

Isoquinolin-1-ylidenes as Electronically Tuneable Ligands

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ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

General Experimental Procedures: Solvents were purified and dried by standard procedures. Flash chromatography was carried out on silica-gel (0.040-0.063 mm or 0.015-0.040 mm). Melting points were measured in a metal block and are uncorrected. ¹H NMR spectra were recorded at 300 MHz, 400 MHz or 500 MHz. ¹³C NMR spectra were recorded at 75 MHz, 100 MHz or 125 MHz with the solvent peak used as the internal reference. IR were recorded in solution (CH₂Cl₂). Reactions were monitored by tlc. Standard schlenk techniques were used for air and moisture sensitive manipulations. Isoquinolines **1a** and **1d** are commercially available; compounds **1b**,¹ **1c**,² **1e**,² **4a**,³ and **5a**³ were prepared following literature procedures.

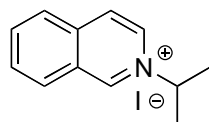
General procedure for the synthesis of isoquinolinium iodides **2a-e**:

A solution of isoquinoline **1a-e** (10 mmol) and 2-iodopropane (3 mL, 30 mmol) in dry toluene (10 mL) was warmed at 90 °C until consumption of the starting material. The mixture was then cooled to RT and cyclohexane (10 mL) was added. The supernatant solution was taken off with a syringe, the residue dissolved in CH₂Cl₂ (20 mL), and ether (50 mL) was added.

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- 1 K. Hirao, R. Tsuchiya, Y. Yano, H. Tsue, *Heterocycles* 1996, **42**, 415.
 - 2 J. B. Hendrickson, C. Rodríguez, *J. Org. Chem.* 1983, **48**, 3344.
 - 3 D. Barbier, C. Marazano, B. C. Das, P. Potier, *J. Org. Chem.* 1996, **61**, 9596.

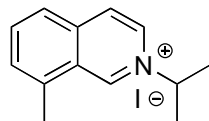
The resulting hygroscopic precipitate was dried *in vacuo*. Starting material, reaction times, yields and characterization data for **2a-e** are as follows:

Isoquinolinium iodide 2a:



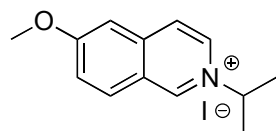
From **1a** (1.2 mL) after 1 d, **2a** (2.36 g, 79%) was obtained as a pale yellow solid. M.p. 95-96 °C. ¹H NMR (CDCl₃, 500 MHz) δ 10.80 (s, 1H), 8.89 (d, *J* = 6.8 Hz, 1H), 8.75 (d, *J* = 8.3 Hz, 1H), 8.39 (d, *J* = 6.8 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 7.99 (t, *J* = 7.8 Hz, 1H), 7.78 (t, *J* = 6.8 Hz, 1H), 5.46 (m, *J* = 6.7 Hz, 1H), 1.74 (d, *J* = 6.7 Hz, 1H). ¹³C NMR (CDCl₃, 125.7 MHz) δ 147.2, 137.2, 136.6, 132.3, 130.7, 130.6, 127.4, 126.6, 126.4, 64.2, 23.1. HRMS (FAB) calc.: C₁₂H₁₄N 172.1126 [M-I]⁺; found: 172.1131. Anal. Calc. for C₁₂H₁₄IN: C 48.12, H 4.72; found: C 47.92, H 5.01.

Isoquinolinium iodide 2b:



From **1b** (1.43 g) after 36 h, **2b** (2.32 g, 74%) was obtained as a pale yellow solid. M.p. 84-85 °C. ¹H NMR (CDCl₃, 500 MHz) δ 10.48 (s, 1H), 8.82 (d, *J* = 7.0 Hz, 1H), 8.75 (d, *J* = 7.0 Hz, 1H), 7.93-7.98 (m, 2H), 7.69 (d, *J* = 6.6 Hz, 1H), 5.95 (m, *J* = 6.8 Hz, 1H), 3.05 (s, 3H), 1.80 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, 125.7 MHz) δ 145.9, 140.4, 138.2, 137.0, 132.0, 131.0, 127.3, 127.1, 125.1, 64.5, 23.3, 20.3. HRMS (FAB) calc.: C₁₃H₁₆N 186.1283 [M-I]⁺; found: 186.1291. Anal. Calc. for C₁₃H₁₆IN: C 49.86, H 5.15; found: C 49.75, H 5.31.

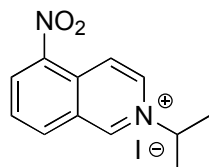
Isoquinolinium iodide 2c:



From **1c** (1.59 g) after 8 h, **2c** (2.27 g, 69%) was obtained as a dark yellow solid. M.p. 122-123 °C. ¹H NMR (CDCl₃, 500 MHz) δ 10.58 (s, 1H), 8.71 (d, *J* = 8.9 Hz, 1H), 8.64 (dd, *J* = 7.0 Hz, *J* = 2.0 Hz, 1H), 8.32 (d, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 8.9 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.42 (d, *J* = 2.4 Hz), 5.41 (m, *J* = 6.7 Hz, 1H), 4.04 (s, 3H), 1.79 (d, *J* = 6.7 Hz, 1H).

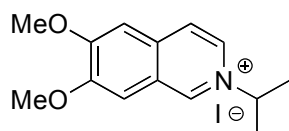
^{13}C NMR (CDCl_3 , 125.7 MHz) δ 166.2, 145.9, 140.6, 132.8, 132.3, 124.8, 124.3, 123.3, 105.2, 63.6, 56.9, 23.4. HRMS (FAB) calc.: $\text{C}_{13}\text{H}_{16}\text{NO}$ 202.1232 $[\text{M}-\text{I}]^+$; found: 202.1234. Anal. Calc. for $\text{C}_{13}\text{H}_{16}\text{INO}$: C 47.43, H 4.90; found: C 47.21, H 5.07.

Isoquinolinium iodide **2d**:



From **1d** (1.74 g) after 3 d, **2d** (2.58 g, 75%) was obtained as a dark pink solid. M.p. 220-222 °C. ^1H NMR ($\text{DMSO}-d_6$, 500 MHz) δ 10.47 (s, 1H), 9.16 (d, $J = 8.0$ Hz, 1H), 9.06 (d, $J = 7.7$ Hz, 1H), 8.96 (d, $J = 8.0$ Hz, 1H), 8.95 (d, $J = 7.7$ Hz, 1H), 8.28 (t, $J = 8.0$ Hz, 1H), 5.52 (m, $J = 6.7$ Hz, 1H), 1.74 (d, $J = 6.7$ Hz, 1H). ^{13}C NMR ($\text{DMSO}-d_6$, 125.7 MHz) δ 149.4, 143.8, 137.4, 135.7, 133.9, 130.3, 129.2, 128.3, 121.7, 64.3, 22.1. HRMS (FAB) calc.: $\text{C}_{12}\text{H}_{13}\text{N}_2\text{O}_2$ 217.0996 $[\text{M}-\text{I}]^+$; found: 217.0997. Anal. Calc. for $\text{C}_{12}\text{H}_{13}\text{IN}_2\text{O}_2$: C 41.88, H 3.81; found: C 41.74, H 3.92.

Isoquinolinium iodide **2e**:

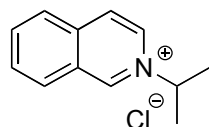


From **1e** (1.89 g) after 1 d, **2e** (2.11 g, 91%) was obtained as a brown pale solid. M.p. 232-234 °C. ^1H RMN (CDCl_3 , 300 MHz) δ 10.51 (s, 1H), 8.42 (d, $J = 6.7$ Hz, 1H), 8.31 (s, 1H), 8.20 (d, $J = 6.7$ Hz, 1H), 7.43 (s, 1H), 5.29 (m, $J = 6.8$ Hz, 1H), 4.11 (s, 3H), 4.09 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H). ^{13}C RMN (CDCl_3 , 75.4 MHz) δ 158.6, 153.4, 143.7, 136.2, 130.7, 125.3, 124.4, 108.7, 105.4, 64.1, 57.7, 57.6, 23.9, 23.9. HRMS (FAB) calc.: $\text{C}_{14}\text{H}_{18}\text{O}_2$ 232.1338 $[\text{M}-\text{I}]^+$; found: 232.1318.

General procedure for the synthesis of isoquinolinium chlorides **3a-e**:

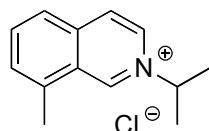
To a suspension of resin Dowex 22 (Cl) (1.5 g, washed with dry methanol and dried *in vacuo*) in dry methanol (5 mL) isoquinolinium iodide **2a-e** (2.5 mmol) was added at once. The resulting suspension was stirred over 1 h and filtered over a celita pad. The filtrate was concentrated to dryness to give pure isoquinolinium chlorides **3a-e**. Starting material, yields and characterization data for compounds **3a-e** are as follows:

Isoquinolinium chloride **3a**:



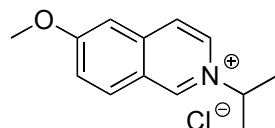
From **2a** (750 mg), **3a** (510 g, 98%) was obtained as a pale yellow green solid. M.p. > 200 °C (dec). ¹H NMR (CDCl₃, 300 MHz) δ 11.02 (s, 1H), 8.90 (d, *J* = 8.1 Hz, 1H), 8.85 (dd, *J* = 7.0, *J* = 1.3 Hz, 1H), 8.43 (d, *J* = 6.8 Hz, 1H), 8.13 (t, *J* = 6.8 Hz, 1H), 7.93 (t, *J* = 7.0 Hz, 1H), 5.60 (m, *J* = 6.8 Hz, 1H), 1.85 (d, *J* = 6.8 Hz, 6H). ¹³C NMR (CDCl₃, 75 MHz) δ 146.3, 136.5, 135.2, 132.1, 130.5, 130.4, 128.9, 126.9, 126.1, 65.1, 25.1. HRMS (FAB) calc.: C₁₂H₁₄N 172.1126 [M-Cl]⁺; found: 172.1123.

Isoquinolinium chloride **3b**:



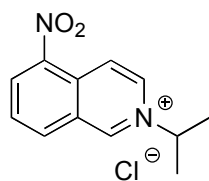
From **2b** (782 mg), **3b** (532 mg, 96%) was obtained as a pale yellow solid. M.p. > 200 °C (dec.). ¹H NMR (CDCl₃, 500 MHz) δ 10.97 (s, 1H), 8.87 (d, *J* = 6.9 Hz, 1H), 8.41 (d, *J* = 6.9 Hz, 1H), 7.95-7.90 (m, 2H), 7.67 (d, *J* = 6.1 Hz, 1H), 6.12 (m, *J* = 6.7 Hz, 1H), 3.06 (s, 3H), 1.78 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (CDCl₃, 125.7 MHz) δ 147.3, 140.8, 138.0, 136.7, 131.7, 130.7, 127.4, 127.0, 124.9, 63.9, 23.3, 19.6. HRMS (FAB) calc.: C₁₃H₁₆N 186.1283 [M-Cl]⁺; found: 186.1285. Anal. Calc. for C₁₃H₁₆ClN: C 70.42, H 7.27; found: C 70.31, H 7.15.

Isoquinolinium chloride **3c**:



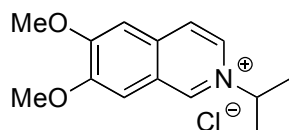
From **2c** (823 mg), **3c** (570 mg, 96%) was obtained as a pale yellow solid. M.p. 195-197 °C. ¹H NMR (CDCl₃, 500 MHz) δ 10.89 (s, 1H), 8.73-8.71 (m, 2H), 8.25 (d, *J* = 7.0 Hz, 1H), 7.39-7.36 (m, 2H), 5.42 (m, *J* = 6.7 Hz, 1H), 3.99 (s, 3H), 1.74 (d, *J* = 6.7 Hz, 6H). ¹³C NMR (CDCl₃, 125.7 MHz) δ 166.1, 147.1, 140.4, 133.3, 132.3, 124.7, 124.0, 123.6, 105.0, 63.4, 56.4, 23.3. Anal. Calc. for C₁₃H₁₆ClNO: C 65.68, H 6.78; found: C 65.37, H 6.99.

Isoquinolinium chloride 3d:



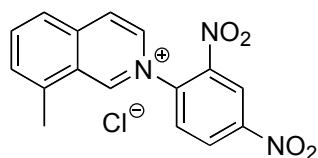
From **2d** (861 mg, 2.5 mmol), **3d** (599 mg, 95%) was obtained as a dark yellow solid. M.p. > 230 °C (dec). ¹H NMR (CDCl₃, 500 MHz) δ 10.30 (s, 1H), 9.16 (d, *J* = 7.3 Hz, 1H), 9.08 (d, *J* = 8.0 Hz, 1H), 9.04 (d, *J* = 7.3 Hz, 1H), 8.93 (d, *J* = 8.0 Hz, 1H), 8.25 (t, *J* = 8.0 Hz, 1H), 5.28 (m, *J* = 6.7 Hz, 1H), 1.85 (d, *J* = 6.7, 6H). ¹³C NMR (CDCl₃, 125.7 MHz) δ 150.5, 145.9, 138.7, 136.7, 135.6, 131.7, 130.5, 123.0, 67.0, 23.0. HRMS (FAB) calc.: C₁₂H₁₃N₂O₂ 217.0977 [M-Cl]⁺; found: 217.0990. Anal. Calc. for C₁₂H₁₃ClN₂O₂: C 57.04, H 5.19; found: C 56.79, H 5.35.

Isoquinolinium chloride 3e:



From **2e** (801 mg), **3e** (667 mg, quant.) was obtained as a white off solid. M.p. 111-113 °C. ¹H RMN (CDCl₃, 400 MHz) δ 10.9 (s, 1H), 8.35 (s, 1H), 8.25 (d, *J* = 6.8 Hz, 1H), 8.03 (d, *J* = 6.8 Hz, 1H), 7.29 (s, 1H), 5.42 (m, *J* = 6.4 Hz, 1H), 4.12 (s, 3H), 4.11 (s, 3H), 1.78 (s, 3H), 1.76 (s, 3H). ¹³C RMN (CDCl₃, 75.4 MHz) δ 158.2, 153.0, 144.6, 135.5, 129.9, 125.1, 123.8, 108.6, 104.8, 63.5, 57.1, 57.0, 23.4, 23.4. HRMS (FAB) calc.: C₁₄H₁₈NO₂ 232.1338 [M-Cl]⁺; found: 232.1325.

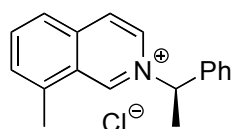
Isoquinolinium chloride 4b:



A mixture of 1-chloro-2,4-dinitrobenzene (1.52 g, 7.5 mmol) and isoquinoline **1b** (1.0 g, 7 mmol) was stirred at 90 °C for 15 min in a two neck round bottom flask equipped with a condenser and a dropping funnel. Acetone (5 mL) was then slowly added, and the resulting solution was refluxed over 30 h. After cooling to RT, the mixture was concentrated to dryness and the red-orange residue was dissolved in boiling MeOH (15 mL). Cold EtOAc (40 mL)

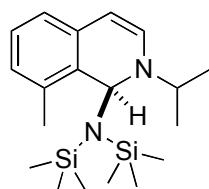
was added under stirring to afford **4b** (1.47 g, 61%) as a pale yellow powder. M.p. 156-159 °C. ¹H NMR (CD₃OD, 500 MHz) δ 10.40 (s, 1H), 9.27 (d, *J* = 2.4 Hz, 1H), 8.94-8.91 (m, 2H), 8.70 (d, *J* = 6.8 Hz, 1H), 8.43 (d, *J* = 8.6, 1H), 8.31-8.27 (m, 2H), 8.00 (d, *J* = 5.6 Hz, 1H), 2.94 (s, 3H). ¹³C NMR (CD₃OD, 125.7 MHz) δ 153.2, 148.2, 147.3, 144.6, 140.4, 139.1, 137.4, 131.2, 129.4, 127.5, 127.4, 125.2, 124.2, 117.9, 23.5. HRMS (FAB) calc.: C₁₆H₁₂N₃O₄ 310.0828 [M-Cl]⁺; found: 310.0824. Anal. Calc. for C₁₆H₁₂ClN₃O₄: C 55.58, H 3.50; found: C 55.49, H 3.71.

Isoquinolium chloride **5b**:



A solution of **4b** (1.04g, 3 mmol) and (*R*)-1-phenylethanamine (447 μL, 3.5 mmol) in dry butanol (10 mL) was refluxed over 2 d and then concentrated. Water was then added to the residue, and the red solid formed was removed by filtration and washed with water (3 x 10 mL). The resulting mother liquor was basicified with saturated aqueous NH₄Cl solution (0.5 mL), and then washed with EtOAc (3 x 30 mL). Concentration of the aqueous solution and column chromatography (99:1→95:5 CH₂Cl₂-MeOH) afforded **5b** as a white off solid (602 mg, 71%). M.p. 126-128 °C. ¹H NMR (CDCl₃, 500 MHz) δ 11.36 (s, 1H), 8.57 (d, *J* = 6.8 Hz, 1H), 8.36 (d, *J* = 7.0 Hz, 1H), 7.98-7.92 (m, 1H), 7.75 (d, *J* = 6.9 Hz, 1H), 7.71 (d, *J* = 6.9 Hz, 1H), 7.48 (q, *J* = 7.0 Hz, 1H), 7.49-7.31 (m, 5H), 3.13 (s, 3H), 2.16 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃, 125.7 MHz) δ 148.0, 141.2, 138.1, 137.0, 137.0, 132.0, 131.2, 129.4, 128.0, 127.5, 127.0, 125.0, 68.9, 20.8, 19.6. [α]_D²⁰ +24.3 (*c* 0.2, CHCl₃). HRMS (FAB) calc.: C₁₈H₁₈N 248.1439 [M-Cl]⁺; found: 248.1438.

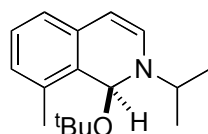
Adduct **6b**:



Inside a dry box, a schlenk flask equipped with a magnetic stir bar was charged with isoquinolinium salt **3b** (221 mg, 1 mmol) and cooled to -78 °C. A solution of KHMDS (200 mg, 1 mmol) in toluene (4 mL) was slowly added *via* cannula. After 10 min, the mixture was

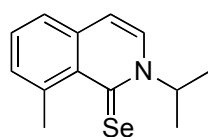
allowed to warm to RT, stirred for 10 min, and then salts were allowed to decant during 1 h. Concentration of the supernatant afforded **6b** (345 mg, quant.) as a light yellow oil that solidifies on standing. ^1H NMR ($[\text{D}_8]$ toluene, 500 MHz) δ 7.03-6.98 (m, 2H), 6.80-6.70 (m, 4H), 6.11-6.08 (m, 4H), 5.35 (d, $J = 7.5$ Hz, 2H), 3.48 (m, $J = 6.5$ Hz, 2H), 2.19 (s, 6H), 1.09 (d, $J = 6.5$ Hz, 6H), 0.93 (d, $J = 6.5$ Hz, 6H). ^{13}C NMR ($[\text{D}_8]$ toluene, 100 MHz) δ 142.2, 141.5, 140.5, 131.9, 126.9, 100.8, 75.9, 53.8, 26.8, 26.3, 25.4, 12.3, 7.4.

Adduct **6'b**:



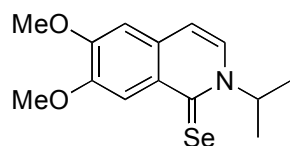
A schlenk flask equipped with a magnetic stir bar was charged with **2b** (313 mg, 1 mmol) and KO t Bu (112 mg, 1 mmol). Dry THF (4 mL) was added and the resulting mixture was stirred for 2 h at RT. Then the solvent was removed and dry toluene (10 mL) was added via syringe. The mixture was decanted, the supernatant separated and concentrated to afford the **6'b** (218 mg, 84%) as a light yellow oil. ^1H RMN (C_6D_6 , 400 MHz) δ 7.12-7.07 (m, 1H), 6.97 (d, $J = 7.6$ Hz, 1H), 6.91 (d, $J = 7.3$ Hz, 1H), 6.20 (dd, $J = 7.3, 1.3$ Hz, 1H), 6.14 (d, $J = 1.3$ Hz, 1H), 5.86 (d, $J = 7.2$ Hz, 1H), 3.37 (m, $J = 6.6$ Hz, 1H), 2.37 (s, 3H), 1.11 (s, 9H), 1.05 (d, $J = 6.5$ Hz, 3H), 0.76 (d, $J = 6.5$ Hz, 3H). ^{13}C RMN (CDCl_3 , 100 MHz) δ 134.8, 134.3, 128.4, 127.4, 127.1, 122.4, 102.9, 82.5, 53.8, 37.7, 30.1, 23.6, 20.6, 19.1. Anal. Calc. for $\text{C}_{17}\text{H}_{25}\text{NS}$: C 78.72, H 9.71, N 5.40; found: C 79.20, H 10.09, N 5.11.

Selenolactam **8b**:



To a solution of **6b** (172 mg, 0.52 mmol) in dry toluene (1.5 mL) under Ar was added Se (80 mg, 1.0 mmol) and the mixture was stirred overnight at RT. Concentration afforded a pale orange solid, which was purified by column chromatography (4:1 EtOAc-hexane) to yield **8b** (121 mg, 93%) as a pale orange syrup. ^1H RMN (CDCl_3 , 400 MHz) δ 7.43 (m, 2H), 7.39 (m, 2H), 6.99 (d, $J = 7.2$ Hz, 1H), 6.80 (m, $J = 6.8$ Hz, 1H), 3.22 (s, 3H), 1.48 (d, $J = 6.8$ Hz, 6H). ^{13}C RMN (CDCl_3 , 100 MHz) δ 184.6, 143.5, 137.6, 133.5, 133.2, 131.1, 128.1, 125.3, 115.1, 57.6, 28.8, 21.9, 21.9. HRMS (CI $^+$) calc.: $\text{C}_{13}\text{H}_{15}\text{NSe}$ 265.0370 $[\text{M}+\text{H}]^+$; found 265.0371.

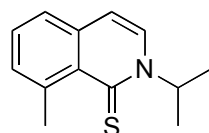
Selenolactam **8e**:



KHMDS (27 mg, 0.13 mmol) and Se (20 mg, 0.25 mmol) were added under Ar to a stirred solution of isoquinolinium chloride **3e** (33 mg, 0.12 mmol) in dry THF (1.5 mL) at RT. After 3 d the solution was concentrated and the residue purified by column chromatography (10:1 EtOAc-hexane) to afford **8e** (17 mg, 45%) as an orange solid. M.p. 164-166 °C. ¹H RMN (CDCl₃, 400 MHz) δ 8.78 (s, 1H), 7.56 (d, *J* = 7.2 Hz, 1H), 7.05 (d, *J* = 7.2 Hz, 1H), 6.88 (m, 1H), 6.86 (s, 1H), 4.07 (s, 3H), 3.99 (s, 3H), 1.50 (s, 3H), 1.48 (s, 3H). ¹³C RMN (CDCl₃, 75.4 MHz) δ 180.3, 154.66, 151.4, 132.5, 128.2, 127.6, 116.5, 114.7, 105.5, 59.5, 56.6, 30.0, 22.3. HRMS (FAB) calc.: C₁₄H₁₈NO₂Se 312.0503 [M+H]⁺; found: 312.0494.

Crystals of **8e** suitable for X-ray diffraction analysis were grown by slow diffusion from a CH₂Cl₂/cyclohexane mixture.

Thiolactame **8'b**:



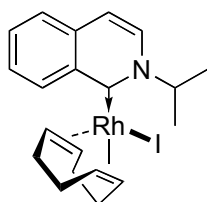
A mixture of **6'b** (130 mg, 0.5 mmol) and S₈ (32 mg, 1 mmol) was charged in a schlenk flask under argon. Dry toluene (2 mL) was added and the mixture was stirred for 1h at 80 °C. Concentration and column chromatography (5:1 EtOAc-hexane) afforded **8'b** (66 mg, 61%) as a yellow oil. ¹H RMN (CDCl₃, 400 MHz) δ 7.50-7.41 (m, 1H), 7.40-7.31 (m, 3H), 6.84 (d, *J* = 7.3 Hz, 1H), 6.61 (m, *J* = 7.3 Hz, 1H), 3.21 (s, 3H), 1.43 (d, *J* = 6.8 Hz, 6H). ¹³C RMN (CDCl₃, 100 MHz) δ 184.0, 143.0, 133.9, 133.8, 132.6, 130.6, 127.1, 124.9, 112.6, 52.2, 28.1, 21.4, 21.4. Anal. Calc. for C₁₃H₁₅NS: C 71.84, H 6.96, N 6.44; found: C 71.80, H 7.08, N 6.31.

General procedure for the synthesis of Rhodium complexes **9a**, **10a-d**, **11**:

A schlenk tube was charged with isoquinolinium salt **2**, **3**, or **5** (1 mmol) and heated *in vacuo*. Anhydrous, desoxygenated THF (5 mL) was added at RT and the resulting suspension was

then cooled to $-30\text{ }^{\circ}\text{C}$. A solution of KHMDS in dry THF (1.1 eq.) was added and the mixture was stirred for 10-60 min at $-20\text{ }^{\circ}\text{C}$. $[\text{RhCl}(\text{COD})]_2$ (270 mg, 1.1 mmol) was added at once and the mixture was stirred at RT for 15 min. The solvent was removed and the residue was purified by column chromatography to afford complex **9-11**. Starting material, reaction times, eluent used for the chromatographic purification, yields, and characterization data for compounds **9a**, **10a-d**, **11** are as follows.

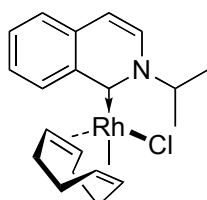
Rhodium complex **9a**:



From **2a** (15 min at $-20\text{ }^{\circ}\text{C}$), column chromatography (95:5 \rightarrow 80:20 pentane-Et₂O) afforded **9a** (360 mg, 71%) as a yellow orange solid. M.p. 89-91 $^{\circ}\text{C}$. ¹H RMN (CDCl₃, 500 MHz) δ 9.83 (d, $J = 8.1\text{ Hz}$, 1H), 7.76 (td, $J = 1.5\text{ Hz}$, $J = 7.5\text{ Hz}$, 1H), 7.71 (dd, $J = 1.1\text{ Hz}$, $J = 8.1\text{ Hz}$, 1H), 7.34 (d, $J = 6.9\text{ Hz}$, 1H), 7.62 (d, $J = 7.7\text{ Hz}$, 1H), 7.29 (d, $J = 7.34\text{ Hz}$, 1H), 7.16 (m, 1H), 5.43 (m, 1H), 5.28 (m, 1H), 3.41 (m, 2H), 2.54 (m, 1H), 2.47-2.32 (m, 3H), 2.12-1.98 (m, 2H), 1.90-1.77 (m, 2H), 1.78 (d, $J = 7.0\text{ Hz}$, 3H), 1.71 (d, $J = 6.6\text{ Hz}$, 3H). ¹³C RMN (CDCl₃, 125.7 MHz) δ 228.0 (d, $J_{\text{C-Rh}} = 44.7\text{ Hz}$), 139.5, 139.0, 132.7, 130.1, 128.9, 127.4, 126.1, 119.0, 97.0 (d, $J_{\text{C-Rh}} = 6.6\text{ Hz}$), 96.6 (d, $J_{\text{C-Rh}} = 6.6\text{ Hz}$), 75.3 (d, $J_{\text{C-Rh}} = 16.4\text{ Hz}$), 70.8 (d, $J_{\text{C-Rh}} = 13.1\text{ Hz}$), 64.9, 53.4, 32.3, 31.7, 29.6, 23.1, 22.5. Anal. Calc. for C₂₀H₂₄INRh: C 47.27, H 4.76; found: C 47.28, H 5.09.

Crystals of **9a** suitable for X-ray diffraction analysis were grown by slow diffusion from a CH₂Cl₂/cyclohexane mixture.

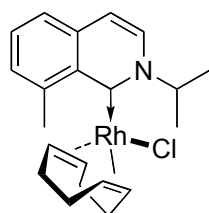
Rhodium complex **10a**:



From **3a** (15 min at $-20\text{ }^{\circ}\text{C}$). Column chromatography (95:5 \rightarrow 80:20 pentane-Et₂O) afforded **10a** (225 mg, 54%) as a yellow solid. M.p. 68-70 $^{\circ}\text{C}$. ¹H RMN (CDCl₃, 500 MHz) δ 10.01 (d, $J = 8.0\text{ Hz}$, 1H), 7.79 (td, $J = 1.2\text{ Hz}$, $J = 6.9\text{ Hz}$, 1H), 7.74 (dd, $J = 1.2\text{ Hz}$, $J = 8.0\text{ Hz}$, 1H),

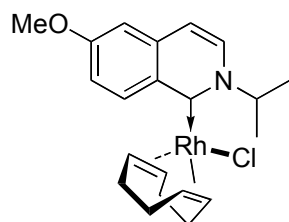
7.71 (d, $J = 6.9$ Hz, 1H), 7.63 (d, $J = 7.5$ Hz, 1H), 7.43 (m, 1H), 7.31 (d, $J = 6.9$ Hz, 1H), 5.25 (m, 1H), 5.08 (m, 1H), 3.24 (m, 1H), 2.65 (m, 1H), 2.55-2.45 (m, 2H), 2.38 (m, 1H), 2.15-1.87 (m, 5H), 1.80 (d, $J = 6.3$ Hz, 3H), 1.71 (d, $J = 6.9$ Hz, 3H). ^{13}C RMN (CDCl_3 , 125.7 MHz) δ 228.1 (d, $J_{\text{C-Rh}} = 44.1$ Hz), 139.5, 138.7, 132.9, 130.4, 129.0, 127.8, 126.2, 119.2, 99.3 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 98.5 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 71.2 (d, $J_{\text{C-Rh}} = 14.8$ Hz), 67.6 (d, $J_{\text{C-Rh}} = 14.8$ Hz), 65.6, 33.3, 32.0, 29.3, 28.3, 23.4, 23.1. Anal. Calcd. for $\text{C}_{20}\text{H}_{24}\text{ClNRh}$: C 57.64, H 5.80; found: C 57.28, H 6.09.

Rhodium complex 10b:



From **3b** (0.5 mmol) (30 min at -20 °C). Column chromatography (95:5 \rightarrow 80:20 pentane- Et_2O) afforded **10b** (176 mg, 82%) as a pale yellow powder. M.p. 125-129 °C. ^1H RMN (CDCl_3 , 500 MHz) δ 8.17 (m, 1H), 7.72 (d, 1H, $J = 6.9$ Hz), 7.64-7.58 (m, 2H), 7.49 (d, 1H, $J = 7.5$ Hz), 7.26 (d, 1H, $J = 7.5$ Hz), 5.19-5.10 (m, 2H), 4.31 (s, 3H), 2.85 (m, 1H), 2.77 (m, 1H), 2.65 (m, 1H), 2.47 (m, 1H), 2.38-2.27 (m, 2H), 2.05 (m, 1H), 1.96 (m, 1H), 1.88 (d, 3H, $J = 6.9$ Hz), 1.84-1.68 (m, 2H), 1.75 (d, 3H, $J = 6.9$ Hz). ^{13}C RMN (CDCl_3 , 125.7 MHz) δ 227.9 (d, $J_{\text{C-Rh}} = 42.7$ Hz), 145.0, 138.5, 132.5, 131.3, 128.6, 125.2, 119.8, 97.6 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 95.0 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 68.7, 68.3, 68.1, 33.6, 31.6, 30.8, 29.4, 27.8, 27.1. Anal. Calc. for $\text{C}_{21}\text{H}_{26}\text{ClNRh}$: C 58.55, H 6.08; found: C 58.21, H 6.07.

Rhodium complex 10c:

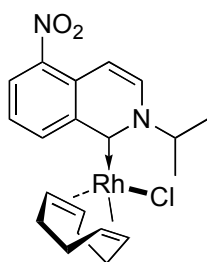


From **3c** (1h at -20 °C). Column chromatography (95:5 \rightarrow 80:20 pentane- Et_2O) afforded **10c** (174 mg, 39%) as a pale yellow solid. M.p. 143-145 °C. ^1H RMN (CDCl_3 , 500 MHz) δ 9.81 (d, $J = 9.2$ Hz, 1H), 7.59 (d, $J = 6.9$ Hz, 1H), 7.33-7.26 (m, 2H), 7.14 (d, $J = 6.9$ Hz, 1H), 6.86 (d, $J = 2.3$ Hz, 1H), 5.15 (m, 1H), 5.00 (m, 1H), 3.88 (s, 3H), 3.17 (m, 1H), 2.58 (m,

1H), 2.43 (m, 2H), 2.31 (m, 1H), 2.08-1.95 (m, 3H), 1.87 (m, 2H), 1.72 (d, $J = 6.9$ Hz, 3H), 1.63 (d, $J = 6.9$ Hz, 3H). ^{13}C RMN (CDCl_3 , 125.7 MHz) δ 224.6 (d, $J_{\text{C-Rh}} = 42.7$ Hz), 163.0, 141.2, 133.8, 132.9, 129.4, 119.0, 118.4, 105.2, 98.9, 98.5 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 71.1 (d, $J_{\text{C-Rh}} = 16.4$ Hz), 67.4 (d, $J_{\text{C-Rh}} = 16.4$ Hz), 65.1, 55.7, 33.3, 32.0, 29.3, 28.3, 23.4, 23.1. Anal. Calc. for $\text{C}_{21}\text{H}_{26}\text{ClNORh}$: C 56.45, H 5.87; found: C 56.01, H 6.29.

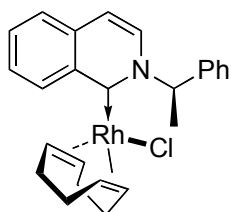
Crystals of **10c** suitable for X-ray diffraction analysis were grown by slow diffusion from a $\text{CH}_2\text{Cl}_2/\text{cyclohexane}$ mixture

Rhodium complex **10 d**:



From **3d** (10 min at -20 °C). Column chromatography (99:1 \rightarrow 90:10 pentane/ Et_2O) afforded **10d** (208 mg, 45%) as an orange solid. M.p. 175-176 °C. ^1H RMN (CDCl_3 , 500 MHz) δ 10.48 (d, $J = 8.0$ Hz, 1H), 8.51 (d, $J = 7.5$ Hz, 1H), 8.15 (dd, $J = 7.5$ Hz, 1H), 7.90 (m, 2H), 7.43 (m, 1H), 5.27 (m, 1H), 5.12 (m, 1H), 3.23 (m, 1H), 3.10 (m, 1H), 2.60 (m, 1H), 2.47 (m, 2H), 2.38 (m, 1H), 2.14-1.91 (m, 4H), 1.81 (d, $J = 6.9$ Hz, 3H), 1.72 (d, $J = 6.9$ Hz, 3H). ^{13}C RMN (CDCl_3 , 125.7 MHz) δ 230.6 (d, $J_{\text{C-Rh}} = 42.7$ Hz), 147.0, 144.4, 139.7, 131.9, 130.0, 126.7, 124.2, 114.3, 100.6 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 99.9 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 71.8 (d, $J_{\text{C-Rh}} = 16.4$ Hz), 68.2 (d, $J_{\text{C-Rh}} = 13.1$ Hz), 66.2, 33.1, 32.1, 29.2, 28.4, 23.2, 23.0. Anal. Calc. for $\text{C}_{20}\text{H}_{23}\text{ClN}_2\text{O}_2\text{Rh}$: C 52.02, H 5.02; found: C 51.75, H 5.48.

Rhodium complex **11**:



From **5b** (15 min at -20 °C). Column chromatography (99:1 \rightarrow 90:10 $\text{CH}_2\text{Cl}_2\text{-Et}_2\text{O}$) afforded **11a** (310 mg, 65 %) as a 4:1 mixture of atropoisomers. Separation of this mixture by medium pressure chromatography afforded the major isomer (215 mg, 45%) in pure form. Data for major **11a**: M.p. 84-86 °C. ^1H RMN (CDCl_3 , 500 MHz) δ 10.09 (d, $J = 8.0$ Hz, 1H), 8.53 (q,

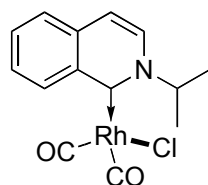
$J = 6.9$ Hz, 1H), 7.85 (m, 1H), 7.78 (m, 1H), 7.67 (d, $J = 8.0$ Hz, 1H), 7.55 (d, $J = 6.9$ Hz, 1H), 7.43 (m, 2H), 7.38 (m, 1H), 7.32 (m, 2H), 7.27 (d, $J = 6.9$ Hz, 1H), 5.25 (m, 1H), 5.16 (m, 1H), 3.46 (m, 1H), 3.31 (m, 1H), 2.67 (m, 1H), 2.57 (m, 1H), 2.35 (m, 1H), 2.19 (d, $J = 7.5$ Hz, 3H), 2.06-1.94 (m, 4H), 1.78 (m, 1H). ^{13}C RMN (CDCl_3 , 125.7 MHz) δ 230.0 (d, $J_{\text{C-Rh}} = 45.9$ Hz), 140.8, 139.7, 139.0, 133.2, 131.3, 130.4, 129.0, 128.0, 127.8, 126.6, 126.5, 119.0, 99.4 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 99.3 (d, $J_{\text{C-Rh}} = 6.6$ Hz), 72.1 (d, $J_{\text{C-Rh}} = 13.1$ Hz), 67.8 (d, $J_{\text{C-Rh}} = 13.1$ Hz), 67.6, 33.0, 32.2, 29.0, 28.5, 21.3. $[\alpha]_{\text{D}}^{20} = -48.2$ (c 0.2, CHCl_3). Anal. Calc. for $\text{C}_{25}\text{H}_{26}\text{ClNRh}$: C 62.71, H 5.47; found: C 62.35, H 5.41.

Crystals of **11a** suitable for X-ray diffraction analysis were grown by slow diffusion from a CH_2Cl_2 /cyclohexane mixture.

General procedure for the synthesis of Rhodium dicarbonyl complexes **12a,c,d**:

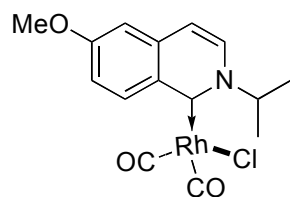
A CO steam (CAUTION: The operation must be done in a well ventilated hood) was bubbled through a deoxygenated solution of rhodium complexes **12a,c,d** (0.1 mmol) in dry CH_2Cl_2 (2 mL) for 5 min. The solution was concentrated and the resulting pale yellow solid was washed with pentane (2×2 mL), and dried *in vacuo*. Starting material, yields, and characterization data for compounds **12a,c,d** are as follows:

Rhodium dicarbonyl complex **12a**:



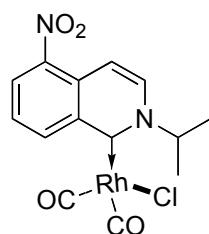
From **10a**, complex **12a** (48 mg, 93%) was isolated as a white off solid. IR (CH_2Cl_2): $\nu(\text{C}=\text{O})$ 2077, 1998 cm^{-1} . ^1H RMN (CDCl_3 , 500 MHz) 9.22 (d, $J = 8.0$ Hz, 1H), 7.91 (d, $J = 6.9$ Hz, 1H), 7.81 (m, 1H), 7.76 (m, 2H), 7.61 (d, $J = 6.9$ Hz, 1H), 6.33 (m, 1H), 1.68 (d, $J = 6.9$ Hz, 3H), 1.63 (d, $J = 6.9$ Hz, 3H). ^{13}C RMN (CDCl_3 , 125.7 MHz) δ 209.2 (d, $J_{\text{C-Rh}} = 36.1$ Hz), 188.2 (d, $J_{\text{C-Rh}} = 52.5$ Hz), 182.8 (d, $J_{\text{C-Rh}} = 82.0$ Hz), 139.0, 138.4, 134.0, 131.5, 129.2, 128.1, 126.2, 121.7, 66.4, 22.6, 21.1.

Rhodium dicarbonyl complex **12c**:



From **10c**, complex **12c** (42 mg, 93%) was isolated as white off solid. IR (CH₂Cl₂): $\nu(\text{C}=\text{O})$ 2076, 1996 cm⁻¹. ¹H RMN (CDCl₃, 500 MHz) δ 9.22 (d, $J = 9.2$ Hz, 1H), 7.80 (d, $J = 6.9$ Hz, 1H), 7.46 (d, $J = 6.9$ Hz, 1H), 7.32 (dd, $J = 6.9, 2.3$ Hz, 1H), 6.97 (d, $J = 2.3$ Hz, 1H), 6.42 (m, 1H), 3.92 (m, 3H), 1.64 (d, $J = 6.9$ Hz, 3H), 1.59 (d, $J = 6.9$ Hz, 3H). ¹³C RMN (CDCl₃, 125.7 MHz) δ 206.7 (d, $J_{\text{C-Rh}} = 36.1$ Hz), 186.5 (d, $J_{\text{C-Rh}} = 52.5$ Hz), 183.7 (d, $J_{\text{C-Rh}} = 76.8$ Hz), 164.0, 140.4, 134.5, 133.9, 128.7, 120.7, 120.2, 105.1, 66.5, 55.9, 22.7, 22.3.

Rhodium dicarbonyl complex **12d**:



From **10d**, complex **12d** (42 mg, 91%) was isolated as a white off solid. IR (CH₂Cl₂): $\nu(\text{C}=\text{O})$ 2081, 2003 cm⁻¹. ¹H RMN (CDCl₃, 500 MHz) δ 9.89 (d, $J = 8.0$ Hz, 1H), 8.65 (d, $J = 8.0$ Hz, 1H), 8.56 (d, $J = 7.5$ Hz, 1H), 8.13 (d, $J = 7.5$ Hz, 1H), 7.91 (d, $J = 8.0$ Hz, 1H), 6.62 (m, 1H), 1.73 (d, $J = 6.9$ Hz, 3H), 1.69 (d, $J = 6.9$ Hz, 3H). ¹³C RMN (CDCl₃, 125.7 MHz) δ 212.6 (d, $J_{\text{C-Rh}} = 39.4$ Hz), 185.9 (d, $J_{\text{C-Rh}} = 55.8$ Hz), 183.0 (d, $J_{\text{C-Rh}} = 75.5$ Hz), 146.2, 144.3, 139.5, 132.1, 131.3, 127.4, 125.4, 117.4, 67.9, 22.6, 22.2.

General procedure for the hydrosilylation of acetophenone

To a solution of Rh-complex **10** (0.004 mmol) in CCl₄ (200 μ L) were added diphenylsilane (237 μ L, 1.28 mmol) and acetophenone (100 μ L, 0.85 mmol) and the mixture was stirred at RT for 6 h. Methanol (1 mL) and a few crystals of *p*-TsOH were added, and after stirring 90 min at RT the solvents were evaporated and the residue analyzed by ¹H NMR. The following peaks were used for analysis: $\delta = 5.07$ ppm (q, PhCHOHCH₃, 1H), $\delta = 2.61$ ppm (s, PhCOCH₃, 3H).