Title: Air-Stable CpCo\textsuperscript{I}-Phosphite-Fumarate Precatalyst in Cyclization Reactions: Comparing Different Methods of Energy Supply

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1. **General methods**

All experiments were carried out under inert gas atmosphere (argon) in flame-dried Schlenk tubes. For microwave-assisted reactions a CEM Discover SP™ with glass tubes was used. For the photochemistry a self-constructed reactor two halogen lamps (460 W each) have been used for irradiation of thermostated Schlenk-type reaction vessels. The anhydrous solvents (THF and toluene) were dried in a solvent purification system MD-5 from Inert (former Innovative Technology). All NMR spectra were recorded on either Bruker AV 300, AV 400 or Fourier 300 NMR spectrometers. HRMS (ESI-TOF) was performed with a Agilent 6210 Time-of-Flight LC/MS and HRMS (EI) and MS (EI) on a Thermo Electron Finnigan MAT 95-XP or an Agilent 6890 N/5973.

The precatalyst 4 was synthesized according to the published procedure[^1] or can be purchased at TCI[^2]. CpCo(CO)₂ (1) and CpCo(COD) were purchased and used as received.

[^1]: Reference number
[^2]: Reference number
2. Substrate synthesis

Most substrates used in this study have been synthesized before. The diynes and triynes were synthesized by literature known procedures and the analytical data were in accordance with the reported data.\textsuperscript{[3,4]} The nitriles were purchased and used either as received or recrystallized before.

**Diethyl 2-(3-(2-methoxynaphthalen-1-yl)prop-2-yn-1-yl)-2-(prop-2-yn-1-yl)malonate (7):**

\[
\text{EtO}_2\text{C} \quad \text{CO}_2\text{Et} \\
\begin{array}{c}
\text{NaH, THF, 25°C} \\
2. \text{Propargyl bromide}
\end{array} \\
\begin{array}{c}
\text{EtO}_2\text{C} \quad \text{CO}_2\text{Et} \\
\text{OMe}
\end{array}
\]

To a suspension of sodium hydride (0.285 g, 7.11 mmol, 1.05 equiv, 60 wt % in oil) in 24 mL of THF was slowly added diethyl 2-(3-(2-methoxynaphthalen-1-yl)prop-2-yn-1-yl)malonate\textsuperscript{[4]} (2.4 g, 6.77 mmol, 1.0 equiv) dissolved in 10 mL of THF via syringe. The solution was stirred for 1 h until the hydrogen evolution ceased. This solution was added slowly to another solution of propargyl bromide (2.0 ml, 13.54 mmol, 2.0 equiv., 80 wt % in toluene) in 10 mL of THF, and the resulting mixture was stirred at 25 °C for 2.5 h. The reaction was monitored by TLC. After no more observable changes, the reaction was quenched with water and extracted with ethyl acetate. The organic phases were washed with brine and dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography with cyclohexane (c-hex)/EE (4:1), and the product 7 (2.4 g, 91%) was obtained as a yellow solid. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz): \( \delta = 1.28 \) (t, \( J = 7.1 \) Hz, 6H), 2.07 (t, \( J = 2.7 \) Hz, 1H), 3.19 (d, \( J = 2.7 \) Hz, 2H), 3.44 (s, 2H), 3.99 (s, 3H), 4.27 (q, \( J = 7.1 \) Hz, 4H), 7.21 (d, \( J = 9.1 \) Hz, 1H), 7.36 (ddd, \( J = 8.2 \), 6.7, 1.2 Hz, 1H), 7.52 (ddd, \( J = 8.5 \), 6.7, 1.3 Hz, 1H), 7.73-7.80 (m, 2H), 8.18 (d, \( J = 8.5 \) Hz, 1H) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 75 MHz): \( \delta = 14.2 \) (2C), 23.0, 24.4, 56.7, 57.0, 62.2 (2C), 71.7, 78.1, 79.0, 93.5, 106.4, 112.9, 124.2, 125.4, 127.3, 128.1, 128.6, 129.8, 134.8, 159.3, 169.1 (2C) ppm; HRMS (EI), C\textsubscript{24}H\textsubscript{24}O\textsubscript{5}: calc.: 392.1618; found: 392.1616.
Diethyl 2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)-2-(prop-2-yn-1-yl)malonate (40)

Sodium hydride (0.195 g, 4.88 mmol, 1.05 equiv, 60 wt % in oil) is suspended in 24 mL of THF and diethyl 2-(3-(naphthalen-1-yl)prop-2-yn-1-yl)malonate (1.509 g, 4.65 mmol, 1.0 equiv) dissolved in 10 mL of THF was slowly added via syringe. The solution was stirred for 1 h until the hydrogen evolution ceased. This solution was added slowly to a solution of propargyl bromide (1.03 ml, 9.3 mmol, 2.0 equiv, 80 wt % in toluene) in 10 mL of THF, and the resulting mixture was stirred at 25 °C for 2.5 h. The reaction was monitored by TLC. After no more observable changes, the reaction was quenched with water and extracted with ethyl acetate. The organic phases were washed with brine and dried over sodium sulfate, and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography with c-hex/EE (4:1), and the product 40 (1.51 g, 90%) isolated as a yellow oil. 

$^1$H NMR (CDCl$_3$, 300 MHz): \( \delta = 1.29 (t, J = 7.1 \text{ Hz}, 6\text{H}), 2.10 (t, J = 2.7 \text{ Hz}, 1\text{H}), 3.16 (d, J = 2.7 \text{ Hz}, 2\text{H}), 3.39 (s, 2\text{H}), 4.29 (q, J = 7.1 \text{ Hz}, 4\text{H}), 7.39 (dd, J = 8.2, 7.2 \text{ Hz}, 1\text{H}), 7.47-7.60 (m, 2\text{H}), 7.62 (dd, J = 7.2, 1.3 \text{ Hz}, 1\text{H}), 7.77-7.85 (m, 2\text{H}), 8.27 (d, J = 8.2 \text{ Hz}, 1\text{H}) \text{ ppm.} \)

$^{13}$C NMR (CDCl$_3$, 75 MHz): \( \delta = 14.2 \text{ (2C)}, 23.1, 24.0, 56.8, 62.2 \text{ (2C)}, 71.9, 78.8, 81.9, 88.9, 120.9, 125.2, 126.2, 126.4, 126.8, 128.3, 128.6, 130.6, 133.2, 135.5, 169.0 \text{ (2C) ppm;} \) HRMS (EI), C$_{23}$H$_{22}$O$_4$: calc.: 362.1513; found: 362.1505.
3. Characterization of cyclization products

General procedures:

**General Procedure 1 (GP1) for [2+2+2] Cycloaddition Reactions under Photochemically Assisted Conditions:** A thermostated photochemical reactor was loaded with precatalyst 4 (5 mol%) under inert conditions and a solution of diyne (0.125 mmol) and the appropriate nitrile (2-5 equiv.) in THF or toluene was added. The reaction mixture was irradiated for the indicated time at 25 °C using medium-pressure metal halide lamps (2*450 W). For stopping the reaction the lamps were turned off and the reaction vessel opened to air. The reaction solution was evaporated to dryness and loaded to a small amount of silica gel. The crude product was purified by flash chromatography, furnishing the pure product.

**General Procedure 2 (GP2) for [2+2+2] Cycloaddition Reactions under Standard Thermal Conditions:** In a Schlenk flask precatalyst 4 was weighted under inert conditions, followed by addition of a solution of diyne (0.125 mmol) and the appropriate nitrile (2-5 equiv.) in THF or toluene. The reaction mixture was heated to 100 °C for the indicated time. After cooling the reaction solution, the solvent was removed in vacuum. The crude product was purified by flash chromatography.

**General Procedure 3 (GP3) for [2+2+2] Cycloaddition Reactions under Microwave Conditions:** In a Schlenk flask precatalyst 4 was weighted under inert conditions, followed by addition either of a solution of diyne (0.125 mmol) and the appropriate nitrile (2-5 equiv.) in toluene or the substrate triyne (0.125 mmol) in 2 mL toluene. The solution was filled under inert conditions into the microwave reaction vial equipped with a stir bar mixture. The reaction in the microwave was executed according to the specified temperature and time. After cooling the reaction solution, the solvent was removed in vacuum. The crude product was purified by automated flash chromatography.
Screening of reaction conditions:
1-(2-Methoxynaphthalen-1-yl)-3-phenyl-5,6,7,8-tetrahydroisoquinoline (6):

Photoassisted reaction:
For the preparation of triaryl 6 from diyne 5 (33 mg, 0.125 mmol) and benzonitrile (2 equiv.) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 5 mL THF were reacted according to GP1 (4 h, 25 °C). After the reaction the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate (3:1, v/v) as eluent furnished product 6 (31 mg, 68% yield). The identification was possible by comparison with published NMR data.[3]

Thermal heating:
According to the GP2 the reaction of diyne 5 (33 mg, 0.125 mmol) and benzonitrile (2 equiv.) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 5 mL toluene was allowed to react for 17 h at 100 °C to yield product 6 (25 mg, 55% yield).

Microwave heating:
According to the GP3 the reaction of diyne 5 (33 mg, 0.125 mmol) and benzonitrile (2 equiv.) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 2 mL toluene were reacted for 0.5 h at 120 °C to yield product 6 (29 mg, 63% yield).
Screening of reaction conditions:

**Diethyl 1-(2-methoxynaphthalen-1-yl)-3-phenyl-5,7-dihydro-6H-cyclopenta[c]pyridine-6,6-dicarboxylate (8):**

![Chemical Structure](image)

**Photoassisted reaction:**

For the preparation of biaryl 8 the diyne 7 (49 mg, 0.125 mmol) and benzonitrile (2 equiv.) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 5 mL THF were reacted according to GP1 (5.5 h, 25 °C). After the reaction the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate (3:1, v/v) as eluent furnished one main fraction, product 8 (62 mg, quantitative yield). ¹H NMR (CDCl₃, 300 MHz): δ = 1.15 (t, J = 7.1 Hz, 3H), 1.26 (t, J = 7.1 Hz, 3H), 3.17 (d, J = 17.2 Hz, 1H), 3.56 (d, J = 17.2 Hz, 1H), 3.77 (bs, 2H), 3.90 (s, 3H), 4.07-4.19 (m, 2H), 4.23 (q, J = 7.1 Hz, 2H), 7.32-7.48 (m, 7H), 7.66 (s, 1H), 7.82-7.87 (m, 1H), 7.94 (d, J = 9.1 Hz, 1H), 7.98-8.03 (m, 2H) ppm; ¹³C NMR (CDCl₃, 75 MHz): δ = 14.0, 14.1, 38.7, 40.8, 56.7, 59.9, 61.9 (2x), 113.6, 115.6, 122.5, 123.7, 125.0, 126.8, 127.4 (2C), 128.0, 128.58, 128.65 (2C), 129.4, 130.4, 133.2, 136.1, 140.0, 150.9, 152.0, 154.3, 156.5, 171.3, 171.4 ppm; HRMS (EI), C₃₁H₂₉O₅N: calc.: 495.2036; found: 495.2040.

**Thermal heating:**

According to the GP2 the reaction of diyne 7 (49 mg, 0.125 mmol) and benzonitrile (2 equiv.) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 5 mL toluene was allowed to react for 17 h at 100 °C to yield product 8 (22 mg, 36% yield).

**Microwave heating:**

According to the GP3 the reaction of diyne 7 (33 mg, 0.125 mmol) and benzonitrile (2 equiv.) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 2 mL toluene were reacted for 0.5 h at 120 °C to yield product 8 (33 mg, 53% yield).
4,5-Dimethyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c']difuran (26):

Photoassisted reaction:
Evaluation of cyclization conditions started irradiation of triyne 25 (96 mg, 0.5 mmol) as well as catalyst 4 (10.8 mg, 5 mol%) dissolved in 2 mL THF in accordance to GP1 (21.5 h, 25 °C). After the reaction the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate (3:1, v/v) as eluent furnished two main fractions (the TLC plates were stained with a solution of vanillin), the substrate 25 (10 mg, 10%) as well as product 26 (19 mg, 20% yield). The NMR data are in accordance to the reported NMR data.[5]

Thermal heating:
According to the GP2 the reaction of triyne 25 (96 mg, 0.5 mmol) in the presence of catalyst 4 (10.8 mg, 5 mol%) dissolved in 2 mL toluene was performed for 18 h at 100 °C. The product 26 (37 mg, 39% yield) as well as unreacted substrate 25 (41 mg, 43%) were isolated.

Microwave heating:
According to the GP3 the triyne 25 (96 mg, 0.5 mmol) as well as catalyst 4 (10.8 mg, 5 mol%) dissolved in 2 mL toluene were reacted for 0.5 h at 120 °C, furnishing product 26 (49 mg, 52% yield) together with separately isolated 25 (35 mg, 36%).
4,5-Diphenyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c']difuran (28):

\[
\text{Photoassisted reaction:}
\]
For the preparation of triaryl 28, the triyne 27 (39 mg, 0.125 mmol) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 2 mL THF were reacted in accordance to GP1 (19 h, 25 °C). After the reaction the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate (3:1, v/v) as eluent furnished two main fractions, the substrate 27 (31%) as well as product 28 (14 mg, 35% yield). The NMR data are in accordance to the reported NMR data.[4]

\[
\text{Thermal heating:}
\]
According to the GP2 the reaction of triyne 27 (39 mg, 0.125 mmol) in the presence of catalyst 4 (2.7 mg, 5 mol%) dissolved in 2 mL toluene was performed for 19 h at 100 °C. The product 28 (17 mg, 44% yield) as well as unreacted substrate 27 (20 mg, 51%) were isolated.

\[
\text{Microwave heating:}
\]
According to the GP3 the triyne 27 (39 mg, 0.125 mmol) as well as catalyst 4 (2.7 mg, 5 mol%) dissolved in 2 mL toluene were reacted for 0.5 h at 120 °C, furnishing product 28 (32 mg, 82% yield).
4,5-Di(naphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c']difuran (30, Table 1, Entry 1-3):

\[
\begin{align*}
\text{Triyne} & \quad 29 \quad (52 \text{ mg, } 0.125 \text{ mmol}) \quad \text{as solution in 2 mL toluene was subjected to microwave} \\
\text{conditions GP3 at } 120 \degree \text{C for 10 min. After completion of the reaction cycle the solvent was} \\
\text{removed in vacuum and the crude product purified by column chromatography on silica gel} \\
\text{using c-hex/ethyl acetate as eluent. The product 30 was isolated in nearly quantitative yield} \\
(51 \text{ mg, } 98\%, \text{ Table 1, Entry 2). Performing the reaction at } 100 \degree \text{C gave no yield at all (Table} \\
1, \text{ Entry 2), applying only } 2.5 \text{ mol\% of 4 as catalyst at } 120 \degree \text{C for 10 min gave } 78\% \text{ yield. The} \\
\text{NMR data are in accordance to the reported NMR data.}\end{align*}
\]

4,5-Bis(2-methoxynaphthalen-1-yl)-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c']difuran (32, Table 1, Entry 4):

\[
\begin{align*}
\text{Triyne} & \quad 31 \quad (60 \text{ mg, } 0.125 \text{ mmol}) \quad \text{as solution in 2 mL toluene was cyclized under microwave} \\
\text{conditions according to the GP3 at } 120 \degree \text{C for 10 min reaction time. After completion of the} \\
\text{reaction cycle the solvent was removed in vacuum and the crude product charged to a small} \\
\text{amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-}
\end{align*}
\]
hex/ethyl acetate as eluent furnished triaryl 32 with 34% yield (20 mg). The NMR data are in accordance to the reported NMR data.\[4\]

4-(2-Methoxynaphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c']difuran (34, Table 1, Entry 5):

Triyne 33 (49 mg, 0.125 mmol) as solution in 2 mL toluene was cyclized under microwave conditions according to the GP3 at 120 °C for 20 min reaction time. After completion of the reaction cycle the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate as eluent furnished triaryl 34 with 62% yield (30 mg). The NMR data are in accordance to the reported NMR data.\[4\]

4-(Naphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydrobenzo[1,2-c:3,4-c']difuran (36, Table 1, Entry 6):

Triyne 35 (46 mg, 0.125 mmol) as solution in 2 mL toluene was subjected to cyclization according GP3 at 120 °C for 20 min reaction time. After completion of the reaction cycle the solvent was removed in vacuum and the crude product charged to a small amount of silica
gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate as eluent furnished pure triaryl 36. Two identical experiments gave 90% yield (44 mg) and 76% (35 mg) yield of product, corresponding to an average of 83% yield. The NMR data are in accordance to the reported NMR data.\(^\text{[4]}\)

**Tetraethyl 4,5-di(naphthalen-1-yl)-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (38, Table 1, Entry 7):**

\[
\text{Triyne } 37 (60 \text{ mg, 0.086 mmol) as solution in 2 mL toluene was cyclized under microwave conditions according to the GP3 at 120 °C for 30 min reaction time. After completion of the reaction cycle the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate as eluent furnished triaryl 38 (11 mg, 15% yield) as well as most of the substrate 37 (38 mg, 63% recovered). The NMR data are in accordance to the reported NMR data.}\(^\text{[4]}\)

**Tetraethyl 4-(naphthalen-1-yl)-5-phenyl-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (40, Table 1, Entry 8):**
Triyne 39 (39 mg, 0.125 mmol) as solution in 2 mL toluene was cyclized under microwave conditions according to GP3 at 120 °C for 30 min. After completion of the reaction cycle the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate as eluent furnished triaryl 40 (32 mg, 40% yield) as well as unreacted substrate 39 (49 mg, 60% recovered). The NMR data are in accordance to the published NMR data.[4]

**Tetraethyl 4-(2-methoxynaphthalen-1-yl)-5-methyl-1,3,6,8-tetrahydro-as-indacene-2,2,7,7-tetracarboxylate (42, Table 1, Entry 9):**

![Chemical Structure](image)

Triyne 41 (77 mg, 0.125 mmol) as solution in 2 mL toluene was cyclized under microwave conditions according to GP3 at 120 °C for 30 min. After completion of the reaction cycle the solvent was removed in vacuum and the crude product charged to a small amount of silica gel in ethyl acetate and dried. Column chromatography on silica gel using c-hex/ethyl acetate as eluent furnished triaryl 42 (12 mg, 15% yield) as well as unreacted substrate 41 (48 mg, 62% recovered). The NMR data are in accordance to the published NMR data.[4]
4. Comparative reactions with CpCo(CO)$_2$ (1)

Procedure: The comparative reactions with precatalyst 1 were performing in accordance to GP3 (Scheme 6 in the manuscript).

Example 1:

In a Schlenk flask CpCo(CO)$_2$ (1) (1.1 mg, 6.3 μmol, 5 mol%) was added 0.1 ml from a stock solution (0.061 mmol CpCo(CO)$_2$/ml in toluene) to a solution of diyne 7 (0.125 mmol) and the piperidine-1-carbonitrile (0.25 mmol, 2 equiv.) in 2 mL of toluene. The solution was filled under inert conditions into the microwave reaction vial equipped with a stir bar mixture. After introduction into the microwave the reaction was heated to 140 °C for 0.5 h. After cooling of the reaction solution to room temperature, the solvent was removed in vacuum. The crude product was purified as described for compound 10 before, yielding the pure biaryl (45 mg, 72%). The NMR data are in accordance to those reported in this work before.

Example 2:

In a Schlenk flask CpCo(CO)$_2$ (1) (1.1 mg, 6.3 μmol, 5 mol%) was added 0.1 ml from a stock solution (0.061 mmol CpCo(CO)$_2$/ml in toluene) to a solution of diyne 5 (0.125 mmol) and 2-(benzo[d]thiazol-2-yl) acetonitrile (0.25 mmol, 2 equiv.) in 2 mL of toluene. The solution was filled under inert conditions into the microwave reaction vial equipped with a stir bar mixture. After introduction into the microwave the reaction was heated to 140 °C for 0.5 h. After cooling of the reaction solution to room temperature, the solvent was removed in vacuum.
The crude product was purified as described for compound 19 before, however, only the starting materials were recovered nearly quantitatively.

**Example 3:**

In a Schlenk flask CpCo(CO)$_2$ (1) (1.1 mg, 6.3 µmol, 5 mol%) was added 0.1 ml from a stock solution (0.061 mmol CpCo(CO)$_2$/ml in toluene) to a solution of triyne 27 (0.125 mmol) in 2 mL of toluene. The solution was filled under inert conditions into the microwave reaction vial equipped with a stir bar mixture. After introduction into the microwave the reaction was heated to 120 °C for 0.5 h. After cooling of the reaction solution to room temperature, the solvent was removed in vacuum. No conversion of 27 was observed and the starting material reisolated.
5. Photochemical catalysis using alternative reaction setup

Procedure: For the photo-catalyzed [2+2+2] cycloadditions the EvoluChem™ PhotoRedOx Box of HepatoChem was utilized (light source: kessil blue 34W, see the following photo), performing the reaction at room-temperature in an air-cooled photo reactor by adoption of GP1 (Scheme 7 in the manuscript).[6]

Reaction setup:

General Procedure: A Schlenk tube was charged with precatalyst 4 (5 mol%) or CpCo(COD) (5 mol%) under argon and a solution of either the diyne (0.125 mmol) and appropriate nitrile (2 equiv.) or the triyne (0.125 mmol) in THF (2 mL) was added. The flask was closed with a glass stopper and subjected to the photo reactor and irradiated (kessil blue 34 W) for the indicated time at 25 °C. For stopping the reaction the lamp was turned off and the reaction vessel opened to air. The reaction solution was evaporated to dryness and loaded to a small amount of silica gel and the subjected to chromatographic purification on silica gel using c-hex/ethyl acetate as eluent.

Synthesis of biaryl 6:
Precatalyst CpCo(COD): According to the General Procedure diyne 5 (33 mg, 0.125 mml), benzonitrile (2 equiv.) and CpCo(COD) (5 mol%) were reacted for 12 h to yield biaryl 6 with 80% (36 mg) yield. The product was identified according to its reported NMR data.[3]

Precatalyst 4: According to the General Procedure diyne 5 (33 mg, 0.125 mml), benzonitrile (2 equiv.) and precatalyst 4 (5 mol%) were reacted for 12 h to yield biaryl 6 with 70% (31 mg) yield.

Synthesis of biaryl 44:

Precatalyst CpCo(COD): According to the General Procedure diyne 43 (45 mg, 0.125 mml), benzonitrile (2 equiv.) and CpCo(COD) (5 mol%) were reacted for 17.5 h to yield biaryl 44 with 90% (52 mg, of syrupy consistency) yield. $^1$H NMR (CDCl$_3$, 300 MHz): $\delta = 1.22$ (m, 6H), 3.43 (s, 2H), 3.77 (s, 2H), 4.14-4.25 (m, 4H), 7.35-7.62 (m, 7H), 7.69 (s, 1H), 7.78-7.83 (m, 1H), 7.91-7.96 (m, 2H), 8.02-8.07 (m, 2H) ppm; $^{13}$C NMR (CDCl$_3$, 75 MHz): $\delta = 14.1$ (2C), 39.1, 40.8 (2C), 60.1, 62.1 (2C), 115.5, 125.5, 126.0, 126.4, 127.0, 127.3 (2C), 128.4, 128.7 (2C), 128.82, 128.84, 131.2, 134.0, 134.4, 137.5, 139.7, 151.4, 154.8, 156.4, 171.3 (2C) ppm; HRMS (EI), C$_{30}$H$_{27}$O$_4$N: calc.: 465.1932; found: 465.1935.

Precatalyst 4: According to the General Procedure diyne 43 (45 mg, 0.125 mml), benzonitrile (2 equiv.) and precatalyst 4 (5 mol%) were reacted for 17.5 h to yield biaryl 44 with 86% (50 mg) yield.
Synthesis of triaryl 29:

Precatalyst CpCo(COD): According to the General Procedure triyne 29 (52 mg, 0.125 mmol) and CpCo(COD) (5 mol%) were reacted for 17 h to yield triaryl 30 with 56% (29 mg) yield. The product was identified according to its reported NMR data.[4]

Precatalyst 4: According to the General Procedure triyne 29 (52 mg, 0.125 mmol) and precatalyst 4 (5 mol%) were reacted for 17.5 h to yield triaryl 30 with 66% (34 mg) yield.

Synthesis of triaryl 32:

Precatalyst CpCo(COD): According to the General Procedure triyne 31 (60 mg, 0.125 mmol) and CpCo(COD) (5 mol%) were reacted for 17 h to yield triaryl 32 with 49% (28 mg) yield. The product was identified according to its reported NMR data.[4]

Precatalyst 4: According to the General Procedure triyne 31 (60 mg, 0.125 mmol), benzonitrile (2 equiv.) and precatalyst 4 (5 mol%) were reacted for 17.5 h to yield triaryl 32 with 50% (30 mg) yield.
6. NMR spectra

Starting materials: Compound 7 (\(^1\)H and \(^{13}\)C)
Starting materials: Compound 40 (\(^1\)H and \(^{13}\)C)
Compound 6 (\(^1\)H)
Compound 8 ($^1$H and $^{13}$C)
Compound 10 (\textsuperscript{1}H and \textsuperscript{13}C)
Compound 11 ($^1$H and $^{13}$C)
Compound 12 (\(^1\)H and \(^{13}\)C)
Compound 13 (\textsuperscript{1}H and \textsuperscript{13}C)
Compound 14 (\(^1\text{H}\) and \(^{13}\text{C}\))
Compound 15 ($^1$H and $^{13}$C)
Compound 16 (\(^1H\) and \(^{13}C\))
Compound 17 (\(^1\)H)

[Chemical structure image]
Compound 18 (\(^1\)H and \(^{13}\)C)
Compound 19 ($^1$H and $^{13}$C)

cyclohexane

cyclohexane
Compound 20 (\(^1\text{H}\) and \(^{13}\text{C}\))
Compound 21 (\(^1\)H and \(^{13}\)C)
Compound 23 (\(^1\)H and \(^{13}\)C)
Compound 24 (\(^1\)H and \(^{13}\)C)
Compound 26 ($^1$H)

Compound 28 ($^1$H)
Compound 30 ($^1$H)

Compound 44 ($^1$H and $^{13}$C)
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