Electronic Supplementary Information

Half sandwich complexes of chalcogenated pyridine based bi–(N, S/Se) and terdentate (N, S/Se, N) ligands with (η^6–benzene) ruthenium(II): Synthesis, structure and catalysis of transfer hydrogenation of ketones and oxidation of alcohols

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1. Table S1 The crystallographic and refinement data of **1-5**

Compounds	**1**	**2**	**3**
Empirical formula	$C_{18}H_{17}ClNRuS.\ PF_6$	$C_{18}H_{17}ClNRuSe.PF_6$	$C_{17}H_{16}ClN_2RuS.PF_6$
Formula wt.	560.89	607.78	561.88
Crystal size [mm]	0.42×0.21×0.17	0.46×0.25×0.18	0.33×0.29×0.21
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	P 21/c	P 21/c	P2(1)/c
Unit Cell dimension	*a* = 11.2800(16)Å *b* = 13.4268(19)Å *c* = 13.4935(19)Å α = 90.00° β = 101.444(2)° γ = 90.00°	*a* = 11.3841(10)Å *b* = 13.2838(12)Å *c* = 13.5948(13)Å α = 90.00° β = 101.647(2)° γ = 90.00°	*a* = 11.2023(10)Å *b* = 13.1735(12)Å *c* = 13.2458(12)Å α = 90.00° β = 101.919(2)° γ = 90.00°
Volume [Å3]	2003.0(5)	2013.5(3)	1919.3(3)
Z	4	4	4
Density(Calc.) [Mg.m-3]	1.860	2.005	1.944
Absorption coeff. [mm-1]	1.160	2.858	1.212
***F*(000)**	1112.0	1184.0	1112.0
θ range [°]	2.39–28.32	2.38–28.21	2.41–28.17
Index ranges	$-13 \le h \le 13$ $-15 \le k \le 15$ $-16 \le l \le 16$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-16 \le l \le 16$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-15 \le l \le 15$
Reflections collected	18493	18587	17826
Independent reflections (*R*int.)	3521(0.0429)	3554(0.0390)	3388(0.0381)
Max./min. Transmission	0.744 / 0.824	0.426 / 0.601	0.674 / 0.778
Data/restraints/ parameters	3521 / 0 / 262	3554 / 0 / 262	3388 / 0 / 262
Goodness-of-fit on *F*2	1.338	1.249	1.154
Final R indices [$I > 2\sigma(I)$]	*R1* = 0.0684 *wR2* = 0.1368	*R1* = 0.0495 *wR2* = 0.0971	*R1* = 0.0364 *wR2* = 0.0770
R indices (all data)	*R1* = 0.0704 *wR2* = 0.1377	*R1* = 0.0512 *wR2* = 0.0979	*R1* = 0.0399 *wR2* = 0.0785
Largest diff. peak/hole [e.Å^{-3}]	0.924 / –1.086	0.703 / –0.697	0.686 / –0.468

Compounds	**4**	**5**
Empirical formula	$C_{18}H_{18}N_2RuS.\ 2PF_6$	$C_{18}H_{18}N_2RuSe.2PF_6$
Formula wt.	685.42	732.31
Crystal size [mm]	0.40×0.22×0.18	0.42×0.21×0.17
Crystal system	Monoclinic	Triclinic
Space group	P 21/c	P -1
Unit Cell dimension	*a* = 17.008(3)Å *b* = 9.1768(14)Å *c* = 15.464(2)Å α = 90.00° β = 97.076(3)° γ = 90.00°	*a* = 15.329(3)Å *b* = 9.1693(18)Å *c* = 17.165(3)Å α = 90.009(4)° β = 97.063(4)° γ = 89.901(4)°
Volume [Å3]	2395.2(6)	2394.3(8)
Z	4	4
Density(Calc.) [Mg.m-3]	1.901	2.032
Absorption coeff. [mm-1]	0.980	2.413
***F*(000)**	1352.0	1424.0
θ range [°]	2.41–25.00	2.39–27.32
Index ranges	$-20 \le h \le 20$ $-10 \le k \le 10$ $-18 \le l \le 18$	$-18 \le h \le 18$ $-10 \le k \le 10$ $-20 \le l \le 20$
Reflections collected	22069	17226
Independent reflections (*R*int.)	4220(0.0387)	8415(0.0523)
Max./min. Transmission	0.840 / 0.770	0.667/ 0.553
Data/restraints/ parameters	4220/ 0 / 325	8415 / 0 / 649
Goodness-of-fit on *F*2	1.072	0.913
Final R indices [*I* >2σ(*I*)]	*R1* = 0.0495 *wR2* = 0.0971	*R1* = 0.0530 *wR2* = 0.1139
R indices (all data)	*R1* = 0.0512 *wR2* = 0.0979	*R1* = 0.0926 *wR2* = 0.1251
Largest diff. peak/hole [e.Å^{-3}]	0.703 / –0.697	0.924 / –0.483

2. Table S2. Bond lengths and bond angles of **1**–**5**

Complex	Bond Length[Å]		Bond Angle[°]	
1	Ru(1)—S(1)	2.3771(18)	N(1)—Ru(1) — S(1)	80.49(15)
	Ru(1)—N(1)	2.095(5)	N(1)—Ru(1)—Cl(1)	85.33(15)
	Ru(1)—C(13)	2.160(7)	N(1)—Ru(1)—C(13)	91.4(3)
	Ru(1)—C(18)	2.193(8)	N(1)—Ru(1)—C(18)	96.1(3)
	Ru(1) —Cl(1)	2.3876(19)	C(13)— Ru(1) — S(1)	114.5(3)
	N(1)—C1(2)	1.348(9)	C(18)— Ru(1) — S(1)	152.4(3)
	S(1)—C(1)	1.783(7)	S(1)— Ru(1) — Cl(1)	93.39(6)
	S(1)—C(7)	1.812(7)	C(13)— Ru(1) — Cl(1)	151.1(3)
			C(18) — Ru(1) — Cl(1)	113.7(3)
			C(1) — S(1) — Ru(1)	116.1(2)
			C(7) — S(1) — Ru(1)	93.8(2)
2	Ru(1) — Se(1)	2.4879(7)	N(1) — Ru(1) — Se(1)	81.49(12)
	N(1) — Ru(1)	2.101(5)	N(1) — Ru(1) — Cl(1)	84.97(13)
	Cl(1) — Ru(1)	2.3955(15)	N(1) — Ru(1) — C(13)	112.9(3)
	C(1) — Se(1)	1.933(6)	N(1) — Ru(1) — C(18)	91.1(2)
	C(7) — Se(1)	1.955(6)	Cl(1) — Ru(1) — Se(1)	92.78(4)
	C(12) — N(1)	1.342(7)	C(13) — Ru(1) — Cl(1)	162.1(3)
	C(13) — Ru(1)	2.171(7)	C(18) — Ru(1) — Cl(1)	150.1(2)
	C(18) — Ru(1)	2.165(6)	C(13) — Ru(1) — Se(1)	89.8(2)
			C(18) — Ru(1) — Se(1)	116.0(2)
			C(1) — Se(1) — Ru(1)	114.13(16)
			C(7) — Se(1) — Ru(1)	89.73(18)
3	Ru(1) — S(1)	2.3740(9)	N(1) — Ru(1) — S(1)	80.82(8)
	N(1) — Ru(1)	2.096(3)	N(1) — Ru(1) — Cl(1)	84.34(8)
	Cl(1) — Ru(1)	2.3989(9)	N(1) — Ru(1) — C(12)	113.49(13)
	C(12) — Ru(1)	2.185(4)	N(1) — Ru(1) — C(17)	90.58(13)
	C(17) — Ru(1)	2.168(4)	N(2) — C(1) — S(1)	115.8(3)
	C(11) — N(1)	1.349(5)	C(11) — N(1) — Ru(1)	120.7(2)
	C(1) — N(2)	1.324(5)	C(12) — Ru(1) — S(1)	88.79(11)
	C(1) — S(1)	1.811(4)	C(17) — Ru(1) — S(1)	115.05(11)
	C(6) — S(1)	1.815(4)	C(12) — Ru(1) —Cl(1)	162.12(11)
			C(17) — Ru(1) — Cl(1)	150.26(11)
			C(1) — S(1) — Ru(1)	115.48(12)
			C(6) — S(1) — Ru(1)	95.12(12)
			S(1) — Ru(1) — Cl(1)	93.09(3)
4	Ru(1) — S(1)	2.3133(15)	N(1) — Ru(1) — S(1)	83.02(13)
	N(1) — Ru(1)	2.098(4)	N(2) — Ru(1) — S(1)	83.13(14)
	N(2) — Ru(1)	2.111(5)	N(1) — Ru(1) — N(2)	83.46(18)
	C(13) — Ru(1)	2.189(6)	N(1) — Ru(1) — C(13)	152.3(2)
	C(18) — Ru(1)	2.192(6)	N(2) — Ru(1) — C(13)	122.7(2)
	C(2) — N(1)	1.344(7)	N(1) — Ru(1) — C(18)	115.2(2)
	C(8) — N(2)	1.351(8)	N(2) — Ru(1) — C(18)	160.3(2)
	C(1) — S(1)	1.798(6)	C(13) — Ru(1) — S(1)	90.84(18)
	C(7) — S(1)	1.810(7)	C(18) — Ru(1) — S(1)	92.57(19)
			C(1) — S(1) — Ru(1)	97.2(2)
			C(7) — S(1) — Ru(1)	101.7(2)
5	Ru(1) — Se(1)	2.4252(9)	N(1) — Ru(1) — Se(1)	83.88(16)
	N(1) — Ru(1)	2.123(6)	N(2) — Ru(1) — Se(1)	83.70(15)

	N(2) — Ru(1)	2.105(5)	N(1) — Ru(1) — N(2)	83.60(2)
	C(13) — Ru(1)	2.180(7)	N(1) — Ru(1) — C(13)	123.7(3)
	C(18) — Ru(1)	2.186(7)	N(2) — Ru(1) — C(13)	151.3(3)
	C(2) — N(1)	1.351(8)	N(1) — Ru(1) — C(18)	161.4(3)
	C(8) — N(2)	1.342(8)	N(2) — Ru(1) — C(18)	114.3(3)
	C(1) — Se(1)	1.939(8)	C(13) — Ru(1) — Se(1)	90.20(2)
	C(7) — Se(1)	1.925(7)	C(18) — Ru(1) — Se(1)	92.8(2)
			C(1) — S(1) — Ru(1)	97.1(2)
			C(7) — S(1) — Ru(1)	92.6(2)

3. Table S3. HOMO-LUMO energy gap of the **1**−**5** and Mulliken partial atomic charge.

Complex	Energy-gap (kcal/mol)	Mulliken partial atomic charge			
		Metal	Calcogen	N pyridine	Cl/ N
1	91.4029	-0.072	+0.329	-0.410	-0.222
2	90.9950	-0.048	+0.198	-0.436	-0.231
3	91. 5849	-0.119	+0.368	-0.427	-0.218
4	101.5123	-0.098	+0.651	-0.458	-0.452
5	99.8745	-0.062	+0.524	-0.460	-0.456

4. **Table S4.** Non-covalent interactions C–H···F distances (Å) of complexes **1**−**5**

1		**2**		**3**	
C(6)–H(6)···F(5)	2.709(8)	C(2)–H(2)···F(1)	2.760(7)	C(6)–H(6A)···F(6)	2.417(3)
C(9)–H(9)···F(3)	2.965(8)	C(14)–H(14)···F(2)	2.573(8)	C(2)–H(2)···F(4)	2.537(2)
C(7)–H(7A)···F(3)	2.548(8)	C(15)–H(15)···F(5)	2.871(7)	C(3)–H(3)···F(1)	2.884(3)
C(10)–H(10)···F(2)	2.712(8)	C(3)–H(3)···F(4)	2.965(7)	C(2)–H(2)···F(6)	2.924(3)
C(11)–H(11)···F(2)	2.768(9)	C(15)–H(15)···F(1)	2.852(7)	C(10)–H(10)···F(1)	2.601(3)
C(16)–H(16)···F(5)	2.815(8)			C(13)–H(13)···F(3)	2.634(4)
C(15)–H(15)···F(6)	2.862(12)			C(17)–H(17)···F(3)	2.465(3)

4		**5**	
C(4)–H(4)···F(12)	2.713(9)	C(4)–H(4)···F(2)	2.840(11)
C(10)–H(10)···F(2)	2.811(10)	C(10)–H(10)···F(11)	2.710(1)
C(13)–H(13)···F(4)	2.552(12)	C(13)–H(13)···F(2)	2.509(12)
C(14)–H(14)···F(1)	2.880(12)	C(14)–H(14)···F(6)	2.451(9)
C(17)–H(17)···F(9)	2.573(5)	C(17)–H(17)···F(10)	2.593(8)
C(15)–H(15)···F(1)	2.421(9)	C(1)–H(1A)···F(9)	2.651(8)

5. Table S5. Non-covalent interactions C–H···Cl distances and C–H···π distances (Å) of complexes **1**−**3**

1		**2**		**3**	
C(3)–H(3)···Cl(1)	2.993(3)	C(5)–H(5)···Cl(1)	3.043(2)	C(5)–H(5)···Cl(1)	2.999(2)
C(12)–H(12)···Cl(1)	2.812(3)	C(12)–H(12)···Cl(1)	2.837(3)	C(16)–H(16)···Cl(1)	2.957(2)
C(14)–H(14)···Cl(1)	2.976(2)	C(13)–H(13)···Cl(1)	2.935(2)	C(12)–H(12)···Cl(1)	2.867(1)
		C(12)–H(12)···Cl(1)	3.114(2)	C(11)–H(11)···Cl(1)	2.817(3)
Non-covalent interactions C–H···π distances (Å)					
C(10)–H(10)····π	2.834(3)	C(10)–H(10)····π	2.859(2)	C(9)–H(9)····π	2.786(2)

6. Secondary C–H···F interactions

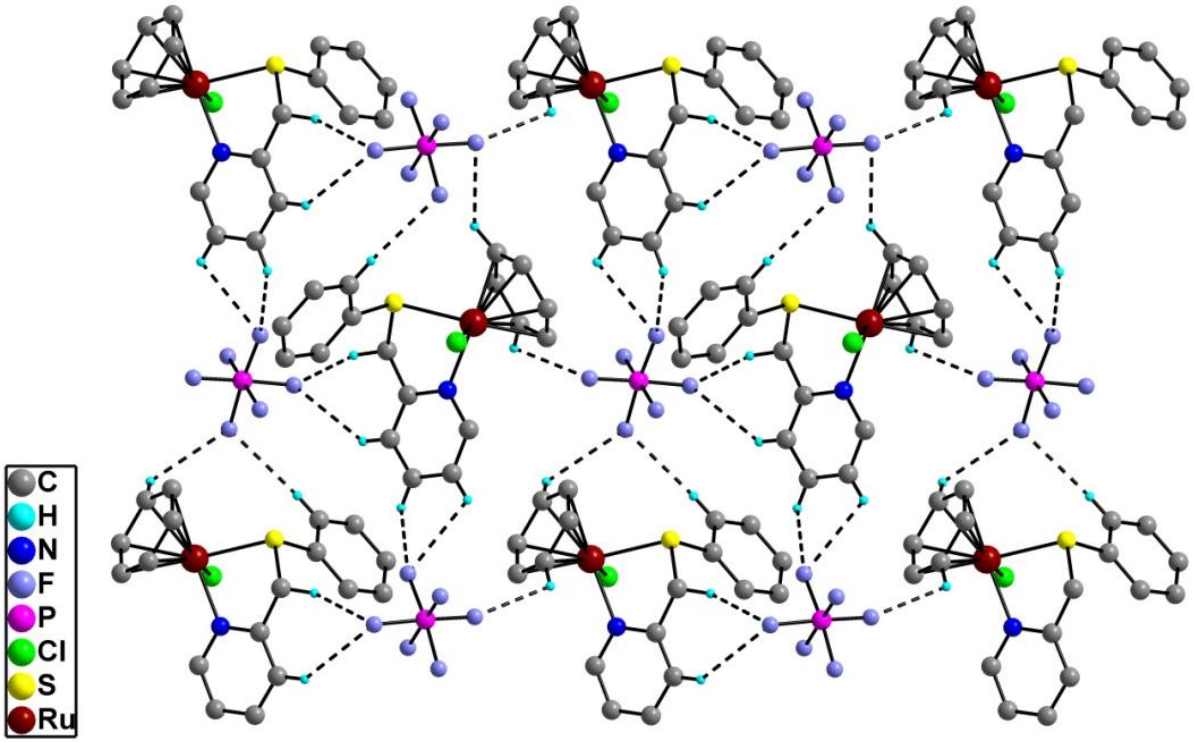

Figure S1. Non-covalent C–H···F interactions in **1**.

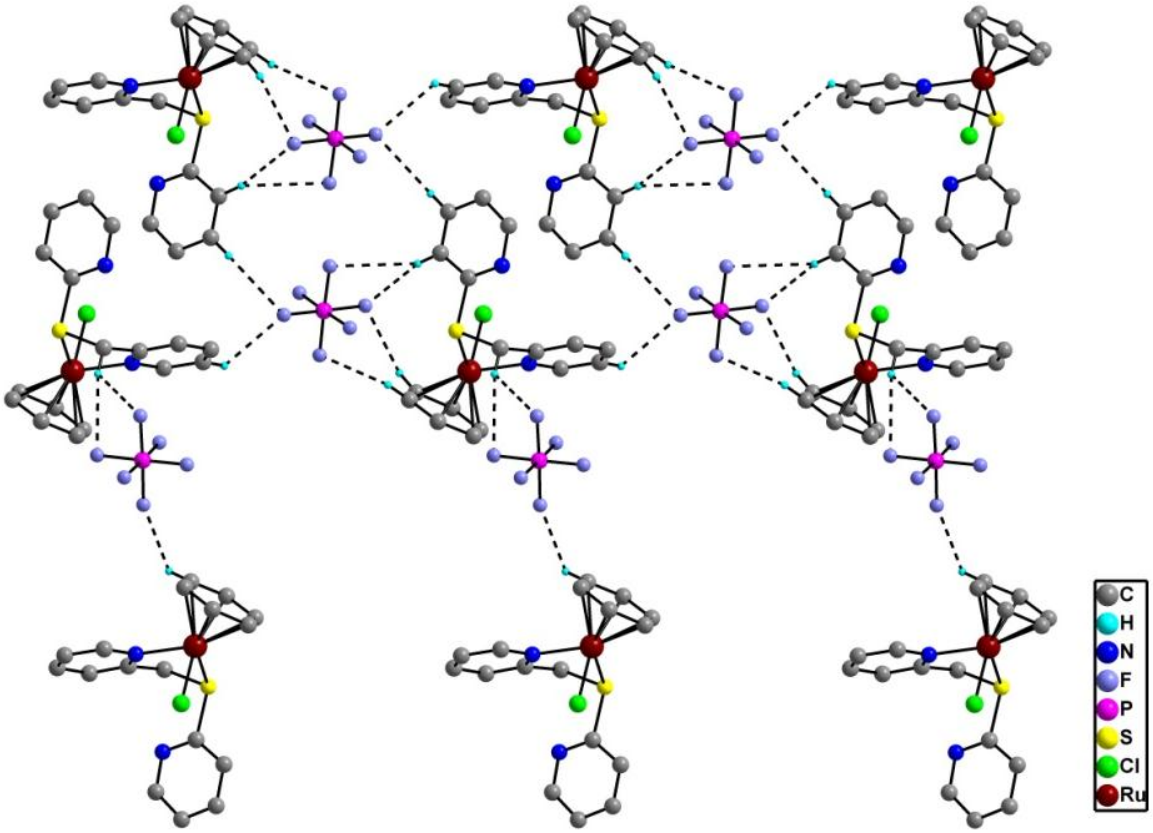

Figure S2. Non-covalent C–H···F interactions in **3**.

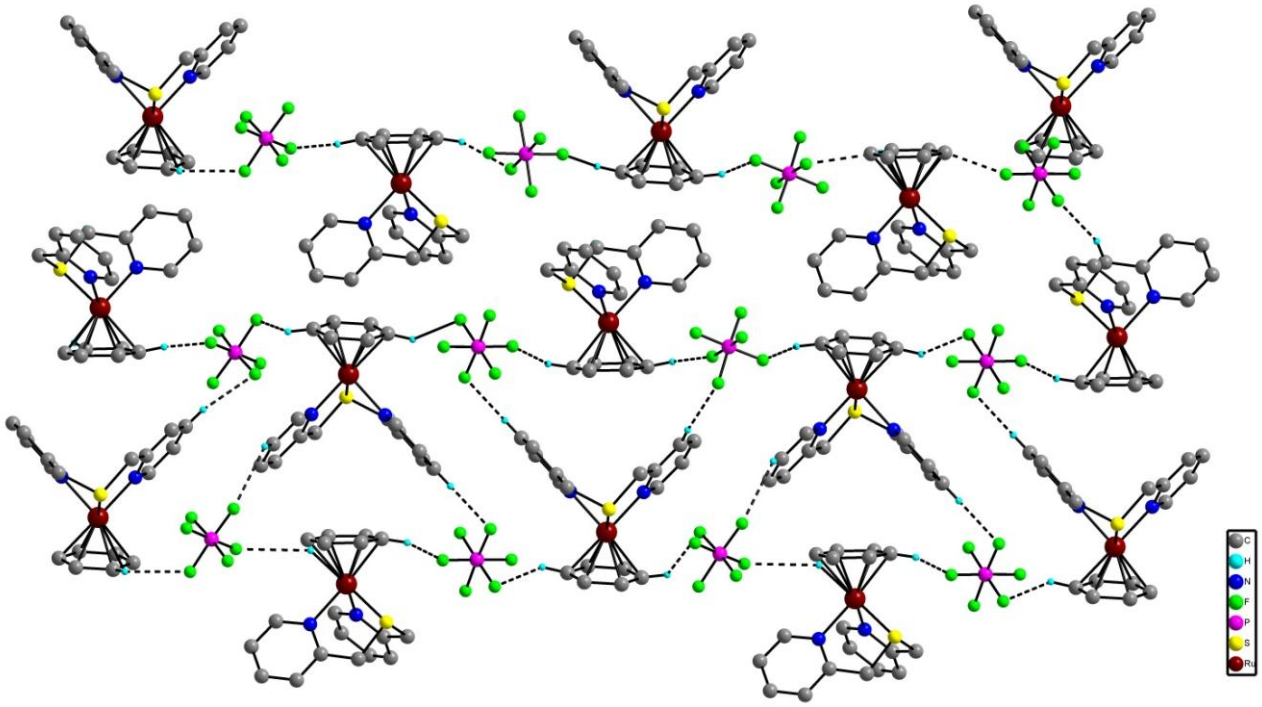

Figure S3. Non-covalent C–H···F interactions in **4**.

7. Secondary C–H···Cl interactions

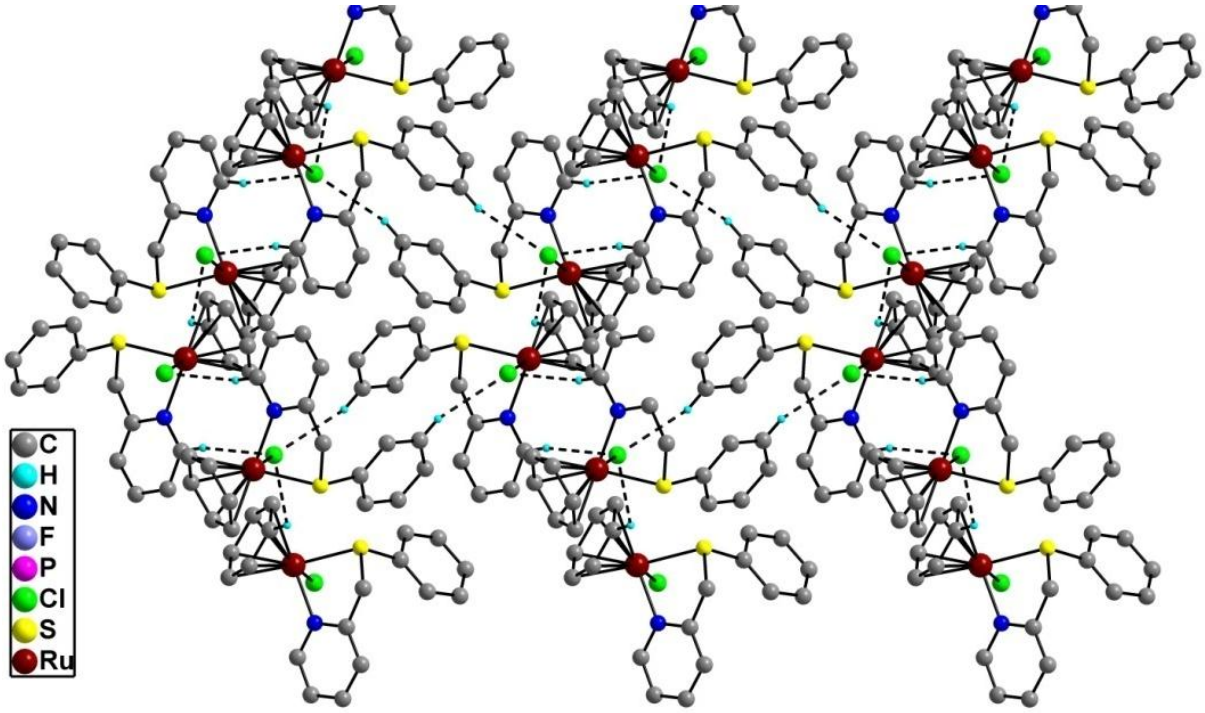

Figure S4. Non-covalent C–H···Cl interactions in **1**.

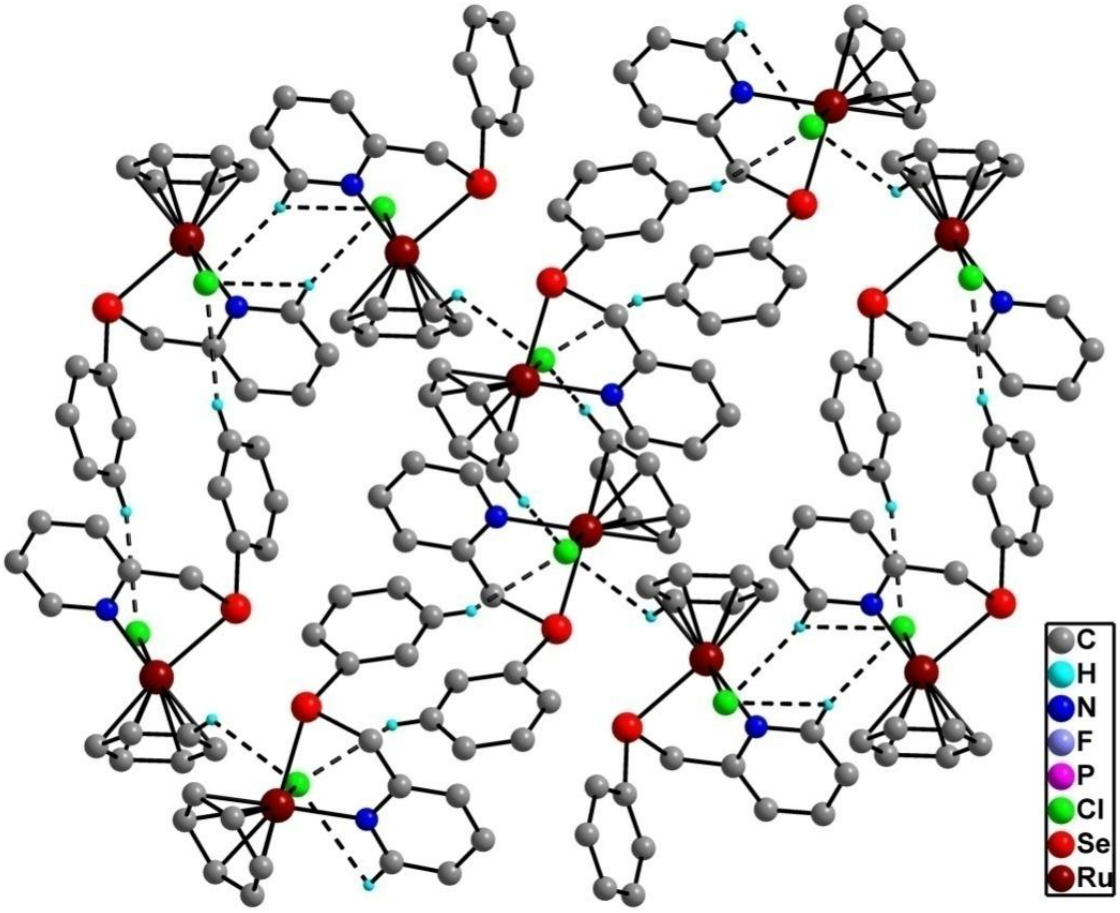

Figure S5. Non-covalent C–H···Cl interactions in **2**.

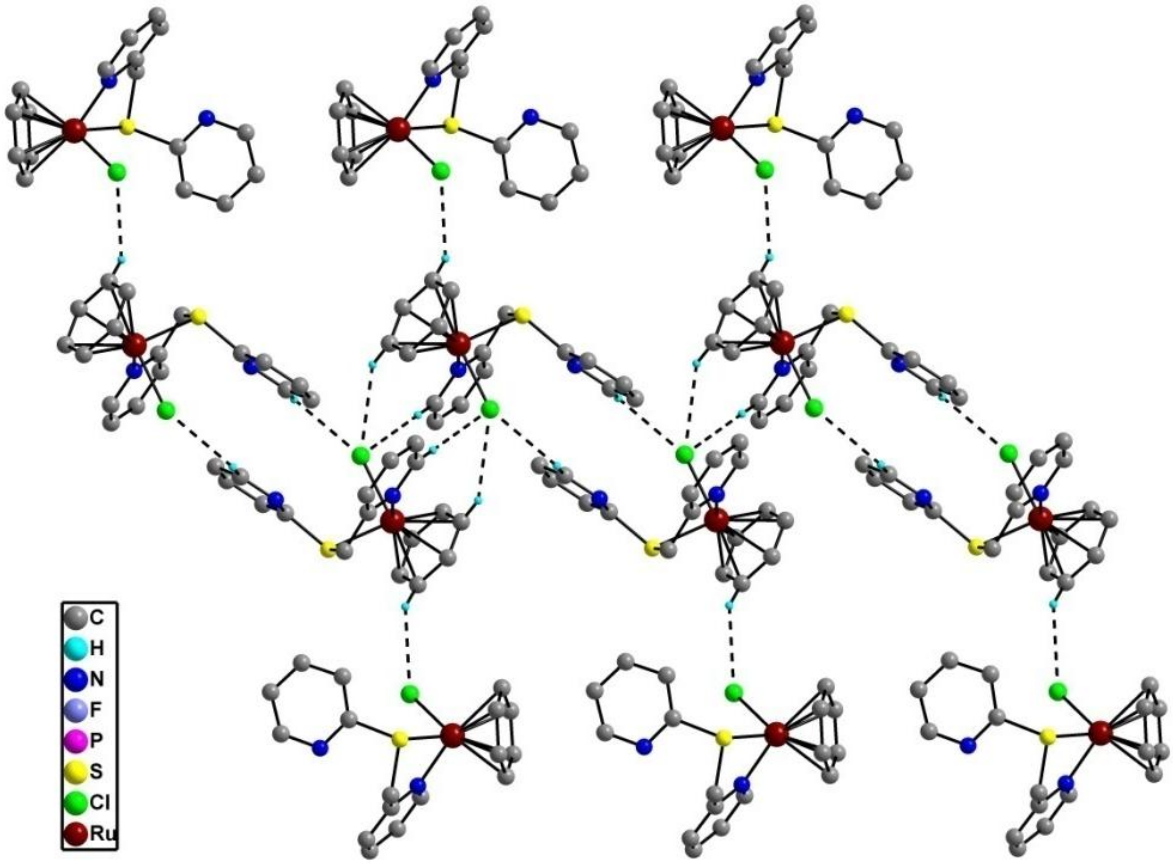

Figure S6. Non-covalent C–H···Cl interactions in **3**

8. Secondary C–H···π interactions

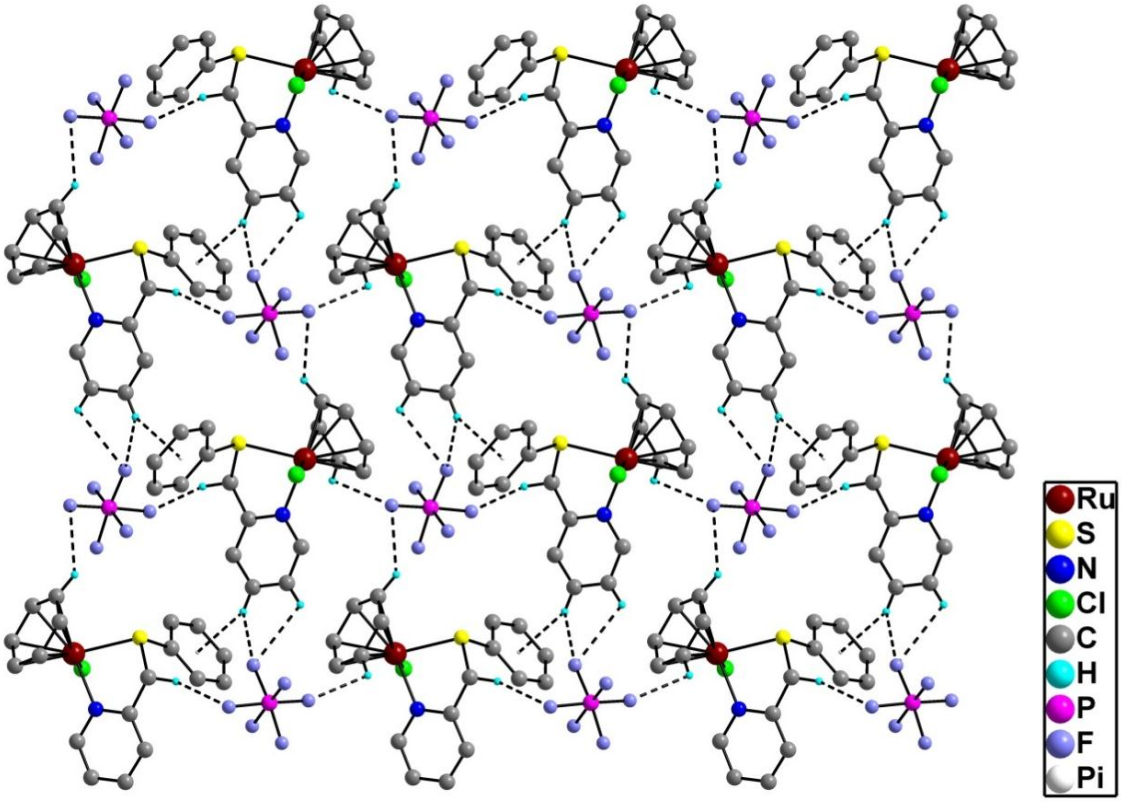

Figure S7. Non-covalent C–H···π interactions in **1**.

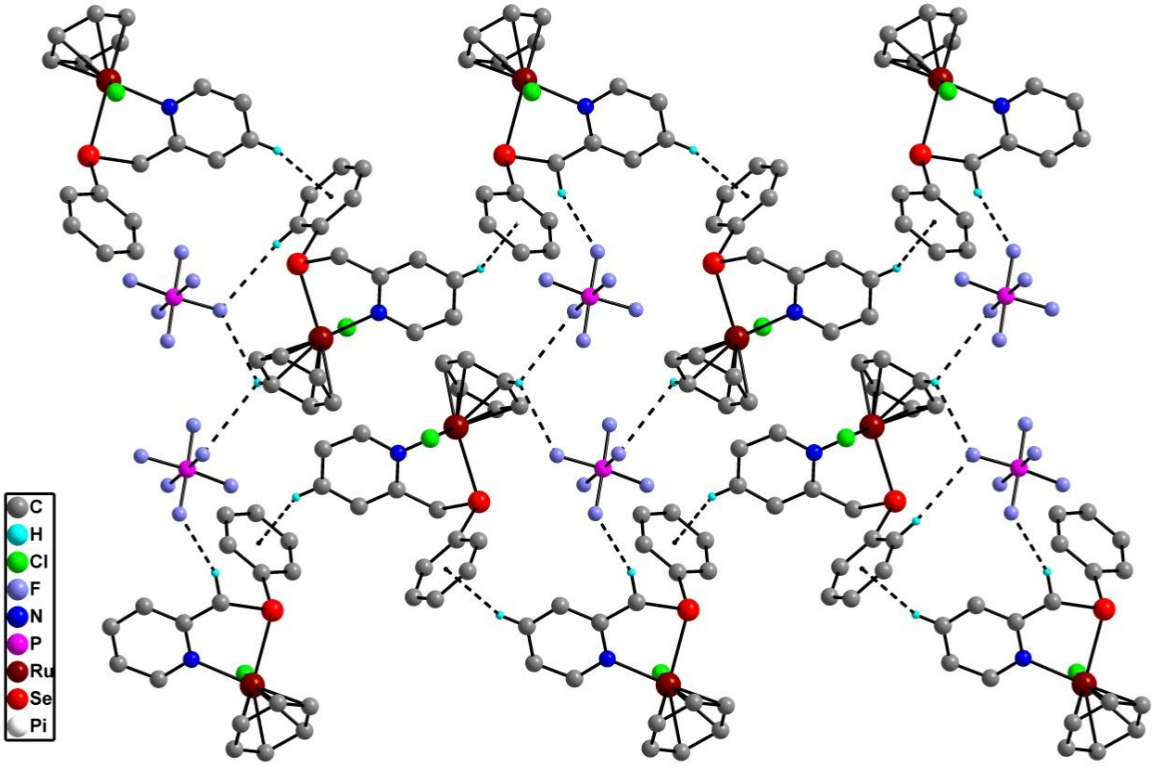

Figure S8. Non-covalent C–H···π interactions in **2**.

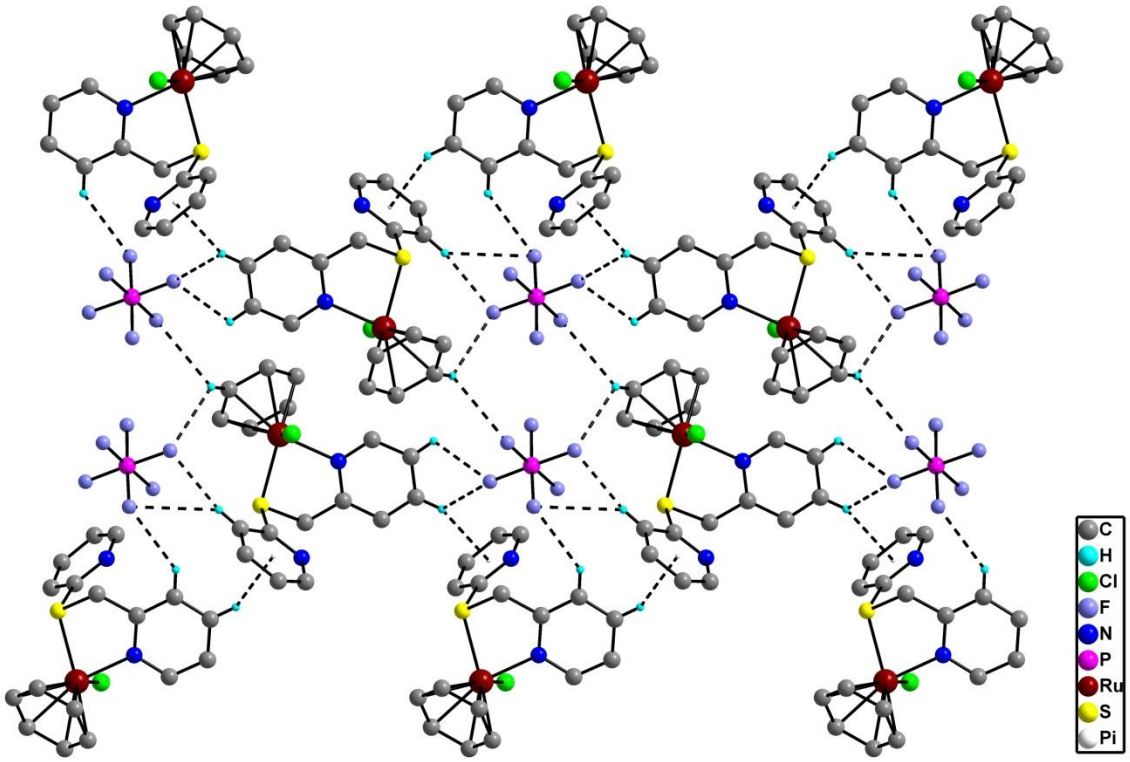

Figure S9. Non-covalent C–H···π interactions in **3**.

9. NMR Spectra

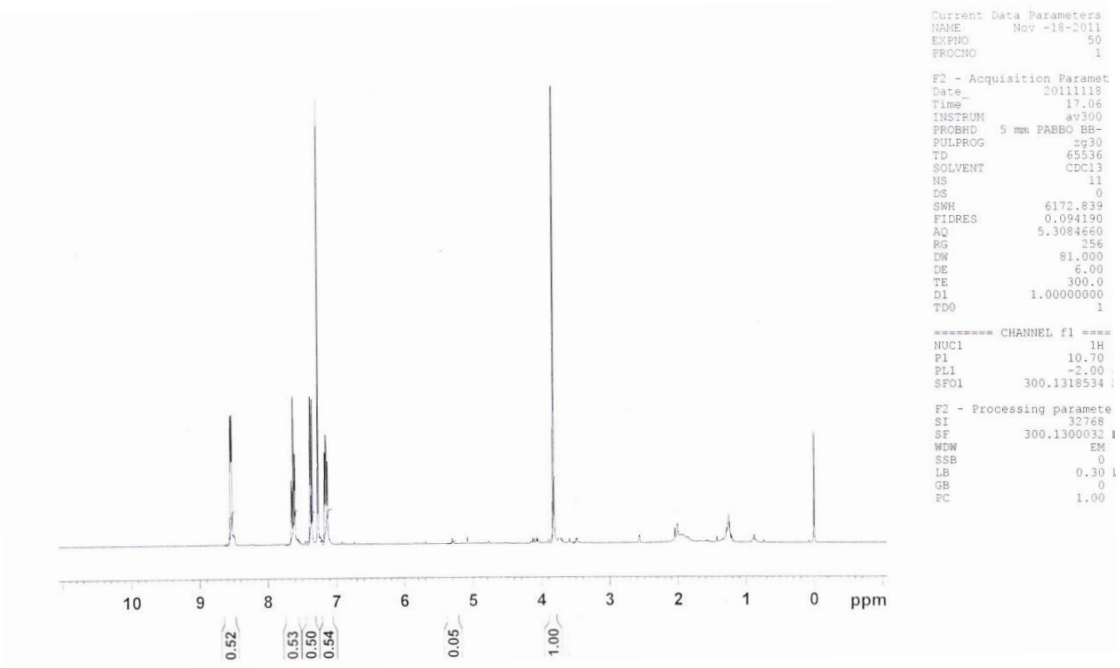

Figure S10. ^{1}H NMR spectra of **L4**

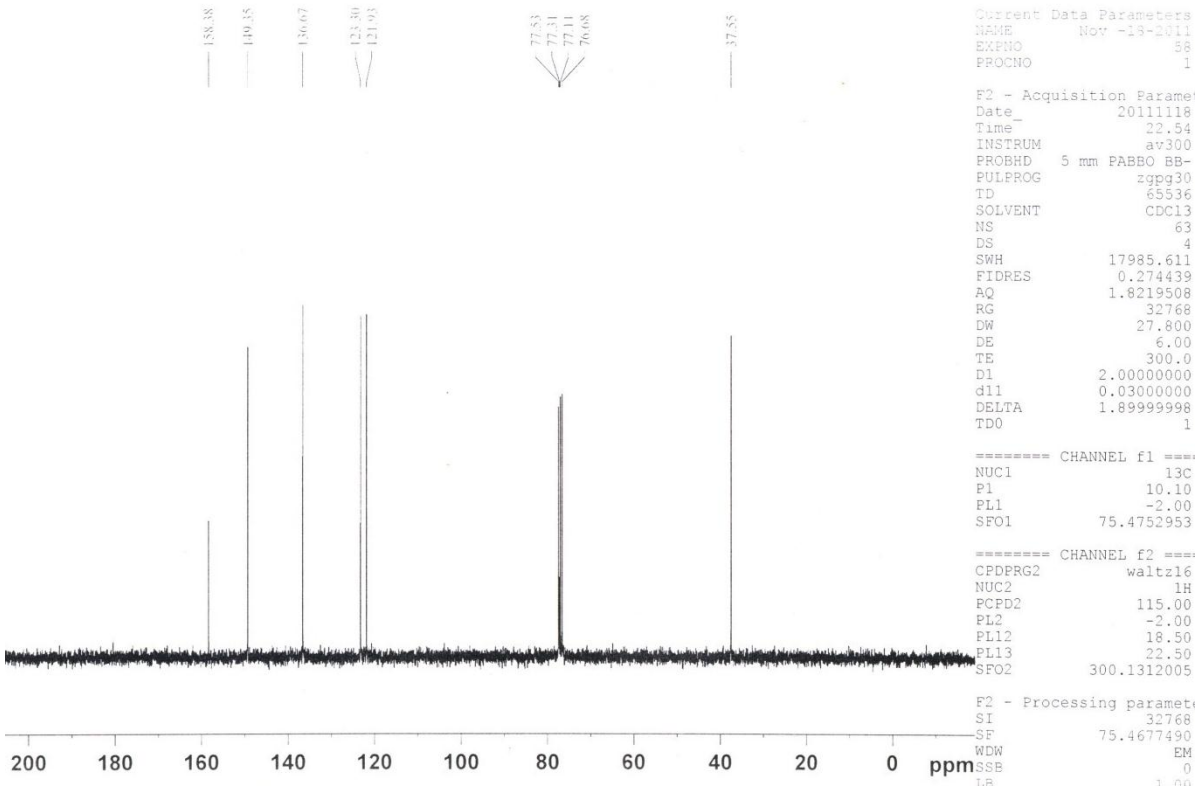

Figure S11. ^{13}C NMR spectra of **L4**

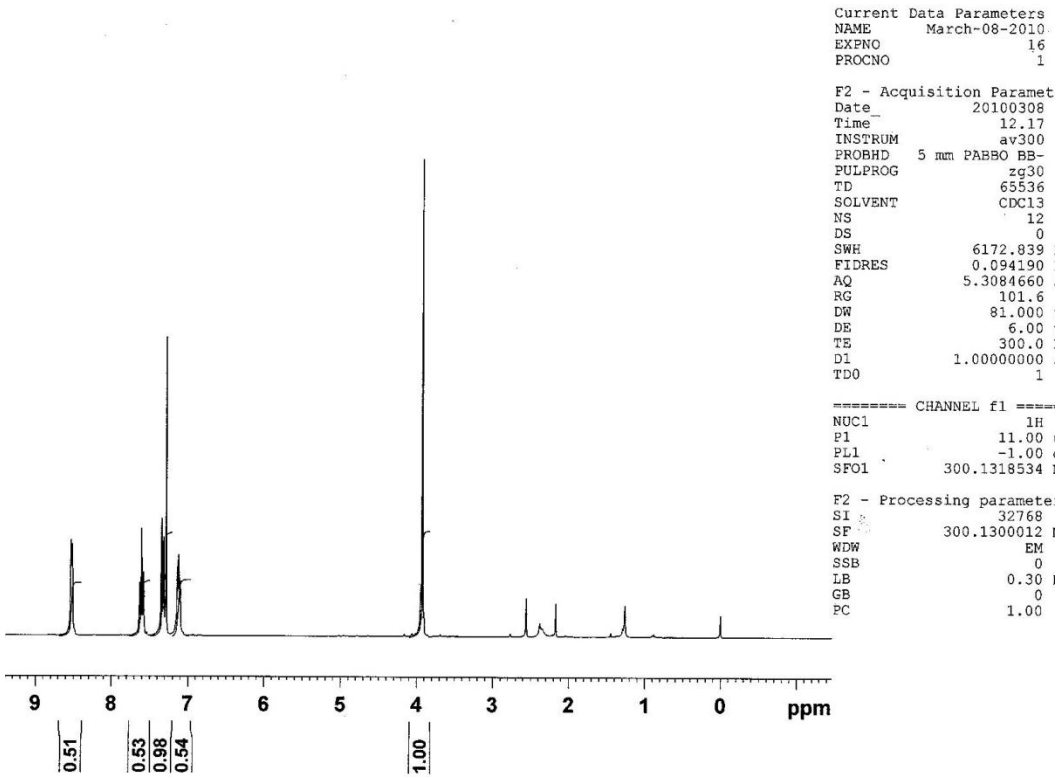

Figure S12. ^{1}H NMR spectra of **L5**

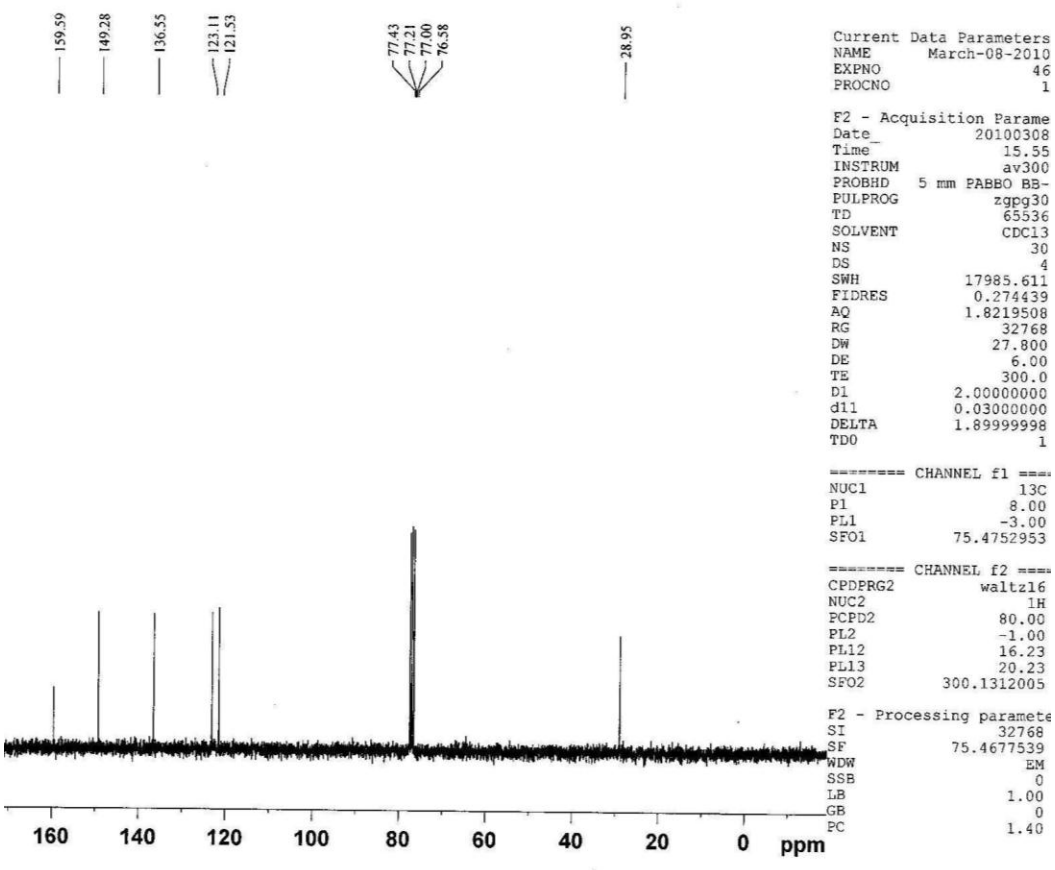

Figure S13. ^{13}C NMR spectra of **L5**

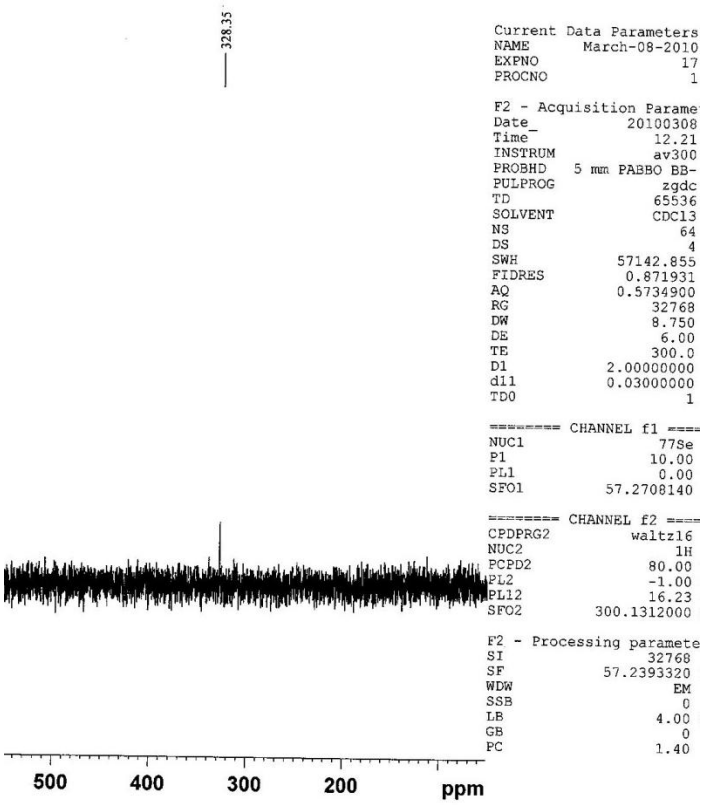

Figure S14. ^{77}SS NMR spectra of **L5**

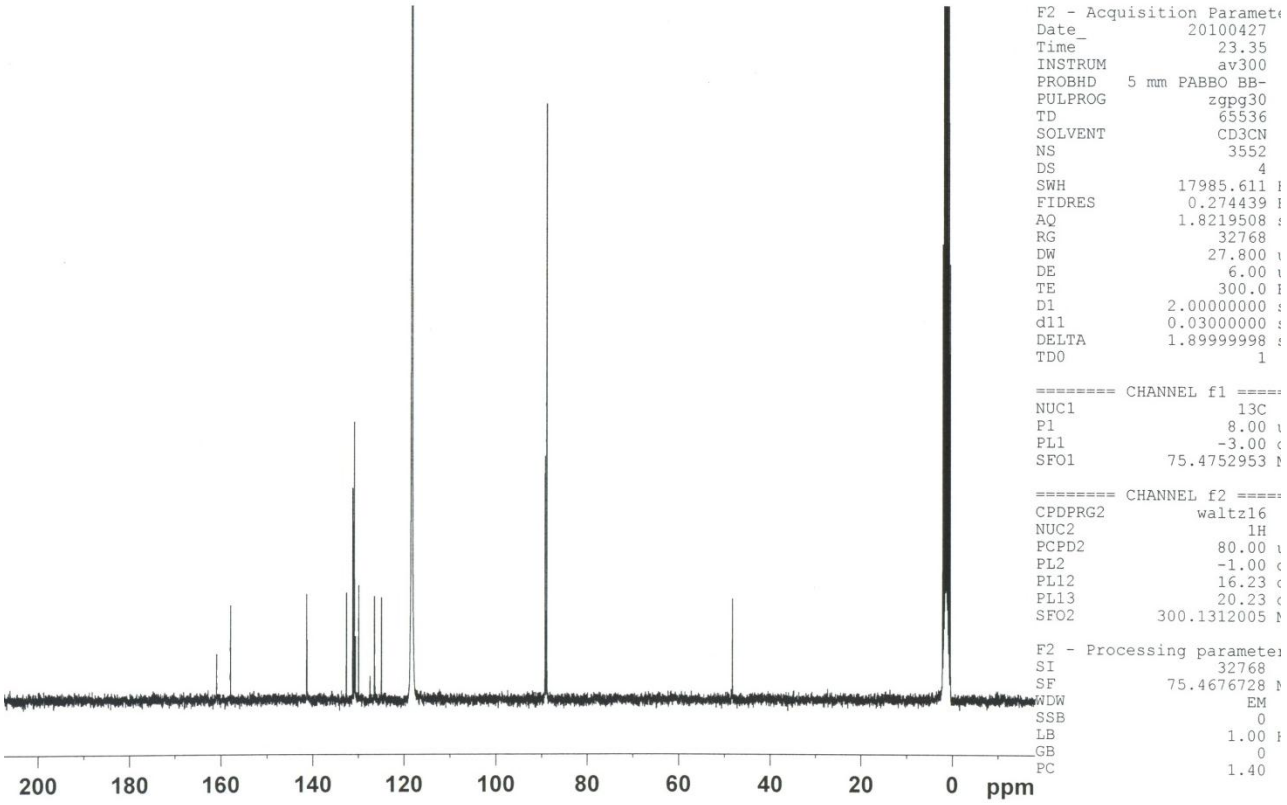

Figure S15. ^{13}C NMR spectra of **1**

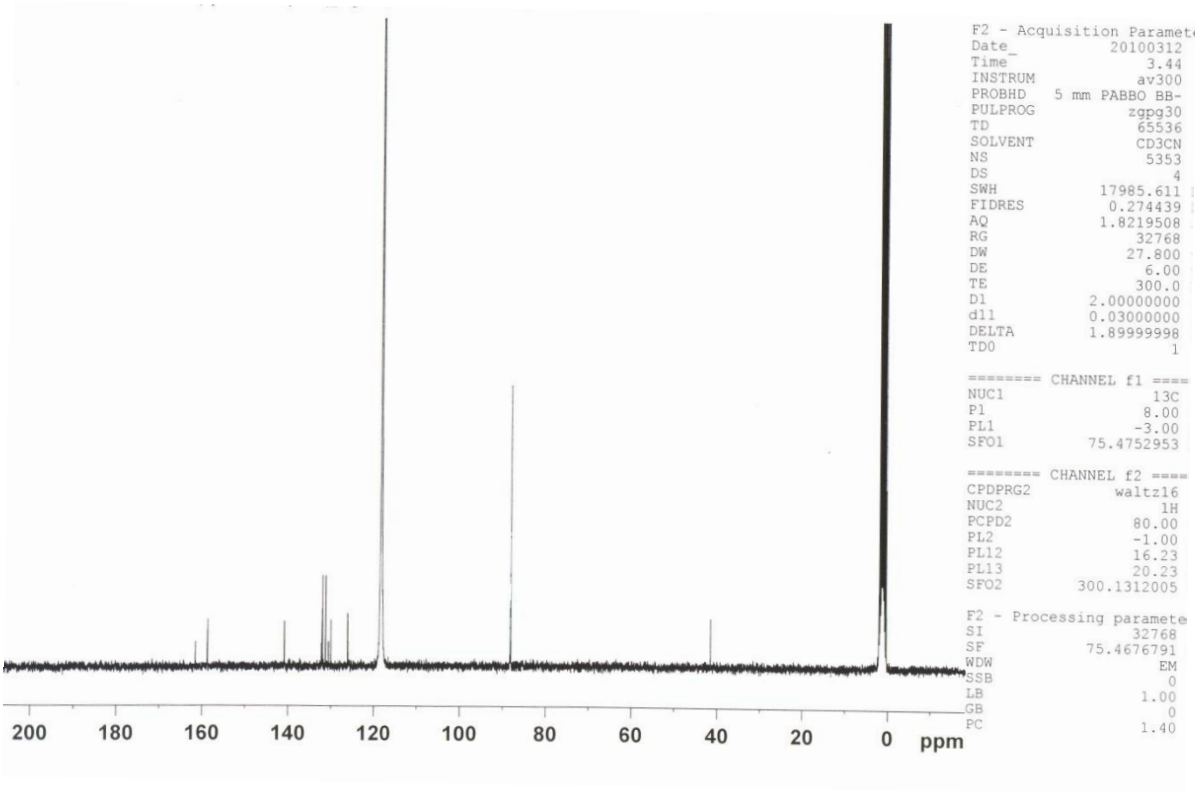

Figure S16. ^{13}C NMR spectra of **2**

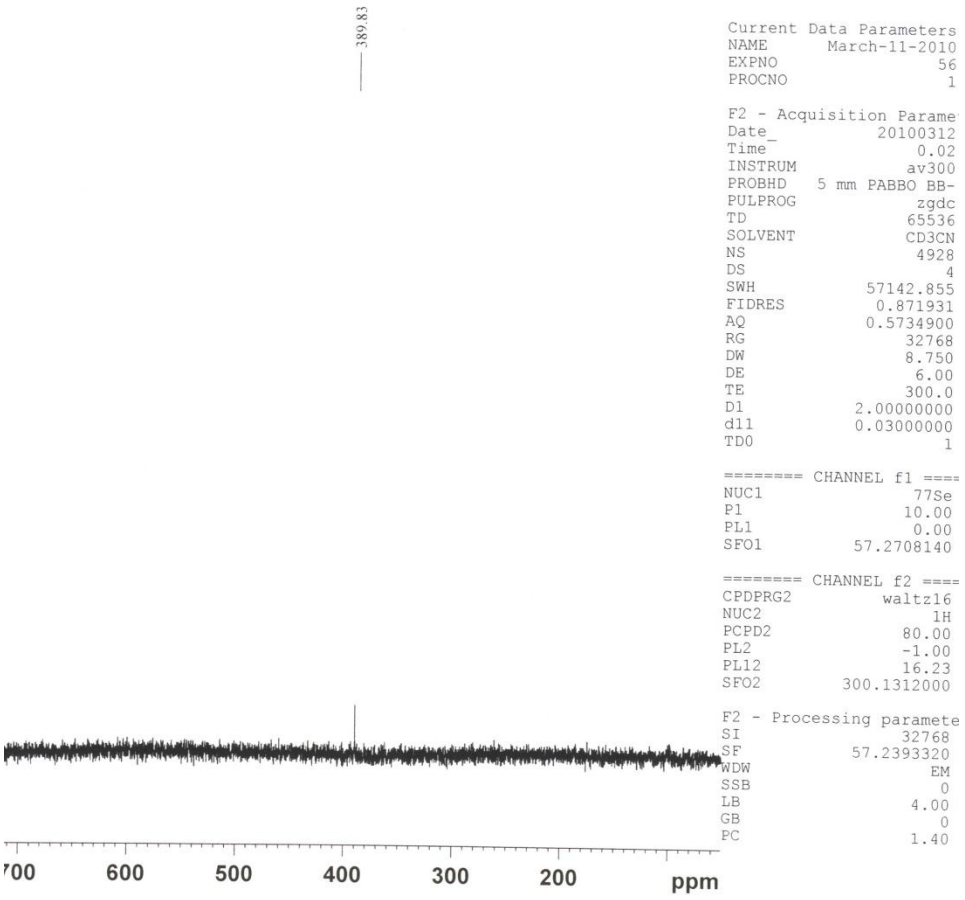

Figure S17. ^{77}Se NMR spectra of **2**

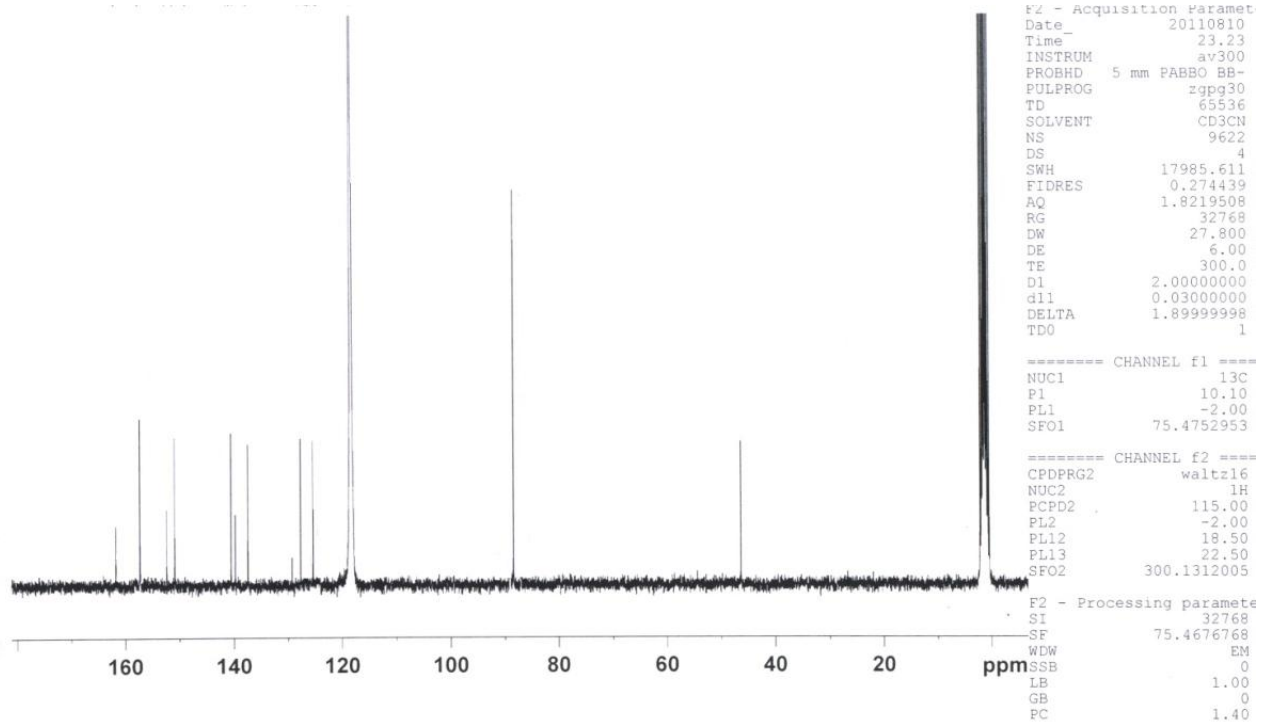

Figure S18. ^{13}C NMR spectra of **3**

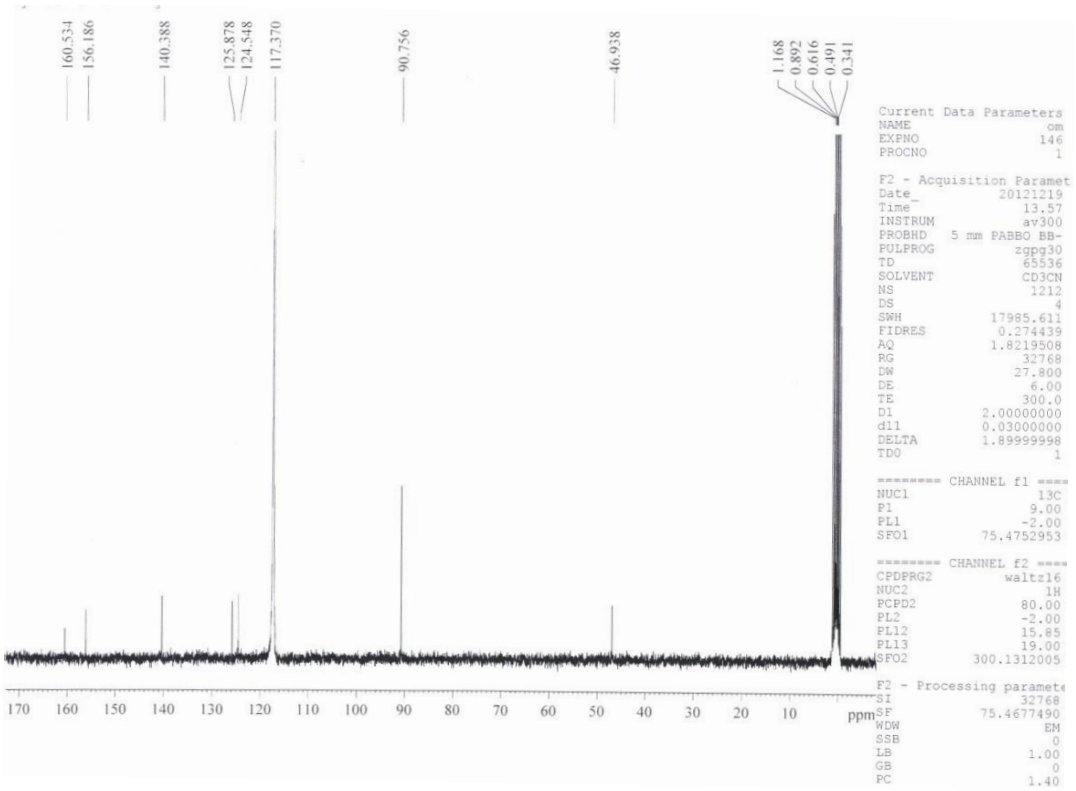

Figure S19. ^{13}C NMR spectra of **4**

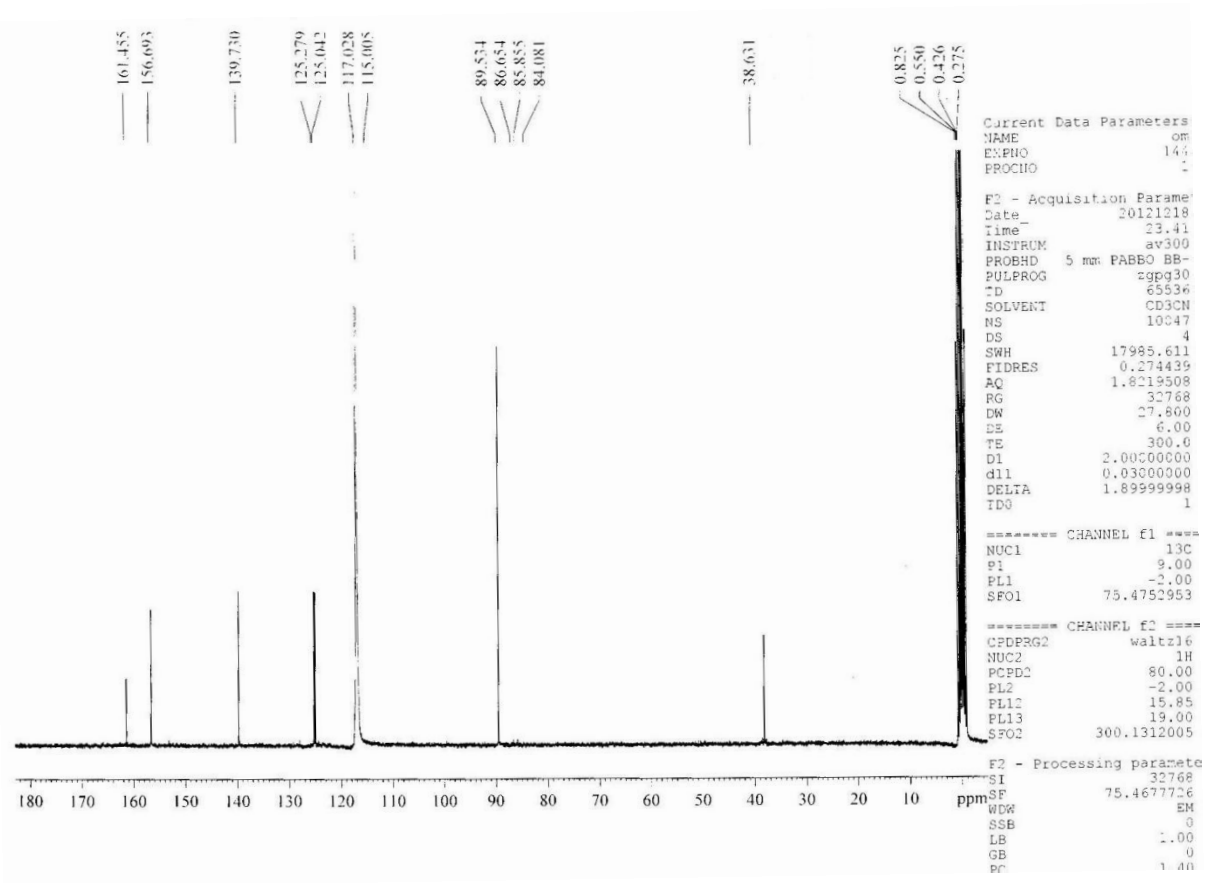

Figure S20. ^{13}C NMR spectra of **5**

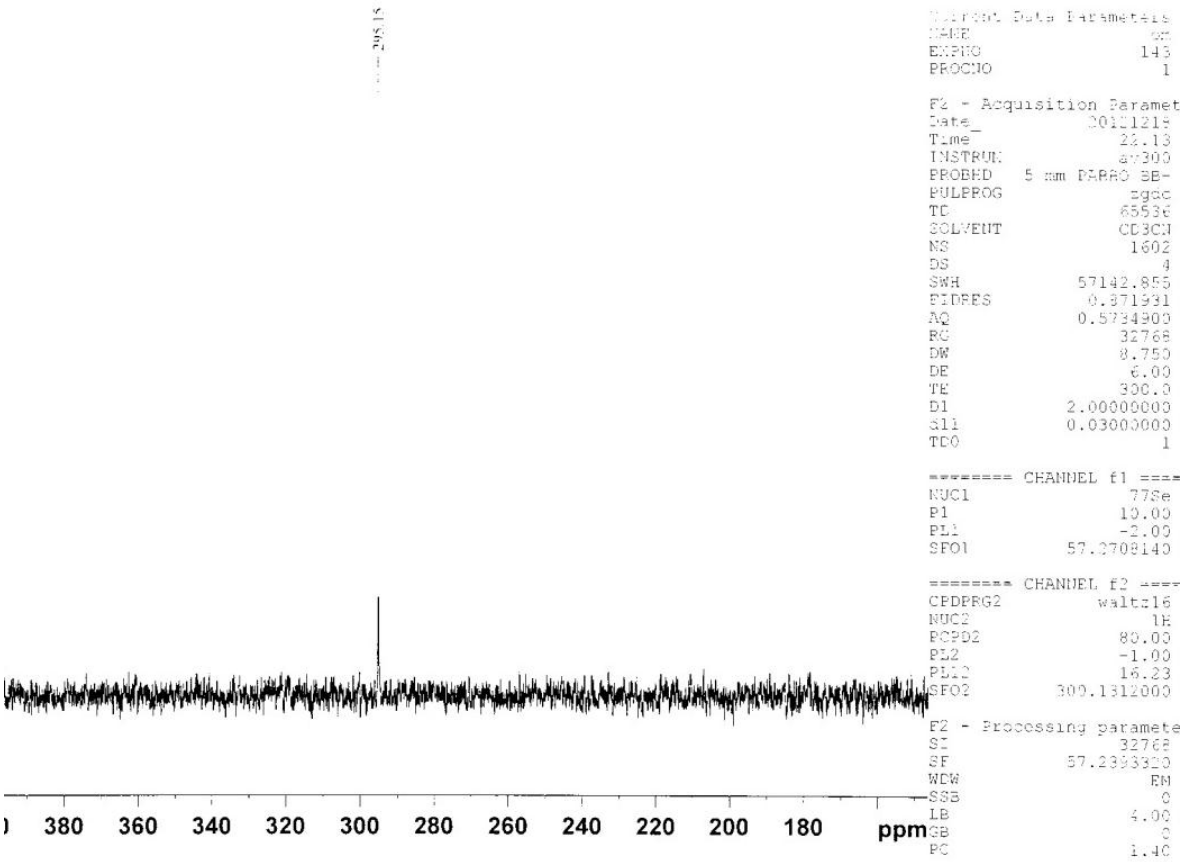

Figure S21. ^{77}Se NMR spectra of **5**