Role of Hemilabile Diamine Ligands in the Amine-Directed C–H Borylation of Arenes

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Supporting Information

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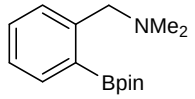
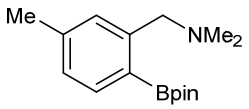
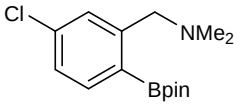
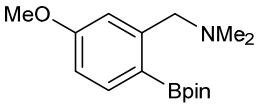
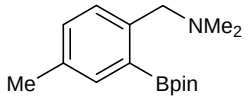
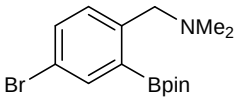
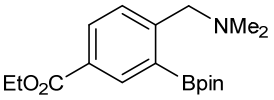
All spectral data for the products obtained in this manuscript were previously reported.[1] The optimized purification conditions of each substrate are listed in Table S-1.

Table S-1. Purification Conditions for Each C–H Borylation Product

Major Product	Product #	Chromatography Conditions	Bulb-to-Bulb[a] Distillation	Isolated Yield (mass, %)
 **1**	**1**:**2**	98:1:1 EtOAc:MeOH:TEA	30 min at 70 °C	0.401 g, 77%
 **21a**	**21a**:**21b**:**21c**	99:0.5:0.5 EtOAc:MeOH:TEA	20 min at 60 °C	0.702 g, 85%
 **22a**	**22a**:**22b**:**22c**	98.5:0.5:1 CH_2Cl_2:MeOH:TEA	30 min at 60 °C	0.453 g, 77%
 **23a**	**23a**:**23b**:**23c**	99:0.5:0.5 CH_2Cl_2:MeOH:TEA	30 min at 90 °C	0.426 g, 73%
 **24a**	**24a**:**24c**	99:0.5:0.5 EtOAc:MeOH:TEA	30 min at 70 °C	0.457 g, 83%
 **25a**	**25a**:**25c**	98.5:0.5:1 CH_2Cl_2:MeOH:TEA	30 min at 80 °C	0.439 g, 65%
 **26a**	**26a**:**26c**	99:0.5:0.5 CH_2Cl_2:MeOH:TEA	30 min at 120 °C	0.573 g, 57%

[a] Bulb-to-bulb distillation was used to remove unreacted starting amine when necessary. All distillation performed at ~0.5 mm Hg.

C–H Borylation of *N*,*N*-Dimethylbenzylamine in the Absence of Added Ligand

N,*N*-Dimethylbenzylamine was subjected to the representative reaction conditions provided in the experimental section of the manuscript without the addition of a ligand. The unpurified

reaction mixture was analyzed by ^{1}H NMR spectroscopy and characteristic peaks for **1**, **2**,[1] and *N*,*N*-dimethylbenzylamine were used to determine the reaction conversion and selectivity, resulting in 89% conversion and a 98:2 mixture of **1**:**2**.

C–H Borylation of *N*,*N*-Dimethylbenzylamine using Pre-Catalyst 27

N,*N*-Dimethylbenzylamine (0.108 g, 0.80 mmol) was subjected to the representative reaction conditions provided in the experimental section of the manuscript using complex **27** (0.0124 g, 0.024 mmol) in place of [Ir(μ-OMe)(COD)]$_2$ and added ligand. The unpurified reaction mixture was analyzed by ^{1}H NMR spectroscopy and characteristic peaks for **1**, **2**,[1] and *N*,*N*-dimethylbenzylamine were used to determine the reaction conversion and selectivity, resulting in 85% conversion and a 98:2 mixture of **1**:**2**.

The conversion and selectivity obtained with complex **27** was compared to other Ir–Cl complexes since [Ir(μ-Cl)(COD)]$_2$ is less reactive than [Ir(μ-OMe)(COD)]$_2$. All reactions were carried out using the same representative procedure provided in the experimental section of the manuscript. The results are summarized in the table below.

Table S-2. Summary of catalytic activity of complex **27** compared to [Ir(μ-Cl)(COD)]$_2$

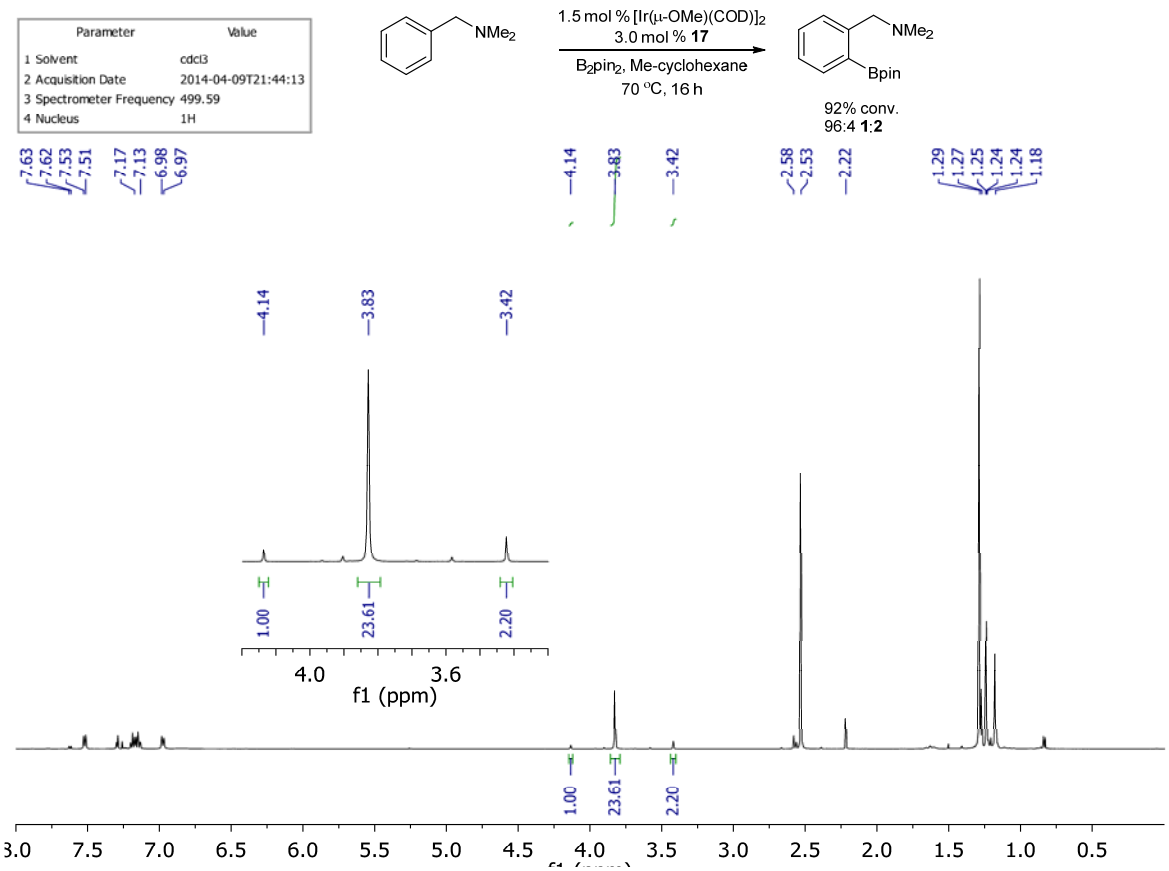
Catalyst	Ligand	Conversion	Selectivity 1:2
27	none	85	98:2
[Ir(μ-Cl)(COD)]$_2$	**17**	83	97:3
[Ir(μ-Cl)(COD)]$_2$	none	71	98:2

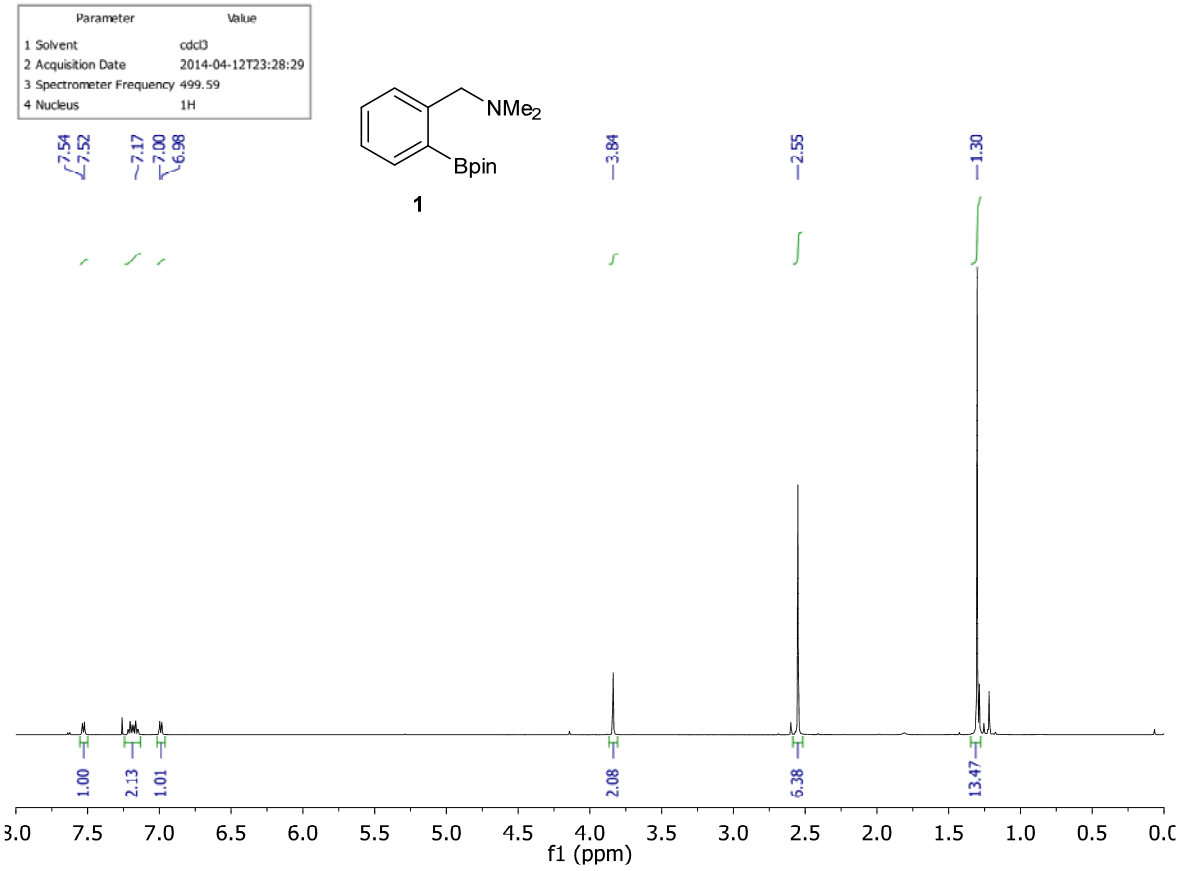
% Conversion and selectivity was determined by ^{1}H NMR spectroscopy. 1.2 equiv. arene to B_2pin_2, conversions are based on the arene substrate.

References:

(1) Roering, A. J.; Hale, L. V. A.; Squier, P. A.; Ringgold, M. A.; Wiederspan, E. R.; Clark, T. B. *Org. Lett.* **2012**, *14*, 3558.

Crude Reaction Mixture





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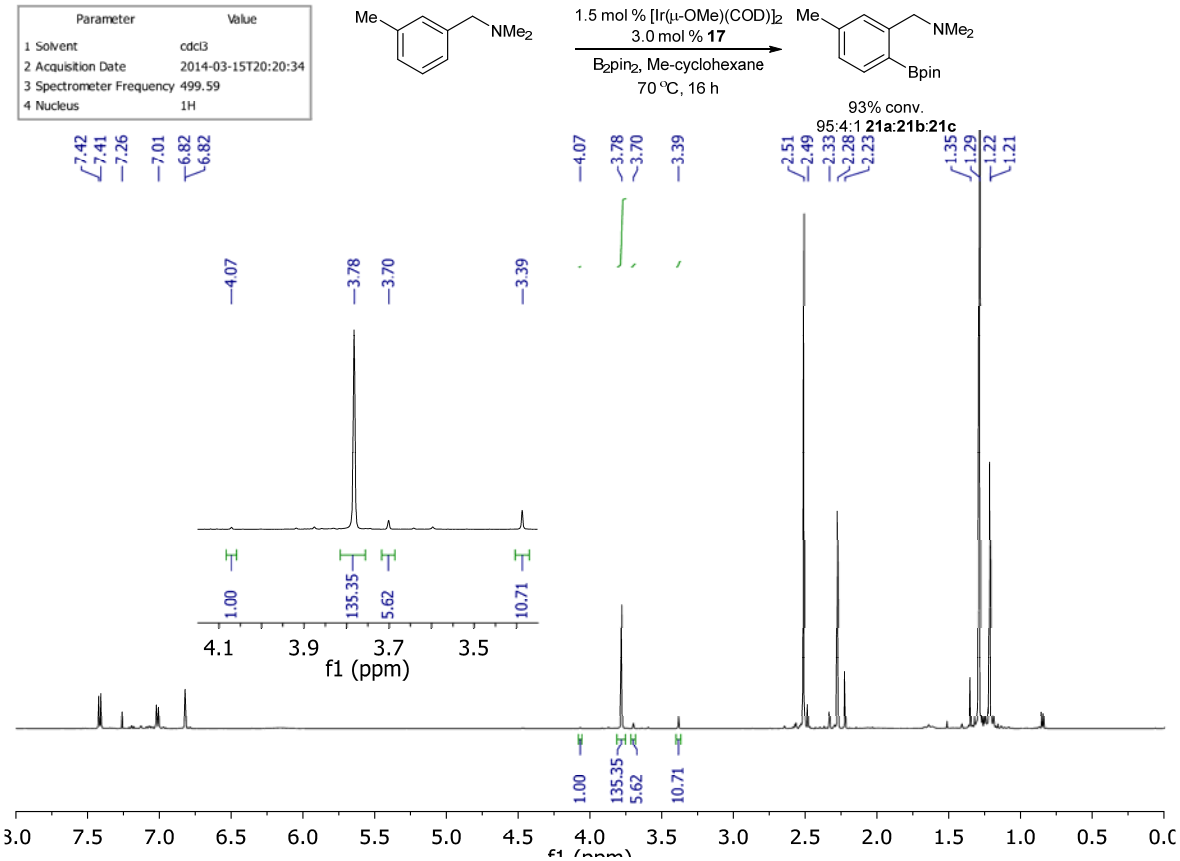

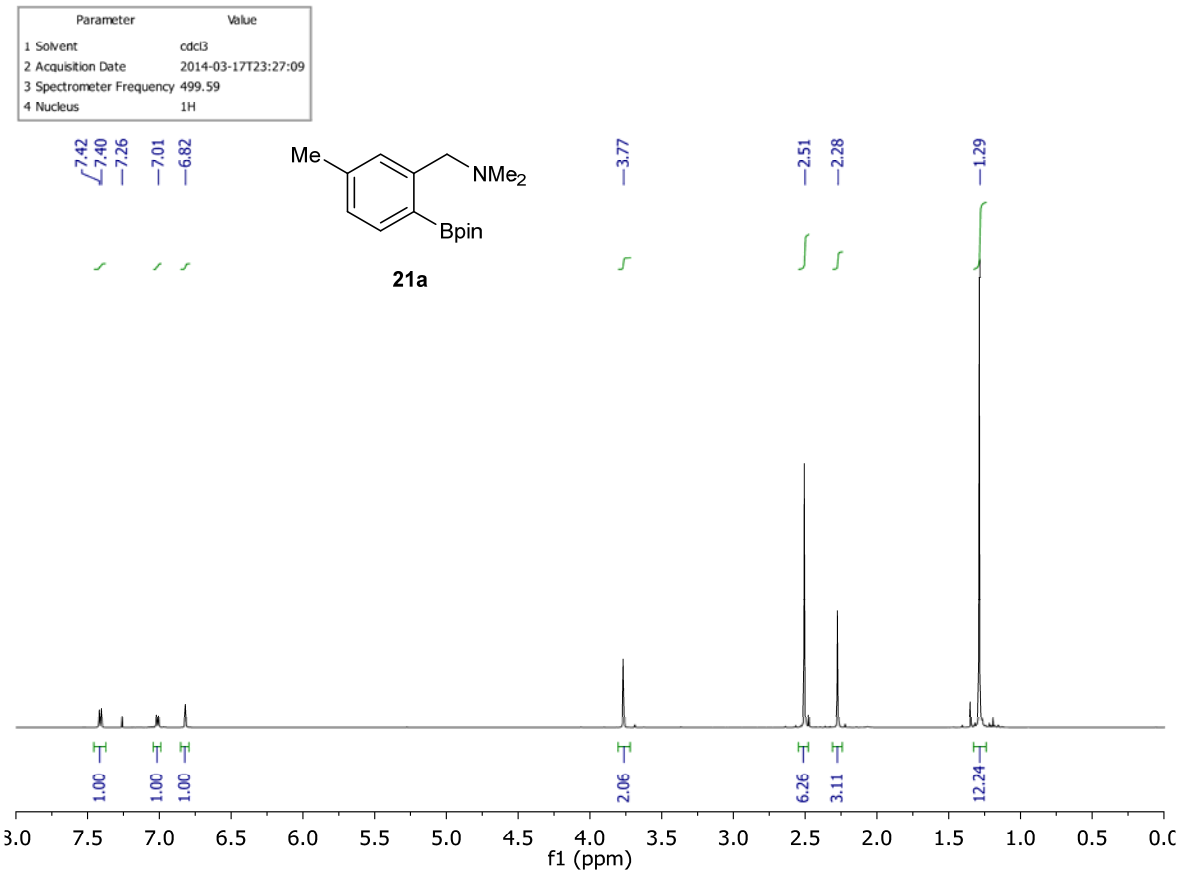

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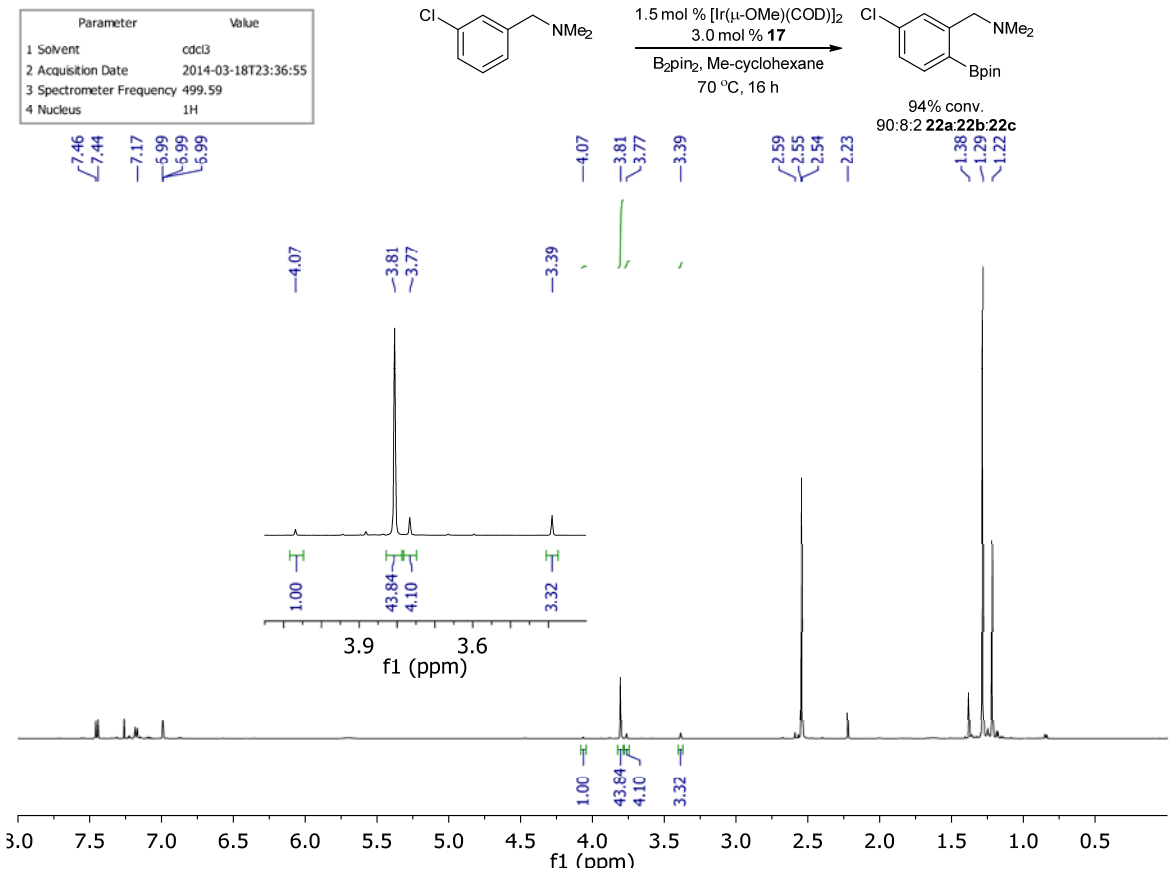

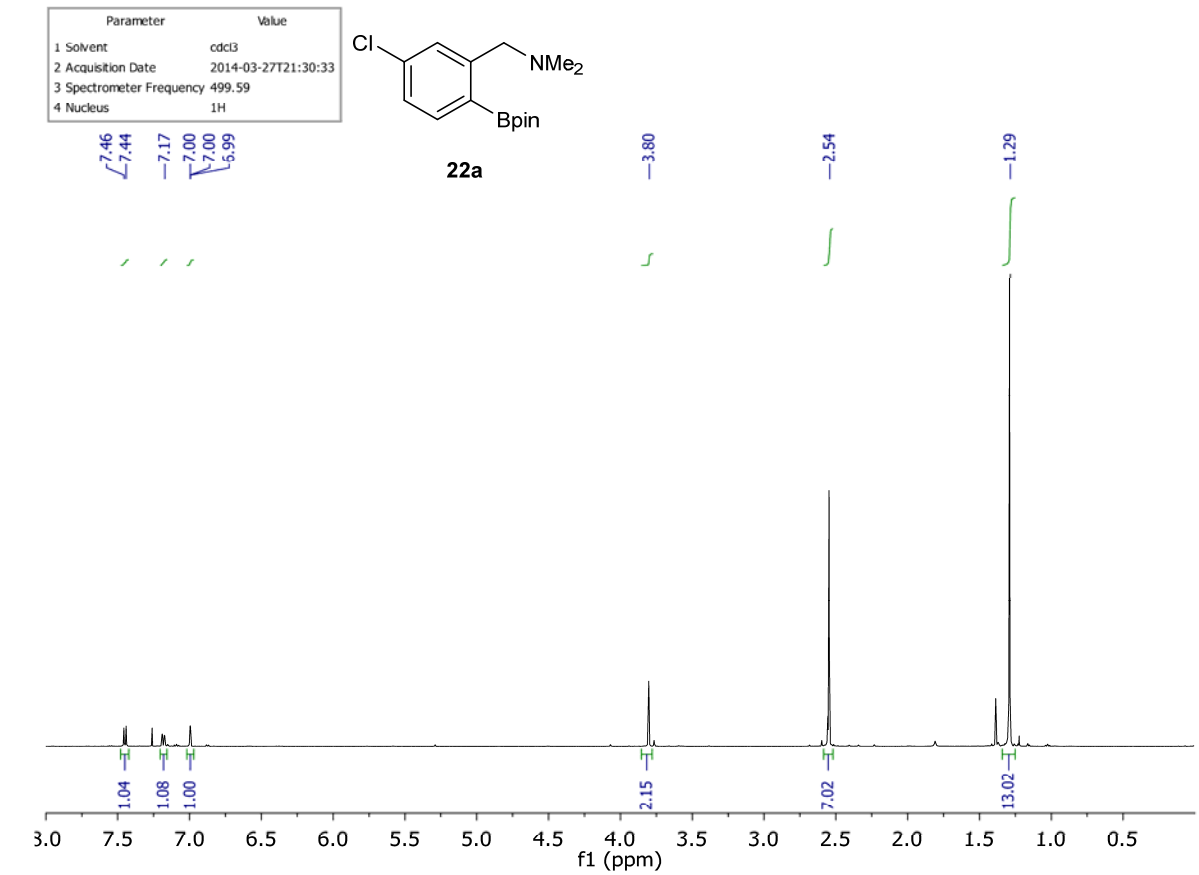

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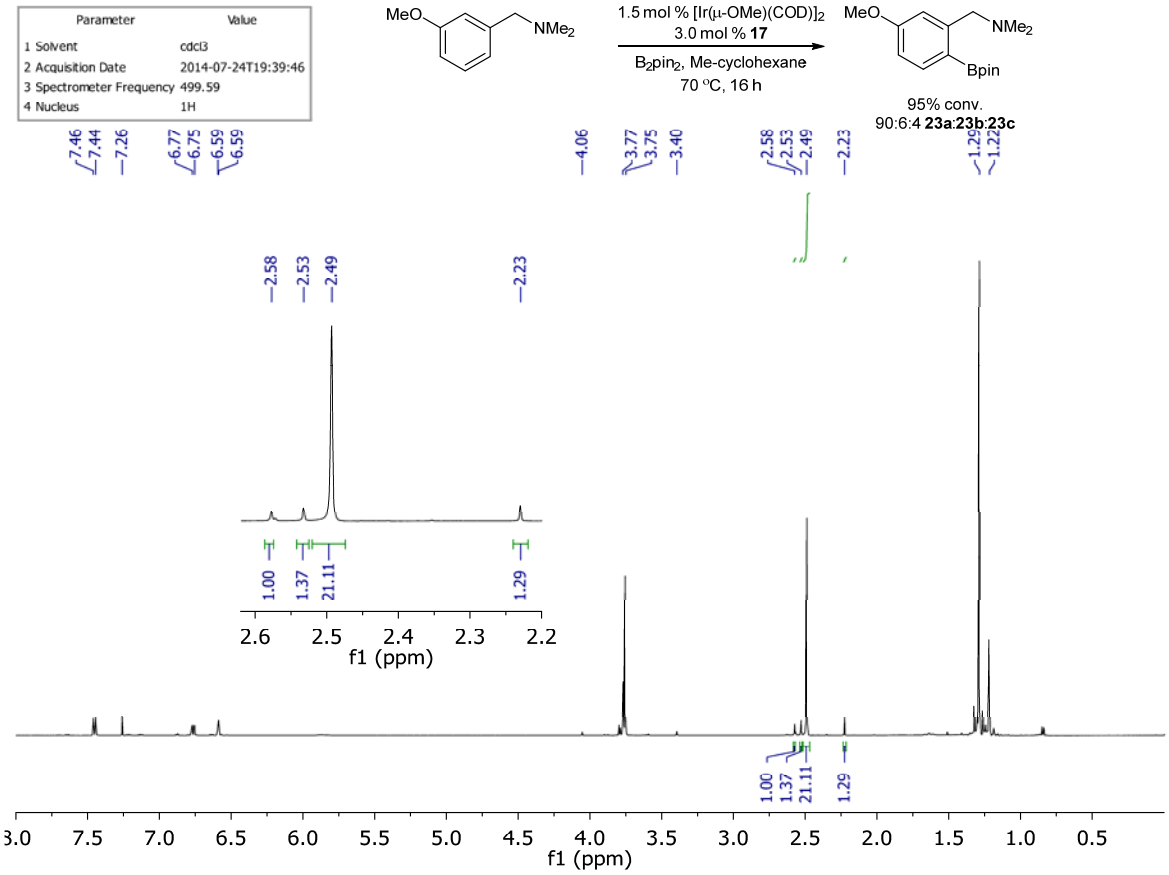

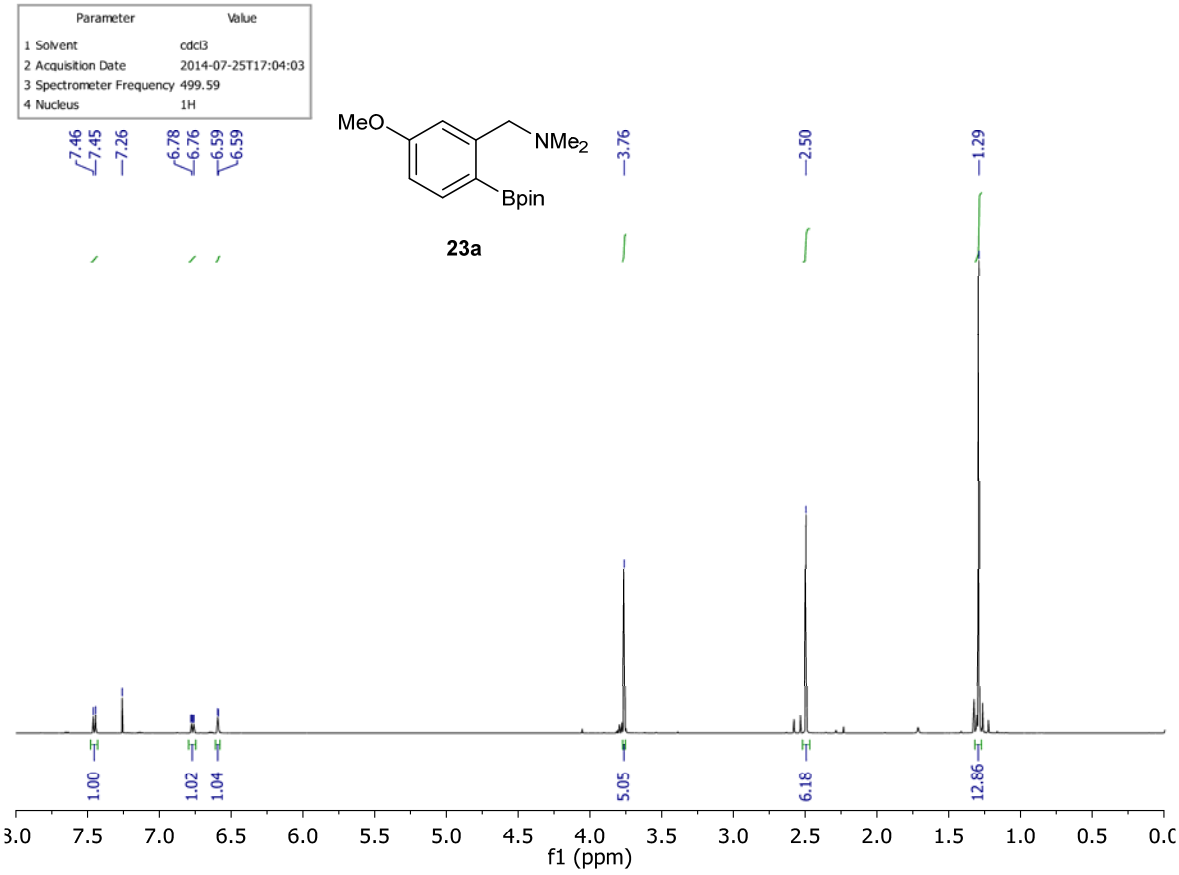

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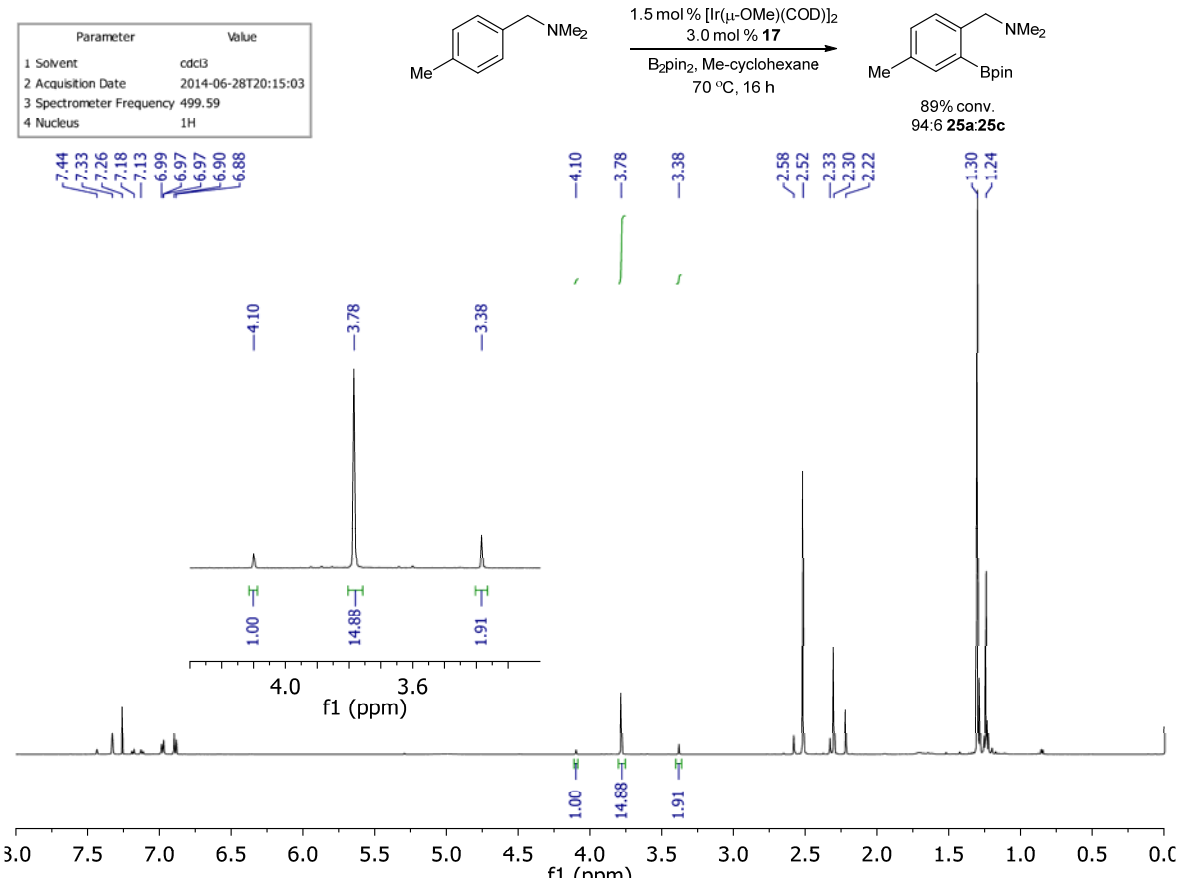

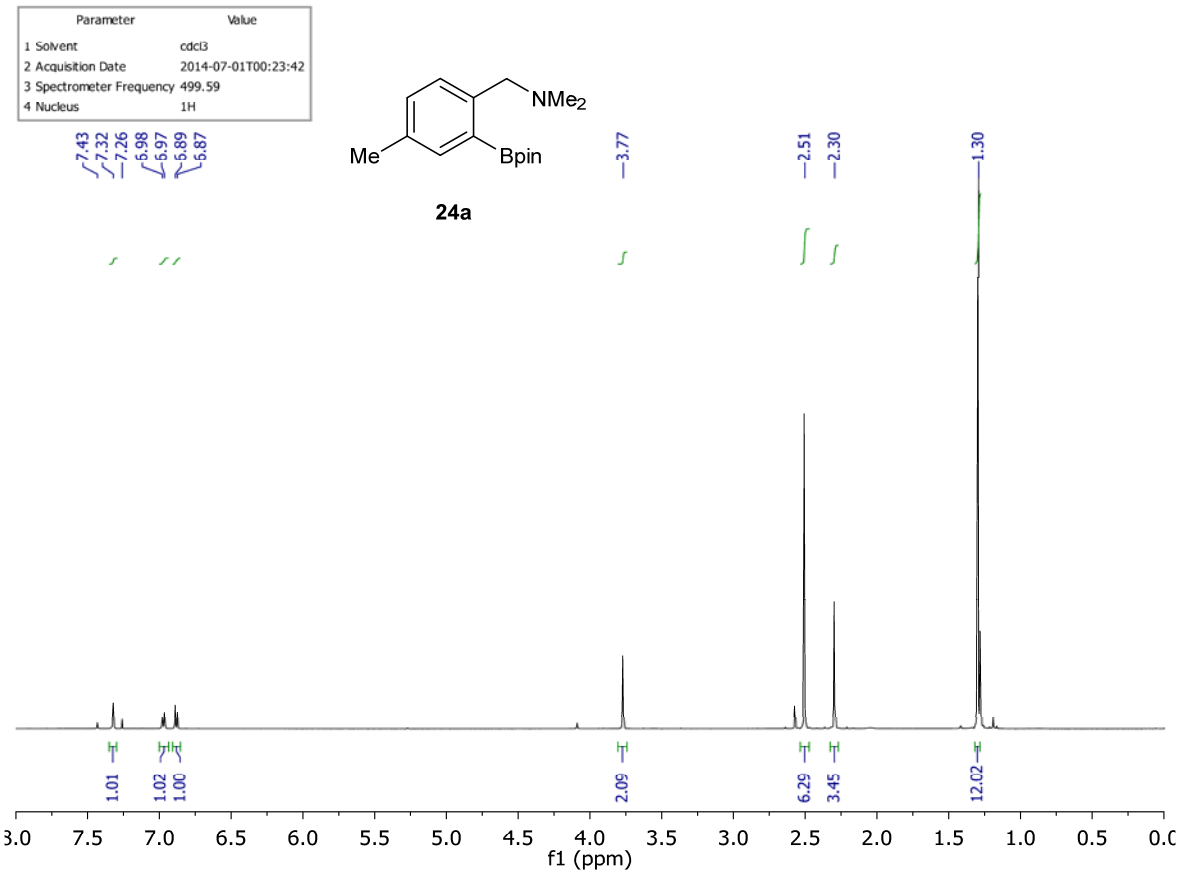

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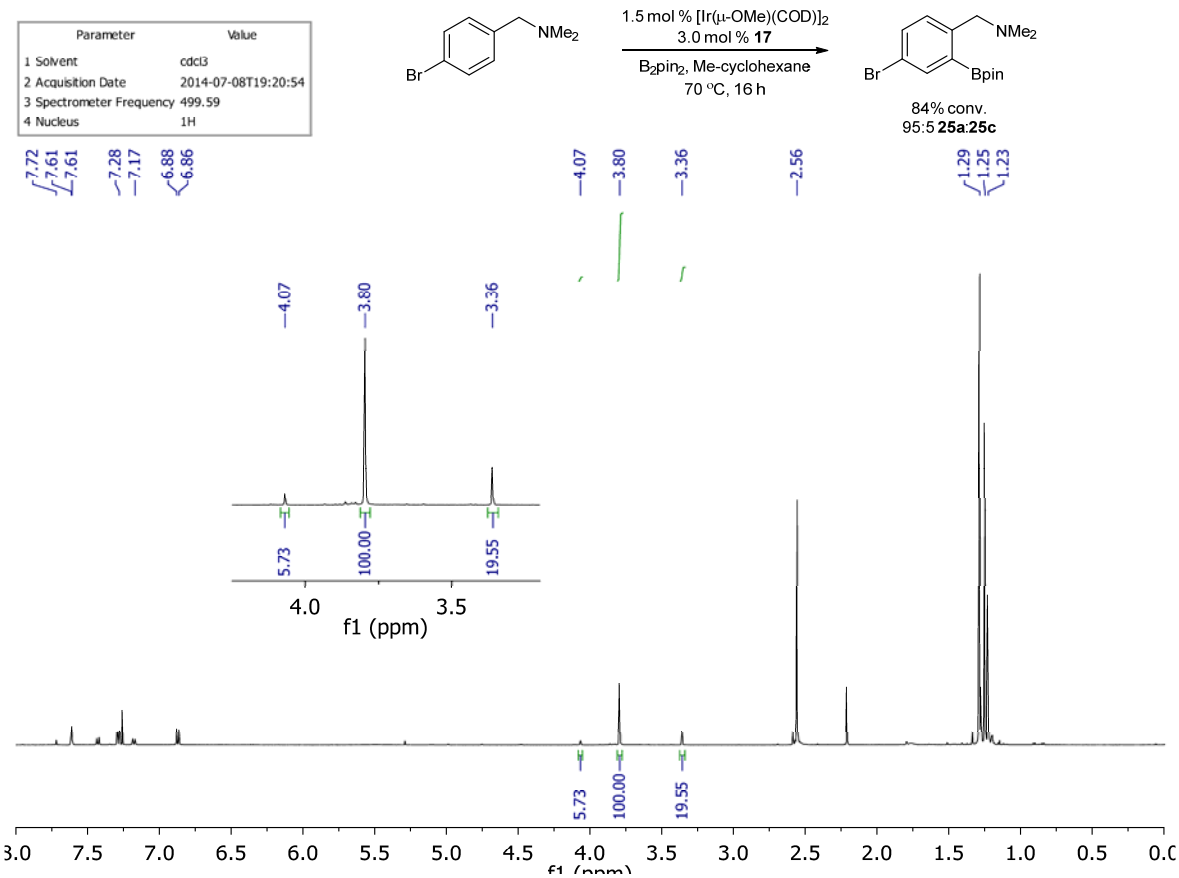

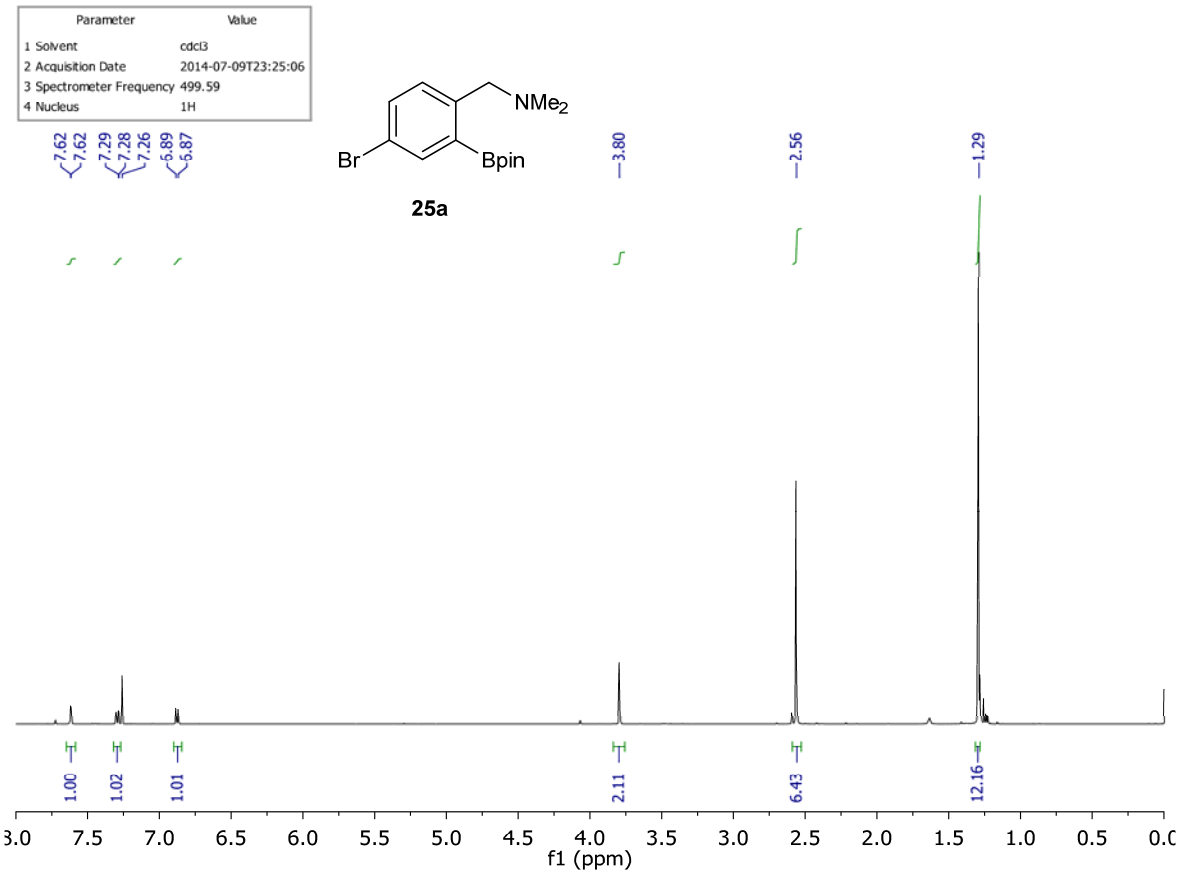

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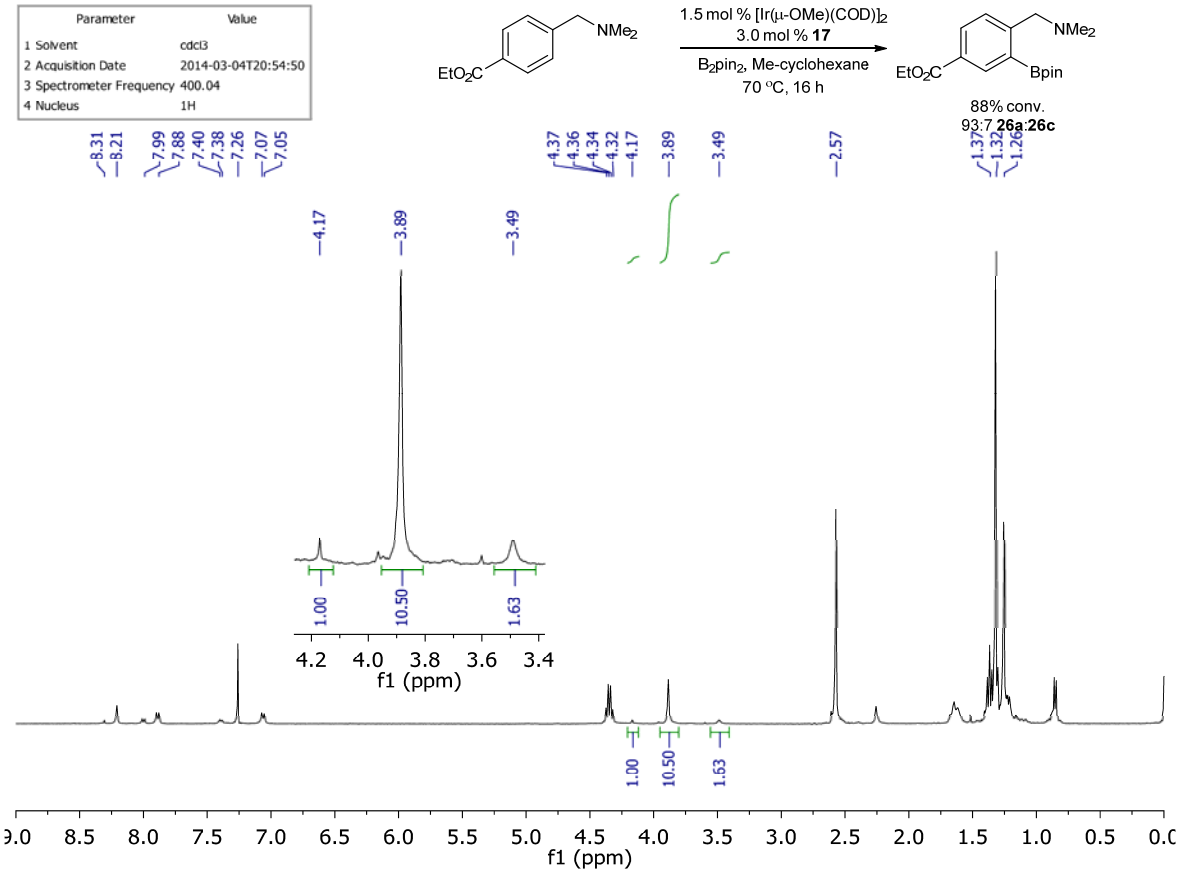

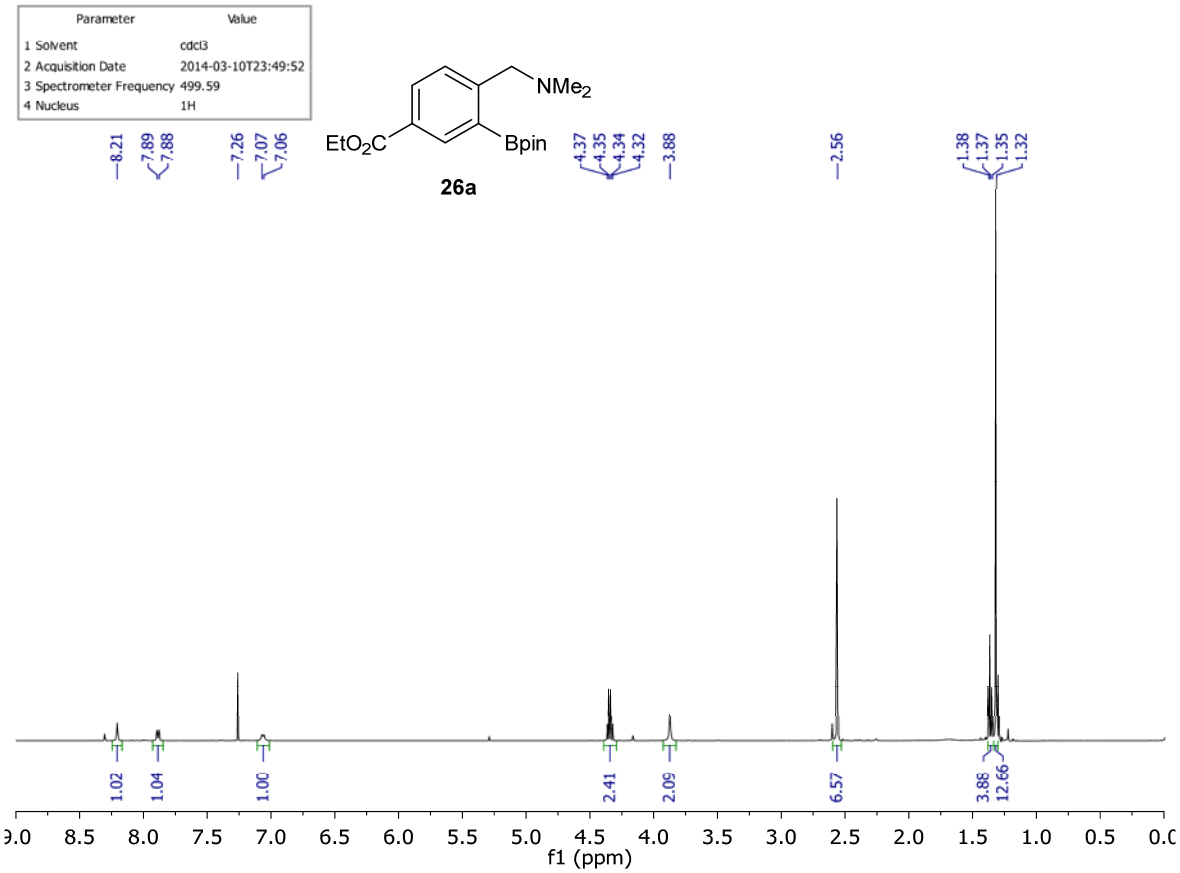

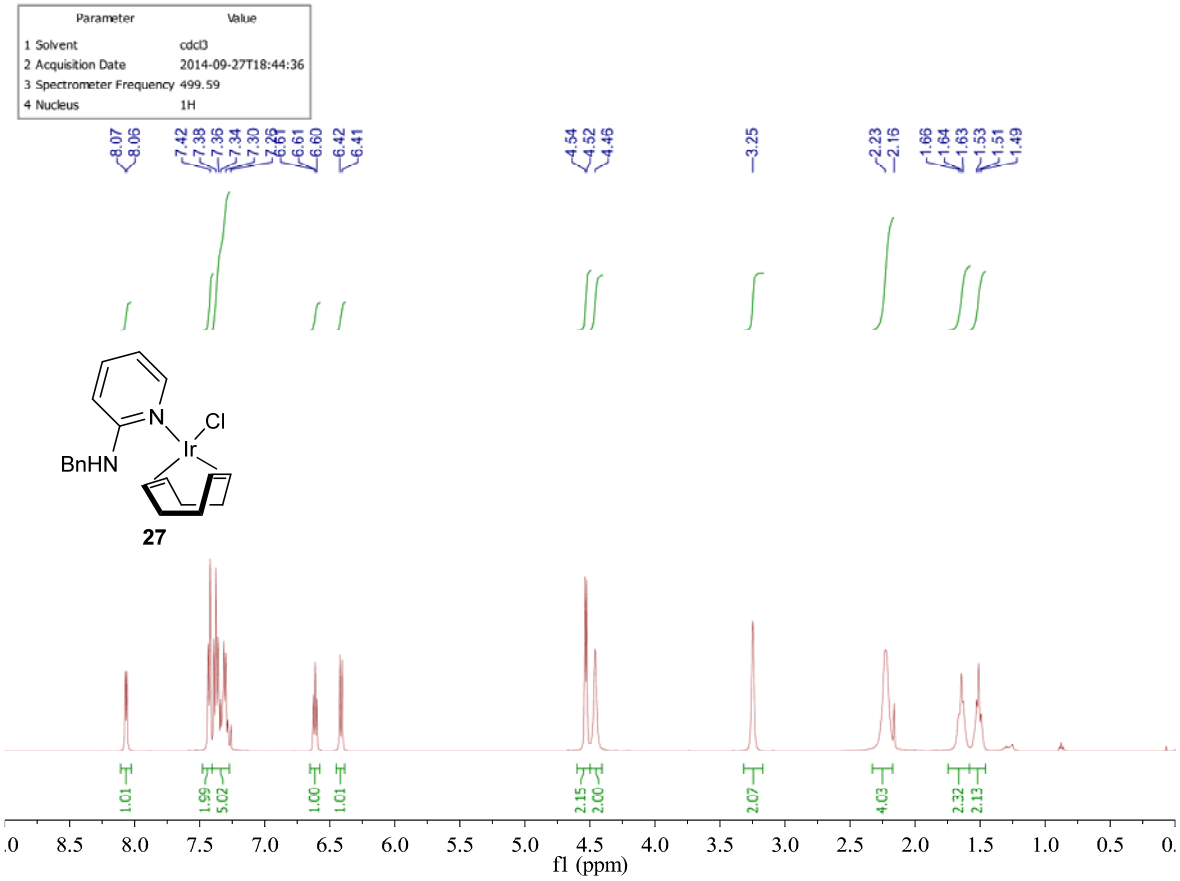
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4 Nucleus 1H
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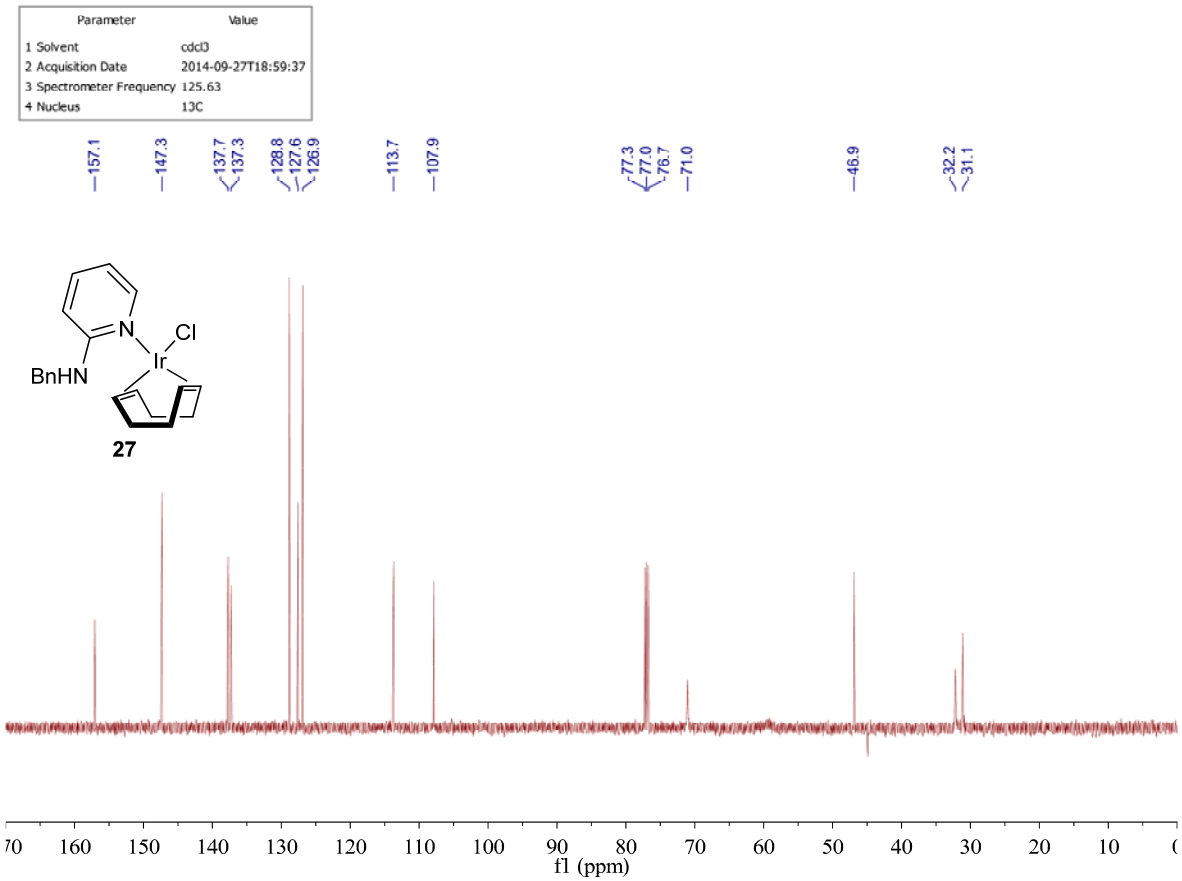
N
Cl
Ir
BnHN
27
1.01 1.99 5.02 1.00 1.01 2.15 2.00 2.07 4.03 2.32 2.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Parameter Value
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3 Spectrometer Frequency 125.63
4 Nucleus 13C
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N
Cl
Ir
BnHN
27
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

Table S-3. Crystal data and structure refinement for Complex 27.

Empirical formula	$C_{40}H_{48}Cl_2Ir_2N_4$	
Formula weight	1040.12	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P-1	
Unit cell dimensions	a = 10.5383(10) Å	α= 105.492(2)°.
	b = 12.6574(12) Å	β= 102.412(2)°.
	c = 14.6343(14) Å	γ = 90.028(2)°.
Volume	1833.7(3) $Å^3$	
Z	2	
Density (calculated)	1.884 Mg/m^3	
Absorption coefficient	7.430 mm^{-1}	
F(000)	1008	
Crystal size	0.427 x 0.312 x 0.184 mm^3	
Theta range for data collection	1.907 to 27.630°.	
Index ranges	-13<=h<=13, -16<=k<=15, 0<=l<=19	
Reflections collected	16626	
Independent reflections	8464 [R(int) = 0.0580]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745553 and 0.332634	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8566 / 0 / 440	
Goodness-of-fit on F^2	1.039	
Final R indices [I>2sigma(I)]	R1 = 0.0379, wR2 = 0.1001	
R indices (all data)	R1 = 0.0460, wR2 = 0.1074	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.768 and -3.169 $e.Å^{-3}$	

Figure S-1. ORTEP drawing for complex 27 with thermal ellipsoids shown at 50% probability. Full asymmetric unit shown viewed down c-axis. Complex 27 is square planar, with ligand-metal-ligand bond angles summing to 360.2(8) degrees and 360.3(8) degrees for the unique complexes.

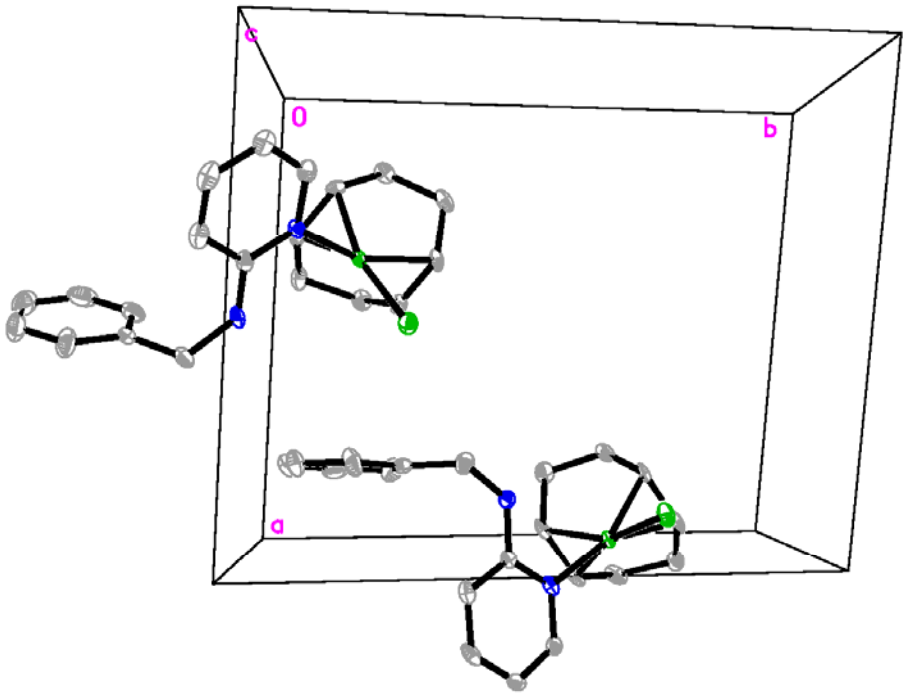

Table S-4. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for Complex 27. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Ir(1)	9915(1)	6665(1)	2771(1)	12(1)
Ir(2)	3733(1)	1669(1)	2834(1)	11(1)
Cl(1)	9265(2)	7586(1)	4203(1)	20(1)
Cl(2)	5149(2)	2636(1)	4298(1)	20(1)
N(1)	10890(6)	5577(5)	3493(4)	15(1)
N(2)	8934(6)	4644(5)	3331(5)	18(1)
N(3)	3170(6)	580(5)	3546(4)	14(1)
N(4)	5017(7)	-382(5)	3418(5)	21(1)
C(1)	12203(7)	5704(6)	3808(5)	16(1)
C(2)	12921(7)	5019(6)	4270(5)	18(2)
C(3)	12254(8)	4149(6)	4424(5)	21(2)
C(4)	10921(8)	3998(6)	4126(5)	18(2)
C(5)	10253(7)	4743(6)	3659(5)	14(1)
C(6)	8124(8)	3810(6)	3500(6)	21(2)
C(7)	8198(7)	2673(6)	2859(6)	19(2)
C(8)	8324(9)	2477(7)	1905(6)	27(2)
C(9)	8318(9)	1404(8)	1319(7)	34(2)
C(10)	8223(9)	528(8)	1707(8)	38(2)
C(11)	8129(10)	712(7)	2658(8)	37(2)
C(12)	8092(9)	1765(7)	3225(7)	31(2)
C(13)	8453(8)	7354(5)	1892(5)	15(1)
C(14)	9588(8)	8053(6)	2219(5)	17(2)
C(15)	10565(8)	8155(6)	1620(6)	20(2)
C(16)	10930(8)	7034(7)	1051(6)	21(2)
C(17)	10886(8)	6181(6)	1622(5)	16(1)
C(18)	9766(7)	5463(6)	1454(5)	15(1)
C(19)	8475(8)	5463(6)	747(6)	22(2)
C(20)	8012(8)	6636(6)	863(6)	20(2)
C(21)	2020(8)	722(6)	3830(5)	20(2)
C(22)	1522(9)	7(6)	4254(5)	21(2)

C(23)	2232(9)	-885(7)	4392(6)	25(2)
C(24)	3391(9)	-1031(6)	4114(5)	21(2)
C(25)	3878(8)	-277(6)	3702(5)	16(1)
C(26)	5857(8)	-1259(6)	3538(6)	22(2)
C(27)	5395(7)	-2347(6)	2773(6)	20(2)
C(28)	5556(10)	-3344(7)	3031(8)	33(2)
C(29)	5217(11)	-4322(8)	2321(10)	45(3)
C(30)	4677(10)	-4359(8)	1357(9)	41(3)
C(31)	4509(9)	-3382(9)	1115(8)	39(2)
C(32)	4866(8)	-2388(7)	1819(7)	30(2)
C(33)	3704(8)	3068(6)	2304(5)	16(1)
C(34)	4664(8)	2412(6)	1972(5)	17(1)
C(35)	4526(8)	1701(6)	939(6)	19(2)
C(36)	4052(8)	504(6)	836(5)	19(2)
C(37)	3147(8)	455(6)	1509(5)	18(2)
C(38)	2112(7)	1137(6)	1659(5)	16(1)
C(39)	1711(8)	1999(6)	1111(5)	18(2)
C(40)	2352(8)	3146(6)	1705(6)	21(2)

Table S-5. Bond lengths [Å] and angles [°] for Complex 27.

Ir(1)-C(18)	2.087(7)
Ir(1)-N(1)	2.093(6)
Ir(1)-C(17)	2.107(7)
Ir(1)-C(14)	2.120(6)
Ir(1)-C(13)	2.130(7)
Ir(1)-Cl(1)	2.3522(18)
Ir(2)-N(3)	2.090(6)
Ir(2)-C(37)	2.098(7)
Ir(2)-C(38)	2.108(7)
Ir(2)-C(33)	2.113(6)
Ir(2)-C(34)	2.146(7)
Ir(2)-Cl(2)	2.3527(18)
N(1)-C(5)	1.354(9)
N(1)-C(1)	1.355(10)
N(2)-C(5)	1.364(10)
N(2)-C(6)	1.459(9)
N(2)-H(2B)	0.94(9)
N(3)-C(25)	1.358(9)
N(3)-C(21)	1.360(10)
N(4)-C(25)	1.348(11)
N(4)-C(26)	1.444(9)
N(4)-H(4B)	0.84(10)
C(1)-C(2)	1.369(10)
C(1)-H(1A)	0.9500
C(2)-C(3)	1.399(11)
C(2)-H(2A)	0.9500
C(3)-C(4)	1.374(11)
C(3)-H(3A)	0.9500
C(4)-C(5)	1.411(10)
C(4)-H(4A)	0.9500
C(6)-C(7)	1.506(11)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(7)-C(8)	1.386(12)
C(7)-C(12)	1.406(11)
C(8)-C(9)	1.398(12)
C(8)-H(8A)	0.9500
C(9)-C(10)	1.387(15)
C(9)-H(9A)	0.9500
C(10)-C(11)	1.374(16)
C(10)-H(10A)	0.9500
C(11)-C(12)	1.374(13)
C(11)-H(11A)	0.9500
C(12)-H(12A)	0.9500
C(13)-C(14)	1.403(11)
C(13)-C(20)	1.509(10)
C(13)-H(13A)	1.0000
C(14)-C(15)	1.514(11)
C(14)-H(14A)	1.0000
C(15)-C(16)	1.536(11)
C(15)-H(15A)	0.9900
C(15)-H(15B)	0.9900
C(16)-C(17)	1.537(10)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
C(17)-C(18)	1.427(11)
C(17)-H(17A)	1.0000
C(18)-C(19)	1.521(10)
C(18)-H(18A)	1.0000
C(19)-C(20)	1.541(10)
C(19)-H(19A)	0.9900
C(19)-H(19B)	0.9900
C(20)-H(20A)	0.9900
C(20)-H(20B)	0.9900
C(21)-C(22)	1.385(11)

C(21)-H(21A)	0.9500	C(38)-H(38A)	1.0000
C(22)-C(23)	1.391(12)	C(39)-C(40)	1.547(11)
C(22)-H(22A)	0.9500	C(39)-H(39A)	0.9900
C(23)-C(24)	1.366(12)	C(39)-H(39B)	0.9900
C(23)-H(23A)	0.9500	C(40)-H(40A)	0.9900
C(24)-C(25)	1.405(10)	C(40)-H(40B)	0.9900
C(24)-H(24A)	0.9500		
C(26)-C(27)	1.526(11)	C(18)-Ir(1)-N(1)	89.0(2)
C(26)-H(26A)	0.9900	C(18)-Ir(1)-C(17)	39.8(3)
C(26)-H(26B)	0.9900	N(1)-Ir(1)-C(17)	92.4(3)
C(27)-C(32)	1.374(12)	C(18)-Ir(1)-C(14)	98.5(3)
C(27)-C(28)	1.411(11)	N(1)-Ir(1)-C(14)	159.7(3)
C(28)-C(29)	1.375(14)	C(17)-Ir(1)-C(14)	81.8(3)
C(28)-H(28A)	0.9500	C(18)-Ir(1)-C(13)	81.8(3)
C(29)-C(30)	1.391(17)	N(1)-Ir(1)-C(13)	161.6(3)
C(29)-H(29A)	0.9500	C(17)-Ir(1)-C(13)	90.5(3)
C(30)-C(31)	1.376(16)	C(14)-Ir(1)-C(13)	38.6(3)
C(30)-H(30A)	0.9500	C(18)-Ir(1)-Cl(1)	155.5(2)
C(31)-C(32)	1.388(13)	N(1)-Ir(1)-Cl(1)	89.55(17)
C(31)-H(31A)	0.9500	C(17)-Ir(1)-Cl(1)	164.7(2)
C(32)-H(32A)	0.9500	C(14)-Ir(1)-Cl(1)	91.2(2)
C(33)-C(34)	1.394(10)	C(13)-Ir(1)-Cl(1)	92.36(19)
C(33)-C(40)	1.522(11)	N(3)-Ir(2)-C(37)	89.1(3)
C(33)-H(33A)	1.0000	N(3)-Ir(2)-C(38)	91.8(3)
C(34)-C(35)	1.515(10)	C(37)-Ir(2)-C(38)	39.2(3)
C(34)-H(34A)	1.0000	N(3)-Ir(2)-C(33)	158.3(3)
C(35)-C(36)	1.554(10)	C(37)-Ir(2)-C(33)	99.2(3)
C(35)-H(35A)	0.9900	C(38)-Ir(2)-C(33)	82.6(3)
C(35)-H(35B)	0.9900	N(3)-Ir(2)-C(34)	163.4(3)
C(36)-C(37)	1.522(11)	C(37)-Ir(2)-C(34)	82.2(3)
C(36)-H(36A)	0.9900	C(38)-Ir(2)-C(34)	90.4(3)
C(36)-H(36B)	0.9900	C(33)-Ir(2)-C(34)	38.2(3)
C(37)-C(38)	1.409(10)	N(3)-Ir(2)-Cl(2)	89.47(18)
C(37)-H(37A)	1.0000	C(37)-Ir(2)-Cl(2)	156.8(2)
C(38)-C(39)	1.528(10)	C(38)-Ir(2)-Cl(2)	164.0(2)

C(33)-Ir(2)-Cl(2)	90.4(2)	C(8)-C(7)-C(12)	118.1(8)
C(34)-Ir(2)-Cl(2)	93.0(2)	C(8)-C(7)-C(6)	122.8(7)
C(5)-N(1)-C(1)	118.3(6)	C(12)-C(7)-C(6)	119.1(8)
C(5)-N(1)-Ir(1)	122.1(5)	C(7)-C(8)-C(9)	120.9(8)
C(1)-N(1)-Ir(1)	119.5(5)	C(7)-C(8)-H(8A)	119.6
C(5)-N(2)-C(6)	122.1(6)	C(9)-C(8)-H(8A)	119.6
C(5)-N(2)-H(2B)	123(6)	C(10)-C(9)-C(8)	119.4(9)
C(6)-N(2)-H(2B)	113(6)	C(10)-C(9)-H(9A)	120.3
C(25)-N(3)-C(21)	119.2(7)	C(8)-C(9)-H(9A)	120.3
C(25)-N(3)-Ir(2)	122.8(5)	C(11)-C(10)-C(9)	120.3(8)
C(21)-N(3)-Ir(2)	117.9(5)	C(11)-C(10)-H(10A)	119.8
C(25)-N(4)-C(26)	122.8(7)	C(9)-C(10)-H(10A)	119.8
C(25)-N(4)-H(4B)	120(7)	C(10)-C(11)-C(12)	120.2(9)
C(26)-N(4)-H(4B)	117(7)	C(10)-C(11)-H(11A)	119.9
N(1)-C(1)-C(2)	123.4(7)	C(12)-C(11)-H(11A)	119.9
N(1)-C(1)-H(1A)	118.3	C(11)-C(12)-C(7)	121.0(9)
C(2)-C(1)-H(1A)	118.3	C(11)-C(12)-H(12A)	119.5
C(1)-C(2)-C(3)	117.7(7)	C(7)-C(12)-H(12A)	119.5
C(1)-C(2)-H(2A)	121.2	C(14)-C(13)-C(20)	123.7(7)
C(3)-C(2)-H(2A)	121.2	C(14)-C(13)-Ir(1)	70.3(4)
C(4)-C(3)-C(2)	120.8(7)	C(20)-C(13)-Ir(1)	113.3(4)
C(4)-C(3)-H(3A)	119.6	C(14)-C(13)-H(13A)	114.0
C(2)-C(3)-H(3A)	119.6	C(20)-C(13)-H(13A)	114.0
C(3)-C(4)-C(5)	118.0(7)	Ir(1)-C(13)-H(13A)	114.0
C(3)-C(4)-H(4A)	121.0	C(13)-C(14)-C(15)	125.5(7)
C(5)-C(4)-H(4A)	121.0	C(13)-C(14)-Ir(1)	71.1(4)
N(1)-C(5)-N(2)	116.6(6)	C(15)-C(14)-Ir(1)	110.6(5)
N(1)-C(5)-C(4)	121.8(7)	C(13)-C(14)-H(14A)	113.9
N(2)-C(5)-C(4)	121.7(7)	C(15)-C(14)-H(14A)	113.9
N(2)-C(6)-C(7)	113.4(6)	Ir(1)-C(14)-H(14A)	113.9
N(2)-C(6)-H(6A)	108.9	C(14)-C(15)-C(16)	112.7(6)
C(7)-C(6)-H(6A)	108.9	C(14)-C(15)-H(15A)	109.1
N(2)-C(6)-H(6B)	108.9	C(16)-C(15)-H(15A)	109.1
C(7)-C(6)-H(6B)	108.9	C(14)-C(15)-H(15B)	109.1
H(6A)-C(6)-H(6B)	107.7	C(16)-C(15)-H(15B)	109.1

H(15A)-C(15)-H(15B)	107.8	C(21)-C(22)-H(22A)	120.9
C(15)-C(16)-C(17)	110.3(6)	C(23)-C(22)-H(22A)	120.9
C(15)-C(16)-H(16A)	109.6	C(24)-C(23)-C(22)	119.7(7)
C(17)-C(16)-H(16A)	109.6	C(24)-C(23)-H(23A)	120.2
C(15)-C(16)-H(16B)	109.6	C(22)-C(23)-H(23A)	120.2
C(17)-C(16)-H(16B)	109.6	C(23)-C(24)-C(25)	120.4(7)
H(16A)-C(16)-H(16B)	108.1	C(23)-C(24)-H(24A)	119.8
C(18)-C(17)-C(16)	122.3(7)	C(25)-C(24)-H(24A)	119.8
C(18)-C(17)-Ir(1)	69.4(4)	N(4)-C(25)-N(3)	117.3(7)
C(16)-C(17)-Ir(1)	114.4(5)	N(4)-C(25)-C(24)	122.7(7)
C(18)-C(17)-H(17A)	114.4	N(3)-C(25)-C(24)	119.9(7)
C(16)-C(17)-H(17A)	114.4	N(4)-C(26)-C(27)	113.1(7)
Ir(1)-C(17)-H(17A)	114.4	N(4)-C(26)-H(26A)	109.0
C(17)-C(18)-C(19)	126.0(6)	C(27)-C(26)-H(26A)	109.0
C(17)-C(18)-Ir(1)	70.9(4)	N(4)-C(26)-H(26B)	109.0
C(19)-C(18)-Ir(1)	112.0(5)	C(27)-C(26)-H(26B)	109.0
C(17)-C(18)-H(18A)	113.5	H(26A)-C(26)-H(26B)	107.8
C(19)-C(18)-H(18A)	113.5	C(32)-C(27)-C(28)	118.5(8)
Ir(1)-C(18)-H(18A)	113.5	C(32)-C(27)-C(26)	121.5(7)
C(18)-C(19)-C(20)	111.0(6)	C(28)-C(27)-C(26)	119.9(8)
C(18)-C(19)-H(19A)	109.4	C(29)-C(28)-C(27)	119.3(10)
C(20)-C(19)-H(19A)	109.4	C(29)-C(28)-H(28A)	120.3
C(18)-C(19)-H(19B)	109.4	C(27)-C(28)-H(28A)	120.3
C(20)-C(19)-H(19B)	109.4	C(28)-C(29)-C(30)	121.9(9)
H(19A)-C(19)-H(19B)	108.0	C(28)-C(29)-H(29A)	119.0
C(13)-C(20)-C(19)	112.3(6)	C(30)-C(29)-H(29A)	119.0
C(13)-C(20)-H(20A)	109.1	C(31)-C(30)-C(29)	118.3(9)
C(19)-C(20)-H(20A)	109.1	C(31)-C(30)-H(30A)	120.8
C(13)-C(20)-H(20B)	109.1	C(29)-C(30)-H(30A)	120.8
C(19)-C(20)-H(20B)	109.1	C(30)-C(31)-C(32)	120.5(10)
H(20A)-C(20)-H(20B)	107.9	C(30)-C(31)-H(31A)	119.7
N(3)-C(21)-C(22)	122.4(7)	C(32)-C(31)-H(31A)	119.7
N(3)-C(21)-H(21A)	118.8	C(27)-C(32)-C(31)	121.4(9)
C(22)-C(21)-H(21A)	118.8	C(27)-C(32)-H(32A)	119.3
C(21)-C(22)-C(23)	118.3(8)	C(31)-C(32)-H(32A)	119.3

C(34)-C(33)-C(40)	125.7(7)
C(34)-C(33)-Ir(2)	72.2(4)
C(40)-C(33)-Ir(2)	109.9(5)
C(34)-C(33)-H(33A)	113.8
C(40)-C(33)-H(33A)	113.8
Ir(2)-C(33)-H(33A)	113.8
C(33)-C(34)-C(35)	124.5(7)
C(33)-C(34)-Ir(2)	69.6(4)
C(35)-C(34)-Ir(2)	113.1(5)
C(33)-C(34)-H(34A)	113.9
C(35)-C(34)-H(34A)	113.9
Ir(2)-C(34)-H(34A)	113.9
C(34)-C(35)-C(36)	111.1(6)
C(34)-C(35)-H(35A)	109.4
C(36)-C(35)-H(35A)	109.4
C(34)-C(35)-H(35B)	109.4
C(36)-C(35)-H(35B)	109.4
H(35A)-C(35)-H(35B)	108.0
C(37)-C(36)-C(35)	112.2(6)
C(37)-C(36)-H(36A)	109.2
C(35)-C(36)-H(36A)	109.2
C(37)-C(36)-H(36B)	109.2
C(35)-C(36)-H(36B)	109.2
H(36A)-C(36)-H(36B)	107.9
C(38)-C(37)-C(36)	125.8(7)
C(38)-C(37)-Ir(2)	70.8(4)
C(36)-C(37)-Ir(2)	110.6(5)
C(38)-C(37)-H(37A)	113.8
C(36)-C(37)-H(37A)	113.8
Ir(2)-C(37)-H(37A)	113.8
C(37)-C(38)-C(39)	123.2(7)
C(37)-C(38)-Ir(2)	70.0(4)
C(39)-C(38)-Ir(2)	113.3(5)
C(37)-C(38)-H(38A)	114.2
C(39)-C(38)-H(38A)	114.2
Ir(2)-C(38)-H(38A)	114.2
C(38)-C(39)-C(40)	111.2(6)
C(38)-C(39)-H(39A)	109.4
C(40)-C(39)-H(39A)	109.4
C(38)-C(39)-H(39B)	109.4
C(40)-C(39)-H(39B)	109.4
H(39A)-C(39)-H(39B)	108.0
C(33)-C(40)-C(39)	111.7(6)
C(33)-C(40)-H(40A)	109.3
C(39)-C(40)-H(40A)	109.3
C(33)-C(40)-H(40B)	109.3
C(39)-C(40)-H(40B)	109.3
H(40A)-C(40)-H(40B)	107.9

Symmetry transformations used to generate equivalent atoms:

Table S-6. Anisotropic displacement parameters ($Å^2 x 10^3$) for Complex 27. 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}
Ir(1)	15(1)	10(1)	12(1)	4(1)	6(1)	5(1)
Ir(2)	13(1)	10(1)	12(1)	4(1)	4(1)	3(1)
Cl(1)	29(1)	16(1)	18(1)	5(1)	12(1)	7(1)
Cl(2)	22(1)	16(1)	18(1)	5(1)	-2(1)	2(1)
N(1)	18(3)	15(3)	13(3)	5(2)	5(2)	7(2)
N(2)	15(3)	13(3)	29(4)	8(3)	7(3)	0(2)
N(3)	16(3)	14(3)	16(3)	9(2)	7(2)	4(2)
N(4)	21(3)	12(3)	33(4)	11(3)	7(3)	5(3)
C(1)	18(4)	13(3)	15(3)	1(3)	3(3)	2(3)
C(2)	15(3)	19(4)	15(3)	-3(3)	0(3)	4(3)
C(3)	26(4)	23(4)	13(3)	6(3)	4(3)	14(3)
C(4)	27(4)	15(3)	12(3)	5(3)	6(3)	5(3)
C(5)	18(3)	14(3)	8(3)	2(2)	2(3)	4(3)
C(6)	24(4)	19(4)	23(4)	5(3)	9(3)	-1(3)
C(7)	11(3)	18(3)	31(4)	6(3)	8(3)	0(3)
C(8)	30(5)	26(4)	24(4)	2(3)	12(4)	-5(3)
C(9)	20(4)	41(5)	37(5)	0(4)	10(4)	-4(4)
C(10)	27(5)	22(4)	56(7)	-2(4)	3(4)	10(4)
C(11)	36(5)	19(4)	58(7)	18(4)	6(5)	8(4)
C(12)	40(5)	22(4)	39(5)	16(4)	15(4)	12(4)
C(13)	23(4)	13(3)	11(3)	5(3)	8(3)	12(3)
C(14)	27(4)	12(3)	18(4)	12(3)	11(3)	11(3)
C(15)	25(4)	15(3)	24(4)	11(3)	7(3)	2(3)
C(16)	21(4)	29(4)	21(4)	15(3)	12(3)	10(3)
C(17)	22(4)	21(3)	13(3)	7(3)	15(3)	12(3)
C(18)	24(4)	16(3)	9(3)	6(3)	8(3)	13(3)
C(19)	26(4)	22(4)	14(4)	4(3)	1(3)	3(3)
C(20)	18(4)	21(4)	24(4)	12(3)	5(3)	8(3)
C(21)	24(4)	16(3)	16(4)	1(3)	4(3)	0(3)
C(22)	30(4)	22(4)	13(4)	2(3)	12(3)	-1(3)

C(23)	40(5)	22(4)	14(4)	6(3)	9(3)	-7(3)
C(24)	34(4)	20(4)	14(4)	12(3)	5(3)	1(3)
C(25)	20(4)	14(3)	14(3)	5(3)	-1(3)	1(3)
C(26)	19(4)	19(4)	28(4)	6(3)	3(3)	8(3)
C(27)	13(3)	15(3)	31(4)	8(3)	4(3)	3(3)
C(28)	42(5)	21(4)	42(5)	13(4)	16(4)	-1(4)
C(29)	42(6)	19(4)	83(9)	15(5)	28(6)	2(4)
C(30)	33(5)	24(5)	57(7)	-11(4)	18(5)	-4(4)
C(31)	20(4)	44(6)	42(6)	-4(4)	6(4)	8(4)
C(32)	19(4)	29(4)	37(5)	5(4)	4(4)	9(3)
C(33)	26(4)	10(3)	15(3)	8(3)	8(3)	5(3)
C(34)	22(4)	15(3)	16(3)	5(3)	7(3)	0(3)
C(35)	23(4)	21(4)	18(4)	7(3)	11(3)	3(3)
C(36)	30(4)	13(3)	14(4)	3(3)	5(3)	2(3)
C(37)	29(4)	11(3)	15(3)	2(3)	11(3)	3(3)
C(38)	11(3)	21(4)	13(3)	3(3)	-3(3)	-3(3)
C(39)	21(4)	22(4)	11(3)	6(3)	2(3)	6(3)
C(40)	26(4)	19(4)	21(4)	11(3)	8(3)	12(3)

Table S-7. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for Complex 27.

	x	y	z	U(eq)
H(2B)	8450(90)	5200(80)	3130(70)	22
H(4B)	5280(100)	90(80)	3180(70)	25
H(1A)	12647	6299	3703	20
H(2A)	13841	5131	4479	22
H(3A)	12727	3657	4737	25
H(4A)	10465	3410	4232	21
H(6A)	7208	4014	3387	25
H(6B)	8398	3802	4189	25
H(8A)	8416	3078	1646	32
H(9A)	8378	1276	660	41
H(10A)	8222	-203	1314	46
H(11A)	8090	110	2926	44
H(12A)	7993	1881	3873	37
H(13A)	7724	7643	2208	18
H(14A)	9514	8746	2724	20
H(15A)	11362	8570	2057	24
H(15B)	10196	8578	1156	24
H(16A)	11817	7103	939	25
H(16B)	10315	6787	410	25
H(17A)	11734	5848	1794	19
H(18A)	9981	4719	1534	18
H(19A)	7812	4995	868	26
H(19B)	8577	5149	73	26
H(20A)	8354	6971	419	24
H(20B)	7050	6600	673	24
H(21A)	1541	1334	3734	23
H(22A)	716	123	4446	25
H(23A)	1913	-1391	4678	30
H(24A)	3872	-1646	4199	26

H(26A)	5907	-1363	4191	27
H(26B)	6745	-1044	3503	27
H(28A)	5895	-3340	3688	39
H(29A)	5355	-4992	2494	54
H(30A)	4431	-5041	879	50
H(31A)	4145	-3388	460	46
H(32A)	4742	-1723	1638	36
H(33A)	4056	3761	2818	19
H(34A)	5572	2720	2299	20
H(35A)	5376	1699	754	23
H(35B)	3895	2014	490	23
H(36A)	3590	161	155	23
H(36B)	4816	75	988	23
H(37A)	3003	-296	1582	21
H(38A)	1372	782	1819	19
H(39A)	752	2032	978	22
H(39B)	1973	1784	479	22
H(40A)	2418	3596	1256	25
H(40B)	1796	3519	2145	25

Table S-8. **Torsion angles [°] for Complex 27.**

C(5)-N(1)-C(1)-C(2)	1.3(10)
Ir(1)-N(1)-C(1)-C(2)	-178.8(6)
N(1)-C(1)-C(2)-C(3)	-0.3(11)
C(1)-C(2)-C(3)-C(4)	-0.5(11)
C(2)-C(3)-C(4)-C(5)	0.3(11)
C(1)-N(1)-C(5)-N(2)	180.0(6)
Ir(1)-N(1)-C(5)-N(2)	0.0(9)
C(1)-N(1)-C(5)-C(4)	-1.6(10)
Ir(1)-N(1)-C(5)-C(4)	178.5(5)
C(6)-N(2)-C(5)-N(1)	-177.3(6)
C(6)-N(2)-C(5)-C(4)	4.2(11)
C(3)-C(4)-C(5)-N(1)	0.8(10)
C(3)-C(4)-C(5)-N(2)	179.2(7)
C(5)-N(2)-C(6)-C(7)	-75.5(9)
N(2)-C(6)-C(7)-C(8)	-35.5(11)
N(2)-C(6)-C(7)-C(12)	146.7(8)
C(12)-C(7)-C(8)-C(9)	1.3(13)
C(6)-C(7)-C(8)-C(9)	-176.5(8)
C(7)-C(8)-C(9)-C(10)	-1.9(14)
C(8)-C(9)-C(10)-C(11)	0.3(14)
C(9)-C(10)-C(11)-C(12)	1.9(15)
C(10)-C(11)-C(12)-C(7)	-2.5(15)
C(8)-C(7)-C(12)-C(11)	0.9(13)
C(6)-C(7)-C(12)-C(11)	178.7(8)
C(20)-C(13)-C(14)-C(15)	-3.1(11)
Ir(1)-C(13)-C(14)-C(15)	102.3(7)
C(20)-C(13)-C(14)-Ir(1)	-105.4(6)
C(13)-C(14)-C(15)-C(16)	-46.1(10)
Ir(1)-C(14)-C(15)-C(16)	34.9(8)
C(14)-C(15)-C(16)-C(17)	-32.2(9)
C(15)-C(16)-C(17)-C(18)	94.9(8)
C(15)-C(16)-C(17)-Ir(1)	14.7(8)
C(16)-C(17)-C(18)-C(19)	-2.8(11)

Ir(1)-C(17)-C(18)-C(19)	103.7(7)
C(16)-C(17)-C(18)-Ir(1)	-106.5(6)
C(17)-C(18)-C(19)-C(20)	-47.6(10)
Ir(1)-C(18)-C(19)-C(20)	34.2(8)
C(14)-C(13)-C(20)-C(19)	94.5(8)
Ir(1)-C(13)-C(20)-C(19)	13.4(8)
C(18)-C(19)-C(20)-C(13)	-30.6(9)
C(25)-N(3)-C(21)-C(22)	-1.7(11)
Ir(2)-N(3)-C(21)-C(22)	176.1(6)
N(3)-C(21)-C(22)-C(23)	0.1(12)
C(21)-C(22)-C(23)-C(24)	0.3(12)
C(22)-C(23)-C(24)-C(25)	0.9(12)
C(26)-N(4)-C(25)-N(3)	-179.6(7)
C(26)-N(4)-C(25)-C(24)	-1.9(12)
C(21)-N(3)-C(25)-N(4)	-179.4(7)
Ir(2)-N(3)-C(25)-N(4)	3.0(9)
C(21)-N(3)-C(25)-C(24)	2.8(11)
Ir(2)-N(3)-C(25)-C(24)	-174.8(5)
C(23)-C(24)-C(25)-N(4)	179.8(8)
C(23)-C(24)-C(25)-N(3)	-2.5(12)
C(25)-N(4)-C(26)-C(27)	78.3(10)
N(4)-C(26)-C(27)-C(32)	38.8(11)
N(4)-C(26)-C(27)-C(28)	-143.8(8)
C(32)-C(27)-C(28)-C(29)	1.9(13)
C(26)-C(27)-C(28)-C(29)	-175.6(8)
C(27)-C(28)-C(29)-C(30)	-2.2(15)
C(28)-C(29)-C(30)-C(31)	1.4(16)
C(29)-C(30)-C(31)-C(32)	-0.3(15)
C(28)-C(27)-C(32)-C(31)	-0.8(13)
C(26)-C(27)-C(32)-C(31)	176.6(8)
C(30)-C(31)-C(32)-C(27)	0.0(14)
C(40)-C(33)-C(34)-C(35)	2.5(12)
Ir(2)-C(33)-C(34)-C(35)	104.6(7)
C(40)-C(33)-C(34)-Ir(2)	-102.0(7)
C(33)-C(34)-C(35)-C(36)	-94.6(9)

Ir(2)-C(34)-C(35)-C(36)	-14.3(8)
C(34)-C(35)-C(36)-C(37)	32.8(9)
C(35)-C(36)-C(37)-C(38)	44.6(10)
C(35)-C(36)-C(37)-Ir(2)	-36.1(8)
C(36)-C(37)-C(38)-C(39)	3.4(12)
Ir(2)-C(37)-C(38)-C(39)	105.4(7)
C(36)-C(37)-C(38)-Ir(2)	-102.0(7)
C(37)-C(38)-C(39)-C(40)	-95.5(8)
Ir(2)-C(38)-C(39)-C(40)	-14.9(8)
C(34)-C(33)-C(40)-C(39)	45.3(10)
Ir(2)-C(33)-C(40)-C(39)	-36.6(7)
C(38)-C(39)-C(40)-C(33)	33.7(9)

Symmetry transformations used to generate equivalent atoms: