EurJOC
European Journal of Organic Chemistry

Full Papers
doi.org/10.1002/ejoc.202001499

Chemistry Europe
European Chemical Societies Publishing

Domino Processes of Arynes Reacting with Three Classes of Nucleophiles for Organic Syntheses

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Synthetic application of arynes is broadened by their reactions with neutral *N*-, *S*-, and *O*-containing nucleophiles to produce three types of compounds. Accordingly, 1,2-dihydroquinolines are synthesized from Schiff bases, alkynes, and arynes through a Diels-Alder reaction. Epoxides are prepared from thioethers and arynes along with aldehydes or ketones through a Johnson-Corey-Chaykovsky reaction. Phenolic ethers are produced from allyl ethers and arynes through a Claisen-type rearrangement. These target molecules, including natural products γ-asarone, asaricin, and a cholesteryl phenolic ether, are formed through reactions initiated by arynes. These new reactions share a prevailing feature of domino processes, which are carried out in a single flask and afford the desired products in good to high yields.

1. Introduction

Arynes are highly reactive intermediates in organic syntheses and commonly involved in the reactions of bond-insertion, nucleophilic additions, pericyclic addition, rearrangement, etc.[1] Recently, Werz and Biju[2] summarize some synthetic applications of arynes through different insertion and addition reactions. Ghorai and Lee[3] publish a review article about aryne-based multicomponent coupling reactions to produce arenes and heterocycles. Benzynes, the simplest members of arynes, are in an oxidized form from benzenes[4a,b,5] and generally function as oxidizing agents. In a few examples, benzynes can act as reducing agents.[5] Application of arynes is still limited as harsh conditions are often required for their generation and thus complicate the sequential reactions to be carried out in situ.[6] Our laboratory plans to broaden the scope of arynes for their capability of reacting with neutral nucleophiles that contain an N-, S-, or O-atom under mild conditions.

Some nucleophiles have been reported to react with arynes and then the third substrates (if any) in situ to yield different classes of organic compounds. For example, Yoshida and co-workers[7] invent a method for the synthesis of benzoxazinones by treating benzyne with Schiff bases in the presence of CO_2. Our group[8] find that arynes react with two equivalents of Schiff bases to produce imidazolidines. Furthermore, reaction of arynes with one equivalent of Schiff bases in the presence of electron-deficient alkenes generates pyrrolidines.[8] Jugé et al.[9] develop an efficient method for the preparation of phosphonium salts by reacting arynes with phosphines. They are also able to synthesize *o*-haloaryl *P*-chirogenic phosphines from phosphine boranes and haloarynes in the presence of *n*-butyllithium.[10] Wang et al.[11] use sulfoxides to react with two equivalents of benzynes and then *N*-methyl isatin in situ. The corresponding spiro[indoline-3,2′-oxiran]-2-ones are produced in a mixture of cis and trans isomers. Moreover, Richmond and Spendel[12] find that benzyne cleaves dialkyl ethers in chloroform. Yoshida and co-workers[13] disclose that two equivalents of arynes react with aldehydes to give *o*-quinones. Herein we report the feasibility of three unprecedented domino reactions. The results can add further value[2,3,6] to arynes for their applications in syntheses of three different classes of compounds shown in Scheme 1.

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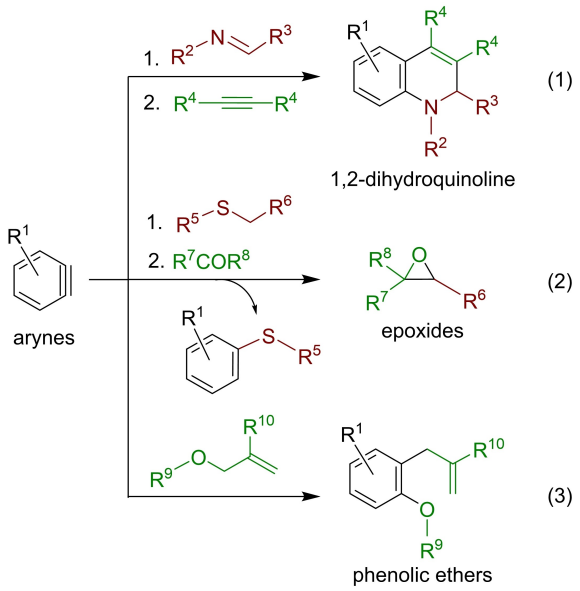
Supporting information for this article is available on the WWW under https://doi.org/10.1002/ejoc.202001499

2. Results and Discussion

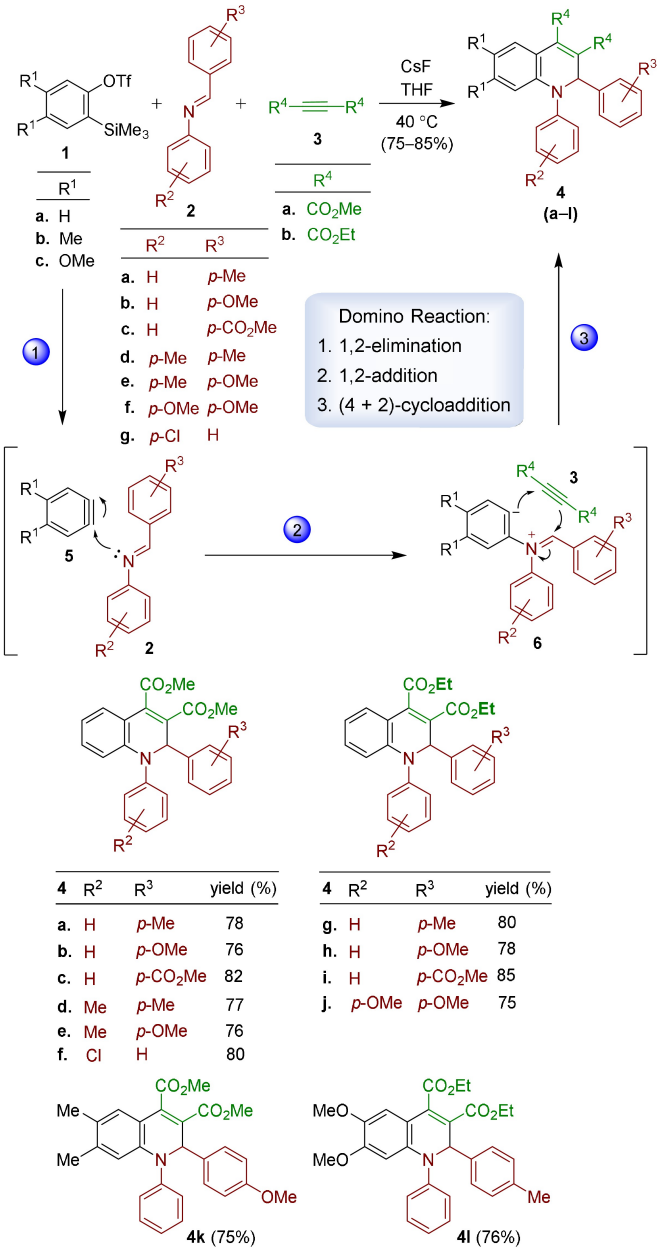
2.1. Synthesis of dihydroquinolines through a domino process including 1,2-elimination, 1,2-addition, and (4 + 2) cycloaddition

A new method as the first category shown in Scheme 2 was developed for the synthesis of dihydroquinolines. It involved the use of silylphenyl triflates **1**, Schiff bases **2**, and alkynes **3** in a ratio of 1:1:1 as the starting materials. This reaction was initiated by use of CsF (1.2 equiv) in THF and carried out at 40 °C for 10–12 hours. Twelve desired 1,2-dihydroquinolines **4a–l** were isolated in 75–85% yields.

In this reaction, aryne intermediates were generated from three different silylphenyl triflates **1a–c**. Various Schiff bases



Scheme 1. New methods for the preparation of dihydroquinolines, *trans*-epoxides, and phenolic ethers by reaction of arynes with Schiff bases/alkynes, thioethers/carbonyl compounds, and allyl ethers, respectively.



Scheme 2. Generation of 1,2-dihydroquinolines 4 and its plausible mechanism.

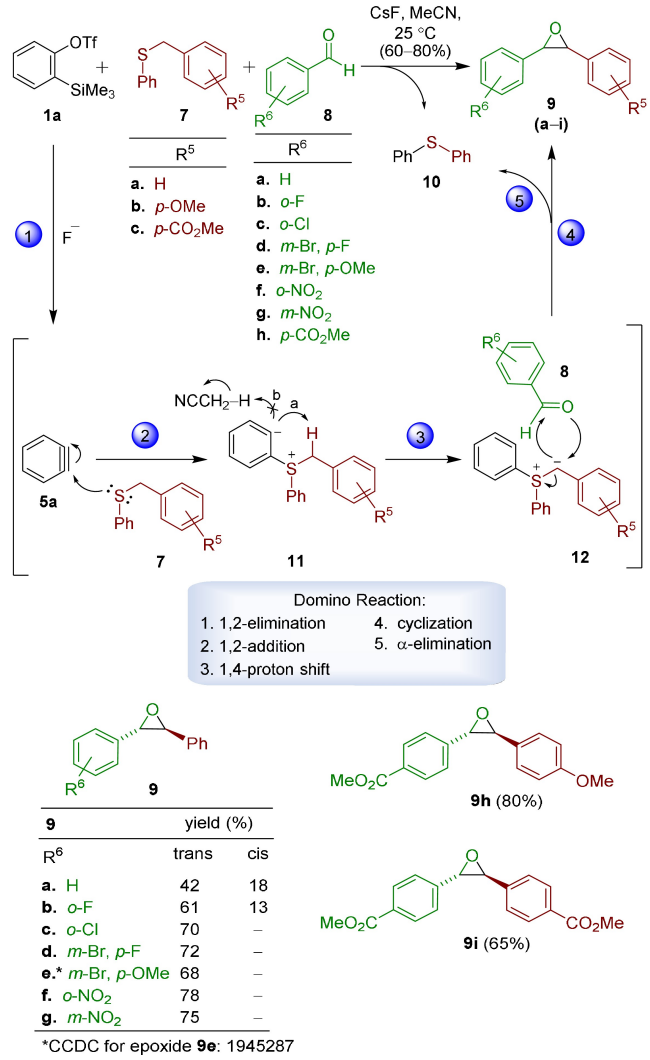
2a–g had an Me, –OMe, or Cl group attached to the phenyl group in the =NPh moiety and an Me, OMe, or CO_2Me group attached to the phenyl group in the N=CHPh moiety. The activated alkynes **3** had two CO_2R groups on both ends of the carbon-carbon triple bond. Such an attachment of electron-withdrawing groups was found necessary to generate the desired products **4** in good yields.

The overall pathway for the formation of dihydroquinolines **4** is shown in Scheme 2. It started with a 1,2-elimination in silylphenyl triflates **1**[7,8] by CsF to generate benzynes **5**, which underwent an established 1,2-nucleophilic addition by Schiff bases **2**.[7,8] Then the resultant betaines **6** performed an unprecedented (4+2) cycloaddition in situ with acetylenes **3** to produce 1,2-dihydroquinolines **4**. Feasibility of this proposed mechanism is supported by the results of Biju et al.[14] who report a related (4+2) cycloaddition between betaines and isatins at their carbonyl group. Furthermore, Coquerel et al.[15] obtain a mechanism and energy profile of the (4+2) cycloaddition between benzyne and *N*-aryl imines by DFT calculation. Their computational outcomes support this type of mechanism proposed by us.

2.2. Preparation of epoxides through a domino process including 1,2-elimination, 1,2-addition, 1,4-proton shift, three-membered ring formation, and α-elimination

In the second category, *trans*-epoxides were formed by reaction of silylphenyl triflates (**1a**) with CsF in acetonitrile and then with phenyl alkyl thioethers **7** and aldehydes **8** in sequence as shown in Scheme 3. After the solution was stirred at 25 °C for 4.0–6.0 hours, *trans*-epoxides **9** were produced as the major or exclusive products; the by-product was biphenyl thioether (**10**).

The methylene units in thioethers **7** were directly connected to a phenyl group (i.e., **7a**), which may be attached by an electron-donating *p*-OMe group (i.e., **7b**) or an electron-withdrawing *p*-CO_2Me group (i.e., **7c**). Most of the epoxides **9** were obtained in the trans form as the exclusive products in 65–80% yields except two epoxides **9a** and **9b**. Their trans isomers were isolated as the major products along with detection of the corresponding cis isomers in 18% yield or less. When electron-withdrawing groups (such as $–NO_2$ and CO_2Me) were attached to the phenyl group in aldehydes **8**, yields of the products **9** were improved.

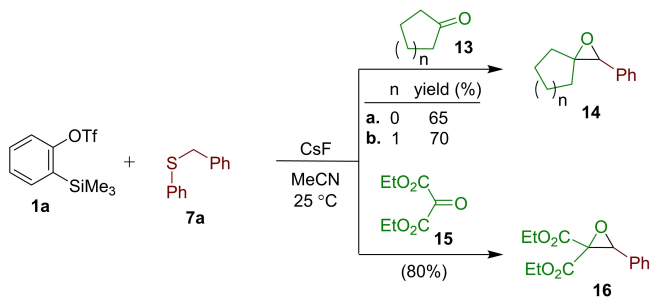


9	yield (%)	
R^6	trans	cis
a. H	42	18
b. *o*-F	61	13
c. *o*-Cl	70	–
d. *m*-Br, *p*-F	72	–
e.* *m*-Br, *p*-OMe	68	–
f. *o*-NO_2	78	–
g. *m*-NO_2	75	–

*CCDC for epoxide **9e**: 1945287

Scheme 3. Generation of *trans*-epoxides **9** and its plausible mechanism.

Furthermore, replacement of aldehydes **8** by cyclic ketones **13a** and **13b** in the reaction mentioned above led to the formation of spiro epoxides **14a** and **14b**, respectively (Scheme 4). Use of diethyl oxomalonate (**15**) with an electron-deficient carbonyl group as the substrate yielded the corresponding epoxide **16** (80% yield).



Scheme 4. Generation of epoxides **14** and **16** from a silylphenyl triflate, thioethers, and ketones.

Two equivalents of arynes would react with aldehydes to give *o*-quinones.[13] The diversity of our reaction shown in Scheme 3 involved three-component coupling processes **5a**+**7**→**11** and **12**+**8**→**9**+**10**. The thioethers **7** were more nucleophilic than aldehydes **8**[16] and thus had priority to react with benzynes **5a**. As a result, we did not detect any quninone as the side product in the reaction mixture.

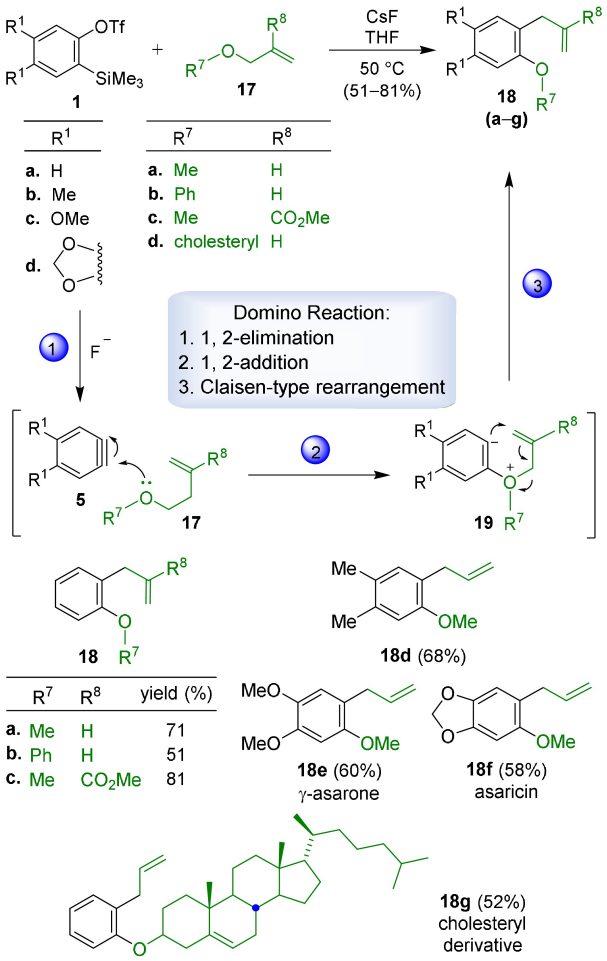
The formation of epoxides **9**, **14**, and **16** includes sequential 1,2-elimination, 1,2-nucleophilic addition, 1,4-proton shift,[16] and the Johnson-Corey-Chaykovsky[17,18] reaction (i.e., three-membered ring formation followed by α-elimination) shown in Scheme 3. Reactions involving arynes as the intermediates are sensitive to the media, such as chloroform and acetonitrile.[19] The protons therein might offer a chance of intermolecular transfer to the betaine intermediates like **11** through the pathway "b". This possible interference, however, was overwhelmed by the intramolecular 1,4-proton shift pathway "a", which led betaines **11** to sulfonium ylides **12**.[16] Then three-membered ring formation followed by α-elimination occurred sequentially to give the epoxides **9** as the major products and biphenyl sulfide (**10**) as the by-product. Peng et al.[20] report that biphenyl sulfides may undergo nucleophilic addition to arynes. This process did not impede the early process of **7**→**11** as biphenyl sulfide was formed at the very last step of **12**→**9**+**10**.

2.3. Synthesis of phenolic ethers through a domino process including 1,2-elimination, 1,2-addition, and Claisen-type rearrangement

After applying the nucleophiles containing *N*- and *S*-atoms, we further explored the possibility of neutral *O*-containing nucleophiles in the third category. As shown in Scheme 5, a mixture containing silylphenyl triflate **1a** (1.0 equiv), CsF (1.2 equiv), and allyl methyl ether **17a** in THF was heated to 50 °C for 26 hours. After separation by flash column chromatography, the product **18a** resulting from benzene-insertion was isolated in 71% yield. When the methyl group in **17a** was replaced by a phenyl group (**17b** with R^7=Ph), *o*-allyl(phenoxyl)benzenes **18b** was obtained in a lower yield (51%) than that of **18a** under thesame reaction conditions. When an electron-withdrawing group (R^8=-CO_2Me) was attached to the allyl methyl ether **17c**, the reaction led to the product **18c** in a very good yield (81%).

Moreover, this reaction was applied to the syntheses of natural products γ-asarone[21] (**18e**) and asaricin[22] (**18f**). Treatment of **1c** (R^1=-OMe) with CsF and **17a** produced γ-asarone in 60% yield; treatment of **1d** (R^1+R^1=-OCH_2O) with CsF and **17a** produced asaricin in 58% yield. The use of allyl cholesteryl ether (**17d**) as the substrate in this reaction led to the formation of the corresponding cholesteryl phenolic ether **18g** in 52% yield.

Greaney et al. discover a benzyne aza-Claisen rearrangement of tertiary allylamines.[23] They use arynes to provide both a pi component and to generate a quaternization *N*-center, which finally leads to anilines as the products. Ethers are less



Scheme 5. Generation of phenolic ethers **18** and its plausible mechanism.

nucleophilic than tertiary amines.[23] However, we were able to allow benzynes **5** to react with alkyl and aryl allylethers **17** to generate phenolic ethers **18** as the final products. Our design of this new reaction involved the generation of oxonium phenyl carbanions **19** as the key intermediate through the process **5** + **17**→**19**. The betaines **19** underwent a charge-accelerated Claisen rearrangement to give allyl *ortho*-phenolic ethers **18**. Consequently, a sequential 1,2-elimination, 1,2-nucleophilic addition, and Claisen-type rearrangement took place through a domino fashion.

2.4. Reaction conditions of the three new reactions

The three new reactions shown in Scheme 1 were performed individually in a single flask. During optimization of the reaction conditions, different combinations of reagents were investigated. Use of the Kobayashi's method[24] for the generation of arynes from 2-silylaryl triflates **1** and CsF provided the best results in these three types of new reactions. Generation of arynes from other compounds, such as halobenzenes, arenediazonium carboxylates, etc., or use of other fluoride sources, such as *n*-Bu_4F, KF, and KF/18-crown-6, were found not applicable to these reactions. Among various solvents, acetonitrile, THF, and 2-Me-THF were found suitable for the generation of the desired products **4**, **9**, and **18**. All of these three reactions proceeded smoothly under moderate temperatures (25–50 °C).

2.5. Comparison of the three reactions in Scheme 1 with the established ones

The new method illustrated in Scheme 2 produced 1,2-dihydroquinolines in a very efficient way. Some 1,2-dihdroquinolines reported in literature possess anti-allergenic, anti-cancer,[25] anti-inflammatory, estrogenic, and psychotropic activities.[26] Several methods have been reported recently for the syntheses of compounds with closely related scaffolds as those in compounds **4**. For example, Li et al.[27] develop a silver-catalyzed process for their preparation from anilines and alkynes. Che et al.[28] report a gold(I)-catalyzed tandem hydroamination-hydroarylation involving the use of aromatic amines and alkynes as the starting materials. Córdova et al.[29] invent an aza-Michael/Aldol reaction for the asymmetric synthesis of 1,2-dihydroquinolidines by using organo catalysts. Tamariz et al.[30] report a solvent-free $MgBr_2$-catalyzed multicomponent reaction. Rueping and co-workers[31] perform an asymmetric synthesis of dihydroquinolines through a combined metal catalysis and organo catalysis process. In comparison with these methods, our newly developed method shown in Scheme 2 did not require a catalyst and proceeded smoothly to give the desired dihydroquinolines in good yields.

Methods for epoxide formation are fruitful in the literature. A comparison of the method (2) in Scheme 3 with some established ones is illustrated in Table 1. Our three-component coupling process involved application of a benzyne intermediate **5a**. It activated thioethers **7** to become zwitterionic intermediates **11** and **12**, in which the Ph_2S^+-moiety functioned as a good leaving group during the conversion of **12**→**9**. With assistance of benzynes, formation of epoxides **9** turned to be feasible at room temperature with good yields. Xu and Tian[18] report a method to generate epoxide from tertiary amines involving benzyne. The reaction requires 60 °C to give epoxides in 28–90 % yields.

For phenolic ether formation shown in Table 1, Sinha et al.[21] report a three-step method with a 21 % overall yield in the absence of metal catalysts. It has been applied to the synthesis of natural products, including γ-asarone. The methods reported separately by Liu et al.[32] and Patil et al.[33] can be carried out at room temperature in the presence of metal catalyst. Our method shown in Scheme 5 required 50 °C for the Claisen-type rearrangement to take place. Without a metal catalyst present, the reaction led to phenolic ethers in good yields.

In the three reactions shown in Scheme 1, phenyl moieties were chosen to be used in substrates including Schiff bases **2**, phenyl alkyl thioethers **7**, and aldehydes **8**. It was due to the formation of zwitterionic intermediates with charges at the appropriate position for ring formations. On the other hand,

Table 1. Comparison of the three methods shown in Scheme 1 with representative and established methods.

Product	Method authors & year	Steps	Temp [°C]	Metal-catalyst	Yields [%]
1,2-dihydrqinoline	Rueping et al. 2014[31]	1	25	yes	47–84
	Tamariz et al. 2013[30]	1	60–90	yes	26–99
	Che et al. 2007[28]	1	150	yes	42–94
	present work	1	40	no	75–85
epoxide	Aggarwal et al. 1996[34]	1	25	yes	38–81
	Hwu et al. 2016[35]	1	25	yes	80–91
	Tian et al. 2019[18]	1	60	no	28–90
	present work	1	25	no	60–80
phenolic ether	Sinha et al. 2002[21]	3	25, 25, 90–120	no	21 overall
	Patil et al. 2017[33]	1	25	yes	41–62
	Liu et al. 2017[32]	1	25	yes	81
	present work	1	50	no	51–81

this concern was not applicable to the substrates including alkynes **3** and ethers **17**, in which alkyl, allyl, electron-withdrawing and -donating groups were involved. While the feasibility of the three reactions was proven, its scope deserves further studies.

3. Conclusion

The three synthetic methods shown in Scheme 1 were initiated by arynes. They underwent nucleophilic attack by a substrate **2**, **7**, or **17** in the sequential step. The aryne moieties became a part of the products including dihydroquinolines in Equation (1) and phenolic ethers in Equation (3). On the other hand, they served as "unsung heroes" during the formation of epoxides in Equation (2): the original aryne moieties were expelled as a moiety in the biphenyl thioether by-products.

The use of arynes to react with neutral nucleophiles containing an *N*, *S*-, or *O*-atom to produce heterocyclic and phenolic products offers the following three advantages. First, the three reactions shown in Scheme 1 involve domino processes, which require simple laboratory manipulations. Second, isolation of the intermediates is no longer necessary and purification procedures are simplified. Third, the desired products are often generated in good-to-high yields under mild conditions.

Experimental Section

General Information: All reactions were carried out in oven-dried glassware (120 °C) under an atmosphere of nitrogen unless as indicated otherwise. Dichloromethane, ethyl acetate, and hexanes from Mallinckrodt Chemical Co. were dried and distilled from CaH_2. Tetrahydrofuran (THF) from Mallinckrodt Chemical Co. was dried by distillation from sodium and benzophenone under an atmosphere of nitrogen. The reagents purchased from Alfa Aesar included diethyl acetylenedicarboxylate, diethyl oxomalonate, dimethyl acetylenedicarboxylate (DMAD), 4-methoxybenzaldehyde, 4-methylbenzaldehyde, and methyl 4-formylbenzoate. The reagents purchased from Sigma-Aldrich included (allyloxy)benzene, benzaldehyde, 3-bromo-4-fluorobenzaldehyde, 3-bromo-4-methoxybenzaldehyde, 2-chlorobenzaldehyde, 2-fluorobenzaldehyde, 3-methoxy-1-propene, 2-nitrobenzaldehyde, and 3-nitrobenzaldehyde. The reagents purchased from Acros included aniline, cesium fluoride (CsF), 4-chloroaniline, 4-methoxyaniline, and 4-methylaniline. The reagents purchased from Tokyo Chemical Industry Co. included cyclohexanone, cyclopentanone, 4,5-dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, 4,5-dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate, and 2-(trimethylsilyl)phenyl trifluoromethanesulfonate.

Analytical thin layer chromatography (TLC) was performed on precoated plates (silica gel 60 F-254). Purification by gravity and dry column chromatography was carried out by use of Silicycle ultrapure silica gel (particle size 40–63 μM, 230–400 mesh). HPLC analysis was performed on high performance liquid chromatography with UV detection monitored at 254 nm by use of Thermo 5 μm Hypersil ODS (250 mm × 4.6 mm i.d.) column with acetonitrile and water as the eluent.

Infrared spectra (IR) were measured on a Fourier transform infrared spectrometer (FT-IR). Absorption intensities are recorded by the following abbreviations: s, strong; m, medium; and w, weak. Proton NMR spectra were obtained on 400 MHz and 600 MHz spectrometers by use of chloroform-*d* ($CDCl_3$) as the solvent. Proton NMR chemical shifts were referenced to the residual protonated solvent (δ 7.24 ppm for chloroform). Carbon-13 NMR spectra were obtained on 100 MHz and 150 MHz spectrometers by use of chloroform-*d* ($CDCl_3$) as the solvents. Carbon-13 chemical shifts were referenced to the center of the $CDCl_3$ triplet (δ 77.0 ppm). Multiplicities are recorded by the following abbreviations: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; q, quartet; m, multiplet; and *J*, coupling constant (hertz). High-resolution mass spectra (HRMS) were measured on an instrument by use of a time-of-flight mass analyzer (TOF) with electrospray ionization (ESI).

Standard Procedure 1 for the Single-Flask Synthesis of 1,2-Dihydroquinolines. To a stirred solution of 2-silylphenyl triflates **1** (1.0 equiv) in dry THF (1.5–3.5 mL) was added Schiff bases **2** (1.1 equiv), alkynes **3** (1.2 equiv), and CsF (1.2 equiv) at room

temperature under nitrogen atmosphere. After the reaction mixture was stirred at 40 °C for 10–12 h, it was cooled to room temperature. The reaction mixture was quenched with water (5.0 mL) and then extracted with EtOAc (3×5.0 mL). The combined organic layers were dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to afford the products. It was then purified by use of column chromatography on silica gel with EtOAc in hexanes as the eluent to give the desired 1,2-dihydroquinolines **4**.

Standard Procedure 2 for the Single-Flask Synthesis of Epoxides. To a stirred solution of 2-silylphenyl triflate **1a** (1.0 equiv) in dry acetonitrile (2.0–3.5 mL) was added thioether **7** (1.1 equiv), aldehydes/ketones **8**, **13**, or **15** (1.2 equiv), and CsF (1.2 equiv) at room temperature under nitrogen atmosphere. After the reaction mixture was stirred at 25 °C for 4.0–6.0 h, it was quenched with water (5.0 mL) and then extracted with EtOAc (3×5.0 mL). The combined organic layers were dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to afford the products. It was then purified by use of column chromatography on silica gel with EtOAc in hexanes as the eluent to give the desired epoxides **9**, **14**, and **16**.

Standard Procedure 3 for the Single-Flask Synthesis of Phenolic Ethers. To a stirred solution of 2-silylphenyl triflate **1** (1.0 equiv) in dry THF (2.5–5.0 mL) was added allyl ethers **17** (2.0 equiv) and CsF (1.2 equiv) at room temperature under nitrogen atmosphere. After the reaction mixture was stirred at 50 °C for 24–30 h, it was cooled to room temperature. The reaction mixture was quenched with water (5.0 mL) and then extracted with EtOAc (3×5.0 mL). The combined organic layers were dried over $MgSO_4$ (s), filtered, and concentrated under reduced pressure to afford the products. It was then purified by use of column chromatography on silica gel with EtOAc in hexanes as the eluent to give the desired phenolic ethers **18**.

Experimental Procedures for the Syntheses of 1,2-Dihydroquinolines 4, Epoxides 9, 14, 16, and Phenolic Ethers 18:

3,4-Dimethoxycarbonyl-2-(*p*-methylphenyl)-*N*-phenyl-1,2-dihydroquinoline (4a). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (343 mg, 1.15 mmol, 1.0 equiv), Schiff base **2a**[36] (246 mg, 1.26 mmol, 1.1 equiv), DMAD (**3a**, 196 mg, 1.38 mmol, 1.2 equiv), and CsF (210 mg, 1.38 mmol, 1.2 equiv) in THF (3.5 mL). After the reaction mixture was stirred at 40 °C for 10 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4a** (371 mg, 0.892 mmol) in 78% yield as a yellow oil: TLC R_f = 0.40 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.47–7.31 (m, 4 H, 4×ArH), 7.29–7.26 (m, 2 H, 2×ArH), 7.11 (d, J = 7.2 Hz, 2 H, 2×ArH), 6.97 (t, J = 7.2 Hz, 1 H, ArH), 6.76 (t, J = 7.2 Hz, 1 H, ArH), 6.60 (d, J = 7.2 Hz, 2 H, 2×ArH), 5.20 (s, 1 H, NCHAr), 3.70 (s, 3 H, CO_2CH_3), 3.61 (s, 3 H, CO_2CH_3), 2.15 (s, 3 H, $ArCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.4 (C=O), 163.3 (C=O), 145.0, 140.1, 138.1, 136.0, 134.9, 130.0, 129.4, 128.2, 128.1, 126.5, 124.3, 123.1, 121.1, 119.1, 117.7, 115.8, 68.2 (NCHAr), 52.2 (CO_2CH_3), 51.9 (CO_2CH_3), 22.0 ($ArCH_3$); IR (neat) 2952 (w), 1734 (s, C=O), 1508 (m), 1437 (w), 1249 (m), 1171 (w), 1032 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+Na]^+$ calcd for $C_{26}H_{23}NO_4$ + Na 436.1524, found 436.1526.

3,4-Dimethoxycarbonyl-2-(*p*-methoxyphenyl)-*N*-phenyl-1,2-dihydroquinoline (4b). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (53.5 mg, 0.179 mmol, 1.0 equiv), Schiff base **2b**[36] (41.6 mg, 0.197 mmol, 1.1 equiv), DMAD (**3a**, 30.5 mg, 0.215 mmol, 1.2 equiv), and CsF (32.6 mg, 0.215 mmol, 1.2 equiv) in THF (1.5 mL). After the reaction mixture was stirred at 40 °C for 12 h, it was quenched and worked up. The residue was purified by use of column chromatography (10⊥% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4b** (58.1 mg, 0.136 mmol) in 76% yield as a colorless oil: TLC R_f = 0.35 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.42–7.30 (m, 4 H, 4×ArH), 7.10 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.00 (t, J = 7.2 Hz, 1 H, ArH), 6.80 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.66 (t, J = 7.2 Hz, 1 H, ArH), 6.61 (d, J = 7.6 Hz, 2 H, 2×ArH), 5.28 (s, 1 H, NCHAr), 3.84 (s, 3 H, $ArOCH_3$), 3.78 (s, 3 H, CO_2CH_3), 3.62 (s, 3 H, CO_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.3 (C=O), 163.2 (C=O), 159.1, 144.9, 140.1, 138.1, 135.6, 130.3, 129.9, 128.8, 126.4, 124.3, 123.9, 121.8, 119.8, 118.2, 116.0, 113.5, 68.1 (NCHAr), 55.1 ($ArOCH_3$), 52.3 (CO_2CH_3), 51.9 (CO_2CH_3); IR (neat) 2952 (w), 1732 (s, C=O), 1602 (m), 1509 (m), 1248 (m), 1171 (w), 1032 (w), 748 (w) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{26}H_{23}NO_5$ + H 430.1654, found 430.1655.

3,4-Dimethoxycarbonyl-2-[(*p*-methoxycarbonyl)phenyl]-*N*-phenyl-1,2-dihydroquinoline (4c). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (56.4 mg, 0.189 mmol, 1.0 equiv), Schiff base **2c**[37] (49.7 mg, 0.208 mmol, 1.1 equiv), DMAD (**3a**, 32.1 mg, 0.226 mmol, 1.2 equiv), and CsF (34.3 mg, 0.226 mmol, 1.2 equiv) in THF (1.5 mL). After the reaction mixture was stirred at 40 °C for 10 h, it was quenched and worked up. The residue was purified by use of column chromatography (8.0% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4c** (70.9 mg, 0.155 mmol) in 82% yield as a yellow oil: TLC R_f = 0.40 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.05 (d, J = 7.6 Hz, 1 H, ArH), 7.94 (d, J = 7.6 Hz, 1 H, ArH), 7.84–7.81 (m, 1 H, ArH), 7.42–7.33 (m, 4 H, 4×ArH), 7.08 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.97 (t, J = 7.2 Hz, 1 H, ArH), 6.77 (t, J = 7.2 Hz, 1 H, ArH), 6.59 (d, J = 7.6 Hz, 2 H, 2×ArH), 5.37 (s, 1 H, NCHAr), 3.85 (s, 3 H, $ArCO_2CH_3$), 3.78 (s, 3 H, CO_2CH_3), 3.64 (s, 3 H, CO_2CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.5 (C=O), 164.0 (C=O), 163.7 (C=O), 145.3, 143.9, 140.0, 136.2, 130.3, 130.0, 129.9, 128.8, 128.1, 126.6, 124.3, 123.8, 122.0, 119.0, 118.3, 116.2, 68.3 (NCHAr), 52.2 ($ArCO_2CH_3$), 51.3 (CO_2CH_3), 51.0 (CO_2CH_3); IR (neat) 2952 (w), 1735 (s, C=O), 1601 (w), 1505 (m), 1437 (w), 1249 (m), 1171 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{23}NO_6$ + H 458.1603, found 458.1602.

3,4-Dimethoxycarbonyl-2,*N*-di(*p*-methylphenyl)-1,2-dihydroquinoline (4d). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (328 mg, 1.09 mmol, 1.0 equiv), Schiff base **2d**[38] (252 mg, 1.21 mmol, 1.1 equiv), DMAD (**3a**, 187 mg, 1.31 mmol, 1.2 equiv), and CsF (201 mg, 1.31 mmol, 1.2 equiv) in THF (3.5 mL). After the reaction mixture was stirred at 40 °C for 12 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4d** (362 mg, 0.847 mmol) in 77% yield as a colorless oil: TLC R_f = 0.35 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.87 (d, J = 7.6 Hz, 1 H, ArH), 7.39–7.25 (m, 6 H, 6×ArH), 7.23–7.15 (m, 4 H, 4×ArH), 6.97 (t, J = 7.2 Hz, 1 H, ArH), 5.20 (s, 1 H, NCHAr), 3.75 (s, 3 H, CO_2CH_3), 3.65 (s, 3 H, CO_2CH_3), 2.16 (s, 3 H, $ArCH_3$), 2.04 (s, 3 H, $ArCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.8 (C=O), 163.0 (C=O), 145.3, 140.0, 138.4, 136.3, 135.0, 130.6, 130.1, 129.9, 129.3, 128.8, 126.7, 124.3, 123.2, 119.5, 118.2, 116.0, 68.1 (NCHAr), 52.5 (CO_2CH_3), 52.3 (CO_2CH_3), 21.5 ($ArCH_3$), 20.7 ($ArCH_3$); IR (neat) 2952 (w), 1735 (s, C=O), 1602 (w), 1504 (m), 1248 (m), 1171 (w), 1032 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{27}H_{25}NO_4$ + H 428.1861, found 428.1865.

3,4-Dimethoxycarbonyl-2-(*p*-methoxyphenyl)-*N*-(*p*-methylphenyl)-1,2-dihydroquinoline (4e). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (55.1 mg, 0.184 mmol, 1.0 equiv), Schiff base **2e**[39] (45.7 mg, 0.203 mmol, 1.1 equiv), DMAD (**3a**, 31.3 mg, 0.221 mmol, 1.2 equiv), and CsF (35.5 mg, 0.221 mmol, 1.2 equiv) in THF (2.0 mL). After the reaction mixture was stirred at 40 °C for 12 h, it was quenched and worked up. The residue was purified by use of column chromatography

(8.0% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4e** (62.2 mg, 0.140 mmol) in 76% yield as a yellow oil: TLC R_f = 0.45 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, J = 7.6 Hz, 1 H, ArH), 7.48 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.40–7.23 (m, 6 H, 6×ArH), 7.00 (t, J = 7.2 Hz, 1 H, ArH), 6.80 (d, J = 7.6 Hz, 2 H, 2×ArH), 5.36 (s, 1 H, NCHAr), 3.82 (s, 3 H, $ArOCH_3$), 3.69 (s, 3 H, CO_2CH_3), 3.62 (s, 3 H, CO_2CH_3), 2.58 (s, 3 H, $ArCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.6 (C=O), 163.8 (C=O), 158.9, 145.5, 140.0, 136.1, 135.4, 130.8, 130.1, 129.9, 128.9, 125.8, 124.6, 123.8, 119.3, 118.6, 116.6, 114.1, 68.4 (NCHAr), 55.4 ($ArOCH_3$), 52.8 (CO_2CH_3), 52.2 (CO_2CH_3), 21.8 ($ArCH_3$); IR (neat) 2953 (w), 1735 (s, C=O), 1601 (m), 1504 (m), 1249 (m), 1172 (m), 1032 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{27}H_{25}NO_5$ + H 444.1811, found 444.1813.

***N*-(*p*-Chlorophenyl)-3,4-dimethoxycarbonyl-2-phenyl-1,2-dihydroquinoline (4f)**. The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (342 mg, 1.14 mmol, 1.0 equiv), Schiff base **2g**[40] (272 mg, 1.26 mmol, 1.1 equiv), DMAD (**3a**, 195 mg, 1.37 mmol, 1.2 equiv), and CsF (208 mg, 1.37 mmol, 1.2 equiv) in THF (3.5 mL). After the reaction mixture was stirred at 40 °C for 10 h, it was quenched and worked up. The residue was purified by use of column chromatography (8.0% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4f** (398 mg, 0.917 mmol) in 80% yield as a yellow oil: TLC R_f = 0.45 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.39-7.33 (m, 5 H, 5×ArH), 7.27 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.20–7.15 (m, 4 H, 4×ArH), 6.96 (t, J = 7.2 Hz, 1 H, ArH), 5.28 (s, 1 H, NCHAr), 3.85 (s, 3 H, CO_2CH_3), 3.77 (s, 3 H, CO_2CH_3); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 164.1 (C=O), 163.5 (C=O), 145.5, 141.2, 139.8, 135.9, 130.4,129.8, 128.8, 128.2, 127.2, 126.7, 126.4, 124.4, 123.9, 120.1, 118.1, 116.3, 68.6 (NCHAr), 52.4 (CO_2CH_3), 52.1 (CO_2CH_3); IR (neat) 2955 (w), 1733 (s, C=O), 1507 (m), 1357 (m), 1249 (m), 1171 (m), 1032 (m), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{25}H_{20}ClNO_4$ + H 434.1159, found 434.1156.

3,4-Diethoxycarbonyl-2-(*p*-methylphenyl)-*N*-phenyl-1,2-dihydroquinoline (4g). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (55.3 mg, 0.185 mmol, 1.0 equiv), Schiff base **2a** (39.6 mg, 0.203 mmol, 1.1 equiv), diethyl acetylenedicarboxylate (**3b**, 37.8 mg, 0.222 mmol, 1.2 equiv), and CsF (33.7 mg, 0.222 mmol, 1.2 equiv) in THF (2.0 mL). After the reaction mixture was stirred at 40 °C for 12 h, it was quenched and worked up. The residue was purified by use of column chromatography (8.0% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4g** (65.6 mg, 0.148 mmol) in 80% yield as a colorless oil: TLC R_f = 0.45 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.47–7.41 (m, 4 H, 4×ArH), 7.39–7.32 (m, 2 H, 2×ArH), 7.17 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.03 (t, J = 7.2 Hz, 1 H, ArH), 6.76 (t, J = 7.2 Hz, 1 H, ArH), 6.61 (d, J = 7.6 Hz, 2 H, 2×ArH), 5.22 (s, 1 H, NCHAr), 4.25–4.21 (m, 2 H, CO_2CH_2), 4.17–4.13 (m, 2 H, CO_2CH_2), 2.18 (s, 3 H, $ArCH_3$), 1.15 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.11 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.5 (C=O), 163.3 (C=O), 145.0, 140.1, 138.2, 136.4, 135.0, 130.1, 129.9, 129.3, 128.8, 126.7, 124.3, 123.9, 120.9, 119.9, 118.1, 116.1, 68.2 (NCHAr), 61.2 (CO_2CH_2), 61.3 (CO_2CH_2), 21.9 ($ArCH_3$), 14.4 (CH_2CH_3), 14.3 (CH_2CH_3); IR (neat) 2952 (w), 1733 (s, C=O), 1602 (w), 1507 (m), 1249 (m), 1171 (w), 1031 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{28}H_{27}NO_4$ + H 422.2018, found 442.2014.

3,4-Diethoxycarbonyl-2-(*p*-methoxyphenyl)-*N*-phenyl-1,2-dihydroquinoline (4h). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (301 mg, 1.01 mmol, 1.0 equiv), Schiff base **2b** (234 mg, 1.11 mmol, 1.1 equiv), diethyl acetylenedicarboxylate (**3b**, 205 mg, 1.21 mmol, 1.2 equiv), and CsF (183 mg, 1.21 mmol, 1.2 equiv) in THF (3.5 mL). After the reaction mixture was stirred at 40 °C for 11 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4h** (359 mg, 0.785 mmol) in 78% yield as a yellow oil: TLC R_f = 0.30 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.42–7.32 (m, 4 H, 4×ArH), 7.07 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.99 (t, J = 7.2 Hz, 1 H, ArH), 6.78 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.68 (t, J = 7.2 Hz, 1 H, ArH), 6.60 (d, J = 7.6 Hz, 2 H, 2×ArH), 5.22 (s, 1 H, NCHAr), 4.20–4.13 (m, 2 H, CO_2CH_2), 4.09–4.02 (m, 2 H, CO_2CH_2), 3.84 (s, 3 H, $ArOCH_3$), 1.28 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.15 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 163.8 (C=O), 163.1 (C=O), 159.4, 144.6, 140.3, 137.7, 135.2, 130.0, 129.4, 128.8, 125.5, 124.3, 123.8, 121.8, 119.3, 118.2, 116.0, 114.1, 68.2 (NCHAr), 61.1 (CO_2CH_2), 60.0 (CO_2CH_2), 55.1 ($ArOCH_3$), 14.0 (CH_2CH_3), 13.9 (CH_2CH_3); IR (neat) 2953 (w), 1731 (s, C=O), 1601 (m), 1505 (m), 1249 (m), 1171 (w), 1032 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{28}H_{27}NO_5$ + H 458.1967, found 458.1965.

3,4-Diethoxycarbonyl-2-[(*p*-methoxycarbonyl)phenyl]-*N*-phenyl-1,2-dihydroquinoline (4i). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (54.3 mg, 0.182 mmol, 1.0 equiv), Schiff base **2c** (48.1 mg, 0.201 mmol, 1.1 equiv), diethyl acetylenedicarboxylate (**3b**, 37.1 mg, 0.218 mmol, 1.2 equiv), and CsF (33.1 mg, 0.218 mmol, 1.2 equiv) in THF (1.5 mL). After the reaction mixture was stirred at 40 °C for 12 h, it was quenched and worked up. The residue was purified by use of column chromatography (8.0% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4i** (75.1 mg, 0.154 mmol) in 85% yield as a yellow oil: TLC R_f = 0.40 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.08 (d, J = 7.6 Hz, 1 H, ArH), 8.00 (d, J = 7.6 Hz, 1 H, ArH), 7.83 (d, J = 7.6 Hz, 1 H, ArH), 7.46–7.39 (m, 4 H, 4×ArH), 7.08 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.97 (t, J = 7.2 Hz, 1 H, ArH), 6.62–6.55 (m, 3 H, 3×ArH), 5.41 (s, 1 H, NCHAr), 4.31–4.24 (m, 2 H, CO_2CH_2), 4.08–4.02 (m, 2 H, CO_2CH_2), 3.83 (s, 3 H, CO_2CH_3), 1.29 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.09 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.4 (C=O), 164.1 (C=O), 163.2 (C=O), 144.6, 143.2, 140.1, 135.5, 130.1, 129.6, 128.6, 128.1, 127.9, 126.8, 124.4, 123.9, 121.8, 119.1, 118.0, 116.4, 68.9 (NCHAr), 61.1 (CO_2CH_2), 60.0 (CO_2CH_2), 52.2 (CO_2CH_3), 14.0 (CH_2CH_3), 13.9 (CH_2CH_3); IR (neat) 2953 (m), 1733 (s, C=O), 1612 (m), 1509 (m), 1437 (w), 1249 (s), 1031 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{29}H_{27}NO_6$ + H 486.1916, found 486.1915.

3,4-Diethoxycarbonyl-2,*N*-di(*p*-methoxyphenyl)-1,2-dihydroquinoline (4j). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1a** (52.2 mg, 0.175 mmol, 1.0 equiv), Schiff base **2f**[38] (45.6 mg, 0.192 mmol, 1.1 equiv), diethyl acetylenedicarboxylate (**3b**, 35.9 mg, 0.210 mmol, 1.2 equiv), and CsF (31.8 mg, 0.210 mmol, 1.2 equiv) in THF (1.5 mL). After the reaction mixture was stirred at 40 °C for 10 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4j** (63.9 mg, 0.131 mmol) in 75% yield as a yellow oil: TLC R_f = 0.30 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.84 (d, J = 7.2 Hz, 1 H, ArH), 7.42-7.35 (m, 4 H, 4×ArH), 7.22 (d, J = 7.8 Hz, 2 H, 2×ArH), 7.10 (t, J = 7.2 Hz, 2 H, 2×ArH), 6.78 (d, J = 7.2 Hz, 1 H, ArH), 6.64 (d, J = 7.8 Hz, 2 H, 2×ArH), 5.22 (s, 1 H, NCHAr), 4.28–4.24 (m, 2 H, CO_2CH_2), 4.15–4.12 (m, 2 H, CO_2CH_2), 3.82 (s, 3 H, $ArOCH_3$), 3.70 (s, 3 H, $ArOCH_3$), 1.30 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.15 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 163.5 (C=O), 162.9 (C=O), 159.2, 159.0, 144.0, 142.2, 138.1, 135.1, 129.7, 128.0, 126.2, 124.5, 123.0, 120.0, 118.0, 116.0, 113.9, 112.3, 68.1 (NCHAr), 61.5 (CO_2CH_2), 61.2 (CO_2CH_2), 55.3 ($ArOCH_3$), 55.2 ($ArOCH_3$), 14.1 (CH_2CH_3), 14.0 (CH_2CH_3); IR (neat) 2955 (m), 1738 (s, C=O), 1505 (m), 1370 (m), 1248 (s), 1172 (m), 1033 (m), 749 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{29}H_{29}NO_6$ + H 488.2073, found 488.2066.

3,4-Dimethoxycarbonyl-6,7-dimethyl-2-(*p*-methoxyphenyl)-*N*-phenyl-1,2-dihydroquinoline (4k). The Standard Procedure 1 was

followed by use of 2-silylphenyl triflate **1b** (53.5 mg, 0.179 mmol, 1.0 equiv), Schiff base **2b** (41.6 mg, 0.197 mmol, 1.1 equiv), DMAD (**3a**, 30.5 mg, 0.215 mmol, 1.2 equiv), and CsF (32.6 mg, 0.215 mmol, 1.2 equiv) in THF (1.5 mL). After the reaction mixture was stirred at 40 °C for 10 h, it was quenched and worked up. The residue was purified by use of column chromatography (8.0% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4k** (61.5 mg, 0.134 mmol) in 75% yield as a colorless oil: TLC R_f = 0.45 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.43 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.17–7.13 (m, 3 H, 3×ArH), 7.05 (s, 1 H, ArH), 6.83 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.74 (t, J = 7.2 Hz, 1 H, ArH), 6.61 (d, J = 7.2 Hz, 2 H, 2×ArH), 5.30 (s, 1 H, NCHAr), 3.83 (s, 3 H, $ArOCH_3$), 3.72 (s, 3 H, CO_2CH_3), 3.65 (s, 3 H, CO_2CH_3), 2.30 (s, 3 H, $ArCH_3$), 2.10 (s, 3 H, $ArCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 165.2 (C=O), 163.4 (C=O), 158.2, 145.5, 138.1, 135.9, 135.3, 135.1, 130.2,129.8, 127.5, 126.2, 125.8, 121.9, 120.8, 119.8, 118.7, 114.5, 68.6 (NCHAr), 55.5 ($ArOCH_3$), 52.5 (CO_2CH_3), 52.3 (CO_2CH_3), 19.8 ($ArCH_3$), 18.8 ($ArCH_3$); IR (neat) 2953 (m), 1732 (s, C=O), 1601 (m), 1507 (m), 1248 (m), 1171 (m), 1031 (m), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{28}H_{27}NO_5$ + H 458.1967, found 458.1965.

6,7-Dimethoxy-3,4-dimethoxycarbonyl-2-(*p*-methylphenyl)-*N*-phenyl-1,2-dihydroquinoline (4l). The Standard Procedure 1 was followed by use of 2-silylphenyl triflate **1c** (54.7 mg, 0.183 mmol, 1.0 equiv), Schiff base **2a** (39.3 mg, 0.201 mmol, 1.1 equiv), diethyl acetylenedicarboxylate (**3b**, 37.2 mg, 0.219 mmol, 1.2 equiv), and CsF (33.2 mg, 0.219 mmol, 1.2 equiv) in THF (1.5 mL). After the reaction mixture was stirred at 40 °C for 10 h, it was quenched and worked up. The residue was purified by use of column chromatography (12% EtOAc in hexanes as the eluent) to give 1,2-dihydroquinoline **4l** (69.8 mg, 0.139 mmol) in 76% yield as a colorless oil: TLC R_f = 0.30 (25% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.35 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.27–7.23 (m, 2 H, 2×ArH), 7.18 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.80 (s, 1 H, ArH), 6.73 (s, 1 H, ArH), 6.67 (t, J = 7.4 Hz, 1 H, ArH), 6.60 (d, J = 7.4 Hz, 2 H, 2×ArH), 5.29 (s, 1 H, NCHAr), 4.29–4.27 (m, 2 H, CO_2CH_2), 4.18–4.16 (m, 2 H, CO_2CH_2), 3.83 (s, 3 H, $ArOCH_3$), 3.72 (s, 3 H, $ArOCH_3$), 2.34 (s, 3 H, $ArCH_3$), 1.30 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$), 1.17 (t, J = 7.2 Hz, 3 H, $CO_2CH_2CH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.6 (C=O), 163.3 (C=O), 152.2, 149.8, 145.0, 140.0, 136.4, 135.5, 133.9, 130.3, 129.8, 128.7, 126.6, 121.2, 119.7, 117.9, 111.4, 110.1, 68.2 (NCHAr), 61.9 (CO_2CH_2), 61.4 (CO_2CH_2), 55.7 ($ArOCH_3$), 55.3 ($ArOCH_3$), 21.3 ($ArCH_3$), 14.3 (CH_2CH_3), 13.9 (CH_2CH_3); IR (neat) 2952 (m), 1733 (s, C=O), 1602 (m), 1510 (m), 1248 (m), 1171 (m), 1032 (m), 748 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{30}H_{31}NO_6$ + H 502.2229, found 502.2228.

1,2-Diphenyloxirane (9a). The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (152 mg, 0.511 mmol, 1.0 equiv), thioether **7a**[41] (112 mg, 0.562 mmol, 1.1 equiv), benzaldehyde (**8a**, 65.1 mg, 0.613 mmol, 1.2 equiv), and CsF (93.5 mg, 0.615 mmol, 1.2 equiv) in acetonitrile (2.5 mL). After the reaction mixture was stirred at 25 °C for 6.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9a** (41.9 mg, 0.214 mmol) in 42% and *cis*-epoxide **9a** (18.0 mg, 0.091 mmol) in 18% yield as colorless oil: TLC R_f = 0.34 for *trans*-epoxide **9a** and R_f = 0.35 for *cis*-epoxide **9a** (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) for *trans*-epoxide **9a**: δ 7.48–7.28 (m, 10 H, 10×ArH), 3.88 (s, 2 H, 2×CHPh); for *cis*-epoxide **9a**: δ 7.18–7.09 (m, 10 H, 10×ArH), 4.36 (s, 2 H, 2×CHPh). These spectroscopic data are in accordance with the literature values.[42]

2-(2-Fluorophenyl)-3-phenyloxirane (9b). The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (110 mg, 0.236 mmol, 1.0 equiv), thioether **7a** (52.1 mg, 0.259 mmol, 1.1 equiv), 2-fluorobenzaldehyde (**8b**, 35.1 mg, 0.283 mmol, 1.2 equiv), and CsF (42.9 mg, 0.286 mmol, 1.2 equiv) in acetonitrile (2.0 mL). After the reaction mixture was stirred at 25 °C for 6.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9b** (30.8 mg, 0.144 mmol) in 61% and *cis*-epoxide **9b** (6.51 mg, 0.031 mmol) in 13% yield as colorless oil: TLC R_f = 0.45 for *trans*-**9b** and R_f = 0.46 for *cis*-**9b** (5.0⊥% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) *trans*-epoxide **9b**: δ 7.42–7.22 (m, 9 H, 9×ArH), 4.21 (d, J = 2.0 Hz, 1 H, CHArF), 3.81 (d, J = 2.0 Hz, 1 H, CHPh); for *cis*-epoxide **9b**: δ 7.42–7.22 (m, 9 H, 10×ArH), 4.26 (d, J = 4.0 Hz, 1 H, CHArF), 3.81 (d, J = 4.0 Hz, 1 H, CHPh). These spectroscopic data are in accordance with the literature values.[43]

***trans*-2-(2-Chlorophenyl)-3-phenyloxirane (9c)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (108 mg, 0.362 mmol, 1.0 equiv), thioether **7a** (79.7 mg, 0.398 mmol, 1.1 equiv), 2-chlorobenzaldehyde (**8c**, 61.3 mg, 0.438 mmol, 1.2 equiv), and CsF (67.1 mg, 0.441 mmol, 1.2 equiv) in acetonitrile (2.0 mL). After the reaction mixture was stirred at 25 °C for 5.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9c** (58.5 mg, 0.253 mmol) in 70% yield as a colorless oil: TLC R_f = 0.35 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.42–7.22 (m, 9 H, 9×ArH), 4.24 (d, J = 2.0 Hz, 1 H, CHArCl), 3.76 (d, J = 2.0 Hz, 1 H, CHPh). These spectroscopic data are in accordance with the literature values.[44]

***trans*-2-(3-Bromo-4-fluorophenyl)-3-phenyloxirane (9d)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (326 mg, 1.09 mmol, 1.0 equiv), thioether **7a** (240 mg, 1.20 mmol, 1.1 equiv), 3-bromo-4-fluorobenzaldehyde (**8d**, 265 mg, 1.30 mmol, 1.2 equiv), and CsF (203 mg, 1.34 mmol, 1.2 equiv) in acetonitrile (3.5 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9d** (230 mg, 0.785 mmol) in 72% yield as yellow solids: TLC R_f = 0.35 (7.0% EtOAc in hexanes as the eluent); mp (recrystallized from EtOH) 149.4–151.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.44–7.24 (m, 6 H, 6×ArH), 6.96 (d, J = 6.8 Hz, 2 H, 2×ArH), 4.09 (s, 1 H, CHArBrF), 3.99 (s, 1 H, CHPh); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 160.4 (d, J_{CF} = 234), 137.4, 135.2, 132.1 (d, J_{CF} = 4.7), 128.8, 128.2, 125.6, 124.3 (d, J_{CF} = 6.4), 117.3 (d, J_{CF} = 22.8), 110.6 (d, J_{CF} = 22.6), 64.4 (CAr), 63.9 (CPh); IR (neat) 2955 (m), 1594 (s), 1502 (m), 1251 (s), 1180 (m), 1118 (m), 1033 (m), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{14}H_{10}BrFO$ + H 292.9977, found 292.9975.

***trans*-2-(3-Bromo-4-methoxyphenyl)-3-phenyloxirane (9e)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (342 mg, 1.15 mmol, 1.0 equiv), thioether **7a** (252 mg, 1.26 mmol, 1.1 equiv), 3-bromo-4-methoxybenzaldehyde (**8e**, 296 mg, 1.38 mmol, 1.2 equiv), and CsF (218 mg, 1.44 mmol, 1.2 equiv) in acetonitrile (3.5 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9e** (237 mg, 0.779 mmol) in 68% yield as yellow solids: TLC R_f = 0.30 (7.0% EtOAc in hexanes as the eluent); mp (recrystallized from EtOH) 156.8–158.4 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.52 (s, 1 H, ArH), 7.40–7.25 (m, 6 H, 6×ArH), 6.90 (d, J = 8.4 Hz, 1 H, ArH), 3.91 (s, 3 H, $ArOCH_3$), 3.82 (s, 1 H, CHArBr), 3.79 (s, 1 H, CHPh); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 155.9, 136.7, 130.6, 130.3, 128.5, 128.3, 126.8, 125.8, 111.9, 111.7, 62.7 (CAr), 61.8 (CPh), 56.3 (OCH_3); IR (neat) 2927 (m), 1597 (m), 1505 (m), 1252 (s), 1180 (m), 1115 (m), 1034 (w), 749 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{15}H_{13}BrO_2$ + H 305.0177, found 305.0175.

***trans*-2-(2-Nitrophenyl)-3-phenyloxirane (9f)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (102 mg, 0.341 mmol, 1.0 equiv), thioether **7a** (75.3 mg, 0.376 mmol, 1.1 equiv), 2-nitrobenzaldehyde (**8f**, 62.8 mg, 0.416 mmol, 1.2 equiv), and CsF (66.3 mg, 0.436 mmol, 1.2 equiv) in acetonitrile (2.5 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9f** (70.6 mg, 0.293 mmol) in 78% yield as yellow solids: TLC R_f = 0.30 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.15 (d, J = 7.6 Hz, 1 H, ArH), 7.72 (d, J = 7.2 Hz, 2 H, 2×ArH), 7.49 (t, J = 6.4 Hz, 1 H, ArH), 7.38–7.28 (m, 5 H, 5×ArH), 4.49 (s, 1 H, $CHArNO_2$), 3.77 (s, 1 H, CHPh). These spectroscopic data are in accordance with the literature values.[45]

***trans*-2-(3-Nitrophenyl)-3-phenyloxirane (9g)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (105 mg, 0.351 mmol, 1.0 equiv), thioether **7a** (77.6 mg, 0.387 mmol, 1.1 equiv), 3-nitrobenzaldehyde (**8g**, 63.6 mg, 0.421 mmol, 1.2 equiv), and CsF (63.9 mg, 0.421 mmol, 1.2 equiv) in acetonitrile (2.5 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9g** (63.4 mg, 0.263 mmol) in 75% yield as a colorless oil: TLC R_f = 0.30 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.20–8.17 (m, 2 H, 2×ArH), 7.67–7.32 (m, 7 H, 7×ArH), 3.96 (d, J = 1.6 Hz, 1 H, $CHArNO_2$), 3.86 (d, J = 1.6 Hz, 1 H, CHPh). These spectroscopic data are in accordance with the literature values.[46]

***trans*-2-(4-Methoxycarbonyl)phenyl-(3-methoxy)phenyloxirane (9h)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (52.1 mg, 0.174 mmol, 1.0 equiv), thioether **7b**[47] (44.1 mg, 0.191 mmol, 1.1 equiv), methyl 4-formylbenzoate (**8h**, 34.3 mg, 0.208 mmol, 1.2 equiv), and CsF (31.7 mg, 0.209 mmol, 1.2 equiv) in acetonitrile (2.0 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (8.0% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9h** (39.5 mg, 0.139 mmol) in 80% yield as a yellow oil: TLC R_f = 0.40 (10⊥% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.00 (d, J = 8.0 Hz, 2 H, 2×ArH), 7.31 (d, J = 8.0 Hz, 2 H, 2×ArH), 7.20 (d, J = 7.6 Hz, 2 H, 2×ArH), 6.88 (d, J = 7.6 Hz, 2 H, 2×ArH), 4.09 (d, J = 1.6 Hz, 1 H, CHAr), 3.89 (s, 3 H, $ArOCH_3$), 3.80 (s, 3 H, CO_2CH_3), 3.75 (d, J = 1.6 Hz, 1 H, CHAr); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 164.3 (C=O), 159.8, 141.9, 130.1, 129.7, 129.6, 125.8, 125.6, 114.3, 64.3 (CAr), 61.1 (CAr), 55.0 ($ArOCH_3$), 51.5 (CO_2CH_3); IR (neat) 2953 (m), 1732 (s, C=O), 1597 (m), 1496 (m), 1252 (s), 1180 (s), 1032 (m), 752 (m) cm^{-1}; HRMS (ESI-TOF) *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}O_4$ + H 285.1126, found 285.1128.

***trans*-2,3-Di(4-methoxycarbonyl)phenyloxirane (9i)**. The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (151 mg, 0.506 mmol, 1.0 equiv), thioether **7c**[48] (143 mg, 0.556 mmol, 1.1 equiv), methyl 4-formylbenzoate (**8h**, 99.5 mg, 0.607 mmol, 1.2 equiv), and CsF (99.1 mg, 0.652 mmol, 1.2 equiv) in acetonitrile (3.0 mL). After the reaction mixture was stirred at 25 °C for 6.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give *trans*-epoxide **9i** (102 mg, 0.329 mmol) in 65% yield as a yellow oil: TLC R_f = 0.30 (10% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.02 (d, J = 8.0 Hz, 4 H, 4×ArH), 7.33 (d, J = 8.0 Hz, 4 H, 4×ArH), 4.10 (s, 2 H, 2×CHAr), 3.95 (s, 6 H, 2×CO_2CH_3). These spectroscopic data are in accordance with the literature values.[49]

2-Phenyl-1-oxaspiro[2.4]heptane (14a). The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (324 mg, 1.08 mmol, 1.0 equiv), thioether **7a** (237 mg, 1.19 mmol, 1.1 equiv), cyclopentanone (**13a**, 109 mg, 1.29 mmol, 1.2 equiv), and CsF (201 mg, 1.31 mmol, 1.2 equiv) in acetonitrile (3.5 mL). After the reaction mixture was stirred at 25 °C for 6.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give epoxide **14a** (112 mg, 0.648 mmol) in 65% yield as a yellow oil: TLC R_f = 0.45 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.39–7.33 (m, 2 H, 2×ArH), 7.29–7.23 (m, 3 H, 3×ArH), 4.02 (s, 1 H, CHPh), 2.10–1.96 (m, 2 H, CH_2), 1.89–1.73 (m, 2 H, CH_2), 1.69–1.52 (m, 4 H, 2×CH_2). These spectroscopic data are in accordance with the literature values.[50]

2-Phenyl-1-oxaspiro[2.5]octane (14b). The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (105 mg, 0.351 mmol, 1.0 equiv), thioether **7a** (78.9 mg, 0.394 mmol, 1.1 equiv), cyclohexanone (**13b**, 43.4 mg, 0.442 mmol, 1.2 equiv), and CsF (68.2 mg, 0.449 mmol, 1.2 equiv) in acetonitrile (2.0 mL). After the reaction mixture was stirred at 25 °C for 6.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give epoxide **14b** (46.2 mg, 0.245 mmol) in 70% yield as a yellow oil: TLC R_f = 0.40 (5.0 % EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32–7.25 (m, 2 H, 2×ArH), 7.22–7.18 (m, 3 H, 3×ArH), 3.78 (s, 1 H, CHPh), 1.78–1.25 (m, 10 H, 5×CH_2). These spectroscopic data are in accordance with the literature values.[51]

Diethyl 3-(phenyl)oxirane-2,2-dicarboxylate (16). The Standard Procedure 2 was followed by use of 2-silylphenyl triflate **1a** (55.5 mg, 0.186 mmol, 1.0 equiv), thioether **7a** (41.2 mg, 0.205 mmol, 1.1 equiv), diethyl oxomalonate (**15**, 38.8 mg, 0.223 mmol, 1.2 equiv), and CsF (34.2 mg, 0.225 mmol, 1.2 equiv) in acetonitrile (2.0 mL). After the reaction mixture was stirred at 25 °C for 4.0 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give epoxide **16** (39.3 mg, 0.148 mmol) in 80% yield as a colorless oil: TLC R_f = 0.40 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.32–7.28 (m, 2 H, 2×ArH), 7.25–7.19 (m, 3 H, 3×ArH), 4.54 (s, 1 H, CHPh), 4.33–4.28 (m, 2 H, OCH_2), 4.04–3.98 (m, 2 H, OCH_2), 1.31 (t, J = 7.2 Hz, CH_3), 0.94 (t, J = 7.2 Hz, CH_3). These spectroscopic data are in accordance with the literature values.[52]

1-Allyl-2-methoxybenzene (18a). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1a** (302 mg, 1.01 mmol, 1.0 equiv), 3-methoxy-1-propene (**17a**, 146 mg, 2.02 mmol, 2.0 equiv), and CsF (184 mg, 1.21 mmol, 1.2 equiv) in THF (3.5 mL). After the reaction mixture was stirred at 50 °C for 26 h, it was quenched and worked up. The residue was purified by use of column chromatography (3.0% EtOAc in hexanes as the eluent) to give phenolic ether **18a** (106 mg, 0.716 mmol) in 71% yield as a colorless oil: TLC R_f = 0.45 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.26 (d, J = 7.2 Hz, 1 H, ArH), 7.15 (d, J = 7.2 Hz, 1 H, ArH), 6.95–6.88 (m, 2 H, 2×ArH), 6.04–5.97 (m, 1 H, HC=C), 5.07–5.03 (m, 2 H, C=CH_2), 3.84 (s, 3 H, OCH_3), 3.42 (d, J = 6.8 Hz, 2 H, $ArCH_2$). These spectroscopic data are in accordance with the literature values.[33]

2-Allyl-1-phenoxybenzene (18b). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1a** (82.4 mg, 0.276 mmol, 1.0 equiv), (allyloxy)benzene (**17b**, 74.2 mg, 0.552 mmol, 2.0 equiv), and CsF (50.3 mg, 0.331 mmol, 1.2 equiv) in THF (2.5 mL). After the reaction mixture was stirred at 50 °C for 30 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give phenolic ether **18b** (29.5 mg, 0.140 mmol) in 51% yield as a colorless oil: TLC R_f = 0.50 (10% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.38 (d, J = 7.6 Hz, 2 H, 2×ArH), 7.30 (d, J = 7.2 Hz, 1 H, ArH), 7.14–7.05 (m, 3 H, 3×ArH), 7.02 (t, J = 7.2 Hz, 1 H, ArH), 6.98–

6.93 (m, 2 H, 2×ArH), 6.03–5.98 (m, 1 H, HC=C), 5.13–5.11 (m, 2 H, C=CH_2), 3.43 (d, J=6.4 Hz, 2 H, $ArCH_2$). These spectroscopic data are in accordance with the literature values.[33]

2-(2-Methoxybenzyl)acrylic acid methyl ester (18c). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1a** (121 mg, 0.406 mmol, 1.0 equiv), methyl 2-(methoxymethyl) acrylate[53] (**17c**, 73.2 mg, 0.812 mmol, 2.0 equiv), and CsF (92.2 mg, 0.486 mmol, 1.2 equiv) in THF (2.5 mL). After the reaction mixture was stirred at 50 °C for 24 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give phenolic ether **18c** (89.9 mg, 0.328 mmol) in 81% yield as a colorless oil: TLC R_f=0.35 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.30 (d, J=7.2 Hz, 1 H, ArH), 6.93–6.88 (m, 3 H, 3×ArH), 6.10 (s, 1 H, C=CH), 5.26 (s, 1 H, C=CH), 3.82 (s, 3 H, $ArOCH_3$), 3.72 (s, 3 H, CO_2CH_3), 3.55 (s, 2 H, $ArCH_2$). These spectroscopic data are in accordance with the literature values.[54]

1-Allyl-4,5-dimethyl-2-methoxybenzene (18d). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1b** (356 mg, 1.09 mmol, 1.0 equiv), 3-methoxy-1-propene (**17a**, 158 mg, 2.19 mmol, 2.0 equiv), and CsF (202 mg, 1.32 mmol, 1.2 equiv) in THF (3.5 mL). After the reaction mixture was stirred at 50 °C for 24 h, it was quenched and worked up. The residue was purified by use of column chromatography (3.0% EtOAc in hexanes as the eluent) to give phenolic ether **18d** (131 mg, 0.743 mmol) in 68% yield as a colorless oil: TLC R_f=0.35 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 (s, 1 H, ArH), 6.83 (s, 1 H, ArH), 6.02–5.93 (m, 1 H, HC=C), 5.08–5.02 (m, 2 H, C=CH_2), 3.78 (s, 3 H, $ArOCH_3$), 3.41 (d, J=6.4 Hz, 2 H, $ArCH_2$), 2.33 (s, 2 H, $ArCH_3$), 2.22 (s, 2 H, $ArCH_3$); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.6, 137.3, 136.7, 132.1, 130.7, 129.6, 115.2, 113.8, 56.1 ($ArOCH_3$), 34.3 ($ArCH_2$), 20.3 ($ArCH_3$), 19.7 ($ArCH_3$); IR (neat) 2927 (m), 2834 (w), 1613 (s), 1584 (m), 1510 (s), 1255 (m), 1042 (m), 747 (w) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{12}H_{16}O$+H 177.1279, found 177.1278.

γ-Asarone (18e). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1c** (365 mg, 1.04 mmol, 1.0 equiv), 3-methoxy-1-propene (**17a**, 150 mg, 2.08 mmol, 2.0 equiv), and CsF (190 mg, 1.25 mmol, 1.2 equiv) in THF (4.5 mL). After the reaction mixture was stirred at 50 °C for 28 h, it was quenched and worked up. The residue was purified by use of column chromatography (3.0% EtOAc in hexanes as the eluent) to give phenolic ether **18e** (129 mg, 0.619 mmol) in 60% yield as a colorless oil: TLC R_f=0.40 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.70 (s, 1 H, ArH), 6.53 (s, 1 H, ArH), 6.01–5.93 (m, 1 H, HC=C), 5.05–5.02 (m, 2 H, C=CH_2), 3.89 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 3.39 (d, J=6.8 Hz, 2 H, $ArCH_2$). These spectroscopic data are in accordance with the literature values.[21]

Asaricin (18f). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1d** (125 mg, 0.365 mmol, 1.0 equiv), 3-methoxy-1-propene (**17a**, 52.6 mg, 0.730 mmol, 2.0 equiv), and CsF (66.5 mg, 0.438 mmol, 1.2 equiv) in THF (2.5 mL). After the reaction mixture was stirred at 50 °C for 24 h, it was quenched and worked up. The residue was purified by use of column chromatography (5.0% EtOAc in hexanes as the eluent) to give phenolic ether **18f** (40.6 mg, 0.211 mmol) in 58% yield as a colorless oil: TLC R_f=0.30 (5.0% EtOAc in hexanes as the eluent); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.64 (s, 1 H, ArH), 6.51 (s, 1 H, ArH), 5.97–5.88 (m, 1 H, HC=C), 6.64 (s, 1 H, ArH) 5.87 (s, 2 H, OCH_2O), 5.05–4.98 (m, 2 H, C=CH_2), 3.75 (s, 3 H, OCH_3), 3.43 (d, J=6.4 Hz, 2 H, $ArCH_2$). These spectroscopic data are in accordance with the literature values.[22]

1-Allyl-2-{[(*3S,8S,10R,13R,14S,17R*)-10,13-dimethyl-17-[(*R*)-6-methylheptan-2-yl]-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-*1H*-cyclopenta[a]phenanthren-3-yl]-oxy} benzene (18g). The Standard Procedure 3 was followed by use of 2-silylphenyl triflate **1a** (206 mg, 0.691 mmol, 1.0 equiv), allyl cholesteryl ether[55] (**17d**, 533 mg, 1.38 mmol, 2.0 equiv), and CsF (126 mg, 0.828 mmol, 1.2 equiv) in THF (5.0 mL). After the reaction mixture was stirred at 50 °C for 30 h, it was quenched and worked up. The residue was purified by use of column chromatography (10% EtOAc in hexanes as the eluent) to give phenolic ether **18g** (180 mg, 0.357 mmol) in 52% yield as white solids: TLC R_f=0.45 (10% EtOAc in hexanes as the eluent); mp (recrystallized from EtOH) 126.6–128.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.27 (d, J=7.2 Hz, 1 H, ArH), 7.16 (d, J=7.2 Hz, 1 H, ArH), 6.96–6.87 (m, 2 H, 2×ArH), 6.96–6.87 (m, 1 H, HC=C), 5.33 (d, J=5.2 Hz, 1 H, MeCC=CH), 5.09–5.03 (m, 2 H, C=CH_2), 4.09–4.01 (m, 1 H, ArOCH), 3.41 (d, J=6.8 Hz, 2 H, $ArCH_2$), 2.50–2.46 (m, 1 H), 2.41–2.36 (m, 1 H), 2.03–1.97 (m, 3 H), 1.89–1.73 (m, 4 H), 1.57–1.42 (m, 6 H), 1.38–1.31 (m, 3 H), 1.28–1.24 (m, 2 H), 1.18–1.09 (m, 8 H), 1.02 (s, 3 H, CH_3), 0.93 (d, J=6.4 Hz, 3 H, CH_3), 0.87 (d, J=6.4 Hz, 6 H, $C(CH_3)_2$), 0.69 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.6, 140.7, 137.2, 132.2, 129.8, 126.7,121.1, 120.3, 116.0, 113.1, 76.6 (ArOC), 56.7, 56.2, 50.1, 42.4, 42.3, 39.8, 39.5, 37.3, 36.5, 36.2, 35.8, 34.7, 31.9, 31.6, 28.3, 28.0, 24.3, 23.9, 22.9 (CH_3), 22.6 (CH_3), 21.1, 19.4 (CH_3), 18.7 (CH_3), 11.9 (CH_3); IR (neat) 2944 (s), 2866 (s), 1609 (m), 1515 (m), 1467 (m), 1372 (m), 1245 (m), 1051 (m) cm^{-1}; HRMS (ESI-TOF) m/z $[M+H]^+$ calcd for $C_{36}H_{54}O$+H 503.4253, found 503.4245.

Deposition Number 1945287 (for **9e**) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

Acknowledgements

For financial support, we thank the Ministry of Science and Technology (MOST, grant nos. 109-2113-M-007-007 and 109-2634-F-007-023) and the Ministry of Education (grant nos. 109QR001I5 and 108QR001I5) of R.O.C. We also thank the MOST in Taiwan to support The Featured Areas Research Center Program within the framework of the Higher Education Sprout Project through the Frontier Research Center on Fundamental and Applied Sciences of Matters. Authors thank Mses. Hui-Chi Tan, Pei-Lin Chen, and Hsin-Ru Wu of Instrumentation Center at NTHU for their assistance with NMR-500, SXRD, and HPLC/MS-MS experiments, respectively.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: Aryne · 1,2-Dihydroquinoline · Domino · Epoxides · Phenolic ethers

[1] P. M. Tadross, B. M. Stoltz, *Chem. Rev.* **2012**, *112*, 3550–3577.
[2] D. B. Werz, A. T. Biju, *Angew. Chem. Int. Ed.* **2020**, *59*, 3385–3398.
[3] S. Ghorai, D. Lee, *Synlett* **2020**, *31*, A–V.
[4] a) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem. Int. Ed.* **2003**, *42*, 502–528; *Angew. Chem.* **2003**, *115*, 518–546; b) C. D. Campbell, C. W. Rees, *J. Chem. Soc. C.* **1969**, 742–747.
[5] J. R. Hwu, D. B. Chandrasekhar, K. C. Hwang, C.-C. Lin, J.-C. Horng, F.-K. Shieh, *ChemistryOpen* **2017**, *6*, 331–335 and references cited therein.

[6] S. S. Bhojgude, A. Bhunia, A. T. Biju, *Acc. Chem. Res.* **2016**, *49*, 1658–1670.
[7] H. Yoshida, H. Fukushima, J. Ohshita, A. Kunai, *J. Am. Chem. Soc.* **2006**, *128*, 11040–11041.
[8] S. P. Swain, Y.-C. Shih, S.-C. Tsay, J. Jacob, C.-C. Lin, K. C. Hwang, J.-C. Horng, J. R. Hwu, *Angew. Chem. Int. Ed.* **2015**, *54*, 9926–9930; *Angew. Chem.* **2015**, *127*, 10064–10068.
[9] E. Rémond, A. Tessier, F. R. Leroux, J. Bayardon, S. Jugé, *Org. Lett.* **2010**, *12*, 1568–1571.
[10] J. Bayardon, H. Laureano, V. Diemer, M. Dutartre, U. Das, Y. Rousselin, J.-C. Henry, F. Colobert, F. R. Leroux, S. Jugé, *J. Org. Chem.* **2012**, *77*, 5759–5769.
[11] M.-M. Lou, H. Wang, L. Song, H.-Y. Liu, Z.-Q. Li, X.-S. Guo, F.-G. Zhang, B. Wang, *J. Org. Chem.* **2016**, *81*, 5915–5921.
[12] G. D. Richmond, W. Spendel, *Tetrahedron Lett.* **1973**, *46*, 4557–4560.
[13] H. Yoshida, M. Watanabe, H. Fukushima, J. Ohshita, A. Kunai, *Org. Lett.* **2004**, *6*, 4049–4051.
[14] A. Bhunia, T. Roy, P. Pachfule, P. R. Rajamohanan, A. T. Biju, *Angew. Chem. Int. Ed.* **2013**, *52*, 10040–10043; *Angew. Chem.* **2013**, *125*, 10224–10227.
[15] J.-C. Castillo, J. Quiroga, R. Abonia, J. Rodriguez, Y. Coquerel, *Org. Lett.* **2015**, *17*, 3374–3377.
[16] H.-D. Xu, M.-Q. Cai, W.-J. He, W.-H. Hua, M.-H. Shen, *RSC Adv.* **2014**, *4*, 7623–7626.
[17] V. K. Aggarwal, C. L. Winn, *Acc. Chem. Res.* **2004**, *378*, 611–620.
[18] Y.-N. Xu, S.-K. Tian, *Tetrahedron* **2019**, *75*, 1632–1638.
[19] Y. Wang, Z.-X. Yu, *J. Org. Chem.* **2018**, *83*, 5384–5391.
[20] L. Zhang, X. Li, Y. Sun, W. Zhao, F. Luo, X. Huang, L. Lin, Y. Yang, B. Peng, *Org. Biomol. Chem.* **2017**, *15*, 7181–7189.
[21] A. K. Sinha, R. Acharya, B. P. Joshi, *J. Nat. Prod.* **2002**, *65*, 764–765.
[22] D. Lorenzo, I. Loayza, L. Leigue, C. Frizzo, E. Dellacassa, P. Moyna, *Nat. Prod. Lett.* **2001**, *15*, 163–170.
[23] A. A. Cant, G. H. V. Bertrand, J. L. Henderson, L. Roberts, M. F. Greaney, *Angew. Chem. Int. Ed.* **2009**, *48*, 51995202.
[24] For related publications, see: a) Y. Himeshima, T. Sonoda, H. Kobayashi, *Chem. Lett.* **1983**, *12*, 1211–1214; b) A. V. Dubrovskiy, N. A. Markina, R. C. Larock, *Org. Biomol. Chem.* **2013**, *11*, 191–218.
[25] X. Ma, Y. Wu, X. Yang, S. Yang, Y. Li, Y. Huang, R. J. Lee, T. Bai, Y. Luo, *Anticancer Res.* **2016**, *36*, 2105–2112.
[26] M. C. Achilonu, D. O. Umesiobi, *J. Chem.* **2015**, 1–22.
[27] Y. Luo, Z. Li, C.-J. Li, *Org. Lett.* **2005**, *7*, 2675–2698.
[28] X.-Y. Liu, P. Ding, J.-S. Huang, C.-M. Che, *Org. Lett.* **2007**, *9*, 2645–2648.
[29] H. Sundén, R. Rios, I. Ibrahem, G.-L. Zhao, L. Eriksson, A. Córdova, *Adv. Synth. Catal.* **2007**, *349*, 827–832.
[30] R. U. Gutiérrez, H. C. Correa, R. Bautista, J. L. Vargas, A. V. Jerezano, F. Delgado, J. Tamariz, *J. Org. Chem.* **2013**, *78*, 9614–9626.
[31] M. Rueping, J. Dufour, L. Bui, *ACS Catal.* **2014**, *4*, 1021–1025.
[32] W.-L. Lei, T. Wang, K.-W. Feng, L.-Z. Wu, Q. Liu, *ACS Catal.* **2017**, *7*, 7941–7945.
[33] M. O. Akram, P. S. Mali, N. T. Patil, *Org. Lett.* **2017**, *19*, 3075–3078.
[34] V. K. Aggarwal, H. Abdel-Rahman, L. Fan, R. V. H. Jones, M. C. H. Standen, *Chem. Eur. J.* **1996**, *2*, 1024–1030.
[35] M. Kapoor, J. R. Hwu, *Sci. Rep.* **2016**, *6*, 36225.
[36] J. L. Carden, L. J. Gierlichs, D. F. Wass, D. L. Browne, R. L. Melen, *Chem. Commun.* **2019**, *55*, 318–321.
[37] N. R. Patel, C. B. Kelly, A. P. Siegenfeld, G. A. Molander, *ACS Catal.* **2017**, *7*, 1766–1770.
[38] M. G. Kallitsakis, P. D. Tancini, M. Dixit, G. Mpourmpakis, I. N. Lykakis, *J. Org. Chem.* **2018**, *83*, 1176–1184.
[39] V. A. Mamedov, V. L. Mamedova, S. F. Kadyrova, V. R. Galimullina, G. Z. Khikmatova, D. E. Korshin, A. T. Gubaidullin, D. B. Krivolapov, I. K. Rizvanov, O. B. Bazanova, O. G. Sinyashin, S. K. Latypov, *J. Org. Chem.* **2018**, *83*, 13132–13145.
[40] A.-S. Cornec, L. Monti, J. Kovalevich, V. Makani, M. J. James, K. G. Vijayendran, K. Oukoloff, Y. Yao, V. M.-Y. Lee, J. Q. Trojanowski III, A. B. Smith, K. R. Brunden, C. Ballatore, *J. Med. Chem.* **2017**, *60*, 5120–5145.
[41] O. S. Akkerman, F. Bickelhaupt, *J. Organomet. Chem.* **1988**, *338*, 159–168.
[42] K. Yamada, Y. Igarashi, T. Betsuyaku, M. Kitamura, K. Hirata, K. Hioki, M. Kunishima, *Org. Lett.* **2018**, *20*, 2015–2019.
[43] A. Solladié-Cavallo, A. Diep-Vohuule, *Tetrahedron: Asymmetry* **1996**, *7*, 1783–1788.
[44] T. Ema, M. Yokoyama, S. Watanabe, S. Sasaki, H. Ota, K. Takaishi, *Org. Lett.* **2017**, *19*, 4070–4073.
[45] P. Lupaptelli, L. Chiummiento, M. Funicello, F. Tramutola, A. Marmo, N. Gliubizzi, D. Tofani, *Tetrahedron* **2015**, *71*, 5662–5668.
[46] V. K. Aggarwal, E. Alonso, I. Bae, G. Hynd, K. M. Lydon, M. J. Palmer, M. Patel, M. Porcelloni, J. Richardson, R. A. Stenson, J. R. Studley, J.-L. Vasse, C. L. Winn, *J. Am. Chem. Soc.* **2003**, *125*, 10926–10940.
[47] W. Li, C. Yang, G.-L. Gao, W. Xia, *Synlett* **2016**, *27*, A–F.
[48] J. I. DeGraw, P. H. Christie, E. G. Brown, L. F. Kelly, R. L. Kisliuk, Y. Gaumont, F. M. Sirotnak, *J. Med. Chem.* **1984**, *27*, 377–380.
[49] F. M. Wong, Y. M. Chan, D. X. Chen, W. Wu, *Tetrahedron Lett.* **2010**, *51*, 6649–6650.
[50] C. P. Burke, L. Shu, Y. Shi, *J. Org. Chem.* **2007**, *72*, 6320–6323.
[51] A. Pereira, C. Martín, C. Maya, T. R. Belderrain, P. J. Pérez, *Adv. Synth. Catal.* **2013**, *355*, 2942–2951.
[52] R. K. Varshnaya, P. Banerjee, *Org. Biomol. Chem.* **2017**, *15*, 5182–5190.
[53] M. L. Quan, C. D. Ellis, A. Y. Liauw, R. S. Alexander, R. M. Knabb, G. Lam, M. R. Wright, P. C. Wong, R. R. Wexler, *J. Med. Chem.* **1999**, *42*, 2760–2773.
[54] I. Kondolff, H. Doucet, M. Santelli, *Tetrahedron Lett.* **2003**, *44*, 8487–8491.
[55] F. E. Ziegler, E. G. Brown, S. B. Sobolov, *J. Org. Chem.* **1990**, *55*, 3693–3695.

Manuscript received: November 16, 2020
Revised manuscript received: November 27, 2020
Accepted manuscript online: November 30, 2020