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# Lithium Diisopropylamide-Mediated Carbolithiation Reactions of Vinylidenecyclopropanes and Further Transformations of the Adducts

**Jian-Mei Lu[a, b] and Min Shi*[a]**

**Abstract:** Highly stereo- and regioselective carbolithiation reactions of vinylidenecyclopropanes **1** were realized by treatment with lithium diisopropylamide (LDA) in THF and by quenching with various electrophiles such as aryl or aliphatic aldehydes, ketones, enones or propargyl bromide. Transformation of these adducts such as vinylcyclopropenes and allenols was also performed in the presence of Lewis acid or Brønsted acid to provide the fused and conjugated aromatic products in good to high yields under mild conditions.

**Keywords:** allenols · Brønsted acids · carbolithiation reactions · electrophilic addition · Lewis acids

## Introduction

Organolithium chemistry is of unquestionable importance in organic synthesis and is no longer limited to academia. A comprehensive survey of scaled procedures used by Pfizer during the last twenty years shows that 68% of C–C bond formations are carbanion-based.[1] Lithium diisopropylamide (LDA) has played a profound role in organolithium chemistry, serving as the base of choice for a broad range of deprotonation reactions, which daily affect synthetic chemists.[2] LDA is also an ideal template for studying organolithium reactivity.[3a] It is well known that the cyclopropylcarbinyl–homoallyl rearrangement operates in one direction, providing the ring-opened product exclusively. This holds not only for cyclopropylmethyl cations[3b] and radicals[3c] but also for simple organometallic species such as cyclopropylmethylmagnesium bromide[3d] or cyclopropylmethyllithium.[3e] Therefore, it was envisioned that LDA-mediated cyclopropylmethyl chemistry would provide an interesting and efficient method for the construction of C–C bond in novel organic compounds.

Vinylidenecyclopropanes[4] are one of the most remarkable organic compounds known. They have an allene moiety connected by a cyclopropane ring and yet they are thermally stable and reactive substances. Thermal and photochemical skeletal conversions of vinylidenecyclopropanes have attracted much attention from mechanistic and synthetic viewpoints since the cyclopropanes can gain additional driving force by the relief of angular strain.[5] Numerous palladium-catalyzed[6] as well as Lewis acid- or Brønsted acid-catalyzed/mediated[7] reactions of vinylidenecyclopropanes have also been disclosed. Recently, we have been investigating the Lewis base- or Brønsted base-catalyzed/mediated reactions of vinylidenecyclopropanes. For example, we previously reported the LDA-mediated selective carbolithiation reactions of vinylidenecyclopropanes **1** with aldehydes **2**, ketones **3** and enones **4** to give vinylcyclopropenes **5**, allenols **6** and 1,3-enynes **7** in good yields (Scheme 1).[8] During our ongoing investigation, we found that when $R^4$ of vinylidenecyclopropanes **1** was a methyl substituent, the carbolithiation reaction with aldehydes gave triene derivatives instead of vinylcyclopropenes. Encouraged by this interesting finding, we further comprehensively investigated the LDA-mediated carbolithiation reactions of vinylidenecyclopropanes with aldehydes, *N*-tosyl imines, enones and propargyl bromide as the electrophiles in detail as well as the further transformations of the adducts. Herein, we wish to disclose these results in this full paper.

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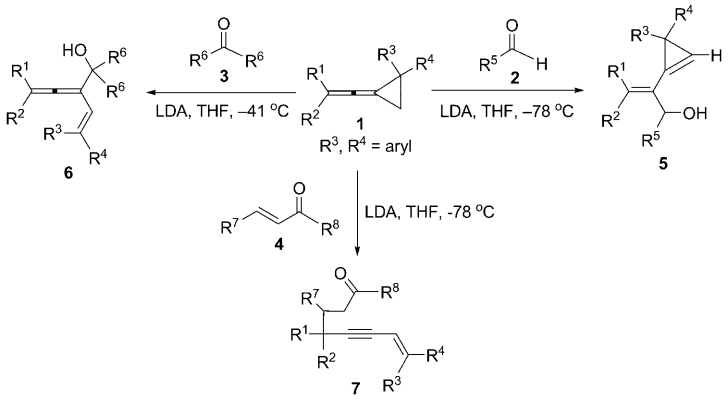
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.200900068: Spectroscopic data of all new compounds shown in Tables 1–8, the detailed descriptions of experimental procedures and X-ray data for compound **11b**, *anti*-**21a** and **22a** are included.



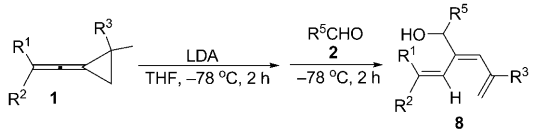

Scheme 1. LDA-mediated carbolithiation reactions of vinylidenecyclopropanes **1** ($R^3$, $R^4$ = aryl).

## Results and Discussion

**LDA-mediated carbolithiation reactions of vinylidenecyclopropanes 1 with aldehydes 2**: Initial examination revealed that when vinylidenecyclopropane **1a** ($R^1=R^2=R^3=C_6H_5$, $R^4$ = Me) was used as the substrate, the LDA-mediated carbolithiation reaction with benzaldehyde **2a** gave triene derivative **8a** in 94% yield rather than the expected vinylcyclopropene product **5** (Table 1, entry 1). Its structure was determined by $^1H$, $^{13}C$ NMR spectroscopic data, and HRMS (see Supporting Information). We next examined several starting materials **1** with various aldehydes **2** in order to evaluate the scope and limitations of this interesting carbolithiation reaction. As can be seen from Table 1, the corresponding trienes **8** were obtained in moderate to good yields in most cases (Table 1). In the reactions with arylaldehydes **2a–f**, the corresponding products **8a–f** were obtained in good yields whether they have electron-donating or -withdrawing substituents on the benzene ring (Table 1, entries 1–6, 10–14). As for 1-naphthaldehyde (**2g**) and 2-furaldehyde (**2h**), the corresponding trienes **8g** and **8h** were obtained in 96 and 77% yields, respectively (Table 1, entries 7 and 8). For α,β-unsaturated aldehyde **2i**, the corresponding 1,2-addition product **8i** was formed similarly as the sole product in 23% yield (Table 1, entry 9). Moreover, in the reactions with aliphatic aldehydes **2j** and **2k**, trienes **8o** and **8p** were obtained in 33 and 38% yield, along with 1,3-enynes **9a** and **9b** in 23 and 22% yields, respectively, suggesting that the steric and electronic nature of aldehyde can significantly affect the reaction outcome (Scheme 2).

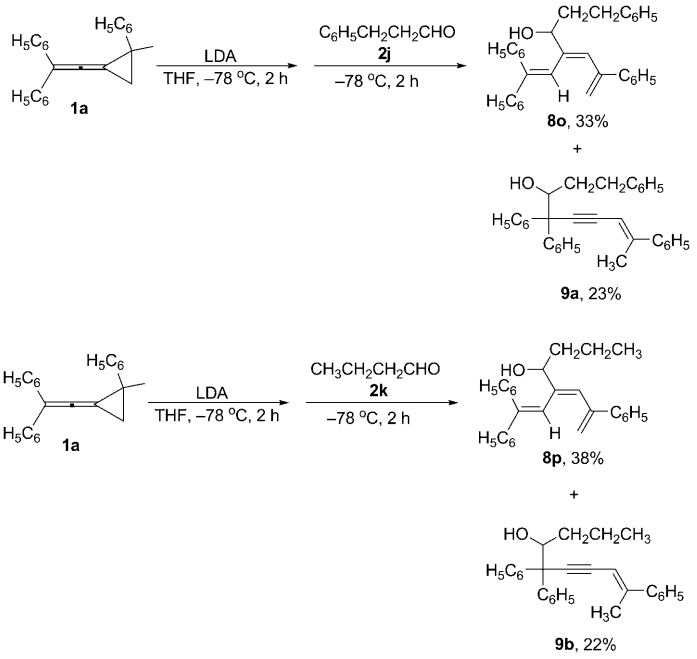
**LDA-mediated carbolithiation reactions of vinylidenecyclopropane 1a with *N*-Ts imines 10**: In order to clarify the structure and configuration of trienes **8**, *N*-Ts imines **10a–c** were used as electrophiles. It was found that the corresponding trienes **11a–c** were formed in moderate to good yields under identical conditions (Table 2, entries 1–3). The structure and the configuration of **11b** were unambiguously determined by X-ray diffraction and its CIF data are presented in the Supporting Information (Figure 1).[9]

Table 1. Reactions of various aldehydes **2** with carbanions derived from vinylidenecyclopropanes **1** ($R^4$ = Me) and LDA.[a]




| | **1** ($R^1/R^2/R^3$) | **2** ($R^5$) | Yield [%][b] |
|---|---|---|---|
| 1 | **1a** ($C_6H_5/C_6H_5/C_6H_5$) | **2a** ($C_6H_5$) | **8a**, 94 |
| 2 | **1a** | **2b** (*p*-$BrC_6H_4$) | **8b**, 88 |
| 3 | **1a** | **2c** (*p*-$ClC_6H_4$) | **8c**, 86 |
| 4 | **1a** | **2d** (*p*-$MeC_6H_4$) | **8d**, 99 |
| 5 | **1a** | **2e** (*m*-$MeC_6H_4$) | **8e**, 86 |
| 6 | **1a** | **2f** (*o*-$BrC_6H_4$) | **8f**, 82 |
| 7 | **1a** | **2g** (1-$C_{10}H_7$) | **8g**, 96 |
| 8 | **1a** | **2h** (2-$C_4H_3O$) | **8h**, 77 |
| 9 | **1a** | **2i** [(*E*)-$C_6H_5CH{=}CH$] | **8i**, 23 |
| 10 | **1b** (*p*-$ClC_6H_4/p$-$ClC_6H_4/p$-$BrC_6H_4$) | **2a** | **8j**, 89 |
| 11 | **1c** (*p*-$MeC_6H_4/p$-$MeC_6H_4/C_6H_5$) | **2a** | **8k**, 81 |
| 12 | **1d** (*p*-$FC_6H_4/p$-$FC_6H_4/C_6H_5$) | **2a** | **8l**, 91 |
| 13 | **1e** ($C_6H_5/C_6H_5/p$-$ClC_6H_4$) | **2a** | **8m**, 85 |
| 14 | **1f** ($C_6H_5/C_6H_5/p$-$MeC_6H_4$) | **2a** | **8n**, 90 |

[a] After vinylidenecyclopropanes **1** (0.2 mmol) were lithiated by LDA (0.4 mmol) at −78 °C for 2 h, aldehydes **2** (0.3 mmol) were added. Then, the reactions were quenched by addition of the aqueous solution of ammonium chloride after 2 h. [b] Yield of isolated products.




Scheme 2. Reactions of vinylidenecyclopropane **1a** with aliphatic aldehydes **2j** and **2k**.

**LDA-mediated carbolithiation reactions of vinylidenecyclopropane 1a with enones 4**: When the carbolithiation reaction was carried out using enones as the electrophiles, the corresponding 1,3-enyne derivatives **12** were obtained exclusively in moderate to good yields (Table 3). For example, as

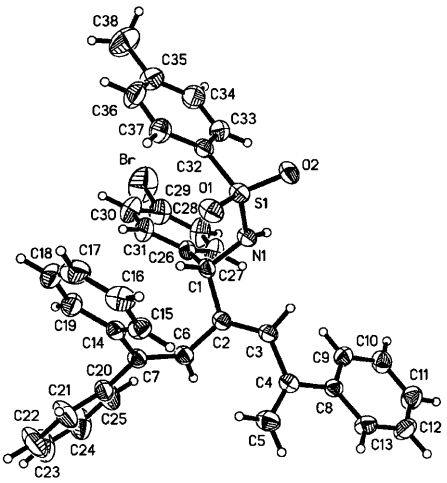
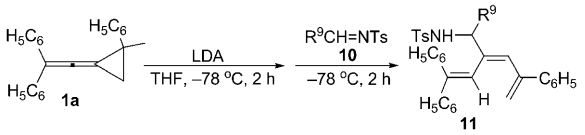



Figure 1. ORTEP drawing of compound **11b**.

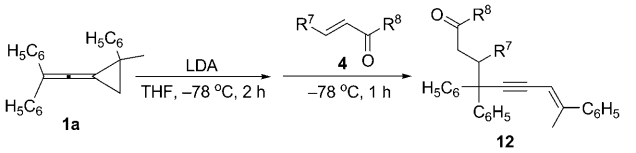
Table 2. Reactions of various imines **10** with carbanion derived from vinylidenecyclopropane **1a** and LDA.




| Entry[a] | **10** ($R^9$) | Yield [%][b] |
|---|---|---|
| 1 | **10a** ($C_6H_5$) | **11a**, 83 |
| 2 | **10b** (*p*-$BrC_6H_4$) | **11b**, 64 |
| 3 | **10c** (*p*-$MeC_6H_4$) | **11c**, 77 |

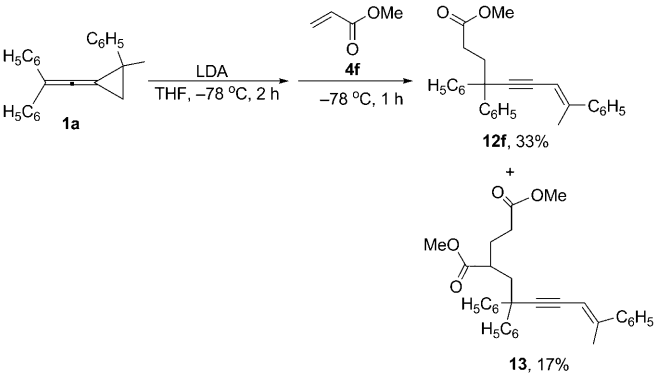
[a] After vinylidenecyclopropane **1a** (0.2 mmol) was lithiated by LDA (0.4 mmol) at −78 °C for 2 h, imines **10** (0.3 mmol) were added. Then, the reactions were quenched by addition of the aqueous solution of ammonium chloride after 2 h. [b] Yield of isolated products.

Table 3. Reactions of various enones **4** with carbanions derived from vinylidenecyclopropane **1a** and LDA.




| Entry[a] | **4** ($R^7$/$R^8$) | Yield [%][b] |
|---|---|---|
| 1 | **4a** (H/Me) | **12a**, 65 |
| 2 | **4b** (H/Et) | **12b**, 63 |
| 3 | **4c** [–$(CH_2)_2$–] | **12c**, 92 |
| 4 | **4d** [–$(CH_2)_3$–] | **12d**, 99 |
| 5 | **4e** (Me/Me) | **12e**, 88 |

[a] After vinylidenecyclopropane **1a** (0.2 mmol) was lithiated by LDA (0.4 mmol) at −78 °C for 2 h, enones **4** (0.3 mmol) were added. Then, the reactions were quenched by addition of the aqueous solution of ammonium chloride after 1 h. [b] Yield of isolated products.




Scheme 3. Reactions of vinylidenecyclopropane **1a** with methyl acrylate **4f**.

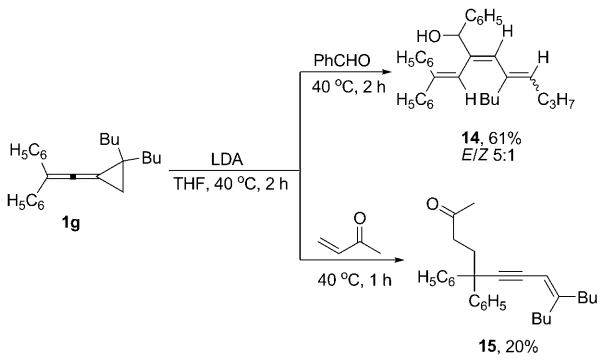
for methyl vinyl ketone (**4a**) and ethyl vinyl ketone (**4b**), the corresponding 1,3-enyne derivatives **12a** and **12b** were obtained in 65 and 63% yield, respectively (Table 3, entries 1 and 2). When 2-cyclopenten-1-one (**4c**) and 2-cyclohexen-1-one (**4d**) were used as the electrophiles, the corresponding 1,3-enyne derivatives **12c** and **12d** were formed in 92 and 99% yield, respectively (Table 3, entries 3 and 4). Using β-methyl substituted enone **4e** as the electrophile, this carbolithiation reaction could also proceed smoothly to afford the corresponding product **12e** in 88% yield (Table 3, entry 5). Surprisingly, no product was obtained when phenyl vinyl ketone was used as an electrophile, perhaps due to that the adjacent phenyl group reduced the nucleophilicity of the olefinic moiety. When methyl acrylate (**4f**) was used as an electrophile, 1,3-enyne derivative **12f** was obtained in 33% yield along with compound **13**, consisting of one molecule of **1a** and two molecules of **4a**, in 17% yield (Scheme 3).

**LDA-mediated carbolithiation reactions of vinylidenecyclopropane 1g with benzaldehyde and methyl vinyl ketone**: As for vinylidenecyclopropane **1g** ($R^3=R^4=Bu$), the reaction temperature of the lithiation should be increased to 40 °C, and when benzaldehyde and methyl vinyl ketone were used as the substrates, triene derivative **14** (*E*/*Z* 5:1) (see the details in the Supporting Information) and 1,3-enyne derivative **15** were obtained in 61 and 20% yield, respectively (Scheme 4).

**LDA-mediated carbolithiation reactions of vinylidenecyclopropanes 1 with propargyl bromide 16**: When propargyl bromide **16** was used as an electrophile in this reaction, hept-1-ene-3,6-diyne derivatives **17** were obtained in good to high yields under the standard conditions (Table 4, entries 1–9).

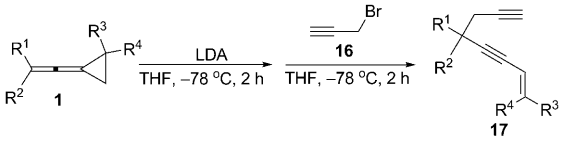
**LDA-mediated carbolithiation reaction of vinylidenecyclopropane 1a with benzophenone 3a**: Carbolithiation reaction of vinylidenecyclopropane **1a** with benzophenone **3a** was also examined under identical reaction conditions and it was found that both of the allenol derivative **18** and triene derivative **19** were obtained in 56% total yield (Scheme 5). Inter-




Scheme 4. Cabolithiation reactions of vinylidenecyclopropane **1g**.

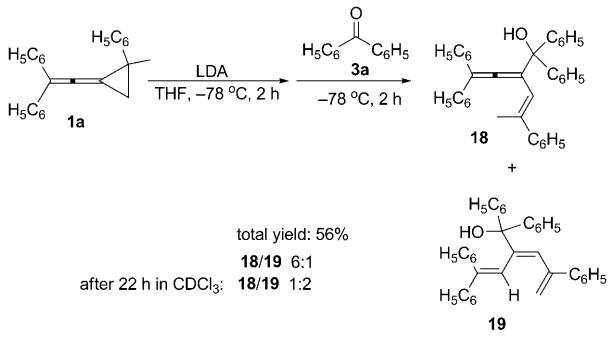
Table 4. Reactions of propargyl bromide **16** with carbanions derived from vinylidenecyclopropanes **1** and LDA.




| Entry[a] | **1** ($R^1/R^2/R^3/R^4$) | Yield [%][b] |
|---|---|---|
| 1 | **1a** ($C_6H_5/C_6H_5/C_6H_5$/Me) | **17a**, 94 |
| 2 | **1b** (*p*-$ClC_6H_4$/*p*-$ClC_6H_4$/*p*-$BrC_6H_4$/Me) | **17b**, 75 |
| 3 | **1c** (*p*-$MeC_6H_4$/*p*-$MeC_6H_4$/$C_6H_5$/Me) | **17c**, 79 |
| 4 | **1e** ($C_6H_5/C_6H_5$/*p*-$ClC_6H_4$/Me) | **17d**, 74 |
| 5 | **1f** ($C_6H_5/C_6H_5$/*p*-$MeC_6H_4$/Me) | **17e**, 90 |
| 6 | **1h** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5$) | **17f**, 75 |
| 7 | **1i** (*p*-$ClC_6H_4$/*p*-$ClC_6H_4/C_6H_5/C_6H_5$) | **17g**, 82 |
| 8 | **1j** ($C_6H_5/C_6H_5$/*p*-$ClC_6H_4$/*p*-$ClC_6H_4$) | **17h**, 75 |
| 9 | **1k** ($C_6H_5/C_6H_5$/*p*-$MeC_6H_4$/*p*-$MeC_6H_4$) | **17i**, 81 |

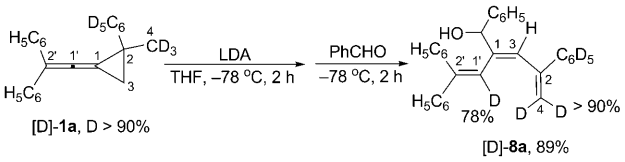
[a] After vinylidenecyclopropanes **1** (0.2 mmol) were lithiated by LDA (0.4 mmol) at −78 °C for 2 h, **16** (0.3 mmol) was added. Then, the reactions were quenched by addition of the aqueous solution of ammonium chloride after 2 h. [b] Yield of isolated products.

estingly, it was also observed that part of allenol derivative **18** can be transformed into triene derivative **19** in $CDCl_3$ solution after 22 h (see the details in the Supporting information).[10]



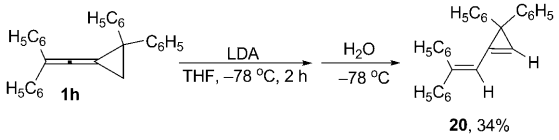

Scheme 5. Cabolithiation reaction of vinylidenecyclopropane **1a** with benzophenone **3a**.

**Proposed mechanism for the carbolithiation reactions**: In order to clarify the mechanism of this reaction, the carbolithiation reaction of [D]-**1a** with benzaldehyde **2a** was carried out under identical conditions (Scheme 6). Based on the observed $^1H$ NMR spectroscopic data, we confirmed that besides the olefinic protons of $C_4$ (D content > 90%), deuterium incorporation also occurred at the olefinic proton of $C_{1'}$ (D content = 78%). On the basis of the deuterium labeling experiment, it is clear that a [1,5]-H shift is concerned in the carbolithiation reaction.[11]




Scheme 6. Deuterium labeling experiment for reaction of **1a–d** with benzaldehyde **2a**.

Another control experiment was also carried out by lithiation of vinylidenecyclopropane **1h** with LDA and then by quenching with the addition of $H_2O$. It was found that vinylcyclopropene derivative **20**[7c] can be obtained in 34% yield, suggesting that the initial lithiation takes place at the cyclopropane along with a [1,3]-Li shift process (Scheme 7).

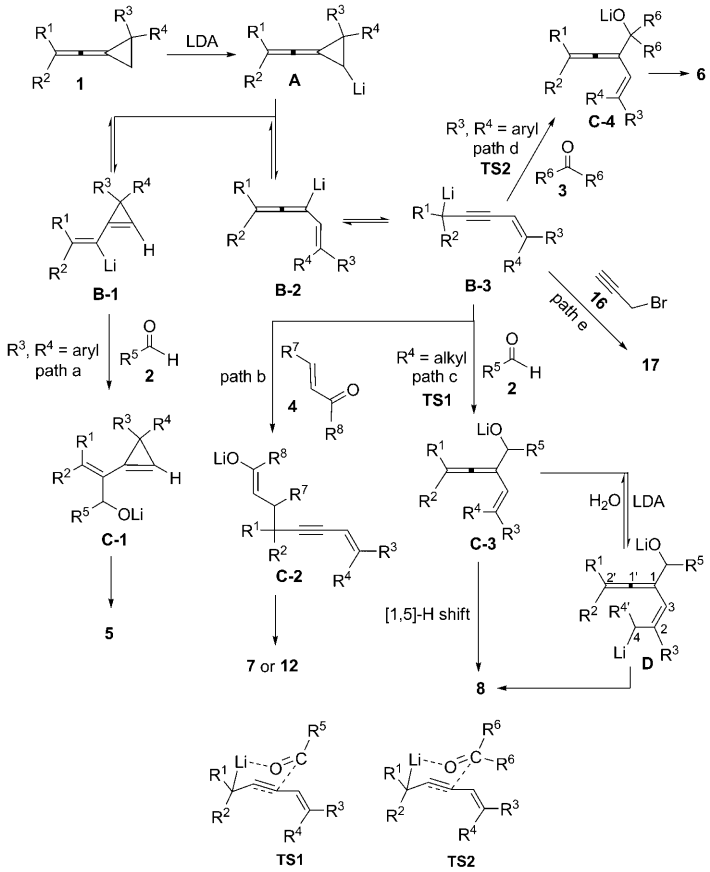



Scheme 7. Lithiation of vinylidenecyclopropane **1h**, which was then quenched with $H_2O$.

A plausible mechanism for the carbolithiation reactions is outlined in Scheme 8 on the basis of above deuterium labeling and control experiments. Initially, the lithiation of cyclopropyl ring of vinylidenecyclopropanes **1** gives the corresponding cyclopropyl carbanion intermediate **A** by treatment with LDA.[12] Intermediate **A** can be transformed to intermediates **B-1**, **B-2** and **B-3** and there is an equilibrium between all these anionic species as **A**, **B-1**, **B-2**, **B-3**.[13] When $R^3$ and $R^4$ are aryl groups and aldehydes **2** are used as electrophiles, vinylcyclopropene derivatives **5** are formed through intermediate **C-1** (Scheme 8, path a). When ketones **3** are used as electrophiles, allenol derivatives **6** are obtained by the reaction of intermediate **B-3** with **3** through intermediate **C-4** and it is conceivable that a six-membered transition state is concerned in the reaction (TS2) (Scheme 8, path d). The different reactivity between aldehydes and ketones may be due to the steric effect of the two electrophiles. When $R^4$ is alkyl group and aldehydes **2** are used as electrophiles, intermediate **C-3** is formed by the reaction of

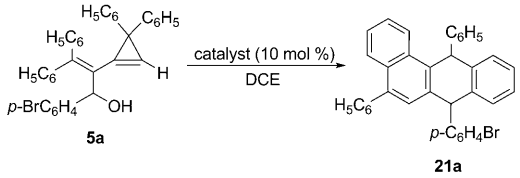
intermediate **B-3** with **2** through a six-membered transition state TS1, which undergoes a [1,5]-H shift to produce the triene derivatives **8**.[11] On the other hand, intermediate **D** can be formed by lithiation of intermediate **C-3** ($R^4$ is alkyl group), which undergoes a [1,5]-lithium shift to give products **8**. During the two possible pathways, the ambient water can take part in the process to partially replace the lithium with proton. This is the reason why the deuterium content in $C_{1'}$ is somewhat lower than that of $C_4$ (Scheme 8, path c). When enones are used as electrophiles, intermediate **C-2** is formed by reaction of intermediate **B-3** with enones and subsequently 1,3-enyne derivatives **7** or **12** is obtained, presumably due to that the lithiated $sp^3$ carboanion prefers such Michael addition (Scheme 8, path b). As for propargyl bromide, products **17** are formed by $S_N2$ reaction with intermediate **B-3** simply (Scheme 8, path e).




Scheme 8. Proposed mechanism for the carbolithiation reactions.

**$Au^I$-catalyzed transformations of vinylcyclopropenes 5**: Interestingly, it was found that vinylcyclopropenes **5** can be transformed to compounds **21** in $CDCl_3$ solution as mixtures of *syn*- and *anti*-isomers, perhaps due to that the weak acidity of $CDCl_3$ can catalyze this transformation. Then we turned our interest to the Lewis acid catalyzed reactions of vinylcyclopropenes **5**. Initial studies using **5a** as the substrate were aimed at finding the optimal reaction conditions for the Lewis acid catalyzed reaction. As can be seen from Table 5, using [AuCl($PPh_3$)]/AgOTf as the catalyst in 1,2-dichloroethane (DCE) at 60 °C, **21a** was formed in 99 % yield as mixtures of *syn*- and *anti*-isomers (Table 5, entry 5). The

Table 5. Optimization for the transformation of **5a** to **21a** in the presence of Lewis acids.




| Entry[a] | Catalyst | $T$ [°C] | $t$ [h] | Yield [%][b,c] |
|---|---|---|---|---|
| 1 | $Sn(OTf)_2$ | 60 | 1.5 | 84 (4.3:1) |
| 2 | $Sc(OTf)_3$ | 60 | 1.5 | 93 (4.2:1) |
| 3 | $Yb(OTf)_3$ | 60 | 8 | NR |
| 4 | $BF_3{\cdot}OEt_2$ | 60 | 1.5 | 93 (3.3:1) |
| 5 | [AuCl($PPh_3$)]/AgOTf | 60 | 1.5 | 99 (3.3:1) |
| 6 | [AuCl($PPh_3$)]/AgOTf | RT | 29 | NR |
| 7 | AgOTf | 60 | 1.5 | 93 (3.3:1) |
| 8 | [AuCl($PPh_3$)] | 60 | 19 | NR |

[a] All reactions were carried out using **5a** (0.05 mmol), catalyst (10 mol %) and DCE (1.0 mL). [b] Yield of isolated products. [c] *anti*/*syn*.

X-ray crystal structure of *anti*-**21a** is shown in Figure 2 and its CIF data are presented in the Supporting Information.[14]

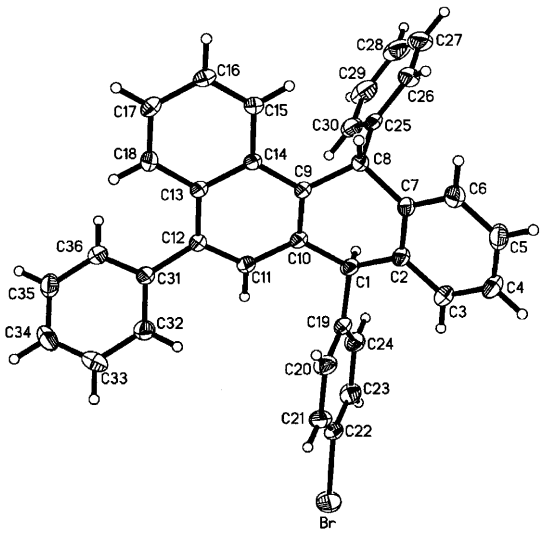


Figure 2. ORTEP drawing of *anti*-**21a**.

Next, we examined a series of vinylcyclopropenes **5** in the presence of [AuCl($PPh_3$)]/AgOTf to determine the scope and limitations of this interesting reaction. It was found that products **21** were formed in moderate to good yields as mixtures of *syn*- and *anti*-isomers whether they have electron-donating or -withdrawing substituent on the benzene ring (Table 6, entries 1–6).

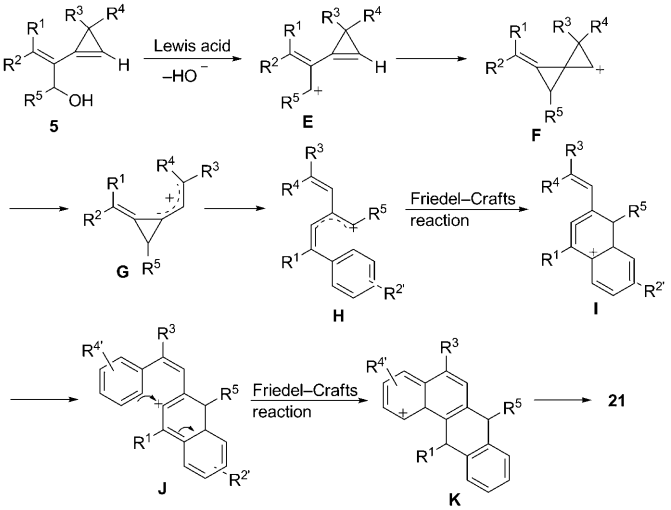
Table 6. $Au^{I}$-catalyzed transformations of **5** to **21**.


**5** **21**

| Entry[a] | **5** ($R^1/R^2/R^3/R^4/R^5$) | Yield [%][b,c] |
|---|---|---|
| 1 | **5b** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5/p$-$ClC_6H_4$) | **21b**, 99 (5.8:1) |
| 2 | **5c** ($C_6H_5/C_6H_5/p$-$ClC_6H_4/p$-$ClC_6H_4/C_6H_5$) | **21c**, 96 (6.7:1) |
| 3 | **5d** ($C_6H_5/C_6H_5/p$-$MeC_6H_4/p$-$MeC_6H_4/C_6H_5$) | **21d**, 92 (2.8:1) |
| 4 | **5e** ($p$-$FC_6H_4/p$-$FC_6H_4/C_6H_5/C_6H_5/p$-$MeC_6H_4$) | **21e**, 79 (7.1:1)[d] |
| 5 | **5f** ($p$-$ClC_6H_4/p$-$ClC_6H_4/C_6H_5/C_6H_5/C_6H_5$) | **21f**, 93 (11.1:1) |
| 6 | **5g** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5/E$-$C_6H_5CH{=}CH$) | **21g**, 88 (2.2:1) |

[a] All reactions were carried out by using **5** (0.05 mmol), [AuCl($PPh_3$)] (10 mol%), AgOTf (10 mol%) and DCE (1.0 mL) at 60°C for 1.5 h. [b] Yield of isolated products. [c] Ratios of *anti*/*syn*. [d] Toluene was used as the solvent.

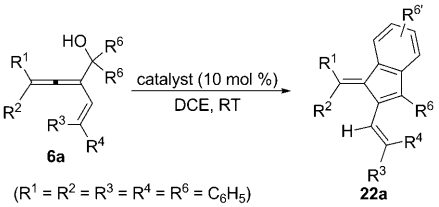
A plausible mechanism for the formation of **21** is outlined in Scheme 9. Initially, allylic carbocation intermediate **E** is formed from vinylcyclopropenes **5** in the presence of Lewis acids. The intramolecular electrophilic addition of intermediate **E** gives spiro intermediate **F** which undergoes ring-opening reaction to give allylic carbocation intermediate **G**. Intermediate **G** also undergoes ring-opening reaction to give intermediate **H**. The intramolecular Friedel–Crafts reaction of intermediate **H** gives intermediate **I** which undergoes rearrangement to give carbocation intermediate **J**. The intramolecular Friedel–Crafts reaction of intermediate **J** gives intermediate **K**. Aromatization of intermediate **K** will furnish product **21** (Scheme 9).




Scheme 9. Proposed mechanism for the formation of **21**.

**TfOH-catalyzed transformation of allenols 6**: Further investigations revealed that allenol derivative **6a** can be transformed to indene derivative **22a** in the presence of Lewis acid or Brønsted acid. As can be seem from Table 7, for most of the Lewis acids screened, indene derivative **22a** could be formed in good yields except for $Yb(OTf)_3$ (Table 7, entries 1, 3–6). When Brønsted acid trifluoromethanesulfonic acid (TfOH) was used as the catalyst, **22a** was obtained in 99% yield within 0.5 h (Table 7, entry 7). The

Table 7. Optimization for the transformation of **6a** to **22a** in the presence of various catalysts.




**6a** **22a**

($R^1 = R^2 = R^3 = R^4 = R^6 = C_6H_5$)

| Entry[a] | Catalyst | $t$ [h] | Yield [%][b] |
|---|---|---|---|
| 1 | $Sc(OTf)_3$ | 8 | 99 |
| 2 | $Yb(OTf)_3$ | 23 | NR |
| 3 | $Sn(OTf)_2$ | 0.5 | 92 |
| 4 | $BF_3{\cdot}OEt_2$ | 0.5 | 99 |
| 5 | $In(OTf)_3$ | 1 | 99 |
| 6 | $Nd(OTf)_3$ | 0.5 | 99 |
| 7 | TfOH | 0.5 | 99 |

[a] All reactions were carried out by using **6a** (0.05 mmol), catalyst (10 mol%) and DCE (0.5 mL) at room temperature. [b] Yield of isolated products.

structure of **22a** was unambiguously determined by an X-ray diffraction and its CIF data are presented in the Supporting Information (Figure 3).[15]

Using TfOH (10 mol%) as the catalyst, we next examined a series of allenol derivatives **6** to evaluate the generality of this interesting reaction and the results of these experiments are summarized in Table 8. It was found that indene derivatives **22** could be formed in high yields for a variety of allenol derivatives **6** under the standard reaction conditions (Table 8). The proposed mechanism for the formation of **22**

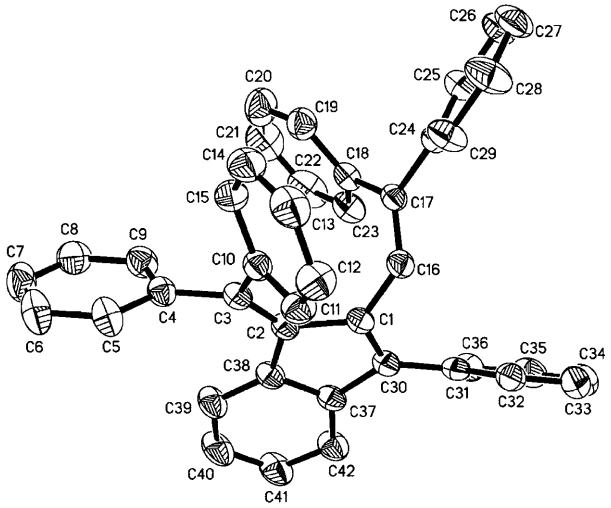
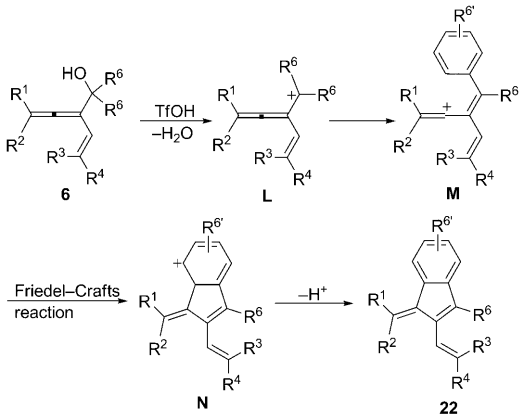


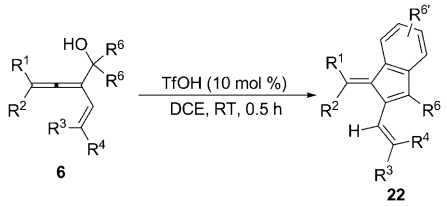

Figure 3. ORTEP drawing of **22a**.

is shown in Scheme 10. Upon treatment of **6** with TfOH, a cationic intermediate **L** is formed.[16] The allylic rearrangement of cationic intermediate **L** produces the corresponding cationic intermediate **M**, which undergoes intramolecular Friedel–Crafts reaction to generate intermediate **N**. Aromatization of intermediate **N** produces the corresponding indene derivatives **22** (Scheme 10).




Scheme 10. Proposed mechanism for the formation of **22**.

Table 8. TfOH-catalyzed transformations of **6** to **22**.




| Entry[a] | **6** ($R^1/R^2/R^3/R^4/R^6$) | Yield [%][b] |
|---|---|---|
| 1 | **6b** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5/p$-$MeC_6H_4$) | **22b**, 93 |
| 2 | **6c** ($C_6H_5/C_6H_5/C_6H_5/C_6H_5/p$-$ClC_6H_4$) | **22c**, 99 |
| 3 | **6d** ($C_6H_5/C_6H_5/p$-$ClC_6H_4/p$-$ClC_6H_4/C_6H_5$) | **22d**, 99 |
| 4 | **6e** ($C_6H_5/C_6H_5/p$-$MeC_6H_4/p$-$MeC_6H_4/C_6H_5$) | **22e**, 96 |
| 5 | **6f** ($p$-$ClC_6H_4/p$-$ClC_6H_4/C_6H_5/C_6H_5/C_6H_5$) | **22f**, 96 |
| 6 | **6g** ($p$-$MeC_6H_4/p$-$MeC_6H_4/C_6H_5/C_6H_5/C_6H_5$) | **22g**, 99 |

[a] All reactions were carried out by using **6** (0.05 mmol), TfOH (10 mol%) and DCE (0.5 mL) at room temperature for 0.5 h. [b] Yield of isolated products.

## Conclusions

We have disclosed highly stereo- and regioselective carbolithiation reactions of vinylidenecyclopropanes **1** by treating with LDA in THF and then quenching with various electrophiles. A variety of vinylcyclopropenes **5**, allenols **6**, 1,3-enynes **7** and **12**, trienes **8** and **11**, hept-1-ene-3,6-diyne derivatives **17** were obtained by quenching with aryl or aliphatic aldehydes, ketones, enones or propargyl bromide. Transformations of vinylcyclopropenes **5** and allenols **6** were also performed in the presence of Lewis acid or Brønsted acid, affording fused and conjugated aromatic products in good to high yields. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

## Experimental Section

$^1H$ and $^{13}C$ NMR spectra were recorded at 300 and 75 MHz, respectively. Mass and HRMS spectra were recorded by EI method. Organic solvents used were dried by standard methods when necessary. Satisfactory CHN microanalyses were obtained with an analyzer. Commercially obtained reagents were used without further purification. All these reactions were monitored by TLC with silica gel coated plates. Flash column chromatography was carried out using silica gel at increased pressure.

**General procedure for LDA-mediated addition reaction of vinylidenecyclopropanes 1 with aldehydes 2**: Under an argon atmosphere, to a solution of vinylidenecyclopropane **1** (0.2 mmol) in THF (2.0 mL) was added LDA (0.4 mmol) at −78 °C, and the resulting reaction mixture was stirred at −78 °C for about 2 h. Then aldehyde **2** (0.3 mmol) was added and the reaction solution was further stirred for 2 h at the same temperature. Then the reaction mixture was quenched by the addition of the aqueous solution of ammonium chloride and warmed to room temperature. The reaction solution was extracted with $Et_2O$ (3×10 mL). The organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

**General procedure for LDA-mediated addition reaction of vinylidenecyclopropanes 1 with imines 10**: Under an argon atmosphere, to a solution of vinylidenecyclopropane **1** (0.2 mmol) in THF (2.0 mL) was added LDA (0.4 mmol) at −78 °C, and the resulting reaction mixture was stirred at −78 °C for about 2 h. Then imine **10** (0.3 mmol) was added and the reaction solution was further stirred for 2 h at the same propargyl bromide temperature. Then the reaction mixture was quenched by addition of the aqueous solution of ammonium chloride and warmed to room temperature. The reaction solution was extracted with $Et_2O$ (3×10 mL). The organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

**General procedure for LDA-mediated addition reaction of vinylidenecyclopropanes 1 with enones 4**: Under an argon atmosphere, to a solution of vinylidenecyclopropane **1** (0.2 mmol) in THF (2.0 mL) was added LDA (0.4 mmol) at −78 °C, and the resulting reaction mixture was stirred at −78 °C for about 2 h. Then enone **4** (0.3 mmol) was added and the reaction solution was further stirred for 1 h at the same temperature. Then the reaction mixture was quenched by addition of the aqueous solution of ammonium chloride and warmed to room temperature. The reaction solution was extracted with $Et_2O$ (3×10 mL). The organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

**General procedure for LDA-mediated addition reaction of vinylidenecyclopropanes 1 with propargyl bromide 16**: Under an argon atmosphere, to a solution of vinylidenecyclopropane **1** (0.2 mmol) in THF (2.0 mL) was added LDA (0.4 mmol) at −78 °C, and the resulting reaction mixture was stirred at −78 °C for about 2 h. Then propargyl bromide **16** (0.3 mmol) was added and the reaction solution was further stirred for 2 h at the same temperature. Then the reaction mixture was quenched by addition of the aqueous solution of ammonium chloride and warmed to room temperature. The reaction solution was extracted with $Et_2O$ (3×10 mL). The organic layers were dried over anhydrous $Na_2SO_4$. The solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

**General procedure for the transformation of 5 to 21 in the presence of [AuCl(PPh$_3$)]/AgOTf**: Under an argon atmosphere, vinylcyclopropene **5** (0.05 mmol), [AuCl(PPh$_3$)] (10 mol%), AgOTf (10 mol%) and DCE (1.0 mL) were added into a Schlenk tube. The reaction mixture was stirred at 60 °C for 1.5 h, then the solvent was removed under reduced

pressure and the residue was purified by a flash column chromatography under reduced pressure and the residue was purified by a flash column chromatography.

**General procedure for the transformation of 6 to 22 in the presence of TfOH**: Under an argon atmosphere, allenol **6** (0.05 mmol) and DCE (1.0 mL) were added into a Schlenk tube, then TfOH (10 mol%) was added. The reaction mixture was stirred at room temperature for 0.5 h, then the solvent was removed under reduced pressure and the residue was purified by a flash column chromatography.

**Compound 8a**: Yellow oil; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 1.94 (br s, 1H, OH), 5.00 (s, 1H), 5.38 (s, 1H), 5.50 (d, $J$=1.2 Hz, 1H), 6.32 (s, 1H), 6.60 (d, $J$=1.2 Hz, 1H), 6.97–7.01 (m, 2H, Ar), 7.15–7.35 ppm (m, 18H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 75.1, 116.8, 126.4, 126.48, 126.52, 127.4, 127.6, 127.8, 127.9, 128.0, 128.1, 128.3, 129.8, 140.4, 141.1, 142.9, 143.6, 143.9, 144.3 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3566, 3446, 3057, 3026, 2925, 1945, 1878, 1800, 1599, 1573, 1492, 1444, 1380, 1181, 1075, 1028, 899, 773, 762, 700 cm$^{-1}$; MS (EI) $m/z$ (%): 396 (100) [$M^+$−18], 397 (30), 305 (21), 317 (15), 318 (14.1), 303 (13.8), 319 (13), 241 (12); HRMS (EI): $m/z$: calcd for $C_{31}H_{26}$: 414.1984; found: 414.1984.

**Compound 11a**: White solid; m.p. 138–139 °C; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 2.33 (s, 3H, $CH_3$), 4.79 (d, $J$=7.2 Hz, 1H), 5.10 (d, $J$=7.2 Hz, 1H), 5.34 (s, 1H), 5.51 (d, $J$=0.9 Hz, 1H), 6.20 (s, 1H), 6.56 (s, 1H), 6.74–6.82 (m, 4H, Ar), 7.05–7.16 (m, 10H, Ar), 7.22–7.26 (m, 5H, Ar), 7.35–7.41 ppm (m, 5H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 21.4, 60.6, 117.2, 126.1, 126.5, 127.10, 127.13, 127.4, 127.47, 127.54, 127.78, 128.81, 127.9, 128.2, 128.4, 129.2, 129.9, 130.2, 137.3, 139.7, 139.8, 140.7, 142.8, 143.0, 143.8, 143.9 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3274, 3057, 3028, 2924, 1945, 1885, 1797, 1598, 1573, 1493, 1444, 1329, 1160, 1094, 1029, 900, 813, 774, 699 cm$^{-1}$; MS (EI): $m/z$ (%): 567 (5) [$M^+$], 396 (100), 260 (46), 412 (42), 397 (31), 307 (29), 411 (26), 319 (17), 306 (15); HRMS (EI): $m/z$: calcd for $C_{38}H_{33}NO_2S$: 567.2232; found: 567.2233.

**Compound 12a**: Yellow oil; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 2.08 (s, 3H, $CH_3$), 2.34 (d, $J$=1.2 Hz, 3H, $CH_3$), 2.55–2.68 (m, 4H), 6.02 (d, $J$=1.2 Hz, 1H), 7.19–7.37 (m, 9H, Ar), 7.43–7.50 ppm (m, 6H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 18.7, 30.1, 34.9, 40.4, 49.5, 84.9, 98.7, 106.6, 125.3, 126.6, 127.2, 128.0, 128.3, 128.4, 140.8, 144.9, 147.9, 208.4 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3082, 3057, 3024, 2924, 1715, 1597, 1493, 1446, 1363, 1160, 1029, 757, 699 cm$^{-1}$; MS (EI): $m/z$ (%): 378 (5) [$M^+$], 229 (100), 320 (85), 305 (81), 307 (43), 215 (34.6), 291 (34.5), 292 (33), 228 (27); HRMS (EI): $m/z$: calcd for $C_{28}H_{26}O$: 378.1984; found: 378.1985.

**Compound 15a**: Yellow oil; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 2.08 (s, 3H, $CH_3$), 2.34 (d, $J$=1.2 Hz, 3H, $CH_3$), 2.55–2.68 (m, 4H), 6.02 (d, $J$=1.2 Hz, 1H), 7.19–7.37 (m, 9H, Ar), 7.43–7.50 ppm (m, 6H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 18.7, 30.1, 34.9, 40.4, 49.5, 84.9, 98.7, 106.6, 125.3, 126.6, 127.2, 128.0, 128.3, 128.4, 140.8, 144.9, 147.9, 208.4 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3082, 3057, 3024, 2924, 1715, 1597, 1493, 1446, 1363, 1160, 1029, 757, 699 cm$^{-1}$; MS (EI): $m/z$ (%): 378 (5) [$M^+$], 229 (100), 320 (85), 305 (81), 307 (43), 215 (34.6), 291 (34.5), 292 (33), 228 (27); HRMS (EI): $m/z$: calcd for $C_{28}H_{26}O$: 378.1984; found: 378.1985.

**Compound 17a**: White solid; m.p. 83–84 °C; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 2.01 (t, $J$=2.4 Hz, 1H), 2.36 (d, $J$=0.9 Hz, 3H, $CH_3$), 3.22 (d, $J$=2.4 Hz, 2H), 6.03 (d, $J$=0.9 Hz, 1H), 7.20–7.34 (m, 9H, Ar), 7.42–7.51 ppm (m, 6H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 18.7, 32.9, 49.9, 71.3, 81.0, 84.3, 98.5, 106.7, 125.4, 126.9, 127.4, 127.9, 128.2, 128.3, 140.9, 144.1, 148.3 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3295, 3058, 3029, 2916, 1946, 1872, 1799, 1597, 1492, 1446, 1378, 1267, 1185, 1071, 1030, 848, 756, 697, 653 cm$^{-1}$; MS (EI): $m/z$ (%): 346 (8) [$M^+$], 307 (100), 229 (74), 308 (29), 215 (26), 228 (24), 291 (19), 129 (19), 128 (15); HRMS (EI): $m/z$: calcd for $C_{27}H_{22}$: 346.1722; found: 345.1720.

**Compound 21a** (*syn*-isomer): White solid; m.p. 194–196 °C; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 5.48 (s, 1H), 6.13 (s, 1H), 6.77 (d, $J$=8.7 Hz, 2H, Ar), 6.95–7.06 (m, 7H, Ar), 7.26–7.76 (m, 11H, Ar), 7.85 (d, $J$=8.4 Hz, 1H, Ar), 7.93 (d, $J$=8.7 Hz, 1H, Ar), 8.08 ppm (d, $J$=8.4 Hz, 1H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 46.2, 50.7, 119.9, 124.5, 125.5, 125.9, 126.5, 126.7, 126.8, 126.9, 127.4, 128.0, 128.2, 128.3, 128.4, 129.5, 130.16, 130.22, 130.7, 131.0, 132.3, 132.5, 136.2, 137.2, 139.5, 139.8, 140.6, 142.7, 143.1 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3060, 3024, 2922, 2851, 1950, 1888, 1595, 1574, 1485, 1454, 1400, 1074, 1031, 1010, 819, 753, 703 cm$^{-1}$; MS (EI): $m/z$ (%): 536 (25.16) [$M^+$], 302 (100), 303 (64), 77 (29), 379 (26.1), 304 (25.9), 189 (25.22), 182 (25.0); HRMS (EI): $m/z$: calcd for $C_{36}H_{25}Br$: 536.1140; found: 536.1147; (*anti*-isomer): White solid; m.p. 200–201 °C; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 5.30 (s, 1H), 6.26 (s, 1H), 6.74 (d, $J$=7.8 Hz, 1H, Ar), 7.05–7.53 (m, 19H, Ar), 7.62 (d, $J$=7.5 Hz, 1H, Ar), 7.86 (d, $J$=8.1 Hz, 1H, Ar), 8.31 ppm (d, $J$=8.4 Hz, 1H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 46.7, 49.1, 120.9, 124.3, 125.5, 126.3, 126.4, 126.8, 127.2, 127.5, 128.2, 128.4, 128.7, 128.8, 130.1, 131.0, 131.3, 131.9, 132.6, 136.0, 138.0, 138.6, 139.2, 140.6, 143.3, 144.5 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3059, 3023, 2924, 2852, 1946, 1898, 1594, 1574, 1487, 1452, 1403, 1385, 1264, 1101, 1072, 1011, 936, 898, 757, 739, 703 cm$^{-1}$; MS (EI): $m/z$ (%): 536 (27) [$M^+$], 302 (100), 303 (65), 380 (39), 379 (31), 538 (28.0), 189 (27.6), 182 (26); HRMS (EI): $m/z$: calcd for $C_{36}H_{25}Br$: 536.1140; found: 536.1153.

**Compound 22a**: Red solid; m.p. 177–178 °C; $^1$H NMR ($CDCl_3$, 300 MHz, TMS): $\delta$ = 6.25 (s, 1H), 6.32 (d, $J$=7.8 Hz, 1H, Ar), 6.70–6.81 (m, 5H, Ar), 6.94–6.96 (m, 2H, Ar), 7.04–7.36 ppm (m, 21H, Ar); $^{13}$C NMR ($CDCl_3$, 75 MHz, TMS): $\delta$ = 119.6, 123.0, 124.8, 126.4, 126.7, 127.0, 127.3, 127.52, 127.54, 127.7, 128.07, 128.11, 128.2, 128.5, 128.87, 128.90, 130.7, 131.9, 135.25, 135.32, 137.7, 138.6, 140.5, 141.8, 142.67, 142.70, 143.0, 143.37, 143.43, 148.3 ppm; IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3055, 3025, 2925, 1936, 1869, 1799, 1595, 1489, 1441, 1352, 1327, 1178, 1156, 1074, 1029, 786, 760, 739, 697 cm$^{-1}$; MS (EI): $m/z$ (%): 534 (100) [$M^+$], 367 (76), 535 (45), 379 (34), 189 (28), 368 (25), 165 (19), 289 (18); elemental analysis calcd (%) for $C_{42}H_{30}$ (3/5 $CH_2Cl_2$): C 87.37, H 5.37; found: C 87.53, H 5.61.

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[14] Crystal data of *anti*-**21a**: empirical formula: $C_{36}H_{25}Br$; formula weight: 537.47; crystal color, habit: colorless, prismatic; crystal system: triclinic; lattice type: primitive; crystal size: 0.507×0.411×0.327 mm; lattice parameters: $a=10.6165(12$ Å, $b=10.9662(12$ Å, $c=11.9919(14$ Å, $\alpha=96.483(2)°$, $\beta=100.051(2)°$, $\gamma=110.137(2)°$, $V=1267.9(2)$ Å$^3$; space group: $P\bar{1}$; $Z=2$; $\rho_{calcd}=1.408$ g cm$^{-3}$; $F_{000}=552$; diffractometer: Rigaku AFC7R; residuals: R.; *R*w: 0.0406, 0.0906. CCDC 641221 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[15] Crystal data of **22a**: empirical formula: $C_{46}H_{38}O_2$; formula weight: 622.76; crystal color, habit: colorless, prismatic; crystal system: triclinic; lattice type: primitive; crystal size: 0.427×0.285×0.191 mm; lattice parameters: $a=11.0883(14)$, $b=13.5128(18)$, $c=14.3661(18)$ Å, $\alpha=96.885(3)$, $\beta=112.443(2)$, $\gamma=111.279(2)°$, $V=1768.4(4)$ Å$^3$; space group: $P\bar{1}$; $Z=2$; $\rho_{calcd}=1.170$ g cm$^{-3}$; $F_{000}=660$; diffractometer: Rigaku AFC7R; residuals: R.; *R*w: 0.0574, 0.1495. CCDC 663242 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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