Visible Light-Promoted Dihydroxylation of Styrenes with Water and Dioxygen

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I. General Information

THF was distilled from sodium benzophenonketyl prior to use. DCM, NEt₃ and iPr₂NEt were distilled from calcium hydride. Alcohols and MeCN was used directly. The Acr⁺MesClO₄⁻ was prepared according to the literature.¹ Unless otherwise noted, all the corresponding ketones from suppliers were used directly without further purification. NMR spectra were recorded on a Bruker-400 instrument.¹H NMR chemical shifts were referenced to the tetramethylsilane (0 ppm),¹³C NMR chemical shifts were referenced to the solvent resonance (77.00 ppm, CDCl₃). The following abbreviations (or combinations thereof) were used to explain multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad, q = quadruplet. IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR spectrometer with diamond ATR accessory. High-resolution
mass spectra (HRMS) were recorded on EI-TOF or ESI-TOF (electrospray ionization-time of flight). Unless noted, all the alkenes were prepared according to the general procedures using the corresponding ketones through Wittig reaction.

II. Procedures for Synthesis of Alkenes

A general procedure to synthesis of alkenes.

To a solution of PPh₃MeBr (36 mmol) in THF (70 mL) was added NaH (60%, 1.1 equiv.), the reaction mixture was refluxed for 1 h. Then the corresponding ketones (30 mmol) in THF (20 mL) were added dropwise at 0 °C. The mixture was refluxed overnight. When the starting material was consumed (monitored by TLC), the reaction mixture was diluted by petroleum ether and filtered through a pad of silica gel. The filtrate was concentrated to give a crude product which was distilled or purified through flash column chromatography to obtain the desired product. The known products were identical to the literature.

(1-cyclohexylvinyl)benzene (1p). To a 100 mL overdried flask, benzaldehyde (5.1 mL, 50 mmol) and THF (50 mL) were added.

Cyclohexylmagnesium chloride (1.3 M in THF) (42 mL, 60 mmol) were added dropwise. Then the reaction mixture was stirred at rt overnight. The mixture was quenched by saturated NH₄Cl solution, diluted by Et₂O and filtered through a short pad of celite. The filtration was concentrated in vacuo to obtain the crude product which was purified by
chromatography through silica gel to obtain the corresponding ketone (4.7545 g, 25.3 mmol, 51% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.96-7.91 (m, 2H), 7.57-7.50 (m, 1H), 7.49-7.42 (m, 2H), 3.31-3.21 (m, 1H), 1.95-1.70 (m, 4H), 1.78-1.69 (m, 1H), 1.56-1.23 (m, 5H).

To a solution of PPh$_3$MeBr (11.17 g, 31.3 mmol) in THF (70 mL) was added NaH (60%, 1.2046 g, 30 mmol), the reaction mixture was refluxed for 1 h, the ketone (3.7094 g, 20 mmol) obtained above in THF (20 mL) were added dropwise at 0 $^\circ$C and then the reaction was refluxing overnight. When the starting material was consumed (monitored by TLC), the reaction was diluted by petroleum ether and filtered through a short pad of silica gel. The filtration was concentrated and distilled to obtain the product (2.4688 g, 13.3 mmol, 67% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35-7.21 (m, 5H), 5.12 (s, 1H), 5.00 (s, 1H), 2.41 (t, $J$ = 11.2 Hz, 1H), 1.89-1.65 (m, 5H), 1.39-1.05 (m, 5H).

4-(prop-1-en-2-yl)benzaldehyde (1i)$^3$ To a over-dried flask cooled under N$_2$ atmosphere, methyl 4-(prop-1-en-2-yl)benzoate (1.4057 g, 8.0 mmol) and THF (20 mL) were added, LiAlH$_4$ (0.1521 g, 4.0 mmol) in THF (5 mL) was added dropwise at 0$^\circ$C. The mixture was stirred overnight at 0 $^\circ$C. NaOH (1.0 M, 4 mL) was added slowly followed by addition of H$_2$O (10 mL). The mixture was filtrated, and the filtration was extracted by Et$_2$O and the combined organic layers were dried over Na$_2$SO$_4$. After filtration, the solvent was removed and the crude product was dissolved in DCM (50 mL), PCC (1.7411 g, 8 mmol) was added and stirred overnight. The reaction mixture was monitored by TLC. When the starting material was consumed, the mixture was diluted with Et$_2$O and filtered through a pad of
silica gel. The filtrate was condensed and the residue was purified by column chromatography to obtain **1i** (0.4413 g, 2.7 mmol, 34% yield). $^1$H NMR (400 MHz, CDCl$_3$) δ 10.00 (s, 1H), 7.84 (d, $J = 8.4$ Hz, 2H), 7.61 (d, $J = 8.0$ Hz, 2H), 5.51 (s, 1H), 5.26-5.23 (m, 1H), 2.19 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 191.8, 147.2, 142.3, 135.3, 129.8, 126.0, 115.4, 21.6.

$N,N$-diethyl-4-(prop-1-en-2-yl)benzamide (**1j**). To a overdried flask cooled under N$_2$, corresponding acid (649.6 mg, 4.0 mmol) and SOCl$_2$ (2.4 mL, 32.8 mmol) was added at 0 °C. Then the mixture was stirred at room temperature for 3 h. The excess SOCl$_2$ was evaporated in vacuo to obtain the crude acyl chloride. The obtained acyl chloride was transferred to a solution of diethylamine (1.96 mL, 19.0 mmol) in Et$_2$O (20 mL). The reaction mixture stirred overnight. Water was added to quench the reaction and extracted by DCM. The combined organic layers were dried by anhydrous Na$_2$SO$_4$. After filtered, the filtration was concentrated and the residue was purified by column chromatography to obtain **1j** (757.3 mg, 3.5 mmol, 87% yield) as a colorless oil. IR ν 2974, 1628, 1428, 1380 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.49 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 5.41 (s, 1H), 5.15-5.11 (m, 1H), 3.63-3.16 (m, 4H), 2.16 (s, 3H), 1.34-1.02 (m, 6H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.1, 142.5, 141.9, 136.1, 126.3, 125.4, 113.2, 43.2, 39.2, 21.7, 14.2, 14.3; HRMS (EI-TOF) Calcd for C$_{14}$H$_{19}$NO [M$^+$]: 217.1467; Found 217.1468.

**prop-1-ene-1,1-diyl dibenzene** (**1aa**). To a 250 mL round flask,
Ethyltriphenylphosphonium bromide (11.17 g, 30 mmol) and THF (100 mL) were added at room temperature. After cooled to 0 °C, tBuOK (3.45 g, 30 mmol) was added and the reaction mixture was stirred for 2 h. Then benzophenone (3.65 g, 20 mmol) was added and stirred at 50 °C overnight. The reaction mixture was diluted with petroleum ether and filtered through a short pad of silica gel. The filtrate was condensed and the residue was purified by column chromatography to obtain 1aa (2.5992 g, 13.4 mmol, 67% yield) as a white solid. ^1H NMR (400 MHz, CDCl₃) δ 7.40-7.33 (m, 2H), 7.32-7.15 (m, 8H), 6.17 (q, J = 7.2 Hz, 1H), 1.76 (d, J = 6.8 Hz, 3H).

1-(((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl)oxy)methyl)4-vinylnaphthalene (1ac). Prepared according to a similar procedure using alkene (2.9560 g, 15.0 mmol), alcohol (2.5781 g, 16.5 mmol), NaH (60 wt%, 0.8806 g, 22.0 mmol), Bu₄NI (775.7 mg, 2.1 mmol) and THF (45 mL) as substrates to afford 1ac. IR ν 3392, 2953, 2923, 2865, 1457, 1094 cm⁻¹; ^1H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 8.0 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 6.71 (dd, J = 17.6, 10.8 Hz, 1H), 5.73 (d, J = 17.6 Hz, 1H), 5.22 (d, J = 10.8 Hz, 1H), 4.64 (d, J = 11.6 Hz, 1H), 4.39 (d, J = 11.6 Hz, 1H), 3.16 (td, J = 10.8, 4.0 Hz, 1H), 2.37-2.23 (m, 1H), 2.23-2.13 (m, 1H), 1.72-1.58 (m, 2H), 1.33-1.22 (m, 1H), 1.03 -0.81 (m, 10H), 0.71 (d, J = 6.8 Hz, 3H); ^13C NMR (101 MHz, CDCl₃) δ 138.8, 136.7, 136.6, 128.0, 126.1, 113.5, 78.7, 70.1, 48.3, 40.3, 34.6, 31.6, 25.5, 23.2, 22.4, 21.0, 16.1; HRMS (El-TOF) Calcd for C₁₉H₂₈O [M]:272.2140; Found 272.2139.

II. General procedure A for dihydroxylation of styrenes
To a 50 mL flask, Acr⁺MesClO₄⁻ (0.009 mmol), 1 (0.3 mmol), Sat.NaHCO₃ (0.25 mL) and MeCN (2.75 mL) were added sequentially under air. The reaction mixture was irradiated by 8W blue LEDs at a distance of 10 cm for 6 h. To the flask, PPh₃ (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et₂O and filtered through a short pad of silica using Et₂O and EA. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel to afford 2.

2-phenylpropane-1,2-diol (2a) Prepared according to the general A procedure employing Acr⁺MesClO₄⁻ (3.7 mg, 0.009 mmol), 1a (34.9 mg, 0.29 mmol), Sat.NaHCO₃ (0.25 mL), MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2a (39.0 mg, 0.26 mmol, 87% yield) as a colourless oil using PE/EA (2:1) as eluent.¹H NMR (400 MHz, CDCl₃) δ 7.43 (dd, J = 8.4, 1.2 Hz, 2H), 7.38-7.31 (m, 2H), 7.29-7.23 m, 1H), 3.75 (d, J = 11.2 Hz, 1H), 3.59 (d, J = 10.4 Hz, 1H), 2.97 (br s, 1H), 2.42 (br s, 1H), 1.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.9, 128.3, 127.1, 125.0, 74.8, 70.93, 25.9.

2-(m-tolyl)propane-1,2-diol (2b) Prepared according to the general procedure A employing Acr⁺MesClO₄⁻ (3.8 mg, 0.009 mmol), 1b (38.1 mg, 0.29 mmol), Sat.NaHCO₃ (0.25 mL), MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2b (31.5 mg, 0.19 mmol, 66% yield) as a white solid using PE/EA (2:1) as eluent.¹H NMR (400 MHz, CDCl₃) δ 7.28-7.19 (m, 3H), 7.11-7.05 (m, 1H), 3.76 (dd, J = 10.8, 2.0
Hz, 1H), 3.60 (dd, J = 10.8, 7.2 Hz, 1H), 2.79 (s, 1H), 2.36 (s, 3H), 2.16 (brs, 1H), 1.50 (s, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 144.9, 138.0, 128.3, 127.9, 125.8, 122.0, 74.8, 71.0, 26.0, 21.6.

2-(4-fluorophenyl)propane-1,2-diol (2c) Prepared according to the general procedure A employing Acr\(^{+}\)MesClO\(_4^-\) (4.0 mg, 0.009 mmol), 1c (42.0 mg, 0.31 mmol), Sat.NaHCO\(_3\) (0.25 mL), MeCN (2.75 mL) and PPh\(_3\) (ca. 1 equiv.) to afford 2c (42.8 mg, 0.25 mmol, 82% yield) as a colourless oil using PE/EA (2:1) as eluent.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.36 (m, 2H), 7.08-6.99 (m, 2H), 3.72 (d, \(J = 11.2\) Hz, 1H), 3.63-3.54 (m, 1H), 2.94 (br s, 1H), 2.37 (br s, 1H), 1.50 (s, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 161.9 (d, \(J = 244.0\) Hz), 140.7 (d, \(J = 3.2\) Hz), 126.8 (d, \(J = 7.9\) Hz), 115.09 (d, \(J = 21.1\) Hz), 74.5, 70.9, 26.1; \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -115.92.

2-(4-chlorophenyl)propane-1,2-diol (2d) Prepared according to the general procedure A employing Acr\(^{+}\)MesClO\(_4^-\) (3.6 mg, 0.009 mmol), 1d (48.0 mg, 0.31 mmol), Sat.NaHCO\(_3\) (0.25 mL), MeCN (2.75 mL) and PPh\(_3\) (ca. 1 equiv.) to afford 2d (52.5 mg, 0.28 mmol, 90% yield) as a yellow oil using PE/EA (2:1) as eluent.

\(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.39-7.27 (m, 4H), 3.70 (d, \(J = 11.2\) Hz, 1H), 3.57 (d, \(J = 11.2\) Hz, 1H), 3.06 (br s, 1H), 2.54 (br s, 1H), 1.47 (s, 3H);

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.5, 133.0, 128.4, 126.6, 74.6, 70.7, 25.9.

2-(2-chlorophenyl)propane-1,2-diol (2e) Prepared according to the general procedure A employing Acr\(^{+}\)MesClO\(_4^-\) (5.9 mg, 0.015 mmol), 1e (45.9 mg,
0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2e (28.8 mg, 0.15 mmol, 51% yield) as a yellow oil using PE/EA (3:1) as eluent. IR ν 3408, 2928, 1466, 1431, 1038 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.77 (dd, J = 8.0, 2.0 Hz, 1H), 7.35 (dd, J = 7.6, 1.2 Hz, 1H), 7.29 (td, J = 7.6, 1.6 Hz, 1H), 7.21 (td, J = 7.6, 2.0 Hz, 1H), 4.27 (d, J = 11.2 Hz, 1H), 3.81 (d, J = 10.8 Hz, 1H), 3.27 (s, 1H), 2.08 (brs, 1H), 1.66 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 141.3, 131.3, 130.8, 128.8, 128.6, 127.1, 75.4, 68.1, 23.9; HRMS (EI-TOF) Calcd for C₉H₉OCl [M-H₂O]⁺: 168.0342; Found 168.0342.

2-(3-chlorophenyl)propane-1,2-diol (2f) Prepared according to the general procedure A employing Acr⁺MesClO₄⁻ (5.9 mg, 0.015 mmol), 1f (45.9 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2f (28.8 mg, 0.15 mmol, 51% yield) as a yellow oil using PE/EA (3:1) as eluent. IR ν 3372, 2928, 2360, 1470, 1417, 1046 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.46 (s, 1H), 7.33-7.22 (m, 3H), 3.75 (dd, J = 11.2, 3.2 Hz, 1H), 3.61 (dd, J = 10.8, 6.8 Hz, 1H), 2.82 (s, 1H), 2.13 (br s, 1H), 1.50 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 147.2, 134.4, 129.7, 127.3, 125.6, 123.3, 74.6, 70.8, 26.0; HRMS (EI-TOF) Calcd for C₉H₉OCl [M-H₂O]⁺: 168.0342; Found 168.0339.

2-(4-bromophenyl)propane-1,2-diol (2g) Prepared according to the general procedure A employing Acr⁺MesClO₄⁻ (3.9 mg, 0.009 mmol), 1g (62.0 mg, 0.31 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and
PPh₃ (ca. 1 equiv.) to afford 2g (63.4 mg, 0.27 mmol, 87% yield) as a yellow oil using PE/EA (3:1) as eluent. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.70 (d, J = 11.2 Hz, 1H), 3.56 (dd, J = 10.4, 4.0 Hz, 1H), 2.98 (br s, 1H), 2.43 (br s, 1H), 1.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.0, 131.4, 127.0, 121.1, 74.6, 70.7, 25.9.

2-(4-iodophenyl)propane-1,2-diol (2h) Prepared according to the general procedure A employing Acr⁺MesClO₄⁻ (3.5 mg, 0.009 mmol), 1h (73.9 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2h (42.0 mg, 0.15 mmol, 50% yield) as a yellow oil using PE/EA (2:1) as eluent. IR ν 3384, 2927, 1586, 1391, 1042 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, J = 8.4 Hz, 2H), 7.22–7.13 (m, 2H), 3.70 (d, J = 10.4 Hz, 1H), 3.63–3.51 (m, 1H), 3.01–2.69 (m, 1H), 2.45–2.01 (m, 1H), 1.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.7, 137.4, 127.2, 92.8, 74.6, 70.7, 25.9; HRMS (EI-TOF) Calcd for C₉H₁₁IO₂ [M]+: 277.9804; Found 277.9804.

4-(1,2-dihydroxypropan-2-yl)benzaldehyde (2i) Prepared according to the general procedure A employing Acr⁺MesClO₄⁻ (4.0 mg, 0.009 mmol), 1i (44.3 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2i (28.3 mg, 0.16 mmol, 52% yield) as a white solid using PE/EA (1:1) as eluent. IR ν 3409, 2924, 2856, 1695, 1608, 1216, 1045 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.89 (s, 1H), 7.78 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 8.4 Hz, 2H), 3.73 (d, J = 10.8 Hz, 1H), 3.61 (d, J = 10.8 Hz, 1H), 3.01 (brs, 1H), 2.36 (brs, 1H), 1.47 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ
192.1, 152.2, 135.2, 129.8, 125.9, 74.9, 70.7, 26.0; HRMS (EI-TOF) Calcd for C_{10}H_{10}O_{2} [M-H$_2$O]$^+$:162.0681; Found 162.0681.

4-(1,2-dihydroxypropan-2-yl)-N,N-diethylbenzamide (2j) Prepared according to the general procedure A employing Acr$^{+}$MesClO$_4^-$ (3.7 mg, 0.009 mmol), 1j (66.0 mg, 0.30 mmol), Sat.NaHCO$_3$ (0.25 mL) MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford 2j(44.1 mg, 0.18 mmol, 58% yield) as a colorless oil using DCM/MeOH (20:1) as eluent. IR ν 3412, 2976, 2933, 1607, 1437, 1289, 1101, 1046 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.42 (d, $J$ = 8.4 Hz, 2H), 7.29 (d, $J$ = 8.4 Hz, 2H), 3.65 (s, 1H), 3.61–3.40 (m, 5H), 3.26 (d, $J$ = 5.6 Hz, 2H), 1.44 (s, 3H), 1.29-1.17 (m, 3H), 1.16-1.05 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.5, 146.8, 135.2, 126.0, 125.3, 74.4, 70.5, 43.3, 39.3, 25.7, 14.1, 12.8; HRMS (EI-TOF) Calcd for C$_{14}$H$_{21}$N$_2$O$_3$ [M]$^+$:251.1521; Found 251.1526.

methyl 4-(1,2-dihydroxypropan-2-yl)benzoate (2k) $^{10}$ Prepared according to the general procedure A employing Acr$^{+}$MesClO$_4^-$ (3.9 mg, 0.009 mmol), 1k (54.5 mg, 0.31 mmol), Sat.NaHCO$_3$ (0.25 mL) MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford 2k (35.6 mg, 0.17 mmol, 55% yield) as a colorless oil using PE/EA (20:1) as eluent. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.00 (d, $J$ = 8.8 Hz, 2H), 7.52 (d, $J$ = 8.4 Hz, 2H), 3.91 (s, 3H), 3.78 (d, $J$ = 11.2 Hz, 1H), 3.65 (d, $J$ = 10.8 Hz, 1H), 3.01 (br s, 1H), 2.34 (br s, 1H), 1.53 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 166.9, 150.3, 129.6, 128.9, 125.2, 74.9, 70.7, 52.1, 25.9.
2-phenylbutane-1,2-diol (2l) Prepared according to the general procedure A employing Acr'MesClO₄⁻ (3.7 mg, 0.009 mmol), 1l (40.0 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2l (43.2 mg, 0.26 mmol, 86% yield) as a colorless oil using PE/EA (4:1) as eluent.¹H NMR (400 MHz, CDCl₃) δ 7.42–7.31 (m, 4H), 7.29–7.22 (m, 1H), 3.79 (d, J = 11.2 Hz, 1H), 3.65 (d, J = 10.4 Hz, 1H), 2.82 (br s, 1H), 2.24 (brs, 1H), 1.89–1.71 (m, 2H), 0.74 (t, J = 7.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.1, 128.3, 126.9, 125.6, 77.5, 70.3, 31.1, 7.4.

2-phenylpentane-1,2-diol (2m) Pre pared according to the general procedure A employing Acr'MesClO₄⁻ (3.9 mg, 0.009 mmol), 1m (41.8 mg, 0.29 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2m (42.9 mg, 0.24 mmol, 83% yield) as a colorless oil using PE/EA (2:1) as eluent.¹H NMR (400 MHz, CDCl₃) δ 7.41–7.31 (m, 4H), 7.28–7.21 (m, 1H), 3.77 (dd, J = 11.2, 2.4 Hz, 1H), 3.63 (dd, J = 10.8, 7.2 Hz, 1H), 2.93 (s, 1H), 2.32 (s, 1H), 1.81–1.63 (m, 2H), 1.37–1.21 (m, 1H), 1.11–0.95 (m, 1H), 0.83 (t, J = 7.2 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 143.5, 128.3, 126.9, 125.5, 77.3, 70.4, 40.8, 16.3, 14.4.

2-(4-fluorophenyl)hexane-1,2,6-triol (2n) Prepared according to the general procedure A employing Acr'MesClO₄⁻ (4.0 mg, 0.009 mmol), 1n (58.8 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2n (43.2 mg, 0.20 mmol, 67% yield) as a colorless oil using PE/EA (1:1) to methanol as eluent. IR ν 3375, 2942, 2873, 1604, 1510, 1228, 1059 cm⁻¹; ¹H NMR (400 MHz,
CDCl$_3$ $\delta$ 7.41-7.32 (m, 2H), 7.04 (dd, $J = 8.8$, 8.4 Hz, 2H), 3.76 (d, $J = 11.2$ Hz, 1H), 3.67 (d, $J = 11.2$ Hz, 1H), 3.57 (t, $J = 6.4$ Hz, 2H), 2.34 (brs, 3H), 1.92-1.71 (m, 2H), 1.54-1.44 (m, 2H), 1.44-1.30 (m, 1H), 1.18-1.02 (m, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 161.8 (d, $J = 244.1$ Hz), 139.1 (d, $J = 3.2$ Hz), 127.2 (d, $J = 8.0$ Hz), 115.2 (d, $J = 21.1$ Hz), 76.9, 70.5, 62.3, 37.9, 32.5, 19.3; $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -116.08; HRMS (EI-TOF) Calcd for C$_{12}$H$_{13}$FO $[M-2\text{H}_2\text{O}]^+$: 192.0950; Found 192.0947.

3-methyl-2-phenylbutane-1,2-diol (2o)$^9$ Prepared according to the general procedure A employing Acrt$^+$MesClO$_4^-$ (3.5 mg, 0.008 mmol), 10 (43.0 mg, 0.29 mmol), Sat.NaHCO$_3$ (0.25 mL) MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford 2o (44.9 mg, 0.25 mmol, 85% yield) as a colorless oil using PE/EA (4:1) as eluent. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42-7.30 (m, 4H), 7.29-7.21 (m, 1H), 3.94 (d, $J = 11.6$ Hz, 1H), 3.77 (dd, $J = 10.8$, 7.6 Hz, 1H), 2.78 (s, 1H), 2.08-1.94 (m, 1H), 1.87 (brs, 1H), 0.91 (d, $J = 6.8$ Hz, 3H), 0.74 (d, $J = 7.2$ Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.8, 128.1, 126.9, 126.2, 79.2, 68.2, 35.1, 17.3, 16.7.

1-cyclohexyl-1-phenylethane-1,2-diol (2p)$^{12}$ Prepared according to the general procedure A employing Acrt$^+$MesClO$_4^-$ (3.8 mg, 0.009 mmol), 1p (54.9 mg, 0.29 mmol), Sat.NaHCO$_3$ (0.25 mL) MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford 2p (48.4 mg, 0.22 mmol, 75% yield) as a white solid using PE/EA (5:1) as eluent. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.43-7.31 (m, 4H), 7.30-7.23 (m, 1H), 3.99 (d, $J = 10.8$ Hz, 1H), 3.83 (dd, $J = 10.4$, 8.0 Hz, 1H), 2.72 (s, 1H), 1.88-1.54 (m, 6H), 1.43 (d, $J = 12.4$ Hz, 1H), 1.29 -0.90 (m, 5H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 128.1, 126.9, 126.1, 79.2, 68.1, 45.5, 27.2, 26.8, 26.6, 26.4, 26.3.
3,3-dimethyl-2-phenylbutane-1,2-diol (2q) Prepared according to the general procedure A employing Acr‘MesClO₄⁻ (3.9 mg, 0.009 mmol), 1q (47.6 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2q (59.7 mg, 0.30 mmol, 99% yield) as a colorless oil using PE/EA (3:1) as eluent. IR ν 3444, 2962, 2360, 1478, 1048 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.45 (d, J = 7.6 Hz, 2H), 7.34 (dd, J = 8.0, 7.2 Hz, 2H), 7.29-7.23 (m, 1H), 4.28 (d, J = 11.2 Hz, 1H), 3.81 (dd, J = 10.8, 9.6 Hz, 1H), 2.89 (br s, 1H), 1.54 (br s, 1H), 0.90 (s, 9H); ¹³C NMR (101 MHz, CDCl₃) δ 141.8, 127.8, 127.6, 126.9, 80.9, 65.2, 36.7, 25.8; HRMS (EI-TOF) Calcd for C₁₂H₁₆O [M-H₂O]⁺: 176.1201; Found 176.1200.

1,1-diphenylethane-1,2-diol (2r) Prepared according to the general procedure A employing Acr‘MesClO₄⁻ (4.0 mg, 0.009 mmol), 1r (53.5 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2r (49.1 mg, 0.23 mmol, 77% yield) as a white solid using PE/EA (3:1) as eluent. ¹H NMR (400 MHz, CDCl₃) δ 7.47-7.40 (m, 4H), 7.38-7.30 (m, 4H), 7.30-7.23 (m, 2H), 4.15 (d, J = 6.0 Hz, 2H), 3.23 (s, 1H), 1.95 (br s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 143.8, 128.4, 127.4, 126.4, 78.5, 69.4.

1-(hydroxymethyl)-2,3-dihydro-1H-inden-1-ol (2s) Prepared according to the general procedure A employing Acr‘MesClO₄⁻ (3.6 mg, 0.009 mmol), 1s (44.4 mg, 0.34 mmol), Sat.KH₂PO₄ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2s (25.5 mg, 0.16 mmol, 46% yield) as a white solid using PE/EA (3:1) as
1-phenylethane-1,2-diol (2t) Prepared according to the general procedure A employing Acr'MesClO₄⁻ (3.9 mg, 0.009 mmol), 1t (35.3 mg, 0.34 mmol), Sat. NaHCO₃ (0.25 mL) MeCN (2.75 mL) and PPh₃ (ca. 1 equiv.) to afford 2t (36.8 mg, 0.27 mmol, 79% yield) as a yellow solid using PE/EA (2:1) as eluent.¹H NMR (400 MHz, CDCl₃) δ 7.37-7.26 (m, 5H), 4.82-4.74 (m, 1H), 3.77-3.67 (m, 1H), 3.67-3.56 (m, 1H), 3.42 (br s, 1H), 3.02 (br s, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 140.4, 128.5, 127.9, 126.0, 74.7, 68.0.

1-(3-chlorophenyl)ethane-1,2-diol (2v) Prepared according to the general procedure A employing Acr'MesClO₄⁻ (4.0 mg, 0.009 mmol),
$1v (42.0 \text{ mg}, 0.30 \text{ mmol})$, Sat. NaHCO$_3$ (0.25 mL), MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford $2v (25.1 \text{ mg}, 0.15 \text{ mmol}, 48\% \text{ yield})$ as a yellow oil using PE/EA (2:1) as eluent.$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (s, 1H), 7.32-7.17 (m, 3H), 4.84-4.70 (m, 1H), 3.81-3.67 (m, 1H), 3.66-3.54 (m, 1H), 3.25 (br s, 1H), 2.62 (br s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.5, 134.5, 129.8, 128.1, 126.2, 124.2, 74.0, 67.8.

$1$-$(4$-$bromophenyl)$ethane-$1,2$-$diol$ ($2w$)$^7$Prepared according to the general procedure A employing Acr$^+\text{MesClO}_4^-$ (3.7 mg, 0.009 mmol), $1w$ (54.5 mg, 0.30 mmol), Sat. NaHCO$_3$ (0.25 mL), MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford $2w (33.8 \text{ mg}, 0.16 \text{ mmol}, 52\% \text{ yield})$ as a white solid using PE/EA (2:1) as eluent.$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J = 8.4$ Hz, 2H), 7.29-7.21 (m, 2H), 4.83-4.71 (m, 1H), 3.81-3.67 (m, 1H), 3.67-3.55 (m, 1H), 2.72 (s, 1H), 2.19 (s, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 139.4, 131.6, 127.8, 121.8, 74.0, 67.9.

$1$-$(4$-$2$-$methyl$-$1,3$dioxolan$-$2$-$yl)phenyl$)ethane-$1,2$-$diol

$(2x)$Prepared according to the general procedure A employing Acr$^+\text{MesClO}_4^-$ (3.9 mg, 0.009 mmol), $1x$ (60.2 mg, 0.32 mmol), Sat. NaHCO$_3$ (0.25 mL), MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford $2x (51.9 \text{ mg}, 0.23 \text{ mmol}, 73\% \text{ yield})$ as a white solid using PE/EA (3:2) as eluent. IR $\nu$ 3318, 2926, 1730, 1251, 1193, 1079, 1037 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 (d, $J = 8.4$ Hz, 2H), 7.34 (d, $J = 8.4$ Hz, 2H), 4.84-4.78 (m, 1H), 4.09-3.97 (m, 1H), 3.82-3.71 (m, 3H), 3.70-3.60 (m, 1H), 2.82 (br s, 1H), 2.38
(s, 1H), 1.64 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 143.1, 140.1, 126.0, 125.5, 108.7, 74.4, 68.0, 64.4, 27.5; HRMS (EI-TOF) Calcd for C$_{11}$H$_{11}$O$_3$ [M-H$_2$O-CH$_3$]$^+$: 191.0708; Found 191.0709.

**4-(1,2-dihydroxyethyl)benzyl acetate (2y).** Prepared according to the general procedure A employing Acr$^+$MesClO$_4$ (3.9 mg, 0.009 mmol), 1y (51.1 mg, 0.29 mmol), Sat. NaHCO$_3$ (0.25 mL), MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford 2y (38.6 mg, 0.18 mmol, 63% yield) as a colorless oil using PE/EA (1:1) as eluent. IR v 3405, 2925, 1736, 1379, 1235, 1078, 1031 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40-7.30 (m, 4H), 5.09 (s, 2H), 4.85-4.76 (m, 1H), 3.80-3.69 (m, 1H), 3.68-3.58 (m, 1H), 2.89 (br s, 1H), 2.42 (br s, 1H), 2.09 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 171.0, 140.6, 135.6, 128.4, 126.3, 74.3, 68.0, 66.0, 21.0; HRMS (EI-TOF) Calcd for C$_{11}$H$_{12}$O$_3$ [M-H$_2$O]$^+$: 192.0786; Found 192.0786.

**1-phenylpropane-1,2-diol (2z)** Prepared according to the general procedure A employing Acr$^+$MesClO$_4$ (4.0 mg, 0.009 mmol), 1z (35.7 mg, 0.30 mmol), Sat. NaHCO$_3$ (0.25 mL), MeCN (2.75 mL) and PPh$_3$ (ca. 1 equiv.) to afford 2z (30.5 mg, 0.20 mmol, 66% yield, $dr$1.9/1) as a colorless oil using PE/EA (3:2) as eluent. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.27 (m, 5H), 4.69-4.63 (m, 0.55 H), 4.36 (dd, $J$ = 7.2, 1.6 Hz, 0.43 H), 4.05-3.90 (m, 0.55H), 3.89-3.80 (m, 0.44H), 2.83 (br s, 0.41H), 2.66 (br, s 0.41H), 2.58 (br s, 0.53H), 2.05 (br s, 0.52 H), 1.08 (d, $J$ = 6.4 Hz, 1.64 H), 1.05 (d, $J$ = 6.4 Hz, 1.33 H).
1,1-diphenylpropane-1,2-diol (2aa) Prepared according to the general procedure A employing Acr\(^+\)MesClO\(_4^-\) (3.9 mg, 0.009 mmol), 1aa (60.9 mg, 0.31 mmol), Sat. NaHCO\(_3\) (0.25 mL), MeCN (2.75 mL) and PPh\(_3\) (ca. 1 equiv.) to afford 2aa (43.3 mg, 0.19 mmol, 61% yield) as a white solid using PE/EA (5:1) as eluent. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.59 (d, \(J = 7.2\) Hz, 2H), 7.42 (d, \(J = 7.2\) Hz, 2H), 7.38-7.22 (m, 5H), 7.22-7.14 (m, 1H), 4.86-4.73 (m, 1H), 3.05 (d, \(J = 1.2\) Hz, 1H), 1.94 (s, 1H), 1.09 (d, \(J = 6.0\) Hz, 3H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 145.6, 143.8, 128.6, 128.1, 127.2, 126.7, 126.2, 125.5, 79.8, 71.6, 16.6.

2-phenylhex-5-ene-1,2-diol (2ab). Prepared according to the general procedure A employing Acr\(^+\)MesClO\(_4^-\) (4.0 mg, 0.009 mmol), 1ab (43.6 mg, 0.27 mmol), Sat. NaHCO\(_3\) (0.25 mL), MeCN (2.75 mL) and PPh\(_3\) (ca. 1 equiv.) to afford 2ab (24.6 mg, 0.13 mmol, 46% yield) as a colorless oil using PE/EA (3:1) as eluent. IR \(\nu\) 3409, 2930, 1736, 1379, 1235, 1031 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44-7.33 (m, 4H), 7.30-7.24 (m, 1H), 5.83-5.70 (m, 1H), 4.99-4.88 (m, 1H), 3.81 (d, \(J = 11.2\) Hz, 1H), 3.68 (d, \(J = 11.2\) Hz, 1H), 2.83 (brs, 1H), 2.13-2.02 (m, 1H), 2.02-1.76 (m, 4H); \(^13\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 143.1, 138.6, 128.4, 127.1, 125.5, 114.6, 77.2, 70.6, 37.4, 27.5; HRMS (EI-TOF) Calcd for C\(_{12}\)H\(_{16}\)O\(_2\) [M+H]\(^+\): 193.1229; Found 193.1220.
eluent. IR ν 3389, 2952, 2867, 1077 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.28 (m, 4H), 4.77 (d, J = 6.0 Hz, 1H), 4.64 (d, J = 11.6 Hz, 1H), 4.38 (d, J = 11.2 Hz, 1H), 3.69 (d, J = 10.4 Hz, 1H), 3.64-3.53 (m, 1H), 3.17 (td, J = 10.8, 4.0 Hz, 1H), 2.85 (br s, 1H), 2.43 (br s, 1H), 2.33-2.23 (m, 1H), 2.18 (d, J = 12.0 Hz, 1H), 1.71-1.56 (m, 1H), 1.45-1.21 (m, 2H), 1.04-0.79 (m, 8H), 0.71 (d, J = 6.8 z, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 139.7, 138.8, 128.1, 126.0, 78.9, 74.4, 70.1, 68.0, 48.2, 40.3, 34.5, 31.5, 25.5, 23.2, 22.3, 21.0, 16.0; HRMS (EI-TOF) Calcd for C₁₈H₂₇O₂ [M-CH₂OH]⁺: 275.2011; Found 275.2012.

III. Transformations of vicinal alcohols

\[ \text{Cl} \quad \text{OH} \quad \text{Cl} \quad \text{OH} \]

1) SOCl₂, CCl₄, reflux
2) NaN₃, DMF, 70 °C, 24 h

\[ \text{Cl} \quad \text{OH} \quad \text{N}_3 \quad \text{Cl} \]

2-azido-2-(3-chlorophenyl)propan-1-ol (3). To a 50 mL overdried flask was added 2f (57.5 mg, 0.31 mmol), CCl₄ (1.5 mL) and SOCl₂ (161 uL) under N₂ atmosphere. The mixture was refluxed for 1 h. After cooled to room temperature, the mixture was washed by saturated NaHCO₃ and brine. The organic phase was dried and concentrated under reduced pressure to give the crude cyclic sulfite, which was transferred to a flask containing NaN₃ (50.0 mg, 0.77 mmol) and DMF (2 mL). The reaction was refluxed overnight. After being cooled to room temperature, the reaction was quenched by diluted H₂SO₄, H₂O and saturated NaHCO₃. The combined organic layers was dried over anhydrous Na₂SO₄, concentrated under reduced pressure and purified by column chromatography using PE/EA (10:1) as eluent to afford 3 (38.8 mg, 0.18 mmol, 61% yield) as a colorless oil. IR ν 3378, 2928, 2108, 1472, 1260, 1049 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.48 (s, 1H), 7.42-7.32 (m, 3H), 3.74 (dd, J = 11.6, 6.0 Hz, 1H), 3.67 (dd, J = 11.2, 7.6 Hz, 1H), 2.01 (br s, 1H), 1.77 (s, 3H); ¹³C
NMR (101 MHz, CDCl$_3$) $\delta$ 143.0, 134.7, 130.0, 128.1, 126.4, 124.2, 70.4, 67.3, 21.3; HRMS (ESI-TOF) Calcd for C$_9$H$_{11}$ClN$_3$O [M+H]$^+$: 212.0591; Found 212.0593.

1-(3-chlorophenyl)ethanone (4)$^{17}$To a 50 mL flask was added 2f (59.5 mg, 0.32 mmol), PCC (129.3 mg, 0.6 mmol) and DCM (10 mL). The mixture was stirred overnight at room temperature. The reaction mixture was diluted with Et$_2$O, filtered through a short pad of silica gel, concentrated under reduced pressure and purified through column chromatography using PE/EA (20:1) to afford 4 (24.5 mg, 0.16 mmol, 51% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.93 (s, 1H), 7.83 (d, $J$ = 7.6 Hz, 1H), 7.54 (d, $J$ = 7.6 Hz, 1H), 7.41 (dd, $J$ = 15.6, 7.6 Hz, 1H), 2.60 (s, 3H).

2-(3-chlorophenyl)-2-methyloxirane (5).$^{18}$To a 50 mL over-dried flask, cooled under N$_2$ atmosphere, was added 2f (58.8 mg, 0.31 mmol), DCM (4 mL) and NEt$_3$ (0.46 mL, 3.4 mmol). The mixture was cooled to 0 °C and then TsCl (70.2 mg, 0.37 mmol) and DMAP (4.9 mg, 0.04 mmol). The reaction was warmed to 50 °C and stirred for 24 h. After being cooled to room temperature, H$_2$O (3 mL) was added to quenched the reaction. The mixture was extracted by DCM. The combined organic layers were dried over anhydrous MgSO$_4$, filtered, concentrated and purified by column chromatography to afford 5 (32.5 mg, 0.19 mmol, 61% yield) as a colorless oil using PE/EA (50:1) as eluent. $^1$H NMR (400
MHz, CDCl$_3$) $\delta$ 7.35 (s, 1H), 7.30-7.22 (m, 3H), 2.97 (d, $J$ = 5.6 Hz, 1H), 2.77 (d, $J$ = 5.6 Hz, 1H), 1.71 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.4, 134.4, 129.6, 127.6, 125.6, 123.5, 57.0, 56.3, 21.6.

To a 50 mL over-dried flask, cooled under N$_2$ atmosphere, were added 2f (55.8 mg, 0.30 mmol), DCM (3.5 mL) and NEt$_3$ (48 uL, 0.36 mmol) . The mixture was cooled to 0 $^\circ$C, TsCl (69.0 mg, 0.36 mmol) and DMAP (6.1 mg, 0.05 mmol) were added. Then the reaction was stirred overnight at 0 $^\circ$C. H$_2$O was added to quench the reaction and extracted with DCM. The combined organic layers were dried over anhydrous Na$_2$SO$_4$, filtered, concentrated and purified by column chromatography to afford 6 (72.5 mg, 0.21 mmol, 71% yield) as a colorless oil using PE/EA (5:1) as eluents. IR $\nu$ 3524, 2985, 1597, 1360, 1179 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.68 (d, $J$ = 8.0 Hz, 2H), 7.30 (d, $J$ = 8.4 Hz, 3H), 7.23 (s, 3H), 4.07 (d, $J$ = 10.0 Hz, 1H), 4.05 (d, $J$ = 10.4 Hz, 1H), 2.72 (s, 1H), 2.44 (s, 3H), 1.52 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.1, 134.3, 132.1, 129.9, 129.6, 127.8, 127.7, 125.4, 123.2, 76.3, 72.9, 26.0, 21.6; HRMS (ESI-TOF) Calcd for C$_{16}$H$_{18}$ClO$_4$S [M+H]$^+$: 341.0614; Found 341.0616.

To a 50 mL over-dried flask, cooled under N$_2$ atmosphere, were added 6 (71.2 mg, 0.21 mmol), DMF (2 mL), NaN$_3$ (48.2 mg, 0.74 mmol) and Bu$_4$NI (12.1 mg, 0.033 mmol). The mixture was heated to 80 $^\circ$C and stirred overnight. After cooled to room temperature, H$_2$O was added and extracted with Et$_2$O. The combined organic layers were washed by H$_2$O and dried by anhydrous Na$_2$SO$_4$. After being filtered, concentrated, the reaction mixture was purified by column chromatography to afford 7 (39.8 mg, 0.19 mmol, 90% yield) as a colorless oil using PE/EA (20:1)
as eluents. IR ν 3449, 2105, 1573, 1295 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (s, 1H), 7.34-7.23 (m, 3H), 3.58 (d, J = 12.4 Hz, 1H), 3.44 (d, J = 12.4 Hz, 1H), 2.38 (s, 1H), 1.57 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 146.8, 134.5, 129.7, 127.6, 125.4, 123.1, 74.3, 61.9, 27.1; HRMS (ESI-TOF) Calcd for C₉H₁₁ClN₃O [M+H]+: 212.0591; Found 212.0590.

IV. Mechanistic studies

![Mechanistic diagram]

1-cyclopropyl-1-phenylethane-1,2-diol (9) To a 50 mL flask, Acr⁺MesClO₄⁻ (3.9 mg, 0.009 mmol), 8 (43.1 mg, 0.30 mmol), Sat.NaHCO₃ (0.25 mL) and MeCN (2.75 mL) were added sequencely under air. The reaction mixture was irradiated by 8W blue LEDS at a distance of 10 cm for 6 h. To the flask, PPh₃ (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et₂O and filtered through a short pad of silica using Et₂O and EA. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel to afford 9 (19.7 mg, 0.11 mmol, 37% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 7.2 Hz, 2H), 7.36 (dd, J = 8.4, 7.2 Hz, 2H), 7.31-7.24 (m, 1H), 3.94 (dd, J = 11.6, 5.2 Hz, 1H), 3.78 (dd, J = 11.2, 6.8 Hz, 1H), 2.54 (s, 1H), 1.86 (br s, 1H), 1.14-1.12 (m, 1H), 0.55-0.42 (m, 2H), 0.40-0.25 (m, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 143.6, 128.2, 127.2, 125.7, 75.1, 70.5, 18.3, 0.8, -0.2
To a 50 mL flask, Acr⁺MesClO₄⁻ (3.9 mg, 0.009 mmol), 1 (34.9 mg, 0.30 mmol), TEMPO (70.8 mg, 0.45 mmol), Sat.NaHCO₃ (0.25 mL) and MeCN (2.75 mL) were added sequentially under air. The reaction mixture was irradiated by 8W blue LEDs at a distance of 10 cm for 6 h. To the flask, PPh₃ (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et₂O and filtered through a short pad of silica using Et₂O and EA. The filtrate was concentrated in vacuo and monitored by ¹H NMR spectroscopy. The results demonstrated that No 2a was obtained.

To a 50 mL over-dried flask, Acr⁺MesClO₄⁻ (3.7 mg, 0.009 mmol), 1 (34.9 mg, 0.3 mmol), Sat.NaHCO₃ (0.25 mL, H₂¹⁸O) and MeCN (2.75 mL) were added sequentially under air. The reaction mixture was irradiated by 8W blue LEDs at a distance of 10 cm for 6 h. To the flask, PPh₃ (1 equiv.) was added and stirred for 30 min at room temperature. The reaction mixture was then diluted with Et₂O and filtered through a short pad of silica using Et₂O and EA. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel to afford 11 (38.2 mg, 0.25 mmol, 84% yield) as a colorless oil. HRMS (ESI-TOF) Calcd for C₉H₁₂O₂ [M+Na]^+: 177.0777; Found 177.0772.

2-hydroperoxy-2-phenylpropan-1-ol (12). Prepared according to the general A
procedure employing Acr′MesClO$_4$ (3.9 mg, 0.009 mmol), 1a (36.7 mg, 0.31 mmol), Sat.NaHCO$_3$ (0.25 mL) and MeCN (2.75 mL). After 6h, the reaction mixture was then diluted with Et$_2$O and filtered through a short pad of silica using Et$_2$O and EA. The filtrate was concentrated in vacuo and purified by flash chromatography on silica gel to afford 12 (42.7 mg, 0.25 mmol, 82% yield) as a colourless oil using PE/EA (2:1) as eluent.$^1$H NMR (400 MHz, CDCl$_3$) δ 8.53 (br s, 1H), 7.47-7.27 (m, 5H), 4.03 (d, $J = 12.0$ Hz, 1H), 3.88 (d, $J = 12.0$ Hz, 1H), 2.61 (br s, 1H), 1.56 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 141.2, 128.6, 127.8, 125.6, 86.2, 66.7, 21.7.

V. General Procedures B for Dioxylation of styrenes

To a 50 mL flask, Acr′MesClO$_4$ (0.015 mmol), 1 (0.3 mmol), alcohol (0.5 mL) and MeCN (5.5 mL) were added sequentially under O$_2$ balloon. The reaction mixture was irradiated by 8W blue LEDs at a distance of 10 cm for 3 h. The reaction mixture was reduced by PPh$_3$ (0.3 mmol) stirred for 30 min at room temperature before it was purified by flash chromatography on silica gel to afford 13.

1-methoxy-2-phenylpropan-2-ol (13a)$^{20}$ Prepared according to the general procedure B employing 1a (35.8 mg, 0.30 mmol), Acr′MesClO$_4$ (6.0 mg, 0.015 mmol), 4Å MS (70.7 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh$_3$ (78.1 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et$_2$O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford 13a (31.7 mg, 0.19 mmol, 63% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 8.0$ Hz, 2H), 7.35 (dd, $J = 7.6, 7.6$ Hz, 2H), 7.28-7.23 (m, 1H), 3.59 (d, $J = 9.2$ Hz, 1H), 3.48 (d, $J = 9.2$ Hz, 1H), 3.37 (s, 3H), 2.93 (s,
1H), 1.51 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.4, 128.1, 126.9, 124.9, 80.7, 73.8, 59.3, 26.7.

1-methoxy-2-(o-tolyl)propan-2-ol (13b). Prepared according to the general procedure B employing the 1-methyl-2-(prop-1-en-2-yl)benzene 13bs (38.6 mg, 0.29 mmol), Acr$^+$MesClO$_4^-$ (6.4 mg, 0.015 mmol), 4Å MS (80.7 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh$_3$ (77.9 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et$_2$O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford 13b (24.9 mg, 0.14 mmol, 47% yield) as a yellow oil. IR $\nu$ 3460, 2928, 1455, 1108 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.44-7.38 (m, 1H), 7.21-7.12 (m, 3H), 3.84 (d, $J$ = 9.2 Hz, 1H), 3.51 (d, $J$ = 9.2 Hz, 1H), 3.42 (s, 3H), 2.92 (s, 1H), 2.56 (s, 3H), 1.56 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.3, 136.0, 132.6, 127.2, 126.1, 125.6, 79.3, 74.9, 59.3, 25.8, 22.3; HRMS (EI-TOF) Calcd for C$_{11}$H$_{16}$O$_2$ [M$^+$]: 180.1150; Found: 180.1145.

1-methoxy-2-(m-tolyl)propan-2-ol (13c). Prepared according to the general procedure B employing 1b (38.7 mg, 0.29 mmol), Acr$^+$MesClO$_4^-$ (6.4 mg, 0.015 mmol), 4Å MS (75.1 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh$_3$ (80.6 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et$_2$O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford 13c (39.7 mg, 0.22 mmol, 75% yield) as a colorless oil. IR $\nu$ 3459, 2926, 1455, 1107 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30 (s, 1H), 7.24 (d, $J$ = 4.8 Hz, 2H), 7.10-7.04 (m, 1H), 3.58 (d,
$J = 9.2$ Hz, 1H), 3.47 (d, $J = 9.2$ Hz, 1H), 3.38 (s, 3H), 2.89 (s, 1H), 2.36 (s, 3H), 1.50 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.3, 137.7, 128.1, 127.7, 125.6, 121.9, 80.7, 73.8, 59.4, 26.7, 21.6;
HRMS (EI-TOF) Calcd for C$_{11}$H$_{16}$O$_2$ [M$^+$]:180.1150; Found 180.1150.

**1-methoxy-2-(p-tolyl)propan-2-ol (13d).** Prepared according to the general procedure B employing 1-methyl-4-(prop-1-en-2-yl)benzene13ds (40.4 mg, 0.30 mmol), Acr$^+$MesClO$_4^-$ (6.4 mg, 0.015 mmol), 4Å MS (76.4 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh$_3$ (77.2 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et$_2$O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford 13d (33.1 mg, 0.18 mmol, 60% yield) as a colorless oil. IR $\nu$ 3463, 2926, 1453, 1106 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 8.0$ Hz, 2H), 7.16 (d, $J = 8.0$ Hz, 2H), 3.58 (d, $J = 9.2$ Hz, 1H), 3.46 (d, $J = 9.2$ Hz, 1H), 3.37 (s, 3H), 2.87 (s, 1H), 2.33 (s, 3H), 1.49 (s, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 142.4, 136.4, 128.8, 124.8, 80.7, 73.7, 59.3, 26.7, 21.0; HRMS (EI-TOF) Calcd for C$_{11}$H$_{16}$O$_2$ [M$^+$]:180.1150; Found 180.1154.

**2-(4-chlorophenyl)-1-methoxypropan-2-ol (13e).** Prepared according to the general procedure B employing 1d (46.8 mg, 0.31 mmol), Acr$^+$MesClO$_4^-$ (6.5 mg, 0.015 mmol), 4Å MS (90.9 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh$_3$ (80.1 mg, 0.31 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et$_2$O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an
eluent to afford **13e** (47.0 mg, 0.23 mmol, 76% yield) as a colorless oil. IR ν 3445, 2930, 1491, 1093 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H), 3.54 (d, J = 9.2 Hz, 1H), 3.45 (d, J = 9.2 Hz, 1H), 3.37 (s, 3H), 2.91 (s, 1H), 1.48 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 144.0, 132.7, 128.2, 126.5, 80.5, 73.5, 59.4, 26.6; HRMS (EI-TOF) Calcd for C₁₀H₁₃O₂Cl [M]⁺: 200.0604; Found 200.0606.

**1-ethoxy-2-phenylpropan-2-ol (13f)**. Prepared according to the general procedure B employing **1a** (35.7 mg, 0.30 mmol), Acr’MesClO₄⁻ (6.3 mg, 0.015 mmol), 4Å MS (70.8 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh₃ (79.3 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et₂O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (30:1) as an eluent to afford **13f** (34.5 mg, 0.19 mmol, 63% yield) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 7.6, 7.2 Hz, 2H), 7.25 (t, J = 6.4 Hz, 1H), 3.60-3.474 (m, 4H), 2.93 (s, 1H), 1.52 (s, 3H), 1.17 (t, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.6, 128.1, 126.8, 125.0, 78.4, 73.7, 67.0, 26.7, 15.0.

**1-isopropoxy-2-phenylpropan-2-ol (13g)**. Prepared according to the general procedure B employing **1a** (36.7 mg, 0.31 mmol), Acr’MesClO₄⁻ (5.8 mg, 0.014 mmol), 4Å MS (70.8 mg), MeCN (5.5 mL) and MeOH (0.5 mL). After 3 h, PPh₃ (80.0 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et₂O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (30:1) as an eluent to afford **13g** (30.6 mg,
0.16 mmol, 51% yield) as a colorless oil. IR ν 3455, 2974, 1449, 1372, 1127, 1085 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 7.6 Hz, 2H), 7.34 (dd, J = 7.6, 7.2 Hz, 2H), 7.24 (t, J = 7.2 Hz, 1H), 3.62-3.56 (m, 1H), 3.54 (d, J = 8.8 Hz, 1H), 3.49 (d, J = 9.2 Hz, 1H), 2.98 (s, 1H), 1.52 (s, 3H), 1.15 (dd, J = 6.4 Hz, 3H), 1.12 (dd, J = 6.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.7, 128.0, 125.0, 126.8, 76.2, 73.6, 72.5, 26.7, 22.00, 21.97; HRMS (EI-TOF) Calcd for C₁₂H₁₈O₂ [M]⁺:194.1307; Found 194.1306.

1-(tert-butoxy)-2-phenylpropan-2-ol (13h). Prepared according to the general procedure B employing 1a (36.0 mg, 0.30 mmol), Acr⁺MesClO₄⁻ (6.7 mg, 0.016 mmol), 4Å MS (71.0 mg), MeCN (5.5 mL) and MeOH (0.5 mL).

After 3 h, PPh₃ (79.7 mg, 0.30 mmol) was added and stirred at rt for 30 min. The reaction mixture was diluted with Et₂O and passed through a short pad of silica gel. The filtrate was condensed and purified by flash column chromatography using PE/EA (10:1) as an eluent to afford 13h (21.1 mg, 0.10 mmol, 33% yield) as a colorless oil. IR ν 3563, 2975, 1365, 1194, 1089 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.47 (d, J = 8.0 Hz, 2H), 7.34 (dd, J = 7.6, 7.6 Hz, 2H), 7.27-7.21 (m, 1H), 3.45 (d, J = 8.4 Hz, 1H), 3.41 (d, J = 8.8 Hz, 1H), 3.06 (s, 1H), 1.51 (s, 3H), 1.16 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 145.9, 128.0, 126.7, 125.0, 73.4, 73.2, 69.8, 27.5, 26.6; HRMS (EI-TOF) Calcd for C₁₃H₂₀O₂ [M]⁺:208.1463; Found 208.1459.

VII. Reference


VIII. NMR Spectra

$^1$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
$^{1}$H NMR
400 M Hz
CDCl$_3$

$^{13}$C NMR
100 M Hz
CDCl$_3$
$^{1}H$ NMR
400 M Hz
CDCl$_{3}$

$^{13}$C NMR
100 M Hz
CDCl$_{3}$
$^{1}H$ NMR
400 MHz
CDCl$_3$

$^{13}C$ NMR
100 MHz
CDCl$_3$
$^{19}$F NMR
376 MHz
CDCl$_3$
$^{1}H$ NMR
400 M Hz
CDCl$_3$

$^{13}C$ NMR
100 M Hz
CDCl$_3$
2f

$^1$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
$^{1}$H NMR
400 M Hz
CDCl$_3$

$^{13}$C NMR
100 M Hz
CDCl$_3$
$2h$

$^1$H NMR
400 MHz
CDCl$_3$

$2h$

$^{13}$C NMR
100 MHz
CDCl$_3$
$^{1}H$ NMR
400 MHz
CDCl$_3$

$^{13}C$ NMR
100 MHz
CDCl$_3$
$^{1}H$ NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
$2k$

$^1$H NMR
400 M Hz
CDCl$_3$

$2k$

$^{13}$C NMR
100 M Hz
CDCl$_3$
$^{1}H$ NMR
400 MHz
CDCl$_3$

$^{13}C$ NMR
100 MHz
CDCl$_3$
$2n$

$^{1}H$ NMR
400 MHz
CDCl$_3$

$^{13}C$ NMR
100 MHz
CDCl$_3$
$^{19}$F NMR
376 MHz
CDCl$_3$
$^{1}$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
2p

$^1$H NMR
400 MHz
CDCl$_3$

2p

$^{13}$C NMR
100 MHz
CDCl$_3$
**1H NMR**
400 MHz
CDCl₃

**1³C NMR**
100 MHz
CDCl₃
$^1$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
$^{1}H$ NMR  
400 MHz  
CDCl$_3$  

$^{13}C$ NMR  
100 MHz  
CDCl$_3$
$\text{Me}$\quad\text{OH}\quad\text{OH}$

$\text{2u}$

$^1\text{H NMR}$

$400$ M Hz

$\text{CDCl}_3$

$\text{Me}$\quad\text{OH}\quad\text{OH}$

$\text{2u}$

$^{13}\text{C NMR}$

$100$ M Hz

$\text{CDCl}_3$
$2v$

$^1$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
$2w$

$^1$H NMR
400 M Hz
CDCl$_3$

$13^C$ NMR
100 M Hz
CDCl$_3$
$\text{2x}$

$^1\text{H NMR}$

$400 \text{ MHz}$

$\text{CDCl}_3$

$\text{2x}$

$^{13}\text{C NMR}$

$100 \text{ MHz}$

$\text{CDCl}_3$
Me\_\_\_ OH
Ph OH
Ph
\underline{2aa}

$^1$H NMR
400 M Hz
CDCl$_3$

\underline{13}$^C$ NMR
100 M Hz
CDCl$_3$
2ab
$^1$H NMR
400 MHz
CDCl$_3$

2ab
$^{13}$C NMR
100 MHz
CDCl$_3$
2ac

$^1$H NMR  
400 MHz  
CDCl$_3$

2ac

$^{13}$C NMR  
100 MHz  
CDCl$_3$
$^1$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
5

$^1$H NMR
400 M Hz
CDCl$_3$

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$^{13}$C NMR
100 M Hz
CDCl$_3$
$^1$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
\[ \text{Cl} - \text{N}_3 - \text{OH} \]

\[ \text{7} \]

$^1$H NMR
400 MHz
CDCl$_3$

\[ \text{Cl} - \text{N}_3 - \text{OH} \]

\[ \text{7} \]

$^{13}$C NMR
100 MHz
CDCl$_3$
$^{1}$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
1H NMR
400 MHz
CDCl₃

13C NMR
100 MHz
CDCl₃
13a
$^1$H NMR
400 MHz
CDCl$_3$

13a
$^{13}$C NMR
100 MHz
CDCl$_3$
13c
$^1$H NMR
400 MHz
CDCl$_3$

13c
$^{13}$C NMR
100 MHz
CDCl$_3$
$^{1}$H NMR
400 MHz
CDCl$_3$

$^{13}$C NMR
100 MHz
CDCl$_3$
$13e$

$^1$H NMR

400 MHz

CDCl$_3$

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$13e$

$^{13}$C NMR

100 MHz

CDCl$_3$
13f
$^1$H NMR
400 MHz
CDCl$_3$

13f
$^{13}$C NMR
100 MHz
CDCl$_3$
$^{13}$C NMR
100 MHz
CDCl$_3$
13h

$^1$H NMR
400 MHz
CDCl$_3$

13h

$^{13}$C NMR
100 MHz
CDCl$_3$