Photoinduced Palladium-Catalyzed Dicarbofunctionalization of Terminal Alkynes

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1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, Fluorochem and Carl Roth.

Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualised by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume.

$^1$H-NMR, $^{19}$F-NMR and $^{13}$C-NMR were recorded on a Varian AV600/AV400 or an Agilent DD2 400 NMR spectrometer in CDCl$_3$. Data are reported in the following order: chemical shift ($\delta$) in ppm; multiplicities are indicated br (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants ($J$) are in Hertz (Hz).

HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV.

IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm$^{-1}$).

2. General Procedure

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, alkynes (3.0 eq., 0.6 mmol), iodide compounds (1.0 eq., 0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and quenched by water and extracted with ethyl acetate (3 times). The organic layers were combined, dried with anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The product was purified by flash column chromatography on silica gel to get the corresponding 1,3-enzyme product.

Primary iodides are not compatible in the reaction system, decomposition of primary alkyl iodides and dimer of alkynes were observed in the reaction crude, only trace 1,3-enzyme products was observed.
3. Preparation of Substrates

General Procedure A: Iodination of secondary and tertiary alcohols. This procedure is according to the corresponding literature.\textsuperscript{1} Imidazole (0.68 g, 10 mmol) and PPh\textsubscript{3} (2.62 g, 10 mmol) were added into a dry round bottom flask equipped with stirring bar under argon atmosphere. Then 12 mL dry DCM was added. The resulting solution was moved to the ice-water bath and cooled to 0 °C and iodine (2.54 g, 10 mmol) were added portion-wise. Then the corresponding alcohol (7.25 mmol) in 8 mL dry DCM was added dropwise. Then the reaction mixture was moved to room temperature and stirred overnight. The solids were removed by passing the reaction mixture through silica gel (washed by ether). The solution was concentrated and the resulting reaction crude was purified by flash column chromatography to get the iodide compounds. Compounds 2d,\textsuperscript{2} 2e,\textsuperscript{3} 2f,\textsuperscript{4} 2g,\textsuperscript{2} 2j,\textsuperscript{5} 2k\textsuperscript{6} were synthesized by the procedure, and their spectra data match previous reports.

General Procedure B: The synthesis of compound 2m is according the previous literature.\textsuperscript{7} To
a suspension of PCC (pyridinium chlorochromate) in dry DCM was added all at once 5-penten-1-ol and the resultant was stirred at room temperature for three hours. Then it was diluted with ether, and the black gum being triturated again in dry ether. The insoluble material was removed through a pad of silica. The product was used directly for the next step. A solution of 5-hexenal in dry ether was cooled to -30 °C and then MeMgBr solution (1 eq.) was added slowly. After the addition, the cooling bath was removed and the reaction mixture was stirred at room temperature for 5 minutes. Then the reaction mixture was cooled to -20 °C and poured into saturated NH₄Cl solution. The layers were separated and the aqueous phase was extracted with ether. The combined organic phase was dried over MgSO₄ and evaporated to give the corresponding 6-hepten-2-ol which was used directly for the next step (General Procedure A) without further purification.

**General Procedure C:** Compound 1r was synthesized according the previous literature.⁸

To S-1r-1 in dry CH₂Cl₂ (15 mL) at 0 °C was added triethylamine (3.8 mmol) and trifluoromethanesulfonic anhydride (4.1 mmol). The reaction mixture was stirred at 0 °C for 20 min before the addition of water. The phases were separated and the aqueous phase was extracted with CH₂Cl₂ (3 times). The combined organic layers are washed with brine and dried over Na₂SO₄. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford S-1r-2 in 85% yield.

To a mixture of S-1r-2 (2.0 mmol), Pd(PPh₃)₂Cl₂ (0.2 mmol) and CuI (0.2 mmol) in DMF (40 mL) was added Et₃N (6.0 mmol), and TMSA (10.0 mmol), then the reaction was stirred at 80 °C for 4 h. Monitored by TLC, when the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 times). The combined organic phases are washed with brine and dried over Na₂SO₄. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford S-1r-3 in 50% yield.

To S-1r-3 (1.0 mmol) in MeOH (10 mL) was added K₂CO₃ (2.0 mmol). The reaction mixture was stirred at 25 °C for 4 h. Monitored by TLC, when the reaction was completed, the mixture was quenched with water and extracted with ethyl acetate (3 times). The combined organic phases are washed with brine and dried over Na₂SO₄. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography to afford 1r in 90% yield. The spectrum data of compound 1r matches previous report.⁸

**Procedure for compound 7:** Compound 7 was synthesized according previous literature.⁹ An oven-dried 30 mL test tup equipped with a stirring bar was charged with zinc powder (294 mg, 4.5 mmol, 1.5 eq.) and DMA solvent (6 mL). Iodine (dissolved in DMA solvent, 0.5 M, 2 mol%) was then added into the reaction mixture. And the mixture was stirred at room temperature until the brown color decolorized. FeBr₂ (65 mg, 10 mol%) was added into the reaction mixture, followed by the addition of phenylacetylene 1a (306 mg, 3 mmol, 1 eq.) and cyclohexane iodide.
2a (945 mg, 4.5 mmol, 1.5 eq.). The mixture was stirred at room temperature for 4 days. After the reaction, IBr (1.8 g, 9 mmol, 3 eq.) was added and the resulting mixture was stirred at room temperature for 1.5 days. Then water and ethyl acetate were added to quench the reaction, the crude was purified by flash chromatography using hexane as eluent. The data of compound 7 matches the previous report. 9

**Procedure for compound 8:** Compound 8 was synthesized according previous literature. 10 A 100 mL flask with a stirring bar was charged under Argon with Pd(PPh$_3$)$_2$Cl$_2$ (0.02 eq.), Cul (0.04 eq.), and 25 mL NEt$_3$. Later, 10 mmol iodobenzene and 12 mmol cyclohexane acetylene were added slowly to the reaction mixture. The solution was stirred at room temperature overnight. After the reaction, the reaction was quenched with water and extracted with ethyl acetate. The organic phase was dried over MgSO$_4$, and the product was purified by column chromatography. The spectrum data of compound 8 matches previous report. 10

**Preparation of compound 2l: Reduction of ketones and iodination of corresponding alcohols.** Reduction step is according the previous literature. 11 The ketone (1.0 eq.) was dissolved in MeOH and cooled to 0 °C in ice-water bath. Then NaBH$_4$ (1.1 eq.) was added into the solution portion-wise and the reaction mixture was stirred for around 1 hour then moved to room temperature overnight. The reaction mixture was quenched by sat. NH$_4$Cl solution and extracted with DCM (3 times). Organic layers were combined, dried over anhydrous Na$_2$SO$_4$ and concentrated under vacuum to provide the corresponding alcohol which is used for the next step (General Procedure A) without further purification. Compound 2l was synthesized by the procedure.

(Cyclopropylidomethyl)benzene (2l)

![Cyclopropylidomethyl)benzene (2l)]

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.37$ (d, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 2H), 7.24 (t, $J = 7.2$ Hz, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.19 – 6.11 (m, 1H), 3.25 (t, $J = 7.2$ Hz, 2H), 2.79 (q, $J = 7.1$ Hz, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 137.0, 132.3, 128.6, 128.5, 127.4, 126.2, 37.0, 5.0$ ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 258.99776, calculated mass for C$_{10}$H$_{12}$I$_2$: 258.99783.

IR (KBr): 3056, 3025, 2957, 2691, 2323, 2105, 1996, 1942, 1799, 1747, 1596, 1492, 1442, 1423, 1324, 1234, 1167, 1070, 1026, 962, 919, 820, 782, 739, 691 cm$^{-1}$. 

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4. Optimization Tables

4.1 Ligands Screening

| entry<sup>a</sup> | [Pd] cat. | Ligand | Solvent | Yield(3a/4)<sup>b</sup> |
|------------------|-----------|--------|---------|--------------------------|
| 1<sup>c</sup>    | Pd(OAc)<sub>2</sub> | Xantphos | PhH     | 30/0                     |
| 2                | Pd(OAc)<sub>2</sub> | Xantphos | PhH     | 40/0                     |
| 3                | Pd(OAc)<sub>2</sub> | Ruphos  | PhH     | 0/64                     |
| 4                | Pd(OAc)<sub>2</sub> | Davephos| PhH     | 0/34                     |
| 5                | Pd(OAc)<sub>2</sub> | dppbe   | PhH     | 29/0                     |
| 6                | Pd(OAc)<sub>2</sub> | tBuXPhos| PhH     | n.r                      |
| 7                | Pd(OAc)<sub>2</sub> | Rac-BINAP| PhH   | 10/0                     |
| 8                | Pd(OAc)<sub>2</sub> | Sphos   | PhH     | 0/43                     |
| 9                | Pd(OAc)<sub>2</sub> | Xphos   | PhH     | 0/19                     |
| 10               | Pd(OAc)<sub>2</sub> | PPh<sub>3</sub> | PhH  | trace                    |
| 11               | Pd(OAc)<sub>2</sub> | dppf    | PhH     | 16/0                     |
| 12               | Pd(OAc)<sub>2</sub> | dpph    | PhH     | n.r                      |
| 13               | Pd(OAc)<sub>2</sub> | P(2-furan)<sub>2</sub> | PhH | 26/0                     |

<sup>a</sup> Reaction condition: 0.2 mmol 1<sub>a</sub>, 0.6 mmol 2<sub>a</sub>, 0.4 mmol Cs<sub>2</sub>CO<sub>3</sub>, 5 mol% Pd(OAc)<sub>2</sub>, 10 mol% Ligand were dissolved in 1 mL PhH under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight.  
<sup>b</sup> The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr<sub>3</sub>.  
<sup>c</sup> reaction time is 6 hours.

4.2 Palladium Screening

| entry<sup>a</sup> | [Pd] cat. | Ligand | Solvent | Yield(3a)<sup>b</sup> |
|------------------|-----------|--------|---------|-----------------------|
| 1                | Pd(OAc)<sub>2</sub> | Xantphos | PhH     | 40                     |
| 2                | Pd(TFA)<sub>2</sub> | Xantphos| PhH     | 24                     |
| 3                | Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> | Xantphos| PhH     | 9                      |
| 4                | PdCl<sub>2</sub> | Xantphos| PhH     | n.r                    |
| 5                | Pd(PPh<sub>3</sub>)<sub>4</sub> | Xantphos| PhH     | 11                     |
| 6                | Pd(dba)<sub>2</sub> | Xantphos| PhH     | 16                     |

<sup>a</sup> Reaction condition: 0.2 mmol 1<sub>a</sub>, 0.6 mmol 2<sub>a</sub>, 0.4 mmol Cs<sub>2</sub>CO<sub>3</sub>, 5 mol% Pd catalyst, 10 mol% Xantphos were dissolved in 1 mL PhH under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight.  
<sup>b</sup> The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr<sub>3</sub>.
4.3 Equivalent Screening

![Chemical structure]

| entry<sup>a</sup> | [Pd] cat. | Ligand | X eq. | Yield<sup>b</sup>(3a) |
|-------------------|----------|--------|-------|-----------------------|
| 1                 | Pd(OAc)<sub>2</sub> | Xantphos | 4     | 45                    |
| 2                 | Pd(OAc)<sub>2</sub> | Xantphos | 3     | 40                    |
| 3                 | Pd(OAc)<sub>2</sub> | Xantphos | 2     | 44                    |
| 4                 | Pd(OAc)<sub>2</sub> | Xantphos | 1     | 27                    |
| 5                 | Pd(OAc)<sub>2</sub> | Xantphos | 0.5   | 31                    |
| 6                 | Pd(OAc)<sub>2</sub> | Xantphos | 0.33  | 55                    |
| 7                 | Pd(OAc)<sub>2</sub> | Xantphos | 0.2   | 53                    |
| 8                 | Pd(OAc)<sub>2</sub> | Xantphos | 0.1   | 30                    |

<sup>a</sup> Reaction condition: 0.2 mmol 1a, x eq. 2a, 0.4 mmol Cs₂CO₃, 5 mol% Pd(OAc)<sub>2</sub>, 10 mol% Xantphos were dissolved in 1 mL PhH under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight. <sup>b</sup> The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr₃.

4.4 Solvent Screening

![Chemical structure]

| entry<sup>a</sup> | [Pd] cat. | Ligand | Solvent | Yield<sup>b</sup>(3a) |
|-------------------|----------|--------|---------|-----------------------|
| 1                 | Pd(OAc)<sub>2</sub> | Xantphos | MeCN    | 28                    |
| 2                 | Pd(OAc)<sub>2</sub> | Xantphos | DCM     | 17                    |
| 3                 | Pd(OAc)<sub>2</sub> | Xantphos | Toluene | 31                    |
| 4                 | Pd(OAc)<sub>2</sub> | Xantphos | THF     | 62                    |
| 5                 | Pd(OAc)<sub>2</sub> | Xantphos | DMF     | 9                     |
| 6                 | Pd(OAc)<sub>2</sub> | Xantphos | EtOH    | n.r                   |
| 7                 | Pd(OAc)<sub>2</sub> | Xantphos | PhCF₃   | n.r                   |
| 8                 | Pd(OAc)<sub>2</sub> | Xantphos | DMA     | trace                 |
| 9                 | Pd(OAc)<sub>2</sub> | Xantphos | DMSO    | 25                    |
| 10                | Pd(OAc)<sub>2</sub> | Xantphos | Et₂O    | 47                    |
| 11                | Pd(OAc)<sub>2</sub> | Xantphos | 1,4-dioxane | 50                 |
| 12                | Pd(OAc)<sub>2</sub> | Xantphos | CHCl₃   | n.r                   |

<sup>a</sup> Reaction condition: 0.6 mmol 1a, 0.2 mmol 2a, 0.4 mmol Cs₂CO₃, 5 mol% Pd(OAc)<sub>2</sub>, 10 mol% Xantphos were dissolved in 1 mL solvent under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight. <sup>b</sup> The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr₃.
4.5 Base Screening

- **Entry**
  - **[Pd] cat.**
  - **Ligand**
  - **Base**
  - **Yield(3a)**

| Entry | [Pd] cat. | Ligand | Base      | Yield(3a) |
|-------|-----------|--------|-----------|-----------|
| 1     | Pd(OAc)$_2$ | Xantphos | K$_2$CO$_3$ | trace     |
| 2     | Pd(OAc)$_2$ | Xantphos | Na$_2$CO$_3$ | trace     |
| 3     | Pd(OAc)$_2$ | Xantphos | KOAc      | trace     |
| 4     | Pd(OAc)$_2$ | Xantphos | NaOAc     | trace     |
| 5     | Pd(OAc)$_2$ | Xantphos | DMAP      | trace     |

[a] Reaction condition: 0.6 mmol 1a, 0.2 mmol 2a, 0.4 mmol base, 5 mol% Pd(OAc)$_2$, 10 mol% Xantphos were dissolved in 1 mL THF under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight. [b] The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr$_3$.

4.6 Catalysts Loading Screening

- **Entry**
  - **x mol%**
  - **y mol%**
  - **Solvent**
  - **Yield(3a)**

| Entry | x mol% | y mol% | Solvent | Yield(3a) |
|-------|--------|--------|---------|-----------|
| 1     | 10     | 20     | THF     | 83        |
| 2     | 10     | 30     | THF     | 35        |
| 3     | 20     | 40     | THF     | 71        |

[a] Reaction condition: 0.6 mmol 1a, 0.2 mmol 2a, 0.4 mmol Cs$_2$CO$_3$, x mol% Pd(OAc)$_2$, y mol% Xantphos were dissolved in 1 mL THF under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight. [b] The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr$_3$. 
### 4.7 Further Screening

![Chemical Reaction Diagram]

| entry<br>a | variations from standard reaction condition | Yield(3a)<br>b |
|---|---|---|
| 1 | without blue led, rt | n.r |
| 2 | without blue led, 60 °C | n.r |
| 3 | no [Pd] cat. | n.r |
| 4 | no Ligand | n.r |
| 5 | no base | n.r |
| 6 | bromocyclohexane as substrate | n.r |

[a] Reaction condition: 0.6 mmol 1a, 0.2 mmol 2a, 0.4 mmol Cs₂CO₃, 10 mol% Pd(OAc)₂, 20 mol% Xantphos were dissolved in 1 mL THF under Argon atmosphere, irradiated with 3W blue led(470 nm) at room temperature overnight. [b] The yield was determined by H-NMR of the reaction crude. The internal standard is CHBr₃.
5. Control experiments

5.1 Air as atmosphere

\[ \text{Pd(OAc)}_2 (10 \text{ mol\%}, 4.5 \text{ mg}) \text{ and Xantphos (20 mol\%, 23.2 mg), Cs}_2\text{CO}_3 (2.0 \text{ eq., 0.4 mmol, 130 mg}) \] were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was under air atmosphere. To those solid, phenylacetylene 1a (3.0 eq., 0.6 mmol), cyclohexane iodide 2a (1.0 eq., 0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under air atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and concentrated under vacuo. Internal standard CHBr₃ was added into the reaction crude and the mixture was submitted to NMR. NMR yield is app. 10%.

5.2 TEMPO trapping experiment

\[ \text{Pd(OAc)}_2 (10 \text{ mol\%, 4.5 mg}) \text{ and Xantphos (20 mol\%, 23.2 mg), Cs}_2\text{CO}_3 (2.0 \text{ eq., 0.4 mmol, 130 mg}) \text{ and TEMPO (0.5 eq., 16 mg}) \] were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, phenylacetylene 1a (3.0 eq., 0.6 mmol), cyclohexane iodide 2a (1.0 eq., 0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and concentrated under vacuo. Internal standard CHBr₃ was added into the reaction crude and the mixture was submitted to NMR. NMR yield is app. 46%.
5.3 Radical Clock Experiments

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, phenylacetylene 1a (0.6 mmol), 5-iodohex-1-ene 2m (0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and concentrated under vacuo. The product was purified by flash column chromatography on silica gel to get the corresponding 1,3-ene product. The inseparable mixture of 5m and 5m’ was obtained as colorless gel in 61% yield (35 mg, 5m : 5m’ = 6:1). The data of 5m and 5m’ is in the physical data part.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The
reaction tube was evacuated and filled with argon for three times. To those solid, phenylacetylene 1a (3 eq.), (cyclopropyliodomethyl)benzene 2l (0.2 mmol, 51.6 mg) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and concentrated under vacuo. Internal standard CHBr₃ was added into the reaction crude and the mixture was submitted to NMR. Iodide compound 2l decomposed and no desired 1,3-enyne product formed.

5.4 Thermal Condition

Pd(OAc)₂ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs₂CO₃ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, phenylacetylene 1a (3.0 eq., 0.6 mmol), iodide compounds 2a (1.0 eq., 0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to 60 °C oil bath or room temperature. The reaction mixture was stirred overnight and quenched by water and extracted with ethyl acetate (3 times). The organic layers were combined, dried with anhydrous Na₂SO₄ and concentrated under vacuo. No desired 1,3-enyne product formed under those conditions.

5.5 On-Off experiment

Serval model reactions followed by General Procedure are setting up parallely at same time under the irradiation of blue led and in the absence of light. Every two hours, one reaction was worked up and analyzed by NMR to detect yield of the corresponding 1,3-enyne.
5.6 Reactivity of aliphatic alkyne vs silylated alkyne

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, alkyne 1s (3.0 eq., 0.6 mmol), iodide compound 2a (1.0 eq., 0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was paraffilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and quenched by water and extracted with ethyl acetate (3 times). The organic layers were combined, dried with anhydrous Na$_2$SO$_4$ and concentrated under vacuum. No desired 1,3-enzyme product formed under those conditions.

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, alkyne 1t (3.0 eq., 0.6 mmol), iodide compound 2a (1.0 eq., 0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was paraffilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and quenched by water and extracted with ethyl acetate (3 times). The organic layers were combined, dried with anhydrous Na$_2$SO$_4$ and concentrated under vacuum. No desired 1,3-enzyme product formed under those conditions.

5.7 Experiment with potential vinyl iodide intermediate

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol,
130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, alkynes (0.2 mmol), vinyl iodide compounds 7 (3.0 eq., 0.6 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb) or under thermal conditions. After the reaction, the solution was quenched by water and extracted with ethyl acetate (3 times). The organic layers were combined, dried with anhydrous Na$_2$SO$_4$ and concentrated under vacuum. The reaction crude was analyzed by crude HNMR.

5.8 Experiment with potential hydroalkylation reaction

\[
\begin{align*}
\text{Pd(OAc)}_2 (10 \text{ mol\%}, 4.5 \text{ mg}) \quad \text{and} \quad \text{Xantphos (20 mol\%, 23.2 mg)}, \\
\text{Cs}_2\text{CO}_3 (2.0 \text{ eq., 0.4 mmol, 130 mg}) \quad \text{were placed in a dry and transparent reaction tube equipped with a stirring bar.} \\
The \text{reaction tube was evacuated and filled with argon for three times. To those solid,} \\
\text{phenylacetylene 1a (0.2 mmol), (cyclohexylethynyl)benzene 8 (3.0 eq., 0.6 mmol) and 1 mL fresh THF} \\
\text{from SPS) were added via a syringe under argon atmosphere. Then the reaction} \\
\text{tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A} \\
\text{cooling fan was put on the top of the reaction tube to make sure the reaction} \\
\text{temperature is near room temperature. The reaction mixture was stirred at room temperature} \\
\text{overnight and quenched by water and extracted with ethyl acetate (3 times). The organic layers} \\
\text{were combined, dried with anhydrous Na}_2\text{SO}_4 \text{ and concentrated under vacuum. No desired} \\
\text{1,3-enzyme product formed under those conditions.}
\end{align*}
\]

5.9 Examination of formation of polymers

\[
\begin{align*}
Pd(OAc)_2 (10 \text{ mol\%, 4.5 mg}) \quad \text{and} \quad \text{Xantphos (20 mol\%, 23.2 mg), Cs}_2\text{CO}_3 (2.0 \text{ eq., 0.4 mmol, 130 mg}) \quad \text{were placed in a dry and transparent reaction tube equipped with a stirring bar.} \\
The \text{reaction tube was evacuated and filled with argon for three times. To those solid,} \\
\text{phenylacetylene 1a (3 eq., 5 eq., or 10 eq., ), cyclohexane iodide 2a (0.2 mmol) and 1 mL fresh THF} \\
\text{from SPS) were added via a syringe under argon atmosphere. Then the reaction} \\
\text{tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A} \\
\text{cooling fan was put on the top of the reaction tube to make sure the reaction} \\
\text{temperature is near room temperature. The reaction mixture was stirred at room temperature} \\
\text{overnight and quenched by water and extracted with ethyl acetate (3 times). Then the sample} \\
\text{was injected to GC-MS to detect higher isomers. No higher isomers were founded in GC-MS.}
\end{align*}
\]
5.10 Cross-over experiments

\[
\text{Si} + 1\text{t} + 1\text{i} + 2\text{a} \xrightarrow{\text{Pd(OAc)}_2, \text{Xantphos}, \text{Cs}_2\text{CO}_3} \text{3i, 60%}
\]

Pd(OAc)$_2$ (10 mol%, 4.5 mg) and Xantphos (20 mol%, 23.2 mg), Cs$_2$CO$_3$ (2.0 eq., 0.4 mmol, 130 mg) were placed in a dry and transparent reaction tube equipped with a stirring bar. The reaction tube was evacuated and filled with argon for three times. To those solid, acetylene 1i (1.5 eq.) and acetylene 1t (1.5 eq.), cyclohexyl iodide 2a (0.2 mmol) and 1 mL fresh THF (from SPS) were added via a syringe under argon atmosphere. Then the reaction tube was parafilmed and moved to under the irradiation of 3W 470 nm blue led (2-3 cm above the light bulb). A cooling fan was put on the top of the reaction tube to make sure the reaction temperature is near room temperature. The reaction mixture was stirred at room temperature overnight and quenched by water and extracted with ethyl acetate (3 times). The product was purified by flash column chromatography on silica gel to get the 1,3-enyne 3i(60%), no cross-over 1,3-enyne was founded in the reaction crude.
6. 2D-NMR of Product 3b

H1-COSY of 3b

The cross-peaks in H1-COSY proves: 1) $H_a$ and $H_d$ are on the same phenyl ring A. 2) $H_b$ and $H_c$ are on the same phenyl ring B.
The cross-peak in HC_HMBC proves phenyl ring A is connected with triplet bond.
The red spectrum is 1D-HNMR, the green spectrum is 1D-NOESY, and H₂ at 2.5 ppm is irradiated in 1D-NOESY. The respondence of H₃ at 7.39 ppm proves the cyclohexane ring and phenyl ring B is the same side. Thus, the conformation of 1,3-enzyme 3b is confirmed and is E.
7. References

1) W. Deng, C. Ye, Y. Li, D. Li, H. Bao, Org. Lett. 2019, 21, 261-265.
2) A. Hazra, J. Chen, G. Lalic, J. Am. Chem. Soc. 2019, 141, 12464-12469.
3) P. Chen, O. Vechorkin, K. V. Allmen, R. Scopelliti, X. Hu, J. Am. Chem. Soc. 2011, 133, 7084-7095.
4) W. Liu, Z. Chen, C.-J. Li, Org. Biomol. Chem. 2015, 13, 6170-6174.
5) N. Iranpoor, H. Firouzabadi, A. Jamalian, F. Kazemi, Tetrahedron, 2005, 61, 5699-5704.
6) L. Thomas, F. H. Lutter, M. S. Hofmyer, K. Karaghiosoff, P. Knochel, Org. Lett. 2018, 20, 2441-2444.
7) C. Meyer, I. Marek, G. Courtemanche. J.-F. Normant, Tetrahedron. 1994, 40, 11665-11692.
8) L. Su, T. Ren, J. Dong, L. Liu, S. Xie, L. Yuan, Y. Zhou, S.-F. Yin, J. Am. Chem. Soc. 2019, 141, 2535-2544.
9) C. W. Cheung, F. E. Zhurkin, X. Hu, J. Am. Chem. Soc. 2015, 137, 4932-4935.
10) K. Semba, T. Fujihara, T. Xu, J. Terao, Y. Tsuji, Adv. Synth. Catal. 2012, 354, 1542-1550.
11) A. Lielpetere, A. Jirgensons, Org. Biomol. Chem. 2018, 16, 5094-5096.
8. Physical Data

(E)-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)dibenzene (3a)

![Chemical structure](image)

Compound 3a was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 81% yield (46 mg) (crude NMR: E/Z > 20:1).

$^1$H NMR (600 MHz, CDCl$_3$): δ = 7.46 – 7.41 (m, 4H), 7.39 (t, $J = 7.3$ Hz, 2H), 7.33 – 7.27 (m, 4H), 6.12 (d, $J = 10.5$ Hz, 1H), 2.53 – 2.20 (m, 1H), 1.71 – 1.63 (overlap, 5H), 1.26 – 1.20 (overlap, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ = 145.9, 137.9, 131.4, 128.6, 128.23, 128.21, 127.8, 127.3, 123.6, 121.7, 91.6, 87.2, 38.0, 32.8, 25.8 ppm.

HRMS (EI) m/z: [M$^+$] mass found: 286.17189, calculated mass for C$_{22}$H$_{22}$: 286.17160.

IR (KBr): 3871, 3411, 3056, 3025, 2923, 2849, 2665, 2327, 2090, 1994, 1941, 1802, 1667, 1595, 1489, 1444, 1361, 1261, 1229, 1141, 1070, 1025, 966, 902, 861, 804, 754, 692 cm$^{-1}$.

(E)-4,4'-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis(fluorobenzene) (3b)

![Chemical structure](image)

Compound 3b was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 88% yield (57 mg) (crude NMR: E/Z > 20:1).

$^1$H NMR (600 MHz, CDCl$_3$): δ = 7.42 (dd, $J = 7.7$, 6.1 Hz, 2H), 7.39 (dd, $J = 7.4$, 6.2 Hz, 2H), 7.09 (t, $J = 8.5$ Hz, 2H), 7.01 (t, $J = 8.5$ Hz, 2H), 6.11 (d, $J = 10.5$ Hz, 1H), 2.35 – 2.33 (m, 1H), 1.79 – 1.63 (m, 5H), 1.22 (overlap, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): δ = 162.3 (d, $J = 249.3$ Hz), 162.0 (d, $J = 246.8$ Hz), 146.1, 133.8 (d, $J = 3.4$ Hz), 133.3 (d, $J = 8.4$ Hz), 130.2 (d, $J = 8.3$ Hz), 120.6, 119.5 (d, $J = 3.5$ Hz), 115.3 (d, $J = 22.0$ Hz), 115.1 (d, $J = 21.4$ Hz), 91.0, 86.3, 38.1, 32.8, 25.8, 25.4 ppm.

$^{19}$F NMR (565 MHz, CDCl$_3$): δ = -111.28 – -111.60 (m, 1F), -114.50 – -114.78 (m, 1F) ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 323.16078, calculated mass for C$_{22}$H$_{21}$F$_2$: 323.16058.

IR (KBr): 3438, 3052, 2926, 2852, 2161, 1890, 1728, 1599, 1504, 1448, 1406, 1365, 1226, 1155, 1093, 1015, 967, 902, 832, 728, 671 cm$^{-1}$.
Compound 3c was prepared according to the general procedure and was obtained as white solid after column chromatography (n-hexane) in 52% yield (36 mg) (crude NMR: E/Z = 7:1).

\( ^1\text{H NMR} \) (600 MHz, CDCl\(_3\))(E isomer): \( \delta = 7.30 – 7.22 \) (m, 6H), 7.19 (d, \( J = 8.8 \) Hz, 2H), 6.04 (d, \( J = 10.5 \) Hz, 1H), 2.28 – 2.18 (m, 1H), 1.68 – 1.53 (m, 5H), 1.21 – 1.03 (m, 5H) ppm.

\( ^{13}\text{C NMR} \) (151 MHz, CDCl\(_3\))(E isomer): \( \delta = 146.7, 136.1, 134.0, 133.3, 132.6, 129.9, 128.6, 128.5, 121.9, 120.5, 92.0, 86.4, 38.1, 32.7, 25.7, 25.3 \) ppm.

\( \text{HRMS (EI)} \) m/z: [M]+ mass found: 354.09382, calculated mass for C\(_{22}\)H\(_{20}\)Cl\(_2\): 354.09366.

\( \text{IR (KBr)} \): 2923, 2850, 1894, 1731, 1590, 1486, 1446, 1396, 1361, 1260, 1229, 1173, 1141, 1089, 1011, 966, 901, 823, 748 cm\(^{-1}\).

(E)-4,4’-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis(methylbenzene) (3d)

Compound 3d was prepared according to the general procedure and was obtained as light pink gel after column chromatography (n-hexane) in 44% yield (24 mg) (crude NMR: E/Z > 20:1)

\( ^1\text{H NMR} \) (600 MHz, CDCl\(_3\)): \( \delta = 7.31 \) (d, \( J = 8.0 \) Hz, 4H), 7.19 (d, \( J = 7.8 \) Hz, 2H), 7.09 (d, \( J = 7.9 \) Hz, 2H), 6.06 (d, \( J = 10.5 \) Hz, 1H), 2.38 (s, 3H), 2.37 – 2.34 (m, 1H), 2.33 (s, 3H), 1.76 – 1.61 (m, 5H), 1.25 – 1.11 (m, 5H) ppm.

\( ^{13}\text{C NMR} \) (151 MHz, CDCl\(_3\)): \( \delta = 145.2, 137.8, 137.0, 135.1, 131.3, 128.9, 128.8, 128.5, 121.7, 120.6, 91.1, 87.1, 38.0, 32.9, 25.8, 25.4, 21.4, 21.2 \) ppm.

\( \text{HRMS (EI)} \) m/z: [M]+ mass found: 314.20416, calculated mass for C\(_{24}\)H\(_{26}\): 314.20290.

\( \text{IR (KBr)} \): 3026, 2924, 2852, 2666, 2327, 2121, 1679, 1605, 1508, 1447, 1361, 1297, 1256, 1216, 1178, 1108, 1041, 965, 898, 815, 728, 683 cm\(^{-1}\).
Compound 3e was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane : ethyl acetate = 20:1) in 46% yield (32 mg) (crude NMR: E/Z > 20:1).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.28 (dd, $J =$ 8.8, 7.1 Hz, 4H), 6.84 (d, $J =$ 8.7 Hz, 2H), 6.75 (d, $J =$ 8.8 Hz, 2H), 5.94 (d, $J =$ 10.4 Hz, 1H), 3.76 (s, 3H), 3.73 (s, 3H), 2.37 – 2.21 (m, 1H), 1.66 – 1.52 (m, 5H), 1.21 – 1.05 (m, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta =$ 159.2, 158.8, 144.5, 132.8, 130.5, 129.7, 121.3, 115.8, 113.8, 113.5, 90.5, 86.9, 55.28, 55.26, 38.0, 32.9, 25.9, 25.4 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 347.20032, calculated mass for C$_{24}$H$_{27}$O$_2$: 347.20056.

IR (KBr): 3459, 3002, 2925, 2848, 2193, 1715, 1602, 1507, 1449, 1366, 1288, 1245, 1171, 1106, 1030, 967, 900, 831, 728 cm$^{-1}$.

Compound 3f was prepared according to the general procedure and was obtained as yellow gel after column chromatography (n-hexane : ethyl acetate = 9:1) in 50% yield (37 mg) (crude NMR: E/Z > 20:1).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta =$ 7.27 (d, $J =$ 8.8 Hz, 2H), 7.23 (d, $J =$ 8.9 Hz, 2H), 6.65 (d, $J =$ 8.8 Hz, 2H), 6.53 (d, $J =$ 8.9 Hz, 2H), 5.86 (d, $J =$ 10.4 Hz, 1H), 2.90 (s, 6H), 2.87 (s, 6H), 2.43 – 2.34 (m, 1H), 1.68 – 1.52 (m, 5H), 1.21 – 1.04 (m, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta =$ 149.7, 149.6, 142.6, 132.5, 129.5, 126.5, 121.9, 111.9, 111.8, 110.9, 90.1, 87.6, 40.5, 40.2, 37.9, 33.2, 26.0, 25.5 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 373.26354, calculated mass for C$_{26}$H$_{33}$N$_2$: 373.26383.

IR (KBr): 3694, 3294, 3088, 3038, 2921, 2851, 2805, 2346, 2193, 2099, 2007, 1883, 1663, 1605, 1518, 1479, 1444, 1355, 1282, 1224, 1164, 1127, 1063, 1034, 944, 897, 815, 754, 691 cm$^{-1}$.
(E)-4,4’-(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis((trifluoromethyl)benzene) (3g)

Compound 3g was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 85% yield (72 mg) (crude NMR: E/Z > 20:1).

1H NMR (600 MHz, CDCl3): δ = 7.66 (d, J = 7.9 Hz, 2H), 7.56 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 10.2 Hz, 4H), 6.23 (d, J = 10.6 Hz, 1H), 2.38 – 2.24 (m, 1H), 1.76 – 1.61 (m, 5H), 1.29 – 1.12 (m, 5H) ppm.

13C NMR (151 MHz, CDCl3): δ = 148.2, 141.1, 131.6, 129.7 (q, J = 32.6 Hz), 129.6 (q, J = 32.6 Hz), 128.9, 127.1, 125.3 (q, J = 3.7 Hz), 125.2 (q, J = 3.6 Hz), 124.1 (q, J = 271.7 Hz), 123.9 (q, J = 272.3 Hz), 120.3, 93.0, 86.5, 38.2, 32.6, 25.7, 25.2 ppm.

19F NMR (565 MHz, CDCl3): δ = -62.53 (s, 3F), -62.80 (s, 3F) ppm.

HRMS (EI) m/z: [M]+ mass found: 422.14641, calculated mass for C24H20F6: 422.14637.

IR (KBr): 3229, 2928, 2853, 2649, 2206, 1796, 1614, 1449, 1407, 1320, 1164, 1123, 1065, 1016, 966, 902, 840, 740, 709 cm⁻¹.

4,4’-(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis((trifluoromethoxy)benzene) (3h)

Compound 3h was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 84% yield (76 mg) (crude NMR: E/Z = 6:1).

1H NMR (600 MHz, CDCl3)(E isomer): δ = 7.44 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.23 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 8.2 Hz, 2H), 6.14 (d, J = 10.5 Hz, 1H), 2.37 – 2.27 (m, 1H), 1.75 – 1.62 (m, 5H), 1.21 (overlap, 5H) ppm.

13C NMR (151 MHz, CDCl3)(E isomer): δ = 148.7, 148.4, 147.0, 136.3, 132.9, 130.0, 122.1, 120.8, 120.7, 120.5 (q, J = 257.7 Hz), 120.3 (q, J = 257.3 Hz), 120.2, 91.8, 86.1, 38.1, 32.7, 25.7, 25.3 ppm.

19F NMR (565 MHz, CDCl3)(E isomer): δ = -57.74 (s, 3F), -57.82 (s, 3F) ppm.

HRMS (EI) m/z: [M]+ mass found: 454.13666, calculated mass for C24H20F6O2: 454.13620.

IR (KBr): 2929, 2854, 1603, 1504, 1449, 1358, 1251, 1206, 1159, 1017, 965, 923, 843, 729,
Compound 3i was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane : ethyl acetate = 9:1) in 84% yield (57 mg) (crude NMR: E/Z = 1:3)

$^1$H NMR (600 MHz, CDCl₃)(both isomers): $\delta = 7.70$ (t, $J = 8.4$ Hz, 3H), 7.65 (dd, $J = 10.1, 8.6$ Hz, 4H), 7.59 (d, $J = 8.2$ Hz, 3H), 7.49 (d, $J = 8.3$ Hz, 1.5 H), 6.50 (d, $J = 9.4$ Hz, 1H), 6.26 (d, $J = 10.7$ Hz, 0.36 H), 2.84 – 2.76 (m, 1H), 2.32 – 2.24 (m, 0.39 H), 1.89 – 1.77 (m, 4.20 H), 1.76 – 1.61 (m, 3 H), 1.44 – 1.35 (m, 2.2 H), 1.32 – 1.17 (m, 5.5 H).

$^{13}$C NMR (151 MHz, CDCl₃)(both isomers): $\delta = 149.4, 148.9, 142.1, 132.3, 132.2, 132.1, 132.0, 131.9, 129.1, 127.8, 126.5, 120.0, 119.9, 118.8, 118.6, 118.45, 118.40, 111.8, 111.5, 111.1, 94.5, 93.8, 89.8, 86.6, 40.9, 38.4, 32.5, 32.1, 25.8, 25.66, 25.64, 25.2 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 337.17095, calculated mass for C$_{24}$H$_{21}$N$_2$: 337.16993.

IR (KBr): 2924, 2851, 2222, 2075, 1600, 1501, 1447, 1408, 1356, 1274, 1174, 1110, 1017, 959, 903, 830, 731 cm$^{-1}$.

Tert-butyl (Z)-4-(2,4-bis(2-fluorophenyl)but-1-en-3-yn-1-yl)piperidine-1-carboxylate (3j)

Compound 3j was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane : ethyl acetate = 20:1) in 61% yield (52 mg) (crude NMR: Z/E > 20:1)

$^1$H NMR (600 MHz, CDCl₃): $\delta = 7.42 – 7.35$ (m, 2H), 7.34 – 7.30 (m, 1H), 7.26 – 7.23 (m, 1H), 7.18 (t, $J = 7.5$ Hz, 1H), 7.12 (t, $J = 9.0$ Hz, 1H), 7.08 – 7.01 (m, 2H), 6.21 (d, $J = 10.3$ Hz, 1H), 4.04 (br, 2H), 2.62 (overlap, 2H), 2.28 – 2.05 (m, 1H), 1.63 (overlap, 1H), 1.45 (s, 9H), 1.43 – 1.41 (m, 1H), 1.39 – 1.31 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl₃): $\delta = 162.5$ (d, $J = 251.27$ Hz), 159.2 (d, $J = 247.26$ Hz), 154.8, 146.3, 133.3, 130.9 (d, $J = 3.28$ Hz), 129.8 (d, $J = 7.57$ Hz), 129.6 (d, $J = 7.63$ Hz), 124.8, 124.7, 903, 830, 731 cm$^{-1}$. 

S24
124.2 (d, J = 3.4 Hz), 123.8 (d, J = 3.59 Hz), 116.4, 115.9 (d, J = 22.04 Hz), 115.4 (d, J = 20.66 Hz), 111.8 (d, J = 15.66 Hz), 95.0, 81.1, 79.4, 37.2, 31.0, 28.4 ppm.

$^{19}$F NMR (565 MHz, CDCl$_3$): $\delta = -109.79 - 110.03$ (m, 1F), -113.74 - -114.08 (m, 1F) ppm.

HRMS (ESI) m/z: [M+Na]$^+$ mass found:446.19016, calculated mass for C$_{26}$H$_{27}$O$_2$NF$_2$Na: 446.19021.

IR (KBr): 3077, 2973, 2925, 2859, 1684, 1614, 1574, 1487, 1426, 1364, 1314, 1280, 1224, 1163, 1104, 1065, 994, 939, 866, 817, 756 cm$^{-1}$.

3,3'-[(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis((trifluoromethyl)benzene) (3k)

Compound 3k was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 82% yield (69 mg) (crude NMR: E/Z = 14:1).

$^1$H NMR (600 MHz, CDCl$_3$)(E isomer): $\delta = 7.61$ (s, 1H), 7.58 (s, 1H), 7.51 (d, J = 7.3 Hz, 3H), 7.46 (t, J = 7.0 Hz, 2H), 7.35 (t, J = 7.8 Hz, 1H), 6.14 (d, J = 10.6 Hz, 1H), 2.29 – 2.14 (m, 1H), 1.62 (overlap, 5H), 1.21 – 1.04 (m, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$)(E isomer): $\delta = 147.9, 138.2, 134.5, 131.8, 130.9$ (q, J = 32.6 Hz), 130.7 (q, J = 32.4 Hz), 128.86, 128.81, 128.2 (q, J = 3.5 Hz), 125.4 (q, J = 3.7 Hz), 124.6 (q, J = 3.6 Hz), 124.3 (q, J = 3.6 Hz), 124.2, 124.0 (q, J = 272.3 Hz), 121.9 (q, J = 272.3 Hz), 120.2, 92.2, 86.3, 38.3, 32.7, 25.7, 25.2 ppm.

$^{19}$F NMR (565 MHz, CDCl$_3$)(E isomer): $\delta = -62.69$ (s, 3F), -62.99 (s, 3F) ppm.

HRMS (EI) m/z: [M]$^+$ mass found: 422.14672, calculated mass for C$_{24}$H$_{20}$F$_6$: 422.14637.

IR (KBr): 3694, 2928, 2854, 2156, 1486, 1437, 1324, 1268, 1225, 1166, 1125, 1072, 969, 903, 868, 800, 739, 696, 661 cm$^{-1}$.

(E)-3,3'-[(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis(methylbenzene) (3I)

Compound 3I was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 45% yield (28 mg) (crude NMR: E/Z > 20:1).

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.29 - 7.26$ (m, 2H), 7.26 - 7.23 (m, 2H), 7.21 (d, J = 7.6 Hz, 1H), 7.18 (t, J = 7.6 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 7.09 (d, J = 7.6 Hz, 1H), 6.09 (d, J = 10.5 Hz, 2H), 6.05 (d, J = 9.3 Hz, 2H), 2.21 - 1.79 (m, 14H), 1.59 - 1.20 (m, 10H) ppm.

HRMS (ESI) m/z: [M+Na]$^+$ mass found: 446.19016, calculated mass for C$_{26}$H$_{27}$O$_2$NF$_2$Na: 446.19021.
Hz, 1H), 2.39 (s, 3H), 2.38 – 2.34 (m, 1H), 2.32 (s, 3H), 1.75 – 1.61 (m, 5H), 1.28 – 1.12 (m, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 145.7, 137.9, 137.83, 137.81, 132.1, 129.3, 128.7, 128.5, 128.1, 128.0, 125.6, 123.4, 121.8, 91.4, 87.3, 38.0, 32.9, 25.8, 25.4, 21.5, 21.2$ ppm (one carbon peak missing due to the overlap).

HRMS (EI) m/z: [M]$^+$ mass found: 314.20305, calculated mass for C$_{24}$H$_{26}$: 314.20290.

IR (KBr): 3440, 3030, 2923, 2851, 2659, 2325, 2111, 1873, 1786, 1599, 1483, 1447, 1361, 1263, 1167, 1091, 1039, 967, 902, 782, 709, 689 cm$^{-1}$.

(E)-3,3’-(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis(methoxybenzene) (3m)

![Chemical structure of compound 3m](image)

Compound 3m was prepared according to the general procedure and was obtained as colorless gel after column chromatography ($n$-hexane : ethyl acetate = 20:1) in 58% yield (40 mg) (crude NMR: E/Z > 20:1)

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.30$ (t, $J = 7.9$ Hz, 1H), 7.20 (t, $J = 8.0$ Hz, 1H), 7.02 (dd, $J = 14.4, 7.6$ Hz, 2H), 6.99 – 6.95 (m, 2H), 6.89 – 6.81 (m, 2H), 6.12 (d, $J = 10.5$ Hz, 1H), 3.84 (s, 3H), 3.79 (s, 3H), 2.45 – 2.38 (m, 1H), 1.74 – 1.62 (m, 5H), 1.25 – 1.14 (m, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 159.4, 159.2, 146.2, 139.2, 129.26, 129.22, 124.6, 124.1, 121.6, 121.0, 116.1, 114.6, 114.2, 113.0, 91.3, 87.2, 55.27, 55.24, 38.1, 32.8, 25.8, 25.4$ ppm.

HRMS (ESI) m/z: [M+Na]$^+$ mass found: 369.18133, calculated mass for C$_{24}$H$_{26}$O$_2$Na: 369.18250.

IR (KBr): 3068, 3001, 2925, 2848, 1741, 1578, 1483, 1456, 1426, 1318, 1282, 1229, 1155, 1082, 1042, 993, 967, 856, 781, 685 cm$^{-1}$.

Tert-butyl 4-(2,4-bis(3-fluorophenyl)but-1-en-3-yn-1-yl)piperidine-1-carboxylate (3n)

![Chemical structure of compound 3n](image)

Compound 3n was prepared according to the general procedure and was obtained as colorless gel after column chromatography ($n$-hexane : ethyl acetate = 20:1) in 70% yield (59 mg) (crude NMR: E/Z = 5:1)

$^1$H NMR (600 MHz, CDCl$_3$)(E isomer): $\delta = 7.40 – 7.34$ (m, 1H), 7.31 – 7.27 (m, 1H), 7.22 (d, $J = 7.8$ Hz, 1H), 7.17 (d, $J = 7.7$ Hz, 1H), 7.15 – 7.09 (m, 2H), 7.08 – 6.99 (m, 2H), 6.11 (d, $J =$
10.3 Hz, 1H), 4.09 (overlap, 2H), 2.68 (overlap, 2H), 2.56 – 2.35 (m, 1H), 1.64 (overlap, 2H), 1.48 (s, 9H), 1.45 – 1.36 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 162.7$ (d, $J = 246.13$ Hz), 162.3 (d, $J = 246.10$ Hz), 154.7, 144.5, 142.9, 139.4 (d, $J = 7.4$ Hz), 129.9 (d, $J = 19.15$ Hz), 129.8 (d, $J = 19.30$ Hz), 127.3 (d, $J = 3.08$ Hz), 124.9 (d, $J = 9.36$ Hz), 124.1 (d, $J = 2.35$ Hz), 118.2 (d, $J = 22.93$ Hz), 115.56 (d, $J = 22.93$ Hz), 115.53 (d, $J = 22.93$ Hz), 114.7 (d, $J = 22.93$ Hz), 91.2, 87.1, 79.5, 36.3, 31.5, 28.4, 28.4 ppm.

$^{19}$F NMR (565 MHz, CDCl$_3$): $\delta = -112.57$ – -112.66 (m, 1F), -112.95 – -113.04 (m, 1F) ppm.

HRMS (ESI) m/z: $[M+Na]^+$ mass found: 446.18909, calculated mass for C$_{26}$H$_{27}$O$_2$NF$_2$Na: 446.19021.

IR (KBr): 3379, 3071, 2974, 2931, 2855, 2167, 1689, 1607, 1580, 1480, 1423, 1366, 1275, 1236, 1157, 1076, 1001, 971, 934, 869, 782, 710, 683 cm$^{-1}$.

3,3'-(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)dipyridine (3o)

Compound 3o was prepared according to the general procedure and was obtained as yellow gel after column chromatography ($n$-hexane: ethyl acetate = 2:1 to 1:1, 1% triethylamine was added) in 94% yield (54 mg) (crude NMR: E/Z = 5:1).

$^1$H NMR (600 MHz, CDCl$_3$)(E isomer): $\delta = 8.65$ (d, $J = 5.6$ Hz, 2H), 8.56 (d, $J = 4.7$ Hz, 1H), 8.49 (d, $J = 4.9$ Hz, 1H), 7.73 – 7.66 (m, 2H), 7.33 (dd, $J = 7.6, 5.1$ Hz, 1H), 7.23 (dd, $J = 7.6, 5.1$ Hz, 1H), 6.24 (d, $J = 10.6$ Hz, 1H), 2.41 – 2.19 (m, 1H), 1.75 – 1.58 (m, 5H), 1.30 – 1.09 (m, 5H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$)(E isomer): $\delta = 152.0$, 149.3, 148.6, 148.5, 148.4, 138.3, 136.0, 133.4, 123.3, 122.9, 120.4, 118.0, 93.8, 84.4, 38.3, 32.7, 25.6, 25.2 ppm.

HRMS (ESI) m/z: $[M+H]^+$ mass found: 289.16998, calculated mass for C$_{20}$H$_{21}$N$_2$: 289.16993.

IR (KBr): 3032, 2927, 2853, 2651, 2217, 1737, 1613, 1514, 1450, 1410, 1324, 1242, 1161, 1113, 1068, 1006, 908, 834, 806, 737, 699, 662 cm$^{-1}$. 

S27
**6,6’-(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis(2-methoxynaphthalene) (3p)**

![Chemical Structure of Compound 3p]

Compound 3p was prepared according to the general procedure and was obtained as light yellow gel after column chromatography (n-hexane: ethyl acetate = 20:1) in 92% yield (82 mg) (crude NMR: E/Z = 5:1)

**^1H NMR** (600 MHz, CDCl₃)(E isomer): δ = 7.81 (s, 1H), 7.74 (s, 1H), 7.69 (dd, J = 8.4, 5.2 Hz, 2H), 7.61 – 7.56 (m, 2H), 7.47 (dd, J = 8.4, 1.6 Hz, 1H), 7.39 (dd, J = 8.4, 1.5 Hz, 1H), 7.12 – 7.07 (m, 2H), 7.05 (dd, J = 8.8, 2.5 Hz, 1H), 7.01 (d, J = 2.3 Hz, 1H), 6.12 (d, J = 10.4 Hz, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 2.43 – 2.33 (m, 1H), 1.72 – 1.54 (m, 5H), 1.18 – 1.06 (m, 5H) ppm.

**^13C NMR** (151 MHz, CDCl₃)(E isomer): δ = 158.1, 157.8, 145.7, 133.9, 133.8, 133.3, 131.0, 129.6, 129.2, 129.1, 128.7, 128.5, 127.3, 127.4, 126.68, 126.62, 126.6, 121.9, 119.2, 118.9, 118.6, 105.8, 105.6, 91.4, 87.9, 55.37, 55.33, 38.1, 32.9, 25.8, 25.4 ppm.

**HRMS (ESI) m/z:** [M+H]^+ mass found: 447.23317, calculated mass for C₃₂H₃₁O₂: 447.23186.

**IR (KBr):** 3262, 3058, 3002, 2925, 2849, 2652, 1627, 1601, 1483, 1456, 1388, 1261, 1165, 1123, 1030, 967, 900, 851, 808, 730 cm⁻¹.

**Compound 3q**

![Chemical Structure of Compound 3q]

Compound 3q was prepared according to the general procedure and was obtained as light-yellow gel after column chromatography (n-hexane) in 77% yield (46 mg) (crude NMR: Z/E > 20:1)

**^1H NMR** (600 MHz, CDCl₃): δ = 7.42 (dd, J = 2.9, 0.7 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.26 – 7.21 (m, 2H), 7.12 (dd, J = 5.0, 0.7 Hz, 1H), 6.05 (d, J = 10.2 Hz, 1H), 2.59 – 2.49 (m, 1H), 1.80 – 1.64 (m, 5H), 1.34 – 1.16 (m, 5H) ppm.

**^13C NMR** (151 MHz, CDCl₃): δ = 145.4, 138.0, 129.8, 128.3, 128.1, 125.1, 125.0, 123.4, 122.5, 116.3, 90.7, 81.7, 38.3, 32.7, 25.8, 25.4 ppm.

**HRMS (ESI) m/z:** [M+H]^+ mass found: 299.09298, calculated mass for C₁₈H₁₈S₂: 299.09227.

**IR (KBr):** 3447, 3106, 2924, 2850, 2159, 1726, 1666, 1512, 1447, 1413, 1354, 1239, 1184,
(8R,8'R,9S,9'S,13S,13'S,14S,14'S)-3,3'-(E)-4-cyclohexylbut-3-en-1-yne-1,3-diyldibenzene (5a)

Compound 5a was prepared according to the general procedure and was obtained as light pink gel after column chromatography (n-hexane) in 55% yield (27 mg) (crude NMR: E/Z > 20:1)

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.48 – 7.39 (m, 6H), 7.38 – 7.29 (m, 4H), 6.12 (d, $J$ = 10.6 Hz, 1H), 2.76 – 2.67 (m, 1H), 1.07 (d, $J$ = 6.0 Hz, 6H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ = 147.3, 137.9, 131.4, 128.6, 128.2, 127.8, 127.3, 126.3, 123.6, 121.5, 121.0, 119.1, 91.2, 87.0, 65.8, 50.57, 50.52, 48.0, 47.9, 44.47, 44.46, 38.1, 38.06, 38.00, 37.9, 35.87, 35.84, 33.0, 31.6, 31.5, 29.5, 29.0, 26.5, 26.3, 26.2, 25.8, 25.6, 25.59, 25.54, 25.4, 21.6, 21.5, 15.2, 13.88, 13.85 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 639.41999, calculated mass for C$_{46}$H$_{55}$O$_2$: 639.41966.

IR (KBr): 3455, 2925, 2855, 2249, 1735, 1495, 1450, 1406, 1372, 1342, 1257, 1215, 1083, 1052, 1007, 967, 907, 822, 783, 728 cm$^{-1}$. 

Compound 3r was prepared according to the general procedure and was obtained as light brown solid after column chromatography (n-hexane) in 42% yield (54 mg) (crude NMR: E/Z > 20:1)

$^1$H NMR (600 MHz, CDCl$_3$): $\delta$ = 7.38 – 7.30 (m, 4H), 7.25 – 7.19 (m, 2H), 6.11 (d, $J$ = 10.5 Hz, 1H), 3.53 (q, $J$ = 7.0 Hz, 1H), 3.02 – 2.90 (m, 6H), 2.60 – 2.52 (m, 3H), 2.51 – 2.44 (m, 4H), 2.39 – 2.32 (m, 3H), 2.24 – 2.18 (m, 3H), 2.15 – 2.07 (m, 6H), 2.07 – 2.00 (m, 3H), 1.72 – 1.49 (m, 12H), 0.98 (s, 3H), 0.96 (s, 3H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta$ = 220.8, 220.7, 145.3, 141.4, 139.7, 138.9, 136.8, 136.4, 136.2, 135.5, 132.9, 131.9, 129.8, 129.1, 128.8, 126.0, 125.5, 125.2, 125.1, 121.5, 121.0, 119.1, 91.2, 87.0, 65.8, 50.57, 50.52, 48.0, 47.9, 44.47, 44.46, 38.1, 38.06, 38.00, 37.9, 35.87, 35.84, 33.0, 31.6, 31.5, 29.5, 29.0, 26.5, 26.3, 26.2, 25.8, 25.6, 25.59, 25.54, 25.4, 21.6, 21.5, 15.2, 13.88, 13.85 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 639.41999, calculated mass for C$_{46}$H$_{55}$O$_2$: 639.41966.

IR (KBr): 3455, 2925, 2855, 2249, 1735, 1495, 1450, 1406, 1372, 1342, 1257, 1215, 1083, 1052, 1007, 967, 907, 822, 783, 728 cm$^{-1}$. 

(8R,8'R,9S,9'S,13S,13'S,14S,14'S)-3,3'-(E)-4-cyclohexylbut-3-en-1-yne-1,3-diyldibenzene (5a)
121.4, 91.4, 87.3, 28.4, 22.8 ppm.

**HRMS (EI) m/z: [M]+** mass found: 246.14061, calculated mass for C_{19}H_{18}: 246.14030.

**IR** (KBr): 3446, 3057, 3027, 2967, 2927, 2867, 1596, 1489, 1445, 1382, 1361, 1272, 1166, 1071, 1026, 948, 913, 880, 841, 754, 692 cm\(^{-1}\).

**HRMS (EI) m/z: [M]+** mass found: 260.15521, calculated mass for C_{20}H_{20}: 260.15595.

**IR** (KBr): 3058, 3027, 2961, 2924, 2336, 1743, 1596, 1489, 1444, 1371, 1283, 1156, 1071, 1024, 974, 914, 883, 753, 692 cm\(^{-1}\).

**HRMS (EI) m/z: [M]+** mass found: 272.15640, calculated mass for C_{21}H_{22}: 272.15595.

**IR** (KBr): 3340, 3056, 3026, 2950, 2864, 1743, 1596, 1489, 1444, 1366, 1159, 1068, 1026, 945, 913, 876, 753, 691 cm\(^{-1}\).
(2,4-diphenylbut-1-en-3-yn-1-yl)cycloheptane (5d)

![Structure of Compound 5d](image)

Compound 5d was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 73% yield (44 mg) (crude NMR: E/Z = 10:1)

$^1$H NMR (600 MHz, CDCl$_3$) (E isomer): $\delta = 7.56 - 7.52$ (m, 2H), 7.45 – 7.38 (m, 4H), 7.37 – 7.33 (m, 4H), 6.21 (d, $J = 10.8$ Hz, 1H), 2.67 – 2.33 (m, 1H), 1.79 – 1.72 (m, 2H), 1.70 – 1.65 (m, 2H), 1.54 – 1.48 (m, 4H), 1.46 – 1.38 (m, 4H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 146.5, 137.9, 131.4, 128.6, 128.2, 127.8, 127.3, 126.3, 123.6, 120.3, 91.7, 87.0, 39.1, 34.6, 28.5, 26.1$ ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found: 301.19582, calculated mass for C$_{23}$H$_{25}$: 301.19508.

IR (KBr): 3058, 3029, 2921, 2853, 1732, 1596, 1489, 1445, 1361, 1315, 1277, 1249, 1174, 1069, 1026, 952, 912, 893, 841 cm$^{-1}$.

(2,4-Diphenylbut-1-en-3-yn-1-yl)cyclooctane (5e)

![Structure of Compound 5e](image)

Compound 5e was prepared according to the general procedure and was obtained as light-yellow gel after column chromatography (n-hexane) in 65% yield (41 mg) (crude NMR: E/Z = 8:1)

$^1$H NMR (600 MHz, CDCl$_3$) (E isomer): $\delta = 7.44 – 7.41$ (m, 2H), 7.39 – 7.35 (m, 5H), 7.31 – 7.27 (m, 3H), 6.10 (d, $J = 10.6$ Hz, 1H), 2.66 – 2.54 (m, 1H), 1.55 – 1.48 (m, 2H), 1.37 – 1.24 (m, 10H), 1.05 – 0.94 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 146.4, 138.2, 131.4, 128.6, 128.3, 128.1, 128.1, 127.8, 127.2, 123.6, 91.4, 87.4, 33.5, 30.3, 23.8, 23.6, 23.2, 22.7, 22.4$ ppm (one carbon peak missing due to the overlap).

HRMS (EI) m/z: [M]$^+$ mass found: 314.20236, calculated mass for C$_{24}$H$_{26}$: 314.20290.

IR (KBr): 3062, 3026, 2931, 2853, 2200, 1727, 1644, 1597, 1488, 1467, 1443, 1353, 1288, 1207, 1170, 1069, 1026, 950, 913, 885, 754, 691 cm$^{-1}$. 
3-(2,4-Diphenylbut-1-en-3-yn-1-yl)tetrahydrofuran (5f)

Compound 5f was prepared according to the general procedure and was obtained as yellow gel after column chromatography (n-hexane : ethyl acetate = 20 :1) in 64% yield (35 mg) (crude NMR: E/Z = 6:1)

$^1$H NMR (600 MHz, CDCl$_3$)(E isomer): $\delta = 7.45 – 7.42$ (m, 2H), 7.42 – 7.39 (m, 3H), 7.37 – 7.32 (m, 2H), 7.32 – 7.28 (m, 3H), 6.18 (d, $J = 10.4$ Hz, 1H), 3.98 – 3.93 (m, 1H), 3.91 (dd, $J = 17.1$, 9.1 Hz, 1H), 3.77 (dd, $J = 15.4$, 8.0 Hz, 1H), 3.57 – 3.50 (m, 1H), 3.22 – 3.10 (m, 1H), 2.16 – 2.07 (m, 1H), 1.88 – 1.76 (m, 1H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 139.9$, 137.3, 131.5, 128.6, 128.3, 128.2, 128.1, 127.7, 126.0, 124.6, 90.7, 88.4, 73.1, 68.3, 39.5, 34.0 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found:275.14385, calculated mass for C$_{20}$H$_{19}$O:275.14304.

IR (KBr): 3056, 3026, 2966, 2931, 2859m 1728, 1596, 1489, 1445, 1363, 1244, 1180, 1068, 966, 908, 755, 693, 532 cm$^{-1}$.

4-(2,4-Diphenylbut-1-en-3-yn-1-yl)tetrahydro-2H-pyran (5g)

Compound 5g was prepared according to the general procedure and was obtained as yellow gel after column chromatography (n-hexane : ethyl acetate = 20 :1) in 78% yield (45 mg) (crude NMR: E/Z = 12:1)

$^1$H NMR (600 MHz, CDCl$_3$)(E isomer): $\delta = 7.45 – 7.42$ (m, 2H), 7.41 – 7.39 (m, 4H), 7.37 – 7.32 (m, 1H), 7.31 – 7.28 (m, 3H), 6.10 (d, $J = 10.3$ Hz, 1H), 3.94 (dt, $J = 11.4$, 3.3 Hz, 2H), 3.37 – 3.30 (m, 2H), 2.67 – 2.58 (m, 1H), 1.62 – 1.54 (m, 1H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 143.4$, 137.6, 131.5, 128.5, 128.3, 128.2, 128.0, 127.6, 123.3, 123.2, 91.1, 88.0, 67.1, 35.3, 32.4 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found:289.15946, calculated mass for C$_{21}$H$_{21}$O:289.15869.

IR (KBr): 3056, 3026, 2930, 2842, 1597, 1490, 1442, 1385, 1237, 1122, 1080, 1012, 984, 915, 871, 821, 754, 693 cm$^{-1}$.
**Tert-butyl-4-(2,4-diphenylbut-1-en-3-yn-1-yl)piperidine-1-carboxylate (5h)**

![Chemical Structure](image)

Compound 5h was prepared according to the general procedure and was obtained as light yellow gel after column chromatography (n-hexane : ethyl acetate = 9:1) in 68% yield (53 mg) (crude NMR: E/Z = 10:1)

$^1$H NMR (600 MHz, CDCl$_3$)(E isomer): $\delta = 7.45 - 7.42$ (m, 2H), 7.41 – 7.39 (m, 4H), 7.36 – 7.33 (m, 1H), 7.30 – 7.28 (m, 3H), 6.07 (d, $J = 10.3$ Hz, 1H), 4.07 (br, 2H), 2.66 (overlap, 2H), 2.57 – 2.46 (m, 1H), 1.65 (overlap, 2H), 1.46 (s, 9H), 1.41 – 1.33 (m, 2H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 154.8$, 143.2, 137.6, 131.5, 128.5, 128.4, 128.2, 128.0, 127.6, 126.0, 123.3, 91.0, 88.0, 79.4, 36.2, 31.7, 28.5, 28.4 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found:388.22626, calculated mass for C$_{26}$H$_{30}$O$_2$N$_1$: 388.22711.

IR (KBr): 2974, 2928, 2853, 1690, 1598, 1418, 1365, 1278, 1244, 1166, 1069, 967, 938, 864, 757, 693, 658 cm$^{-1}$.

**{(E)}-(5,5-Dimethylhex-3-en-1-yn-1,3-diyl)dibenzene (5i)**

![Chemical Structure](image)

Compound 5i was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 63% yield (33 mg) (crude NMR: E/Z > 20:1)

$^1$H NMR (600 MHz, CDCl$_3$): $\delta = 7.42 – 7.39$ (m, 2H), 7.37 – 7.34 (m, 4H), 7.34 – 7.31 (m, 1H), 7.30 – 7.26 (m, 3H), 6.31 (s, 1H), 0.99 (s, 9H) ppm.

$^{13}$C NMR (151 MHz, CDCl$_3$): $\delta = 149.9$, 138.8, 131.4, 129.1, 128.1, 127.9, 127.7, 127.2, 123.6, 122.1, 92.6, 87.2, 34.6, 30.9 ppm.

HRMS (ESI) m/z: [M+H]$^+$ mass found:261.16467, calculated mass for C$_{20}$H$_{21}$:261.16378.

IR (KBr): 3058, 2957, 2867, 1736, 1597, 1488, 1443, 1364, 1265, 1200, 1069, 1026, 949, 914, 879, 838 cm$^{-1}$.
1-((E)-2,4-Diphenylbut-1-en-3-yn-1-yl)adamantane (5j)

Compound 5j was prepared according to the general procedure and was obtained as light-yellow gel after column chromatography (n-hexane) in 84% yield (57 mg) (crude NMR: E/Z > 20:1)

\[^1\text{H}\text{ NMR}\] (600 MHz, CDCl\textsubscript{3}): \(\delta = 7.40 - 7.36\) (m, 2H), 7.35 - 7.33 (m, 4H), 7.33 - 7.29 (m, 1H), 7.29 - 7.25 (m, 3H), 6.06 (s, 1H), 1.86 (s, 3H), 1.65 - 1.56 (m, 12H) ppm.

\[^{13}\text{C}\text{ NMR}\] (151 MHz, CDCl\textsubscript{3}): \(\delta = 150.1, 139.1, 131.4, 129.2, 128.1, 127.7, 127.7, 127.2, 123.7, 121.9, 92.9, 87.3, 42.7, 37.1, 36.5, 28.3\) ppm.

HRMS (EI) m/z: [M]\(^+\) mass found:338.20429, calculated mass for C\textsubscript{26}H\textsubscript{36}:338.2029.

IR (KBr): 3057, 2902, 2848, 2660, 2199, 1879, 1729, 1595, 1488, 1446, 1364, 1314, 1283, 1207, 1175, 1101, 1069, 1027, 986, 914, 873, 754, 694 cm\(^{-1}\).

(3S,5S,8R,9S,10S,13S,14S)-3-(2,4-Diphenylbut-1-en-3-yn-1-yl)-10,13-dimethylhexadecahydro-17H-cyclopenta[a]phenanthren-17-one (5k)

Compound 5k was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane : ethyl acetate = 20 :1) in 50% yield (48 mg) (crude NMR: E/Z = 1:2)

\[^1\text{H}\text{ NMR}\] (600 MHz, CDCl\textsubscript{3}): \(\delta = 7.40 - 7.40\) (m, 5H), 7.40 - 7.34 (m, 4H), 7.32 - 7.27 (m, 6H), 6.75 (d, J = 11.0 Hz, 1H), 6.10 (d, J = 10.5 Hz, 0.44H), 2.87 - 2.79 (m, 1H), 2.49 - 2.38 (m, 2H), 2.14 - 2.00 (m, 2H), 1.99 - 1.87 (m, 2H), 1.85 - 1.67 (m, 7H), 1.61 - 1.45 (m, 10H), 1.36 - 1.20 (m, 14H), 1.12 - 1.02 (m, 2H), 0.87 (s, 3H), 0.85 (s, 1.5H), 0.83 (s, 1.5H), 0.82 (s, 3H) ppm.

\[^{13}\text{C}\text{ NMR}\] (151 MHz, CDCl\textsubscript{3}): \(\delta = 221.45, 145.58, 143.24, 137.83, 131.50, 128.70, 128.24, 128.22, 127.94, 127.39, 123.54, 122.33, 91.85, 87.21, 65.86, 54.70, 51.59, 47.86, 45.69, 40.95, 38.57, 37.62, 36.47, 35.87, 35.11, 33.71, 33.60, 32.56, 31.62, 30.86, 28.61, 26.53, 21.77, 20.10, 15.28, 13.86, 11.82.

HRMS (ESI) m/z: [M+Na]\(^+\) mass found:499.29581, calculated mass for C\textsubscript{35}H\textsubscript{40}ONa:499.29714.

IR (KBr): 3457, 3025, 2921, 2854, 2165, 1735, 1597, 1489, 1446, 1373, 1249, 1173, 1062,
(E)-(5-Methylnona-3,8-dien-1-yn-1,3-diyldibenzene and (E)-(4-(3-Methyl-cyclopentyl)but-3-en-1-yn-1,3-diyldibenzene (5m, 5m′)

Inseparable compound 5m and 5m′ were prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 61% yield (35 mg) (5m : 5m′ = 6:1).

^1H NMR (600 MHz, CDCl₃)(mixture of 5m and 5m′): δ = 7.45 − 7.42 (m, 2.2H), 7.41 − 7.35 (m, 4.6H), 7.32 − 7.27 (m, 4.8H), 6.07 (d, J = 11.0 Hz, 0.16 H), 6.05 (d, J = 10.7 Hz, 1H), 5.77 − 5.63 (m, 1H), 4.94 − 4.83 (m, 2H), 2.61 − 2.51 (m, 1.2 H), 2.10 − 1.99 (m, 1.22 H), 1.96 − 1.89 (m, 1.18H), 1.45 − 1.40 (m, 2.36H), 1.06 (d, J = 6.6 Hz, 3H), 1.01 (d, J = 6.6 Hz, 0.5 H) ppm.

^13C NMR (151 MHz, CDCl₃)(mixture of 5m and 5m′): δ = 146.0, 138.5, 137.9, 131.4, 128.6, 128.2, 127.8, 127.3, 123.5, 122.7, 114.4, 91.4, 87.4, 36.5, 33.0, 31.5, 29.7, 20.8 ppm.

HRMS (EI) m/z: [M]^+ mass found: 286.1715, calculated mass for C₂₂H₂₂: 286.1716.

IR (KBr): 3340, 3062, 3025, 2922, 2854, 2162, 1729, 1641, 1597, 1556, 1489, 1447, 1372, 1030, 911, 754, 694 cm⁻¹.

(Z)-(4-Cyclohexylbut-3-en-1-yne-1,3-diyldibis(trimethylsilane) (3t)

Compound 3t was prepared according to the general procedure and was obtained as colorless gel after column chromatography (n-hexane) in 45% yield (25 mg) (crude NMR: Z/E > 20:1)(due to the low boiling point of 3t, the solvent of DCM and ethyl acetate can’t be removed).

^1H NMR (600 MHz, CDCl₃): δ = 5.94 (d, J = 8.6 Hz, 1H), 2.70 − 2.60 (m, 1H), 1.75 − 1.61 (m, 6H), 1.23 − 1.03 (m, 4H), 0.18 (s, 9H), 0.12 (s, 9H) ppm.

^13C NMR (151 MHz, CDCl₃): δ = 160.0, 124.4, 106.7, 103.5, 34.0, 28.0, 27.7, 16.2, 2.2, -0.0 ppm.

HRMS (ESI) m/z: [M+H]^+ mass found: 279.19613, calculated mass for C₁₆H₂₃Si₂: 279.19588.

IR (KBr): 3854, 2925, 2851, 2664, 2329, 2121, 1993, 1801, 1600, 1447, 1406, 1349, 1310, 1247, 1171, 1137, 1094, 987, 961, 906, 837, 754, 694 cm⁻¹.
9. NMR Spectrum

\((E)-(4\text{-Cyclohexylbut-3-en-1-yn}-1,3\text{-diyl})\text{dibenzene (3a)}\)

\(\text{\(^1\)H NMR (600 MHz, CDCl}_3\)\)

\(\text{\(^{13}\)C NMR (151 MHz, CDCl}_3\)\)
(E)-4,4'-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis(fluorobenzene) (3b)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
$^{19F}$ NMR (565 MHz, CDCl$_3$)
4,4′-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis(chlorobenzene) (3c)

\(^1\text{H NMR}\) (600 MHz, CDCl\(_3\))

\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\))
\((E)-4,4'-(4\text{-Cyclohexylbut}-3\text{-en}-1\text{-yne}-1,3\text{-diyl})\text{bis(methylbenzene)}\) (3d)

\(^1H\text{ NMR}\ (600\text{ MHz, CDCl}_3)

\(^{13}C\text{ NMR}\ (151\text{ MHz, CDCl}_3)\)
(E)-4,4'-(4-Cyclohexylbut-3-en-1-ynyl)bis(methoxybenzene) (3e)

\(^1\)H NMR (600 MHz, CDCl\(_3\))

\(^{13}\)C NMR (151 MHz, CDCl\(_3\))
(E)-4,4'-(4-Cyclohexylbut-3-en-1-ynyl)bis(N,N-dimethylaniline) (3f)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(E)-4,4’-(4-cyclohexylbut-3-en-1-yne-1,3-diyl)bis((trifluoromethyl)benzene) (3g)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
$^{19}$F NMR (565 MHz, CDCl$_3$)
4,4'-((4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis((trifluoromethoxy)benzene) (3h)

$^1$H NMR (600 MHz, CDCl₃)

$^{13}$C NMR (151 MHz, CDCl₃)
$^{19}\text{F NMR}$ (565 MHz, CDCl$_3$)
4,4’-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)dibenzonitrile (3i)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
Tert-butyl (Z)-4-(2,4-bis(2-fluorophenyl)but-1-en-3-yn-1-yl)piperidine-1-carboxylate (3j)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
$^{19}$F NMR (565 MHz, CDCl₃)
3,3'-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis((trifluoromethyl)benzene) (3k)

**$^1H$ NMR** (600 MHz, CDCl₃)

**$^{13}C$ NMR** (151 MHz, CDCl₃)
$^{19}\text{F NMR}$ (565 MHz, CDCl$_3$)
(E)-3,3’-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis(methylbenzene) (3l)

^1^H NMR (600 MHz, CDCl₃)

^13^C NMR (151 MHz, CDCl₃)
(E)-3,3’-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)bis(methoxybenzene) (3m)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
Tert-butyl 4-(2,4-bis(3-fluorophenyl)but-1-en-3-yn-1-yl)piperidine-1-carboxylate (3n)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
$^{19}$F NMR (565 MHz, CDCl$_3$)
3,3’-(4-Cyclohexylbut-3-en-1-yn-1,3-diyl)dipyridine (3o)

**1H NMR** (600 MHz, CDCl₃)

**13C NMR** (151 MHz, CDCl₃)
6,6'-(4-Cyclohexylbut-3-en-1-yne-1,3-diyl)bis(2-methoxynaphthalene) (3p)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(Z)-3,3’-(4-Cyclohexylbut-3-en-1-yn-1-yl)-dithiophene (3q)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(8R,8'R,9S,9'S,13S,13'S,14S,14'S)-3,3'-(E)-4-cyclohexylbut-3-en-1-yn-1,3-diyl)bis(13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one) (3r)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(E)-(5-Methylhex-3-en-1-yn-1,3-diyl)dibenzene (5a)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(E)-(5-Methylhept-3-en-1-yne-1,3-diyl)dibenzene (5b)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(E)-(4-Cyclopentylbut-3-en-1-yne-1,3-diyl)dibenzene (5c)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(2,4-diphenylbut-1-en-3-yn-1-yl)cycloheptane (5d)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(2,4-Diphenylbut-1-en-3-yn-1-yl)cyclooctane (5e)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
3-(2,4-Diphenylbut-1-en-3-yn-1-yl)tetrahydrofuran (5f)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
4-(2,4-Diphenylbut-1-en-3-yn-1-yl)tetrahydro-2H-pyran (5g)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
Tert-butyl-4-[2,4-diphenylbut-1-en-3-yn-1-yl]piperidine-1-carboxylate (5h)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(E)-(5,5-Dimethylhex-3-en-1-yn-1,3-diyl)dibenzene (5i)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
1-((E)-2,4-Diphenylbut-1-en-3-yn-1-yl)adamantane (5j)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(5S,8R,9S,10S,13S,14S)-3-((E)-2,4-diphenylbut-1-en-3-yn-1-yl)-10,13-dimethyl-hexadecahydro-17H-cyclopenta[a]phenanthren-17-one (5k)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(E)-(5-Methylnona-3,8-dien-1-yne-1,3-diyl)dibenzene and (E)-(4-(3-Methyl-cyclopentyl)but-3-en-1-yne-1,3-diyl)dibenzene (5m, 5m')

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)
(Z)-(4-Cyclohexylbut-3-en-1-yn-yne-1,3-diyl)bis(trimethylsilane) (3t)

$^1$H NMR (600 MHz, CDCl$_3$)

$^{13}$C NMR (151 MHz, CDCl$_3$)