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"Click" generated 1,2,3-triazole based organosulfur/selenium ligands and their Pd(II) and Ru(II) complexes: their synthesis, structure and catalytic applications

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Contents

Table S1 Crystal Data and Structural Refinement Parameters of 1-4

	Complex 1	**Complex 2**
Empirical formula	C21 H25 Cl2 N3 Pd S	C21 H25 Cl2 N3 Pd Se
Formula weight	528.81	575.70
Colour	Orange	Orange
Crystal size, mm^3	0.34 × 0.26 × 0.24	0.35 × 0.26 × 0.24
Crystal system	Triclinic	Triclinic
Space group	*P -1*	*P -1*
Unit Cell dimension	a = 8.6557(19) Å b = 13.346(3) Å c = 21.148(5) Å α = 94.225(5)° β = 92.885(4)° γ = 106.421(5)	a = 8.6059(13) Å b = 13.194(2) Å c = 21.170(3) Å α = 94.485(3)° β = 93.455(3)° γ = 106.073(3)°
Volume [$Å^3$]	2330.5(9)	2294.3(6)
Z	4	4
ρ, (calc.) Mg/m^3	1.507	1.667
μ, mm^{-1}	1.127	2.640
F(000)	1072.0	1144.0
θ, range (°)	2.53 to 24.47	2.53 to 24.47
Index ranges	$-10 \le h \le 10$ $-15 \le k \le 15$ $-25 \le l \le 25$	$-10 \le h \le 9$ $-15 \le k \le 13$ $-21 \le l \le 25$
Reflections collected/unique	22651 / 8190 [R_{int} = 0.0897]	12066 / 7982 [R_{int} = 0.0222]
Completeness to max. θ, %	99.7	98.6
Max./min. Transmission	0.164 / 0.237	0.426 / 0.534
Data/restraints/ parameters	8211 / 0 / 513	8099 / 0/ 513
Goodness–of–fit on F^2	1.180	1.004
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0987, wR_2 = 1665	R_1 = 0.0368, wR_2 = 0.0888
R indices (all data)	R_1 = 0.1416, wR_2 = 0.1822	R_1 = 0.0495, wR_2 = 0.0972
Largest diff. peak/hole [$e.Å^{-3}$]	0.727/−1.576	0.846 /−0.402
CCDC No.	1472950	1472951

	Complex 3	**Complex 4**
Empirical formula	C27H31ClN3RuS,F6P	C27H31ClN3RuSe,F6P
Formula weight	711.11	758.00
Colour	Yellow	Orange
Crystal size, mm^3	0.38 × 0.29 × 0.24	0.36 × 0.28 × 0.25
Crystal system	Monoclinic	Monoclinic
Space group	*P 21/n*	*P -21/n*
Unit Cell dimension	a = 9.624(3) Å b = 19.312(6) Å c = 16.689(5) Å α = 90.00° β = 100.152(5)° γ = 90.00°	a = 9.7255(7) Å b = 19.3313(13)Å c = 16.6941(11)Å α = 90.00° β = 100.3640(10)° γ = 90.00°
Volume [$Å^3$]	3053.2(16)	3087.4(4)
Z	4	4
ρ, (calc.) Mg/m^3	1.547	1.631
μ, mm^{-1}	0.784	1.883
F(000)	1440.0	1512.0
θ, range (°)	2.28 to 20.72	2.26 to 23.80
Index ranges	$-11 \le h \le 11$ $-22 \le k \le 22$ $-19 \le l \le 19$	$-11 \le h \le 11$ $-22 \le k \le 22$ $-19 \le l \le 19$
Reflections collected/unique	29060 / 5387[R_{int} = 0.0506]	29274 / 5444 [R_{int} = 0.0398]
Completeness to max. θ, %	99.9	98.9
Max./min. Transmission	0.760 / 825	0.533 / 0.628
Data/restraints/ parameters	5387 / 0 / 365	5444 / 0/ 365
Goodness–of–fit on F^2	1.051	1.028
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0482, wR_2 = 0.1261	R_1 = 0.0448, wR_2 = 0.1155
R indices (all data)	R_1 = 0.0627, wR_2 = 0.1341	R_1 = 0.0546, wR_2 = 0.1215
Largest diff. peak/hole [$e.Å^{-3}$]	0.801/−0.392	0.787 /−0.432
CCDC No.	1472952	1472953

Table S2 Selected Bond Lengths and Bond Angles of Complex 1

Bond Distance (Å)		Bond Angle (°)	
Pd(1)—N(3)	2.002(8)	N(3)—Pd(1)—S(1)	84.7(2)
Pd(1)—S(1)	2.277(3)	N(3)—Pd(1)—Cl(1)	173.9(2)
Pd(1)—Cl(1)	2.295(3)	S(1)—Pd(1)—Cl(1)	89.52(11)
Pd(1)—Cl(2)	2.297(3)	N(3)—Pd(1)—Cl(2)	93.6(2)
S(1)—C(1)	1.778(12)	S(1)—Pd(1)—Cl(2)	177.44(10)
S(1)— C(7)	1.811(10)	Cl(1)—Pd(1)—Cl(2)	92.07(11)
N(3)—N(2)	1.306(11)	C(1)—S(1)—C(7)	103.7(5)
N(3)—C(8)	1.385(12)	C(1)—S(1)—Pd(1)	101.0(3)
N(2)—N(1)	1.348(11)	C(7)—S(1)—Pd(1)	99.3(3)
N(1)—C(9)	1.346(11)	N(2)—N(3)—C(8)	110.2(8)
N(1)—C(10)	1.455(12)	N(2)—N(3) —Pd(1)	129.6(6)

Table S3 Selected Bond Lengths and Bond Angles of Complex 2

Bond Distance (Å)		Bond Angle (°)	
Pd(1)—N(3)	2.011(3)	N(3)—Pd(1)— Cl(2)	175.20(11)
Pd(1)—Cl(2)	2.2815(12)	N(3)—Pd(1)—Cl(1)	93.13(11)
Pd(1)— Cl(1)	2.3188(12)	Cl(2)—Pd(1)—Cl(1)	91.57(4)
Pd(1)—Se(1)	2.3840(6)	N(3)—Pd(1)—Se(1)	85.05(10)
Se(1)— C(6)	1.937(4)	Cl(2)—Pd(1)—Se(1)	90.23(4)
Se(1)— C(7)	1.968(4)	Cl(1)—Pd (1)—Se(1)	177.62(3)
N(3)—N(2)	1.317(5)	C(6)—Se(1)—C(7)	96.71(18)
N(3)— C(8)	1.374(5)	C(6)—Se(1)—Pd(1)	103.69(15)
N(2)— N(1)	1.338(5)	C(7)—Se(1)—Pd(1)	95.56(13)
N(1)—C(9)	1.357(5)	N(2)—N(3)—C(8)	111.2(3)

Table S4 Selected Bond Lengths and Bond Angles of Complex 3

Bond Distance (Å)		Bond Angle (°)	
C(30)—Ru(1)	2.152(6)	N(3)—Ru(1)—C(25)	92.27(18)
C(29)—Ru(1)	2.177(7)	N(3)—Ru(1)—C(30)	133.6(4)
C(28)—Ru(1)	2.174(5)	N(3)—Ru(1)—C(24)	142.9(3)
Ru(1)—N(3)	2.082(3)	N(3)—Ru(1)—C(23)	169.5(3)
Ru(1)—C(25)	2.143(6)	N(3)—Ru(1)—C(28)	108.1(2)
Ru(1)—C(24)	2.168(5)	N(3)—Ru(1)—C(29)	103.0(3)
Ru(1)—C(23)	2.169(5)	N(3)—Ru(1)—S(1)	80.42(9)
Ru(1)—Cl(1)	2.3993(14)	C(25)—Ru(1)—S(1)	141.9(3)
Ru(1)—S(1)	2.3728(12)	C(30)—Ru(1)—S(1)	93.22(19)
S(1)—C(21)	1.781(5)	C(24)—Ru(1)—S(1)	134.9(3)
S(1)—C(3)	1.825(4)	C(23)—Ru(1)—S(1)	103.7(2)
N(3)—N(2)	1.317(4)	C(28)—Ru(1)—S(1)	170.85(18)
N(1)—N(2)	1.340(4)	S(1)—Ru(1)—Cl(1)	80.89(5)

Table S5 Selected Bond Lengths and Bond Angles of Complex 4

Bond Distance (Å)		Bond Angle (°)	
Ru(1)—N(3)	2.081(3)	N(3)—Ru(1)—C(7)	130.3(3)
Ru(1)—C(7)	2.154(6)	N(3)—Ru(1)—C(11)	92.6(2)
Ru(1)—C1(1)	2.157(6)	N(3)— Ru(1)—C(8)	167.4(3)
Ru(1)—C(8)	2.159(6)	N(1)— Ru(1)—C(9)	145.1(3)
Ru(1)—C(9)	2.168(6)	N(3)—Ru(1)— C(12)	100.9(3)
Ru(1)—C(12)	2.171(7)	N (3)—Ru(1)— C(10)	110.0(2)
Ru(1)—C(10)	2.181(6)	N(3)—Ru(1)— Cl(1)	84.53(10)
Ru(1)—Cl(1)	2.3973(14)	N(3)—Ru(1)—Se(1)	81.36(9)
Ru(1)—Se(1)	2.4741(6)	C(7)—Ru (1)—Se(1)	93.3(2)
Se(1)—C(6)	1.931(5)	C(11)—Ru(1)—Se(1)	145.5(4)
Se(1)— C(13)	1.957(4)	C(8)—Ru(1)—Se(1)	101.3(2)
N(3)—N(2)	1.316(4)	C (9)—Ru(1)—Se(1)	131.8(2)
N(3)—C(14)	1.358(5)	C(12)—Ru(1)—Se(1)	111.7(3)
N(2)—N(3)	1.337(5)	C(10)—Ru(1)—Se(1)	168.6(2)
N(3)—C(15)	1.354(6)	Cl(1)—Ru(1)—Se(1)	80.15(4)

Table S6 Selected bond lengths (Å) and angles (°) for 1─4 calculated from DFT studies

Complex 1		**Complex 2**	
Bond lengths (Å)	calculated value	Bond lengths (Å)	calculated value
Pd−S	2.473	Pd−Se	2.520
Pd−N	2.089	Pd−N	2.088
Pd−Cl(1)	2.302	Pd−Cl(1)	2.312
Pd−Cl(2)	2.302	Pd−Cl(2)	2.309
Bond angles(°)		Bond angles(°)	
N−Pd−S	82.96	N−Pd−Se	84.40
N−Pd−Cl(1)	93.75	N−Pd−Cl	93.48
S−Pd−Cl(2)	91.16	Se−Pd−Cl(2)	89.83
Cl(1)−Pd−Cl(2)	92.19	Cl(1)−Pd−Cl(2)	92.37
S−Pd−Cl(1)	176.00	Se−Pd−Cl(1)	176.61
N−Pd−Cl(2)	173.89	N−Pd−Cl(2)	173.92
Complex 3		**Complex 4**	
Bond lengths (Å)	calculated value	Bond lengths (Å)	calculated value
Ru−S	2.373	Ru−Se	2.474
Ru−N	2.082	Ru−N	2.081
Ru−Cl(1)	2.399	Ru−Cl(1)	2.397
Ru−C	0.800	Ru−C	1.678
Bond angles(°)		Bond angles(°)	
N−Ru−S	80.42	N−Ru−Se	81.36
N−Ru−Cl(1)	84.94	N−Ru−Cl(1)	84.52
S−Ru−Cl(1)	80.89	Se−Ru−Cl(1)	80.15

Poisoning test for coupling reactions:

General procedure: A mixture of 4-bromobenzaldehyde (0.5 mmol), phenylboronic acid (0.6 mmol) (for SMC)/phenyl acetylene (0.6 mmol) (for Sonogashira coupling), K_2CO_3 (0.8 mmol), solvent (3 mL), in the presence of complex **1** was heated at optimum temperature. Then excess of poisoning agent (*viz.* Hg(0) (Hg:Pd = 400:1 or 4 mol% (10 mg) of PPh_3) was added after 10 min (Table S7) / 1h (Table S8) and the reaction mixture was stirred at same temperature up to optimum time. After the standard workup of the reaction mixture, % conversion was determined by ^1H NMR. The results are shown in Tables S7 and S8. In fresh reaction mixtures poisoning was made after 20 min (Table S7) / 2 or 4 h (Table S8) and % conversion determined after continuing reaction for optimum time.

Table S7 Poisoning experiments for SMC.[a]

Entry No.	time	No Poison % conversion (NMR)	Addition of Hg(0)/ PPh_3: % conversion (NMR)[b]
1	10 min	35	74/80
2	20 min	78	83/91

[a]Reaction conditions: 4-bromobenzaldehyde (0.092 g, 0.5 mmol), phenylboronic acid (0.6 mmol, 0.072 g), K_2CO_3 (0.11 g, 0.8 mmol), 3 mL water, temperature of bath 100 °C, 0.1 mol % complex **1**. [b]Conversion after 2 h (by standard workup of whole reaction mixture).

Table S8. Poisoning experiments for Sonogashira coupling.[a]

Entry No.	time	No Poison % conversion (NMR)	Addition of Hg(0)/ PPh_3: % conversion (NMR)[b]
1	1 h	<10	42/51
2	2 h	35	73/77
3	4 h	79	79/85

[a]Reaction conditions: 4-bromobenzaldehyde (0.092 g, 0.5 mmol), 0.6 mmol (0.061 g) of phenylacetylene, 0.8 mmol (0.110 g) of K_2CO_3, CuI equiv. to 2 mol%, 3 mL DMF, temperature of bath 120 °C, N_2 atmosphere, 1 mol % complex **1**, [b]Conversion after 10 h (by standard workup of whole reaction mixture).

Poisoning test for hydrogen transfer reaction:

General procedure: Three sets of aldehyde (0.5 mmol), KOH (0.028 g, 0.5 mmol), glycerol (0.184 g, 2.0 mmol) and complex **4** (0.1 mol %) were mixed in water (3 mL) and the mixture heated at 110 °C. At time intervals given in Tables S9, excess of poisoning reagent *viz.* Hg (Hg:Ru = 500:1) or PPh_3 (0.013 g; 5 mol%) was added (i.e. in one after 1h, second after 2h and third after 3 h) and the reaction was further carried under similar conditions for optimum

time. Conversion into corresponding product (alcohol) was monitored by ^{1}H NMR. The results are given in Table S9.

Table S9. Poisoning experiments for transfer hydrogenation.[a]

Entry No.	time	No Poison % conversion (NMR)	Addition of Hg(0)/ PPh_3: % conversion (NMR)[b]
1	1 h	21	91/82
2	2 h	37	90/79
3	3 h	63	95/85

[a]Reaction conditions: benzaldehyde (0.053 g, 0.5 mmol), 0.5 mmol of K_2CO_3, 3 mL DMF, temperature of bath 110 °C, 0.1 mol % complex **4**, [b]Conversion after 8 h (by standard workup of reaction mixture).

NMR spectra of ligands and complexes:

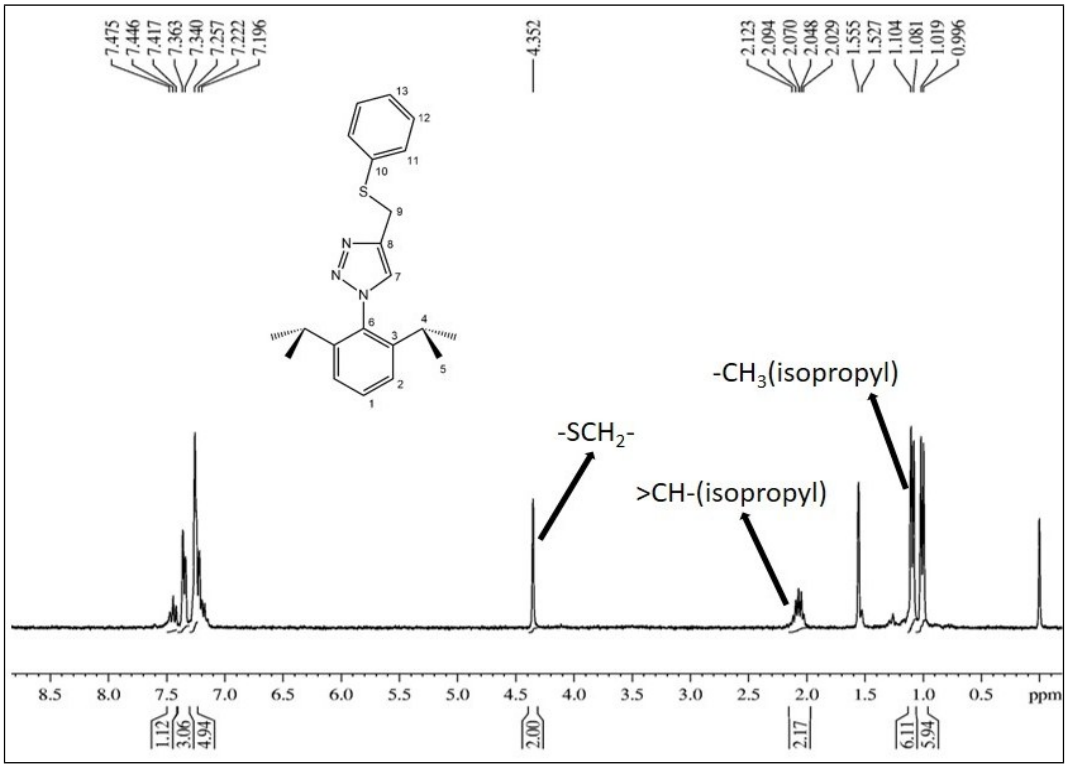


Figure S1 ^{1}H NMR Spectrum of **L1**

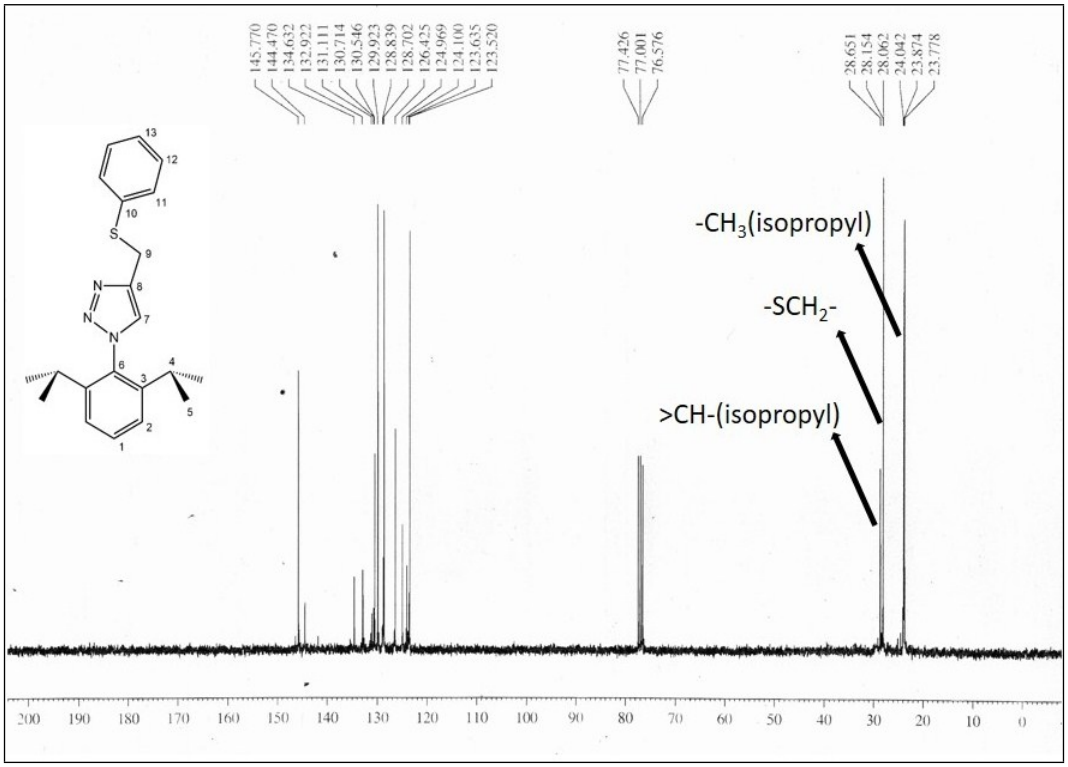


Figure S2 $^{13}C\{^{1}H\}$ NMR Spectrum of **L1**

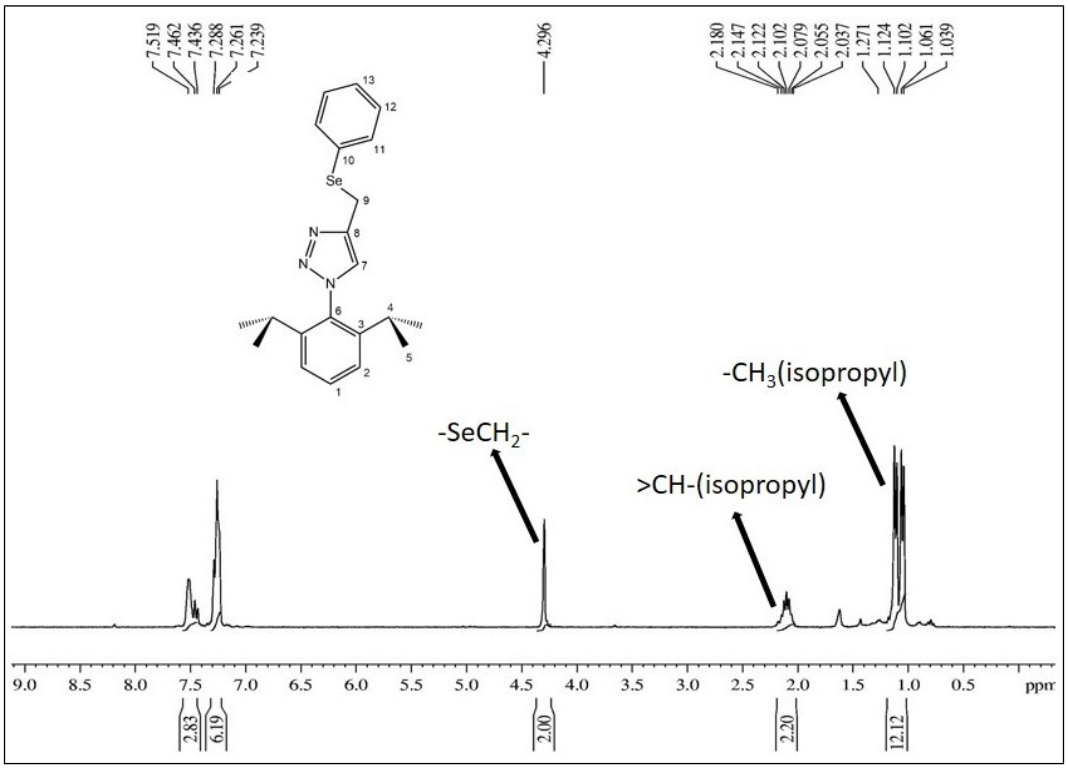


Figure S3 ^{1}H NMR Spectrum of **L2**

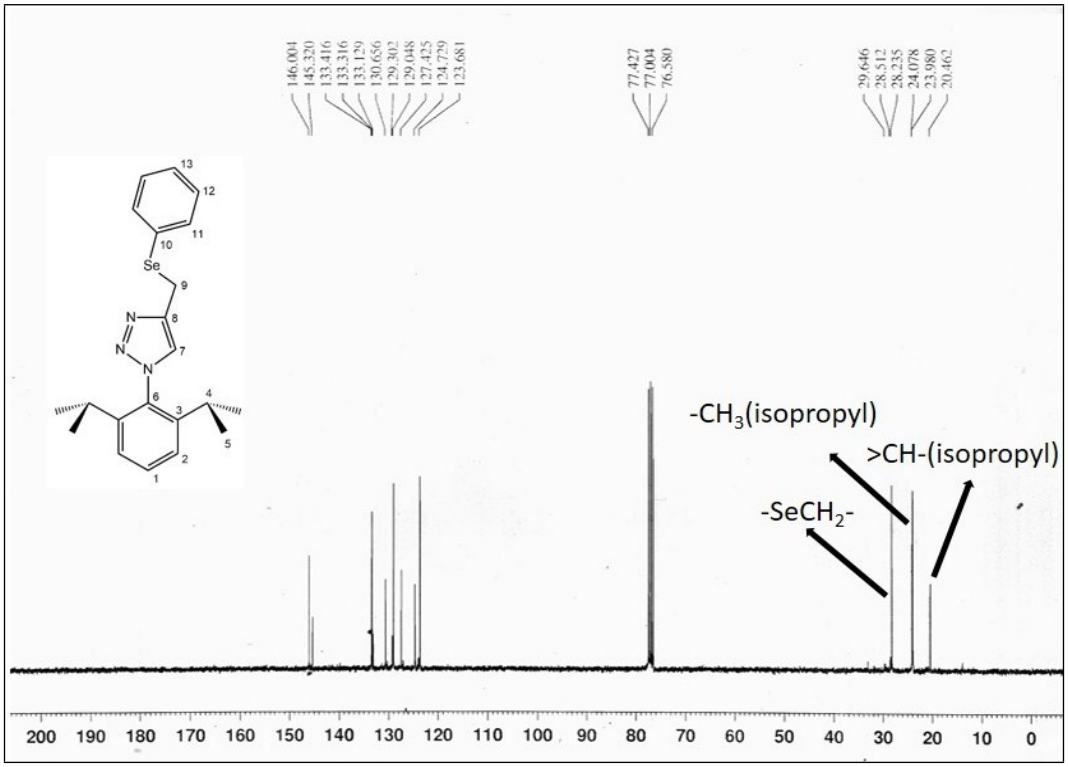


Figure S4 $^{13}C\{^{1}H\}$ NMR Spectrum of **L2**

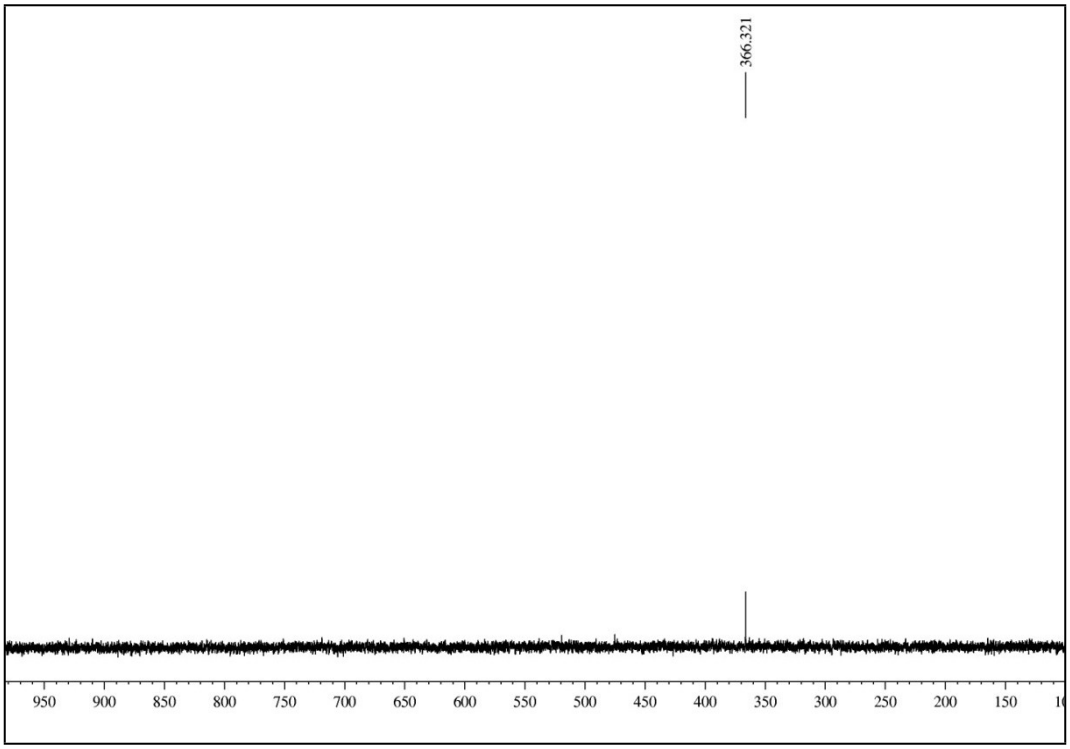


Figure S5 $^{77}Se\{^{1}H\}$ NMR Spectrum of **L2**

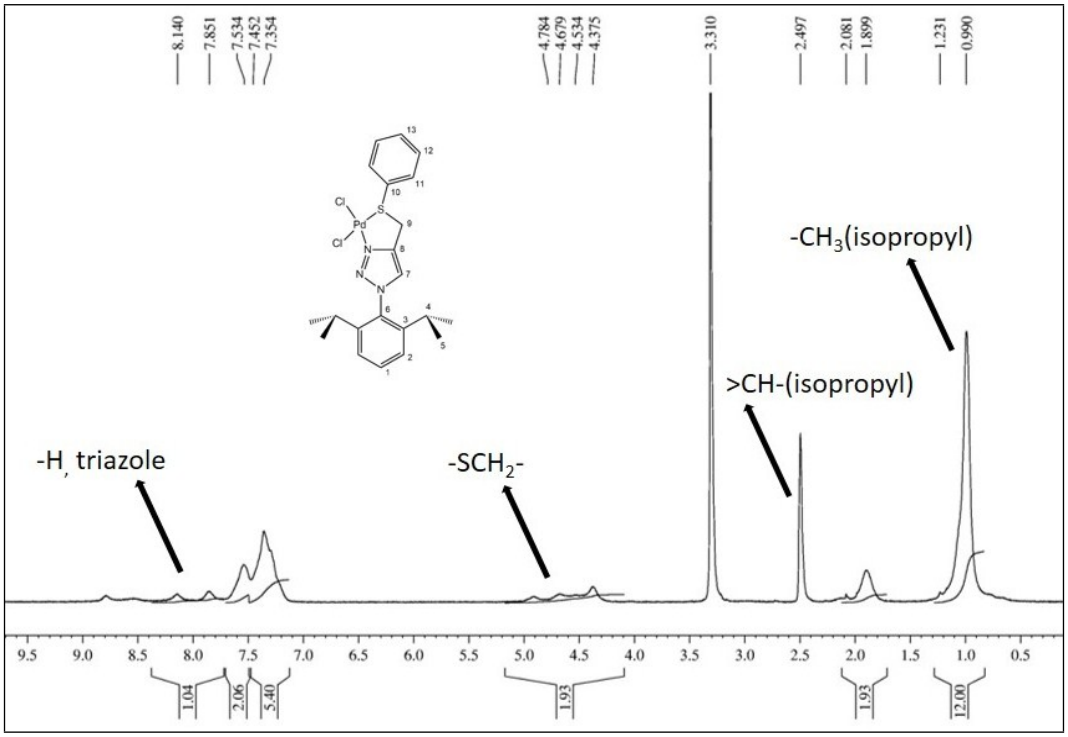


Figure S6 ^{1}H NMR Spectrum of Complex **1**

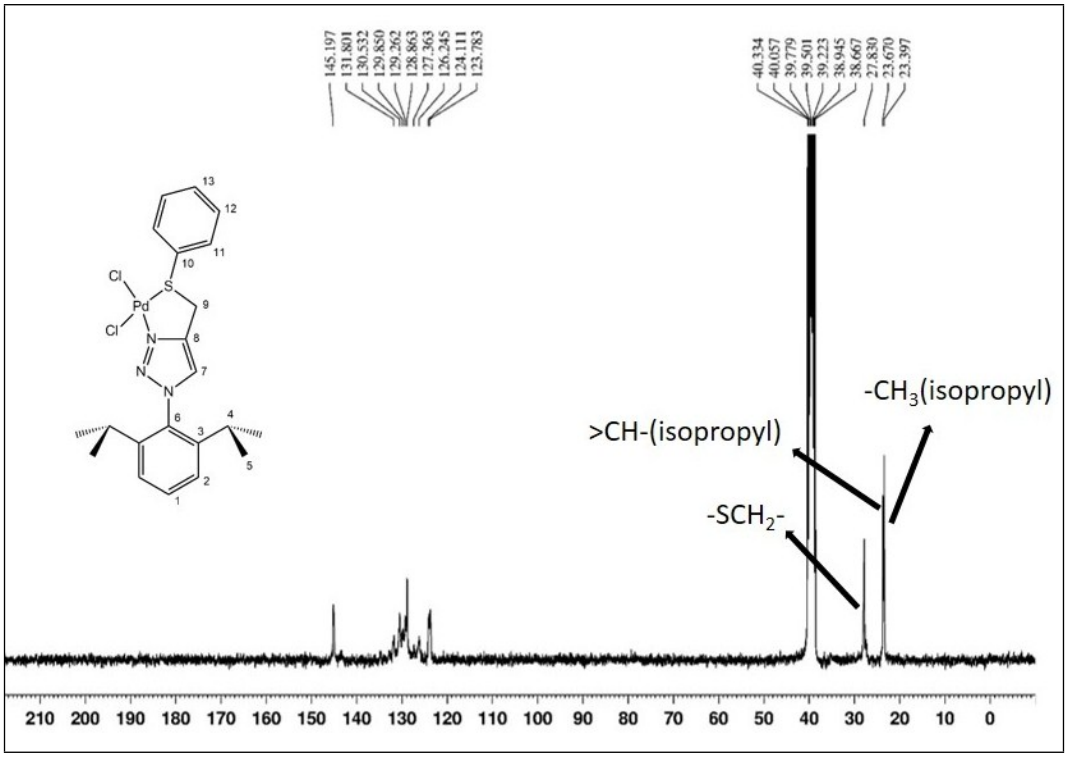


Figure S7 ^{13}C{^{1}H} NMR Spectrum of Complex **1**

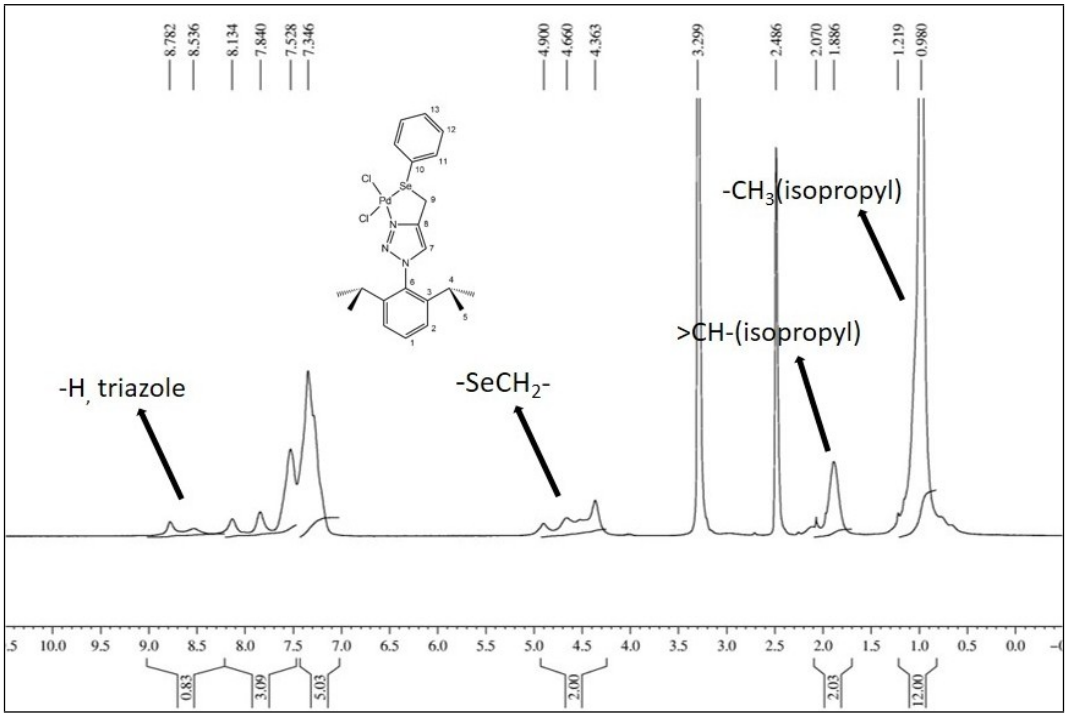


Figure S8 ^{1}H NMR Spectrum of Complex **2**

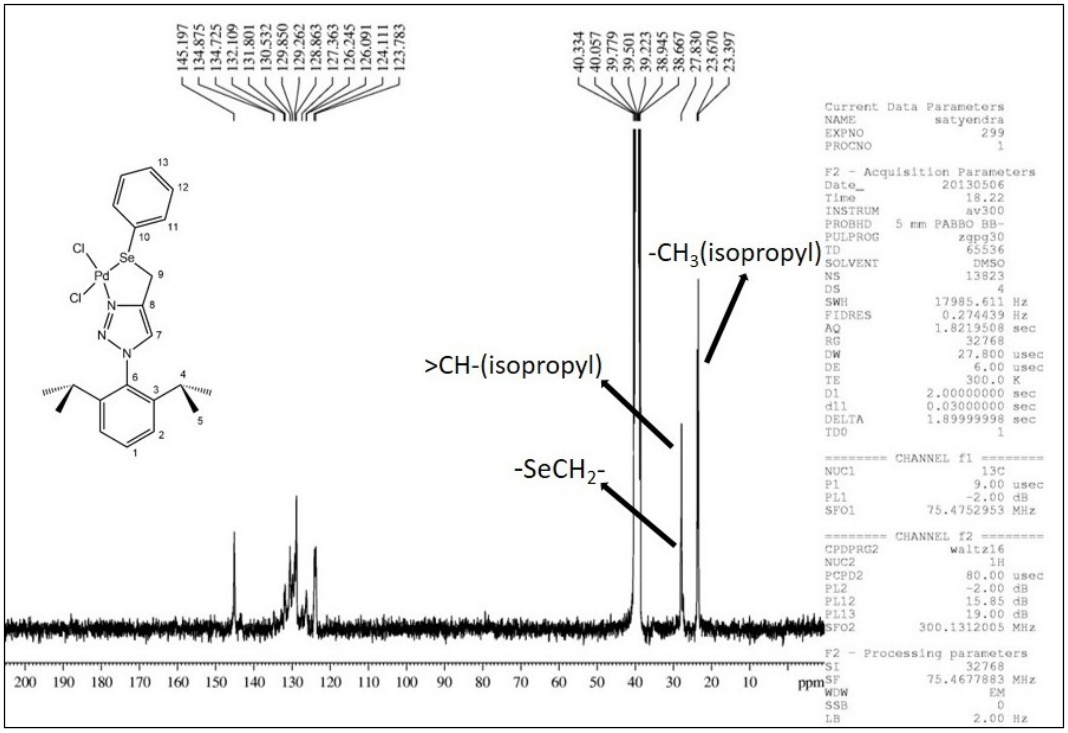


Figure S9 ^{13}C{^{1}H} NMR Spectrum of Complex **2**

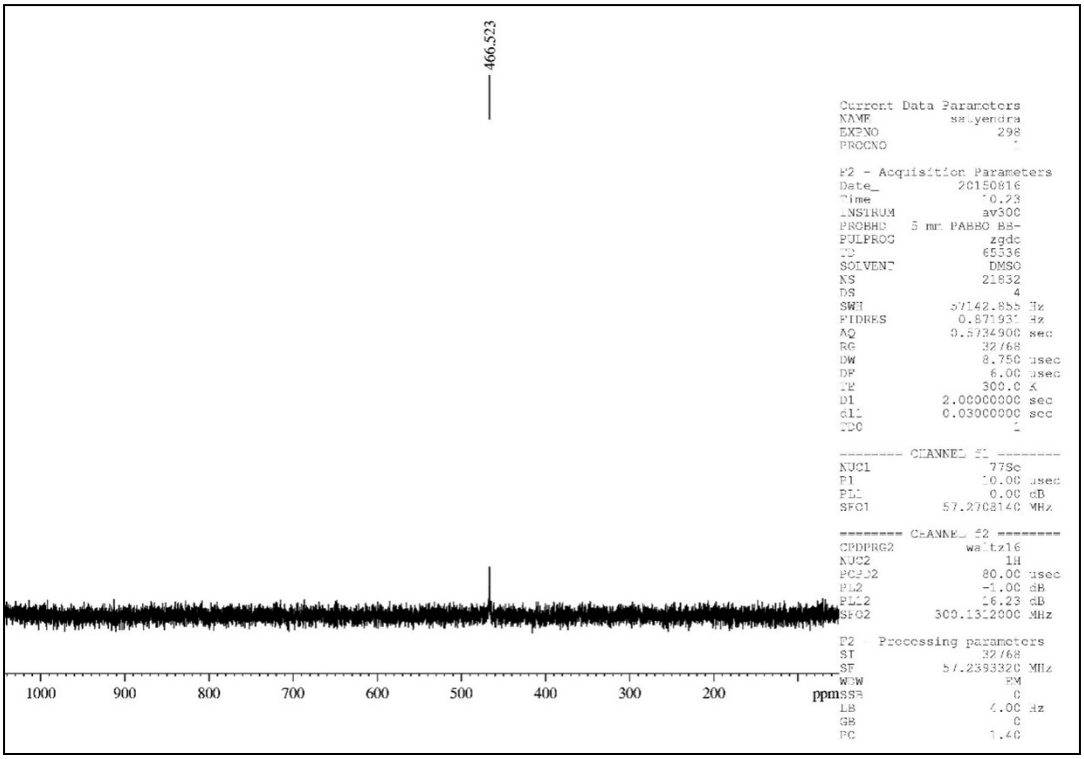


Figure S10 $^{77}Se\{^{1}H\}$ NMR Spectrum of Complex **2**

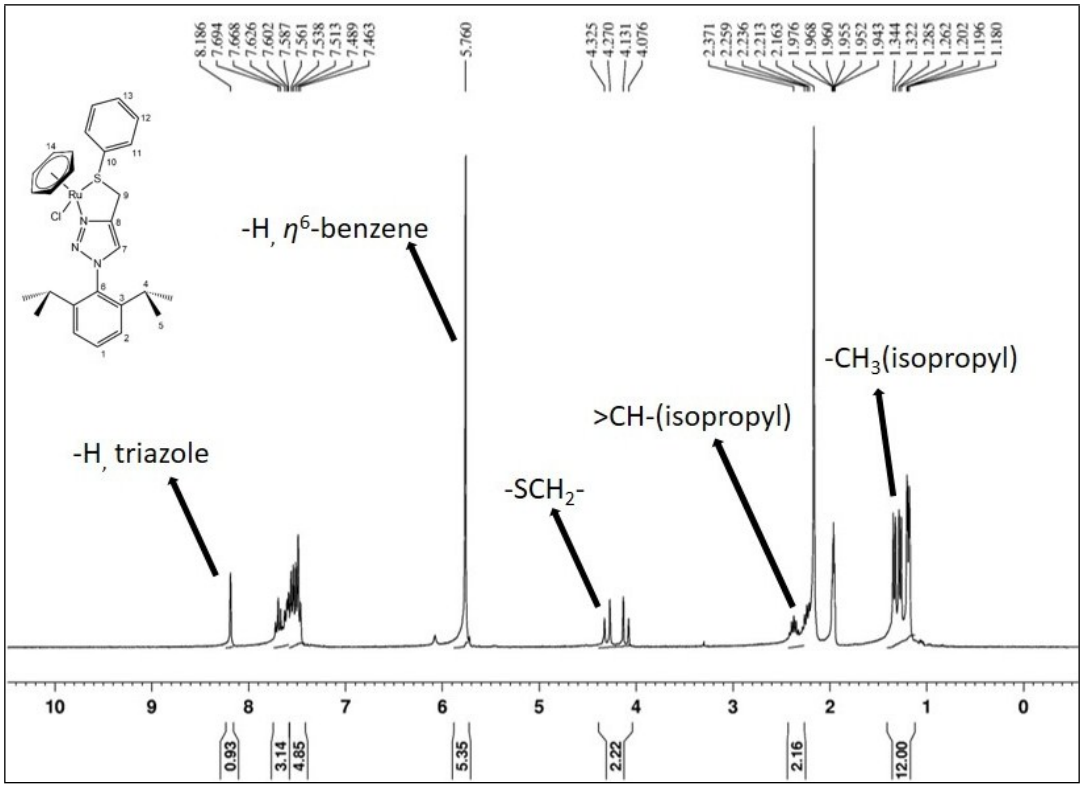


Figure S11 ^{1}H NMR Spectrum of Complex **3**

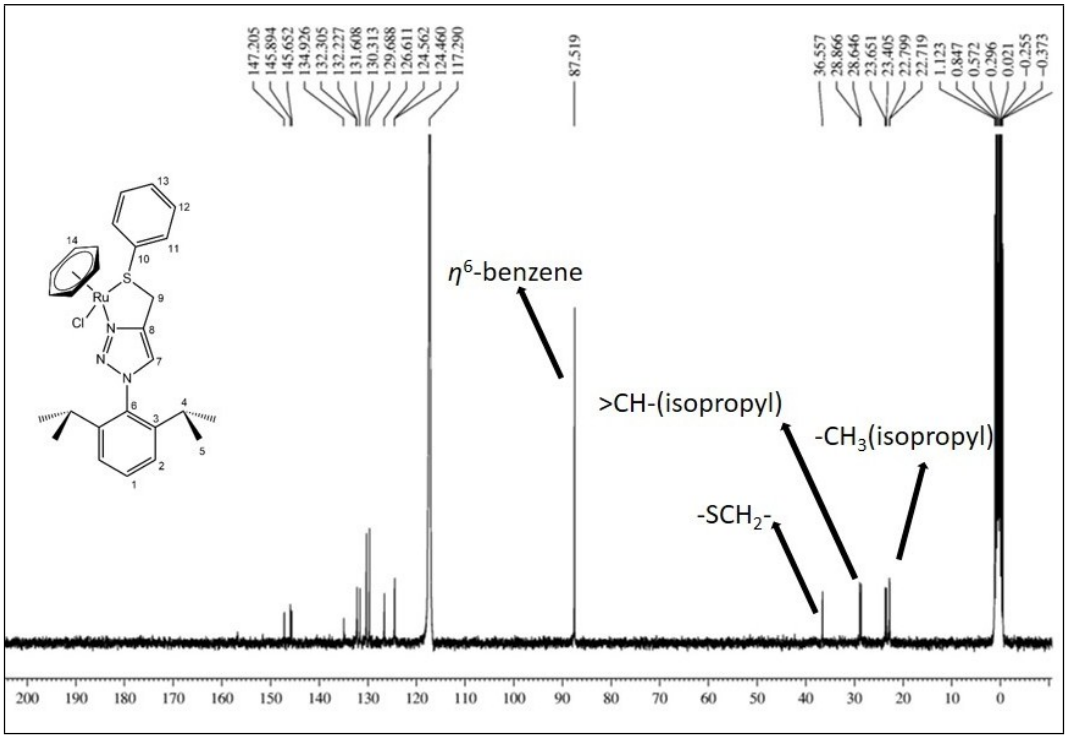


Figure S12 $^{13}C\{^{1}H\}$ NMR Spectrum of Complex **3**

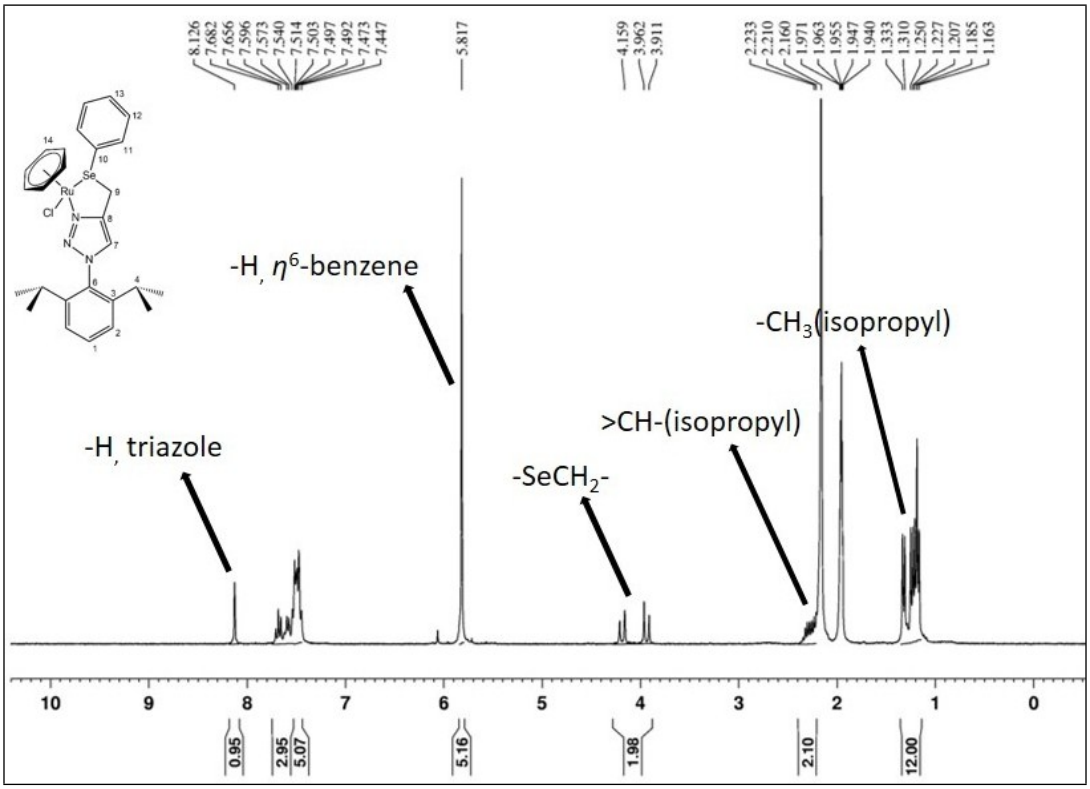


Figure S13 ^{1}H NMR Spectrum of Complex **4**

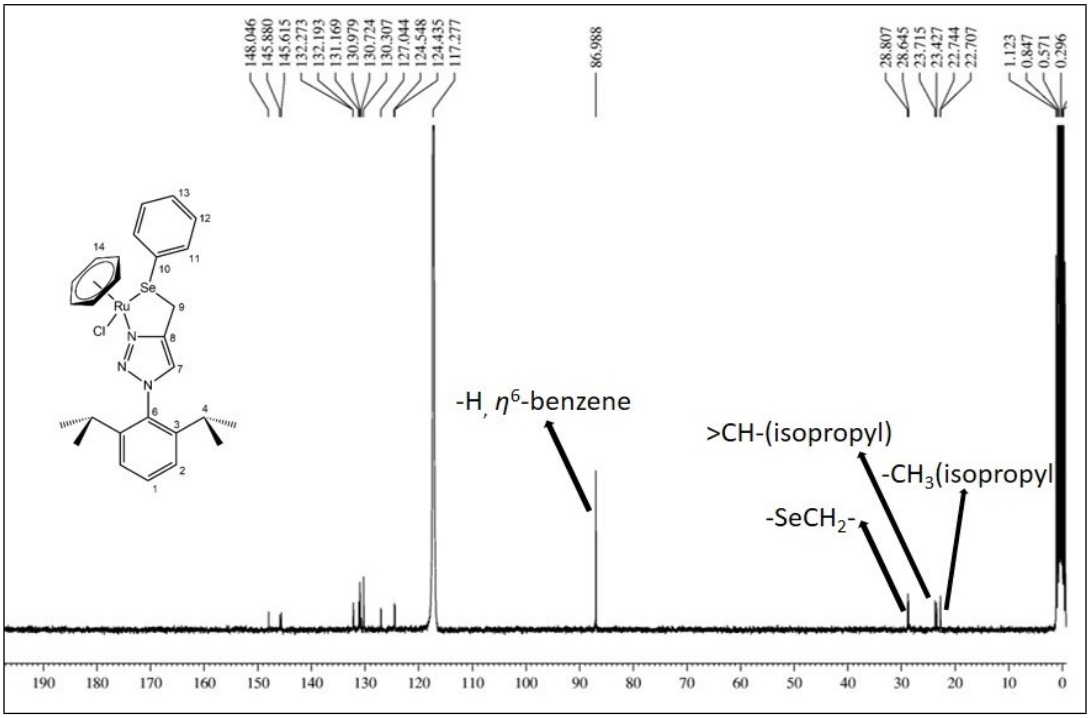


Figure S14 $^{13}C\{^{1}H\}$ NMR Spectrum of Complex **4**

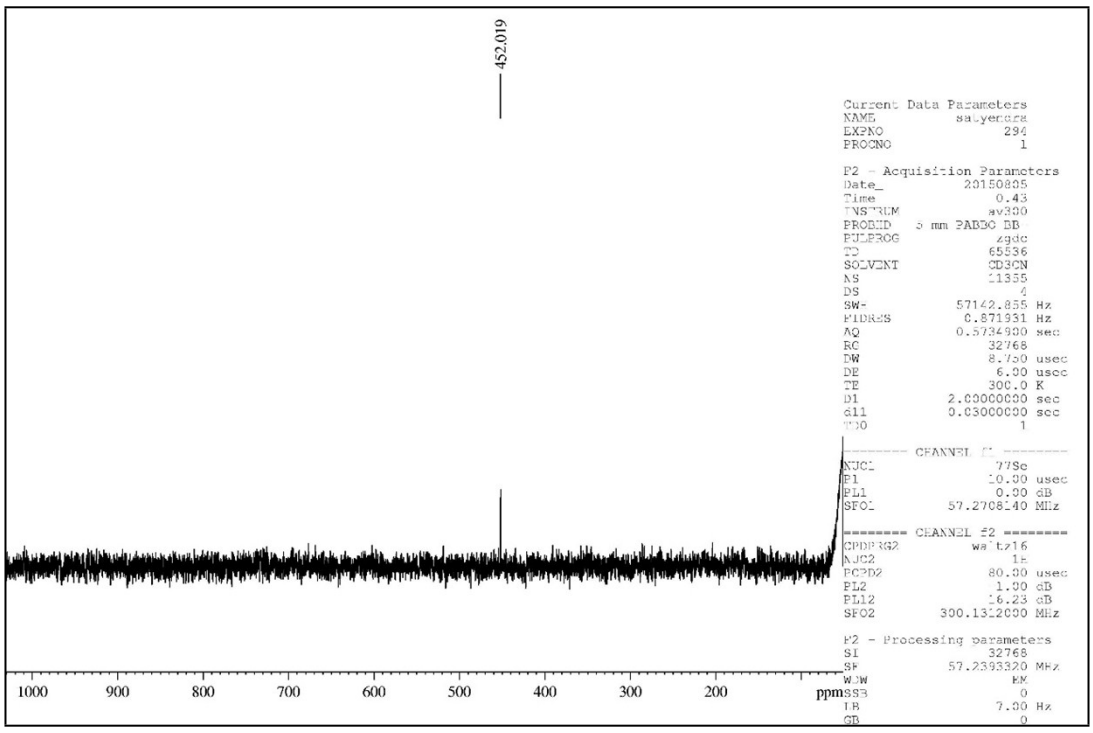
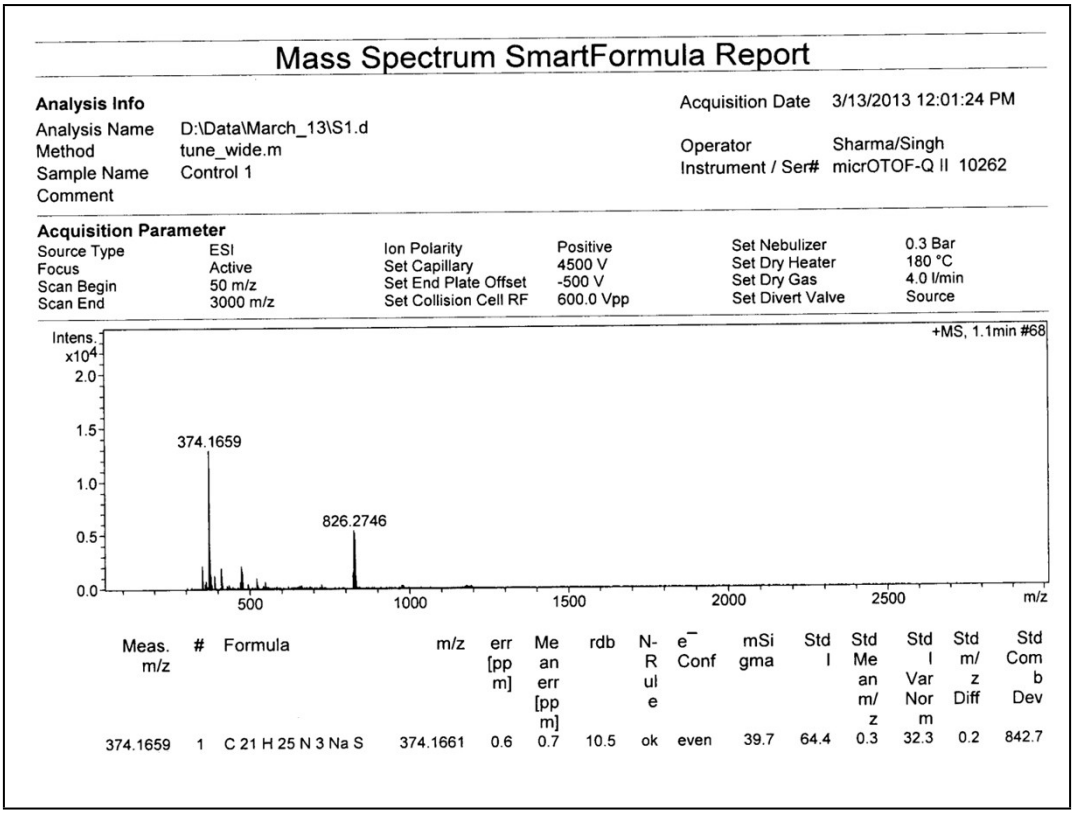


Figure S15 $^{77}Se\{^{1}H\}$ NMR Spectrum of Complex **4**



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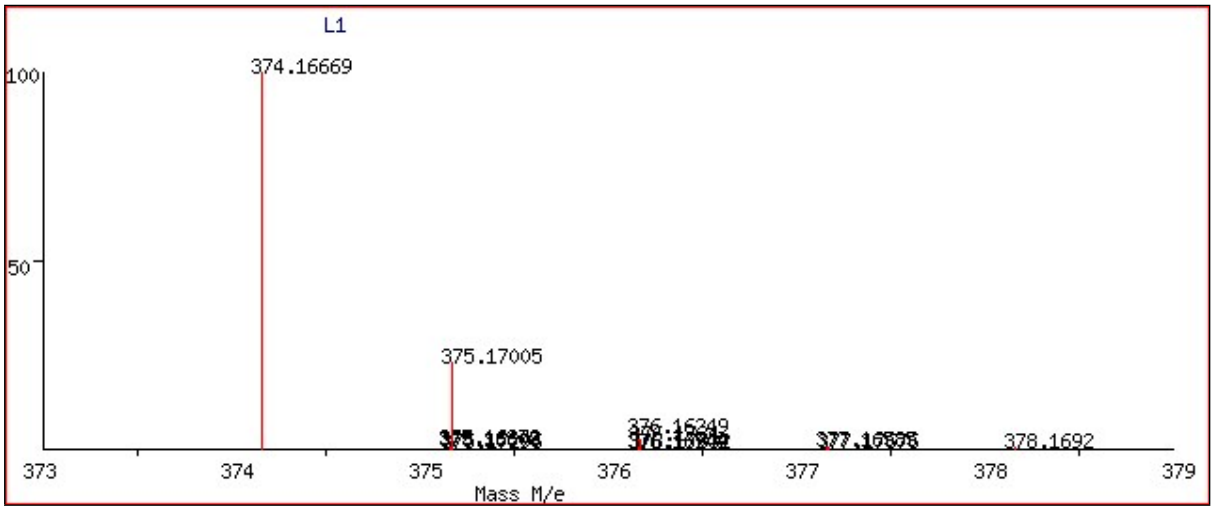
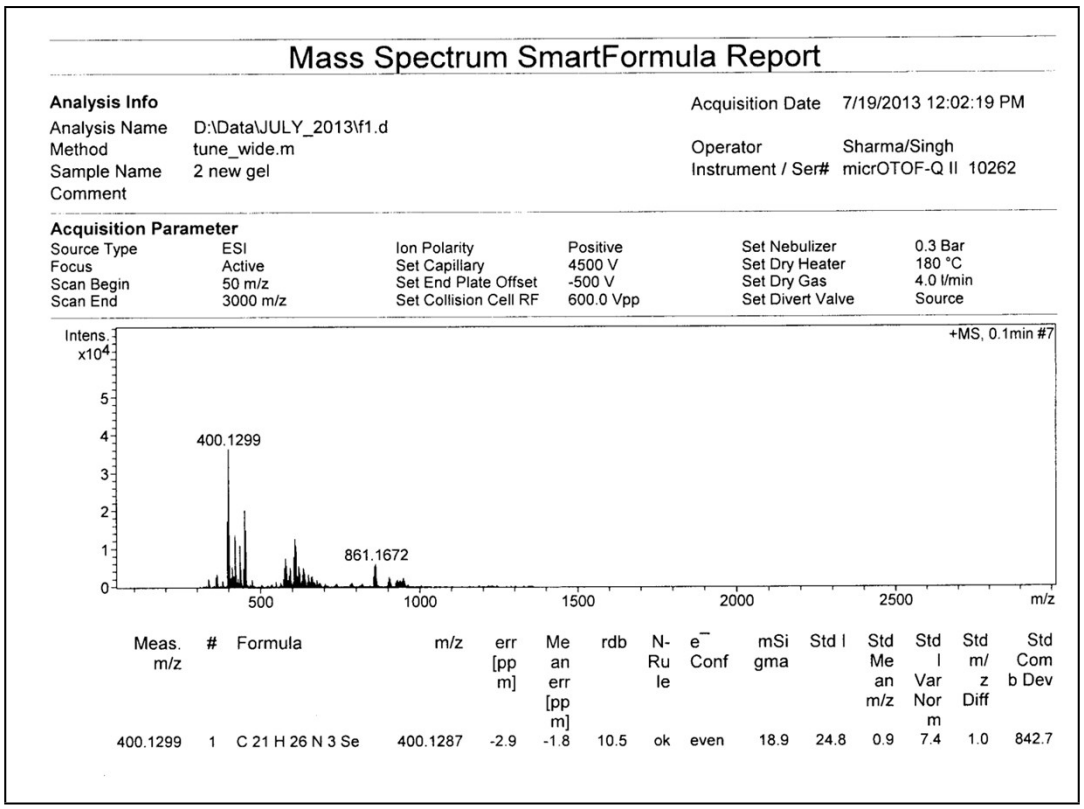


(b)

Figure S16 Mass Spectra of **L1 (a)** Experimental; **(b)** Simulated



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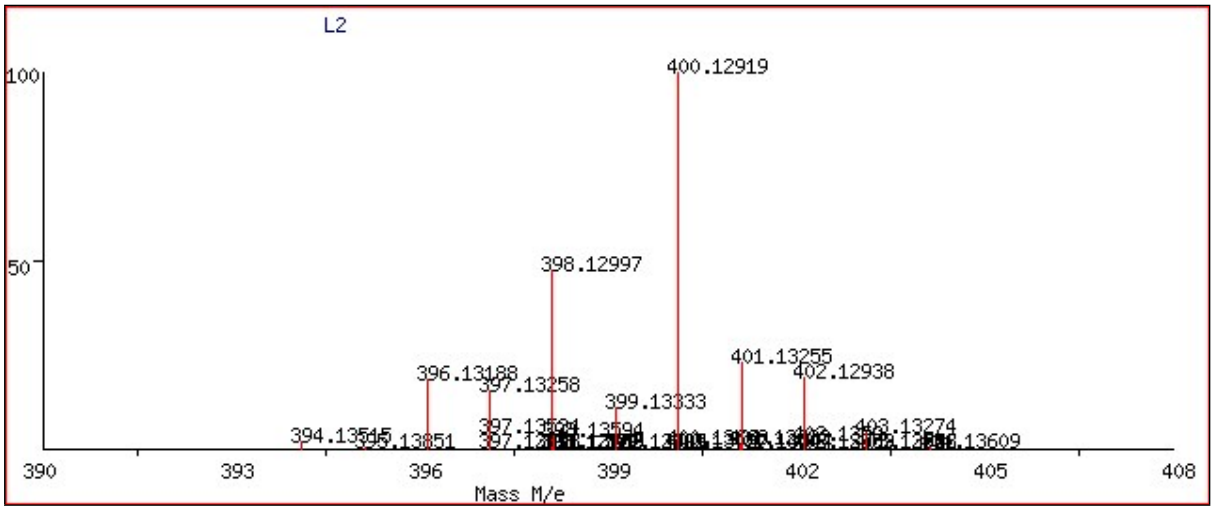
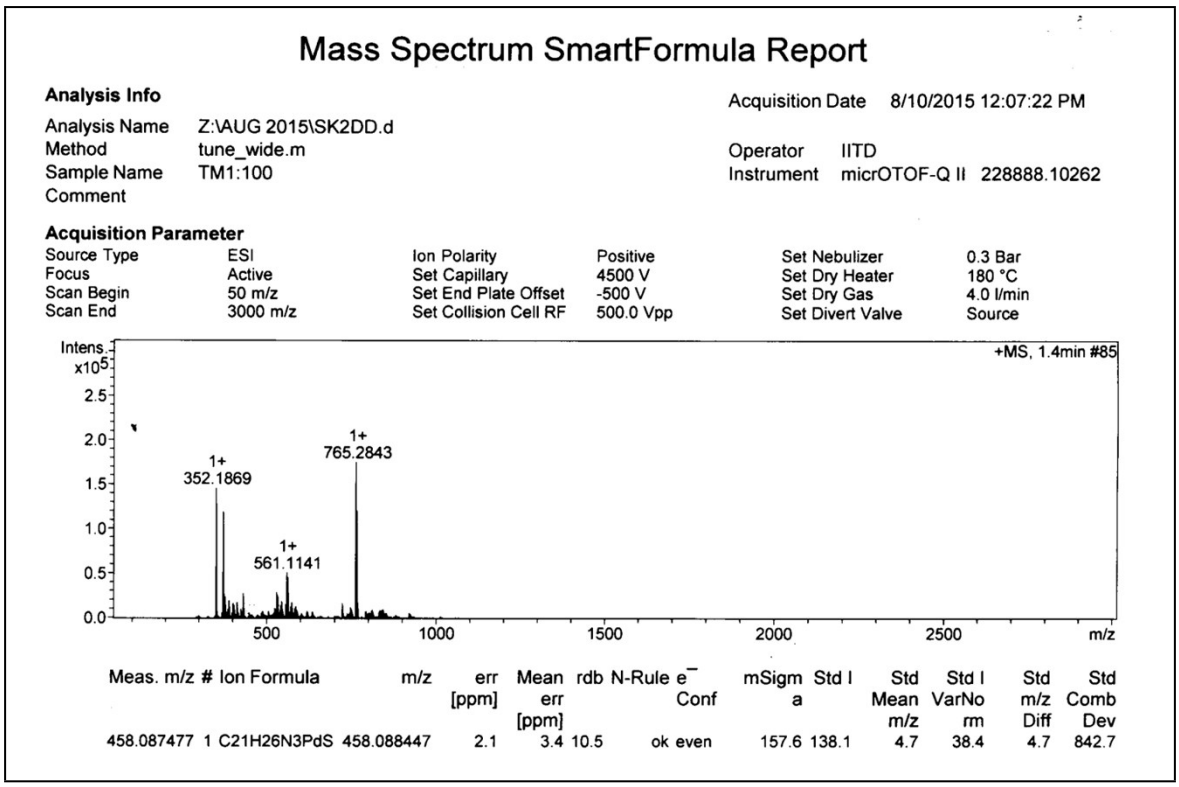


(b)

Figure S17 Mass Spectra of **L2 (a)** Experimental; **(b)** Simulated



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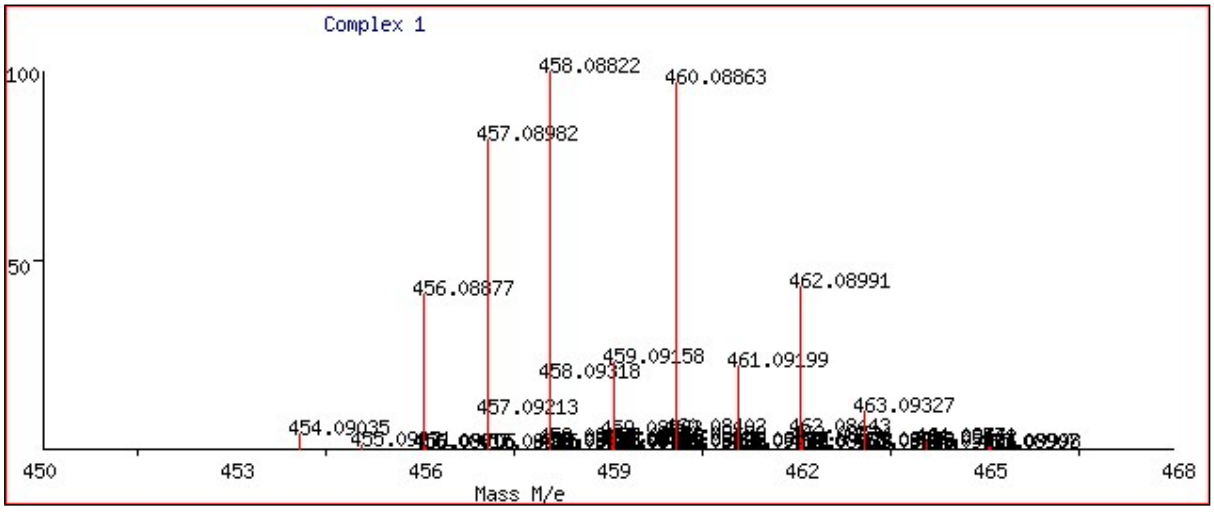
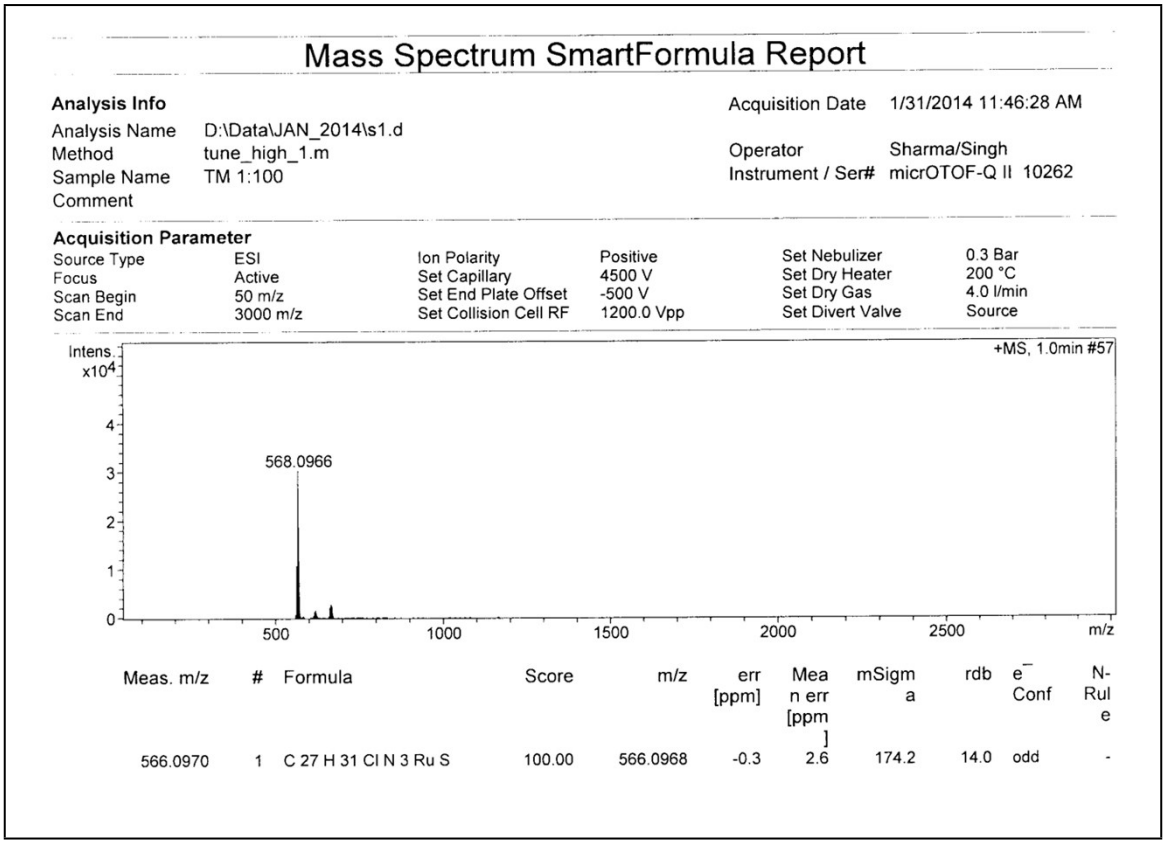
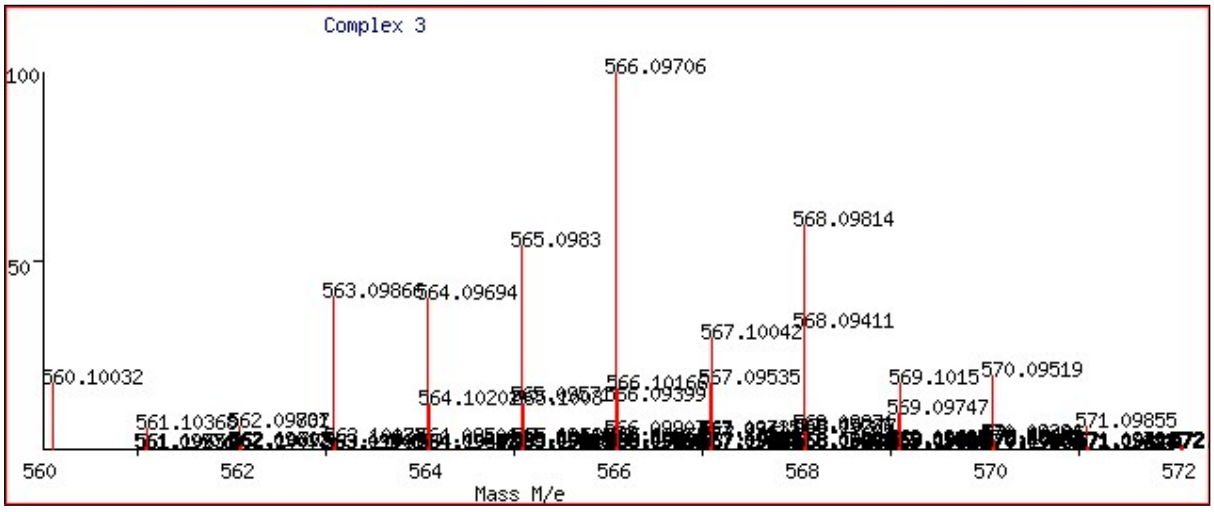


(b)

Figure S18 Mass Spectra of complex **1 (a)** Experimental; **(b)** Simulated

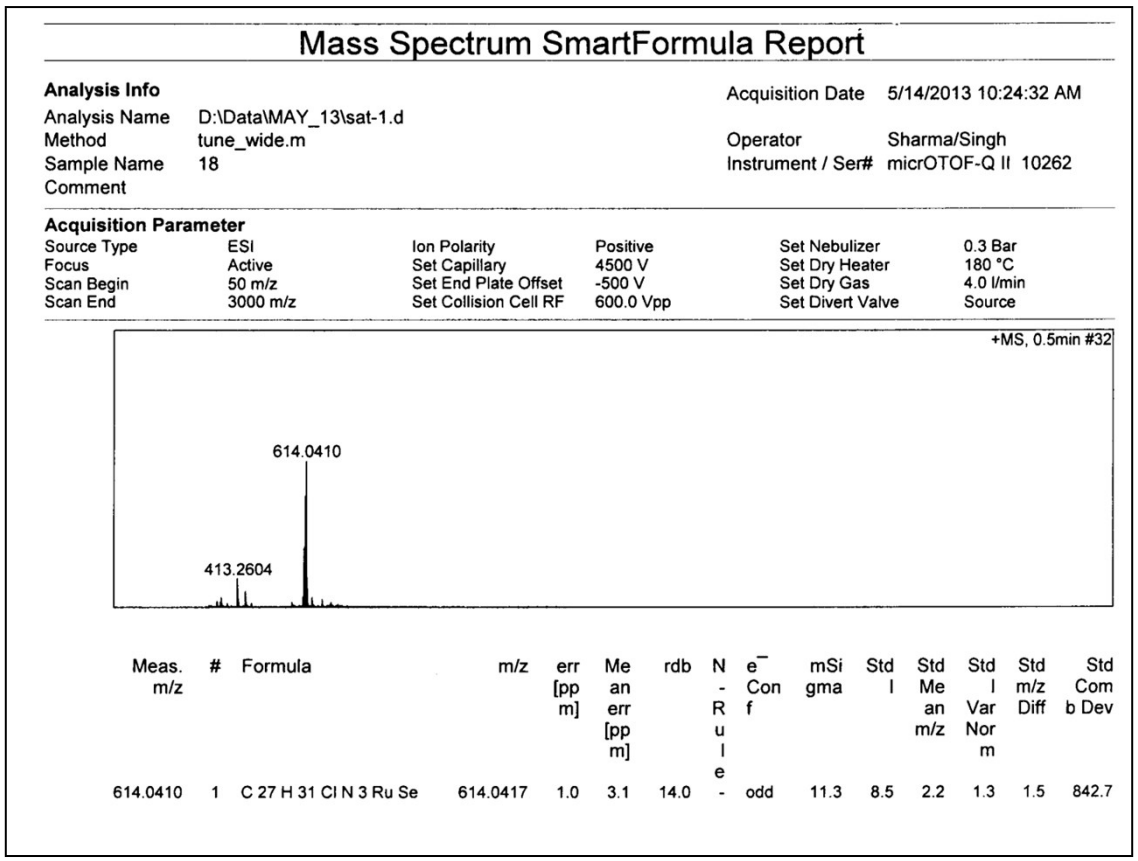


(a)

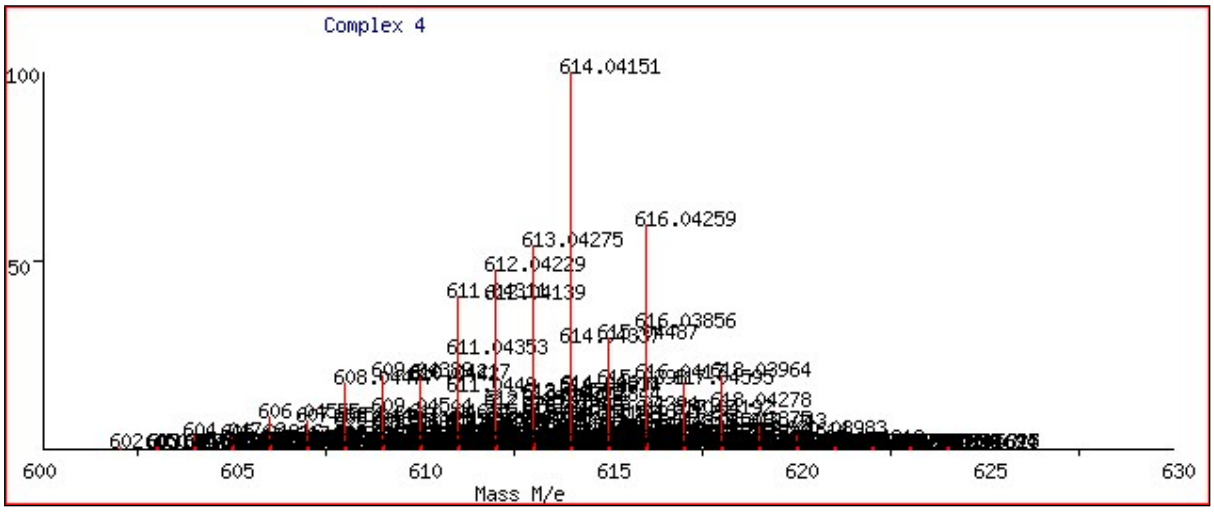


(b)

Figure S19 Mass Spectra of complex **3 (a)** Experimental; **(b)** Simulated



(a)



(b)

Figure S20 Mass Spectra of complex **4 (a)** Experimental; **(b)** Simulated

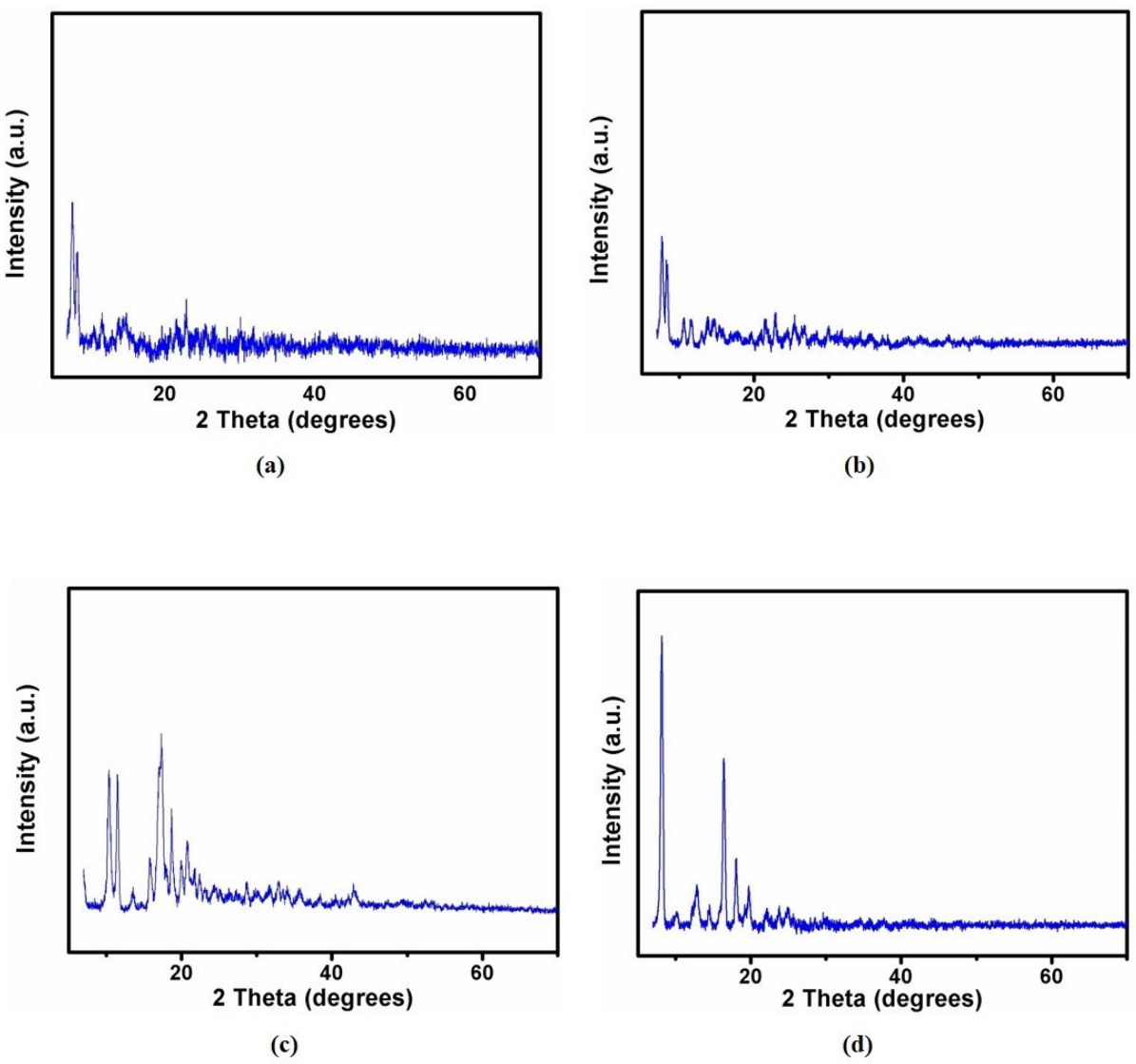


Figure S21 Powder-XRD pattern of metal complexes (*a*) Pd(II) complex **1**; (*b*) Pd(II) complex **2**; (*c*) Ru(II) complex **3**; (*d*) Ru(II) complex **4**.

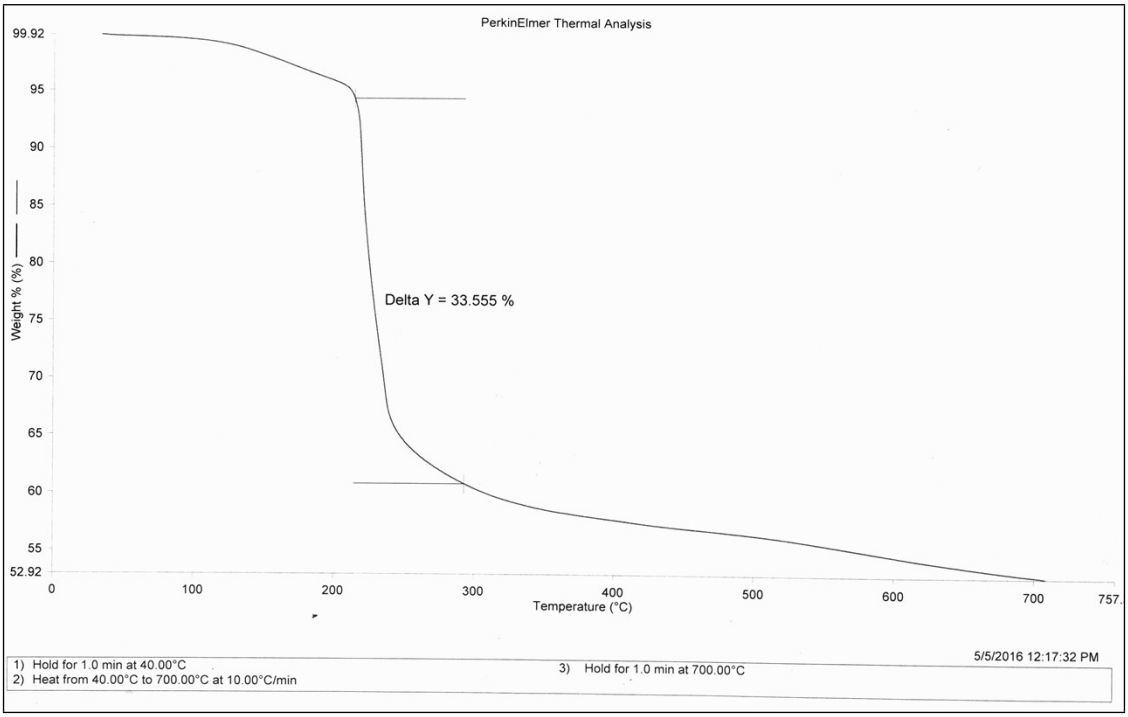


Figure S22 TGA of complex **1**

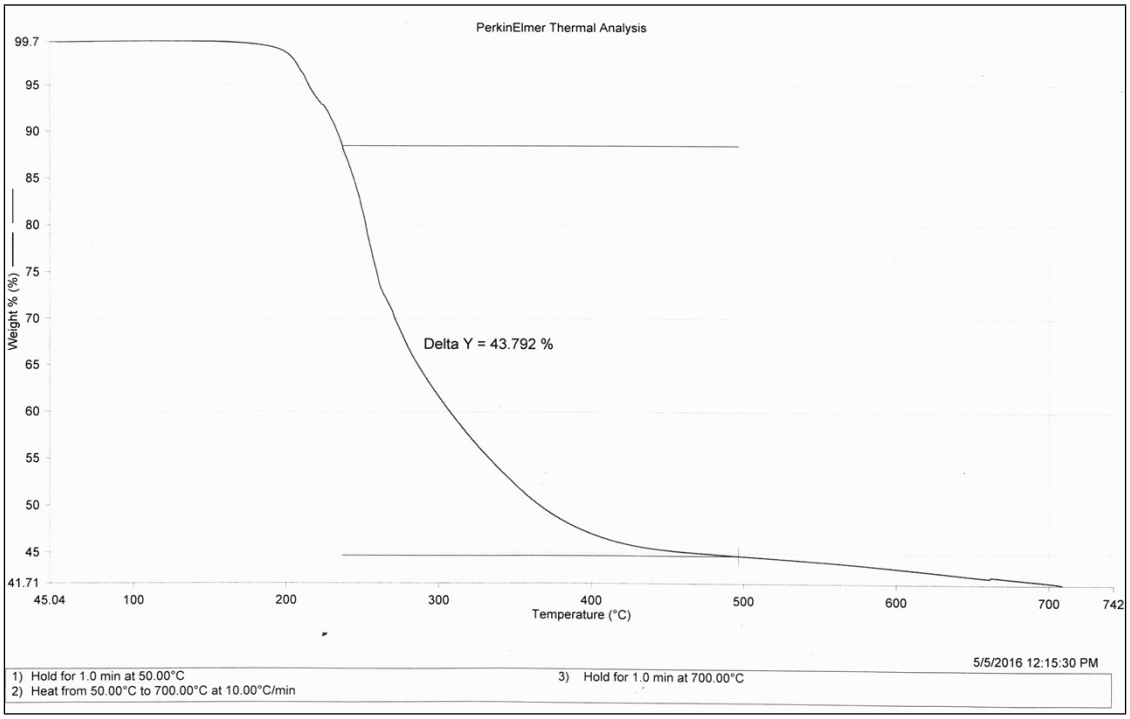


Figure S23 TGA of complex **2**

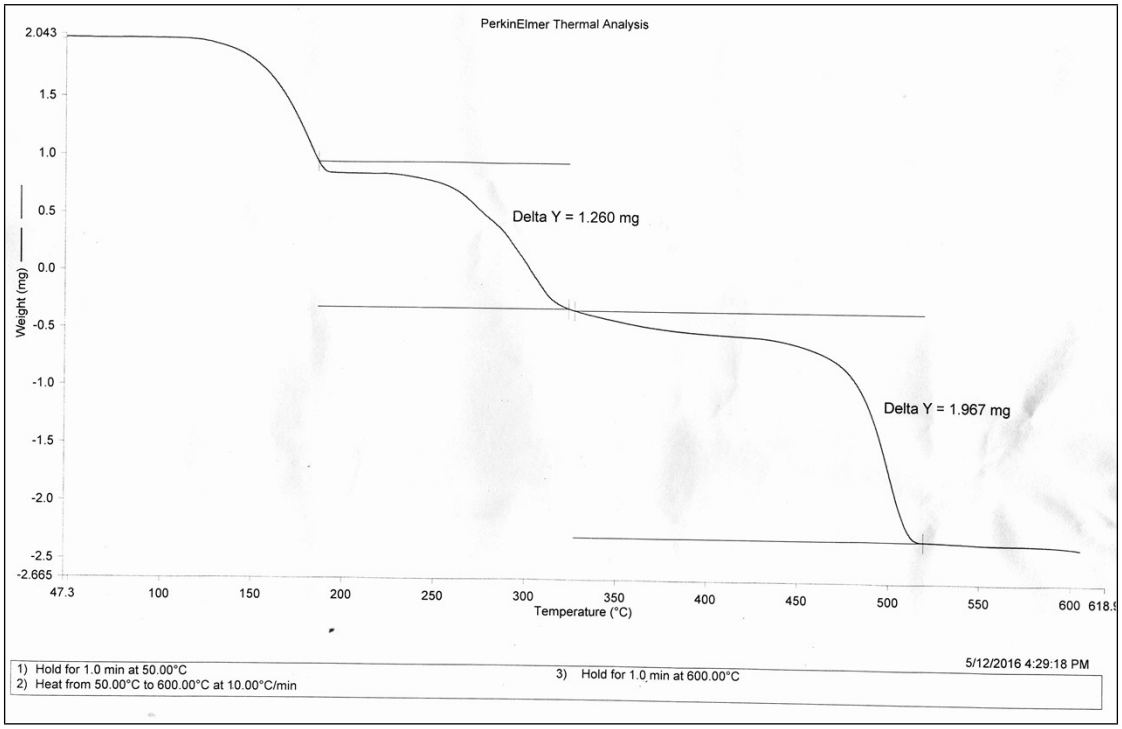


Figure S24 TGA of complex **3**

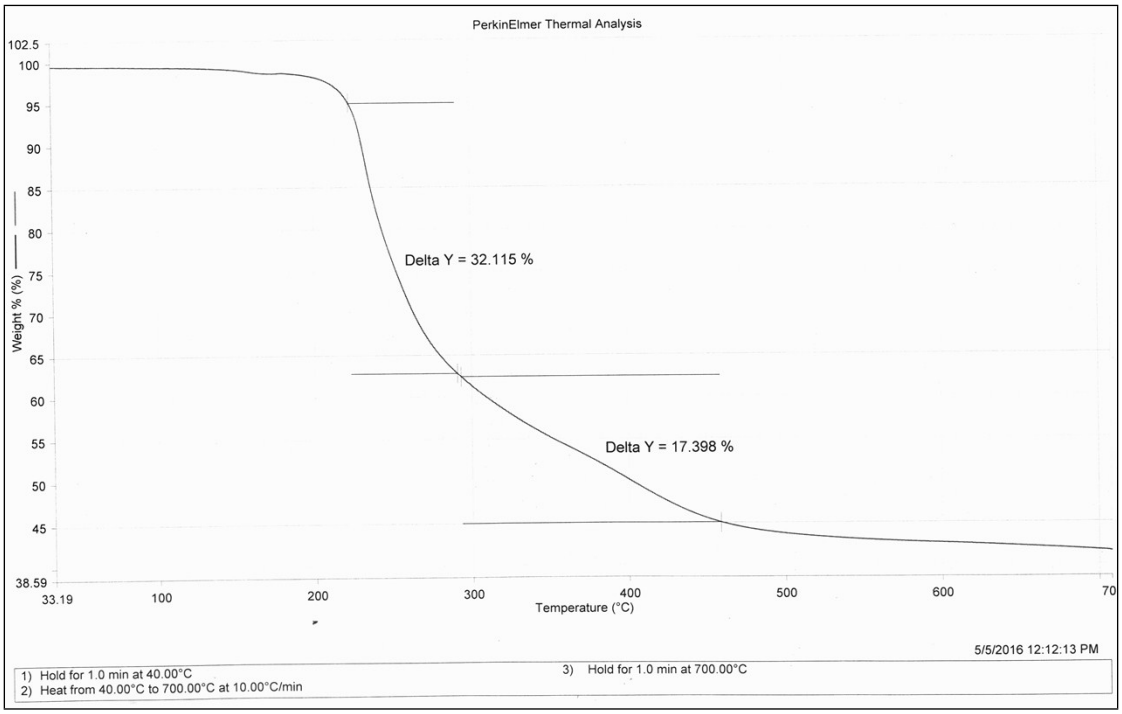


Figure S25 TGA of complex **4**

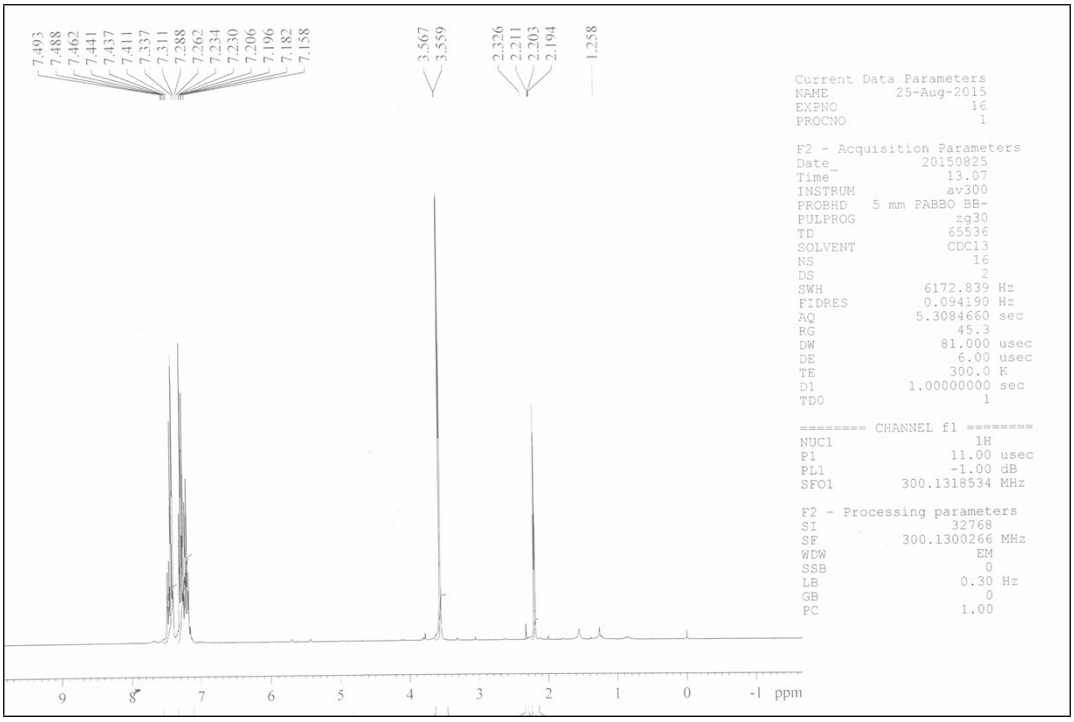


Figure S26 ^{1}H NMR of phenyl propargyl sulphide

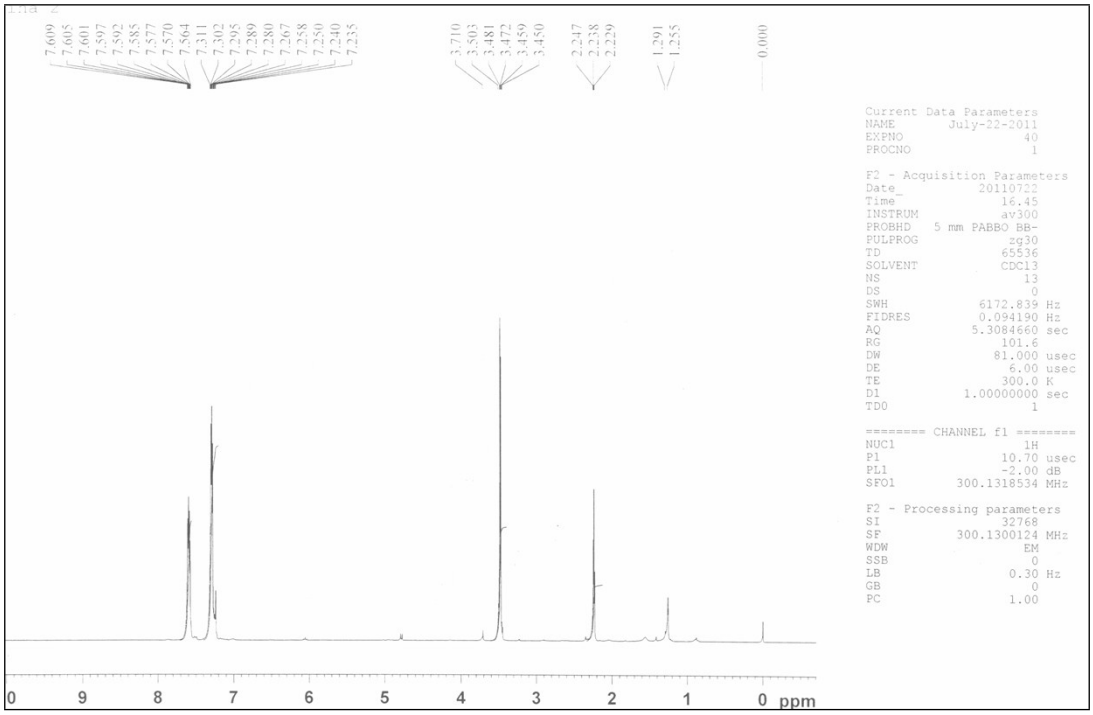


Figure S27 ^{1}H NMR of phenyl propargyl selenide

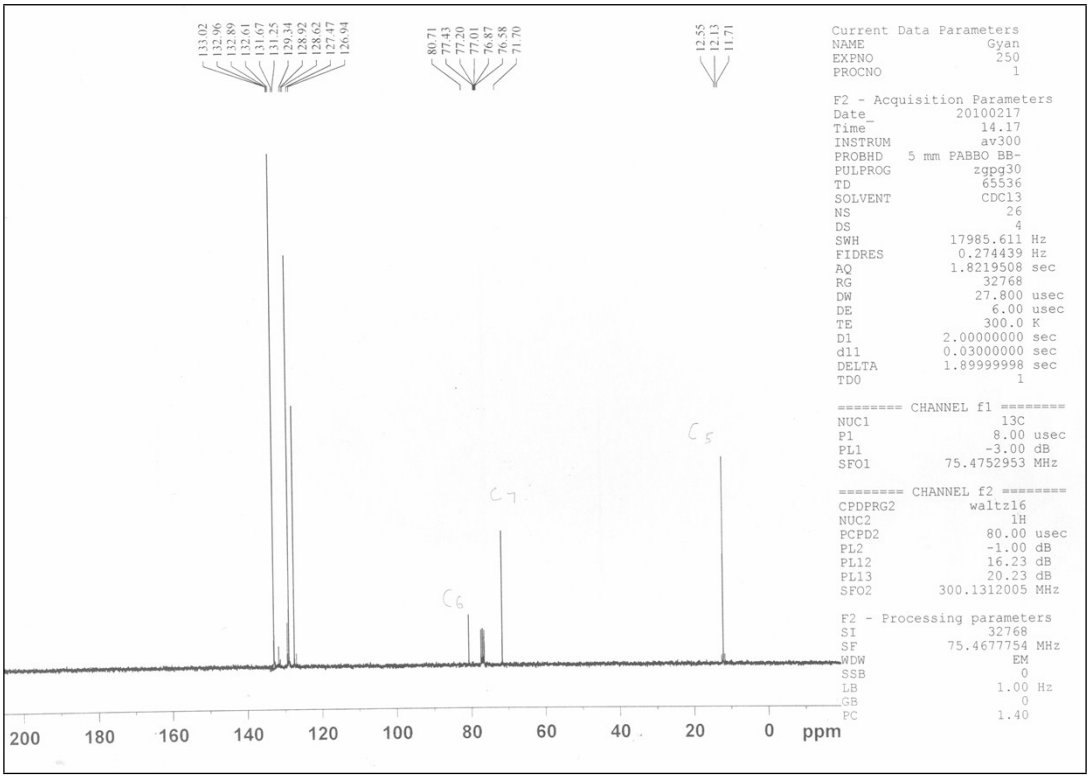


Figure S28 $^{13}C\{^{1}H\}$ NMR of phenyl propargyl selenide

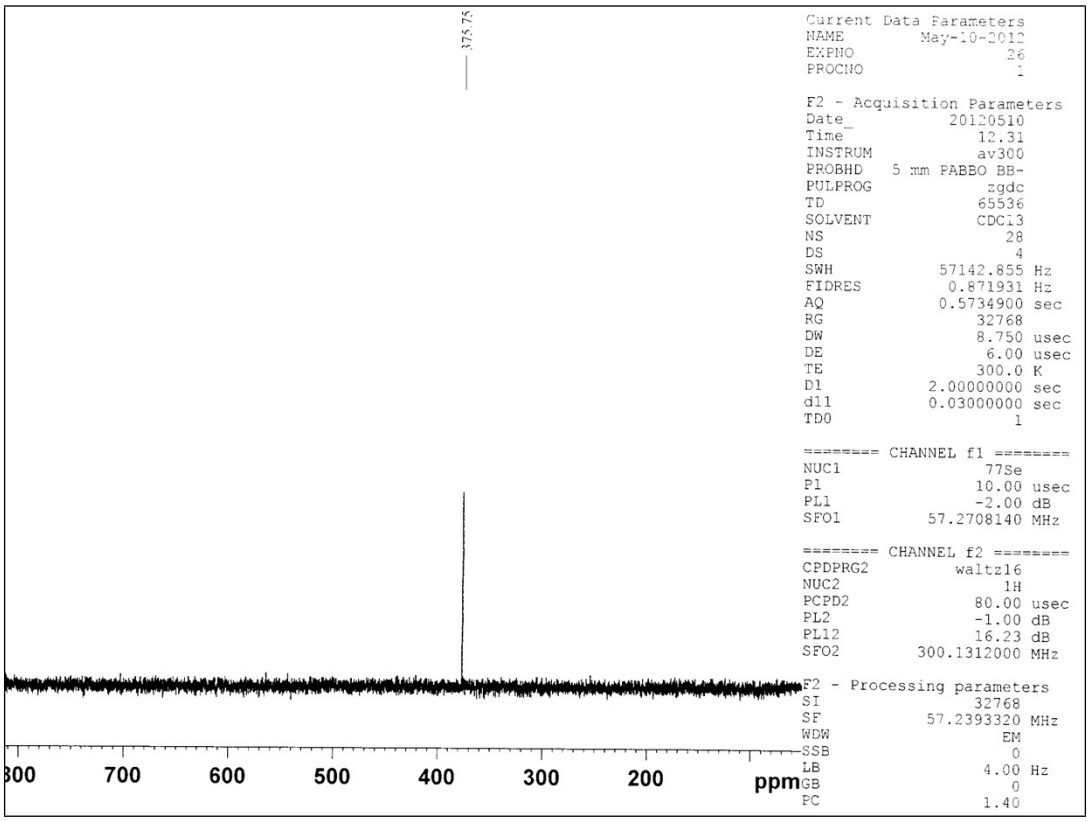


Figure S29 $^{77}Se\{^{1}H\}$ NMR of phenyl propargyl selenide

NMR Spectra of Catalysis Products

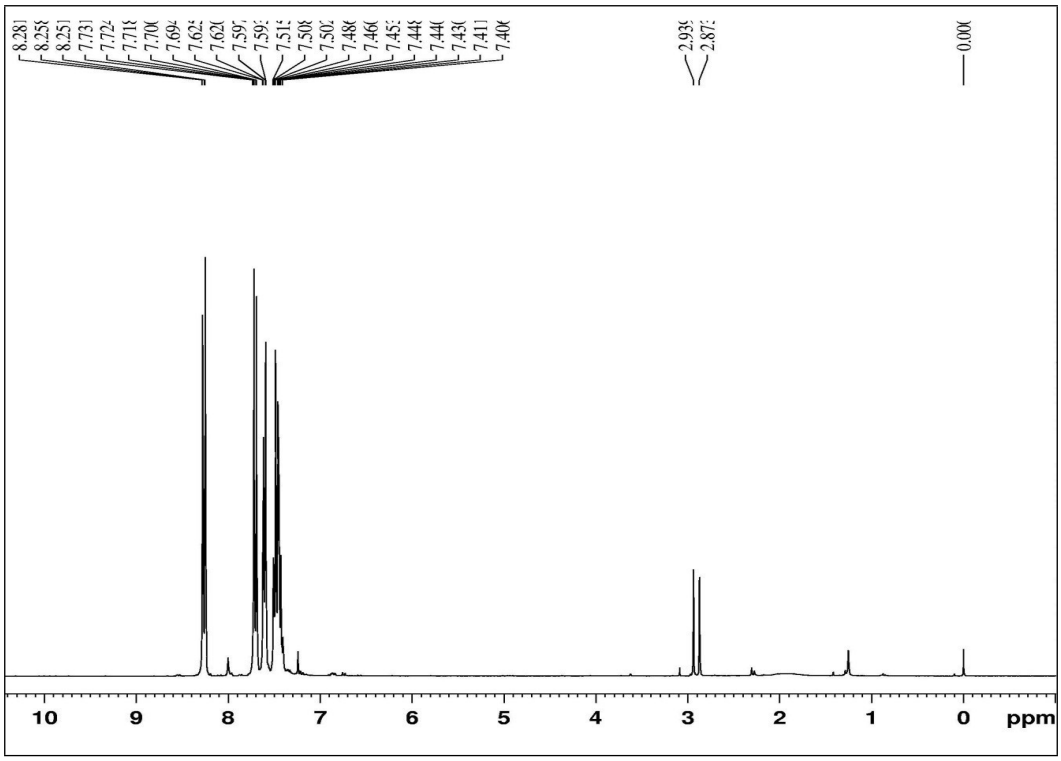


Figure S30 ^{1}H NMR of 4-Nitrobiphenyl

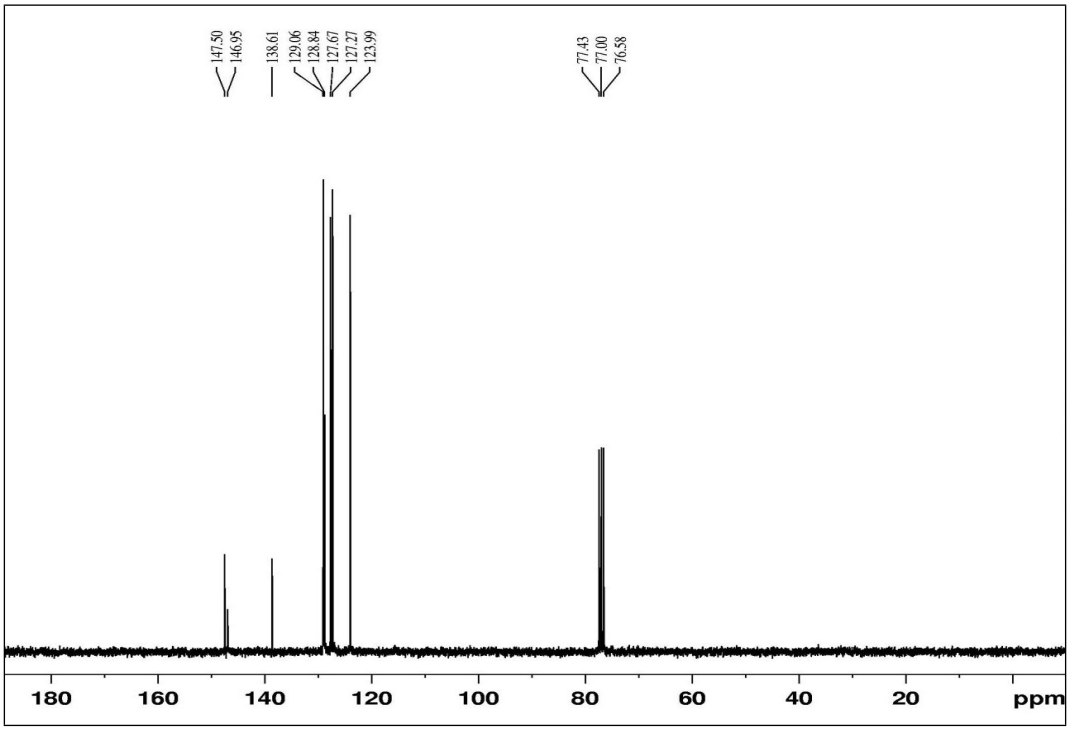


Figure S31 $^{13}C\{^{1}H\}$ NMR of 4-Nitrobiphenyl

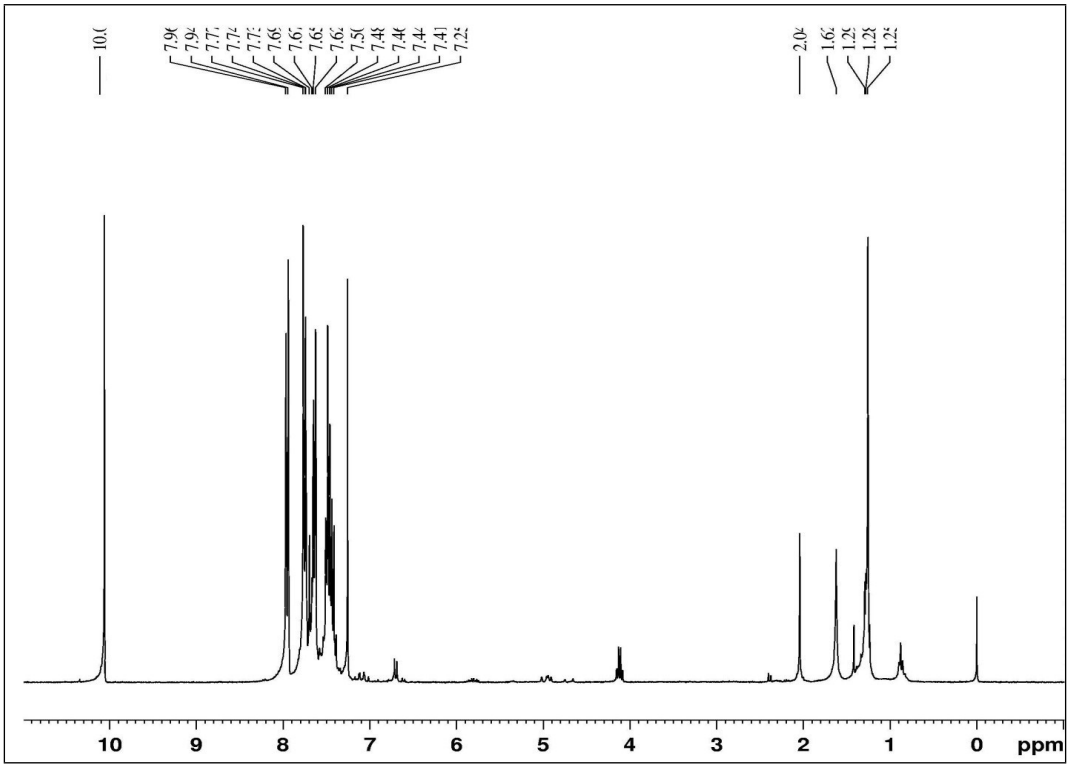


Figure S32 ^{1}H NMR of 4−phenylbenzaldehyde

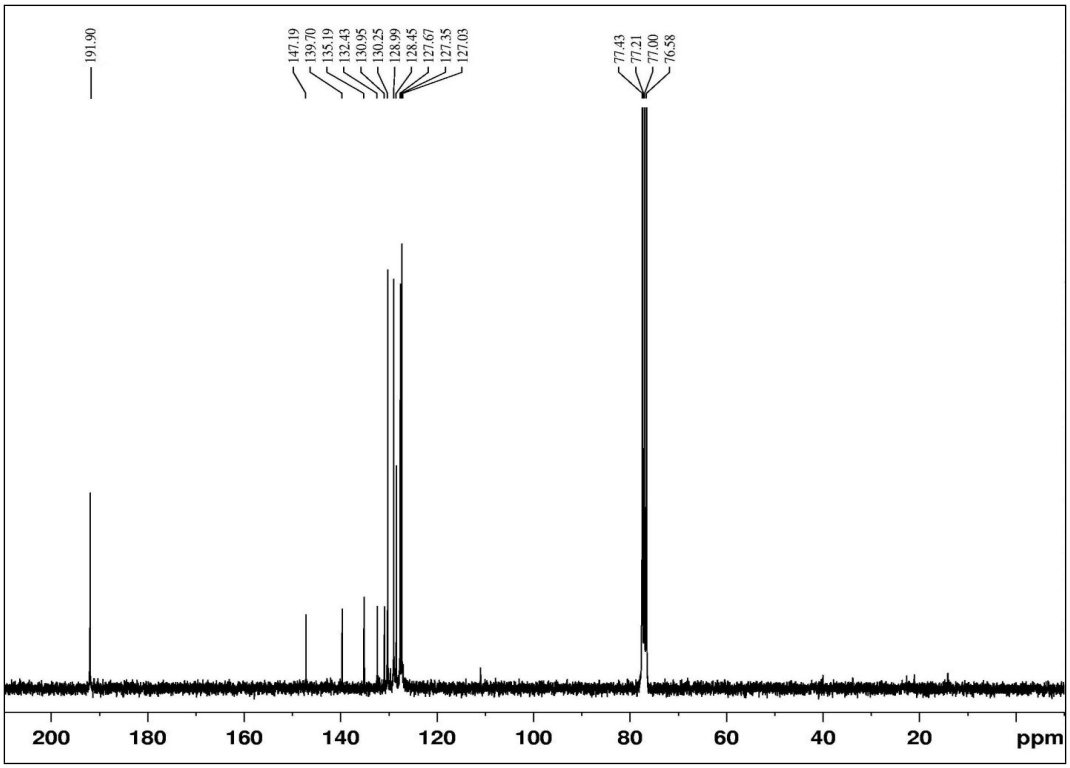


Figure S33 ^{13}C{^{1}H} NMR of 4−Phenylbenzaldehyde

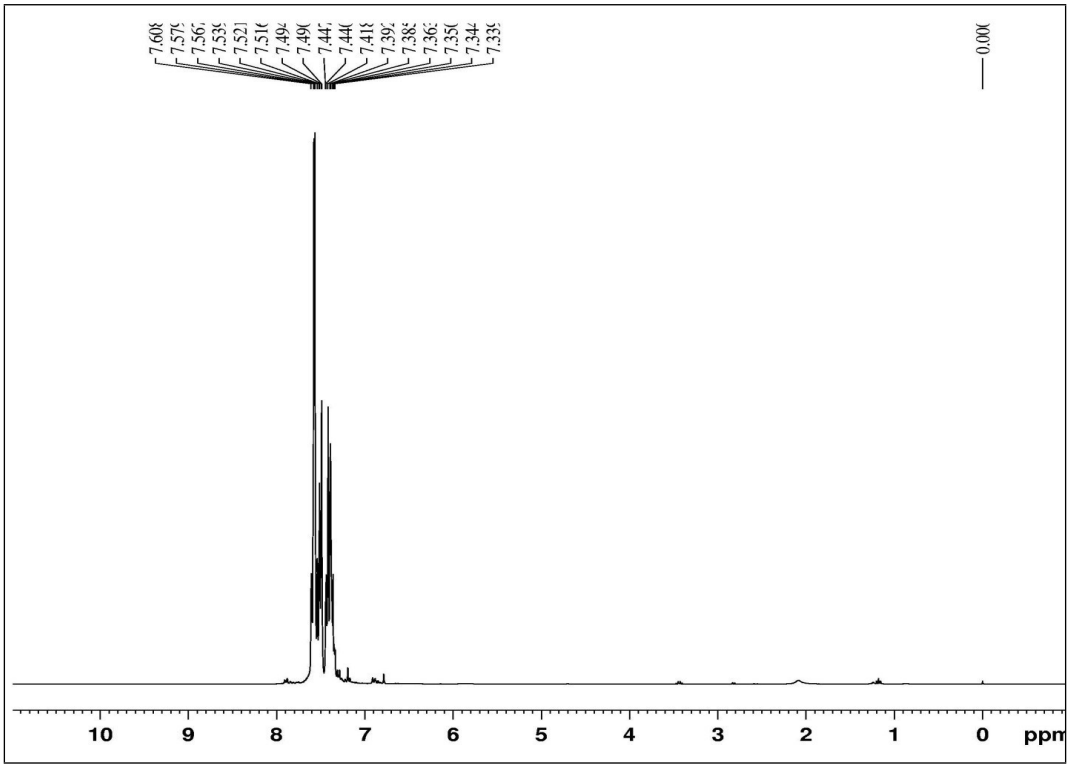


Figure S34 ^{1}H NMR of 4-Phenylbenzonitrile

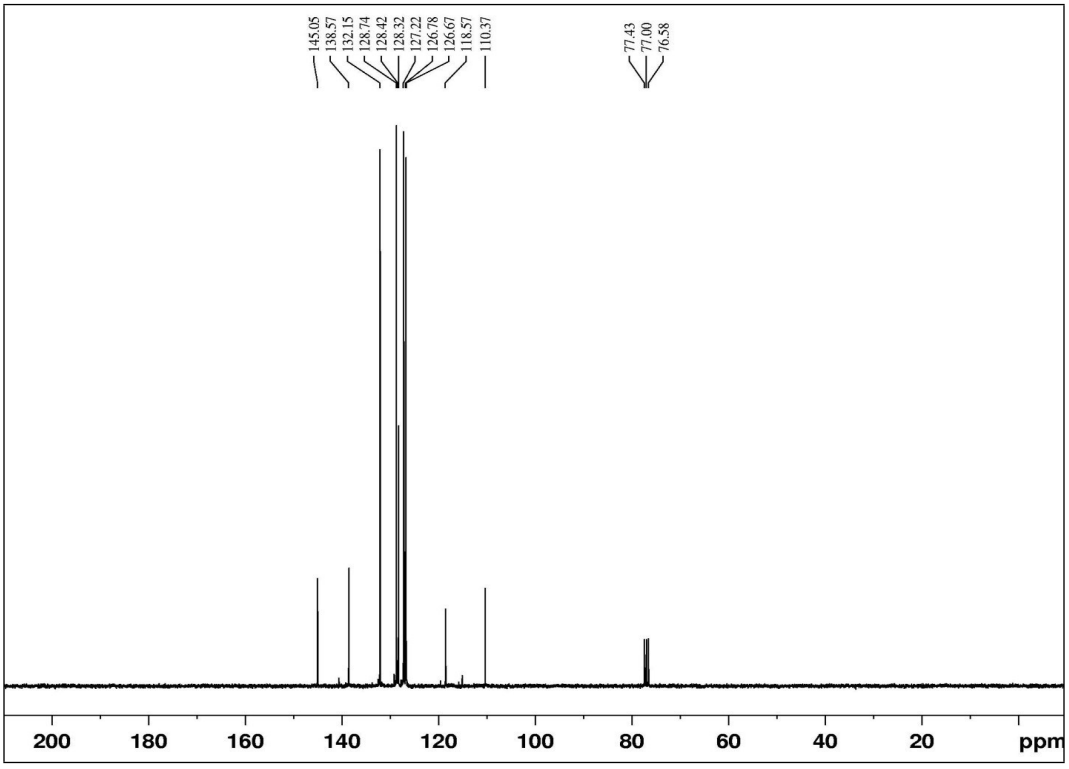


Figure S35 ^{13}C{^{1}H} NMR of 4-Phenylbenzonitrile

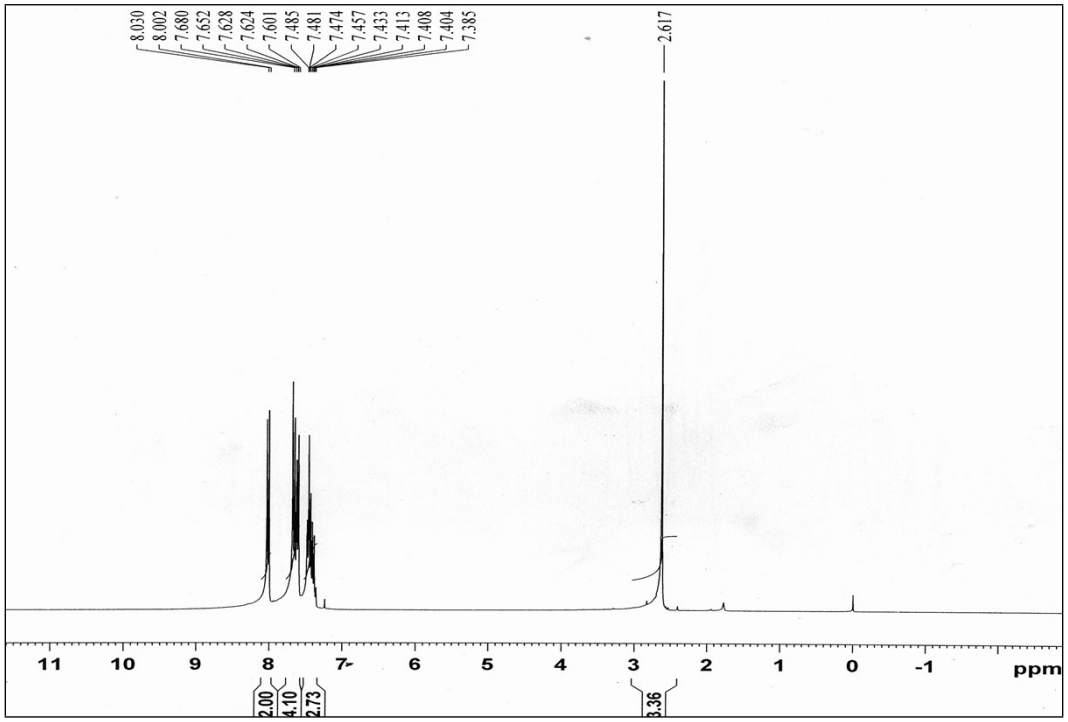


Figure S36 ^{1}H NMR of 4-Acetylbiphenyl

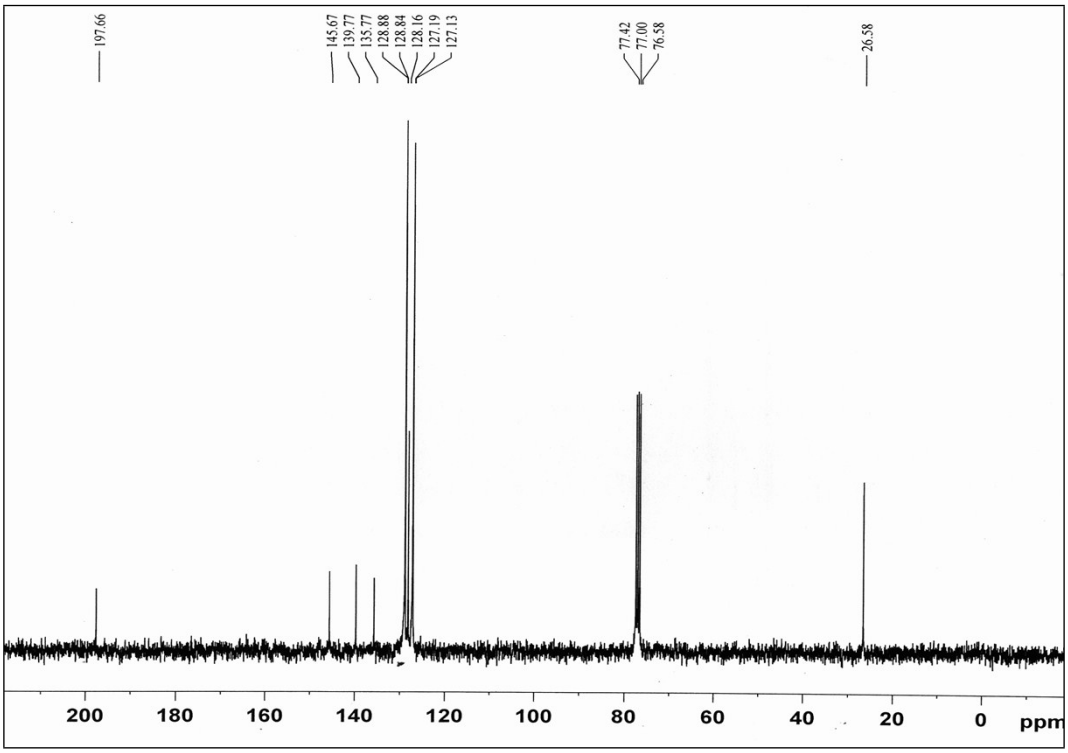


Figure S37 ^{13}C{^{1}H} NMR of 4-Acetylbiphenyl

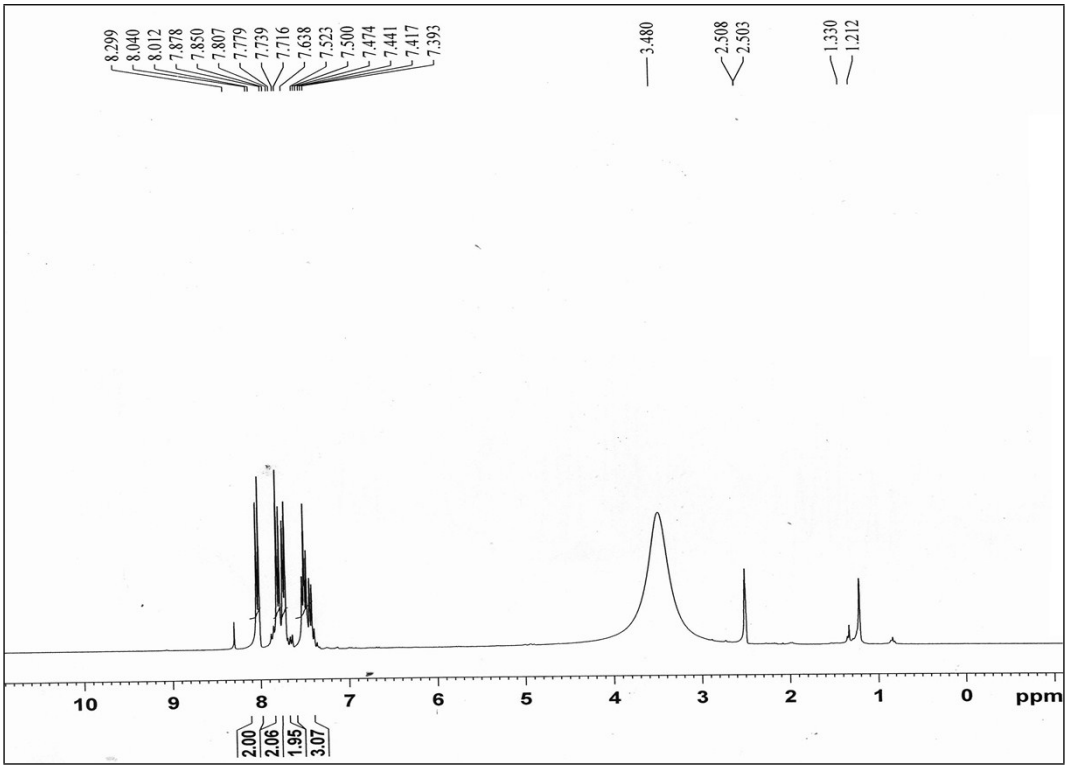


Figure S38 ^{1}H NMR of 4-Carboxylicbiphenyl

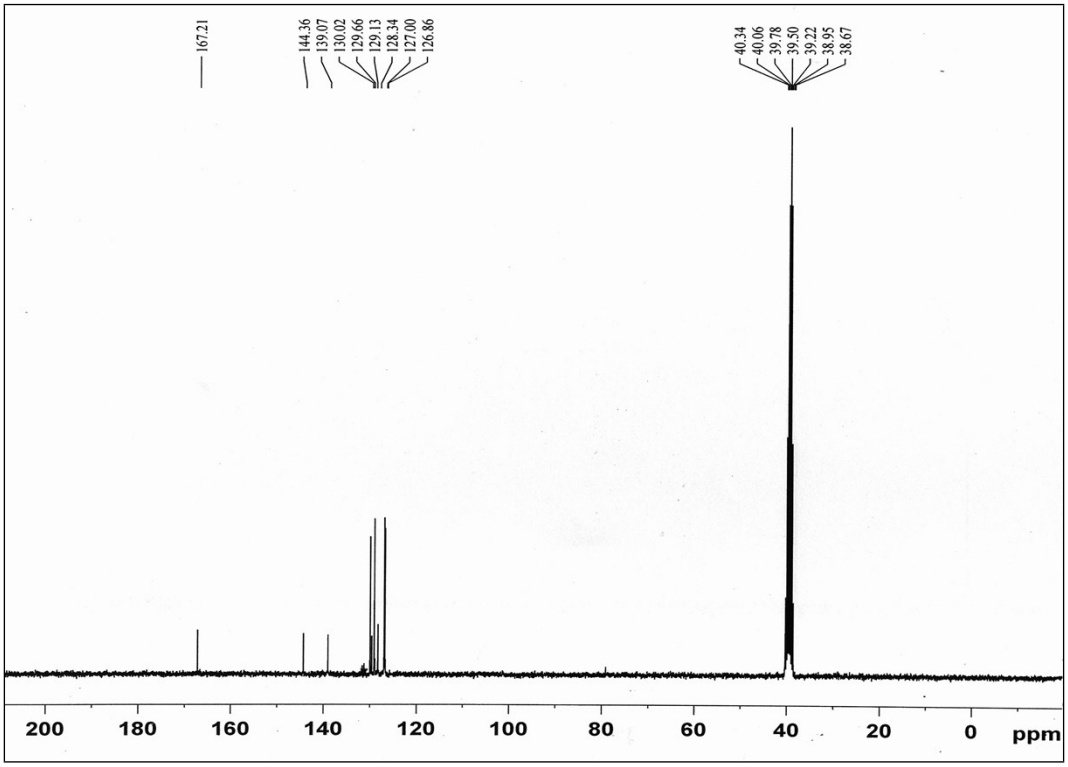


Figure S39 ^{13}C{^{1}H} NMR of 4-Carboxylicbiphenyl

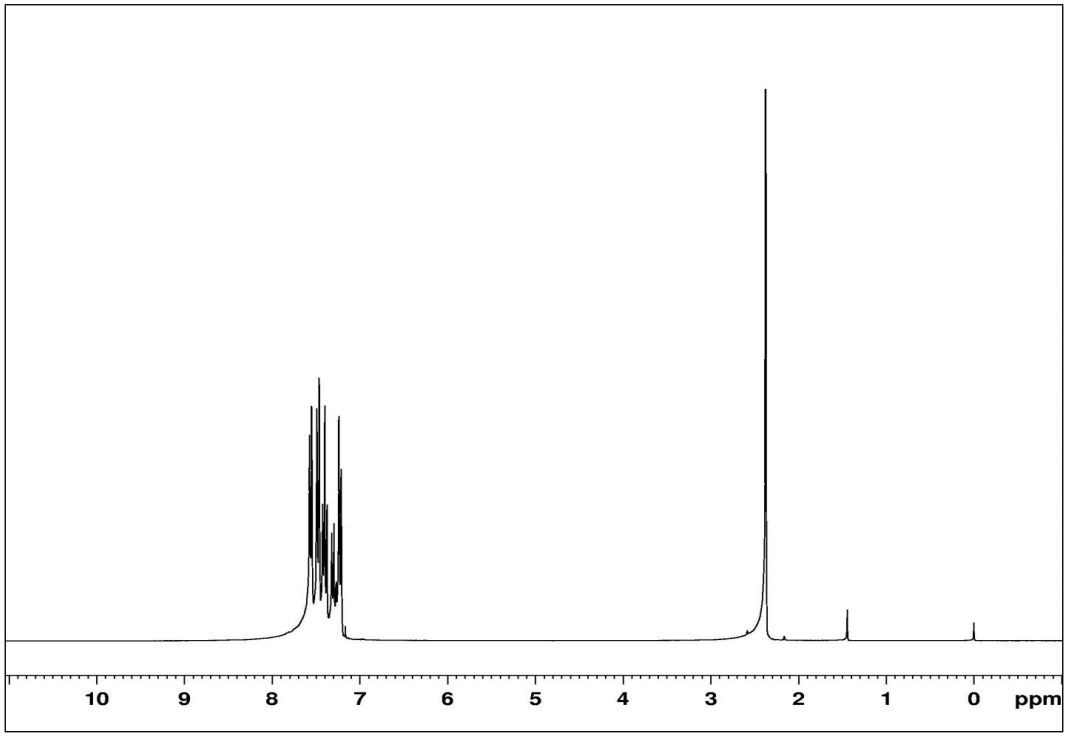


Figure S40 ^{1}H NMR of 4-Methylbiphenyl

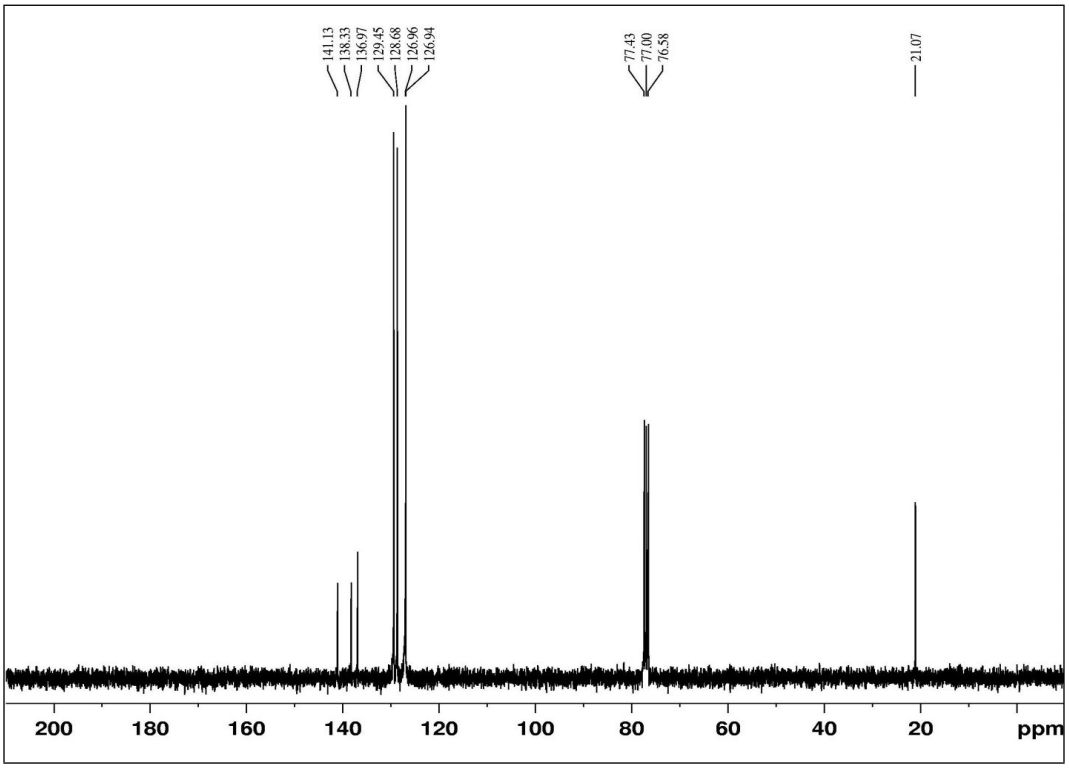


Figure S41 $^{13}C\{^{1}H\}$ NMR of 4-Methylbiphenyl

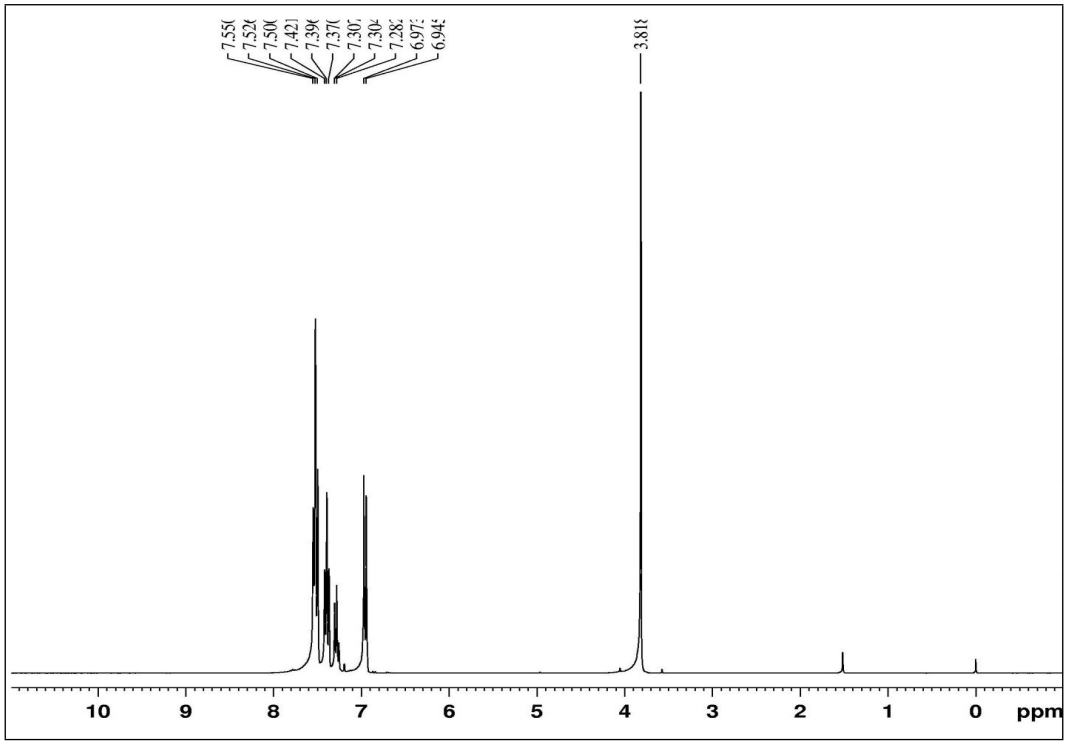


Figure S42 ^{1}H NMR of 4-Methoxybiphenyl

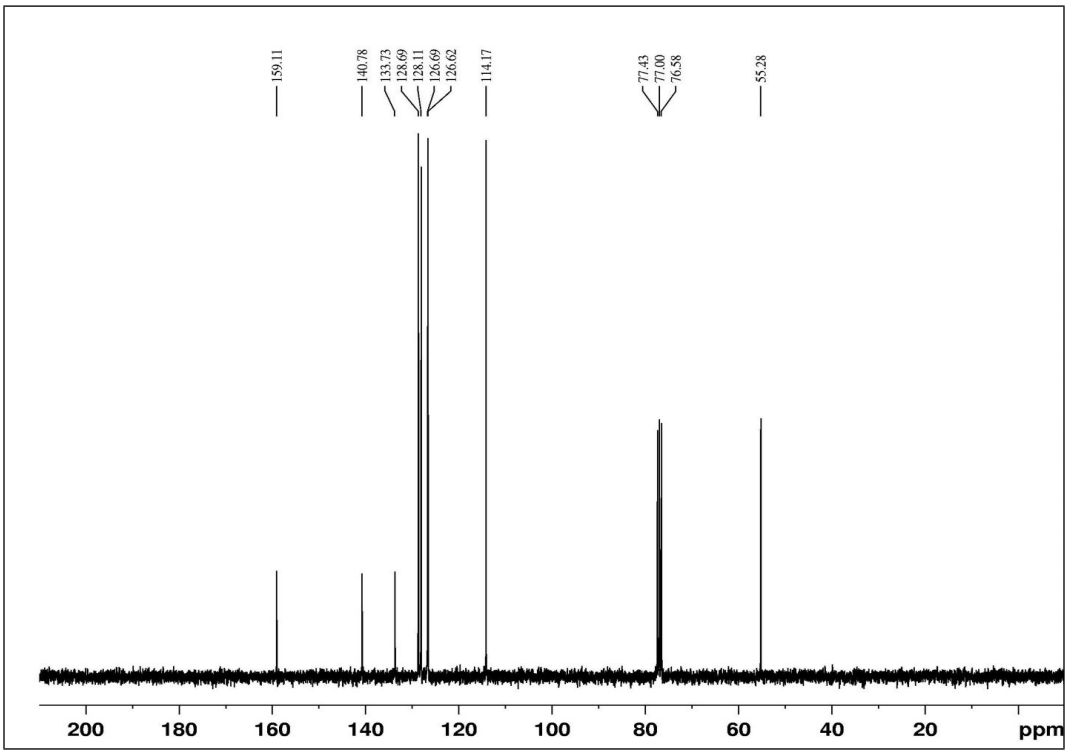


Figure S43 ^{13}C{^{1}H} NMR of 4-Methoxybiphenyl

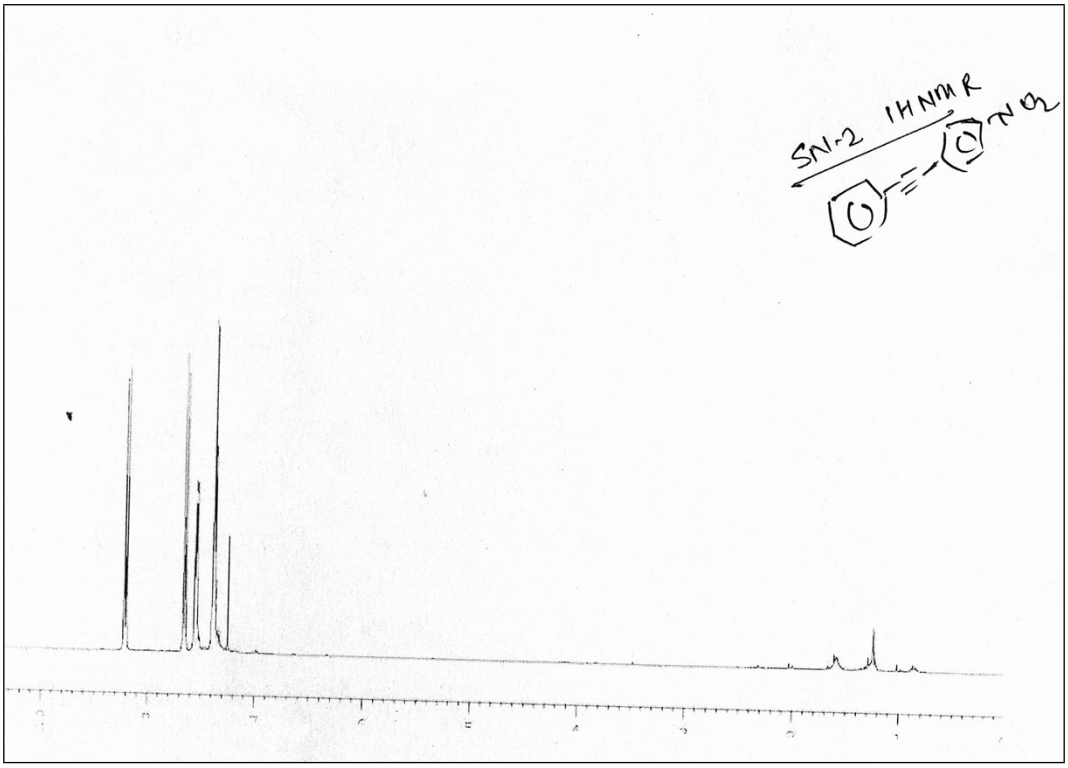


Figure S44 ^{1}H NMR of 1-Nitro-4-(phenylethynyl)benzene

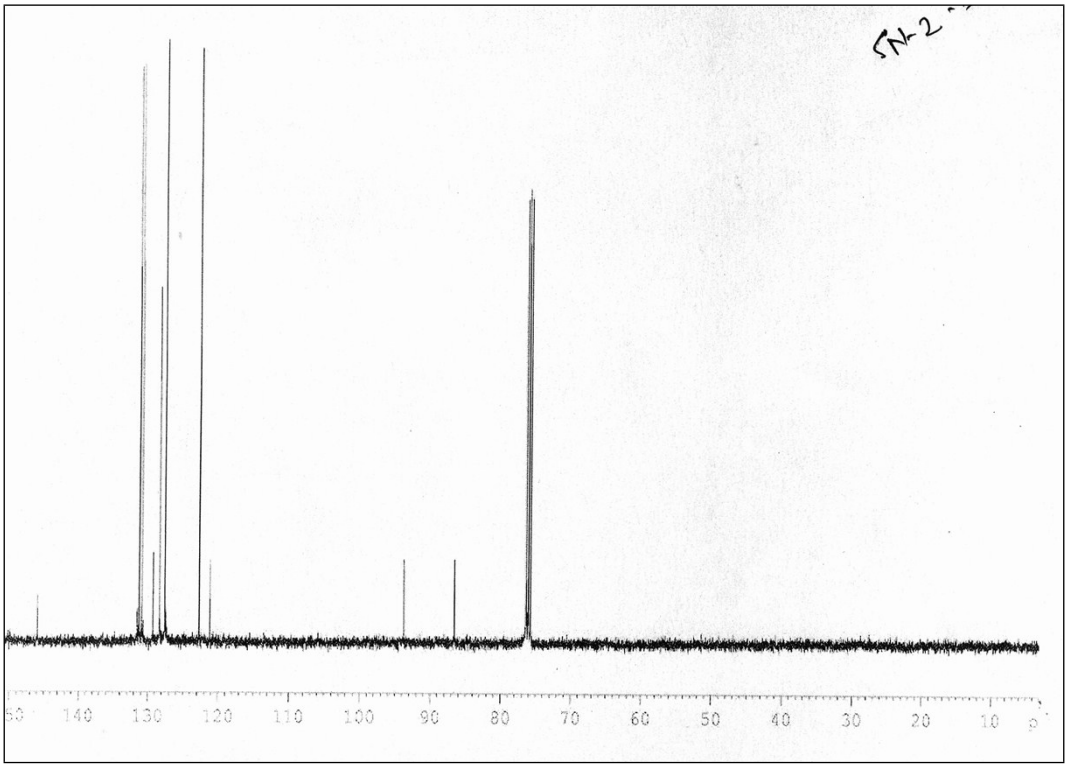


Figure S45 ^{13}C{^{1}H} NMR of 1-Nitro-4-(phenylethynyl)benzene

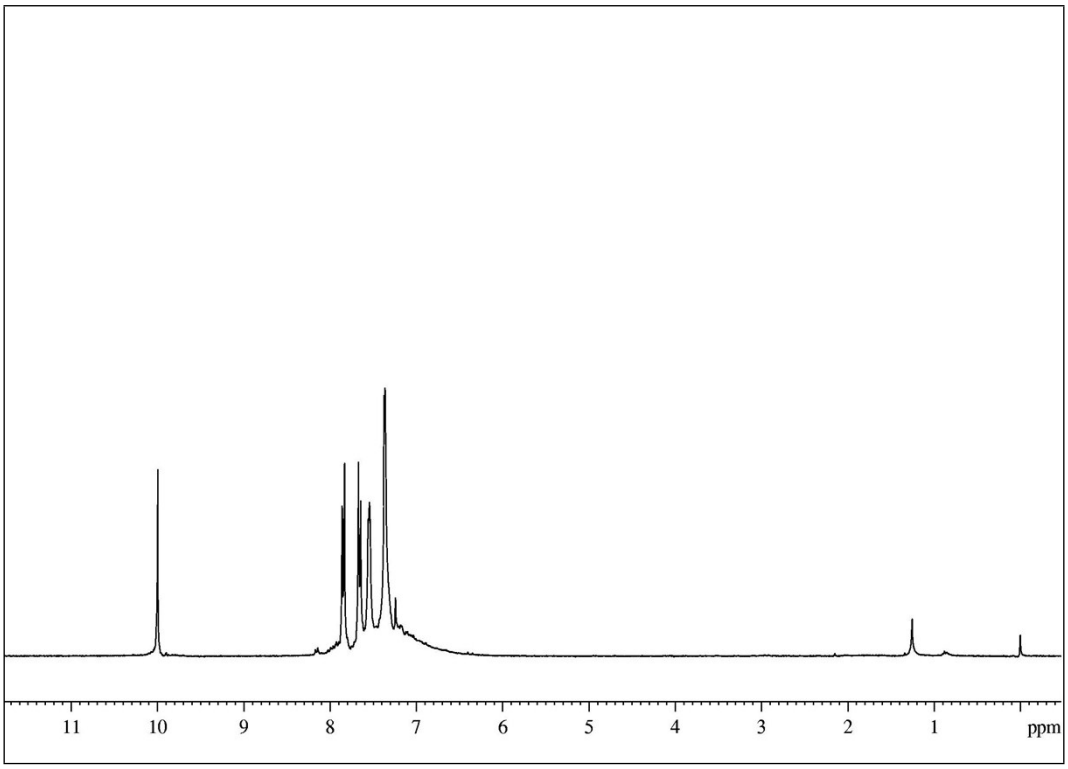


Figure S46 ^{1}H NMR of 4-(Phenylethynyl)benzaldehyde

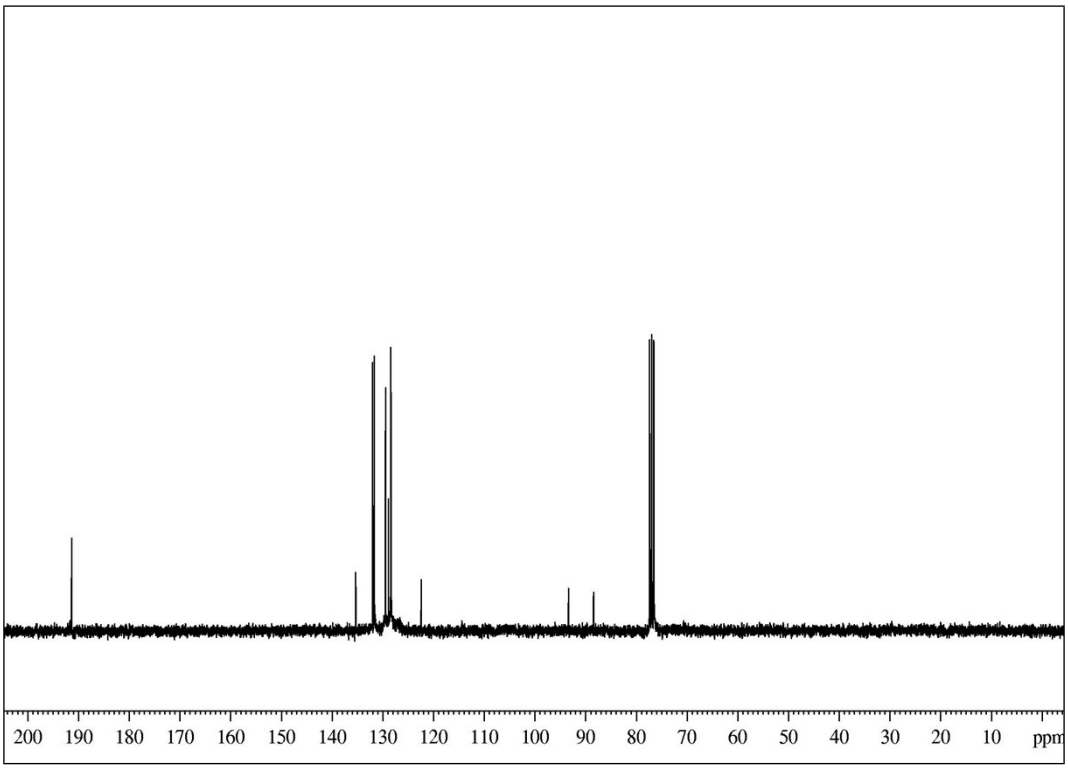


Figure S47 ^{13}C{^{1}H} NMR of 4-(Phenylethynyl)benzaldehyde

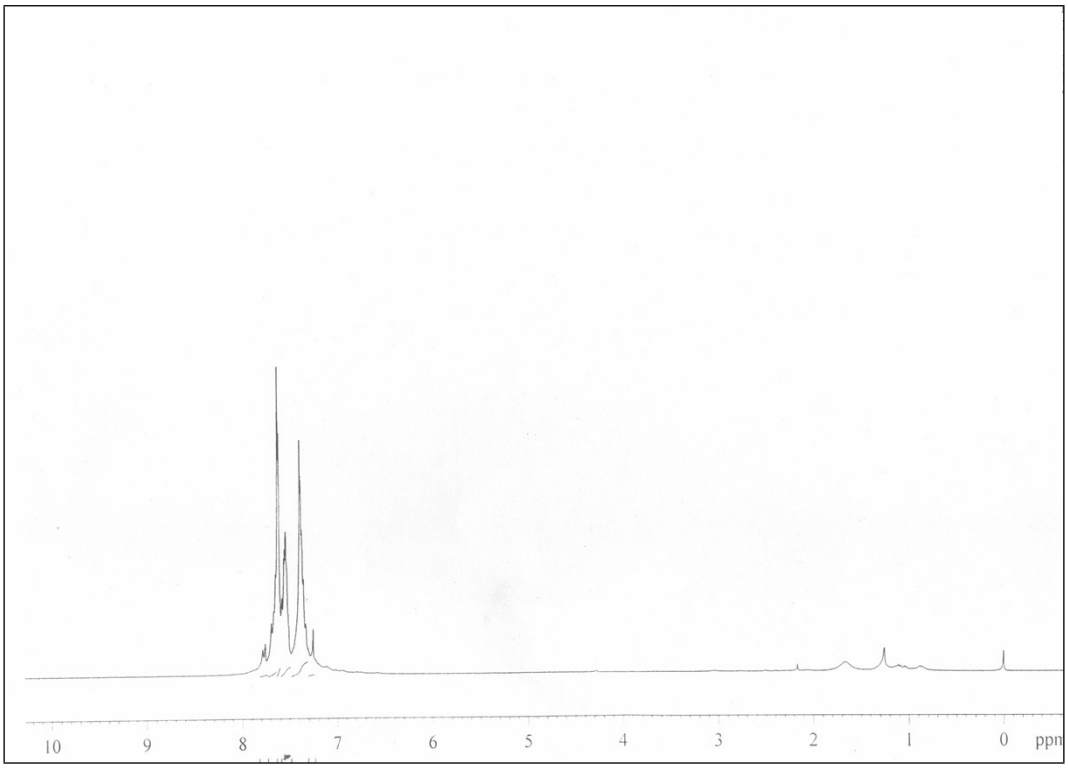


Figure S48 ^{1}H NMR of 4-(Phenylethynyl)benzonitrile

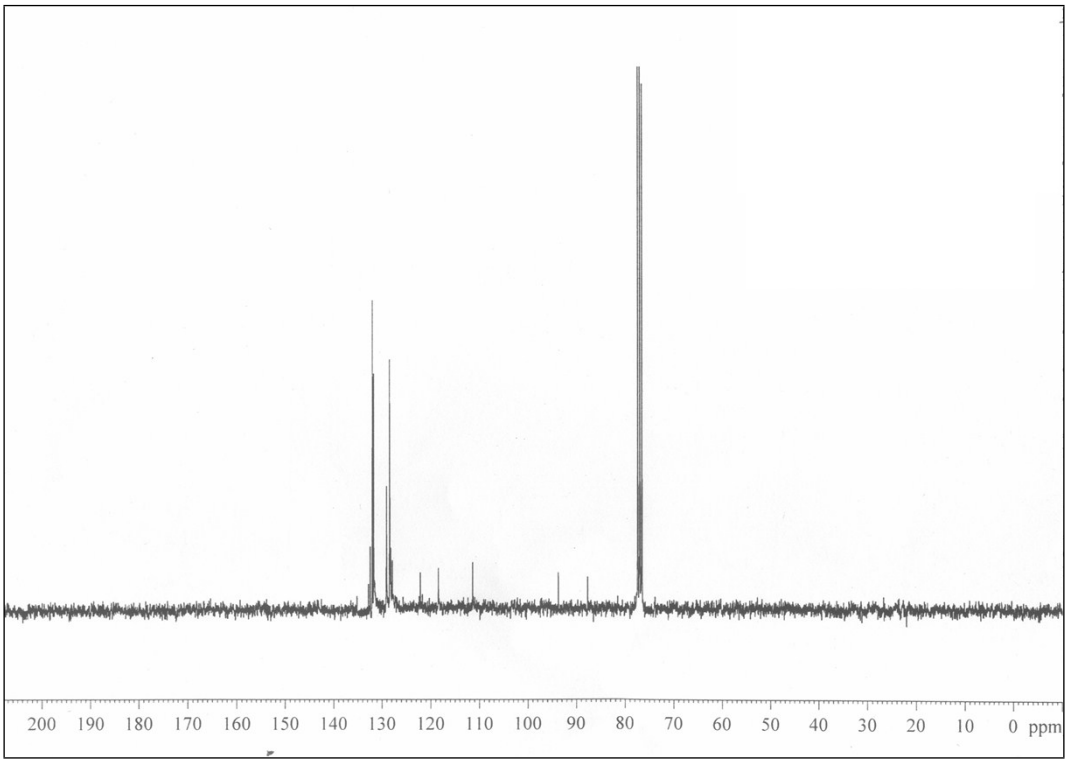


Figure S49 ^{13}C{^{1}H} NMR of 4-(Phenylethynyl)benzonitrile

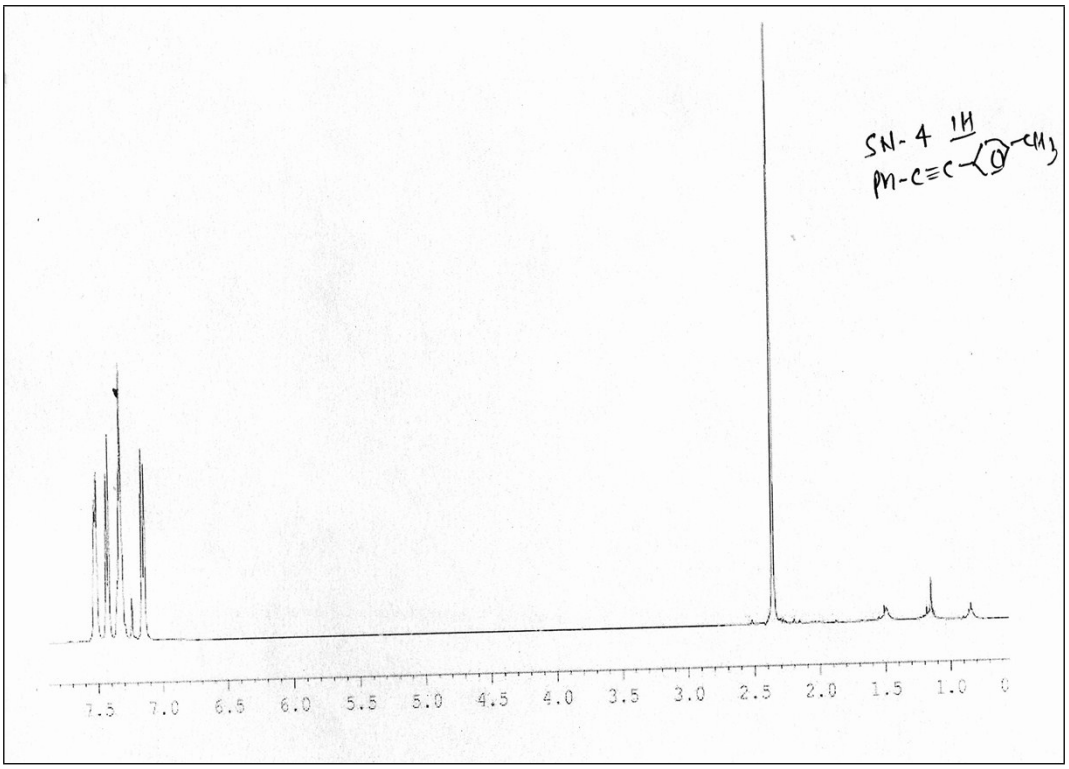


Figure S50 ^{1}H NMR of 1-Methyl-4-(phenylethynyl)benzene

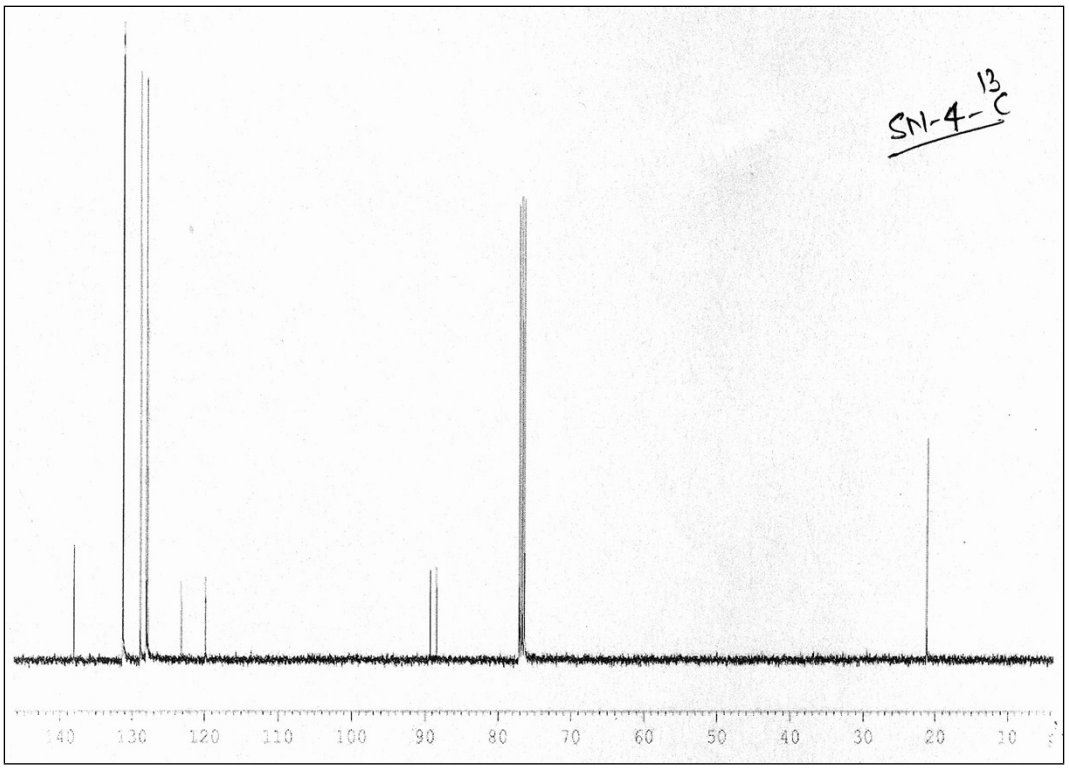


Figure S51 ^{13}C{^{1}H} NMR of 1-Methyl-4-(phenylethynyl)benzene

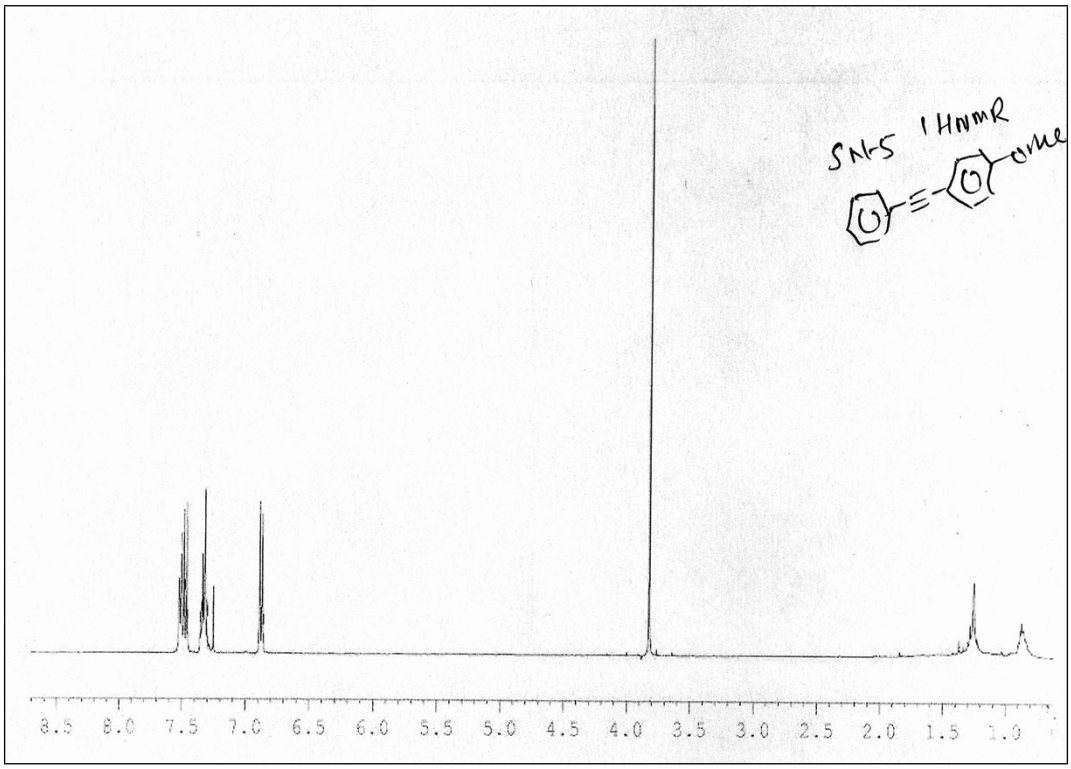


Figure S52 $^{13}C\{^{1}H\}$ NMR of 1-Methoxy-4-(phenylethynyl)benzene

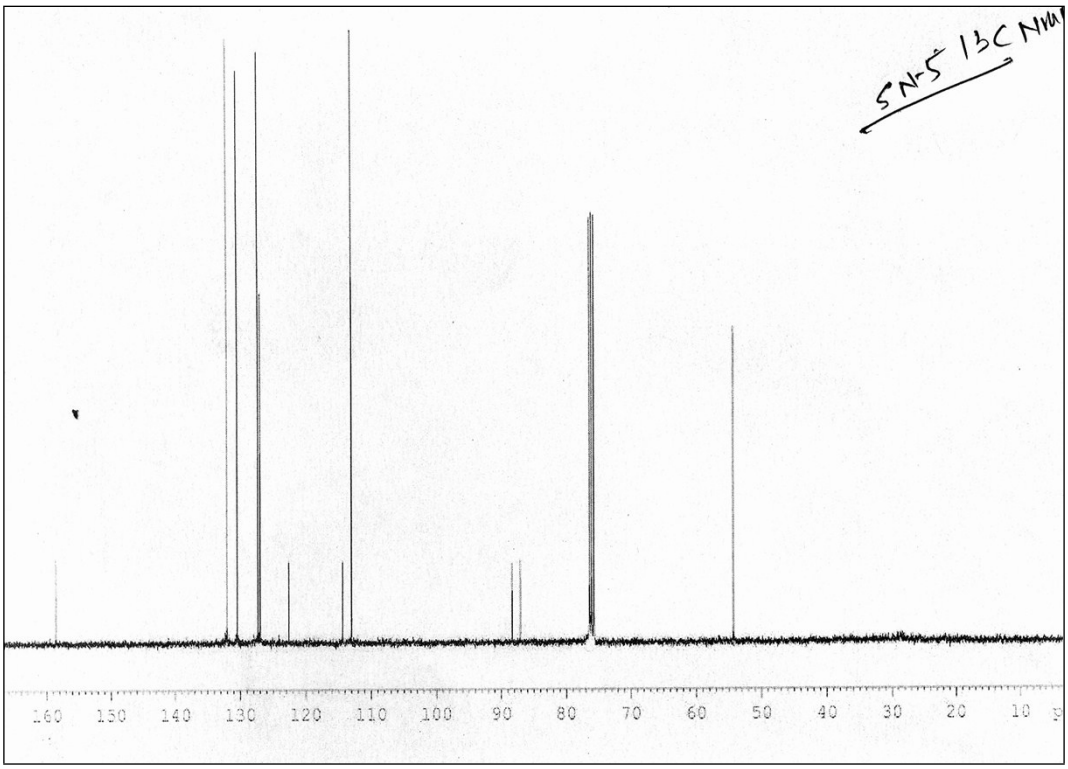


Figure S53 $^{13}C\{^{1}H\}$ NMR of 1-Methoxy-4-(phenylethynyl)benzene

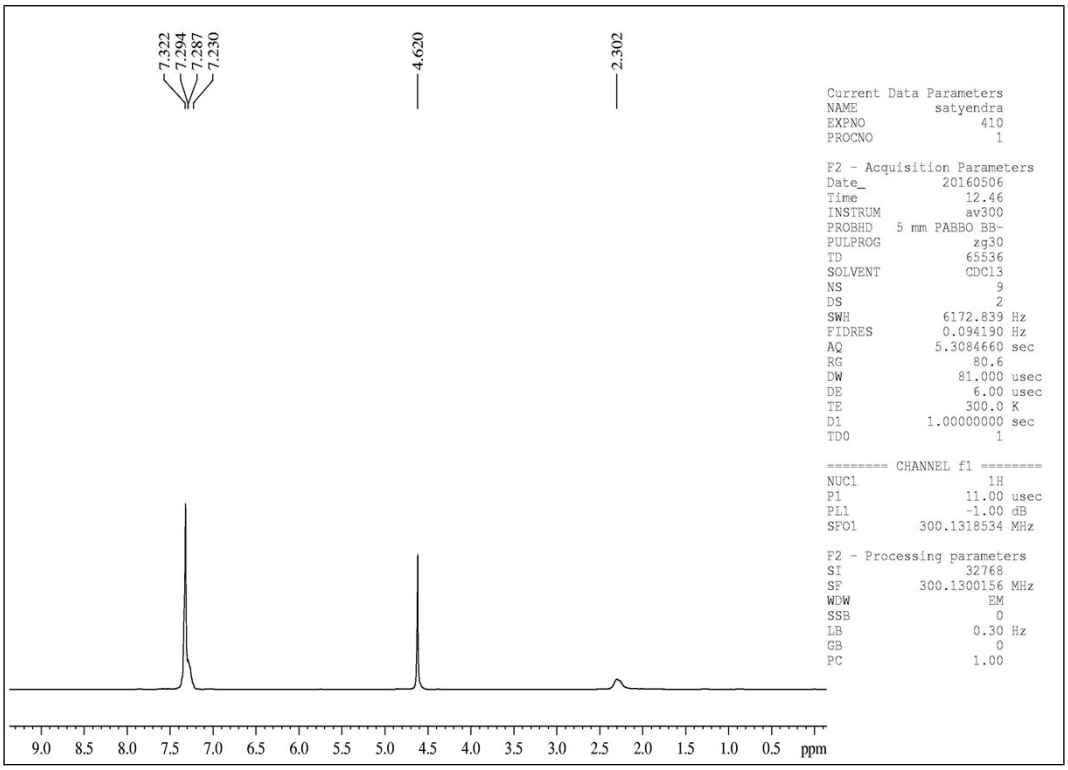


Figure S54 ^{1}H NMR of Phenylmethanol

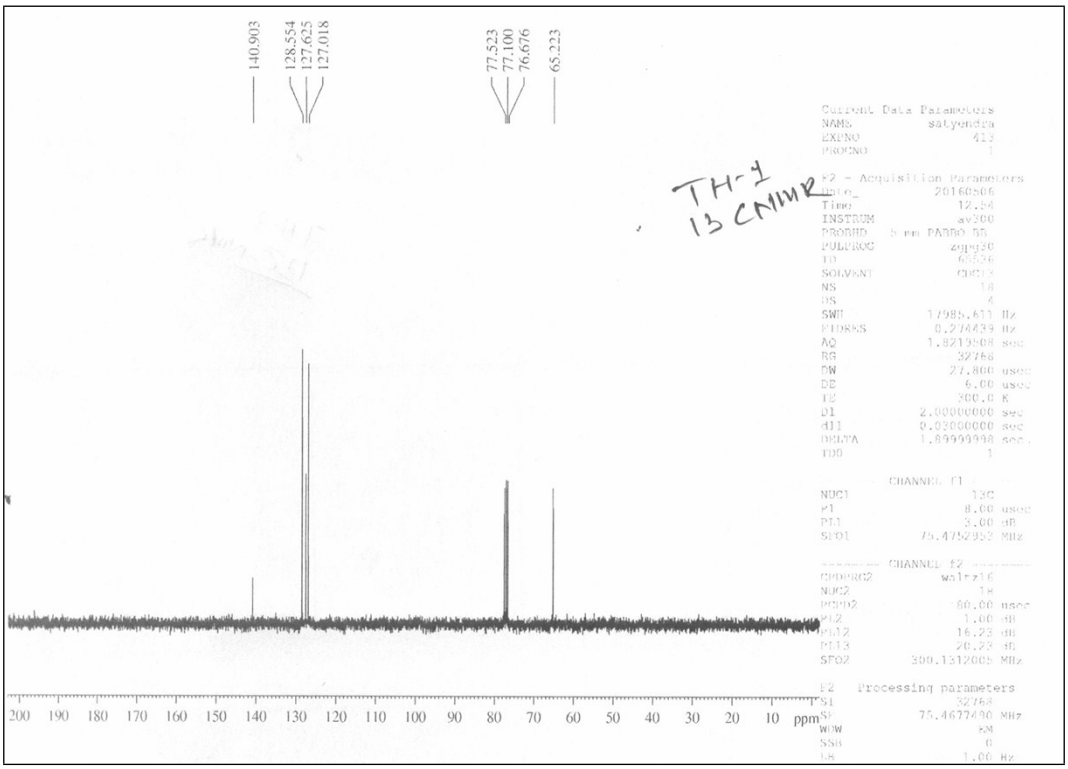


Figure S55 $^{13}C\{^{1}H\}$ NMR of Phenylmethanol

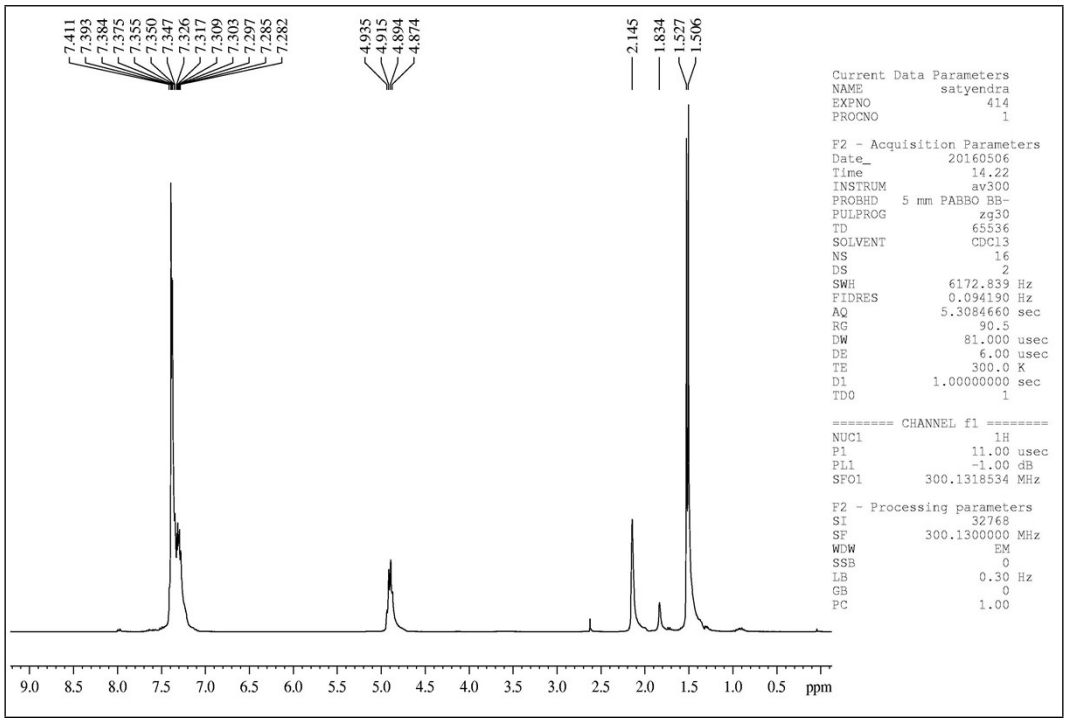


Figure S56 ^{1}H NMR of 1-Phenylethanol

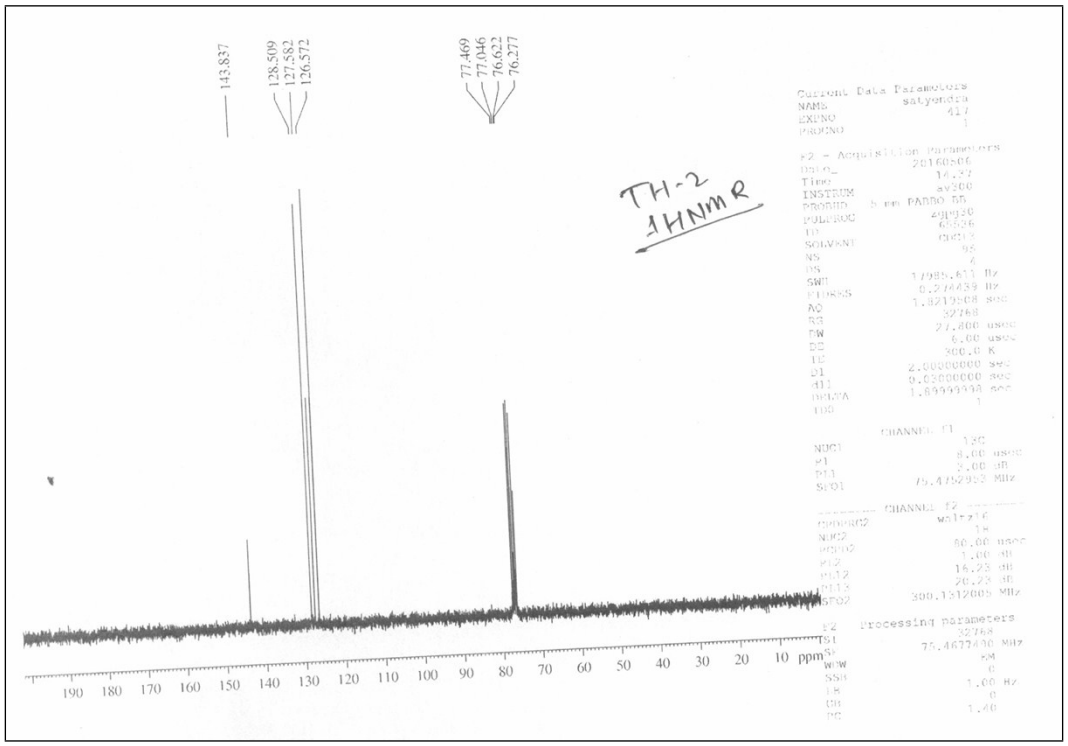


Figure S57 $^{13}C\{^{1}H\}$ NMR of 1-Phenylethanol

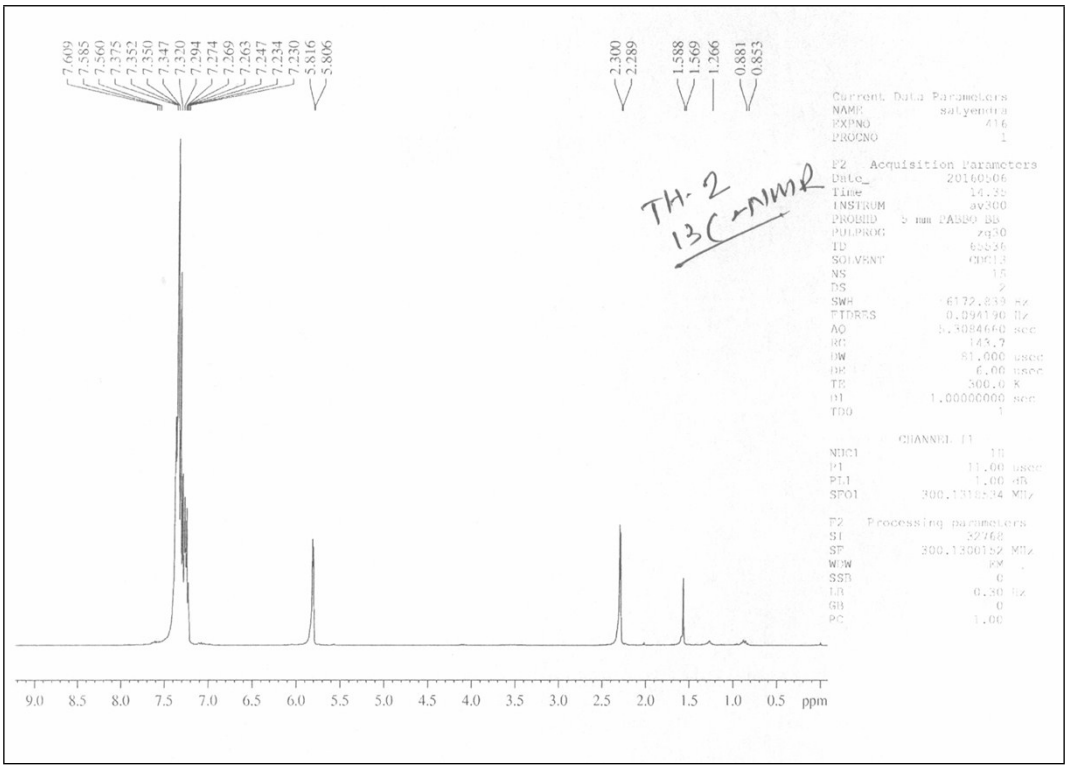


Figure S58 ^{1}H NMR of Diphenylmethanol

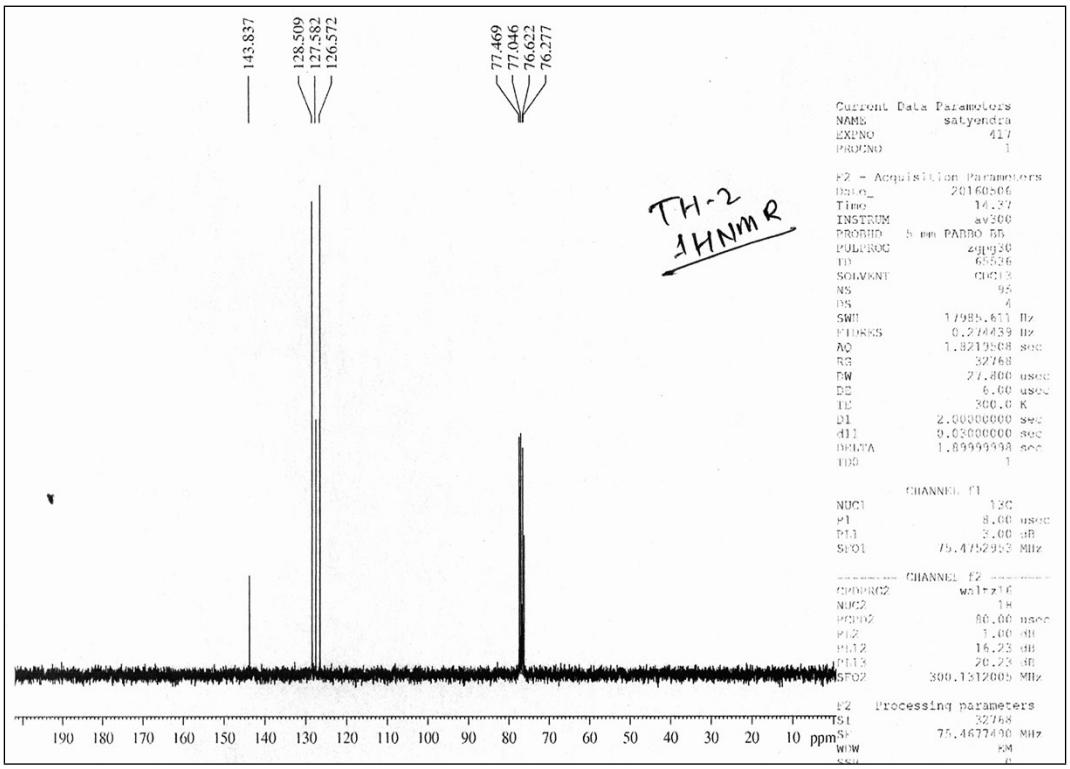


Figure S59 ^{13}C{^{1}H} NMR of Phenylmethanol

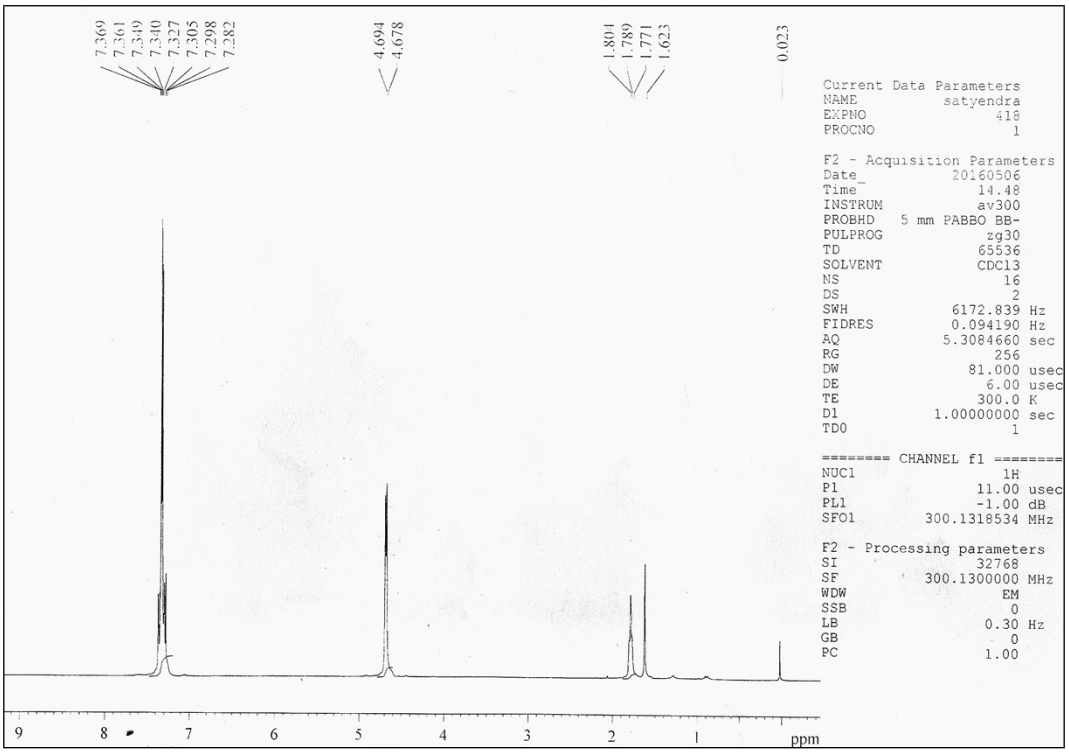


Figure S60 ^{1}H NMR of (4-Chlorophenyl)methanol

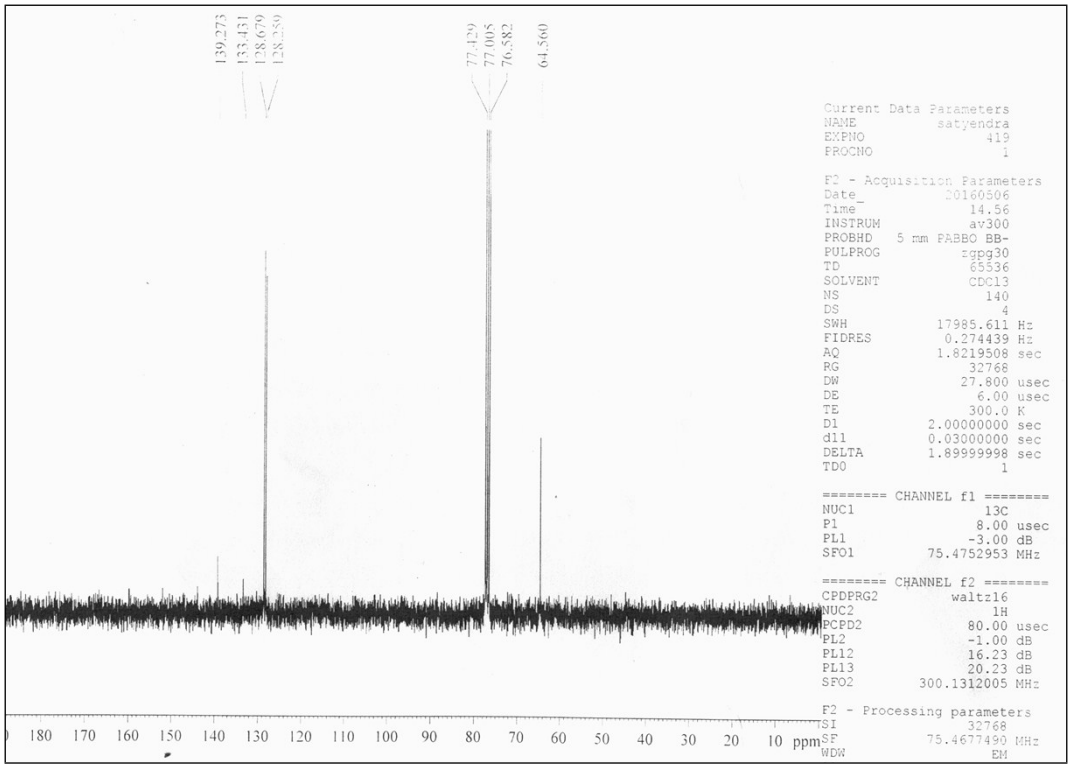


Figure S61 ^{13}C{^{1}H} NMR of (4-Chlorophenyl)methanol

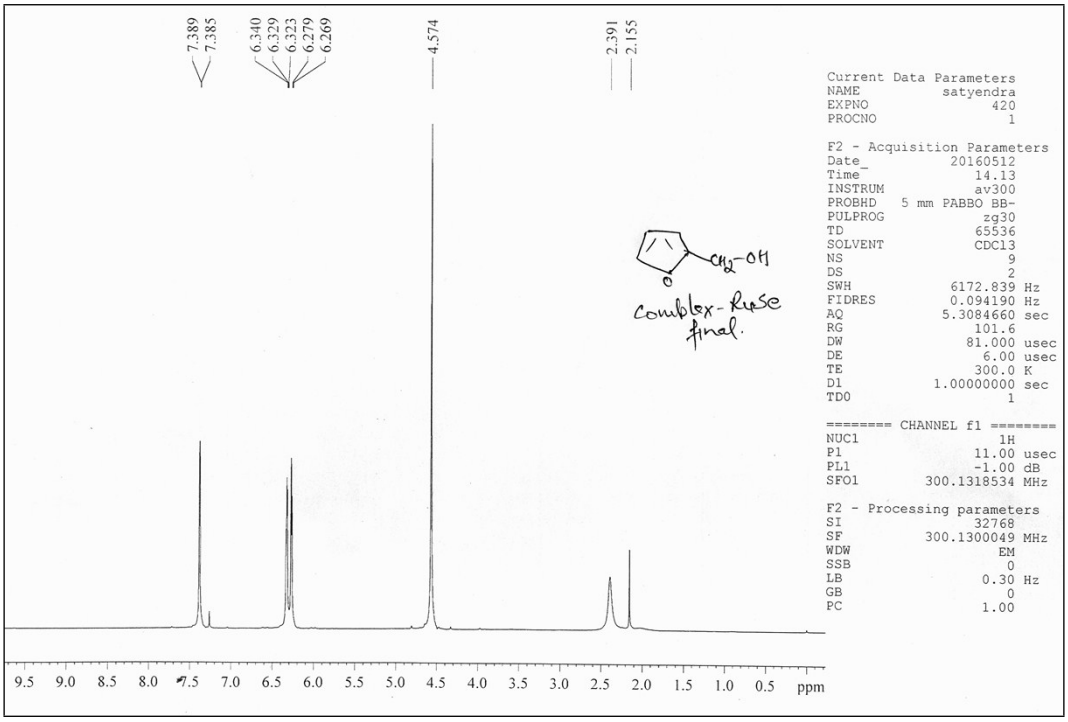


Figure S62 ^{1}H NMR of furan-2-ylmethanol

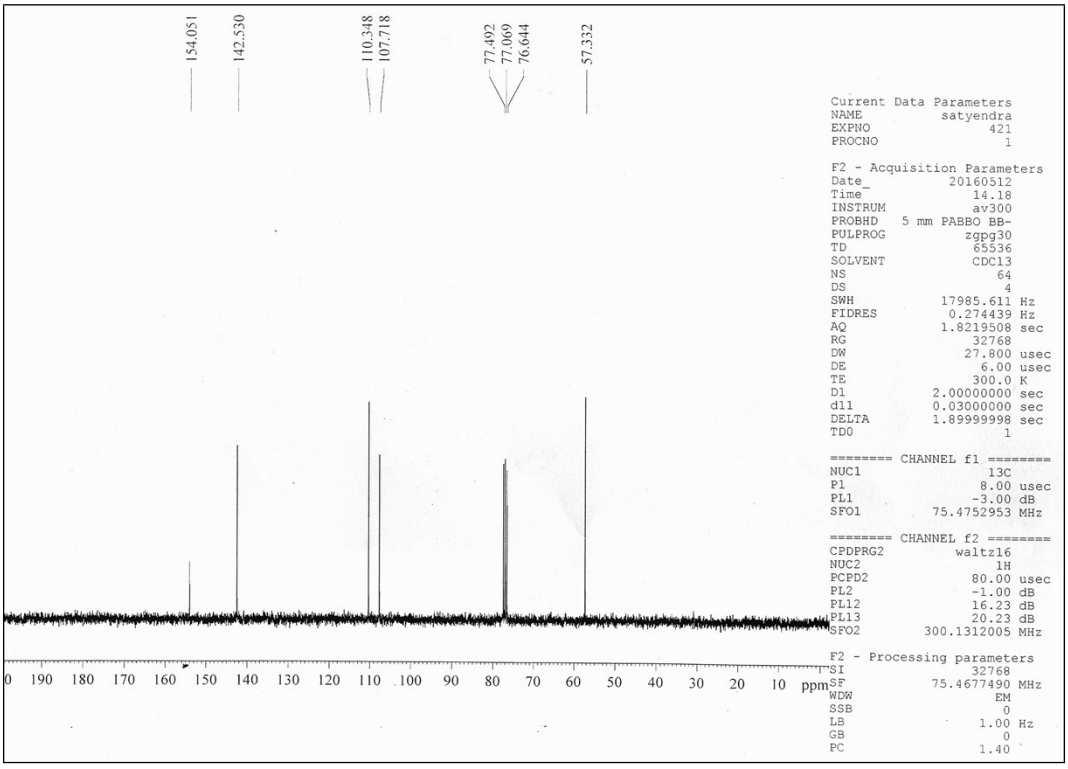


Figure S63 ^{13}C{^{1}H} NMR of furan-2-ylmethanol