Supporting Information

Rapid and high sensitive detection of mercury ions using a fluorescence-based paper test strip with a *N*-alkylaminopyrazole ligand as receptor

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1. Characterization of complexes

Compound **1** (0.084 g, 81%). (Found C 55.52, H 5.37, N 9.09. $C_{21}H_{25}Cl_2N_3Zn$ (453.1) requires C 55.30, H 5.50, N 9.20 %). Conductivity ($\Omega^{-1}cm^2mol^{-1}$, 1.1 × 10^{-3} M in methanol) 37.2. IR ν_{max} (KBr)/cm^{-1} ν(C-H)$_{ar}$ 3062, ν(C-H)$_{al}$ 2978-2878, ν(C=C)$_{ph}$ 1608, [ν(C=C)$_{pz}$, ν(C=N)$_{pz}$] 1553, [δ(C=C)$_{ar}$, δ(C=N)$_{ar}$] 1471, 1454, δ(C-H)$_{ip}$ 1020, δ(C-H)$_{oop\ ph}$ 764, δ(C-H)$_{oop\ pz}$ 696. ν_{max} (polyethylene)/ cm^{-1} ν(Zn-N) 556, ν(Zn-Cl) 322. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 7.86 (d, 2H, ^3J = 7.2 Hz, $H_{ortho\text{-}3\text{-}ph}$), 7.50 (m, 8H, H_{ph}), 6.61 (s, 1H, C$H_{(pz)}$), 4.57 (ddd, 2H, $N_{pz}CH_2CH_2N$), 3.36 (ddd, 2H, $N(CH_2CH_3)_2$), 3.10 (m, 2H, $N_{pz}CH_2CH_2N$), 2.87 (ddd, 2H, $N(CH_2CH_3)_2$), 1.21 (t, 6H, ^3J = 7.2 Hz, $N(CH_2CH_3)_2$).*^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K) δ 155.2-128.3 (C_{pz}, C_{ph}), 106.8 ($CH_{(pz)}$), 55.8 ($N(CH_2CH_3)_2$), 48.9 ($N_{pz}CH_2CH_2N$), 44.8 ($N_{pz}CH_2CH_2N$), 9.3 ($N(CH_2CH_3)_2$). Fluorescence: (2.0 x 10^{-5} M in HCl), λ_{exc} 254 nm; λ_{em} 359 nm (1911 rfu). *m/z* (ESI+): 478.1 (100%, $[ZnCl_2(\mathbf{L1}) + Na]^+$), 418.1 (87%, $[ZnCl(\mathbf{L1})]^+$).

* Study of the $N_{pz}CH_2CH_2N_{am}$ fragment of compound **1** as an AA'XX' system gave a set of coupling constants gathered in Table SI1. In the same way, $N_{am}(CH_2)_2$ terminal chains were also treated and the coupling constants obtained are gathered in Table SI1. These constants are consistent with the simulated spectra for compound **1** obtained with the aid of *g* NMR program.[1] Figure SI1 shows the experimentally determined and simulated spectra for compound **1**.

Compound **2** (0.090 g, 63%). (Found C 63.38, H 8.09, N 6.56. $C_{33}H_{49}Cl_2N_3Zn$ (621.3) requires C 63.50, H 7.90, N 6.70 %). Conductivity ($\Omega^{-1}cm^2mol^{-1}$, 9.9 × 10^{-4} M in methanol) 37.3. IR ν_{max} (KBr)/cm^{-1} ν(C-H)$_{ar}$ 3051, ν(C-H)$_{al}$ 2955-2776, ν(C=C)$_{ph}$ 1602,

[ν(C=C)$_{pz}$, ν(C=N)$_{pz}$] 1571, 1551, [δ(C=C)$_{ar}$, δ(C=N)$_{ar}$] 1463, δ(C-H)$_{ip}$ 1072, δ(C-H)$_{oop\ ph}$ 759, δ(C-H)$_{oop\ pz}$ 691. ν_{max} (polyethylene)/ cm^{-1} ν(Zn-N) 586, ν(Zn-Cl) 323. ^{1}H NMR (250 MHz, $CDCl_3$, 298 K) δ 7.84 (d, 2H, ^{3}J = 7.2 Hz, $H_{ortho\text{-}3\text{-}ph}$), 7.49 (m, 8H, H_{ph}), 6.61 (s, 1H, C$H_{(pz)}$), 4.55 (m, 2H, $N_{pz}CH_2CH_2N$), 3.20 (m, 2H, $N(CH_2(CH_2)_6CH_3)_2$), 3.10 (m, 2H, $N_{pz}CH_2CH_2N$), 2.72 (m, 2H, $N(CH_2(CH_2)_6CH_3)_2$), 1.68 (br, 2H, $N(CH_2CH_2(CH_2)_5CH_3)_2$), 1.51 (br, 2H, $N(CH_2CH_2(CH_2)_5CH_3)_2$), 1.26 (br, 20H, $N(CH_2CH_2(CH_2)_5CH_3)_2$), 0.88 (t, 6H, ^{3}J = 7.4 Hz, $N((CH_2)_7CH_3)_2$). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K) δ 169.9-126.1 (C_{pz}, C_{ph}), 106.2 (C$H_{(pz)}$), 51.7 ($N(CH_2(CH_2)_6CH_3)_2$), 50.4 ($N_{pz}CH_2CH_2N$), 47.5 ($N_{pz}CH_2CH_2N$), 32.3-23.0 ($N(CH_2(CH_2)_6CH_3)_2$), 14.3 ($N(CH_2(CH_2)_6CH_3)_2$). Fluorescence: (2.0 x 10^{-5} M in HCl), λ_{exc} 254 nm; λ_{em} 354 nm (277 rfu). *m/z* (ESI+): 586.3 (100%, [ZnCl(**L2**)]$^{+}$).

Compound **3** (0.039 g, 34%). (Found C 49.82, H 4.87, N 8.19. $C_{21}H_{25}Cl_2N_3Cd$ (503.1) requires C 50.02, H 5.00, N 8.40 %). Conductivity (Ω^{-1}cm^{2}mol^{-1}, 1.2 × 10^{-3} M in methanol) 63.7.IR ν_{max} (KBr)/cm^{-1} ν(C-H)$_{ar}$ 3035, ν(C-H)$_{al}$ 2974-2848, ν(C=C)$_{ph}$ 1601, [ν(C=C)$_{pz}$, ν(C=N)$_{pz}$] 1553, 1480, [δ(C=C)$_{ar}$, δ(C=N)$_{ar}$] 1464, δ(C-H)$_{ip}$ 1026, δ(C-H)$_{oop\ ph}$ 764, δ(C-H)$_{oop\ pz}$ 697. ν_{max} (polyethylene)/ cm^{-1} ν(Cd-N) 517, ν(Cd-Cl) 226. ^{1}H NMR (250 MHz, DMSO, 298 K) δ 7.84 (d, 2H, ^{3}J = 7.2 Hz, $H_{ortho\text{-}3\text{-}ph}$), 7.45 (m, 8H, H_{ph}), 6.82 (s, 1H, C$H_{(pz)}$), 4.19 (br, 2H, $N_{pz}CH_2CH_2N$), 2.85 (br, 2H, $N_{pz}CH_2CH_2N$), 2.42 (br, 4H, $N(CH_2CH_3)_2$), 0.82 (t, 6H, ^{3}J = 7.4 hZ, $N(CH_2CH_3)_2$). ^{13}C{^{1}H} NMR (63 MHz, $CDCl_3$, 298 K) δ 149.4-125.1 (C_{pz}, C_{ph}), 103.2 (C$H_{(pz)}$), 52.1 ($N(CH_2CH_3)_2$), 46.9, 46.7 ($N_{pz}CH_2CH_2N$), 11.5 ($N(CH_2CH_3)_2$). ^{113}Cd{^{1}H} NMR (80 MHz, DMSO, 298 K) δ +387 (s). Fluorescence: (2.0 x 10^{-5} M in HCl), λ_{exc} 254 nm; λ_{em} 359 nm (2493 rfu). *m/z* (ESI+): 468.1 (100%, [CdCl(**L1**)]$^{+}$).

Compound **4** (0.074 g, 48%). (Found C 58.88, H 7.23, N 6.16. $C_{33}H_{49}Cl_2N_3Cd$ (671.2) requires C 59.10, H 7.40, N 6.30 %). Conductivity (Ω^{-1}cm^{2}mol^{-1}, 1.1 × 10^{-3} M in methanol) 62.1. IR ν_{max} (KBr)/cm^{-1} ν(C-H)$_{ar}$ 3062, ν(C-H)$_{al}$ 2959-2854, ν(C=C)$_{ph}$ 1617, [ν(C=C)$_{pz}$, ν(C=N)$_{pz}$] 1579, 1480, [δ(C=C)$_{ar}$, δ(C=N)$_{ar}$] 1464, δ(C-H)$_{ip}$ 1026, δ(C-H)$_{oop\ ph}$ 762, δ(C-H)$_{oop\ pz}$ 694. ν_{max} (polyethylene)/ cm^{-1} ν(Cd-N) 505, ν(Cd-Cl) 202. ^{1}H NMR (250 MHz, DMSO, 298 K) δ 7.83 (d, 2H, ^{3}J = 7.2 Hz, $H_{ortho\text{-}3\text{-}ph}$), 7.49 (m, 8H, H_{ph}), 6.79 (s, 1H, C$H_{(pz)}$), 4.16 (br, 2H, $N_{pz}CH_2CH_2N$), 2.75 (br, 2H, $N_{pz}CH_2CH_2N$), 2.20 (br, 4H, $N(CH_2(CH_2)_6CH_3)_2$), 1.13 (br, 24H, $N(CH_2(CH_2)_6CH_3)_2$), 0.83 (t, 6H, ^{3}J = 7.4 Hz, $N((CH_2)_7CH_3)_2$). ^{13}C{^{1}H} NMR (63 MHz, DMSO, 298 K) δ 150.4-125.4 (C_{pz}, C_{ph}),

103.4 ($CH_{(pz)}$), 54.3 ($N(CH_2(CH_2)_6CH_3)_2$), 54.0 ($N_{pz}CH_2CH_2N$), 53.8 ($N_{pz}CH_2CH_2N$), 31.6-22.5 ($N(CH_2(CH_2)_6CH_3)_2$), 14.3 ($N(CH_2)_7CH_3)_2$). $^{113}Cd\{^1H\}$ NMR (80 MHz, DMSO, 298 K) δ +446 (s). Fluorescence: (2.0 x 10^{-5} M in HCl), λ_{exc} 254 nm; λ_{em} 354 nm (311 rfu). *m/z* (ESI+): 636.2 (100%, $[CdCl(\mathbf{L2})]^+$).

Compound **5** (0.096 g, 71%). (Found C 42.92, H 4.48, N 6.89. $C_{21}H_{25}Cl_2N_3Hg$ (590.9) requires C 42.70, H 4.30, N 7.10 %). Conductivity ($\Omega^{-1}cm^2mol^{-1}$, 1.1 × 10^{-3} M in methanol) 55.3.IR ν_{max} (KBr)/cm^{-1} $\nu(C\text{-}H)_{ar}$ 3040, $\nu(C\text{-}H)_{al}$ 2973-2856, $\nu(C{=}C)_{ph}$ 1603, [$\nu(C{=}C)_{pz}$, $\nu(C{=}N)_{pz}$] 1549, 1481, [$\delta(C{=}C)_{ar}$, $\delta(C{=}N)_{ar}$] 1463, $\delta(C\text{-}H)_{ip}$ 1026, $\delta(C\text{-}H)_{oop\ ph}$ 763, $\delta(C\text{-}H)_{oop\ pz}$ 696. ν_{max} (polyethylene)/ cm^{-1} $\nu(Hg\text{-}N)$ 517, $\nu(Hg\text{-}Cl)$ 223. ^1H NMR (250 MHz, $CDCl_3$, 298 K) δ 7.77 (d, 2H, ^3J = 7.2 Hz, $H_{ortho\text{-}3\text{-}ph}$), 7.49 (m, 8H, H_{ph}), 6.63 (s, 1H, $CH_{(pz)}$), 4.72 (br, 2H, $N_{pz}CH_2CH_2N$), 3.79 (br, 2H, $N_{pz}CH_2CH_2N$), 3.34 (br, 4H, $N(CH_2CH_3)_2$), 1.35 (t, 6H, ^3J = 7.4 Hz, $N(CH_2CH_3)_2$). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 298 K) δ 151.5-125.5 (C_{pz}, C_{ph}), 104.0 ($CH_{(pz)}$), 51.6 ($N(CH_2CH_3)_2$), 48.0 ($N_{pz}CH_2CH_2N$), 43.6 ($N_{pz}CH_2CH_2N$), 9.4 ($N(CH_2CH_3)_2$). Fluorescence: (2.0 x 10^{-5} M in HCl), λ_{exc} 254 nm; λ_{em} 359 nm (1123 rfu). *m/z* (ESI+): 320.2 (100%, $[\mathbf{L1}]^+$).

Compound **6** (0.145 g, 79%). (Found C 52.49, H 6.72, N 5.45. $C_{33}H_{49}Cl_2N_3Hg$ (759.3) requires C 52.20, H 6.50, N 5.53 %). Conductivity ($\Omega^{-1}cm^2mol^{-1}$, 1.2 × 10^{-3} M in methanol) 72.5. IR ν_{max} (KBr)/cm^{-1} $\nu(C\text{-}H)_{ar}$ 3011, $\nu(C\text{-}H)_{al}$ 2918-2849, $\nu(C{=}C)_{ph}$ 1604, [$\nu(C{=}C)_{pz}$, $\nu(C{=}N)_{pz}$] 1546, 1483, [$\delta(C{=}C)_{ar}$, $\delta(C{=}N)_{ar}$] 1462, 1432, $\delta(C\text{-}H)_{ip}$ 1019, $\delta(C\text{-}H)_{oop\ ph}$ 761, $\delta(C\text{-}H)_{oop\ pz}$ 693. ν_{max} (polyethylene)/ cm^{-1} $\nu(Hg\text{-}N)$ 565, $\nu(Hg\text{-}Cl)$ 221. ^1H NMR (250 MHz, $CDCl_3$, 298 K) δ 7.77 (d, 2H, ^3J = 7.2 Hz, $H_{ortho\text{-}3\text{-}ph}$), 7.47 (m, 8H, H_{ph}), 6.65 (s, 1H, $CH_{(pz)}$), 4.66 (br, 2H, $N_{pz}CH_2CH_2N$), 3.70 (br, 2H, $N_{pz}CH_2CH_2N$), 3.06 (br, 4H, $N(CH_2(CH_2)_6CH_3)_2$), 1.67 (m, 4H, $N(CH_2CH_2(CH_2)_5CH_3)_2$), 1.21 (br, 20H, $N(CH_2CH_2(CH_2)_5CH_3)_2$), 0.87 (t, 6H, ^3J = 7.4 Hz, $N((CH_2)_7CH_3)_2$). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, 298 K) δ 151.1-126.1 (C_{pz}, C_{ph}), 104.7 ($CH_{(pz)}$), 60.3 ($N(CH_2(CH_2)_6CH_3)_2$), 56.9 ($N_{pz}CH_2CH_2N$), 53.8 ($N_{pz}CH_2CH_2N$), 47.9-22.7 ($N(CH_2(CH_2)_6CH_3)_2$), 14.8 ($N(CH_2(CH_2)_6CH_3)_2$). Fluorescence: (2.0 x 10^{-5} M in HCl), λ_{exc} 254 nm; λ_{em} 354 nm (61 rfu). *m/z* (ESI+): 488.4 (100%, $[\mathbf{L2}]^+$).

2. Tables

Table SI1.

$\delta(CH_2)(16)$	4.57	$\delta(CH_2)(18a,20a)$	3.36
$\delta(CH_2)(17)$	3.10	$\delta(CH_2)(18b,20b)$	2.87
$^2J(16a,16b)$	13.8	$\delta(CH_3)(19,21)$	1.21
$^2J(17a,17b)$	13.8	$^2J(18a,18b) = {}^2J(20a,20b)$	13.2
$^3J(16a,17a) = {}^3J(17b,16b)$	8.0	$^3J(18,19) = {}^3J(20,21)$	7.2
$^3J(16a,17b) = {}^3J(17a,16b)$	1.2		

Table SI2. Crystallographic data for $[ZnCl_2(\mathbf{L1})]$.

	1
Formula	$C_{21}\ H_{25}\ Cl_2\ N_3\ Zn$
M	455.71
Temperature [K]	293(2)
Crystal System	Triclinic
Space group	*P* (-1)
Unit cell dimensions	
a (Å)	11.725(9)
b (Å)	13.240(8)
c (Å)	14.250(7)
Z	4
U (Å^3)	2140(2)
D_{calc} [g cm^{-3}]	1.414
μ [mm^{-1}]	1.408
F(000)	944
Crystal size (mm)	0.16 x 0.14 x 0.14
θ range [º]	2.64 to 32.48
Index range	$-17 \le h \le 17$, $-18 \le k \le 19$, $-21 \le l \le 18$
Reflections collected/unique	27147 / 13855 [*R*(int) = 0.1460]
Completeness to θ [%]	93.9
Absorption correction	Empirical
Data/restraints/parameters	13855 / 8 / 487
Goodness-of-fit	0.997
Final R_1, ωR_2	0.0770, 0.1412
R_1 (all data), ωR_2	0.2133, 0.1716
Residual electron density [eÅ^{-3}]	0.597 and -0.317

Table SI3. Selected bond lengths (Å) and bond angles (º) for [$ZnCl_2$(**L1**)]

Molecule A		**Molecule B**	
Zn(1A)-N(1A)	2.052(4)	Zn(2B)-N(1B)	2.059(4)
Zn(1A)-N(3A)	2.111(4)	Zn(2B)-N(3B)	2.101(4)
Zn(1A)-Cl(1A)	2.2492(17)	Zn(2B)-Cl(1B)	2.2277(19)
Zn(1A)-Cl(2A)	2.2216(19)	Zn(2B)-Cl(2B)	2.229(2)
N(1A)-Zn(1A)-N(3A)	96.90(16)	N(1B)-Zn(2B)-N(3B)	98.42(15)
N(1A)-Zn(1A)-Cl(1A)	115.90(12)	N(1B)-Zn(2B)-Cl(1B)	117.28(11)
N(1A)-Zn(1A)-Cl(2A)	111.49(12)	N(1B)-Zn(2B)-Cl(2B)	104.73(13)
N(3A)-Zn(1A)-Cl(1A)	107.04(11)	N(3B)-Zn(2B)-Cl(1B)	108.18(12)
N(3A)-Zn(1A)-Cl(2A)	110.27(12)	N(3B)-Zn(2B)-Cl(2B)	109.33(12)
Cl(1A)-Zn(1A)-Cl(2A)	113.74(7)	Cl(1B)-Zn(2B)-Cl(2B)	117.17(7)

3. Figures.

Figure SI1. Experimental and simulated ^{1}H NMR spectra for complex **1**.

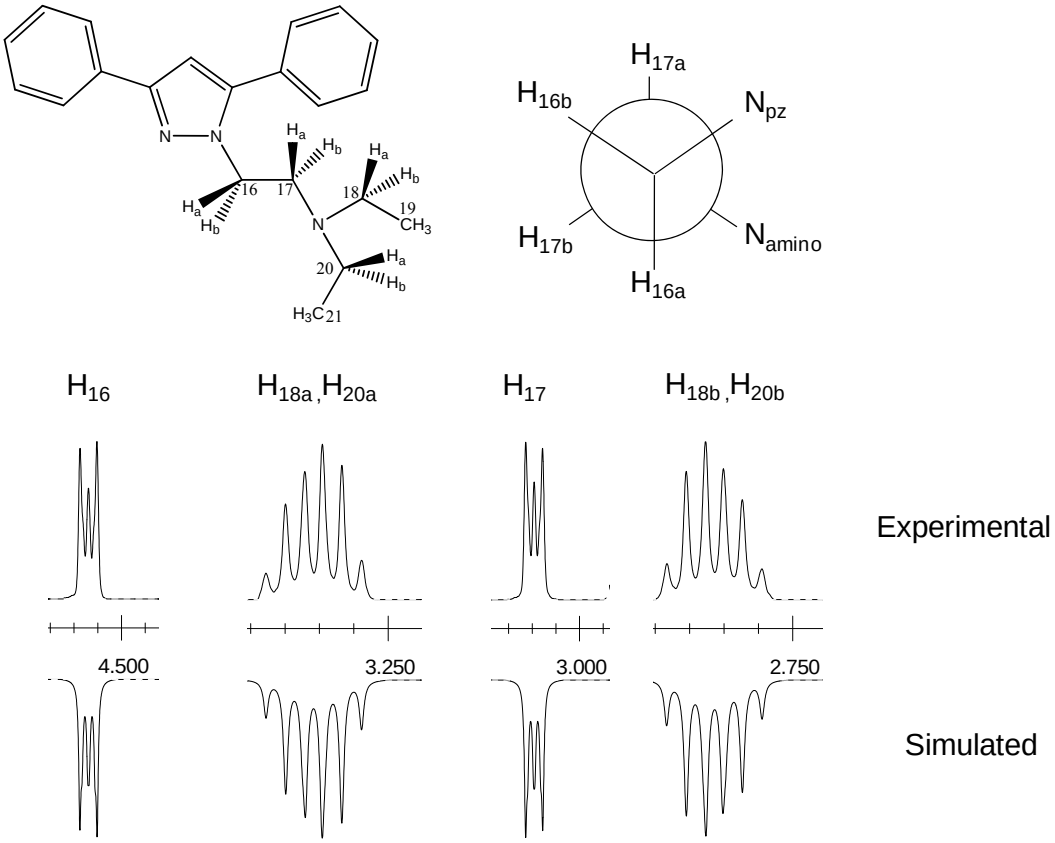
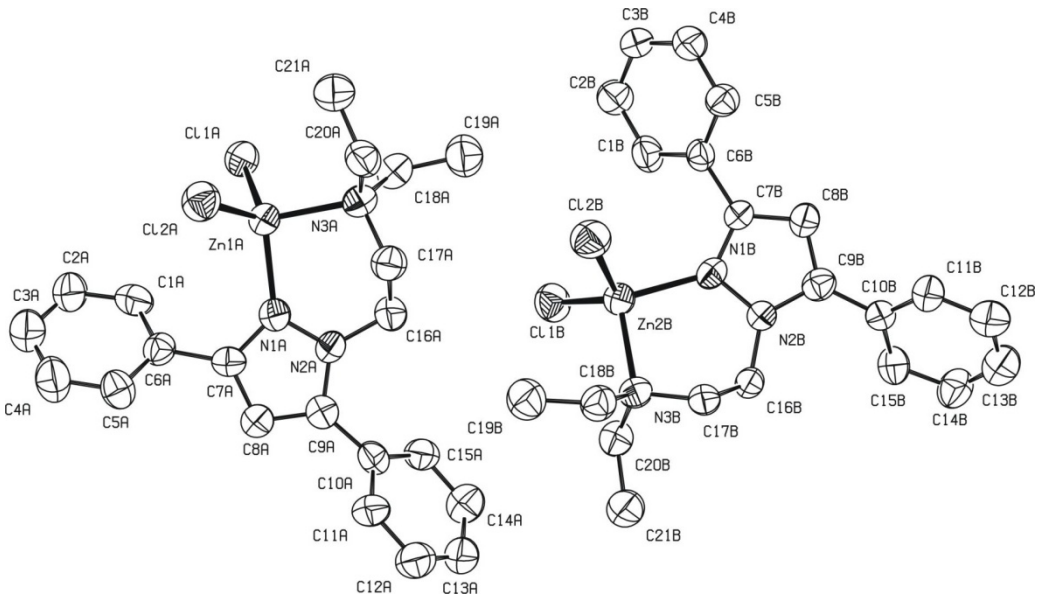


Figure SI2. ORTEP drawing of complex **1**, showing all non-hydrogens atoms and the atom numbering scheme; 50% probability amplitude displacement ellipsoids are shown.



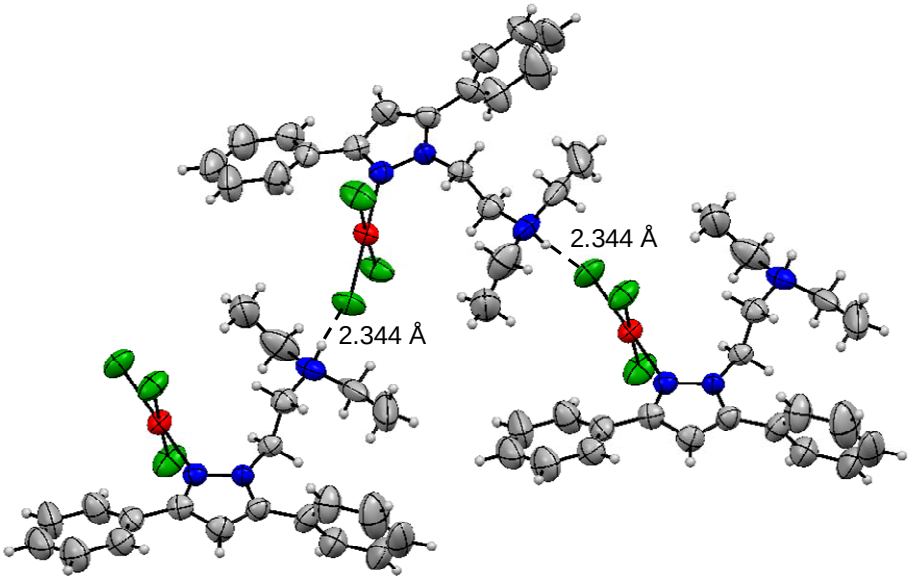
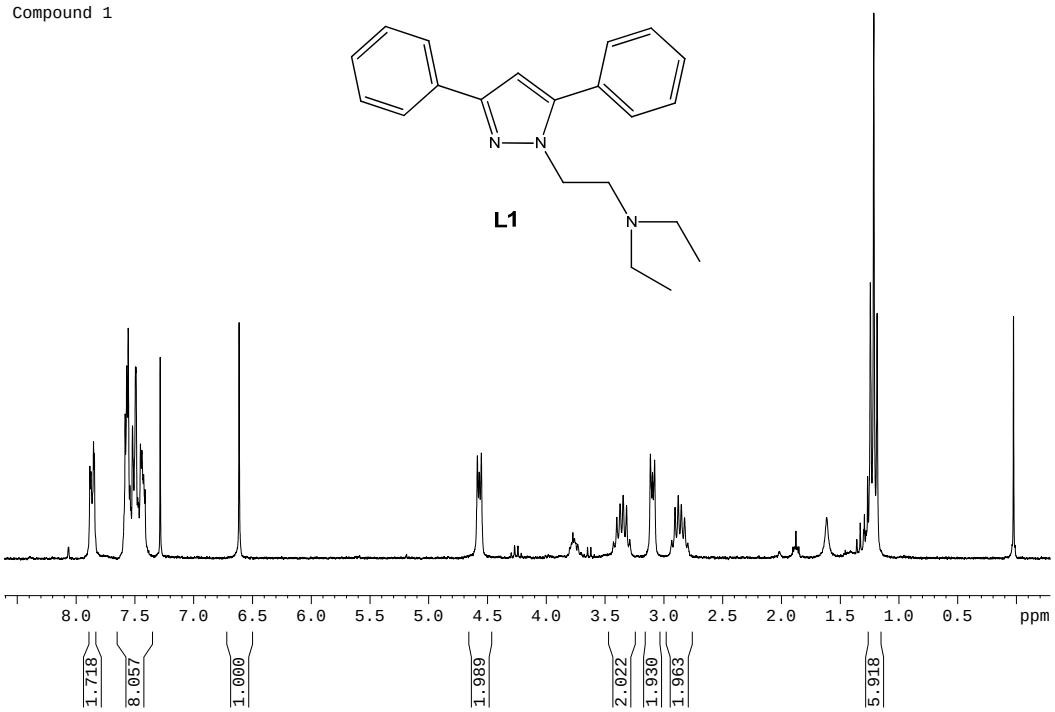


Figure SI3. Hydrogen bond interactions in [Pd(**L1**)]Cl_3 complex.

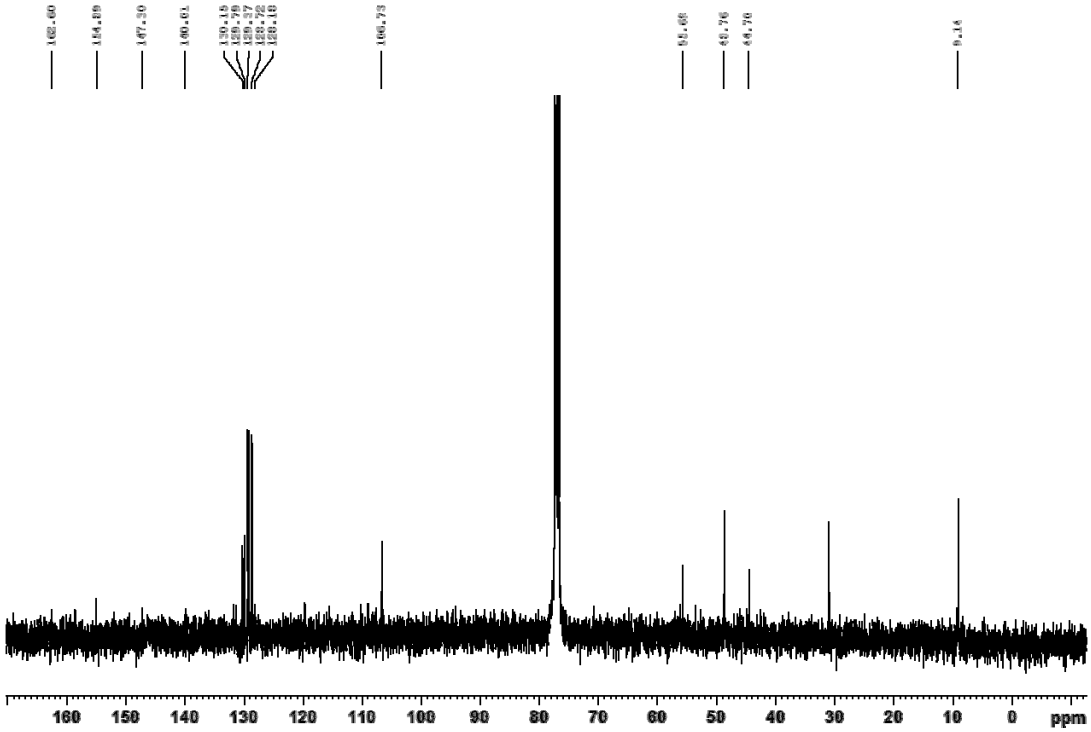
Spectra of the compounds

Compound 1 Characterization ([$ZnL1Cl_2$])

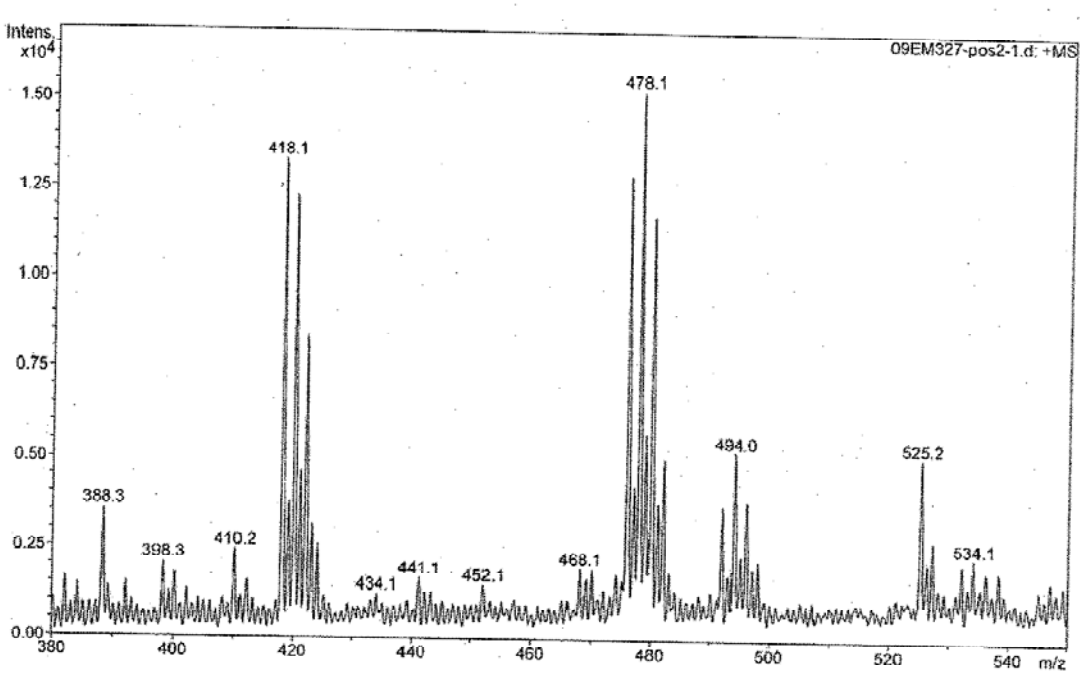
^{1}H NMR spectrum



^{13}C {^{1}H} NMR spectrum

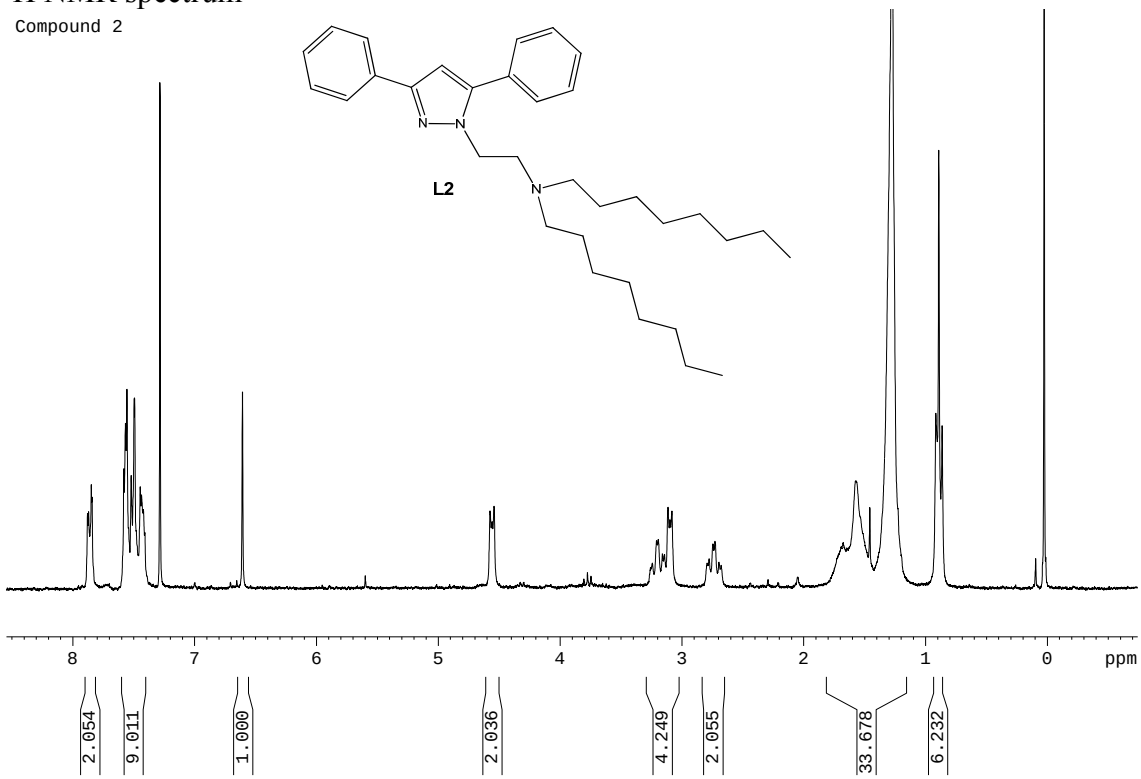


Mass spectrometry

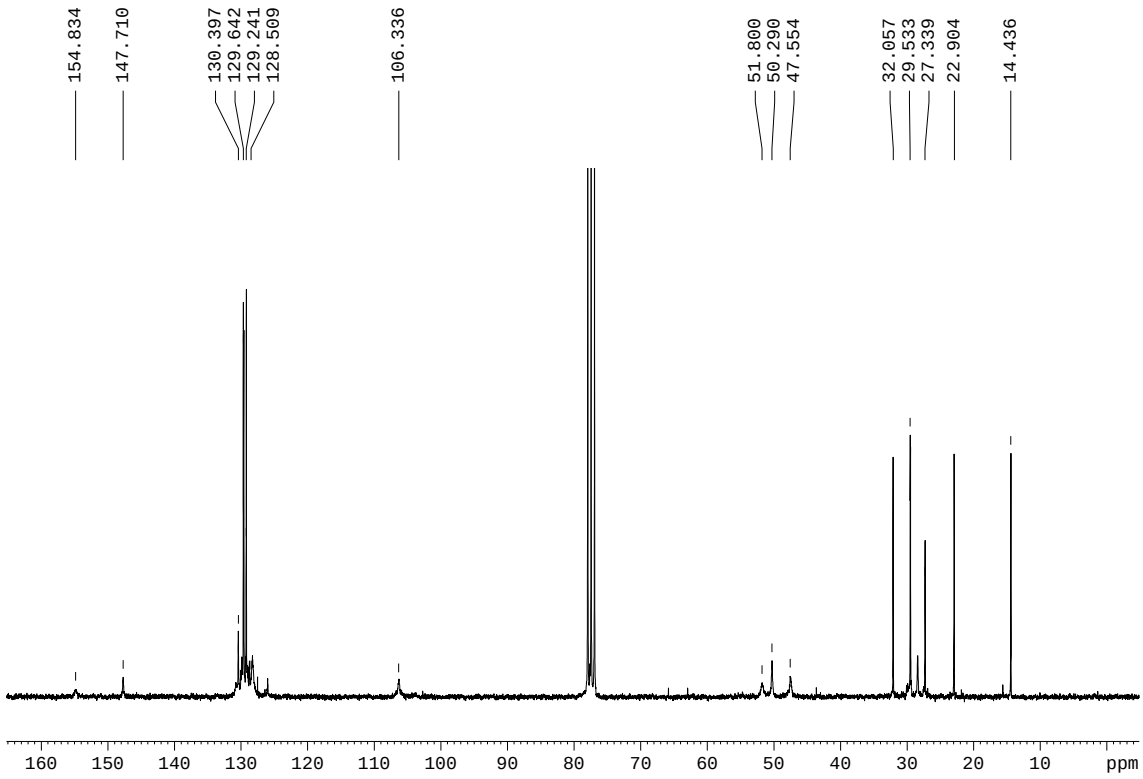


Compound 2 Characterization ([ZnL2Cl$_2$])

^{1}H NMR spectrum



^{13}C {^{1}H} NMR spectrum



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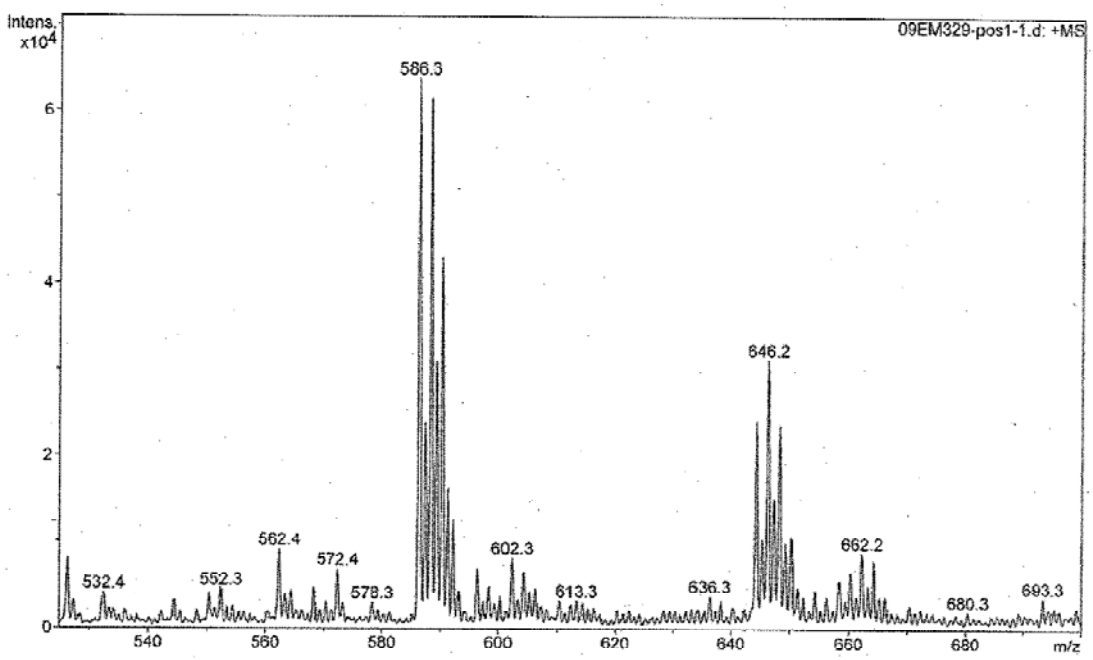
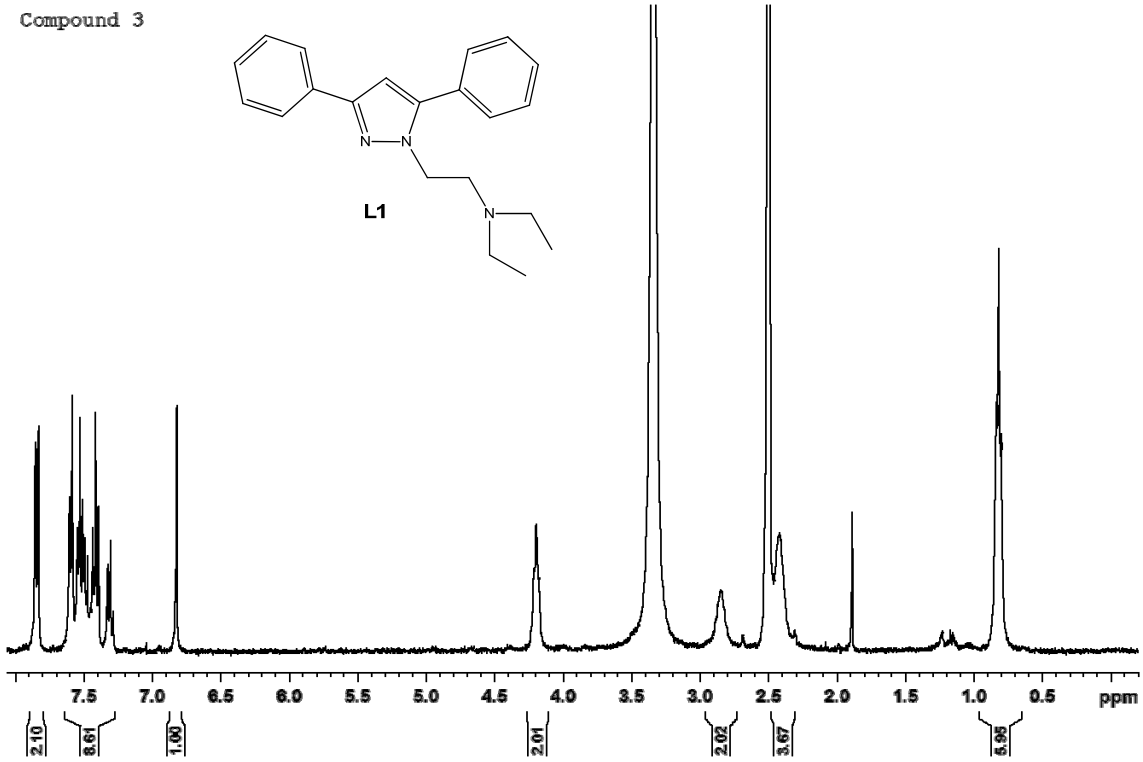
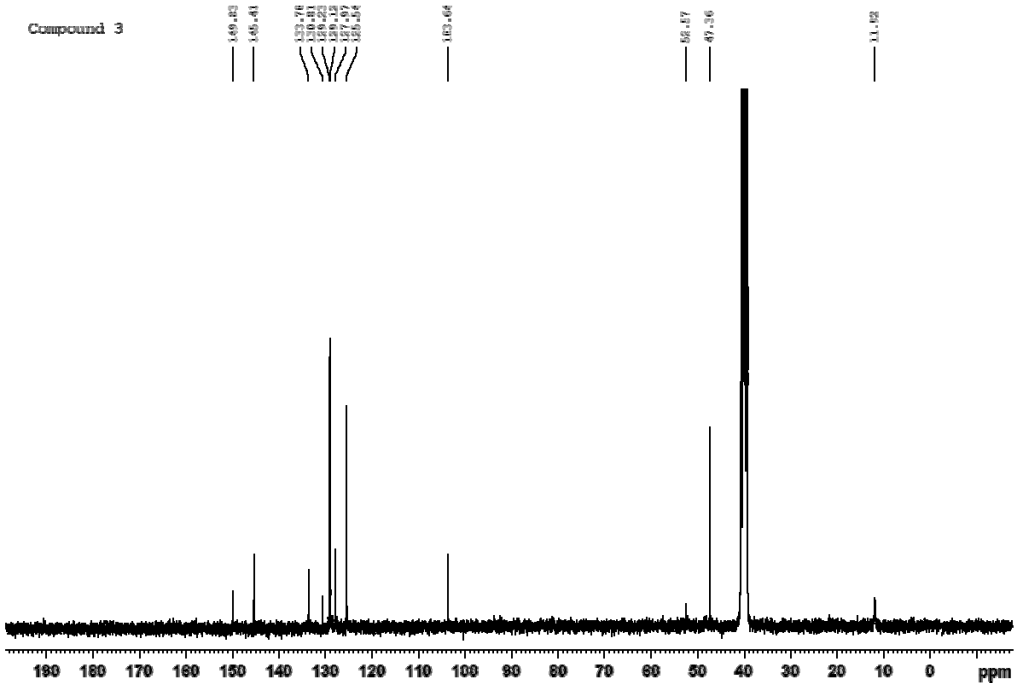


Compound 3 Characterization ([$CdL1Cl_2$])

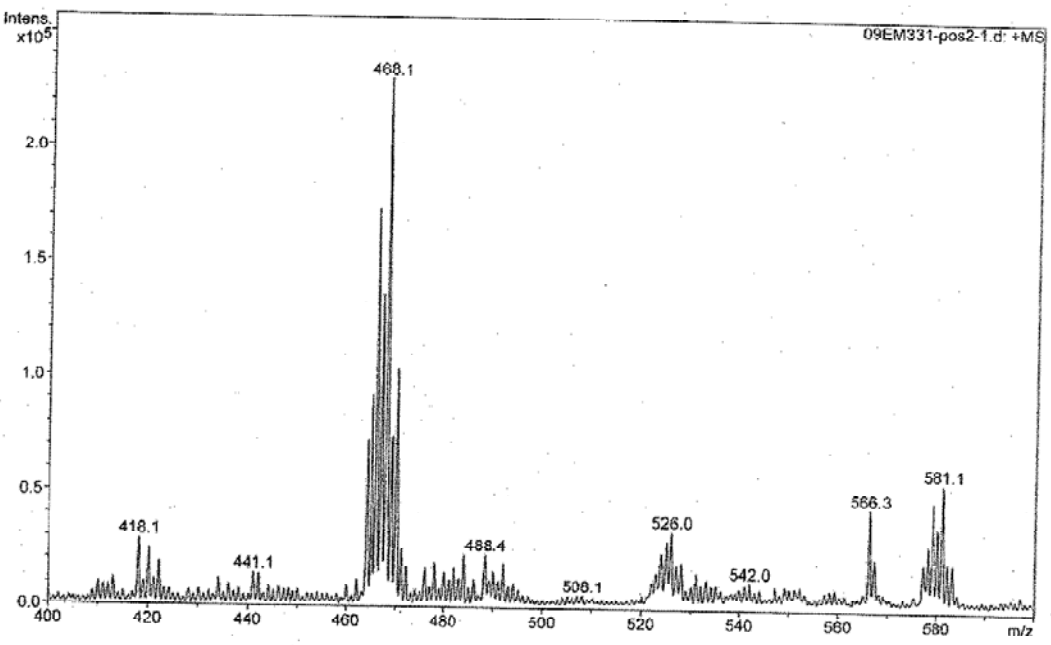
^{1}H NMR spectrum



^{13}C {^{1}H} NMR spectrum

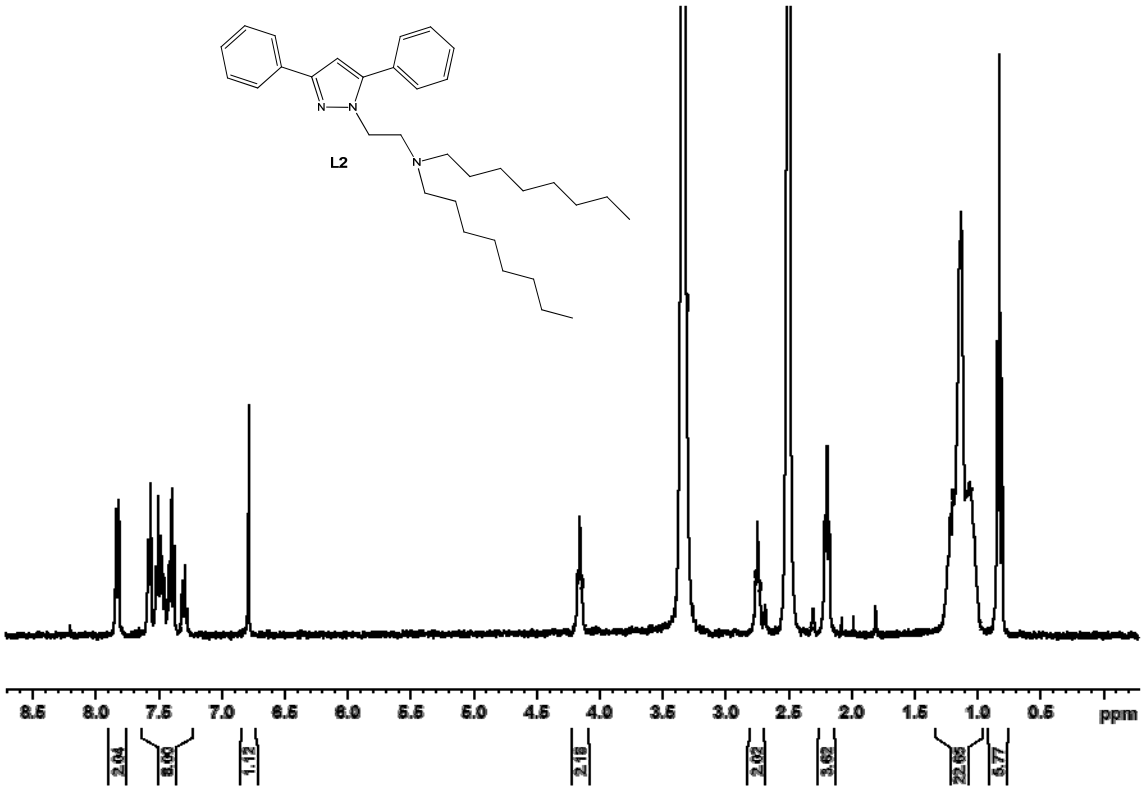


Mass spectrometry

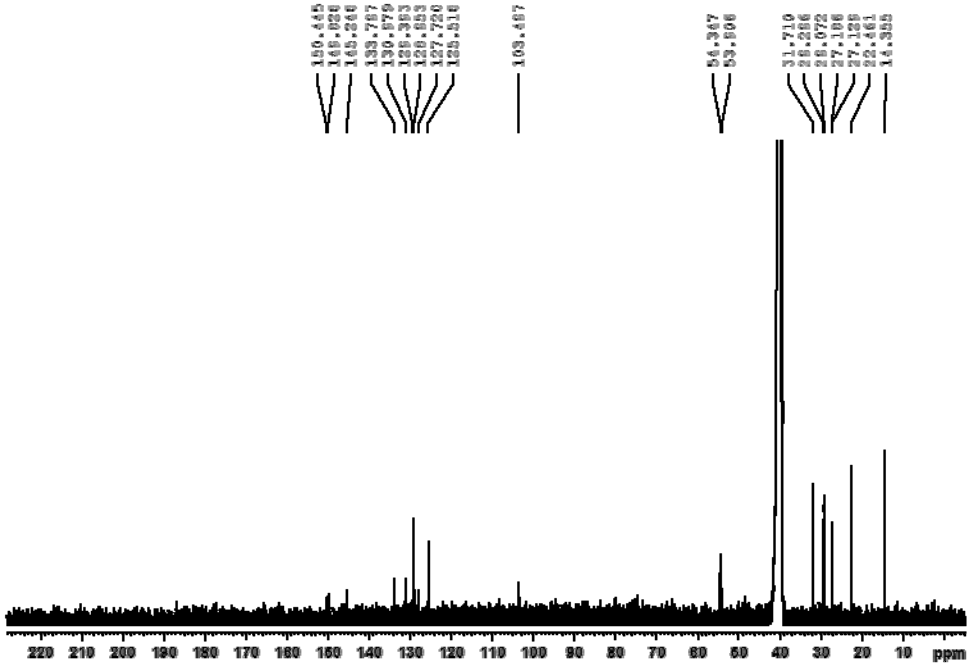


Compound 4 Characterization ([$CdL2Cl_2$])

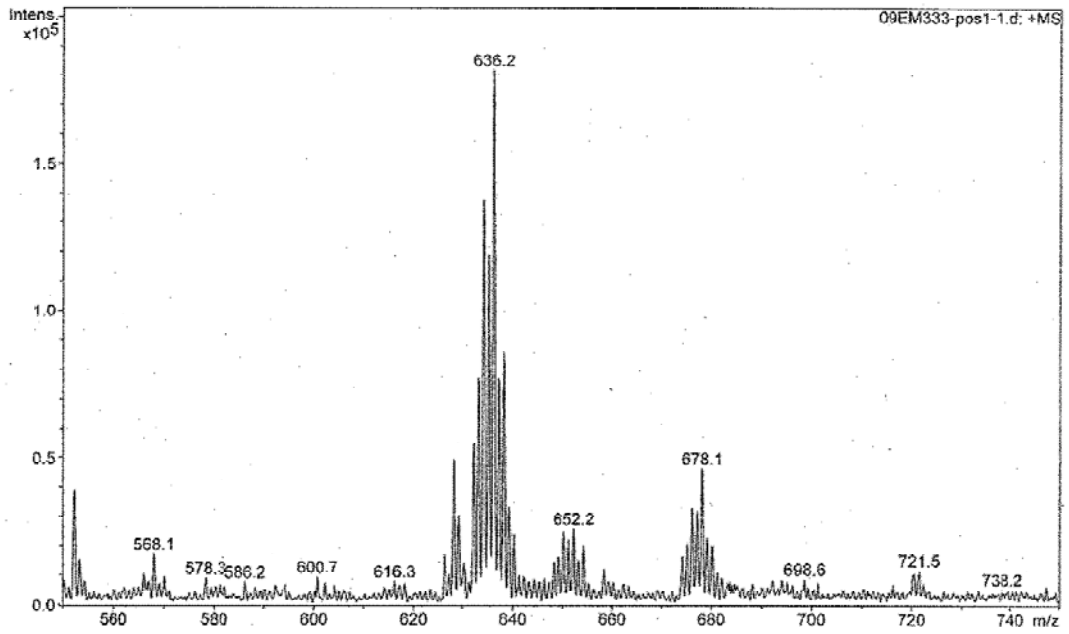
^{1}H NMR spectrum



^{13}C {^{1}H} NMR spectrum

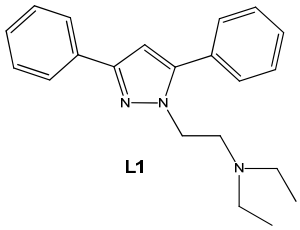


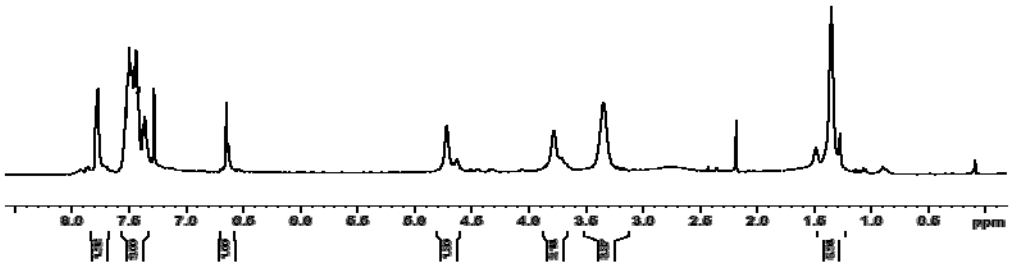
Mass spectrometry



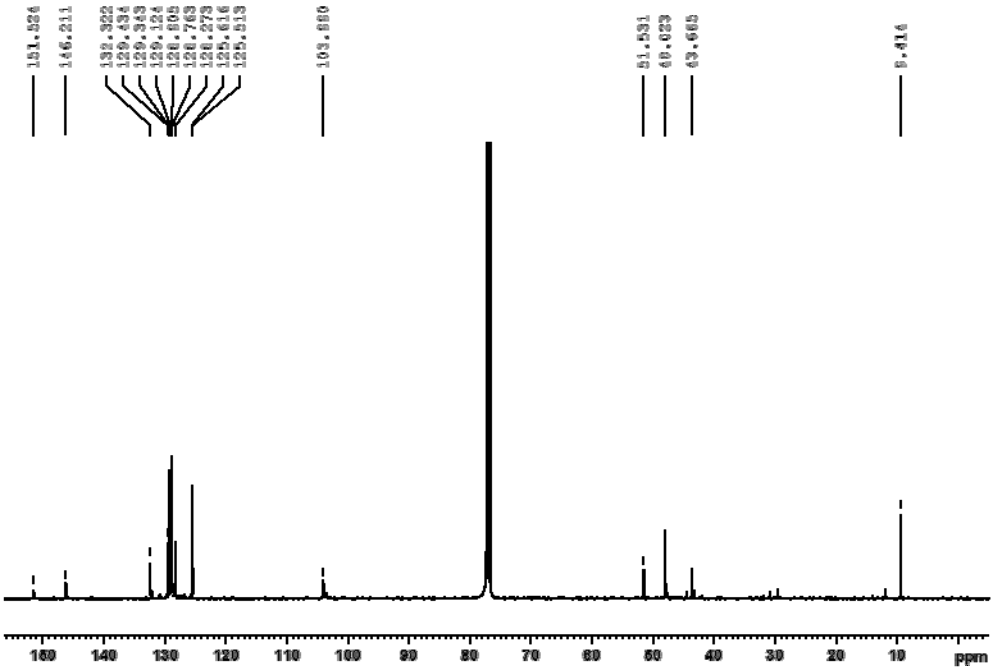
Compound 5 Characterization ([$HgL1Cl_2$])

^{1}H NMR spectrum

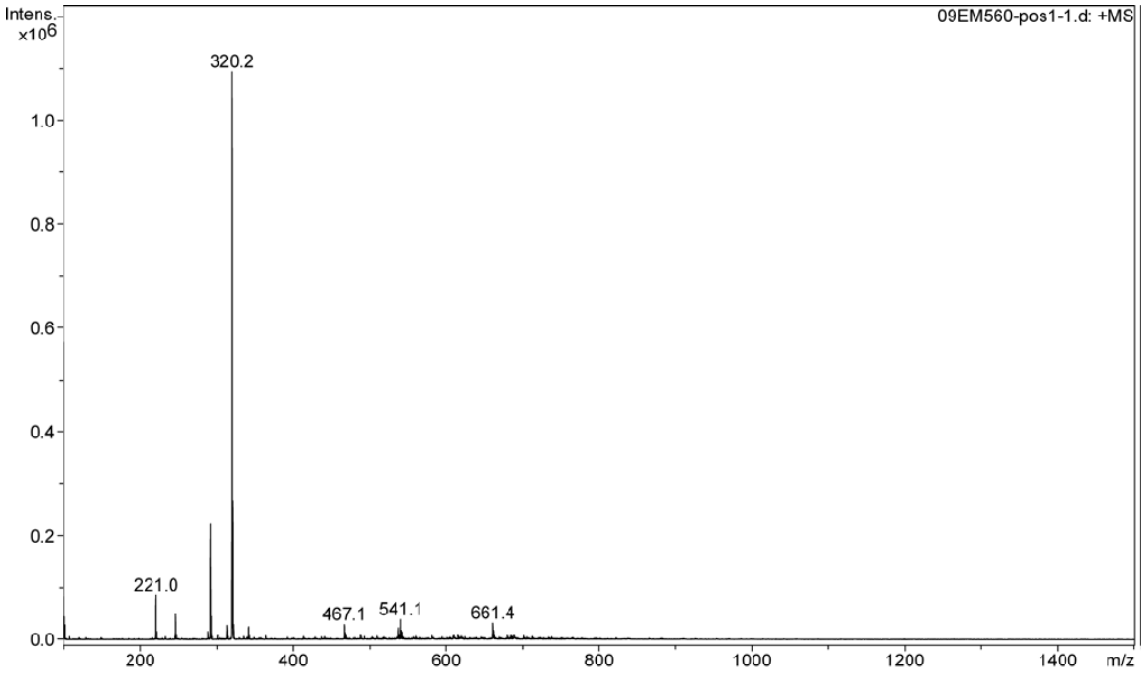




^{13}C {^{1}H} NMR spectrum

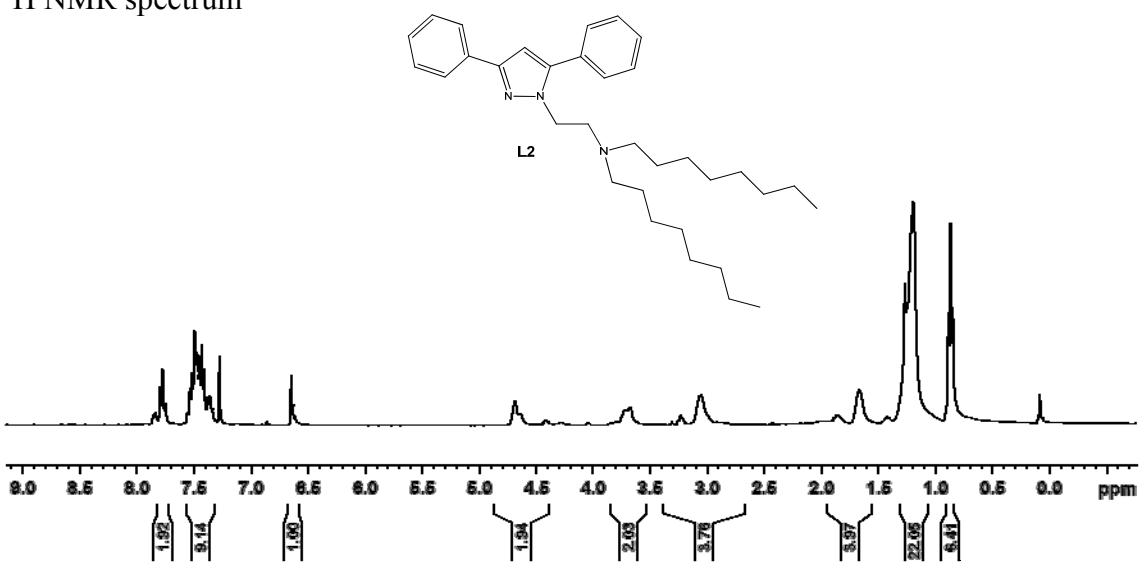


Mass spectrometry

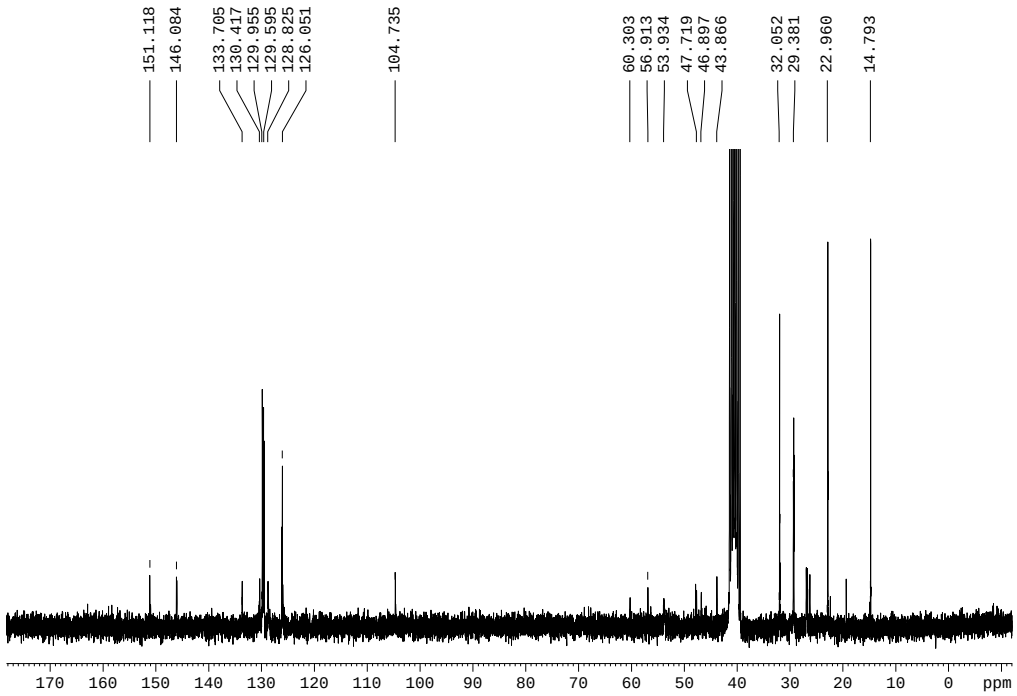


Compound 6 Characterization ([$HgL2Cl_2$])

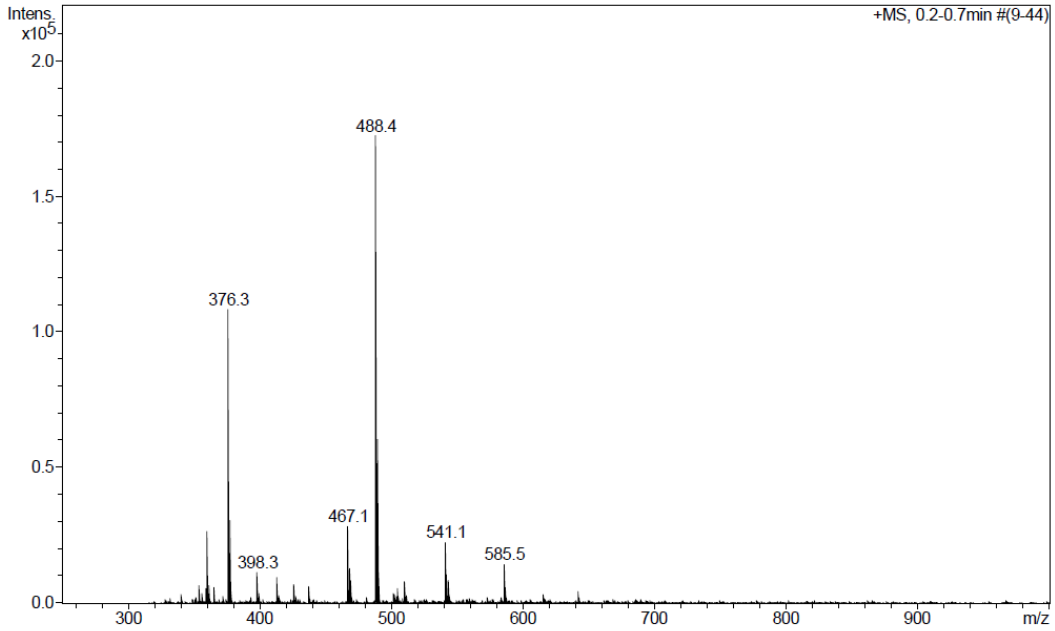
^{1}H NMR spectrum



^{13}C {^{1}H} NMR spectrum



Mass spectrometry



4. References

1 Budzelaar, P.H.M. *g* NMR-*Version 4.0.* IvorySoft **1997** (Cherwell Scientific: Oxford, UK).