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Sulfur-Mediated Allylic C-H Arylation, Epoxidation and Aziridination

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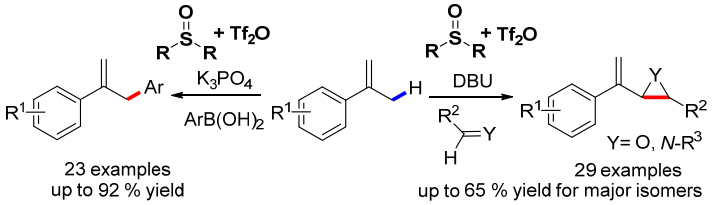
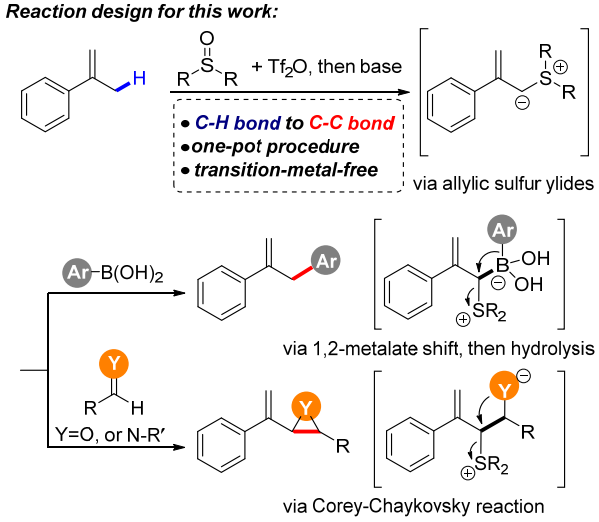
Supporting Information Placeholder



ABSTRACT: Transition-metal-free, sulfur mediated allylic C-H arylation, epoxidation and aziridination were realized through one-pot procedures. The reaction design involved initial addition between olefins and triflic anhydride activated sulfoxides, followed by subsequent reactions of the allylic sulfur ylides generated under basic conditions with arylboronic acids, aldehydes, or aldimines, to give allylic arylation, epoxidation or aziridination products, respectively.

INTRODUCTION

The C–C bond formation at allylic positions has been an attractive research topic for decades.[1] Apart from Alder ene type reactions, the most influential method for allylic functionalization is arguably the Tsuji-Trost type allylation. While palladium-catalyzed allylic substitutions enabled the synthesis of a broad range of molecules,[2] seminal studies on palladium-catalyzed allylic C-H alkylation provided new opportunity for converting C-H bond directly to C-C bond at allylic positions.[3] In addition, oxidative cross-dehydrogenative coupling reaction was another alternative for allylic C-H functionalization.[4] However, reports on allylic C-H arylation reactions were still rare in the literature, while most metal-catalyzed coupling of allyl electrophiles with aryl-partners required functionalized olefins.[5] Nakamura and co-workers realized iron-catalyzed allylic arylation of simple olefins with aryl-Grignard reagents.[6] MacMillan and Cuthbertson accomplished the direct arylation of allylic C-H bond by using cyanoarenes as coupling partner via dual photoredox and organocatalysis.[7] Rueping's group reported direct allylic arylation of olefins with aryl- and vinylbromides by the combined use of nickel and visible light catalysis.[8] Recently, Glorius and co-workers explored rhodium catalyzed allyl-aryl coupling of arylboron reagents or heteroarenes with unfunctionalized olefins.[9] Herein, we report a transition-metal-free, sulfur mediated route for converting allylic C-H bond to C-C bond via the allylic sulfur ylide intermediates, which provides the arylation, epoxidation and aziridination products in one-pot fashion (Scheme 1).[10]



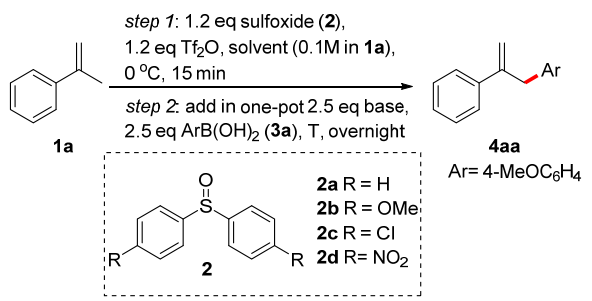
Scheme 1. Sulfur mediated allylic C-H arylation, epoxidation, and aziridination reactions

Sulfur ylides have been widely used for synthetic chemistry since the pioneering work by Johnson, Corey and Chaykovsky in the 1960s.[11a-d] Conventionally, there are two main methods for generating sulfur ylides: deprotonation of sulfonium salts, which are usually prepared through sulfide substitution of alkyl halides; or alternatively, reaction between sulfides and metal carbenoids, which could be generated from metal-catalyzed

decomposition of diazo compounds. Certain other strategies for the synthesis of sulfur ylides have also been explored.[11e-h] Allylic and benzylic sulfur ylides, classified as semi-stabilized ylides, generally exhibited good reactivity in epoxidation or aziridination reactions with carbonyl or imine type compounds.[12] Asymmetric reaction of chiral sulfur ylides are also well-established.[11a,11b,13] On the other hand, sulfur ylides could also react with organoboron reagents through 1,2-metalate shift of the corresponding ate complex.[14] In 2018, Huang and co-workers further achieved sulfide catalyzed cross-coupling between benzyl halides and arylboronic acids.[15a] Wang's group also reported a non-transition-metal catalyzed coupling between benzyl halides and arylboronic acids via Friedel-Crafts-type reaction pathway.[15b]

Based on many precedents for the reactions with alkenes and alkynes involving activated sulfoxides,[16,17] we hypothesize that allylic sulfur ylides could be directly generated from simple olefins, through electrophilic addition of activated sulfoxides with olefins, followed by subsequent deprotonation, which could then react with arylboronic acids via 1,2-metalate shift and hydrolysis, or with aldehydes/aldimines via Corey-Chaykovsky reaction, to give the desired allylic functionalized products (Scheme 1).

Table 1. Optimization of reaction conditions



entry	sulfoxide	base	Solvent	T (°C)	yield[a] (%)
1[b]	**2a**	DBU	DCM	rt	0
2[b]	**2a**	$K_2HPO_4·2H_2O$	DCM	rt	18
3[b]	**2a**	Cs_2CO_3	DCM	rt	21
4[b]	**2a**	KOH	DCM	rt	<5
5	**2a**	$LiOH·2H_2O$	Toluene	rt	36
6	**2a**	$K_3PO_4·3H_2O$	Toluene	rt	42
7	**2a**	$K_3PO_4·3H_2O$	Toluene	110	48
8	**2b**	$K_3PO_4·3H_2O$	Toluene	110	77
9[c]	**2b**	$K_3PO_4·3H_2O$	Toluene	150	62
10	**2c**	$K_3PO_4·3H_2O$	Toluene	110	88
11	**2d**	$K_3PO_4·3H_2O$	Toluene	110	<5
12[d]	**2c**	$K_3PO_4·3H_2O$	DCE	80	64
13[e]	**2c**	$K_3PO_4·3H_2O$	Toluene	110	92
14[f]	**2c**	$K_3PO_4·3H_2O$	Toluene	110	80

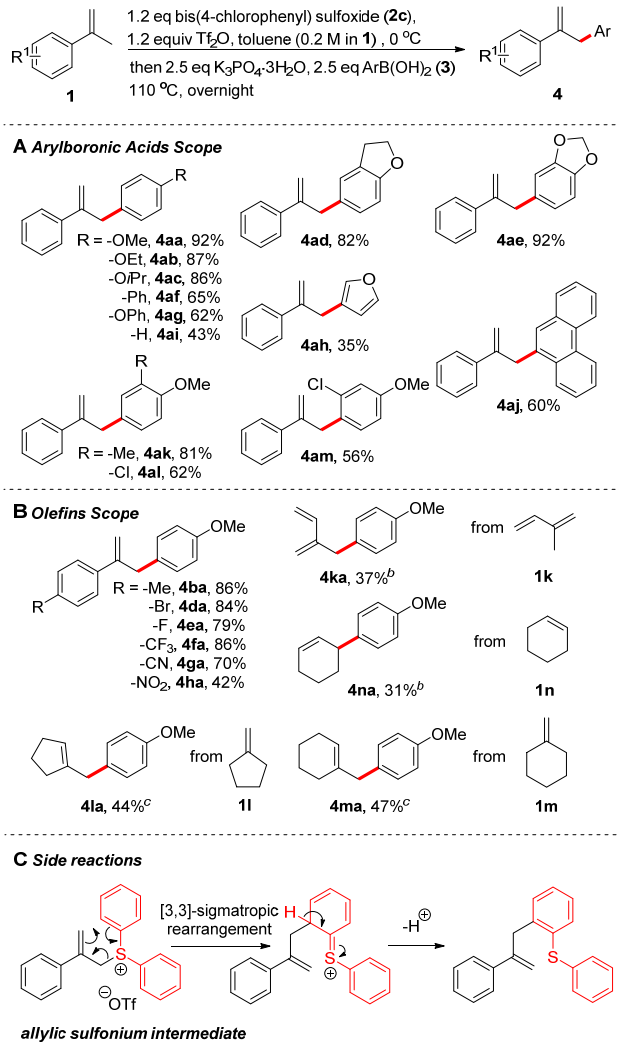
Reaction conditions: a solution of **1a** (0.4 mmol) and sulfoxide (**2**) in 1 mL of solvent was treated Tf_2O (0.48 mmol) at 0 °C, added base (1 mmol) and 4-methoxylphenyl boronic acid (1 mmol), and warmed up, stirred for overnight. [a]Isolated yield after column chromatography. [b]Instead of adding Tf_2O at 0 °C, step 1 was conducted at - 78 °C. [c]Microwave heating in a sealed tube. [d]Instead of adding Tf_2O at 0 °C, step 1 was conducted at - 43 °C. [e]Using 2 mL solvent (0.2 M in **1a**). [f]Reaction conducted on 1 mmol scale.

RESULT AND DISCUSSION

We initially optimized the conditions for allylic C-H arylation of α-methylstyrene (**1a**) (Table 1). The formation of allylic sulfonium salt through electrophilic addition between α-methylstyrene (**1a**) and triflic anhydride activated sulfoxides (**2**) took place in step 1. After that, boronic acid **3a** and base were added to complete the transformation in step 2. It was found that inorganic base worked better than strong organic base (i.e. DBU, entry 1) for this transformation, affording desired product **4aa** (entries 2-4) at room temperature. Instead of dichloromethane (DCM), toluene or dichloroethane (DCE) could also be used as solvent for this reaction, and thus allowing increased reaction temperature for step 2 (entries 5-7, 12). Although higher temperature exhibited the potential of promoting yields, it also facilitated other competitive side reactions. In order to avoid the major side product, which was formed through [3,3]-sigmatropic rearrangement of allylic sulfonium intermediates and then rearomatization (Table 2C),[16f,16i] we tried using different sulfoxides bearing either electron-donating or electron-withdrawing groups at the phenyl rings' para-position (entries 8-11). Gratifyingly, it was found that bis(4-chlorophenyl) sulfoxide (**2c**) could adequately suppress such unintended rearrangement. When reaction concentration was lowered to 0.2 M, such optimal condition achieved 92% yield of arylation product **4aa** (entry 13).

We then explored the substrate scope of different arylboronic acids (Table 2A) under the optimized conditions. This arylation protocol worked nicely for electron-rich arylboronic acids, e.g. *para*-alkyloxy substrates gave the corresponding products **4aa**-**4ae** in 82% to 92% yields, while less electron-rich arylboronic acids gave products **4af**, **4ag**, and **4ai** with lower yields. For electron-rich heterocyclic boronic acids, furan-3-boronic acid only gave desired product **4ah** in 35% yield. Halogen substituted products **4al** and **4am** were obtained in 56% and 62% yields, respectively. However, arylboronic acids with strong electron-withdrawing groups gave no desired product (see supporting information for details). Protodeboronation of those boronic acids was predominant under our current reaction conditions. Presumably, 1,2-migration of the aryl group on boron-ate complex (see our proposed reaction mechanism in Scheme 1) would be less favored for electron-deficient aryl groups. Next, we evaluated a variety of substituted α-methylstyrenes, and the desired products **4ba**-**4ha** were isolated in 42% to 86% yields (Table 2B). In addition, isoprene (**1k**) and cyclohexene (**1n**) could also afford the coupling products **4ka** and **4na** in 37% and 31% yields, respectively. For alkenes **1l** and **1m** with exocyclic methylene groups, it was found that bis(4-methoxylphenyl) sulfoxide (**2b**) favored this transformation, since its electron-rich aryl group on the sulfur atom probably enhanced the stability of corresponding sulfonium intermediate. Furthermore, tri-substituted alkenes failed to give the desired products (see supporting information for details), presumably, the corresponding allylic sulfur ylides formed from tri-substituted olefins were steric hindered to participate in these reactions.

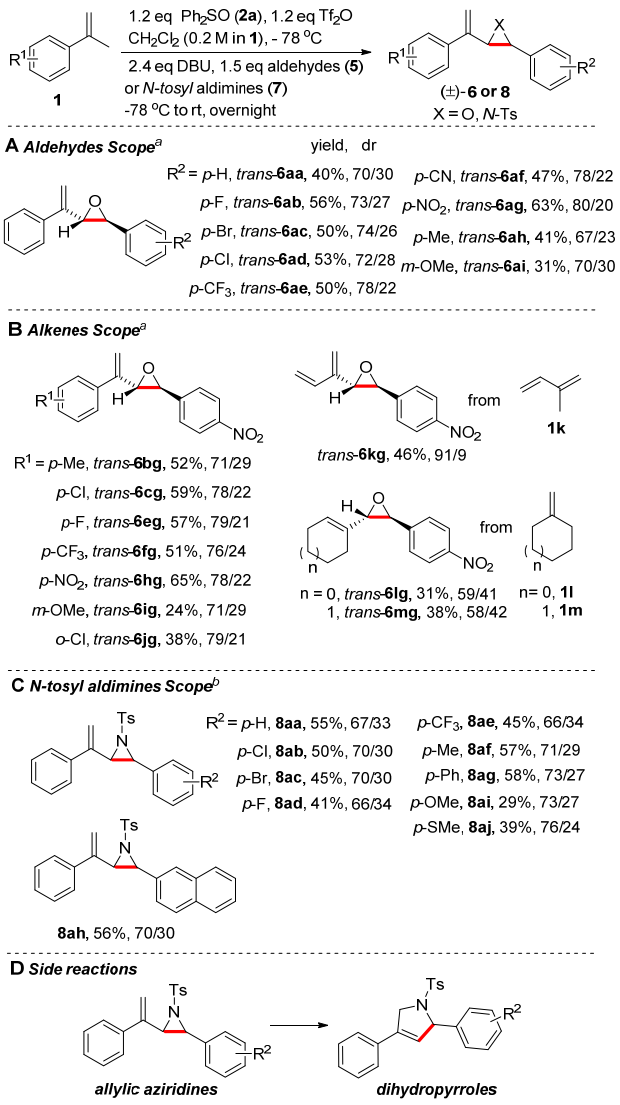
Table 2. Allylic C-H arylation[a]



[a]Isolated yields. [b]DCE was used instead of toluene as solvent, heated at 80 °C. [c]Used sulfoxide **2b** instead of **2c**.

For the allylic C-H epoxidation or aziridination reactions, another set of reaction condition was optimized, and DBU was found to be most suitable base for generating sulfur ylides in situ to participate in the Corey-Chaykovsky type reactions (see supporting information for details). The substrate scope and side reactions are shown in Table 3. Electron-deficient aromatic aldehydes afforded the major *trans*-epoxides **6ab-6ag** in moderate yields with 3:1-4:1 dr (Table 3A). *Meta*-methoxy substituted aromatic aldehyde only gave 31% yield of *trans*-**6ai**. When trying some electron-rich aromatic aldehydes, the corresponding allylic epoxide products were prone to decompose under acidic condition. Meanwhile, a variety of electron-rich and electron-deficient α-methylstyrenes **1a-1j** were also tolerated, affording the major *trans*-epoxides products in 24% to 65% yields with moderate dr (Table 3B). In addition, Isoprene (**1k**) afforded major *trans*-**6kg** in 46% with excellent dr. The use of alkenes **1l** and **1m** with exocyclic methylene group afforded *trans*- **6lg** and *trans*-**6mg** in lower yields with poor dr. We tried to enhance the diastereoselectivity by using different sulfoxides, but achieved no significant improvement (see supporting information for details). Similarly,

Table 3. Allylic C-H epoxidation[a] **and aziridination**[b]



Reaction conditions: a solution of alkenes **1** (0.4 mmol) and diphenylsulfoxide (**2a**) in 2 mL of CH_2Cl_2 was treated Tf_2O (0.48 mmol) at - 78 °C, added DBU (0.96 mmol) and aldehydes (**5**) or *N*-tosyl aldimines (**6**) (0.6 mmol), warmed up slowly to rt, stirred overnight. The dr (trans : cis) was determined by crude ^1H NMR analysis. [a]Isolated yields of *trans*-isomers. [b]MeCN was used as solvent instead of CH_2Cl_2, and the reaction temperature was initially -43 °C, isolated yields for the mixture of two diastereomers were given.

N-tosyl aldimines provided allylic aziridination products **8aa-8aj** in moderate yields and dr (Table 3C). In those cases, ring expansion rearrangement of allylic aziridine products toward dihydropyrroles partly contributed to the diminished yields (Table 3D).[18]

In conclusion, we have developed a novel sulfur mediated allylic C-H functionalization strategy to access arylation, epoxidation or aziridination products without the involvement of transition metal or photoredox catalysts, which complements our previous reports on sulfur mediated allylic/propargylic C-H alkylation reactions.[17a,17c] The use of readily available reagents under robust reaction condition is an attractive feature of this chemistry involving triflic anhydride activated sulfoxides.

EXPERIMENTAL SECTION

General Information. All reactions were carried out in oven-dried glassware under a nitrogen atmosphere employing standard techniques unless otherwise noted. Dichloromethane was refluxed over CaH_2, and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200-300 mesh). Petroleum ether used for column chromatography were 60-90 ºC fraction, and the removal of residue solvent was accomplished under rotovap with repeated azeotrope with chloroform, and then evaporation under vacuum (< 1 mmHg pressure). Reactions were monitored by thin-layer chromatography on silica gel 60-F254 coated 0.2 mm plates. The plates were visualized under UV light. ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer, usually in $CDCl_3$ with TMS as an internal standard, and the chemical shifts (δ) were reported in parts per million (ppm). The IR spectra (KBr pellets, ν [cm^{-1}]) were taken on a FTIR spectrometer. HRMS measurements were carried out on a TOF mass spectrometer. Substituted alkenes **1b**,[19] **1c**, [19] **1d**, [19] **1e**, [19] **1f**, [19] **1g**,[20] **1h**,[19] **1i**,[21] **1j**,[19] **1l**,[17a] **1m**,[17a] and sulfoxide substrates **2b**,[22] **2d,**[22] *N*-tosylaldimines substrates **7a**,[23] **7b**,[24] **7c**,[24] **7d**,[25] **7e**,[24] **7f**,[24] **7g**,[23] **7h**,[24] **7i**[24] were known compounds, and prepared according to published procedures.

Preparation of *N*-tosylaldimine 7j: To the solution of the 4-(methylthio)benzaldehyde (5 mmol, 1 equiv) in PhMe (30 mL) was added $TsNH_2$ (5 mmol, 1 equiv) and $BF_3{\cdot}Et_2O$ (0.06 ml, 0.5 mmol, 0.1 equiv). The mixture was refluxed using a Dean-Stark apparatus for 20 hours in an oil bath. After the reaction was complete as monitored by TLC, the solution was cooled to room temperature, concentrated under reduced pressure, and recrystallized from EtOAc/Hexanes to give 0.61 g (40% yield) **7j** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (s, 1H), 7.88 (d, J = 8.3 Hz, 2H), 7.81 (d, J = 8.5 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.27 (d, J = 7.7 Hz, 2H), 2.52 (s, 3H), 2.43 (s, 3H). ^{13}C NMR {^{1}H} NMR (100 MHz, $CDCl_3$) δ 169.3, 149.1, 144.4, 135.5, 131.5, 129.8, 128.5, 128.0, 125.2, 21.7, 14.6. HRMS (ESI) calcd for $C_{15}H_{16}NO_2S_2^+$ $[M+H]^+$ *m/z* 306.0617, found 306.0624.

General Procedure A for arylation reaction: To a flame-dried 10 mL tube, alkene (**1**) (0.4 mmol) and bis(4-chlorophenyl) sulfoxide (**2b**) (131 mg, 0.48 mmol) were added, and then dissolved with toluene (2 mL) under nitrogen atmosphere before cooling down to 0 ºC. Tf_2O (81 µL, 0.48 mmol) were added dropwise and kept 15 minutes, then $K_3PO_4{\cdot}3H_2O$ (266 mg, 1 mmol) and arylboronic (**3**) (1 mmol) was added. After fully stirred, warm up to 110 ºC in an oil bath, and kept 12 hours of reaction at reflux temperature. The solution was quenched by 10 mL water, and then the aqueous phase extracted with CH_2Cl_2 (10 mL×3). The combined organic phases were dried with Na_2SO_4 and concentrated under reduced pressure to give the crude products. The crude product was then purified by repeated flash column chromatography and preparative thin layer chromatography to give pure isolated products. If some pure products are hard to separate from sulfide, Oxone (0.8 mmol) could add to a solution of crude product in MeOH (10 mL). After the reaction was complete as monitored by TLC, the solution was quenched by saturated sodium bicarbonate, and then aqueous phase extracted with CH_2Cl_2 (10 mL×3). The combined organic phases were dried with Na_2SO_4 and concentrated under reduced pressure to give the crude products for further purification.

Methoxy-4-(2-phenylallyl)benzene (4aa): yellow oil (92%, 82 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A. 1 mmol scale reaction for compound **4aa** was similarly conducted using 118 mg (1 mmol) α-methylstyrene (**1a)** to yield 179 mg product **4aa** (80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.2 Hz, 2H), 7.31 – 7.19 (m, 3H), 7.13 (d, J = 8.5 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 5.46 (s, 1H), 5.00 (s, 1H), 3.77 (m, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 147.7, 141.3, 131.9, 130.2, 128.6, 127.8, 126.5, 114.6, 114.1, 55.6, 41.1;IR (KBr) ν (cm^{-1}) 2931, 1611, 1511, 1246, 1177, 1036, 899, 818, 780, 702; HRMS (ESI) calcd for $C_{16}H_{17}O^+[M+H]^+$ *m/z* 225.1274, found 225.1281.

1-Ethoxy-4-(2-phenylallyl)benzene (4ab): yellow oil (87%, 83 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.4 Hz, 2H), 7.30 – 7.18 (m, 3H), 7.11 (d, J = 8.4 Hz, 2H), 6.79 (d, J = 8.4 Hz, 2H), 5.45 (s, 1H), 4.99 (s, 1H), 3.97 (q, J = 7.0 Hz, 2H), 3.76 (s, 2H), 1.37 (t, J = 7.0 Hz, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.7, 147.7, 141.3, 131.7, 130.2, 128.6, 127.7, 126.5, 114.7, 114.6, 63.7, 41.1, 15.2; IR (KBr) ν (cm^{-1}) 3031, 2979, 2906, 1611, 1582, 1477, 922, 899, 780, 740; HRMS (ESI) calcd for $C_{17}H_{19}O^+$ $[M+H]^+$ *m/z* 239.1430, found 239.1430.

1-Isopropoxy-4-(2-phenylallyl)benzene (4ac): yellow oil (86%, 87 mg), R_f = 0.51 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) 7.35 (d, J = 7.1 Hz, 2H), 7.23 – 7.12 (m, 3H), 7.03 (d, J = 8.6 Hz, 2H), 6.71 (d, J = 8.6 Hz, 2H), 5.38 (s, 1H), 4.92 (d, J = 1.2 Hz, 1H), 4.50 – 4.31 (m, 1H), 3.68 (s, 2H), 1.23 (d, J = 6.1 Hz, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.6, 147.7, 141.3, 131.7, 130.2, 128.6, 127.7, 126.5, 116.1, 114.59, 70.2, 41.1, 22.4; IR (KBr) ν (cm^{-1}) 2976, 2918, 1611, 1508, 1383, 1242, 1120, 956, 898, 779; HRMS (ESI) calcd for $C_{18}H_{21}O^+$ $[M+H]^+$ *m/z* 253.1587, found 253.1590.

5-(2-Phenylallyl)-2,3-dihydrobenzofuran (4ad): yellow oil (82%, 77 mg), R_f = 0.33 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.3 Hz, 2H), 7.31 – 7.19 (m, 3H), 7.04 (s, 1H), 6.95 (d, J = 8.1 Hz, 1H), 6.68 (d, J = 8.1 Hz, 1H), 5.46 (s, 1H), 5.00 (s, 1H), 4.51 (t, J = 8.7 Hz, 2H), 3.75 (s, 2H), 3.13 (t, J = 8.7 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.8, 147.8, 141.2, 131.7, 128.7, 128.6, 127.7, 127.3, 126.5, 125.7, 114.6, 109.3, 71.5, 41.3, 30.1; IR (KBr) ν (cm^{-1}) 3020, 2894, 1624, 1489, 1384, 1243, 1099, 984, 899, 780, 704; HRMS (ESI) calcd for $C_{17}H_{17}O^+$ $[M+H]^+$ *m/z* 237.1274, found 237.1280.

5-(2-Phenylallyl)benzo[d][1,3]dioxole (4ae): yellow oil (92%, 92 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 2H), 7.31 – 7.20 (m, 3H), 6.71 – 6.66 (m, 3H) 5.89 (s, 2H), 5.47 (s, 1H), 5.03 (s, 1H), 3.74 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.9, 147.4, 146.2, 141.0, 133.6, 128.6, 127.8, 126.5, 122.2, 114.8, 109.6, 108.5, 101.1, 41.7; IR (KBr) ν (cm^{-1}) 2893, 1621, 1487, 1360, 1244,

1040, 933, 783, 708; HRMS (ESI) calcd for $C_{16}H_{15}O_2^+$ $[M+H]^+$ *m/z* 239.1067, found 239.1066.

4-(2-Phenylallyl)-1,1'-biphenyl (4af): white solid (65%, 70 mg), R_f = 0.33 (petroleum ether), mp 63-65 °C, was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.36 (m, 8H), 7.33 – 7.25 (m, 5H), 7.23 (d, J = 2.8 Hz, 1H), 5.52 (s, 1H), 5.07 (s, 1H), 3.87 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.2, 141.3, 141.1, 139.4, 139.0, 129.7, 129.0, 128.6, 127.9, 127.43, 127.4, 127.3, 126.5, 115.0, 41.6; IR (KBr) ν (cm^{-1}) 3054, 2974, 1625, 1444, 1265, 907, 751, 702; HRMS (ESI) calcd for $C_{21}H_{19}^+$ $[M+H]^+$ *m/z* 271.1481, found 271.1484.

1-Phenoxy-4-(2-phenylallyl)benzene (4ag): yellow oil (62%, 71 mg), R_f = 0.58 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 7.6 Hz, 2H), 7.33 – 7.22 (m, 5H), 7.17 (d, J = 7.9 Hz, 2H), 7.05 (dd, J = 7.3 Hz, J = 7.3 Hz, 1H), 6.97 (d, J = 7.8 Hz, 2H), 6.91 (d, J = 7.7 Hz, 2H), 5.49 (s, 1H), 5.03 (s, 1H), 3.81 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 157.8, 155.8, 147.4, 141.1, 134.8, 130.5, 130.0, 128.6, 127.8, 126.5, 123.4, 119.3, 119.0, 114.9, 41.3; IR (KBr) ν (cm^{-1}) 3058, 2919, 1589, 1488, 1239, 871, 777, 704; HRMS (ESI) calcd for $C_{21}H_{19}O^+$ $[M+H]^+$ *m/z* 287.1430, found 287.1423.

3-(2-Phenylallyl)furan (4ah): yellow oil (35%, 26 mg), R_f = 0.34 (petroleum ether), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.39 (m, 2H), 7.34 – 7.22 (m, 4H), 6.26 (dd, J = 3.0, 2.0 Hz, 1H), 6.01 (dd, J = 3.0, 0.6 Hz, 1H), 5.48 (s, 1H), 5.10 (d, J = 1.1 Hz, 1H), 3.83 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.8, 144.7, 141.6, 140.7, 128.6, 127.9, 126.3, 114.9, 110.7, 107.0, 34.6; IR (KBr) ν (cm^{-1}) 3057, 2920, 1600, 1504, 1445, 1384, 1010, 899, 788, 701; HRMS (ESI) calcd for $C_{13}H_{13}O^+$ $[M+H]^+$ *m/z* 185.0961, found 185.0961.

Prop-2-ene-1,2-diyldibenzene (4ai): yellow oil (43%,33 mg), R_f = 0.88 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.31 – 7.14 (m, 8H), 5.49 (s, 1H), 5.01 (d, J= 1.2 Hz, 1H), 3.83 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 147.27, 141.16, 139.86, 129.27, 128.68, 128.59, 127.79, 126.47, 126.43, 114.92, 41.96; IR (KBr) ν (cm^{-1}) 3059, 2924, 1625, 1493, 1073, 899, 777, 697; HRMS (ESI) calcd for $C_{15}H_{15}^+$ $[M+H]^+$ *m/z* 195.1168, found 195.1172.

9-(2-Phenylallyl)phenanthrene (4aj): white solid (60%, 71 mg), R_f = 0.34 (petroleum ether), mp 160-162 °C, was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, J = 8.1 Hz, 2H), 8.06 – 8.01 (m, 1H), 7.82 – 7.78 (m, 1H), 7.68 – 7.53 (m, 7H), 7.39 – 7.23 (m, 3H), 5.55 (d, J = 0.8 Hz, 1H), 4.87 (d, J = 1.0 Hz, 1H), 4.28 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 146.3, 141.6, 134.1, 132.2, 131.8, 131.0, 130.2, 128.8, 128.6, 128.2, 128.0, 127.0, 126.6, 126.6, 126.2, 125.3, 123.5, 122.8, 115.4, 39.2; IR (KBr) ν (cm^{-1}) 2918, 2849, 1625, 1492, 1384, 1275, 1180, 906, 764, 724; HRMS (ESI) calcd for $C_{23}H_{19}^+$ $[M+H]^+$ *m/z* 295.1481, found 295.1477.

1-Methoxy-2-methyl-4-(2-phenylallyl)benzene (4ak): yellow oil (81%, 77 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 7.9 Hz, 2H), 7.32 – 7.15 (m, 3H), 6.98 (d, J = 6.4 Hz, 2H), 6.70 (d, J = 8.9 Hz, 1H), 5.46 (s, 1H), 4.99 (s, 1H), 3.75 (s, 3H), 3.73 (s, 2H), 2.17 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 156.47, 147.71, 141.31, 131.59, 131.37, 128.54, 127.69, 127.30, 126.69, 126.45, 114.53, 110.14, 55.59, 41.06, 16.55; IR (KBr) ν (cm^{-1}) 2918, 2848, 1663, 1448, 1273, 971, 757, 700; HRMS (ESI) calcd for $C_{17}H_{19}O^+$ $[M+H]^+$ *m/z* 239.1430, found 239.1430.

2-Chloro-1-methoxy-4-(2-phenylallyl)benzene (4al): yellow oil (81%, 77 mg), R_f = 0.29 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.36 (m, 2H), 7.30 – 7.19 (m, 4H), 7.07 – 7.01 (m, 1H), 6.80 (d, J = 8.4 Hz, 1H), 5.48 (s, 1H), 5.02 (s, 1H), 3.83 (s, 3H), 3.74 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 153.7, 146.9, 140.8, 133.0, 130.87, 128.6, 128.3, 127.9, 126.4, 122.5, 115.1, 112.3, 56.4, 40.8; IR (KBr) ν (cm^{-1}) 2918, 2849, 1625, 1492, 1384, 1275, 1180, 906, 745, 724; HRMS (ESI) calcd for $C_{16}H_{16}ClO^+$ $[M+H]^+$ *m/z* 259.0884, found 259.0887

2-Chloro-4-methoxy-1-(2-phenylallyl)benzene (4am): yellow oil (56%, 58 mg), R_f = 0.32 (petroleum ether), was synthesized according to General Procedure A; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.3, 2H), 7.34 – 7.23 (m, 3H), 7.11 (d, J = 8.5 Hz, 1H), 6.93 (d, J = 2.6 Hz, 1H), 6.72 (dd, J = 8.5, 2.6 Hz, 1H), 5.48 (s, 1H), 4.87 (d, J = 1.1 Hz, 1H), 3.85 (s, 2H), 3.77 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 159.0, 146.2, 141.1, 135.1, 131.6, 129.4, 128.7, 127.9, 126.4, 115.0, 114.6, 113.3, 55.8, 38.2; IR (KBr) ν (cm^{-1}) 3020, 2958, 2922, 1626, 1493, 1383, 1028, 899, 777, 700; HRMS (ESI) calcd for $C_{16}H_{16}ClO^+$ $[M+H]^+$ *m/z* 259.0884, found 259.0844.

1-Methoxy-4-(2-(p-tolyl)allyl)benzene (4ba): yellow oil (86%, 82 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from 1-methyl-4-(prop-1-en-2-yl)benzene (**1b**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (d, J = 8.1 Hz, 2H), 7.13 (dd, J = 17.1, 8.3 Hz, 4H), 6.83 (d, J = 8.6 Hz, 2H), 5.46 (s, 1H), 4.98 (d, J = 1.2 Hz, 1H), 3.78 (s, 5H), 2.33 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 147.4, 138.2, 137.5, 132.0, 130.2, 129.3, 126.3, 114.1, 113.8, 55.5, 41.1, 21.4; IR (KBr) ν (cm^{-1}) 2931, 1610, 1511, 1392, 1246, 1177, 1036, 902, 831, 778, 755; HRMS (ESI) calcd for $C_{17}H_{19}O^+$ $[M+H]^+$ *m/z* 239.1430, found 239.1427.

1-Bromo-4-(3-(4-methoxyphenyl)prop-1-en-2-yl)benzene (4da): yellow oil (84%,102 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from 1-bromo-4-(prop-1-en-2-yl)benzene (**1d**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H), 7.13 (d, J = 8.5 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 5.48 (s, 1H), 5.08 (d, J = 0.9 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.4, 146.6, 140.0, 131.6, 131.4, 130.1, 128.2, 121.7, 115.2, 114.2, 55.5, 41.0; IR (KBr) ν (cm^{-1}) 2920, 1610, 1511, 1247, 1177, 1035, 825; HRMS (ESI) calcd for $C_{16}H_{16}BrO^+$ $[M+H]^+$ *m/z* 303.0379, found 303.0387.

1-Fluoro-4-(3-(4-methoxyphenyl)prop-1-en-2-yl)benzene (4ea): yellow oil (79%, 76 mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from 1-fluoro-4-(prop-1-en-2-yl)benzene(**1e**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (dd, J = 8.7, 5.5 Hz, 2H), 7.16 (d, J = 8.5 Hz, 2H), 7.02 – 6.96 (m, 2H), 6.85 (d, J = 8.6 Hz, 2H), 5.44 (s, 1H), 5.05 (s, 1H), 3.80 (s, 3H), 3.78 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 162.5 (d, J = 246.3

Hz), 158.4, 146.6, 137.2, 131.5, 130.1, 128.1 (d, J = 7.9 Hz), 115.3 (d, J = 21.3 Hz)114.5, 114.1, 55.5, 41.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.09; IR (KBr) ν (cm^{-1}) 2934, 2836, 1601, 1511, 1301, 1247, 1038, 838, 767; HRMS (ESI) calcd for $C_{16}H_{16}FO^+$ $[M+H]^+$ *m/z* 243.1180, found 243.1171.

1-Methoxy-4-(2-(4-(trifluoromethyl)phenyl)allyl)benzene (4fa): yellow oil (86%, 100mg), R_f = 0.43 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from 1-(prop-1-en-2-yl)-4-(trifluoromethyl)benzene (**1f**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.50 (m, 4H), 7.14 (d, J = 8.4 Hz, 2H), 6.84 (d, J = 8.5 Hz, 2H), 5.55 (s, 1H), 5.16 (s, 1H), 3.80 (s, 2H), 3.79 (s, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 146.6, 144.7, 131.1, 130.1, 129.7 (q, J = 32.3 Hz), 126.8, 125.5 (q, J = 3.6 Hz), 121.9 (q, J = 271.5 Hz), 116.6, 114.2, 55.5, 41.0; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.48; IR (KBr) ν (cm^{-1}) 2935, 2836, 1614, 1511, 1404, 1326, 1247, 1119, 847; HRMS (ESI) calcd for $C_{17}H_{16}F_3O^+$ $[M+H]^+$ *m/z* 293.1148, found 293.1146.

4-(3-(4-Methoxyphenyl)prop-1-en-2-yl)benzonitrile (4ga): yellow oil (70%, 70 mg), R_f = 0.12 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from 4-(prop-1-en-2-yl)benzonitrile (**1g**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.44 (m, 4H), 7.10 (d, J = 8.6 Hz, 2H), 6.82 (d, J = 8.6 Hz, 2H), 5.56 (s, 1H), 5.20 (d, J = 1.0 Hz, 1H), 3.77 (s, 5H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.5, 146.2, 145.6, 132.4, 130.8, 130.0, 127.1, 119.2, 117.5, 114.2, 111.2, 55.5, 40.8; IR (KBr) ν (cm^{-1}) 2955, 2931, 2227, 1606, 1510, 1301, 1246, 1177, 1035, 874, 740; HRMS (ESI) calcd for $C_{17}H_{16}NO^+$ $[M+H]^+$ *m/z* 250.1226, found 250.1234.

1-Methoxy-4-(2-methylenebut-3-en-1-yl)benzene (4ka): yellow oil (37%, 26 mg), R_f = 0.58 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from isoprene (**1k**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 8.6 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 6.43 (dd, J = 17.6, 10.8 Hz, 1H), 5.25 (d, J = 17.6 Hz, 1H), 5.15 (s, 1H), 5.06 (d, J = 10.8 Hz, 1H), 4.90 (s, 1H), 3.79 (s, 3H), 3.50 (s, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 146.0, 138.9, 131.8, 130.1, 118.3, 114.6, 114.1, 55.6, 37.5; IR (KBr) ν (cm^{-1}) 2919, 1610, 1511, 1384, 1247, 1179, 1036; HRMS (ESI) calcd for $C_{12}H_{15}O^+$ $[M+H]^+$ *m/z* 175.1117, found 175.1111.

1-(Cyclopent-1-en-1-ylmethyl)-4-methoxybenzene (4la): yellow oil (44%, 33 mg), R_f = 0.48 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from methylenecyclopentane (**1l**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.5 Hz, 2H), 5.32 (s, 1H), 3.80 (s, 3H), 3.33 (s, 2H), 2.31 (t, J = 6.1 Hz, 2H), 2.20 (t, J = 7.1 Hz, 2H), 1.90 – 1.80 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 144.6, 132.6, 130.0, 125.4, 114.0, 55.6, 37.4, 35.1, 32.8, 23.9; IR (KBr) ν (cm^{-1}) 3054, 2973, 1609, 1512, 1448, 1384, 1037, 745, 704; HRMS (ESI) calcd for $C_{13}H_{17}O^+$ $[M+H]^+$ *m/z* 189.1274, found 189.1269.

1-(Cyclohex-1-en-1-ylmethyl)-4-methoxybenzene (4ma): yellow oil (43%, 38 mg), R_f = 0.48 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from methylenecyclohexane(**1m**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (d, J = 8.5 Hz, 2H), 6.83 (d, J = 8.6 Hz, 2H), 5.45 (s, 1H), 3.79 (s, 3H), 3.18 (s, 2H), 2.06 – 1.96 (m, 2H), 1.89 – 1.81 (m, 2H), 1.61 – 1.48 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.3, 138.0, 132.9, 130.2, 123.0, 114.0, 55.7, 44.2, 28.4, 25.8, 23.4, 22.9; IR (KBr) ν (cm^{-1}) 2926, 2839, 1610, 1510, 1300, 125, 821, 800; HRMS (ESI) calcd for $C_{14}H_{19}O^+$ $[M+H]^+$ *m/z* 203.1430, found 203.1433.

4'-Methoxy-1,2,3,4-tetrahydro-1,1'-biphenyl (4na): yellow oil (31%,23 mg), R_f = 0.66 (petroleum ether/dichloromethane = 3:1), was synthesized according to General Procedure A from cyclohexene (**1n**); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, J = 8.6 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 5.87 (dt, J = 9.7, 6.0, 3.5 Hz, 1H), 5.70 (dd, J = 10.1, 2.1 Hz, 1H), 3.80 (s, 3H), 3.39 – 3.32 (m, 1H), 2.12 – 2.04 (m, 2H), 2.04 – 1.95 (m, 1H), 1.78 – 1.48 (m, 3H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 158.2, 139.2, 130.9, 129.0, 128.5, 114.0, 55.6, 41.3, 33.1, 25.4, 21.5; IR (KBr) ν (cm^{-1}) 3017, 2928, 1610, 1511, 1463, 1246, 1177, 1036, 827; HRMS (ESI) calcd for $C_{13}H_{17}O^+$ $[M+H]^+$ *m/z* 189.1274, found 189.1269.

General Procedure B for epoxidation reaction: To a flame-dried Schlenk tube, alkene (**1**) (47 mg, 0.4 mmol) and diphenyl sulfoxide (**2a**) (97 mg, 0.48 mmol) were added, and then dissolved with dichloromethane (2 mL) under nitrogen atmosphere before cooling down to -78 ºC (liquid nitrogen/ethyl acetate bath). Tf_2O (81 μL, 0.48 mmol) were added dropwise and kept 15 minutes, Then DBU (143 μL, 0.48mmol) and aldehyde (0.6 mmol) was added. After 12 hours of reaction at -78 ºC and warm up slowly to room temperature. The solution was quenched by 10 mL water. The aqueous phase extracted with CH_2Cl_2 (10 mL×3). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure to give the crude products. Crude ^{1}H NMR was taken for determination of diastereomeric ratio (see SI page 67-76 for the characteristic peaks used for dr determination). The crude product was then purified by repeated flash column chromatography and preparative thin layer chromatography to give pure isolated products.

2-Phenyl-3-(1-phenylvinyl)oxirane (*trans*-) (6aa): yellow oil (40%, 35mg), R_f = 0.58 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, DMSO- d_6) δ 7.56 – 7.30 (m, 10H), 5.63 (s, 1H), 5.43 (s, 1H), 3.96 (s, 1H), 3.87 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO- d_6) δ 144.6, 138.1, 137.7, 129.6, 129.5, 129.3, 129.2, 126.9, 126.6, 112.6, 62.3, 61.5; IR (KBr) ν (cm^{-1}) 2918, 1629, 1560, 1164, 1025, 878, 806, 668; HRMS (ESI) calcd for $C_{16}H_{15}O^+$ $[M+H]^+$ *m/z* 223.1117, found 223.1110.

2-(4-Fluorophenyl)-3-(1-phenylvinyl)oxirane (*trans*-) (6ab): yellow oil (56%, 54 mg), R_f = 0.52 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, DMSO- d_6) δ 7.56 – 7.48 (m, 4H), 7.45 – 7.35 (m, 3H), 7.28 (m, 2H), 5.63 (s, 1H), 5.41 (s, 1H), 3.98 (s, 1H), 3.91 (d, J = 1.4 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, DMSO- d_6) δ 163.1 (d, J = 244.3 Hz), 144.5, 138.1, 133.9 (d, J = 2.8 Hz), 129.6, 129.1 (d, J = 7.6 Hz), 129.0, 126.6, 116.4 (d, J = 21.6 Hz), 112.7, 62.3, 60.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.47; IR (KBr) ν (cm^{-1}) 2918, 2850, 1654, 1560, 1179, 1080, 810, 669; HRMS (ESI) calcd for $C_{16}H_{14}FO^+$ $[M+H]^+$ *m/z* 241.1023, found 241.1021.

2-(4-Bromophenyl)-3-(1-phenylvinyl)oxirane (*trans*-) (6ac): yellow oil (50%, 61 mg), R_f = 0.54 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.3 Hz,

2H), 7.43 – 7.31 (m, 5H), 7.24 (d, J = 8.3 Hz, 2H), 5.53 (s, 1H), 5.47 (s, 1H), 3.69 (s, 1H), 3.64 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 144.0, 137.9, 136.4, 132.1, 129.0, 128.6, 127.6, 126.4, 122.7, 112.7, 63.0, 61.2; IR (KBr) ν (cm^{-1}) 2981, 2926, 1629, 1594, 1180, 1104, 862, 823, 713, 694; HRMS (ESI) calcd for $C_{16}H_{14}BrO^+$ $[M+H]^+$ *m/z* 301.0223, found 301.0221.

2-(4-Chlorophenyl)-3-(1-phenylvinyl)oxirane (*trans*-) (6ad) : yellow oil (53%, 58 mg), R_f = 0.53 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^1H NMR (400 MHz, DMSO- d_6) δ 7.54 – 7.46 (m, 6H), 7.45 – 7.34 (m, 3H), 5.64 (s, 1H), 5.42 (s, 1H), 3.97 (s, 1H), 3.92 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO- d_6) δ 144.4, 138.0, 136.8, 133.9, 129.6, 129.5, 129.2, 128.8, 126.6, 112.8, 62.4, 60.7; IR (KBr) ν (cm^{-1}) 2918, 1654, 1560, 1180, 1090, 825, 774, 692; HRMS (ESI) calcd for $C_{16}H_{14}ClO^+$ $[M+H]^+$ *m/z* 257.0728, found 257.0721.

2-(1-Phenylvinyl)-3-(4-(trifluoromethyl)phenyl)oxirane (*trans*-) (6ae): yellow oil (50%, 58 mg) was synthesized according to General Procedure B; ^1H NMR (400 MHz, DMSO- d_6) δ 7.81 (d, J = 7.1 Hz, 2H), 7.69 (d, J = 7.6 Hz, 2H), 7.51 (d, J = 7.3 Hz, 2H), 7.45 – 7.35 (m, 3H), 5.66 (s, 1H), 5.45 (s, 1H), 4.05 (s, 1H), 4.01 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 143.5, 141.1, 137.5, 130.6 (q, J = 32.5 Hz, 1C), 128.6, 128.3, 126.1, 125.9, 125.7 (q, J = 3.6 Hz, 1C), 124.1 (q, J = 272.0 Hz, 1C), 113.0, 62.9, 60.6; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.56; IR (KBr) ν (cm^{-1}) 2919, 2849, 1655, 1458, 1166, 1066, 867, 837, 709; HRMS (ESI) calcd for $C_{17}H_{14}F_3O^+$ $[M+H]^+$ *m/z* 291.0991, found 291.0996.

4-(3-(1-Phenylvinyl)oxiran-2-yl)benzonitrile (*trans*-) (6af): yellow oil (47%, 46 mg), R_f = 0.37 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^1H NMR (400 MHz, DMSO- d_6) δ 7.92 (d, J = 8.0 Hz, 2H), 7.67 (d, J = 8.1 Hz, 2H), 7.50 (d, J = 7.4 Hz, 2H), 7.45 – 7.34 (m, 3H), 5.66 (s, 1H), 5.44 (s, 1H), 4.04 (s, 1H), 4.02 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO-d_6) δ 144.1, 143.4, 137.9, 133.4, 129.6, 129.2, 127.8, 126.7, 119.6, 113.2, 112.0, 62.8, 60.5; IR (KBr) ν (cm^{-1}) 2918, 2227, 1655, 1560, 1142, 1075, 848, 694; HRMS (ESI) calcd for $C_{17}H_{14}NO^+$ $[M+H]^+$ *m/z* 248.1070, found 248.1076.

2-(4-Nitrophenyl)-3-(1-phenylvinyl)oxirane (*trans*-) (6ag): yellow solid (63%, 67 mg), R_f = 0.43 (petroleum ether/ethyl acetate = 15:1), mp 120-122 ℃ was synthesized according to General Procedure B; ^1H NMR (400 MHz, DMSO- d_6) δ 8.29 (d, J = 8.5 Hz, 2H), 7.74 (d, J = 8.5 Hz, 2H), 7.54 – 7.32 (m, 5H), 5.67 (s, 1H), 5.46 (s, 1H), 4.12 (s, 1H), 4.03 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO- d_6) δ 148.4, 145.5, 144.1, 137.9, 129.6, 129.3, 128.1, 126.7, 124.7, 113.3, 63.0, 60.3; IR (KBr) ν (cm^{-1}) 2920, 1597, 1521, 1496, 1345, 1180, 1074, 899, 775, 692; HRMS (ESI) calcd for $C_{16}H_{13}NO_3^+$ $[M+H]^+$ *m/z* 268.0968, found 268.0969.

2-(1-Phenylvinyl)-3-(p-tolyl)oxirane (*trans*-) (6ah): yellow oil (41%, 39 mg), R_f = 0.58 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^1H NMR (400 MHz, DMSO- d_6) δ 7.49 (d, J = 7.6 Hz, 2H), 7.44 – 7.32 (m, 5H), 7.24 (d, J = 7.8 Hz, 2H), 5.62 (s, 1H), 5.40 (s, 1H), 3.93 (s, 1H), 3.81 (d, J = 1.0 Hz, 1H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, DMSO- d_6) δ 144.6, 138.7, 138.1, 134.7, 130.0, 129.6, 129.1, 126.9, 126.6, 112.4, 62.2, 61.5, 21.7; IR (KBr) ν (cm^{-1}) 2917, 2860, 1651, 1550, 1470, 1384, 1072, 810; HRMS (ESI) calcd for $C_{17}H_{17}O^+$ $[M+H]^+$ *m/z* 237.1274, found 237.1274.

2-(3-Methoxyphenyl)-3-(1-phenylvinyl)oxirane (*trans*-) (6ai): yellow oil (31%, 31 mg), R_f = 0.44 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, J = 6.7 Hz, 2H), 7.39 – 7.27 (m, 4H), 6.98 (d, J = 7.6 Hz, 1H), 6.89 (d, J = 6.4 Hz, 2H), 5.52 (s, 1H), 5.47 (s, 1H), 3.83 (s, 3H), 3.71 (s, 1H), 3.68 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 160.4, 144.3, 139.1, 138.0, 130.0, 128.9, 128.5, 126.4, 118.4, 114.5, 112.4, 110.9, 62.8, 61.8, 55.6; IR (KBr) ν (cm^{-1}) 2912, 1685, 1577, 1458, 1383, 1151, 872, 772, 692; HRMS (ESI) calcd for $C_{17}H_{17}O_2^+$ $[M+H]^+$ *m/z* 253.1223, found 253.1226.

2-(4-Nitrophenyl)-3-(1-(p-tolyl)vinyl)oxirane (*trans*-) (6bg): white solid (52%, 59 mg), R_f = 0.64 (petroleum ether/ethyl acetate = 15:1), mp 126-128 ℃, was synthesized according to General Procedure B; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 5.52 (s, 1H), 5.44 (s, 1H), 3.81 (s, 1H), 3.66 (s, 1H), 2.35 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.3, 144.9, 143.4, 138.7, 134.7, 129.7, 126.6, 126.2, 124.3, 112.7, 63.6, 60.5, 21.5; IR (KBr) ν (cm^{-1}) 3075, 2918, 1655, 1560, 1458, 1380, 1345, 1187, 1106, 892, 690; HRMS (ESI) calcd for $C_{17}H_{16}NO_3^+$ $[M+H]^+$ *m/z* 282.1125, found 282.1127.

2-(1-(4-Chlorophenyl)vinyl)-3-(4-nitrophenyl)oxirane (*trans*-) (6cg): yellow solid (59%, 71 mg), R_f = 0.45 (petroleum ether/ethyl acetate = 15:1), mp 124-126 ℃, was synthesized according to General Procedure B; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.6 Hz, 2H), 7.51 (d, J = 8.6 Hz, 2H), 7.32 (s, 4H), 5.55 (s, 1H), 5.51 (s, 1H), 3.80 (d, J = 1.0 Hz, 1H), 3.64 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.3, 144.5, 142.6, 136.0, 134.7, 129.2, 127.8, 126.6, 124.4, 114.5, 63.33, 60.22; IR (KBr) ν (cm^{-1}) 2918, 2852, 1601, 1518, 1346, 1180, 1094, 893, 853, 745, 693; HRMS (ESI) calcd for $C_{16}H_{13}ClNO_3^+$ $[M+H]^+$ *m/z* 302.0578, found 302.0575.

2-(1-(4-Fluorophenyl)vinyl)-3-(4-nitrophenyl)oxirane (*trans*-) (6eg): white solid (57%, 65 mg), R_f = 0.57 (petroleum ether/ethyl acetate = 15:1), , mp 128-130 ℃, was synthesized according to General Procedure B; ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.3 Hz, 2H), 7.51 (d, J = 8.2 Hz, 2H), 7.40 – 7.31 (m, 2H), 7.09 – 6.97 (m, 2H), 5.50 (s, 1H), 5.48 (s, 1H), 3.80 (s, 1H), 3.63 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 163.1 (d, J = 248.0 Hz), 148.3, 144.6, 142.7, 133.7, 128.2 (d, J = 8.1 Hz), 126.6, 124.3, 115.9 (d, J = 21.6 Hz), 114.0, 63.5, 60.2; ^{19}F NMR (377 MHz, $CDCl_3$) δ -113.32; IR (KBr) ν (cm^{-1}) 2918, 2853, 1655, 1560, 1346, 1160, 894, 873, 751, 694; HRMS (ESI) calcd for $C_{16}H_{13}FNO_3^+$ $[M+H]^+$ *m/z* 286.0874, found 286.0874.

2-(4-Nitrophenyl)-3-(1-(4-(trifluoromethyl)phenyl)vinyl)oxirane (*trans*-) (6fg): yellow solid (51%, 69 mg), R_f = 0.48 (petroleum ether/ethyl acetate = 15:1), mp 109-112 ℃, was synthesized according to General Procedure B; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, J = 8.4 Hz, 2H), 7.61 (d, J = 8.1 Hz, 2H), 7.55 – 7.48 (m, 4H), 5.64 (s, 1H), 5.61 (s, 1H), 3.81 (s, 1H), 3.67 (s, 1H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 148.1, 144.0, 142.4, 140.7, 130.4 (q, J = 32.7 Hz), 126.6, 126.3, 125.6 (q, J = 3.8 Hz), 124.0, 124.0 (q, J = 272.1 Hz), 115.8, 62.9, 59.9; ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.71; IR (KBr) ν (cm^{-1}) 2919, 2860, 1616, 1519, 1197, 1060,

849, 742, 690; HRMS (ESI) calcd for $C_{17}H_{13}F_3NO_3^+$ $[M+H]^+$ *m/z* 336.0842, found 336.0845.

2-(4-Nitrophenyl)-3-(1-(4-nitrophenyl)vinyl)oxirane (*trans*-) (6hg): yellow solid (65%, 81 mg), R_f = 0.31 (petroleum ether/ethyl acetate = 20:1), mp 135-138 ℃, was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.1 Hz, 2H), 7.51 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 5.56 (s, 1H), 5.51 (s, 1H), 3.79 (s, 1H), 3.63 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.3, 144.5, 142.7, 138.1, 137.0, 128.3, 126.6, 124.4, 114.6, 94.5, 63.2, 60.2; IR (KBr) ν (cm^{-1}) 2921, 2851, 1653, 1558, 1345, 1141, 1089, 874, 690; HRMS (ESI) calcd for $C_{16}H_{13}N_2O_5^+$ $[M+H]^+$ *m/z* 313.0819, found 313.0823.

2-(1-(3-Methoxyphenyl)vinyl)-3-(4-nitrophenyl)oxirane (*trans*-) (6ig): white solid (24%, 25 mg), R_f = 0.44 (petroleum ether/ethyl acetate = 15:1), mp 118-120 ℃, was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 7.27 (t, J = 7.9 Hz, 1H), 6.99 – 6.85 (m, 3H), 5.56 (s, 1H), 5.49 (s, 1H), 3.82 (s, 1H), 3.80 (s, 3H), 3.65 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.1, 145.2, 144.7, 143.5, 139.1, 130.0, 126.6, 124.3, 118.9, 113.8, 113.8, 112.5, 63.5, 60.5, 55.6; IR (KBr) ν (cm^{-1}) 2919, 2850, 1655, 1560, 1384, 1343, 1125, 1066, 896, 837, 692; HRMS (ESI) calcd for $C_{17}H_{16}NO_4^+$$[M+H]^+$ *m/z* 298.1074, found 298.1078.

2-(1-(2-Chlorophenyl)vinyl)-3-(4-nitrophenyl)oxirane (*trans*-) (6jg): yellow solid (38%, 46 mg) , R_f = 0.50 (petroleum ether/ethyl acetate = 15:1), mp 87-90 ℃, was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 8.7 Hz, 2H), 7.41 – 7.34 (m, 1H), 7.30 – 7.26 (m, 3H), 5.70 (s, 1H), 5.36 (s, 1H), 3.79 (d, J = 1.3 Hz, 1H), 3.54 (d, J = 1.3 Hz, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.2, 144.8, 143.7, 137.3, 133.0, 131.6, 129.9, 129.9, 127.2, 126.6, 124.2, 118.7, 63.8, 60.8; IR (KBr) ν (cm^{-1}) 2919, 2848, 1654, 1560, 1324, 1165, 1066, 867, 708; HRMS (ESI) calcd for $C_{16}H_{13}ClNO_3^+$ $[M+H]^+$ *m/z* 302.0578, found 302.0575.

2-(Buta-1,3-dien-2-yl)-3-(4-nitrophenyl)oxirane (*trans*-) (6kg): white solid (45%, 39 mg), R_f = 0.48 (petroleum ether/ethyl acetate = 15:1), mp 60-63 ℃, was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.5 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 6.45 (dd, J = 17.9, 11.1 Hz, 1H), 5.36 (s, 1H), 5.24 (d, J = 17.7 Hz, 1H), 5.23 (s, 1H), 5.15 (d, J = 11.0 Hz, 1H), 3.76 (s, 1H), 3.55 (s, 1H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.3, 144.9, 141.7, 135.9, 126.6, 124.3, 115.8, 115.4, 61.8, 59.8; IR (KBr) ν (cm^{-1}) 3085, 2963, 2851, 1648, 1571, 1347, 1179, 1095, 908, 851, 695; HRMS (ESI) calcd for $C_{12}H_{12}NO_3^+$ $[M+H]^+$ *m/z* 218.0812, found 218.0813.

2-(Cyclopent-1-en-1-yl)-3-(4-nitrophenyl)oxirane (*trans*-) (6lg): yellow oil (31%, 29 mg), R_f = 0.40 (petroleum ether/ethyl acetate = 20:1), was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.6 Hz, 2H), 7.45 (d, J = 8.6 Hz, 2H), 6.00 (t, J = 3.2 Hz 1H), 3.99 (d, J = 1.3 Hz, 1H), 3.54 (s, 1H), 2.48 – 2.33 (m, 3H), 2.32 – 2.19 (m, 1H), 2.02 – 1.88 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.1, 145.6, 140.1, 133.1, 126.5, 124.1, 62.2, 57.8, 33.2, 30.7, 23.4; IR (KBr) ν (cm^{-1}) 2962, 2824, 1603, 1520, 1384, 1141, 1090, 798, 706; HRMS (ESI) calcd for $C_{13}H_{14}NO_3^+$ $[M+H]^+$ *m/z* 232.0968, found 232.0970.

2-(Cyclohex-1-en-1-yl)-3-(4-nitrophenyl)oxirane (*trans*-) (6mg): yellow oil (38%, 37 mg), R_f = 0.58 (petroleum ether/ethyl acetate = 15:1), was synthesized according to General Procedure B; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.7 Hz, 2H), 7.45 (d, J = 8.7 Hz, 2H), 5.96 (m, 1H), 3.96 (d, J = 1.4 Hz, 1H), 3.27 (s, 1H), 2.12 – 1.98 (m, 3H), 1.92 – 1.81 (m, 1H), 1.79 – 1.55 (m, 4H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 148.0, 145.8, 133.1, 129.3, 126.5, 124.1, 66.9, 56.7, 25.6, 23.0, 22.7, 22.4; IR (KBr) ν (cm^{-1}) 3010, 2930, 1599, 1520, 1345, 1141, 1095, 823, 710, 617; HRMS (ESI) calcd for $C_{14}H_{16}NO_3^+$ $[M+H]^+$ *m/z* 246.1125, found 246.1128.

General Procedure C for aziridination reaction: To a flame-dried Schlenk tube, alkene (**1**) (0.4 mmol) and diphenyl sulfoxide (**2a**) (97 mg, 0.48 mmol) were added, and then dissolved with acetonitrile (2 mL) under nitrogen atmosphere before cooling down to - 43 ºC (liquid nitrogen/acetonitrile bath). Tf_2O (81 μL, 0.48 mmol) were added dropwise and kept for 15 minutes. Then DBU (143 μL, 0.48mmol) and imine (**7**) (0.6 mmol) were added. After 12 hours of reaction at - 43 ºC and warming up slowly to room temperature, the solution was quenched by 10 mL water. The aqueous phase extracted with CH_2Cl_2 (10 mL×3). The combined organic phase was dried with Na_2SO_4 and concentrated under reduced pressure to give the crude products. Crude ^{1}H NMR was taken for determination of diastereomeric ratio, Crude ^{1}H NMR was taken for determination of diastereomer ratio (see SI page 77-81 for the characteristic peaks used for dr determination). The crude product was then purified by repeated flash column chromatography (alumina) and preparative thin layer chromatography to give pure isolated products.

2-Phenyl-3-(1-phenylvinyl)-1-tosylaziridine (8aa): oil (55%, 84 mg), R_f = 0.57 (petroleum ether/ethyl acetate = 5:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.2 Hz), 7.64 (d, J = 8.3 Hz), 7.47 – 7.14 (m), 5.60 (s, 1H *trans*), 5.43 (s, 1H *trans*), 5.40 (s, 1H *cis*), 5.25 (s, 1H *cis*), 4.25 (d, J = 7.2 Hz, 1H *cis*), 4.19 (d, J = 4.6 Hz, 1H *trans*), 4.01 – 3.95 (m, 2H *trans* and *cis*), 2.44 (s, 3H *cis*), 2.38 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 144.2, 141.4, 138.6, 138.1, 137.6, 137.4, 135.2, 132.5, 132.2, 130.1, 129.7, 129.2, 129.2, 128.8, 128.7, 128.5, 128.3, 128.2, 128.0, 128.0, 126.5, 126.1, 116.4, 116.3, 51.4, 49.3, 48.4, 47.5, 22.0, 21.9; IR (KBr) ν (cm^{-1}) 3021, 1597, 1447, 1328, 1162, 1089, 901, 752, 698; HRMS (ESI) calcd for $C_{23}H_{22}NO_2S^+$ $[M+H]^+$ *m/z* 376.1366, found 376.1374.

2-(4-Chlorophenyl)-3-(1-phenylvinyl)-1-tosylaziridine (8ab): oil (50%, 82 mg), R_f = 0.51 (petroleum ether/ethyl acetate = 5:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz), 7.66 (d, J = 8.2 Hz), 7.45 – 7.08 (m), 5.58 (s, 1H *trans*), 5.42 (s), 5.39 (s, 1H *trans*), 5.22 (s, 1H *cis*), 4.20 (d, J = 7.2 Hz, 1H *cis*), 4.16 (d, J = 4.6 Hz, 1H *trans*), 3.97 (d, J = 7.3 Hz, 1H *cis*), 3.92 (d, J = 4.7 Hz, 1H *trans*), 2.45 (s, 3H *cis*), 2.40 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.5, 141.3, 138.5, 137.3, 135.2, 131.1, 130.6, 130.2, 129.8, 129.4, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 127.9, 126.5, 125.9, 116.5, 116.4, 50.7, 49.4, 48.5, 46.6, 22.0, 21.9; IR (KBr) ν (cm^{-1}): 2921, 1700, 1598, 1494, 1329, 1160, 1092, 908, 812, 780; HRMS (ESI) calcd for $C_{23}H_{21}ClNO_2S^+$ $[M+H]^+$ *m/z* 410.0976, found 410.0979

2-(4-Bromophenyl)-3-(1-phenylvinyl)-1-tosylaziridine (8ac): oil (45%, 81 mg), R_f = 0.57 (petroleum ether/ethyl acetate = 5:1) was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.2 Hz), 7.65 (d, J = 8.2 Hz), 7.48 (d, J = 8.4 Hz), 7.44 – 7.15 (m), 7.05 (d, J = 8.3 Hz), 5.58 (s, 1H *trans*), 5.42 (s, 1H *cis*), 5.39 (s, 1H *trans*), 5.22 (s, 1H *cis*), 4.18 (d, J = 7.2 Hz, 1H *cis*), 4.14 (d, J = 4.5 Hz, 1H *trans*), 3.97 (d, J = 7.2 Hz, 1H *cis*), 3.91 (d, J = 4.7 Hz, 1H *trans*), 2.44 (s, 3H *cis*), 2.40 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.5, 141.2, 138.5, 137.2, 132.0, 131.6, 131.4, 130.8, 130.3, 129.8, 129.7, 128.9, 128.8, 128.6, 128.5, 128.3, 127.9, 126.4, 125.9, 123.4, 116.5, 116.4, 50.6, 49.4, 48.4, 46.7, 22.0, 21.9; IR (KBr) ν (cm^{-1}): 3057, 2923, 1597, 1492, 1397, 1328, 1161, 911, 813, 707; HRMS (ESI) calcd for $C_{23}H_{21}BrNO_2S^+$ $[M+H]^+$ *m/z* 454.0471, found 454.0477.

2-(4-Fluorophenyl)-3-(1-phenylvinyl)-1-tosylaziridine (8ad): oil (41%, 65 mg), R_f = 0.57 (petroleum ether/ethyl acetate = 5:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz), 7.65 (d, J = 8.2 Hz), 7.48 – 7.12 (m), 7.05 (t, J = 8.6 Hz), 6.86 (t, J = 8.7 Hz), 5.57 (s, 1H *trans*), 5.41 (s, 1H *cis*), 5.38 (s, 1H *trans*), 5.21 (s, 1H *cis*), 4.22 (d, J = 7.2 Hz, 1H *cis*), 4.18 (d, J = 4.7 Hz, 1H *trans*), 3.97 – 3.91 (m, 2H *trans* and *cis*), 2.46 (s, 3H *cis*), 2.41 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 164.6, 162.1, 145.2, 144.4, 141.4, 138.5, 137.9, 137.6, 137.4, 131.2, 131.1, 130.2, 129.8, 129.6, 128.9, 128.7, 128.6, 128.5, 128.4, 128.2, 127.9, 126.5, 125.98, 116.5, 116.2, 116.0, 115.8, 115.4, 115.2, 51.0, 49.2, 48.5, 46.6, 22.0, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -112.34, -113.96; IR (KBr) ν (cm^{-1}): 2920, 1599, 1513, 1446, 1328, 1162, 1088, 913, 816, 707; HRMS (ESI) calcd for $C_{23}H_{21}FNO_2S^+$ $[M+H]^+$ *m/z* 394.1272, found 394.1278.

2-(1-Phenylvinyl)-1-tosyl-3-(4-(trifluoromethyl)phenyl)aziridine (8ae): oil (45%, 80 mg), R_f = 0.60 (petroleum ether/ethyl acetate = 5:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.9 Hz), 7.66 (d, J = 7.9 Hz), 7.58 (m), 7.45 – 7.17 (m), 5.63 (s, 1H *trans*), 5.44 (s, 1H *trans*), 5.42 (s, 1H *cis*), 5.23 (s, 1H *cis*), 4.27 (d, J = 7.3 Hz, 1H *cis*), 4.15 (d, J = 4.6 Hz, 1H *trans*), 4.06 – 3.98 (m, 2H *trans* and *cis*), 2.46 (s, 3H *cis*), 2.40 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.4, 144.6, 140.9, 138.5, 137.7, 137.3, 137.1, 137.0, 134.9, 131.1, 130.3, 129.8, 129.4, 128.9, 128.8, 128.6, 128.6, 128.4, 128.4, 128.0, 126.5, 125.9, 125.9, 125.8, 125.8, 125.8, 116.8, 116.6, 50.1, 50.0, 48.5, 46.6, 22.1, 21.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.64, -62.69; IR (KBr) ν (cm^{-1}) 2921, 1597, 1494, 1328, 1162, 1088, 928, 802; HRMS (ESI) calcd for $C_{24}H_{21}F_3NO_2S^+$ $[M+H]^+$ *m/z* 444.1240, found 444.1248

2-(1-Phenylvinyl)-3-(p-tolyl)-1-tosylaziridine (8af): oil (57%, 89 mg), R_f = 0.46 (petroleum ether/ethyl acetate = 5:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.89 (m), 7.65 (d, J = 8.1 Hz), 7.47 – 7.12 (m), 7.08 (d, J = 7.9 Hz), 6.97 (d, J = 7.9 Hz), 5.55 (s, 1H *trans*), 5.41 (s, 1H *cis*), 5.37 (s, 1H *trans*), 5.26 (s, 1H *cis*), 4.27 – 4.18 (m, 2H *trans* and *cis*), 3.97 – 3.88 (m, 2H *trans* and *cis*), 2.43 (s, 3H *cis*), 2.39 (s, 3H *trans*), 2.36 (s, 3H *trans*), 2.22 (s, 3H *cis*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.0, 144.2, 141.7, 139.1, 138.6, 138.2, 138.0, 137.7, 137.6, 135.2, 130.1, 129.7, 129.5, 129.3, 129.2, 129.2, 129.0, 128.8, 128.7, 128.5, 128.3, 127.9, 126.4, 126.1, 116.3, 115.9, 52.0, 48.8, 48.4, 47.5, 22.0, 21.9, 21.6, 21.4; IR (KBr) ν (cm^{-1}): 3030, 2922, 1598, 1446, 1328, 1161, 1089, 911, 812, 776, 707; HRMS (ESI) calcd for $C_{24}H_{24}NO_2S^+$ $[M+H]^+$ *m/z* 390.1522 , found 390.1514.

2-([1,1'-Biphenyl]-4-yl)-3-(1-phenylvinyl)-1-tosylaziridine (8ag): oil (58%, 105 mg) was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, J = 8.2 Hz), 7.67 (d, J = 8.2 Hz), 7.62 – 7.17 (m), 5.60 (s, 1H *trans*), 5.46 – 5.40 (m, 2H *trans* and *cis*), 5.29 (s, 1H *cis*), 4.29 (d, J = 7.2 Hz, 1H *cis*), 4.25 (d, J = 4.7 Hz, 1H *trans*), 4.02 – 3.97 (m, 2H *trans* and *cis*), 2.45 (s, 3H *cis*), 2.40 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 144.3, 142.1, 141.1, 141.1, 140.8, 140.7, 138.6, 137.7, 137.4, 131.4, 130.2, 129.7, 129.2, 129.0, 128.9, 128.7, 128.5, 128.5, 128.4, 128.0, 127.9, 127.7, 127.5, 127.5, 127.3, 126.9, 126.5, 126.1, 116.5, 116.2, 51.4, 49.2, 48.5, 47.3, 22.0, 21.9; IR (KBr) ν (cm^{-1}): 3030, 2922, 1598, 1328, 1162, 1089, 912, 812, 763, 696; HRMS (ESI) calcd for $C_{29}H_{26}NO_2S^+$ $[M+H]^+$ *m/z* 452.1679, found 452.1674.

2-(Naphthalen-2-yl)-3-(1-phenylvinyl)-1-tosylaziridine (8ah): oil (56%, 96 mg), R_f = 0.46 (petroleum ether/ethyl acetate = 5:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, J = 8.3 Hz), 7.87 – 7.17 (m), 7.13 (d, J = 8.1 Hz), 5.64 (s), 5.50 (s, 1H *trans*), 5.39 (s, 1H *trans*), 5.31 (s, 1H *cis*), 4.40 (d, J = 7.2 Hz), 4.30 (d, J = 4.4 Hz, 1H *trans*), 4.15 (d, J = 4.7 Hz, 1H *trans*), 4.04 (d, J = 7.2 Hz, 1H *cis*), 2.44 (s, 3H *cis*), 2.35 (s, 3H *trans*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 144.3, 141.5, 138.7, 137.3, 133.7, 133.3, 130.2, 129.9, 129.7, 129.1, 128.9, 128.7, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.5, 127.0, 126.8, 126.5, 126.5, 126.4, 126.2, 126.1, 125.6, 116.5, 116.4, 51.6, 49.5, 48.6, 47.7, 22.0, 21.9; IR (KBr) ν (cm^{-1}): 3054, 2916, 1598, 1446, 1328, 1162, 1088, 912, 815, 707; HRMS (ESI) calcd for $C_{27}H_{24}NO_2S^+$ $[M+H]^+$ *m/z* 426.1522, found 426.1529.

2-(4-Methoxyphenyl)-3-(1-phenylvinyl)-1-tosylaziridine (8ai): oil (29%, 47 mg), R_f = 0.66 (petroleum ether/ethyl acetate = 3:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.3 Hz), 7.65 (d, J = 8.3 Hz), 7.47 – 7.19 (m), 7.12 (d, J = 8.7 Hz), 6.89 (d, J = 8.7 Hz), 6.73 – 6.68 (m), 5.54 (s, 1H *cis*), 5.42 (s, 1H *trans*), 5.36 (s, 1H *cis*), 5.25 (s, 1H *trans*), 4.24 (d, J = 4.8 Hz, 1H *trans*), 4.20 (d, J = 7.2 Hz, 1H *cis*), 3.92 (d, J = 7.2 Hz, 1H *cis*), 3.89 (d, J = 4.7 Hz, 1H *trans*), 3.82 (s, 3H *cis*), 3.71 (s, 3H *trans*), 2.44 (s, 3H *trans*), 2.40 (s, 3H *cis*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 160.4, 159.7, 145.0, 144.2, 141.9, 138.5, 138.2, 137.8, 137.6, 135.3, 130.9, 130.1, 129.7, 129.2, 128.9, 128.7, 128.5, 128.3, 127.9, 126.4, 126.1, 124.3, 123.8, 116.3, 115.6, 114.2, 113.7, 55.6, 55.5, 52.3, 48.5, 48.4, 47.2; IR (KBr) ν (cm^{-1}): 2921, 1598, 1496, 1328, 1161, 1090, 912, 803, 707; HRMS (ESI) calcd for $C_{24}H_{24}NO_3S^+$ $[M+H]^+$ *m/z* 406.1471, found 406.1478.

2-(4-(Methylthio)phenyl)-3-(1-phenylvinyl)-1-tosylaziridine (8aj): oil (39%, 66 mg), R_f = 0.67 (petroleum ether/ethyl acetate = 3:1), was synthesized according to General Procedure C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, J = 8.2 Hz), 7.65 (d, J = 8.2 Hz), 7.45 – 7.16 (m), 7.08 (m), 5.56 (s, 1H *trans*), 5.42 (s), 5.38 (s, 1H *trans*), 5.25 (s), 4.22 – 4.17 (m, 2H *trans* and *cis*), 3.95 (d, J = 7.2 Hz, 1H *cis*), 3.90 (d, J = 4.8 Hz, 1H *trans*), 2.48 (s, 3H *trans*), 2.44 (s, 3H *cis*), 2.40 (s, 3H *trans*), 2.38 (s, 3H *cis*); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ 145.1, 144.3, 141.5, 140.1, 138.7, 138.5, 138.0, 137.6, 137.4, 135.1, 130.2, 129.8, 129.7, 129.0, 128.9, 128.7, 128.5, 128.5, 128.4, 128.3, 127.91, 126.4, 126.4, 126.1, 126.0, 116.4, 116.0, 51.6, 48.9, 48.5, 47.2, 22.0, 21.9, 15.8, 15.8; IR (KBr) ν (cm^{-1}): 2973, 2933, 1606, 1445,

1380, 1334, 1046, 881, 748, 691; HRMS (ESI) calcd for $C_{24}H_{24}NO_2S_2^+$ $[M+H]^+$ *m/z* 422.1243, found 422.1249.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Optimization of reaction conditions, copies of spectra

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All authors have given approval to the final version of the manuscript.

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