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Supporting Information

Supramolecular Control of the Oxidative Addition as a Way To Improve the Catalytic Efficiency of Pincer-Rhodium (I) Complexes

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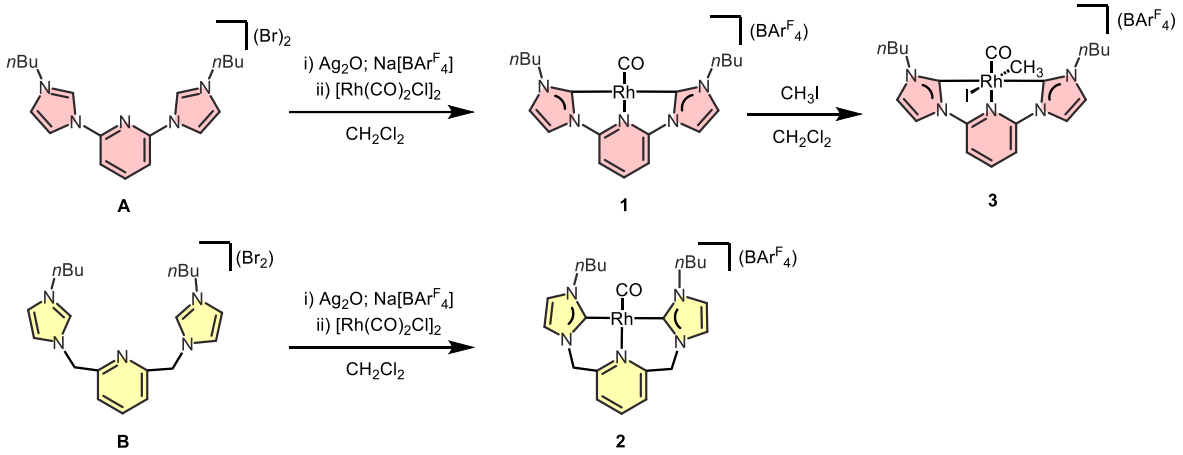
Supporting Information

General considerations

2,6-Bis(1-*n*-butylimidazolium-3-yl)pyridine bromide (compound **A**) was prepared as described in the literature.[1] Anhydrous solvents were dried using a solvent purification system (SPS M BRAUN) or purchased and degassed prior to use by purging them with dry nitrogen. All the other reagents were used as received from the commercial suppliers. Column chromatography was performed using silica gel (60-120 mesh). NMR spectra recorded on a Bruker 400 or 300 MHz using CD_2Cl_2, CD_3CN and $CDCl_3$ as solvents, chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard. All coupling constants (*J*) are expressed in hertz (Hz). Signals marked with an asterisk (*) in the NMR spectra correspond to Apiezon brand H grease.[2] Infrared spectra (FTIR) were performed on an Agilent Cary 630 KBr Engine FTIR spectrometer with a spectral window of 7000-350 cm^{-1}. Electrospray mass spectra (ESI-MS) were recorded on a Micromass Quatro LC instrument; nitrogen was employed as drying and nebulizing gas.

1. Synthesis and characterization of the compounds



Scheme S1. Synthesis of the NHC-based pincer complexes described in this work.

Synthesis and characterization of salt B. A mixture of 2,6-bis(bromomethyl)pyridine (2.21 mmol, 0.586 g, 1 equiv.) and 1-butylimidazole (4.42 mmol, 0.580 mL, 2 equiv.) in dioxane (15 mL) was refluxed for 16 h. The solvent was then removed under vacuum and the residue was washed with cold acetone and Et_2O. The isolated oil was dried under vacuum. Compound **B** was isolated as a brown oil in 55% yield (621 mg). **^{1}H NMR** (300 MHz, CD_3CN): 9.89 (s, 2H, NC*H*N), 7.81 (t, $^3J_{H\text{-}H}$ = 1.7 Hz, 2H, C*H*$_{imid}$), 7.80 (overlapped t, 1H, C*H*$_{pyr}$), 7.63 (t, $^3J_{H\text{-}H}$ = 1.6 Hz, 2H, C*H*$_{imid}$), 7.59 (d, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, C*H*$_{pyr}$), 5.64 (s, 4H, C*H*$_{2\ pyr\text{-}imid}$), 4.33 (t, $^3J_{H\text{-}H}$ = 7.2 Hz, 4H, NC*H*$_2$CH$_2$CH$_2$CH$_3$), 1.81 (q, $^3J_{H\text{-}H}$ = 7.3 Hz, 4H, NCH$_2$C*H*$_2$CH$_2$CH$_3$), 1.29 (sext, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, NCH$_2$CH$_2$C*H*$_2$CH$_3$), 0.87 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 6H, NCH$_2$CH$_2$CH$_2$C*H*$_3$). **^{13}C {^{1}H} NMR** (75 MHz, CD_3CN): δ 154.4 (*C*$_{pyr}$), 139.6 (*C*H$_{pyr}$), 137.8 (N*C*HN), 124.0 (*C*H$_{pyr}$), 123.7 (*C*H$_{imid}$), 122.8 (*C*H$_{imid}$), 53.8 (*C*H$_{2pyr\text{-}imid}$), 50.0 (N*C*H$_2$CH$_2$CH$_2$CH$_3$), 32.5 (NCH$_2$*C*H$_2$CH$_2$CH$_3$), 19.8 (NCH$_2$CH$_2$*C*H$_2$CH$_3$), 13.6 (NCH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 176.6 [M-2Br]$^{2+}$. (Calcd. for 176.7 [M-2Br]$^{2+}$).

- **Synthesis of the Rh(I) pincer complexes 1 and 2. General procedure.**

The corresponding bis-imidazolium salt (1 equiv.), Na[BAr$^F_4$] (1.10 equiv.) and Ag_2O (1 equiv.) were placed together in a Schlenk tube fitted with a Teflon cap. The tube was evacuated and filled with nitrogen three times. The mixture reaction was suspended in

CH_2Cl_2 (4 mL) and stirred at room temperature in the absence of light overnight. The solution was then filtered through Celite into a flask charged with 0.5 equivalents of $[Rh(CO)_2Cl]_2$. The suspension was stirred for 2h and then was passed through a column chromatography using dichloromethane as eluent.

Synthesis and characterization of 1. Complex **1** was prepared employing the general procedure by reacting 2,6-bis(1-*n*-butylimidazolium-3-yl)pyridine bromide (compound **A**, 150 mg, 0.309 mmol), $[Rh(CO)_2Cl]_2$ (60 mg, 0.155 mmol), $Na[BAr^F{}_4]$ (261.6 mg, 0.324 mmol) and Ag_2O (71.6 mg, 0.309 mmol). Complex **1** was isolated as red solid in 73% yield (298 mg). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 8.07 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, CH_{pyr}), 7.75-7.65 (m, 8H, Ar^F), 7.55 (br, 4H, Ar^F), 7.47 (d, $^3J_{H\text{-}H}$ = 2.2 Hz, 2H, CH_{imid}), 7.19 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 2H, CH_{pyr}), 7.12 (d, $^3J_{H\text{-}H}$ = 2.2 Hz, 2H, CH_{imid}), 4.14 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 4H, CH_2CH$_2$CH$_2$CH$_3$), 1.90 (q, $^3J_{H\text{-}H}$ = 7.5 Hz, 4H, CH$_2$CH_2CH$_2$CH$_3$), 1.45 (sext, $^3J_{H\text{-}H}$ = 7.7 Hz, 4H, CH$_2$CH$_2$CH_2CH$_3$), 1.00 (t, $^3J_{H\text{-}H}$ = 7.3 Hz, 6H, CH$_2$CH$_2$CH$_2$CH_3). **^{13}C {^{1}H} NMR** (75 MHz, CD_2Cl_2): δ 196.2 (d, $^1J_{RhC}$ = 76.2 Hz, Rh-CO), 186.6 (d, $^1J_{RhC}$ = 47.4 Hz, Rh-C_{NHC}), 162.3 (q, $^1J_{CB}$ = 49.5 Hz, Ar^F), 152.7 ($C_{pyr\text{-}imid}$), 146.3 (*C*H$_{pyr}$), 135.4 (Ar^F), 130.6 (Ar^F), 129.7 (q, $^2J_{CF}$ = 2.9 Hz, Ar^F), 129.3 (q, $^1J_{CF}$ = 2.9 Hz, Ar^F), 127.0 (Ar^F), 123.8 (*C*H$_{imid}$), 123.4 (Ar^F), 119.8 (Ar^F), 118.0 (sept, $^3J_{FC}$ = 4.0 Hz, Ar^F), 117.0, (*C*H$_{imid}$), 106.7 (*C*H$_{pyr}$), 52.8 (*C*H$_2$CH$_2$CH$_2$CH$_3$), 33.7 (CH$_2$*C*H$_2$CH$_2$CH$_3$), 20.3 (CH$_2$CH$_2$*C*H$_2$CH$_3$), 13.9 (CH$_2$CH$_2$CH$_2$*C*H$_3$). Electrospray MS (20 V, m/z): 454.2 $[M]^+$. (Calcd. for $[M]^+$: 454.4). IR (CH_2Cl_2): ν(CO) 1992.0 cm^{-1}.

Synthesis and characterization of 2. Complex **2** was prepared employing the general procedure by reacting compound **B** (200 mg, 0.389 mmol), $[Rh(CO)_2Cl]_2$ (76 mg, 0.195 mmol), $Na[BAr^F{}_4]$ (362 mg, 0.409 mmol) and Ag_2O (90.2 mg, 0.389 mmol). Complex **2** was isolated as yellow solid in 52% yield (248 mg). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 7.80 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, CH_{pyr}), 7.75-7.65 (m, 8H, Ar^F), 7.57 (br, 4H, Ar^F), 7.45 (d, $^3J_{H\text{-}H}$ = 7.8 Hz, 2H, CH_{pyr}), 7.12 (d, $^3J_{H\text{-}H}$ = 1.9 Hz, 2H, CH_{imid}), 6.97 (d, $^3J_{H\text{-}H}$ = 1.9 Hz, 2H, CH_{imid}), 5.55-5.35 (br, 2H, C$H_{2\ pyr\text{-}imid}$), 5.10-4.88 (br, 2H, C$H_{2\ pyr\text{-}imid}$), 4.15 (t, $^3J_{H\text{-}H}$ = 7.5 Hz, 4H, NCH_2CH$_2$CH$_2$CH$_3$), 1.86 (br, 4H, NCH$_2$CH_2CH$_2$CH$_3$), 1.37 (sext, $^3J_{H\text{-}H}$ = 7.4 Hz, 4H, NCH$_2$CH$_2$CH_2CH$_3$), 0.94 (t, $^3J_{H\text{-}H}$ = 7.4

Hz, 6H, $NCH_2CH_2CH_2CH_3$). **^{13}C {^{1}H} NMR** (75 MHz, CD_2Cl_2): δ 194.0 (d, $^1J_{RhC}$ = 79.0 Hz, Rh-*C*O), 182.4 (d, $^1J_{RhC}$ = 41.4 Hz, Rh-C_{NHC}), 162.4 (q, $^1J_{CB}$ = 49.5 Hz, Ar^F), 156.2 (C_{pyr}), 141.4 (CH_{pyr}), 135.4 (Ar^F), 130.6 (Ar^F), 129.7 (q, $^2J_{CF}$ = 2.9 Hz, Ar^F), 129.4 (q, $^1J_{CF}$ = 2.9 Hz, Ar^F) , 127.0 (Ar^F), 124.7 (CH_{pyr}), 123.4 (Ar^F), 121.8 (CH_{imid}), 121.3 (CH_{imid}), 119.8 (Ar^F), 118.1 (sept, $^3J_{FC}$ = 3.9 Hz, Ar^F), 55.9 ($CH_{2\ pyr\text{-}imid}$), 51.2 ($NCH_2CH_2CH_2CH_3$), 34.0 ($NCH_2CH_2CH_2CH_3$), 20.3 ($NCH_2CH_2CH_2CH_3$), 13.9 ($NCH_2CH_2CH_2CH_3$). Electrospray MS (20 V, m/z): 482.3 $[M]^+$. (Calcd. for $[M]^+$: 482.4). IR (CH_2Cl_2): ν(CO) 1975.5 cm^{-1}.

Synthesis and characterization of 3. Complex **1** (80 mg, 0.0606 mmol, 1 equiv.) was dissolved in 5 mL of CH_2Cl_2, forming a purple solution. Then, CH_3I (20 μL, 0.32 mmol, 75 equiv.) was added, and the resulting mixture was stirred at room temperature for 3h. The resulting solution was concentrated to dryness and purified by column chromatography using dichloromethane as eluent. Complex **3** was isolated as a cream powder in 80% yield (71 mg). **^{1}H NMR** (300 MHz, CD_2Cl_2): δ 8.32 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, CH_{pyr}), 7.77 (d, $^3J_{H\text{-}H}$ = 2.3 Hz, 2H, CH_{imid}), 7.75-7.65 (m, 8H, Ar^F), 7.56 (br, 4H, Ar^F), 7.53 (overlapped d, 2H, CH_{pyr}), 7.27 (d, $^3J_{H\text{-}H}$ = 2.3 Hz, 2H, CH_{imid}), 4.34-4.22 (m, 4H, $CH_2CH_2CH_2CH_3$), 2.14-1.95 (m, 4H, $CH_2CH_2CH_2CH_3$), 1.51 (sext, $^3J_{H\text{-}H}$ = 7.6 Hz, 4H, $CH_2CH_2CH_2CH_3$), 1.03 (t, $^3J_{H\text{-}H}$ = 7.4 Hz, 6H, $CH_2CH_2CH_2CH_3$), 0.53 (d, $^2J_{Rh\text{-}H}$ = 2.1 Hz, 3H, Rh-CH_3). **^{13}C {^{1}H} NMR** (75 MHz, CD_2Cl_2): δ 180.4 (d, $^1J_{RhC}$ = 37.2 Hz, Rh-C_{NHC}), 162.3 (q, $^1J_{CB}$ = 49.6 Hz, Ar^F), 150.2 ($C_{pyr\text{-}imid}$), 145.7 (CH_{pyr}), 135.4 (Ar^F), 130.6 (Ar^F), 129.6 (q, Ar^F), 129.2 (q, Ar^F), 126.1 (Ar^F), 124.5 (CH_{imid}), 123.4 (Ar^F), 119.8 (Ar^F), 118.1 (sept, $^3J_{FC}$ = 3.8 Hz, Ar^F), 118.0 (CH_{imid}), 108.7 (C_{pyr}), 53.2 ($CH_2CH_2CH_2CH_3$), 32.9 ($CH_2CH_2CH_2CH_3$), 20.4 ($CH_2CH_2CH_2CH_3$), 13.8 ($CH_2CH_2CH_2CH_3$), -3.0 (d, $^1J_{RhC}$ = 18.3 Hz, Rh-CH_3). Electrospray MS (20 V, m/z): 596.2 $[M]^+$. (Calcd. for $[M]^+$: 596.3). IR (CH_2Cl_2): ν(CO) 2074.3 cm^{-1}.

2. Spectroscopic data

2.1. ^{1}H and ^{13}C{^{1}H} NMR spectra of B

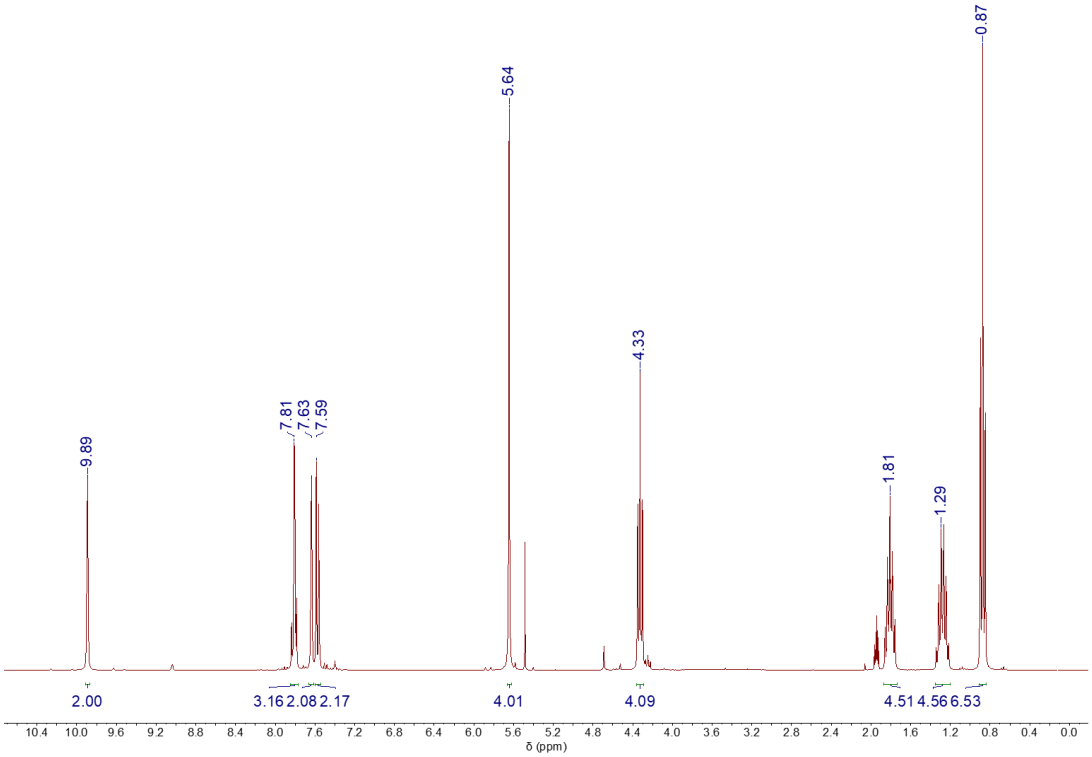


Figure S1. ^{1}H NMR spectrum (300 MHz, CD_3CN) of **B**

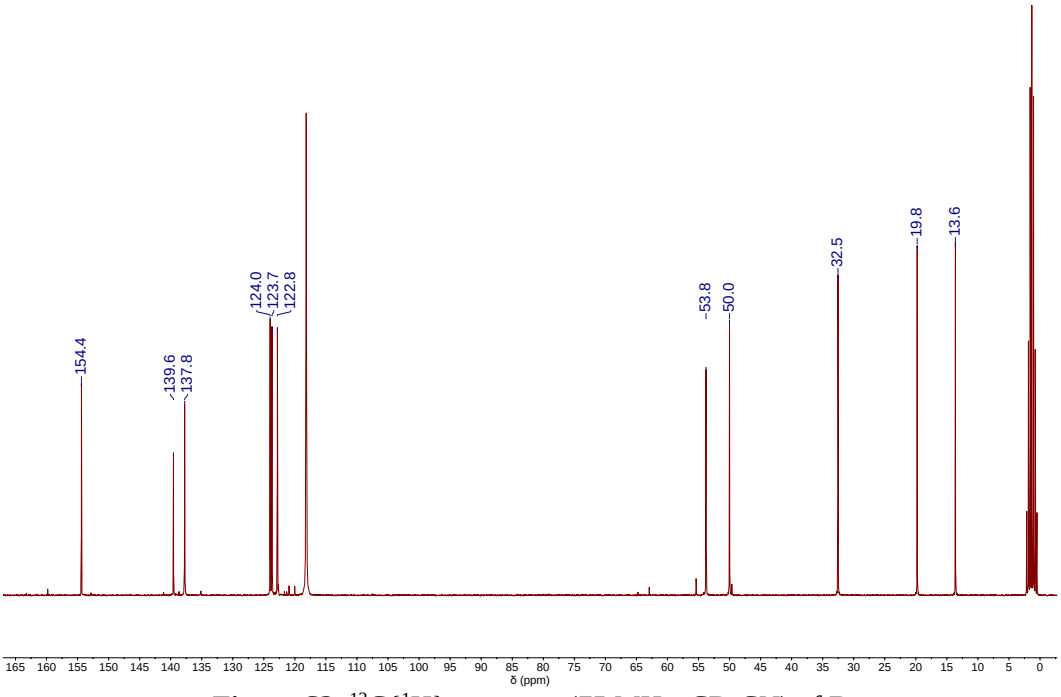


Figure S2. ^{13}C{^{1}H} spectrum (75 MHz, CD_3CN) of **B**

2.2. ^{1}H and ^{13}C{^{1}H} NMR spectra of 1

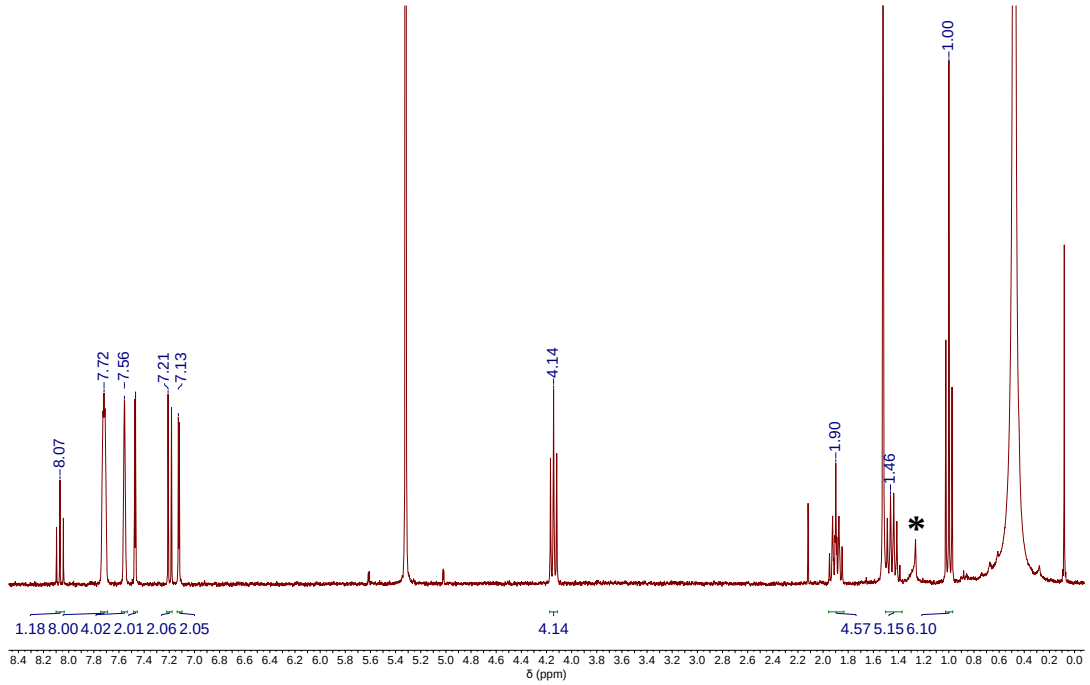


Figure S3. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **1**

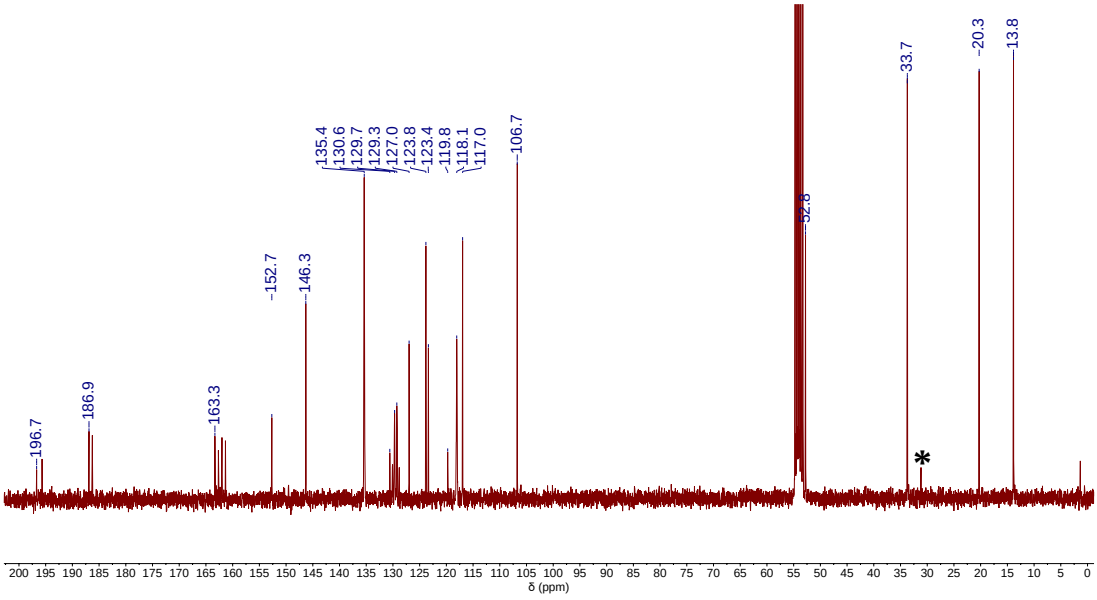


Figure S4. ^{13}C{^{1}H} spectrum (75 MHz, CD_2Cl_2) of **1**

2.3. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 2

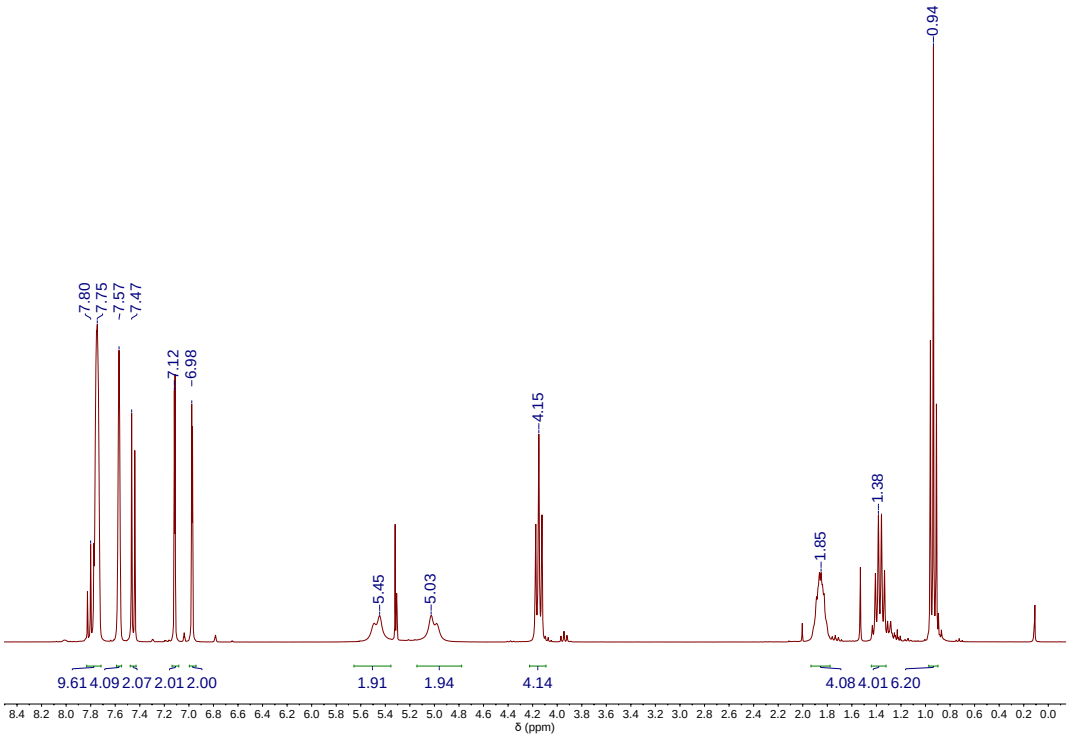


Figure S5. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **2**

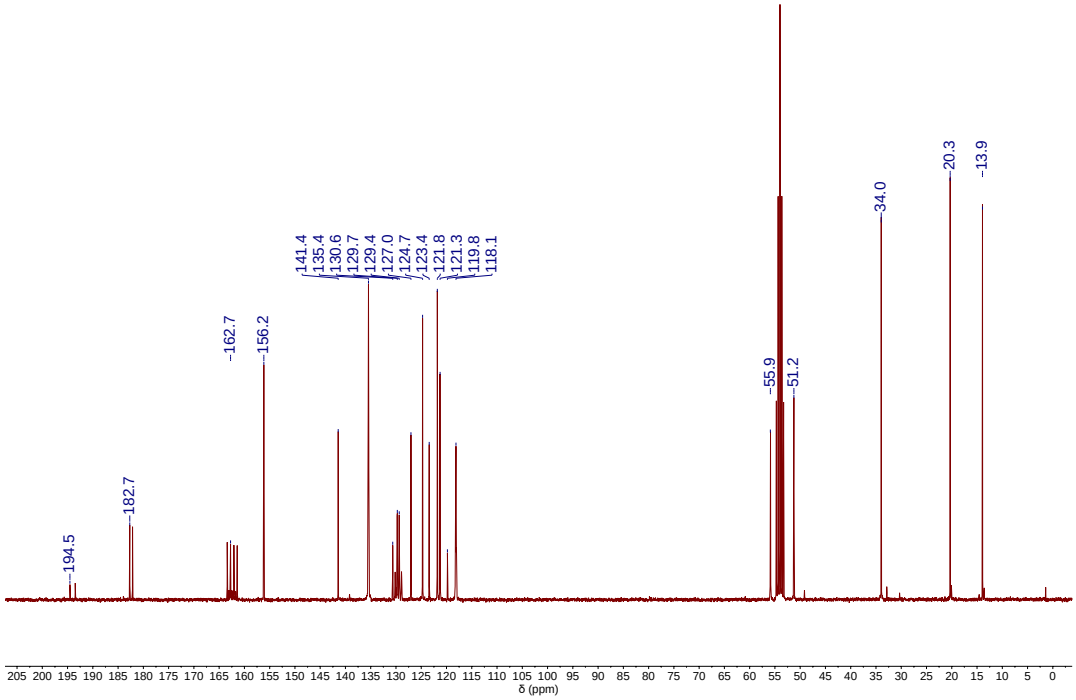


Figure S6. $^{13}C\{^{1}H\}$ spectrum (75 MHz, CD_2Cl_2) of **2**

2.4. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra of 3

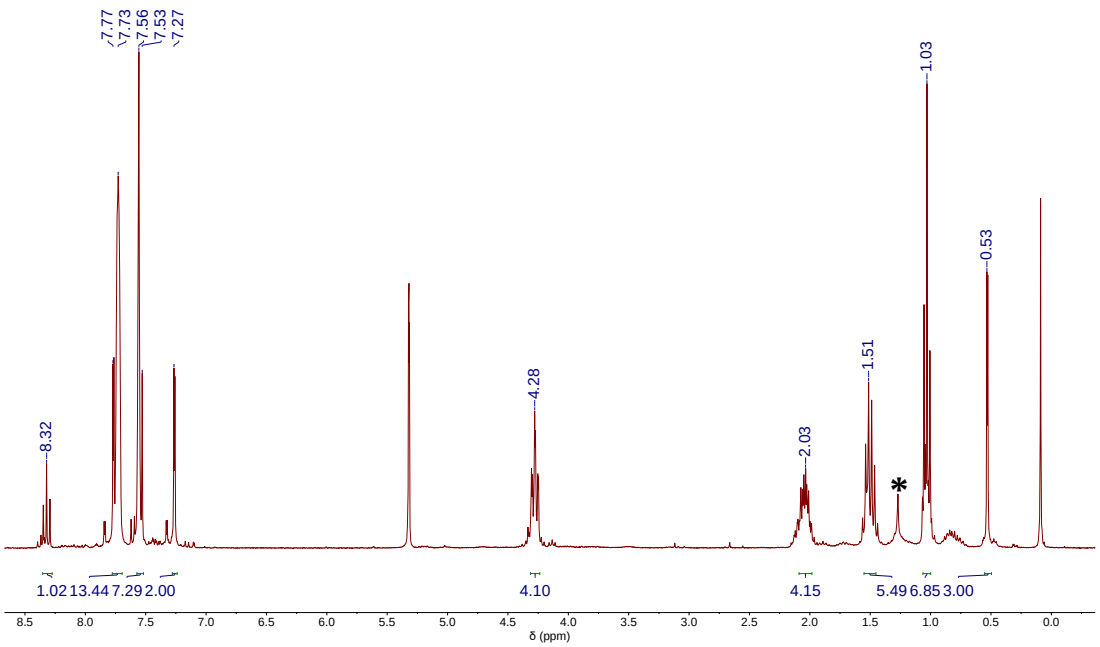


Figure S7. ^{1}H NMR spectrum (300 MHz, CD_2Cl_2) of **3**

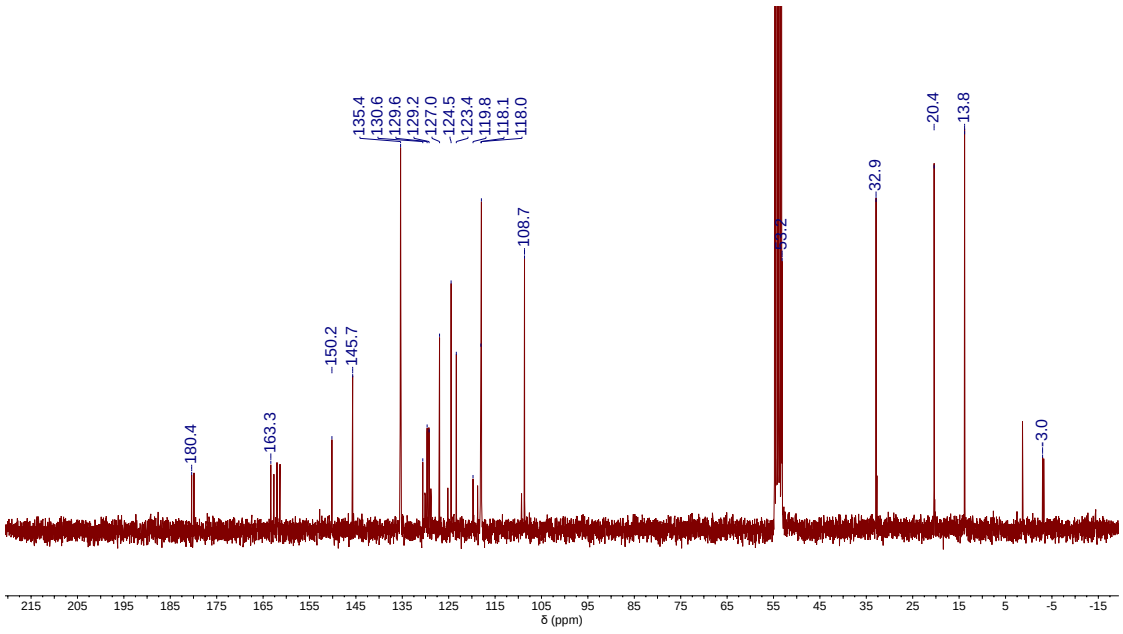


Figure S8. $^{13}C\{^{1}H\}$ spectrum (75 MHz, CD_2Cl_2) of **3**

3. Titration experiments

The recognition capability of complex **1** (host) was studied by means of ^{1}H NMR titration experiments, by adding increasing amounts of coronene or pyrene (guest) to a solution of complex **1**. The experiments were carried out in CD_2Cl_2, at constant concentrations of the host (0.233 mM). Two solutions were prepared: solution A (only containing host at 0.233 mM) and solution B (containing host at 0.233 mM and guest at 10.1 mM). The addition of increasing amounts of solution B to solution A, produced perturbations on many of the signals of the pincer host when coronene was employed as guest molecule. The association constants were calculated by nonlinear least-square analysis, by using the BindFitv0.5 program.

3.1. Titration of 1 with pyrene

Table S1. Data values from the titration study of **1** with pyrene

[**1**] / M	[pyrene] / M	δ CH_{imid} (ppm)	δ CH_{pyr} (ppm)	δ CH_{imid} (ppm)	δ NCH_2 (ppm)	Equiv. pyrene
0,00053129	0	7,49	7,22	7,14	4,15	0
0,00053129	0,00024041	7,49	7,22	7,14	4,15	0,45
0,00053129	0,00026431	7,49	7,22	7,14	4,15	0,50
0,00053129	0,00106921	7,48	7,21	7,13	4,14	2,01
0,00053129	0,00168285	7,48	7,21	7,13	4,14	3,18
0,00053129	0,00201623	7,47	7,20	7,13	4,14	3,80
0,00053129	0,00349054	7,47	7,19	7,13	4,14	6,57
0,00053129	0,00585742	7,45	7,18	7,12	4,13	11,03
0,00053129	0,00884988	7,43	7,14	7,11	4,12	16,66
0,00053129	0,01164843	7,42	7,12	7,10	4,12	21,92
0,00053129	0,01427563	7,40	7,10	7,10	4,11	26,87

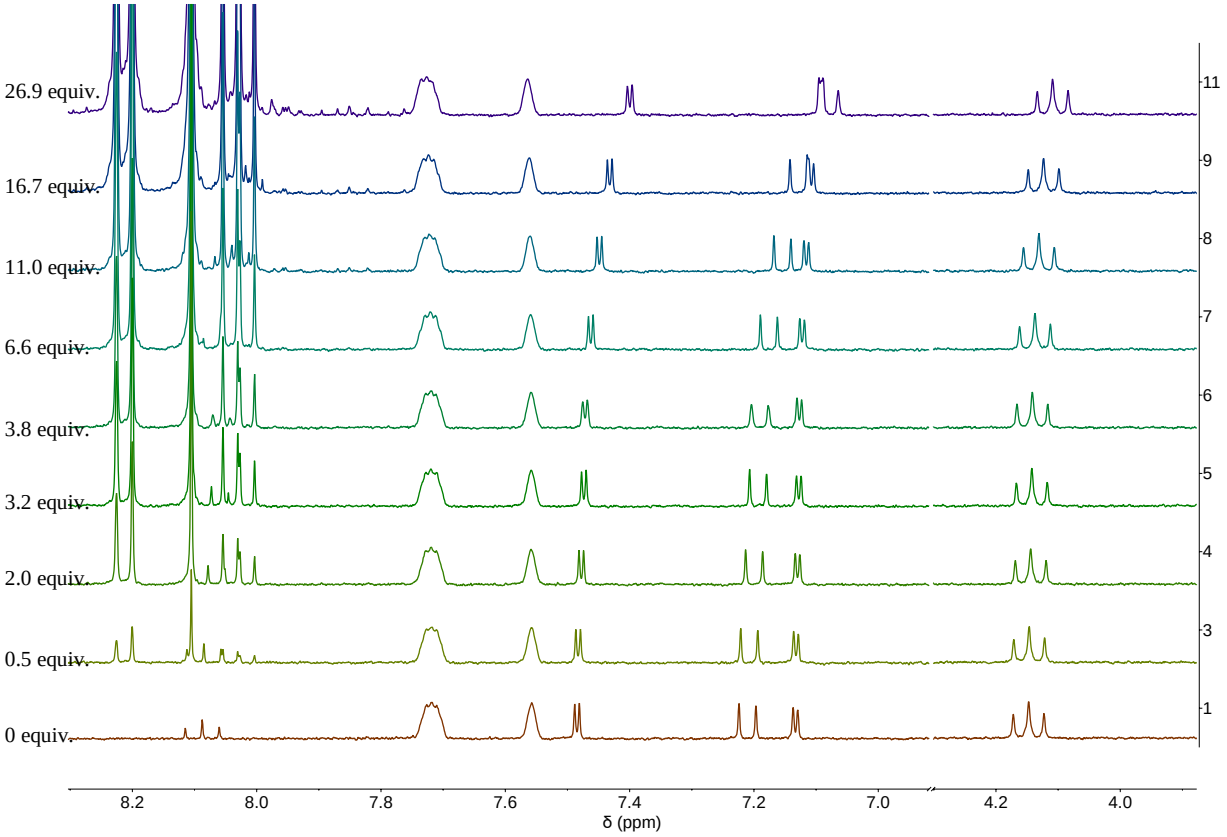


Figure S9. Selected region of the ^{1}H NMR (300 MHz) showing the perturbations observed during the titration of **1** with pyrene.

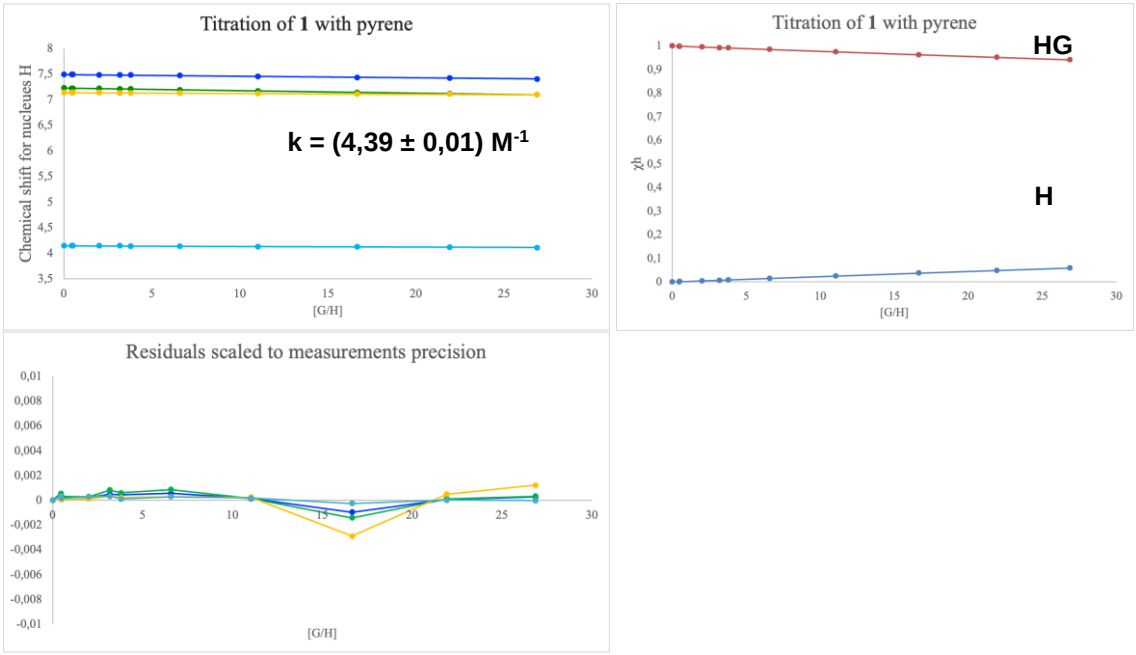


Figure S10. Non-linear least-squares fitting of the chemical shift changes of H during titration experiments of **1** with pyrene. The figure on the left represents the speciation profiles.

3.2. Titration of 1 with coronene

Table S2. Data values from the titration study of **1** with coronene

[**1**] / M	[coronene] / M	δ CH_{pyr} (ppm)	δ CH_{imid} (ppm)	δ CH_{pyr} (ppm)	δ CH_{imid} (ppm)	δ NCH_2 (ppm)	Equiv. coronene
0,000232753	0	8,10	7,49	7,23	7,14	4,15	0
0,000232753	0,0000692442	8,09	7,48	7,22	7,13	4,14	0,29
0,000232753	0,000125105	8,08	7,47	7,21	7,13	4,13	0,53
0,000232753	0,000205017	8,07	7,47	7,19	7,12	4,13	0,88
0,000232753	0,000249046	8,06	7,46	7,18	7,12	4,12	1,07
0,000232753	0,000313829	8,05	7,45	7,17	7,11	4,11	1,34
0,000232753	0,000392578	8,03	7,43	7,15	7,11	4,11	1,68
0,000232753	0,000462016	8,03	7,43	7,14	7,10	4,10	1,98
0,000232753	0,000541346	8,01	7,41	7,12	7,09	4,09	2,32
0,000232753	0,000755479	7,97	7,37	7,08	7,07	4,06	3,24
0,000232753	0,001026831	7,94	7,34	7,03	7,06	4,04	4,41
0,000232753	0,001365099	7,89	7,30	6,97	7,04	4,01	5,86
0,000232753	0,001572832	7,85	7,26	6,91	7,02	3,99	6,75
0,000232753	0,00217353	7,80	7,2171	6,85	7,00	3,96	9,33
0,000232753	0,002449536	7,72	7,17	6,80	6,98	3,93	10,52
0,000232753	0,00276259	7,72	7,14	6,76	6,96	3,91	11,86
0,000232753	0,002888471	7,71	7,12	6,73	6,95	3,90	12,41
0,000232753	0,003066721	7,68	7,10	6,70	6,94	3,89	13,17
0,000232753	0,005472422	7,64	7,06	6,65	6,92	3,86	23,51

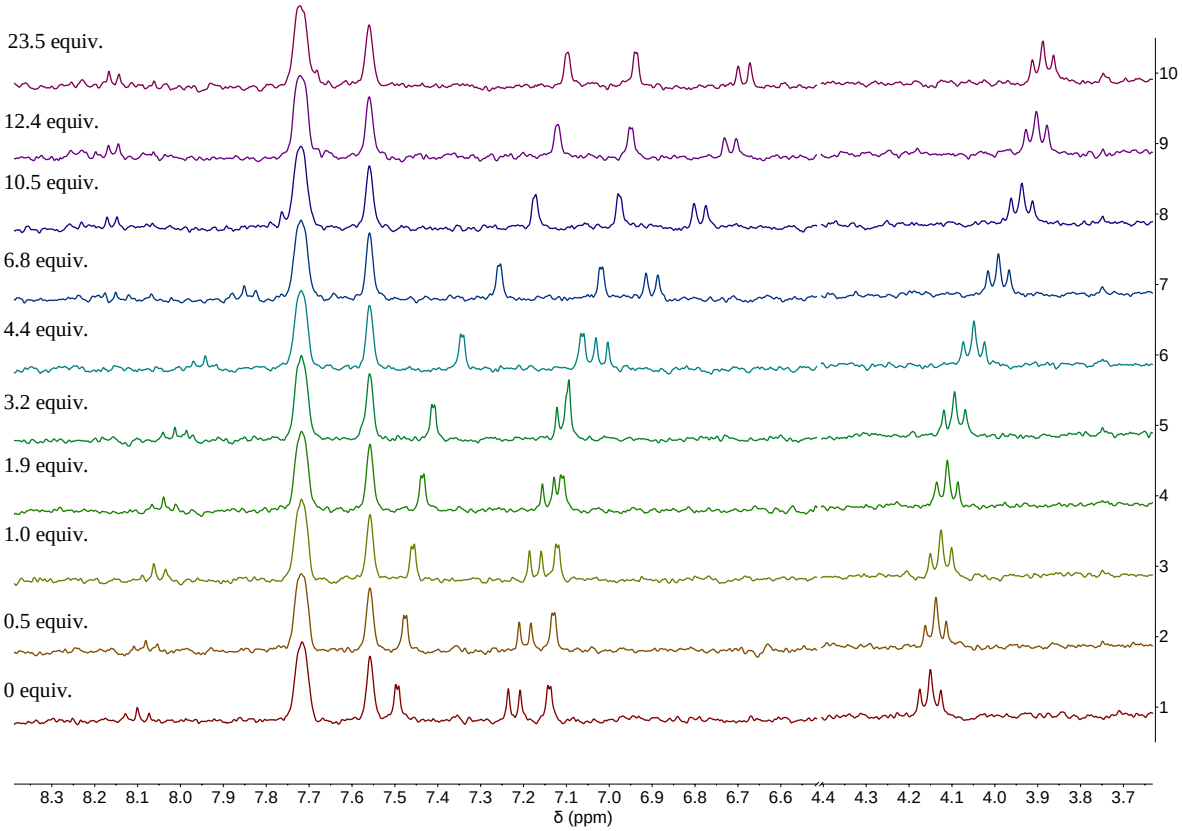


Figure S11. Selected region of the ^{1}H NMR (300 MHz) showing the perturbations observed during the titration of **1** with coronene.

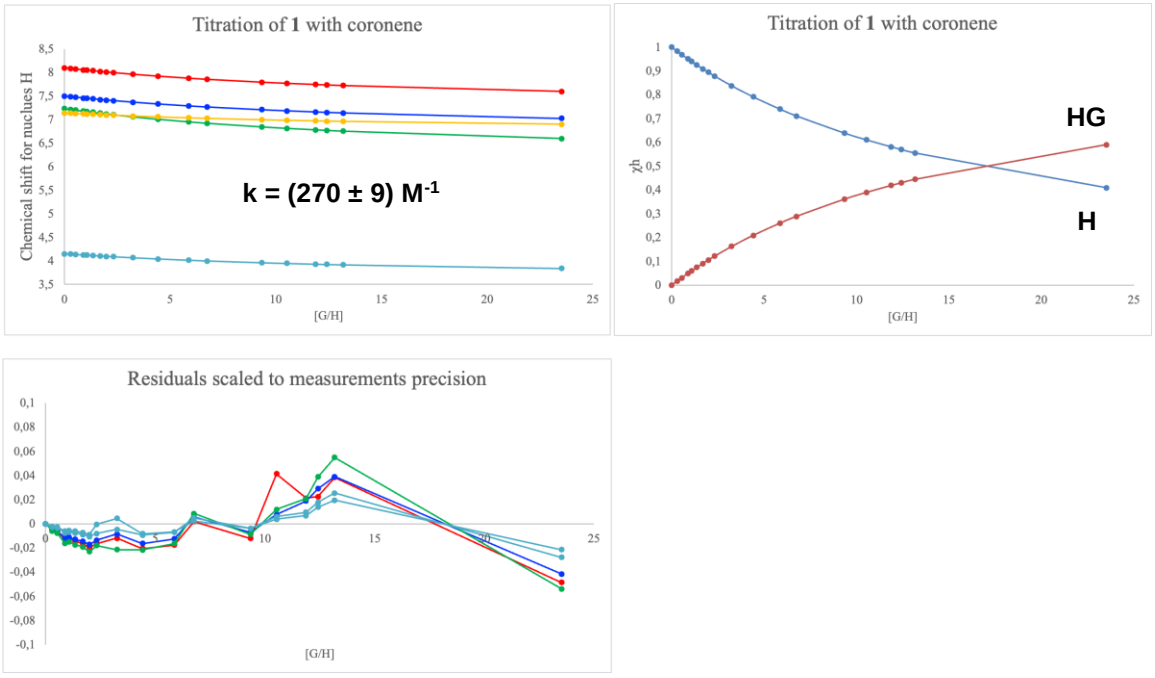


Figure S12. Non-linear least-squares fitting of the chemical shift changes of H during titration experiments of **1** with coronene. The figure on the left represents the speciation profiles.

3.3. Study of the recognition capabilities of 2

The binding affinity of complex **2** (host) with coronene (guest) was studied by means of ^{1}H NMR spectroscopy, by adding 27 equivalents of coronene to a solution of complex **2**. The experiment was carried out in CD_2Cl_2, at constant concentration of the host (0.233 mM). As can be seen in Figure S13, the addition of coronene did not produced perturbations on any of the resonances of the pincer host.

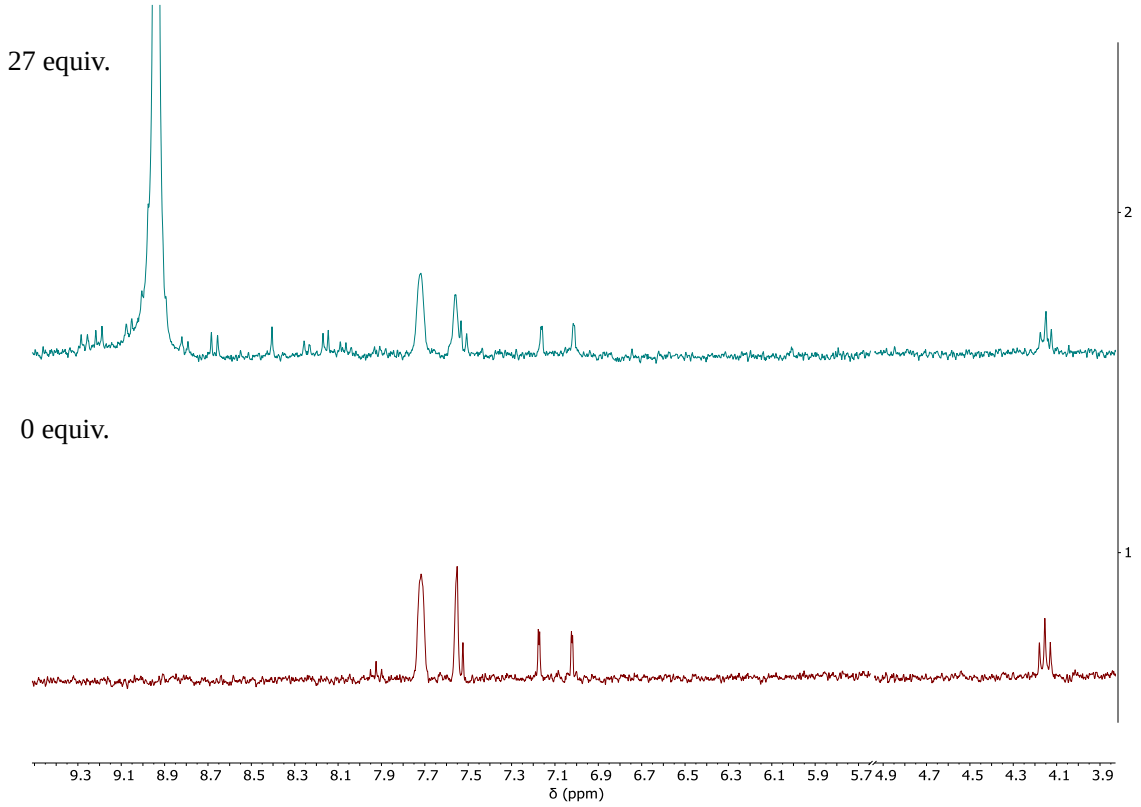


Figure S13. Selected region of the ^{1}H NMR (300 MHz) showing the spectrum of complex **2** (down) and the spectrum of complex **2** upon the addition of 27 equivalents of coronene (up). The solvent residual signal of CD_2Cl_2 at 5.32 ppm has been omitted for clarity.

3.4. Job Plot analysis

The stoichiometry of the aggregate formed between complex **1** and coronene was determined by means of a Job Plot ^{1}H NMR experiment using CD_2Cl_2 as solvent. We prepared a solution of the host (**1**) and a solution of the guest (coronene) at the same concentration (1.66 mM). Using these two stock solutions, 10 solutions were prepared with different [**1**]/[Coronene] ratios.

Table S3. Data values of the Job Plot of **1** with coronene

χ (host)	δ CH_2 (ppm)	Δδ CH_2 (ppm)	χ (host) x Δδ CH_2 (ppm)
1.00	4.14	0	0
0.81	4.12	0.02	0.0202
0.77	4.11	0.03	0.0245
0.69	4.10	0.04	0.0294
0.62	4.09	0.05	0.0326
0.52	4.07	0.06	0.0337
0.37	4.06	0.07	0.0313
0.31	4.06	0.08	0.0282
0.19	4.05	0.09	0.0196

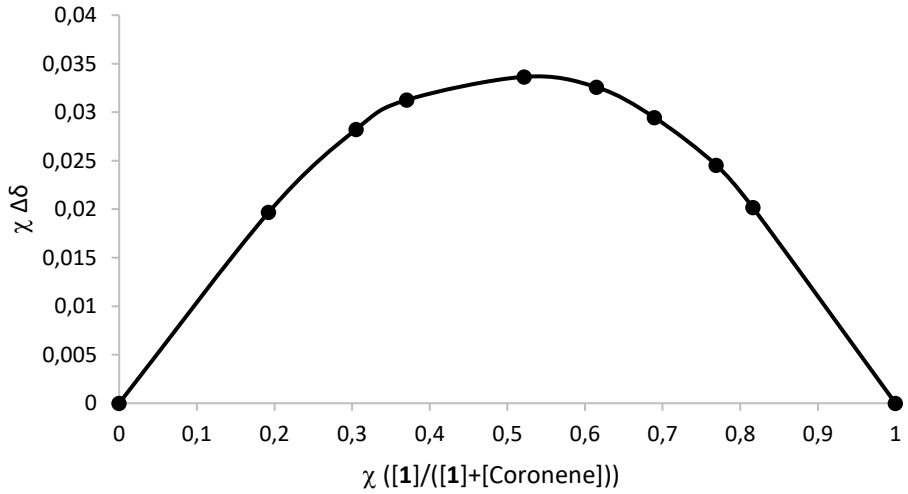


Figure S14. Job plot for the inclusion complex formed between **1** and coronene, indicating a 1:1 stoichiometry. Experiments were carried out in CD_2Cl_2, at a concentration of [**1**] + [coronene] = 4 mM.

4. Infrared Spectroscopy measurements

We prepared a solution of the host complex (**1** or **2**) and a solution of coronene or pyrene (guest) at the same concentration. FTIR-ATR experiments were performed using these two stock solutions with different [**1**]/[Guest] or [**2**]/[Guest] ratios.

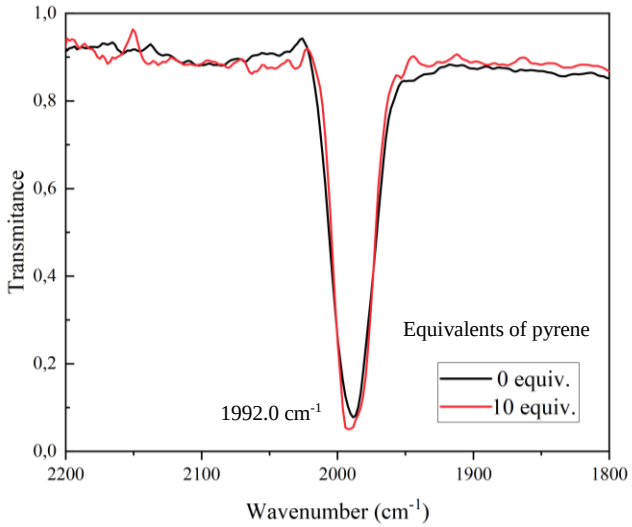


Figure S15. Infrared spectra recorded for complex **1** in the presence of 10 equivalents of pyrene.

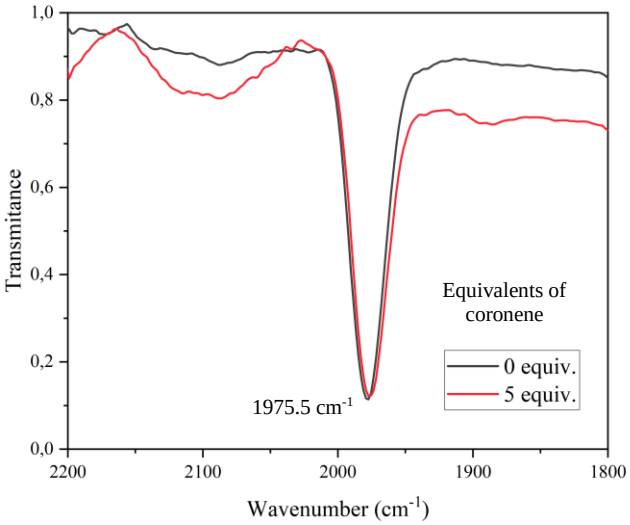


Figure S16. Infrared spectra recorded for complex **2** in the presence of 5 equivalents of coronene.

4. Kinetic studies: oxidative addition of MeI to 1 and 2

An NMR tube was charged with a CD_2Cl_2 solution (0.5 mL) of **1** or **2** (4.04 mM) and 10 μL of MeI (52 mM, 13 equiv.). For the reactions performed in the presence of a π-π-stacking additive, coronene (5 mg, 8.32 mM, 2 equiv.) or pyrene (3.37 mg, 8.32 mM, 2 equiv.) were also introduced in the NMR tube. A ^{1}H NMR spectrum was collected every 5 min using an arrayed experiment. Each data point involved eight scans with a delay time of 3 s. The formation of the oxidative product was monitored by using the ^{1}H NMR integrals of the Rh-C*H*$_3$ signal. The reactions were carried out under constant temperature of 313, 308, 303 and 293 K.

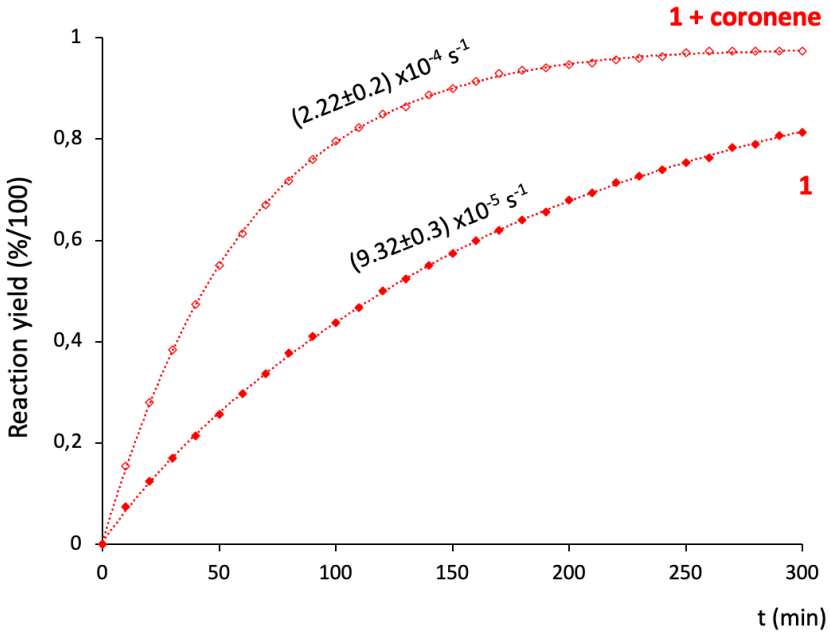


Figure S17. Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of coronene a 313K. The pseudo-first order kinetic constants are also depicted in the graphic.

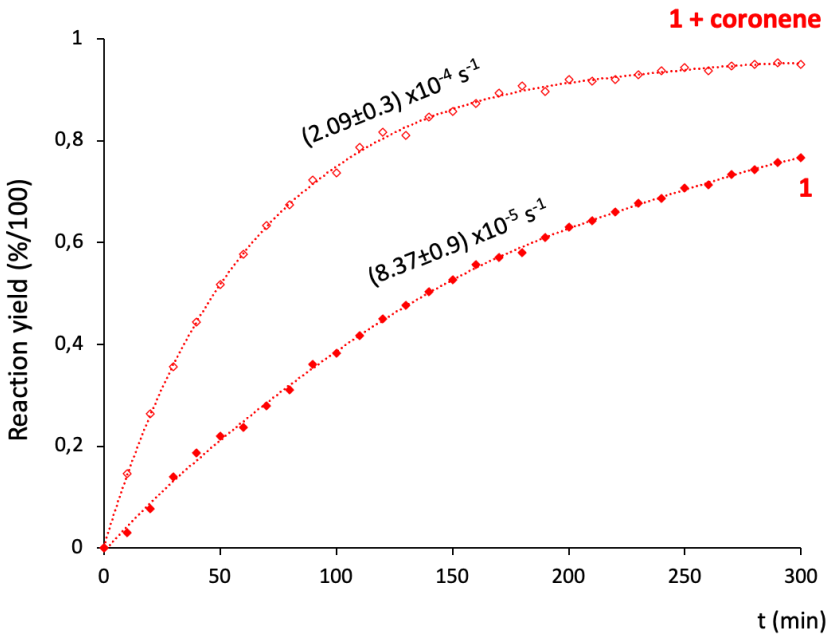


Figure S18. Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of coronene a 308K. The pseudo-first order kinetic constants are also depicted in the graphic.

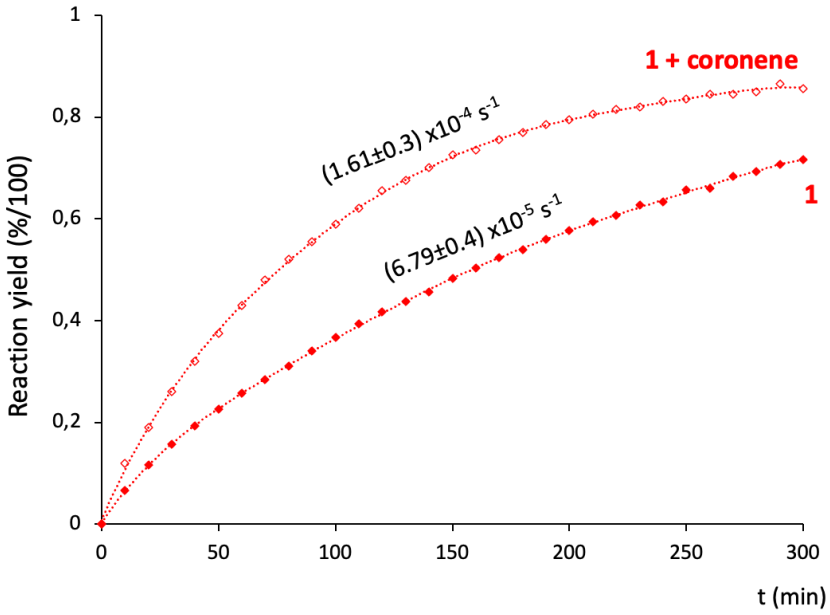


Figure S19. Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of coronene a 303K. The pseudo-first order kinetic constants are also depicted in the graphic.

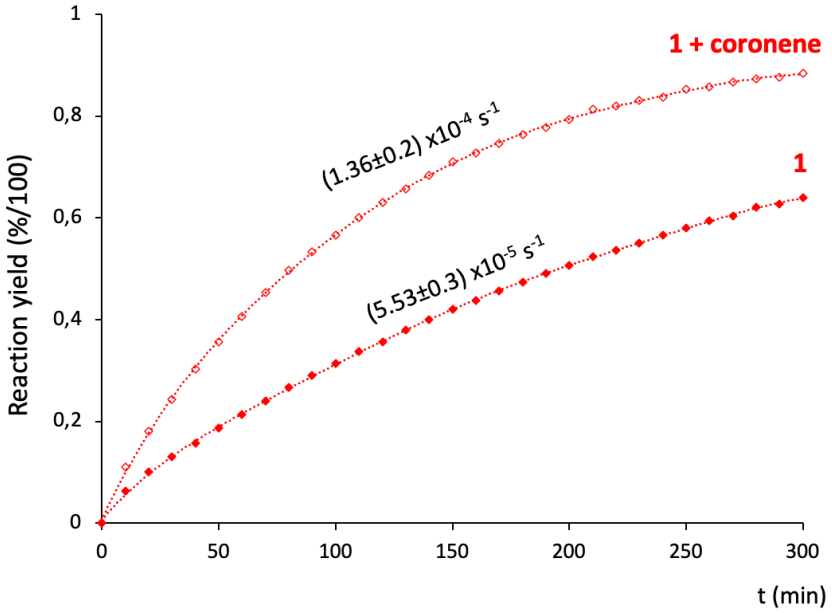


Figure S20. Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of coronene a 298K. The pseudo-first order kinetic constants are also depicted in the graphic.

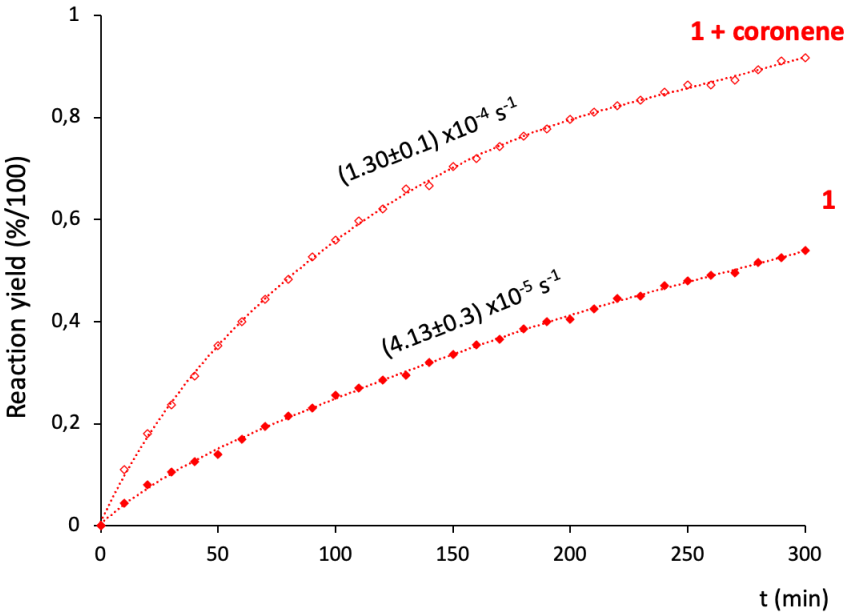


Figure S21. Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of coronene a 293K. The pseudo-first order kinetic constants are also depicted in the graphic.

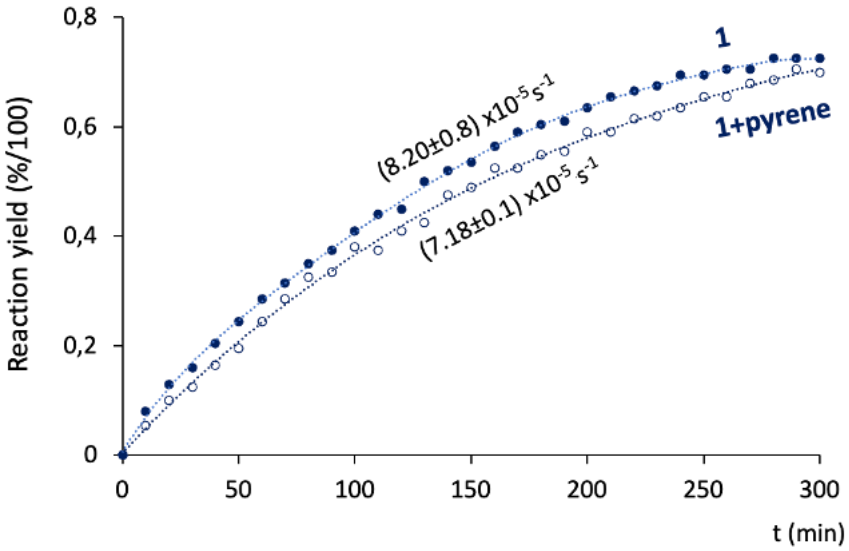


Figure S22. Time-dependent reaction profiles of the reactions of **1** with MeI, in the presence and in the absence of pyrene a 313K. The pseudo-first order kinetic constants are also depicted in the graphic.

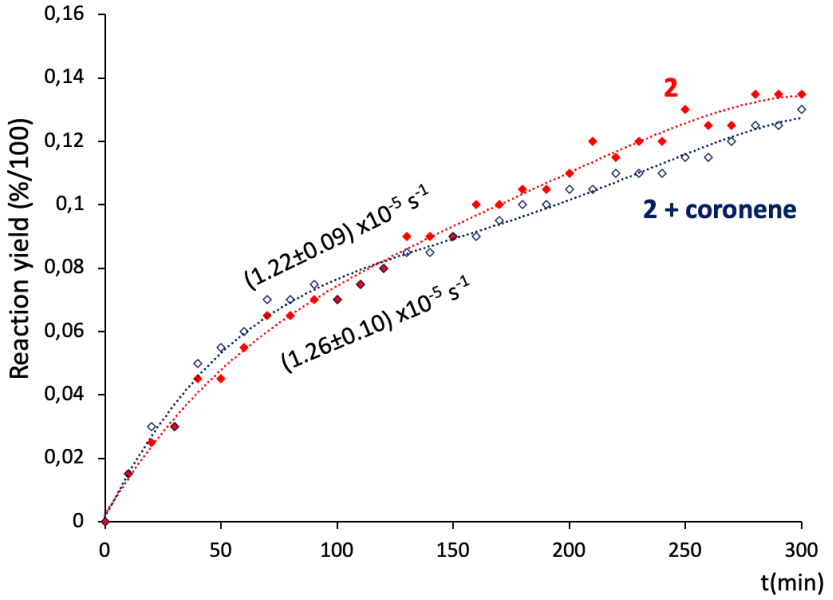


Figure S23. Time-dependent reaction profiles of the reactions of **2** with MeI, in the presence and in the absence of coronene a 313K. The pseudo-first order kinetic constants are also depicted in the graphic.

Eyring plots: determination of the thermodynamic parameters.

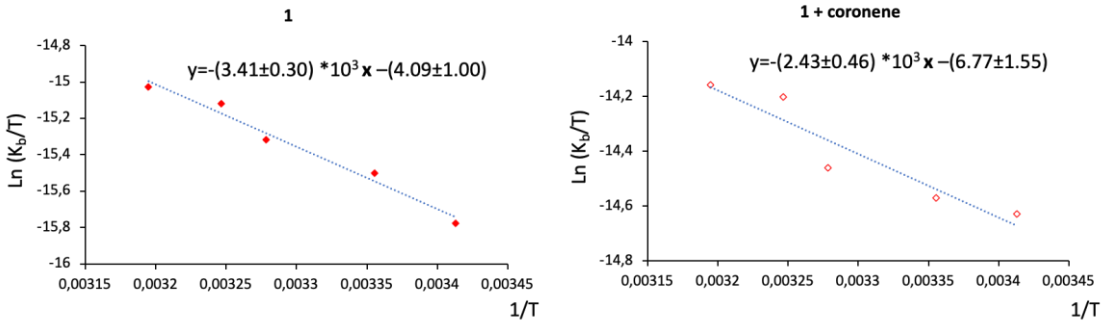
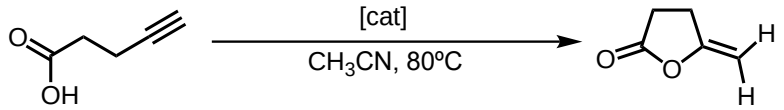


Figure S24. Eyring plot for the oxidative addition of MeI to **1**. $\Delta H^{\neq}$ and $\Delta S^{\neq}$ calculated from the linear equation y = mx + b as: $\Delta H^{\neq}$ = m x R; $\Delta S^{\neq}$ = [b - ln(k_B/h)] x R, with R = 1.98 $calmol^{-1}K^{-1}$; k_B = $1.38x10^{-23}$ $calK^{-1}$ and h = $6.626x10^{-34}$ Js^{-1}.

5. Catalytic studies

Cyclization of 4-pentynoic acid to γ-methylene-γ-butyrolactone



Scheme S2. Cyclization of 4-pentynoic acid to γ-methylene-γ-butyrolactone.

General procedure. All the catalytic experiments and manipulations were conducted under nitrogen atmosphere. In a high pressure Schlenk tube fitted with a Teflon cap, complex **1** (1.0 mol %) was added to a 0.15 M solution of 4-pentynoic acid (0.30 mmol) and 1,3,5-trimethoxybenzene (0.15 mmol) in CH_3CN (2 mL). For the reactions carried out in the presence of a π-π-stacking additive, coronene or pyrene (10 mol % with respect to the substrate) was also introduced in the reaction vessel. The mixture was heated at 80 °C. Yields were determined by ^{1}H-NMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. γ-Methylene-γ-butyrolactone was isolated as the only product. Spectroscopic data were consistent with those reported in the literature.[3] **^{1}H NMR** (300 MHz, CD_3Cl): δ 4.74-4.69 (m, 1H, C=CH_2), 4.32-4.26 (m, 1H, C=CH_2), 2.88-2.83 (m, 2H, CH_2), 2.65-2.61 (m, 2H, CH_2).

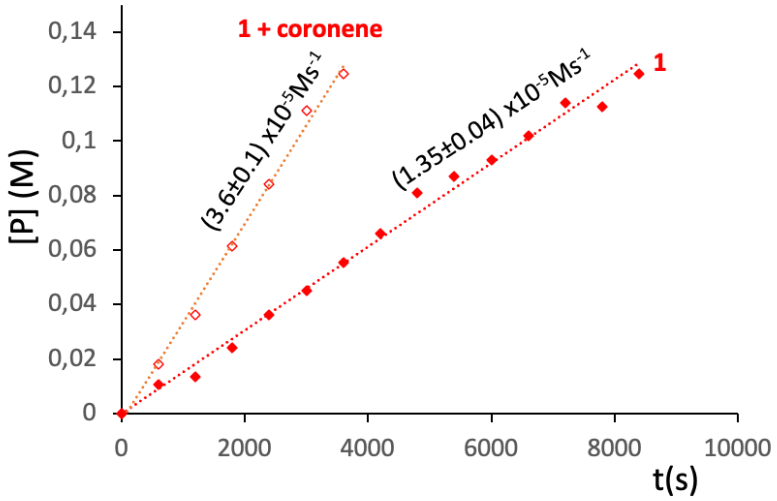


Figure S25. Time-dependent reaction profiles for the cyclization of 4-pentynoic acid using catalyst **1** in the presence and in the absence of coronene. The figure also shows the kinetic constants for each reaction.

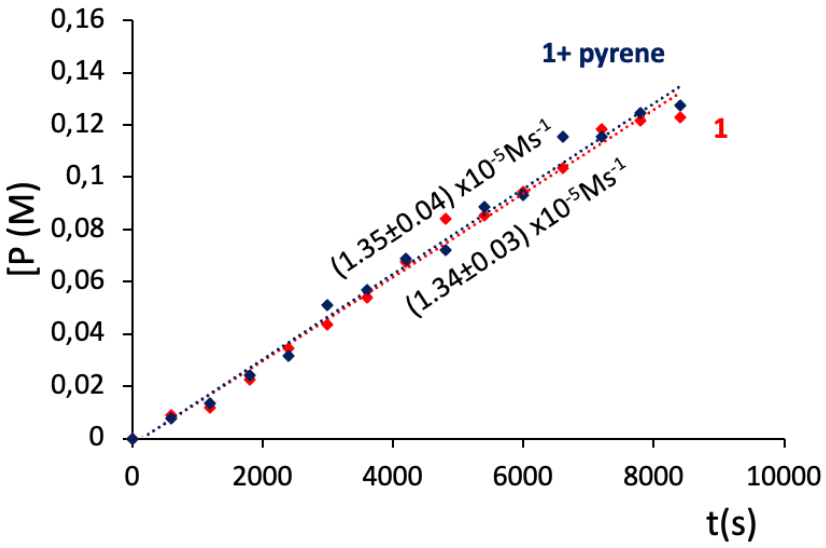


Figure S26. Time-dependent reaction profiles f or the cyclization of 4-pentynoic acid using catalyst **1** in the presence and in the absence of pyrene. The figure also shows the kinetic constants for each reaction.

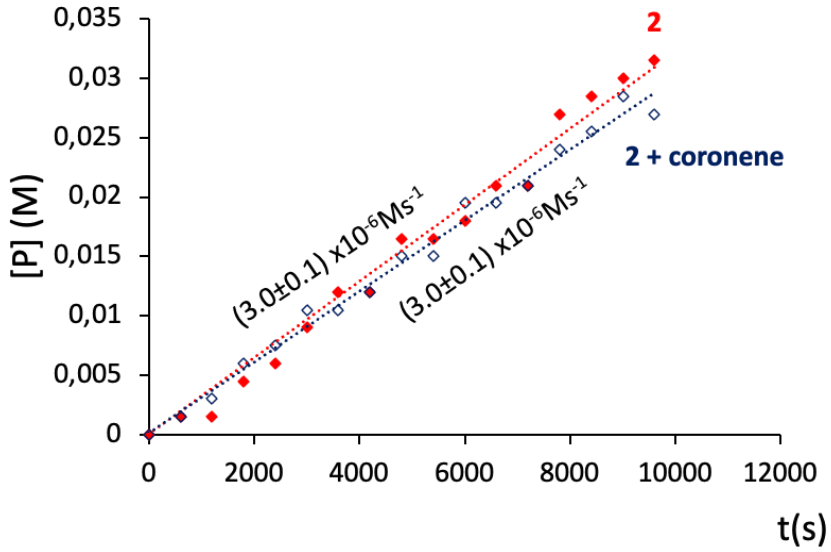


Figure S27. Time-dependent reaction profiles f or the cyclization of 4-pentynoic acid using catalyst **2** in the presence and in the absence of coronene. The figure also shows the kinetic constants for each reaction.

6. References

[1] E. Peris, J. A. Loch, J. Mata, R. H. Crabtree, *Chem. Commun.* **2001**, 201-202.

[2] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176-2179.

[3] S. Elgafi, L. D. Field, B. A. Messerle, *J. Organomet. Chem.* **2000**, *607*, 97-104.