Abnormal N-Heterocyclic Carbene Palladium Complex: Living Catalyst for Activation of Aryl Chlorides in Suzuki–Miyaura Cross Coupling

Samaresh Chandra Sau, Subhankar Santra, Tamal K. Sen, Swadhin K. Mandal* and Debasis Koley

Department of Chemical Sciences, Indian Institute of Science Education and Research-Kolkata, Mohanpur-741252, India,

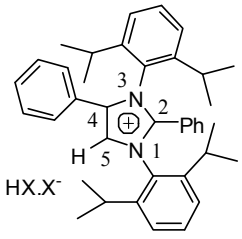
Email: swadhin.mandal@iiserkol.ac.in

Supplementary Information

Contents

Experimental Section:

Materials and Instrumentation: All manipulations were performed under a dry and oxygen free atmosphere (Argon) using standard Schlenk techniques or inside a glovebox maintained at below 0.1 ppm of O_2 and H_2O level, utilizing glasswares that were oven-dried (130 °C) and evacuated while hot prior to use. All solvents were distilled from Na/benzophenone prior to use. All other chemicals were purchased from Sigma-Aldrich and used as received. The HRMS data was obtained using a Finnigan MAT 8230 instrument. Elemental analyses were carried out using a Perkin-Elmer 2400 CHN analyser and samples were prepared by keeping under reduced pressure (10^{-2} mbar) for overnight. The melting point was measured in a sealed glass tube on a Büchi B-540 melting point apparatus and was uncorrected. Analytical TLC was performed on a Merck 60 F254 silica gel plate (0.25 mm thickness). Column chromatography was performed on Merck 60 silica gel (100-200 mesh). NMR spectra were recorded on a JEOL ECS 400 MHz spectrometer and on a Bruker Avance III 500 MHz spectrometer. All chemical shifts were reported in ppm using tetramethylsilane as a reference. Chemical shifts (δ) downfield from the reference standard were assigned positive values. Abnormal *N*-heterocyclic carbene salt 1,3-bis(2,6-diisopropylphenyl)-2,4-diphenyl-imidazolium salts (**IA** and **IB** in Chart 1) were prepared starting from *N,N′*-bis(2,6-diisopropylphenyl)benzamidine[1] following modified literature protocol.[2]



X= Cl ; **IA**
X= Br ; **IB**

Chart 1. The drawing of salts **IA** and **IB** employed in the present study.

Synthesis of complex 1:

Under an Ar atmosphere, a 50 mL Schlenk flask was charged with $Pd(OAc)_2$ (112 mg, 0.5 mmol), **IA** (Chart 1, 308 mg, 0.5 mmol), and 1,4-dioxane (10 mL). The reaction mixture was heated to 80 ^{o}C for 8 h. After cooling to room temperature, all volatiles were removed under reduced pressure. The product was isolated by column chromatography using CH_2Cl_2 as an eluent. Complex **1**(yellow crystals, 273 mg, 0.20 mmol, 80 %) was obtained by recrystallization from CH_2Cl_2/Et_2O. Mp: 275-280 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.55-7.52 (t, J = 8 Hz, 1 H), 7.46-7.43 (t, J = 8 Hz, 1 H), 7.30-7.29 (d, J = 7.5 Hz, 2 H), 7.25-7.23 (d, J = 7.5 Hz, 1 H), 7.19-7.17(d, J = 8 Hz, 2 H), 7.12-7.10(m, 1 H), 7.03-7.00(t, J = 8.5 Hz, 2 H), 6.94-6.93(d, J = 8.5 Hz, 2 H), 6.65-6.61(t, J = 7.7 Hz, 1 H), 6.55-6.52(t, J = 7.5 Hz, 1 H), 5.62-5.60 (d, J = 7.5 Hz, 1 H), 2.87-2.81(m, 2 H), 2.76-2.71 (m, 2 H), 1.56-1.53(d, J = 7 Hz, 6 H), 1.06-1.04(d, J = 7 Hz, 6 H), 0.94-0.91(m, 12 H) ^{13}C NMR (125 MHz, 25 ºC, TMS): δ 155.7, 152.9, 145.4, 144.7, 144.2, 139.8, 138.0, 135.7, 134.3, 131.0, 130.9, 129.7, 129.3, 128.9, 127.9, 124.8, 124.2, 124.1, 123.9, 122.5, 118.6, 29.0, 28.7, 25.3, 24.4, 23.0, 22.9. ESI-MS: m/z (%): 1365 [M^+], Elemental analysis: Anal. Calcd for $C_{78}H_{88}Cl_2N_4Pd_2$: C, 68.62; H, 6.50; N, 4.10. Found: C, 67.75; H, 6.48; N, 3.90.

Synthesis of complex 2:

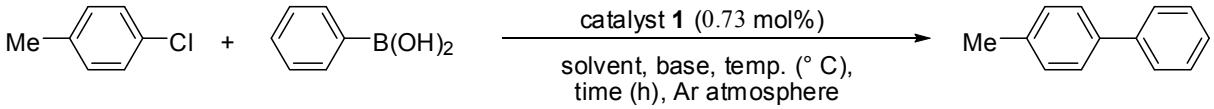
Under an Ar atmosphere, a Schlenk flask was charged with $Pd(OAc)_2$ (112 mg, 0.5 mmol), **IB** (Chart 1, 353 mg, 0.5 mmol), and 1,4-dioxane (10 mL). The reaction mixture was heated to 80 ^{o}C for 8 h. After cooling to room temperature, all volatiles were removed. The product was isolated by column chromatography using CH_2Cl_2 as an eluent. Complex **2** (yellow crystals, 280 mg, 0.19 mmol, 77 %) was obtained by recrystallization from CH_2Cl_2/Et_2O. Mp: 295-300 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C, TMS): δ 7.54-7.52 (t, J = 5 Hz, 1 H), 7.49-7.43 (m, 2 H), 7.30-7.28 (d,

J = 8 Hz, 2 H), 7.19-7.17 (d, *J* = 8 Hz, 2 H), 7.13-7.08(m, 1 H), 7.02-6.98(m, 2 H), 6.91-6.90(d, *J* = 8.25 Hz, 2 H), 6.64-6.61(t, *J* = 7.5Hz, 1 H), 6.55-6.51(t, *J* = 7.5 Hz, 1 H), 5.62-5.60 (d, *J* = 7.5 Hz, 1 H), 2.89-2.84(m, 2 H), 2.76-2.69 (m, 2 H), 1.54-1.53(d, *J* = 6.5 Hz, 6 H), 1.05-1.04(d, *J* = 6.5 Hz, 6 H), 0.93-0.92(d, *J* = 6.5 Hz, 6 H), 0.88-0.86(d, *J* = 7 Hz, 6 H) ^{13}C NMR (125 MHz, 25 ºC, TMS): *δ* 156.6, 153.8, 145.4, 144.8, 144.4, 139.9, 138.1, 137.1, 134.5, 131.1, 130.9, 129.9, 129.3, 129.0, 127.9, 124.9, 124.6, 124.4, 124.2, 122.5, 118.9, 29.0, 28.7, 25.3, 24.4, 23.11, 22.9. ESI-MS: *m*/*z* (%): 1454 [M^+], Elemental analysis: Anal. Calcd for $C_{78}H_{88}Br_2N_4Pd_2$: C, 64.42; H, 6.10; N, 3.85. Found: C, 63.80; H, 5.95; N, 3.70.

Catalytic Suzuki-Miyaura reaction for aryl chloride substrates:

We standardized the Suzuki-Miyaura reaction usuing 4-chlorotoluene as substrate and **1** as catalyst under different reaction condition as listed in Table 1. The first solvent/base mixture tested was acetonitrile/K_2CO_3, and no coupling product was observed (entries 1-2, Table 1). Then we tested using EtOH/NaOMe and EtOH/Cs_2CO_3 as solvent/base combination and no coupling product was observed (entries 3-4, Table 1). Using 1,4-dioxane and KO^{t}Bu combination a small amount of desired product was obtained (10 % yield) at room temperature (entry 5, Table 1). Using 1,4-dioxane/Cs_2CO_3 combination resulted in 40% yield of the desired product at room temperature and this yield can be improved to 78 % on heating at 80 °C (entries 6-7, Table 1). 1,4-dioxane as solvent and NaOMe as base resulted in the desired biphenyl product in 99% yield using 0.73 mol% of catalyst loading after 4 h at 25 °C (entry 8, Table 1). Thus 1,4-dioxane/NaOMe and dioxane/Cs_2CO_3 are the most effective combination for this particular catalytic system to carry out Suzuki–Miyaura reaction.

Table 1. Screening of conditions Suzuki-Miyaura coupling reactions of 4-chlorotoluene using catalyst **1**[a]



Entry	Solvent	Base	Temp. (° C)	Time (h)	Yield (%)[b]
1	Acetonitrile	K_2CO_3	25	48	--
2	Acetonitrile	K_2CO_3	80	12	--
3	EtOH	NaOMe	25	12	--
4	EtOH	Cs_2CO_3	25	12	--
5	Dioxane	KO^{t}Bu	25	12	10
6	Dioxane	Cs_2CO_3	25	48	40
7	Dioxane	Cs_2CO_3	80	12	78
8	Dioxane	NaOMe	25	3	99

[a] Reaction condition: Complex **1** (10 mg, 0.73 mol%) was used for the above catalytic reactions with 4-chlorotoluene (1 mmol), phenylboronic acid (1.5 mmol) and base (2 mmol) in 5 mL of dry 1,4-dioxane. [b] Isolated yield**.**

Procedure for Catalytic Suzuki-Miyaura coupling reactions:

10 mg (0.73 mol%) of the catalyst (complex **1** or complex **2**) together with the phenylboronic acid (1.5 mmol), base (2 mmol) and aryl chloride (1 mmol) were kept in 50 mL Schlenk falsk. Dry 1,4-dioxane (5 mL) was added to it. Then the catalytic reactions were performed at room temperature under dry nitrogen atmosphere for appropriate time. After completion of the reaction, the reaction mixture was dried under reduced pressure and purified through a short column chromatography (silica gel 100-200 mesh) using the appropriate ratio of hexane and ethyl acetate to provide pure biaryls.

Conversion Vs. time monitored by ^{1}H NMR spectroscopy:

Under an Ar atmosphere, a Schlenk flask was charged with complex **1** (10 mg, 0.73 mmol), NaOMe (2 mmol), phenylboronic acid (1.5 mmol) and 4-chlorotoluene(1 mmol) in 1,4-dioxane (3 mL). The reaction mixture was monitored by ^{1}H NMR spectroscopy by taking aliquots of the reaction mixture after 15 min. time interval and the time vs. conversion indicates that with 75 min. the conversion reaches over 90% (Fig. 1).

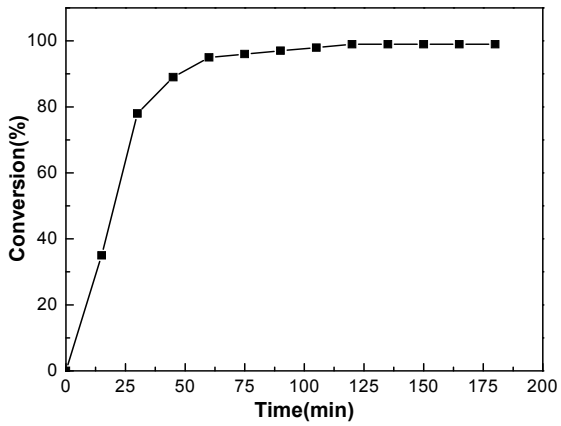


Fig. 1. Plots of conversion [%] versus time (t) in the coupling of 4-chlorotoluene (1 mmol) with phenylboronic acid (1.5 mmol) catalyzed by complex **1**(0.73 mol %).

Procedure for catalyst longevity experiment:

In a 100 mL Schlenk flask 10 mg of catalyst (**1**, 0.73 mol %), 5 mL of 1,4-dioxane, 2 mmol of NaOMe, 1 mmol of 4-chlorotoluene and 1.5 mmol of phenylboronic acid were taken and catalytic reaction was performed at 25 °C following the protocol mentioned above. The reaction mixture was monitored by ^{1}H NMR spectroscopy by taking aliquots of the reaction mixture after

4 h to check for complete consumption of 4-chlorotoluene substrate. After each 4 h, a fresh batch of substrate (4-chlorotoluene, 1mmol), phenylboronic acid (1.5 mmol), NaOMe (2 mmol) and dry 1,4-dioxane (5 mL) were added without any additional catalyst or solvent and the catalytic reaction was performed for the next catalytic cycle. The catalyst is soluble in 1,4-dioxan, however, the base remains as a suspension in the reaction medium. Similarly, the process was repeated for a total of ten consecutive catalytic runs revealing that the 4-chlorotoluene can be coupled for 10 catalytic runs with equal efficiency (Fig. 2). Also the isolated yield after column chromatography revealed 95% which indicates that the catalyst used at beginning stays live for ten catalytic runs.

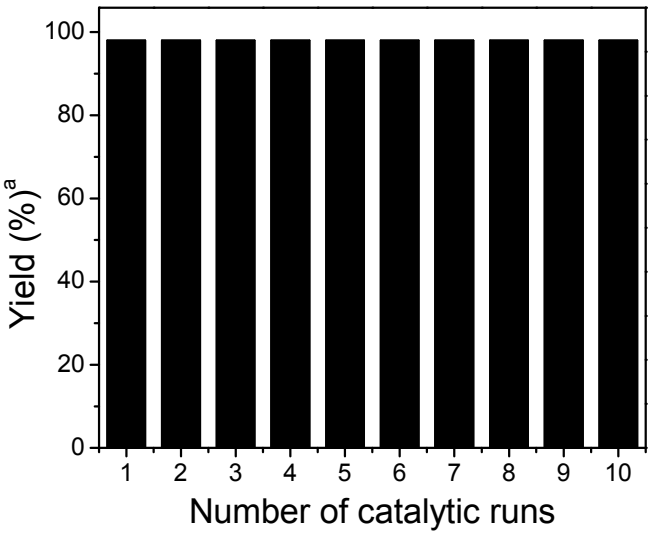


Fig. 2. Longevity of the catalyst was tested by monitoring the time required for complete consumption of substrate by ^{1}H NMR spectroscopy in ten consecutive catalytic cycles. Reaction condition: 0.73 mol% catalyst **1**, 4-chlorotoluene (1 mmol), phenylboronic acid (1.5 mmol), NaOMe (2 mmol) and 5 mL dry 1,4-dioxane. After completion of each catalytic cycle fresh 4-chlorotoluene (1 mmol), phenylboronic acid (1.5 mmol) and NaOMe (2 mmol) were added and no additional catalyst was added. [a] Yields were determined for each cycle after 4 h by ^{1}H NMR of reaction mixture.

X-ray crystallographic details:

The single-crystal X-ray diffraction data of the crystals were collected on a Bruker Kappa APEX-II CCD DUO diffractometer at 100 K using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Crystallographic parameters are listed in Table 2. Multi-Scan absorption correction was applied. The lattice parameters were determined from least-squares analysis, and reflection data were integrated using the program SHELXTL.[3] The crystal structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares refinement on F^2 with anisotropic displacement parameters for non-H atoms using SHELXL-97.[4] The hydrogen atoms were fixed at their calculated geometrical positions and allowed to ride on the non-hydrogen atoms to which they are attached. The summary of crystal data is given below:

Crystal data for **1**: $C_{83}H_{98}Cl_4N_4OPd_2$, M_r = 1522.27, 0.25 ×0.20 ×0.15 mm^3, orthorombic, space group 'pbca', a = 16.3712(18)Å, b = 23.523(3) Å, c = 39.955(5) Å, α = β = γ = 90.00, V = 15386(3) $Å^3$, Z = 8, Calculated density = 1.316 Mg/m^3, μ (MoKα) = 0.653 mm^{-1}, T = 100(2) K, θ range for data collection=1.60–27.00, 76173 reflections measured, 16790 independent (R_{int} = 0.0683), R_1 = 0.0458 (I>2σ(I)), wR_2 = 0.1195(all data), CCDC 843993 contains the supplementary crystallographic data for this paper.

Crystal data for **2**: $C_{83}H_{98}Cl_2Br_2N_4O\ Pd_2$, M_r = 1611.16, 0.30 × 0.25 × 0.2 mm^3, orthorombic, space group 'pbca', a = 16.4356(11)Å, b = 23.3770(16)Å, c = 40.098(3)Å, α = β = γ = 90.00, V = 15406.2(18)$Å^3$, Z = 8, Calculated density = 1.389 Mg/m^3, μ (MoKα) = 1.627 mm^{-1}, T = 100(2) K, θ range for data collection=1.60–27.00, 122829 reflections measured, 16807 independent (R_{int} = 0.0481), R_1 = 0.0430 (I>2σ(I)), wR_2 = 0.0873 (all data), CCDC 843992 contains the supplementary crystallographic data for this paper. These data can be obtained

free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif.

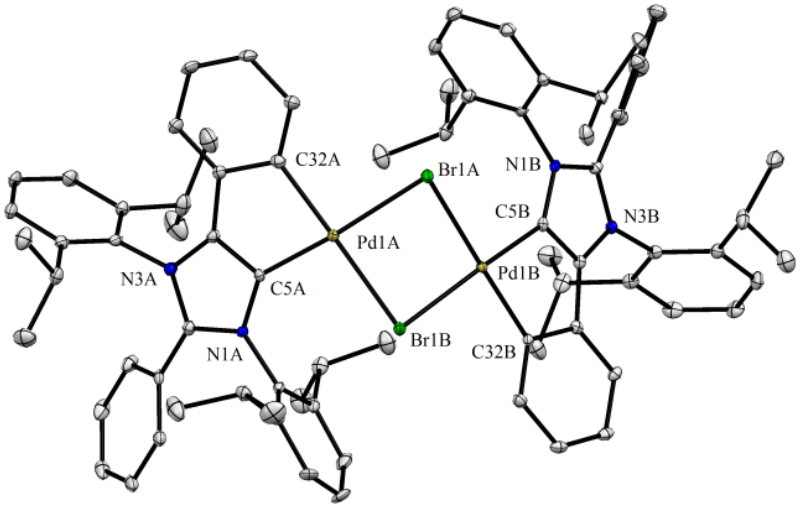


Fig. 3. Perspective ORTEP views of the molecular structure of **2**. Thermal ellipsoids are drawn with 30% probability. Hydrogen atoms and lattice held solvent molecules (dichlormethane and diethyl ether) have been omitted for the sake of clarity.

Table 2. Crystallographic and data collection parameters for **1** and **2**.

	Complex **1**	Complex **2**
Empirical formula	$C_{78}H_{86}Cl_2N_4Pd_2.C_4H_{10}O.CH_2Cl_2$	$C_{78}H_{86}Br_2N_4Pd_2.C_4H_{10}O.CH_2Cl_2$
Formula weight	1522.27	1611.16
Temperature (K)	100	100
Wavelength (A˚)	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca
Unit cell dimensions		
a (Å)	16.3712(18)	16.4356(11)
b (Å)	23.523(3)	23.3770(16)
c (Å)	39.955(5)	40.098(3)
α (°)	90.00	90.00
β (°)	90.00	90.00
γ(°)	90.00	90.00
Volume ($Å^3$)	15386(3)	15406.2(18)
Z	8	8
Calculated density (Mg/m^3)	1.316	1.389
Absorption coefficient (mm^{-1})	0.653	1.627
F(000)	6336	6624
Crystal size (mm)	0.25 × 0.2 × 0.15	0.30 x 0.25 x 0.20
Theta range for data collection(°)	1.60-27.00	1.60-27.00
Index ranges	$-20 \le h \le 20$, $-30 \le k \le 16$, $-51 \le l \le 50$	$-20 \le h \le 20$, $-29 \le k \le 19$, $-51 \le l \le 50$
Reflections collected/unique[R(int)]	76173/ 16790/ 0.0683	122829/ 16807/ 0.0481
Completeness to 2θ = 25.00	100 %	100 %
Absorption correction	'multi-scan'	'multi-scan'
Maximum and minimum transmission	0.907and 0.855	0.722 and 0.620
Refinement method	Full matrix least square on F^2	Full matrix least square on F^2
Data/restraints/parameters	16790/1/ 841	16807/0/ 865
Goodness-of-fit on F^2	1.027	1.162
Final R indices [I > 2σ(I)]	$R_1 = 0.0458$, $wR_2 = 0.1007$	$R_1 = 0.0430$, $wR_2 = 0.0815$
R indices (all data)	$R_1 = 0.0798$, $wR_2 = 0.1195$	$R_1 = 0.0578$, $wR_2 = 0.0873$
Largest difference peak and hole (e $Å^{-3}$)	1.159 and -0.985	1.820 and -1.322

Table 3. Selected bond distances (Å) and angles (°) for **1** and **2**.

Complex **1**			
	Bond distances (Å)		Bond angles (°)
Pd1A–C5A	1.989(4)	C5A– Pd1A–C32A	79.49(15)
Pd1A–C32A	2.017(4)	C5A–Pd1A–Cl1B	171.24(10)
Pd1A–Cl1B	2.3864(9)	C32A–Pd1A–Cl1B	95.57(11)
Pd1A–Cl1A	2.4541(10)	C5A–Pd1A–Cl1A	102.11(11)
Pd1B– C5B	1.979(4)	C32A–Pd1A–Cl1A	175.67(10)
Pd1B–C32B	2.018(4)	Cl1B–Pd1A–Cl1A	83.35(3)
Pd1B–Cl1A	2.3853(10)	C5B–Pd1B–C32B	79.60(15)
Pd1B–Cl1B	2.4492(10)	C5B–Pd1B–Cl1A	169.45(10)
		C32B–Pd1B–Cl1A	95.77(11)
		C5B–Pd1B–Cl1B	102.15(11)
		C32B–Pd1B–Cl1B	173.67(11)
		Cl1A–Pd1B–Cl1B	83.48(3)
		Pd1B–Cl1A–Pd1A	83.34(3)
		Pd1A–Cl1B–Pd1B	83.42(3)
Complex **2**			
Pd1A–C5A	1.980(3)	C5A–Pd1A–C32A	79.90(14)
Pd1A–C32A	2.031(4)	C5A–Pd1A–Br1A	169.18(10)
Pd1A–Br1A	2.4888(4)	C32A–Pd1A–Br1A	95.39(10)
Pd1A–Br1B	2.5611(4)	C5A–Pd1A–Br1B	101.62(10)

Pd1B–C5B	1.987(3)	C32A–Pd1A–Br1B	173.54(10)
Pd1B–C32B	2.021(3)	Br1A–Pd1A–Br1B	84.153(14)
Pd1B–Br1B	2.4997(4)	C5B–Pd1B–C32B	80.01(14)
Pd1B–Br1A	2.5601(4)	C5B–Pd1B–Br1B	170.70(10)
		C32B–Pd1B–Br1B	95.16(10)
		C5B–Pd1B–Br1A	101.50(10)
		C32B–Pd1B–Br1A	175.27(10)
		Br1B–Pd1B–Br1A	83.953(14)
		Pd1A–Br1A–Pd1B	82.759(14)
		Pd1B–Br1B–Pd1A	82.525(14)

Final coordinates and equivalent isotropic displacement parameters of different atoms:

Complex **1**

Atom	x	y	z	U(eq) [Ang^2]
Pd1A	0.49239(1)	0.20296(1)	0.16213(1)	0.0134(1)
Pd1B	0.49631(2)	0.22223(1)	0.08242(1)	0.0141(1)
Cl1A	0.53144(6)	0.14119(4)	0.11529(2)	0.0195(3)
Cl1B	0.55658(5)	0.27484(4)	0.12920(2)	0.0188(3)
N1A	0.38663(18)	0.09822(13)	0.18691(8)	0.0154(9)
N1B	0.42531(18)	0.34076(13)	0.05944(8)	0.0157(9)
N3A	0.33541(17)	0.13712(13)	0.23194(8)	0.0160(9)
N3B	0.36528(18)	0.31287(13)	0.01359(8)	0.0181(9)
C2A	0.3323(2)	0.09036(16)	0.21202(10)	0.0165(11)

C2B	0.3752(2)	0.35822(15)	0.03423(10)	0.0165(11)
C4A	0.3925(2)	0.17425(16)	0.21842(10)	0.0165(11)
C4B	0.4092(2)	0.26761(16)	0.02640(10)	0.0182(11)
C5A	0.4245(2)	0.15119(15)	0.18998(9)	0.0151(10)
C5B	0.4465(2)	0.28381(15)	0.05553(10)	0.0163(10)
C21A	0.2789(2)	0.04044(16)	0.21656(10)	0.0208(11)
C21B	0.3352(2)	0.41408(16)	0.03114(10)	0.0188(11)
C22A	0.1962(2)	0.04719(19)	0.22376(11)	0.0270(12)
C22B	0.2552(3)	0.41774(19)	0.01868(11)	0.0273(12)
C23A	0.1455(3)	0.0002(2)	0.22731(12)	0.0357(16)
C23B	0.2163(3)	0.4697(2)	0.01592(11)	0.0337(14)
C24A	0.1778(3)	-0.0542(2)	0.22385(12)	0.0390(17)
C24B	0.2557(3)	0.51912(19)	0.02508(11)	0.0307(12)
C25A	0.2601(3)	-0.06123(19)	0.21693(12)	0.0347(16)
C25B	0.3342(3)	0.51619(18)	0.03808(11)	0.0277(12)
C26A	0.3103(3)	-0.01401(17)	0.21305(11)	0.0277(12)
C26B	0.3740(2)	0.46409(16)	0.04083(10)	0.0217(12)
C31A	0.4200(2)	0.23081(15)	0.22773(10)	0.0164(10)
C31B	0.4190(2)	0.20847(16)	0.01625(10)	0.0211(11)
C32A	0.4692(2)	0.25361(15)	0.20174(10)	0.0158(10)
C32B	0.4593(2)	0.17789(16)	0.04193(10)	0.0189(11)
C33A	0.5019(2)	0.30782(15)	0.20662(10)	0.0195(11)
C33B	0.4744(3)	0.12052(17)	0.03650(11)	0.0267(12)
C34A	0.4881(2)	0.33744(16)	0.23643(10)	0.0215(11)
C34B	0.4523(3)	0.09447(18)	0.00631(12)	0.0363(16)
C35A	0.4409(2)	0.31416(16)	0.26165(11)	0.0212(11)

C35B	0.4146(3)	0.12571(19)	-0.01874(12)	0.0380(16)
C36A	0.4061(2)	0.26042(16)	0.25760(10)	0.0201(11)
C36B	0.3970(3)	0.18267(18)	-0.01398(11)	0.0297(12)
C41A	0.3961(2)	0.06115(15)	0.15804(10)	0.0168(11)
C41B	0.4475(2)	0.37509(16)	0.08811(9)	0.0170(11)
C42A	0.3428(2)	0.06898(17)	0.13139(10)	0.0209(11)
C42B	0.3886(2)	0.38485(17)	0.11249(10)	0.0210(12)
C43A	0.3561(3)	0.03566(18)	0.10317(11)	0.0277(12)
C43B	0.4095(3)	0.42142(19)	0.13851(11)	0.0310(12)
C44A	0.4197(3)	-0.00268(18)	0.10164(11)	0.0283(12)
C44B	0.4858(3)	0.44613(19)	0.13967(12)	0.0350(16)
C45A	0.4709(3)	-0.00979(17)	0.12872(11)	0.0247(12)
C45B	0.5444(3)	0.43335(17)	0.11618(11)	0.0287(14)
C46A	0.4606(2)	0.02189(16)	0.15798(10)	0.0190(11)
C46B	0.5270(2)	0.39715(15)	0.08939(10)	0.0180(11)
C47A	0.5185(2)	0.01443(16)	0.18751(10)	0.0211(11)
C47B	0.5917(2)	0.38127(17)	0.06331(11)	0.0224(11)
C48A	0.5355(3)	-0.04894(17)	0.19464(12)	0.0303(14)
C48B	0.6777(3)	0.3763(2)	0.07833(13)	0.0380(16)
C49A	0.5981(3)	0.0468(2)	0.18187(12)	0.0327(16)
C49B	0.5920(3)	0.4222(2)	0.03385(14)	0.0503(17)
C50A	0.2719(2)	0.11154(18)	0.13209(11)	0.0263(12)
C50B	0.3063(2)	0.35467(18)	0.11274(11)	0.0260(12)
C51A	0.1898(3)	0.0805(2)	0.13096(13)	0.0393(16)
C51B	0.2348(3)	0.3963(2)	0.11439(13)	0.0413(16)
C52A	0.2792(3)	0.1544(2)	0.10354(13)	0.0413(17)
C52B	0.3023(3)	0.3120(2)	0.14162(13)	0.0383(16)

C53A	0.2889(2)	0.14851(16)	0.26206(10)	0.0176(11)
C53B	0.3173(2)	0.30932(16)	-0.01715(10)	0.0201(11)
C54A	0.3147(2)	0.12477(17)	0.29227(11)	0.0223(11)
C54B	0.2391(2)	0.28490(17)	-0.01511(11)	0.0237(12)
C55A	0.2721(3)	0.13967(18)	0.32100(11)	0.0270(12)
C55B	0.1957(2)	0.27941(18)	-0.04519(12)	0.0274(14)
C56A	0.2068(3)	0.17710(18)	0.31958(12)	0.0300(14)
C56B	0.2294(3)	0.29592(18)	-0.07517(11)	0.0273(12)
C57A	0.1825(2)	0.19990(18)	0.28977(11)	0.0265(13)
C57B	0.3078(3)	0.31937(17)	-0.07628(11)	0.0250(12)
C58A	0.2224(2)	0.18643(16)	0.25975(11)	0.0212(11)
C58B	0.3535(2)	0.32656(16)	-0.04705(10)	0.0210(11)
C59A	0.1941(2)	0.21282(19)	0.22707(11)	0.0290(14)
C59B	0.4396(2)	0.35183(18)	-0.04846(11)	0.0267(12)
C60A	0.2021(3)	0.27781(19)	0.22727(13)	0.0377(16)
C60B	0.4906(3)	0.3265(2)	-0.07653(12)	0.0370(16)
C61A	0.1046(3)	0.1975(2)	0.21976(16)	0.053(2)
C61B	0.4349(3)	0.4164(2)	-0.05212(14)	0.0413(17)
C62A	0.3866(3)	0.08362(19)	0.29414(11)	0.0310(14)
C62B	0.2018(3)	0.2642(2)	0.01750(12)	0.0340(16)
C63A	0.4476(3)	0.1016(2)	0.32108(12)	0.0363(16)
C63B	0.1904(4)	0.1997(2)	0.01705(15)	0.0510(19)
C64A	0.3559(3)	0.02299(19)	0.30089(13)	0.0393(16)
C64B	0.1187(3)	0.2924(3)	0.02470(17)	0.061(2)
O1S	0.6282(3)	0.8384(2)	0.15418(14)	0.0950(16)
C2S	0.7548(5)	0.8756(3)	0.1769(2)	0.0950(16)

C3S	0.7065(5)	0.8240(3)	0.1588(2)	0.0950(16)
C4S	0.5781(5)	0.7938(3)	0.1392(2)	0.0950(16)
C5S	0.4903(5)	0.8119(3)	0.1352(2)	0.0950(16)
Cl1S	0.26012(8)	0.46569(5)	0.89170(3)	0.0460(4)
Cl2S	0.12846(9)	0.50161(5)	0.93611(3)	0.0470(4)
C1S	0.1877(3)	0.44378(19)	0.92185(13)	0.0393(16)

Atom	x	y	z	U(iso) [Ang^2]
H22A	0.17470	0.08350	0.22620	0.0320
H22B	0.22800	0.38480	0.01220	0.0330
H23A	0.09030	0.00510	0.23200	0.0430
H23B	0.16320	0.47140	0.00780	0.0400
H24A	0.14410	-0.08580	0.22620	0.0470
H24B	0.22990	0.55410	0.02260	0.0370
H25A	0.28190	-0.09760	0.21490	0.0420
H25B	0.36040	0.54920	0.04500	0.0330
H26A	0.36530	-0.01900	0.20800	0.0330
H26B	0.42690	0.46270	0.04920	0.0260
H33A	0.53330	0.32440	0.18990	0.0240
H33B	0.49960	0.09910	0.05310	0.0320
H34A	0.51090	0.37330	0.23930	0.0260
H34B	0.46310	0.05600	0.00300	0.0440
H35A	0.43240	0.33430	0.28140	0.0250
H35B	0.40100	0.10830	-0.03890	0.0450
H36A	0.37420	0.24460	0.27440	0.0240
H36B	0.37090	0.20350	-0.03060	0.0350
H43A	0.32120	0.03930	0.08490	0.0330
H43B	0.37170	0.42930	0.15520	0.0370

H44A	0.42810	-0.02380	0.08230	0.0340
H44B	0.49790	0.47190	0.15660	0.0420
H45A	0.51310	-0.03620	0.12750	0.0300
H45B	0.59630	0.44900	0.11810	0.0340
H47A	0.49190	0.03060	0.20730	0.0250
H47B	0.57710	0.34370	0.05450	0.0270
H48A	0.48470	-0.06860	0.19790	0.0460
H48B	0.56830	-0.05230	0.21450	0.0460
H48C	0.56400	-0.06540	0.17600	0.0460
H48D	0.71470	0.36240	0.06160	0.0570
H48E	0.67660	0.35050	0.09690	0.0570
H48F	0.69550	0.41310	0.08590	0.0570
H49A	0.62420	0.03300	0.16190	0.0490
H49B	0.63370	0.04110	0.20070	0.0490
H49C	0.58660	0.08660	0.17950	0.0490
H49D	0.53960	0.42140	0.02300	0.0760
H49E	0.63350	0.41100	0.01820	0.0760
H49F	0.60300	0.46000	0.04170	0.0760
H50A	0.27470	0.13250	0.15320	0.0310
H50B	0.30160	0.33330	0.09180	0.0310
H51A	0.18430	0.06110	0.10990	0.0590
H51B	0.14620	0.10750	0.13340	0.0590
H51C	0.18720	0.05330	0.14890	0.0590
H51D	0.23400	0.41450	0.13590	0.0620
H51E	0.18450	0.37610	0.11110	0.0620
H51F	0.24080	0.42450	0.09720	0.0620

H52A	0.33200	0.17210	0.10430	0.0620
H52B	0.23760	0.18290	0.10590	0.0620
H52C	0.27260	0.13520	0.08250	0.0620
H52D	0.34590	0.28500	0.13950	0.0580
H52E	0.25080	0.29240	0.14100	0.0580
H52F	0.30750	0.33180	0.16250	0.0580
H55A	0.28760	0.12430	0.34150	0.0320
H55B	0.14320	0.26430	-0.04490	0.0330
H56A	0.17930	0.18680	0.33910	0.0360
H56B	0.19980	0.29140	-0.09490	0.0330
H57A	0.13850	0.22490	0.28940	0.0320
H57B	0.32980	0.33030	-0.09670	0.0300
H59A	0.22800	0.19780	0.20890	0.0350
H59B	0.46690	0.34330	-0.02720	0.0320
H60A	0.16960	0.29320	0.24510	0.0560
H60B	0.18330	0.29280	0.20630	0.0560
H60C	0.25820	0.28810	0.23050	0.0560
H60D	0.49130	0.28580	-0.07440	0.0550
H60E	0.54540	0.34080	-0.07520	0.0550
H60F	0.46720	0.33670	-0.09770	0.0550
H61A	0.09700	0.15730	0.22250	0.0790
H61B	0.09140	0.20810	0.19720	0.0790
H61C	0.06960	0.21760	0.23500	0.0790
H61D	0.48900	0.43200	-0.05200	0.0620
H61E	0.40410	0.43200	-0.03380	0.0620
H61F	0.40850	0.42580	-0.07290	0.0620
H62A	0.41460	0.08390	0.27250	0.0370

H62B	0.23920	0.27380	0.03580	0.0410
H63A	0.46300	0.14060	0.31760	0.0540
H63B	0.49530	0.07800	0.31980	0.0540
H63C	0.42290	0.09770	0.34280	0.0540
H63D	0.15140	0.18960	0.00010	0.0760
H63E	0.17090	0.18720	0.03850	0.0760
H63F	0.24170	0.18170	0.01230	0.0760
H64A	0.33140	0.02130	0.32270	0.0590
H64B	0.40090	-0.00310	0.29990	0.0590
H64C	0.31600	0.01280	0.28430	0.0590
H64D	0.12480	0.33300	0.02420	0.0910
H64E	0.09970	0.28090	0.04640	0.0910
H64F	0.07990	0.28100	0.00800	0.0910
H4S1	0.58030	0.76020	0.15330	0.1140
H4S2	0.60030	0.78390	0.11750	0.1140
H5S1	0.48500	0.83490	0.11540	0.1420
H5S2	0.47370	0.83350	0.15440	0.1420
H5S3	0.45630	0.77890	0.13310	0.1420
H3S1	0.73180	0.81580	0.13740	0.1140
H3S2	0.70970	0.79010	0.17250	0.1140
H2S1	0.74810	0.90980	0.16410	0.1420
H2S2	0.81180	0.86640	0.17840	0.1420
H2S3	0.73310	0.88120	0.19900	0.1420
H1S1	0.21590	0.42660	0.94070	0.0470
H1S2	0.15210	0.41530	0.91210	0.0470

Complex **2**

Atom	x	y	z	U(eq) [Ang^2]
Pd1A	0.49655(2)	0.22274(1)	0.08098(1)	0.0112(1)
Pd1B	0.49296(1)	0.20203(1)	0.16333(1)	0.0103(1)
Br1A	0.53430(2)	0.13736(1)	0.11467(1)	0.0165(1)
Br1B	0.55916(2)	0.27882(1)	0.12948(1)	0.0157(1)
N1A	0.42336(17)	0.34136(12)	0.05848(7)	0.0117(8)
N1B	0.38725(17)	0.09655(12)	0.18736(7)	0.0119(8)
N3A	0.36390(18)	0.31350(13)	0.01312(7)	0.0155(8)
N3B	0.33494(17)	0.13539(12)	0.23180(7)	0.0123(8)
C2A	0.3728(2)	0.35899(16)	0.03367(9)	0.0156(10)
C2B	0.3325(2)	0.08840(15)	0.21219(9)	0.0138(10)
C4A	0.4082(2)	0.26802(15)	0.02551(8)	0.0145(10)
C4B	0.3920(2)	0.17271(15)	0.21880(8)	0.0125(10)
C5A	0.4455(2)	0.28470(14)	0.05460(8)	0.0127(9)
C5B	0.4247(2)	0.14934(15)	0.19036(8)	0.0118(9)
C21A	0.3322(2)	0.41478(16)	0.03075(8)	0.0171(10)
C21B	0.2792(2)	0.03816(16)	0.21638(9)	0.0166(10)
C22A	0.2526(3)	0.41765(18)	0.01837(9)	0.0243(11)
C22B	0.3098(3)	-0.01668(17)	0.21335(10)	0.0243(12)
C23A	0.2125(3)	0.46969(19)	0.01594(10)	0.0300(14)
C23B	0.2593(3)	-0.06370(18)	0.21685(10)	0.0310(14)
C24A	0.2510(3)	0.51948(18)	0.02554(9)	0.0290(14)

C24B	0.1776(3)	-0.05629(19)	0.22294(10)	0.0320(14)
C25A	0.3289(3)	0.51712(17)	0.03819(9)	0.0238(11)
C25B	0.1460(3)	-0.0018(2)	0.22587(10)	0.0307(14)
C26A	0.3693(2)	0.46559(16)	0.04089(9)	0.0200(11)
C26B	0.1967(2)	0.04561(18)	0.22284(10)	0.0230(12)
C31A	0.4191(2)	0.20920(15)	0.01524(9)	0.0169(10)
C31B	0.4194(2)	0.22925(15)	0.22850(8)	0.0131(9)
C32A	0.4598(2)	0.17772(16)	0.04037(9)	0.0172(10)
C32B	0.4699(2)	0.25262(15)	0.20310(8)	0.0130(9)
C33A	0.4759(3)	0.12054(16)	0.03455(10)	0.0235(11)
C33B	0.5027(2)	0.30653(15)	0.20889(9)	0.0174(10)
C34A	0.4536(3)	0.09523(17)	0.00426(10)	0.0299(14)
C34B	0.4884(2)	0.33563(15)	0.23891(9)	0.0182(10)
C35A	0.4156(3)	0.12672(18)	-0.02024(11)	0.0317(14)
C35B	0.4395(2)	0.31220(15)	0.26314(9)	0.0186(10)
C36A	0.3979(3)	0.18391(17)	-0.01510(10)	0.0251(11)
C36B	0.4050(2)	0.25855(16)	0.25825(9)	0.0161(10)
C41A	0.4458(2)	0.37701(15)	0.08672(8)	0.0133(9)
C41B	0.3971(2)	0.05861(15)	0.15886(8)	0.0135(10)
C42A	0.3882(2)	0.38556(16)	0.11181(9)	0.0172(10)
C42B	0.3442(2)	0.06618(16)	0.13208(9)	0.0176(11)
C43A	0.4096(3)	0.42334(18)	0.13718(10)	0.0268(11)
C43B	0.3585(2)	0.03249(17)	0.10422(9)	0.0223(11)
C44A	0.4845(3)	0.44974(19)	0.13757(10)	0.0323(14)
C44B	0.4215(3)	-0.00637(17)	0.10327(9)	0.0238(11)
C45A	0.5419(3)	0.43753(16)	0.11327(10)	0.0265(11)

C45B	0.4719(2)	-0.01321(16)	0.13049(9)	0.0209(11)
C46A	0.5240(2)	0.40016(15)	0.08737(9)	0.0163(10)
C46B	0.4610(2)	0.01954(15)	0.15935(9)	0.0154(10)
C47A	0.5870(2)	0.38436(17)	0.06101(9)	0.0203(11)
C47B	0.5177(2)	0.01233(15)	0.18889(9)	0.0175(11)
C48A	0.6741(3)	0.3860(2)	0.07416(13)	0.0400(16)
C48B	0.5967(2)	0.04514(19)	0.18375(10)	0.0273(12)
C49A	0.5795(3)	0.4207(2)	0.02968(12)	0.0413(17)
C49B	0.5357(3)	-0.05078(17)	0.19612(10)	0.0263(12)
C50A	0.3074(2)	0.35420(18)	0.11251(10)	0.0229(11)
C50B	0.2749(2)	0.10914(18)	0.13218(10)	0.0223(11)
C51A	0.2356(3)	0.3954(2)	0.11450(12)	0.0377(16)
C51B	0.1924(3)	0.0781(2)	0.13097(11)	0.0343(14)
C52A	0.3065(3)	0.3120(2)	0.14184(11)	0.0347(14)
C52B	0.2825(3)	0.1518(2)	0.10351(12)	0.0357(16)
C53A	0.3166(2)	0.30934(15)	-0.01748(9)	0.0161(10)
C53B	0.2884(2)	0.14636(15)	0.26194(9)	0.0149(10)
C54A	0.3534(2)	0.32629(16)	-0.04715(9)	0.0182(11)
C54B	0.3160(2)	0.12316(16)	0.29187(9)	0.0192(11)
C55A	0.3084(2)	0.31809(17)	-0.07642(9)	0.0216(11)
C55B	0.2742(3)	0.13903(18)	0.32063(9)	0.0248(11)
C56A	0.2315(2)	0.29432(17)	-0.07557(9)	0.0239(11)
C56B	0.2091(2)	0.17559(17)	0.31937(10)	0.0247(12)
C57A	0.1972(2)	0.27769(17)	-0.04550(10)	0.0238(11)
C57B	0.1833(2)	0.19814(17)	0.28944(10)	0.0233(11)
C58A	0.2394(2)	0.28471(16)	-0.01559(9)	0.0194(11)
C58B	0.2223(2)	0.18421(16)	0.25953(9)	0.0172(10)

C59A	0.2017(2)	0.26412(19)	0.01704(10)	0.0273(14)
C59B	0.1929(2)	0.20982(18)	0.22698(10)	0.0242(11)
C60A	0.1176(3)	0.2902(2)	0.02308(15)	0.054(2)
C60B	0.2035(3)	0.27487(19)	0.22624(11)	0.0317(12)
C61A	0.1946(3)	0.1994(2)	0.01775(13)	0.0440(17)
C61B	0.1029(3)	0.1962(2)	0.22103(13)	0.0390(16)
C62A	0.4381(2)	0.35207(17)	-0.04851(9)	0.0211(11)
C62B	0.3876(3)	0.08237(18)	0.29381(9)	0.0256(11)
C63A	0.4902(3)	0.3264(2)	-0.07606(10)	0.0317(14)
C63B	0.4492(3)	0.1012(2)	0.32036(11)	0.0333(14)
C64A	0.4336(3)	0.41693(19)	-0.05207(12)	0.0340(14)
C64B	0.3580(3)	0.02128(19)	0.30039(11)	0.0367(14)
O3S	0.8739(3)	0.33752(17)	0.15329(10)	0.0583(14)
C1S	0.7478(4)	0.3765(4)	0.1735(2)	0.102(4)
C2S	0.7952(4)	0.3245(3)	0.15548(19)	0.077(3)
C4S	0.9214(5)	0.2930(3)	0.1388(2)	0.089(3)
C5S	1.0102(5)	0.3106(4)	0.1361(2)	0.116(4)
Cl1S	0.75698(8)	0.03666(5)	0.10963(3)	0.0399(4)
Cl2S	0.62829(8)	0.00003(5)	0.06470(3)	0.0398(4)
C6S	0.6965(3)	0.05511(18)	0.07502(11)	0.0300(12)

Atom	x	y	z	U(iso) [Ang^2]
H22A	0.22640	0.38430	0.01170	0.0290
H22B	0.36480	-0.02200	0.20890	0.0290
H23A	0.15950	0.47100	0.00780	0.0360

H23B	0.28070	-0.10040	0.21510	0.0370
H24A	0.22450	0.55450	0.02350	0.0350
H24B	0.14370	-0.08790	0.22510	0.0380
H25A	0.35450	0.55060	0.04500	0.0280
H25B	0.09070	0.00320	0.22990	0.0370
H26A	0.42180	0.46470	0.04950	0.0240
H26B	0.17550	0.08230	0.22510	0.0280
H33A	0.50170	0.09880	0.05080	0.0280
H33B	0.53470	0.32360	0.19260	0.0210
H34A	0.46450	0.05670	0.00060	0.0360
H34B	0.51220	0.37120	0.24250	0.0220
H35A	0.40170	0.10940	-0.04030	0.0380
H35B	0.42960	0.33220	0.28280	0.0220
H36A	0.37230	0.20520	-0.03160	0.0300
H36B	0.37240	0.24230	0.27470	0.0190
H43A	0.37260	0.43090	0.15420	0.0320
H43B	0.32470	0.03620	0.08570	0.0270
H44A	0.49660	0.47600	0.15430	0.0390
H44B	0.43010	-0.02810	0.08420	0.0290
H45A	0.59290	0.45460	0.11430	0.0320
H45B	0.51380	-0.04000	0.12970	0.0250
H47A	0.57600	0.34470	0.05440	0.0240
H47B	0.49050	0.02840	0.20850	0.0210
H48A	0.71000	0.36930	0.05800	0.0600
H48B	0.67720	0.36470	0.09460	0.0600
H48C	0.68970	0.42490	0.07820	0.0600

H48D	0.62240	0.03240	0.16360	0.0410
H48E	0.63230	0.03840	0.20230	0.0410
H48F	0.58510	0.08530	0.18220	0.0410
H49A	0.58760	0.46020	0.03530	0.0620
H49B	0.52630	0.41580	0.02020	0.0620
H49C	0.61990	0.40900	0.01380	0.0620
H49D	0.48550	-0.07150	0.19790	0.0400
H49E	0.56520	-0.05390	0.21670	0.0400
H49F	0.56780	-0.06650	0.17830	0.0400
H50A	0.30250	0.33220	0.09180	0.0280
H50B	0.27760	0.13060	0.15320	0.0270
H51A	0.23840	0.41660	0.13500	0.0560
H51B	0.18570	0.37420	0.11380	0.0560
H51C	0.23760	0.42150	0.09600	0.0560
H51D	0.18760	0.05780	0.11020	0.0510
H51E	0.14920	0.10550	0.13270	0.0510
H51F	0.18900	0.05150	0.14920	0.0510
H52A	0.35100	0.28570	0.13960	0.0520
H52B	0.25610	0.29130	0.14190	0.0520
H52C	0.31190	0.33270	0.16240	0.0520
H52D	0.33470	0.17020	0.10450	0.0540
H52E	0.24040	0.18010	0.10540	0.0540
H52F	0.27710	0.13210	0.08260	0.0540
H55A	0.33060	0.32880	-0.09680	0.0260
H55B	0.29080	0.12450	0.34110	0.0290
H56A	0.20250	0.28940	-0.09530	0.0290
H56B	0.18200	0.18530	0.33890	0.0300

H57A	0.14540	0.26160	-0.04530	0.0290
H57B	0.13920	0.22300	0.28910	0.0280
H59A	0.23750	0.27590	0.03540	0.0330
H59B	0.22480	0.19330	0.20870	0.0290
H60A	0.08120	0.27850	0.00560	0.0810
H60B	0.12180	0.33120	0.02320	0.0810
H60C	0.09700	0.27740	0.04420	0.0810
H60D	0.17360	0.29170	0.24430	0.0480
H60E	0.18350	0.28960	0.20550	0.0480
H60F	0.26020	0.28420	0.22850	0.0480
H61A	0.16030	0.18690	-0.00020	0.0660
H61B	0.17130	0.18760	0.03860	0.0660
H61C	0.24760	0.18270	0.01530	0.0660
H61D	0.09420	0.15570	0.22330	0.0580
H61E	0.08780	0.20800	0.19900	0.0580
H61F	0.07030	0.21620	0.23710	0.0580
H62A	0.46490	0.34370	-0.02720	0.0250
H62B	0.41520	0.08270	0.27210	0.0310
H63A	0.49040	0.28550	-0.07400	0.0480
H63B	0.54480	0.34060	-0.07420	0.0480
H63C	0.46820	0.33700	-0.09740	0.0480
H63D	0.46360	0.14050	0.31670	0.0500
H63E	0.49700	0.07780	0.31890	0.0500
H63F	0.42540	0.09710	0.34210	0.0500
H64A	0.40940	0.42650	-0.07310	0.0510
H64B	0.48750	0.43270	-0.05100	0.0510

H64C	0.40120	0.43240	-0.03430	0.0510
H64D	0.33360	0.01930	0.32210	0.0550
H64E	0.40320	-0.00460	0.29930	0.0550
H64F	0.31840	0.01080	0.28380	0.0550
H5S1	1.01780	0.33310	0.11630	0.1730
H5S2	1.04370	0.27700	0.13490	0.1730
H5S3	1.02510	0.33280	0.15530	0.1730
H1S1	0.76700	0.38040	0.19600	0.1530
H1S2	0.69050	0.36860	0.17370	0.1530
H1S3	0.75780	0.41130	0.16150	0.1530
H2S1	0.78840	0.28970	0.16830	0.0920
H2S2	0.77300	0.31830	0.13340	0.0920
H4S1	0.90050	0.28420	0.11680	0.1070
H4S2	0.91710	0.25880	0.15240	0.1070
H6S1	0.66610	0.08960	0.08000	0.0360
H6S2	0.73130	0.06300	0.05600	0.0360

Computational Details:

The DFT optimized (BP86/6-31G(d) level) structure of complex **1** is shown in Fig. 4. The optimized structure shows a good resemblance with the X-ray crystal structure data. In solution mixture the dimeric Pd(II) complex will dissociate to form the three-coordinated monomeric Pd(II) species ($\mathbf{1_m}$). All calculations are performed in Gaussian03 quantum code.[5] The geometries of all the compounds are optimized with the generalized approximation (GGA) to

DFT by using the exchange functional of the Becke[6] in addition with the correlation functional of Perdew[7] (BP86).

Standard 6-31G(d) basis[8] was used for all the atoms, except for palladium which was described by the LANL2DZ valence basis set in combination with the corresponding effective core potential.[9] In all our DFT treatments, the resolution-of-the-identity (RI) approximation (also called "density fitting") for the two electron integrals was employed.[10] The geometries were optimized without any symmetry constraints. For validation, single-point BP86 calculations were performed at the optimized BP86/6-31G(d) geometries employing larger basis sets: Palladium was described by LANL2TZ effective core potential and the associate (5s5p4d)/[5s5p3d] valence basis set;[9] TZVP (triple-ζ valence polarization) basis was employed for N, Cl and C atoms coordinated to the metal center and the imidazole ring,[11] H and rest of the C atoms using SVP basis.[11] The charge distribution around the metal center was analyzed using Weinhold's NPA (Natural Population Analysis) approach.[12] Wiberg bond indices were also calculated to quantify covalent interactions.[13] We have applied Bader's AIM (Atoms-in-molecule) concept[14] to characterize the electron distribution in the Pd(II) complex. Any bonded pair of atoms has a bond path, i.e. a connecting line with maximum electron density. The bond critical point (BCP) is a point on this line where the gradient $\nabla\rho$ of the density is equal to zero. The magnitude of the electron density (ρ) and its Laplacian ($\nabla^2\rho$) at the BCP provide information about the strength and type of bond. The Laplacian indicates whether the density is locally concentrated ($\nabla^2\rho<0$) or depleted ($\nabla^2\rho>0$). Natural bond orbitals are plotted in the Chemcraft visualization software.[15]

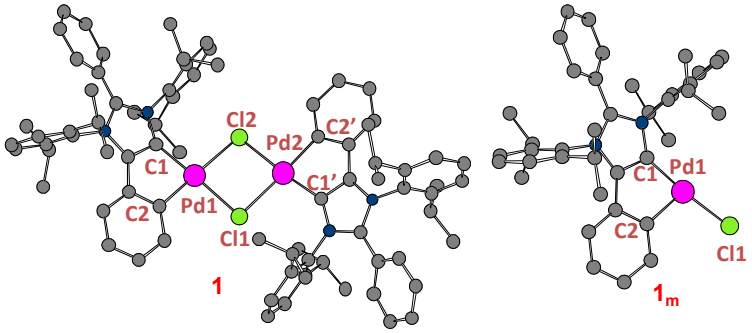


Fig. 4. DFT optimized structures of **1** and $\mathbf{1_m}$. Hydrogen atoms are removed for clarity. Color code: C grey, Cl green, N blue and Pd pink.

Table 4. Cartesian coordinates (Å) of the DFT optimized structures.

1	172			
	XYZ			
	Pd	1.50754	17.58908	16.89255
	Pd	1.59783	16.78095	13.32648
	Cl	0.97729	18.71876	14.71160
	Cl	1.39335	15.55521	15.51160
	N	2.33001	13.93147	12.08967
	N	1.51659	20.53946	18.11033
	N	3.04332	14.62332	10.11734
	C	5.37887	15.20434	7.25557
	H	6.41092	15.52656	7.07642
	C	-0.50918	13.26111	12.47655
	H	-0.04110	13.81602	11.64328
	N	2.40326	20.05774	20.07543
	C	1.83988	17.83465	11.61168
	C	1.69402	19.15342	18.11715
	C	0.94240	21.28373	17.00140
	C	2.38657	17.13431	10.48538
	C	1.52546	19.19395	11.45799
	H	1.10749	19.75492	12.30006
	C	1.74579	19.84838	10.22761
	H	1.49003	20.91096	10.12877
	C	2.16360	15.31870	12.09184
	C	2.21882	18.86426	19.38089

C	2.38363	17.46096	19.72551
C	2.28372	19.15441	9.13275
H	2.45138	19.66741	8.17859
C	2.87321	13.49299	10.89338
C	2.99962	12.61024	14.06696
C	3.56756	14.68237	8.76562
C	2.60545	17.79240	9.25568
H	3.01777	17.25176	8.39750
C	1.97524	13.06699	13.20383
C	1.93680	22.52701	19.67152
C	2.98309	20.14802	21.40229
C	2.69882	14.38810	7.68492
C	2.58448	15.73326	10.82393
C	1.95377	21.10647	19.29643
C	3.19189	12.11312	10.50356
C	0.60628	12.73954	13.38864
C	2.07194	15.24480	18.76751
H	1.80803	14.59048	17.93040
C	2.12007	20.28428	22.51833
C	4.91354	15.10101	8.58102
C	1.80839	21.98974	16.13204
C	4.39504	20.04421	21.52842
C	0.28807	11.89862	14.47223
H	-0.75985	11.63269	14.65089
C	-1.34644	12.11525	11.85977
H	-0.72637	11.41393	11.27265
H	-2.11528	12.53316	11.18476
H	-1.87269	11.53081	12.63646
C	-0.46671	21.25514	16.83186
C	2.02631	16.63842	18.60614
C	2.62013	11.76290	15.12646
H	3.38853	11.39247	15.81426
C	1.21446	22.72341	15.08650
H	1.85628	23.28031	14.39446
C	2.76706	16.88840	20.95740
H	3.03042	17.52284	21.81015
C	-0.17316	22.73582	14.90433
H	-0.61224	23.30894	14.07956
C	2.96814	23.08898	20.47042
H	3.79783	22.46515	20.80734
C	4.46402	13.02431	13.91354
H	4.54304	13.68627	13.03224
C	1.28172	11.40732	15.32835
H	1.00852	10.75418	16.16514
C	2.94353	24.44163	20.83357
H	3.75680	24.84374	21.44812
C	-1.42124	14.25837	13.22914
H	-1.93766	13.76790	14.07485
H	-2.19143	14.65808	12.54376
H	-0.83577	15.10323	13.62984

C	4.54810	14.90886	6.16681
H	4.93353	14.99798	5.14465
C	1.90052	25.27844	20.40486
H	1.88700	26.33724	20.68589
C	4.93077	20.10731	22.82986
H	6.01590	20.03277	22.96329
C	0.88752	23.38645	19.24909
H	0.07713	22.99425	18.63231
C	0.87680	24.73985	19.60874
H	0.05215	25.37492	19.26635
C	2.38452	11.02313	10.92452
H	1.51140	11.20364	11.55383
C	4.10519	20.25948	23.95152
H	4.54636	20.30615	24.95374
C	4.31470	11.82460	9.68324
H	4.96519	12.63342	9.34619
C	2.45750	14.67568	19.99970
H	2.48260	13.58360	20.10459
C	2.69257	9.71099	10.54399
H	2.04877	8.89273	10.88543
C	2.71664	20.34280	23.79378
H	2.07645	20.44843	24.67674
C	1.23451	13.98919	7.87981
H	1.04069	13.90832	8.96385
C	3.22497	14.50583	6.38264
H	2.57880	14.28683	5.52512
C	3.80301	9.44312	9.72706
H	4.03852	8.41540	9.42951
C	-1.00023	22.00168	15.76351
H	-2.08375	21.99695	15.59931
C	0.59632	20.32736	22.38766
H	0.34318	20.35952	21.31319
C	2.80338	15.49020	21.08912
H	3.09840	15.04250	22.04526
C	0.28877	15.08049	7.32386
H	0.42180	15.20978	6.23385
H	0.47299	16.05481	7.80883
H	-0.76457	14.79895	7.50372
C	4.93449	13.84091	15.14062
H	4.27523	14.70784	15.31643
H	5.96721	14.20304	14.98246
H	4.93264	13.22241	16.05703
C	0.93050	12.60961	7.25154
H	1.06959	12.62366	6.15495
H	-0.11932	12.32712	7.44918
H	1.58317	11.82377	7.66886
C	4.60890	10.51026	9.29896
H	5.48488	10.32205	8.66807
C	-1.40650	20.45671	17.74185
H	-0.80013	19.98189	18.53368

C	3.33213	21.94991	16.26011
H	3.58688	21.34028	17.14549
C	5.33554	19.86209	20.33103
H	4.72693	19.85296	19.40931
C	5.85152	15.44511	9.74442
H	5.32589	15.21924	10.68964
C	6.19707	16.95384	9.75727
H	6.84953	17.18434	10.61875
H	5.28958	17.57500	9.83714
H	6.73585	17.24624	8.83680
C	-0.03757	19.04104	22.97022
H	0.35443	18.13896	22.46900
H	-1.13413	19.06150	22.83449
H	0.16725	18.94780	24.05280
C	3.93037	23.35948	16.47376
H	3.73599	24.01337	15.60384
H	5.02677	23.29280	16.59851
H	3.50988	23.84997	17.36875
C	-2.45585	21.36055	18.43208
H	-3.10121	20.75343	19.09272
H	-3.11183	21.85685	17.69362
H	-1.98710	22.14816	19.04958
C	-2.09985	19.31785	16.95721
H	-2.74126	18.72685	17.63660
H	-1.35617	18.64337	16.50046
H	-2.73848	19.72083	16.14937
C	6.07882	18.50641	20.40328
H	6.70900	18.37466	19.50536
H	5.37157	17.66176	20.45255
H	6.73960	18.45819	21.28873
C	3.96381	21.25325	15.03100
H	3.53052	20.25037	14.87687
H	5.05621	21.15355	15.17071
H	3.79533	21.84021	14.10929
C	5.38261	11.80499	13.66691
H	5.36936	11.11212	14.52834
H	6.42751	12.13746	13.52602
H	5.07651	11.23786	12.77082
C	7.14720	14.59975	9.71566
H	6.93884	13.51587	9.74610
H	7.77428	14.84694	10.59100
H	7.74673	14.80425	8.81000
C	-0.00399	21.59321	23.04128
H	-1.09703	21.61773	22.88164
H	0.42755	22.51335	22.61160
H	0.17107	21.61043	24.13270
C	6.35047	21.02467	20.21173
H	7.00380	21.08483	21.10136
H	5.85128	22.00206	20.08995
H	6.99956	20.86681	19.33168

1_m

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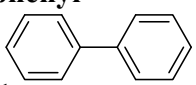
xyz

Pd	1.25412	17.78085	16.90649
Cl	0.80764	16.17372	15.25682
N	1.42839	20.66719	18.19553
N	2.38233	20.12929	20.11373
C	1.58283	19.28392	18.17063
C	0.91407	21.38799	17.04221
C	2.16225	18.95699	19.39537
C	2.36784	17.53891	19.63752
C	1.90349	22.61403	19.77860
C	2.98482	20.16886	21.43426
C	1.91596	21.20348	19.37692
C	2.05935	15.38690	18.49963
H	1.75646	14.81127	17.62107
C	2.13561	20.23316	22.56717
C	1.83793	21.98434	16.14791
C	4.40005	20.08230	21.53228
C	-0.48679	21.38067	16.81135
C	1.96550	16.78316	18.48881
C	1.31209	22.61796	15.00464
H	1.99904	23.08440	14.28978
C	2.84134	16.87185	20.78688
H	3.13484	17.44150	21.67514
C	-0.06520	22.64129	14.75487
H	-0.44973	23.13157	13.85342
C	2.91537	23.16266	20.61046
H	3.73364	22.53253	20.96324
C	2.88270	24.51103	20.98791
H	3.67929	24.90479	21.62893
C	1.85243	25.35459	20.54178
H	1.83350	26.40987	20.83496
C	4.95414	20.08655	22.82769
H	6.04206	20.02338	22.94218
C	0.86401	23.47850	19.34235
H	0.06292	23.09100	18.70982
C	0.84665	24.82780	19.71542
H	0.03045	25.46821	19.36315
C	4.14300	20.16697	23.96726
H	4.59886	20.16879	24.96386
C	2.54531	14.73546	19.65474
H	2.61670	13.64129	19.65961
C	2.75098	20.23661	23.83508
H	2.12397	20.28696	24.73212
C	-0.95069	22.02382	15.64691
H	-2.02530	22.03028	15.43371
C	0.60955	20.26078	22.46014
H	0.33937	20.32903	21.39135
C	2.92884	15.46935	20.78798
H	3.29655	14.95141	21.68095

C	-1.48438	20.69976	17.75351
H	-0.93475	20.36388	18.65163
C	3.35263	21.91115	16.34898
H	3.54925	21.47925	17.34658
C	5.32356	19.98448	20.31234
H	4.69933	20.02219	19.40143
C	-0.00059	18.94609	23.00329
H	0.39283	18.06773	22.46263
H	-1.09910	18.95867	22.88483
H	0.22139	18.81430	24.07827
C	4.01320	23.30771	16.31861
H	3.90868	23.78887	15.32911
H	5.09451	23.21952	16.52828
H	3.56857	23.98005	17.07278
C	-2.59847	21.66506	18.22266
H	-3.26214	21.15114	18.94103
H	-3.22649	22.00577	17.37963
H	-2.18921	22.56178	18.72207
C	-2.09488	19.44167	17.09140
H	-2.80598	18.95286	17.78193
H	-1.31063	18.70368	16.83585
H	-2.63914	19.69969	16.16470
C	6.08783	18.63877	20.29118
H	6.71483	18.57587	19.38376
H	5.39539	17.78061	20.28828
H	6.75449	18.54280	21.16803
C	3.98675	20.95922	15.30616
H	3.55029	19.94696	15.37548
H	5.07653	20.87838	15.47264
H	3.82707	21.33032	14.27734
C	0.00447	21.49436	23.16883
H	-1.09093	21.51216	23.02558
H	0.41996	22.43470	22.76782
H	0.19510	21.47274	24.25740
C	6.31898	21.16794	20.24712
H	6.99525	21.17737	21.12126
H	5.80297	22.14322	20.20681
H	6.94719	21.08098	19.34247

^{1}H and ^{13}C data for Suzuki-Miyaura Product:

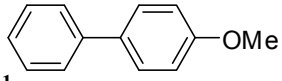
Biphenyl



^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.73-7.76 (d, J = 8.3 Hz, 4H), 7.56-7.60 (t, J_1 = 7.4 Hz, J_2 = 7.7 Hz, 4H), 7.47-7.51 (t, J_1 = 7.8 Hz, J_2 = 6.9 Hz, 2H)

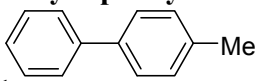
ppm.
^{13}C NMR ($CDCl_3$, 125 MHz): δ 141.2, 128.7, 127.2, 127.1 ppm.
Eluent: Hexane:Ethyl acetate = 100:1

4-Methoxybiphenyl



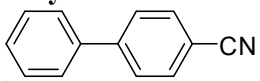
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66-7.71 (m, 4H), 7.53-7.57 (t, J_1 = 7.3 Hz, J_2 = 7.8 Hz, 2H), 7.42-7.46 (t, J_1 = 7.4 Hz, J_2 = 7.8 Hz, 1H), 7.09-7.13 (d, J = 8.7 Hz, 2H), 3.93 (s, 3H) ppm.
^{13}C NMR ($CDCl_3$, 100 MHz): δ 159.1, 140.8, 133.8, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3 ppm.
Eluent: Hexane:Ethyl acetate = 100:2.5

4-Methylbiphenyl



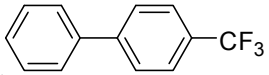
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.70-7.72 (d, J = 8.0 Hz, 2H), 7.62-7.64 (d, J = 7.9 Hz, 2H), 7.53-7.57 (t, J_1 = 8.1 Hz, J_2 = 6.7 Hz, 2H), 7.43-7.47 (t, J = 7.3 Hz, 1H), 7.36-7.38 (d, J = 7.9 Hz, 2H), 2.52 (s, 3H) ppm.
^{13}C NMR ($CDCl_3$, 100 MHz): δ 141.1, 138.3, 136.9, 129.4, 128.7, 126.9, 21.0 ppm.
Eluent: Hexane:Ethyl acetate = 100:1.5

Biphenyl-4-carbonitrile



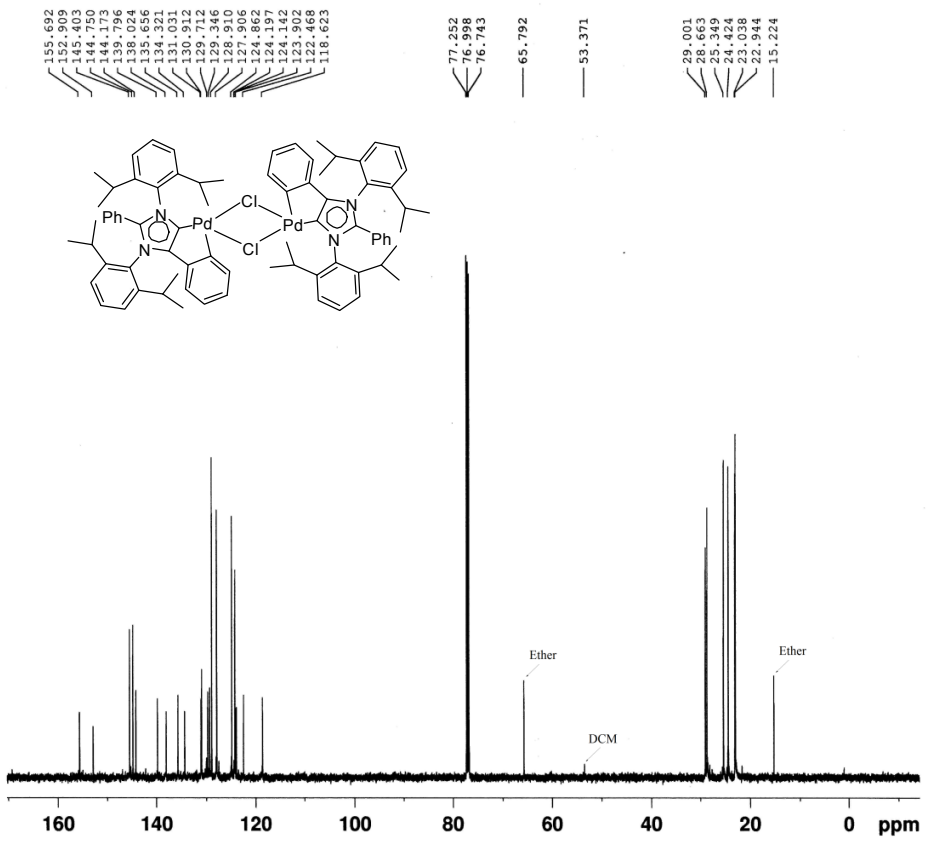
^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.67-7.74 (m, 4H), 7.58-7.60 (d, J = 7.9 Hz, 2H), 7.41-7.51 (m, 3H) ppm.
^{13}C NMR ($CDCl_3$, 100 MHz): δ 145.6, 139.1, 132.5, 129.1, 128.6, 127.7, 127.2, 118.9, 110.9 ppm.
Eluent: Hexane:Ethyl acetate = 100:2

4-(Trifluoromethyl)biphenyl

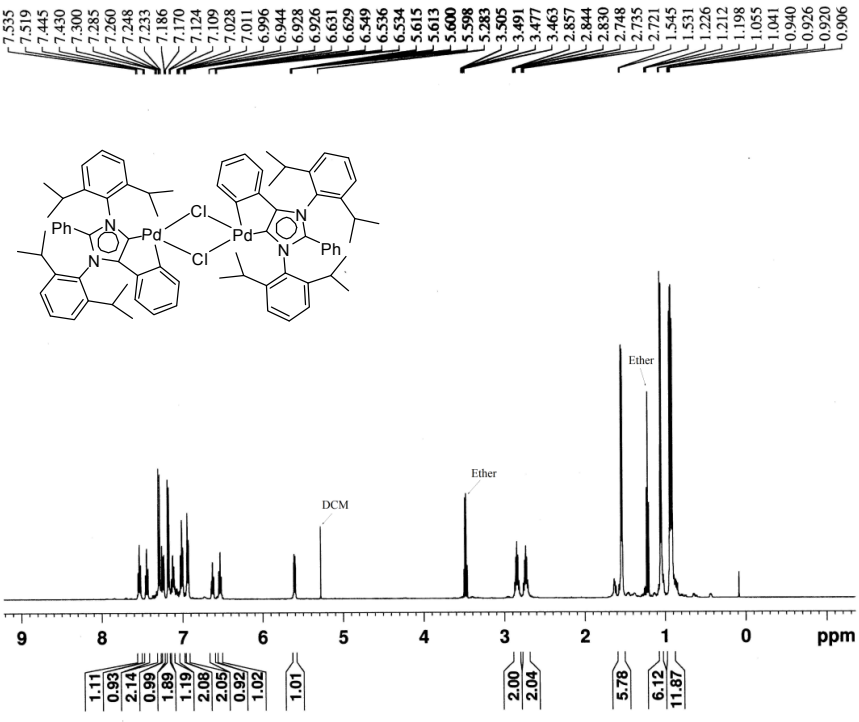


^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.71 (s, 4H), 7.61-7.63 (m, 2H), 7.48-7.52 (t, J_1 = 7.3 Hz, J_2 = 6.1 Hz, 2H), 7.41-7.45 (m, 1H) ppm.
^{13}C NMR ($CDCl_3$, 100 MHz): δ 144.7, 139.7, 128.9, 128.2, 127.4, 127.3, 125.7, 125.6 ppm.
Eluent: Hexane:Ethyl acetate = 100:2.5

^{1}H and ^{13}C NMR spectra of complex **1**

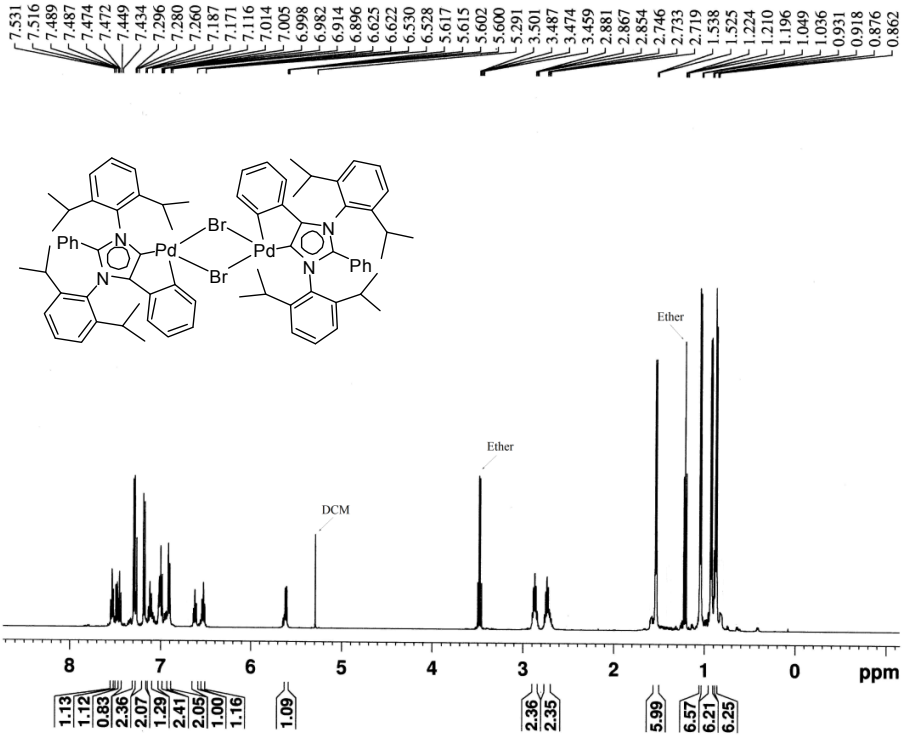



```
NAME            Jul19-2011
EXPNO                   11
PROCNO                   1
Date_             20110719
Time                 9.49
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG            zgpg30
TD                  65536
SOLVENT             CDCl3
NS                    245
DS                      4
SWH             29761.904 Hz
FIDRES          0.454131 Hz
AQ              1.1010548 sec
RG                    203
DW                16.800 usec
DE                 6.50 usec
TE                300.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.50 usec
PL1                -0.50 dB
PL1W         90.18825531 W
SFO1        125.7753938 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                  1H
PCPD2              80.00 usec
PL2                 1.30 dB
PL12               16.00 dB
PL13               20.00 dB
PL2W         15.30635643 W
PL12W         0.51864696 W
PL13W         0.20647706 W
SFO2        500.1520006 MHz
SI                  32768
SF          125.7628267 MHz
WDW                    EM
SSB                     0
LB                 1.00 Hz
GB                      0
PC                 1.40
```

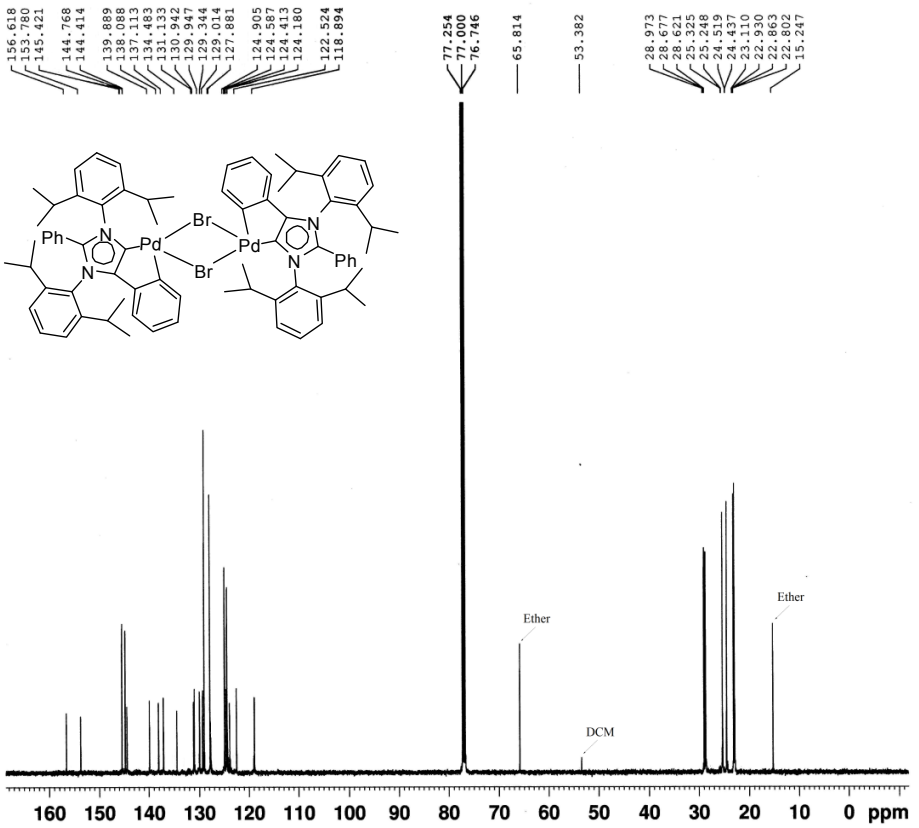



```
NAME            Jul19-2011
EXPNO                   10
PROCNO                   1
Date_             20110719
Time                 9.44
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG             zg30
TD                  65536
SOLVENT             CDCl3
NS                      8
DS                      2
SWH             10330.578 Hz
FIDRES          0.157632 Hz
AQ              3.1719923 sec
RG                     36
DW                48.400 usec
DE                 6.50 usec
TE                299.2 K
D1             1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                 14.25 usec
PL1                 1.30 dB
PL1W         15.30635643 W
SFO1        500.1530886 MHz
SI                  32768
SF          500.1500126 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                 1.00
```

^{1}H and ^{13}C NMR spectra of complex **2**

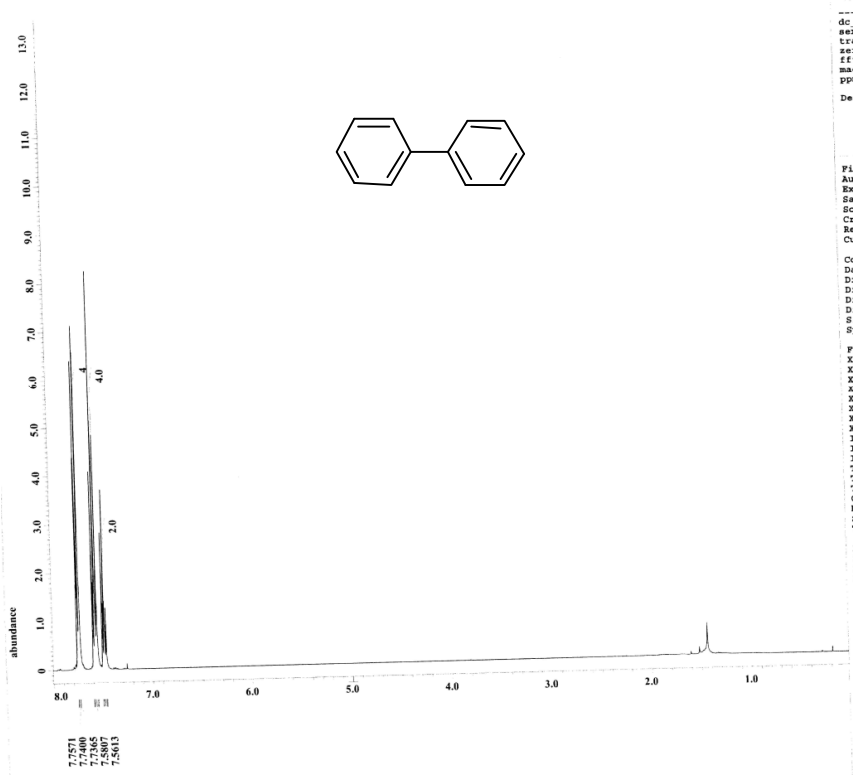



```
NAME            Jun27-2011
EXPNO                   20
PROCNO                   1
Date_             20110627
Time                 11.13
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                   65536
SOLVENT              CDCl3
NS                      19
DS                       2
SWH              10330.578 Hz
FIDRES           0.157632 Hz
AQ               3.1719923 sec
RG                    45.2
DW                  48.400 usec
DE                   6.50 usec
TE                  298.7 K
D1             1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.25 usec
PL1                   1.30 dB
PL1W         15.30635643 W
SFO1         500.1530886 MHz
SI                   32768
SF           500.1500126 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```



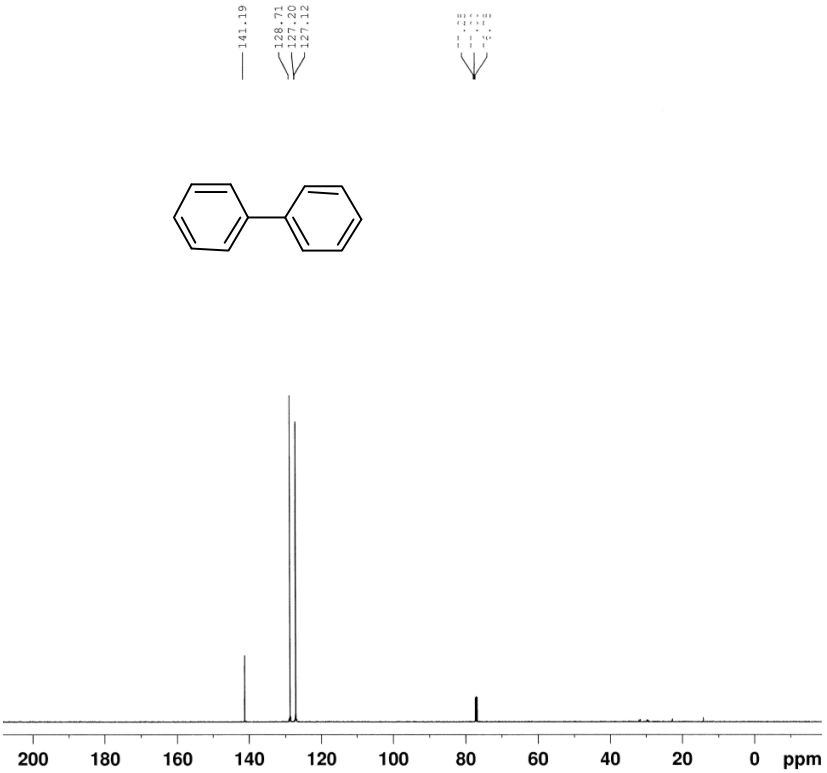

```
NAME            Jun27-2011
EXPNO                   21
PROCNO                   1
Date_             20110627
Time                 11.26
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG             zgpg30
TD                   65536
SOLVENT              CDCl3
NS                    2000
DS                       4
SWH              29761.904 Hz
FIDRES           0.454131 Hz
AQ               1.1010548 sec
RG                     203
DW                  16.800 usec
DE                   6.50 usec
TE                  300.1 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                   9.50 usec
PL1                  -0.50 dB
PL1W         90.18825531 W
SFO1         125.7753938 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                    1H
PCPD2                80.00 usec
PL2                   1.30 dB
PL12                 16.00 dB
PL13                 20.00 dB
PL2W         15.30635643 W
PL12W         0.51864696 W
PL13W         0.20647706 W
SFO2         500.1520006 MHz
SI                  131072
SF           125.7628237 MHz
WDW                     EM
SSB                      0
LB                    1.00 Hz
GB                       0
PC                    1.40
```

^{1}H and ^{13}C NMR spectra of biphenyl



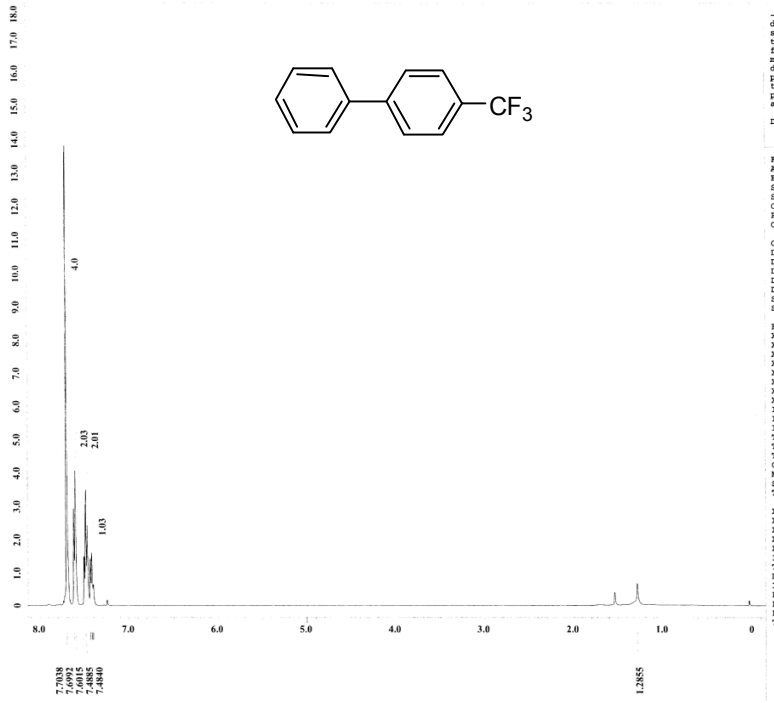

```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: B166A-1.jdf
```

Filename	= B166A-4.jdf
Author	= delta
Experiment	= single_pulse.ex2
Sample_id	= SKM_SS_B166A
Solvent	= CHLOROFORM-D
Creation_time	= 8-MAR-2011 09:26:13
Revision_time	= 8-MAR-2011 09:50:21
Current_time	= 8-MAR-2011 09:50:42
Comment	= SKM_SS_B166A
Data_format	= 1D COMPLEX
Dim_size	= 13107
Dim_title	= 1H
Dim_units	= [ppm]
Dimensions	= X
Site	= ECS 400
Spectrometer	= JNM-ECS400
Field_strength	= 9.389766[T] (400[MHz]
X_acq_duration	= 2.18365952[s]
X_domain	= 1H
X_freq	= 399.78219838[MHz]
X_offset	= 5[ppm]
X_points	= 16384
X_prescans	= 1
X_resolution	= 0.45794685[Hz]
X_sweep	= 7.5030012[kHz]
Irr_domain	= 1H
Irr_freq	= 399.78219838[MHz]
Irr_offset	= 5[ppm]
Tri_domain	= 1H
Tri_freq	= 399.78219838[MHz]
Tri_offset	= 5[ppm]
Clipped	= FALSE
Mod_return	= 1
Scans	= 4
Total_scans	= 4
X_90_width	= 9.5[us]
X_acq_time	= 2.18365952[s]
X_angle	= 45[deg]
X_atn	= 0.3[dB]
X_pulse	= 4.75[us]
Irr_mode	= Off
Tri_mode	= Off
Dante_presat	= FALSE
Initial_wait	= 1[s]
Recvr_gain	= 22
Relaxation_delay	= 5[s]
Repetition_time	= 7.18365952[s]
Temp_get	= 20.9[dC]

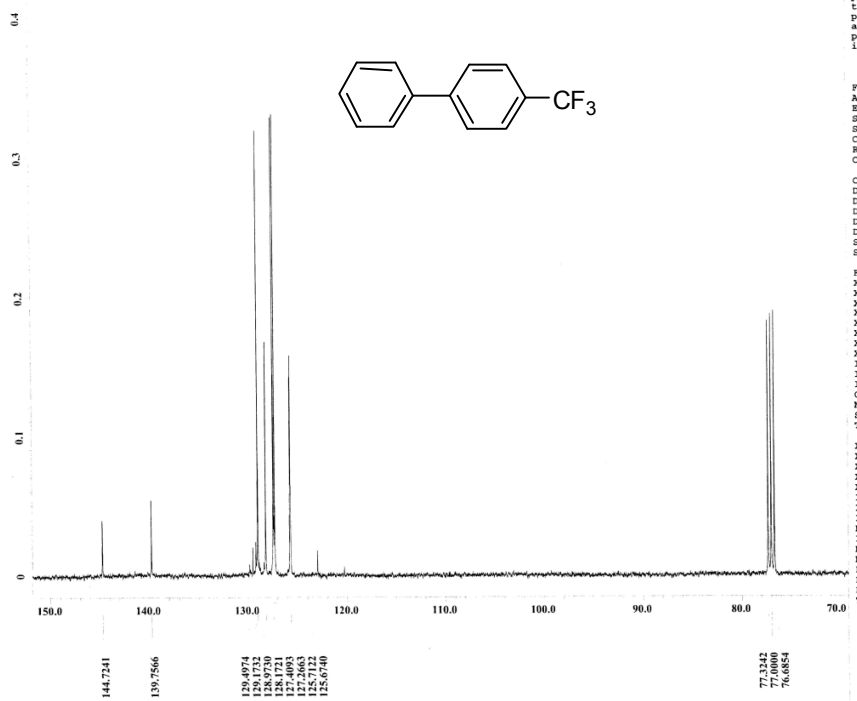


NAME	Mar08-2011
EXPNO	30
PROCNO	1
Date_	20110308
Time	10.05
INSTRUM	spect
PROBHD	5 mm PABBO BB-
PULPROG	zgpg30
TD	65536
SOLVENT	CDCl3
NS	172
DS	4
SWH	29761.904 Hz
FIDRES	0.454131 Hz
AQ	1.1010548 sec
RG	203
DW	16.800 usec
DE	6.50 usec
TE	298.9 K
D1	2.00000000 sec
D11	0.03000000 sec
TD0	1
======== CHANNEL f1 ========	
NUC1	13C
P1	9.50 usec
PL1	-0.50 dB
PL1W	90.18825531 W
SFO1	125.7753938 MHz
======== CHANNEL f2 ========	
CPDPRG2	waltz16
NUC2	1H
PCPD2	80.00 usec
PL2	1.30 dB
PL12	16.00 dB
PL13	20.00 dB
PL2W	15.30635643 W
PL12W	0.51864696 W
PL13W	0.20647706 W
SFO2	500.1520006 MHz
SI	32768
SF	125.7628449 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

^{1}H and ^{13}C NMR spectra of trifluoromethyl biphenyl

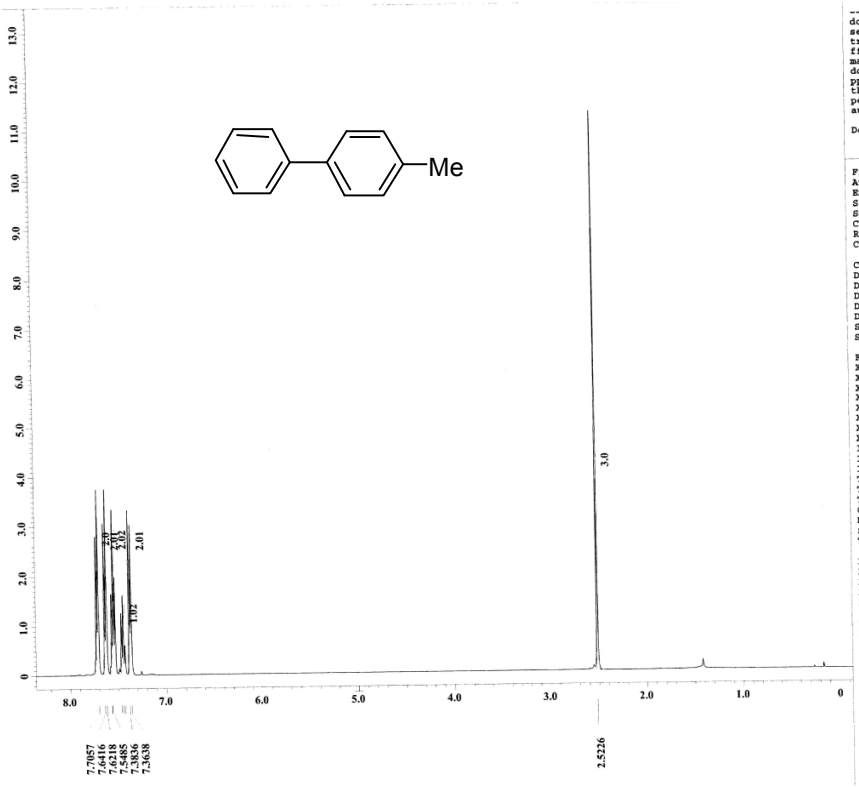



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 0.2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Both : 0[
auto_reference : 5[%]

Derived from: B140A_PROTON-3.jdf

Filename          = B140A_PROTON-9.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = SKM/SS/B140A
Solvent           = CHLOROFORM-D
Creation_time     = 27-JAN-2011 19:34:44
Revision_time     = 27-JAN-2011 19:57:47
Current_time      = 27-JAN-2011 19:58:56

Comment           = SKM_SS_B140A
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.6384[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.61035156[Hz]
X_sweep           = 10[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 9.5[us]
X_acq_time        = 1.6384[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 4.75[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 34
Relaxation_delay  = 4[s]
Repetition_time   = 5.6384[s]
Temp_get          = 23.3[dC]
```

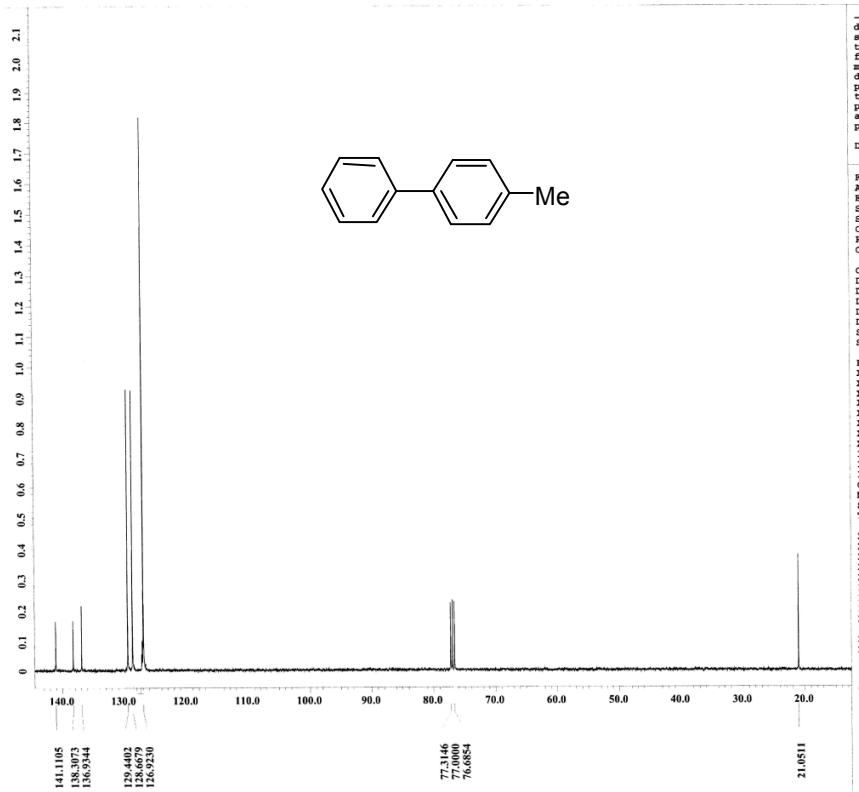



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Peaks : 0
auto_reference : 5[%]
phase : -30 : -30 : 39.00293[%]
ibase_correct :  : FALSE

Filename          = B140A_CARBON-9.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = SKM/SS/B140A
Solvent           = CHLOROFORM-D
Creation_time     = 27-JAN-2011 19:59:45
Revision_time     = 27-JAN-2011 20:23:13
Current_time      = 27-JAN-2011 20:23:43

Comment           = SKM_SS_B140A
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 198
Total_scans       = 198

X_90_width        = 8.25[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 5[dB]
X_pulse           = 2.75[us]
Irr_atn_dec       = 21.96[dB]
Irr_atn_noe       = 21.96[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 42
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 23.5[dC]
```

^{1}H and ^{13}C NMR spectra of methylbiphenyl

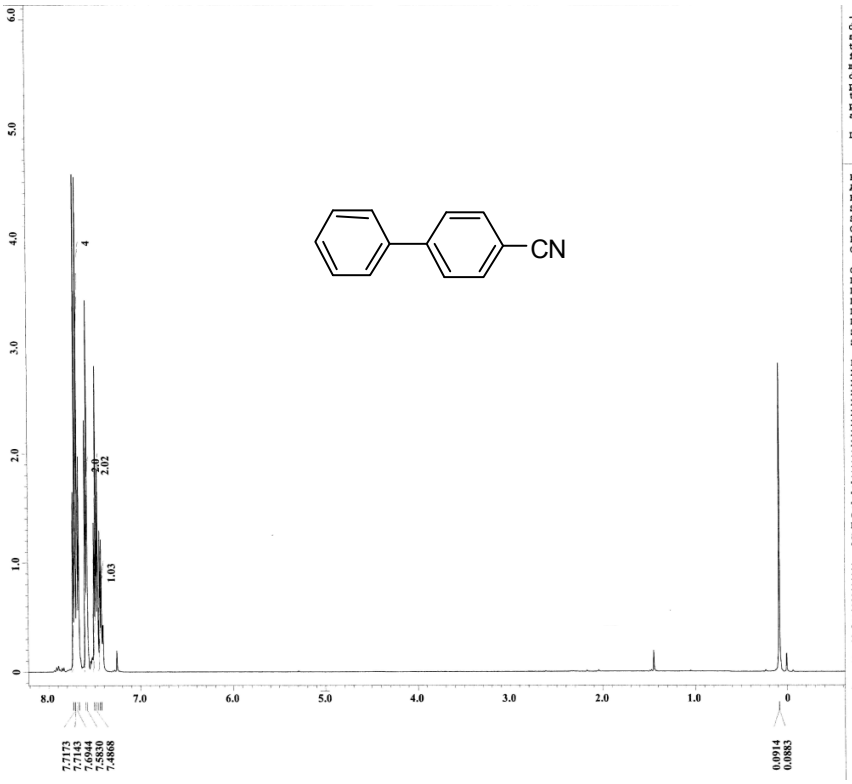



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 0.2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Both : 0[
auto_reference : 5[%]

Derived from: B114A_PROTON-3.jdf

Filename          = B114A_PROTON-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = SKM/SS/B114A
Solvent           = CHLOROFORM-D
Creation_time     =  5-JAN-2011 18:02:47
Revision_time     =  5-JAN-2011 18:26:28
Current_time      =  5-JAN-2011 18:26:55

Comment           = SKM_SS_B114A
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.6384[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.61035156[Hz]
X_sweep           = 10[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 4
Total_scans       = 4

X_90_width        = 9.5[us]
X_acq_time        = 1.6384[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 4.75[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 24
Relaxation_delay  = 4[s]
Repetition_time   = 5.6384[s]
Temp_get          = 22.2[dC]
```

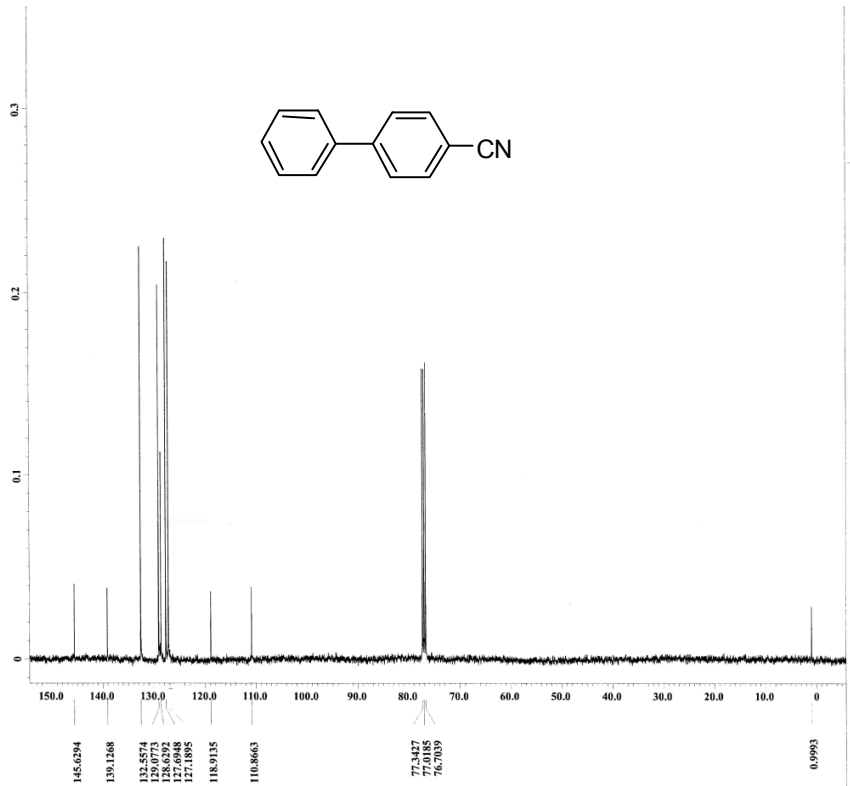



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Peaks : 0
auto_reference : 5[%]
phase : -4 : -15 : 38.9484[%]

Derived from: B114A_CARBON-3.jdf

Filename          = B114A_CARBON-6.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = SKM/SS/B114A
Solvent           = CHLOROFORM-D
Creation_time     =  5-JAN-2011 18:16:51
Revision_time     =  5-JAN-2011 18:40:25
Current_time      =  5-JAN-2011 18:40:51

Comment           = SKM_SS_B114A
Data_format       = 1D COMPLEX
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 56
Total_scans       = 56

X_90_width        = 8.25[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 5[dB]
X_pulse           = 2.75[us]
Irr_atn_dec       = 21.96[dB]
Irr_atn_noe       = 21.96[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 44
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 22.4[dC]
```

^{1}H and ^{13}C NMR spectra of cyanobiphenyl

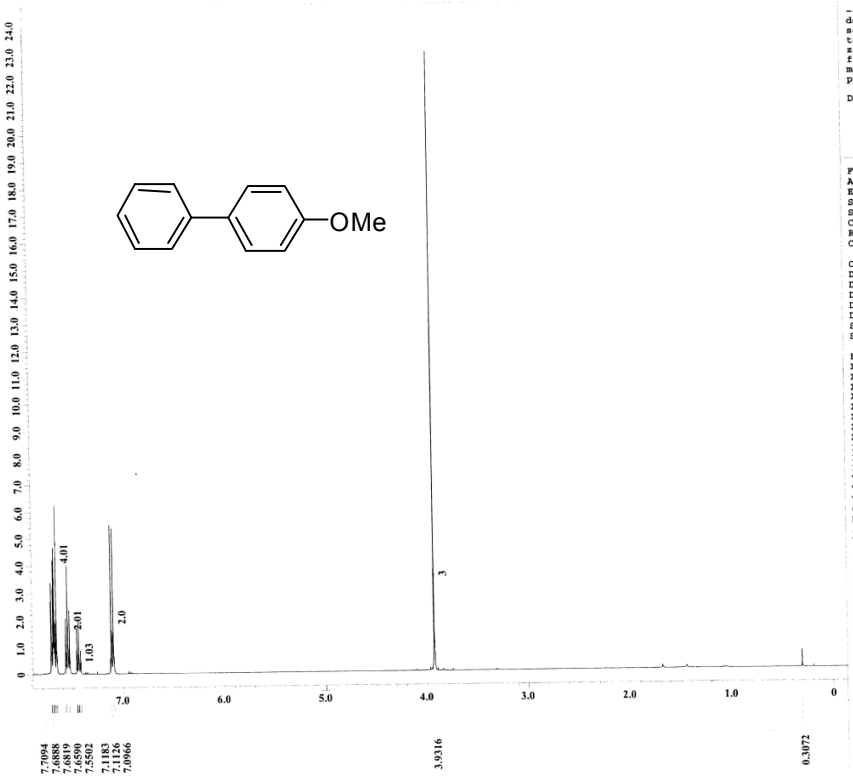



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 0.2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Both : 0[
auto_reference : 5[%]

Derived from: B132A_PROTON-3.jdf

Filename          = B132A_PROTON-13.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = SKM/SS/B132A
Solvent           = CHLOROFORM-D
Creation_time     = 31-JAN-2011 18:06:23
Revision_time     = 31-JAN-2011 18:31:33
Current_time      = 31-JAN-2011 18:32:02

Comment           = SKM_SS_B132A
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T]  (400[MHz]
X_acq_duration    = 1.6384[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.61035156[Hz]
X_sweep           = 10[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 8
Total_scans       = 8

X_90_width        = 9.5[us]
X_acq_time        = 1.6384[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 4.75[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 34
Relaxation_delay  = 4[s]
Repetition_time   = 5.6384[s]
Temp_get          = 23.1[dC]
```

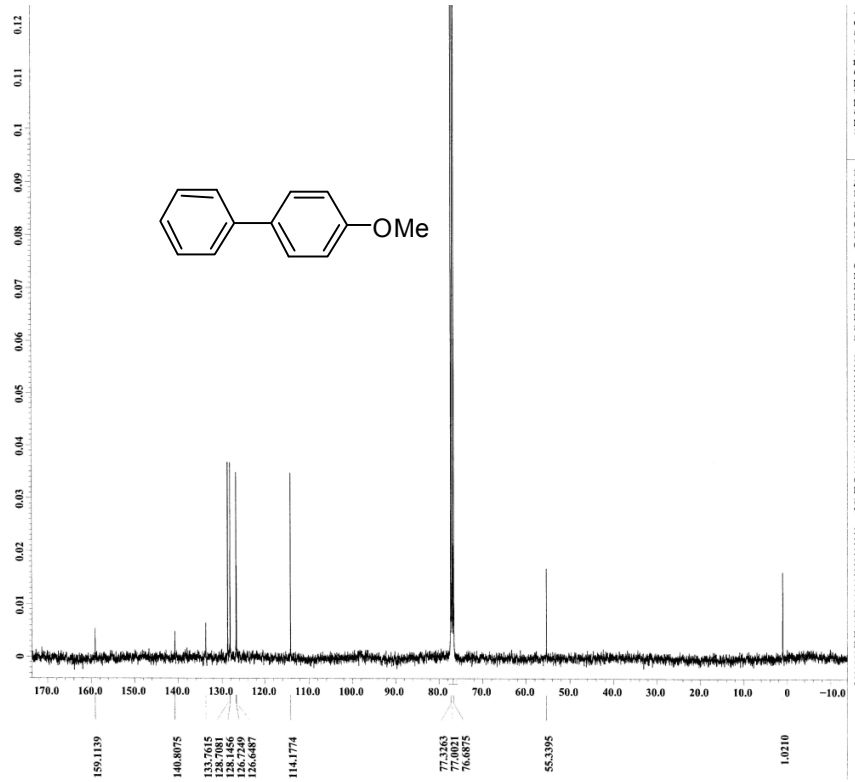



```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Peaks : 0
auto_reference : 5[%]
phase : 55 : -10 : 39.19844[%]
ibase_correct :  : FALSE

Filename          = B132A_CARBON-8.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = SKM/SS/B132A
Solvent           = CHLOROFORM-D
Creation_time     = 31-JAN-2011 18:33:16
Revision_time     = 31-JAN-2011 19:00:04
Current_time      = 31-JAN-2011 19:00:32

Comment           = SKM_SS_B132A
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T]  (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 106
Total_scans       = 106

X_90_width        = 8.25[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 5[dB]
X_pulse           = 2.75[us]
Irr_atn_dec       = 21.96[dB]
Irr_atn_noe       = 21.96[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 40
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 23.5[dC]
```

^{1}H and ^{13}C NMR spectra of methoxybiphenyl




```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp : 0.2[Hz] : 0.0[s]
trapezoid3 : 0[%] : 80[%] : 100[%]
zerofill : 1
fft : 1 : TRUE : TRUE
machinephase
ppm

Derived from: B165A-1.jdf

Filename          = B165A-5.jdf
Author            = delta
Experiment        = single_pulse.ex2
Sample_id         = SKM_SS_B165A
Solvent           = CHLOROFORM-D
Creation_time     =  8-MAR-2011 09:19:56
Revision_time     =  8-MAR-2011 09:44:22
Current_time      =  8-MAR-2011 09:44:43

Comment           = SKM_SS_B165A
Data_format       = 1D COMPLEX
Dim_size          = 13107
Dim_title         = 1H
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 2.18365952[s]
X_domain          = 1H
X_freq            = 399.78219838[MHz]
X_offset          = 5[ppm]
X_points          = 16384
X_prescans        = 1
X_resolution      = 0.45794685[Hz]
X_sweep           = 7.5030012[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Tri_domain        = 1H
Tri_freq          = 399.78219838[MHz]
Tri_offset        = 5[ppm]
Clipped           = FALSE
Mod_return        = 1
Scans             = 4
Total_scans       = 4

X_90_width        = 9.5[us]
X_acq_time        = 2.18365952[s]
X_angle           = 45[deg]
X_atn             = 0.3[dB]
X_pulse           = 4.75[us]
Irr_mode          = Off
Tri_mode          = Off
Dante_presat      = FALSE
Initial_wait      = 1[s]
Recvr_gain        = 20
Relaxation_delay  = 5[s]
Repetition_time   = 7.18365952[s]
Temp_get          = 20.6[dC]
```




```
---- PROCESSING PARAMETERS ----
dc_balance : 0 : FALSE
sexp_auto : 2
trapezoid3 : 0[%] : 80[%] : 100[%]
fft : 1
machinephase
dc_correct
ppm
thresh : 5[%] : 1
peak_pick : 0[Hz] : 0.1[ppm] : Peaks : 0
auto_reference : 5[%]
phase : 42 : 0 : 59.23753[%]
ibase_correct :  : FALSE

Filename          = B147A_CARBON-11.jdf
Author            = delta
Experiment        = single_pulse_dec
Sample_id         = SKM/SS/B147A
Solvent           = CHLOROFORM-D
Creation_time     =  3-FEB-2011 15:20:10
Revision_time     =  3-FEB-2011 15:45:36
Current_time      =  3-FEB-2011 15:45:59

Comment           = SKM_SS_B147A
Data_format       = 1D REAL
Dim_size          = 26214
Dim_title         = 13C
Dim_units         = [ppm]
Dimensions        = X
Site              = ECS 400
Spectrometer      = JNM-ECS400

Field_strength    = 9.389766[T] (400[MHz]
X_acq_duration    = 1.04333312[s]
X_domain          = 13C
X_freq            = 100.52530333[MHz]
X_offset          = 100[ppm]
X_points          = 32768
X_prescans        = 4
X_resolution      = 0.95846665[Hz]
X_sweep           = 31.40703518[kHz]
Irr_domain        = 1H
Irr_freq          = 399.78219838[MHz]
Irr_offset        = 5[ppm]
Clipped           = TRUE
Mod_return        = 1
Scans             = 512
Total_scans       = 512

X_90_width        = 8.25[us]
X_acq_time        = 1.04333312[s]
X_angle           = 30[deg]
X_atn             = 5[dB]
X_pulse           = 2.75[us]
Irr_atn_dec       = 21.96[dB]
Irr_atn_noe       = 21.96[dB]
Irr_noise         = WALTZ
Decoupling        = TRUE
Initial_wait      = 1[s]
Noe               = TRUE
Noe_time          = 2[s]
Recvr_gain        = 42
Relaxation_delay  = 2[s]
Repetition_time   = 3.04333312[s]
Temp_get          = 21.8[dC]
```

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