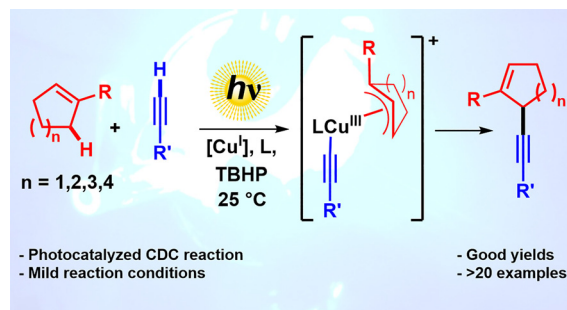


Allylic C–H Alkynylation via Copper-Photocatalyzed Cross-Dehydrogenative Coupling

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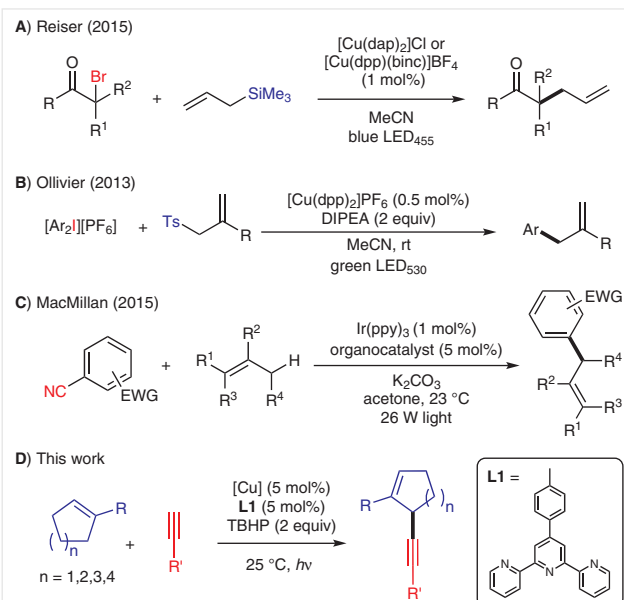
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Abstract An efficient, novel photocatalyzed allylic-alkynylation methodology via copper-based cross-dehydrogenative coupling (CDC) is described. Different types of 1,4-enyne compounds were synthesized in one step at room temperature using copper(I) terpyridyl complex as photocatalyst/initiator. This procedure is an improvement and to some extent complementary to previously reported thermal CDC methods. Preliminary investigations on the reaction mechanism are also presented.

Key words C–C bond, copper catalyst, C–H functionalization, photocatalyst, allylic-alkynylation, 1,4-enyne

The search for more efficient and ‘environmentally friendlier’ processes is one of the major tasks to be accomplished by chemists, in response to the growing society’s concern about pollution, energy, and resources. Therefore, the development of new catalytic strategies of high selectivity, low energy demand, and reduced waste are of paramount importance. Among these strategies, photocatalysis has been in the spotlight during the last decades.¹ Remarkably, among the plethora of reported photocatalyzed reactions, allylic functionalization represents only a small fraction, in spite of the ubiquity of the allylic moiety in natural products and pharmaceuticals.² In a pioneering report, Reiser developed the first photocatalyzed allylation of α -halocarbonyls with allyltributylstannane using homoleptic $[\text{Cu}(\text{dpa})_2]$ as photosensitizer.³ Later on, the same group improved the reaction scope by using allylsilanes and heteroleptic copper(I) complexes having longer excited state lifetimes and stronger reductive capabilities (Scheme 1 A).⁴ Alkylation of allyl sulfones by aryl radicals generated from diaryliodonium salts using $[\text{Cu}(\text{dpp})_2]\text{PF}_6$ as photocatalyst was reported by Ollivier in 2013 (Scheme 1 B).⁵ Two years later, MacMillan reported a more benign approach towards

allylic C–H functionalizations avoiding the use of stoichiometric amounts of oxidant, leading to the direct arylation of allylic C–H bonds under mild conditions (Scheme 1 C).⁶ An important drawback of this methodology is that it relies on the use of expensive iridium photosensitizers.



Scheme 1 Recent examples of photocatalyzed allylic functionalizations; dap: 2,9-bis(4-methoxyphenyl)-1,10-phenanthroline; dpp: 2,9-diphenyl-1,10-phenanthroline; py: 2-phenylpyridine.

Very recently, we reported the alkynylation of underivatized allylic substrates under oxidative conditions using terminal alkynes.⁷ This is an example of a thermal cross-dehydrogenative coupling (CDC) reaction, which can be described as the coupling of a pre-nucleophile and a pre-electrophile, both devoid of leaving groups.⁸ CDC reactions

have been thoroughly studied in the last decade⁹ and several photocatalyzed CDC processes either using a sacrificial oxidant or a proton reductant have been reported.¹⁰ In most cases (thermal and photocatalyzed), the derivatization takes place at sp³ carbons adjacent to nitrogen, and allylic substrates have been neglected. Herein, we combine for the first time the advantages of CDC and photocatalysis for the alkylation of allylic substrates, using a Cu(I) terpyridine complex as photocatalyst and *tert*-butyl hydroperoxide (TBHP) as sacrificial oxidant at room temperature (Scheme 1, D).

We began our investigation on the photocatalyzed CDC between phenylacetylene (**1a**) and cyclohexene (**2a**) as model reactants using white light (xenon lamp, $\lambda = 300\text{--}700\text{ nm}$) at room temperature (23–26 °C) (Scheme 2). We employed the reaction conditions from our previous report⁷ (except the reaction temperature) using DTBP as oxidant and terpyridine ligand **L1** (Table 1). Terpyridines are important chelating ligands in many applications spawning from supramolecular¹¹ and macromolecular chemistry to luminescent devices¹² and photoelectrical cells.¹³ However, the low photoabsorption and quantum yield of metallic mono- and bis-terpyridyl complexes compared to their bipyridine analogues has discouraged their application as photoredox catalysts in organic synthesis.¹⁴ Furthermore, most of the studied copper terpyridine complexes are of Cu(II),^{14a,15} with only few Cu(I) examples.^{16,17} Under these conditions, only 10% of the desired product **3a** was obtained (Table 1, entry 1). No product was detected without the copper complex or the oxidant (entries 2 and 3). Having **1a** as the sole ligand (entry 4) was not effective in our case, in contrast to previous reports on Sonogashira-type photoinduced coupling reactions.¹⁸ Using TBHP instead of DTBP was sufficient to increase the yield to 55% (entry 5). Motivated by this observation, different oxidants were tested, but no product was produced (entries 6–10). By lowering the amount of oxidant, a decreased yield was observed (entry 11, 41%). The addition of an excess of **L1** (1.5 and 2 equiv relative to Cu) resulted in an increase of product yield (entries 12 and 13, 61 and 60%, respectively). An increased excess of **2a** was also beneficial, giving **3a** in 72% (entry 14). Conversely, further increase on the amount of **2a** or oxidant showed to be detrimental (entries 15 and 16). At this stage, we turned our attention to the role of the ligand, for which different terpyridine derivatives **L2–L4**, 4,7-diphenyl-1,10-phenanthroline (**L6**), and 2,6-bis(1*H*-benzo[*d*]imidazol-2-yl)pyridine (**L7**), were tested. In all cases, either lower conversion or no reaction was observed (Table S1, SI).

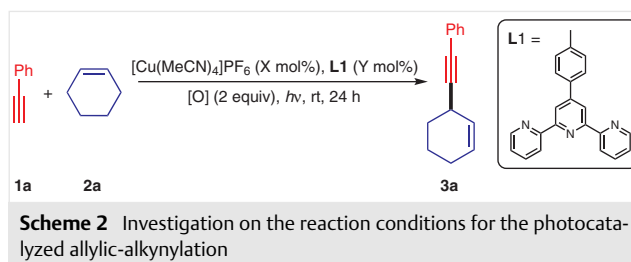


Table 1 Screening of Optimal Reaction Conditions^a

Entry	2a (equiv)	X (mol%)	Y (mol%)	[O]	Solvent	3a Yield (%) ^b
1	10	5	5	DTBP	DMSO	10
2	10	–	–	DTBP	DMSO	nd
3	10	5	5	–	DMSO	nd
4	10	5	–	DTBP	DMSO	nd
5	10	5	5	TBHP	DMSO	55
6	10	5	5	DDQ	DMSO	nd
7	10	5	5	BPO	DMSO	nd
8	10	5	5	air	DMSO	nd
9	10	5	5	O ₂	DMSO	nd
10	10	5	5	H ₂ O ₂	DMSO	nd
11 ^c	10	5	5	TBHP	DMSO	41
12	10	5	7.5	TBHP	DMSO	61
13	10	5	10	TBHP	DMSO	60
14	20	5	5	TBHP	DMSO	72
15	30	5	5	TBHP	DMSO	43
16 ^d	20	5	5	TBHP	DMSO	35
17 ^e	20	5	5	TBHP	MeCN	54
18	20	5	5	TBHP	MeCN/MeOH (3:1)	72
19	20	5	5	TBHP	MeCN	78
20	20	5	5	TBHP	MeOH	43
21	20	5	5	TBHP	DCM	4
22	20	5	5	TBHP	DMF	34
23	20	5	5	TBHP	THF	0
24 ^f	20	5	5	TBHP	MeCN	70
25 ^g	20	5	5	TBHP	MeCN	30

^a Reaction conditions: **1a** (0.5 mmol), *tert*-butyl hydroperoxide (TBHP) solution in decane 5.5 M, DTBP (di-*tert*-butylperoxide), DDQ (2,3-dichloro-5,6-dicyano-1,4-benzoquinone), BPO (benzoyl peroxide), temperature was kept at 24–26 °C by flowing dry air through the reactor.

^b GC-MS yield; nd: not detected.

^c TBHP: 1 equiv.

^d TBHP: 3 equiv.

^e $\lambda = 400\text{--}700\text{ nm}$.

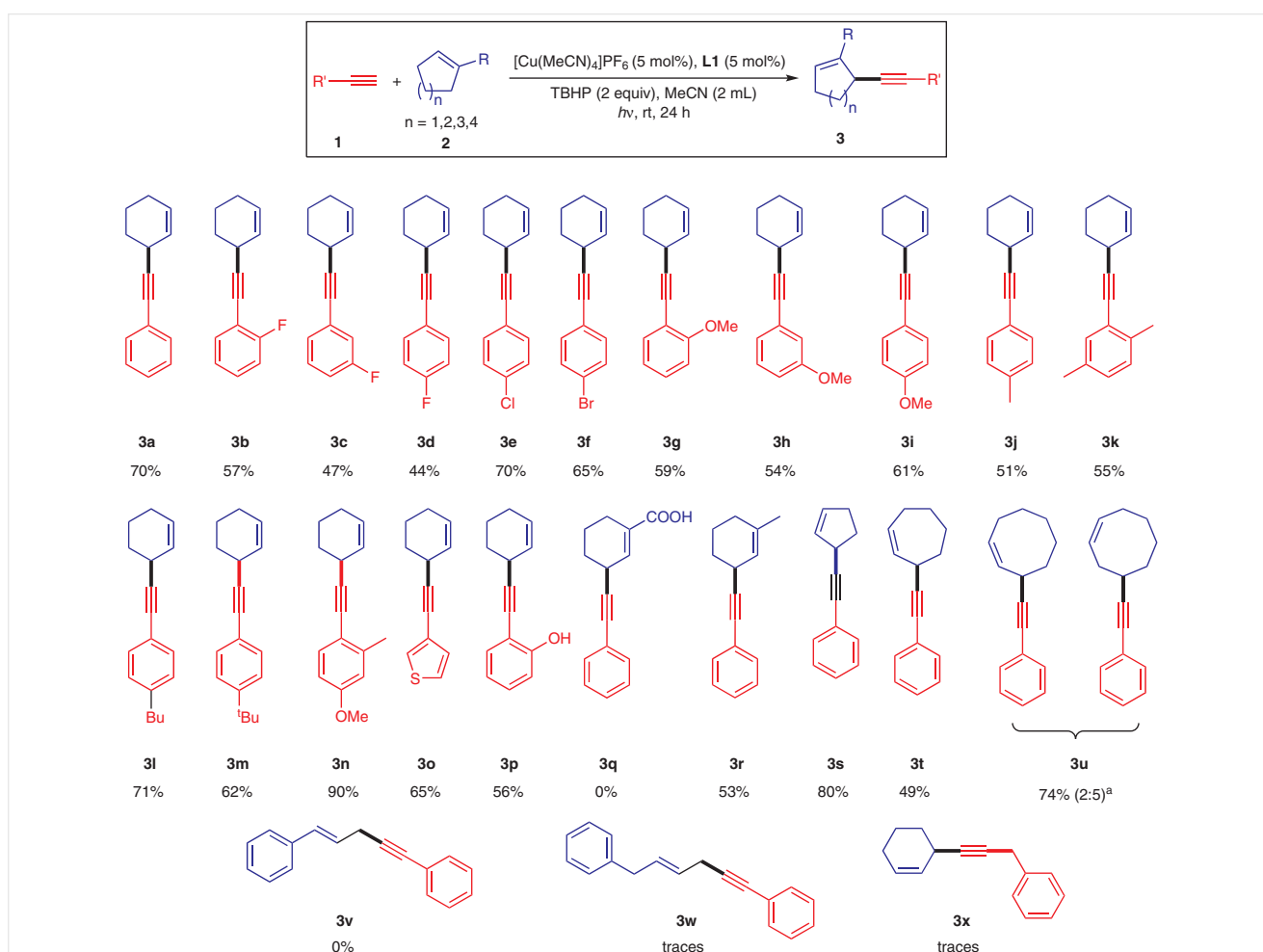
^f With isolated Cu^I-L1.

^g With 5 mol% [Cu(CF₃SO₃)₂].

Moreover, we tested the effect of different light sources, including LED strips and household bulbs. To our delight all tested light sources were able to produce the desired product, however, only in moderate yields (Table S1, SI). By removing the UV radiation of the Xenon light source, that is, using only visible light ($\lambda_{\text{exc}} = 420\text{--}600\text{ nm}$), a yield of 54% was obtained (Table 1, entry 17). This decrease can be due to the reduction of the light intensity resulting from the use of the long pass filter. We also investigated the solvent effect (entries 18–23) and found that MeCN gives the best results (entry 19, 78%). Interestingly, coupling by-products resulting from a reaction between **1a** with DMF¹⁹ and THF²⁰ were produced. The nature of the copper species was briefly investigated. By using the isolated complex [Cu^I-L1] (see SI) as catalyst, very similar results were obtained as when it is produced in situ (entry 24, 70%). Interestingly, and contrary to what we observed under thermal conditions,⁷ using Cu^{II} instead of Cu^I resulted in 30% yield of **3a** (entry 25). Importantly, high selectivity towards the allylic alkynylation product was achieved in all cases, in strong contrast to the

results under thermal conditions. There, a variety of by-products were always present, for instance the Glaser coupling product of **1a** being practically unavoidable. In this case, only the CDC product **3** is produced.

Once we have identified a suitable set of reaction conditions, we proceeded with the investigations on the substrate scope. In general, all phenylacetylene derivatives **1** tested produced the CDC products with **2a** in moderate to good yields (Scheme 3, **3a–p**). The highest yield was obtained for the electronically enriched 1-ethynyl-4-methoxy-2-methylbenzene (**1n**) (90% of **3n**), while the lowest was obtained for the electron-poor 1-ethynyl-4-fluorobenzene (**1d**) (44% of **3d**). Interestingly, halogenated substrates **1b–f** gave satisfactory results in spite of their propensity to form radical species by reacting with analogous catalysts.²¹ Importantly, the presence of reactive functionalities like thiophene and phenol did not inhibit the product formation (**3o** and **3p**, respectively). The presence of a carboxyl moiety at position 1 of the allyl substrate **2q** resulted in complete reaction inhibition, while the methyl-substituted



Scheme 3 Substrate scope for the photocatalyzed allylic alkynylation reaction. Isolated yields are reported. ^a Determined by GC-MS.

analogue produced the desired product **3r** in moderate yield (53%). Under the same conditions, cyclopentene and cycloheptene produced exclusively the expected products **3s** and **3t** in 80% and 49% yield, respectively. Unfortunately, the regioselectivity was not controlled in the case of cyclooctene, producing a mixture of isomers **3u**. The lack of regioselectivity for **3u** and the high regioselectivity for **3s** are in strong contrast with the thermal method where the complete opposite behavior was observed.⁷ The difference in selectivity between the two sets of conditions (thermal vs photoinduced) relays on the stability and reactivity of the metal-allyl intermediates **6** and **8**, common to both mechanism, but that can undergo different side reactions (like thermal isomerization) before the product-forming step (vide infra). Moreover, the use of open-chain allylic substrates or a not-conjugated alkyne did not yield the desired products **3v** and **3w** or **3x**, respectively. We believe that for the former, it is due to unintended photoexcitation of the substrates while for the latter, due the lower acidity of the alkyne. The thermal method, on the other hand, was effective for the coupling of both alkylic and open-chain substrates. This makes, to some extent, the two approaches complementary. Kinetic investigations of the reaction between **1a** and **2a** showed that the formation of product **3a** is of zero order and is not complete after 24 hours of irradiation under the above-described conditions (Figure S3, SI).

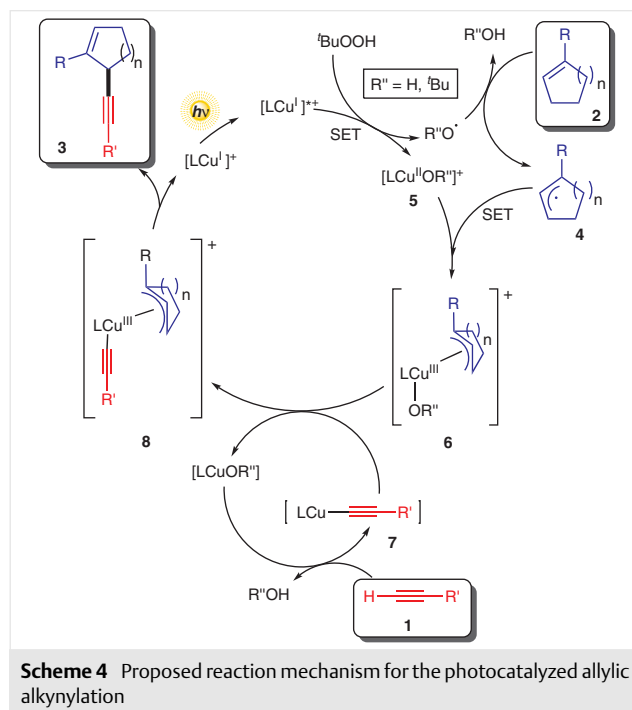
Furthermore, when the reaction was irradiated for only one hour and then further stirred in the dark, it yields **3a** in 54% (Table S1, SI). This suggests that the active (radical) species are generated during the induction (irradiation) period and a thermal reaction follows in the dark without the intervention of photoexcited copper species. Hence, the reaction should be better described as 'photoinitiated' rather than 'photosensitized'.²² To assess the role of the copper catalyst as photoinitiator, we measured the UV absorption of the different species and the luminescence quenching of the complex upon addition of the different substrates.

The UV/Vis absorption spectra in acetonitrile (Figure S4, SI) of the free ligand **L1**, copper(I) complex (Cu-L1), and its mixtures with the different substrates (**1a**, **2a**, and TBHP) show in all cases only absorption bands below 360 nm. This is rather puzzling, not only considering the strong maroon color of the reaction mixture (under catalytic conditions), but also the fact that there is considerable catalytic turnover even after suppression of the UV wavelengths of the irradiation source (see the above discussion and SI). It is thus very plausible, that the photoactive copper species are of polymeric and/or multimetallic nature, although this hypothesis has to be supported by experimental data (currently being collected in our laboratories). Preliminary photoluminescence quenching experiments ($\lambda_{\text{ex}} = 317 \text{ nm}$) for complex Cu-L1 with the three different substrates showed that only the peroxide (TBHP) is capable of effectively quenching the excited state emission of the copper complex. This suggests that, as expected, the photoexcited cop-

per catalyzes the peroxide splitting, presumably by single electron transfer (SET) during the irradiation period (Figures S5 to S7, SI).

The addition of an excess of the radical-trapping reagent TEMPO only resulted in a decrease on the reaction yield to 56%, also in strong contrast to the use if DTBP under thermal conditions where the addition of the scavenger resulted in complete inhibition of the reaction.⁷ Under thermal conditions, the main open-shell species formed by the peroxide decomposition showed to be methyl radicals, which were presumably also responsible for the hydrogen abstraction at the allylic substrate. In the present case, the methyl radical seems to play only a minor role, if any (a very small amount of methylated TEMPO was detected. See Figure S8, SI).

Although a detailed reaction mechanism cannot be proposed with the available data, based in our preliminary observations and our previous report,⁷ we anticipate that the reaction pathway might be as depicted in Scheme 4. After photon absorption, the excited copper species $[\text{Cu}^{\text{I}}]^*$ shall react with TBHP via SET to produce the oxidized complex copper(II) **5**, which shall be feasible considering the enhanced reductive power of photoexcited copper complexes {for instance, $[\text{Cu}(\text{XyBnta})(\text{dppb})]^+$ is a very strong photoreductant: $E_{\text{ox}}^* = -2.40 \text{ V vs. SCE}$ in THF; XyBnta: *N*-[2-(1-benzyl-1*H*-1,2,3-triazol-4-yl)phenyl]-2,6-dimethylaniline; dppb: 1,2-bis(diphenylphosphanyl)benzene}²³ The radicals resulting from the peroxide splitting can then abstract a hydrogen from the allyl substrate **2**, to yield an open-shell species **4** that shall react quickly with complex **5**²⁴ to produce a transient copper(III) intermediate **6**.²⁵ Under the re-



action condition it is expected that organocuprates **7** are formed from **1**.²⁶ Finally, ligand exchange between **6** and **7** followed by reductive elimination from **8** shall regenerate the copper(I) catalyst and lead to the cross-coupling product **3**.

In conclusion, we have developed a new photocatalytic method for the synthesis of substituted 1,4-enynes via cross-dehydrogenative coupling of underivatized cyclic alkenes and terminal alkynes under very mild conditions. This methodology poses a dramatic improvement over our previous reports under thermal conditions and, to some extent, is complementary to it on the substrate scope. Moreover, the use of copper complex as photocatalyst/photoinitiator at room temperature for this reaction poses an attractive alternative to previous CDC methodologies relying on precious metals. Further investigations on the underlying reaction mechanism, the role and nature of the photocatalyst and the application of this methodology in asymmetric allylic functionalization are currently under investigation and will be the subject of a later report.

Chemicals, reagents, and solvents were purchased from commercial suppliers and used without further purification. The ligands **L2**, **L3**, and **L4** were synthesized following reported procedures.²⁷ TLC was performed on silica HSGF254 plates. ¹H and ¹³C NMR spectra were recorded in CDCl₃ using a Bruker Avance 300 spectrometer with a QNP probe head (¹H: 300 MHz, ¹³C: 75 MHz) or Bruker Avance 400 (¹H: 400 MHz, ¹³C: 101 MHz). The calibration of the spectra were carried out on referenced with residual solvent shifts (CDCl₃, ¹H = 7.26, ¹³C = 77.16) and were reported as parts per million relative to SiMe₄. All the NMR samples were measured at 297 K. ESI-TOF spectra were recorded using a Waters Q-ToF micro mass spectrometer. GC analysis was performed on Hewlett-Packard 6890 Series. Samples were dissolved in DCM and sampled in to the GC column. The chromatogram peak ratios of the (cyclohex-2-en-1-ylethynyl)benzene (**3a**) and internal standard naphthalene (AE/AS) were used for calibration (exemplary calibration curve in Figure S0, SI). The GC-yields were calculated with the corresponding calibration curve with naphthalene as an internal standard. Asahi Spectra Max-303 Xenon Light Source was used.

Allylic C–H Alkynylation; General Procedure

In an oven-dried glass Schlenk tube equipped with a stirring bar, Cu(MeCN)₄PF₆ and ligand **L1** were mixed under argon. The tube was evacuated and carefully refilled with argon three times. Then anhyd MeCN (2.0 mL) was injected into the tube through a syringe. After stirring for 15 min at rt, TBHP, a 20-fold excess of the allyl substrate **2**, and the corresponding alkyne **1** were subsequently injected into the reaction tube. The reaction was then irradiated with white light (Xenon lamp, 300–700 nm) for 24 h (9 cm was the distance between the light source and the Schlenk tube) while keeping the temperature (23–26 °C) by a stream of dry air. After stirring for 24 h, H₂O was added and the product was extracted with DCM (3 × 50 mL). The pure product **3** was obtained by flash column chromatography on silica gel. Importantly, most of the obtained compounds were found to be unstable in solution under bench conditions, most probably due to polymerization.

1-(Cyclohex-2-en-1-ylethynyl)benzene (**3a**)

Following the general procedure, using Cu(MeCN)₄PF₆ (9.4 mg, 0.024 mmol), ligand **L1** (8.3 mg, 0.024 mmol), cyclohexene (**2a**; 788 mg, 9.6 mmol), phenylacetylene (**1a**; 50 mg, 0.5 mmol), and TBHP (86.5 mg, 0.959 mmol), the pure product was obtained by flash column chromatography on silica gel with pentane as eluent; colorless oil; yield: 61 mg (70%, 0.33 mmol); *R*_f = 0.62.

¹H NMR (400 MHz, CDCl₃): δ = 7.34–7.31 (m, 2 H), 7.21–7.18 (m, 3 H), 5.74–5.68 (m, 1 H), 5.65 (ddt, *J* = 10.0, 3.5, 1.8 Hz, 1 H), 3.22 (ddp, *J* = 7.6, 5.1, 2.6 Hz, 1 H), 1.98–1.87 (m, 3 H), 1.81–1.69 (m, 2 H), 1.59–1.49 (m, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 131.8, 128.3, 128.2, 127.7, 127.2, 124.0, 93.0, 80.4, 29.5, 28.1, 24.8, 20.8.

The NMR data matched with the previous report.²⁸

MS: *m/z* = 182 (72), 167 (81), 153 (100), 128 (56), 115 (89).

HRMS (ESI-TOF): *m/z* calcd for C₁₄H₁₄ [M + H]⁺: 182.10900; found: 182.10905.

1-(Cyclohex-2-en-1-ylethynyl)-2-fluorobenzene (**3b**)

Following the general procedure, using Cu(MeCN)₄PF₆ (7.8 mg, 0.02 mmol), ligand **L1** (7 mg, 0.02 mmol), cyclohexene (**2a**; 663 mg, 8.07 mmol), 1-ethynyl-2-fluorobenzene (**1b**; 50 mg, 0.4 mmol), and TBHP (72 mg, 0.8 mmol), the pure product was obtained by flash column chromatography on silica gel with Et₂O/pentane (5:95) as eluent; colorless oil; yield: 46 mg (57%, 0.22 mmol); *R*_f = 0.7.

¹H NMR (300 MHz, CDCl₃): δ = 7.43–7.37 (m, 1 H), 6.87–6.78 (m, 2 H), 6.76–6.70 (m, 1 H), 5.89–5.82 (m, 1 H), 5.73–5.66 (m, 1 H), 3.28 (tq, *J* = 5.7, 2.4 Hz, 1 H), 1.90–1.81 (m, 4 H), 1.79–1.72 (m, 1 H), 1.45–1.35 (m, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 164.8, 161.5, 133.5, 129.0, 128.1, 127.8, 127.4, 126.8, 123.7, 115.2, 98.6, 74.1, 29.2, 28.4, 24.6, 20.5.

¹⁹F NMR (282 MHz, CDCl₃): δ = -110.4.

MS: *m/z* = 200 (100), 185 (49), 172 (68), 165 (39), 159 (35), 133 (48).

HRMS (ESI-TOF): *m/z* calcd for C₁₄H₁₃F [M + H]⁺: 200.09958; found: 200.09983.

1-(Cyclohex-2-en-1-ylethynyl)-3-fluorobenzene (**3c**)

Following the general procedure, using Cu(MeCN)₄PF₆ (8.1 mg, 0.02 mmol), ligand **L1** (8 mg, 0.02 mmol), cyclohexene (**2a**; 670 mg, 8.07 mmol), 1-ethynyl-3-fluorobenzene (**1c**; 50 mg, 0.4 mmol), and TBHP (73 mg, 0.8 mmol), the pure product was obtained by flash column chromatography on silica gel with Et₂O/pentane (2:98) as eluent; colorless oil; yield: 38 mg (47%, 0.19 mmol); *R*_f = 0.8.

¹H NMR (400 MHz, CDCl₃): δ = 7.24–7.18 (m, 2 H), 6.84–6.78 (m, 1 H), 6.76–6.69 (m, 1 H), 5.84 (ddt, *J* = 10.1, 3.6, 2.1 Hz, 1 H), 5.75–5.69 (m, 1 H), 3.24 (tp, *J* = 5.7, 2.5 Hz, 1 H), 1.90–1.81 (m, 4 H), 1.80–1.71 (m, 1 H), 1.48–1.37 (m, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 163.8, 161.4, 129.7, 128.0, 127.8, 127.5, 126.8, 118.4, 114.7, 94.1, 79.7, 29.2, 28.1, 24.6, 20.6.

¹⁹F NMR (282 MHz, CDCl₃): δ = -112.4.

HRMS (ESI-TOF): *m/z* calcd for C₁₄H₁₃F [M + H]⁺: 200.09958; found: 200.09880.

1-(Cyclohex-2-en-1-ylethynyl)-4-fluorobenzene (**3d**)

Following the general procedure, using Cu(MeCN)₄PF₆ (7.9 mg, 0.02 mmol), ligand **L1** (6.8 mg, 0.02 mmol), cyclohexene (**2a**; 656 mg, 8 mmol), 1-fluoro-4-ethynylbenzene (**1d**; 50 mg, 0.4 mmol), and TBHP

(72 mg, 0.8 mmol), the pure product was obtained by flash column chromatography on silica gel with Et₂O/pentane (5:95) as eluent; colorless oil; yield: 35 mg (44%, 0.18 mmol); *R*_f = 0.7.

¹H NMR (400 MHz, CDCl₃): δ = 7.38 (dd, *J* = 8.9, 5.4 Hz, 2 H), 6.99–6.94 (m, 2 H), 5.79 (dtd, *J* = 9.3, 3.5, 2.1 Hz, 1 H), 5.71 (dtd, *J* = 9.9, 3.5, 2.0 Hz, 1 H), 3.28 (ddp, *J* = 7.9, 5.4, 2.6 Hz, 1 H), 2.06–2.01 (m, 2 H), 2.00–1.94 (m, 1 H), 1.90–1.82 (m, 1 H), 1.82–1.75 (m, 1 H), 1.66–1.55 (m, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 163.5, 161.0, 133.6, 133.5, 128.3, 127.0, 120.1, 115.6, 115.4, 92.6, 79.4, 29.5, 28.1, 24.8, 20.8.

¹⁹F NMR (282 MHz, CDCl₃): δ = –112.0.

1-Chloro-4-(cyclohex-2-en-1-ylethynyl)benzene (3e)

Following the general procedure, using Cu(MeCN)₄PF₆ (7 mg, 0.018 mmol), ligand **L1** (6.1 mg, 0.018 mmol), cyclohexene (**2a**; 590 mg, 7.2 mmol), 1-chloro-4-ethynylbenzene (**1e**; 50 mg, 0.35 mmol), and TBHP (64 mg, 0.71 mmol), the pure product was obtained by flash column chromatography on silica gel with pentane as eluent; colorless oil; yield: 55 mg (70%, 0.25 mmol); *R*_f = 0.76.

¹H NMR (300 MHz, CDCl₃): δ = 7.27 (d, *J* = 8.7 Hz, 2 H), 7.18 (d, *J* = 8.8 Hz, 2 H), 5.77–5.70 (m, 1 H), 5.65 (dtd, *J* = 10.0, 3.7, 1.9 Hz, 1 H), 3.22 (ddp, *J* = 7.6, 5.2, 2.4 Hz, 1 H), 1.99–1.87 (m, 3 H), 1.79–1.68 (m, 2 H), 1.61–1.51 (m, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 133.6, 133.0, 128.6, 128.4, 126.9, 122.5, 94.0, 79.4, 29.4, 28.1, 24.8, 20.7.

1-Bromo-4-(cyclohex-2-en-1-ylethynyl)benzene (3f)

Following the general procedure, using Cu(MeCN)₄PF₆ (5.5 mg, 0.013 mmol), ligand **L1** (5.1 mg, 0.013 mmol), cyclohexene (**2a**; 445 mg, 5.4 mmol), 1-bromo-4-ethynylbenzene (**1f**; 50 mg, 0.27 mmol), and TBHP (94 mg, 0.54 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane as eluent; colorless oil; yield: 46 mg (65%, 0.18 mmol); *R*_f = 0.54.

¹H NMR (300 MHz, CDCl₃): δ = 7.40 (d, *J* = 8.6 Hz, 2 H), 7.27–7.24 (m, 2 H), 5.82–5.75 (m, 1 H), 5.71 (ddd, *J* = 7.9, 4.2, 2.5 Hz, 1 H), 3.28 (ddp, *J* = 7.6, 5.1, 2.4 Hz, 1 H), 2.05–2.00 (m, 2 H), 1.87 (ddd, *J* = 14.1, 6.2, 2.9 Hz, 1 H), 1.82–1.73 (m, 2 H), 1.67–1.58 (m, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 133.2, 131.5, 128.4, 126.8, 123.0, 121.8, 94.3, 79.5, 29.4, 28.1, 24.8, 20.7.

1-(Cyclohex-2-en-1-ylethynyl)-2-methoxybenzene (3g)

Following the general procedure, using Cu(MeCN)₄PF₆ (7.1 mg, 0.018 mmol), ligand **L1** (6.1 mg, 0.018 mmol), cyclohexene (**2a**; 603 mg, 7.3 mmol), 1-ethynyl-2-methoxybenzene (**1g**; 50 mg, 0.37 mmol), and TBHP (66 mg, 0.73 mmol), the pure product was obtained by flash column chromatography on silica gel using Et₂O/pentane (1:30) as eluent; colorless oil; yield: 42 mg (59%, 0.2 mmol); *R*_f = 0.6.

¹H NMR (400 MHz, CDCl₃): δ = 7.39 (d, *J* = 9.3 Hz, 1 H), 7.23 (ddd, *J* = 8.3, 7.5, 1.8 Hz, 1 H), 6.88 (dd, *J* = 7.5, 1.1 Hz, 1 H), 6.84 (d, *J* = 8.7 Hz, 1 H), 5.77 (d, *J* = 1.4 Hz, 2 H), 3.86 (s, 3 H), 3.40–3.34 (m, 1 H), 2.06–1.98 (m, 3 H), 1.91 (ddd, *J* = 13.2, 5.7, 2.5 Hz, 1 H), 1.87–1.80 (m, 1 H), 1.67–1.57 (m, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 159.9, 133.8, 129.0, 128.0, 127.3, 120.4, 113.1, 110.7, 97.2, 76.5, 55.9, 29.5, 28.4, 24.8, 20.8.

HRMS (ESI-TOF): *m/z* calcd for C₁₅H₁₆O [M + H]⁺: 212.11957; found: 212.11889.

1-(Cyclohex-2-en-1-ylethynyl)-3-methoxybenzene (3h)

Following the general procedure, using Cu(MeCN)₄PF₆ (7.1 mg, 0.018 mmol), ligand **L1** (6.1 mg, 0.018 mmol), cyclohexene (**2a**; 603 mg, 7.3 mmol), 1-ethynyl-3-methoxybenzene (**1h**; 50 mg, 0.37 mmol), and TBHP (66 mg, 0.73 mmol), the pure product was obtained by flash column chromatography on silica gel using Et₂O/pentane (1:99) as eluent; colorless oil; yield: 46 mg (54%, 0.21 mmol); *R*_f = 0.7.

¹H NMR (300 MHz, CDCl₃): δ = 7.22–7.16 (m, 1 H), 7.04–7.00 (m, 1 H), 6.96 (dd, *J* = 2.6, 1.4 Hz, 1 H), 6.86–6.81 (m, 1 H), 5.83–5.77 (m, 1 H), 5.74 (ddd, *J* = 9.9, 3.0, 1.6 Hz, 1 H), 3.79 (s, 3 H), 3.35–3.27 (m, 1 H), 2.07–1.95 (m, 3 H), 1.90 (ddd, *J* = 13.2, 5.6, 2.4 Hz, 1 H), 1.85–1.79 (m, 1 H), 1.69–1.57 (m, 1 H).

¹³C NMR (75 MHz, CDCl₃): δ = 159.3, 129.3, 128.2, 127.1, 125.0, 124.3, 116.5, 114.4, 92.8, 80.3, 77.2, 55.3, 29.5, 28.1, 24.8, 20.8.

MS: *m/z* = 212 (100), 197 (65), 184 (45), 165 (41), 131 (74), 118 (57).

HRMS (ESI-TOF): *m/z* calcd for C₁₅H₁₆O [M + H]⁺: 212.11957; found: 212.11901.

1-(Cyclohex-2-en-1-ylethynyl)-4-methoxybenzene (3i)

Following the general procedure, using Cu(MeCN)₄PF₆ (7 mg, 0.018 mmol), ligand **L1** (6.3 mg, 0.018 mmol), cyclohexene (**2a**; 610 mg, 7.4 mmol), 1-ethynyl-4-methoxybenzene (**1i**; 50 mg, 0.37 mmol), and TBHP (64 mg, 0.74 mmol), the pure product was obtained by flash column chromatography on silica gel using Et₂O/pentane (1:30) as eluent; yellowish oil; yield: 48 mg (61%, 0.22 mmol); *R*_f = 0.56.

¹H NMR (300 MHz, CDCl₃): δ = 7.34 (d, *J* = 8.9 Hz, 2 H), 6.80 (d, *J* = 8.9 Hz, 2 H), 5.81–5.69 (m, 2 H), 3.79 (s, 3 H), 3.28 (dtd, *J* = 7.1, 5.4, 4.8, 2.2 Hz, 1 H), 2.04–1.95 (m, 3 H), 1.85–1.74 (m, 2 H), 1.65–1.56 (m, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 159.1, 133.7, 133.0, 128.0, 127.4, 116.1, 114.0, 113.8, 91.3, 80.1, 77.2, 75.9, 55.3, 29.6, 28.1, 24.8, 20.8.

1-(Cyclohex-2-en-1-ylethynyl)-4-methylbenzene (3j)

Following the general procedure, using Cu(MeCN)₄PF₆ (8.4 mg, 0.021 mmol), ligand **L1** (7.2 mg, 0.021 mmol), cyclohexene (**2a**; 693 mg, 8.4 mmol), 1-ethynyl-4-methylbenzene (**1j**; 50 mg, 0.42 mmol), and TBHP (76 mg, 0.84 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane as eluent; colorless oil; yield: 42 mg (51%, 0.21 mmol); *R*_f = 0.6.

¹H NMR (400 MHz, CDCl₃): δ = 7.32 (dd, *J* = 8.1, 1.8 Hz, 2 H), 7.10 (dd, *J* = 8.5, 0.7 Hz, 2 H), 5.83–5.78 (m, 1 H), 5.78–5.73 (m, 1 H), 3.31 (tdt, *J* = 7.2, 4.1, 2.5 Hz, 1 H), 2.35 (s, 3 H), 2.10–2.03 (m, 2 H), 2.00 (ddd, *J* = 13.2, 5.1, 3.0 Hz, 1 H), 1.94–1.86 (m, 1 H), 1.85–1.78 (m, 1 H), 1.68–1.56 (m, 1 H).

¹³C NMR (101 MHz, CDCl₃): δ = 137.6, 132.5, 131.6, 129.3, 129.0, 128.0, 127.3, 120.9, 92.1, 80.4, 77.2, 29.6, 28.1, 24.8, 21.5, 20.8.

2-(Cyclohex-2-en-1-ylethynyl)-1,4-dimethylbenzene (3k)

Following the general procedure, using Cu(MeCN)₄PF₆ (7.3 mg, 0.018 mmol), ligand **L1** (6.7 mg, 0.018 mmol), cyclohexene (**2a**; 612 mg, 7.4 mmol), 2-ethynyl-1,4-dimethylbenzene (**1k**; 50 mg, 0.37 mmol), and TBHP (67 mg, 0.74 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane as eluent; colorless oil; yield: 43 mg (55%, 0.25 mmol); *R*_f = 0.67.

¹H NMR (400 MHz, CDCl₃): δ = 7.23 (s, 1 H), 7.07 (d, *J* = 7.7 Hz, 1 H), 6.99 (d, *J* = 9.4 Hz, 1 H), 5.82–5.74 (m, 2 H), 3.35 (dtt, *J* = 6.7, 3.4, 1.9 Hz, 1 H), 2.39 (s, 3 H), 2.29 (s, 3 H), 2.07–1.98 (m, 3 H), 1.95–1.89 (m, 1 H), 1.87–1.80 (m, 1 H), 1.70–1.62 (m, 1 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 137.0, 134.9, 132.4, 129.3, 128.5, 128.0, 127.4, 123.5, 96.7, 79.5, 77.2, 29.7, 28.3, 24.8, 20.9, 20.8, 20.3.

1-Butyl-4-(cyclohex-2-en-1-ylethynyl)benzene (3l)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (5.8 mg, 0.015 mmol), ligand **L1** (5.2 mg, 0.015 mmol), cyclohexene (**2a**; 500 mg, 6 mmol), 1-butyl-4-ethynylbenzene (**1l**; 50 mg, 0.3 mmol), and TBHP (55 mg, 0.61 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane as eluent; colorless oil; yield: 51 mg (71%, 0.21 mmol); R_f = 0.52.

^1H NMR (300 MHz, CDCl_3): δ = 7.33 (d, J = 8.3 Hz, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 5.82–5.70 (m, 2 H), 3.30 (dtd, J = 7.1, 5.4, 4.8, 2.0 Hz, 1 H), 2.62–2.56 (m, 2 H), 2.08–1.75 (m, 5 H), 1.66–1.53 (m, 3 H), 1.35 (dq, J = 14.3, 7.2 Hz, 2 H), 0.93 (t, J = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 142.6, 132.5, 131.6, 128.7, 128.4, 128.0, 127.4, 121.1, 92.2, 80.5, 35.6, 33.6, 29.6, 28.2, 24.8, 22.4, 20.8, 14.1.

1-(tert-Butyl)-4-(cyclohex-2-en-1-ylethynyl)benzene (3m)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (5.8 mg, 0.015 mmol), ligand **L1** (5.1 mg, 0.015 mmol), cyclohexene (**2a**; 500 mg, 6 mmol), 1-(tert-butyl)-4-ethynylbenzene (**1m**; 50 mg, 0.3 mmol), and TBHP (54 mg, 0.6 mmol), the pure product was obtained by flash column chromatography on silica gel using pure pentane as eluent; colorless oil; yield: 564 mg (62%, 0.18 mmol); R_f = 0.44.

^1H NMR (400 MHz, CDCl_3): δ = 7.37 (d, J = 8.7 Hz, 2 H), 7.32 (d, J = 6.6 Hz, 2 H), 5.83–5.73 (m, 2 H), 3.32 (qt, J = 5.3, 2.3 Hz, 1 H), 2.08–1.97 (m, 3 H), 1.92–1.78 (m, 2 H), 1.68–1.58 (m, 1 H), 1.32 (s, 9 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 150.8, 132.4, 131.4, 128.0, 127.4, 125.2, 121.0, 92.2, 80.4, 77.2, 34.8, 31.3, 29.6, 28.2, 24.8, 20.8.

1-(Cyclohex-2-en-1-ylethynyl)-4-methoxy-methylbenzene (3n)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (6.5 mg, 0.017 mmol), ligand **L1** (5.9 mg, 0.017 mmol), cyclohexene (**2a**; 545 mg, 6.6 mmol), 1-ethynyl-4-methoxy-2-methylbenzene (**1n**; 50 mg, 0.33 mmol), and TBHP (60 mg, 0.66 mmol), the pure product was obtained by flash column chromatography on silica gel using Et_2O /pentane (1:30) as eluent; colorless oil; yield: 68 mg (90%, 0.3 mmol); R_f = 0.5.

^1H NMR (400 MHz, CDCl_3): δ = 7.30 (d, J = 8.5 Hz, 1 H), 6.72 (d, J = 2.7 Hz, 1 H), 6.65 (dd, J = 8.0, 2.7 Hz, 1 H), 5.80–5.72 (m, 2 H), 3.78 (s, 3 H), 3.32 (dtt, J = 6.7, 3.6, 1.8 Hz, 1 H), 2.40 (s, 3 H), 2.01 (dddt, J = 20.7, 10.7, 5.4, 2.2 Hz, 3 H), 1.93–1.85 (m, 1 H), 1.84–1.77 (m, 1 H), 1.68–1.58 (m, 1 H).

^{13}C NMR (101 MHz, CDCl_3): δ = 159.05, 141.83, 133.07, 127.88, 127.59, 116.10, 115.02, 111.10, 95.39, 79.10, 77.16, 55.29, 29.79, 28.30, 24.84, 21.12, 20.79.

MS: m/z = 226 (100), 211 (34), 198 (70), 165 (39), 146 (68).

HRMS (ESI-TOF): m/z calcd for $\text{C}_{16}\text{H}_{18}\text{O}$ [$\text{M} + \text{H}$] $^+$: 226.13522; found: 226.13481.

3-(Cyclohex-2-en-1-ylethynyl)thiophene (3o)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (8.7 mg, 0.022 mmol), ligand **L1** (7.8 mg, 0.022 mmol), cyclohexene (**2a**; 736 mg, 9 mmol), 3-ethynylthiophene (**1o**; 50 mg, 0.45 mmol), and TBHP (81 mg, 0.9 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane as eluent; colorless oil; yield: 55 mg (65%, 0.3 mmol); R_f = 0.6.

^1H NMR (400 MHz, CDCl_3): δ = 7.36 (d, J = 4.1 Hz, 1 H), 7.22 (d, J = 3.0 Hz, 1 H), 7.09–7.07 (m, 1 H), 5.78 (dtd, J = 9.1, 3.5, 2.1 Hz, 1 H), 5.72 (ddt, J = 9.9, 3.5, 1.9 Hz, 1 H), 3.28 (ddp, J = 7.8, 5.4, 2.8 Hz, 1 H), 2.05–1.94 (m, 3 H), 1.91–1.83 (m, 1 H), 1.82–1.75 (m, 1 H), 1.66–1.57 (m, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 130.2, 128.2, 127.8, 127.1, 125.0, 122.9, 92.5, 77.6, 77.2, 76.7, 75.4, 29.4, 28.1, 24.8, 20.8.

2-(Cyclohex-2-en-1-ylethynyl)phenol (3p)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (7.8 mg, 0.021 mmol), ligand **L1** (6.7 mg, 0.021 mmol), cyclohexene (**2a**; 810 mg, 8.04 mmol), 2-ethynylphenol (**1p**; 50 mg, 0.4 mmol), and TBHP (72 mg, 0.8 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane/EtOAc (8:2) as eluent; colorless oil; yield: 45 mg (56%, 0.22 mmol); R_f = 0.6.

Note: Extensive drying of the product under high vacuum leads to decomposition of the product.

^1H NMR (300 MHz, CDCl_3): δ = 7.14 (t, J = 7.9 Hz, 1 H), 6.98 (d, J = 7.7 Hz, 1 H), 6.89–6.86 (m, 1 H), 6.75 (dd, J = 8.1, 3.5 Hz, 1 H), 5.82–5.75 (m, 1 H), 5.74–5.67 (m, 1 H), 3.28 (pt, J = 6.0, 3.2 Hz, 1 H), 2.07–2.00 (m, 2 H), 1.96 (dd, J = 11.3, 4.0 Hz, 1 H), 1.92–1.83 (m, 1 H), 1.83–1.72 (m, 1 H), 1.67–1.55 (m, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 155.3, 129.6, 128.3, 127.1, 125.3, 124.5, 118.5, 115.2, 93.2, 80.1, 77.2, 29.4, 28.1, 24.8, 20.8.

[(3-Methylcyclohex-2-en-1-yl)ethynyl]benzene (3r)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (9.2 mg, 0.024 mmol), ligand **L1** (8.4 mg, 0.024 mmol), 1-methylcyclohex-1-ene (**2e**; 923 mg, 9.6 mmol), phenylacetylene (**1a**; 50 mg, 0.48 mmol), and TBHP (86 mg, 0.96 mmol), the pure product was obtained by flash column chromatography on silica gel using pentane as eluent; colorless oil; yield: 50 mg (53%, 0.25 mmol); R_f = 0.8.

^1H NMR (300 MHz, CDCl_3): δ = 7.39–7.35 (m, 2 H), 7.23–7.20 (m, 3 H), 5.42 (dh, J = 3.0, 1.5 Hz, 1 H), 3.24 (dddq, J = 7.4, 5.5, 4.1, 2.1 Hz, 1 H), 1.89 (ddd, J = 10.9, 6.1, 2.8 Hz, 3 H), 1.85–1.77 (m, 1 H), 1.75–1.67 (m, 1 H), 1.65 (ddd, J = 2.2, 1.8, 0.8 Hz, 3 H), 1.57 (ddd, J = 9.0, 4.8, 2.6 Hz, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 135.5, 131.7, 128.2, 127.6, 124.1, 121.2, 93.5, 80.2, 77.2, 29.8, 29.3, 28.4, 23.9, 21.2.

(Cyclopent-2-en-1-ylethynyl)benzene (3s)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (9.2 mg, 0.024 mmol), ligand **L1** (8.4 mg, 0.024 mmol), cyclopentene (**2b**; 653 mg, 9.6 mmol), phenylacetylene (**1a**; 50 mg, 0.48 mmol), and TBHP (86 mg, 0.96 mmol), the pure product was obtained by flash column chromatography on silica gel using Et_2O /pentane (0.5:99.5) as eluent; colorless oil; yield: 65 mg (80%, 0.38 mmol); R_f = 0.8.

Note: Extensive drying of the product under high vacuum leads to decomposition of the product.

^1H NMR (300 MHz, CDCl_3): δ = 7.35–7.31 (m, 2 H), 7.21–7.17 (m, 3 H), 5.81–5.76 (m, 1 H), 5.71–5.65 (m, 1 H), 3.64 (dddt, J = 9.2, 7.1, 4.6, 2.3 Hz, 1 H), 2.47–2.38 (m, 1 H), 2.36–2.29 (m, 1 H), 2.29–2.21 (m, 1 H), 1.99–1.88 (m, 1 H).

^{13}C NMR (75 MHz, CDCl_3): δ = 132.3, 132.0, 131.8, 131.4, 128.4, 128.3, 127.7, 124.2, 92.8, 80.8, 77.2, 36.7, 32.2, 31.9, 26.0.

MS: m/z = 167 (100), 153 (53), 141 (11), 128 (8), 115 (16).

3-(Phenylethynyl)cyclohept-1-ene (3t)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (9.5 mg, 0.024 mmol), ligand **L1** (8.4 mg, 0.024 mmol), cycloheptene (**2c**; 941 mg, 9.6 mmol), phenylacetylene (**1a**; 50 mg, 0.48 mmol), and TBHP (86 mg, 0.96 mmol), the pure product was obtained by flash column chromatography on silica gel using Et_2O /pentane (1:99) as eluent; colorless oil; yield: 50 mg (49%, 0.25 mmol); $R_f = 0.8$.

^1H NMR (300 MHz, CDCl_3): $\delta = 7.40\text{--}7.36$ (m, 2 H), 7.26–7.23 (m, 3 H), 5.85–5.82 (m, 2 H), 3.50–3.43 (m, 1 H), 2.30–2.18 (m, 1 H), 2.05 (dddd, $J = 13.6, 10.1, 6.8, 3.2$ Hz, 2 H), 1.94–1.86 (m, 1 H), 1.81–1.68 (m, 2 H), 1.55 (ddt, $J = 15.7, 8.9, 3.2$ Hz, 2 H).

^{13}C NMR (75 MHz, CDCl_3): $\delta = 133.5, 132.8, 131.7, 128.3, 127.6, 124.1, 93.1, 80.9, 77.2, 33.8, 32.6, 29.7, 28.5, 26.9$.

3-(Phenylethynyl)cyclooct-1-ene (3u, Mixture of Isomers)

Following the general procedure, using $\text{Cu}(\text{MeCN})_4\text{PF}_6$ (9.3 mg, 0.024 mmol), ligand **L1** (8.2 mg, 0.024 mmol), *cis*-cyclooctene (**2d**; 1 g, 9.6 mmol), phenylacetylene (**1a**; 50 mg, 0.48 mmol), and TBHP (86 mg, 0.96 mmol), a mixture of isomeric products was obtained. This was purified by flash column chromatography on silica gel using pentane as eluent. A colorless oil consisting of two main products was obtained; yield: 75 mg (74%, 0.35 mmol); $R_f = 0.6$.

^{13}C NMR (75 MHz, CDCl_3): δ [for the 3-(phenylethynyl)cyclooct-1-ene assigned from 2D NMR] = 131.7, 131.1, 130.2, 128.3, 127.7, 124.1, 93.7, 80.6, 37.1, 29.4, 29.1, 26.6, 26.1, 25.5.

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Supporting Information

Supporting information for this article is available online at <https://doi.org/10.1055/s-0039-1690014>.

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