Supporting Information

Ferrocenyl substituted calixarenes: synthesis, structure, and properties

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General: Chemicals were used as received unless otherwise indicated. All oxygen or moisture sensitive reactions were performed under nitrogen/argon atmosphere using standard schlenk method. Triethylamine (TEA) was received from commercial source, and distilled on KOH prior to use. ^{1}H NMR (400 MHz), and ^{13}C NMR (100MHz) spectra were recorded on the Bruker Avance (III) 400 MHz, using $CDCl_3$ as solvent. Tetramethylsilane (TMS) was used as reference for recording ^{1}H (of residual proton; δ = 7.26 ppm), and ^{13}C (δ = 77.0 ppm) spectra in $CDCl_3$. UV-visible absorption spectra of all compounds in Dichloromethane were recorded on a Carry-100 Bio UV-visible Spectrophotometer. Cyclic voltamograms (CVs) were recorded on a CHI620D electrochemical analyzer using Platinum as a working electrode, Pt wire as the counter electrode, and Ag/Ag^{+} as the reference electrode. HRMS was recorded on Brucker-Daltonics, micrO TOF-Q II mass spectrometer.

Synthesis and Characterization

The reactant **5a** was purchased from Sigma-Aldrich, and the reactants **5b-5c** were synthesized via diazotization of 4-ethynylaniline, and 3-ethynylaniline respectively, according to known methods.[1]

General procedure for synthesis of 5a-5c.

5,11,17,23-Tetraiodo-25,26,27,28-tetra-(*n*-propoxy)calix[4]arene **4** (160 mg, 0.14 mmol) was stirred together with $Pd(PPh_3)_2Cl_2$ (40 mg, 0.05 mmol) and CuI (0.09 mg, 0.05 mmol) in degassed diisopropylamine (20 mL) and THF (20ml) for 30 min at room temperature before the corresponding ethynyl ferrocene (6 equivalent, 0.875mmol) was added. The mixture was heated at 80 ºC for 48 h. The solvent was removed; the remaining residue was suspended in water (50 mL) and extracted with EtOAc (3 x 20 mL). The combined organic layers were dried ($MgSO_4$) and concentrated in vacuum. The resulting crude product was purified by column chromatography on silica gel eluting with CH_2Cl_2/hexane (2:3). The desired compound obtained

from the column was recrystalized from chloroform/methanol to give compounds **5a-5c** in 70-80% yield.

Compound **5a**: Orange solid (164 mg, 79%) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.93 (s, 8H), 4.40-4.43 (m, 12H), 4.19 (s, 20H), 4.11 (s, 8H), 3.88 (t, 8H), 3.16 (d, 4H, *J* = 12.23 Hz), 1.94 (m, 8H), 0.99 (t, 12H)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.57, 134.74, 131.19, 117.18, 86.88, 86.25, 71.59, 70.02, 68.58, 66.23, 31.03, 23.36, 10.49. HRMS (ESI) m/z, calcd for MH^+ ($C_{88}H_{80}Fe_4O_4$): 1424.3462; found: 1424.3516.

Compound **5b**: Orange solid (176 mg, 70%) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36 (d, 8H, *J* = 8.55 Hz), 7.27 (d, 8H, *J* = 8.29 Hz), 6.99 (s, 8H), 4.57 (m, 8H), 4.45 (d, 4H, *J* = 13.31 Hz), 4.27 (m, 8H), 3.97 (s, 20H), 3.91 (t, 8H), 3.20 (d, 4H, *J* = 13.31 Hz), 1.99-1.93 (m, 8H), 1.00 (t, 12H)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.96, 139.21, 134.88, 132.06, 131.84, 125.77, 121.09, 117.50, 90.17, 88.61, 84.61, 69.86, 69.38, 66.69, 31.05, 23.43, 10.52. HRMS (ESI) m/z, calcd for MH^+ ($C_{112}H_{96}Fe_4O_4$): 1729.4740; found: 1729.4737.

Compound **5c**: Orange solid (170 mg, 70%) ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.56 (s, 4H), 7.29 (d, 4H, *J* = 8.88 Hz), 7.24 (d, 4H, *J* = 8.68 Hz), 6.97-7.01 (m, 12H), 4.60 (m, 8H), 4.48 (d, 4H, *J* = 12.87 Hz), 4.24 (m, 8H), 3.99 (s, 20H), 3.92 (t, 8H), 3.22 (d, 4H, *J* = 13.79 Hz), 1.91-2.01 (m, 8H), 1.02 (t, 12H)); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.94, 139.28, 134.77, 132.00, 129.25, 128.79, 128.21, 125.55, 123.57, 117.14, 89.65, 88.50, 84.60, 69.64, 69.01, 66.51, 30.92, 23.26, 10.36. HRMS (ESI) m/z, calcd for MH^+ ($C_{112}H_{96}Fe_4O_4$): 1729.4740; found: 1729.4737.

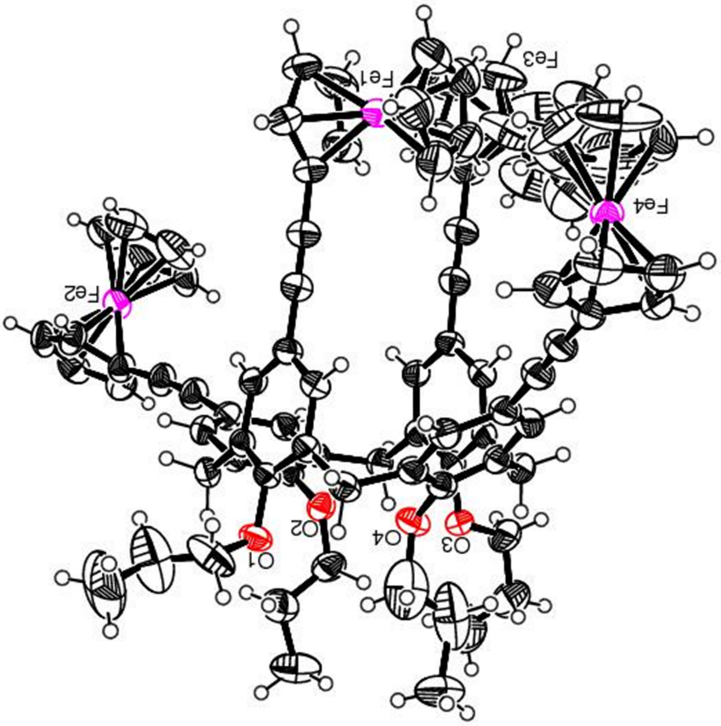

Figure S1. ORTEP view of **5a.** Thermal ellipsoids are plotted at the 50 % level.

Single crystal X-ray diffraction Studies

Single crystal X-ray structural studies of **5a** were performed on a CCD Agilent Technologies (Oxford Diffraction) SUPER NOVA diffractometer. Data were collected at 293(2) K using graphite-monochromated Mo Kα radiation (λ_α = 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, refining on $F^{2.1}$. The positions of all the atoms were obtained by direct methods. All non-hydrogen atoms were refined anisotropically. The remaining hydrogen

atoms were placed in geometrically constrained positions, and refined with isotropic temperature factors, generally 1.2U_{eq} of their parent atoms. The crystal and refinement data are summarized in Table 2. The CCDC number 903776 contains the supplementary crystallographic data for **5a**. This data can be obtained free of charge via www.ccdc.cam.ac.uk (or from the Cambridge Crystallographic Data Centre, 12 union Road, Cambridge CB21 EZ, UK; Fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystal data and structure refinement parameter for compound **5a**.

Compound	**5a**
Empirical formula	C_{88} H_{80} Fe_4 O_4
Formula weight	1424.92
Temperature/K	150(2) K
Wavelength/A	0.71073
Crystal system, space group	Orthorhombic, *P cab*
Unit cell dimensions	a = 15.7383(4) A alpha = 90 deg.
	b = 50.6519(11) A beta = 90 deg.
	c = 18.0535(4) A gamma = 90 deg.
Volume	14391.8(6) A^3
Z, Calculated density	8, 1.315 Mg/m^3
Absorption coefficient	0.842 mm^{-1}
F(000)	5952
Crystal size	0.34 x 0.28 x 0.22 mm
Theta range for data collection/(°)	2.96 to 25.00
Limiting indices	-18<=h<=18, -48<=k<=60, -21<=l<=21

Reflections collected / unique	111276 / 12648 [R(int) = 0.0597]
Completeness to theta = 25.00	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8364 and 0.7627
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12648 / 0 / 869
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0672, wR2 = 0.1628
R indices (all data)	R1 = 0.0788, wR2 = 0.1715
Largest diff. peak and hole	0.954 and -0.667 $e.A^{-3}$

Table S2: Selected bond length of intermolecular interactions in the crystal structure **5a.**

C-H- π Interactions	Bond length Å
H83----C18, C13, C14, C16, C17, C15	2.675
H56----C66, C67, C68, C65, C64	3.026
H26----C80, C81, C82, C83, C79	3.19
H51----C86, C87, C88, C84, C85	3.597

Electrochemical Data for 5b, 5c.

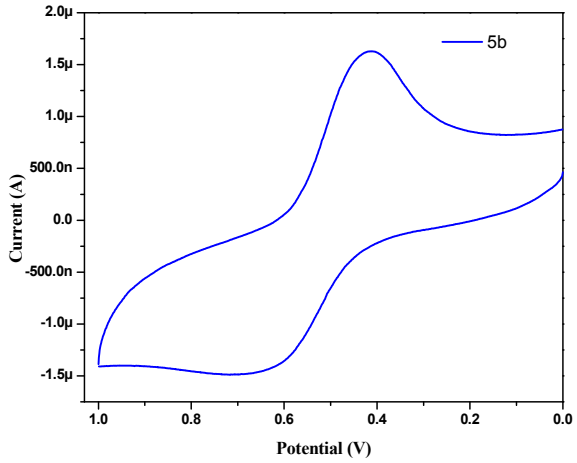

Figure S2. Cyclic voltammogram of calixarene **5b.**

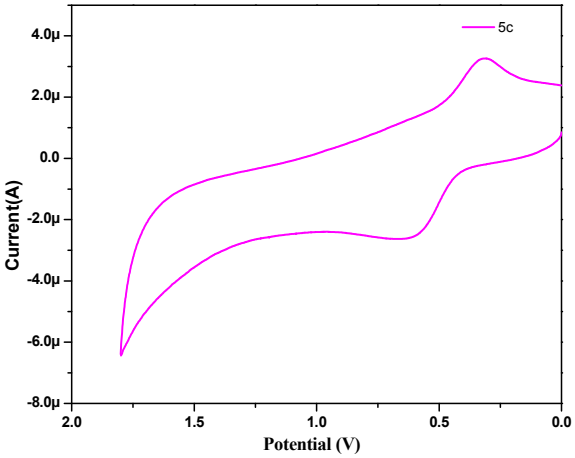

Figure S3. Cyclic voltammogram of calixarene **5c.**

Copies of ^{1}H NMR, ^{13}C NMR and HRMS Spectra of the Compounds 5a-5c.

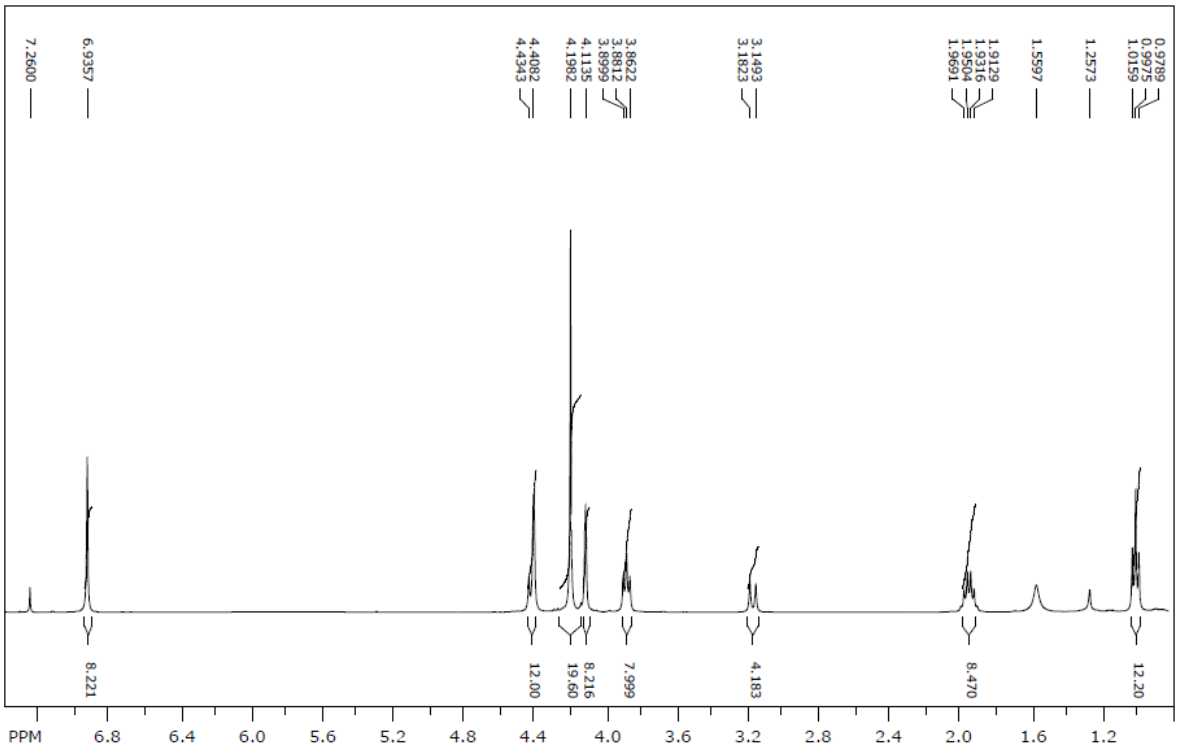

Figure S4. ^{1}H NMR Spectra of **5a.**

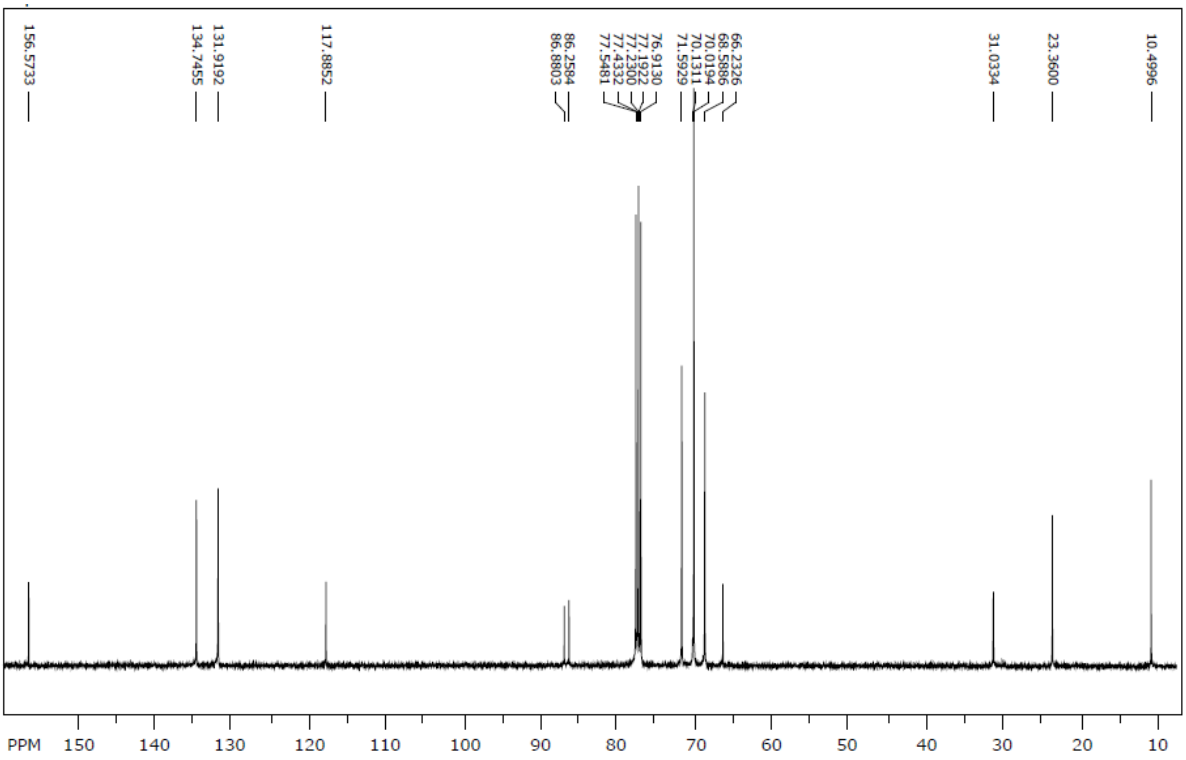

Figure S5. ^{13}C NMR Spectra of **5a.**

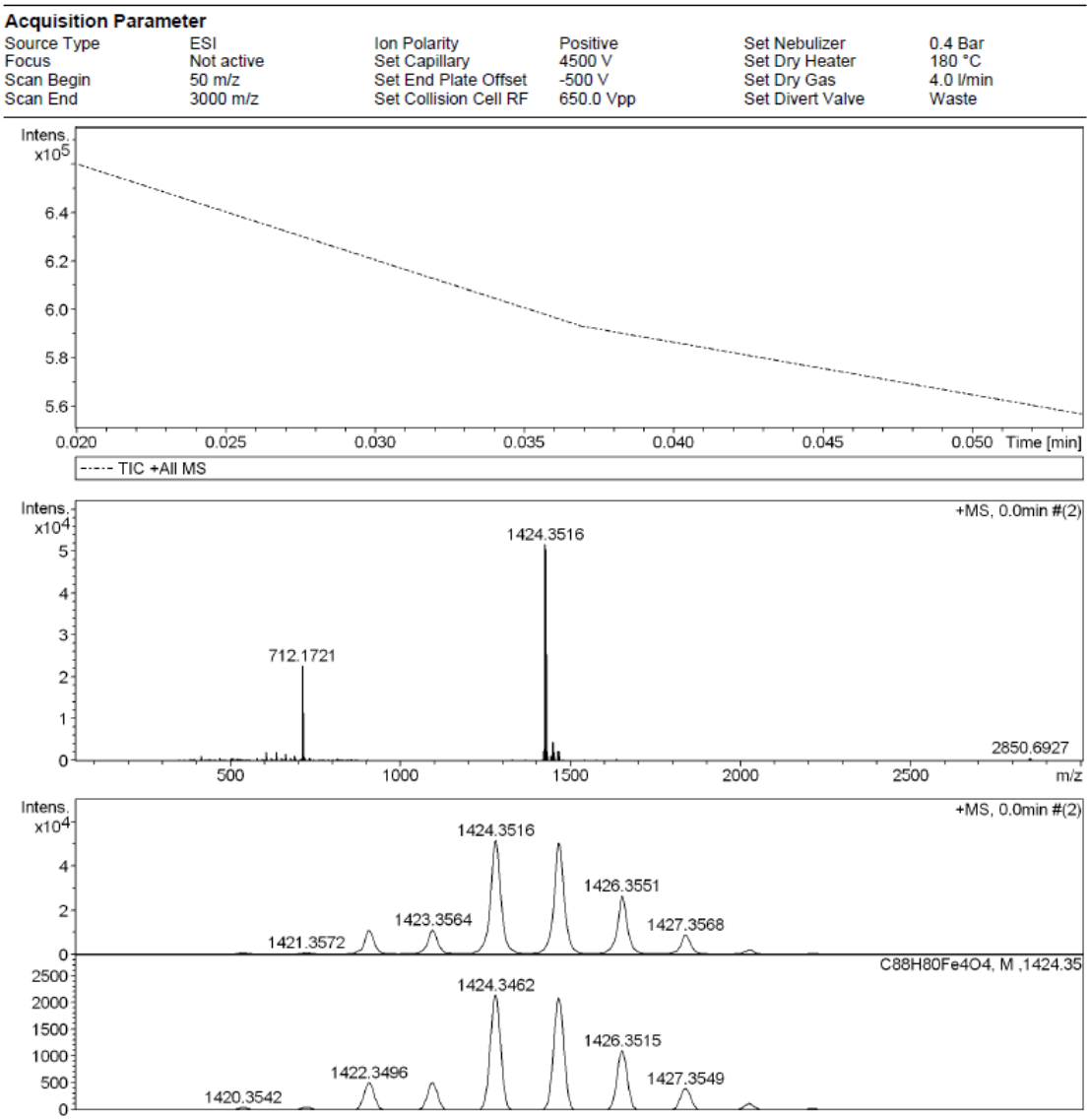

Figure S6. HRMS Spectra of **5a.**

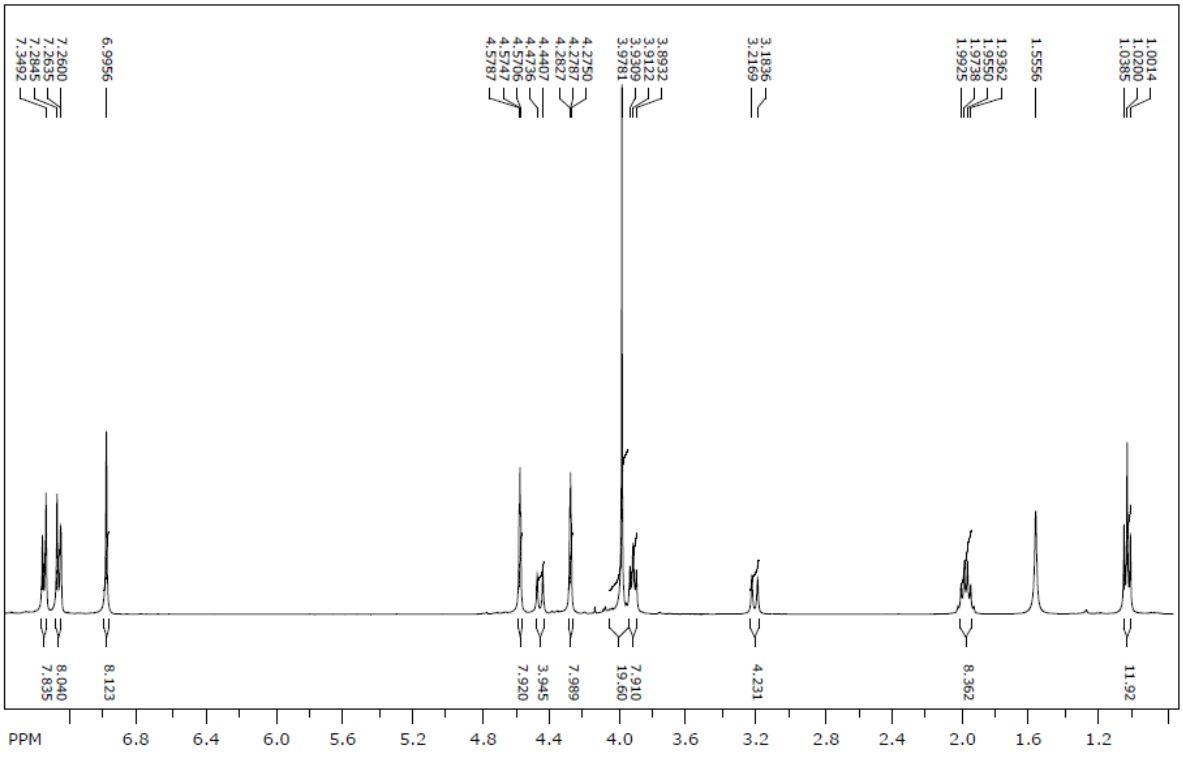

Figure S7. ^{1}H NMR Spectra of **5b.**

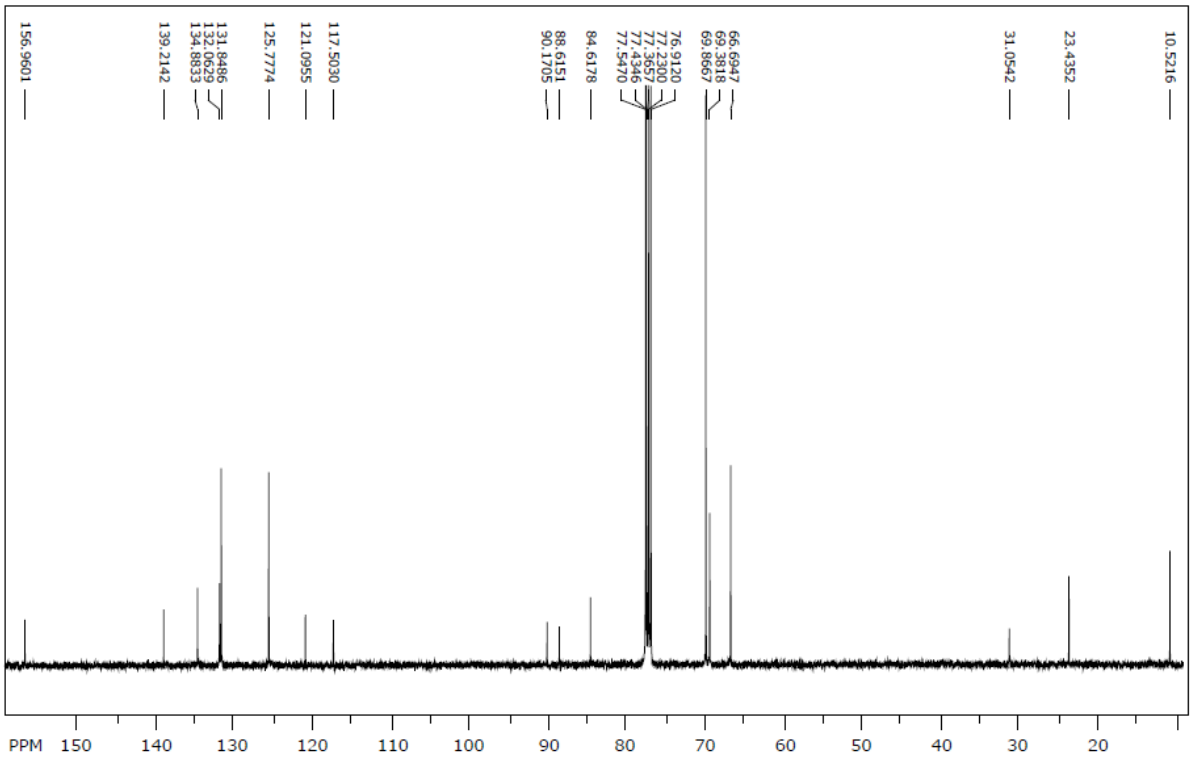

Figure S8. ^{13}C NMR Spectra of **5b.**

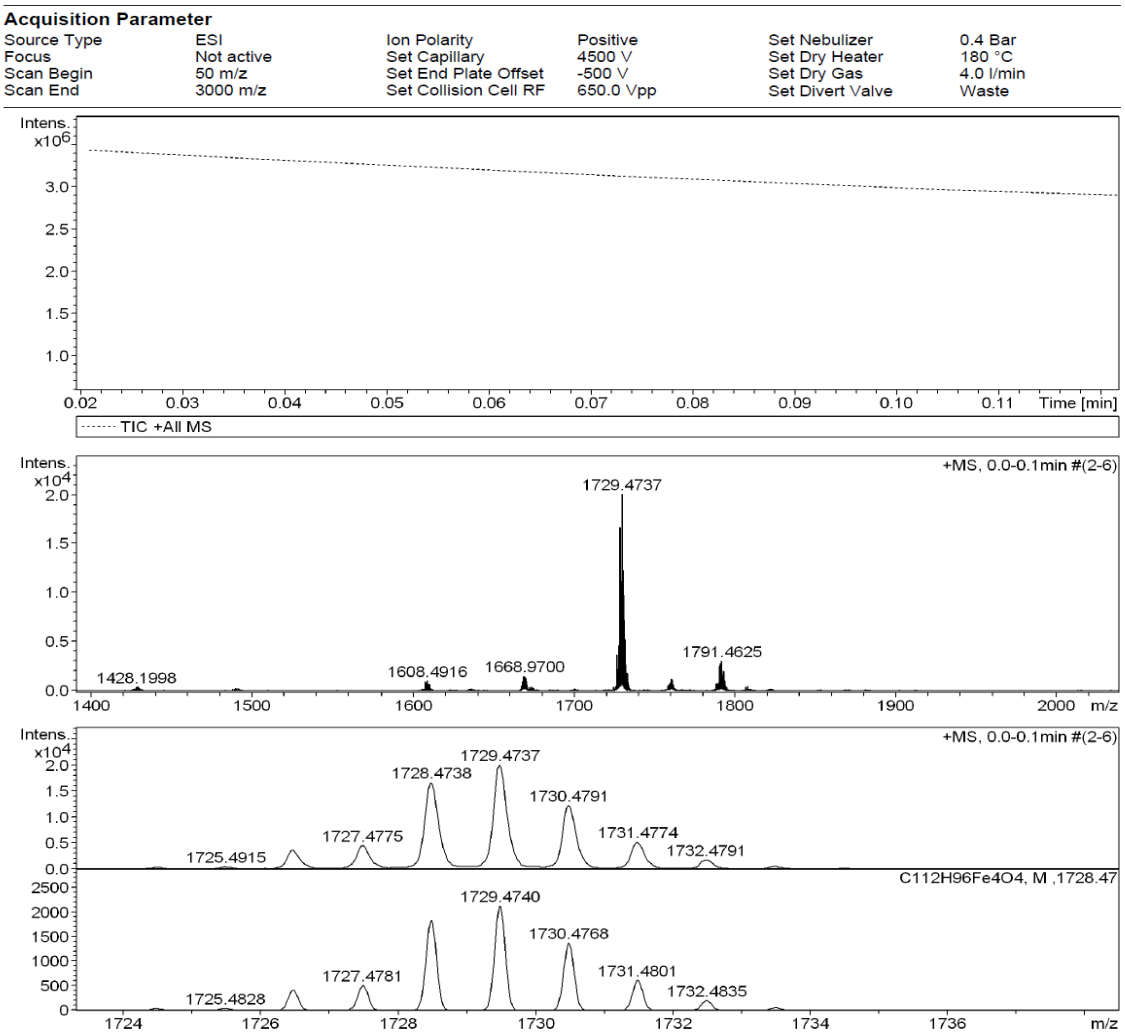

Figure S9. HRMS Spectra of **5b.**

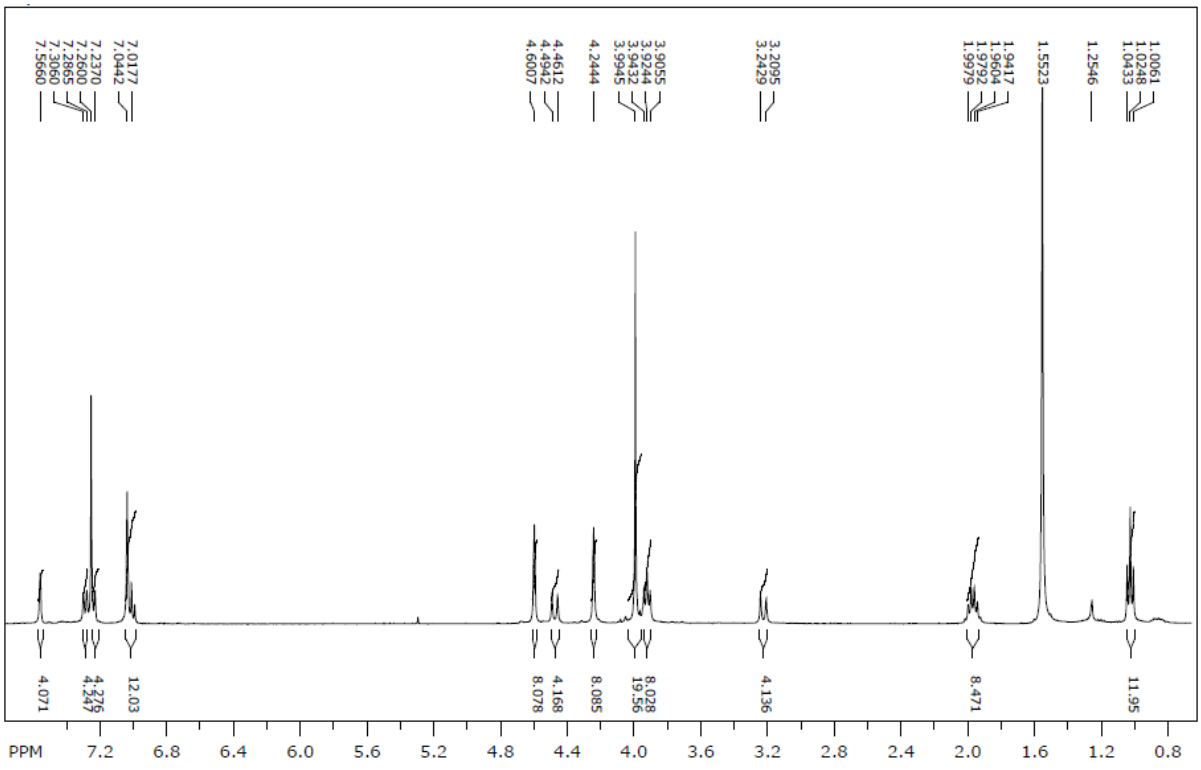

Figure S10. ^{1}H NMR Spectra of **5c.**

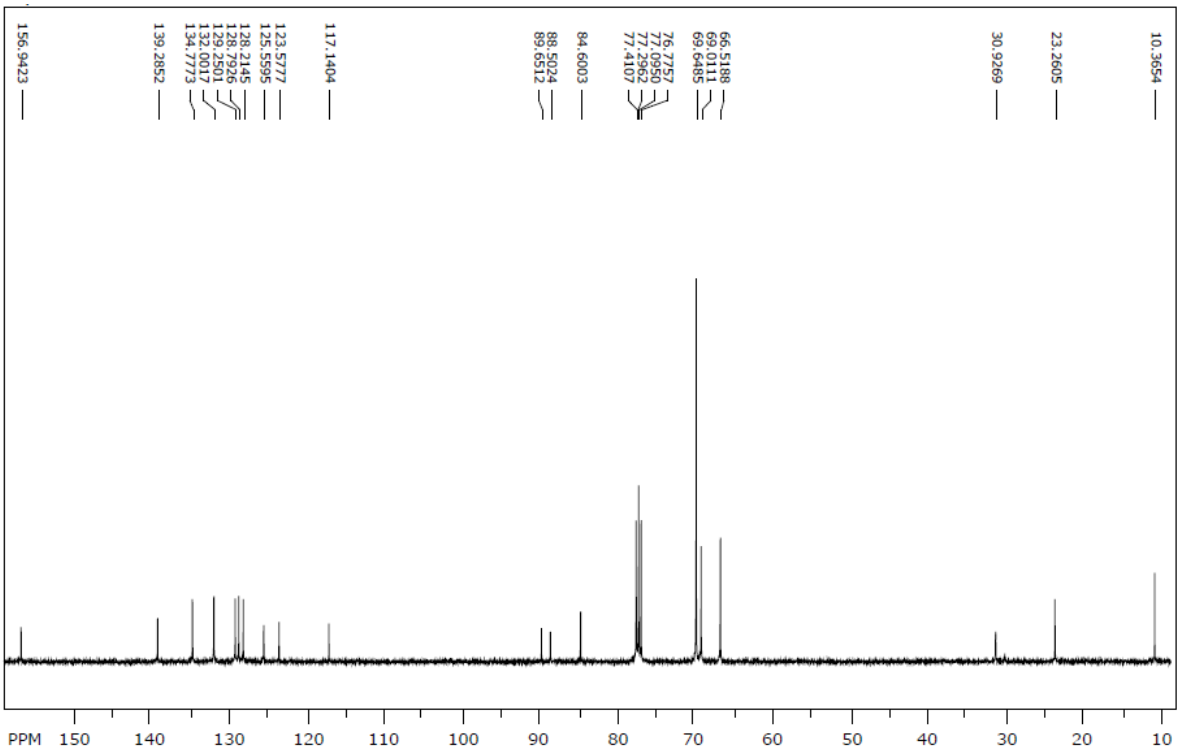

Figure S11. ^{13}C NMR Spectra of **5c.**

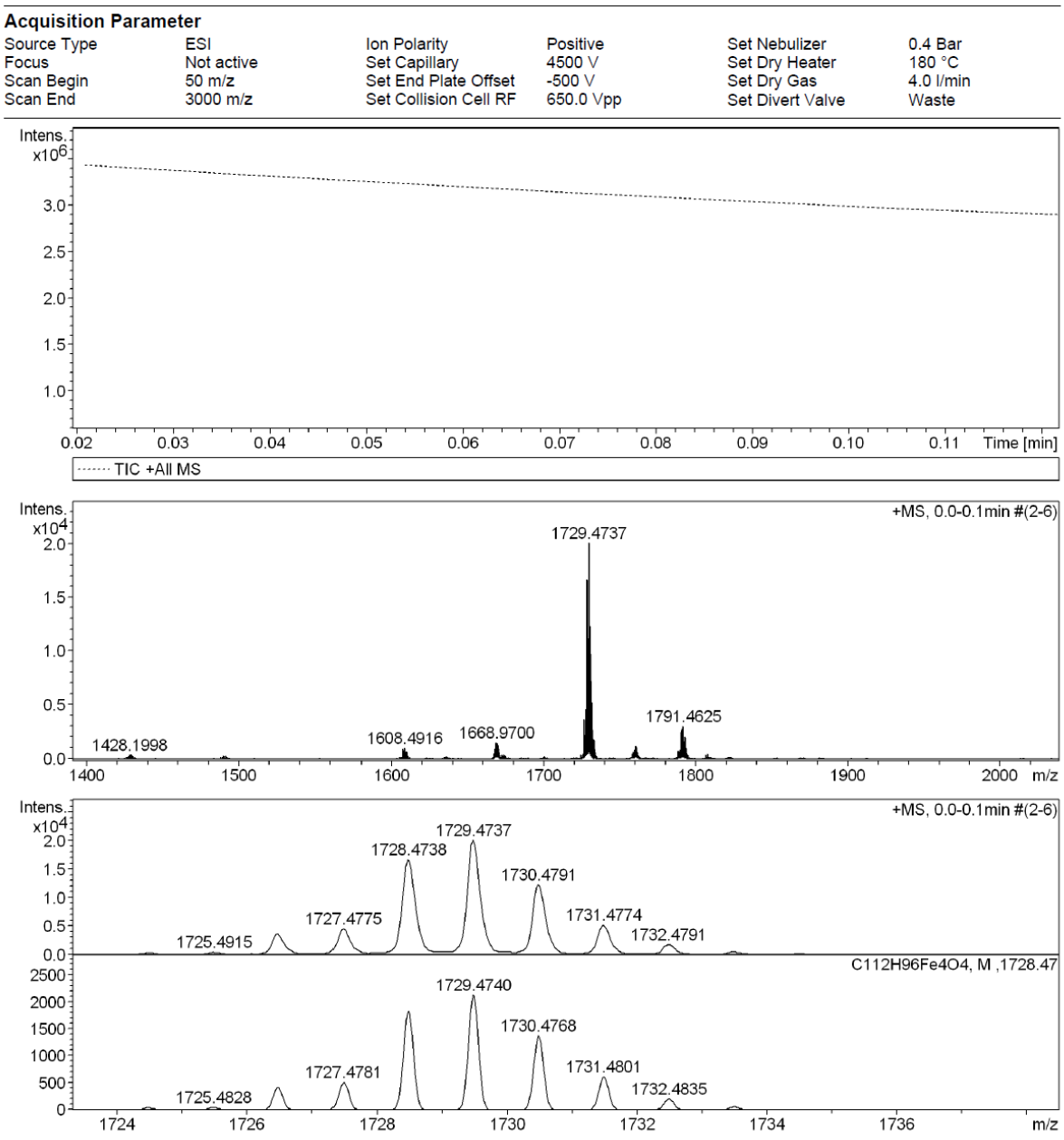

Figure S12. HRMS Spectra of **5c.**

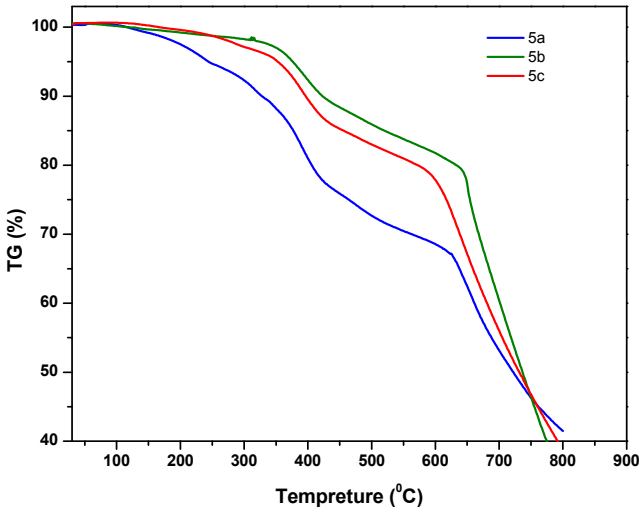

Figure S13. TGA plots of compounds **5a**−**5c**.

References

1 S. Kopacka, K. Wurst, K. H. Ongania and K. Kirchner, *J.Organomet. Chem.,* 2001, 558–576.