Copper-Free One-Pot Sonogashira-Type Coupling for the Efficient Preparation of Symmetric Diarylalkyne Ligands for Metal-Organic Cages

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Submitted date: 22/01/2021 • Posted date: 25/01/2021
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Citation information: Lehr, Marc; Paschelke, Tobias; Bendt, Victoria; Petersen, Andre; Pietsch, Lorenz; Harders, Patrick; et al. (2021): Copper-Free One-Pot Sonogashira-Type Coupling for the Efficient Preparation of Symmetric Diarylalkyne Ligands for Metal-Organic Cages. ChemRxiv. Preprint. https://doi.org/10.26434/chemrxiv.13625783.v1

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Copper-Free One-Pot Sonogashira-Type Coupling for the Efficient Preparation of Symmetric Diarylalkyne Ligands for Metal-Organic Cages

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Bipyridine- and benzimidazole-based ligands for the self-assembly of Co₄L₄ cages were synthesised in short reaction times and high isolated yields directly from aryl halide precursors using a copper-free one-pot Sonogashira-type coupling. This one-pot method circumvents the often time-consuming and challenging ligand synthesis for the preparation and application of cages.

Palladium catalysed cross-coupling reactions are powerful synthetic methods for carbon-carbon bond formation in modern organic chemistry.¹ In particular, Sonogashira cross-coupling reactions²-⁴ have been used extensively for the synthesis of diarylalkynes in natural products,⁵ conjugated oligomers/polymeris in materials science,⁶,⁷ and ligands/building blocks⁸-²⁰ in coordination chemistry and supramolecular chemistry due to their typically high yields and tolerance of a wide range of functional groups.

Symmetric diarylalkynes find application in diverse fields since they are precursors in the synthesis of hexaarylbenzene derivatives,²¹,²² building blocks for light-emitting materials²³ and inorganic heterocycles²⁴ as well as building blocks in supramolecular architectures.⁹, ¹⁰, ¹³ However, their preparation is typically a multi-step synthesis, often involving long reaction times and multiple purification steps, resulting in overall lower yields and making scale-up for applications difficult (black route, Scheme 1).²³ Glaser coupling²⁵-²⁷ can also take place in the presence of the copper co-catalyst with traces of oxygen, leading to side-product formation² and difficult purifications. As a result, one-pot cross-coupling methods using a variety of acetylene sources (e.g. gaseous acetylene,²⁹-³¹ calcium carbide,³² propionic acid³³ and silyl-protected alkynes³⁴-³⁶) as well as copper-free Sonogashira-type couplings³², ³³, ³⁵, ³⁷, ³⁸ (e.g. replacing the copper co-catalyst and amine with tetrabutylammonium fluoride (TBAF)³⁷, ³⁸) have been developed to overcome these problems, respectively.

Ligand synthesis is a bottleneck for the self-assembly and application of metal-organic cages¹⁴-²⁰ due to multi-step syntheses and challenging purifications. Diarylalkyne-based ligands are appealing given their potential synthesis via a one-pot procedure and further functionalisation via the alkyne functionality, e.g. through post-assembly modification.¹⁰ However, most one-pot Sonogashira couplings have been reported for carbocyclic rather than heterocyclic diarylalkynes.³⁶

We report the efficient synthesis of symmetric diarylalkyne ligands 1a-c and 2a-b for metal-organic cages 3a-c and 4a-b (Figure 1) via a copper-free one-pot procedure using trimethylsilylethylene as the acetylene source and TBAF functioning as a base, activator and deprotection reagent (blue route, Scheme 1). In addition to significantly reducing the synthetic burden from a 3 step synthesis with long overall reaction time to a single 3 hour step, the ligands were prepared in high isolated yields (32-92%) for a one-pot procedure. The proof-of-principle for large scale ligand synthesis was also demonstrated. Thus, this method enables rapid access to ligands for metal-organic cages from suitable aryl halide building blocks and this will facilitate the discovery of new cages as well as the translation of cages to applications.

We recently reported that the synthesis of ligand 1a³⁹-⁴¹ could be reduced from three to two steps using TBAF for the in situ deprotection of the TMS protected alkyne (first step in black route, Scheme 2).¹³ However, the Glaser by-product was also obtained in the final Sonogashira coupling using copper(I) iodide in some instances. Mori³⁷ and Li³⁸ reported copper- and amine-free Sonogashira couplings between terminal alkynes and aryl halides, including aryl chlorides, with short reaction times and good to excellent yields using TBAF as an activator. It is proposed that the TBAF activates and stabilises the Pd(0) species, deprotonates the alkyne and acts as a phase-transfer catalyst.³⁸ Therefore, we envisaged TBAF could play the role of not only a deprotection reagent but also activator and base in a one-pot procedure while preventing the formation of Glaser by-products.

Scheme 1. Multi-step synthesis of diarylacetylenes via sequential Sonogashira cross-coupling reactions (black) and the copper-free one-pot Sonogashira method (blue) in this work.
Having demonstrated that TBAF functions in both the deprotection and Sonogashira-type steps (black route, Scheme 2), the one-pot synthesis of ligand 1a was carried out under analogous conditions, using 1 eq. of 5a and 0.5 eq. of TMSA (blue route, Scheme 2). Ligand 1a was isolated in 40% yield and 12% of the starting material 5a was also recovered (Table 1, entry 1). This with the observation of intense gas release upon addition of TBAF suggested immediate deprotection of TMSA’s silyl protecting group, resulting in the release of gaseous acetylene. While no starting material was recovered upon increasing the TMSA to 1 eq., a similar yield was obtained (Table 1, entry 2).

Table 1. Initial one-pot Sonogashira-type experiments for the preparation of 1a from 5a.\(^a\)

| entry | TMSA (eq.) | Reaction Vessel | Yield\(^c\) (%) |
|-------|------------|----------------|-----------------|
| 1     | 0.5        | RBF            | 40              |
| 2     | 1          | RBF            | 35              |
| 3     | 0.5        | PT             | 40              |
| 4     | 1          | PT             | 53              |
| 5\(^a\)| 1          | RBF            | 54              |

\(^{a}\)Reaction conditions: 1 eq. 5a (723 \(\mu\)mol), 5 mol\% Pd(PPh\(_3\))Cl\(_2\), 6 eq. 1 M TBAF in THF (not degassed), N\(_2\) atmosphere. RBF = round bottom flask, PT = pressure tube. \(^{b}\)Degassed 1 M TBAF in THF. \(^{c}\)Isolated yield after column chromatography.

The reaction vessel was then changed to a pressure tube to investigate if acetylene loss over the course of the reaction was significant. While the yield did not improve with a stoichiometric amount of TMSA (Table 1, entry 3), the yield could be improved to 53% by using an excess of TMSA (Table 1, entry 4). In entries 1-4 the reactions were carried out under a nitrogen atmosphere without degassing the TBAF solution in THF before addition to the reagents. Degassing of the TBAF solution by bubbling nitrogen was unnecessary as a similar yield was obtained when this additional step was performed (Table 1, entry 5).

In an effort to optimise the yield further, various palladium catalysts were screened (Table 2). Compared to Pd(PPh\(_3\))Cl\(_2\) (Table 2, entry 1), the catalysts Pd(OAc)\(_2\) (Table 2, entry 2) and Pd(dppf)Cl\(_2\) (Table 2, entry 3) gave lower yields. However, the reaction with Pd(PPh\(_3\))Cl\(_2\) (Table 2, entry 4) gave the product in the improved yield of 62%. As a precaution, the TBAF solution for this reaction was degassed due to the oxygen sensitivity of the catalyst.\(^{42}\)

Table 2. Catalyst screening of one-pot Sonogashira-type experiments for the preparation of 1a from 5a.\(^a\)

| entry | Pd catalyst | Temp. (°C) | Time (h) | Yield\(^c\) (%) |
|-------|-------------|------------|----------|-----------------|
| 1     | Pd(PPh\(_3\))Cl\(_2\) | 70         | 3        | 53              |
| 2     | Pd(OAc)\(_2\)       | 70         | 3        | 13              |
| 3     | Pd(dppf)Cl\(_2\)    | 70         | 3        | 40              |
| 4\(^a\)| Pd(PPh\(_3\))Cl\(_2\) | 70         | 3        | 62              |

\(^{a}\)Reaction conditions: 1 eq. 5a (723 \(\mu\)mol), 1 eq. TMSA, 5 mol\% Pd catalyst, 6 eq. non-degassed 1 M TBAF in THF, pressure tube, N\(_2\) atmosphere. \(^{b}\)Degassed 1 M TBAF in THF. \(^{c}\)Isolated yield after column chromatography.

Further experiments were carried out to investigate if the reaction parameters (time, temperature, catalytic loading, aryl halide reactivity) can be reduced without significantly impacting the yield (Table 3). With a 1 hour...
instead of a 3 hour reaction time, ligand 1a was still isolated in good yield and no starting material was recovered (Table 3, entry 2). However, reducing the reaction time further to 30 mins led to a significant decrease in the yield and 40% of the starting material was recovered (Table 3, entry 3). Although a shorter reaction time is possible, 3 hours was chosen for subsequent experiments to ensure full consumption of the starting material. Heating the reaction was necessary since the coupling did not take place at room temperature and 98% of the starting material was recovered, even with a longer reaction time of 20 hours (Table 3, entry 4). Although a ten-fold lower catalytic loading of 0.5 mol% still gave 1a in 32% yield, the reaction was not complete within 3 hours since 41% of the starting material was recovered (Table 3, entry 5). Given the short reaction time with aryl bromide 1a, the one-pot procedure was also extended to the less reactive aryl chloride 5d (SI, Section S2.1.2) but no product was obtained (Scheme S2).

| Table 3. Catalyst loading, temperature and reaction time screening of one-pot Sonogashira-type experiments for the preparation of 1a from 5a. |
|---|---|---|---|
| entry | Pd cat. (mol%) | Temp. (°C) | Time (h) | Yield* (%) |
| 1 | 5 | 70 | 3 | 62 |
| 2 | 5 | 70 | 1 | 50 |
| 3 | 5 | 70 | 0.5 | 23 (40) |
| 4 | 5 | rt | 20 | 0 (98) |
| 5 | 0.5 | 70 | 3 | 32 (41) |

*Reaction conditions: 1 eq. 5a (723 µmol), Pd(PPh₃)₄, 1 eq. TMSA, 6 eq. degassed 1 M TBAF in THF, pressure tube, N₂ atmosphere. * Isolated yield after column chromatography. * Recovered 5a.

Through the development and optimisation of the copper-free one-pot procedure (SI, Section 2.1.3.2), ligand 1a can now be prepared both more efficiently and without the formation of Glaser by-products. Li and co-authors proposed a mechanism for TBAF promoted cross-couplings38 and we propose a similar mechanism for the one-pot procedure. Compared to the previous 3 step synthesis of ligand 1a with a total reaction time over 40 hours,39, 40, 43, 44 this one-pot procedure gives the ligand in the significantly reduced overall reaction time of 3 hours. Furthermore, the overall isolated ligand yield has been significantly improved from 35% for the shortened 2 step synthesis (black route, Scheme 2) and 40% yield in initial one-pot experiments to 62% yield following optimisation (blue route, Scheme 2). This optimised yield corresponds to an average yield of 85% for each of the 3 steps (Scheme 1). Finally, the scalability of the procedure was investigated by increasing the reaction scale ten-fold to 1.7 g of 1a (SI, Section 2.1.3.3). A similar isolated yield of 60% was obtained following a chromatography-free purification (Scheme 2).

Having optimised the one-pot conditions for the synthesis of 1a, we extended the reaction scope to the related ligands 1b, 1c and 2a based on 6-methyl-2,2’-bipyridine and benzimidazole coordination motifs, respectively (Figure 1). Ligand 1b was synthesised in a comparable yield to 1a, whereas 1c was obtained in a lower yield, attributed to a steric clash of the methyl substituent in close proximity to the cross-coupling site (Scheme S1). The synthesis of NH-benzimidazole 2a was attempted using the same conditions (Scheme S5), however, only starting material was recovered. We proposed deuteration of the imidazole under the basic conditions prevented the coupling taking place and therefore, the NH was substituted with a methyl (6b) or benzyl (6c) group (Scheme S5). Indeed, ligands 2b and 2c were isolated in good to excellent yields.‡

We previously reported the self-assembly of cage 3a3 from 1a and Co(NTf₂)₂ in CD₃CN. Self-assemblies with ligands 1b-c and 2b-c were investigated using analogous conditions; four equivalents of Co(NTf₂)₂ and six equivalents of the respective ligand were heated at 50 °C in CD₃CN for 20 hours. Cage 4b was prepared in situ only, whereas cages 3b, 3c and 4a were isolated by precipitation with diethyl ether. Characterisation using our recently reported paramagnetic NMR spectroscopy toolbox¹³ and mass spectrometry was consistent with tetrahedral Co₄L₆ cages (Figures S55-81). Further investigation of these cages and their properties will be the focus of future work.

In summary, we have reported a copper-free one-pot Sonogashira-type procedure for the preparation of symmetric heterocyclic diarylalkynes. We have applied this method to the synthesis of ligands 1a-c and 2b-c, which can be used to self-assemble a series of novel metal-organic cages 3b-c and 4a-b. This procedure has the following advantages: reduction of a 3 step synthesis to 1 step; good to excellent isolated yields (32-92%) for a one-pot synthesis; short reaction times of typically 3 hours; scalability; copper-free conditions preventing the formation of Glaser side-products; commonly used reagents that are commercially available and relatively inexpensive.

This one-pot procedure now enables rapid access to symmetric diarylalkynes ligands directly from aryl halide substrates both on a small and large scale. This reduces the synthetic burden for scale-up as well as incorporating additional functionality for applications. Libraries of ligands could also be generated for high-throughput screening of self-assembly conditions enabling the discovery of new cages. Given the application of symmetric diarylalkynes in numerous fields, this straightforward copper-free one-pot procedure could also be extended to other carbocyclic and heterocyclic aryl halide substrates and allow scale-up for applications.

Conflicts of interest
There are no conflicts to declare.

Acknowledgements
We thank the Deutsche Forschungsgemeinschaft (DFG, project numbers 413396832 and 429518153) for financial support. We thank the spectroscopy department and Dr Claus Bier for NMR and mass spectral data collection. We thank Felix Piontek and Etienne Rommens for preliminary studies and Niclas Grocholski for the synthesis of additional ligand.
Supporting Information

Copper-Free One-Pot Sonogashira-Type Coupling for the Efficient Preparation of Symmetric Diarylalkyne Ligands for Metal-Organic Cages

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Materials andMethods

Solvents and reagents were commercially obtained and used without further purification. Anhydrous tetrahydrofuran was dried using a Pure Solv MD-5 apparatus from Innovative Technologies. Tetrabutylammonium fluoride (1 M in tetrahydrofuran) for use in reactions with Pd(PPh₃)₄ was degassed by bubbling nitrogen through the solution for 24 h ensuring solvent evaporation did not affect the reagent’s concentration. Pd(PPh₃)₄ was stored under a nitrogen atmosphere due to its air sensitivity. Pressure tubes (15 mL) were purchased from FengTecEx GmbH and as a precaution, the reactions using pressure tubes were performed behind a blast shield.

For thin-layer chromatography Macherey Nagel plates (Polygram®SIL G/UV254, coating thickness 0.2 mm) equipped with a fluorescence indicator were used. Silica gel with a pore diameter of 0.040-0.063 mm was purchased from Merck. For flash chromatography Biotage® SNAP Ultra columns (10 g, 25 g, 50 g) and Biotage® Sfär Silica HC D columns (10 g, 25 g) were used on an Isolera One from Biotage®.

Centrifugation of the cages was performed using a Grant-Bio LMC-3000.

1.1 NMR Spectroscopy

NMR spectra were recorded on a Bruker Avance 200, a Bruker AvanceNeo 500, or a Bruker Avance 600 spectrometer, the latter being equipped with a cryogenically cooled triple-resonance probe head. Chemical shifts for ¹H, ¹³C, and ¹⁹F spectra are expressed in parts per million (ppm) and coupling constants (J) are reported in Hertz (Hz). ¹H and ¹³C spectra of the diamagnetic compounds were referenced to TMS at 0.0 ppm or TFA-d₁ (δ_H = 11.6 ppm, δ_C = 164.4 ppm) and the chemical shifts of the paramagnetic cages are reported relative to the resonance of the residual methyl proton and carbon of CD₃CN (δ_H = 1.94 ppm, δ_C = 1.32 ppm). The paramagnetic cages were characterised using the paramagnetic NMR toolbox we previously reported.[¹] ¹⁹F spectra were referenced to C₆F₆ at -164.9 ppm. All measurements were carried out at 298 K unless reported otherwise. The following abbreviations are used to describe signal multiplicity for ¹H, ¹³C and ¹⁹F NMR spectra: s: singlet, d: doublet, t: triplet, m: multiplet, br: broad.

1.2 Mass Spectrometry

Mass spectra using electron ionization (EI-MS) were recorded on a Jeol AccuTOF™. High resolution electrospray ionisation mass spectrometry (ESI-MS) was carried out on a Thermo Scientific Q Exactive™ Plus (spray voltage 3-4 eV, capillary temperature 40-50 °C) infused from a Harvard syringe pump at a rate of 5-10 μL per minute.

1.3 Infrared Spectroscopy

Infrared spectra were recorded on a 1600 series FT-IR spectrometer from Perkin Elmer, equipped with an A531-G Golden-Gate-Diamond-ATR-Unit. For analysis, the intensities were classified as weak (w), medium (m) and strong (s).

1.4 Melting Point

Melting points were measured using a Melting Point M-560 from Büchi.
2 Ligand Synthesis

2.1 Bipyridine-Based Ligands

The bipyridine-based ligands 1a-c were prepared according to Scheme S1. The precursor 5-bromo-2,2'-bipyridine (5a) was prepared according to a literature known procedure\cite{2} and the precursors 5-bromo-6'-methyl-2,2'-bipyridine (5b) and 5-bromo-6-methyl-2,2'-bipyridine (5c) were synthesised adapting this procedure. Although the three step synthesis of 1,2-di([2',2''-bipyridin]-5'-yl)ethyne (1a) is literature known,\cite{3} we previously reported a shortened synthesis with an in situ deprotection of the TMS-protected alkyne using tetrabutylammonium fluoride.\cite{1}

Scheme S1. Synthesis of the bipyridine-based ligands 1a-1c.

5-Chloro-2,2'-bipyridine (5d) was also prepared from the Negish coupling of 2-bromo-5-chloropyridine and 2-pyridylzinc(II) bromide to test the one-pot procedure with a less reactive aryl halide, however, no product formation was observed (Scheme S2).

Scheme S2. Attempted one-pot synthesis of 1a using the less reactive aryl chloride 5d.
2.1.1 5-Bromo-2,2′-bipyridine (5a)

Adapted from literature procedure.[2]

Under a nitrogen atmosphere 2-iodo-5-bromopyridine (2.00 g, 7.04 mmol) and Pd(PPh₃)₄ (408 mg, 5 mol%) were dissolved in a solution of 2-pyridylzinc(II) bromide (0.5 M in tetrahydrofuran, 14.0 mL, 7.00 mmol). The reaction mixture was heated at 75 °C for 20 h. After cooling to room temperature, sat. ethylenediaminetetraacetic acid (20 mL) and sat. sodium bicarbonate solution (20 mL) were added and the reaction mixture was stirred at room temperature for another 24 h. The aqueous layer was extracted with dichloromethane (3 x 150 mL), the organic layers were combined, dried over magnesium sulfate and filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 5-15 % ethyl acetate/cyclohexane) and the product was obtained as a yellowish solid.

**Yield:** 1.19 g (72%, 5.06 mmol)

The synthesis of compound 5a was also performed on a larger scale with a longer reaction time.

Under a nitrogen atmosphere 2-iodo-5-bromopyridine (7.10 g, 25.0 mmol) and Pd(PPh₃)₄ (1.44 g, 5 mol%) were dissolved in a solution of 2-pyridylzinc(II) bromide (0.5 M in tetrahydrofuran, 50.0 mL, 25.0 mmol). The reaction mixture was heated at 75 °C for 48 h. After cooling to room temperature, sat. ethylenediaminetetraacetic acid (150 mL) and sat. sodium bicarbonate solution (150 mL) were added and the reaction mixture was stirred at room temperature for another 24 h. The aqueous layer was extracted with dichloromethane (3 x 150 mL), the organic layers were combined, dried over magnesium sulfate and filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 5-15 % ethyl acetate/cyclohexane) and the product was obtained as a yellowish solid.

**Yield:** 4.19 g (71%, 17.8 mmol)

The analytical data was consistent with literature data.[4]

1H NMR (500 MHz, CDCl₃, 298 K, TMS) δ (ppm): 8.72 (d, 4J = 2.4 Hz, 1H, H₄), 8.67 (ddd, 3J = 4.8 Hz, 4J = 1.8 Hz, 5J = 0.8 Hz, 1H, H₅), 8.38 (dt, 3J = 7.8 Hz, 4J = 1.0 Hz, 1H, H₆), 8.33 (d, 3J = 8.5 Hz, 1H, H₇), 7.94 (dd, 3J = 8.5 Hz, 4J = 2.4 Hz, 1H, H₈), 7.83 (td, 3J = 7.8 Hz, 4J = 1.8 Hz, 1H, H₉), 7.33 (ddd, 3J = 7.8 Hz, 3J = 4.8 Hz, 4J = 1.2 Hz, 1H, H₁₀).

13C NMR (126 MHz, CDCl₃, 298 K) δ (ppm): 155.1 (C₆), 154.5 (C₇), 150.2 (C₈), 149.2 (C₉), 139.5 (C₁₀), 137.1 (C₁₁), 124.0 (C₁₂), 122.4 (C₁₃), 121.2 (C₁₄), 121.0 (C₁₅).

HRMS (EI, 70 eV) m/z: 233.97939 [M]+ (calculated: 233.97926 for C₁₁H₇Br₂N₂), 235.97764 [M]+ (calculated: 235.97721 for C₁₁H₇Br₂N₂).

FT-IR: v = 3260.2 (w), 2248.9 (w), 1586.2 (w), 1570.3 (w), 1542.1 (m), 1496.9 (w), 1458.4 (s), 1433.5 (m), 1370.6 (w), 1243.1 (w), 1145.3 (w), 1090.0 (w), 1061.1 (w), 1021.9 (m), 992.5 (w), 927.9 (w), 905.9 (w), 858.2 (m), 797.3 (s), 749.6 (s), 648.9 (w), 620.4 (w), 593.8 (w), 564.0 (w) cm⁻¹.

M. p.: 76 °C.
2.1.2 5-Chloro-2,2'-bipyridine (5d)

Under a nitrogen atmosphere 2-bromo-5-chloropyridine (577 mg, 3.00 mmol) and Pd(PPh₃)₄ (173 mg, 5 mol%) were dissolved in a solution of 2-pyridylzinc(II) bromide (0.5 M in tetrahydrofuran, 6.0 mL, 3.00 mmol). The reaction mixture was heated at 75 °C for 18 h. After cooling to room temperature, sat. ethylenediaminetetraacetic acid (40 mL) and sat. sodium bicarbonate solution (40 mL) were added and the reaction mixture was stirred at room temperature for another 2 h. The aqueous layer was extracted with dichloromethane (3 x 100 mL), the organic layers were combined, dried over magnesium sulfate and filtered. The solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 5-15% ethyl acetate/cyclohexane) and the product was obtained as a colourless solid.

**Yield:** 276 mg (48%, 1.45 mmol)

**1H NMR** (600 MHz, CDCl₃, 298 K, TMS) δ (ppm): 8.66 (unres. ddd, ³J = 4.7 Hz, 1H, H₉), 8.61 (d, ⁴J = 2.2 Hz, 1H, H₇), 8.37 (d, ³J = 8.5 Hz, 1H, H₅), 8.36 (d, ³J = 7.8 Hz, 1H, H₆), 7.81 (td, ³J = 7.8 Hz, ⁴J = 1.7 Hz, 1H, H₄), 7.78 (dd, ³J = 8.5 Hz, ⁴J = 2.2 Hz, 1H, H₆), 7.32 (ddd, ³J = 7.8 Hz, ³J = 4.7 Hz, ⁴J = 0.9 Hz, 1H, H₆).
$^{13}$C NMR (151 MHz, CDCl$_3$, 298 K, TMS) δ (ppm): 155.1 ($C_e$), 154.3 ($C_f$), 149.2 ($C_a$), 148.0 ($C_i$), 137.0 ($C_e$), 136.7 ($C_h$), 132.4 ($C_i$), 124.0 ($C_b$), 121.9 ($C_g$), 121.0 ($C_d$).

HRMS (ESI) m/z: 191.03689 [M+H]$^+$ (calculated: 191.03705 for C$_{10}$H$_8$N$_2$Cl).

M. p.: 76 °C.

Figure S3. $^1$H NMR spectrum (600 MHz, CDCl$_3$, 298 K, TMS) of 5-chloro-2,2'-bipyridine (5d).

Figure S4. $^{13}$C NMR spectrum (151 MHz, CDCl$_3$, 298 K, TMS) of 5-chloro-2,2'-bipyridine (5d).
Figure S5. $^1$H-$^1$H COSY NMR spectrum (600 MHz, CDCl$_3$, 298 K, TMS) of 5-chloro-6'-methyl-2,2'-bipyridine (5d).

Figure S6. $^1$H-$^{13}$C HSQC NMR spectrum (600 MHz/151 MHz, CDCl$_3$, 298 K, TMS) of 5-chloro-6'-methyl-2,2'-bipyridine (5d).
**Figure S7.** $^1$H-$^{13}$C HMBC NMR spectrum (600 MHz/151 MHz, CDCl$_3$, 298 K, TMS) of 5-chloro-6'-methyl-2,2'-bipyridine (5d).

2.1.3 1,2-Di([2',2''-bipyridin]-5'-yl)ethyne (1a)

2.1.3.1 Procedure in a Round-Bottomed Flask

5-Ethynyl-2,2'-bipyridine (6) was prepared according to the literature procedure.$^{[1]}$ Ligand 1a was synthesised from 5a and 6 (Scheme S3) adapting reported conditions$^{[1]}$ but replacing copper(I) iodide and the amine with TBAF based on the precedence by Mori and co-workers.$^{[5]}$ To have the same amount of palladium catalyst available as for the one-pot reaction, a catalytic loading of 10 mol% relative to 5a was used for the reaction.

![Scheme S3](image)

**Scheme S3.** Synthesis of 1a from Sonogashira-type coupling of 5a and 6 using TBAF.
Under a nitrogen atmosphere 5-bromo-2,2'-bipyridine (5a) (85.1 mg, 362 µmol), 5-ethynyl-2,2'-bipyridine (6) (65.2 mg, 362 µmol) and Pd(PPh₃)₂Cl₂ (25.4 mg, 10 mol%), to have the same amount of palladium catalyst as the one-pot conditions) were added to a three-neck flask. Tetrabutylammonium fluoride (1 M in tetrahydrofuran, 4.3 mL, 4.30 mmol) was added and the reaction mixture heated at 70 °C for 3 h. After cooling to room temperature water was added, the mixture was extracted with dichloromethane (3 x 33 mL), dried over magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 10-20 % ethyl acetate/cyclohexane).

**Yield:** 66.3 mg (55%, 198 µmol)

### 2.1.3.2 Procedure for the Optimised One-Pot Reaction in a Pressure Tube

All reactions to optimise the reaction conditions for the one-pot synthesis of 1a were performed on the same scale (Scheme S4). As a precaution, the pressure tube reactions were performed behind a blast shield. Initial optimisation attempts used the catalyst Pd(PPh₃)₂Cl₂ and purification by column chromatography was necessary for removal of TBAF. The use of Pd(PPh₃)₄ instead of Pd(PPh₃)₂Cl₂ simplified removal of TBAF since ligand 1a precipitated after cooling the reaction mixture down to room temperature. Nevertheless, purification by column chromatography was still performed to ensure no product loss due to the partial solubility of 1a in THF, the same for 1c. For the analogous one-pot syntheses of ligands 1b, 2b-2c, column chromatography was not necessary since the ligands are not soluble in THF and pure ligand could be isolated in good yields by washing the precipitate with cold THF and in some cases, a subsequent acid extraction.

In cases where impure ligand was obtained following column chromatography or washing with cold THF, purification by acid extraction was performed as described: the crude product was dissolved in dichloromethane (10 mL) and extracted with hydrochloric acid (3 x 10 mL, 6 M). The layers were separated, the pH value of the aqueous layer was adjusted to 7 with 25% ammonia solution. The product was either filtered and dried or reextracted with dichloromethane (25 mL) and the solvent was removed in vacuo.

![Diagram](image.png)

**Scheme S4.** Synthesis of 1a from one-pot Sonogashira-type coupling of 5a.

5-Bromo-2,2'-bipyridine (5a) (170 mg, 723 µmol) and Pd(PPh₃)₄ (41.8 mg, 5 mol%) were added to a pressure tube and evacuated for five minutes. Using counterflow technique, degassed tetrabutylammonium fluoride (1 M in tetrahydrofuran, 4.30 mL, 4.30 mmol) and trimethylsilylacetylene (100 µL, 723 µmol) were added. The pressure tube was immediately closed and the reaction mixture was heated at 70 °C for 3 h. After cooling to room temperature, the mixture was washed with water (50 mL) and the aqueous layer was extracted with dichloromethane (3 x 33 mL). The organic layers were combined, dried over magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 10-20% ethyl acetate/cyclohexane) to give the product as a colourless solid.

**Yield:** 74.9 mg (62%, 224 µmol)
2.1.3.3 Large Scale Reaction
5-Bromo-2,2'-bipyridine (5a) (1.70 g, 7.23 mmol) and Pd(PPh$_3$)$_4$ (418 mg, 5 mol%) were added to a pressure tube and evacuated for five minutes. Using counterflow technique, degassed tetrabutylammonium fluoride (1 M in tetrahydrofuran, 43 mL, 43.0 mmol) and trimethylsilylacetylene (1.0 mL, 7.23 mmol) were added. The pressure tube was immediately closed and the reaction mixture was heated at 70 °C for 3 h. After cooling to room temperature, the precipitate was collected by filtration and was dissolved in dichloromethane (100 mL) and the organic layer was extracted with hydrochloric acid (3 x 30 mL, 6 M). The layers were separated and the pH value of the aqueous layer was adjusted to 7 with 25% ammonia solution and the precipitate was collected.

**Yield:** 720 mg (60%, 2.15 mmol)

The analytical data from the various reactions was consistent with literature data.$^{[3a, 3c]}$

$^1$H NMR (500 MHz, CDCl$_3$, 298 K, TMS) δ (ppm): 8.85 (dd, $^3$J = 2.2 Hz, $^5$J = 0.8 Hz, 2H, $H_I$), 8.71 (ddd, $^3$J = 4.8, $^4$J = 1.8 Hz, $^5$J = 0.8 Hz, 2H, $H_B$), 8.47-8.45 (m, 2H, $H_D$), 8.45-8.43 (m, 2H, $H_H$), 7.99 (dd, $^3$J = 8.3 Hz, $^4$J = 2.2 Hz, 2H, $H_H$), 7.85 (td, $^3$J = 7.7 Hz, $^4$J = 1.8, 2H, $H_B$), 7.34 (ddd, $^3$J = 7.7 Hz, $^4$J = 4.8 Hz, $^5$J = 1.2 Hz, 2H, $H_B$).

$^{13}$C NMR (126 MHz, CDCl$_3$, 298 K, TMS) δ (ppm): 155.3 ($C_e$), 155.2 ($C_i$), 151.7 ($C_j$), 149.2 ($C_a$), 139.5 ($C_h$), 137.1 ($C_c$), 124.1 ($C_b$), 121.5 ($C_d$), 120.5 ($C_g$), 119.7 ($C_c$), 90.5 ($C_k$).

HRMS (EI, 70 eV) $m/z$: 334.12117 [M]$^+$ (calculated: 334.12185 for C$_{22}$H$_{14}$N$_4$).

FT-IR: $\tilde{\nu}$ = 2360.2 (w), 2248.9 (w), 1586.2 (w), 1570.3 (w), 1542.1 (m), 1496.9 (w), 1458.4 (s), 1433.5 (m), 1370.6 (w), 1243.1 (w), 1145.3 (w), 1090.0 (w), 1061.1 (w), 1021.9 (m), 992.5 (w), 927.9 (w), 905.9 (w), 858.2 (m), 797.3 (s), 749.6 (s), 648.9 (w), 620.4 (w), 593.8 (w), 564.0 (w) cm$^{-1}$.

**M. p.:** 228 °C.

![1H NMR spectrum](image)

**Figure S8.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([2',2''-bipyridin]-5'-yl)ethyne (1a).
Figure S9. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([2',2''-bipyridin]-5'-yl)ethyne (1a).

2.1.4 5-Bromo-6'-methyl-2,2'-bipyridine (5b)

Under a nitrogen atmosphere 2-bromo-6-methylpyridine (1.42 g, 8.25 mmol) was suspended in anhydrous tetrahydrofuran (20 mL). The solution was degassed three times using the freeze-pump-thaw technique. Afterwards, the solution was cooled to -78 °C, n-butyllithium (2.5 M in hexane, 3.9 mL, 9.75 mmol) was slowly added and the mixture was stirred at -78 °C for 1 h. Zinc(II) chloride (1 M in tetrahydrofuran, 1.31 g, 9.6 mL, 9.63 mmol) was added and the solution was stirred at -78 °C for 2 h. At this temperature, 2-iodo-5-bromopyridine (1.95 g, 6.87 mmol) and Pd(PPh$_3$)$_4$ (398 mg, 5 mol%) were added and the reaction mixture was stirred at 75 °C for 18 h. After cooling to room temperature, sat. ethylenediaminetetraacetic acid (50 mL) and sat. sodium bicarbonate solution (50 mL) were added and the mixture was stirred for further 2 h. The layers were separated, the aqueous layer was extracted with dichloromethane (3 x 100 mL), the organic layers were combined, dried over magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 10% ethyl acetate/cyclohexane) to obtain the product as a colourless solid.

Yield: 1.21 g (71%, 4.86 mmol)

$^1$H NMR (500 MHz, CDCl$_3$, 298 K, TMS) δ (ppm): 8.70 (dd, $^4$J = 2.4 Hz, $^5$J = 0.6 Hz, 1H, H$_k$), 8.33 (dd, $^3$J = 8.4 Hz, $^5$J = 0.6 Hz, 1H, H$_l$), 8.15 (d, $^3$J = 7.8 Hz, 1H, H$_d$), 7.92 (dd, $^3$J = 8.4 Hz, $^4$J = 2.4 Hz, 1H, H$_i$), 7.70 (t, $^3$J = 7.8 Hz, 1H, H$_s$), 7.18 (d, $^3$J = 7.8 Hz, 1H, H$_d$), 2.63 (s, 3H, H$_a$).

$^{13}$C NMR (126 MHz, CDCl$_3$, 298 K, TMS) δ (ppm): 158.1 (C$_b$), 155.0 (C$_g$), 154.6 (C$_i$), 150.1 (C$_d$), 139.4 (C$_i$), 137.2 (C$_g$), 123.6 (C$_o$), 122.5 (C$_h$), 120.9 (C$_e$), 118.0 (C$_o$), 24.6 (C$_a$).

HRMS (El, 70 eV) m/z: 247.99469 [M]$^+$ (calculated: 247.99491 for C$_{11}$H$_9$BrN$_2$), 249.99278 [M]$^+$ (calculated: 249.99286 for C$_{11}$H$_9$BrN$_2$).

FT-IR: $\tilde{\nu}$ = 2920.3 (w), 2307.9 (w), 1751.1 (w), 1593.9 (w), 1566.3 (m), 1547.9 (m), 1448.8 (m), 1366.0 (m), 1285.2 (w), 1247.9 (w), 1154.9 (w), 1124.8 (w), 1082.1 (m), 1003.4 (s).
927.5 (w), 870.0 (w), 848.3 (s), 789.6 (s), 752.9 (s), 738.3 (m), 696.4 (w), 656.1 (w), 631.8 (m), 595.1 (m), 540.9 (w), 513.3 (w) cm\(^{-1}\).

**M. p.:** 91 °C.

**Figure S10.** \(^1\)H NMR spectrum (500 MHz, CDCl\(_3\), 298 K, TMS) of 5-bromo-6'-methyl-2,2'-bipyridine (5b).

**Figure S11.** \(^{13}\)C NMR spectrum (126 MHz, CDCl\(_3\), 298 K, TMS) of 5-bromo-6'-methyl-2,2'-bipyridine (5b).
Figure S12. $^1$H-$^1$H COSY NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 5-bromo-6'-methyl-2,2'-bipyridine (5b).

Figure S13. $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K, TMS) of 5-bromo-6'-methyl-2,2'-bipyridine (5b).
2.1.5 1,2-Di([6"-methyl-2',2''-bipyridin]-5'-yl)ethyne (1b)

5-Bromo-6'-methyl-2,2'-bipyridine (5b) (180 mg, 723 µmol) and Pd(PPh₃)₄ (41.8 mg, 5 mol%) were added to a pressure tube and evacuated for five minutes. Using counterflow technique, degassed tetrabutylammonium fluoride (1 M in tetrahydrofuran, 4.3 mL, 4.30 mmol) and trimethylsilylacetylene (100 µL, 723 µmol) were added, the pressure tube was immediately closed and the reaction mixture was heated at 70 °C for 3 h. Upon cooling, the product precipitated and the precipitate was filtered and was washed with cold tetrahydrofuran (10 mL). The layers were separated and the pH value of the aqueous layer was adjusted to 7 with 25% ammonia solution and the precipitate was collected.

**Yield:** 75.3 mg (58%, 208 µmol)

**'H NMR** (500 MHz, CDCl₃, 298 K, TMS) δ (ppm): 8.84 (dd, ⁴J = 2.1 Hz, ⁵J = 0.8 Hz, 2H, H₈), 8.48 (d, ³J = 8.2 Hz, 2H, H₁₁), 8.23 (d, ³J = 7.8 Hz, 2H, H₁₀), 7.96 (dd, ³J = 8.2 Hz, ⁴J = 2.1 Hz, 2H, H₉), 7.73 (t, ³J = 7.8 Hz, 2H, H₇), 7.19 (d, ³J = 7.8 Hz, 2H, H₈), 2.65 (s, 6H, H₃).

**¹³C NMR** (126 MHz, CDCl₃, 298 K, TMS) δ (ppm): 158.1 (C₇), 155.5 (C₉), 154.7 (C₈), 151.7 (C₄), 139.4 (C₁), 137.3 (C₂), 123.7 (C₃), 120.5 (C₅), 119.5 (C₆), 118.5 (C₈), 90.4 (C₁), 24.6 (C₃).

**HRMS** (El, 70 eV) m/z: 362.15253 [M]+ (calculated: 362.15315 for C₂₄H₁₈N₄).
FT-IR: $\tilde{\nu} = 2920.9$ (w), 2359.9 (w), 1738.9 (w), 1589.9 (m), 1568.0 (w), 1545.6 (m), 1487.1 (w), 1453.3 (m), 1372.2 (m), 1244.7 (w), 1157.0 (w), 1133.6 (w), 1082.9 (m), 1022.9 (w), 997.9 (w), 983.9 (w), 926.3 (w), 901.3 (w), 861.9 (s), 846.3 (w), 799.3 (s), 754.9 (s), 693.6 (m), 644.1 (m), 598.3 (m), 553.1 (w), 517.0 (w) cm$^{-1}$.

M. p.: 227 °C.

Figure S15. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6''-methyl-2',2''-bipyridin]-5'-yl)ethyne (1b).

Figure S16. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6''-methyl-2',2''-bipyridin]-5'-yl)ethyne (1b).
Figure S17. $^1$H-$^1$H COSY NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6"'-methyl-2',2"'-bipyridin]-5'-yl)ethyne. (1b)

Figure S18. $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6"'-methyl-2',2"'-bipyridin]-5'-yl)ethyne (1b).
Under a nitrogen atmosphere, 2-bromopyridine (390 µL, 3.90 mmol) was suspended in anhydrous tetrahydrofuran (12 mL). The solution was degassed using the freeze-pump-thaw technique. Afterwards, the solution was cooled to -78 °C, n-butyllithium (2.5 M in hexane, 1.9 mL, 4.75 mmol) was slowly added and the mixture was stirred at -78 °C for 1 h. Zinc(II) chloride (1 M in tetrahydrofuran, 681 mg, 5.00 mmol) was added and the solution was further stirred at -78 °C for 2 h. At -78 °C, 3,6-dibromo-2-methylpyridine (1.00 g, 3.90 mmol) and Pd(PPh₃)₄ (230 mg, 5 mol%) were added and the reaction mixture was stirred at 75 °C for 19 h. After cooling to room temperature, sat. ethylenediaminetetraacetic acid (25 mL) and sat. sodium bicarbonate solution (25 mL) were added and the mixture was stirred for further 1.5 h. The layers were separated, the aqueous layer was extracted with dichloromethane (3 x 50 mL), the organic layers were combined, dried over magnesium sulfate and the solvent was removed in vacuo. The crude product was purified by flash chromatography (silica gel, 5% ethyl acetate/cyclohexane) to obtain the product as a colourless solid.

**Yield:** 714 mg (74%, 2.87 mmol)

**¹H NMR** (500 MHz, CDCl₃, 298 K, TMS) δ (ppm): 8.66 (ddd, ³J = 4.8 Hz, ⁴J = 1.8 Hz, ⁵J = 0.9 Hz, 1H, H₄), 8.40 (dt, ³J = 7.8 Hz, ⁵J = 0.9 Hz, 1H, H₆), 8.10 (d, ³J = 8.3 Hz, 1H, H₉), 7.91 (d, ³J = 8.3 Hz, 1H, H₆), 7.81 (td, ³J = 7.8 Hz, ⁴J = 1.8 Hz, 1H, H₇), 7.31 (ddd, ³J = 7.8 Hz, ⁴J = 4.8 Hz, ⁵J = 1.2 Hz, 1H, H₈), 2.74 (s, 3H, H₉).

**¹³C NMR** (126 MHz, CDCl₃, 298 K, TMS) δ (ppm): 156.6 (C₁), 155.5 (C₉), 154.2 (C₁), 149.1 (C₈), 140.6 (C₉), 137.0 (C₆), 123.8 (C₈), 121.8 (C₁), 121.1 (C₉), 119.9 (C₇), 25.2 (C₉).
HRMS (EI, 70 eV) m/z: 247.99492 [M]^+ (calculated: 247.99491 for C_{11}H_{9}BrN_{2}), 249.99355 [M]^+ (calculated: 249.99286 for C_{11}H_{9}BrN_{2}).

FT-IR: \( \tilde{\nu} = 2923.9 \text{ (w)}, 2853.05 \text{ (w)}, 1571.8 \text{ (w)}, 1554.9 \text{ (m)}, 1419.5 \text{ (s)}, 1382.5 \text{ (w)}, 1246.8 \text{ (m)}, 1095.6 \text{ (m)}, 1029.7 \text{ (s)}, 996.0 \text{ (w)}, 977.6 \text{ (w)}, 845.7 \text{ (s)}, 789.8 \text{ (s)}, 741.6 \text{ (s)}, 733.0 \text{ (s)}, 718.3 \text{ (m)}, 620.2 \text{ (m) cm}^{-1} \).

M. p.: 88 °C.

**Figure S20.** \(^1\text{H} \text{NMR spectrum (500 MHz, CDCl}_3, 298 \text{ K, TMS)} \) of 5-bromo-6-methyl-2,2'-bipyridine (5c).

**Figure S21.** \(^{13}\text{C} \text{NMR spectrum (126 MHz, CDCl}_3, 298 \text{ K, TMS)} \) of 5-bromo-6-methyl-2,2'-bipyridine (5c).
Figure S22. $^1$H-$^1$H COSY NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 5-bromo-6-methyl-2,2'-bipyridine (5c).

Figure S23. $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K, TMS) of 5-bromo-6-methyl-2,2'-bipyridine (5c).
Figure S24. $^1$H-$^{13}$C HMBC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K, TMS) of 5-bromo-6-methyl-2,2'-bipyridine (5c).

2.1.7 1,2-Di([6'-methyl-2',2''-bipyridin]-5'-yl)ethyne (1c)

5-Bromo-6-methyl-2,2'-bipyridine (5c) (180 mg, 723 µmol) and Pd(PPh$_3$)$_2$Cl$_2$ (41.8 mg, 5 mol%) were added to a pressure tube and evacuated for five minutes. Using counterflow technique, degassed tetrabutylammonium fluoride (1 M in tetrahydrofuran, 4.3 mL, 4.30 mmol) and trimethylsilylacetylene (100 µL, 723 µmol) were added, the pressure tube immediately closed and the reaction mixture stirred at 70 °C for 24 h. After cooling to room temperature, the precipitate was collected by filtration, dissolved in tetrahydrofuran (200 mL) and the solvent removed in vacuo. The crude product was purified by flash chromatography (silica gel, 20-40% ethyl acetate/cyclohexane) to obtain the product as a colourless solid.

Yield: 42.3 mg (32%, 117 µmol)

$^1$H NMR (500 MHz, CDCl$_3$, 298 K, TMS) δ (ppm): 8.69 (d, ³J = 4.9 Hz, ⁴J = 1.8 Hz, ⁵J = 0.9 Hz, 2H, H$_8$), 8.47 (ddd, ³J = 7.9 Hz, ⁴J = 1.2 Hz, ⁵J = 0.9 Hz, 2H, H$_6$), 8.27 (d, ³J = 8.1 Hz, 2H, H$_7$), 7.92 (d, ³J = 8.1 Hz, 2H, H$_6$), 7.83 (td, ³J = 7.9 Hz, ⁴J = 1.8 Hz, 2H, H$_6$), 7.31 (ddd, ³J = 7.9 Hz, ⁴J = 4.9 Hz, ⁵J = 1.2 Hz, 2H, H$_6$), 2.87 (s, 6H, H$_k$).

$^{13}$C NMR (126 MHz, CDCl$_3$, 298 K) δ (ppm): 159.7 (C$_l$), 155.7 (C$_e$), 154.5 (C$_i$), 149.3 (C$_a$), 139.9 (C$_o$), 136.9 (C$_b$), 124.0 (C$_o$), 121.4 (C$_d$), 118.9 (C$_c$), 118.1 (C$_b$), 93.7 (C$_l$), 24.1 (C$_k$).

HRMS (EI, 70 eV) m/z: 362.15271 [M]$^+$ (calculated: 362.15315 for C$_{24}$H$_{18}$N$_4$).
FT-IR: $\tilde{\nu} = 2987.4$ (w), 2252.5 (w), 1572.1 (w), 1546.4 (w), 1450.5 (m), 1433.8 (m), 1393.1 (w), 1246.0 (w), 1094.7 (w), 993.5 (w), 848.8 (m), 794.5 (s), 747.9 (s), 718.1 (w), 615.1 (m) cm$^{-1}$.

M. p.: 218 °C.

**Figure S25.** $^1$H NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6'-methyl-2',2''-bipyridin]-5'-yl)ethyne (1c).

**Figure S26.** $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6'-methyl-2',2''-bipyridin]-5'-yl)ethyne (1c).
Figure S27. $^1$H-$^1$H COSY NMR spectrum (500 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6'-methyl-2',2''-bipyridin]-5'-yl)ethyne (1c).

Figure S28. $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([6'-methyl-2',2''-bipyridin]-5'-yl)ethyne (1c).
Figure S29. $^1$H-$^{13}$C HMBC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K, TMS) of 1,2-di([(6'-methyl-2',2''-bipyridin]-5'-yl)ethyne (1c).

2.2 Benzimidazole-Based Ligands

The benzimidazole-based ligands 2b and 2c were prepared according to Scheme S5. The synthesis of ligand 2a was also attempted from 6a but no coupling took place, attributed to deprotonation of the NH. The synthesis of the benzimidazole based precursors 2-(5'-bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a) and compounds 6b and 6c were adapted from literature procedures.[6]

Scheme S5. Synthesis of the benzimidazole-based ligands 2b and 2c.
2.2.1 2-(5'-Bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a)

In a three-neck flask polyphosphoric acid (40 mL) was added and was preheated to 140 °C. o-Phenylenediamine (1.34 g, 12.4 mmol) and 5-bromopicolinic acid (2.50 g, 12.4 mmol) were added and the reaction mixture was heated at 180 °C for 24 h. The mixture was cooled to 140 °C, poured into water (200 mL) and neutralised to pH 7 with ammonia solution (25%). The precipitate was collected by filtration and, after intensive drying in vacuo, the product was obtained as a colourless solid.

**Yield:** 2.96 g (87%, 10.8 mmol)

The analytical data was consistent with literature data.[6a]

**$^1$H NMR** (500 MHz, DMSO-$d_6$, 298 K) δ (ppm): 13.2 (s, 1H, $H_a$), 8.86 (dd, $^4J = 2.3$ Hz, $^5J = 0.8$ Hz, 1H, $H_b$), 8.26 (dd, $^3J = 8.5$ Hz, $^5J = 0.8$ Hz, 1H, $H_j$), 8.23 (dd, $^3J = 8.5$ Hz, $^4J = 2.3$ Hz, 1H, $H_i$), 7.71 (d, $^3J = 7.8$ Hz, 1H, $H_c$), 7.54 (d, $^3J = 7.8$ Hz, 1H, $H_d$), 7.29-7.18 (m, 2H, $H_{d,e}$).

**$^{13}$C NMR** (126 MHz, DMSO-$d_6$, 298 K) δ (ppm): 150.0 ($C_m$), 149.7 ($C_h$), 147.2 ($C_i$), 143.7 ($C_{b/g}$), 140.1 ($C_l$), 134.9 ($C_{c/f}$), 123.3 ($C_{a/e}$), 122.9 ($C_{a/e}$), 122.0 ($C_{a/e}$), 119.3 ($C_{c/f}$), 112.0 ($C_{c/f}$).

**HRMS** (EI, 70 eV) m/z: 272.98975 [M]$^+$ (calculated: 272.99016 for $C_{12}H_{87}^9BrN_3$), 274.98788 [M]$^+$ (calculated: 274.98811 for $C_{12}H_{87}^9BrN_3$).

**FT-IR:** $\tilde{\nu} = 3386$ (m), 3049 (w), 1422 (s), 1005 (s) cm$^{-1}$.

**M. p.:** 227 °C.

![Figure S30. $^1$H NMR spectrum (500 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a).](image-url)
Figure S31. $^{13}$C NMR spectrum (126 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a).

Figure S32. $^1$H-$^1$H COSY NMR spectrum (500 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a).
**Figure S33.** $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a).

**Figure S34.** $^1$H-$^{13}$C HMBC NMR spectrum (500 MHz/126 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a).
2.2.2 2-(5'-Bromopyridin-2'-yl)-1-methyl-1H-benzo[d]imidazole (6b)

2-(5'-Bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a) (1.60 g, 5.84 mmol) and potassium carbonate (milled, 2.50 g, 18.1 mmol) were dissolved in dimethylformamide (25 mL). Methyl iodide (500 µL, 8.03 mmol) was added and the reaction mixture was stirred at room temperature for 17 h. Water (100 mL) was added and the aqueous layer extracted with ethyl acetate (3 x 50 mL). The organic layers were combined, washed with brine (150 mL) and sodium hydroxide solution (10%, 100 mL), dried over magnesium sulfate and the solvent was removed in vacuo. The product was obtained as a greyish solid.

Yield: 1.33 g (79%, 4.62 mmol)

The analytical data was consistent with literature data.[6b]

$^1$H NMR (600 MHz, DMSO-d$_6$, 298 K) δ (ppm): 8.88 (unres. dd, 1H, $H_m$), 8.29-8.23 (m, 2H, $H_b$), 7.73 (d, $^3$J = 8.1 Hz, 1H, $H_j$), 7.66 (d, $^3$J = 8.1 Hz, 1H, $H_k$), 7.35 (t, $^3$J = 7.6 Hz, 1H, $H_l$), 7.29 (t, $^3$J = 7.6 Hz, 1H, $H_h$), 4.21 (s, 3H, $H_a$).

$^{13}$C NMR (151 MHz, DMSO-d$_6$, 298 K) δ (ppm): 149.6 (C$_m$), 148.8 (C$_h$), 148.7 (C$_i$), 142.0 (C$_b$), 140.1 (C$_k$), 137.2 (C$_d$), 126.0 (C$_i$), 123.4 (C$_d$), 122.5 (C$_e$), 120.9 (C$_c$), 119.5 (C$_g$), 110.9 (C$_l$), 110.9 (C$_c$), 32.7 (C$_a$).

MS (EI, 70 eV) m/z: 288.01 (100) [M]$^+$.  
HRMS (ESI) m/z: 288.01275 [M+H]$^+$ (calculated: 288.01309 for C$_{13}$H$_{11}$N$_3$Br).

FT-IR: $\tilde{\nu}$ = 3041 (w), 1434 (m), 1004 (m), 727 (s) cm$^{-1}$.

M. p.: 137 °C.

**Figure S35.** $^1$H NMR spectrum (600 MHz, DMSO-d$_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-methyl-1H-benzo[d]imidazole (6b).
**Figure S36.** $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-methyl-1$H$-benzo[d]imidazole (6b).

**Figure S37.** $^1$H-$^1$H COSY NMR spectrum (600 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-methyl-1$H$-benzo[d]imidazole (6b).
Figure S38. $^1$H-$^{13}$C HSQC NMR spectrum (600 MHz/151 MHz, DMSO-\textit{d}_6, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-methyl-1\textit{H}-benzo[d]imidazole (6b).

Figure S39. $^1$H-$^{13}$C HMBC NMR spectrum (600 MHz/151 MHz, DMSO-\textit{d}_6, 298 K) of 2(5'-bromopyridin-2'-yl)-1-methyl-1\textit{H}-benzo[d]imidazole (6b).
2.2.3 1,2-Di(6''-(1’-methyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b)

![Chemical Structure](image)

2-(5'-Bromopyridin-2'-yl)-1-methyl-1H-benzo[d]imidazole (6b) (208 mg, 722 µmol) and Pd(PPh₃)₄ (41.8 mg, 5 mol%) were added to a pressure tube and evacuated for five minutes. Using counterflow technique, degassed tetrabutylammonium fluoride (1 M in tetrahydrofuran, 4.3 mL, 4.30 mmol) and trimethylsilylacetylene (100 µL, 723 µmol) were added, the tube was immediately closed and the reaction mixture was heated at 70 °C for 3 h. The product precipitated, was filtered and washed with cold tetrahydrofuran (100 mL). The product was obtained as a yellow to green solid.

**Yield:** 112 mg (70%, 254 µmol)

1H NMR (600 MHz, CDCl₃, 298 K) δ (ppm): 8.87 (d, 4J = 1.9 Hz, 2H, Hₙ), 8.48 (d, 3J = 8.2 Hz, 2H, H₁), 8.00 (dd, 3J = 8.2 Hz, 4J = 1.9 Hz, 2H, H₂), 7.85 (d, 3J = 7.8 Hz, 2H, H₃), 7.47 (d, 3J = 7.8 Hz, 2H, H₄), 7.39-7.32 (m, 4H, H₅, H₆, H₇, H₈).

13C NMR (126 MHz, CDCl₃, 298 K) δ (ppm): 151.1 (Cₙ), 149.8 (C₁), 149.4 (C₂), 142.6 (C₃), 139.2 (C₄), 137.4 (C₅), 124.0 (C₆), 123.7 (C₇), 122.9 (C₈), 120.2 (C₉), 119.5 (C₁₀), 110.0 (C₁₁), 90.7 (C₁₂), 32.9 (C₁₃).

HRMS (EI, 70 eV) m/z: 440.17491 [M]+ (calculated: 440.17494 for C₂₈H₂₀N₆).

FT-IR: ν = 3050 (w), 1466 (m), 725 (s) cm⁻¹.

M. p.: decomposed at >220 °C.

![NMR Spectrum](image)

**Figure S40.** 1H NMR spectrum (600 MHz, CDCl₃, 298 K) of 1,2-di(6''-(1’-methyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b).
Figure S41. $^{13}$C NMR spectrum (126 MHz, CDCl$_3$, 298 K) of 1,2-di(6''-(1'-methyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b).

Figure S42. $^1$H-$^1$H COSY NMR spectrum (500 MHz, CDCl$_3$, 298 K) of 1,2-di(6''-(1'-methyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b).
Figure S43. $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K) of 1,2-di(6''-(1'-methyl-1$H$-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b).

Figure S44. $^1$H-$^{13}$C HMBC NMR spectrum (500 MHz/126 MHz, CDCl$_3$, 298 K) of 1,2-di(6''-(1'-methyl-1$H$-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b).
2.2.4 2-(5'-Bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c)

2-(5'-Bromopyridin-2'-yl)-1H-benzo[d]imidazole (6a) (614 mg, 2.24 mmol) and potassium carbonate (milled, 496 mg, 3.59 mmol) were dissolved in dry dimethylformamide (5 mL). Benzyl bromide (350 µL, 2.94 mmol) was added and the reaction mixture stirred at room temperature for 4.5 h. The solvent was removed in vacuo (55 °C, 20 mbar). Water (50 mL) was added and the aqueous layer was extracted with ethyl acetate (1 x 50 mL). The organic layers were combined, washed with brine (2 x 125 mL) and sodium hydroxide solution (10%, 1 x 50 mL), dried over magnesium sulfate and the solvent was removed in vacuo. The product was obtained as a greyish solid.

Yield: 663 mg (81%, 1.82 mmol)

1H NMR (600 MHz, DMSO-d6, 298 K) δ (ppm): 8.82 (dd, 4J = 2.3 Hz, 5J = 0.6 Hz, 1H, Hq), 8.32 (dd, 3J = 8.6 Hz, 5J = 0.6 Hz, 1H, Hn), 8.25 (dd, 3J = 8.6 Hz, 4J = 2.3 Hz, 1H, Ho), 7.78-7.74 (m, 1H, Hi), 7.61-7.57 (m, 1H, Hg), 7.32-7.26 (m, 2H, Hj,g), 7.26-7.22 (m, 2H, Hb), 7.20-7.17 (m, 1H, Ha), 7.14-7.11 (m, 2H, Hc), 6.17 (s, 2H, He).

13C NMR (151 MHz, DMSO-d6, 298 K) δ (ppm): 149.6 (Cq), 148.6 (Cl), 148.4 (Cm), 142.2 (Cj), 140.3 (Cq), 137.7 (Cq), 136.6 (Cq), 128.6 (Cj), 127.3 (Cq), 126.7 (Cq), 126.0 (Cj), 123.8 (Ci,g), 122.9 (Ci,g), 121.2 (Cj), 119.8 (Cj), 111.5 (Cj), 48.1 (Ce).

MS (EI, 70 eV) m/z: 364.02 (100) [M]+.

HRMS (ESI) m/z: 364.04380 [M+H]+ (calculated: 364.04439 for C19H15N3Br).

FT-IR: ν = 3252.9 (w), 2158.9 (w), 1572.4 (w), 1496.22 (w), 1434.8 (m), 1407.8 (m), 1328.6 (m), 1291.5 (w), 1259.3 (w), 1236.2 (m), 1157.5 (m), 1089.5 (m), 1009.8 (m), 977.5 (w), 923.7 (w), 845.9 (m), 778.1 (w), 763.1 (m), 736.7 (s), 717.9 (s), 692.8 (m), 641.8 (w) cm⁻¹.

M. p.: 131 °C.

Figure S45. 1H NMR spectrum (600 MHz, DMSO-d6, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c).
Figure S46. $^{13}$C NMR spectrum (151 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c).

Figure S47. $^1$H-$^1$H COSY NMR spectrum (500 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c).
Figure S48. $^1$H-$^{13}$C HSQC NMR spectrum (500 MHz/126 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c).

Figure S49. $^1$H-$^{13}$C HMBC NMR spectrum (500 MHz/126 MHz, DMSO-$d_6$, 298 K) of 2-(5'-bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c).
2.2.5 1,2-Di(6''-(1'-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c)

2-(5'-Bromopyridin-2'-yl)-1-benzyl-1H-benzo[d]imidazole (6c) (263 mg, 722 µmol) and Pd(PPh₃)₄ (41.8 mg, 5 mol%) were added to a pressure tube and evacuated for five minutes. Using counterflow technique, degassed tetrabutylammonium fluoride (1 M in tetrahydrofuran, 4.3 mL, 4.30 mmol) and trimethylsilylacetylene (100 µL, 723 µmol) were added, the tube was immediately closed and the reaction mixture was heated at 70 °C for 3 h. The product precipitated, was filtered and washed with cold tetrahydrofuran (1 x 200 mL). The product was obtained as a neon green solid.

**Yield:** 196 mg (92%, 331 µmol)

**¹H NMR** (500 MHz, TFA-d₁, 298 K) δ (ppm): 9.42 (dd, ⁴J = 2.0 Hz, ⁵J = 0.8 Hz, 2H, Hₖ), 8.65 (dd, ³J = 8.2 Hz, ⁴J = 2.0 Hz, 2H, Hₖ), 8.41 (dd, ³J = 8.2 Hz, ⁵J = 0.8 Hz, 2H, Hₖ), 8.21 (d, ³J = 7.8 Hz, 2H, Hₙ), 8.09-8.00 (m, 6H, Hₕ,h,i), 7.64-7.59 (m, 4H, Hₐ,b), 7.45-7.40 (m, 2H, Hₙ), 6.18 (s, 4H, Hₙ).

**¹³C NMR** (126 MHz, TFA-d₁, 298 K) δ (ppm): 154.8 (Cₗ), 147.1 (Cₘ), 145.3 (Cₙ), 141.6 (Cₖ), 135.6 (Cₙ), 134.5 (C₉), 132.6 (C₈), 132.0 (C₉₉), 131.9 (C₉₉₉), 131.7 (C₉₉₉₉), 131.2 (C₉₉₉₉₉), 128.8 (C₉₉₉₉₉₉), 128.6 (C₉₉₉₉₉), 126.8 (C₉₉₉₉₉₉), 117.0 (C₉₉₉), 115.6 (C₉₉₉), 93.4 (C₉₉₉), 52.8 (C₉₉₉₉₉₉).

**HRMS** (EI, 70 eV) m/z: 592.23610 [M]+ (calculated: 592.23754 for C₄₀H₂₈N₆).

**FT-IR:** ν = 1972.9 (w), 1592.1 (w), 1519.5 (w), 1495.9 (w), 1465.8 (m), 1442.3 (m), 1405.5 (m), 1368.3 (m), 1330.4 (m), 1296.8 (s), 1240.1 (w), 1166.5 (w), 1069.5 (w), 853.7 (m), 743.2 (s), 726.1 (s), 452.3 (m) cm⁻¹.

**M. p.:** >300 °C.

![Figure S50](image-url)  
**Figure S50.** ¹H NMR spectrum (500 MHz, TFA-d₁, 298 K) of 1,2-di(6''-(1'-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c).
Figure S51. $^{13}$C NMR spectrum (126 MHz, TFA-$d_1$, 298 K) of 1,2-di(6''-(1''-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c).

Figure S52. $^1$H-$^1$H COSY NMR spectrum (500 MHz, TFA-$d_1$, 298 K) of 1,2-di(6''-(1''-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c).
Figure S53. $^1$H-13C HSQC NMR spectrum (500 MHz/126 MHz, TFA-d$_1$, 298 K) of 1,2-di(6''-(1'-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c).

Figure S54. $^1$H-13C HMBC NMR spectrum (500 MHz/126 MHz, TFA-d$_1$, 298 K) of 1,2-di(6''-(1'-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c).
3 Co₄L₆ Cages

3.1 Cage 3a

Cage 3a has been previously reported.[1]

3.2 Cage 3b

Cobalt bis(trifluoromethylsulfonylimide (10.9 mg, 17.6 μmol) and 1,2-di([6''-methyl-2',2'-bipyridin]-5'-yl)ethyne (1c) (9.56 mg, 26.4 μmol) were dissolved in acetonitrile (1.5 mL) and were heated at 50 °C for 22.5 h. After cooling to room temperature, the solution was added dropwise to diethyl ether (10 mL) and was centrifuged. The organic layer was decanted and the residue washed with diethyl ether (10 mL) to obtain the product as a red solid.

Yield: 16.3 mg (3.50 μmol, 80%)

1H NMR (600 MHz, CD3CN, 298 K) δ (ppm): 81.5 (s, 2H, Hk), 72.1 (br, 2H, Hl), 71.5 (s, 2H, Hg), 51.0 (s, 2H, Hc), 18.9 (s, 2H, Hd), 6.7 (s, 2H, Hi), -57.7 (s, 6H, Ha).

13C NMR (151 MHz, CD3CN, 298 K) δ (ppm): 667.4 (s, Cj), 624.5 (d, 1J = 166 Hz, Cc), 413.9 (d, 1J = 171 Hz, Cn), 336.9 (d, 1J = 160 Hz, Cc), 233.7 (br, Ca), 217.4 (s, Ci), 162.8 (d, 1J = 164 Hz, Cc), 160.5 (d, 1J = 170 Hz, Ca), 53.0 (br, Cb/k), 0.7 (br, Cb/k), -121.6 (s, Cg/k), -181.9 (s, Cg/k).

19F NMR (471 MHz, CD3CN, 298 K, C6F6) δ (ppm): -80.3 (NTf₂).

HRMS (ESI): m/z = 2045.0792 [3b + 6NTf2]^{2+}, 1270.0787 [3b + 5NTf2]^{3+}, 882.5788 [3b + 4NTf2]^{4+}, 650.0451 [3b + 3NTf2]^{5+}, 495.0399 [3b + 2NTf2]^{6+}, 384.2237 [3b + NTf2]^{7+}, 301.3173 [3b]^{8+}. 
Quaternary carbons were tentatively assigned by comparison to reference complexes and cages\[1\] since an HMBC experiment could not be adapted for the paramagnetic NMR toolbox\[1\] for long-range C-H couplings. Carbons \(a, b, k\) in close proximity to the paramagnetic centre were similarly assigned since cross-peaks were not observed in the HMQC spectra and the multiplicity of the carbon signal could not be determined due to the broadness of the signal.

**Figure S55.** \(^1\)H NMR spectrum (600 MHz, CD\(_3\)CN, 298 K) of cage 3b.

**Figure S56.** \(^{13}\)C NMR spectrum (151 MHz, CD\(_3\)CN, 298 K) of cage 3b.
Figure S57. $^1$H-$^1$H COSY NMR spectrum (600 MHz, CD$_3$CN, 298 K) of cage 3b.

Figure S58. $^1$H-$^{13}$C HMQC NMR spectrum (600 MHz/151 MHz, CD$_3$CN, 298 K) of cage 3b.
Figure S59. $^{19}$F NMR spectrum (471 MHz, CD$_3$CN, 298 K, C$_6$F$_6$) of cage 3b.

Figure S60. High resolution ESI mass spectrum of cage 3b showing in the inset the observed (top) and theoretical (bottom) isotope patterns.
Cobalt bis(trifluoromethylsulfonyl)imide (21.8 mg, 35.3 μmol) and 1,2-di([6’-methyl-2’,2”-bipyridin]-5’-yl)ethyne (1c) (19.2 mg, 53.0 μmol) were dissolved in acetonitrile (3 mL) and heated at 50 °C for 15 d. After cooling to room temperature, the solution was added dropwise to diethyl ether (20 mL) and centrifuged. The organic layer was decanted and the residue washed with diethyl ether (20 mL) to obtain the product as a red/brown solid.

Yield: 30.4 mg (73%, 6.52 μmol)

\( ^1H \text{NMR} \) (600 MHz, CD\(_3\)CN, 298 K) \( \delta \) (ppm): 87.9 (s, 2H, \( H_d \)), 78.6 (br, 2H, \( H_b \)), 69.6 (s, 2H, \( H_d \)), 43.0 (s, 2H, \( H_b \)), 16.8 (s, 2H, \( H_h \)), 12.6 (s, 2H, \( H_h \)), -70.5 (s, 6H, \( H_k \)).

\( ^{13}C \text{NMR} \) (151 MHz, CD\(_3\)CN, 298 K) \( \delta \) (ppm): 681.7 (s, \( C_i \)), 591.0 (d, \( ^1J = 171 \text{ Hz}, C_b \)), 437.7 (d, \( ^1J = 160 \text{ Hz}, C_a \)), 325.4 (d, \( ^1J = 165 \text{ Hz}, C_g \)), 278.1 (s, \( C_i \)), 229.3 (s, \( C_i \)), 164.9 (s, \( C_i/j \)), 89.7 (s, \( C_i/j \)), 4.1 (s, \( C_i/j \)), -87.0 (s, \( C_e/f \)), -166.3 (s, \( C_e/f \)).

\( ^{19}F \text{NMR} \) (471 MHz, CD\(_3\)CN, 298 K, C\(_6\)F\(_6\)) \( \delta \) (ppm): -83.6 (NTf\(_2\)).

HRMS (ESI): \( m/z = 1269.7429 \ [3c + 5\text{NTf}_2]^3+, \ 882.5771 \ [3c + 4\text{NTf}_2]^4+, \ 649.8775 \ [3c + 3\text{NTf}_2]^5+ \). Signals for the other charges were not observed since the cage is not stable to dilution (Figure S67).

**Figure S61.** \( ^1H \text{NMR} \) spectrum (600 MHz, CD\(_3\)CN, 298 K) of cage 3c.

Quaternary carbons were tentatively assigned by comparison to reference complexes and cages\(^{[1]}\) since an HMBC experiment could not be adapted for the paramagnetic NMR toolbox\(^{[1]}\) for long-range C-H couplings. Carbons \( a, j, k \) in close proximity to the paramagnetic centre were similarly assigned since cross-peaks were not observed in the
HMQC spectra and the multiplicity of the carbon signal could not be determined due to the broadness of the signal.

Figure S62. $^{13}$C NMR spectrum (151 MHz, CD$_3$CN, 298 K) of cage 3c.

Figure S63. $^1$H-$^1$H COSY NMR spectrum (600 MHz, CD$_3$CN, 298 K) of cage 3c.
Figure S64. $^1$H-$^{13}$C HMQC NMR spectrum (600 MHz/151 MHz, CD$_3$CN, 298 K) of cage 3c.

Figure S65. $^{19}$F NMR spectrum (471 MHz, CD$_3$CN, 298 K, C$_6$F$_6$) of cage 3c.
Figure S66. High resolution ESI mass spectrum of cage 3c showing in the inset the observed (top) and theoretical (bottom) isotope patterns.
Figure S67. $^1$H NMR dilution experiment for cage 3c: black (0.2 mmol/L), red (0.4 mmol/L), blue (0.6 mmol/L), pink (0.8 mmol/L), violet (1.0 mmol/L).

3.4 Cage 4a

Cobalt bis(trifluoromethylsulfonyl)imide (10.9 mg, 17.6 μmol) and 1,2-bis(6''-(1'-methyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2b) (11.6 mg, 26.3 μmol) were dissolved in acetonitrile (3 mL) and heated at 50 °C for 18 h. After cooling to room temperature, the solution was added dropwise to diethyl ether (20 mL) and centrifuged. The organic layer was decanted and the residue washed with diethyl ether (20 mL) to obtain the cage as a brown solid.

Yield: 10.9 mg (48%, 2.13 μmol)

$^1$H NMR (600 MHz, CD$_3$CN, 298 K) δ (ppm): 75.0 (s, 2H, $H_j$), 61.3 (br, 2H, $H_n$), 35.4 (s, 2H, $H_c$), 17.5 (s, 6H, $H_a$), 9.4 (s, 2H, $H_k$), 3.17 (s, 2H, $H_d$), -1.1 (s, 2H, $H_e$), -32.1 (s, 2H, $H_f$).
$^{13}$C NMR (151 MHz, CD$_3$CN, 298 K) δ (ppm): 758.8 (s, C$_l$), 635.7 (s, C$_{o_9}$), 602.0 (s, C$_{o_9}$), 381.4 (d, $^1J = 162$ Hz, C$_j$), 227.2 (d, $^1J = 163$ Hz, C$_d$), 222.0 (s, C$_n$), 182.2 (d, $^1J = 170$ Hz, C$_n$). 165.4 (d, $^1J = 136$ Hz, C$_i$), 140.2 (q, $^1J = 140$ Hz, C$_d$), 136.8 (d, $^1J = 162$ Hz, C$_d$), 88.0 (d, $^1J = 161$ Hz, C$_d$), -32.1 (s, C$_{h/i}$), -155.1 (s, C$_{h/i}$).

$^{19}$F NMR (471 MHz, CD$_3$CN, 298 K, C$_6$F$_6$) δ (ppm): -82.5 (NTf$_2$).

HRMS (ESI): $m/z = 2279.1484$ [4a + 6NTf$_2$]$^{2+}$, 1426.1242 [4a + 5NTf$_2$]$^{3+}$, 999.6138 [4a + 4NTf$_2$]$^{4+}$, 743.7069 [4a + 3NTf$_2$]$^{5+}$, 573.1030 [4a + 2NTf$_2$]$^{6+}$.

**Figure S68.** $^1$H NMR spectrum (600 MHz, CD$_3$CN, 298 K) of cage 4a.

Quaternary carbons were tentatively assigned by comparison to reference complexes and cages$^{[1]}$ since an HMBC experiment could not be adapted for the paramagnetic NMR toolbox$^{[1]}$ for long-range C-H couplings. Carbon $f$ in close proximity to the paramagnetic centre was similarly assigned since a cross-peak was not observed in the HMQC spectra and carbon $m$ could not be identified, most likely since it overlapped with the signal for carbon $e$ and a cross-peak is likely to be unobservable in the HMQC spectrum due to the broadness of the signal.
Figure S69. $^{13}$C NMR spectrum (151 MHz, CD$_3$CN, 298 K) of cage 4a.

Figure S70. $^1$H-$^1$H COSY NMR spectrum (600 MHz, CD$_3$CN, 298 K) of cage 4a.
Figure S71. $^1$H-$^{13}$C HMQC NMR spectrum (600 MHz/151 MHz, CD$_3$CN, 298 K) of cage 4a.

Figure S72. $^1$H-$^{13}$C HMQC NMR spectrum (600 MHz/151 MHz, CD$_3$CN, 298 K) of cage 4a.
Figure S73. $^{19}$F NMR spectrum (471 MHz, CD$_3$CN, 298 K, C$_6$F$_6$) of cage 4a.

Figure S74. High resolution ESI mass spectrum of cage 4a showing in the inset the observed (top) and theoretical (bottom) isotope patterns.

3.5 Cage 4b
The cage was prepared *in situ* by heating a mixture of cobalt bis(trifluoromethylsulfonylimide (5.38 mg, 8.69 μmol) and 1,2-bis(6''-(1'-benzyl-1H-benzo[d]imidazol-2'-yl)pyridin-3''-yl)ethyne (2c) (7.72 mg, 13.0 μmol) in CD$_3$CN (0.5 mL) at 50 °C for 16 h.

$^1$H NMR (600 MHz, CD$_3$CN, 298 K) δ (ppm): 76.4 (s, 2H, $H_n$), 62.3 (br, 2H, $H_o$), 35.6 (s, 2H, $H_g$), 21.9 (s, 1H, $H_e$), 16.3 (s, 1H, $H_h$), 13.8 (s, 4H, $H_c$), 10.5 (s, 4H, $H_e$), 10.3 (s, 2H, $H_o$), 8.6 (s, 2H, $H_g$), 3.10 (s, 2H, $H_i$), -1.1 (s, 2H, $H_i$), -33.2 (s, 2H, $H_j$).

$^{13}$C NMR (151 MHz, CD$_3$CN, 298 K) δ (ppm): 762.5 (s, $C_p$), 631.0 (s, $C_f/k$), 583.6 (s, $C_f/k$), 382.6 (d, $^1J = 164$ Hz, $C_n$), 225.7 (d, $^1J = 168$ Hz, $C_q$), 222.1 (s, $C_i$), 187.5 (d, $^1J = 166$ Hz, $C_o$), 164.8 (d, $^1J = 135$ Hz, $C_j$), 153.7 (t, $^1J = 135$ Hz, $C_a$), 140.3 (s, $C_d$), 138.0 (d, $^1J = 165$ Hz, $C_b$), 135.6 (d, $^1J = 159$ Hz, $C_b$), 133.5 (d, $^1J = 159$ Hz, $C_e$), 132.4 (d, $^1J = 154$ Hz, $C_b$), 88.1 (d, $^1J = 162$ Hz, $C_i$), 77.8 (s, $C_c$), -25.9 (s, $C_{im}$), -147.6 (s, $C_{im}$).

$^{19}$F NMR (471 MHz, CD$_3$CN, 298 K, C$_6$F$_6$) δ (ppm): -83.0 (NTf$_2^-$).

HRMS (ESI): $m/z = 2736.8430$ [4b + 6NTf$_2^-$]$^{2+}$, 1730.5841 [4b + 5NTf$_2^-$]$^{3+}$, 1227.7072 [4b + 4NTf$_2^-$]$^{4+}$, 926.3818 [4b + 3NTf$_2^-$]$^{5+}$, 725.1650 [4b + 2NTf$_2^-$]$^{6+}$, 581.5817 [4b + NTf$_2^-$]$^{7+}$.

**Figure S75.** $^1$H NMR spectrum (600 MHz, CD$_3$CN, 298 K) of cage 4b.

Quaternary carbons were tentatively assigned by comparison to reference complexes and cages[1] since an HMBC experiment could not be adapted for the paramagnetic NMR toolbox[1] for long-range C-H couplings. Carbons $j$, $q$ in close proximity to the paramagnetic centre were similarly assigned since cross-peaks were not observed in the HMQC spectra and the multiplicity of the carbon signal could not be determined due to the broadness of the signal.
Figure S76. $^{13}$C NMR spectrum (151 MHz, CD$_3$CN, 298 K) of cage 4b.

Figure S77. $^1$H-$^1$H COSY NMR spectrum (600 MHz, CD$_3$CN, 298 K) of cage 4b.
Figure S78. $^1$H-$^{13}$C HMQC NMR spectrum (600 MHz/151 MHz, CD$_3$CN, 298 K) of cage 4b.

Figure S79. $^1$H-$^{13}$C HMQC NMR spectrum (600 MHz/151 MHz, CD$_3$CN, 298 K) of cage 4b.
Figure S80. $^{19}$F NMR spectrum (471 MHz, CD$_3$CN, 298 K, C$_6$F$_6$) of cage 4b.

Figure S81. High resolution ESI mass spectrum of cage 4b showing in the inset the observed (top) and theoretical (bottom) isotope patterns.

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