ESI

For

Ultra-small Palladium Nano-particles Synthesized Using Bulky S/Se and N Donor Ligands as a Stabilizer: Application as Catalysts for Suzuki-Miyaura Coupling

Preeti Oswal[1], Aayushi Arora[1], Jolly Kaushal[1], Gyandshwar Kumar Rao[2], Sushil Kumar[1], Ajai K Singh[3], Arun Kumar[1]*

[1]*Department of Chemistry, School of Physical Sciences, Doon University, Dehradun, India*

[2]*Amity School of Applied Sciences, Amity University, Gurgaon, Haryana, India*

[3]*Department Of Chemistry, Indian Institue of Technology, Delhi, New Delhi*

Corresponding author: Arun Kumar, e-mail: arunkaushik@gmail.com,

akumar.ch@doonuniversity.ac.in

CONTENTS

S1. Syntheses of ligands L1' and L2'

Synthesis of L1' and L2': 9-Anthracenecarboxaldehyde (0.412 g, 2.0 mmol) was stirred in dry ethanol (5 mL) for 10 minutes at room temperature. The solution of 2-(phenylthio)ethylamine (0.306 g, 2.0 mmol) / 2-(phenylseleno)ethylamine (0.398 g, 2.0 mmol) was added drop wise with stirring. The mixture was further stirred for 8 h at room temperature. After completion of the reaction, the solvent was removed with a rotary evaporator resulting **L1'/L2'** as a yellow solid.

L1': Yield: Yellow solid (0.30 g) 86%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ(ppm): 3.62 (t, 2H, SCH_2), 4.36 (t, 2H, NCH_2), 7.20 (m, 1H, Ar-H), 7.35-7.40 (m, 2H, Ar-H), 7.48-7.60 (m, 6H, Ar-H), 8.03 (m, 2H, Ar-H), 8.49-8.60 (m, 3H, Ar-H), 9.40 (s,1H,CH=N). ^{13}C{^{1}H}NMR (125 MHz, $CDCl_3$, 25 °C, TMS):34.5 (SCH_2), 61.3(NCH_2), 124.6, 124.8, 125.2, 126.7, 128, 128.5, 129, 129.5, 131.1, 135.8 (Ar-C), 162.1 (N=C).

L2':^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ(ppm): 3.43 (t, 2H, $SeCH_2$), 4.18 (t, 2H, C-CH_2-N), 7.21-7.28 (m, 3H, Ar-H), 7.43-7.51 (m, 4H, Ar-H), 7.59 (m, 2H,Ar-H), 7.9 (m, 2H, Ar-H), 8.4-8.51 (m, 3H, Ar-H), 9.31 (s, 1H, CH=N).^{13}C{^{1}H}NMR (125MHz, CDCl3, 25°C, TMS):28.5($SeCH_2$), 62.2 (NCH_2), 124.7, 125.18, 126.2, 126.9, 127.8, 128.7, 129.1, 129.4, 129.7, 129.8, 131.1,131.7 (Ar-C), 161.7 (N=C).

TABLE S1. Crystal data and structural refinements for ligand L1

	L1
Empirical formula	$C_{23}H_{21}NS$
Formula weight	343.47
Temperature	150.01(10) K
Wavelength	1.541
Crystal system, space group	Triclinic, *P−1*
Unit cell dimension	a = 5.3825(7) Å b = 15.3166(13) Å c = 21.472(3) Å α = 89.910(8)° β = 84.752(10)° γ = 89.905(9)°
V	1762.8 (4) Å^3
Z	4
Absorption coefficient	1.639
F(000)	728
Crystal color	Light yellow
Theta range for data collection	3.5470 to 67.0830 deg.
Density	1.294
Limiting indices	−6<h<4, −15<h<18, −24<h<25
Goodness –of –fit on F^2	1.131
$R1^b$ [$I > 2\sigma(I)$]	0.0821
*R*1[all data]	0.1042
$wR2^c$ [$I > 2\sigma(I)$]	0.2427
*wR*2 [all data]	0.2912
CCDC	1887878

Table S2. Selected bond distances and bond angles of L1

Bond Length(Å)		**Bond Angles(°)**	
S(2)–C(27)	1.765(6)	C(27)–S(2)–C(13)	104.5(3)
S(2)–C(13)	1.826(6)	C(45)–N(3)–C(33)	113.9(4)
N(3)–C(45)	1.436(8)		
N(3)–C(33)	1.492(7)		

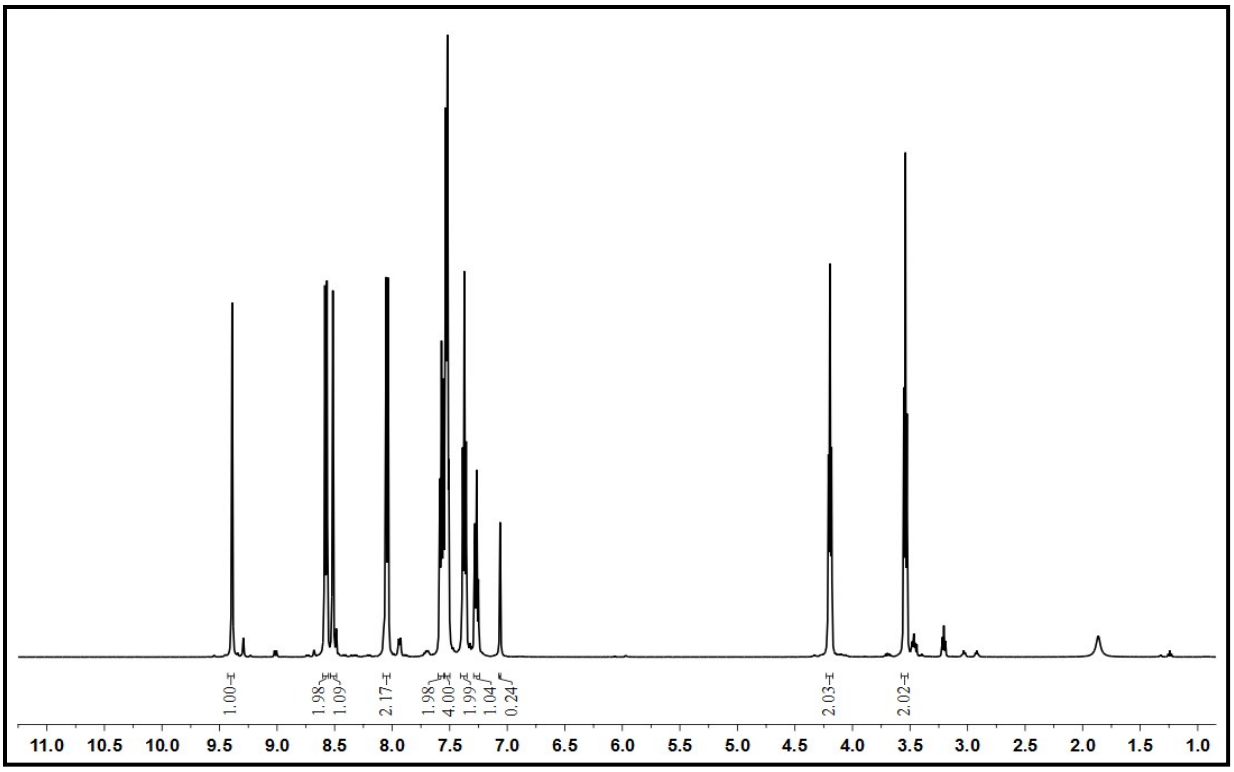


Fig. S1. ^{1}H NMR of ligand **L1'**

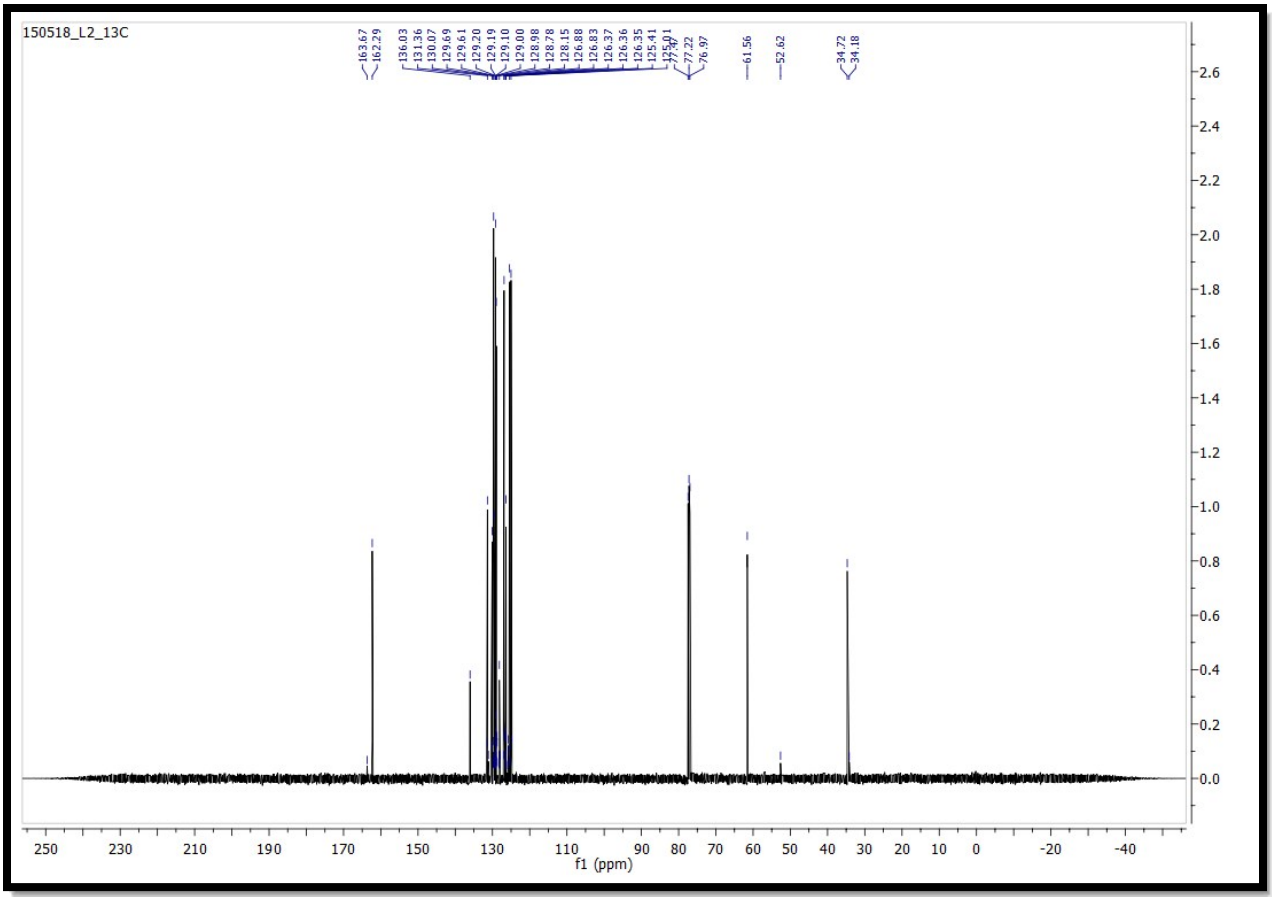


Fig. S2. $^{13}C\{^{1}H\}$ NMR of ligand **L1'**

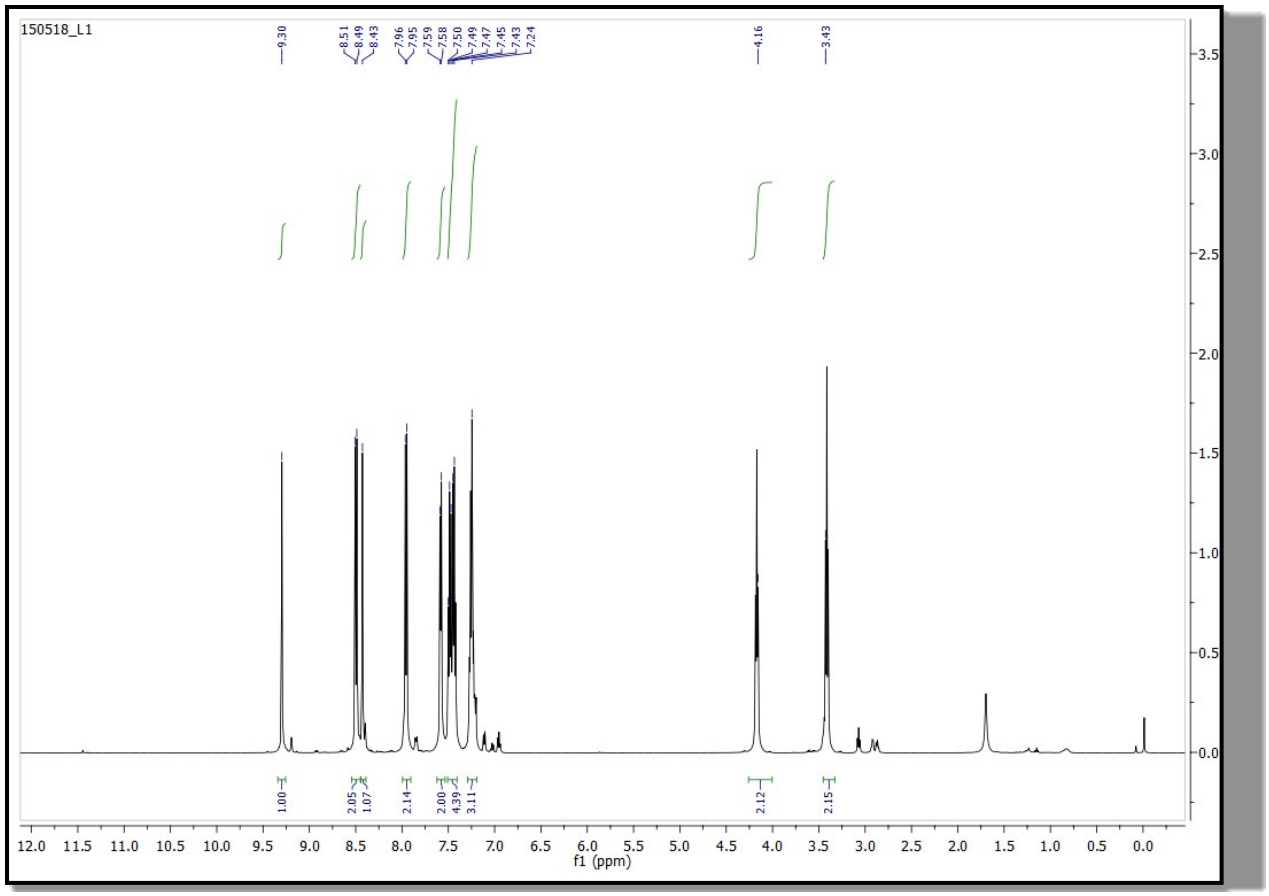


Fig. S3. ^{1}H NMR of ligand **L2'**

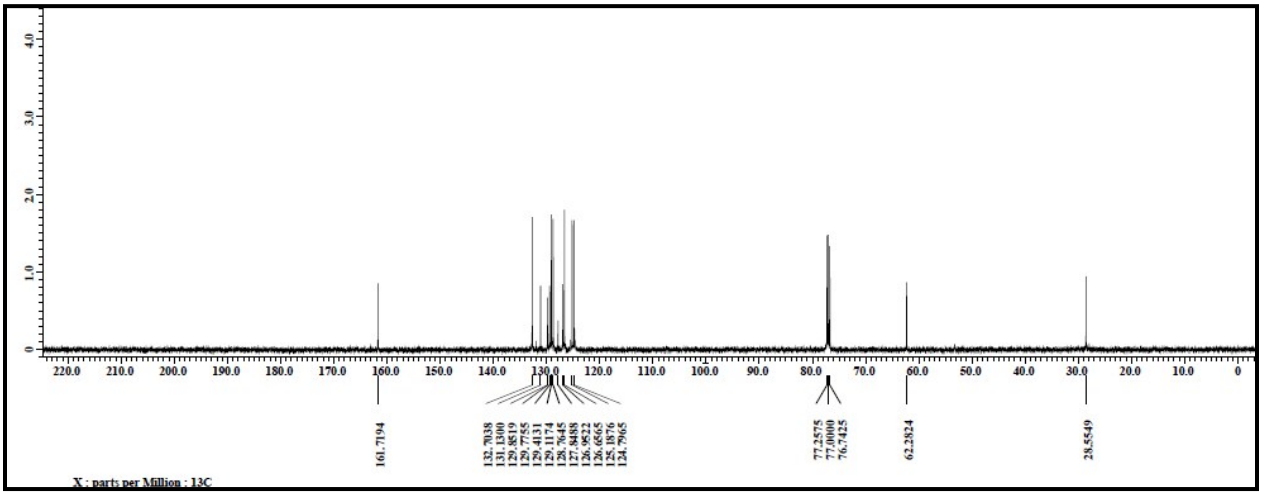


Fig. S4. ^{13}C{^{1}H} NMR of ligand **L2'**

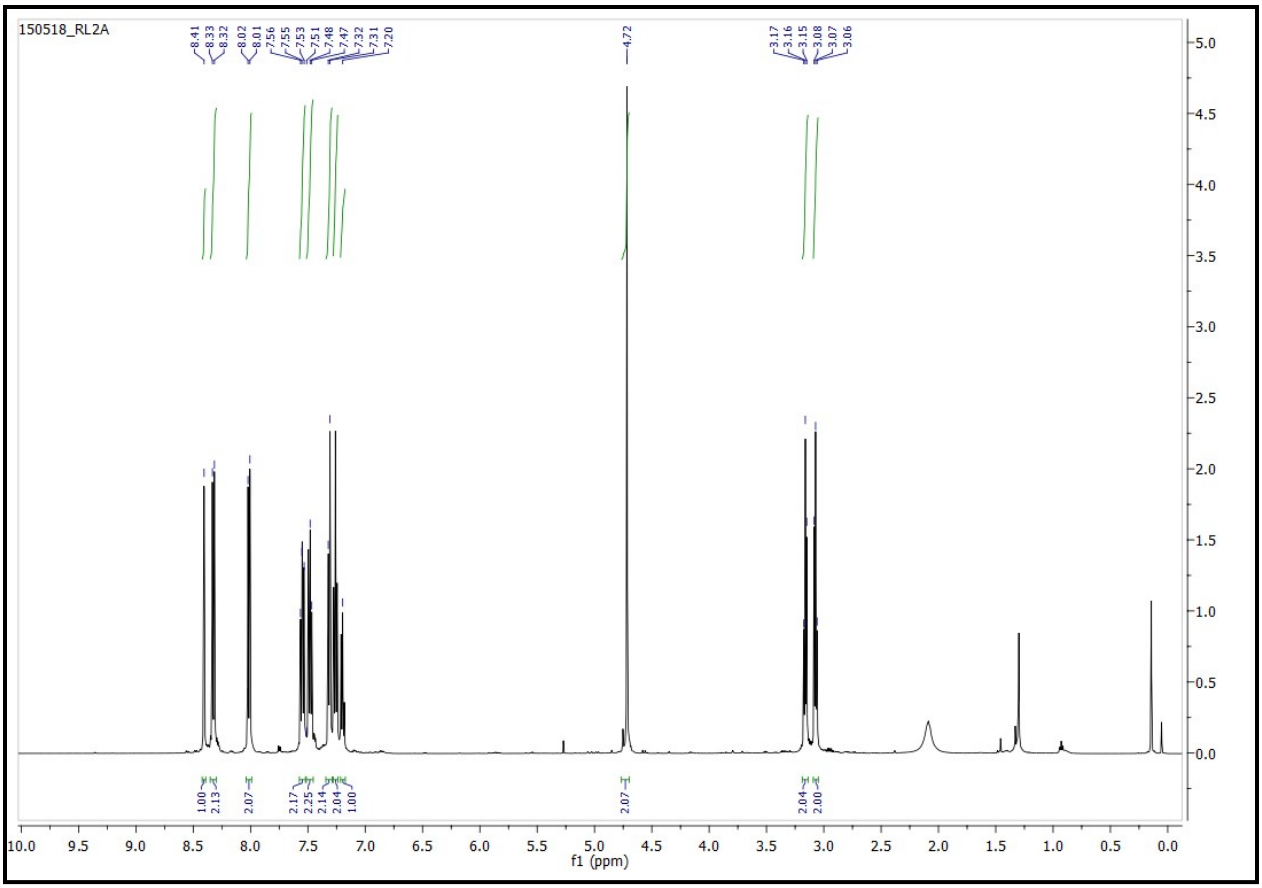


Fig. S5. ^{1}H NMR of ligand **L1**

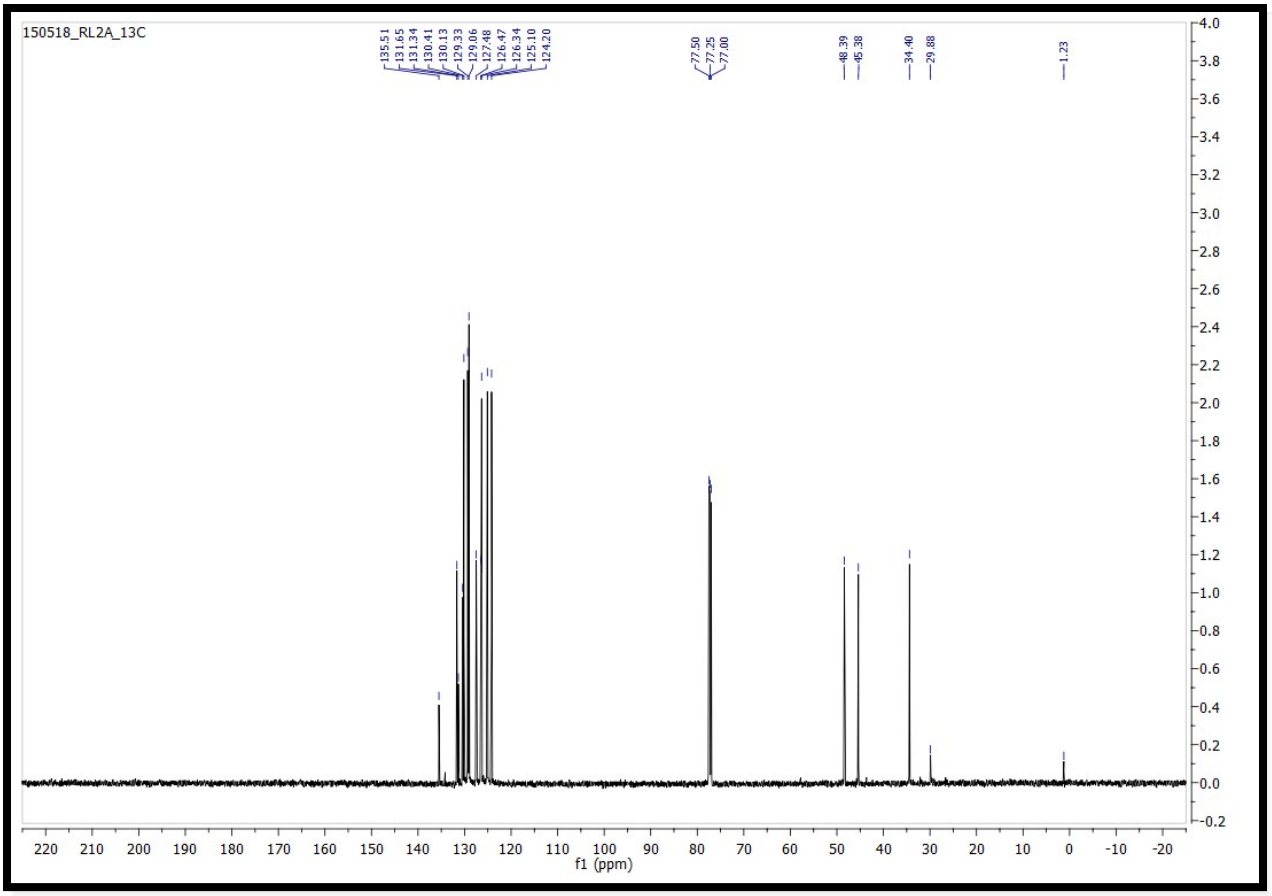


Fig. S6. $^{13}C\{^{1}H\}$ NMR of ligand **L1**

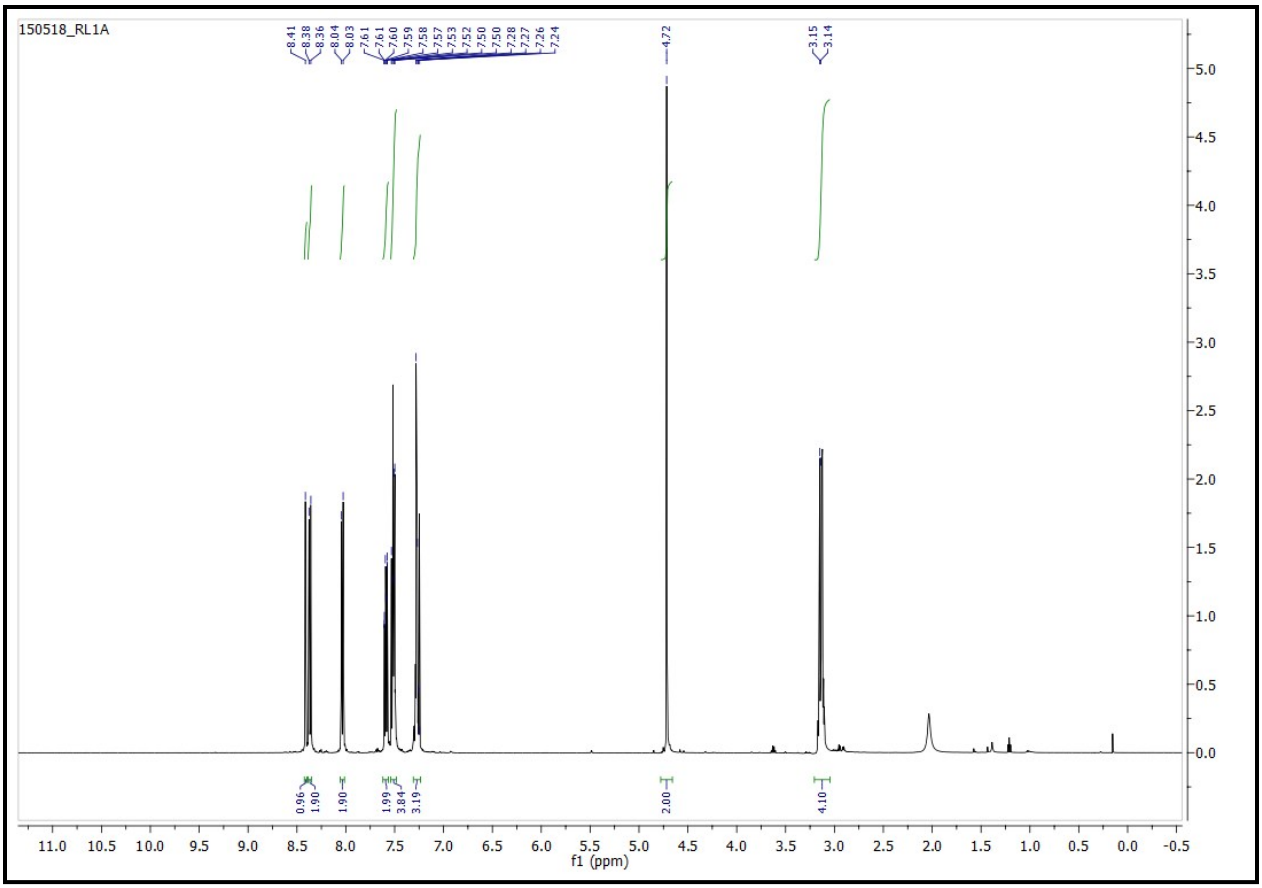


Fig. S7. ^{1}H NMR of ligand **L2**

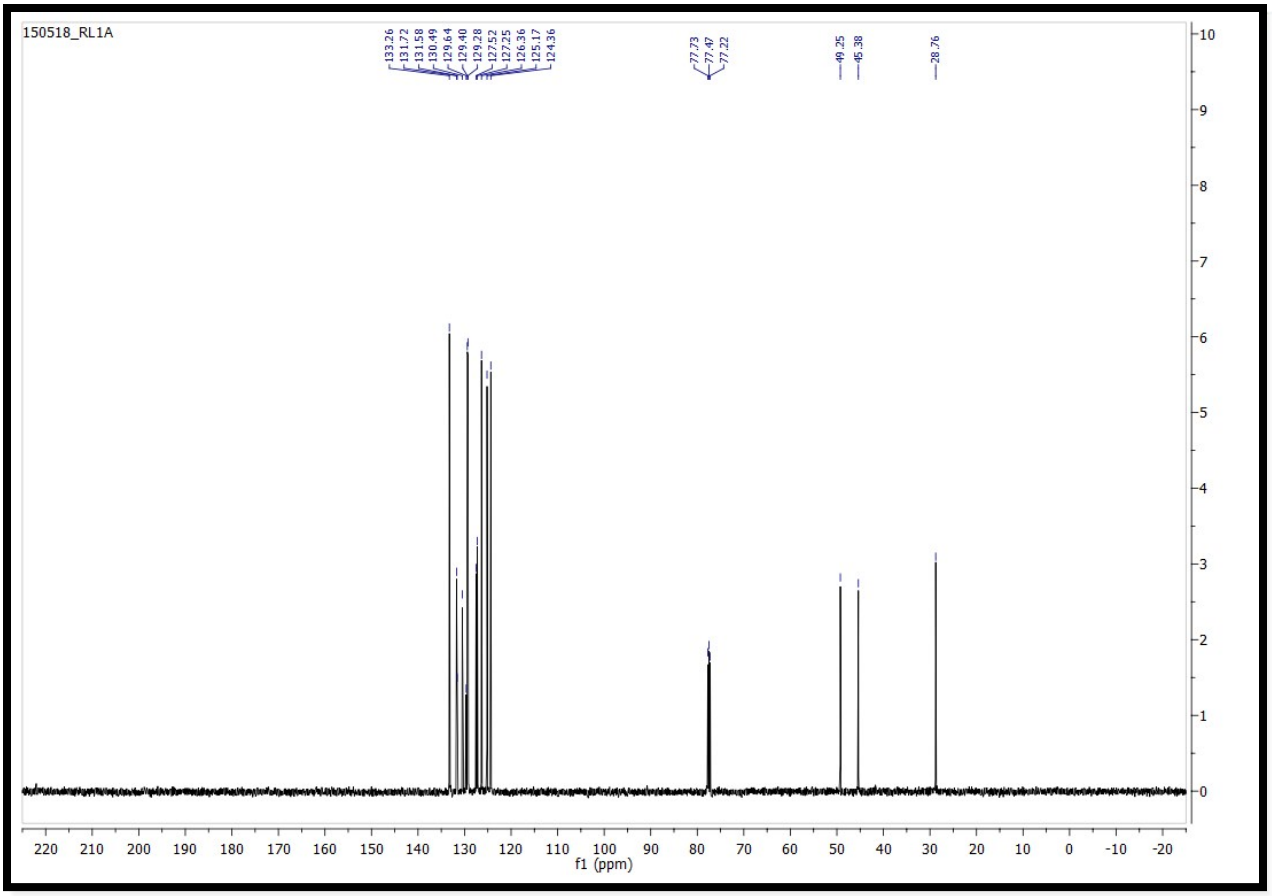
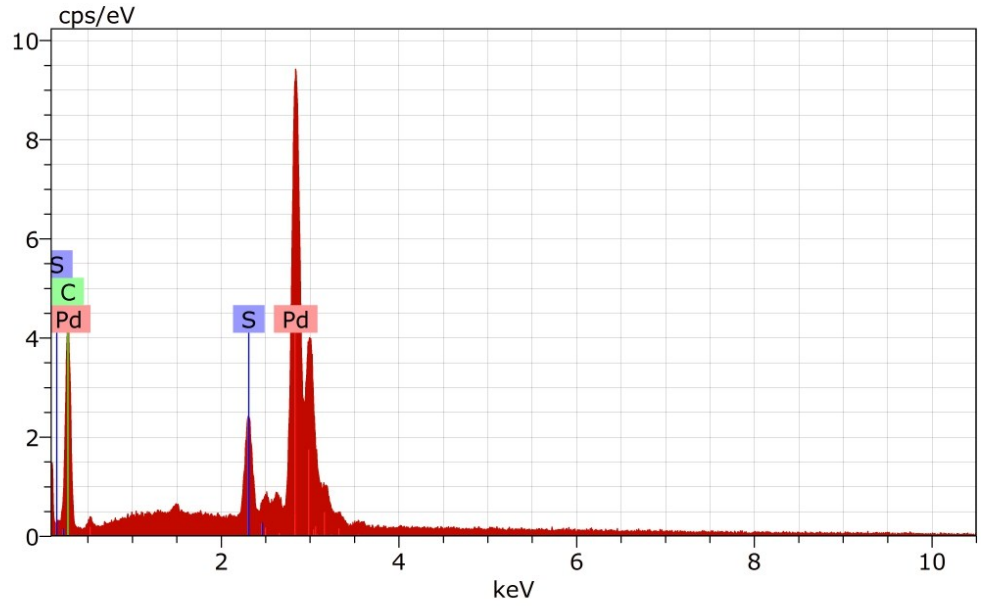


Fig. S8. $^{13}C\{^{1}H\}$ NMR of ligand **L2**



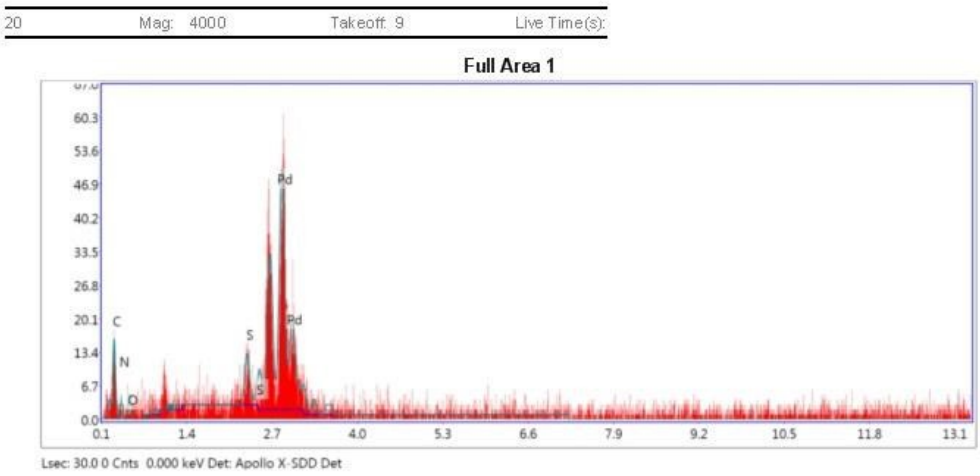
Spectrum: test 2700

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Palladium	L-series	62.10	78.70	33.02	6.04
Carbon	K-series	12.67	16.05	59.67	5.11
Sulfur	K-series	4.14	5.25	7.30	0.54
	Total:	78.91	100.00	100.00	

Fig. S9. SEM−EDX analysis of NP's **1**

EDAX TEAM

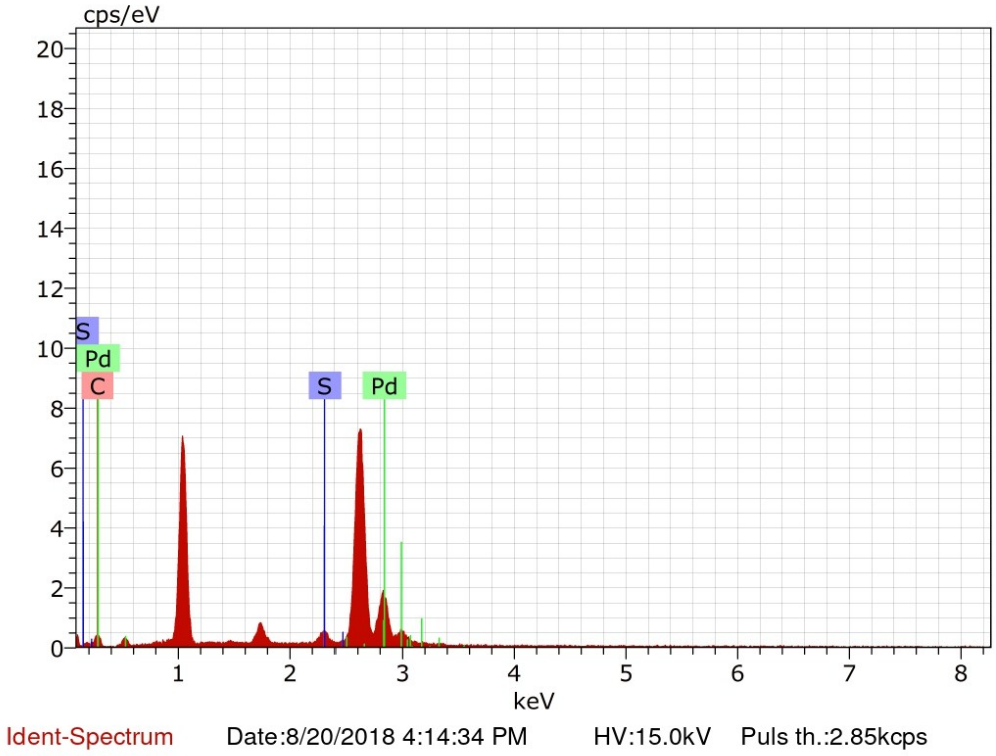
Full Area 1



eZAF Smart Quant Results

Element	Weight %	Atomic %	Error %
C K	0.21	0.54	99.99
N K	19.41	42.52	48.70
O K	18.57	35.60	43.44
S K	5.26	5.03	27.33
PdL	56.55	16.31	9.82

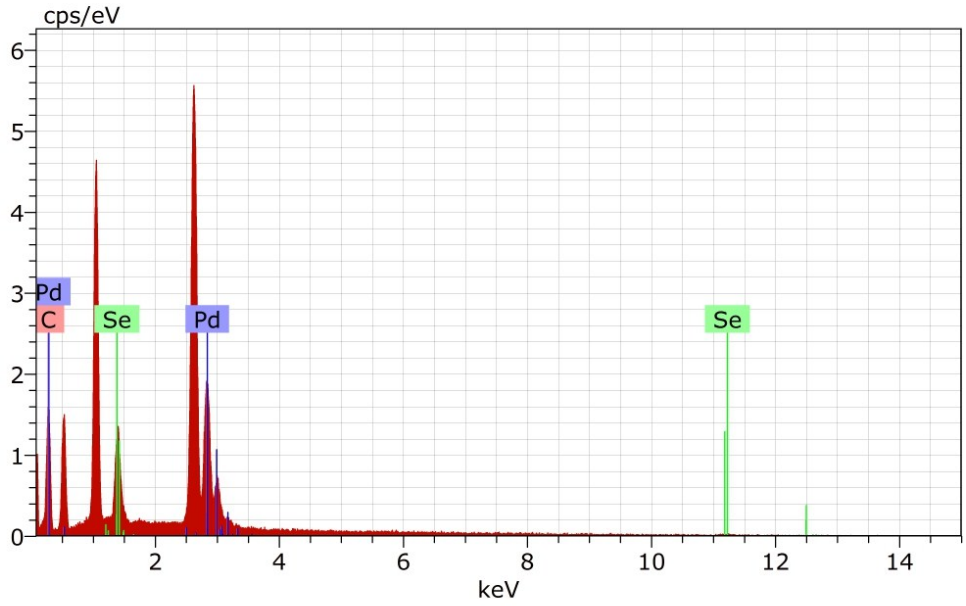
Fig. S10. SEM−EDX analysis of NP's **2**



Spectrum: test 2729

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	1.25	3.05	19.18	1.36
Palladium	L-series	36.75	89.72	63.77	3.79
Sulfur	K-series	2.96	7.23	17.05	0.48
	Total:	40.96	100.00	100.00	

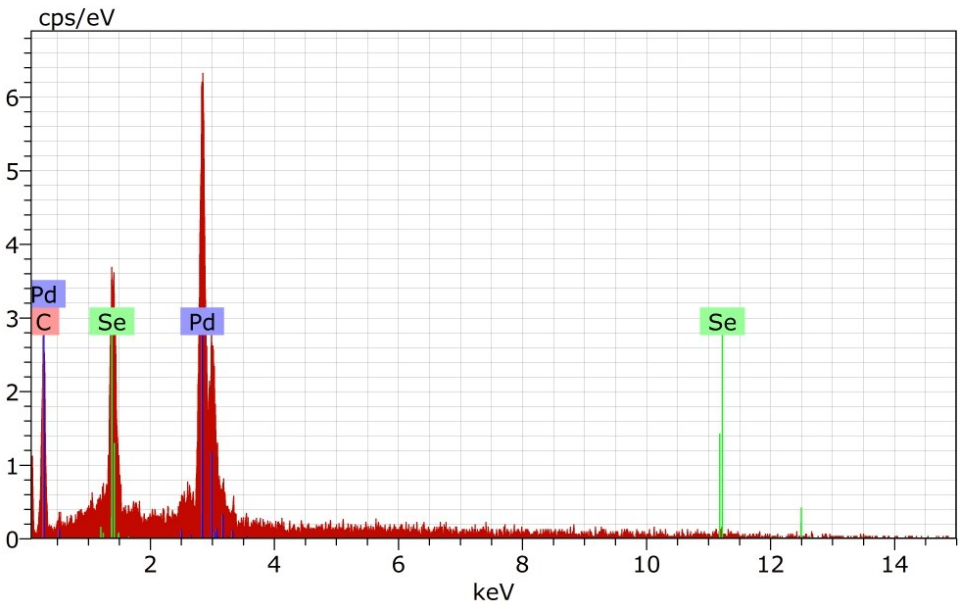
Fig. S11. SEM−EDX analysis of NP's **3**



Spectrum: test 2704

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	5.80	10.99	50.13	3.23
Selenium	L-series	11.92	22.58	15.67	1.91
Palladium	L-series	35.06	66.43	34.20	3.50
	Total:	52.77	100.00	100.00	

Fig. S12. SEM−EDX analysis of NP's **4**



Spectrum: test 2705

Element	Series	unn. C [wt.%]	norm. C [wt.%]	Atom. C [at.%]	Error (3 Sigma) [wt.%]
Carbon	K-series	12.89	16.40	61.64	9.15
Selenium	L-series	15.43	19.62	11.22	2.77
Palladium	L-series	50.30	63.98	27.14	5.41
	Total:	78.62	100.00	100.00	

Fig. S13. SEM−EDX analysis of NP's **6**

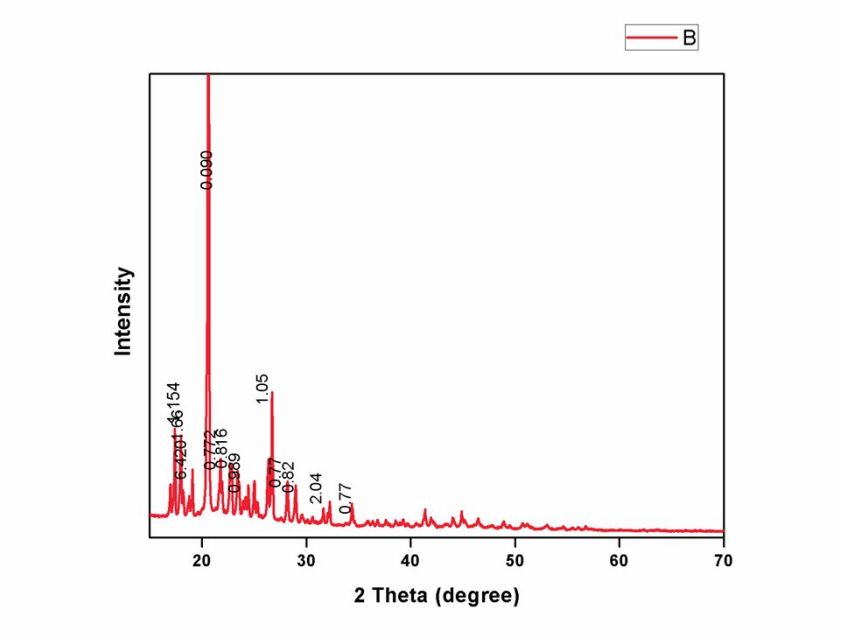


Fig. S14. PXRD analysis of ligand **L1**

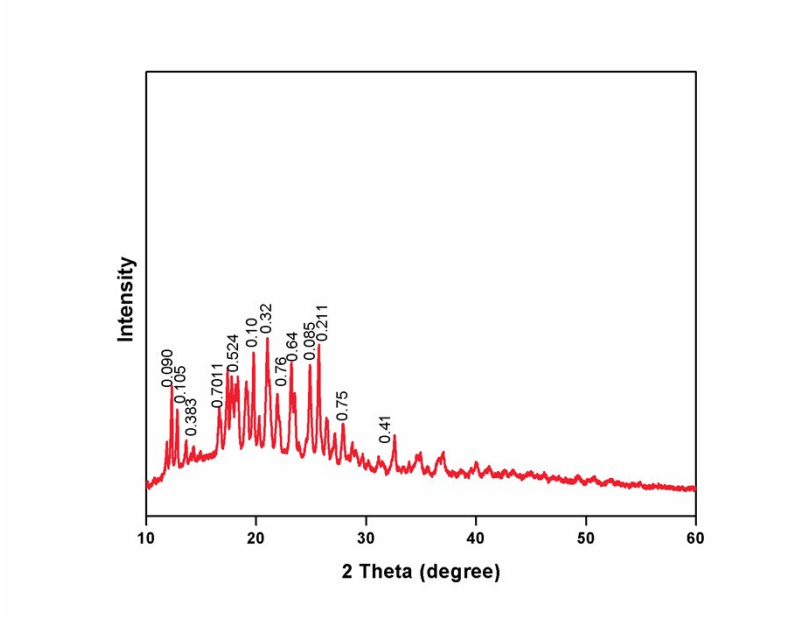


Fig. S15. PXRD analysis of ligand **L2**

S2. NMR Data of Coupled Products of Suzuki reaction

4-Nitrobiphenyl.[1] Pale yellow solid. ^{1}H NMR (500 MHz, $CdCl_3$): δ 7.406-7.515 (m, 3H), 7.609 (d, 2H), 7.709 (d, 2H), 8.266 (d, 2H).

4-Phenylbenzonitrile.[1] Pale yellow solid. ^{1}H NMR (500 MHz, $CdCl_3$): δ 7.339-7.447 (m, 3H, aromatic), 7.490-7.521(m, 3H, aromatic), 7.539-7.608(m, 3H, aromatic).

Biphenyl-4-carboxaldehyde.[2] Light yellow solid. ^{1}H NMR (500 MHz, $CdCl_3$): δ 7.391-7.508 (m, 3H), 7.628-7.655 (m, 3H), 7.755 (d, 2H), 7.955 (d, 2H), 10.058 (s, 1H).

Biphenyl-4-carboxylic acid.[3] White solid. ^{1}H NMR (500 MHz, $CdCl_3$): δ 7.393-7.523 (m, 3H), 7.727 (d, 2H), 7.793 (d, 2H), 8.026 (d, 2H).

4-Methylbiphenyl.[1] Colorless solid. ^{1}HNMR (300 MHz, $CDCl_3$): δ 2.375 (s, 3H), 7.228 (d, 2H), 7.274-7.323 (m, 1H), 7.378-7.427 (m, 2H), 7.479 (d, 2H), 7.552-7.580(m, 2H).

4−Phenylaniline.[1] Brown solid. ^{1}H NMR (500 MHz, CDCl3): δ 3.722 (s, 2H), 6.752 (d, 2H), 7.246−7.286 (m, 1H), 7.364−7.428 (m, 4H), 7.533 (d, 2H).

4-Hydroxybiphenyl.[3] Brown solid. ^{1}H NMR (500 MHz, CDCl3): δ 4.915 (s, 1H, OH), 6.998 (d, 2H), 7.300−7.548 (m, 7H).

S3. References

1. R. K. Arvela and N. E. Leadbeater, *Org. Lett.,* 2005, **7,** 2101.

2. B. Tao and D. W. J. Boykin, *Org. Chem.,* 2004, **69,** 4330.

3. G. M. Scheuermann, L. Rumi, P. Steurer, W. Bannwarth, R. Mulhaupt, *J. Am. Chem. Soc.*, 2009, **131,** 8262.