Electronic Supplementary Material (ESI) for Dalton Transactions.

Enhancements in Catalytic Reactivity and Selectivity of Homobimetallic Complexes Containing Heteroditopic Ligands

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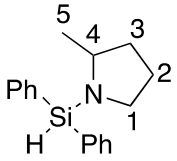
1. NMR Characterisation Data

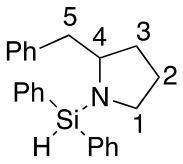
The N-silylamines **18c** and **19c** could not be isolated and purified due to their ability to hydrolyse in air. Therefore the N-silylamines were identified by diagnostic signals in the ^{1}H NMR spectra. **18c** and **19c** were hydrolysed with water, purified and confirmed by comparison of the ^{1}H NMR spectra with literature.[1]

1.1 Diagnostic signals for 19c



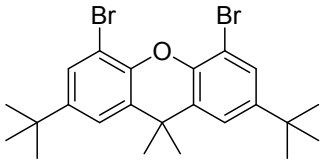
^{1}H NMR (500 MHz, C7D8): δ 7.60 (m, 2H, Ar**H**), 7.17 (m, 3H, Ar**H**), 5.76 (s, 1H, **H**SiPh2), 3.53 (m, 1H, H**4**), (3.04, 1.78, 1.64, 1.54, 1.27 (multiplets, 6H, belonging to H**1-3**)), 1.00 (d, $^{3}J_{H\text{-}H}$ = 6.3 Hz, 3H, H**5**) ppm.

1.2 Diagnostic signals for 20c



^{1}H NMR (600 MHz, C_7D_8): *δ* 7.60 (m, 5H, Ar**H**), 7.18 (m, 5H, Ar**H**), 7.02 (m, 2H, Ar**H**), 6.97 (m, Ar**H**), 6.87 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 2H, Ar**H**), 5.48 (1H, **H**$SiPh_2$), 3.69 (m, 1H, H**4**), 3.06 (t, $^{3}J_{H\text{-}H}$ = 6.2 Hz, 2H, H**1**), 2.79 (dd, $^{2}J_{H\text{-}H}$ = 13.2 Hz, $^{3}J_{H\text{-}H}$ = 4.7 Hz, 1H, H**5**), 2.41 (dd, $^{2}J_{H\text{-}H}$ = 13.2 Hz, $^{3}J_{H\text{-}H}$ = 9.3 Hz, 1H, H**5**), 1.65-1.49 (m, 4H, H**2** and H**3**) ppm.

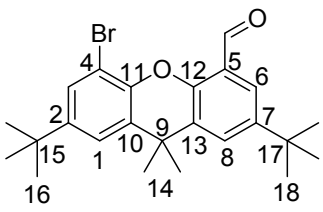
1.3 NMR Data for 6



^{1}H NMR (300 MHz, $CDCl_3$): *δ* 7.5 (d, $^{4}J_{H\text{-}H}$ = 2.19 Hz, 2H, Ar**H**), 7.3 (d $^{4}J_{H\text{-}H}$ = 2.22 Hz, 2H, Ar**H**), 1.6 (s, 6H, 2 x C$\mathbf{H}_3$), 1.3 (s, 18H, 6 x C$\mathbf{H}_3$) ppm.

^{13}C{^{1}H} NM (151 MHz, $CDCl_3$): δ 147.4 (Ar**C**), 145.4 (Ar**C**), 131.3 (Ar**C**), 128.61 (Ar**C**), 121.7 (Ar**C**), 110.6 (Ar**C**), 35.9 (tert-butyl quart-**C**), 34.8 (dimethyl quart-**C**), 32.0 (dimethyl **C**H_3), 31.6 (tert-butyl **C**H_3) ppm.

1.4 NMR Data for 7

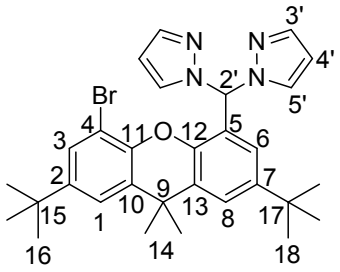


^{1}H NMR (300 MHz, $CDCl_3$): *δ* 10.85 (s, 1H, C**H**O), 7.81 (d, $^{4}J_{H\text{-}H}$ = 2.45 Hz, 1H, Ar**H**), 7.67 (d, $^{4}J_{H\text{-}H}$ = 2.49 Hz, 1H, Ar**H**), 7.49 (d, $^{4}J_{H\text{-}H}$ = 2.25 Hz, 1H, Ar**H**), 7.37 (d, $^{4}J_{H\text{-}H}$ = 2.25 Hz, 1H, Ar**H**), 1.66 (s, 6H, 2 x C$\mathbf{H}_3$), 1.35 (s, 9H, 3 x C$\mathbf{H}_3$), 1.33 (s, 9H, 3 x C$\mathbf{H}_3$) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): *δ* 189.9 (**C**HO), 150.8 (Ar**C**), 147.7 (Ar**C**), 146.3 (Ar**C**), 144.4 (Ar**C**), 131.0 (Ar**C**), 130.8 (Ar**C**), 129.5 (Ar**C**), 129.2 (Ar**C**), 128.5 (Ar**C**), 124.1

(Ar**C**), 123.3 (Ar**C**), 122.7 (Ar**C**), 121.8 (Ar**C**), 110.4 (Ar**C**), 35.1 (tert-butyl quart-**C**), 34.7 (dimethyl quart-**C**), 32.0 (dimethyl **C**H_3), 31.4 (tert-butyl **C**H_3) ppm.

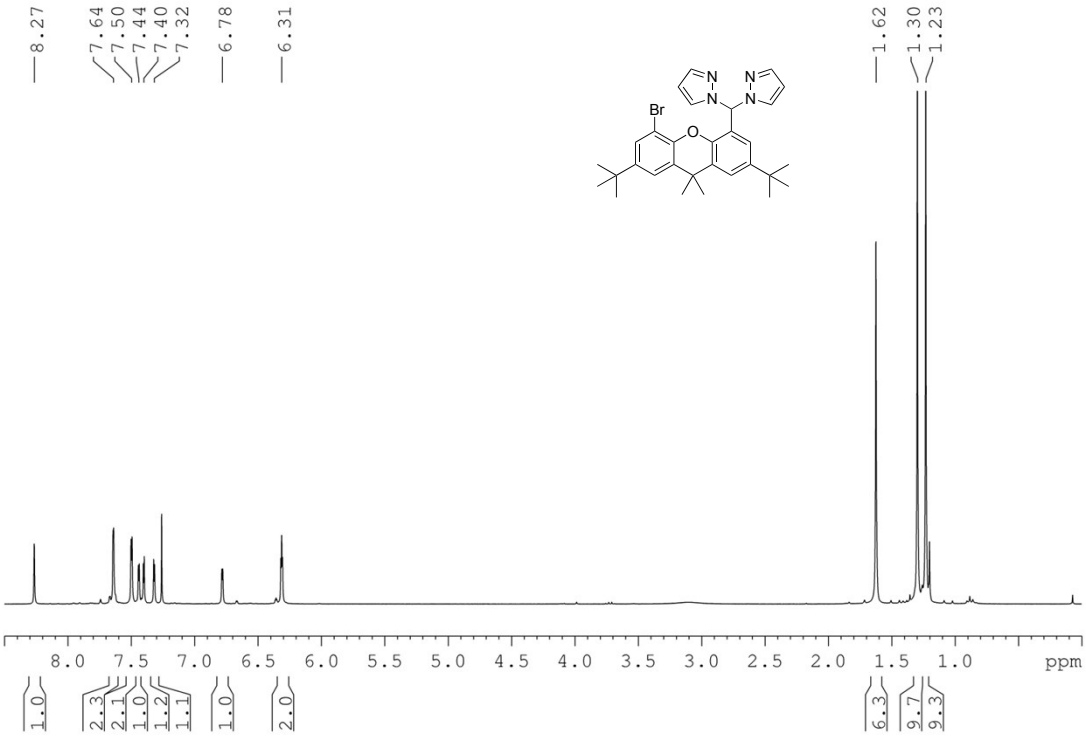
1.5 NMR Data for 8



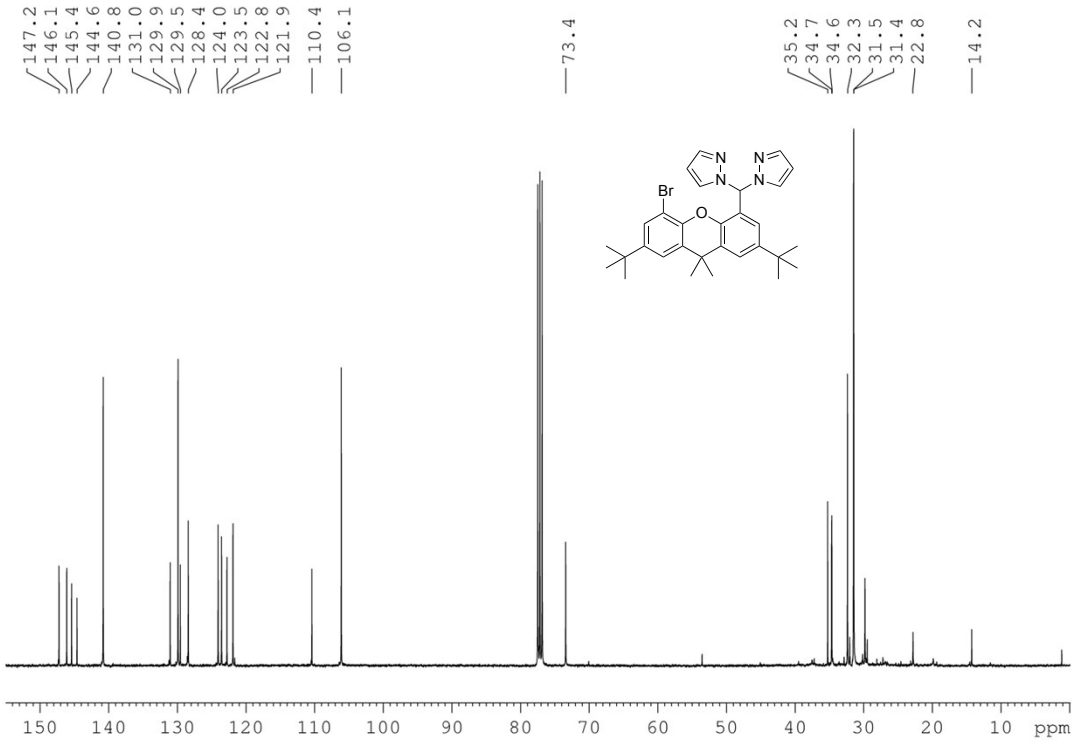
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (s, 1H, **H**2'), 7.64 (d, $^3J_{H\text{-}H}$ = 1.42 Hz, 2H, **H**3'), 7.50 (d, $^3J_{H\text{-}H}$ = 2.31 Hz, 2H, **H**5'), 7.44 (d, $^4J_{H\text{-}H}$ = 2.16 Hz, 1H, **H**8), 7.40 (d, $^4J_{H\text{-}H}$ = 2.21 Hz, 1H, **H**3), 7.32 (d, $^4J_{H\text{-}H}$ = 2.16 Hz, 1H, **H**1), 6.78 (d, $^4J_{H\text{-}H}$ = 2.16 Hz, 1H, **H**6), 6.31 (t, $^3J_{H\text{-}H}$ = 2.06 Hz, 2H, **H**4'), 1.62 (s, 6H, **H**14), 1.30 (s, 9H, **H**16), 1.23 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (100.6 MHz, $CDCl_3$): δ 147.2 (**C**2), 146.1 (**C**7), 145.4 (**C**12), 144.60 (**C**11), 140.8 (**C**3'), 131.0 (**C**10), 129.9 (**C**5'), 129.6 (**C**13), 128.4 (**C**3), 124.0 (**C**8), 123.5 (**C**6), 122.8 (**C**5), 121.9 (**C**1), 110.4 (**C**4), 106.1 (**C**4'), 73.4 (**C**2'), 35.2 (**C**9), 34.7 (**C**15), 35.6 (**C**17), 32.4 (**C**14), 31.5 (**C**16), 31.4 (**C**18) ppm.

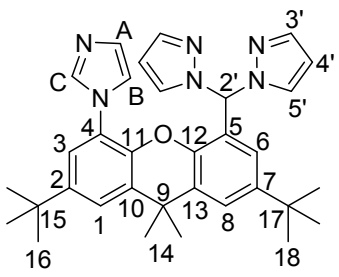
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (**8**)



$^{13}C\{^{1}H\}$ NMR (100.6 MHz, $CDCl_3$) spectrum of **8**



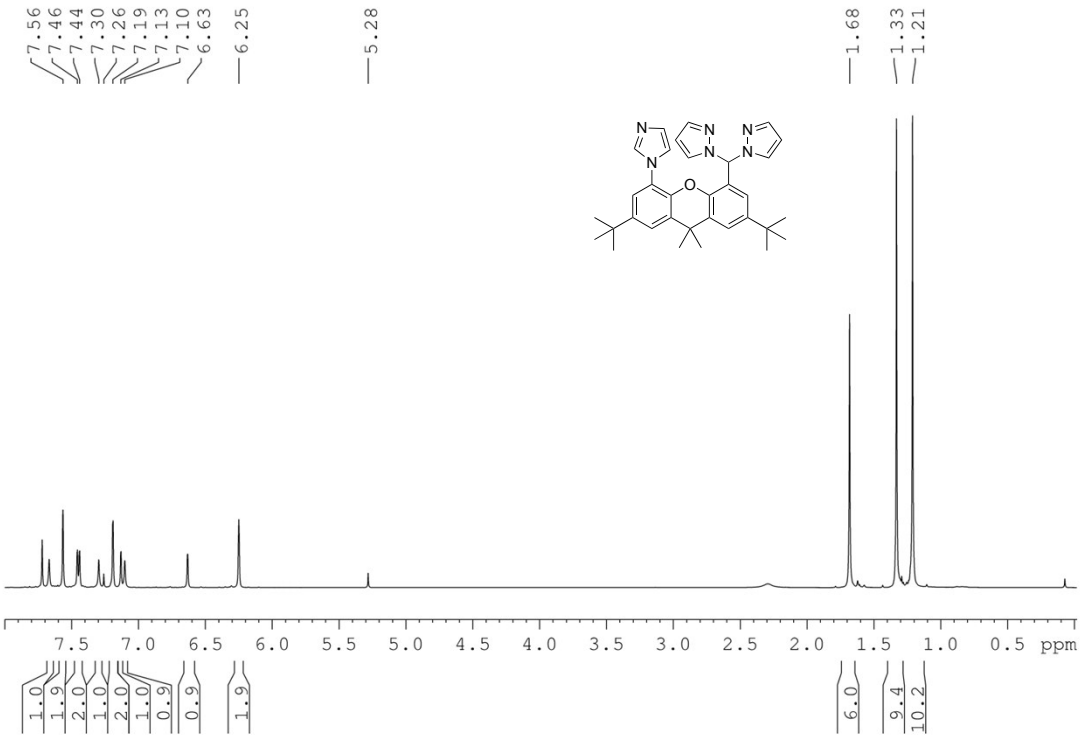
1.6 NMR Data for 9



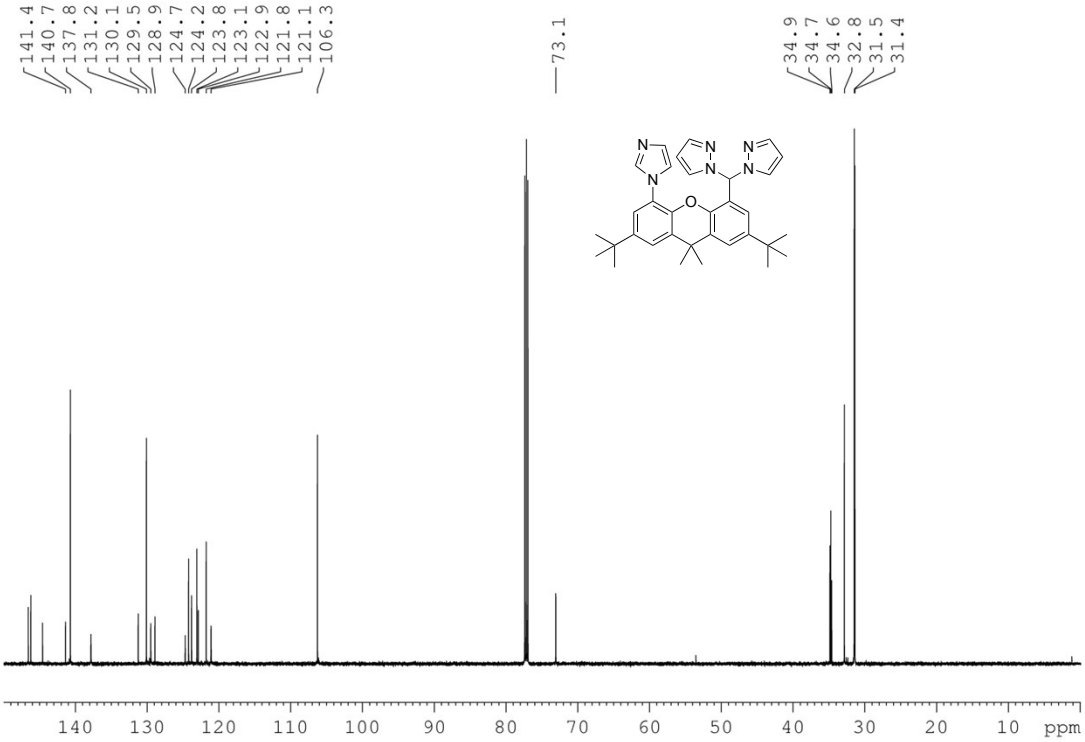
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.72 (s, 1H, **H**2'), 7.67 (br s, 1H, **H**A/B), 7.56 (br s, 2H, **H**3'), 7.46 (d, $^{4}J_{H\text{-}H}$ = 1.76 Hz, 1H, **H**1), 7.44 (d, $^{4}J_{H\text{-}H}$ = 1.76 Hz, 1H, **H**8), 7.30 (br s, 1H, **H**A/B), 7.19 (d, $^{3}J_{H\text{-}H}$ = 1.85 Hz, 2H, **H**5'), 7.13 (d, $^{4}J_{H\text{-}H}$ = 1.76 Hz, 1H, **H**3), 7.10 (br s, 1H, **H**C), 6.63 (br d, 1H, **H**6), 6.25 (br t, 2H, **H**4'), 1.68 (s, 6H, **H**14), 1.33 (s, 9H, **H**16), 1.21 (s, 9H, **H**18) ppm.

$^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$): δ 146.6 (**C**2), 146.2 (**C**7), 144.6 (**C**12), 141.4 (**C**11), 140.7 (**C**3'), 137.8 (**C**A/B), 131.2 (**C**10), 130.1 (**C**5'), 129.5 (**C**A/B), 128.9 (**C**13), 124.7 (**C**4), 124.2 (**C**8), 123.8 (**C**6), 123.1 (**C**1), 122.9 (**C**5), 121.8 (**C**3), 121.1 (**C**C), 106.3 (**C**4'), 73.1 (**C**2'), 34.9 (**C**9), 34.7 (**C**15), 34.6 (**C**17), 32.8 (**C**14), 31.5 (**C**16), 31.4 (**C**18) ppm.

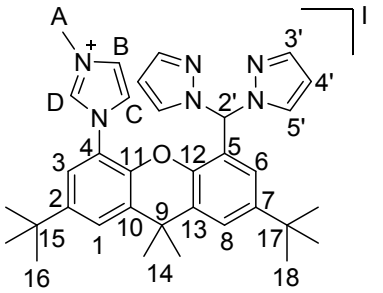
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **9**



^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$) spectrum of **9**



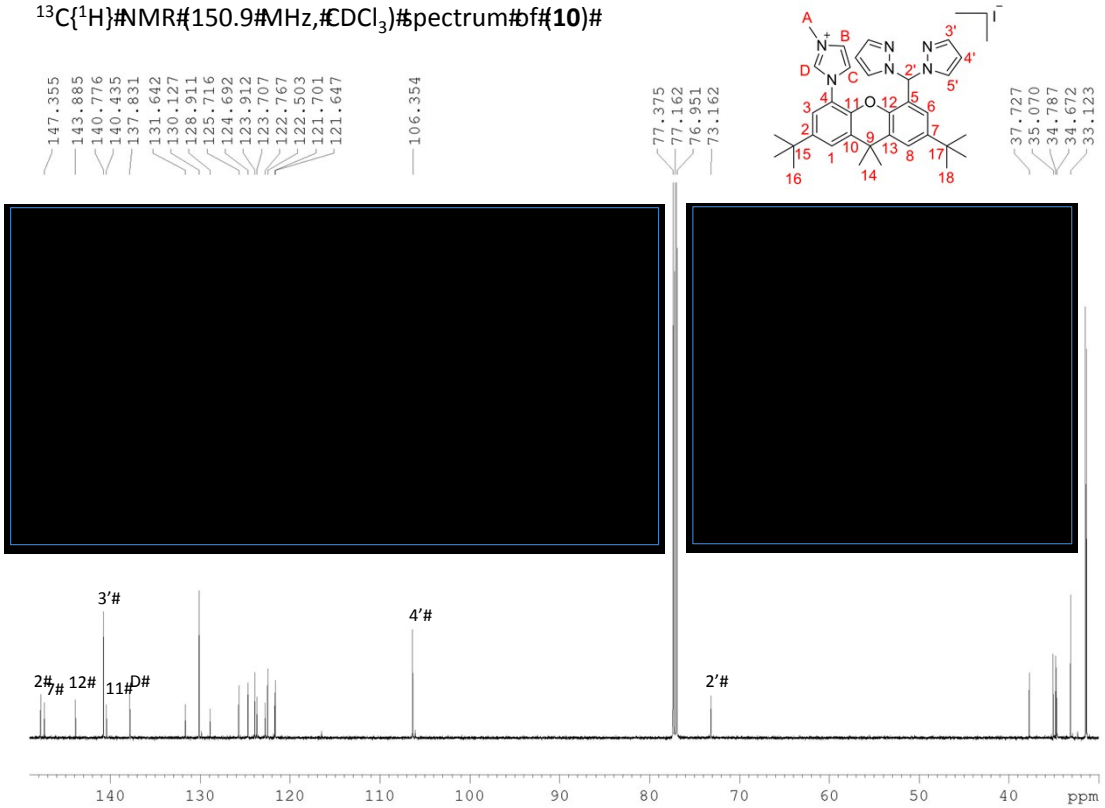
1.7 NMR Data for 10



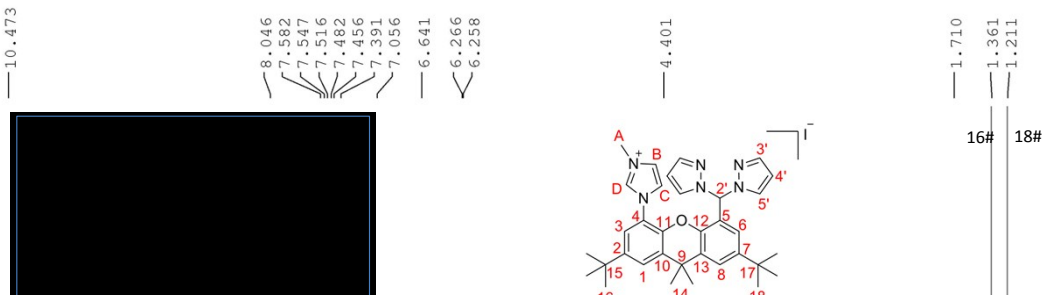
^{1}H NMR (600 MHz, $CDCl_3$): δ 10.36 (s, 1H, **H**D), 8.07 (s, 1H, **H**2'), 7.56 (d, $^{4}J_{H\text{-}H}$ = 2.15 Hz, 1H, **H**1), 7.54 (br d, 4H, **H**3' & **H**5'), 7.51 (br t, 1H, **H**B), 7.47 (d, $^{4}J_{H\text{-}H}$ = 2.15 Hz, 1H, **H**8), 7.42 (d, $^{4}J_{H\text{-}H}$ = 2.15 Hz, 1H, **H**3), 7.07 (br t, 1H, **H**C), 6.63 (d, $^{4}J_{H\text{-}H}$ = 2.02 Hz, 1H, **H**6), 6.24 (t, $^{3}J_{H\text{-}H}$ = 1.99 Hz, 2H, **H**4'), 4.38 (s, 3H, **H**A), 1.70 (s, 6H, **H**14), 1.34 (s, 9H, **H**16), 1.20 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): δ 147.8 (**C**2), 147.4 (**C**7), 143.9 (**C**12), 140.8 (**C**3'), 140.4 (**C**11), 137.8 (**C**D), 131.6 (**C**10), 130.1 (**C**5'), 128.9 (**C**13), 125.7 (**C**1), 124.7 (**C**8), 123.9 (**C**B), 123.7 (**C**6), 122.8 (**C**5), 122.5 (**C**C), 121.7 (**C**4), 121.6 (**C**3), 106.3 (**C**4'), 73.2 (**C**2'), 37.7 (**C**A), 35.1 (**C**15), 34.8 (**C**9), 34.7 (**C**17), 33.1 (**C**14), 31.5 (**C**16), 31.3 (**C**18) ppm.

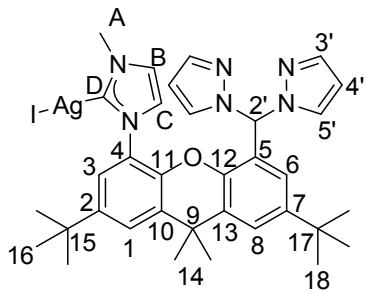
^{13}C{^{1}H}#NMR#(150.9#MHz,#$CDCl_3$)#spectrum#bf#(**10**)#



^{1}H#NMR#(300#MHz,#$CDCl_3$)#spectrum#bf#(**10**)#



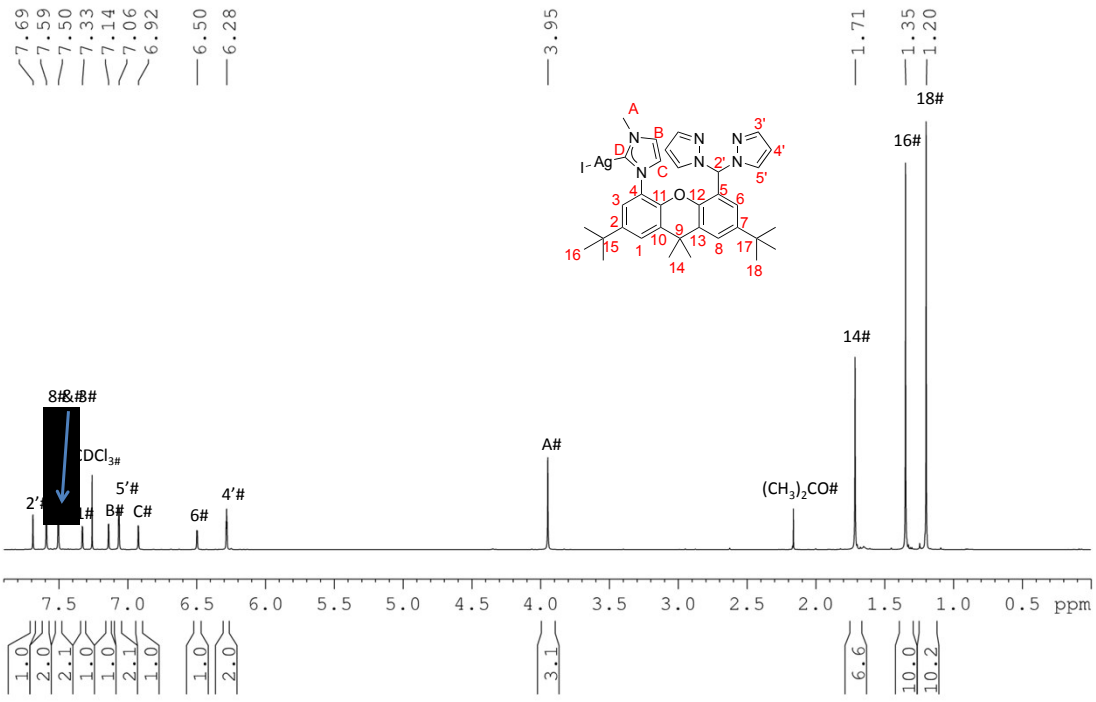
1.8 NMR Data for 11



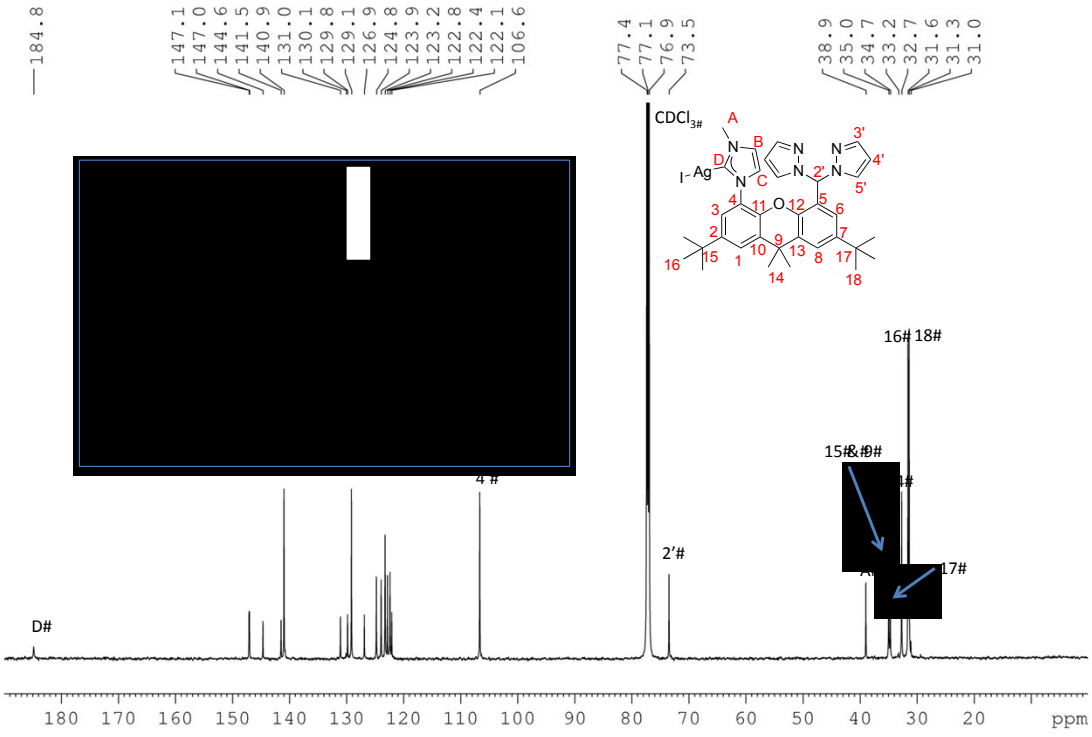
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.69 (s, 1H, **H**2'), 7.59 (d, $^{3}J_{H\text{-}H}$ = 1.53 Hz, 2H, **H**3'), 7.50 (br d, 2H, **H**8 & 3), 7.33 (d, $^{4}J_{H\text{-}H}$ = 2.27 Hz, 1H, **H**1), 7.14 (d, $^{3}J_{H\text{-}H}$ = 1.69 Hz, 1H, **H**B), 7.06 (d, $^{3}J_{H\text{-}H}$ = 2.48 Hz, 2H, **H**5'), 6.92 (d, $^{3}J_{H\text{-}H}$ = 1.69 Hz, 1H, **H**C), 6.50 (d, $^{4}J_{H\text{-}H}$ = 2.04 Hz, 1H, **H**6), 6.28 (dd, $^{3}J_{H\text{-}H}$ = 2.18 Hz, 2H, **H**4'), 3.95 (s, 3H, **H**A), 1.71 (s, 6H, **H**14), 1.35 (s, 9H, **H**16), 1.20 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): δ 184.8 (**C**D), 147.1 (**C**2), 147.0 (**C**7), 144.6 (**C**12), 141.5 (**C**11), 140.9 (**C**3'), 131.0 (**C**10), 129.7 (**C**13), 129.1 (**C**5'), 126.9 (**C**4), 124.8 (**C**8), 123.9 (**C**3), 123.22 (**C**6), 123.22 (**C**C), 122.8 (**C**1), 122.4 (**C**B), 122.1 (**C**5), 106.6 (**C**4'), 73.5 (**C**2'), 38.9 (**C**A), 35.0 (**C**15), 35.0 (**C**9), 34.7 (**C**17), 32.7 (**C**14), 31.6 (**C**16), 31.3 (**C**18) ppm.

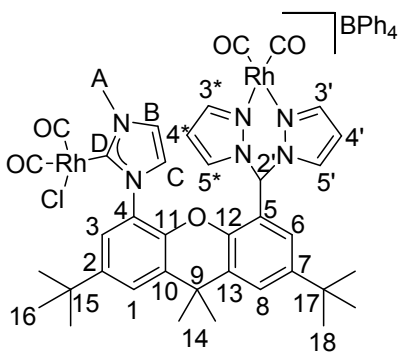
^{1}H#NMR#(600#MHz,#$CDCl_3$)#spectrum#bf#(**11**)##



$^{13}C\{^{1}H\}$ NMR (150.9 MHz, $CDCl_3$) spectrum of **11**



1.9 NMR Data for 12

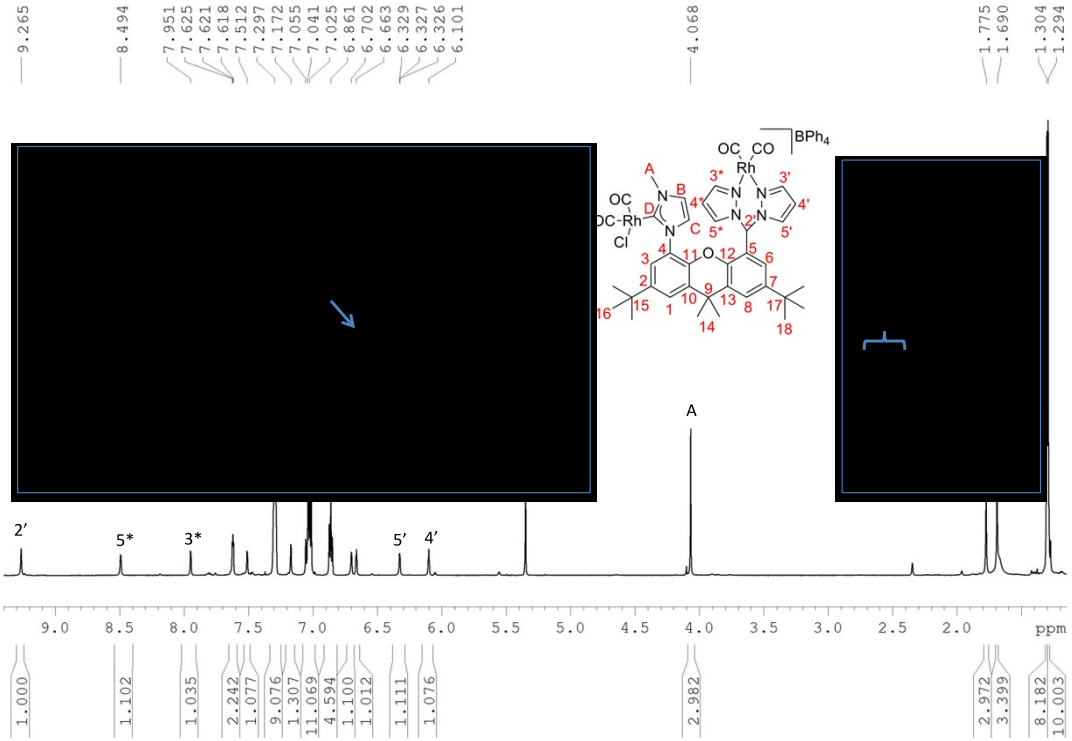


^{1}H NMR (600 MHz, CD_2Cl_2, 238 K): δ 9.27 (br s, 1H, **H**2'), 8.49 (br d, 1H, **H**5*), 7.95 (br d, 1H, **H**3*), 7.63 (d, $^{4}J_{H\text{-}H}$ = 2.23 Hz, 1H, **H**8), 7.62 (d, $^{4}J_{H\text{-}H}$ = 2.30 Hz, 1H, **H**1), 7.51 (br d, 1H, **H**3'), 7.29 (br s, 8H, *o*-C**H** of BPh_4), 7.17 (br d, 1H, **H**B), 7.06 (d, $^{3}J_{H\text{-}H}$ = 1.58 Hz, 1H, **H**C), 7.05 (br d, 1H, **H**3), 7.03 (t, $^{3}J_{H\text{-}H}$ = 7.56 Hz, 8H, *m*-C**H** of BPh_4), 6.86 (t, $^{3}J_{H\text{-}H}$ = 7.13 Hz, 4H, *p*-C**H** of BPh_4), 6.70 (br d, 1H, **H**6), 6.66 (br t, $^{3}J_{H\text{-}H}$ = 2.36 Hz, 1H, **H**4*), 6.33 (br d, 1H, **H**5'), 6.10 (br t, 1H, **H**4'), 4.07 (s, 3H, **H**A), 1.77 (s, 3H, **H**14), 1.69 (s, 3H, **H**14), 1.30 (s, 9H, **H**18), 1.29 (s, 9H, **H**16) ppm.

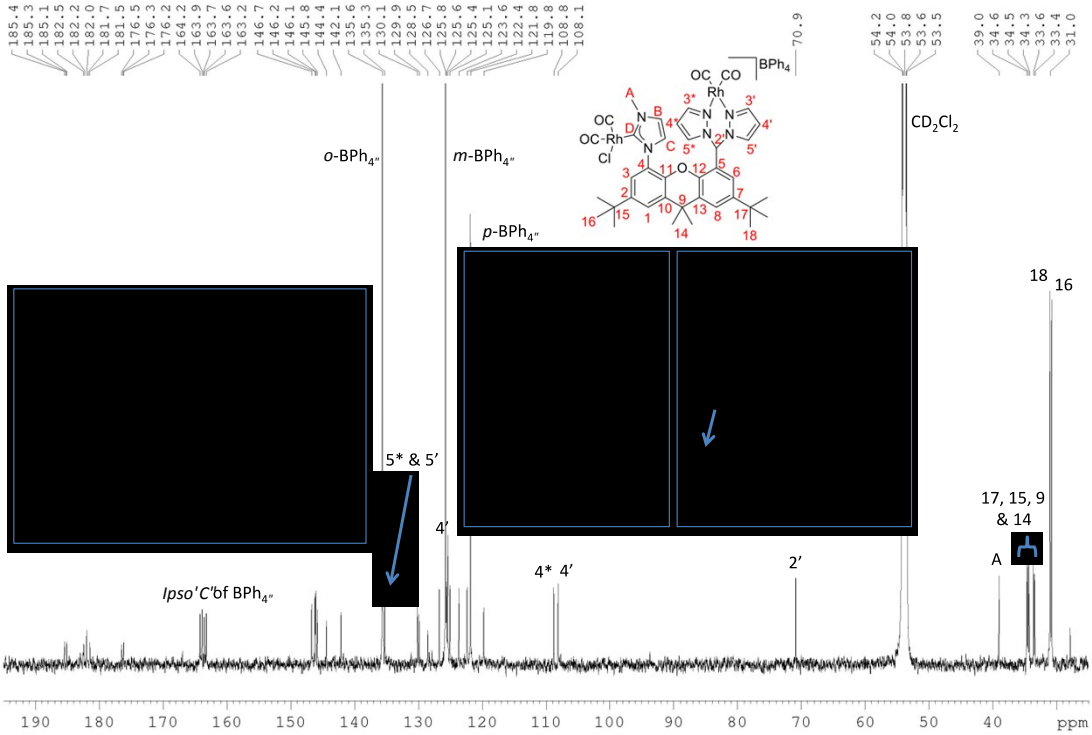
$^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2, 238 K): δ 185.26 (d, $^{1}J_{RhNHC\text{-}CO}$ = 53.43 Hz, **C**O), 182.23 (d, $^{1}J_{RhBpm\text{-}CO}$ = 72.13 & 69.8 Hz 2x **C**O), 181.71(d, $^{1}J_{RhNHC\text{-}CO}$ = 75.69 Hz, **C**O), 176.33 (d, $^{1}J_{Rh\text{-}C}$ = 44.86 Hz, **C**D), 163.72 (d, $^{1}J_{B\text{-}C}$ = 49.85 Hz, *ipso*-**C** of BPh_4), 146.74 (**C**2), 146.19 (**C**3*), 146.08 (**C**3'), 145.85 (**C**7), 144.42 (**C**12), 142.11 (**C**11), 135.64 (*o*-**C** of BPh_4), 135.61 (**C**5*), 135.27 (**C**5'), 130.14 (**C**10), 129.90 (**C**13), 128.54 (**C**4), 126.73 (**C**8), 125.76 (*m*-**C** of BPh_4), 125.60 (**C**3), 125.39 (**C**1), 125.05 (**C**C), 123.65 (**C**B), 122.37 (**C**6), 121.84 (*p*-**C** of BPh_4), 119.76 (**C**5), 108.79 (**C**4*),

108.10 (**C**4'), 70.86 (**C**2'), 39.01 (**C**A), 34.64 (**C**17), 34.46 (**C**15), 34.28 (**C**9), 33.61 (**C**14), 33.42 (**C**14), 31.02 (**C**18), 30.76 (**C**16) ppm.

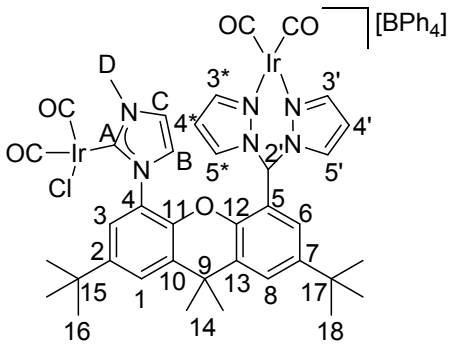
^{1}H NMR (600 MHz, CD_2Cl_2, 238K) spectrum of (**12**)



^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, 238K) spectrum of (**12**)



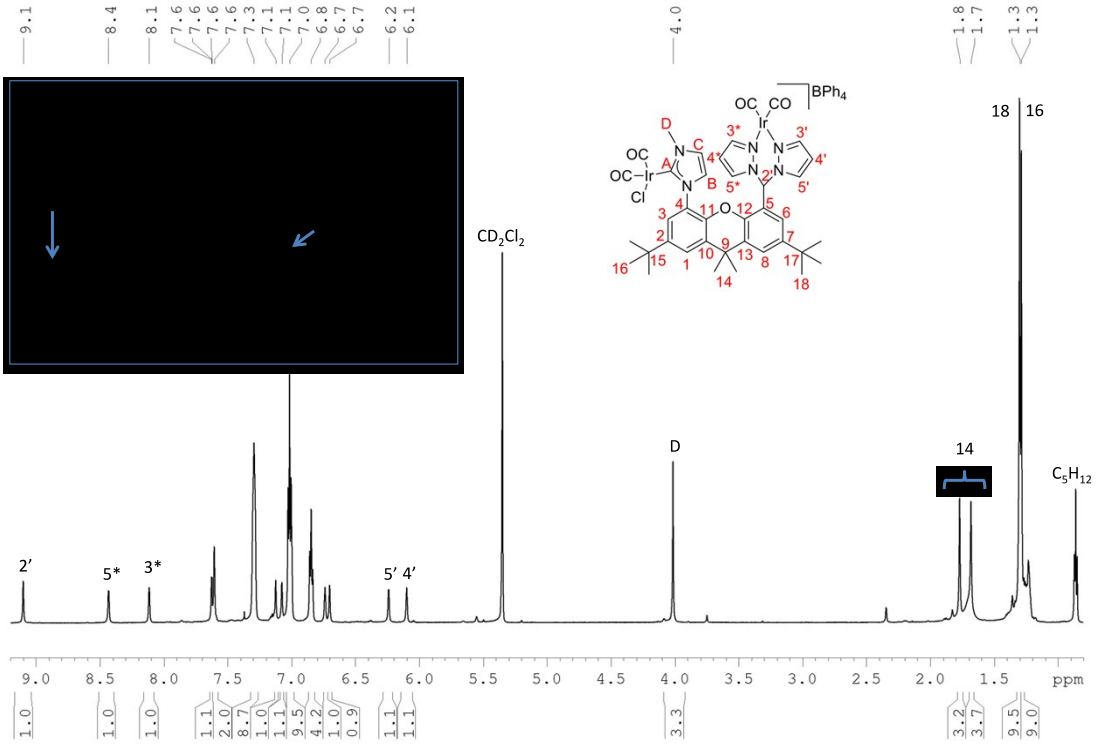
1.10 NMR Data for 13



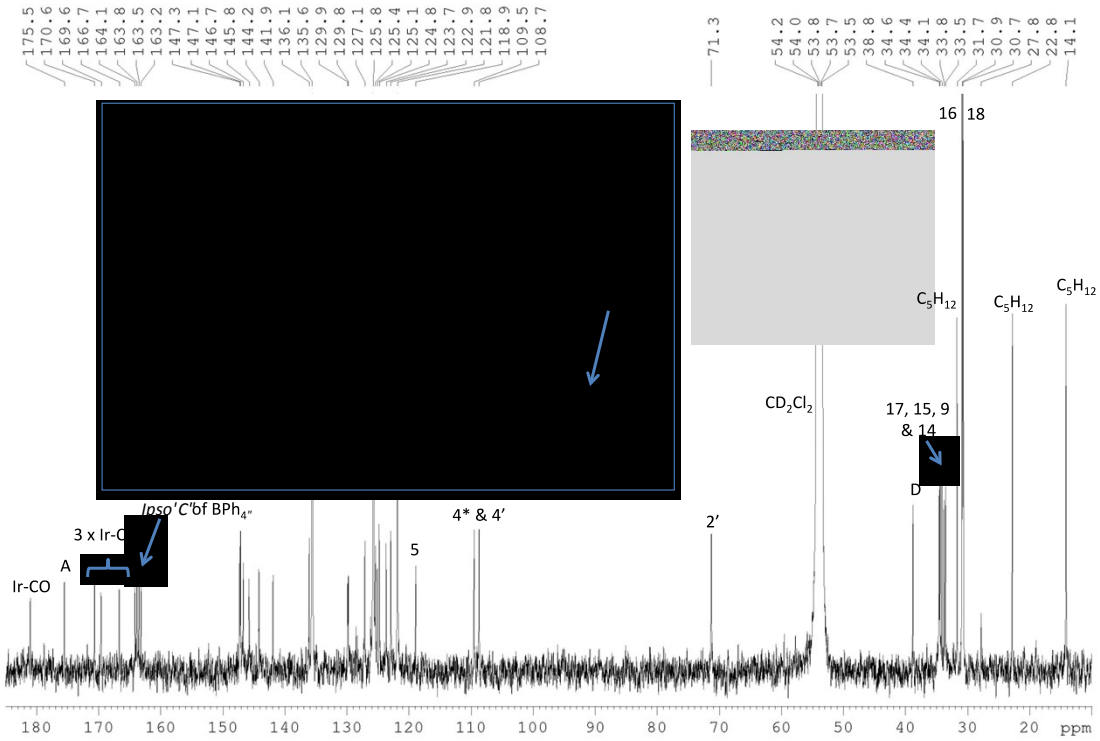
^{1}H NMR (600 MHz, CD_2Cl_2, 233 K) δ 9.10 (s, 1H, **H**2'), 8.43 (d, $^{3}J_{H\text{-}H}$ = 2.9 Hz, 1H, **H**5*), 8.11 (d, $^{3}J_{H\text{-}H}$ = 2.5 Hz, 1H, **H**3*), 7.63 (d, $^{4}J_{H\text{-}H}$ = 1.52 Hz, 1H, **H**3), 7.61 (br s, 2H, **H**3' & **H**6), 7.30 (br t, J = 5.8 Hz, 8H, *o*-C**H** of BPh_4), 7.12 (br d, 1H, **H**C), 7.08 (br d, 1H, **H**1), 7.02 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 9H, *m*-C**H** of BPh_4 & **H**B), 6.85 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 4H, *p*-C**H** of BPh_4), 6.74 (br t, $^{4}J_{H\text{-}H}$ = 2.8 Hz, 1H, **H**4*), 6.70 (br d, 1H, **H**8), 6.24 (br d, $^{3}J_{H\text{-}H}$ = 2.7 Hz, 1H, **H**5'), 6.10 (ap t, 1H, **H**4'), 4.01 (s, 3H, **H**D), 1.77 (s, 3H, **H**14), 1.68 (s, 3H, **H**14), 1.30 (s, 9H, **H**18), 1.29 (s, 9H, **H**16) ppm.

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 233 K): δ 181.02 (Ir_{NHC}-**C**O), 175.53 (**C**A), 170.65 (Ir_{Bpm}-**C**O), 169.60 (Ir_{Bpm}-**C**O), 166.69 (Ir_{NHC}-**C**O), 164.14-163.17 (q, $^{1}J_{B\text{-}C}$ = 48.86 Hz, *ipso*-**C** of BPh_4), 147.27 (**C**3'), 147.13 (**C**3*), 146.70 (**C**7), 145.76 (**C**2), 144.17 (**C**12), 141.91 (**C**11), 136.08 (**C**5*), 135.59 (*o*-**C** of BPh_4 & **C**5'), 129.88 (**C**10), 129.76 (**C**13), 127.12 (**C**6), 125.75 (*m*-**C** of BPh_4 & **C**3), 125.42 (**C**1), 125.11 (**C**4), 124.80 (**C**B), 123.68 (**C**C), 122.92 (**C**8), 121.83 (*p*-**C** of BPh_4), 118.91 (**C**5), 109.51 (**C**4*), 108.70 (**C**4'), 71.28 (**C**2'), 38.78 (**C**D), 34.59 (**C**17), 34.42 (**C**15), 34.14 (**C**9), 33.79 (**C**14), 33.54 (**C**14), 30.88 (**C**16), 30.70 (**C**18) ppm.

^{1}H NMR (600 MHz, CD_2Cl_2, 233K) spectrum of (**13**)



$^{13}C\{^{1}H\}$ NMR (150.9 MHz, CD_2Cl_2, 233K) spectrum of (**13**)



2. Crystallographic Experimental Data Tables

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Chemical formula	$C_{51.25}H_{67}Cl_2N_6O_2Rh_2$
M (g mol^{-1})	1075.82
Crystal System	Monoclinic
Space Group	C2/c
Crystal Habit	Plates
Temperature (K)	100
a (Å)	15.018 (3)
b (Å)	25.511 (5)
c (Å)	27.991 (6)
α (°)	90
β (°)	93.13 (3)
γ (°)	90
V (Å^3)	10708 (4)
Z	8
Radiation type	Synchrotron, λ = 0.71073 Å
μ (mm^{-1})	0.76
Crystal size (mm)	0.02 × 0.02 × 0.01
Refl. measured	68600
Unique reflections	9437
Obsd. Reflections	7457
[I > 2σ(I)]	
Rint	0.06
R[F^2> 2σ(F^2)]	0.055
wR(F^2)	0.166
S	1.06
Reflections used	9437
Parameters	7457
Restraints	H-atom parameters constrained
Δρmax, Δρmin (e Å^{-3})	1.40, -1.21

3. References

[1] a) H. V. Secor and J. I. Seeman, *Heterocycles* **1986**, *24*, 1687-1698; b) C. Quinet, P. Jourdain, C. Hermans, A. Ates, I. Lucas and I. E. Marko, *Tetrahedron* **2007**, *64*, 1077-1087.