

Supporting Information

A new halide-free efficient reaction-controlled phase-transfer catalyst based on silicotungstate of $[(C_{18}H_{37})_2(CH_3)_2N]_3[SiO_4H(WO_5)_3]$ for olefin epoxidation, oxidation of sulfides and alcohols with hydrogen peroxide

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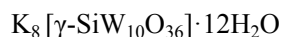
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Preparation of catalysts



Sodium metasilicate (2.2 g, 10 mmol) was dissolved in 20 mL of water (Solution A). Sodium tungstate (36.4 g, 0.11 mol) was dissolved in 60 mL of water in a separate 250 ml beaker containing a magnetic stirring bar. To this solution, 33 mL of 4 M HCl was added in 1mL portions over 10 min, with vigorous stirring (there was local formation of hydrated tungstic acid that slowly disappears). Then, solution A was poured into the tungstate solution, and the pH was adjusted to 5.5 by addition of the 4 M HCl solution (~ 8 mL). This pH was maintained by addition of small amounts of 4 M HCl for 100 min. Solid potassium chloride (18 g) was then added to the solution with gentle stirring. After 15 min, the precipitate was collected by filtering through a sintered glass filter. Purification was achieved by dissolving the product in 170 mL of water. The insoluble material was rapidly removed by filtration on a funnel, and the salt was precipitated again by addition of solid KCl (16 g). The precipitate was separated by filtration, washed with 2M potassium chloride solution (2 portions of 10mL), and air dried. Yield: 12.9 g (40%). IR spectrum (KBr, cm^{-1}): 991, 950, 879, 863, 803, 728, 610, 532, 513, 397, 360, 322, 270.



The potassium salt of the β_2 isomer of undecatungstosilicate (5 g, 1.67 mmol) was dissolved in 50 mL of water maintained at 298 K. Impurities in the $\text{K}_8[[\beta_2\text{-SiW}_{11}\text{O}_{39}]$ salt gave insoluble materials, which have to be removed rapidly by filtration on a funnel. The pH of the solution was quickly adjusted to 9.1 by addition of a 2 M aqueous solution of K_2CO_3 . The pH of the solution was kept at this value by addition of the K_2CO_3 solution for exactly 16 min. The potassium salt of

the γ -decatungstosilicate was then precipitated by addition of solid potassium chloride (13.3 g). During the precipitation (10 min), the pH must be maintained at 9.1 by addition of small amounts of the K_2CO_3 solution. The solid was removed by filtering, washed with 1 M KCl solution, and air dried. Yield: 3.2 g (64%). IR spectrum (KBr, cm^{-1}): 990, 946, 907, 865, 817, 742, 654, 554, 525, 479, 393, 361, 323, 279, 250. ^{29}Si MAS NMR (79.5 MHz): -85.0 ppm.

$[(C_{18}H_{37})_2(CH_3)_2N]_2[W_3O_{18}]$:

A suspension of H_2WO_4 (2.0 g, 8.0 mmol) in 30% aqueous H_2O_2 (6.7 ml, 67 mmol) was stirred at 323 K for 60 min until a pale yellow solution was obtained. The solution was cooled to ambient temperature and filtered to remove insoluble materials. To this solution 1.0 g (1.7 mmol) of dioctadecyl dimethyl ammonium chloride (DDAC) dissolved in 20 ml of tert-butanol was added. The mixture was stirred vigorously for 4 h at 318 K. A white floccule was filtered off and then washed with warm water (~ 318 K, about 60 ml) and diethyl ether (25 ml). After dried in air, a white powder was obtained. Anal. calcd for $[DDA]_2[W_3O_{18}]$: C, 47.14; H, 8.27; N, 1.45; W, 28.51; Found: C, 46.87; H, 7.95; N, 1.31; W, 26.82. Yield: 1.8 g. IR spectrum (KBr, cm^{-1}): 2920, 2851, 2359, 1718, 1643, 1466, 1374, 1079, 977, 880, 816, 719, 681, 627, 558, 446.

$[(C_{18}H_{37})_2(CH_3)_2N]_8[\beta_2-SiW_{11}O_{39}]$:

$K_8[\beta_2-SiW_{11}O_{39}] \cdot 12H_2O$ was prepared according to ref. [1]. A solution of $K_8[\beta_2-SiW_{11}O_{39}] \cdot 12H_2O$ (0.65 g, 0.2 mmol) in 20 ml water was stirred vigorously. And to this solution 0.94 g (1.6 mmol) of dioctadecyl dimethyl ammonium chloride dissolved in 18 ml tert-butanol was added. The mixture was stirred for 2 h. The resulting white precipitate of $[DDA]_8[\beta_2-SiW_{11}O_{39}]$ was collected by the filtration and washed with an excess amount of H_2O and a small quantity of diethyl ether, then dried in air. Yield: 0.9 g. IR spectrum (KBr, cm^{-1}): 2920, 2850,

2361, 1644, 14686, 1374, 988, 942, 874, 793, 744, 553.

[(C₁₈H₃₇)₂(CH₃)₂N]₈[γ-SiW₁₀O₃₆]:

K₈[γ-SiW₁₀O₃₆]·12H₂O (0.74 g, 0.25 mmol) was dissolved in 12 ml H₂O. The solution was stirred vigorously. Dioctadecyl dimethyl ammonium chloride (1.2 g, 2 mmol) dissolved in 10 ml tert-butanol was added to this solution. The mixture was stirred for 2 h. A white precipitate was collected by the filtration and washed with an excess amount of H₂O and a small quantity of diethyl ether, then dried in air. Yield: 1.4 g. IR spectrum (KBr, cm⁻¹): 2920, 2850, 2361, 1643, 1468, 1368, 988, 941, 905, 969, 832, 741, 672, 557.

[(C₁₈H₃₇)₂(CH₃)₂N]₄[SiW₁₂O₄₀]:

A solution of H₄SiW₁₂O₄₀·XH₂O (0.72 g, 0.25 mmol) in 25ml water was stirred vigorously at 318 K. And to this solution 0.59 g (1.0 mmol) of dioctadecyl dimethyl ammonium chloride dissolved in 15 ml tert-butanol was added. The mixture was stirred for 2 h at 318 K. A white precipitate of was collected by the filtration and washed with an excess amount of H₂O and a small quantity of diethyl ether, and dried in vacuo. Yield: 0.80 g. IR spectrum (KBr, cm⁻¹): 2922, 2851, 1615, 1465, 1373, 1014, 972, 920, 883, 791, 532, 484.

[(C₁₈H₃₇)₂(CH₃)₂N]₃[PW₁₂O₄₀]:

A solution of H₃PW₁₂O₄₀·XH₂O (0.73 g, 0.25 mmol) in 25 ml water was stirred vigorously at 318 K. And to this solution 0.59 g (1.0 mmol) of dioctadecyl dimethyl ammonium chloride dissolved in 15 ml tert-butanol was added. The mixture was stirred for 2 h at 318 K. A white precipitate of was collected by the filtration and washed with an excess amount of H₂O and a small quantity of diethyl ether, and dried in vacuo. Yield: 0.85 g. IR spectrum (KBr, cm⁻¹): 2920, 2851, 1466, 1368, 1080, 979, 897, 807, 723, 596, 518. ³¹P MAS NMR: -15.5 ppm.

Reference

[1] A Te'ze', G. Herve', Inorg Synth. 27 (1990) 85.

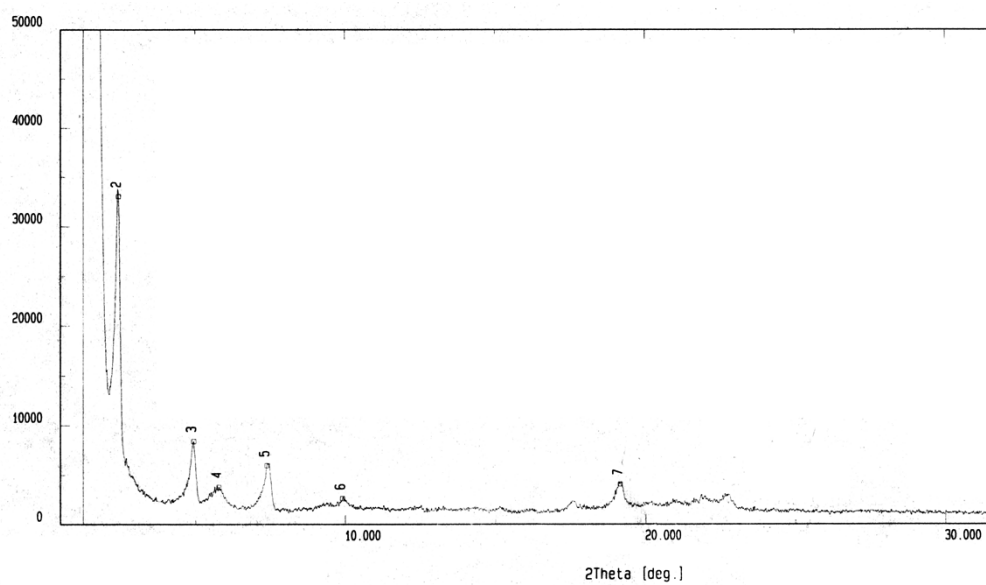


Fig S1 XRD pattern of catalyst I.

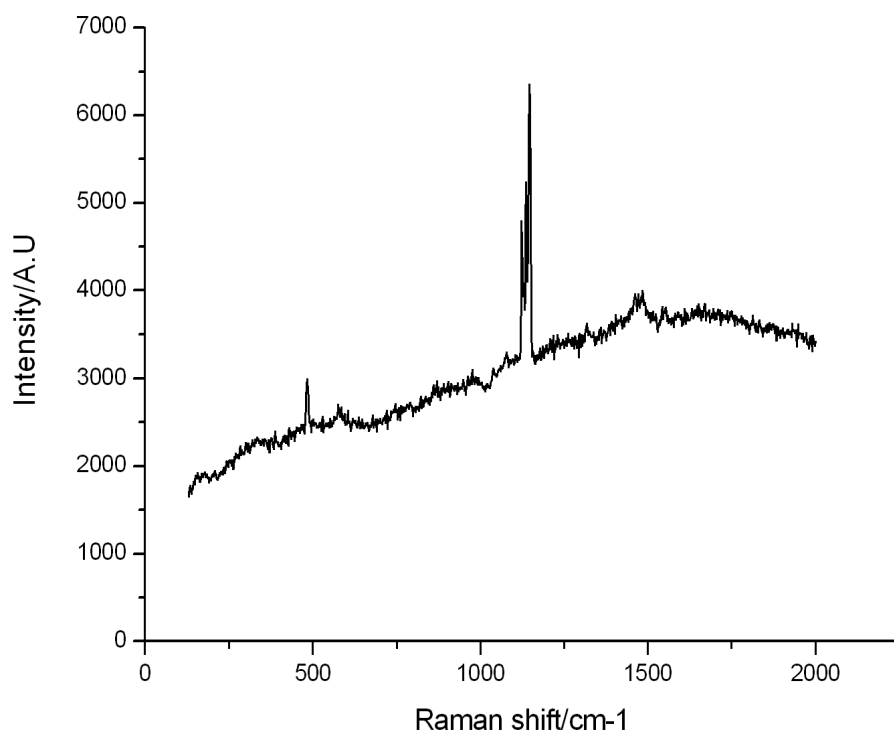


Fig. S2 Raman spectrum of catalyst I

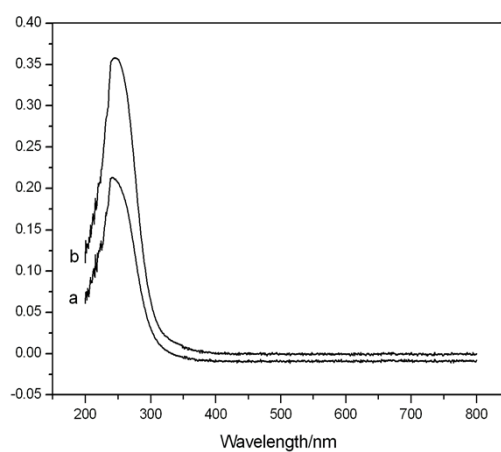


Fig.S3 UV-vis spectra of a) fresh catalyst I; b) catalyst I treated with H₂O₂

Table S1 Epoxidation of 1-octene with H₂O₂ catalyzed by I ^a

Cycle times	Reaction time (h)	Conversion (mol%)	Selectivity (mol%)	Yield (mol%)
1	3	98	>99	97
2	3	92	>99	91
3	3	86	>99	85
4	3	88	>99	87
5	3	81	>99	80
6	4	91	>99	90
7	4	81	>99	80
8	4	84	>99	83
9	4	84	>99	83
10	4	82	>99	81
11	4	62	>99	61
12	5	80	>99	79
13	5	84	>99	83
14	5	85	>99	84
15	5	62	>99	61
16	6	80	>99	79
17	6	74	>99	73
18	7	90	>99	89
19	7	84	>99	83
20	7	82	>99	81

^a Reaction conditions: 2.5 mmol 1-octene; 0.5mmol H₂O₂; 20 μ mol catalyst of I; 2 ml ethyl acetate; reaction temperature: 60 °C, Conversion (%) =consumed 1-octene (mol)/H₂O₂ used (mol) \times 100. Yield (%) =1-octene epoxide (mol)/H₂O₂ used (mol) \times 100. Selectivity of epoxide was more than 99% for all cycles.

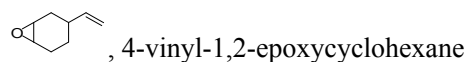
Table S2 Oxidation of thioanisole with hydrogen peroxide catalyzed by I for different cycles ^a

Cycle times	Reaction time (h)	Conversion (mol%)	Selectivity (mol%)	Yield (mol%)
1	2	100	>99	>99
2	2	100	>99	>99
3	2	100	>99	>99
4	2	100	>99	>99
5	2	100	>99	>99


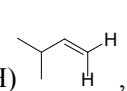
^a Reaction conditions: time 2 h; 2mL solvent ethyl acetate; 10 μ mol (25 mg) cat I; 1 mmol substrate; 2 mmol H₂O₂; Reaction temperature: 333 K; Yield (%) = products (mol)/ substrate used (mol) \times 100. Conversions and selectivity were determined by gas chromatography using an internal standard technique were based on the substrate.

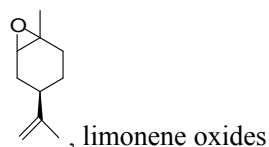
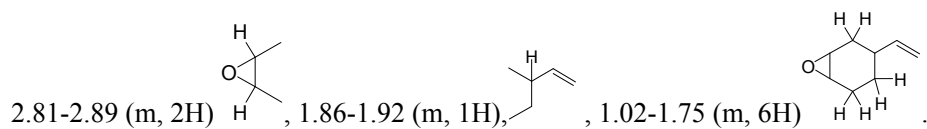
Characterization of oxidation products:

The data (GC retention time, mass, and NMR) of epoxides were listed below:

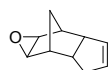


GC (SE-54 capillary column, 30 m \times 0.32 mm \times 0.33 μ m, GC-9AM, Shimadzu Corporation) carrier gas (N₂, 1.2 kg /cm²), column temperature (130 $^{\circ}$ C), injection temperature (220 $^{\circ}$ C), detection temperature (220 $^{\circ}$ C), retention time (2.3 min). MS (70 eV, EI): m/z (%): 124 (4) [M⁺], 123(6), 109(8), 107(14), 95 (20), 79 (64), 55 (89), 41(100). Colorless liquid,

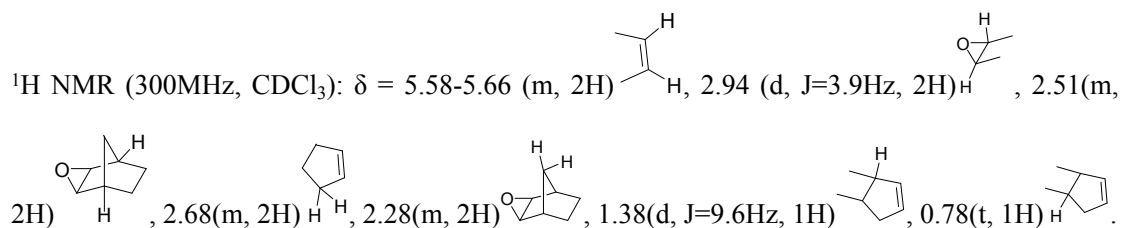
¹H NMR (300MHz, CDCl₃): δ = 5.34-5.51 (m, 1H)  , 4.61-4.71 (tt, J=9.3Hz, 2H)  ,



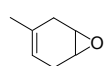
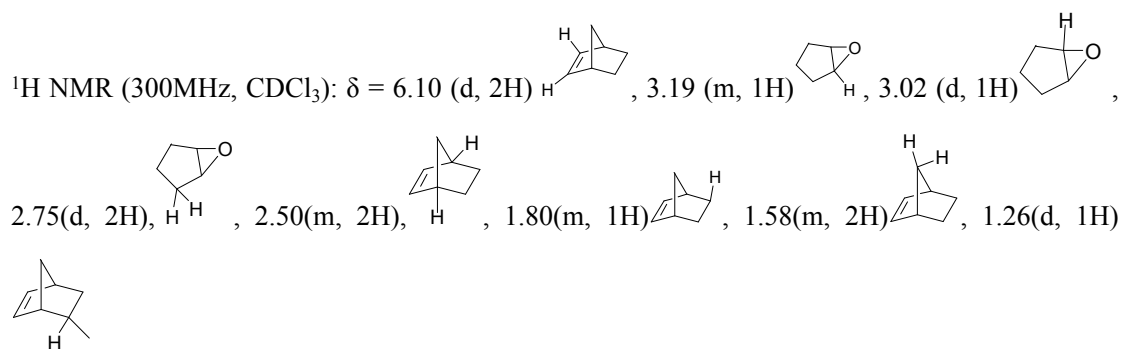
GC (SE-54 capillary column, 30 m×0.32 mm×0.33 μm, GC-9AM, Shimadzu Corporation) carrier gas (N₂, 1.2 kg /cm²), initial column temperature (130 °C), final column temperature (180 °C), progress rate (20 °C/min), injection temperature (220 °C), detection temperature (220 °C), retention time (2.8 min). MS (70 eV, EI): m/z (%):152 (2) [M⁺], 108(21), 94(40), 93(25), 81 (17), 67 (40), 55(21), 43(100), 41(41).



GC (SE-54 capillary column, 30 m×0.32 mm×0.33 μm, GC-9AM, Shimadzu Corporation) carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.2 min).MS (70 eV, EI): m/z (%):148 (5) [M⁺], 120(13), 92 (13), 91(26), 82 (79), 81 (100), 79(23), 66(43), 39(27).

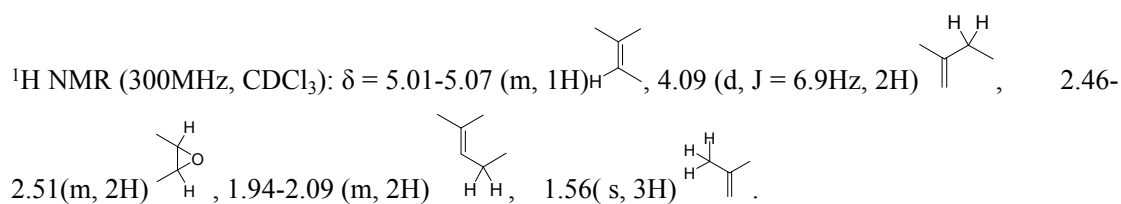


GC (SE-54 capillary column, 30m×0.32mm×0.33μm, GC-9AM, Shimadzu Corporation) carrier gas (N₂, 1.2kg /cm²), column temperature (130 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (3.5 min).MS (70 eV, EI): m/z (%):148 (7) [M⁺], 91(10), 83(10), 82(10), 81 (15), 77 (7), 66(100), 39(17), 27(6).



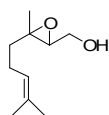
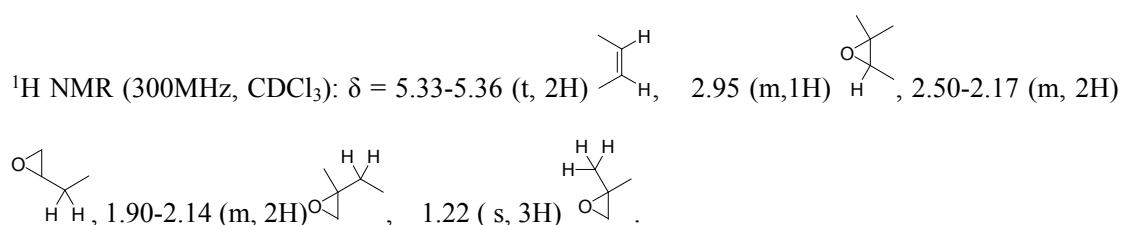
1-Methyl-4,5-epoxy-1-cyclohexene

GC (SE-54 capillary column, 30 m×0.32 mm×0.33 μm, GC-9AM, Shimadzu Corporation)
 carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),
 detection temperature (220 °C), retention time (1.8 min). MS (70 eV, EI): m/z (%): 110
 (100) [M⁺], 95 (86), 91 (25), 82 (19), 81 (98), 80 (21), 79 (91), 77 (38).



1-Methyl-1,2-epoxy-4-cyclohexene











GC (SE-54 capillary column, 30 m×0.32 mm×0.33 μm, GC-9AM, Shimadzu Corporation)
 carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),
 detection temperature (220 °C), retention time (1.5 min). MS (70 eV, EI): m/z (%): 110
 [M⁺] (4), 95 (8), 91 (10), 81(42), 67 (28), 50 (17), 43 (100).

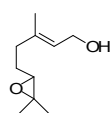


2,3-Epoxy-3,7-dimethyloct-6-en-1-ol

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








carrier gas (N₂, 1.0 kg /cm²), initial column temperature (110 °C), final column temperature (200 °C), progress rate (20 °C/min), injection temperature (220 °C), detection temperature (220 °C), retention time (3.6 min). MS (70 eV, EI): m/z (%): 170 (2) [M⁺], 111(21), 94(40), 93(25), 81 (15), 68 (40), 59(100), 55(48), 43(60), 41(31). ¹³C NMR (100 MHz, CDCl₃): 132.04, 123.29, 63.07, 61.32, 61.14, 38.43, 25.56, 23.60, 17.55, 16.66.

¹H NMR (400 MHz, CDCl₃): 5.08 (t, *J* = 1.2 Hz, 1H) , 3.80-3.83 (m, 1H) , 3.64-3.69 (m, 1H) , 2.97-2.99 (m, 1H) , 2.59(s, br, 1H) , 2.05-2.11 (m, 2H) , 1.64-1.70 (m, 4H) , 1.61(s, 3H) , 1.43-1.51 (m, 1H) , 1.30 (s, 3H) .



6,7-Epoxy-3,7-dimethyloct-2-en-1-ol

GC (SE-54 capillary column, 30 m×0.32 mm×0.33 μm, GC-9AM, Shimadzu Corporation) carrier gas (N₂, 1.0 kg /cm²), initial column temperature (110 °C), final column temperature (200 °C), progress rate (20 °C/min), injection temperature (220 °C), detection temperature (220 °C), retention time (3.8 min). ¹³C NMR (100 MHz, CDCl₃): 138.28, 124.04, 63.99, 59.09, 58.36, 36.16, 27.04, 24.75, 18.65, 16.16.

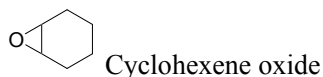
¹H NMR (400 MHz, CDCl₃): 5.45 (t, *J* = 8.8 Hz, 1H) , 4.15 (d, *J* = 9.6 Hz, 2H) , 2.72 (t, *J* = 8.4 Hz, 1H) , 2.09-2.24 (m, 2H) , 1.86 (s, br, 1H) , 1.70 (s, 3H) , 1.63-1.67(m, 2H) , 1.31 (s, 3H) , 1.27 (s, 3H) .



cyclopentene oxide

GC (SE-54 capillary column, 30 m×0.32 mm×0.33 μm, GC-9AM, Shimadzu Corporation) carrier gas (N₂, 1.2 kg /cm²), column temperature (100 °C), injection temperature (220 °C), detection temperature (220 °C), retention time (1.3 min). MS (70 eV, EI): m/z (%): 84 (10) [M⁺],

83 (38) [M⁺], 69 (13), 56 (42), 55 (100), 41(54), 39 (30), 27(22)



GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)

carrier gas (N₂, 1.2 kg /cm²), column temperature (110 °C), injection temperature (220 °C),

detection temperature (220 °C), retention time (1.8 min).MS (70 eV, EI): m/z (%): 98 (18) [M⁺],

83 (100), 70 (28), 69 (35), 57 (45), 54(58), 42 (60), 39(43).

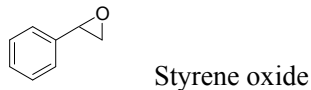


GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)

carrier gas (N₂, 1.2kg /cm²), column temperature (110 °C), injection temperature (220 °C),

detection temperature (220 °C), retention time (3.5 min).MS (70 eV, EI): m/z (%): 126 (4) [M⁺],

97 (22), 83 (28), 67 (60), 57 (53), 55(100), 54(41), 41(75).



GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)

carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),

detection temperature (220 °C), retention time (2.0 min).MS (70 eV, EI): m/z (%): 120 (44) [M⁺],

119 (22), 92 (31), 91 (100), 90 (29), 89(28), 65(17), 63(10).

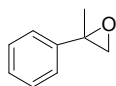


GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)

carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),

detection temperature (220 °C), retention time (1.9 min).MS (70 eV, EI): m/z (%): 110 (10) [M⁺],

109 (7), 95 (19), 92 (15), 82 (29), 81(100), 79(65), 67(40), 55(43), 54(31), 39(25).



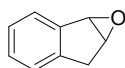
α -Methylstyrene oxide

GC (SE-54 capillary column, 30 m \times 0.32 mm \times 0.33 μ m, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (2.8 min).MS (70 eV, EI): m/z (%): 134 (37) [M⁺],
133(65), 105 (100), 103(40), 91 (15), 77 (29), 51(14).



1-Methylcyclohexene oxide

GC (SE-54 capillary column, 30 m \times 0.32 mm \times 0.33 μ m, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2kg /cm²), column temperature (130 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.4 min).MS (70 eV, EI): m/z (%): 112 (18) [M⁺],
97(82), 83 (17), 69(25), 55(48), 43 (100), 41(50).



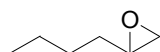
Indene oxide

GC (SE-54 capillary column, 30 m \times 0.32 mm \times 0.33 μ m, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (180 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (4.2 min).MS (70 eV, EI): m/z (%): 132 (30) [M⁺],
104(100), 103 (27), 78(27), 77(17), 63 (13), 52 (12), 51(29).



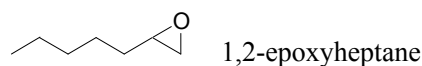
Propylene oxide

GC (SE-54 capillary column, 30 m \times 0.32 mm \times 0.33 μ m, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (100 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.8 min).

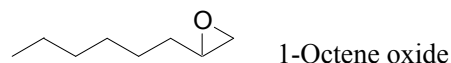


1-Hexene oxide

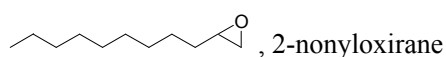
GC (SE-54 capillary column, 30m×0.32mm×0.33um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2kg /cm²), column temperature (130 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.3min).MS (70 eV, EI): m/z (%): 100 (3) [M⁺],
85(2), 71 (100), 58(32), 55(41), 42(65), 41 (71), 39(33).



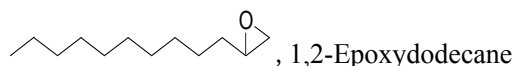
GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.3 min).MS (70 eV, EI): m/z (%): 114 (7) [M⁺],
85(10), 71 (100), 58(40), 56(50), 55(41), 43(34), 41 (50).



GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.7 min).MS (70 eV, EI): m/z (%): 128 (4) [M⁺],
85 (19), 81 (30), 71(100), 69(29), 58(41), 55(65), 41 (70).

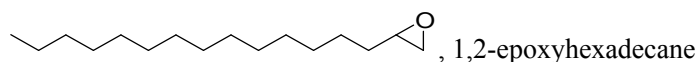


GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (180 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (3.5 min).MS (70 eV, EI): m/z (%): 170 (5) [M⁺],
126(11), 110 (15), 96(25), 82(50), 71(100), 55(75), 43 (90), 41(82), 29(50).

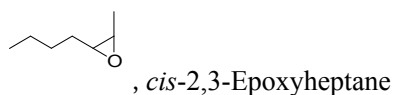


GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (180 °C), injection temperature (220 °C),

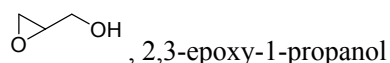
detection temperature (220 °C), retention time (3.8 min). MS (70 eV, EI): m/z (%): 184 (2) [M⁺], 95(21), 82(35), 71(82), 69 (46), 55(78), 43(75), 41 (100), 29(30).



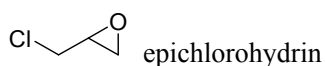
GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (180 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (6.9 min). MS (70 eV, EI): m/z (%): 240 (2) [M⁺],
180(4), 109(23), 96(60), 82 (90), 68(55), 57(46), 55 (85), 41(100), 29 (51).



GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (130 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.8 min). MS (70 eV, EI): m/z (%):114 (9) [M⁺],
85(87), 71 (54), 57(72), 55 (86), 45 (100), 42 (96), 41 (80), 29(60).



GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg /cm²), column temperature (60 °C), injection temperature (220 °C),
detection temperature (220 °C), retention time (1.3 min). MS (70 eV, EI): m/z (%): 74 (4) [M⁺],
45(85), 44 (100), 42(72), 31 (53), 29 (41), 26 (78), 15 (10).

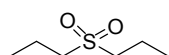
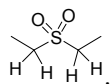


GC (SE-54 capillary column, 30 m×0.32 mm×0.33 um, GC-9AM, Shimadzu Corporation)
carrier gas (N₂, 1.2 kg/cm²), column temperature (50 °C), injection temperature (220 °C),

detection temperature (220 °C), retention time (1.6 min). MS (70 eV, EI): m/z (%): 92 (2) [M⁺], 64 (6), 57 (100), 49 (25), 42 (11), 31 (30), 29 (22), 27 (42).

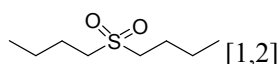


¹H NMR (CDCl₃, 400 MHz) δ 1.31-1.34 (t, J=15.2 Hz, 6H), 2.91-2.96 (m, 4H)



¹H NMR (CDCl₃, 400 MHz) δ 1.04-1.08 (m, 6H), 1.80-1.90 (m, 4H)

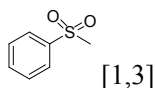
2.89-2.93 (m, 4H)



¹H NMR (CDCl₃, 400 MHz) δ 0.79-0.83 (t, J= 14.4Hz, 6H), 1.30-1.36 (m,

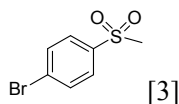
4H), 1.63-1.67 (t, J= 14.4Hz, 4H), 2.81-2.85 (t, J= 15.6 Hz,

4H)

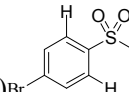


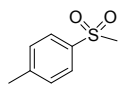
¹H NMR (CDCl₃, 400 MHz) δ 3.07 (s, 3H), 7.57-7.61 (t, J= 15.2 Hz, 2H),

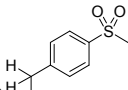
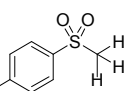
7.65-7.69 (t, J= 14.8Hz, 1H), 7.95-7.97 (t, J= 8.8Hz, 2H)

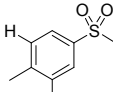
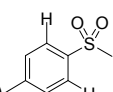


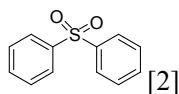
¹H NMR (CDCl₃, 400 MHz) δ 3.04 (d, J= 2.4 Hz, 3H), 7.68-7.71 (m, 2H)

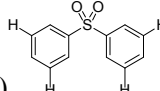
7.78-7.81 (m, 2H)  .

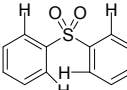


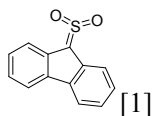
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 2.39 (s, 3H)  , 2.98 (d, $J=1.2$ Hz, 3H)  , 7.30-

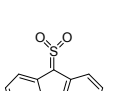
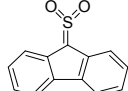
7.32 (t, $J=8$ Hz, 2H)  , 7.75-7.77 (t, $J=8$ Hz, 2H)  .

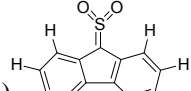


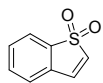
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.47-7.51 (t, $J=15.2$ Hz, 4H)  , 7.53-7.57 (m, 2H)


7.93-7.96 (t, $J=9.6$ Hz, 4H)  .

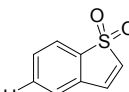
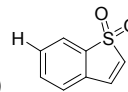


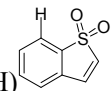
$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 7.52-7.56 (m, 2H)  , 7.63-7.67 (m, 2H)  , 7.80-

7.85 (m, 4H)  .



$^1\text{H NMR}$ (CDCl_3 , 400 MHz) δ 6.71-6.72 (d, $J=6.8$ Hz, 1H)  , 7.22-7.23 (t, $J=7.6$ Hz, 1H)

7.35-7.37 (t, $J=7.6$ Hz, 1H)  , 7.50-7.58 (m, 2H)  , 7.69-7.71(d,

$J=7.2$ Hz, 1H)  .

References

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- [3] K. Kamata, M. Kotani, K. Yamaguchi, S. Hikichi, N. Mizuno. *Chem. Eur. J.* 13 (2007) 639-648