Supplementary Material (ESI) for New Journal of Chemistry

SUPPORTING INFORMATION

A Supramolecular Approach to Modifying Chiral Ligands: Co-ordination Chemistry of a Multifunctionalised Tridentate Amine-Phosphine Ligand.

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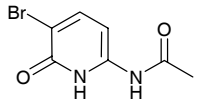
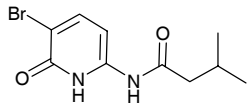
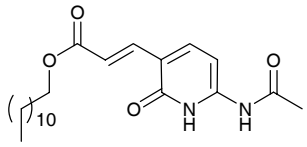
pyridinone derivatives



A1.[1] White solid. ^{1}H NMR (300 MHz, CD_3OD) δ= 2.05 (3H, s), 6.37 (1H, d, *J* 7.9 Hz), 7.60 (1H, d, *J* 7.9 Hz); ^{13}C NMR (75 MHz, DMSO-d_6) δ= 23.9, 96.6, 103.3, 143.0, 147.0, 162.0, 169.4; MS (ESI) m/z: 254.95 (MNa^+, 95%), 252.95 (MNa^+, 100), 232.98 (MH^+, 5).

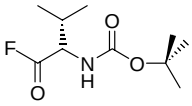


A2.[2] White solid. Mp 209-210 ºC; IR (KBr, cm^{-1}) 1644, 1586, 1453, 1450, 1215, 1153 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ= 0.92 (6H, d, *J* 6.5 Hz), 1.19 (1H, s), 2.07-2.19 (1H, m), 2.23 (2H, d, *J* 6.7 Hz), 6.45 (1H, d, *J* 8.2 Hz), 7.69 (1H, d, *J* 8.2 Hz), 9.67 (1H, br s); ^{13}C NMR (75 MHz, CD_3OD) δ= 23.1, 23.1, 27.5, 47.3, 96.3, 106.3, 146.1, 146.6, 160.0, 176.6; MS (EI) m/z: 274.01 (M^+, 23%), 272.01 (M^+, 24), 218.99 (9), 189.95 (99), 187.95 (100), 159.96 (19), 118.93 (5), 57.07 (8); Found (TOF EI) 272.0152 (M^+), $C_{10}H_{13}N_2O_2{}^{(79)}Br$ requires 272.0160. Found (TOF EI) 274.0142 (M^+), $C_{10}H_{13}N_2O_2{}^{(81)}Br$ requires 274.0140.



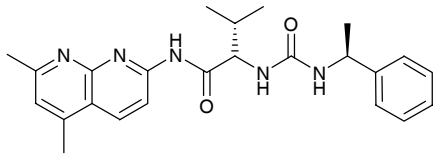
A3.[2] Yellow solid. Mp 140-142 ºC; IR ($CDCl_3$, cm^{-1}) 3157, 2927, 2856, 1706, 1653, 1614, 1567, 1467, 1376, 1249, cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 0.80 (3H, t, *J* 6.7 Hz), 1.18-1.24 (m, 18H), 1.54-1.63 (2H, m), 2.13 (1H, br s), 2.14 (3H, s), 4.08 (2H, t, *J* 6.8 Hz), 6.36 (1H, d, *J* 8.0 Hz), 6.73 (1H, d, *J* 15.9 Hz), 7.48 (1H, d, *J* 15.9 Hz), 7.53 (1H, d, *J* 8.0 Hz), 10.40 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 14.1, 22.7, 24.5, 26.0, 28.8, 29.3, 29.4, 29.5, 29.6, 29.6, 29.7, 31.9, 64.7, 94.9, 117.7, 117.9, 139.3, 144.2, 144.6, 160.4, 168.0, 171.5; MS (TOF ES) m/z: 413.10 (MNa^+, 100%); Found (TOF ES) 413.2413 (MNa^+), $C_{22}H_{34}N_2O_4Na$ requires 413.2416.

N-Boc-amino acid fluoride 2[3]



To a stirred solution of the *N*-Boc-*L*-Valine (0.868 g, 4 mmol) in dry DCM (10 ml) and pyridine (0.324 ml, 4 mmol) under a N_2 atmosphere was added cyanuric fluoride (0.8 ml, 9 mmol) at -30 °C. A white precipitate formed and gradually increased in amount. After stirring at -30 to -10 °C for 2 h, crushed ice was added along with 10 ml of additional DCM. The organic layer was separated and the aqueous layer extracted with DCM (3 x 20 ml). The combined organic layers were washed with 30 ml of water, dried over anhydrous $MgSO_4$ and the solvent was removed with a rotary evaporator at room temperature to give *N*-Boc-amino acid fluoride **2** (0.728 g, 83%) as colourless oil. ^1H-NMR (δ, $CDCl_3$) 0.92 (3H, d *J* 6.9 Hz, CH_3), 0.98 (3H, d *J* 6.9 Hz, CH_3), 1.39 (9H, s, 3xCH_3), 2.09-2.22 (1H, m, CH), 4.32 (1H, dd, *J* 9.1, 4.7 Hz, CH), 4.90 (1H, br d *J* 9.1 Hz, NH). ^{19}F-NMR (δ, $CDCl_3$) 33.43 (s, F-C=O).

Synthesis of diastereomeric ureas from amine 5



(*S*)-(*S*)-Urea. To a solution of (*S*)-amine **4** (14.6 mg, 0.054 mmol) in $CHCl_3$ (2 ml) was added (–)-(*S*)-1-Phenylethyl isocyanate (9.5 mg, 0.064 mmol). The resulting solution was stirred for 4.5 hours until there was no unreacted (*S*)-amine and then evaporated to dryness. The residue was purified by column chromatography using ethyl acetate and then ethyl acetate/ethanol (4:1) as eluent to afford the urea (16 mg, 71%) as a white solid. Mp 131-133 ºC; $[\alpha]_D^{20}$ +15.2 (*c* 0.5, $CHCl_3$); IR ($CDCl_3$, cm^{-1}) 3356, 3300, 3018, 2968, 2929, 1655, 1601, 1569, 1510, 1407, 1313, 1216 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ= 0.73 (3H, d *J* 6.9 Hz), 0.87 (3H, d *J* 6.9 Hz), 1.32 (3H, d *J* 6.9 Hz), 2.19-2.30 (1H, m), 2.48 (3H, s), 2.56 (3H, s), 4.38 (1H, dd *J* 5.6, 3.5 Hz), 4.88 (1H, m), 6.47 (1H, br d *J* 5.6 Hz), 6.61 (1H, br d *J* 6.7 Hz), 7.02-7.23 (6H, m), 8.20 (1H, d *J* 9.0 Hz), 8.41 (1H, d *J* 9.0 Hz), 9.52 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ= 17.6, 18.1, 19.4, 23.2, 24.9, 30.5, 50.1, 61.0, 114.1, 118.7, 122.4, 126.0, 126.7, 128.3, 135.7, 144.8, 145.9, 153.1, 154.2, 158.3, 162.7, 173.3; MS (ES) m/z: 420.2 (MH^+, 100%), 174.1 (12); Found (ES) 420.2401 (MH^+), $C_{24}H_{30}N_5O_2$ requires 420.2400. (*R*)-(*S*)-Urea was prepared using the same procedure.

General procedure for imine hydrogenation.

DCM (2 ml) was added to a vial containing ligand **5** (0.01 mmol), additive (0.01 mmol) and $[Ir(COD)Cl]_2$ (0.005 mmol) under a N_2 atmosphere. The mixture was stirred for 30 minutes and then $AgBF_4$ (0.01 mmol) was added, stirred for 15 min and the filtered through a cotton plug into a vial under a N_2 atmosphere. 2,3,3-Trimethylindoline (1 mmol) was added and the reaction mixture was transferred to an autoclave. The autoclave was pressurised to 50 bar H_2 gas and the mixture was stirred for the required time. After pressure release, the solvent was partially evaporated and then filtered through a sort plug of silica gel eluting with DCM. The filtrate was analysed by ^{1}H NMR and chiral HPLC to determine conversion and enantioselectivity, ee determined by HPLC using chiralpak OD-H column at 254 nm (hexane:2-propanol 98:2), 1 ml/min; t_r= 7.1 min (minor), 8.2 min (major).

General procedure for ketone hydrosilylation.

To a mixture of ligand **5** (0.02 mmol), additive (0.02 mmol) and $[Rh(COD)Cl]_2$ (0.005 mmol) in toluene (1 ml) which has been pre-stirred at room temperature for 30 min, was added a solution of ketone (1 mmol) in toluene (0.5 ml). Then Ph_2SiH_2 (2 mmol) was added at –78 ºC, and the resultant mixture was stirred at room temperature for 19 h. After being cooled to 0 ºC, 1M HCl aq (2.5 ml) and acetone (4 ml) were successively added and the mixture stirred for 2 h at room temperature. The reaction mixture extracted with DCM (3 x 10 ml). The combined organic layers were washed with brine (10 ml x 1), dried over anhydrous $MgSO_4$, filtered and partially evaporated under reduced pressure. The filtrate was analysed by ^{19}F NMR and chiral GC/MS to determine conversion and enantioselectivity.

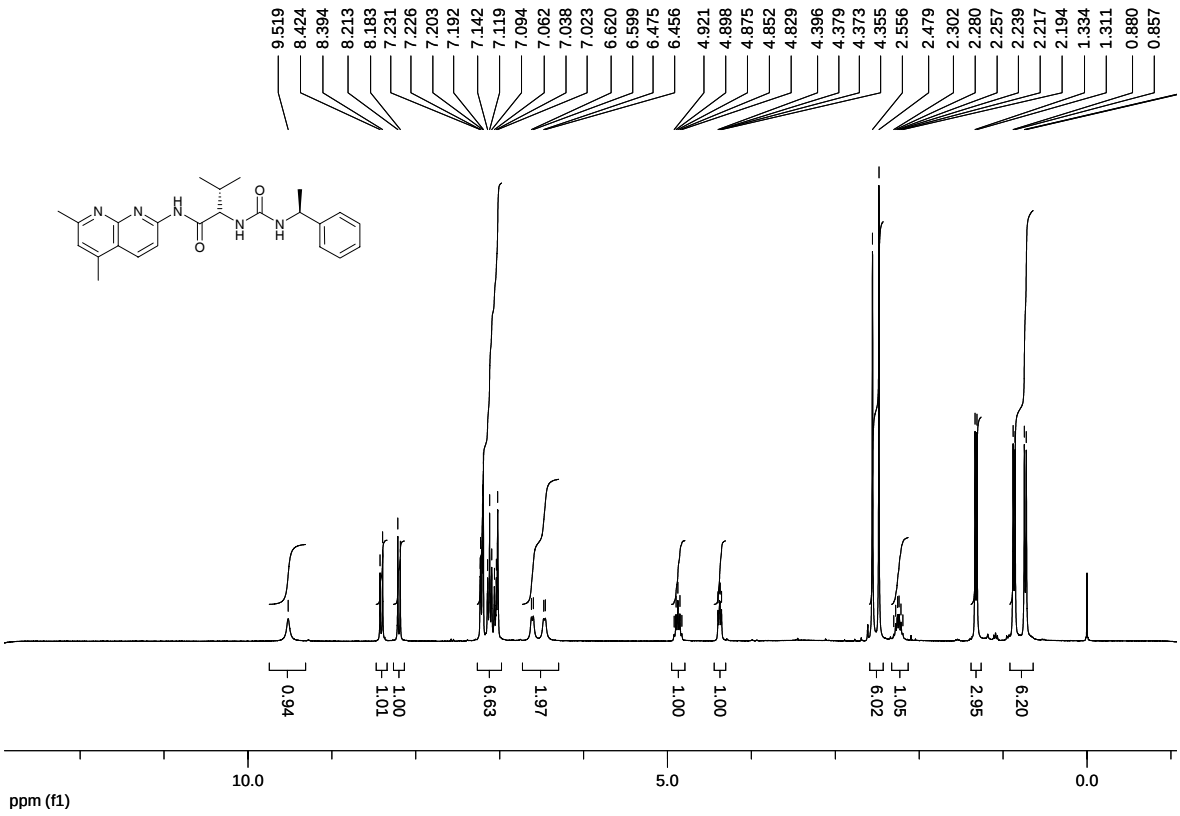
References

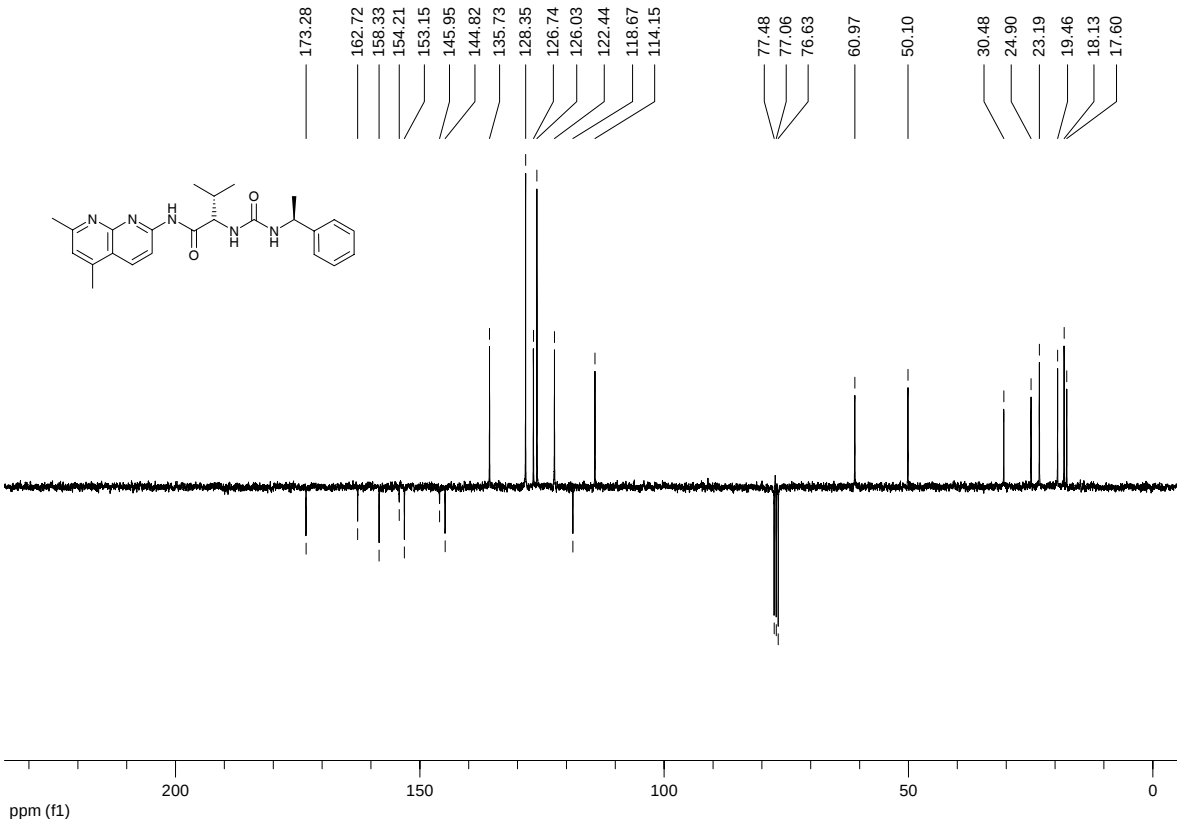
[1] M. Sollogoub, K. R. Fox, V. E. C. Powers, T. Brown. *Tetrahedron Lett.* 2002, **43**, 3121.

[2] M. L. Clarke and J. A. Fuentes, *Angew. Chem. Int. Ed.*, 2007, **46**, 930; *Angew. Chem.*, 2007, **119**, 948.

[3] L. A. Carpino; E. M. E. Mansour; D. Sadat-Aallaee *J. Org. Chem.* 1991, **56**, 2611

NMR spectra of (*S*)-(*S*)-Urea





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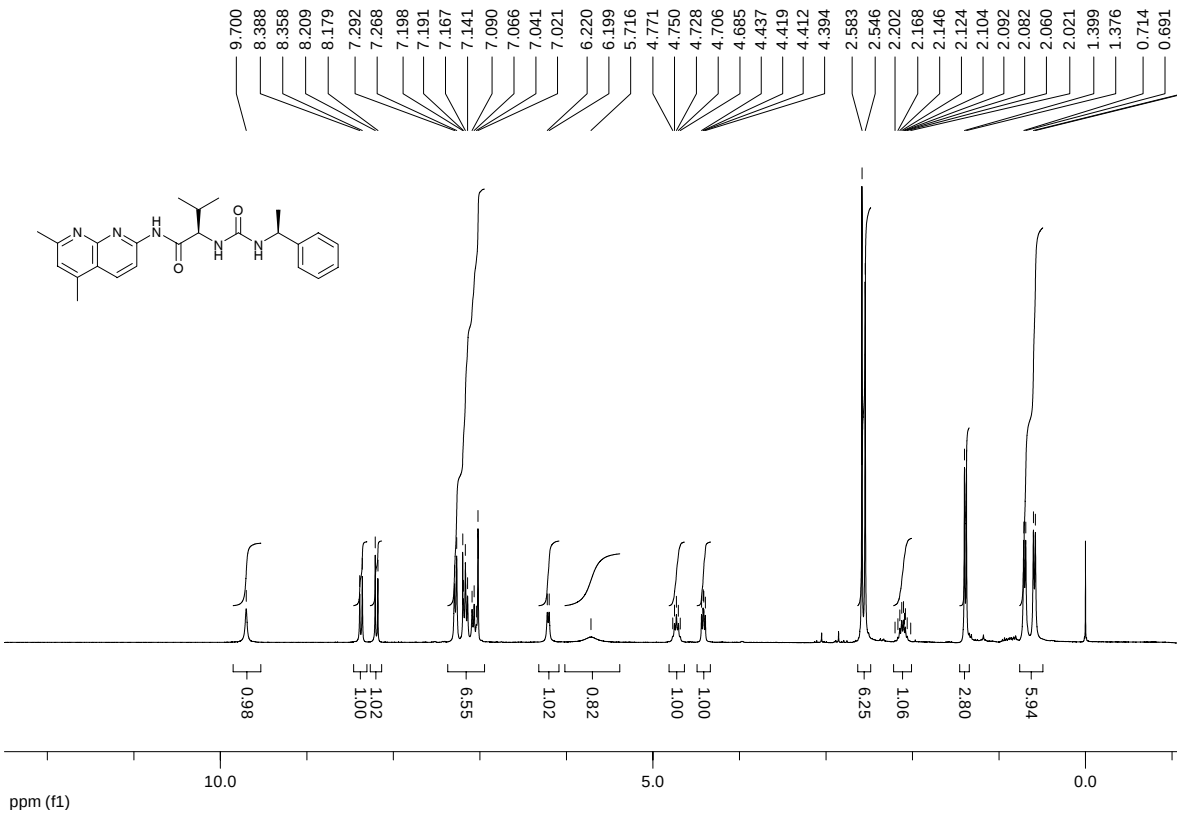
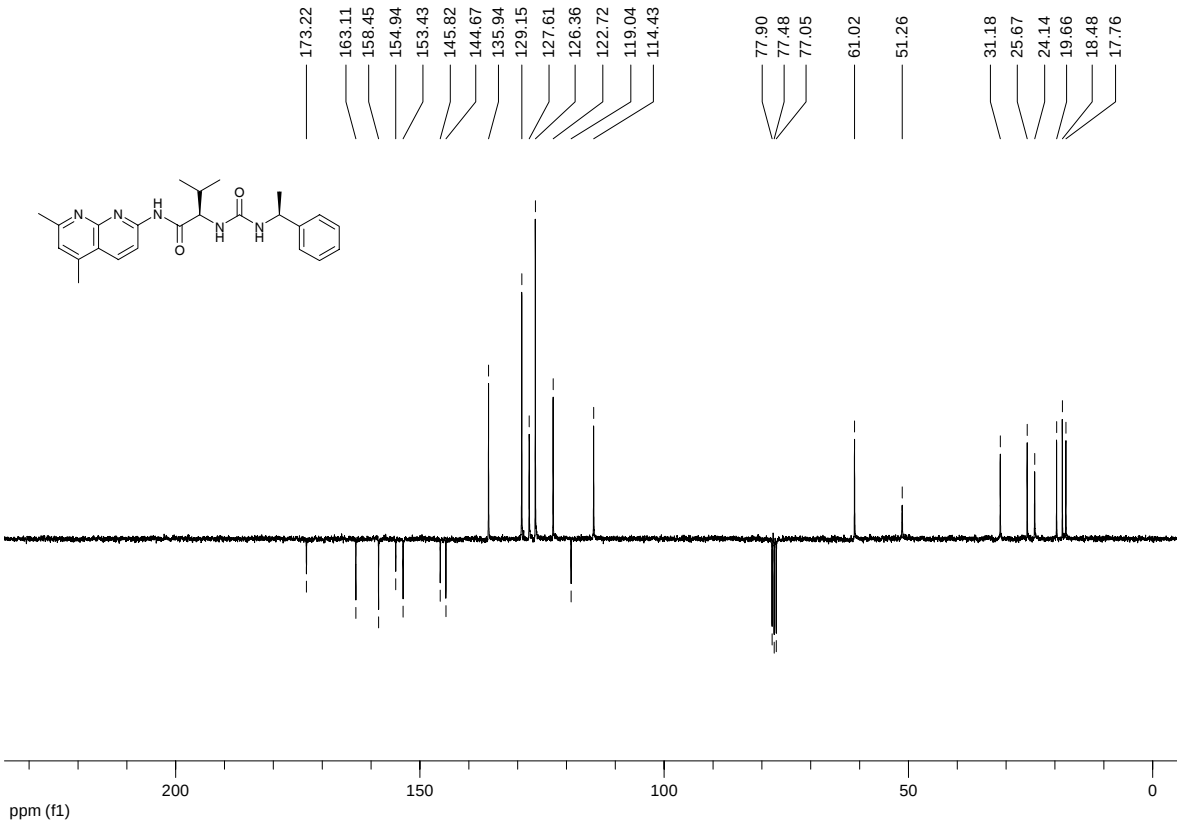
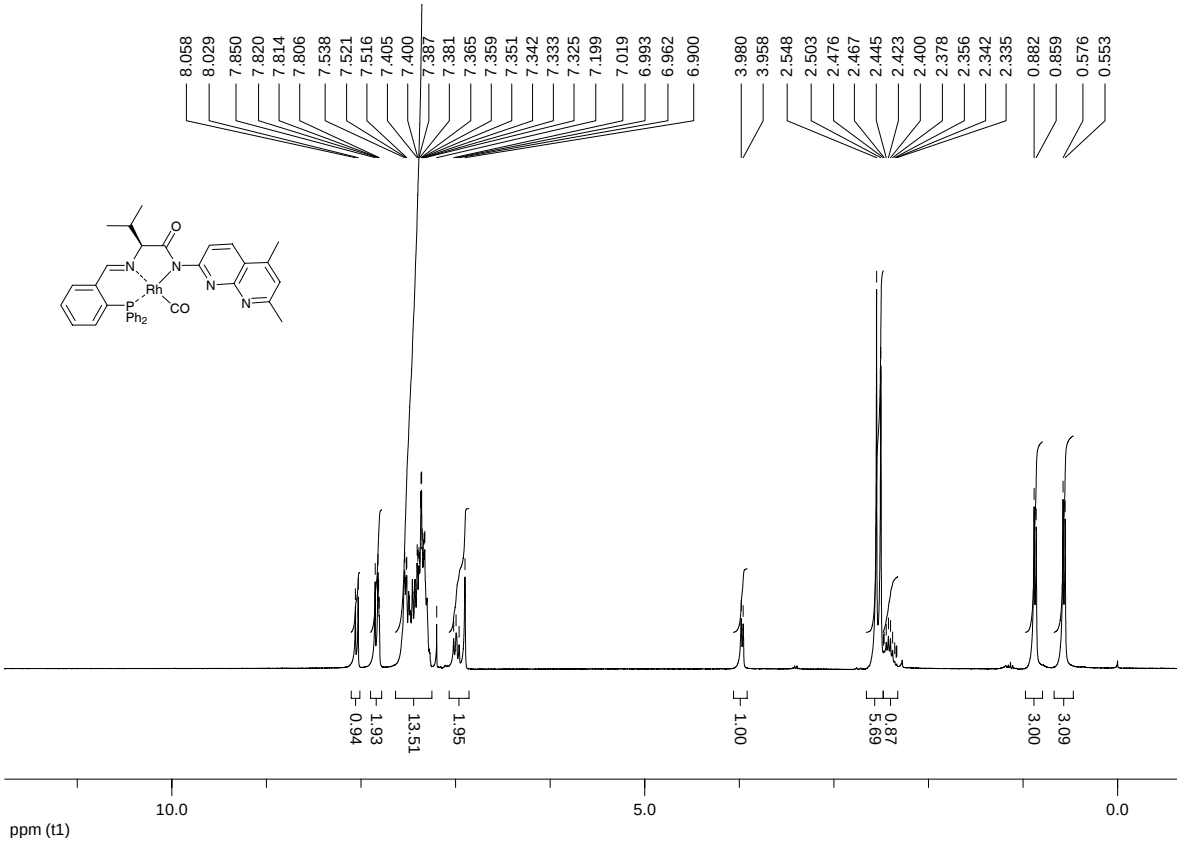
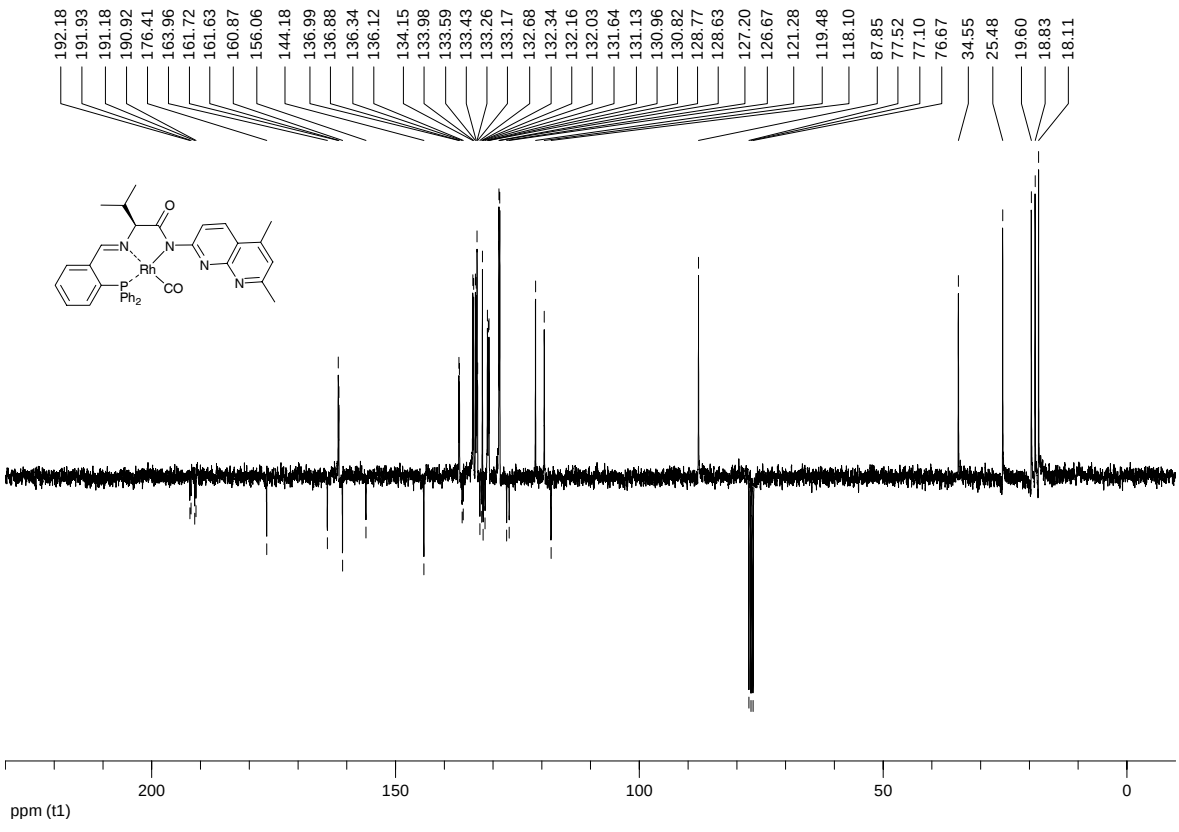
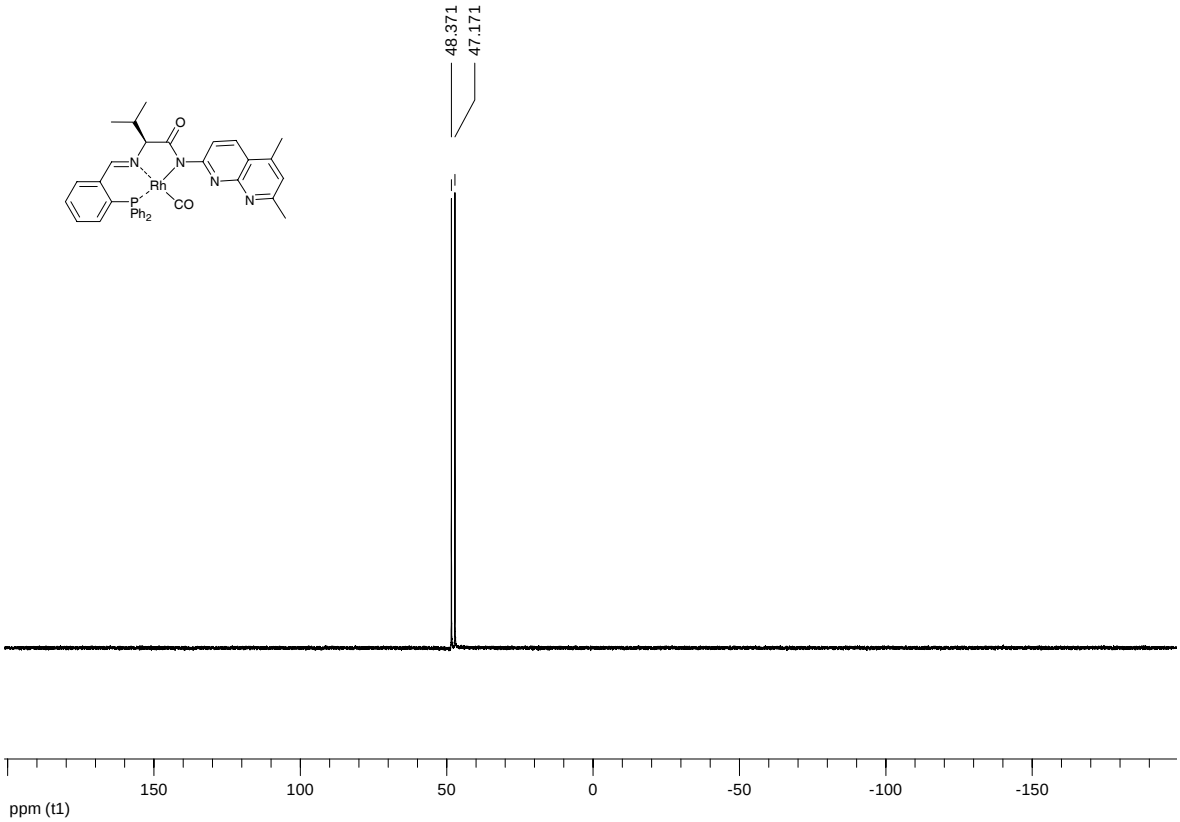




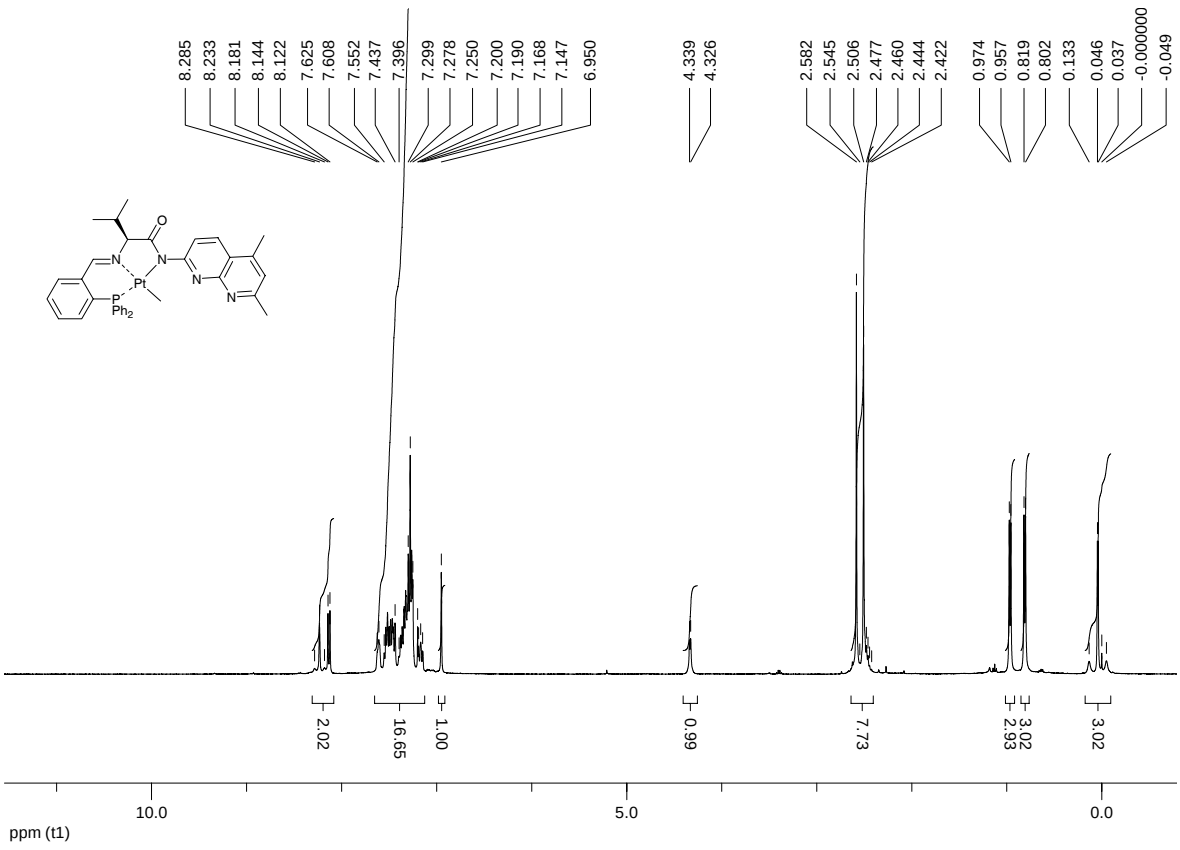
NMR spectra of complex 6

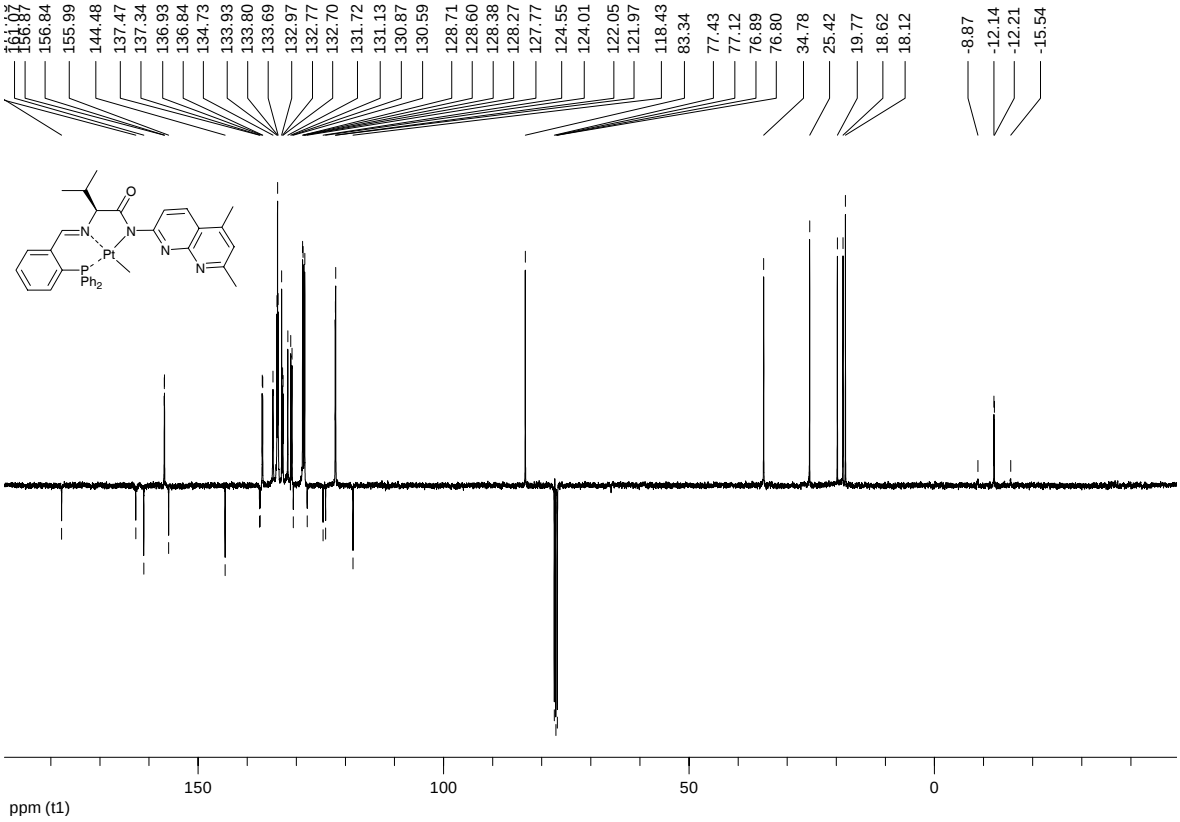


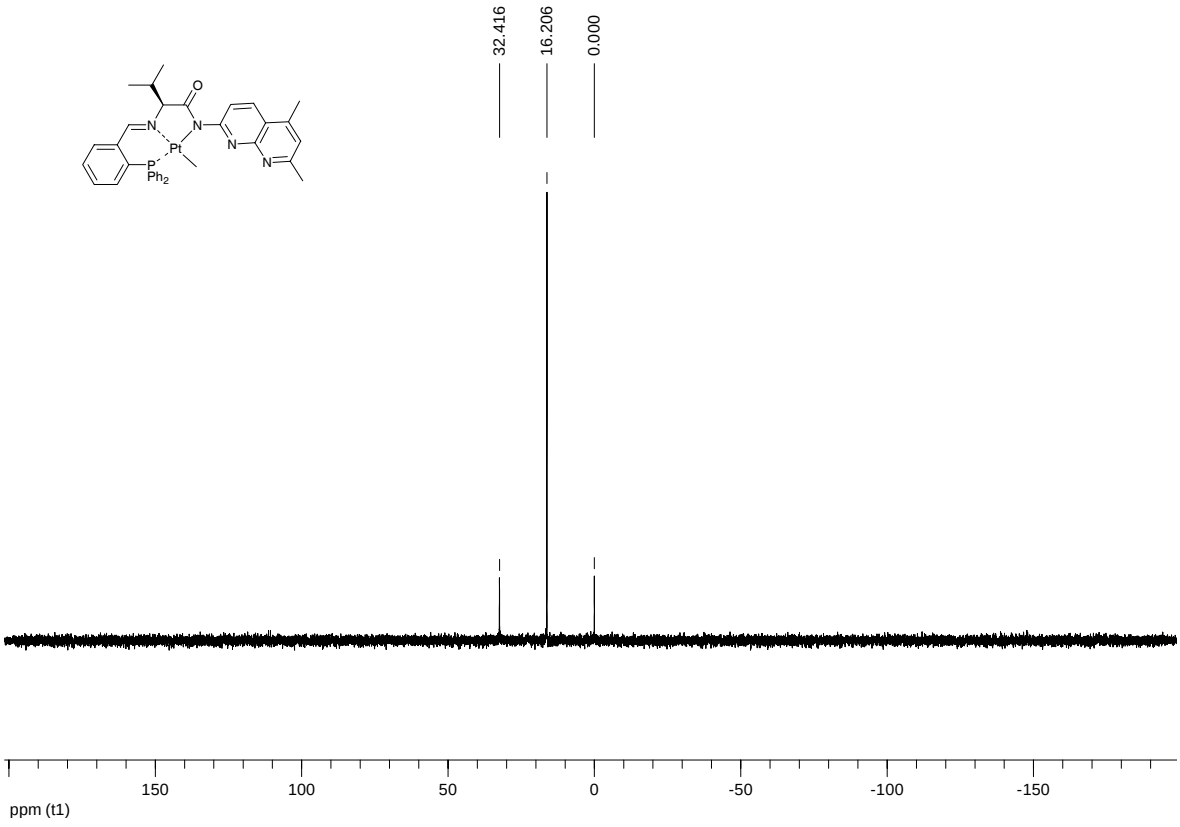




NMR spectra of complex 7

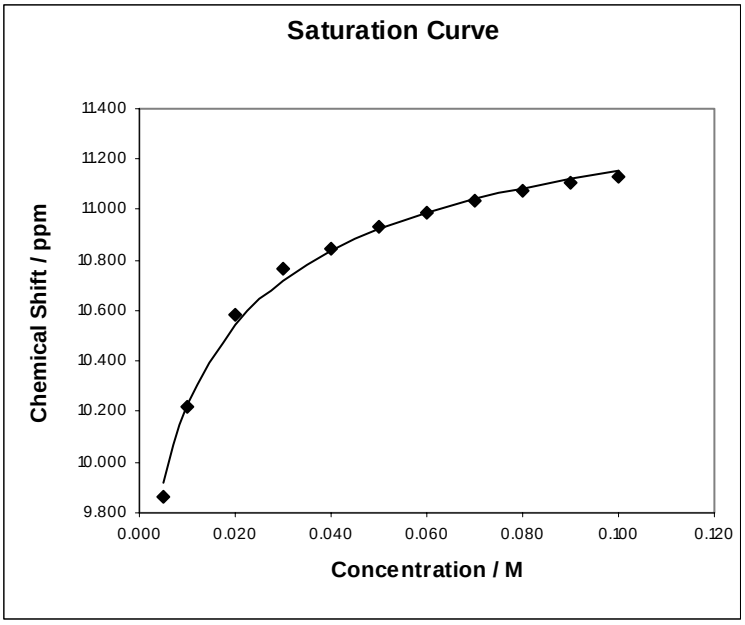



161.07
156.87
156.84
155.99
144.48
137.47
137.34
136.93
136.84
134.73
133.93
133.80
133.69
132.97
132.77
132.70
131.72
131.13
130.87
130.59
128.71
128.60
128.38
128.27
127.77
124.55
124.01
122.05
121.97
118.43
83.34
77.43
77.12
76.89
76.80
34.78
25.42
19.77
18.62
18.12
-8.87
-12.14
-12.21
-15.54
150
100
50
0
ppm (t1)

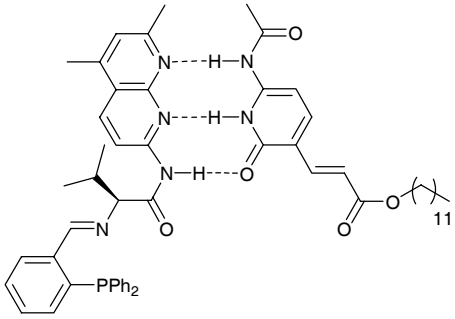

32.416
16.206
0.000
150
100
50
0
-50
-100
-150
ppm (t1)

Binding Constant determination for Ligand 5 and Additive A3

The binding constant value (Ka) was calculated from ^{1}H NMR dilution (1:1 model) data. Titration experiments were carried out in $CDCl_3$ at 273K



Host:Guest pair



Optimised Value of Ka 106
ΔG/Kcalmol^{-1} -2.63
SSR 7.59 E-3

Crystallographic data of complex 7 (jafmc5)

Table 1. Crystal data and structure refinement for JAFMC5.

Identification code	jafmc5	
Empirical formula	C35 H37 N4 O2 P Pt	
Formula weight	771.75	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)/c	
Unit cell dimensions	a = 8.7388(15) Å	α= 90°.
	b = 14.988(2) Å	β= 94.227(2)°.
	c = 25.469(4) Å	γ = 90°.
Volume	3326.7(10) $Å^3$	
Z	4	
Density (calculated)	1.541 Mg/m^3	
Absorption coefficient	4.302 mm^{-1}	
F(000)	1536	
Crystal size	0.0800 x 0.0300 x 0.0300 mm^3	
Theta range for data collection	2.77 to 25.34°.	
Index ranges	-10<=h<=9, -18<=k<=16, -30<=l<=30	
Reflections collected	28683	
Independent reflections	5887 [R(int) = 0.0686]	
Completeness to theta = 25.00°	96.8 %	
Absorption correction	Multiscan	
Max. and min. transmission	0.8790 and 0.7125	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5887 / 0 / 401	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.1068	
R indices (all data)	R1 = 0.0479, wR2 = 0.1095	
Largest diff. peak and hole	2.221 and -2.552 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for JAFMC5. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Pt(1)	5990(1)	8222(1)	3167(1)	20(1)
P(1)	4959(2)	8312(1)	2359(1)	20(1)
C(1)	3537(6)	9207(4)	2341(2)	22(1)
C(2)	2579(6)	9317(4)	2762(2)	24(1)
C(3)	1450(6)	9978(4)	2725(2)	27(1)
C(4)	1284(7)	10557(4)	2304(3)	32(1)
C(5)	2243(7)	10473(4)	1900(3)	33(1)
C(6)	3347(7)	9793(4)	1917(2)	30(1)
C(7)	2664(6)	8795(4)	3250(2)	24(1)
N(8)	3840(5)	8357(3)	3441(2)	22(1)
C(9)	3765(7)	7909(4)	3957(2)	28(1)
C(10)	5323(6)	8002(4)	4273(2)	25(1)
O(10)	5341(5)	7924(3)	4753(2)	35(1)
N(11)	6544(6)	8173(3)	3981(2)	20(1)
C(12)	7953(6)	8387(4)	4242(2)	23(1)
N(13)	8685(5)	9061(3)	4046(2)	22(1)
C(14)	10043(6)	9326(4)	4301(2)	25(1)
N(15)	10723(5)	10028(4)	4066(2)	26(1)
C(16)	12026(7)	10350(5)	4306(2)	32(1)
C(17)	12699(7)	9977(5)	4777(2)	33(2)
C(18)	12063(7)	9272(5)	5015(2)	30(1)
C(19)	10678(6)	8916(4)	4763(2)	27(1)
C(20)	9893(7)	8166(4)	4951(2)	31(1)
C(21)	8543(7)	7890(5)	4687(2)	31(1)
C(22)	3222(8)	6945(5)	3928(3)	42(2)
C(23)	1564(10)	6868(6)	3681(4)	58(2)
C(24)	4262(10)	6353(6)	3666(4)	56(2)
C(25)	3822(6)	7337(4)	2162(2)	23(1)
C(26)	4593(7)	6515(4)	2157(2)	28(1)
C(27)	3814(7)	5768(4)	1992(2)	27(1)
C(28)	2257(7)	5797(4)	1832(2)	29(1)
C(29)	1487(7)	6599(4)	1848(3)	31(1)
C(30)	2273(7)	7366(4)	2003(2)	31(1)
C(31)	6097(7)	8530(4)	1804(2)	25(1)
C(32)	7435(7)	9029(4)	1875(3)	33(1)
C(33)	8360(8)	9165(5)	1457(3)	45(2)
C(34)	7920(9)	8814(5)	968(3)	48(2)
C(35)	6562(10)	8333(5)	884(3)	45(2)
C(36)	5670(8)	8188(4)	1302(3)	34(2)
C(37)	12787(8)	11097(5)	4042(3)	42(2)
C(38)	12786(7)	8872(6)	5510(2)	40(2)
C(39)	8234(6)	7979(4)	2982(2)	24(1)
O(61)	2120(20)	6230(30)	5405(9)	225(19)
O(62)	2690(50)	4950(30)	5409(9)	280(20)

Table 3. Bond lengths [Å] and angles [°] for JAFMC5.

Pt(1)-N(8)	2.061(5)
Pt(1)-C(39)	2.083(6)
Pt(1)-N(11)	2.094(5)
Pt(1)-P(1)	2.1904(15)
P(1)-C(31)	1.815(6)
P(1)-C(25)	1.817(6)
P(1)-C(1)	1.826(6)
C(1)-C(6)	1.394(8)
C(1)-C(2)	1.417(8)
C(2)-C(3)	1.396(8)
C(2)-C(7)	1.466(8)
C(3)-C(4)	1.378(9)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.381(9)
C(4)-H(4A)	0.9500
C(5)-C(6)	1.402(9)
C(5)-H(5A)	0.9500
C(6)-H(6A)	0.9500
C(7)-N(8)	1.284(7)
C(7)-H(7A)	0.9500
N(8)-C(9)	1.484(7)
C(9)-C(22)	1.522(10)
C(9)-C(10)	1.535(8)
C(9)-H(9A)	1.0000
C(10)-O(10)	1.226(7)
C(10)-N(11)	1.369(8)
N(11)-C(12)	1.394(7)
C(12)-N(13)	1.314(8)
C(12)-C(21)	1.421(8)
N(13)-C(14)	1.369(7)
C(14)-N(15)	1.369(8)
C(14)-C(19)	1.404(8)
N(15)-C(16)	1.342(8)
C(16)-C(17)	1.412(9)
C(16)-C(37)	1.489(10)
C(17)-C(18)	1.356(10)
C(17)-H(17A)	0.9500
C(18)-C(19)	1.431(8)
C(18)-C(38)	1.493(9)
C(19)-C(20)	1.418(9)
C(20)-C(21)	1.377(9)
C(20)-H(20A)	0.9500
C(21)-H(21A)	0.9500
C(22)-C(24)	1.465(12)
C(22)-C(23)	1.541(10)
C(22)-H(22A)	1.0000
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-C(30)	1.384(8)
C(25)-C(26)	1.405(9)
C(26)-C(27)	1.360(9)
C(26)-H(26A)	0.9500
C(27)-C(28)	1.393(8)
C(27)-H(27A)	0.9500

C(28)-C(29)	1.379(9)
C(28)-H(28A)	0.9500
C(29)-C(30)	1.382(9)
C(29)-H(29A)	0.9500
C(30)-H(30A)	0.9500
C(31)-C(32)	1.388(9)
C(31)-C(36)	1.403(9)
C(32)-C(33)	1.397(10)
C(32)-H(32A)	0.9500
C(33)-C(34)	1.380(11)
C(33)-H(33A)	0.9500
C(34)-C(35)	1.392(11)
C(34)-H(34A)	0.9500
C(35)-C(36)	1.381(10)
C(35)-H(35A)	0.9500
C(36)-H(36A)	0.9500
C(37)-H(37A)	0.9800
C(37)-H(37B)	0.9800
C(37)-H(37C)	0.9800
C(38)-H(38A)	0.9800
C(38)-H(38B)	0.9800
C(38)-H(38C)	0.9800
C(39)-H(39A)	0.9800
C(39)-H(39B)	0.9800
C(39)-H(39C)	0.9800

N(8)-Pt(1)-C(39)	172.2(2)
N(8)-Pt(1)-N(11)	79.60(19)
C(39)-Pt(1)-N(11)	93.7(2)
N(8)-Pt(1)-P(1)	89.40(14)
C(39)-Pt(1)-P(1)	97.26(16)
N(11)-Pt(1)-P(1)	168.99(14)
C(31)-P(1)-C(25)	104.5(3)
C(31)-P(1)-C(1)	105.1(3)
C(25)-P(1)-C(1)	103.1(3)
C(31)-P(1)-Pt(1)	122.1(2)
C(25)-P(1)-Pt(1)	112.88(19)
C(1)-P(1)-Pt(1)	107.44(19)
C(6)-C(1)-C(2)	118.0(5)
C(6)-C(1)-P(1)	121.6(5)
C(2)-C(1)-P(1)	120.4(4)
C(3)-C(2)-C(1)	119.1(6)
C(3)-C(2)-C(7)	115.2(5)
C(1)-C(2)-C(7)	125.7(5)
C(4)-C(3)-C(2)	122.2(6)
C(4)-C(3)-H(3A)	118.9
C(2)-C(3)-H(3A)	118.9
C(3)-C(4)-C(5)	119.2(6)
C(3)-C(4)-H(4A)	120.4
C(5)-C(4)-H(4A)	120.4
C(4)-C(5)-C(6)	119.8(6)
C(4)-C(5)-H(5A)	120.1
C(6)-C(5)-H(5A)	120.1
C(1)-C(6)-C(5)	121.6(6)
C(1)-C(6)-H(6A)	119.2
C(5)-C(6)-H(6A)	119.2
N(8)-C(7)-C(2)	125.6(5)
N(8)-C(7)-H(7A)	117.2
C(2)-C(7)-H(7A)	117.2
C(7)-N(8)-C(9)	118.7(5)

C(7)-N(8)-Pt(1)	130.3(4)
C(9)-N(8)-Pt(1)	110.8(3)
N(8)-C(9)-C(22)	114.9(5)
N(8)-C(9)-C(10)	109.1(5)
C(22)-C(9)-C(10)	111.9(5)
N(8)-C(9)-H(9A)	106.8
C(22)-C(9)-H(9A)	106.8
C(10)-C(9)-H(9A)	106.8
O(10)-C(10)-N(11)	127.3(5)
O(10)-C(10)-C(9)	117.3(5)
N(11)-C(10)-C(9)	115.4(5)
C(10)-N(11)-C(12)	118.7(5)
C(10)-N(11)-Pt(1)	114.3(4)
C(12)-N(11)-Pt(1)	126.6(4)
N(13)-C(12)-N(11)	115.6(5)
N(13)-C(12)-C(21)	123.3(5)
N(11)-C(12)-C(21)	121.1(5)
C(12)-N(13)-C(14)	118.1(5)
N(15)-C(14)-N(13)	113.8(5)
N(15)-C(14)-C(19)	123.1(5)
N(13)-C(14)-C(19)	123.1(6)
C(16)-N(15)-C(14)	117.2(5)
N(15)-C(16)-C(17)	122.2(6)
N(15)-C(16)-C(37)	117.1(6)
C(17)-C(16)-C(37)	120.6(6)
C(18)-C(17)-C(16)	121.9(6)
C(18)-C(17)-H(17A)	119.1
C(16)-C(17)-H(17A)	119.1
C(17)-C(18)-C(19)	116.8(6)
C(17)-C(18)-C(38)	121.8(6)
C(19)-C(18)-C(38)	121.3(6)
C(14)-C(19)-C(20)	117.2(5)
C(14)-C(19)-C(18)	118.8(6)
C(20)-C(19)-C(18)	124.0(6)
C(21)-C(20)-C(19)	119.5(6)
C(21)-C(20)-H(20A)	120.2
C(19)-C(20)-H(20A)	120.2
C(20)-C(21)-C(12)	118.5(6)
C(20)-C(21)-H(21A)	120.7
C(12)-C(21)-H(21A)	120.7
C(24)-C(22)-C(9)	113.3(7)
C(24)-C(22)-C(23)	111.4(7)
C(9)-C(22)-C(23)	111.8(6)
C(24)-C(22)-H(22A)	106.6
C(9)-C(22)-H(22A)	106.6
C(23)-C(22)-H(22A)	106.6
C(22)-C(23)-H(23A)	109.5
C(22)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(22)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(22)-C(24)-H(24A)	109.5
C(22)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
C(22)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
C(30)-C(25)-C(26)	119.0(5)
C(30)-C(25)-P(1)	124.0(5)

C(26)-C(25)-P(1)	117.0(4)
C(27)-C(26)-C(25)	119.7(6)
C(27)-C(26)-H(26A)	120.2
C(25)-C(26)-H(26A)	120.2
C(26)-C(27)-C(28)	121.4(6)
C(26)-C(27)-H(27A)	119.3
C(28)-C(27)-H(27A)	119.3
C(29)-C(28)-C(27)	119.1(6)
C(29)-C(28)-H(28A)	120.4
C(27)-C(28)-H(28A)	120.4
C(28)-C(29)-C(30)	120.0(6)
C(28)-C(29)-H(29A)	120.0
C(30)-C(29)-H(29A)	120.0
C(29)-C(30)-C(25)	120.8(6)
C(29)-C(30)-H(30A)	119.6
C(25)-C(30)-H(30A)	119.6
C(32)-C(31)-C(36)	118.6(6)
C(32)-C(31)-P(1)	120.1(5)
C(36)-C(31)-P(1)	121.3(5)
C(31)-C(32)-C(33)	120.6(7)
C(31)-C(32)-H(32A)	119.7
C(33)-C(32)-H(32A)	119.7
C(34)-C(33)-C(32)	119.5(7)
C(34)-C(33)-H(33A)	120.2
C(32)-C(33)-H(33A)	120.2
C(33)-C(34)-C(35)	120.9(7)
C(33)-C(34)-H(34A)	119.5
C(35)-C(34)-H(34A)	119.5
C(36)-C(35)-C(34)	119.1(7)
C(36)-C(35)-H(35A)	120.5
C(34)-C(35)-H(35A)	120.5
C(35)-C(36)-C(31)	121.2(7)
C(35)-C(36)-H(36A)	119.4
C(31)-C(36)-H(36A)	119.4
C(16)-C(37)-H(37A)	109.5
C(16)-C(37)-H(37B)	109.5
H(37A)-C(37)-H(37B)	109.5
C(16)-C(37)-H(37C)	109.5
H(37A)-C(37)-H(37C)	109.5
H(37B)-C(37)-H(37C)	109.5
C(18)-C(38)-H(38A)	109.5
C(18)-C(38)-H(38B)	109.5
H(38A)-C(38)-H(38B)	109.5
C(18)-C(38)-H(38C)	109.5
H(38A)-C(38)-H(38C)	109.5
H(38B)-C(38)-H(38C)	109.5
Pt(1)-C(39)-H(39A)	109.5
Pt(1)-C(39)-H(39B)	109.5
H(39A)-C(39)-H(39B)	109.5
Pt(1)-C(39)-H(39C)	109.5
H(39A)-C(39)-H(39C)	109.5
H(39B)-C(39)-H(39C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for JAFMC5. 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}
Pt(1)	18(1)	20(1)	22(1)	-5(1)	-1(1)	1(1)
P(1)	19(1)	20(1)	21(1)	-4(1)	0(1)	0(1)
C(1)	24(3)	17(3)	25(3)	-1(2)	0(2)	0(2)
C(2)	24(3)	21(3)	26(3)	-8(2)	-4(2)	2(2)
C(3)	22(3)	27(3)	33(3)	-4(3)	2(2)	5(2)
C(4)	26(3)	29(4)	41(4)	-2(3)	-1(3)	7(3)
C(5)	37(3)	31(4)	29(3)	8(3)	-5(3)	4(3)
C(6)	32(3)	35(4)	22(3)	-6(3)	-4(2)	4(3)
C(7)	16(3)	28(3)	27(3)	-7(2)	3(2)	-1(2)
N(8)	18(2)	23(3)	24(3)	-4(2)	2(2)	0(2)
C(9)	22(3)	36(4)	25(3)	10(3)	2(2)	-2(3)
C(10)	21(3)	29(3)	26(3)	0(2)	0(2)	-4(2)
O(10)	28(2)	51(3)	25(2)	-3(2)	2(2)	-4(2)
N(11)	23(2)	21(3)	15(2)	-1(2)	0(2)	2(2)
C(12)	21(3)	33(3)	14(3)	-4(2)	0(2)	0(2)
N(13)	19(2)	21(3)	24(2)	-7(2)	-1(2)	-1(2)
C(14)	17(3)	35(3)	23(3)	-7(2)	2(2)	5(2)
N(15)	18(2)	32(3)	27(3)	-7(2)	4(2)	-2(2)
C(16)	24(3)	39(4)	32(3)	-13(3)	3(2)	-2(3)
C(17)	20(3)	48(4)	30(3)	-19(3)	-2(2)	0(3)
C(18)	25(3)	41(4)	24(3)	-8(3)	3(2)	5(3)
C(19)	20(3)	39(4)	22(3)	-6(3)	4(2)	7(3)
C(20)	28(3)	42(4)	22(3)	3(3)	-5(2)	6(3)
C(21)	29(3)	32(4)	30(3)	7(3)	-1(2)	0(3)
C(22)	41(4)	38(4)	45(4)	5(3)	-10(3)	-10(3)
C(23)	47(5)	53(5)	72(6)	8(4)	-16(4)	-15(4)
C(24)	48(5)	60(6)	59(5)	-3(4)	11(4)	-12(4)
C(25)	26(3)	24(3)	19(3)	-3(2)	3(2)	-1(2)
C(26)	25(3)	29(3)	30(3)	0(3)	-2(2)	2(3)
C(27)	32(3)	28(3)	23(3)	6(2)	4(2)	2(3)
C(28)	33(3)	31(4)	21(3)	-2(2)	2(2)	-9(3)
C(29)	22(3)	35(4)	36(4)	-7(3)	1(3)	-5(3)
C(30)	28(3)	28(3)	34(3)	-8(3)	-1(3)	2(3)
C(31)	26(3)	22(3)	27(3)	-1(2)	6(2)	3(2)
C(32)	28(3)	28(4)	42(4)	1(3)	5(3)	-2(3)
C(33)	36(4)	41(4)	58(5)	9(4)	14(3)	-4(3)
C(34)	53(5)	44(5)	49(4)	1(4)	27(4)	1(4)
C(35)	67(5)	39(4)	30(4)	-8(3)	21(3)	-3(4)
C(36)	37(4)	29(4)	35(4)	-6(3)	7(3)	-5(3)
C(37)	34(4)	50(5)	43(4)	-6(3)	2(3)	-20(3)
C(38)	28(3)	66(5)	24(3)	-9(3)	-4(3)	4(3)
C(39)	21(3)	25(3)	23(3)	-4(2)	-3(2)	-1(2)
O(61)	54(11)	530(60)	93(15)	-10(30)	-7(10)	80(20)
O(62)	410(60)	360(50)	57(13)	-90(20)	-20(20)	100(50)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for JAFMC5.

	x	y	z	U(eq)
H(3A)	775	10030	2999	32
H(4A)	519	11008	2293	38
H(5A)	2155	10875	1611	39
H(6A)	3981	9730	1631	36
H(7A)	1772	8780	3442	28
H(9A)	3003	8247	4154	33
H(17A)	13624	10227	4932	40
H(20A)	10295	7857	5256	37
H(21A)	8017	7378	4801	37
H(22A)	3208	6729	4300	51
H(23A)	1253	6239	3670	87
H(23B)	1509	7109	3322	87
H(23C)	874	7206	3893	87
H(24A)	5307	6424	3828	83
H(24B)	4240	6506	3292	83
H(24C)	3933	5733	3704	83
H(26A)	5652	6481	2269	34
H(27A)	4344	5215	1986	33
H(28A)	1731	5272	1713	34
H(29A)	416	6624	1752	38
H(30A)	1744	7920	2001	37
H(32A)	7724	9281	2210	39
H(33A)	9285	9496	1510	53
H(34A)	8553	8902	685	57
H(35A)	6252	8107	544	54
H(36A)	4751	7852	1248	40
H(37A)	12005	11483	3865	63
H(37B)	13450	10856	3783	63
H(37C)	13407	11444	4305	63
H(38A)	13634	9252	5649	59
H(38B)	13179	8276	5434	59
H(38C)	12020	8824	5770	59
H(39A)	8734	7576	3244	35
H(39B)	8800	8544	2982	35
H(39C)	8224	7705	2633	35

Table 6. Torsion angles [°] for JAFMC5.

N(8)-Pt(1)-P(1)-C(31)	164.3(3)
C(39)-Pt(1)-P(1)-C(31)	-19.7(3)
N(11)-Pt(1)-P(1)-C(31)	162.2(7)
N(8)-Pt(1)-P(1)-C(25)	-69.9(2)
C(39)-Pt(1)-P(1)-C(25)	106.1(3)
N(11)-Pt(1)-P(1)-C(25)	-72.0(7)
N(8)-Pt(1)-P(1)-C(1)	43.1(2)
C(39)-Pt(1)-P(1)-C(1)	-141.0(3)
N(11)-Pt(1)-P(1)-C(1)	41.0(7)
C(31)-P(1)-C(1)-C(6)	9.3(6)
C(25)-P(1)-C(1)-C(6)	-99.9(5)
Pt(1)-P(1)-C(1)-C(6)	140.7(5)
C(31)-P(1)-C(1)-C(2)	-171.4(5)
C(25)-P(1)-C(1)-C(2)	79.4(5)
Pt(1)-P(1)-C(1)-C(2)	-40.0(5)
C(6)-C(1)-C(2)-C(3)	2.5(8)
P(1)-C(1)-C(2)-C(3)	-176.8(4)
C(6)-C(1)-C(2)-C(7)	-176.8(5)
P(1)-C(1)-C(2)-C(7)	3.9(8)
C(1)-C(2)-C(3)-C(4)	-3.2(9)
C(7)-C(2)-C(3)-C(4)	176.2(6)
C(2)-C(3)-C(4)-C(5)	1.2(9)
C(3)-C(4)-C(5)-C(6)	1.3(10)
C(2)-C(1)-C(6)-C(5)	-0.1(9)
P(1)-C(1)-C(6)-C(5)	179.2(5)
C(4)-C(5)-C(6)-C(1)	-1.8(10)
C(3)-C(2)-C(7)-N(8)	-157.9(6)
C(1)-C(2)-C(7)-N(8)	21.4(9)
C(2)-C(7)-N(8)-C(9)	176.3(5)
C(2)-C(7)-N(8)-Pt(1)	1.1(9)
C(39)-Pt(1)-N(8)-C(7)	178.6(13)
N(11)-Pt(1)-N(8)-C(7)	146.9(5)
P(1)-Pt(1)-N(8)-C(7)	-32.6(5)
C(39)-Pt(1)-N(8)-C(9)	3.1(16)
N(11)-Pt(1)-N(8)-C(9)	-28.6(4)
P(1)-Pt(1)-N(8)-C(9)	151.8(4)
C(7)-N(8)-C(9)-C(22)	91.9(7)
Pt(1)-N(8)-C(9)-C(22)	-92.0(5)
C(7)-N(8)-C(9)-C(10)	-141.4(5)
Pt(1)-N(8)-C(9)-C(10)	34.7(6)
N(8)-C(9)-C(10)-O(10)	158.1(6)
C(22)-C(9)-C(10)-O(10)	-73.6(8)
N(8)-C(9)-C(10)-N(11)	-21.4(8)
C(22)-C(9)-C(10)-N(11)	106.9(6)
O(10)-C(10)-N(11)-C(12)	-8.0(10)
C(9)-C(10)-N(11)-C(12)	171.4(5)
O(10)-C(10)-N(11)-Pt(1)	178.6(5)
C(9)-C(10)-N(11)-Pt(1)	-2.0(7)
N(8)-Pt(1)-N(11)-C(10)	17.1(4)
C(39)-Pt(1)-N(11)-C(10)	-158.9(4)
P(1)-Pt(1)-N(11)-C(10)	19.2(10)
N(8)-Pt(1)-N(11)-C(12)	-155.7(5)
C(39)-Pt(1)-N(11)-C(12)	28.4(5)
P(1)-Pt(1)-N(11)-C(12)	-153.5(5)
C(10)-N(11)-C(12)-N(13)	-135.4(6)
Pt(1)-N(11)-C(12)-N(13)	37.0(7)
C(10)-N(11)-C(12)-C(21)	45.3(8)
Pt(1)-N(11)-C(12)-C(21)	-142.2(5)

N(11)-C(12)-N(13)-C(14)	177.1(5)
C(21)-C(12)-N(13)-C(14)	-3.7(9)
C(12)-N(13)-C(14)-N(15)	179.6(5)
C(12)-N(13)-C(14)-C(19)	-0.5(8)
N(13)-C(14)-N(15)-C(16)	177.2(5)
C(19)-C(14)-N(15)-C(16)	-2.7(8)
C(14)-N(15)-C(16)-C(17)	1.2(9)
C(14)-N(15)-C(16)-C(37)	178.4(6)
N(15)-C(16)-C(17)-C(18)	-0.2(10)
C(37)-C(16)-C(17)-C(18)	-177.3(6)
C(16)-C(17)-C(18)-C(19)	0.5(9)
C(16)-C(17)-C(18)-C(38)	179.3(6)
N(15)-C(14)-C(19)-C(20)	-176.9(5)
N(13)-C(14)-C(19)-C(20)	3.1(9)
N(15)-C(14)-C(19)-C(18)	3.1(9)
N(13)-C(14)-C(19)-C(18)	-176.8(5)
C(17)-C(18)-C(19)-C(14)	-1.9(8)
C(38)-C(18)-C(19)-C(14)	179.4(6)
C(17)-C(18)-C(19)-C(20)	178.2(6)
C(38)-C(18)-C(19)-C(20)	-0.6(9)
C(14)-C(19)-C(20)-C(21)	-1.8(9)
C(18)-C(19)-C(20)-C(21)	178.2(6)
C(19)-C(20)-C(21)-C(12)	-2.0(10)
N(13)-C(12)-C(21)-C(20)	5.0(10)
N(11)-C(12)-C(21)-C(20)	-175.9(6)
N(8)-C(9)-C(22)-C(24)	64.0(8)
C(10)-C(9)-C(22)-C(24)	-61.3(8)
N(8)-C(9)-C(22)-C(23)	-62.9(8)
C(10)-C(9)-C(22)-C(23)	171.9(6)
C(31)-P(1)-C(25)-C(30)	-105.0(5)
C(1)-P(1)-C(25)-C(30)	4.6(6)
Pt(1)-P(1)-C(25)-C(30)	120.2(5)
C(31)-P(1)-C(25)-C(26)	73.0(5)
C(1)-P(1)-C(25)-C(26)	-177.4(5)
Pt(1)-P(1)-C(25)-C(26)	-61.8(5)
C(30)-C(25)-C(26)-C(27)	0.8(9)
P(1)-C(25)-C(26)-C(27)	-177.3(5)
C(25)-C(26)-C(27)-C(28)	-0.7(9)
C(26)-C(27)-C(28)-C(29)	-0.8(9)
C(27)-C(28)-C(29)-C(30)	2.3(9)
C(28)-C(29)-C(30)-C(25)	-2.2(10)
C(26)-C(25)-C(30)-C(29)	0.7(9)
P(1)-C(25)-C(30)-C(29)	178.6(5)
C(25)-P(1)-C(31)-C(32)	-158.9(5)
C(1)-P(1)-C(31)-C(32)	92.9(5)
Pt(1)-P(1)-C(31)-C(32)	-29.4(6)
C(25)-P(1)-C(31)-C(36)	19.8(6)
C(1)-P(1)-C(31)-C(36)	-88.4(6)
Pt(1)-P(1)-C(31)-C(36)	149.3(4)
C(36)-C(31)-C(32)-C(33)	-1.9(10)
P(1)-C(31)-C(32)-C(33)	176.8(5)
C(31)-C(32)-C(33)-C(34)	1.3(11)
C(32)-C(33)-C(34)-C(35)	0.5(12)
C(33)-C(34)-C(35)-C(36)	-1.7(12)
C(34)-C(35)-C(36)-C(31)	1.1(11)
C(32)-C(31)-C(36)-C(35)	0.7(10)
P(1)-C(31)-C(36)-C(35)	-178.0(6)

Symmetry transformations used to generate equivalent atoms: