Practical synthesis of polysubstituted naphthalene derivatives via HNTf$_2$-catalyzed benzannulation reaction

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Dedicated to Professor J. S. Yadav on the occasion of his 65th birthday

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Abstract
The synthesis of polysubstituted naphthalenes using the triflimide-catalyzed benzannulation of arylacetaldehydes with alkynes at room temperature is described. This method demonstrates a high functional group tolerance and, in the case of halogen substituted naphthalenes, opens the route for further functionalization by palladium-catalyzed cross-coupling reactions. With an analogous organocatalytic strategy, arylepoxides or 2-arylacetal derivatives are also suitable partners in the related benzannulation reactions with aryl-alkynes.

Keywords: Organocatalysis, naphthalene, benzannulation, triflimide

Introduction
Substituted naphthalene derivatives are important pharmacophores in many biologically active compounds which possess anti-inflammatory, antibacterial, antimicrobial and anticancer activities.\(^1\)-\(^9\) Additionally, this particular aromatic structure can be found in numerous optical and electronic materials\(^10\)-\(^12\) and constitutes the backbone of many chiral ligands.\(^13\) Nafacillin,\(^14\) suramin,\(^15,16\) which play a vital role in the control of microbial infection, are typical examples of drugs that present a naphthalene moiety (Figure 1). Therefore, the development of new and efficient methods for the synthesis of naphthalene skeletons has been a subject of great interest in recent years.\(^17\)-\(^42\) Most of the traditional approaches toward naphthalene derivatives involve the stepwise introduction of a substituent through electrophilic substitution or coupling reactions.\(^17,18\) Construction of the second aromatic ring of the naphthalene core \textit{via} a formal [4+2] process
under various catalytic conditions is definitely one of the most direct and efficient methods.\textsuperscript{19-42} In particular, TiCl$_4$ or FeCl$_3$ in stoichiometric quantities as well as catalytic GaCl$_3$ or AuCl$_3$/AgSbF$_6$ systems were found to promote the benzannulation reaction of arylacetaldehydes with alkynes.\textsuperscript{29-32} Boron trifluoride etherate complex was also described as an appropriate catalyst for this transformation, in the specific case of terminal arylacetylenes.\textsuperscript{34}

![Figure 1. Two representative naphthalene containing drugs.](image)

In this field, we recently discovered that triflimide (HNTf$_2$)\textsuperscript{43-47} is also an efficient catalyst for the benzannulation of arylacetaldehyde derivatives with alkynes.\textsuperscript{48} This organocatalytic metal-free reaction proceeds under mild reaction conditions at room temperature and leads to a variety of substituted naphthalene compounds with, in the vast majority of cases, perfect regioselectivity. We report herein a more detailed study of this benzannulation reaction for the synthesis of a larger number of naphthalene derivatives displaying various useful functionalities. Additionally, this strategy could be applied to the analogous benzannulation of arylepoxides and arylacetals. The further functionalization of these aromatic scaffolds by palladium-catalyzed cross-coupling reactions is also presented.

### Results and Discussion

Initial optimization studies allowed us to determine that the benzannulation reactions of phenylacetaldehydes with 1.5 equivalents of alkynes in DCE at room temperature were efficiently catalyzed by 15 mol % HNTf$_2$.\textsuperscript{48} Accordingly, these reaction conditions were applied for the synthesis of a wide variety of naphthalenes in order to evaluate the scope and limitations of this novel protocol. At first, various 2-methyl-phenylacetaldehydes 1a-h were reacted with 1-phenyl-1-propyne 2 to assess the influence of the aromatic substitution of the aldehyde partner over benzannulation efficiency (Table 1 & Scheme 1). This reaction gave almost similar yields (62-70%) when the aryl group was not substituted 1a (R = H) or when it bears an electron-
donating substituent \(1b-c\) (\(R = \text{Me}, \text{OMe}\)) on 4-position of the aromatic ring (Table 1, entries 1-3). In the specific case of 2-(3,5-dimethoxyphenyl)-propionaldehyde \(1d\), a degradation of the reaction mixture was observed so that naphthalene \(3d\) was isolated in a low yield of 8% as a probable consequence of the increased electron-richness of this substrate (Table 1, entry 4). With \(1e\), which presents a nitro group at the \(para\) position of its aromatic moiety, a slightly diminished yield of 46% was obtained which is in good correlation with the deactivating effect of such group in electrophilic aromatic substitutions (Table 1, entry 5).

**Table 1.** Influence of electronic factors induced by the substitution of the aldehyde aromatic ring

![Chemical reaction diagram](image)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Aldehyde</th>
<th>Product</th>
<th>(t) (h)</th>
<th>Yield (%)</th>
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<td>20</td>
<td>46</td>
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</table>

\(^a\)Isolated yield.

We were pleased to observe a relatively small influence of the steric effect induced by the substitution of the aromatic ring. Indeed, the \(ortho\), \(meta\) or \(para\)-bromo phenylacetaldehydes \(1f-h\) afforded the corresponding naphthalenes \(3f-h\) in almost identical yields (Scheme 1). Whereas \(3f\) and \(3h\) were obtained as single regiosomers in 59% and 66% yield respectively, the
benzannulation of 3-bromo phenylacetaldehyde 1g led to a 1:1 regioisomeric mixture of naphthalenes 3g and 3g’ in 63% yield.

Scheme 1. Influence of steric factors induced by the substitution of the aldehyde aromatic ring.

We next moved our attention toward the influence of the α-substitution of the aldehyde partner and the evaluation of the reactivity of few ketones (Table 2). Switching from a methyl group to phenyl, ethyl or cyclohexyl α-substituents had a limited impact over the efficiency of the benzannulation process since compounds 3i-k were obtained in good 69-78% yields (Table 2, entries 1–3). Unsubstituted phenylacetaldehyde 1l reacted with somewhat lower efficiency to give the naphthalene adduct 3l in 49% yield (Table 2, entry 4), which tended to support that α-substitution of the aldehyde group may prove itself beneficial to achieve better yields. On the other hand, ketones 1m-o were tested. However, only 2-phenylcyclohexanone 1o resulted in the formation of the desired benzannulation product 3o in low 25% yield (Table 2, entry 7), thus suggesting that this HNTf₂-catalyzed benzannulation process is poorly efficient with ketones.

To further determine the scope of our organocatalyzed benzannulation reaction, we investigated the reactivity of different alkyne partners with 2-phenylpropionaldehyde 1a (Table 3 & Table 4). We began our studies by performing some reactions with phenylacetylenes possessing various alkyl groups and we were pleased to observe that the reaction of alkynes 4a, 4b and 4c (R¹ = Ph and R² = Et, nPr, nBu) afforded the corresponding naphthalenes 5a-c in 66-70% yields (Table 3, entries 1-3). We then decided to examine the influence of the aromatic substitution of the arylalkyne partner. Accordingly, the 4-chloro-, 4-bromo- and 4-methyl- substituted alkynes 4d-f were submitted to reaction and gave access to desired products 5d-f with comparable satisfactory results (Table 3, entries 4-6). In the case of alkynes 4g and 4h, which are bearing electron-withdrawing/donating 4-trifluoromethyl and 4-methoxy groups, a reduced reaction efficiency could however be noticed (Table 3, entries 7-8). Notably, the reaction of the electron rich alkyne 4h was faster and the aldehyde 1a was converted to 5h in 44% yield along with some
unidentified by-products (Table 3, entry 8). Diaryl-substituted alkynes were also prone to react under these catalytic conditions. The reaction of symmetrical alkynes 4i and 4j led to naphthalene compounds 5i and 5j in 46 and 49% yields respectively (Table 3, entries 9-10). On the other hand the unsymmetrical alkyne 4k generated a 1:1 mixture of the two regioisomers 5k/5k' in 39% yield (Table 3, entry 11). Trimethylsilyl-substituted phenylacetylene 4l gave only degradation of starting materials (Table 3, entry 12).

Table 2. Influence of α-substitution of the aldehyde partner and evaluation of ketones

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\(^a\)Isolated yield.
Table 3. Benzannulation scope for di-substituted aryl-alkynes

![Chemical structure](image)

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<sup>a</sup> Isolated yield. <sup>b</sup> 1.5:1 aldehyde:alkyne ratio. <sup>c</sup> 1:1 mixture of regioisomers.

Afterwards, we turned our attention toward a wider range of aromatic alkynes and aliphatic alkynes (Table 4). In the case of terminal aromatic alkynes, the benzannulation process proved to be more challenging so that, for this particular class, the alkyne-loading was increased to 3 equivalents. Under the corresponding reaction conditions, phenylacetylene 4m yielded the
desired 1,4-disubstituted naphthalene 5m in 41% yield (Table 4, entry 1). The substitution of the phenylacetylene aromatic core with 4-fluoro or 4-bromo moiety did not affect the outcome of the benzannulation and produced the expected compounds 5n and 5o with similar results (Table 4, entries 2-3). Conversely, electron-richer 4-methyl and 4-methoxy terminal alkynes 4p and 4q provided complex mixtures of products from which only the naphthalene 5p could be isolated in low 11% yield (Table 4, entries 4-5). Interestingly, the keto- and ester-substituted naphthalenes 5r and 5s were obtained in 46% and 35% yields respectively using alkynes 4r and 4s bearing electron-withdrawing groups (Table 4, entries 6-7). This method could also be extended to halogen-substituted phenylacetylenes. Indeed, the corresponding alkynes 4t-v were converted to 2-chloro-, 2-bromo- substituted naphthalene compounds 5t and 5u with useful 43% and 42% yields respectively (Table 4, entries 8-9), and to the 2-iodonaphthalene 5v with 34% yield (Table 4, entry 10). When opposed to diphenylacetaldehyde 1i, bromo-alkyne 4u led to naphthalene 6 in 37% yield (Table 4, entry 11). Then, terminal and internal aliphatic alkynes 4w and 4x were tested but reacted much more sluggishly than their aryl-alkyne counterparts resulting in the limited formation of the naphthalenes 5w and 5x in 21% and 11% respectively (Table 4, entries 12-13).

Table 4. Benzannulation scope for terminal aryl-alkynes, carbo-alkynes, halogeno alkynes and aliphatic alkynes

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Table 4 (continued)

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</table>
Considering literature precedents, we envisioned that this Brønsted acid catalyzed benzannulation reaction could be extended to the use of epoxides or acetals. Pleasingly, epoxides reacted with 1-phenyl-1-propyne in the presence of 15 mol% HNTf₂ in DCE at room temperature to provide the corresponding naphthalenes in 12-61% yields. On the other hand, acetals, under the same reaction conditions, furnished the desired products with slightly better efficiency (Scheme 2).

\[ \text{Scheme 2. Scope of epoxides and acetals for the synthesis of naphthalene derivatives.} \]
To further demonstrate the usefulness of this method of access to polyfunctionalized naphthalene derivatives, we then studied the reactivity of the iodonaphthalene 5v in palladium catalyzed Sonogashira and Suzuki-Miyaura cross-couplings (Scheme 3). Satisfyingly, compound 5v reacted well with various aryl and aliphatic alkynes to give the corresponding alkynyl-naphthalenes 9a-e in 51-81% yields and when engaged with 4-(trifluoromethyl)phenylboronic acid allowed to obtain the polyaromatic 10 in good 76% yield.

\[
\text{Reagents and conditions: (i) Pd(PPh}_3\text{)}_2\text{Cl}_2 (5 \text{ mol\%}), \text{CuI (5 mol\%}, \text{DMF/NEt}_3 (7:3), \text{rt, 13h. (ii) Pd(OAc)}_2 (5 \text{ mol\%}), \text{dppf (5 mol\%}, \text{K}_2\text{CO}_3 (3 \text{ equiv.}, \text{DMF, 80 }^\circ\text{C, 13h.}}
\]

Scheme 3. Pd-catalyzed cross-coupling reactions.

Conclusions

We have developed a practical and easy protocol to access naphthalene derivatives from readily available starting materials through the triflimide (HNTf$_2$) organocatalyzed benzannulation reactions of arylacetaldehyde, arylepoxide and arylacetal derivatives with alkynes. Attractive features of these organocatalytic transformations involve the mild reaction conditions and the wide substrate scope allowing the straightforward access to highly substituted naphthalenes with, in most cases, perfect regioselectivity. We could also demonstrate that this method may lead to valuable platforms such as iodonaphthalenes which can be further functionalized via palladium-catalyzed cross-coupling reactions.

Acknowledgements

This work was supported by the Ministère de l’Education Supérieure et de la Recherche (MESR) and the Centre National de la Recherche Scientifique (CNRS). S. Ponra is grateful to the “Fondation Pierre-Gilles de Gennes pour la Recherche” for a postdoctoral grant.
**Experimental Section**

**General.** All reactions were performed under argon atmosphere. 1,2-Dichloroethane was distilled from CaH$_2$. All products were purified by flash chromatography using silica gel (230-400 mesh). $^1$H-NMR and $^{13}$C-NMR were recorded in CDCl$_3$ with chemical shifts reported relative to residual CHCl$_3$ peak for $^1$H NMR (7.26 ppm) or the central peak of CDCl$_3$ for $^{13}$C NMR (77.16 ppm). HRMS data for new compounds were obtained using an atmospheric pressure photo ionization source (APPI) coupled to a LTQ-Orbitrap high resolution detector. Unless otherwise noted, all the reagents were ordered and used without further purification. Starting materials were prepared according to literature (see supplementary information for more details). Naphthalene derivatives 3a-c, 3e-f, 3h-l and 5a-f, 5i-j, 5m-o, 5r, 5t-u have already been described in our previous report. 48

**Procedure for the benzannulation reaction:** In a screw cap vial under argon atmosphere were sequentially added the arylaldehyde 1 or arylepoxides 7 or 2-arylacetal 8 (1 mmol, 1 equiv.), the alkyne 2 or 4 (1.5 mmol, 1.5 equiv.), 1,2-dichloroethane (1 mL) and HNTf$_2$ (42 mg, 0.15 mmol, 0.15 equiv.). The resulting mixture was stirred at room temperature until TLC analysis showed completion of the reaction. The reaction mixture was then diluted with dichloromethane (5 mL) and water (15 mL) and transferred to a separating funnel. The aqueous phase was extracted with dichloromethane (3 x 15 mL) and the combined organic extracts washed by water (2 x 40 mL) and brine (40 mL) before being dried over MgSO$_4$. After filtration and evaporation of the solvents under reduced pressure, the crude material was purified by flash column chromatography on silica gel to afford the desired naphthalene 3 or 5. In specific cases, this first purification step was followed by a bulb to bulb distillation under reduced pressure in order to remove residual alkyne.

**6,8-Dimethoxy-2,4-dimethyl-1-phenylnaphthalene (3d).** Starting from 2-(3,5-dimethoxyphenyl)-propanal 1d (194 mg, 1.0 mmol) and 1-phenyl-1-propyne 2 (174 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (98:2) as eluent. The desired naphthalene 3d was obtained as a pale yellow oil (22 mg, 8% yield). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 7.24 (s, 1H), 7.17 – 7.12 (m, 2H), 6.85 (d, $J$ 2.4 Hz, 1H), 6.42 (d, $J$ 2.4 Hz, 1H), 3.94 (s, 3H), 3.32 (s, 3H), 2.64 (d, $J$ 0.7 Hz, 3H), 2.05 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.4, 157.3, 144.9, 135.3, 133.7, 131.9, 131.8, 130.8, 128.7, 127.2, 125.3, 120.6, 99.2, 95.5, 55.6, 55.4, 21.0, 20.4; HRMS (APPI) $m/z$: [M]$^+$ calcd for C$_{20}$H$_{20}$O$_2$ 292.1458, found: 292.1461.

**6-Bromo-2,4-dimethyl-1-phenylnaphthalene (3g) and 8-bromo-2,4-dimethyl-1-phenylnaphthalene (3g').** Starting from 2-(3-bromophenyl)-propanal 1g (209 mg, 0.98 mmol) and 1-phenyl-1-propyne 2 (171 mg, 1.47 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane as eluent. The desired naphthalenes 3g and 3g' (1:1 mixture) were obtained as a colorless oil (192 mg, 63%...
yield. $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.21 (d, $J$ 1.9 Hz, 1H), 8.08 (dd, $J$ 8.4, 1.2 Hz, 1H), 7.83 (dd, $J$ 7.4, 1.2 Hz, 1H), 7.61 – 7.43 (m, 7H), 7.36 (d, $J$ 7.5 Hz, 3H), 7.33 – 7.24 (m, 5H), 2.77 (s, 3H), 2.74 (s, 3H), 2.25 (s, 3H), 2.19 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.6, 139.5, 136.7, 136.4, 136.2, 134.2, 134.0, 133.7, 133.4, 132.6, 132.5, 131.7, 131.3, 130.6, 130.5, 130.4, 130.3, 128.8 (2C), 128.6, 127.9, 127.3, 127.0, 126.4, 125.0, 124.6, 120.5, 119.2, 22.1, 20.8, 20.4, 19.4; HRMS (APPI) m/z: [M]$^+$ calcd for C$_{18}$H$_{15}$Br 310.0352, found: 310.0357.

10-Methyl-9-phenyl-1,2,3,4-tetrahydrophenanthrene (3o). Starting from 2-phenyl-cyclohexanone 1o (174 mg, 1.0 mmol) and 1-phenyl-1-propyne 2 (174 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane as eluent. The desired naphthalene 3o was obtained as a white low melting solid (68 mg, 25% yield). $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J$ 8.5 Hz, 1H), 7.55 – 7.40 (m, 4H), 7.37 – 7.24 (m, 4H), 3.23 (t, $J$ 5.2 Hz, 2H), 2.85 (t, $J$ 5.2 Hz, 2H), 2.12 (s, 3H), 2.05 – 1.90 (m, 4H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 141.0, 136.6, 134.1, 133.0, 131.4, 131.3, 131.0, 130.6, 128.4, 127.1, 126.9, 126.4, 125.0, 28.4, 26.7, 23.4, 23.0, 17.6. These analytical data are in accordance with literature.

2,4-Dimethyl-1-(4-(trifluoromethyl)-phenyl)-naphthalene (5g). Starting from 2-phenyl-propionaldehyde 1a (134 mg, 1.0 mmol) and 1-(prop-1-ynyl)-4-(trifluoromethyl)benzene 4g (276 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent followed by bulb to bulb distillation of residual alkyne at 100°C/0.3 Torr during 1 hour. The desired naphthalene 5g was obtained as a white solid (108 mg, 36% yield). mp 121-123°C; $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.07 (d, $J$ 8.4, 1H), 7.85 – 7.78 (m, 2H), 7.57 – 7.49 (m, 1H), 7.48 – 7.38 (m, 4H), 7.34 (s, 1H), 2.78 (d, $J$ 1.0 Hz, 3H), 2.24 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.1, 135.1, 134.2, 132.8, 131.2, 131.0, 129.5, 129.4 (q, $^{3}$J$_{C,F}$ 32.2 Hz), 126.4, 126.0, 125.5 (q, $^{2}$J$_{C,F}$ 3.8 Hz), 125.0, 124.5 (q, $^{1}$J$_{C,F}$ 271.5 Hz), 124.2, 20.7, 19.5; $^{19}$F NMR (282 MHz, CDCl$_3$) $\delta$ -63.2 (s); HRMS (APPI) m/z: [M]$^+$ calcd for C$_{19}$H$_{15}$F$_3$ 300.1120, found: 300.1124.

1-(4-Methoxyphenyl)-2,4-dimethylnaphthalene (5h). Starting from 2-phenylpropionaldehyde 1a (134 mg, 1.0 mmol) and 1-methoxy-4-(prop-1-ynyl)benzene 4h (219 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent followed by bulb to bulb distillation of residual alkyne at 100°C/0.3 Torr during 1 hour. The desired naphthalene 5h was obtained as a white solid (114 mg, 44% yield). mp 103-105°C; $^{1}$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.99 (dt, $J$ 8.1, 1.0 Hz, 1H), 7.50 – 7.40 (m, 2H), 7.38 – 7.30 (m, 1H), 7.28 – 7.24 (m, 4H), 3.91 (s, 3H), 2.72 (d, $J$ 1.0 Hz, 3H), 2.22 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 158.7, 136.3, 133.6, 133.3, 133.2, 132.3, 131.5, 131.2, 129.6, 126.9, 125.6, 124.7, 124.0, 113.9, 55.4, 20.9, 19.5; HRMS (APPI) m/z: [M]$^+$ calcd for C$_{19}$H$_{18}$O 262.1352, found: 262.1354.

1-(4-Chlorophenyl)-4-methyl-2-phenylnaphthalene (5k) and 2-(4-chlorophenyl)-4-methyl-1-phenylnaphthalene (5k'). Starting from 2-phenylpropionaldehyde 1a (201 mg, 1.5 mmol) and 1-chloro-4-(phenylethynyl)benzene 4k (212 mg, 1.0 mmol) and following the general procedure,
the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent. The desired naphthalenes 5k and 5k′ (1:1 mixture) were obtained as a white low melting solid (128 mg, 39% yield). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.14 – 8.03 (m, 2H), 7.71 – 7.60 (m, 2H), 7.59 – 7.51 (m, 2H), 7.47 – 7.37 (m, 4H), 7.33 – 7.24 (m, 6H), 7.22 – 7.04 (m, 12H), 2.79 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 141.9, 140.7, 139.0, 138.3, 137.9, 136.8, 136.2, 134.7, 134.3, 134.1, 133.1, 132.9, 132.7, 132.6, 132.3, 132.1, 132.0, 131.7, 131.5, 130.2, 129.2, 128.8, 128.6, 128.2, 127.9, 127.6, 127.2, 126.9, 126.5, 126.2 (2C), 125.9, 125.8, 124.3, 124.2, 19.7 (2C); HRMS (APPI) m/z: [M]$^+$ calcd for C$_{23}$H$_{17}$Cl 328.1013, found: 328.1013.

1-Methyl-4-(p-tolyl)-naphthalene (5p). Starting from 2-phenylpropionaldehyde 1a (134 mg, 1.0 mmol) and p-tolylacetylene 4p (348 mg, 3.0 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent. The desired naphthalene 5p was obtained as a white solid (25 mg, 11% yield). mp 95-97 °C; $^1$H NMR (300 MHz, CDCl$_3$) δ 8.11 (dd, J 8.4, 0.7 Hz, 1H), 8.01 (dd, J 8.4, 0.7 Hz, 1H), 7.59 (ddd, J 8.4, 6.8, 1.4 Hz, 1H), 7.54 – 7.31 (m, 7H), 2.80 (d, J 0.7 Hz, 3H), 2.51 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 138.8, 138.2, 136.9, 133.7, 132.9, 131.9, 130.2, 129.1, 126.9, 126.7, 126.3, 125.7 (2C), 124.5, 21.4, 19.7; MS (EI) for C$_{18}$H$_{16}$O m/z 232 (100) [M]$^+$, 217 (22) [M-Me]$^+$.

2-Carbomethoxy-4-methyl-1-phenylnaphthalene (5s). Starting from 2-phenylpropionaldehyde 1a (134 mg, 1.0 mmol) and methyl 3-phenylpropionate 4s (240 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (98:2) as eluent followed by bulb to bulb distillation of residual alkyne at 115°C/0.3 Torr during 1 hour. The desired naphthalene 5s was obtained as a pale yellow low melting solid (96 mg, 35% yield). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.10 – 8.03 (m, 1H), 7.79 (d, J 0.9 Hz, 1H), 7.65 – 7.56 (m, 2H), 7.49 – 7.39 (m, 4H), 7.33 – 7.26 (m, 2H), 3.61 (s, 3H), 2.77 (d, J 0.9 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 169.0, 140.0, 139.3, 134.3, 134.1, 132.8, 129.9, 128.6, 127.9, 127.6, 127.4, 126.3, 126.2, 125.7 (2C), 124.5, 21.4, 19.7; MS (EI) for C$_{18}$H$_{16}$O$_2$ m/z 232 (100) [M]$^+$, 217 (22) [M-Me]$^+$.

2-Iodo-4-methyl-1-phenylnaphthalene (5v). Starting from 2-phenylpropionaldehyde 1a (134 mg, 1.0 mmol) and 2-iodoethynylbenzene 4v (342 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent. The desired naphthalene 5v was obtained as a pale orange solid (118 mg, 34% yield). $^1$H NMR (300 MHz, CDCl$_3$) δ 8.02 (dt, J 8.5, 1.0 Hz, 1H), 7.91 (d, J 1.0 Hz, 1H), 7.64 – 7.45 (m, 5H), 7.42 – 7.34 (m, 1H), 7.33 – 7.26 (m, 2H), 2.72 (d, J 1.0 Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 143.6, 142.9, 135.9, 135.7, 133.4, 132.2, 130.3, 128.5, 127.9, 127.8, 126.5, 126.1, 124.3, 98.5, 19.1; HRMS (APPI) m/z: [M]$^+$ calcd for C$_{17}$H$_{13}$I 344.0056, found: 344.0058. These analytical data are in accordance with literature.

2-Bromo-1,4-diphenylnaphthalene (6). Starting from diphenylacetaldehyde 1i (196 mg, 1.0 mmol) and 2-bromoethylbenzene 4u (272 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum
ether as eluent. The desired naphthalene 6 was obtained as a white solid (132 mg, 37% yield). mp 134-136 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.01 – 7.93 (m, 1H), 7.78 (s, 1H), 7.64 – 7.39 (m, 13H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.5, 139.8, 139.4, 139.3, 134.3, 130.8, 130.6, 130.3, 130.1, 128.5 (2C), 127.9 (2C), 127.20, 126.8, 126.4, 126.1, 121.2; HRMS (APPI) \(m/z\): [M]+ calcd for C\(_{22}\)H\(_{15}\)Br 358.0357, found: 358.0354.

1-(\(n\)-Butyl)-4-methylnaphthalene (5w). Starting from 2-phenylpropionaldehyde 1a (134 mg, 1.0 mmol) and 1-hexyne 4w (123 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent. The desired naphthalene 5w was obtained as a white low melting solid (42 mg, 21% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.18 – 8.04 (m, 2H), 7.62 – 7.55 (m, 2H), 7.33 – 7.26 (m, 2H), 3.17 – 3.07 (m, 2H), 2.74 (s, 3H), 1.87 – 1.72 (m, 2H), 1.61 – 1.45 (m, 2H), 1.04 (t, \(J\) 7.3 Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 137.3, 133.1, 132.4, 132.1, 126.4, 125.7, 125.4, 125.3, 125.0, 124.6, 33.3, 32.9, 23.0, 19.6, 14.2. These analytical data are in accordance with literature.\(^{29}\)

4-Methyl-1,2-di-(\(n\)-propyl-naphthalene (5x). Starting from 2-phenylpropionaldehyde 1a (134 mg, 1 mmol) and 4-octyne 4x (165 mg, 1.5 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using petroleum ether as eluent. The desired naphthalene 5x was obtained as colorless oil (25 mg, 11% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.09 – 8.03 (m, 1H), 8.02 – 7.95 (m, 1H), 7.55 – 7.42 (m, 2H), 7.18 (s, 1H), 3.10 – 2.99 (m, 2H), 2.85 – 2.70 (m, 2H), 2.67 (s, 3H), 1.78 – 1.61 (m, 4H), 1.12 (t, \(J\) 7.3 Hz, 3H), 1.05 (t, \(J\) 7.3 Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 137.3, 133.7, 132.6, 131.9, 131.8, 129.5, 125.5, 124.7 (2C), 124.5, 35.9, 30.5, 25.0, 24.7, 19.6, 14.9, 14.6. These analytical data are in accordance with literature.\(^{29}\)

**General procedure for the Sonogashira reaction:** Iodonaphthalene derivative 5v (50 mg, 0.145 mmol), Pd(PPh\(_3\))\(_2\)Cl\(_2\) (5 mg, 0.007 mmol, 5 mol%) and CuI (1.4 mg, 0.007 mmol, 5 mol%) were weighed out to a round bottom flask equipped with a magnetic stir bar and fitted with a rubber septa. The flask was purged with argon and DMF (0.5 mL) followed by triethylamine (0.25 mL) and the corresponding alkyne (0.217 mmol, 1.5 eq.) were added to the mixture and the reaction was stirred overnight at room temperature. After completion and hydrolysis (H\(_2\)O, 10 mL) the reaction mixture was transferred to a separating funnel. The aqueous phase was extracted with ethyl acetate (3 \(\times\) 15 mL) and the combined organic extracts washed by water (4 \(\times\) 40 mL) and brine (40 mL) before being dried over MgSO\(_4\). After filtration and evaporation of the solvents under reduced pressure, the crude material was purified by flash column chromatography on silica gel to afford the desired naphthalene 9. In specific cases, this first purification step was followed by a bulb to bulb distillation under reduced pressure in order to remove residual alkyne.

4-Methyl-1-phenyl-2-(phenylethynyl)-naphthalene (9a). Starting from iodonaphthalene derivative 5v (50 mg, 0.145 mmol) and phenylacetylene (22.2 mg, 0.217 mmol) and following
the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (500:1) as eluent. The desired naphthalene 9a was obtained as a white low melting solid (30 mg, 65% yield). mp 96-98 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.95 (d, \(J\) 8.0 Hz, 1H), 7.61 (dd, \(J\) 8.4, 0.8 Hz, 1H), 7.53 – 7.32 (m, 8H), 7.22 – 7.03 (m, 5H), 2.66 (d, \(J\) 0.8 Hz, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.7, 139.3, 133.9, 132.6, 132.5, 131.5, 131.0, 128.9, 128.3, 128.1 (2C), 127.5 (2C), 126.4, 126.2, 124.3, 123.7, 119.9, 93.1, 90.3, 19.5; MS (EI) for C\(_{25}\)H\(_{18}\) m/z 318.19 (100) [M]+.

2-(Cyclopropylethynyl)-4-methyl-1-phenylnaphthalene (9b). Starting from iodonaphthalene derivative 5v (50 mg, 0.145 mmol) and ethynylcyclopropane (14.3 mg, 0.217 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (500:1) as eluent. The desired naphthalene 9b was obtained as a yellow colored low melting solid (21 mg, 51% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.02 – 7.90 (m, 1H), 7.55 – 7.65 (m, 1H), 7.54 – 7.32 (m, 8H), 2.70 (d, \(J\) 0.9 Hz, 3H), 1.31 – 1.21 (m, 1H), 0.82 – 0.61 (m, 2H), 0.50 – 0.35 (m, 2H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.1, 139.6, 133.6, 132.5, 132.1, 130.8, 129.3, 127.9, 127.2 (2C), 126.0, 125.9, 124.2, 120.5, 97.5, 75.9, 19.4, 8.8, 0.4; MS (EI) for C\(_{22}\)H\(_{18}\) m/z 282.17 (92) [M]+.

2-(3-Methoxyprop-1-ynyl)-4-methyl-1-phenylnaphthalene (9c). Starting from iodonaphthalene derivative 5v (50 mg, 0.145 mmol) and 3-methoxyprop-1-yne (15.2 mg, 0.217 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (99.5:0.5) as eluent. The desired naphthalene 9c was obtained as a yellow colored solid (22.8 mg, 55% yield). mp 64-66 °C; \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.02 (d, \(J\) 8.4 Hz, 1H), 7.61 (d, \(J\) 8.4 Hz, 1H), 7.57 – 7.35 (m, 8H), 4.14 (s, 2H), 3.14 (s, 3H), 2.72 (s, 3H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.6, 139.2, 133.9, 132.6, 132.4, 130.7, 129.2, 128.1, 127.5 (2C), 126.4, 126.2, 124.2, 119.2, 88.4, 86.9, 60.4, 57.2, 19.4; MS (EI) for C\(_{21}\)H\(_{18}\)O m/z 286.15 (85) [M]+.

2-(5-Chloropent-1-ynyl)-4-methyl-1-phenylnaphthalene (9d). Starting from iodonaphthalene derivative 5v (50 mg, 0.145 mmol) and 5-chloropent-1-yne (22.2 mg, 0.217 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (500:1) as eluent. The desired naphthalene 9d was obtained as a yellow oil (26 mg, 56% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.08 – 7.88 (m, 1H), 7.58 (ddd, \(J\) 8.4, 1.3, 0.6 Hz, 1H), 7.55 – 7.34 (m, 8H), 3.27 (t, \(J\) 6.5 Hz, 2H), 2.71 (d, \(J\) 0.9 Hz, 3H), 2.43 (t, \(J\) 6.5 Hz, 2H), 1.76 (p, \(J\) 6.5 Hz, 2H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 141.3, 139.6, 133.8, 132.5, 132.2, 130.7, 129.2, 128.1, 127.4, 127.3, 126.1 (2C), 124.2, 120.1, 91.7, 82.0, 43.5, 31.4, 19.4, 17.0; MS (EI) for C\(_{22}\)H\(_{19}\)Cl m/z 318.10 (100) [M]+.

4-(4-Methyl-1-phenynaphthalen-2-yl)-but-3-yn-1-ol (9e). Starting from iodonaphthalene derivative 5v (50 mg, 0.145 mmol) and but-3-yn-1-ol (15.2 mg, 0.217 mmol) and following the general procedure, the crude material was purified by flash column chromatography on silica gel using cyclohexane:ethyl acetate (500:1) as eluent. The desired naphthalene 9e was obtained as yellow oil (33.5 mg, 81% yield). \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 8.01 (dd, \(J\) 8.3, 0.7 Hz, 1H), 7.66
– 7.34 (m, 9H), 3.48 (q, \(J = 5.9\) Hz, 2H), 2.72 (d, \(J = 0.9\) Hz, 3H), 2.49 (t, \(J = 5.9\) Hz, 2H), 1.24 (t, \(J = 5.9\) Hz, 1H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta = 141.4, 139.8, 133.9, 132.4, 132.3, 130.6, 128.9, 128.2\) (2C), 127.6, 127.3, 126.2, 124.3, 119.8, 90.2, 83.2, 61.0, 24.1, 19.4; MS (EI) for \(\text{C}_{21}\text{H}_{18}\text{O}\) \(m/z = 286.12\) (69) [M] \(^+\).

4-Methyl-1-phenyl-2-(4-(trifluoromethyl)-phenyl)-naphthalene (10). In a screw cap vial under argon atmosphere were sequentially added the iodonaphthalene derivative 5\(v\) (42 mg, 0.121 mmol), Pd(OAc)$_2$ (1.3 mg, 0.006 mmol, 5 mol%), K$_2$CO$_3$ (50.5 mg, 0.365 mmol, 3 equiv.), dppf (3 mg, 0.006 mmol, 5 mol%), 4-(trifluoromethyl)-phenylboronic acid (46 mg, 0.243 mmol, 2 equiv.) and DMF (0.5 mL). The reaction was stirred overnight at 80 °C. After completion and hydrolysis (H$_2$O, 10 mL) the reaction mixture was transferred to a separating funnel. The aqueous phase was extracted with ethyl acetate (3 x 15 mL) and the combined organic extracts washed by water (4 x 40 mL) and brine (40 mL) before being dried over MgSO$_4$. After filtration and evaporation of the solvents under reduced pressure, the crude material was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford the desired naphthalene 10 as a white solid (33.7 mg, 76% yield). mp 126-128 °C; \(^1\)H NMR (300 MHz, CDCl$_3$) \(\delta = 8.11\) (d, \(J = 8.4\) Hz, 1H), 7.75 – 7.67 (m, 1H), 7.61-7.55 (m, 1H), 7.49 – 7.39 (m, 4H), 7.35 – 7.24 (m, 5H), 7.22 – 7.14 (m, 2H), 2.81 (d, \(J = 0.9\) Hz, 3H); \(^{13}\)C NMR (75 MHz, CDCl$_3$) \(\delta = 146.0, 138.8, 136.6, 136.5, 134.3, 132.9, 132.3, 131.7, 130.5, 128.6, 128.1, 127.7, 127.1\) (2C), 126.3, 126.1, 124.7, 124.6, 124.2, 19.7; \(^{19}\)F NMR (282 MHz, CDCl$_3$) \(\delta = -63.34\). MS (EI) for \(\text{C}_{24}\text{H}_{17}\text{F}_3\) \(m/z = 362.15\) (100) [M] \(^+\).

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