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Note

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Nucleophilic Organic Base DABCO-Mediated Chemospecific Meinwald Rearrangement of Terminal Epoxides into Methyl Ketones

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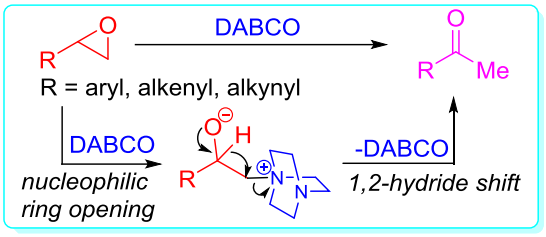
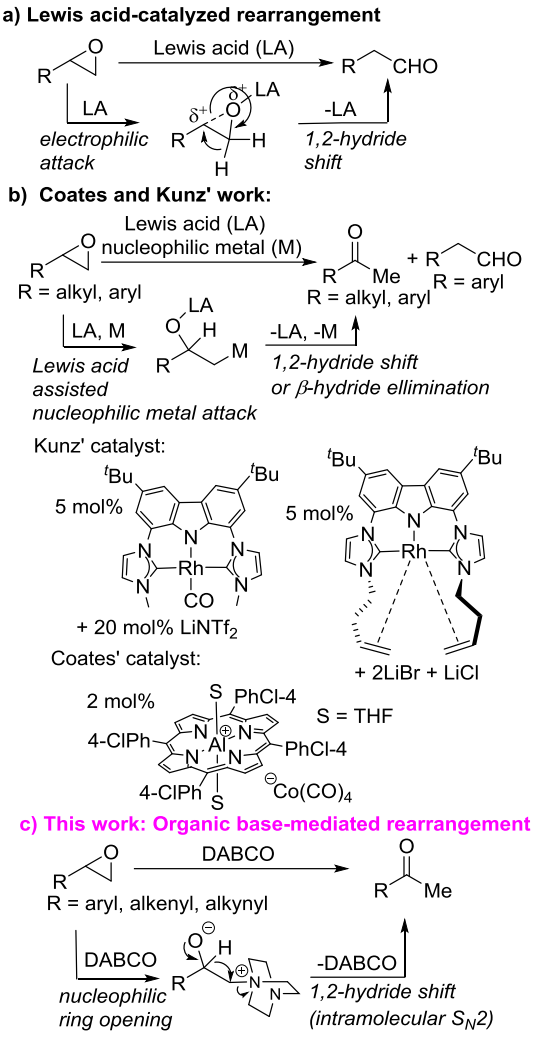
Supporting Information



ABSTRACT: Nucleophilic organic base DABCO (1,4-diazabicyclo[2.2.2]octane)-mediated Meinwald rearrangement of various epoxides was investigated. 2-Aryl, alkenyl, and alkynylepoxides generate the corresponding methyl ketones chemospecifically in good to excellent yields. The current DABCO-mediated Meinwald rearrangement of epoxides features readily accessible starting materials, wide substrate scope, transition metal and acid-free environment, and chemospecificity in the isomerization of epoxides.

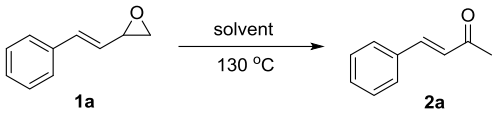
Epoxides are readily available and important intermediates in organic synthesis.[1] They undergo the nucleophilic ring-opening reactions to generate 2-hydroxyalkylated derivatives,[1,2] the acid-catalyzed rearrangements to yield carbonyl compounds,[1a] and strong base-promoted isomerization to give rise to allylic alcohols.[3] The isomerization of epoxides into carbonyl compounds is well known as the Meinwald rearrangement or Meinwald reaction.[4] The acid-catalyzed, including various protonic and Lewis acids, Meinwald rearrangements of epoxides have been widely investigated,[5] in which terminal epoxides generate the corresponding aldehydes as sole or major products (Scheme 1, a),[6] companied with methyl ketones as byproducts in some cases,[6d,6e] while internal epoxides generally afford the corresponding ketones with aldehydes as side products in certain reactions,[7] especially for aryl epoxides.[8] Occasionally, aldehydes are obtained as major products.[9] To realize the isomerization of terminal epoxides into the corresponding methyl ketones (the inverse selectivity from that in the acid-catalyzed rearrangements), some transition metal catalysts[10] and Lewis acid-nucleophilic metal systems with (transition) metal-organic ligand complexes have been designed and applied in the Meinwald rearrangement of terminal epoxides (Scheme 1, b).[11] 2-Alkylepoxides were converted into the desired methyl ketones chemospecifically in good yields. However, 2-arylepoxides generated the desired acetophenones with arylethanals as byproducts in most cases. The isomerization is very attractive in organic synthesis because it could be an alternative to Wacker oxidation by a two step epoxidation-Meinwald rearrangement sequence for Lewis acid-sensitive olefins and displace the sequence of methyl-Grignard reagent addition-alcohol oxidation after the combination with the Corey-Chaychovsky epoxidation for nonoxidation transformation of aldehydes into methyl ketones. After carefully considering and analyzing the mechanism of the Meinwald rearrangement,[1a,5] we designed an organic base-mediated Meinwald rearrangement. Nucleophilic tertiary or aromatic organic bases can serve as nucleophiles to open epoxides at their more electrophilic ring carbon atom (usually less substituted one)[2] to generate zwitterionic intermediates, which undergo a 1,2-hydride-shift with loss of the organic base (similar to an intramolecular substitution) to afford the desired methyl ketones because the organic bases can work as leaving groups in the zwitterionic intermediates as well (Scheme 1, c). In continuation of our interest in the synthetic application of small heterocycles,[12] herein, we present our nucleophilic organic base DABCO-mediated chemospecific Meinwald rearrangement of various nonalkyl terminal epoxides into the corresponding methyl ketones in good yields. The current strategy is a mild basic, metal-free, and chemospecific isomerization of nonalkyl terminal epoxides into methyl ketones. It is a good complement for the Meinwald rearrangement, especially for Lewis acid-nucleophilic metal systems. The current method can be applied in the acid-sensitive epoxides.

Scheme 1. Rearrangement of terminal epoxides to carbonyl compounds. a) Lewis acid-catalyzed rearrangement; b) Costes and Kunz's work; c) This work: Organic base-mediated rearrangement.



To avoid the existence of a protonic acid and to extend the scope of substrates, we directly selected acid-sensitive 2-styrylepoxide (**1a**) as a model substrate to react with tertiary or aromatic organic amine bases under thermal conditions. Stoichiometric amount of organic amines can rule out the possible involvement of a trace amount of acid from silica borate glassware's residue acidic sites. We started our optimization with 2-styrylepoxide (**1a**) and two representative tertiary organic bases TEA (triethylamine) and DABCO (1,4-diazabicyclo[2.2.2]octane)**.** When 2-styrylepoxide (**1a**) and 2 equivalents of TEA were stirred in anhydrous toluene at 40 °C, 80 °C, and 100 °C for 12 hrs, no reaction occurred (Table 1, entries 1, 3 and 5). However, the reaction of 2-styrylepoxide (**1a**) and 2 equivalents of DABCO produced the desired product 4-phenyl-but-3-en-2one (**2a**) in 58% and 65% yields, respectively, at 80 °C and 100 °C for 12 hrs (Table 1, entries 4 and 6). The yield was further improved to 80% when 2-styrylepoxide (**1a**) and DABCO were stirred in anhydrous mesitylene ($Me_3C_6H_3$) at 130 °C for 12 hrs (Table 1, entry 8). However, triethylamine was still not efficient at 130 °C (Table 1, entry 7). Furthermore, a number of organic amine bases, including pyridine (Py), 2-chloropyridine (2-ClPy), 4-methylpyridine (4-MePy), 2,6-dimethylpyridine (2,6-Me_2Py), 4-(dimethylamino)pyridine (DMAP), *N*-methylimidazole (*N*-MeIm), *N*-ethyl-*N*-isopropylpropan-2-amine (DIPEA), 4-methylmorpholine, morpholine, and hexamethylenetetramine (HMTA), was screened, only the reaction with DMAP as a base produced product **2a** in 8% yield (Table 1, entries 9-18). Strong organic nucleophile PPh_3 was test. However, it was inefficient (Table 1, entry 19). The results indicate that DABCO is an efficient base for the isomerization due to its strong nucleophilicity. According to the nucleophilicity scale described by Mayr and coworkers,[13] DABCO is a much more potent nucleophile than other organic amines tested. This could explain its exceptional performance in this reaction. Solvent evaluation revealed that mesitylene was the best choice (Table 1, entries 8, 20, and 21). Lengthening the time to 24 h had a positive influence on the yield, the product **2a** was isolated in an excellent yield of 91% (Table 1, entry 22) (Method A). Decreasing the amount of DABCO to 1.5 to 1.0 to 0.5 equivalents gave lower yields of 79%, 63%, and 47%, respectively (Table 1, entries 23-25). Raising the reaction temperature to 165 °C (refluxing conditions) resulted in a slightly decreased yield (Table 1, entry 26).

Table 1. Optimization of base-mediated reaction conditions[a]

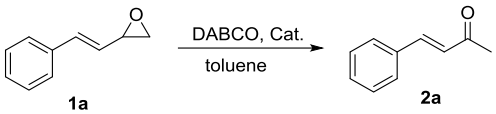


Entry	Base.	Base equiv.	Solvent	Time h	Yield[b] %
1	TEA	2	Toluene	12	NR[c]
2	DABCO	2	Toluene	12	NR[c]
3	TEA	2	Toluene	12	NR[d]
4	DABCO	2	Toluene	12	58[d]
5	TEA	2	Toluene	12	NR[e]
6	DABCO	2	Toluene	12	65[e]
7	TEA	2	$Me_3C_6H_3$	12	NR
8	DABCO	2	$Me_3C_6H_3$	12	80
9	Py	2	$Me_3C_6H_3$	12	NR
10	2-ClPy	2	$Me_3C_6H_3$	12	NR
11	4-MePy	2	$Me_3C_6H_3$	12	NR
12	2,6-Me_2Py	2	$Me_3C_6H_3$	12	NR
13	DMAP	2		12	8
14	*N*-MeIm	2	$Me_3C_6H_3$	12	NR
15	DIPEA	2	$Me_3C_6H_3$	12	NR
16	4-Memorpholine	2	$Me_3C_6H_3$	12	NR
17	Morpholine	2	$Me_3C_6H_3$	12	NR
18	HMTA	2	$Me_3C_6H_3$	12	NR
19	PPh_3	2	$Me_3C_6H_3$	12	NR
20	DABCO	2	ClC_6H_5	12	59
21	DABCO	2	DMSO	12	Mess
22	DABCO	2	$Me_3C_6H_3$	24	91
23	DABCO	1.5	$Me_3C_6H_3$	24	79
24	DABCO	1	$Me_3C_6H_3$	24	63
25	DABCO	0.5	$Me_3C_6H_3$	24	47
26	DABCO	2	$Me_3C_6H_3$	24	86[f]

[a] Unless otherwise specified, reactions were performed on a 0.5 mmol scale at 130 °C. [b] Isolated yield. [c] Reaction was conducted

at 40 °C. [d] Reaction was conducted at 80 °C. [e] Reaction was conducted at 100 °C. [f] Reaction was conducted at 165 °C.

Table 2. Optimization of the Lewis acid-catalyzed base-mediated reaction conditions[a]



Entry	Catalyst (equiv.)	T (°C)	Yield (%)[b]
1	-	80	58
2	$MgSO_4$ (0.2)	80	58
3	$Mg(ClO_4)_2$ (0.2)	80	67
4	MgI_2 (0.2)	80	68
5	$LiOAc{\cdot}2H_2O$ (0.2)	80	52
6	LiCl (0.2)	80	49
7	LiBr (0.2)	80	51
8	$SnCl_2{\cdot}2H_2O$ (0.2)	80	67
9	$Sc(OTf)_3$ (0.2)	80	59
10	$MnSO_4{\cdot}H_2O$ (0.2)	80	67
11	AgOAc (0.2)	80	33
12	$AgNO_3$ (0.2)	80	38
13	$FeCl_2{\cdot}7H_2O$ (0.2)	80	56
14	$FeCl_3$ (0.2)	80	56
15	$Fe(NO_3){\cdot}9H_2O$ (0.2)	80	0
16	$CoCl_2{\cdot}2H_2O$ (0.2)	80	52
17	$CeCl_3{\cdot}7H_2O$ (0.2)	80	73
18	$CuSO_4{\cdot}5H_2O$ (0.2)	80	46
19	CuBr (0.2)	80	53
20	$Cu(OAc)_2$ (0.2)	80	55
21	$Cu(SO_4)_2$ (0.2)	80	64
22	$Cu(OTf)_2$ (0.2)	80	49
23	$CuBr_2$ (0.2)	80	79
24	$CuCl_2{\cdot}2H_2O$ (0.2)	80	78
25	$CuCl_2{\cdot}2H_2O$ (0.1)	80	71
26	$CuCl_2{\cdot}2H_2O$ (0.3)	80	74
27	$CuCl_2{\cdot}2H_2O$ (0.2)	90	58
28	$CuCl_2{\cdot}2H_2O$ (0.2)	70	45
29	$CuCl_2{\cdot}2H_2O$ (0.2)	80	59[c]
30	$CuCl_2{\cdot}2H_2O$ (0.2)	80	84[d]
31	$CuCl_2{\cdot}2H_2O$ (0.2)	80	0[e,f]
32	$TsOH{\cdot}H_2O$ (0.2)	80	mess[e]

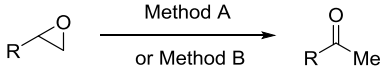
[a] Unless otherwise specified, 2 equiv of DABCO . [b] Isolated yields; [c] 1.5 equiv of DABCO; [d] 3 equiv of DABCO. [e] Without DABCO. [f] $PhCH_2CH{=}CHCHO$ generated in a trace amount.

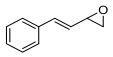
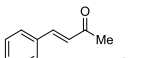
Considering that the reaction temperature of 130 °C is somewhat high for certain thermally unstable epoxides in possible synthetic applications, and the fact that our DABCO-mediated rearrangement works at 80 °C with a relatively low yield (Table 1, entry 4), we hope to decrease the reaction temperature with the assistance of Lewis acids to activate the epoxides. We evaluated many weak acidic Lewis acids as catalysts for the DABCO-mediated reaction at 80 °C, including $MgSO_4$, $Mg(ClO_4)_2$, MgI_2, $LiOAc{\cdot}2H_2O$, LiCl, LiBr, $SnCl_2{\cdot}2H_2O$, $Sc(OTf)_3$, $MnSO_4{\cdot}H_2O$, AgOAc, $AgNO_3$, $FeCl_2{\cdot}7H_2O$, $FeCl_3$, $Fe(NO_3)_3{\cdot}9H_2O$, $CoCl_2{\cdot}2H_2O$, $CeCl_3{\cdot}7H_2O$, $CuSO_4{\cdot}5H_2O$, CuBr, $Cu(OAc)_2$, $Cu(SO_4)_2$, $Cu(OTf)_2$, $CuBr_2$, and $CuCl_2{\cdot}2H_2O$ (Table 2). After all these attempts, $Mg(ClO_4)_2$, MgI_2, $SnCl_2{\cdot}2H_2O$, $MnSO_4{\cdot}H_2O$, $CeCl_3{\cdot}7H_2O$, $Cu(SO_4)_2$, CuBr, and $CuCl_2{\cdot}2H_2O$ can improve the yield (Table 2, entries 3, 4, 8, 10, 17, 21, 23, and 24). The others decreased the yield possibly due to strong conjunction between the Lewis acids and base DABCO. The conjunction not only quenched the Lewis acid, but also decreased the amount of free DABCO, resulting in the decrease of the yield. $CuCl_2{\cdot}2H_2O$ was chosen as the best catalyst due to its cheaper price. Both increasing and decreasing reaction temperatures resulted in loss of the yield (Table 2, entries 27 and 28). Adjusting the amount of DABCO to 3 equivalents and $CuCl_2{\cdot}2H_2O$ to 0.2 equivalent gave the best yield of 84% (Table 2, entry 30) (Method B). The representative Lewis and protonic acid-catalyzed conditions were evaluated as well. However, no reaction was observed (Table 2, entries 31 and 32).

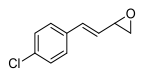
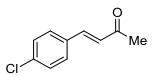
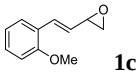
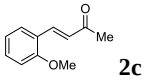
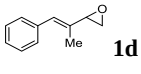
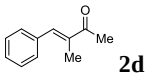
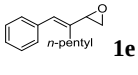
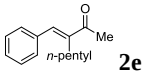
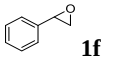
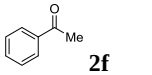
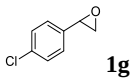
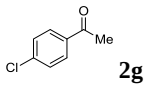
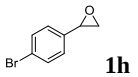
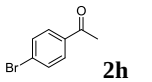
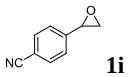
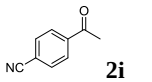
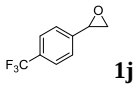
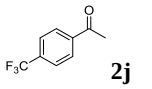
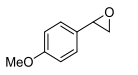
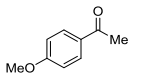
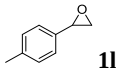
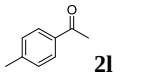
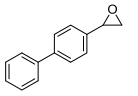
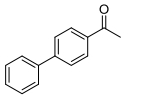
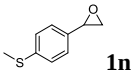
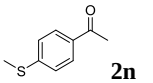
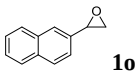
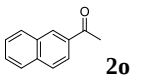
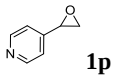
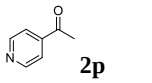
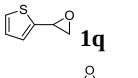
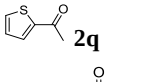
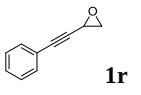
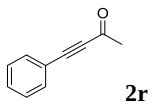
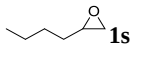
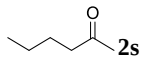
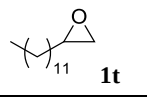
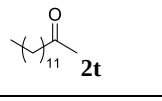
With the optimal conditions (Method A) in hand, substituted 2-styrylepoxides **1b**−**1e** were treated with DABCO in mesitylene at 130 °C, the corresponding methyl ketones **2b**−**2e** were isolated as sole products in good to excellent yields with chemospecificity (Table 3, entries 2-5, Method A). To extend the scope of substrates, 2-arylepoxides **1f**−**1o** with both electron-donating and electron-withdrawing substituents, as well as 2-heteroarylepoxides **1p** and **1q**, were subjected to the rection conditions, affording the desired products in satisfactory to excellent yields (Table 3, entries 6-17, Method A). The results indicates that 2-arylepoxides with electron-withdrawing substituents generally gave the corresponding methyl ketones in higher yields that those with electron-donating substituents possibly because the electron-deficient aryls are favorable to stabilize the generated alkoxide anions in the reactions (Scheme 1, c). The reaction was further extended to 2-alkynylepoxide **1r**, affording the desired methyl alkynyl ketone **2p** in 42% yield (Table 3, entry 18). However, alkyl substituted terminal epoxides 2-butylepoxide (**1s**) and 2-dodecylepoxide (**1t**) showed no reactivity under the reaction conditions (Table 3, enmtries 19 and 20).

The Lewis acid-catalyzed conditions were applied in the isomerization reactions of epoxides **1a**-**1t** at 80 °C, the corresponding methyl ketones **2a**-**2r** were obtained in comparable yields except for **1s** and **1t** (Table 3, Method B). Even under the Lewis acid catalysis conditions, they did not work either.

Table 3. Scope of epoxides



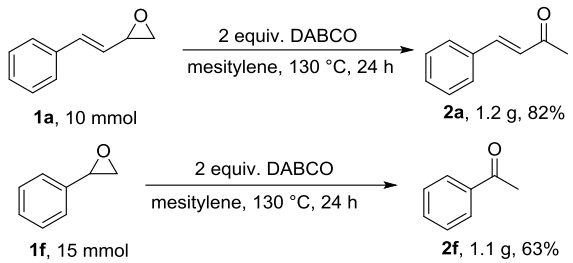
Entry	Substrate	Product	Yield[a] in Method (%)	
			A[b]	B[c]
1	 **1a**	 **2a**	91	85

2	 **1b**	 **2b**	69	90
3	 **1c**	 **2c**	74	75
4	 **1d**	 **2d**	66	65
5	 **1e**	 **2e**	73	39
6	 **1f**	 **2f**	70	58
7	 **1g**	 **2g**	94	95
8	 **1h**	 **2h**	75	56
9	 **1i**	 **2i**	95	99
10	 **1j**	 **2j**	89	84
11	 **1k**	 **2k**	56	13
12	 **1l**	 **2l**	41	33
13	 **1m**	 **2m**	50	48
14	 **1n**	 **2n**	71	49
15	 **1o**	 **2o**	90	95
16	 **1p**	 **2p**	96	92
17	 **1q**	 **2q**	84	53
18	 **1r**	 **2r**	42	31
19	 **1s**	 **2s**	0	0
20	 **1t**	 **2t**	0	0

[a]Yields are isolated yields. [b]Method A: **1** (0.5 mmol) and DABCO (112 mg, 1 mmol) in 2 mL of mesitylene were stirred at 130 °C for 24 hrs. [c]Method B: **1** (0.5 mmol), DABCO (112 mg, 1 mmol), and $CuCl_2{\cdot}2H_2O$ (17 mg, 0.1 mmol) in 2 mL of toluene were stirred at 80 °C for 24 hrs.

Gram-scale preparations of methyl ketones **2a** and **2f** were realized in 82% and 63% isolated yields, respectively (Scheme 2).

Scheme 2. Meinwald Rearrangement of Epoxides into Methyl Ketones in Gram-Scale Reactions



In conclusion, we have realized nucleophilic organic base DABCO-mediated Meinwald rearrangement of monosubstituted nonalkylepoxides under thermal conditions, specifically affording methyl ketone products. Most Lewis acids can catalyze the rearrangement at relatively low temperature, while $CeCl_3{\cdot}7H_2O$, $CuBr_2$, and $CuCl_2{\cdot}2H_2O$ are efficient ones. Compared with previously reported Meinwald rearrangements, DABCO-mediated rearrangement can be metal-free, acid-free, specific, and suitable for monosubstituted nonalkylepoxides. Our current strategy can be taken as a complementary method for the acid-catalyzed isomerization of epoxides.

EXPERIMENTAL SECTION

General Information. Unless otherwise noted, all materials were purchased from commercial suppliers. Reactions were conducted in base-washed and flame-dried glassware under nitrogen atmosphere. Mesitylene was refluxed with sodium/benzophenone, and freshly distilled prior to use. Flash column chromatography was performed using silica gel (normal phase, 200–300 mesh) from Qingdao Haiyang Chemical. Petroleum ether used for column chromatography was 60–90 °C 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 from Yantai Chemical Industry Institute. The plates were visualized under UV light, as well as other TLC stains (phosphomolybdic acid: 10% in ethanol; potassium permanganate: 1% in water; iodine: 10 g iodine absorbed on 30g silica gel). ^1H and ^{13}C NMR spectra were recorded on a Bruker 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). IR spectra (KBr pellets, ν (cm^{-1})) were taken on an FT-IR spectrometer. The high-resolution mass spectra were obtained under ESI ionization using an LC/MSD TOF mass spectrometer.

General procedure for the DABCO-mediated Meinwald rearrangement of epoxides 1. *Method A.* Epoxide **1** (0.5 mmol) was dissolved in 2 mL of mesitylene in a 10 mL reaction tube. DABCO (112 mg, 1.0 mmol) was added at room temperature, and then the reaction mixture was heated at 130 °C for 24 h. After cooling to room temperature, the reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:50, *v/v*) to afford product **2**.

Method B. Epoxide **1** (0.5 mmol) was dissolved with 2 mL of toluene in a 10 mL reaction tube. DABCO (112 mg, 1.5 mmol) and $CuCl_2{\cdot}2H_2O$ (17 mg, 0.1 mmol) were added at room temperature, and then the reaction mixture was heated at 80 °C for 24 h. After cooling to room temperature, the reaction mixture was directly subjected to flash column chromatography with ethyl acetate/ petroleum ether (1:50, *v/v*) to afford product **2**.

(E)-4-Phenylbut-3-en-2-one (2a).[14] Purified by flash column chromatography (PE/EA 100:1, *v/v*) on silica gel to give the desired product as red-brown oil, method A: 133 mg, 91% yield (from 1.0 mmol **1a**), method B: 62 mg, 85% yield (from 0.5 mmol **1a**). R_f = 0.30, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.47 (m, 3H), 7.42 – 7.35 (m, 3H), 6.71 (d, J = 16.3 Hz, 1H), 2.37 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.3, 143.4, 134.4, 130.5, 128.9, 128.2, 127.1, 27.5.

(E)-4-(4-Chlorophenyl)but-3-en-2-one (2b).[14] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow oil, method A: 125 mg, 69% yield (from 1.0 mmol **1b**), method B: 81 mg, 90% yield (from 0.5 mmol **1b**). R_f = 0.25, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 3H), 7.40 – 7.35 (m, 2H), 6.69 (d, *J* = 16.3 Hz, 1H), 2.38 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.0, 141.8, 136.4, 132.9, 129.3, 129.2, 127.4, 27.6.

(E)-4-(2-Methoxyphenyl)but-3-en-2-one (2c).[14] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow oil, method A: 104 mg, 74% yield (from 0.80 mmol **1c**), method B: 40 mg, 75% yield (from 0.3 mmol **1c**). R_f = 0.20, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 16.4 Hz, 1H), 7.54 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.39 – 7.35 (m, 1H), 6.97 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.75 (d, *J* = 16.8 Hz, 1H), 3.90 (s, 3H), 2.39 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 199.1, 158.3, 138.7, 131.8, 128.3, 127.8, 123.4, 120.8, 111.1, 55.5, 27.1.

(E)-3-Methyl-4-phenylbut-3-en-2-one (2d).[15] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, method A: 106 mg, 66% yield (from 1.0 mmol **1d**), method B: 31 mg, 65% yield (from 0.3 mmol **1d**). R_f = 0.28, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 1.2 Hz, 1H), 7.45-7.40 (m, 4H), 7.36 – 7.32 (m, 1H), 2.47 (s, 3H), 2.06 (d, *J* = 1.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.3, 139.6, 137.8, 135.9, 129.7, 128.5, 128.4, 25.8, 12.9.

(E)-3-Benzylideneoctan-2-one (2e).[15] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow oil, method A: 129 mg, 73% yield (from 0.82 mmol **1e**), method B: 42 mg, 39% yield (from 0.5 mmol **1e**). R_f = 0.18, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.29 (m, 6H), 2.52 – 2.45 (m, 2H), 2.44 (s, 3H), 1.50 – 1.40 (m, 2H), 1.40 – 1.10 (m, 4H), 0.92-0.84 (m, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 200.3, 137.3, 134.3, 130.6, 128.6, 128.2, 126.7, 52.0, 31.7, 31.7, 27.5, 22.4, 14.0.

1-Phenylethan-1-one (2f).[16] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, method A: 70 mg, 70% yield (from 0.83 mmol **1f**), method B: 70 mg, 58% yield (from 0.5 mmol **1f**). R_f = 0.27, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.92 (m, 2H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.47 (dd, *J* = 7.6 7.6, Hz, 2H), 2.61 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.1, 137.0, 133.0, 128.5, 128.2, 26.5.

1-(4-Chlorophenyl)ethan-1-one (2g).[17] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, method A: 145 mg, 94% yield (from 1.0 mmol **1g**), method B: 73 mg, 95% yield (from 0.5 mmol **1g**). R_f = 0.38, 5% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.8 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.8, 139.5, 135.4, 129.7, 128.8, 26.5.

1-(4-Bromophenyl)ethan-1-one (2h).[18] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as white solid, method A: 75 mg, 75% yield. (from 0.5 mmol **1h**), method B: 56 mg, 56% yield (from 0.5 mmol **1h**). M.p. 57–58 °C (Lit.[19] M.p. 52−53 °C). R_f = 0.30, 6.67% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.61 (d, *J* = 8.5 Hz, 2H), 2.59 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.0, 135.8, 131.9, 129.8, 128.3, 26.5.

4-Acetylbenzonitrile (2i).[20] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as white solid, method A: 69 mg, 95% yield (from 0.5 mmol **2i**), method B: 45 mg, 99% yield (from 0.3 mmol **1i**). M.p. 60–63 °C (Lit.[21] M.p. 59−60 °C). R_f = 0.14, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.4 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 2H), 2.66 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.4, 139.8, 132.4, 128.6, 117.8, 116.3, 26.7.

1-(4-(Trifluoromethyl)phenyl)ethan-1-one (2j).[20] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow liquid, method A: 85 mg, 89% yield (from 0.5 mmol **1j**), method B: 47 mg, 84% yield (from 0.3 mmol **1j**). R_f = 0.46, 6.67% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 2.63 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.9, 139.6, 134.4 (q, $J_{C\text{-}F}$ = 32.6 Hz), 128.6, 125.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 123.6 (q, $J_{C\text{-}F}$ = 272.8 Hz), 26.7. ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.14.

1-(4-Methoxyphenyl)ethan-1-one (2k).[22] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, method A: 84 mg, 56 % yield (from 1.0 mmol **1k**), method B: 10 mg, 13% yield (from 0.5 mmol **1k**). R_f = 0.18, 6.67% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.3.

1-(4-Methylphenyl)ethan-1-one (2l).[20] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow liquid, method A: 41 mg, 41% yield (from 0.75 mmol **1l**), method B: 13 mg, 33% yield (from 0.3 mmol **1l**). R_f = 0.37, 6.67% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 2H), 7.26 (d, *J*

= 7.9 Hz, 2H), 2.58 (s, 3H), 2.41 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.8, 143.9, 134.7, 129.2, 128.4, 26.5, 21.6.

1-([1,1'-Biphenyl]-4-yl)ethan-1-one (2m).[23] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow solid, method A: 50 mg, 50% yield (from 0.5 mmol **1m**), method B: 47 mg, 48% yield (from 0.5 mmol **1m**). M.p. 125–128 °C (Lit.[24] M.p. 123−124 °C). R_f = 0.46, 10% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.01 (m, 2H), 7.71 – 7.67 (m, 2H), 7.65 – 7.61 (m, 2H), 7.50 – 7.44 (m, 2H), 7.42 –7.39 (m, 1H), 2.64 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.7, 145.8, 139.9, 135.8, 128.9, 128.9, 128.2, 127.3, 127.2, 26.7.

1-(4-Methylthiophenyl)ethan-1-one (2n).[25] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as white solid, method A: 60 mg, 71% yield (from 0.5 mmol **1n**), method B: 41 mg, 49% yield (from 0.5 mmol **1n**). M.p. 82–84 °C (Lit.[25] M.p. 80.6−81.4 °C). R_f = 0.44, 20% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, J = 8.5 Hz, 2H), 7.26 (d, J = 8.4 Hz, 2H), 2.56 (s, 3H), 2.52 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.1, 145.8, 133.4, 128.7, 124.9, 26.4, 14.7.

1-(Naphthalen-2-yl)ethan-1-one (2o).[20] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as yellow oil, method A: 90 mg, 91% yield (from 0.6 mmol **1o**), method B: 81 mg, 95% yield (from 0.5 mmol **1o**). R_f = 0.29, 5% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 8.51 – 8.42 (m, 1H), 8.06 – 7.80 (m, 4H), 7.65 – 7.48 (m, 2H). 2.72 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 198.0, 135.6, 134.5, 132.5, 130.1, 129.5, 128.4, 128.4, 127.7, 126.7, 123.9, 26.6.

1-(Pyridin-4-yl)ethan-1-one (2p).[23] Purified by flash column chromatography (PE/EA 2:1, *v/v*) on silica gel to give the desired product as colorless liquid, method A: 48 mg, 96% yield (from 0.4 mmol **1p**), method B: 55 mg, 92% yield (from 0.5 mmol **1p**). R_f = 0.22, 50% ethyl acetate in petroleum eth. ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 – 8.73 (m, 2H), 8.00 – 7.41 (m, 2H), 2.60 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 197.2, 150.9, 142.7, 121.1, 26.6.

1-(Thiophen-2-yl)ethan-1-one (2q).[20] Purified by flash column chromatography (PE/EA 20:1, *v/v*) on silica gel to give the desired product as yellow liquid, method A: 53 mg, 84% yield (from 0.5 mmol **1q**), method B: 33 mg, 53% yield (from 0.5 mmol **1q**). R_f = 0.50, 20% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, J = 3.7, 1.2 Hz, 1H), 7.64 (dd, J = 4.9, 1.2 Hz, 1H), 7.13 (dd, J = 5.0, 3.7 Hz, 1H), 2.57 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 190.7, 144.6, 133.7, 132.4, 128.1, 26.9.

4-Phenylbut-3-yn-2-one (2r).[26] Purified by flash column chromatography (PE/EA 50:1, *v/v*) on silica gel to give the desired product as colorless oil, method A: 30 mg, 42% yield (from 0.5 mmol **1r**), method B: 28 mg, 31% % (from 0.5 mmol **1r**). R_f = 0.60, 20% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.1 Hz, 2H), 7.46 (dd, J = 7.4, 7.1 Hz, 1H), 7.39 (dd, J = 7.4, 7.1 Hz, 2H), 2.46 (s, 3H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 184.6, 133.0, 130.7, 128.6, 119.9, 90.3, 88.3, 32.7.

General procedure for the synthesis of epoxides 1. Styrylepoxides **1a-1e** and arylepoxides **1g-1q** were prepared from trimethylsulfonium iodide with the corresponding cinnamaldehydes and aromatic aldehydes using Johnson-Corey-Chaykovsky reaction.[27] Sodium hydride (0.9 g, 22.5 mmol, 60% mineral oil dispersion) was washed with petroleum ether (3 × 5 mL). The residual petroleum ether was removed under vacuum. Under atmosphere of nitrogen, dry THF (15 mL) and dry DMSO (15 mL) were added and the reaction mixture was cooled in an ice bath. A solution of trimethylsulfonium iodide (3.67 g, 18 mmol) in DMSO (4 mL) was added. After addition, cinnamyl aldehyde (1.98 g, 15 mmol) was added in one portion. The reaction mixture was stirred at 0 °C for 30 min and at room temperature for an additional 12 h. The reaction mixture was slowly quenched with a mixture of water and ice (20 mL) and extracted with methylene chloride (3 × 10 mL). The combined organic extracts were washed with brine (2 × 30 mL), dried over sodium sulfate, filtered. The reaction mixture was directly subjected to flash column chromatography with ethyl acetate/petroleum ether (1:25, *v/v*) to give (*E*)-2-styryloxirane (**1a**)

2-(Phenylethynyl)oxirane (**1r**) was prepared from but-3-en-1-yn-1-ylbenzene using the *m*-CPBA epoxidation reaction.[28] To a solution of but-3-en-1-yn-1-ylbenzene (640 mg, 5.0 mmol) in DCM (20 mL) in a 100 mL flask was added *m*-CPBA (1.5 g, 7.5 mmol, 85%) and $Na_2HPO_4{\cdot}12H_2O$ (2.15 g, 6 mmol) at 0 °C. The reaction mixture was allowed to stir at room temperature overnight. The solution was then washed with $NaHCO_3$ aq (20 mL), and dried over Na_2SO_4. After evaporation of the solvent, the crude product was purified on silica gel column chromatography with a mixture of petroleum ether/EtOAc (20:1, *v/v*) to afford the desired epoxide **1r**.

All prepared epoxides except **1e** are known compounds with the same analytical data as reported ones. Epoxides **1f**, **1s**, and **1t** are commercially available.

(E)-2-Styryloxirane (**1a**)[29] Yellow liquid, 1.23 g, 56% yield. R_f = 0.68, 20% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.36 (t, J = 7.4 Hz, 2H), 7.33 – 7.27 (m, 1H), 6.85 (d, J = 16.0 Hz, 1H), 5.92 (dd, J = 16.0, 8.0 Hz, 1H), 3.64 – 3.45 (m, 1H), 3.09 (dd, J = 5.0, 4.2 Hz, 1H), 2.81 (dd, J = 5.1, 2.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 136.1, 134.5, 128.6, 128.0, 126.9, 126.4, 52.5, 49.1.

(E)-2-(4-Chlorostyryl)oxirane (1b).[29] Yellow liquid, 0.53 g, 59% yield. R_f = 0.65, 20% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.19 (m, 4H), 6.76 (d, J = 16.0 Hz, 1H), 5.86 (dd, J = 16.0, 7.9 Hz, 1H), 3.63 – 3.38 (m, 1H), 3.06 (dd, J = 4.8, 4.6 Hz, 1H), 2.77 (dd, J = 5.0, 2.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 134.6, 133.7, 133.2, 128.8, 127.7, 127.6, 52.4, 49.2

(E)-2-(2-Methoxystyryl)oxirane (**1c**)[30] Yellow oil, 483 mg, 55% yield. R_f = 0.72, 20% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.31 (d, J = 7.6 Hz, 1H), 7.16 –7.14 (m, 1H), 7.05 (d, J = 16.1 Hz, 1H), 6.86 – 6.75 (m, 2H), 5.80 (dd, J = 16.1, 8.2 Hz, 1H), 3.75 (s, 3H), 3.53 – 3.29 (m, 1H), 2.95 (dd, J= 5.1, 4.6 Hz, 1H), 2.67 (dd, J = 5.1, 2.6 Hz, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 156.6, 129.6, 129.0, 127.6, 127.0, 125.1, 120.6, 110.8, 55.3, 53.1, 49.1.

(E)-2-(1-Phenylprop-1-en-2-yl)oxirane (1d)[29] Colorless oil, 1.552 g, 97% yield. R_f = 0.5, 10% ethyl acetate in petroleum ether. ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 4H), 7.26 – 7.20 (m, 1H), 6.67 (s, 1H), 3.52 – 3.47 (m, 1H), 2.94 (dd, J = 5.0, 4.6 Hz, 1H), 2.81 (dd, J = 5.0, 2.6 Hz, 1H), 1.74 (s, 1H). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 137.1, 134.0, 128.9, 128.8, 128.2, 126.7, 56.1, 46.8, 11.8.

(E)-2-(1-Phenylhept-1-en-2-yl)oxirane (1e) Colorless oil, 2.086 g, 97% yield. R_f = 0.58, 10% ethyl acetate in petroleum

ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.30 (m, 2H), 7.28 – 7.18 (m, 3H), 6.56 (s, 1H), 3.58 – 3.30 (m, 1H), 2.96 (dd, J = 5.6, 4.1 Hz, 1H), 2.69 (dd, J = 5.6, 2.7 Hz, 1H), 2.26 (ddd, J = 13.6, 10.8, 5.6 Hz, 1H), 2.14 (ddd, J = 13.6, 10.7, 5.4 Hz, 1H).1.60 – 1.52 (m, 1H), 1.51 – 1.41 (m, 1H), 1.32 – 1.27 (m, 4H), 0.89 – 0.86 m, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.8, 137.1, 128.6, 128.2, 126.6, 126.3, 54.7, 48.8, 32.0, 28.8, 27.8, 22.4, 14.0. HRMS (ESI-TOF) *m/z*: $[M+H]^+$ calcd for $C_{15}H_{21}O^+$ 217.1587, found 217.1584.

2-(4-Chlorophenyl)oxirane (1g)[12h] Colorless oil, 262 mg, 32% yield. R_f = 0.5, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.2 Hz, 2H), 3.85–3.79 (m, 1H), 3.13 (t, J = 4.7 Hz, 1H), 2.74 (dd, J = 5.0, 2.1 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.1, 133.9, 128.7, 126.8, 51.7, 51.2.

2-(4-Bromophenyl)oxirane(1h)[12h] Colorless oil, 600 mg, 60% yield. R_f = 0.43, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.4 Hz, 2H), 3.82 (dd, J = 3.9, 2.6 Hz, 1H), 3.14 (dd, J = 5.4, 4.1 Hz, 1H), 2.75 (dd, J = 5.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 136.7, 131.6, 127.1, 122.0, 51.8, 51.2.

4-(Oxiran-2-yl)benzonitrile(1i)[32] Colorless liquid, 320 mg, 44% yield. R_f = 0.28, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, J = 8.3 Hz, 2H), 7.39 (d, J = 8.3 Hz, 2H), 3.91 (dd, J = 4.1, 2.5 Hz, 1H), 3.21 (dd, J = 5.5, 4.1 Hz, 1H), 2.76 (dd, J = 5.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.2, 132.3, 126.1, 118.6, 111.9, 51.6, 51.5.

2-(4-(Trifluoromethyl)phenyl)oxirane(1j)[11c]: Colorless liquid, 0.456 g, 48% yield. R_f = 0.56, 10% ethyl acetate in petroleum ether.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.0 Hz, 2H), 3.91 (dd, J = 4.1, 2.5 Hz, 1H), 3.18 (dd, J = 5.5, 4.1 Hz, 1H), 2.77 (dd, J = 5.5, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.8, 130.34 (q, $J_{C\text{-}F}$ = 32.5 Hz), 125.7, 125.4 (q, $J_{C\text{-}F}$ = 4.0 Hz), 124.0 (q, $J_{C\text{-}F}$ = 266.6 Hz), 51.7, 51.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -62.60.

2-(4-Methoxyphenyl)oxirane (1k)[33] Colorless liquid, 1.04 g, 77% yield. R_f = 0.83, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (d, J = 8.6 Hz, 2H), 6.88 (d, J = 8.6 Hz, 2H), 3.89 – 3.76 (m, 4H), 3.15 – 3.10 (m, 1H), 2.81 (dd, J = 5.2, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.7, 129.4, 126.8, 114.0, 55.3, 52.2, 51.0.

2-(4-Methylphenyl)oxirane (1l)[34] Colorless liquid, 665 mg, 98% yield. R_f = 0.80, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.13 (m,4H), 3.83 (dd, J = 4.1, 2.6 Hz, 1H), 3.12 (dd, J = 5.5, 4.1 Hz, 1H), 2.79 (dd, J = 5.5, 2.6 Hz, 1H), 2.34 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.0, 134.5, 129.2, 125.4, 52.3, 51.1, 21.2.

2-([1,1'-Biphenyl]-4-yl)oxirane (1m)[34]: Yellow solid, 292 mg, 30% yield. M.p. 103–105℃. R_f = 0.57, 10% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 4H), 7.48 – 7.41 (m, 2H), 7.38 – 7.31 (m, 3H), 3.91 (dd, J = 4.1, 2.6 Hz, 1H), 3.18 (dd, J = 5.5, 4.1 Hz, 1H), 2.85 (dd, J = 5.5, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 140.6, 136.6, 128.8, 127.4, 127.2, 127.0, 125.9, 52.2, 51.2.

2-(4-Methylthiophenyl)oxirane (1n)[35] Colorless oil, 967 mg, 58% yield. R_f = 0.63, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 3.80 (dd, J = 4.0, 2.7 Hz, 1H), 3.11 (dd, J = 5.4, 4.1 Hz, 1H), 2.77 (dd, J = 5.4, 2.6 Hz, 1H), 2.46 (s, 3H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 138.4, 134.3, 126.5, 125.9, 52.0, 51.0, 15.7.

2-(Naphthalen-2-yl)oxirane (1o)[34]: White solid, 300 mg, 17% yield. M.p. 57−58 °C (Lit.[36] M.p. 57−58 °C). R_f = 0.70, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 – 7.76 (m, 3H), 7.55 – 7.46 (m, 3H), 7.36 (dd, J = 8.5, 1.8 Hz, 1H), 4.06 (dd, J = 4.1, 2.6 Hz, 1H), 3.26 (dd, J = 5.4, 4.1 Hz, 1H), 2.94 (dd, J = 5.5, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 135.0, 133.2, 133.1, 128.3, 127.7, 126.3, 126.0, 125.1, 122.6, 58.1, 52.6, 51.2.

4-(Oxiran-2-yl)pyridine (1p)[37] Brown liquid, 60 mg, 10% yield. R_f = 0.22, 50% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, J = 6.0 Hz, 2H), 7.21 (d, J = 6.0 Hz, 2H), 3.84 (dd, J = 4.1, 2.5 Hz, 1H), 3.19 (dd, J = 5.5, 4.2 Hz, 1H), 2.76 (dd, J = 5.6, 2.5 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.9, 146.8, 120.3, 51.2, 50.9.

2-(Thiophen-2-yl)oxirane (1q)[38] Colorless liquid, 248 mg, 98% yield. R_f = 0.35, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (dd, J = 4.9, 1.4 Hz, 1H), 7.13 (dd, J = 3.5, 1.2 Hz, 1H), 6.98 (dd, J = 5.0, 3.5 Hz, 1H), 4.10 (dd, J = 4.0, 2.6 Hz, 1H), 3.19 (dd, J = 5.2, 4.0 Hz, 1H), 3.00 (dd, J = 5.1, 2.6 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.3, 127.0, 126.3, 125.1, 51.5, 49.3.

2-(Phenylethynyl)oxirane (1r)[39] Yellow oil, 317 mg, 44% yield. R_f = 0.81, 20% ethyl acetate in petroleum ether. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, J = 7.6, 1.8 Hz, 2H), 7.36 – 7.29 (m, 3H), 3.59 (t, J = 3.3 Hz, 1H), 3.01 (d, J = 3.2 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 131.9, 128.8, 128.3, 121.9, 85.7, 83.4, 49.1, 40.2.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Copies of ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra for all isolated products **1** and **2** (PDF)

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Notes

The authors declare no competing financial interest.

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