Supplementary Information

Synthesis, structural analysis, electrochemical and magnetic properties of tetrachloroferrate(III) ionic liquids

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1. **Supplementary crystallographic data for (2) and (6)**

Table S1. Bond lengths for (**2**) and (**6**).

Atom	Atom	Length/Å	Atom	Atom	Length/Å
(2)					
Fe1	Cl4	2.1853(8)	N2	C3	1.387(3)
Fe1	Cl3	2.1912(8)	N2	C9	1.463(4)
Fe1	Cl2	2.1938(8)	C2	C7	1.383(4)
Fe1	Cl1	2.1967(7)	C2	C3	1.388(4)
N1	C1	1.313(3)	C3	C4	1.382(4)
N1	C2	1.380(3)	C4	C5	1.376(5)
N1	C8	1.471(3)	C5	C6	1.387(5)
N2	C1	1.317(3)	C6	C7	1.355(5)
(6)					
Fe1	Cl1	2.1991(5)	C2	C3	1.377(3)
Fe1	Cl4	2.1948(5)	C16	C21	1.382(2)
Fe1	Cl2	2.1957(5)	C16	C17	1.385(2)
Fe1	Cl3	2.1937(5)	C16	C15	1.509(2)
N1	C14	1.392(2)	C21	C20	1.387(3)
N1	C8	1.328(2)	C10	C11	1.382(3)
N1	C1	1.471(2)	C17	C18	1.382(3)
N2	C9	1.391(2)	C13	C12	1.375(3)
N2	C8	1.323(2)	C20	C19	1.375(3)
N2	C15	1.474(2)	C19	C18	1.383(3)
C14	C9	1.390(2)	C12	C11	1.393(3)
C14	C13	1.391(2)	C7	C6	1.394(3)

Table S2. Bond Angles for (**2**) and (**6**).

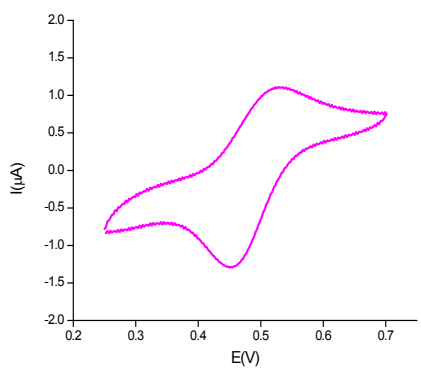
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
(2)							
Cl4	Fe1	Cl3	110.00(3)	N1	C1	N2	111.0(2)
Cl4	Fe1	Cl2	110.39(3)	N1	C2	C7	131.6(2)
Cl3	Fe1	Cl2	109.12(3)	N1	C2	C3	106.1(2)
Cl4	Fe1	Cl1	111.13(3)	C7	C2	C3	122.2(3)
Cl3	Fe1	Cl1	110.09(3)	C4	C3	N2	132.3(3)
Cl2	Fe1	Cl1	106.02(3)	C4	C3	C2	121.1(3)
C1	N1	C2	108.5(2)	N2	C3	C2	106.6(2)
C1	N1	C8	126.5(2)	C5	C4	C3	116.3(3)

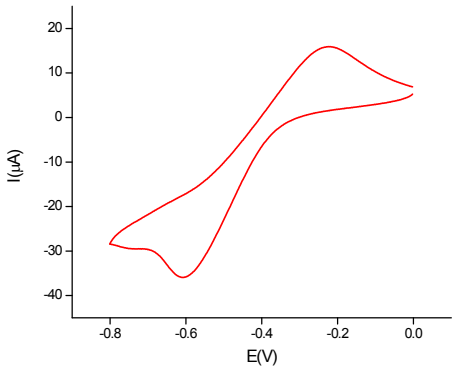
Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
(2)							
C2	N1	C8	125.0(2)	C4	C5	C6	122.0(3)
C1	N2	C3	107.7(2)	C7	C6	C5	122.2(3)
C1	N2	C9	126.6(3)	C6	C7	C2	116.2(3)
C3	N2	C9	125.6(3)				
(6)							
Cl4	Fe1	Cl1	107.16(2)	C21	C16	C17	119.18(16)
Cl4	Fe1	Cl2	110.66(2)	C21	C16	C15	120.57(16)
Cl2	Fe1	Cl1	109.49(2)	C17	C16	C15	120.24(16)
Cl3	Fe1	Cl1	111.17(2)	N2	C8	N1	110.80(14)
Cl3	Fe1	Cl4	110.05(2)	C16	C21	C20	120.25(17)
Cl3	Fe1	Cl2	108.31(2)	C11	C10	C9	115.87(17)
C14	N1	C1	126.57(14)	C18	C17	C16	120.60(16)
C8	N1	C14	107.94(14)	C12	C13	C14	115.85(17)
C8	N1	C1	125.48(14)	C19	C20	C21	120.27(17)
C9	N2	C15	125.94(15)	C20	C19	C18	119.81(17)
C8	N2	C9	108.19(13)	N2	C15	C16	111.43(14)
C8	N2	C15	125.86(15)	C17	C18	C19	119.90(17)
C9	C14	N1	106.55(14)	C13	C12	C11	122.05(17)
C9	C14	C13	122.18(15)	N1	C1	C2	113.05(14)
C13	C14	N1	131.27(15)	C2	C7	C6	119.76(19)
C14	C9	N2	106.50(14)	C2	C3	C4	120.97(19)
C10	C9	N2	131.73(16)	C10	C11	C12	122.26(17)
C10	C9	C14	121.75(16)	C5	C4	C3	119.9(2)
C7	C2	C1	121.88(17)	C4	C5	C6	119.90(19)
C3	C2	C1	119.01(17)	C5	C6	C7	120.4(2)
C3	C2	C7	119.02(17)				

2. Cyclic voltammetric diagrams (1-8)

Positive Potential **Negative Potential**

(1)





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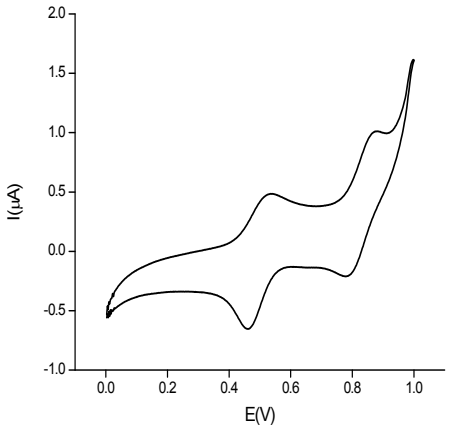

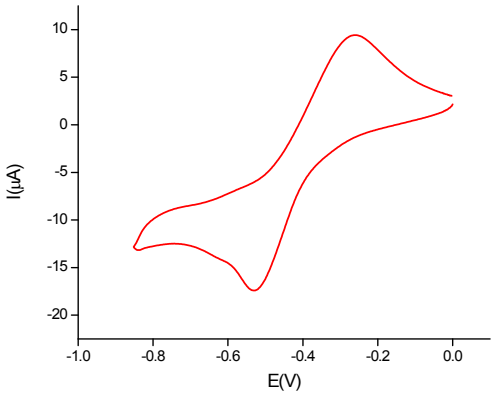

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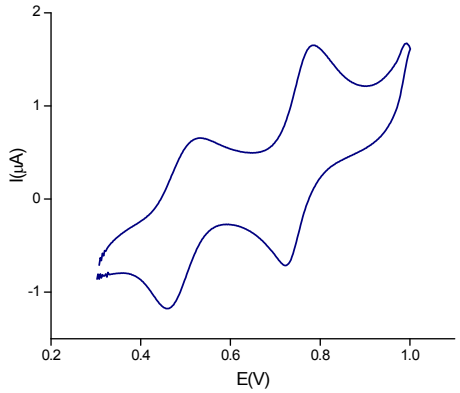

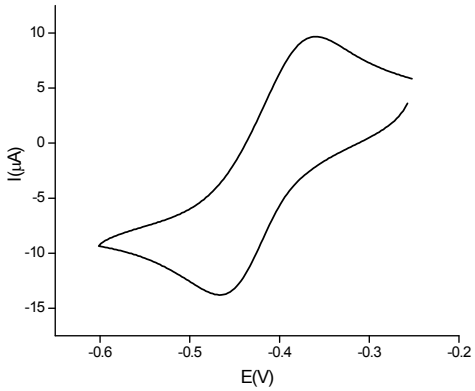

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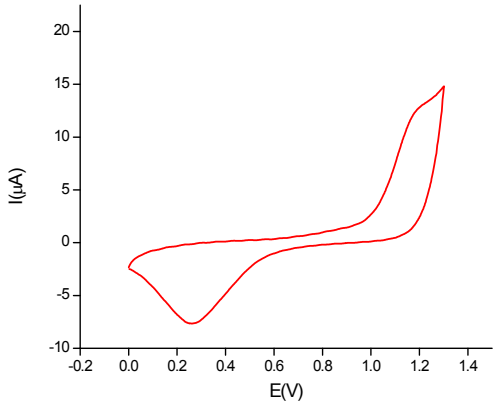

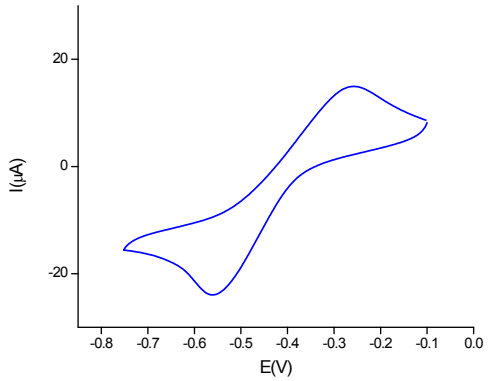

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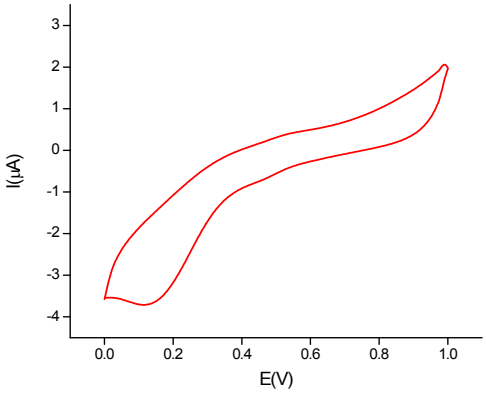

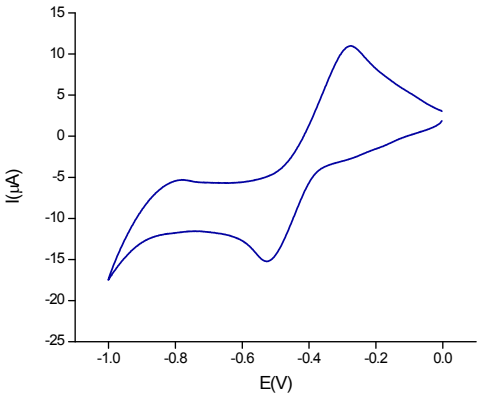

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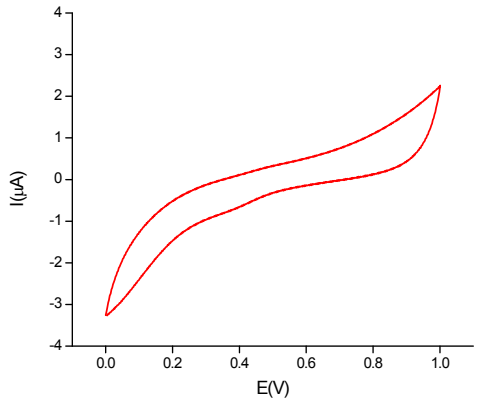

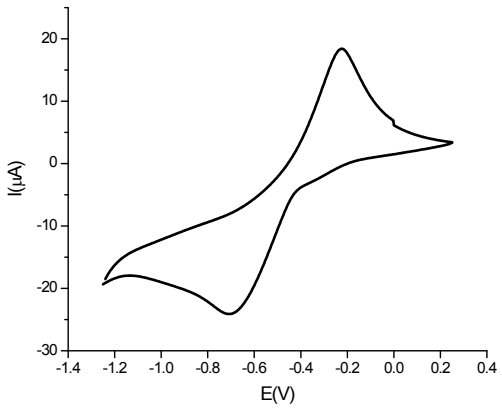

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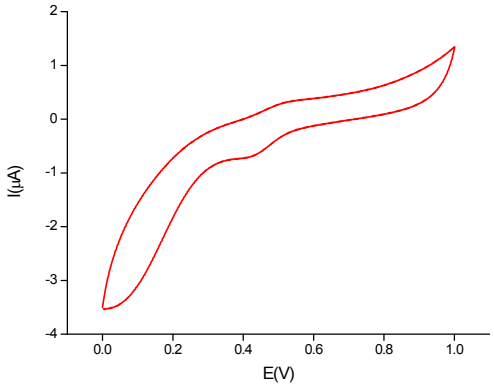

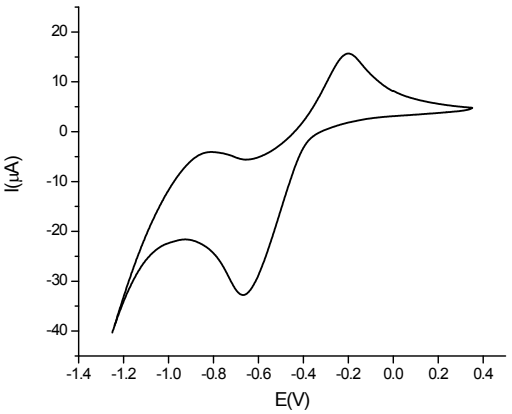

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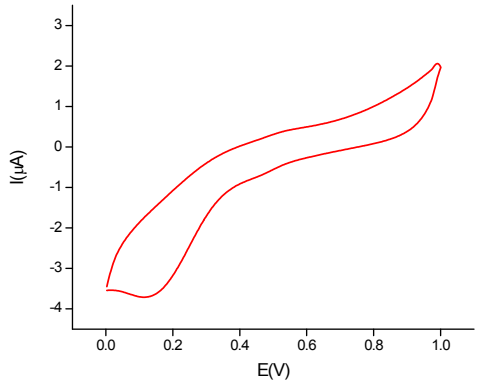

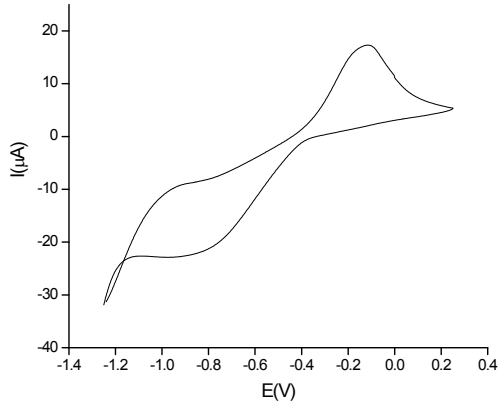

3. Peak search results in positive potential

Table S3. Electrochemical peak search results in positive potential

MILs	Position	Height	Area (C)	Width (1/2)	Derivative	Ep-Ep/2 (/V)
(1)						
	5.209e-01	8.004e-07	2.258e-06	1.343e-01	1.731e-05	5.764e-02
	4.575e-01	-1.104e-0	2.389e-06	1.001e-01	3.101e-05	-4.804e-02
(2)						
	5.502e-01	1.032e-07	1.802e-07	8.789e-02	5.793e-06	3.092e-02
	8.994e-01	2.868e-08	2.853e-08	4.883e-02	2.914e-06	1.856e-02
	7.895e-01	-4.227e-07	1.156e-06	1.221e-01	8.953e-06	-5.418e-02
	4.697e-01	-4.902e-07	9.531e-07	9.277e-02	1.469e-05	-4.542e-02
(3)						
	5.344e-01	1.276e-07	1.772e-07	7.080e-02	9.344e-06	2.694e-02
	7.785e-01	8.257e-07	1.681e-06	9.766e-02	2.507e-05	3.756e-02
	7.248e-01	-8.176e-07	1.646e-06	9.033e-02	2.503e-05	-3.513e-02
	4.636e-01	-6.497e-07	1.257e-06	9.033e-02	2.007e-05	-4.313e-02
(4)						
	2.368e-01	-6.316e-06	3.413e-05	2.563e-01	6.960e-05	-1.460e-01

4. Peak search results in negative potential

Table S4. Electrochemical peak search results in negative potential

MILs	Position	Height	Area (C)	Width (1/2)	Derivative	Ep-Ep/2 (/V)
(1)						
	-5.640e-01	-2.065e-05	8.153e-05	1.855e-01	3.051e-04	-9.712e-02
	-2.417e-01	1.816e-05	9.480e-05	2.490e-01	1.921e-04	1.405e-**01**
(2)						
	-5.835e-01	-2.744e-06	6.370e-06	1.025e-01	1.036e-04	-4.425e-02
	-2.515e-01	9.574e-06	4.646e-05	2.319e-01	1.072e-04	1.209e-01
(3)						
	-4.599e-01	-8.575e-06	1.956e-05	1.099e-01	2.273e-04	-4.640e-02
	-3.745e-01	8.860e-06	1.984e-05	1.099e-01	2.247e-04	4.892e-02
(4)						
	-5.492e-01	-1.554e-05	5.592e-05	1.685e-01	2.626e-04	-9.090e-02
	-2.782e-01	1.229e-05	5.096e-05	2.026e-01	1.676e-04	1.131e-01
(5)						
	-5.518e-01	-7.858e-06	2.663e-05	1.611e-01	1.363e-04	-8.025e-02
	-3.003e-01	1.146e-05	5.693e-05	2.368e-01	1.228e-04	1.061e-01
(6)						
	-2.295e-01	2.070e-05	1.394e-04	2.832e-01	1.789e-04	1.367e-01
	-7.104e-01	-5.796e-06	2.804e-05	2.197e-01	1.096e-04	-8.528e-02
(7)						

	-2.075e-01	1.662e-05	1.205e-04	3.076e-01	1.417e-04	1.369e-01
	-6.519e-01	-2.127e-05	1.170e-04	2.612e-01	2.326e-04	-1.437e-01
(8)						
	-1.270e-01	1.655e-05	1.221e-04	3.076e-01	1.712e-04	1.727e-01
	-9.863e-01	-2.214e-07	4.505e-07	1.025e-01	8.034e-06	-5.513e-02

5. Mass spectrometry

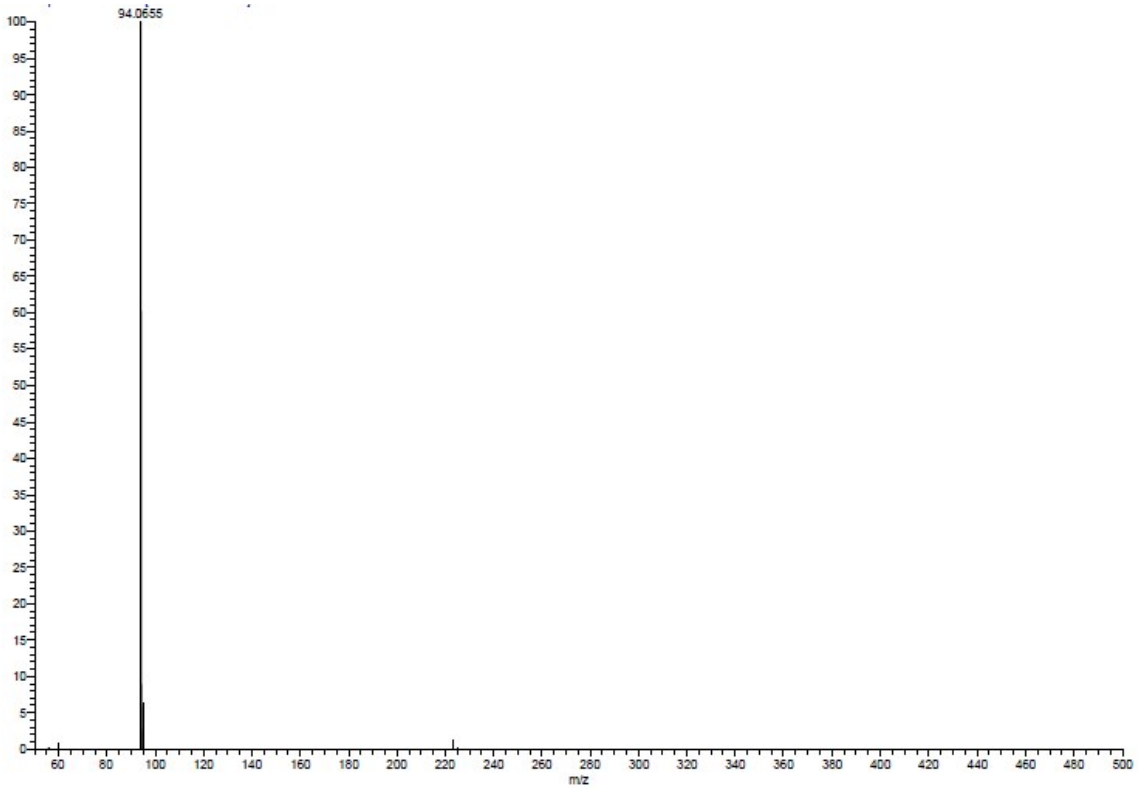

Figure S1. ESI$^+$ mass spectrum for (**1**)

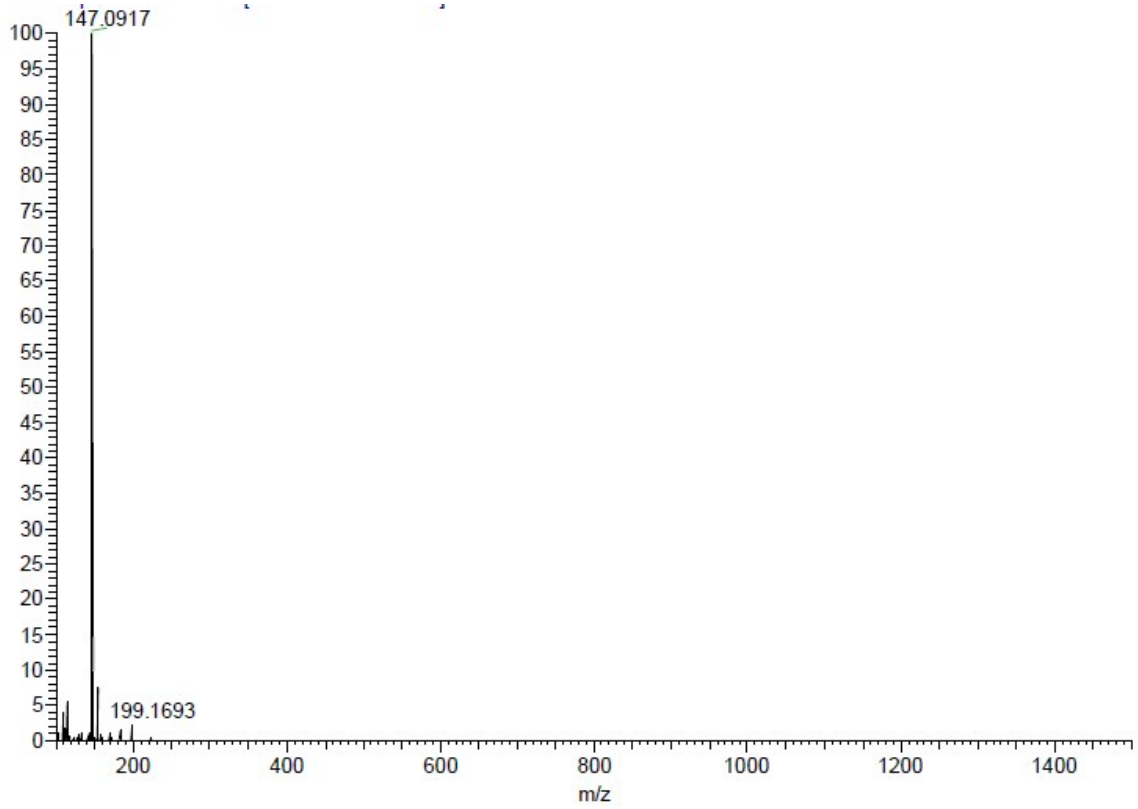

Figure S2. ESI$^+$ mass spectrum for (**2**)

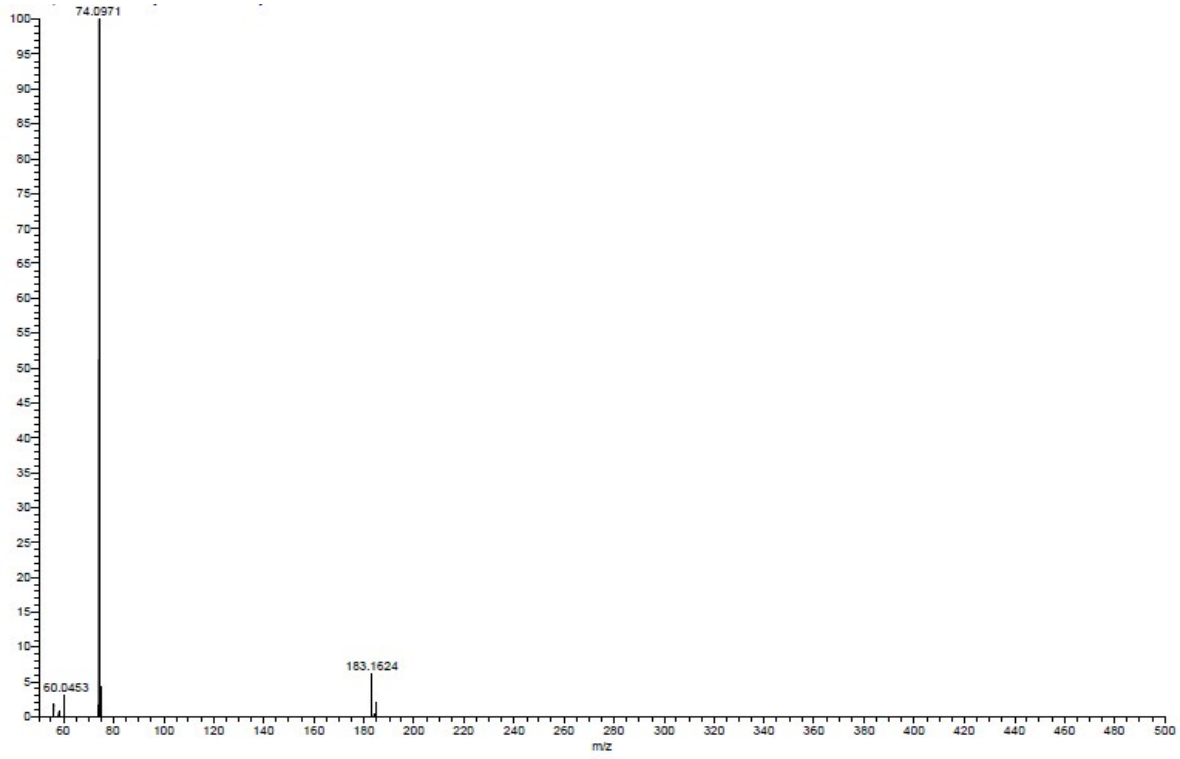

Figure S3. ESI$^+$ mass spectrum for (**3**)

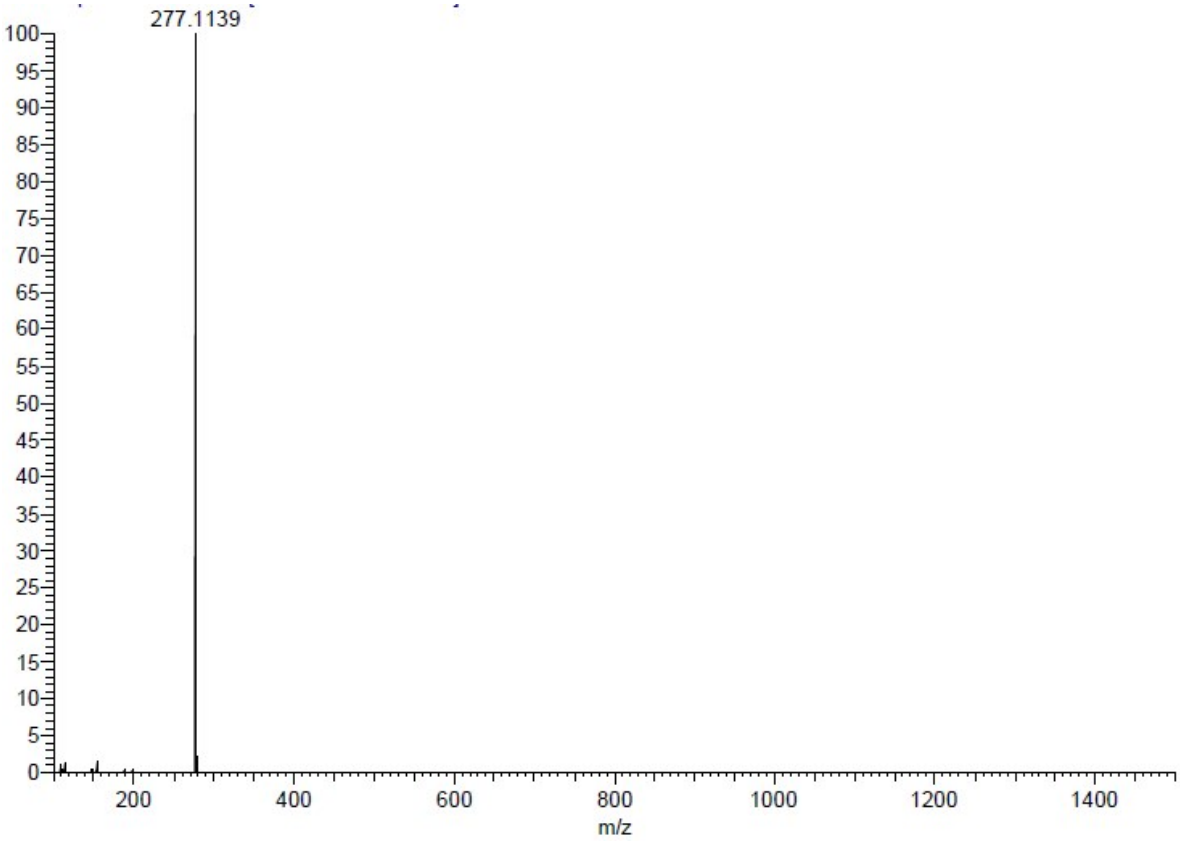

Figure S4. ESI^+ mass spectrum for (**4**)

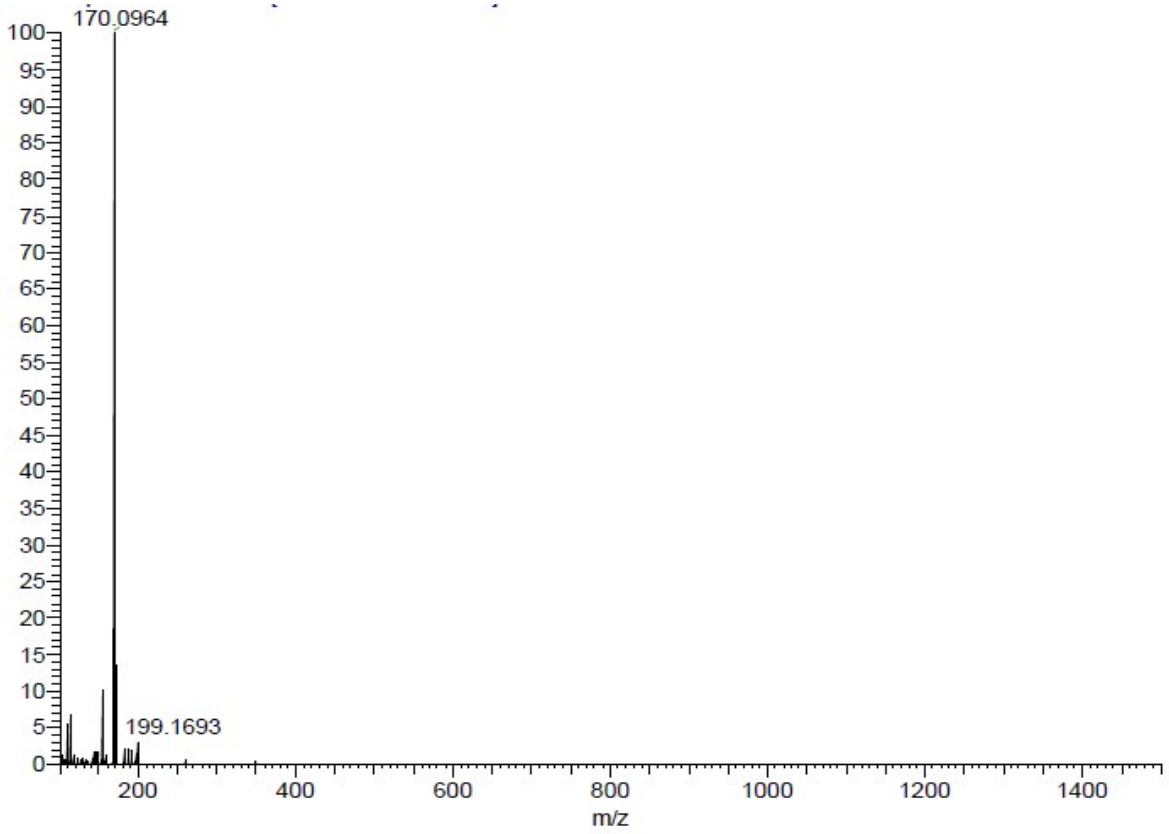

Figure S5. ESI$^+$ mass spectrum for (**5**)

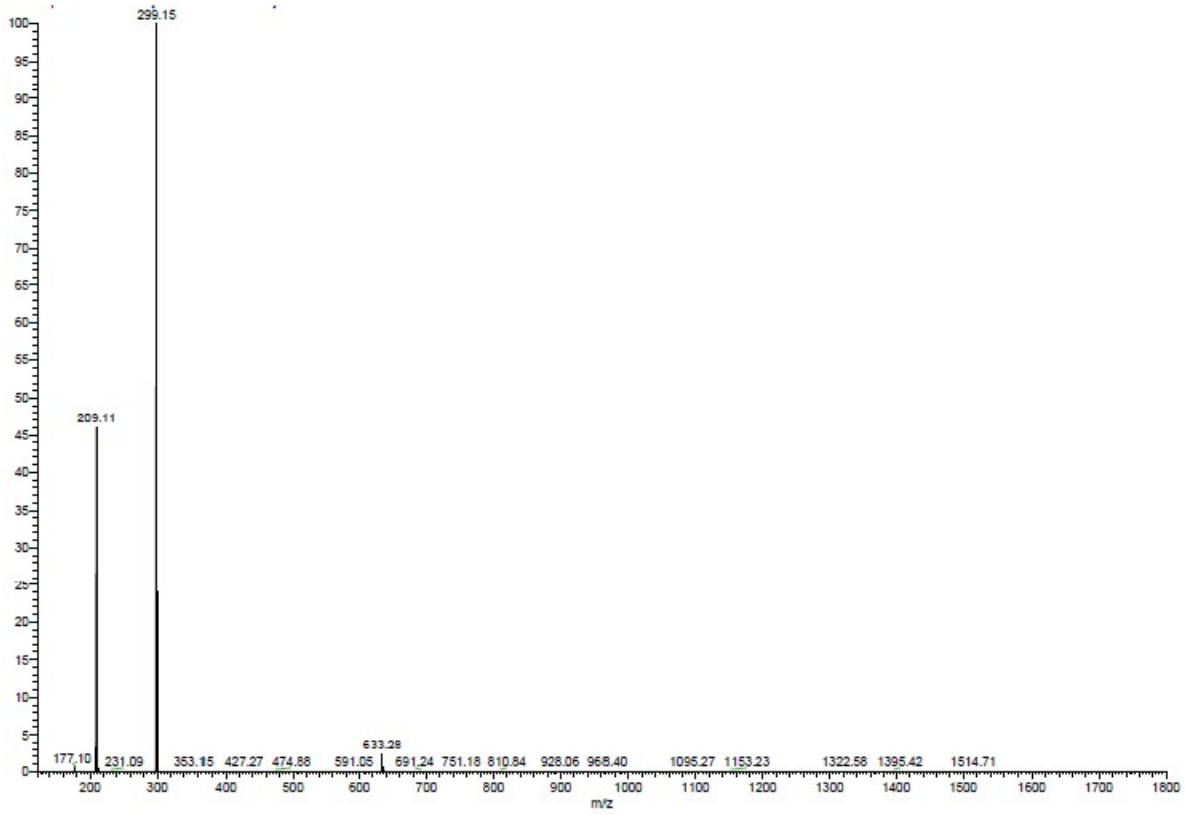

Figure S6. ESI$^+$ mass spectrum for (**6**)

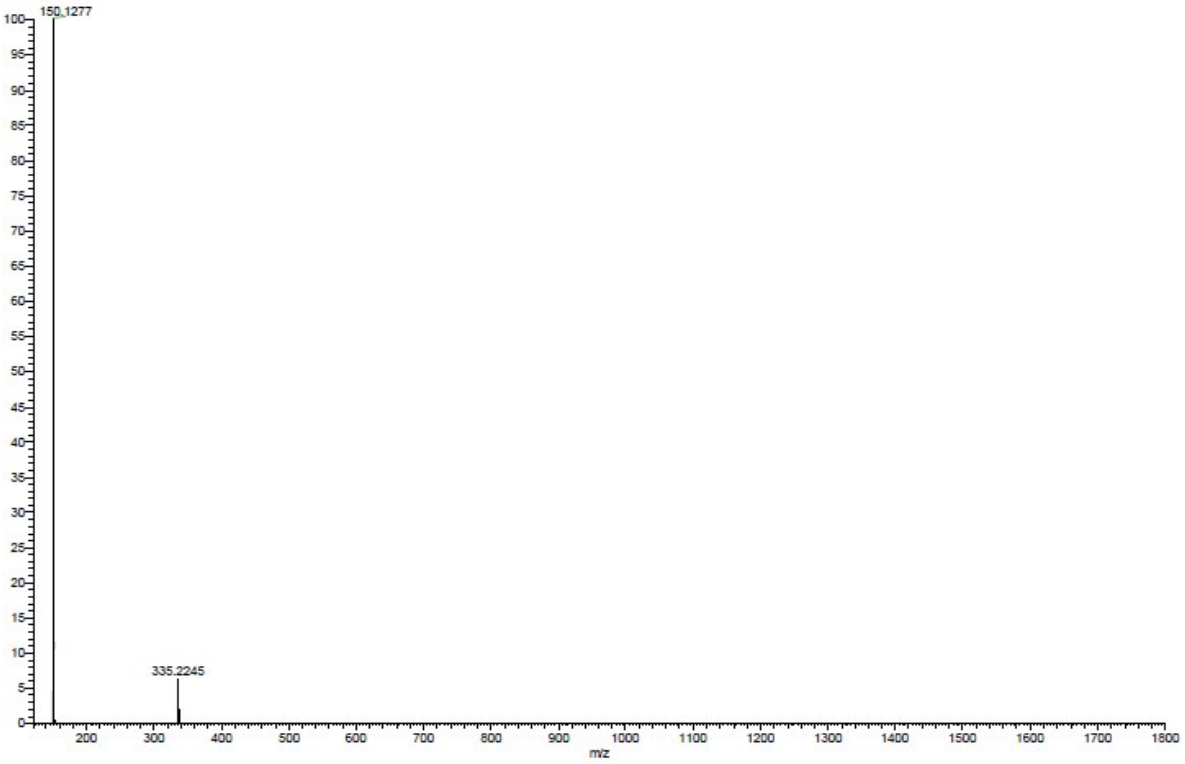

Figure S7. ESI$^+$ mass spectrum for (**7**)

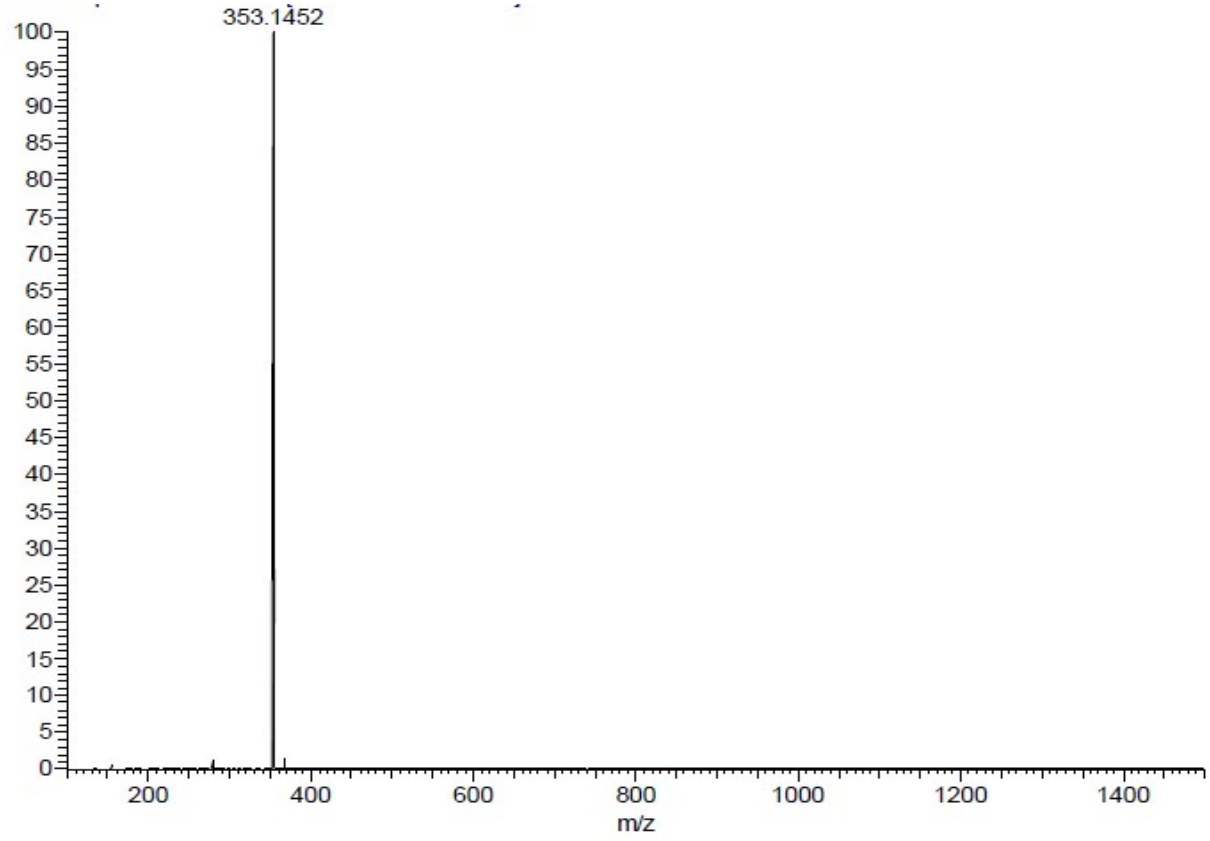

Figure S8. ESI^+ mass spectrum for (8)

6. NMR spectroscopy

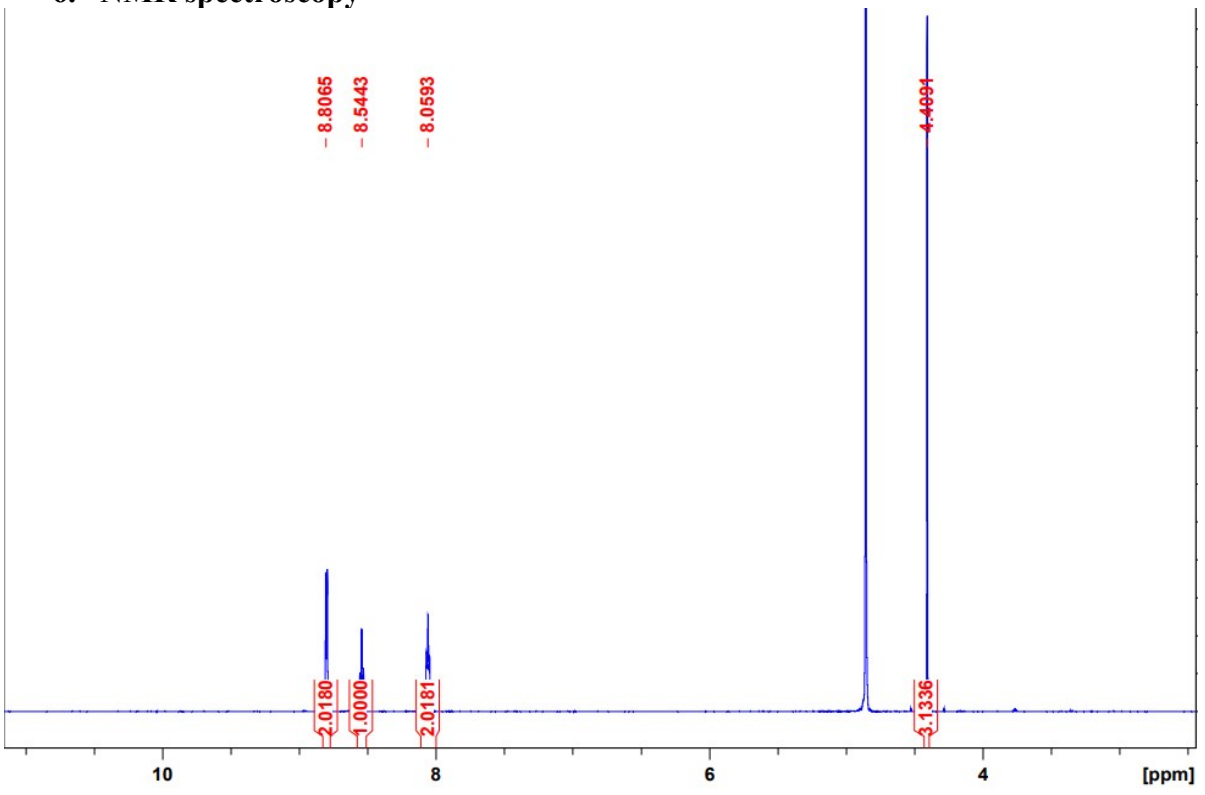

Figure S9. ^1H NMR spectrum for (**1**)

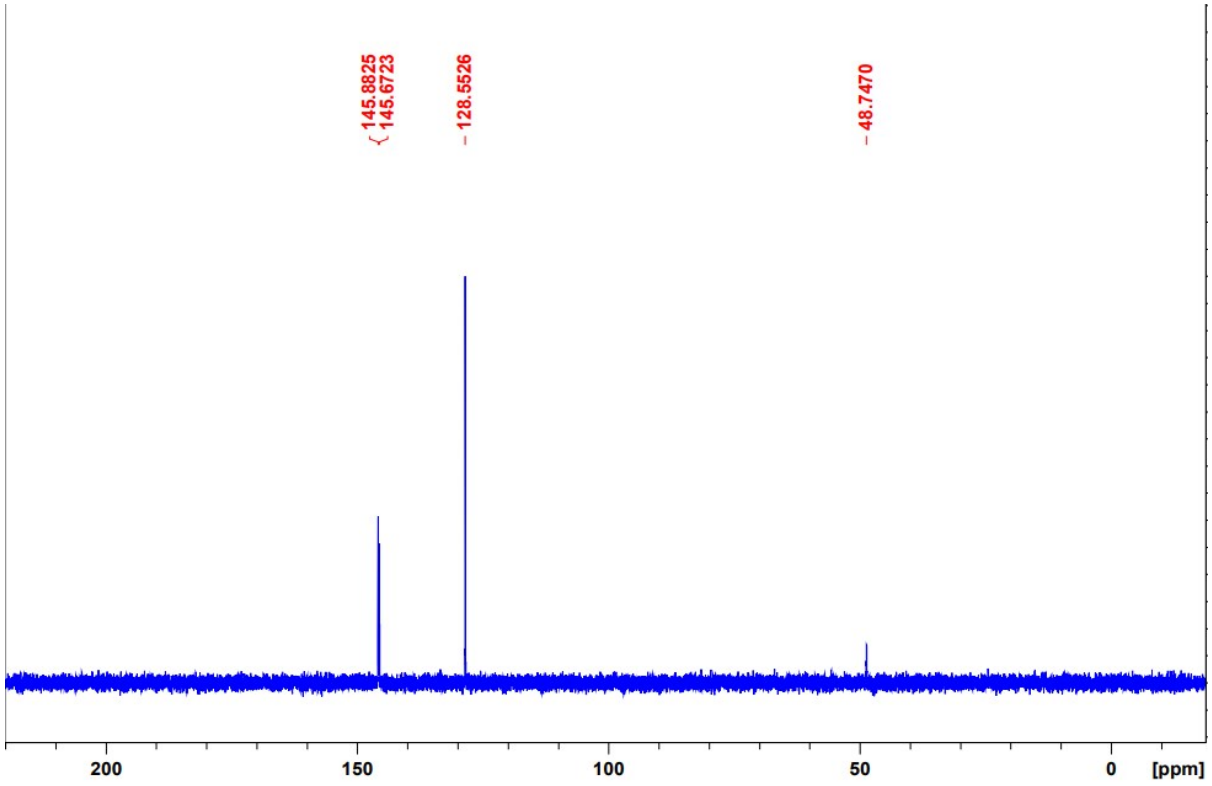

Figure S10. ^{13}C NMR spectrum for (**1**)

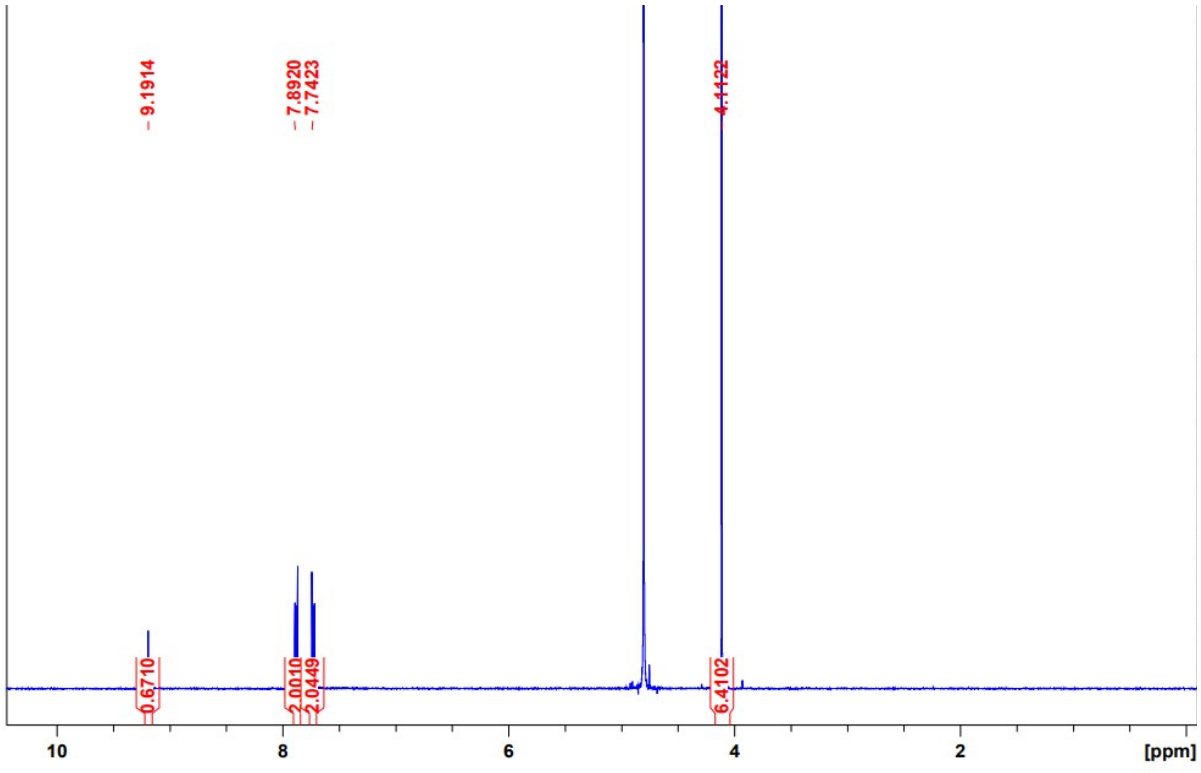

Figure S11. ^{1}H NMR spectrum for (**2**)

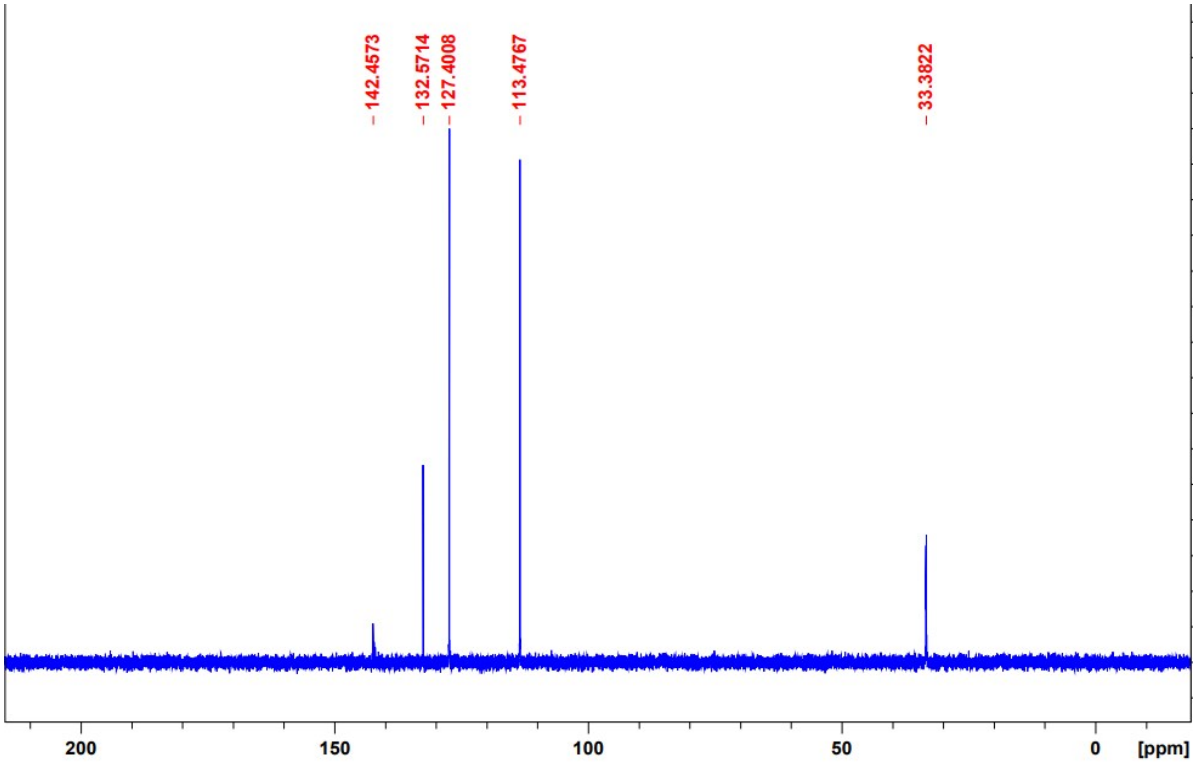

Figure S12. ^{13}C NMR spectrum for (**2**)

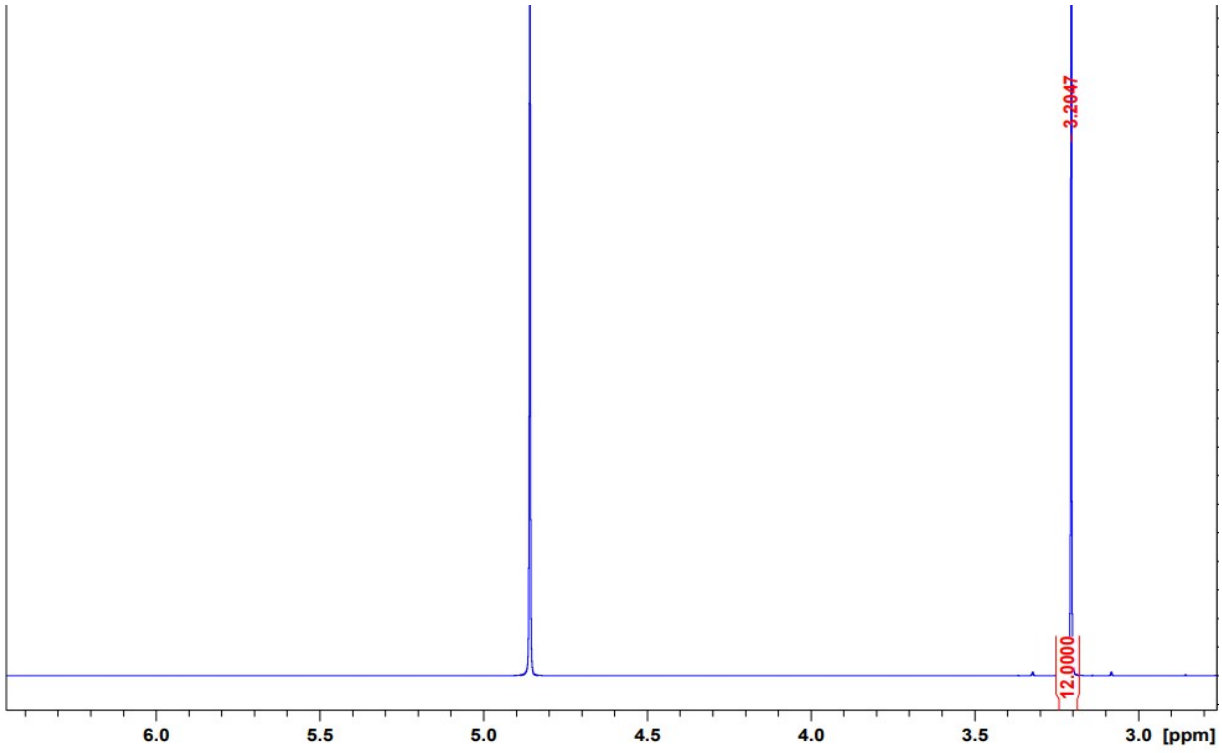

Figure S13. ^{1}H NMR spectrum for (**3**)

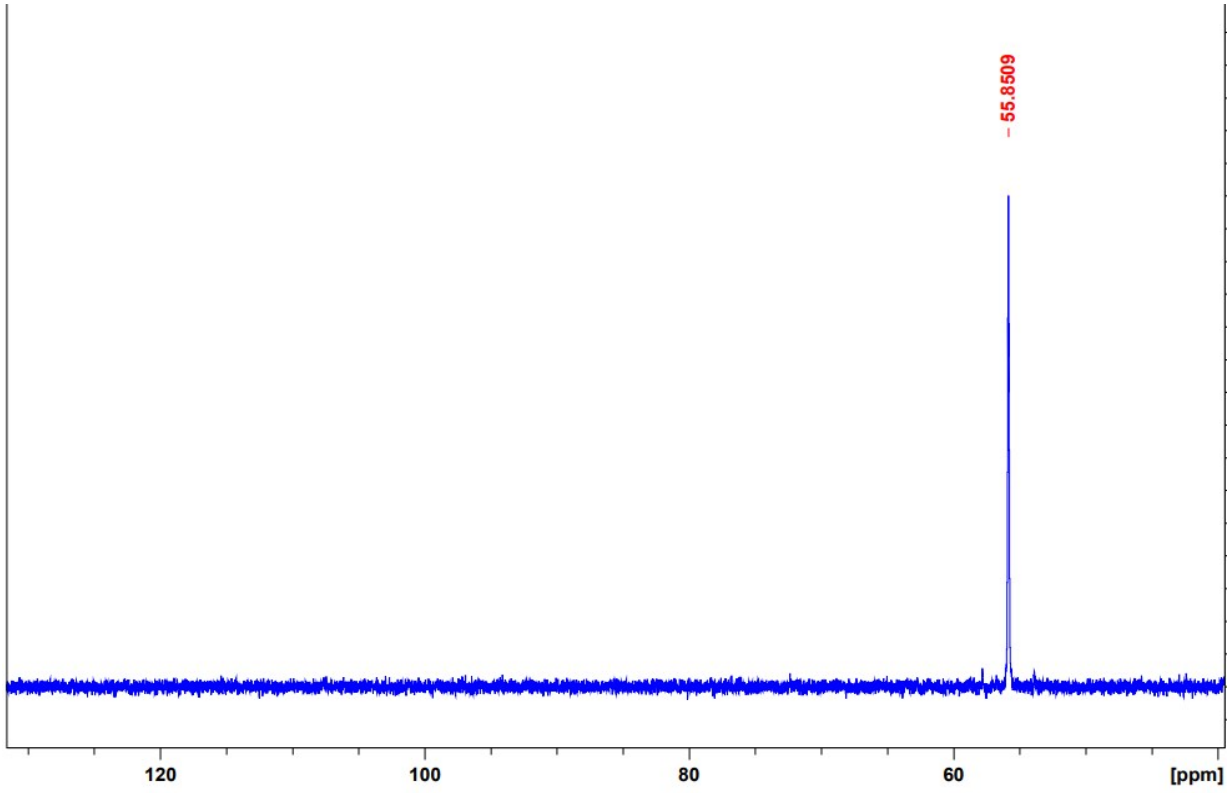

Figure S14. ^{13}C NMR spectrum for (**3**)

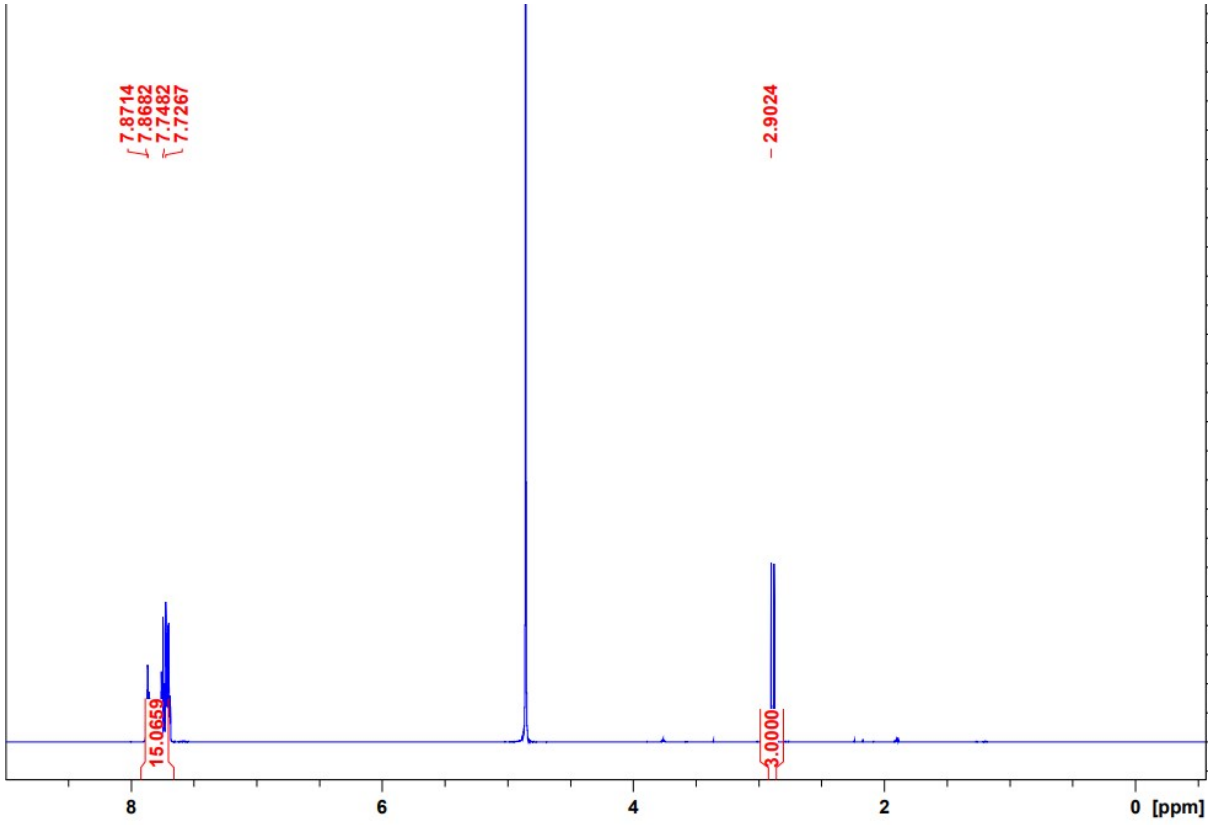

Figure S15. ^{1}H NMR spectrum for (**4**)

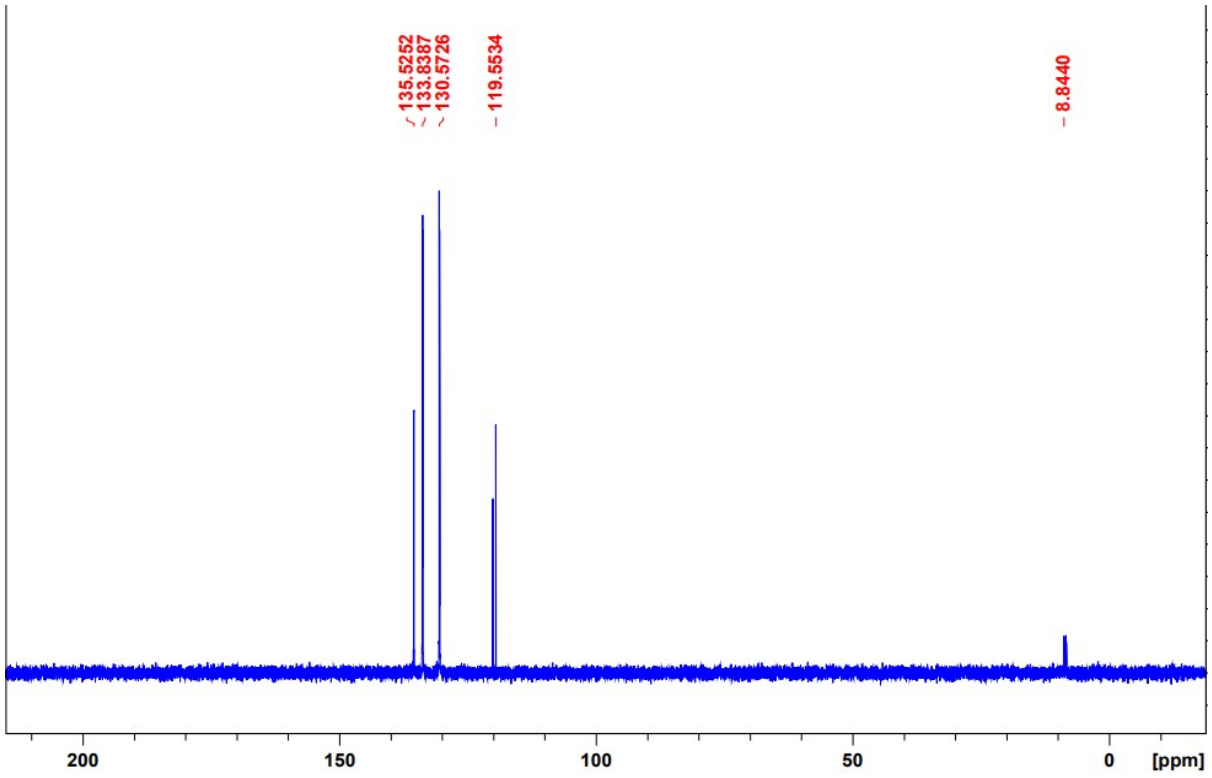

Figure S16. ^{13}C NMR spectrum for (**4**)

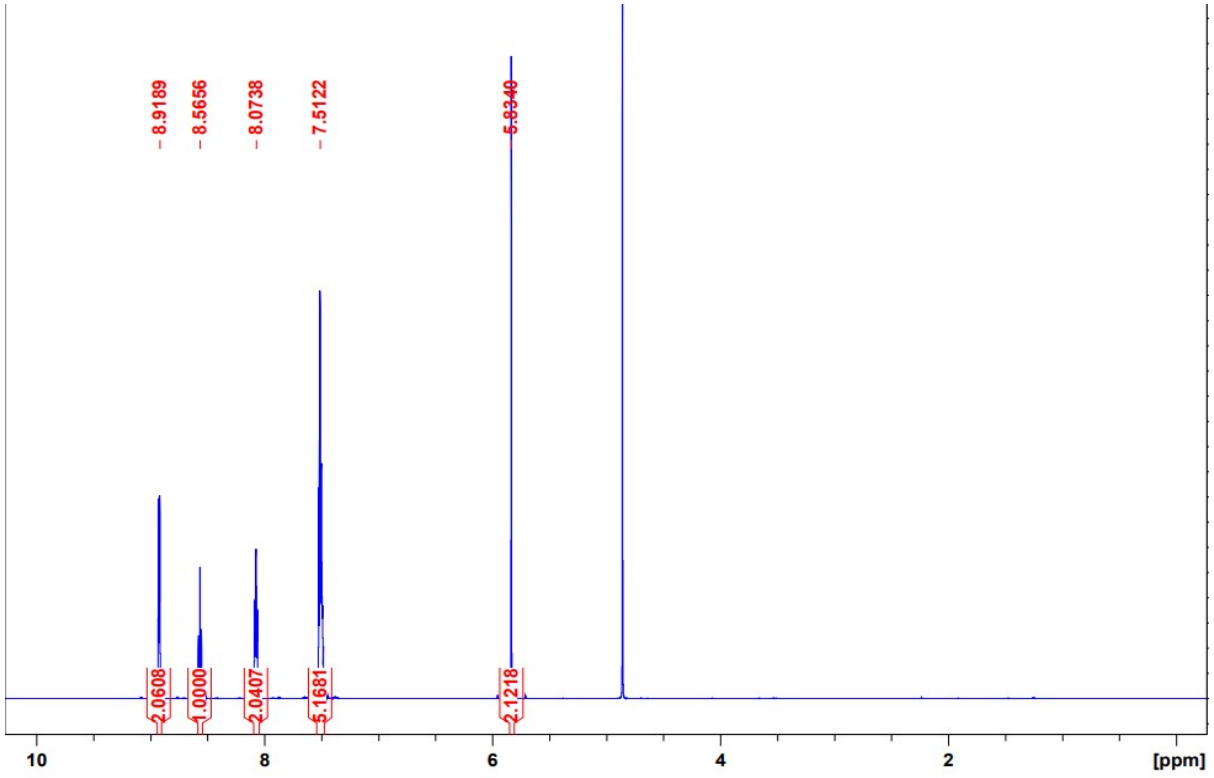

Figure S17. ^{1}H NMR spectrum for (**5**)

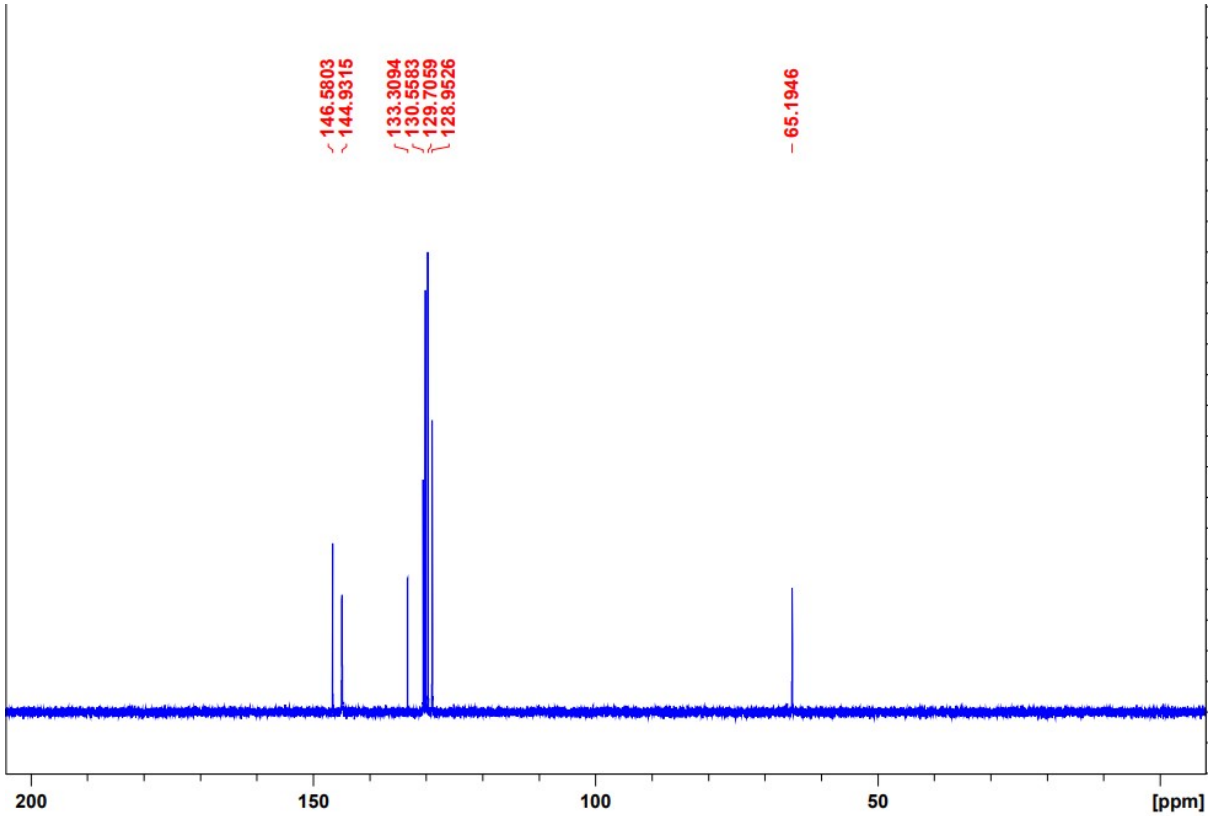

Figure S18. ^{13}C NMR spectrum for (**5**)

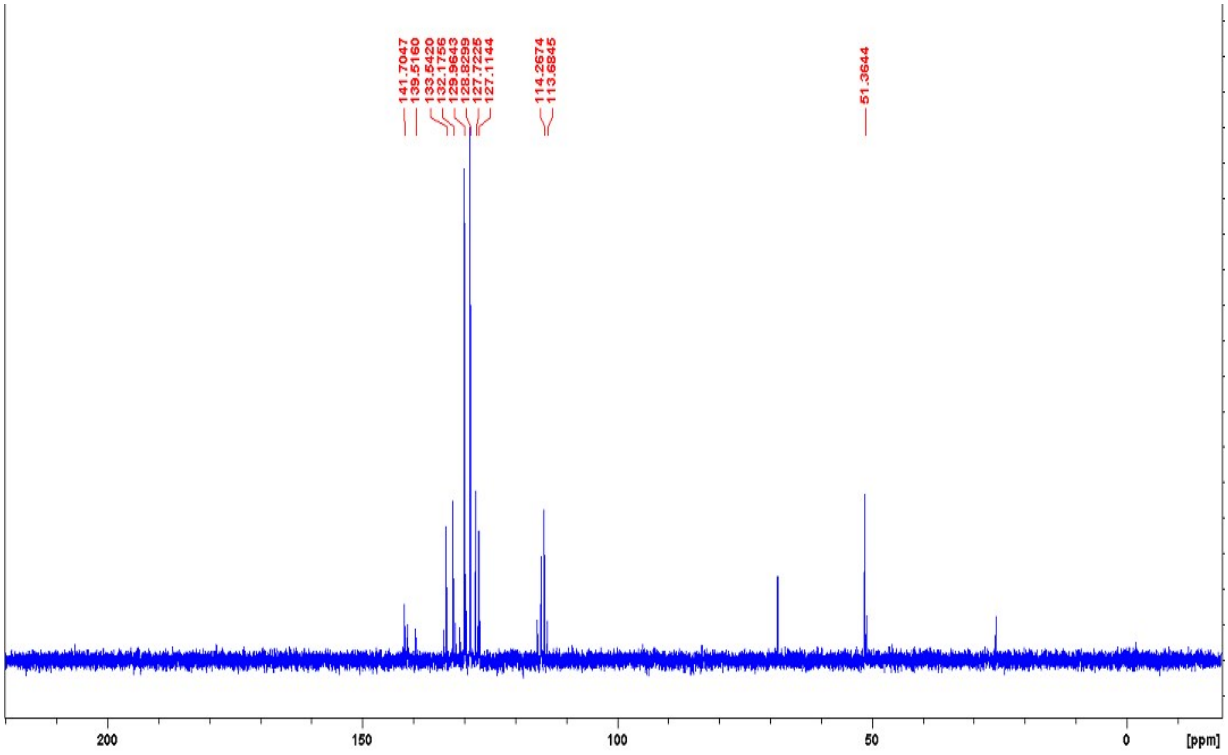

Figure S19. ^{13}C NMR spectrum for (**6**)

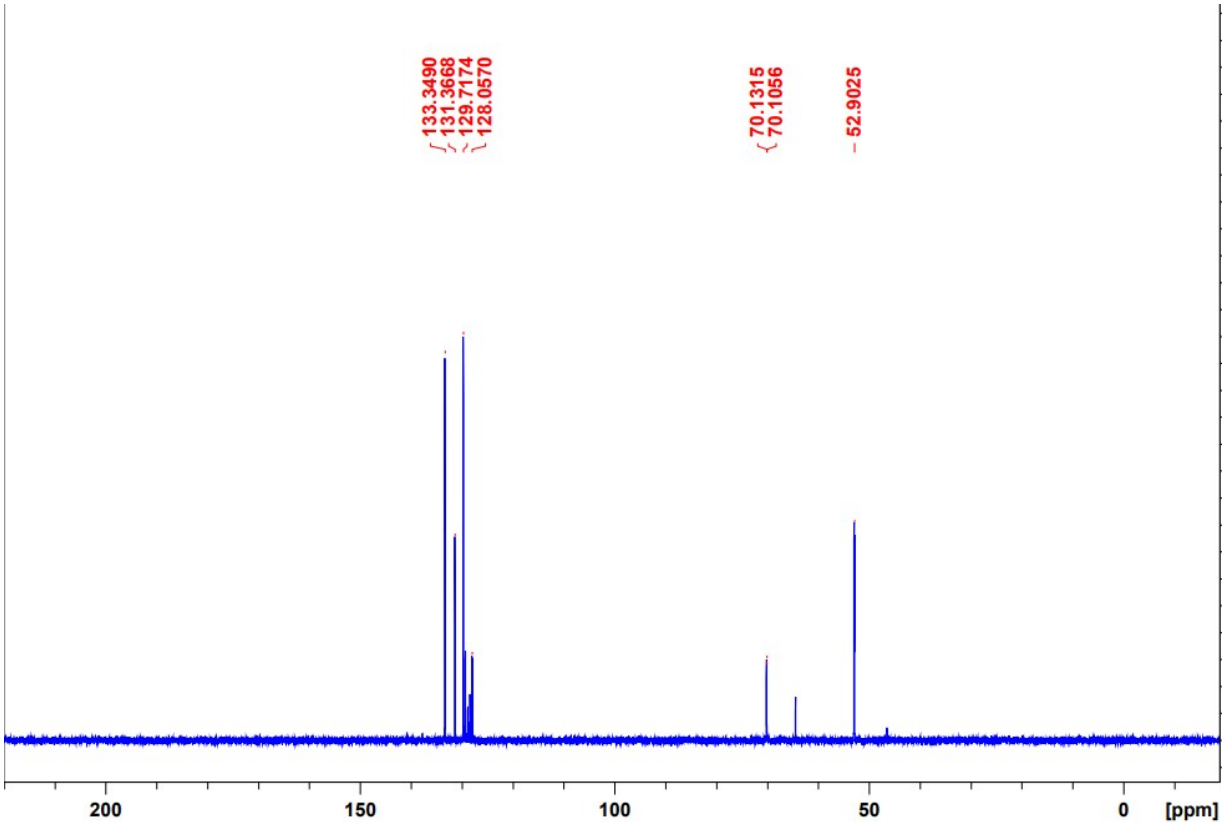

Figure S20. ^{13}C NMR spectrum for (**7**)

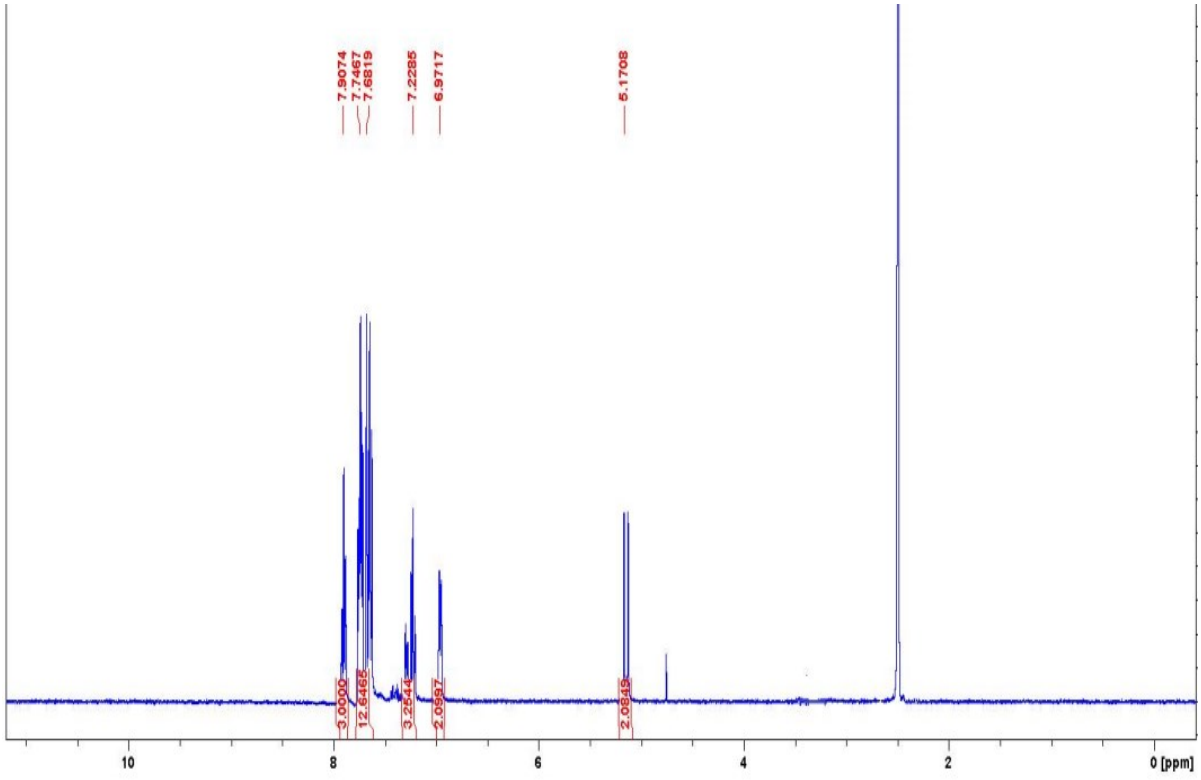

Figure S21.. ^{1}H NMR spectrum for (**8**)

7. Raman Spectroscopy

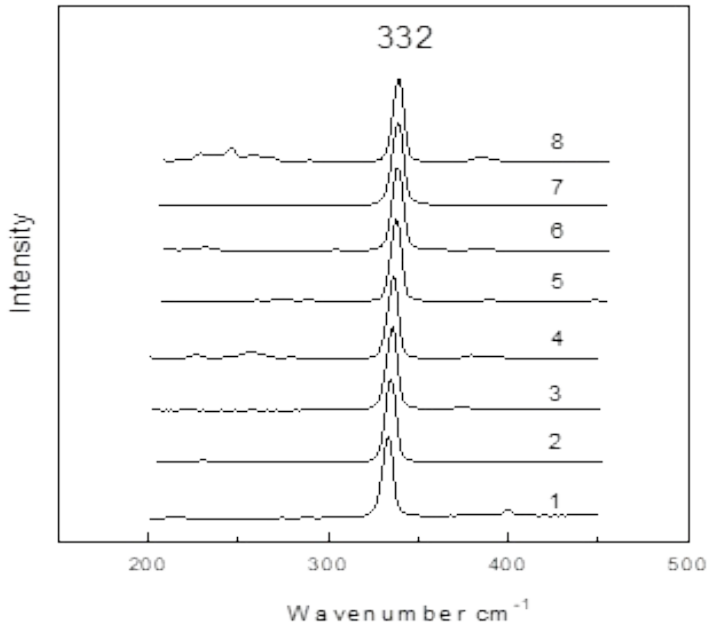

Figure S22.. Raman spectra for compounds (**1-8**) – see main manuscript for compound numbers

8. Magnetic studies

Table S5. Gram and molar susceptibilities for (**1-8**)

MILs	(χ_g) (emu.g^{-1} Oe^{-1})	(χ_{mol}) $^{(corr)}$ (emu.mol^{-1} Oe^{-1})
1	45×10^{-6}	0.013
2	34×10^{-6}	0.011
3	46×10^{-6}	0.012
4	31×10^{-6}	0.015
5	35×10^{-6}	0.013
6	32×10^{-6}	0.013
7	41×10^{-6}	0.014
8	26×10^{-6}	0.015