Supporting Information

Unprecedented formation of π-copper complexes during Sonogashira coupling: Synthesis of a unique, recyclable, ethynyl ferrocene derived Cu(I) specific ligand

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A. Table- S1: Optimization of reaction conditions:

Entry no.	Reactant	X on ***Aryl halide***	R on ***oxazoline***	Time (h)	Temp (^{o}C)	Yield (%)
1	Fc-C≡CH	I	i-Pr	24	50	42[a]
2	Fc-C≡CH	Br	i-Pr	24	50	8[a]
3	Fc-C≡CH	I	Ph	24	50	2[a]
4	**Fc-C≡C-Cu**	**I**	**i-Pr**	**3**	**RT**	**65[b]**
5	Fc-C≡C-Cu	I	i-Pr	3	50	40[b]
6	Fc-C≡C-Cu	I	i-Pr	3	70	25[b]
7	Fc-C≡C-Cu	I	i-Pr	24	RT	62[b]
8	Fc-C≡C-Cu	Br	i-Pr	3	RT	56[b]
9	Fc-C≡C-Cu	I	Ph	3	RT	53[b]
10	Fc-C≡C-Cu	I	H	3	RT	0[b]
11	Fc-C≡C-Cu	Br	H	3	RT	0[b]
12	Fc-C≡C-Cu	I	H	24	50	0[b]
13	Fc-C≡CH	I	i-Pr	24	RT	3[c]
14	Fc-C≡CH	Br	i-Pr	24	RT	2[c]
15	Fc-C≡CH	I	Ph	24	RT	2[c]

Fc = Ferrocenyl; RT = Room temperature. [a]Carried out with 1.1 equiv of CuI and triethylamine as base and solvent, [b]Carried out in a co-catalyst free and base free condition, [c]Carried out with 4 mol% of CuI co-catalyst, with triethylamine as base and solvent. (All yields are isolated yields)

B. Recyclability studies of metal-free Cu(I) specific ligand (5a):

Table-S2

No of cycle	Yield of the CuX complex isolated from 5a (%)*	Time of the reaction
1	97	60 seconds
2	96	60 seconds
3	94	60 seconds
4	93	60 seconds

*Isolated yields with respected to the amount of free ligand **5a** used before the 1st cycle.

C. UV-vis spectroscopy of the un-complexed (5a) and complexed form (4a):

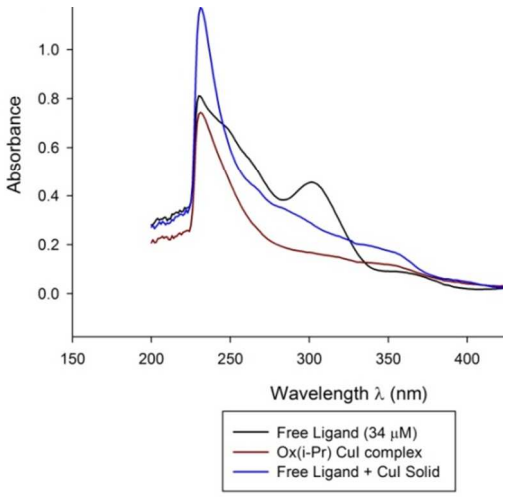

Figure S1: Plot of Absorbance vs wavelength of the complexed and un-complexed forms.

Table- S3 (Measurement was performed in dry-dichloromethane as solvent)

Serial no	Substance	λ_{max}(nm)	Color of the curve
1	Complexed form **4a**	231	Red curve
2	Metal-free ligand **5a**	301	Black curve
3	**5a + CuI →**	231**	Blue curve

** *Solution was filtered before the measurement of Absorbance.*

Fate of Copper in the synthesis of Cu-free ligands (5a-b):

The aq. layer obtained in section E, was examined by measuring the UV-vis spectra. The λ_{max} was found to be at 633 nm. The identity of the blue complex was confirmed by reacting $CuCl_2.6H_2O$ in DMF with aq. NH_3. The complex obtained was found to absorb λ_{max} 632 nm. The literature[1] for UV-vis spectroscopy for Cu(II) complexes reveals that $Cu(NH_3)_4(H_2O)_2$ absorbs at λ_{max} 620-630 nm.

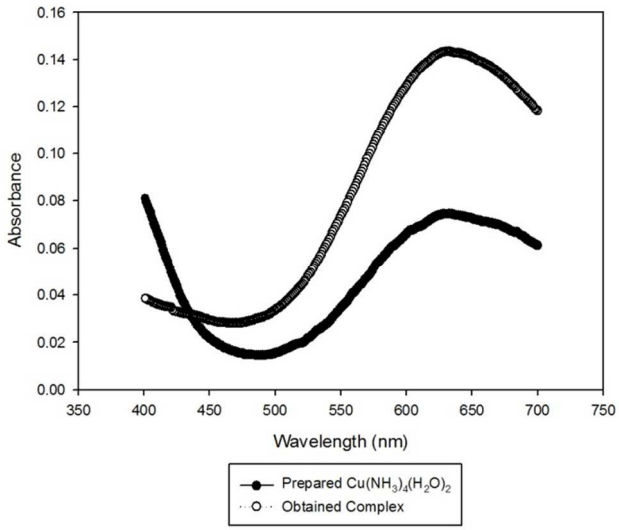

Figure S2: Plot of Absorbance *vs.* wavelength of the prepared $Cu(NH_3)_4(H_2O)_2$ complex in DMF and obtained blue colored aq. layer in section E.

D. Important bond lengths and bond angles of compounds (4a-c) (Tables S4-S6):

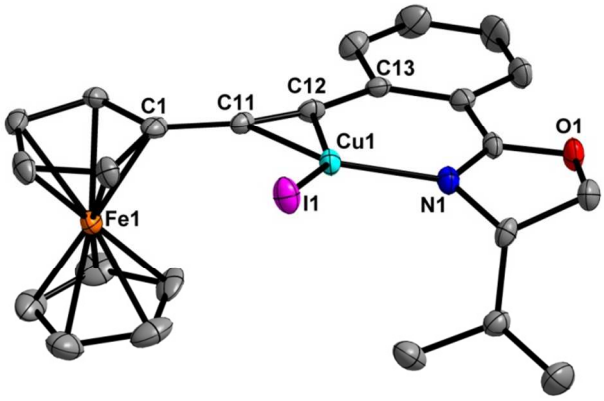

Fig S3: Molecular structure of **4a**

Table-S4 (4a)

Bond lengths (Å)	
N(1)-Cu(1)	1.963(6)
I(1)-Cu(1)	2.5151(11)
C(11)-C(12)	1.233(10)
Cu(1)-C(11)	2.017(7)
Cu(1)-C(12)	1.966(7)
Bond Angles (deg)	
N(1)-Cu(1)-C(12)	94.3(3)
N(1)-Cu(1)-C(11)	129.6(3)
C(12)-Cu(1)-C(11)	36.0(3)
N(1)-Cu(1)-I(1)	112.87(18)
C(11)-Cu(1)-I(1)	117.5(2)

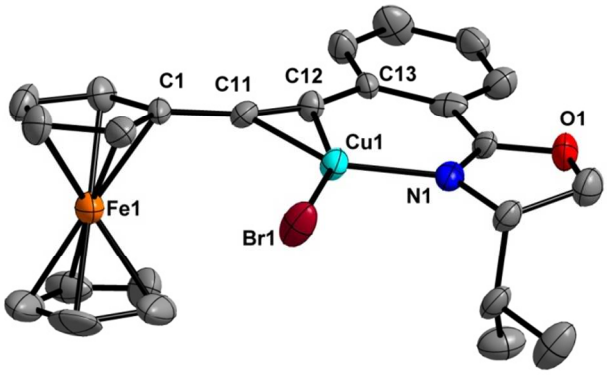

Fig S4: Molecular structure of **4b**

Table-S5 (4b)

Bond lengths (Å)	
N(1)-Cu(1)	1.971(11)
Br(1)-Cu(1)	2.307(2)
C(11)-C(12)	1.261(17)
Cu(1)-C(11)	1.996(12)
Cu(1)-C(12)	1.927(12)
Bond Angles (deg)	
C(12)-Cu(1)-N(1)	95.2(5)
N(1)-Cu(1)-C(11)	132.6(5)
C(12)-Cu(1)-C(11)	37.4(5)
N(1)-Cu(1)-Br(1)	111.8(3)
C(11)-Cu(1)-Br(1)	115.5(4)

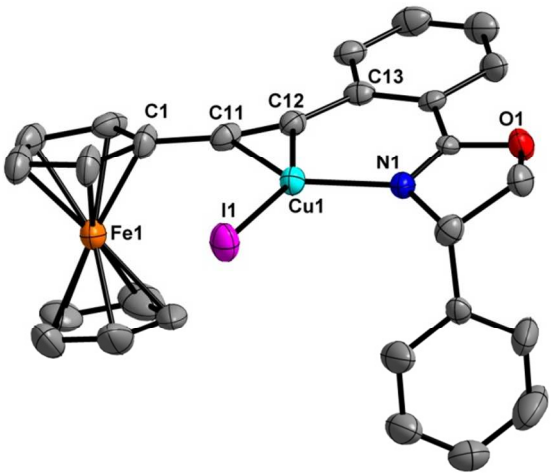

Fig S5: Molecular structure of **4c**

Table-S6 (4c)

Bond lengths (Å)	
I(1)-Cu(1)	2.5008(11)
Cu(1)-C(12)	1.947(7)
Cu(1)-N(1)	1.951(6)
Cu(1)-C(11)	2.004(7)
C(11)-C(12)	1.226(10)
Bond Angles (deg)	
C(12)-Cu(1)-N(1)	94.7(3)
C(12)-Cu(1)-C(11)	36.1(3)
N(1)-Cu(1)-C(11)	130.8(3)
C(12)-Cu(1)-I(1)	151.2(2)
N(1)-Cu(1)-I(1)	113.90(19)
C(11)-Cu(1)-I(1)	115.3(2)

E. Table-S7: X-ray crystallographic data for compounds 4a-c:

Parameters	**4a**	**4b**	**4c**
Formula	$C_{24}H_{23}CuFeINO$	$C_{48}H_{46}Br_2Cu_2Fe_2N_2O_2$	$C_{27}H_{21}CuFeINO$
MW	587.73	1078.11	621.75
crystal system	orthorhombic	triclinic	orthorhombic
Space group	P212121	P1	P212121
a (Å)	9.231(13)	8.846(3)	9.5006(12)
b (Å)	13.687(2)	11.295(4)	13.0647(16)
c (Å)	17.612(3)	12.422(4)	19.113(2)
α (deg)	90	72.460(7)	90
β (deg)	90	73.915(6)	90
γ (deg)	90	70.961(7)	90
V (Å^3)	2225.2(6)	1096.5(6)	2372.4(5)
Z	4	1	4
T /K	298(2)	298(2)	298(2)
λ (Å)	0.71073	0.71073	0.71073
ρ_{calcd} (g/cm3)	1.754	1.633	1.741
μ (mm-1)	3.010	3.468	2.828
Goodness of fit	1.293	0.960	1.198
θ range	1.88 to 24.99	1.96 to 25.00	2.13 to 24.99
Total reflections	21468	5665	23083
Unique reflections	3917	4707	4173
# Ovserved data[$I > \sigma(I)$]	3759	3047	3742
R_{int}	0.0767	0.0412	0.0635
R_1, wR_2 [(I > 2σ(I)]	0.0536, 0.1121	0.0614, 0.1177	0.0554, 0.1094
R_1, wR_2 (all data)	0.0567, 0.1135	0.1070, 0.1356	0.0637, 0.1125
Flack parameter	0.03(4)	0.01(2)	0.03(4)

$R_1 = \Sigma|F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma\ (|F_o|^2 - |F_c|^2)^2]\}^{1/2}$

F. ^{1}H and ^{13}C{1H} NMR spectra of the new compounds: (300 MHz and 75.4 MHz respectively, in CDCl3):

2a

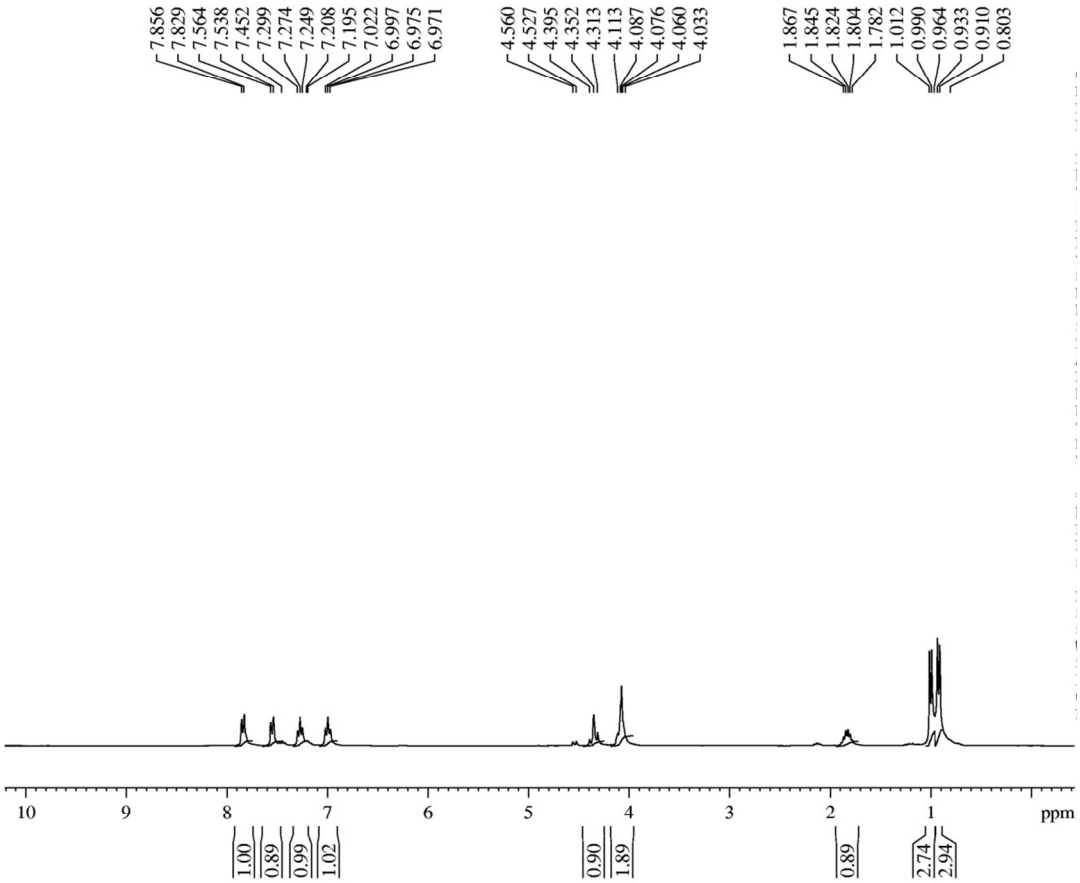

Fig S6: ^{1}H NMR spectrum of **2a**

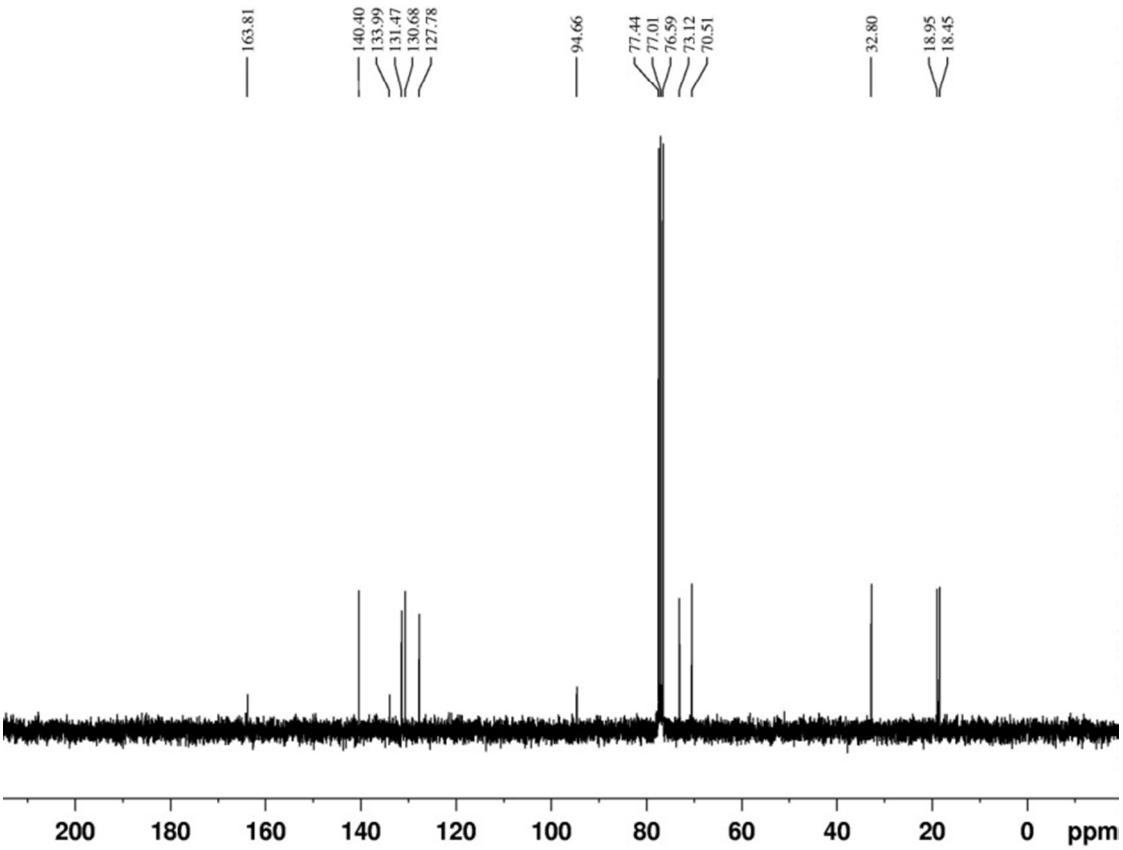

Fig S7: $^{13}C\{1H\}$ NMR spectrum of **2a**

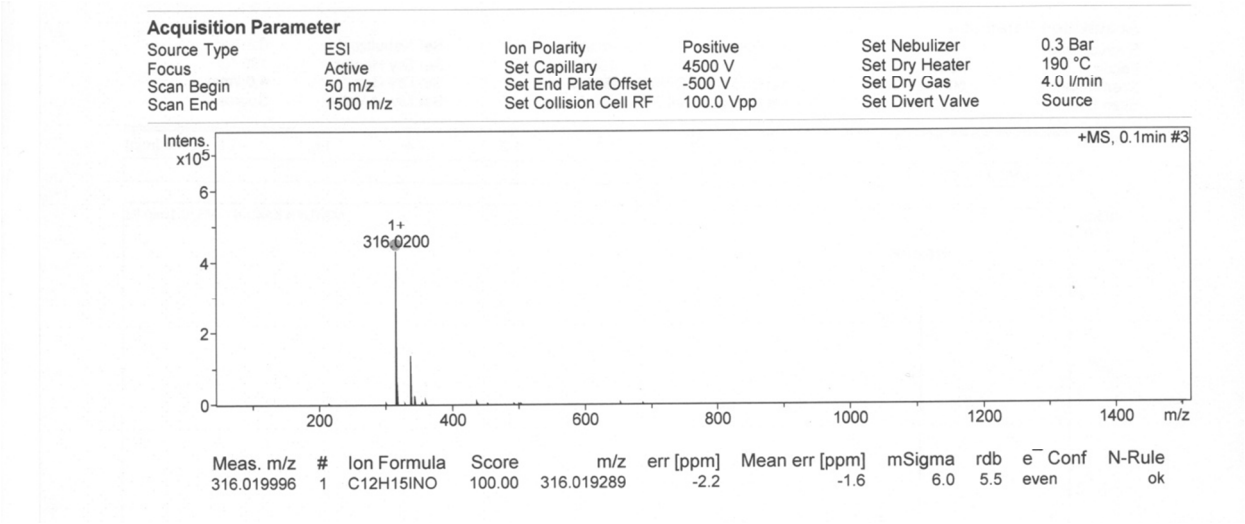

Fig S8: ESI-MS HRMS spectrum of **2a**

2b

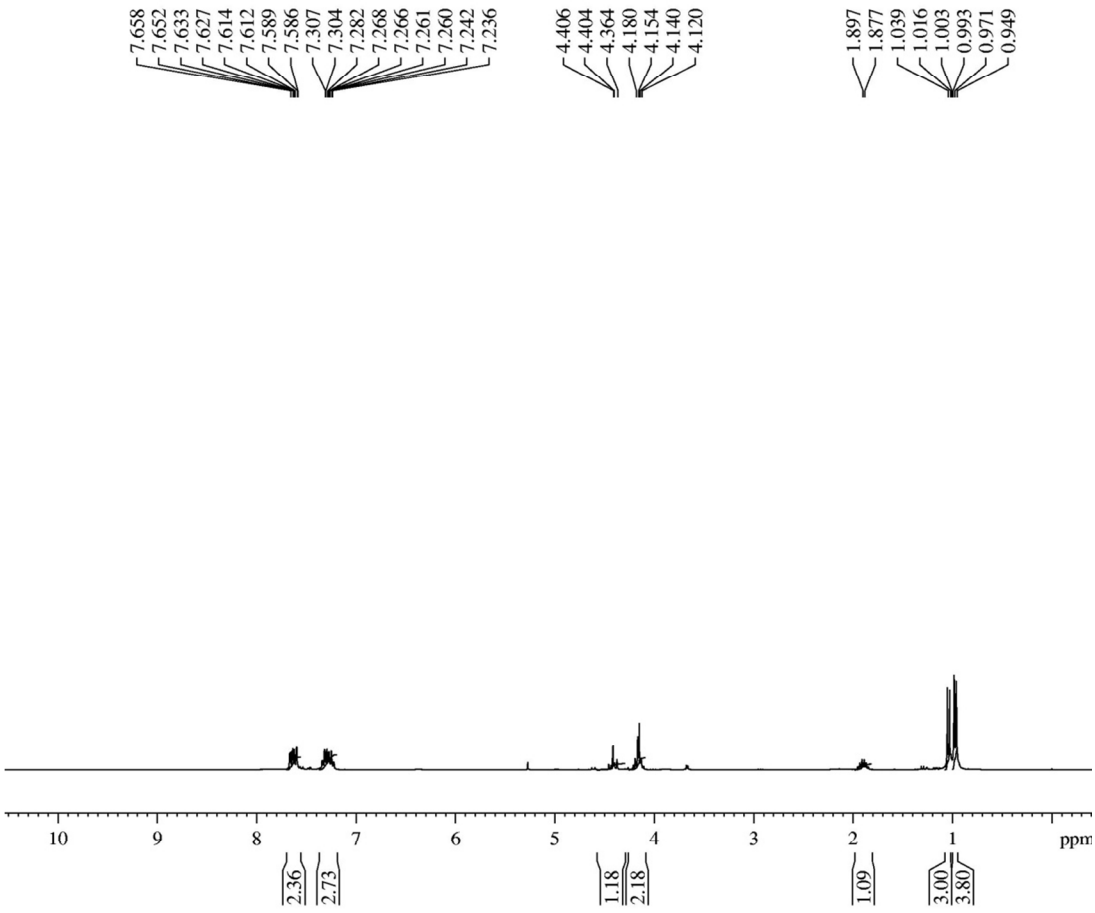

Fig S9: ^{1}H NMR spectrum of **2b**

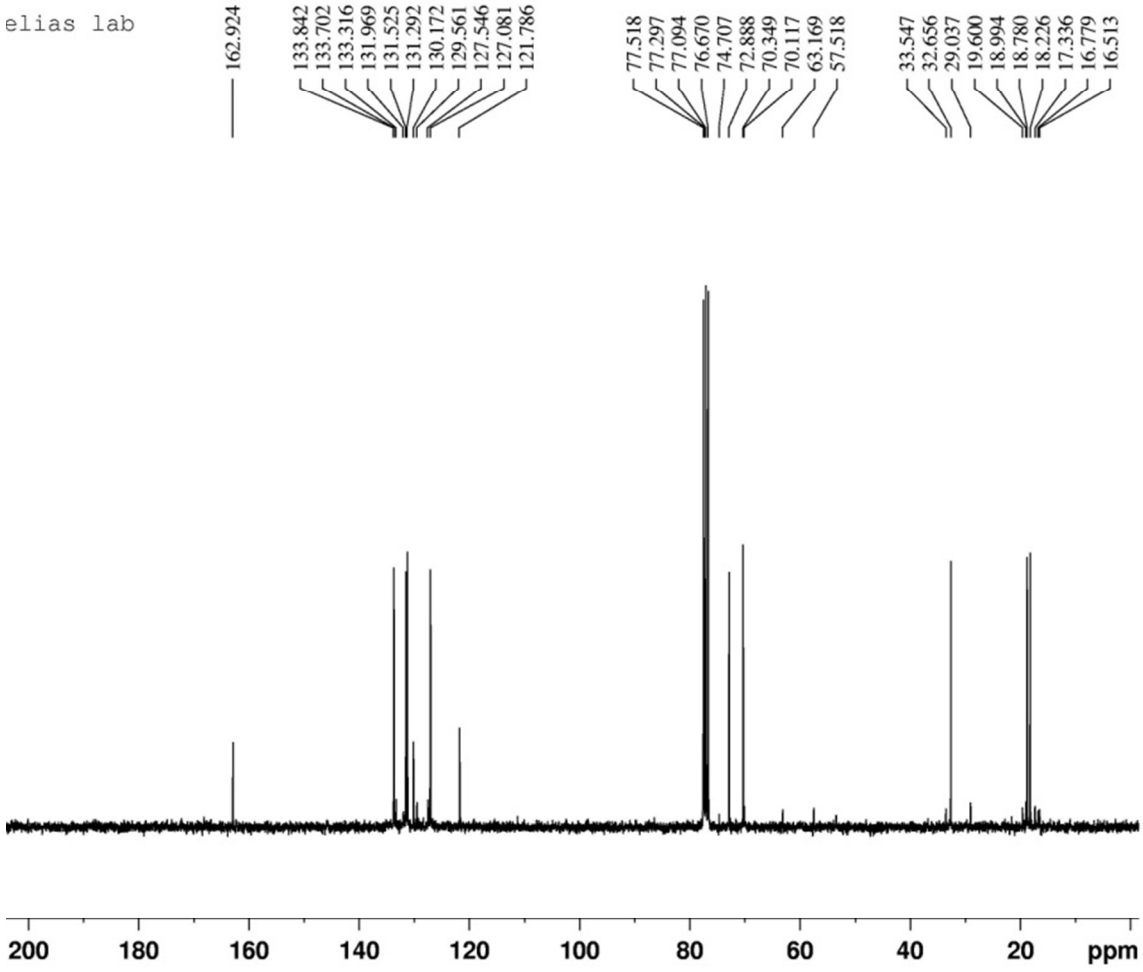

Fig S10: $^{13}C\{1H\}$ NMR spectrum of **2b**

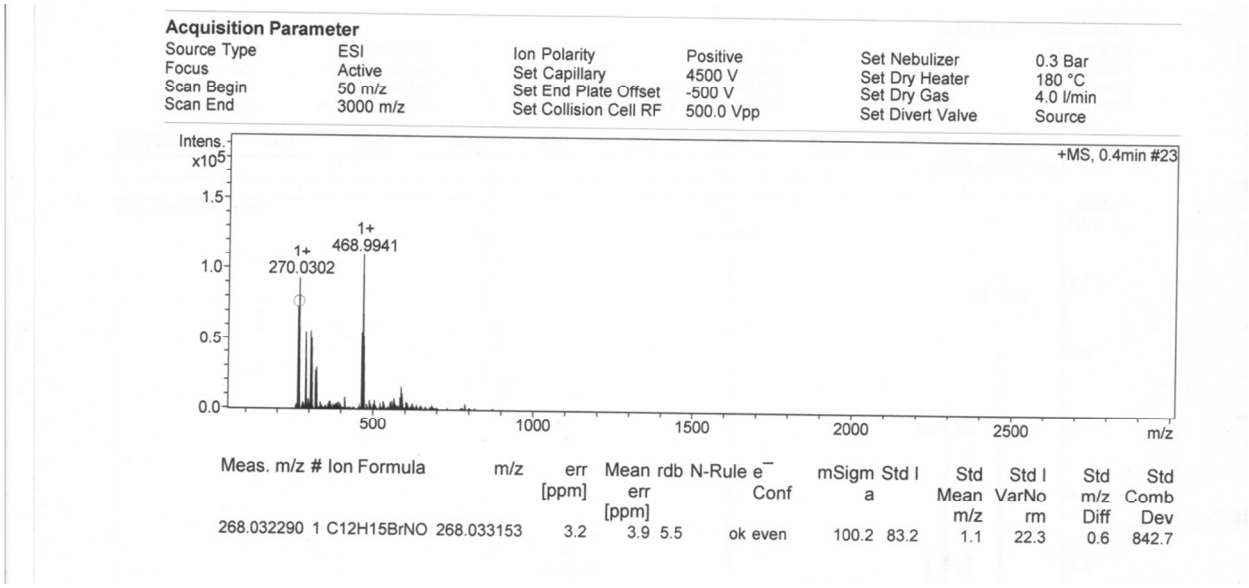

Fig S11: ESI-MS HRMS spectrum of **2b**

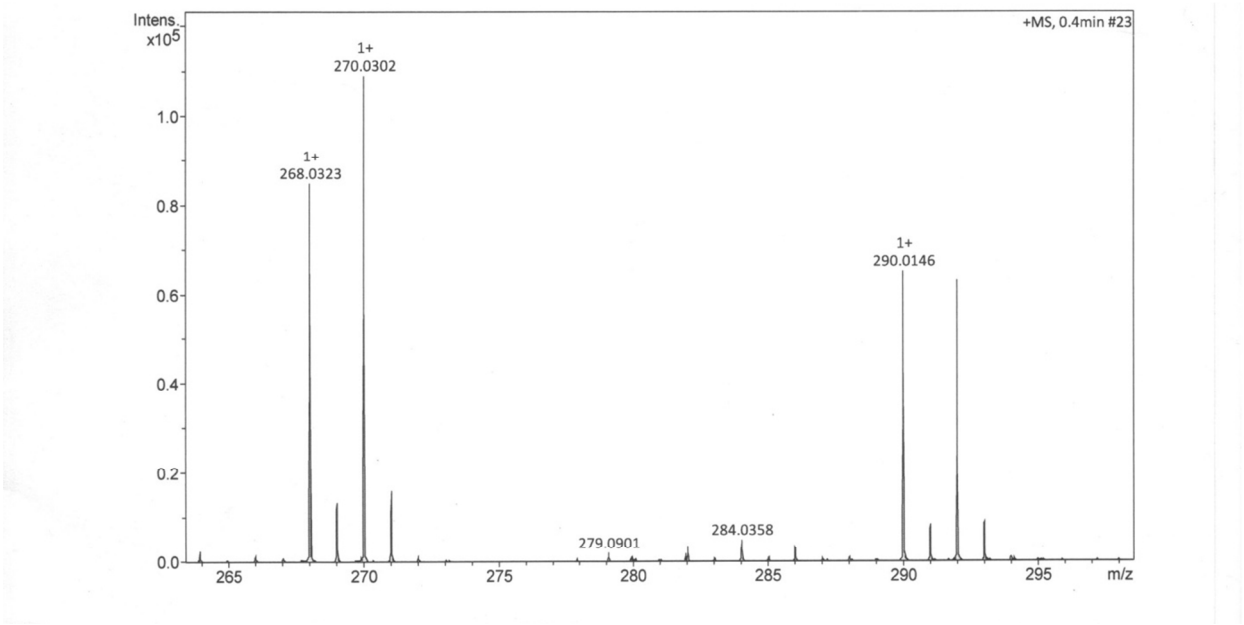

Fig S12: ESI-MS HRMS spectrum of **2b (Expanded)**

2c

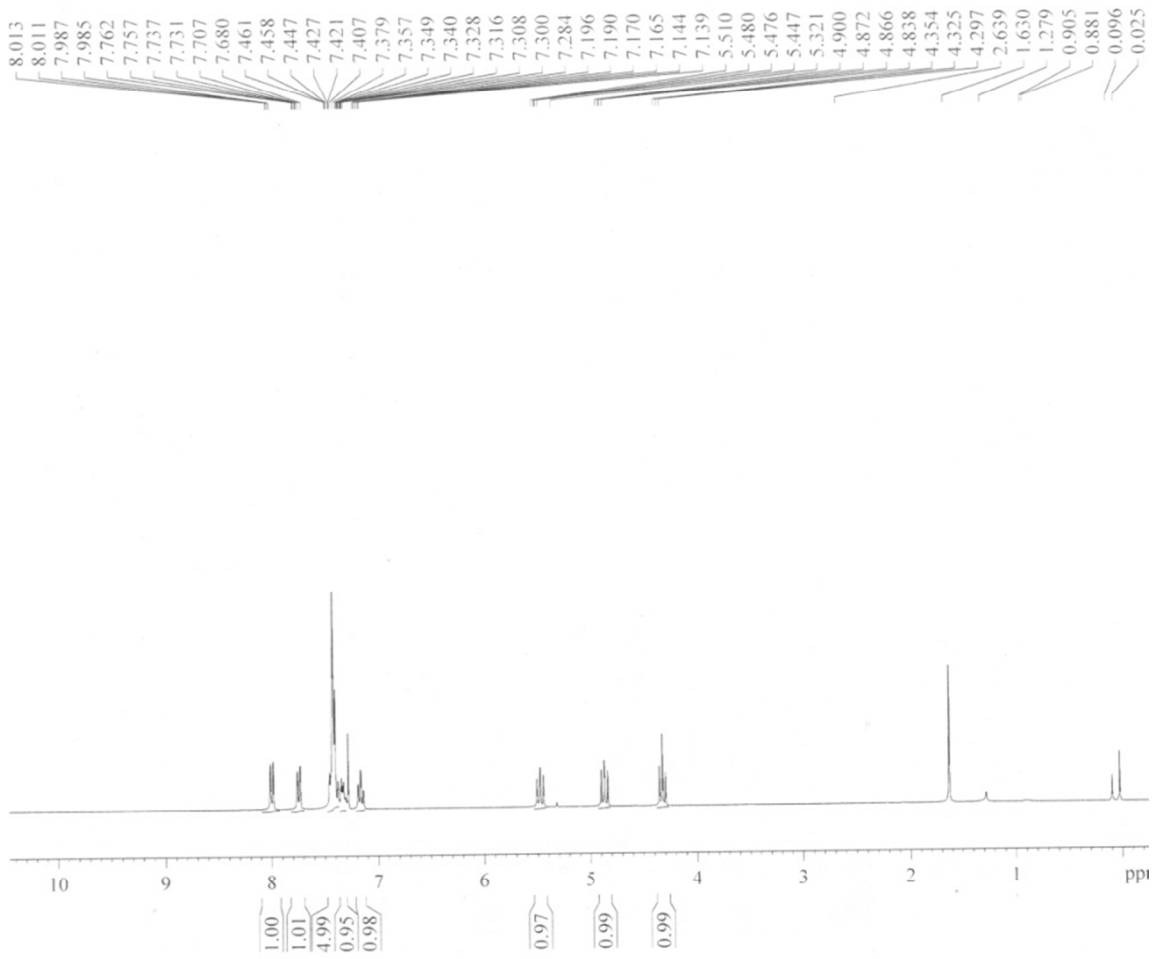

Fig S13: ^{1}H NMR spectrum of **2c**

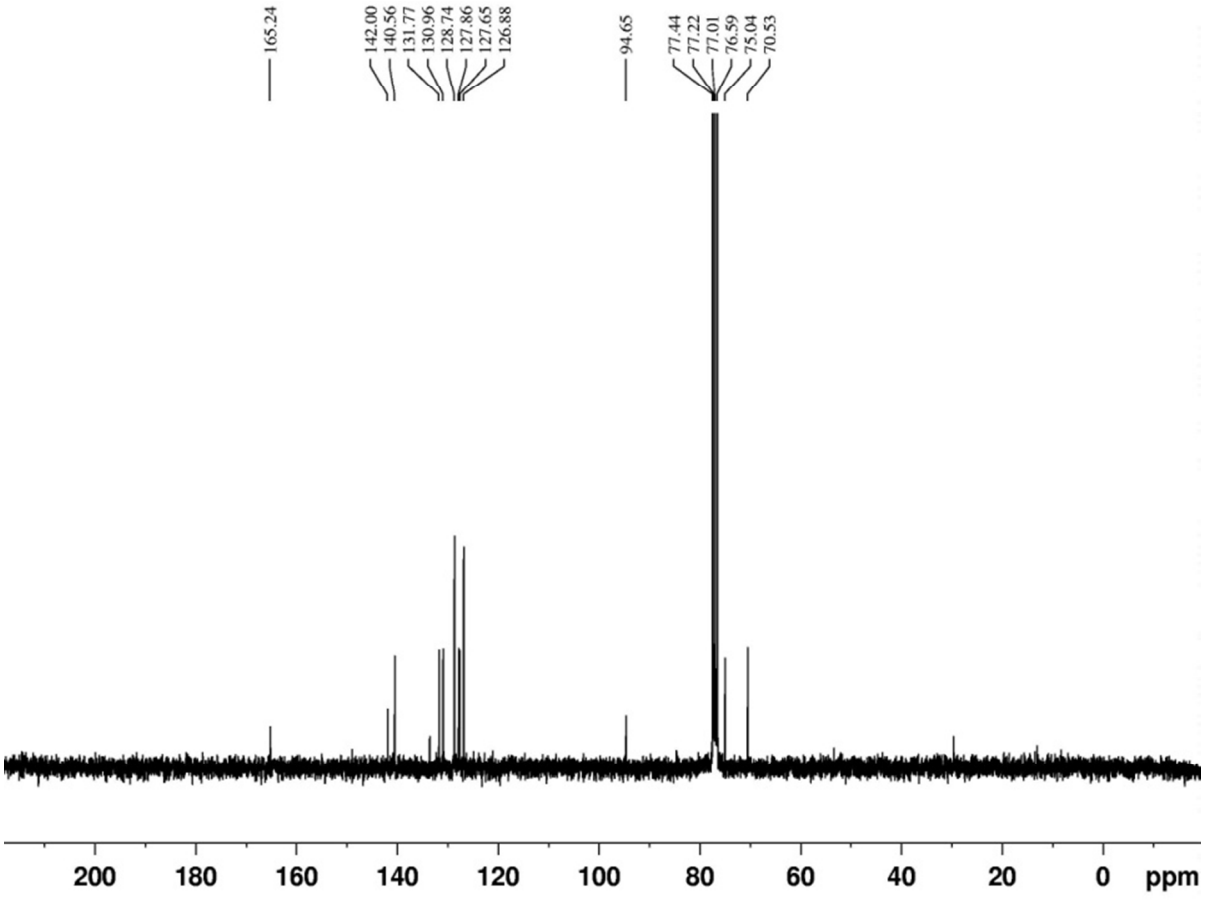

Fig S14: $^{13}C\{1H\}$ NMR spectrum of **2c**

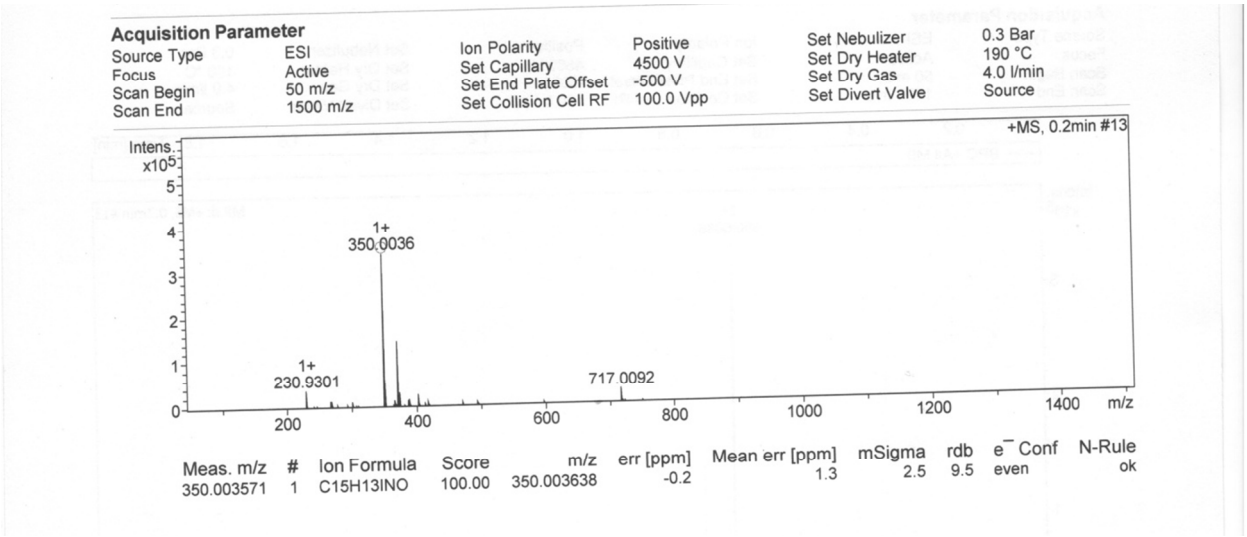

Fig S15: ESI-MS HRMS spectrum of **2c**

5a

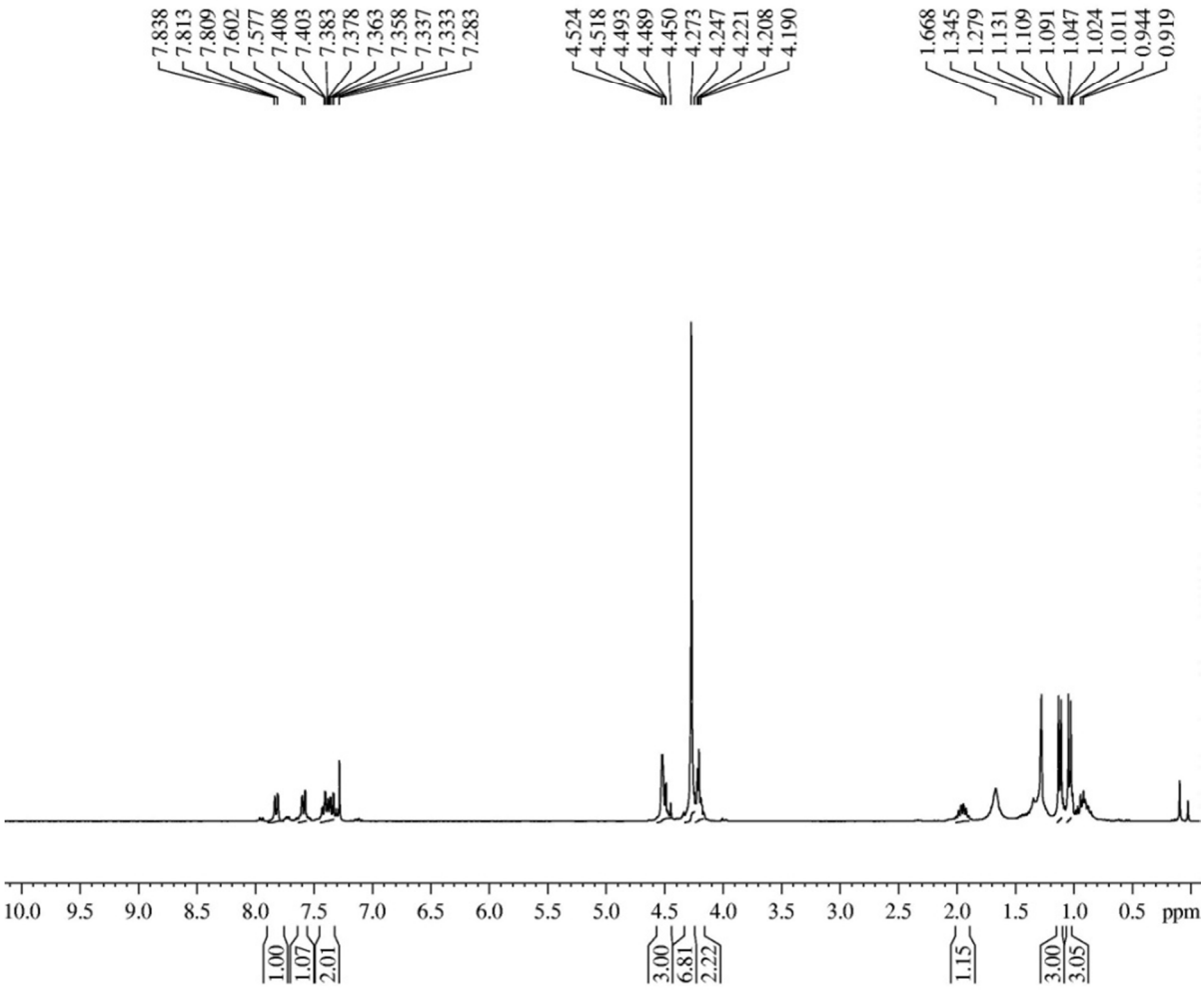

Fig S16: ^{1}H NMR spectrum of **5a**

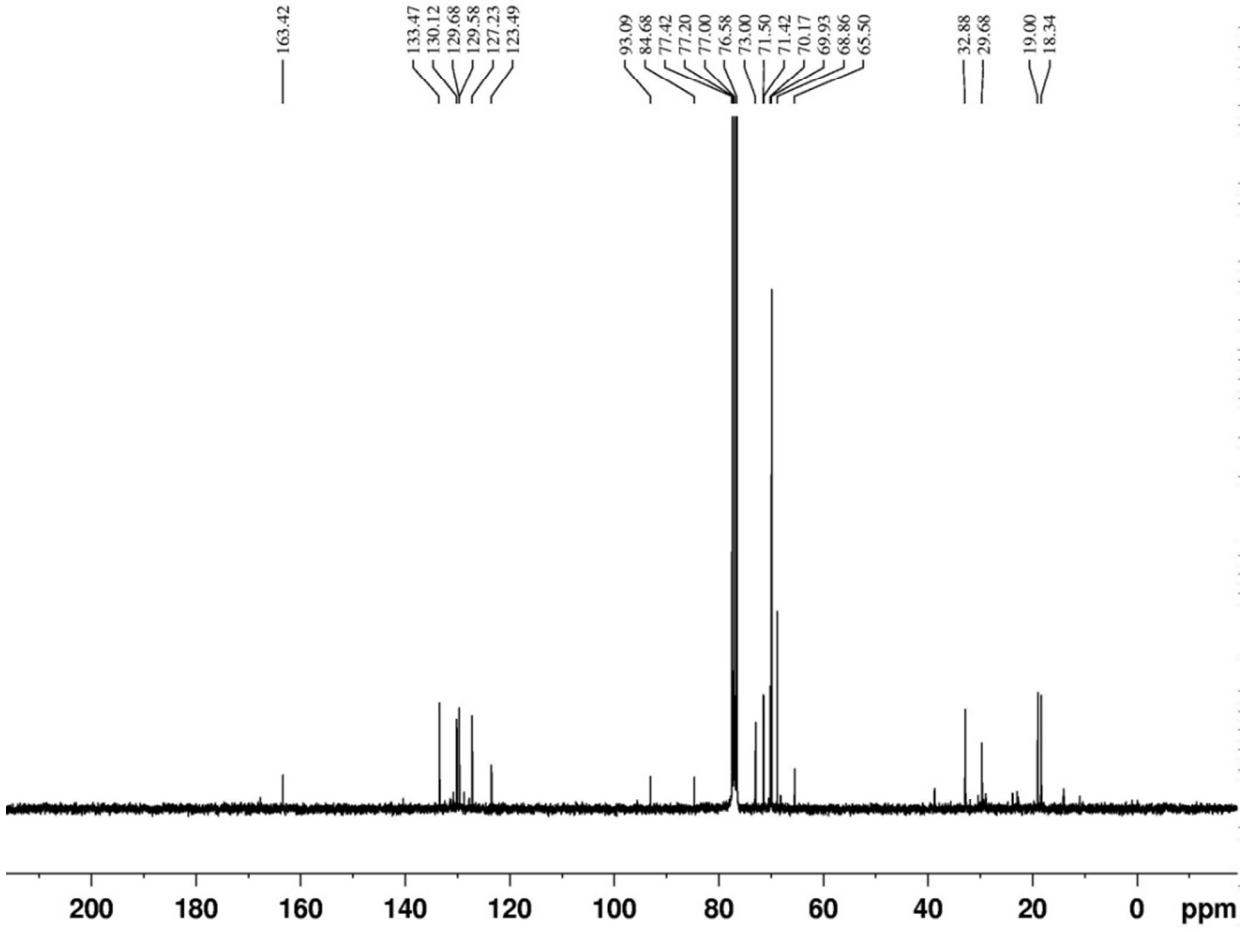

Fig S17: $^{13}C\{1H\}$ NMR spectrum of **5a**

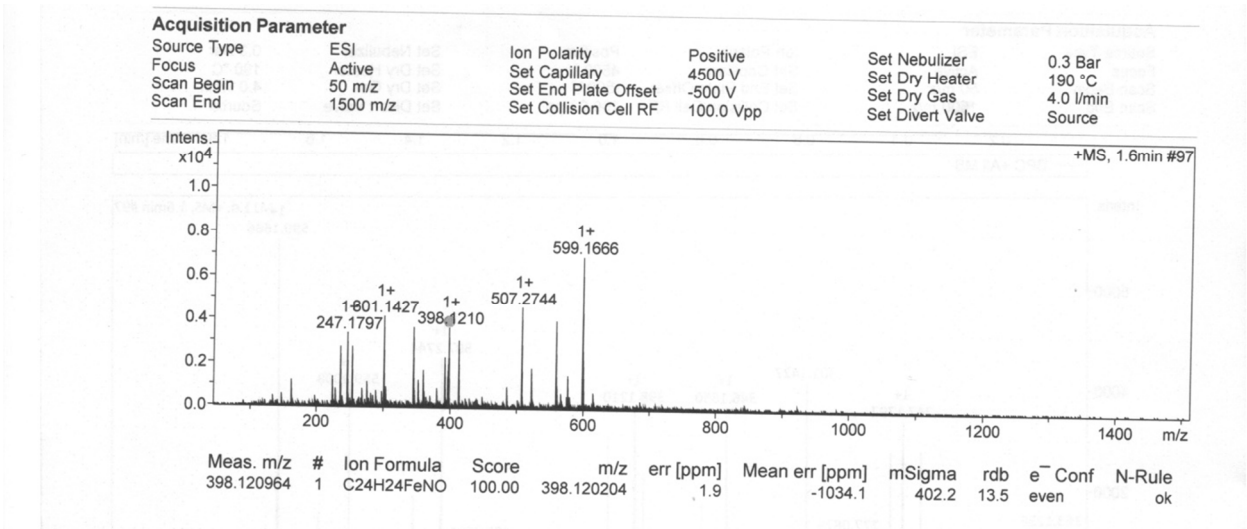

Fig S18: ESI-MS HRMS spectrum of **5a**

5b

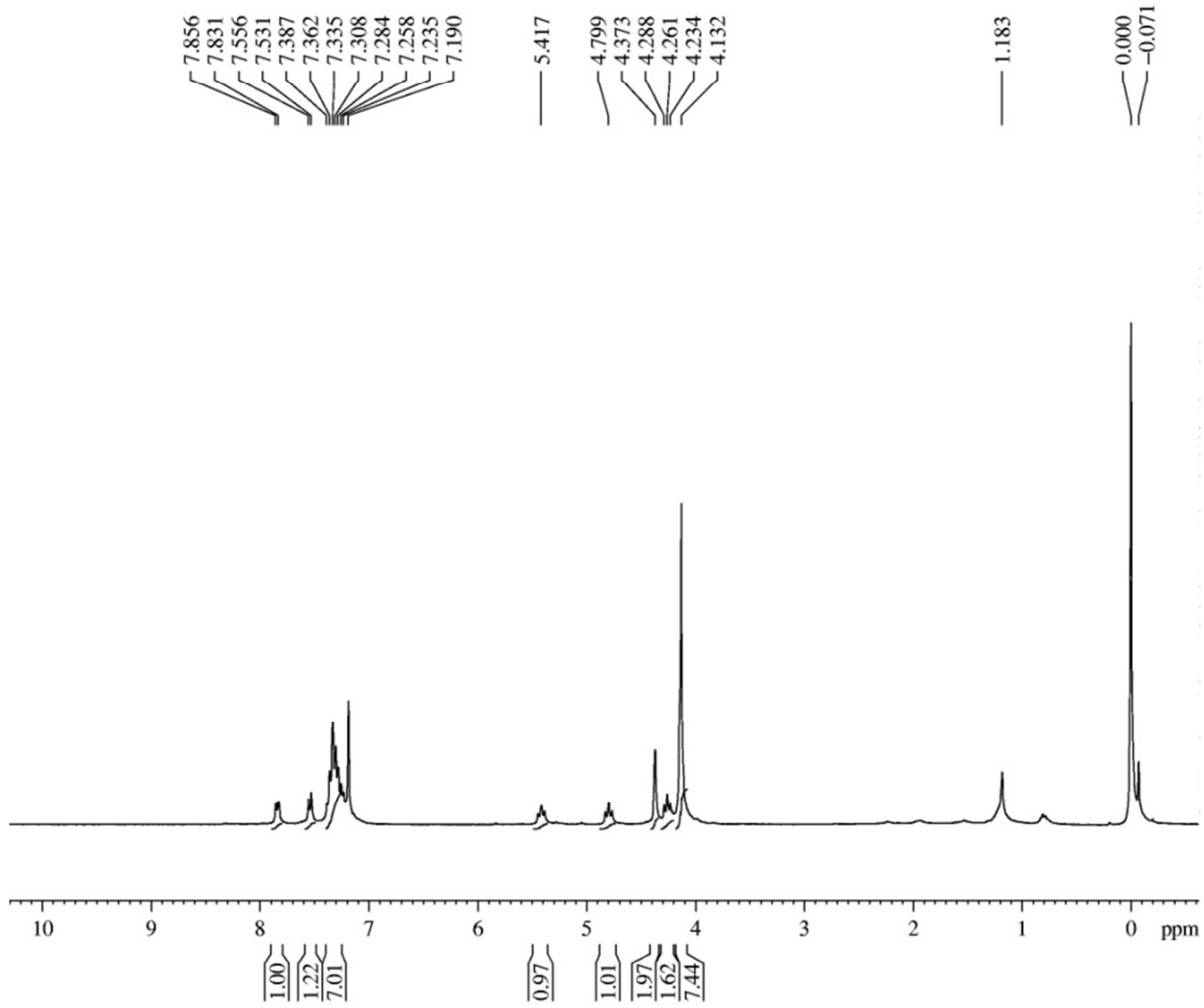

Fig S19: ^{1}H NMR spectrum of **5b**

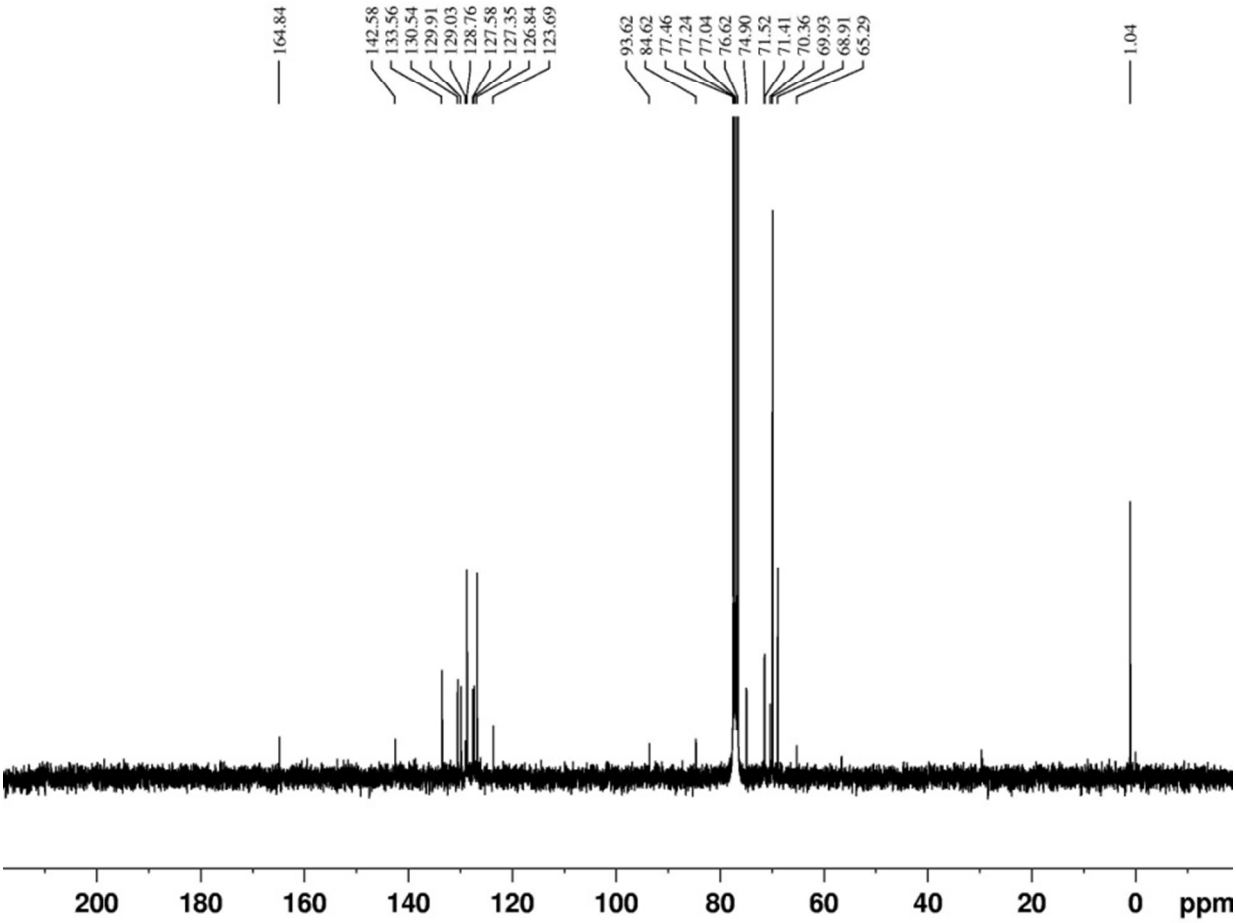

Fig S20: $^{13}C\{1H\}$ NMR spectrum of **5b**

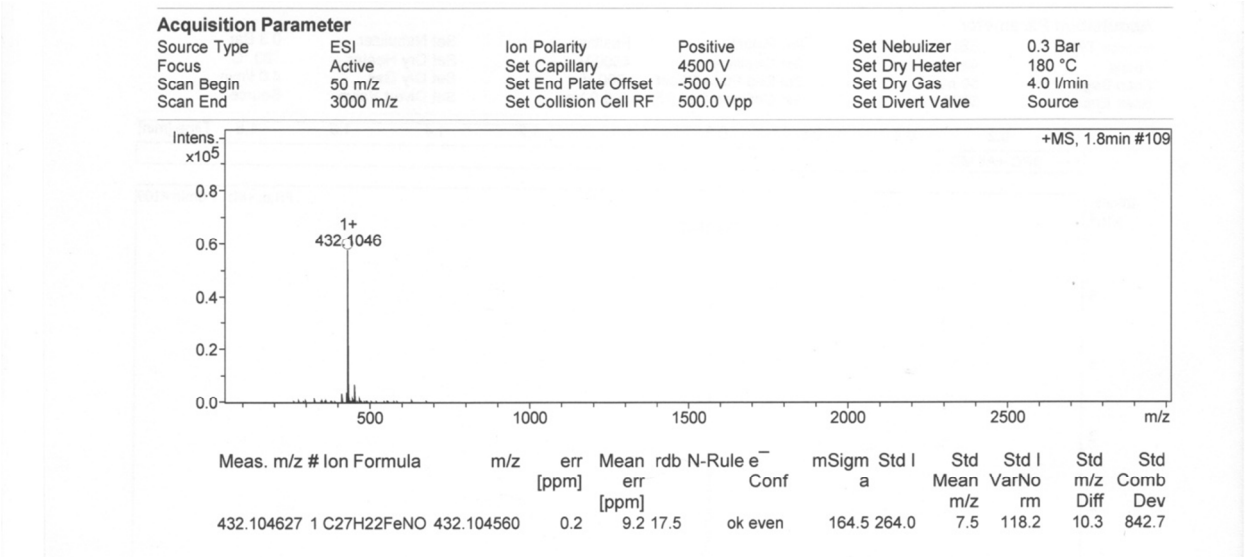

Fig S21: ESI-MS HRMS spectrum of **5b**

G. References:

1. Faust, B. *Modern Chemical Techniques: An Essential Reference for Students and Teachers,* The Royal Society of Chemistry, 1997.