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PAPER

Efficient synthetic method for the preparation of allyl- and propargyl-epoxides by allylation and propargylation of α-haloketones with organozinc reagents†

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A simple, efficient, and non-metal catalyzed synthetic method for the preparation of substituted allyl- and propargyl-epoxides by allylation and propargylation of α-halo ketones with organozinc reagents in mild conditions is reported in this paper. The present method complements the existing synthetic methods due to some advantageous properties of the organozinc reagents such as availability, selectivity, operational simplicity and low toxicity.

Introduction

Epoxides, with their reactive oxirane groups, are versatile organic tools as both building blocks and synthetic intermediates in various organic syntheses.[1] These epoxides are widely used as epoxy resins, paints, and surfactants in various organic chemistry applications. Most epoxides are frequently used as electrophiles in ring-opening nucleophilic addition reactions,[2] especially, one of the useful reactions is the Meinwald rearrangement from epoxides to afford carbonyl compounds with a number of reagents including a variety of Lewis acids.[3]

Epoxides are prepared in a number of ways: epoxidation of olefins,[4] Darzens reaction,[5] catalytic reactions of α-halo ketones with organometallic reagents,[6] and so on.[7] Most epoxides are prepared by epoxidation of olefins, especially asymmetric epoxidation, which is the focus of methodological developments.[8] This method has two types: a convenient type is the oxidation of olefins with hydrogen peroxide or alkyl peroxides in the presence of transition metal complexes.[9] However, in general, the activity of the catalyst is limited and the metal catalyst, as well as modifying ligands, has to be separated after the reaction. Another type is the oxidation of olefins with hydrogen peroxide in the presence of acetic or formic acid.[10] A drawback of this method is the potential side reactions of the acid. Epoxidation of alkenes using peroxyacids is also one of the most fundamental reactions in organic chemistry.[11] However, these methods for the epoxidation of olefins cannot be used to selectively synthesize epoxides which contain other functional groups. For these reasons, the development of an effective preparation procedure for epoxides would be significant.

Zinc is a relatively non-toxic metal and it is an essential element for humans and all forms of plant and animal life. Although known for more than 150 years,[12] the applications of organozinc reagents in organic synthesis were limited to very rare reactions due to their moderate reactivity. The reagents were replaced by the more reactive organomagnesium and organolithium reagents which were found to have broad applications in organic synthesis.

However, it became apparent that this high reactivity has also some drawbacks, such as low chemoselectivity and excessively high reactivity for some functional groups. It was noticed that organozinc reagents could be easily prepared and could have higher functional group compatibility in comparison with organolithium and Grignard reagents. Furthermore, the low reactivity of organozinc reagents could be increased by adding transition metal catalyst.[13] Nowadays, organozinc reagents have been widely used in organic synthesis,[14] and are important reagents in organic chemistry.[15]

Research work on organozinc halides has been performed in our laboratory over the past few years. We have reported a novel environmentally benign reaction of allylzinc bromide with α-haloketones leading to three different products depending on the different reaction conditions.[16] Allylic epoxides were obtained without any additives (Scheme 1). Based on these initial results we proceeded to examine the scope of this reaction. We report herein a full account of our research that has efficiently prepared a series of epoxides by various organozinc halides with α-haloketones.

Results and discussion

In our initial study, α-bromoacetophenone (**1a**) was chosen as a model substrate to react with organozinc bromides (**2**) in THF at room temperature (Scheme 2), and then different epoxides (**3**) were obtained. As shown in Table 1, this reaction procedure is applicable to several highly reactive substituted allylzinc reagents and one propargylzinc reagent.

Treatment of **1a** with allylzinc reagents (**2a**, **2c** and **2d**) at room temperature for 2 h gave the corresponding epoxides (**3a**, **3c** and **3d**) in moderate to good yields (Table 1, entries 1, 3 and 4). Cinnamylzinc bromide (**2b**) was also used in this reaction,

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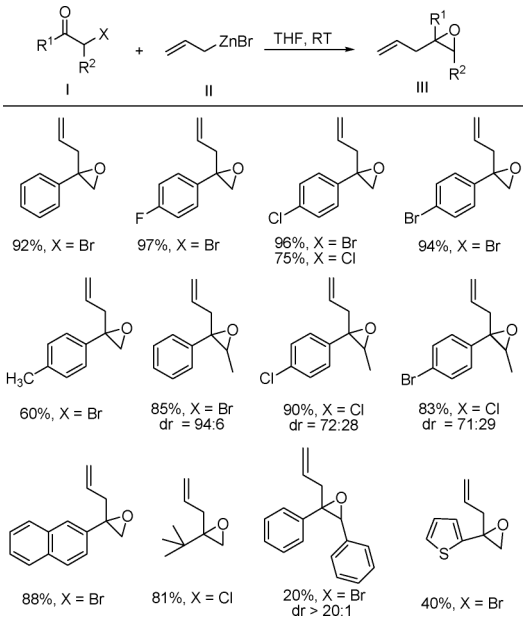
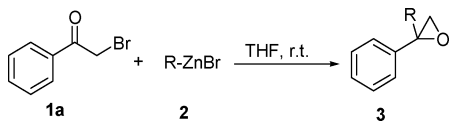


Scheme 1 Products obtained by the allylation of α-haloketones with allylzinc bromide.



Scheme 2 Reactions of α-bromoacetophenone with organozinc bromides.

which displayed no marked stereoselectivity (Table 1, entry 2). The reaction of **1a** took place in the case of propargylzinc bromide (**2e**) to give **3e** in 75% yield (Table 1, entry 5). However, alkylzinc bromides (**2f** and **2g**) and phenylzinc iodide (**2h**) in this reaction did not give the corresponding epoxides (Table 1, entries 6–8).

To research our methodology synthetically, we investigated the generality of this method. A number of α-halo ketones were further subjected to reaction with several highly reactive substituted acyclic allylzinc reagents, cyclic allylzinc reagents and propargylzinc reagent.

First of all, the results of α-bromoketones with acyclic allylic organozinc bromides are summarized in Table 2. We investigated the factors electronic effect and steric hindrance at the phenyl- and halo-substituted compounds. The results clearly show that electronic features have a very great impact on the processes. Electron-deficient groups at the *para* position of the phenyl ring were well tolerated and we obtained the product in good yields (Table 2, entries 1–3). However, an electron-rich group at the *para* position resulted in relatively diminished efficiency (Table 2, entry 4). Examination of the result of the investigation reveals that high reactivity was observed for 2-bromoacetylnaphthalene (Table 2, entry 5). Substrates bearing big sterically hindered groups could not yield the corresponding epoxide, but allyl-ketone (**4f**) can be obtained in 76% yield (Table 2, entry 6). The reactions of α-bromoketones with cinnamylzinc bromide reveal that an electron-deficient group at the *para* position of the phenyl ring was little better than an electron-rich group (Table 2, entries 7–8). And the diastereo-selectivity was also poor (57 : 43, 60 : 40).

Table 1 Comparison of different organozinc bromides react with α-bromoacetophenone[a]

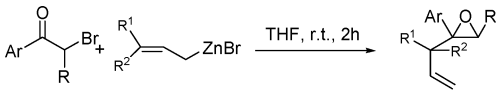
Entry	Organozinc bromide	Time (h)	Product	Yield (%)[b]
1	ZnBr **2a**	2	**3a**	90
2	Ph ZnBr **2b**	2	**3b**	53 dr = 58 : 42[c]
3	ZnBr **2c**	2	**3c**	92 dr > 20 : 1[c]
4	ZnBr **2d**	2	**3d**	82 dr > 20 : 1[c]
5	ZnBr **2e**	3	**3e**	75
6	ZnBr **2f**	24	—	none
7	ZnBr **2g**	24	—	none
8	ZnI **2h**	24	—	none

[a] Reaction conditions: α-bromoacetophenone (0.5 mmol), organozinc bromide (1.0 mmol) and THF (6 mL) at room temperature under nitrogen. [b] Isolated yield based on **1a** after silica gel chromatography. [c] Diastereomeric ratio (dr) determined by ^{1}H NMR analysis, relative stereochemistry not determined.

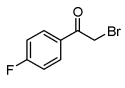
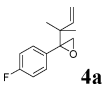
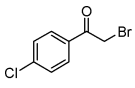
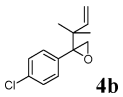
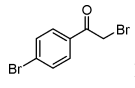
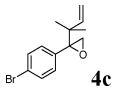
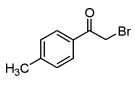
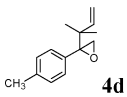
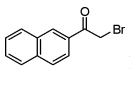
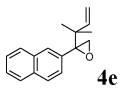
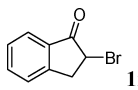
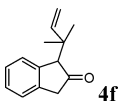
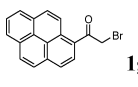
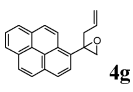
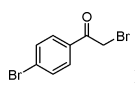
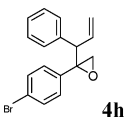
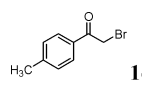
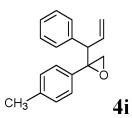
From the results of cyclohexenylzinc bromide and cyclooctenylzinc bromide with α-haloketones (Table 3), we can see that cyclohexenylzinc bromide could yield more epoxides compared with cyclooctenylzinc bromide. For the two cyclic allylic organozinc bromides, electron-deficient groups at the *para* position of the phenyl ring were well tolerated in good yields (Table 3, entries 1–3). However, an electron-rich group at the *para* position resulted in a slightly lower yield (Table 3, entry 4). We also found that sterically hindered epoxides can be obtained in good yield (Table 3, entry 5). Furthermore, epoxide (**5cf**) also can be obtained in 89% yield (Table 3, entry 6). For the aliphatic ketones, when X = Cl, the reaction showed a lower product yield (61%) than X = Br of 78%. The reason, probably, is that the leaving ability of the Br atom is higher than Cl (Table 3, entries 7–8).

At last, we performed the reaction of propargylzinc bromide with other α-bromoketones. Some experimental results are summarised in Table 4. It was clear that bromoketones bearing electron-deficient groups at the *para* position of the phenyl ring underwent reaction smoothly to afford the desired products with moderate yields (Table 4, entries 1–3). Substrates bearing more sterically hindered groups still yielded the corresponding product (**6d**) in good yield; the diastereomeric ratio was up to 93 : 7

Table 2 Products obtained by the allylation of α-bromoketones with acyclic allylic organozinc bromides[a,b]



1 2a 4

Entry	α-Haloketones	Product	Yield (%)[c]
1	 **1a**	 **4a**	89
2	 **1b**	 **4b**	90
3	 **1c**	 **4c**	91
4	 **1d**	 **4d**	63
5	 **1e**	 **4e**	89
6	 **1f**	 **4f**	76
7[d]	 **1g**	 **4g**	72
8[e]	 **1c**	 **4h**	56 dr = 57 : 43[f]
9[e]	 **1d**	 **4i**	44 dr = 60 : 40[f]

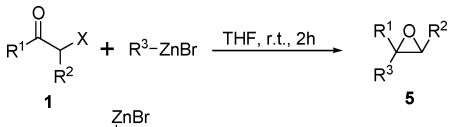
[a] Reaction conditions: α-bromoketone (0.5 mmol), acyclic allylic organozinc bromide (1.0 mmol) and THF (6 mL) at room temperature under nitrogen. [b] $R^1 = R^2 = CH_3$. [c] Isolated yield based on **1** after silica gel chromatography. [d] $R^1 = H$, $R^2 = H$. [e] $R^1 = H$, $R^2 = Ph$. [f] Diastereomeric ratio (dr) determined by ^1H NMR analysis, relative stereochemistry not determined.

(Table 4, entry 4). And 2-bromoacetylnaphthalene also afforded the corresponding epoxide in good yield (Table 4, entry 5).

Conclusions

In summary, we have successfully developed a cost effective, environmentally benign, highly efficient, non-metal catalyzed and simple manner for the synthesis of a series of epoxides by allylation and propargylation of α-haloketones with organozinc

Table 3 Products obtained by the allylation of α-haloketones with cyclic allylic organozinc bromides[a]



1 5

2c 2d

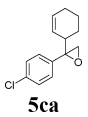
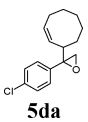
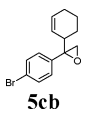
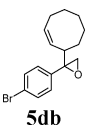
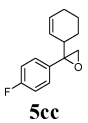
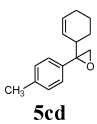
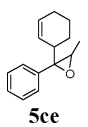
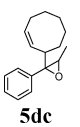
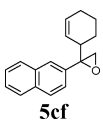
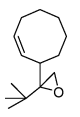
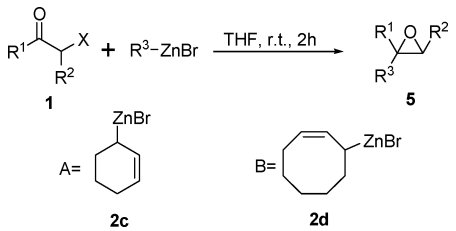
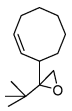
Entry	R^1	R^2	X	R^3–ZnBr	Product	Yield (%)[b,c]
1	*p*-ClC_6H_4	H	Br	A	 **5ca**	90 dr > 20 : 1
				B	 **5da**	81 dr > 20 : 1
2	*p*-BrC_6H_4	H	Br	A	 **5cb**	92 dr > 20 : 1
				B	 **5db**	80 dr > 20 : 1
3	*p*-FC_6H_4	H	Br	A	 **5cc**	88 dr > 20 : 1
4	*p*-$CH_3C_6H_4$	H	Br	A	 **5cd**	65 dr > 20 : 1
5	C_6H_5	CH_3	Br	A	 **5ce**	80
				B	 **5dc**	75
6	2-Naphthyl	H	Br	A	 **5cf**	89 dr > 20 : 1
7	t-Butyl	H	Cl	B	 **5dd**	61 dr > 20 : 1

Table 3 (*Contd.*)

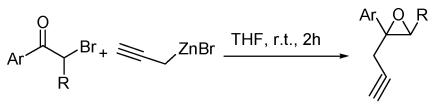


1 5 2c 2d

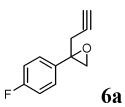
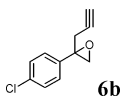
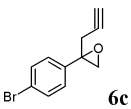
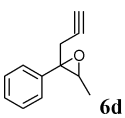
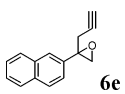
Entry	R^1	R^2	X	R^3–ZnBr	Product	Yield (%)[b,c]
8	t-Butyl	H	Br	B	 **5dd**	78 dr > 20 : 1

[a] Reaction conditions: α-haloketone (0.5 mmol), cyclic allylic organozinc bromide (1.0 mmol) and THF (6 mL) at room temperature under nitrogen. [b] Isolated yield based on **1** after silica gel chromatography. [c] Diastereomeric ratio (dr) determined by ^{1}H NMR analysis, relative stereochemistry not determined.

Table 4 Products obtained by the propargylation of α-bromoketones with propargylzinc bromide[a]



1 2e 6

Entry	Ar	*R*	Product	Yield (%)[b]
1	*p*-FC_6H_4	H	 **6a**	69
2	*p*-ClC_6H_4	H	 **6b**	70
3	*p*-BrC_6H_4	H	 **6c**	72
4	C_6H_5	CH_3	 **6d**	68 dr = 93 : 7[c]
5	2-Naphthyl	H	 **6e**	67

[a] Reaction conditions: α-bromoketone (0.5 mmol), propargylzinc bromide (1.0 mmol) and THF (6 mL) at room temperature under nitrogen. [b] Isolated yield based on **1** after silica gel chromatography. [c] Diastereomeric ratio (dr) determined by ^{1}H NMR analysis, relative stereochemistry not determined.

reagents. This high yielding procedure is very attractive for large-scale preparations since it is performed under mild reaction conditions using organozinc reagents, which are the most common commercially available organometallic reagents.

Experimental section

General

Tetrahydrofuran was distilled from sodium and benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Metallic zinc and all other solvents were purchased from a commercial source, without further purification before use. The flash column chromatography was carried out on Merck silica gel (300–400 mesh). The IR spectra was measured on a Varian 1000 FT-IR spectrometer as KBr disks (4000–400 cm^{-1}). ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Varian Mercury 300 or 400 MHz spectrometer. Chemical shifts in ^{1}H NMR spectra are reported in parts per million (ppm, δ) downfield from the internal standard Me_4Si (TMS). Chemical shifts in ^{13}C NMR spectra are reported relative to the central line of the chloroform signal (δ = 77.50 ppm). High-resolution mass spectra were obtained with a GCT-TOF instrument.

General procedure for the synthesis of epoxides

The solution of substrate (*a*-haloketones, 0.5 mmol, in 3 mL THF) was added to the mixture of organozinc bromide (1 mmol) in dry THF (3 mL). The reaction mixture was stirred for 2 h (the reaction was monitored by TLC) and then was quenched with water. The resulting mixture was extracted with diethyl ether (3 × 10 mL), and the organic layer was dried over anhydrous Na_2SO_4. The solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded epoxides (petroleum ether and ethyl acetate as eluent).

Preparation of organozinc bromides (2a–2e)[16]

Bromide **2a** (1 mmol) and zinc powder (1.25 mmol, 0.080 g) were added to dry THF (3 mL) under a nitrogen atmosphere at room temperature. The mixture was stirred for about 15–30 min, and the zinc powder disappeared. Stirring was continued for one hour to complete the synthesis of the organozinc reagent.

Preparation of organozinc bromides (2f–2h)[17]

Anhydrous LiCl (1 mmol) was placed in an N_2-flushed flask and dried for 20 min at 150–170 °C under high vacuum (1 mbar). Zinc powder (1.4 mmol, 1.4 equiv.) was added under N_2 and the reaction flask was evacuated and refilled with nitrogen three times. THF (1 mL) was added and the Zn was activated with $BrCH_2CH_2Br$ (5 mol%) and Me_3SiCl (1 mol%). **2f** (1 mmol) was then added neat at room temperature. The insertion reaction was complete after 24 h.

General procedure for the prepare of acyclic and cyclic allylic bromide cinnamyl bromide[18]

Triphenylphosphine (5.32 g, 20.4 mmol) was dissolved in 20 mL of dry acetonitrile, and then Br_2 (3.2 g, 20 mmol) was added dropwise over a 15 min period with cooling to maintain the solution at T = 0–10 °C. The solution was allowed to warm to room temperature, and cinnamyl alcohol (2.7 g, 20 mmol) was added in acetonitrile

(5 mL) whereupon an exotherm occurred ($T = 32$ °C). After being stirred at this temperature for 1 h, the mixture was poured into 500 mL of ether. Triphenylphosphine oxide precipitated from this solution upon standing overnight. The solution was filtered, and the solvent was removed by evaporation under reduced pressure. Purification by column chromatography on silica gel afforded the product. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.41–7.24 (m, 5H), 6.70–6.62 (m, 1H), 6.46–6.37 (m, 1H), 4.17 (d, $J = 8.0$ Hz, 2H).

3-Bromocyclohexene[19]

To a suspension of AIBN and *N*-bromosuccinimide (NBS, 23.1 g, 0.13 mol) in tetrachloromethane (75 mL), cyclohexene (20 mL, 0.2 mol), was added under argon. The mixture was refluxed until the disappearance of NBS. The mixture was then filtered, concentrated and distilled under vacuum (63–64 °C, 15 mbar). The colourless liquid was stored in the absence of light (12.8 g, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.94–5.90 (m, 1H), 5.85–5.80 (m, 1H), 4.86–4.84 (m, 1H), 2.30–1.64 (m, 6H).

(*Z*)-3-Bromocyclooct-1-ene[20]

A mixture of the cyclooctene (20 mL, 154 mmol), NBS (27.4 g, 154 mmol), and benzoyl peroxide (70%, 100 mg, 0.29 mmol) in CCl_4 (100 mL) was heated at reflux for 1 h. The reaction mixture was cooled to 0 °C then filtered. The filtrate was washed with 5% aq. $NaHCO_3$ then dried and concentrated in vacuo. Purification *via* fractional distillation at reduced pressure gave the product as a colourless oil (17.8 g, 61%); bp: 68–70 °C (3 mmHg). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.82–5.74 (m, 1H), 5.65–5.57 (m, 1H), 5.00–4.90 (m, 1H), 2.30–1.24 (m, 10H).

2-(2-Methylbut-3-en-2-yl)-2-phenyloxirane (3a)

Colourless oil. Isolated yield 90%. Compound purity: 100% (confirmed by HPLC). IR (KBr): 3058, 2972, 2932, 2874, 1637, 1603, 1495, 1469, 1446, 1414, 1342, 1178, 1053, 1023, 918, 837, 753, 702, 564 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.40–7.20 (m, 5H), 5.97–5.90 (m, 1H), 5.04–4.96 (m, 2H), 3.05 (d, J = 4.7 Hz, 1H), 2.63 (d, $J = 4.7$ Hz, 1H), 1.07 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.16, 139.22, 129.08, 127.59, 127.48, 113.22, 66.13, 50.96, 40.02, 24.06, 23.29; HRMS (EI$^+$) calcd for $C_{13}H_{16}O$ (M^+): 188.1201; found: 188.1201.

2-(4-Fluorophenyl)-2-(2-methylbut-3-en-2-yl)oxirane (4a)

Colourless oil. Isolated yield 89%. ^{1}H NMR (400 MHz,$CDCl_3$): δ (ppm) 7.33–7.30 (m, 2H), 6.99–6.94 (t, 2H), 5.95–5.87 (m, 1H), 5.05–4.95 (m, 2H), 3.06 (d, $J = 5.0$ Hz, 1H), 2.60 (d, $J = 5.0$ Hz, 1H), 1.06 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.15, 130.91, 130.83, 114.69, 114.48, 113.64, 65.80, 51.24, 40.22, 24.14, 23.36; HRMS (EI$^+$) calcd for $C_{13}H_{15}OF$(M^+): 206.1107; found: 206.1106.

2-(4-Chlorophenyl)-2-(2-methylbut-3-en-2-yl)oxirane (4b)

Colourless oil. Isolated yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.30–7.24 (m, 4H), 5.94–5.89 (m, 1H), 5.05–4.95 (m, 2H), 3.06 (d, $J = 5.0$ Hz, 1H), 2.60 (d, $J = 5.0$ Hz, 1H), 1.05 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.07, 137.98, 133.67, 130.59, 127.91, 113.77, 65.82, 51.21, 40.17, 24.13, 23.36; HRMS (EI$^+$) calcd for $C_{13}H_{15}{}^{35}ClO$ (M^+): 222.0811; found: 222.0806.

2-(4-Bromophenyl)-2-(2-methylbut-3-en-2-yl)oxirane (4c)

Colourless oil. Isolated yield 91%. Compound purity: 100% (confirmed by HPLC). IR (KBr): 3053, 2971, 2932, 2874, 1637, 1592, 1489, 1448, 1415, 1393, 1169, 1070, 1010, 919, 823, 776, 701, 564, 536 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.45–7.40 (s, 2H), 7.23–7.21 (m, 2H), 5.94–5.87 (m, 1H), 5.06–4.96 (m, 2H), 3.06 (s, 1H), 2.59 (s, 1H), 1.05–1.02 (d, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 143.81, 138.26, 130.70, 130.63, 121.64, 113.58, 65.64, 50.96, 39.91, 23.90, 23.14; HRMS (EI$^+$) calcd for $C_{13}H_{15}{}^{79}BrO$ (M^+): 266.0306; found: 266.0310; $C_{13}H_{15}{}^{81}BrO$ (M^+): 268.0286; found: 268.0260.

2-(2-Methylbut-3-en-2-yl)-2-*p*-tolyloxirane (4d)

Colourless oil. Isolated yield 63%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.24–7.22 (m, 2H), 7.09–7.07 (m, 2H), 5.97–5.90 (m, 1H), 5.03–4.95 (m, 2H), 3.03 (d, $J = 5.2$ Hz, 1H), 2.60 (d, $J = 5.2$ Hz, 1H), 2.32 (s, 3H), 1.06 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 144.29, 137.21, 136.30, 129.00, 128.18, 113.12, 66.01, 51.06, 40.08, 24.10, 23.31, 21.43; HRMS (EI$^+$) calcd for $C_{14}H_{18}O$ (M^+): 202.1358; found: 202.1356.

2-(2-Methylbut-3-en-2-yl)-2-(naphthalen-3-yl)oxirane (4e)

Colourless oil. Isolated yield 89%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.80–7.72 (m, 4H), 7.49–7.43 (m, 3H), 6.02–5.95 (m, 1H), 5.06–4.97 (m, 2H), 3.10 (d, $J = 5.1$ Hz, 1H), 2.69 (d, $J = 5.1$ Hz, 1H), 1.11 (s, 3H), 1.08 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.58, 131.25, 127.29, 127.11, 122.65, 122.41, 122.26, 121.58, 121.36, 120.71, 120.65, 107.82, 60.74, 45.63, 34.67, 18.59, 17.80; HRMS (EI$^+$) calcd for $C_{17}H_{18}O$ (M^+): 238.1358; found: 238.1361.

1-(2-Methylbut-3-en-2-yl)-1*H*-inden-2(3H)-one (4f)

Colourless oil. Isolated yield 76%. IR (KBr): 3081, 2964, 2930, 2871, 1707, 1608, 1597, 1464, 1364, 1275, 1205, 1096, 1001, 916, 749, 685 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.71–7.52 (m, 2H), 7.43–7.24 (m, 2H), 5.84 (dd, $J = 10.8$ Hz, $J = 17.4$ Hz, 1H), 5.02–4.93 (m, 2H), 3.14 (dd, $J = 8.0$ Hz, $J = 17.5$ Hz, 1H), 2.91 (dd, $J = 3.8$ Hz, $J = 17.5$ Hz, 1H), 2.58 (dd, $J = 4.0$ Hz, $J = 7.9$ Hz, 1H), 1.24 (s, 3H), 1.14 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 207.53, 153.62, 145.81, 138.12, 134.72, 127.41, 126.43, 123.76, 112.09, 55.61, 40.23, 30.52, 26.15, 23.63; HRMS (EI$^+$) calcd for $C_{14}H_{16}O$ (M^+): 200.1201; found: 200.1203.

2-Allyl-2-(pyren-6-yl)oxirane (4g)

Colourless oil. Isolated yield 72%. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.33–8.30 (m, 1H), 8.14–7.91 (m, 8H), 5.85–5.71 (m, 1H), 5.07–5.00 (m, 2H), 3.28 (d, $J = 5.2$ Hz, 1H), 3.02 (d, $J = 5.2$ Hz, 1H), 3.00–2.91 (m, 1H), 2.87–2.79 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 134.16, 132.93, 131.63, 131.30, 131.05, 128.47, 128.31, 127.86, 127.76, 126.43, 126.00, 125.81, 125.69, 125.12, 124.97, 124.90, 123.86, 119.13, 61.17, 53.44, 42.46; HRMS (EI$^+$) calcd for $C_{21}H_{16}O$ (M^+): 284.1201; found: 284.1200.

2-Phenyl-2-(1-phenylallyl)oxirane (3b)

Colourless oil. Isolated yield 53%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.26–7.10 (m, 10H), 6.18–5.96 (m, 1H), 5.25–5.01 (m, 2H), 4.02–3.99 (m, 1H), 3.15–2.65 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.70, 139.72, 139.67, 139.46, 137.31, 136.76, 129.41, 128.94, 128.60, 128.23, 128.15, 127.76, 127.50, 127.31, 126.91, 118.42, 118.00, 62.90, 62.76, 54.36, 54.17, 53.39, 53.12; HRMS (EI$^+$) calcd for $C_{17}H_{16}O$ (M^+): 236.1201; found: 236.1199.

2-(4-Bromophenyl)-2-(1-phenylallyl)oxirane (4h)

Colourless oil. Isolated yield 56%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.37–7.06 (m, 9H), 6.13–5.92 (m, 1H), 5.25–5.01 (m, 2H), 3.98–3.92 (m, 1H), 3.15–2.60 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 140.39, 139.08, 138.82, 136.94, 136.39, 131.77, 131.70, 131.35, 131.30, 129.33, 129.09, 128.84, 128.74, 128.66, 128.62, 127.41, 127.06, 121.79, 121.50, 118.72, 118.26, 62.50, 62.35, 54.03, 54.00, 53.36, 53.09; HRMS (EI$^+$) calcd for $C_{17}H_{15}{}^{79}BrO$ (M^+): 314.0306; found: 314.0310.

2-(1-Phenylallyl)-2-*p*-tolyloxirane (4i)

Colourless oil. Isolated yield 44%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 6.97–7.28 (m, 9H), 5.95–6.14 (m, 1H), 5.01–5.24 (m, 2H), 3.97–3.99 (d, 1H), 2.64–3.14 (m, 2H), 2.23–2.29 (d, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 141.01, 139.81, 137.63, 137.57, 137.27, 137.09, 136.92, 136.84, 129.59, 129.15, 129.12, 129.04, 128.77, 128.73, 127.41, 127.02, 118.53, 118.07, 62.92, 62.82, 54.60, 54.35, 53.68, 53.38, 21.63, 21.57; HRMS (EI$^+$) calcd for $C_{18}H_{18}O$ (M^+): 250.1358; found: 250.1360.

2-(Cyclohex-2-enyl)-2-phenyloxirane (3c)

Colourless oil. Isolated yield 92%. Compound purity: 99.50% (confirmed by HPLC). IR (KBr): 3026, 2933, 2861, 2835, 1651, 1603, 1495, 1447, 1377, 1252, 1138, 1026, 937, 910, 829, 761, 700, 653 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.38–7.24 (m, 5H), 5.80 (d, J = 9.8 Hz, 1H), 5.71 (d, J = 10.1 Hz, 1H), 3.04 (d, J = 5.0 Hz, 1H), 2.72 (d, J = 5.0 Hz, 1H), 2.65 (s, 1H), 1.93 (s, 2H), 1.76–1.71 (m, 2H), 1.51–1.41 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 139.81, 130.32, 128.21, 127.70, 127.43, 126.25, 63.51, 52.84, 40.57, 25.65, 25.24, 21.50; HRMS (EI$^+$) calcd for $C_{14}H_{16}O$ (M^+): 200.1201; found: 200.1199.

2-(4-Chlorophenyl)-2-(cyclohex-2-enyl)oxirane (5ca)

Colourless oil. Isolated yield 90%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.31 (s, 4H), 5.81 (d, J = 9.8 Hz, 1H), 5.68 (d, J = 10.0 Hz, 1H), 3.04 (d, J = 5.1 Hz, 1H), 2.70 (d, J = 5.1 Hz, 1H), 2.60 (s, 1H), 1.94 (s, 2H), 1.76–1.71 (m, 2H), 1.53–1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 138.34, 133.53, 130.60, 128.86, 128.40, 125.91, 62.99, 52.89, 40.51, 25.66, 25.20, 21.42; HRMS (EI$^+$) calcd for $C_{14}H_{15}{}^{35}ClO$ (M^+): 234.0811; found: 234.0810. $C_{14}H_{15}{}^{37}ClO$ (M^+): 236.0782; found: 236.0813.

2-(4-Bromophenyl)-2-(cyclohex-2-enyl)oxirane (5cb)

Colourless oil. Isolated yield 92%. Compound purity: 100% (confirmed by HPLC). IR (KBr): 3024, 2932, 2860, 2835, 1651, 1593, 1488, 1448, 1394, 1253, 1140, 1071, 1010, 912, 824, 749, 725, 563 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44 (d, J = 7.9 Hz, 2H), 7.25 (d, J = 8.0 Hz, 2H), 5.81 (d, J = 9.5 Hz, 1H), 5.67 (d, J = 10.0 Hz, 1H), 3.03 (d, J = 4.6 Hz, 1H), 2.68 (d, J = 4.4 Hz, 1H), 2.60 (s, 1H), 1.93 (s, 2H), 1.74–1.71 (m, 2H), 1.50–1.38 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 138.82, 131.34, 130.65, 129.19, 125.84, 121.70, 63.05, 52.86, 40.44, 25.65, 25.18, 21.40; HRMS (EI$^+$) calcd for $C_{14}H_{15}{}^{79}BrO$ (M^+): 278.0306; found: 278.0305; $C_{14}H_{15}{}^{81}BrO$ (M^+): 280.0286; found: 280.0303.

2-(Cyclohex-2-enyl)-2-(4-fluorophenyl)oxirane (5cc)

Colourless oil. Isolated yield 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36–7.32 (m, 2H), 7.02–6.98 (m, 2H), 5.81 (d, J = 8.5 Hz, 1H), 5.70 (d, J = 10.1 Hz, 1H), 3.03 (d, J = 5.0 Hz, 1H), 2.71 (d, J = 5.0 Hz, 1H), 2.59 (s, 1H), 1.94 (s, 2H), 1.77–1.70 (m, 2H), 1.51–1.38 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 130.64, 129.44, 129.36, 126.27, 115.37, 115.16, 63.27, 53.12, 41.03, 25.83, 25.37, 21.60; HRMS (EI$^+$) calcd for $C_{14}H_{15}FO$ (M^+): 218.1107; found: 218.1134.

2-(Cyclohex-2-enyl)-2-*p*-tolyloxirane (5cd)

Colourless oil. Isolated yield 65%. ^{1}H NMR (400 MHz, $CDCl_3$). δ (ppm) 7.26 (d, J = 7.4 Hz, 2 H), 7.12 (d, J = 7.5 Hz, 2H), 5.79 (d, J = 7.5 Hz, 1H), 5.71 (d, J = 10.2 Hz, 1H), 3.01 (d, J = 4.9 Hz, 1H), 2.70 (d, J = 4.9 Hz, 1H), 2.61 (s, 1H), 2.33 (s, 3H), 1.93 (s, 2H), 1.76–1.71 (m, 2H), 1.48–1.42 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.53, 136.99, 130.36, 129.09, 127.58, 126.64, 63.58, 53.11, 40.94, 25.88, 25.44, 21.73, 21.62; HRMS (EI$^+$) calcd for $C_{15}H_{18}O$ (M^+): 214.1358; found: 214.1361.

2-(Cyclohex-2-enyl)-3-methyl-2-phenyloxirane (5ce)

Colourless oil. Isolated yield 80%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33–7.26 (m, 5H), 5.78–5.71 (t, 2H), 3.28–3.24 (m, 1H), 2.50 (s, 1H), 1.91 (s, 2H), 1.73–1.68 (m, 2H), 1.48–1.46 (m, 2H), 1.13 (d, J = 5.3 Hz; *trans*, 3H), 0.98 (d, J = 5.3 Hz; *cis*, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 137.85, 130.06, 128.13, 127.92, 127.35, 126.31, 68.36, 57.80, 42.21, 25.81, 25.22, 21.55, 15.47; HRMS (EI$^+$) calcd for $C_{15}H_{18}O$ (M^+): 214.1358; found: 214.1358.

2-(Cyclohex-2-enyl)-2-(naphthalen-3-yl)oxirane (5cf)

Colourless oil. Isolated yield 89%. Compound purity: 99.12% (confirmed by HPLC). IR (KBr): 3054, 3022, 2930, 2860, 1633, 1601, 1506, 1448, 1352, 1140, 950, 896, 858, 815, 748, 702, 478 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84–7.77 (m, 4H), 7.51–7.44 (m, 3H), 5.80–5.74 (m, 2H), 3.10 (d, J = 5.0 Hz, 1H), 2.78 (d, J = 5.0 Hz, 2H), 1.92 (s, 2H), 1.77–1.72 (m, 2H), 1.52–1.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 137.40, 133.17, 132.96, 130.69, 130.49, 128.23, 127.89, 126.40, 126.32, 126.22, 126.18, 125.39, 63.69, 52.99, 40.51, 25.74, 25.24, 21.51; HRMS (EI$^+$) calcd for $C_{18}H_{18}O$ (M^+): 250.1358; found: 250.1357.

2-(Cyclooct-2-enyl)-2-phenyloxirane (3d)

Colourless oil. Isolated yield 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42–7.26 (m, 5H), 5.80–5.73 (m, 1H), 5.32 (t, J = 9.6 Hz, 1H), 3.30–3.24 (m, 1H), 3.01 (d, J = 4.9 Hz, 1H), 2.62 (d, J = 4.9 Hz, 1H), 2.25–2.05 (m, 2H), 1.69–1.23 (m, 8H); ^{13}C NMR (75 MHz,

$CDCl_3$): δ (ppm) 140.77, 131.27, 128.95, 128.42, 127.49, 126.53, 62.43, 53.93, 39.00, 31.49, 29.84, 27.32, 27.26, 25.57; HRMS (EI^+) calcd for $C_{16}H_{20}O$ (M^+): 228.1514; found: 228.1513.

2-(4-Chlorophenyl)-2-(cyclooct-2-enyl)oxirane (5da)

Colourless oil. Isolated yield 81%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.36–7.29 (m, 4H), 5.81–5.74 (m, 1H), 5.29 (t, J = 9.6 Hz, 1H), 3.26–3.21 (m, 1H), 3.01 (d, J = 4.9 Hz, 1H), 2.59 (d, J = 4.8 Hz, 1H), 2.22–2.10 (m, 2H), 1.67–1.20 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 139.38, 133.28, 131.53, 128.61, 127.93, 127.24, 62.01, 53.86, 38.87, 31.39, 29.77, 27.30, 27.22, 25.50; HRMS (EI^+) calcd for $C_{16}H_{19}{}^{35}ClO$ (M^+): 262.1124; found: 262.1122.

2-(4-Bromophenyl)-2-(cyclooct-2-enyl)oxirane (5db)

Colourless oil. Isolated yield 80%. ^1H NMR (400 MHz,$CDCl_3$): δ (ppm) 7.46 (d, J = 8.2 Hz, 1H), 7.29 (d, J = 8.2 Hz, 1H), 5.80–5.74 (m, 1H), 5.28 (t, J = 9.8 Hz, 1H), 3.26–3.20 (m, 1H), 3.01 (d, J = 5.1 Hz, 1H), 2.58 (d, J = 5.1 Hz, 1H), 2.22–2.08 (m, 2H), 1.70–1.20 (m, 8H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 139.92, 131.54, 128.91, 128.58, 128.27, 121.43, 62.02, 53.81, 38.79, 31.39, 29.77, 27.31, 27.23, 25.50; HRMS (EI^+) calcd for $C_{16}H_{19}{}^{79}BrO$ (M^+): 306.0619; found: 306.0603; $C_{14}H_{15}{}^{81}BrO$ (M^+): 308.0599; found: 308.0577.

2-(Cyclooct-2-enyl)-3-methyl-2-phenyloxirane (5dc)

Colourless oil. Isolated yield 75%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.33 (s, 5H), 5.79–5.72 (m, 1H), 5.33 (t, J = 9.9 Hz, 1H), 3.23–3.20 (m, 1H), 3.11 (t, J = 9.3 Hz, 1H), 2.24–2.08 (m, 2H), 1.70–1.22 (m, 8H), 1.08 (d, J = 5.3 Hz; *trans*, 1H), 0.93 (d, J = 5.2 Hz; *cis*, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 138.72, 131.12, 128.92, 128.13, 127.63, 127.26, 67.68, 58.37, 40.77, 31.73, 29.86, 27.37, 27.27, 25.52, 14.83; HRMS (EI^+) calcd for $C_{17}H_{22}O$ (M^+): 242.1671; found: 242.1667.

2-*tert*-Butyl-2-(cyclooct-2-enyl)oxirane (5dd)

Colourless oil. Isolated yield 78%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 5.66–5.59 (m, 1H), 5.39 (t, J = 9.8 Hz, 1H), 3.15–3.09 (m, 1H), 2.76 (d, J = 4.1 Hz, 1H), 2.67 (d, J = 4.0 Hz, 1H), 2.23–2.07 (m, 2H), 1.75–1.08 (m, 8H), 0.96 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 131.24, 128.45, 66.38, 48.31, 35.38, 34.59, 34.16, 29.83, 27.17, 27.03, 26.57, 25.55; HRMS (EI^+) calcd for $C_{14}H_{24}O$ (M^+): 208.1827; found: 208.1802.

2-Phenyl-2-(prop-2-ynyl)oxirane (3e)

Colourless oil. Isolated yield 75%. Compound purity: 99.99% (confirmed by HPLC). IR (KBr): 3302, 3077, 2923, 2854, 1638, 1604, 1554, 1422, 1383, 1261, 1128, 1017, 899, 804, 746, 636 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.44–7.29 (m, 5H), 3.23 (d, J = 4.8 Hz, 1H), 2.90 (s, 2H), 2.82 (d, J = 4.7 Hz, 1H), 2.06 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 139.43, 128.95, 128.54, 126.40, 79.44, 71.80, 58.40, 55.09, 26.60; HRMS (EI^+) calcd for $C_{11}H_{10}O$ (M^+): 158.0732; found: 158.0735.

2-(4-Fluorophenyl)-2-(prop-2-ynyl)oxirane (6a)

Colourless oil. Isolated yield 69%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.42–7.39 (m, 2H), 7.06–7.02 (m, 2H), 3.21 (d, J = 5.0 Hz, 1H), 2.90 (s, 2H), 2.80 (d, J = 5.0 Hz, 1H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 128.19, 128.11, 115.85, 115.63, 79.14, 71.86, 57.99, 56.05, 26.70; HRMS (EI^+) calcd for $C_{11}H_9OF$(M^+): 176.0637; found: 176.0635.

2-(4-Chlorophenyl)-2-(prop-2-ynyl)oxirane (6b)

Colourless oil. Isolated yield 70%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39–7.25 (m, 4H), 3.22 (d, J = 5.0 Hz, 1H), 2.91 (s, 2H), 2.80 (d, J = 5.0 Hz, 1H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 137.61, 134.12, 128.81, 127.56, 78.81, 71.73, 57.73, 54.93, 26.27; HRMS (EI^+) calcd for $C_{11}H_9{}^{35}ClO$ (M^+): 192.0342; found: 192.0340. $C_{14}H_{15}{}^{37}ClO$ (M^+): 194.0312; found: 194.0340.

2-(4-Bromophenyl)-2-(prop-2-ynyl)oxirane (6c)

Colourless oil. Isolated yield 72%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.48 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 8.3 Hz, 2H), 3.21 (d, J = 5.2 Hz, 1H), 2.90 (s, 2H), 2.79 (d, J = 5.1 Hz, 1H), 2.08 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 138.34, 131.97, 128.09, 122.48, 79.00, 72.00, 57.99, 55.13, 26.40; HRMS (EI^+) calcd for $C_{11}H_9{}^{79}BrO$ (M^+): 235.9837; found: 235.9835; $C_{11}H_9{}^{81}BrO$ (M^+): 237.9816; found: 237.9811.

3-Methyl-2-phenyl-2-(prop-2-ynyl)oxirane (6d)

Colourless oil. Isolated yield 68%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.49–7.26 (m, 5H), 3.48–3.44 (m, 1H), 2.85 (s, 1H), 2.04 (s, 1H), 1.51 (d, J = 5.4 Hz; *trans*, 3H), 1.01 (d, J = 5.3 Hz; *cis*, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 137.86, 128.39, 127.96, 127.20, 79.33, 71.33, 63.26, 59.30, 28.37, 14.66; HRMS (EI^+) calcd for $C_{12}H_{12}O$ (M^+): 172.0888; found: 172.0888.

2-(Naphthalen-6-yl)-2-(prop-2-ynyl)oxirane (6e)

Colourless oil. Isolated yield 67%. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91–7.81 (m, 4H), 7.51–7.46 (m, 3H), 3.29 (d, J = 5.2 Hz, 1H), 3.04 (s, 2H), 2.90 (d, J = 5.1 Hz, 1H), 2.08 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 136.51, 133.23, 133.14, 128.45, 128.27, 128.86, 126.59, 126.48, 125.36, 123.69, 79.10, 71.57, 58.30, 54.95, 26.35; HRMS (EI^+) calcd for $C_{15}H_{12}O$ (M^+): 208.0888; found: 208.0887.

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