

Supporting information to:

Metal-ion induced amplification of three receptors from dynamic combinatorial libraries of peptide-hydrazones

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NMR and IR data of the Li⁺ complexes of (mPF)₂, (pPF)₃ and (pPC)₃. The complexes were generated in solution by addition of 1 equivalent of LiI to solutions of the cyclic receptors in CDCl₃:MeOD / 98:2 (v/v) followed by sonication.

Li-(mPF)₂: (S, S) *N*-(3-Dimethoxymethyl-benzoyl)-proline-phenylalanine carboxylic acid hydrazide dimer - lithium complex

IR (CDCl₃:MeOD / 98:2) ν = 1676 (br, C=Os) cm⁻¹; ¹H NMR (500 MHz (cryoprobe), CDCl₃:MeOD / 98:2) δ = 11.81 (2H, br, NHNC), 8.48 (2H, s, HCN), 7.99 (2H, br m, Ar-H), 7.71 (2H, s, Ar-H), 7.55-7.35 (4H, m, Ar-H), 7.21-7.12 (10H, br m, Ar-H), 6.42 (2H, br m, NH), 5.38 (2H, br, α -H), 4.72 (2H, br m, Pro- α -H), 3.74 (2H, br m, Pro-NCH_aH_b), 3.38 (2H, br m, Pro-NCH_aH_b), 3.24 (2H, br m, CH_aH_bPh), 2.65 (2H, br m, CH_aH_bPh), 2.18 (2H, br m, Pro-CH_aH_b), 1.90 (2H, br m, Pro-CH_cH_d), 1.58-1.42 (4H, br m, Pro-CH₂); ¹³C NMR (125 MHz (cryoprobe), CDCl₃:MeOD / 98:2) δ = 172.1, 170.3, 169.6 (C=O), 150.0 (CN), 136.0, 133.1, 132.5, 131.7, 129.5, 128.7, 128.4, 128.2, 126.9, 123.4 (Ar), 65.2 (Pro-C α -H), 51.1 (C α -H), 50.1 (Pro-NCH₂), 38.7 (CH₂Ph), 29.3, 25.0 (CH₂).

Li-(pPC)₃: (S, S) *N*-(4-Dimethoxymethyl-benzoyl)-proline-cyclohexylalanine carboxylic acid hydrazide trimer - lithium complex

IR (CDCl₃:MeOD / 98:2) ν = 1667 (br, C=Os) cm⁻¹; ¹H NMR (500 MHz (cryoprobe), CDCl₃:MeOD / 98:2) δ = 11.01 (3H, br, NHNC), 8.42 (3H, s, HCN), 8.14 (6H, d, J = 7.3 Hz, Ar-H), 7.43 (6H, d, J = 7.3 Hz, Ar-H), 5.08 (3H, d, J = 10.5 Hz, α -H), 4.90 (3H, m, Pro-NCH_aH_b), 4.40 (3H, dd, J_1 = 11.0 Hz, J_2 = 7.0 Hz Pro- α -H), 3.48 (3H, m, Pro-NCH_aH_b), 2.63 (3H, m, CH_aH_b(C₆H₁₁)), 2.47 (3H, m, Pro-CH_aH_b), 2.30 (3H, m, Pro-CH_aH_b), 2.04 (3H, m, Pro-CH_cH_d), 1.90 (3H, m, CH_aH_b(C₆H₁₁)), 1.87 (3H, m, Pro-CH_cH_d), 1.85-0.77 (11H, ring CH₂); ¹³C NMR (125 MHz (cryoprobe), CDCl₃:MeOD / 98:2) δ = 173.4, 173.1, 170.8 (C=O), 150.8 (CN), 136.9, 134.9, 129.3, 127.0 (Ar), 65.0 (Pro-C α -H), 51.1 (Pro-NCH₂), 49.1 (C α -H), 35.0, 33.4, 31.1, 30.0, 29.6, 26.5, 26.1 (ring and chain CH₂).

Li-(pPF)₃: (S, S) *N*-(3-Dimethoxymethyl-benzoyl)-proline-phenylalanine carboxylic acid hydrazide dimer- lithium complex

IR (CDCl₃:MeOD / 98:2) ν = 1668 (br, C=Os) cm⁻¹; ¹H NMR (500 MHz (cryoprobe), CDCl₃:MeOD / 98:2) δ = 11.06 (3H, br, NHNC), 8.60 (3H, s, HCN), 8.01 (3H, br, NH), 7.98 (12H, m, Ar-H), 7.64 (6H, d, J = 6.0 Hz, Ar-H), 7.39-7.28 (9H, m, Ar-H), 5.27 (3H, dd, J_1 = 11.6 Hz, J_2 = 2.7 Hz, α -H), 4.06 (3H, dd, J_1 = 11.6 Hz, J_2 = 7.0 Hz, Pro- α -H), 3.72 (3H, br m, CH_aH_bPh), 3.64 (3H, br m, CH_aH_bPh), 3.33 (3H, br m, Pro-NCH_aH_b), 3.10 (3H, br m, Pro-NCH_aH_b), 1.82 (3H, br m, Pro-CH_aH_b), 1.11 (3H, br m, Pro-CH_cH_d), 0.92 (3H, br m, Pro-CH_aH_b), 0.49 (3H, br m, Pro-CH_cH_d); ¹³C NMR (125 MHz (cryoprobe), CDCl₃:MeOD / 98:2) δ = 171.4, 171.7, 171.1 (C=O), 152.8 (CN), 137.0, 136.3, 134.5, 130.3, 129.5, 128.6, 128.3, 126.7 (Ar), 64.3 (Pro-C α -H), 51.8 (C α -H), 51.2 (Pro-NCH₂), 34.8 (CH₂Ph), 29.5, 24.8 (CH₂).

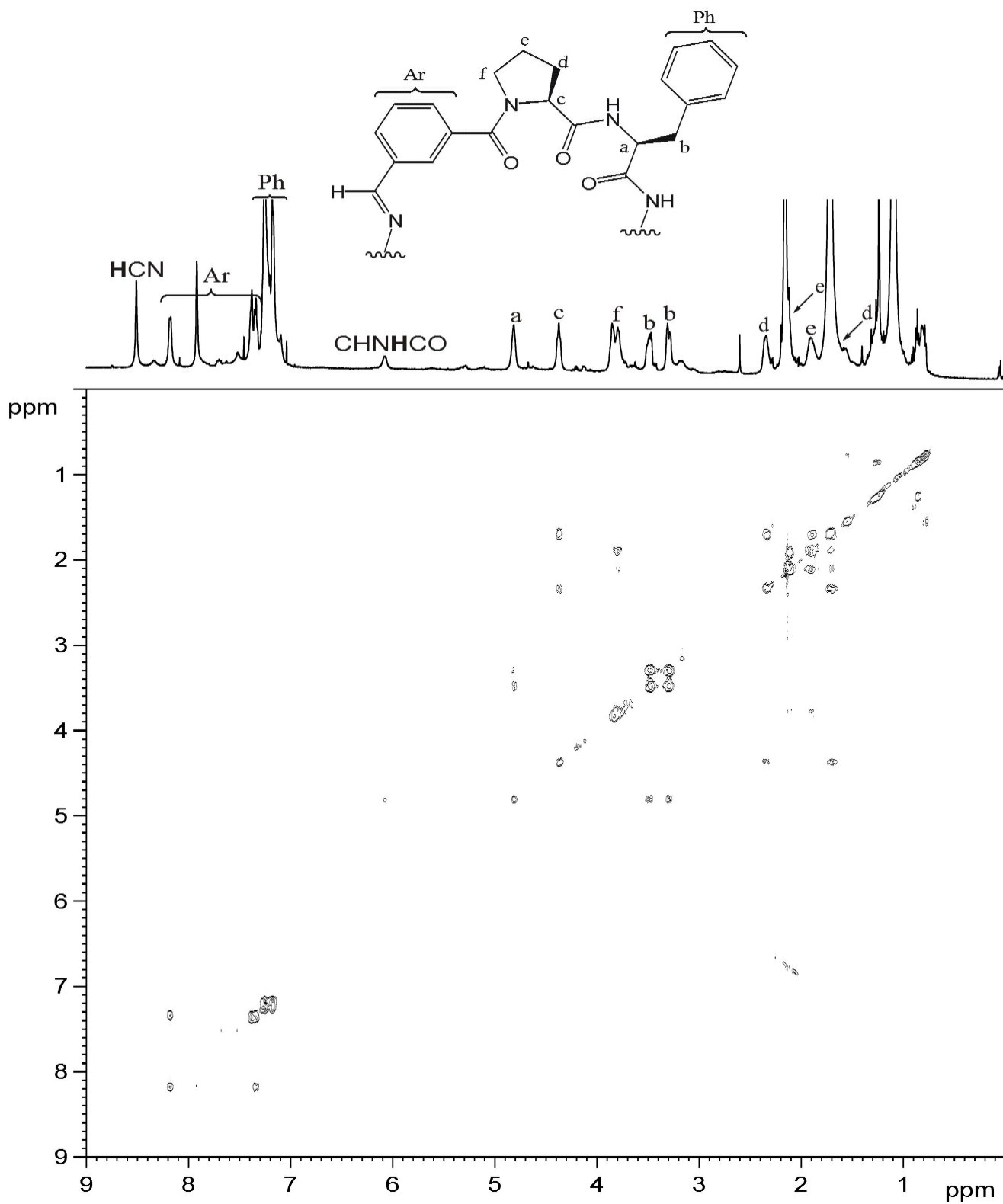


Fig. S1 COSY spectrum of $(mPF)_2$

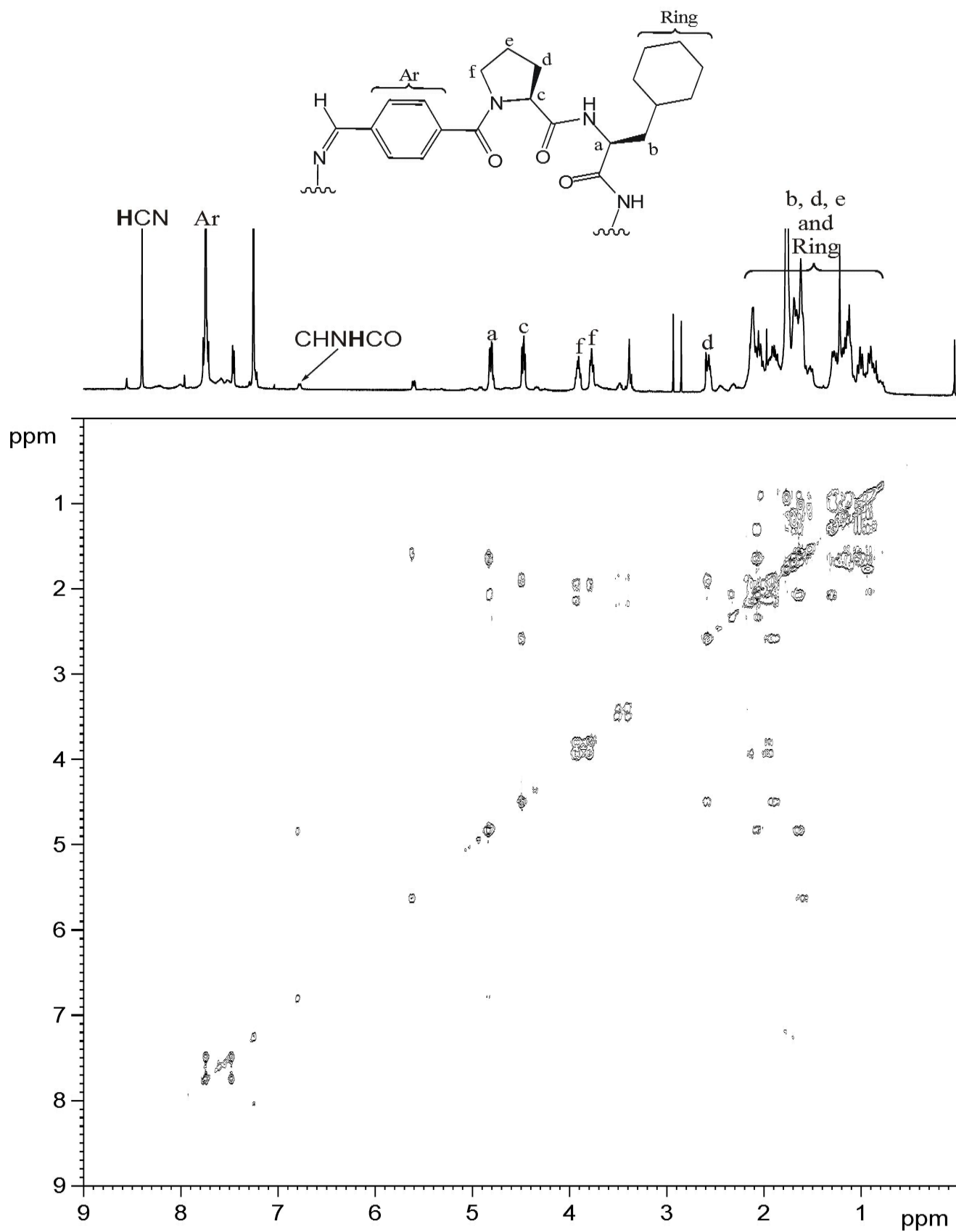


Fig. S2 COSY spectrum of (pPC)₃.

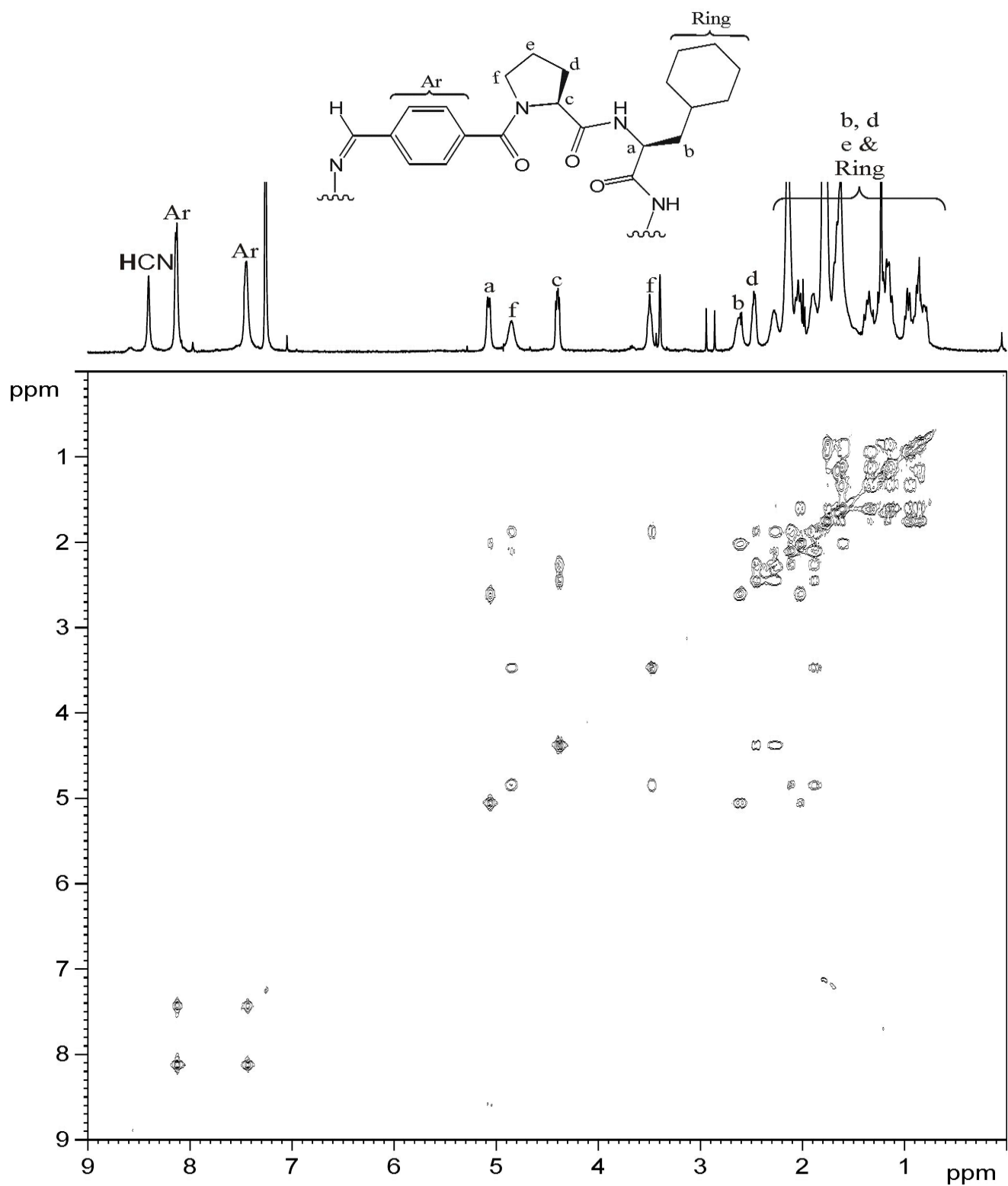


Fig. S3 COSY spectrum of $(\text{pPC})_3 \cdot \text{Li}^+$.