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$_3$)$_2$SO) VT spectra of (16)
2. NMR Characterisation Data

2.1 NMR Data for 2

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 11.11\) (br s, 1H, HA), 8.32 (s, 1H, \(H2'\)), 7.74 (br s, 2H, \(H5'\)), 7.73 (br s, 1H, HC), 7.57 (d, \(4\)\(J_{HH} = 2.1\) Hz, 1H, H1), 7.48 (br d, 2H, \(H3'\)), 7.44 (d, \(4\)\(J_{HH} = 2.2\) Hz, 1H, H6), 7.28 (d, \(4\)\(J_{HH} = 2.1\) Hz, 1H, H3), 7.13 (br s, 1H, HB), 6.68 (d, \(4\)\(J_{HH} = 2.2\) Hz, 1H, H8), 6.21 (br t, 2H, \(H4'\)), 5.93 (d, \(4\)\(J_{HH} = 2.3\) Hz, 2H, HD), 2.71 (t, \(4\)\(J_{HH} = 2.3\), 1H, HF), 1.70 (s, 6H, H14), 1.33 (s, 9H, H16), 1.20 (s, 9H, H18) ppm.

\(^{13}\)C\((^1\)H\)) NMR (151 MHz, CDCl\(_3\)): \(\delta 147.5\) (C2), 147.2 (C7), 143.7 (C12), 140.6 (C3'), 140.5 (C11), 138.3 (CA), 131.7 (C10), 130.6 (C5'), 128.5 (C13), 126.0 (C1), 124.6 (C6), 124.0 (C8), 123.2 (C5), 122.1 (CB), 121.7 (C4), 121.6 (CC), 121.2 (C3), 106.1 (C4'), 77.8 (CE), 74.6 (CF), 73.0 (C2'), 40.8 (CD), 35.0 (C15), 34.7 (C9 \(\times\) C17), 33.4 (C14), 31.4 (C16), 31.3 (C18) ppm.

\(^1\)H NMR (600 MHz, CDCl\(_3\)) spectrum of (2)
2.2 NMR Data for 3

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 11.36 (br s, 1H, H1*), 8.52 (s, 1H, H2*), 8.44 (s, 1H, H6*), 7.94 (d, $^3$J$_{H-H}$ = 2.3 Hz, 2H, H5*), 7.81 (br d, 1H, H3*), 7.54 (d, $^4$J$_{H-H}$ = 2.1 Hz, 1H, H1), 7.41 (d, $^4$J$_{H-H}$ = 2.2 Hz, 1H, H8), 7.33 (d, $^3$J$_{H-H}$ = 1.5 Hz, 2H, H3*), 7.29 (m, 3H, H10* and H11*), 7.19 (m, 2H, H9*), 7.11 (d, $^4$J$_{H-H}$ = 2.2 Hz, 1H, H3), 7.02 (br d, 1H, H2*), 6.74 (d, $^4$J$_{H-H}$ = 2.1 Hz, 1H, H6), 6.27 (br s, 2H, H4*), 6.17 (t, $^3$J$_{H-H}$ = 2.0 Hz, 2H, H4*), 5.27 (br s, 2H, H7*), 1.68 (br s, 6H, H14), 1.31 (br s, 9H, H16), 1.20 (br s, 9H, H18) ppm.

$^{13}$C($^1$H) NMR (101 MHz, CDCl$_3$): $\delta$ 147.2 (C2), 147.1 (C7), 143.7 (C12), 141.1 (C5*), 140.6 (C11), 140.2 (C3*), 139.0 (C1*), 134.4 (C8*), 131.7 (C10), 130.7 (C5'), 129.1 (C10*), 128.8 (C11*), 128.3 (C9*), 128.2 (C13), 126.2 (C6*), 125.8 (C1), 124.3 (C8), 124.0 (C6), 123.7 (C5), 122.5 (C3*), 121.9 (C4), 121.7 (C2*), 121.0 (C3), 105.9 (C4*), 72.7 (C2*), 54.2 (C7*), 44.6 (C4*), 34.9 (C15), 34.7 (C17 & C9), 33.5 (C14), 31.4 (C16 & C18) 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

\[ ^1H \text{NMR (600 MHz, CDCl}_3): \delta 7.63 \text{ (br s, 1H, H2'), 7.62 \text{ (d, } ^4J_{HH} = 2.1 \text{ Hz, 1H, H1'), 7.52 \text{ (d, } ^4J_{HH} = 2.1 \text{ Hz, 1H, H8), 7.50 \text{ (d, } ^3J_{HH} = 1.4 \text{ Hz, 2H, H3'). 7.36-7.33 \text{ (m, 11H, o-CH of BPh}_4, \text{ H10' \& H11*), 7.23 \text{ (d, } ^3J_{HH} = 2.3 \text{ Hz, 2H, H5'), 7.21 \text{ (m, 2H, H9*)}, 7.05 \text{ (br s, 2H, H1' \& H6*), 6.94 \text{ (br t, 1H, H3*), 6.93 \text{ (d, } ^4J_{HH} = 2.1 \text{ Hz, 1H, H3}), 6.89 \text{ (t, } ^3J_{HH} = 7.4 \text{ Hz, 8H, m-CH of BPh}_4, 6.78 \text{ (t, } ^3J_{HH} = 7.2 \text{ Hz, 4H, p-CH of BPh}_4, 6.66 \text{ (d, } ^4J_{HH} = 1.9 \text{ Hz, 1H, H6), 6.64 \text{ (br t, 1H, H2*), 6.25 \text{ (t, } ^3J_{HH} = 1.9 \text{ Hz, 2H, H4*), 5.34 \text{ (s, 2H, H7*), 4.86 \text{ (s, 2H, H4*), 1.73 \text{ (s, 6H, H14), 1.31 \text{ (s, 9H, H16), 1.23 \text{ (s, 9H, H18) ppm.)}}

\[ ^{13}C\text{(^1H) NMR (151 MHz, CDCl}_3): \delta 164.0 \text{ (q, } ^1J_{B\text{-C}} = 48.9 \text{ Hz, ipso-C of BPh}_4, 148.0 \text{ (C2), 147.7 \text{ (C7), 143.9 \text{ (C12), 141.1 \text{ (C3'), 140.6 \text{ (C11), 139.2 \text{ (C5*)}, 136.3 \text{ (o-C of BPh}_4), 135.8 \text{ (C4 & C6*), 134.2 \text{ (C8*), 131.7 \text{ (C10), 129.4 \text{ (C5*), 129.3 \text{ (C10*), 129.1 \text{ (C13 \& C11*), 128.3 \text{ (C9*), 126.0 \text{ (C1), 125.9 \text{ (m-C of BPh4), 124.9 \text{ (C8), 124.8 \text{ (C1*}, 123.7 \text{ (C6), 122.8 \text{ (C3*), 122.7 \text{ (C2*), 122.6 \text{ (C5), 122.2 \text{ (p-C of BPh4), 121.5 \text{ (C3), 106.7 \text{ (C4*), 73.3 \text{ (C2'), 54.4 \text{ (C7*), 44.7 \text{ (C4*), 35.0 \text{ (C15), 34.9 \text{ (C9), 34.8 \text{ (C17), 33.2 \text{ (C14), 31.4 \text{ (C16 \& C18) ppm.)}}

S7
$^1$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

\[ \delta \]

\[ \delta \] NMR (600 MHz, CDCl₃): δ 8.40 (d, J₁-H₂ = 2.3 Hz, 1H, H1), 7.68 (br s, 1H, H2'), 7.65 (dd, J₃-H₄ = 1.8 Hz, J₄-H₃ = 0.5 Hz, 1H, H5*), 7.56 (br d, 2H, H5' & H3), 7.52 (d, J₁-H₃ = 2.3 Hz, 1H, H8), 7.10 (d, J₃-H₈ = 2.4 Hz, 1H, H3*), 7.02 (br d, 1H, H3'), 6.98 (br d, 1H, H2), 6.62 (d, J₃-H₆ = 2.0 Hz, 1H, HC), 6.55 (d J₄-H₆ = 2.2 Hz, 1H, H6), 6.29 (dd, J₃-H₅ = 1.9 Hz, 1H, H4*), 6.22 (dd, J₃-H₄ = 1.9 Hz, 1H, H4'), 5.10 (m, 1H, CH of COD), 4.93 (m, 1H, CH of COD), 4.07 (s, 3H, HA), 3.24 (m, 1H, CH of COD), 2.59 (m, 1H, CH of COD), 2.30-2.05 (m, 3H, CH₂ of COD), 1.80 (s, 3H, H14 & m, 1H for CH₂ of COD), 1.67 (s, 3H, H14 & m, 1H for CH₂ of COD), 1.55 (s, 3H, H14), 1.62 (m, 1H, CH₂ of COD), 1.55 (m, 9H, H18), 1.26 (m, 2H, CH₂ of COD), 1.21 (s, 9H, H16) ppm.

\[ \delta \] C NMR (150.9 MHz, CDCl₃): δ 183.8 (d, CD, assigned indirectly by ¹H-¹³C HMBC), 146.6 (C7), 146.5 (C2), 144.4 (C12), 141.1 (C3*), 140.9 (C3'), 140.7 (C11), 129.3 (C10), 129.3 (C5*), 129.2 (C13), 129.0 (C5'), 127.2 (C4), 127.0 (C1), 125.3 (C8), 123.6 (C6), 123.1 (C3), 123.0 (CC), 122.6 (CB), 121.9 (C5), 106.4 (C4*), 106.2 (C4'), 98.3 (CH of COD), 96.9 (CH of COD), 73.3 (C2'), 68.8 (CH of COD), 67.4 (CH of COD), 38.0 (CA), 35.3 (C15), 34.7 (C17), 34.6 (C14), 32.8 (C9 & 2 x CH₂ of COD), 32.2 (2 x CH₂ of COD), 31.7 (C18), 31.4 (C16), 29.6 (2 x CH₂ of COD), 28.0 (2 x CH₂ of COD) ppm.

S9
$^1$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

\[ \delta \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{):} \delta \text{ 8.09 (d, } J_{HH} = 2.3 \text{ Hz, 1H, H3'), 7.72 (s, 1H, H2'), 7.67 (d, } J_{HH} = 1.8 \text{ Hz, 1H, H3*), 7.56 (d, } J_{HH} = 1.8 \text{ Hz, 1H, H3*), 7.50 (ap t, 2H, H1 & H8), 7.12 (d, } J_{HH} = 2.4 \text{ Hz, 1H, H5*), 7.00 (d, } J_{HH} = 2.4 \text{ Hz, 1H, HB), 6.54 (d, } J_{HH} = 1.96 \text{ Hz, 1H, HC), 6.53 (d, } J_{HH} = 2.2 \text{ Hz, 1H, H6), 6.30 (ap t, } J_{HH} \text{ ppm.} \]

\[ \text{C\{H\}} \text{ NMR (101 MHz, CDCl}_3\text{):} \delta \text{ 180.9 (CD), 146.5 (C7), 146.2 (C2), 144.3 (C5), 141.1 (C3*), 141.0 (C3'), 140.6 (C4), 129.3 (C5* & C5'), 129.1 & 129.0 (C10 & C13), 127.3 (C3), 126.7 (C11), 125.3 (C8), 123.5 (C6), 123.0 (C1), 122.5 (CC), 122.4 (CB), 121.8 (C12), 106.4 (C4*), 106.3 (C4'), 84.0 (CH of COD), 82.9 (CH of COD), 73.2 (C2'), 52.3 (CH of COD), 51.1 (CH of COD), 37.7 (CA), 35.1 (C15), 34.6 (C9, C14 & C17), 33.6 (CH of COD), 32.8 (C14 & CH of COD), 31.5 (C16), 31.4 (C18), 30.4 (CH of COD), 28.4 (CH of COD) ppm.} \]
2.6 NMR Data for 9

**1H NMR (600 MHz, CDCl₃):** δ 9.91 (s, 1H, H2'), 8.40 (br d, 1H, H3*), 7.63 (d, 3J_HH = 1.9 Hz, 1H, H8), 7.61 (br d, 1H, H5*), 7.61 (br d, 1H, H1), 7.41 (br s, 8H, o-C of BPh₄), 7.05 (br d, 1H, H5'), 6.98 (t, 3J_HH = 7.5 Hz, 8H, m-C of BPh₄), 6.82 (br d, 1H, H3), 6.80 (t, 3J_HH = 7.1 Hz, 4H, p-C of BPh₄), 6.69 (br d, 1H, H4), 6.60 (d, 3J_HH = 1.6 Hz, 1H, H6), 6.54 (br t, 1H, H4*), 6.45 (d, 3J_HH = 2.2 Hz, 1H, H3*), 6.20 (br d, 1H, H6), 5.70 (br t, 1H, H4*), 4.70 (q, 3J_HH = 7.1 Hz, 1H, CH of COD), 4.52 (br q, 1H, CH of COD), 4.36 (t, 3J_HH = 7.1 Hz, 1H, CH of COD), 4.16 (s, 3H, HA), 3.79 (t, 3J_HH = 7.1 Hz, 1H, CH of COD), 3.54 (t, 3J_HH = 7.1 Hz, 1H, CH of COD), 3.54 (t, 3J_HH = 7.1 Hz, 1H, CH of COD) 2.59 (br q, 1H, CH of COD), 2.47 (m, 2H, CH₂ of COD), 2.10 (m, 3H, CH₂ of COD), 1.94 (m, 4H, CH₂ of COD), 1.87 (s, 3H, H14), 1.73 (m, 3H, CH₂ of COD), 1.68 (s, 3H, H14), 1.58 (m, 1H, CH₂ of COD), 1.39 (m, 3H, CH₂ of COD), 1.33 (s, 9H, H16), 1.27 (s, 9H, H18) ppm.

**13C{1H} NMR (151 MHz, CDCl₃):** δ 183.0 (CD, assigned indirectly by 1H-13C HMBC), 164.4 (q, 1J_{C-B} = 49.1 Hz, ipso-C of BPh₄), 146.7 (C2), 145.4 (C7), 143.1 (C4), 142.9 (C5'), 141.6 (C5*), 136.5 (o-C of BPh₄), 135.8 (C3'), 135.4 (C3*), 131.0 (C13), 130.2 (C10), 128.5 (C11), 126.8 (C12), 126.0 (C3 & C8), 125.7 (m-C of BPh₄), 125.4 (CC), 124.3 (C1), 123.1 (CB), 122.4 (C6), 121.8 (p-C of BPh₄), 121.6 (C5), 108.8 (C4'), 108.2 (C4*), 98.0 (CH of COD), 72.0 (C2'), 71.2 (CH of COD), 70.8 (CH of COD), 69.4 (CH of COD), 67.0 (CH of COD), 65.4 (CH of COD), 65.1 (CH of COD), 38.9 (CA), 34.8 (C9), 34.7 (C15 & C17), 33.78 & 33.08 (CH₂ of COD), 32.7 (C14), 31.7 (CH₂ of COD), 31.5 (C18), 31.4 (C16), 30.9, 29.9, 28.7, 28.4 & 27.3 (CH₂ of COD) ppm.
1H NMR (600 MHz, CDCl₃) spectrum of (9)

13C{¹H} NMR (151 MHz, CDCl₃) spectrum of (9)
2.7 NMR Data for 11

\(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\), 233 K): \(\delta\) 9.33 (s, 1H, H2\(^\prime\)), 8.55 (br d, 1H, H5\(^\prime\)), 8.09 (br d, 1H, H8), 7.62 (br d, 1H, H3) 7.61 (br d, 1H, H8), 7.58 (br d, 1H, H3*) 7.30 (br m, 8H, ipso-C of BPh\(_4\)), 7.10 (br d, 1H, HB), 7.05 (br d, 1H, H1), 7.02 (t, \(3\)J\(_{H-H}\) = 7.3 Hz, 8H, m-CH of BPh\(_4\)), 6.85 (t, \(3\)J\(_{H-H}\) = 7.1 Hz, 4H, p-CH of BPh\(_4\)), 6.72 (br t, 1H, H4\(^\prime\)), 6.68 (br d, 1H, H6), 6.25 (br d, 1H, H5\(^\prime\)), 6.07 (br d, 1H, H4\(^\prime\)), 4.04 (s, 3H, HA), 1.77 (s, 3H, H14), 1.70 (s, 3H, H14), 1.30 (s, 9H, H16), 1.29 (s, 9H, H18) ppm.

\(^{13}\)C\(^{1}\)H NMR (151 MHz, CD\(_2\)Cl\(_2\), 233 K): \(\delta\) 185.2 (d, \(1\)J\(_{Rh-CO}\) = 53.6 Hz, CO), 181.7 (d, \(1\)J\(_{Rh-CO}\) = 75.5 Hz, CO), 176.2 (d, \(1\)J\(_{Rh-C} = 43.8 Hz, CD\)), 170.7 (s, Ir-CO), 169.7 (s, Ir-CO), 163.8 (q, \(1\)J\(_{B-C}\) = 49.4 Hz, ipso-C of BPh\(_4\)), 147.1 (C3\(^\prime\)), 147.0 (C3\(^\prime\)), 146.7 (C2), 145.7 (C7), 144.2 (C12), 142.0 (C11), 136.2 (C5\(^\prime\)), 135.8 (C5\(^\prime\)), 135.6 (o-C of BPh\(_4\)), 130.0 (C10), 129.7 (C13), 127.0 (C8), 126.2 (C4), 125.8 (m-C of BPh\(_4\)), 125.5 (C1 & C3), 125.0 (CC), 123.7 (CB), 123.0 (C6), 121.8 (p-C of BPh\(_4\)), 119.1 (C5), 109.4 (C4\(^\prime\)), 108.7 (C4\(^\prime\)), 71.2 (C2\(^\prime\)), 39.0 (CA), 34.6 (C17), 34.4 (C15), 34.2 (C9), 33.8 (C14), 33.6 (C14), 30.9 (C16), 30.7 (C18) ppm.

\(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\), 233 K) spectrum of (11)
2.8 NMR Data for 12

$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ 9.02 (s, 1H, H2'), 8.37 (br d, 1H, H5*), 7.95 (br d, 1H, H3*), 7.62 (br m, 2H, H1 & H8), 7.49 (br d, 1H, H3'), 7.30 (br t, 8H, o-C$_6$H$_4$ of BPh$_4$), 7.12 (br d, 1H, H3), 7.02 (t, $J_{H\text{-}H} = 7.4$ Hz, 8H, m-C$_6$H$_4$ of BPh$_4$), 6.99 (br d, 1H, H5), 6.85 (t, $J = 7.2$ Hz, 4H, p-C$_6$H$_4$ of BPh$_4$), 6.72 (br d, 1H, H6), 6.67 (br t, 1H, H4*), 6.28 (br d, 1H, H5'), 6.08 (br t, 1H, H4'), 4.02 (s, 3H, HA), 1.77 (s, 3H, H14), 1.67 (s, 3H, H14), 1.30 (br s, 18H, H16 & H18) ppm.

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 233 K): $\delta$ 182.7 (d, $^1$J$_{Rh\text{-}CO} = 69.3$ Hz, Rh-CO), 182.1 (d, $^1$J$_{Rh\text{-}CO} = 68.0$ Hz, Rh-CO), 181.1 (Ir-CO), 175.5 (CA), 166.7 (Ir-CO), 163.7 (q, $^1$J$_{B. C} = 49.9$ Hz, ipso-C of BPh$_4$), 146.6 (C2), 146.3 (C3*), 146.2 (C3*), 145.8 (C7), 144.3 (C12), 142.0 (C11), 135.6 (o-C of BPh$_4$), 135.4 (C5*), 135.0 (C5*), 129.9 (C10), 129.8 (C13), 126.8 (C8), 125.8 (m-C of BPh$_4$), 125.6 (C1), 125.4 (C3), 125.2 (C4), 124.8 (CB), 123.6 (CC), 122.3 (C6), 121.8 (p-C of BPh$_4$), 119.5 (C5), 108.9 (C4*), 108.2 (C4*), 70.9 (C2*), 38.8 (CD), 34.6 (C17), 34.4 (C15), 34.2 (C9), 33.7 (C14), 33.4 (C14), 30.1 (C16), 30.7 (C18) ppm.
$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 233 K) spectrum of (12)

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 233 K) spectrum of (12)
2.9 NMR Data for 13

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ 7.61 (m, 2H, H3’ & H3*), 7.60 (br s, 1H, H2’), 7.56 (d, $^4$J$_{HH} = 2.3$ Hz, 1H, H1), 7.47 (br d, 1H, H8 & m, 8H, o-CH of BPh$_4$), 7.35 (m, 3H, HJ & HK), 7.31 (d, $^4$J$_{HH} = 2.2$ Hz, 1H, H3), 7.11 (m, 2H, H1), 7.06 (d, $^3$J$_{HH} = 2.4$ Hz, 1H, H5’), 7.04 (d, $^3$J$_{HH} = 2.2$ Hz, 1H, H5*), 7.01 (t, $^3$J$_{HH} = 2.0$ Hz, 1H, H14), 6.88 (t, $^3$J$_{HH} = 1.8$ Hz, 1H, HB), 6.63 (d, $^3$J$_{HH} = 1.9$ Hz, 1H, HC), 6.49 (d, $^4$J$_{HH} = 2.1$ Hz, 1H, H6), 6.33 (t, $^3$J$_{HH} = 2.0$ Hz, 1H, H4’), 6.30 (t, $^3$J$_{HH} = 2.1$ Hz, 1H, H4*), 6.18 (br s, 1H, HF), 5.24 (br t, 1H, CH of COD), 5.04 (d, $^2$J$_{HH} = 15.0$ Hz, 1H, HG), 4.98 (d, $^2$J$_{HH} = 14.6$ Hz, 1H, HG), 4.73 (d, $^2$J$_{HH} = 15.4$ Hz, 1H, HD), 4.36 (br q, 1H, CH of COD), 4.28 (d, $^2$J$_{HH} = 15.4$ Hz, 1H, HD), 3.49 (br t, 1H, CH of COD), 2.73 (br q, 1H, CH of COD), 2.42 (m, 1H, CH$_2$ of COD), 2.16 (m, 2H, CH$_2$ of COD), 1.96 (m, 2H, CH$_2$ of COD), 1.77 (s, 3H, H14), 1.65 (m, 2H, CH$_2$ of COD), 1.61 (s, 3H, H14), 1.52 (m, 1H, CH$_2$ of COD), 1.41 (s, 9H, H16), 1.22 (s, 9H, H18) ppm.

$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$): $\delta$ 175.0 (d, $^1$J$_{C-Rh} = 51.5$ Hz, CA), 164.3 (q, $^1$J$_{B-C} = 49.5$ Hz, ipso-C of BPh$_4$), 146.9 (C7), 146.7 (C2), 144.1 (C12), 142.3 (C11), 141.1 (C3’), 140.9 (C3*), 139.2 (CE), 136.4 (o-CH of BPh$_4$), 133.3 (CH), 130.6 (C10), 129.3 (CJ, CK & C5*), 129.0 (C5’), 128.7 (C13), 128.5 (C1), 126.3 (C4), 125.9 (m-C of BPh$_4$), 124.9 (C8), 124.7 (C3), 124.5 (C1), 124.2 (CF), 123.7 (C6), 122.9 (CB & CC), 122.5 (C5), 122.1 (p-C of BPh$_4$), 106.5 (C4’ & C4*), 96.2 (2C, CH of COD), 80.2 & 76.0 (CH of COD), 73.4 (C2’), 55.1 (CG), 44.7 (CD), 34.9 (C15), 34.7 (C9 & C17), 34.3 (C14), 34.1 (CH$_2$ of COD), 32.3 (C14), 31.6 (C16), 31.4 (C18), 30.7, 30.1 & 27.5 (CH$_2$ 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$_2$Cl$_2$, 235 K):
δ 7.95 (d, $^3$$J_{H-H} = 2.2$ Hz, 1H, H5*), 7.89 (d, $^4$$J_{H-H} = 2.0$ Hz, 1H, H8), 7.68 (d, $^4$$J_{H-H} = 2.1$ Hz, 1H, H1), 7.59 (d, $^3$$J_{H-H} = 2.1$ Hz, 1H, H5'), 7.44 – 7.39 (m, 3H, H J & K), 7.37 (m, 16H, o-CH of BPh$_4$), 7.35 (d, $^3$$J_{H-H} = 2.8$ Hz, 1H, H3*), 7.28 – 7.24 (m, 3H, HI & H3), 7.16 (d, $^4$$J_{H-H} = 2.0$ Hz, 1H, H6), 7.10 (d, $^3$$J_{H-H} = 2.9$ Hz, 1H, H3'), 7.04 (br s, 1H, H2'), 6.96 (t, $^3$$J_{H-H} = 7.2$ Hz, 16H, m-CH of BPh$_4$), 6.81 (t, $^3$$J_{H-H} = 7.2$ Hz, 8H, p-CH of BPh$_4$), 6.36 (t, $^3$$J_{H-H} = 2.5$ Hz, 1H, H4*), 6.27 (br m, 2H, H4' & HF), 6.19 (d, $^3$$J_{H-H} = 1.6$ Hz, 1H, HC), 5.70 (d, $^3$$J_{H-H} = 1.6$ Hz, 1H, HB), 5.32 (d, $^2$$J_{H-H} = 14.8$ Hz, 1H, HG), 5.29 (d, $^2$$J_{H-H} = 14.8$ Hz, 1H, HG), 3.54 (d, $^2$$J_{H-H} = 15.8$ Hz, 1H, HD), 3.27 (d, $^2$$J_{H-H} = 15.8$ Hz, 1H, HD), 1.84 (s, 3H, H14), 1.80 (d, 3H, H14), 1.36 (s, 9H, H16), 1.32 (s, 9H, H18) ppm.

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 235 K): δ 184.9 (d, $^1$$J_{Rh-CO} = 71.3$ Hz, CO), 184.0 (d, $^1$$J_{Rh-CO} = 56.3$ Hz, CO), 172.3 (d, $^1$$J_{Rh-C} = 47.9$ Hz, CA), 169.7 (s, Ir-CO), 169.5 (s, Ir-CO), 163.8 (q, $^1$$J_{B-C} = 48.9$ Hz, ipso-C of BPh$_4$), 149.3 (C7), 148.5 (C5*), 147.5 (C2), 146.9 (C5'), 143.6 (C12), 139.7 (C11), 139.0 (C13), 135.5 (o-C of BPh$_4$), 135.3 (C3*), 134.7 (C3'), 132.5 (CH), 131.2 (C10), 130.6 (C8), 129.8 (C13), 129.5 (C6 & CK), 129.2 (CJ), 128.5 (CI), 126.9 (C3), 126.0 (m-C of BPh$_4$), 125.8 (C1), 124.8 (C4), 123.8 (CF), 122.0 (p-C of BPh$_4$), 121.2 (CC), 121.1 (CB), 111.1 (C5), 109.8 (C4*), 109.3 (C4'), 76.9 (C2'), 55.5 (CG), 42.8 (CD), 35.2 (C14), 34.8 (C15), 34.7 (C17), 34.5 (C9), 31.9 (C14), 30.8 (C16 & C18) ppm.
$^1$H NMR (600 MHz, CD$_2$Cl$_2$, 235 K) spectrum of (14)

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$, 235 K) spectrum of (14)
2.11 NMR Data for 15

$^1$H NMR (600 MHz, CDCl$_3$): δ 7.80 (s, 1H, H2'), 7.59 (d, $^3$J$_{HH}$ = 1.3 Hz, 2H, H3'), 7.53 (d, $^4$J$_{HH}$ = 2.2 Hz, 1H, H3), 7.50 (br s, 2H, H1 & H8), 7.13 (d, $^3$J$_{HH}$ = 2.2 Hz, 2H, H5'), 7.11 (d, $^3$J$_{HH}$ = 1.8 Hz, 1H, HB), 6.86 (d, $^3$J$_{HH}$ = 1.8 Hz, 1H, HC), 6.56 (d, $^4$J$_{HH}$ = 1.9 Hz, 1H, H6), 6.28 (t, $^3$J$_{HH}$ = 2.0 Hz, 2H, H4'), 3.99 (s, 3H, HA), 1.71 (s, 6H, H14), 1.36 (s, 9H, H16), 1.21 (s, 9H, H18) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ 182.1 (CD), 147.0 (C7), 146.8 (C12), 141.3 (C11), 140.1 (C3'), 130.8 (C10 or C13), 129.7 (C10 or C13), 129.2 (C5'), 126.0 (C4), 124.8 (C8), 123.9 (C1), 123.6 (C3), 123.4 (C6), 122.7 (CC), 122.2 (C5), 122.0 (CB), 106.6 (C4'), 73.4 (C2'), 38.3 (CA), 35.0 (C15), 35.0 (C9), 34.7 (C17), 32.8 (C14), 31.5 (C16), 31.4 (C18) ppm.

$^1$H NMR (600 MHz, CDCl$_3$) spectrum of (15)
$^{13}\text{C}^{1\text{H}}$ 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): $\delta$ 8.58 (br d, 1H, H3), 7.84 (s, 1H, H2'), 7.70 (br d, 1H, H3'), 7.63 (br d, 1H, H3*), 7.49 (br d, 1H, H8), 7.47 (br d, 1H, H1), 7.28 (br d, 1H, H5'), 7.26 (1H, HB), 6.92 (2H, HC & H5*), 6.77 (br d, 1H, H6), 6.34 (br t, 1H, H4'), 6.30 (br t, 1H, H4*), 4.13 (s, 3H, HA), 1.83 (br s, 3H, H14), 1.52 (br s, 3H, H14), 1.38 (br s, 9H, H16), 1.19 (br s, 9H, H18), 1.17 (s, 15H, Cp*CH$_3$) ppm.

$^{13}$C($^1$H) NMR (151 MHz, CDCl$_3$, 233 K): $\delta$ 158.1 (CD), 146.6 (C7), 145.6 (C2), 144.0 (C12), 142.1 (C11), 141.6 (C3'), 141.1 (C3*), 129.8 (C5'), 129.7 (C13), 128.7 (C3), 128.2 (C5*), 128.1 (C10), 125.8 (CC), 125.2 (C8), 123.7 (C1 & CB), 123.5 (C6), 122.0 (C4), 121.0 (C5), 106.8 (C4*), 106.4 (C4*), 88.8 (Cq of Cp*), 71.7 (C2'), 40.2 (CA), 36.1 (C14), 35.1 (C15), 34.6 (C9), 34.5 (C17), 31.4 (C16), 31.3 (C18), 30.1 (C14), 8.5 (CH$_3$ of Cp*) ppm.

$^1$H NMR (600 MHz, CDCl$_3$, 233 K) spectrum of (18)
2.13 NMR Data for 19

$^1$H NMR (600 MHz, CD$_2$Cl$_2$): $\delta$ 8.98 (s, 1H, H$_2^2$), 8.46 (d, $^3$$J_{H-H} = 2.7$ Hz, 1H, H$_3^3$), 7.70 (d, $^4$$J_{H-H} = 2.2$ Hz, 1H, H$_8$), 7.60 (d, $^4$$J_{H-H} = 2.3$ Hz, 1H, H$_1$), 7.45 (d, $^3$$J_{H-H} = 2.3$ Hz, 1H, H$_5^5$), 7.35 (br t, 9H, o-CH of BPh$_4$ and H$_5^*$), 7.16 (d, $^3$$J_{H-H} = 2.0$ Hz, 1H, HB), 7.04 (t, $^3$$J_{H-H} = 7.4$ Hz, 8H, m-CH of BPh$_4$), 6.98 (d, $^3$$J_{H-H} = 2.6$ Hz, 1H, H$_3^*$), 6.89 (t, $^3$$J_{H-H} = 7.25$ Hz, 5H, p-CH of BPh$_4$ and H$_3$), 6.70 (d, $^3$$J_{H-H}$= 2.0 Hz, 1H, HC), 6.48 (br d, 1H, H$_6$), 6.06 (t, $^3$$J_{H-H}$= 2.5 Hz, 1H, H$_4^*$), 4.66 (t, $^3$$J_{H-H}$= 7.2 Hz, 1H, CH of COD), 4.12 (s, 3H, HA), 4.04 – 3.95 (m, 2H, CH of COD), 3.92 (t, $^3$$J_{H-H}$= 7.3 Hz, 1H, CH of COD), 2.84 – 2.76 (m, 1H, CH$_2$ of COD), 2.24 (m, 2H, CH$_2$ of COD), 2.01 (s, 3H, H$_{14}$), 2.00 – 1.92 (m, 2H, CH$_2$ of COD), 1.90-1.80 (m, 1H, CH$_2$ of COD), 1.65-1.54 (m, 2H, CH$_2$ 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$_2$Cl$_2$): $\delta$ 164.5 (q, $^1$$J_{B-C} = 49.1$ Hz, ipso-C of BPh$_4$), 156.0 (CD), 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 (CC), 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 (CB), 123.2
(C1), 122.7 (C6), 122.1 (p-C of BPh₄), 107.8 (C4'), 107.5 (C4*), 89.7 (Cq of Cp*),
85.8 (d, \(^1J_{C-Rh} = 12.3\) Hz, CH of COD), 85.3 (d, \(^1J_{C-Rh} = 12.3\) Hz, CH of COD), 80.7 (d,
\(^1J_{C-Rh} = 12.3\) Hz, CH of COD), 80.1 (d, \(^1J_{C-Rh} = 12.3\) Hz, CH of COD), 74.1 (C2'), 40.1
(CA), 36.2 (C9), 35.0 (C17), 34.9 (C15), 33.8 (C14), 33.1 (CH₂ of COD), 33.0 (CH₂ of
COD), 31.6 (C18), 31.5 (C16), 28.1 (CH₂ of COD), 28.0 (CH₂ of COD), 23.4 (C14),
9.7 (CH₃ of Cp*) ppm.

\(^1H\) NMR (600 MHz, CD₂Cl₂) spectrum of (19)
2.14 NMR Data for 20

**1H NMR (400 MHz, CD$_2$Cl$_2$)**: δ 7.97 (d, $^4J_{H-H} = 2.1$ Hz, 1H, H3), 7.72 (m, 2H, H1 & H2'), 6.76 (br d, 1H, H3'), 7.65 (d, $^4J_{H-H} = 2.0$ Hz, 1H, H8), 7.51 (br d, 1H, H3*), 7.44 (m, 3H, HJ & HK), 7.40-7.33 (m, 9H, H5* & ortho-C of BPh$_4$), 7.32 (br d, 1H, H5'), 7.15 (d, $^3J_{H-H} = 2.1$ Hz, 1H, H5'), 7.01 (t, $^3J_{H-H} = 7.3$ Hz, 8H, meta-CH of BPh$_4$), 6.90 (d, $^4J_{H-H} = 1.8$ Hz, 1H, H6), 6.86 (t, $^3J_{H-H} = 7.2$ Hz, 4H, para-CH of BPh$_4$), 6.82 (br s, 1H, HF), 6.40 (br t, 1H, H4'), 6.34 (br s, 1H, Hz of Ru), 5.51 (d, $^3J_{H-H} = 14.8$ Hz, 1H, HG), 5.42 (d, $^4J_{H-H} = 14.8$ Hz, 1H, HG), 5.03 (br s, 6H, Hz of Ru), 5.02 (d, $^3J_{H-H} = 15.9$ Hz, 1H, HD), 4.82 (d, $^3J_{H-H} = 15.9$, 1H, HD), 1.88 (s, 3H, H14), 1.71 (s, 1H, H14), 1.43 (s, 9H, H16), 1.29 (s, 9H, H18) ppm.

**13C{'1H} NMR (101 MHz, CD$_2$Cl$_2$)**: δ 174.4 (C A), 164.4 (q, $^1J_{B-C} = 49.25$, ipso-C of BPh$_4$), 148.0 (C2), 147.6 (C7), 144.5 (C12), 143.3 (C11), 141.3 (C3' & C3*), 140.8 (C E), 136.4 (o-C of BPh$_4$), 133.5 (C H), 130.6 (C13), 130.2 (C10), 130.1 (C5*), 129.7 (C K & C J), 129.1 (C5'), 128.7 (C I), 127.3 (C3), 127.0 (C4), 126.2 (meta-C of BPh$_4$), 125.7 (C B), 125.5 (C8), 125.1 (C1), 124.0 (C6), 123.9 (C C), 123.7 (C F), 122.5 (C5), 122.3 (p-C of BPh$_4$), 107.2 (C4*), 105.6.
(C4'), 88.0 (Cbz of Ru), 73.2 (C2'), 56.2 (CG), 44.9 (CD), 35.4 (C15), 35.3 (C9), 35.0 (C17), 34.4 (C14), 31.5 (C16), 31.4 (C18 & C14) ppm.

$^1$H NMR (400 MHz, CD$_2$Cl$_2$) spectrum of (20)

$^{13}$C($^1$H) NMR (101 MHz, CD$_2$Cl$_2$) spectrum of (20)
2.15 NMR Data for 21

$^1$H NMR (600 MHz, CD$_2$Cl$_2$): δ 9.00 (s, 1H, H2'), 8.35 (d, $^3$J$_{H-H}$ = 2.7 Hz, 1H, H3'), 7.85 (d, $^4$J$_{H-H}$ = 2.3 Hz, 1H, H3), 7.75 (d, $^4$J$_{H-H}$ = 2.2 Hz, 1H, H8), 7.74 (d, $^3$J$_{H-H}$ = 2.5 Hz, 1H, H5*), 7.54 (d, $^3$J$_{H-H}$ = 2.4 Hz, 1H, H5*), 7.50-7.45 (m, 3H, HJ & HK), 7.35 (br t, 16H, o-CH of BPh$_4$), 7.31 (d, $^4$J$_{H-H}$ = 2.3 Hz, 1H, H1), 7.30-7.28 (m, 2H, HI), 6.99 (t, 7.4 Hz, 17H, m-CH of BPh$_4$ & HB), 6.84 (t, $^3$J$_{H-H}$ = 7.1 Hz, 8H, p-CH of BPh$_4$), 6.80 (d, $^3$J$_{H-H}$ = 2.0 Hz, 1H, HC), 6.64 (t, $^3$J$_{H-H}$ = 2.5 Hz, 1H, H4*), 6.57 (s, 1H, HF), 6.46 (d, $^3$J$_{H-H}$ = 2.6 Hz, 1H, H3*), 6.24 (t, $^3$J$_{H-H}$ = 2.6 Hz, 1H, H5*), 6.16 (d, $^4$J$_{H-H}$ = 1.8 Hz, 1H, H6), 5.35 (d, $^2$J$_{H-H}$ = 14.4 Hz, 1H, HG), 5.26 (d, $^2$J$_{H-H}$ = 14.4 Hz, 1H, HG), 4.99 (s, 6H, Hbz of Ru), 4.88 (d, $^2$J$_{H-H}$ = 16.0 Hz, 1H, HD), 4.46 (t, $^3$J$_{H-H}$ = 6.9 Hz, 1H, CH of COD), 4.12 (d, $^2$J$_{H-H}$ = 16.0 Hz, 1H, HD), 3.84 (m, 1H, CH of COD), 3.76-3.69 (m, 2H, CH of COD), 2.50 (m, 1H, CH$_2$ of COD), 2.20 (m, 1H, CH$_2$ of COD), 2.10 (m, 1H, CH$_2$ of COD), 2.03 (s, 3H, H14), 1.96 (m, 1H, CH$_2$ of COD), 1.88 (m, 1H, CH$_2$ of COD), 1.65 (m, 1H, CH$_2$ of COD), 1.49-1.40 (m, 11H, H16 & CH$_2$ of COD), 1.40 (s, 3H, H14), 1.32 (s, 9H, H18) ppm.

$^{13}$C($^1$H) NMR (150.9 MHz, CDCl$_3$): δ 169.1 (CA), 164.4 (q, $^1$J$_{B-C}$ = 49.5 Hz, ipso-C of BPh$_4$), 149.4 (C2), 147.9 (C7), 147.2 (C12), 145.0 (C11), 143.0 (C5*), 143.0 (C5'), 139.8 (CE), 136.3 (o-CH of BPh$_4$), 135.5 (C3'), 135.4 (C3*), 134.5 (C13), 132.9 (CH), 132.0 (C10), 130.0 (CK), 129.8 (CJ), 129.1 (Cl), 127.85 (C4), 126.4 (C1), 126.2 (m-CH of BPh$_4$), 125.4 (C3), 125.3 (C8), 124.5 (CF), 124.2 (CC), 122.8 (C6), 122.3 (CB & p-CH of BPh$_4$), 122.1 (C5), 109.1 (C4'), 108.7 (C4*), 89.1 (Cbz of Ru), 72.4 (C2'), 71.0, 70.5, 67.1 & 65.5 (4 x CH of COD), 56.2 (CG), 44.8 (CD), 36.0 (C9), 35.3 (C15), 35.2 (C17), 34.3 (C14), 33.7 & 33.0 (2 x CH$_2$ of COD), 31.5 (C16 & C18), 29.1, 28.9 (2 x CH$_2$ of COD) ppm.
$^1$H NMR (600 MHz, CD$_2$Cl$_2$) spectrum of (21)

$^{13}$C($^1$H) NMR (151 MHz, CD$_2$Cl$_2$) 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, ArH), 7.17 (m, 3H, ArH), 5.76 (s, 1H, HSiPh2), 3.53 (m, 1H, H4), (3.04, 1.78, 1.64, 1.54, 1.27 (multiplets, 6H, belonging to H1-3)), 1.00 (d, $^3$J$_{H-H}$ = 6.3 Hz, 3H, H5) ppm.

28c

$^1$H NMR (600 MHz, C7D8): δ 7.60 (m, 5H, ArH), 7.18 (m, 5H, ArH), 7.02 (m, 2H, ArH), 6.97 (m, ArH), 6.87 (d, $^3$J$_{H-H}$ = 7.6 Hz, 2H, ArH), 5.48 (1H, HSiPh2), 3.69 (m, 1H, H4), 3.06 (t, $^3$J$_{H-H}$ = 6.2 Hz, 2H, H1), 2.79 (dd, $^2$J$_{H-H}$ = 13.2 Hz, $^3$J$_{H-H}$ = 4.7 Hz, 1H, H5), 2.41 (dd, $^2$J$_{H-H}$ = 13.2 Hz, $^3$J$_{H-H}$ = 9.3 Hz, 1H, H5), 1.65-1.49 (m, 4H, H2 and H3) ppm.
### 3. Crystallographic Experimental Data Tables

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**Data collection**

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<td>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 i/2 correction factor is 0.0015.</td>
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<td>1.43, -3.24</td>
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</tbody>
</table>
4. References