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Benzoquinone-imidazole hybrids as selective colorimetric sensors for cyanide in aqueous, solid and gas phases

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Supporting Information

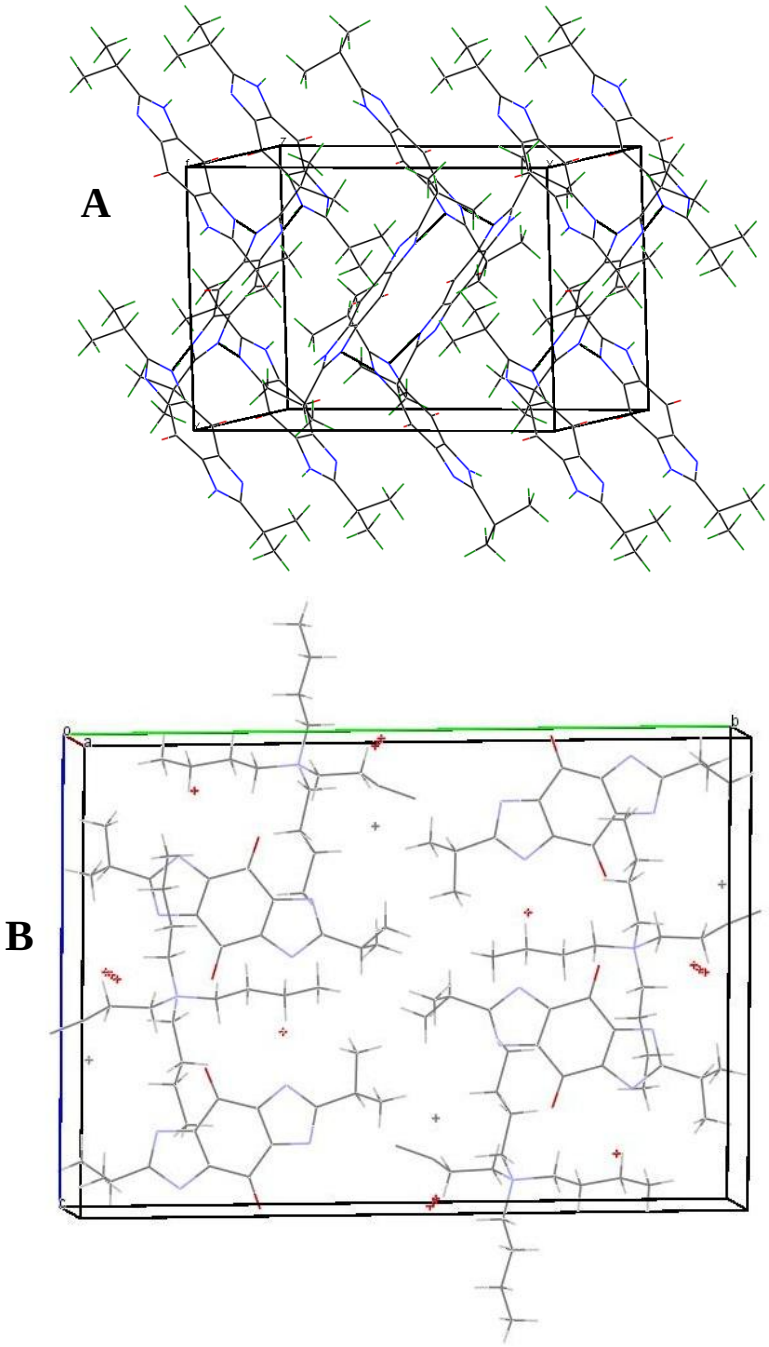

Figure S1. The packing diagram of (A) **R5** and (B) **R5-CN$^-$**.

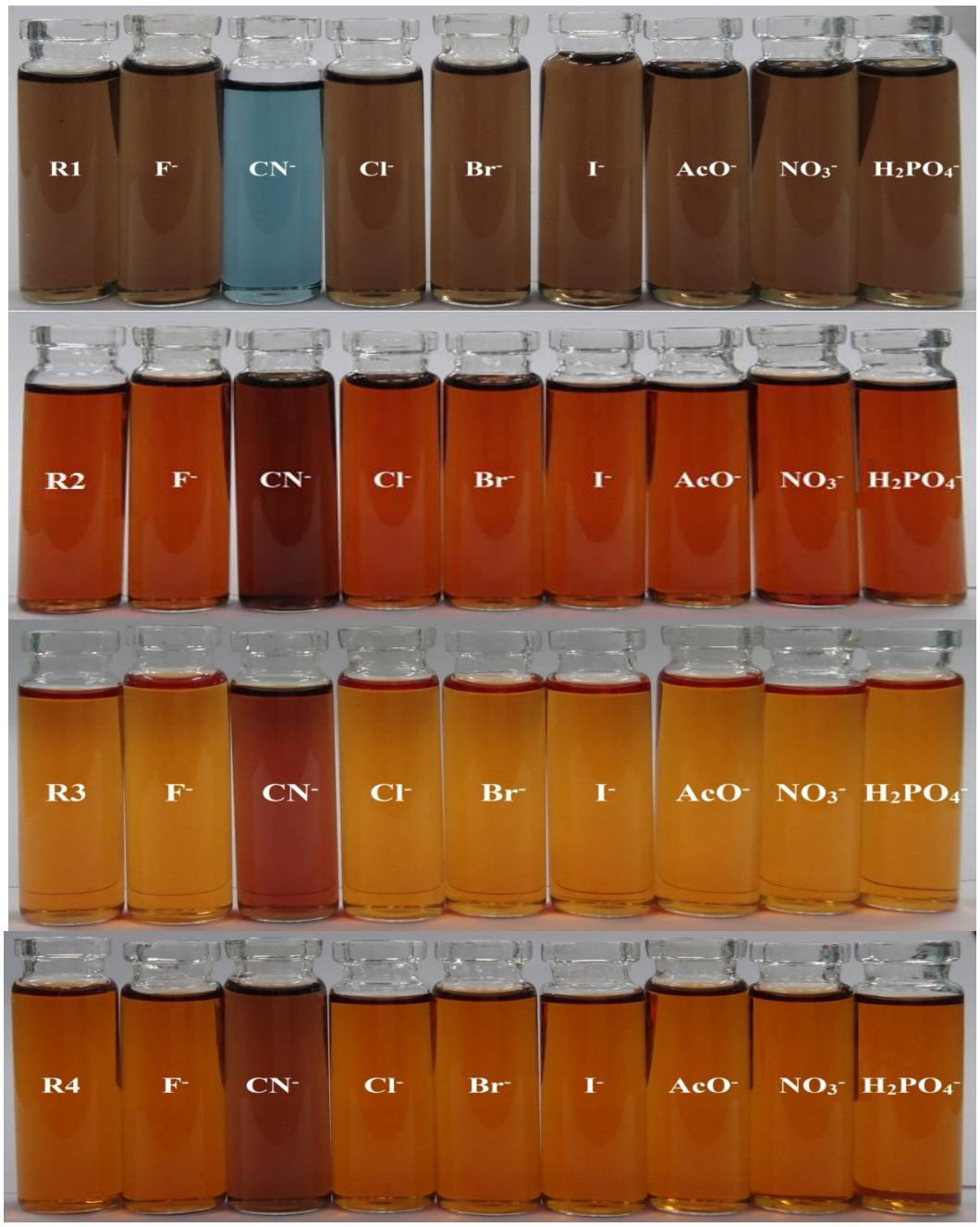

Figure S2. Color changes observed in DMF solution of **R1**-**R4** (6.25×10^{-4} M) upon addition of various anions.

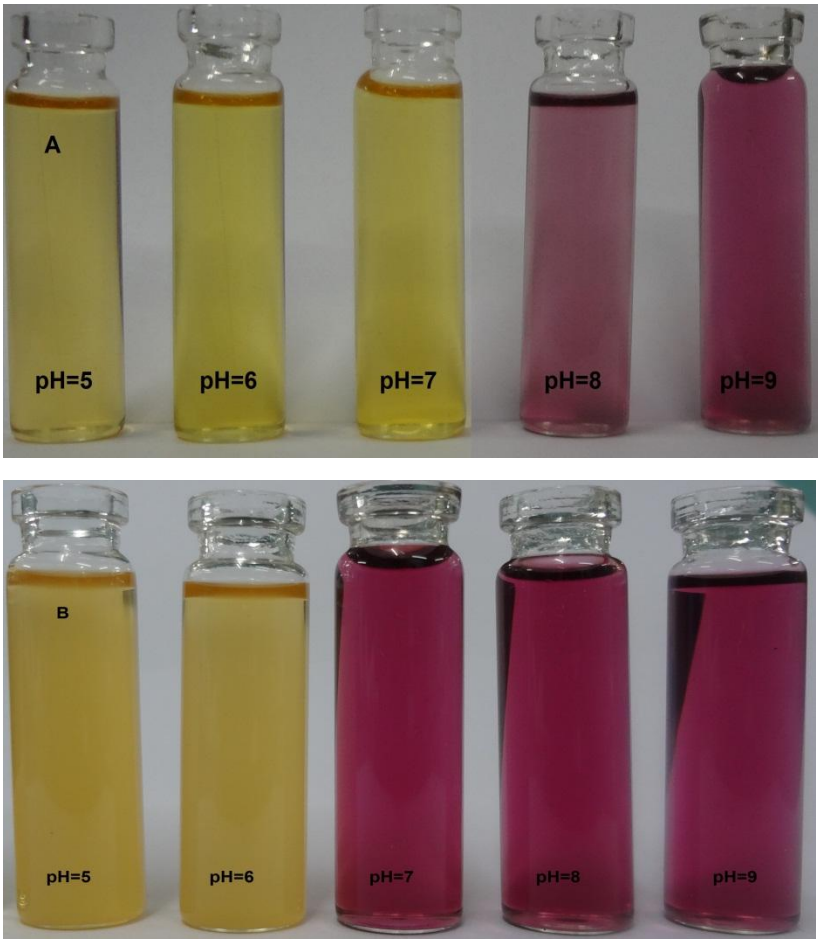

Figure S3. Color changes observed for **R5** at different pH values: A) free **R5** and B) after the addition of cyanide ion.

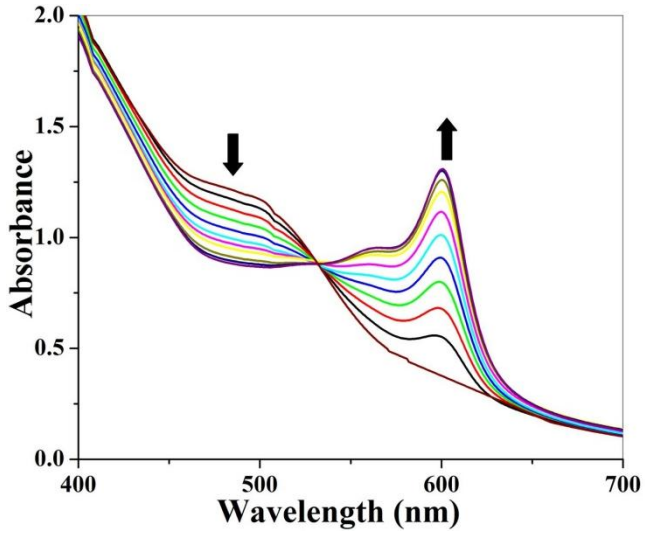

Figure S4. UV-Vis spectra of **R1** (6.25×10^{-4} M) with the incremental addition of TBACN (0 - 6.25×10^{-7} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

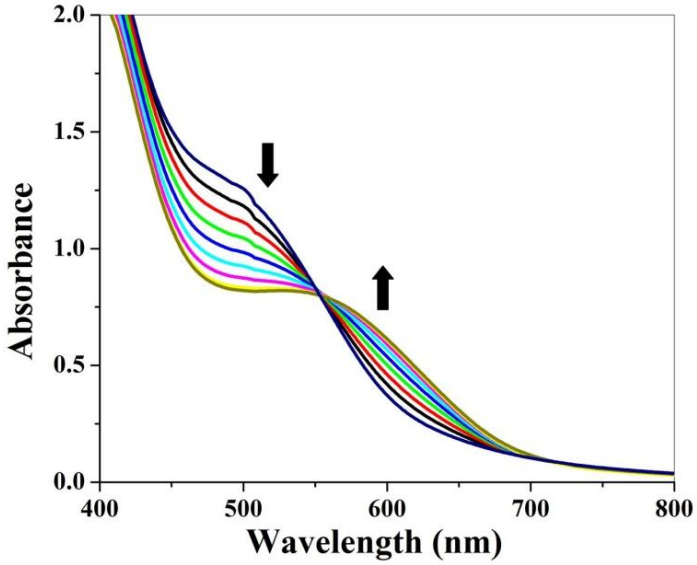

Figure S5. UV-Vis spectra of **R2** (6.25×10^{-4} M) with the incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

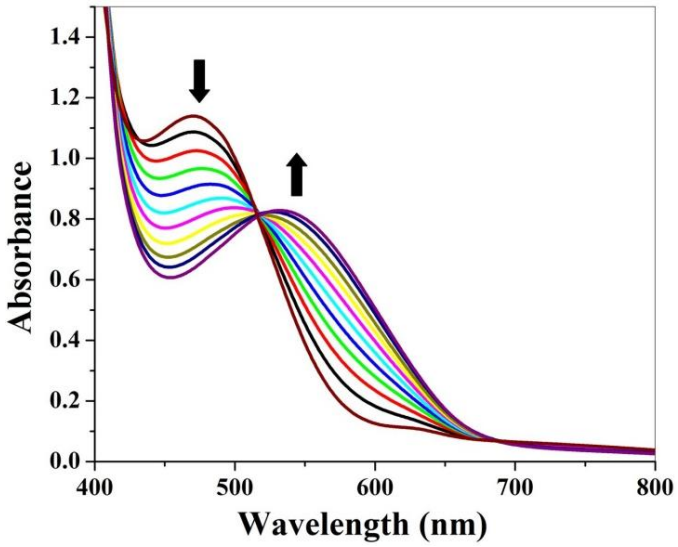

Figure S6. UV-Vis spectra of **R3** (6.25×10^{-4} M) with the incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

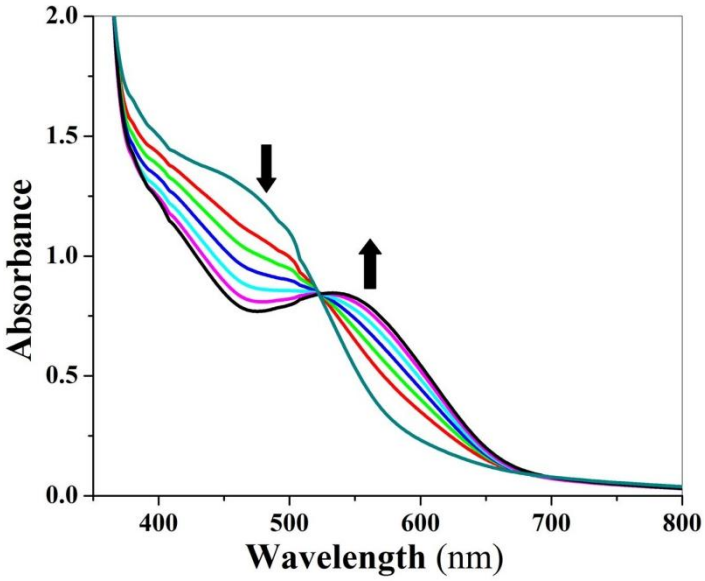

Figure S7. UV-Vis spectra of **R4** (6.25×10^{-4} M) with the incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

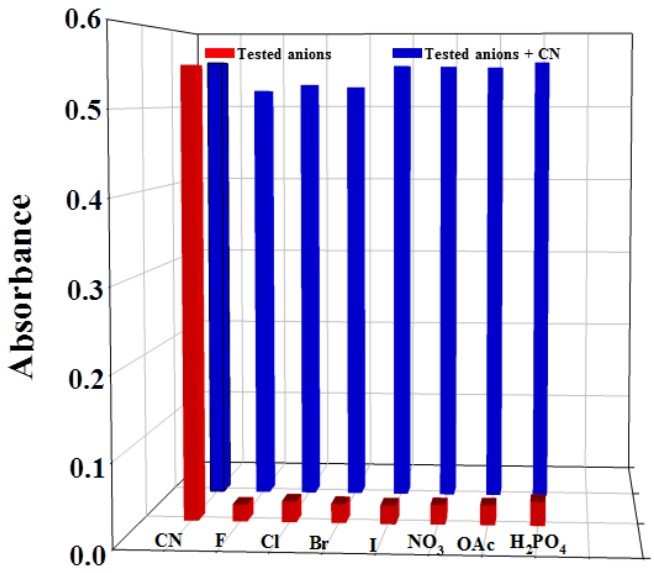

Figure S8. UV-Vis absorption changes of **R5** with cyanide ion in presence of other anions.

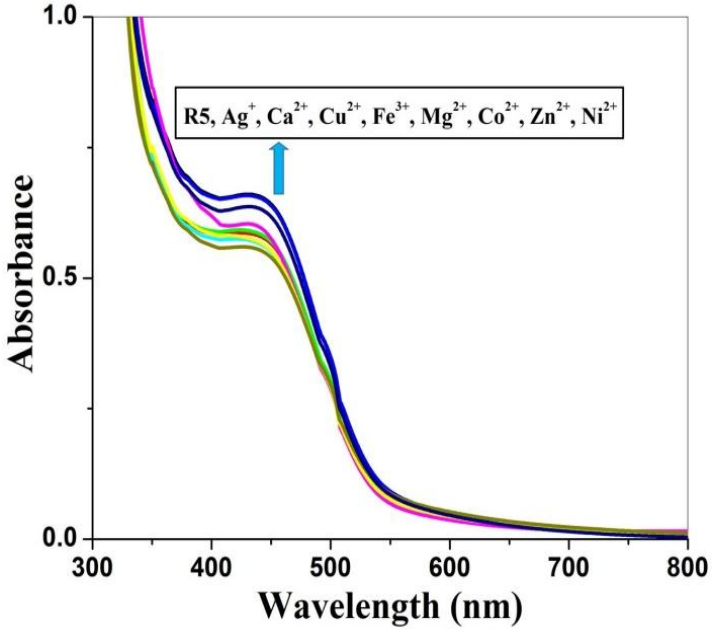

Figure S9. UV-Vis absorption changes of **R5** (6.25×10^{-4} M) upon addition of 1 eqv. of Ag^{+}, Ca^{2+}, Cu^{2+}, Fe^{3+}, Mg^{2+}, Co^{2+}, $Zn^{2+}$and Ni^{2+}.

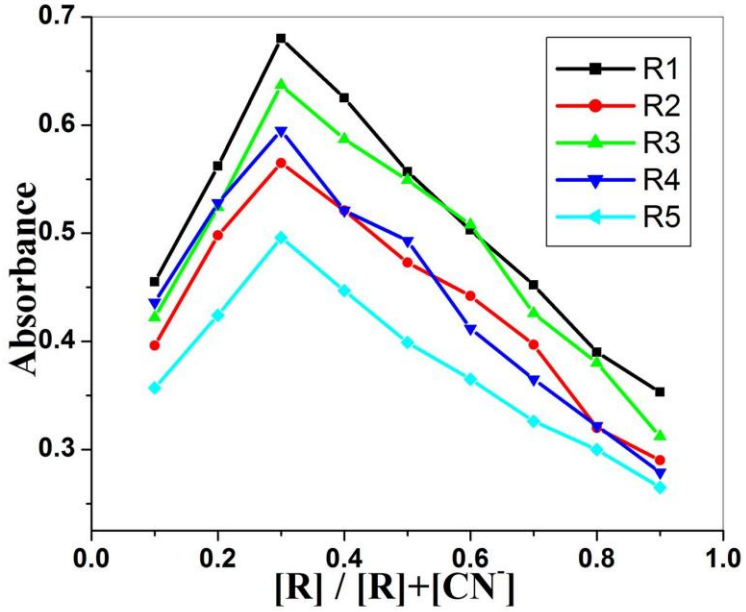

Figure 10. Job's plots for the receptor-cyanide complexes.

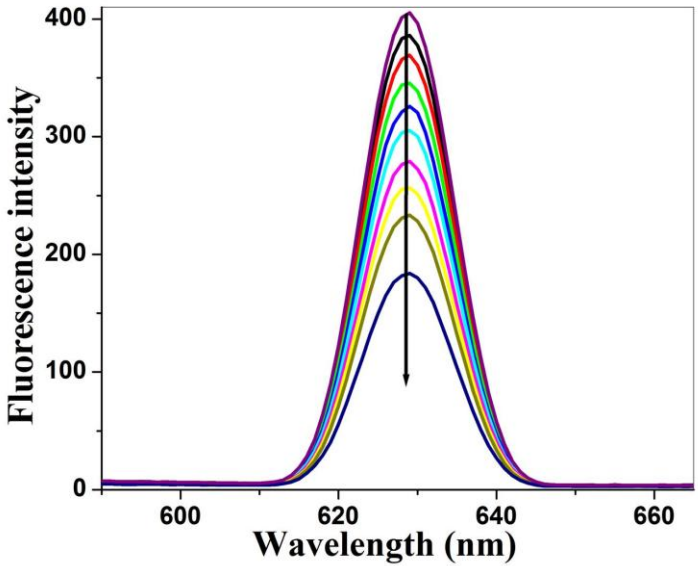

Figure S11. Fluorescence emission spectra of **R1** (6.25×10^{-4} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

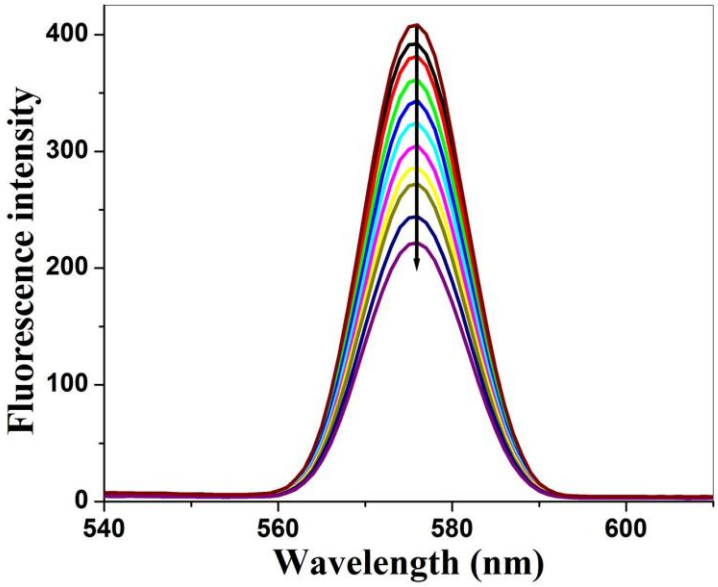

Figure S12. Fluorescence emission spectra of **R2** (6.25×10^{-4} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

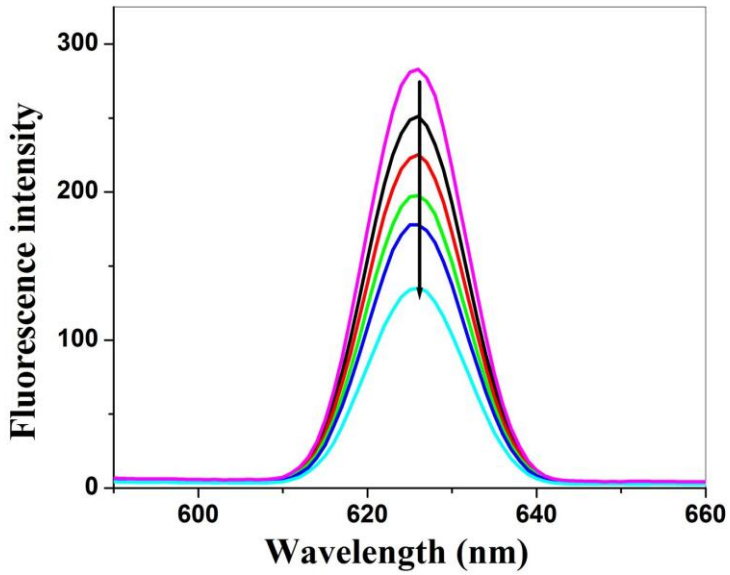

Figure S13. Fluorescence emission spectra of **R3** (6.25×10^{-4} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

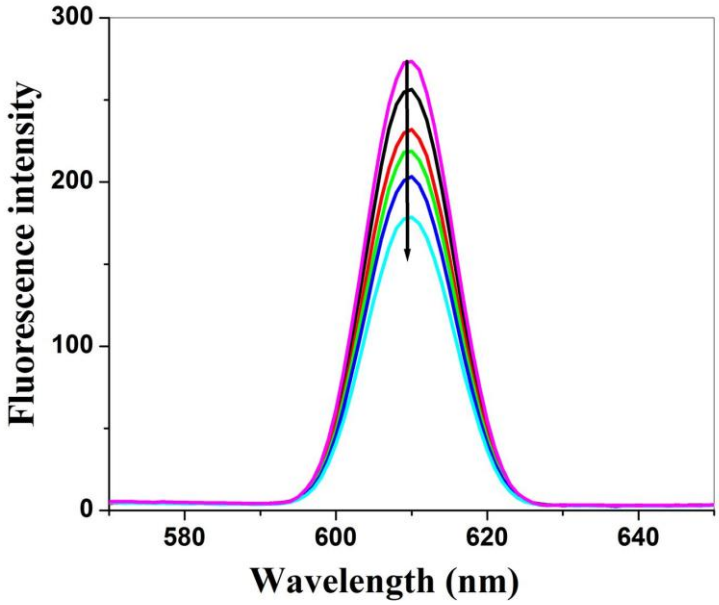

Figure S14. Fluorescence emission spectra of **R4** (6.25×10^{-4} M) with incremental addition of TBACN (0 - 6.25×10^{-6} M) in aq. HEPES buffer-DMF (9:1 v/v) medium (pH = 7.26).

Table S1. ^{1}H NMR spectral data for the interaction of the receptors with CN^{-}

Receptor	δ_{N-H} in free receptor	δ_{N-H} in complex*	$\Delta\delta$ (ppm)
R1	14.324	14.466	0.142
R2	14.276	14.379	0.103
R3	14.213	14.316	0.103
R4	14.132	14.245	0.113
R5	13.400	13.534	0.134

* After the addition of 0.5 equivalents of CN^{-} ion.

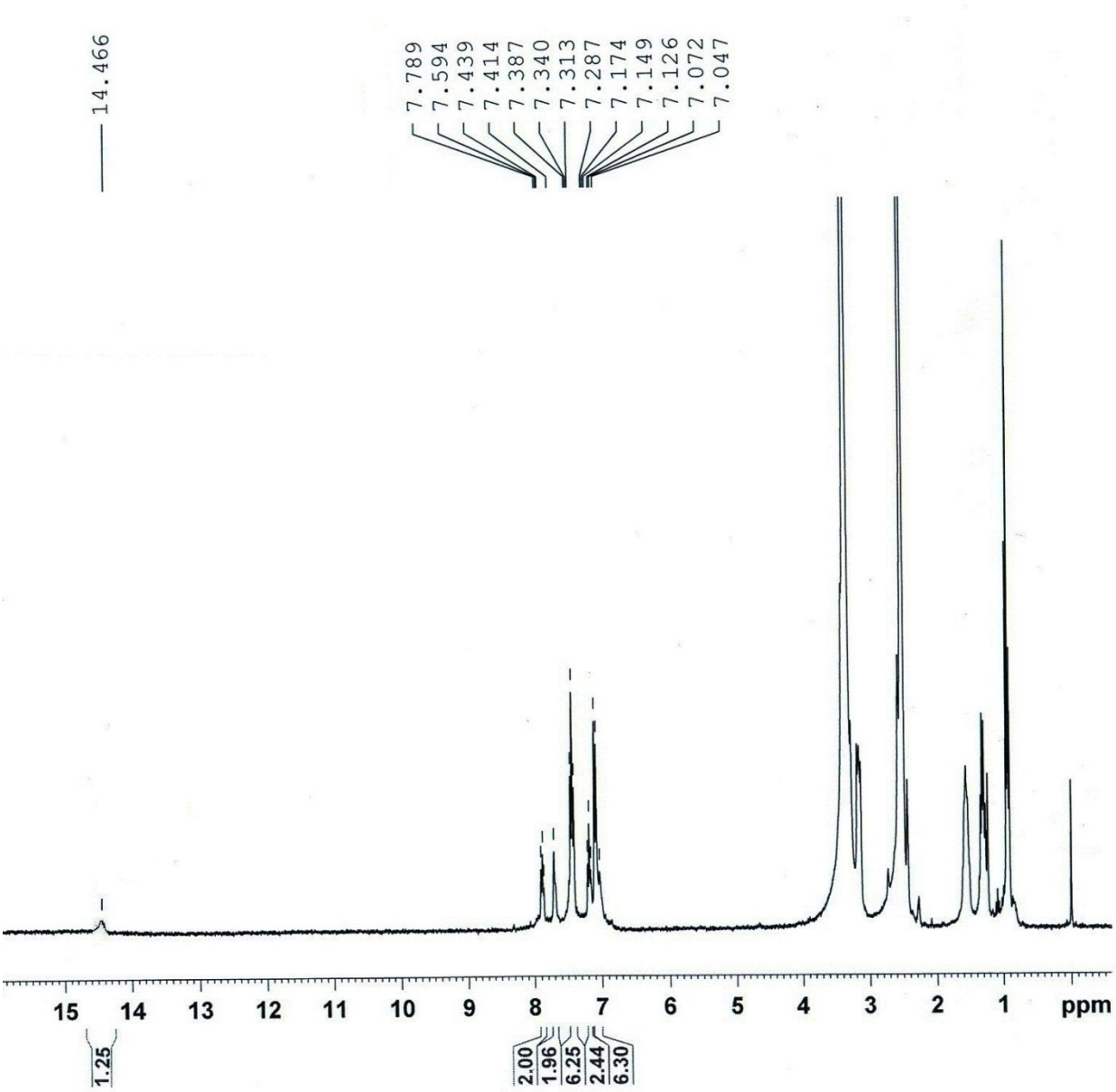

Figure S15. ^{1}H NMR spectrum of **R1** with addition of 0.5 eqv. of CN^- ion in DMSO-d_6.

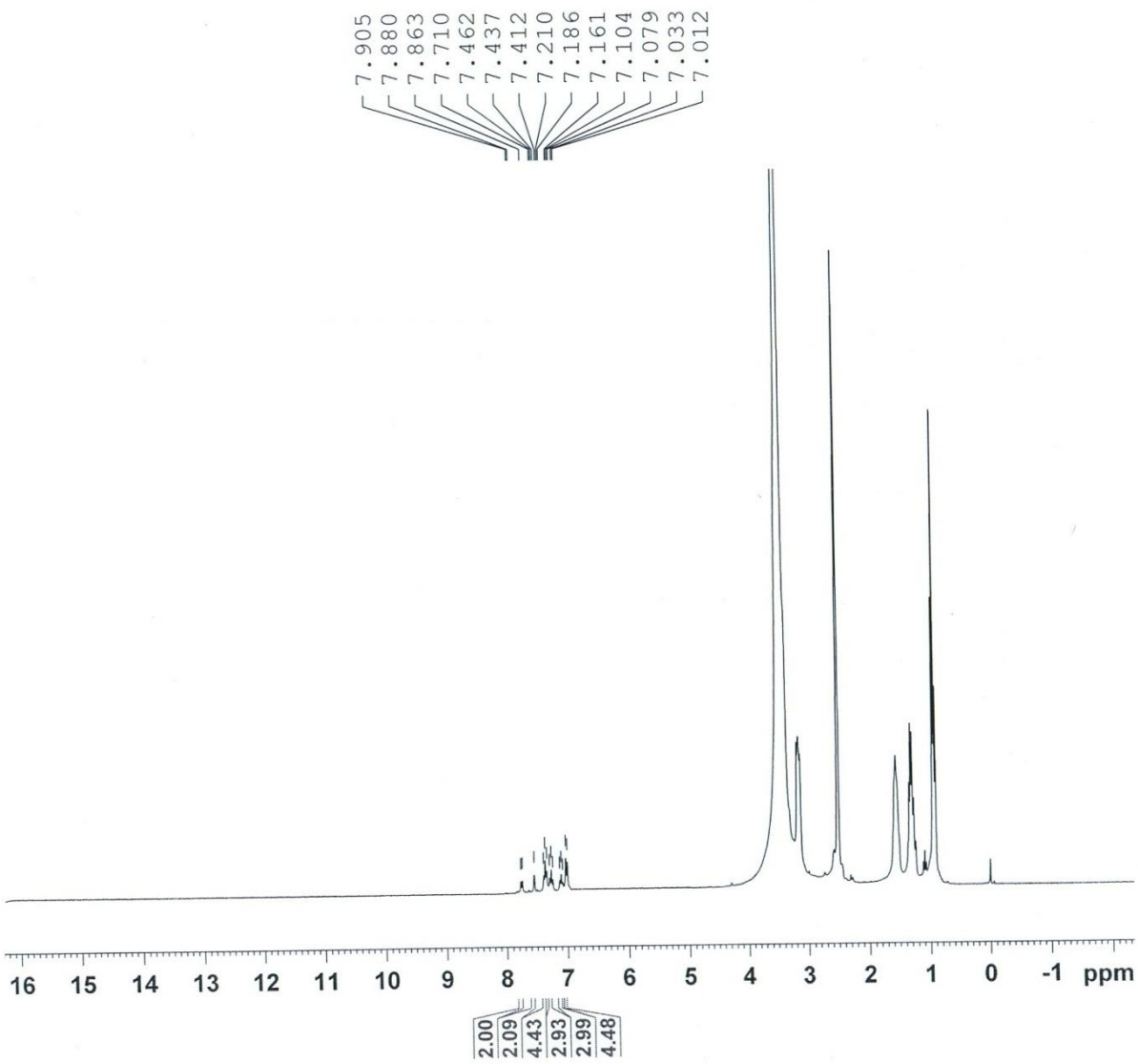

Figure S16. ^{1}H NMR spectrum of **R1** with addition of 2.0 eqv. of CN^- ion in DMSO-d_6.

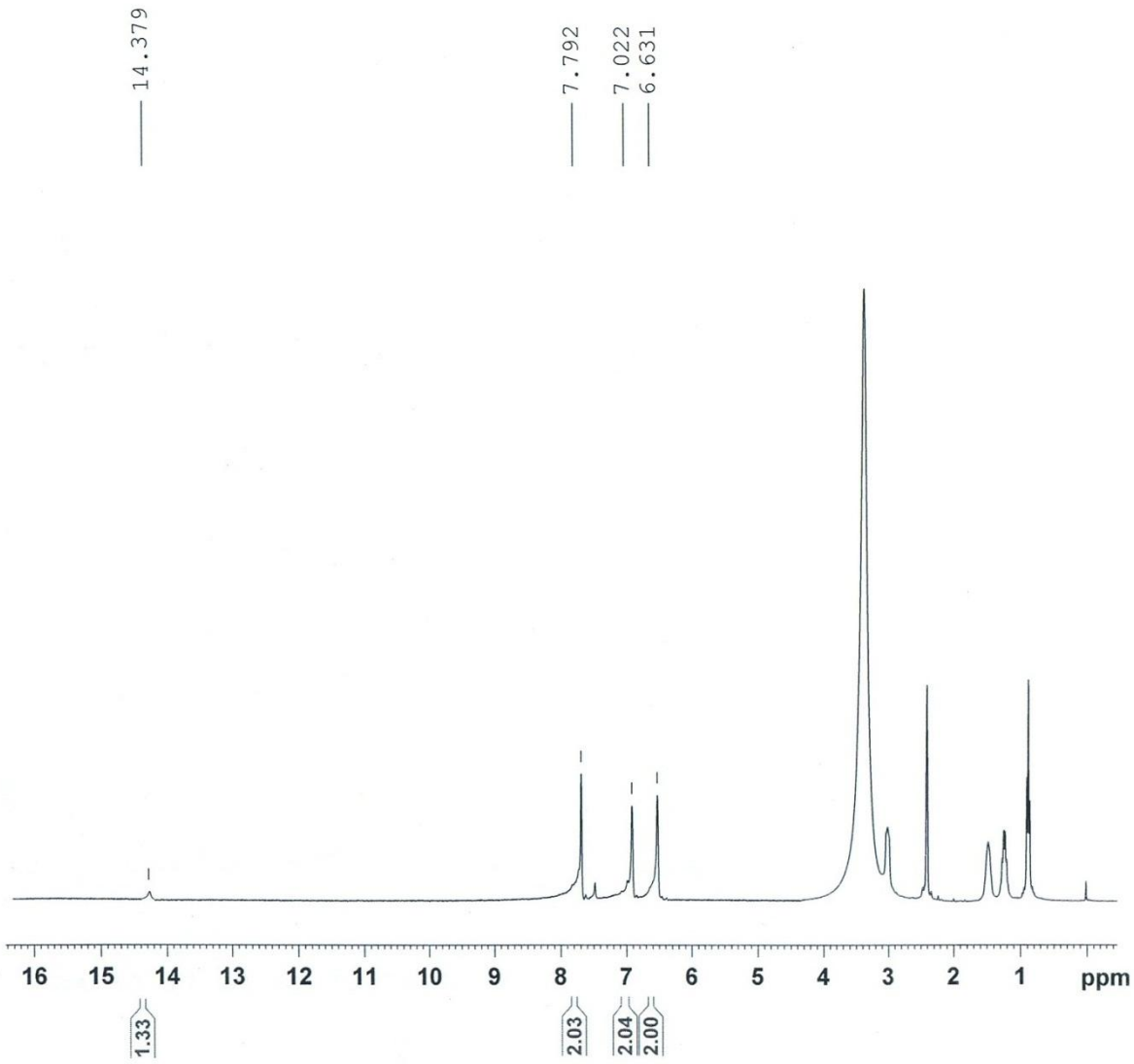

Figure S17. ^{1}H NMR spectrum of **R2** with addition of 0.5 eqv. of CN^- ion in DMSO-d_6.

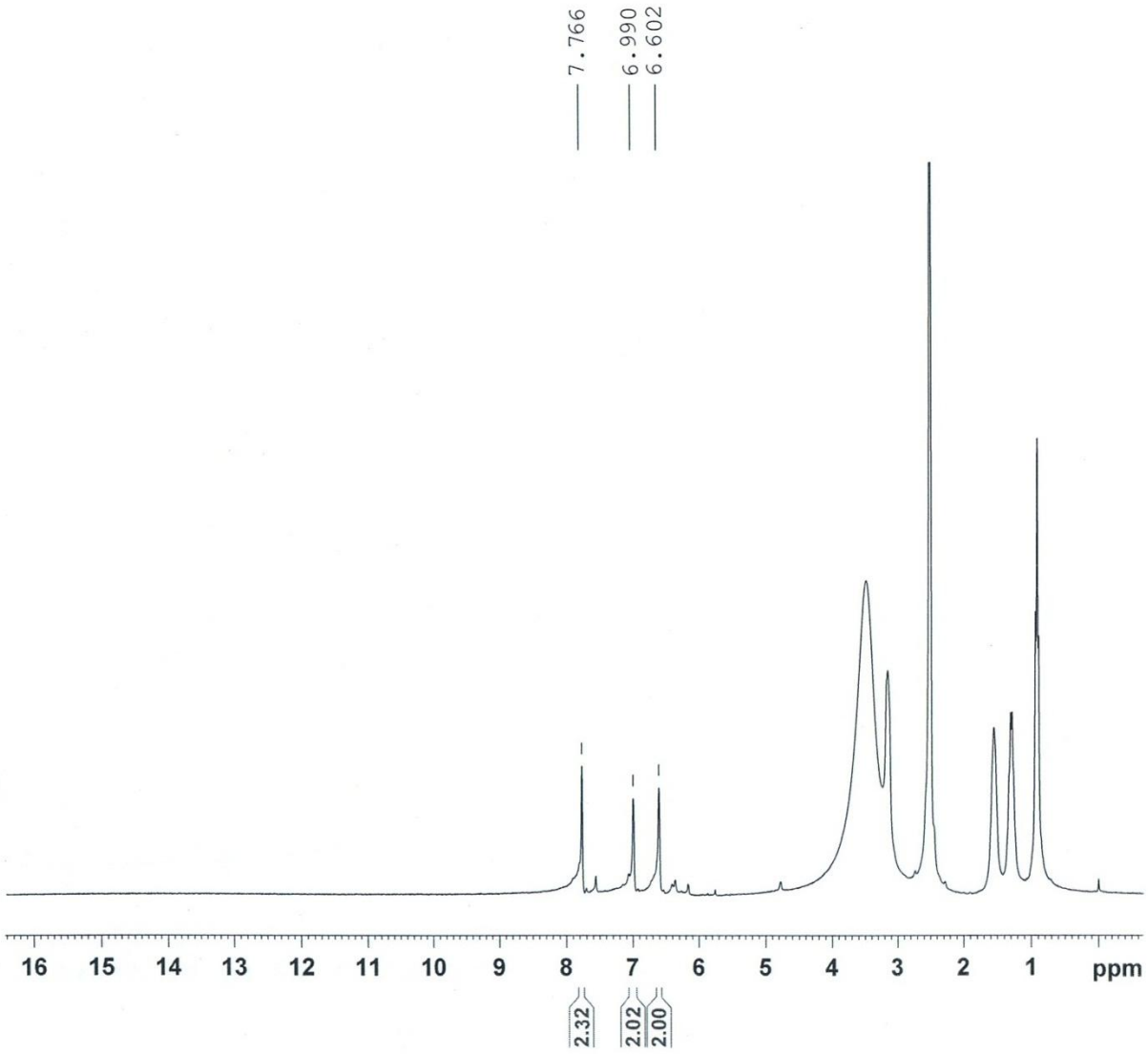

Figure S18. ^{1}H NMR spectrum of **R2** with addition of 2.0 eqv. of CN^- ion in DMSO-d_6.

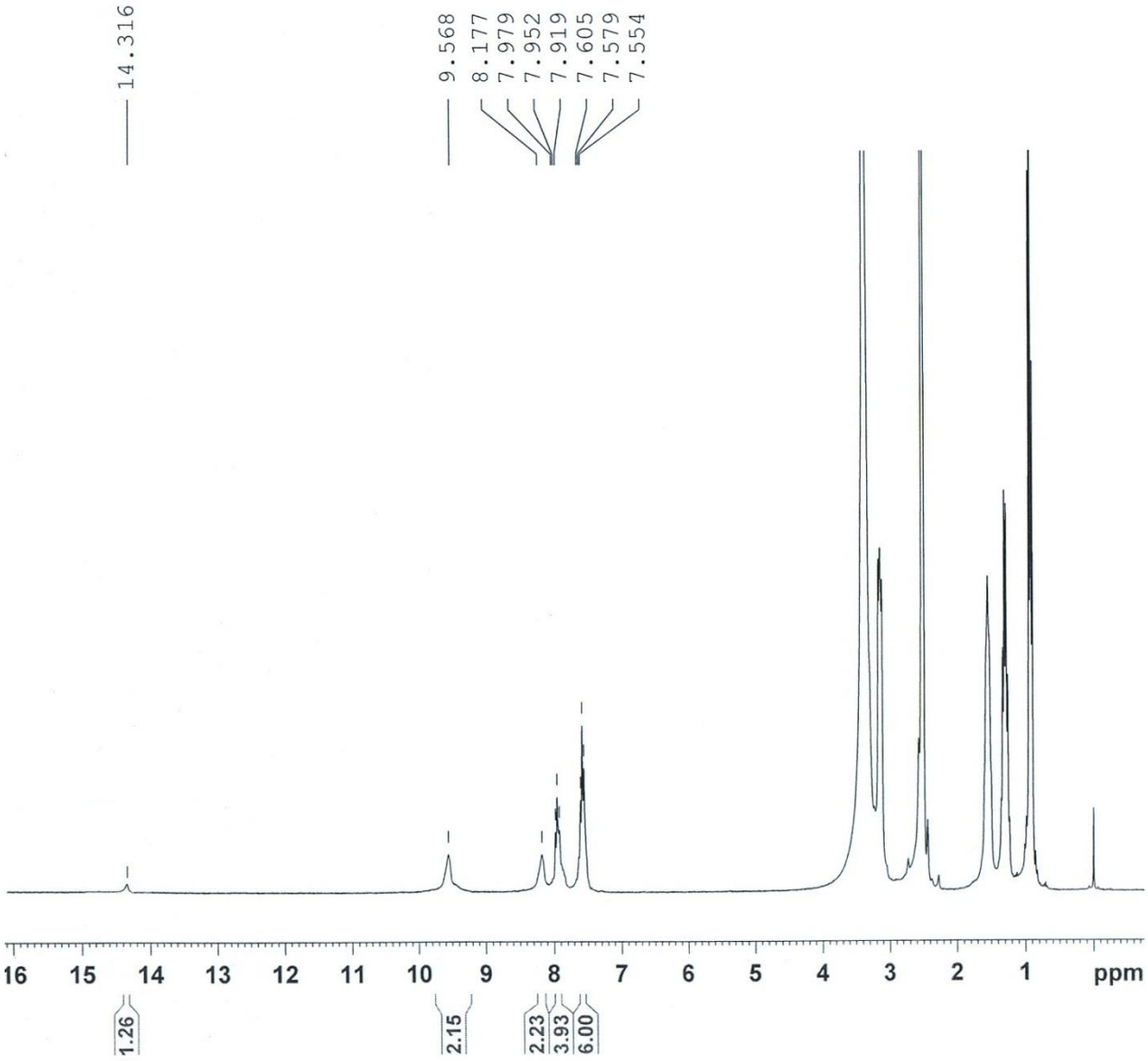

Figure S19. ^{1}H NMR spectrum of **R3** with addition of 0.5 eqv. of CN^- ion in DMSO-d_6.

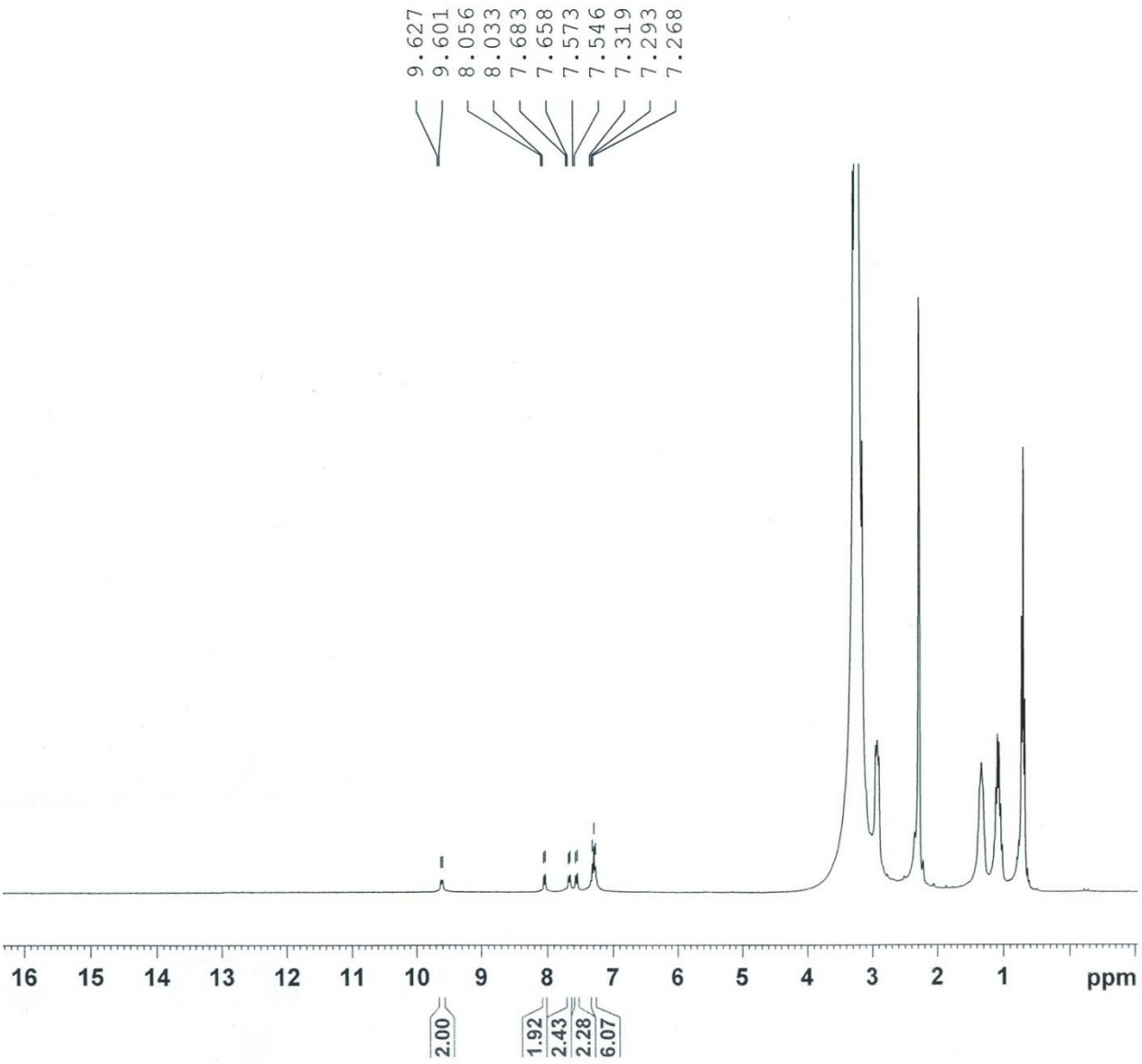

Figure S20. ^{1}H NMR spectrum of **R3** with addition of 2.0 eqv. of CN^- ion in DMSO-d_6.

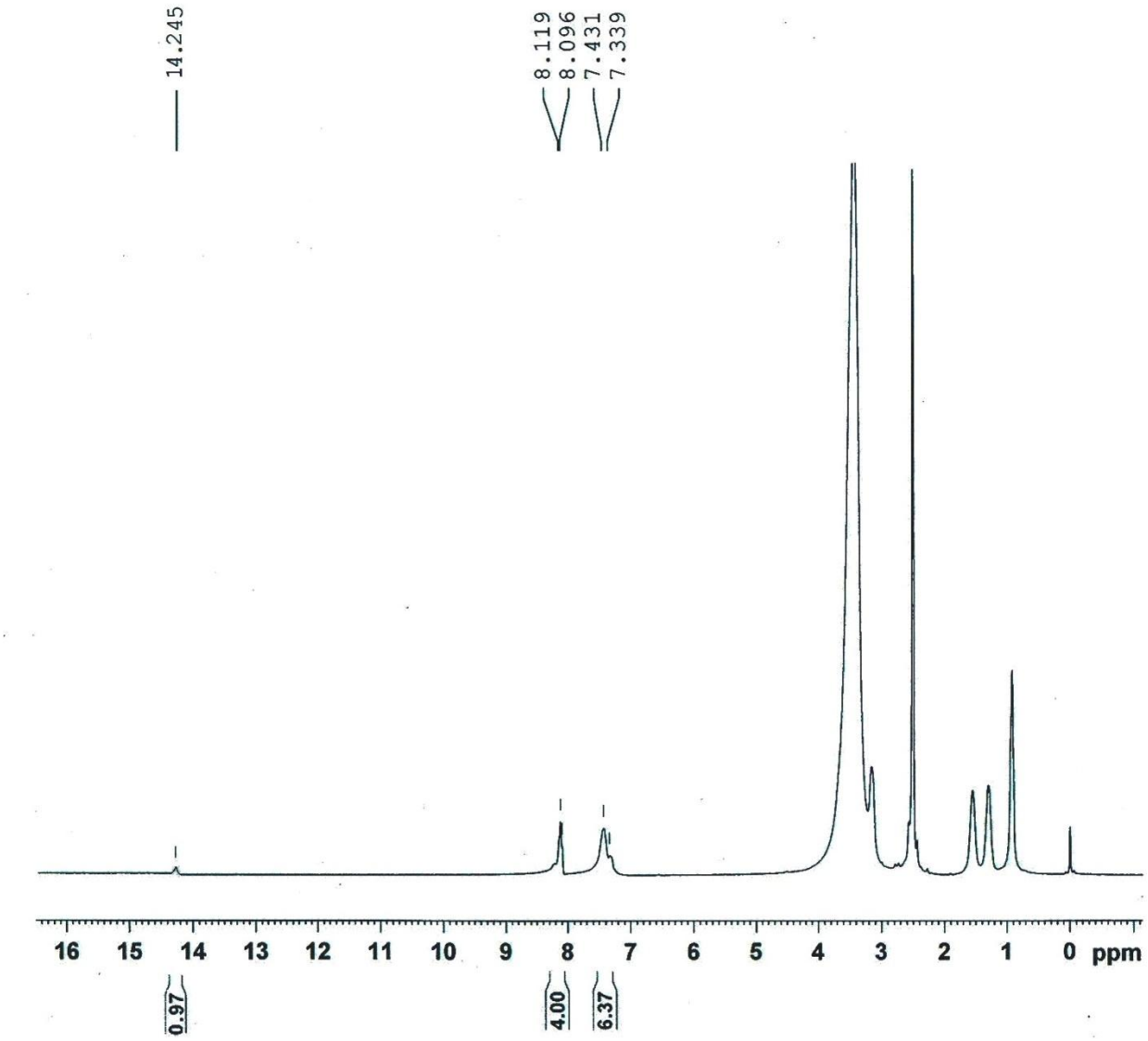

Figure S21. ^{1}H NMR spectrum of **R4** with addition of 0.5 eqv. of CN^- ion in DMSO-d_6.

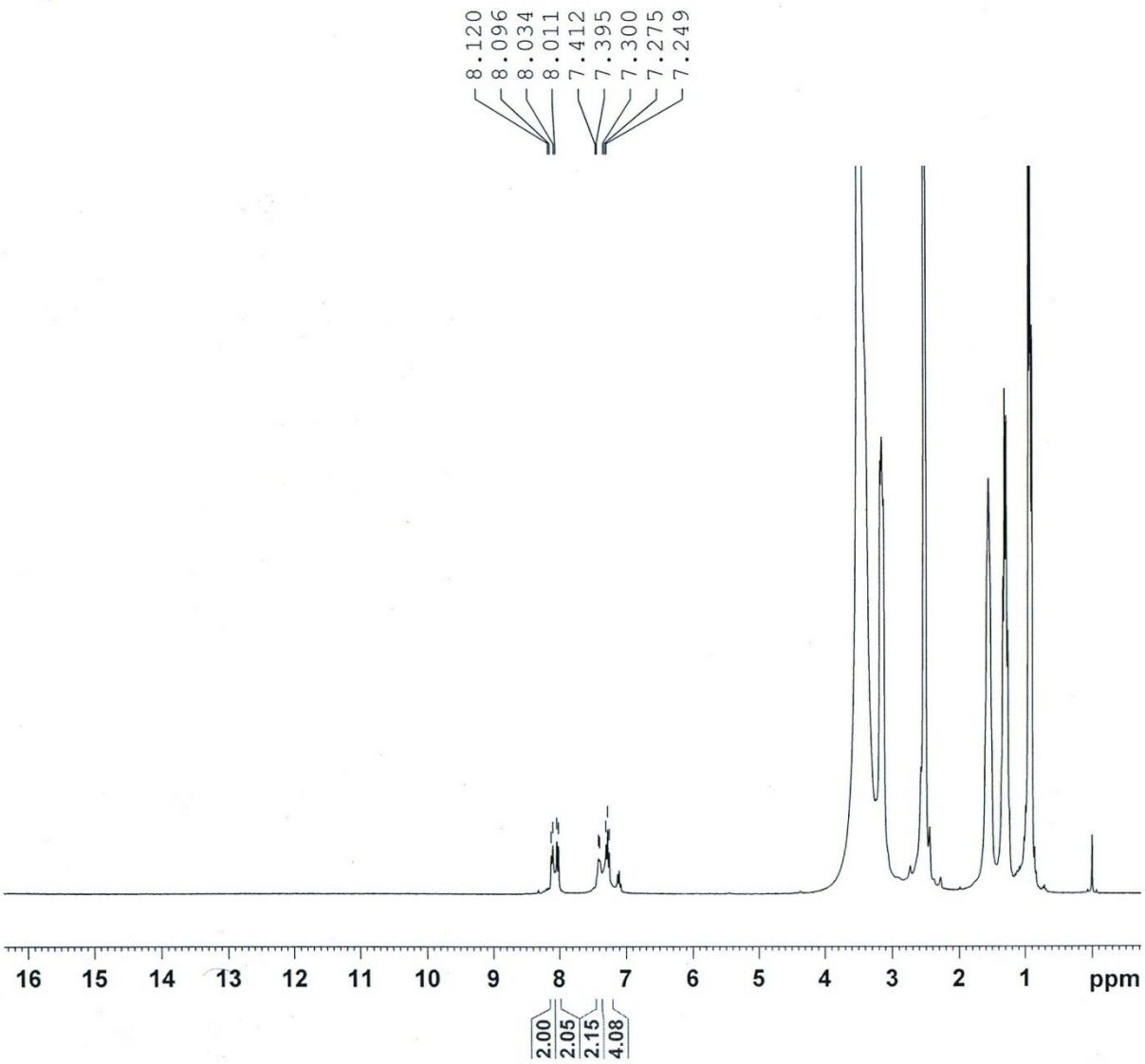

Figure S22. ^{1}H NMR spectrum of **R4** with addition of 2.0 eqv. of CN^- ion in DMSO-d_6.

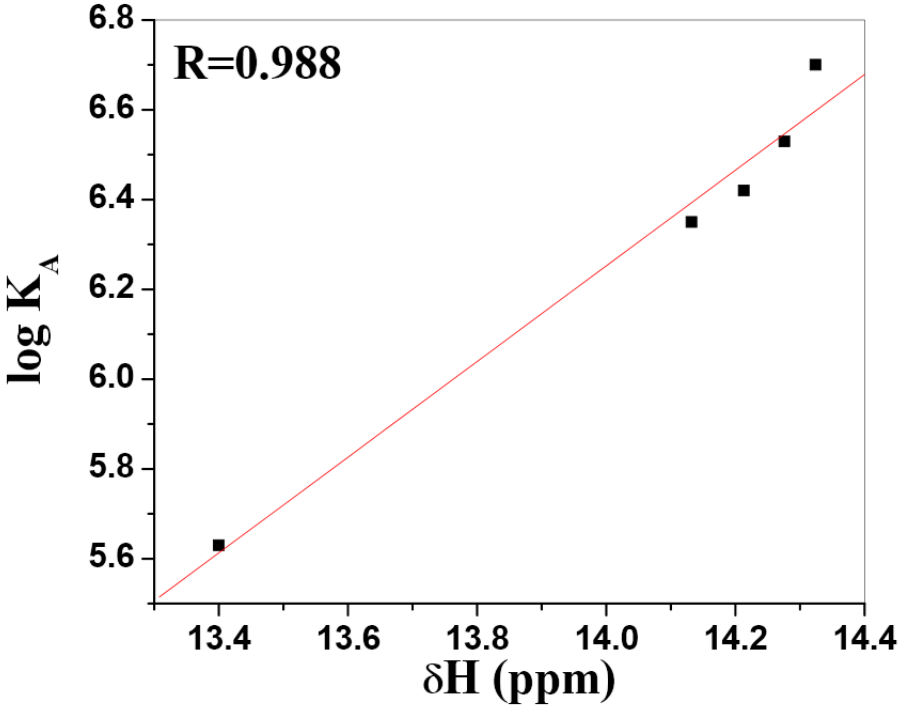

Figure S23. Correlation between association constant (K_A) and chemical shift (δ_H).

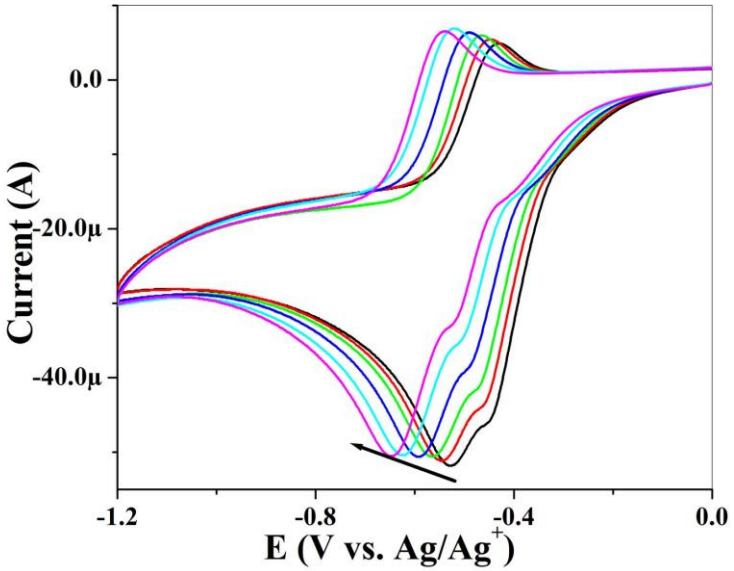

Figure S24. CV response of receptor **R1** with CN^- ion.

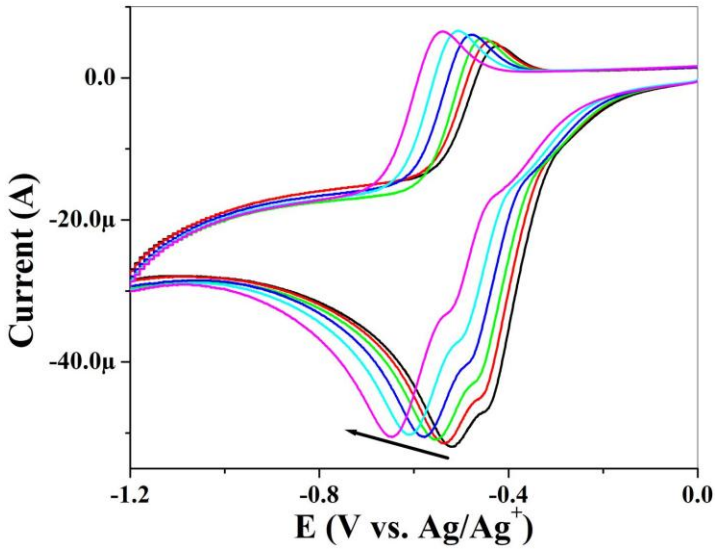

Figure S25. CV response of receptor **R2** with CN^- ion.

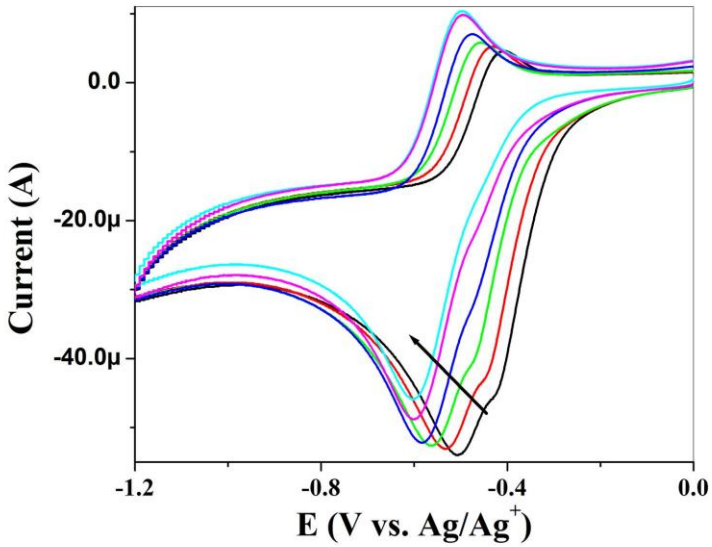

Figure S26. CV response of receptor **R3** with CN^- ion.

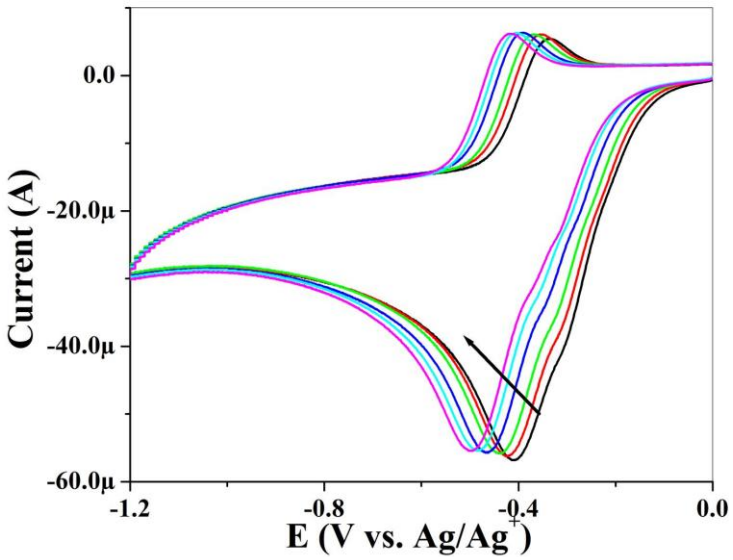

Figure S27. CV response of receptor **R4** with CN^- ion.

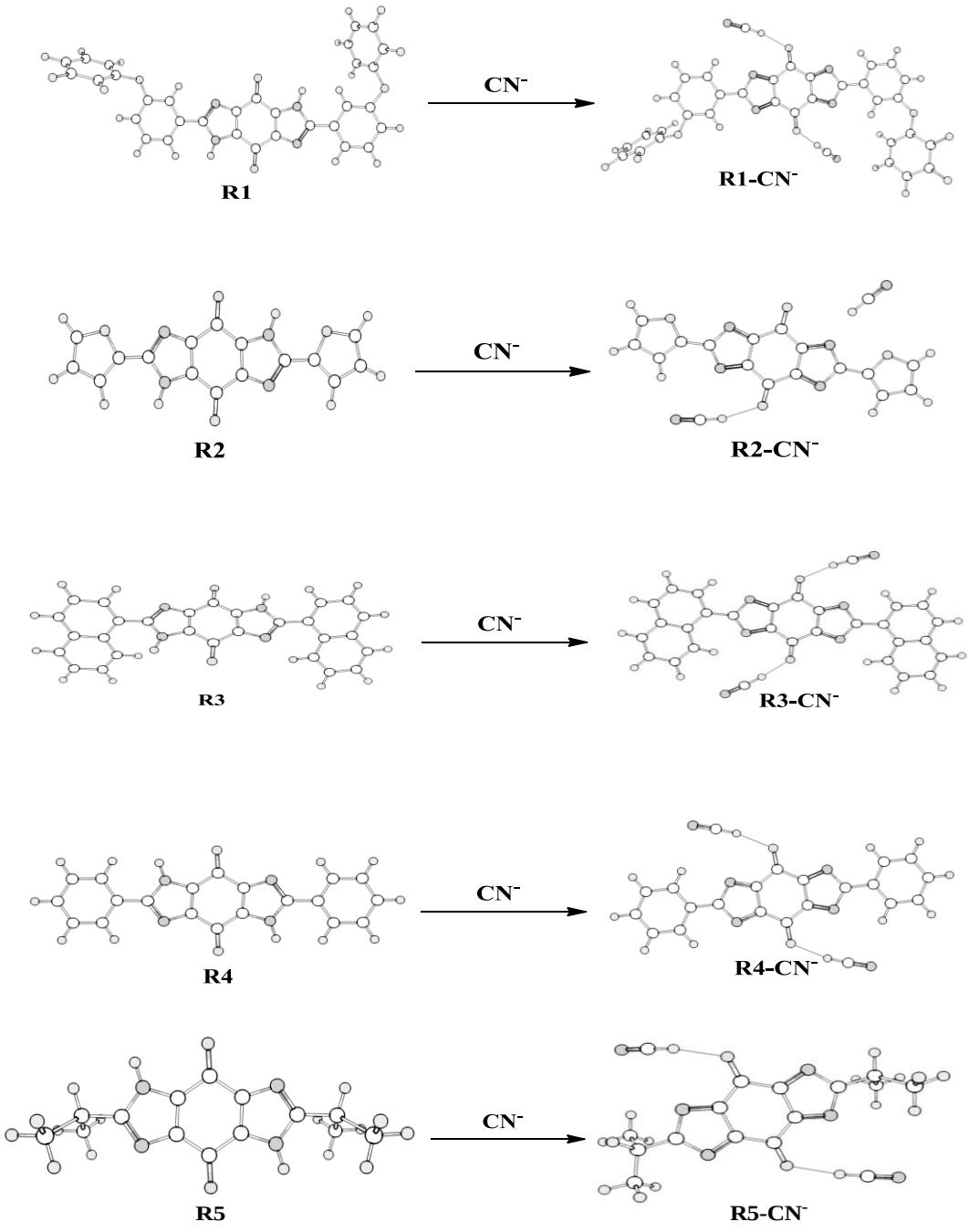

Figure S28. Optimized structure for receptors **R1**-**R5** and its Cyanide complexes.

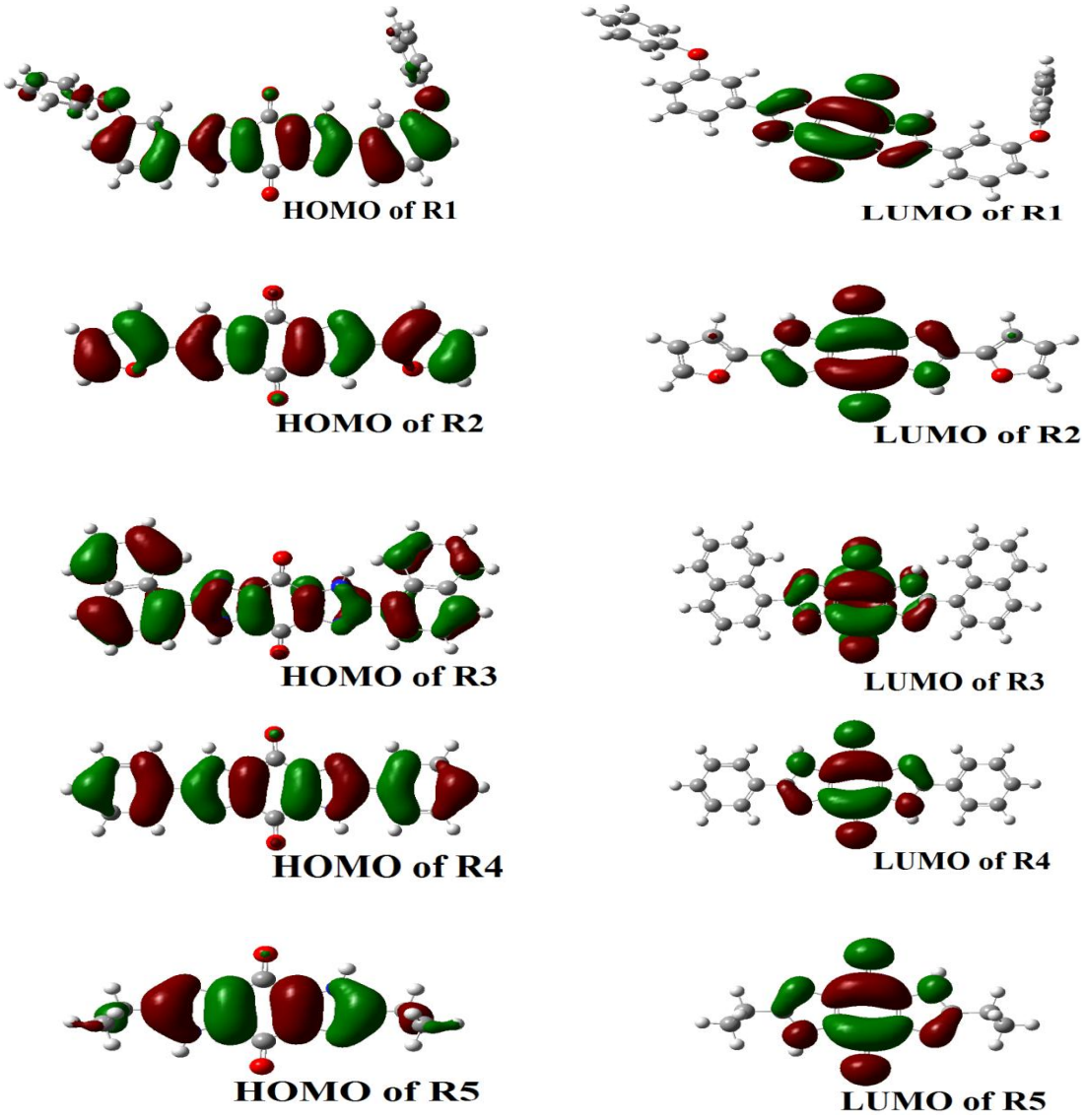

Figure S29. Molecular orbitals (HOMO–LUMO) of receptors **R1-R5.**

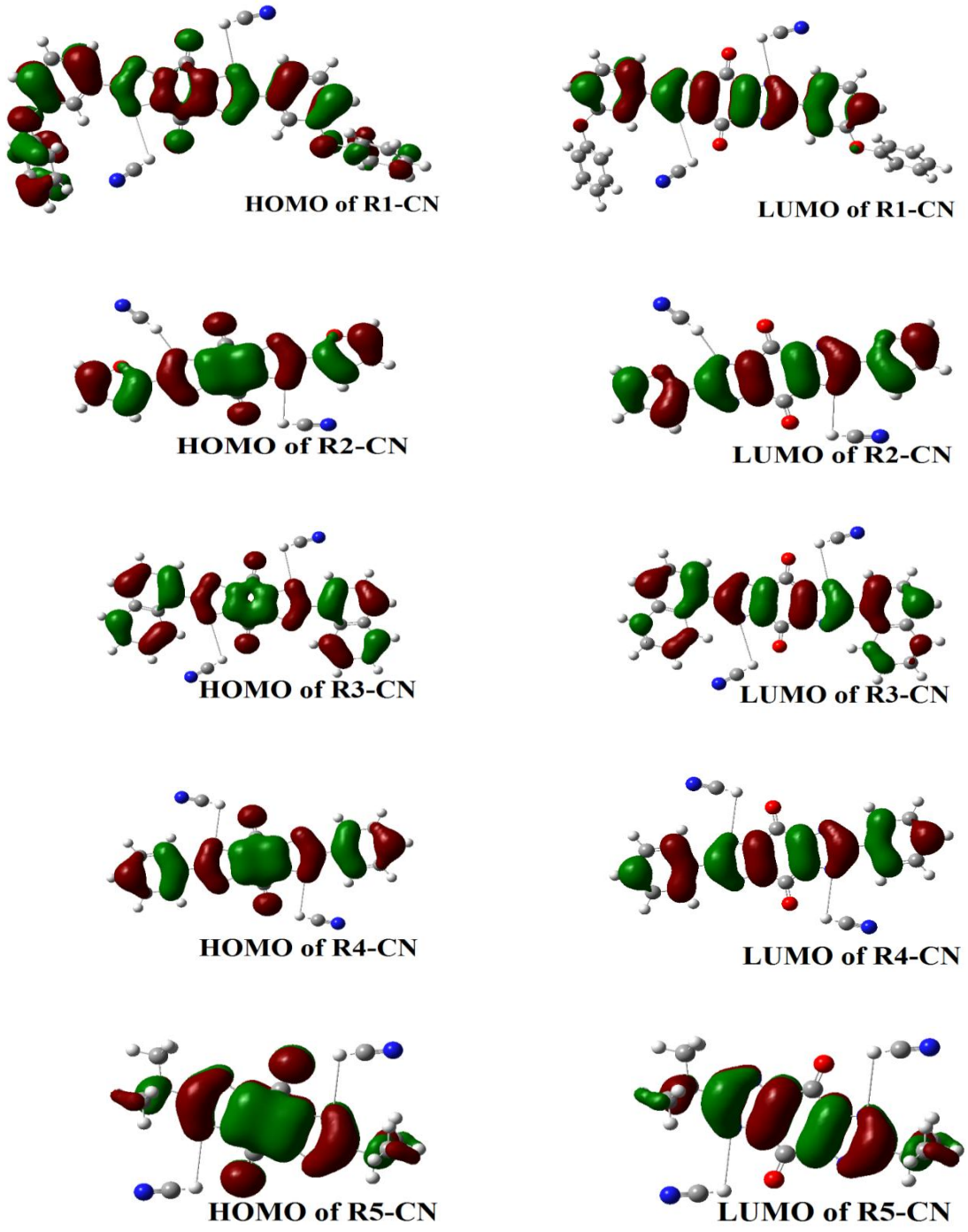

Figure S30. Molecular orbitals (HOMO –LUMO) of receptors–CN^- complexes.

Table S2. Energies (in eV) of the MOs in free receptors and in receptor-CN^- complexes

Receptor	Free receptor			Receptor-CN^- complex		
	E_{HOMO}	E_{LUMO}	ΔE	E_{HOMO}	E_{LUMO}	ΔE
R1	-6.3305	-3.3908	2.9397	-6.720	-5.6951	1.0569
R2	-6.2472	-3.3932	2.8540	-6.8257	-5.7136	1.1121
R3	-6.0975	-3.3818	2.7157	-6.3136	-5.3343	0.9793
R4	-6.3990	-3.3897	3.0093	-6.9245	-5.7152	1.2093
R5	-6.8004	-3.2738	3.5266	-7.9955	-6.4872	1.5083

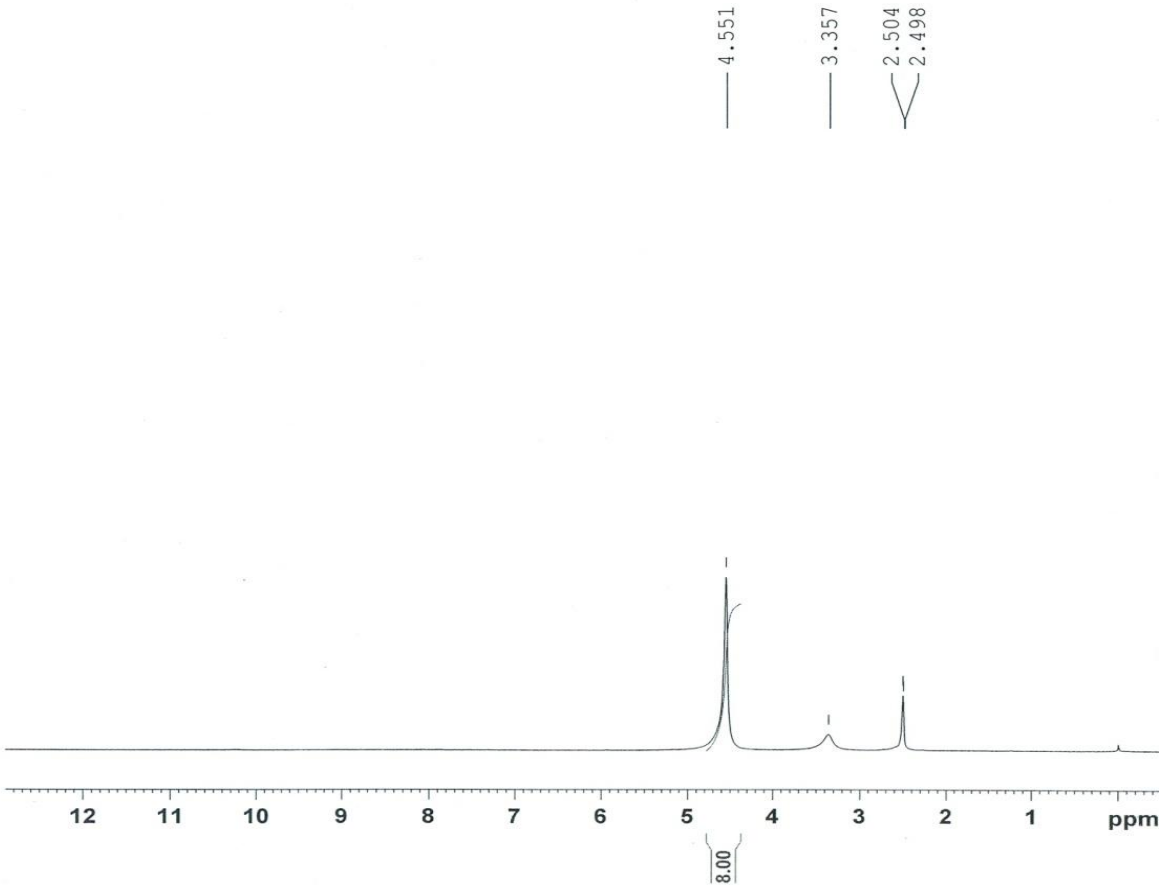

Figure S31. ^{1}H NMR spectrum of **1**

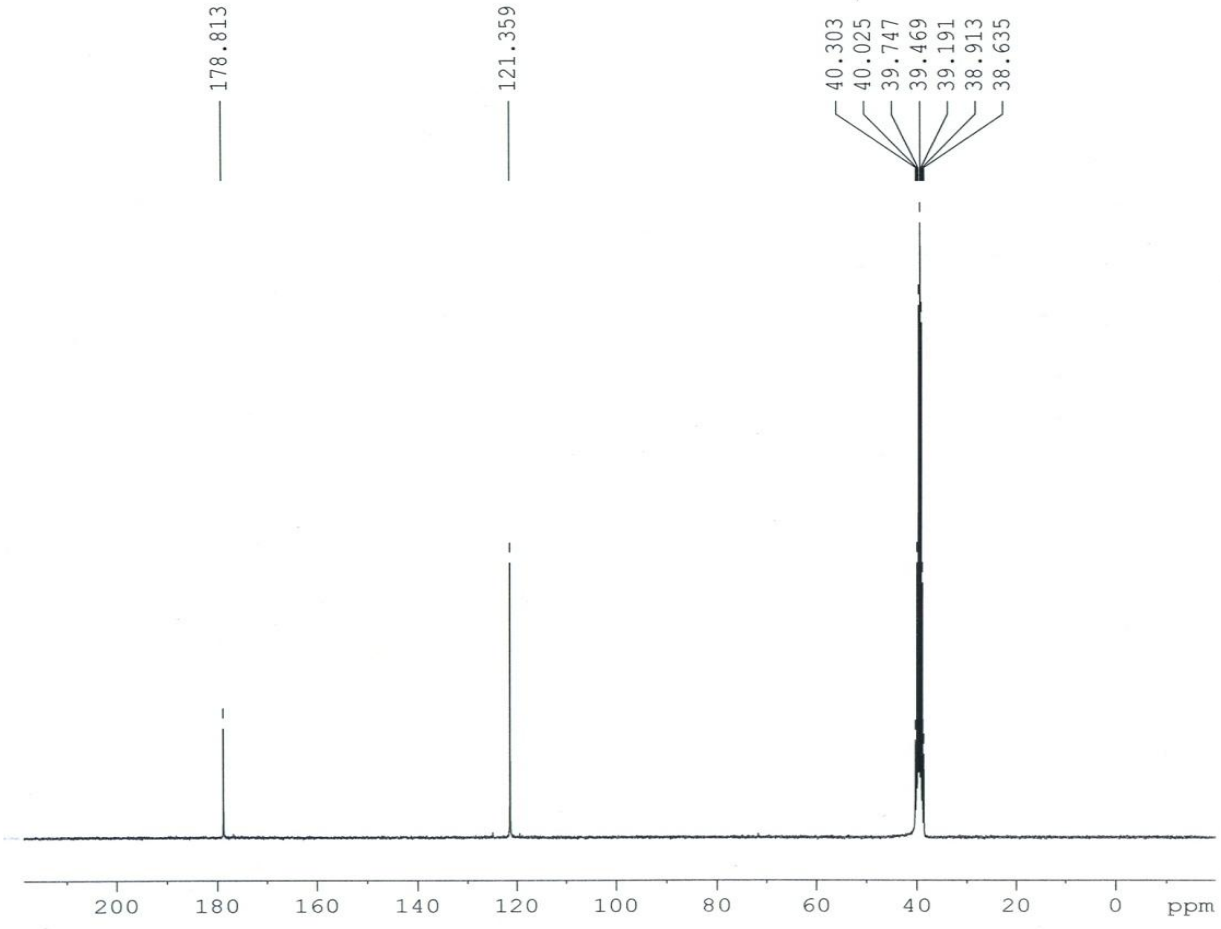

Figure S32. ^{13}C NMR spectrum of **1**

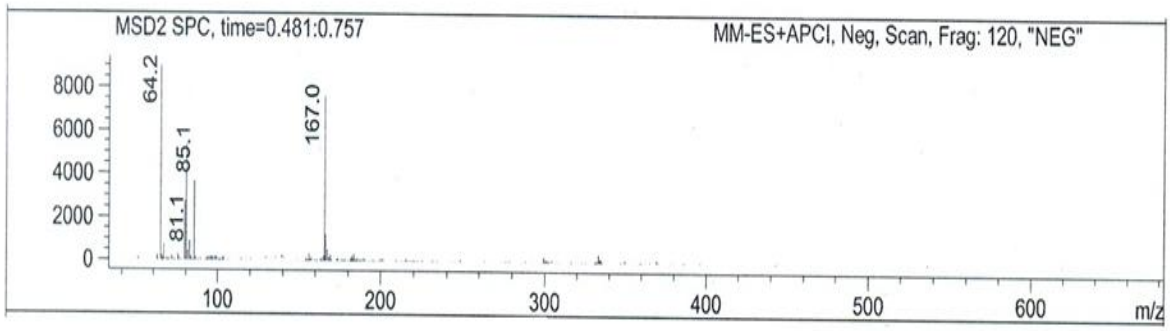

Figure S33. LCMS spectrum of **1**

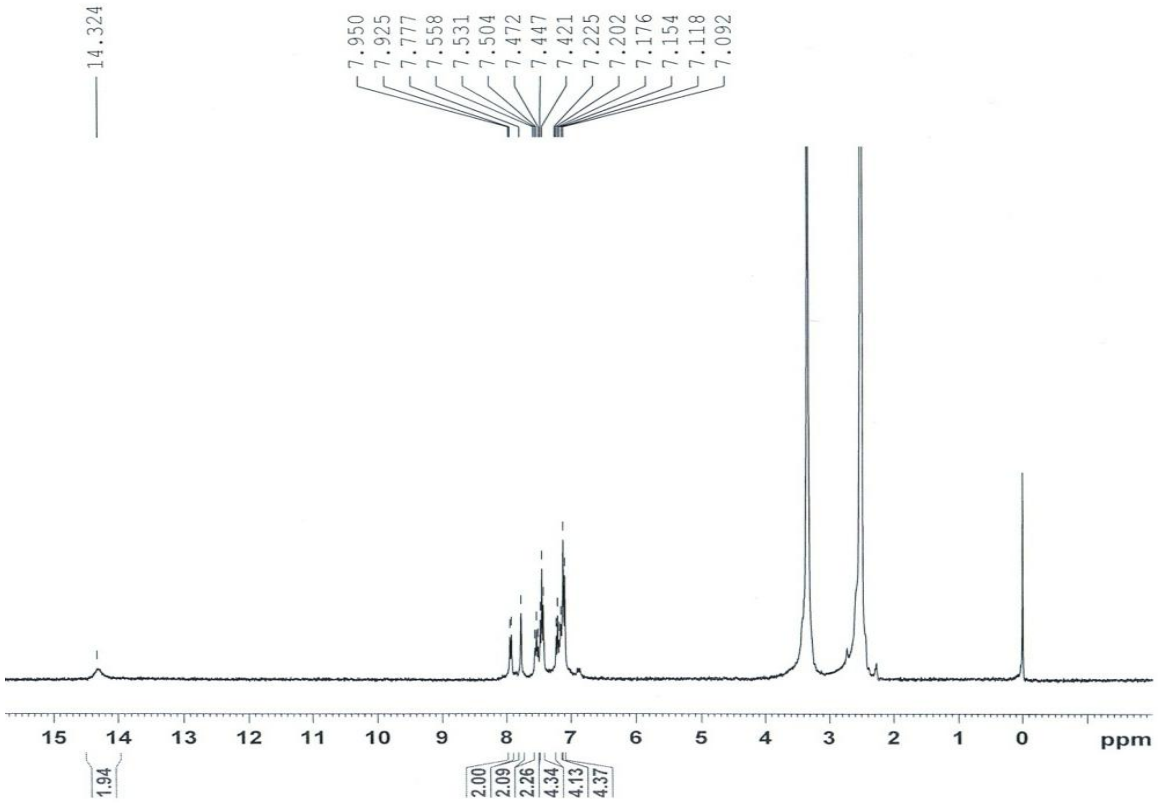

Figure S34. ^{1}H NMR spectrum of **R1.**

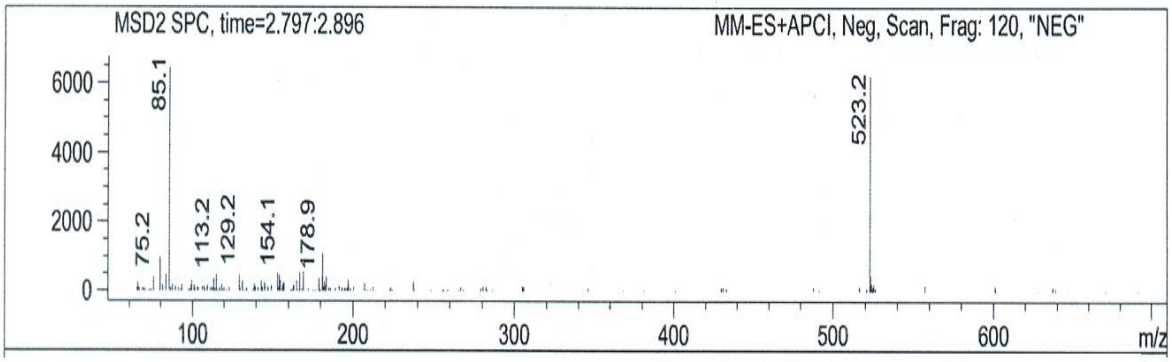

Figure S35. LCMS spectrum of **R1.**

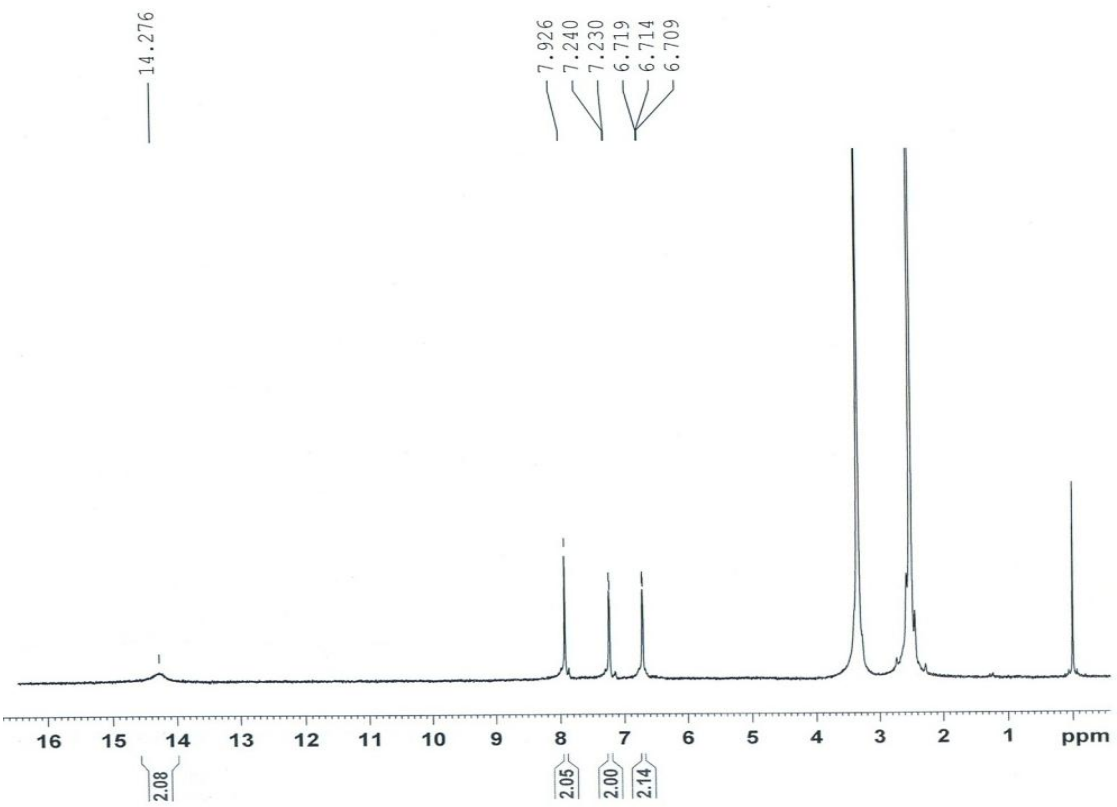

Figure S36. ^{1}H NMR spectrum of **R2.**

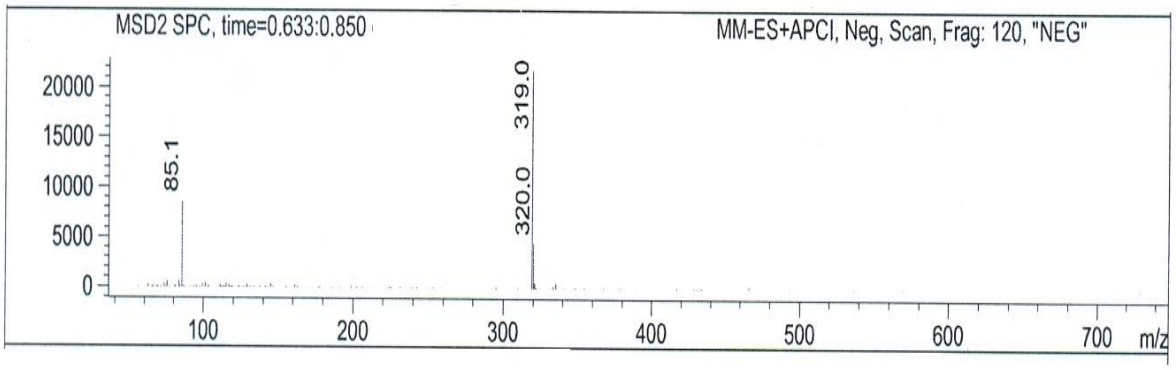

Figure S37. LCMS spectrum of **R2.**

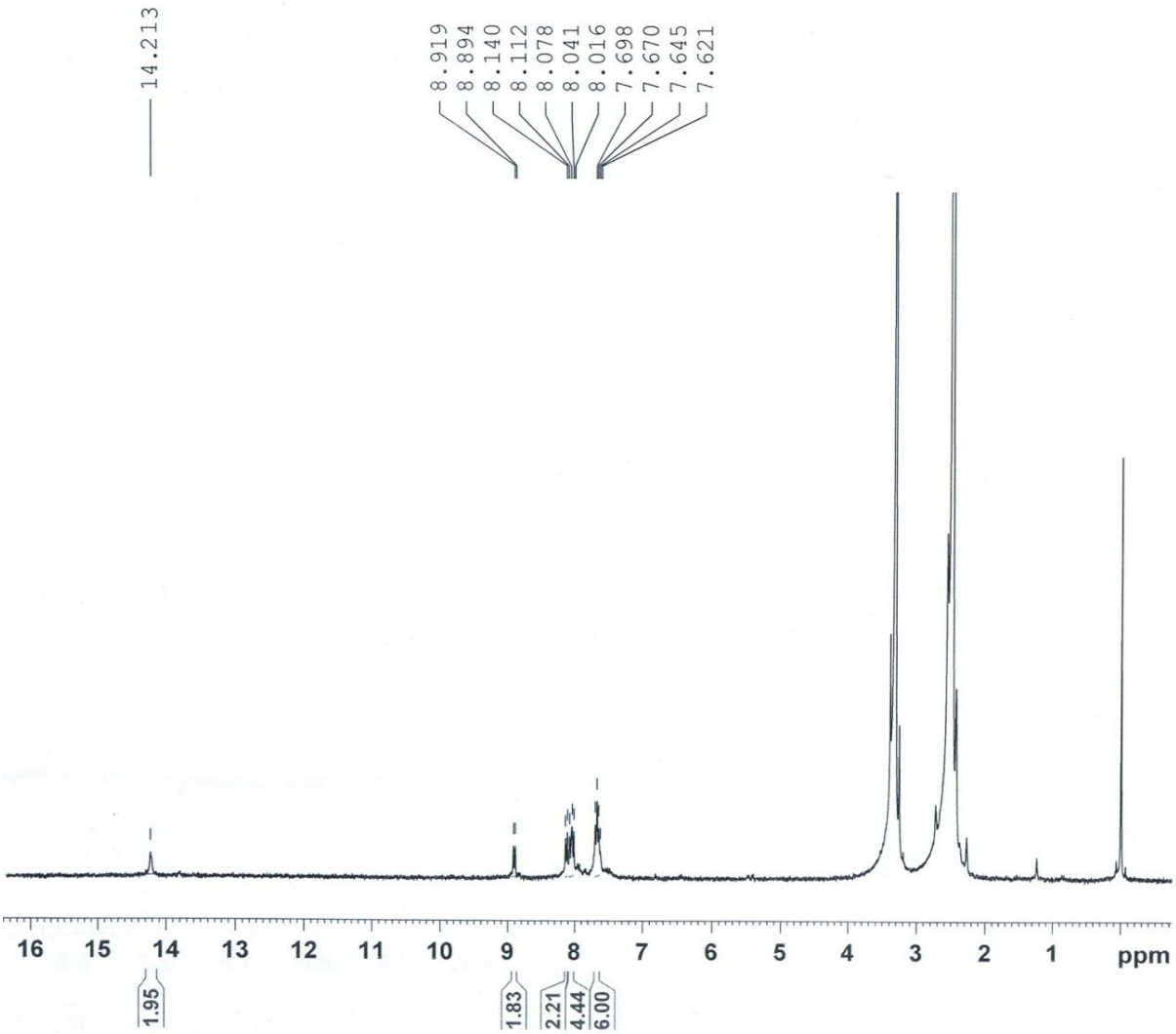

Figure S38. ^{1}H NMR spectrum of **R3.**

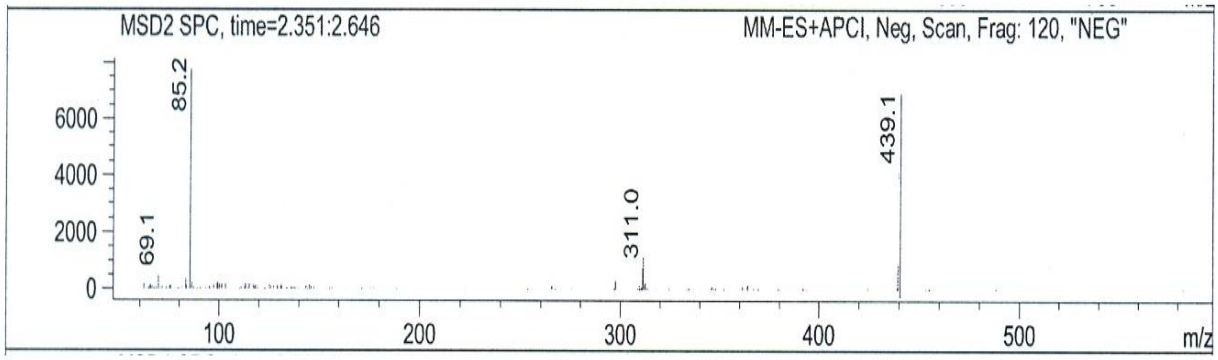

Figure S39. LCMS spectrum of **R3.**

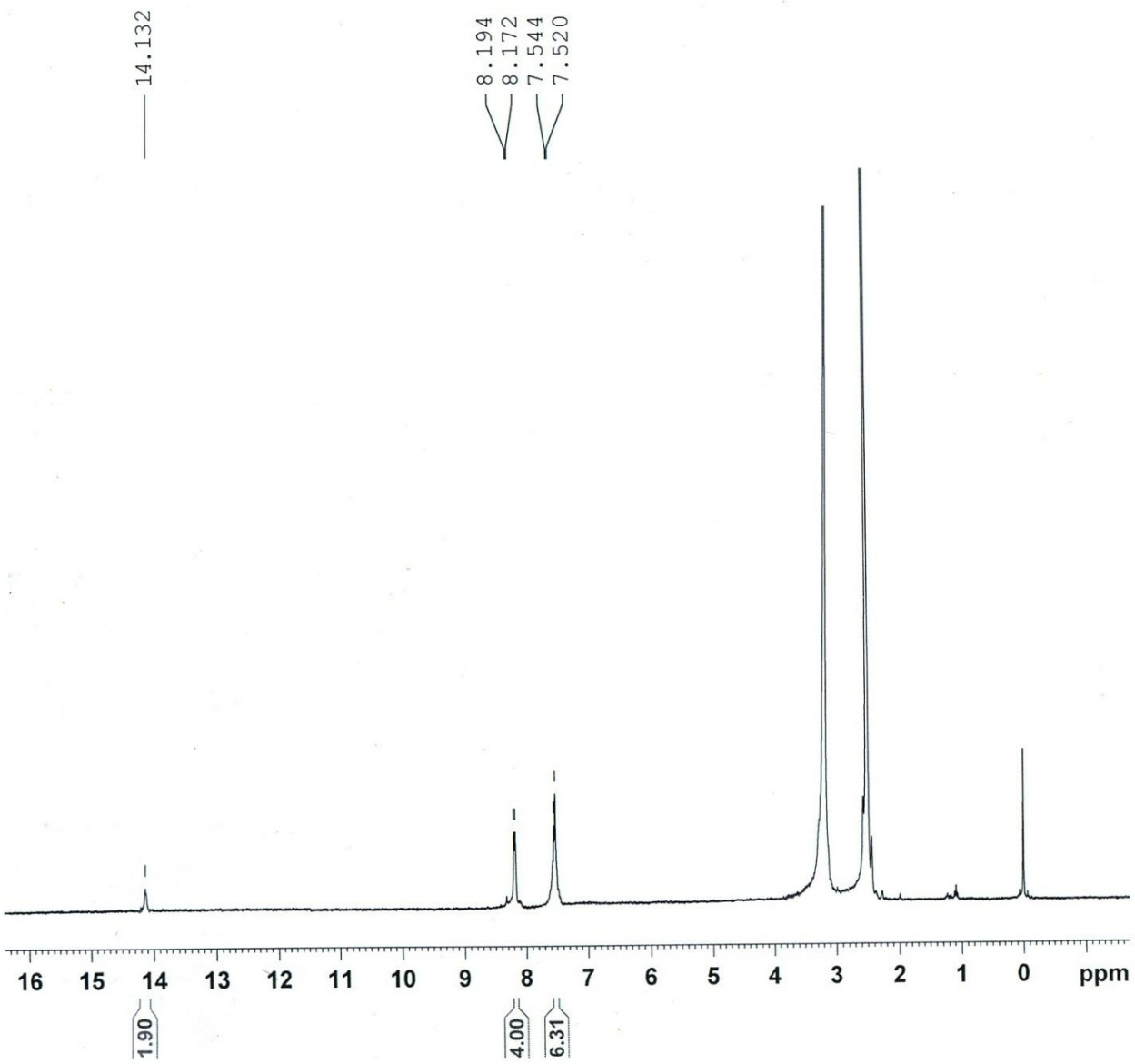

Figure S40. ^{1}H NMR spectrum of **R4.**

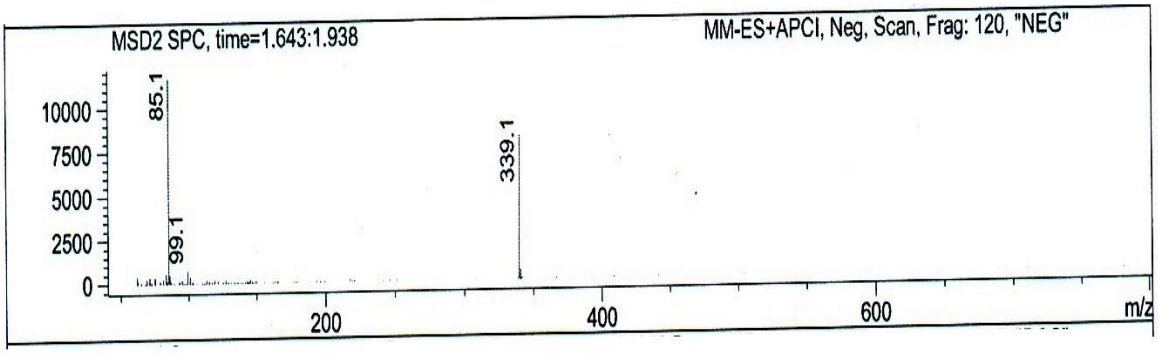

Figure S41. LCMS spectrum of **R4.**

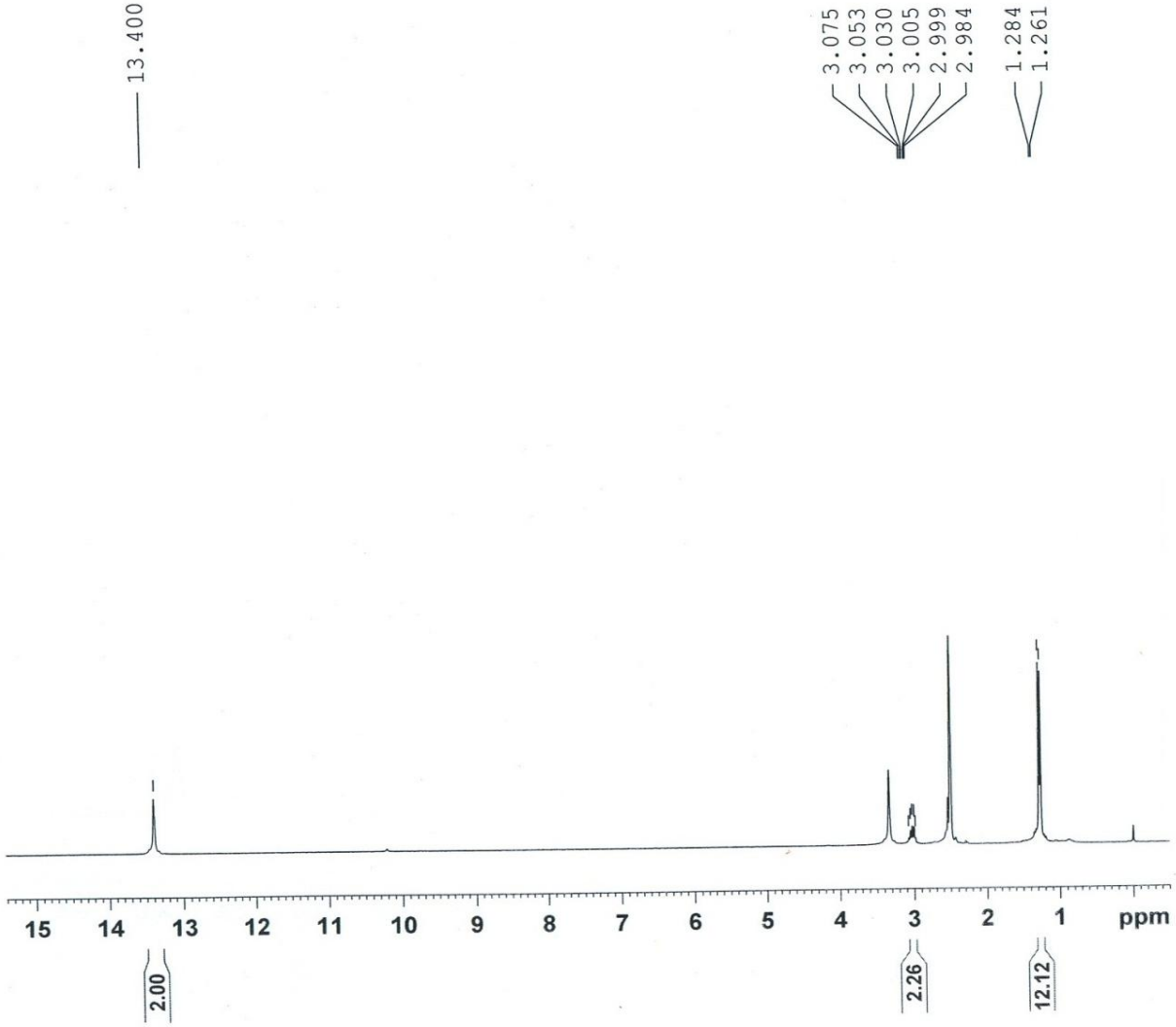

Figure S42. ^{1}H NMR spectrum of **R5.**

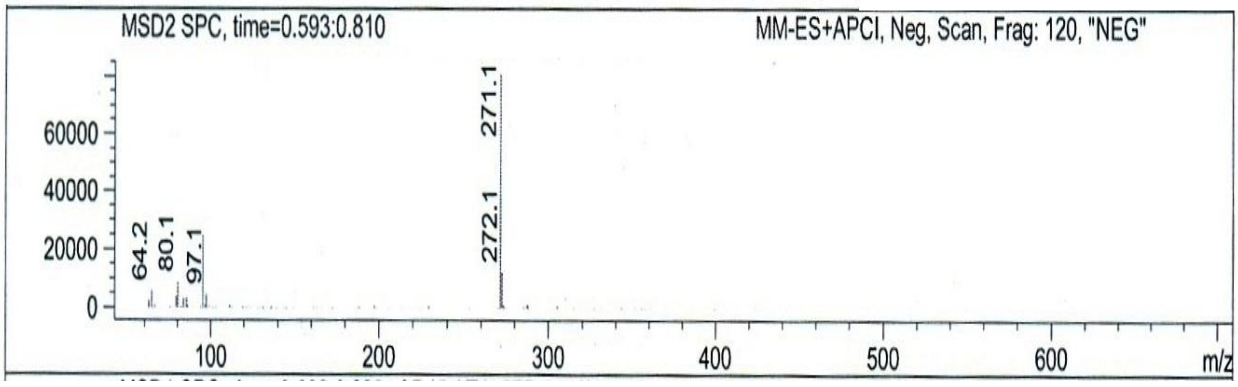

Figure S43. LCMS spectrum of **R5.**