ESI *for*

Palladacycles having normal and spiro chelate rings designed from bi- and tridentate ligands with indole core: structure, synthesis and applications as catalysts

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Contents:

Table S1. Crystal data and structural refinements for ligand precursors aldehydes

Compounds	**A**	**B**
Empirical formula	$C_{15}H_{12}N_2O$	$C_{12}H_9NO$
Formula Wt.	236.27	183.20
Crystal size [mm]	0.33×0.29×0.27	0.34×0.32×0.29
Crystal system	Monoclinic	Monoclinic
Space group	*P 21/c*	*P 21/c*
Unit cell dimension	a = 11.737(3) Å b = 12.583(3) Å c = 8.430(2) Å α = 90.00° β = 104.108(6) ° γ = 90.00°	a = 8.5285(18) b = 15.890(3) c = 7.5691(16) α = 90.00 β = 114.881(3) γ = 90.00
Volume [Å^3]	1207.5(6)	930.5 (3)
Z	4	4
Density (Calc.) [Mg·m^{-3}]	1.300	1.308
Absorption Coeff. [mm^{-1}]	0.083	0.084
F(000)	496.0	384.0
θ range [°]	2.41–25.00	2.93–24.99
Index ranges	$-8 \le h \le 13$ $-13 \le k \le 14$ $-10 \le l \le 8$	$-10 \le h \le 10$ $-18 \le k \le 18$ $-8 \le l \le 8$
Reflections collected	5054	8759
Independent reflections ($R_{int.}$)	2066(0.0375)	1627(0.0291)
Completeness to max. θ [%]	97.8	99.8
Max./min. Transmission	0.968/0.957	0.965/0.953
Data/restraints/parameters	2066/0/163	1627/0/127
Goodness-of-fit on F^2	1.024	1.078
Final R indices [I >2σ(I)]	R_1 = 0.0469, wR_2 = 0.1036	R_1 = 0.0383 wR_2 = 0.1049
R indices (all data)	R_1 = 0.0768, wR_2 = 0.1142	R_1 = 0.0468 wR_2 = 0.1106
Largest diff. peak/hole [e.Å^{-3}]	0.151/-0.135	0.179/- 0.157
CCDC No.	1524513	1524514

Table S2 Crystal data and structural refinements for ligand **L1** and **L3**

Compounds	**L1**	**L3**
Empirical formula	$C_{22}H_{19}N_3$	$C_{13}H_{10}N_2S$
Formula Wt.	325.40	226.29
Crystal size [mm]	0.34× 0.30 × 0.28	0.35× 0.31× 0.28
Crystal system	Triclinic	Orthorhombic
Space group	*P-1*	*Pbca*
Unit cell dimension	a = 9.727(4)Å b = 10.001(4)Å c = 11.403(4)Å α = 113.392(10)° β = 96.236(10)° γ = 113.408(8)°	a = 8.1295(19) Å b = 15.338(4) Å c = 18.901(4) Å α = 90.00° β = 90.00° γ = 90.00°
Volume [Å^3]	886.3(6)	2356.8(9)
Z	2	8
Density (Calc.) [Mg.m^{-3}]	1.219	1.276
Absorption Coeff. [mm^{-1}]	0.073	0.247
F(000)	344.0	944.0
θ range [°]	2.37–24.99	2.66–25.00
Index ranges	$-11 \le h \le 9$ $-11 \le k \le 11$ $-13 \le l \le 11$	$-9 \le h \le 9$ $-18 \le k \le 18$ $-22 \le l \le 22$
Reflections collected	4545	21062
Independent reflections ($R_{int.}$)	3072(0.0467)	2076(0.0535)
Completeness to max. θ [%]	98.5	99.9
Max./min. Transmission	0.982/0.973	0.933/0.915
Data/restraints/parameters	3072/0/226	2076/0/149
Goodness-of-fit on F^2	0.885	0.950
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0688, wR_2 = 0.1075	R_1 = 0.0453 wR_2 = 0.1175
R indices (all data)	R_1 = 0.2039, wR_2 = 0.1437	R_1 = 0.0636 wR_2 = 0.1299
Largest diff. peak/hole [e.Å^{-3}]	0.154/–0.152	0.293/–0.112
CCDC No.	1524516	1524517

Table S3 Crystal data and structural refinements for complex **2** and **3**

Compounds	**2**	**3**
Empirical formula	$C_{26}H_{22}ClN_5Pd$	C_{26} H_{18} Cl_2 N_4 Pd_2 S_2,C H_2 Cl_2
Formula Wt.	546.34	819.19
Crystal size [mm]	0.35× 0.30 × 0.28	0.33× 0.29 ×0.26
Crystal system	Monoclinic	Monoclinic
Space group	*P 21/c*	*C2/c*
Unit cell dimension	a = 10.450(6)Å b = 12.734(8)Å c = 18.174(11)Å α = 90.00° β = 104.019(11)° γ = 90.00°	a = 14.7535(16) Å b = 13.5197(15) Å c = 15.248(17) Å α = 90.00° β = 111.195(2)° γ = 90.00°
Volume [Å^3]	2347 (2)	2889.0(5)
Z	4	4
Density (Calc.) [Mg.m^{-3}]	1.547	1.883
Absorption Coeff. [mm^{-1}]	0.929	1.786
F(000)	1104.0	1608.0
θ range [°]	2.57–24.99	2.11–25.00
Index ranges	$-12 \le h \le 12$ $-15 \le k \le 15$ $-21 \le l \le 21$	$-17 \le h \le 17$ $-16 \le k \le 16$ $-18 \le l \le 18$
Reflections collected	21242	13706
Independent reflections ($R_{int.}$)	4126(0.1182)	2542(0.0333)
Completeness to max. θ [%]	99.7	99.8
Max./min. Transmission	0.892/0.924	0.632/0.558
Data/restraints/parameters	4126/0/298	2542/0/177
Goodness-of-fit on F^2	1.168	1.042
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0873 wR_2 = 0.1527	R_1 = 0.0297 wR_2 = 0.0734
R indices (all data)	R_1 = 0.1273, wR_2 = 0.1687	R_1 = 0.0335 wR_2 = 0.0753
Largest diff. peak/hole [e.Å^{-3}]	0.741/–1.220	0.561/–0.661
CCDC No.	1524518	1524519

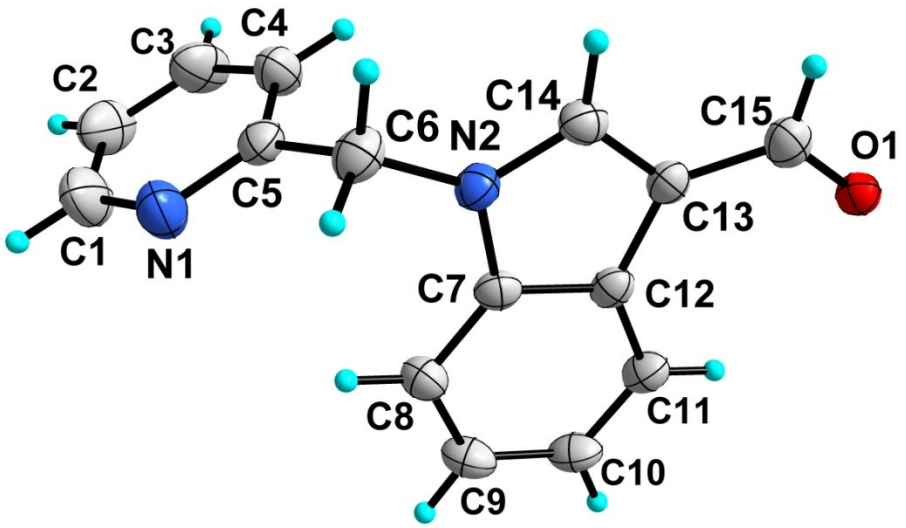


Figure **S1.** Molecular structure of **A.** Selected bond angles (°): N(2)—C14 1.346(2), N(2)—C(7) 1.395(2), N(2)—C(6) 1.454(2), N(1)—C(1) 1.330(3), C(5)—N(1) 1.322(2), O(1)—C(15) 1.219(2), C(13)—C(15) 1.428(3), C(14)—C(13) 1.370(2). Selected bond angles (°):C(7)—N(2)—C(6) 124.97(16) , N(2)—C(14)—C(13) 111.41(17), C(14)—N(2)—C(7) 108.29(15), C(14)—N(2)—C(6) 126.47(16), N(2)—C(6)—C(5) 113.41(16), C(5)—N(1)—C(1) 117.5(2).

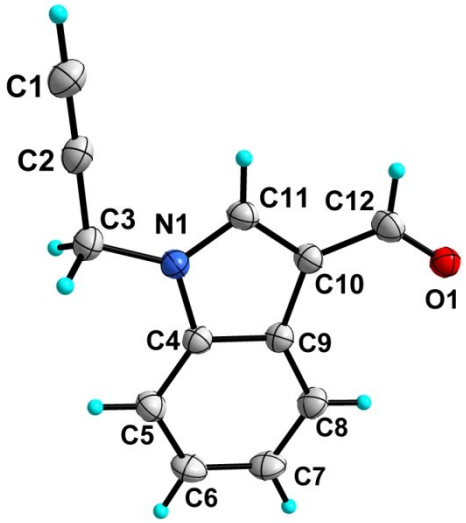
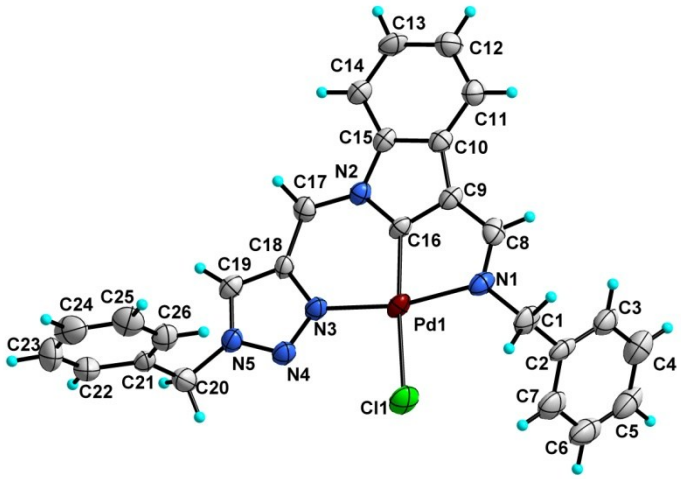


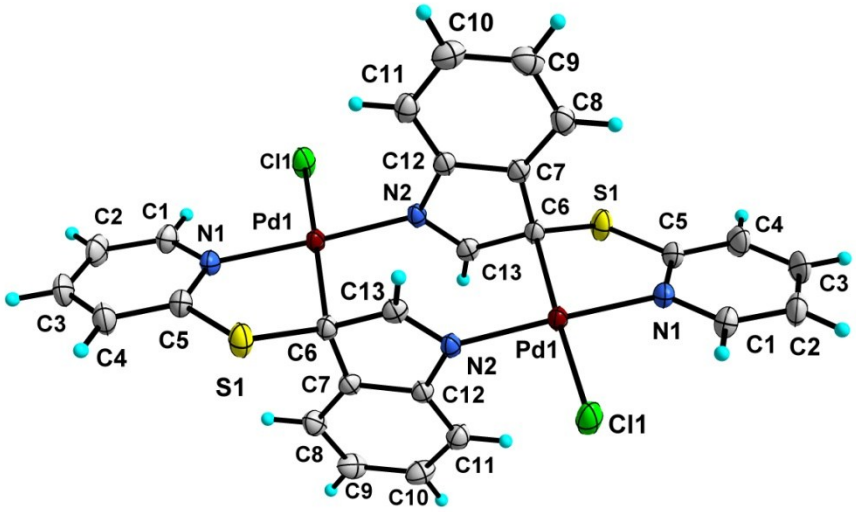
Figure **S2.** Molecular structure of **B.** Selected bond angles (°): N(1)—C(11) 1.3449(18), N(1)—C(4) 1.3888(17), N(1)— C(3) 1.4628(19), O(1)—C(12) 1.2211(19), C(2)—C(1) 1.171(2), C(2)—C(3) 1.454(2). Selected bond angles (°):C(11)—N(1)—C(4) 108.70(12), C(11)—N(1)—C(3) 128.25(12), C(4)—N(1)—C(30 122.96(12), C(1)—C(2)—C(3) 179.11(19).

Table S4 Selected bond lengths and bond angles of complex **2**



Bond Distance (Å)		Bond Angle (°)	
Pd(1)—C(16)	1.932(8)	C(16)—Pd(1)—N(1)	78.9(3)
Pd(1)—N(3)	2.028(7)	C(16)—Pd(1)—N(3)	88.2(3)
Pd(1)—N(1)	2.063(7)	N(3)—Pd(1)—N(1)	167.0(3)
Pd(1)—Cl(1)	2.390(3)	C(16)—Pd(1)—Cl(1)	174.5(3)
N(3)—N(4)	1.313(9)	N(3)—Pd(1)—Cl(1)	96.8(2)
N(1)—C(8)	1.287(11)	N(1)—Pd(1)—Cl(1)	96.2(2)
N(4)—N(5)	1.335 (9)	N(4)—N(3)—C(18)	109.6(7)
N(3)—C(18)	1.369(9)	N(4)—N(3)—Pd(1)	122.3(5)
N(2)—C(16)	1.359(9)	C(18)—N(3)—Pd(1)	128.1(6)
N(1)—C(1)	1.487(10)	C(16)—N(2)—C(15)	108.1(7)
C(17)—C(18)	1.500(11)	C(16)—N(2)—C(17)	127.1(7)
C(8)—C(9)	1.422(11)	C(15)—N(2)—C(17)	124.5(7)
		C(8)—N(1)—C(1)	118.0(8)
		C(8)—N(1)—Pd(1)	114.1(6)
		C(1)—N(1)—Pd(1)	127.8(6)
		C(13)—C(14)—C(15)	117.1(9)
		N(2)—C(16)—C(9)	110.0(7)
		N(2)—C(16)—Pd(1)	132.5(7)
		C(9)—C(16)—Pd(1)	117.4(6)
		C(19)—C(18)—N(3)	107.2(7)
		C(19)—C(18)—C(17)	125.9(7)
		N(4)—N(5)—C(19)	110.7(7)

Table S5 Bond lengths and bond angles of complex **3**



Bond Distance (Å)		Bond Angle (°)	
Pd(1)—C(6)	2.115(3)	C(6)—Pd(1)—N(2)	93.11(12)
Pd(1)—N(1)	2.053(3)	C(6)—Pd(1)—N(1)	84.34(12)
Pd(1)—N(2)	2.019(3)	N(2)—Pd(1)—Cl(1)	88.31(8)
Pd(1)—Cl(1)	2.3360(10)	N(1)—Pd(1)—Cl(1)	94.82(9)
S(1)—C(5)	1.743(4)	N(2)—Pd(1)—N(1)	173.15(11)
S(1)—C(6)	1.795(3)	C(6)—Pd(1)—Cl(1)	174.46(10)
N(2)—C(13)	1.310(4)	C(5)—S(1)—C(6)	99.99(16)
N(2)—C(12)	1.421(4)	C(13)—N(2)—Pd(1)	129.5(2)
C(6)—C(13)	1.457(5)	C(12)—N(2)—Pd(1)	119.9(2)
N(1)—C(1)	1.349(5) 1.351(5)	C(1)—N(1)—C(5)	117.8(3)
N(1)—C(5)	1.385(5)	C(1)—N(1)—Pd(1)	123.1(2)
C(12)—C(11)		C(5)—N(1)—Pd(1)	119.0(2)
		C(13)—C(6)—C(7)	102.9(3)
		C(13)—C(6)—Pd(1)	103.6(2)

		C(7)—C(6)—Pd(1)	103.7(2)
		S(1)—C(6)—Pd(1)	109.08(16)
		N(2)—C(13)—C(6)	112.1(3)
		C(11)—C(12)—C(7)	122.4(3)
		N(1)—C(5)—C(4)	121.5(4)
		N(1)—C(5)—S(1)	118.5(3)
		C(4)—C(3)—C(2)	119.7(4)
		C(11)—C(10)—C(9)	121.4(4)

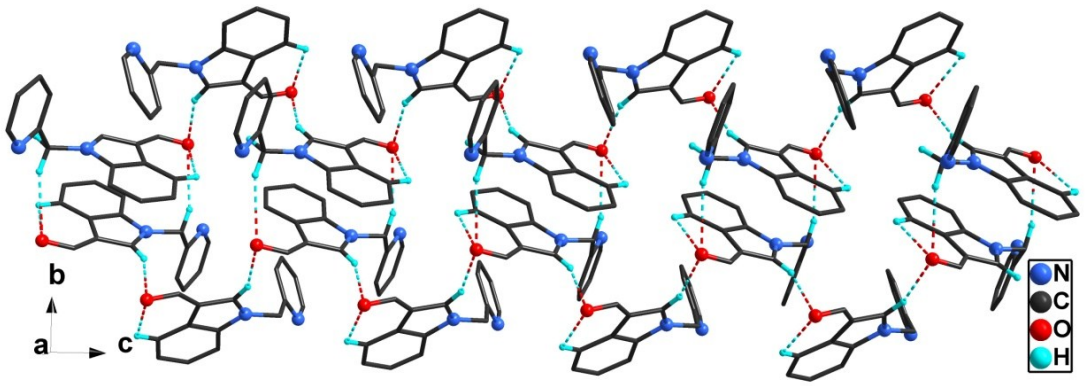


Figure S3. Molecular packing framework showing non-covalent C–H···O interactions in the crystal lattice of **A**.

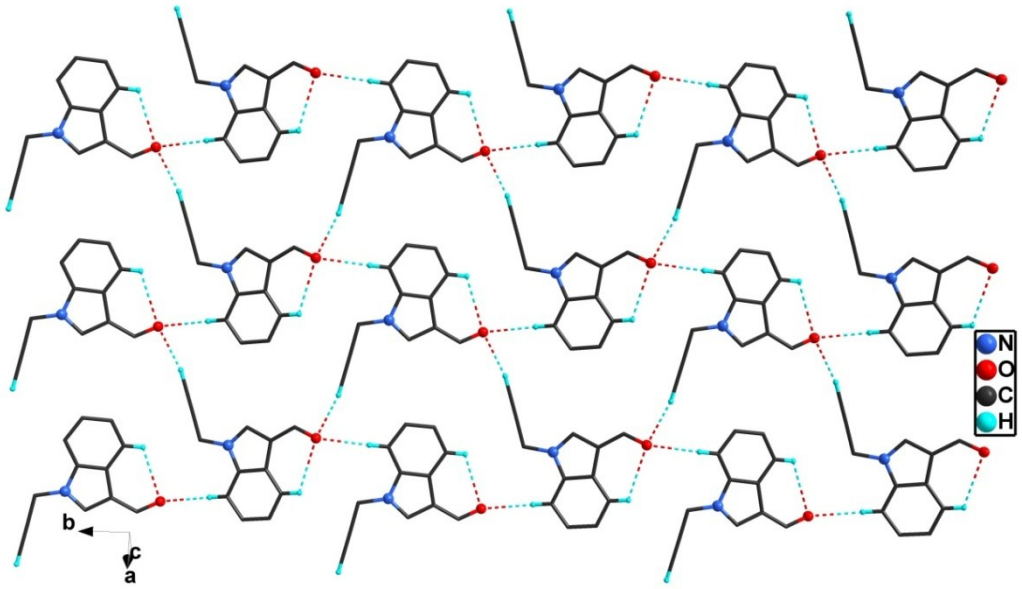


Figure S4. Molecular packing framework showing non-covalent C–H···O interactions in the crystal lattice of **B**.

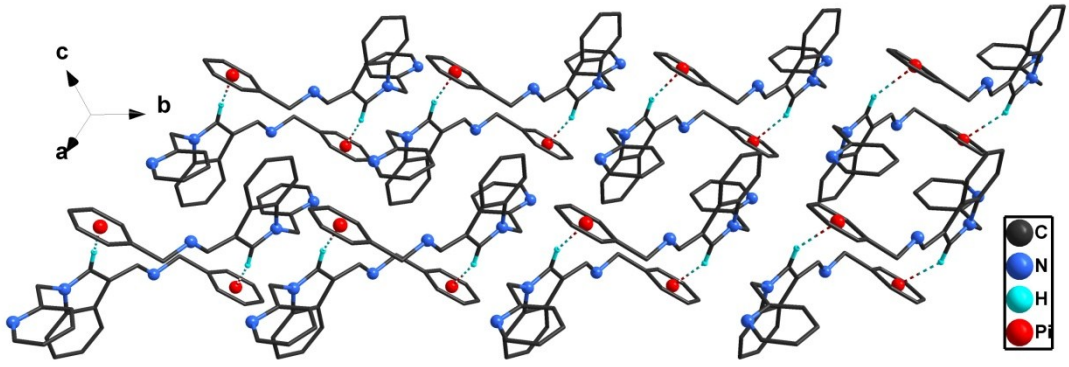


Figure S5. Molecular packing framework showing non-covalent C–H···π interactions in the crystal lattice of ligand **L1**.

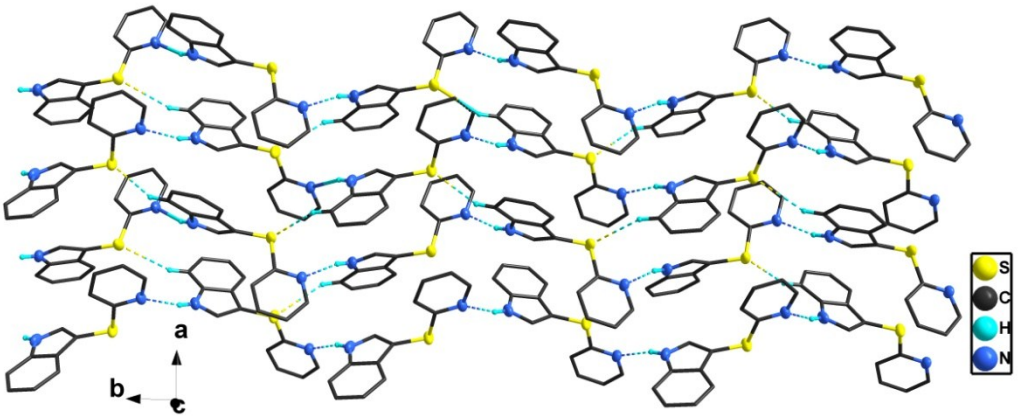


Figure S6. Molecular packing framework showing non-covalent C–H···S and N–H···N secondry interactions in the crystal lattice of ligand **L3**

Table S6 Distances [Å] of non-covalent interactions for **A** and **B**

A		**B**	
C(6)—H(6B)···O(1) Inter-molecular	2.6862	C(1)—H(1)···O(1) Inter-molecular	2.3920
C(11)—H(11)···O(1) Intra-molecular	2.8190	C(8)—H(8)···O(1) Intra-molecular	2.8292

Table S7 Distances [Å] of non-covalent interactions for **L1** and **L3**

L1		**L3**	
C(18)—H(18)···π Inter-molecular	2.8975		
		C(11)—H(11)···S(1) Inter-molecular	2.9960
		N(1)—H(1)···N(2) Inter-molecular	2.1375

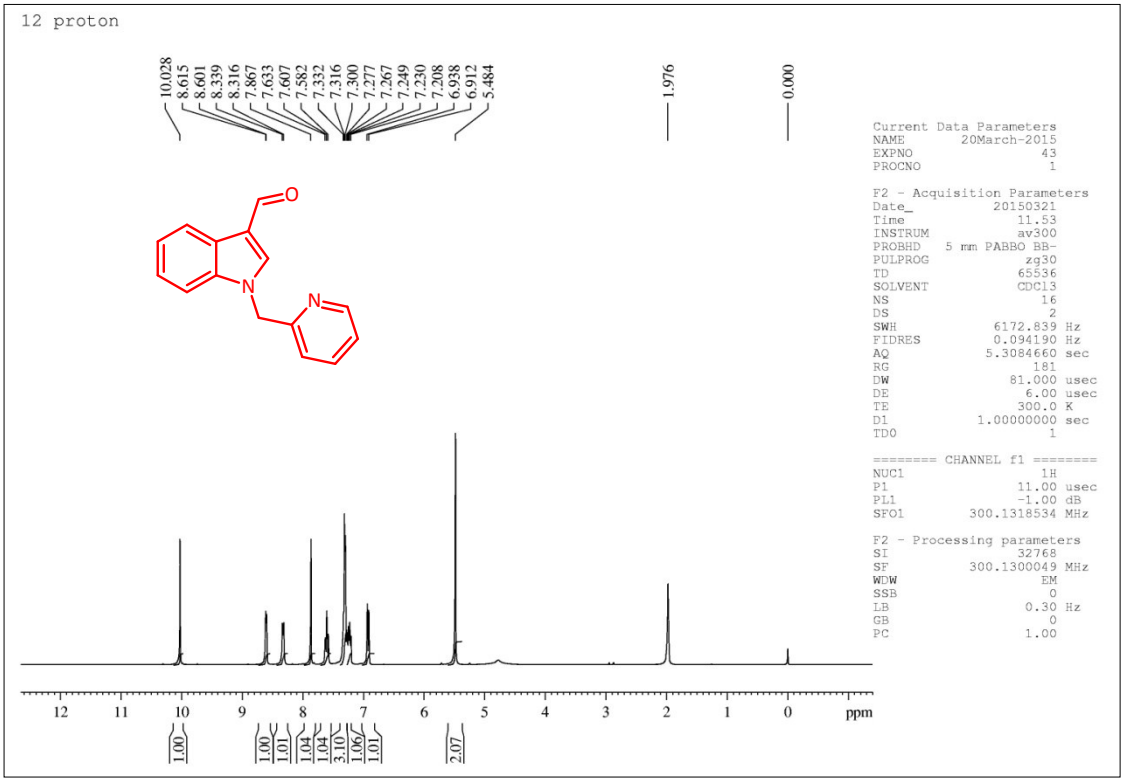


Figure S7. ^{1}H NMR spectrum of 1-(pyridin-2-ylmethyl)-1*H*-indole-3-carbaldehyde (**A**)

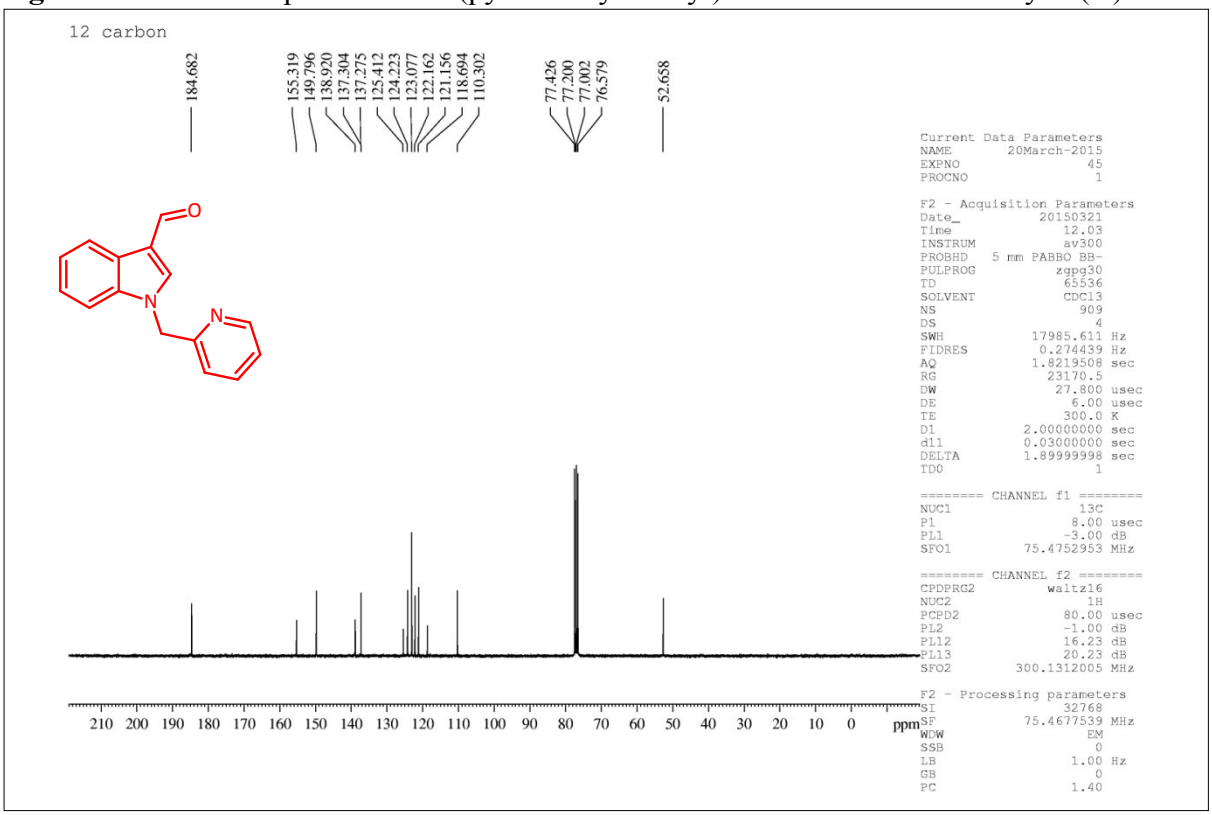


Figure S8. ^{13}C{^{1}H} NMR spectrum of 1-(pyridin-2-ylmethyl)-1*H*-indole-3-carbaldehyde (**A**)

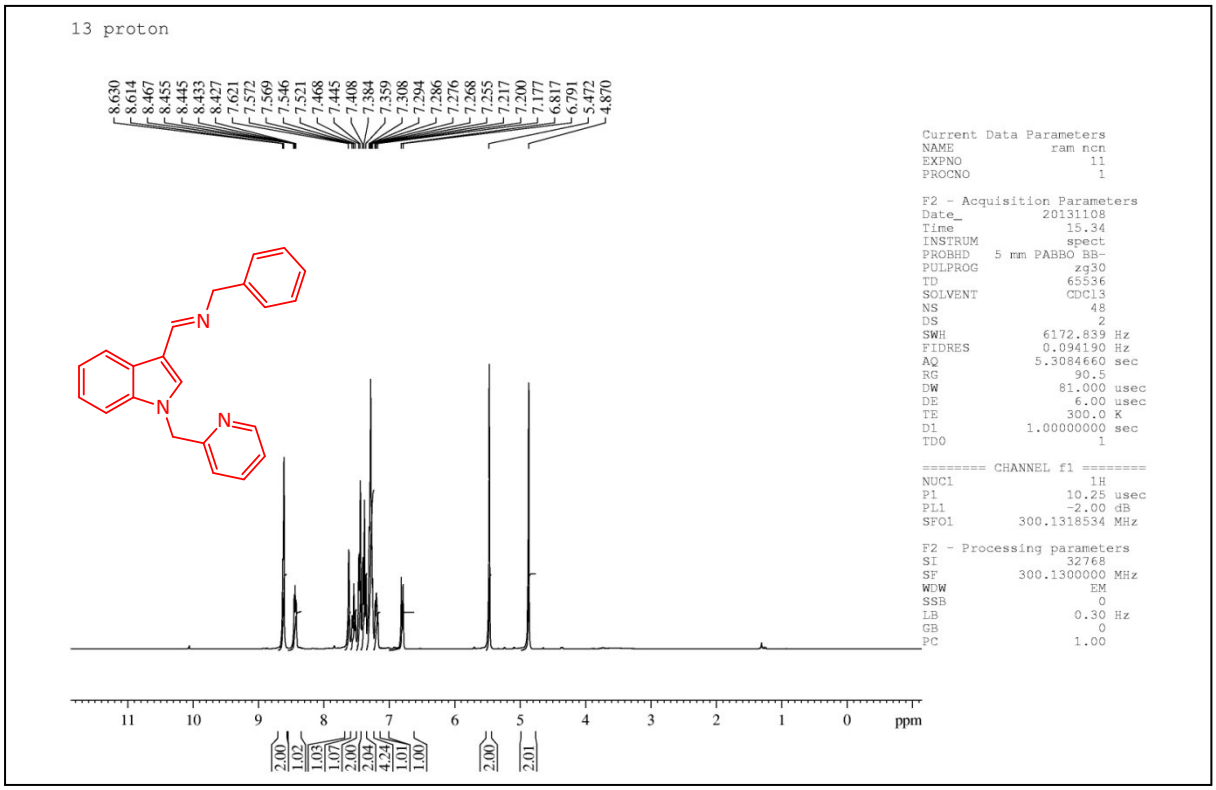


Figure 9. ^{1}H NMR spectrum of **L1**

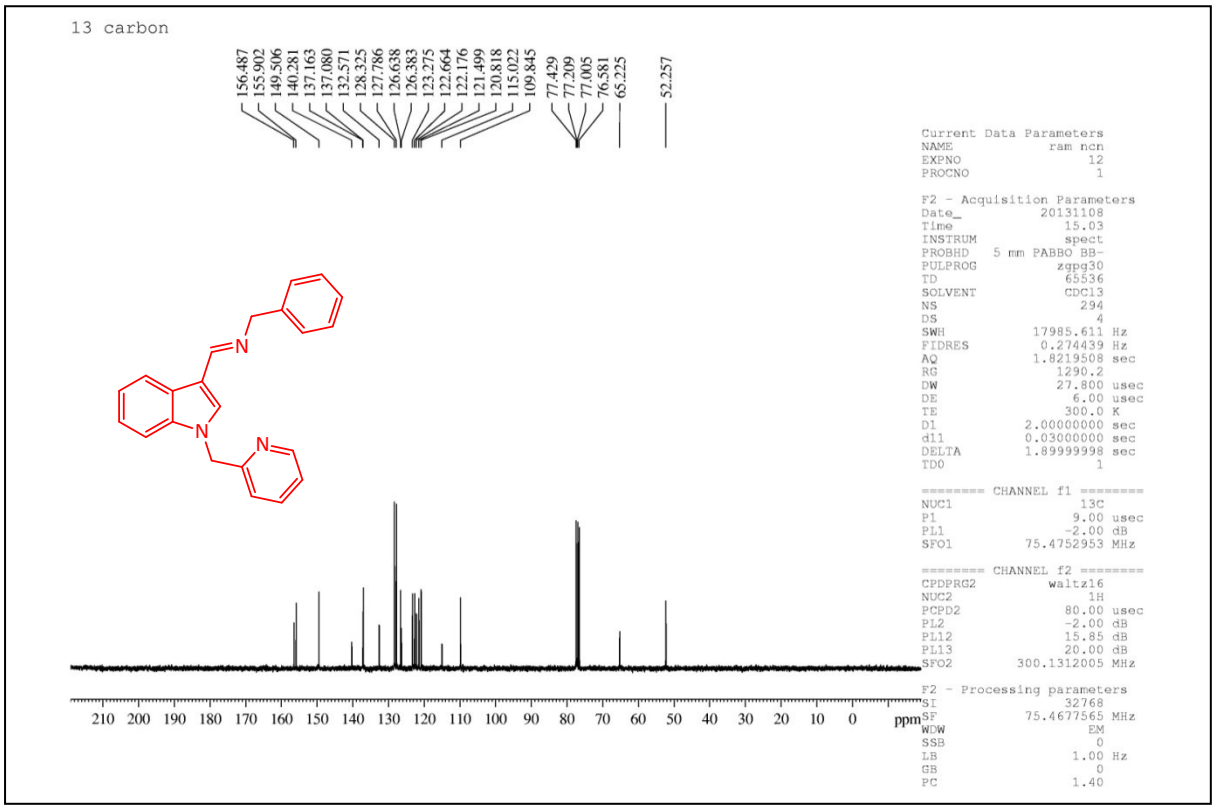


Figure S10. ^{13}C{^{1}H} NMR spectrum of **L1**

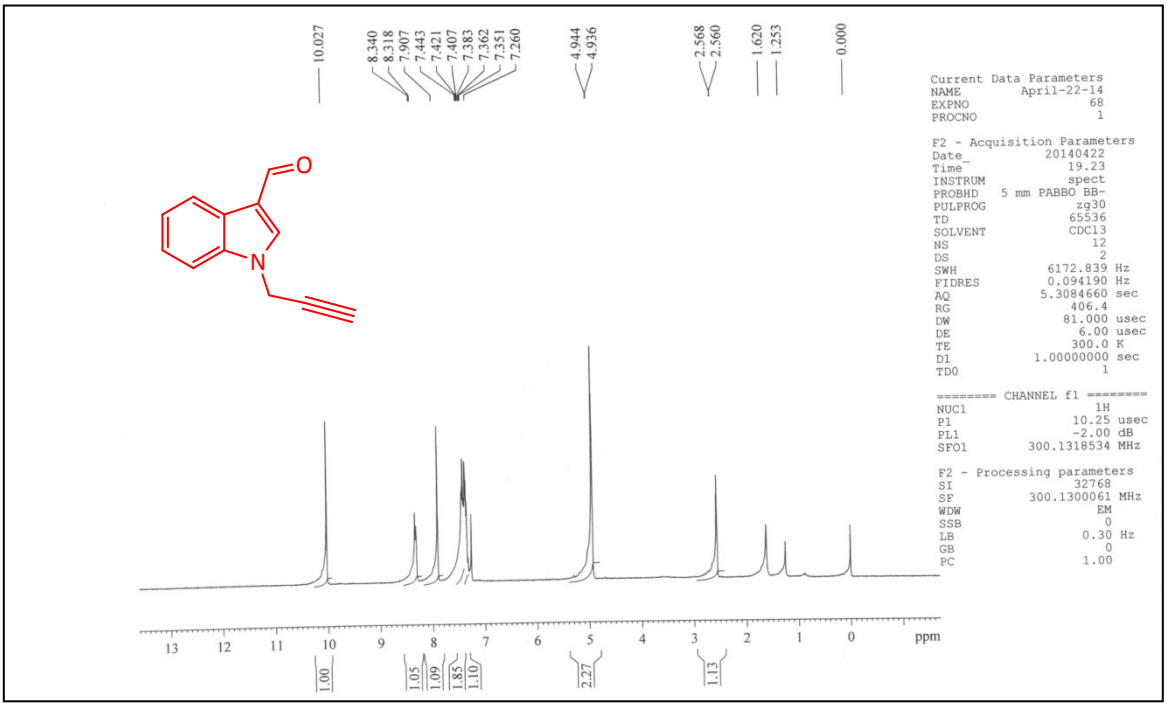


Figure S11. ^{1}H NMR spectrum of 1-prop-2-ynyl-1H-indole-3-carbaldehyde (**B**)

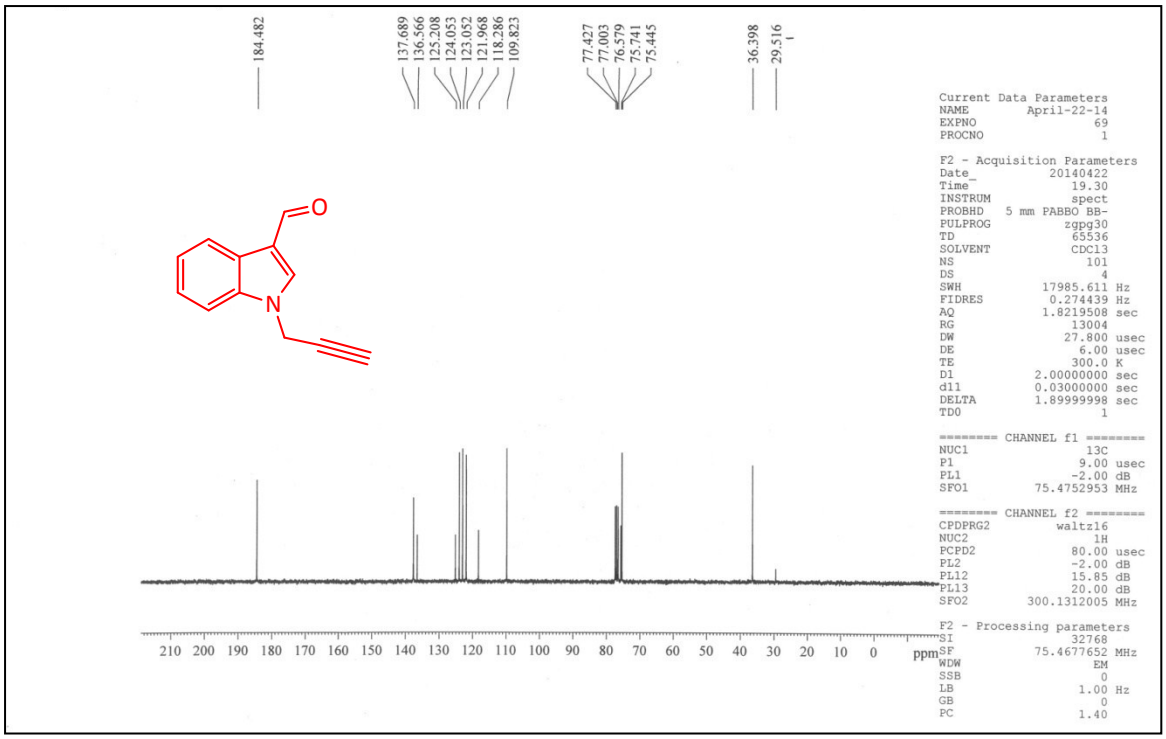


Figure S12. ^{13}C{^{1}H} NMR spectrum of 1-prop-2-ynyl-1H-indole-3-carbaldehyde (**B**)

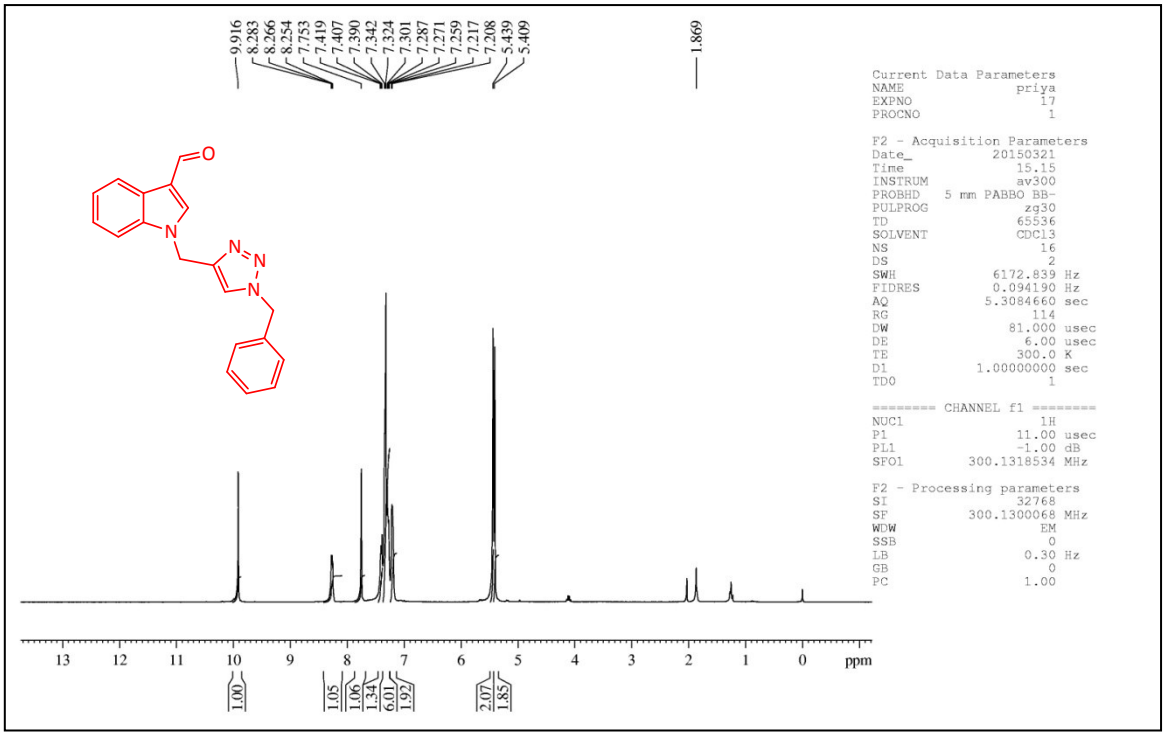


Figure S13. ^{1}H NMR spectrum of 1-(1-benzyl-1H-[1,2,3]-triazole-4ylmethyl)-1H-indole-3-carbaldehyde (**B1**)

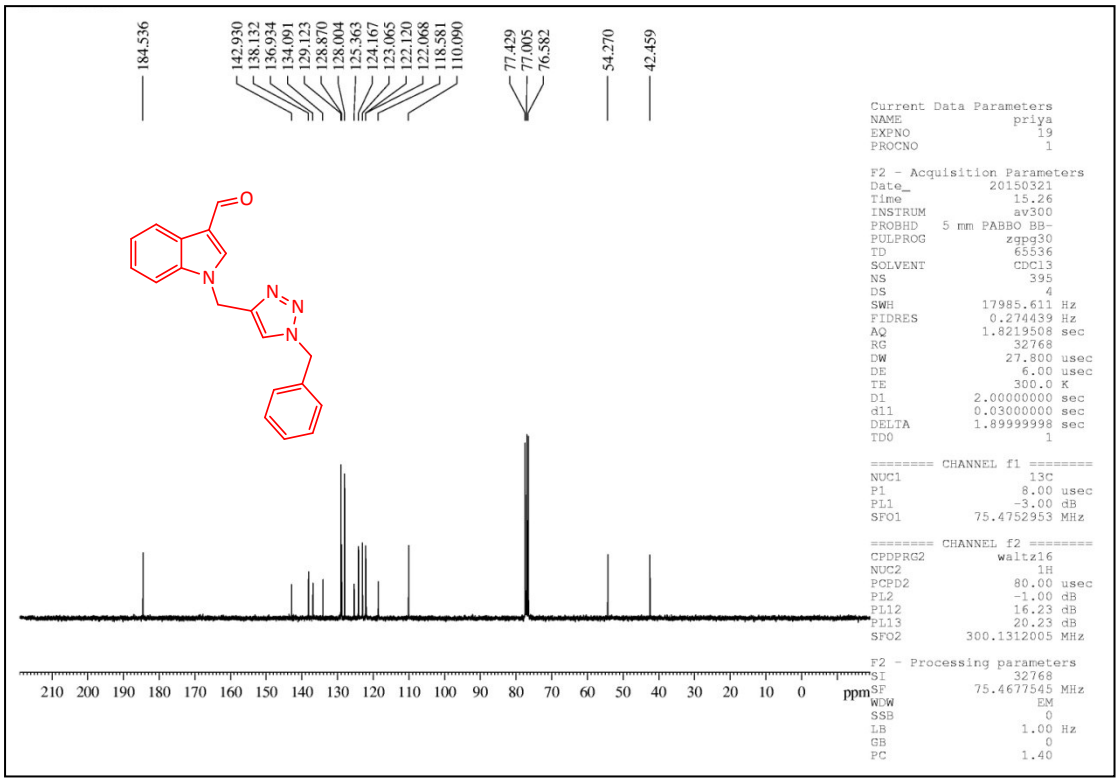


Figure S14. ^{13}C{^{1}H} NMR spectrum of 1-(1-benzyl-1*H*-[1,2,3]-triazole-4ylmethyl)-1H-indole-3-carbaldehyde (**B1**)

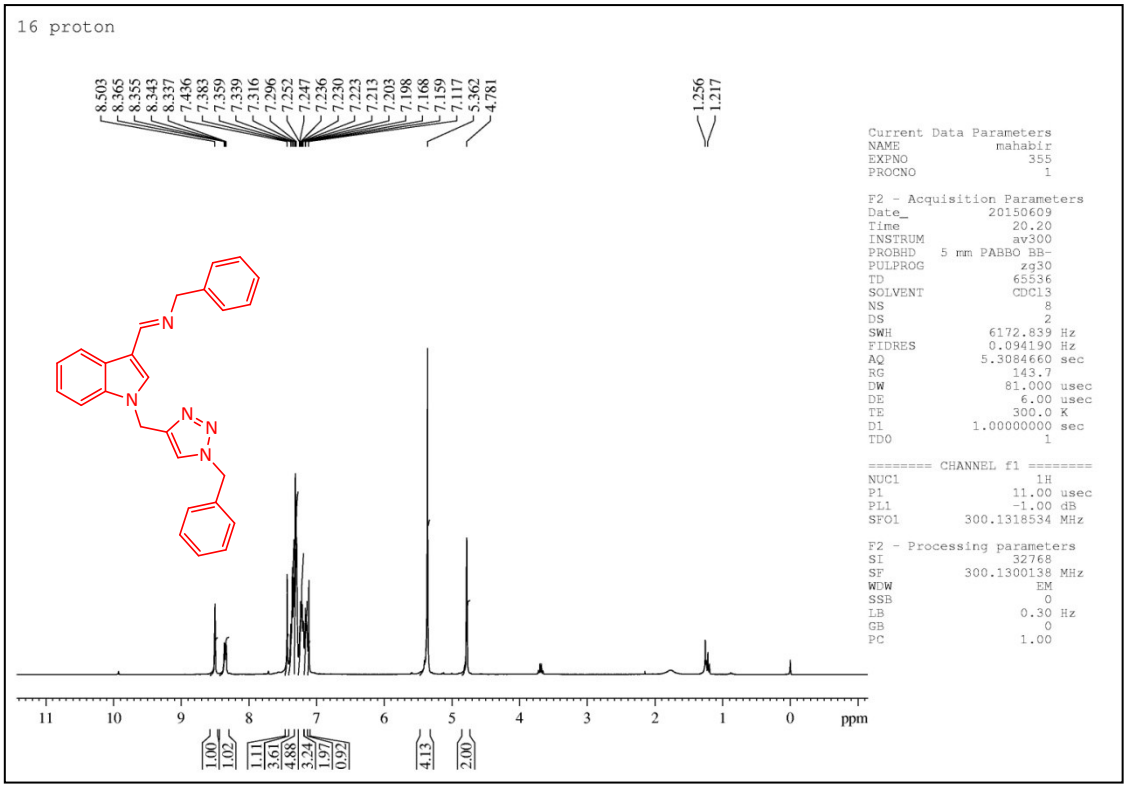


Figure S15. ^{1}H NMR spectrum of **L2**

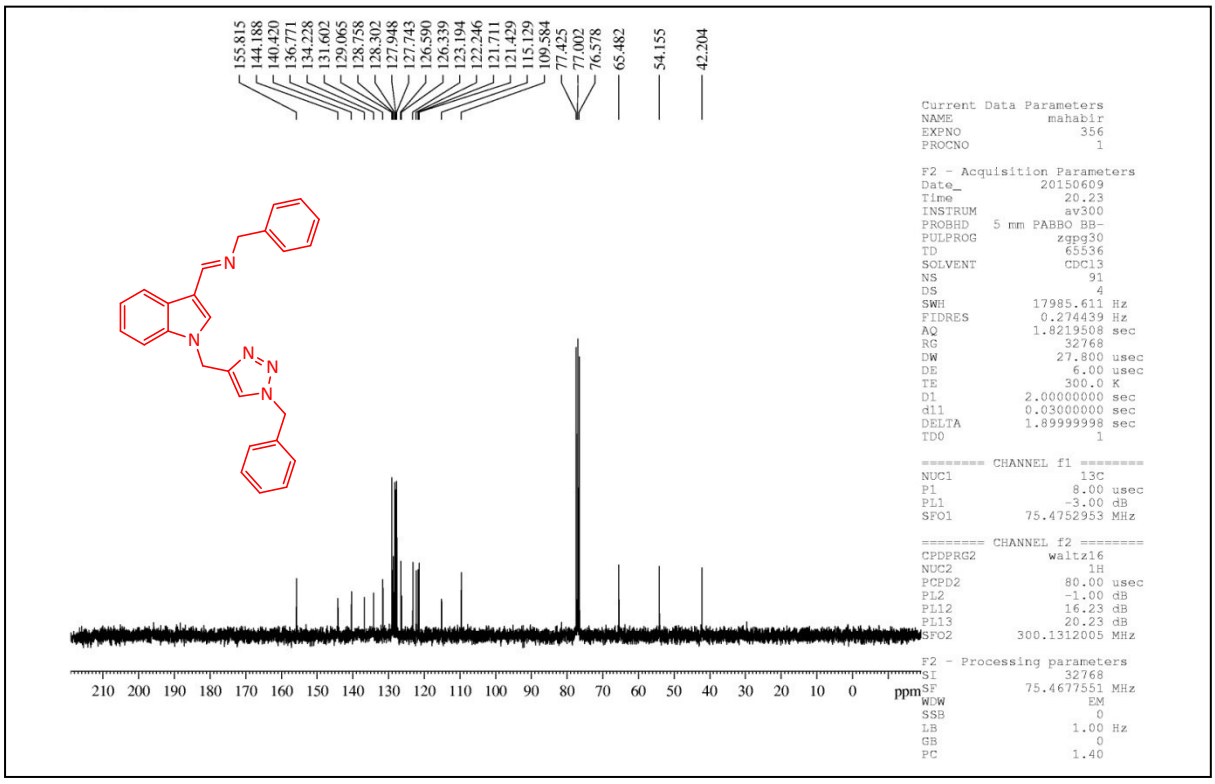


Figure S16. ^{13}C{^{1}H} NMR spectrum of **L2**

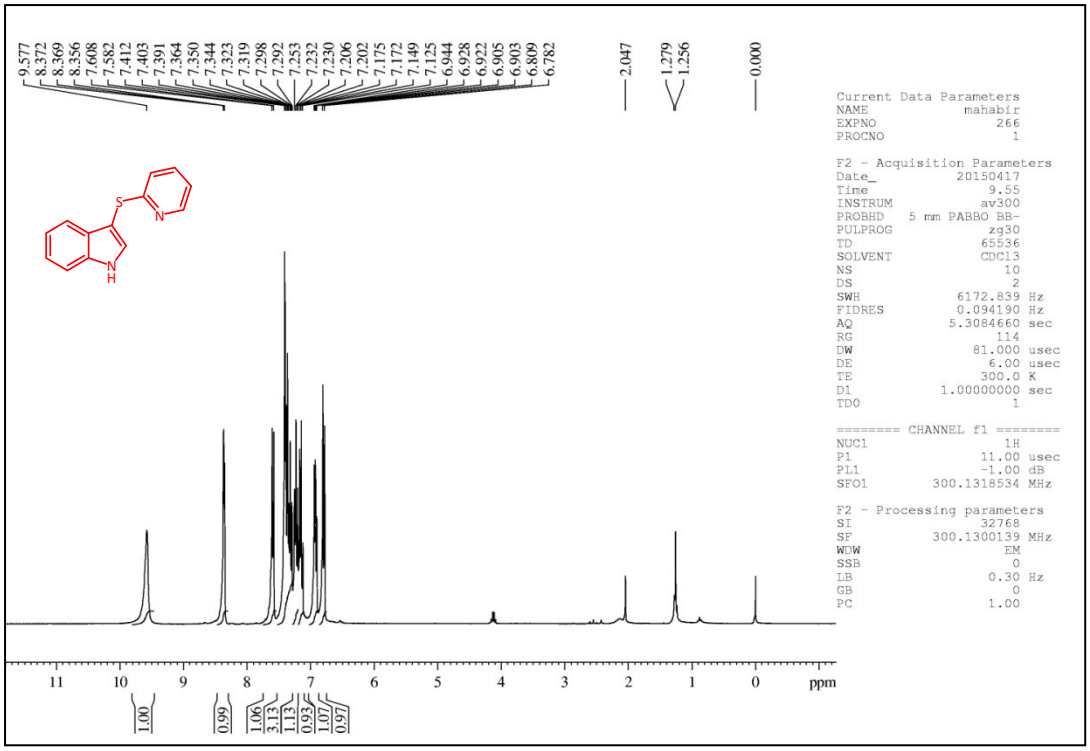


Figure S17. ^{1}H NMR spectrum of **L3**

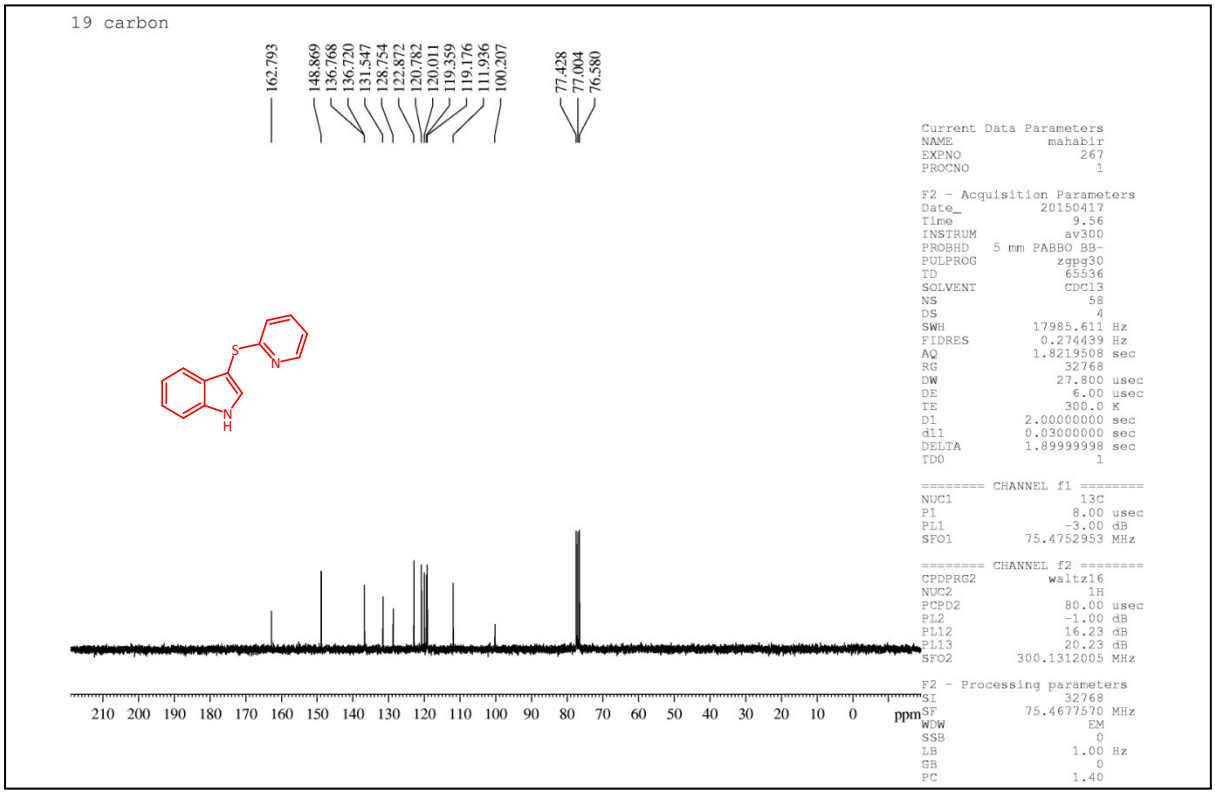


Figure S18. ^{13}C{^{1}H} NMR spectrum of ligand **L3**

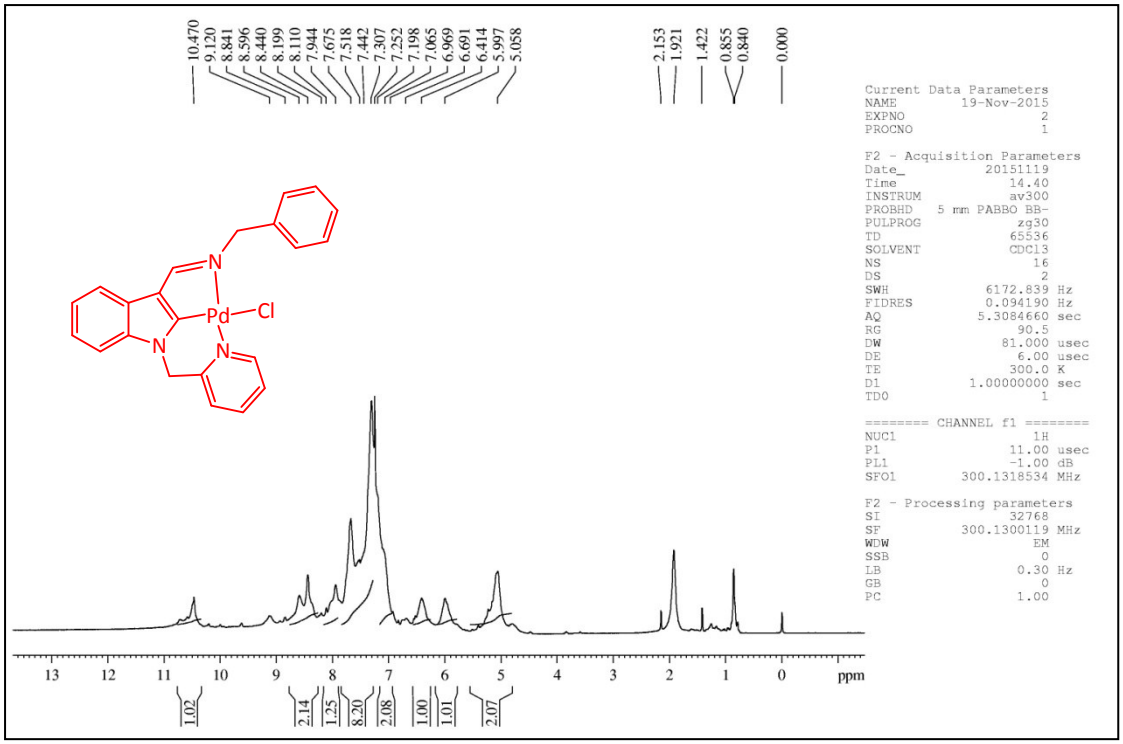


Figure S19. ^{1}H NMR spectrum of **1**

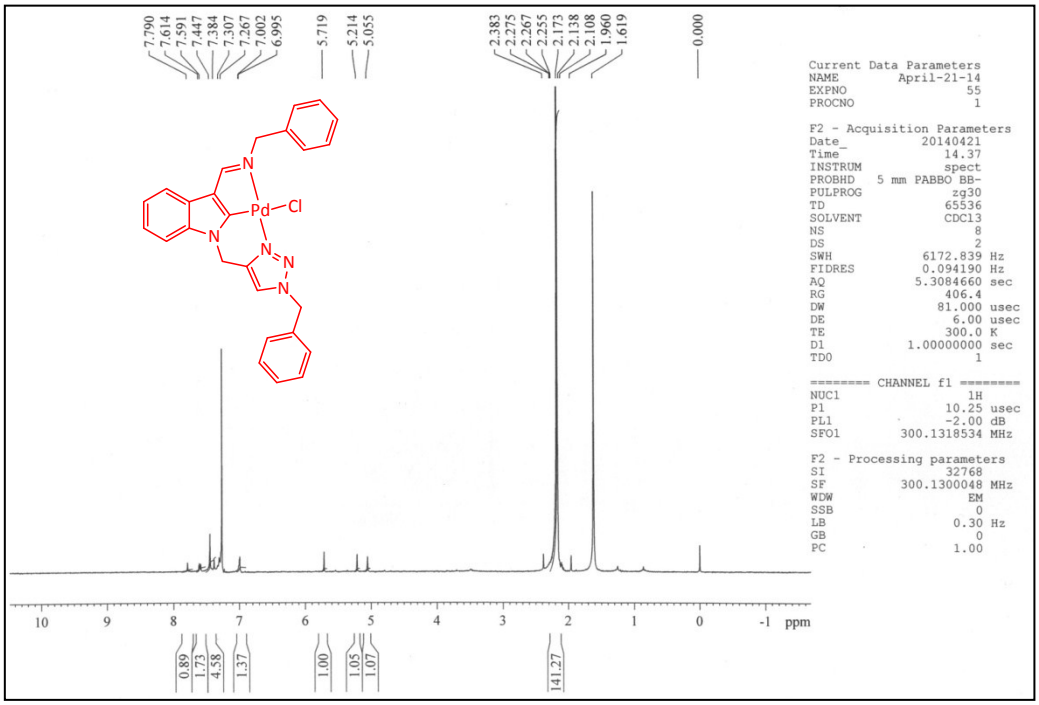


Figure S20. ^{1}H NMR spectrum of **2**

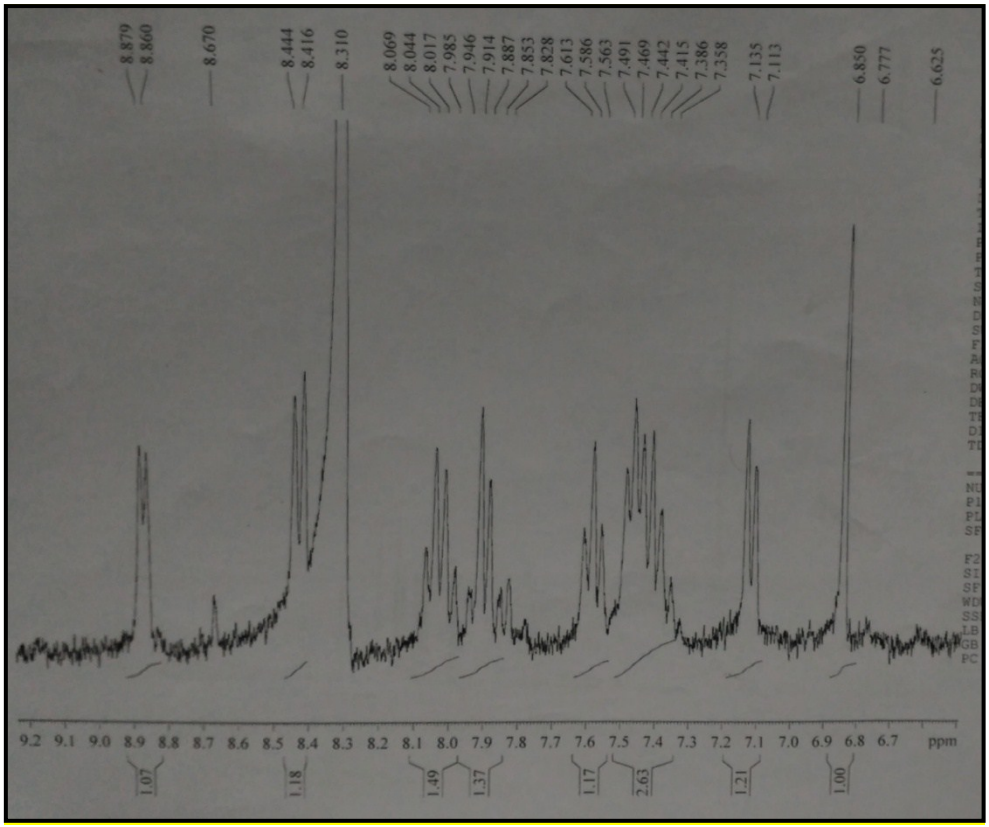
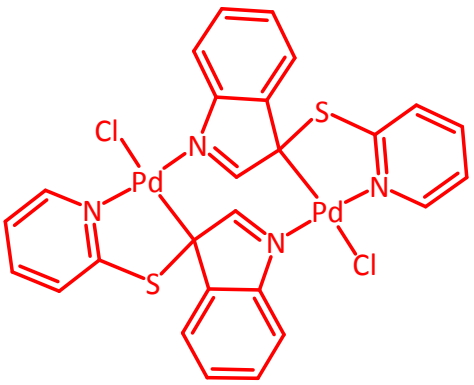


Figure S21. ^{1}H NMR spectrum of **3** in DMSO-d_6 at 300 MHz



3

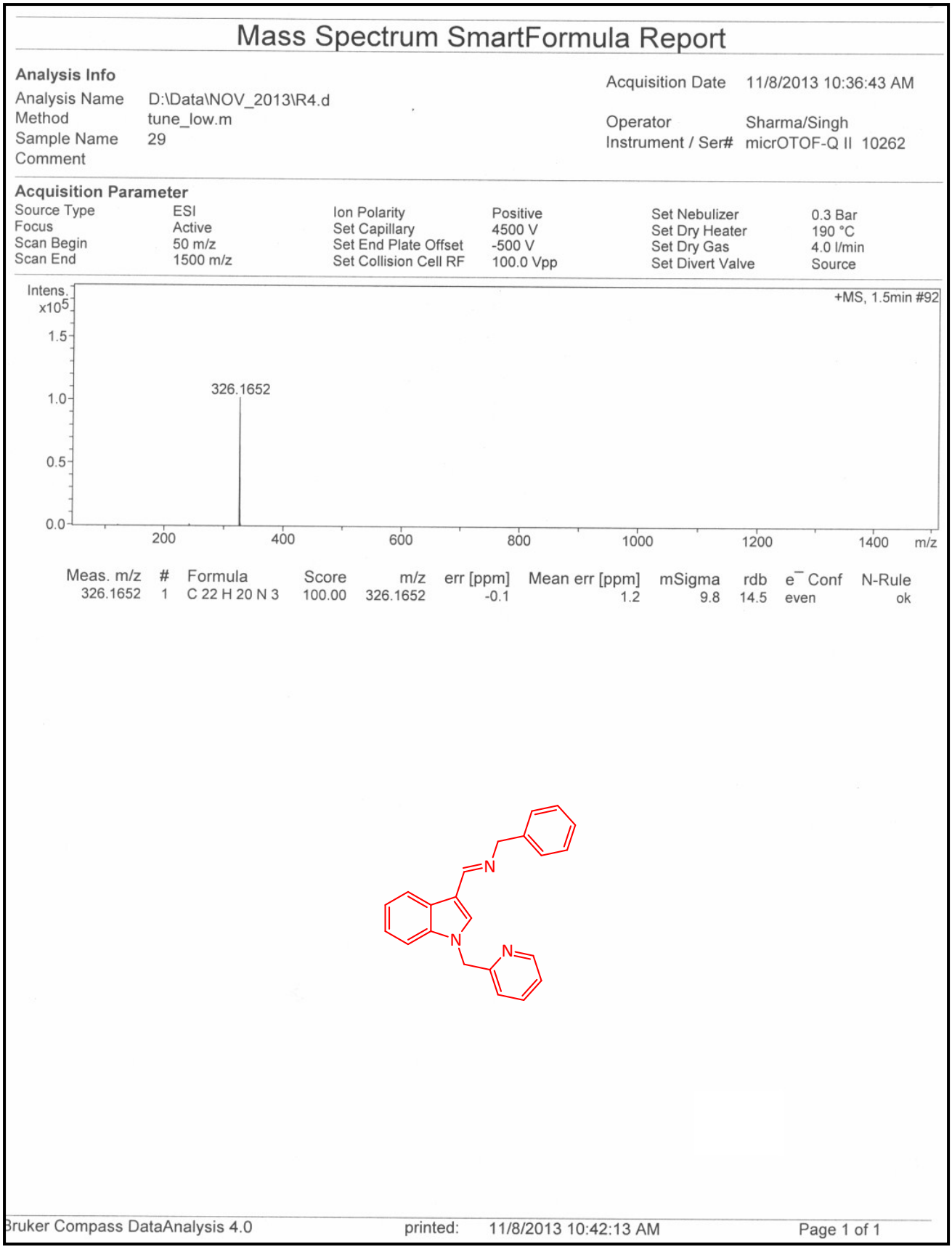


Figure S22. Mass spectrum of **L1**

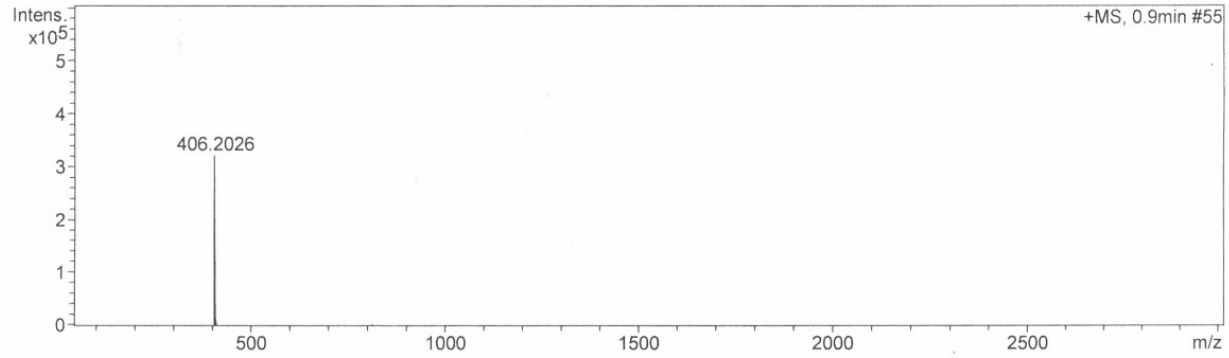
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\APRIL_2014\R1.d	Acquisition Date	4/29/2014 11:53:51 AM
Method	tune_wide.m	Operator	Sharma/Singh
Sample Name	TM 1:100	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	600.0 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 Var Norm	Std m/z Diff	Std Comb Dev
406.2026	1	C 26 H 24 N 5	406.2026	0.0	3.3	17.5	ok	even	12.0	17.4	2.6	7.5	4.4	842.7

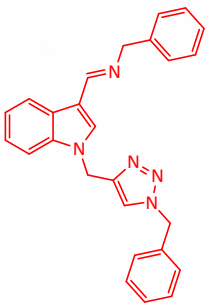


Figure S23. Mass spectrum of **L2**

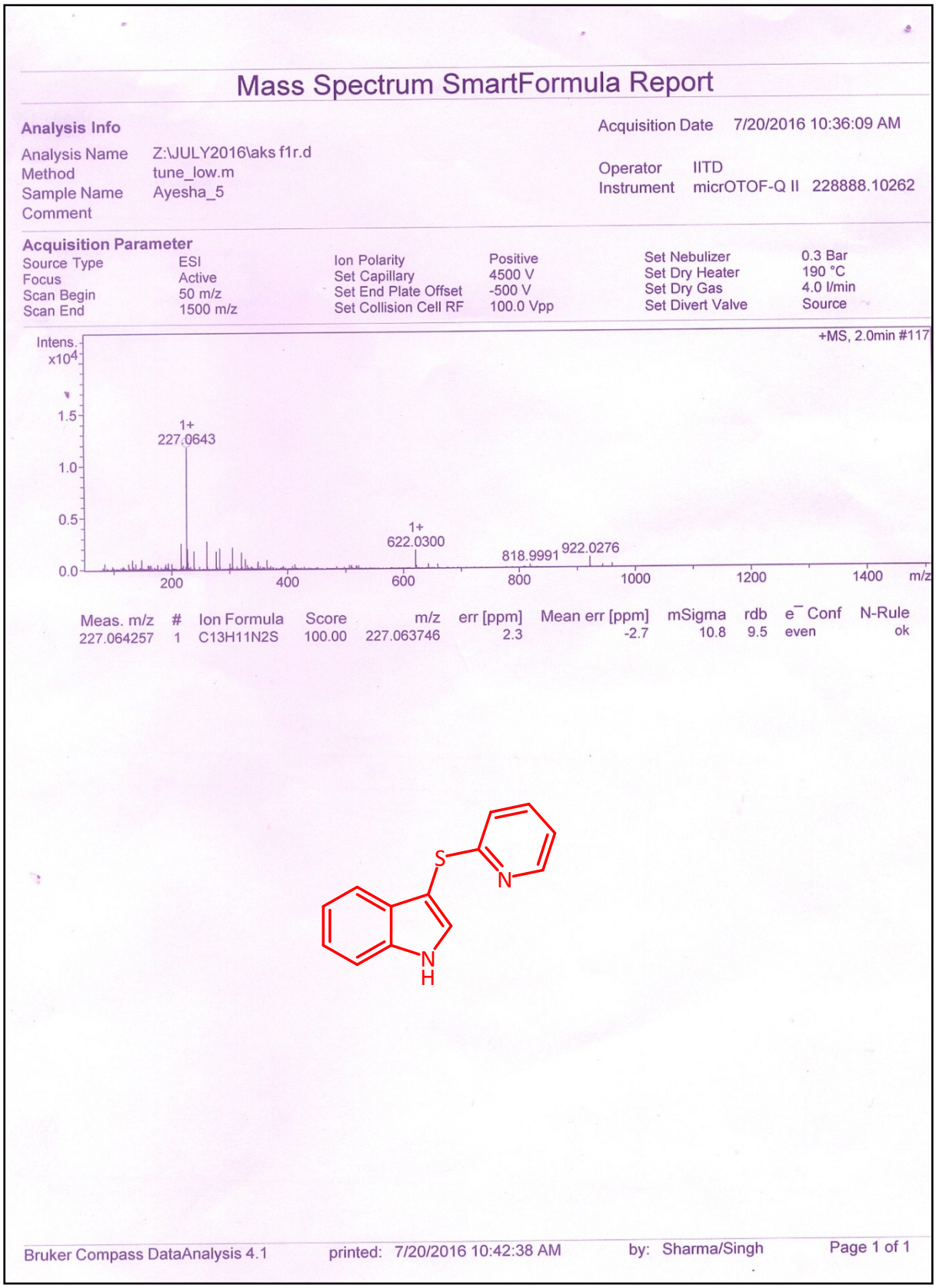


Figure S24. Mass spectrum of **L3**

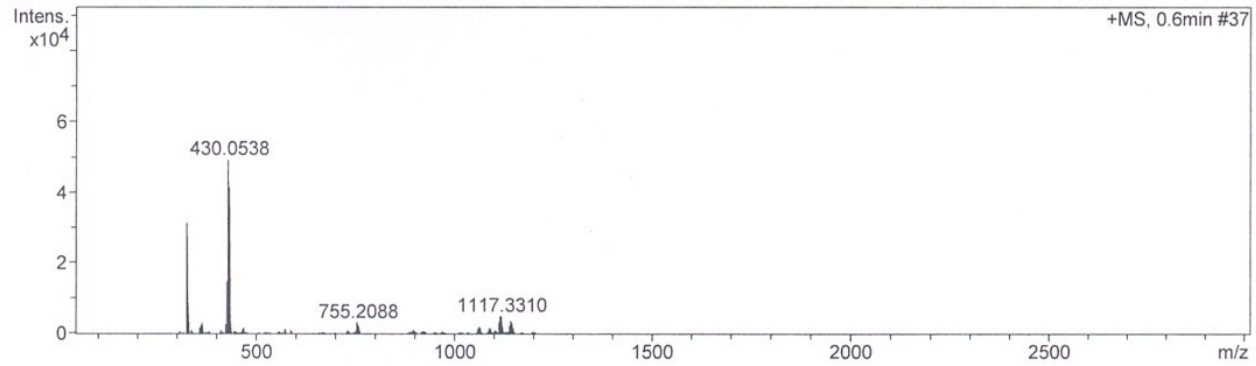
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\Feb_2014\RAM1.d	Acquisition Date	2/13/2014 12:15:45 PM
Method	tune_wide.m	Operator	Sharma/Singh
Sample Name	TM 1:100	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	600.0 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 Var Norm	Std m/z Diff	Std Comb Dev
430.0538	1	C 22 H 18 N 3 Pd	430.0539	0.2	3.3	15.5	ok	even	33.8	28.9	1.9	6.5	2.1	842.7

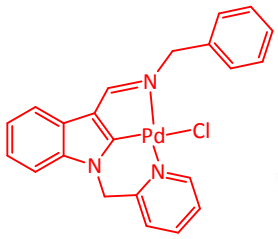


Figure S25. Mass spectrum of **1**

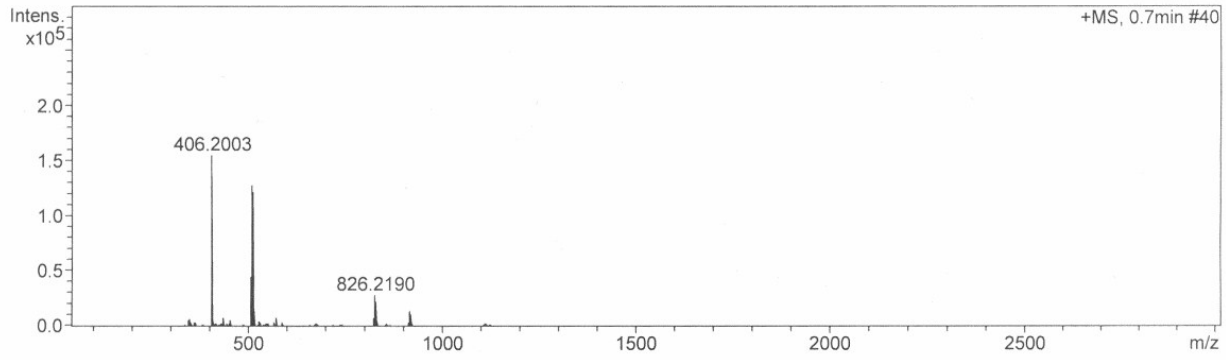
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\APRIL_2014\R2.d	Acquisition Date	4/29/2014 11:59:58 AM
Method	tune_wide.m	Operator	Sharma/Singh
Sample Name	TM 1:100	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	600.0 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 Var Norm	Std m/z Diff	Std Comb Dev
510.0887	1	C 26 H 22 N 5 Pd	510.0914	5.3	7.7	18.5	ok	even	67.7	34.6	4.1	6.2	1.8	842.7

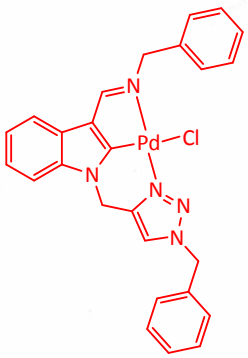


Figure S26. Mass spectrum of **2**

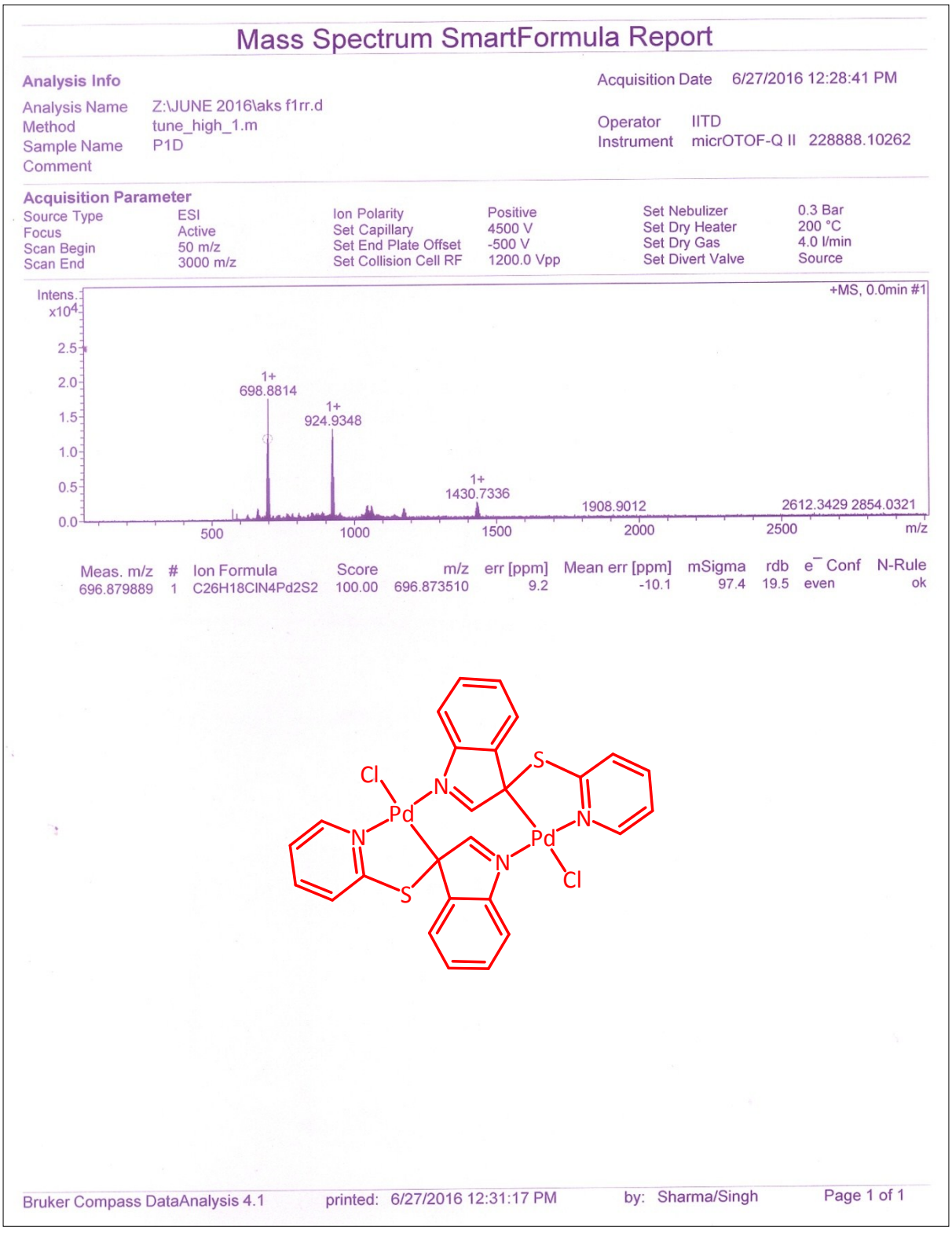


Figure S27. Mass spectrum of **3**