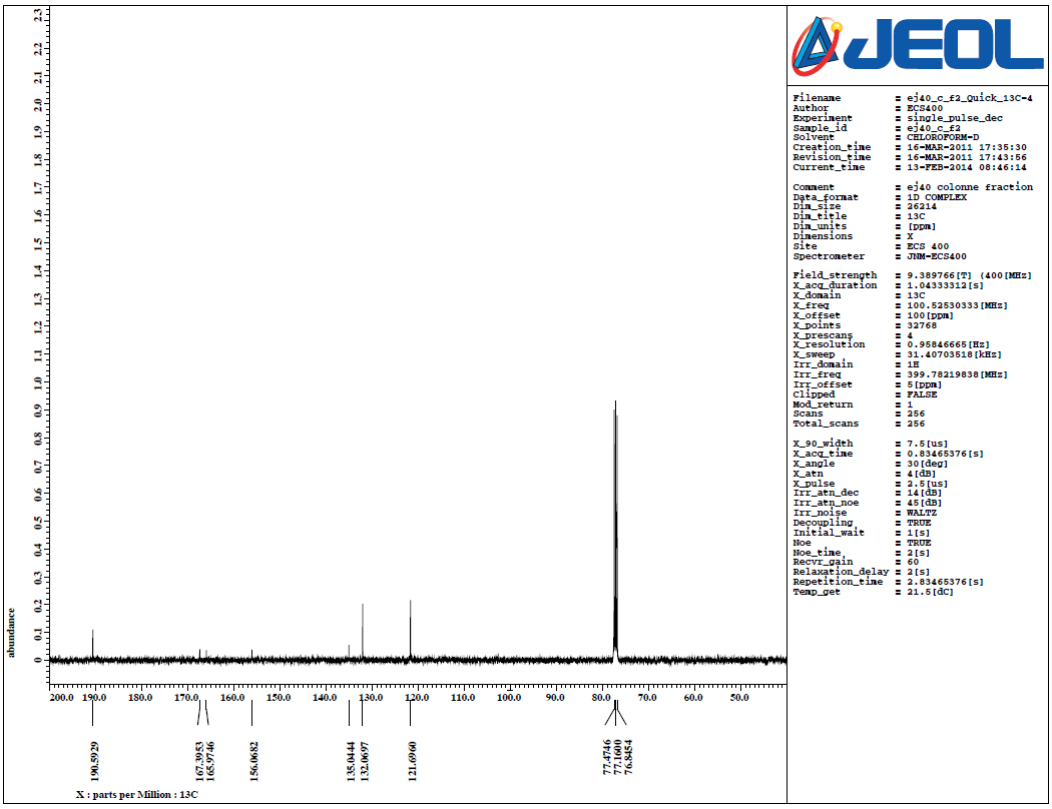


Figure 13: ^{1}H NMR of 3-methoxy-6-(4-nitrophenoxy)-*s*-tetrazine **2c**

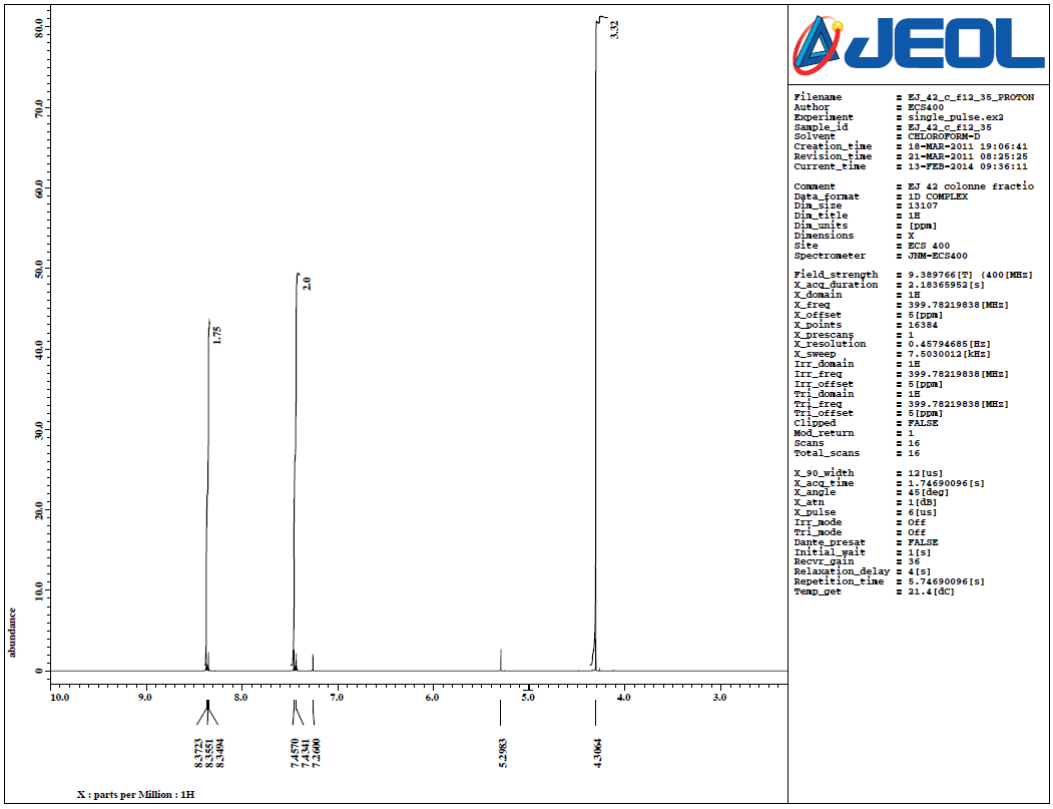


Figure 14: ^{13}C NMR of 3-methoxy-6-(4-nitrophenoxy)-*s*-tetrazine **2c**

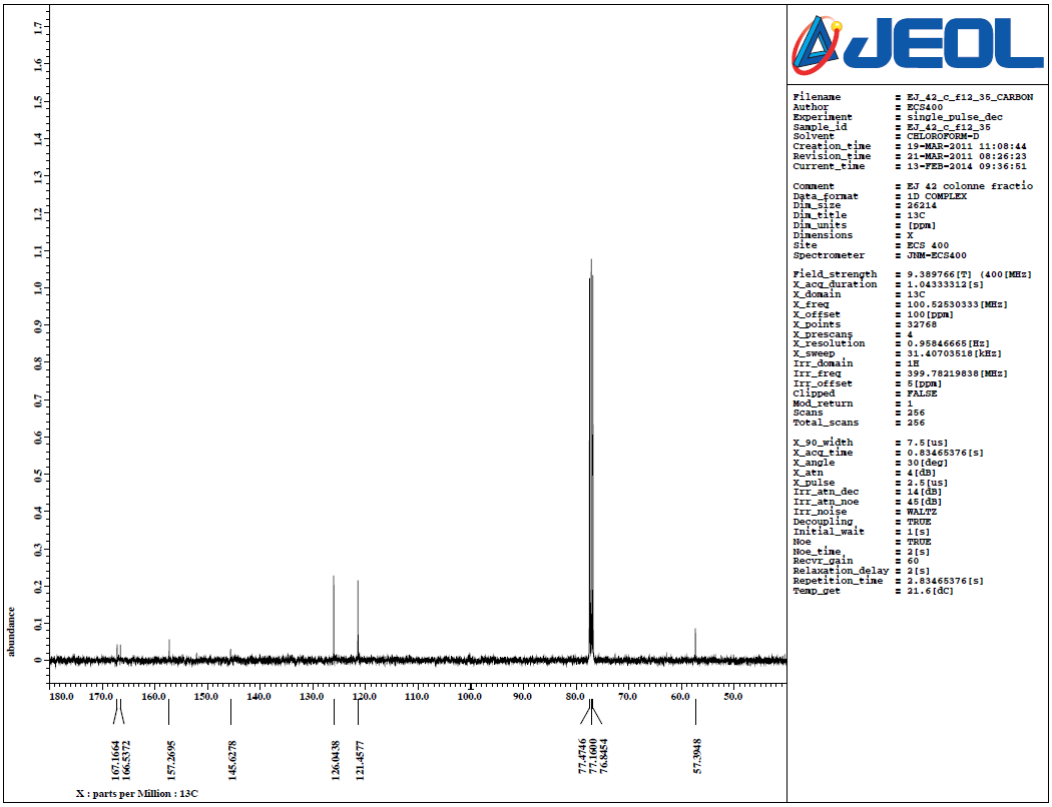


Figure 15: ^{1}H NMR of 3,6-di-(4-nitrophenoxy)-*s*-tetrazine **3c**

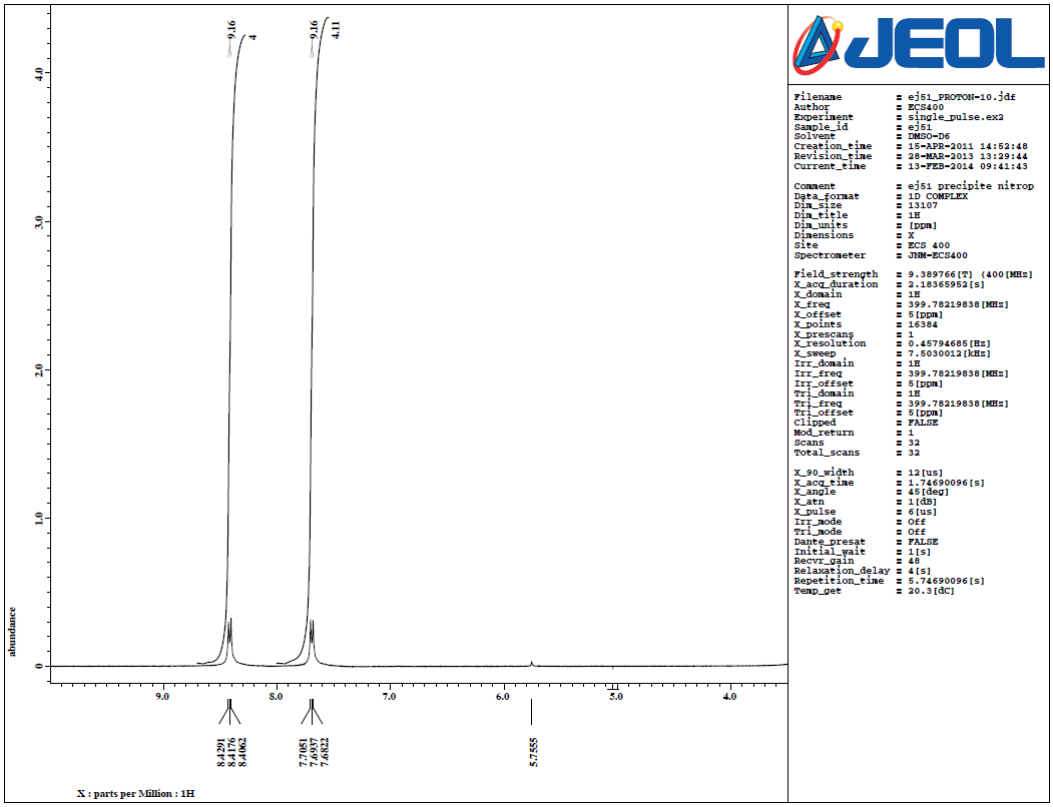


Figure 16: ^{13}C NMR of 3,6-di-(4-nitrophenoxy)-*s*-tetrazine **3c**

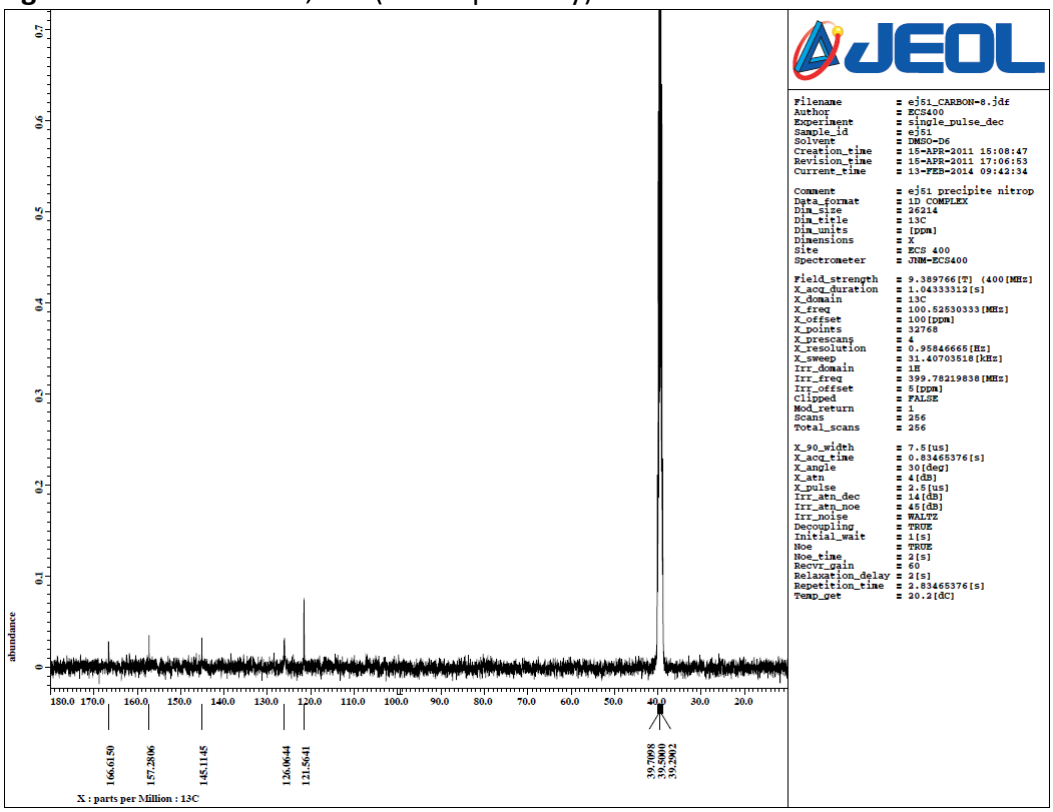


Figure 17: ^{1}H NMR of 3-chloro-6-(4-bromophenoxy)-*s*-tetrazine **1d**

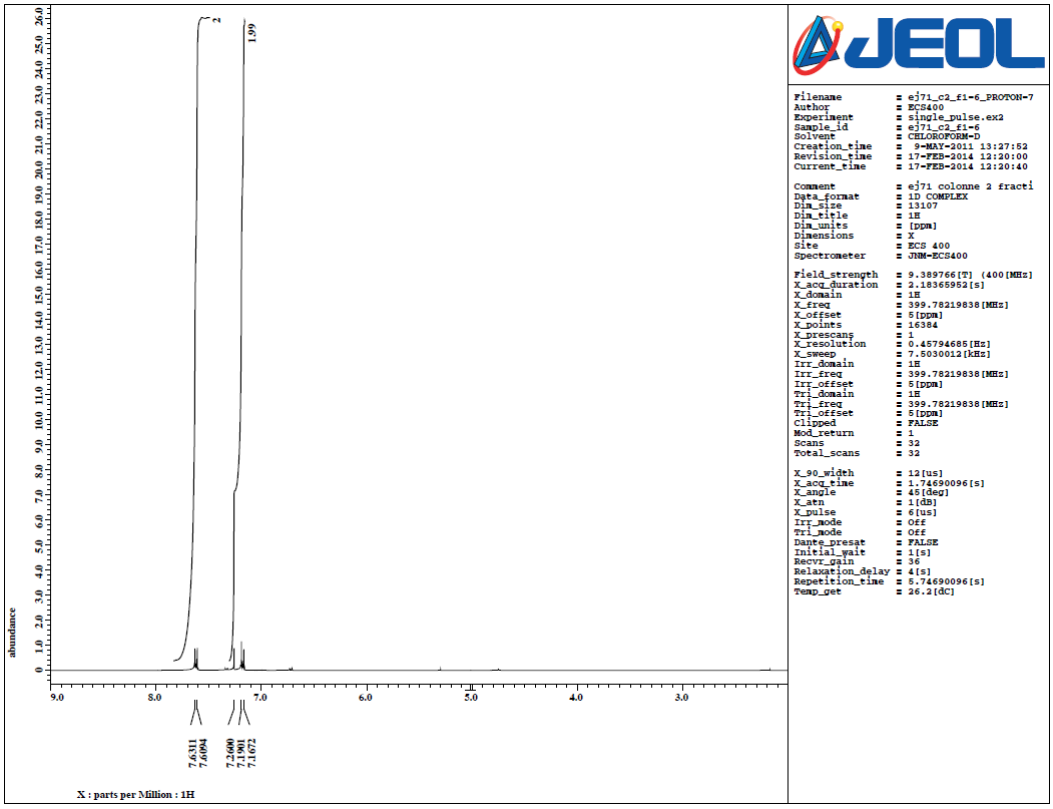


Figure 18: ^{13}C NMR of 3-chloro-6-(4-bromophenoxy)-*s*-tetrazine **1d**

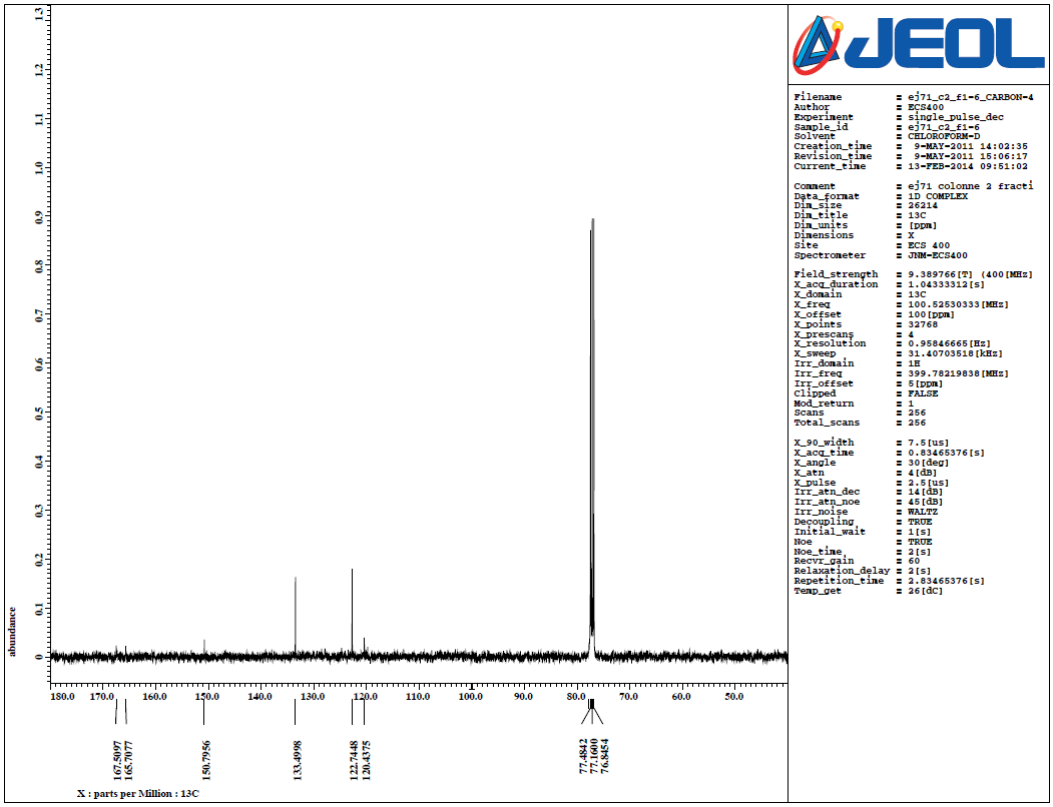


Figure 19: ^{1}H NMR of 3-methoxy-6-(4-bromophenoxy)-*s*-tetrazine **2d**

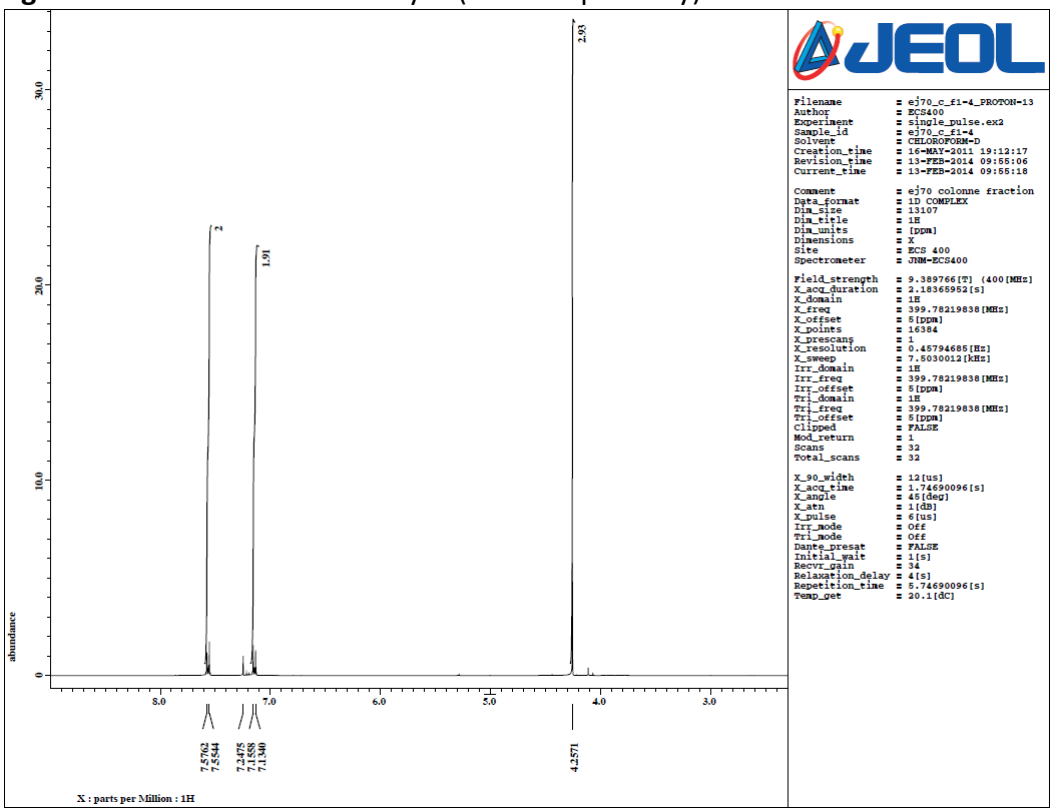


Figure 20: ^{13}C NMR of 3-methoxy-6-(4-bromophenoxy)-*s*-tetrazine **2d**

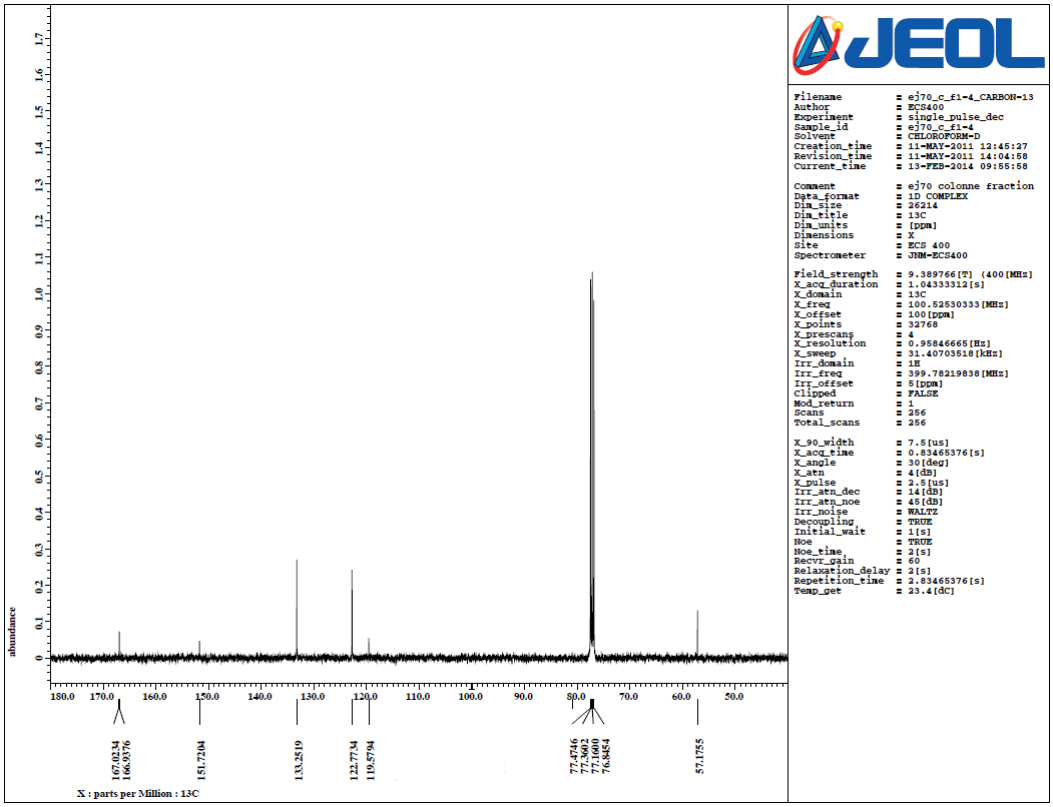


Figure 21: ^{1}H NMR of 3,6-di-(4-bromophenoxy)-*s*-tetrazine **3d**

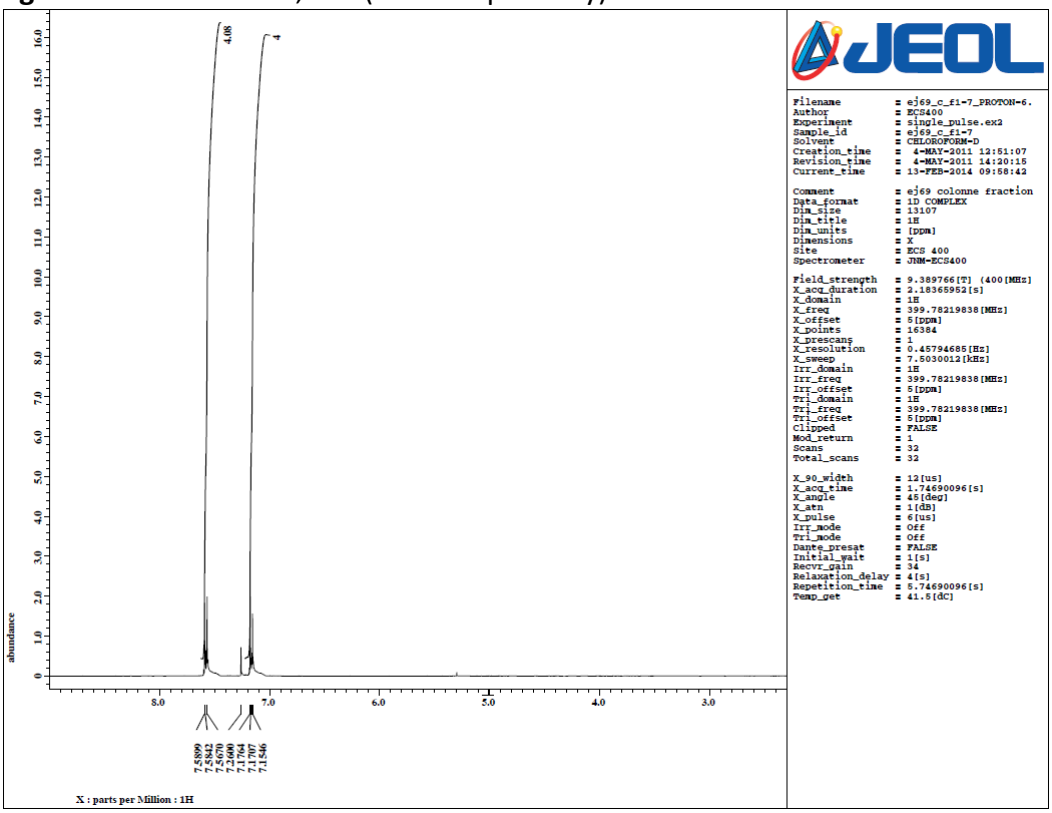


Figure 22: ^{13}C NMR of 3,6-di-(4-bromophenoxy)-*s*-tetrazine **3d**

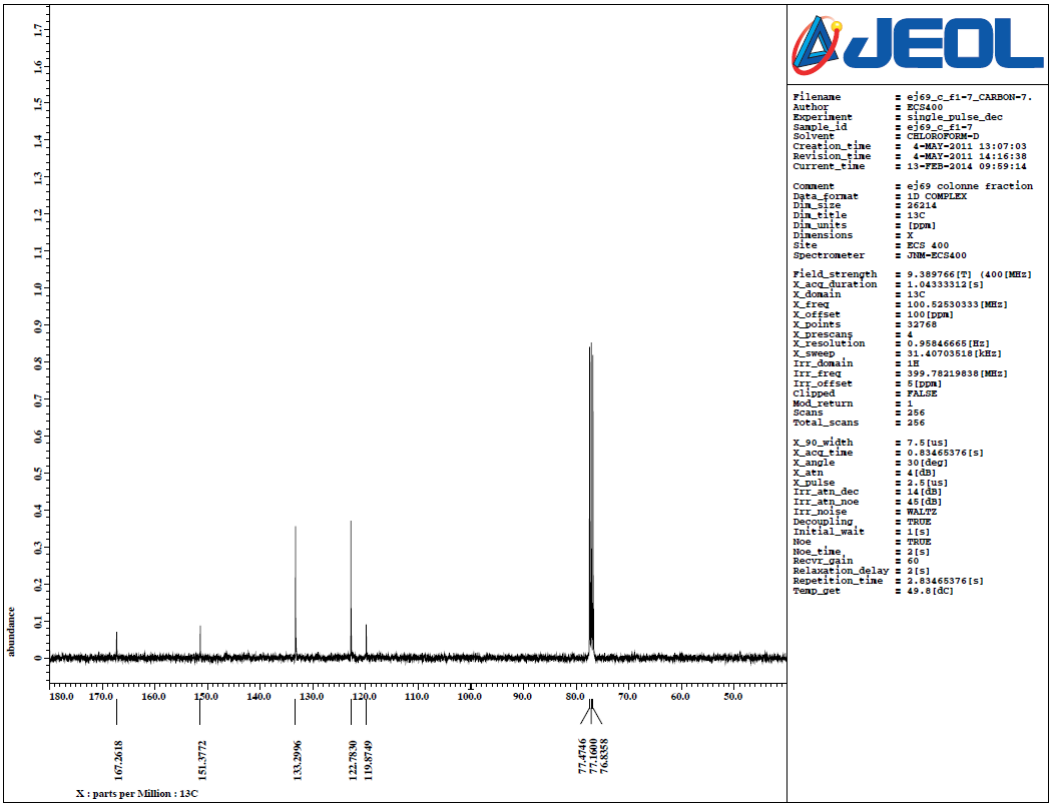


Figure 23: ^{1}H NMR of 3-chloro-6-(4-chlorophenoxy)-*s*-tetrazine **1e**

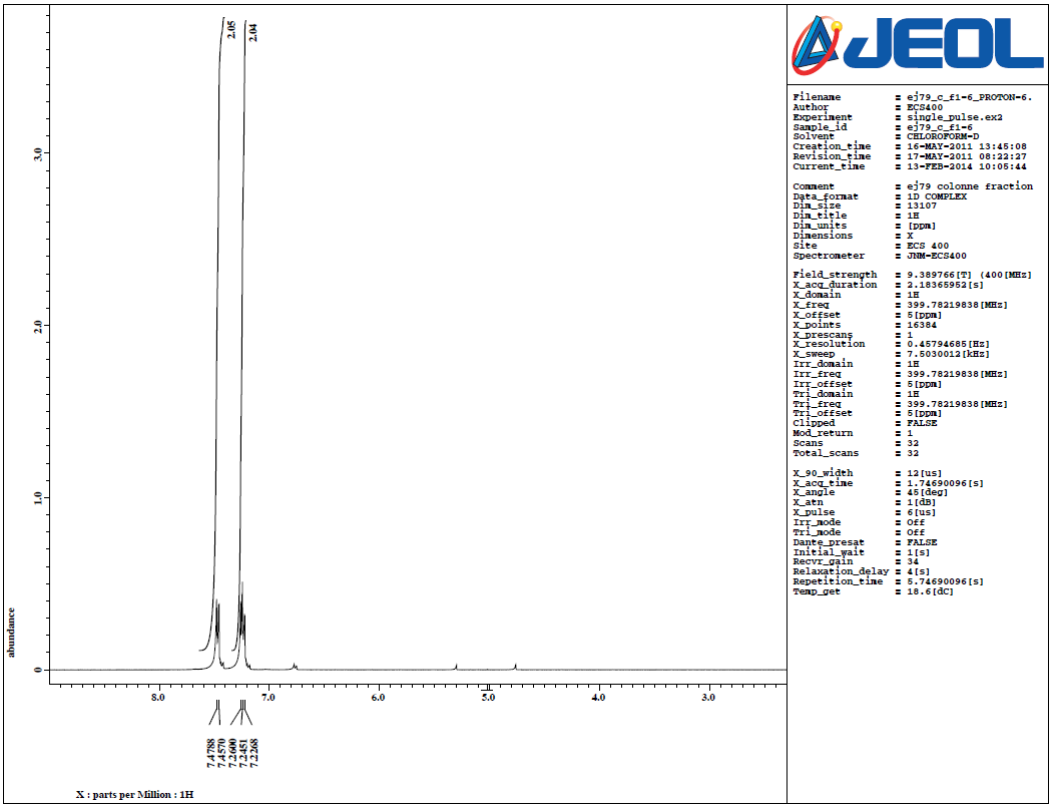


Figure 24: ^{13}C NMR of 3-chloro-6-(4-chlorophenoxy)-*s*-tetrazine **1e**

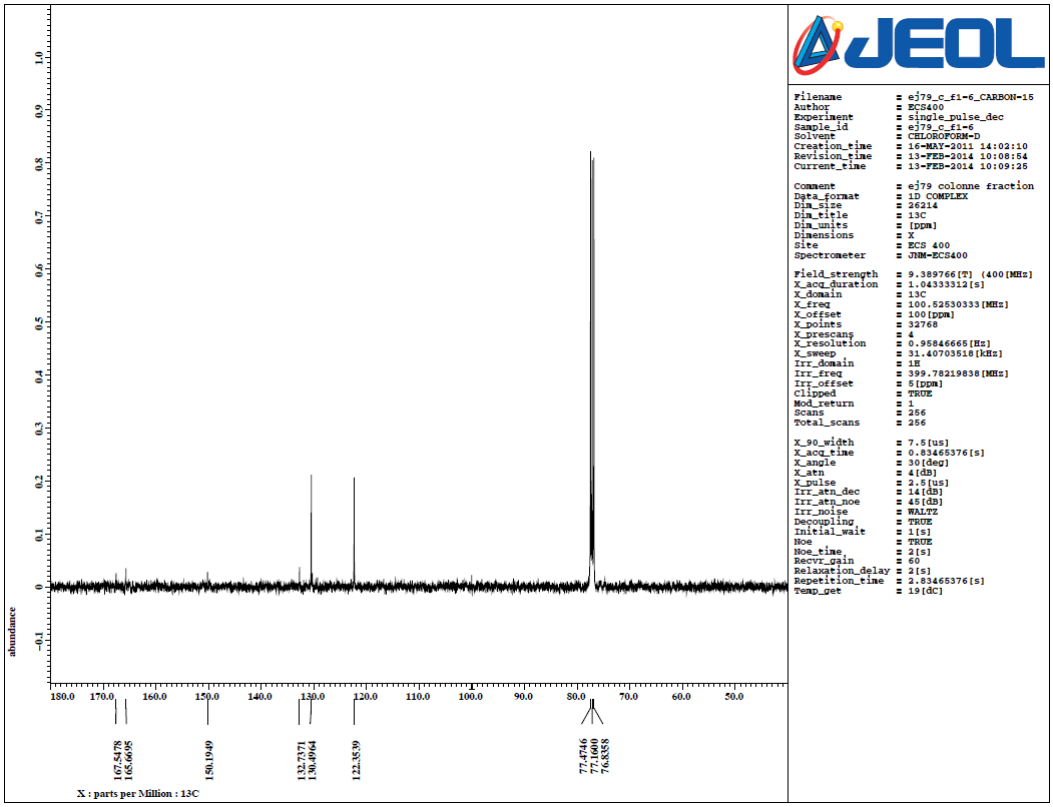


Figure 25: ^{1}H NMR of 3-methoxy-6-(4-chlorophenoxy)-*s*-tetrazine **2e**

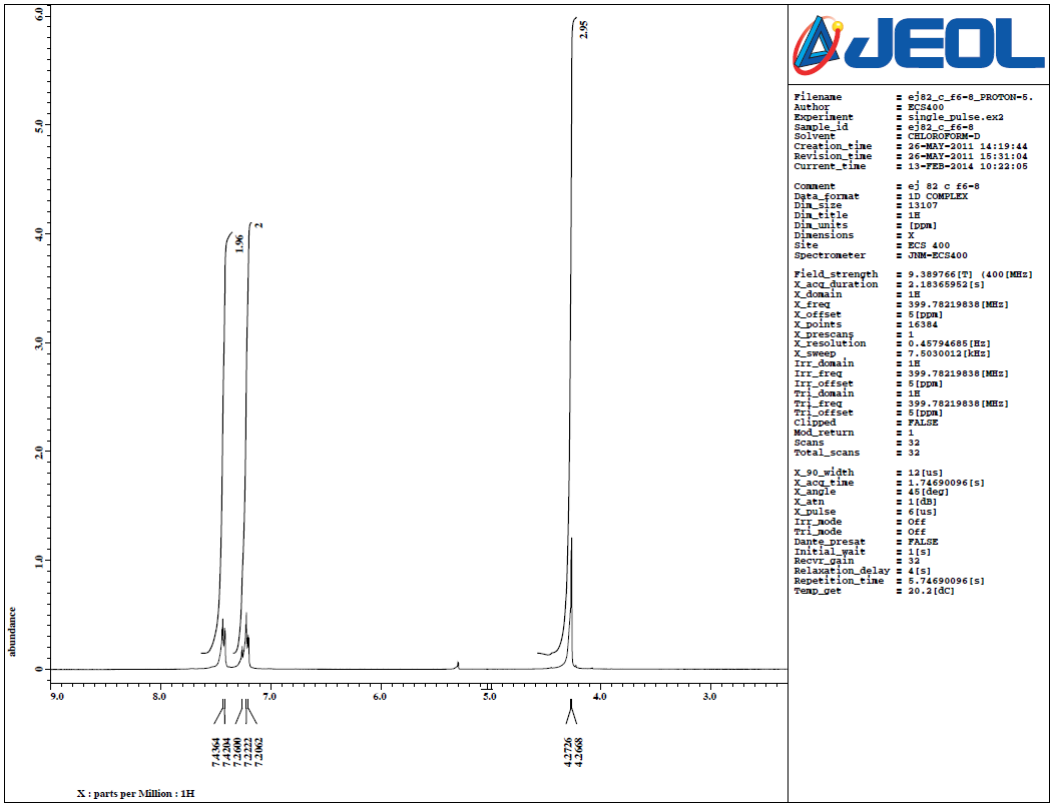


Figure 26: ^{13}C NMR of 3-methoxy-6-(4-chlorophenoxy)-*s*-tetrazine **2e**

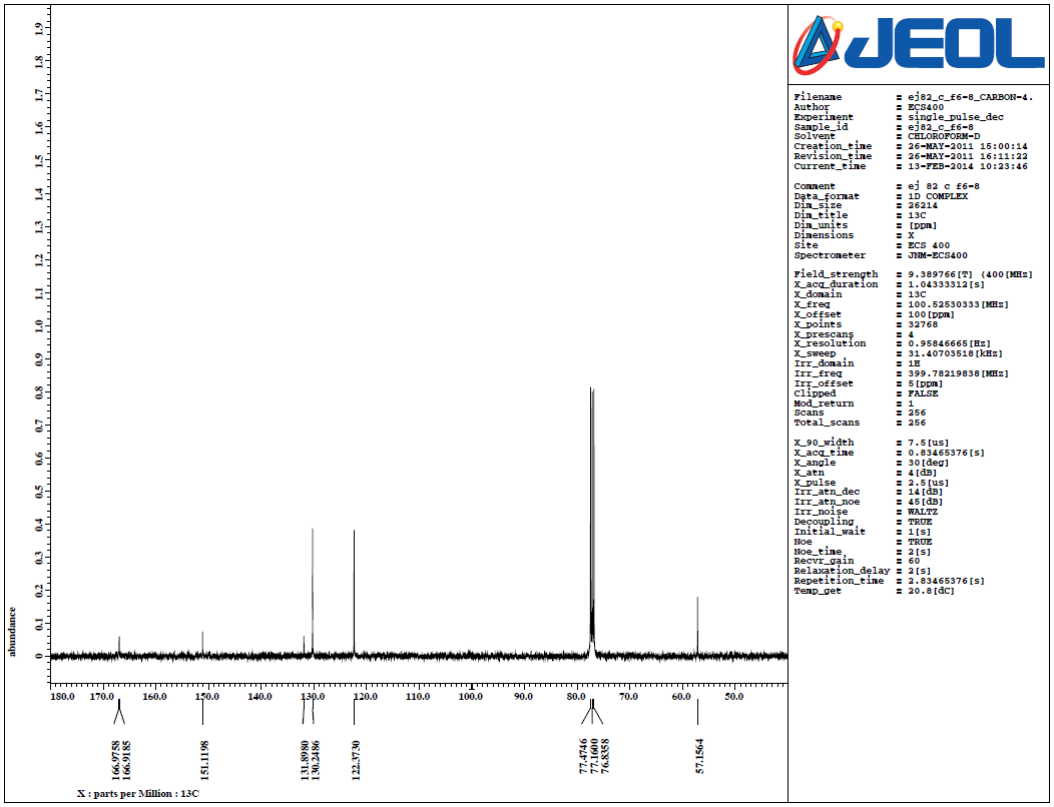


Figure 27: ^{1}H NMR of 3,6-di-(4-chlorophenoxy)-*s*-tetrazine **3e**

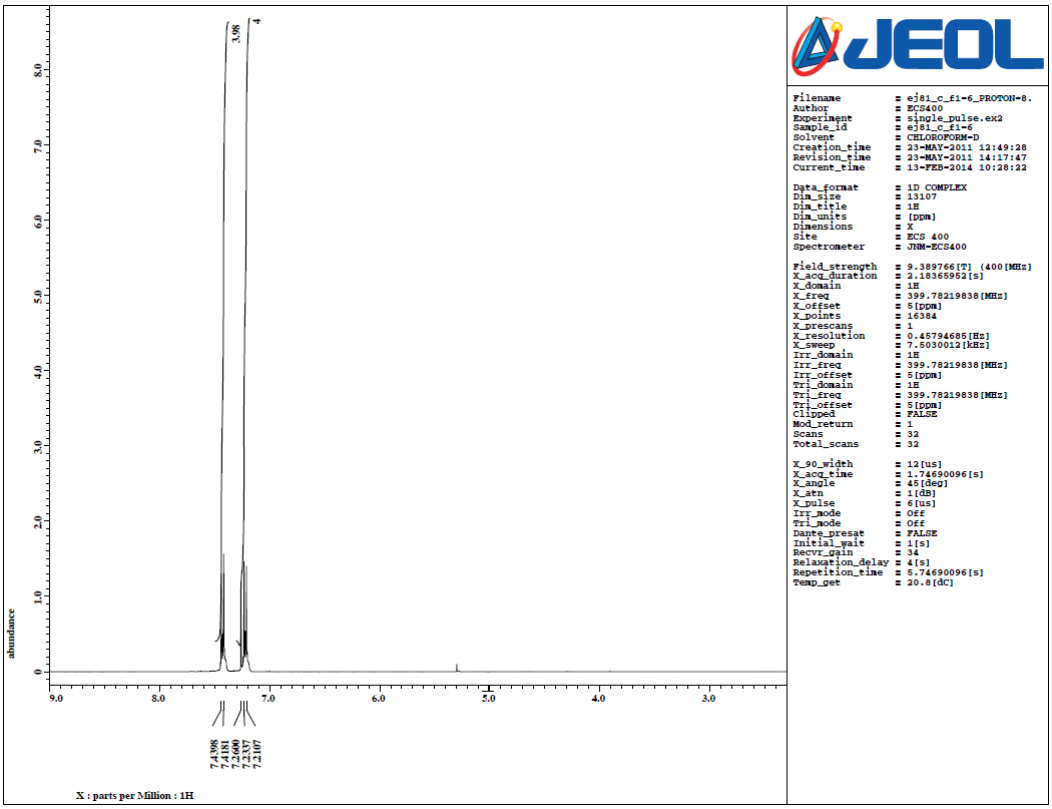


Figure 28: ^{13}C NMR of 3,6-di-(4-chlorophenoxy)-*s*-tetrazine **3e**

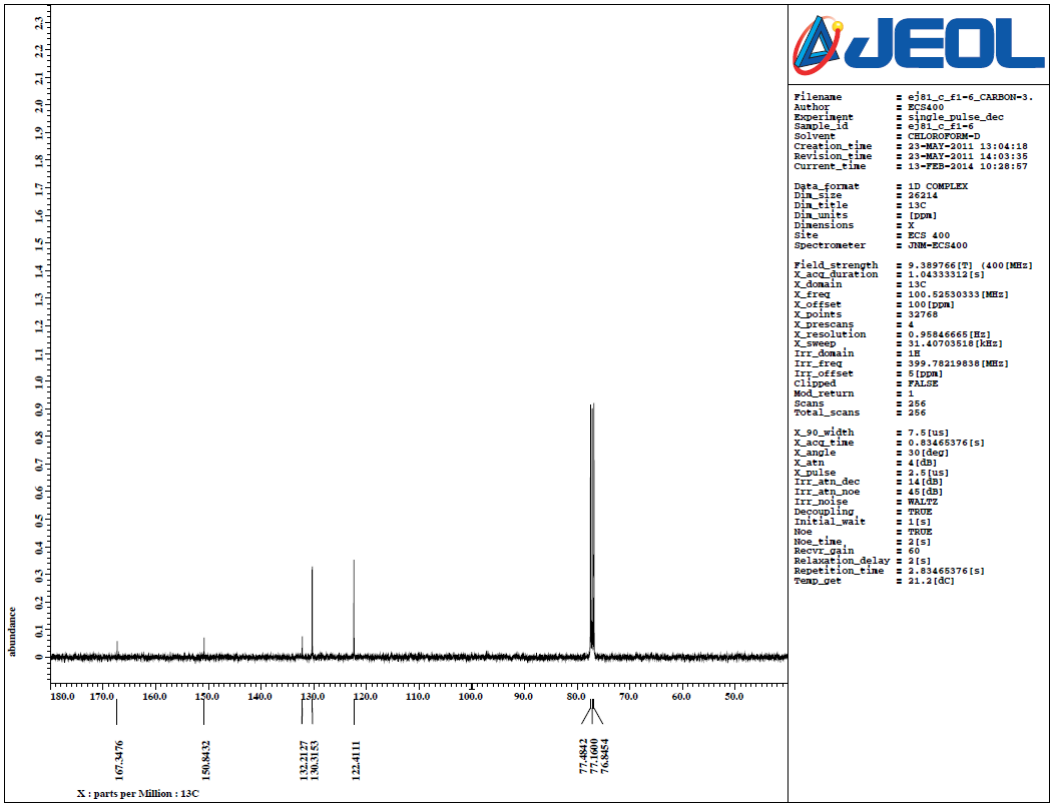


Figure 29: ^{1}H NMR of 3-chloro-6-(3-chlorophenoxy)-*s*-tetrazine **1f**

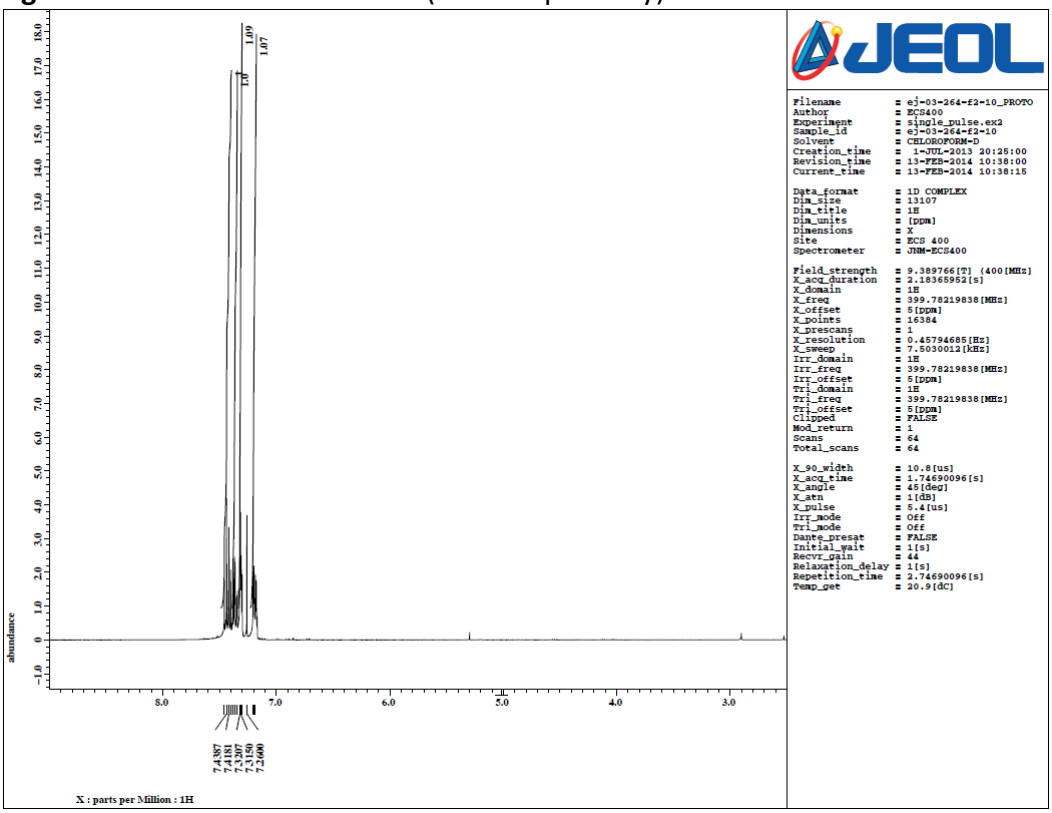


Figure 30: ^{13}C NMR of 3-chloro-6-(3-chlorophenoxy)-*s*-tetrazine **1f**

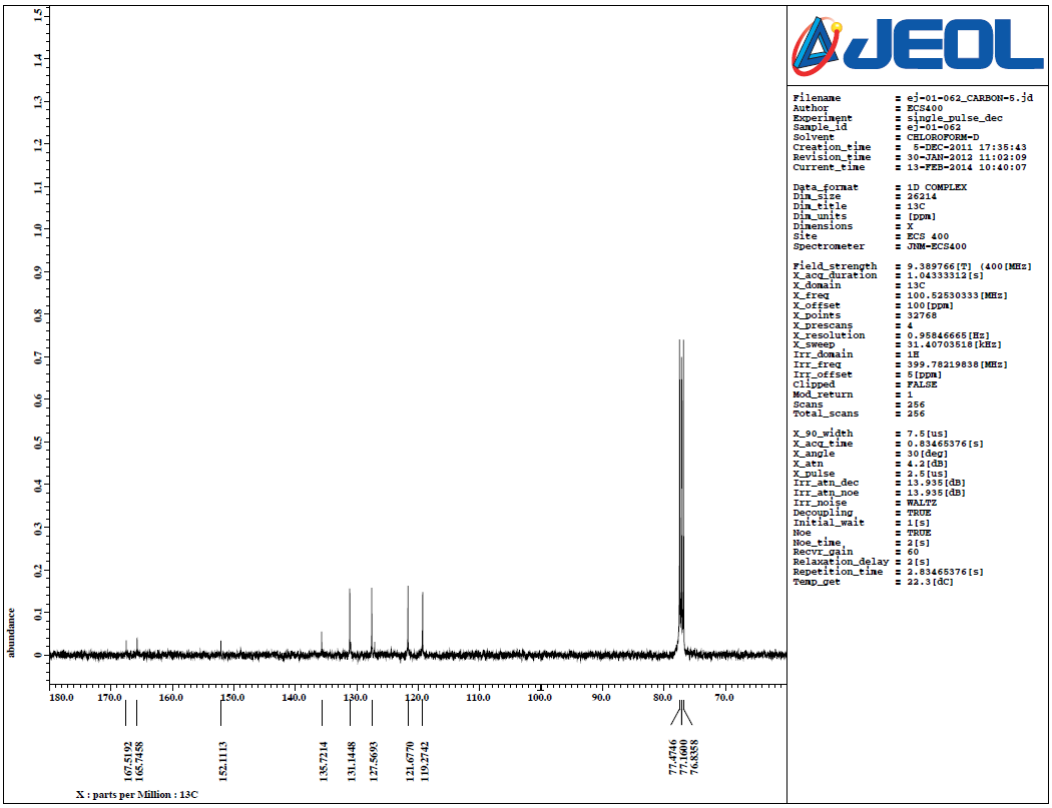


Figure 31: ^{1}H NMR of 3-methoxy-6-(3-chlorophenoxy)-*s*-tetrazine **2f**

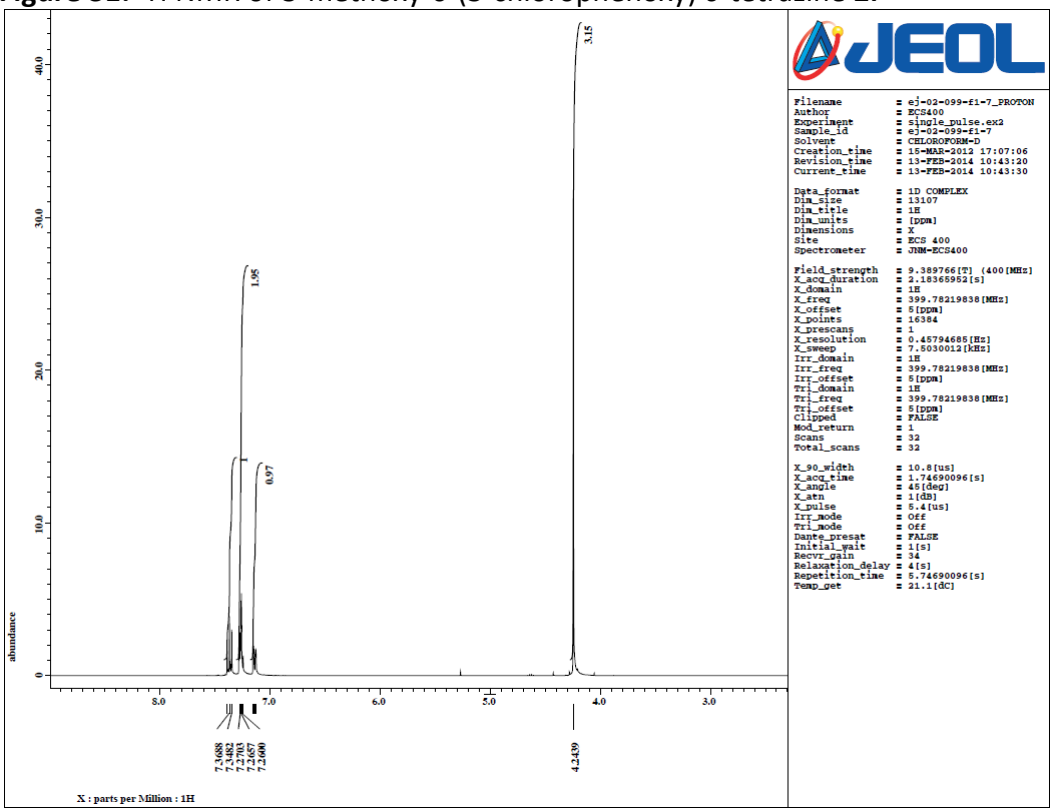


Figure 32: ^{13}C NMR of 3-methoxy-6-(3-chlorophenoxy)-*s*-tetrazine **2f**

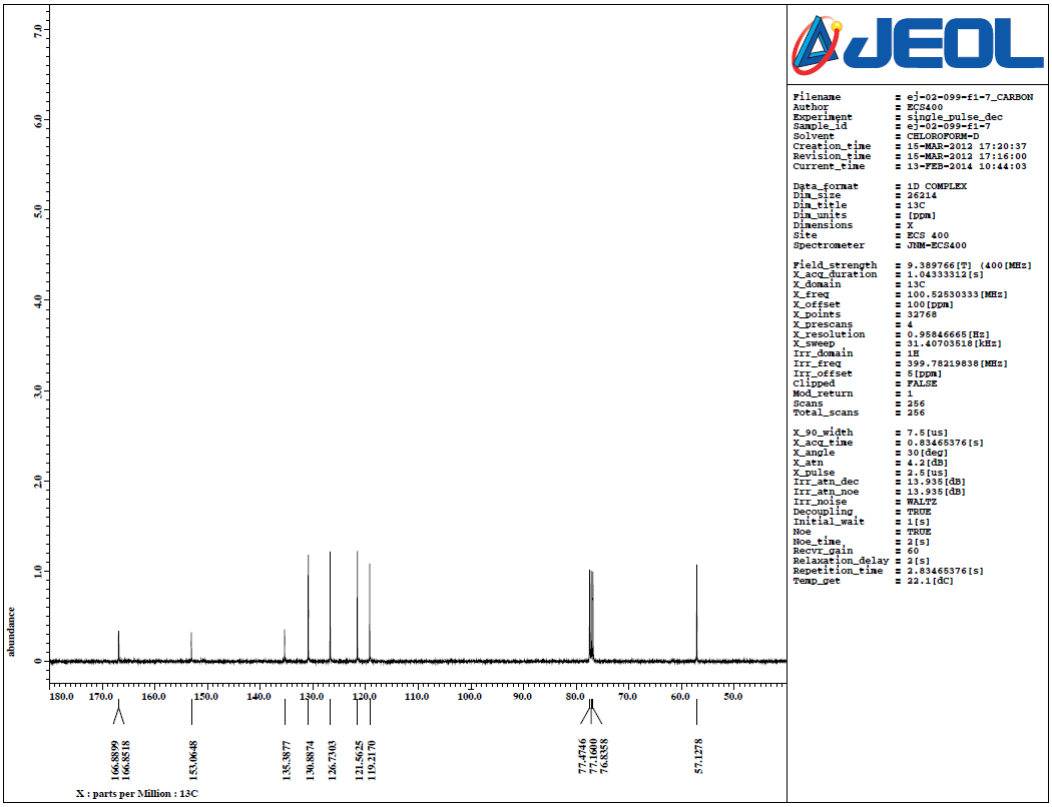


Figure 33: ^{1}H NMR of 3,6-di-(3-chlorophenoxy)-*s*-tetrazine **3f**

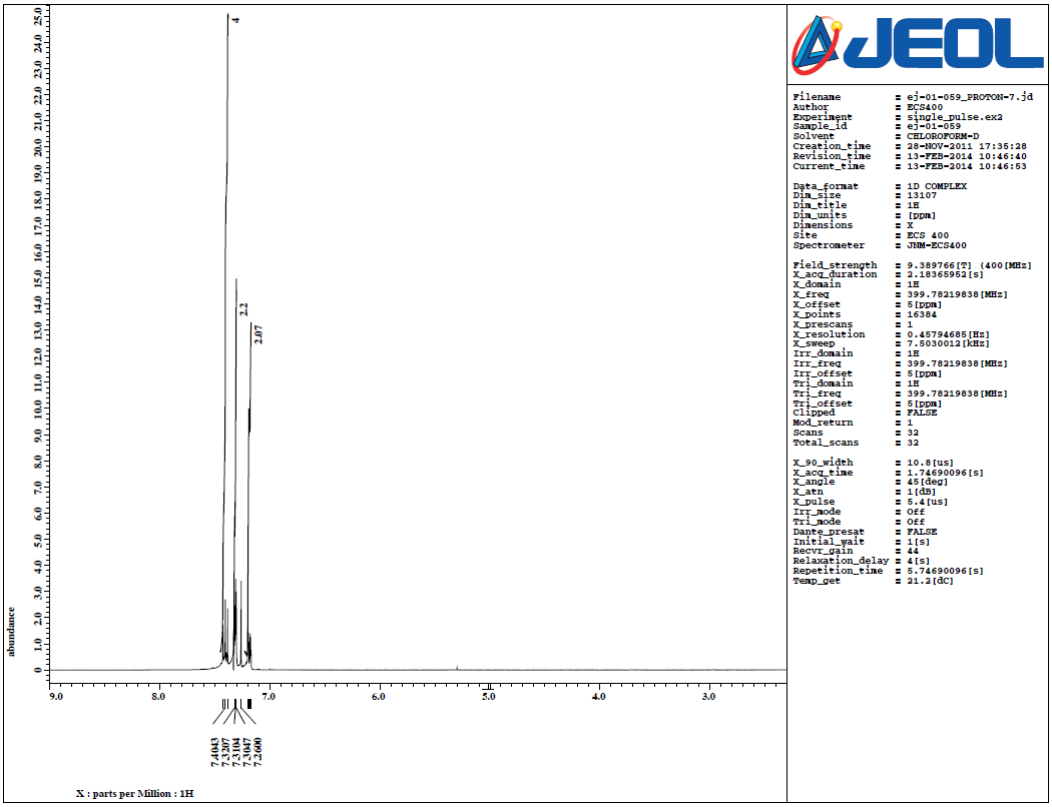


Figure 34: ^{13}C NMR of 3,6-di-(3-chlorophenoxy)-*s*-tetrazine **3f**

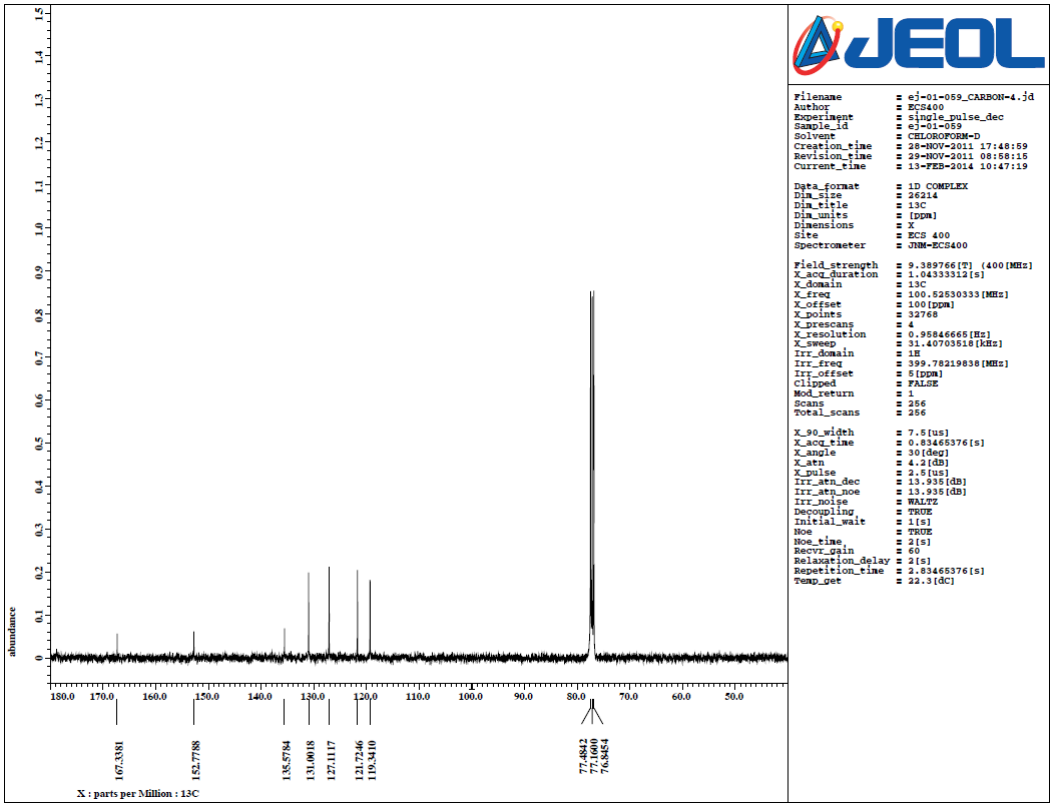


Figure 35: ^{1}H NMR of 3-chloro-6-(4-tertbutylphenoxy)-*s*-tetrazine **1g**

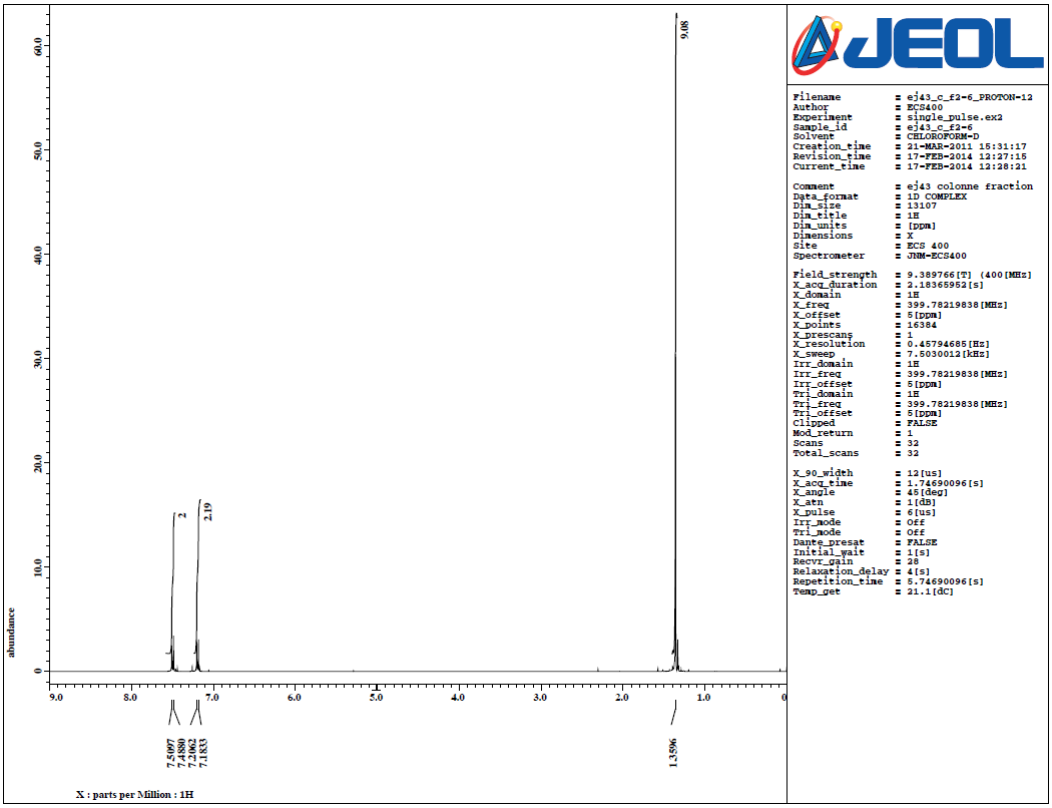


Figure 36: ^{13}C NMR of 3-chloro-6-(4-*tert*butylphenoxy)-*s*-tetrazine **1g**

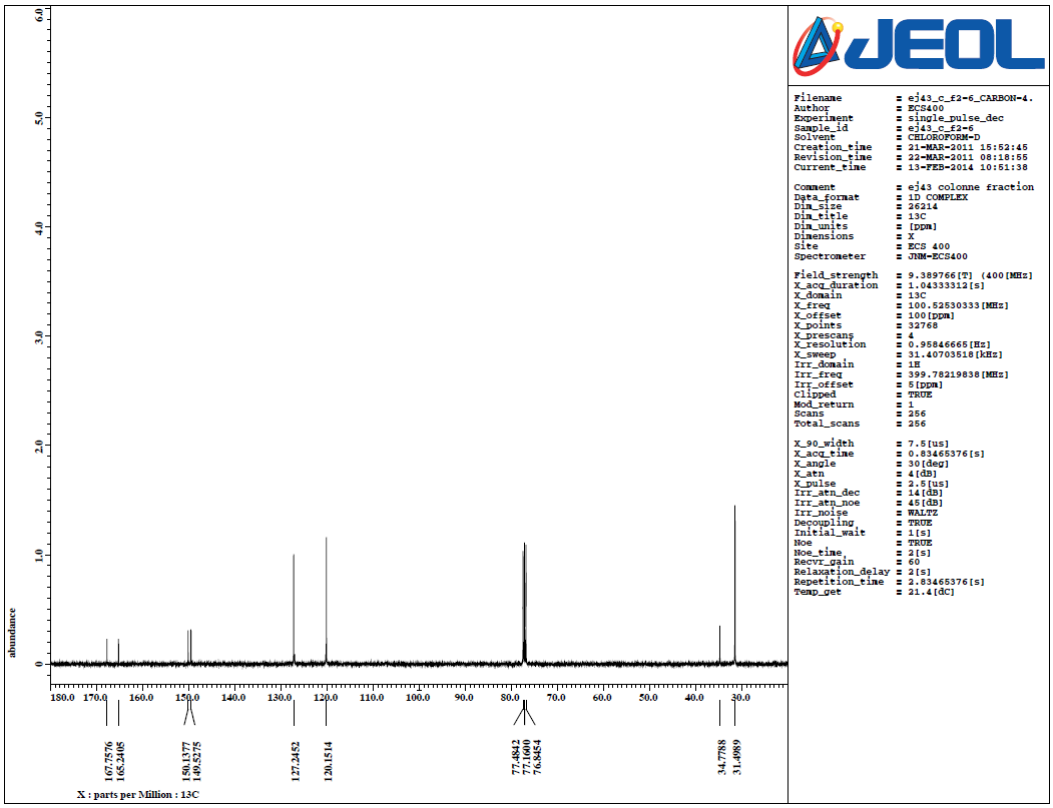


Figure 37: ^{1}H NMR of 3-methoxy-6-(4-*tert*butylphenoxy)-*s*-tetrazine **2g**

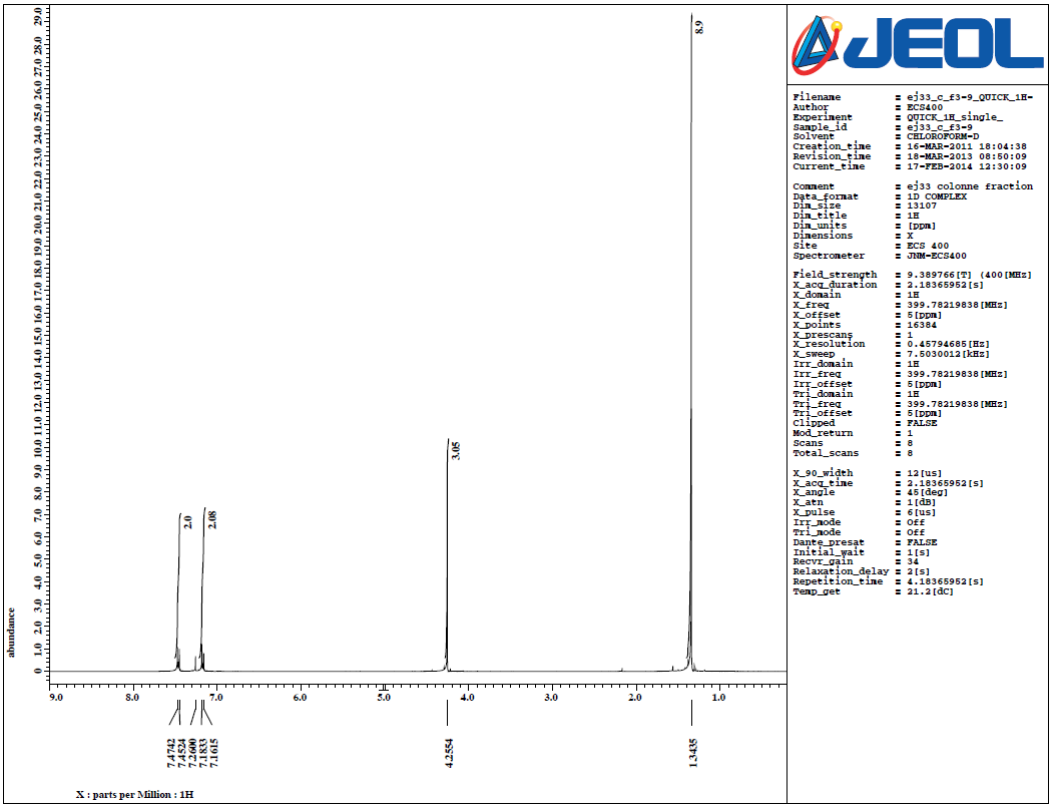


Figure 38: ^{13}C NMR of 3-methoxy-6-(4-*tert*butylphenoxy)-*s*-tetrazine **2g**

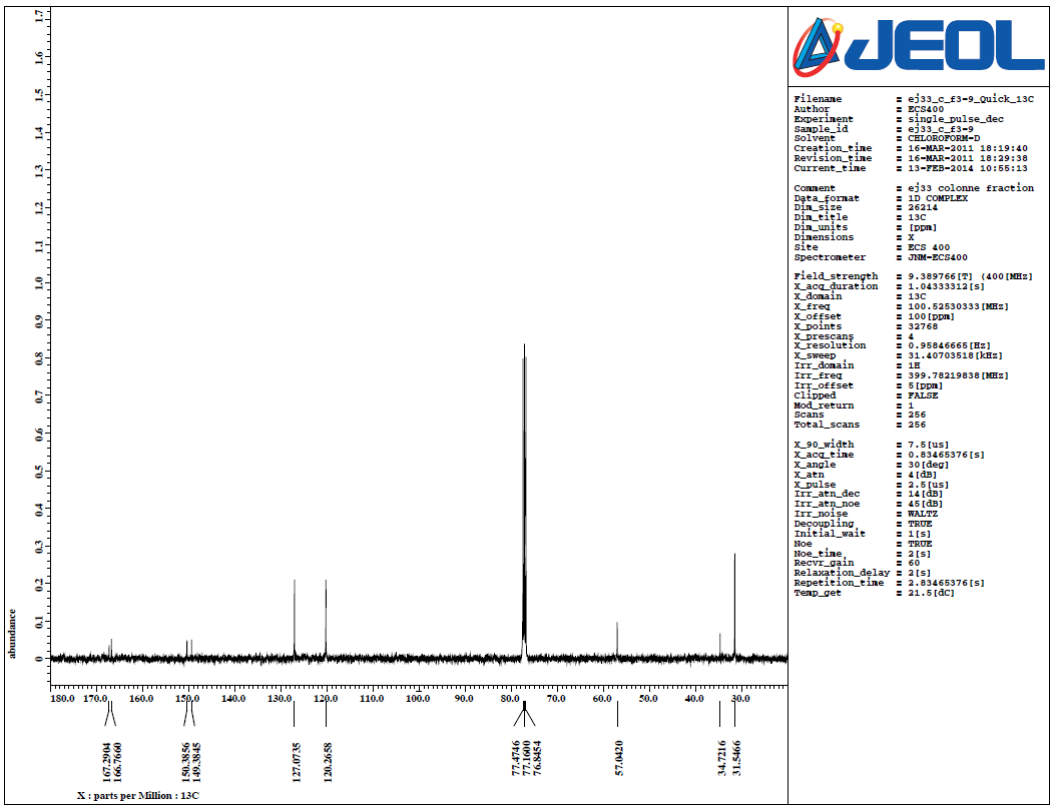


Figure 39: ^{1}H NMR of 3,6-di-(4-*tert*butylphenoxy)-*s*-tetrazine **3g**

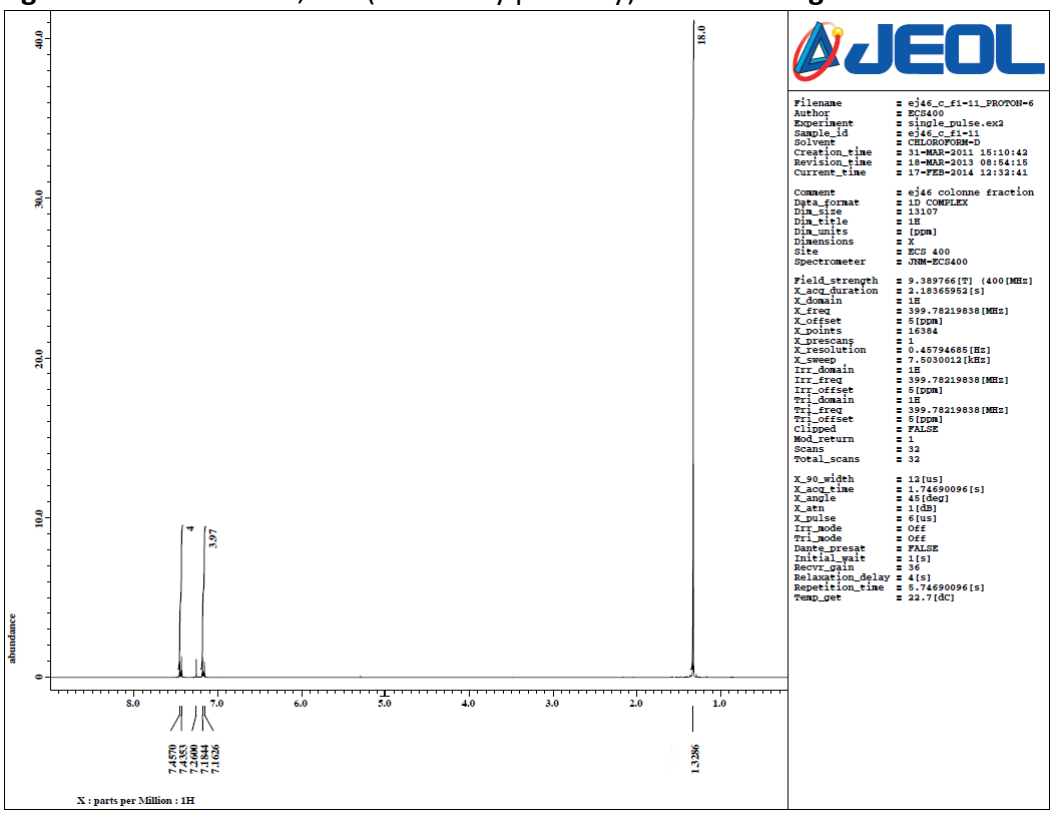


Figure 40: ^{13}C NMR of 3,6-di-(4-*tert*butylphenoxy)-*s*-tetrazine **3g**

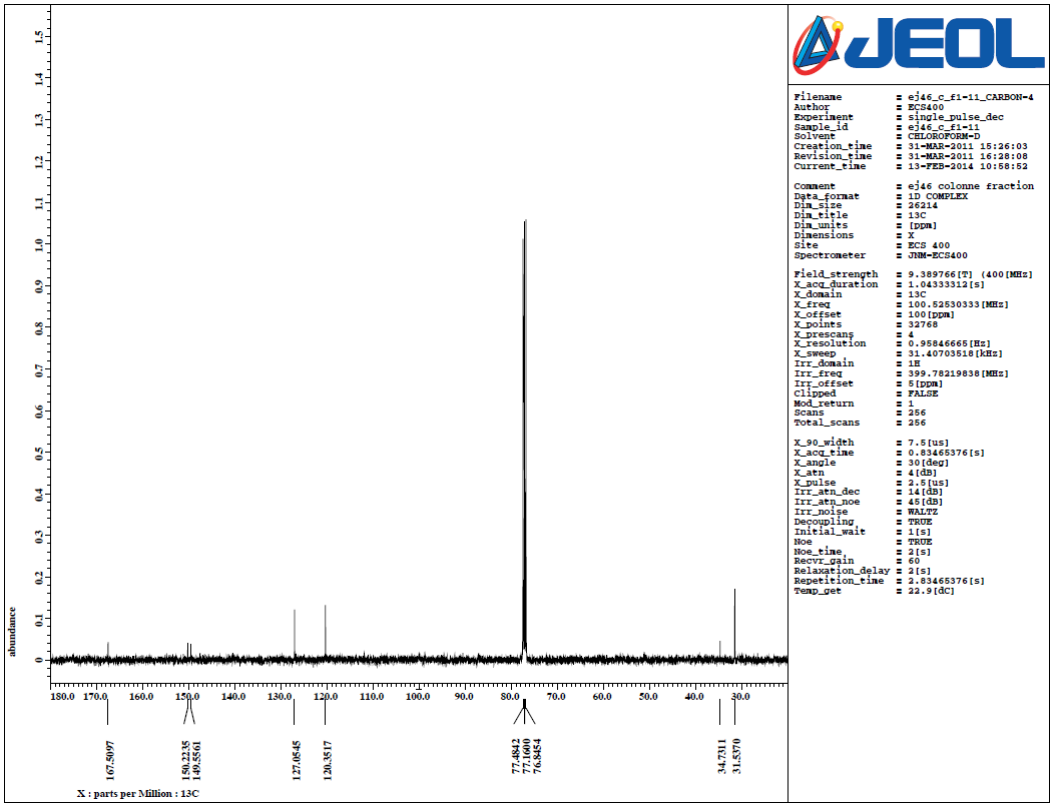


Figure 41: ^{1}H NMR of 4-decyloxyphenol **h**

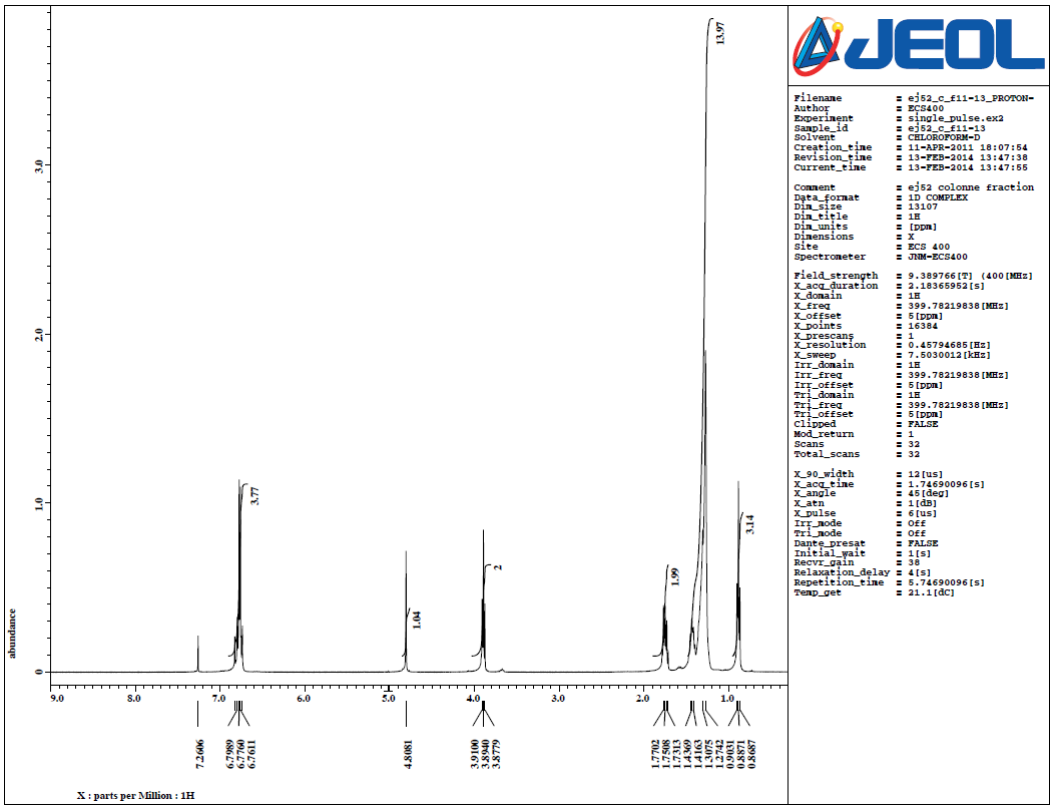


Figure 42: ^{13}C NMR of 4-decyloxyphenol **h**

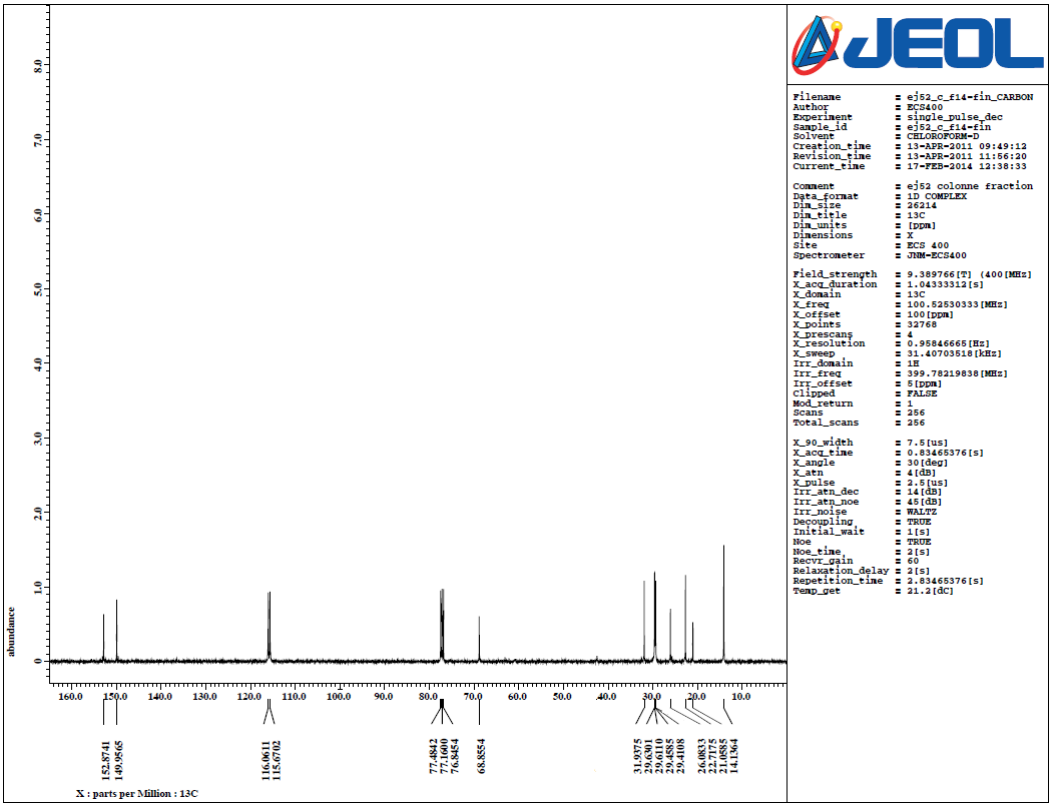


Figure 43: ^{1}H NMR of 3-chloro-6-(4-decyloxyphenoxy)-*s*-tetrazine **1h**

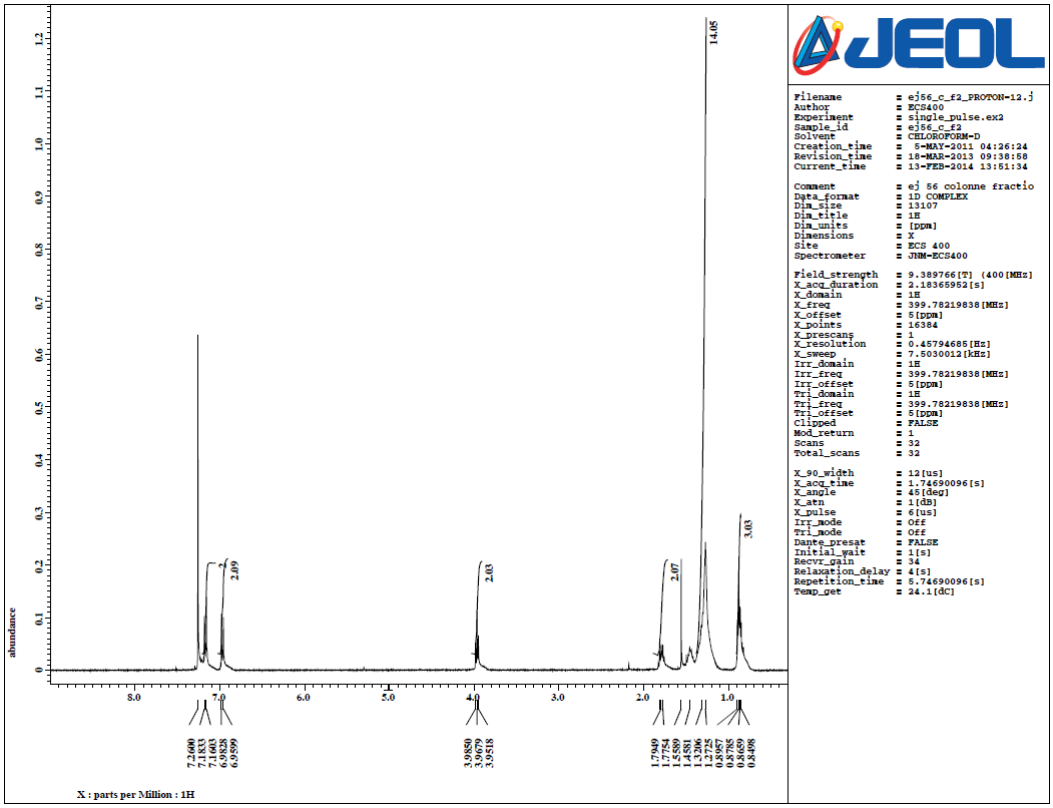


Figure 44: ^{13}C NMR of 3-chloro-6-(4-decyloxyphenoxy)-*s*-tetrazine **1h**

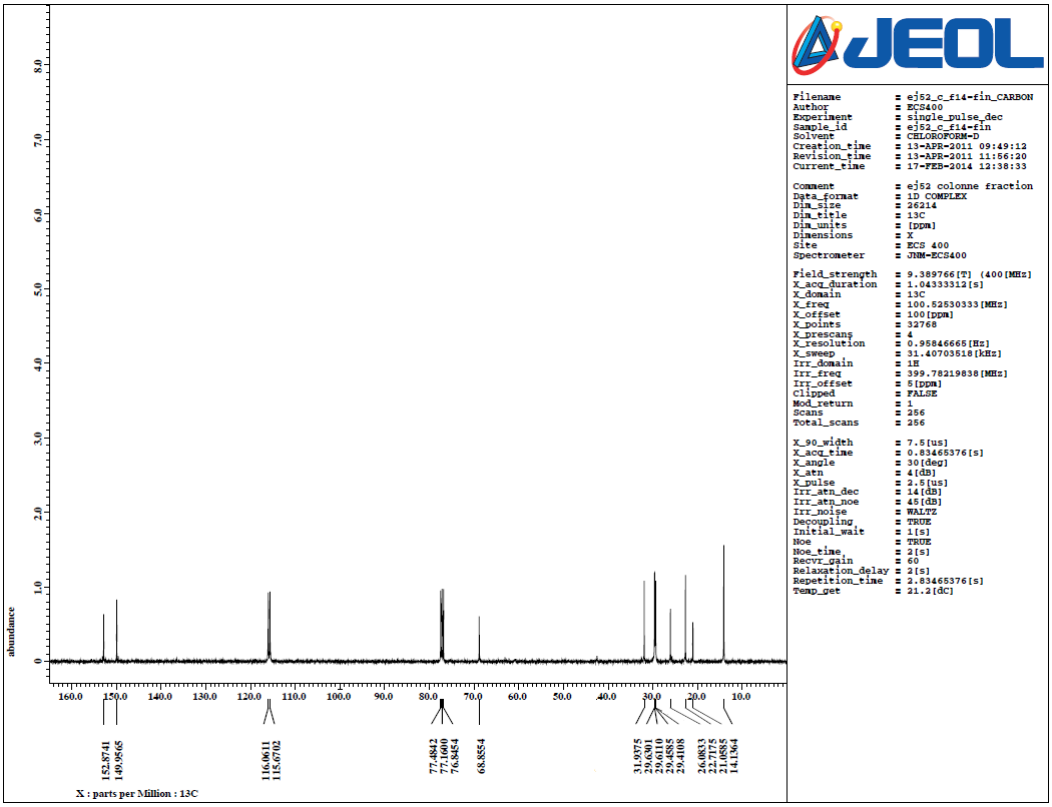


Figure 45: ^{1}H NMR of 3-methoxy-6-(4-decyloxyphenoxy)-*s*-tetrazine **2h**

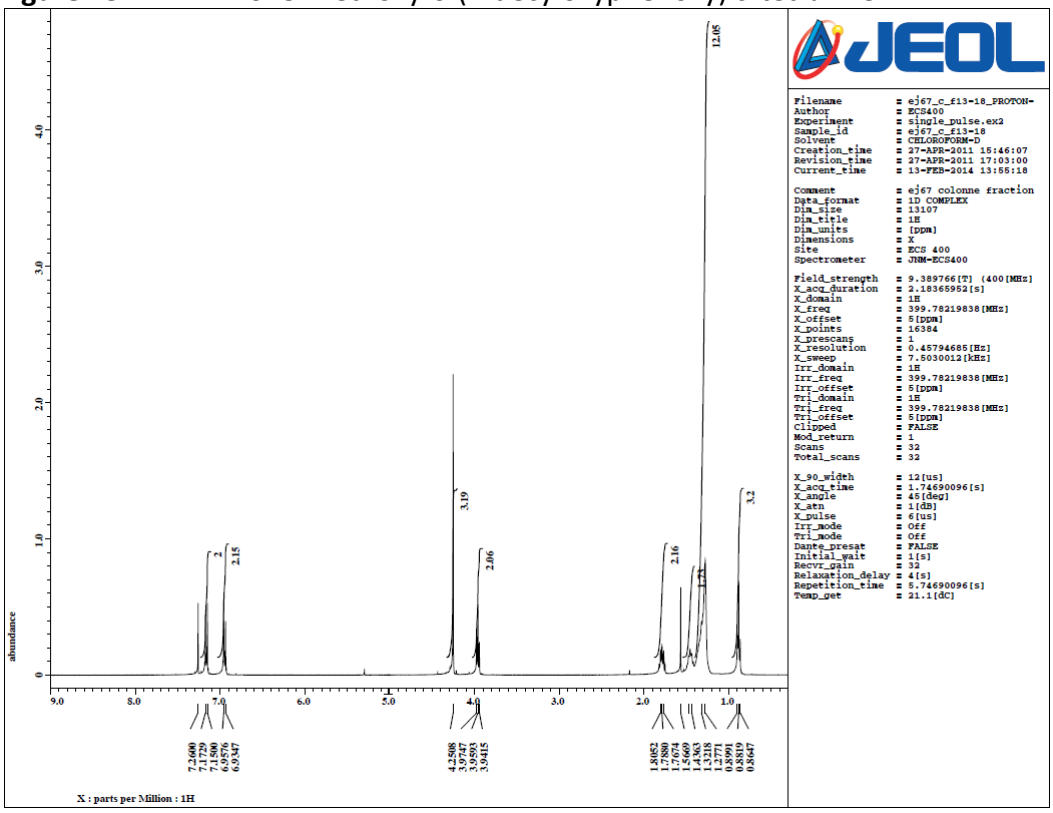


Figure 46: ^{13}C NMR of 3-methoxy-6-(4-decyloxyphenoxy)-*s*-tetrazine **2h**

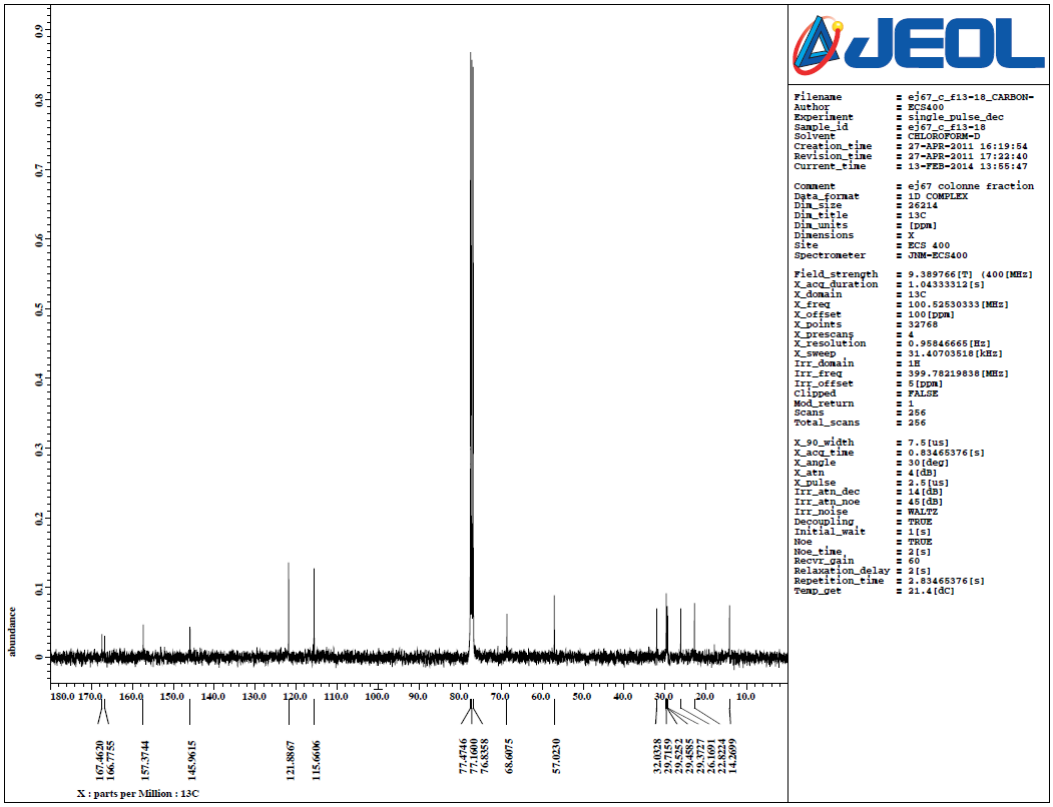


Figure 47: ^{1}H NMR of 3,6-di-(4-decyloxyphenoxy)-*s*-tetrazine **3h**

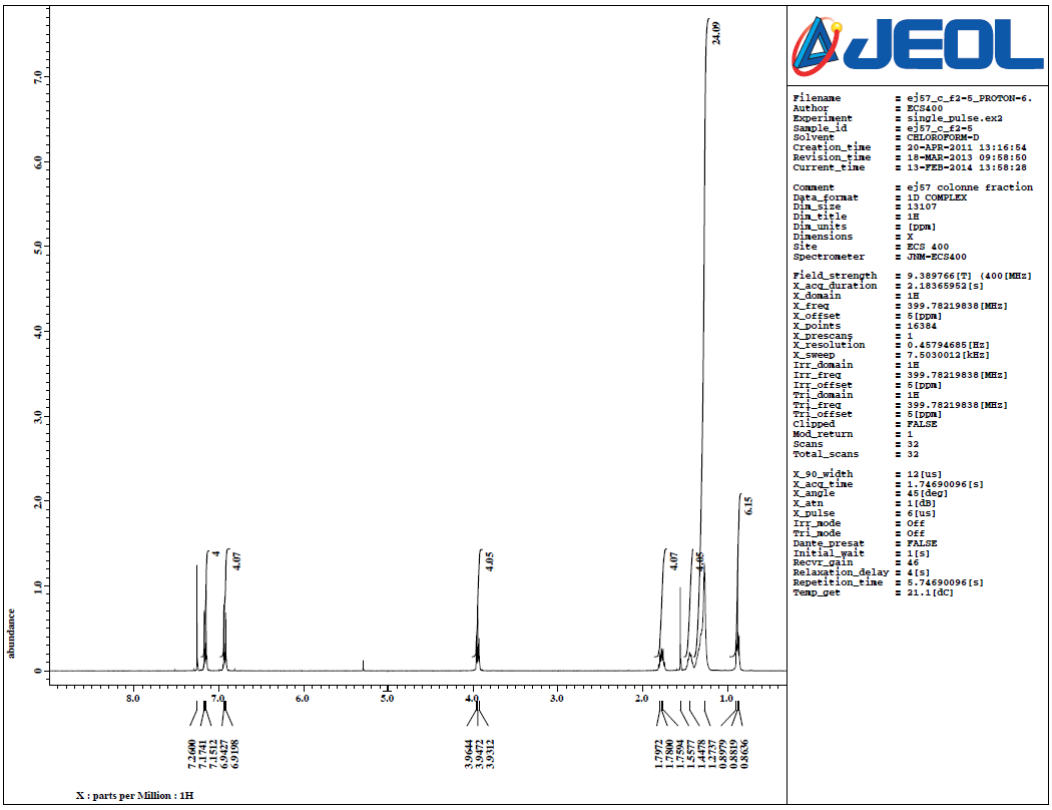
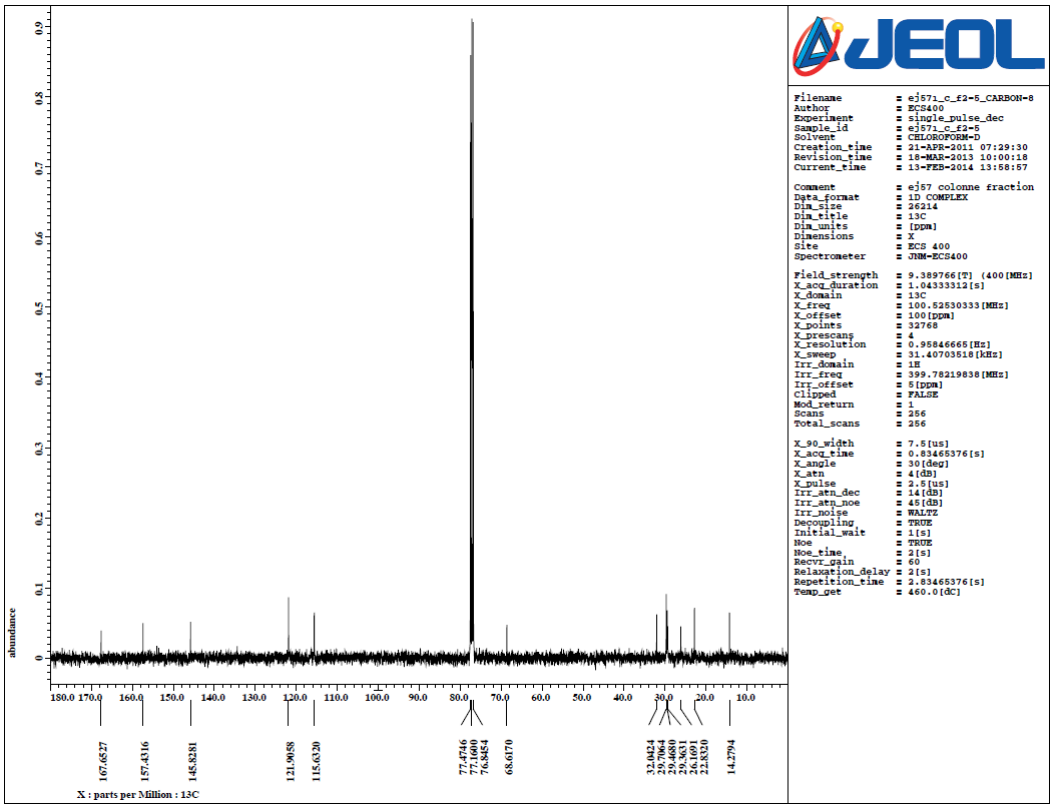


Figure 48: ^{13}C NMR of 3,6-di-(4-decyloxyphenoxy)-*s*-tetrazine **3h**



Time-resolved quenching experiments

Figure 49: Fluorescence decays of 3-chloro-6-(4-oxophenoxy)-*s*-tetrazine **1b** (5.0.10-4 M in dichloromethane) in the presence of increasing amounts of toluene (excitation 355 nm, emission 566 nm)

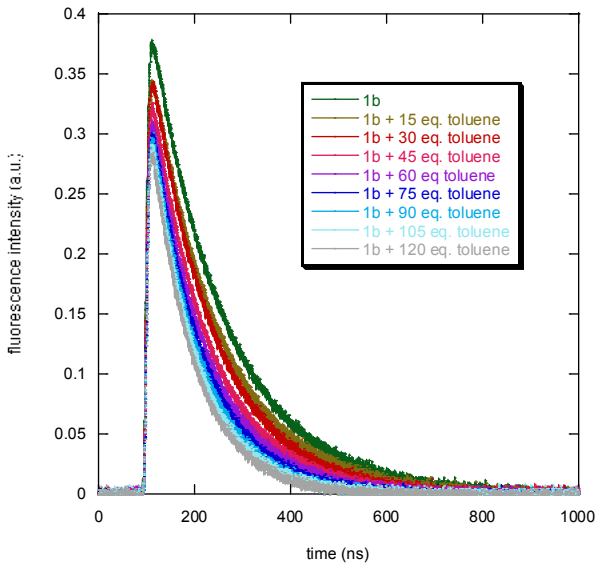


Figure 50: Fluorescence decays of 3,6-di-(4-nitrophenoxy)-*s*-tetrazine **3c** (3.8.10-4 M in dichloromethane) in the presence of increasing amounts of xylene (excitation 355 nm, emission 575 nm)

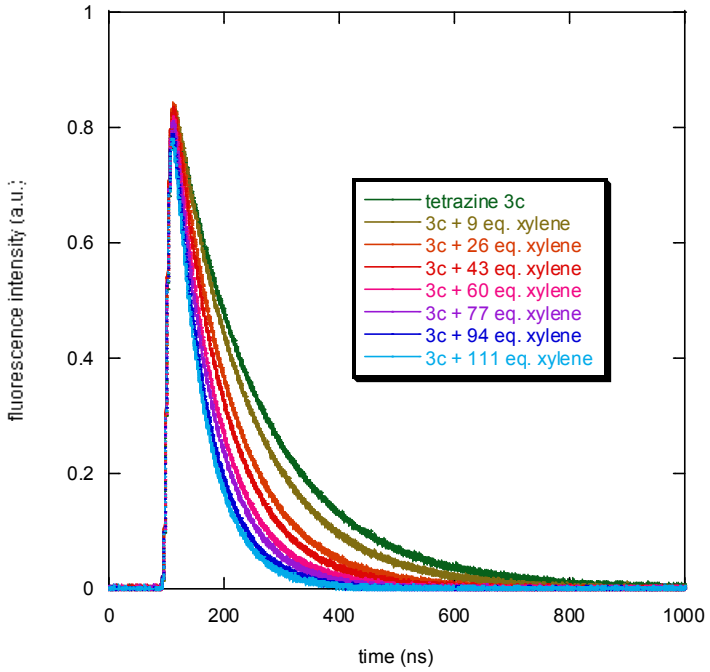


Figure 51: Fluorescence decays of 3-chloro-6-(3-chlorophenoxy)-*s*-tetrazine **1f** (5.0.10-4 M in dichloromethane) in the presence of increasing amounts of styrene (excitation 355 nm, emission 571 nm)