Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

C_3 Symmetric Ferrocenyl Triazines: Synthesis, Structure, and Properties

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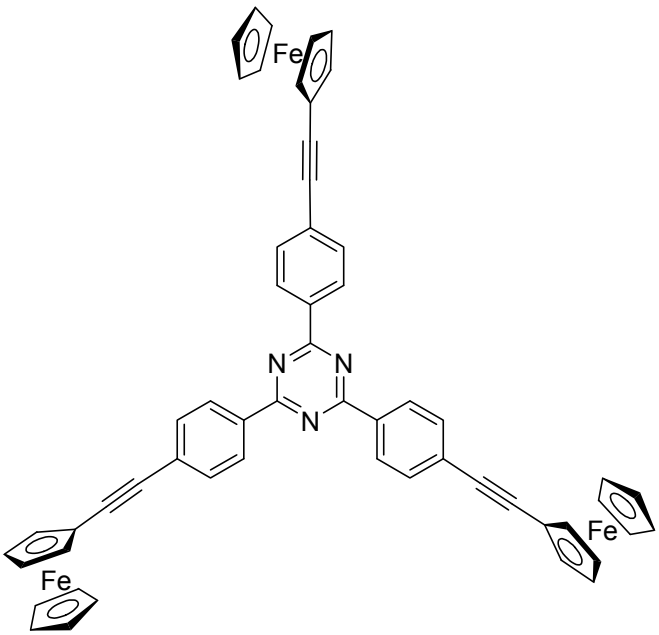
1) **General Experimental**. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on Bruker Advance (III) 400 MHz. Chemical shifts in 1H, and 13C NMR spectra were reported in parts per million (ppm) with TMS (0 ppm), and CDCl3 (77.23 ppm) as standards. UV-Visible absorption spectra of all compounds in CH2Cl2 were recorded on Carry-100 Bio UV-Visible Spectrophotometer. All microwave reactions were performed on CEM Discover microwave instrument (Model No – 908010). Electrochemical characterization of all compounds was done by cyclic voltametry. Cyclic voltammograms (CVs) was recorded on CHI620D electrochemical analyzer using Glassy carbon as a working electrode, Platinum wire as the counter electrode, and Ag/AgCl as the reference electrode. The scan rate was 100 mVS-1. A solution of tetrabutylammonium - hexafluorophosphate ($TBAPF_6$) in THF (0.1 M) was employed as the supporting electrolyte. The half-wave oxidation potential of ferrocene was measured to be 0.58 V against Ag/AgCl. HRMS was recorded on Brucker-Daltonics, Micro-TOF-Q II mass spectrometer. Column chromatography was performed on Merck silica gel (230-400 mesh). All reagents were obtained from commercial sources, and used as received unless otherwise stated.

2) Synthesis, and Structures and ^{1}H NMR, ^{13}C NMR, and Mass (HRMS) spectroscopy data and TGA, DSC data, cyclic voltammograms of ferrocene substituted triazine 3-6

2,4,6-Tris-(4-ferrocenylethynyl-phenyl)-1,3,5-triazine (3)

The triazine **2a** (0.200 g, 0.36 mmol) was dissolved in the mixture of toluene 30 ml, and THF 10 ml (3:1), triethylamine (5 ml), and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.04 mmol), PPh_3 (0.0106 g, 0.04mmol), ethynyl ferrocene (0.260 g, 1.23 mmol) was added under argon atmosphere, and stirred for 16 h at 60 ^oC, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica gel, using hexane/ DCM (60:40) to get triazine **3** as a orange solid (0.136 g, 40%); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.67 (d, 6H, *J* = 8.3 Hz), 7.61 (d, 6H, *J* = 8.3 Hz), 4.50 (s, 7H), 4.22 (s, 7H), 4.22 (s, 13H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.13, 135.06, 131.56, 128.86, 128.36 , 91.93, 85.85, 71.62, 70.07, 69.15, 64.76 ppm; HRMS (ESI): calcd. for $C_{57}H_{39}Fe_3N_3$ 933.1191 [M^+]; found 933.1155.



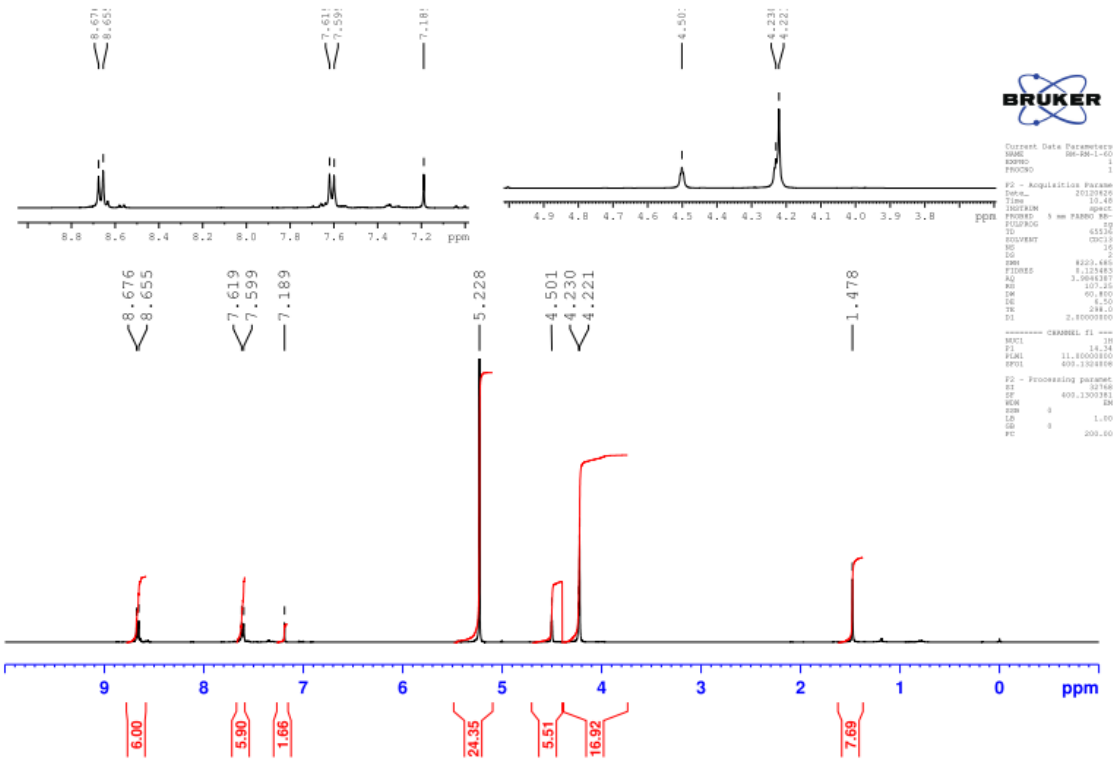


Fig. S-1: ^{1}H-NMR spectrum of compound **3** recorded in $CDCl_3$.

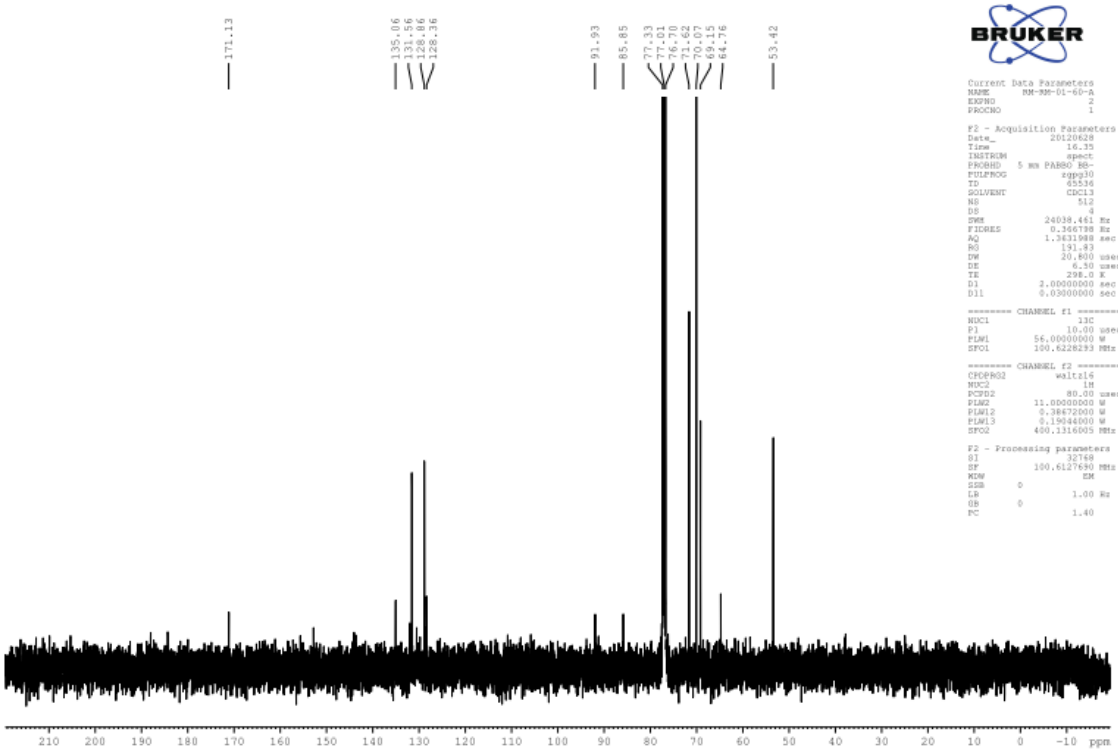


Fig. S-2: ^{13}C-NMR spectrum of compound **3** recorded in $CDCl_3$.

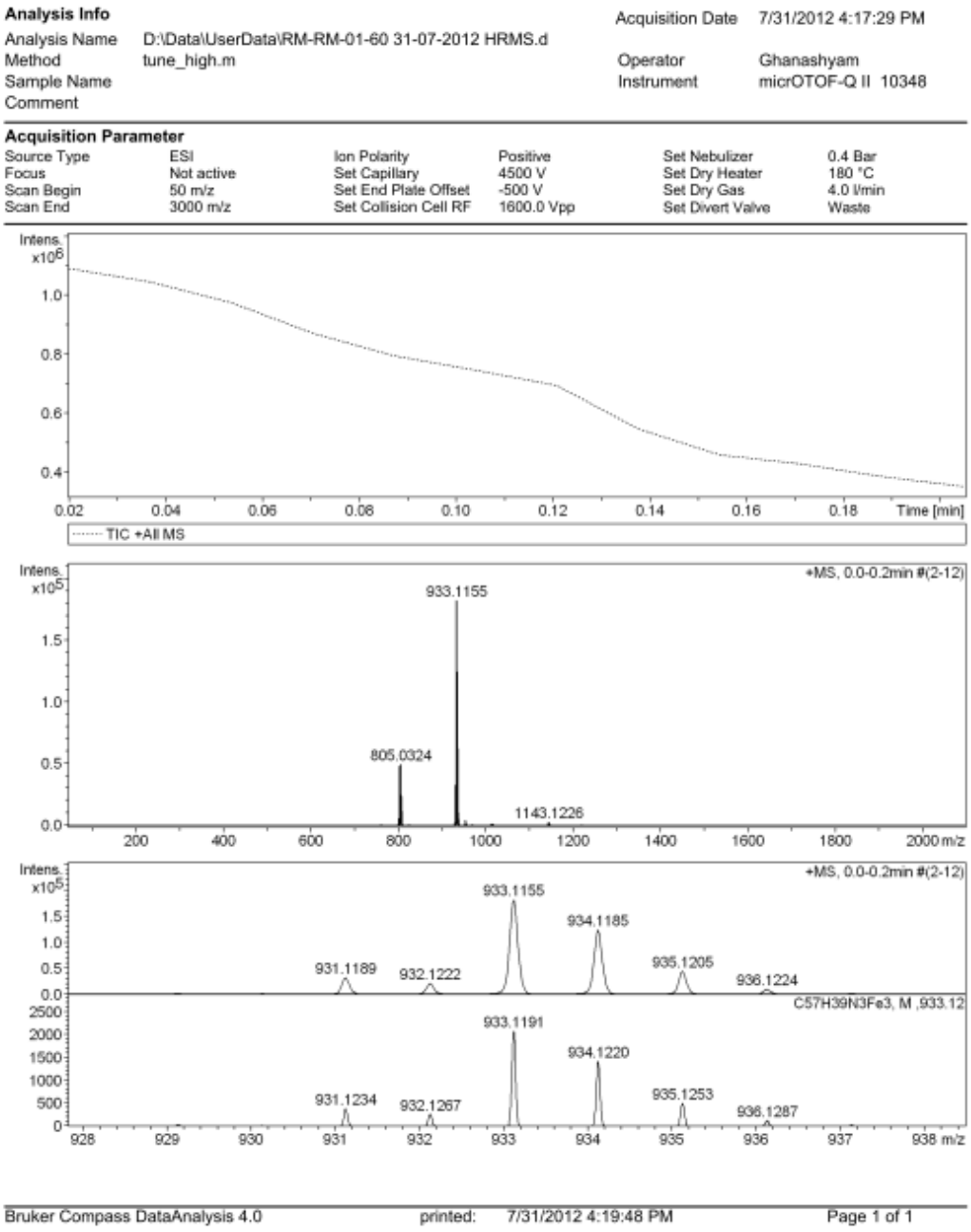


Fig. S-3: HRMS mass spectrum of compound **3**

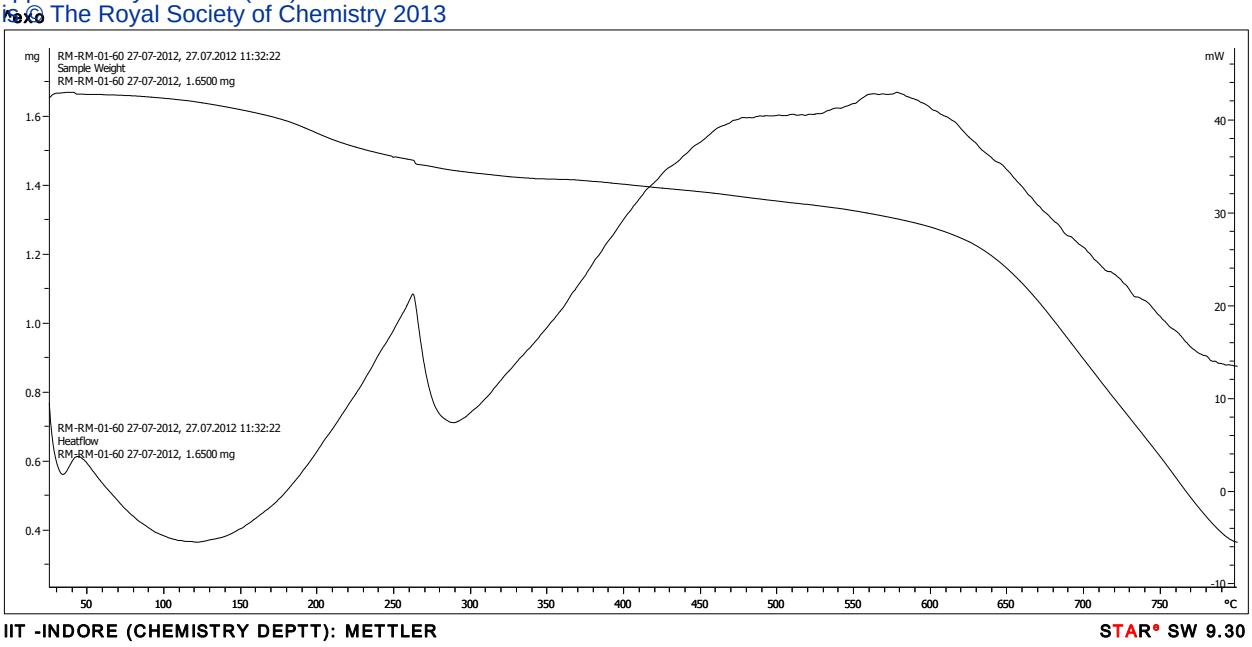


Fig. S-4: TGA and DSC spectrum of compound **3**

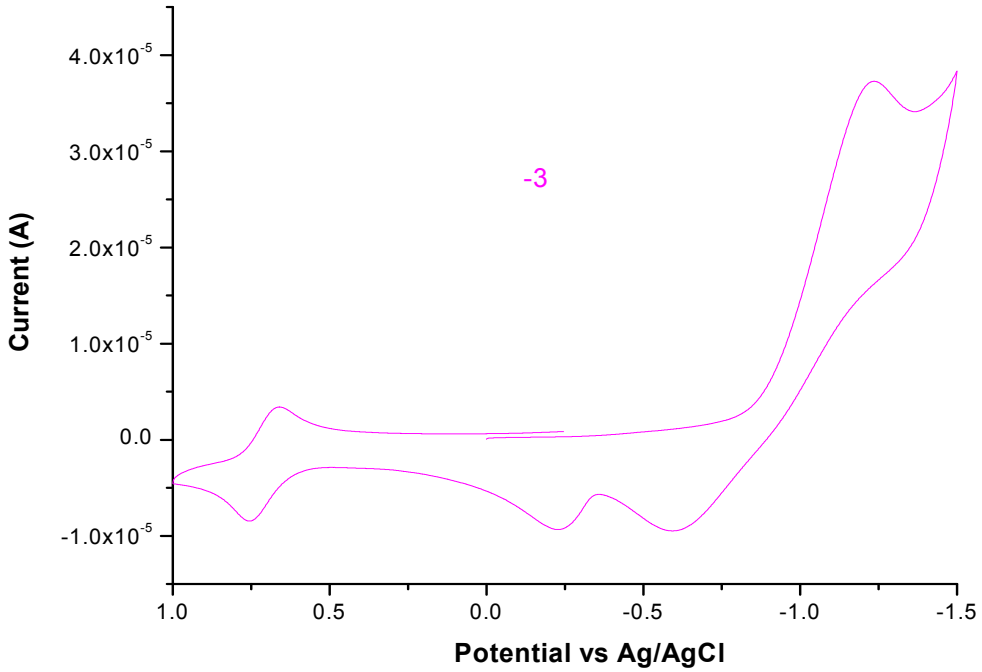
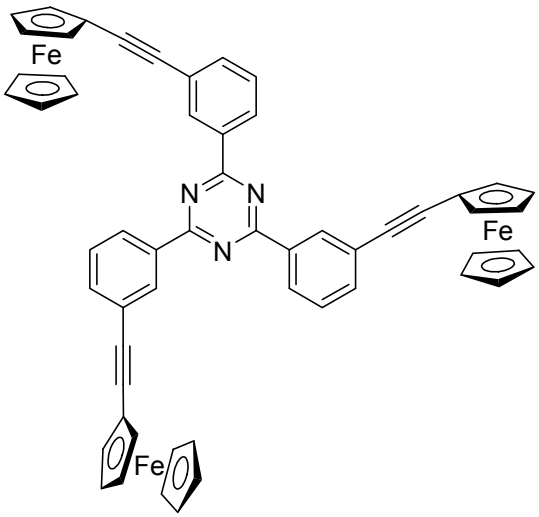


Fig.S-5: Cyclic voltammogram of compound **3** in 0.1 M solution of Bu_4NPF_6 in THF (1.0×10^{-4} M) at 100 mV S^{-1} scan rate.

2,4,6-Tris-(3-ferrocenylethynyl-phenyl)-1,3,5-triazine (4)

The triazine **2b** (0.200 g, 0.36 mmol) was dissolved in the mixture of toluene 30 ml and THF 10 ml (3;1), triethylamine (5 ml), and $Pd(PPh_3)_2Cl_2$ (0.035 g, 0.04 mmol), PPh_3 (0.0106 g, 0.04mmol), ethynyl ferrocene (0.260 g, 1.23 mmol) was added under argon atmosphere, and stirred for 16 h at 60 ^oC, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica gel, using hexane/ DCM (70:30) to get triazine **4** as a yellow solid (0.120 g, 34%); ^1H NMR (400 MHz, $CDCl_3$): δ = 8.81 (s, 3H), 8.68 (d, 3H), 7.68 (d, 3H), 7.51 (t, 3H) 4.51 (t, 6H), 4.22 (s, 12H), 4.20 (t, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.35, 136.29, 135.43, 131.79, 128.27, 124.65, 89.39, 85.45, 71.57, 70.05, 69.78, 68.96, 65.02, 31.59, 29.71, 22.66, 14.12. ppm; HRMS (ESI): calcd. for $C_{57}H_{39}Fe_3N_3$ 933.1191 $[M^+]$; found 933.1204.



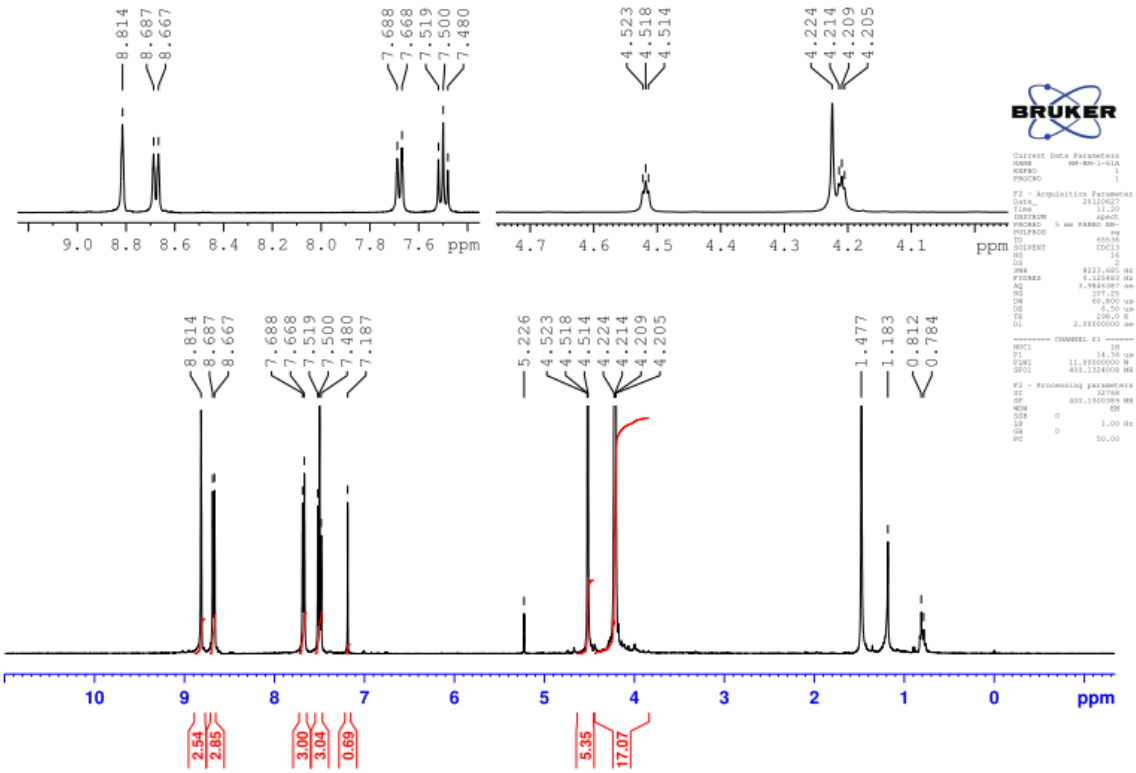


Fig. S-6: ^{1}H-NMR spectrum of compound **4** recorded in $CDCl_3$

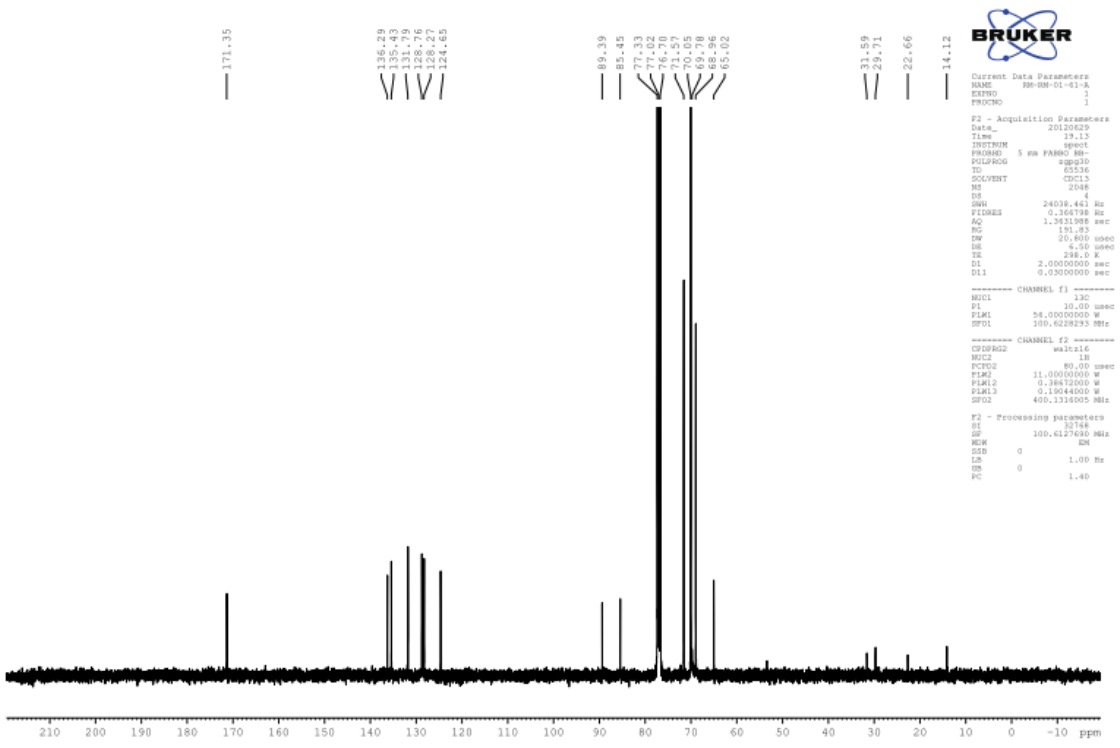


Fig. S-7: ^{13}C-NMR spectrum of compound **4** recorded in $CDCl_3$.

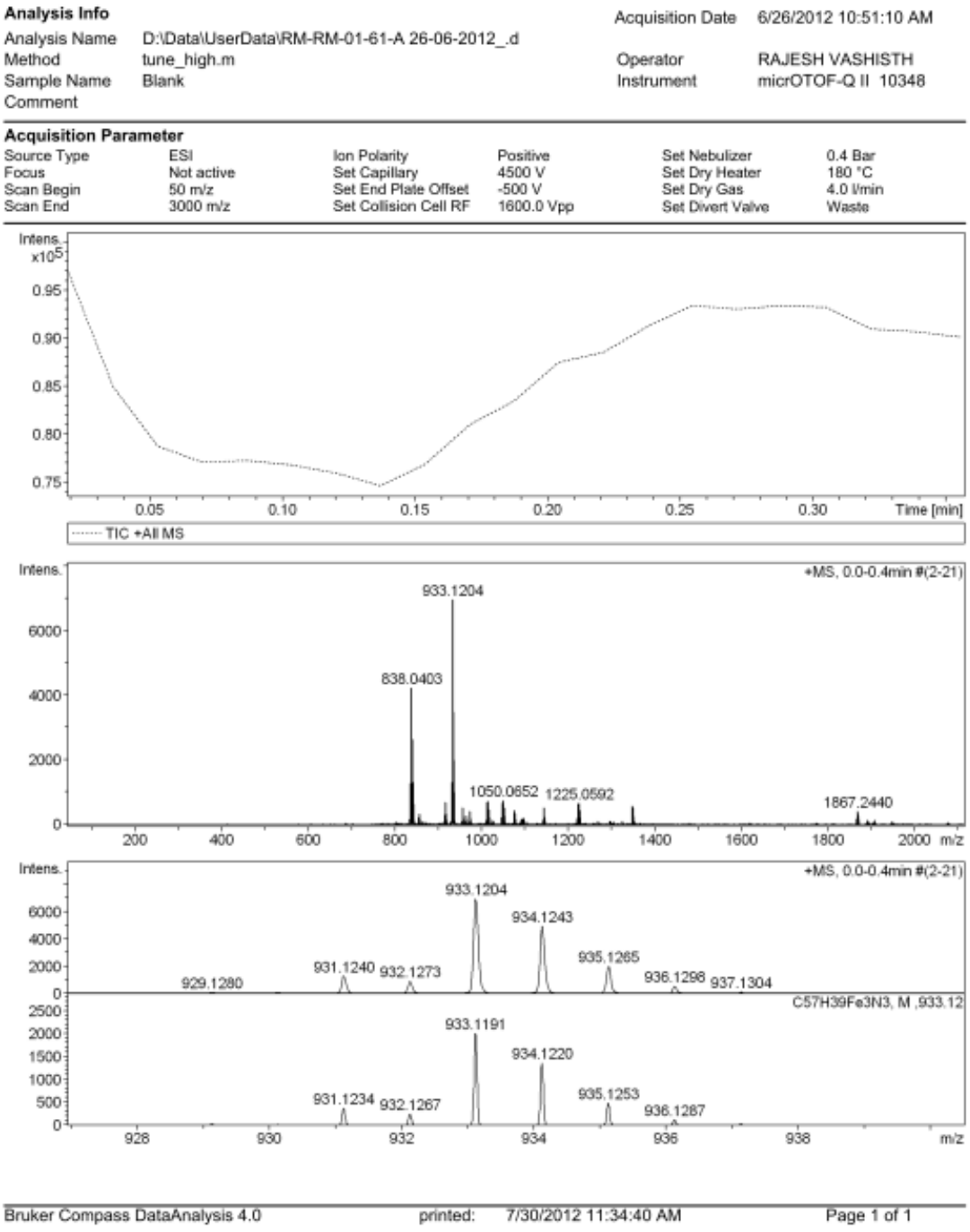


Fig. S-8: HRMS mass spectrum of compound **4**

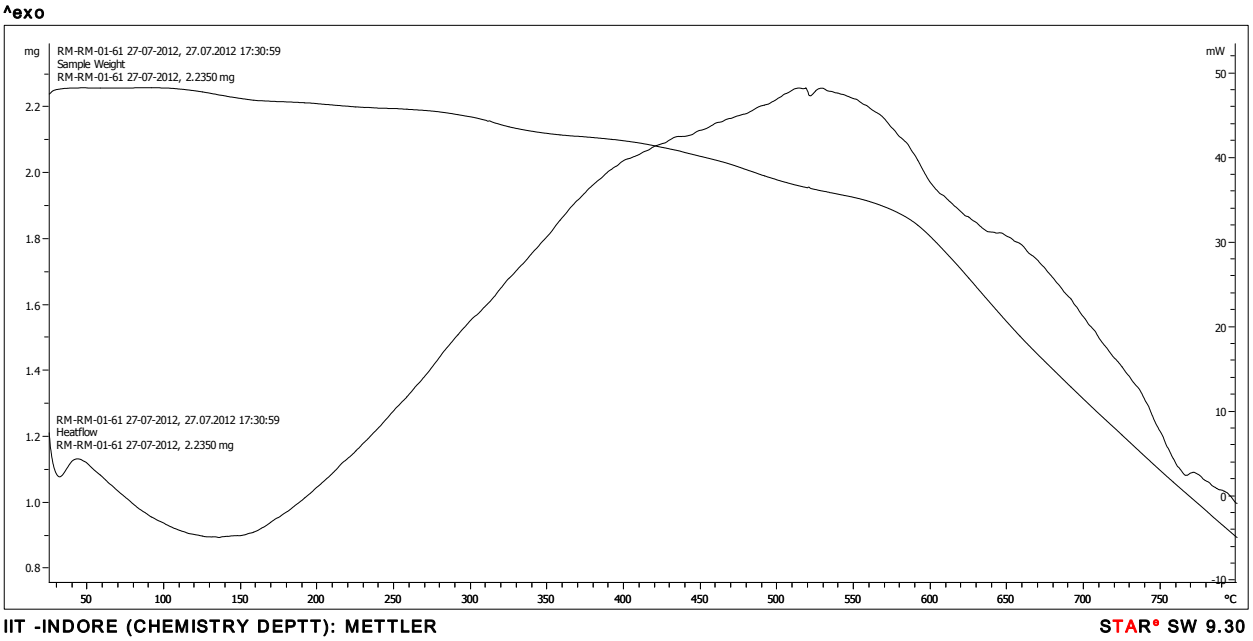


Fig. S-9: TGA and DSC spectrum of compound **4**

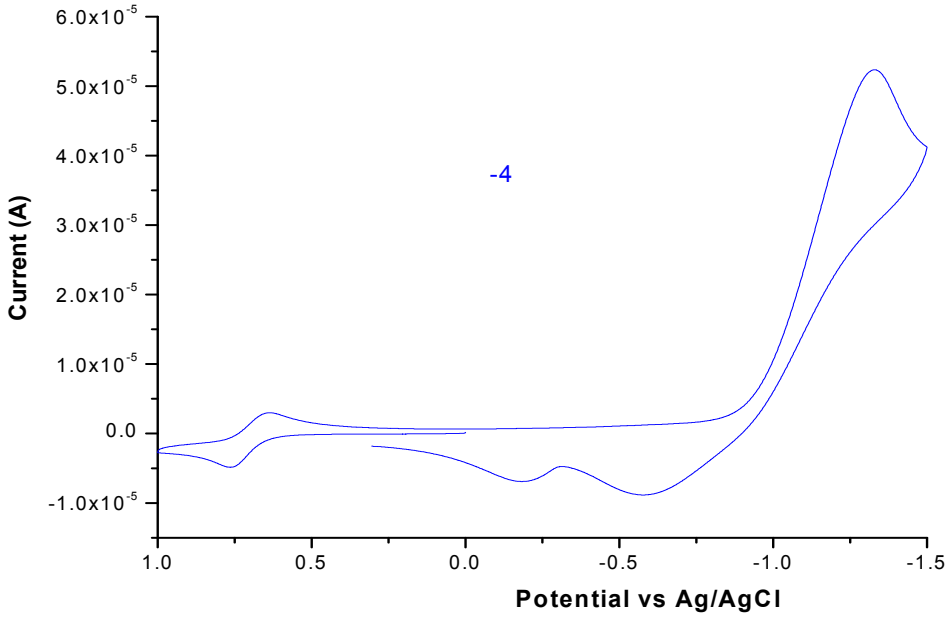
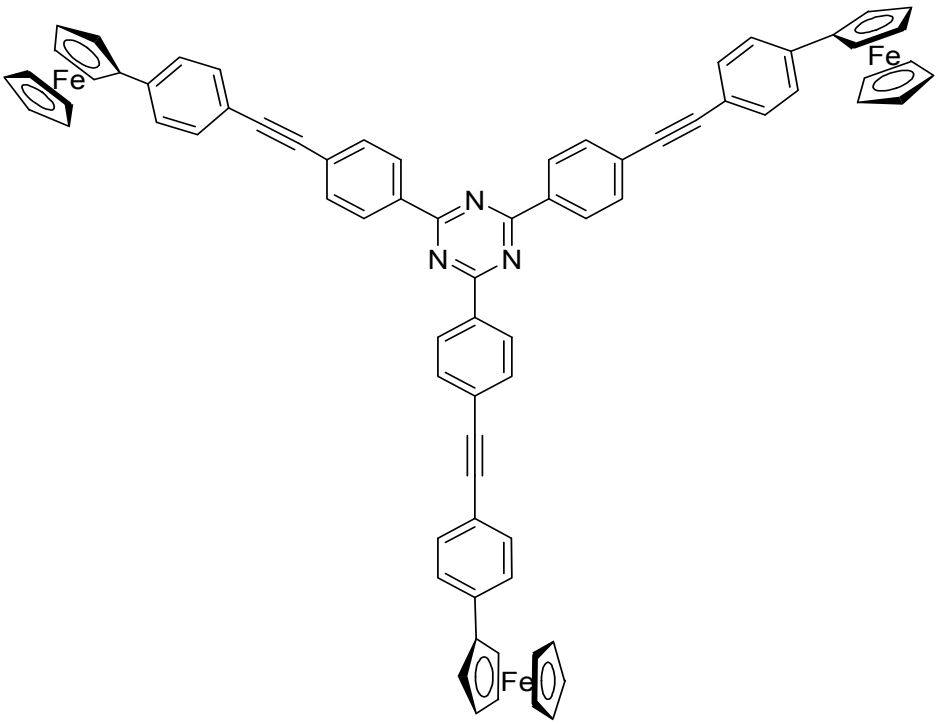


Fig.S-10: Cyclic voltammogram of compound **4** in 0.1 M solution of Bu_4NPF_6 in THF (1.0×10^{-4} M) at 100 mV S^{-1} scan rate.

2,4,6-Tris-(4-(4-ferrocene-phenylethynyl)-phenyl)-(1,3,5)triazine (5)

The triazine **2a** (0.100 g, 0.18 mmol) was dissolved in the mixture of toluene 10 ml, and THF 3 ml (3;1), triethylamine (3 ml), and $Pd(PPh_3)_4$ (0.030 g, 0.02 mmol), ferrocene-4-ethynyl benzene (0.171 g, 0.59 mmol) was added under argon atmosphere, and stirred for 8 h at 85 ^{o}C in microwave, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica gel, using hexane/ DCM (50:50), to get triazine **5** as a yellow solid (0.075 g, 35%); ^{1}H NMR (400 MHz, $CDCl_3$): δ =8.71 (d, 6H, J = 8.4 Hz), 7.68 (d, 6H, J = 8.4 Hz), 7.43 (q, 12H), 4.62 (s, 7H), 4.30 (s, 7H), 3.98 (s, 13H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 179.26, 171.12, 162.96, 140.48, 135.50, 131.82, 131.78, 128. 93, 127.88, 125.89, 119.97, 92.84, 89.39, 84.10, 69.76, 69.47, 66.58. ppm; HRMS (ESI): calcd. for $C_{75}H_{51}Fe_3N_3$ 1161.2133 [M^+]; found 1161.2402.



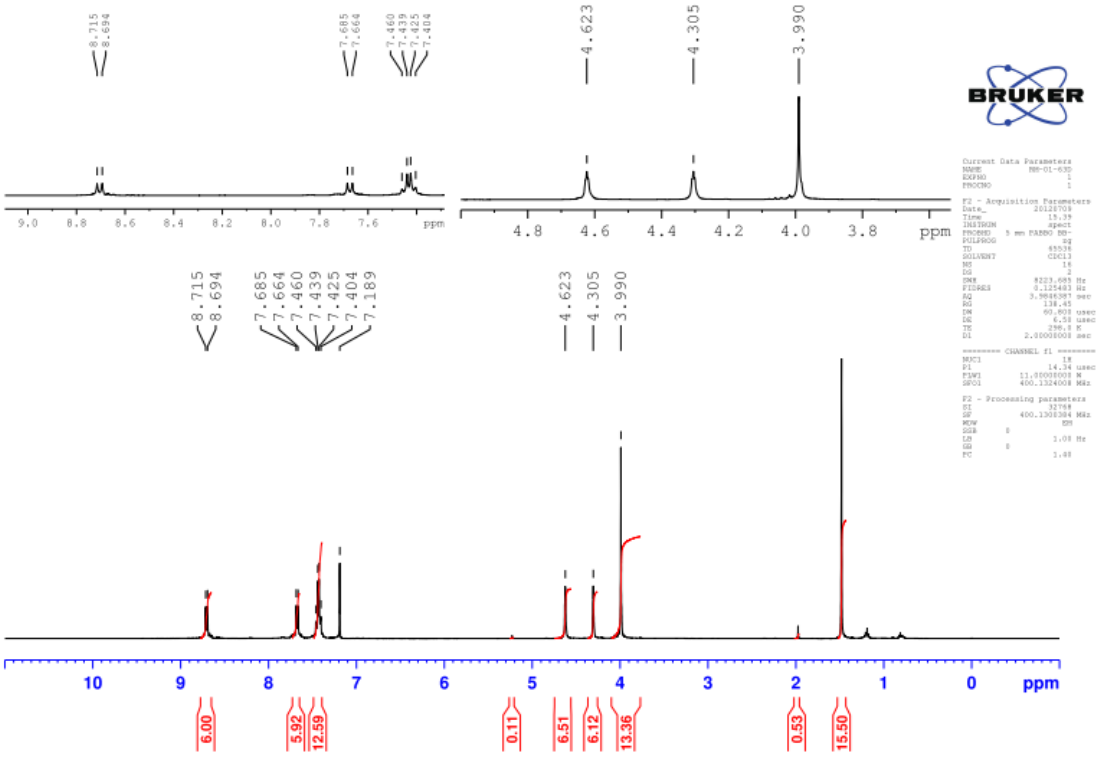


Fig. S-11: ^{1}H-NMR spectrum of compound **5** recorded in $CDCl_3$.

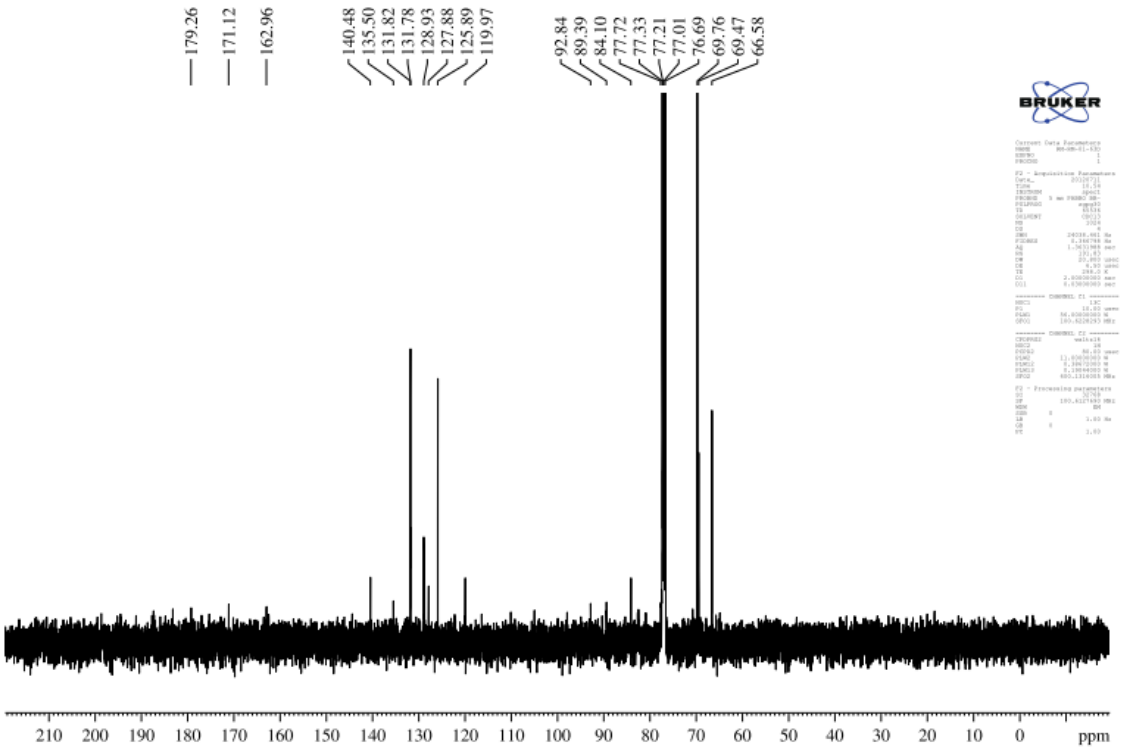


Fig. S-12: ^{13}C-NMR spectrum of compound **5** recorded in $CDCl_3$.

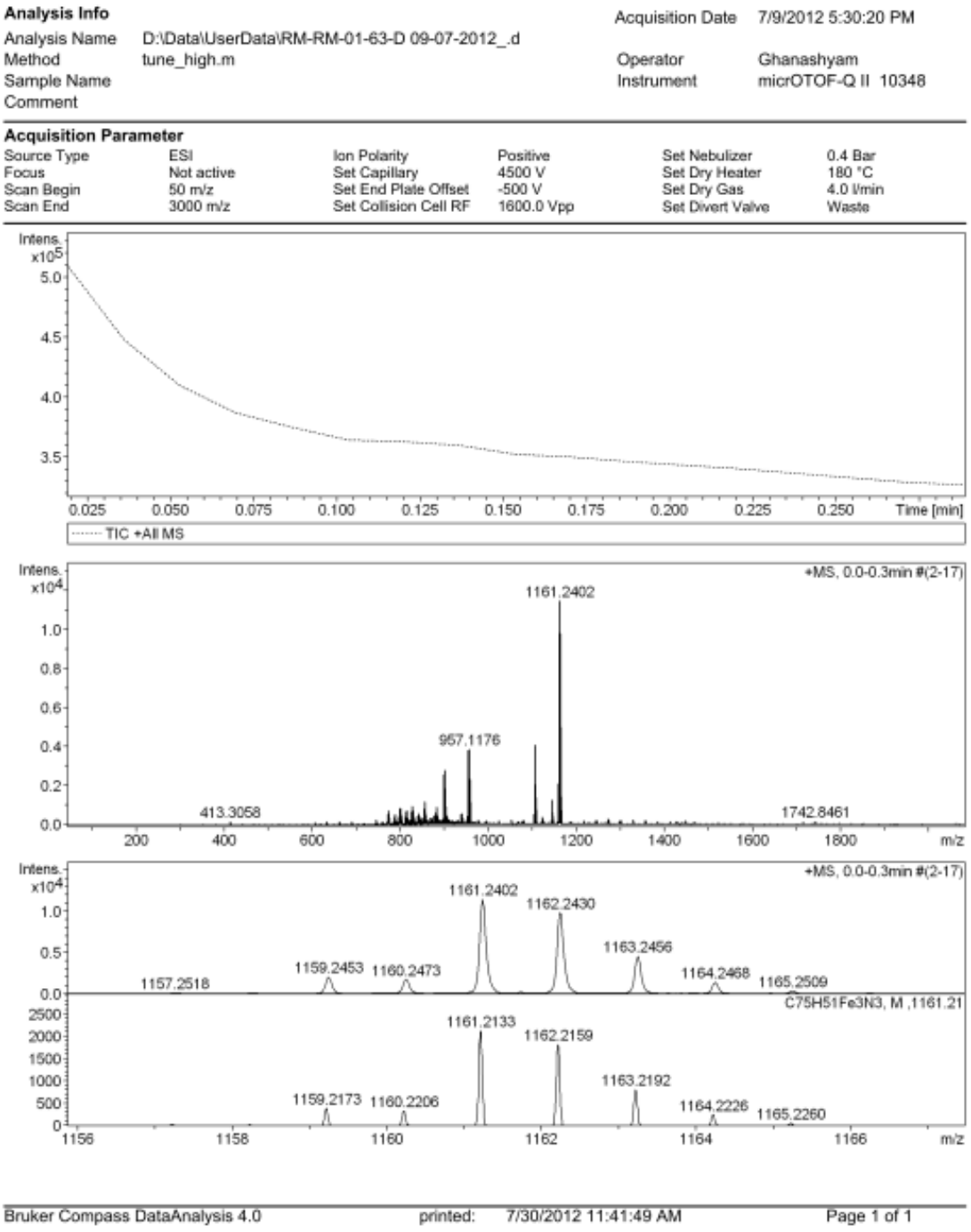


Fig. S-13: HRMS mass spectrum of compound **5**.

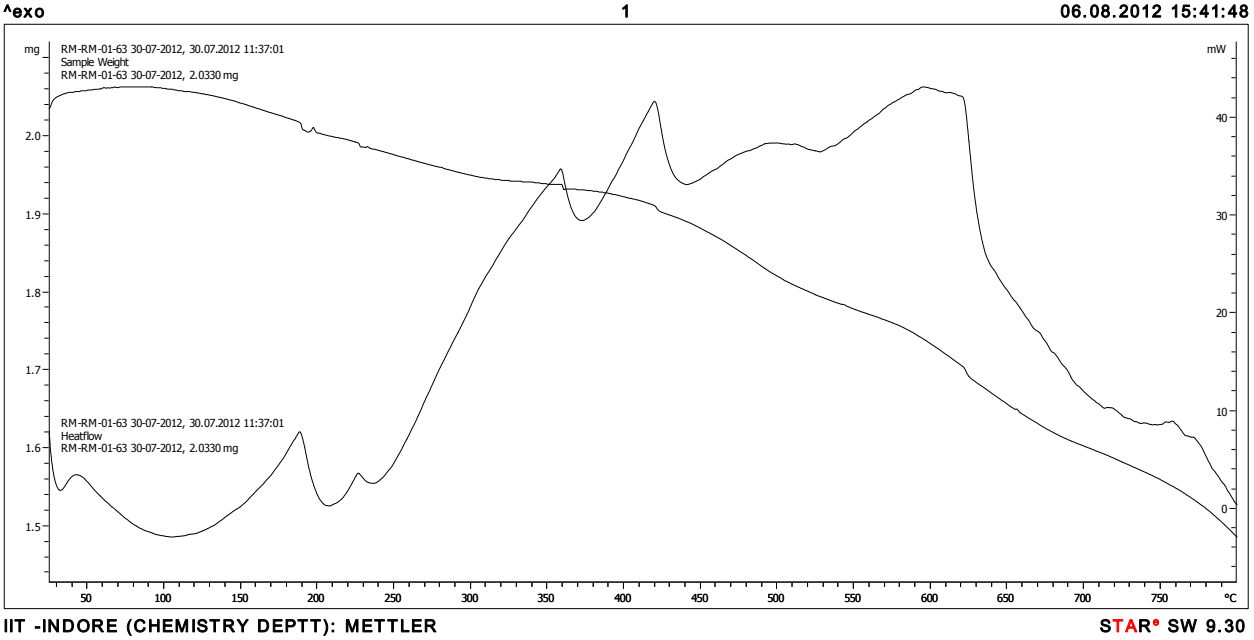


Fig. S-14: TGA and DSC spectrum of compound **5**

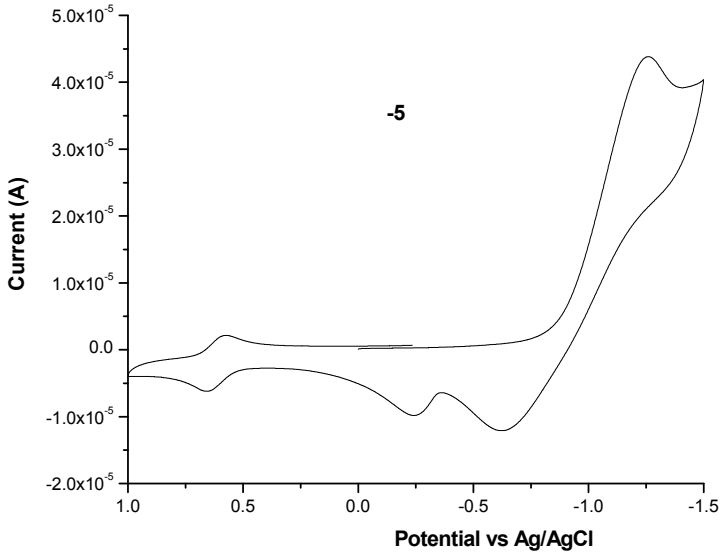
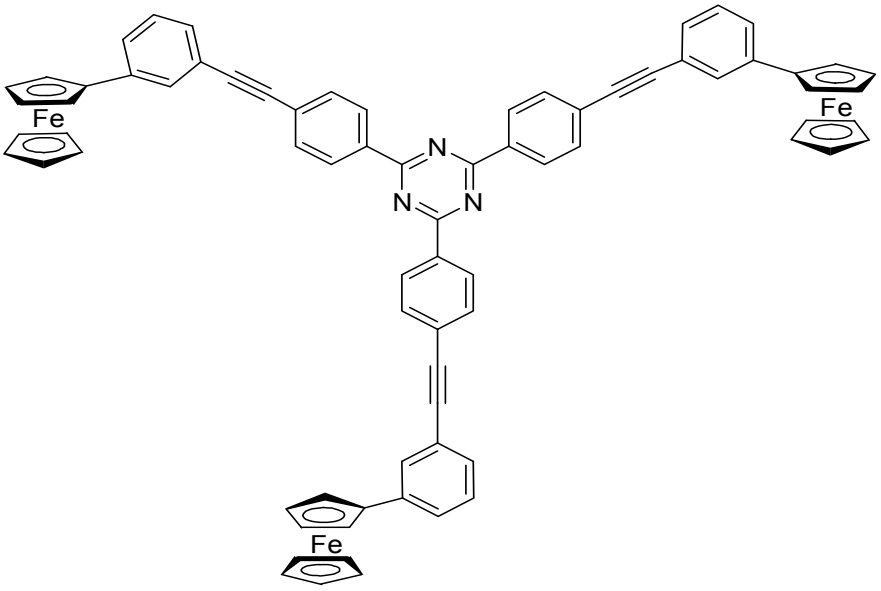


Fig.S-15: Cyclic voltammogram of compound **5** in 0.1 M solution of Bu_4NPF_6 in THF (1.0×10^{-4} M) at 100 mV S^{-1} scan rate.

2,4,6-Tris-(4-(3-ferrocene-phenylethynyl)-phenyl)-(1,3,5)triazine (6)

The triazine **2a** (0.100 g, 0.18 mmol) was dissolved in the mixture of toluene 10 ml, and THF 3 ml (3;1), triethylamine (3 ml), and $Pd(PPh_3)_4$ (0.030 g, 0.02 mmol), ferrocene-3-ethynyl benzene (0.171 g, 0.59 mmol) was added under argon atmosphere, and stirred for 8 h at 85 ^{o}C in microwave, after completion of the reaction, the reaction mixture was concentrated under reduced pressure, the crude compound was purified by column chromatography on silica gel, using hexane/ DCM (60:40) to get triazine **6** as a yellow solid (0.069 g, 32%); ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.80 (d, 6H, J = 7.9 Hz), 7.80 (d, 6H, J = 8 Hz), 7,72 (s, 3H), 7,53 (d, 3H), 7.47 (d, 3H), 7.33 (t, 3H), 4.73 (s, 6H), 4.38 (s, 6H), 4.11 (s, 15H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.06, 139.91, 135.65, 131.92, 130.52, 129.29, 129.01, 128.95, 128.52, 127.66, 126.49, 122.90, 92.58, 89.10, 84.23, 69.73, 69.26, 66.56 ppm; HRMS (ESI): calcd. for $C_{75}H_{51}Fe_3N_3$ 1161.2133 [M^+]; found 1161.2226.



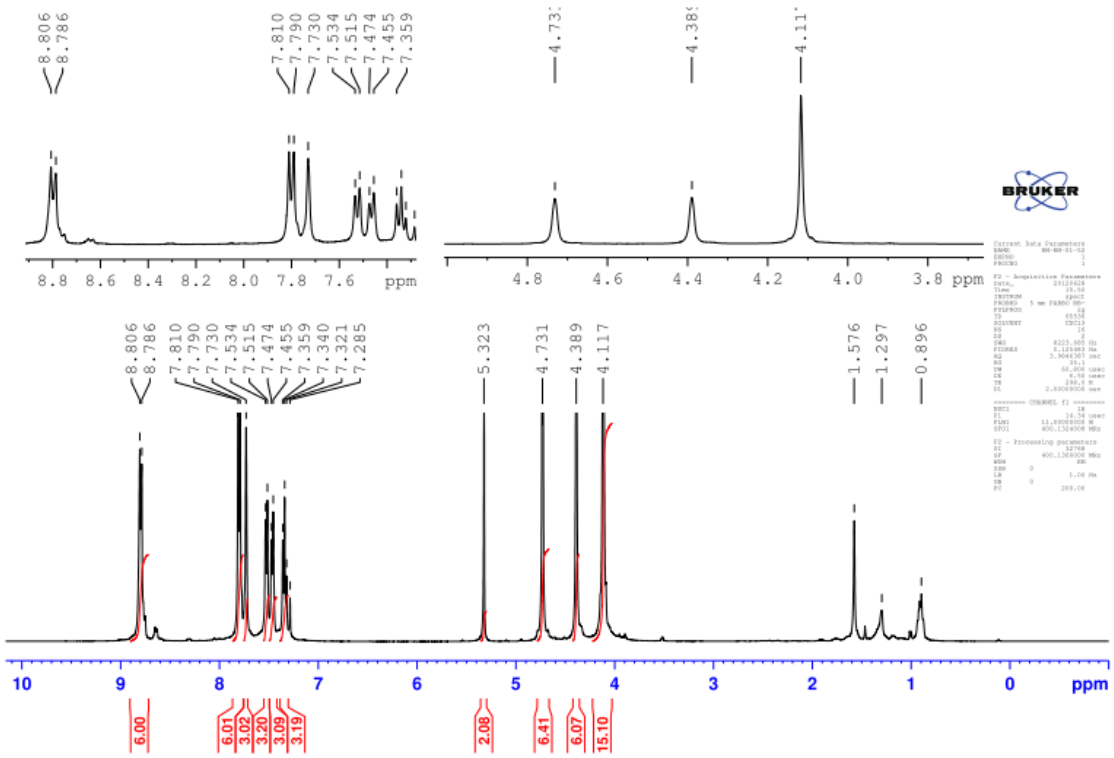


Fig. S-16: ^{1}H-NMR spectrum of compound **6** recorded in $CDCl_3$.

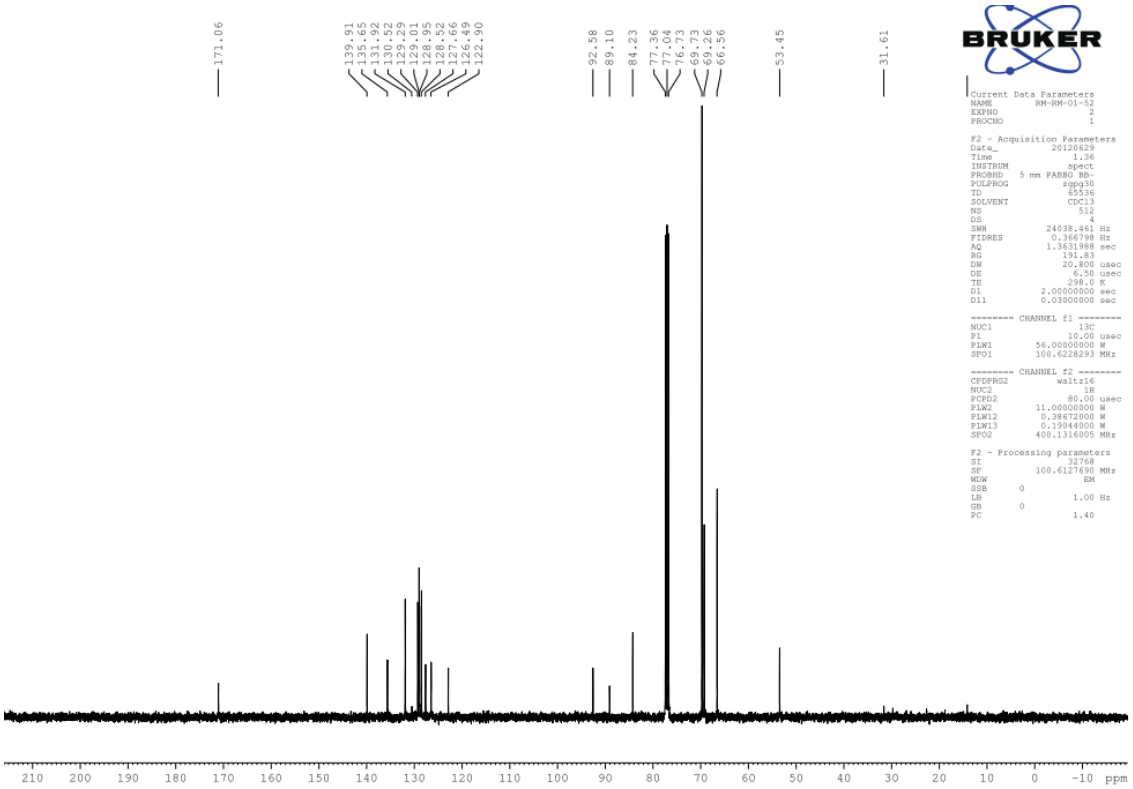


Fig. S-17: ^{13}C-NMR spectrum of compound **6** recorded in $CDCl_3$.

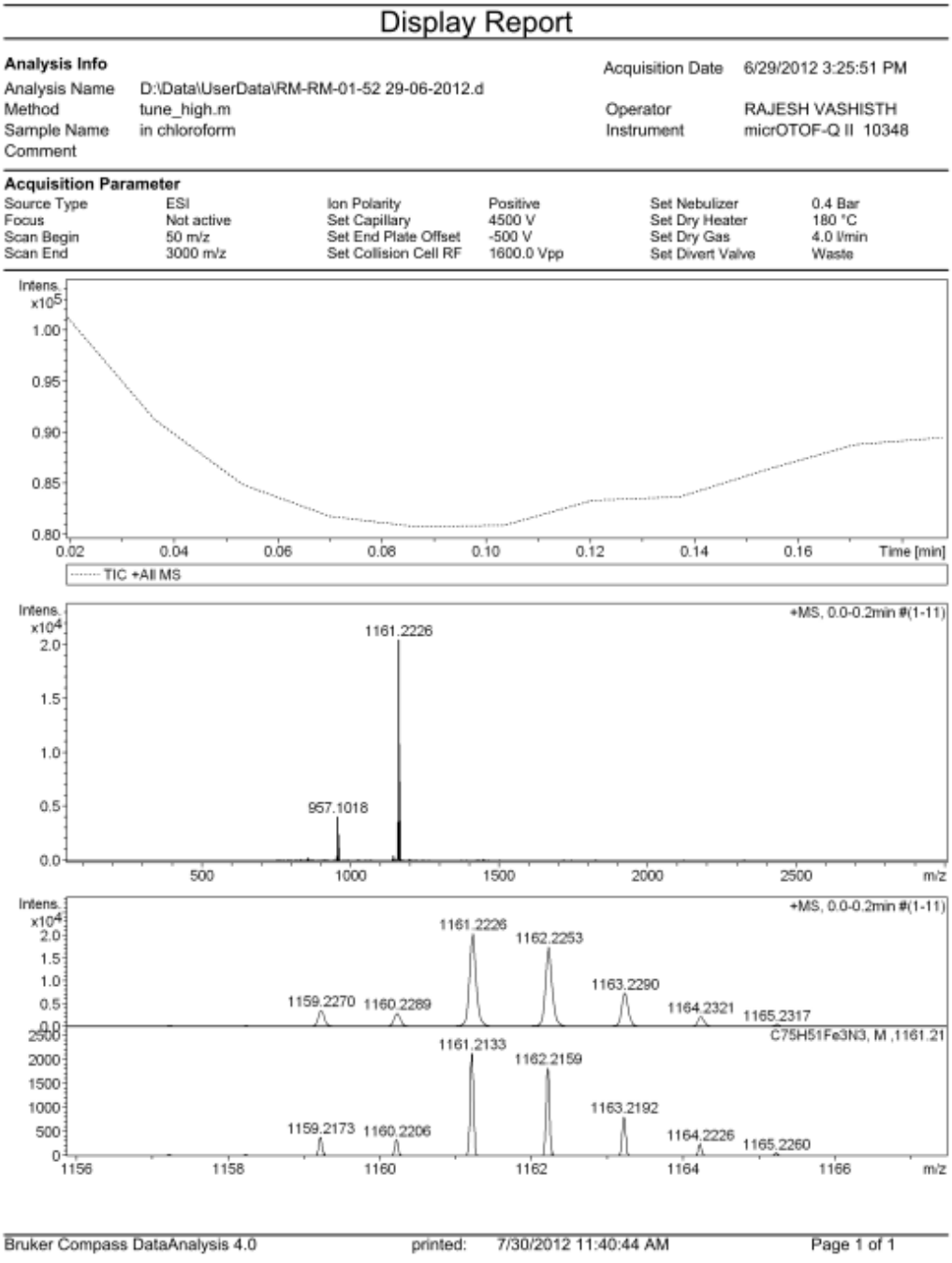


Fig. S-18: HRMS mass spectrum of compound **6**.

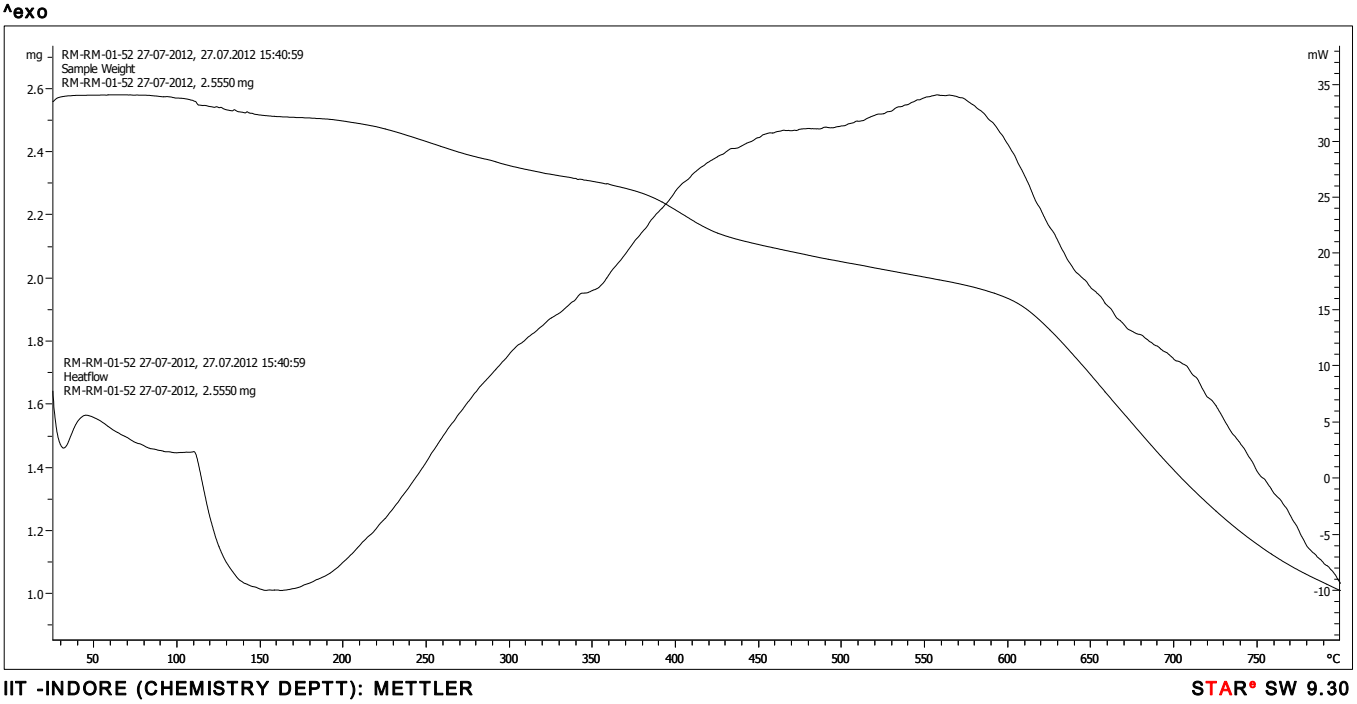


Fig. S-19: TGA and DSC spectrum of compound **6**

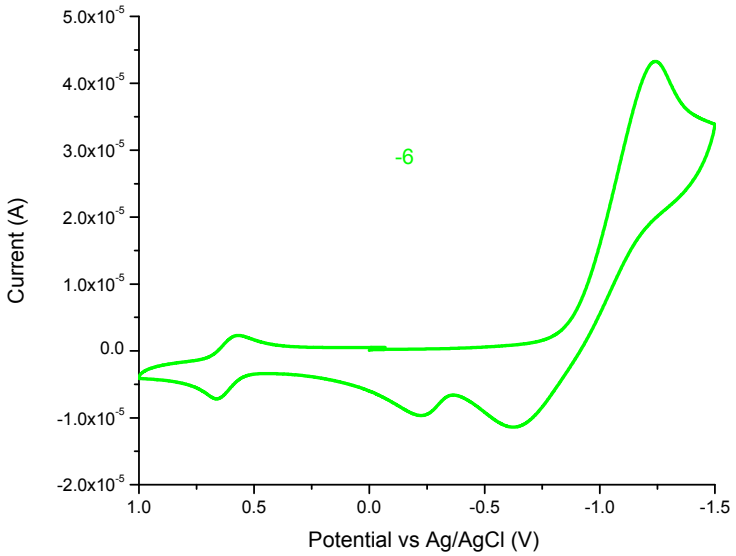


Fig.S-20: Cyclic voltammogram of compound **6** in 0.1 M solution of Bu_4NPF_6 in THF (1.0×10^{-4} M) at 100 mV S^{-1} scan rate.

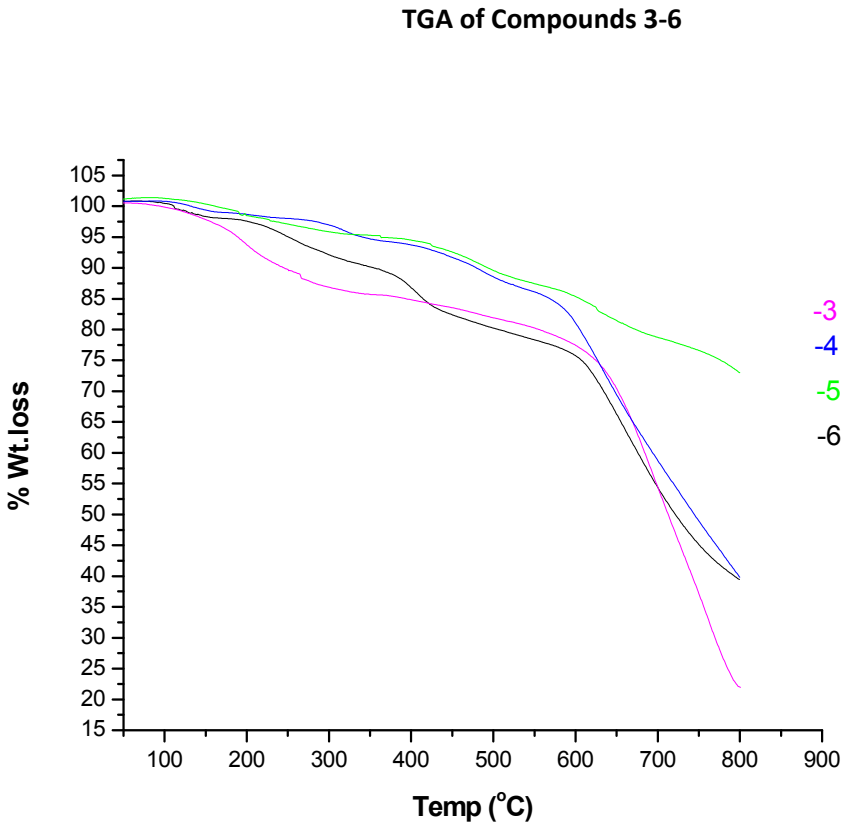


Fig.S-21: The triazines **3-6** shows 10 % wt. loss around 260 °C to 500 °C

X-ray crystallography

Single crystal X-ray structural studies of **3** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromoated Mo Kα radiation (λα = 0.71073 Å). The strategy for the Data collection was evaluated by using the CrysAlisPro CCD software. The data were collected by the standard 'phi-omega scan techniques, and were scaled and reduced using CrysAlisPro RED software. The structures were solved by direct methods using SHELXS-97 and refined by full matrix least-squares with SHELXL-97. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropic ally. The remaining hydrogen atoms were placed in geometrically constrained positions and refined with isotropic temperature factors, generally 1.2Ueq of their parent atoms. The crystal and refinement data are summarized in Table 3. The CCDC–899827 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

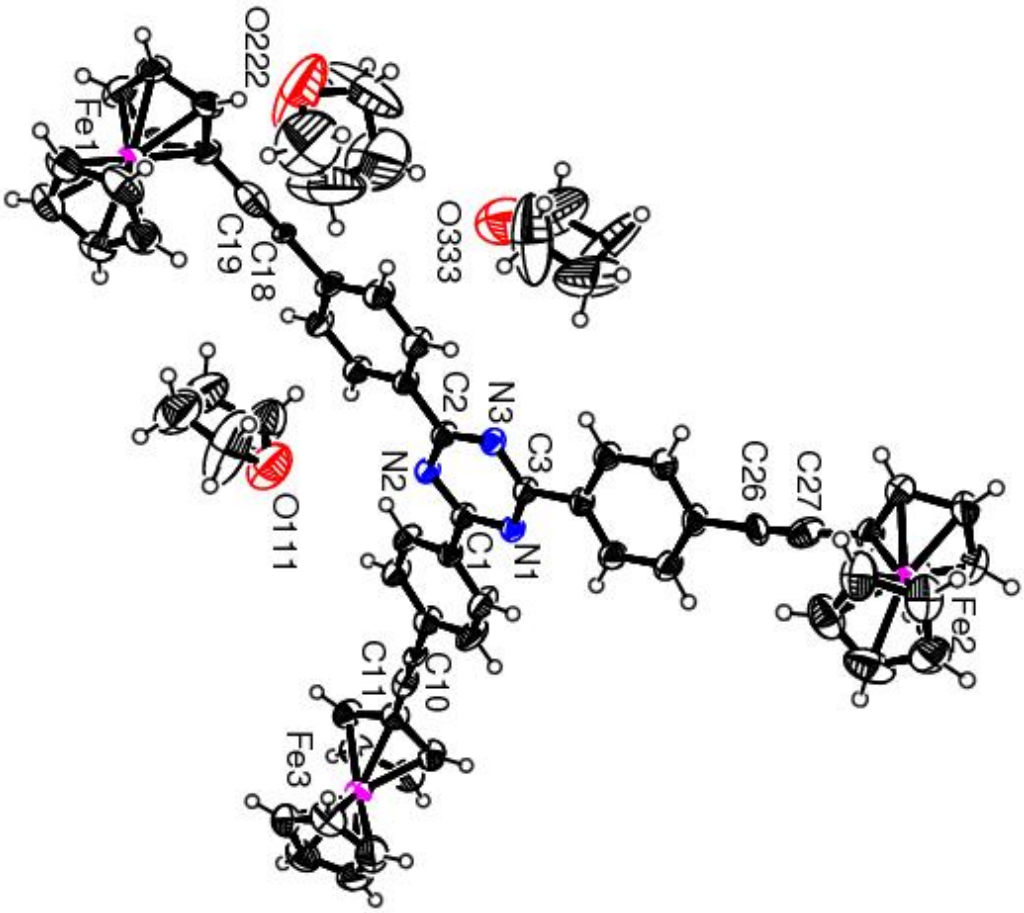


Fig.S-22: Single crystal X-ray structure of triazine **3, (**50 % probability chosen for ellipsoids).

Table 2. The selected bond lengths, and bond angles of compound **3**

Bond lengths (Å)		**Bond angles °**	
N(1)-C(1)	1.337(5)	C(1)-N(1)-C(3)	115.0(4)
N(1)-C(3)	1.340(6)	C(1)-N(2)-C(2)	115.2(4)
N(2)-C(1)	1.335(5)	C(2)-N(3)-C(3)	114.5(4)
N(2)-C(2)	1.341(5)	N(2)-C(1)-N(1)	124.9(4)
N(3)-C(2)	1.341(5)	N(2)-C(1)-C(4)	117.7(4)
N(3)-C(3)	1.343(5)	N(1)-C(1)-C(4)	117.3(4)
C(1)-C(4)	1.485(6)	N(2)-C(2)-N(3)	125.1(4)
C(2)-C(12)	1.484(6)	N(2)-C(2)-C(12)	117.3(4)
C(3)-C(20)	1.479(6)	N(3)-C(2)-C(12)	117.7(4)
C(23)-C(26)	1.502(6)	N(1)-C(3)-N(3)	125.2(4)
C(26)-C(27)	1.108(7)	N(1)-C(3)-C(20)	117.0(4)
C(27)-C(48)	1.453(7)	C(18)-C(19)-C(38)	179.6(6)
C(10)-C(11)	1.069(7)	C(26)-C(27)-C(48)	177.9(6)
C(11)-C(28)	1.467(7)	C(10)-C(11)-C(28)	175.5(6)
C(7)-C(10)	1.525(7)	C(5)-C(4)-C(1)	120.3(4)
C(15)-C(18)	1.546(6)	C(13)-C(12)-C(2)	120.5(4)
C(18)-C(19)	1.033(7)	C(21)-C(20)-C(3)	120.3(4)
C(19)-C(38)	1.486(8)		

Table 3. Crystallographic data and structure refinement detail for compound **3**

Compound	**3**
Empirical formula	$C_{69}\ H_{63}\ Fe_3\ N_3\ O_3$
Formula weight	1149.77
Crystal system	Triclinic
Space group	$P\ \bar{1}$
Unit cell dimensions	
a (A°)	11.750(5)
b (A°)	15.514(5)
c (A°)	16.213(5)
Volume	2703.5(17) A^3
Z, Calculated density	2, 1.412 Mg/m^3
Absorption coefficient	0.848 mm^-1
Max. and min. transmission	0.8345 and 0.7569
F (000)	1200
Crystal size	0.23 x 0.18 x 0.13 mm
Theta range for data collection	2.93 to 25.00 deg.
Completeness to theta	25.00 99.8 %
Reflections collected / unique	21732 / 9514 [R (int) = 0.0242]
Data / restraints / parameters	9514 / 0 / 703
Goodness-of-fit on F^2	1.038
Refinement method	Full-matrix least-squares on F^2
	R1 = 0.0720, wR2 = 0.2014

Final R indices [I>2sigma (I)]	R1 = 0.0839, wR2 = 0.2135
R indices (all data)	
Largest diff. peak and hole	1.117 and -0.903 e.A^-3