Electronic Supplementary Material (ESI) for Dalton Transactions.

Highly Versatile Heteroditopic Ligand Scaffolds for Accommodating Group 8, 9 & 11 Heterobimetallic Complexes

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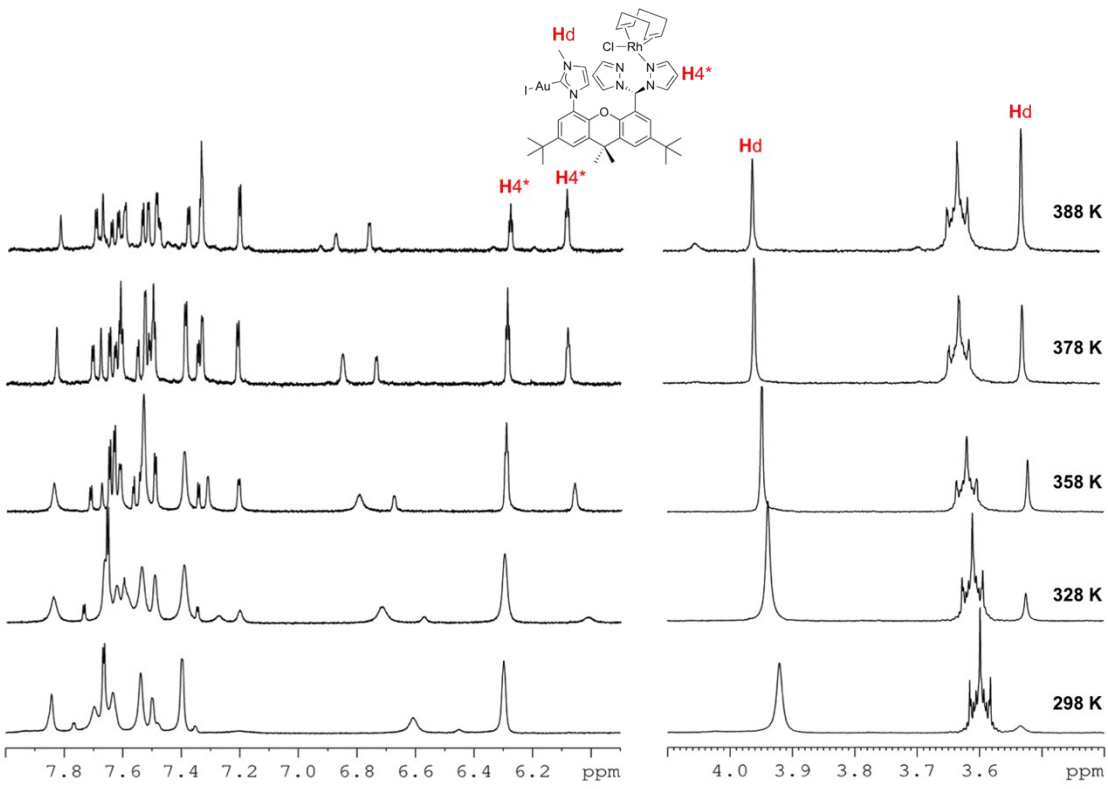
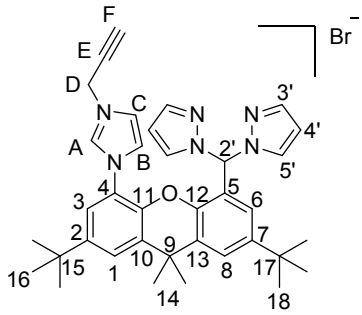
1. Variable Temperature NMR

^{1}H NMR (600 MHz, $(CD_3)_2SO$) VT spectra of (16)



2. NMR Characterisation Data

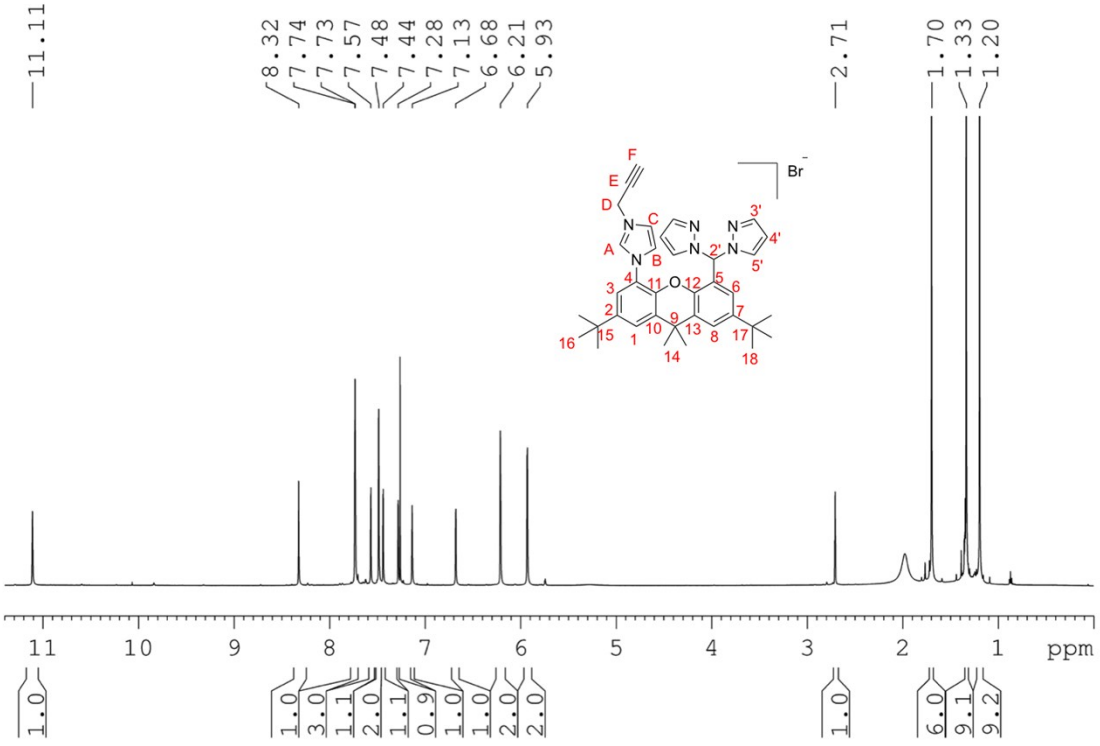
2.1 NMR Data for 2



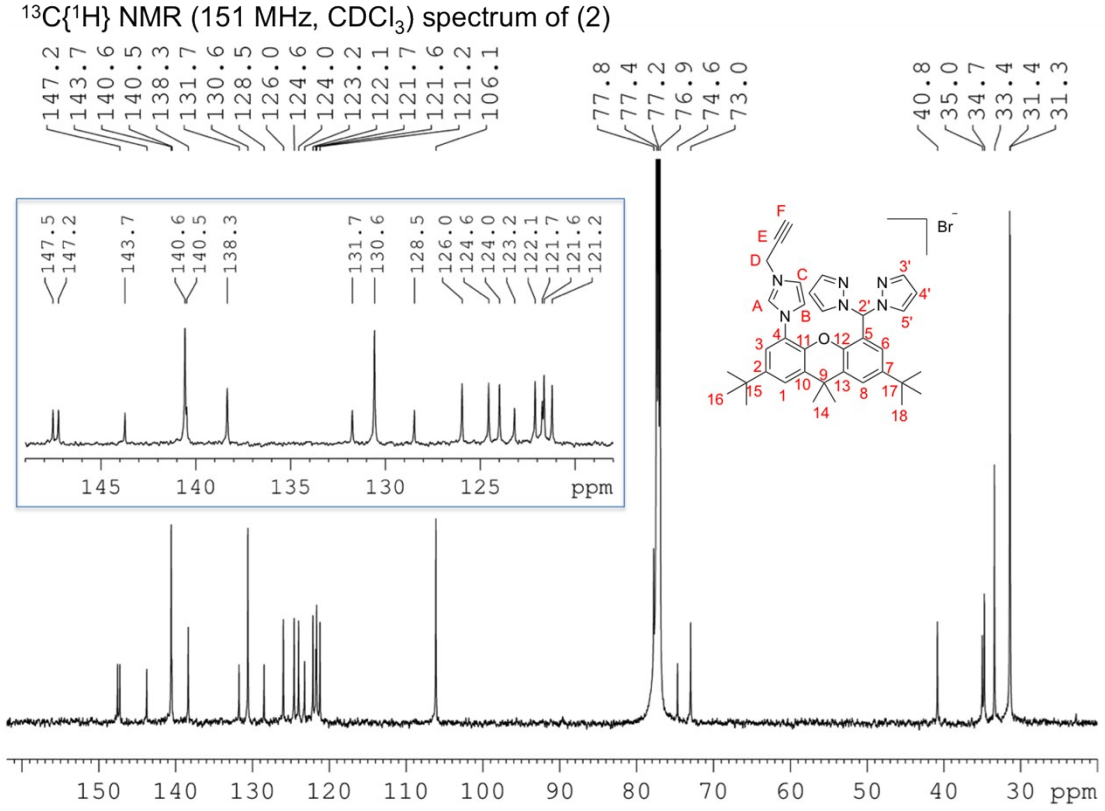
^{1}H NMR (600 MHz, $CDCl_3$): δ 11.11 (br s, 1H, **H**A), 8.32 (s, 1H, **H**2'), 7.74 (br s, 2H, **H**5'), 7.73 (br s, 1H, **H**C), 7.57 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**1), 7.48 (br d, 2H, **H**3'), 7.44 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**6), 7.28 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**3), 7.13 (br s, 1H, **H**B), 6.68 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**8), 6.21 (br t, 2H, **H**4'), 5.93 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**D), 2.71 (t, $^{4}J_{H\text{-}H}$ = 2.3, 1H, **H**F), 1.70 (s, 6H, **H**14), 1.33 (s, 9H, **H**16), 1.20 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 147.5 (**C**2), 147.2 (**C**7), 143.7 (**C**12), 140.6 (**C**3'), 140.5 (**C**11), 138.3 (**C**A), 131.7 (**C**10), 130.6 (**C**5'), 128.5 (**C**13), 126.0 (**C**1), 124.6 (**C**6), 124.0 (**C**8), 123.2 (**C**5), 122.1 (**C**B), 121.7 (**C**4), 121.6 (**C**C), 121.2 (**C**3), 106.1 (**C**4'), 77.8 (**C**E), 74.6 (**C**F), 73.0 (**C**2'), 40.8 (**C**D), 35.0 (**C**15), 34.7 (**C**9 * **C**17), 33.4 (**C**14), 31.4 (**C**16), 31.3 (**C**18) ppm.

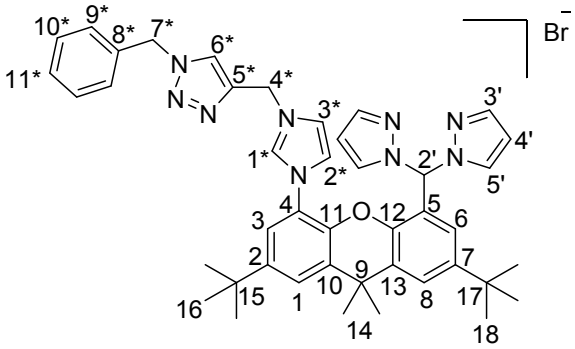
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (2)



$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of (2)



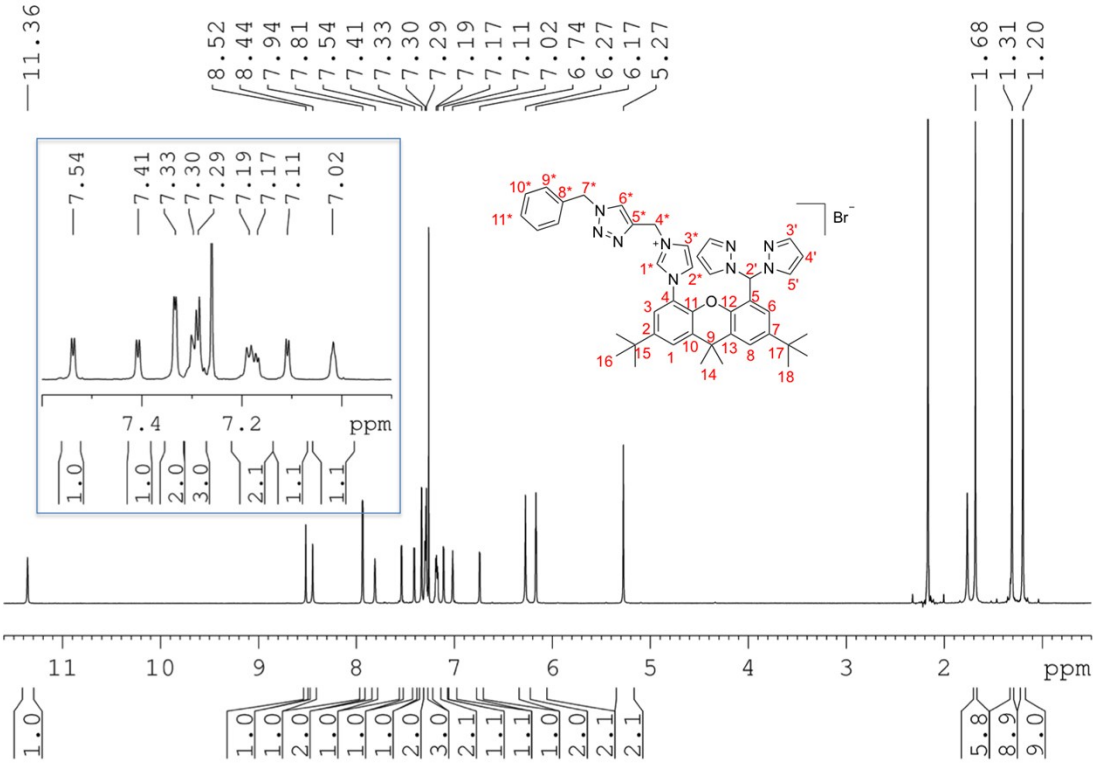
2.2 NMR Data for 3



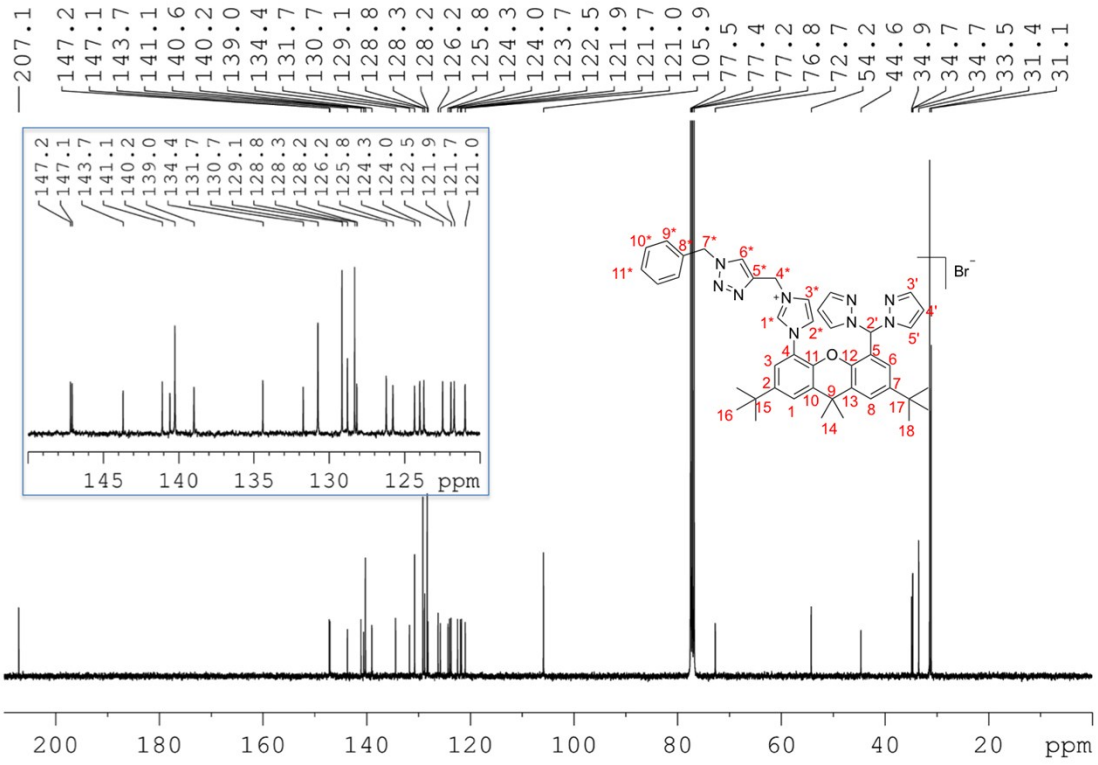
^{1}H NMR (400 MHz, $CDCl_3$): δ 11.36 (br s, 1H, **H**1*), 8.52 (s, 1H, **H**2'), 8.44 (s, 1H, **H**6*), 7.94 (d, $^{3}J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**5'), 7.81 (br d, 1H, **H**3*), 7.54 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**1), 7.41 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**8), 7.33 (d, $^{3}J_{H\text{-}H}$ = 1.5 Hz, 2H, **H**3'), 7.29 (m, 3H, **H**10* and **H**11*), 7.19 (m, 2H, **H**9*), 7.11 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**3), 7.02 (br d, 1H, **H**2*), 6.74 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**6), 6.27 (br s, 2H, **H**4*), 6.17 (t, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 2H, **H**4'), 5.27 (br s, 2H, **H**7*), 1.68 (br s, 6H, **H**14), 1.31 (br s, 9H, **H**16), 1.20 (br s, 9H, **H**18) ppm.

$^{13}C\{^{1}H\}$ NMR (101MHz, $CDCl_3$): δ 147.2 (**C**2), 147.1 (**C**7), 143.7 (**C**12), 141.1 (**C**5*), 140.6 (**C**11), 140.2 (**C**3'), 139.0 (**C**1*), 134.4 (**C**8*), 131.7 (**C**10), 130.7 (**C**5'), 129.1 (**C**10*), 128.8 (**C**11*), 128.3 (**C**9*), 128.2 (**C**13), 126.2 (**C**6*), 125.8 (**C**1), 124.3 (**C**8), 124.0 (**C**6), 123.7 (**C**5), 122.5 (**C**3*), 121.9 (**C**4), 121.7 (**C**2*), 121.0 (**C**3), 105.9 (**C**4'), 72.7 (**C**2'), 54.2 (**C**7*), 44.6 (**C**4*), 34.9 (**C**15), 34.7 (**C**17 & **C**9), 33.5 (**C**14), 31.4 (**C**16 & **C**18) ppm.

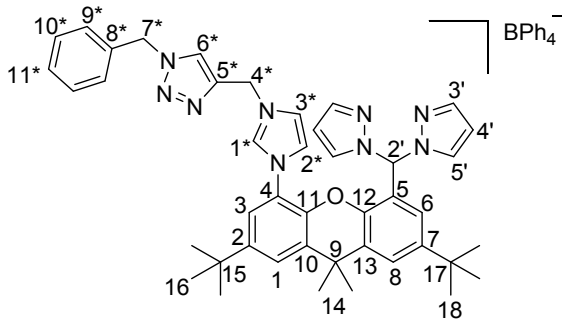
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (3)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (3)



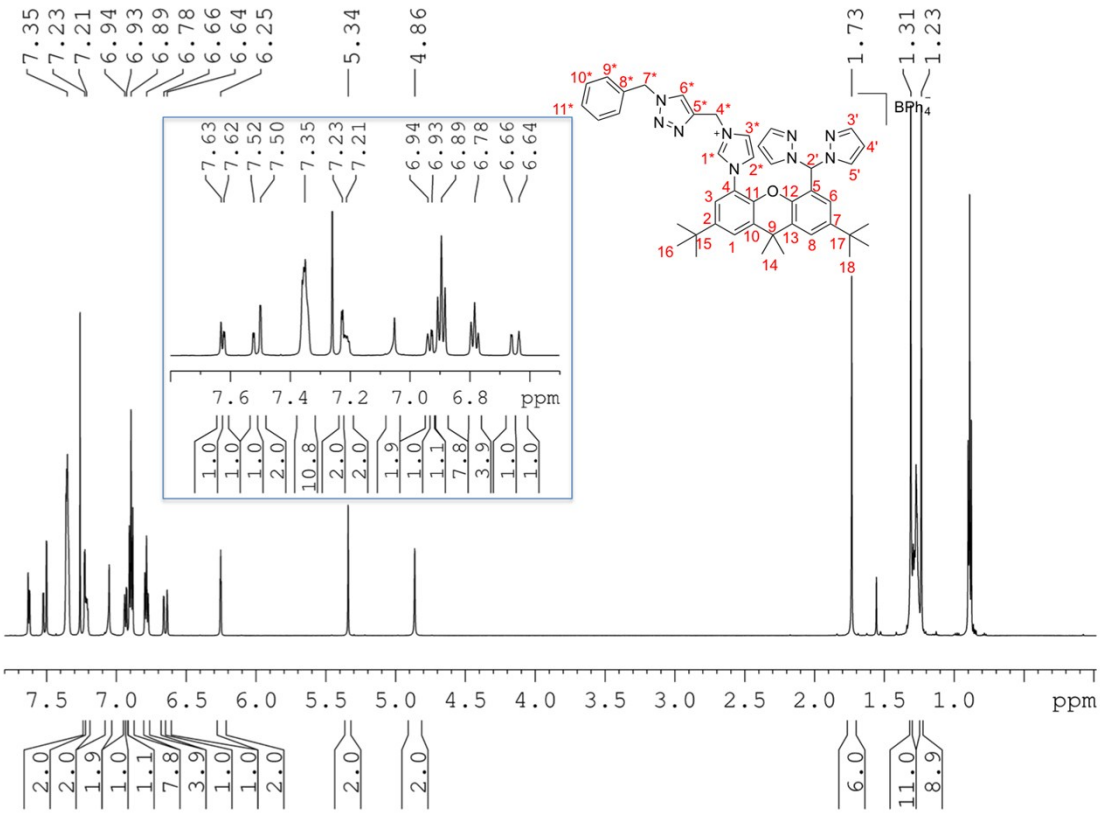
2.3 NMR Data for 4



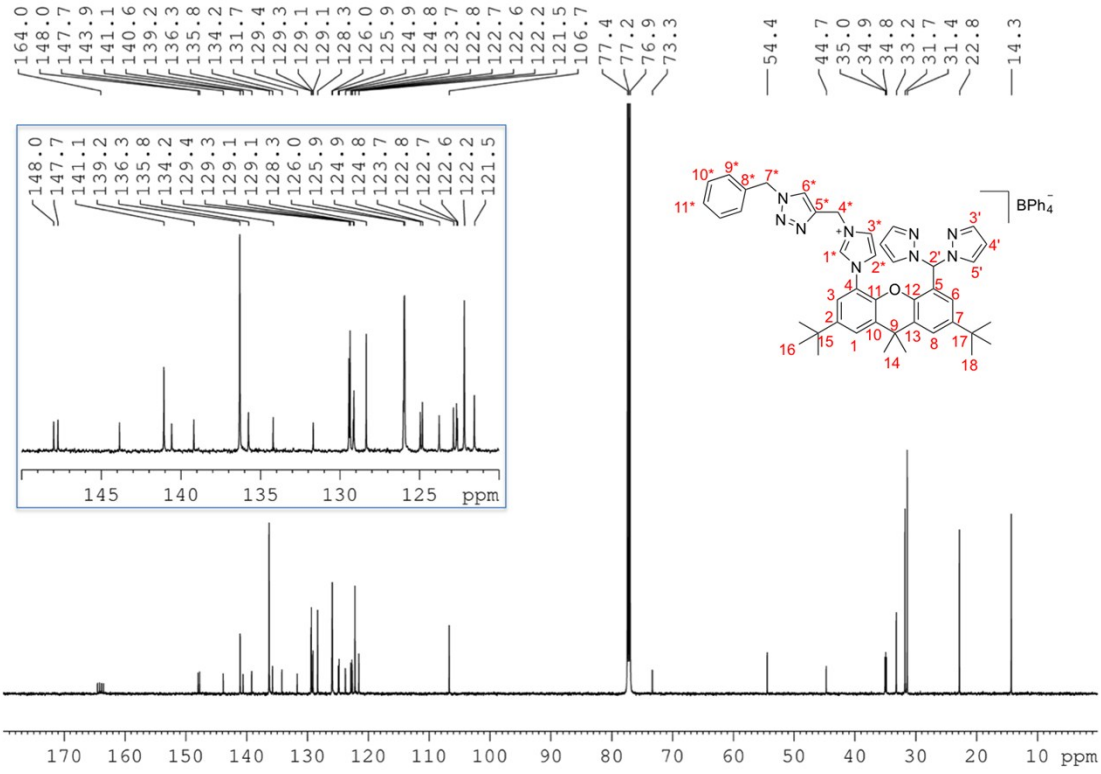
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.63 (br s, 1H, **H**2'), 7.62 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**1), 7.52 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**8), 7.50 (d, $^{3}J_{H\text{-}H}$ = 1.4 Hz, 2H, **H**3'), 7.36-7.33 (m, 11H, o-C**H** of BPh_4, **H**10* & **H**11*), 7.23 (d, $^{3}J_{H\text{-}H}$ = 2.3 Hz, 2H, **H**5'), 7.21 (m, 2H, **H**9*), 7.05 (br s, 2H, **H**1* & **H**6*), 6.94 (br t, 1H, **H**3*), 6.93 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**3), 6.89 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 8H, *m*-C**H** of BPh_4), 6.78 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of BPh_4), 6.66 (d, $^{4}J_{H\text{-}H}$ = 1.9 Hz, 1H, **H**6), 6.64 (br t, 1H, **H**2*), 6.25 (t, $^{3}J_{H\text{-}H}$ = 1.9 Hz, 2H, **H**4'), 5.34 (s, 2H, **H**7*), 4.86 (s, 2H, **H**4*), 1.73 (s, 6H, **H**14), 1.31 (s, 9H, **H**16), 1.23 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 164.0 (q, $^{1}J_{B\text{-}C}$ = 48.9 Hz, *ipso*-**C** of BPh_4), 148.0 (**C**2), 147.7 (**C**7), 143.9 (**C**12), 141.1 (**C**3'), 140.6 (**C**11), 139.2 (**C**5*), 136.3 (*o*-**C** of BPh_4), 135.8 (**C**4 & **C**6*), 134.2 (**C**8*), 131.7 (**C**10), 129.4 (**C**5'), 129.3 (**C**10*), 129.1 (**C**13 & **C**11*), 128.3 (**C**9*), 126.0 (**C**1), 125.9 (*m*-**C** of BPh4), 124.9 (**C**8), 124.8 (**C**1*), 123.7 (**C**6), 122.8 (**C**3*), 122.7 (**C**2*), 122.6 (**C**5), 122.2 (*p*-**C** of BPh_4), 121.5 (**C**3), 106.7 (**C**4'), 73.3 (**C**2'), 54.4 (**C**7*), 44.7 (**C**4*), 35.0 (**C**15), 34.9 (**C**9), 34.8 (**C**17), 33.2 (**C**14), 31.4 (**C**16 & **C**18) ppm.

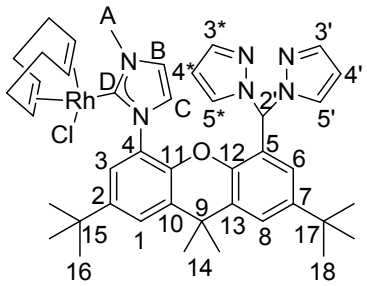
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (4)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of (4)



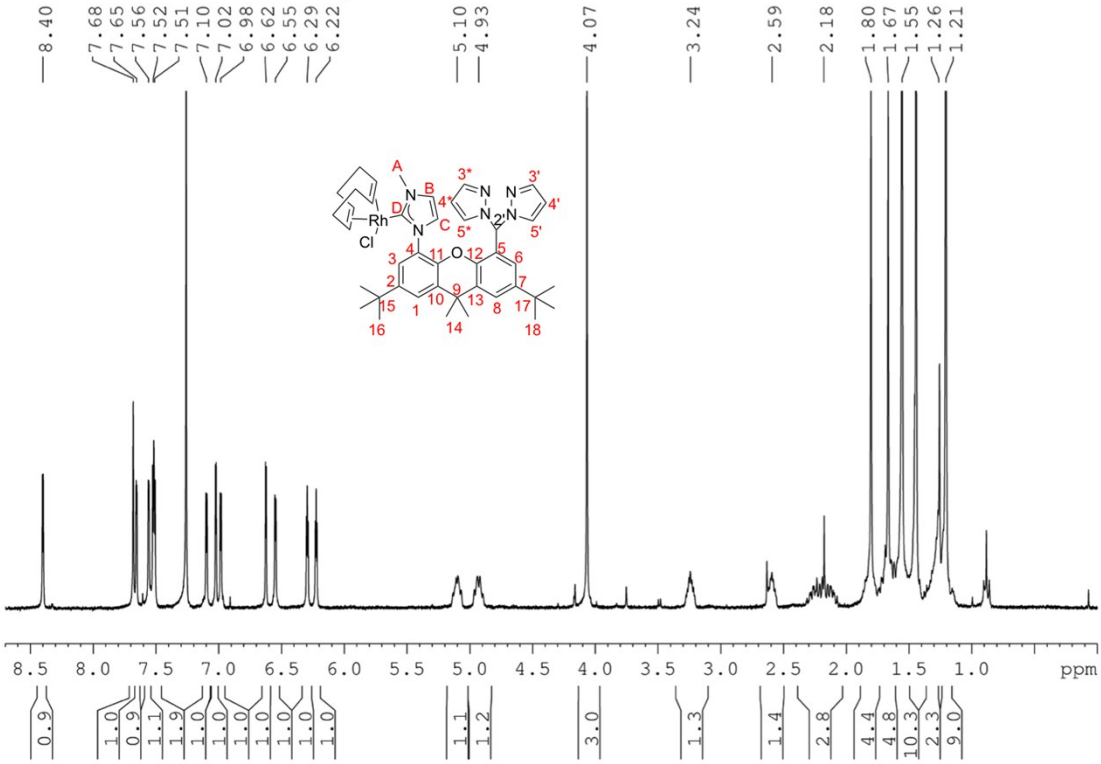
2.4 NMR Data for 7



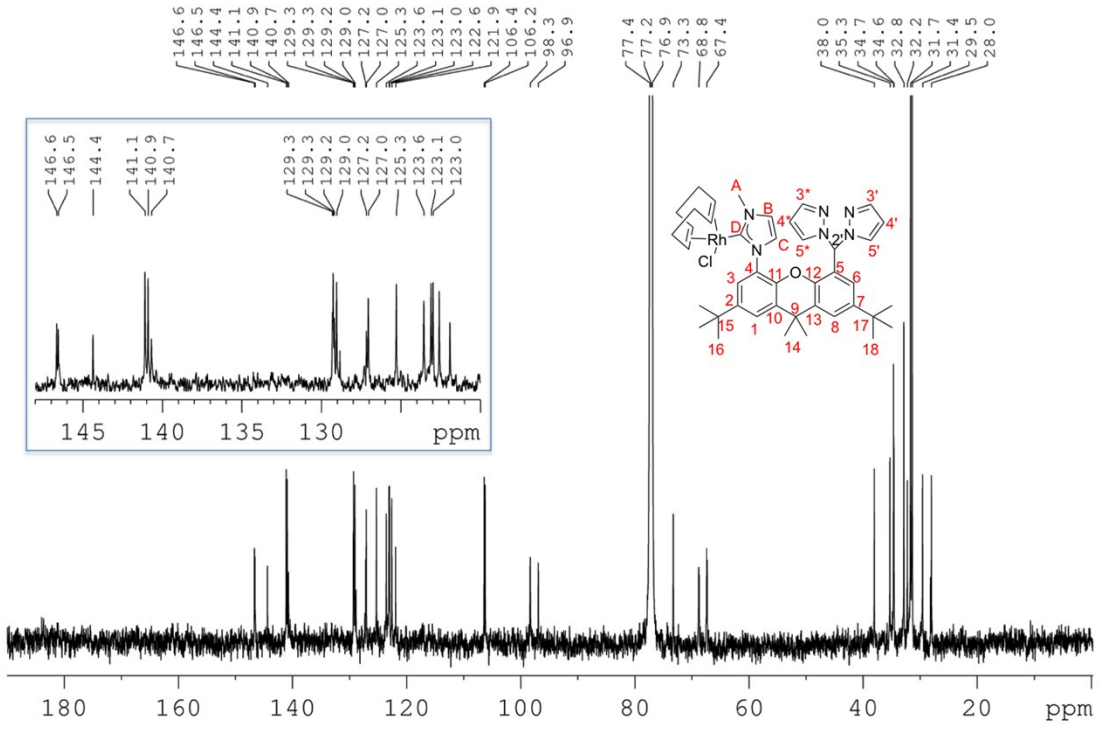
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, **H**1), 7.68 (br s, 1H, **H**2'), 7.65 (dd, $^{3}J_{H\text{-}H}$ = 1.8 Hz, $^{4}J_{H\text{-}H}$ = 0.5 Hz, 1H, **H**5*), 7.56 (br d, 2H, **H**5' & **H**3), 7.52 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, **H**8), 7.10 (d, $^{3}J_{H\text{-}H}$ = 2.4 Hz, 1H, **H**3*), 7.02 (br d, 1H, **H**3'), 6.98 (br d, 1H, **H**B), 6.62 (d, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**C), 6.55 (d $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**6), 6.29 (dd, $^{3}J_{H\text{-}H}$ = 1.9 Hz, 1H, **H**4*), 6.22 (dd, $^{3}J_{H\text{-}H}$ = 1.9 Hz, 1H, **H**4'), 5.10 (m, 1H, C**H** of COD), 4.93 (m, 1H, C**H** of COD), 4.07 (s, 3H, **H**A), 3.24 (m, 1H, C**H** of COD), 2.59 (m, 1H, C**H** of COD), 2.30-2.05 (m, 3H, C$\mathbf{H_2}$ of COD), 1.80 (s, 3H, **H**14 & m, 1H for C$\mathbf{H_2}$ of COD), 1.67 (s, 3H, **H**14 & m, 1H for C$\mathbf{H_2}$ of COD), 1.55 (s, 3H, **H**14), 1,62 (m, 1H, C$\mathbf{H_2}$ of COD), 1.55 (s, 9H, **H**18), ,1.26 (m, 2H, C$\mathbf{H_2}$ of COD), 1.21 (s, 9H, **H**16) ppm.

^{13}C NMR (150.9 MHz, $CDCl_3$): δ 183.8 (d, **C**D, assigned indirectly by ^{1}H-^{13}C HMBC), 146.6 (**C**7), 146.5 (**C**2), 144.4 (**C**12), 141.1 (**C**3*), 140.9 (**C**3'), 140.7 (**C**11), 129.3 (**C**10), 129.3 (**C**5*), 129.2 (**C**13), 129.0 (**C**5'), 127.2 (**C**4), 127.0 (**C**1), 125.3 (**C**8), 123.6 (**C**6), 123.1 (**C**3), 123.0 (**C**C), 122.6 (**C**B), 121.9 (**C**5), 106.4 (**C**4*), 106.2 (**C**4'), 98.3 (**C**H of COD), 96.9 (**C**H of COD), 73.3 (**C**2'), 68.8 (**C**H of COD), 67.4 (**C**H of COD), 38.0 (**C**A), 35.3 (**C**15), 34.7 (**C**17), 34.6 (**C**14), 32.8 (**C**9 & 2 x **C**H_2 of COD), 32.2 (2 x **C**H_2 of COD), 31.7 (**C**18), 31.4 (**C**16), 29.6 (2 x **C**H_2 of COD), 28.0 (2 x **C**H_2 of COD) ppm.

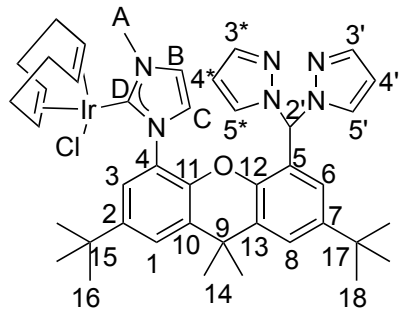
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (7)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of (7)



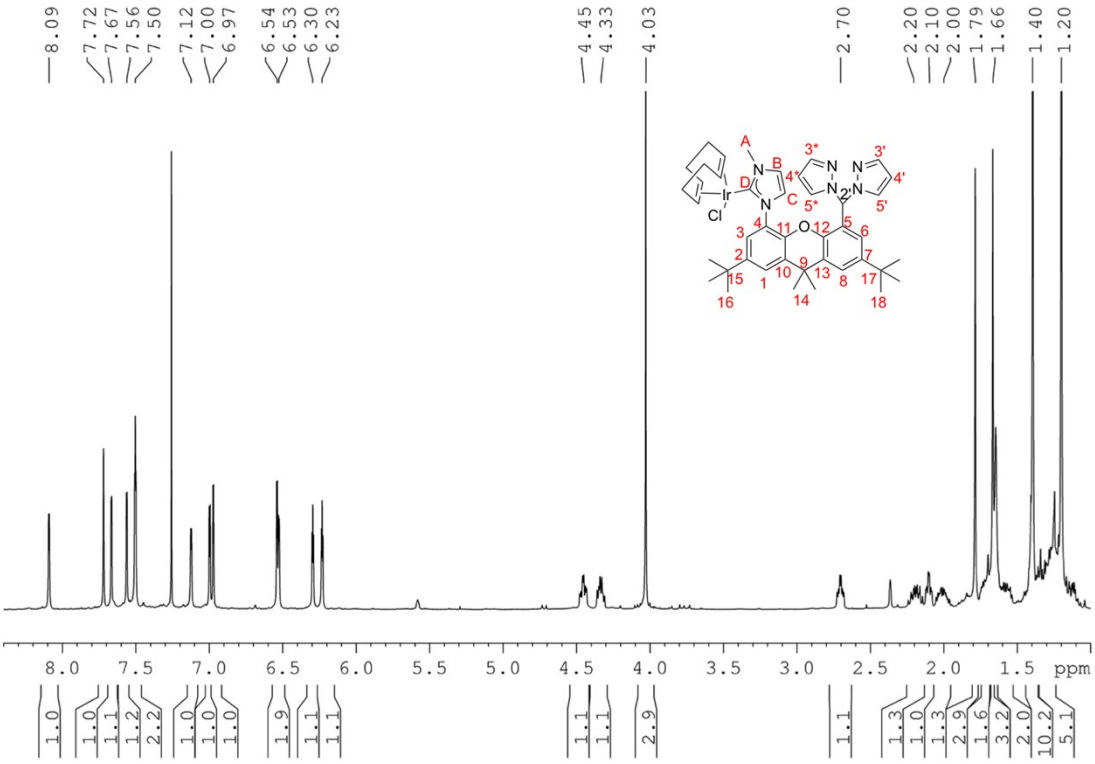
2.5 NMR Data for 8



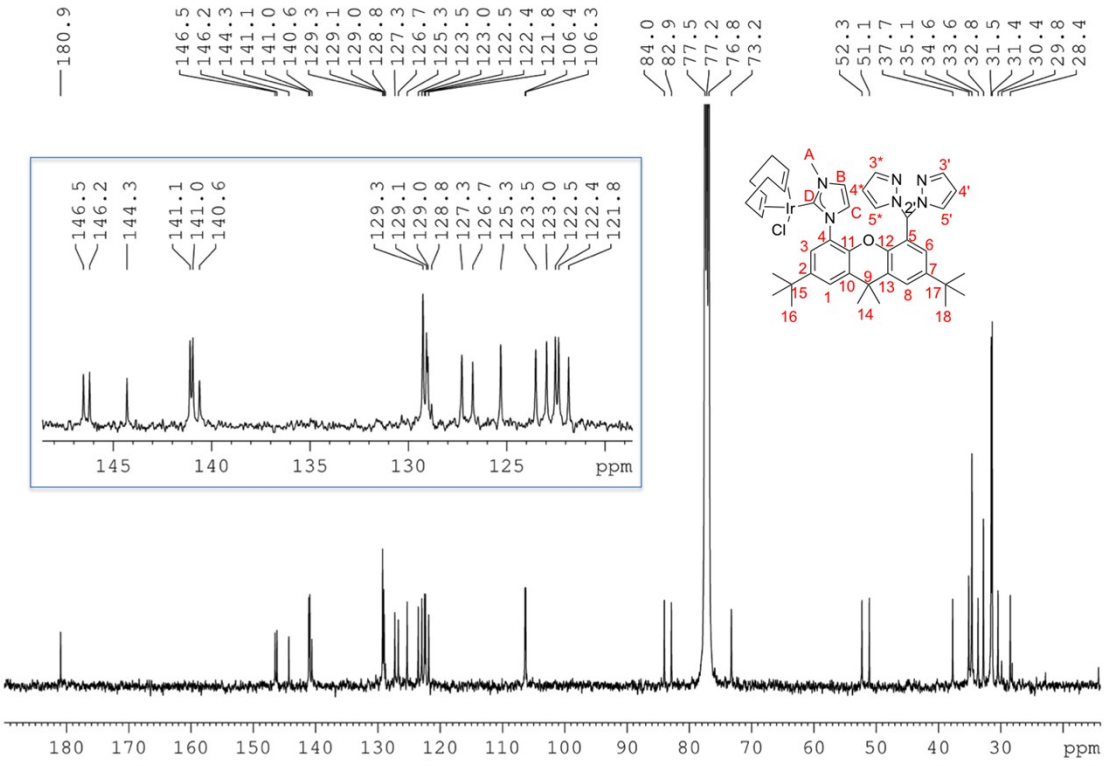
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, **H**3), 7.72 (s, 1H, **H**2'), 7.67 (d, $^{3}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**3*), 7.56 (d, $^{3}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**3'), 7.50 (ap t, 2H, **H**1 & **H**8), 7.12 (d, $^{3}J_{H\text{-}H}$ = 2.4 Hz, 1H, **H**5*), 7.00 (d, $^{3}J_{H\text{-}H}$ = 2.4 Hz, 1H, **H**5'), 6.97 (d, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**B), 6.54 (d, $^{3}J_{H\text{-}H}$ = 1.96 Hz, 1H, **H**C), 6.53 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**6), 6.30 (ap t, $^{3}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**4*), 6.23 (ap t, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**4'), 4.45 (td, $^{2}J_{H\text{-}H}$ = 7.7, $^{3}J_{H\text{-}H}$ = 3.2 Hz, 1H, C**H** of COD), 4.33 (td, $^{2}J_{H\text{-}H}$ 7.8, $^{3}J_{H\text{-}H}$ = 4.2 Hz, 1H, C**H** of COD), 4.03 (s, 3H, **H**A), 2.70 (td, $^{2}J_{H\text{-}H}$ = 7.4, $^{3}J_{H\text{-}H}$ = 3.5 Hz, 1H, C**H** of COD), 2.27 – 2.14 (m, 1H, C**H$_2$** of COD), 2.10 (td, $^{2}J_{H\text{-}H}$ = 7.1, $^{3}J_{H\text{-}H}$ = 2.4 Hz, 1H, C**H** of COD), 2.07 – 1.95 (m, 1H, C**H$_2$** of COD) 1.79 (s, 3H, **H**14), 1.75 – 1.69 (m, 1H, C**H$_2$** of COD), 1.66 (s, 3H, **H**14), 1.62 – 1.53 (m, 1H, C**H$_2$** of COD), 1.40 (s, 9H, **H**16), 1.35 – 1.22 (m, 2H, C**H$_2$** of COD), 1.20 (s, 9H, **H**18), 1.20 – 1.05 (m, 2H, C**H$_2$** of COD)ppm.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 180.9 (**C**D), 146.5 (**C**7), 146.2 (**C**2), 144.3 (**C**5), 141.1 (**C**3*), 141.0 (**C**3'), 140.6 (**C**4), 129.3 (**C**5* & **C**5'), 129.1 & 129.0 (**C**10 & **C**13), 127.3 (**C**3), 126.7 (**C**11), 125.3 (**C**8), 123.5 (**C**6), 123.0 (**C**1), 122.5 (**C**C), 122.4 (**C**B), 121.8 (**C**12), 106.4 (**C**4*), 106.3 (**C**4'), 84.0 (**C**H of COD), 82.9 (**C**H of COD), 73.2 (**C**2'), 52.3 (**C**H of COD), 51.1 (**C**H of COD), 37.7 (**C**A), 35.1 (**C**15), 34.6 (**C**9, **C**14 & **C**17), 33.6 (**C**H$_2$ of COD), 32.8 (**C**14 & **C**H$_2$ of COD), 31.5 (**C**16), 31.4 (**C**18), 30.4 (**C**H$_2$ of COD), 28.4 (**C**H$_2$ of COD)ppm.

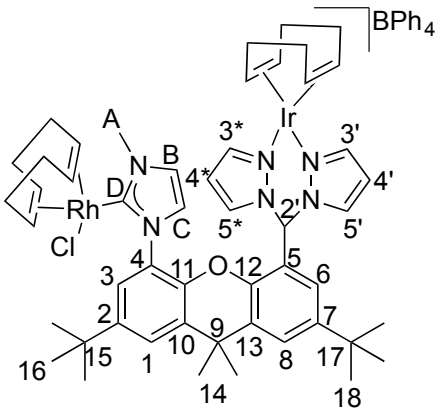
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of (8)



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of (8)



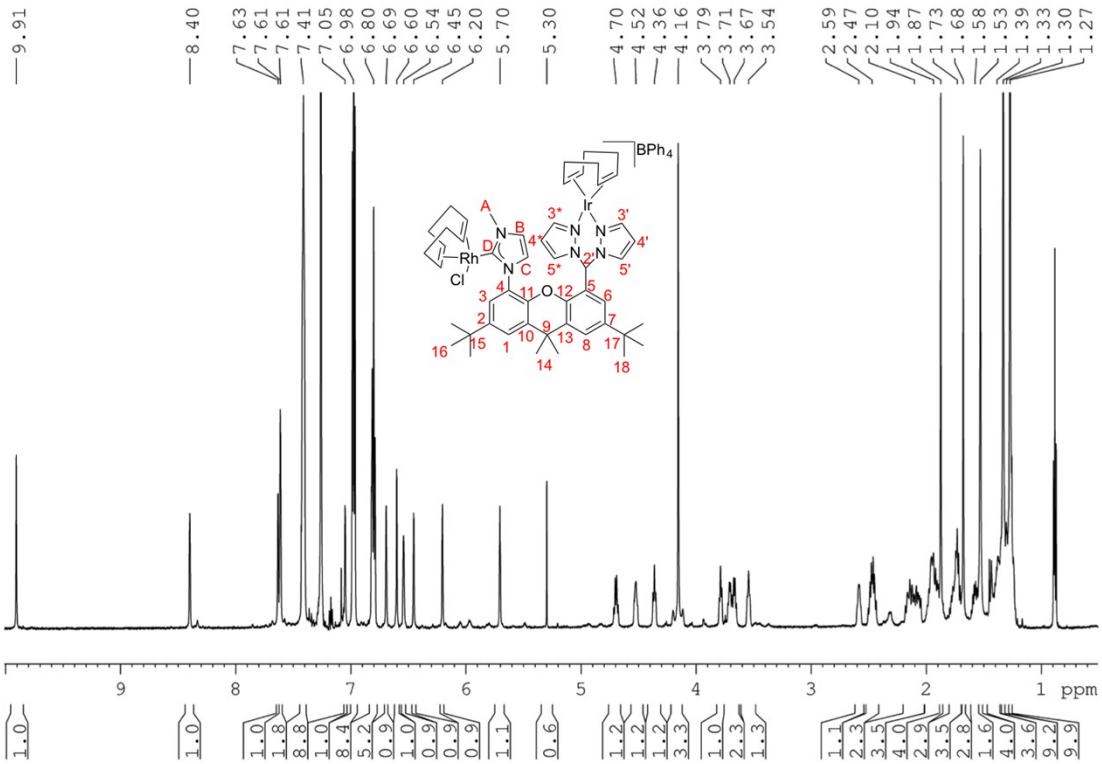
2.6 NMR Data for 9



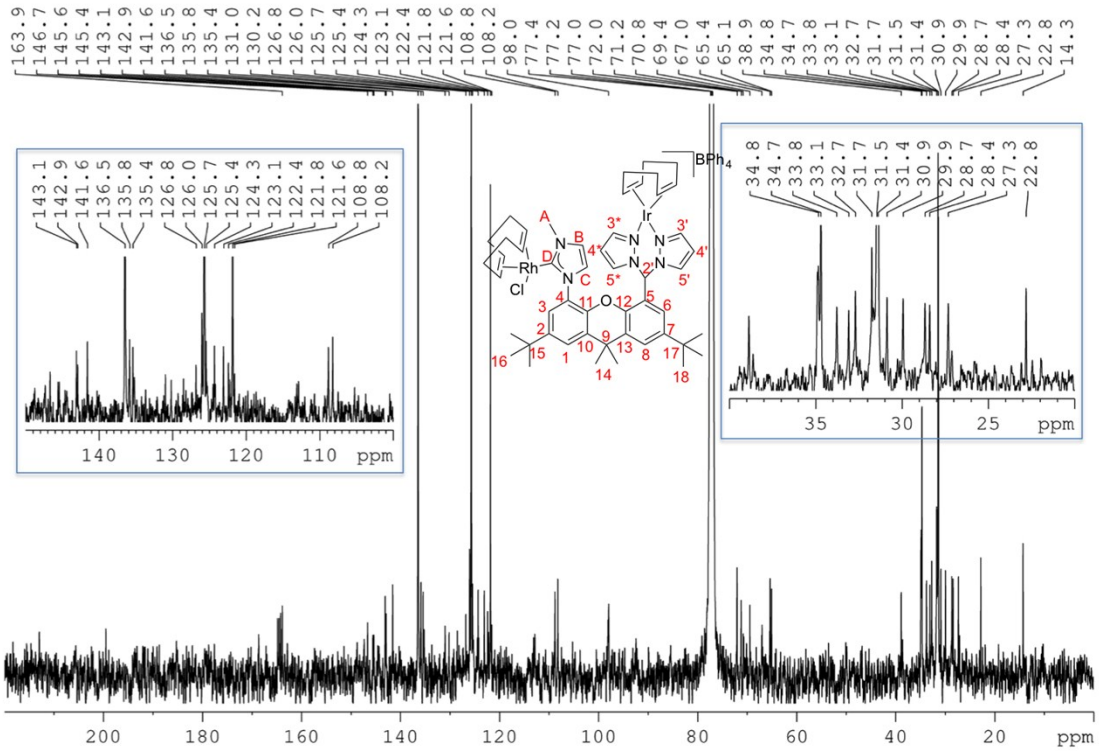
^{1}H NMR (600 MHz, $CDCl_3$): δ 9.91 (s, 1H, **H**2'), 8.40 (br d, 1H, **H**3*), 7.63 (d, $^{4}J_{H\text{-}H}$ = 1.9 Hz, 1H, **H**8), 7.61 (br d, 1H, **H**5*), 7.61 (br d, 1H, **H**1), 7.41 (br s, 8H, *o*-C**H** of BPh_4), 7.05 (br d, 1H, **H**5'), 6.98 (t, $^{3}J_{H\text{-}H}$ = 7.5 Hz, 8H, *m*-C**H** of BPh_4), 6.82 (br d, 1H, **H**3), 6.80 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 4H, *p*-C**H** of BPh_4), 6.69 (br d, 1H, **H**B), 6.60 (d, $^{3}J_{H\text{-}H}$ = 1.6 Hz, 1H, **H**C), 6.54 (br t, 1H, **H**4*), 6.45 (d, $^{3}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**3'), 6.20 (br d, 1H, **H**6), 5.70 (br t, 1H, **H**4'), 4.70 (q, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, C**H** of COD), 4.52 (br q, 1H, C**H** of COD), 4.36 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, C**H** of COD), 4.16 (s, 3H, **H**A), 3.79 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, C**H** of COD), 3.71 (q, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, C**H** of COD), 3.67 (q, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, C**H** of COD), 3.54 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 1H, C**H** of COD) 2.59 (br q, 1H, C**H** of COD), 2.47 (m, 2H, C$\mathbf{H_2}$ of COD), 2.10 (m, 3H, C$\mathbf{H_2}$ of COD), 1.94 (m, 4H, C$\mathbf{H_2}$ of COD), 1.87 (s, 3H, **H**14), 1.73 (m, 3H, C$\mathbf{H_2}$ of COD), 1.68 (s, 3H, **H**14), 1.58 (m, 1H, C$\mathbf{H_2}$ of COD), 1.39 (m, 3H, C$\mathbf{H_2}$ of COD), 1.33 (s, 9H, **H**16), 1.27 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 183.0 (**C**D, assigned indirectly by ^{1}H-^{13}C HMBC), 164.4 (q, $^{1}J_{C\text{-}B}$ = 49.1 Hz, *ipso*-**C** of BPh_4), 146.7 (**C**2), 145.4 (**C**7), 143.1 (**C**4), 142.9 (**C**5'), 141.6 (**C**5*), 136.5 (*o*-**C** of BPh_4), 135.8 (**C**3'), 135.4 (**C**3*), 131.0 (**C**13), 130.2 (**C**10), 128.5 (**C**11), 126.8 (**C**12), 126.0 (**C**3 & **C**8), 125.7 (*m*-**C** of BPh_4), 125.4 (**C**C), 124.3 (**C**1), 123.1 (**C**B), 122.4 (**C**6), 121.8 (*p*-**C** of BPh_4), 121.6 (**C**5), 108.8 (**C**4'), 108.2 (**C**4*), 98.0 (**C**H of COD), 72.0 (**C**2'), 71.2 (**C**H of COD), 70.8 (**C**H of COD), 69.4 (**C**H of COD), 67.0 (**C**H of COD), 65.4 (**C**H of COD), 65.1 (**C**H of COD), 38.9 (**C**A), 34.8 (**C**9), 34.7 (**C**15 & **C**17), 33.78 & 33.08 (**C**H_2 of COD), 32.7 (**C**14), 31.7 (**C**H_2 of COD), 31.5 (**C**18), 31.4 (**C**16), 30.9, 29.9, 28.7, 28.4 & 27.3 (**C**H_2 of COD) ppm.

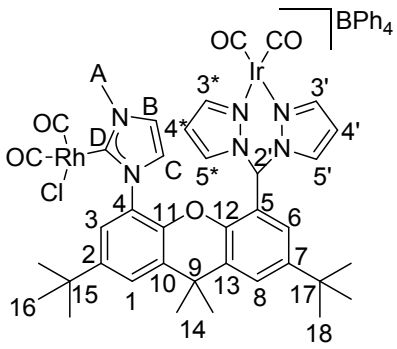
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (9)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of (9)



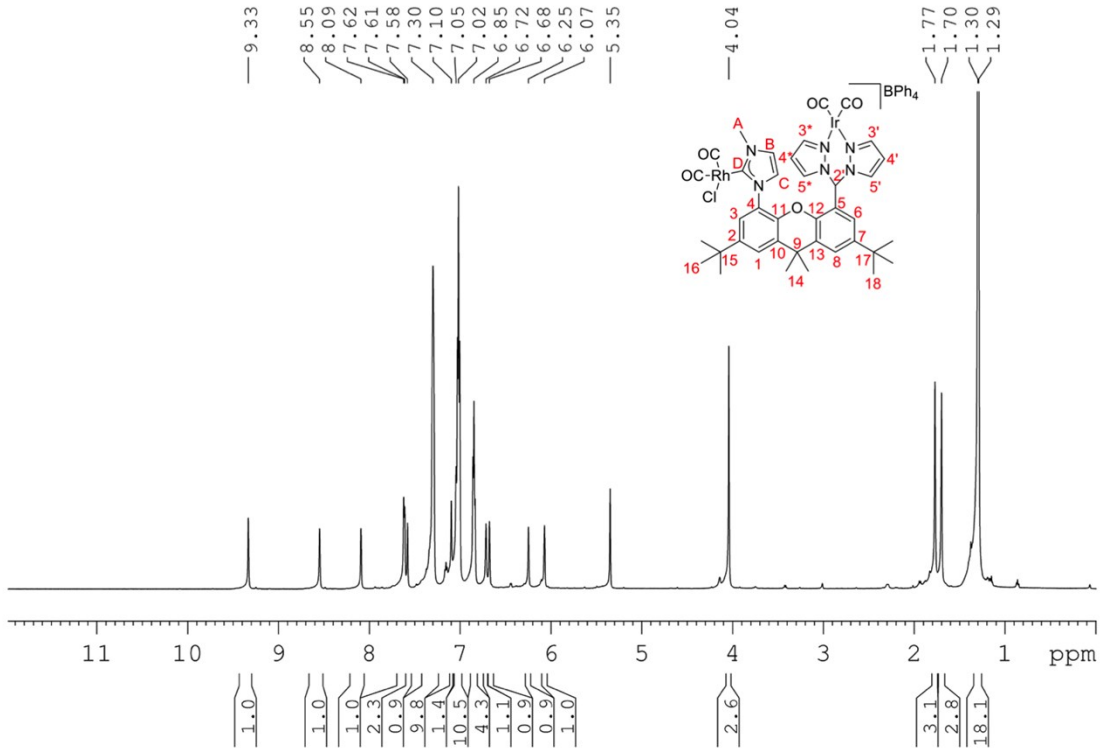
2.7 NMR Data for 11



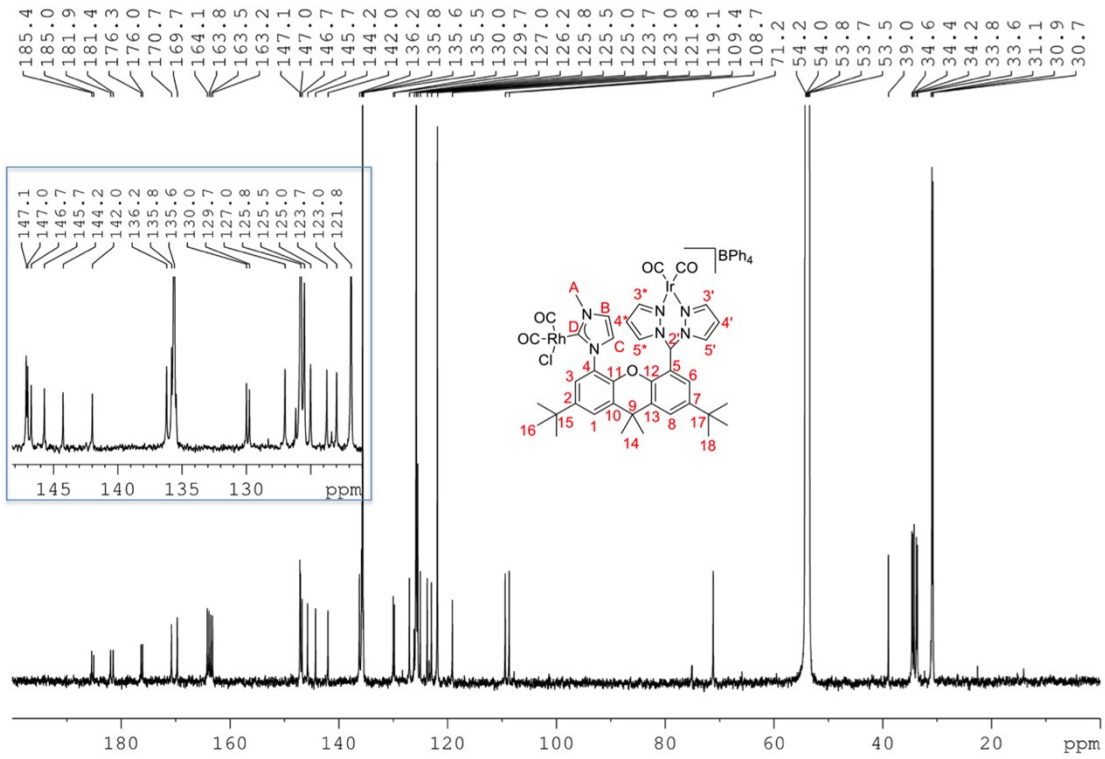
^{1}H NMR (600 MHz, CD_2Cl_2, 233 K): δ 9.33 (s, 1H, **H**2'), 8.55 (br d, 1H, **H**5'), 8.09 (br d, $^{3}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**3'), 7.62 (br d, 1H, **H**3) 7.61 (br d, 1H, **H**8), 7.58 (br d, 1H, **H**3*) 7.30 (br m, 8H, *o*-C**H** of BPh_4), 7.10 (br d, 1H, **H**B), 7.05 (br d, 1H, **H**1), 7.02 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 8H, *m*-C**H** of BPh_4 & 1H, **H**C), 6.85 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 4H, *p*-C**H** of BPh_4), 6.72 (br t, 1H, **H**4'), 6.68 (br d, 1H, **H**6), 6.25 (br d, 1H, **H**5*), 6.07 (br d, 1H, **H**4*), 4.04 (s, 3H, **H**A), 1.77 (s, 3H, **H**14), 1.70 (s, 3H, **H**14), 1.30 (s, 9H, **H**16), 1.29 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 233 K): δ 185.2 (d, $^{1}J_{Rh\text{-}CO}$ = 53.6 Hz, **C**O), 181.7 (d, $^{1}J_{Rh\text{-}CO}$ = 75.5 Hz, **C**O), 176.2 (d, $^{1}J_{Rh\text{-}C}$ = 43.8 Hz, **C**D), 170.7 (s, Ir-**C**O), 169.7 (s, Ir-**C**O), 163.8 (q, $^{1}J_{B\text{-}C}$ = 49.4 Hz, *ipso*-**C** of BPh_4), 147.1 (**C**3*), 147.0 (**C**3'), 146.7 (**C**2), 145.7 (**C**7), 144.2 (**C**12), 142.0 (**C**11), 136.2 (**C**5'), 135.8 (**C**5*), 135.6 (*o*-**C** of BPh_4), 130.0 (**C**10), 129.7 (**C**13), 127.0 (**C**8), 126.2 (**C**4), 125.8 (*m*-**C** of BPh_4), 125.5 (**C**1 & **C**3), 125.0 (**C**C), 123.7 (**C**B), 123.0 (**C**6), 121.8 (*p*-**C** of BPh_4), 119.1 (**C**5), 109.4 (**C**4*), 108.7 (**C**4'), 71.2 (**C**2'), 39.0 (**C**A), 34.6 (**C**17), 34.4 (**C**15), 34.2 (**C**9), 33.8 (**C**14), 33.6 (**C**14), 30.9 (**C**16), 30.7 (**C**18) ppm.

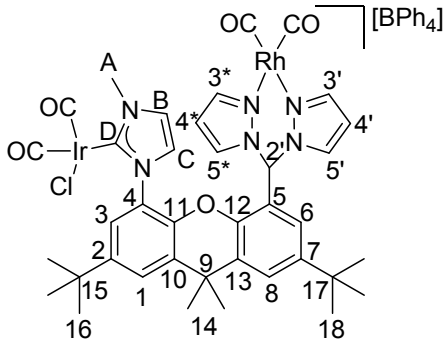
^{1}H NMR (600 MHz, CD_2Cl_2, 233 K) spectrum of (11)



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 233 K) spectrum of (11)



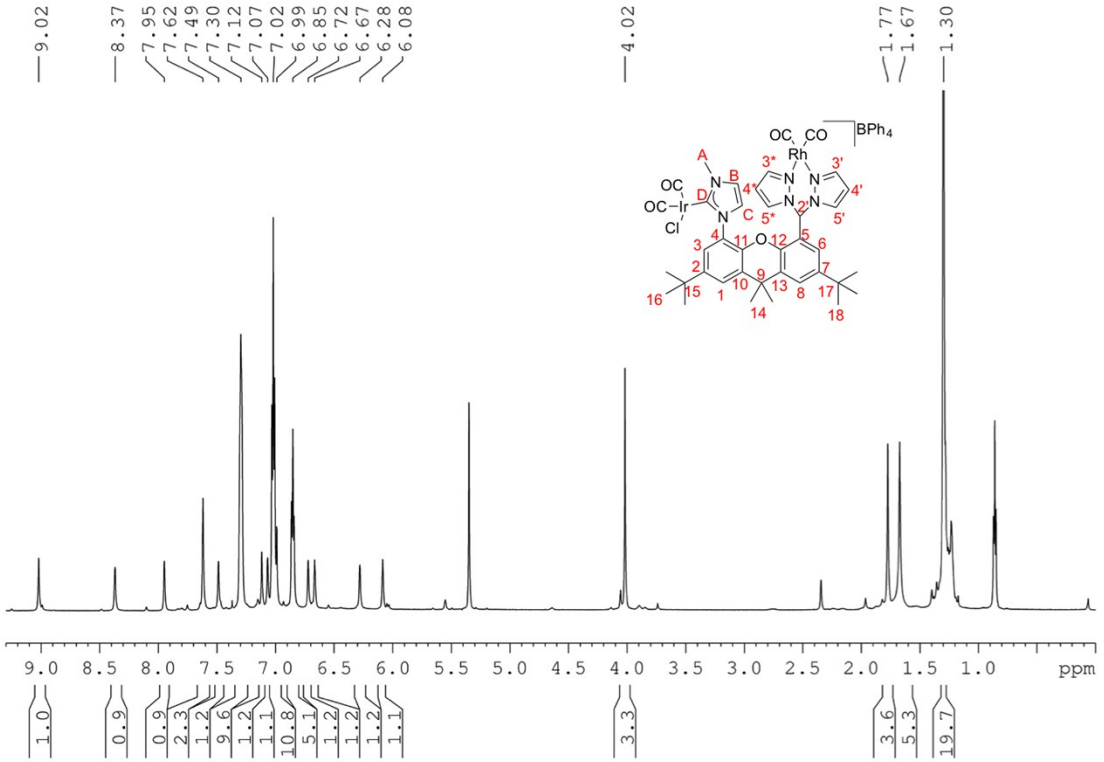
2.8 NMR Data for 12



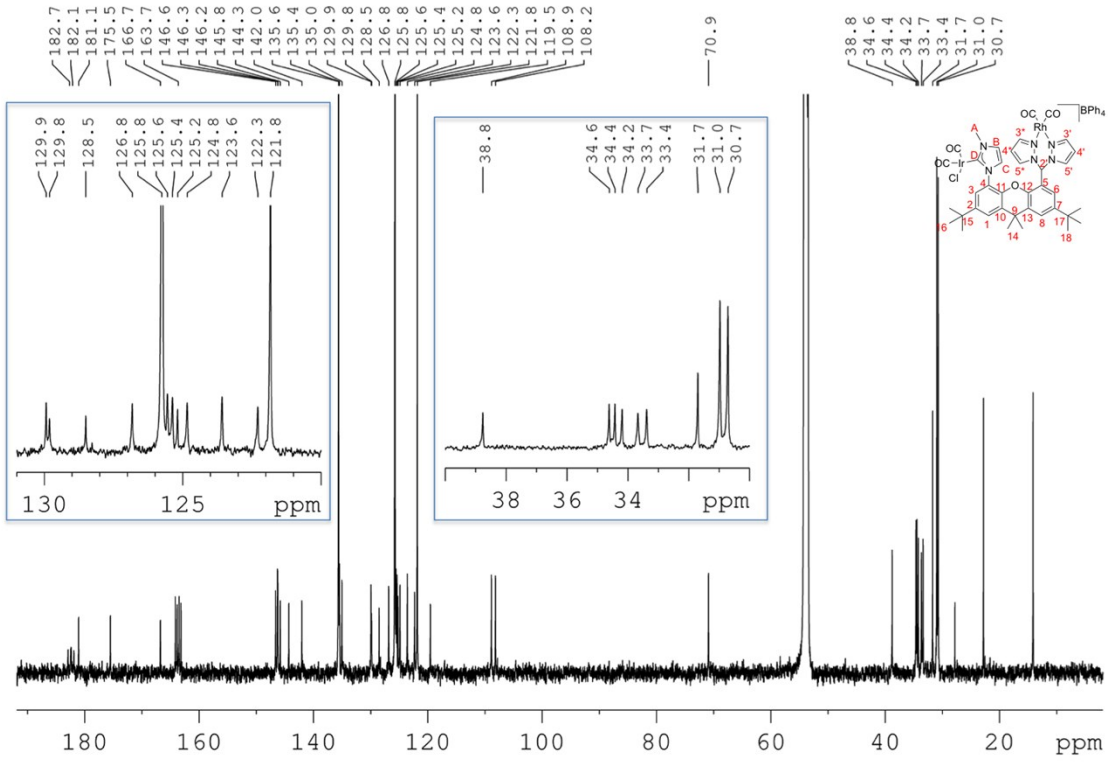
^{1}H NMR (600 MHz, CD_2Cl_2, 233 K): δ 9.02 (s, 1H, **H**2'), 8.37 (br d, 1H, **H**5*), 7.95 (br d, 1H, **H**3*), 7.62 (br m, 2H, **H**1 & **H**8), 7.49 (br d, 1H, **H**3'), 7.30 (br t, 8H, *o*-C**H** of BPh_4), 7.12 (br d, 1H, **H**C), 7.07 (br d, 1H, **H**3), 7.02 (t, $^{3}J_{H\text{-}H}$ = 7.4 Hz, 8H, *m*-C**H** of BPh_4), 6.99 (br d, 1H, **H**B), 6.85 (t, J = 7.2 Hz, 4H, *p*-C**H** of BPh_4), 6.72 (br d, 1H, **H**6), 6.67 (br t, 1H, **H**4*), 6.28 (br d, 1H, **H**5'), 6.08 (br t, 1H, **H**4'), 4.02 (s, 3H, **H**A), 1.77 (s, 3H, **H**14), 1.67 (s, 3H, **H**14), 1.30 (br s, 18H, **H**16 & **H**18) ppm.

$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2, 233 K): δ 182.7 (d, $^{1}J_{Rh\text{-}CO}$ = 69.3 Hz, Rh-**C**O), 182.1 (d, $^{1}J_{Rh\text{-}CO}$ = 68.0 Hz, Rh-**C**O), 181.1 (Ir-**C**O), 175.5 (**C**A), 166.7 (Ir-**C**O), 163.7 (q, $^{1}J_{B\text{-}C}$ = 49.9 Hz, *ipso*-**C** of BPh_4), 146.6 (**C**2), 146.3 (**C**3*), 146.2 (**C**3'), 145.8 (**C**7), 144.3 (**C**12), 142.0 (**C**11), 135.6 (*o*-**C** of BPh_4), 135.4 (**C**5*), 135.0 (**C**5'), 129.9 (**C**10), 129.8 (**C**13), 126.8 (**C**8), 125.8 (*m*-**C** of BPh_4), 125.6 (**C**1), 125.4 (**C**3), 125.2 (**C**4), 124.8 (**C**B), 123.6 (**C**C), 122.3 (**C**6), 121.8 (*p*-**C** of BPh_4), 119.5 (**C**5), 108.9 (**C**4*), 108.2 (**C**4'), 70.9 (**C**2'), 38.8 (**C**D), 34.6 (**C**17), 34.4 (**C**15), 34.2 (**C**9), 33.7 (**C**14), 33.4 (**C**14), 30.1 (**C**16), 30.7 (**C**18) ppm.

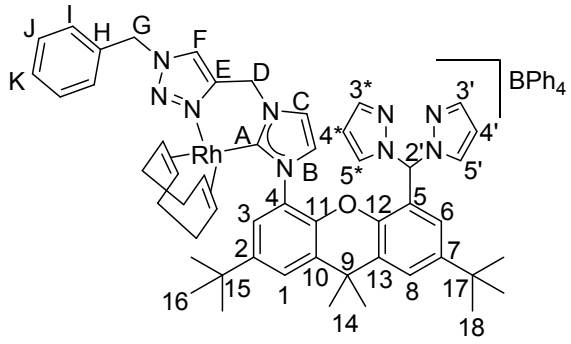
^{1}H NMR (600 MHz, CD_2Cl_2, 233 K) spectrum of (12)



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 233 K) spectrum of (12)



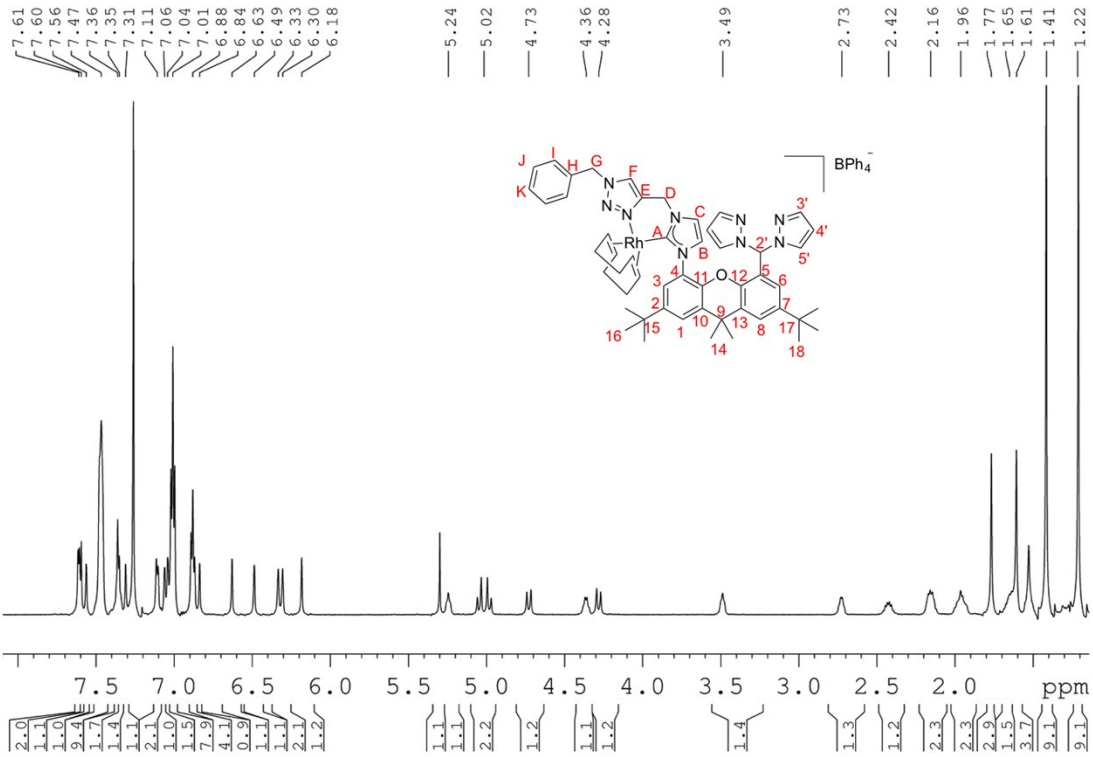
2.9 NMR Data for 13



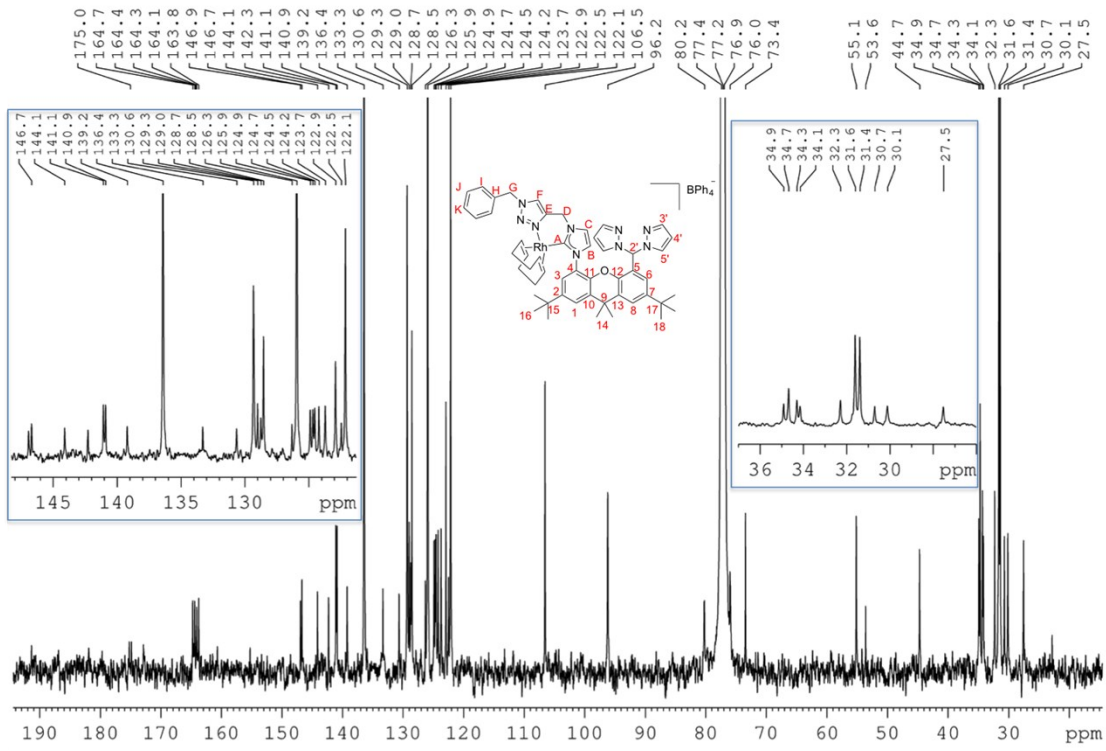
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 (m, 2H, **H**3' & **H**3*), 7.60 (br s, 1H, **H**2'), 7.56 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, **H**1), 7.47 (br d, 1H, **H**8 & m, 8H, *o*-C**H** of BPh_4), 7.35 (m, 3H, **H**J & **H**K), 7.31 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**3), 7.11 (m, 2H, **H**I), 7.06 (d, $^{3}J_{H\text{-}H}$ = 2.4 Hz, 1H, **H**5'), 7.04 (d, $^{3}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**5*), 7.01 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 8H, *m*-C**H** of BPh_4), 6.88 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 4H, *p*-C**H** of BPh_4), 6.84 (d, $^{3}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**B), 6.63 (d, $^{3}J_{H\text{-}H}$ = 1.9 Hz, 1H, **H**C), 6.49 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**6), 6.33 (t, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**4'), 6.30 (t, $^{3}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**4*), 6.18 (br s, 1H, **H**F), 5.24 (br t, 1H, C**H** of COD), 5.04 (d, $^{2}J_{H\text{-}H}$ = 15.0 Hz, 1H, **H**G), 4.98 (d, $^{2}J_{H\text{-}H}$ = 14.6 Hz, 1H, **H**G), 4.73 (d, $^{2}J_{H\text{-}H}$ = 15.4 Hz, 1H, **H**D), 4.36 (br q, 1H, C**H** of COD), 4.28 (d, $^{2}J_{H\text{-}H}$ = 15.4 Hz, 1H, **H**D), 3.49 (br t, 1H, C**H** of COD), 2.73 (br q, 1H, C**H** of COD), 2.42 (m, 1H, C$\mathbf{H}_2$ of COD), 2.16 (m, 2H, C$\mathbf{H}_2$ of COD), 1.96 (m, 2H, C$\mathbf{H}_2$ of COD), 1.77 (s, 3H, **H**14), 1.65 (m, 2H, C$\mathbf{H}_2$ of COD), 1.61 (s, 3H, **H**14), 1.52 (m, 1H, C$\mathbf{H}_2$ of COD), 1.41 (s, 9H, **H**16), 1.22 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ 175.0 (d, $^{1}J_{C\text{-}Rh}$ = 51.5 Hz, **C**A), 164.3 (q, $^{1}J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** of BPh_4), 146.9 (**C**7), 146.7 (**C**2), 144.1 (**C**12), 142.3 (**C**11), 141.1 (**C**3'), 140.9 (**C**3*), 139.2 (**C**E), 136.4 (*o*-**C** of BPh_4), 133.3 (**C**H), 130.6 (**C**10), 129.3 (**C**J, **C**K & **C**5*), 129.0 (**C**5'), 128.7 (**C**13), 128.5 (**C**I), 126.3 (**C**4), 125.9 (*m*-**C** of BPh_4), 124.9 (**C**8), 124.7 (**C**3), 124.5 (**C**1), 124.2 (**C**F), 123.7 (**C**6), 122.9 (**C**B & **C**C), 122.5 (**C**5), 122.1 (*p*-**C** of BPh_4), 106.5 (**C**4' & **C**4*), 96.2 (2C, **C**H of COD), 80.2 & 76.0 (**C**H of COD), 73.4 (**C**2'), 55.1 (**C**G), 44.7 (**C**D), 34.9 (**C**15), 34.7 (**C**9 & **C**17), 34.3 (**C**14), 34.1 (**C**H_2 of COD), 32.3 (**C**14), 31.6 (**C**16), 31.4 (**C**18), 30.7, 30.1 & 27.5 (**C**H_2 of COD) ppm.

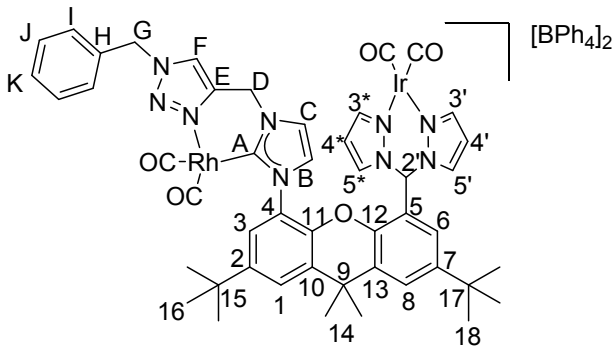
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (13)



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of (13)



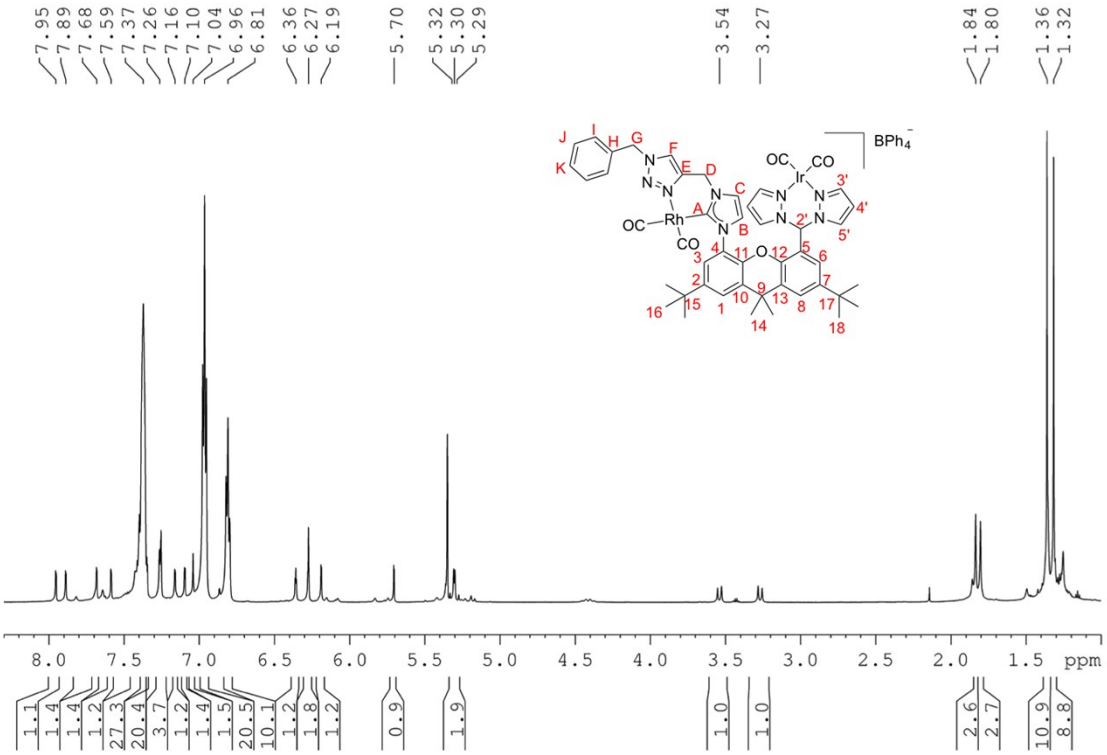
2.10 NMR Data for 14



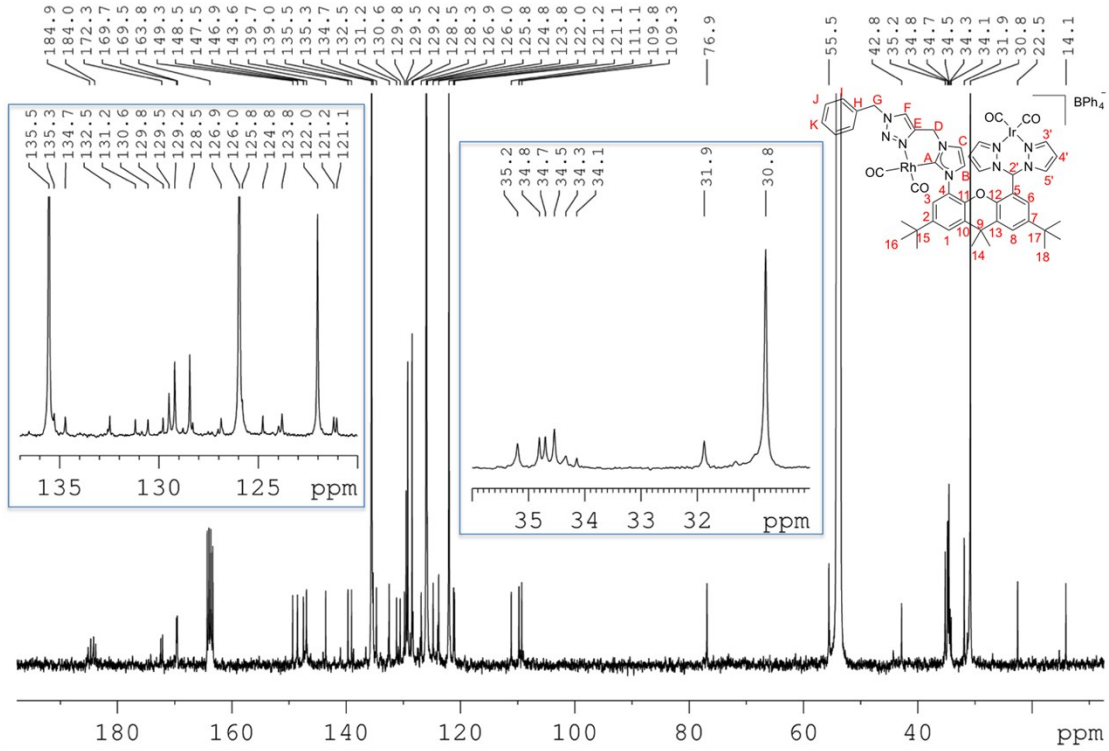
^{1}H NMR (600 MHz, CD_2Cl_2, 235 K): δ 7.95 (d, $^{3}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**5*), 7.89 (d, $^{4}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**8), 7.68 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**1), 7.59 (d, $^{3}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**5'), 7.44 – 7.39 (m, 3H, **H**J & **H**K), 7.37 (m, 16H, *o*-C**H** of BPh_4), 7.35 (d, $^{3}J_{H\text{-}H}$ = 2.8 Hz, 1H, **H**3*), 7.28 – 7.24 (m, 3H, **H**I & **H**3), 7.16 (d, $^{4}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**6), 7.10 (d, $^{3}J_{H\text{-}H}$ = 2.9 Hz, 1H, **H**3'), 7.04 (br s, 1H, **H**2'), 6.96 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 16H, *m*-C**H** of BPh_4), 6.81 (t, $^{3}J_{H\text{-}H}$ =7.2 Hz, 8H, *p*-C**H** of BPh_4), 6.36 (t, $^{3}J_{H\text{-}H}$ = 2.5 Hz, 1H, **H**4*), 6.27 (br m, 2H, **H**4' & **H**F), 6.19 (d, $^{3}J_{H\text{-}H}$ = 1.6 Hz, 1H, **H**C), 5.70 (d, $^{3}J_{H\text{-}H}$ = 1.6 Hz, 1H, **H**B), 5.32 (d, $^{2}J_{H\text{-}H}$ = 14.8 Hz, 1H, **H**G), 5.29 (d, $^{2}J_{H\text{-}H}$ = 14.8 Hz, 1H, **H**G), 3.54 (d, $^{2}J_{H\text{-}H}$ = 15.8 Hz, 1H, **H**D), 3.27 (d, $^{2}J_{H\text{-}H}$ = 15.8 Hz, 1H, **H**D), 1.84 (s, 3H, **H**14), 1.80 (d, 3H, **H**14), 1.36 (s, 9H, **H**16), 1.32 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 235 K): δ 184.9 (d, $^{1}J_{Rh\text{-}CO}$ = 71.3 Hz, **C**O), 184.0 (d, $^{1}J_{Rh\text{-}CO}$ = 56.3 Hz, **C**O), 172.3 (d, $^{1}J_{Rh\text{-}C}$ = 47.9 Hz, **C**A), 169.7 (s, Ir-**C**O), 169.5 (s, Ir-**C**O), 163.8 (q, $^{1}J_{B\text{-}C}$ = 48.9 Hz, *ipso*-**C** of BPh_4), 149.3 (**C**7), 148.5 (**C**5*), 147.5 (**C**2), 146.9 (**C**5'), 143.6 (**C**12), 139.7 (**C**11), 139.0 (**C**E), 135.5 (*o*-**C** of BPh_4), 135.3 (**C**3*), 134.7 (**C**3'), 132.5 (**C**H), 131.2 (**C**10), 130.6 (**C**8), 129.8 (**C**13), 129.5 (**C**6 & **C**K), 129.2 (**C**J), 128.5 (**C**I), 126.9 (**C**3), 126.0 (*m*-**C** of BPh_4), 125.8 (**C**1), 124.8 (**C**4), 123.8 (**C**F), 122.0 (*p*-**C** of BPh_4), 121.2 (**C**C), 121.1 (**C**B), 111.1 (**C**5), 109.8 (**C**4*), 109.3 (**C**4'), 76.9 (**C**2'), 55.5 (**C**G), 42.8 (**C**D), 35.2 (**C**14), 34.8 (**C**15), 34.7 (**C**17), 34.5 (**C**9), 31.9 (**C**14), 30.8 (**C**16 & **C**18) ppm.

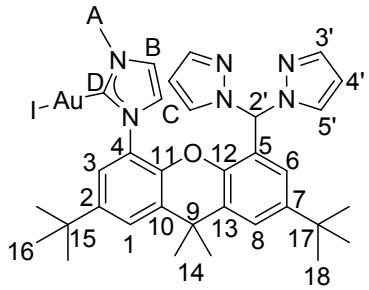
^{1}H NMR (600 MHz, CD_2Cl_2, 235 K) spectrum of (14)



^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2, 235 K) spectrum of (14)



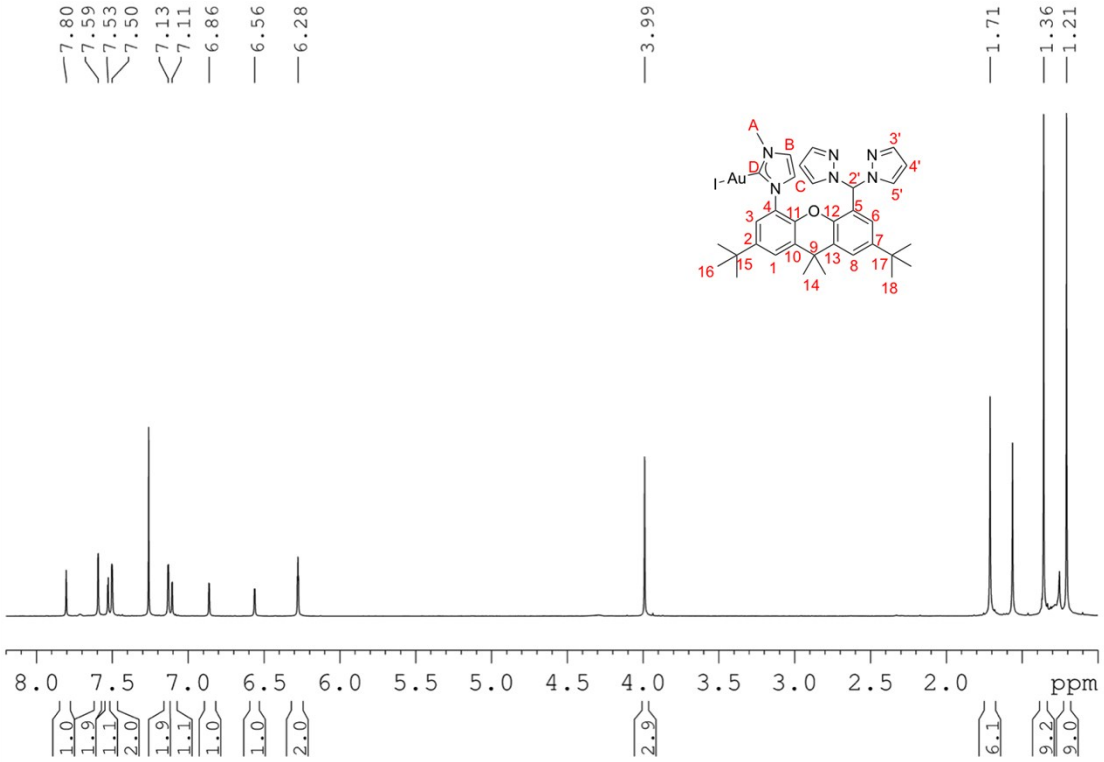
2.11 NMR Data for 15



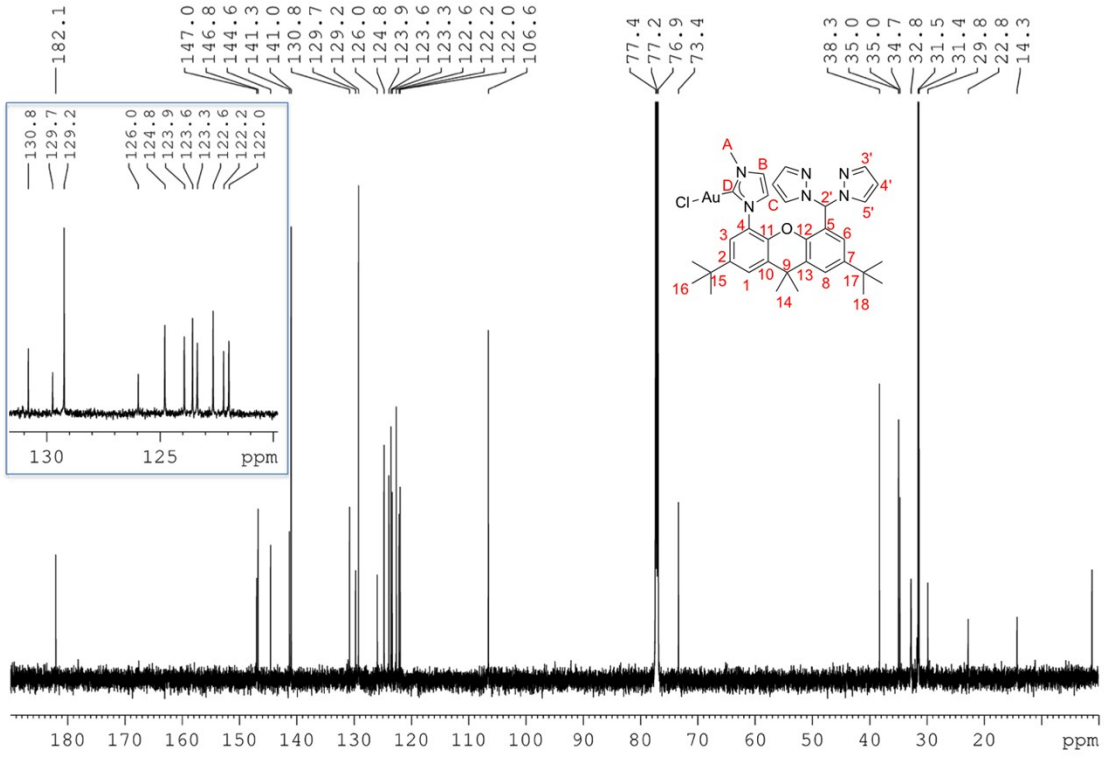
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.80 (s, 1H, **H**2'), 7.59 (d, $^{3}J_{H\text{-}H}$ = 1.3 Hz, 2H, **H**3'), 7.53 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**3), 7.50 (br s, 2H, **H**1 & **H**8), 7.13 (d, $^{3}J_{H\text{-}H}$ = 2.2 Hz, 2H, **H**5'), 7.11 (d, $^{3}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**B), 6.86 (d, $^{3}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**C), 6.56 (d, $^{4}J_{H\text{-}H}$ = 1.9 Hz, 1H, **H**6), 6.28 (t, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 2H, **H**4'), 3.99 (s, 3H, **H**A), 1.71 (s, 6H, **H**14), 1.36 (s, 9H, **H**16), 1.21 (s, 9H, **H**18) ppm.

^{13}C NMR (151 MHz, $CDCl_3$): δ 182.1 (**C**D), 147.0 (**C**7), 146.8 (**C**12), 141.3 (**C**11), 140.1 (**C**3'), 130.8 (**C**10 or **C**13), 129.7 (**C**10 or **C**13), 129.2 (**C**5'), 126.0 (**C**4), 124.8 (**C**8), 123.9 (**C**1), 123.6 (**C**3), 123.4 (**C**6), 122.7 (**C**C), 122.2 (**C**5), 122.0 (**C**B), 106.6 (**C**4'), 73.4 (**C**2'), 38.3 (**C**A), 35.0 (**C**15), 35.0 (**C**9), 34.7 (**C**17), 32.8 (**C**14), 31.5 (**C**16), 31.4 (**C**18) ppm.

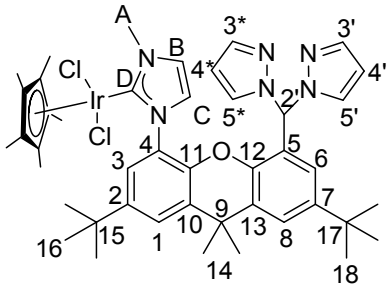
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of (15)



$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of (15)



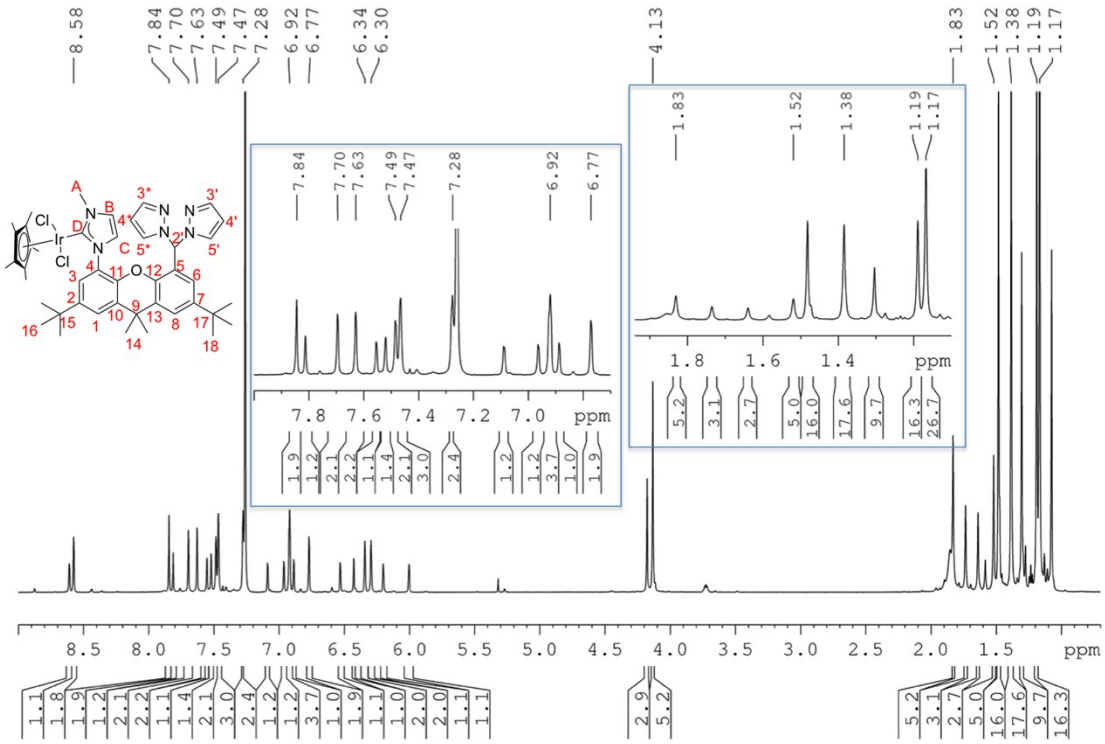
2.12 NMR Data for 18



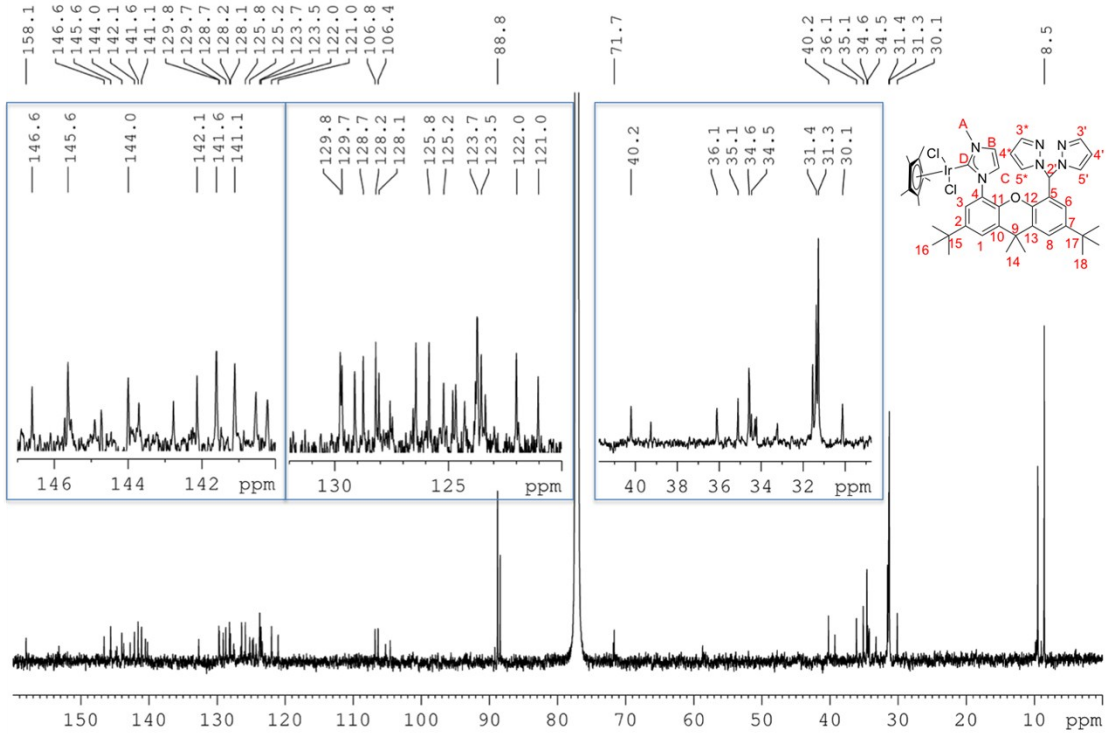
Assigned NMR of major conformation only: ^{1}H NMR (600 MHz, $CDCl_3$, 233 K): δ 8.58 (br d, 1H, **H**3), 7.84 (s, 1H, **H**2'), 7.70 (br d, 1H, **H**3'), 7.63 (br d, 1H, **H**3*), 7.49 (br d, 1H, **H**8), 7.47 (br d, 1H, **H**1), 7.28 (br d, 1H, **H**5'), 7.26 (1H, **H**B), 6.92 (2H, **H**C & **H**5*), 6.77 (br d, 1H, **H**6), 6.34 (br t, 1H, **H**4'), 6.30 (br t, 1H, **H**4*), 4.13 (s, 3H, **H**A), 1.83 (br s, 3H, **H**14), 1.52 (br s, 3H, **H**14), 1.38 (br s, 9H, **H**16), 1.19 (br s, 9H, **H**18), 1.17 (s, 15H, Cp*C**H$_3$**) ppm.

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$, 233 K): δ 158.1 (**C**D), 146.6 (**C**7), 145.6 (**C**2), 144.0 (**C**12), 142.1 (**C**11), 141.6 (**C**3'), 141.1 (**C**3*), 129.8 (**C**5'), 129.7 (**C**13), 128.7 (**C**3), 128.2 (**C**5*), 128.1 (**C**10), 125.8 (**C**C), 125.2 (**C**8), 123.7 (**C**1 & **C**B), 123.5 (**C**6), 122.0 (**C**4), 121.0 (**C**5), 106.8 (**C**4'), 106.4 (**C**4*), 88.8 (**C**q of Cp*), 71.7 (**C**2'), 40.2 (**C**A), 36.1 (**C**14), 35.1 (**C**15), 34.6 (**C**9), 34.5 (**C**17), 31.4 (**C**16), 31.3 (**C**18), 30.1 (**C**14), 8.5 (**C**H$_3$ of Cp*) ppm.

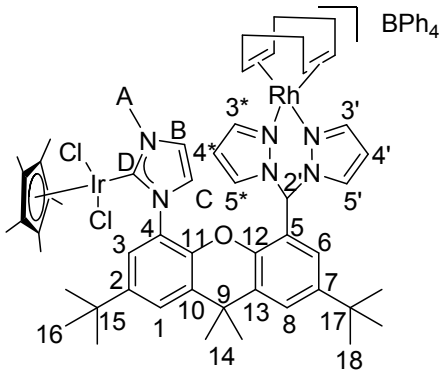
^{1}H NMR (600 MHz, $CDCl_3$, 233 K) spectrum of (18)



$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$, 233 K) spectrum of (18)



2.13 NMR Data for 19

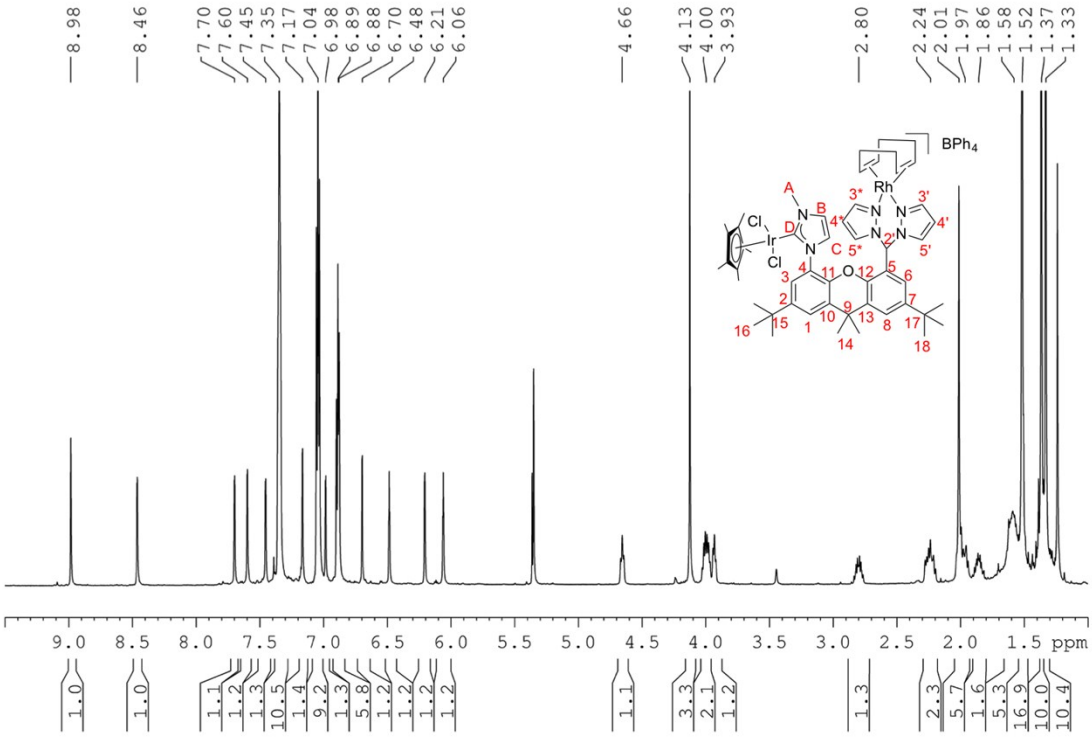


^{1}H NMR (600 MHz, CD_2Cl_2): δ 8.98 (s, 1H, H**2'**), 8.46 (d, $^{3}J_{H\text{-}H}$ = 2.7 Hz, 1H, H**3'**), 7.70 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, H**8**), 7.60 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, H**1**), 7.45 (d, $^{3}J_{H\text{-}H}$= 2.3 Hz, 1H, H**5'**), 7.35 (br t, 9H, *o*-C**H** of BPh_4 and H**5***), 7.16 (d, $^{3}J_{H\text{-}H}$= 2.0 Hz, 1H, H**B**), 7.04 (t, $^{3}J_{H\text{-}H}$= 7.4 Hz, 8H, *m*-C**H** of BPh_4), 6.98 (d, $^{3}J_{H\text{-}H}$= 2.6 Hz, 1H, H**3***), 6.89 (t, $^{3}J_{H\text{-}H}$= 7.25 Hz, 5H, *p*-C**H** of BPh_4 and H**3**), 6.70 (d, $^{3}J_{H\text{-}H}$= 2.0 Hz, 1H, H**C)**, 6.48 (t, $^{3}J_{H\text{-}H}$= 2.5 Hz, 1H, H**4'**), 6.20 (br d, 1H, H**6**), 6.06 (t, $^{3}J_{H\text{-}H}$= 2.5 Hz, 1H, H**4***), 4.66 (t, $^{3}J_{H\text{-}H}$= 7.2 Hz, 1H, C**H** of COD), 4.12 (s, 3H, H**A**), 4.04 – 3.95 (m, 2H, C**H** of COD), 3.92 (t, $^{3}J_{H\text{-}H}$= 7.3 Hz, 1H, C**H** of COD), 2.84 – 2.76 (m, 1H, C$\mathbf{H_2}$ of COD), 2.24 (m, 2H, C$\mathbf{H_2}$ of COD), 2.01 (s, 3H, H**14**), 2.00 – 1.92 (m, 2H, C$\mathbf{H_2}$ of COD), 1.90-1.80 (m, 1H, C$\mathbf{H_2}$ of COD), 1.65-1.54 (m, 2H, C$\mathbf{H_2}$ of COD), 1.52 (s, 15H, Cp*H), 1.37 (s, 9H, H**16**), 1.33 (s, 9H, H**18**), 1.24 (s, 3H, H**14**) ppm.

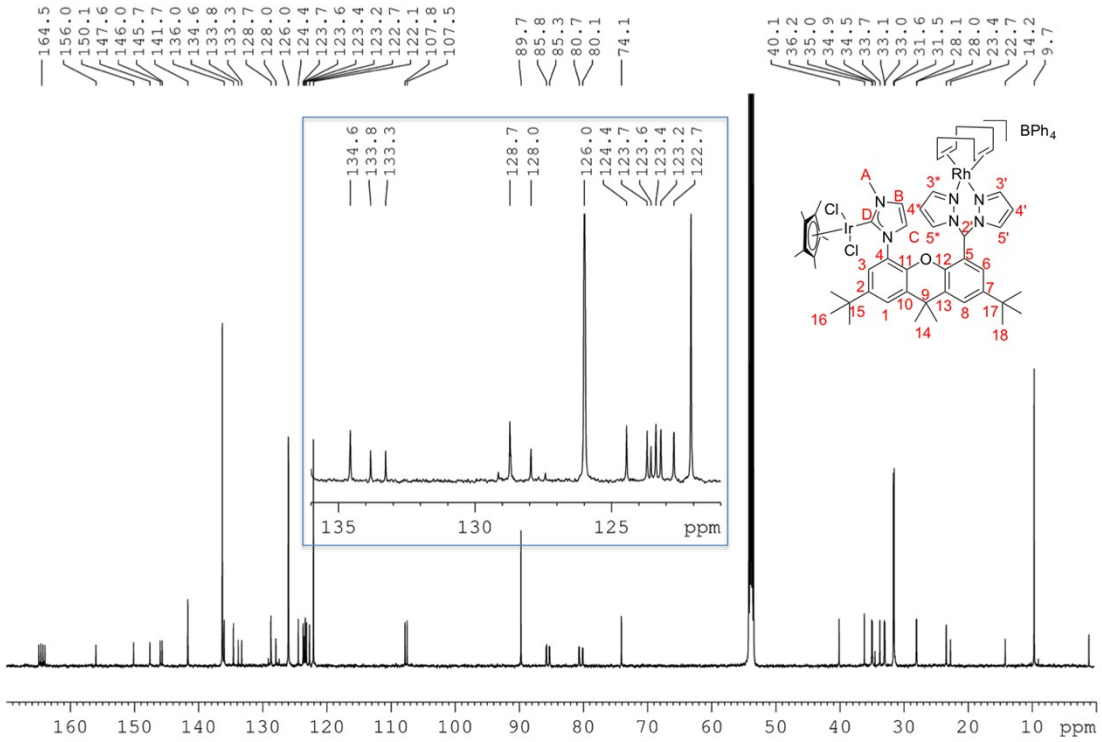
^{13}C NMR (151 MHz, CD_2Cl_2): δ 164.5 (q, $^{1}J_{B\text{-}C}$ = 49.1 Hz, *ipso*-**C** of BPh_4), 156.0 (**C**D), 150.1 (**C**12), 147.6 (**C**11), 146.0 (**C**7), 146.0 (**C**2), 141.7 (**C**5' & **C**5*), 136.3 (*o*-**C** of BPh_4), 136.0 (**C**3'), 134.6 (**C**3*), 133.8 (**C**10), 133.3 (**C**13), 128.7 (**C**C), 127.9 (**C**4), 126.0 (*m*-**C** of BPh_4), 124.4 (**C**3), 123.7 (**C**8), 123.5 (**C**5), 123.4 (**C**B), 123.2

(**C**1), 122.7 (**C**6), 122.1 (*p*-**C** of BPh_4), 107.8 (**C**4'), 107.5 (**C**4*), 89.7 (**C**q of Cp*), 85.8 (d, $^1J_{C\text{-}Rh}$ = 12.3 Hz, **C**H of COD), 85.3 (d, $^1J_{C\text{-}Rh}$ = 12.3 Hz, **C**H of COD), 80.7 (d, $^1J_{C\text{-}Rh}$ = 12.3 Hz, **C**H of COD), 80.1 (d, $^1J_{C\text{-}Rh}$ = 12.3 Hz, **C**H of COD), 74.1 (**C**2'), 40.1 (**C**A), 36.2 (**C**9), 35.0 (**C**17), 34.9 (**C**15), 33.8 (**C**14), 33.1 (**C**H_2 of COD), 33.0 (**C**H_2 of COD), 31.6 (**C**18), 31.5 (**C**16), 28.1 (**C**H_2 of COD), 28.0 (**C**H_2 of COD), 23.4 (**C**14), 9.7 (**C**H_3 of Cp*) ppm.

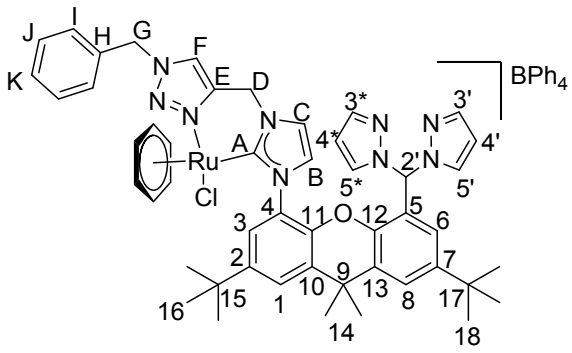
^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of (19)



$^{13}C\{^{1}H\}$ NMR (151 MHz, CD_2Cl_2) spectrum of (19)



2.14 NMR Data for 20

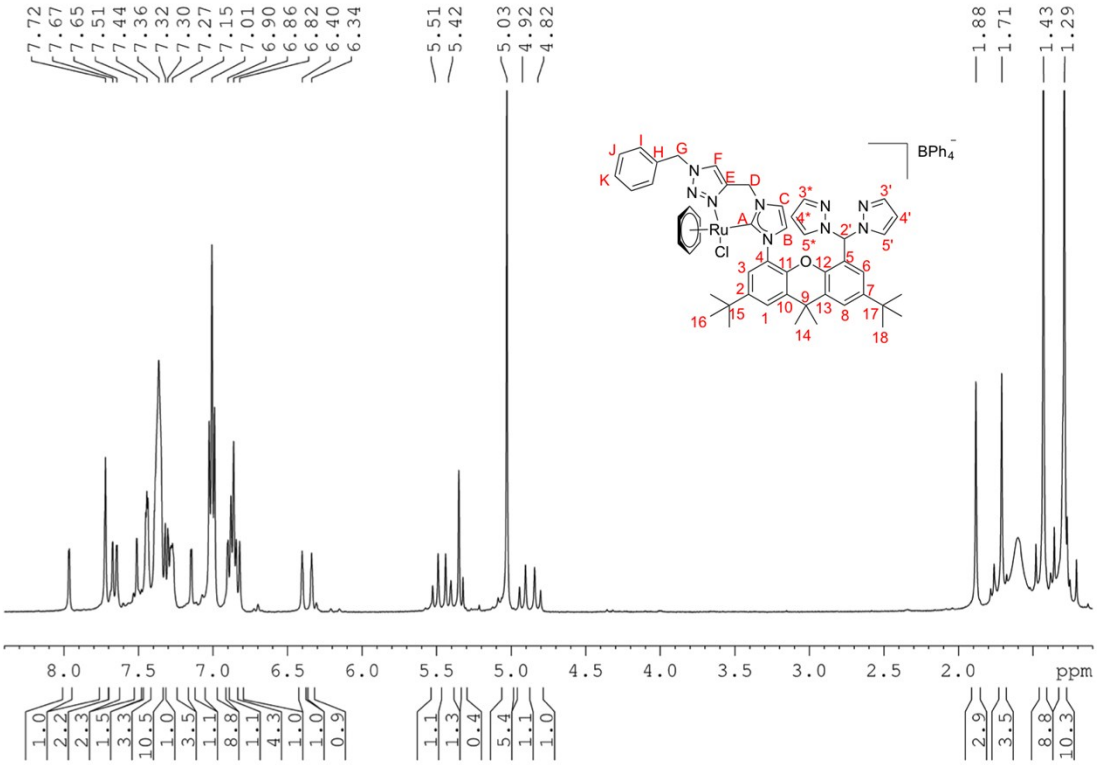


^{1}H NMR (400 MHz, CD_2Cl_2): δ 7.97 (d, $^{4}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**3), 7.72 (m, 2H, **H**1 & **H**2'), 6.76 (br d, 1H, **H**3'), 7.65 (d, $^{4}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**8), 7.51 (br d, 1H, **H**3*), 7.44 (m, 3H, **H**J & **H**K), 7.40-7.33 (m, 9H, H5* & *o*-C**H** of BPh_4), 7.32 (br d, 1H, **H**B), 7.30 (br d, 1H, **H**B), 7.27 (m, 2H, **H**I), 7.15 (d, $^{3}J_{H\text{-}H}$ = 2.1 Hz, 1H, **H**5'), 7.01 (t, $^{3}J_{H\text{-}H}$ = 7.3 Hz, 8H, *m*-C**H** of BPh_4), 6.90 (d, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**6), 6.86 (t, $^{3}J_{H\text{-}H}$ = 7.2 Hz, 4H, *p*-C**H** of BPh_4), 6.82 (br s, 1H, **H**F), 6.40 (br t, 1H, **H**4'), 6.34 (br t, 1H, **H**4*), 5.51 (d, $^{2}J_{H\text{-}H}$ = 14.8 Hz, 1H, **H**G), 5.42 (d, $^{2}J_{H\text{-}H}$ = 14.8 Hz, 1H, **H**G), 5.03 (br s, 6H, **H**bz of Ru), 4.92 (d, $^{2}J_{H\text{-}H}$ = 15.9 Hz, 1H, **H**D), 4.82 (d, $^{2}J_{H\text{-}H}$ = 15.9, 1H, **H**D), 1.88 (s, 3H, **H**14), 1.71 (s, 1H, **H**14), 1.43 (s, 9H, **H**16), 1.29 (s, 9H, **H**18) ppm.

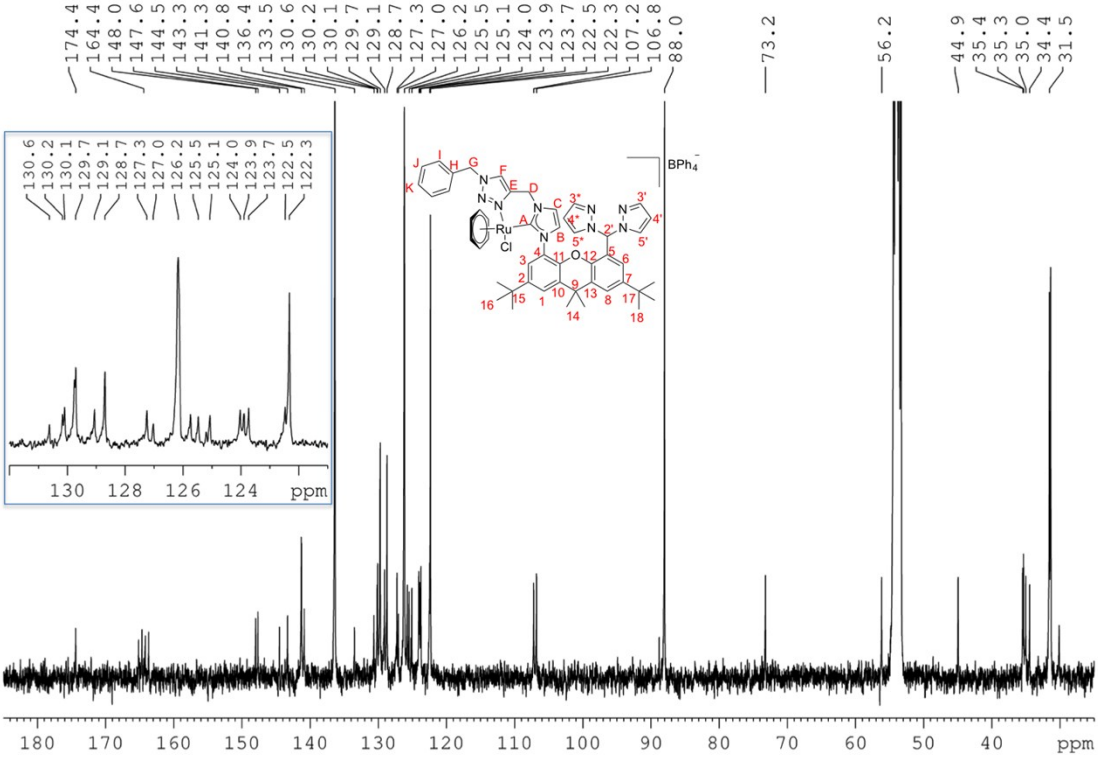
$^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ 174.4 (**C**A), 164.4 (q, $^{1}J_{B\text{-}C}$ = 49.25, *ipso*-**C** of BPh_4), 148.0 (**C**2), 147.6 (**C**7), 144.5 (**C**12), 143.3 (**C**11), 141.3 (**C**3' & **C**3*), 140.8 (**C**E), 136.4 (*o*-**C** of BPh_4), 133.5 (**C**H), 130.6 (**C**13), 130.2 (**C**10), 130.1 (**C**5*), 129.7 (**C**K & **C**J), 129.1 (**C**5'), 128.7 (**C**I), 127.3 (**C**3), 127.0 (**C**4), 126.2 (*m*-**C** of BPh_4), 125.7 (**C**B), 125.5 (**C**8), 125.1 (**C**1), 124.0 (**C**6), 123.9 (**C**C), 123.7 (**C**F), 122.5 (**C**5), 122.3 (*p*-**C** of BPh_4), 107.2 (**C**4*), 106.8

(**C**4'), 88.0 (**C**bz of Ru), 73.2 (**C**2'), 56.2 (**C**G), 44.9 (**C**D), 35.4 (**C**15), 35.3 (**C**9), 35.0 (**C**17), 34.4 (**C**14), 31.5 (**C**16), 31.4 (**C**18 & **C**14) ppm.

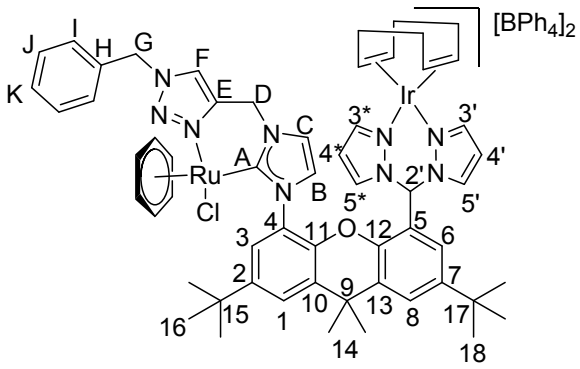
^{1}H NMR (400 MHz, CD_2Cl_2) spectrum of (20)



^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2) spectrum of (20)



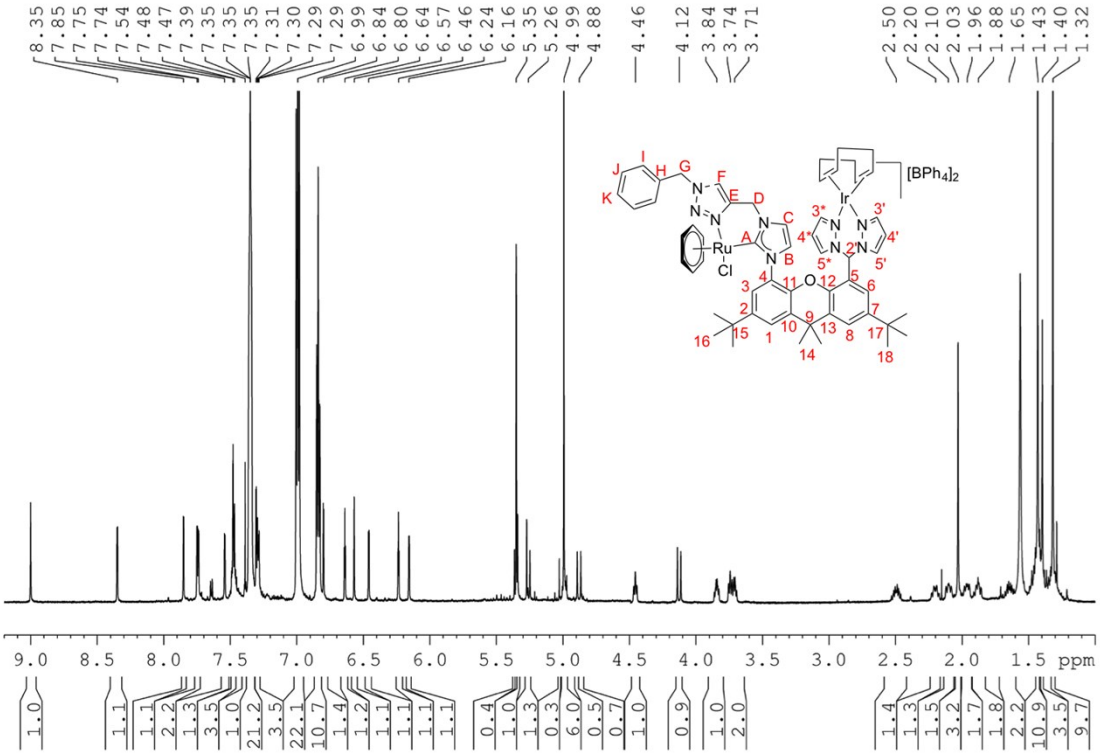
2.15 NMR Data for 21



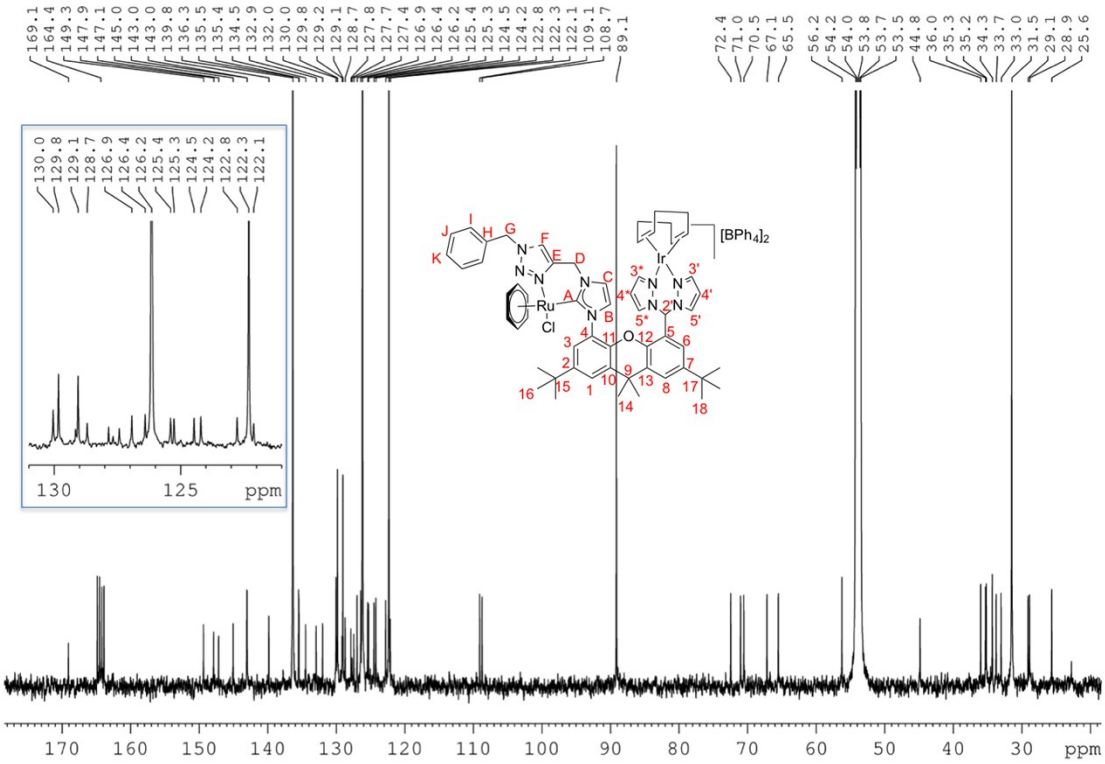
^{1}H NMR (600 MHz, CD_2Cl_2): δ 9.00 (s, 1H, **H**2'), 8.35 (d, $^{3}J_{H\text{-}H}$ = 2.7 Hz, 1H, **H**3'), 7.85 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, **H**3), 7.75 (d, $^{4}J_{H\text{-}H}$ = 2.2 Hz, 1H, **H**8), 7.74 (d, $^{3}J_{H\text{-}H}$ = 2.5 Hz, 1H, **H**5'), 7.54 (d, $^{3}J_{H\text{-}H}$ = 2.4 Hz, 1H, **H**5*), 7.50-7.45 (m, 3H, **H**J & **H**K), 7.35 (br t, 16H, *o*-C**H** of BPh_4), 7.31 (d, $^{4}J_{H\text{-}H}$ = 2.3 Hz, 1H, **H**1), 7.30-7.28 (m, 2H, **H**I), 6.99 (t, 7.4 Hz, 17H, *m*-C**H** of BPh_4 & **H**B), 6.84 (t, $^{3}J_{H\text{-}H}$ = 7.1 Hz, 8H, *p*-C**H** of BPh_4), 6.80 (d, $^{3}J_{H\text{-}H}$ = 2.0 Hz, 1H, **H**C), 6.64 (t, $^{3}J_{H\text{-}H}$ = 2.5 Hz, 1H, **H**4'), 6.57 (s, 1H, **H**F), 6.46 (d, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, **H**3*), 6.24 (t, $^{3}J_{H\text{-}H}$ = 2.6 Hz, 1H, **H**4*), 6.16 (d, $^{4}J_{H\text{-}H}$ = 1.8 Hz, 1H, **H**6), 5.35 (d, $^{2}J_{H\text{-}H}$ = 14.4 Hz, 1H, **H**G), 5.26 (d, $^{2}J_{H\text{-}H}$ = 14.4 Hz, 1H, **H**G), 4.99 (s, 6H, **H**bz of Ru), 4.88 (d, $^{2}J_{H\text{-}H}$ = 16.0 Hz, 1H, **H**D), 4.46 (t, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 1H, C**H** of COD), 4.12 (d, $^{2}J_{H\text{-}H}$ = 16.0 Hz, 1H, **H**D), 3.84 (m, 1H, C**H** of COD), 3.76-3.69 (m, 2H, C**H** of COD), 2.50 (m, 1H, C$\mathbf{H_2}$ of COD), 2.20 (m, 1H, C$\mathbf{H_2}$ of COD), 2.10 (m, 1H, C$\mathbf{H_2}$ of COD), 2.03 (s, 3H, **H**14), 1.96 (m, 1H, C$\mathbf{H_2}$ of COD), 1.88 (m, 1H, C$\mathbf{H_2}$ of COD), 1.65 (m, 1H, C$\mathbf{H_2}$ of COD), 1.49-1.40 (m, 11H, **H**16 & C$\mathbf{H_2}$ of COD), 1.40 (s, 3H, **H**14), 1.32 (s, 9H, **H**18) ppm.

^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$): δ 169.1 (**C**A), 164.4 (q, $^{1}J_{B\text{-}C}$ = 49.5 Hz, *ipso*-**C** of BPh_4), 149.4 (**C**2), 147.9 (**C**7), 147.2 (**C**12), 145.0 (**C**11), 143.0 (**C**5*), 143.0 (**C**5'), 139.8 (**C**E), 136.3 (*o*-**C** of BPh_4), 135.5 (**C**3'), 135.4 (**C**3*), 134.5 (**C**13), 132.9 (**C**H), 132.0 (**C**10), 130.0 (**C**K), 129.8 (**C**J), 129.1 (**C**I),127.85 (**C**4), 126.4 (**C**1), 126.2 (*m*-**C** of BPh_4), 125.4 (**C**3), 125.3 (**C**8), 124.5 (**C**F), 124.2 (**C**C), 122.8 (**C**6), 122.3 (**C**B & *p*-**C** of BPh_4), 122.1 (**C**5), 109.1 (**C**4'), 108.7 (**C**4*), 89.1 (**C**bz of Ru), 72.4 (**C**2'), 71.0, 70.5, 67.1 & 65.5 (4 x **C**H of COD), 56.2 (**C**G), 44.8 (**C**D), 36.0 (**C**9), 35.3 (**C**15), 35.2 (**C**17), 34.3 (**C**14), 33.7 & 33.0 (2 x **C**H_2 of COD), 31.5 (**C**16 & **C**18), 29.1, 28.9 (2 x **C**H_2 of COD) ppm.

^{1}H NMR (600 MHz, CD_2Cl_2) spectrum of (21)



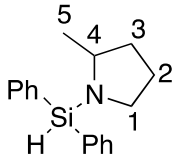
^{13}C{^{1}H} NMR (151 MHz, CD_2Cl_2) spectrum of (21)



2.16 Diagnostic Signals for 27c & 28c

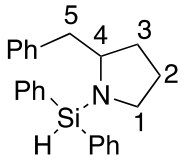
The N-silylamines **27c** and **28c** could not be isolated and purified due to their ability to hydrolyse in air. Therefore the N-silylamines were identified by diagnostic signals in the ^{1}H NMR spectra. **27c** and **28c** were hydrolysed with water, purified and confirmed by comparison of the ^{1}H NMR spectra with literature.[1]

27c



^{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.

28c



^{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.

3. Crystallographic Experimental Data Tables

	9	**13**	**16**	**17**
Chemical formula	$C_{50}H_{64}ClIrN_6ORh \cdot C_{24}H_{20}B$	$C_{76}H_{82}BCl_2N_9ORh$	$C_{42}H_{52}AuClIN_6ORh \cdot 0.5(C_4H_8O)$	$C_{34}H_{40}AuClN_6O$
M_r	1414.84	1322.12	1155.17	781.13
Crystal system, space group	Monoclinic, $P2_1/c$	Monoclinic, $P2_1/c$	Monoclinic, $C2/c$	Monoclinic, $P2_1/n$
Temperature (K)	100	150	150	150
a, *b*, *c* (Å)	19.462 (4), 23.367 (5), 16.797 (3)	13.5268 (19), 36.756 (5), 14.0701 (18)	33.393 (4), 15.0582 (13), 21.186 (2)	9.9529 (9), 12.3931 (11), 30.588 (3)
b (°)	104.72 (3)	108.382 (4)	96.356 (8)	95.433 (4)
V (Å^3)	7388 (3)	6638.6 (16)	10587.4 (18)	3756.0 (6)
Z	4	4	8	4
m (mm^{-1})	2.10	0.39	3.75	4.02
Crystal size (mm)	0.17 × 0.06 × 0.04	0.16 × 0.10 × 0.07	0.12 × 0.07 × 0.03	0.30 × 0.26 × 0.12
Data collection				
Diffractometer	Australian Synchrotron	Bruker kappa APEXII CCD Diffractometer	Bruker *APEX*-II CCD	Bruker kappa APEXII CCD Diffractometer
Absorption correction	–	Multi-scan *SADABS* (Bruker, 2001)	Multi-scan *SADABS2012*/1 (Bruker,2012) was used for absorption correction. wR2(int) was 0.1068 before and 0.0622 after correction. The Ratio of minimum to maximum transmission is 0.8459. The l/2 correction factor is 0.0015.	Multi-scan *SADABS* (Bruker, 2001)
T_{min}, T_{max}	–	0.942, 0.975	0.631, 0.746	0.383, 0.646
No. of measured, independent and observed [$I > 2s(I)$] reflections	155483, 22328, 16946	48783, 11669, 5504	83515, 9300, 7111	19350, 6407, 5771
R_{int}	0.086	0.184	0.083	0.027
$(\sin q/l)_{max}$ (Å^{-1})	0.741	0.595	0.595	0.595
Refinement				
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.048, 0.127, 1.09	0.062, 0.116, 0.83	0.052, 0.140, 1.03	0.043, 0.083, 1.20

No. of reflections	22328	11669	9300	6407
No. of parameters	805	819	607	397
No. of restraints	18	0	310	0
	$w = 1/[s^2(F_o^2) + (0.0658P)^2 + 6.3847P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o^2) + (0.0253P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o^2) + (0.0609P)^2 + 122.2848P]$ where $P = (F_o^2 + 2F_c^2)/3$	$w = 1/[s^2(F_o^2) + (0.0125P)^2 + 18.137P]$ where $P = (F_o^2 + 2F_c^2)/3$
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	2.13, -3.75	0.53, -1.52	2.58, -2.06	1.43, -3.24

4. 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.