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Rh-Catalyzed Reactions of 1,4-Benzoquinones with Electrophiles: C-H Iodination, Bromination and Phenylselenation

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Contents

A) General experimental details S2
B) Synthesis of substrates and known compounds S3
C) General procedure for halogenation/selenylation at the 2-position S4
D) Intermolecular competition experiment between 1a and deuterio-1a S18
E) Copies of NMR spectra of novel compounds S20
General Experimental Details

Starting materials sourced from commercial suppliers were used as received unless otherwise stated. All reagents requiring purification were purified using standard laboratory techniques according to methods published by Perrin, Armarego, and Perrin (Pergamon Press, 1966). Catalytic reactions were run under an atmosphere of dry nitrogen or argon; glassware, syringes and needles were either flame dried immediately prior to use or placed in an oven (200 °C) for at least 2 h and allowed to cool either in a desiccator or under an atmosphere of nitrogen or argon; liquid reagents, solutions or solvents were added via syringe through rubber septa; solid reagents were added inside a glovebox. All optimization reactions were filtered through a sinter funnel charged with a pad of celite and silica for copper removal. Coupling partners for Stille reactions were distilled before use. Anhydrous solvents were obtained by distillation using standard procedures or by passage through drying columns supplied by Anhydrous Engineering Ltd. Anhydrous dichloromethane (CH₂Cl₂) was purged with argon for 10 minutes prior use. Flash column chromatography (FCC) was performed using silica gel (Aldrich 40-63 μm, 230-400 mesh). Thin layer chromatography (TLC) was performed using aluminium backed 60 F254 silica plates. Visualization was achieved by UV fluorescence or a basic KMnO₄ solution and heat. Proton nuclear magnetic resonance spectra (NMR) were recorded using either a Varian 400 MHz, Varian 500 MHz or Bruker AVANCE DRX400 MHz. ¹³C NMR spectra were recorded at 100 MHz or 125 MHz as stated. Chemical shifts (δ) are given in parts per million (ppm). Peaks are described as singlets (s), doublets (d), double doublets (dd), triplets (t), double triplets (dt), and multiplets (m). ¹H and ¹³C NMR spectra were referenced to the appropriate residual solvent peak. Coupling constants (J) are quoted to the nearest 0.5 Hz. All assignments of NMR spectra were based on 2D NMR data (DEPT-135, COSY, HSQC and HMBC). In situ yields were determined by employing 1,4-dinitrobenzene as an internal standard. Mass spectra were recorded using a Brüker Daltonics FT-ICRMS Apex 4e 7.0T FT-MS (ESI⁺ mode) and Shimadzu GCMS QP2010+ (EI⁺ mode). Infrared spectra were recorded on a Perkin Elmer Spectrum One FTIR spectrometer as thin films or solids compressed on a diamond plate. Melting points were determined using Stuart SMP30 melting point apparatus and are uncorrected.
**Synthesis of Substrates and Known Compounds:**

All commercially available benzoquinones and further commercial chemicals were purchased from Sigma Aldrich, Alfa Aesar, Strem Chemicals and Santa Cruz Biotechnology. \([\text{RhCp}^\ast\text{Cl}_2]\_2\) and \([\text{RhCp}^\prime\text{Cl}_2]\_2\) were purchased from Sigma Aldrich. \([\text{RhCp}^\prime\text{Cl}_2]\_2\), \([\text{RhCp}^{\text{CF3}}\text{Cl}_2]\_2\) and \([\text{RhCp}^\prime\text{Pr}\text{Cl}_2]\_2\) were synthesised via literature procedures already described by our research group.\(^1\)

**2-Methoxy-1,4-benzoquinone (1b)**

Compound 1b was synthesized (267.9 mg, 97% yield) as a yellow powder using a previously reported procedure.\(^3\) **m.p.** (°C) = 133.8-134.1 (Petrol/CH\(_2\)Cl\(_2\)); **HRMS (EI\(^+\))**: 138.0311 [M]. Calcd. for [C\(_7\)H\(_6\)O\(_3\)]: 138.0317; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 6.69 (s, 2H), 5.92 (s, 1H), 3.81 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 187.4, 181.7, 158.6, 137.2, 134.4, 107.7, 56.2. Data are consistent with those reported in the literature.\(^3\)

**2,3-Dimethyl-1,4-benzoquinone (1c)**

Compound 1c was synthesised (1.68 g, 90% yield) as yellow crystals using previously reported procedures.\(^2,3\) **m.p.** (°C) = 54.9-56.4 (Petrol/CH\(_2\)Cl\(_2\)); **HRMS (EI\(^+\))**: 136.0569 [M]. Calld. for [C\(_8\)H\(_8\)O\(_2\)]: 136.0524; \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\): 6.70 (s, 2H), 2.01 (s, 6H); \(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\): 187.4, 141.0, 136.2, 12.2. Data are consistent with those reported in the literature.\(^3\)
2,3-Dichloro-1,4-benzoquinone (1f)

Compound 1f was synthesised (1.79 g, 60% yield) as yellow crystals using previously reported procedure.\textsuperscript{4} m.p. (°C) = 102.9-103.7 (Petrol/CH\textsubscript{2}Cl\textsubscript{2}); HRMS (EI\textsuperscript{+}): 175.9421 [M]\textsuperscript{+}. Cald. for [C\textsubscript{6}H\textsubscript{2}Cl\textsubscript{2}O\textsubscript{2}]: 175.9432; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\): 6.97 (s, 2H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\): 177.4, 141.2, 136.1. Data are consistent with those reported in the literature.\textsuperscript{4}

General procedure for halogenation/selenylation at the 2-position:

In a glovebox, an oven dried re-sealable tube was charged with the corresponding benzoquinone (0.10 mmol), [RhCp'Cl\textsubscript{2}]\textsubscript{2} (3.75 mol%, 2.6 mg), silver bis(trifluoromethanesulfonyl)imide (20 mol%, 7.8 mg), the electrophile source (see below) and anhydrous copper sulfate (220 mol%, 0.22 mmol, 34.9 mg). The tube was removed from the glovebox and an inert atmosphere was maintained. Anhydrous CH\textsubscript{2}Cl\textsubscript{2} (1 mL) was added via syringe and tube was sealed. The mixture was heated at 100 °C for 18h. After cooling, the mixture was filtered through a pad of celite and purified by FCC, under the conditions noted.
2-Iodo-1,4-benzoquinone (2a)

The product was obtained by the general procedure described above using 1,3-diiodo-5,5-dimethylhydantoin (DIH) (150 mol %, 0.12 mmol, 56.9 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 2a (22 mg, 95% yield) as orange crystals; m.p. (°C) = 58.3-58.9 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) v: 3042 (w), 1644 (s), 1269 (s), 914 (s); HRMS (EI⁺): 233.9174 [M⁺]. Calcd. for [C₆H₃IO₂]: 233.9178;

Elemental analysis – Calculated (%) C: 30.80 H: 1.29. Found (%) C: 31.01 H: 1.30; ¹H NMR (400 MHz, CDCl₃) δ: 7.67 (d, J = 2.4 Hz, C3-H), 7.00 (d, J = 10.0 Hz, C6-H), 6.84 (dd, J = 10.1, 2.4 Hz, C5-H); ¹³C NMR (100 MHz, CDCl₃) δ: 184.0 (C4), 180.2 (C1), 146.1 (C3), 136.6 (C5), 134.56 (C6), 119.6 (C2). Data are consistent with those reported in the literature.⁵

![Figure 1: Crystal structure of compound 2a.](image)

2-Iodo-3-methoxy-1,4-benzoquinone (2b)

The product was obtained by the general procedure described above using 1,3-diiodo-5,5-dimethylhydantoin (DIH) (120 mol %, 0.12 mmol, 45.5 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 2b (24.0 mg, 91% yield) as orange crystals; m.p. (°C) = 98.1-99.9 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) v: 3027 (w), 1698 (s),
1354 (s), 991 (s); **HRMS (EI**⁺): 261.9493 [M]⁺. Calcd. for [C₇H₅IO₃]: 263.9283; **Elemental analysis – Calculated (%) C: 31.85 H: 1.91. Found (%) C: 32.10 H: 1.93; ¹H NMR (400 MHz, CDCl₃) δ: 6.91 (d, J = 10.0 Hz, C₆-H), 6.67 (d, J = 10.0 Hz, C₅-H), 4.21 (s, C₇-H₃); ¹³C NMR (100 MHz, CDCl₃) δ: 181.73 (C₁), 179.36 (C₄), 161.43 (C₃), 135.10 (C₆), 134.66 (C₅), 100.93 (C₂), 61.67 (C₇).

**Figure 2:** Crystal structure of compound 2b.

2-Iodo-5,6-dimethyl-1,4-benzoquinone (2c)

The product was obtained by the general procedure described above using 1,3-diiodo-5,5-dimethylhydantoin (DIH) (150 mol%, 0.15 mmol, 56.9 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 2c (21.2 mg, 81% yield) as a red oil; **IR (solid, cm⁻¹) ν:** 2921 (w), 1638 (s), 1236 (s), 838 (s); **HRMS (EI**⁺): 261.9493 [M]⁺. Calcd. for [C₈H₇IO₂]: 261.9491; ¹H NMR (400 MHz, CDCl₃) δ: 7.60 (s, C₃-H), 2.11 (d, J = 1.2 Hz, C₈-H₃), 2.03 (d, J = 1.2 Hz, C₇-H₃); ¹³C NMR (100 MHz, CDCl₃) δ: 184.4 (C₄), 180.4 (C₁) 146.0 (C₃), 141.4 (C₅), 140.0 (C₆), 119.0 (C₂), 13.7 (C₈), 12.4 (C₇). The structural assignment of the product was supported by **HMBC analysis, as indicated above.**
2-Iodo-6-methyl-1,4-benzoquinone (2da) and 2-Iodo-5-methyl-1,4-benzoquinone (2db)

The product was obtained by the general procedure described above using 1,3-diiodo-5,5-dimethylhydantoin (DIH) (150 mol%, 0.15 mmol, 56.9 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded products 2da and 2db (mixture of isomers, 5:4/a:b) (20 mg, 81% yield) as an orange powder; HRMS (EI⁺): 247.9326 [M]+. Calcd. for [C₇H₅IO₂]: 247.9334; ¹H NMR (500 MHz, CDCl₃) δ: 7.64 (d, J = 1.4 Hz, C₃b-H), 7.59 (dd, J = 2.4, 1.5 Hz, C₃a-H), 6.84 (t, J = 1.6 Hz, C₆b-H), 6.66 (dt, J = 2.4, 1.5 Hz, C₅a-H), 2.14 (t, J = 1.5 Hz, C₇a-H₃), 2.07 (t, J = 1.5 Hz, C₇b-H₃); ¹³C NMR (125 MHz, CDCl₃) δ: 184.6 (C₄b), 184.5 (C₄a), 180.8 (C₁a), 180.4 (C₁b), 146.4 (C₅b), 146.2 (C₃a), 146.1 (C₃b), 144.6 (C₆a), 133.5 (C₅a), 131.4 (C₆b), 119.7 (C₂-Ib), 119.3 (C₂-Ia), 17.3 (C₇a), 15.8 (C₇b). The structural assignments of the products were supported by HMBC analysis, as indicated above.

2-Iodo-5-(tert-butyl)-1,4-benzoquinone (2e)

The product was obtained by the general procedure described above using 1,3-diiodo-5,5-dimethylhydantoin (DIH) (120 mol%, 0.12 mmol, 45.5 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 2e (19.2 mg, 66% yield) as a deep
yellow solid; m.p. (°C) = 70.5-71.0 (Petrol/CH\textsubscript{2}Cl\textsubscript{2}); IR (solid, cm\textsuperscript{-1}) ν: 2960 (s), 1651 (s), 1180 (s), 1009 (s); HRMS (EI\textsuperscript{+}): 289.9798 [M]+. Cald. for [C\textsubscript{10}H\textsubscript{11}IO\textsubscript{2}]: 289.9804; Elemental analysis – Calculated (%) C: 41.40 H: 3.82. Found (%) C: 41.69 H: 3.85; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.54 (s, C\textsubscript{3}-H), 6.81 (s, C\textsubscript{6}-H), 1.27 (s, C\textsubscript{8}-H\textsubscript{9}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 184.2 (C\textsubscript{4}), 181.3 (C1), 156.6 (C5), 147.9 (C3), 129.8 (C6), 117.5 (C2), 35.5 (C7), 29.0 (C8). The structural assignment of the product was supported by HMBC analysis, as indicated above.

2-Iodo-6-(tert-butyl)-1,4-benzoquinone (2e')

Continued elution afforded product 2e' (5.2 mg, 18% yield) as a deep yellow solid; m.p. (°C) = 71.8-72.9 (Petrol/CH\textsubscript{2}Cl\textsubscript{2}); IR (solid, cm\textsuperscript{-1}) ν: 2965 (s), 1689 (s), 1218 (s), 1124 (s); HRMS (EI\textsuperscript{+}): 289.9807 [M]+. Cald. for [C\textsubscript{10}H\textsubscript{11}IO\textsubscript{2}]: 289.9804; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.54 (d, J = 2.4 Hz, C\textsubscript{3}-H), 6.65 (d, J = 2.4 Hz, C\textsubscript{5}-H), 1.28 (s, C\textsubscript{8}-H\textsubscript{9}); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 185.3 (C4), 179.9 (C1), 155.1 (C6), 145.1 (C3), 131.9 (C5), 122.7 (C2), 36.2 (C7), 29.1 (C8). The structural assignment of the product was supported by HMBC analysis, as indicated above.

2-Iodo-5,6-dichloro-1,4-benzoquinone (2f)

The product was obtained by the general procedure described above using 1,3-diodo-5,5-dimethylhydantoin (DIH) (150 mol%, 0.15 mmol, 56.9 mg) and a reaction time of
18 h. Purification by FCC (toluene) afforded product \(2f\) (16.9 mg, 56% yield) as yellow crystals; \(\text{m.p. (°C) = 162.8-163.5 (Petrol/CH}_2\text{Cl}_2)\); \(\text{IR (solid, cm}^{-1}) \nu: 2973 \text{ (w), 1667 (s), 1046 (m), 881 (s); HRMS (EI\(^+\)): 301.8402 [M]\(^+\). Cald. for [C\(_6\)H\(_5\)Cl\(_2\)O\(_2\)]: 301.8398; Elemental analysis – Calculated (%) C: 23.79 H: 0.33. Found (%) C: 23.98 H: 0.33; \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta: 7.83 \text{ (s, C}\_3\text{-H)}); \(^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta: 175.3 \text{ (C4), 171.9 (C1), 145.2 (C3), 141.6 (C5), 138.2 (C6), 117.4 (C2). The structural assignment of the product was supported by HMBC analysis, as indicated above.\)

2-Bromo-1,4-benzoquinone (3a)

![HMBC analysis](image.png)

The product was obtained by the general procedure described above using 1,3-dibromo-5,5-dimethylhydantoin (DBH) (120 mol\%, 0.12 mmol, 34.3 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product \(3a\) (15.3 mg, 82% yield) as yellow crystals; \(\text{m.p. (°C) = 54.5-55.1 (Petrol/CH}_2\text{Cl}_2)\); \(\text{IR (solid, cm}^{-1}) \nu: 3042 \text{ (w), 1661 (s), 1276 (s), 967 (s); HRMS (EI\(^+\)): 185.9312 [M]\(^+\). Cald. for [C\(_6\)H\(_3\)BrO\(_2\)]: 185.9316; Elemental analysis – Calculated (%) C: 38.54 H: 1.62. Found (%) C: 38.77 H: 1.63; \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta: 7.29 \text{ (d, } J = 2.4 \text{ Hz, C}\_3\text{-H), 6.96 (d, } J = 10.1 \text{ Hz, C}\_6\text{-H), 6.82 (dd, } J = 10.1, 2.4 \text{ Hz, C}\_5\text{-H); }^{13}\text{C NMR (100 MHz, CDCl}_3\) \(\delta: 184.55 \text{ (C4), 179.17 (C1), 138.12 (C3), 137.50 (C2), 136.63 (C5), 135.79 (C6). Data are consistent with those reported in the literature. The structural assignment of the product was supported by HMBC analysis, as indicated above.\)
2-Bromo-3-methoxy-1,4-benzoquinone (3b)

The product was obtained by the general procedure described above using 1,3-dibromo-5,5-dimethylhydantoin (DBH) (120 mol%, 0.12 mmol, 34.3 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 3b (16.1 mg, 74% yield) as an orange powder; m.p. (°C) = 85.7-86.3 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) ν: 2960 (w), 1651 (s), 1555 (s), 1092 (s); HRMS (EI⁺): 215.9410 [M⁺]. Calcd. for [C₇H₅BrO₃]: 215.9422; Elemental analysis – Calculated (%) C: 38.74 H: 2.32. Found (%) C: 39.09 H: 2.34; ¹H NMR (400 MHz, CDCl₃) δ: 6.87 (d, J = 10.0 Hz, C₆-H), 6.68 (d, J = 10.1 Hz, C₅-H), 4.21 (s, C₇-H₃); ¹³C NMR (100 MHz, CDCl₃) δ: 180.8 (C₄), 180.3 (C₁), 157.0 (C₃), 135.8 (C₆), 134.6 (C₅), 118.5 (C₂), 61.6 (C₇). The structural assignment of the product was supported by HMBC analysis, as indicated above.

2-Bromo-3-methyl-1,4-benzoquinone (3d)

The product was obtained by the general procedure described above using 1,3-dibromo-5,5-dimethylhydantoin (DBH) (120 mol%, 0.12 mmol, 34.3 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 3d (13.7 mg, 68% yield) as a yellow powder; m.p. (°C) = 55.1-56.7 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) ν: 2987 (w), 1596 (s), 1233 (s), 870 (s); HRMS (EI⁺): 199.9461 [M⁺]. Calcd. for [C₇H₅BrO₂]: 199.9473; Elemental analysis – Calculated (%) C: 41.83 H: 2.51. Found (%) C:
41.74 \( \text{H}: 2.66 \); \( ^1\text{H NMR} \ (400 \text{ MHz, CDCl}_3) \delta: \) 6.92 (d, \( J = 10.0 \text{ Hz, C6-H} \)), 6.81 (d, \( J = 10.0 \text{ Hz, C5-H} \)), 2.23 (s, C7-H); \( ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \delta: \) 183.9 (C4), 179.1 (C1), 146.2 (C3), 136.3 (C5), 136.1 (C2), 135.8 (C6), 16.9 (C7). The structural assignment of the product was supported by \textit{HMBC} analysis, as indicated above.

\textit{2-Bromo-5-(tert-butyl)-1,4-benzoquinone (3e)}

\begin{align*}
\text{The product was obtained by the general procedure described above using 1,3-dibromo-5,5-dimethylhydantoin (DBH) (120 \text{ mol\%}, 0.12 \text{ mmol, 34.3 mg}) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 3e (13.9 mg, 57\% yield) as a yellow powder; m.p. (°C) = 100.2-101.1 (Petrol/CH}_2\text{Cl}_2); \text{IR (solid, cm}^{-1}\text{)} \nu: \) 2963 (s), 1654 (s), 1013 (s), 733 (s); \text{HRMS (EI\textsuperscript{+})}: \) 241.9932 [M\textsuperscript{+}]. \text{Cald. for [C}_{10}\text{H}_{11}\text{BrO}_2]: 241.9942; \text{Elemental analysis – Calculated (\%)} \text{ C: 49.39 H: 4.56. Found (\%) C: 49.39 \ H: 4.44; \text{H NMR} \ (500 \text{ MHz, CDCl}_3) \delta: \) 7.19 (s, C3-H), 6.78 (s, C6-H), 1.28 (s, C8-H); \( ^{13}\text{C NMR} \ (100 \text{ MHz, CDCl}_3) \delta: \) 184.7 (C4), 180.4 (C1), 156.7 (C5), 139.9 (C3), 135.7 (C2), 130.9 (C6), 35.5 (C7), 29.1 (C8). The structural assignment of the product was supported by \textit{HMBC} analysis, as indicated above. Minor traces of regioisomer 3e' (10:1 3e:3e'), where bromination had occurred at C3, were detected, but, due to the low quantities of material formed, good quality NMR data could not be obtained. Assignment was made by comparison to 2e': \( ^1\text{H NMR} \ (500 \text{ MHz, CDCl}_3) \delta: \) 7.43 (d, \( J = 2.2 \text{ Hz, 1H} \)), 6.54 (d, \( J = 2.2 \text{ Hz, 1H} \)), 1.26 (s, 9H).}
2-Bromo-5,6-dichloro-1,4-benzoquinone (3f)

The product was obtained by the general procedure described above using 1,3-dibromo-5,5-dimethylhydantoin (DBH) (120 mol%, 0.12 mmol, 34.3 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 3f (11.5 mg, 45% yield) as yellow crystals; m.p. (°C) = 153.9-155.1 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) ν: 2970 (w), 1671 (s), 1187 (m), 1052 (s); HRMS (EI⁺): 253.8542 [M⁺]. Calcd. for [C₆HBrCl₂O₂]: 253.8537; Elemental analysis – Calculated (%) C: 28.16 H: 0.39. Found (%) C: 28.30 H: 0.39; ¹H NMR (400 MHz, CDCl₃) δ: 7.46 (s, C₃-H); ¹³C NMR (100 MHz, CDCl₃) δ: 175.3 (C₄), 141.4 (C5), 137.4 (C₁), 134.1 (C₆), 136.6 (C₂). The structural assignment of the product was supported by HMBC analysis, as indicated above.

2-(Phenylselanyl)-1,4-benzoquinone (4a)

The product was obtained by the general procedure described above using N-phenyl selenium phthalimide (100 mol%, 0.1 mmol, 30.2 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 4b (16.0 mg, 61% yield) as a red powder; m.p. (°C) = 100.4-101.1 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) ν: 2921 (w), 1631 (s), 1279 (m), 967 (s); HRMS (EI⁺): 263.9682 [M⁺]. Calcd. for [C₁₂H₈SeO₂]: 263.9690; Elemental analysis – Calculated (%) C: 54.77 H: 3.06. Found (%) C: 54.99 H: 3.07; ¹H NMR (400 MHz, CDCl₃) δ: 7.64-7.53 (m, C₈-H, C₁₂-H), 7.53-7.39 (m, C₉-H, C₁₀-H, C₁₁-H), 6.85 (d, J = 10.0 Hz, C₆-H), 6.68 (dd, J = 10.0, 2.4 Hz, C₅-H), 6.15
(d, J = 2.4 Hz, C3-H); 13C NMR (100 MHz, CDCl3) δ: 184.8 (C1), 184.1 (C4), 154.5 (C2), 137.5 (C5), 137.0 (C8), 135.9 (C6), 130.5 (C3), 130.4 (C9), 130.2 (C10), 123.9 (C7). The structural assignment of the product was supported by HMBC analysis, as indicated above. Compound 4a' was eluted first and obtained (5.4 mg, 13% yield) as an orange powder. The data for this compound are given at the end of the next procedure.

2,5-Bis(phenylselanyl)-1,4-benzoquinone (4a')

The product was obtained by the general procedure described above using N-phenyl selenium phthalimide (250 mol%, 0.25 mmol, 75.5 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 4a (30.9 mg, 74% yield) as an orange powder; m.p. (°C) = 230.3-231.0 (Petrol/CH2Cl2); IR (solid, cm⁻¹) ν: 3055 (w), 1634 (s), 1546 (m), 990 (s); HRMS (ESI⁺): 420.9263 [M+H]⁺. Calcd. for [C18H13Se2O2]: 420.9244; Elemental analysis – Calculated (%) C: 51.70 H: 2.89. Found (%) C: 52.11 H: 2.91; 1H NMR (400 MHz, CDCl3) δ: 7.63-7.53 (m, C8-H), 7.54-7.39 (m, C9-H, C10-H), 6.21 (s, C3-H, C6-H); 13C NMR (100 MHz, CDCl3) δ: 181.38 (C1, C4), 157.1 (C2, C5), 136.9 (C8), 130.4 (C9), 129.4 (C3, C6), 124.1 (C7). The structural assignment of the product was supported by HMBC analysis, as indicated above.

2,3-Dimethyl-5-(phenylselanyl)-1,4-benzoquinone (4c)
The product was obtained by the general procedure described above using N-phenyl selenium phthalimide (120 mol%, 0.12 mmol, 36.2 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 4c (21.3 mg, 73% yield) as red crystals; m.p. (°C) = 98.1-99.0 (Petrol/CH2Cl2); IR (solid, cm⁻¹) ν: 2930 (w), 1634 (s), 1236 (m), 746 (s); HRMS (EI⁺): 292.0006 [M⁺]. Calcd. for [C14H12SeO2]: 292.0003; Elemental analysis – Calculated (%) C: 57.74 H: 4.15. Found (%) C: 58.17 H: 4.18; ¹H NMR (500 MHz, CDCl₃) δ: 7.62-7.54 (m, C₈-H), 7.51-7.37 (m, C₉-H, C₁₀-H), 6.11 (s, C₃-H), 2.06 (s, C₁₃-H₃), 1.99 (s, C₁₄-H₃); ¹³C NMR (125 MHz, CDCl₃) δ: 184.9 (C₁a), 184.2 (C₄b), 153.6 (C₂), 141.9 (C₆), 140.5 (C₅), 137.0 (C₈), 130.5 (C₃), 130.2 (C₉), 129.9 (C₁₀), 124.5 (C₇), 12.4 (C₁₃, C₁₄). The structural assignment of the product was supported by HMBC analysis, as indicated above.

5-(tert-Butyl)-2-(phenylselanyl)-1,4-benzoquinone (4ea) and 6-(tert-butyl)-2-(phenylselanyl)-1,4-benzoquinone (4eb)

The product was obtained by the general procedure described above using N-phenyl selenium phthalimide (120 mol%, 0.12 mmol, 36.2 mg) and a reaction time of 18h. Purification by FCC (toluene) afforded products 4ea and 4eb (mixture of isomers, 5:2/a:b) (19.5 mg, 61% yield) as a red oil; HRMS (EI⁺): 321.0405 [M+H⁺]. Calcd. for [C₁₆H₁₇O₂Se]: 321.0393; ¹H NMR (400 MHz, CDCl₃) δ: 7.65-7.58 (m, C₅-H), 7.51-7.37 (m, C₆-H, C₁₂-H), 6.69 (s, C₃a-H), 6.52 (d, J = 2.4 Hz, C₃b-H), 6.11 (d, J = 2.4 Hz, C₆b-H), 6.07 (s, C₆a-H), 1.32 (s, C₈b-H), 1.27 (s, C₈a-H); ¹³C NMR (125 MHz, CDCl₃) δ: 185.7 (C₁a), 185.0 (C₄b), 184.8 (C₁b), 184.3 (C₄a), 157.2 (C₅a), 155.8 (C₆a) 152.0
The product was obtained by the general procedure described above using N-phenyl selenium phthalimide (120 mol%, 0.12 mmol, 36.2 mg) and a reaction time of 18 h. Purification by FCC (toluene) afforded product 6 (26.9 mg, 86% yield) as orange crystals; m.p. (°C) = 152.8-153.7 (Petrol/CH₂Cl₂); IR (solid, cm⁻¹) ν: 2930 (w), 1664 (s), 1296 (m), 690 (s); HRMS (EI⁺): 313.9848 [M⁺]. Calcd. for [C₁₆H₁₀SeO₂]: 313.9846.

Elemental analysis – Calculated (%) C: 61.36 H: 3.22. Found (%) C: 61.43 H: 3.56.

¹H NMR (400 MHz, CDCl₃) δ: 8.14 (dd, J = 7.2, 1.9 Hz, C₈-H), 8.03 (dd, J = 6.1, 1.9 Hz, C₅-H), 7.82-7.67 (m, C₆-H, C₇-H), 7.68-7.61 (m, C₁₀-H), 7.57-7.42 (m, C₁₁-H, C₁₂-H), 6.40 (s, C₃-H); ¹³C NMR (100 MHz, CDCl₃) δ: 183.0 (C₁), 181.7 (C₄), 157.0 (C₂), 137.1 (C₁₀), 134.3 (C₆), 133.3 (C₇), 132.8 (C₃), 132.3 (C₄a), 131.6 (C₈a), 130.4 (C₁₁), 130.2 (C₁₂), 126.9 (C₈), 126.7 (C₅), 124.4 (C₉). Data are consistent with those reported in the literature.⁷

Figure 3: Crystal structure of compound 6.
2-Phenoxy-1,4-benzoquinone (7a)

Product 7a was synthesised using a previously reported procedure.8 A 5 mL reaction tube was charged with 2a (0.10 mmol, 23.4 mg) or 3a (0.1 mmol, 18.7 mg), phenol (0.11 mmol, 10.3 mg), KF (0.3 mmol, 17.4 mg) and DMF (1 mL). The mixture was stirred and heated at 90 °C for 1h. After cooling and solvent removal, the mixture was purified by FCC (toluene) to afford 7a (16.2 mg, 81% yield from 2a, 15.8 mg, 79% yield from 3a) as a yellow solid; m.p. (°C) = 133.8-134.1 (Petrol/CH₂Cl₂); HRMS (EI⁺): 200.0468 [M]+. Cald. for [C₁₂H₈O₃]: 200.0473; ¹H NMR (400 MHz, CDCl₃) δ: 7.49-7.39 (m, 2H), 7.35-7.28 (m, 1H), 7.14-7.05 (m, 2H), 6.81 (d, J = 10.1 Hz, 1H), 6.72 (dd, J = 10.1, 2.3 Hz, 1H), 5.73 (d, J = 2.3 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ: 187.5, 181.5, 158.6, 152.3, 137.0, 137.0, 134.5, 130.4, 126.7, 120.9, 111.0. Data are consistent with those reported in the literature.⁹

2-Phenylamino-1,4-benzoquinone (7b)

Compound 7b was synthesised using a previously reported procedure.¹⁰ A 5 mL reaction tube was charged with 2a (0.10 mmol, 23.4 mg), aniline (0.12 mmol, 11.2 µL) and H₂O (0.5 mL). The mixture was stirred for 1h. The precipitate was collected by filtration and purified by FCC (toluene) to afford 7b (19.1 mg, 96% yield) as a dark yellow powder; m.p. (°C) = 131.5-133.4 (Petrol/CH₂Cl₂); MS (EI⁺): 199.1 [M]+. Cald. for [C₁₂H₉NO₂]: 199.1; ¹H NMR (400 MHz, CDCl₃) δ: 8.14 (s, 1H), 7.10-6.95 (m, 4H), 6.63-6.51 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 184.9, 181.6, 159.0, 158.5, 146.5, 138.4, 129.8, 128.6, 127.0, 123.0. Data are consistent with those reported in the literature.¹¹
2-Phenyl-1,4-benzoquinone (7c)

Compound 7c was synthesised using a previously reported procedure.\textsuperscript{1} A oven dried re-sealable tube was charged with 2a (0.10 mmol, 23.4 mg), Pd(d'bpf)Cl\textsubscript{2} (5 mol %, 3.7 mg), CuI (20 mol %, 4.0 mg) and CsF (0.20 mmol, 30.0 mg). The tube was purged with N\textsubscript{2} and PhSnBu\textsubscript{3} (0.12 mmol, 40.0 µL) and N,N-dimethylacetamide (1 mL) were added via syringe. The tube was sealed and the mixture was heated at 45 °C for 18h. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) and filtered through a pad of celite. The filtrate was concentrated under reduced pressure and the residue was purified by FCC (hexane/EtOAc 5:1) to afford 7c (13.1 mg, 71% yield) as an golden powder; m.p. (°C) = 108.8-110.0 (Petrol/CH\textsubscript{2}Cl\textsubscript{2}); HRMS (EI\textsuperscript{+}): 184.0511 [M]+. Cald. for [C\textsubscript{12}H\textsubscript{8}O\textsubscript{2}]: 184.0524; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ: 7.52-7.39 (m, 5H), 6.92-6.79 (m, 3H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ: 187.6, 186.6, 145.9, 137.0, 136.2, 132.7, 130.1, 129.2, 128.5. Data are consistent with those reported in the literature.\textsuperscript{12}

2-(4-fluorophenyl)-1,4-benzoquinone (7d)

Compound 7d was synthesised using a previously reported procedure\textsuperscript{13} with small modifications. A oven dried re-sealable tube was charged with 2a (0.10 mmol, 23.4 mg), Pd(d'bpf)Cl\textsubscript{2} (5 mol %, 3.7 mg), Na\textsubscript{2}CO\textsubscript{3} (200 mol %, 21.2 mg) and (4-fluorophenyl)boronic acid (0.11 mmol, 15.4 mg). The tube was purged with N\textsubscript{2} and N,N-dimethylacetamide (1 mL) were added via syringe. The tube was sealed and the mixture was heated at 50 °C for 14h. After cooling, the solvent was removed under reduced pressure. The residue was dissolved in CH\textsubscript{2}Cl\textsubscript{2} (5 mL) and filtered through a
pad of celite. The filtrate was concentrated under reduced pressure and the residue was purified by FCC (toluene) to afford 7d (11.1 mg, 55% yield) as an golden powder; m.p. (°C) = 149.8-152.2 (Petrol/CH₂Cl₂); MS (EI⁺): 202.0 [M]+. Calcd. for [C₁₂H₇FO₂]: 202.0; ¹H NMR (400 MHz, CDCl₃) δ: 7.48-7.51 (m, 2H), 7.12-7.14 (m, 2H), 6.80-6.89 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 187.6, 186.8, 165.2, 144.7, 136.9, 136.7, 132.7, 131.2 (d, J = 8.2 Hz), 129.5, 115.6 (d, J = 21.6 Hz). Data are consistent with those reported in the literature.¹⁴

**Intermolecular competition experiment between 1a and d₄-1a**

\[ \text{[RhCp}^1\text{Cl}_2]_2 \text{ (3.75 mol %), AgNTf}_2 \text{ (20 mol %), DIH (100 mol %)}} \]
\[ \text{CuSO}_4 \text{ (220 mol %), CH}_2\text{Cl}_2 \text{ (0.1 M), 100 °C, 18 h (sealed tube)}} \]
\[ \text{1a} \quad \text{d₄-1a} \quad \text{2a} \quad \text{d₃-2a} \]

A competition experiment involving the iodination of equimolar quantities of 1a and deuterio-1a was conducted. At 30% conversion, a 1.6:1 ratio of 2a to d₃-2a was obtained as determined by ¹H/²H NMR analysis against a 1:1 mixture of 1a and d₄-1a. This result confirms that C-H cleavage is kinetically significant, but does not elucidate whether or not this is the rate determining step.
Figure 4: $^1$H NMR spectra (400 MHz, CDCl$_3$) and $^2$H NMR spectra (400 MHz, CHCl$_3$) for determination of the 2a/d$_3$-2a ratio. A 1:1 ratio of benzoquinone:d$_4$-benzoquinone was used as a standard.
Figure 4: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2a.

Figure 5: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2a.
Figure 6: \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\)) of compound 2b.

Figure 7: \(^{13}\)C NMR spectrum (100 MHz, CDCl\(_3\)) of compound 2b.
Figure 8: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2c.

Figure 9: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2c.
**Figure 10:** $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 2d.

**Figure 11:** $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of compound 2d.
Figure 12: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2e.

Figure 13: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2e.
**Figure 14:** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2e$^\text{a}$. 

**Figure 15:** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2e$^\text{a}$. 

S25
Figure 16: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 2f.

Figure 17: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 2f.
Figure 18: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3a.

Figure 19: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3a.
Figure 20: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3b.

Figure 21: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3b.
**Figure 22:** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3d.

**Figure 23:** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3d.
Figure 24: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3e.

Figure 25: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3e.
Figure 26: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 3f.

Figure 27: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 3f.
**Figure 28:** $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 4a'.

**Figure 29:** $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 4a'.
Figure 30: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 4a.

Figure 31: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 4a.
Figure 32: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of compound 4c.

Figure 33: $^{13}$C NMR spectrum (125 MHz, CDCl$_3$) of compound 4c.
Figure 34: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 4e.

Figure 35: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 4e.
Figure 36: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of compound 6.

Figure 37: $^{13}$C NMR spectrum (100 MHz, CDCl$_3$) of compound 6.
References