Supporting Information

Accelerated Ru–Cu Trinuclear Cooperative C–H Bond Functionalization of Carbazoles: A Kinetic and Computational Investigation

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Supporting Information

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General methods

All reactions were carried out in dried reaction vessels with sealed Teflon screw caps under oxygen or nitrogen, unless otherwise specified. NMR spectra were obtained on Bruker Avance 400 using CDCl$_3$, CD$_2$Cl$_2$ or (CD$_3$)$_2$SO as solvents, with proton and carbon resonances at 400 MHz and 101 MHz, respectively. Coupling constants ($J$) are quoted in Hz. Flash chromatography was performed on silica gel (40-63 mesh) by standard technique. For the preparative HPLC the following conditions were used: HPLC, UltiMate 3000 Pump, UltiMate 3000 Autosampler, UltiMate 3000 Variable Wavelength Detector, UltiMate 3000 Fraction Collector, column: Supelco™ Ascentis® C18, 25 cm x 21.2 mm, 5 μm. Analysis was performed on the program Chromeleon 6.8. Temperature: 25 °C; Flow: 10 mL/min; Gradient (water/acetonitrile): 0–20 min, linear increase from 65% to 95% ACN; 20–40 min, 95% ACN; 40–55 min 100% ACN; 55–761 min, linear decrease to 65% ACN. HRMS spectra were recorded on WATERS GCT-Premier™ mass spectrometer. Some substrates were purchased either from Sigma Aldrich, Acros, ABCR, chemPUR, or TCI, and engaged directly. Other substrates were prepared according to standard procedures.
I: Optimization

Note: The absence of the Ru-salt leads to complete loss of conversion (2a, 0%). Moreover, it is possible to work with catalytic loadings of Cu-salts, down to 2 mol% (see manuscript: kinetic investigations). However, 1.1 equivalent of Cu-salt is usually employed as a precaution, in particular when exploring new potentially onerous substrates.

| solvents\(^1\) | ratio | isolated yield (%) |
|----------------|-------|--------------------|
| **p-DCB**      | 4     |                    |
| PhCl           | 1     | 40 (150 °C)        |
| AcOH           | 1     |                    |
| **p-DCB**      | 1     |                    |
| C\(_2\)Cl\(_4\) | 4     | 24 (150 °C)        |
| AcOH           | 1     |                    |
| **p-DCB**      | 5     | 36 (150 °C)        |
| AcOH           | 1     |                    |
| C\(_2\)Cl\(_4\) | 1     |                    |
| PhCl           | 4     | 40 (150 °C)        |
| AcOH           | 1     |                    |
| PhCl           | 5     | 39 (140 °C)        |
| AcOH           | 1     | 42 (150 °C)        |
| C\(_2\)Cl\(_4\) | 1     |                    |
| PhCl           | 4     | 37 (140 °C)        |
| AcOH           | 1     |                    |
| C\(_2\)Cl\(_4\) | 4     | 43 (140 °C)        |
| PhCl           | 1     | 52 (150 °C)        |
| AcOH           | 1     |                    |

\(^1\) p-DCB = 1,4-dichlorobenzene, AcOH = acetic acid, C\(_2\)Cl\(_4\) = tetrachloroethylene, PhCl = chlorobenzene
II: General procedure

General procedure for dehydrogenative amination reaction of carbazoles

Unless otherwise specified, the substrate 1 (1.00 mmol), ([Ru-complex6]$_2$ = dichlorodi-$\mu$-chlorobis[[1,2,3,6,7,8-$\eta$-2,7-dimethyl-2,6-octadiene-1,8-diyl]diruthenium(IV) (3.10 mg, 5.00 $\times$ 10$^{-3}$ mmol) (cond. B) or ([Ru-complex3]$_2$L$_4$) = [Ru(p-cymene)Cl$_2$]$_2$ (3.10 mg, 5.00 $\times$ 10$^{-3}$ mmol) with the ligand (L$_4$) 1,1'-bis(diphenylphosphino)ferrocene (2.80 mg, 5.00 $\times$ 10$^{-3}$ mmol) (cond. C), Cu(OAc)$_2$ (200 mg, 1.10 mmol), C$_2$Cl$_4$ (1.00 mL), AcOH (0.250 mL) and PhCl (0.250 mL) were united under air in a 85 mL reactor equipped with a Teflon screw cap. The reactor was flushed with oxygen and sealed (oxygen pressure of approx. 1.5 bars), after which the reaction mixture was stirred at 150 °C for 24 h. The reactor was then cooled to room temperature and the crude directly engaged (unless otherwise specified) on SiO$_2$ gel column chromatography for purification, which gave the desired product after concentration in vacuo.

III: Product characterization

Synthesis of 2a

Following general procedure A, using 9H-carbazole (167 mg, 1.00 mmol). The crude product was purified over a plug of SiO$_2$ with DCM in order to remove metals and ease the following purification. After concentration, the mixture was engaged by SiO$_2$ gel column chromatography pentane/CH$_2$Cl$_2$ = 6:4. Isolated yield: cond. B: 65%, cond. C: 80% (white solid).

$^1$H-NMR (400 MHz, DMSO-d$_6$): δ (ppm) = 11.00 (s, NH), 8.35 (d, $^3$J = 8.0 Hz, 1H), 8.32 (d, $^3$J = 8.0 Hz, 2H), 8.24 (d, $^3$J = 8.0 Hz, 1H), 7.53 (d, $^3$J = 7.4 Hz, 1H), 7.42–7.37 (m, 5H), 7.33–7.29 (m, 2H), 7.24–7.20 (m, 1H), 7.06 (d, $^3$J = 8.0 Hz, 2H).
$^{13}$C-$^1$H-NMR (101 MHz, DMSO-d$_6$): $\delta$ (ppm) = 140.7 (s, C$_{quat}$), 140.1 (s, C$_{quat}$), 136.3 (s, C$_{quat}$), 126.1 (s, CH), 125.0 (s, C$_{quat}$), 124.7 (s, CH), 122.9 (s, C$_{quat}$), 122.5 (s, C$_{quat}$), 120.5 (s, CH), 120.4 (s, C$_{quat}$), 119.8 (s, CH), 119.3 (s, CH), 119.1 (s, CH), 111.5 (s, CH), 109.8 (s, CH). Two CH lines overlapped.

**Elemental Analysis:** C$_{24}$H$_{16}$N$_2$

Calculated:  N: 8.43%  C: 86.72%  H: 4.85%
Found:  N: 8.31%  C: 86.25%  H: 5.15%

HRMS-TOF [EI]: m/z calc.: 332.1313 [C$_{24}$H$_{16}$N$_2$]+, measured 332.1313.

IR (neat, cm$^{-1}$): $\tilde{\nu}$ = 3454, 3391, 3059, 1624, 1585, 1448, 1429, 1369, 1313, 1229, 1197, 1161, 1148, 1117, 745, 722, 766.

**Synthesis of 2b**

Following general procedure A, using 3,6-dichloro-9H-carbazole (236 mg, 1.00 mmol). The crude product was purified by SiO$_2$ gel column chromatography pentane/CH$_2$Cl$_2$ = 6:4. Isolated yield: **cond. B:** 78%, **cond. C:** 73% (white solid).

$^1$H-NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) = 11.27 (s, NH), 8.49 (d, $^{4}J$ = 1.9 Hz, 1H), 8.43 (d, $^{4}J$ = 2.0 Hz, 2H), 8.35 (d, $^{4}J$ = 2.0 Hz, 1H), 7.63 (d, $^{4}J$ = 2.0 Hz, 1H), 7.47–7.41 (m, 3H), 7.35 (d, $^{3}J$ = 8.5 Hz, 1H), 7.04 (d, $^{3}J$ = 8.8 Hz, 2H).

$^{13}$C-$^1$H-NMR (101 MHz, DMSO-d$_6$): $\delta$ (ppm) = 139.6 (s, C$_{quat}$), 139.1 (s, C$_{quat}$), 135.4 (s, C$_{quat}$), 127.0 (s, CH), 127.0 (s, CH), 125.3 (s, CH), 125.2 (s, C$_{quat}$), 125.0 (s, C$_{quat}$), 124.0 (s, C$_{quat}$), 123.6 (s, C$_{quat}$), 123.4 (s, C$_{quat}$), 123.1 (s, C$_{quat}$), 121.4 (s, CH), 120.8 (s, CH), 120.7 (s, CH), 120.3 (s, C$_{quat}$), 113.3 (s, CH), 111.7 (s, CH).

$^1$H-NMR (400 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 8.20 (d, $^{4}J$ = 1.9 Hz, 1H), 8.15 (d, $^{4}J$ = 1.9 Hz, 2H), 8.11 (d, $^{4}J$ = 2.1 Hz, 1H), 7.92 (broad s, NH), 7.62 (d, $^{4}J$ = 1.9 Hz, 1H), 7.45–7.39 (m, 3H), 7.28 (d, $^{3}J$ = 8.6 Hz, 1H), 7.15 (d, $^{3}J$ = 8.8 Hz, 2H).

$^{13}$C-$^1$H-NMR (101 MHz, CD$_2$Cl$_2$): $\delta$ (ppm) = 139.8 (s, C$_{quat}$), 138.8 (s, C$_{quat}$), 135.4 (s, C$_{quat}$), 128.1 (s, CH), 127.7 (s, CH), 126.9 (s, CH), 126.5 (s, C$_{quat}$), 126.3 (s, C$_{quat}$), 125.9 (s, C$_{quat}$), 125.9
(s, C_{quat.}), 124.4 (s, C_{quat.}), 124.1 (s, C_{quat.}), 121.2 (s, CH), 121.0 (s, CH), 121.0 (s, CH), 113.0 (s, CH), 111.9 (s, CH). One C_{quat.} line overlapped.

**HRMS-TOF [EI^+]:** m/z calc.: 467.9755 [C_{24}H_{1235}Cl_4N_2]^+, measured: 467.9722
469.9725 [C_{24}H_{1235}Cl_3ClN_2]^+, measured: 469.9707
471.9696 [C_{24}H_{1235}Cl_2Cl_2N_2]^+, measured: 471.9688
473.9666 [C_{24}H_{1235}Cl_3N_2]^+, measured: 473.9673.

**IR (neat, cm⁻¹):** 3423, 2917, 1584, 1472, 1441, 1279, 1231, 1063, 861, 812, 799, 757, 684.

**Synthesis of 2c**

Following general procedure A, using 3,6-dibromo-9H-carbazole (325 mg, 1.00 mmol). The crude product was purified by SiO₂ gel column chromatography pentane/CH₂Cl₂ = 6:4. Isolated yield: **cond. B:** 40%, **cond. C:** 71% (light green solid).

**¹H-NMR (400 MHz, DMSO-d₆):** δ (ppm) = 11.38 (s, NH), 8.73–8.59 (m, 4H), 7.81 (s, 1H), 7.55 (d, 3J = 8.0 Hz, 3H), 7.33 (d, 3J = 8.0 Hz, 1H), 7.08 (d, 2J = 8.0 Hz, 2H).

**¹³C{¹H}-NMR (101 MHz, DMSO-d₆):** δ (ppm) = 139.6 (s, Cₜ₅), 139.1 (s, Cₜ₅), 135.6 (s, Cₜ₅), 129.5 (s, CH), 127.7 (s, CH) 125.6 (s, Cₜ₅), 124.3 (s, CH), 124.0 (s, Cₜ₅), 123.7 (s, CH), 123.7 (s, CH), 123.5 (s, Cₜ₅), 120.4 (s, Cₜ₅), 113.6 (s, CH), 112.6 (s, Cₜ₅), 112.0 (s, CH), 111.7 (s, Cₜ₅), 110.6 (s, Cₜ₅). One CH line overlapped.

**HRMS-TOF [EI^+]:** m/z calc.: 467.7734 [C_{24}H_{1235}Br_4N_2]^+, measured: 467.7734
469.7693 [C_{24}H_{1235}Br_3BrN_2]^+, measured: 469.7695
651.7652 [C_{24}H_{1235}Br_3N_2]^+, measured: 651.7726.

**IR (neat, cm⁻¹):** 3067, 2998, 2951, 1719, 1597, 1584, 1477, 1433, 1393, 1276, 1180, 1107, 1087, 1068, 1017, 761, 751, 742, 720, 692, 673.
Synthesis of 2d

Following general procedure A, using 3,6-diphenyl-9H-carbazole (319 mg, 1.00 mmol). The crude product was purified by SiO₂ gel column chromatography pentane/CH₂Cl₂ = 6:4. Isolated yield: cond. B: 81%, cond. C: 95% (white solid).

¹H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.53–8.52 (m, 3H), 8.46 (d, J = 1.6 Hz, 1H), 7.95 (d, J = 1.6 Hz, 1H), 7.85 (broad s, NH), 7.82–7.74 (m, 8H), 7.71–7.67 (m, 3H), 7.54–7.49 (m, 8H), 7.42–7.39 (m, 6H), 7.34 (s, 1H).

¹³C{¹H}-NMR (101 MHz, CDCl₃): δ (ppm) = 141.9 (s, C_quat.), 141.2 (s, C_quat.), 140.7 (s, C_quat.), 139.4 (s, C_quat.), 135.8 (s, C_quat.), 134.4 (s, C_quat.), 134.2 (s, C_quat.), 134.0 (s, C_quat.), 129.2 (s, CH), 129.0 (s, CH), 127.5 (s, CH), 127.2 (s, CH), 126.9 (s, CH), 126.6 (s, CH), 126.2 (s, CH), 124.5 (s, C_quat.), 124.3 (s, CH), 124.3 (s, C_quat.), 121.0 (s, C_quat.), 119.3 (s, CH), 118.9 (s, CH), 111.6 (s, CH), 110.7 (s, CH). Many lines are overlapped.

HRMS-TOF [EI+]: am/z calc.: 636.2565 [C₄₈H₃₂N₂]+, measured 636.2571.

IR (neat, cm⁻¹): ɵ = 3412, 3029, 2921, 1597, 1577, 1473, 1460, 1399, 1373, 1281, 1267, 1229, 1188, 1134, 878, 869, 813, 756, 734, 692, 660.
Synthesis of 2e

Following general procedure A, using 3,6-di-tert-butyl-9H-carbazole (279 mg, 1.00 mmol). The crude product was purified over a plug of SiO₂ with DCM in order to remove metals and ease the following purification. After concentration, the mixture was engaged by SiO₂ gel column chromatography pentane/CH₂Cl₂ = 6:4. Isolated yield: cond. B: 97%, cond. C: 84% (white solid).

^1H-NMR (400 MHz, CDCl₃): δ (ppm) = 8.24–8.18 (m, 4H), 7.64 (broad s, NH), 7.63 (s, 1H), 7.49–7.45 (m, 3H), 7.22 (d, 3J = 8.0 Hz, 1H), 7.15 (d, 3J = 8.0 Hz, 2H), 1.50 (s, 27H), 1.48 (s, 9H).

^13C{^1H}-NMR (101 MHz, CDCl₃): δ (ppm) = 143.4 (s, C_quat.), 142.9 (s, C_quat.), 142.8 (s, C_quat.), 139.1 (s, C_quat.), 137.8 (s, C_quat.), 134.2 (s, C_quat.), 125.4 (s, C_quat.), 124.2 (s, CH), 123.8 (s, CH), 123.4 (s, C_quat.), 123.4 (s, C_quat.), 122.4 (s, CH), 120.4 (s, C_quat.), 116.4 (s, CH), 116.4 (s, CH), 115.7 (s, CH), 110.4 (s, CH), 35.0 (s, C_quat.), 34.8 (s, C_quat.), 34.8 (s, C_quat.), 32.1 (s, CH₃), 32.0 (s, CH₃). One tBu line overlapped.

^1H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 10.65 (s, NH), 8.35 (m, 3H), 8.26 (d, 3J = 1.8 Hz, 1H), 7.46–7.41 (m, 4H), 7.27 (d, 3J = 8.5 Hz, 1H), 6.96 (d, 3J = 8.6 Hz, 2H), 1.44 (s, 9H), 1.43 (s, 18H), 1.41 (s, 9H).

HRMS-TOF [EI⁺]: m/z calc.: 556.3817 [C₄₀H₄₈N₂]^+; measured 556.3826.

IR (neat, cm⁻¹): ̅ = 3407, 3059, 2920, 2853, 1574, 1484, 1464, 1435, 1393, 1349, 1317, 1278, 1237, 1226, 1145, 1133, 1052, 1019, 981, 857, 850, 792, 759, 740.
Synthesis of 2f

Following general procedure A, using 3,6-dimethyl-9H-carbazole (195 mg, 1.00 mmol). The crude product was purified by SiO₂ gel column chromatography pentane/CH₂Cl₂ = 6:4. Isolated yield: cond. B: 48%, cond. C: 54% (white solid).

\(^1\)H-NMR (400 MHz, CDCl₃): \(\delta\) (ppm) = 8.00 (s, 2H), 7.98 (s, 1H), 7.94 (s, 1H), 7.55 (broad s, NH), 7.41 (s, 1H), 7.22–7.20 (m, 3H), 7.14 (d, \(J = 8.0\) Hz, 2H), 7.11 (d, \(J = 8.0\) Hz, 1H), 2.63 (s, 3H), 2.59 (s, 6H), 2.56 (s, 3H).

\(^{13}\)C{\(^1\)H}-NMR (101 MHz, CDCl₃): \(\delta\) (ppm) = 139.3 (s, C_{quat.}), 138.0 (s, C_{quat.}), 134.5 (s, C_{quat.}), 129.5 (s, C_{quat.}), 129.3 (s, C_{quat.}), 129.2 (s, C_{quat.}), 127.7 (s, CH), 127.4 (s, CH), 125.7 (s, CH), 125.6 (s, C_{quat.}), 123.6 (s, C_{quat.}), 123.6 (s, C_{quat.}), 120.7 (s, C_{quat.}), 120.5 (s, CH), 120.0 (s, CH), 110.7 (s, CH), 109.9 (s, CH), 21.6 (s, CH₃). One CH and two CH₃ lines are overlapped.

HRMS-TOF [EI⁺]: \(m/z\) calc.: 388.1939 [C₂₈H₂₄N₂]⁺, measured 388.1928.

IR (neat, cm⁻¹): \(\tilde{\nu}\) = 3405, 3022, 2917, 2857, 1593, 1464, 1396, 1367, 1294, 1270, 1235, 1201, 1139, 1034, 869, 851, 799, 766, 731, 669, 660, 654.

Synthesis of 2g

Following general procedure A, using 2-trifluoromethyl-9H-carbazole (235 mg, 1.00 mmol). The crude product was purified over a plug of SiO₂ with DCM in order to remove metals and ease the following purification. After concentration, the mixture was engaged by SiO₂ gel column chromatography pentane/CH₂Cl₂ = 6:4. Isolated yield: cond. B: 41%, cond. C: 8% (white solid).
**1H-NMR (400 MHz, CD$_2$Cl$_2$):** $\delta$ (ppm) = 8.36 (d, $^3J = 8.0$ Hz, 2H), 8.30 (d, $^3J = 8.1$ Hz, 2H), 8.05 (s, NH), 7.71 (dd, $^3J = 7.5$ Hz, $J = 0.8$ Hz, 1H), 7.64 (d, $^3J = 8.2$ Hz, 1H), 7.58–7.54 (m, 4H), 7.49 (~td, $^3J = 7.0$ Hz, $J = 1.1$ Hz, 1H), 7.41 (~td, $^3J = 7.0$ Hz, $J = 0.9$ Hz, 1H), 7.20 (d, $^3J = 8.2$ Hz, 1H).

**13C{1H}-NMR (101 MHz, CD$_2$Cl$_2$):** $\delta$ (ppm) = 142.1 (s, C$_{quat}$), 140.5 (s, C$_{quat}$), 139.0 (s, C$_{quat}$), 137.4 (s, C$_{quat}$), 128.6 (q, $^3J = 31.9$ Hz, C$_{quat}$), 128.3 (q, $^3J = 31.9$ Hz, C$_{quat}$), 128.1 (s, CH), 126.7 (s, CH), 126.4 (s, C$_{quat}$), 125.3 (s, C$_{quat}$), 125.2 (q, $^3J = 272.6$ Hz, C$_{quat}$), 125.2 (q, $^3J = 272.6$ Hz, C$_{quat}$), 123.0 (s, C$_{quat}$), 121.9 (s, CH), 121.6 (s, CH), 121.5 (s, CH), 121.4 (s, CH), 121.4 (s, CH), 120.6 (s, C$_{quat}$), 117.4 (q, $^3J = 3.6$ Hz, CH), 117.2 (q, $^3J = 3.6$ Hz, CH), 110.7 (s, CH), 108.8 (q, $^3J = 3.7$ Hz, CH), 107.6 (q, $^3J = 3.6$ Hz, CH). One CH and one C$_{quat}$ lines are overlapped.

**19F{1H}-NMR (376 MHz, CD$_2$Cl$_2$):** $\delta$ (ppm) = -61.15, -61.40.

**HRMS-TOF [EI⁺]:** m/z calc.: 468.1061 [C$_{26}$H$_{14}$F$_6$N$_2$]$,^+$, measured: 468.1052.

**IR (neat, cm$^{-1}$):** $\tilde{\nu} = 3460, 3069, 1631, 1591, 1509, 1476, 1460, 1442, 1365, 1320, 1279, 1255, 1238, 1213, 1199, 1159, 1107, 1080, 1053, 972, 945, 915, 868, 822, 792, 770, 748, 726, 706, 664.

**Synthesis of 2h**

![Chemical Structure](Image)

Chemical Formula: C$_{28}$H$_{20}$N$_2$O$_2$

Molecular Weight: 392.4492

m/z: 392.1525 (100.0%), 393.1558 (28.1%), 394.1592 (3.8%)

Elemental Analysis: C, 79.57; H, 5.14; N, 7.14; O, 8.15

Following general procedure A, using 3-methoxy-9H-carbazole (197 mg, 1.00 mmol). The crude product was purified by SiO$_2$ gel column chromatography pentane/toluene = 1:1. Isolated yield: cond. B: 36%, cond. C: 68% (NMR yield) (white solid).

**1H-NMR (400 MHz, CD$_2$Cl$_2$):** $\delta$ (ppm) = 8.17 (d, $^3J = 7.7$ Hz, 1H), 8.12 (d, $^3J = 7.9$ Hz, 1H), 7.73 (d, $^3J = 2.3$ Hz, 1H), 7.72 (broad s, NH), 7.69 (d, $^3J = 2.4$ Hz, 1H), 7.42–7.39 (m, 2H), 7.32–7.20 (m, 5H), 7.16 (d, $^3J = 8.9$ Hz, 1H), 7.05–7.01 (m, 1H), 3.97 (s, 3H), 3.94 (s, 3H).

**13C{1H}-NMR (101 MHz, CD$_2$Cl$_2$):** $\delta$ (ppm) = 155.2 (s, C$_{quat}$), 154.8 (s, C$_{quat}$), 141.6 (s, C$_{quat}$), 140.7 (s, C$_{quat}$), 136.0 (s, C$_{quat}$), 131.3 (s, C$_{quat}$), 127.0 (s, CH), 126.7 (s, CH), 126.3 (s, C$_{quat}$), 124.5 (s, C$_{quat}$), 124.0 (s, C$_{quat}$), 123.8 (s, C$_{quat}$), 121.8 (s, C$_{quat}$), 121.0 (s, CH), 120.9 (s, CH), 120.3 (s, CH), 120.0 (s, CH), 115.6 (s, CH), 113.8 (s, CH), 111.6 (s, CH), 111.4 (s, CH), 110.7 (s, CH), 103.9 (s, CH), 103.8 (s, CH), 56.8 (s, OCH$_3$), 56.5 (s, OCH$_3$).

**HRMS-TOF [EI⁺]:** m/z calc.: 392.1525 [C$_{26}$H$_{20}$N$_2$O$_2$]$^+$, measured: 392.1527.
IR (neat, cm⁻¹): δ = 3401, 3308, 2928, 2833, 1592, 1484, 1455, 1428, 1321, 1285, 1202, 1148, 1031, 905, 747, 730.

Synthesis of 2i

Following general procedure A, using 2-methoxy-9H-carbazole (197 mg, 1.00 mmol). The crude product was purified by SiO₂ gel column chromatography pentane/EA = 9:1. Isolated yield: cond. B: 26%, cond. C: 30% (NMR yield: 37%)(light yellow solid).

¹H-NMR (400 MHz, DMSO-d₆): δ (ppm) = 10.77 (s, NH), 8.29 (d, ³J = 8.6 Hz, 1H), 8.17–8.12 (m, 3H), 7.29–7.14 (m, 6H), 6.89 (dd, ³J = 8.6 Hz, ⁴J = 2.3 Hz, 1H), 6.82 (m, 1H), 6.35 (d, ⁴J = 2.3 Hz, 1H), 3.73 (s, CH₃), 3.66 (s, CH₃).

¹³C{¹H}-NMR (101 MHz, DMSO-d₆): δ (ppm) = 158.8 (s, C_quat.), 154.6 (s, C_quat.), 142.0 (s, C_quat.), 140.6 (s, C_quat.), 140.4 (s, C_quat.), 138.4 (s, C_quat.), 124.9 (s, CH), 124.5 (s, CH), 123.1 (s, C_quat.), 122.8 (s, C_quat.), 121.4 (s, CH), 121.2 (s, CH), 119.6 (s, CH), 119.5 (s, CH), 119.4 (s, CH), 119.0 (s, CH), 118.3 (s, C_quat.), 116.7 (s, C_quat.), 111.1 (s, CH), 109.5 (s, CH), 108.2 (s, CH), 106.9 (s, C_quat.), 104.7 (s, CH), 93.6 (s, CH), 56.2 (s, CH₃), 55.2 (s, CH₃).

HRMS-TOF [EI⁺]: m/z calc.: 392.1525 [C₂₆H₂₀N₂O₂]*, measured: 392.1548.

IR (neat, cm⁻¹): δ = 3336, 2918, 2846, 1628, 1614, 1598, 1517, 1499, 1490, 1460, 1432, 1399, 1321, 1291, 1258, 1230, 1205, 1194, 1171, 1159, 1151, 1127, 1118, 1082, 1073, 1030, 1015, 997, 946, 931, 819, 811, 801, 782, 735, 722.
Synthesis of \(2j\)

Following general procedure A, using 9,3',6',9''-ter-9\(H\)-carbazole (498 mg, 1.00 mmol). The crude product was purified by SiO\(_2\) gel column chromatography pentane/toluene = 1:2. Isolated yield: \textbf{cond. B}: 56\%, \textbf{cond. C}: 57\% (light yellow solid).

\(^1\)H-NMR (400 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 11.90 (s, NH), 8.85 (s, 1H), 8.75 (s, 2H), 8.69 (s, 1H), 8.18 (m, 8H), 8.03 (s, 1H), 7.80 (d, \(J = 8.5\) Hz, 1H), 7.64 (m, 5H), 7.56 (d, \(J = 8.2\) Hz, 2H), 7.43–7.37 (m, 14H), 7.25–7.21 (m, 8H).

\(^{13}\)C\(^{\text{1H}}\)-NMR (101 MHz, DMSO-\(d_6\)): \(\delta\) (ppm) = 141.3 (s, C\(_{\text{quat.}}\)), 141.2 (s, C\(_{\text{quat.}}\)), 141.1 (s, C\(_{\text{quat.}}\)), 140.6 (s, C\(_{\text{quat.}}\)), 140.1 (s, C\(_{\text{quat.}}\)), 136.6 (s, C\(_{\text{quat.}}\)), 129.8 (s, C\(_{\text{quat.}}\)), 128.9 (s, C\(_{\text{quat.}}\)), 126.3 (s, CH), 126.2 (s, CH), 126.2 (s, CH), 126.1 (s, C\(_{\text{quat.}}\)), 124.8 (s, CH), 124.2 (s, C\(_{\text{quat.}}\)), 123.8 (s, C\(_{\text{quat.}}\)), 122.6 (s, C\(_{\text{quat.}}\)), 122.5 (s, C\(_{\text{quat.}}\)), 121.2 (s, CH), 120.8 (s, C\(_{\text{quat.}}\)), 120.5 (s, CH), 120.4 (s, CH), 119.9 (s, CH), 119.8 (s, CH), 119.7 (s, CH), 113.3 (s, CH), 111.7 (s, CH), 109.9 (s, CH), 109.7 (s, CH). Many overlapped lines.

IR (neat, cm\(^{-1}\)): \(\tilde{\nu} = 3398, 3048, 2921, 2851, 1625, 1596, 1494, 1467, 1449, 1400, 1333, 1313, 1280, 1226, 1172, 1154, 1118, 1020, 1003, 918, 877, 813, 744, 720.\)
Synthesis of 2k

Following general procedure A, using 3-methyl-9H-carbazole (181 mg, 1.00 mmol). The crude product was purified by SiO\textsubscript{2} gel column chromatography pentane/CH\textsubscript{2}Cl\textsubscript{2} = 7:3. Isolated yield: cond. B: 58\% (regioisomeric ratio = 1.3:1), cond. C: 66\% (regioisomeric ratio = 1.5:1) (white solid).

Observed NMR lines:

\textsuperscript{1}H-NMR (400 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 8.09 (d, \(J = 8.0\) Hz), 8.08 (d, \(J = 8.0\) Hz), 7.94 (s), 7.93 (s), 7.87 (s), 7.55 (broad s), 7.50 (dd, \(J = 7.5\) Hz, \(J = 1.0\) Hz), 7.34–7.00 (m), 2.54 (s), 2.49 (s), 2.46 (s).

\textsuperscript{13}C\{\textsuperscript{1}H\}-NMR (101 MHz, CDCl\textsubscript{3}): \(\delta\) (ppm) = 140.9 (s, C\textsubscript{quat.}), 140.9 (s, C\textsubscript{quat.}), 139.6 (s, C\textsubscript{quat.}), 139.0 (s, C\textsubscript{quat.}), 138.9 (s, C\textsubscript{quat.}), 137.5 (s, C\textsubscript{quat.}), 136.2 (s, C\textsubscript{quat.}), 134.1 (s, C\textsubscript{quat.}), 129.7 (s, C\textsubscript{quat.}), 129.5 (s, C\textsubscript{quat.}), 129.4 (s, C\textsubscript{quat.}), 127.8 (s, CH), 127.5 (s, CH), 126.3 (s, CH), 126.0 (s, CH), 125.8 (s, CH), 125.7 (s, C\textsubscript{quat.}), 125.5 (s, C\textsubscript{quat.}), 124.6 (s, CH), 123.3 (s, C\textsubscript{quat.}), 122.7 (s, C\textsubscript{quat.}), 120.5 (s, CH), 120.4 (s, CH), 120.1 (s, CH), 120.0 (s, CH), 119.9 (s, CH), 119.9 (s, CH), 119.9 (s, CH), 119.7 (s, CH), 111.0 (s, CH), 110.6 (s, CH), 110.1 (s, CH), 109.8 (s, CH), 21.5 (s, CH\textsubscript{3}), 21.4 (s, CH\textsubscript{3}). Many lines are overlapped.

HRMS-TOF [EI\textsuperscript{+}]: \(m/z\) calc.: 360.1626 [C\textsubscript{26}H\textsubscript{20}N\textsubscript{2}]\textsuperscript{+}, measured: 360.1616.

IR (neat, cm\textsuperscript{-1}): \(\tilde{\nu}\) = 3401, 3043, 2917, 1859, 1592, 1485, 1453, 1395, 1371, 1317, 1292, 1269, 1229, 1148, 1028, 905, 873, 847, 800, 769, 736, 724, 666.
Synthesis of 2m

Following general procedure A, using 2,7-dibromo-9H-carbazole (325 mg, 1.00 mmol). The crude product was purified over a plug of SiO$_2$ with DCM in order to remove metals and ease the following purification. After concentration, the mixture was engaged by SiO$_2$ gel column chromatography pentane/toluene = 2:1. Isolated yield: **cond. B**: 24%, **cond. C**: 43% (NMR: 49%) (white solid).

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ (ppm) = 8.11 (d, $^3J = 8.3$ Hz, 1H), 8.04 (d, $^3J = 8.3$ Hz, 2H), 8.00 (d, $^3J = 8.3$ Hz, 1H), 7.78 (broad s, NH), 7.69 (d, $^3J = 8.3$ Hz, 1H), 7.49–7.46 (m, 3H), 7.44 (d, $^3J = 8.3$ Hz, 1H), 7.13 (d, $^3J = 1.5$ Hz, 2H).

$^{13}$C{$^1$H}-NMR (101 MHz, CDCl$_3$): $\delta$ (ppm) = 140.8 (s, C$_{quat}$), 137.4 (s, C$_{quat}$), 124.4 (s, C$_{quat}$), 124.2 (s, CH), 124.1 (s, CH), 123.5 (s, CH), 123.2 (s, CH), 123.1 (s, CH), 121.8 (s, C$_{quat}$), 121.3 (s, C$_{quat}$), 120.9 (s, C$_{quat}$), 119.6 (s, C$_{quat}$), 118.2 (s, C$_{quat}$), 118.2 (s, C$_{quat}$), 114.4 (s, CH), 112.4 (s, CH). One CH and one C$_{quat}$ overlapping.

$^1$H-NMR (400 MHz, DMSO-d$_6$): $\delta$ (ppm) 11.44 (s, NH), 8.38 (d, $^3J = 8.4$ Hz, 1H), 8.32 (d, $^3J = 8.4$ Hz, 2H), 8.24 (d, $^3J = 8.4$ Hz, 1H), 7.70 (d, $^3J = 8.4$ Hz, 1H), 7.54–7.46 (m, 3 H), 7.40 (d, $^3J = 8.4$ Hz, $^4J = 1.8$ Hz, 1H), 7.07 (d, $^3J = 1.5$ Hz, 2H).

$^{13}$C{$^1$H}-NMR (101 MHz, DMSO-d$_6$): $\delta$ (ppm) = 141.2 (s, C$_{quat}$), 138.7 (s, C$_{quat}$), 123.9 (s, C$_{quat}$), 123.7 (s, CH), 123.5 (s, CH), 122.8 (s, CH), 122.7 (s, CH), 122.6 (s, CH), 121.8 (s, C$_{quat}$), 121.6 (s, C$_{quat}$), 120.3 (s, C$_{quat}$), 119.6 (s, C$_{quat}$), 119.4 (s, C$_{quat}$), 117.4 (s, C$_{quat}$), 114.2 (s, CH), 112.4 (s, CH). One CH and one C$_{quat}$ overlapping.

HRMS-TOF [EI$^+$]: $m/z$ calc.: 643.7693 [C$_{24}$H$_{12}^{129}$Br$_4$N$_2$]$^+$, measured: 643.7792
645.7713 [C$_{24}$H$_{12}^{129}$Br$_3^{13}$BrN$_2$]$^+$, measured: 645.7751
647.7693 [C$_{24}$H$_{12}^{129}$Br$_2^{13}$Br$_2$N$_2$]$^+$, measured: 647.7747.

IR (neat, cm$^{-1}$): $\tilde{v} = 3424, 2922, 2853, 1585, 1439, 1423, 1231, 1050, 951, 898, 792, 759, 736, 670.$
IV: Ru catalyst screening

The C1-N dehydrogenative dimerization of unfunctionalized 9H-carbazole served as the starting point for the optimization (Fig. S1). A broad screening of commercially available or easily accessible Ru catalyst candidates was thereafter performed (Ru-complexes 1-11, Fig. S1). Interestingly, [Ru-complex6]2 showed the best performance compared to all other Ru candidates with a significantly higher yield of 65% of the C1-N bicarbazole product. This represents a surprising finding because as far as we know, this isoprene based Ru-complex has never been utilized in C–H bond activation methods before. In contrast, the norbornadiene based Ru-complex10 catalyst candidate did not yield any conversion, perhaps because of solubility issues. In general, it can be noted that many of these Ru complexes display at least some catalytic activity in the reaction, indicating that catalytic activity is not limited to π-arene-Ru systems.

![Screening of various Ru catalysts](image)

Figure S1. Screening of various Ru catalysts, isolated yields. Note: Omitting the Ru-salt leads to complete loss of conversion (2a, 0%).

The effect of some phosphine ligands was then evaluated. In Buchwald-Hartwig amination methods, phosphorus-containing ligands are essential and have a large structural impact on the efficiency of the C-N bond formation process. Therefore, we started with the preparation of some Ru-catalysts that contain P-based ligands (Fig. S2). Interestingly, the performance of some of the Ru-phosphine-complexes were found to be in the same range as the best phosphine-free catalyst Ru-complex6 despite a reaction atmosphere of pure oxygen, possibly rendering the ligand inactive due to oxidation to phosphine oxide. RuCl2L2, containing XPhos, performed poorly, which was somewhat disappointing in the light of some promising C–H activation literature precedent by Ackermann. In the case of [Ru-complex3]2L4, the phosphine-based...
system even outperformed phosphine-free Ru-complex6 (Fig. S1). To our delight, this catalyst does not need to be pre-isolated in order to achieve a high yield of 80% of the C1-N bicarbazole.

Indeed, in situ formation from commercially available Ru-complex3 and dppf affords the same yield. Notably, any ferrocene-based deviations as well as any change in the Ru precursor did not increase the yield beyond 80% (see beneath). Thereby, we have identified two new Ru catalyst precursors which perform significantly better compared to the state of the art. One is based on the dppf ligand: \([\text{Ru-complex3}]_2P_4\), and the other is phosphine-free: the isoprene based Ru-complex6. These arguably constitute important findings as neither of them has ever been utilized in cross dehydrogenative couplings before.

**General procedure for catalyst screening:**

Unless otherwise specified, the substrate 1a (167 mg, 1.00 mmol), [Ru] (1.00 mol%) and ligand L (1 mol%), Cu(OAc)\(_2\) (200 mg, 1.10 mmol), C\(_2\)Cl\(_4\) (1.00 mL), AcOH (0.250 mL) and PhCl (0.250 mL) were united under air in a 85 mL reactor equipped with a Teflon screw cap. The reactor was flushed with oxygen and sealed, after which the reaction mixture was stirred at 150 °C for 24 h. The reactor was then cooled to room temperature and the crude directly engaged on SiO\(_2\) gel column chromatography for purification, with pentane/CH\(_2\)Cl\(_2\) = 6:4, which gave the desired product after concentration in vacuo.

### i. Ligand screening

| entry\(^1\) | ligand                        | yield (%) |
|------------|------------------------------|-----------|
| 0          | -                            | 40        |
| 1          | tppb (0.330 mol%)            | 61        |
| 2          | 4-(diphenylphosphino)benzoic acid (1.00 mol%) | 47        |
triphenylphosphine (1.00 mol%) | 47
--- | ---
**dppf (0.50 mol%)** | 80
Xantphos (1.00 mol%) | 63

2 reaction conditions: general procedure for cat. screening with [Ru(p-cymene)Cl]₂ (3.10 mg, 5.00·10⁻³ mmol) as catalyst.

tppb | 1,3,5-tris(4-diphenylphosphinophenyl)benzene
dppf | 1,1′-bis(diphenylphosphino)ferrocene
Xantphos | 4,5-bis(diphenylphosphino)-9,9-dimethyl-xanthene

### ii. Iron source screening

| entry | iron source | yield (%) |
|-------|-------------|-----------|
| 1     | dppf        | 80        |
| 2     | Fe(OAc)₂    | 69        |
| 3     | Ferrocene   | 69        |
| 4     | FcPPh₂      | 67        |
| 5     | Q-Phos      | 69        |
| 6     | dtbpf       | 78        |
| 7     | dchpf       | 80        |
| 8     | 1-diphenylphosphino-1′-di-tert-butyl-phosphinoferrocene | 79 |

1 reaction conditions: general procedure for cat. screening with [Ru(p-cymene)Cl]₂ (3.10 mg, 5.00·10⁻³ mmol) as catalyst.

FcPPh₂ | 1-(diphenylphosphino)ferrocene
Q-Phos | 1,2,3,4,5-Pentaphenyl-1′-(di-tert-butylphosphino)ferrocene
dtbpf | 1,1′-Bis(di-tert-butylphosphino)ferrocene
dchpf | 1,1′-Bis(dicyclohexylphosphino)ferrocene

### iii. Ruthenium catalyst screening

| entry | ruthenium catalyst | yield (%) |
|-------|--------------------|-----------|
| 1     | dichloro(p-cymene) ruthenium(II) | 80        |
| 2     | dichloro(benzene) ruthenium(II)  | 66        |
| 3     | dichlorodim-chlorobis[(1,2,3,6,7,8-η₂,2,7-dimethyl-2,6-octadiene-1,8-diyl)diruthenium(IV)] | 70        |
| 4     | dichloro(hexamethylbenzene) ruthenium(II) | 73        |

1 reaction conditions: general procedure for cat. screening with dppf (2.80 mg, 5.00·10⁻³ mmol) as ligand.
iii. Pre-synthesized vs. in situ generated catalyst

| entry | catalytic system | yield (%) |
|-------|----------------|-----------|
| 1     | [Ru(p-cymene)Cl₂ (0.500 mol%) + dppf (0.500 mol%)] | 80 |
| 2     | [Ru(p-cymene)Cl₂(dppf)Ru(p-cymene)Cl₂] (0.500 mol%) | 80 |

1 reaction conditions: general for cat. screening with dppf (2.80 mg, 5.00·10⁻³ mmol) as ligand.

V: Ru kinetic orders (t = 1h) and H/D Scrambling experiments

Figure S3. Top: Ru kinetic order: [Ru-complex6]₂ (black fit) and [Ru-complex3]₂L₄ (red fit), in the interval: 0.125 mol% < [Ru] < 1 mol%, in otherwise standard conditions, 1 h reaction time, ¹H-NMR yields, 1,3,5-trimethylbenzene as internal standard, Bottom: H/D scrambling experiments. No detectable H/D scrambling occurs in the absence of any of components, in particular the Ru, or alternatively the Cu salt.
All the calculations were carried out with the Gaussian09 (revision D.01) program package\textsuperscript{1} using density functional theory (DFT). The B97D functional was selected to compute the reaction mechanisms,\textsuperscript{2} due to the good performance demonstrated for a similar reaction studied before (a benchmark study can be found in the previous manuscript).\textsuperscript{3} All structures were optimized without symmetry restrictions and vibrational frequency calculations were computed for all stationary points to establish their nature as minima (without imaginary frequencies) or transition states (with one imaginary frequency). In the case of transition state optimizations, relaxation to reactant and product was done in all the cases (or IRC calculation when the relaxation was inconclusive), confirming the connectivity between intermediates. Free energy corrections were calculated for all species at 298.15 K and 1 atm pressure, including zero point energy corrections (ZPE).

The influence of the solvent was considered implicitly in all the optimizations and single point corrections through the SMD model,\textsuperscript{4} using diphenylether ($\varepsilon = 3.73$). Diphenylether was selected due to the dielectric constant value between those of chlorobenzene ($\varepsilon = 5.6968$) and tetrachloroethene ($\varepsilon = 2.268$) used as solvent mixture in the experimental reaction.

In order to minimize the basis set superposition error (BSSE), especially considering that aggregated species are involved in the catalytic cycles, we refined the potential energies by introducing an extended basis set. Firstly, we used basis set (I) for optimization and frequency calculations and then, all potential energies were recomputed using basis set (II) in single-point calculations. Basis set (I) was LANL2DZ and the associated pseudopotential for metals (Ru and Cu)\textsuperscript{5} and 6-31G(d) for the rest of atoms (C, H, O, N, Cl).\textsuperscript{6} Basis set (II) was upgraded to the triple-zeta level using LANL2TZ(f) (including the corresponding pseudopotential)\textsuperscript{7} for metals and 6-311++G(d,p) for the rest of the atoms.\textsuperscript{8}

The legend of colors used in 3D structures is:

- Carbon: \[\text{Carbon: } \]
- Hydrogen: \[\text{Hydrogen: } \]
- Oxygen: \[\text{Oxygen: } \]
- Nitrogen: \[\text{Nitrogen: } \]
- Chloride: \[\text{Chloride: } \]
- Copper: \[\text{Copper: } \]
- Ruthenium: \[\text{Ruthenium: } \]
VIb: Structure of 3t with Spin Distribution

Figure S4. 2D and 3D structures of intermediate 3t, with spin densities in top and relevant bond lengths in Å.

VIC: Catalyst Regeneration Pathway

Figure S5. Free energy pathway for catalyst regeneration. Energies in kcal/mol.
Once the lauternazole product has been formed after the cooperative reductive elimination, intermediate 11t releases the reaction product, forming the intermediate 12t. We did not explore this steps in detail because they are thermodynamically favored and the regeneration of the catalytic cycle has been demonstrated experimentally with TOF values. From 12t, the coordination of acetic acid is favored and the initial ruthenium catalyst can be liberated directly, forming intermediate 14t at -13.2 kcal/mol. The direct protonation of the OH group by the coordinated acetic acid can also facilitate the release of the Ru fragment forming 15t exergonically. Finally, the side product water molecule is de-coordinated from the copper dimer, and the copper diacetate dimeric structure is recovered. The overall free energy change of the carbazole homocoupling is therefore -35.6 kcal/mol.

**VId: Alternative Mechanism based on Ru(III)**

![Diagram of Alternative Mechanism based on Ru(III)](image)

*Figure S6. Free energy pathway for alternative pathway based on Ru(III) C–H activation. Energies in kcal/mol.*
We considered an alternative mechanism which also fulfills the kinetic experimental results, where copper, ruthenium and oxygen are involved since the C–H activation. This possibility implies the reduction of 5t by chloride transfer to the copper dimer, producing 17t, which is less stable by 6.1 kcal/mol. From here onwards, the coordination vacancy of Ru can be filled by acetic acid in the media, protonating the oxo group and generating 18t. This intermediate can change the coordination mode of acetate from bidentate to monodentate ligand, giving space to the second carbazole to coordinate, activating in that way the C–H bond. Then, we explored the acetate assisted deprotonation (CMD transition state) and the OH– mediated deprotonation. The free energy barriers of TS 19t-20tOAc and TS 19t-20tOH are 24.4 and 32.3 kcal/mol, respectively. If we compare these results with the Ru/Cu cooperative C–H activation (TS 8t-9t, at 3.9 kcal/mol), it is evident that this pathway is much hindered. In addition, the reductive elimination based on Ru(III) is also higher in energy, at 21.4 kcal/mol, which is consistent with the lower oxidation state of ruthenium center. For all of this, this mechanism has been discarded for the homocoupling of carbazoles.

**VIe: 3D Structures for the Transition States for C–H Activation at Regioselective Positions**

![3D Structures](Figure S7. 3D views of the concerted metallation deprotonation transition states (TS 8t-9t). Relevant bond distances in Å and copper dimer is shown in wireframe for clarity reasons. The energies are referred to the initial point 1t.)

The C1 activation has the lowest transition state at 3.9 kcal/mol. C3 is also low in energy, at 4.5 kcal/mol, followed by C2, which is at 8.5 kcal/mol. Finally, C4 has the highest barrier at 10.6 kcal/mol. This barrier is even higher than the C1-reductive elimination (TS 10t-11t, 10.5 kcal/mol), explaining why C4 C–H activation is negligible. The 3D structures of these transition
states show that the relative position of C–H bond during the activation is strongly related with the distortion of the system. C1 and C3 transition states have the shorter Ru-C bonds (2.10 Å), while C2 and C4 bond lengths increase up to 2.12 Å, showing a worse activation of the C–H bond. The same tendency is observed for C–H bond lengths while the contrary is true for O–H bonds, since the three interactions are strongly correlated in the transition state.

**VII:** Mulliken Spin Populations of Relevant Intermediates along the Reaction Pathway.

**Table S1.** Mulliken spin populations of relevant atoms/fragments of relevant intermediates.

| Intermediate | Cu1<sup>a</sup> | Cu2<sup>b</sup> | Ru | O | Carbazole |
|--------------|----------------|----------------|----|---|-----------|
| 1t           | 0.97           | 0.97           | 0.00 | 1.00 | 0.00       |
| 2t           | 0.94           | 0.69           | 0.00 | 1.00 | 0.35       |
| TS 2t-3t     | 0.95           | 0.56           | 0.00 | 1.00 | 0.38       |
| 3t           | 0.56           | 0.62           | 0.00 | 1.00 | 0.85       |
| 4t           | 0.54           | 0.62           | 0.00 | 1.00 | 0.85       |
| 5t           | 0.54           | 0.62           | 1.39 | 0.49 | 0.85       |
| (4t + CpRuCl2(O)) | 0.54     | 0.62           | 1.39 | 0.49 | 0.85       |
| 6t           | -0.09          | -0.45          | 1.40 | 0.35 | 0.71       |
| 7t           | 0.61           | -0.52          | 1.19 | 0.19 | 0.35       |
| 8t           | 0.55           | -0.46          | 1.37 | 0.27 | 0.10       |
| TS 8t-9t     | 0.34           | -0.66          | 2.46 | 0.20 | -0.31      |
| 9t           | -0.70          | 0.40           | 1.19 | 0.02 | 0.70       |
| 9t(quin)     | 0.75           | 0.54           | 1.20 | 0.17 | 0.70       |
| 10t          | -0.68          | -0.07          | 2.81 | 0.04 | -0.71      |
| TS 10t-11t   | 0.34           | -0.66          | 2.46 | 0.23 | -0.20      |
| 11t          | -0.15          | -0.49          | 2.33 | 0.16 | -0.06      |
| 11t(quin)    | 0.50           | 0.48           | 2.32 | 0.21 | 0.12       |

<sup>a</sup> Copper center close to ruthenium. Spin densities of coordinated oxygens from acetates are added to the spin density of copper.  
<sup>b</sup> Copper center far to ruthenium. Spin densities of coordinated oxygens from acetates are added to the spin density of copper.

The spin populations of key points along the reaction path are supplied in Table S1. As a general comment, the large spin coupling in all the structures makes difficult the assignment of integer spin states to the metals. In most of the cases, the quintuplet state were also computed and it was only slightly higher in energy (1-2 kcal/mol) and were used to assign those spin states.
Additionally, the spin state of Ru(III) was changing between doublet (in relaxed intermediates) or quadruplet (in transition states or in the crowded intermediate 10t). Due to the similar energies of triplet/quintuplet states, we did not calculate the minimum energy crossing points (MECP).
**VIg:** Cartesian Coordinates (Å) and Calculated Potential Energies with Basis set (II) and Free Energy Correction (atomic units)

| Species | E\(_{\text{Enthalpy}}\) | \(G_{\text{corr}}\) | \(G_{\text{corr}}\) | \(G_{\text{corr}}\) |
|---------|-----------------|-----------------|-----------------|-----------------|
| O\(_2\)  | -150.299477 H   | -0.016412 H     |                  |                  |
| H\(_2\)O | -76.423059 H    | 0.002275 H      |                  |                  |
| HOAc    | -229.029638 H   | 0.033121 H      |                  |                  |
| Carbazole | -517.221970 H | 0.138325 H      |                  |                  |
| [C\(_6\)H\(_6\)RuCl\(_2\)] | -2493.622124 H | 0.156450 H      |                  |                  |

**Product**

| Species | E\(_{\text{Enthalpy}}\) | \(G_{\text{corr}}\) |
|---------|-----------------|-----------------|
| C       | -1033.239900 H  | 0.278735 H      |
| C       | -0.60453000 H   | -0.65413600 H   |
| C       | 0.75888300 H    | 1.01893200 H    |
| C       | 1.42270900 H    | 0.99395700 H    |
| C       | 0.68245100 H    | 2.36150400 H    |
| C       | -0.69573200 H   | 2.45339300 H    |
| C       | -1.33703500 H   | -3.70666800 H   |
| H       | -1.08808900 H   | -5.81007000 H   |
| H       | 1.30796500 H    | 5.61227900 H    |
| H       | 2.47450500 H    | 3.39898470 H    |
| H       | -2.38831300 H   | -7.98050000 H   |
| C       | 0.02008500 H    | -0.27029700 H   |
| C       | -0.03001100 H   | 1.11909200 H    |
| C       | -1.25264700 H   | 1.63959900 H    |
| C       | -2.37995800 H   | 0.81151900 H    |
| C       | -2.32602100 H   | -0.56850100 H   |
| C       | -1.12119400 H   | -1.11284900 H   |
| C       | -1.30880000 H   | 2.70841700 H    |
| C       | -3.30706700 H   | 1.25319000 H    |
| C       | -2.30268400 H   | -1.93256000 H   |
| N       | 1.08612200 H    | 1.03867700 H    |
| C       | 2.00491800 H    | -0.67816700 H   |
| C       | 1.11637900 H    | 1.92501100 H    |
| C       | 1.71525000 H    | 2.68522600 H    |
| C       | 1.90834800 H    | 2.01532600 H    |
| C       | 1.30808000 H    | 2.87286100 H    |
| C       | 2.91299900 H    | 3.27269100 H    |
| C       | 1.70106100 H    | 1.43836800 H    |
| C       | 3.03959000 H    | 2.84155600 H    |
| C       | 2.10291600 H    | 3.67965600 H    |
| C       | 0.39969600 H    | 2.40582100 H    |
| C       | 3.69948400 H    | 4.07945500 H    |
| C       | 2.66615700 H    | 1.68389200 H    |
| C       | 0.82069700 H    | 0.82959800 H    |
| C       | 3.99956500 H    | 3.07251700 H    |
| C       | 3.32756200 H    | 4.28061400 H    |
| C       | 1.80474500 H    | 3.84497700 H    |
| C       | 4.61903500 H    | 4.35602200 H    |
| C       | 3.80109500 H    | 2.48697000 H    |
| C       | 2.53304000 H    | 1.24768500 H    |
| C       | 4.86265300 H    | 3.70053200 H    |
| C       | 3.88663500 H    | 4.90562100 H    |
| C       | 4.53633400 H    | 2.65584500 H    |

**Free Energy Correction (atomic units)**

\[ \Delta E = -76.423059 \text{H} \]

\[ \Delta G_{\text{corr}} = 0.278735 \text{H} \]

\[ \Delta G_{\text{corr}} = 0.016412 \text{H} \]

\[ \Delta G_{\text{corr}} = 0.002275 \text{H} \]

\[ \Delta G_{\text{corr}} = 0.033121 \text{H} \]

\[ \Delta G_{\text{corr}} = 0.138325 \text{H} \]

\[ \Delta G_{\text{corr}} = 0.156450 \text{H} \]
\[
\begin{align*}
&\text{C} \quad 0.53209100 \quad -3.69386000 \quad 3.17340500 \\
&\text{C} \quad 0.82126000 \quad -2.51229000 \quad 3.94599100 \\
&\text{C} \quad -0.24067500 \quad -1.63579400 \quad 4.31371700 \\
&\text{C} \quad -1.60289200 \quad -1.93570000 \quad 3.95007400 \\
&\text{H} \quad -1.88043200 \quad -3.11013700 \quad 3.81410100 \\
&\text{H} \quad 1.35008400 \quad -4.29401000 \quad 2.78010100 \\
&\text{H} \quad 1.85378400 \quad -2.22808300 \quad 4.13808500 \\
&\text{H} \quad -2.38993800 \quad -1.21191600 \quad 4.13695900 \\
&\text{H} \quad -2.88172800 \quad -3.52683800 \quad 2.78818700 \\
&\text{H} \quad -1.00861400 \quad -4.80433400 \quad 2.10278700 \\
&\text{H} \quad -0.01079300 \quad -0.67977100 \quad 2.79180700 \\
\end{align*}
\]

\text{[Cu(OAc)\textsubscript{2}]}

\[
\begin{align*}
E_{\text{high}} &= -1246.797057 \text{ H} \quad | \quad G_{\text{corr}} = 0.066569 \text{ H} \\
\text{Ru} &= -1.00640400 \quad 0.34621000 \quad -0.86469200 \\
\text{Cl} &= -1.83651500 \quad -1.79264900 \quad -0.28227200 \\
\text{Cl} &= -0.94549700 \quad 0.99224600 \quad 1.41549000 \\
\text{C} &= -0.96618200 \quad -0.65254000 \quad -0.37261700 \\
\text{C} &= 0.35544400 \quad 0.99443500 \quad -2.55907900 \\
\text{C} &= 0.71591300 \quad 1.28968500 \quad -0.83427800 \\
\text{C} &= -0.24651300 \quad 2.32031200 \quad -0.26223900 \\
\text{C} &= -1.59598300 \quad 2.16655000 \quad -0.32223900 \\
\text{C} &= -1.95609800 \quad 0.91263300 \quad -0.27592470 \\
\text{H} &= 1.07100900 \quad -0.72282100 \quad -0.63820600 \\
\text{H} &= 1.69902100 \quad 1.36165800 \quad -1.37181200 \\
\text{H} &= 2.37418700 \quad 2.80094400 \quad -1.71896000 \\
\text{H} &= -3.00268400 \quad 0.71842700 \quad -2.99404000 \\
\text{H} &= -1.26132000 \quad -1.00913000 \quad -3.52597100 \\
\text{H} &= -0.00165300 \quad 3.16758900 \quad -0.98474800 \\
\end{align*}
\]

\text{[Cu(OAc)\textsubscript{2}]}

\[
\begin{align*}
E_{\text{high}} &= -565.539360 \text{ H} \quad | \quad G_{\text{corr}} = 0.060887 \text{ H} \\
\text{Cu} &= -2.43581700 \quad 0.24349400 \quad -1.45953900 \\
\text{O} &= -3.99911800 \quad 1.01412700 \quad -0.36655800 \\
\text{C} &= -4.63588200 \quad 1.19125100 \quad -1.46103100 \\
\text{O} &= -4.06719100 \quad 0.83739900 \quad -2.55377300 \\
\text{O} &= -0.80420400 \quad -0.37216600 \quad -0.36620200 \\
\text{O} &= -0.22369900 \quad -0.68188000 \quad -1.45956400 \\
\text{O} &= -0.87511600 \quad -0.51875900 \quad -2.55370500 \\
\text{C} &= 1.17172700 \quad -1.24128000 \quad -1.44717900 \\
\text{H} &= 1.46722300 \quad -1.57575900 \quad -2.45152900 \\
\text{H} &= 1.87018400 \quad -0.46483500 \quad -1.09701200 \\
\text{H} &= 1.22660300 \quad -0.20818000 \quad -0.73779900 \\
\text{C} &= -6.00712200 \quad 1.81426600 \quad -1.54514500 \\
\text{H} &= -5.91288100 \quad 2.88150400 \quad -1.19331500 \\
\text{H} &= -6.48378100 \quad 1.72762600 \quad -2.43292600 \\
\text{H} &= -6.62985500 \quad 1.33593200 \quad -0.68288000 \\
\end{align*}
\]

\text{[Cu(OAc)\textsubscript{2}]}

\[
\begin{align*}
E_{\text{high}} &= -1307.127939 \text{ H} \quad | \quad G_{\text{corr}} = 0.146007 \text{ H} \\
\text{Cu} &= -2.31181000 \quad 0.35529200 \quad 1.09471600 \\
\text{Cu} &= -2.31311700 \quad 0.40596800 \quad -1.43671000 \\
\text{O} &= -1.66615600 \quad 2.27916400 \quad 0.98829000 \\
\text{C} &= -1.31849800 \quad 2.78524300 \quad -0.13273800 \\
\text{O} &= -1.41204800 \quad 2.21774400 \quad -1.27345600 \\
\text{O} &= -0.39199900 \quad -0.28939500 \quad 0.94536500 \\
\text{C} &= 0.09144900 \quad -0.61444300 \quad -0.19141400 \\
\text{O} &= -0.49876400 \quad -0.49799700 \quad -1.31826900 \\
\end{align*}
\]
\[
\begin{align*}
\text{TS 3t-3t} & \\
E_{\text{high}} &= -1824.361778 \text{ H} | G_{\text{corr}} = 0.304922 \text{ H} \\
E_{\text{corr}} &= 0.250213 \text{ H} \\
\end{align*}
\]
TS 8t-9t

\[ E_{\text{high}} = -366.53585800 \text{ H} \quad |G_{\text{corr}}| = 0.552074 \text{ H} \]

\[ \begin{align*}
H &\quad -1.14010800 & 1.59824100 & 2.93704500 \\
C &\quad -4.58022900 & 4.88941700 & 2.12391700 \\
O &\quad -2.02439500 & 4.35855300 & 3.25799200 \\
O &\quad -4.69215800 & 4.26969900 & 1.03224300 \\
C &\quad -4.84762900 & 6.38886970 & 2.18508100 \\
H &\quad -5.32787500 & 6.73060610 & 1.25902100 \\
H &\quad -5.47994200 & 6.63805500 & 3.05141700 \\
H &\quad -3.88902300 & 6.91483500 & 2.31720600 \\
O &\quad -3.94765100 & 2.09686300 & 1.71197600 \\
H &\quad -3.97631200 & 2.87586900 & 1.23985700 \\
H &\quad -6.91044500 & -0.15980900 & 4.023191900 \\
C &\quad -6.22649700 & 0.58172500 & 3.07227300 \\
H &\quad -6.01833400 & 2.01144700 & 3.21537000 \\
H &\quad -6.66186600 & 2.67178100 & 4.36505000 \\
C &\quad -7.38486600 & 1.84784100 & 5.32943600 \\
C &\quad -7.49609500 & 0.46826900 & 5.15889900 \\
H &\quad -7.01466600 & -1.23766300 & 3.89680700 \\
C &\quad -5.83113500 & 1.04327000 & 2.18029400 \\
C &\quad -5.97212300 & 2.58430500 & 2.28438200 \\
H &\quad -8.01689400 & -0.13636600 & 5.89939000 \\
C &\quad -7.39506200 & -3.07350600 & 5.91568800 \\
C &\quad -7.36964300 & 5.23755600 & 6.65708000 \\
C &\quad -8.35587400 & -0.19004200 & 7.85152500 \\
C &\quad -8.81511300 & 3.29879500 & 8.28693000 \\
C &\quad -8.56565500 & 2.66970900 & 7.53728700 \\
C &\quad -7.84567100 & 2.70821400 & 6.33704400 \\
H &\quad -7.28240700 & 6.21074100 & 6.31337400 \\
C &\quad -8.56130400 & 5.97759200 & 8.45819900 \\
H &\quad -9.36811300 & 3.75537600 & 9.22424600 \\
C &\quad -9.18713500 & 1.66923400 & 7.88269600 \\
N &\quad -6.72625100 & 3.92769400 & 6.49679500 \\
H &\quad -6.07907900 & 4.60907600 & 4.29348400 \\
\end{align*} \]

TS 8t-9t-C2
\[ E_{\text{high}} = -3434.589937 \text{ H} \mid G_{\text{corr}} = 0.506510 \text{ H} \]

\[ E_{\text{high}} = -2401.320228 \text{ H} \mid G_{\text{corr}} = 0.202356 \text{ H} \]
| H  | -1.05879300 | 3.33690200 | 4.20547800 |
| C  | -0.17379700 | 3.53390300 | 1.87361400 |
| C  | -3.44984200 | 5.41317000 | 2.90995800 |
| C  | -3.39091900 | 6.20662200 | 0.89344500 |
| C  | -3.15207000 | 4.53497900 | 4.85598200 |
| C  | -4.36160400 | 5.94104600 | 3.17976700 |
| H  | -3.91723500 | 2.28235200 | 1.89206200 |
| H  | -3.64957800 | 2.65176200 | 2.68346400 |

**E_{high} = -2630.375027 H | G_{corr} = 0.257986 H**

13t

| O  | -1.42484100 | 0.54123100 | 2.40326100 |
| C  | -0.24490200 | 0.79699300 | 2.05179800 |
| O  | 0.14644900 | 1.02376200 | 0.83673900 |
| C  | -0.40421900 | 1.81210100 | -0.76636300 |
| C  | -3.66527600 | 1.55995800 | -1.99877300 |
| C  | -2.49609900 | 1.20971400 | -2.29547900 |
| C  | -3.14596700 | -1.18338300 | 0.40593300 |
| C  | -2.23977100 | -1.66824600 | -0.35353800 |
| C  | -1.52685700 | -1.04354000 | -0.86072000 |
| C  | -2.37954900 | -3.13543500 | -0.68861700 |
| C  | -3.30303500 | -3.29988600 | -1.27717600 |
| C  | -1.51950100 | -3.15452100 | -2.16665000 |
| C  | -2.47383700 | -3.70349400 | 0.24338800 |
| C  | 0.84959400 | 0.85522200 | 3.11154000 |
| C  | 1.60996600 | 0.80952300 | 2.88644400 |
| H  | 1.35147400 | 1.83041000 | 3.07419900 |
| H  | 0.43839200 | 0.68420800 | 4.11387500 |
| C  | -4.74713100 | 1.61567700 | -3.05517000 |
| C  | -5.13037500 | 2.64452600 | -3.09616000 |
| C  | -4.35039800 | 1.31708200 | -0.03735700 |
| H  | -5.57455600 | 0.95724600 | -2.76201800 |
| Cu | -1.02655800 | 1.00389100 | -0.85929600 |
| Cu | -3.15271100 | 0.63734100 | 1.16145900 |
| Ru | -3.98443500 | 3.66894300 | 0.25839000 |
| Cl | -6.20498300 | 4.45691300 | 0.69123000 |
| Cl | -3.64131800 | 4.88306600 | -1.78074800 |
| C  | -1.71648900 | 4.86586200 | 1.01391900 |
| C  | -1.49704100 | 0.01436400 | 3.28637300 |
| C  | -1.04709000 | 0.62080900 | 1.95854900 |
| C  | -2.86343000 | 5.61426400 | 1.40560200 |
| C  | -1.34256000 | 4.95281000 | -0.00525400 |
| C  | -2.63380300 | 4.75736000 | -3.69868000 |
| C  | -0.97261400 | 3.39644500 | 4.01714500 |
| C  | -0.17127500 | 3.49416000 | 1.65543800 |
| C  | -3.31608700 | 5.54738200 | 2.74671500 |
| C  | -3.30801200 | 6.32947900 | 0.71257800 |
| C  | -2.98124000 | 4.70778700 | 4.71312200 |
| C  | -4.19508300 | 6.11861000 | 3.04505700 |
| C  | -3.88671700 | 2.37444600 | 1.80206100 |
| C  | -3.45527500 | 2.76524100 | 2.59147900 |
| C  | -0.91909000 | 4.04445600 | -1.05944800 |
| O  | -0.10748400 | 2.82858000 | -1.48368400 |
| O  | 1.65578300 | 2.95522200 | -0.05292600 |
| H  | 1.20953600 | 2.13138400 | 0.34823300 |
| H  | 1.40507400 | 4.70079800 | -1.65078200 |
| H  | 1.40770800 | 5.47926500 | -0.87152700 |
| H  | 2.44379600 | 4.57939200 | -1.99697900 |
| H  | 0.76190900 | 5.00570300 | -2.48481600 |

**E_{high} = -1383.536958 H | G_{corr} = 0.168473 H**

15t

**E_{high} = -1383.562543 H | G_{corr} = 0.169710 H**
**17t**

$E_{\text{high}} = -861.698599 \text{ H} \ | \ G_{\text{corr}} = 0.066138 \text{ H}$

**18t**

$E_{\text{high}} = -1090.744687 \text{ H} \ | \ G_{\text{corr}} = 0.121262 \text{ H}$

**TS 19t-20t**

$E_{\text{high}} = -1607.959063 \text{ H} \ | \ G_{\text{corr}} = 0.275664 \text{ H}$
|  | X      | Y      | Z      |
|---|--------|--------|--------|
| H | -0.648458 | 0.614017 | 3.154414 |
| H | -2.449249 | -1.119276 | 3.196083 |
| H | -4.712962 | -0.611542 | 2.336791 |
| H | -5.362050 | 1.785369 | 2.644240 |
| C | -1.941870 | 2.141102 | 3.149120 |
| C | -5.360250 | 1.785369 | 2.336791 |
| C | -4.712962 | -0.611542 | 2.336791 |
| C | -2.449249 | -1.119276 | 3.149120 |
| H | 0.020027 | 6.994194 | 1.382713 |
| C | -1.941870 | 2.141102 | 3.149120 |
| C | -1.662970 | 5.646502 | 2.840267 |
| C | -0.328539 | 5.981347 | 1.595454 |
| O | -3.908060 | 3.966837 | 0.606723 |
| H | -3.693350 | 0.397300 | 4.609004 |
| H | -1.525689 | 1.634693 | 0.451213 |
| N | -2.634949 | 3.855600 | 0.830834 |
| H | -3.098260 | 4.074666 | -0.044760 |
| C | 0.509550 | 3.726632 | 2.422943 |
| H | 0.160442 | 5.329154 | 2.334969 |
| C | 0.020027 | 6.994194 | 1.382713 |
| C | -2.359291 | 6.376070 | 0.906526 |
| C | 0.859271 | 2.999932 | 2.840267 |
| C | -3.627434 | 2.430102 | 1.849111 |
| C | -4.322209 | 1.461009 | 1.831591 |
| C | -3.948400 | 0.616160 | 2.322669 |
| C | -2.668240 | -0.120628 | 2.812608 |
| C | -1.650708 | 0.855614 | 2.793529 |
| C | -1.941870 | 2.141102 | 3.149120 |
| H | -3.562050 | 1.785369 | 2.336791 |
| H | -4.712962 | -0.611542 | 2.336791 |
| H | -2.449249 | -1.119276 | 3.149120 |
| H | 0.648580 | 0.614107 | 3.154414 |
| N | -3.314960 | 3.740180 | 1.440533 |
| H | -4.174581 | 4.415458 | 1.054953 |

**TS 19t-20t**

\[ E_{\text{high}} = -1607.975974 \text{ H} \mid G_{\text{corr}} = 0.280760 \text{ H} \]

|  | X      | Y      | Z      |
|---|--------|--------|--------|
| C | -5.576166 | 1.960329 | -0.017510 |
| C | -7.153942 | 3.948108 | -2.493697 |
| C | -7.061498 | 2.546201 | -2.519743 |
| C | -8.066773 | 4.573037 | -1.635960 |
| C | -6.504555 | 4.544909 | -3.136102 |
| C | -7.884550 | 1.766979 | -1.677510 |
| C | -6.353007 | 2.052507 | -3.186154 |
| C | -8.909192 | 3.797927 | -0.801214 |
| C | -8.136099 | 5.665212 | -1.610360 |
| C | -8.815390 | 2.400255 | -0.825290 |
| C | -7.827174 | 0.678539 | -1.766690 |
| C | -9.620453 | 4.289566 | -0.146104 |
| C | -9.452274 | 1.797829 | -0.764410 |
| Cl | -3.835115 | 2.166080 | -1.619980 |
| C | -6.693431 | -0.155560 | 0.793018 |
| C | -6.592067 | -0.178424 | 0.017940 |
| C | -7.069867 | 1.001358 | 1.207330 |
| C | -7.389899 | -1.141194 | 1.219732 |
| Cl | -7.613619 | -1.372386 | 2.295145 |
| C | -8.348682 | -1.490466 | 0.679436 |
| C | -6.776523 | -2.293418 | 0.990570 |
| C | -5.862105 | 3.885555 | 0.627308 |
| C | -6.834472 | 3.995349 | 0.768040 |
| C | 1.093615 | 4.860570 | 2.369157 |
| C | 0.661000 | 5.530677 | 1.191273 |
| C | -0.553190 | 5.262459 | 0.587754 |
| C | -1.369412 | 4.301408 | 0.999880 |
| C | -0.972948 | 3.606979 | 2.381170 |
| C | 0.270595 | 3.897670 | 2.971246 |
| C | 2.063483 | 5.095506 | 2.811620 |
| C | 1.347841 | 6.273552 | 0.741400 |
| C | -0.863728 | 5.786810 | -0.319202 |
| C | 0.590235 | 3.381226 | 3.878234 |
| C | -3.065520 | 2.880692 | 1.692281 |
| C | -4.319699 | 2.188055 | 1.714640 |
| C | -4.485200 | 2.188840 | 2.809749 |
| C | -3.505826 | 1.089464 | 3.792841 |
| C | -2.284779 | 1.791532 | 3.742802 |
| C | -2.061746 | 2.705910 | 2.707890 |
| C | -5.221630 | 3.188303 | 1.592195 |

**21t**

\[ E_{\text{high}} = -3434.538739 \text{ H} \mid G_{\text{corr}} = 0.499217 \text{ H} \]

|  | X      | Y      | Z      |
|---|--------|--------|--------|
| O | -2.011566 | 0.449840 | 1.922489 |
| O | -0.880670 | 0.223410 | 1.383060 |
| O | -0.631851 | 0.065057 | 0.140584 |
| O | -5.200830 | 0.038866 | -0.483266 |
| C | -3.654540 | -0.476930 | -0.100320 |
VII: Spectra
