Urea-Substituted Tetramethylcyclopentadienyl Ligands for Supramolecularly Accelerated Rh$^{III}$-Catalyzed ortho-C–H Olefination of Benzoic Acid Derivatives

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1 General Materials and Methods

All reactions were performed in flame- or oven-dried glassware with magnetic stirring under a nitrogen or argon (Argon 5.0, Sauerstoffwerk Friedrichshafen) atmosphere. All commercial reagents were used without purification unless otherwise noted. Air and moisture sensitive liquids and solutions were transferred via stainless steel syringe or cannula and introduced into the reaction vessel through rubber septa. Reaction temperatures were measured in degrees Celsius (°C). Reaction times were recorded in minutes (min) or hours (h). Organic extracts were dried over sodium sulfate. Reactions conducted below room temperature were cooled by an external bath: dry ice in acetone for −78 °C or ice water for 0 °C.

1.1 Solvents

Cyclohexane (CH) was purchased in technical grade quality and distilled before use.
Dichloromethane (DCM) was purchased in HPLC grade quality and used as received.
Diethyl ether (Et₂O) was purchased in p.a. grade quality and used as received.
Dimethyl sulfoxide (DMSO) was purchased in p.a. grade and used as received.
Ethyl acetate (AcOEt) was purchased in technical grade quality and distilled before use.
Tetrahydrofuran (THF) was purchased in HPLC grade quality, heated to reflux over potassium and distilled under argon.
Toluene (PhMe) was purchased in p.a. grade quality, heated to reflux over sodium and distilled under argon.

1.2 Evaporation

Organic solutions were concentrated by rotary evaporation at 40 °C on a Heidolph Laborata 4001 - efficient. Reaction mixtures containing only non-volatile products were further concentrated at a vacuubrand® vacuum pump (pressure < 0.5 mbar).

1.3 Thin-Layer Chromatography

Analytical TLC was performed on silica gel 60 F₂₅₄ plates (0.25 mm, Merck KGaA). Visualization of developed chromatograms was performed by fluorescence quenching and staining with an aqueous solution of potassium permanganate (1.0 g potassium permanganate, 7.0 g potassium carbonate and 0.1 g sodium hydroxide per 100 mL of water).

1.4 Column Chromatography

Chromatographic purification of products was accomplished using forced-flow chromatography on silica gel 60 (particle size 0.040 - 0.063 mm, 230 - 240 mesh ASTM) from Macherey-Nagel GmbH & Co. KG.

1.5 Melting points

Melting points were measured using a Stuart® SMP10 digital melting point apparatus and are uncorrected.

1.6 Nuclear Magnetic Resonance Spectroscopy

All NMR experiments were performed by the analytics department of the Institut für Organische Chemie at the University of Freiburg. ¹H and ¹³C NMR spectra were recorded on a Bruker 400 Avance NMR spectrometer with BBO probe head at a frequency of 400.1 MHz or 100.6 MHz, respectively, at a temperature of 300 K. Unequivocal ¹H and ¹³C assignments were made with the aid of two-dimensional HH-COSY, CH-COSY or HMBC spectra using a Bruker Avance III HD (500 MHz) spectrometer with TBI or BBFO (for ³¹P-decoupled spectra) probe head at a frequency of 499.6 MHz (¹H) or 125.6 MHz (¹³C) at a temperature of 300 K. Chemical shifts (δ) are reported in parts per million (ppm) relative to residual protio solvent signals; in case of CDCl₃: δ (CHCl₃) = 7.26 ppm; in case of DMSO-d₆: δ (CD₃S(O)CD₂H) = 2.50 ppm for ¹H spectra; in case of CD₂OD: δ (CD₂OD) = 3.31 ppm for ¹H spectra. In ¹³C NMR spectra, chemical shifts were referenced to the signal of the deuterated solvent; in case of CDCl₃: δ = 77.16 ppm, in case of DMSO-d₆: δ = 39.52 ppm; in case of CD₂OD: δ = 49.00 ppm. All ¹³C spectra were proton broad-band decoupled. Coupling constants (J) were expressed in Hertz (Hz). Multiplicities were recorded as s (singlet), d (doublet), t (triplet), q (quartet), hept (heptet) or m (multiplet). All isolated characterized compounds were >95% pure as judged by H-NMR spectroscopic analysis unless noted otherwise.
1.7 Mass Spectrometry

Mass spectra were recorded by the analytics department of the Institut für Organische Chemie at the University of Freiburg. Ions were given as a mass-to-charge ratio \((m/z)\). High resolution mass spectrometry (HRMS) was performed on an Exactive mass spectrometer (ESI: needle voltage 2.5 – 5.0 kV, ion transfer tube 250°, sheath / aux gas \(\text{N}_2\); or APCI: corona current 5 – 10 µA, vaporizer temperature 50 – 400 °C, sheath gas \(\text{N}_2\), aux gas \(\text{N}_2/\text{NH}_3\)) with orbitrap analyzer (Thermo Fisher Scientific Inc.). The analyzer was calibrated externally (mass accuracy < 5 ppm) and had a resolution of \(M/\Delta M = 10\,000 – 100\,000\).

1.8 X-ray crystal structures

X-Ray structure analysis was performed at the Institut für Anorganische Chemie at the University of Freiburg. All structures were solved by Dr. Daniel Kratzert. Images were rendered with POV-Ray 3.6 using CYLview v10.561 BETA.\(^{[1,2]}\)

1.9 Elemental Analysis

Due to their high fluorine content, the novel catalysts described in this work could not be analyzed reliably by elemental analysis.

1.10 Nomenclature

Nomenclature was automatically generated with the help of ChemBioDraw 16.0 by PerkinElmer. Whenever available, trivial names were preferentially used.
2 Kinetic Evaluation

2.1 Procedure for kinetic studies

![Chemical Reaction Diagram]

1-Naphthoic acid (0.4 mmol, 68.8 mg), Rh(III)-catalyst (0.04 mmol, 10 mol% for monomeric compounds OR 0.02 mmol, 5 mol% for dimeric compounds), Cu(CO₂CF₃)₂ (116 mg, 0.4 mmol, 1.0 equiv.), AgSbF₆ (27.6 mg, 0.08 mmol, 20 mol%), KOAc (39.2 mg, 0.4 mmol, 1.0 equiv.) and toluene (8.0 mL) were added to a Schlenk tube under an argon atmosphere and ethyl acrylate (132 μL, 1.2 mmol, 3 equiv.) was added dropwise. The resulting reaction mixture was heated to 90 °C and stirred at this temperature. Samples of 0.5 mL of the reaction mixture were taken with a syringe at different time points (cf. results table) under a slight argon overpressure. An aq. solution of HCl (0.5 mL, 1 M) was added to these samples and the resulting mixture was extracted with ethyl acetate (3×). The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo. The crude product was dissolved in a solution of 1,3,5-trimethoxybenzene in CDCl₃ (1.00 mL, 8 μmol, 0.33 equiv. relative to sample size) and the conversion was determined by ¹H-NMR spectroscopy.

Integrals were determined relative to the aromatic ¹H-NMR signal of 1,3,5-trimethoxybenzene (s, 6.09 ppm). The following signals NMR signals were used to quantify the amounts of chemical species:- starting material (Intₐ): d (9.09 ppm); - intermediate product (olefin, Intₐ): d (6.59 ppm); - major product (lactone, Intₐ): d (9.00 ppm), t (5.97 ppm), d (2.96 ppm), (average of integral values).

Result table S1 contains conversion to the major product (lactone, Intₐ) relative to remaining starting material (conversion = Intₐ / (Intₐ + Intₐ)). All experiments were carried out at least twice to identify potential outliers. Table S1 contains averaged conversion values of those two experiments. The amount of the intermediate product (olefin, Intₐ) remained constant within the limits of experimental error over the course of the studied time frame. Therefore, a kinetic model including a quasi-stationary approximation was applied in order to determine the reaction’s rate constant via linear regression of – ln(1 – [P]/[A₀]) (cf. figures S3 and S4).

[P]: product concentration at given time; [A₀]: initial concentration of starting material.
2.2 Results of kinetic studies

Table S1: Kinetic study of Rh(III) catalyzed C−H olefination of 1-naphtoic acid. All values are conversions relative to remaining starting material (%, average of two experiments).

| t/min | [RhCp*Cl₂]₂ | catalyst 3 | catalyst 4a | catalyst 4b | catalyst 4c |
|-------|-------------|------------|-------------|-------------|-------------|
| 0     | 0           | 0          | 0           | 0           | 0           |
| 30    | 5           | 10         | 11          | 11          | 9           |
| 60    | 10          | 20         | 20          | 29          | 23          |
| 90    | 15          | 27         | 24          | 38          | 33          |
| 150   | 26          | 42         | 32          | 59          | 47          |
| 210   | 36          | 55         | 39          | 69          | 58          |
| 270   | 50          | 63         | 44          | 74          | 65          |
| 330   | 58          | 72         | 57          | 85          | 78          |

| t/min | catalyst 4d | catalyst 4e | [RhCp*Cl₂]₂ + Urea 5a | [RhCp*Cl₂]₂ + PPh₃ | [RhCp*Cl₂]₂ + 6-DPPOn 5b |
|-------|-------------|-------------|------------------------|---------------------|-------------------------|
| 0     | 0           | 0           | 0                      | 0                   | 0                       |
| 30    | 3           | 0           | 0                      | 0                   | 0                       |
| 60    | 15          | 11          | 2                      | 0                   | 5                       |
| 90    | 24          | 15          | 9                      | 0                   | 10                      |
| 150   | 37          | 34          | 22                     | 9                   | 23                      |
| 210   | 46          | 40          | 39                     | 18                  | 30                      |
| 270   | 58          | 59          | 53                     | 28                  | 41                      |
| 330   | 67          | 65          | 60                     | 33                  | 50                      |

Table S2: Rate constants, error and coefficient of determination resulting from linear regression of $-\ln (1 - [P])/[A_0]$.

| catalyst 3 | catalyst 4a | catalyst 4b | catalyst 4c | catalyst 4d |
|------------|-------------|-------------|-------------|-------------|
| $k / 10^{-5} \text{ min}^{-1}$ | 37.6 | 24.6 | 54.7 | 42.9 | 32.0 |
| $\Delta k / 10^{-5} \text{ min}^{-1}$ | 0.3 | 1.0 | 1.2 | 1.1 | 0.8 |
| $R^2$ | 0.9989 | 0.9682 | 0.9910 | 0.9878 | 0.9903 |

| catalyst 3 | [RhCp*Cl₂]₂ + Urea 5a | [RhCp*Cl₂]₂ + PPh₃ | [RhCp*Cl₂]₂ + 6-DPPOn | catalyst 4e |
|------------|------------------------|---------------------|------------------------|-------------|
| $k / 10^{-5} \text{ min}^{-1}$ | 24.4 | 25.1 | 10.5 | 19.1 | 29.8 |
| $\Delta k / 10^{-5} \text{ min}^{-1}$ | 1.0 | 1.9 | 1.1 | 0.9 | 1.6 |
| $R^2$ | 0.9742 | 0.9265 | 0.8727 | 0.9637 | 0.9579 |
2.3 Determination of rate constants

**Figure S1:** Kinetic study of Rh(III) catalyzed C−H olefination of 1-naphthoic acid (graphical representation, part 1).

**Figure S2:** Kinetic study of Rh(III) catalyzed C−H olefination of 1-naphthoic acid (graphical representation, part 2).
Figure S3: Kinetic study of Rh(III) catalyzed C–H olefination of 1-naphthoic acid (part 3):
Determination of rate constant via linear regression of \(-\ln (1 - [P]/[A_0])\) (quasi-stationary approximation).

Figure S4: Kinetic study of Rh(III) catalyzed C–H olefination of 1-naphthoic acid (part 4):
Determination of rate constant via linear regression of \(-\ln (1 - [P]/[A_0])\) (quasi-stationary approximation).
3 NMR Experiments

3.1 Procedure for determination of binding constants via titration

Rh(III) catalyst (0.01 mmol) was dissolved in d$_6$-DMSO (4.00 mL) to prepare the host solution (0.0025 M). The guest solution (0.250 M) was prepared by dissolving the substrate (0.45 mmol) in host solution (1.80 mL) to avoid dilution effects. Increasing volumes of guest solution were added to an NMR tube containing initially 0.50 mL of the host solution. $^1$H-NMR spectra were measured at 300 MHz and 298 K and the catalyst’s urea- NH$^1$H-NMR signals (ppm) were determined relative to the residual solvent signal of d$_6$-DMSO (2.500 ppm). NMR data was fitted using the bindfit online tool (http://app.supramolecular.org/bindfit). Modelization was performed via the Nelder-Mead method assuming a 1:1 host/guest interaction.

3.2 Results of titration experiments

Permanent URLs containing the raw data and modelization details for each experiment are given in table S3.

Table S3: Association constants determined via NMR titration experiments for 1-naphthoic acid as guest and Rh(III) catalyst as host.

| Catalyst | K / M$^{-1}$ | ΔK / % | permanent link (including NMR data) |
|----------|-------------|--------|----------------------------------|
| 3        | 19.64       | 10.6   | http://app.supramolecular.org/bindfit/view/74a16081-0249-4da8-9cfb-b79085a87b4c |
|          | 21.35       | 4.9    | http://app.supramolecular.org/bindfit/view/0967e556-268a-471f-b0c6-884f73165f15 |
| 4a       | 2.80        | 3.4    | http://app.supramolecular.org/bindfit/view/74fd1096-674d-4ad3-b36a-a8ef31a9a91 |
|          | 3.89        | 2.2    | http://app.supramolecular.org/bindfit/view/cfb7ee0a-64ec-4f77-810a-ec461c76e8d0 |
| 4b       | 106.79      | 14.4   | http://app.supramolecular.org/bindfit/view/023954c1-847f-4cf6-e27c-e30540d818701 |
|          | 84.58       | 19.3   | http://app.supramolecular.org/bindfit/view/4b96638e-9309-410d-8271-60611119f8ae |
| 4c       | 37.07       | 16.3   | http://app.supramolecular.org/bindfit/view/78d6c2c6-14aa-4d54-ad07-70d97092cd |
|          | 37.03       | 13.0   | http://app.supramolecular.org/bindfit/view/598d76b6-35a8-4576-b2ff-c6e3b210e5b |
| 4d       | 8.57        | 1.9    | http://app.supramolecular.org/bindfit/view/7949c2c6-650f-4775-a07b-3b22b39d3f8b |
|          | 6.54        | 2.1    | http://app.supramolecular.org/bindfit/view/811b76eb-35a8-4576-b2ff-c6e3b210e5b |
| 4e       | 3.30        | 2.8    | http://app.supramolecular.org/bindfit/view/7ecf1bb8-6a00-4fa9-b5ef-145bee32a63 |
|          | 3.79        | 2.5    | http://app.supramolecular.org/bindfit/view/7ecf1bb8-6a00-4fa9-b5ef-145bee32a63 |

Free energies of complex formation $\Delta G_{rel}$ were calculated relative to the lowest association constant (reference: catalyst 4a) as follows:

$\Delta G_{rel} = RT \ln(K_n/K_{4a})$ for $T = 298$ K

$K_n$: average association constant of catalyst n; $K_{4a}$: average association constant of catalyst 4a

Table S4 summarizes the average association constants and relative Gibbs free energies of complex formation.
Table S4: Average association constants $K$ and relative Gibbs free energies $\Delta G_{rel} = RT \ln (Kn/K_{4a})$

| Catalyst | $\Delta G_{in}$ / kJ mol$^{-1}$ | $\Delta (\Delta G_{in})$ / kJ mol$^{-1}$ | $K$ / M$^{-1}$ | $\Delta K$ / M$^{-1}$ |
|----------|-------------------------------|------------------------------------------|----------------|------------------|
| 4b       | 8.4                           | 1.0                                      | 96             | 11               |
| 4c       | 6.0                           | 1.0                                      | 37             | 6                |
| 3        | 4.5                           | 0.4                                      | 20.5           | 1.9              |
| 4d       | 2.1                           | 0.3                                      | 7.6            | 1.0              |
| 4e       | 0.2                           | 0.1                                      | 3.5            | 0.3              |
| 4a       | 0.0                           | -                                        | 3.3            | 0.6              |

Dimerization of catalyst 4b as observed in its crystal structure (see Figure 3) was examined by a $^1$H-NMR dilution experiment (see Figure S5).

![Dimerization of catalyst 4b](image)

Figure S5: $^1$H-NMR data (urea NH-signals) obtained for catalyst 4b at different concentrations fitted as non-cooperative dimer aggregation.$^{30}$

An association constant of 41 M$^{-1}$ (± 33%) was determined using [http://app.supramolecular.org/bindfit/](http://app.supramolecular.org/bindfit/).

(NMR Dimer Aggregation, Nelder-Mead-Method, permanent link, including NMR data: [http://app.supramolecular.org/bindfit/view/dea1b17d-48e6-46d6-bbab-633ad6d0245a](http://app.supramolecular.org/bindfit/view/dea1b17d-48e6-46d6-bbab-633ad6d0245a))
3.3 Variable-temperature NMR experiments

Variable-temperature $^1$H-NMR experiments of a 10 mM solution of catalyst 4b and naphthoic acid 1a in d$_6$-DMSO were performed between 303 and 393 K (see Table S5).

**Table S5:** NMR shifts obtained for nitrogen-bound H-atoms at variable temperature.

| Temp / K | DPPon NH | Urea NH s | Urea NH t |
|----------|----------|-----------|-----------|
| 303      | 11,1516  | 9,2888    | 6,5270    |
| 313      | 11,1385  | 9,2430    | 6,5055    |
| 323      | 11,1269  | 9,1986    | 6,4836    |
| 333      | 11,1167  | 9,1559    | 6,4619    |
| 343      | 11,1039  | 9,1065    | 6,4356    |
| 353      | 11,0942  | 9,0640    | 6,4124    |
| 363      | 11,0827  | 9,0236    | 6,3890    |
| 373      | 11,0793  | 8,9828    | 6,3660    |
| 383      | *        | 8,9468    | 6,3446    |
| 393      | *        | 8,9174    | 6,3168    |

*DPPon NH-signal too broad to be picked.

Increasing the temperature shifted the nitrogen-bound H-atoms’ NMR signals upfield in a significant manner. A linear relationship between the shift difference $\Delta\delta$ of the examined peaks and the change of temperature $\Delta T$ was observed over the complete range of 30 to 120 °C (see Figure S6), thereby confirming the existence of H-bonding at our reaction temperature.

![Figure S6](image-url)

*Figure S6:* Graphical plot of chemical shift difference $\Delta\delta$ between 303 and 393 K including linear regression.
4 Optimization of Reaction Conditions

General Procedure for C-H-Olefination Reactions

Substrate (0.1 mmol), acrylate (0.3 mmol, 3 equiv.), Rh(III)-catalyst (0.001 mmol, 10 mol%; in case of dimeric catalysts: 0.005 mmol, 5 mol%), Cu(CO₂CF₃)₂ (29 mg, 0.1 mmol, 1.0 equiv.), AgSbF₆ (6.9 mg, 0.02 mmol, 20 mol%), base (0.1 mmol, 1.0 equiv.) and solvent (2.0 mL) were added to a Schlenk tube under an argon atmosphere. The resulting reaction mixture was stirred at T (90 or 120 °C) for 16 h. After cooling to rt, the reaction was interrupted by addition of an aq. solution of HCl (2 mL, 1 M) and the resulting mixture was extracted with ethyl acetate (3×). The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo. The conversion was determined by ¹H-NMR-spectroscopy using 1,3,5-trimethoxybenzene (5.6 mg, 0.033 mmol, 0.33 equiv.) as an internal standard.

Table S6: Solvent screening of ortho-C–H functionalization of 1-naphthoic acid (1a).

| catalyst | solvent | NMR yield* / % |
|----------|---------|----------------|
|          |         | ortho | olefine |
| DCE      |         | 65    | 0       |
| DCE      | 3       | 82    | 5       |
| PhMe     | 3       | 69    | 0       |
| PhMe     | 3       | 85    | 11      |
| HFIP     | 3       | 4     | 0       |
| THF      | 3       | 15    | 48      |
| AcOH     | 3       | 0     | 0       |
| MeCN     | 3       | 30    | 0       |
| EtOH     | 3       | 15    | 0       |
| t-AmylOH | 3       | 55    | 0       |
| i-PrOH   | 3       | 2     | 0       |

All reactions were performed at a 0.1 mmol scale.

*All yields were determined by ¹H-NMR analysis of the crude reaction mixture relative to 1,3,5-trimethoxybenzene as the internal standard.
### Table S7: Base screening of ortho-C–H functionalization of 1-naphthoic acid (1a).

| catalyst   | base          | NMR yield* / % |
|------------|---------------|----------------|
|            |               | ortho | olefine |
| [RhCp*Cl₂]₂ | KOAc          | 69    | 0       |
| 3          | KOAc          | 85    | 11      |
| [RhCp*Cl₂]₂ | Cs₂CO₃       | 58    | 15      |
| 3          | Cs₂CO₃       | 58    | 25      |
| [RhCp*Cl₂]₂ | CsOAc        | 52    | 17      |
| 3          | CsOAc        | 80    | 8       |
| 3          | NaHCO₃       | 46    | 13      |

All reactions were performed at a 0.1 mmol scale.

*All yields were determined by ¹H-NMR analysis of the crude reaction mixture relative to 1,3,5-trimethoxybenzene as the internal standard.

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### Table S8: Oxidant screening of ortho-C–H functionalization of 1-naphthoic acid (1a).

| catalyst   | oxidant (equivalents) | NMR yield* / % |
|------------|-----------------------|----------------|
|            |                       | ortho | olefine |
| [RhCp*Cl₂]₂ | Cu(CO₂CF₃)₂ (1.0)     | 69    | 0       |
| 3          | Cu(CO₂CF₃)₂ (1.0)     | 85    | 11      |
| 3          | Cu(CO₂CF₃)₂ (2.0)     | 87    | 9       |
| 3          | Cu(CO₂CF₃)₂ (0.5)     | 38    | 7       |
| 3          | Cu(CO₂CF₃)₂ (0.2)**   | 14    | 4       |
| 3          | Cu(OAc)₂ (1.0)        | 81    | 6       |
| 3          | AgOAc (2.0)           | 78    | 5       |

All reactions were performed at a 0.1 mmol scale.

*All yields were determined by ¹H-NMR analysis of the crude reaction mixture relative to 1,3,5-trimethoxybenzene as the internal standard.

**Reaction performed under air.
5 Scope of Catalyses

Olefin scope

**Ethyl 2-(1-oxo-1,3-dihydropaphtho[1,2-c]furan-3-yl)acetate (2a)**

\[
\text{C}_{16}H_{12}O_4
\]

\[
270.28 \text{ g/mol}
\]

\[
R_f = 0.56 \ (\text{CH/EtOAc} = 2:1).
\]

\[ ^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) \delta = 1.28 \ (t, J = 7.2 \text{ Hz}, 3H, \text{CH}_3CH_2), 2.95 \ (d, J = 6.6 \text{ Hz}, 2H, \text{CH}_2CO_2Et), 4.24 \ (q, J = 7.2 \text{ Hz}, 2H, \text{CH}_2CH_3), 5.95 \ (t, J = 6.6 \text{ Hz}, 1H, \text{OCHCH}_2), 7.53 \ (d, J = 8.4 \text{ Hz}, 1H, H_A), 7.64 \ (ddd, J = 8.3, 6.9, 1.3 \text{ Hz}, 1H, H_A), 7.73 \ (ddd, J = 8.4, 6.9, 1.3 \text{ Hz}, 1H, H_A), 7.97 \ (d, J = 8.4 \text{ Hz}, 1H, H_A), 8.14 \ (d, J = 8.4, 1H, H_A), 9.00 \ (dd, J = 8.4, 1.1 \text{ Hz}, 1H, H_A).
\]

\[ ^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) \delta = 14.3 \ (\text{CH}_2CH_3), 39.6 \ (\text{CH}_2CO_2Et), 61.5 \ (\text{CH}_2CO_2Et), 76.5 \ (\text{OCHCH}_2), 118.6 \ (C_A), 120.5 \ (C_A), 123.7 \ (C_A), 127.7 \ (C_A), 128.6 \ (C_A), 129.3 \ (C_A), 129.4 \ (C_A), 133.7 \ (C_A), 135.9 \ (C_A), 150.6 \ (C_A), 169.5 \ (\text{C(O)OEt}), 170.2 \ (\text{C(O)OCH}).
\]

HRMS (pos. ESI, Chloroform): [M + H$^+$], calcd: 271.0965; found: 271.0964.

Spectral data matched reported values.$[^6]$

**Methyl 2-(1-oxo-1,3-dihydropaphtho[1,2-c]furan-3-yl)acetate (2b)**

\[
\text{C}_{15}H_{12}O_4
\]

\[
256.26 \text{ g/mol}
\]

\[
R_f = 0.44 \ (\text{CH/EtOAc} = 2:1).
\]

\[ ^1H \text{ NMR} \ (500 \text{ MHz, CDCl}_3) \delta = 2.92 - 2.99 \ (m, 2H, \text{CH}_2CO_2Me), 3.79 \ (s, 3H, \text{CO}_2\text{CH}_3), 5.96 \ (t, J = 6.7 \text{ Hz}, 1H, \text{OCHCH}_2), 7.52 \ (d, J = 8.4 \text{ Hz}, 1H, H_A), 7.65 \ (ddd, J = 8.1, 6.9, 1.2 \text{ Hz}, 1H, H_A), 7.74 \ (ddd, J = 8.2, 6.9, 1.3 \text{ Hz}, 1H, H_A), 7.98 \ (d, J = 8.2 \text{ Hz}, 1H, H_A), 8.15 \ (d, J = 8.4 \text{ Hz}, 1H, H_A), 9.01 \ (dd, J = 8.4, 1.1 \text{ Hz}, 1H, H_A).
\]

\[ ^{13}C \text{ NMR} \ (126 \text{ MHz, CDCl}_3) \delta = 39.4 \ (\text{CH}_2CO_2Me), 52.4 \ (\text{CO}_2\text{CH}_3), 76.4 \ (\text{OCHCH}_2), 118.6 \ (C_A), 120.4 \ (C_A), 123.7 \ (C_A), 127.7 \ (C_A), 128.6 \ (C_A), 129.3 \ (C_A), 129.4 \ (C_A), 133.7 \ (C_A), 135.9 \ (C_A), 150.5 \ (C_A), 170.0 \ (\text{C(O)OMe}), 170.2 \ (\text{C(O)OCH}).
\]

HRMS (pos. ESI, APCI): [M + H$^+$], calcd: 257.0808; found: 257.0807.

Spectral data matched reported values.$[^6]$
**SUPPORTING INFORMATION**

_Benzyl 2-(1-oxo-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (2c)

![Structure of Benzyl 2-(1-oxo-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (2c)]

C_{21}H_{19}O_4

332.36 g/mol

R_f = 0.56 (CH/EtOAc = 2:1).

**1H NMR** (500 MHz, CDCl_3) δ = 2.94 – 3.07 (m, 2H, CH_2CO_2Bn), 4.97 – 5.41 (m, 2H, CH_2C_6H_5), 5.97 (t, J = 6.6 Hz, 1H, OCHCH_2), 7.29 – 7.40 (m, 5H, CH_2C_6H_5), 7.45 (d, J = 8.4 Hz, 1H, H_α), 7.65 (dd, J = 8.2, 6.9, 1.3 Hz, 1H, H_α), 7.74 (ddd, J = 8.3, 6.8, 1.3 Hz, 1H, H_α), 7.96 (d, J = 8.1 Hz, 1H, H_α), 8.10 (d, J = 8.5 Hz, 1H, H_α), 8.99 (dd, J = 8.3, 1.1 Hz, 1H, H_α).

**13C NMR** (126 MHz, CDCl_3) δ = 39.6 (CCH_2CO_2Bn), 67.3 (CCH_2C_6H_5), 76.4 (OCCH_2), 118.5 (C_α), 120.4 (C_α), 123.7 (C_α), 127.7 (C_α), 128.6 (C_α), 128.8 (2 × C_α), 129.7 (C_α), 129.8 (2 × C_α), 132.3 (C_α), 133.7 (C_α), 135.3 (C_α), 135.9 (C_α), 150.4 (C_α), 169.3 (COOBn), 170.2 (COOCH).

**HRMS** (pos. APCI, CHCl_3): [M + NH_4]^+, calcd: 350.1387; found: 350.1385.

**tert-Butyl 2-(1-oxo-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (2d)

![Structure of tert-Butyl 2-(1-oxo-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (2d)]

C_{19}H_{18}O_4

298.34 g/mol

R_f = 0.62 (CH/EtOAc = 2:1).

**1H NMR** (500 MHz, CDCl_3) δ = 1.45 (s, 9H, C(CH_3)_3), 2.89 (d, J = 6.5 Hz, 2H, CH_2CO_2Bu), 5.91 (t, J = 6.5 Hz, 1H, OCHCH_2), 7.54 (d, J = 8.4 Hz, 1H, H_α), 7.64 (ddd, J = 8.2, 6.9, 1.3 Hz, 1H, H_α), 7.74 (ddd, J = 8.3, 6.9, 1.3 Hz, 1H, H_α), 7.97 (d, J = 8.2 Hz, 1H, H_α), 8.14 (d, J = 8.4 Hz, 1H, H_α), 9.01 (dd, J = 8.4, 1.1 Hz, 1H, H_α).

**13C NMR** (126 MHz, CDCl_3) δ = 28.2 (C(CH_3)_3), 40.6 (CH_2CO_2Bu), 76.8 (OCCH_2), 82.2 (C(CH_3)_3), 118.7 (C_α), 120.5 (C_α), 123.7 (C_α), 127.6 (C_α), 128.6 (C_α), 129.3 (C_α), 129.4 (C_α), 133.6 (C_α), 135.8 (C_α), 150.8 (C_α), 168.6 (COOBU), 170.5 (COOCH).

**HRMS** (pos. APCI, CHCl_3): [M + NH_4]^+, calcd: 316.1543; found: 316.1540.
2-(1-Oxo-1,3-dihyronaphtho[1,2-c]furan-3-yl)acetonitrile (2e)

\[
\begin{align*}
\text{C}_{14} \text{H}_{9} \text{NO}_2 \\
\text{223.23 g/mol}
\end{align*}
\]

\[R_f = 0.30 \ (\text{DCM/MeOH} = 20:1).\]

\[^{1}H\text{ NMR} \ (500 \text{ MHz, CDCl}_3) \delta = 2.97 - 3.20 \ (\text{m, } 2\text{H, } \text{CH}_2\text{CN}), 5.74 \ (\text{dd, } J = 6.9, 5.3 \text{ Hz, } 1\text{H, OCHCH}_3), 7.62 - 7.75 \ (\text{m, } 2\text{H, } 2\times \text{H}_a), 7.78 \ (\text{ddd, } J = 8.3, 6.8, 1.2 \text{ Hz, } 1\text{H, H}_a), 8.02 \ (\text{d, } J = 8.2 \text{ Hz, } 1\text{H, H}_a), 8.23 \ (\text{d, } J = 8.4 \text{ Hz, } 1\text{H, H}_a), 9.00 \ (\text{dd, } J = 8.4, 1.1 \text{ Hz, } 1\text{H, H}_a).\]

\[^{13}C\text{ NMR} \ (126 \text{ MHz, CDCl}_3) \delta = 23.8 \ (\text{CH}_2\text{CN}), 74.2 \ (\text{OCHCH}_2), 114.9 \ (\text{CH}_2\text{CN}), 118.1 \ (\text{C}_a), 120.5 \ (\text{C}_a), 123.8 \ (\text{C}_a), 128.2 \ (\text{C}_a), 128.8 \ (\text{C}_a), 129.3 \ (\text{C}_a), 129.8 \ (\text{C}_a), 134.1 \ (\text{C}_a), 136.6 \ (\text{C}_a), 148.2 \ (\text{C}_a), 169.1 \ (\text{C}(O)\text{OCH}).\]

\[^{1}H\text{ NMR} \ (500 \text{ MHz, CDCl}_3) \delta = 2.97 - 3.20 \ (\text{m, } 2\text{H, } \text{CH}_2\text{CN}), 5.74 \ (\text{dd, } J = 6.9, 5.3 \text{ Hz, } 1\text{H, OCHCH}_3), 7.62 - 7.75 \ (\text{m, } 2\text{H, } 2\times \text{H}_a), 7.78 \ (\text{ddd, } J = 8.3, 6.8, 1.2 \text{ Hz, } 1\text{H, H}_a), 8.02 \ (\text{d, } J = 8.2 \text{ Hz, } 1\text{H, H}_a), 8.23 \ (\text{d, } J = 8.4 \text{ Hz, } 1\text{H, H}_a), 9.00 \ (\text{dd, } J = 8.4, 1.1 \text{ Hz, } 1\text{H, H}_a).\]

\[^{13}C\text{ NMR} \ (126 \text{ MHz, CDCl}_3) \delta = 23.8 \ (\text{CH}_2\text{CN}), 74.2 \ (\text{OCHCH}_2), 114.9 \ (\text{CH}_2\text{CN}), 118.1 \ (\text{C}_a), 120.5 \ (\text{C}_a), 123.8 \ (\text{C}_a), 128.2 \ (\text{C}_a), 128.8 \ (\text{C}_a), 129.3 \ (\text{C}_a), 129.8 \ (\text{C}_a), 134.1 \ (\text{C}_a), 136.6 \ (\text{C}_a), 148.2 \ (\text{C}_a), 169.1 \ (\text{C}(O)\text{OCH}).\]

HRMS (neg. ESI, CHCl_3): [M - H\textsuperscript{+}], calcd: 222.0561; found: 222.0560.

Spectral data matched reported values.\[^{[6]}\]
Aryl carboxylic acid derivative scope

*Ethyl 2-(3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2f mono)*

\[
\begin{align*}
\text{C}_{12} \text{H}_{12} \text{O}_4 & \quad 220.22 \text{ g/mol} \\
R_f & = 0.54 \text{ (CH/EtOAc = 5:1)}.
\end{align*}
\]

\[\begin{align*}
^1H \text{ NMR} \ (400 \text{ MHz, CDCl}_3) & \delta = 1.27 \text{ (t, } J = 7.2 \text{ Hz, 3H, CH}_2 \text{C}_6 \text{H}_3 \text{)}, \ 2.82 - 3.00 \text{ (m, 2H, CH}_2 \text{CO}_2 \text{Et), 4.22 \text{ (q, } J = 7.1 \text{ Hz, 2H, CH}_2 \text{CH}_3 \text{)}, 5.89 \text{ (t, } J = 6.6 \text{ Hz, 1H, OCCH}_3 \text{)}, 7.50 \text{ (dd, } J = 7.7, 0.9 \text{ Hz, 1H, H}_a \text{)}, 7.56 \text{ (dd, } J = 7.5 \text{ Hz, 1H, H}_a \text{)}, 7.68 \text{ (ddd, } J = 7.6, 1.1 \text{ Hz, 1H, H}_a \text{)}, 7.92 \text{ (ddd, } J = 7.7, 0.9 \text{ Hz, 1H, H}_a \text{)}.
\end{align*}\]

\[\begin{align*}
^{13}C \text{ NMR} \ (101 \text{ MHz, CDCl}_3) & \delta = 14.3 \text{ (CH}_2 \text{C}_6 \text{H}_3 \text{)}, 39.8 \text{ (CH}_2 \text{CO}_2 \text{Et}, 61.4 \text{ (CH}_2 \text{CH}_3 \text{)}, 77.1 \text{ (OCHCH}_3 \text{)}, 122.2 \text{ (C}_a \text{)}, 126.0 \text{ (C}_a \text{)}, 126.2 \text{ (C}_a \text{)}, 129.7 \text{ (C}_a \text{)}, 134.4 \text{ (C}_a \text{)}, 149.0 \text{ (C}_a \text{)}, 169.4 \text{ (C}(O)\text{OCH}), 170.0 \text{ (CO}_2 \text{Et}).
\end{align*}\]

\[\begin{align*}
\text{HRMS (pos. APCI, CHCl}_3\text{): [M + H}^+\text{], calcd: 221.0808; found: 221.0807.}
\end{align*}\]

Spectral data matched reported values.\(^{[6]}\)

*Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2f bis)*

\[
\begin{align*}
\text{C}_{17} \text{H}_{18} \text{O}_6 & \quad 318.33 \text{ g/mol} \\
R_f & = 0.42 \text{ (CH/EtOAc = 5:1)}.
\end{align*}
\]

\[\begin{align*}
^1H \text{ NMR} \ (500 \text{ MHz, CDCl}_3) & \delta = 1.26 \text{ (t, } J = 7.2 \text{ Hz, 3H, CH}_2 \text{CH}_3 \text{)}, 1.35 \text{ (t, } J = 7.1 \text{ Hz, 3H, CH}_2 \text{CH}_3 \text{)}, 2.83 - 2.98 \text{ (m, 2H, CH}_2 \text{CO}_2 \text{Et), 4.21 \text{ (q, } J = 7.1 \text{ Hz, 2H, CH}_2 \text{CH}_3 \text{)}, 4.29 \text{ (q, } J = 7.2 \text{ Hz, 2H, CH}_2 \text{CH}_3 \text{)}, 5.85 \text{ (t, } J = 6.5 \text{ Hz, 1H, OCCH}_3 \text{)}, 6.60 \text{ (d, } J = 16.2 \text{ Hz, 1H, CH=CHCO}_2 \text{Et), 7.49 \text{ (d, } J = 7.6 \text{ Hz, 1H, H}_a \text{)}, 7.66 \text{ (t, } J = 7.7 \text{ Hz, 1H, H}_a \text{)}, 7.78 \text{ (d, } J = 7.7 \text{ Hz, 1H, H}_a \text{)}, 8.89 \text{ (d, } J = 16.2 \text{ Hz, 1H, CH=CHCO}_2 \text{Et}).
\end{align*}\]

\[\begin{align*}
^{13}C \text{ NMR} \ (126 \text{ MHz, CDCl}_3) & \delta = 14.2 \text{ (CH}_2 \text{CH}_3 \text{)}, 14.4 \text{ (CH}_2 \text{CH}_3 \text{)}, 39.6 \text{ (CH}_2 \text{CO}_2 \text{Et), 61.0 \text{ (CH}_2 \text{CH}_3 \text{)}, 61.5 \text{ (CH}_2 \text{CH}_3 \text{)}, 76.2 \text{ (OCHCH}_3 \text{)}, 123.2 \text{ (CH=CHCO}_2 \text{Et), 122.2 \text{ (C}_a \text{)}, 123.3 \text{ (C}_a \text{)}, 126.8 \text{ (C}_a \text{)}, 134.4 \text{ (C}_a \text{)}, 135.2 \text{ (C}_a \text{)}, 137.4 \text{ (CH=CHCO}_2 \text{Et), 149.9 \text{ (C}_a \text{)}, 166.2 \text{ (CO}_2 \text{Et), 169.0 \text{ (C}(O)\text{OCH), 169.3 \text{ (CO}_2 \text{Et).}}
\end{align*}\]

\[\begin{align*}
\text{HRMS (pos. ESI, CHCl}_3\text{): [M + Na}^+\text{], calcd: 341.0996; found: 341.0994.}
\end{align*}\]

Spectral data matched reported values.\(^{[6]}\)
**SUPPORTING INFORMATION**

_Ethyl 2-(4-fluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2g)_

![Structure of 2g]

C_{12}H_{11}FO_4
238.21g/mol

R_f = 0.26 (CH/EtOAc = 2:1).

^1H NMR (500 MHz, CDCl_3) δ = 1.27 (t, J = 7.1 Hz, 3H, CH_2CH_3), 2.83 – 3.01 (m, 2H, CH_2CO_2Et), 4.21 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.87 (t, J = 6.5 Hz, 1H, OCHCH_2), 7.18 (dd, J = 8.5 , 1H, H_6), 7.29 (d, J = 7.6 Hz, 1H, H_5), 7.67 (ddd, J = 7.9, 4.6 Hz, 1H, H_3).

^13C NMR (126 MHz, CDCl_3) δ = 14.3 (CH_2CH_3), 39.6 (CH_2CO_2Et), 61.5 (OCHCH_2), 114.0 (d, J = 14.3 Hz, C_6), 116.7 (d, J = 18.7 Hz, C_5), 118.2 (d, J = 4.5 Hz, C_7), 137.0 (d, J = 7.7 Hz, C_8), 151.5 (d, J = 1.5 Hz, C_9), 159.8 (d, J = 265.2 Hz, C_10), 166.0 (C(O)OEt), 169.1 (C(O)OCH).

^19F NMR (471 MHz, CDCl_3) δ = -113.7 (dd, J = 8.7, 4.4 Hz).

HRMS (pos. APCI, CHCl_3): [M + H^+] calcd: 239.0720; found: 239.0716.

Spectral data matched reported values.[6]

_Ethyl 2-(3-oxo-4-(trifluoromethyl)-1,3-dihydroisobenzofuran-1-yl)acetate (2h)_

![Structure of 2h]

C_{13}H_{13}F_3O_4
288.22 g/mol

R_f = 0.33 (CH/EtOAc = 2:1).

^1H NMR (500 MHz, CDCl_3) δ = 1.26 (t, J = 7.1 Hz, 3H, CH_2CH_3), 2.91 (dd, J = 16.7, 6.3 Hz, 1H, CH_2CO_2Et), 2.99 (dd, J = 16.6, 6.6 Hz, 1H, CH_2CO_2Et), 4.21 (q, J = 7.2, 2H, CH_2CH_3), 5.90 (t, J = 6.4 Hz, 1H, OCHCH_2), 7.74 (d, J = 7.7 Hz, 1H, H_6), 7.80 (dd, J = 7.6 Hz, 1H, H_5), 7.86 (d, J = 7.6 Hz, 1H, H_4).

^13C NMR (126 MHz, CDCl_3) δ = 14.2 (CH_2CH_3), 39.4 (CH_2CO_2Et), 61.6 (CH_2CH_3), 76.3 (OCHCH_2), 122.2 (q, J = 273.8 Hz, CF_3), 123.5 (d, J = 1.6 Hz, C_7), 126.0 (C_6), 127.3 (q, J = 5.6 Hz, C_8), 129.0 (q, J = 35.3 Hz, C_9), 134.3 (C_9), 151.3 (C_9), 165.9 (C(O)OCH), 169.1 (C(O)OEt).

^19F NMR (471 MHz, CDCl_3) δ = -61.0.

HRMS (pos. APCI, CHCl_3): [M + H^+] calcd: 289.0688; found: 289.0679.
Ethyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2i)

R_f = 0.58 (CH/EtOAc = 5:1).

^1H NMR (500 MHz, CDCl_3) δ = 1.27 (t, J = 7.2 Hz, 3H, CH_2CH_3), 2.69 (s, 3H, CH_3), 2.77 – 2.92 (m, 2H, CH_2CO_2Et), 4.21 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.81 (t, J = 6.5 Hz, 1H, OCHCH_2), 7.19 – 7.38 (m, 2H, 2 × H_Ar), 7.52 (t, J = 7.6 Hz, 1H, H_Ar).

^13C NMR (126 MHz, CDCl_3) δ = 14.3 (CH_2CH_3), 17.5 (CH_3), 40.0 (CH_2CO_2Et), 61.4 (CH_2CH_3), 76.2 (OCHCH_2), 119.4 (C_Ar), 123.6 (C_Ar), 131.3 (C_Ar), 134.1 (C_Ar), 140.1 (C_Ar), 149.4 (C_Ar), 169.5 (O(O)OEt), 170.2 (O(O)OCH).

HRMS (pos. ESI, CHCl_3): [M + H]^+, calcd: 235.0965; found: 235.0964.

Spectral data matched reported values.\[6\]

Ethyl 2-(4-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2j)

R_f = 0.50 (DCM/MeOH = 20:1).

^1H NMR (500 MHz, CDCl_3) δ = 1.28 (t, J = 7.2 Hz, 3H, CH_2CH_3), 2.80 – 2.91 (m, 2H, CH_2CO_2Et), 4.00 (s, 3H, CH_3), 4.22 (q, J = 7.2 Hz, 2H, CH_2CH_3), 5.80 (t, J = 6.6 Hz, 1H, OCHCH_2), 6.95 (d, J = 8.2 Hz, 1H, H_Ar), 7.00 (d, J = 7.5 Hz, 1H, H_Ar), 7.61 (dd, J = 7.9 Hz, 1H, H_Ar).

^13C NMR (126 MHz, CDCl_3) δ = 14.3 (CH_2CH_3), 39.9 (CH_2CO_2Et), 56.2 (CH_3), 61.4 (CH_2CH_3), 76.1 (OCHCH_2), 111.3 (C_Ar), 113.6 (C_Ar), 113.7 (C_Ar), 136.6 (C_Ar), 151.8 (C_Ar), 158.9 (C_Ar), 168.9 (O(O)OEt), 169.4 (O(O)OCH).

HRMS (pos. ESI, CHCl_3): [M + H]^+, calcd: 251.0914; found: 251.0917.

Spectral data matched reported values.\[6\]
**Ethyl 2-(4,7-difluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2k)**

![Structure of ethyl 2-(4,7-difluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2k)](image)

C_{12}H_{19}F_{2}O_{4}

256.20 g/mol

R_f = 0.22 (CH/EtOAc = 2:1).

**1H NMR** (500 MHz, CDCl_3) δ = 1.28 (t, J = 7.2 Hz, 3H, CH_2C_H_3), 2.85 (dd, J = 16.8, 6.8 Hz, 1H, CH_2CO_2Et), 3.00 (dd, J = 16.8, 6.3 Hz, 1H, CH_2CO_2Et), 4.22 (q, J = 7.2 Hz, 2H, CH_2CH_3), 5.82 (t, J = 6.5 Hz, 1H, OCHCH_2), 6.94 (ddd, J = 8.8, 2.0 Hz, 1H, H_Ar), 7.06 (dd, J = 7.2, 1.9 Hz, 1H, H_Ar).

**13C NMR** (126 MHz, CDCl_3) δ = 14.2 (CH_2C_H_3), 39.2 (CH_2CO_2Et), 61.7 (CH_2CH_3), 76.5 (d, J = 3.0 Hz, OCHCH_2), 105.5 – 106.7 (m, 2 × C_Ar), 110.6 (dd, J = 14.5, 2.6 Hz, C_A), 153.3 (dd, J = 11.5, 3.0 Hz, C_A), 160.34 (dd, J = 268.0, 13.8 Hz, C_A), 165.0 (d, J = 3.3 Hz, C(O)OCH), 167.51 (dd, J = 259.6, 10.2 Hz, C_A), 168.9 (C(O)OEt).

**19F NMR** (471 MHz, CDCl_3) δ = -108.2 (dd, J = 13.0, 8.6 Hz), -96.8 (dd, J = 13.2, 8.2 Hz).

**HRMS** (pos. ESI, CHCl_3): [M + H^+], calcd: 257.0620; found: 257.0624.

**Ethyl 2-(6-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2l mono)**

![Structure of ethyl 2-(6-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2l mono)](image)

C_{13}H_{14}O_4

234.25 g/mol

R_f = 0.51 (DCM/MeOH = 100:1).

**1H NMR** (400 MHz, CDCl_3) δ = 1.28 (t, J = 7.1 Hz, 3H, CH_2CH_3), 2.49 (s, 3H, CH_3), 2.80 – 2.96 (m, 2H, CH_2CO_2Et), 4.23 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.83 (t, J = 6.6 Hz, 1H, OCHCH_2), 7.28 (s, 1H, H_Ar), 7.35 (d, J = 7.9 Hz, 1H, H_Ar), 7.79 (d, J = 7.8 Hz, 1H, H_Ar).

**13C NMR** (101 MHz, CDCl_3) δ = 14.3 (CH_2CH_3), 22.3 (CH_3), 39.8 (CH_2CO_2Et), 61.4 (CH_2CH_3), 76.9 (OCHCH_2), 122.5 (C_A), 123.6 (C_A), 125.8 (C_A), 130.8 (C_A), 145.7 (C_A), 149.5 (C_A), 169.5 (C(O)OEt), 170.0 (C(O)OCH).

**HRMS** (pos. APCI, CHCl_3): [M + H^+], calcd: 235.0965; found: 235.0963.

Spectral data matched reported values.[7]
Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-6-methyl-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2l bis)

\[
\text{EtO}_2\text{C} \quad \text{O} \quad \text{CO}_2\text{Et}
\]

C_{18}H_{20}O_{6}

332.35 g/mol

R_f = 0.29 (DCM/MeOH = 100:1).

\(^1\)H NMR (400 MHz, CDCl_3) δ = 1.27 (t, J = 7.1 Hz, 3H, CH_2C,H_3), 1.35 (t, J = 7.1 Hz, 3H, CH_2C,H_3), 2.49 (s, 3H, C,H_3), 2.78 – 2.97 (m, 2H, CH_2CO_2Et), 4.22 (q, J = 7.1 Hz, 2H, CH_2CH_2), 4.29 (q, J = 7.1 Hz, 2H, CH_2CH_2), 5.79 (t, J = 6.5 Hz, 1H, OCHCH_2), 6.59 (d, J = 16.3 Hz, 1H, CH=CHCO_2Et), 7.27 (s, 1H, HAr), 7.56 (s, 1H, HAr), 8.63 (d, J = 16.3 Hz, 1H, CH=CHCO_2Et).

\(^{13}\)C NMR (101 MHz, CDCl_3) δ = 14.3 (CH_2C,H_3), 14.4 (CH_2C,H_3), 22.2 (CH_3), 39.7 (CH_2CO_2Et), 60.9 (CH_2CH_2), 61.4 (CH_2CH_2), 76.0 (OCHCH_2), 121.0 (CH=CHCO_2Et), 123.0 (C_ar), 123.6 (C_ar), 127.9 (C_ar), 134.9 (C_ar), 137.6 (CH=CHCO_2Et), 145.6 (C_ar), 150.4 (C_ar), 166.3 (O(\text{O})\text{OE}t), 169.0 (O(\text{O})\text{OCH}), 169.4 (O(\text{O})\text{OE}t).

HRMS (pos. APCI, CHCl_3): [M + NH_4]^+, calcd: 350.1598; found: 350.1595.

Spectral data matched reported values.[8]

Ethyl 2-(6-amino-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2m)

\[
\text{O} \quad \text{O} \quad \text{CO}_2\text{Et}
\]

C_{12}H_{12}NO_4

235.24 g/mol

Analytic sample contained impurities due to decomposition in solution.

R_f = 0.58 (CH/EtOAc = 1:1).

\(^1\)H NMR (500 MHz, CDCl_3) δ = 1.29 (d, J = 7.1 Hz, 3H, CH_2C,H_3), 2.74 – 2.94 (m, 2H, CH_2CO_2Et), 4.22 (q, J = 7.1 Hz, 2H, CH_2CH_2), 5.72 (t, J = 6.6 Hz, 1H, OCHCH_2), 6.62 (d, J = 1.9 Hz, 1H, HAr), 6.73 (dd, J = 8.3, 2.0 Hz, 1H, HAr), 7.65 (d, J = 8.3 Hz, 1H, HAr).

\(^{13}\)C NMR (126 MHz, CDCl_3) δ = 14.3 (CH_2CH_2), 39.9 (CH_2CO_2Et), 61.4 (CH_2CH_2), 76.2 (OCHCH_2), 106.0 (C_ar), 115.3 (C_ar), 116.3 (C_ar), 127.6 (C_ar), 152.1 (C_ar), 152.5 (C_ar), 169.8 (O(\text{O})\text{OCH}), 170.2 (CO_2Et).

HRMS (pos. APCI, MeOH): [M + H]^+, calcd: 236.0917; found: 236.0914.
**SUPPORTING INFORMATION**

*Ethyl 2-(6-hydroxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2n mono)*

![Chemical Structure](image)

\[
C_{12}H_{15}O_5 \\
236.22 \text{ g/mol}
\]

R_f = 0.58 (DCM/MeOH = 20:1).

**^1H NMR** (500 MHz, CDCl_3) δ = 1.28 (t, J = 7.2 Hz, 3H, CH_2CH_3), 2.79 – 2.97 (m, 2H, CH_2CO_2Et), 4.22 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.79 (t, J = 6.6 Hz, 1H, OCH_2CH_2), 6.38 (br s, 1H, OH), 6.92 (d, J = 2.1 Hz, 1H, H_b), 6.99 (dd, J = 8.3, 2.1 Hz, 1H, H_a), 7.78 (d, J = 8.3 Hz, 1H, H_a).

**^13C NMR** (126 MHz, CDCl_3) δ = 14.3 (CH_2CH_3), 39.7 (CH_2CO_2Et), 61.5 (CH_2CH_3), 108.6 (C_a), 117.9 (C_b), 118.3 (C_b), 127.9 (C_b), 152.0 (C_b), 161.7 (CH=OCH), 170.1 (CO_2Et).

**HRMS** (pos. APCI, CHCl_3): [M + H]^+ calcd: 237.0757; found: 237.0760.

*Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-6-hydroxy-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2n bis)*

![Chemical Structure](image)

\[
C_{17}H_{16}O_7 \\
334.32 \text{ g/mol}
\]

R_f = 0.48 (DCM/MeOH = 20:1).

**^1H NMR** (500 MHz, CDCl_3) δ = 1.27 (t, J = 7.1 Hz, 3H, CH_2CH_3), 1.35 (t, J = 7.1 Hz, 3H, CH_2CH_3), 2.82 – 2.96 (m, 2H, CH_2CO_2Et), 4.21 (q, J = 7.1 Hz, 2H, CH_2CH_3), 4.30 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.77 (t, J = 6.5 Hz, 1H, OCHCH_3), 6.55 (d, J = 16.2 Hz, 1H, CH=CHCO_2Et), 6.94 (d, J = 2.0 Hz, 1H, H_b), 7.23 (d, J = 2.0 Hz, 1H, H_a), 8.60 (d, J = 16.2 Hz, 1H, CH=CHCO_2Et).

**^13C NMR** (126 MHz, CDCl_3) δ = 14.3 (CH_2CH_3), 14.4 (CH_2CH_3), 39.6 (CH_2CO_2Et), 61.3 (CH_2CH_3), 61.6 (CH_2CH_3), 75.9 (OCHCH_3), 110.1 (C_a), 114.5 (C_b), 115.7 (C_b), 123.1 (CH=CHCO_2Et), 136.7 (C_b), 137.8 (CH=CHCO_2Et), 152.9 (C_b), 161.8 (C_b), 166.7 (CO_2Et), 169.1 (O(O)OCH), 169.6 (CO_2Et).

**HRMS** (pos. APCI, CHCl_3): [M + NH_4]^+ calcd: 352.1391; found: 352.1387.
**Ethyl 2-(7-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2o mono)**

\[
\text{C}_{12}H_{17}BrO_4
\]

\[299.12 \text{ g/mol}\]

**Rf = 0.51 (CH/EtOAc = 5:1).**

**1H NMR** (500 MHz, CDCl\(_3\)) \(\delta = 1.23 (t, J = 7.1 \text{ Hz}, 3H, \text{CH}_2\text{CH}_3), 2.78 (dd, J = 16.7, 8.3 \text{ Hz}, 1H, \text{CH}_2\text{CO}_2\text{Et}), 3.48 (dd, J = 16.7, 2.9 \text{ Hz}, 1H, \text{CH}_2\text{CO}_2\text{Et}), 4.17 (q, J = 7.2 \text{ Hz}, 2H, \text{CH}_2\text{CH}_2), 5.84 (dd, J = 8.4, 2.9 \text{ Hz}, 1H, O\text{CHCH}_2), 7.46 (dd, J = 7.7 \text{ Hz}, 1H, H\text{Ar}), 7.82 (dd, J = 7.9, 0.8 \text{ Hz}, 1H, H\text{Ar}), 7.88 (d, J = 7.5 \text{ Hz}, 1H, H\text{Ar}).

**13C NMR** (126 MHz, CDCl\(_3\)) \(\delta = 14.2 (\text{CH}_2\text{CH}_3), 37.0 (\text{CH}_2\text{CO}_2\text{Et}), 61.4 (\text{CH}_2\text{CH}_2), 77.8 (\text{OCHCH}_2), 116.5 (\text{CA}), 125.0 (\text{CA}), 128.9 (\text{CA}), 131.4 (\text{CA}), 137.7 (\text{CA}), 147.4 (\text{CA}), 168.6 (\text{C(O)OCH}), 168.8 (\text{CO}_2\text{Et}).

**HRMS** (pos. APCI, CHCl\(_3\)): [M + NH\(_4\)]\(^+\), calcd: 316.0179; found: 316.0178.

**Ethyl (E)-3-(7-bromo-1-(2-ethoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2o bis)**

\[
\text{C}_{12}H_{17}BrO_5
\]

\[397.22 \text{ g/mol}\]

**Rf = 0.38 (CH/EtOAc = 5:1).**

**1H NMR** (500 MHz, CDCl\(_3\)) \(\delta = 1.23 (t, J = 7.1 \text{ Hz}, 3H, \text{CH}_2\text{CH}_3), 1.35 (t, J = 7.1 \text{ Hz}, 3H, \text{CH}_2\text{CH}_3), 2.81 (dd, J = 16.7, 8.0 \text{ Hz}, 1H, \text{CH}_2\text{CO}_2\text{Et}), 3.46 (dd, J = 16.7, 3.0 \text{ Hz}, 1H, \text{CH}_2\text{CO}_2\text{Et}), 4.16 (q, J = 7.1 \text{ Hz}, 2H, \text{CH}_2\text{CH}_2), 4.29 (q, J = 7.1 \text{ Hz}, 2H, \text{CH}_2\text{CH}_2), 5.79 (dd, J = 8.0, 3.0 \text{ Hz}, 1H, O\text{CHCH}_2), 6.59 (d, J = 16.2 \text{ Hz}, 1H, CH=CH\text{CO}_2\text{Et}), 7.65 (d, J = 8.3 \text{ Hz}, 1H, H\text{Ar}), 7.78 (d, J = 8.3 \text{ Hz}, 1H, H\text{Ar}), 8.65 (d, J = 16.3 \text{ Hz}, 1H, CH=CH\text{CO}_2\text{Et}).

**13C NMR** (126 MHz, CDCl\(_3\)) \(\delta = 14.2 (\text{CH}_2\text{CH}_3), 14.4 (\text{CH}_2\text{CH}_2), 36.9 (\text{CH}_2\text{CO}_2\text{Et}), 61.1 (\text{CH}_2\text{CH}_3), 61.5 (\text{CH}_2\text{CH}_2), 77.4 (\text{OCHCH}_2), 117.5 (\text{CA}), 123.8 (\text{CH=CH\text{CO}_2\text{Et}}), 125.8 (\text{CA}), 128.4 (\text{CA}), 134.5 (\text{CA}), 136.5 (\text{CH=CH\text{CO}_2\text{Et}}), 137.7 (\text{CA}), 148.3 (\text{CA}), 166.0 (\text{CO}_2\text{Et}), 167.9 (\text{C(O)OCH}), 168.8 (\text{CO}_2\text{Et}).

**HRMS** (pos. APCI, CHCl\(_3\)): [M + NH\(_4\)]\(^+\), calcd: 414.0547; found: 414.0547.
Ethyl 2-(5-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2p mono isomer 1)

![Chemical structure of Ethyl 2-(5-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate]

Rf = 0.61 (toluene/EtOAc = 3:1).

1H NMR (500 MHz, CDCl3) δ = 1.28 (t, J = 7.2 Hz, 3H, CH2CH3), 2.74 – 2.99 (m, 2H, CH2CH3), 3.87 (s, 3H, OC6H3), 4.22 (q, J = 7.1 Hz, 2H, CH2CH3), 5.83 (t, J = 6.6 Hz, 1H, OCHCH2), 7.23 (dd, J = 8.4, 2.4 Hz, 1H, HAr), 7.34 (d, J = 2.4 Hz, 1H, HAr), 7.38 (d, J = 8.4 Hz, 1H, HAr).

13C NMR (126 MHz, CDCl3) δ = 14.2 (CH2CH3), 39.9 (CH2CO2Et), 55.9 (OCH3), 61.3 (CH2CH3), 77.0 (OCHCH2), 107.7 (CAr), 123.1 (CAr), 123.2 (CAr), 127.5 (CAr), 141.3 (CAr), 161.1 (CAr), 169.4 (O(O)OEt), 170.0 (O(O)OCH).

HRMS (pos. ESI, CHCl3): [M + H]+, calcd: 251.0914; found: 251.0912.

Spectral data matched reported values.[7]

Analytic sample contained traces of regio isomer 2p mono isomer 1.

Rf = 0.50 (toluene/EtOAc = 3:1).

1H NMR (500 MHz, CDCl3) δ = 1.25 (t, J = 7.1 Hz, 3H, CH2CH3), 2.64 (dd, J = 16.3, 8.8 Hz, 1H, CH2CO2Et), 3.31 (dd, J = 16.3, 3.2 Hz, 1H, CH2CO2Et), 3.92 (s, 3H, OCH3), 4.18 (q, J = 7.2 Hz, 2H, CH2CH3), 5.89 (dd, J = 8.8, 3.2 Hz, 1H, OCHCH2), 7.11 (dd, J = 6.7, 2.0 Hz, 1H, HAr), 7.45 – 7.56 (m, 2H, 2 × HAr).

13C NMR (126 MHz, CDCl3) δ = 14.3 (CH2CH3), 38.0 (CH2CO2Et), 55.8 (OCH3), 61.2 (CH2CH3), 76.4 (OCHCH2), 115.2 (CAr), 117.5 (CAr), 128.2 (CAr), 131.5 (CAr), 138.4 (CAr), 154.3 (CAr), 169.6 (O(O)OEt), 170.1 (O(O)OCH).

HRMS (pos. ESI, CHCl3): [M + H]+, calcd: 251.0914; found: 251.0912.

1H NMR data matched reported values.[9]
Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-7-methoxy-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2p bis)

Rf = 0.34 (DCM/MeOH = 20:1).

$^1$H NMR (500 MHz, CDCl$_3$) δ = 1.25 (d, J = 7.1 Hz, 3H, CH$_2$C$_6$H$_3$), 1.34 (t, J = 7.1 Hz, 3H, CH$_2$C$_6$H$_3$), 2.65 (dd, J = 16.4 Hz, 8.5, 1H, CH$_2$CO$_2$Et), 3.29 (dd, J = 16.4, 3.3 Hz, 1H, CH$_2$CO$_2$Et), 3.95 (s, 3H, C$_6$H$_3$), 4.17 (q, J = 7.1 Hz, 2H, CH$_2$C$_6$H$_3$), 4.28 (q, J = 7.1 Hz, 2H, CH$_2$C$_6$H$_3$), 5.83 (dd, J = 8.5, 3.2 Hz, 1H, OCH$_2$CH$_3$), 6.50 (d, J = 16.2 Hz, 1H, CH=CHOEt), 7.11 (d, J = 8.5 Hz, 1H, H$_{Ar}$), 7.76 (d, J = 8.5 Hz, 1H, H$_{Ar}$), 8.62 (d, J = 16.2 Hz, 1H, CH=CHOEt).

$^{13}$C NMR (126 MHz, CDCl$_3$) δ = 14.3 (CH$_2$C$_6$H$_3$), 14.5 (CH$_2$C$_6$H$_3$), 37.8 (CH$_2$CO$_2$Et), 56.1 (CH$_3$), 60.8 (CH$_2$CH$_3$), 61.3 (CH$_2$CH$_3$), 75.4 (OCH$_2$CH$_3$), 115.4 (C$_{Ar}$), 120.7 (CH=CHOEt), 125.4 (C$_{Ar}$), 127.0 (C$_{Ar}$), 129.1 (C$_{Ar}$), 137.0 (C$_{Ar}$), 137.3 (C$_{Ar}$), 155.2 (C$_{Ar}$), 166.6 (CO$_2$Et), 169.0 (C(O)OCH), 169.4 (CO$_2$Et).

HRMS (pos. ESI, CHCl$_3$): [M + H$^+$], calcd: 366.1547; found: 366.1544.

Ethyl 2-(1-oxo-3,6-dihydro-1H-furo[3,4-e]indol-3-yl)acetate (2q)

Rf = 0.53 (DCM/MeOH = 20:1).

$^1$H NMR (400 MHz, CDCl$_3$) δ = 1.29 (t, J = 7.2 Hz, 3H, CH$_2$C$_6$H$_3$), 2.91 (d, J = 6.6 Hz, 2H, CH$_2$CO$_2$Et), 4.24 (q, J = 7.2 Hz, 2H, CH$_2$CH$_3$), 5.96 (t, J = 6.6 Hz, 1H, OCH$_2$CH$_3$), 7.11 – 7.17 (m, 1H, H$_{Ar}$), 7.23 (d, J = 8.3 Hz, 1H, H$_{Ar}$), 7.46 (d, J = 2.9 Hz, 1H, H$_{Ar}$), 7.70 (dd, J = 8.3, 0.9 Hz, 1H, H$_{Ar}$), 8.56 (s, 1H, NH$_3$).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ = 14.3 (CH$_2$CH$_3$), 40.5 (CH$_2$CO$_2$Et), 61.3 (CH$_2$CH$_3$), 77.4 (OCH$_2$CH$_3$), 101.9 (C$_{Ar}$), 114.4 (C$_{Ar}$), 117.4 (C$_{Ar}$), 117.6 (C$_{Ar}$), 124.1 (C$_{Ar}$), 127.8 (C$_{Ar}$), 136.7 (C$_{Ar}$), 143.6 (C$_{Ar}$), 169.8 (C(O)OEt), 170.8 (C(O)OCH).

HRMS (pos. ESI, CHCl$_3$): [M + H$^+$], calcd: 260.0917; found: 260.0916.
SUPPORTING INFORMATION

Ethyl 2-(7-oxo-5,7-dihydro-1H-furo[3,4-f]indol-5-yl)acetate (2r mono)

\[
\begin{align*}
\text{C}_{14}\text{H}_{12}\text{NO}_4 \\
259.26 \text{ g/mol}
\end{align*}
\]

\( R_f = 0.43 \) (DCM/MeOH = 20:1).

\(^1\text{H NMR}\) (500 MHz, CDCl\(_3\)) \( \delta = 1.29 \) (t, \( J = 7.1 \) Hz, 3H, CH\(_2\)CH\(_3\)), 2.82 – 3.04 (m, 2H, CH\(_2\)CO\(_2\)Et), 4.24 (q, \( J = 7.1 \) Hz, 2H, CH\(_2\)CH\(_3\)), 5.96 (t, \( J = 6.6 \) Hz, 1H, OCHCHO), 6.66 (dd, \( J = 2.2 \) Hz, 1H, CH\(_2\)), 7.49 (dd, \( J = 2.9 \) Hz, 1H, H\(_a\)), 7.65 (s, 1H, H\(_b\)), 7.95 (s, 1H, H\(_a\)), 8.59 (s, 1H, NH).

\(^13\text{C NMR}\) (126 MHz, CDCl\(_3\)) \( \delta = 14.3 \) (CH\(_2\)CH\(_3\)), 40.8 (CH\(_2\)CO\(_2\)Et), 61.3 (CH\(_2\)CH\(_3\)), 77.1 (OCHCHO), 103.4 (C\(_a\)), 108.7 (C\(_a\)), 113.4 (C\(_a\)), 120.1 (C\(_a\)), 129.4 (C\(_a\)), 133.8 (C\(_a\)), 136.4 (C\(_a\)), 139.8 (C\(_a\)), 169.9 (C(O)OEt), 171.2 (C(O)OCH).

HRMS (pos. ESI, CDCl\(_3\)): [M + H\(^+\)], calcd: 260.0917; found: 260.0912.

Ethyl 3-(5-(2-ethoxy-2-oxoethyl)-7-oxo-5,7-dihydro-1H-furo[3,4-f]indol-8-yl)propanoate (2r bis)

\[
\begin{align*}
\text{C}_{18}\text{H}_{16}\text{NO}_6 \\
358.38 \text{ g/mol}
\end{align*}
\]

The initial product’s double bond was hydrogenated prior to isolation in order to be separable from remaining starting material and monofunctionalized product 2r mono.

\( R_f = 0.38 \) (DCM/MeOH = 20:1).

\(^1\text{H NMR}\) (500 MHz, Methanol-\( d_4 \)) \( \delta = 1.16 \) (t, \( J = 7.1 \) Hz, 3H, CH\(_2\)CH\(_3\)), 1.23 (t, \( J = 7.1 \) Hz, 3H, CH\(_2\)CH\(_3\)), 2.72 – 2.76 (m, 2H, CH\(_2\)CH\(_2\)CO\(_2\)Et), 2.79 (dd, \( J = 16.3, 8.0 \) Hz, 1H, CH\(_2\)CO\(_2\)Et), 3.12 (dd, \( J = 16.3, 4.5 \) Hz, 1H, CH\(_2\)CO\(_2\)Et), 3.58 – 3.69 (m, 2H, CH\(_2\)CH\(_2\)CO\(_2\)Et), 4.07 (q, \( J = 7.2 \) Hz, 2H, CH\(_2\)CH\(_3\)), 4.17 (q, \( J = 7.1 \) Hz, 2H, CH\(_2\)CH\(_3\)), 5.87 (dd, \( J = 8.0, 4.6, 1.0 \) Hz, 1H, OCHCHO), 6.59 (d, \( J = 3.1 \) Hz, 1H, H\(_b\)), 7.52 – 7.59 (m, 2H, 2 \times H\(_a\)).

\(^13\text{C NMR}\) (126 MHz, Methanol-\( d_4 \)) \( \delta = 14.4 \) (CH\(_2\)CH\(_3\)), 14.4 (CH\(_2\)CH\(_3\)), 22.5 (CH\(_2\)CH\(_2\)CO\(_2\)Et), 35.3 (CH\(_2\)CH\(_2\)CO\(_2\)Et), 41.4 (CH\(_2\)CO\(_2\)Et), 61.6 (CH\(_2\)CH\(_3\)), 62.0 (CH\(_2\)CH\(_3\)), 77.8 (OCHCHO), 103.5 (C\(_a\)), 112.2 (C\(_a\)), 116.4 (C\(_a\)), 126.4 (C\(_a\)), 131.4 (C\(_a\)), 135.3 (C\(_a\)), 137.2 (C\(_a\)), 141.2 (C\(_a\)), 171.4 (C(O)OEt), 173.3 (C(O)OCH), 174.6 (C(O)OEt).

HRMS (pos. ESI, MeOH): [M + H\(^+\)], calcd: 360.1442; found: 360.1446.
Ethyl (E)-3-[(2-[(methyl)carbamoyl]phenyl)acrylate (2s mono)

![Chemical structure of 2s mono]

R_f = 0.18 (CH/EtOAc = 1:1).

^1H NMR (500 MHz, CDCl_3) δ = 1.32 (t, J = 7.1 Hz, 3H, CH_2CH_3), 3.00 (d, J = 4.9 Hz, 3H, NCH_3), 4.24 (q, J = 7.1 Hz, 2H, CH_2CH_3), 5.91 (s, 1H, N), 6.36 (d, J = 15.9 Hz, 1H, CH=CHCO_2Et), 7.34 – 7.51 (m, 3H, HAr), 7.60 (dd, J = 7.7, 1.2 Hz, 1H, HAr), 7.97 (d, J = 16.0 Hz, 1H, CH=CHCO_2Et).

^13C NMR (126 MHz, CDCl_3) δ = 14.4 (CH_2CH_3), 27.0 (NCH_3), 60.7 (CH_2CH_3), 121.0 (CH=CHCO_2Et), 127.3 (CAr), 127.7 (CAr), 129.9 (CAr), 130.4 (CAr), 132.9 (CAr), 137.3 (CAr), 141.9 (CH=CHCO_2Et), 166.6 (CO_2Et), 169.5 (CO(N)).

HRMS (pos. ESI, CHCl_3): [M + H]^+ calcd: 234.1125; found: 234.1126.

Spectral data matched reported values.^[10]^ 

Diethyl 3,3′-(2-[(methyl)carbamoyl]1,3-phenylene)(2E,2′E)-diacylate (2s bis)

![Chemical structure of 2s bis]

R_f = 0.33 (CH/EtOAc = 1:1).

^1H NMR (500 MHz, CDCl_3) δ = 1.32 (t, J = 7.1 Hz, 6H, 2 × CH_2CH_3), 3.08 (d, J = 4.9 Hz, 3H, NCH_3), 4.25 (q, J = 7.1 Hz, 4H, 2 × CH_2CH_3), 5.70 (q, J = 4.5 Hz, 1H, NH), 6.43 (d, J = 15.9 Hz, 2H, 2 × CH=CHCO_2Et), 7.43 (t, J = 7.9 Hz, 1H, HAr), 7.64 (d, J = 7.8 Hz, 2H, HAr), 7.73 (d, J = 16.0 Hz, 2H, 2 × CH=CHCO_2Et).

^13C NMR (126 MHz, CDCl_3) δ = 14.4 (2 × CH_2CH_3), 27.0 (NCH_3), 60.9 (2 × CH_2CH_3), 121.9 (2 × CH=CHCO_2Et), 127.9 (2 × CAr), 129.8 (CAr), 132.7 (CAr), 138.4 (2 × CAr), 140.7 (2 × CH=CHCO_2Et), 166.4 (2 × CO_2Et), 168.3 (CO(N)).

HRMS (pos. ESI, CHCl_3): [M + H]^+ calcd: 332.1492; found: 332.1492.

Spectral data matched reported values.^[11]^ 

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S25
6 Synthesis of Catalysts

\((E)-2-(2,3,4,5-Tetramethylcyclopent-2-en-1-ylidene)acetonitrile\)

A solution of acetonitrile (2.00 mL, 38.1 mmol, 1.1 equiv.) in dry THF (40 mL) was cooled to −78 °C and a solution of n-BuLi in hexanes (1.6 M, 23.8 mL, 38 mmol, 1.1 equiv.) was added dropwise. The reaction mixture was stirred at −78 °C for 15 min. 2,3,4,5-Tetramethylcyclopent-2-en-1-one (5.20 mL, 34.5 mmol) was added dropwise over a period of 30 min and the resulting solution was allowed to warm up to 0 °C over 3 h. The reaction was interrupted by addition of water (8 mL) and the resulting layers were separated. The organic layer was washed with water (2×3 mL) and an aq. solution of HCl in water (2 M, 4 mL) was added. The reaction mixture was stirred at rt for 20 h and the layers were separated. The organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by flash column chromatography (silica, CH/EtOAc = 40:1 → 20:1) and the product was obtained as a colorless oil (5.20 g, 32.2 mmol, 93%, mixture of isomers). Alternatively, the crude product can be purified by distillation in vacuo (b.p. 69–72 °C at 0.8 mbar).

\[ R_f = 0.46 \text{(CH/EtOAc = 5:1).} \]

\[^1H\text{NMR} (300 \text{ MHz, CDCl}_3, \text{ signals of main isomer}) \delta = 1.07 \text{ (d, } J = 7.1 \text{ Hz, 3H, CHCH}_3), 1.27 \text{ (d, } J = 7.2 \text{ Hz, 3H, CHCH}_3), 1.65 – 1.67 \text{ (m, 3H, C=C(CH}_3)), 1.83 – 1.84 \text{ (m, 3H, C=C(CH}_3)), 2.17 – 2.26 \text{ (m, 1H, CHCH}_3), 2.56 – 2.65 \text{ (m, 1H, CHCH}_3), 4.89 \text{ (dt, } J = 2.0, 0.6 \text{ Hz, 1H, C≡CHCN).} \]

The preparation of this product was performed according to a published procedure.\[^{12}\]
Spectral data matched reported values.
A solution of (E)-2-(2,3,4,5-tetramethylcyclopent-2-en-1-ylidene)acetonitrile (1.00 g, 6.2 mmol) in dry Et₂O (3 mL) was added dropwise to a suspension of LiAlH₄ (365 mg, 9.61 mmol, 1.5 equiv.) in dry Et₂O (10 mL) at 0 °C. The reaction mixture was heated to reflux, was stirred at that temp. for 3 h and then cooled to 0 °C. The reaction was interrupted by successive addition of H₂O (0.4 mL), an aq. solution of NaOH (15%, 0.8 mL) and H₂O (1.2 mL) and the resulting mixture was allowed to warm up to rt. After 15 min, dry Na₂SO₄ was added and the suspension was stirred at rt for another 15 min. The resulting salts were filtered off and thoroughly washed with Et₂O. The combined filtrates were concentrated under reduced pressure and the residue was purified by distillation in vacuo (b.p. 53–57 °C at 0.8 mbar). The title compound was obtained as a light-yellow oil (0.81 g, 4.9 mmol, 79%, mixture of isomers).

NMR spectra were collected for the isomerically pure hydrochloride of the title compound.

¹HNMR (500 MHz, Methanol-d₄) δ = 1.77 (s, 6H, 2 × CH₃), 1.85 (s, 6H, 2 × CH₃), 2.02 – 2.10 (m, 2H, CH₂CH₂NH₃Cl), 2.29 – 2.37 (m, 2H, CH₂CH₂NH₃Cl), 2.71 – 2.77 (m, 1H, CH=C).

¹³CNMR (126 MHz, Methanol-d₄) δ = 11.1 (2 × CH₃), 11.6 (2 × CH₃), 26.2 (CH₂CH₂NH₃Cl), 36.3 (CH₂CH₂NH₃Cl), 54.8 (CHC=C), 134.7 (2 × CH=C), 138.1 (2 × CH=C).

The preparation of this product was performed according to a published procedure,[¹²] spectral data matched reported values.
To a solution of (1-isocyanato-3,5-bis(trifluoromethyl)benzene (0.42 mL, 2.4 mmol, 1.3 equiv.) in THF (4.0 mL) was added (E)-2-(2,3,4,5-tetramethylcyclopent-2-en-1-ylidene)ethan-1-amine (320 mg, 1.9 mmol) dropwise. The resulting solution was stirred at rt overnight. The reaction was interrupted by addition of a sat. aq. solution of NH₄Cl and the resulting mixture was extracted with ethyl acetate (3×). The combined organic layers were dried over Na₂SO₄, filtered and concentrated in vacuo. The residue was purified by recrystallization from Et₂O/n-pentane. (Alternatively, the crude product can be purified by flash column chromatography (silica, CH/EtOAc = 10:1 → 5:1). The title compound was obtained as a colorless solid (578 mg, 1.37 mmol, 77%).

m.p. 104 – 106 °C.

¹H NMR (500 MHz, DMSO-d₆) δ = 0.95 (d, J = 7.0 Hz, 3H, CH₃), 1.01 (d, J = 7.0 Hz, 3H, CH₃), 1.57 (s, 3H, C=C(CH₃)), 1.70 (s, 3H, C=C(CH₃)), 2.04 (q, J = 7.0 Hz, 1H, CH₂CH₃), 2.41 (q, J = 7.1 Hz, 1H, CH₂CH₃), 3.74 – 3.87 (m, 2H, CH₂CH=C), 5.06 (ddd, J = 7.0, 1.7 Hz, 1H, CH₂CH=C), 6.54 (t, J = 5.5 Hz, 1H, NH), 7.52 (s, 1H, Ar-H), 8.06 (s, 2H, Ar-H), 9.16 (s, 1H, NH).

¹³C NMR (126 MHz, DMSO-d₆) δ = 9.9 (C=C(CH₃)), 12.9 (C=C(CH₃)), 19.3 (CH₂CH₃), 21.5 (CH₂CH₃), 37.8 (CH₂CH=C), 41.4 (CH₃), 50.7 (CH₂CH₃), 112.5 (CH₂CH=C), 113.4 (hept, J = 3.7 Hz, C₆H₆), 117.2 (q, J = 4.0 Hz, 2 × C₆H₆), 123.3 (q, J = 272.7 Hz, 2 × CF₃), 129.8 (C₆H₆), 130.6 (q, J = 32.3 Hz, 2 × C₆H₆), 142.6 (C=C(CH₃)), 144.8 (CH₂CH=C), 153.7 (C=C(CH₃)), 154.6 (NC(O)N).

HRMS (pos. ESI, EtOH): [M + H⁺], calcd: 421.1709; found: 421.1711.
Dichloro[η^5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea]rhodium(III) dimer (3)

(E)-1-(3,5-Bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopent-2-en-1-ylidene)ethyl)urea (454 mg, 1.08 mmol, 1.3 equiv.) was dissolved in dry EtOH (11 mL) and RhCl₃ · n H₂O (222 mg, 0.84 mmol) was added. The reaction mixture was heated to 80 °C and stirred at that temp. for 24 h. The reaction mixture was stored in the freezer (−20 °C) overnight to complete precipitation of the crude product. The solvent was removed after centrifugation and the solid crude product was washed successively with cold EtOH, Et₂O and n-pentane. The title compound was obtained as an orange powder (427 mg, 0.36 mmol, 86%).

m.p. 265 – 267 °C.

¹H NMR (500 MHz, DMSO-d₆) δ = 1.52 (s, 6H, 2 × CH₃), 1.62 (s, 6H, 2 × CH₃), 2.30 (t, J = 6.6 Hz, 2H, CH₂CH₂NH), 3.28 (t, J = 6.6 Hz, 2H, CH₂CH₂NH), 7.52 (s, 1H, Hₐ), 7.86 (s, 2H, 2 × Hₐ).

¹³C NMR (126 MHz, DMSO-d₆) δ = 9.5 (CH₃), 9.7 (CH₃), 25.7 (CH₂CH₂NH), 37.5 (CH₂CH₂NH), 98.9 (d, J = 7.7 Hz, Cₖₐ), 101.2 (d, J = 7.2 Hz, 2 × Cₖₐ), 102.0 (d, J = 7.2 Hz, 2 × Cₖₐ), 115.6 (Cₖₐ), 118.7 (2 × Cₖₐ), 124.2 (q, J = 273.2 Hz, 2 × CF₃), 132.1 (q, J = 32.9 Hz, 2 × Cₖₐ), 142.6 (Cₖₐ), 156.4 (NC(O)(N)).

HRMS (pos. ESI, Chloroform): [M – Cl], calcd: 1149.0286; found: 1149.0288.

The complex formation was adapted from a literature known procedure.[13]
General Procedure for Rhodium(III)Cp* Monomer Synthesis

Dichloro[η5-(3,5-bis(trifluoromethyl)phenyl)-3-(2,3,4,5-tetramethylcyclopentadienyl)ethyl]urea] rhodium(III) dimer (1.0 equiv.) and phosphine ligand (3.0 equiv.) were dissolved in DMSO (0.04 M) under an argon atmosphere. The resulting reaction mixture was stirred at rt for 16 h. The solvent was removed at high vacuum and the resulting crude product was recrystallized from either MeOH or acetone/Et₂O. After washing thoroughly with Et₂O and n-pentane, the products were obtained as orange or red crystalline solids.

The product was synthesized according to the general procedure using Dichloro[η5-(3,5-bis(trifluoromethyl)phenyl)-3-(2,3,4,5-tetramethylcyclopentadienyl)ethyl]urea]rhodium(III) dimer (3, 60 mg, 0.05 mmol) and triphenylphosphine (40 mg, 0.15 mmol, 3 equiv.). The title compound was obtained as an orange powder (76 mg, 0.09 mmol, 88%).

m.p. 229 – 231 °C (decomp.).

1H NMR (500 MHz, DMSO-d₆) δ = 1.27 (d, J = 3.8 Hz, 6H, 2 × CH₃), 1.32 (d, J = 3.2 Hz, 6H, 2 × CH₃), 1.86 (t, J = 7.4 Hz, 2H, CH₂CH₂NH), 3.11 (q, J = 6.2 Hz, 2H, CH₂CH₂NH), 6.55 (t, J = 5.9 Hz, 1H, CH₂CH₂NH), 7.44 (s, 9H, HAr), 7.55 (s, 1H, HAr), 7.73 (q, J = 9.0 Hz, 6H, HAr), 8.04 (s, 2H, HAr), 9.30 (s, 1H, NH).

13C NMR (126 MHz, DMSO-d₆) δ = 8.3 (d, J = 1.4 Hz, 2 × CH₃), 8.5 (d, J = 1.0 Hz, 2 × CH₃), 24.4 (CH₂CH₂NH₂), 36.7 (CH₂CH₂NH₂), 98.1 (C₆H₅), 99.0 (2 × C₆H₅), 100.4 (2 × C₆H₅), 113.6 (C₆H₅), 117.2 (C₆H₅), 113.3 (q, J = 272.5 Hz, 2 × CF₃), 128.7 (d, J = 11.9 Hz, C₆H₅), 130.6 (q, J = 32.3 Hz, 2 × C₆H₅), 131.5 (d, J = 9.7 Hz, C₆H₅), 134.3 (d, J = 10.0 Hz, C₆H₅), 142.4 (C₆H₅), 154.6 (NC(O)N).

19F NMR (282 MHz, DMSO-d₆) δ = -61.7.

31P NMR (122 MHz, DMSO-d₆) δ = 29.5 (d, J = 145.0 Hz).

HRMS (pos. ESI, MeOH): [M - Cl], calcd: 819.1208; found: 819.1203.
Dichloro[η⁵-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea][6-oxo-1,6-dihydropyridin-2-yl]diphenylphosphine]rhodium(III) (4b)

The product was synthesized according to the general procedure using Dichloro[η⁵-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea]rhodium(III) dimer (3, 64.8 mg, 0.055 mmol) and 6-diphenylphosphanyl-1H-pyridin-2-one (46 mg, 0.16 mmol, 3 equiv.). The title compound was obtained as a red crystalline solid (85.0 mg, 0.097 mmol, 89%).

m.p. 222 – 224 °C (decomp.).

**¹H NMR** (500 MHz, DMSO-d₆) δ = 1.34 (d, J = 3.9 Hz, 6H, 2 × CH₃), 1.37 (d, J = 3.4 Hz, 6H, 2 × CH₃), 1.90 (t, J = 6.4 Hz, 2H, CH₂CH₂NH), 5.94 (t, J = 5.7 Hz, 1H, HAr), 6.27 (d, J = 9.3 Hz, 1H, HAr), 6.53 (t, J = 6.0 Hz, 1H, CH₂CH₂NH), 7.24 – 7.35 (m, 1H, HAr), 7.50 – 7.74 (m, 11H, HAr), 8.02 (s, 2H, HAr), 9.31 (s, 1H, NH), 11.15 (s, 1H, NH).

**¹³C NMR** (126 MHz, DMSO-d₆) δ = 8.4 (d, J = 1.2 Hz, 2 × CH₃), 8.5 (d, J = 1.0 Hz, 2 × CH₃), 24.3 (CH₂CH₂NH), 36.7 (CH₂CH₂NH), 98.9 (d, J = 8.6 Hz, CAr), 99.9 (d, J = 8.7 Hz, 2 × CAr), 101.5 (d, J = 9.9 Hz, 2 × CAr), 111.0 (CAr), 113.6 (CAr), 117.2 (d, J = 3.5 Hz, CAr), 121.9 (CAr), 123.3 (q, J = 272.5 Hz, 2 × CF₃), 128.9 (d, J = 10.3 Hz, CAr), 130.5 (q, J = 32.6 Hz, 2 × CAr), 132.1 (CAr), 134.2 (d, J = 10.9 Hz, CAr), 139.4 (d, J = 8.3 Hz, CAr), 142.4 (CAr), 154.6 (NCOON), 161.4 (d, J = 6.4 Hz, NCO).

**¹⁹F NMR** (282 MHz, DMSO-d₆) δ = -61.7.

**³¹P NMR** (202 MHz, DMSO-d₆) δ = 32.0 (d, J = 158.2 Hz).

**HRMS** (pos. ESI, MeOH): [M - Cl]’, calcd: 836.1109; found: 836.1104.

**X-ray structure**
Dichloro[η5-(3,5-bis(trifluoromethyl)phenyl)-3-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl]urea][3-oxo-2,3-dihydroisoquinolin-1-yl]diphenylphosphine/rhodium(III) (4c)

The product was synthesized according to the general procedure using Dichloro[η5-(3,5-bis(trifluoromethyl)phenyl)-3-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl]urea/rhodium(III) dimer (3, 60 mg, 0.05 mmol) and 1-(diphenylphosphaneyl)isoquinolin-3(2H)-one (49 mg, 0.15 mmol, 3 equiv.). The title compound was obtained as an orange powder (82 mg, 0.09 mmol, 88%).

**m.p.** 227 – 229 °C (decomp.).

**1H NMR** (500 MHz, Methanol-$d_4$) δ = 1.43 (d, $J = 3.9$ Hz, 6H, $2 \times$ C$_{CH_3}$), 1.51 (d, $J = 3.3$ Hz, 6H, $2 \times$ C$_{CH_3}$), 2.07 (td, $J = 6.7$, 1.6 Hz, 2H, C$_{CH_2NH}$), 3.28 (q, $J = 6.7$ Hz, 2H, CH$_2$CH$_2$NH), 6.55 (d, $J = 8.0$ Hz, 2H, H$_{Ar}$), 7.46 – 7.50 (m, 2H, H$_{Ar}$), 7.52 (t, $J = 7.1$ Hz, 1H, H$_{Ar}$), 7.56 – 7.69 (m, 7H, H$_{Ar}$), 7.81 – 7.88 (m, 4H, H$_{Ar}$), 7.94 (s, 2H, H$_{Ar}$), 8.17 (d, $J = 7.8$ Hz, 2H, H$_{Ar}$).

**13C NMR** (126 MHz, DMSO-$d_6$) δ = 8.4 (d, $J = 1.4$ Hz, 2 x CH$_3$), 8.6 (d, J = 1.1, 2 x CH$_3$), 24.4 (CH$_2$CH$_2$NH$_2$), 36.7 (CH$_3$CH$_2$NH$_2$), 98.9 (C$_{CH_3}$), 99.9 (2 x C$_{CH_3}$), 101.4 (2 x C$_{Ar}$), 111.9 (C$_{CH_2NH}$), 113.6 (C$_{Ar}$), 117.2 (C$_{Ar}$), 123.3 (q, $J = 273.8$, 2 x CF$_3$), 125.8 (C$_{Ar}$), 126.5 (C$_{Ar}$), 127.3 (C$_{Ar}$), 128.0 (C$_{Ar}$), 128.9 (d, $J = 10.0$ Hz, C$_{Ar}$), 130.6 (q, $J = 32.5$ Hz, 2 x C$_{Ar}$), 132.0 (C$_{Ar}$), 132.7 (C$_{Ar}$), 134.3 (d, $J = 10.9$ Hz, C$_{Ar}$), 135.9 (d, $J = 9.1$ Hz, C$_{Ar}$), 142.4 (C$_{Ar}$), 154.6 (NCOON), 160.8 (d, $J = 7.2$ Hz, NC(O)).

**19F NMR** (471 MHz, Methanol-$d_4$) δ = -64.6.

**31P NMR** (202 MHz, Methanol-$d_4$) δ = 31.8 (d, $J = 144.5$ Hz).

**HRMS** (neg. ESI, MeOH): [M - H$^+$], calcd: 920.0887; found: 920.0879.

**X-ray structure**
Dichloro[η5-(3,5-bis(trifluoromethyl)phenyl)-3-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl]urea[(6-oxo-1,6-dihydropyridin-2-yl)(3,5-bis(trifluoromethyl)phenyl)phosphine]rhodium(III) (4d)

The product was synthesized according to the general procedure using Dichloro[η5-(3,5-bis(trifluoromethyl)phenyl)-3-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl]urea[rhodium(III) dimer (3, 61.0 mg, 0.051 mmol) and 6-bis(3,5-bis(trifluoromethyl)phenyl)phosphanyl)pyridin-2(1H)-one (85.0 mg, 0.154 mmol, 3 equiv.). The title compound was obtained as a red crystalline solid (113.0 mg, 0.099 mmol, 96%).

m.p. 210 – 212 °C (decomp.).

$^1$H NMR (500 MHz, DMSO-d$_6$) δ = 1.30 – 1.45 (m, 12H, 4 × C$_2$H$_3$), 1.74 – 1.97 (m, 2H, CH$_2$CH$_2$NH), 3.00 – 3.17 (m, 2H, CH$_2$CH$_2$NH), 6.50 (t, J = 6.0 Hz, 1H, H$_6$), 6.84 (s, 1H, H$_2$), 7.54 (s, 1H, H$_6$), 8.03 (s, 2H, H$_2$), 8.17 – 8.41 (m, 2H, H$_4$), 8.50 – 8.64 (m, 3H, H$_7$), 9.30 (s, 1H, NH), 11.26 (s, 1H, NH).

$^{13}$C NMR (126 MHz, DMSO-d$_6$, not all expected signals detected) δ = 8.3 (4 × C$_2$H$_3$), 24.1 (CH$_2$CH$_2$NH), 36.8 (CH$_2$CH$_2$NH), 98.4 (C$_6$), 99.1 (2 × C$_6$), 100.3 (2 × C$_6$), 108.0 (C$_6$), 113.5 (C$_6$), 117.2 (C$_6$), 121.8 (q, J = 273.7 Hz, 2 × CF$_3$), 123.3 (q, J = 272.8 Hz, 2 × CF$_3$), 124.8 (C$_6$), 130.5 (q, J = 32.3 Hz, C$_6$), 135.2 – 135.6 (m, C$_6$), 144.2 (C$_6$), 154.6 (NC(O)N), 163.2 (NC(O)).

$^{19}$F NMR (471 MHz, DMSO-d$_6$) δ = -61.8, -61.5.

$^{31}$P NMR (202 MHz, DMSO-d$_6$) δ = 26.3 (d, J = 149.9 Hz).

HRMS (pos. ESI, MeOH): [M - Cl]$^+$, calcd: 1108.0605; found: 1108.0607.

X-ray structure
The product was synthesized according to the general procedure using Dichloro[η5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea][6-methoxypyridin-2-yl]diphenylphosphine]rhodium(III) dimer (3, 60 mg, 0.05 mmol) and 2-(diphenylphosphaneyl)-6-methoxypyridine (44 mg, 0.15 mmol, 3 equiv.). The title compound was obtained as an orange powder (59 mg, 0.07 mmol, 66%).

m.p. 209 – 211 °C (decomp.).

\(^1\text{H NMR}\) (500 MHz, DMSO-d\(_6\)) \(\delta = 1.28\) (d, \(J = 3.6\) Hz, 6H, 2 × CH\(_3\)), 1.34 (d, \(J = 3.3\) Hz, 6H, 2 × CH\(_3\)), 1.90 (t, \(J = 6.9, 2H\) Hz, CH\(_2\)CH\(_2\)NH), 3.12 (q, \(J = 6.6\) Hz, 2H, CH\(_2\)CH\(_2\)NH), 3.76 (s, 3H, OC\(_3\)H\(_3\)), 6.48 (t, \(J = 6.1\) Hz, 1H, CH\(_2\)CH\(_2\)NH), 6.82 (dd, \(J = 8.5, 2.1\) Hz, 1H, H\(_{\text{Ar}}\)), 7.35 – 7.54 (m, 8H, H\(_{\text{Ar}}\)), 7.62 – 7.73 (m, 1H, H\(_{\text{Ar}}\)), 7.88 – 8.01 (m, 4H, H\(_{\text{Ar}}\)), 8.03 (s, 2H, H\(_{\text{Ar}}\)), 9.20 (s, 1H, NH).

\(^{13}\text{C NMR}\) (126 MHz, DMSO-d\(_6\)) \(\delta = 8.3\) (d, \(J = 1.6\) Hz, 2 × CH\(_3\)), 8.4 (d, \(J = 0.9\) Hz, 2 × CH\(_3\)), 24.2 (CH\(_2\)CH\(_2\)NH), 36.7 (CH\(_2\)CH\(_2\)NH), 53.4 (OCH\(_3\)), 97.8 (d, \(J = 6.8\) Hz, C\(_{\text{Ar}}\)), 99.3 (d, \(J = 4.9\) Hz, 2 × C\(_{\text{Ar}}\)), 100.5 (2 × C\(_{\text{Ar}}\)), 111.5 (C\(_{\text{Ar}}\)), 113.5 (C\(_{\text{Ar}}\)), 117.2 (d, \(J = 4.4\) Hz, C\(_{\text{Ar}}\)), 123.3 (q, \(J = 272.8\) Hz, 2 × CF\(_3\)), 127.4 (d, \(J = 10.0\) Hz, C\(_{\text{Ar}}\)), 130.3 (C\(_{\text{Ar}}\)), 130.5 (q, \(J = 32.5\) Hz, C\(_{\text{Ar}}\)), 134.9 (C\(_{\text{Ar}}\)), 138.8 (C\(_{\text{Ar}}\)), 142.5 (C\(_{\text{Ar}}\)), 153.4 (d, \(J = 63.3\) Hz, C\(_{\text{Ar}}\)), 154.6 (NCO(N)), 162.0 (d, \(J = 12.5\) Hz, (NCO)).

\(^{19}\text{F NMR}\) (471 MHz, DMSO-d\(_6\)) \(\delta = -61.7\).

\(^{31}\text{P NMR}\) (122 MHz, Methanol-d\(_4\)) \(\delta = 27.9\) (d, \(J = 134.9\) Hz).

HRMS (pos. ESI, MeOH): [M - Cl], calcd: 850.1266; found: 850.1249.

X-ray structure
The compound was crystallized from acetone/cyclohexene by solvent layering. The data for cu_BreitLB_1_36_0m-a-final.cif were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used CuKα radiation (λ = 1.54184 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS-2016/2 and refined by full matrix least-squares methods against $F^2$ by SHELXL-2018/3.[16,17] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their $U_{eq}$ values constrained to 1.5 times the $U_{eq}$ of their pivot atoms for terminal sp$^3$ carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[18] CCDC 1977992 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Table S9: Crystal data and structure refinement for catalyst 4b

| Atom       | $x$    | $y$    | $z$    | $U_{eq}$ |
|------------|--------|--------|--------|----------|
| Rh1        | 0.62690(2) | 0.29175(3) | 0.49714(2) | 0.02015(9) |
| N1         | 0.42546(18) | 0.2927(14) | 0.30708(17) | 0.0253(8) |
| C1         | 0.39581(17) | 0.358537 | 0.299496 | 0.030 |
| F1         | 0.71691(17) | 0.2300(4) | 0.21966(17) | 0.0660(11) |
| O1         | 0.51339(15) | 0.1835(3) | 0.27543(14) | 0.0274(7) |
| C1         | 0.58643(5) | 0.19456(10) | 0.57157(5) | 0.0238(12) |
| C1         | 0.53998(2) | 0.2556(4) | 0.41727(19) | 0.0215(8) |
| P1         | 0.72666(5) | 0.22587(11) | 0.57147(5) | 0.0209(2) |
| C2         | 0.5929(2) | 0.15774(4) | 0.4165(2) | 0.0238(9) |
| F2         | 0.67632(19) | 0.15934(3) | 0.1247(2) | 0.0752(12) |
| C2         | 0.64684(3) | 0.50556(10) | 0.55244(5) | 0.0255(2) |
| N2         | 0.47897(19) | 0.3892(4) | 0.23168(18) | 0.0272(8) |
| H2         | 0.447514 | 0.451127 | 0.230263 | 0.033 |
| O2         | 0.62958(16) | 0.4452(3) | 0.74645(15) | 0.0299(7) |
| C3         | 0.65317(2) | 0.2257(4) | 0.4042(2) | 0.0228(9) |
| O3         | 0.59283(3) | 0.7007(5) | 0.2740(2) | 0.0706(13) |
| F3         | 0.74318(16) | 0.3282(4) | 0.13858(18) | 0.0604(10) |
| N3         | 0.68072(18) | 0.3310(4) | 0.67572(17) | 0.0242(8) |
| H3         | 0.667534 | 0.394127 | 0.649781 | 0.029 |
| C5         | 0.5678(2) | 0.3837(4) | 0.4078(2) | 0.0231(9) |
| F5         | 0.50154(17) | 0.7393(3) | 0.07374(19) | 0.0590(10) |
| C4         | 0.6385(2) | 0.3686(4) | 0.4009(2) | 0.0251(9) |
| F4         | 0.54630(3) | 0.6327(5) | 0.00570(18) | 0.0965(17) |
| C6         | 0.5822(2) | 0.0108(4) | 0.4166(2) | 0.0269(10) |
| H6A        | 0.555969 | -0.017146 | 0.373926 | 0.040 |
| H6B        | 0.566794 | -0.012573 | 0.450572 | 0.040 |
| H6C        | 0.628744 | -0.03168 | 0.425344 | 0.040 |
| F6         | 0.60890(19) | 0.7441(5) | 0.0783(3) | 0.0108(19) |
| C7         | 0.7166(2) | 0.1596(5) | 0.3927(2) | 0.0296(10) |
| H7A        | 0.711380 | 0.138050 | 0.346247 | 0.044 |
SUPPORTING INFORMATION

Table S11: Bond lengths and angles for catalyst 4b.

| Atom–Atom | Length [Å] |
|-----------|------------|
| Rh1–C2    | 2.166(4)   |
| Rh1–C4    | 2.198(4)   |
| Rh1–C3    | 2.207(4)   |
| Rh1–C1    | 2.216(4)   |
| Rh1–C5    | 2.332(11)  |
| Rh1–P1    | 2.4018(10) |
| Rh1–C12   | 2.4347(11) |
| N1–C11    | 1.355(5)   |

\( \sigma_{\text{UC}} \) is defined as 1/3 of the trace of the orthogonalized \( \sigma_{\text{UC}} \) tensor.
| Atom-Atom-Atom | Angle [°] |
|----------------|-----------|
| C2-RH1-C4      | 64.72(16) |
| C2-RH1-C3      | 38.73(16) |
| C4-RH1-C3      | 38.25(16) |
| C2-RH1-C1      | 38.69(16) |
| C4-RH1-C1      | 64.24(16) |
| C3-RH1-C1      | 64.30(15) |
| C2-RH1-C5      | 64.17(16) |
| C4-RH1-C5      | 38.57(16) |
| C3-RH1-C5      | 63.97(16) |
| C1-RH1-C5      | 37.72(16) |
| C2-RH1-P1      | 116.31(12) |
| C4-RH1-P1      | 119.54(12) |
| C3-RH1-P1      | 101.61(11) |
| C1-RH1-P1      | 153.47(12) |
| C5-Rh1-P1      | 157.53(12) |
| C2-Rh1-C11     | 96.66(12) |
| C4-Rh1-C11     | 152.72(12) |
| C3-Rh1-C11     | 133.44(12) |
| C5-Rh1-C11     | 88.68(11) |
| C5-Rh1-C11     | 116.44(12) |
| P1-Rh1-C1     | 86.03(4) |
| C2-RH1-C12 | 156.09(12) |
| C4-RH1-C12 | 95.99(12) |
| C3-RH1-C12 | 130.56(12) |
| C1-RH1-C12 | 121.49(12) |
| C5-RH1-C12 | 91.98(12) |
| C1-RH1-C12 | 95.62(4) |
| C2-RH1-C12 | 121.9(4) |
| C5-C1-C2 | 107.9(4) |
| C5-C1-C10 | 126.4(4) |
| C2-C1-C10 | 125.6(4) |
| C5-C1-RH1 | 71.5(2) |
| C2-C1-RH1 | 69.1(2) |
| C10-C1-RH1 | 126.9(3) |
| C26-P1-C32 | 105.4(2) |
| C26-P1-C21 | 102.12 |
| C26-P1-C21 | 102.8(2) |
| C26-P1-RH1 | 113.89(14) |
| C32-P1-RH1 | 117.46(15) |
| C21-P1-RH1 | 113.40(14) |
| C3-C2-C1 | 108.1(4) |
| C3-C2-C6 | 126.3(4) |
| C1-C2-C6 | 124.8(4) |
| C3-C2-RH1 | 71.8(2) |
| C1-C2-RH1 | 72.2(2) |
| C6-C2-RH1 | 129.8(3) |
| C12-N2-C13 | 126.2(4) |
| C12-N2-H2 | 116.9 |
| C13-N2-H2 | 116.9 |
| C4-C3-C2 | 107.8(4) |
| C4-C3-C7 | 126.8(4) |
| C2-C3-C7 | 125.3(4) |
| C4-C3-RH1 | 70.6(2) |
| C2-C3-RH1 | 69.4(2) |
| C7-C3-RH1 | 128.4(3) |
| C25-N3-C21 | 125.6(4) |
| C25-N3-C21 | 125.6(4) |
| C25-N3-H3 | 117.2 |
| C21-N3-H3 | 117.2 |
| C1-C5-C4 | 108.3(4) |
| C1-C5-C9 | 127.7(4) |
| C4-C5-C9 | 124.0(4) |
| C1-C5-RH1 | 70.8(2) |
| C4-C5-RH1 | 69.8(2) |
| C9-C5-RH1 | 125.9(3) |
| C3-C4-C5 | 107.8(4) |
| C3-C4-C8 | 127.9(4) |
| C5-C4-C8 | 123.4(4) |
| C3-C4-RH1 | 71.2(4) |
| C5-C4-RH1 | 71.6(2) |
| C8-C4-RH1 | 131.5(3) |
| C2-C6-H6A | 109.5 |
| C2-C6-H6B | 109.7(16) |
| H6A-C6-H6B | 109.5 |
| H6B-C6-H6C | 109.5 |
| H6B-C6-H6C | 109.5 |
Table S12: Hydrogen bonds for catalyst 4b.

| D-H-A [Å] | d(O-H) [Å] | d(H...A) [Å] | <(DHA) [°] |
|------------|------------|---------------|-------------|
| N1-H1-O21 | 0.88       | 2.21          | 166.9       |
| N2-H2-O20 | 0.88       | 2.00          | 159.9       |

Symmetry transformations used to generate equivalent atoms: #1: 1-X, 1-Y, 1-Z;

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Catalyst 4c

The compound was crystallized from methanol by evaporation. The data for cu_BreitLB_1_37_0m_a-final cif were collected from a shock-cooled single crystal at 110(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used CuKα radiation (λ = 1.5418 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied. The structure were solved by direct methods using SHELXTL 2014/5 and refined by full-matrix least-squares methods against F² by SHELXL-2018/3.[16,17] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their Uiso values constrained to 1.5 times the Ueq of their pivot atoms for terminal sp³ carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[18] CCDC 1982180 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.[19]

Table S13: Crystal data and structure refinement for catalyst 4c.

| Crystallographic data | value |
|-----------------------|-------|
| CCDC number           | 1982180 |
| Empirical formula     | CuH₁₀Cl₂F₆N₅O₂PrH |
| Formula weight        | 954.56 |
| Temperature [K]       | 110(2) |
| Crystal system        | monoclinic |
| Space group (number)  | C2/c (15) |
| a [Å]                 | 28.5889 (15) |
| b [Å]                 | 15.4635 (3) |
| c [Å]                 | 19.8925 (8) |
| α [°]                 | 90 |
| β [Å]                 | 109.913 (3) |
| γ [Å]                 | 90 |
| Volume [Å³]           | 8271.3 (6) |
| Z                     | 8 |
| μ [mm⁻¹]              | 5.502 |
| F(000)                | 3886 |
| Crystal size [mm²]    | 0.200 × 0.120 × 0.060 |
| Crystal colour        | red |
| Radiation             | CuKα (λ=1.5418 Å) |
| 2θ range [°]          | 6.57 to 14.62 (0.00 Å) |
| Index ranges          | -35 ≤ h ≤ 35 |
| -19 ≤ k ≤ 19          |
| -24 ≤ l ≤ 24          |
| Reflections collected | 187852 |
| μ [mm⁻¹]              | 8220 |
| Independent reflections | R = 0.0326 |
| R₁ = 0.0098           |
| Completeness to θ = 67.684 ° | 99.9 % |
| Data / Restraints / Parameters | 8220/285/611 |
| Goodness-of-fit on F² | 1.075 |
| Final R indexes       | R₁ = 0.0216 |
| Final R indexes       | R = 0.0216 |
| [all data]            | wR₁ = 0.0541 |
| Largest peak/hole [e Å⁻³] | 0.53/0.40 |

Table S14: Atomic coordinates and Ueq [Å²] for catalyst 4c.

| Atom | x     | y     | z     | Ueq |
|------|-------|-------|-------|-----|
| Rh1  | 0.37863(2) | 0.55237(2) | 0.38722(2) | 0.01426(4) |
| F1   | 0.38881(5) | 0.96733(11) | 0.47904(8) | 0.0556(4) |
| C1   | 0.41347(2) | 0.41499(2) | 0.36733(2) | 0.01992(8) |
| P1   | 0.26962(4) | 0.50726(2) | 0.32174(2) | 0.01454(8) |
| C1   | 0.44898(8) | 0.62087(10) | 0.39962(8) | 0.0185(3) |
| O1   | 0.33876(4) | 0.20523(7) | 0.40551(6) | 0.0206(2) |
| N1   | 0.55677(5) | 0.69846(9) | 0.46310(8) | 0.0209(3) |
| H1N  | 0.5762(7) | 0.6735(12) | 0.5013(9) | 0.025 |
| C2   | 0.43122(8) | 0.64918(10) | 0.45389(9) | 0.0185(3) |
| F2   | 0.39892(5) | 1.05889(9) | 0.56311(11) | 0.0675(5) |
| N2   | 0.55481(5) | 0.81270(10) | 0.53548(8) | 0.0255(3) |
| H2N  | 0.5586(5) | 0.8013(13) | 0.5562(10) | 0.031 |
| C12  | 0.36389(2) | 0.49276(3) | 0.49151(2) | 0.02048(8) |
| O2   | 0.49391(4) | 0.79671(8) | 0.42514(7) | 0.0259(3) |
| C3   | 0.38197(6) | 0.68556(10) | 0.42012(9) | 0.0239(3) |
| F3   | 0.3802(3) | 0.92431(11) | 0.57912(10) | 0.0649(4) |
| O1A  | 0.50277(7) | 0.46033(4) | 0.2596(11) | 0.042(4) |
| H1A  | 0.512665 | 0.496809 | 0.236334 | 0.063 |
| C1A  | 0.42063(5) | 0.17214(3) | 0.2134(2) | 0.048(3) |
| H1AA | 0.440104 | 0.459077 | 0.177622 | 0.072 |
| H1AB | 0.4405682 | 0.3949958 | 0.241217 | 0.072 |
| H1AC | 0.470757 | 0.370299 | 0.189147 | 0.072 |
| O2A  | 0.46581(10) | 0.429(2) | 0.2366(16) | 0.097(9) |
| H2A  | 0.459077 | 0.460108 | 0.200835 | 0.145 |
| C2A  | 0.5095(12) | 0.382(2) | 0.245(3) | 0.143(14) |
| H2AA | 0.535312 | 0.393494 | 0.293196 | 0.215 |
| H2AB | 0.523623 | 0.400555 | 0.209188 | 0.215 |
| H2AC | 0.501962 | 0.320358 | 0.240153 | 0.215 |
Table S15: Bond lengths and angles for catalyst 4c.

| Atom–Atom | Length [Å] | Angle [°] |
|-----------|------------|-----------|
| H38–C39  | 0.194161   | 0.098426  |
| C39–C59  | 0.24635(6)  | 0.16525(11) |
| H59–C40  | 0.270886    | 0.119827  |
| C40–C41  | 0.250777(10)| 0.2466(10) |
| C41–N1   | 0.30533(6)  | 0.26033(10) |

$U_{ii}$ is defined as 1/3 of the trace of the orthogonalized $U_{ij}$ tensor.

### Bond Angles

- **C10–C19–C20**: 113.11(4)°
- **C12–C11–C10**: 114.75(4)°
- **C16–C17–C18**: 118.97(4)°
- **C20–C19–C18**: 122.4(2)°
- **C21–C22–C23**: 122.2(2)°
- **C24–C25–C26**: 122.2(2)°
- **C27–C28–C29**: 122.2(2)°
- **C30–C31–C32**: 122.2(2)°

### Bond Lengths

- **C10–C19**: 1.403(18) Å
- **C12–C11**: 1.384(2) Å
- **C16–C17**: 1.496(2) Å
- **C20–C19**: 1.406(2) Å
- **C24–C25**: 1.401(2) Å
- **C27–C26**: 1.403(2) Å
- **C30–C31**: 1.406(2) Å
- **C33–C34**: 1.406(2) Å
- **C36–C37**: 1.401(2) Å
- **C39–C40**: 1.403(2) Å
- **C42–C43**: 1.406(2) Å

### Additional Information

Atom–Atom–Atom Angles:

- **C3–Rh1–C5**: 64.72(6)°
- **C3–Rh1–C4**: 36.73(7)°
- **C5–Rh1–C4**: 36.17(7)°
- **C3–Rh1–C1**: 64.04(6)°
- **C5–Rh1–C1**: 36.81(6)°
- **C4–Rh1–C1**: 63.8(3)°
- **C5–Rh1–C2**: 36.76(6)°
- **C5–Rh1–C2**: 63.73(6)°
- **C4–Rh1–C2**: 63.97(6)°
- **C1–Rh1–C2**: 37.0(6)°
- **C3–Rh1–P1**: 113.11(4)°
- **C5–Rh1–P1**: 114.75(4)°
- **C4–Rh1–P1**: 96.70(4)°
- **C1–Rh1–P1**: 153.14(4)°
- **C2–Rh1–P1**: 151.44(4)°
- **C3–Rh1–C2**: 96.30(5)°
- **C5–Rh1–C2**: 154.52(4)°
- **C4–Rh1–C2**: 132.34(5)°
- **C1–Rh1–C2**: 118.97(4)°
- **C2–Rh1–C2**: 90.80(4)°
- **P1–Rh1–C2**: 87.714(13)°
- **C3–Rh1–C1**: 154.62(4)°
Table S16: Hydrogen bonds for catalyst 4c.

|         | D-H-A  [Å] | d(D-H) [Å] | d(H-A) [Å] | d(D-A) [Å] | <DHA [°] |
|---------|------------|------------|------------|------------|----------|
| N3-H3N-C1 | 0.807(14)  | 2.338(14)  | 3.1248(13) | 165.2(18)  |
| N1-H1N-C1  | 0.865(14)  | 2.874(16)  | 3.6368(15) | 148.0(17)  |
| N2-H2N-O1  | 0.854(14)  | 2.036(15)  | 2.8780(18) | 169(2)     |

Symmetry transformations used to generate equivalent atoms: #2: 1-X, 1-Y, 1-Z.
Catalyst 4d

The compound was crystallized from methanol/cyclohexane by solvent layering. The data for BreitLB_1_38B were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength Mo/Cu three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoKα radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABS was applied.

SUPPORTING INFORMATION

| Atom | x | y | z | Ueq |
|------|---|---|---|-----|
| F1   | 0.77981(18) | 0.72242(5) | 0.27197(17) | 0.0264(4) |
| N1   | 0.7509(2) | 0.58653(7) | 0.3440(2) | 0.0212(5) |
| H1   | 0.694165 | 0.591437 | 0.286891 | 0.025 |
| Rh1  | 0.49135(2) | 0.42824(2) | 0.47431(2) | 0.0281(4) |
| Cl1  | 0.66246(8) | 0.39580(2) | 0.56126(6) | 0.01640(13) |
| C2   | 0.45265(6) | 0.45305(2) | 0.67036(6) | 0.01816(13) |
| F2   | 0.7291(2) | 0.74716(7) | 0.4407(2) | 0.0402(6) |
| N2   | 0.7360(2) | 0.52647(7) | 0.2727(2) | 0.0175(5) |
| H2A  | 0.678616 | 0.534449 | 0.22050(2) | 0.021 |
| P1   | 0.39353(6) | 0.37415(2) | 0.50757(6) | 0.01287(13) |
| F4   | 1.0458(2) | 0.61629(9) | 0.7271(2) | 0.0650(9) |
| F11  | -0.07432(17) | 0.45623(6) | 0.6178(2) | 0.0340(5) |
| F12  | 0.10143(18) | 0.47789(6) | 0.6365(2) | 0.0380(5) |
| F13  | 0.6663(2) | 0.27631(9) | 0.1580(2) | 0.0607(8) |
| N3   | 0.4514(2) | 0.36805(8) | 0.7501(2) | 0.0205(5) |
| H3A  | 0.441758 | 0.392354 | 0.743685 | 0.025 |
| F5   | 0.8798(2) | 0.61728(9) | 0.7971(2) | 0.0628(9) |
| C18  | 0.7940(3) | 0.61608(8) | 0.4176(3) | 0.0186(6) |
| C19  | 0.7816(3) | 0.65238(6) | 0.3706(3) | 0.0185(6) |
| H19  | 0.740572 | 0.656204 | 0.290869 | 0.022 |
| C25  | 0.8223(3) | 0.68261(9) | 0.4402(3) | 0.0192(6) |
| C24  | 0.9475(3) | 0.63532(10) | 0.7273(3) | 0.0276(7) |
| C22  | 0.8103(3) | 0.72158(9) | 0.3906(3) | 0.0247(7) |
| C21  | 0.8475(3) | 0.61114(9) | 0.5393(3) | 0.0210(6) |
| H22  | 0.856226 | 0.586805 | 0.568949 | 0.025 |
| H23  | 0.8879(3) | 0.64198(9) | 0.6028(3) | 0.0209(6) |
| H21  | 0.906471 | 0.698779 | 0.5568(3) | 0.0216(6) |
| H2   | 0.906471 | 0.698779 | 0.603473 | 0.026 |

Table S17: Crystal data and structure refinement for catalyst 4d.

| CCDC number | 1999742 |
|-------------|---------|
| Empirical formula | Cu2Rh8Cl14F19N10O10 |
| Formula weight | 1173.51 |
| Temperature [K] | 100(2) |
| Crystal system | monoclinic |
| Space group (number) | Cc (9) |
| a [Å] | 11.5072(8) |
| b [Å] | 35.835(3) |
| c [Å] | 11.1242(9) |
| α [Å] | 90 |
| β [Å] | 95.979(3) |
| γ [Å] | 90 |
| Volume [Å³] | 4562.2(6) |
| Z | 4 |
| ρcalc [g/cm³] | 1.709 |
| μ (mm⁻¹) | 0.643 |
| F(000) | 2344 |
| Crystal size [mm³] | 0.110×0.070×0.030 |
| Crystal colour | red |
| Crystal shape | block |
| Radiation | MoKα (λ=0.71073 Å) |
| 2Θ range [°] | 3.74 to 61.05 (0.70 Å) |
| Index ranges | -16 ≤ h ≤ 16 |
| -15 ≤ l ≤ 15 |
| Reflections collected | 107960 |
| Independent reflections | 13409 |
| Completeness to θ = 25.24° | 100.0 % |
| Data / Restraints / Parameters | 13409/228/668 |
| Goodness-of-fit on F² | 1.028 |
| Final R indexes | R = 0.0281 |
| wR = 0.0546 |
| Final R indexes | R = 0.0340 |
| [all data] | wR = 0.0567 |
| Largest peak/hole [eÅ³] | 0.48/0.63 |
| Flack X parameter | -0.011(5) |

Table S18: Atomic coordinates and Ueq [Å²] for catalyst 4d.

1999742 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.¹⁹
\[ U_{ij}^{\text{tensor}} \] is defined as 1/3 of the trace of the orthogonalized \( U_{ij} \) tensor.
### Table S19: Bond lengths and angles for catalyst 4d.

| Atom–Atom | Length [Å] |
|-----------|------------|
| F1–C24    | 1.332(4)   |
| N1–C8     | 1.381(4)   |
| N1–C18    | 1.398(4)   |
| N1–H1     | 0.8800     |
| Rh1–C10   | 2.157(3)   |
| Rh1–C12   | 2.184(3)   |
| Rh1–C9    | 2.195(3)   |
| Rh1–C11   | 2.196(3)   |
| Rh1–C13   | 2.213(3)   |
| Rh1–P1    | 2.3210(7)  |
| Rh1–C1    | 2.4189(7)  |
| Rh1–C2    | 2.4259(7)  |
| F2–C24    | 1.344(4)   |
| N2–C8     | 1.351(4)   |
| N2–C7     | 1.454(4)   |
| N2–H2A    | 0.8800     |
| P1–C34    | 1.817(3)   |
| P1–C26    | 1.823(3)   |
| P1–C1     | 1.843(3)   |
| F4–C25    | 1.321(4)   |
| F11–C33   | 1.335(4)   |
| F12–C33   | 1.333(4)   |
| F13–C40   | 1.326(4)   |
| N3–C1     | 1.365(4)   |
| N3–C5     | 1.400(4)   |
| N3–H3A    | 0.8800     |
| F5–C25    | 1.324(4)   |
| C18–C23   | 1.396(4)   |
| C18–C19   | 1.404(4)   |
| C19–C20   | 1.385(4)   |
| C19–H19   | 0.9500     |
| C20–C21   | 1.392(4)   |
| C20–C24   | 1.502(4)   |
| C25–F6    | 1.343(4)   |
| C25–C22   | 1.500(4)   |
| C24–F3    | 1.338(4)   |
| C23–C22   | 1.388(4)   |
| C23–H23   | 0.9500     |
| C22–C21   | 1.388(4)   |
| C21–H21   | 0.9500     |
| C26–C31   | 1.388(4)   |
| C26–C27   | 1.404(4)   |
| C27–C28   | 1.389(4)   |
| C27–H27   | 0.9500     |
| C28–C29   | 1.390(4)   |
| C28–C32   | 1.504(4)   |
| C29–C30   | 1.389(4)   |
| C29–H29   | 0.9500     |
| C35–C36   | 1.383(4)   |
| C35–C34   | 1.406(4)   |
| C35–H35   | 0.9500     |
| C34–C39   | 1.390(4)   |
| C33–F10   | 1.338(4)   |
| C33–C30   | 1.503(4)   |
| C32–F6    | 1.329(4)   |
| C32–F7    | 1.339(4)   |
| C32–F9    | 1.340(4)   |
| C31–C30   | 1.390(4)   |
| C31–H31   | 0.9500     |
| C37–C38   | 1.383(5)   |
| C37–C36   | 1.390(5)   |
| C37–H37   | 0.9500     |
| C38–C39   | 1.395(4)   |
| C38–C41B  | 1.496(8)   |
| C38–C41A  | 1.540(17)  |
| C39–H39   | 0.9500     |
| C40–F14   | 1.302(5)   |
| C40–F15   | 1.304(4)   |
| C40–C36   | 1.498(5)   |
| C41A–F3A  | 1.332(17)  |
| C41A–F1A  | 1.332(16)  |
| C41A–F2A  | 1.344(17)  |
| C41B–F6A  | 1.327(10)  |
| C41B–F5A  | 1.327(8)   |
| C41B–F4A  | 1.332(8)   |
| N4–C42    | 1.420(6)   |
| C42–H42A  | 0.9800     |
| C42–H42B  | 0.9800     |

| Atom–Atom–Atom | Angle [°] |
|----------------|----------|
| C8–N1–C18     | 124.8(3) |
| C8–N1–H1      | 117.6    |
| C10–Rh1–C12   | 64.64(11)|
| C10–Rh1–C9    | 39.09(10)|
| C12–Rh1–C9    | 63.99(10)|
| C12–Rh1–C11   | 38.39(11)|
| C12–Rh1–C11   | 37.90(11)|
| C9–Rh1–C11    | 63.86(10)|
| C10–Rh1–C13   | 64.45(11)|
| C12–Rh1–C13   | 36.62(10)|
| C9–Rh1–C13    | 37.52(10)|
| C11–Rh1–C13   | 63.63(11)|
| C10–Rh1–P1    | 111.14(8)|
| C12–Rh1–P1    | 119.39(9)|
| C9–Rh1–P1     | 148.58(7)|
| C11–Rh1–P1    | 99.00(8) |
| C13–Rh1–P1    | 158.00(8)|
| C10–Rh1–C11   | 95.85(8) |
| C12–Rh1–C11   | 154.51(8)|
| C9–Rh1–C11    | 91.07(7) |
| C11–Rh1–C11   | 136.53(9)|
| C13–Rh1–C11   | 117.35(8)|
| P1–Rh1–G1     | 84.44(2) |
| C10–Rh1–C2    | 155.66(8)|
| C12–Rh1–C2    | 96.26(8) |
| C9–Rh1–C2     | 120.21(7)|
| C8–N2–C7      | 131.07(9)|
| C11–Rh1–C2    | 91.22(8) |
| C13–Rh1–C2    | 91.06(3) |
| C11–Rh1–C2    | 91.88(2) |
| C8–N2–H2A     | 119.52    |
| C7–N2–H2A     | 120.3     |
| C34–P1–C26    | 106.42(13)|
| C34–P1–C1    | 103.18(13)|
| C26–P1–C1    | 98.84(13)|
| C34–P1–Rh1   | 111.89(9)|
| C26–P1–Rh1   | 117.23(10)|
| C1–P1–Rh1    | 117.51(10)|
| C1–N3–C5     | 125.03(3)|
| C1–N3–H3A    | 117.5     |
| Bond                  | Angle (°) |
|----------------------|-----------|
| C17–C13–Rh1          | 126.2(2)  |
| C10–C14–H14A         | 109.5     |
| C10–C14–H14B         | 109.5     |
| H14A–C14–H14B        | 109.5     |
| C10–C14–H14C         | 109.5     |
| H14A–C14–H14C        | 109.5     |
| H14B–C14–H14C        | 109.5     |
| C11–C15–H15A         | 109.5     |
| C11–C15–H15B         | 109.5     |
| H15A–C15–H15B        | 109.5     |
| C11–C15–H15C         | 109.5     |
| H15A–C15–H15C        | 109.5     |
| H15B–C15–H15C        | 109.5     |
| C12–C16–H16A         | 109.5     |
| C12–C16–H16B         | 109.5     |
| H16A–C16–H16B        | 109.5     |
| C12–C16–H16C         | 109.5     |
| H16A–C16–H16C        | 109.5     |
| H16B–C16–H16C        | 109.5     |
| C13–C17–H17A         | 109.5     |
| C13–C17–H17B         | 109.5     |
| H17A–C17–H17B        | 109.5     |
| C13–C17–H17C         | 109.5     |
| H17A–C17–H17C        | 109.5     |
| H17B–C17–H17C        | 109.5     |
The compound was crystallized from MeOH/Et2O (5:1) at room temperature. The data for mo_Breit_LB_1_39rc_0m-finalcif.cif were collected from a shock-cooled single crystal at 100(2) K on a Bruker D8 VENTURE dual wavelength MoKα three-circle diffractometer with a microfocus sealed X-ray tube using mirror optics as monochromator and a Bruker PHOTON III detector. The diffractometer was equipped with an Oxford Cryostream 800 low temperature device and used MoKα radiation (λ = 0.71073 Å). All data were integrated with SAINT and a multi-scan absorption correction using SADABs 2016/2 was applied.\[14][15] The structure were solved by direct methods using SHELXTL XT-CRYSTAL STRUCTURE SOLUTION VERSION 2014/5 and refined by full-matrix least-squares methods against \(F^2\) by SHELXL-2018/3.\[16][17] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their \(U_{iso}\) values constrained to 1.5 times the \(U_{iso}\) of their pivot atoms for terminal sp\(^3\) carbon atoms and 1.2 times for all other carbon atoms. Crystallographic data (including structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.\[18] CCDC 1993238 contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report and the CIF file were generated using FinalCif.\[19]

**Table S21: Atomic coordinates and \(U_{iso} [\text{Å}^2]\) for catalyst 4e.**

| Atom | \(x\) | \(y\) | \(z\) | \(U_{iso}\) |
|------|-------|-------|-------|-----------|
| Rh1  | 0.39984(2) | 0.25001(2) | 0.30444(2) | 0.01458(4) |
| F1   | 1.09174(18) | 0.63521(14) | 1.04369(9) | 0.0570(4) |
| Cl1  | 0.36667(4) | 0.25022(3) | 0.44644(3) | 0.01966(8) |
| N1   | 0.26358(15) | 0.04235(12) | 0.10068(9) | 0.0215(3) |
| C1   | 0.02112(19) | -0.00159(15) | 0.01451(11) | 0.0234(3) |
| P1   | 0.30706(4) | 0.05188(3) | 0.27551(3) | 0.01560(8) |
| O1   | 0.27100(16) | 0.05522(12) | -0.03654(9) | 0.0341(3) |
| N2   | 0.85029(15) | 0.60120(12) | 0.57047(9) | 0.0202(3) |
| H2A  | 0.843690 | 0.662261 | 0.095440 | 0.024 |
| F2   | 1.2944(2) | 0.7363(18) | 1.04283(12) | 0.0884(7) |
| Cl2  | 0.16100(4) | 0.24239(3) | 0.23118(3) | 0.01942(8) |
| C2   | 0.07682(19) | -0.09540(15) | -0.01862(12) | 0.0254(4) |
| H2   | 0.034956 | -0.124106 | -0.030429 | 0.030 |
| N3   | 0.97119(16) | 0.58360(13) | 0.71073(10) | 0.0240(3) |
| H3A  | 0.949340 | 0.637739 | 0.727432 | 0.029 |
| F3   | 1.2654(3) | 0.5793(2) | 1.09026(10) | 0.1143(10) |
| C3   | 0.01735(19) | -0.14464(15) | 0.04183(12) | 0.0263(4) |
| H3   | -0.067745 | -0.207777 | 0.021692 | 0.032 |
| F5   | 1.27123(12) | 0.33850(10) | 0.73674(8) | 0.0339(3) |
| C5   | 0.20447(17) | -0.08333(14) | 0.15821(11) | 0.0183(3) |
| F4   | 1.20090(14) | 0.25501(10) | 0.83625(11) | 0.0489(4) |
| C4   | 0.06181(18) | -0.10200(14) | 0.13245(12) | 0.0226(3) |
| H4   | 0.043109 | -0.135878 | 0.174951 | 0.027 |
| F6   | 1.49377(12) | 0.38414(10) | 0.87322(8) | 0.0363(3) |
| C6   | 0.18854(17) | -0.02239(13) | 0.33340(11) | 0.0182(3) |
| O008 | 0.94665(13) | 0.46320(10) | 0.58845(8) | 0.0253(5) |
| C8   | 0.09403(19) | -0.18508(15) | 0.39675(12) | 0.0249(4) |
| H8   | 0.09414(15) | -0.256050 | 0.415011 | 0.030 |
| C7   | 0.18788(18) | -0.12744(14) | 0.35779(11) | 0.0200(3) |
| H7   | 0.251909 | -0.159326 | 0.346251 | 0.026 |
SUPPORTING INFORMATION

Table S22: Bond lengths and angles for catalyst 4e.

| Atom–Atom | Length [Å] | O1–C18 | 1.436(2) |
|-----------|------------|--------|-----------|
| Rh1–C22   | 2.160(16)  | N2–C30 | 1.362(2)  |
| Rh1–C20   | 2.1719(16) | N2–C29 | 1.457(2)  |
| Rh1–C23   | 2.1797(16) | N2–H2A | 0.8850    |
| Rh1–C21   | 2.1999(16) | N2–H2A | 0.8850    |
| Rh1–C19   | 2.2105(16) | F2–C37 | 1.337(4)  |
| Rh1–P1    | 2.3432(6)  | C2–C3  | 1.380(3)  |
| Rh1–C11   | 2.3966(5)  | C2–H2  | 0.9500    |
| Rh1–C2    | 2.4400(5)  | N3–C30 | 1.387(2)  |
| F1–C17    | 1.344(4)   | N3–C31 | 1.394(2)  |
| N1–C1     | 1.336(2)   | N3–H3A | 0.8800    |
| N1–C5     | 1.344(2)   | F5–C38 | 1.339(2)  |
| C1–O1     | 1.351(2)   | C5–C4  | 1.388(2)  |
| C1–C2     | 1.403(3)   | F4–C38 | 1.335(2)  |
| P1–C12    | 1.8249(16) | C4–H4  | 0.9500    |
| P1–C6     | 1.8362(17) | F6–C38 | 1.346(2)  |
| P1–C5     | 1.8409(17) | C6–C11 | 1.404(2)  |

Table S50: 

\[
U_{ii} = (1/3) \text{trace of the orthogonalized } U_i \text{ tensor.}
\]
### SUPPORTING INFORMATION

| Atom–Atom–Atom | Angle [°] |
|----------------|----------|
| C22–Rh1–C20    | 64.66(6) |
| C22–Rh1–C23    | 39.14(6) |
| C20–Rh1–C23    | 64.46(6) |
| C22–Rh1–C21    | 38.22(6) |
| C20–Rh1–C21    | 38.48(6) |
| C23–Rh1–C21    | 64.40(6) |
| C22–Rh1–C19    | 64.11(6) |
| C20–Rh1–C19    | 38.73(6) |
| C23–Rh1–C19    | 37.53(6) |
| C21–Rh1–C19    | 64.00(6) |
| C22–Rh1–P1     | 120.61(5) |
| C20–Rh1–P1     | 110.96(4) |
| C23–Rh1–P1     | 159.74(4) |
| C21–Rh1–P1     | 99.28(4)  |
| C19–Rh1–P1     | 147.64(4) |
| C22–Rh1–C1     | 149.02(5) |
| C20–Rh1–C1     | 104.77(5) |
| C23–Rh1–C1     | 104.77(5) |
| C22–Rh1–C2     | 119.78(5) |
| C20–Rh1–C2     | 119.78(5) |
| C23–Rh1–C2     | 119.78(5) |
| C21–Rh1–C2     | 119.78(5) |
| C20–Rh1–C3     | 119.78(5) |
| C23–Rh1–C3     | 119.78(5) |
| C21–Rh1–C3     | 119.78(5) |
| C20–Rh1–C4     | 119.78(5) |
| C23–Rh1–C4     | 119.78(5) |
| C21–Rh1–C4     | 119.78(5) |
| C20–Rh1–C5     | 119.78(5) |
| C23–Rh1–C5     | 119.78(5) |
| C21–Rh1–C5     | 119.78(5) |
| C20–Rh1–C6     | 119.78(5) |
| C23–Rh1–C6     | 119.78(5) |
| C21–Rh1–C6     | 119.78(5) |
| C20–Rh1–C7     | 119.78(5) |
| C23–Rh1–C7     | 119.78(5) |
| C21–Rh1–C7     | 119.78(5) |
| C20–Rh1–C8     | 119.78(5) |
| C23–Rh1–C8     | 119.78(5) |
| C21–Rh1–C8     | 119.78(5) |
| C20–Rh1–C9     | 119.78(5) |
| C23–Rh1–C9     | 119.78(5) |
| C21–Rh1–C9     | 119.78(5) |
| C20–Rh1–C10    | 119.78(5) |
| C23–Rh1–C10    | 119.78(5) |
| C21–Rh1–C10    | 119.78(5) |
| C20–Rh1–C11    | 119.78(5) |
| C23–Rh1–C11    | 119.78(5) |
| C21–Rh1–C11    | 119.78(5) |
| C20–Rh1–C12    | 119.78(5) |
| C23–Rh1–C12    | 119.78(5) |
| C21–Rh1–C12    | 119.78(5) |
| C20–Rh1–C13    | 119.78(5) |
| C23–Rh1–C13    | 119.78(5) |
| C21–Rh1–C13    | 119.78(5) |
| C20–Rh1–C14    | 119.78(5) |
| C23–Rh1–C14    | 119.78(5) |
| C21–Rh1–C14    | 119.78(5) |
| C20–Rh1–C15    | 119.78(5) |
| C23–Rh1–C15    | 119.78(5) |
| C21–Rh1–C15    | 119.78(5) |
| C20–Rh1–C16    | 119.78(5) |
| C23–Rh1–C16    | 119.78(5) |
| C21–Rh1–C16    | 119.78(5) |
| C20–Rh1–C17    | 119.78(5) |
| C23–Rh1–C17    | 119.78(5) |
| C21–Rh1–C17    | 119.78(5) |
| C20–Rh1–C18    | 119.78(5) |
| C23–Rh1–C18    | 119.78(5) |
| C21–Rh1–C18    | 119.78(5) |
| C20–Rh1–C19    | 119.78(5) |
| C23–Rh1–C19    | 119.78(5) |
| C21–Rh1–C19    | 119.78(5) |
| C20–Rh1–C20    | 119.78(5) |
| C23–Rh1–C20    | 119.78(5) |
| C21–Rh1–C20    | 119.78(5) |
| C20–Rh1–C21    | 119.78(5) |
| C23–Rh1–C21    | 119.78(5) |
| C21–Rh1–C21    | 119.78(5) |
| C20–Rh1–C22    | 119.78(5) |
| C23–Rh1–C22    | 119.78(5) |
| C21–Rh1–C22    | 119.78(5) |
| C20–Rh1–C23    | 119.78(5) |
| C23–Rh1–C23    | 119.78(5) |
| C21–Rh1–C23    | 119.78(5) |
| C20–Rh1–C24    | 119.78(5) |
| C23–Rh1–C24    | 119.78(5) |
| C21–Rh1–C24    | 119.78(5) |
| C20–Rh1–C25    | 119.78(5) |
| C23–Rh1–C25    | 119.78(5) |
| C21–Rh1–C25    | 119.78(5) |
| C20–Rh1–C26    | 119.78(5) |
| C23–Rh1–C26    | 119.78(5) |
| C21–Rh1–C26    | 119.78(5) |
| C20–Rh1–C27    | 119.78(5) |
| C23–Rh1–C27    | 119.78(5) |
| C21–Rh1–C27    | 119.78(5) |
| C20–Rh1–C28    | 119.78(5) |
| C23–Rh1–C28    | 119.78(5) |
| C21–Rh1–C28    | 119.78(5) |
| C20–Rh1–C29    | 119.78(5) |
| C23–Rh1–C29    | 119.78(5) |
| C21–Rh1–C29    | 119.78(5) |
| C20–Rh1–C30    | 119.78(5) |
| C23–Rh1–C30    | 119.78(5) |
| C21–Rh1–C30    | 119.78(5) |
### Table S23: Torsion angles for catalyst 4e.

| Atom–Atom–Atom–Atom | Torsion Angle [°] |
|---------------------|-------------------|
| C5–N1–C1–C2        | -179.04(14)       |
| N1–C1–O1–C18       | 173.60(16)        |
| C2–C1–O1–C18       | -6.8(3)           |
| N1–C1–C2–C3        | -0.4(3)           |
| C1–C1–C2–C3        | -179.95(16)       |
| C1–C2–C3–C4        | -0.9(3)           |
| C1–N1–C5–C4        | -1.0(2)           |
| C1–N1–C5–P1        | 175.14(12)        |
| C12–P1–C5–N1       | -81.73(13)        |
| C6–P1–C5–N1        | 172.99(12)        |
| Rh1–P1–C5–N1       | 43.07(13)         |
| C12–P1–C5–C4       | 94.50(15)         |
| C6–P1–C5–C4        | -10.76(15)        |
| Rh1–P1–C5–C4       | -140.71(12)       |
| N1–C5–C4–C3        | -0.2(2)           |
| P1–C5–C4–C3        | -176.10(13)       |
| C2–C3–C4–C5        | 1.2(3)            |
| C12–P1–C6–C11      | 164.17(13)        |
| C5–P1–C6–C11       | -89.52(14)        |
| Rh1–P1–C6–C11      | 37.20(15)         |
| C12–P1–C6–C7       | -18.95(15)        |
| C5–P1–C6–C7        | 87.36(14)         |
| Rh1–P1–C6–C7       | -145.92(15)       |
| C9–C8–C7–C6        | 0.0(3)            |
| C11–C6–C7–C8       | -0.7(2)           |
| P1–C6–C7–C8        | -177.63(13)       |
| C7–C8–C9–C10       | 0.9(3)            |
| C7–C6–C11–C10      | 0.6(2)            |
| P1–C6–C11–C10      | 177.51(13)        |
| C8–C11–C10–C9      | 0.3(3)            |
| C8–C8–C10–C11      | -1.1(3)           |
| C15–C14–C13–C12    | 0.2(3)            |
| C14–C13–C12–C17    | -1.3(2)           |
| C14–C13–C12–P1     | 173.58(13)        |
| C6–P1–C12–C17      | 104.62(15)        |
| C5–P1–C12–C17      | -1.27(16)         |
| Rh1–P1–C12–C17     | -125.61(13)       |
| C6–P1–C12–C13      | -70.08(14)        |
| C5–P1–C12–C13      | -175.98(13)       |
| Rh1–P1–C12–C13     | 59.69(14)         |
| C13–C14–C15–C16    | 1.0(3)            |
| C13–C12–C17–C16    | 1.2(3)            |
| P1–C12–C17–C16     | -173.41(14)       |
| C14–C15–C16–C17    | -1.1(3)           |
| C12–C17–C16–C15    | 0.0(3)            |
| C23–C19–C20–C21    | 3.33(18)          |
| C28–C19–C20–C21    | -176.93(15)       |
| Rh1–C19–C20–C21    | 63.40(11)         |
| C23–C19–C20–C24    | 173.29(16)        |
| C28–C19–C20–C24    | -7.0(3)           |
| Rh1–C19–C20–Rh1    | -126.64(17)       |
| C23–C19–C20–Rh1    | -60.07(11)        |
| C28–C19–C20–Rh1    | 119.67(15)        |
| C19–C20–C21–C22    | -4.08(18)         |
| C24–C20–C21–C22    | -173.82(16)       |
| Rh1–C20–C21–C22    | 59.49(11)         |
| C19–C20–C21–C22    | 169.23(15)        |
| Rh1–C20–C21–C25    | -0.5(3)           |
| C19–C20–C21–C25    | -127.19(17)       |

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| Bond | Distance (Å) | Angle (°) |
|------|--------------|-----------|
| C24-C20-C21-Rh1 | 126.69(17) | |
| C20-C21-C22-C23 | 3.30(18) | |
| C25-C21-C22-C23 | -169.88(16) | |
| Rh1-C21-C22-C23 | 62.79(11) | |
| C20-C21-C22-C26 | 178.58(16) | |
| C25-C21-C22-C26 | 5.4(3) | |
| Rh1-C21-C22-C26 | -121.94(17) | |
| C20-C21-C22-Rh1 | -59.49(11) | |
| C25-C21-C22-Rh1 | 127.33(17) | |
| C20-C19-C23-C22 | -1.29(18) | |
| C28-C19-C23-C22 | 178.99(15) | |
| Rh1-C19-C23-C22 | -60.40(11) | |
| C20-C19-C23-C27 | 178.49(15) | |
| C28-C19-C23-C27 | -1.2(3) | |
| Rh1-C19-C23-C27 | 119.38(17) | |
| C20-C19-C23-Rh1 | 59.11(11) | |
| C28-C19-C23-Rh1 | -120.62(17) | |
| C21-C22-C23-C19 | -1.25(18) | |
| C26-C22-C23-C19 | -176.52(16) | |
| Rh1-C22-C23-C19 | 61.90(11) | |
| C21-C22-C23-C27 | 178.98(15) | |
| C26-C22-C23-C27 | 3.7(3) | |
| Rh1-C22-C23-C27 | -117.87(16) | |
| C21-C22-C23-Rh1 | -63.15(11) | |
| C26-C22-C23-Rh1 | 121.57(17) | |
| C23-C19-C28-C29 | -95.70(19) | |
| C20-C19-C28-C29 | 84.62(19) | |
| Rh1-C19-C28-C29 | 171.94(11) | |
| C30-N2-C29-C28 | 83.19(18) | |
| C19-C28-C29-N2 | -165.23(13) | |
| C29-N2-C30-O008 | 6.7(3) | |
| C29-N2-C30-N3 | -174.63(15) | |
| C31-N3-C30-O008 | 4.2(3) | |
| C31-N3-C30-N2 | -174.48(17) | |
| C30-N3-C31-C32 | -176.16(18) | |
| C30-N3-C31-C36 | 5.2(3) | |
| N3-C31-C32-C33 | -177.80(19) | |
| C36-C31-C32-C33 | 1.0(3) | |
| C31-C32-C33-C34 | -0.7(3) | |
| C31-C32-C33-C37 | 176.8(2) | |
| C32-C33-C34-C35 | 0.0(3) | |
| C37-C33-C34-C35 | -177.6(2) | |
| C33-C34-C35-C36 | 0.6(3) | |
| C33-C34-C35-C38 | -177.54(18) | |
| C34-C35-C36-C31 | -0.4(3) | |
| C38-C35-C36-C31 | 177.75(16) | |
| N3-C31-C36-C35 | 178.25(17) | |
| C32-C31-C36-C35 | -0.4(3) | |
| C32-C33-C37-F3 | 165.7(3) | |
| C34-C33-C37-F3 | -16.7(4) | |
| C32-C33-C37-F2 | -73.6(3) | |
| C34-C33-C37-F2 | 104.0(3) | |
| C32-C33-C37-F1 | 44.8(3) | |
| C34-C33-C37-F1 | -137.6(2) | |
| C36-C35-C38-F4 | -100.1(2) | |
| C34-C35-C38-F4 | 78.1(2) | |
| C36-C35-C38-F5 | 20.6(2) | |
| C34-C35-C38-F5 | -161.24(17) | |
| C36-C35-C38-F6 | 140.68(17) | |
| C34-C35-C38-F6 | -41.1(2) | |
8 DFT Calculation

Geometry optimization was performed using the BP86-functional\textsuperscript{[20,21]} in combination with the def2SVP\textsuperscript{[22]} basis set in Gaussian 09, Revision B.01\textsuperscript{[23]}. Shown is ortho-metalated benzoic acid coordinated by a simplified version of catalyst 4b (trifluormethyl-groups were omitted from N-phenyl residue).

|   |   |   |
|---|---|---|
| Rh | -0.68490 | -0.72061 | -0.78431 |
| N  | 2.82571  | -1.59307 | 0.77603  |
| H  | 2.25609  | -0.74799 | 0.58203  |
| O  | 4.90820  | -2.42556 | 1.31846  |
| C  | 0.27089  | -2.89662 | -0.62894 |
| P  | -2.15680 | 0.31366  | 0.70108  |
| C  | 0.50092  | -2.24182 | -1.92737 |
| N  | 4.69305  | -0.27027 | 0.45007  |
| H  | 3.99407  | 0.40563  | 0.08824  |
| O  | 0.85650  | 4.24164  | 1.42603  |
| C  | -0.77685 | -2.05914 | -2.57099 |
| N  | -0.72266 | 2.60342  | 1.04000  |
| H  | 0.05470  | 1.92068  | 0.97301  |
| C  | -1.13688 | -2.98866 | -0.43492 |
| C  | -1.80738 | -2.42739 | -1.62096 |
| C  | 1.84761  | 2.01428  | -2.54968 |
| H  | 2.20224  | 2.93371  | -3.06732 |
| C  | 2.60077  | -1.75176 | -1.78121 |
| C  | 1.81871  | -1.20017 | -3.30013 |
| C  | -0.98530 | -1.68149 | -4.00680 |
| C  | -0.90863 | -2.59271 | -4.64906 |
| C  | -0.22648 | -0.95665 | -4.36263 |
| C  | -1.98320 | -1.23750 | -4.18332 |
| C  | -3.27175 | -2.55870 | -1.92490 |
| H  | -3.61155 | -1.79356 | -2.64999 |

Table S24: Coordinates resulting from DFT calculations.
|   |   |   |   |
|---|---|---|---|
| C | -0.67843 | 0.92440 | -2.00559 |
| C | -1.63654 | 1.34064 | -2.95029 |
| C | 0.55032  | 1.63064 | -1.94725 |
| C | -1.36829 | 2.42778 | -3.80861 |
| H | -2.59924  | 0.81239 | -3.04523 |
| C | 0.83066  | 2.70186 | -2.81806 |
| C | -0.13655  | 3.10778 | -3.74963 |
| H | -2.13368  | 2.74259 | -4.53759 |
| H | 1.80865  | 3.20303 | -2.73558 |
| H | 0.06310  | 3.95177 | -4.42842 |
| C | 1.51626  | 1.18769 | -0.89895 |
| O | 0.95748  | 0.37667 | 0.00802 |
| O | 2.70149  | 1.52582 | -0.83254 |
| H | 9.27047  | -0.68142 | 1.13667 |
| H | 7.72313  | 3.00430 | -0.56102 |
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10 NMR Spectra

Ethyl 2-(1-oxo-1,3-dihyronaphtho[1,2-c]furan-3-yl)acetate (2a)

$$\text{C}_{16}\text{H}_{14}\text{O}_4$$
270.28 g/mol
$^1\text{H}$ NMR (400 MHz, CDCl$_3$)

$^{13}\text{C}$ NMR (101 MHz, CDCl$_3$)
Methyl 2-(1-oxo-1,3-dihydronaphtho[1,2-c]furan-3-yl)acetate (2b)

C_{15}H_{12}O_{4}
256.26 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

C_{12}H_{12}O_{4}
256.26 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)
Benzyl 2-(1-oxo-1,3-dihyronaphtho[1,2-c]furan-3-yl)acetate (2c)

C₂₁H₁₉O₄
332.36 g/mol

¹H NMR (500 MHz, CDCl₃)

C₂₁H₁₉O₄
332.36 g/mol

¹³C NMR (126 MHz, CDCl₃)
tert-Butyl 2-(1-oxo-1,3-dihydropaphtho[1,2-c]furan-3-yl)acetate (2d)

C_{19}H_{18}O_{4}
298.34 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

C_{19}H_{18}O_{4}
298.34 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)
2-(1-Oxo-1,3-dihydropyrido[1,2-c]furano-3-yl)acetonitrile (2e)

C_{16}H_{12}NO_{2}
223.23 g/mol

^1H NMR (500 MHz, CDCl₃)

C_{16}H_{12}NO_{2}
223.23 g/mol

^13C NMR (126 MHz, CDCl₃)
Ethyl 2-(3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2f mono)

C_{12}H_{12}O_4
220.22 g/mol

$^1$H NMR (400 MHz, CDCl$_3$)

C_{12}H_{12}O_4
220.22 g/mol

$^{13}$C NMR (101 MHz, CDCl$_3$)
Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2f bis)
Supporting Information

Ethyl 2-(4-fluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2g)

$\text{C}_9\text{H}_9\text{FO}_4$
238.21 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

$\text{C}_{12}\text{H}_{11}\text{FO}_4$
238.21 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)
Ethyl 2-(3-oxo-4-(trifluoromethyl)-1,3-dihydroisobenzofuran-1-yl)acetate (2h)

$\text{C}_{13}\text{H}_{11}\text{F}_{3}\text{O}_{4}$

288.22 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Supporting Information

Ethyl 2-(4-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2i)

C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>
234.25 g/mol

1H NMR (500 MHz, CDCl<sub>3</sub>)

C<sub>13</sub>H<sub>14</sub>O<sub>4</sub>
234.25 g/mol

13C NMR (126 MHz, CDCl<sub>3</sub>)
Ethyl 2-(4-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2j)

$\text{C}_{13} \text{H}_{14} \text{O}_5$

250.25 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

$\text{C}_{13} \text{H}_{14} \text{O}_5$

250.25 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)
Ethyl 2-(4,7-difluoro-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2k)

C\textsubscript{12}H\textsubscript{8}F\textsubscript{2}O\textsubscript{4}  
256.20 g/mol

\textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3})

\textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3})
Ethyl 2-(6-methyl-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2I mono)

\[
\text{C}_{12}\text{H}_{14}\text{O}_4 \\
234.25 \text{ g/mol} \\
^1\text{H NMR (400 MHz, CDCl}_3\text{)}
\]

\[
\text{C}_{13}\text{H}_{14}\text{O}_4 \\
234.25 \text{ g/mol} \\
^{13}\text{C NMR (101 MHz, CDCl}_3\text{)}
\]
Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-6-methyl-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2l **bis**)

C_{18}H_{20}O_{6}
332.35 g/mol
^1H NMR (400 MHz, CDCl$_3$)

C_{18}H_{20}O_{6}
332.35 g/mol
^13C NMR (101 MHz, CDCl$_3$)
Ethyl 2-(6-amino-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2m)

C₁₂H₁₃NO₄
235.24 g/mol
¹H NMR (500 MHz, CDCl₃)

Analytic sample contained impurities due to decomposition in solution.

C₁₂H₁₃NO₄
235.24 g/mol
¹³C NMR (126 MHz, CDCl₃)
Ethyl 2-(6-hydroxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2n mono)

$\text{C}_{12}\text{H}_{12}\text{O}_{6}$
236.22 g/mol

$^1\text{H}$ NMR (500 MHz, CDCl$_3$)

$\text{C}_{12}\text{H}_{12}\text{O}_{6}$
236.22 g/mol

$^{13}\text{C}$ NMR (126 MHz, CDCl$_3$)
**Supporting Information**

Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-3-hydroxy-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2n bis)

![Chemical Structure](image1)

C$_{17}$H$_{18}$O$_7$

334.32 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

![NMR Spectrum](image2)

C$_{17}$H$_{18}$O$_7$

334.32 g/mol

$^{13}$C NMR (125 MHz, CDCl$_3$)

![NMR Spectrum](image3)
Ethyl 2-(7-bromo-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2o mono)
Ethyl (E)-3-(7-bromo-1-(2-ethoxy-2-oxoethyl)-3-oxo-1,3-dihydroisobenzofuran-4-yI)acrylate (2o bis)
Ethyl 2-(5-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2p mono isomer 1)

$\text{C}_{13}\text{H}_{14}\text{O}_5$
$250.25 \text{ g/mol}$

$^1\text{H NMR (500 MHz, CDCl}_3)$

$\text{C}_{13}\text{H}_{14}\text{O}_5$
$250.25 \text{ g/mol}$

$^{13}\text{C NMR (126 MHz, CDCl}_3)$
Ethyl 2-(7-methoxy-3-oxo-1,3-dihydroisobenzofuran-1-yl)acetate (2p mono isomer 2)

**Chemical Structure**

**Formula:** $C_{13}H_{14}O_5$

**Molecular Weight:** 250.25 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
Ethyl (E)-3-(1-(2-ethoxy-2-oxoethyl)-7-methoxy-3-oxo-1,3-dihydroisobenzofuran-4-yl)acrylate (2p bis)

**$C_{18}H_{20}O_7$**
348.35 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

**$C_{18}H_{20}O_7$**
348.35 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)
Ethyl 2-(1-oxo-3,6-dihydro-1H-furo[3,4-e]indol-3-yl)acetate (2q)

C_{14}H_{12}NO_{4}
259.26 g/mol

$^1$H NMR (400 MHz, CDCl$_3$)

C_{14}H_{12}NO_{4}
259.26 g/mol

$^{13}$C NMR (101 MHz, CDCl$_3$)
Ethyl 2-(7-oxo-5,7-dihydro-1H-furo[3,4-f]indol-5-yl)acetate (2r mono)

C_{14}H_{13}NO_4
259.26 g/mol

{sup}H NMR (500 MHz, CDCl_3)

C_{14}H_{13}NO_4
259.26 g/mol

{sup}C NMR (126 MHz, CDCl_3)
SUPPORTING INFORMATION

**Ethyl 3-(5-(2-ethoxy-2-oxoethyl)-7-oxo-5,7-dihydro-1H-furo[3,4-f]indol-8-yl) propanoate (2r bis)**

![Chemical structure](image)

**C$_{19}$H$_{21}$NO$_6$**

359.38 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

![NMR spectrum 1](image)

**C$_{19}$H$_{21}$NO$_6$**

359.38 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)

![NMR spectrum 2](image)
Ethyl (E)-3-{(2-(methylcarbamoyl)phenyl)acrylate} (2s mono)

$\text{C}_{13}\text{H}_{13}\text{NO}_3$

233.27 g/mol

$^1$H NMR (500 MHz, CDCl$_3$)

$\text{C}_{13}\text{H}_{13}\text{NO}_3$

233.27 g/mol

$^{13}$C NMR (126 MHz, CDCl$_3$)
Diethyl 3,3'-(2-(methylcarbamoyl)-1,3-phenylene)(2E,2'E)-diacrylate (2s bis)

\[ \text{C}_{18}\text{H}_{20}\text{NO}_5 \]

\[ 331.37 \text{ g/mol} \]

\(^1\text{H NMR (500 MHz, CDCl}_3)\)

\[ \text{C}_{18}\text{H}_{20}\text{NO}_5 \]

\[ 331.37 \text{ g/mol} \]

\(^{13}\text{C NMR (126 MHz, CDCl}_3)\)
SUPPORTING INFORMATION

(E)-2-(2,3,4,5-Tetramethylcyclopent-2-en-1-ylidene)acetonitrile

\[
\text{C}_{11}\text{H}_{12}\text{N}
\]

161.25 g/mol

\(^1\)H NMR (300 MHz, CDCl\(_3\))

\[
2-(2,3,4,5-Tetramethylcyclopenta-2,4-dien-1-yl)ethan-1-aminium chloride
\]

\[
\text{C}_{11}\text{H}_{20}\text{NCl}
\]

201.74 g/mol

\(^1\)H NMR (500 MHz, CD\(_3\)OD)
(E)-1-(3,5-Bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopent-2-en-1-ylidene)ethyl)urea

$\text{C}_{29}\text{H}_{32}\text{F}_{2}\text{N}_{2}\text{O}$

420.40 g/mol

$^1\text{H NMR (500 MHz, DMSO-}$d$_6$)

$^{13}\text{C NMR (126 MHz, DMSO-}$d$_6$)
Dichloro[η5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea]rhodium(III) dimer (3)

\[
\text{C}_{60}\text{H}_{52}\text{Cl}_2\text{F}_{32}\text{N}_2\text{O}_2\text{Rh}_2
\]

1186.39 g/mol

\[1^H\text{ NMR (500 MHz, DMSO-d}_6)\]

\[
\text{C}_{60}\text{H}_{42}\text{Cl}_4\text{F}_{12}\text{N}_2\text{O}_2\text{Rh}_2
\]

1186.39 g/mol

\[1^3C\text{ NMR (126 MHz, DMSO-d}_6)\]
**Supporting Information**

Dichloro[η5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea] (triphenylphosphine)rhomodium(III) (4a)

\[
\text{C}_{39}\text{H}_{34}\text{Cl}_{2}\text{F}_6\text{N}_2\text{OPRh}
\]

855.49 g/mol

\(^{1}H\) NMR (500 MHz, DMSO-\(d_6\))

\[
\text{C}_{39}\text{H}_{34}\text{Cl}_{2}\text{F}_6\text{N}_2\text{OPRh}
\]

855.49 g/mol

\(^{13}C\) NMR (126 MHz, DMSO-\(d_6\))
Dichloro[η5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethy]urea][(6-oxo-1,6-dihydropyridin-2-yl)diphenylphosphine]rhodium(III) (4b)

\[\text{C}_{37}\text{H}_{35}\text{Cl}_2\text{F}_6\text{N}_2\text{O}_4\text{PRh} \]
872.48 g/mol

\(\text{'H NMR (500 MHz, DMSO-}d_6\text{)}\)

\[\text{C}_{37}\text{H}_{35}\text{Cl}_2\text{F}_6\text{N}_2\text{O}_4\text{PRh} \]
872.48 g/mol

\(\text{\(^{13}\text{C NMR (126 MHz, DMSO-}d_6\text{)}}\)
Dichloro[η5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopentadienyl)ethyl)urea][3-oxo-2,3-dihydroisoquinolin-1-yl]diphenylphosphine]rhodium(III) (4c)
Dichloro[η5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea][(6-oxo-1,6-dihydropyridin-2-yl)di(3,5-bis(trifluoromethyl)phenyl) phosphine]rhodium(III) (4d)
Dichloro[η^5-1-(3,5-bis(trifluoromethyl)phenyl)-3-(2-(2,3,4,5-tetramethylcyclopenta-dienyl)ethyl)urea][6-methoxypyridin-2-yl)diphenylphosphine]rhodium(III) (4e)

\[ \text{C}_{36} \text{H}_{32} \text{Cl}_2 \text{F}_6 \text{N}_2 \text{O}_2 \text{Prh} \]

\[ \text{886.50 g/mol} \]

\[ ^1H \text{NMR (500 MHz, DMSO-}d_6) \]

\[ ^13\text{C NMR (126 MHz, DMSO-}d_6) \]