Enantioselective Incorporation of Carbon Dioxide into Epoxides Catalyzed by Optically Active Cobalt(II) Complexes

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The enantioselective chemical fixation of CO_2 into an epoxide was developed using an optically active ketoiminatocobalt(II) complex as a chiral Lewis acid. In the presence of a catalytic amount of the cobalt complex and amine base, enantioselective CO_2 fixation with an epoxide proceeded with kinetic resolution to afford the corresponding carbonate along with unreacted epoxide, both of which were optically active. To improve their enantioselectivities, the ligand structures of the cobalt complexes and amine bases were examined. Thus, the optimized catalytic system was successfully applied to various epoxides to obtain the corresponding optically active cyclic carbonates and to recover epoxides with good-to-high enantioselectivities.

Carbon dioxide has drawn much attention from the viewpoint of global warming.[1] In order to suppress its greenhouse effect, much effort has been devoted to the development of ways to reduce effectively its exhaust from industries. Since it is ubiquitous, safe and abundant and can be regarded as a C1 chemical feedstock[2] from the viewpoint of economic benefit, its utilization has been a focus of organic chemists. Carbon dioxide has been industrially employed as a raw material for manufacturing various basic chemicals. For example, urea has been manufactured from CO_2 and ammonia gases and remains one of the most important materials as a fertilizer, resin and animal feed. From the reaction of CO_2 with sodium phenolate, called the Korbe–Schmidt process, a large amount of salicylic acid has been produced for the pharmaceutical industries. Also, its reaction with propylene oxide or ethylene oxide has been used for production of organic carbonate, which is employed as a solvent or is converted to other compounds, such as carbonate resins.[3] Although CO_2 fixation has been extensively employed in specific industrial processes, its application to fine organic syntheses has so far been limited to only a few examples. Metal-complex-catalyzed reactions are expected to expand the applicability of the CO_2 fixation reaction to various substrates. It has been reported that by using nickel or palladium complex catalysts, oxidative cyclization reactions of an alkyne and diene with CO_2 occurs.[4] The ruthenium-catalyzed hydrogenation of CO_2 has been examined to afford formic acid and DMF under supercritical conditions.[5] Supercritical CO_2 has been considered to be a good reaction medium for various organic reactions, such as hydrogenation,[6] oxidation,[7] metathesis,[8] hydroboration,[9] and hydrovinylation,[10] because of its safety, noncombustibility, and readily accessible critical point.[11] Among the various incorporation reactions of CO_2, the synthesis of carbonates has been extensively studied, including stereochemical control, and the well-defined complex catalysts are expected to be the most promising for regulating chemical fixation of CO_2. Since the pioneering report on this chemistry by using a diethylzinc-derived catalyst, several catalyst systems for the copolymerization of propylene oxide or cyclohexene oxide have been proposed in order to achieve a high turnover frequency, high carbonate linkage in polymers, and high regioselectivity of the epoxide.[12] It has been reported that optically active polycarbonates can be obtained from a meso-epoxide using an optically active zinc complex catalyst.[13] Because of the thermodynamic stability of CO_2, severe reaction conditions have been applied for the chemical fixation of CO_2 with epoxides to form cyclic carbonates, e.g., high-pressure,[14] high-temperature,[15] supercritical conditions,[16] and electrochemical reactions.[17] Since the alternating copolymerization of CO_2 with epoxides to polycarbonates was reported in the 1960s,[16,18] various catalyst systems have been proposed to achieve remarkable catalytic activities. The reaction of epoxides and CO_2 can also afford five-membered cyclic carbonates, which can be used as a monomer for polycarbonates and as the masked 1,2-diol equivalents, etc. However, concerning the enantioselective version, it has been reported that high enantioselectivity is very hard to achieve because high temperatures are required for these reactions.[19] Using optically active salen complexes, enantioselective CO_2 coupling has been reported, although the enantioselectivity is low compared to other enantioselective reactions.[20] We have determined that an optically active ketoiminatocobalt complex catalyzed chemical fixation of CO_2 with high enantioselectivity.[21] Most recently, it has been reported that the asymmetric incorporation of CO_2 into propylene oxide occurs with a good enantioselectivity by using a salen complex combined with a quaternary ammonium salt.[22] In this article, we report that CO_2 was smoothly inserted into epoxides at ambient temperature under mild reaction conditions in the presence of a catalytic amount of an optically active ketoiminatocobalt complex and amine bases. As the result of kinetic resolution, the corresponding five-membered cyclic

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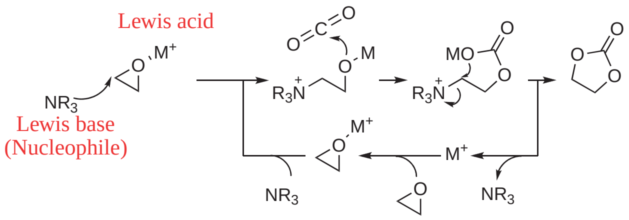


Fig. 1. Proposed catalytic cycle.

carbonate was obtained in a high enantioselectivity along with the starting epoxides in high enantiomeric excess.

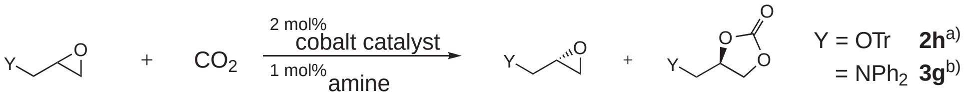
Results and Discussion

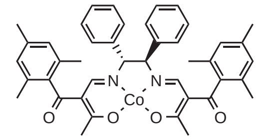
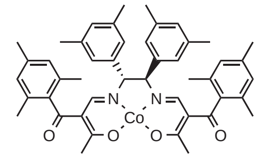
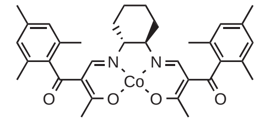
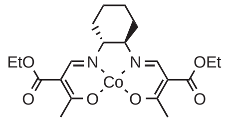
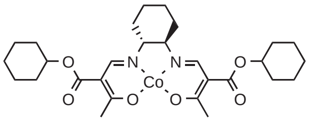
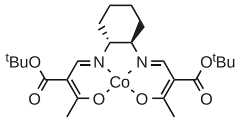
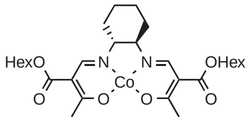
The Ligand Structures of the Optically Active 3-Oxobutylideneaminatocobalt Complex Catalysts. It has been proposed that the chemical fixation reaction of CO_2 to form a five-membered cyclic carbonate is cocatalyzed by a Lewis base amine and Lewis acids.[21] The epoxide, activated by the coordination of the Lewis acid, reacts with the Lewis base to generate the alkoxide intermediate, which captures CO_2, and recyclization with the release of an amine base affords the corresponding five-membered cyclic carbonate (Fig. 1). Consequently, amine bases are indispensable for this reaction, and an optically active Lewis acid that can operate even in the presence of a Lewis base is expected to bring about the enantioselective fixation of CO_2 to afford optically active cyclic carbonates. Based on the reaction mechanism, optically active cobalt complexes and cocatalysts have been assumed essential for the reactivity and enantioselectivity. Ketoiminatocobalt complexes have been employed as the chiral Lewis acid for the enantioselective hetero-Diels–Alder reaction[23] and carbonyl-ene[24] reaction to afford the corresponding products in high yield and high enantioselectivity. It has also been reported that cationic cobalt complexes can effectively activate the carbonyl group even in the presence of a strong electron-donating group, such as nitrones and amines. The normal- and inverse-electron-demanding 1,3-dipolar cycloaddition of the nitrone with electron rich or deficient olefins has been reported using a cationic cobalt complex catalyst.[25] An enantioselective Henry reaction has also been proposed which uses a tertiary amine and an optically active cobalt complex.[26] Various cobalt complexes were prepared, and their catalytic activities as well as enantioselectivities for the CO_2 incorporation reaction were examined (Table 1). The racemic glycidyl trityl ether (**2h**) as a model substrate was treated with 2 MPa of CO_2 in the presence of 2 mol % of the cobalt complex and 1 mol % of the amine base at room temperature to afford the corresponding optically active cyclic carbonate and starting epoxide. The selectivity factor (s) was calculated from Kagan's equation estimated from the chemical yield and the optical purity of the recovered epoxide.[27] Cobalt complexes possessing an ester group on the side chain (**1d**–**1g**) afforded the corresponding cyclic product with s values of 4.6–10.7 (Entries 7, 9, 11, and 13), while the cobalt complexes possessing a bulky diaryl backbone or the bulky side chain (**1a**–**1c**) gave poor results (Entries 1, 3, and 5). Cobalt complex **1g** possessing the hexyl ester group on the side chain was found to be an effective catalyst for the CO_2 insertion reaction to give the corresponding cyclic carbonate with a 59% ee in 34% yield and the recovered epoxide with a 68% ee in 47% yield. Although complex **1e** showed good enantioselectivity ($s = 10.7$), it took 10 days to reach sufficient conversion. The ligands of the cobalt complexes were screened again for the reaction of CO_2 with *N*,*N*-diphenylaminomethyloxirane (**3g**). Cobalt complexes **1a** and **1c** catalyzed the CO_2 fixation into *N*,*N*-diphenylaminomethyloxirane to afford the corresponding cyclic carbonate and the recovered epoxide with s values of 2.7 and 2.5 (Entries 2 and 6), respectively, while **1b** did not catalyze the reaction at all (Entries 3 and 4). Cobalt complexes **1d**–**1g** smoothly catalyzed the reaction with improved enantioselectivity, and the s value was calculated to be 6.4–14.0 (Entries 8, 10, 12, and 14). In the presence of cobalt complex **1g**, the cyclic carbonate in 64% ee was obtained in 19% yield, and the epoxide in 91% ee was recovered in a 42% yield (Entry 14). The cobalt complex bearing an optically active 1,2-cyclohexanediamine and ester group on the side chain was found to be a suitable ligand for enantioselective CO_2 incorporation reaction.

Three by-products were observed using TLC after the reaction. One of them was determined to be the corresponding diol via the hydrolysis of the starting epoxide. The other by-products were analyzed by IR and NMR. In the IR spectrum, a peak at 1752 cm^{-1} assigned to be the carbonyl stretch for one of the by-products was observed, while the other has no carbonyl group. Thus, the former was assumed to be a polycarbonate and the latter a polyether. On the basis of the proposed mechanism, the polyether is obtained when the alkoxide, generated after the ring-opening reaction with an amine base, attacks another epoxide without any subsequent ring-closing reaction. The high pressure of CO_2 is proposed to enhance the generation of the carbonate intermediate and reduce the amount of polyether, therefore, the effect of CO_2 pressure was examined using *N*,*N*-diphenylaminomethyloxirane (**3g**) as a model substrate. It was found that the yield of the cyclic product was influenced by the CO_2 pressure (Table 2). The cyclic carbonate was obtained in low yield under a CO_2 pressure of 0.1 MPa, but the material balance (MB) reached 98% yield at 0.7 MPa (Entries 1–5), because the high-pressure CO_2 reduced the polyether production. Carbon dioxide pressures higher than 0.7 MPa slightly reduced the MB, probably due to an increase in the producing polycarbonate (Entry 6).

Examination of Nucleophiles as Cocatalysts. Nucleophiles were examined in the reaction catalyzed by the cobalt complex **1g**. No cyclic carbonate was observed without amine bases, while a catalytic amount of the amine base promoted the reaction. The amine bases thus play a significant role in the reaction. It was found that a catalytic amount of potassium cyanide along with 18-crown-6 could be used as cocatalyst to produce the cyclic carbonate with a high catalytic activity (Table 3, Entry 1). Although MB was unsatisfactory for the polymerization, it is noted that a high nucleophilicity of the cocatalyst can cause polymerization. Phosphonium salts have often been used in mono- or poly-carbonate syntheses,[28] and so, triphenylphosphine was used as a nucleophile giving an s value of 4.0 (Entry 2). Use of *N*-methylpyrrolidine afforded the cyclic product with an s value of 2.8 (Entry 3). In contrast, *N*-methylpiperidine did not catalyze the reaction at all (Entry 4). As anticipated, 2,6-lutidine and diisopropylethylamine

Table 1. CO_2 Insertion Reaction Catalyzed by Various Optically Active Cobalt Complexes

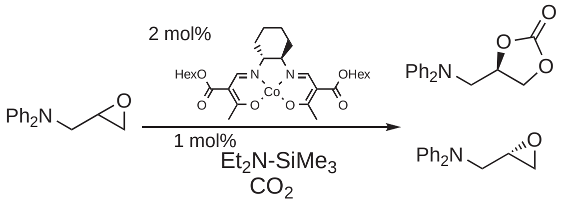


Entry	Cobalt Catalyst	Epoxide	Reaction time/days	Yield/%[c] (Ee/%[d]) Epoxide	Yield/%[c] (Ee/%[d]) Carbonate	MB[e]	s[f]
1	 **1a**	**2h**		No reaction			
2		**3g**	3	54 (29)	8 (41)		2.7
3	 **1b**	**2h**		No reaction			
4		**3g**		No reaction			
5	 **1c**	**2h**		No reaction			
6		**3g**	3	89 (5)	5 (65)		2.5
7	 **1d**	**2h**	3	31 (79)	30 (41)	61	4.6
8		**3g**	4	55 (54)	18 (70)	73	8.3
9	 **1e**	**2h**	10	63 (44)	11 (77)	74	10.7
10		**3g**	4	55 (49)	25 (67)	80	6.4
11	 **1f**	**2h**	3	47 (64)	18 (77)	65	6.8
12		**3g**	3	35 (93)	47 (57)	82	9.4
13	 **1g**	**2h**	3	34 (59)	47 (68)	81	8.0
14		**3g**	3	42 (91)	19 (64)	61	14.0

Reaction conditions: a) the reaction was performed in 0.5 mL of dichloromethane using 2.0 mol % cobalt(II) catalyst, 1.0 mol % *N*-trimethylsilyldiethylamine and 1.0 mmol of epoxide under 2.0 MPa CO_2. b) The reaction was carried out using 1.0 mol % *N*-methylimidazole under 0.1 MPa CO_2. c) Isolated yield. d) Enantiomeric excess was determined by HPLC analysis. e) Material balance: the sum of the yields of the recovered epoxide and the cyclic carbonate. f) The selective factor s value was calculated on the basis of the recovered epoxide.

were inert toward the CO_2 fixation due to the steric bulkiness (Entries 5 and 6). *N*-Trimethylsilyldiethylamine in conjunction with the cobalt complex **1g** was found to effectively catalyze the CO_2 incorporation reaction into the glycidyl trityl ether to afford a mixture of the five-membered cyclic carbonate and starting epoxide with an s value of 7.7 (Entry 7). Examination of the amine bases revealed that sterically hindered nucleophiles were inert for the ring-opening reaction. On the other hand, highly nucleophilic cocatalyst catalyzed the ring-opening reaction, although a cocatalyst with too strong a nucleophilicity, such as the cyanide anion, generated from potassium cyanide, caused copolymerization of the epoxide with CO_2. It should be noted that secondary amines could be used for the CO_2 fixation. Diethylamine, dibutylamine, and dihexylamine accompanied by a cobalt complex **1g** was successfully applied to the CO_2 fixation, giving s values from 7.1 to 7.6 (Entries 8–10). Morpholine showed a slightly lower selectivity with an s value of 5.2 (Entry 11). A sterically demanding secondary amine, diisopropylamine, was inactive for the reaction (Entry 12). This is to the best of our knowledge, the first example of a CO_2 fixation catalyzed by a secondary amine with a metal complex. To expand the generality of the epoxides, nucleophiles were again examine using *N*,*N*-diphenylaminomethyloxirane (**3g**) as a substrate in the presence of cobalt complex **1g**. 4-Dimethylaminopyridine, *N*-alkylimidazoles, and *N*-trimethylsilylimidazole were used a cocatalyst affording the

Table 2. Effect of CO_2 Pressure



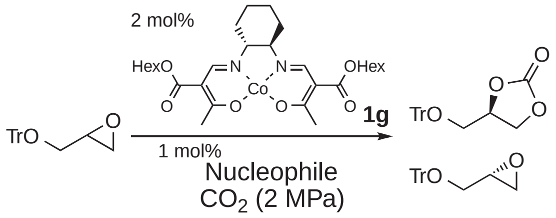
Entry[a)]	Pressure /MPa	Yield/%[b)] (Ee/%[c)])		MB
		Epoxide	Carbonate	
1	0.1	53 (80)	25 (87)	78
2	0.2	52 (77)	37 (88)	89
3	0.3	63 (53)	34 (88)	97
4	0.5	44 (99)	51 (78)	95
5	0.7	49 (87)	49 (86)	98
6	1.0	43 (99)	51 (78)	94

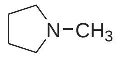
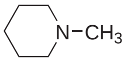
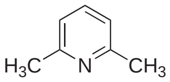
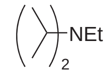
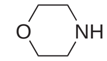
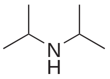
a) Reaction conditions: the reaction was carried out in 0.5 mL of dichloromethane using 2.0 mol % cobalt(II) complex catalyst, 1.0 mol % $Et_2N–SiMe_3$ under 0.1 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis.

cyclic carbonate with *s* values of 5 to 10 (Table 4, Entries 1–4). When pyridine *N*-oxide, or an electron-rich or deficient *N*-oxide was employed, the *s* value was slightly improved, ranging from 9 to 13 (Entries 9–11). Cyclic amines, such as *N*-methylmorpholine, piperidine, and pyrrolidine, improved the *s* value to 13–22 (Entries 5–7). Triethylamine showed almost the same performance as the cyclic amines, and the *s* value was calculated to be 15 (Entry 8). Although the morpholine derivative having a *tert*-butyldimethylsilyl group on the nitrogen gave an *s* value of 18 (Entry 13), the *s* value was improved to 28 using *N*-trimethylsilylmorpholine (Entry 12). The steric demand around the nitrogen atom and the electronic properties of the cocatalysts are thought to be important for the reactivity. It was found that when a catalytic amount of trimethyl silyldiethylamine was combined with cobalt complex **1d**, and the racemic epoxide was treated with 0.1 MPa of CO_2, the *s* value increased to 48 (Entry 14).

Enantio-Discrimination in Enantioselective CO_2 Incorporation Reaction. As mentioned above, a catalytic amount of a Lewis acid and nucleophile catalyzed the chemical fixation of CO_2. Based on the reaction mechanism, a Lewis acid possessing a chiral ligand should help to achieve the asymmetric CO_2 incorporation reaction, and the reaction should produce the epoxide and cyclic carbonate in optically active forms through a kinetic resolution process. Glycidyl derivatives were used to afford the corresponding carbonate along with the recovered epoxide both in optically active forms, though the reaction of 4-phenyl-1-butene oxide or styrene oxide scarcely proceeded in the presence of the cobalt(II) complex catalyst. When the corresponding cationic cobalt(III) complex was employed in place of the cobalt(II) complex, CO_2 was effectively incorporated into these epoxides to afford the cyclic carbonates in good yields, but the epoxides were recovered as a racemic. These observations suggest that the heteroatoms adjacent to the oxirane in the glycidyl derivatives are essential for the enantio-discrimination of the epoxide as well as activation of the oxirane to incorporate CO_2. By comparing the optical rotation with the reported value, the absolute configuration of the recovered epoxide was determined to be *R* corresponding to the (*R*,*R*)-cobalt complex catalyst (Fig. 2).[29] These enantioselections can be explained as follows (Fig. 3). As the d_{z^2} orbital of the cobalt(II) ion in the catalyst becomes occupied by one electron, its Lewis acidity could can become rather weak. The substrate can then approach the cobalt(II) complex while maintaining the interaction between the cobalt atom and the oxygen atom in the oxirane as well as the heteroatom adjacent to the oxirane. Finally, the oxirane can be activated by the cobalt(II) complex catalyst through the coordination of the oxygen atom of the oxirane. The enantiodiscrimination was regulated by the steric repulsion with the optically active (*R*,*R*)-cyclohexanediamine moiety (Fig. 4). Coordination of the (*R*)-epoxide to the cobalt(II) complex is unfavored due to the steric repulsion with the optically active (*R*,*R*)-cyclohexanediamine moiety, whereas coordination of the (*S*)-epoxide avoids steric repulsion. The (*S*)-epoxide is then activated by the (*R*,*R*)-cobalt(II) complex for attack by a nucleophile and reacts with CO_2 to afford the corresponding cyclic carbonate. Nucleophilic attack on the (*R*)-epoxide activated by (*R*,*R*)-co-

Table 3. Various Nucleophiles for CO_2 Fixation into Glycidyl Trityl Ether



Entry[a)]	Nucleophile	MB	*s*[b)]
1	KCN 18-Crown-6	56	2.7
2	Ph_3P	37	4.0
3		84	2.8
4		trace	
5		trace	
6		trace	
7	$Et_2N–SiMe_3$	87	7.7
8	Et_2NH	93	7.6
9	Bu_2NH	67	7.1
10	Hex_2NH	80	7.3
11		91	5.2
12		No Reaction	

a) Reaction conditions: the reaction was carried out in 0.5 mL of dichloromethane using 2.0 mol % cobalt(II) complex catalyst, 1.0 mol % nucleophile, and 1.0 mmol of epoxide under 2.0 MPa CO_2 pressure. b) *s* was calculated on the basis of the recovered epoxide.

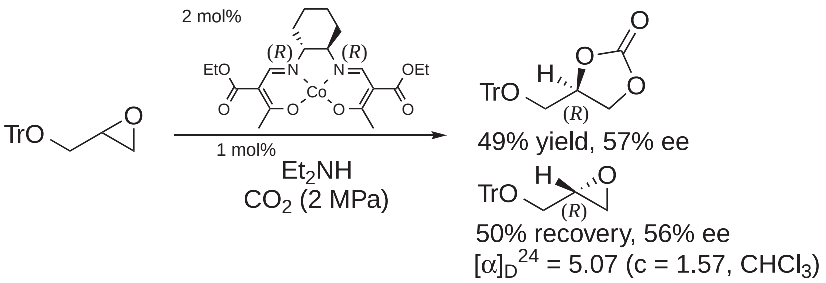
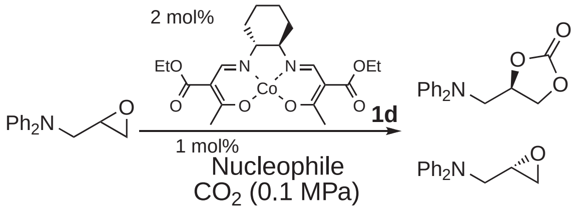
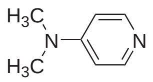
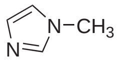
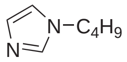
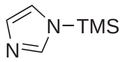
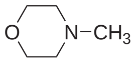
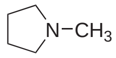
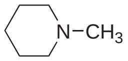
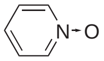
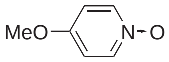
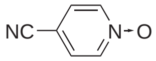
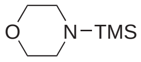
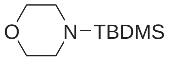


Fig. 2. Absolute configuration of the products.

Table 4. Various Nucleophiles for CO_2 Fixation into *N,N*-Diphenylaminomethyloxirane



Entry[a]	Nucleophile	MB	*s*[b]
1		57	5
2		73	10
3		58	6
4		40	9
5		82	13
6		87	22
7		80	16
8	Et_3N	84	15
9		60	13
10		82	11
11		61	9
12		77	28
13		79	18
14	$Et_2N–SiMe_3$	77	48

a) Reaction conditions: the reaction was carried out in 0.5 mL of dichloromethane using 2.0 mol % cobalt(II) complex catalyst, 1.0 mol % nucleophile under 0.1 MPa CO_2 pressure. b) *s* was calculated on the basis of the recovered epoxide.

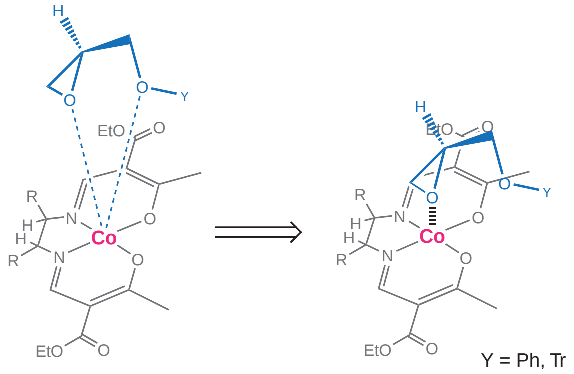


Fig. 3. Approach and activation of epoxide by cobalt(II) complex.

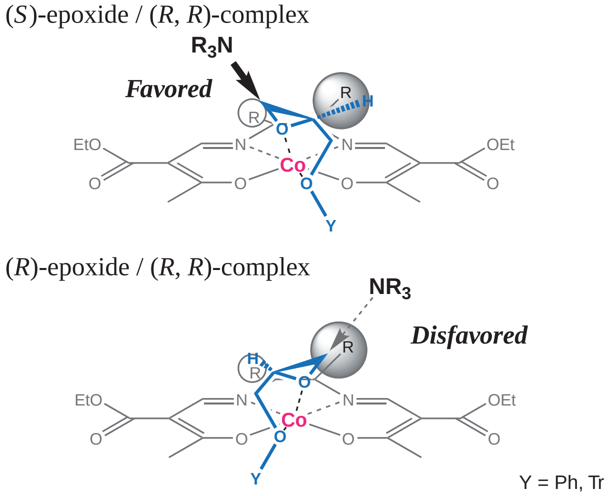
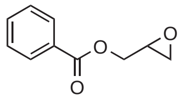
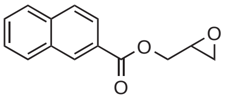
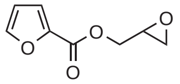
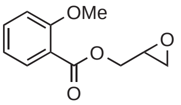
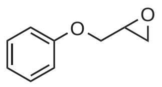
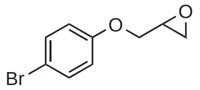
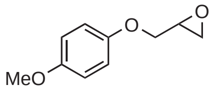
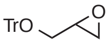


Fig. 4. Enantiomer discrimination of glycidol derivatives.

balt(II) complex should also be disfavored, because the steric-demanding group on the chiral diamine prevents the nucleophile from approaching the reaction center. In fact, the *s* values were found to depend on the structure of nucleophiles. Thus, unreacted optically active (*R*)-epoxide was recovered. The enantioselectivity of the reaction using the glycidyl amine derivatives was relatively better than that of the glycidyl ester or ether. These results support a two-point-coorination mechanism in the present CO_2 fixation reaction.

Enantioselective CO_2 Insertion into Glycidyl Derivatives. The optimized ketoiminatocobalt(II) complexes were successfully applied to the chemical fixation of glycidol derivatives and glycidyl esters with CO_2 (Table 5). The epoxides derived from benzoic acid (**2a**), naphthoic acid (**2b**), *o*-methoxy benzoic acid (**2c**), and furan carboxylic acid (**2d**) were examined for the asymmetric CO_2 incorporation reaction

Table 5. Enantioselective Carbon Dioxide Insertion Reaction into Glycidol Dervatives

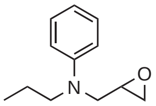
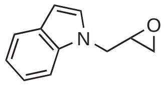
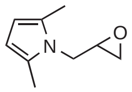
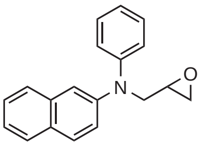
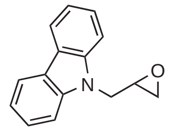
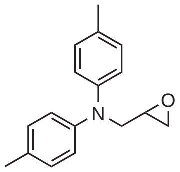
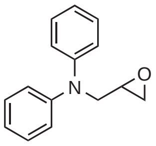
Entry[a]	Epoxide		Reaction time/h	Yield/%[b] (Ee/%[c])		MB	*s*[d]
				Epoxide	Carbonate		
1		**2a**	36	49 (27)	33 (33)	82	2.1
2		**2b**	20	50 (26)	25 (23)	75	2.2
3		**2c**	48	48 (32)	34 (25)	82	2.6
4		**2d**	24	55 (55)	24 (30)	79	8.8
5		**2e**	40	40 (35)	47 (25)	87	2.2
6		**2f**	36	56 (22)	37 (33)	93	2.2
7		**2g**	36	43 (39)	49 (26)	92	2.6
8		**2h**	72	54 (57)	44 (59)	98	8.8

a) Reaction conditions: the reaction was carried out in 0.5 mL of dichloromethane using 2.0 mol % cobalt(II) catalyst **1g**, 1.0 mol % diethylamine, and 1.0 mmol of epoxide under 2.0 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis. d) *s* was calculated on the basis of the recovered epoxide.

(Entries 1, 2, 3, and 4). Carbon dioxide smoothly inserted into **2a** to afford a cyclic product with $s = 2.1$ (Entry 1). Substrate **2b** afforded the optically active cyclic product, although the chemical yield was low (Entry 2). Epoxide **2c** sufficiently reactive to give the optically active cyclic carbonate in 34% yield with a 25% ee, and the starting ester was recovered in 48% yield with a 32% ee (Entry 3). When **2d** was employed as the epoxide, the *s* value improved to 8.8 (Entry 4). This slightly higher enantioselectivity suggested that the methyl ether moiety might coordinate to the cobalt(II) complex. The present reaction system could also catalyze CO_2 insertion into the glycidyl ethers (Entries 5, 6, 7, and 8). Glycidyl phenyl ether (**2e**) was converted into the corresponding cyclic carbonate in 47% yield with a 25% ee along with the recovery of the epoxide in 40% yield with a 35% ee (Entry 5), whereas 4-phenyl-1-butene oxide did not afford the cyclic carbonate. An electron-rich or -poor substituent (**2f** or **2g**) reacted with CO_2 in a high yield with *s* values of 2.2–2.6 (Entries 6 and 7). An epoxide possessing a protective group in the molecule, glycidyl trityl ether (**2h**), was converted into the corresponding cyclic carbonate (44% yield, 59% ee) along with the recovery of the starting epoxide in 54% yield with a 59% ee. The *s* value was calculated to be 8.8 (Entry 8).

The enantioselective incorporation of CO_2 could be applied to glycidyl amines (Table 6). Glycidyl amines having various substituents on the nitrogen were allowed to react with CO_2 to afford the optically active cyclic carbonate. *N*-Propyl-*N*-phenylaminomethyloxirane (**3a**) reacted with CO_2 in a high yield with $s = 6.3$ (Entry 1). The epoxide derived from the indole (**3b**) afforded the optically active epoxide and the cyclic carbonate in a good yield with $s = 6.4$ (Entry 2). The protected form of the glycidylamines could be subjected to the present catalyst system. [*N*-(2,5-Dimethylpyrrolyl)methyl]oxirane (**3c**) reacted with CO_2 to give the optically active cyclic product, although the yield was unsatisfactory, because of the partial decomposition of the starting epoxide (Entry 3). This investigation showed that glycidyl amines afforded a relatively higher enantioselectivity compared to be glycidyl ester or glycidyl ethers. Further examination of the glycidyl amines improved the *s* value to a satisfactory level. The ketoiminatocobalt complex catalyzed the CO_2 insertion even in the presence of a bulky substituent on the nitrogen without any loss of activity. The racemic *N*-β-naphthyl-*N*-phenylaminomethyloxirane (**3d**) reacted with CO_2 in good yield, and the *s* value was calculated to be 14.6 (Entry 4). Epoxides having symmetrical amine moieties improved the enantioselectivity (Entries 5, 6, and 7). In the presence of cobalt complex **1g**, *N*,*N*-ditolylaminomethyloxirane (**3f**) reacted with high-pressure CO_2 to give the cyclic product and the starting epoxide with $s = 13.9$ (Entry 6). *N*-Carbazolylmethyloxirane (**3e**) and *N*,*N*-diphenylaminomethyloxirane (**3g**) were also used and they showed remarkable enantioselectivities with *s* values of 41.7 and 43.5, respectively

Table 6. Enantioselective Carbon Dioxide Insertion Reaction into Glycidyl Amines

Entry$^{a)}$	Epoxide		Reaction time/h	Yield/%$^{b)}$ (Ee/%$^{c)}$)		MB	$s^{d)}$
				Epoxide	Carbonate		
1		**3a**	36	47 (62)	44 (54)	91	6.3
2		**3b**	8	57 (46)	30 (68)	87	6.4
3		**3c**	8	50 (24)	14 (82)	64	2.0
4		**3d**	27	55 (63)	33 (87)	88	14.6
5		**3e**	29	53 (79)	45 (92)	98	41.7
6		**3f**	14	44 (86)	27 (74)	71	13.9
7		**3g**	75	47 (95)	43 (82)	90	43.5

a) Reaction conditions: the reaction was carried out in 0.5 mL of dichloromethane using 2.0 mol % cobalt(II) catalyst **1g**, 1.0 mol % diethylamine, and 1.0 mmol of epoxide under 2.0 MPa CO_2 pressure. b) Isolated yield. c) Enantiomeric excess was determined by HPLC analysis. d) s was calculated on the basis of the recovered epoxide.

(Entries 5 and 7). This is considered to be a practical level of enantioselectivity for asymmetric CO_2 reactions. The reaction was carried out under a high pressure of CO_2 using *N*,*N*-diphenylaminomethyloxirane (**3g**) as a model substrate and a catalytic amount of the cobalt(II) complex **1g** and dipropylamine. The reaction was quenched at different conversion amounts, and the s value was determined each time. The ee values at each conversion were plotted on the theoretical curve for $s = 100$ (Fig. 5). It was confirmed that they fit the theoretical values and the present catalyst system achieved a high enantioselectivity. The s value reached ca. 100. It is noted that the optically active ketoiminatocobalt(II) complex efficiently catalyzed the enantioselective CO_2 incorporation into various glycidol derivatives to afford the corresponding cyclic carbonate along with the epoxide, both with high ee values. The obtained results nearby fit on the $s = 100$ curve.

Conclusion

Optically active cobalt(II) complexes catalyzed the asymmetric CO_2 insertion reaction into epoxides via a kinetic resolution process. The optimization of the cobalt ligand and co-catalyst improved both the reactivity and enantioselectivity. The heteroatoms adjacent to the oxirane in the glycidyl derivatives appear to be crucial for the enantiodiscrimination. Various glycidol derivatives were applied to the present catalyst system to afford the corresponding optically active cyclic carbonates along with the recovery of the epoxides with good-to-high enantioselectivities.

Experimental

General. The melting point were measured on an Electrothermal IA9100 apparatus and were uncorrected. The ^1H NMR spectra and ^{13}C spectra were measured using a JEOL model GX-400 (400 MHz) spectrometer with $CDCl_3$ (77.7 ppm) as the solvent and tetramethylsilane (0.00 ppm) as the internal standard. Infrared (IR) spectra were recorded using a JASCO Model FT/IR-410 infrared spectrometer with KBr pellets or liquid film on NaCl. Elemental analyses were done using an Elemental Vario EL apparatus. High-resolution mass spectra (HRMS) were obtained using a Hitachi M-80B. For the thin-layer chromatography (TLC) analysis throughout this study, Merck precoated TLC plates (silica gel 60F254, 0.25 mm) were used. High-performance liquid chroma-

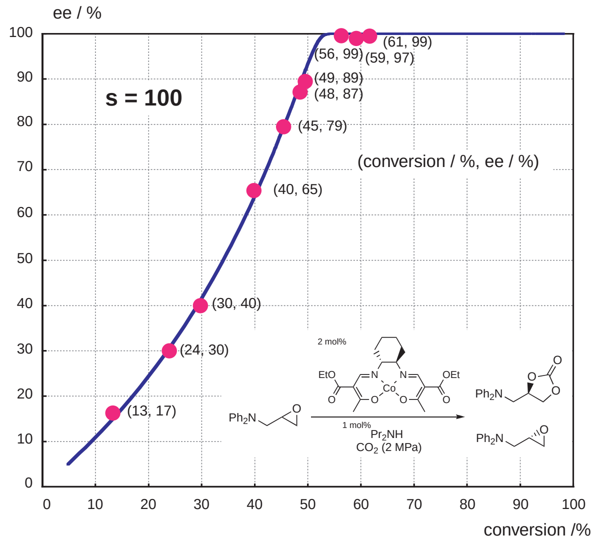


Fig. 5. Optical purity of the epoxide for the conversion of *N*,*N*-diphenylaminomethyloxirane (**3g**).

tography (HPLC) analyses were performed on a Shimadzu LC-6A chromatograph using an optically active column (Daicel Chiralcel OD-H, Chiralpak AD-H, Chiralpak IB, and Chiralpak IA); the peak areas were obtained by using a Shimadzu Chromatopak CR-4A, Shimadzu SPD-M10A or Varian Dynamax MacIntegrator. Optical rotations were measured using a JASCO DIP-370 digital polarimeter.

General Procedure for Preparation of Optically Active Cobalt Complexes. These ligands were prepared by the reported method from 3-oxo-2-(alkoxycarbonyl)butanal and the corresponding optically active diamines. Optically active cobalt(II) complexes were also prepared by the reported method.[30]

Preparation of Glycidyl Ethers. The glycidyl ether derivatives were prepared from the corresponding phenol and epichlorohydrin according to the literature method.[31]

Preparation of Glycidyl Esters.[32] Various glycidyl esters were prepared from the corresponding carboxylic acids and epichlorohydrin. A carboxylic acid was added to a methanol solution of sodium methoxide and stirred for about 30 min. The methanol was then evaporated under reduced pressure. The obtained carboxylic acid sodium salt was added to excess epichlorohydrin and heated at 100 °C for several hours. The reaction was quenched by adding water and extracted with EtOAc. The combined organic layer was washed with brine and dried over sodium sulfate, and then the excess solvent and epichlorohydrin were removed under reduced pressure. Purification by bulb-to-bulb distillation under reduced pressure gave the corresponding glycidyl esters.

Preparation of Glycidyl Amines. A secondary amine in DMF was added to a DMF solution of sodium hydride and stirred overnight at room temperature. Excess epichlorohydrin was added dropwise to the solution at 0 °C. The resulting mixture was stirred for 6 h. The reaction was quenched by slowly adding water at 0 °C and extracted with diethyl ether. The combined organic layer was washed with brine and dried over sodium sulfate, and then the excess solvent and epichlorohydrin were removed under reduced pressure. Purification by column chromatography on silica gel gave the corresponding glycidyl amines.

General Procedure for Enantioselective Incorporation of Epoxides with CO_2. A racemic of each epoxide was added to a solution of the optically active cobalt(II) complex catalyst (11.3 mg, 0.02 mmol, 2 mol %) in dichloromethane (0.4 mL), and then, 0.1 mL of a solution of diethylamine (7.3 mg, 0.1 mmol) in dichloromethane (1.0 mL) was added to the mixture. The reaction mixture was stirred for the amount of time shown in Tables 5 and 6 under a CO_2 pressure of 2.0 MPa at 30 °C. Purification by column chromatography on silica gel gave the corresponding cyclic carbonate along and the starting epoxide. The enantiomeric excess was determined by HPLC analysis using Daicel Chiralcel OD-H, Daicel Chiralpak AD-H, IA and IB.

Glycidyl Benzoate (2a): ^{1}H NMR ($CDCl_3$) δ 2.73 (dd, 1H, $J = 2.4, 4.8$ Hz), 2.90 (t, 1H, $J = 4.8$ Hz), 3.32–3.37 (1H, m), 4.18 (dd, 1H, $J = 6.4, 12.4$ Hz), 4.66 (dd, 1H, $J = 2.8, 12.4$ Hz), 7.45 (t, 2H, $J = 8.0$ Hz), 7.56–7.60 (m, 1H), 8.07 (dd, 2H, $J = 0.80, 8.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 44.7, 49.4, 65.4, 128.3, 129.5, 129.6, 133.1, 166.1; IR (neat) 3057, 1590, 1495, 1362, 1257, 749, 695 cm^{-1}. HPLC Daicel chiralpak AD-H (2% ethanol in hexane; flow = 1.0 mL min^{-1}), 14.3 min (minor), 15.7 min (major). $[\alpha]_D^{25} = -3.69°$ ($c = 0.84$ in $CHCl_3$).

4-(Benzoyloxymethyl)-1,3-dioxolan-2-one (2a′):[33] HPLC Daicel chiralpak IA (10% ethanol; flow = 1.0 mL min^{-1}), 29.6 min (major), 36.9 min (minor). $[\alpha]_D^{25} = -4.99°$ ($c = 0.74$ in $CHCl_3$).

Glycidyl Naphthoate (2b): ^{1}H NMR ($CDCl_3$) δ 2.77 (dd, 1H, $J = 2.4, 4.9$ Hz), 2.93 (t, 1H, $J = 4.9$ Hz), 3.38–3.42 (m, 1H), 4.23 (dd, 1H, $J = 6.3, 12.2$ Hz), 4.73 (dd, 1H, $J = 2.9, 12.2$ Hz), 7.53–7.62 (m, 2H), 7.80–7.97 (m, 3H), 8.07 (dd, 1H, $J = 1.7, 8.6$ Hz), 8.64 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 44.8, 49.6, 65.6, 125.1, 126.6, 126.8, 127.7, 128.1, 128.3, 129.3, 131.2, 132.3, 135.5, 166.3; IR (neat) 3059, 1719, 1284, 1227, 1197, 1130, 1094, 779 cm^{-1}. HRMS: calcd for $C_{14}H_{12}O_3$: (M$^+$), 228.0786. Found: m/z 228.0777. HPLC Daicel chiralpak IB (2% ethanol in hexane; flow = 1.0 mL min^{-1}), 13.7 min (minor), 14.8 min (major); $[\alpha]_D^{25} = -5.3°$ ($c = 0.48$ in EtOH).

4-(2-Naphthoyloxymethyl)-1,3-dioxolane-2-one (2b′): ^{1}H NMR ($CDCl_3$) δ 4.47 (dd, 1H, $J = 5.9, 8.8$ Hz), 4.57 (dd, 1H, $J = 3.8, 12.7$ Hz), 4.61–4.69 (m, 2H), 5.08–5.13 (m, 1H), 7.55–7.64 (m, 2H), 7.88–8.04 (m, 4H), 8.61 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 63.8, 66.1, 73.9, 76.7, 124.8, 125.8, 126.8, 127.7, 128.4, 128.6, 129.4, 131.6, 132.3, 135.7, 154.4, 166.0; IR (KBr) 1784, 1715, 1283, 1187, 1090 cm^{-1}. Mp 122.0–123.1 °C; HRMS: calcd for $C_{15}H_{12}O_5$: (M$^+$), 272.0669. Found: m/z 272.0669. HPLC Daicel chiralcel OD-H (10% ethanol in hexane; flow = 1.0 mL min^{-1}), 29.6 min (major), 35.4 min (minor); $[\alpha]_D^{25} = -36.0°$ ($c = 0.21$ in $CHCl_3$).

Glycidyl Furoate (2c): ^{1}H NMR ($CDCl_3$) δ 2.73 (dd, 1H, $J = 2.9, 4.7$ Hz), 2.89 (t, 1H, $J = 4.7$ Hz), 3.30–3.34 (m, 1H), 4.17 (dd, 1H, $J = 6.3, 12.2$ Hz), 4.63 (dd, 1H, $J = 3.4, 12.2$ Hz), 6.53 (dd, 1H, $J = 2.0, 3.4$ Hz), 7.24 (dd, 1H, $J = 1.0, 3.4$ Hz), 7.61 (dd, 1H, $J = 1.0, 2.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 44.7, 49.3, 65.3, 111.8, 118.4, 144.0, 146.5, 158.1; IR (neat) 3141, 3004, 1728, 1580, 1394, 1346, 1297, 1181, 1116, 762 cm^{-1}. HRMS: calcd for $C_8H_8O_4$: (M$^+$), 168.0423. Found: m/z 168.0419. HPLC Daicel chiralcel OD-H (0.5% 2-propanol in hexane; flow = 1.0 mL min^{-1}), 35.0 min (minor), 37.2 min (major); $[\alpha]_D^{25} = -11.6°$ ($c = 0.83$ in EtOH).

4-(Furyloxymethyl)-1,3-dioxolan-2-one (2c′): ^{1}H NMR ($CDCl_3$) δ 4.40 (dd, 1H, $J = 5.9, 8.8$ Hz), 4.50 (dd, 1H, $J = 4.4, 12.2$ Hz), 4.57 (dd, 1H, $J = 3.4, 12.2$ Hz), 4.62 (t, 1H, $J = 8.8$ Hz), 5.02–5.06 (m, 1H), 6.55 (dd, 1H, $J = 1.0, 3.4$ Hz), 7.25 (d, 1H, $J = 3.4$ Hz), 7.63 (d, 1H, $J = 1.0$ Hz); ^{13}C NMR ($CDCl_3$) δ 63.3, 66.0, 73.7, 112.0, 119.2, 143.1, 147.1, 154.2, 157.6; IR (KBr) 1785, 1720, 1471, 1402, 1298, 1187, 1090, 1052, 774

cm^{-1}. Mp 85.7–87.0 °C; HRMS: calcd for $C_9H_8O_6$: (M^+), 212.0320. Found: *m/z* 212.0320. HPLC Daicel chiralpak AD-H (10% ethanol in hexane; flow $= 1.0\,\text{mL}\,\text{min}^{-1}$), 64.4 min (major), 70.3 min (minor); $[\alpha]_D^{25} = -22.4°$ ($c = 0.16$ in $CHCl_3$).

Glycidyl *o*-Anisoate (2d): ^{1}H NMR ($CDCl_3$) δ 2.76 (dd, 1H, $J = 2.9$, 4.9 Hz), 2.88 (t, 1H, $J = 4.9$ Hz), 3.31–3.35 (m, 1H), 3.91 (s, 3H), 4.18 (dd, 1H, $J = 6.1$, 12.5 Hz), 4.62 (dd, 1H, $J = 3.4$, 12.5 Hz), 6.97–7.00 (m, 2H), 7.46–7.51 (m, 1H), 7.83–7.86 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 45.2, 47.7, 50.9, 101.8, 109.2, 119.5, 120.9, 121.7, 128.1, 128.5, 136.2; IR (neat) 2948, 2839, 1728, 1600, 1491, 1252, 1075, 757 cm^{-1}. HRMS: calcd for $C_{11}H_{12}O_4$: (M^+), 208.0736; Found: *m/z* 208.0729. HPLC Daicel chiralcel OD-H (3% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 14.0 min (minor), 15.2 min (major); $[\alpha]_D^{25} = -4.7°$ ($c = 1.14$ in EtOH).

4-(*o*-Anisyloyloxymethyl)-1,3-dioxolan-2-one (2d′): ^{1}H NMR ($CDCl_3$) δ 3.91 (s, 3H), 4.46 (dd, 1H, $J = 1.5$, 2.7 Hz), 4.49 (dd, 1H, $J = 1.0$, 2.7 Hz), 4.59–4.63 (m, 2H), 5.01–5.06 (m, 1H), 6.98–7.02 (m, 2H), 7.50–7.54 (m, 1H), 7.83 (dd, 1H, $J = 1.5$, 7.8 Hz); ^{13}C NMR ($CDCl_3$) δ 55.8, 63.1, 65.9, 73.8, 112.0, 118.2, 120.1, 132.1, 134.4, 154.4, 159.5, 165.7; IR (neat) 2949, 1798, 1727, 1600, 1492, 1300, 1250, 1169, 1049 cm^{-1}. HRMS: calcd for $C_{12}H_{12}O_6$: (M^+), 252.0633. Found: *m/z* 252.0644. HPLC Daicel chiralcel OD-H (4% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 78.0 min (minor), 82.8 min (major); $[\alpha]_D^{25} = -45.8°$ ($c = 0.59$ in EtOH).

Glycidyl Phenyl Ether (2e): HPLC Daicel chiralpak AD-H (1% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 11.3 min (major), 12.3 min (minor); $[\alpha]_D^{25} = -4.24°$ ($c = 1.23$ in EtOH).

4-Phenyl-1,3-dioxolan-2-one (2e′):[34] HPLC Daicel chiralpak IB (5% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 33.2 min (minor), 36.8 min (major); $[\alpha]_D^{25} = +5.46°$ ($c = 0.39$ in EtOH).

***p*-Bromophenyl Glycidyl Ether (2f):** ^{1}H NMR ($CDCl_3$) δ 2.75 (dd, 1H, $J = 2.4$, 4.9 Hz), 2.90 (t, 1H, $J = 4.9$ Hz), 3.32–3.36 (m, 1H), 3.91 (dd, 1H, $J = 5.4$, 11.0 Hz), 4.21 (dd, 1H, $J = 2.9$, 11.0 Hz), 6.81 (dd, 2H, $J = 3.4$, 11.0 Hz), 7.37 (dd, 2H, $J = 3.4$, 11.0 Hz): ^{13}C NMR ($CDCl_3$) δ 44.6, 50.0, 68.9, 113.3, 116.3, 132.2, 157.4; IR (KBr) 2926, 1589, 1488, 1286, 1241, 1174, 1071, 1031, 822 cm^{-1}. Mp 54.6–55.6 °C; HRMS: calcd for $C_9H_9BrO_2$: (M^+), 227.9786. Found: 227.9793. HPLC Daicel chiralpak IA (0.5% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 16.1 min (minor), 17.4 min (major); $[\alpha]_D^{25} = -1.9°$ ($c = 1.25$ in $CHCl_3$).

4-[(4-Bromophenoxy)methyl]-1,3-dioxolan-2-one (2f′): ^{1}H NMR ($CDCl_3$) δ 4.12 (dd, 1H, $J = 3.9$, 10.7 Hz), 4.22 (dd, 1H, $J = 4.4$, 10.7 Hz), 4.52 (dd, 1H, $J = 5.9$, 8.8 Hz), 4.62 (t, 1H, $J = 8.8$ Hz), 5.00–5.05 (m, 1H), 6.80 (d, 2H, $J = 6.8$ Hz), 7.41 (d, 2H, $J = 8.6$ Hz); ^{13}C NMR (C_6D_6) δ 65.3, 67.0, 73.3, 114.3, 116.58, 116.60, 132.6, 157.1; IR (KBr) 1795, 1488, 1232, 1175, 1067, 822, 771 cm^{-1}. Mp 118.0–118.9 °C; HRMS: calcd for $C_{10}H_9BrO_4$: (M^+), 271.9684. Found: *m/z* 271.9677. HPLC Daicel chiralpak IA (10% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 19.3 min (major), 23.3 min (minor); $[\alpha]_D^{25} = +4.7°$ ($c = 0.49$ in acetone).

Glycidyl-*p*-Methoxyphenyl Ether (2g):[35] HPLC Daicel chiralpak IB (1% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 13.1 min (major), 15.0 min (minor); $[\alpha]_D^{25} = -0.68°$ ($c = 0.72$ in ethyl acetate).

4-[(4-Methoxyphenoxy)methyl]-1,3-dioxolan-2-one (2g′): ^{1}H NMR ($CDCl_3$) δ 3.77 (s, 3H), 3.93 (dd, 1H, $J = 3.6$, 10.9 Hz), 4.18 (dd, 1H, $J = 3.9$, 10.9 Hz), 4.49–4.62 (m, 2H), 4.95–5.03 (m, 1H), 6.84 (s, 4H); ^{13}C NMR ($CDCl_3$) δ 55.7, 66.2, 67.8, 74.2, 114.7, 115.7, 151.8, 154.50, 154.55; IR (KBr) 1779, 1511, 1238, 1184, 1089, 1038 cm^{-1}. Mp 79.1–80.1 °C; HRMS: calcd for $C_{11}H_{12}O_5$: (M^+), 224.0685. Found: *m/z* 224.0687. HPLC Daicel chiralpak IA (10% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 21.4 min (major), 27.6 min (minor); $[\alpha]_D^{25} = -9.9°$ ($c = 1.0$ in $CHCl_3$).

Glycidyl Trityl Ether (2h): HPLC Daicel chiralpak IA (1% tetrahydrofuran in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$) 7.9 min (minor), 10.0 min (major); $[\alpha]_D^{25} = +4.77°$ ($c = 1.59$ in $CHCl_3$).

4-(Triphenylmethoxy)methyl-1,3-dioxolan-2-one (2h′): ^{1}H NMR ($CDCl_3$) δ 3.17 (dd, 1H, $J = 3.2$, 10.8 Hz), 3.54 (dd, 1H, $J = 3.2$, 10.8 Hz), 4.33 (dd, 1H, $J = 5.2$, 7.6 Hz), 4.43 (t, 1H, $J = 7.6$ Hz), 4.72–4.77 (m, 1H), 7.22–7.43 (m, 15H); ^{13}C NMR ($CDCl_3$) δ 63.0, 66.3, 75.1, 87.1, 127.3, 128.0, 128.4, 143.0, 154.9; IR (KBr) 1787, 1172, 1057, 1175, 697 cm^{-1}. Mp 220.2–221.6 °C; HRMS: *m/z*: calcd for $C_{23}H_{20}O_4$: (M^+), 360.1362. Found: *m/z* 360.1358. HPLC Daicel chiralpak IA (7% ethyl acetate in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 23.2 min (minor), 26.9 min (major); $[\alpha]_D^{25} = +4.25°$ ($c = 1.81$ in $CHCl_3$).

***N*-Phenyl-*N*-propylaminomethyloxirane (3a):** ^{1}H NMR ($CDCl_3$) δ 0.93 (t, 3H, $J = 7.6$ Hz), 1.58–1.68 (m, 2H), 2.56 (dd, 1H, $J = 2.4$, 4.9 Hz), 2.78 (t, 1H, $J = 4.9$ Hz), 3.12–3.15 (m, 1H), 3.29 (t, 2H, $J = 7.8$ Hz), 3.41 (dd, 1H, $J = 4.4$, 16.1 Hz), 3.62 (dd, 1H, $J = 3.4$, 16.1 Hz), 6.67–6.73 (m, 3H), 7.19–7.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.4, 20.1, 45.6, 50.7, 52.5, 53.4, 112.0, 116.2, 129.2, 148.1; IR (neat): 3053, 1462, 1316, 1254, 1199, 850, 741 cm^{-1}. HRMS: calcd for $C_{12}H_{17}NO$: (M^+), 191.1310. Found: *m/z* 191.1296. HPLC: Daicel Chiralcel OD-H (0.1% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 15.4 min (minor), 16.4 min (major) $[\alpha]_D^{25} = +28.9°$ ($c = 0.86$ in $CHCl_3$).

4-(*N*-Phenyl-*N*-propylaminomethyl)-1,3-dioxolan-2-one (3a′): ^{1}H NMR ($CDCl_3$) δ 0.92 (t, 3H, $J = 7.8$ Hz), 3.11 (sextet, 2H, $J = 7.8$ Hz), 3.25–3.40 (m, 2H), 3.59 (dd, 1H, $J = 4.9$, 15.6 Hz), 3.67 (dd, 1H, $J = 5.9$, 15.6 Hz), 4.20 (t, 1H, $J = 8.8$ Hz), 4.51 (t, 1H, $J = 8.8$ Hz), 4.89–4.95 (m, 1H), 6.68–6.79 (m, 3H), 7.22–7.27 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 11.3, 19.9, 53.2, 54.4, 67.3, 75.1, 113.1, 117.7, 129.5, 147.4, 154.5; IR (neat) 2962, 1805, 1599, 1505, 1381, 1170, 1079, 749 cm^{-1}. HRMS: calcd for $C_{13}H_{17}NO_3$: (M^+), 235.1208. Found: *m/z* 235.1221. HPLC Chiralpak AD-H (5% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 15.3 min (major), 17.1 min (minor). $[\alpha]_D^{25} = +10.6°$ ($c = 1.01$ in EtOH).

***N*-Indolylmethyloxirane (3b):** ^{1}H NMR ($CDCl_3$) δ 2.43 (dd, 1H, $J = 2.4$, 4.8 Hz), 2.77 (t, 1H, $J = 4.8$ Hz), 3.22–3.27 (m, 1H), 4.16 (dd, 1H, $J = 5.4$, 15.1 Hz), 4.39 (dd, 1H, $J = 2.9$, 15.1 Hz), 6.51 (d, 1H, $J = 2.9$ Hz), 7.10–7.24 (m, 3H), 7.36 (d, 1H, $J = 8.3$ Hz), 7.63 (d, 1H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 45.2, 47.7, 50.9, 101.8, 109.2, 119.5, 120.9, 121.7, 128.1, 128.4, 136.2; IR (neat) 2960, 1598, 1505, 1388, 1235, 1192, 949, 828, 748, 693 cm^{-1}. HRMS: calcd for $C_{11}H_{11}NO$: (M^+), 173.0841. Found: *m/z* 173.0833. Daicel chiralcel OD-H (5% 2-propanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 12.8 min (minor), 13.8 min (major); $[\alpha]_D^{25} = +3.06°$ ($c = 0.93$ in $CHCl_3$).

4-(*N*-Indolylmethyl)-1,3-dioxolan-2-one (3b′): ^{1}H NMR ($CDCl_3$) δ 4.13 (dd, 1H, $J = 6.8$, 8.8 Hz), 4.42–4.47 (m, 3H), 5.01–5.04 (m, 1H), 6.58 (d, 1H, $J = 3.4$ Hz), 7.12–7.31 (m, 4H), 7.65 (d, 1H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 47.4, 66.8, 75.1, 103.3, 108.5, 120.2, 121.0, 122.0, 122.4, 127.9, 128.7, 153.8; IR (KBr) 1805, 1461, 1396, 1311, 1163, 1084, 1033 cm^{-1}. Mp 91.4–92.4 °C; HRMS: calcd for $C_{12}H_{11}NO_3$: (M^+), 217.0739. Found: *m/z* 217.0737. HPLC Daicel chiralpak AD-H (5% ethanol in hexane; flow = 1.0 $\text{mL}\,\text{min}^{-1}$), 50.3 min (major), 55.5 min (minor); $[\alpha]_D^{25} = -49.4°$ ($c = 0.59$ in $CHCl_3$).

[*N*-(2,5-Dimethylpyrrolyl)methyl]oxirane (3c): ^{1}H NMR ($CDCl_3$) δ 2.22 (s, 6H), 2.38 (dd, 1H, $J = 2.5$, 4.9 Hz), 2.76 (t, 1H, $J = 4.9$ Hz), 3.11–3.14 (m, 1H), 3.91 (dd, 1H, $J = 4.4$, 15.6 Hz), 4.06 (dd, 1H, $J = 12.2$, 15.6 Hz), 5.77 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 12.6, 44.4, 45.2, 51.2, 105.4, 127.9; IR (neat) 3055, 1407, 1299, 1111, 757 cm^{-1}. HRMS: calcd for $C_9H_{13}NO$: (M^+), 151.0997. Found: m/z 151.1008. HPLC: Daicel chiralcel OD-H (0.5% 2-propanol in hexane; flow = 1.0 mL min^{-1}), 9.73 min (minor), 11.0 min (major) $[\alpha]_D^{25} = +8.63°$ ($c = 0.87$ in $CHCl_3$).

4-[*N*-(2,5-Dimethylpyrrolyl)methyl]-1,3-dioxolan-2-one (3c′): ^{1}H NMR ($CDCl_3$) δ 2.23 (s, 6H), 4.02–4.16 (m, 3H), 4.51 (t, 1H, $J = 8.3$ Hz), 4.84–4.90 (m, 1H), 5.83 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 12.8, 45.2, 66.6, 75.7, 106.8, 127.6, 153.9; IR (KBr) 1800, 1400, 1170, 1083 cm^{-1}. Mp 88.3–88.6 °C; HRMS: calcd for $C_8H_{13}NO_3$: (M^+) 195.0895. Found: m/z 195.0902. HPLC Daicel chiralcel OD-H (2% 2-propanol in hexane; flow = 1.0 mL min^{-1}), 14.5 min (minor), 16.2 min (major) $[\alpha]_D^{25} = -43.9°$ ($c = 0.04$ in DMSO).

***N*-2-Naphthalenyl-*N*-phenylaminomethyloxirane (3d):** ^{1}H NMR ($CDCl_3$) δ 2.59 (dd, 1H, $J = 2.9$, 4.9 Hz), 2.79 (dd, 1H, $J = 3.9$, 4.9 Hz), 3.27–3.30 (m, 1H), 3.96 (dd, 1H, $J = 2.0$, 15.6 Hz), 4.08 (dd, 1H, $J = 3.4$, 15.6 Hz), 7.00–7.43 (m, 9H), 7.67–7.74 (m, 3H); ^{13}C NMR ($CDCl_3$) δ 46.0, 50.3, 54.1, 115.7, 121.4, 122.0, 122.1, 123.9, 126.2, 126.7, 127.4, 128.8, 129.25, 129.31, 134.5, 145.3, 147.8; IR (neat) 2977, 1407, 1299, 1111, 757 cm^{-1}. HRMS: calcd for $C_{19}H_{17}NO$: (M^+), 275.1310. Found: m/z 275.1301. HPLC Daicel chiralpak AD-H (10% ethanol in hexane; flow = 1.0 mL min^{-1}), 7.3 min (major), 9.1 min (minor); $[\alpha]_D^{25} = +34.0°$ ($c = 0.28$ in EtOH).

4-(*N*-2-Naphthalenyl-*N*-phenylaminomethyl)-1,3-dioxolan-2-one (3d′): ^{1}H NMR ($CDCl_3$) δ 3.99–4.14 (m, 3H), 4.33–4.37 (m, 1H), 4.91–4.93 (m, 1H), 6.94–7.67 (m, 12H); ^{13}C NMR ($CDCl_3$) δ 54.3, 67.4, 74.3, 116.0, 121.5, 121.9, 122.8, 124.3, 126.4, 126.7, 127.3, 129.2, 129.4, 129.5, 134.2, 144.7, 147.3, 154.3; IR (KBr) 1797, 1595, 1498, 1396, 1168, 1080 cm^{-1}. HRMS: calcd for $C_{20}H_{17}NO_3$: (M^+), 319.1208. Found: m/z 319.1196. HPLC Daicel chiralpak AD-H (10% ethanol in hexane; flow = 1.0 mL min^{-1}), 18.7 min (minor), 22.5 min (major); $[\alpha]_D^{25} = -33.7°$ ($c = 0.24$ in EtOH).

***N*-Carbazolylmethyloxirane (3e):** ^{1}H NMR ($CDCl_3$) δ 2.57 (dd, 1H, $J = 2.9$, 4.9 Hz), 2.80 (t, 1H, $J = 4.9$ Hz), 3.33–3.37 (m, 1H), 4.40 (dd, 1H, $J = 4.9$, 15.6 Hz), 4.63 (dd, 1H, $J = 3.7$, 15.6 Hz), 7.23–7.27 (m, 2H), 7.44–7.49 (m, 4H), 8.09 (d, 2H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 44.6, 45.4, 50.6, 108.7, 119.3, 120.3, 123.0, 125.8, 140.6; IR (KBr) 1485, 1457, 1221, 1153, 909, 747, 721 cm^{-1}. Mp 111.8–112.6 °C; elemental analysis calcd (%) for $C_{15}H_{13}NO$: C, 80.69; H, 5.87; N, 6.27%. Found: C, 80.53; H, 5.77; N, 6.20%. HPLC Daicel chiralpak AD-H (5% ethanol in hexane; flow = 1.0 mL min^{-1}), 11.0 min (minor), 11.9 min (major); $[\alpha]_D^{25} = +11.1°$ ($c = 1.02$ in $CHCl_3$).

4-(Carbazolylmethyl)-1,3-dioxolan-2-one (3e′): ^{1}H NMR ($CDCl_3$) δ 4.28 (dd, 1H, $J = 6.6$, 8.8 Hz), 4.47 (t, 1H, $J = 8.8$ Hz), 4.60 (dd, 1H, $J = 5.3$, 15.9 Hz), 4.65 (dd, 1H, $J = 5.4$, 15.9 Hz), 5.16–5.22 (m, 1H), 7.26–7.52 (m, 6H), 8.10 (d, 2H, $J = 7.8$ Hz); ^{13}C NMR ($CDCl_3$) δ 44.6, 66.9, 74.9, 108.2, 120.0, 120.6, 123.3, 126.3, 140.3, 153.9; IR (KBr) 3447, 1781, 1456, 1162, 1042, 754 cm^{-1}. Mp 189.6–191.1 °C; HRMS: calcd for $C_{16}H_{13}NO_3$: (M^+), 267.0895. Found: m/z 267.0902. Daicel chiralpak IA (10% ethanol in hexane; flow = 1.0 mL min^{-1}), 15.0 min (major), 17.3 min (minor); $[\alpha]_D^{25} = +7.8°$ ($c = 1.65$ in $CHCl_3$).

***N*,*N*-Ditolylaminomethyloxirane (3f):** ^{1}H NMR ($CDCl_3$) δ 2.29 (s, 6H), 2.55 (dd, 1H, $J = 2.4$, 4.9 Hz), 2.76 (t, 1H, $J = 4.9$ Hz), 3.19–3.23 (m, 1H), 3.82 (dd, 1H, $J = 4.4$, 15.6 Hz), 3.88 (dd, 1H, $J = 3.9$, 15.6 Hz), 6.92 (d, 4H, $J = 8.3$ Hz), 7.07 (d, 4H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.7, 46.1, 50.5, 54.0, 120.8, 129.8, 130.9, 145.7; IR (KBr) 2914, 1607, 1510, 1359, 1230, 1114, 906, 868, 812 cm^{-1}. Mp 59.8–60.4 °C; HRMS: calcd for $C_{17}H_{19}NO$: (M^+), 253.1467. Found: m/z 253.1467. HPLC Daicel chiralpak AD-H (10% ethanol in hexane; flow = 1.0 mL min^{-1}), 6.7 min (minor), 8.0 min (major); $[\alpha]_D^{25} = +38.8°$ ($c = 0.54$ in EtOH).

4-(*N*,*N*-Ditolylaminomethyl)-1,3-dioxolan-2-one (3f′): ^{1}H NMR ($CDCl_3$) δ 2.30 (s, 6H), 3.94 (dd, 1H, $J = 6.4$, 15.1 Hz), 4.07 (dd, 1H, $J = 5.8$, 15.1 Hz), 4.20 (dd, 1H, $J = 2.0$, 8.3 Hz), 4.44 (t, 1H, $J = 8.3$ Hz), 4.91–4.96 (m, 1H), 6.84 (d, 4H, $J = 8.3$ Hz), 7.09 (d, 4H, $J = 8.3$ Hz); ^{13}C NMR ($CDCl_3$) δ 20.6, 54.5, 67.7, 74.5, 121.0, 130.1, 132.0, 145.3, 154.5; IR (KBr) 1782, 1509, 1165, 1071, 809 cm^{-1}. Mp 147.0–148.2 °C; elemental analysis calcd (%) for $C_{18}H_{19}NO_3$: C, 72.71; H, 6.44; N, 4.71%. Found: C, 72.63; H, 6.33; N, 4.62%. HPLC Daicel chiralpak AD-H (5% ethanol in hexane; flow = 1.0 mL min^{-1}), 22.7 min (minor), 28.2 min (major); $[\alpha]_D^{25} = -14.3°$ ($c = 0.39$ in $CHCl_3$).

***N*,*N*-Diphenylaminomethyloxirane (3g):** ^{1}H NMR ($CDCl_3$) δ 2.57 (dd, 1H, $J = 2.9$, 4.9 Hz), 2.78 (t, 1H, $J = 4.9$ Hz), 3.21–3.25 (m, 1H), 3.87 (dd, 1H, $J = 4.9$, 15.6 Hz), 3.96 (dd, 1H, $J = 3.4$, 15.6 Hz), 6.95–7.06 (m, 6H), 7.25–7.29 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 46.0, 50.4, 53.9, 120.9, 121.6, 129.3, 147.8; IR (neat) 3003, 1723, 1601, 1452, 1345, 1315, 1273, 1111, 1071, 1025, 908 cm^{-1}. Mp 60.1–60.4 °C; elemental analysis calcd (%) for $C_{15}H_{15}NO$: C, 79.97; H, 6.71; N, 6.22%. Found: C, 79.87; H, 6.66; N, 6.24%. HPLC Daicel chiralpak IB (0.1% 2-propanol in hexane; flow = 1.0 mL min^{-1}), 24.7 min (minor), 26.0 min (major). $[\alpha]_D^{25} = +41.4°$ ($c = 1.06$ in EtOH).

4-(*N*,*N*-Diphenylaminomethyl)-1,3-dioxolan-2-one (3g′): ^{1}H NMR ($CDCl_3$) δ 4.02 (dd, 1H, $J = 6.3$, 15.1 Hz), 4.13 (dd, 1H, $J = 5.9$, 15.1 Hz), 4.19 (dd, 1H, $J = 6.8$, 8.8 Hz), 4.46 (t, 1H, $J = 8.8$ Hz), 4.94–5.00 (m, 1H), 6.97–7.05 (m, 6H), 7.26–7.33 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 54.4, 67.6, 74.4, 121.2, 122.7, 129.7, 147.4, 154.2; IR (KBr) 1789, 1497, 1182, 1078, 754, 697 cm^{-1}. Mp 98.9–99.1 °C; elemental analysis calcd (%) for $C_{16}H_{15}NO_3$: C, 71.36; H, 5.61; N, 5.20%. Found: C, 71.24; H, 5.57; N, 5.15%. HPLC Daicel chiralpak IA (7% ethylacetate in hexane; flow = 1.0 mL min^{-1}), 16.5 min (minor), 18.1 min (major). $[\alpha]_D^{25} = -13.8°$ ($c = 1.18$ in $CHCl_3$).

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