ESI *for*

Complexes of (η^5-Cp*)Ir(III) with 1-Benzyl-3-Phenylthio/selenomethyl-1,3-Dihydrobenzoimidazole-2-Thione/Selenone: Catalysts for Oxidation and 1,2-Substituted Benzimidazole Synthesis

Alpesh K. Sharma, Hemant Joshi, Renu Bhaskar and Ajai K. Singh*

Department of Chemistry, Indian Institute of Technology Delhi, New Delhi – 110016, India

E-mail: aksingh@chemistry.iitd.ac.in

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Table S1. Crystal data and structural refinement parameters for complexes 1-4

Compounds	**1**	**2**	**3**	**4**
Empirical formula	$C_{31}H_{33}ClF_6IrN_2PSe_2$	$C_{31}H_{33}ClF_6IrN_2PSeS$	$C_{31}H_{33}ClF_6IrN_2PSSe$	$C_{31}H_{33}ClF_6IrN_2PS_2$
Formula wt.	964.15	917.25	917.25	870.35
Crystal size [mm]	0.34×0.25×0.22	0.43 × 0.21 × 0.19	0.38×0.24×0.17	0.31×0.28×0.13
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P 21/n*	*P 21/n*	*P 21/n*	*P 21/n*
Unit Cell dimension	*a* = 8.0384(18) *b* = 19.300(4) *c* = 22.282(5) α = 90.00° β = 91.219(4) γ = 90.00°	a = 7.980(4) b = 19.271(9) c = 22.304(10) α = 90.00 β = 91.000(9) γ = 90.00	a = 8.0837(16) b = 19.099(4) c = 22.104(4) α =90.00 β = 91.680(3) γ =90.00	a = 8.0195(14) b = 19.158(3) c = 22.138(4) α =90.00 β = 91.279(3) γ =90.00
Volume [Å^3]	3456.1(13)	3429(3)	3411.2(12)	3400.4(10)
Z	4	4	4	4
Density (Calc.) [Mg·m^{-3}]	1.853	1.777	1.786	1.700
Absorption coeff. [mm^{-1}]	6.150	5.197	5.225	4.232
F(000)	1856.0	1784.0	1784.0	1712.0
θ range [°]	2.30–19.50	2.30 – 19.04	2.13- 19.72	2.32- 22.31
Index ranges	-9≤ *h* ≤ 9 -22≤ *k* ≤ 22 -26 ≤ *l* ≤ -26	-9 ≤ *h* ≤ 9 -22 ≤ *k* ≤ 22 -26 ≤ *l* ≤ 26	-9 ≤ *h* ≤ 9 -22 ≤ *k* ≤ 22 -26 ≤ *l* ≤ 26	-9≤ *h* ≤ 9 -22≤ *k* ≤ 22 -26≤ *l* ≤ 26
Reflections collected	32943	31761	31700	31686
Independent reflections ($R_{int.}$)	6092 (0.0760)	6045 (0.1110)	6020(0.0976)	6001(0.0831)
Max./min. Transmission	0.258 /0.172	0.620/0.493	0.371 / 0.279	0.358/0.447
Data/restraints/parameters	6092 /0/402	6045 /0/ 402	6020 /0/ 402	6001/0/402
Goodness-of-fit on F^2	1.275	1.179	1.189	1.156
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0827 wR_2 = 0.1363	R_1 = 0.0818 wR_2 = 0.1168	R_1 = 0.1025 wR_2 = 0.1922	R_1 = 0.0617 wR_2 = 0.1103
R indices (all data)	R_1 = 0.0668, wR_2 = 0.1303	R_1 = 0.0818 wR_2 = 0.1111	R_1 = 0.0761 wR_2 = 0.1824	R_1 = 0.0503 wR_2 = 0.1062
Largest diff. peak/hole [e.Å^{-3}]	1.267/-2.079	1.461 /-2.610	3.712/-1.739	1.681/-2.228

Table S2. Bond Lengths and Bond Angles of Complexes 1-4

Complex	Bond length [Å]	Bond angle [°]
1	Ir1— Se1 2.4663(12) Ir1— Se2 2.5159(12) Ir1— Cl1 2.439(3) Se2 —C14 1.840(11) Se1— C6 1.939(11) Se1— C7 1.973(10) C14— N1 1.369(13) C14— N2 1.352(13) N1— C8 1.393(13)	Se1— Ir1— Se2 95.99(4) Cl1— Ir1— Se2 90.79(8) Cl1— Ir1— Se1 78.31(8) C6— Se1— Ir1 113.8(3) C7— Se1— Ir1 102.1(3) C14— Se2— Ir1 105.6(3) C14— N2— C15 123.4(9) C14— N1— C7 123.2(9) N1— C7— Se1 111.9(7) N2— C15— C16 113.3(8) C(6) —Se(1) —C(7) 96.6(5)
2.	Ir1— Se1 2.4663(13) Ir1 —S1 2.417(2) Cl1— Ir1 2.436(3) C14— S1 1.692(10) C14 —N2 1.365(11) C6 —Se1 1.945(10) C7 —Se1 1.945(10) C8 —N1 1.365(11) C14— N1 1.363(11)	S1— Ir1— Se1 95.41(7) Cl1— Ir1— S1 90.69(10) Cl1— Ir1— Se1 78.08(7) C6— Se1— Ir1 113.3(3) C7— Se1— Ir1 100.7(3) C14— S1— Ir1 108.9(3) C14— N2— C15 124.2(8) C14— N1— C7 122.7(8) N1— C7— Se1 122.7(8) C16— C15— N2 113.6(8) C6 —Se1— C7 95.4(4)
3	Ir1 —S1 2.355(4) Ir1— Se1 2.5141(16) Cl1— Ir1 2.427(4) C14— Se1 1.844(15) C14 —N2 1.344(18) C6 —S1 1.777(15) C7 —S1 1.823(15) C8 —N1 1.386(17) C14— N1 1.351(17)	S1— Ir1— Se1 94.99(9) Cl1— Ir1— Se1 90.85(12) Cl1— Ir1— S1 79.62(14) C6— S1— Ir1 116.2(5) C7— S1— Ir1 106.5(5) C14— Se1—Ir1 104.8(4) C14— N2— C15 125.6(12) C14— N1— C7 123.2(12) N1— C7— S1 111.9(9) C16— C15— N2 112.2(12) C6 —S1— C7 98.6(7)

4	Ir1— S1 2.3469(18) Ir1— S2 2.4146(19) N1— C14 1.364(9) N1— C8 1.392(9) C14— N2 1.346(8) S2 —C14 1.685(7) S1— C6 1.782(8) S1— C7 1.834(7)	S1— Ir1 —S2 94.61(6) S1— Ir1— Cl1 79.33(7) S2— Ir1 —Cl1 90.55(8) C6— S1— Ir1 116.0(3) C7 —S1— Ir1 104.4(3) C14 —S2— Ir1 108.0(2) C14— N1— C7 123.2(6) C14— N2 —C15 124.0(6) N1— C7— S1 112.3(5) N2— C15— C16 113.4(6) C6— S1— C7 98.9(3)

Table S3. Non-covalent Interactions C–H···F Distances (Å) of Complexes 1-4

Complex 1	**Complex 2**	**Complex 3**	**Complex 4**
H30C-F4 2.453	H7B –F2 2.486	H9 –F5 2.580	H28B-F2 2.632
H27A-F3 2.531	H30B-F5 2.581	H7B-F3 2.489	H9-F6 2.606
H15A-F3 2.606	H15b-F3 2.619	H15A-F1 2.546	H7B-F6 2.501
H7B-F2 2.530	H28B-F3 2.541	H28C-F6 2.612	H2-F5 2.668
H7B-F1 2.480	H12-Cl1 2.883	H7B-F3 2.489	H12-Cl1 2.865
		H12-Cl1 2.829	

Secondary Interaction-

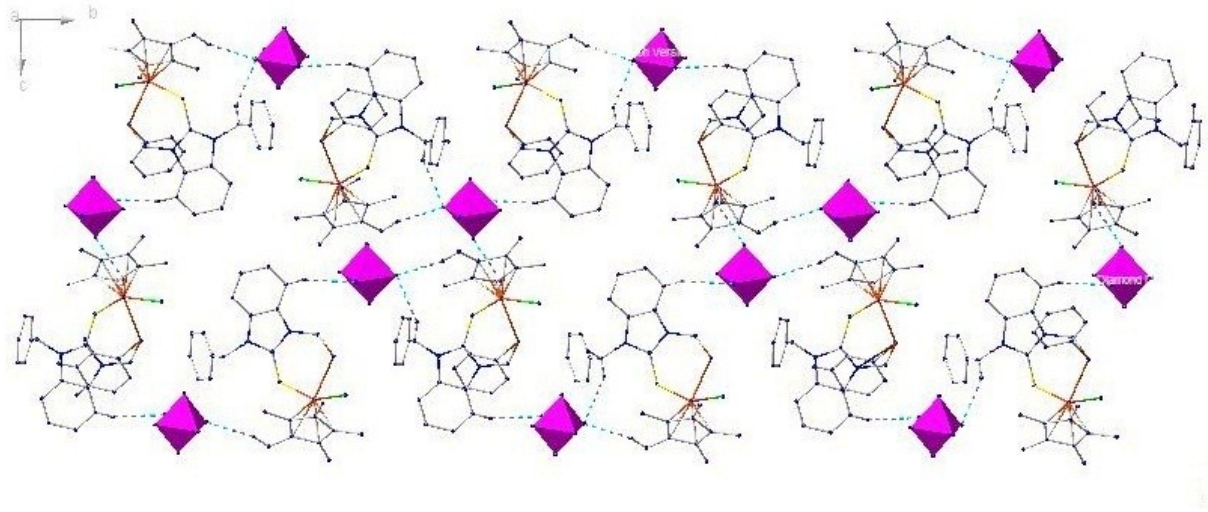


Figure S1 Three dimensional packing framework showing non-covalent C–H···F interactions in the crystal lattice contain PF_6 in polyhedral form of **2**

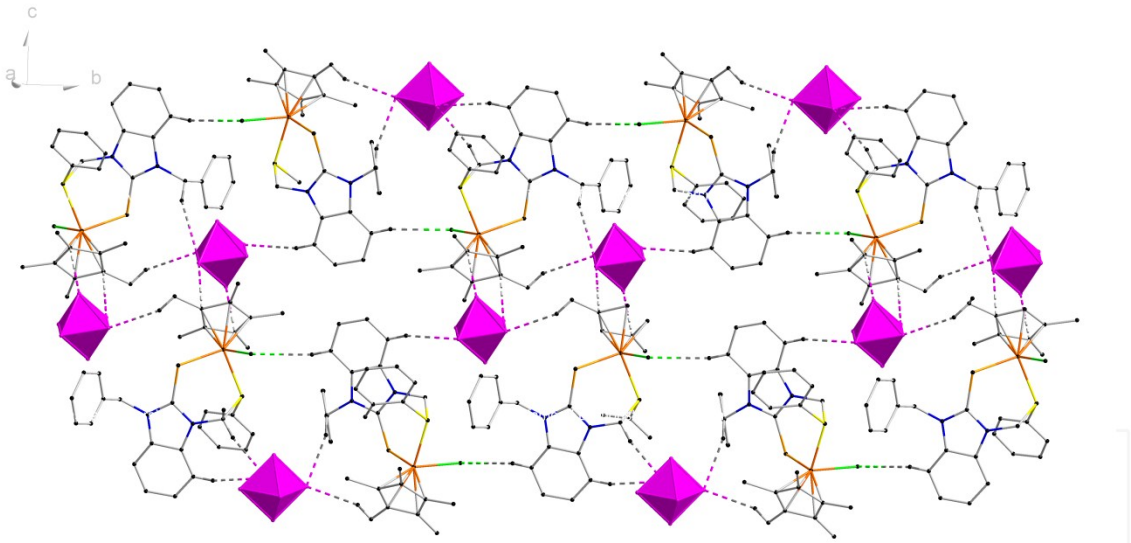


Figure S2 Three dimensional packing framework showing non-covalent C–H···F interactions in the crystal lattice contain PF_6 in polyhedral form of **3**

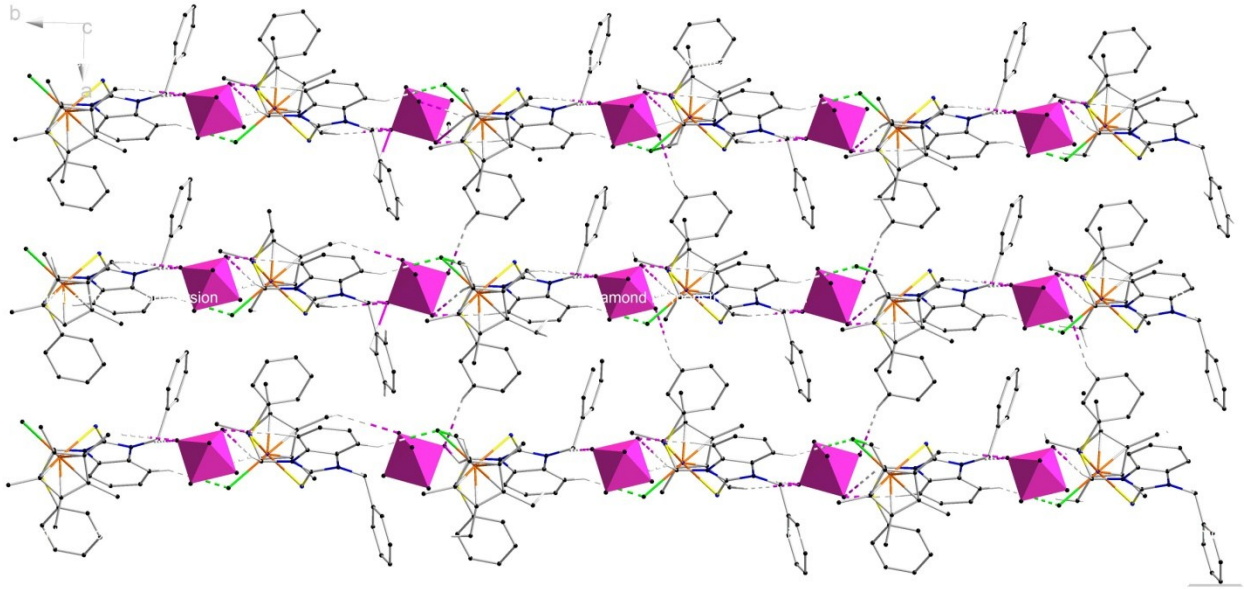


Figure S3 Three dimensional packing framework showing non-covalent C–H···F interactions in the crystal lattice contain PF_6 in polyhedral form of **4**

Mass Spectrum-

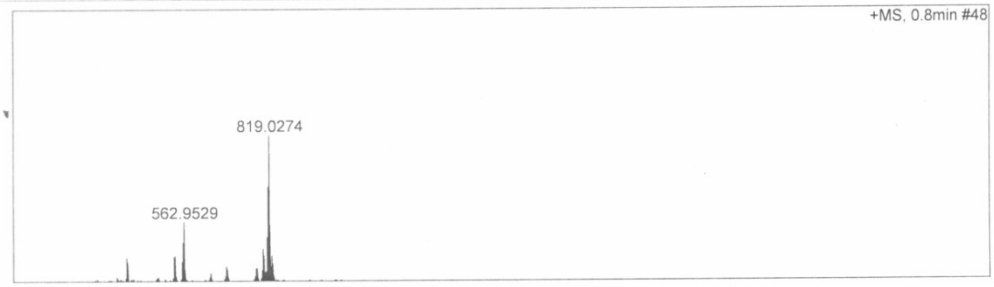
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\MAR 2016\aks A2.d	Acquisition Date	3/30/2016 11:23:18 AM
Method	tune_wide.m	Operator	IITD
Sample Name	TM1:100	Instrument / Ser#	micrOTOF-Q II 10262
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	500.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
821.0276	1	C 31 H 33 Cl Ir N 2 Se 2	821.0281	0.6	-0.8	16.5	ok	even	28.3	25.1	4.9	7.3	3.7	842.7

Fig S4 Mass spectrum of complex **1**

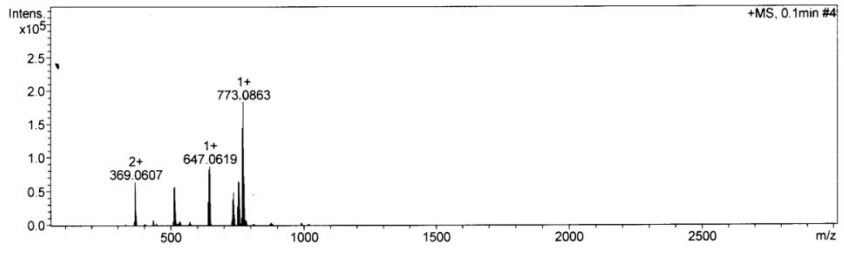
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	Z:\Aug_2014\ALP1.d	Acquisition Date	8/5/2014 10:12:34 AM
Method	tune_wide.m	Operator	Sharma/Singh
Sample Name	TM1:100	Instrument	micrOTOF-Q II 228888.10262
Comment			

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.3 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	3000 m/z	Set Collision Cell RF	600.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Ion Formula	m/z	err [ppm]	Mean err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma	Std I	Std Mean m/z	Std I VarNorm	Std m/z Diff	Std Comb Dev
773.086288	1	C31H33ClIrN2SSe	773.083333	-3.8	-1.9	16.5	ok	even	28.6	24.7	2.2	4.2	2.2	842.7

Fig S5 Mass spectrum of complex **2**

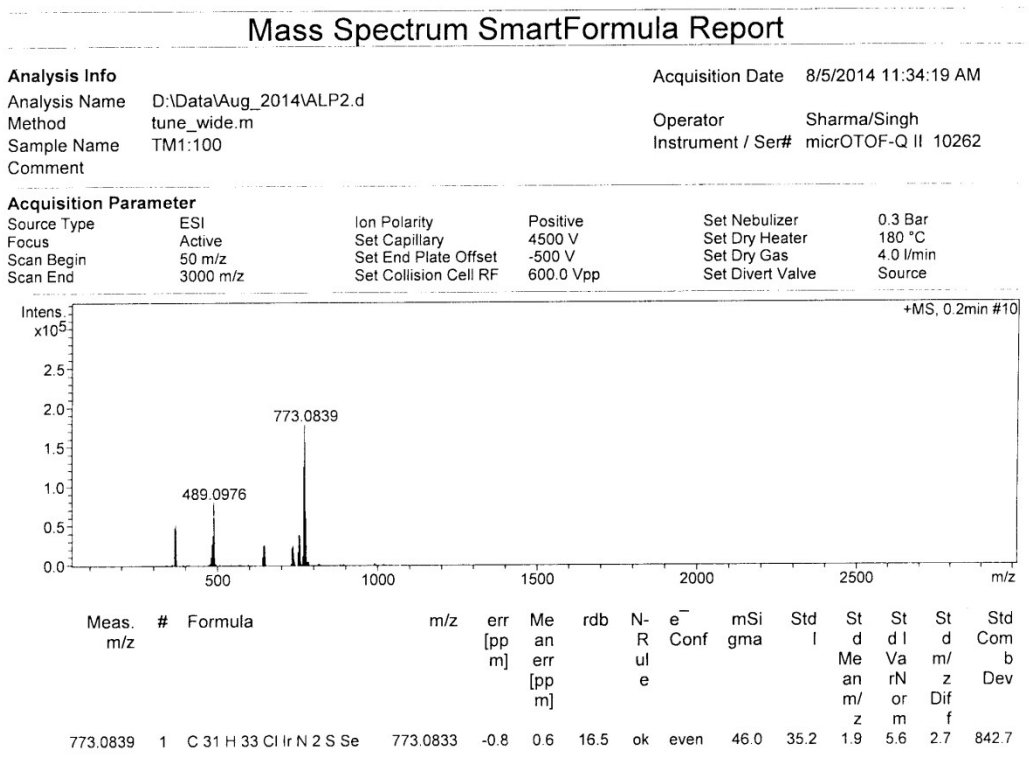


Fig S6 Mass spectrum of complex **3**

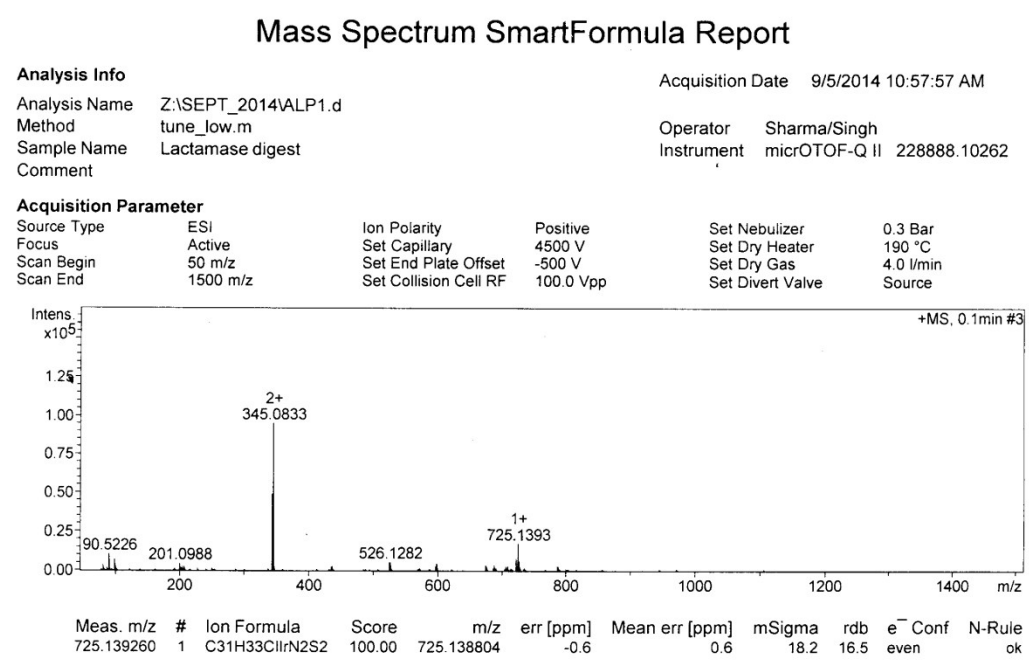
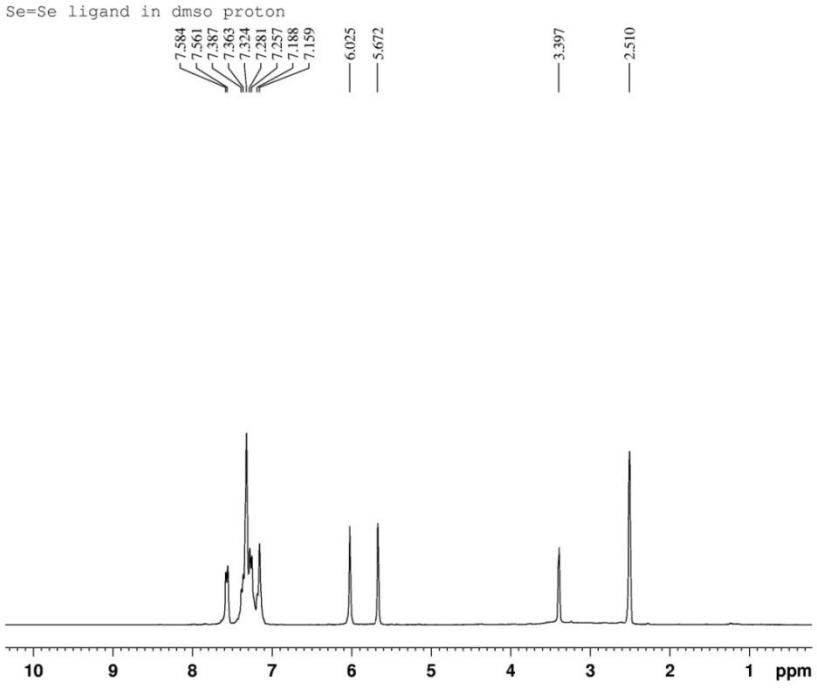
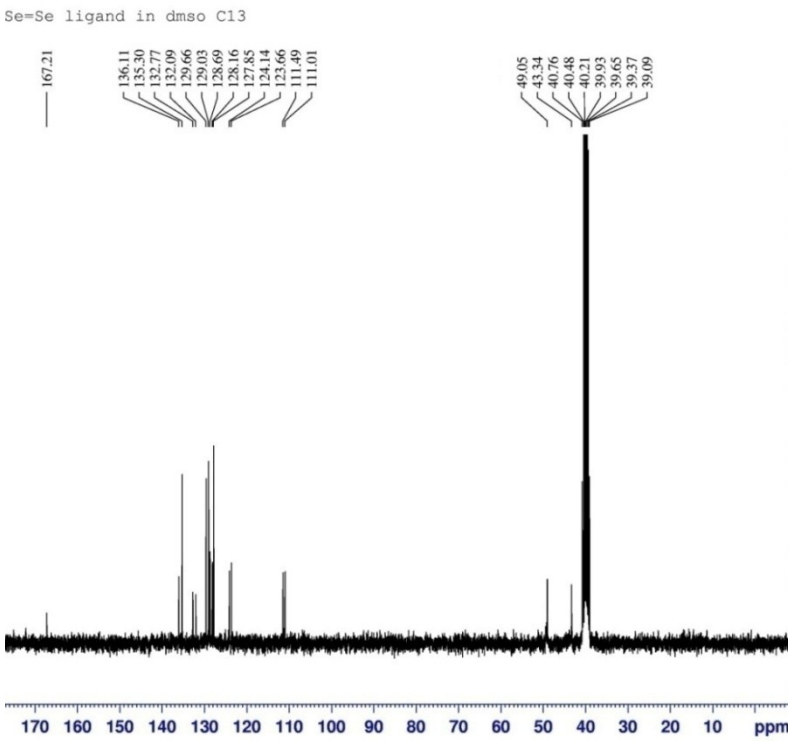


Fig S7 Mass spectrum of complex **4**

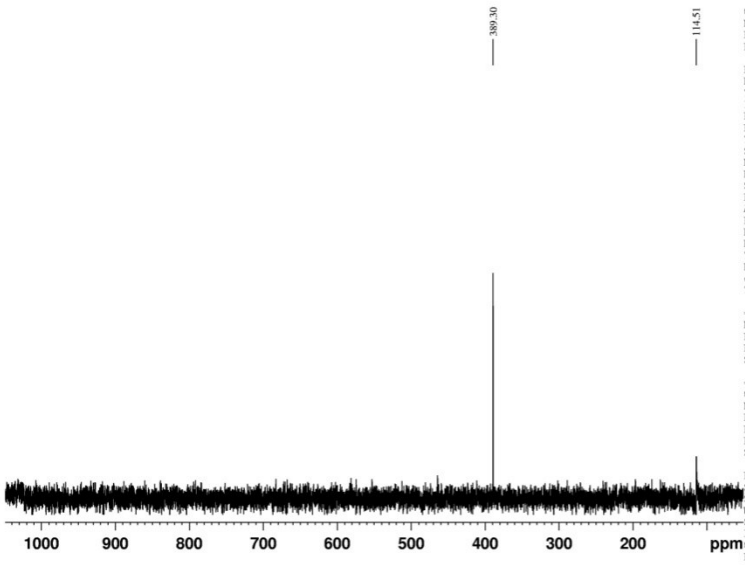
NMR Spectra-



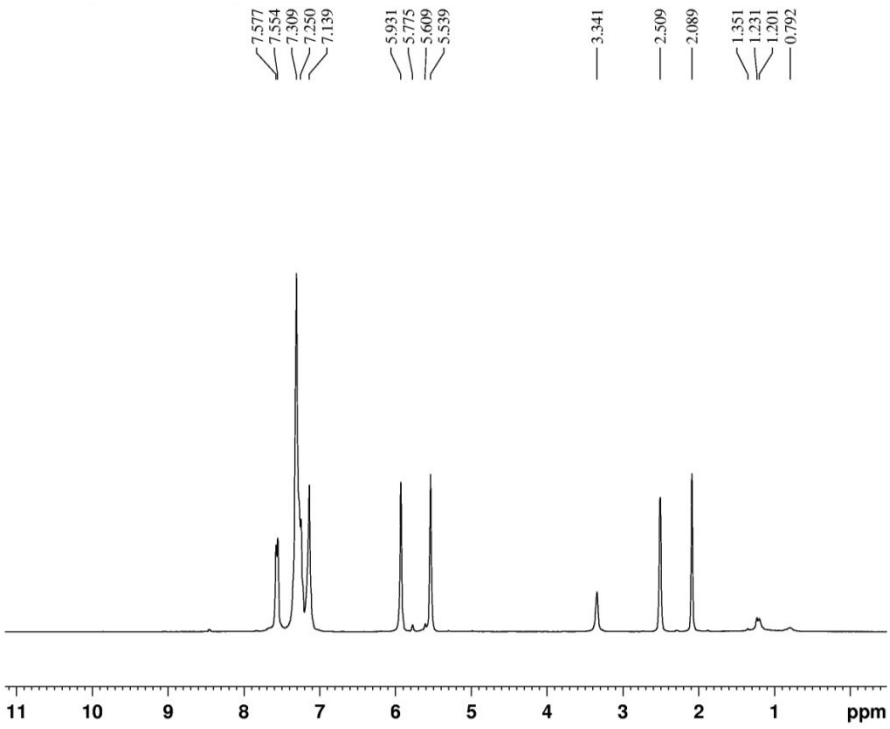
FigureS8 ^{1}H NMR spectrum of ligand **L1**



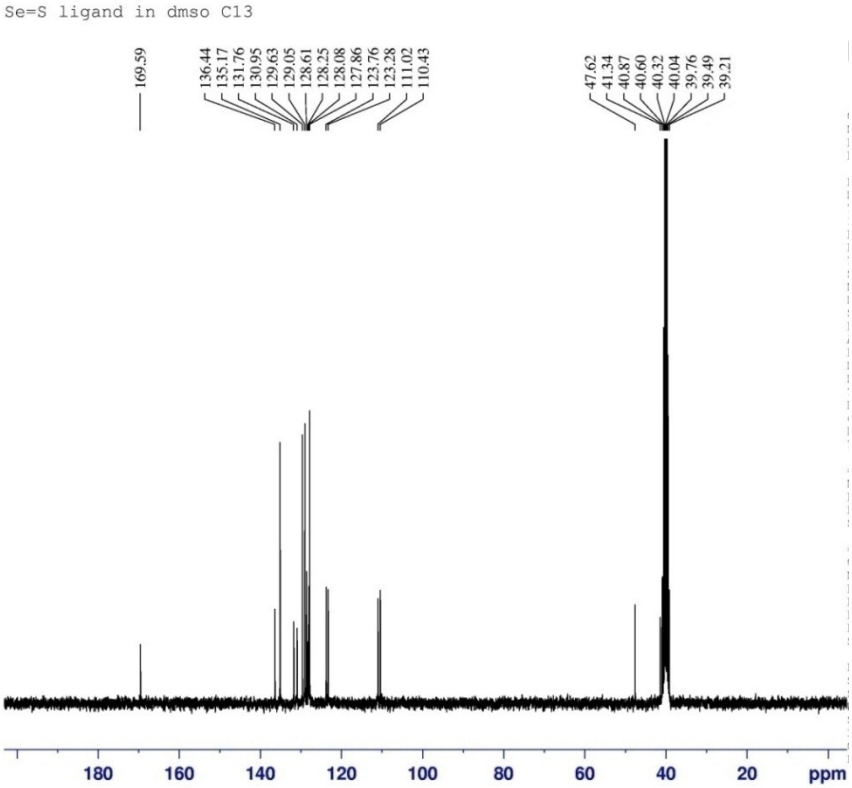
FigureS9 ^{13}C{^{1}H} NMR spectrum of ligand **L1**



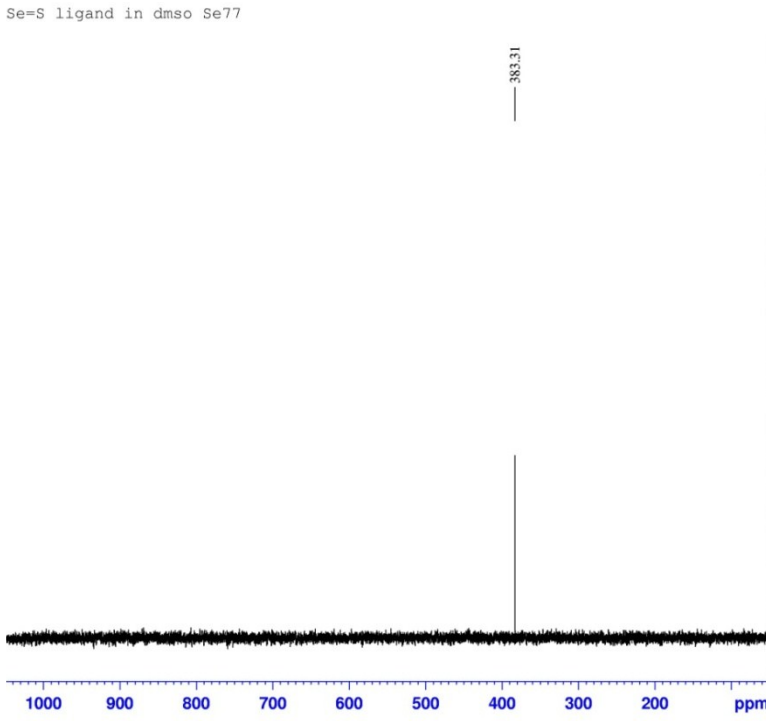
FigureS10 $^{77}Se\{^{1}H\}$ NMR spectrum of ligand **L1**



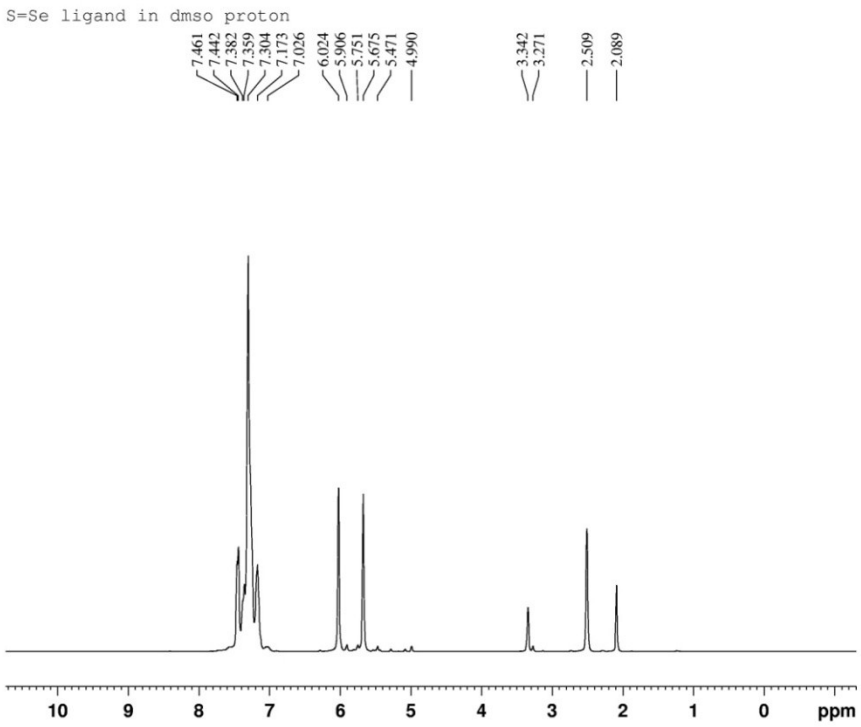
FigureS11 ^{1}H NMR spectrum of ligand **L2**



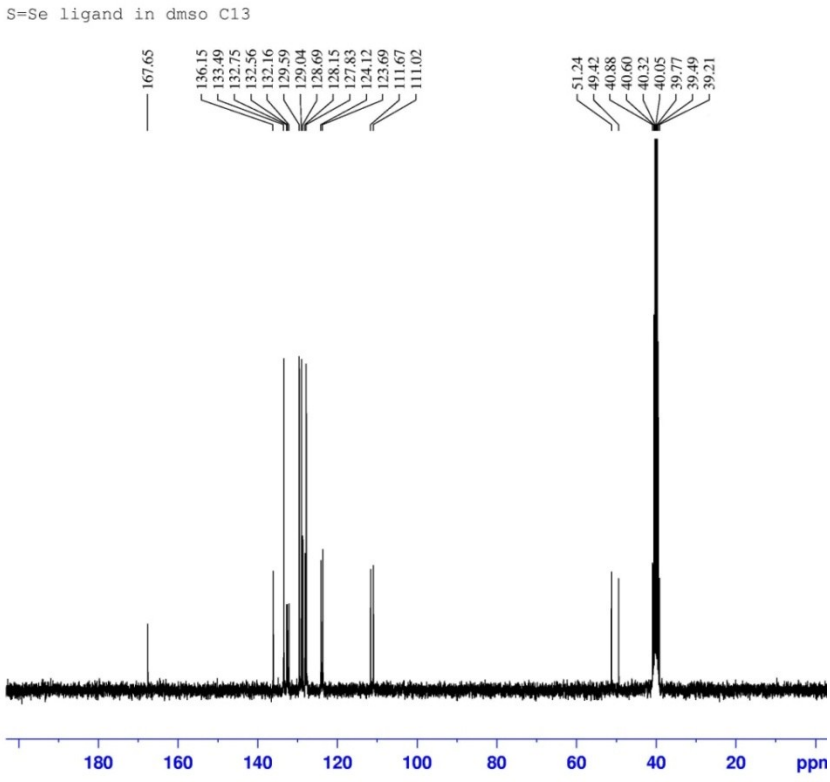
FigureS12 $^{13}C\{^{1}H\}$ NMR spectrum of ligand **L2**



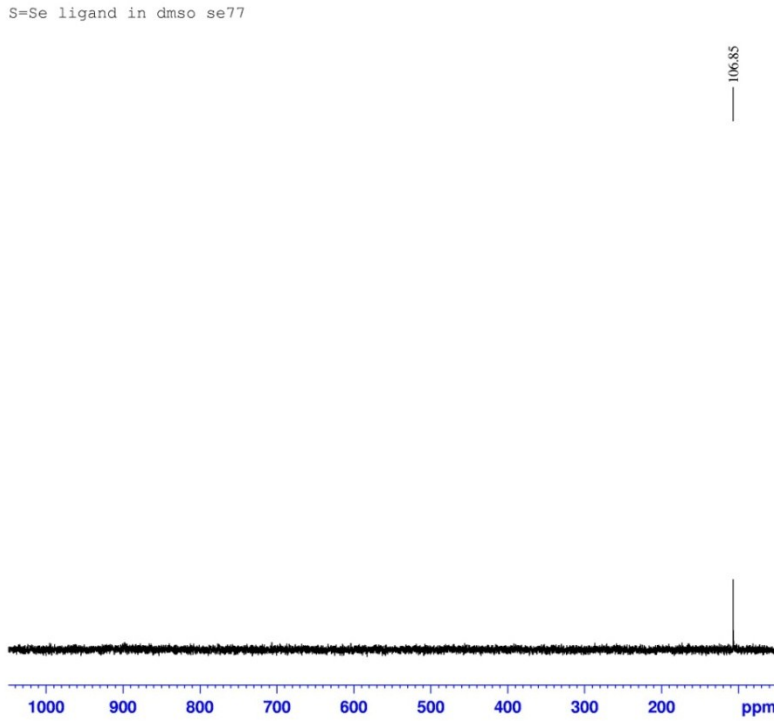
FigureS13 $^{77}Se\{^{1}H\}$ NMR spectrum of ligand **L2**



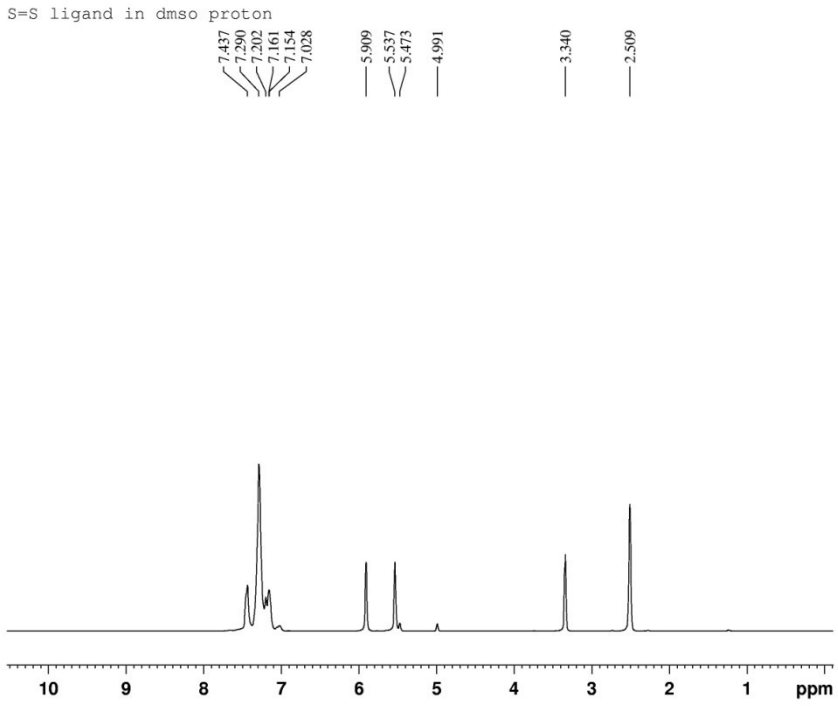
FigureS14 ^{1}H NMR spectrum of ligand **L3**



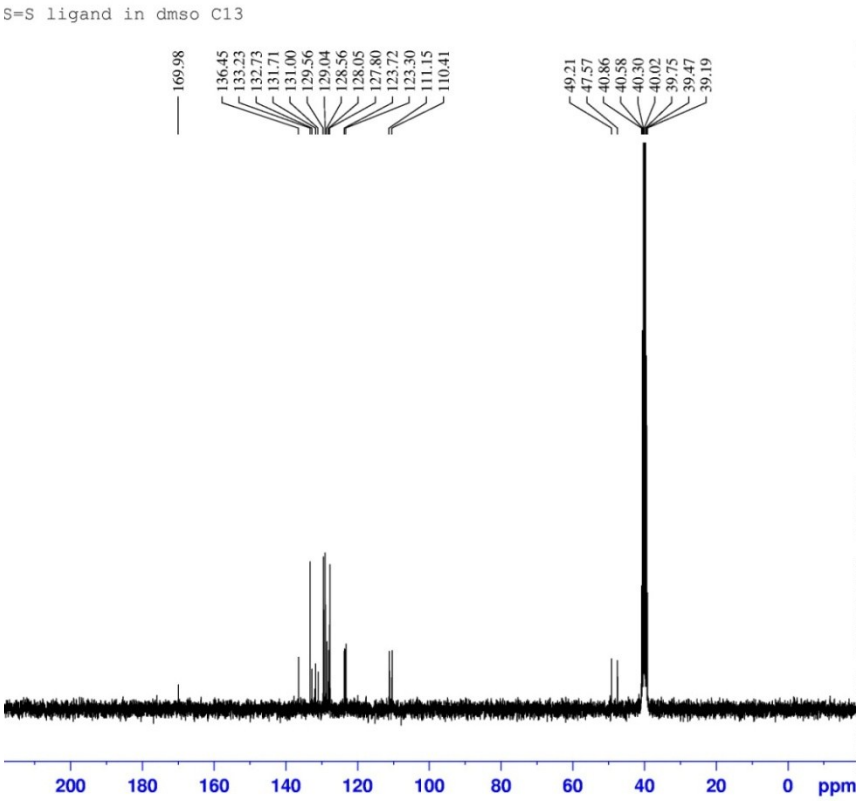
FigureS15 ^{13}C{^{1}H} NMR spectrum of ligand **L3**



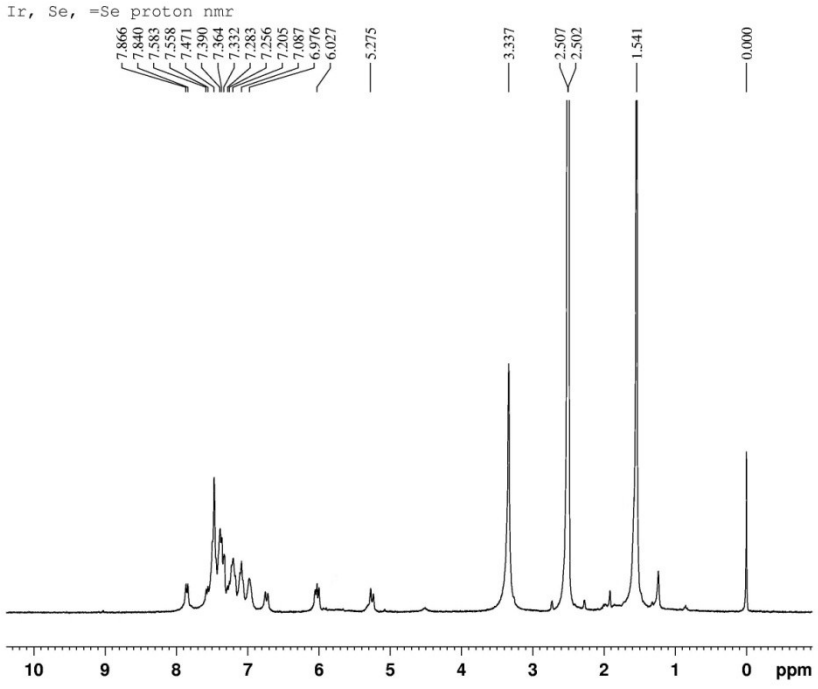
FigureS16 $^{77}Se\{^{1}H\}$ NMR spectrum of ligand **L3**



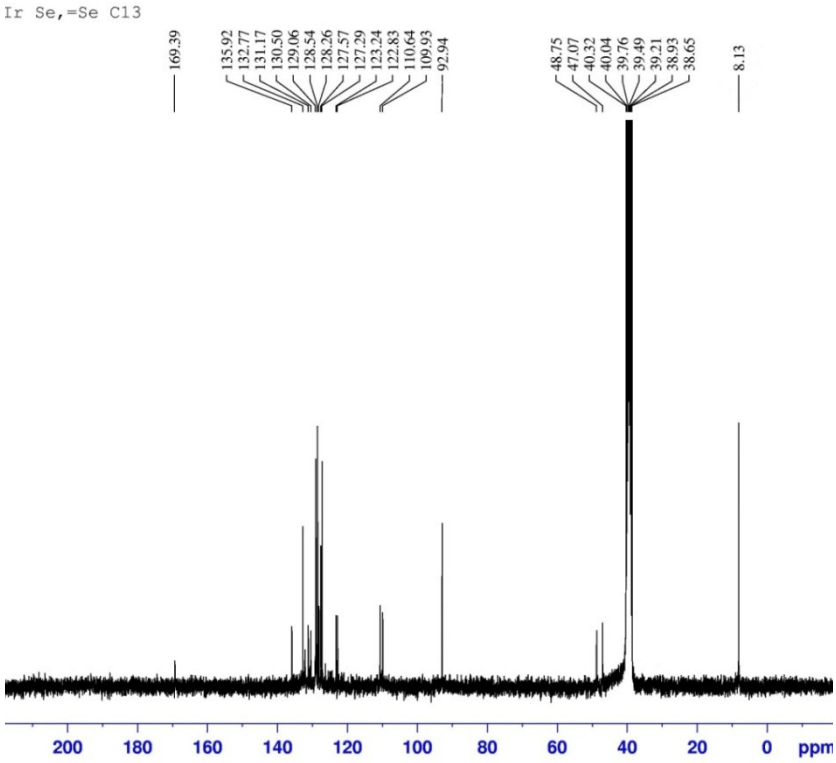
FigureS17 ^{1}H NMR spectrum of ligand **L4**



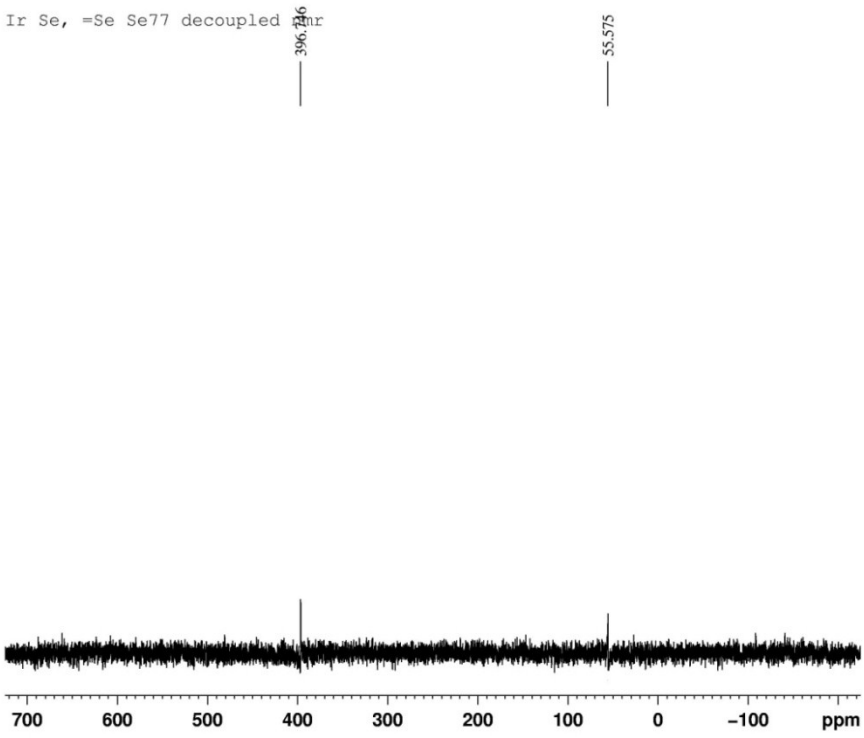
FigureS18 $^{13}C\{^{1}H\}$ NMR spectrum of ligand **L4**



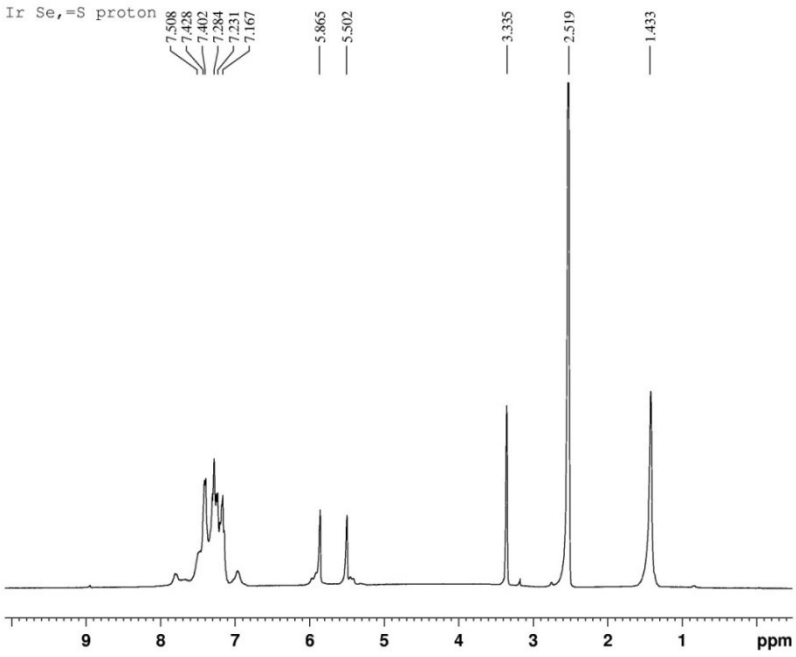
FigureS19 ^{1}H NMR spectrum of complex **1**



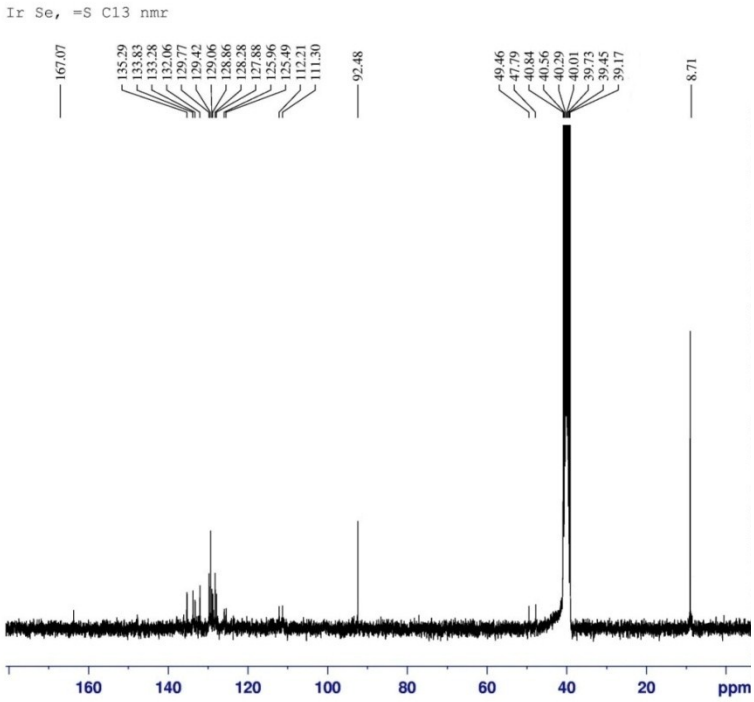
FigureS20 $^{13}C\{^{1}H\}$ NMR spectrum of complex **1**



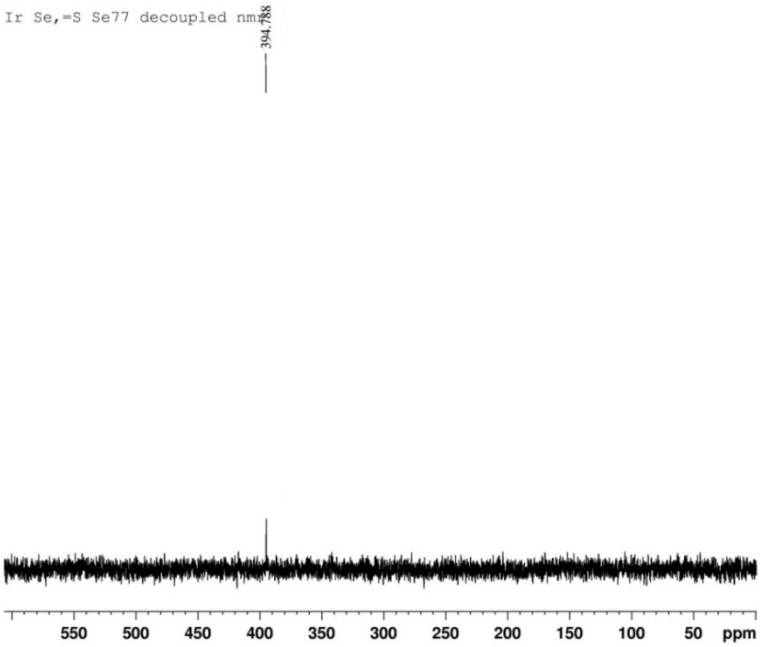
FigureS21 $^{77}Se\{^{1}H\}$ NMR spectrum of complex **1**



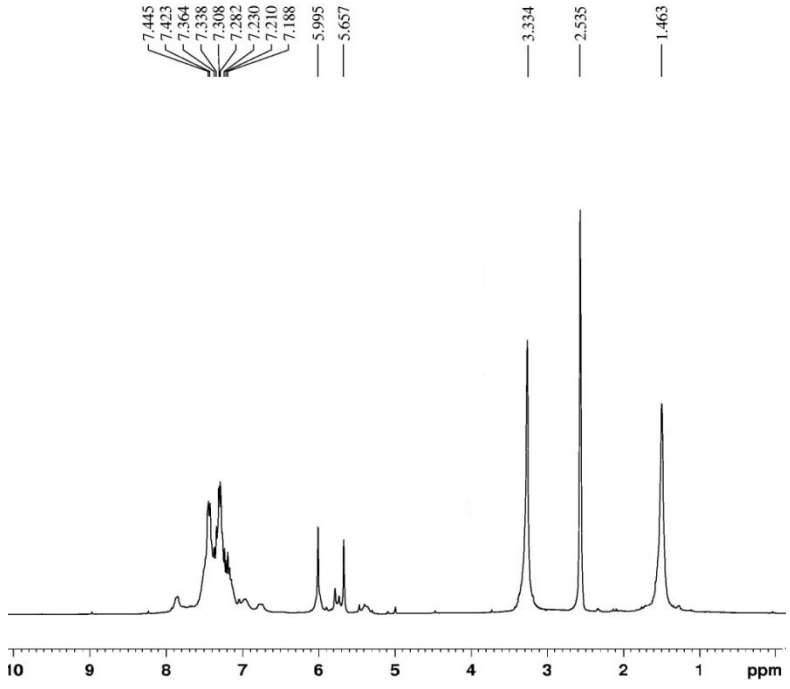
FigureS22 ^{1}H NMR spectrum of complex **2**



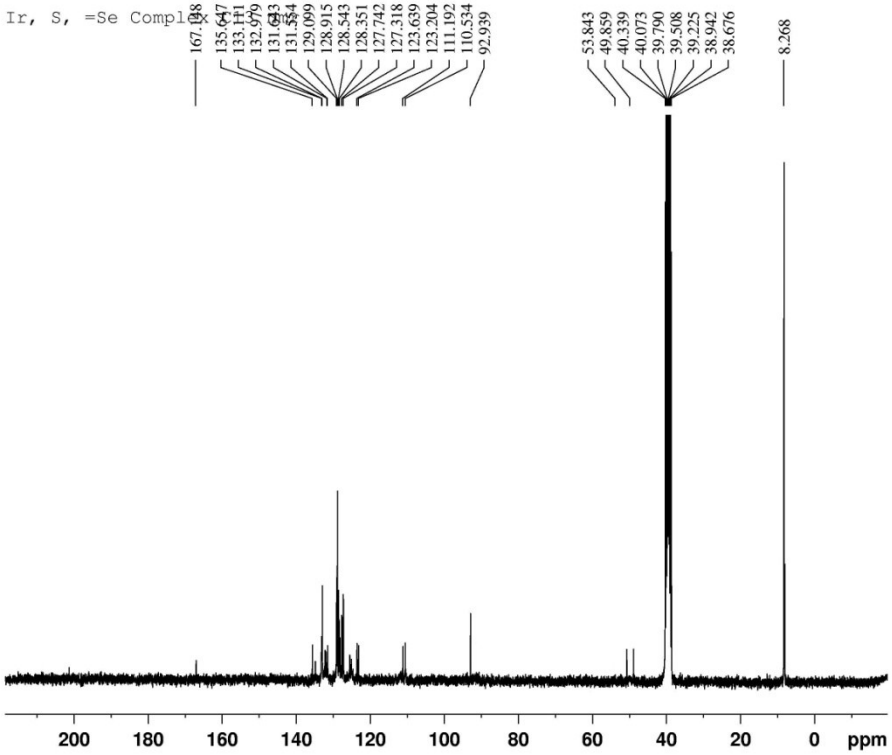
FigureS23 ^{13}C{^{1}H} NMR spectrum of complex **2**



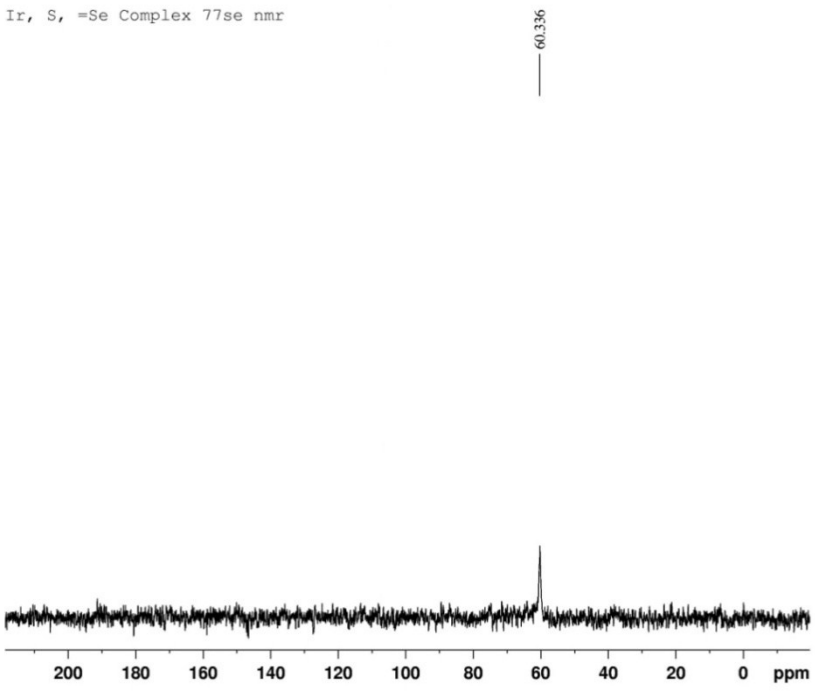
FigureS24 $^{77}Se\{^{1}H\}$ NMR spectrum of complex **2**



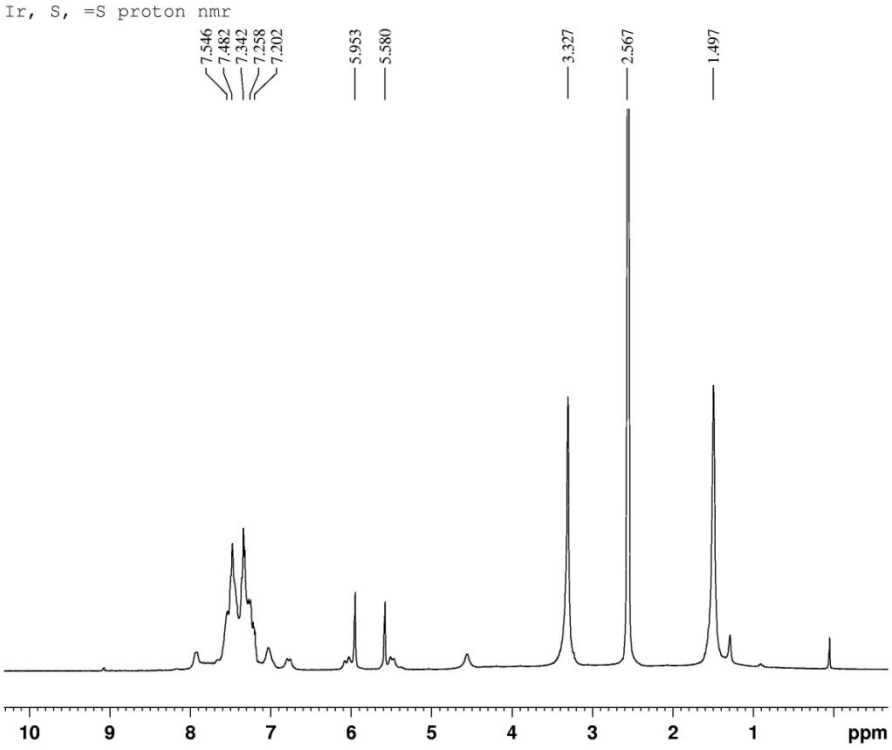
FigureS25 ^{1}H NMR spectrum of complex **3**



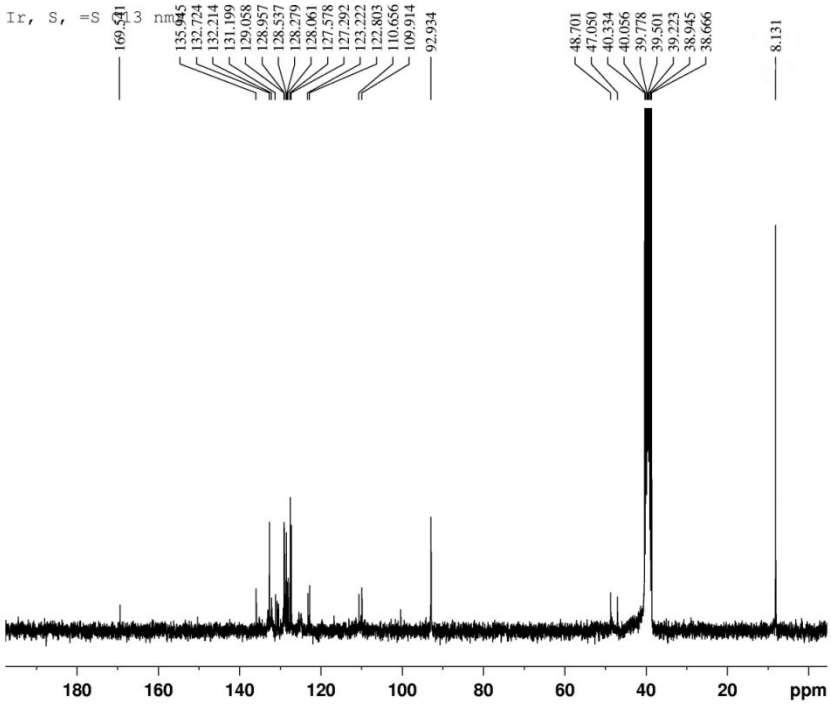
FigureS26 $^{13}C\{^{1}H\}$ NMR spectrum of complex **3**



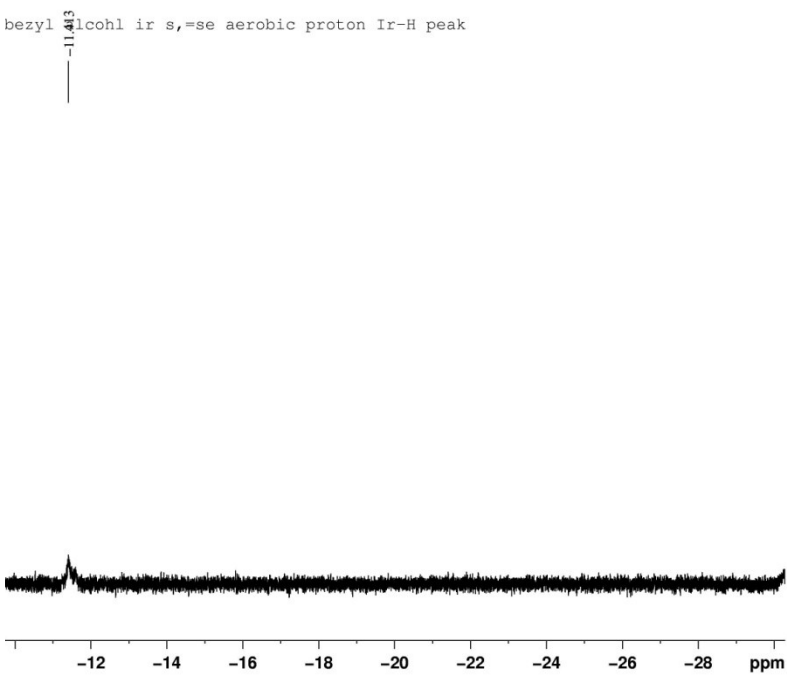
FigureS27 $^{77}Se\{^{1}H\}$ NMR spectrum of complex **3**



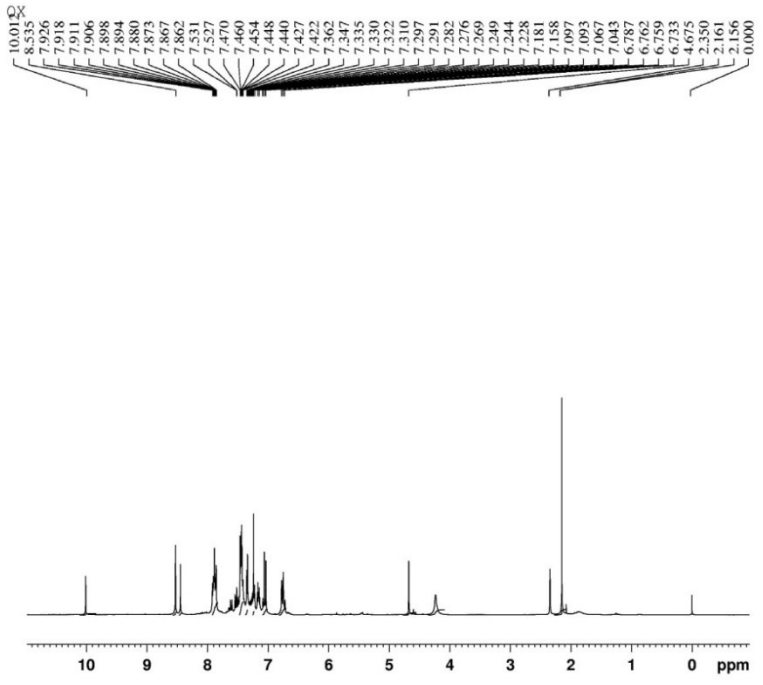
FigureS28 ^{1}H NMR spectrum of complex **4**



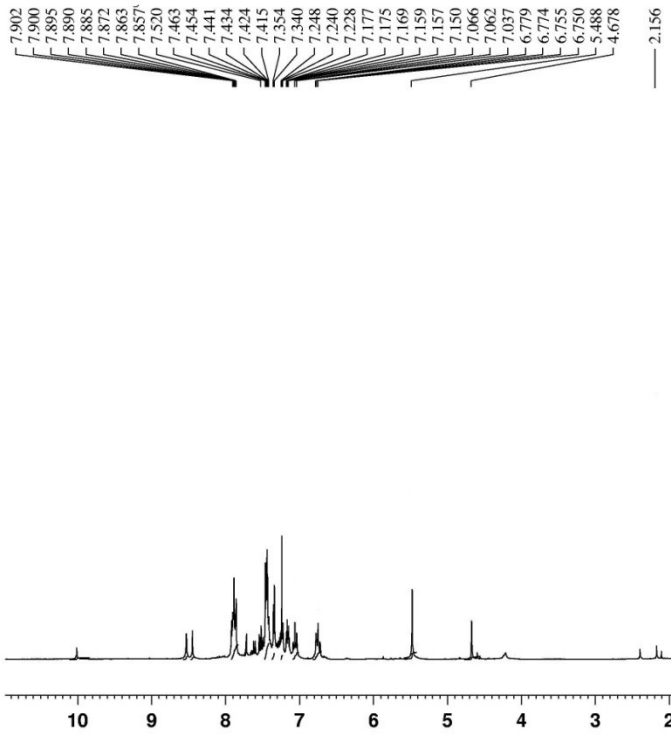
FigureS29 $^{13}C\{^{1}H\}$ NMR spectrum of complex **4**



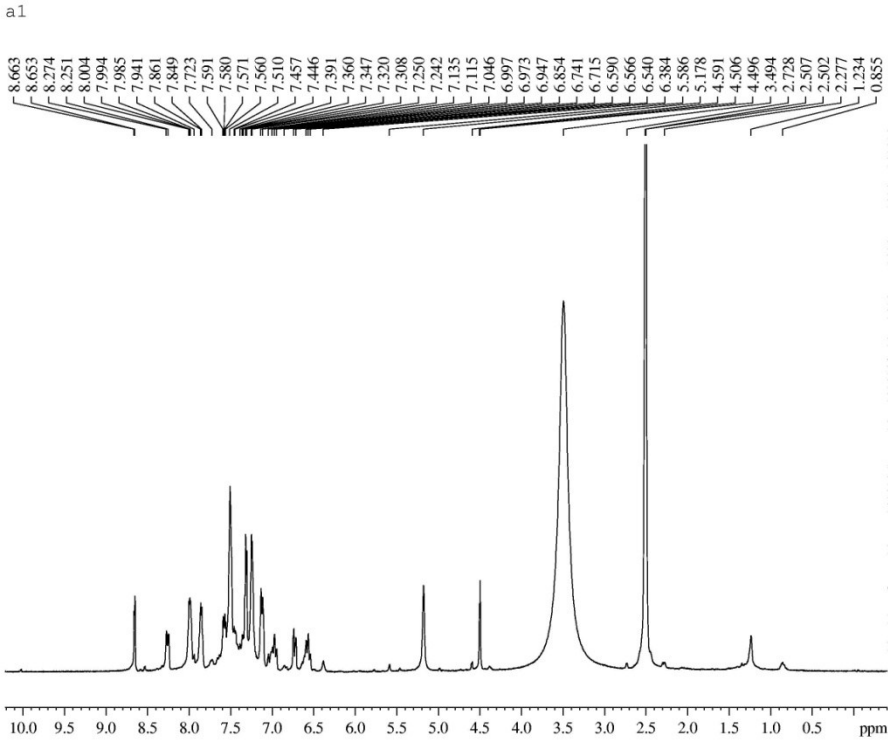
FigureS30 [1]H NMR spectrum for Ir-H species



FigureS31 [1]H NMR spectrum after 30 min of catalysis reaction progress (1,2-phenylenediamine and benzyl alcohol)



FigureS32 [1]H NMR spectrum after 90 min of catalysis reaction progress1,2-phenylenediamine and benzyl alcohol



FigureS33 [1]H NMR spectrum of catalytic reaction mixture

NMR Spectra of compound (3a-3g)-

1-Benzyl-2-phenyl-1H-benzimidazole (3a)[1,3]- White solid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si): δ (ppm): 7.87 (d, J = 6.1Hz, 1H), 7.70−7.68 (m, 2H), 7.47−7.41 (m, 3H), 7.34−7.30 (m, 4H), 7.25−7.20 (m, 2H), 7.12−7.10 (m, 2H), 5.47 (s, 2H).

1-(4-Methylbenzyl)-2-(4-methylphenyl)-1H-benzimidazole (3b)[1,2]- White solid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si): δ (ppm) 7.83 (d, J = 6.4 Hz, 1H), 7.60 (d, J = 6.2 Hz, 2H), 7.32−7.20 (m, 5H), 7.13(d, J = 6.2 Hz, 2H), 6.98 (d, J = 6.1 Hz, 2H), 5.41 (s, 2H), 2.41 (s, 3H), 2.36 (s, 3H).

1-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-1H-benzimidazole (3c)[1,2]- White solid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si): δ (ppm) 7.67 (d, J = 6.2 Hz, 3H), 7.45 (d, J = 6.4 Hz, 1H), 7.27−7.18 (m, 2H), 7.06 (d, J = 5.2 Hz, 2H), 6.96 (d, J = 5.6 Hz, 2H), 6.85 (d, J = 6.5 Hz, 2H), 5.46 (s, 2H), 3.84 (s, 3H), 3.63 (s, 3H).

1-(3-Methoxybenzyl)-2-(3-methoxyphenyl)-1H-benzimidazole (3d)[2]- White solid; ^{1}H NMR (DMSO, 25°C vs Me_4Si): δ (ppm) 7.54 (d, J = 6.2 Hz, 1H), 7.47-7.32 (d, J = 6.8 Hz, 2H), 7.28−7.19 (m, 1H), 7.13−7.05 (m, 3H), 6.98-6.92 (d, J = 6.2 Hz, 2H), 6.82-6.72 (d, J = 6.2 Hz, 2H), 5.21 (s, 2H), 3.84 (s, 3H), 3.80 (s,3H).

1-(2-Methoxybenzyl)-2-(2-methoxyphenyl)-1H-benzimidazole (3e)[2]- White solid; ^{1}H NMR (DMSO, 25°C vs Me_4Si): δ (ppm) 7.82 (d, J = 7.6 Hz, 1H), 7.63 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz, 1H), 7.24−7.22 (m, 1H), 7.19−7.17 (m, 3H), 7.11 (d, J = 6.2 Hz, 2H), 7.10 (d, J = 6.0 Hz, 2H), 5.41 (s, 2H), 2.32 (s, 3H), 2.27 (s,3H).

2-(Furan-2-yl)-1-(furan-2-ylmethyl)-1H-benzimidazole (3f)[1,2]. White solid; ^{1}H NMR (DMSO, 25°C vs Me_4Si): δ (ppm) 7.78−7.73 (m, 1H), 7.64 (s, 1H), 7.55−7.49 (m, 1H), 7.30−7.28(m, 3H), 7.22 (d, J = 7.4 Hz, 1H), 7.63-7.58 (m, 1H), 6.31−6.25 (m, 2H), 5.66 (s, 2H).

1-(4-Nitrobenzyl)-2-(4-nitrophenyl)-1H-benzimidazole (3g)[2]. Yellow solid; ^{1}H NMR (DMSO, 25°C vs Me_4Si): δ (ppm) 8.45−8.31 (m, 4H), 8.29 (d, J = 6.4 Hz, 2H), 8.17-8.09 (m, 1H), 7.36−7.23 (m, 2H), 7.21-7.15 (m, 1H), 7.13-7.12 (m, 1H), 6.79 (m, 1H), 6.56 (m, 1H), 5.40 (s, 2H).

NMR Spectra of compound (5a-g, 7a-d)-

Benzaldehyde (5a)[3] - Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si) δ (ppm): 9.98 (s, 1H), δ 7.44-7.478 (m, 2 H), 7.51-7.59 (m, 1 H), 7.78-7.83 (m, 2 H).

4-Methylbenzaldehyde (5b)[3]- Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 2.43(s, 3H), 7.33(d, J = 6.3 Hz, 2H), 7.78 (d, J = 6.2 Hz, 2H), 9.96 (s, 1H).

4-Methoxybenzaldehyde(5c)[3]- Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 9.82 (s, 1H), 7.82 (d, J = 6.6 Hz, 2H), 6.95 (d, J = 6.4 Hz, 2H), 3.91 (s, 3H).

3-Methoxybenzaldehyde (5d)[3]- Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 3.82(s, 3H), 7.18(d, J = 6.2 Hz, 2H), 7.38(d, J = 6.2 Hz, 2H), 7.43(d, J = 6.8 Hz, 2H), 9.93(s, 1H).

2-Methoxybenzaldehyde (5e)[5]**-** Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si): δ (ppm): 3.92(s, 3H), 7.02-7.04(m, 2H), 7.53-7.58(m, 1H), 7.82-7.85(q, 1H), 10.49(s, 1H).

2-Furaldehyde (5f)[4] – Pale yellow liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 9.65 (s, 1H), 7.69-7.67 (m, 1H), 7.52-7.44 (m, 1H), 6.60-6.59 (m, 1H).

4-Nitrobenzaldehyde (5g)[3,4]- Pale yellow solid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 10.1 (s, 1H), 8.71 (s, 1H), 8.46-8.50 (m, 1H), 8.22-8.20 (m1H), 7.72-7.80 (m, 1H).

Acetophenone (7a)[3]- Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 7.93-7.90 (m, 2H), 7.55-7.50 (m, 1H), 7.46-7.40 (m, 2H), 2.59 (s, 3H).

2-Pentanone (7b)[6] - Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 0.92 (t, J = 6.2 Hz, 3H), 1.61(m, 3H), 2.15(s, 3H), 2.40(t, J = 6.6 Hz, 2H).

2-octanone (7c)[6] - Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 0.89 (t, J = 6.4 Hz, 3H), 1.22-1.39 (m, 6H), 1.53-1.64 (m, 2H), 2.11(s, 3H), 2.42 (t, J = 8.4 Hz, 2H).

Cyclopentanone (7d)[4] - Colorless liquid; ^{1}H NMR ($CDCl_3$, 25°C vs Me_4Si); δ (ppm): 1.90-1.78 (m, 4H), 2.16-2.00 (m, 4H).

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