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A convenient ruthenium-catalyzed alkene epoxidation with hydrogen peroxide as oxidant

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Abstract

A general procedure for the epoxidation of various olefins using hydrogen peroxide as the oxidant in the presence of ruthenium trichloride has been developed. Aromatic and aliphatic olefins gave the corresponding epoxides at room temperature in good to excellent yield. For turnover numbers (TON) up to 16,000 the key factor for obtaining high yield and chemoselectivity is the use of pyridine-2,6-dicarboxylic acid (pydic) as ligand.

Keywords: Ruthenium; Epoxidation; Hydrogen peroxide; Oxidation; Homogeneous catalysis

1. Introduction

The development of environmentally benign and clean synthetic methodologies is one of the most important goals of current chemical research (recent examples from our group [1]). In this regard reactions should proceed with high atom-economy [2], thereby minimizing the cost of raw materials and of waste disposal. Although oxidation reactions constitute core technologies for converting bulk chemicals to useful products of a higher oxidation state, they are still among the more problematic processes. Even today most of the known textbook oxidation methods lead to a significant amount of waste and therefore are unacceptable for industrial applications. Hence, there is a significant need for the development of cleaner and safer oxidation procedures. Obviously, molecular oxygen is the ideal oxidant for oxidation reactions [3]. However, the use of O_2 is sometimes difficult to control and in general only one oxygen atom from both oxygen atoms in O_2 is used productively for oxidation (50% atom efficiency) (for recent examples see [4,5]). Thus, oxidation with molecular oxygen often require certain reducing agents to capture the second oxygen atom during the reaction. One of the few examples in which both oxygen atoms are used productively in oxidation reactions is the aerobic dihydroxylation of olefines, which we have developed some time ago [6].

Apart from molecular oxygen, hydrogen peroxide (H_2O_2) is a "green", waste-avoiding oxidant [7]. It can oxidize organic compounds with an atom efficiency of 47% and generates theoretically only water as coproduct. Moreover, it is relatively cheap, less than 0.6$ kg^{-1} (100% H_2O_2) and on million metric ton-scale available [8]. Due to its properties, H_2O_2 is particularly useful for liquid-phase oxidations for the synthesis of fine chemicals, pharmaceuticals or agrochemicals and electronic materials. The discovery of new catalysts for oxidation reactions using H_2O_2 is an important and challenging goal in oxidation chemistry (selected recent examples using H_2O_2 as oxidant [9,10]).

Among the different oxidation methods, the epoxidation of olefins is of major importance for organic synthesis. Nowadays, especially asymmetric epoxidation reactions are in the focus of methodological developments (selected reviews [11]). Nevertheless, the synthesis of racemic epoxides catalyzed by transition metal complexes is still important on laboratory as well as industrial scale [12,13].[1] Based on our recent work on epoxidations using chiral ruthenium–pybox

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[1] Apart from fine chemical applications, there is a trend to use hydrogen peroxide for industrial large scale processes, e.g. propylene oxide production (Dow, BASF, Degussa).

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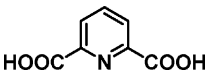
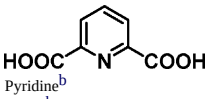
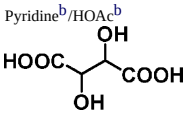
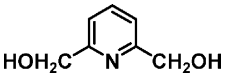
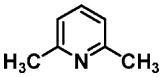
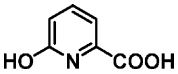
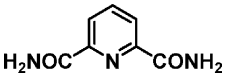
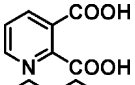
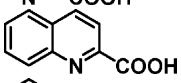
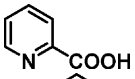
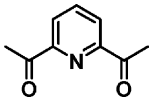
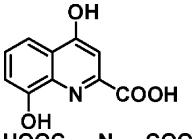
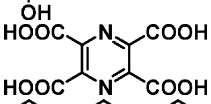
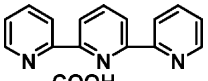
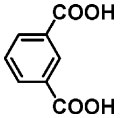
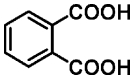
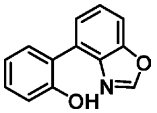
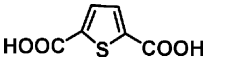
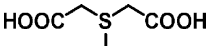
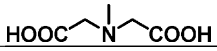
Table 1
Epoxidation of β-methylstyrene with H_2O_2 in the presence of different catalysts[a]

Entry	Catalyst	Ligand	Conversion (%)	Yield (%)	Selectivity (%)
1	–	–	0	0	0
2	$RuCl_3$	–	34		0
3	$RuCl_3$		100	>99	>99
4	–		0	0	0
5	$RuCl_3$	Pyridine[b]	0	0	0
6	$RuCl_3$	HOAc[b]	34	9	26
7	$RuCl_3$	Pyridine[b]/HOAc[b]	0	0	0
8	$RuCl_3$		23	0	0
9	$RuCl_3$		100	96	96
10	$RuCl_3$		20	0	0
11	$RuCl_3$		2	0	0
12	$RuCl_3$		26	10	38
13	$RuCl_3$		30	25	83
14	$RuCl_3$		8	0	0
15	$RuCl_3$		5	0	0
16	$RuCl_3$		26	0	0
17	$RuCl_3$		71	59	83
18	$RuCl_3$		100	81	81
19	$RuCl_3$		3	0	0
20	$RuCl_3$		29	0	0
21	$RuCl_3$		22	0	0
22	$RuCl_3$		22	0	0
23	$RuCl_3$		31	0	0
24	$RuCl_3$		13	0	0
25	$RuCl_3$		56	46	82

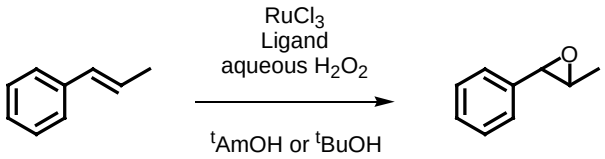
[a] General conditions: 0.5 mmol *trans*-β-methylstyrene, 1 mol% $RuCl_3 \cdot xH_2O$ in 9 mL ^{t}AmOH, 12 h slow addition of 3.0 eq. 30% H_2O_2 in 1 mL ^{t}AmOH, 1000 rpm stirring, room temperature, 10 mol% ligand.
[b] 1 eq. of ligand.

complexes in the presence of different oxidants [14], we became interested in using ruthenium complexes in various oxidation reactions. Here, we report a simple and convenient procedure for epoxidation of olefins using hydrogen peroxide as the final oxidant. While significant work has been done on ruthenium-catalyzed epoxidations using other more complicated oxidants, [12]. Only few examples of such reactions using H_2O_2 have been described so far [15].

2. Results and discussion

During our studies on the Ru(II)(pyridine-2,6-bisoxazoline)(pyridine-2,6-dicarboxylic acid)-catalyzed asymmetric epoxidation of olefines using various oxidants [16], we discovered that slow addition of alkyl peroxides or hydrogen peroxide significantly improved the yield of chiral epoxides [17].[2] Thus, the well-known unproductive decomposition of the oxidant is minimized. Since no epoxidation reaction applying hydrogen peroxide was known with simple ruthenium salts, e.g. $RuCl_3$, we set out to study this effect in more detail. As a model system the epoxidation of *trans*-β-methylstyrene (Scheme 1) was chosen. Initially, we investigated the influence of different catalysts and reaction conditions. The most relevant results are summarized in Tables 1 and 2.

In general, the reactions were run at room temperature in the presence of 1 mol% of $RuCl_3{\cdot}xH_2O$ and 10 mol% of pyridine-type or carboxylate ligands. Due to safety reasons all experiments were performed with a H_2O_2 concentration of 30% or below. As shown in Table 1 (entries 1–2) without catalyst no reaction occurred and $RuCl_3{\cdot}xH_2O$ alone gave only unspecific decomposition of hydrogen peroxide and β-methylstyrene. To our delight under similar conditions in the presence of 10 mol% of 2,6-pyridinedicarboxylic acid (pydic) a remarkable increase in activity and selectivity was observed leading to a nearly quantitative yield (>99%) of the desired epoxide (Table 1, entry 3)! Using pyridine and acetic acid, as mimic of pydic (Table 1, entries 5–7) no epoxide formation is observed. Here, we used the additives in a stoichiometric amount due to the expected decreased binding ability compared to the tridentate ligand pydic. Next, we tested various substituted pyridines, which resemble pydic (Table 1, entries 9–19). Good epoxide yields (81–96%) were obtained in the presence of pyrazinetetracarboxylic acid and 2,6-bis(hydroxymethyl)pyridine, the latter of which is likely to be oxidized to pydic under the reaction conditions. Pyridine-2,6-dicarboxylic acid amide, pyridine-2,3-dicarboxylic acid, a substituted quinolinecarboxylic acid and an aliphatic analog of pydic (Table 1, entries 12, 13, 17, 25) gave low yield of epoxide. All other pyridine-type ligands gave no yield of the desired epoxide. Interestingly, even in the presence of pyridine-2-carboxylic acid no epoxide formation was observed, demonstrating the importance of a tridentate coordination. Also other aromatic and heteroaromatic as well as aliphatic carboxylic acid ligands were not capable to promote the epoxidation of *trans*-β-methylstyrene (Table 1, entries 8, 10, 11, 14–16, 19–24).



Scheme 1. Epoxidation of *trans*-β-methylstyrene.

Interestingly, in case of successful transformations we observed a color change from initially light brown through dark brown upon addition of oxidant to finally nice violet near or after finishing the reaction. As solvents, tertiary alcohols have proven to be the best reaction media (Table 2). Although *tert*-butanol and *tert*-amyl alcohol gave similar results, we generally employed the latter due to its lower melting point. Apart from these solvents, dichloromethane can also be used with some success, however, it required the oxidant to be dissolved in tertiary amyl alcohol during the slow addition process.

As shown in Table 3 under optimized conditions different aliphatic and aromatic olefins can be oxidized in good to very good yield. In most cases the reactions run smoothly and generally with a high selectivity under mild conditions. In case of styrene and substituted styrenes solvolytic opening of the epoxide or rearrangement of the epoxide to phenylacetaldehydes is observed as side-reactions (Table 3, entries 6, 7, 9 and 16). The reaction rate is substrate dependent, e.g. electron-rich alkenes react faster than electron-deficient ones. Thus, 4-vinylcyclohexene is epoxizidized selectively at the internal double bond (Table 3, entry 3). The most active substrates (1-methylcyclohexene, β-methylstyrene and 1-phenylcyclohexene; Table 3, entries 5, 11 and 15) required as little as 0.01 mol% of ruthenium trichloride, thus representing a turnover number (TON) of 10,000. However, at a catalyst concentration of 0.001 mol% of ruthenium the conversion dropped considerably to 16% (yield 16%, substrate 1-phenylcyclohexene), which represents a TON of 16,000.

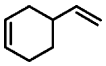
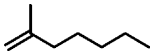
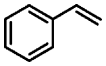
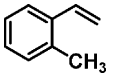
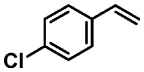
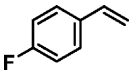
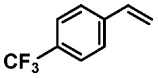
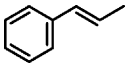
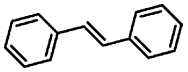
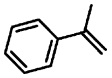
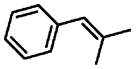
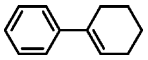
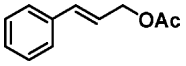
Table 2
Influence of solvent on the epoxidation of *trans*-β-methylstyrene[a]

Entry	Solvent	Conversion (%)	Yield (%)	Selectivity (%)	Remarks
1	^{t}AmOH	100	>99	>99	–
2	^{t}BuOH	100	95	95	–
3	H_2O	47	0	0	Two phases
4	Cyclohexane	11	0	0	Two phases
5	Dichloromethane	53	47	89	
6	CH_3CN	18	14	78	

[a] General conditions: 0.5 mmol *trans*-β-methylstyrene, 1 mol% $RuCl_3{\cdot}xH_2O$ in 9 mL solvent, 12 h slow addition of 3 eq. 30% H_2O_2 in 1 mL ^{t}AmOH,or respective solvent, 1000 rpm stirring, room temperature, 10 mol% pyridine-2,6-dicarboxylic acid.

[2] Recently, we have also achieved the first catalytic asymmetric epoxidations with chiral Ru(pyridine-2,6-bisoxazoline)(pyridine-2,6-dicarboxylic acid) complexes using hydrogen peroxide.

Table 3
Ru-catalyzed epoxidation of different olefins with H_2O_2[a]

Entry	Substrate	$RuCl_3$ (mol%)	Conversion (%)	Yield (%)	Selectivity (%)
1		5	78	74	95
2		1[b]	100	90	90
3		0.1	79	66	83[c]
4		0.1	100	95	95
5		0.01	100	>99	>99
6		1	100	71	71
7		1	100	70	70
8		1[b]	100	>99	>99
9		1	100	76	76
10		1[b]	49	46	93
11		0.01	100	96	96
12		0.1	100	93	93
13		0.1	100	90	90
14		0.1	100	96	96
15		0.01	100	97	97[d]
16		1	100	80	80

[a] General conditions: 0.5 mmol substrate, 10 mol% pyridine-2,6-dicarboxylic acid in 9 mL ^{t}AmOH, 12 h slow addition of 3 eq. 3% H_2O_2 in 1 mL ^{t}AmOH, room temperature.
[b] 20 mol% pyridine-2,6-dicarboxylic acid.
[c] Product: 3-vinyl-7-oxabicyclo[4.1.0]heptane.
[d] Respective values for Ru—concentration of 0.001 mol%: conversion 16%, yield 16%, selectivity >99%.

3. Conclusion

In summary, an easy and general epoxidation procedure of olefins using hydrogen peroxide has been developed. The addition of pyridine-2,6-dicarboxylic acid as ligand to $RuCl_3$ led to a remarkable increase of activity and selectivity. For the first time epoxidations of olefins with hydrogen peroxide in the presence of simple ruthenium salts are possible. Apart from styrenes, disubstituted and trisubstituted aliphatic and aromatic olefins reacted in good to excellent yields (up to >99%) under mild reaction conditions (room temperature). The major advances of this method are simplicity, the cheapness of the ligand and the use of aqueous hydrogen peroxide as the oxidant.

4. Experimental section

4.1. General information

All reactions were carried out without any special precautions under an atmosphere of air. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX 400 spectrometer (^{1}H: 400.1 MHz, ^{13}C 100.6 MHz). Chemical shifts (δ) are given in ppm and refer to the residual solvent as the internal standard. Gas chromatography was performed on a Hewlett-Packard HP 6890 chromatograph with a HP5 column (5% phenyl methyl siloxane, 30 m, 250 and 0.25 μm). Mass spectra were recorded on a AMD 402/3 mass spectrometer. Chemicals and solvents

were purchased from Fluka and Aldrich used as received.

4.1.1. General procedure for epoxidation of olefins

In a 25 ml Schlenk tube, substrate (0.5 mmol), catalyst solution (1 mL, 0.005 mmol, the catalyst solution was prepared by dissolving 10.4 mg, 0.05 mmol $RuCl_3 \cdot xH_2O$ in *tert*-amyl alcohol to 10 mL) and pyridine-2,6-dicarboxylic acid (8.4 mg, 0.05 mmol) were dissolved in *tert*-amyl alcohol (8 mL). Then dodecane (100 μL) was added as an internal GC standard. To this reaction mixture, a solution of hydrogen peroxide (170 μL, 1.67 mmol, 3.3 eq.) in *tert*-amyl alcohol (1 mL) was added over a period of 12 h by a syringe pump. After 2 h of further stirring, aliquots were taken from the reaction mixture and subjected to GC analysis for determination of yield and conversion data. For isolation of the products the reaction mixture was quenched with Na_2SO_3 solution (∼10 mL) and then extracted with dichloromethane (10 mL × 2) and washed with water (∼20 mL). The combined organic layers were dried over $MgSO_4$ and evaporated to give the crude epoxides. The epoxides were purified by silica gel column chromatography (70–230 mesh), saturated with triethylamine (∼3%), and *n*-hexane/ethyl acetate (100:1) as the eluent.

4.1.2. Analytical data

All epoxides are known compounds [18].

4.1.3. 2-Methyl-2-pentyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 2.58 (d, J = 4.9 Hz, 1H), δ = 2.54 (d, J = 4.9 Hz, 1H), 1.2–1.6 (m, 14H), 1.28 (s, 3H), 0.86 t, (J = 6.7 Hz, 3H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 57.1, 53.9, 36.7, 31.8, 24.9, 22.6, 20.9, 14. EIMS (70 eV): m/z = 128 (M^+, 1), 99 (8), 85 (100), 72 (38), 55 (37), 41 (32)

4.1.4. trans-Stilbene oxide

Colorless solid, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.24–7.31 (m, 10H), 3.87 (s, 2H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 137.1, 128.6, 128.6, 125.5, 62.8. EIMS (70 eV): m/z = EIMS (70 eV): m/z = 197 ($M^+ + 1$, 18), 196 (M^+, 100), 195 (72), 178 (28), 167 (85), 90 (66), 89 (65).

4.1.5. 2,2-Dimethyl-3-phenyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$, ppm): δ = 7.37–7.27 (m, 5H), 3.88 (s, 1H), 1.09 (s, 3H), 1.49 (s, 3H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$, ppm): δ = 137.0, 128.4, 127.8, 126.8, 61.6, 25.2, 18.4. EIMS (70 eV): m/z = MS (i.e. 70 eV): m/z = 148 ($[M]^+$, 48), 147 (27), 133 (16), 119 (15), 107 (13), 105 (47), 91 (55), 90 (100), 89 (51), 77 (41), 39 (37).

4.1.6. (4-Chloro)phenyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.12–7.26 (m, 4H), 3.76 (dd, J = 4.0, 2.6 Hz, 1H), 3.07 (dd, J = 5.6, 4.0 Hz, 1H), 2.68 (dd, J = 5.6, 2.6 Hz, 1H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 136.3, 134.1, 128.8, 127, 51.9, 51.4. EIMS (70 eV): m/z = 156 ($M + 2^+$, 9), 155 ($M + 1^+$, 10), 154 (M^+, 28), 153 ($M - 1^+$, 23), 125 (53), 119 (74), 89 (106).

4.1.7. 1,2-Epoxy-1-methylcyclohexane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 2.87 (s, 1H), 1.82–1.78 (m, 2H), 1.59 (m, 2H), 1.36−1.31 (m, 2H), 1.22 (m, 5H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$, ppm): δ = 59.6, 57.8, 29.9, 25.0, 22.7, 20.1, 19.7. EIMS (70 eV): m/z = 112 (M^+), 111, 97 (100), 55, 43.

4.1.8. 3-Phenyloxiranylmethyl acetate

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.17–7.32 (m, 5H), 4.41 (dd, J = 12.28, 3.37 Hz, 1H), 4.02 (dd, J = 2.28, 5.95 Hz, 1H), 3.73 (d, 1H, J = 1.98 Hz), 3.18–3.20 (m, 1H), 2.04 (s, 3H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 170.7, 136.1, 128.5, 128.4, 125.6, 64.2, 59.2, 56.4, 20.7. EIMS (70 eV): m/z = 192 (M^+, 2), 150 (10), 149 (79), 133 (26), 107 (95), 105 (67), 91 (54), 90 (45), 89 (42), 79 (31), 77 (31), 43 (100).

4.1.9. Phenyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.16–7.29 (m, 5H), 3.78 (dd, J = 4.16, 2.57 Hz, 1H), 3.06 (dd, J = 5.55, 4.16 Hz, 1H), 2.72 (dd, J = 5.55, 2.57 Hz, 1H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 137.7, 128.6, 128.3, 125.6, 52.5, 51.3. EIMS (70 eV): m/z = 120 (M^+, 41), 119 (65), 92 (37), 91 (100), 90 (64), 89 (79).

4.1.10. 3-Oxatricyclo[3.2.1.0^{2,4}]octane (norbornene epoxide)

White crystals, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 3.04 (s, 2H), 2.42 (s, 2H), 1.42–1.49 (m, 2H), 1.26–1.31 (m, 1H), 1.15–1.21 (m, 2H), 0.65–0.69 (m, 1H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 51.4, 36.6, 26.2, 25.1. EIMS (70 eV): m/z = 110 (M^+, 3), 109 (5), 95 (19), 92 (16), 91 (15), 82 (31), 81 (100), 79 (55), 55 (40), 54 (32), 41 (39), 39 (62), 27 (45).

4.1.11. trans-2-Methyl-3-phenyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.23–7.4 (m, 5H), 3.57 (d, J = 1.97 Hz, 1H), 3.03 (dq, J = 5.17, 1.97 Hz, 1H), 1.44 (d, J = 5.17 Hz, 3H). ^{13}C NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 137.9, 128.5, 128.1, 125.7, 59.6, 59.2, 18. EIMS (70 eV): m/z = 134 (M^+, 52), 133 (65), 105 (51), 91 (42), 90 (100), 89 (77), 77 (23).

4.1.12. trans-2,3-Dibutyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 2.65 (m, 2H), 1.25–1.6 (m, 14H), 0.91 (t, J = 7.14 Hz, 6H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 59, 32, 28.3, 22.7, 14.1. EIMS (70 eV): m/z = 127 (13), 113 (13), 99 (71), 69 (100), 57 (78), 55 (37), 41 (43).

4.1.13. 3-Vinyl-7-oxabicyclo[4.1.0]heptane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 5.6–5.74 (m, 1H), 4.85–4.99 (m, 2H), 3.08–3.19 (m, 2H), 0.98–2.22 (m, 8H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 142.9, 112.8, 52.3, 51.3, 33.4, 29.9, 25, 23.2. EIMS (70 eV): m/z = 124 (M^+, 5), 123 (15), 110 (10), 109 (11), 105 (20), 95 (52), 81 (41), 79 (49), 77 (30), 67 (53), 55 (100).

4.1.14. 4-Flurophenyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.12–7.17 (m, 2H), 6.91–6.96 (m, 2H), 3.75 (dd, J = 3.96, 2.58 Hz, 1H), 3.04 (dd, J = 5.55, 3.96 Hz, 1H) 2.67 (dd, J = 5.55, 2.58 Hz, 1H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 163.1 (d, J = 24), 133.7 (d, J = 2), 127.6 (d, J = 7), 115.9 (d, J = 20), 52.2, 51.6. EIMS (70 eV): m/z = 138 (M^+), 137 ($M-1^+$), 122 (86), 109 (100), 96.

4.1.15. 4-Trifluoromethylphenyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, $CDCl_3$): δ = 7.6 (d, J = 8.12 Hz, 2H), 7.4 (d, J = 8.12 Hz, 2H), 3.92 (dd, J = 3.97, 2.58 Hz, 1H), 3.19 (dd, J = 5.55, 3.97 Hz, 1H), 2.77 (dd, J = 5.55, 2.58 Hz, 1H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 141.9, 125.9, 125.4 (q, J = 3.82 Hz), 51.6, 51.4. EIMS (70 eV): m/z = 188 (M^+, 14), 187 (20), 159 (49), 158 (48), 119 (100), 91 (37).

4.1.16. 2-Tolyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, CD_2Cl_2): δ = 7.14–7.22 (m, 4H), 3.98 (dd, J = 3.97, 2.58 Hz, 1H), 3.13 (dd, J = 5.75, 3.97 Hz, 1H), 2.65 (dd, J = 5.75, 2.58 Hz, 1H), 2.42 (s, 3H). ^{13}C NMR (100.6 MHz, 25 °C, CD_2Cl_2): δ = 136.4, 136.2, 129.8, 127.6, 126, 124, 50.3, 50.1. EIMS (70 eV): m/z = 134 (M^+, 53), 119 (44), 118 (42), 117 (64), 105 (100), 103 (48), 91 (52), 78 (33), 77 (35).

4.1.17. 4-Tolyloxirane

Colorless oil, ^{1}H NMR (400.1 MHz, 25 °C, CD_2Cl_2): δ = 7.05–7.25 (m, 4H, arom.), 3.79 (dd, J = 3.96, 2.6 Hz, 1H), 3.09 (dd, J = 5.56, 3.96 Hz, 1H), 2.77 (dd, J = 5.56, 2.6 Hz, 1H), 2.33 (s, 3H). ^{13}C NMR (100.6 MHz, 25 °C, $CDCl_3$): δ = 138.8, 135.5, 129.9, 126.2, 52.8, 51.6, 21.6. EIMS (70 eV): m/z = 134 (M^+, 37), 119 (17), 118 (48), 117 (52), 115 (22), 106 (24), 105 (100), 103 (34), 91 (43).

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