Electronic Supplementary Information for Dalton Transactions

SUPPORTING INFORMATION

Ruthenium Xantphos Complexes in Hydrogen Transfer Processes: Reactivity and Mechanistic Studies

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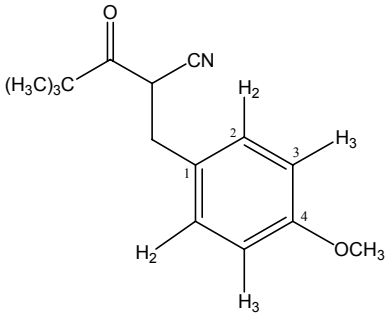
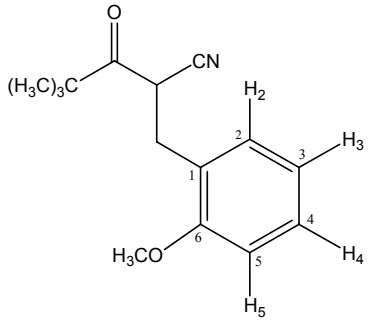
1. Spectroscopic and analytical data for alkylation products 7b-k from ketonitrile 6 listed in Table 2.

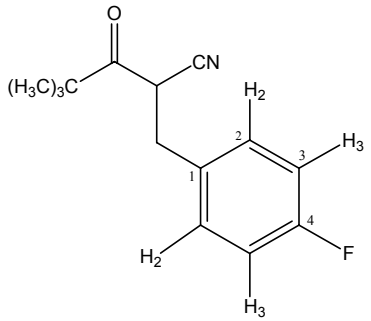


7b: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.10 (m, 2H; *H2*), 6.82 (m, 2H; *H3*), 3.99 (app t, $^{3}J_{HH}$ = 7.7 Hz, 1H; C*H*CN), 3.76 (s, 3H; OCH_3), 3.13 (dd, $^{2}J_{HH}$ = 13.8, $^{3}J_{HH}$ = 7.7 Hz, 1H; C*H*H), 3.05 (dd, $^{2}J_{HH}$ = 13.8, $^{3}J_{HH}$ = 7.7 Hz, 1H; CH*H*), 1.07 (s, 9H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 205.3 (*C*O), 159.2 (*C4*), 130.4 (*C2*), 128.4 (*C1*), 117.4 (*C*N), 114.4 (*C3*), 55.5 (O*C*H$_3$), 45.7 (*C*(CH$_3$)$_3$), 39.2 (*C*HCN), 35.5 (*C*H$_2$), 25.8 (C(*C*H$_3$)$_3$). HR-MS (ESI): m/z: calcd for [M+NH$_4$]$^{+}$: 263.1754; found: 263.1752.

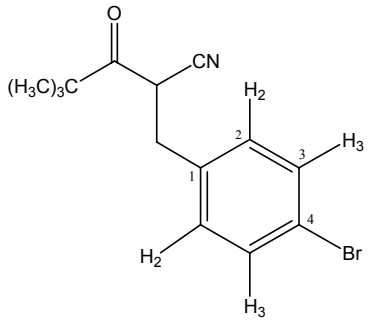


7c: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.18 (m, 1H; *H4*), 7.08 (m, 1H; *H2*), 6.82 (m, 1H; *H3*), 6.78 (m, 1H; *H5*), 4.23 (dd, $^{3}J_{HH}$ = 7.9, $^{3}J_{HH}$ = 7.0 Hz, 1H; C*H*CN), 3.78 (s, 3H; OCH_3), 3.10 (dd, $^{2}J_{HH}$ = 13.1, $^{3}J_{HH}$ = 7.0 Hz, 1H; C*H*H), 3.00 (dd, $^{2}J_{HH}$ = 13.1, $^{3}J_{HH}$ = 7.9 Hz, 1H; CH*H*), 1.02 (s,

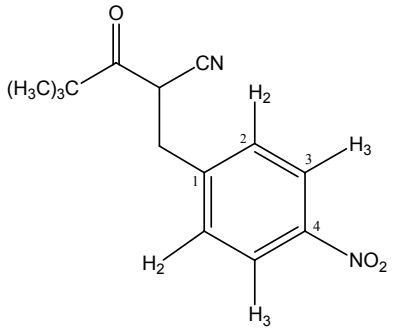
9H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 206.0 (*C*O), 157.6 (*C6*), 131.8 (*C2*), 129.4 (*C4*), 124.6 (*C1*), 121.2 (*C3*), 117.9 (*C*N), 110.6 (*C5*), 55.6 (O*C*H$_3$), 45.7 (*C*(CH$_3$)$_3$), 36.4 (*C*HCN), 32.3 (*C*H$_2$), 25.8 (C(*C*H$_3$)$_3$). HR-MS (ESI): m/z: calcd for [M+NH$_4$]$^+$: 263.1754; found: 263.1755.



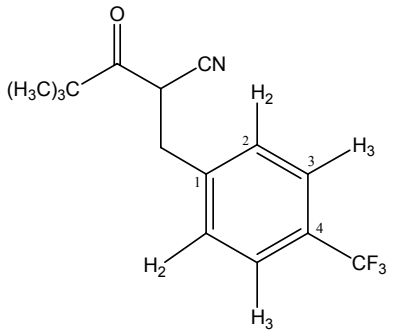
7d: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.16 (m, 2H; *H2*), 6.97 (m, 2H; *H3*), 4.00 (app t, $^3J_{HH}$ = 7.5 Hz, 1H; C*H*), 3.16 (dd, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 7.5 Hz, 1H; C*H*H), 3.08 (dd, $^2J_{HH}$ = 13.8, $^3J_{HH}$ = 7.5 Hz, 1H; CH*H*), 1.08 (s, 9H; C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 205.0 (*C*O), 162.4 (d, ^1J(C,F) = 246.1 Hz; *C4*), 132.2 (d, ^4J(C,F) = 3.4 Hz; *C1*), 131.0 (d, ^3J(C,F) = 8.1 Hz; *C2*), 117.1 (*C*N), 115.9 (d, ^2J(C,F) = 21.5 Hz; *C3*), 45.7 (*C*(CH$_3$)$_3$), 39.0 (*C*H), 35.3 (*C*H$_2$), 25.8 (C(*C*H$_3$)$_3$). IR (nujol, cm^{-1}): ν_{CN} = 2255 (s), 2244 (s), ν_{CO} = 17123 (s). HR-MS (ESI): m/z: calcd for [M+NH$_4$]$^+$: 251.1554; found: 251.1553.



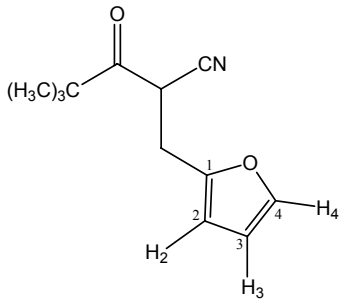
7e: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.44 (m, 2H; *H3*), 7.09 (m, 2H; *H2*), 3.96 (app t, $^{3}J_{HH}$ = 7.6 Hz, 1H; C*H*CN), 3.16 (dd, $^{2}J_{HH}$ = 13.6, $^{3}J_{HH}$ = 7.6 Hz, 1H; C*H*H), 3.08 (dd, $^{2}J_{HH}$ = 13.6, $^{3}J_{HH}$ = 7.6 Hz, 1H; CH*H*), 1.12 (s, 9H; C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 204.8 (*C*O), 135.5 (*C1*), 132.3 (*C3*), 131.2 (*C2*), 122.0 (*C4*), 117.0 (*C*N), 45.8 (*C*(CH$_3$)$_3$), 38.9 (*C*H), 35.5 (*C*H$_2$), 26.0 (C(*C*H$_3$)$_3$). HR-MS (ESI): m/z: calcd for $[M+NH_4]^+$: 311.0754; found: 311.0754.



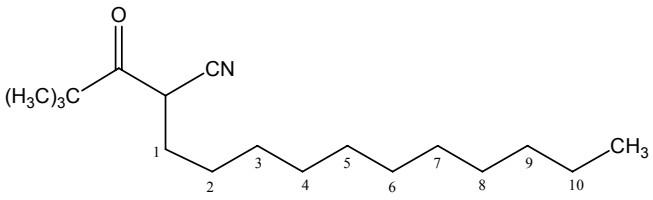
7f: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 8.18 (m, 2H; *H3*), 7.41 (m, 2H; *H2*), 4.03 (app t, $^{3}J_{HH}$ = 7.6 Hz, 1H; C*H*), 3.30 (dd, $^{2}J_{HH}$ = 13.7, $^{3}J_{HH}$ = 7.6 Hz, 1H; C*H*H), 3.23 (dd, $^{2}J_{HH}$ = 13.7, $^{3}J_{HH}$ = 7.6 Hz, 1H; CH*H*), 1.15 (s, 9H; C(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 204.3 (*C*O), 147.8 (*C1*), 144.0 (*C4*), 130.6 (*C2*), 124.4 (*C3*), 116.6 (*C*N), 45.9 (*C*(CH$_3$)$_3$), 38.6 (*C*H), 35.5 (*C*H$_2$), 26.2 (C(*C*H$_3$)$_3$). HR-MS (ESI): m/z: calcd for $[M+NH_4]^+$: 278.1499; found: 278.1502.



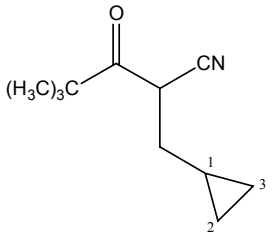
7g: ^{1}H NMR ($CDCl_3$, 300 MHz, 209 K): δ = 7.58 (m, 2H; *H3*), 7.35 (m, 2H; *H2*), 4.01 (app t, $^{3}J_{HH}$ = 7.6 Hz, 1H; C*H*), 3.25 (dd, $^{2}J_{HH}$ = 13.7, $^{3}J_{HH}$ = 7.6 Hz, 1H; C*H*H), 3.18 (dd, $^{2}J_{HH}$ = 13.7, $^{3}J_{HH}$ = 7.6 Hz, 1H; CH*H*), 1.13 (s, 9H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 204.7 (*C*O), 140.6 (*C1*), 130.3 (q, $^{2}J_{CF}$ = 32.9 Hz; *C4*), 129.9 (*C2*), 126.1 (q, $^{3}J_{CF}$ = 3.8 Hz; *C3*), 124.3 (q, $^{1}J_{CF}$ = 272.4 Hz; CF_3), 116.9 (*C*N), 45.9 (*C*(CH$_3$)$_3$), 38.9 (*C*H), 35.7 (*C*H$_2$), 26.1 (C(*C*H$_3$)$_3$). HR-MS (ESI): m/z: calcd for [M+NH$_4$]$^{+}$: 301.1522; found: 301.1521.



7h: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 7.32 (m, 1H; *H4*), 6.28 (m, 1H; *H3*), 6.15 (m, 1H; *H*$_2$), 4.18 (dd, $^{3}J_{HH}$ = 8.0, $^{3}J_{HH}$ = 6.9 Hz, 1H; C*H*), 3.27 (dd, $^{2}J_{HH}$ = 15.0, $^{3}J_{HH}$ = 8.0 Hz, 1H; C*H*H), 3.17 (dd, $^{2}J_{HH}$ = 15.0, $^{3}J_{HH}$ = 6.9 Hz, 1H; CH*H*), 1.14 (s, 9H; C(CH_3)$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 204.7 (*C*O), 149.8 (*C1*), 142.6 (*C4*), 117.0 (*C*N), 111.0 (*C3*), 108.8 (*C2*), 46.1 (*C*(CH$_3$)$_3$), 36.2 (*C*H), 28.9 (*C*H$_2$), 26.0 (C(*C*H$_3$)$_3$).

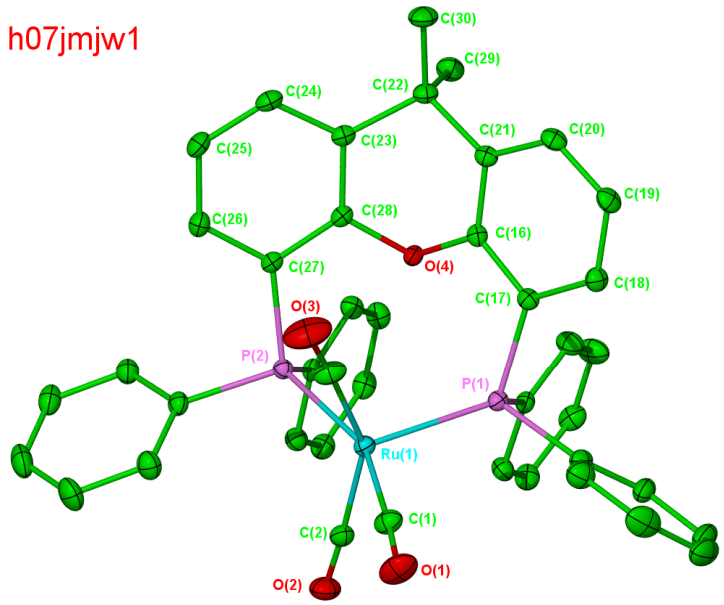


7j: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 3.79 (dd, $^{3}J_{HH}$ = 8.4, $^{3}J_{HH}$ = 6.4 Hz, 1H; C*H*), 1.85-1.25 (m, 20H, alkyl CH_2), 1.23 (s, 9H; C(CH_3)$_3$), 0.87 (t, $^{3}J_{HH}$ = 6.7 Hz, 3H; CH_3). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 205.9 (*C*O), 117.8 (*C*N), 45.8 (*C*(CH$_3$)$_3$), 37.4 (*C*H), 32.2 (*C1*), 30.3 (*C2*), 29.9 (*C3/4*), 29.8 (*C5*), 29.6 (*C6*), 29.5 (*C7*), 29.3 (*C8*), 27.5 (*C9*), 26.4 (C(*C*H$_3$)$_3$), 23.0 (*C10*), 14.4 (*C*H$_3$). HR-MS (ESI): m/z: calcd for [M+NH$_4$]$^{+}$: 297.2900; found: 297.2900.



7k: ^{1}H NMR ($CDCl_3$, 300 MHz, 298 K): δ = 3.91 (app t, $^{3}J_{HH}$ = 7.4 Hz, 1H; C*H*), 1.76 (m, 2H; CH_2), 1.22 (s, 9H; C(CH_3)$_3$), 0.77 (m, 1H; *H1*), 0.52 (m, 2H, *H2*/*H3*), 0.15 (m, 2H; *H2H3*). ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz, 298 K): δ = 205.8 (*C*O), 117.9 (*C*N), 45.9 (*C*(CH$_3$)$_3$), 37.5 (*C*H), 35.6 (*C*H$_2$), 26.4 (C(*C*H$_3$)$_3$), 9.4 (*C1*), 5.1 (*C2/3*). HR-MS (ESI): m/z: calcd for [M+NH$_4$]$^{+}$: 197.1648; found: 197.1647.

2. X-ray crystal structure of 22



Molecular structure of **22**. All hydrogen atoms are omitted. Thermal ellipsoids are shown at the 30% probability level

Table S-1. Crystal data and structure refinement for **22**.

Compound	**22**
Empirical formula	$C_{48}H_{38}O_4P_2Ru$
Formula weight	841.79
T / K	150(2)
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	*P*21/*c*
a / Å	10.7330(1)
b / Å	28.5420(2)
c / Å	3.0640(1)
β / º	96.661(1)
U / Å^3	3975.03(6)
Z	4
D_{calc} / Mg/m^3	1.407
μ / mm^{-1}	0.520
F(000)	1728
Crystal size / mm	0.25 x 0.25 x 0.10
Theta range for data collection / º	3.55 to 27.50
Index ranges	-13<=h<=12; -36<=k<=37; -16<=l<=16
Reflections collected	57366

Independent reflections, R_{int}	9072, 0.0489
Reflections observed (>2σ)	7068
Data Completeness	0.995
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.91, 0.85
Data / restraints / parameters	9072 / 0 / 499
Goodness-of-fit on F^2	1.027
Final $R1$, $wR2$ indices [I>2σ(I)]	0.0344, 0.0840
Final $R1$, $wR2$ indices (all data)	0.0540, 0.0917
Largest diff. peak and hole / eÅ^{-3}	0.454, -0.506

Notes: Asymmetric unit also contains 1 molecule of benzene.