Supplementary Material

New symmetrical N^N^N palladium(II) pincer complexes: synthesis, characterization and catalytic evaluation in the Suzuki-Miyaura cross-coupling reaction

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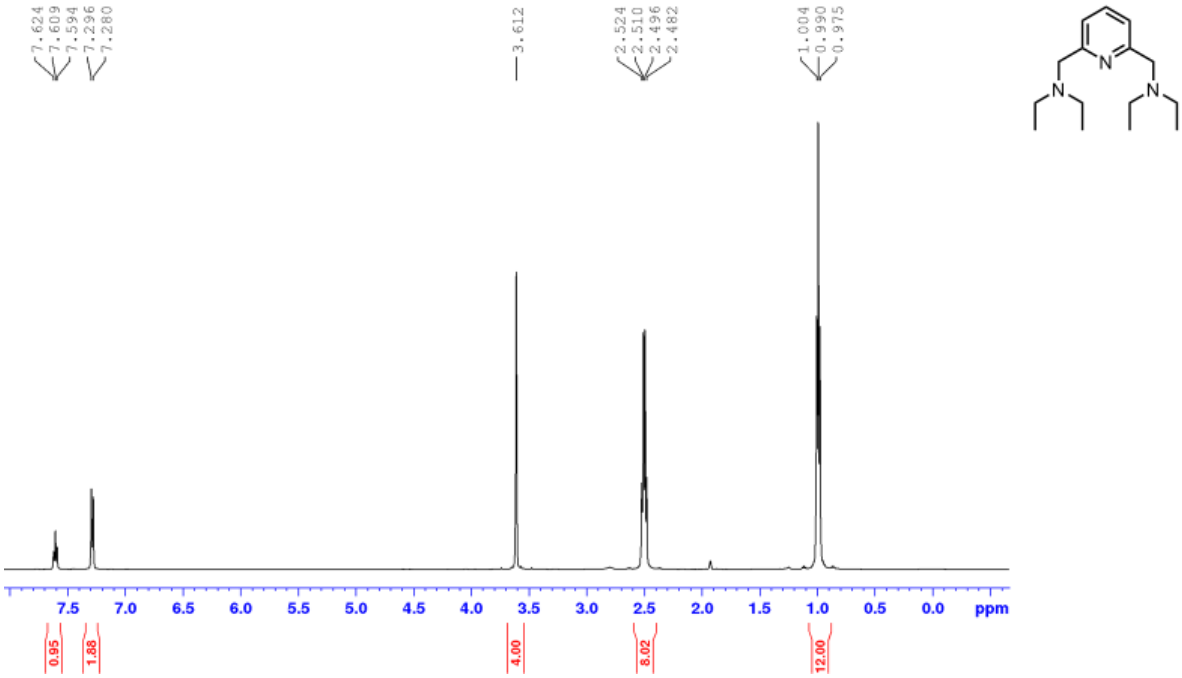


Figure A1: ^{1}H NMR of **10a** recorded in CD_3CN

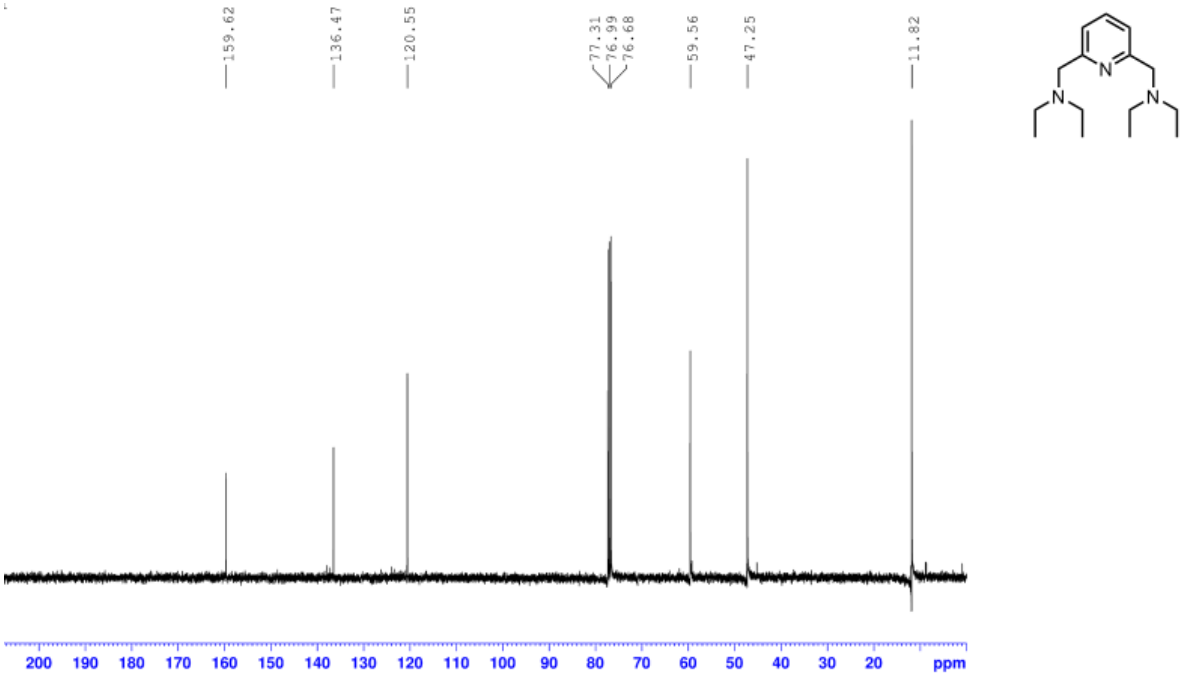


Figure A2: ^{13}C NMR of **10a** recorded in $CDCl_3$

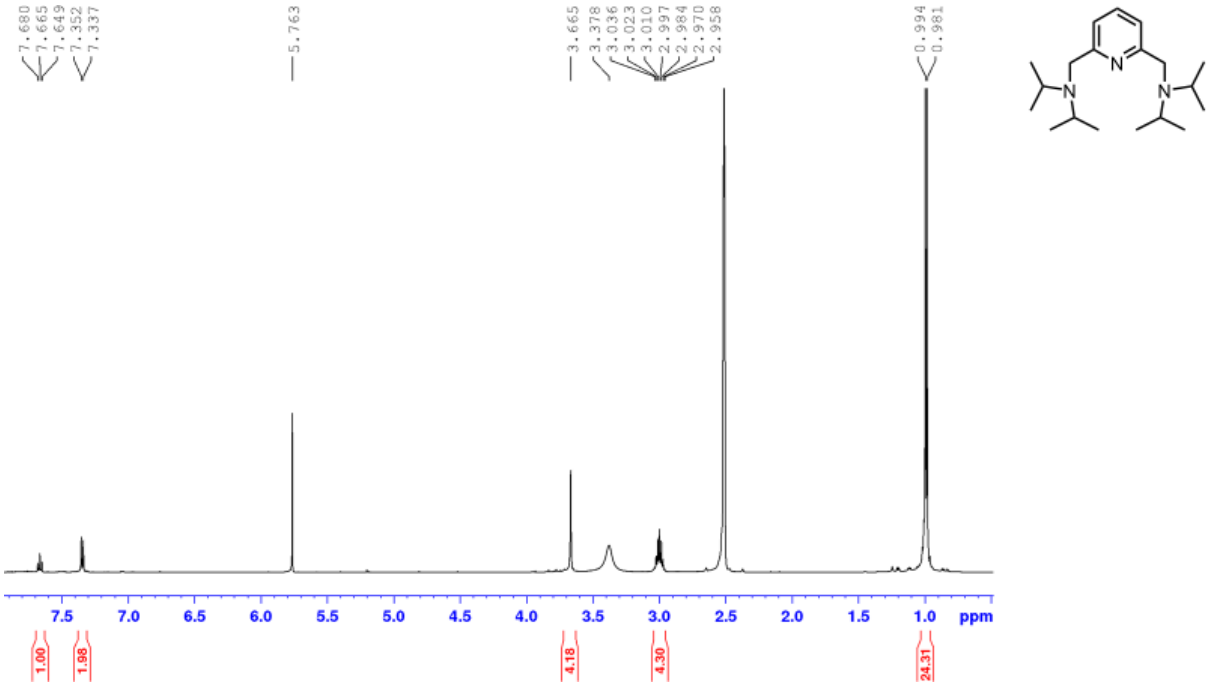


Figure A3: ^{1}H NMR of **10b** recorded in DMSO-d_6

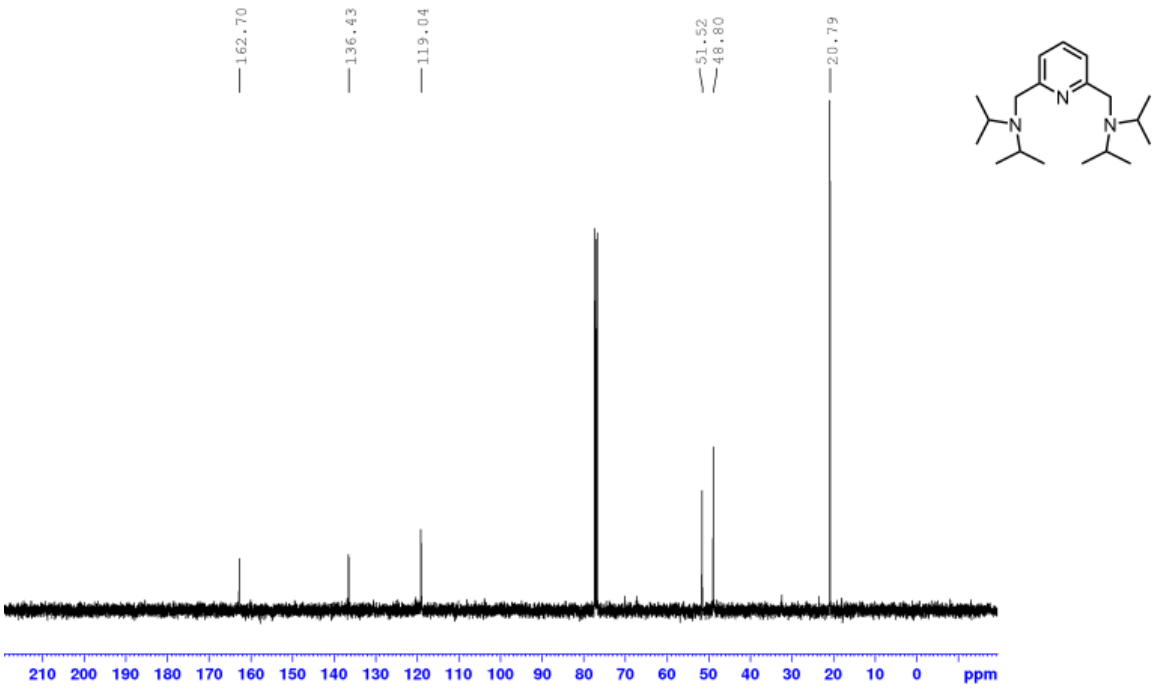


Figure A4: ^{13}C NMR of **10b** recorded in $CDCl_3$

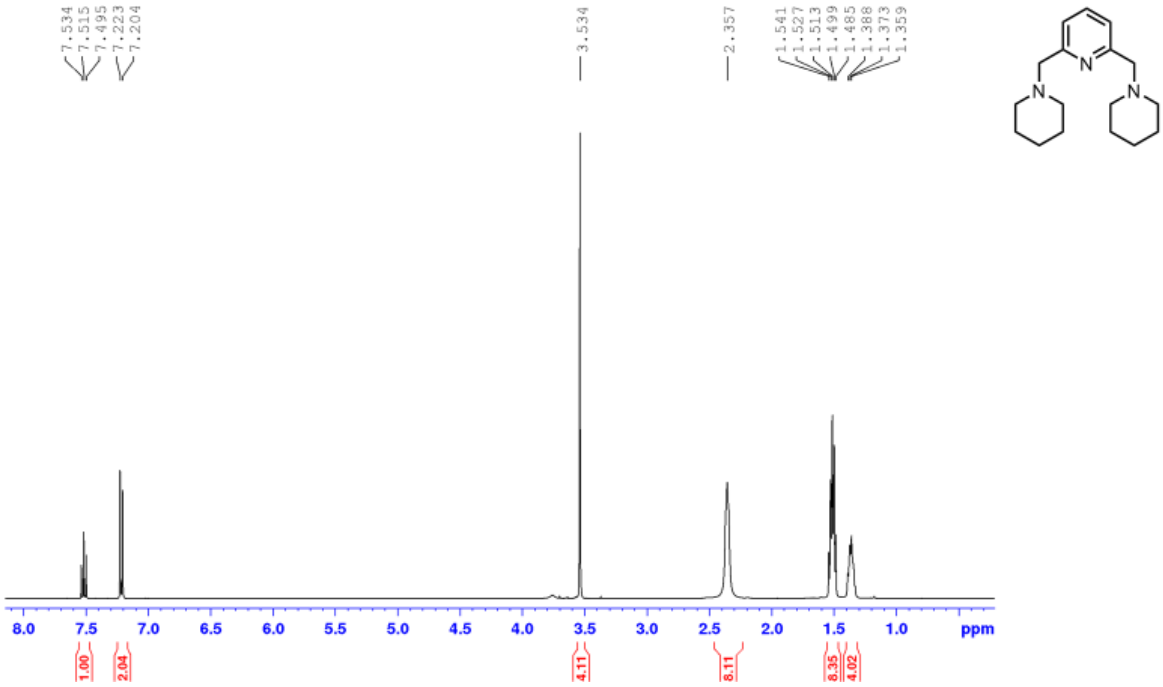


Figure A5: ^{1}H NMR of **10c** recorded in $CDCl_3$

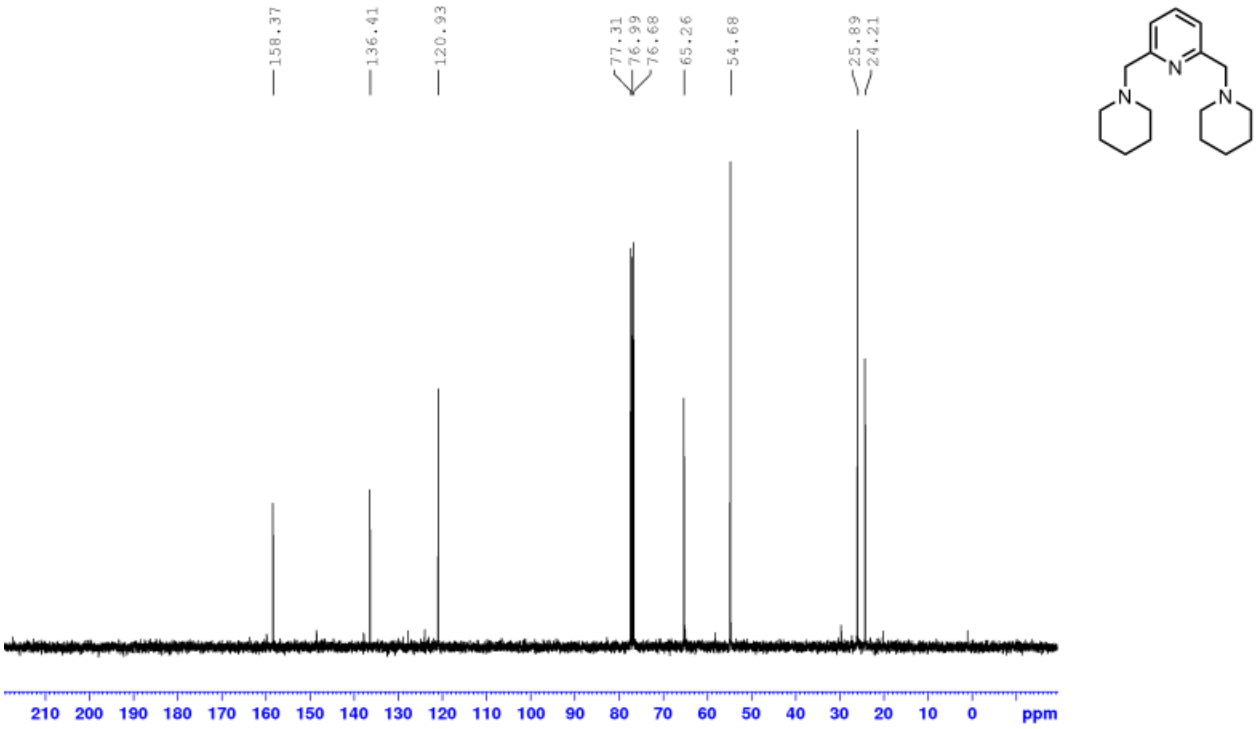


Figure A6: ^{13}C NMR of **10c** recorded in $CDCl_3$

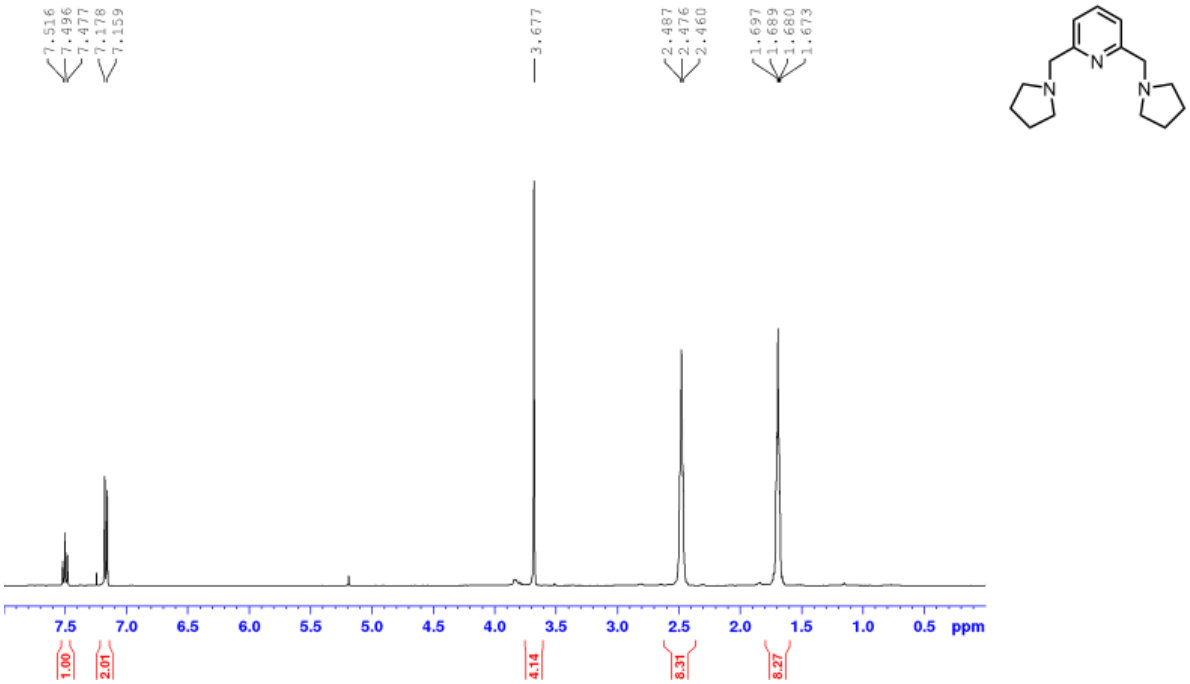


Figure A7: ^{1}H NMR of **10d** recorded in $CDCl_3$

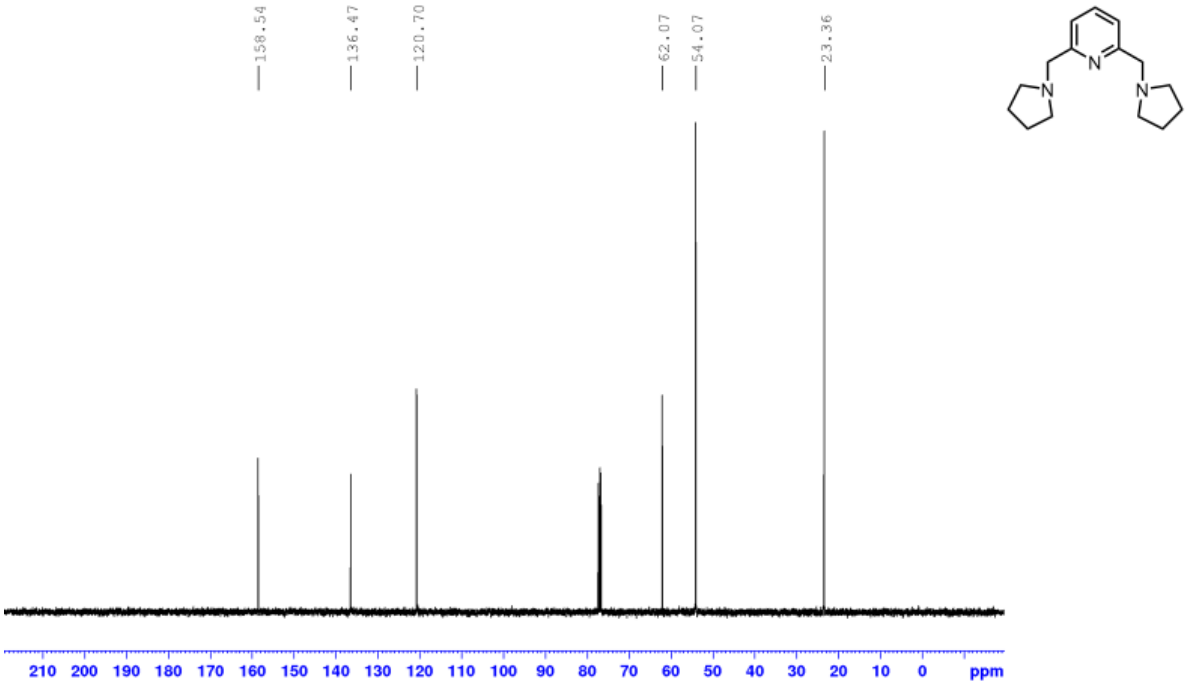


Figure A8: ^{13}C NMR of **10d** recorded in $CDCl_3$

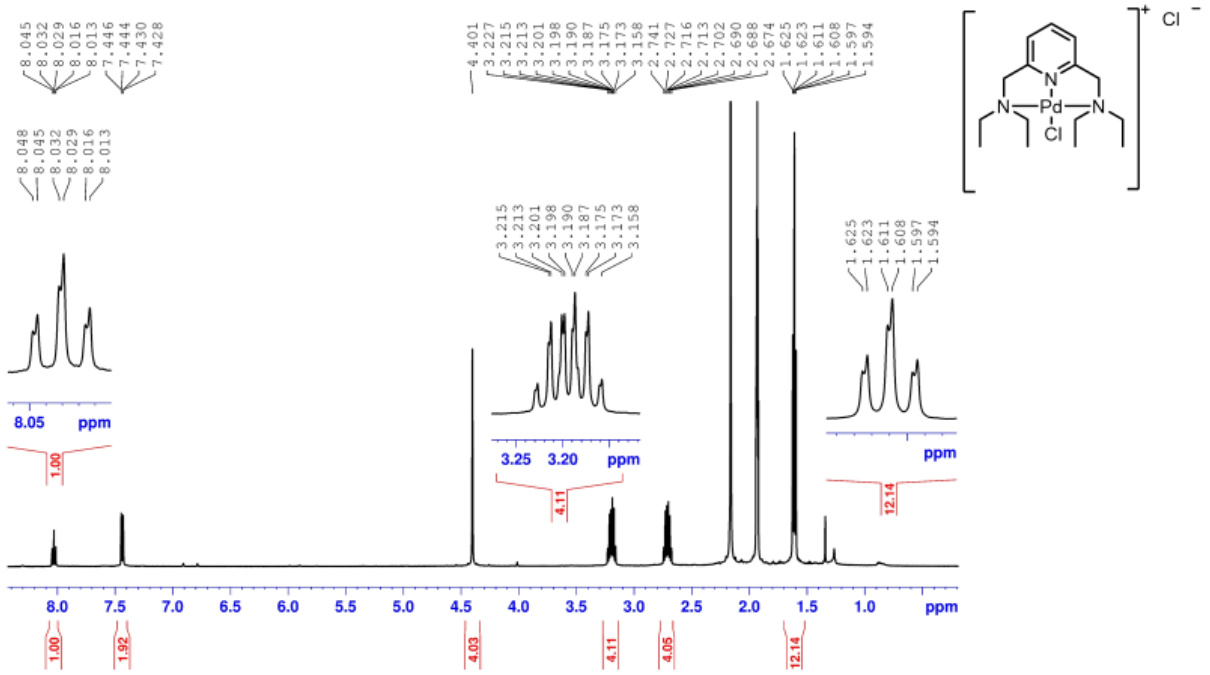


Figure A9: ^{1}H NMR of **8a** recorded in CD_3CN

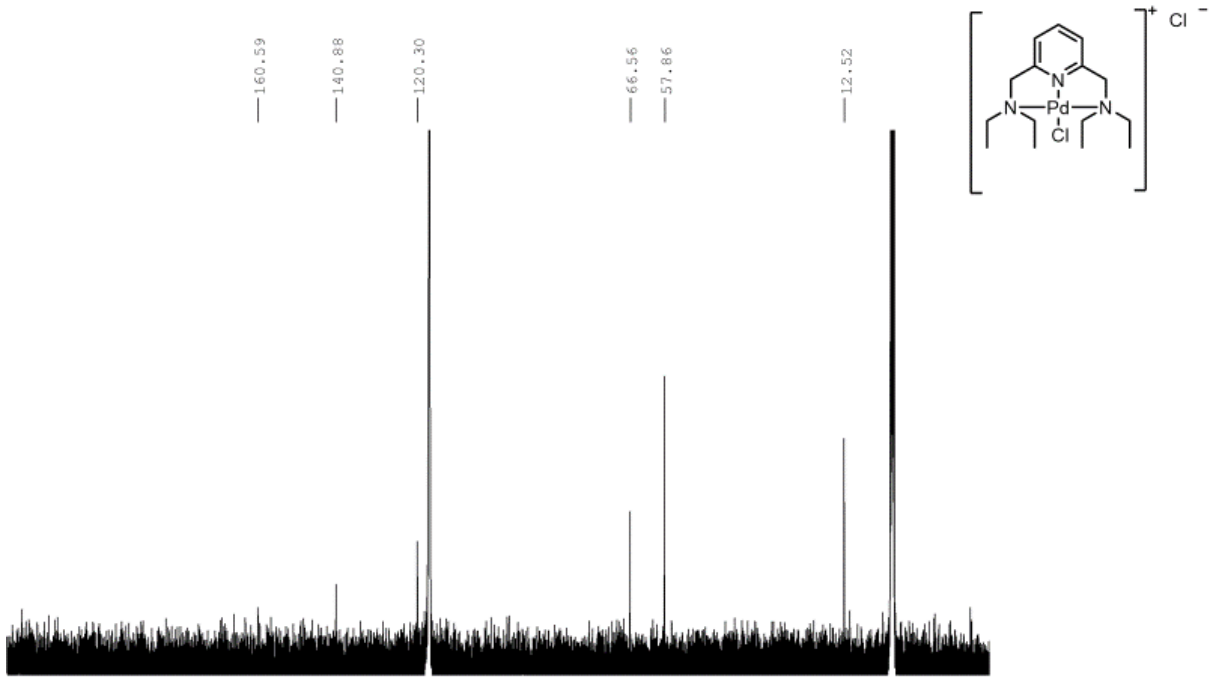


Figure A10: ^{13}C NMR of **8a** recorded in CD_3CN

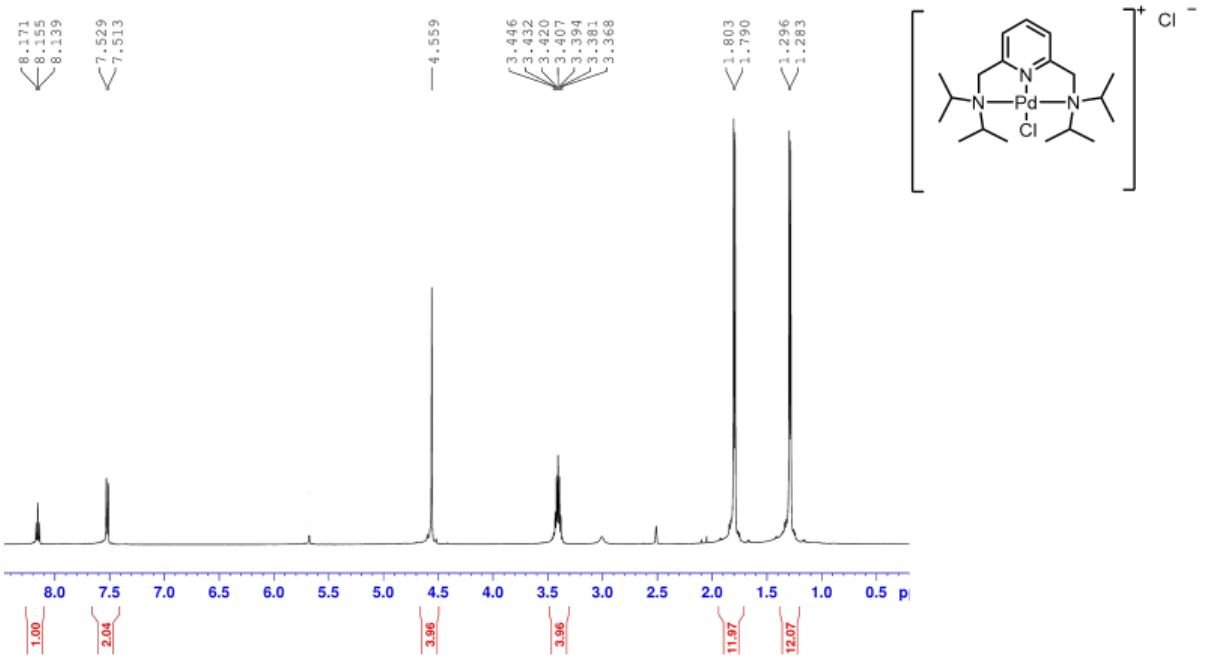


Figure A11: ^{1}H NMR of **8b** recorded in DMSO-d_6

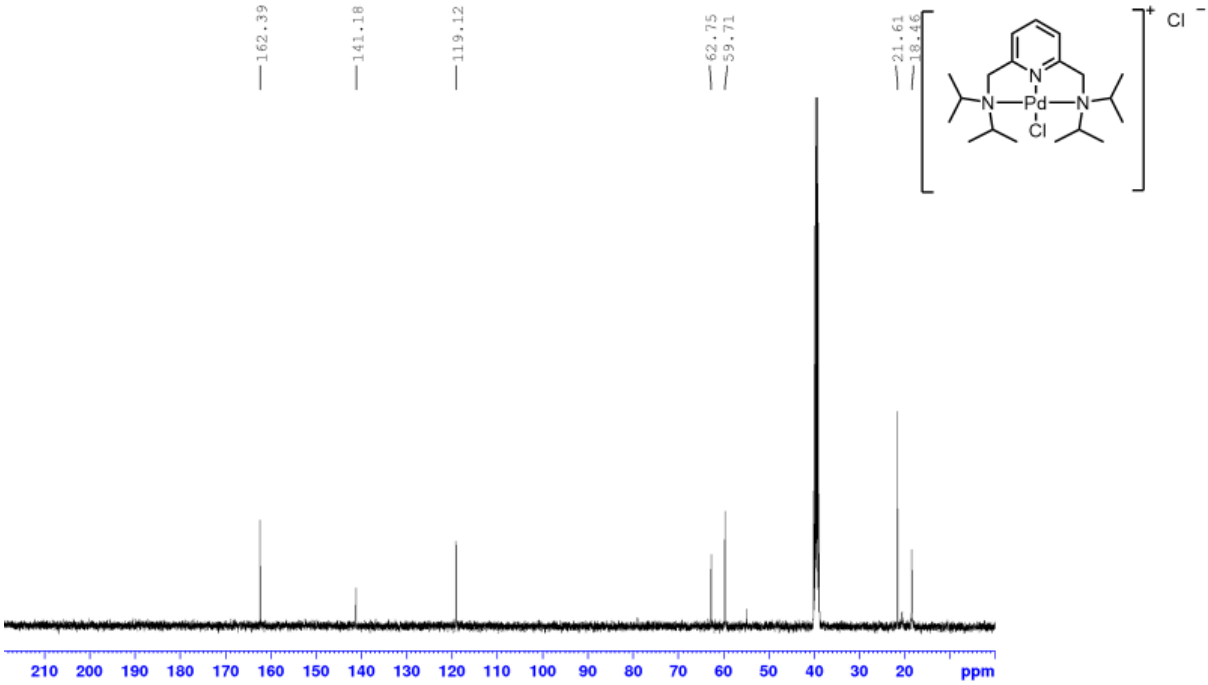


Figure A12: ^{13}C NMR of **8b** recorded in DMSO-d_6

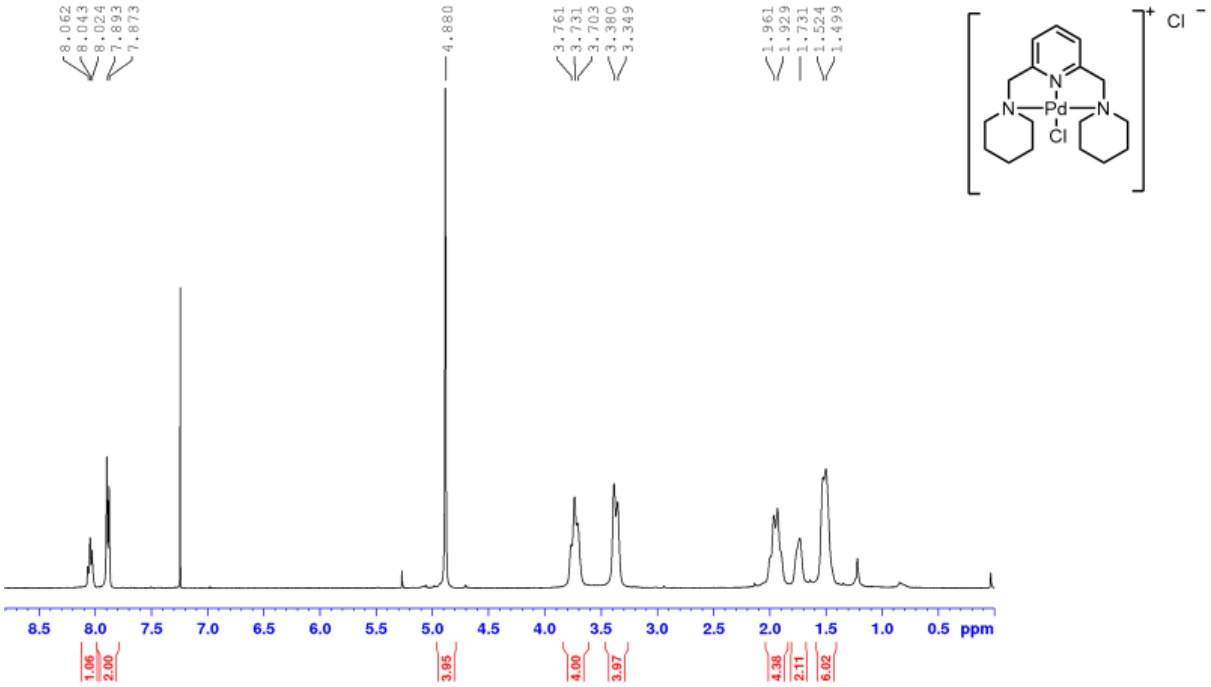


Figure A13: ^{1}H NMR of **8c** recorded in $CDCl_3$

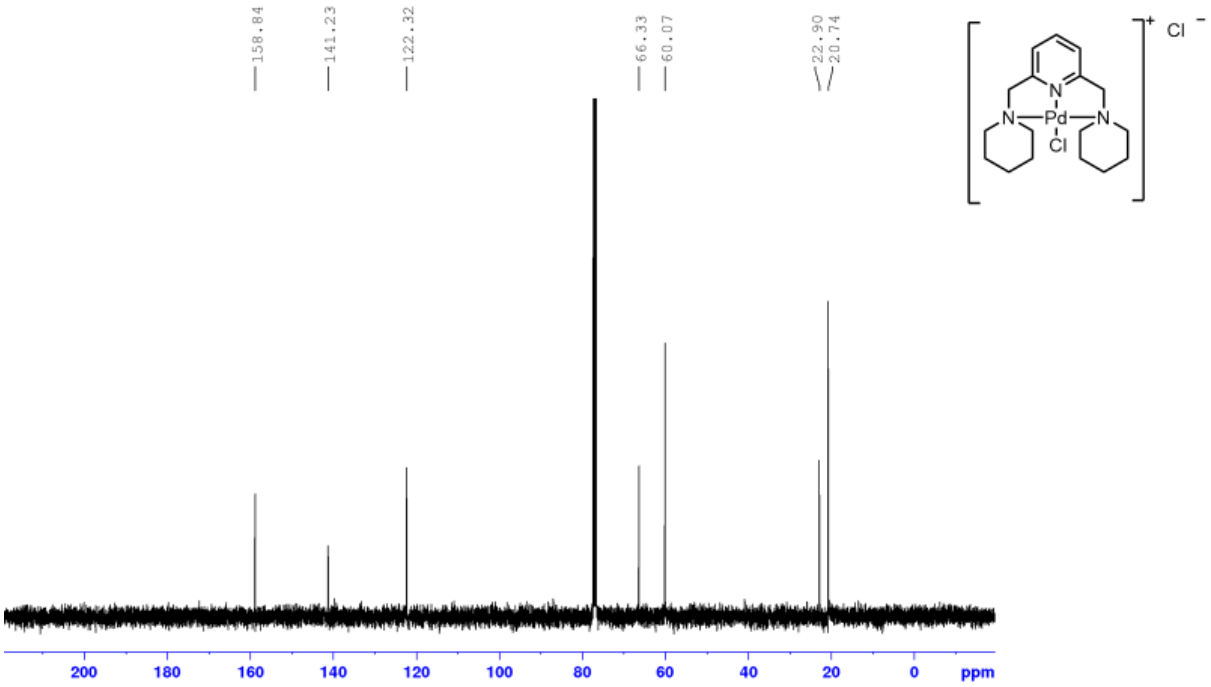


Figure A14: ^{13}C NMR of **8c** recorded in $CDCl_3$

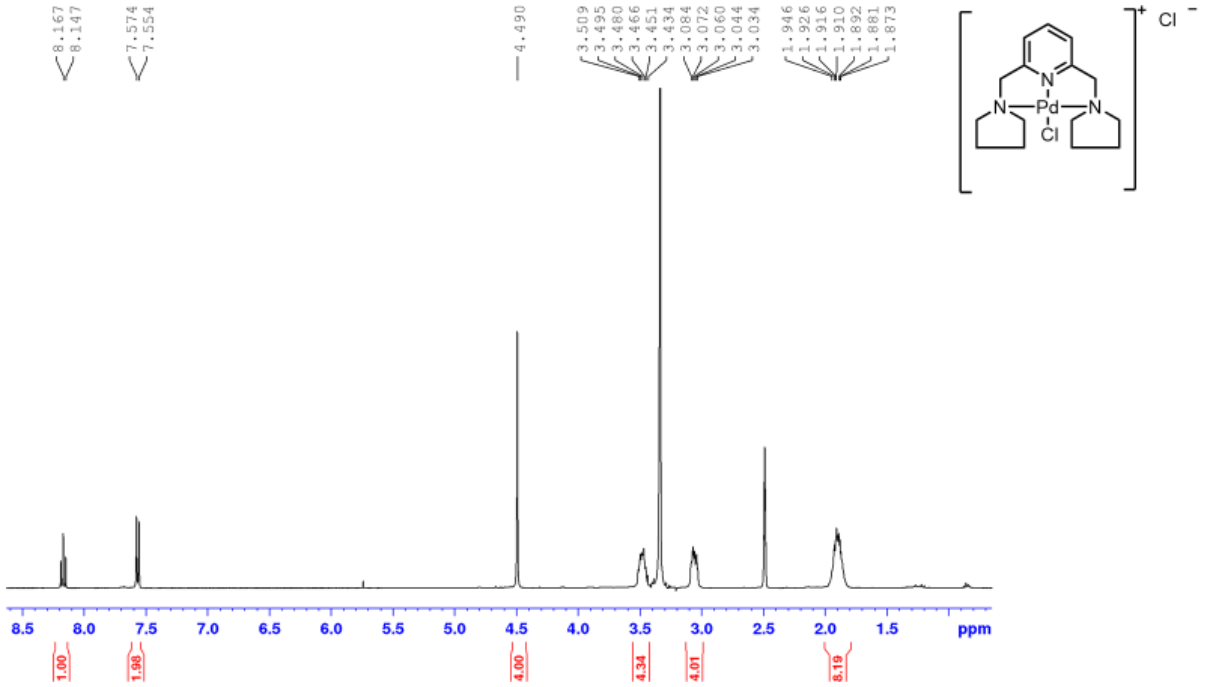


Figure A15: ^{1}H NMR of **8d** recorded in DMSO-d_6

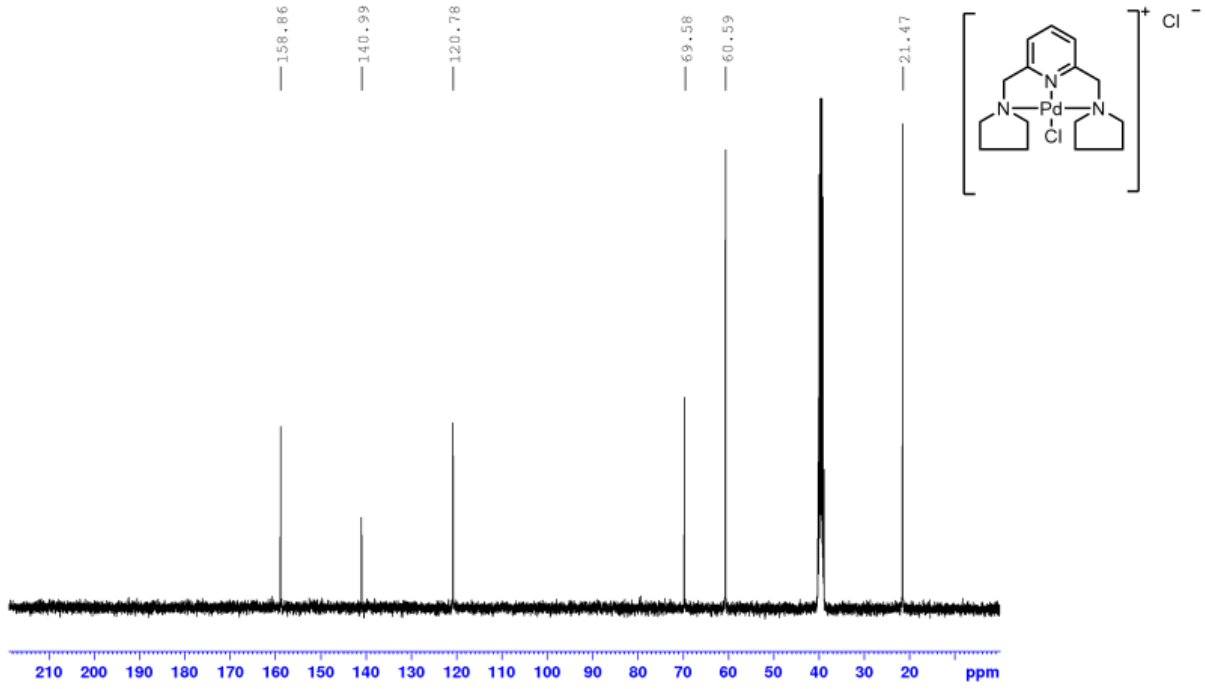


Figure A16: ^{13}C NMR of **8d** recorded in DMSO-d_6

S2 HRMS of the Complexes(8a- 8d)

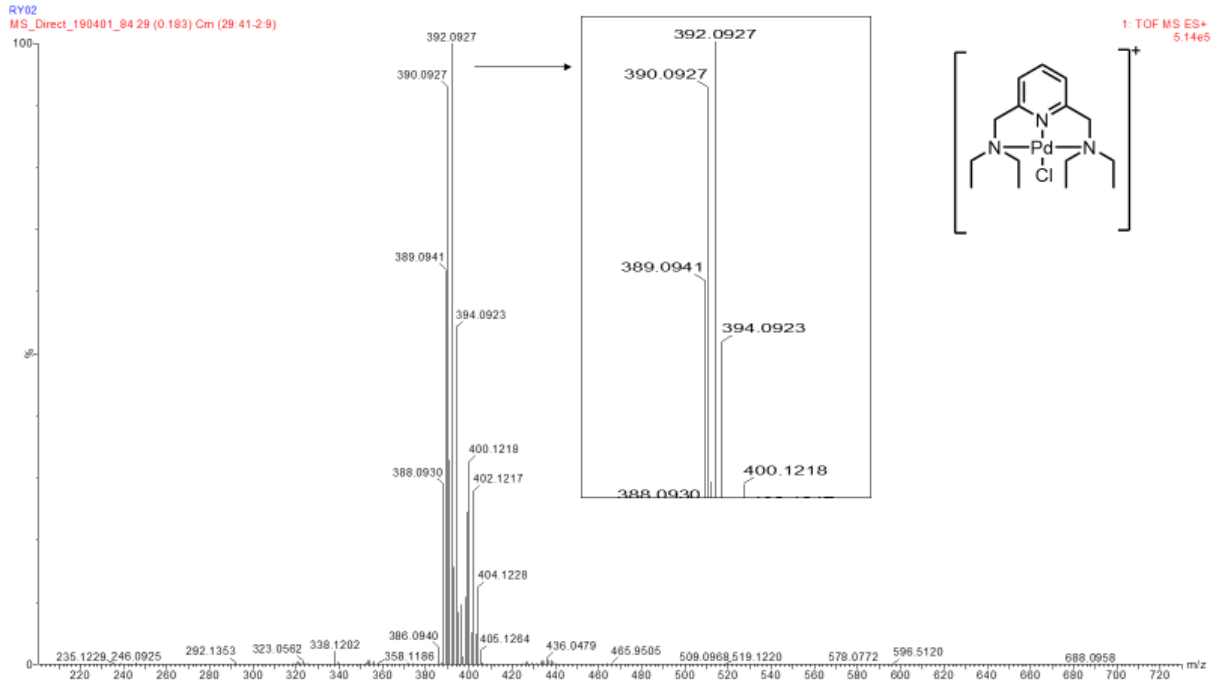


Figure A17: HR-MS (ESI+) of **8a**

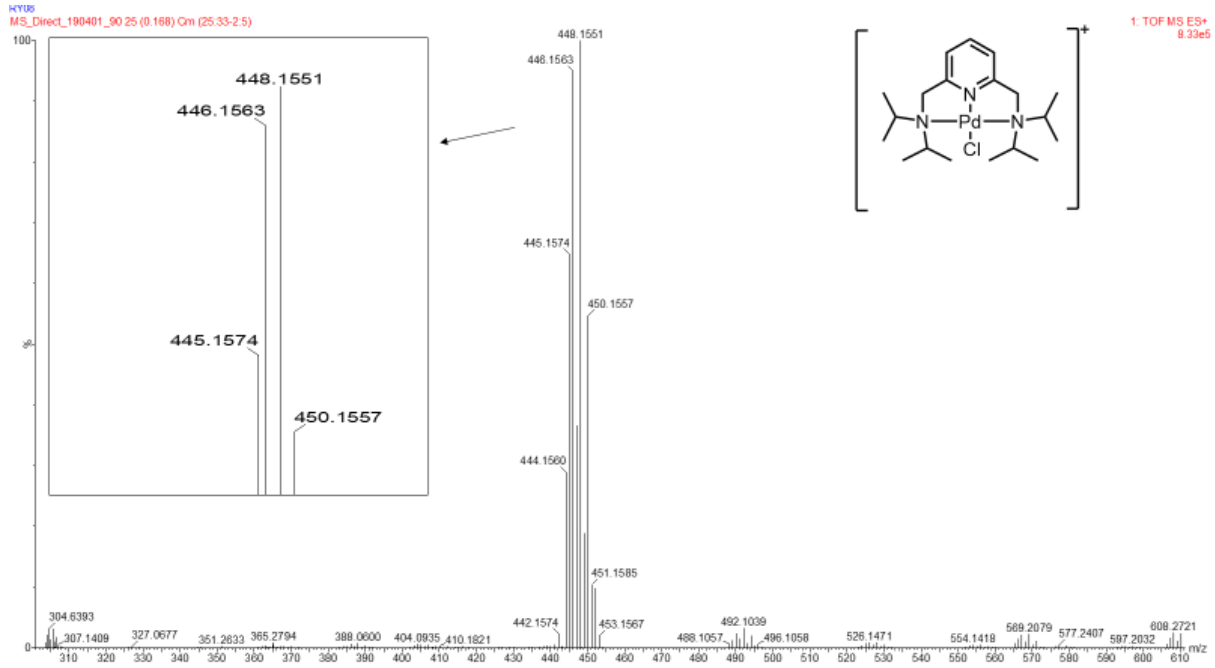


Figure A18: HR-MS (ESI+) of **8b**

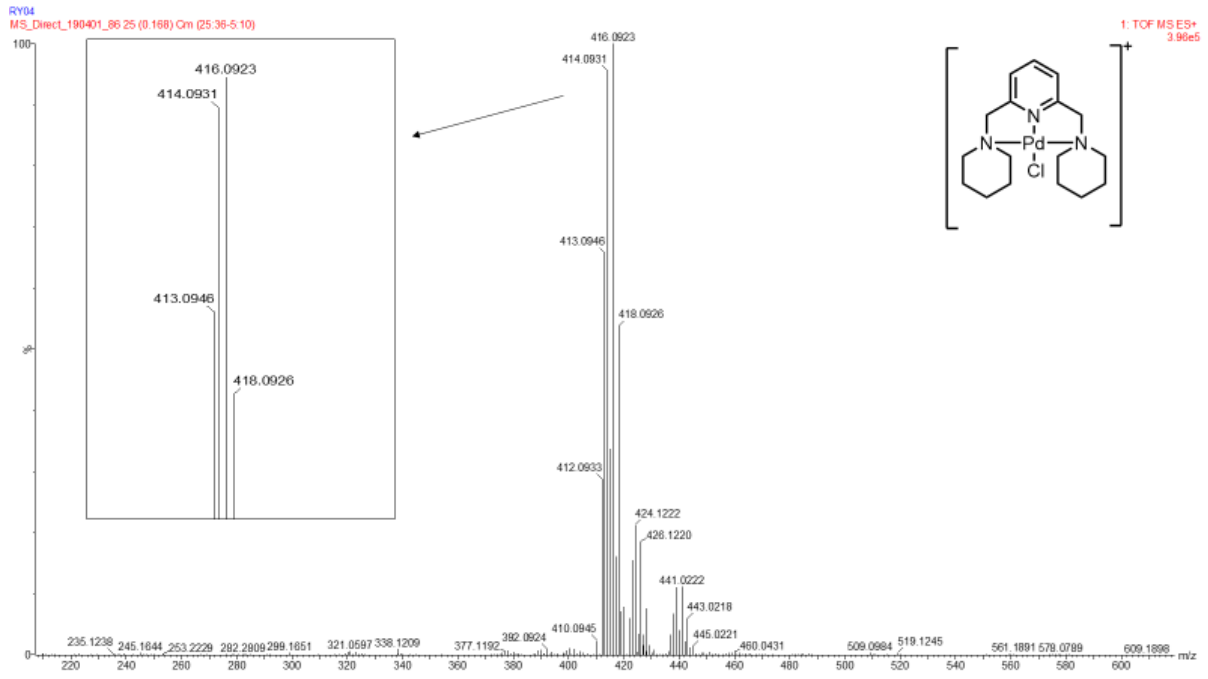


Figure A19: HR-MS (ESI+) of **8c**

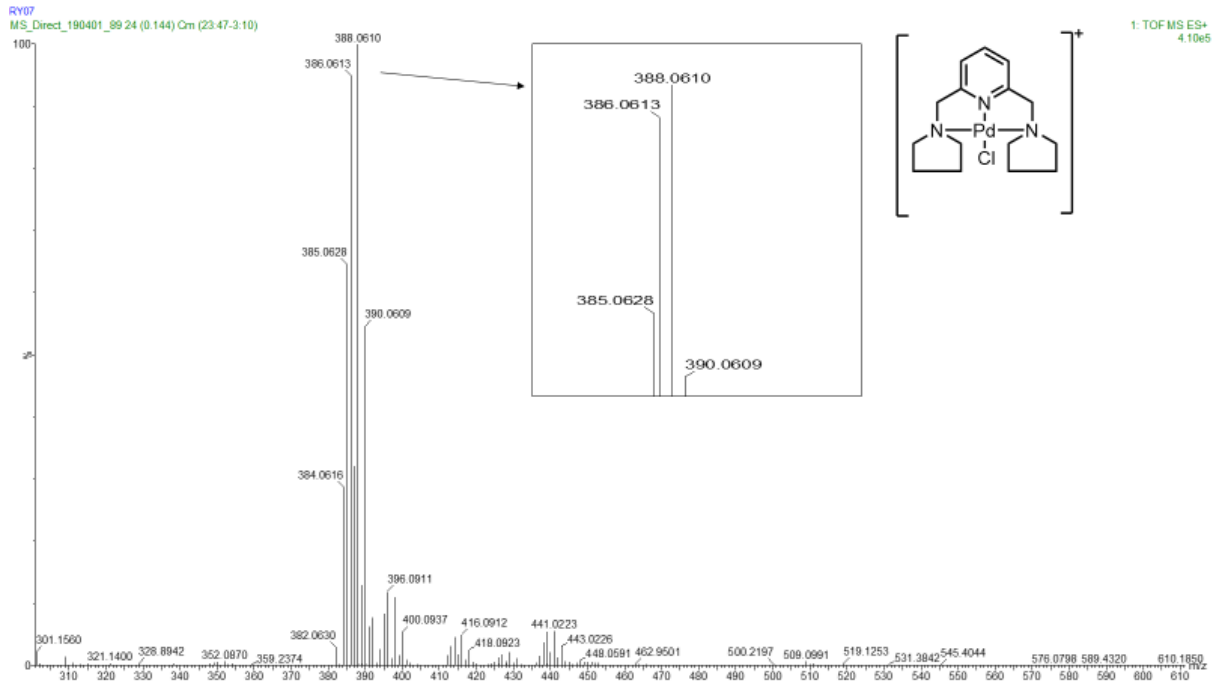


Figure A20: HR-MS (ESI+) of **8d**

S3 FT-IR of the Ligands (10a-10d) and Complexes(8a- 8d)

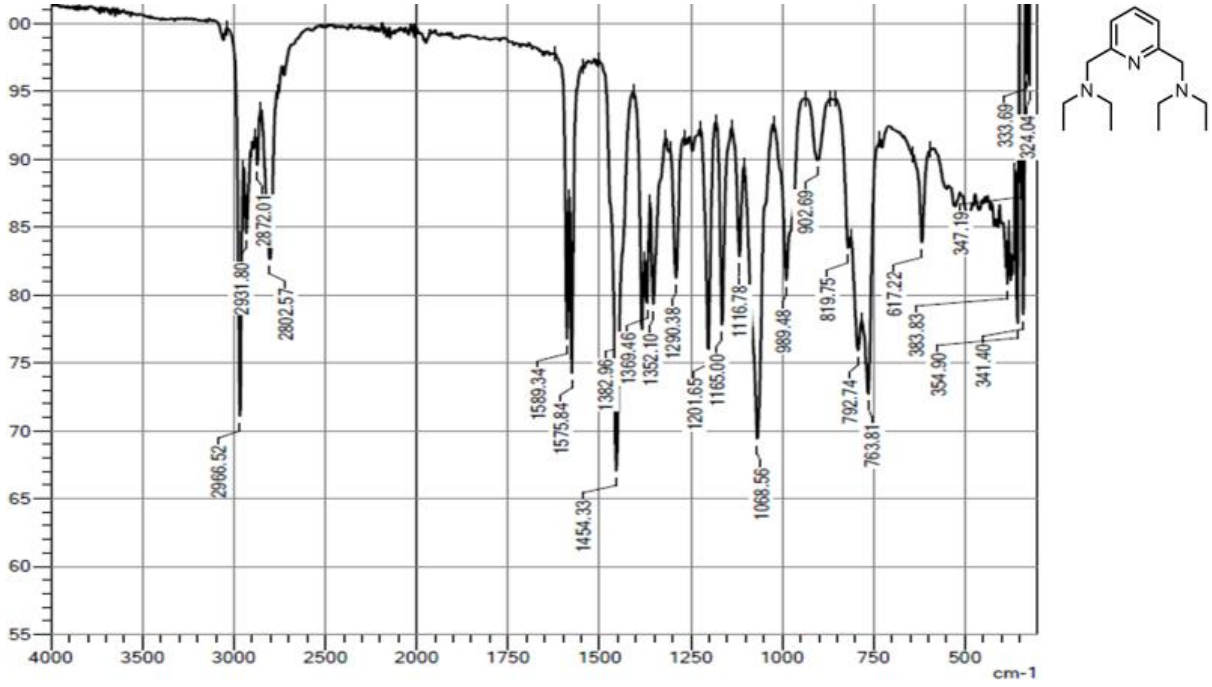


Figure A21: FT-IR of **10a**

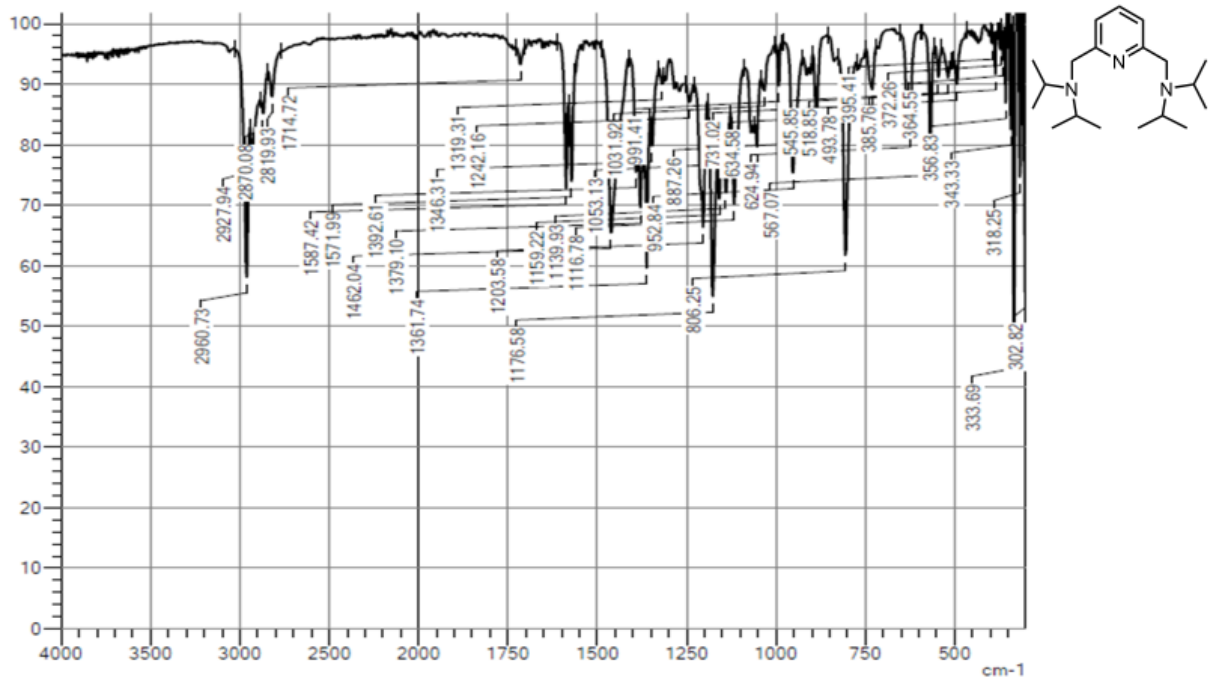


Figure A22: FT-IR of **10b**

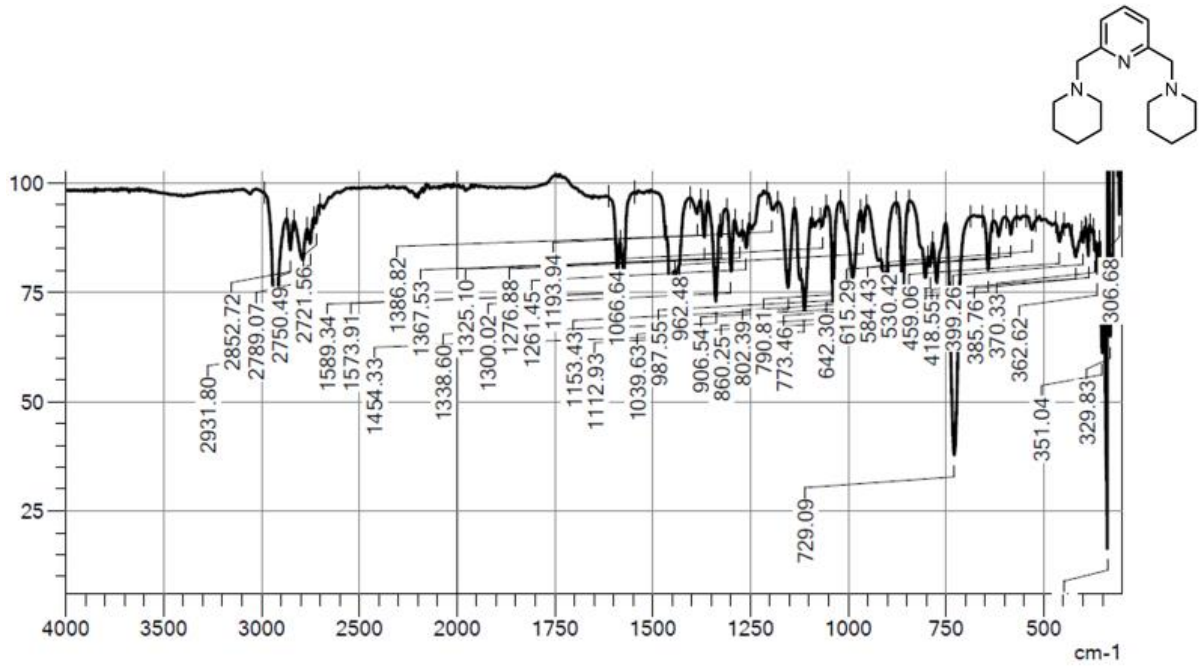


Figure A23: FT-IR of **10c**

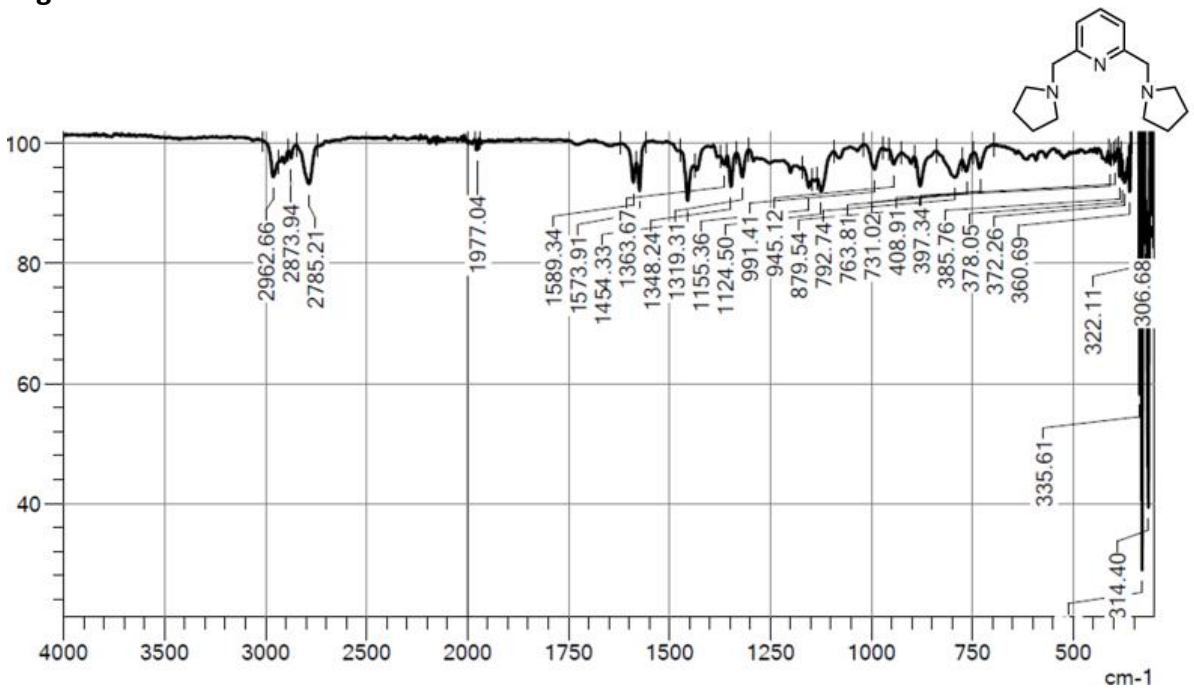


Figure A24: FT-IR of **10d**

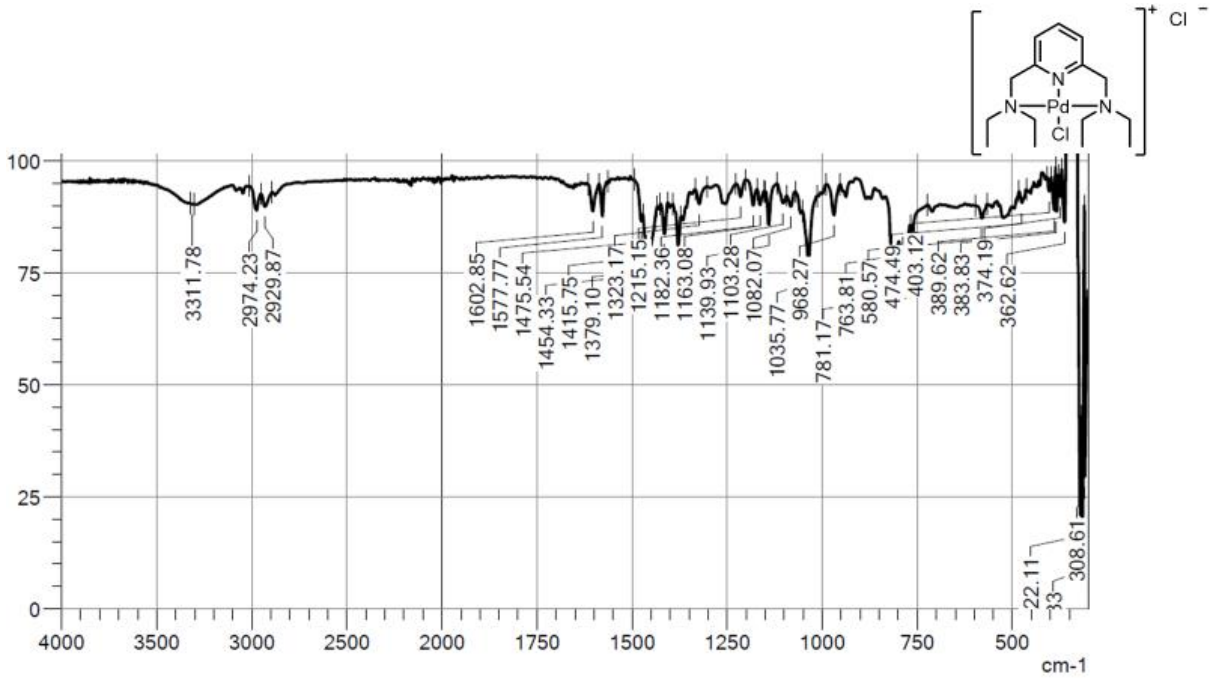


Figure A25: FT-IR of **8a**

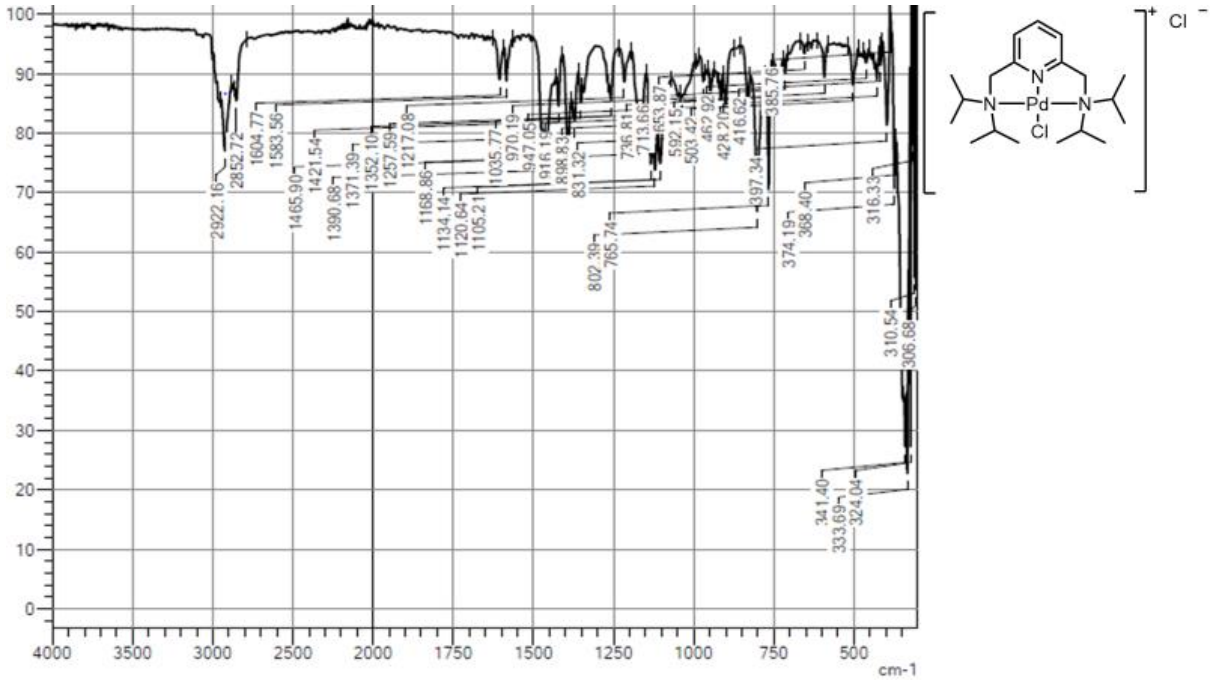


Figure A26: FT-IR of **8b**

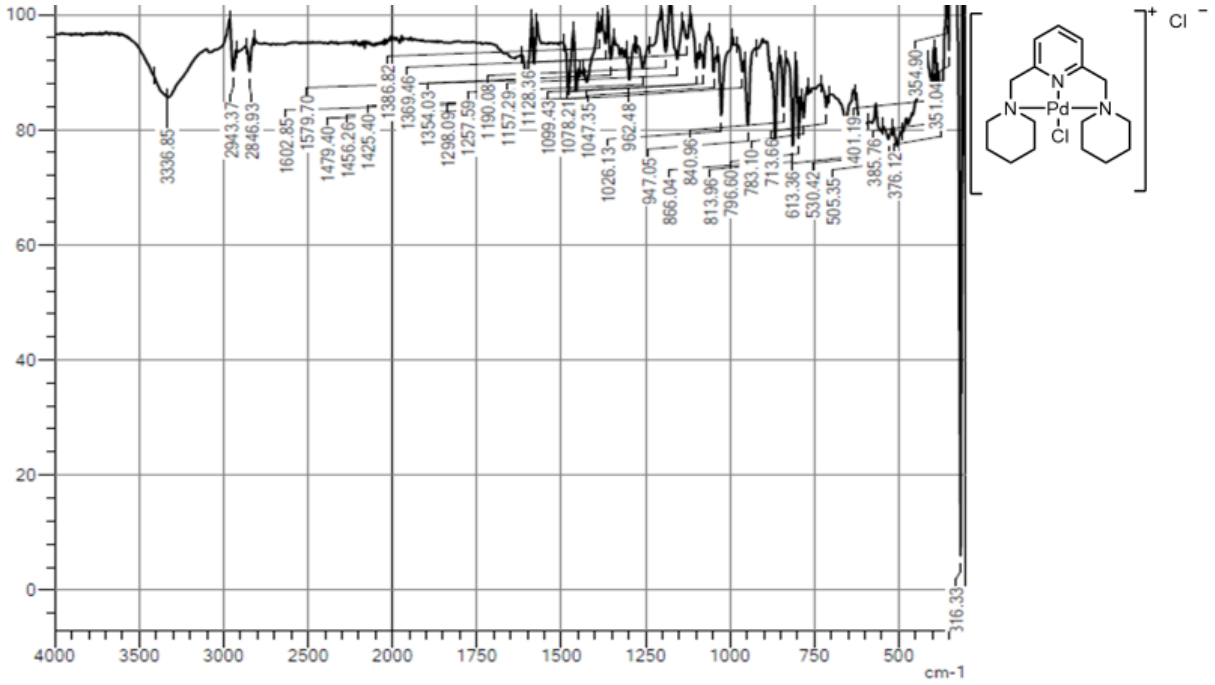


Figure A27: FT-IR of **8c**

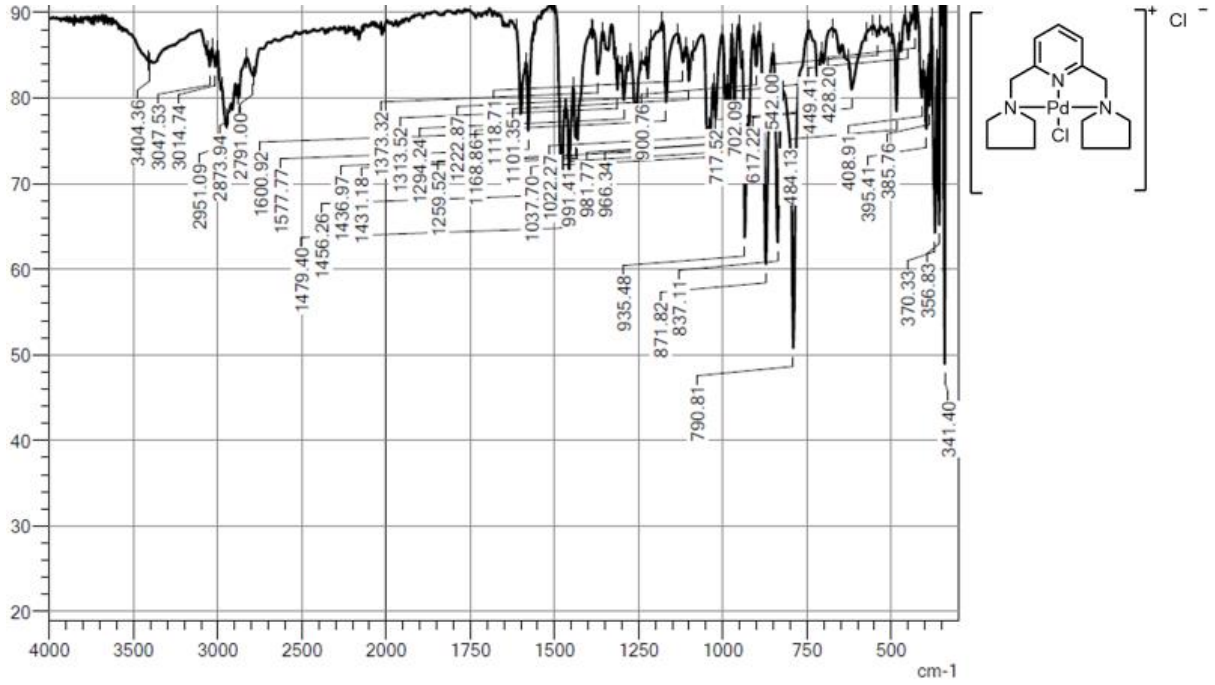


Figure A28: FT-IR of **8d**

S4 ^{1}H and ^{13}C NMR of the Coupling Products (13a-13o)

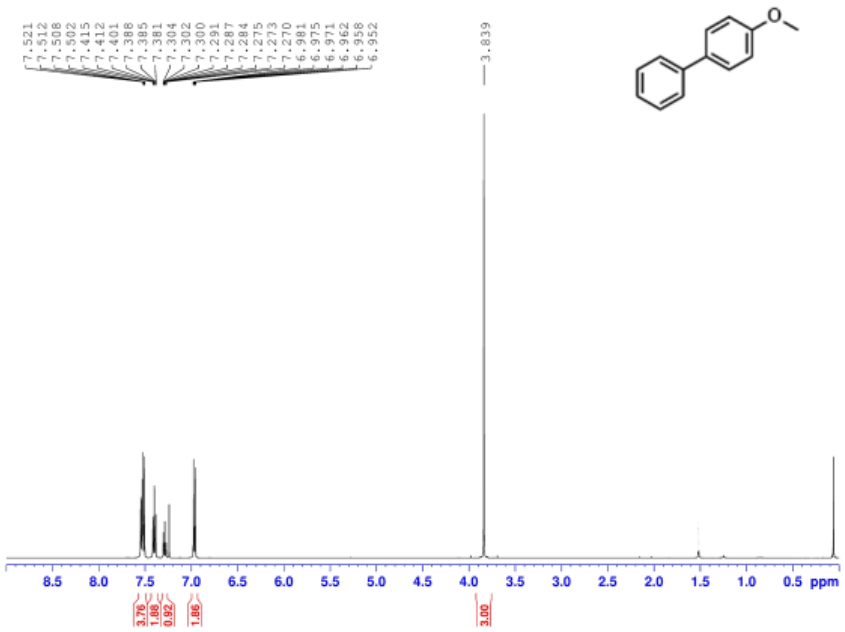


Figure A29: ^{1}H NMR of **13a** recorded in $CDCl_3$

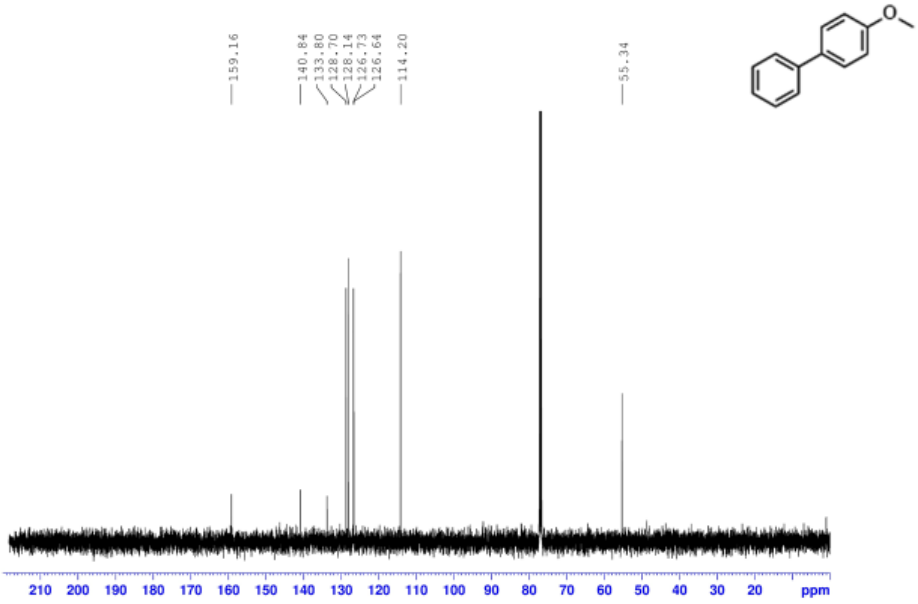


Figure A30: ^{13}C NMR of **13a** recorded in $CDCl_3$

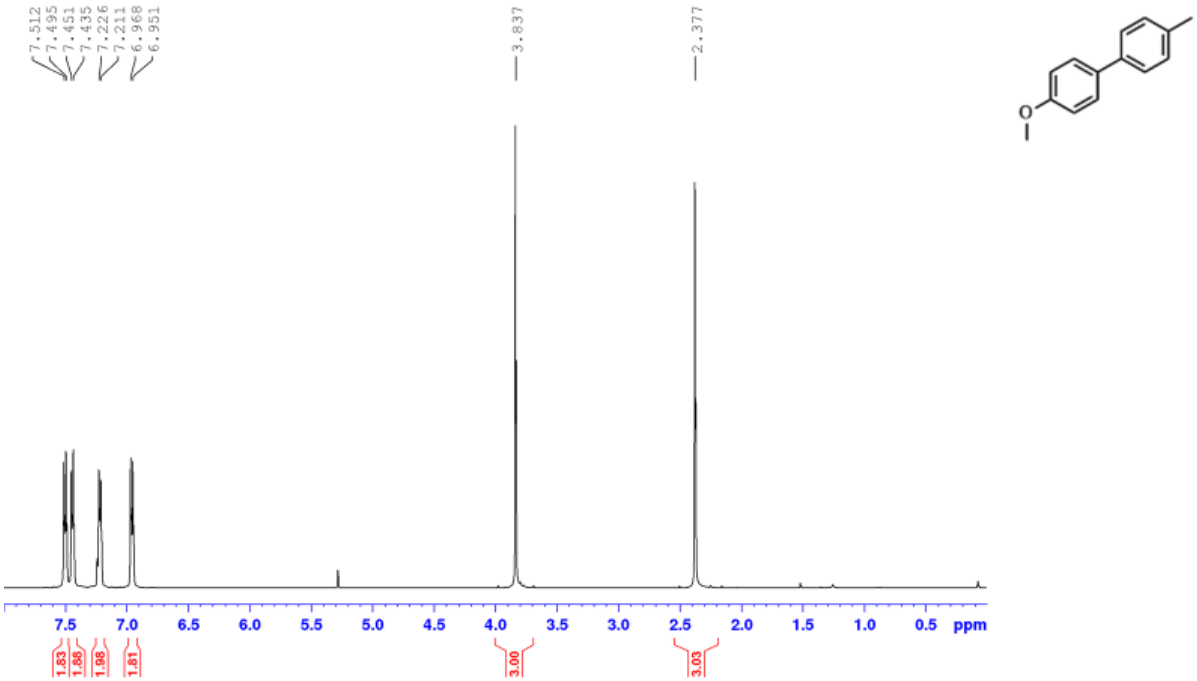


Figure A31: ^{1}H NMR of **13b** recorded in $CDCl_3$

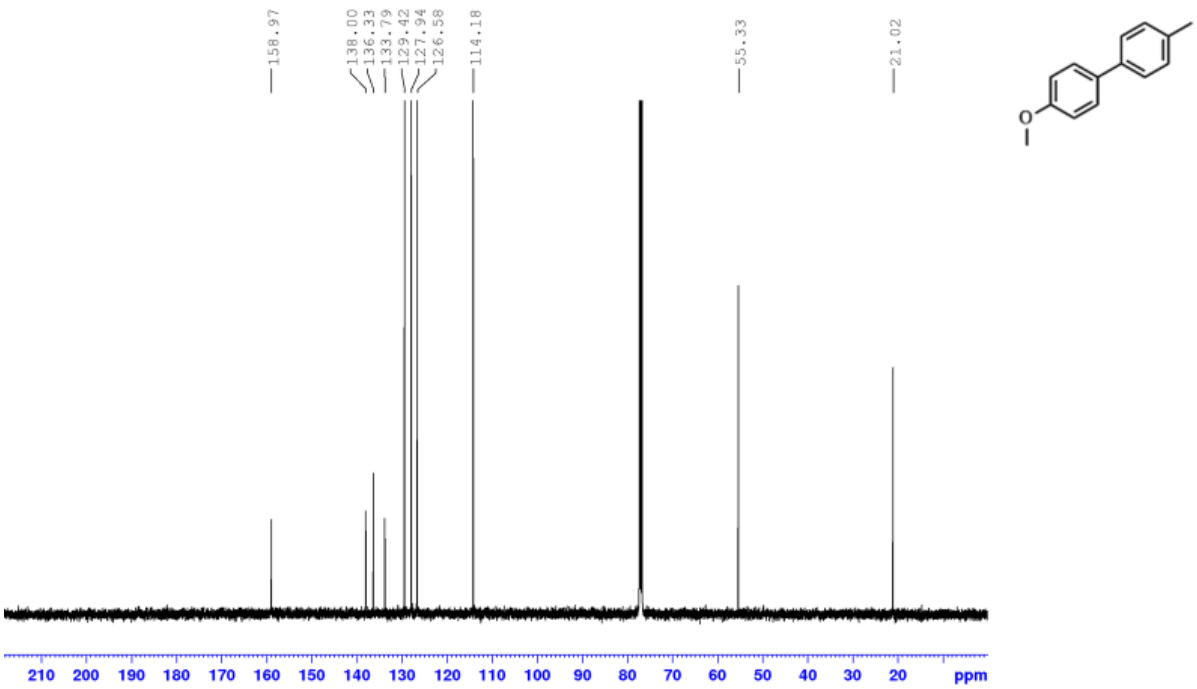


Figure A32: ^{13}C NMR of **13b** recorded in $CDCl_3$

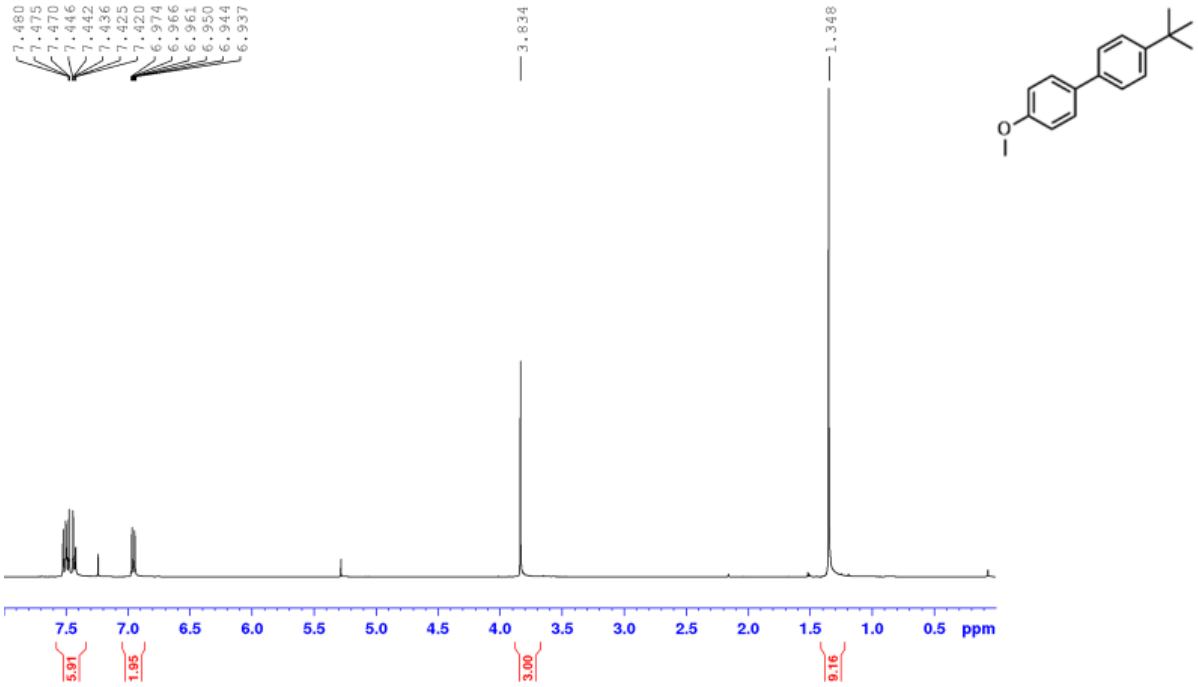


Figure A33: ^{1}H NMR of **13c** recorded in $CDCl_3$

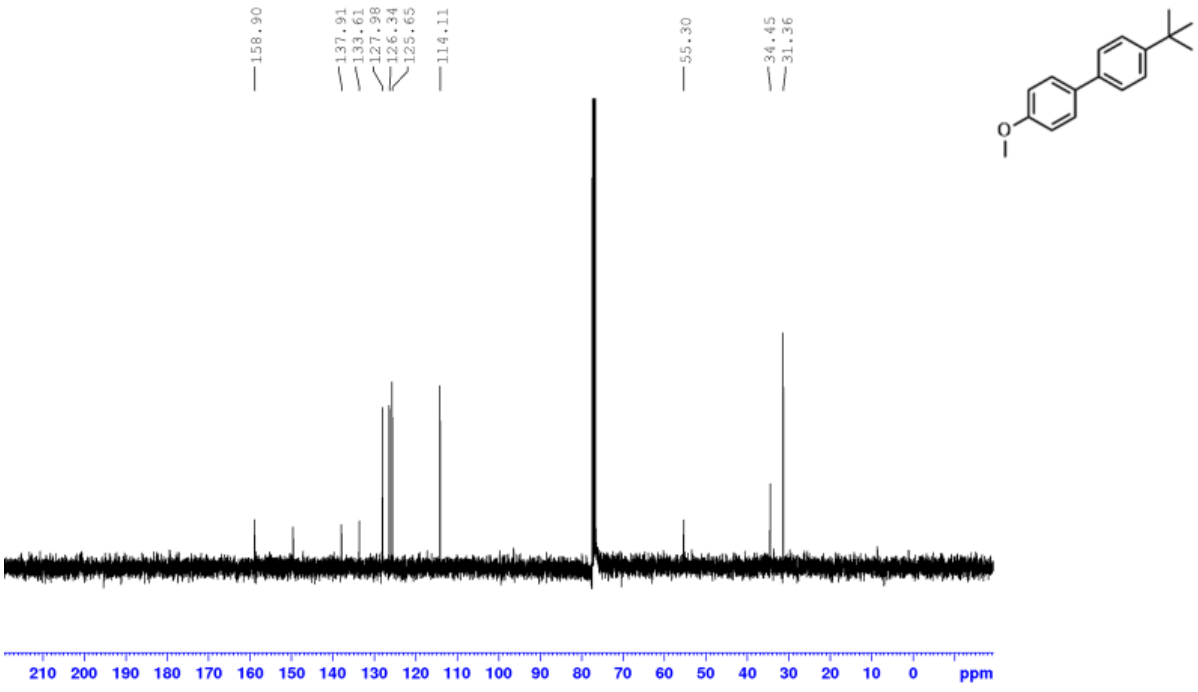


Figure A34: ^{13}C NMR of **13c** recorded in $CDCl_3$

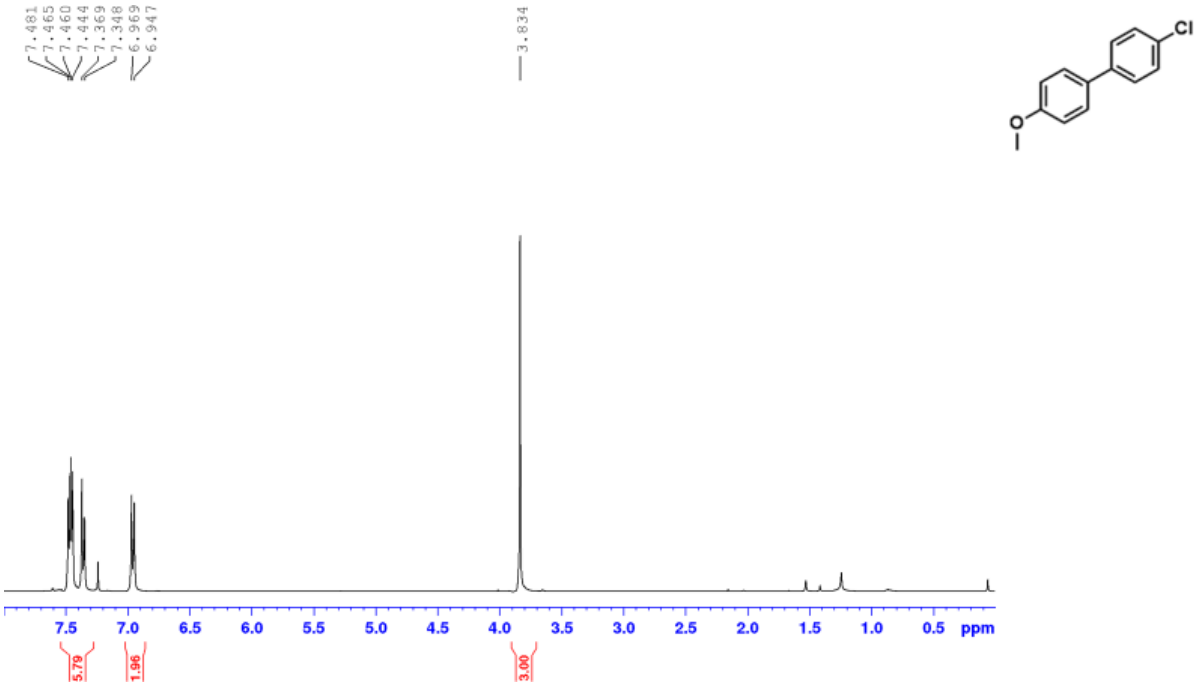


Figure A35: ^{1}H NMR of **13d** recorded in $CDCl_3$

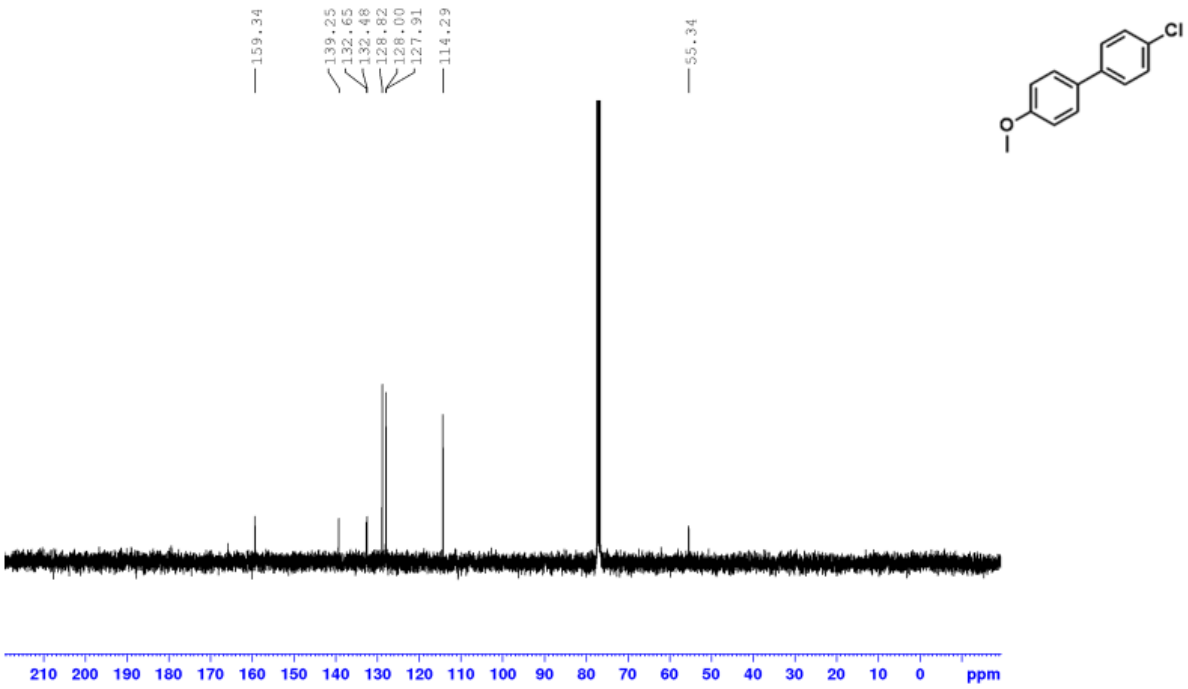


Figure A36: ^{13}C NMR of **13d** recorded in $CDCl_3$

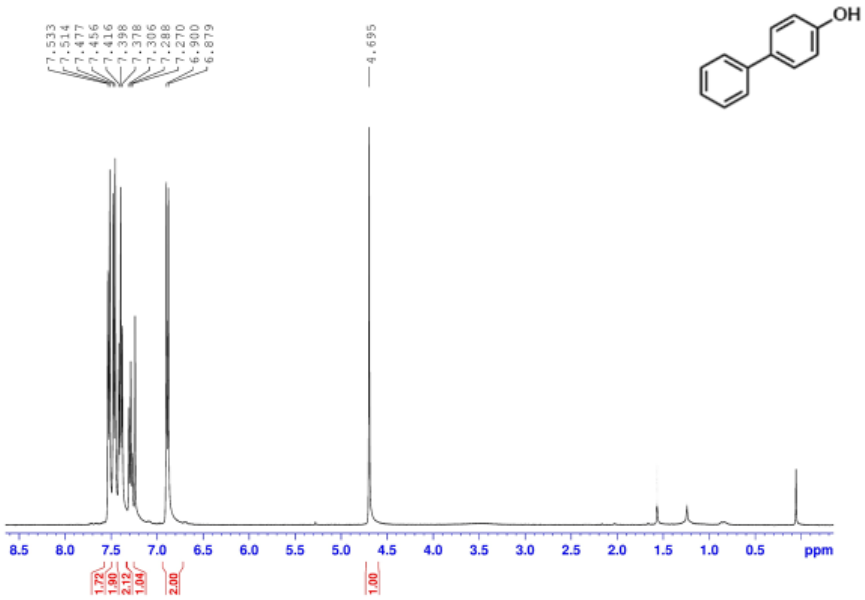


Figure A37: ^{1}H NMR of **13e** recorded in $CDCl_3$

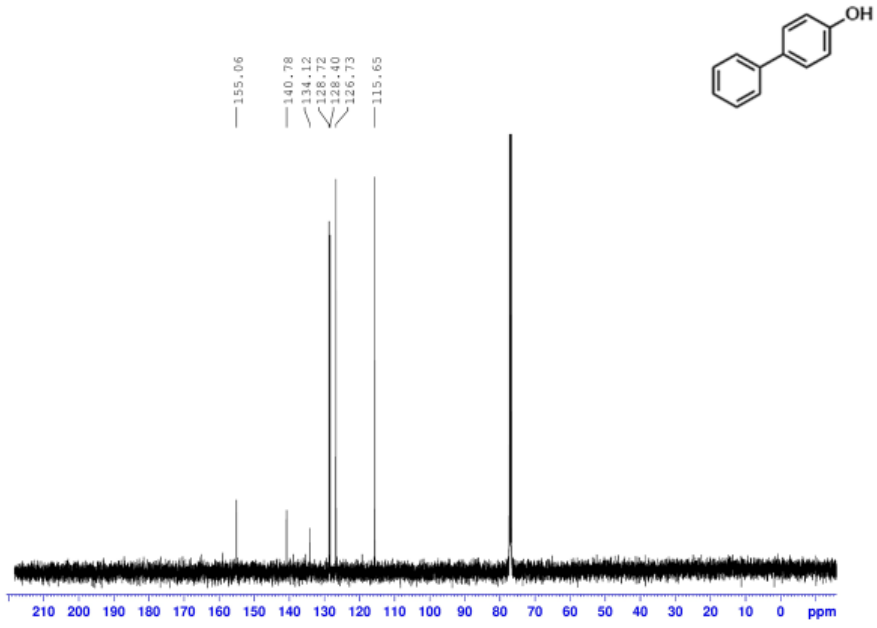


Figure A38: ^{13}C NMR of **13e** recorded in $CDCl_3$

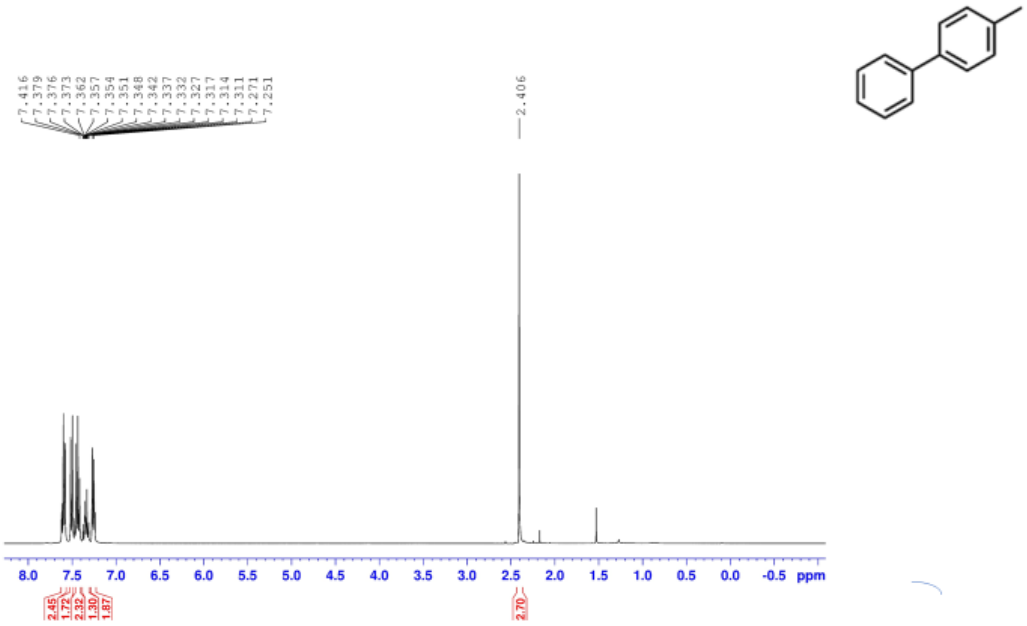


Figure A39: ^{1}H NMR of **13f** recorded in $CDCl_3$

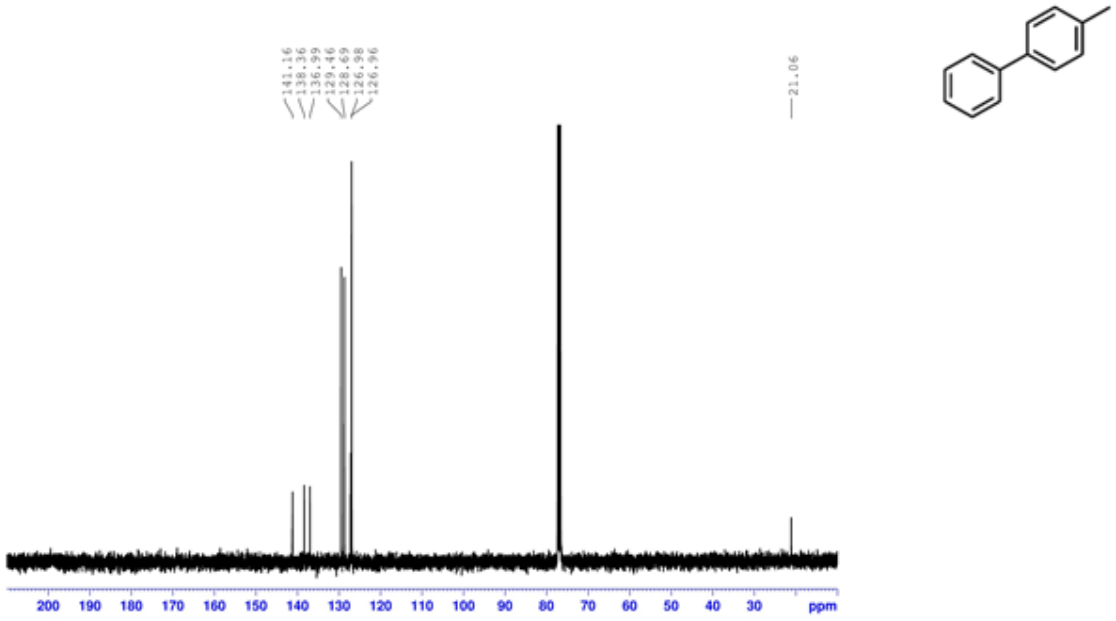


Figure A40: ^{13}C NMR of **13f** recorded in $CDCl_3$

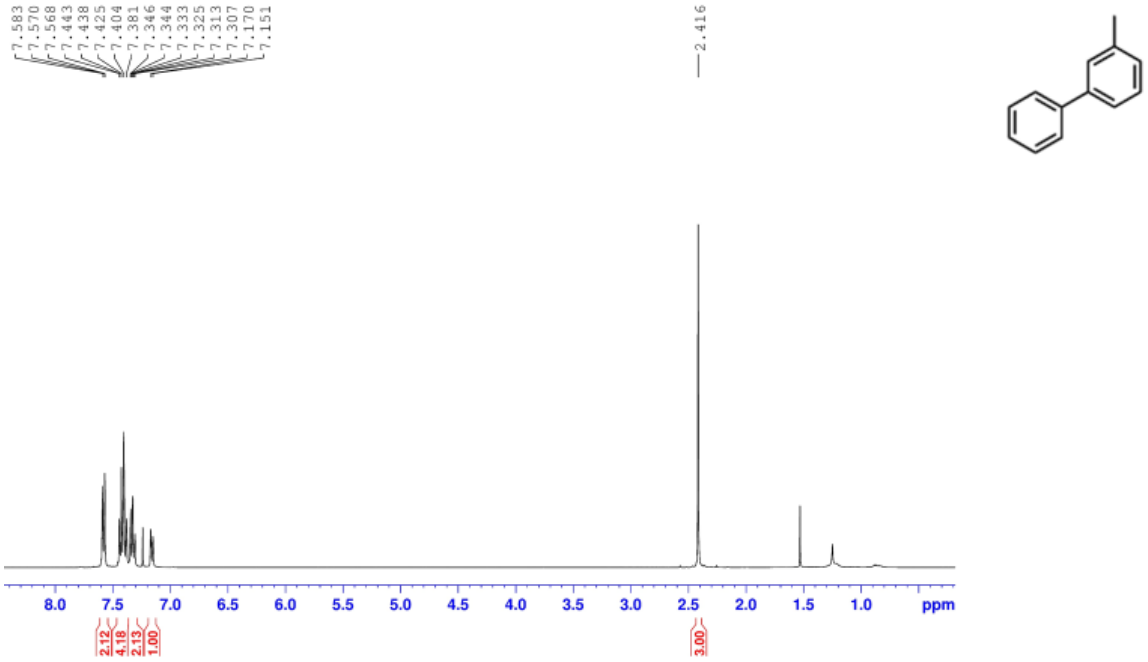


Figure A41: ^{1}H NMR of **13g** recorded in $CDCl_3$

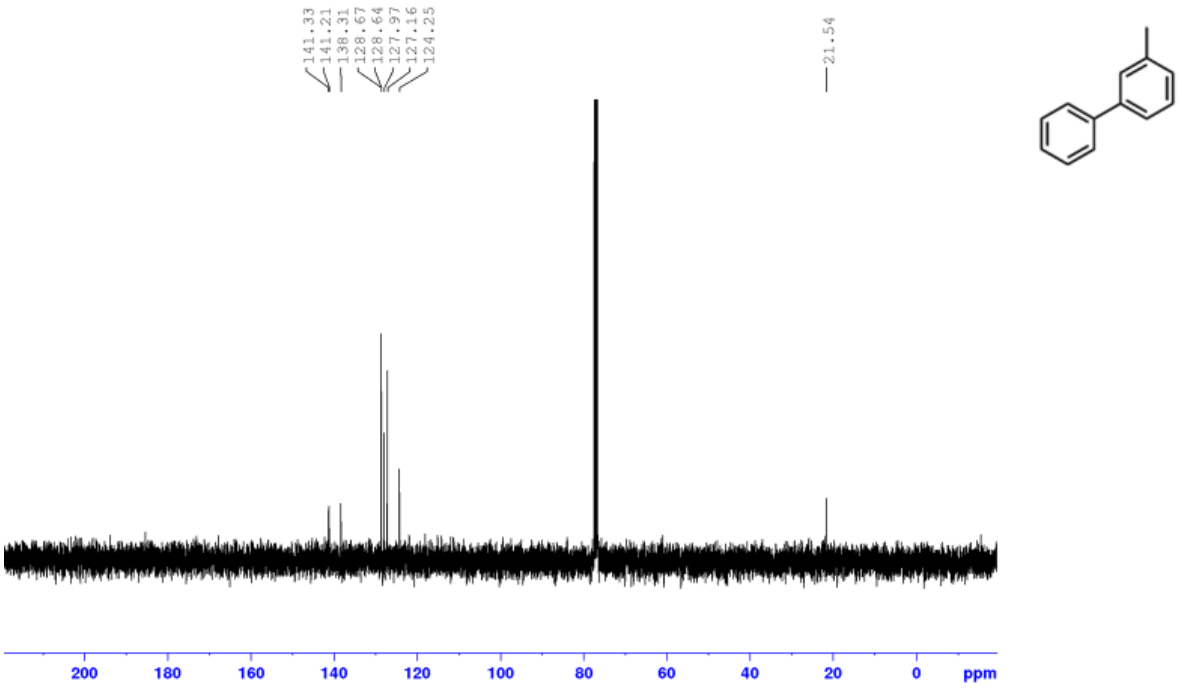


Figure A42: ^{13}C NMR of **13g** recorded in $CDCl_3$

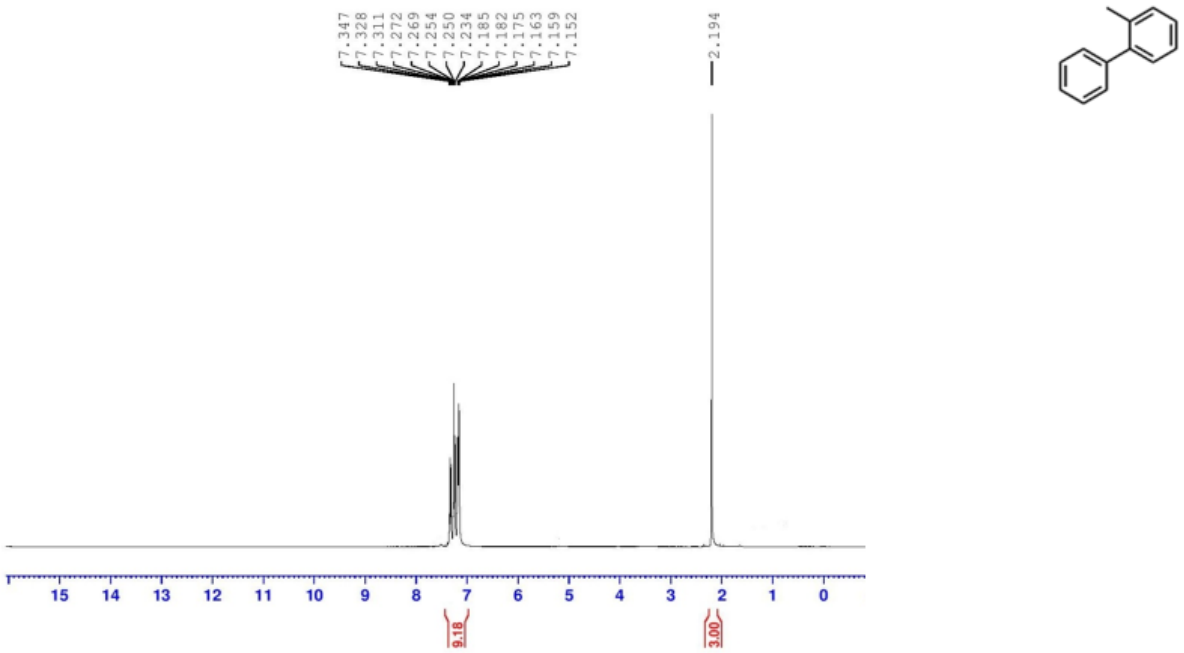


Figure A43: ^{1}H NMR of **13h** recorded in $CDCl_3$

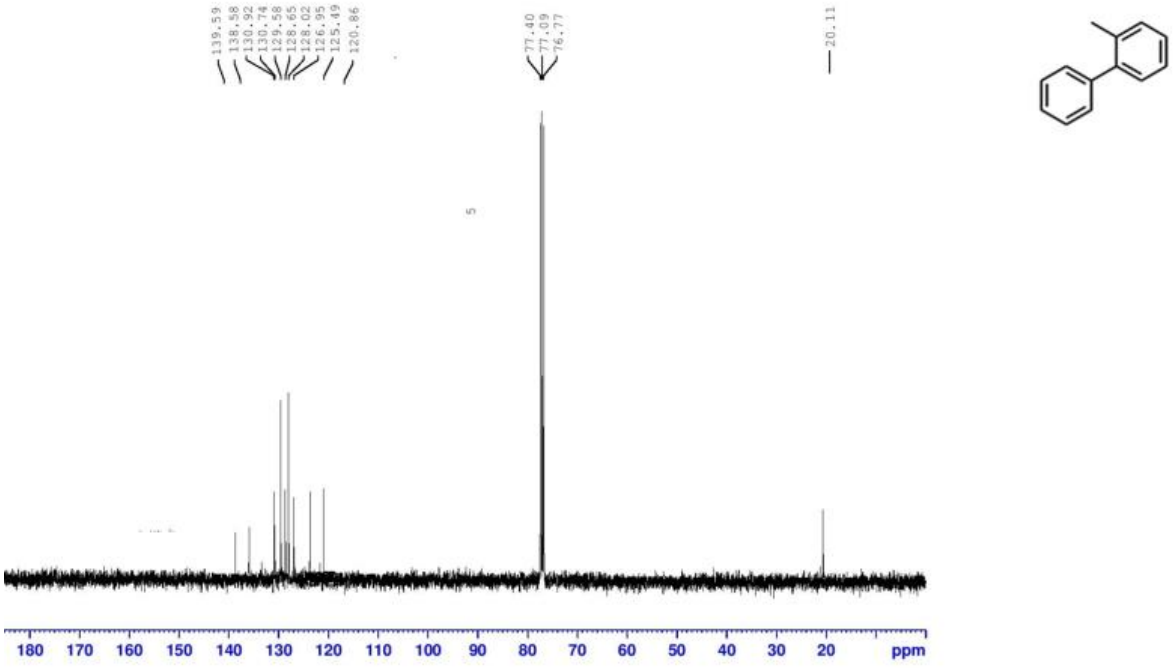


Figure A44: ^{13}C NMR of **13h** recorded in $CDCl_3$

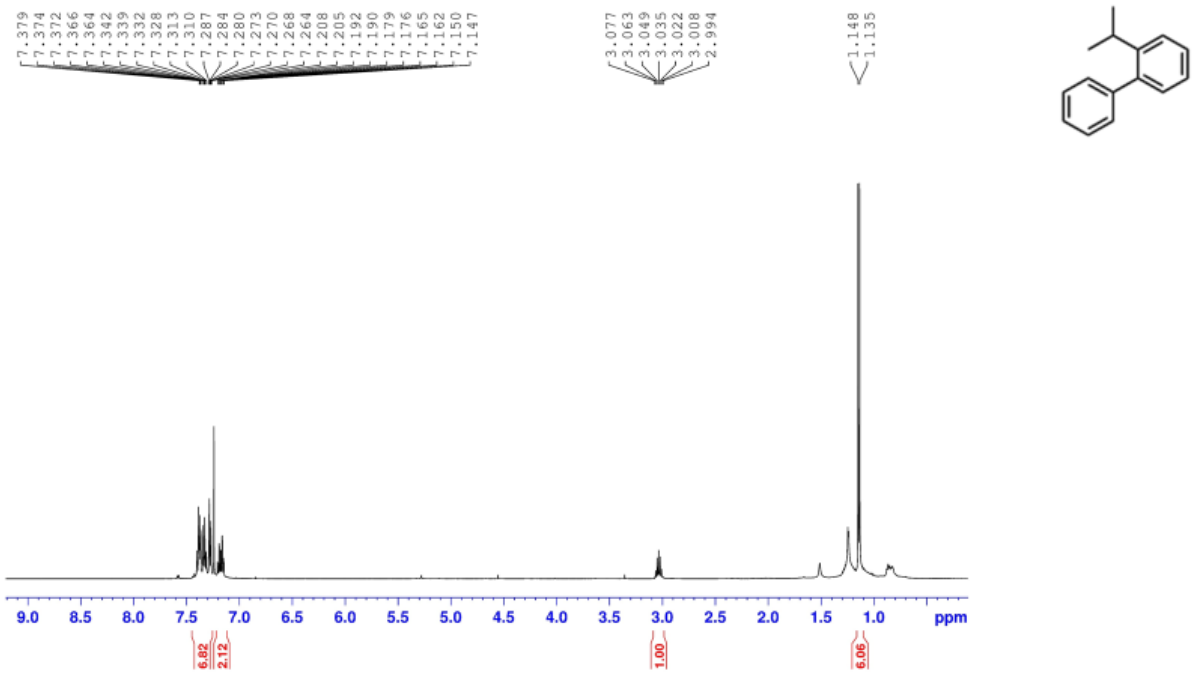


Figure A45: ^{1}H NMR of **13i** recorded in $CDCl_3$

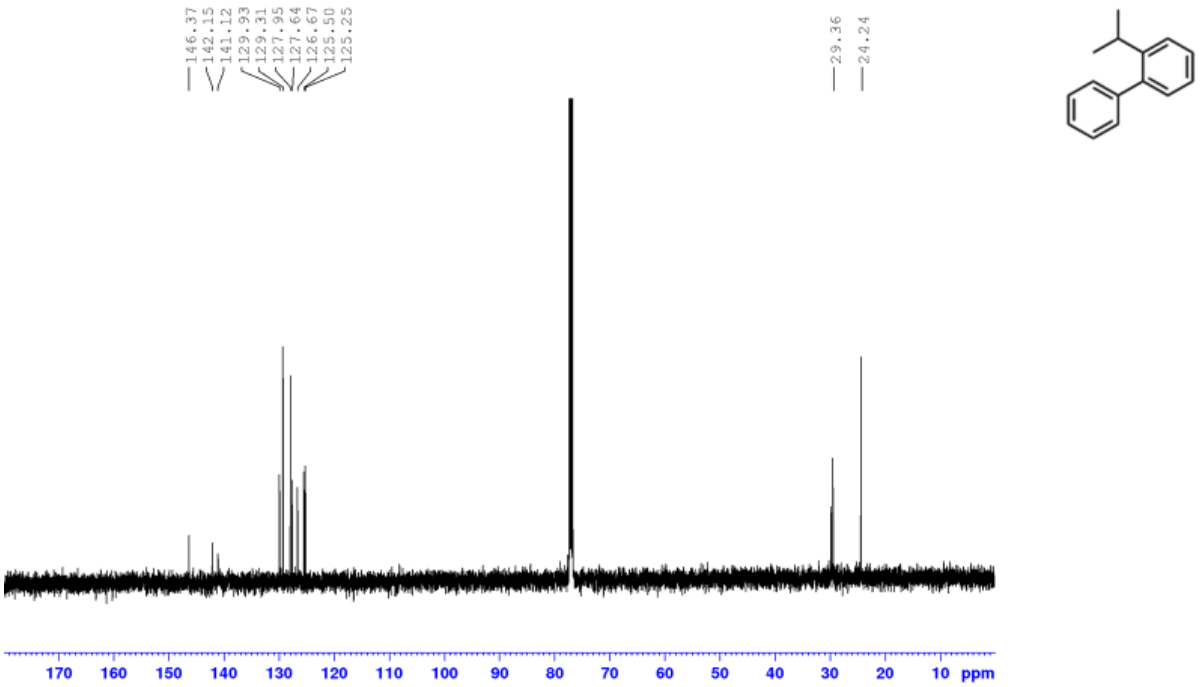


Figure A46: ^{13}C NMR of **13i** recorded in $CDCl_3$

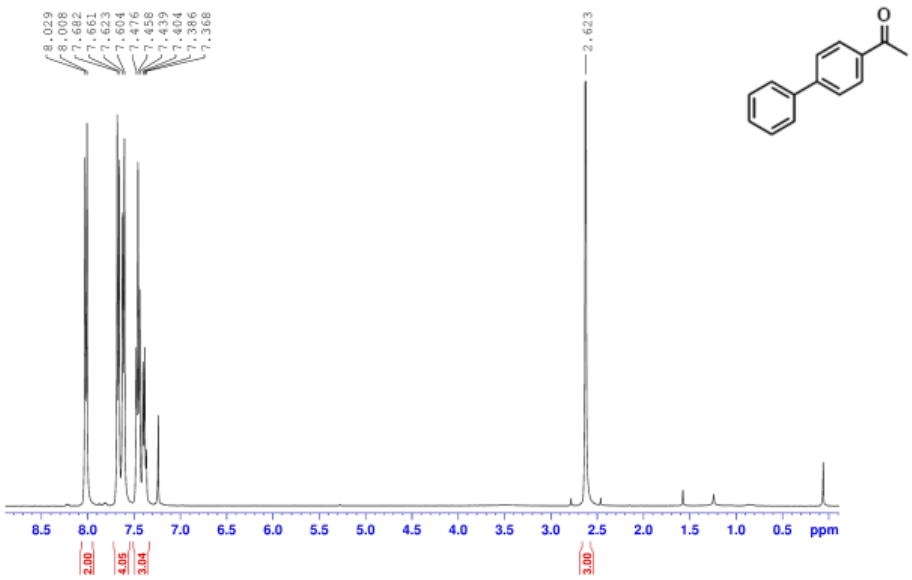


Figure A47: ^{1}H NMR of **13j** recorded in $CDCl_3$

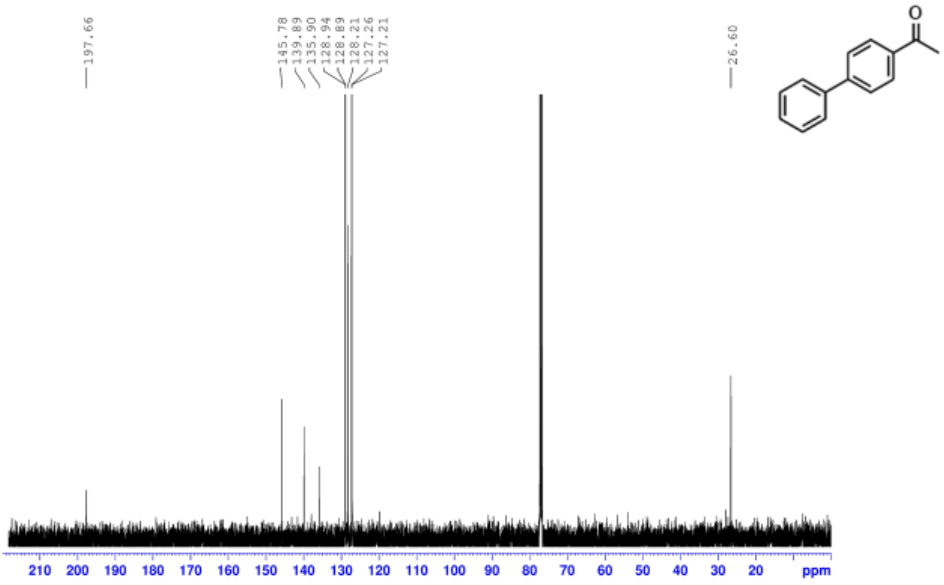


Figure A48: ^{13}C NMR of **13j** recorded in $CDCl_3$

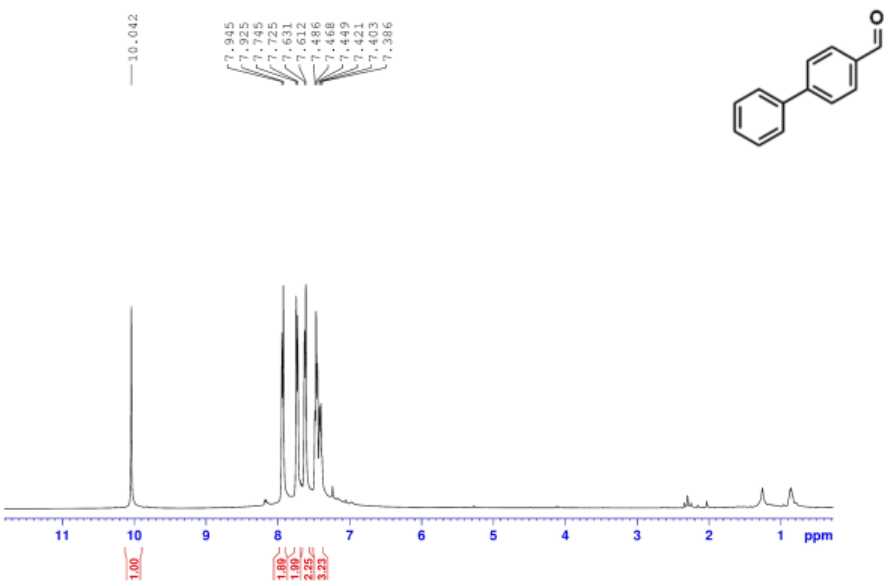


Figure A49: ^{1}H NMR of **13k** recorded in $CDCl_3$

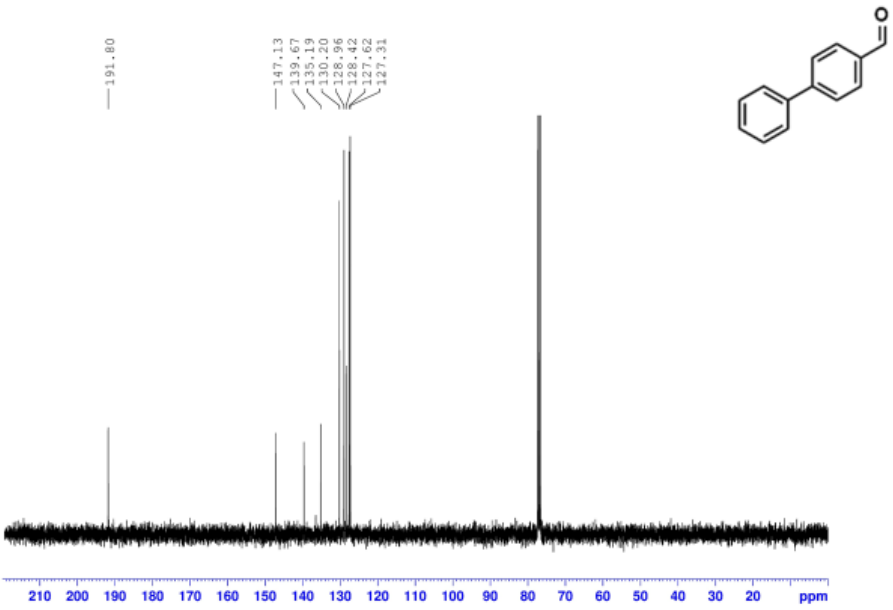
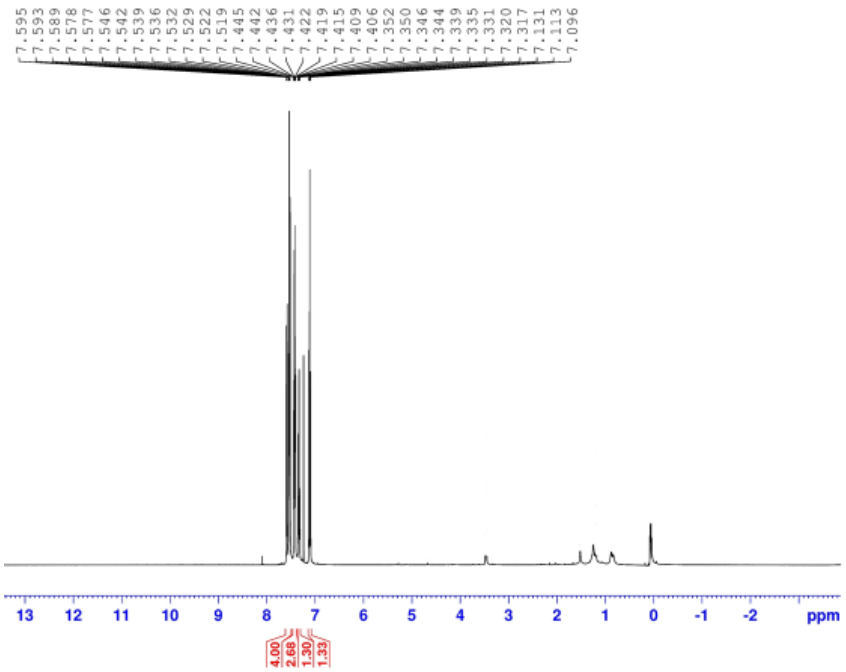


Figure A50: ^{13}C NMR of **13k** recorded in $CDCl_3$



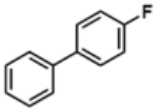
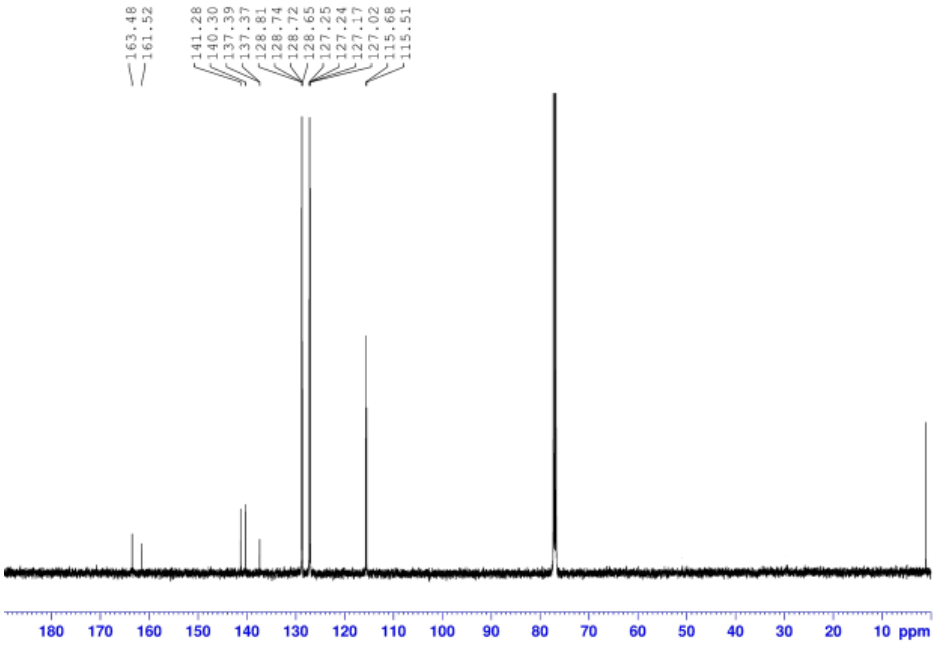


Figure A51: ^{1}H NMR of **13l** recorded in $CDCl_3$



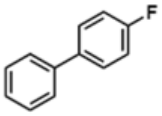


Figure A52: ^{13}C NMR of **13l** recorded in $CDCl_3$

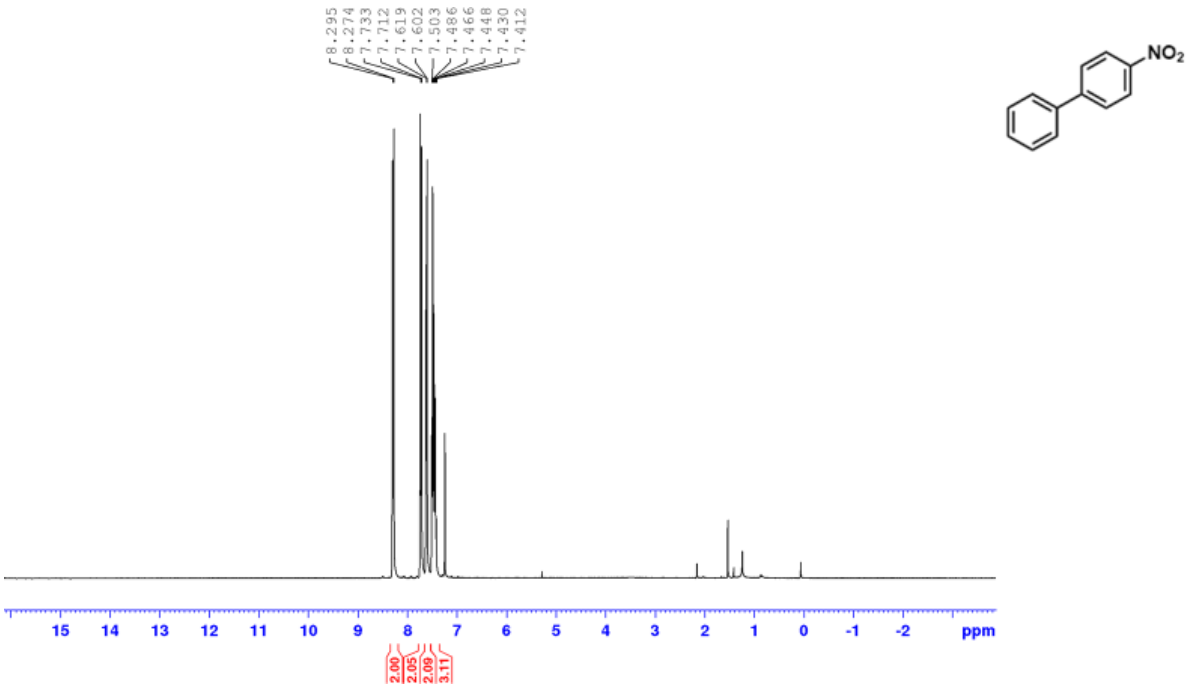


Figure A53: ^{1}H NMR of **13m** recorded in $CDCl_3$

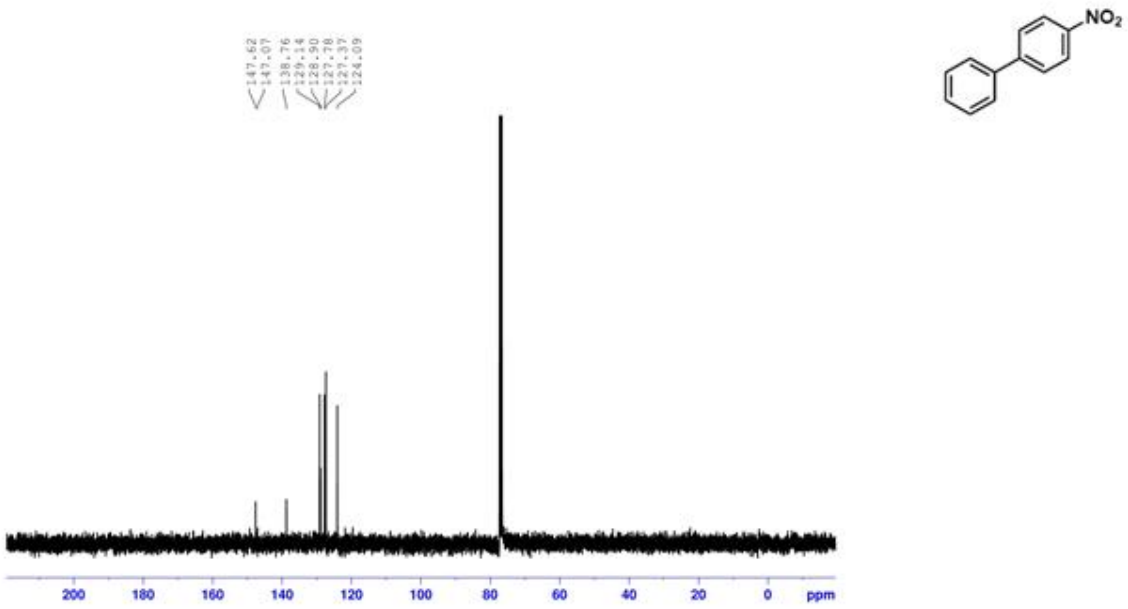
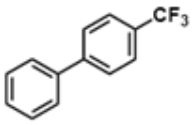


Figure A54: ^{13}C NMR of **13m** recorded in $CDCl_3$



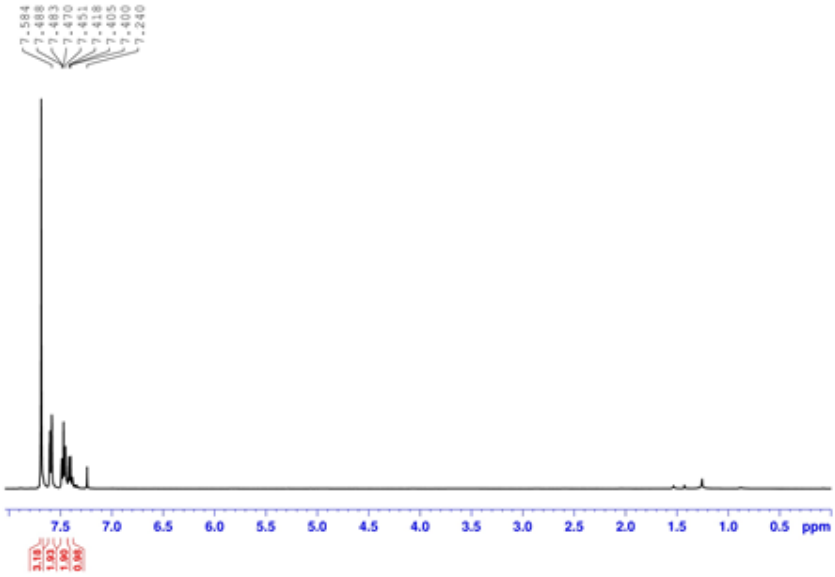
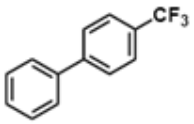


Figure A55: ^{1}H NMR of **13n** recorded in $CDCl_3$



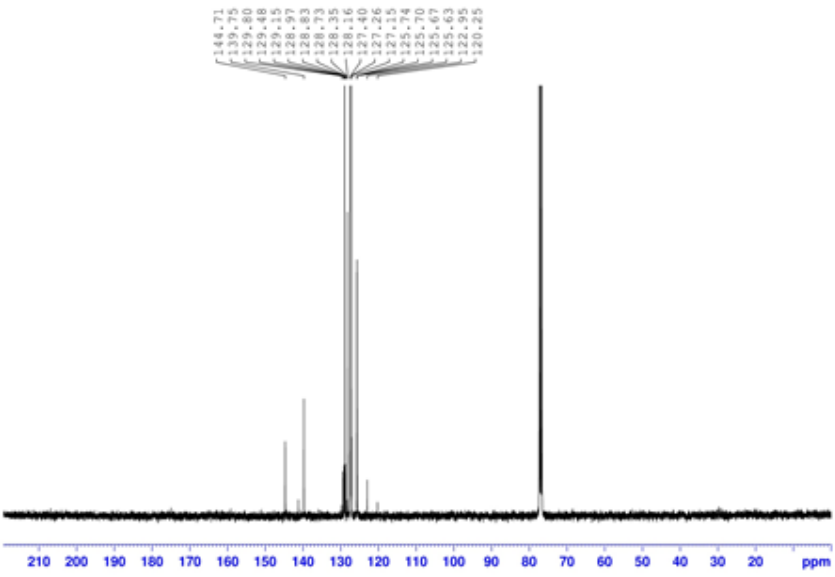


Figure A56: ^{13}C NMR of **13n** recorded in $CDCl_3$

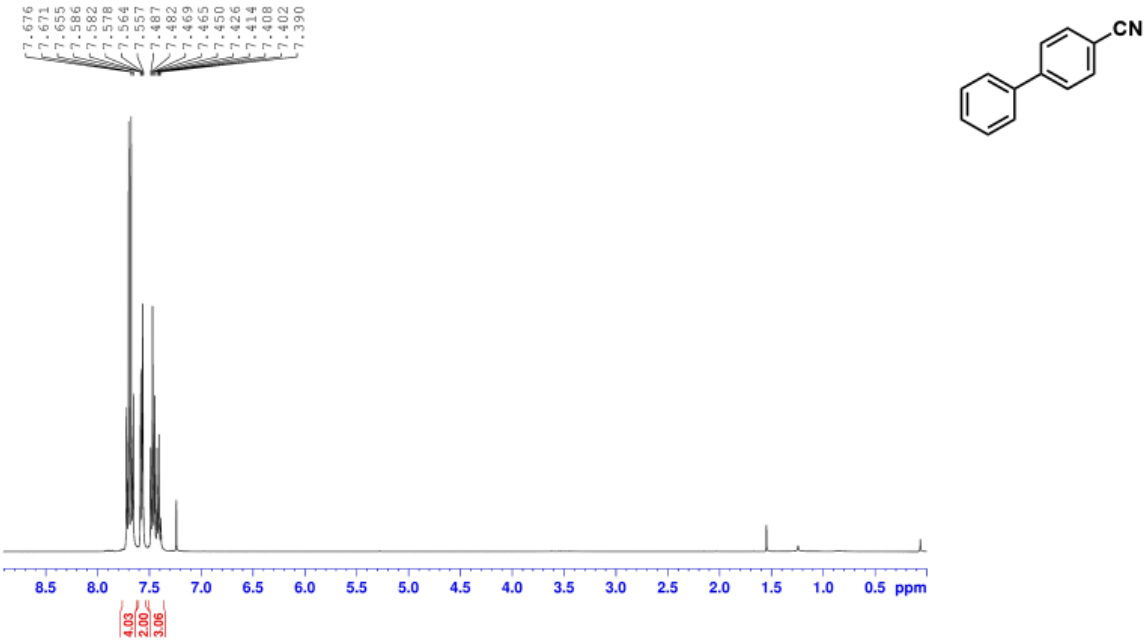


Figure A57: ^{1}H NMR of **13o** recorded in $CDCl_3$

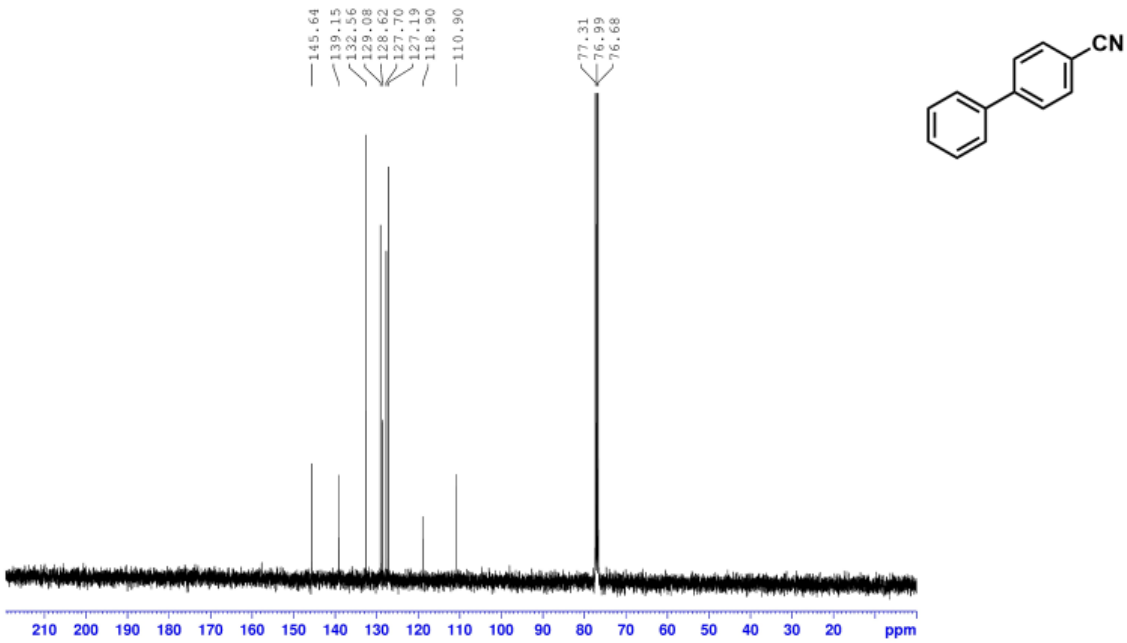


Figure A58: ^{13}C NMR of **13o** recorded in $CDCl_3$

S5 Crystal Data for 8a

Identification code	**8a**
Empirical formula	$C_{15}H_{31}Cl_2N_3O_2Pd$
Formula weight	462.73
Temperature/K	293.15
Crystal system	monoclinic
Space group	P21/n
a/Å	16.2366(10)
b/Å	6.9626(4)
c/Å	19.1339(12)
α/°	90
β/°	111.0000(10)
γ/°	90
Volume/Å3	2019.4(2)
Z	4
ρcalcg/cm3	1.522
μ/mm^{-1}	1.195
F(000)	952.0
Crystal size/mm3	0.302 × 0.186 × 0.165
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	6.392 to 52.482
Index ranges	-20 ≤ h ≤ 20, -8 ≤ k ≤ 8, -23 ≤ l ≤ 23
Reflections collected	46361
Independent reflections	4067 [Rint = 0.0221, Rsigma = 0.0103]
Data/restraints/parameters	4067/0/216
Goodness-of-fit on F2	1.059
Final R indexes [I>=2σ (I)]	R1 = 0.0229, wR2 = 0.0581
Final R indexes [all data]	R1 = 0.0264, wR2 = 0.0600
Largest diff. peak/hole / e Å-3	0.48/-0.57
CCDC no.	1991901

Table A2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for solve_a. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*Z*	U(eq)
Pd1	7445.2(2)	10401.9(5)	4338.2(2)	28.02(15)
Cl1	8466.1(8)	9391(2)	3837.9(7)	51.0(4)
Cl2	9554.1(10)	-1294(2)	7759.5(8)	57.7(4)
N2	6597(2)	11269(5)	4774.1(19)	30.7(7)
N1	8219(3)	9811(6)	5447(2)	35.8(8)
N3	6457(2)	11146(6)	3332(2)	34.5(8)
C10	5796(3)	11810(6)	4311(2)	34.3(9)
C9	5189(3)	12469(7)	4609(3)	45.1(11)
C8	5424(4)	12539(8)	5372(3)	50.2(13)
C7	6266(4)	11956(8)	5844(3)	45.7(11)
C6	6847(3)	11325(7)	5521(2)	36.6(9)
C11	5627(3)	11522(8)	3494(3)	41.8(11)
C5	7795(3)	10785(8)	5938(3)	45.1(12)
C14	6306(4)	9498(8)	2782(3)	47.6(12)
C2	8235(4)	7678(8)	5555(3)	47.5(12)
C3	9151(3)	10510(8)	5662(3)	45.8(12)
C4	9230(4)	12539(9)	5431(4)	63.4(16)
C15	5635(5)	9866(11)	2012(3)	64.8(17)
C13	6741(4)	12881(8)	3013(3)	51.4(13)
C1	7334(4)	6793(8)	5373(3)	57.8(14)
C12	7028(5)	14493(8)	3535(4)	69.0(19)
C16	8343(3)	-4897(6)	7195(2)	31.3(9)
C17	8347(3)	1804(8)	8043(3)	41.3(10)

Table A3 Anisotropic Displacement Parameters ($Å^2×10^3$) for solve_a. The Anisotropic displacement factor exponent takes the form: $-2π^2[h^2a^{*2}U_{11}+2hka*b*U_{12}+…]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pd1	24.7(2)	34.8(2)	23.0(2)	-0.15(11)	6.57(14)	3.83(11)
Cl1	36.0(6)	78.7(10)	40.5(6)	-13.0(6)	16.5(5)	9.0(6)
Cl2	56.3(8)	57.3(8)	63.0(8)	0.9(7)	25.4(7)	0.0(6)
N2	29.9(17)	32.8(18)	28.6(17)	2.5(14)	9.5(14)	7.4(14)
N1	34(2)	44(2)	24.7(17)	0.2(15)	5.2(15)	12.0(16)
N3	28.8(17)	42(2)	28.7(17)	7.9(16)	5.5(14)	-1.5(16)
C10	30(2)	34(2)	38(2)	6.8(18)	11.6(17)	4.6(17)
C9	35(2)	46(3)	55(3)	7(2)	18(2)	11(2)
C8	51(3)	49(3)	63(3)	2(3)	36(3)	12(2)
C7	57(3)	49(3)	37(2)	-1(2)	24(2)	12(2)
C6	41(2)	37(2)	32(2)	2.2(18)	13.4(18)	9.3(19)
C11	27(2)	60(3)	33(2)	8(2)	5.6(17)	8(2)
C5	46(3)	58(3)	28(2)	-4(2)	8(2)	15(2)
C14	45(3)	55(3)	36(3)	-6(2)	7(2)	-1(2)
C2	53(3)	46(3)	41(2)	7(2)	14(2)	18(2)
C3	29(2)	63(3)	36(2)	-4(2)	0.1(19)	10(2)
C4	42(3)	61(4)	70(4)	-16(3)	-1(3)	-6(3)
C15	57(4)	90(5)	36(3)	0(3)	3(3)	-12(3)
C13	52(3)	48(3)	53(3)	24(2)	19(2)	0(2)
C1	72(4)	43(3)	59(3)	8(3)	23(3)	4(3)
C12	81(5)	42(3)	73(4)	11(3)	13(4)	-1(3)
C16	36(2)	25.7(18)	32(2)	7.9(16)	12.5(18)	5.5(17)
C17	36(2)	48(3)	41(2)	0(2)	15.2(19)	3(2)

Table A4 Bond Lengths for solve_a.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Pd1	Cl1	2.3010(12)	N3	C13	1.499(6)
Pd1	N2	1.943(3)	C10	C9	1.382(6)
Pd1	N1	2.082(4)	C10	C11	1.501(6)
Pd1	N3	2.082(3)	C9	C8	1.370(7)
N2	C10	1.339(5)	C8	C7	1.401(8)
N2	C6	1.339(5)	C7	C6	1.371(6)
N1	C5	1.509(6)	C6	C5	1.506(6)
N1	C2	1.499(7)	C14	C15	1.507(8)
N1	C3	1.500(7)	C2	C1	1.508(8)
N3	C11	1.510(6)	C3	C4	1.499(8)
N3	C14	1.516(6)	C13	C12	1.463(9)

Table A5 Bond Angles for solve_a.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
N2	Pd1	Cl1	179.14(11)	C13	N3	Pd1	109.2(3)
N2	Pd1	N1	83.44(14)	C13	N3	C11	111.8(4)
N2	Pd1	N3	83.69(15)	C13	N3	C14	108.9(4)
N1	Pd1	Cl1	95.85(11)	N2	C10	C9	119.2(4)
N1	Pd1	N3	167.08(15)	N2	C10	C11	115.0(4)
N3	Pd1	Cl1	97.03(11)	C9	C10	C11	125.7(4)
C10	N2	Pd1	118.3(3)	C8	C9	C10	118.9(4)
C6	N2	Pd1	118.5(3)	C9	C8	C7	120.7(4)
C6	N2	C10	123.2(4)	C6	C7	C8	118.2(4)
C5	N1	Pd1	107.6(3)	N2	C6	C7	119.7(4)
C2	N1	Pd1	108.1(3)	N2	C6	C5	114.8(4)
C2	N1	C5	110.4(4)	C7	C6	C5	125.4(4)
C2	N1	C3	108.5(4)	C10	C11	N3	113.2(3)
C3	N1	Pd1	113.4(3)	C6	C5	N1	112.9(4)
C3	N1	C5	108.9(4)	C15	C14	N3	115.5(5)
C11	N3	Pd1	107.5(3)	N1	C2	C1	113.9(4)
C11	N3	C14	109.9(4)	C4	C3	N1	114.2(4)
C14	N3	Pd1	109.4(3)	C12	C13	N3	114.1(5)

Table A6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for solve_a.

Atom	*x*	*y*	*z*	U(eq)
H9	4629.55	12858.39	4297.73	54
H8	5020.81	12978.64	5578.69	60
H7	6427	11996.24	6361.46	55
H11A	5338.59	12656.52	3221.19	50
H11B	5227.51	10445.43	3312.92	50
H5A	7824.61	9931.52	6346.99	54
H5B	8127.32	11934.83	6152.2	54
H14A	6864.63	9183.17	2731.6	57
H14B	6120.26	8383.24	2991.05	57
H2A	8588.83	7387.01	6071.17	57
H2B	8518.88	7089.47	5240.37	57
H3A	9437.37	10411.82	6201.07	55
H3B	9463.92	9673.38	5436.34	55
H4A	8941.5	12658.32	4898.63	95
H4B	9842.18	12867.53	5568.22	95
H4C	8957.2	13390.83	5678.19	95
H15C	5088.56	10263.01	2054.56	97
H15B	5542.52	8710.01	1720.59	97
H15A	5846.66	10859.29	1771.53	97
H13A	7222.57	12519.68	2851.48	62
H13B	6254.02	13301.4	2573.53	62
H1A	7058.85	7315.26	5699.18	87
H1B	7391.84	5426.54	5440.55	87
H1C	6977.01	7073.04	4862.18	87
H12A	6550.9	14887.13	3687.51	103
H12B	7200.1	15546.31	3293.78	103
H12C	7520.31	14102.77	3966.66	103