Advanced Synthesis & Catalysis

Supporting Information

Supporting Information

Modular Palladium Bipyrazoles for the Isomerization of Allylbenzenes – Insights into Catalyst Design and Activity, Role of Solvent, Additive Effects and Mechanistic Considerations

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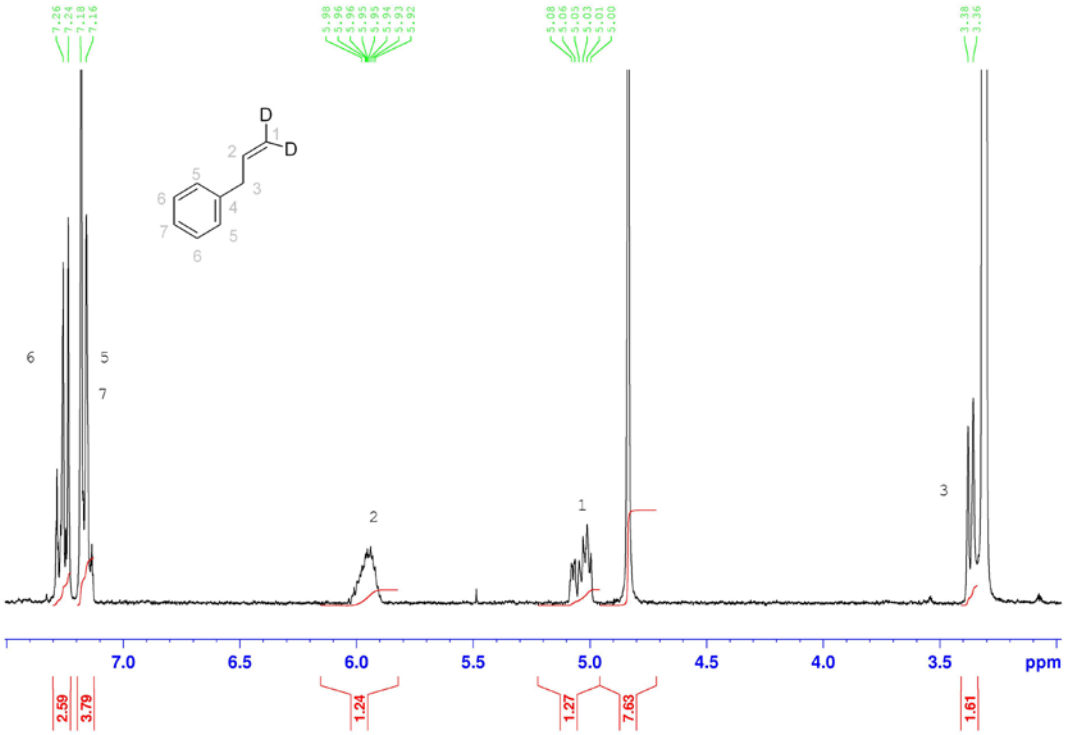
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4
5
6
7
6
5
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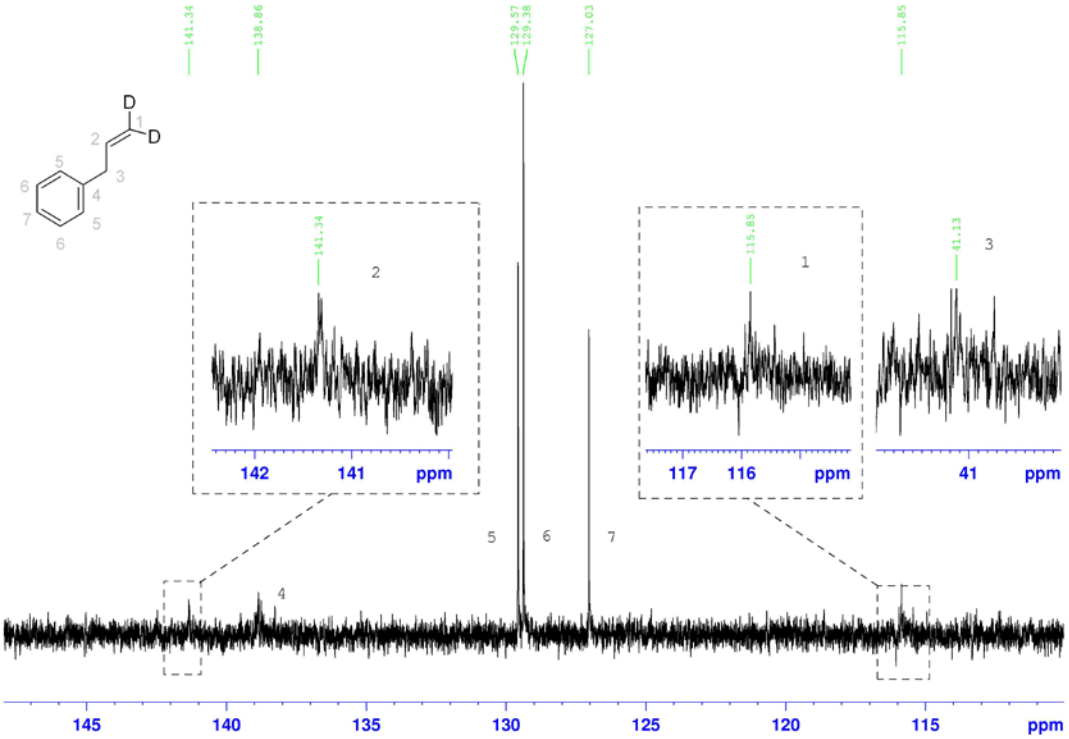
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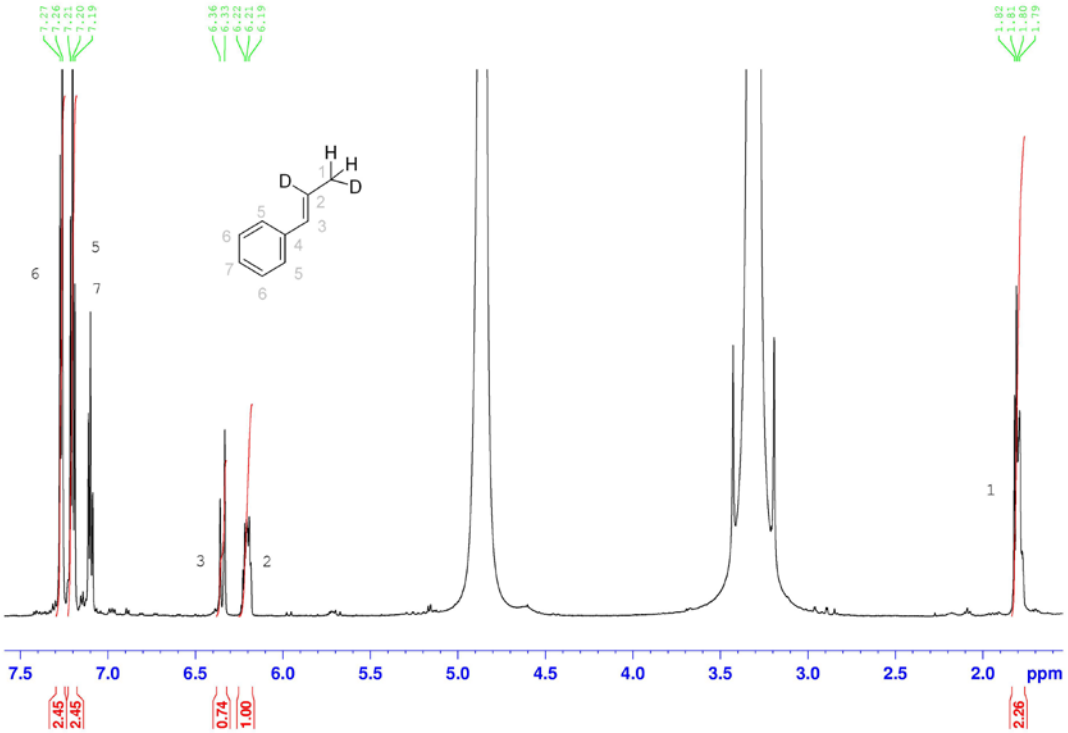
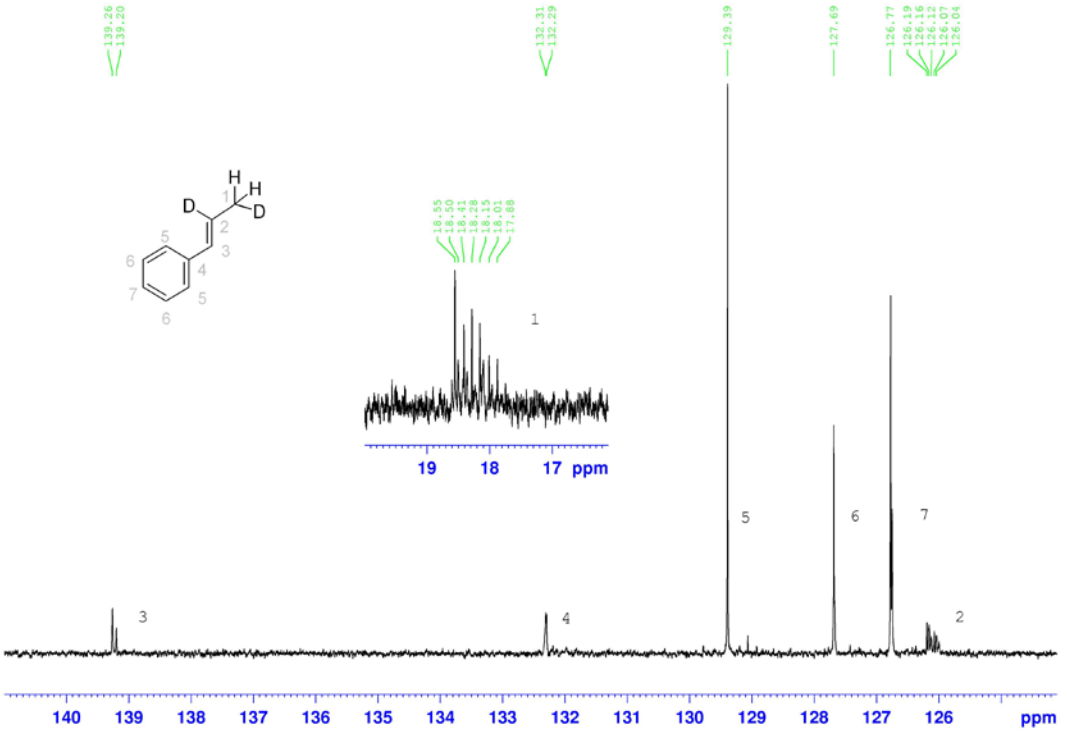




1 General Methods

All reagents and solvents were obtained from Acros, ABCR, Alfa Aesar, Sigma-Aldrich or VWR and were used without further purification unless otherwise noted. Deuterated solvents were purchased from Euriso-Top. NMR spectra were recorded on Bruker Avance 500, Bruker Avance 300 and Bruker ARX-250 spectrometers at RT. Chemical shifts (in ppm) were referenced to residual solvent protons. GC-and GC-MS measurements were performed on a Thermo Trace-Ultra GC-MS, equipped with split injector (250°C), FID (250°C) and a quadrupole MS (Thermo, San Jose, CA). MS spectra were recorded on a JEOL JMS-700 spectrometer. IR spectra were recorded on a Bruker Vector 22 FT-IR. Elemental analyses were performed by the analytical laboratories of the chemical institute of the University of Heidelberg. Melting points were determined on a Büchi melting point apparatus and temperatures were uncorrected. Crystal structure analysis was accomplished on Bruker Smart CCD and Bruker APEX diffractometers.

2 Reaction Kinetics

2.1 Reaction rate orders (catalyst, substrate and solvent)

Reactions for the determination of dependency on catalyst, substrate and solvent concentration were carried out as described in the experimental part.

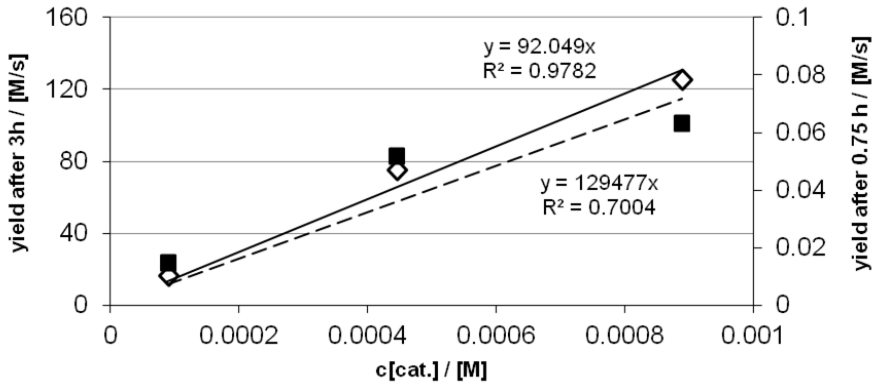


Figure 1: Catalyst concentration versus yield of *E*-propenylbenzene (6 h data not included to improve readability).

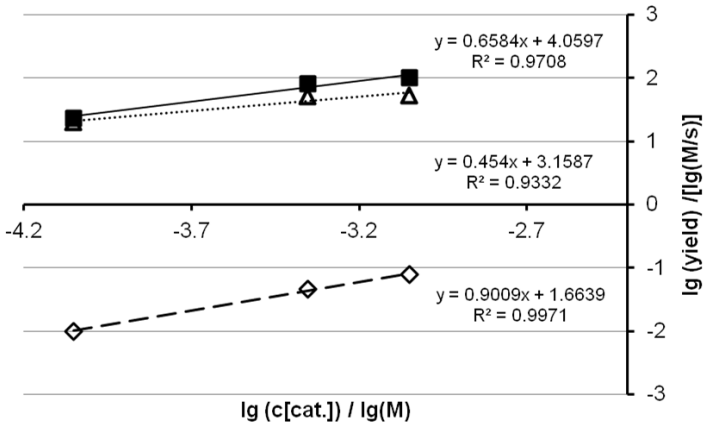


Figure 2: **Logarithmic projection of catalyst concentration versus yield of *E*-propenylbenzene.**

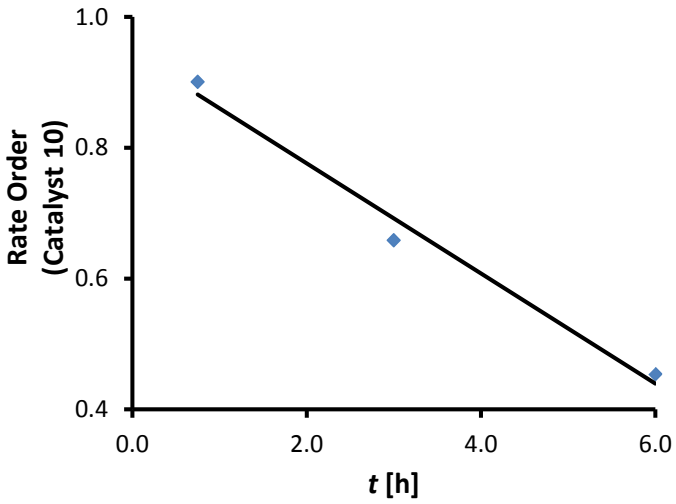


Figure 3: **Determination of time-independent reaction-rate order of catalyst 10.**

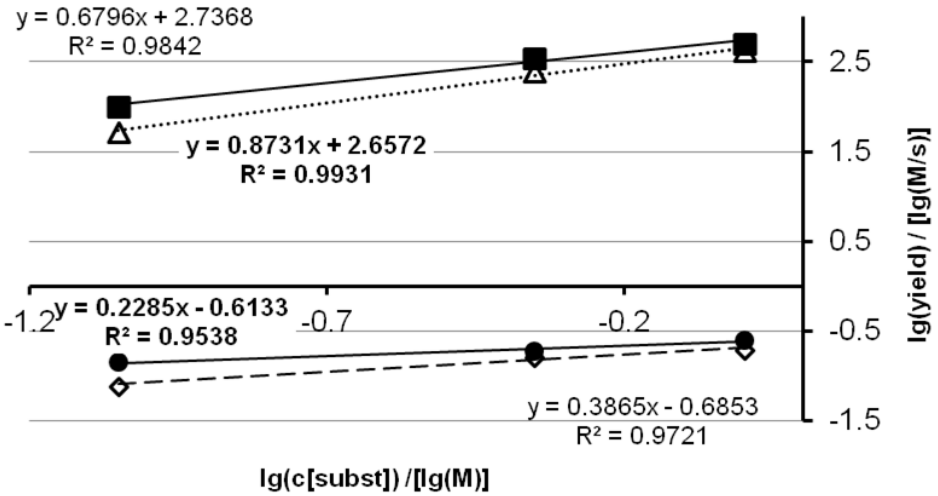


Figure 4: **Logarithmic projection of substrate concentration versus yield of *E*-propenylbenzene.**

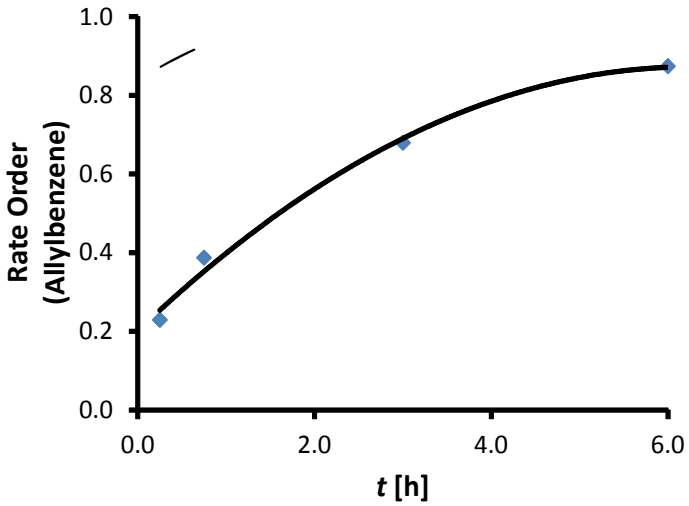


Figure 5: **Determination of time-independent reaction-rate order of substrate.**

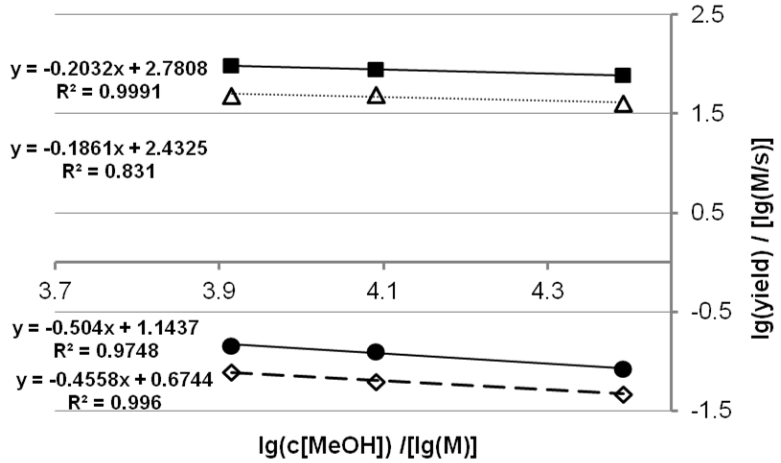


Figure 6: **Logarithmic projection of methanol concentration versus yield of *E*-propenylbenzene.**

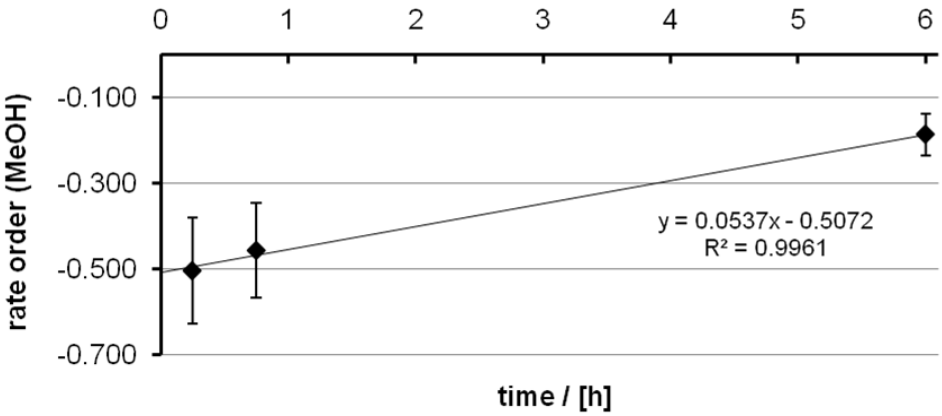


Figure 7: **Determination of time-independent reaction-rate order of methanol.**

2.2 Multiple addition-reaction cycles using Palladium(II)bis(acetonitrile) dichloride

The isomerization was carried out using $Pd(MeCN)_2Cl_2$, (1 mol%, 2.6 mg, 10 µmol), allylbenzene (117.4 mg, 0.993 mmol, 89 mM) and 10 µL undecane as internal standard in 11.2 mL of a 2:1 mixture of methanol/ toluene at 60 °C. Reaction progress was monitored by GC-measurements and after consumption of all starting material usually after 24 h latest allylbenzene was added again (117.4 mg, 89 mM). The re-addition-reaction cycle was repeated 21 times and samples were taken 15 min after each addition and analyzed by GC-measurements. Similar procedure was used for multiple addition-reaction cycles using catalyst 10 (4.1 mg, 1 mol%), allylbenzene (58.7 mg, 89 mm) and internal standard in 5.6 mL solvent.

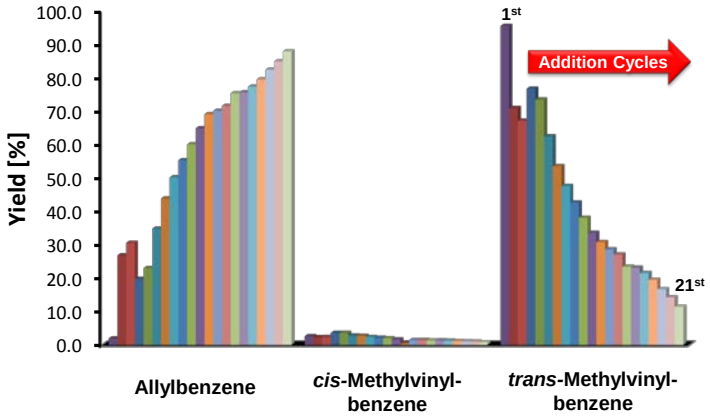
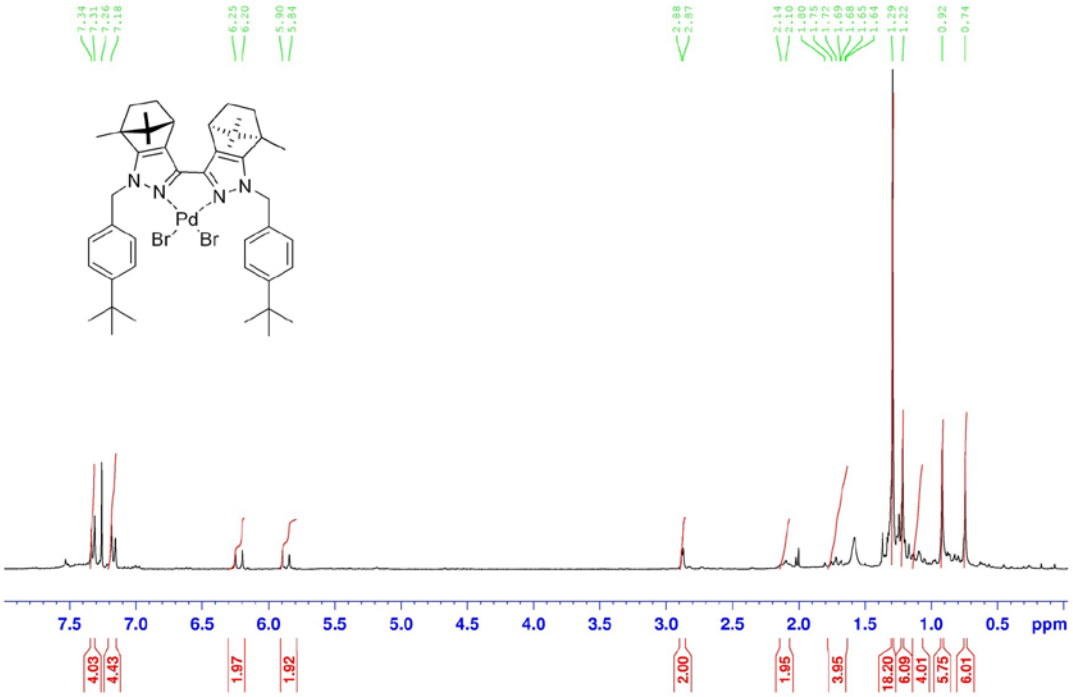
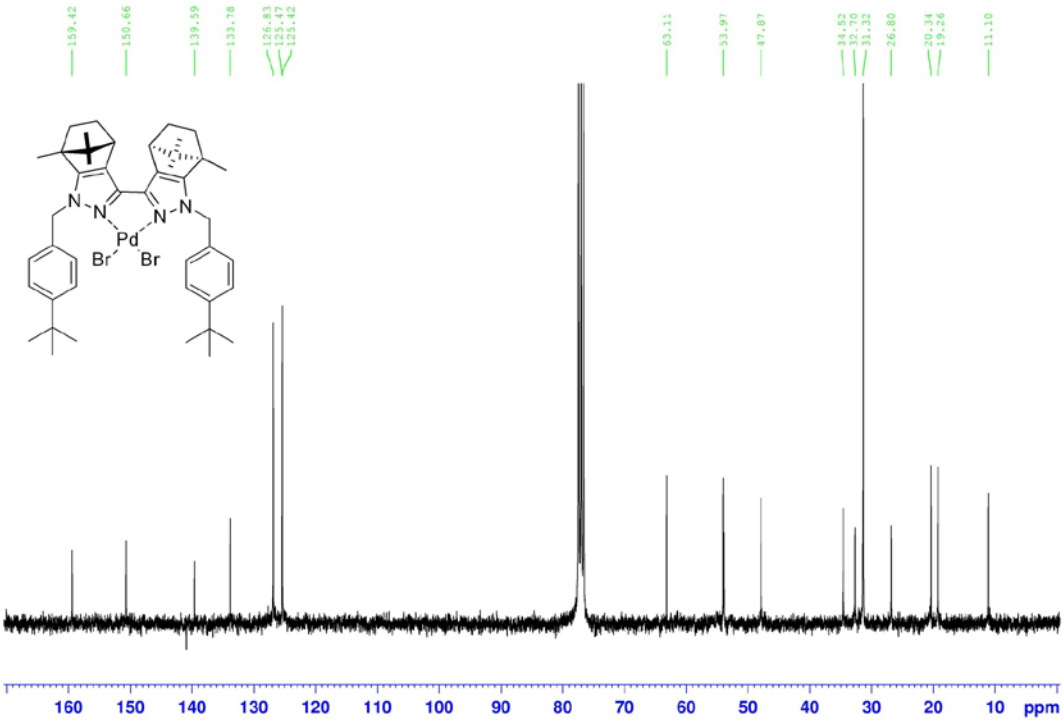


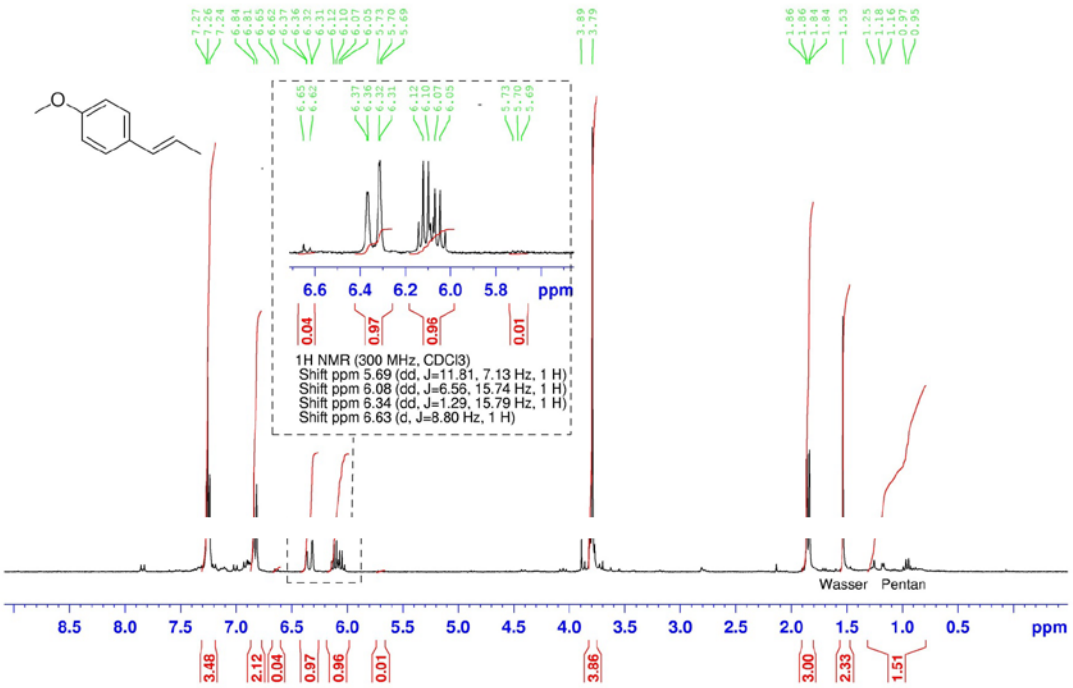
Figure 8: **Catalyst lifetime and conversion measured 15 min after addition of allylbenzene using $Pd(MeCN)_2Cl_2$ over multiple addition-reaction cycles. Complete consumption of starting material was ensured each time before re-addition of starting material (GC).**

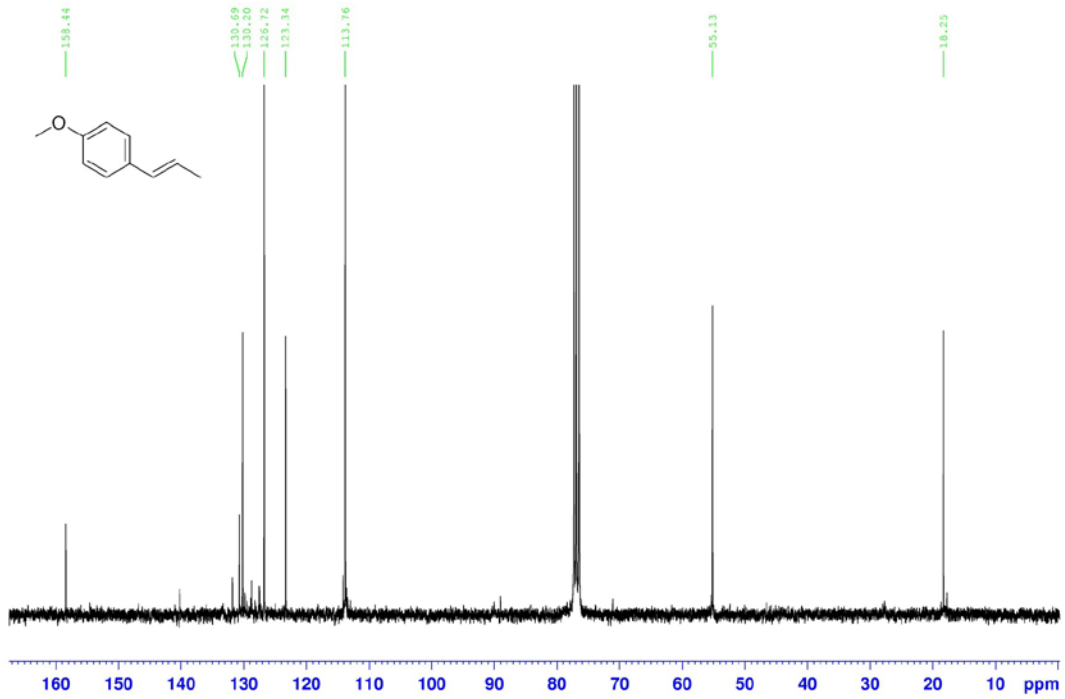
3 ^{1}H and ^{13}C-NMR spectra of catalyst 10^{Br} and samples

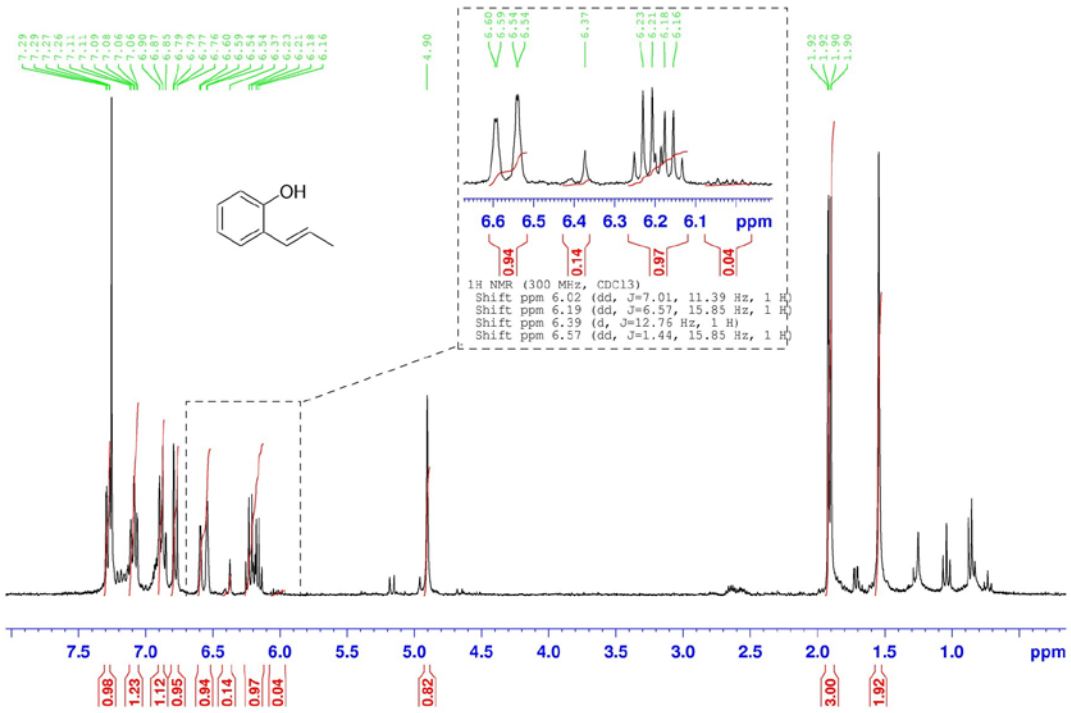
Compounds were prepared as described in the experimental part (R = -*p*-OMe, -*o*-OH, -*p*-CF_3, -*p*-OAc/ -*o*-OMe).






1H NMR (300 MHz, CDCl3)
Shift ppm 5.69 (dd, J=11.81, 7.13 Hz, 1 H)
Shift ppm 6.08 (dd, J=6.56, 15.74 Hz, 1 H)
Shift ppm 6.34 (dd, J=1.29, 15.79 Hz, 1 H)
Shift ppm 6.63 (d, J=8.80 Hz, 1 H)
Wasser
Pentan
ppm


ppm


OH
1H NMR (300 MHz, CDCl3)
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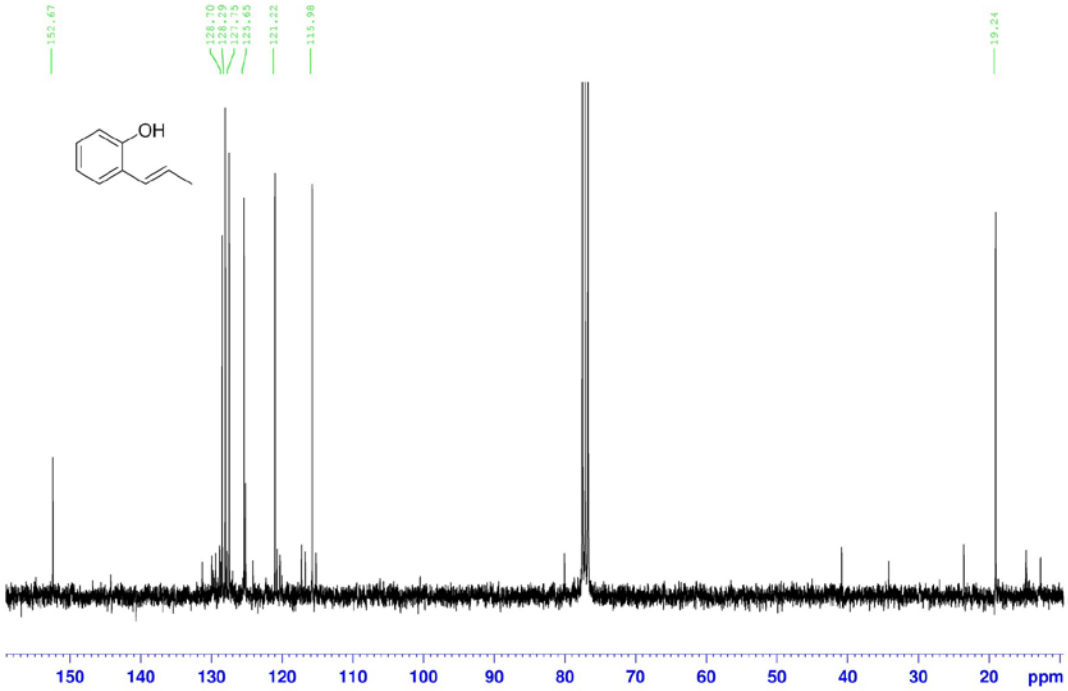
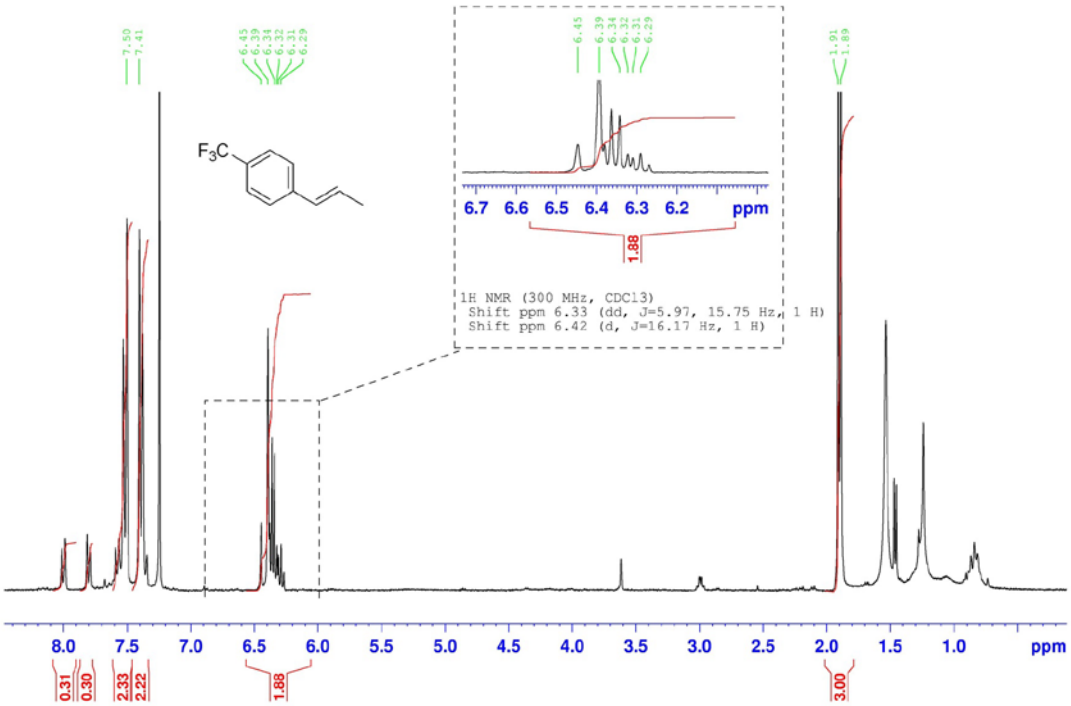
Shift ppm 6.19 (dd, J=6.57, 15.85 Hz, 1 H)
Shift ppm 6.39 (d, J=12.76 Hz, 1 H)
Shift ppm 6.57 (dd, J=1.44, 15.85 Hz, 1 H)
ppm


OH
ppm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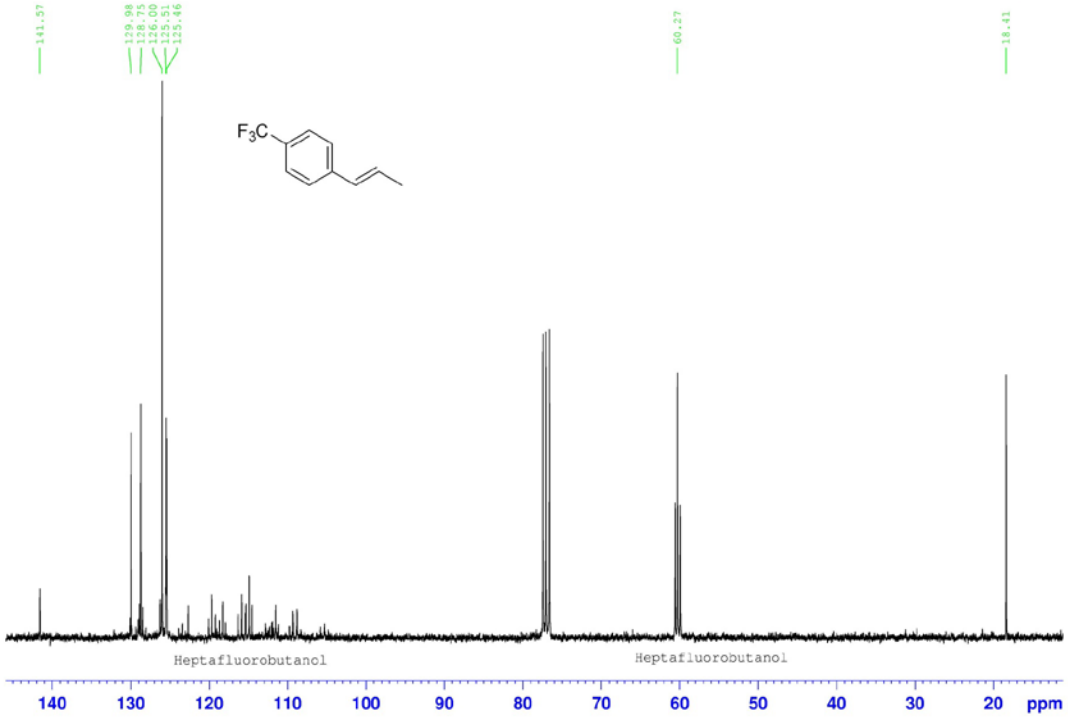
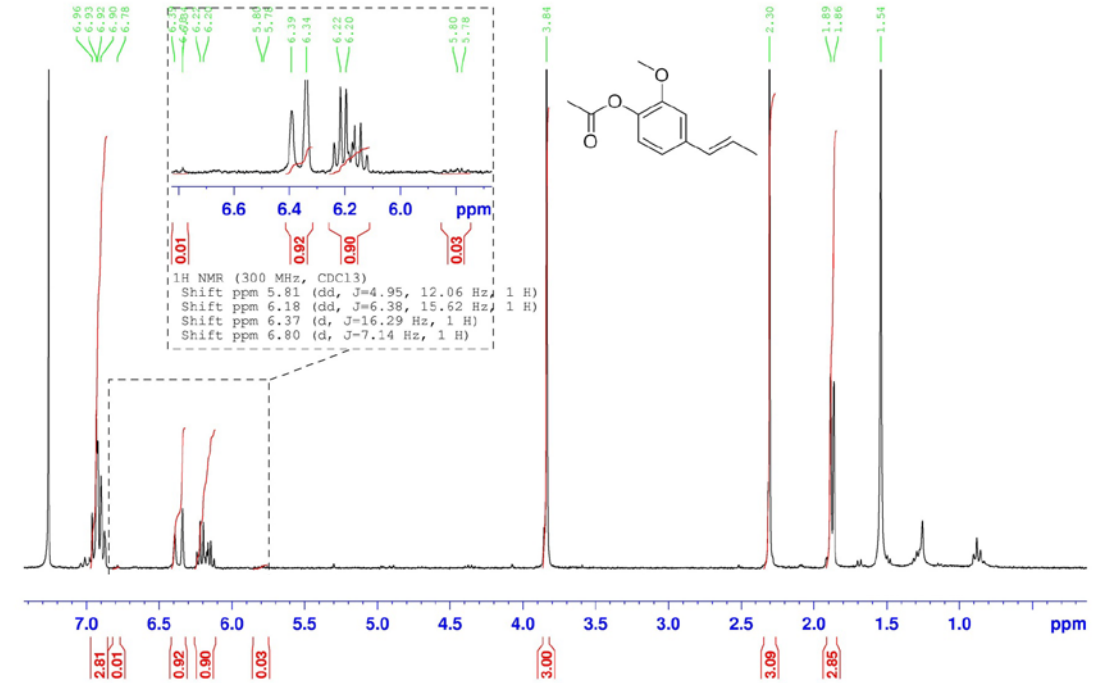
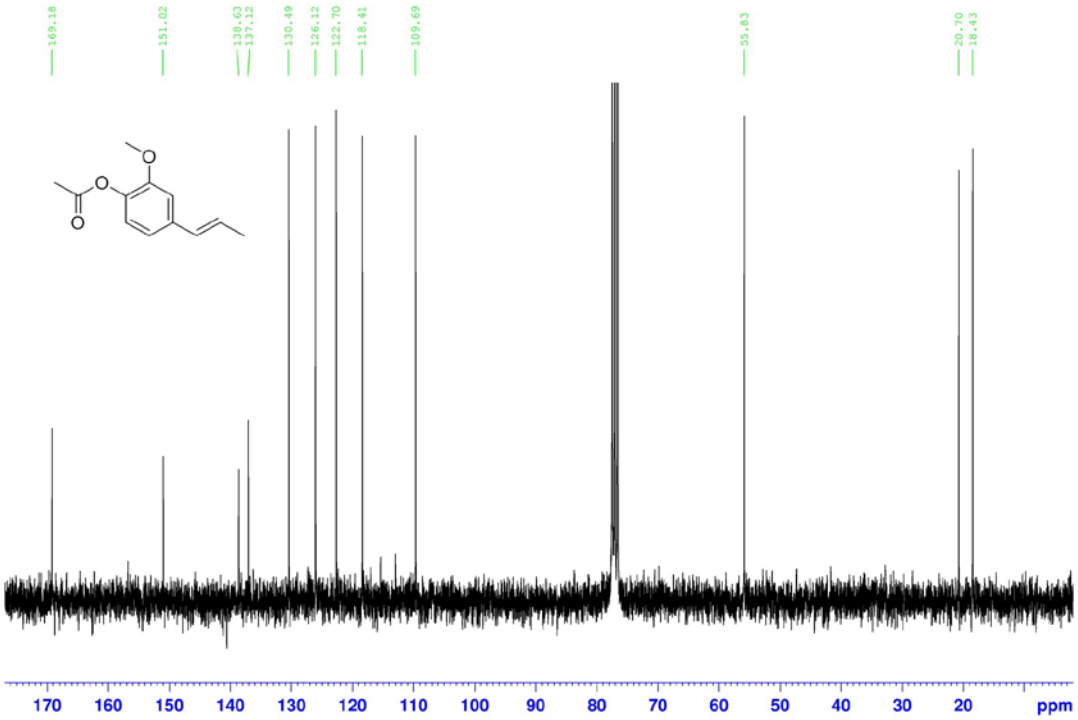
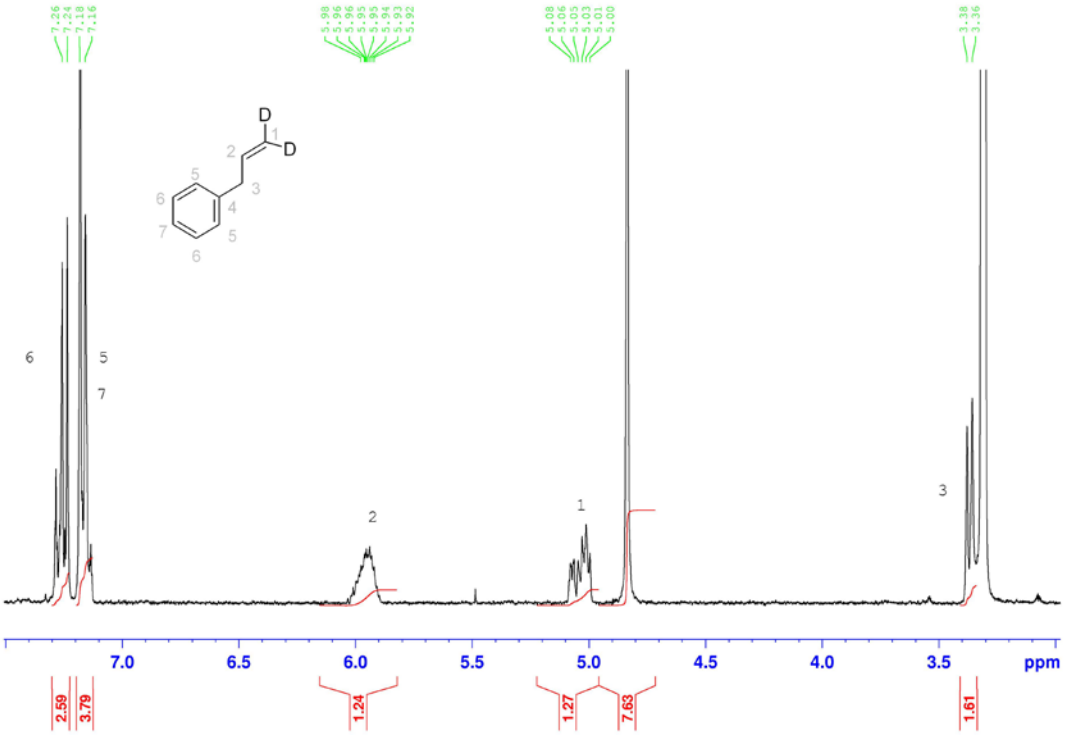
6.45
6.39
6.34
6.32
6.31
6.29
1.91
1.89
F3C
6.7 6.6 6.5 6.4 6.3 6.2 ppm
1.88
1H NMR (300 MHz, CDCl3)
Shift ppm 6.33 (dd, J=5.97, 15.75 Hz, 1 H)
Shift ppm 6.42 (d, J=16.17 Hz, 1 H)
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
0.31
0.30
2.33
2.22
1.88
3.00

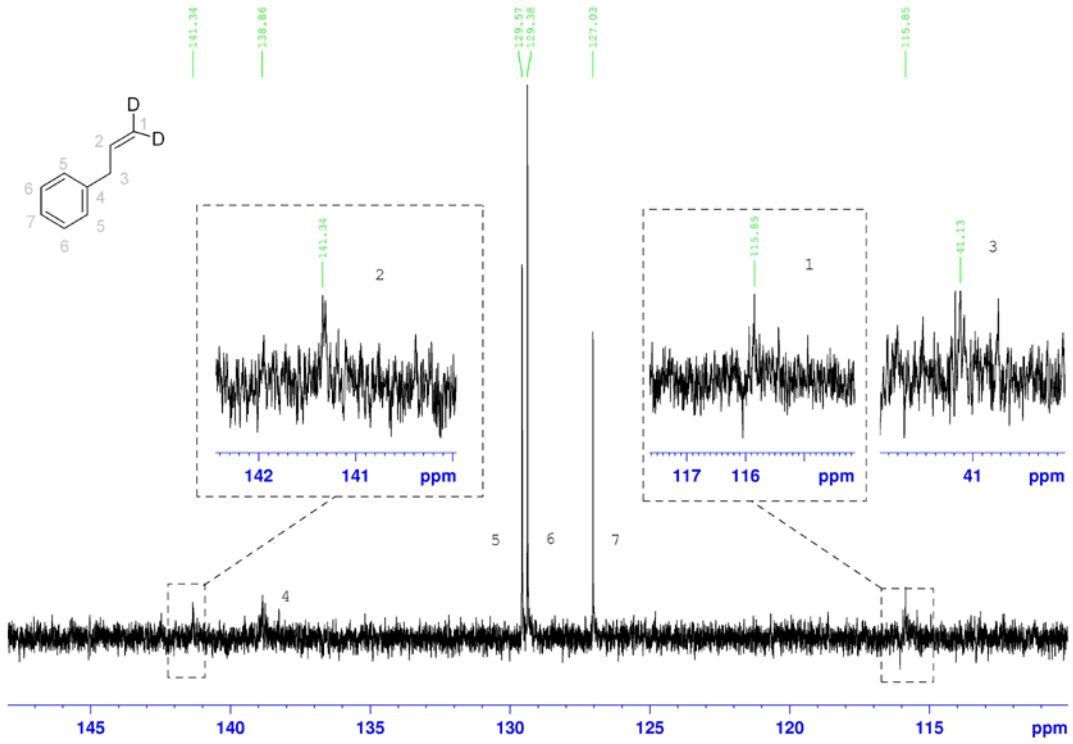

141.57
129.98
128.75
126.00
125.51
125.46
60.27
18.41
F3C
Heptafluorobutanol
Heptafluorobutanol
140 130 120 110 100 90 80 70 60 50 40 30 20 ppm

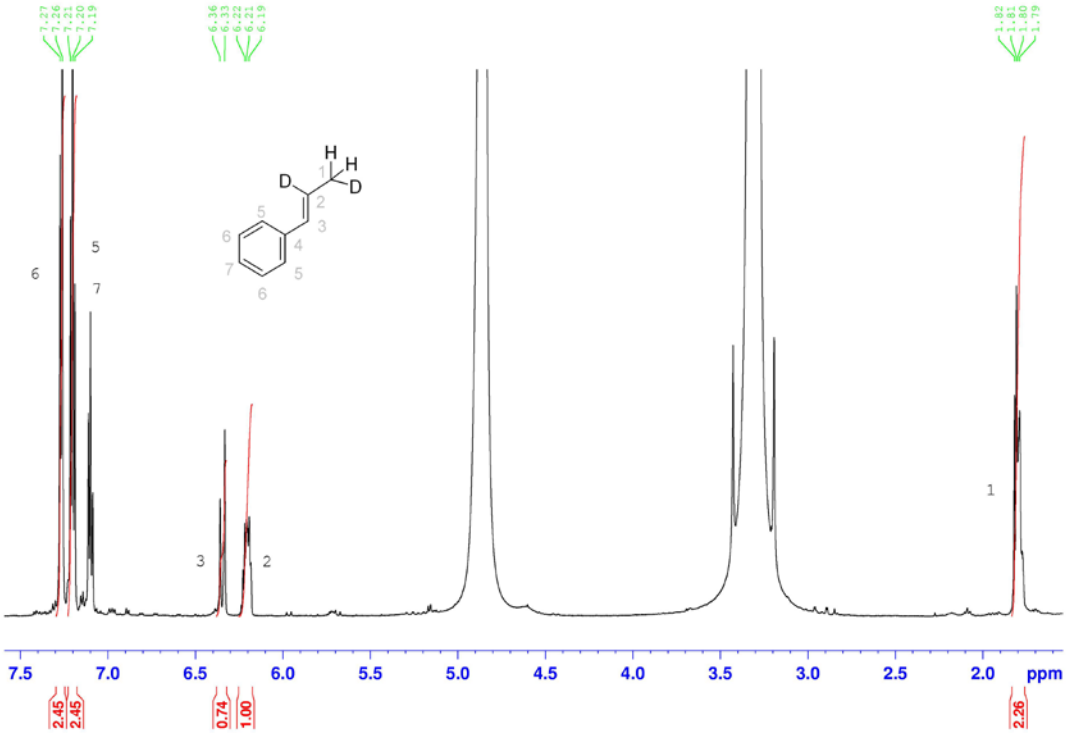

1H NMR (300 MHz, CDCl3)
Shift ppm 5.81 (dd, J=4.95, 12.06 Hz, 1 H)
Shift ppm 6.18 (dd, J=6.38, 15.62 Hz, 1 H)
Shift ppm 6.37 (d, J=16.29 Hz, 1 H)
Shift ppm 6.80 (d, J=7.14 Hz, 1 H)
ppm


ppm

4 ^{1}H and ^{13}C-NMR spectra of 1,1-d_2-prop-1-en-3-yl benzene and 2,3-d_2-(*E*)-prop-1-en-1-yl benzene



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H
H
D
D
1
2
3
4
5
6
7
5
6
7
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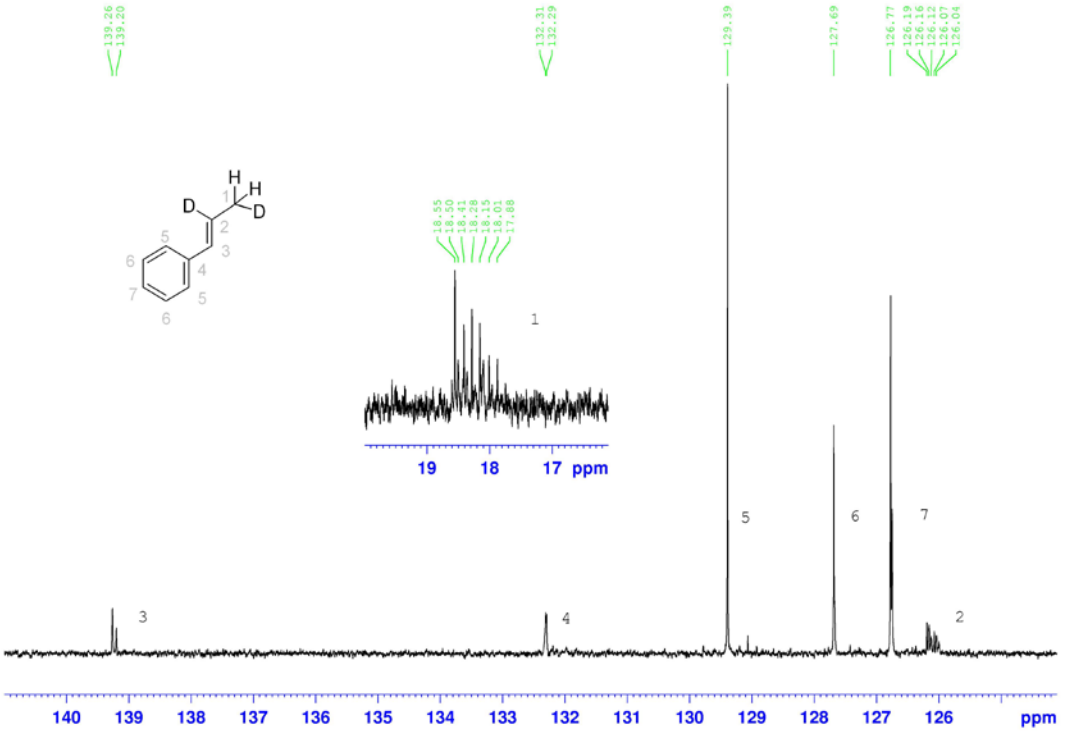
2.26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126.07
126.04
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18.15
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6
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ppm

5 Single crystal X-ray structure determination of 6

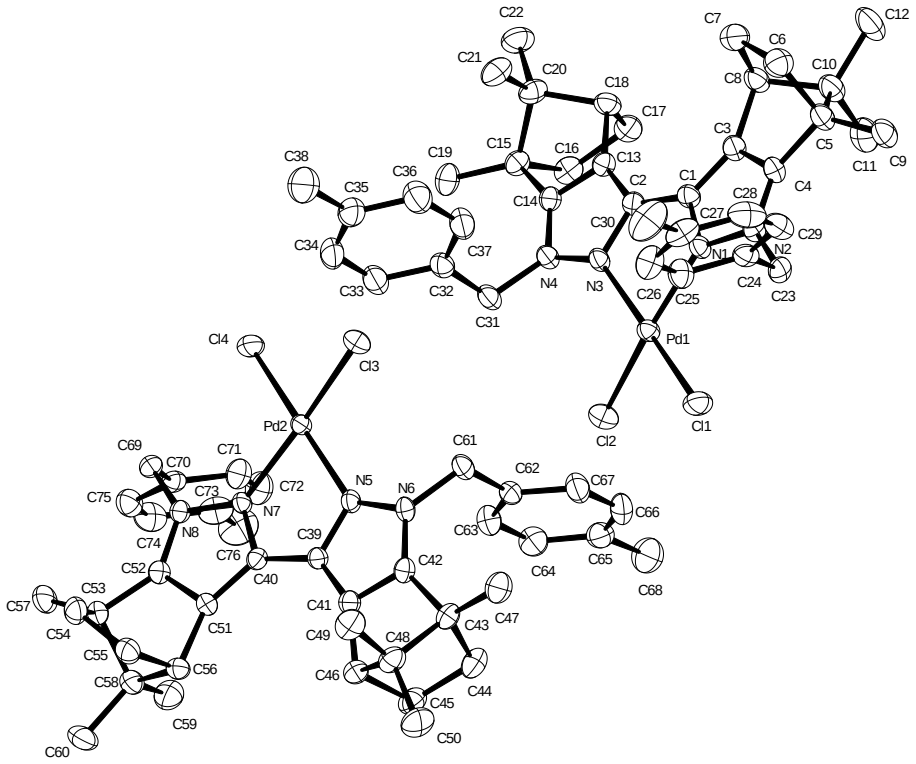

Figure 9: The crystal structure of 6, showing the two independent molecules in the asymmetric unit, which are related by an approximate centre of symmetry. Atomic displacement ellipsoids shown at the 50% probability level. H atoms are omitted for clarity.

It was difficult to integrate intensities at high diffraction angles owing to the large number of weak reflections caused by the very small size of the crystal (105 x 78 x 10 microns). The completeness was 98.7% to 0.86 Å (see following intensity statistics).

INTENSITY STATISTICS FOR DATASET

Resolution	#Data	#Theory	%Complete	Redundancy	Mean I	Mean I/s	R(int)	Rsigma
Inf - 2.12	787	800	98.4	9.27	105.7	60.20	0.0391	0.0162
2.12 - 1.69	794	795	99.9	9.79	80.4	61.27	0.0351	0.0143
1.69 - 1.47	813	813	100.0	9.39	48.1	54.29	0.0341	0.0158
1.47 - 1.34	816	816	100.0	8.74	37.2	48.31	0.0316	0.0176
1.34 - 1.24	846	846	100.0	8.03	30.6	42.74	0.0330	0.0197
1.24 - 1.16	874	874	100.0	7.51	26.3	38.51	0.0328	0.0215
1.16 - 1.10	874	874	100.0	7.04	24.3	36.54	0.0335	0.0232
1.10 - 1.05	893	893	100.0	6.69	22.8	33.74	0.0372	0.0246
1.05 - 1.01	820	821	99.9	6.35	19.6	31.50	0.0420	0.0271
1.01 - 0.97	981	981	100.0	6.03	17.1	28.78	0.0496	0.0302
0.97 - 0.94	845	847	99.8	5.81	15.0	26.05	0.0573	0.0331
0.94 - 0.91	984	991	99.3	5.40	13.3	24.10	0.0669	0.0371
0.91 - 0.88	1088	1093	99.5	5.20	10.5	20.50	0.0807	0.0435
0.88 - 0.86	820	831	98.7	4.82	9.6	18.47	0.0882	0.0486
0.86 - 0.84	894	920	97.2	4.65	9.0	17.54	0.0941	0.0514
0.84 - 0.82	980	1002	97.8	4.18	8.0	15.03	0.1123	0.0601
0.82 - 0.80	949	1071	88.6	2.01	7.4	9.82	0.1143	0.0949
0.80 - 0.76	564	1643	34.3	0.44	6.1	6.45	0.1286	0.1395

0.86 - 0.76	3811	5070	75.2	2.65	7.9	13.43	0.1023	0.0736
Inf - 0.76	15622	16911	92.4	5.79	26.3	31.50	0.0405	0.0247

There is a solvent accessible void of 35 $Å^3$ at x = 0.520, y = -0.032, z = 0.560 between the complexes, but no electron density is observed in that region. The hydrophobic nature of the surrounding molecules suggests that this region was previously occupied by organic solvent. Acetonitrile is a possible candidate, since it is small and was one of the solvents used for crystallisation.

Four reflections show high disagreements between Fo^2 and Fc^2 (see below), with $Fo^2 > Fc^2$ at high resolution. This may be due to an underestimation of the weights at high angles caused by the chosen weighting scheme.

Most Disagreeable Reflections (Delta(F^2)/esd > 10.0)

h	k	l	Fo^2	Fc^2	Delta(F^2)/esd	Fc/Fc(max)	Res(A)
11	4	20	1728.33	38.26	11.68	0.024	0.79
11	-7	16	2082.05	141.42	11.66	0.046	0.79
8	4	23	1534.83	99.96	11.08	0.039	0.78
16	4	13	1250.48	137.96	10.24	0.046	0.78

The two independent molecules form an almost centrosymmetric arrangement, which may explain why the Flack parameter is relatively poorly determined.

Highest peak 0.50 at 0.6744 0.7720 0.1174 [0.97 A from PD2]
Deepest hole -0.58 at 0.6290 0.7788 0.0509 [0.77 A from PD2]

Table S-1. Crystal data and structure refinement for 6.

Identification code	7105	
Empirical formula	$C_{38}H_{46}Cl_2N_4Pd$	
Color	pale yellow	
Formula weight	736.09 g · mol^{-1}	
Temperature	150 K	
Wavelength	0.80000 Å	
Crystal system	Monoclinic	
Space group	**$P2_1$, (no. 4)**	
Unit cell dimensions	a = 16.196(5) Å	α= 90°.
	b = 10.248(3) Å	β= 96.143(4)°.
	c = 21.795(7) Å	γ = 90°.
Volume	3596.6(19) Å^3	
Z	4	
Density (calculated)	1.359 Mg · m^{-3}	
Absorption coefficient	0.696 mm^{-1}	
F(000)	1528 e	
Crystal size	0.148 x 0.139 x 0.010 mm^3	
θ range for data collection	1.86 to 31.57°.	
Index ranges	$-20 \le h \le 20$, $-12 \le k \le 13$, $-28 \le l \le 27$	
Reflections collected	97835	
Independent reflections	15609 [R_{int} = 0.0406]	
Reflections with I>2σ(I)	14879	
Completeness to θ = 31.57°	95.0 %	
Absorption correction	Gaussian	
Max. and min. transmission	0.99 and 0.93	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	15609 / 1 / 827	
Goodness-of-fit on F^2	1.173	
Final R indices [I>2σ(I)]	R_1 = 0.0272	wR^2 = 0.0577
R indices (all data)	R_1 = 0.0313	wR^2 = 0.0610
Absolute structure parameter	-0.145(13)	
Largest diff. peak and hole	0.499 and -0.580 e · Å^{-3}	

Table S-2. Atomic coordinates and equivalent isotropic displacement parameters (Å²) for 6.

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
C(1)	0.2407(2)	0.9827(3)	0.5789(1)	0.024(1)
C(2)	0.2770(2)	0.9189(3)	0.6347(1)	0.023(1)
C(3)	0.2492(2)	1.1049(3)	0.5541(1)	0.026(1)
C(4)	0.1983(2)	1.1053(3)	0.4989(1)	0.024(1)
C(5)	0.2097(2)	1.2324(3)	0.4654(1)	0.030(1)
C(6)	0.3008(2)	1.2216(4)	0.4468(2)	0.038(1)
C(7)	0.3578(2)	1.2249(3)	0.5093(1)	0.039(1)
C(8)	0.2943(2)	1.2346(3)	0.5582(1)	0.030(1)
C(9)	0.1447(2)	1.2780(3)	0.4146(1)	0.035(1)
C(10)	0.2245(2)	1.3226(3)	0.5245(1)	0.033(1)
C(11)	0.1486(2)	1.3357(4)	0.5597(2)	0.041(1)
C(12)	0.2535(3)	1.4613(3)	0.5099(2)	0.049(1)
C(13)	0.3362(2)	0.9539(3)	0.6831(1)	0.023(1)
C(14)	0.3466(2)	0.8446(3)	0.7199(1)	0.023(1)
C(15)	0.4045(2)	0.8756(3)	0.7774(1)	0.026(1)
C(16)	0.3503(2)	0.9709(3)	0.8131(1)	0.032(1)
C(17)	0.3420(2)	1.0973(3)	0.7729(1)	0.032(1)
C(18)	0.3877(2)	1.0608(3)	0.7160(1)	0.029(1)
C(19)	0.4464(2)	0.7649(4)	0.8149(1)	0.035(1)
C(20)	0.4616(2)	0.9771(3)	0.7470(1)	0.031(1)
C(21)	0.5157(2)	0.9153(4)	0.7005(2)	0.039(1)
C(22)	0.5197(2)	1.0517(4)	0.7957(2)	0.041(1)
C(23)	0.1033(2)	0.9426(3)	0.4383(1)	0.027(1)
C(24)	0.1502(2)	0.8769(3)	0.3905(1)	0.026(1)
C(25)	0.1879(2)	0.7557(3)	0.4026(1)	0.032(1)
C(26)	0.2291(2)	0.6926(4)	0.3582(2)	0.041(1)
C(27)	0.2341(2)	0.7488(4)	0.3005(1)	0.038(1)
C(28)	0.1962(2)	0.8686(4)	0.2884(1)	0.042(1)
C(29)	0.1542(2)	0.9323(3)	0.3326(1)	0.035(1)
C(30)	0.2790(2)	0.6791(5)	0.2525(2)	0.060(1)
C(31)	0.3065(2)	0.6071(3)	0.7064(1)	0.029(1)
C(32)	0.3802(2)	0.5548(3)	0.6763(1)	0.029(1)
C(33)	0.4219(2)	0.4436(3)	0.7013(2)	0.036(1)
C(34)	0.4870(2)	0.3909(4)	0.6728(2)	0.042(1)

C(35)	0.5137(2)	0.4439(3)	0.6200(2)	0.040(1)
C(36)	0.4729(2)	0.5555(4)	0.5963(2)	0.044(1)
C(37)	0.4071(2)	0.6093(3)	0.6240(2)	0.038(1)
C(38)	0.5836(2)	0.3832(4)	0.5884(2)	0.059(1)
C(39)	0.1917(2)	0.0985(3)	0.8911(1)	0.020(1)
C(40)	0.2392(2)	0.0319(3)	0.9417(1)	0.020(1)
C(41)	0.1253(2)	0.0638(3)	0.8478(1)	0.023(1)
C(42)	0.1117(2)	0.1715(3)	0.8104(1)	0.023(1)
C(43)	0.0337(2)	0.1523(3)	0.7663(1)	0.027(1)
C(44)	-0.0371(2)	0.1597(3)	0.8101(2)	0.036(1)
C(45)	-0.0231(2)	0.0362(3)	0.8521(2)	0.036(1)
C(46)	0.0551(2)	-0.0306(3)	0.8294(1)	0.028(1)
C(47)	0.0219(2)	0.2358(4)	0.7084(1)	0.037(1)
C(48)	0.0414(2)	-0.0009(3)	0.7581(1)	0.031(1)
C(49)	0.1138(2)	-0.0433(3)	0.7232(1)	0.037(1)
C(50)	-0.0377(2)	-0.0641(4)	0.7251(2)	0.044(1)
C(51)	0.2375(2)	-0.0942(3)	0.9660(1)	0.022(1)
C(52)	0.3056(2)	-0.1006(3)	1.0099(1)	0.021(1)
C(53)	0.3181(1)	-0.2403(3)	1.0316(1)	0.025(1)
C(54)	0.3443(2)	-0.3101(3)	0.9724(1)	0.030(1)
C(55)	0.2646(2)	-0.3093(3)	0.9257(1)	0.031(1)
C(56)	0.2015(2)	-0.2304(3)	0.9597(1)	0.026(1)
C(57)	0.3723(2)	-0.2699(3)	1.0908(1)	0.034(1)
C(58)	0.2230(2)	-0.2796(3)	1.0283(1)	0.029(1)
C(59)	0.1751(2)	-0.2080(4)	1.0748(2)	0.040(1)
C(60)	0.2116(2)	-0.4275(3)	1.0370(2)	0.042(1)
C(61)	0.1588(2)	0.4063(3)	0.8144(1)	0.026(1)
C(62)	0.0905(2)	0.4687(3)	0.8471(1)	0.025(1)
C(63)	0.0781(2)	0.4354(3)	0.9073(1)	0.033(1)
C(64)	0.0175(2)	0.4972(3)	0.9372(2)	0.036(1)
C(65)	-0.0322(2)	0.5956(3)	0.9089(2)	0.036(1)
C(66)	-0.0206(2)	0.6266(3)	0.8482(2)	0.041(1)
C(67)	0.0397(2)	0.5645(3)	0.8172(2)	0.036(1)
C(68)	-0.0951(2)	0.6665(4)	0.9434(2)	0.055(1)
C(69)	0.4094(2)	0.0600(3)	1.0621(1)	0.024(1)
C(70)	0.3710(2)	0.1108(3)	1.1174(1)	0.025(1)
C(71)	0.3223(2)	0.2234(3)	1.1132(1)	0.032(1)
C(72)	0.2869(2)	0.2698(4)	1.1645(1)	0.039(1)
C(73)	0.2984(2)	0.2055(3)	1.2208(2)	0.039(1)
C(74)	0.3486(2)	0.0944(3)	1.2255(1)	0.039(1)

C(75)	0.3840(2)	0.0472(3)	1.1743(1)	0.033(1)
C(76)	0.2589(2)	0.2548(5)	1.2764(2)	0.055(1)
Cl(1)	0.0406(1)	0.6804(1)	0.5149(1)	0.035(1)
Cl(2)	0.0984(1)	0.5993(1)	0.6551(1)	0.033(1)
Cl(3)	0.3662(1)	0.4314(1)	0.8609(1)	0.030(1)
Cl(4)	0.4435(1)	0.3372(1)	0.9918(1)	0.034(1)
N(1)	0.1857(1)	0.9090(2)	0.5408(1)	0.023(1)
N(2)	0.1595(1)	0.9890(2)	0.4919(1)	0.024(1)
N(3)	0.2524(1)	0.7938(2)	0.6424(1)	0.022(1)
N(4)	0.2951(1)	0.7487(2)	0.6966(1)	0.024(1)
N(5)	0.2181(1)	0.2204(2)	0.8789(1)	0.021(1)
N(6)	0.1673(1)	0.2655(2)	0.8285(1)	0.022(1)
N(7)	0.3030(1)	0.1015(2)	0.9722(1)	0.020(1)
N(8)	0.3451(1)	0.0158(2)	1.0129(1)	0.021(1)
Pd(1)	0.1470(1)	0.7428(1)	0.5861(1)	0.022(1)
Pd(2)	0.3302(1)	0.2728(1)	0.9272(1)	0.019(1)

Table S-3. Bond lengths [Å] and angles [°] for 6.

C(1)-C(3)	1.376(4)	C(1)-N(1)	1.377(3)
C(1)-C(2)	1.450(4)	C(2)-N(3)	1.358(4)
C(2)-C(13)	1.393(4)	C(3)-C(4)	1.382(4)
C(3)-C(8)	1.515(4)	C(4)-N(2)	1.348(4)
C(4)-C(5)	1.515(4)	C(5)-C(9)	1.517(4)
C(5)-C(6)	1.576(4)	C(5)-C(10)	1.582(4)
C(6)-C(7)	1.561(4)	C(7)-C(8)	1.563(4)
C(8)-C(10)	1.565(4)	C(10)-C(11)	1.524(5)
C(10)-C(12)	1.541(4)	C(13)-C(14)	1.378(4)
C(13)-C(18)	1.511(4)	C(14)-N(4)	1.351(4)
C(14)-C(15)	1.517(4)	C(15)-C(19)	1.517(4)
C(15)-C(16)	1.575(4)	C(15)-C(20)	1.582(4)
C(16)-C(17)	1.562(4)	C(17)-C(18)	1.555(4)
C(18)-C(20)	1.566(4)	C(20)-C(22)	1.543(4)
C(20)-C(21)	1.546(4)	C(23)-N(2)	1.481(3)
C(23)-C(24)	1.511(4)	C(24)-C(29)	1.392(4)
C(24)-C(25)	1.396(4)	C(25)-C(26)	1.393(4)
C(26)-C(27)	1.393(5)	C(27)-C(28)	1.386(5)
C(27)-C(30)	1.515(5)	C(28)-C(29)	1.399(5)
C(31)-N(4)	1.476(4)	C(31)-C(32)	1.519(4)
C(32)-C(37)	1.382(4)	C(32)-C(33)	1.404(4)
C(33)-C(34)	1.389(5)	C(34)-C(35)	1.384(5)
C(35)-C(36)	1.392(5)	C(35)-C(38)	1.519(5)
C(36)-C(37)	1.392(5)	C(39)-N(5)	1.356(3)
C(39)-C(41)	1.397(4)	C(39)-C(40)	1.448(4)
C(40)-N(7)	1.368(3)	C(40)-C(51)	1.397(4)
C(41)-C(42)	1.376(4)	C(41)-C(46)	1.514(4)
C(42)-N(6)	1.348(4)	C(42)-C(43)	1.516(4)
C(43)-C(47)	1.520(4)	C(43)-C(44)	1.569(4)
C(43)-C(48)	1.586(4)	C(44)-C(45)	1.564(4)
C(45)-C(46)	1.566(4)	C(46)-C(48)	1.576(4)
C(48)-C(49)	1.528(4)	C(48)-C(50)	1.543(4)
C(51)-C(52)	1.383(4)	C(51)-C(56)	1.512(4)
C(52)-N(8)	1.353(4)	C(52)-C(53)	1.514(4)
C(53)-C(57)	1.512(4)	C(53)-C(54)	1.573(4)
C(53)-C(58)	1.587(4)	C(54)-C(55)	1.557(4)
C(55)-C(56)	1.554(4)	C(56)-C(58)	1.581(4)
C(58)-C(59)	1.526(4)	C(58)-C(60)	1.542(4)

C(61)-N(6)	1.478(4)	C(61)-C(62)	1.519(4)
C(62)-C(63)	1.392(4)	C(62)-C(67)	1.395(4)
C(63)-C(64)	1.388(4)	C(64)-C(65)	1.392(5)
C(65)-C(66)	1.393(5)	C(65)-C(68)	1.516(5)
C(66)-C(67)	1.398(5)	C(69)-N(8)	1.483(3)
C(69)-C(70)	1.508(4)	C(70)-C(71)	1.394(4)
C(70)-C(75)	1.395(4)	C(71)-C(72)	1.394(4)
C(72)-C(73)	1.387(5)	C(73)-C(74)	1.395(5)
C(73)-C(76)	1.516(4)	C(74)-C(75)	1.396(4)
Cl(1)-Pd(1)	2.2820(9)	Cl(2)-Pd(1)	2.3022(9)
Cl(3)-Pd(2)	2.2909(8)	Cl(4)-Pd(2)	2.2879(8)
N(1)-N(2)	1.375(3)	N(1)-Pd(1)	2.097(2)
N(3)-N(4)	1.382(3)	N(3)-Pd(1)	2.061(2)
N(5)-N(6)	1.379(3)	N(5)-Pd(2)	2.071(2)
N(7)-N(8)	1.375(3)	N(7)-Pd(2)	2.081(2)

C(3)-C(1)-N(1)	110.3(2)	C(3)-C(1)-C(2)	133.8(3)
N(1)-C(1)-C(2)	115.9(2)	N(3)-C(2)-C(13)	109.7(2)
N(3)-C(2)-C(1)	115.6(2)	C(13)-C(2)-C(1)	134.7(3)
C(1)-C(3)-C(4)	105.6(3)	C(1)-C(3)-C(8)	147.4(3)
C(4)-C(3)-C(8)	106.7(2)	N(2)-C(4)-C(3)	108.9(2)
N(2)-C(4)-C(5)	141.7(3)	C(3)-C(4)-C(5)	109.3(2)
C(4)-C(5)-C(9)	120.4(3)	C(4)-C(5)-C(6)	103.3(2)
C(9)-C(5)-C(6)	115.4(2)	C(4)-C(5)-C(10)	97.2(2)
C(9)-C(5)-C(10)	116.6(3)	C(6)-C(5)-C(10)	100.7(2)
C(7)-C(6)-C(5)	104.9(2)	C(6)-C(7)-C(8)	103.0(2)
C(3)-C(8)-C(7)	104.6(2)	C(3)-C(8)-C(10)	99.1(2)
C(7)-C(8)-C(10)	102.2(2)	C(11)-C(10)-C(12)	107.6(3)
C(11)-C(10)-C(8)	113.3(3)	C(12)-C(10)-C(8)	114.1(3)
C(11)-C(10)-C(5)	113.7(3)	C(12)-C(10)-C(5)	113.2(3)
C(8)-C(10)-C(5)	94.9(2)	C(14)-C(13)-C(2)	105.2(2)
C(14)-C(13)-C(18)	106.7(2)	C(2)-C(13)-C(18)	147.8(3)
N(4)-C(14)-C(13)	109.9(2)	N(4)-C(14)-C(15)	139.9(3)
C(13)-C(14)-C(15)	109.7(2)	C(14)-C(15)-C(19)	119.4(3)
C(14)-C(15)-C(16)	102.2(2)	C(19)-C(15)-C(16)	116.0(2)
C(14)-C(15)-C(20)	97.5(2)	C(19)-C(15)-C(20)	118.0(2)
C(16)-C(15)-C(20)	100.4(2)	C(17)-C(16)-C(15)	104.8(2)
C(18)-C(17)-C(16)	103.2(2)	C(13)-C(18)-C(17)	105.5(2)
C(13)-C(18)-C(20)	99.5(2)	C(17)-C(18)-C(20)	101.2(2)
C(22)-C(20)-C(21)	107.8(3)	C(22)-C(20)-C(18)	114.0(3)

C(21)-C(20)-C(18)	113.7(2)	C(22)-C(20)-C(15)	112.3(2)
C(21)-C(20)-C(15)	113.7(3)	N(2)-C(23)-C(24)	112.1(2)
C(29)-C(24)-C(25)	118.2(3)	C(29)-C(24)-C(23)	121.2(3)
C(25)-C(24)-C(23)	120.5(2)	C(26)-C(25)-C(24)	120.9(3)
C(25)-C(26)-C(27)	120.9(3)	C(28)-C(27)-C(26)	118.1(3)
C(28)-C(27)-C(30)	121.4(3)	C(26)-C(27)-C(30)	120.5(4)
C(27)-C(28)-C(29)	121.4(3)	C(24)-C(29)-C(28)	120.5(3)
N(4)-C(31)-C(32)	112.1(2)	C(37)-C(32)-C(33)	117.8(3)
C(37)-C(32)-C(31)	123.0(3)	C(33)-C(32)-C(31)	119.1(3)
C(34)-C(33)-C(32)	120.0(3	C(35)-C(34)-C(33)	122.6(3)
C(34)-C(35)-C(36)	116.9(3)	C(34)-C(35)-C(38)	122.0(3)
C(36)-C(35)-C(38)	121.1(3)	C(35)-C(36)-C(37)	121.4(3)
C(32)-C(37)-C(36)	121.4(3)	N(5)-C(39)-C(41)	109.7(2)
N(5)-C(39)-C(40)	115.5(2)	C(41)-C(39)-C(40)	134.6(3)
N(7)-C(40)-C(51)	110.1(2)	N(7)-C(40)-C(39)	115.9(2)
C(51)-C(40)-C(39)	133.9(2)	C(42)-C(41)-C(39)	105.0(2)
C(42)-C(41)-C(46)	106.7(2)	C(39)-C(41)-C(46)	147.4(3)
N(6)-C(42)-C(41)	109.9(2)	N(6)-C(42)-C(43)	139.7(3)
C(41)-C(42)-C(43)	110.0(2)	C(42)-C(43)-C(47)	118.4(2)
C(42)-C(43)-C(44)	102.8(2)	C(47)-C(43)-C(44)	116.2(2)
C(42)-C(43)-C(48)	97.4(2)	C(47)-C(43)-C(48)	117.9(3)
C(44)-C(43)-C(48)	100.8(2)	C(45)-C(44)-C(43)	104.3(2)
C(44)-C(45)-C(46)	103.9(2)	C(41)-C(46)-C(45)	104.3(2)
C(41)-C(46)-C(48)	99.3(2)	C(45)-C(46)-C(48)	101.1(2)
C(49)-C(48)-C(50)	107.0(3)	C(49)-C(48)-C(46)	113.6(2)
C(50)-C(48)-C(46)	113.6(3)	C(49)-C(48)-C(43)	114.3(3)
C(50)-C(48)-C(43)	113.4(3)	C(46)-C(48)-C(43)	94.9(2)
C(52)-C(51)-C(40)	105.0(2)	C(52)-C(51)-C(56)	106.8(2)
C(40)-C(51)-C(56)	147.4(2)	N(8)-C(52)-C(51)	109.3(2)
N(8)-C(52)-C(53)	140.5(2)	C(51)-C(52)-C(53)	109.4(2)
C(57)-C(53)-C(52)	120.2(2)	C(57)-C(53)-C(54)	115.2(2)
C(52)-C(53)-C(54)	102.3(2)	C(57)-C(53)-C(58)	117.4(2)
C(52)-C(53)-C(58)	97.4(2)	C(54)-C(53)-C(58)	101.2(2)
C(55)-C(54)-C(53)	104.8(2)	C(56)-C(55)-C(54)	103.4(2)
H(55A)-C(55)-H(55B)	109.0	C(51)-C(56)-C(55)	104.8(2)
C(51)-C(56)-C(58)	99.6(2)	C(55)-C(56)-C(58)	101.3(2)
C(59)-C(58)-C(60)	108.4(3)	C(59)-C(58)-C(56)	113.4(2)
C(60)-C(58)-C(56)	114.4(3)	C(59)-C(58)-C(53)	114.1(2)
C(60)-C(58)-C(53)	111.9(2)	C(56)-C(58)-C(53)	94.3(2)
N(6)-C(61)-C(62)	111.7(2)	C(63)-C(62)-C(67)	118.4(3)

C(63)-C(62)-C(61)	121.6(3)	C(67)-C(62)-C(61)	120.0(3)
C(64)-C(63)-C(62)	120.7(3)	C(63)-C(64)-C(65)	121.8(3)
C(64)-C(65)-C(66)	117.1(3)	C(64)-C(65)-C(68)	120.9(3)
C(66)-C(65)-C(68)	122.0(3)	C(65)-C(66)-C(67)	121.8(3)
C(62)-C(67)-C(66)	120.1(3)	C(71)-C(70)-C(75)	118.5(3)
C(71)-C(70)-C(69)	120.7(2)	C(75)-C(70)-C(69)	120.8(3)
C(70)-C(71)-C(72)	120.4(3)	C(73)-C(72)-C(71)	121.3(3)
C(72)-C(73)-C(74)	118.3(3)	C(72)-C(73)-C(76)	121.3(3)
C(74)-C(73)-C(76)	120.4(3)	C(73)-C(74)-C(75)	120.7(3)
C(70)-C(75)-C(74)	120.7(3)	N(2)-N(1)-C(1)	105.4(2)
N(2)-N(1)-Pd(1)	140.00(17)	C(1)-N(1)-Pd(1)	111.62(17)
C(4)-N(2)-N(1)	109.8(2)	C(4)-N(2)-C(23)	127.8(2)
N(1)-N(2)-C(23)	122.1(2)	C(2)-N(3)-N(4)	107.1(2)
C(2)-N(3)-Pd(1)	113.66(17)	N(4)-N(3)-Pd(1)	137.02(17)
C(14)-N(4)-N(3)	108.1(2)	C(14)-N(4)-C(31)	126.7(2)
N(3)-N(4)-C(31)	119.8(2)	C(39)-N(5)-N(6)	106.9(2)
C(39)-N(5)-Pd(2)	114.62(16)	N(6)-N(5)-Pd(2)	137.25(17)
C(42)-N(6)-N(5)	108.4(2)	C(42)-N(6)-C(61)	126.3(2)
N(5)-N(6)-C(61)	121.7(2)	C(40)-N(7)-N(8)	106.1(2)
C(40)-N(7)-Pd(2)	113.42(17)	N(8)-N(7)-Pd(2)	136.60(17)
C(52)-N(8)-N(7)	109.4(2)	C(52)-N(8)-C(69)	126.6(2)
N(7)-N(8)-C(69)	122.2(2)	N(3)-Pd(1)-N(1)	78.73(9)
N(3)-Pd(1)-Cl(1)	173.17(7)	N(1)-Pd(1)-Cl(1)	98.63(6)
N(3)-Pd(1)-Cl(2)	95.25(7)	N(1)-Pd(1)-Cl(2)	165.13(7)
Cl(1)-Pd(1)-Cl(2)	88.77(3)	N(5)-Pd(2)-N(7)	78.64(8)
N(5)-Pd(2)-Cl(4)	172.02(6)	N(7)-Pd(2)-Cl(4)	98.63(6)
N(5)-Pd(2)-Cl(3)	97.54(6)	N(7)-Pd(2)-Cl(3)	167.59(6)
Cl(4)-Pd(2)-Cl(3)	86.65(3)		

Table S-4. Anisotropic displacement parameters (Å²) for 6.

The anisotropic displacement factor exponent takes the form:
$-2\pi^2[h^2 a^{*2}U_{11} + ... + 2 h k a^* b^* U_{12}]$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C(1)	0.026(1)	0.020(1)	0.024(1)	-0.002(1)	-0.001(1)	-0.001(1)
C(2)	0.024(1)	0.022(1)	0.022(1)	-0.002(1)	0.000(1)	0.001(1)
C(3)	0.029(1)	0.023(2)	0.024(1)	-0.002(1)	-0.004(1)	0.000(1)
C(4)	0.031(1)	0.019(1)	0.023(1)	0.000(1)	0.002(1)	0.003(1)
C(5)	0.037(1)	0.023(1)	0.028(1)	0.004(1)	-0.001(1)	0.000(1)
C(6)	0.039(2)	0.040(2)	0.035(2)	0.004(1)	0.004(1)	-0.002(2)
C(7)	0.034(2)	0.039(2)	0.043(2)	0.006(1)	0.000(1)	-0.005(1)
C(8)	0.036(1)	0.023(2)	0.031(1)	0.002(1)	-0.005(1)	-0.004(1)
C(9)	0.042(2)	0.029(2)	0.032(1)	0.007(1)	-0.001(1)	0.001(1)
C(10)	0.041(2)	0.024(2)	0.033(2)	0.001(1)	-0.005(1)	-0.003(1)
C(11)	0.051(2)	0.034(2)	0.039(2)	-0.008(2)	0.003(2)	0.007(2)
C(12)	0.066(2)	0.022(2)	0.054(2)	0.002(2)	-0.010(2)	-0.002(2)
C(13)	0.023(1)	0.025(1)	0.022(1)	-0.001(1)	0.001(1)	0.001(1)
C(14)	0.024(1)	0.024(1)	0.021(1)	0.000(1)	0.002(1)	0.002(1)
C(15)	0.026(1)	0.030(2)	0.022(1)	-0.001(1)	-0.002(1)	-0.001(1)
C(16)	0.031(1)	0.036(2)	0.027(2)	-0.007(1)	0.004(1)	-0.001(1)
C(17)	0.033(2)	0.029(2)	0.033(2)	-0.008(1)	0.002(1)	-0.001(1)
C(18)	0.031(2)	0.025(1)	0.029(2)	0.000(1)	-0.001(1)	-0.007(1)
C(19)	0.034(1)	0.041(2)	0.028(1)	0.002(2)	-0.006(1)	0.008(2)
C(20)	0.026(1)	0.040(2)	0.025(1)	-0.001(1)	-0.003(1)	-0.006(1)
C(21)	0.026(2)	0.052(2)	0.039(2)	0.000(2)	0.007(1)	-0.001(1)
C(22)	0.034(2)	0.046(2)	0.040(2)	-0.001(2)	-0.006(1)	-0.012(2)
C(23)	0.027(1)	0.028(2)	0.024(1)	-0.001(1)	-0.007(1)	0.001(1)
C(24)	0.028(1)	0.027(2)	0.022(1)	0.000(1)	-0.004(1)	-0.007(1)
C(25)	0.036(1)	0.034(2)	0.027(1)	0.004(1)	0.003(1)	0.004(1)
C(26)	0.037(2)	0.048(2)	0.038(2)	-0.002(2)	0.003(1)	0.009(1)
C(27)	0.027(1)	0.055(2)	0.032(1)	-0.007(2)	0.005(1)	-0.004(2)
C(28)	0.049(2)	0.053(2)	0.023(2)	0.003(1)	0.004(1)	-0.020(2)
C(29)	0.044(2)	0.030(2)	0.029(2)	0.003(1)	-0.003(1)	-0.008(1)
C(30)	0.045(2)	0.094(3)	0.042(2)	-0.009(2)	0.012(2)	0.010(2)
C(31)	0.035(2)	0.021(1)	0.029(2)	0.006(1)	0.001(1)	-0.001(1)
C(32)	0.031(2)	0.022(2)	0.032(2)	-0.002(1)	-0.004(1)	-0.002(1)
C(33)	0.042(2)	0.027(2)	0.038(2)	0.004(1)	-0.001(1)	0.002(1)
C(34)	0.037(2)	0.028(2)	0.058(2)	0.000(2)	-0.005(2)	0.008(1)

C(35)	0.033(2)	0.033(2)	0.054(2)	-0.005(2)	0.002(2)	0.003(1)
C(36)	0.047(2)	0.040(2)	0.048(2)	0.008(2)	0.014(2)	0.006(2)
C(37)	0.041(2)	0.032(2)	0.041(2)	0.006(1)	0.005(1)	0.008(1)
C(38)	0.048(2)	0.046(2)	0.085(3)	-0.004(2)	0.016(2)	0.011(2)
C(39)	0.020(1)	0.018(1)	0.022(1)	-0.001(1)	0.003(1)	0.001(1)
C(40)	0.019(1)	0.023(1)	0.020(1)	0.001(1)	0.002(1)	0.001(1)
C(41)	0.023(1)	0.022(1)	0.023(1)	-0.002(1)	0.004(1)	0.002(1)
C(42)	0.023(1)	0.024(1)	0.022(1)	-0.001(1)	0.002(1)	0.005(1)
C(43)	0.022(1)	0.033(2)	0.025(1)	0.000(1)	-0.002(1)	0.002(1)
C(44)	0.024(1)	0.046(2)	0.038(2)	0.001(2)	0.004(1)	0.007(1)
C(45)	0.024(1)	0.046(2)	0.037(2)	0.006(1)	0.006(1)	-0.001(1)
C(46)	0.024(1)	0.028(2)	0.030(2)	0.000(1)	-0.002(1)	-0.002(1)
C(47)	0.036(1)	0.043(2)	0.030(1)	0.003(2)	-0.006(1)	0.003(2)
C(48)	0.026(1)	0.035(2)	0.031(2)	-0.006(1)	-0.002(1)	-0.002(1)
C(49)	0.036(2)	0.039(2)	0.034(2)	-0.012(1)	0.000(1)	0.001(1)
C(50)	0.036(2)	0.049(2)	0.043(2)	-0.008(2)	-0.012(1)	-0.008(2)
C(51)	0.023(1)	0.019(1)	0.023(1)	0.002(1)	0.002(1)	0.001(1)
C(52)	0.023(1)	0.023(1)	0.017(1)	0.001(1)	0.002(1)	0.001(1)
C(53)	0.024(1)	0.022(1)	0.029(1)	0.004(1)	-0.001(1)	0.001(1)
C(54)	0.030(1)	0.025(2)	0.035(2)	-0.002(1)	0.000(1)	0.005(1)
C(55)	0.032(2)	0.024(1)	0.036(2)	-0.002(1)	-0.001(1)	0.000(1)
C(56)	0.024(1)	0.023(1)	0.029(1)	0.002(1)	-0.001(1)	-0.004(1)
C(57)	0.037(2)	0.031(2)	0.032(2)	0.010(1)	-0.006(1)	0.000(1)
C(58)	0.029(1)	0.027(2)	0.030(1)	0.007(1)	0.000(1)	-0.002(1)
C(59)	0.034(2)	0.050(2)	0.037(2)	0.011(2)	0.009(1)	0.001(2)
C(60)	0.043(2)	0.032(2)	0.050(2)	0.014(2)	-0.002(2)	-0.012(1)
C(61)	0.032(1)	0.021(2)	0.025(1)	0.005(1)	0.000(1)	0.001(1)
C(62)	0.026(1)	0.020(1)	0.029(2)	-0.001(1)	0.001(1)	0.000(1)
C(63)	0.038(2)	0.031(2)	0.030(2)	0.004(1)	0.002(1)	0.006(1)
C(64)	0.038(2)	0.037(2)	0.035(2)	-0.001(1)	0.008(1)	0.002(1)
C(65)	0.030(2)	0.029(2)	0.049(2)	-0.004(1)	0.008(1)	-0.001(1)
C(66)	0.036(2)	0.031(2)	0.056(2)	0.009(2)	0.006(2)	0.012(1)
C(67)	0.040(2)	0.029(2)	0.038(2)	0.007(1)	0.003(1)	0.006(1)
C(68)	0.045(2)	0.049(2)	0.073(3)	-0.003(2)	0.021(2)	0.011(2)
C(69)	0.022(1)	0.024(1)	0.024(1)	-0.001(1)	-0.003(1)	-0.002(1)
C(70)	0.022(1)	0.027(2)	0.023(1)	0.000(1)	-0.002(1)	-0.005(1)
C(71)	0.032(1)	0.037(2)	0.025(1)	-0.001(1)	0.000(1)	0.005(1)
C(72)	0.038(2)	0.041(2)	0.037(2)	-0.005(2)	0.004(1)	0.008(2)
C(73)	0.038(2)	0.048(2)	0.033(2)	-0.007(1)	0.008(1)	-0.009(1)
C(74)	0.045(2)	0.046(2)	0.025(2)	0.005(1)	0.002(1)	-0.007(2)

C(75)	0.037(2)	0.031(2)	0.030(2)	0.002(1)	-0.002(1)	-0.001(1)
C(76)	0.056(2)	0.073(3)	0.038(2)	-0.006(2)	0.018(2)	-0.001(2)
Cl(1)	0.031(1)	0.037(1)	0.037(1)	0.003(1)	-0.005(1)	-0.010(1)
Cl(2)	0.039(1)	0.030(1)	0.031(1)	0.002(1)	0.008(1)	-0.006(1)
Cl(3)	0.035(1)	0.025(1)	0.031(1)	0.005(1)	0.006(1)	-0.004(1)
Cl(4)	0.027(1)	0.032(1)	0.041(1)	0.007(1)	-0.006(1)	-0.009(1)
N(1)	0.026(1)	0.020(1)	0.021(1)	0.003(1)	-0.001(1)	-0.001(1)
N(2)	0.028(1)	0.022(1)	0.020(1)	-0.001(1)	-0.003(1)	0.000(1)
N(3)	0.027(1)	0.018(1)	0.021(1)	0.003(1)	-0.002(1)	0.000(1)
N(4)	0.029(1)	0.020(1)	0.023(1)	0.001(1)	0.000(1)	-0.001(1)
N(5)	0.022(1)	0.020(1)	0.021(1)	0.003(1)	-0.001(1)	0.002(1)
N(6)	0.025(1)	0.021(1)	0.019(1)	0.002(1)	-0.001(1)	0.004(1)
N(7)	0.021(1)	0.018(1)	0.020(1)	0.003(1)	-0.002(1)	0.000(1)
N(8)	0.021(1)	0.023(1)	0.018(1)	0.002(1)	-0.001(1)	0.001(1)
Pd(1)	0.024(1)	0.020(1)	0.022(1)	-0.001(1)	0.001(1)	-0.002(1)
Pd(2)	0.020(1)	0.017(1)	0.020(1)	0.001(1)	0.002(1)	-0.001(1)