ELECTRONIC SUPPORTING INFORMATION (ESI) FOR

Palladium(II)-(E,N,E) pincer ligand (E = S/Se/Te) complex catalyzed Suzuki coupling reactions in water via in situ generated palladium quantum dots

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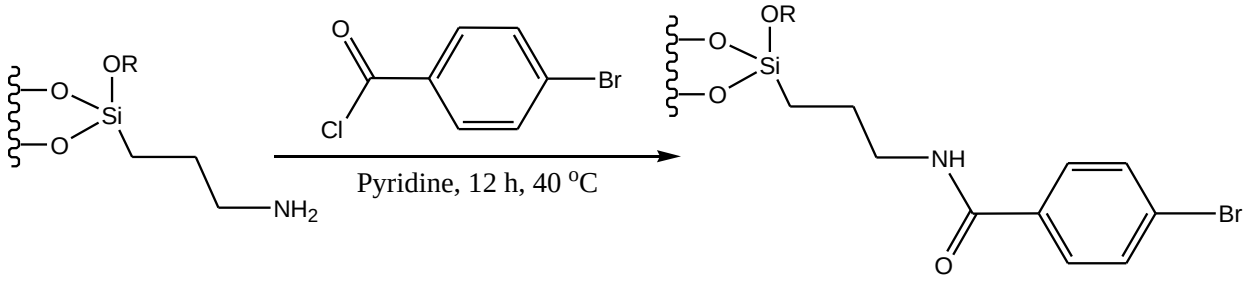
Contents

S1. Immobilisation of 4-Bromobenzoic Acid on Silica[1]

4-Bromobenzoic acid (1.99 g, 10 mmol) was refluxed with dry $SOCl_2$ (20 mL) for 3 h. After that the solution was cooled and thionyl chloride was distilled off to give 4-bromobenzoyl chloride as a white solid. 3-Aminopropyl trimethoxysilane-modified silica (1.00 g, Aldrich), pyridine



Scheme S1. Immobilisation of 4-Bromobenzoic Acid on Silica

(0.404 mL), dry THF (10 mL) and 4-bromobenzoyl chloride (1.150 g, 5.25 mmol) were stirred at 40 °C for 12 h in a round bottom flask under a N_2 atmosphere. The suspension was filtered through G-4 crucible and washed with 5% (v/v) HCl (3 × 20 mL) followed by 0.02 M aqueous K_2CO_3 (2 × 20 mL) and rinsed with distilled water (40 mL) and ethanol (40 mL). The resulting solid was washed with excess dichloromethane and dried at room temperature in air, resulting in white powder.

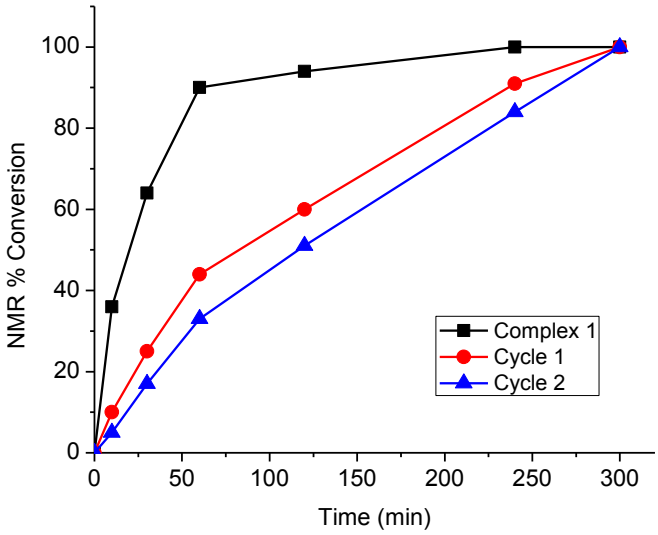


Figure S1. NMR % conversion with time for Suzuki coupling of 4-bromobenzoic acid in presence of complex **1** and nanoparticles obtained from complex **1**

Reference

(1) J.D. Webb, S. MacQuarrie, K. McEleney, C.M. Crudden, *J. Catal*. 2007, **252**, 97.

Table S1. Crystal Data and Structural Refinement Parameters of 2 and 3

	Complex 2	**Complex 3**
Empirical formula	$C_{16}H_{19}ClNPdSe_2ClH_2O$	$C_{18}H_{23}Cl\ NO_2PdTe_2ClH_2O$
Formula weight	578.56	735.89
Colour	Orange	Orange
Crystal size, mm^3	0.34 × 0.25 × 0.23	0.35 × 0.26 × 0.24
Crystal system	Monoclinic	Monoclinic
Space group	*P 21*	*P 21/n*
Unit Cell dimension	a = 5.7585(9) Å b = 10.0664(16) Å c = 16.847(3) Å α = 90 ° β = 96.071(2)° γ = 90 °	a = 18.500(2) Å b = 10.3779(14) Å c = 37.183(5) Å α = 90 ° β = 98.127(3) ° γ = 90 °
Volume [$Å^3$]	971.1(3)	7067.1(15)
Z	2	12
ρ, (calc.) Mg/m^3	1.979	2.075
μ, mm^{-1}	4.981	3.460
F(000)	560	4176
θ, range (°)	2.36 to 28.28	2.80 to 24.99
Index ranges	$-6 \le h \le 6$ $-11 \le k \le 11$ $-20 \le l \le 20$	$-22 \le h \le 22$ $-12 \le k \le 12$ $-44 \le l \le 44$
Reflections collected/unique	8789 / 3399 [R_{int} = 0.0370]	66570 / 12446 [R_{int} = 0.1027]
Completeness to max. θ, %	99.8	100.0
Max./min. Transmission	0.260 / 0.291	0.336 / 0.439
Data/restraints/ parameters	3374 / 4 / 220	12446 / 9 / 769
Goodness–of–fit on F^2	0.871	1.339
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0206, wR_2 = 0.0465	R_1 = 0.1153, wR_2 = 0.1889
R indices (all data)	R_1 = 0.0216, wR_2 = 0.0468	R_1 = 0.1492, wR_2 = 0.2014
Largest diff. peak/hole [$e.Å^{-3}$]	0.561/−0.383	1.446 /−1.788
CCDC No.	945010	945011

Table S2. Selected Bond Lengths and Bond Angles of Complex 2

Bond Distance (Å)		Bond Angle (°)	
Se(1)—C(6)	1.946(4)	C(6)—Se(1)—C(7)	100.2(2)
Se(1)—C(7)	1.962(4)	C(6)—Se(1)—Pd(1)	101.3(1)
Se(1)—Pd(1)	2.4104(5)	C(7)—Se(1)—Pd(1)	93.3(1)
Pd(1)—N(1)	2.046(3)	N(1)—Pd(1)—Cl(1)	178.8(1)
Pd(1)—Cl(1)	2.297(1)	N(1)—Pd(1)—Se(1)	87.8(1)
Pd(1)—Se(2)	2.422(6)	Cl(1)—Pd(1)—Se(1)	92.36(3)
Se(2)—C(11)	1.934(4)	N(1)—Pd(1)—Se(2)	87.3(1)
Se(2)—C(10)	1.970(4)	Cl(1)—Pd(1)—Se(2)	92.42(3)
C(6)—C(5)	1.374(5)	Se(1)—Pd(1)—Se(2)	174.04(2)
C(6)—C(1)	1.388(5)	C(11)—Se(2)—C(10)	97.7(2)
C(11)—C(16)	1.380(5)	C(11)—Se(2)—Pd(1)	105.4(1)
C(11)—C(12)	1.383(5)	C(10)—Se(2)—Pd(1)	93.8(1)
N(1)—C(8)	1.477(5)	C(5)—C(6)—C(1)	121.4(4)
N(1)—C(9)	1.490(5)	C(5)—C(6)—Se(1)	121.4(3)
C(1)—C(2)	1.390(5)	C(1)—C(6)—Se(1)	117.1(3)
C(16)—C(15)	1.391(6)	C(16)—C(11)—C(12)	120.9(3)
C(8)—C(7)	1.516(6)	C(16)—C(11)—Se(2)	117.4(3)
C(5)—C(4)	1.397(6)	C(12)—C(11)—Se(2)	121.5(3)
C(10)—C(9)	1.506(7)	C(8)—N(1)—C(9)	112.7(3)
C(4)—C(3)	1.374(5)	C(8)—N(1)—Pd(1)	113.9(2)
C(12)—C(13)	1.381(6)	C(9)—N(1)—Pd(1)	112.3(3)
C(2)—C (3)	1.377(6)	C(6)—C(1)—C(2)	118.8(4)
C(14)—C(15)	1.373(6)	C(11)—C(16)—C(15)	119.2(4)
C(14)—C(13)	1.387(6)	N(1)—C(8)—C(7)	110.0(3)
		C(6)—C(5)—C(4)	118.9(4)
		C(9)—C(10)—Se (2)	111.0(3)
		C(3)—C(4)—C(5)	120.3(4)
		C(13)—C(12)—C(11)	119.3(4)
		C(3)—C(2)—C(1)	120.3(4)
		C(15)—C(14)—C(13)	120.2(4)
		C(8)—C(7)—Se (1)	109.6(3)
		C(12)—C(13)—C(14)	120.1(4)
		C(14)—C(15)—C(16)	120.3(4)
		C(4)—C(3)—C(2)	120.3(4)
		N(1)—C(9)—C(10)	110.5(3)
		H(1B)—O(1)—H(1C)	106.0(2)

Table S3. Selected Bond Lengths and Bond Angles of Complex 3

Bond Distance (Å)		Bond Angle (°)	
Pd(2)—N(2D)	2.070(13)	N(2D)—Pd(2)—Cl(2)	178.8(4)
Pd(2)— Cl(2)	2.288(4)	N(2D)—Pd(2)—Te(3)	89.6(4)
Pd(2)—Te(3)	2.5592(18)	Cl(2)—Pd(2)—Te(3)	90.00(13)
Pd(2)—Te(4)	2.5878(18)	N(2D)—Pd(2)—Te(4)	87.4(4)
Te(4)—C(30)	2.127(16)	Cl(2)—Pd(2)—Te(4)	92.96(13)
Te(4)— C(29)	2.16(2)	Te(3)—Pd(2)—Te(4)	176.35(6)
Te(3)—C(23)	2.131(14)	C(30)—Te(4)—C(29)	96.9(7)
Te(3)—C(26)	2.161(16)	C(30)—Te(4)—Pd(2)	96.8(5)
N(2D)—C(28)	1.47(2)	C(29)—Te(4)—Pd(2)	89.5(5)
N(2D)—C(27)	1.48(2)	C(23)—Te(3)—C(26)	95.6(6)
N(2D)—H(2D)	0.84(16)	C(23)—Te(3)—Pd(2)	96.6(4)
C(26)—C(27)	1.47(2)	C(26)—Te(3)—Pd(2)	88.4(5)
C(29)—C(28)	1.49(2)	C(28)—N(2D)—C(27)	109.6(13)
C(23)—C(24)	1.36(2)	C(28)—N(2D)—Pd(2)	115.5(10)
C(23)—C(22)	1.39(2)	C(27)—N(2D)—Pd(2)	115.1(11)
C(20)—C(21)	1.37(2)	C(27)—C(26)—Te(3)	110.2(11)
C(20)—C(25)	1.37(2)	C(26)—C(27)—N(2D)	115.3(14)
C(20)—O(3)	1.375(19)	C(28)—C(29)—Te(4)	110.6(13)
C(24)—C(25)	1.39(2)	C(24)—C(23)—C(22)	116.6(14)
O(3)—C(19)	1.41(2)	C(24)—C(23)—Te(3)	121.8(12)
C(22)—C(21)	1.37(2)	C(22)—C(23)—Te(3)	121.5(12)
C(6)—C(5)	1.39(2)	C(21)—C(20)—C(25)	119.3(17)
C(30)—C(31)	1.33(2)	C(21)—C(20)—O(3)	116.5(14)
C(30)—C(35)	1.36(2)	C(25)—C(20)—O(3)	124.2(16)
C(33)—C(34)	1.34(2)	C(23)—C(24)—C(25)	122.3(15)
C(33)—O(4)	1.368(19)	N(2D)—C(28)—C(29)	113.3(15)
C(33)—C(32)	1.38(3)	C(20)—C(25)—C(24)	119.7(16)
C(31)—C(32)	1.41(2)	C(20)—O(3)—C(19)	117.8(14)
C(31)—H(31)	0.9300	C(31)—C(30)—C(35)	120.7(17)
C(32)—H(32)	0.9300	C(31)—C(30)—Te(4)	117.2(14)
O(4)—C(36)	1.43(2)	C(35)—C(30)—Te(4)	122.0(13)
C(35)—C(34)	1.42(2)	C(34)—C(33)—O(4)	122.8(18)
		C(34)—C(33)—C(32)	120.5(16)
		O(4)—C(33)—C(32)	116.7(17)
		C(30)—C(31)—C(32)	119.1(18)
		C(33)—C(32)—C(31)	120.2(17)
		C(33)—O(4)—C(36)	119.5(16)
		C(30)—C(35)—C(34)	120.9(17)

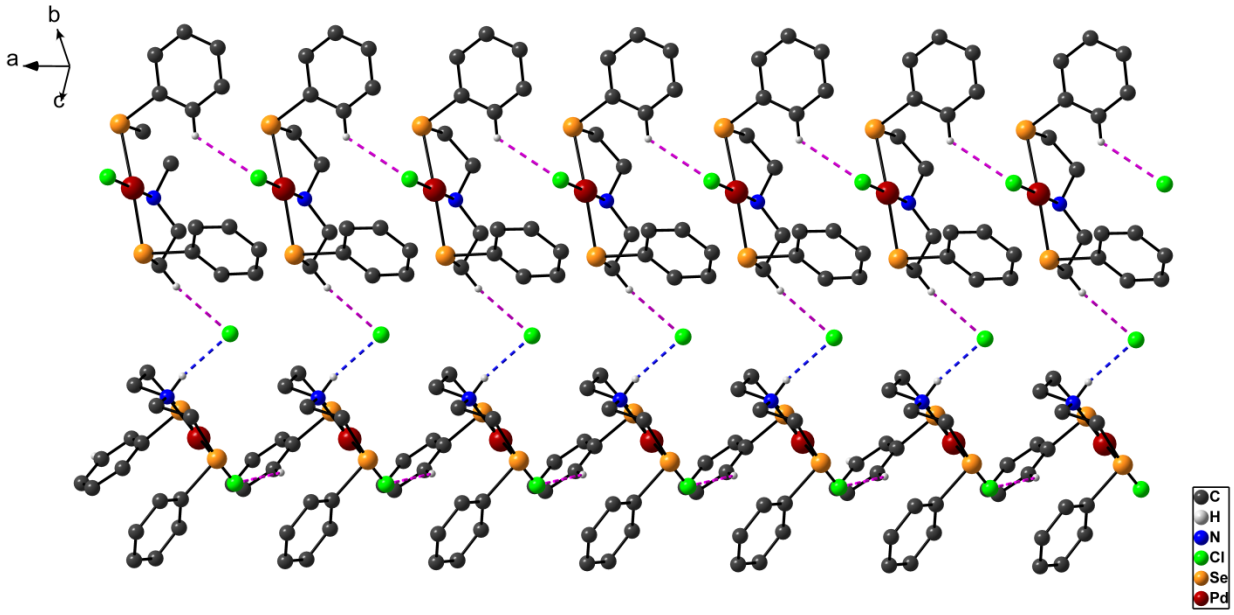


Figure S2. Intermolecular C−H···Cl, N−H···Cl and Pd−Cl···H interactions in complex **2**

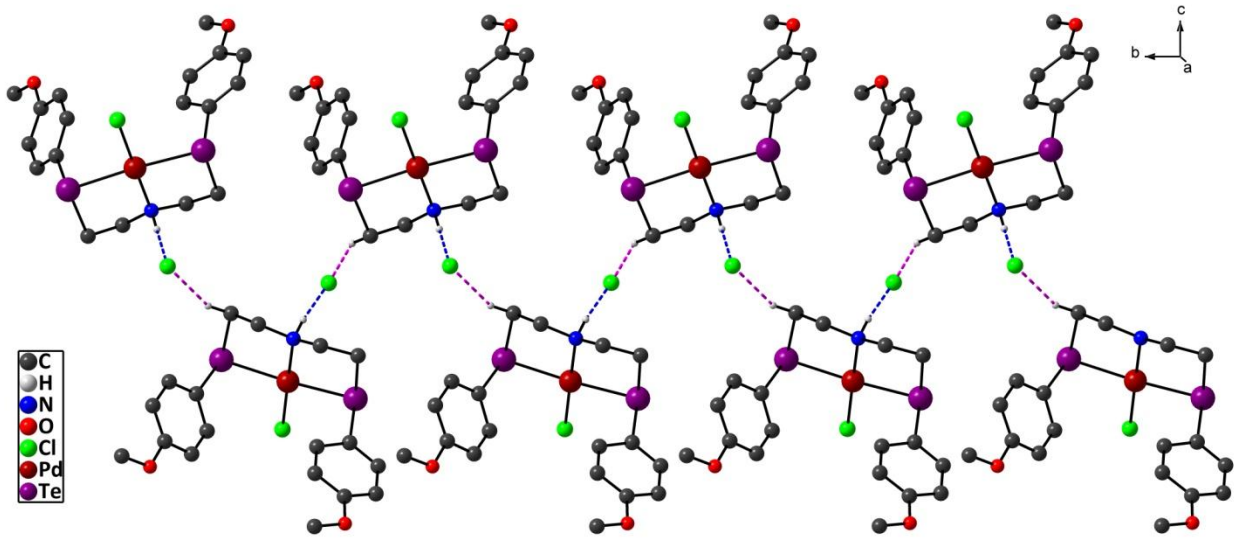


Figure S3. Intermolecular N−H···Cl and C−H···Cl interactions in complex **3**

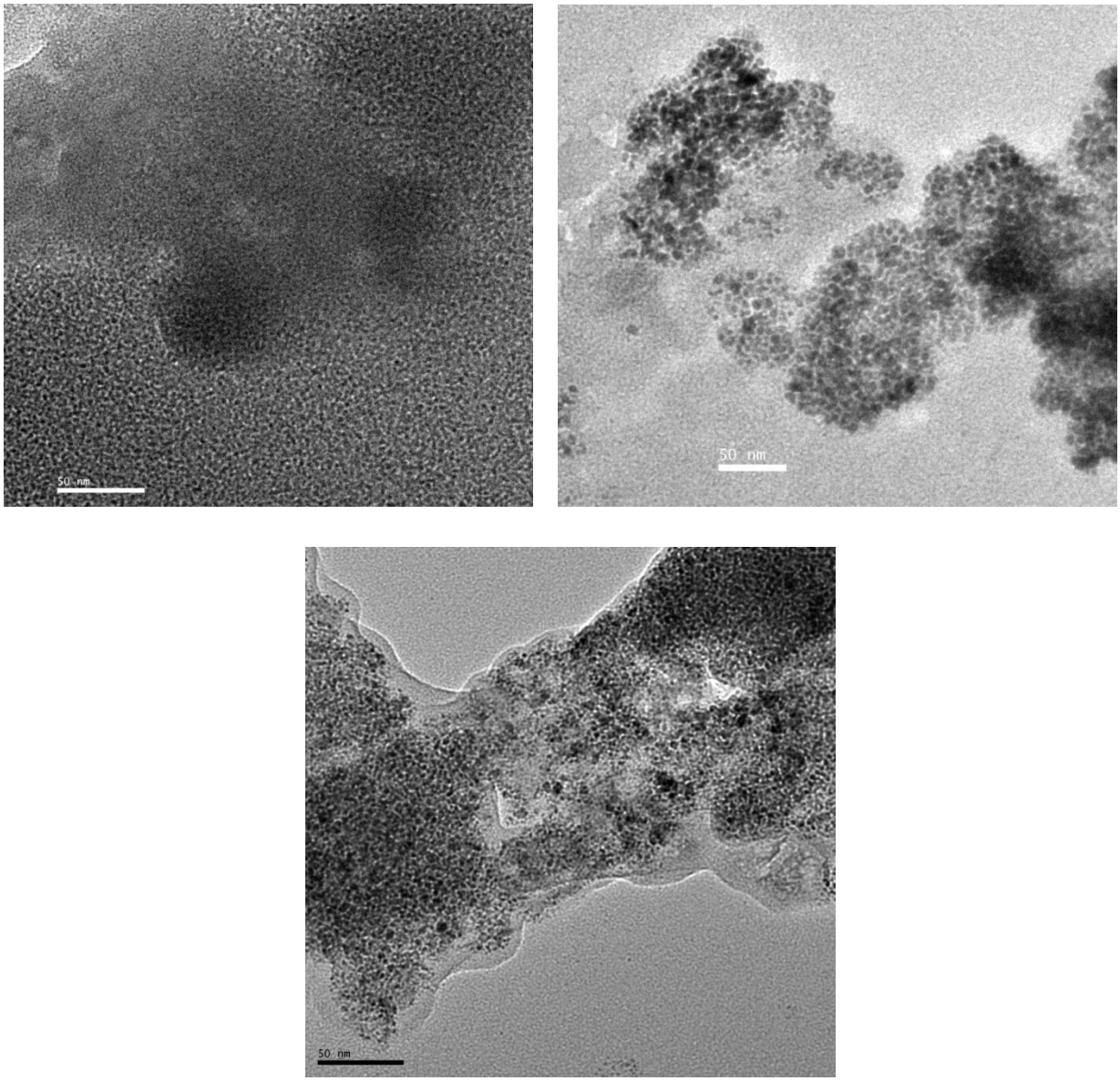


Figure. S4. HRTEM images for NPs obtained from complexes **1**, **2** and **3** respectively (Scale bar 50 nm)

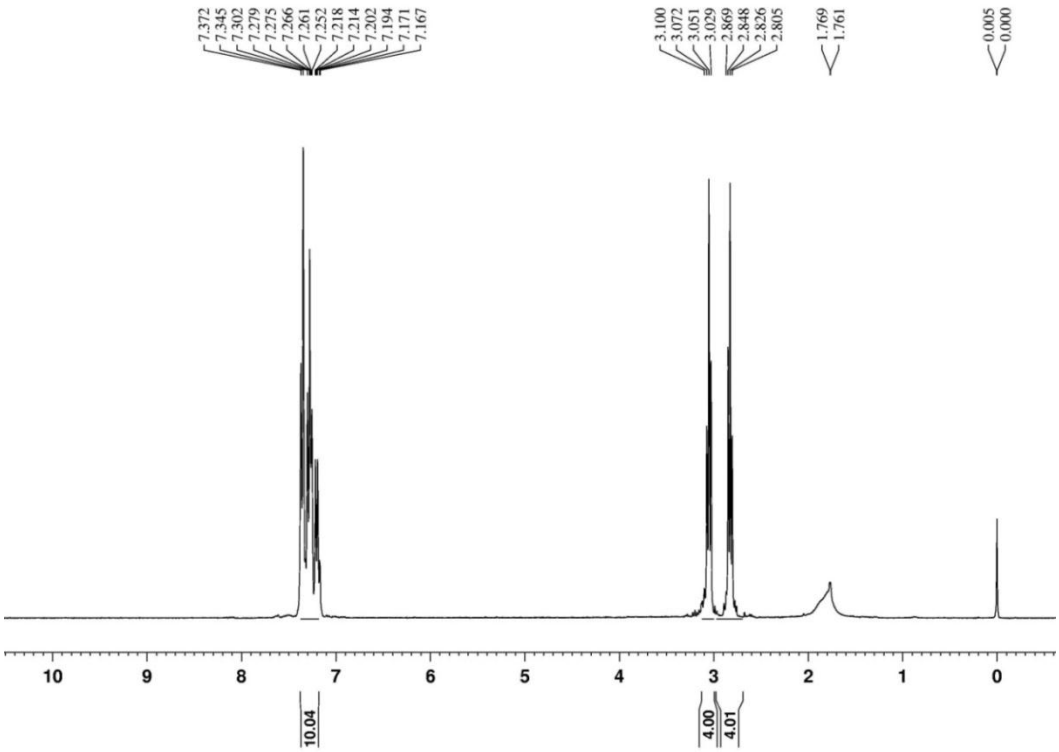


Figure S5. ^{1}H NMR Spectrum of **L1**

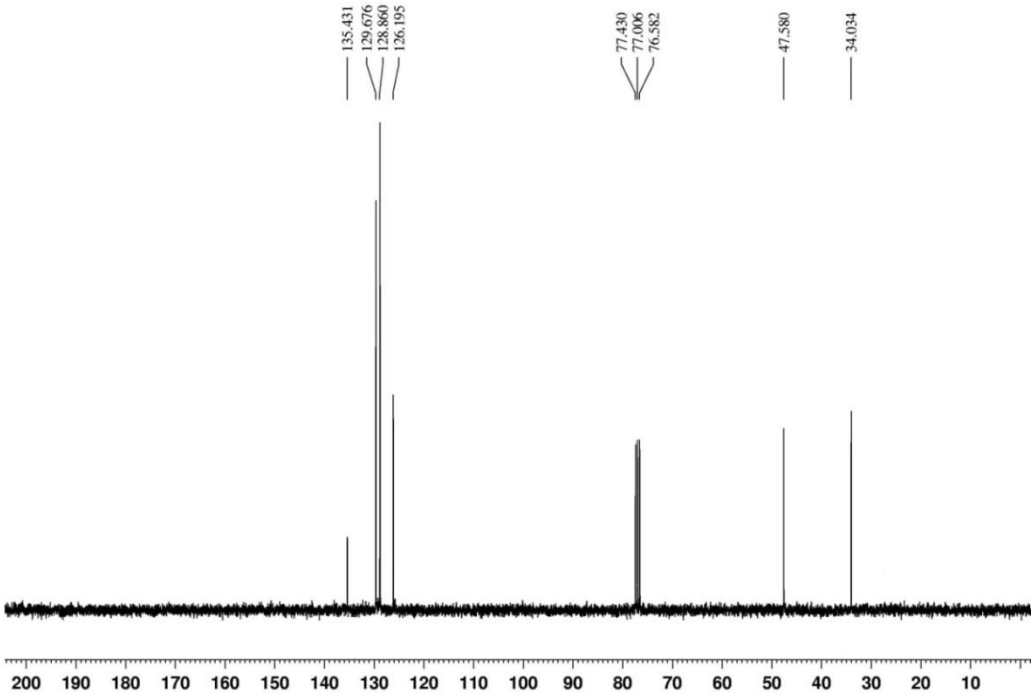


Figure S6. ^{13}C{^{1}H} NMR Spectrum of **L1**

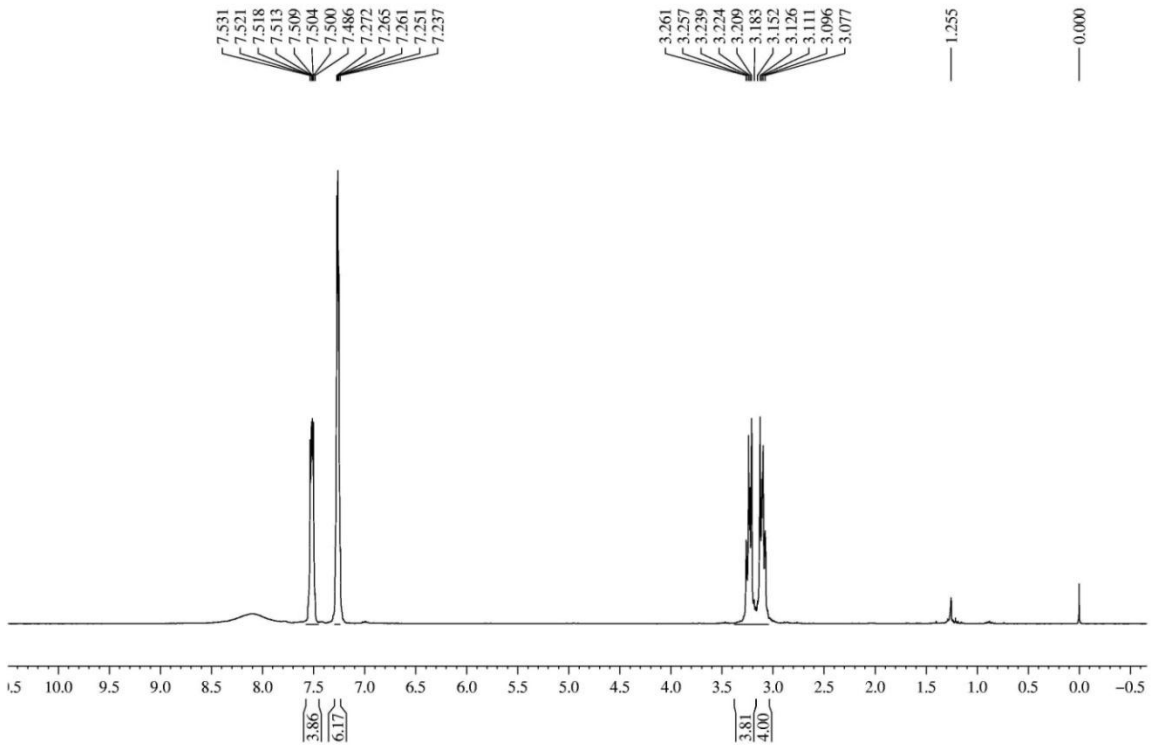


Figure S7. ^{1}H NMR Spectrum of **L2**

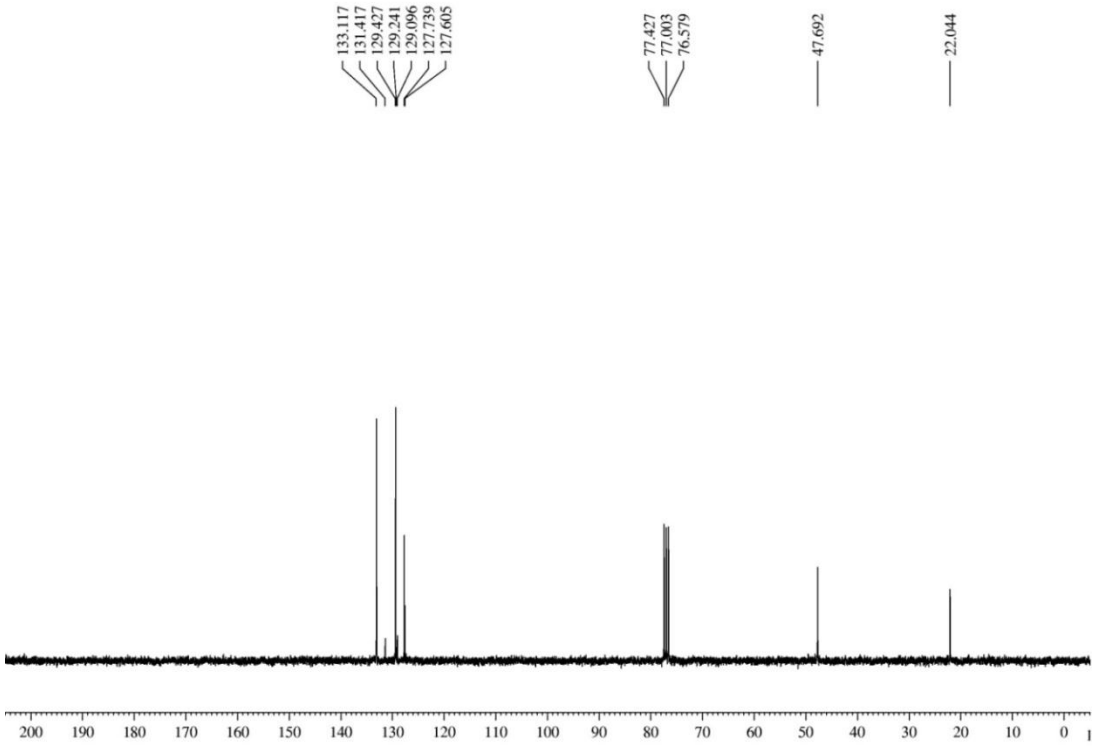


Figure S8. ^{13}C{^{1}H} NMR Spectrum of **L2**

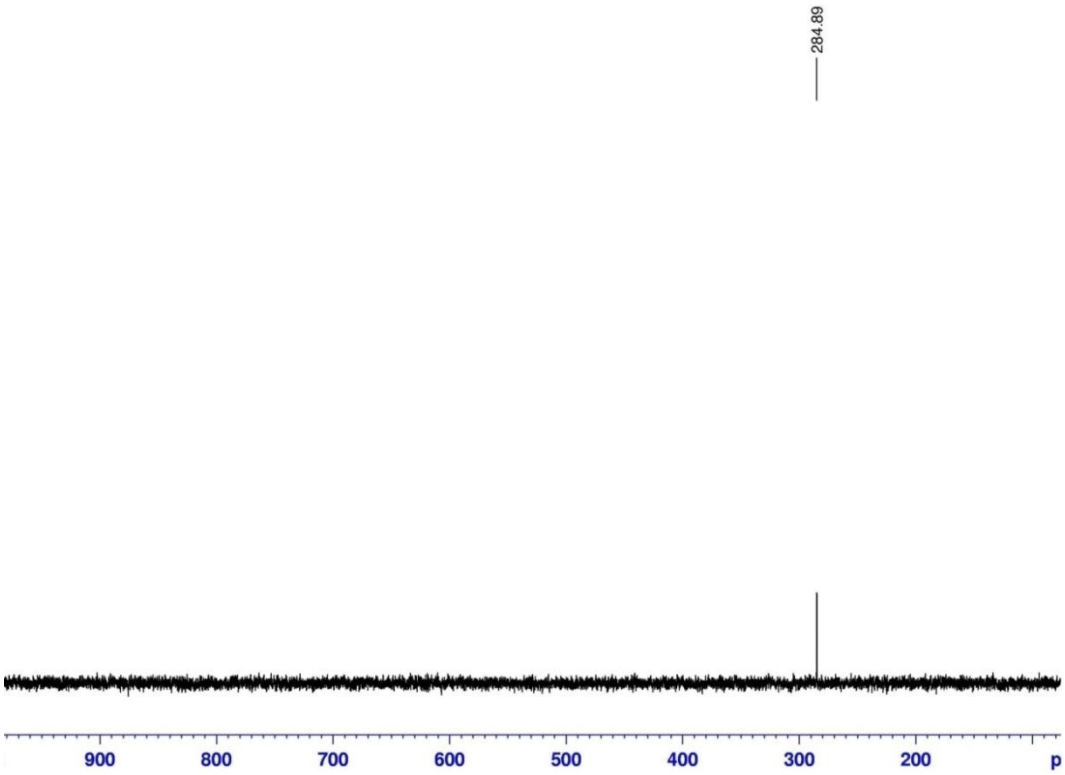


Figure S9. $^{77}Se\{^{1}H\}$ NMR Spectrum of **L2**

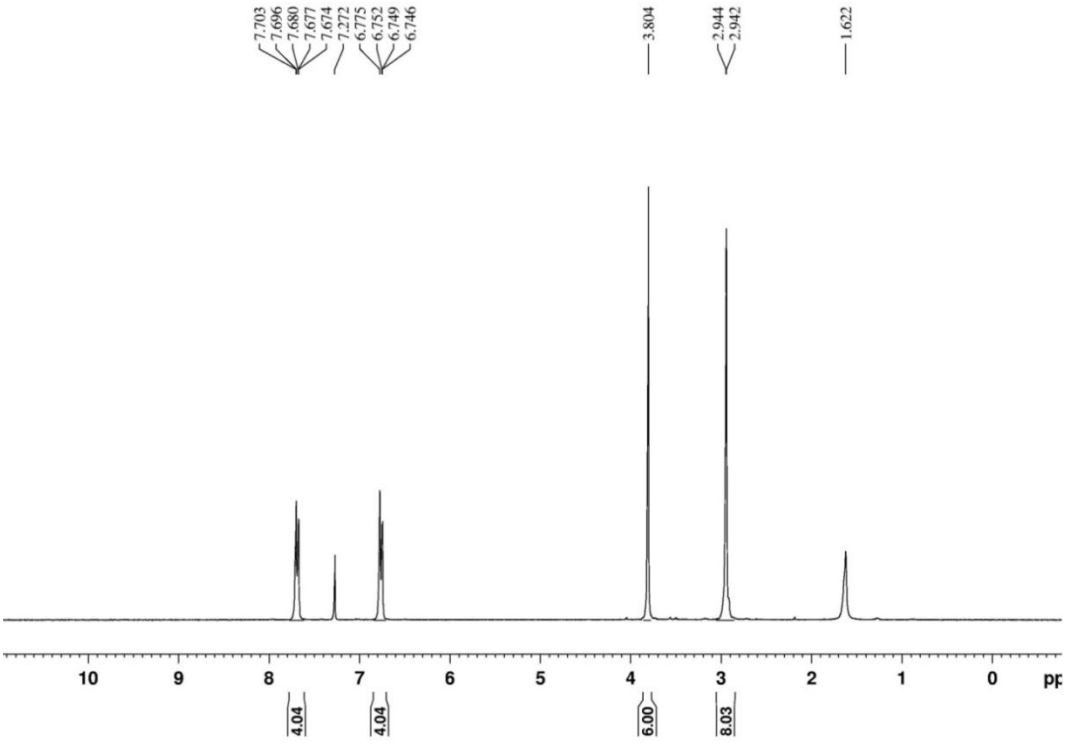


Figure S10. ^{1}H NMR Spectrum of **L3**

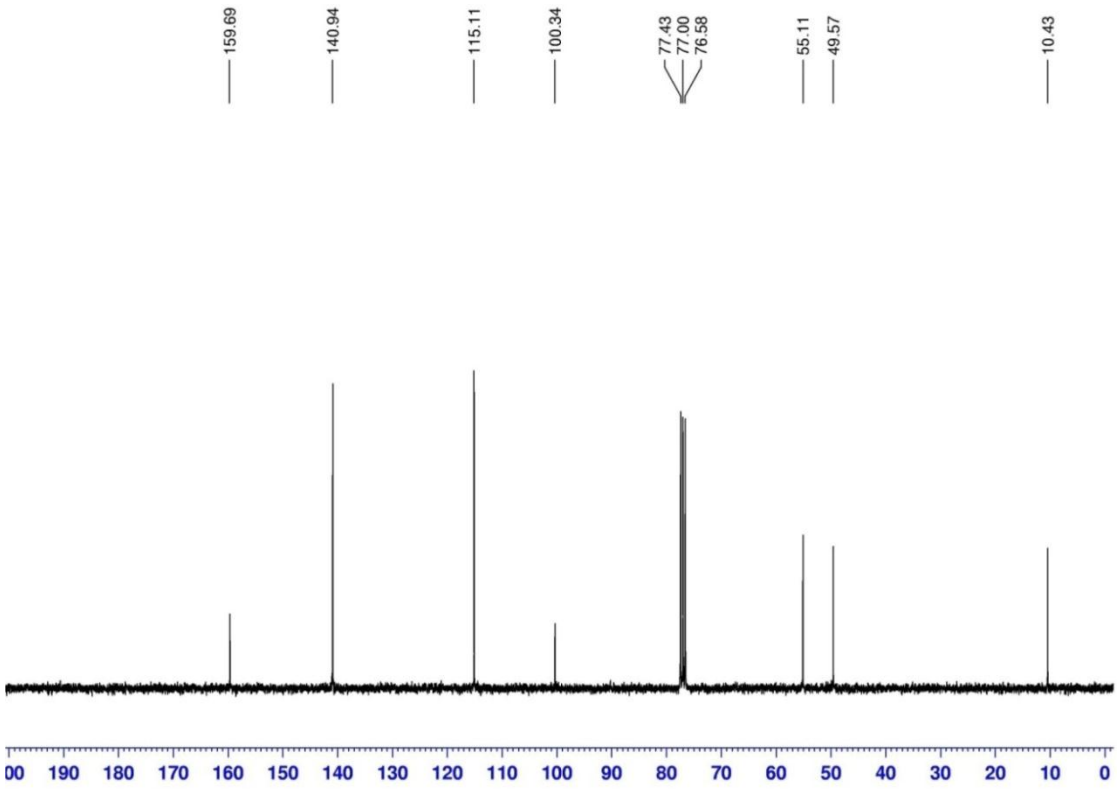


Figure S11. $^{13}C\{^{1}H\}$ NMR Spectrum of **L3**

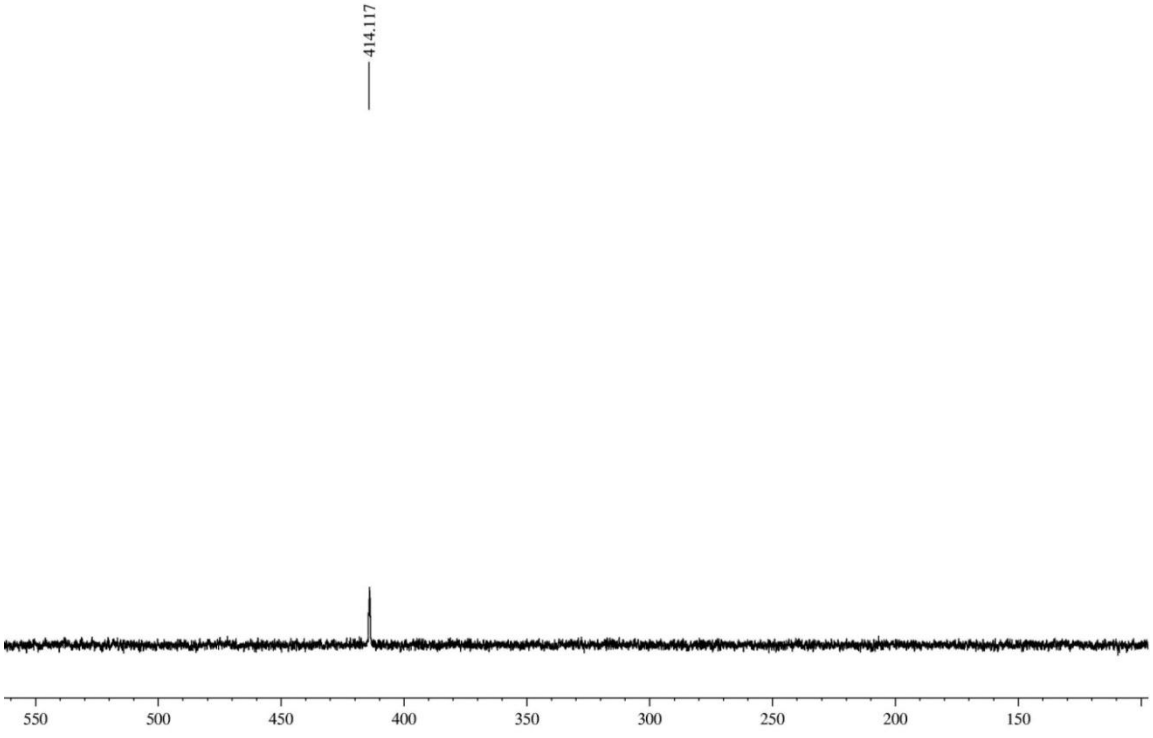


Figure S12. $^{125}Te\{^{1}H\}$ NMR Spectrum of **L3**

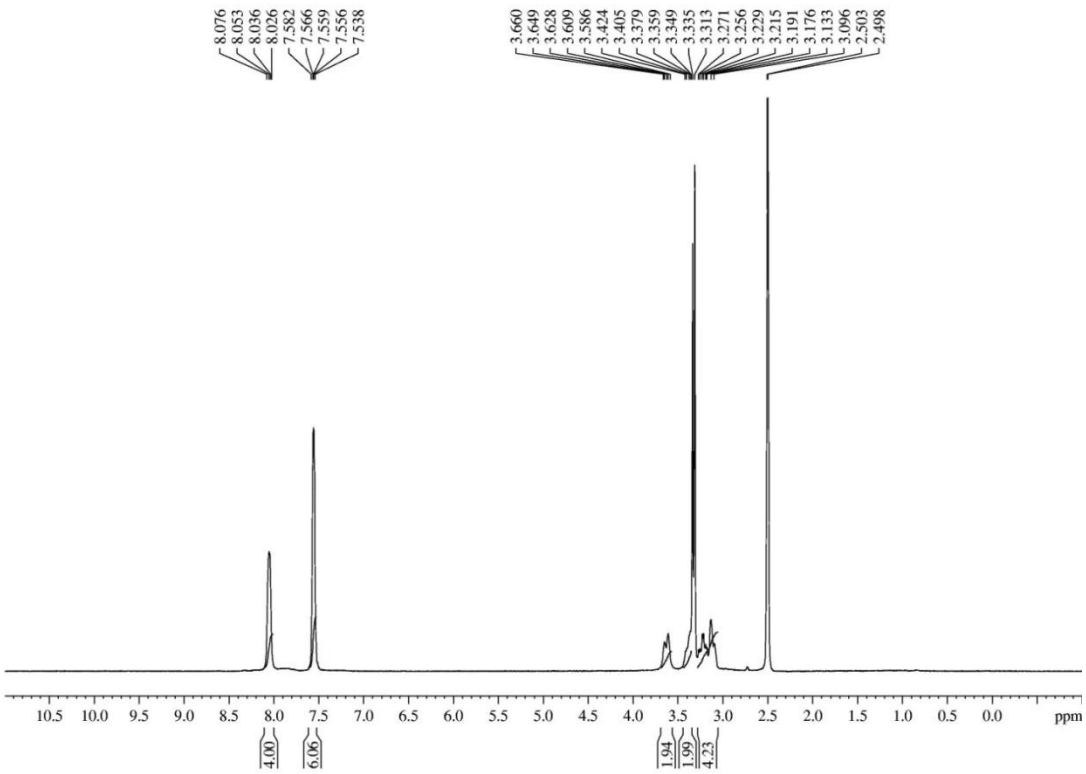


Figure S13. ^{1}H NMR Spectrum of Complex **1**

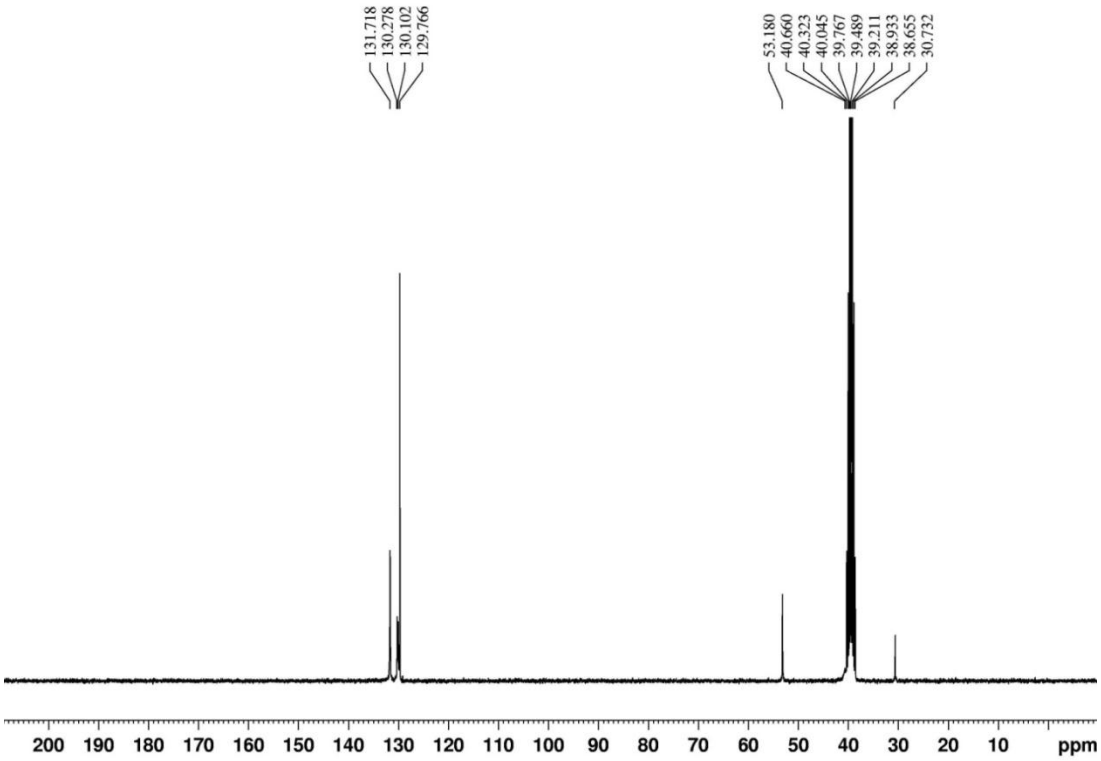


Figure S14. ^{13}C{^{1}H} NMR Spectrum of Complex **1**

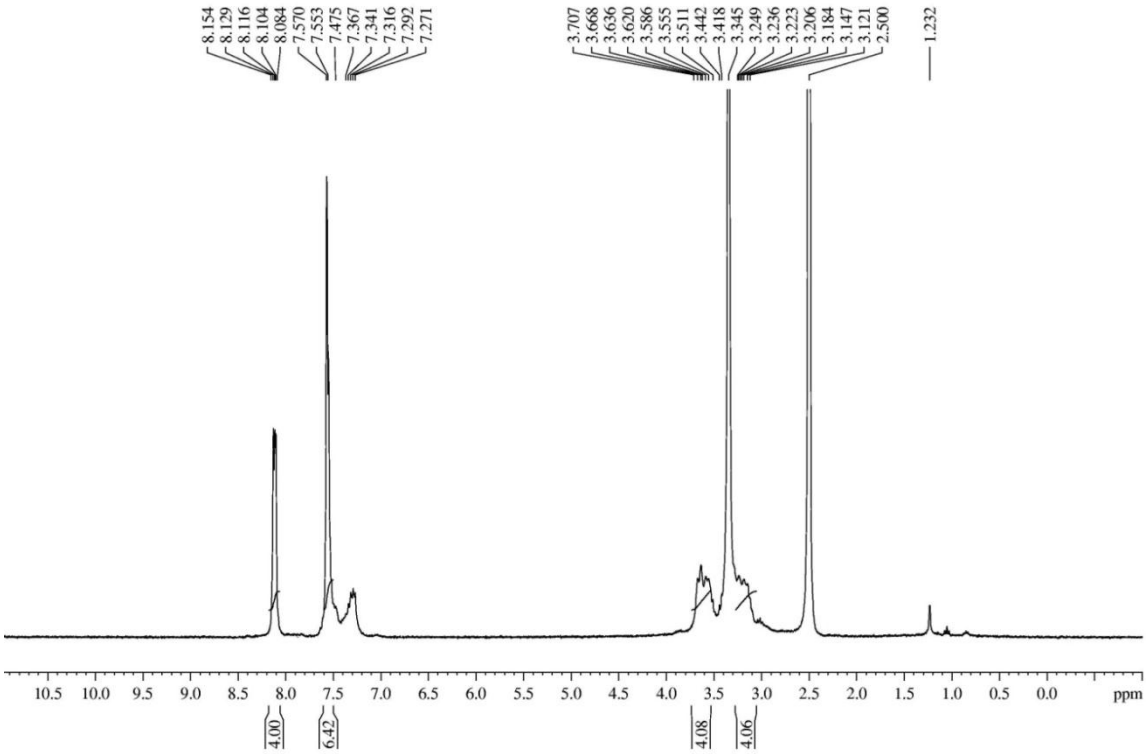


Figure S15. ^{1}H NMR Spectrum of Complex **2**

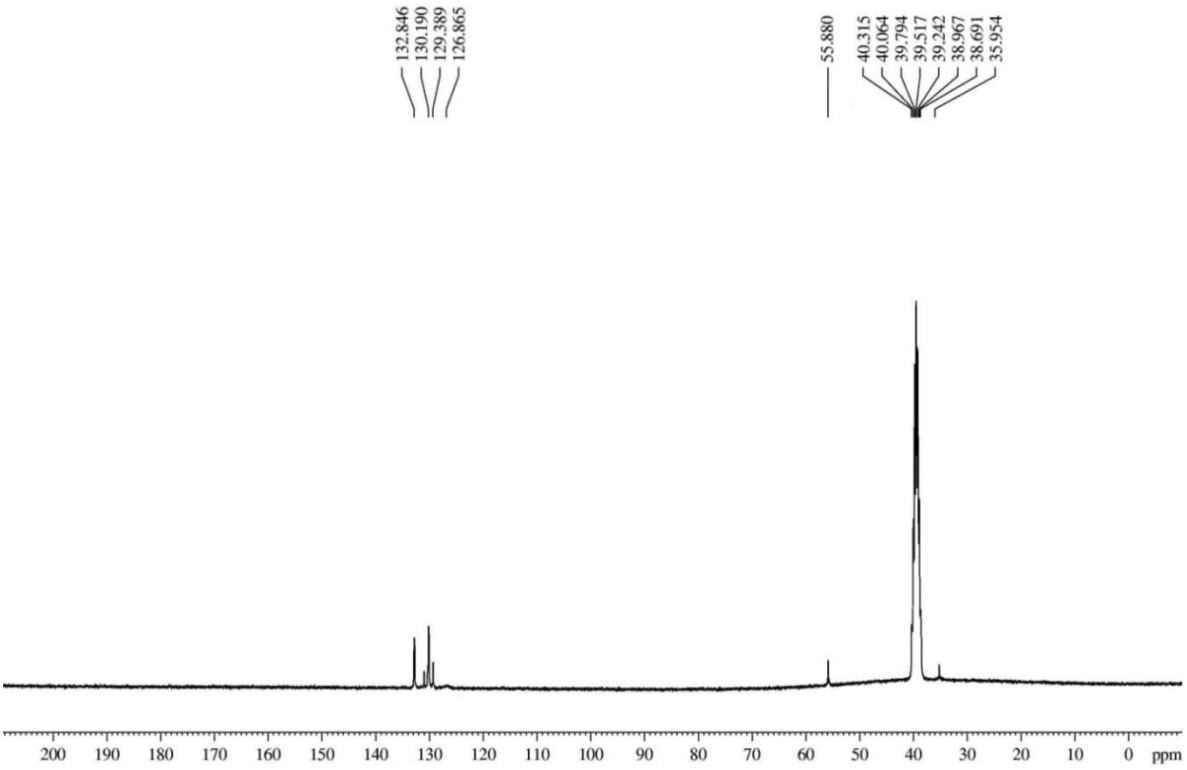


Figure S16. ^{13}C{^{1}H} NMR Spectrum of Complex **2**

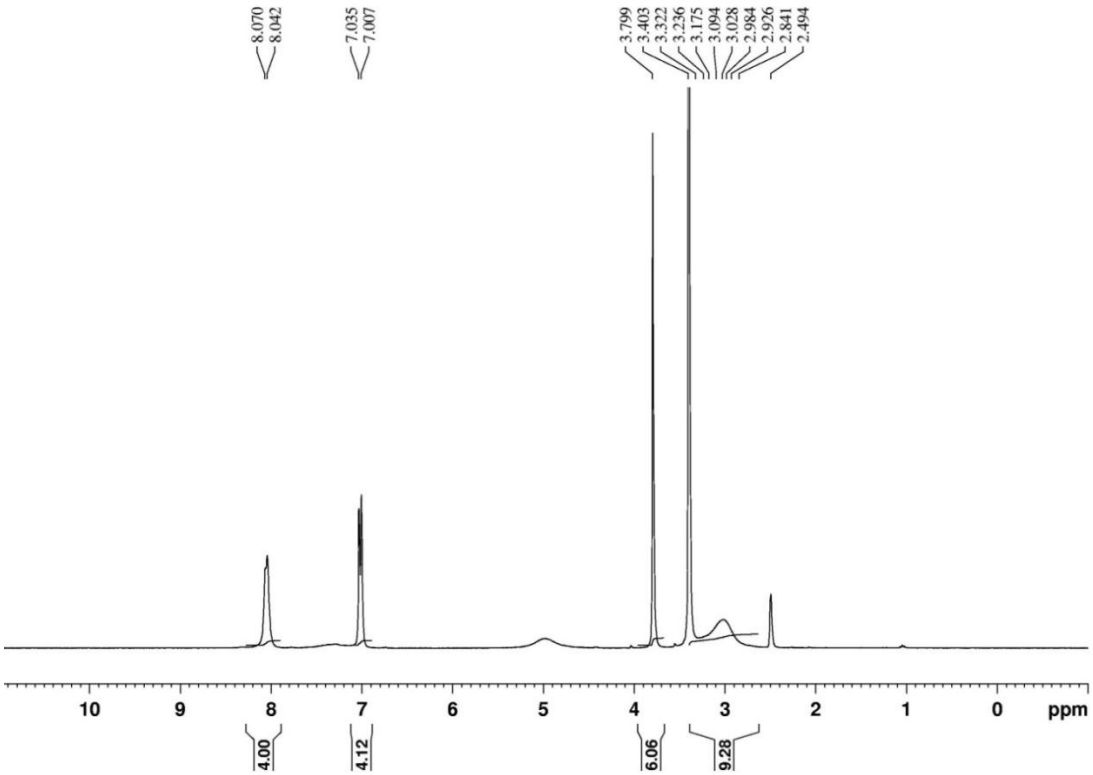


Figure S17. ^{1}H NMR Spectrum of Complex **3**

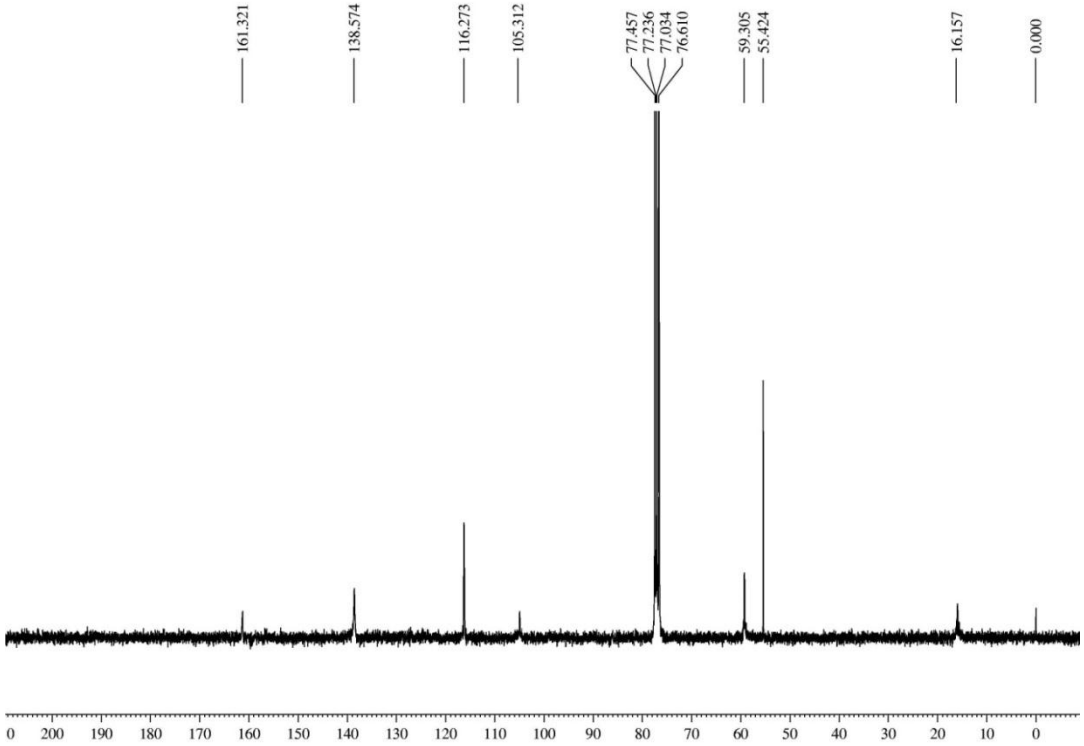


Figure S18. ^{13}C{^{1}H} NMR Spectrum of Complex **3**

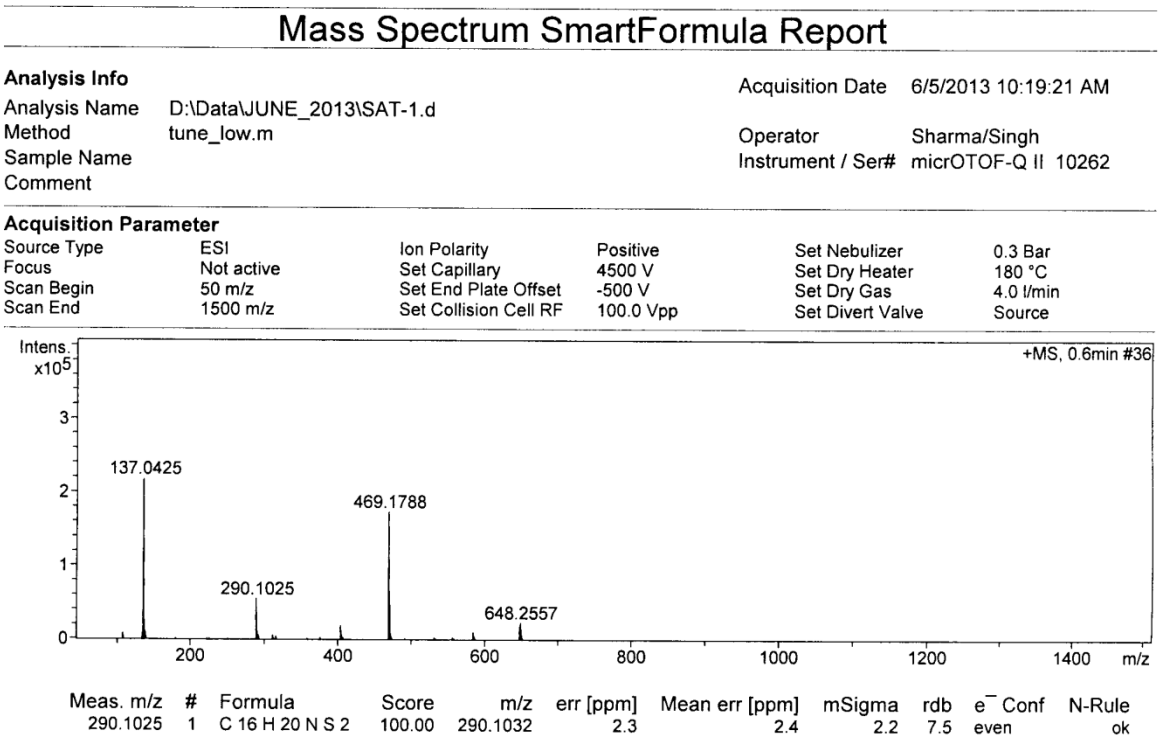


Figure S19. Mass Spectra of **L1**

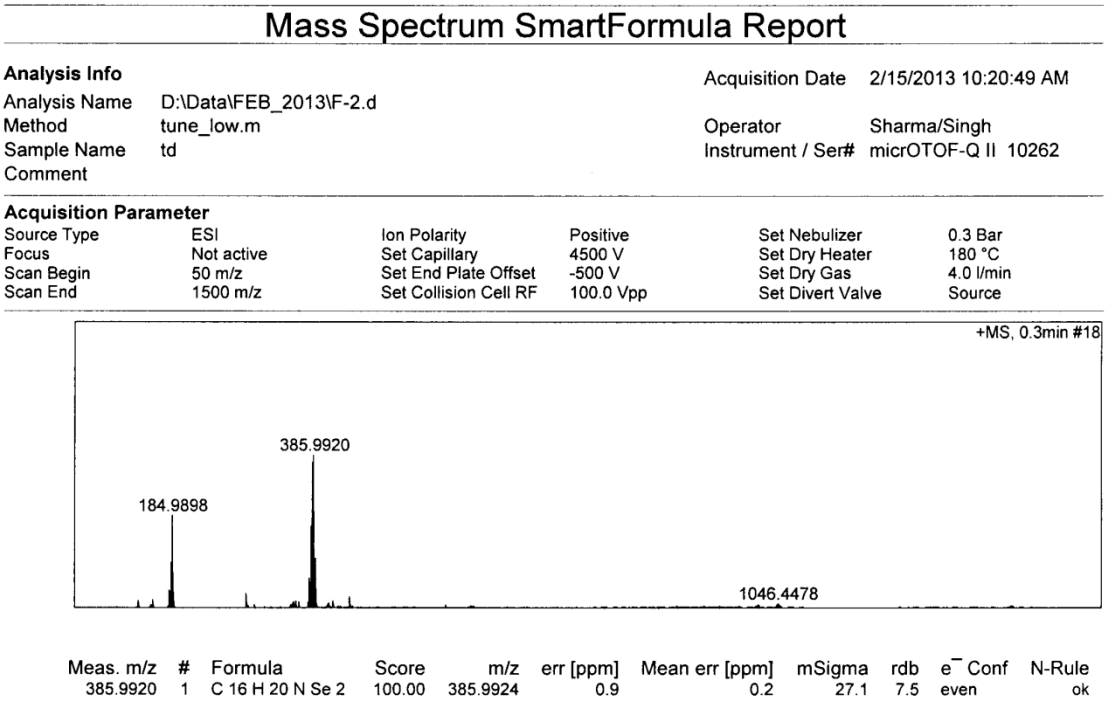


Figure S20. Mass Spectra of **L2**

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name		Instrument / Ser#	micrOTOF-Q II 10262
Comment			

Acquisition Parameter

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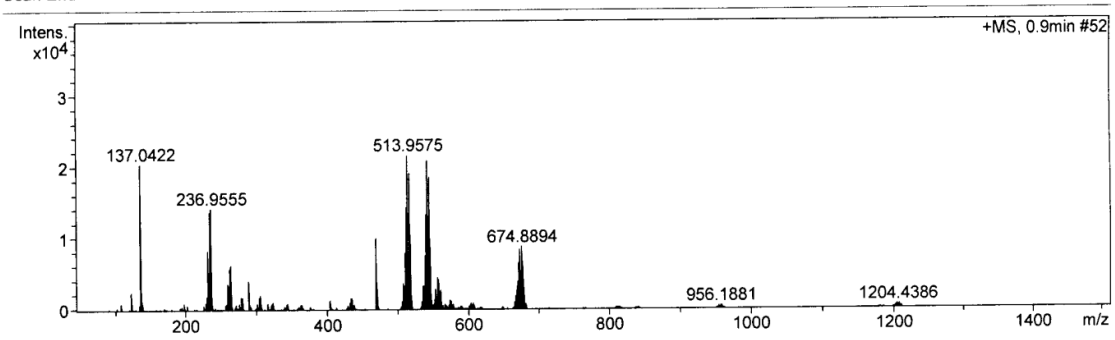
Scan End	1500 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
545.9928	1	C 18 H 24 N O 2 Te 2	100.00	545.9926	-0.3	1.4	14.6	7.5	even	ok

Figure S21. Mass Spectra of **L3**

Mass Spectrum SmartFormula Report

Analysis Info

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Sample Name	td	Instrument / Ser#	micrOTOF-Q II 10262
Comment			

Acquisition Parameter

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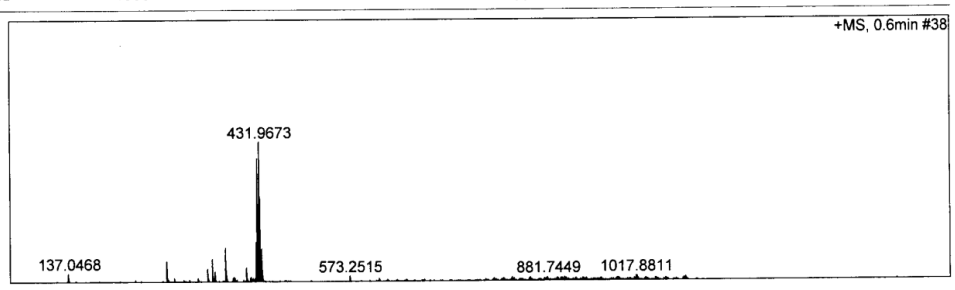
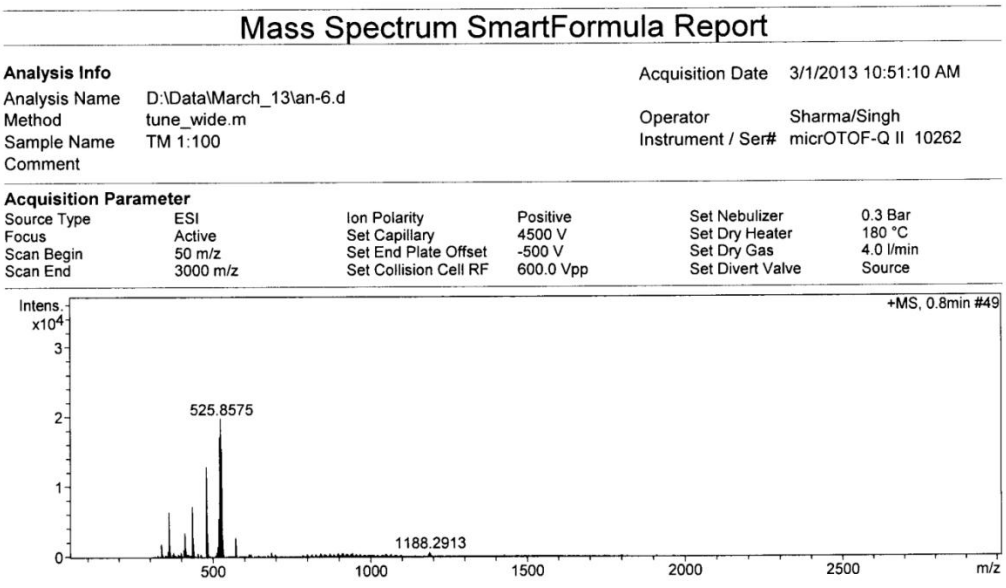
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1500 m/z	Set Collision Cell RF	100.0 Vpp	Set Divert Valve	Source



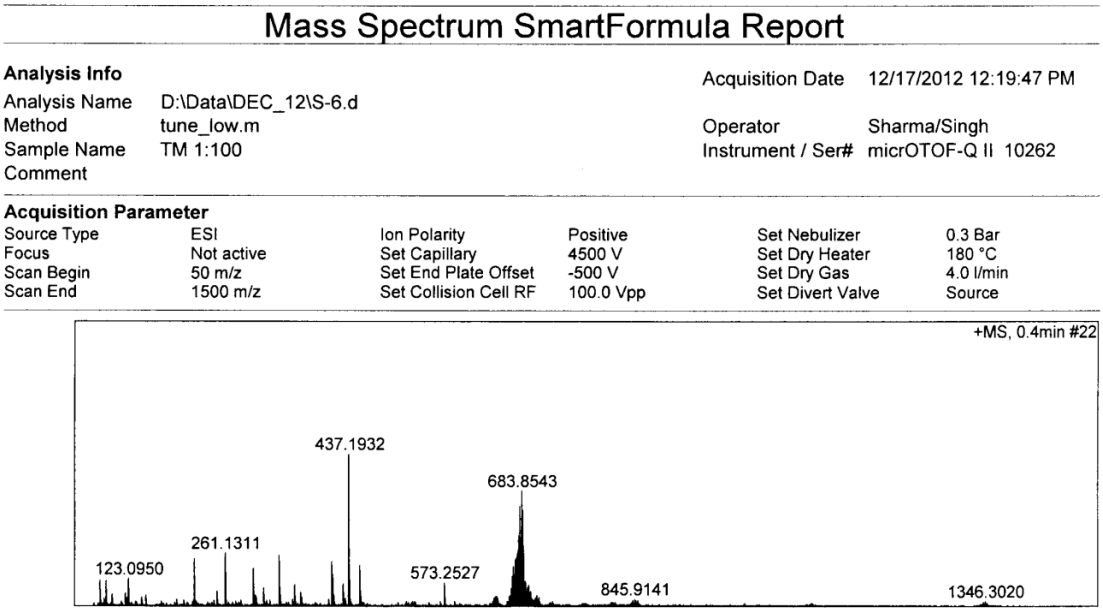
Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
429.9678	1	C 16 H 19 Cl N Pd S 2	100.00	429.9679	0.1	0.8	16.9	7.5	even	ok

Figure S22. Mass Spectra of Complex **1**



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
525.8575	1	C 16 H 19 Cl N Pd Se 2	525.8576	0.1	0.3	7.5	ok	even	18.3	12.9	1.6	2.3	1.7	842.7

Figure S23. Mass Spectra of Complex **2**



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
685.8570	1	C 18 H 23 Cl N O 2 Pd Te 2	100.00	685.8554	-2.4	-14.7	143.2	7.5	even	ok

Figure S24. Mass Spectra of Complex **3**

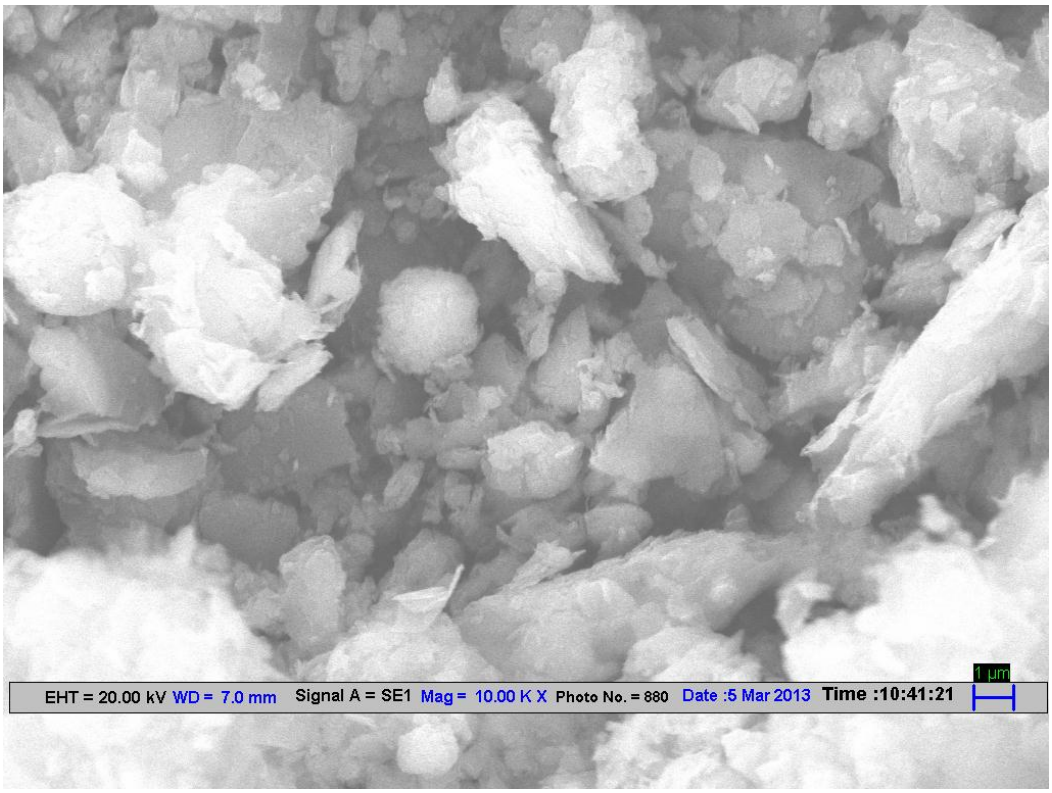


Figure S25. SEM image of NPs obtained from Complex **1** during Suzuki-Miyaura Coupling

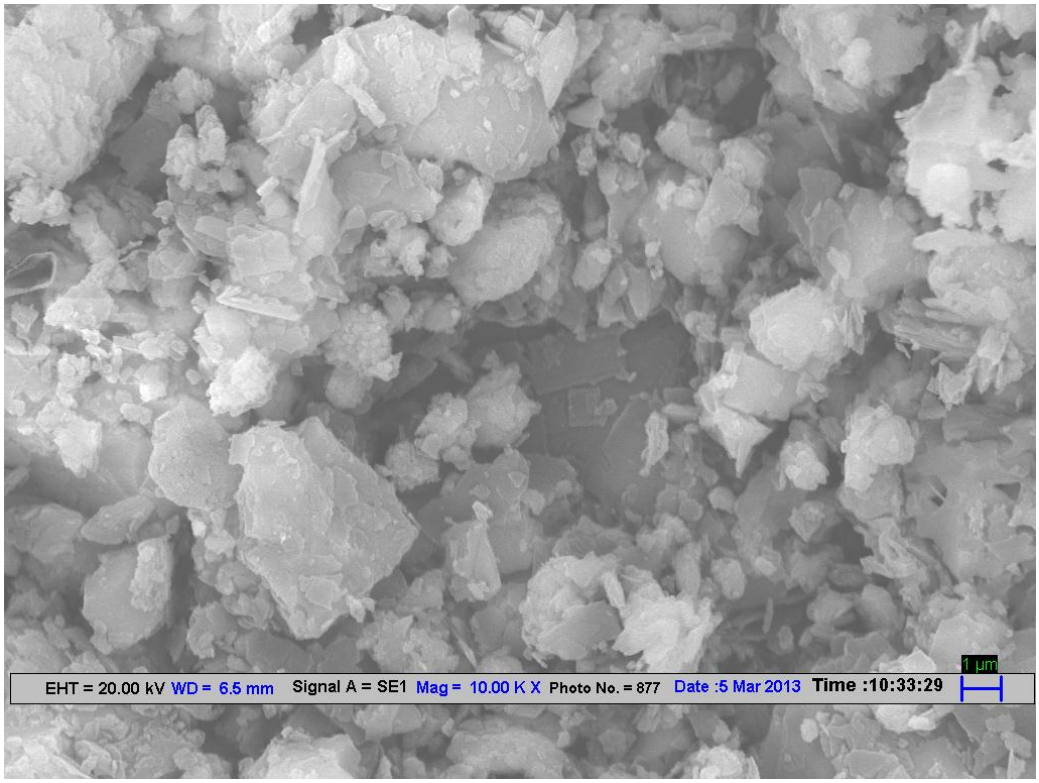


Figure S26. SEM image of NPs obtained from Complex **2** during Suzuki-Miyaura Coupling

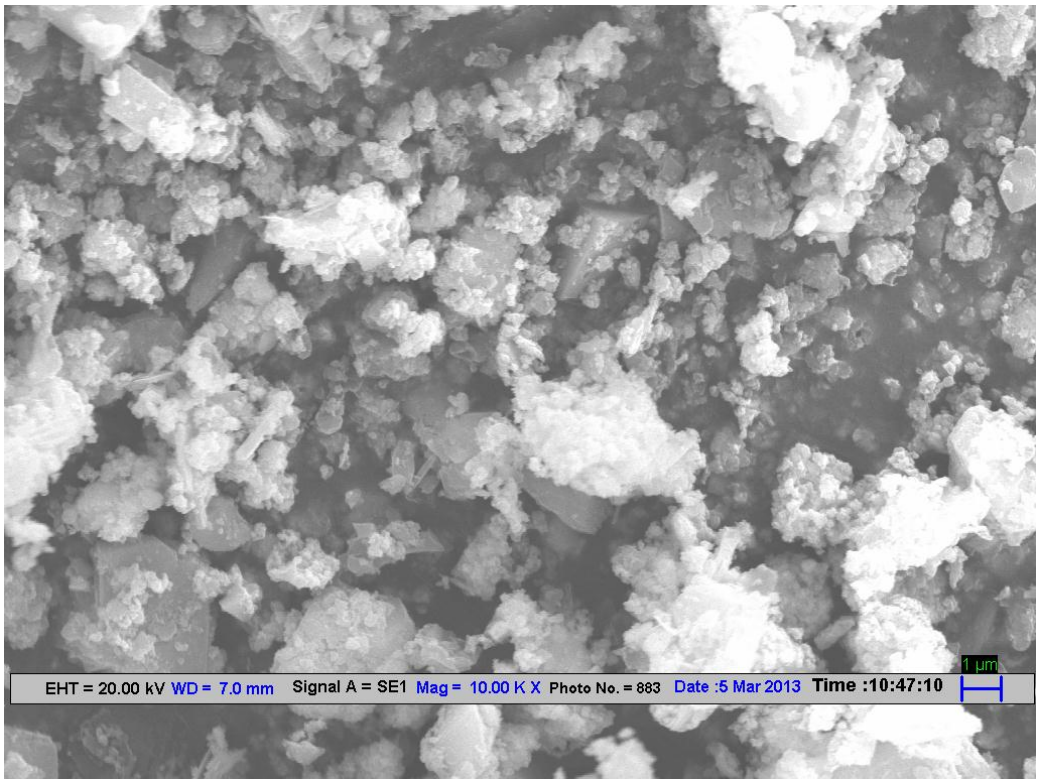
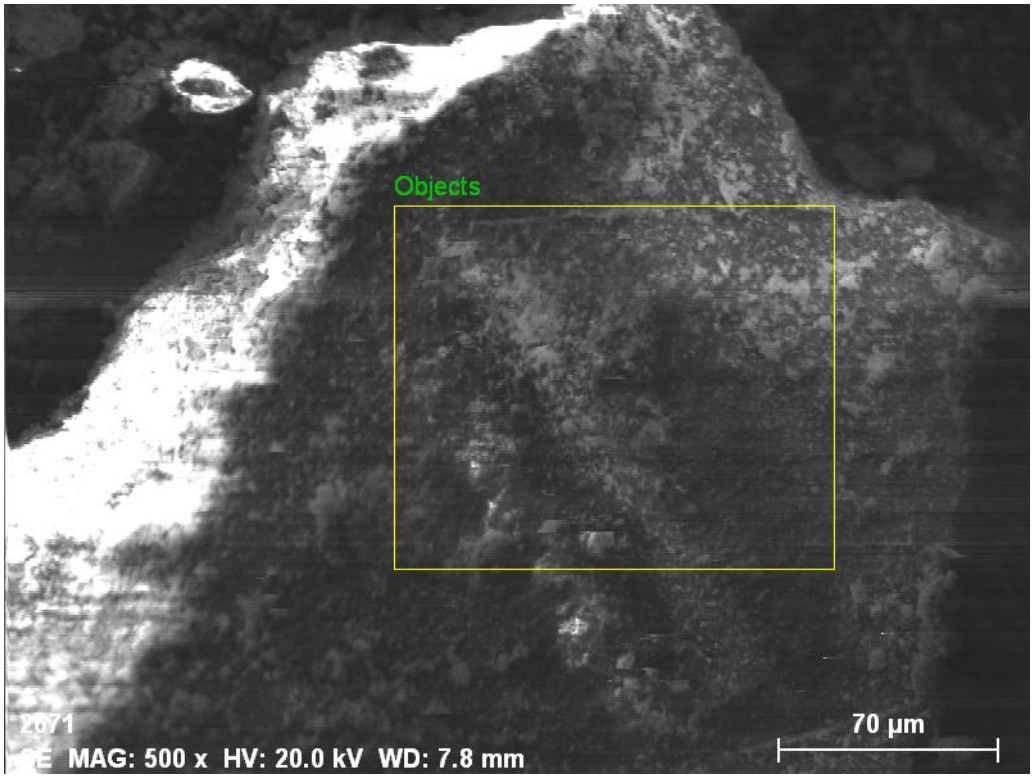


Figure S27. SEM image of NPs obtained from Complex **3** during Suzuki-Miyaura Coupling



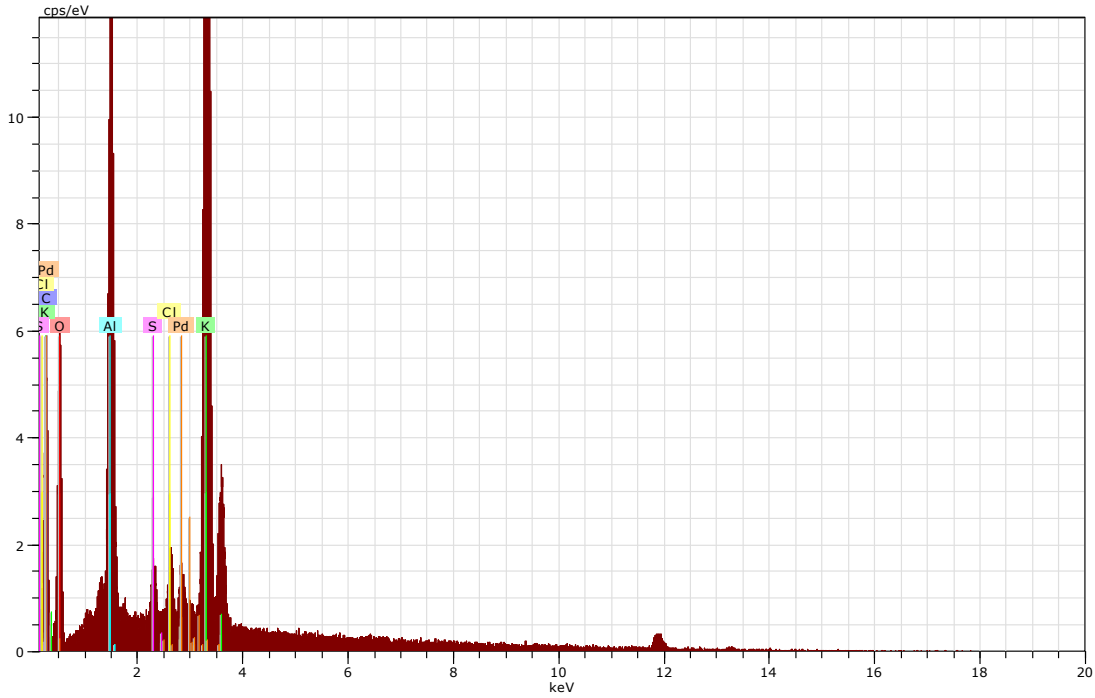
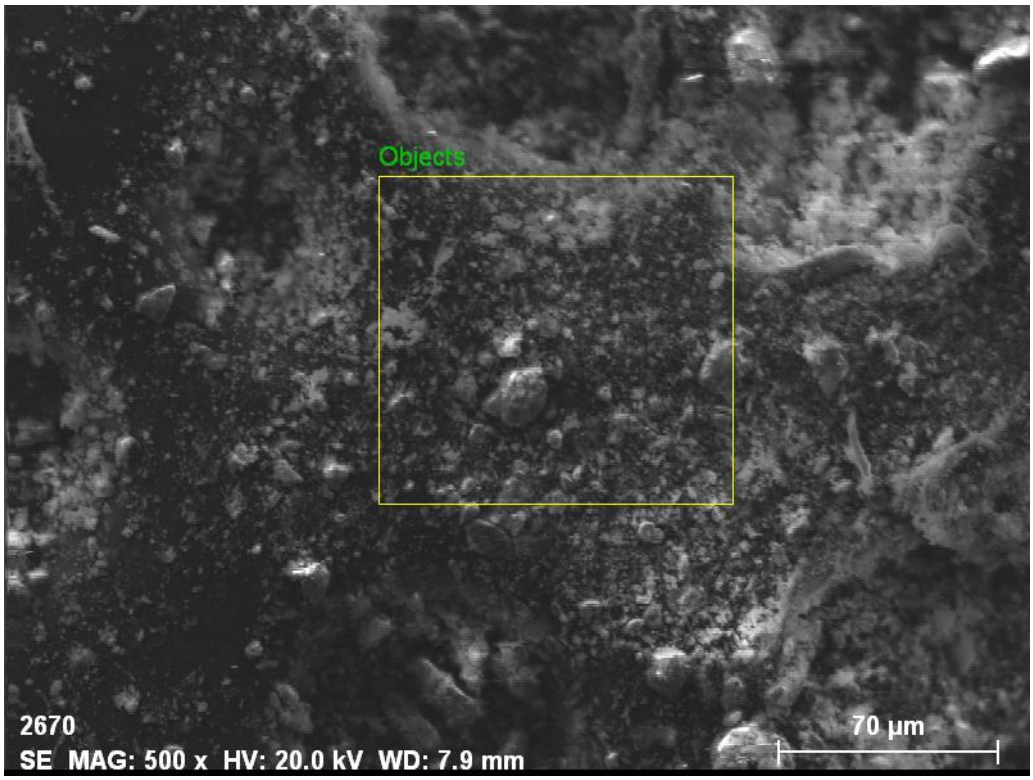


Figure S28. SEM−EDX of NPs obtained from Complex **1** during Suzuki-Miyaura Coupling



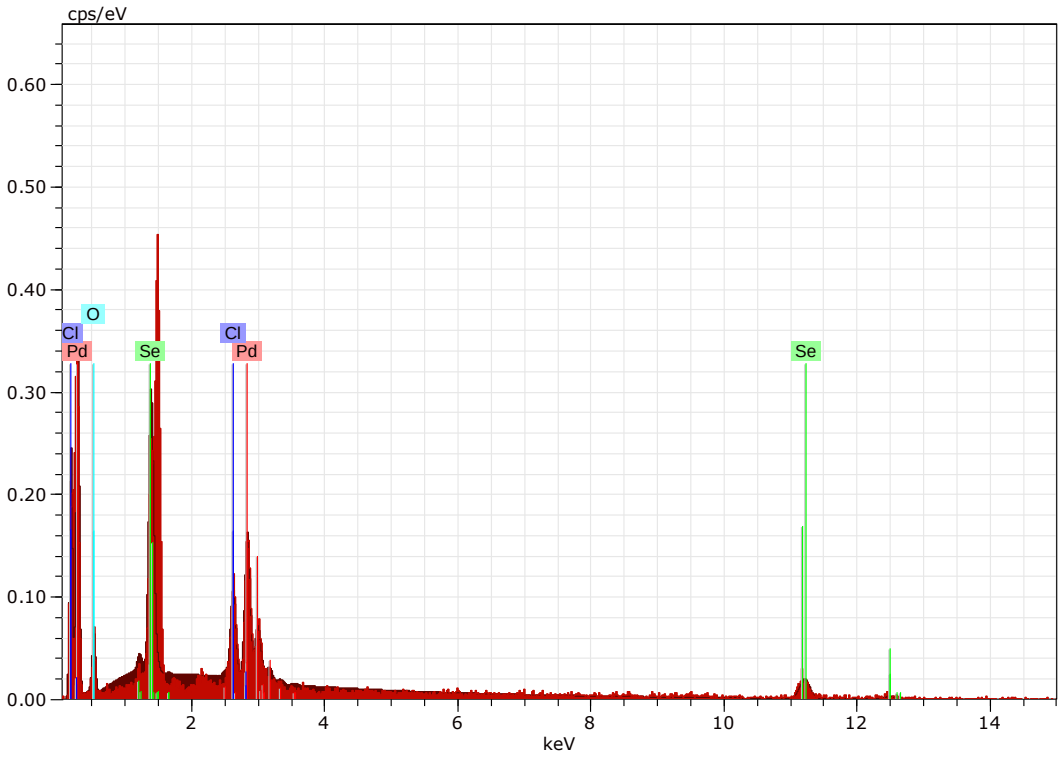
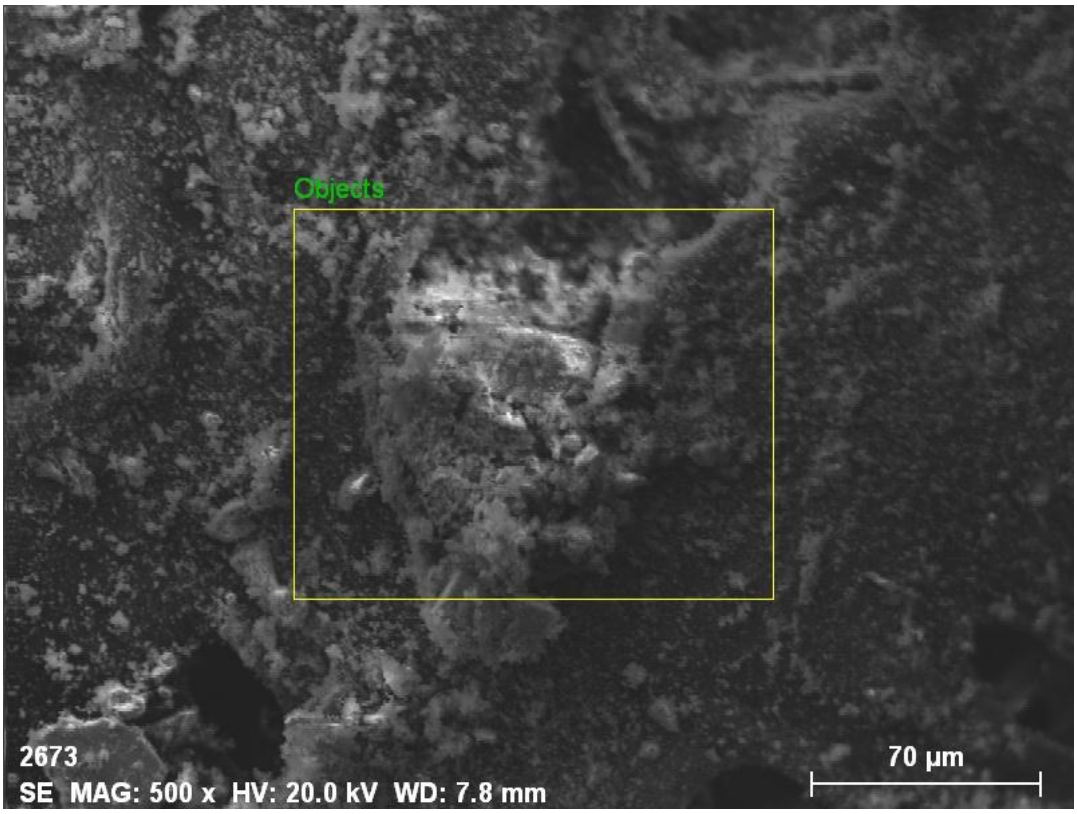


Figure S29. SEM−EDX of NPs obtained from Complex **2** during Suzuki-Miyaura Coupling



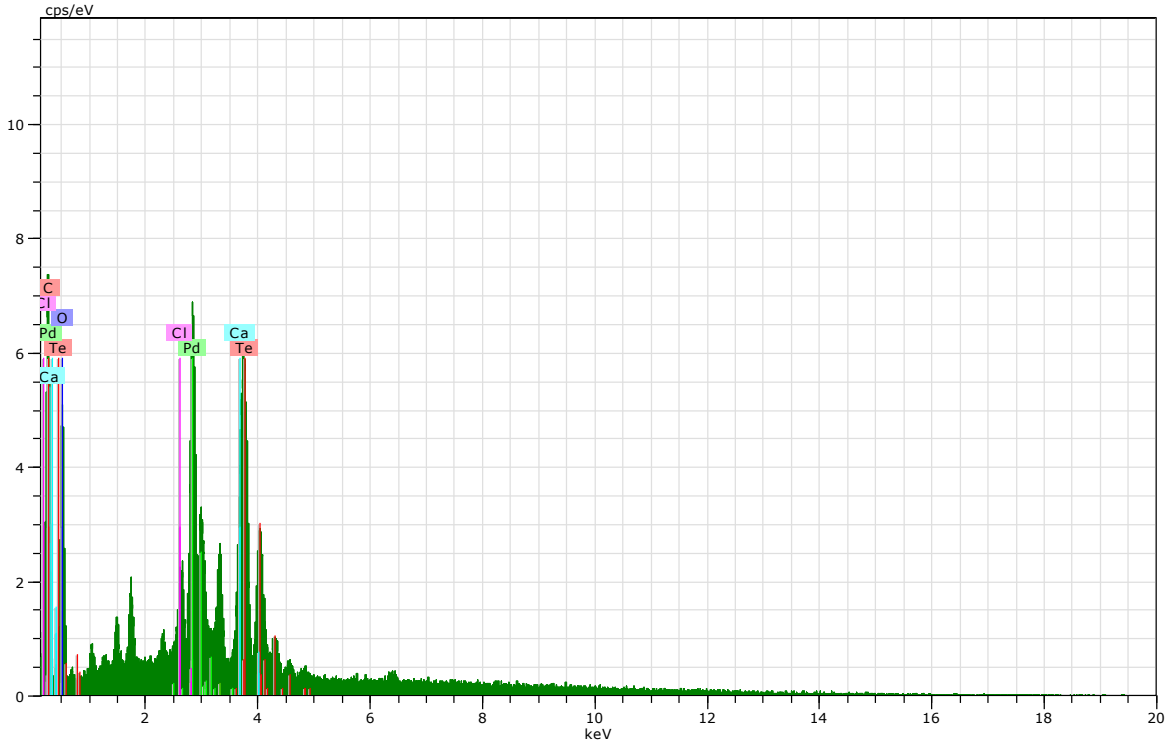


Figure S30. SEM−EDX of NPs obtained from Complex **3** during Suzuki-Miyaura Coupling

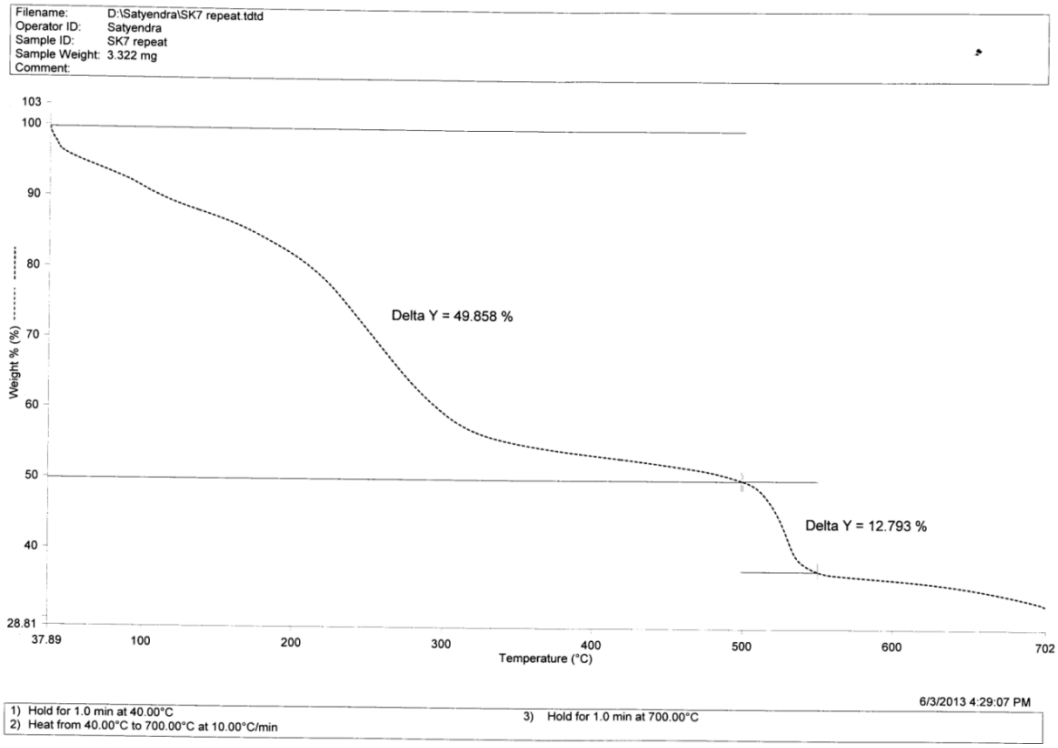


Figure S31. TGA of NPs obtained from Complex **1** during Suzuki−Miyaura Coupling

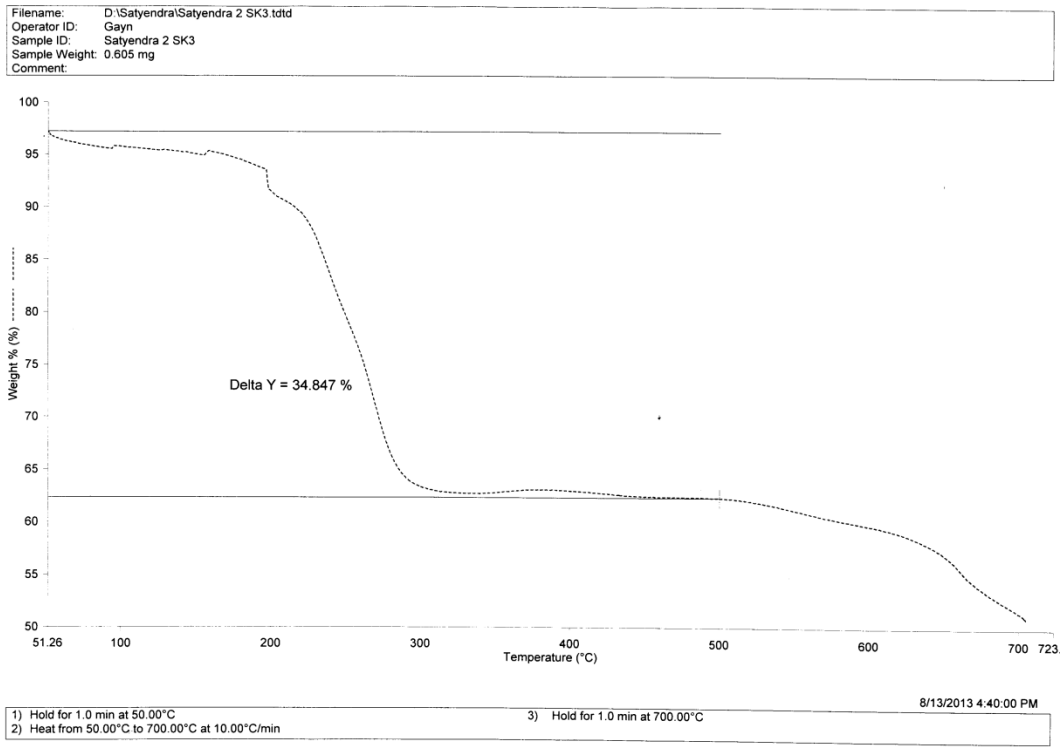


Figure S32. TGA of NPs obtained from Complex **2** during Suzuki−Miyaura Coupling

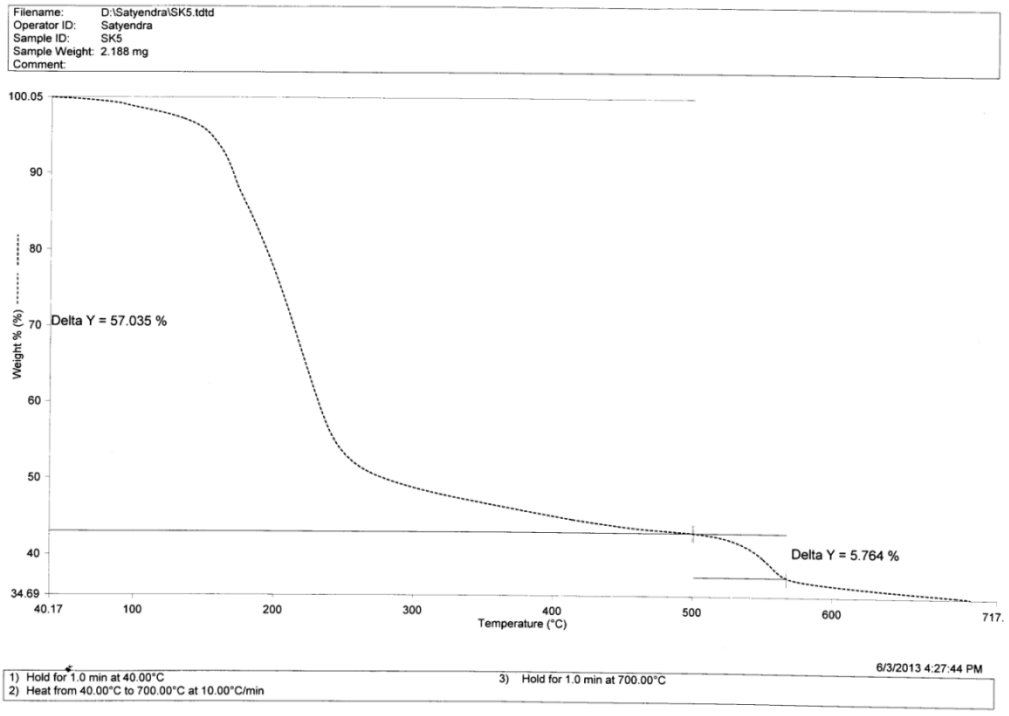


Figure S33. TGA of NPs obtained from Complex **3** during Suzuki−Miyaura Coupling