

1 **Complexity from simplicity: intramolecular *meta*-thermocycloadditions of**  
2 **benzene rings via Wheland intermediates**

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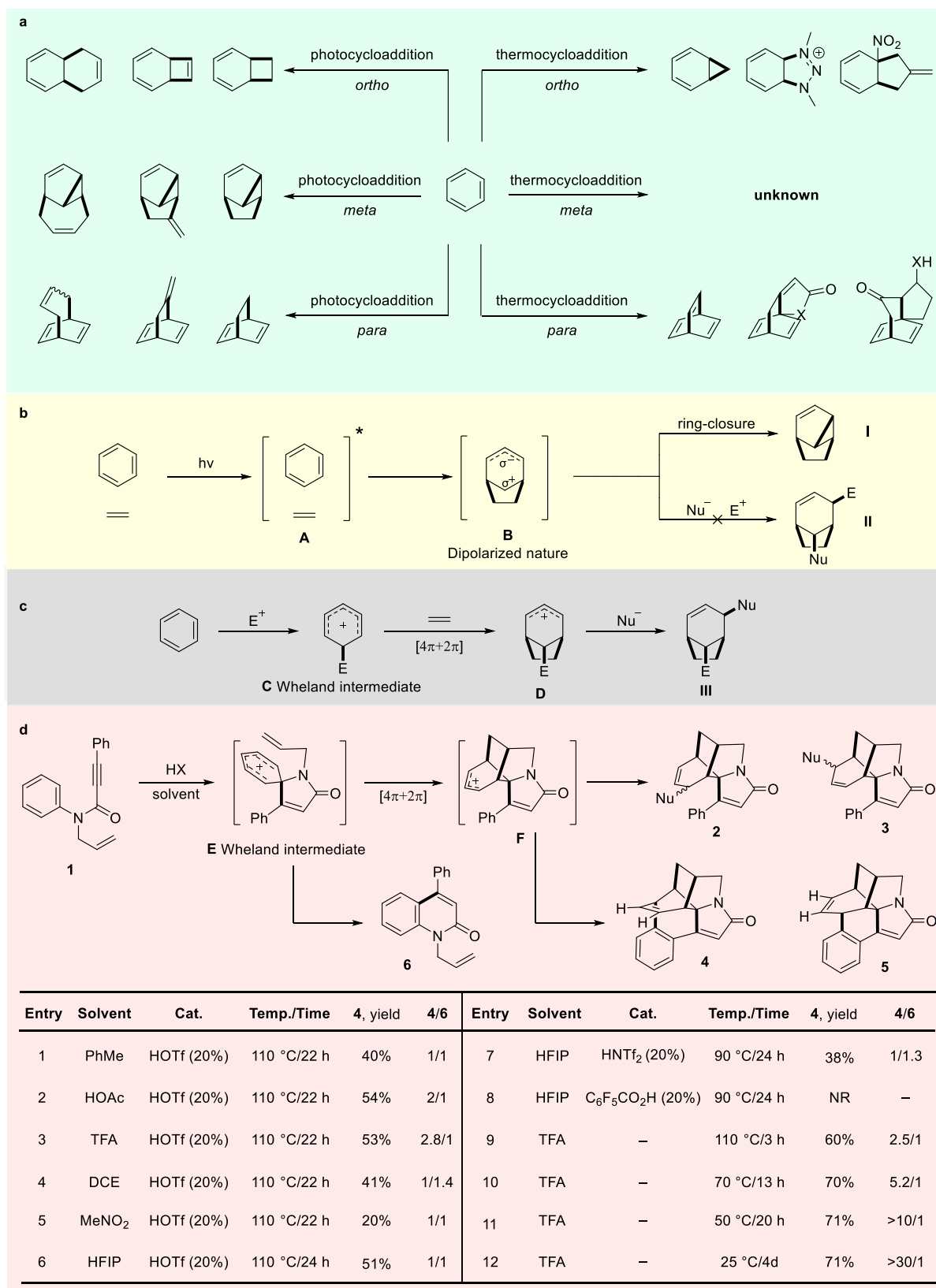
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10  
11 **Abstract**

12 Dearomative cycloadditions are powerful synthetic transformations utilizing aromatic  
13 compounds for cycloaddition reactions<sup>1-4</sup>. Diverse complex three-dimensional architectures  
14 could be built upon the flat land of aromatic compounds. In addition, such transformations are  
15 atom- and step-economical and, thus, have been widely applied to the preparations of complex  
16 biologically relevant compounds<sup>5-7</sup>. For the ubiquitous and most studied yet challenging  
17 benzene ring systems<sup>8</sup>, *ortho*- and *para*-cycloadditions are feasible both photochemically and  
18 thermally, while the *meta*-cycloadditions are still limited to the photochemical processes from  
19 the 1960s<sup>9,10</sup>. Herein, we have realized the *meta*-thermocycloadditions of benzene rings in an  
20 intramolecular fashion. The reaction was proposed to proceed via  $[4\pi+2\pi]$  cycloadditions of  
21 Wheland intermediates from the electrophilic dearomatization of benzene rings. A broad  
22 spectrum of readily available C(sp<sup>2</sup>)-rich aniline-tethered enynes were transformed into  
23 C(sp<sup>3</sup>)-rich 3D complex polycyclic architectures simply by stirring in TFA. Moreover, the

1 reaction could be performed in gram-scales and the products could be diversely elaborated.



2

3 Fig. 1 | Research background and the discovery of *meta*-thermocycloadditions of

1 **benzene rings. a**, Dearomative cycloadditions of benzene rings. **b**, Mechanism of the  
2 *meta*-photocycloadditions of benzene rings. **c**, General scheme of the proposed thermal  
3 counterpart to the *meta*-photocycloadditions of benzene rings. **d**, Proof of concept and  
4 reaction discovery and optimizations. The yields of **4** and the ratios of **4/6** were determined  
5 by crude <sup>1</sup>H NMR using dibutyl phthalate as internal standard.

6 Dearomative cycloadditions are a class of transformations that convert C(sp<sup>2</sup>)-rich planar  
7 aromatics into C(sp<sup>3</sup>)-rich 3D complex polycyclic structures<sup>1-4</sup>. They have been extensively  
8 applied to the synthesis of biologically relevant compounds not only because of the  
9 complexity generated from simplicity but also the atom- and step-economy<sup>5-7</sup>. Moreover, the  
10 aromatics are readily available and easily editable and are much more stable than the regular  
11 cycloaddition partners, such as alkenes and dienes, towards acidic, basic, and redox  
12 conditions. Therefore, the aromatics could be treated as “sleeping” cycloaddition partners to  
13 carry through multi-step synthesis for late-stage cycloadditions. However, the dearomative  
14 cycloadditions are considerably challenging due to the disruption of aromaticity, especially  
15 for the benzene ring systems<sup>8</sup>. Indeed, the pioneering discoveries required highly energetic  
16 ultraviolet light irradiation<sup>9,10</sup>. Nevertheless, ever since the pioneering discoveries in 1960s,  
17 quite a few new systems have been developed utilizing aromatics for cycloadditions<sup>11-33</sup>. In  
18 particular, significant advancement has been achieved recently using visible light catalysis<sup>27</sup>.

19 From the topological point view, the cycloadditions of benzene rings could be classified  
20 into three types: *ortho*-, *meta*-, and *para*-cycloadditions (Fig. 1a). While the *ortho*- and  
21 *para*-ones have been realized both photochemically and thermally, leading to diversified  
22 structural types, the *meta*-cycloadditions are still limited to the photochemical processes from

1 the 1960s. Moreover, the products from the *meta*-cycloadditions are restricted to the  
2 tricyclic-type **I** with few exceptions in sluggish efficiency<sup>34,35</sup>. In this context, we envisioned  
3 that the *meta*-thermocycloadditions of benzene rings might be feasible via the proposed  
4  $[4\pi+2\pi]$  cycloadditions of Wheland intermediate **C** with alkenes (Fig. 1c) based on the  
5 following two facts: 1) benzene rings could be dearomatized by various electrophiles to  
6 generate Wheland intermediates and 2) pentadienyl cations could facilely react with alkenes  
7 in a  $[4\pi+2\pi]$  cycloaddition fashion<sup>36</sup>. After the proposed cycloaddition of the Wheland  
8 intermediate **C**, subsequent nucleophilic interception of the resulting allyl cation **D** would  
9 afford the bicyclo[3.2.1]octane-type product **III**, a structural type complementary to the  
10 *meta*-photocycloadduct **I**. Specifically, although it is now commonly accepted that the  
11 *meta*-photocycloaddition reactions progressed from an arene-alkene exciplex **A** to a  
12 dipolarized intermediate **B** and finally to the cyclopropane ring-closing product **I**<sup>37</sup>, attempts  
13 to intercept the bicyclo[3.2.1]octenyl intermediate **B** with nucleophiles and electrophiles all  
14 failed to furnish the bicyclo[3.2.1]octane-type product **II** (Fig. 1b)<sup>38-42</sup>.

### 15 **Reaction discovery and optimizations**

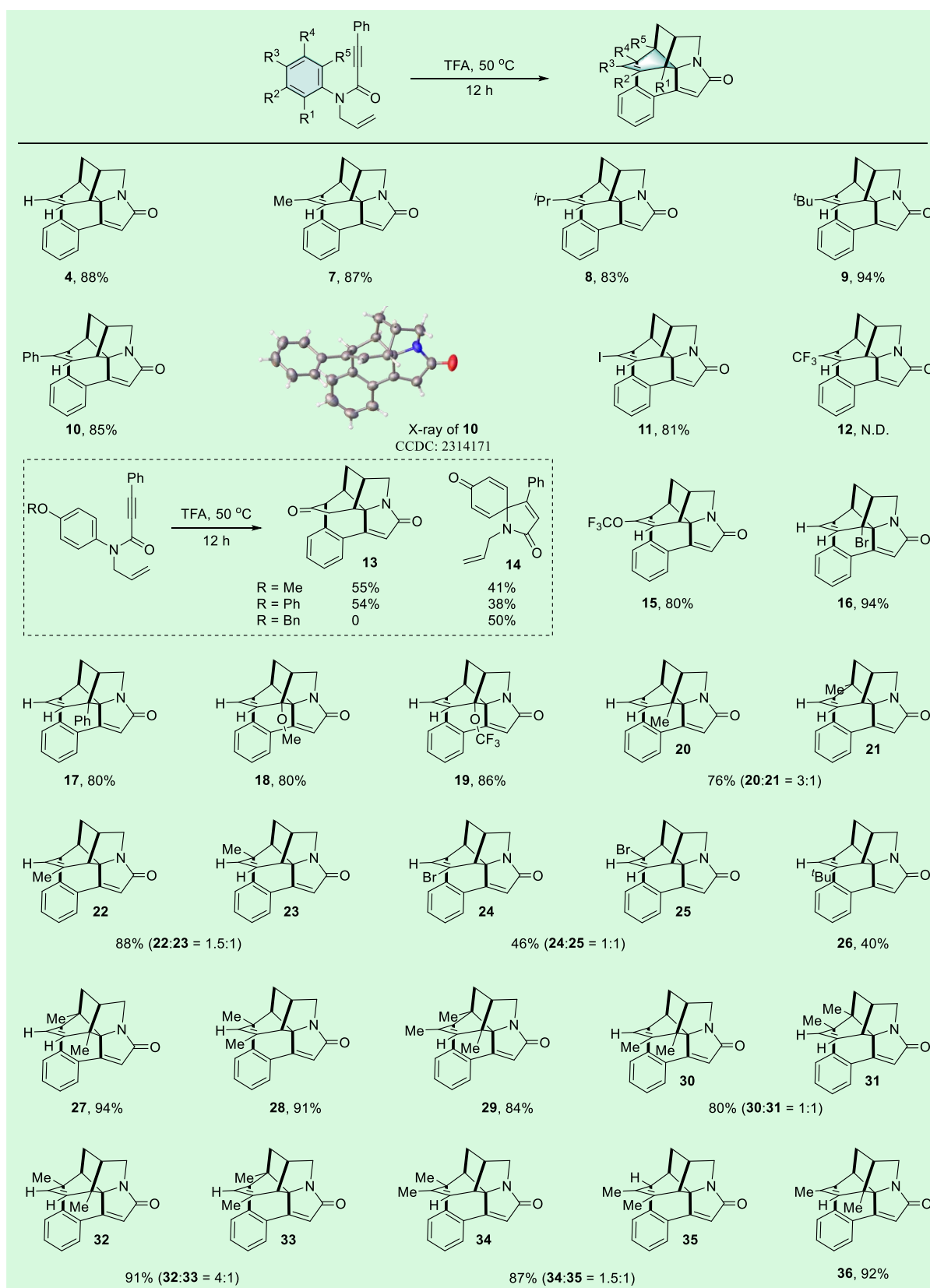
16 However, one imminent challenge posed for the above proposal is the great rearomatization  
17 tendency of the Wheland intermediates **C**. In order to intercept them with alkenes prior to  
18 rearomatization, we employed the aniline-tethered enyne **1** as the model substrate to  
19 implement the proposed *meta*-thermocycloaddition reaction intramolecularly (Fig. 1d). In this  
20 scenario, Brønsted acid was envisioned to first promote the *ipso*-cyclization of aniline's  
21 benzene ring to the acetylenic bond to furnish the spirocyclic Wheland intermediate **E**<sup>43</sup>.  
22 Then, the proposed intramolecular  $[4\pi+2\pi]$  cycloaddition between the pentadienyl cation

1 entity and the olefin entity in **E** would afford the cationic species **F**, which might be trapped  
2 by the solvent, leading to several possible isomeric products **2** and **3**. Interestingly, when  
3 triflic acid (HOTf) was utilized as the Brønsted acid catalyst and toluene, acetic acid, or  
4 trifluoroacetic acid (TFA) as the solvent (Fig. 1d, entries 1-3), none of the initially proposed  
5 solvent trapping products was detected. Instead, an even more complex polycyclic compound  
6 **4** was identified, originating from an unexpected trapping of the allyl cation entity of **F** via an  
7 intramolecular Friedel-Crafts reaction. The other regioisomer **5** was not detected. Meanwhile,  
8 substantial amount of rearomatized side product **6** was formed in these conditions. Further  
9 screening of the solvent and acid did not improve the chemoselectivity (entries 4-8).  
10 Surprisingly, without HOTf, the *meta*-thermocycloaddition of **1** still worked simply stirring in  
11 TFA (entry 9). Moreover, the chemoselectivity between **4** and **6** could be improved by  
12 lowering the reaction temperature and excellent selectivity in 71% yield was achieved at  
13 room temperature albeit in prolonged reaction time (entries 10-12).

#### 14 **Substrate scope study**

15 With the reactivity disclosed and conditions optimized, we then systematically investigated  
16 the substrate scope. The aniline-tethered enyne substrates could be easily prepared in two  
17 steps from anilines, arylpropionic acids, and allyl (pseudo)halides via amide formation and  
18 N-alkylation reactions. At the outset, substrates derived from various anilines were examined  
19 (Fig. 2). Substituents ranging from electron donating to weakly electron withdrawing groups  
20 such as Me, <sup>i</sup>Pr, <sup>t</sup>Bu, Ph, and I were allowed at the *para*-positions of the aniline rings (**7-11**),  
21 while the strongly electron withdrawing CF<sub>3</sub> group caused no product **12** but a messy reaction.  
22 When the aniline ring was substituted with 4-methoxy group, a cyclohexanone-type product

1 **13** was isolated in 55% yield presumably from the hydrolysis of the original vinyl ether  
2 product. Meanwhile, significant amount of spirocyclic cyclohexadienone **14** was isolated,  
3 shedding light on the proposed Wheland intermediate **E**. The 4-phenoxy substrate worked  
4 similarly with the 4-methoxy one. Interestingly, when the aniline ring was substituted with  
5 4-benzyloxy group, no desired product but **14** was obtained presumably due to the rapid  
6 debenylation of the corresponding Wheland intermediate. To the opposite, the  
7 4-trifluoromethoxy substrate led to the *meta*-cycloadduct **15** but no **14** and the vinyl ether  
8 functionality remained intact. Furthermore, for non-symmetrical substrates derived from  
9 *ortho*-Ph, Br, OMe, or OCF<sub>3</sub> substituted anilines, excellent regioselectivities were observed  
10 for the [4π+2π] cycloaddition step (**16-19**). Among all the tested substrates, one exception  
11 was the *ortho*-Me one, giving **20** and **21** in 3:1 regioselectivity. For the *meta*-Me or Br  
12 substituted substrates, poor regioselectivities were observed (**22-25**) while the *meta*-<sup>t</sup>Bu one  
13 led to one single regioisomer **26** albeit in only 40% yield. The aniline ring could be doubly or  
14 triply substituted, leading to densely substituted polycyclic products **27-36**. For the  
15 symmetrical substrates derived from 2,6-dimethylaniline, 3,5-dimethylaniline, and  
16 2,4,6-trimethylaniline, good to excellent yields were obtained despite the steric hindrance  
17 (**27-29**). For the non-symmetrical substrates derived from 2,3-dimethylaniline,  
18 2,5-dimethylaniline, and 3,4-dimethylaniline, poor to moderate regioselectivities were  
19 observed (**30-35**). Interestingly, for the 2,4-dimethylaniline-derived non-symmetrical  
20 substrate, the reaction was regiospecific with excellent yield (**36**). The structure of **10** was  
21 confirmed by X-ray crystallography (CCDC 2314171), and the structures of all other  
22 cycloadducts were assigned by analogy and NMR analysis.



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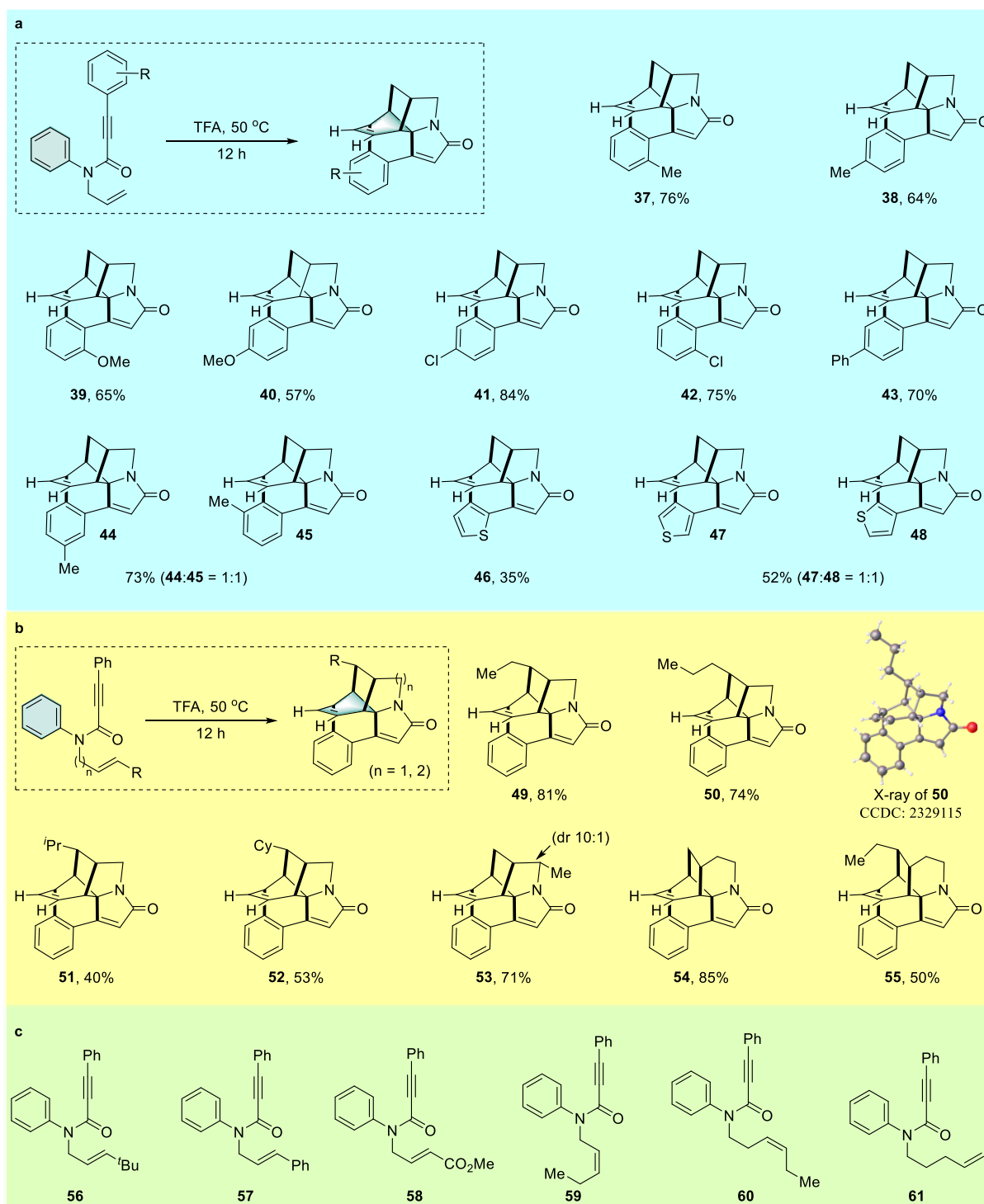
2 **Fig. 2 | Scope study of the N-aryl part of the aniline-tethered enyne substrate.**

3 Efforts were then turned to explore the phenylacetylene part of the enyne substrate (Fig.

1 3a). In general, the phenyl ring could be substituted with either electron donating or  
2 withdrawing groups at either the *ortho*- or *para*-positions, affording the cycloadducts **37-43**  
3 in moderate to good yields. A methyl group at the phenyl ring's *meta*-position caused 1:1  
4 mixture of two regioisomeric products **44** and **45**. Heterocycles such as thienyl group could  
5 facilely participate in the reaction (**46-48**). Again, when 3-thienyl group was involved, two  
6 regioisomers **47** and **48** were generated in 1:1 ratio.

7 Ultimately, the olefin part of the enyne substrate was varied (Fig. 3b). It turned out the  
8 olefin was not limited to terminal ones. Internal olefins in *trans*-configuration facilely took  
9 part in the *meta*-cycloadditions (**49-52**). In addition to the primary alkyl groups (**49,50**), bulky  
10 groups such as *i*Pr and Cy on the olefin were tolerated (**51,52**) while extremely bulky *t*Bu  
11 group (**56**), phenyl group (**57**), or electron withdrawing group (**58**) all caused no desired  
12 products. Substrate **59** in *cis*-configuration led to neither the desired product nor the isomeric  
13 product **49** but messy mixtures. Moreover, the allylic position could be substituted and the  
14 reaction proceeded smoothly affording **53** in good diastereoselectivity (10:1). Much to our  
15 delight, substrate with a homoallyl group worked equally efficiently, affording the polycyclic  
16 product **54** with a unique piperidine ring. Again, internal *trans*-olefin was allowed in the  
17 homoallyl system (**55**) while the *cis*-counterpart **60** was still unsuccessful. Finally, substrate  
18 with the olefin further away from nitrogen (**61**) led to no desired product. Again, the structure  
19 of **50** was confirmed by X-ray crystallography (CCDC 2329115), and the other structures  
20 were assigned by analogy and NMR analysis.



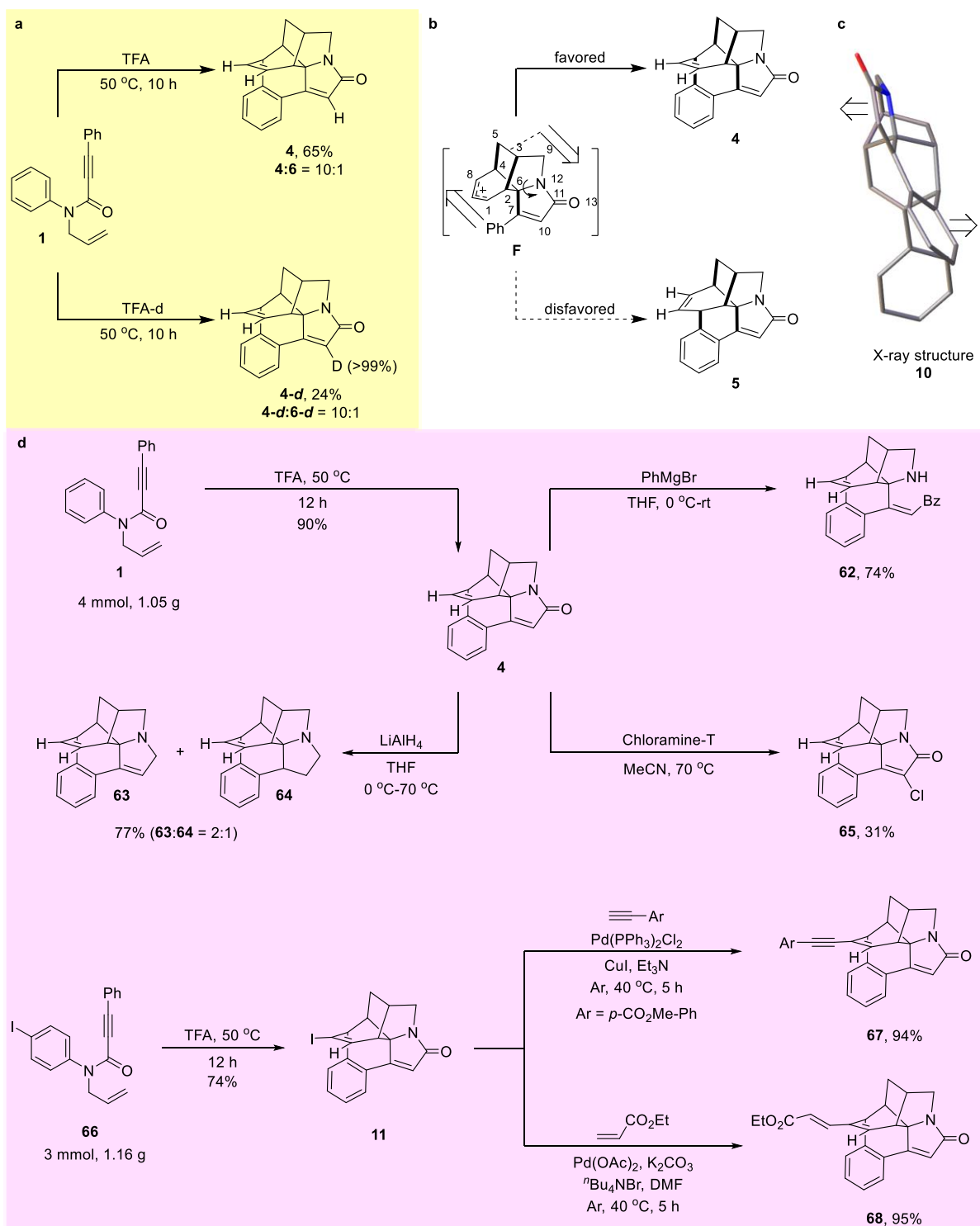


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2 **Fig. 3 | Scope study of the enyne part of the aniline-tethered enyne substrate. a,**

3 Variations of the alkyne part of the enyne substrate. **b,** Variations of the alkene part of the

4 enyne substrate. **c,** Unsuccessful substrates.



1

2 **Fig. 4 | Mechanistic considerations and synthetic applications.** a, Kinetic effect of the

3 deuterated TFA solvent. b, Rationale of the regioselective ring-closure step. c, Topological

4 analysis of the X-ray structure of **10**. d, Gram-scale reactions and the downstream

5 diversifications of the *meta*-thermocycloadducts.

## 1 **Mechanistic considerations and synthetic applications**

2 To get more insight into the reaction mechanism, we conducted the reaction in deuterated  
3 TFA (Fig. 4a). It turned out the reaction was significantly slowed down. Only 24% yield was  
4 obtained after 10 hours, while the regular conditions enabled 65% yield. Interestingly, the  
5 chemoselectivities between the *meta*-cycloadduct and the rearomatized side product for both  
6 reactions were identical (10:1). Moreover, the  $\alpha$ -positions of the  $\alpha,\beta$ -unsaturated lactams of  
7 **4-d** and **6-d** were completely deuterated. Thus, it was unambiguous that the alkyne  
8 protonation step was one of the slowest steps even if not the rate-determining one. The  
9 regioselective formation of **4** over **5** could be explained by the conformational analysis as  
10 depicted in Fig. 4b. Without the C3-C9 bond, intermediate **F** should be symmetrical and the  
11 lactam ring should be in the plane of symmetry, with C9-N12 bond being perpendicular to the  
12 C3-C5 bond. Once C3 was bonded to C9, the molecular symmetry was broken and the lactam  
13 ring was tilted, directing C9 outside of the plane and the phenyl ring inside. Thus, the phenyl  
14 ring will be proximal to C8 and distal to C1, in accordance with the observed regioselective  
15 formation of **4** over **5**. The above rationale based on conformational analysis could be  
16 supported by the X-ray structure of **10**, where the lactam ring was tilted and obliquely fused  
17 to the bicyclo[3.2.1]octane core (Fig. 4c).

18 To highlight the synthetic potential of the above *meta*-thermocycloaddition reaction,  
19 gram-scale reactions were performed, affording **4** and **11** in 90% and 74% yield respectively  
20 (Fig. 4d). Beyond the scalability, the synthetic potential could be further demonstrated by the  
21 divergent downstream elaborations of the products. For instance, the lactam ring of **4** could  
22 be facilely cleaved by phenylmagnesium bromide, affording compound **62** in 74% yield with

1 simplified ring system. Alternatively, the lactam unit could be reduced to amine by LiAlH<sub>4</sub>  
2 with partial reduction of the adjacent double bond (**63,64**). Interestingly, treatment of **4** with  
3 chloramine-T led to no aziridination product but the chlorination one (**65**) in a serviceable  
4 yield. Finally, the vinyl iodide unit of **11** served as an excellent handle for Heck and  
5 Sonogashira reactions to give the cross-coupled products **67** and **68** in near quantitative  
6 yields.

## 7 **Conclusion**

8 In summary, we have realized the *meta*-thermocycloadditions of benzene rings in an  
9 intramolecular fashion. A broad spectrum of readily available C(sp<sup>2</sup>)-rich aniline-tethered  
10 enynes were transformed into C(sp<sup>3</sup>)-rich 3D complex polycyclic architectures simply by  
11 stirring in TFA. The reaction was proposed to proceed via [4π+2π] cycloadditions of Wheland  
12 intermediates. Moreover, the reaction could be performed in gram-scales and the products  
13 could be diversely elaborated. We believe this methodology will not only set stage for  
14 developing new *meta*-thermocycloadditions of benzene rings but also open up new chemical  
15 space to biologically relevant molecules.

## 16 **Methods**

17 N-allyl-N,3-diphenylpropiolamide (0.2 mmol, 52.3 mg, 1.0 equiv.) was added to a dried vial.  
18 The reaction was stirred at 50 °C after adding trifluoroacetic acid (2 mL). After complete  
19 consumption of starting material observed by TLC (12 h), the reaction mixture was washed  
20 with saturated aqueous solution of NaHCO<sub>3</sub> then extracted with CH<sub>2</sub>Cl<sub>2</sub>. The organic phase  
21 was concentrated and the residue was purified by column chromatography on silica gel  
22 (petroleum ether/ethyl acetate = 3/1) to afford the corresponding product **4** (46.0 mg, 88%

1 yield).

## 2 **Data availability**

3 The data supporting the findings of this study are available within this article and its  
4 Supplementary Information.

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#### 10 **Author contributions**

11 Y.W. designed and conceived the project. S.L., T.X., and Y.L. carried out the reactions. S.L.  
12 and Y.W. wrote the manuscript with input from all authors. All authors analyzed the data and  
13 discussed the results. S.L. and T.X. contributed equally to this work.

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#### 15 **Competing interests**

16 The authors declare no competing interests.