

Communication

In(III)-TMSBr-Catalyzed Cascade Reaction of Diarylalkynes with Acrylates for the Synthesis of Aryldihydronaphthalene Derivatives

Qiu-Chi Zhang ^{1,†}, Wen-Wei Zhang ^{2,†}, Liang Shen ¹, Zhi-Liang Shen ³ and Teck-Peng Loh ^{1,3,*}

¹ Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore; zhan0413@e.ntu.edu.sg (Q.-C.Z.); lshen003@e.ntu.edu.sg (L.S.)

² BGI, BGI-Shenzhen, Shenzhen 518083, China; zhangww@genomics.cn

³ Institute of Advanced Synthesis, School of Chemistry and Molecular Engineering, Jiangsu National Synergetic Innovation Center for Advanced Materials, Nanjing Tech University, Nanjing 210009, China; ias_zlshen@njtech.edu.cn

* Correspondence: teckpeng@ntu.edu.sg; Tel.: +65-6316-8899

† These authors contributed equally to this work.

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Abstract: A combined Lewis acid system comprising of two or more Lewis acids occasionally exhibits augmented catalytic activity in organic transformations which are otherwise unrealizable by either of the components exclusively. On the other hand, the efficient construction of multiple new C-C bonds and polycyclic structures in minimal steps remains a subject of great interest in both academia and industry. Herein we report an efficient method to assemble aryldihydronaphthalene derivatives via a cascade reaction of diarylalkynes with acrylates under the catalysis of a combined Lewis acid derived from In(III) salt and TMSBr.

Keywords: indium; combined Lewis acid; catalysis; cascade reaction; aryldihydronaphthalene

1. Introduction

In the context of green chemistry, efficient methods to forge multiple new C-C bonds and to introduce molecular complexity in minimal steps have been a long-standing and important goal in the development of modern organic chemistry [1,2]. In this regard, aryldihydronaphthalene derivatives are particularly attractive targets mainly due to their widespread occurrence in natural products and bioactive compounds (Figure 1) [3–7]. They are also employed as fluorescent ligands in biochemistry studies or building blocks towards the synthesis of several biologically-active cyclic molecules [8–11]. Consequently, their significant roles have driven the establishment of several synthetic methodologies for their preparation. Prominently, the intramolecular hydroarylation of 4-phenyl-1-butyne or its derivatives is one of the most versatile protocols for the construction of aryldihydronaphthalene derivatives [12–15]. Since the pioneering studies by Fujiwara et al. [16,17], numerous catalytic methods have been developed in this field in which a series of transition metals, Lewis and Bronsted acids have been found effective for catalyzing the hydroarylation [18–39]. More recently, Corey [24] and Pérez Sestelo and Martínez [38,39] have independently reported the formation of six-membered oxa- and carbocycles by an In(III)-catalyzed hydroarylation of acetylenic substrates.

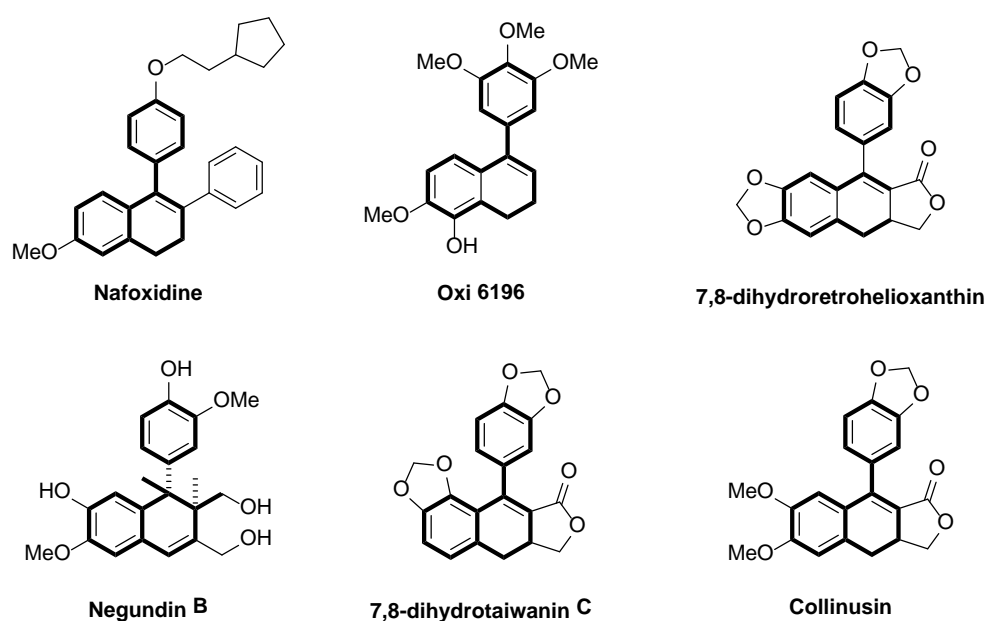
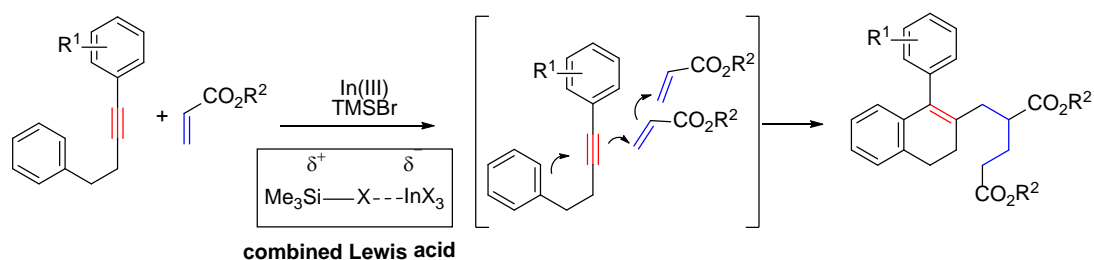


Figure 1. Representative natural products and bioactive compounds containing aryldihydronaphthalene structures [3–7].

On the other hand, although indium(III) salts (InX_3 ($X = \text{Cl}, \text{Br}, \text{I}, \text{OTf}, \text{NTf}_2$, etc.)) have been widely applied as Lewis acids in organic synthesis [40–42], their relatively weak Lewis acidity nonetheless limit their applications. Unlike other group III elements, such as aluminum and boron, trimethylsilyl halide is often employed together with InX_3 as a robust combined Lewis acid catalyst, as observed in various reactions developed by Baba [43,44], Lee [45], Corey [24,46], our group [47–49], and others. As a continuation of our research interest in the application of indium in organic synthesis [47–51], herein we wish to report the first example of the In(III) - TMSBr -catalysed cascade reaction of diarylalkynes with acrylates to access a series of dihydronaphthalene derivatives in a one-pot manner (Scheme 1).



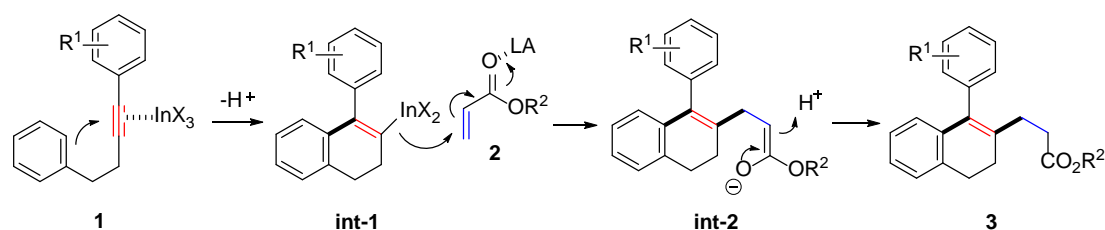
Scheme 1. In(III) - TMSBr -catalysed cascade reaction of diarylalkynes with acrylates for the synthesis of dihydronaphthalene derivatives.

2. Results

2.1. Preliminary Result of In(III) - TMSBr -Catalyzed Cascade Reaction of Diarylalkynes with Acrylates

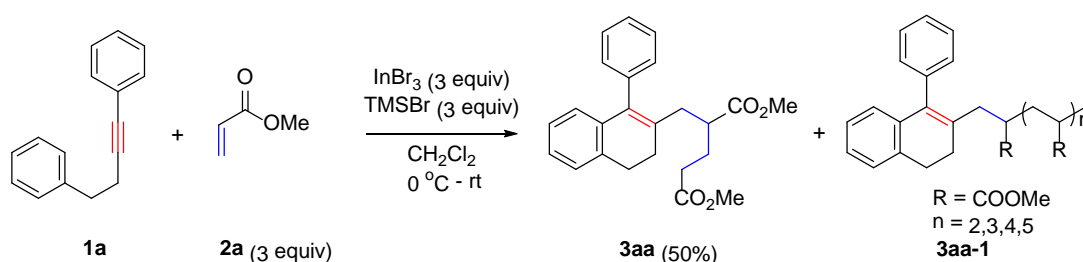
More recently, our group has demonstrated that the combined Lewis acid of In(III) salt and TMSBr could effectively activate acrylate component for the reaction with aryl alkynes [49]. Inspired by this activation mode, we envisaged a cascade reaction between diarylalkyne **1** and acrylate **2** to prepare aryldihydronaphthalene derivatives with this combined Lewis acid via the reaction sequence shown in Scheme 2. Initially, an intramolecular Friedel-Crafts type arylation reaction might occur, to give alkenyl indium species **int-1** which will then undergo nucleophilic attack on the activated acrylate

2 to give the dihydronaphthalene enolate **int-2**. A further enolate protonation will give the final 1,2-dihydronaphthalene derivative **3**.



Scheme 2. Proposed In(III)-TMSBr-catalysed cascade reaction of diarylalkynes with acrylates.

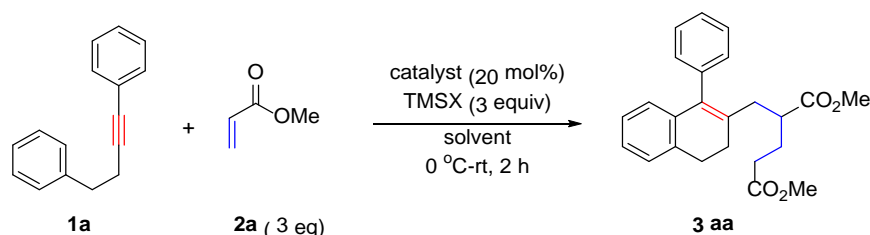
To begin with, the model reaction involving but-1-yne-1,4-diylidibenzene (**1a**) and methyl acrylate (**2a**) were investigated to probe the proposed cascade reaction. In the presence of InBr_3 and TMSBr, a 1,2-dihydronaphthalene derivative **3aa** with two propionate motifs was obtained in moderate yield with trace amounts of intractable mixture of 1,2-dihydronaphthalene derivatives containing more propionate motifs (Scheme 3). Interestingly, no 1,2-dihydronaphthalene derivative with a single propionate motif in original proposal could be obtained.



Scheme 3. Initial results of In(III)-TMSBr-catalysed cascade reaction of but-1-yne-1,4-diylidibenzene (**1a**) with methyl acrylates (**2a**).

2.2. Optimization of In(III)-TMSBr-Catalyzed Cascade Reaction of Diarylalkynes with Acrylates

We subsequently optimized the reaction conditions by using but-1-yne-1,4-diylidibenzene (**1a**) and methyl acrylate (**2a**) as model substrates. The results are summarized in Table 1. At the outset, it was found that both In(III) catalyst and TMSBr were indispensable for the efficient progress of this reaction, because the reaction could not take place in the absence of either of them (entries 2–3). Among the different indium catalysts studied (entries 1 and 4–8), $\text{In}(\text{tfacac})_3$ was found to exhibit the best catalytic activity to afford the desired product **3aa** with 61% yield (entry 7). Other common Lewis acid catalysts (e.g., AlBr_3 and ZnCl_2 , entries 9 and 10) were also screened, which mostly resulted in no product formation. In addition, this reaction was found to proceed only in chlorinated solvents, such as CH_2Cl_2 or 1,2-dichloroethane, with the latter giving a higher yield of 70% (entry 7 vs. entry 11). In comparison, when TMSBr was replaced by TMSCl, the product yield eroded significantly to less than 5% (entry 12). An attempt to decrease the amount of TMSBr or $\text{In}(\text{tfacac})_3$ led to lower yields (entries 13–14). Finally, reducing the stoichiometry of methyl acrylate (**2a**) to only one equivalent resulted in a significantly decreased yield of **3aa**, and 1,2-dihydronaphthalene derivative with a single propionate motif remained absent (entry 15).

Table 1. The In(III)-TMSBr-catalyzed cascade reaction of diarylalkyne **1a** with methyl acrylate (**2a**)^a.

Entry	Catalyst	Solvent	TMSX	Yield (%) ^b
1	InBr ₃	CH ₂ Cl ₂	TMSBr	50
2	InBr ₃	CH ₂ Cl ₂	-	0
3	-	CH ₂ Cl ₂	TMSBr	0 ^c
4	InCl ₃	CH ₂ Cl ₂	TMSBr	14
5	InI ₃	CH ₂ Cl ₂	TMSBr	47
6	In(OTf) ₃	CH ₂ Cl ₂	TMSBr	37
7	In(tfacac) ₃	CH ₂ Cl ₂	TMSBr	61
8	In(acac) ₃	CH ₂ Cl ₂	TMSBr	0
9	AlBr ₃	CH ₂ Cl ₂	TMSBr	0
10	ZnCl ₂	CH ₂ Cl ₂	TMSBr	0
11	In(tfacac) ₃	ClCH ₂ CH ₂ Cl	TMSBr	70
12	In(tfacac) ₃	ClCH ₂ CH ₂ Cl	TMSCl	<5
13	In(tfacac) ₃	ClCH ₂ CH ₂ Cl	TMSBr	60 ^c
14	In(tfacac) ₃	ClCH ₂ CH ₂ Cl	TMSBr	57 ^d
15	In(tfacac) ₃	ClCH ₂ CH ₂ Cl	TMSBr	33 ^e

^a Unless otherwise noted, all reactions were performed with **1a** (0.4 mmol), **2a** (1.2 mmol), catalyst (20 mol %), TMSX (3 equiv), 0 °C-rt, 2 h, N₂. ^b Isolated yields. ^c 2.0 equiv of TMSBr was added. ^d 10 mol % of In(tfacac)₃ was added. ^e 1.0 equiv of **2a** was added.

2.3. Substrate Scope of In(III)-TMSBr-Catalyzed Cascade Reaction of Diarylalkynes with Acrylates

With the optimized reaction conditions in hand (Table 1, entry 11), the generality of diarylalkyne substrate scope of this reaction with respect to methyl acrylate (**2a**) was investigated, and the results are listed in Figure 2a. Various substituted but-1-yne-1,4-diylidibenzene derivatives on the phenyl ring were well suited for this protocol, producing the corresponding product **3** in 47% to 73% yields (**3aa-j**). Expectedly, substrates with *ortho*-substituent on phenyl ring gave respective products in lower yields than those with *meta*- or *para*-substituents (**3ga** vs. **3ha**, **3fa** vs. **3ia**) and no cyclization product could be detected when **1l** was used under the same conditions. Additionally, the incompatibility of 4-phenyl-1-butyne (**1k**) with the current transformation emphasized the importance of the phenyl ring moiety for this reaction. Finally, a substrate with a strong aryl electron-withdrawing substituent (e.g., **1m**) was also unsuitable for this reaction.

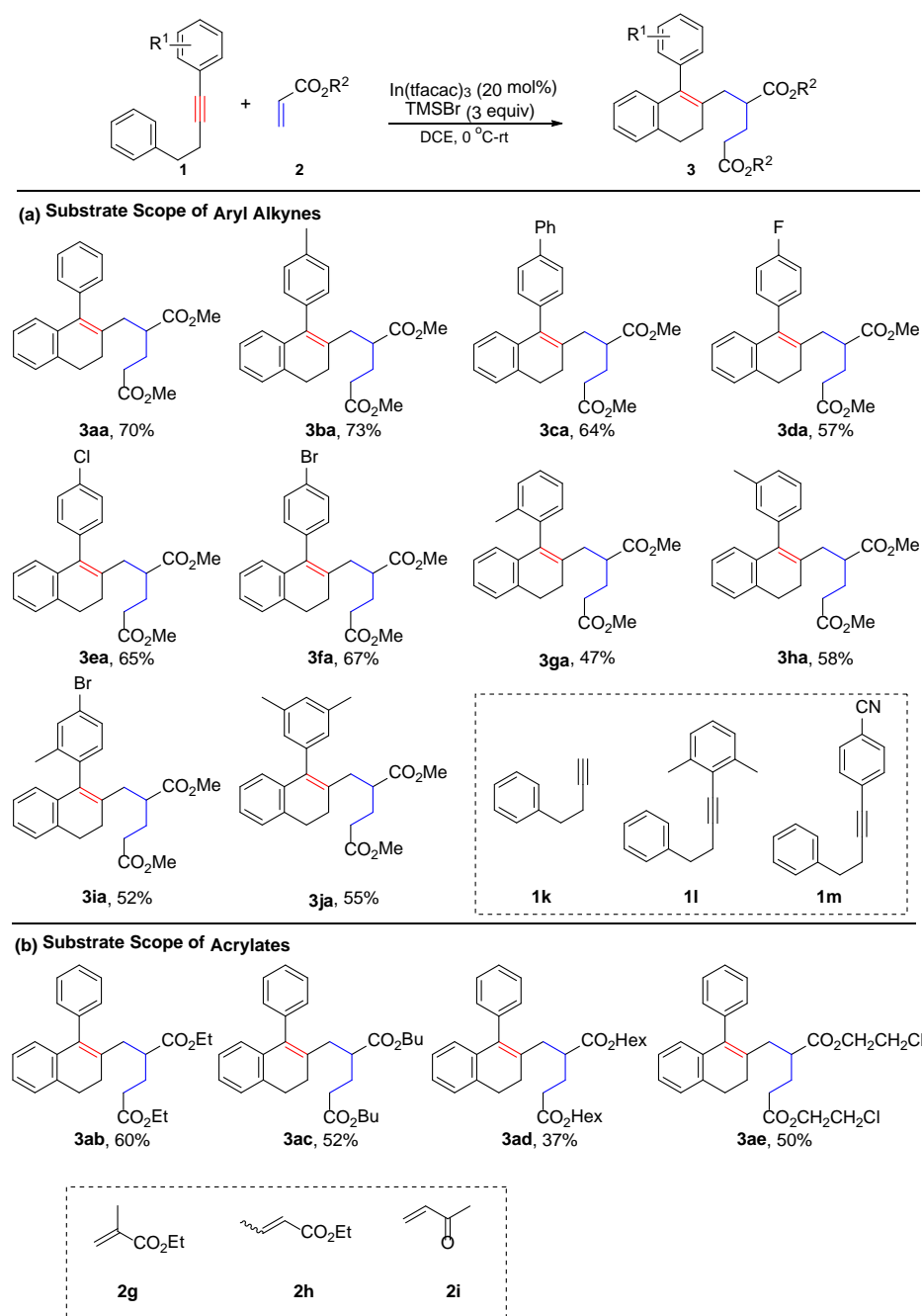
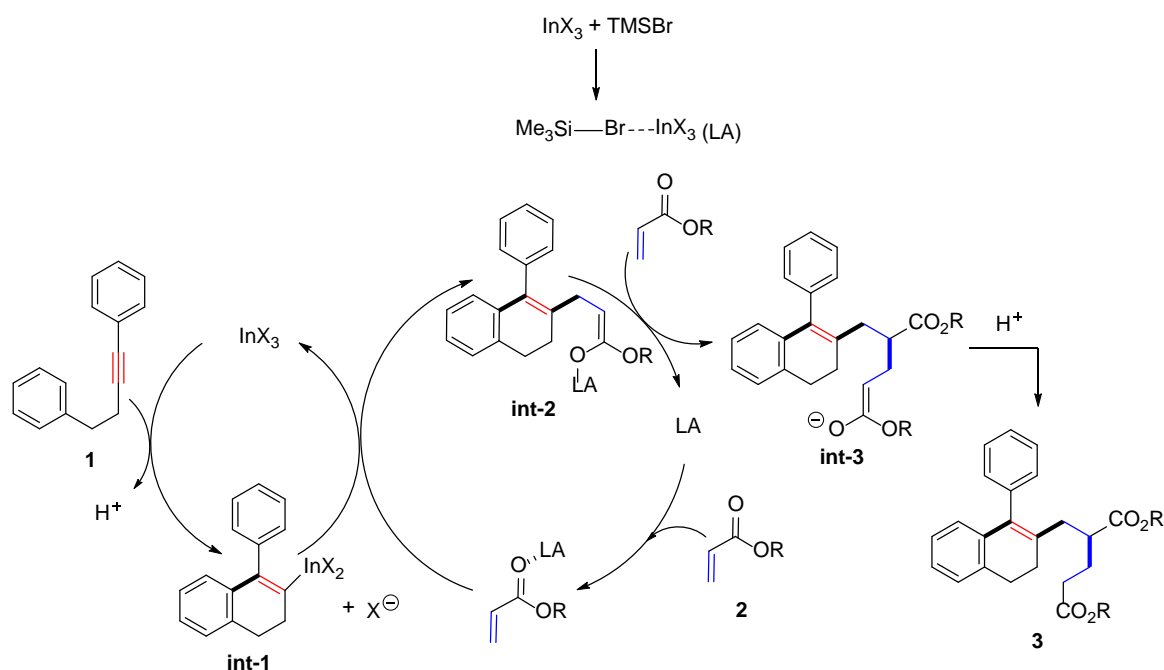


Figure 2. Substrate scope for the In(III)-TMSBr-catalysed cascade reaction of diarylalkyne with acrylates ^{a,b}. ^a Unless otherwise noted, all reactions were performed with **1** (0.4 mmol), **2** (1.2 mmol), In(tfacac)₃ (20 mol %), TMSBr (3 equiv), 0 °C-rt, N₂. ^b Isolated yields.

With but-1-yne-1,4-diylidibenzene (**1a**) as the standard coupling partner, next, the scope of acrylate **2** in the present protocol was examined (Figure 2b). In addition to methyl acrylate (**3a**), acrylates carrying longer *O*-alkyl chains also reacted smoothly to give 1,2-dihydronaphthalene products **3ab–ad**, albeit in relatively low yields (37–60%). Aside from the alkyl chain, reactions of acrylates tethering the chloroethyl group proceeded well to give **3ae** in moderate yield (50%). However, the use of other olefinic substrates, such as ethyl methacrylate (**2g**), ethyl but-2-enoate (**2h**), and but-3-en-2-one (**2i**), could not provide any desired product.

3. Discussion

On the basis of above experimental results and precedent literature reports [38,39,43,44,49], a plausible reaction pathway for this $\text{In}(\text{tfacac})_3$ -TMSBr-catalyzed cascade reaction of diarylalkynes with acrylates was put forward in Scheme 4: $\text{In}(\text{tfacac})_3$ and TMSBr would first form a combined Lewis acid complex (LA) with heightened acidity than either of them solely; second, an intramolecular Friedel-Crafts type arylation reaction takes place to generate an alkenyl indium species **int-1**; this is followed by a nucleophilic attack of **int-1** onto activated acrylate **2**, giving rise to **int-2**, which subsequently attacks another molecule of acrylate to give **int-3**; finally, the **int-3** is quenched by the proton generated from the first step to furnish the final product **3**.



Scheme 4. Plausible reaction mechanism of the $\text{In}(\text{tfacac})_3$ -TMSBr-catalyzed cascade reaction of diarylalkynes with acrylates.

4. Materials and Methods

4.1. General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial sources and used as received. The TMSBr and InBr_3 used was purchased from Sigma-Aldrich, Singapore. The $\text{In}(\text{tfacac})_3$ used was purchased from Strem Chemicals (Newburyport, MA, USA) and its purity is 99%. Thin layer chromatography (TLC) was used to monitor the reaction progress on Merck (Frankfurter Strasse, Darmstadt, Germany) 60 F254 precoated silica gel plates (0.2 mm thickness). TLC spots were visualized by UV-light irradiation on a Spectro line model ENF-24061/F (Spectroline, Westbury, NY, USA) at 254 nm. Another visualization method was staining with a basic solution of potassium permanganate or acidic solution of ceric molybdate, followed by heating. Flash column chromatography was performed using Merck silica gel 60 (Frankfurter Strasse, Darmstadt, Germany) with analytical grade solvents as eluents. $^1\text{H-NMR}$, $^{13}\text{C-NMR}$, and 2D NMR spectra were recorded using Bruker Avance 400 MHz spectrometers (Bruker Corporation, Billerica, MA, USA). Corresponding chemical shifts are reported in ppm downfield relative to TMS and were referenced to the signal of chloroform-d ($\delta = 7.26$, singlet). Multiplicities were given as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, brs = broad singlet, dd = doublet of doublets, and td = triplet of doublets. Values of coupling constants are reported as J in Hz.

4.2. General Procedure for In(III)-TMSBr-Catalysed Cascade Reaction of Diarylalkyne with Acrylates

A dry reaction tube was charged with aryl alkyne **1** (0.4 mmol), acrylate **2** (1.2 mmol), indium(III) trifluoroacetate ($\text{In}(\text{tfacac})_3$, 20 mol %, 0.08 mmol, 45.9 mg) and DCE (1 mL) under N_2 atmosphere at 0 °C. Bromotrimethylsilane (TMSBr, 3 equiv, 1.2 mmol, 183.6 mg) was added and the reaction mixture was stirred at room temperature for 2 h. Upon completion of the reaction as indicated by TLC analysis, the residue was directly purified by flash column chromatography on silica gel (eluent: hexane/ethyl acetate 10:1) to afford the desired product **3**.

4.3. Product Characterization

Dimethyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3aa). Colorless oil, 106.2 mg, 0.281 mmol, 70% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.45–7.41 (m, 2H), 7.38–7.34 (m, 1H), 7.18–7.10 (m, 4H), 7.05–7.02 (m, 1H), 6.58 (d, $J = 7.5$ Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.91 (t, $J = 7.7$ Hz, 2H), 2.66–2.61 (m, 1H), 2.44–2.31 (m, 4H), 2.22–2.18 (m, 2H), 1.79–1.76 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.4, 173.3, 139.2, 136.7, 136.3, 135.2, 134.3, 130.2, 128.4, 127.0, 126.9, 126.4, 126.2, 125.8, 51.6, 51.5, 43.5, 37.0, 31.6, 28.4, 27.4, 26.7.

Dimethyl 2-((1-(p-tolyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ba). Colorless oil, 114.5 mg, 0.292 mmol, 73% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.24–7.22 (m, 2H), 7.17–7.12 (m, 1H), 7.11–7.08 (m, 1H), 7.05–7.01 (m, 3H), 6.60 (d, $J = 7.0$ Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.89 (t, $J = 7.8$ Hz, 2H), 2.66–2.62 (m, 1H), 2.44 (s, 3H), 2.43–2.35 (m, 4H), 2.22–2.18 (m, 2H), 1.79–1.74 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.5, 173.3, 136.8, 136.4, 136.2, 136.0, 135.2, 134.2, 130.1, 129.1, 127.0, 126.3, 126.2, 125.9, 51.6, 51.5, 43.4, 37.0, 31.6, 28.4, 27.4, 26.6, 21.2.

Dimethyl 2-((1-([1,1'-biphenyl]-4-yl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ca). Colorless oil, 116.3 mg, 0.256 mmol, 64% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.71–7.66 (m, 4H), 7.51–7.47 (m, 2H), 7.44–7.37 (m, 2H), 7, 23 (brs, 2H), 7.15–7.11 (m, 1H), 7.08–7.04 (m, 1H), 6.67 (d, $J = 7.6$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.94–2.90 (m, 2H), 2.70–2.66 (m, 1H), 2.50–2.41 (m, 4H), 2.25–2.19 (m, 2H), 1.83–1.77 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.5, 173.3, 140.9, 139.6, 138.2, 136.7, 135.9, 135.2, 134.5, 130.7 ($\times 2$), 128.8, 127.3, 127.1 ($\times 2$), 126.4, 126.2, 125.9, 51.7, 51.6, 43.5, 37.0, 31.6, 28.4, 27.4, 26.6.

Dimethyl 2-((1-(4-fluorophenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3da). Colorless oil, 90.3 mg, 0.228 mmol, 57% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.18–7.16 (m, 1H), 7.14–7.10 (m, 5H), 7.07–7.03 (m, 1H), 6.56–6.54 (d, $J = 7.5$ Hz, 1H), 3.68 (s, 3H), 3.65 (s, 3H), 2.90 (t, $J = 7.9$ Hz, 2H), 2.66–2.61 (m, 1H), 2.44–2.29 (m, 4H), 2.24–2.19 (m, 2H), 1.80–1.73 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.3, 173.3, 161.9 (d, $J_{\text{C-F}} = 243.7$ Hz), 136.5, 135.3, 135.2, 134.9 (d, $J_{\text{C-F}} = 4.0$ Hz), 134.8, 131.8 (d, $J_{\text{C-F}} = 7.8$ Hz), 127.1, 126.5, 126.2, 125.7, 115.3 (d, $J_{\text{C-F}} = 21.1$ Hz), 51.7, 51.6, 43.4, 37.0, 31.5, 28.3, 27.4, 26.7.

Dimethyl 2-((1-(4-chlorophenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ea). Colorless oil, 107.1 mg, 0.26 mmol, 65% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.61–7.59 (m, 2H), 7.22–7.14 (m, 3H), 7.10–7.06 (m, 2H), 6.58 (d, $J = 7.6$ Hz, 1H), 3.72 (s, 3H), 3.69 (s, 3H), 2.93 (t, $J = 7.8$ Hz, 2H), 2.71–2.67 (m, 1H), 2.48–2.41 (m, 4H), 2.37–2.32 (m, 2H), 1.83–1.77 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.3, 173.2, 138.1, 136.2, 135.2, 135.1, 134.8, 132.0, 131.6, 127.1, 126.6, 126.3, 125.7, 121.0, 51.7, 51.6, 43.3, 37.0, 31.5, 28.3, 27.3, 26.7.

Dimethyl 2-((1-(4-bromophenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3fa). Colorless oil, 122.2 mg, 0.268 mmol, 67% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.41–7.39 (m, 2H), 7.17–7.02 (m, 5H), 6.54 (d, $J = 7.6$ Hz, 1H), 3.67 (s, 3H), 3.65 (s, 3H), 2.89 (t, $J = 7.9$ Hz, 2H), 2.68–2.61 (m, 1H), 2.43–2.26 (m, 4H), 2.24–2.19 (m, 2H), 1.79–1.75 (m, 2H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3): δ (ppm) 175.3, 173.2, 137.6, 136.3, 135.1, 134.9, 132.9, 131.7, 128.7 ($\times 2$), 127.1, 126.6, 126.3, 125.7, 51.7, 51.6, 43.3, 37.0, 31.5, 28.3, 27.3, 26.7.

Dimethyl 2-((1-(o-tolyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ga). Colorless oil, 73.7 mg, 0.188 mmol, 47% yield. $^1\text{H-NMR}$ (400 MHz, CDCl_3): δ (ppm) 7.28–7.22 (m, 3H), 7.18–7.17 (m, 1H), 7.12–7.08 (m, 2H), 7.03–7.00 (m, 1H), 6.49 (d, $J = 7.4$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.92–2.90 (m, 2H),

2.64–2.61 (m, 1H), 2.46–2.29 (m, 4H), 2.19–2.15 (m, 2H), 2.05 (s, 3H), 1.79–1.72 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.7, 173.3, 138.3, 136.8, 135.8, 135.4, 135.1, 134.2, 130.6, 130.4, 130.1, 127.3, 127.0, 126.4, 125.8, 125.1, 51.6, 51.5, 43.3, 36.8, 31.5, 28.4, 27.1, 26.5, 19.3.

*Dimethyl 2-((1-(*m*-tolyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ha)*. Colorless oil, 90.9 mg, 0.232 mmol, 58% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.32–7.30 (m, 1H), 7.17–7.15 (m, 2H), 7.12–7.08 (m, 1H), 7.05–7.01 (m, 1H), 6.97–6.93 (m, 2H), 6.59 (d, $J = 7.5$ Hz, 1H), 3.66 (s, 3H), 3.65 (s, 3H), 2.91–2.87 (m, 2H), 2.65–2.62 (m, 1H), 2.43–2.34 (m, 4H), 2.39 (s, 3H), 2.22–2.17 (m, 2H), 1.79–1.76 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.6, 173.3, 139.0, 136.7, 136.3, 135.1, 134.1, 130.8, 128.2, 127.6 ($\times 2$), 127.2, 127.0, 126.3, 126.2, 125.9, 51.6, 51.5, 43.4, 36.9, 31.6, 28.4, 27.3, 26.6, 21.5.

Dimethyl 2-((1-(4-bromo-2-methylphenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ia). Colorless oil, 97.8 mg, 0.208 mmol, 52% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.44 (s, 1H), 7.38 (d, $J = 8.1$ Hz, 1H), 7.17 (d, $J = 7.1$ Hz, 1H), 7.13–7.10 (m, 1H), 7.04–7.00 (m, 1H), 6.97 (d, $J = 8.1$ Hz, 1H), 6.45 (d, $J = 7.4$ Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 2.92–2.88 (m, 2H), 2.64–2.62 (m, 1H), 2.46–2.34 (m, 4H), 2.22–2.11 (m, 2H), 2.03 (s, 3H), 1.80–1.70 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.5, 173.2, 139.4, 137.3, 135.3, 135.1, 134.8, 134.3, 133.0, 132.1, 129.0, 127.2, 126.6, 126.4, 124.9, 121.1, 51.7, 51.6, 43.2, 36.9, 31.5, 28.3 ($\times 2$), 27.0, 26.5.

Dimethyl 2-((1-(3,5-dimethylphenyl)-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ja). Colorless oil, 89.4 mg, 0.220 mmol, 55% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.17–7.15 (m, 1H), 7.12–7.08 (m, 1H), 7.06–7.02 (m, 1H), 6.98 (s, 1H), 6.78 (s, 1H), 6.73 (s, 1H), 6.62 (d, $J = 7.5$ Hz, 1H), 3.67 (s, 3H), 3.66 (s, 3H), 2.91–2.86 (m, 2H), 2.66–2.61 (m, 1H), 2.44–2.37 (m, 4H), 2.35 (s, 6H), 2.24–2.14 (m, 2H), 1.81–1.75 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.7, 173.3, 139.0, 137.7, 136.8, 136.4, 135.1, 133.9, 128.4, 127.9, 126.9, 126.2, 126.1, 125.9, 51.6, 51.5, 43.5, 37.0, 31.6, 28.4, 27.3, 26.6, 21.3.

Diethyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ab). Colorless oil, 97.5 mg, 0.240 mmol, 60% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.44–7.40 (m, 2H), 7.37–7.33 (m, 1H), 7.18–7.16 (m, 3H), 7.12–7.09 (m, 1H), 7.05–7.01 (m, 1H), 6.58 (d, $J = 7.6$ Hz, 1H), 4.17–4.08 (m, 4H), 2.90 (t, $J = 8.3$ Hz, 1H), 2.65–2.58 (m, 1H), 2.43–2.30 (m, 4H), 2.21–2.14 (m, 2H), 1.79–1.74 (m, 2H), 1.29–1.27 (m, 6H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.1, 172.9, 139.2, 136.7, 136.2, 135.2, 134.5, 130.3, 128.4, 127.0, 126.8, 126.3, 126.2, 125.8, 60.4, 60.3, 43.5, 37.0, 31.8, 28.4, 27.4, 26.8, 14.2.

Dibutyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ac). Colorless oil, 96.2 mg, 0.208 mmol, 52% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.44–7.40 (m, 2H), 7.37–7.33 (m, 1H), 7.17–7.09 (m, 4H), 7.05–7.01 (m, 1H), 6.58 (d, $J = 7.0$ Hz, 1H), 4.07–4.03 (m, 4H), 2.91 (t, $J = 8.1$ Hz, 2H), 2.66–2.57 (m, 1H), 2.47–2.30 (m, 4H), 2.21–2.12 (m, 2H), 1.81–1.73 (m, 2H), 1.65–1.54 (m, 4H), 1.42–1.29 (m, 4H), 0.97–0.89 (m, 6H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.1, 173.0, 139.2, 136.7, 136.2, 135.1, 134.4, 130.3, 128.4, 127.0, 126.8, 126.3, 126.2, 125.8, 64.4, 64.3, 43.5, 37.0, 31.9, 30.7, 30.6, 28.4, 27.4, 26.8, 19.1 ($\times 2$), 13.7, 13.6.

Dihexyl 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ad). Colorless oil, 66.1 mg, 0.148 mmol, 37% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.44–7.40 (m, 2H), 7.37–7.35 (m, 1H), 7.17–7.16 (m, 3H), 7.12–7.08 (m, 1H), 7.05–7.01 (m, 1H), 6.57 (d, $J = 7.5$ Hz, 1H), 4.09–4.02 (m, 4H), 2.92–2.88 (m, 2H), 2.64–2.62 (m, 1H), 2.45–2.32 (m, 4H), 2.22–2.16 (m, 2H), 1.79–1.71 (m, 2H), 1.65–1.56 (m, 6H), 1.32–1.28 (m, 10H), 0.93–0.87 (m, 6H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 175.1, 173.0, 139.2, 136.7, 136.2, 135.1, 134.4, 130.3, 128.4, 127.0, 126.8, 126.3, 126.2, 125.8, 64.7, 64.6, 43.5, 37.0, 31.8, 31.4, 31.3, 28.6, 28.5, 28.4, 27.4, 26.7, 25.6 ($\times 2$), 22.5, 22.4, 14.0 ($\times 2$).

Bis(2-chloroethyl) 2-((1-phenyl-3,4-dihydronaphthalen-2-yl)methyl)pentanedioate (3ae). Colorless oil, 89.2 mg, 0.200 mmol, 50% yield. ^1H -NMR (400 MHz, CDCl_3): δ (ppm) 7.45–7.43 (m, 2H), 7.38–7.36 (m, 1H), 7.18–7.10 (m, 4H), 7.06–7.02 (m, 1H), 6.58 (d, $J = 7.6$ Hz, 1H), 4.35–4.29 (m, 4H), 3.70–3.63 (m, 4H), 2.94–2.89 (m, 2H), 2.73–2.67 (m, 1H), 2.50–2.33 (m, 4H), 2.31–2.26 (m, 2H), 1.84–1.79 (m, 2H); ^{13}C -NMR (100 MHz, CDCl_3): δ (ppm) 174.6, 172.4, 139.1, 136.6, 136.4, 135.1, 134.0, 130.2, 128.4, 127.0, 126.9, 126.4, 126.2, 125.9, 64.0, 63.9, 43.2, 41.5, 41.4, 36.9, 31.5, 28.4, 27.4, 26.4.

Product characterization data, and ^1H - and ^{13}C -NMR spectra are available from supplementary material.

5. Conclusions

In a nutshell, we described an efficient method to assemble aryldihydronaphthalene derivatives via the cascade reaction of diarylalkynes with acrylates employing the catalysis of a combined Lewis acid system formed from In(III) salt and TMSBr. Both indium(III) and TMSBr are indispensable for the efficient progress of the reaction. In most cases, the reaction proceeded efficiently to afford the corresponding aryldihydronaphthalene derivatives in moderate to good yields. With reference to current experimental observations and literature reports, a possible mechanistic pathway for this reaction was also provided.

Supplementary Materials: Supplementary materials are available online: general experimental procedures, product characterization data, and ^1H - and ^{13}C -NMR spectra.

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Sample Availability: Samples of the compounds **3aa–ja** and **3ab–ae** are available from the authors.



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