

Supplementary material: Complete list of ^1H and ^{13}C NMR data for compounds **5-24**, **26**, **27**, **30** and **31**.

Compound **5**: NMR (CD_2Cl_2): δ_{H} (400 MHz) 6.93 [1 H, d, $J(\text{H,H})$ 12.6, RuCH], 4.75 [1 H, dt, $J(\text{H,H})$ 12.6, $J(\text{P,H})$ 2.3, =CHtBu], 2.73 [6 H, m; in $^1\text{H}\{^{31}\text{P}\}$ sept, $J(\text{H,H})$ 7.2, PCHCH₃], 1.28, 1.26 [18 H each, both dvt, N 14.4, $J(\text{H,H})$ 7.2, PCHCH₃], 0.88 (9 H, s, CCH₃); δ_{C} (100.6 MHz) 203.4 [t, $J(\text{P,C})$ 13.4, CO], 143.7 [t, $J(\text{P,C})$ 3.8, RuC=C], 132.8 [t, $J(\text{P,C})$ 10.5, RuCH], 35.7 (s, CCH₃), 29.9 (s, CCH₃), 24.1 (vt, N 19.1, PCHCH₃), 19.7 (s, PCHCH₃).

Compound **6**: NMR (CD_2Cl_2): δ_{H} (400 MHz) 7.63 [1 H, dd, $J(\text{H,H})$ 14.2, $J(\text{H,H})$ 6.3, RuCH], 4.83 (1 H, m, one H of =CH₂ *cis* to RuCH), 4.55 [1 H, br d, $J(\text{H,H})$ 14.2, one H of =CH₂ *trans* to RuCH], 2.41-1.09 (66 H, br m, C₆H₁₁); δ_{C} (100.6 MHz) 203.3 [t, $J(\text{P,C})$ 12.7, CO], 152.8 [t, $J(\text{P,C})$ 10.2, RuCH], 119.1 [t, $J(\text{P,C})$ 3.2, RuC=C], 34.7 (vt, N 19.1, C1 of C₆H₁₁), 30.2, 29.9 (both s, C3,5 of C₆H₁₁), 28.1, 27.9 (both vt, N 10.2, C2,6 of C₆H₁₁), 26.8 (s, C4 of C₆H₁₁).

Compound **7**: NMR (CD_2Cl_2): δ_{H} (400 MHz) 8.55 [1 H, d, $J(\text{H,H})$ 13.5, RuCH], 7.04 (5 H, m, C₆H₅), 5.92 [1 H, d, $J(\text{H,H})$ 13.5, =CHPh], 2.52-1.14 (66 H, br m, C₆H₁₁); δ_{C} (100.6 MHz) 202.9 [t, $J(\text{P,C})$ 12.7, CO], 151.2 [t, $J(\text{P,C})$ 10.7, RuCH], 139.1 (s, *ipso*-C of C₆H₅), 133.3 [t, $J(\text{P,C})$ 3.6, RuC=C], 128.2, 123.8, 123.5 (all s, C₆H₅), 34.6 (vt, N 18.3, C1 of C₆H₁₁), 30.1, 29.7 (both s, C3,5 of C₆H₁₁), 27.9, 27.8 (both vt, N 10.2, C2,6 of C₆H₁₁), 26.6 (s, C4 of C₆H₁₁).

Compound **8**: NMR (CD_2Cl_2): δ_{H} (400 MHz) 6.92 [1 H, d, $J(\text{H,H})$ 12.8, RuCH], 4.66 [1 H, d, $J(\text{H,H})$ 12.8, =CHtBu], 2.43-1.14 (66 H, br m, C₆H₁₁), 0.80 (9 H, s, CCH₃); δ_{C} (100.6 MHz)

203.2 [t, $J(\text{P,C})$ 13.4, CO], 142.8 [t, $J(\text{P,C})$ 3.8, RuC=C], 132.5 [t, $J(\text{P,C})$ 10.5, RuCH], 35.6 (s, CCH₃), 34.2 (vt, N 18.1, C1 of C₆H₁₁), 30.0 (s, CCH₃), 29.9, 29.5 (both s, C3,5 of C₆H₁₁), 27.8, 27.6 (both vt, N 10.5, C2,6 of C₆H₁₁), 26.5 (s, C4 of C₆H₁₁).

Compound **9**: NMR (CD₂Cl₂): δ_{H} (200 MHz) 16.82 [1 H, q, $J(\text{H,H})$ 4.9, Ru=CH], 3.05 (3 H, m, CH₃), 2.78 (6 H, m, PCHCH₃), 1.30 (36 H, m, PCHCH₃); δ_{C} (50.3 MHz, 253 K) 328.9 (br s, Ru=CH), 195.0 (br s, CO), 50.4 (s, CH₃), 25.2 (vt, N 22.8, PCHCH₃), 19.3, 18.5 (both s, PCHCH₃).

Compound **10**: NMR (CD₂Cl₂): δ_{H} (200 MHz, 253 K) 16.95 [1 H, q, $J(\text{H,H})$ 5.4, Ru=CH], 7.35 (5 H, m, C₆H₅), 4.36 (2 H, m, CH₂Ph), 2.76 (6 H, m, PCHCH₃), 1.24 (36 H, m, PCHCH₃); δ_{C} (50.3 MHz, 253 K) 328.4 (br s, Ru=CH), 194.8 [t, $J(\text{P,C})$ 10.2, CO], 133.7 (s, *ipso*-C of C₆H₅), 129.2, 128.2, 127.8 (all s, C₆H₅), 65.6 (s, CH₂Ph), 25.2 (vt, N 22.9, PCHCH₃), 19.4, 18.7 (both s, PCHCH₃).

Compound **11**: NMR (CD₂Cl₂): δ_{H} (400 MHz) 17.40 (1 H, br s, Ru=CH), 2.97 [2 H, m; in ¹H{³¹P} d, $J(\text{H,H})$ 3.9, CH₂*t*Bu], 2.83 [6 H, m; in ¹H{³¹P} sept, $J(\text{H,H})$ 7.0, PCHCH₃], 1.33, 1.32 [18 H each, both dvt, N 14.9, $J(\text{H,H})$ 7.0, PCHCH₃], 1.03 (9 H, s, CCH₃); δ_{C} (100.6 MHz) 333.3 (br s, Ru=CH), 195.0 [t, $J(\text{P,C})$ 10.8, CO], 72.2 (s, CH₂*t*Bu), 33.7 (s, CCH₃), 29.2 (s, CCH₃), 25.5 (vt, N 22.9, PCHCH₃), 19.9, 19.0 (both s, PCHCH₃).

Compound **12**: NMR (CD₂Cl₂): δ_{H} (200 MHz, 253 K) 16.82 [1 H, q, $J(\text{H,H})$ 4.9, Ru=CH], 2.96 (3 H, m, CH₃), 2.50-1.15 (66 H, br m, C₆H₁₁); δ_{C} (50.3 MHz, 253 K) 326.3 (br s, Ru=CH), 195.1 [t, $J(\text{P,C})$ 10.2, CO], 50.0 (s, CH₃), 34.1 (vt, N 22.5, C1 of C₆H₁₁), 29.5, 28.5 (both s, C3,5 of C₆H₁₁), 26.9, 26.8 (both vt, N 10.2, C2,6 of C₆H₁₁), 25.3 (s, C4 of C₆H₁₁).

Compound **13**: NMR (CD₂Cl₂): δ_H (200 MHz, 253 K) 16.92 (1 H, br s, Ru=CH), 7.30 (5 H, m, C₆H₅), 4.33 (2 H, m, CH₂Ph), 2.52-1.28 (66 H, br m, C₆H₁₁).

Compound **14**: NMR (CD₂Cl₂): δ_H (200 MHz) 17.13 (1 H, br s, Ru=CH), 2.80 (2 H, br s, CH₂*t*Bu), 2.47-1.16 (66 H, br m, C₆H₁₁), 0.98 (9 H, s, CCH₃); δ_C (50.3 MHz) 329.0 (br s, Ru=CH), 194.9 [t, *J*(P,C) 10.2, CO], 70.9 (s, CH₂*t*Bu), 34.4 (vt, *N* 21.6, C1 of C₆H₁₁), 33.3 (s, CCH₃), 29.8, 28.8 (both s, C3,5 of C₆H₁₁), 28.9 (s, CCH₃), 27.0, 26.8 (both vt, *N* 10.2, C2,6 of C₆H₁₁), 25.7 (s, C4 of C₆H₁₁).

Compound **15**: NMR (CD₂Cl₂): δ_H (400 MHz) 6.81 [1 H, dd, *J*(P,H) 41.4, *J*(H,H) 13.1, one H of =CH₂ *cis* to PCH], 6.46 [1 H, dd, *J*(P,H) 19.1, *J*(H,H) 19.1, one H of =CH₂ *trans* to PCH], 6.21 [1 H, ddd, *J*(P,H) 13.1, *J*(H,H) 19.1, *J*(H,H) 13.1, PCH], 2.80 [3 H, m; in ¹H{³¹P} d, *J*(H,H) 7.4, PCHCH₃], 1.40 [18 H, dd, *J*(P,H) 16.3, *J*(H,H) 7.4, PCHCH₃]; δ_C (100.6 MHz) 143.5 [d, *J*(P,C) 2.6, =CH₂], 113.7 [d, *J*(P,C) 70.2, PCH], 20.7 [d, *J*(P,C) 43.2, PCHCH₃], 16.3 [d, *J*(P,C) 3.8, PCHCH₃].

Compound **16**: NMR (CD₂Cl₂): δ_H (400 MHz) 6.76 [1 H, dd, *J*(P,H) 41.4, *J*(H,H) 13.0, one H of =CH₂ *cis* to PCH], 6.35 [1 H, dd, *J*(P,H) 18.8, *J*(H,H) 18.8, one H of =CH₂ *trans* to PCH], 6.15 [1 H, ddd, *J*(P,H) 13.0, *J*(H,H) 18.8, *J*(H,H) 13.0, PCH], 2.49-1.25 (33 H, br m C₆H₁₁); δ_C (100.6 MHz) 142.8 [d, *J*(P,C) 2.0, =CH₂], 114.0 [d, *J*(P,C) 70.2, PCH], 29.8 [d, *J*(P,C) 41.7, C1 of C₆H₁₁], 27.9 [d, *J*(P,C) 3.1, C3,5 of C₆H₁₁], 26.4 [d, *J*(P,C) 18.3, C2,6 of C₆H₁₁], 25.4 (s, C4 of C₆H₁₁).

Compound **17**: NMR (CD₂Cl₂): δ_H (400 MHz) 2.67 (6 H, m, PCHCH₃), 2.52, 2.45 (3 H each, both s, CH₃CN), 1.40 (36 H, m, PCHCH₃); δ_C (100.6 MHz) 203.6 [t, *J*(P,C) 13.2, CO], 130.0,

127.6 (both s, CN), 24.2 (vt, *N* 20.3, PCHCH₃), 19.5, 19.2 (both s, PCHCH₃), 4.5, 4.2 (both s, CH₃CN).

Compound **18b**: NMR (CD₂Cl₂): δ_H (400 MHz) 2.33 [6 H, m; in ¹H{³¹P} sept, *J*(H,H) 7.0, PCHCH₃], 2.30, 2.29 (3 H each, both s, CH₃CN), 1.30, 1.29 [18 H each, both dvt, *N* 14.1, *J*(H,H) 7.0, PCHCH₃], -14.19 [1 H, t, *J*(P,H) 18.8, RuH]; δ_C (100.6 MHz) 203.7 [t, *J*(P,C) 13.4, CO], 126.0, 125.3 (both s, CN), 25.3 (vt, *N* 21.0, PCHCH₃), 19.0 (s, PCHCH₃), 3.4, 3.1 (both s, CH₃CN).

Compound **19**: NMR (C₆D₆): δ_H (400 MHz) 2.23-1.25 (69 H, br m, C₆H₁₁ and O₂CCH₃), -17.40 [1 H, t, *J*(P,H) 19.7, RuH]; δ_C (100.6 MHz) 207.8 (br s, CO), 181.7 (s, O₂CCH₃), 35.5 (vt, *N* 18.3, C1 of C₆H₁₁), 30.8, 29.8 (both s, C3,5 of C₆H₁₁), 28.5, 28.3 (both vt, *N* 10.2, C2,6 of C₆H₁₁), 27.0 (s, C4 of C₆H₁₁), 24.7 (s, O₂CCH₃).

Compound **20**: NMR (C₆D₆): δ_H (200 MHz) 8.46 [1 H, dd, *J*(H,H) 16.5, *J*(H,H) 9.1, RuCH], 5.99 [1 H, dd, *J*(H,H) 9.1, *J*(H,H) 1.8, one H of =CH₂ *cis* to RuCH], 5.47 [1 H, dd, *J*(H,H) 16.5, *J*(H,H) 1.8, one H of =CH₂ *trans* to RuCH], 2.36-1.25 (69 H, br m, C₆H₁₁ and O₂CCH₃); δ_C (100.6 MHz) 209.6 [t, *J*(P,C) 14.2, CO], 181.4 (s, O₂CCH₃), 164.6 [t, *J*(P,C) 11.2, RuCH], 118.8 (s, RuC=C), 34.9 (vt, *N* 16.3, C1 of C₆H₁₁), 30.0, 29.9 (both s, C3,5 of C₆H₁₁), 28.4, 28.3 (both vt, *N* 10.2, C2,6 of C₆H₁₁), 27.0 (s, C4 of C₆H₁₁), 22.7 (s, O₂CCH₃).

Compound **21**: NMR (C₆D₆): δ_H (400 MHz) 9.17 [1 H, d, *J*(H,H) 15.3, RuCH], 7.22 (5 H, m, C₆H₅), 6.65 [1 H, d, *J*(H,H) 15.3, =CHPh], 2.40-1.18 (69 H, br m, C₆H₁₁ and O₂CCH₃); δ_C (100.6 MHz) 209.5 [t, *J*(P,C) 14.2, CO], 181.7 (s, O₂CCH₃), 161.4 [t, *J*(P,C) 11.2, RuCH], 133.6, 130.6, 128.8, 128.3, 124.1, 123.8 (all s, C₆H₅ and RuC=C), 35.2 (vt, *N* 17.3, C1 of

C₆H₁₁), 30.0, 29.9 (both s, C3,5 of C₆H₁₁), 28.5, 28.4 (both vt, N 10.2, C2,6 of C₆H₁₁), 26.9 (s, C4 of C₆H₁₁), 22.7 (s, O₂CCH₃).

Compound **22**: NMR (CD₂Cl₂): δ_H (200 MHz) 17.31 [1 H, q, *J*(H,H) 6.5, Ru=CH], 2.90 [3 H, d, *J*(H,H) 6.5, =CHCH₃], 2.11-1.26 (69 H, br m, C₆H₁₁ and O₂CCH₃).

Compound **23**: NMR (C₆D₆): δ_H (400 MHz) 8.24 [1 H, dd, *J*(H,H) 19.6, *J*(H,H) 11.7 RuCH], 6.44 [1 H, dd, *J*(H,H) 11.7, *J*(H,H) 2.9, one H of =CH₂ *cis* to RuCH], 5.88 [1 H, dd, *J*(H,H) 19.6, *J*(H,H) 2.9, one H of =CH₂ *trans* to RuCH], 2.66 [6 H, m; in ¹H{³¹P} sept, *J*(H,H) 7.2, PCHCH₃], 1.35, 1.11 [18 H each, both dvt, *N* 14.4, *J*(H,H) 7.2, PCHCH₃]; δ_C (100.6 MHz) 201.5 [t, *J*(P,C) 11.0, CO], 197.2 [t, *J*(P,C) 9.1, CO], 166.4 [t, *J*(P,C) 12.4, RuCH], 124.2 (s, RuC=C), 23.9 (vt, *N* 21.0, PCHCH₃), 19.5, 18.3 (both s, PCHCH₃).

Compound **24a**: NMR (CD₂Cl₂): δ_H (400 MHz) 7.19 [1 H, dd, *J*(H,H) 17.1, *J*(H,H) 7.5, RuCH], 5.54 [1 H, br d, *J*(H,H) 7.5, one H of =CH₂ *cis* to RuCH], 5.08 [1 H, d, *J*(H,H) 17.1, one H of =CH₂ *trans* to RuCH], 2.52-1.25 (72 H, br m, C₆H₁₁ and CH₃CN); δ_C (100.6 MHz) 206.2 [t, *J*(P,C) 13.7, CO], 153.3 (br s, RuCH), 128.3, 127.3 (both s, CN), 123.4 (s, RuC=C), 34.9 (vt, *N* 18.3, C1 of C₆H₁₁), 29.3, 29.1 (both s, C3,5 of C₆H₁₁), 27.9 (m, C2,6 of C₆H₁₁), 26.4 (s, C4 of C₆H₁₁), 4.3, 3.1 (both s, CH₃CN).

Compound **24b**: NMR (CD₂Cl₂): δ_H (400 MHz) 7.34-6.86 (21 H, br m, C₆H₅ and RuCH), 5.41 (1 H, br m, one H of =CH₂ *cis* to RuCH), 5.00 [1 H, d, *J*(H,H) 17.0, one H of =CH₂ *trans* to RuCH], 2.27-1.26 (72 H, br m, C₆H₁₁ and CH₃CN); δ_C (100.6 MHz) 205.8 (br s, CO), 164.2 [q, *J*(B,C) 49.5, *ipso*-C of BC₆H₅], 136.0 (s, CH of BC₆H₅), 128.4, 127.3 (both s, CN), 125.7 [q, *J*(B,C) 3.0, CH of BC₆H₅], 123.6 (s, RuC=C), 121.8 (s, CH of BC₆H₅), 35.1 (vt, *N*

18.3, C1 of C₆H₁₁), 29.5, 29.3 (both s, C_{3,5} of C₆H₁₁), 27.9 (vt, *N* 10.2, C_{2,6} of C₆H₁₁), 26.8 (s, C₄ of C₆H₁₁), 3.5, 2.9 (both s, CH₃CN), signal of RuCH not exactly located.

Compound **26**: NMR (CD₂Cl₂): δ_H (200 MHz, 273 K) 8.21-7.24 (20 H, m, C₆H₅), 4.64, 4.32, 3.98, 3.77 (2 H each, all s, C₅H₄), 1.71-0.82 (33 H, br m, C₆H₁₁), -19.58 (1 H, m, RuH); δ_H (200 MHz, 203 K) 8.23-6.67 (20 H, m, C₆H₅), 5.37, 4.71, 4.12, 3.90, 3.83, 3.80, 3.74, 3.66 (1 H each, all s, C₅H₄), 2.17-0.76 (33 H, br m, C₆H₁₁), -19.64 [1 H, dt, *J*(P,H) 43.6, *J*(P,H) 18.0, RuH); δ_C (100.6 MHz, 273 K) 140.8 [d, *J*(P,C) 44.8, *ipso*-C of C₆H₅], 137.3 [d, *J*(P,C) 11.4, C₆H₅], 135.1 [d, *J*(P,C) 38.1, *ipso*-C of C₆H₅], 132.5 [d, *J*(P,C) 8.6, C₆H₅], 129.7, 128.3 (both s, C₆H₅), 127.6 [d, *J*(P,C) 8.6, C₆H₅], 127.0 [d, *J*(P,C) 9.5, C₆H₅], 77.7 [d, *J*(P,C) 11.4, C₅H₄], 73.7 [d, *J*(P,C) 5.7, C₅H₄], 71.8 [d, *J*(P,C) 4.8, C₅H₄], 34.9 [d, *J*(P,C) 14.3, C1 of C₆H₁₁], 29.5 (s, C_{3,5} of C₆H₁₁), 27.5 [d, *J*(P,C) 8.6, C_{2,6} of C₆H₁₁], 26.5 (s, C₄ of C₆H₁₁).

Compound **27**: NMR (CD₂Cl₂): δ_H (200 MHz, 273 K) 7.38-6.74 (15 H, m, C₆H₅), 2.86 (6 H, s, CH₂), 1.92-1.25 (66 H, br m, C₆H₁₁), -15.40 (1 H, br s, RuH).

Compound **30**: NMR (CD₂Cl₂): δ_H (400 MHz) 2.50 (3 H, br s, CH₃CN), 2.40-1.18 (66 H, br m, C₆H₁₁), -15.96 (1 H, br s, RuH); δ_C (100.6 MHz) 129.9 (s, CN), 34.5 (vt, *N* 18.1, C1 of C₆H₁₁), 29.5 (s, C_{3,5} of C₆H₁₁), 27.0 (vt, *N* 10.5, C_{2,6} of C₆H₁₁), 25.9 (s, C₄ of C₆H₁₁), 3.9 (s, CH₃CN).

Compound **31**: NMR (CD₂Cl₂): δ_H (200 MHz) 9.63 [1 H, d, *J*(HH) 14.7, RuCH], 6.92 (5 H, m, C₆H₅), 5.82 [1 H, d, *J*(HH) 14.7, =CHPh], 2.52 (3 H, s, CH₃CN), 2.43-1.23 (66 H, br m, C₆H₁₁); δ_C (50.3 MHz) 150.0 [t, *J*(P,C) 10.2, RuCH], 139.5 (s, *ipso*-C of C₆H₅), 132.5 (br s, RuC=C), 128.2 (s, CN), 128.0, 124.3, 122.9 (all s, C₆H₅), 33.2 (vt, *N* 14.5, C1 of C₆H₁₁), 29.8,

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29.6 (both s, C3,5 of C₆H₁₁), 28.3, 27.8 (both m, C2,6 of C₆H₁₁), 26.8 (s, C4 of C₆H₁₁), 5.8 (s, CH₃CN).