Supplementary Information

Fenton-like Chemistry Enables Catalytic Oxidative Desulfurization of Thioacetals and Thioketals with Hydrogen Peroxide

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1. General Information

Reactions were carried out in a round-bottom flask with vigorous stirring at room temperature with open-air condition, unless otherwise noted. Anhydrous ethanol (EtOH), acetonitrile (MeCN), tetrahydrofuran (THF), dichloromethane (DCM), dimethyl sulfoxide (DMSO), N,N-dimethylformamide (DMF), 1-butanol (n-BuOH) and pyridine were used as received without further purification unless otherwise noted. Anhydrous CeBr₃, FeBr₂ and FeBr₃ were purchased from Sigma-Aldrich and dried under vacuum before use. Solvents were used as received from commercial suppliers without prior purification for workup, extraction and column chromatography. Reactions were monitored by thin-layer chromatography (TLC, 0.25 mm) on pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040-0.062 mm). ¹Hand ¹³C-NMR spectra were recorded on a 400 MHz spectrometer (400 MHz for ¹H, 100 MHz for ¹³C). Chemical shifts are reported in parts per million (ppm) as values relative to the internal chloroform (7.26 ppm for ¹H and 77.16 ppm for ¹³C) or DMSO (2.50 ppm for ¹H and 39.52 ppm for ¹³C). Abbreviations for signal coupling are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were detected by ESI-TOF (Agilent 6520 or G6125B) or GC-MS (Agilent 7890A/5975C). Infrared spectrometry was recorded on Nicolet iS10 FT-IR (Thermo). Fluorescence emission spectra were recorded on LS-45 fluorescence spectrophotometer (PerkinElmer). Optical rotations were measured on Autopol I polarimeter (Rudolph Research Analytical) with $[\alpha]_{D}$ values reported in degrees. Melting points were determined on MP70 instrument (Mettler Toledo) without correction.

2. [Br⁺] from CeBr₃-H₂O₂ system was confirmed to be HOBr.



To a stirred solution of fluorescent probe **BPP**¹ (compound **1**, 108 mg, 0.5 mmol) in MeCN/H₂O (3/1, 10 mL) were added CeBr₃ (56.9 mg, 0.15 mmol) and H₂O₂ (30%, 150 µL, 1.5 mmol). After completion of the addition, the reaction mixture was stirred at room temperature (rt) for 1.5 h. The reaction was quenched by aqueous Na₂S₂O₃ solution (0.1 M, 50 mL) and ethyl acetate (50 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2×20 mL). The combined organic fractions were washed with H₂O, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Compound **2**¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:1 to 3:1) as a gray solid (85.3 mg, 80%). M.P. 142–144 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.95 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.63–7.57 (m, 1H), 7.42 (d, *J* = 4.6 Hz, 2H), 7.34–7.27 (m, 1H), 7.22 (d, *J* = 8.2 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 2.35 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 148.7, 132.6, 131.9, 130.5, 127.6, 125.8, 124.8, 124.6, 124.3, 123.6, 120.8, 119.8, 32.1. IR 2971.9, 2895.4, 1590.2, 1563.1, 1465.4, 1413.1, 1280.4, 1218.5, 1148.6, 1109.4, 1037.1, 738.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₂NS [M+H]⁺ 214.0685; found 214.0683.

Notably, no product **2** was furnished after the combination of Br₂ (38.4 μ L, 0.75 mmol) or H₂O₂ (30%, 150 μ L, 1.5 mmol) with fluorescent probe **BPP** (108 mg, 0.5 mmol) following the above protocol (1.5 h at rt in MeCN/H₂O 3/1), further indicating the specificity of fluorescent probe **BPP** for HOBr¹ detection.

The emission spectra of fluorescent probe **BPP 1** (0.9 mM in MeCN, black) and **2** (7.5 mM in MeCN, blue) were got under the excitation wavelength of 375 nm and 480 nm respectively, and the emission wavelength collected were 400-600 nm (for **BBP**) and 500-700 nm (for compound **2**), which were reported in the literature¹.

3. Optimization of the 1,3-dithiane deprotection.



General Procedure: To a stirred solution of compound **3a** (21.0 mg, 0.1 mmol) in solvent (1 mL) were added MBr_x (0.01 mmol) and H₂O₂ (30 wt%, 30 μ L, 0.3 mmol). After completion of the addition, the reaction mixture was allowed to stir at room temperature (rt) for 1.5 h. The reaction was quenched by dilute aqueous Na₂S₂O₃ solution (0.1 M, 10 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic fractions were washed with H₂O, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Yield was determined by ¹H-NMR of the crude reaction mixture using CH₂Br₂ as the internal reference.

<i>entry</i> ^a	$MBr_x(0.1 \ eq)$	Solvent	Yield ^c (%)
1	CeBr ₃	DCM/H ₂ O (10/1)	<5
2	CeBr ₃	DMSO/H ₂ O (10/1)	<5
3	CeBr ₃	DMF/H ₂ O (10/1)	<5
4	CeBr ₃	THF/H ₂ O (10/1)	13
5	CeBr ₃	<i>n</i> -BuOH/H ₂ O (10/1)	32
6	CeBr ₃	MeCN/H ₂ O (10/1)	70
7	CeBr ₃	EtOH/H ₂ O (10/1)	75
8	CeBr ₃	EtOH	77
9	FeBr ₂	EtOH	69
10	FeBr ₃	EtOH	73
11 ^b	CeBr ₃	EtOH	86

^{*a*}Reaction was carried out at rt: **3a** (0.1 mmol) was dissolved in solvent (1 mL), then CeBr₃, FeBr₂ or FeBr₃ (0.01 mmol), and H₂O₂ (30%, 30 μ L, 0.3 mmol) were added and stirred at rt for 1.5 h. ^b0.005 mmol CeBr₃ and 0.2 mmol H₂O₂ were added, and the reaction was stirred at 40°C for 15 min. ^cYield was determined by ¹H-NMR of the crude reaction mixture using CH₂Br₂ as the internal reference.

4. Preparation of thioacetals, thioketals and methylthiomethyl ether.

4.1. Substrates $3c^2$, $3g^3$, $3h^4$, $3k^5$, $3l^6$, $3n^7$, $3p-t^8$, $3u^9$, $3v^{10}$, $3x^{11}$, $3y^{12}$, $3ab^7$, $3am^{13}$, $5a^{14}$, $5b^{15}$ and $5n^{16}$ were prepared according to the published procedure.



4.2. Synthesis of 4ac and 6t: To a stirred solution of compound **S1** or **S2** (20 mmol) in anhydrous pyridine (40 mL) or dichloromethane (DCM: 100 mL) were added acetic anhydride (Ac₂O: 9.4 mL, 100 mmol) and 4-dimethylaminopyridine (DMAP: 244 mg, 2 mmol) or *tert*-butyldimethylsilyl chloride (TBSCI: 3.01 g, 20 mmol) and imidazole (2.04 g, 30 mmol). After completion of the addition, the reaction mixture was allowed to stir at rt for 1 h. Then the mixture was quenched by cooled aqueous HCl or NaHCO₃ solution and DCM (200 mL). The organic fractions were collected, and the aqueous phase was extracted with DCM (2×100 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) to give **4ac** (4.72 g, 71%) or **6t** (5.42 g, 80%). The detail spectra data was described in detail below (Part 5).



4.3. Others were synthesized according to "General Procedure I or II" as below:

$$\begin{array}{c} O \\ R_1 \\ R_2 \end{array} \xrightarrow{BF_3 \bullet OEt_2, \text{ Thiol}} \\ DCM, RT, 3 \text{ h} \\ \textbf{K}_1 \\ \textbf{K}_2 \\ \textbf{K}_1 \\ \textbf{K}_2 \\ \textbf{K}_1 \\ \textbf{K}_2 \\ \textbf{K}_2 \\ \textbf{K}_1 \\ \textbf{K}_2 \\ \textbf{K}$$

General Procedure I: To a stirred solution of compound **4** (8 mmol) in DCM (40 mL) were added thiol (1,3-propanedithiol, 1,2-ethanedithiol, 2-mercaptoethanol, 3-mercaptopropanol, 2-mercaptophenol, 2-aminothiophenol or L-cysteine ethyl ester hydrochloride: 8 mmol; 4-methylbenzenethiol or benzyl

mercaptan: 16 mmol) and BF3•OEt2 (1.97 mL, 16 mmol) at rt. After completion of the addition, the reaction mixture was allowed to stir at rt for 3 h. Then the mixture was quenched by saturated aqueous NaHCO₃ solution (100 mL) and CH₂Cl₂ (100 mL). The organic fractions were collected, and the aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound 3.

2-Methyl-2-phenyl-1,3-dithiane (3a)



 $3a^{17}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.26 g, 75%). ¹H-NMR (400 MHz, CDCl₃) δ: 7.96–7.91 (m, 2H), 7.38–7.33 (m, 2H), 7.26–7.21 (m, 1H), 2.76–2.64 (m, 4H), 1.95–1.89 (m, 2H), 1.78 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 143.8, 128.5, 127.7, 127.0, 53.9, 32.8, 28.1, 24.6. IR 3055.6, 2907.4, 1593.1, 1485.7, 1440.9, 1368.0, 1275.1, 1179.9, 1062.5, 906.6, 866.5, 760.5 cm⁻¹; HRMS

 (ESI^{+}) (m/z) calcd. for C₁₁H₁₅S₂ [M+H]⁺ 211.0610; found 211.0610.

2-Methyl-2-(4-phenylphenyl)-1,3-dithiane (3b)



3b was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (1.83 g, 80%). M.P. 135–137 °C. ¹H-NMR (400 MHz, CDCl₃) δ: 8.03-7.99 (m, 2H), 7.65-7.60 (m, 4H), 7.48-7.43 (m, 2H), 7.39-7.34 (m, 1H), 2.81-2.75 (m, 4H), 2.02–1.95 (m, 2H), 1.85 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 143.1, 140.7, 140.0, 128.9, 128.4, 127.5, 127.4, 127.2, 53.9, 32.9, 28.3, 24.8. IR 2878.7,

1591.8, 1478.2, 1390.6, 1275.8, 1175.3, 1069.9, 999.6, 845.7, 761.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₇H₁₉S₂ [M+H]⁺ 287.0923; found 287.0922.

2-Methyl-2-(4-benzyloxyphenyl)-1,3-dithiane (3d)



3d was purified by flash column chromatography (dichloromethane/hexane = 1:1 to 2:1) as a white solid (1.77 g, 70%). M.P. 98–100 °C. ¹H-NMR (400 MHz, CDCl₃) δ: 7.87-7.82 (m, 2H), 7.49-7.36 (m, 5H), 7.00-6.95 (m, 2H), 5.08 (s, 2H), 2.81-2.69 (m, 4H), 1.99–1.93 (m, 2H), 1.81 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 158.0, 137.1, 136.2, 129.3, 128.7, 128.1, 127.7, 114.8, 70.2, 53.6, 32.3, 28.3, 24.9. IR

3030.9, 2906.3, 1600.2, 1573.8, 1498.1, 1453.7, 1383.7, 1287.4, 1236.1, 1169.8, 1070.4, 1007.1, 835.9, 736.5 cm^{-1} ; HRMS (ESI⁺) (m/z) calcd. for $C_{18}H_{21}OS_2 [M+H]^+ 317.1028$; found 317.1028.

2-Methyl-2-(4-acetoxyphenyl)-1,3-dithiane (3e)



 $3e^{18}$ was purified by flash column chromatography (dichloromethane/hexane = 1:1) to 2:1) as a light-yellow oil (1.70 g, 79%). ¹H-NMR (400 MHz, CDCl₃) δ: 7.96-7.92 (m, 2H), 7.10-7.05 (m, 2H), 2.75-2.69 (m, 4H), 2.30 (s, 3H), 1.99-1.88 (m, 2H), 1.77 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 169.5, 149.7, 141.5, 129.2, 121.6, 53.7, 33.1, 28.2, 24.7, 21.3. IR 2900.7, 1763.3, 1591.2, 1494.0, 1415.5, 1363.6, 1277.8, 1189.2, 1067.1, 1011.1, 903.9, 846.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₇O₂S₂ [M+H]⁺ 269.0664; found 269.0666.

2-Methyl-2-(4-fluorophenyl)-1,3-dithiolane (3f)



3f was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.37 g, 80%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.76–7.69 (m, 2H), 7.01–6.94 (m, 2H), 3.52–3.43 (m, 2H), 3.42–3.34 (m, 2H), 2.13 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 160.7 (d, *J* = 245 Hz), 141.9 (d, *J* = 3.2 Hz), 128.8 (d, *J* = 8 Hz),

114.7 (d, J = 21.3 Hz), 68.1, 40.6, 34.0. IR 2922.4, 1599.3, 1501.2, 1445.3, 1372.8, 1273.8, 1224.2, 1106.3, 1067.1, 1013.2, 833.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₀H₁₂FS₂ [M+H]⁺ 215.0359; found 215.0357.

2-Methyl-2-(4-iodophenyl)-1,3-dithiolane (3i)



3i was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.86 g, 72%). ¹H-NMR (400 MHz, CDCl₃) δ: 7.65–7.58 (m, 2H), 7.53–7.46 (m, 2H), 3.49–3.39 (m, 2H), 3.38–3.28 (m, 2H), 2.11 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 146.0, 137.0, 129.0, 92.9, 68.1, 40.5, 33.5. IR 2916.4, 1568.7, 1465.3,

1435.9, 1374.9, 1263.5, 1172.4, 1102.9, 1066.4, 817.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{10}H_{12}IS_2 [M+H]^+$ 322.9420; found 322.9412.

2-Methyl-2-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-1,3-dithiane (3j)



3j was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (1.78 g, 66%). M.P. 153–155 °C. ¹H-NMR (400 MHz, CDCl₃) δ: 7.98–7.93 (m, 2H), 7.84–7.81 (m, 2H), 2.73–2.67 (m, 4H), 1.96–1.90 (m, 2H), 1.76 (s, 3H), 1.35 (s, 12H). ¹³C-NMR (100 MHz, CDCl₃) δ: 147.2, 135.3, 127.3, 84.0, 54.4, 33.0, 28.2, 25.0, 24.7. IR 2972.6, 2906.4, 1600.9, 1391.9, 1356.7, 1324.0,

1265.7, 1209.9, 1138.7, 1066.6, 1013.9, 849.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{17}H_{26}BO_2S_2$ [M+H]⁺ 337.1462; found 337.1468.

2-(2,3-dihydrobenzofuran-5-yl)-1,3-dithiane (3m)



3m was purified by flash column chromatography (dichloromethane/hexane = 1:1 to 2:1) as a white solid (1.33 g, 70%). M.P. 167–169 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.32 (s, 1H), 7.18 (dd, J = 8.2, 2.0 Hz, 1H), 6.71 (d, J = 8.2 Hz, 1H), 5.11 (s, 1H), 4.52 (t, J = 8.7 Hz, 2H), 3.15 (t, J = 8.7 Hz, 2H), 3.08–2.99 (m, 2H), 2.91–2.84 (m,

2H), 2.18–2.11 (m, 1H), 1.95–1.83 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 160.3, 131.3, 127.8, 127.6, 124.4, 109.3, 71.5, 51.1, 32.3, 29.6, 25.1. IR 2926.3, 2891.1, 1602.5, 1483.4, 1417.2, 1319.8, 1275.6, 1237.0, 1174.2, 1099.0, 898.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₅OS₂ [M+H]⁺ 239.0559; found 239.0550.

2-(2-ethynylphenyl)-1,3-dithiane (30)



THF (40 mL) was used as the reaction solvent instead of DCM, and **30** was purified by flash column chromatography (dichloromethane/hexane = 1:1 to 2:1) as a white solid (1.15 g, 65%). M.P. 102–104 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.65 (dd, J = 7.9, 1.2 Hz, 1H), 7.47 (dd, J = 7.7, 1.4 Hz, 1H), 7.34 (td, J = 7.6, 1.4 Hz, 1H), 7.22 (td, J = 7.6,

1.4 Hz, 1H), 5.73 (s, 1H), 3.37 (s, 1H), 3.14–3.05 (m, 2H), 2.87 (dt, J = 14.4, 4.2 Hz, 2H), 2.20–2.10 (m, 1H), 1.99–1.86 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 141.0, 133.1, 129.6, 128.14, 128.09, 120.7, 82.2, 80.9, 48.9, 32.3, 25.2. IR 3236.8, 3048.4, 2945.9, 2891.1, 2103.2, 1475.4, 1443.1, 1271.2, 1243.2, 1191.3, 756.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₃S₂ [M+H]⁺ 221.0453; found 221.0452.

2-(benzofuran-2-yl)-1,3-dithiane (3w)



3w was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.40 g, 74%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.50 (d, *J* = 7.5 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.28–7.22 (m, 1H), 7.22–7.16 (m, 1H), 6.77 (s, 1H), 5.26 (s, 1H), 3.02–2.94 (m, 2H), 2.93–2.85 (m, 2H), 2.14–2.04 (m, 1H),

2.04–1.92 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 154.7, 154.6, 128.0, 124.5, 122.9, 121.0, 111.3, 104.7, 41.9, 29.8, 25.2. IR 3087.7, 2901.8, 1583.8, 1446.1, 1419.2, 1341.4, 1273.4, 1244.7, 1199.0, 1159.7, 1124.6, 1005.2, 748.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₃OS₂ [M+H]⁺ 237.0402; found 237.0399.

2,2-Dipentyl-1,3-dithiane (3z)



 $3z^{19}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.50 g, 72%). ¹H-NMR (400 MHz, CDCl₃) δ : 2.77–2.74 (m, 4H), 1.92–1.88 (m, 2H), 1.82–1.79 (m, 4H), 1.40–1.35 (m, 4H), 1.32–1.27 (m, 4H), 1.27–1.22 (m, 4H), 0.85 (t, J = 4.0 Hz, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 52.4, 37.1, 31.0,

25.0, 24.7, 22.7, 21.6, 13.1. IR 2930.2, 2860.7, 1458.2, 1421.8, 1376.4, 1272.9, 1239.0, 1120.4, 907.5, 734.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{14}H_{29}S_2$ [M+H]⁺ 261.1705; found 261.1704.

9-Phenyl-1,5-dithiaspiro[5.5]undecane (3aa)



3aa²⁰ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (1.44 g, 68%). M.P. 110–112 °C; ¹H-NMR (400 MHz, CDCl₃) δ: 7.31–7.26 (m, 2H), 7.25–7.21 (m, 2H), 7.21–7.16 (m, 1H), 2.93–2.89 (m, 2H), 2.80–2.75 (m, 2H), 2.50 (tt, *J* = 12.1, 3.7 Hz, 1H), 2.50–2.44 (m, 2H), 2.05–1.94 (m, 4H), 1.87–1.78 (m, 2H), 1.76–1.69 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 146.7, 128.5, 127.0, 126.3, 49.8, 44.3, 38.2, 29.7, 26.4, 25.9. IR 3018.4, 2918.7, 1596.0, 1487.4, 1417.4, 1268.8, 1232.2, 1099.8, 1066.0, 993.0,

831.9, 755.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{15}H_{21}S_2$ [M+H]⁺ 265.1079; found 265.1076.

(5S)-17-Acetyl-4,5-dihydrotestosterone Cyclic 1,3-Propanediyl Dithioacetal (3ac)



3ac was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (2.03 g, 60%). M.P. 213–215 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 4.57 (t, *J* = 8.5 Hz, 1H), 2.90–2.84 (m, 2H), 2.76–2.71 (m, 2H), 2.23–2.08 (m, 2H), 2.02 (s, 3H), 2.00–1.93 (m, 2H), 1.92–1.78 (m, 2H), 1.73–1.53 (m, 6H), 1.52–1.38 (m, 4H), 1.33–1.19 (m, 4H), 1.18–0.88 (m, 4H), 0.80 (s, 3H), 0.76 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 171.3, 83.0,

54.1, 50.9, 50.6, 42.8, 41.5, 40.6, 37.0, 36.6, 35.4, 34.6, 34.0, 31.5, 28.1, 27.7, 26.41, 26.35, 26.1, 23.6, 21.3, 20.6, 12.2, 12.0. IR 2920.5, 2851.3, 1722.8, 1439.0, 1378.6, 1246.6, 1028.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{24}H_{39}O_2S_2$ [M+H]⁺ 423.2386; found 423.2388. [α]_D²⁵ = +21 (*c* 1, CHCl₃).

1-(Bisbenzylthio)indane (3ad)



InCl₃ (177 mg, 0.8 mmol) was used as the reaction solvent instead of BF₃•OEt₂, and **3ad** was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.45 g, 50%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.28–7.16 (m, 14H), 3.89 (d, *J* = 12.0 Hz, 2H), 3.71 (d, *J* = 12.0 Hz, 2H), 2.96 (t, *J* = 6.9 Hz, 2H), 2.44 (t, *J* = 6.9

Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 144.0, 142.8, 137.4, 129.3, 128.6, 128.4, 127.1, 126.5, 125.5, 123.9, 67.7, 43.1, 36.0, 30.6. IR 2936.2, 2879.2, 1616.9, 1407.2, 1321.9, 1162.9, 1117.5, 1013.0, 758.9, 710.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₃H₂₃S₂ [M+H]⁺ 363.1236; found 363.1223.

1-[Bis(4-tolylthio)methyl]-4-tert-butylbenzene (3ae)



3ae was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (2.39 g, 76%). M.P. 84–86 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.28–7.20 (m, 8H), 7.03 (d, *J* = 7.8 Hz, 4H), 5.31 (s, 1H), 2.30 (s, 6H), 1.29 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 151.0, 138.0, 137.0, 133.1, 131.4, 129.7, 127.6, 125.5,

61.3, 34.7, 31.5, 21.3. IR 2959.1, 2864.1, 1600.8, 1487.9, 1401.0, 1360.7, 1265.9, 1213.2, 1084.3, 1015.4, 800.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₅H₂₈NaS₂ [M+Na]⁺ 415.1525; found 415.1534.

1-[Bis(4-tolylthio)methyl]-4-methoxybenzene (3af)



3af²¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (2.11 g, 72%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.31–7.24 (m, 6H), 7.05 (d, *J* = 7.9 Hz, 4H), 6.78–6.83 (m, 2H), 5.33 (s, 1H), 3.80 (s, 3H), 2.32 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 159.3, 138.0, 133.1, 132.1, 131.2,

129.7, 129.2, 113.8, 60.7, 55.4, 21.3. IR 2919.6, 1605.7, 1501.7, 1452.4, 1301.2, 1247.4, 1098.2, 1028.6, 835.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₂H₂₂NaOS₂ [M+Na]⁺ 389.1004; found 389.0998.

1-[Bis(4-tolylthio)methyl]-4-phenylbenzene (3ag)



3ag was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (2.48 g, 75%). M.P. 113–115 °C. ¹H-NMR (400 MHz, DMSO) δ : 7.67–7.58 (m, 4H), 7.56–7.51 (m, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.38–7.33 (m, 1H), 7.29 (d, *J* = 8.0 Hz, 4H), 7.10 (d, *J* = 8.0 Hz, 4H), 6.00 (s, 1H), 2.25 (s, 6H).

¹³C-NMR (100 MHz, DMSO) δ: 139.6, 139.4, 138.5, 137.2, 131.5, 130.5, 129.6, 128.9, 128.4, 127.6, 126.6, 57.1, 20.6. IR 3023.1, 2918.1, 1599.7, 1482.0, 1444.8, 1399.8, 1176.5, 1106.3, 1008.9, 838.2, 758.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{27}H_{24}NaS_2$ [M+Na]⁺ 435.1212; found 435.1208.

1-[Bis(2-Hydroxyethyl)thio]pyrene (3ah)



TsOH (800 mg, 4.64 mmol) was used instead of BF₃•OEt₂, and the mixture was refluxed with 2-mercaptoethanol (1.69 mL, 24 mmol) in EtOH for 24 h under nitrogen atmosphere. **3ah**²² was purified by flash column chromatography (ethyl acetate/hexane =1:5 to 2:1) as a yellow solid (2.21 g, 75%). M.P. 132–134 °C. ¹H-NMR (400 MHz, DMSO) δ : 8.65 (d, *J* = 9.4 Hz, 1H), 8.40–8.24 (m, 5H), 8.21–8.14 (m, 2H), 8.06 (t, *J* = 7.6 Hz, 1H), 6.43 (s, 1H), 4.80 (t, *J* = 5.4 Hz, 2H), 3.60–3.49 (m, 4H), 2.85–2.76 (m, 2H), 2.70–

2.62 (m, 2H). ¹³C-NMR (100 MHz, DMSO) δ : 134.4, 130.8, 130.3, 130.2, 127.54, 127.46, 127.3, 126.4, 126.0, 125.5, 125.3, 124.9, 124.1, 123.9, 60.8, 35.0. IR 3221.3, 2912.0, 1592.9, 1394.2, 1284.6, 1231.6, 1161.3, 1004.6, 823.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₁H₂₀NaO₂S₂ [M+Na]⁺ 391.0797; found 391.0789.

1-Oxa-5-thiaspiro[5.11]heptadecane (3ai)



THF (40 mL) was used as the reaction solvent instead of DCM, and **3ai** was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (1.23 g, 60%). M.P. 59–61 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 3.81 (t, *J* = 5.4 Hz, 2H), 2.86–2.82 (m, 2H), 2.17–2.08 (m, 2H), 1.83–1.68 (m, 4H), 1.34 (m, 18H). ¹³C-NMR (100 MHz, CDCl₃) δ : 85.5, 61.9, 33.3, 26.3, 26.2, 25.7, 24.1, 22.5, 22.1, 19.3. IR 2909.4, 2853.6, 1468.0, 1439.6, 1211.9, 1074.0, 1021.3, 722.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd.

for $C_{15}H_{29}OS [M+H]^+ 257.1934$; found 257.1929.

2-[2-(Ethoxycarbonyl)ethyl]-2-methyl-1,3-oxathiane (3aj)



THF (40 mL) was used as the reaction solvent instead of DCM, and **3aj** was purified by flash column chromatography (ethyl acetate/petroleum ether = 1:20 to 1:5) as a light-yellow oil (1.36 g, 78%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.03 (q, *J* = 7.1 Hz, 2H), 3.83–3.72 (m, 2H), 2.82–2.76 (m, 2H), 2.46–2.32 (m, 2H), 2.23–2.03 (m, 2H),

1.74–1.67 (m, 2H), 1.48 (s, 3H), 1.17 (t, J = 7.2 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 173.5, 80.7, 61.9,

60.4, 35.4, 29.1, 26.1, 25.1, 24.3, 14.2. IR 2939.4, 2873.1, 1729.8, 1438.2, 1373.7, 1171.7, 1094.4, 1015.8 cm^{-1} ; HRMS (ESI⁺) (m/z) calcd. for $C_{10}H_{19}O_3S$ [M+H]⁺ 219.1049; found 219.1039.

2-(2,4-Dichlorophenyl)-1,3-oxathiane (3ak)



THF (40 mL) was used as the reaction solvent instead of DCM, and 3ak was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (1.46 g, 73%). M.P. 60–62 °C. ¹H-NMR (400 MHz, CDCl₃) δ: 7.62 (d, J = 8.4 Hz, 1H), 7.34 (d, J = 2.1 Hz, 1H), 7.27 (dd, J = 8.4, 2.2 Hz, 1H), 6.03 (s, 1H), 4.36–4.29 (m, 1H), 3.79 (td, J = 12.5, 2.2 Hz, 1H), 3.21 (td, J = 13.2, 2.8 Hz, 1H), 2.86–2.79 (m, 1H), 2.18–2.05 (m, 1H), 1.82–1.74 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ: 135.9, 134.8, 132.0, 129.7, 129.2, 127.7, 80.7, 70.9, 29.3, 25.7. IR 2912.8, 2865.5, 1585.1, 1465.8, 1376.8, 1342.9, 1227.9, 1072.8, 852.5, 752.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{10}H_{11}Cl_2OS [M+H]^+ 248.9902$; found 248.9896.

2-Methyl-2-(4-trifluoromethylphenyl)-1,3-oxathiolane (3al)



THF (40 mL) was used as the reaction solvent instead of DCM, and 3al was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.41 g, 71%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.63 (d, J = 4.7 Hz, 2H), 7.59 (d, J = 5.1 Hz, 2H), 4.38–4.34 (m, 1H), 4.04–4.00 (m, 1H), 3.25–3.21 (m,

1H), 3.09–3.05 (m, 1H), 1.92 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 151.1, 129.2 (q, J = 18.4 Hz), 125.4, 125.2 (q, J = 2.1 Hz), 121.9 (q, J = 155 Hz), 95.0, 71.0, 34.6, 32.2. IR 2980.1, 2879.2, 1616.9, 1407.2, 1321.9, 1162.8, 1117.6, 1067.9, 1013.0, 840.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{11}H_{12}F_{3}OS$ [M+H]⁺ 249.0555; found 249.0567.

2-Ethyl-2-(6-methoxynaphthalen-2-yl)-1,3-oxathiolane (3an)



THF (40 mL) was used as the reaction solvent instead of DCM, and 3an was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.54 g, 70%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.93 (d, J = 1.2 Hz, 1H), 7.78 (d, J = 5.2 Hz, 1H), 7.74 (d, J = 4.9 Hz, 1H), 7.54 (dd, J = 4.9,

1.1 Hz, 1H), 7.20 (dd, J = 5.1, 1.5 Hz, 1H), 7.16 (d, J = 1.6 Hz, 1H), 4.42–4.39 (m, 1H), 4.04–4.00 (m, 1H), 3.92 (s, 3H), 3.21-3.16 (m, 1H), 3.08-3.04 (m, 1H), 2.26 (q, J = 4.1 Hz, 2H), 0.97 (t, J = 4.2 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 157.8, 140.4, 133.7, 129.7, 128.3, 126.8, 124.8, 123.8, 118.9, 105.5, 100.0, 70.7, 55.2, 37.4, 34.0, 9.8. IR 3055.1, 2927.4, 2871.1, 1599.1, 1473.2, 1378.9, 1335.2, 1220.3, 1122.3, 1024.7, 884.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{16}H_{19}O_2S$ [M+H]⁺ 275.1100; found 275.1096.

2-(Anthracen-9-yl)benzothiazoline (3ao)



EtOH (40 mL) was used as the reaction solvent instead of DCM, and no BF₃•OEt₂ was needed. **3ao** was purified by flash column chromatography (dichloromethane/hexane = 1:5 to 1:2) as a yellow solid (1.63 g, 65%). M.P. 126–128 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 8.75 (d, *J* = 8.1 Hz, 2H), 8.48 (s, 1H), 8.12 (s, 1H), 8.05–7.99 (m, 2H), 7.53–7.45 (m, 4H), 7.18 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.01 (td, *J* = 7.6, 1.3 Hz, 1H), 6.85 (td, *J* = 7.6, 1.2 Hz, 1H), 6.67 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.42

(s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 146.7, 131.7, 130.7, 130.1, 129.6, 128.0, 127.9, 126.2, 125.9, 125.1, 124.4, 122.1, 121.0, 110.5, 65.7. IR 3337.9, 3040.1, 1576.7, 1447.7, 1366.9, 1072.6, 1015.9, 844.1, 731.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₁H₁₆NS [M+H]⁺ 314.0998; found 314.1012.

2-(*n*-Heptyl)benzothiazoline (3ap)



EtOH (40 mL) was used as the reaction solvent instead of DCM, and no $BF_3 \cdot OEt_2$ was needed. **3ap**²³ was purified by flash column chromatography (dichloromethane/hexane = 1:5 to 1:2) as a light-yellow oil (1.32 g, 70%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.06 (dd, *J* = 7.6, 1.3 Hz, 1H), 6.89 (td, *J* = 7.6, 1.4 Hz, 1H), 6.72 (td, *J* = 7.5, 1.2 Hz, 1H), 6.63 (dd, *J* = 7.8, 1.2 Hz, 1H), 5.25 (t, *J* = 6.6 Hz, 1H), 3.99 (s, 1H), 1.91–1.85 (m, 2H), 1.43–1.29 (m, 10H), 0.89 (t, *J* = 7.0 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 146.7, 127.6, 125.2,

122.0, 120.8, 110.9, 69.0, 38.7, 31.8, 29.33, 29.25, 26.2, 22.7, 14.2. IR 3298.3, 2920.6, 2850.9, 1583.0, 1462.7, 1400.6, 1366.5, 1211.3, 1118.0, 1019.5, 736.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{14}H_{22}NS$ [M+H]⁺ 236.1467; found 236.1472.

2-(3-Bromo-4-fluorophenyl)-2-methyl-1,3-benzoxathiole (3aq)



CHCl₃ (40 mL) was used as the reaction solvent instead of DCM, and the mixture was refluxed under nitrogen for 3 h. **3aq** was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.56 g, 60%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.81 (dd, *J* = 6.4, 2.4 Hz, 1H), 7.49 (ddd, *J* = 8.6, 4.5, 2.4 Hz, 1H), 7.13–7.04 (m, 3H), 6.98–6.89 (m, 2H), 2.14 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 157.5 (d, *J* = 247 Hz), 154.6, 142.2 (d, *J* = 3.7 Hz), 130.4, 126.3, 125.9, 125.8 (d, *J*

= 7.5 Hz), 122.9, 122.2, 116.2 (d, J = 22.5 Hz), 111.0, 109.0 (d, J = 21.1 Hz), 98.3, 31.1. IR 1579.4, 1491.9, 1456.9, 1384.7, 1228.9, 1083.4, 1045.5, 1017.0, 852.7, 739.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₄H₁₁BrFOS [M+H]⁺ 324.9693; found 324.9690.

2-Ethyl-2-(3-fluorophenyl)-1,3-benzoxathiole (3ar)



CHCl₃ (40 mL) was used as the reaction solvent instead of DCM, and the mixture was refluxed under nitrogen for 3 h. **3ar** was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.35 g, 65%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.30–7.19 (m, 3H), 7.04 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.02–6.90 (m, 3H), 6.82 (td, *J* = 7.5, 1.3 Hz, 1H), 2.44–2.24 (m, 2H), 0.96 (t, *J* = 7.3 Hz, 3H). ¹³C-NMR

(100 MHz, CDCl₃) δ : 161.5 (d, *J* = 245 Hz), 155.2, 146.7 (d, *J* = 6.6 Hz), 129.9 (d, *J* = 8.1 Hz), 126.0, 125.8, 122.6, 122.1, 120.8 (d, *J* = 2.9 Hz), 114.8 (d, *J* = 21.1 Hz), 112.4 (d, *J* = 23.2 Hz), 110.6, 102.7 (d, *J* = 1.9 Hz), 36.7, 9.3. IR 2935.2, 1585.8, 1458.3, 1229.1, 1119.9, 862.9, 781.6, 739.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₅H₁₄FOS [M+H]⁺ 261.0744; found 261.0757.

2-(4-Bromophenyl)benzothiazoline (3as)



EtOH (40 mL) was used as the reaction solvent instead of DCM, and no BF₃•OEt₂ was needed. **3as** was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a yellow solid (1.64 g, 70%). M.P. 81–83 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.50–7.46 (m, 2H), 7.42–7.38 (m, 2H), 7.04 (dd, J = 7.6, 1.3 Hz, 1H), 6.96 (td, J = 7.7, 1.3 Hz, 1H), 6.77 (td, J = 7.5, 1.2 Hz, 1H),

6.65 (dd, J = 7.7, 1.2 Hz, 1H), 6.30 (s, 1H), 4.03 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 146.1, 140.9, 131.9, 128.3, 126.3, 125.7, 122.7, 121.7, 120.9, 110.0, 69.3. IR 3342.5, 1576.4, 1461.9, 1391.1, 1250.2, 1064.1, 826.1, 746.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₁BrNS [M+H]⁺ 291.9790; found 291.9789.

2-Methyl-2-(6-methoxynaphthalen-2-yl)-1,3-benzoxathiole (3at)



THF (40 mL) was used as the reaction solvent instead of DCM, and **3at** was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a white solid (1.83 g, 74%). M.P. 122–124 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.99 (d, *J* = 2.0 Hz, 1H), 7.76 (d, *J* = 8.7 Hz, 2H), 7.68 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.18 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.16–7.13 (m, 2H), 7.11–7.06 (m, 1H), 7.02 (dd, *J* = 8.0, 1.4 Hz, 1H), 6.90 (td, *J* = 7.4, 1.4 Hz, 1H), 3.93 (s, 3H), 2.29

(s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 158.3, 155.1, 139.3, 134.3, 130.0, 128.2, 127.3, 126.6, 126.0, 124.0, 123.3, 122.5, 122.1, 119.3, 110.9, 105.8, 99.8, 55.4, 31.0. IR 2963.1, 1600.9, 1454.0, 1368.9, 1268.9, 1232.1, 1198.7, 1089.4, 1027.8, 841.8, 742.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₉H₁₇O₂S [M+H]⁺ 309.0944; found 309.0941.

(2RS,4R) Ethyl-2-(4-methylphenyl)thiazolidine-4-carboxylate (3au)



EtOH (40 mL) was used as the reaction solvent instead of DCM, and Et₃N (1.11 mL, 8 mmol) was added. **3au²⁴** was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:2) as a light-yellow oil (1.51 g, 75%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.44–7.35 (m, 2H), 7.19–

7.11 (m, 2H), 5.81–5.52 (m, 1H), 4.30–4.21 (m, 2H), 4.21–3.93 (m, 1H), 3.48–3.35 (m, 1H), 3.22–3.07 (m, 1H), 2.69 (s, 1H), 2.36–2.32 (m, 3H), 1.33–1.27 (m, 3H). 13 C-NMR (100 MHz, CDCl₃) δ : 171.8, 171.2, 138.6, 138.3, 137.6, 135.2, 129.4, 129.1, 127.4, 126.9, 72.6, 70.8, 65.7, 64.4, 61.7, 61.6, 39.3, 38.2, 21.2, 21.1, 14.2. IR 3312.5, 2926.5, 1734.2, 1512.8, 1449.1, 1374.1, 1266.3, 1190.4, 1094.2, 1025.5, 763.0 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₈NO₂S [M+H]⁺ 252.1053; found 252.1061.

(2RS,4R) Ethyl-2-(2-fluorophenyl)thiazolidine-4-carboxylate (3av)



EtOH (40 mL) was used as the reaction solvent instead of DCM, and Et₃N (1.11 mL, 8 mmol) was added. **3av** was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:2) as a light-yellow oil (0.92 g, 45%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.64–7.49 (m, 1H), 7.35–7.21 (m, 1H), 7.19–7.00 (m, 2H),

6.04–5.78 (m, 1H), 4.30–4.24 (m, 2H), 4.24–3.93 (m, 1H), 3.50–3.37 (m, 1H), 3.17–3.08 (m, 1H), 2.82 (s, 1H), 1.34–1.29 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 171.6, 171.1, 159.5 (d, *J* = 247 Hz), 159.2 (d, *J* = 246 Hz), 130.3 (d, *J* = 8.5 Hz), 129.4 (d, *J* = 12.3 Hz), 129.3 (d, *J* = 8.1 Hz), 128.6 (d, *J* = 3.3 Hz), 127.2 (d, *J* = 3.6 Hz), 125.3 (d, *J* = 12.5 Hz), 124.6 (d, *J* = 3.5 Hz), 124.1 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 21.7 Hz), 115.5 (d, *J* = 21.1 Hz), 65.8, 65.7 (d, *J* = 3.7 Hz), 64.8, 64.3 (d, *J* = 2.2 Hz), 61.82, 61.79, 39.2, 38.0, 14.2. IR 3319.3, 2981.4, 1732.5, 1585.7, 1487.0, 1454.9, 1374.6, 1265.0, 1192.1, 1090.0, 1025.9, 753.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₅FNO₂ S [M+H]⁺ 256.0802; found 256.0811.

(2RS,4R) Ethyl-2-(3-methoxyphenyl)thiazolidine-4-carboxylate (3aw)



EtOH (40 mL) was used as the reaction solvent instead of DCM, and Et₃N (1.11 mL, 8 mmol) was added. **3aw** was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:2) as a light-yellow oil (1.07 g, 50%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.30–7.21 (m, 1H), 7.13–

7.04 (m, 2H), 6.89–6.78 (m, 1H), 5.82–5.52 (m, 1H), 4.29–4.21 (m, 2H), 4.19–3.93 (m, 1H), 3.82–3.79 (m, 3H), 3.48–3.35 (m, 1H), 3.19–3.07 (m, 1H), 2.67 (s, 1H), 1.34–1.28 (m, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 171.8, 171.2, 159.9, 159.7, 143.2, 139.8, 129.8, 129.5, 119.8, 119.3, 114.4, 113.4, 113.0, 112.5, 72.6, 70.8, 65.8, 64.5, 61.8, 61.7, 55.4, 55.3, 39.3, 38.3, 14.2. IR 3313.8, 2934.5, 1733.3, 1595.0, 1458.4, 1373.2, 1255.3, 1154.5, 1039.1, 758.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₈NO₃S [M+H]⁺ 268.1002; found 268.1012.

$$R^{OH} \xrightarrow{Ac_2O, AcOH} R^{O} \xrightarrow{S} Me$$

General Procedure II: To a solution of compound **6** (6.5 mmol) in dimethyl sulfoxide (20 mL) was added a mixture of acetic anhydride (14 mL) and acetic acid (2.5 mL) at rt. After completion of the addition, the mixture was allowed to stand for 24-72 h (primary alcohol: 24 h; secondary alcohol: 48 h; tertiary alcohol: 72 h). Then the mixture was quenched by saturated aqueous NaHCO₃ solution (200 mL) and ethyl acetate (100 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (3 × 50 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography to give compound **5**.

Methylthiomethyl 2-phenoxyethyl ether (5c)



5c was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.97 g, 75%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.28–7.23 (m, 2H), 6.95–6.90 (m, 3H), 4.72 (s, 2H), 4.12 (t, *J* = 4.6 Hz, 2H), 3.88 (t, *J* = 4.8 Hz, 2H), 2.15 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 158.8, 129.5, 121.0,

114.7, 75.6, 67.1, 66.3, 13.9. IR 2922.2, 1742.0, 1594.6, 1493.0, 1430.0, 1369.6, 1299.1, 1241.8, 1212.4, 1174.3, 1085.1, 1022.9, 959.4, 922.2, 840.6, 752.9, 607.8, 509.7, 464.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{10}H_{15}O_2S$ [M+H]⁺ 199.0787; found 199.0786.

Cyclohexylmethyl methylthiomethyl ether (5d)



5d was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.76 g, 67%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.61 (s, 2H), 3.30 (d, *J* = 7.8 Hz, 2H), 2.13 (s, 3H), 1.77–1.67 (m, 5H), 1.60–1.54 (m, 1H), 1.26–1.16 (m, 3H), 0.99–0.89 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 75.4, 74.0,

37.9, 30.2, 26.7, 26.0, 13.9. IR 2919.9, 2850.1, 1445.0, 1299.1, 1260.0, 1068.3, 956.6, 882.2, 728.9, 678.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₁₉OS [M+H]⁺ 175.1151; found 175.1154.

Cyclopentylmethyl methylthiomethyl ether (5e)



5e was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.89 g, 85%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.60 (s, 2H), 3.36 (d, *J* = 7.0 Hz, 2H), 2.14–2.08 (m, 4H), 1.76–1.68 (m, 2H), 1.60–1.47 (m, 4H), 1.24–1.19 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 75.4, 72.8, 39.3, 29.8,

25.6, 13.9. IR 2948.4, 2863.9, 1434.8, 1299.5, 1256.9, 1070.2, 960.0, 923.7, 728.7, 678.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_{20}NOS [M+NH_4]^+$ 178.1260; found 178.1253.

Methylthiomethyl n-undecanyl ether (5f)

 $\begin{array}{l} \text{Me} \underbrace{0}_{11} \underbrace{$

3-[(tert-Butyloxycarbonyl)amino]propanyl methylthiomethyl ether (5g)



5g was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (1.16 g, 76%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.81 (s, 1H), 4.59 (s, 2H), 3.54 (t, *J* = 6.0 Hz, 2H), 3.23–3.18 (m, 2H),

2.12 (s, 3H), 1.78–1.72 (m, 2H), 1.41 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 156.1, 79.1, 75.5, 66.3, 38.5, 29.6, 28.5, 14.1. IR 3357.9, 2925.7, 1693.2, 1511.7, 1447.5, 1391.5, 1364.8, 1246.3, 1166.8, 1072.9, 859.7, 779.1, 728.6, 678.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₀H₂₂NO₃S [M+H]⁺ 236.1315; found 236.1313.

3-(3-Trifluoromethylphenyl)propanyl methylthiomethyl ether (5h)



5h was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.53 g, 89%) as colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ : 7.46–7.38 (m, 4H), 4.64 (s, 2H), 3.53 (t, *J* = 6.1 Hz, 2H), 2.76 (t, *J* = 7.7 Hz, 2H), 2.17 (s, 3H),

1.90 (p, J = 6.7 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 142.9, 132.0, 130.3 (q, J = 32.0 Hz), 128.9, 125.3 (q, J = 4.0 Hz), 122.8 (q, J = 4.0 Hz), 120.3 (q, J = 270.0 Hz), 75.5, 67.2, 32.4, 31.0, 14.2. IR 2924.4, 1744.4, 1442.0, 1326.4, 1210.6, 1162.4, 1121.3, 1068.2, 1017.9, 959.7, 907.4, 800.3, 732.7, 701.1, 458.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₆F₃OS [M+H]⁺ 265.0868; found 265.0876.

2-(Naphthalen-1-yl)ethyl methylthiomethyl ether (5i)



5i was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.22 g, 81%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.09 (d, *J* = 8.3 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 9.4 Hz, 1H), 7.57–7.49 (m, 2H), 7.46–7.41 (m, 2H), 4.67 (s, 2H), 3.90 (t, *J* = 7.2 Hz, 2H),

3.40 (t, J = 7.2 Hz, 2H), 2.11 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 134.8, 133.9, 132.2, 128.9, 127.2, 126.9, 126.1, 125.61, 125.59, 123.8, 75.4, 68.3, 33.1, 14.0. IR 3046.2, 2916.7, 1727.2, 1594.8, 1510.1, 1431.4, 1392.6, 1299.2, 1258.9, 1163.6, 1062.2, 955.8, 862.1, 775.0, 728.8, 678.0, 596.5, 520.6, 478.0, 422.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₄H₁₆NaOS [M+Na]⁺ 255.0814; found 255.0810.

Cyclohexyl methylthiomethyl ether (5j)

5j²⁵ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.78 g, 75%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.63 (s, 2H), 3.61–3.56 (m, 1H), 2.14 (s, 3H), 1.88–1.83 (m, 2H), 1.73–1.69 (m, 2H), 1.54–1.50 (m, 1H), 1.25 (t, J = 9.7 Hz, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ : 74.5, 72.0, 32.1, 25.9, 24.3, 13.9. IR 2927.1, 2855.1, 1444.5, 1298.0, 1263.2, 1060.9, 931.2, 890.3, 792.7, 728.5, 677.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₁₇OS [M+H]⁺ 161.0995; found 161.0993.

Tetrahydropyran-4-yl methylthiomethyl ether (5k)

5k was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.97 g, 92%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.63 (s, 2H), 3.87 (dt, J = 11.7, 4.4 Hz, 2H), 3.85–3.81 (m, 1H), 3.45–3.39 (m, 2H), 2.12 (s, 3H), 1.86–1.81 (m, 2H), 1.60–1.51 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 71.8, 70.7, 65.7, 32.2, 13.8. IR 2922.6, 2846.8, 1743.6, 1435.3, 1366.7, 1296.9, 1155.5, 1067.9, 1004.2, 947.1, 858.9, 818.5, 728.7, 678.0, 599.6, 515.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₇H₁₅O₂S [M+H]⁺ 163.0787; found 163.0784.

trans-1-[(tert-Butyloxycarbonyl)amino]-4-methylthiomethyloxy cyclohexane (51)



51 was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (1.32 g, 74%) as white solid. M.P. 92–94 °C; ¹H-NMR (400 MHz, CDCl₃) δ : 4.64 (s, 2H), 4.44 (s, 1H), 3.61–3.55 (m,

1H), 3.44 (s, 1H), 2.15 (s, 3H), 2.05–1.97 (m, 4H), 1.44 (s, 9H), 1.39–1.35 (m, 2H), 1.21–1.15 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 155.3, 79.3, 73.7, 72.3, 49.0, 31.2, 30.4, 28.5, 13.8. IR 3320.8, 2976.9, 2931.6, 2860.4, 1676.0, 1522.4, 1445.2, 1365.5, 1310.0, 1271.2, 1229.5, 1164.3, 1076.5, 1038.5, 962.2, 926.7, 896.2, 856.6, 785.9, 735.4, 677.4, 646.4, 463.0 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₂₆NO₃S [M+H]⁺ 276.1628; found 276.1624.

(1R,2S,5R) 2-Isopropyl-5-methyl-1-methylthiomethyloxy cyclohexane (5m)

(1S,2R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl methylthiomethyl ether (50)



50 was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.53 g, 38%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.69–4.51 (m, 2H), 3.92 (ddd, J = 9.5, 3.2, 1.8 Hz, 1H), 2.14–2.10 (m, 4H), 1.97–1.90 (m, 1H), 1.74–1.68 (m, 1H), 1.62 (t, J = 4.6 Hz, 1H), 1.24–1.19 (m, 2H), 0.98

(dd, J = 13.0, 3.4 Hz, 1H), 0.86–0.83 (m, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 81.6, 74.0, 49.0, 47.9, 45.2, 35.9, 28.3, 27.0, 19.8, 19.0, 13.9, 13.7. IR 2947.3, 1450.2, 1368.8, 1301.0, 1261.9, 1112.7, 1062.9, 818.6, 728.7, 678.4, 473.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₂₂NaOS [M+Na]⁺ 237.1284; found 237.1282. $[\alpha]_D^{25} = -160$ (*c* 0.1, EtOH).

1,1-Dimethyl-2-phenylethyl methylthiomethyl ether (5p)

 $\begin{array}{c} \textbf{5p} \text{ was purified by flash column chromatography (ethyl acetate/hexane = 1:40} \\ \textbf{Me} \quad \textbf{5p} \end{array} \\ \begin{array}{c} \textbf{5p} \text{ was purified by flash column chromatography (ethyl acetate/hexane = 1:40} \\ \textbf{to 1:10) as a light-yellow oil (0.74 g, 54\%). ^{1}H-NMR (400 MHz, CDCl_3) \delta: \\ \textbf{7.26-7.20 (m, 5H), 4.56 (s, 2H), 2.81 (s, 2H), 2.16 (s, 3H), 1.19 (s, 6H). \\ \textbf{1^3C-NMR (100 MHz, CDCl_3) } \delta: 138.1, 130.7, 127.9, 126.3, 77.1, 66.9, 47.9, 25.2, 14.4. IR 3028.1, 2973.1, \\ \textbf{2919.5, 1494.2, 1449.7, 1372.8, 1302.7, 1219.8, 1130.7, 1040.6, 856.3, 763.6, 698.8, 610.6, 514.6, 468.5 cm^{-1}; \\ \textbf{HRMS (ESI^+) (m/z) calcd. for C_{12}H_{19}OS [M+H]^+ 211.1151; found 211.1149. \end{array}$

3,7,7-Trimethyl-7-methylthiomethyloxy heptaldehyde (5q)



5q was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.91 g, 60%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.74 (t, *J* = 2.3 Hz, 1H), 4.48 (s, 2H), 2.36 (ddd, *J* = 16.1, 5.7, 2.0 Hz, 1H), 2.24 (td, *J* = 8.1, 2.5 Hz, 1H),

2.18 (s, 3H), 2.10–2.02 (m, 1H), 1.48–1.29 (m, 6H), 1.19 (s, 6H), 0.95 (d, J = 6.7 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 203.1, 76.6, 66.8, 51.2, 41.0, 37.4, 28.3, 25.73, 25.71, 21.4, 20.1, 14.6. IR 2926.4, 2716.2, 1723.0, 1462.3, 1371.9, 1304.9, 1213.1, 1151.5, 1045.1, 961.7, 733.9, 683.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₂₄NaO₂S [M+Na]⁺ 255.1389; found 255.1389.

1-Ethyl-1,5-dimethylhexyl methylthiomethyl ether (5r)

Ме



5r was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (0.75 g, 53%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.44 (s, 2H), 2.18 (s, 3H), 1.55–1.50 (m, 3H), 1.45–1.41 (m, 2H), 1.30–1.28

(m, 2H), 1.16–1.14 (m, 5H), 0.87–0.85 (m, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 78.9, 66.2, 39.7, 38.1, 30.8, 28.0, 22.8, 22.75, 22.73, 21.4, 14.6, 8.1. IR 2949.1, 1462.0, 1374.5, 1300.5, 1154.3, 1042.0, 872.3, 733.2, 683.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₂₇OS [M+H]⁺ 219.1777; found 219.1775.

1-Adamantyl methylthiomethyl ether (5s)



5s²⁷ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (1.02 g, 74%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.58 (s, 2H), 2.17 (s, 3H), 2.14 (s, 3H), 1.79 (d, J = 2.8 Hz, 6H), 1.62–1.60 (m, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 74.1, 65.7, 41.9, 36.4, 30.6, 14.4. IR 2906.3, 2850.6, 1446.8, 1353.4, 1298.5, 1104.9, 1073.4, 1035.9, 905.6, 875.8, 813.9, 777.6, 679.3, 548.9, 464.9 cm⁻¹;

HRMS (ESI⁺) (m/z) calcd. for $C_{12}H_{21}OS [M+H]^+ 213.1308$; found 213.1301.

1-[4-[2-(tert-Butyldimethylsilyloxy)ethoxy]phenyl]-2-methyl-2-methylthiomethyloxypropan-1-one (5t)



5t was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:10) as a light-yellow oil (2.31 g, 89%) as colorless oil. ¹H-NMR (400 MHz, CDCl₃) δ : 8.28 (d, *J* = 5.2 Hz, 2H), 6.92 (d, *J* = 5.1 Hz, 2H), 4.45 (s, 2H), 4.10 (d, *J* = 3.0 Hz, 2H), 3.99–3.98 (m, 2H), 2.06 (s, 3H),

1.57 (s, 6H), 0.90 (s, 9H), 0.10 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 201.0, 162.8, 132.6, 127.5, 114.1, 83.8, 69.9, 69.6, 62.0, 26.0, 25.6, 18.5, 15.3, -5.1. IR 2929.3, 1742.6, 1670.7, 1598.3, 1506.0, 1427.0, 1371.0, 1254.7, 1211.6, 1159.7, 1129.4, 1014.4, 958.7, 912.1, 834.5, 775.6, 697.5, 599.3, 560.5, 516.5, 463.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₀H₃₅O₄SSi [M+H]⁺ 399.2020; found 399.2008.

2-(Thiophen-2-yl)ethyl methylthiomethyl ether (5u)



5u was purified by flash column chromatography (dichloromethane/hexane = 1:2 to 1:1) as a light-yellow oil (0.43 g, 35%). ¹H-NMR (400 MHz, CDCl₃) δ :

7.14 (dd, J = 5.1, 1.2 Hz, 1H), 6.93 (dd, J = 5.1, 3.4 Hz, 1H), 6.88–6.86 (m, 1H), 4.66 (s, 2H), 3.77 (t, J = 6.6 Hz, 2H), 3.11 (t, J = 7.3 Hz, 2H), 2.12 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 141.3, 126.8, 125.3, 123.8, 75.4, 68.6, 30.3, 14.1. IR 3071.5, 2856.1, 1761.7, 1431.4, 1300.7, 1201.8, 1083.0, 1050.1, 985.7, 954.2, 825.3, 688.3, 476.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₁₃OS₂ [M+H]⁺ 189.0402; found 189.0404.

5. Deprotections of thioacetals, thioketals and methylthiomethyl ether.



General Procedure III: To a stirred solution of compound **3** (1 mmol) in ethanol (EtOH: 10 mL) were added CeBr₃ (19.0 mg, 0.05 mmol) and 30% H₂O₂ (200 μ L, 2 mmol) at rt. After completion of the addition, the resulting mixture was allowed to stir at 40 °C for 15 min. Then the mixture was quenched by aqueous Na₂S₂O₃ (0.1 M, 40 mL) and ethyl acetate (50 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give compound **4**.

Acetophenone (4a)



4a²⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (103 mg, 86%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.98–7.93 (m, 2H), 7.59–7.53 (m, 1H), 7.44 (t, *J* = 7.9 Hz, 2H), 2.60 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 198.3, 137.3, 133.2, 128.7, 128.4, 26.7. IR 3062.1, 1680.2, 1593.2, 1445.1, 1357.9,

1179.6, 758.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₉O [M+H]⁺ 121.0648; found 121.0649.

4'-Phenylacetophenone (4b)



4b²⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a white solid (165 mg, 84%). M.P. 118–120 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 8.06–8.02 (m, 2H), 7.71–7.67 (m, 2H), 7.65–7.61 (m, 2H), 7.50–7.45 (m, 2H), 7.43–7.38 (m, 1H), 2.64 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 197.9, 145.9,

140.0, 136.0, 129.10, 129.06, 128.4, 127.42, 127.38, 26.8. IR 1672.5, 1592.6, 1479.6, 1398.6, 1356.5, 1202.2, 1122.2, 835.3, 759.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{14}H_{13}O$ [M+H]⁺ 197.0961; found 197.0957.

4'-Methoxyacetophenone (4c)



4c²⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (138 mg, 92%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.96–7.91 (m, 2H), 6.95–6.91 (m, 2H), 3.87 (s, 3H), 2.55 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 196.9, 163.6, 130.7, 130.5, 113.8, 55.6, 26.5. IR 1667.0, 1597.7, 1505.8,

1416.7, 1356.4, 1248.1, 1171.5, 1018.7, 829.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_9H_{11}O_2$ [M+H]⁺ 151.0754; found 151.0755.

4'-Benzyloxyacetophenone (4d)



4d²⁹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a white solid (186 mg, 82%). M.P. 93–95 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.96–7.92 (m, 2H), 7.45–7.30 (m, 5H), 7.04–6.99 (m, 2H), 5.13 (s, 2H), 2.55 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 196.8, 162.7, 136.3, 130.7, 130.6, 128.8, 128.3,

127.6, 114.6, 70.2, 26.4. IR 3060.5, 2939.3, 2881.9, 1674.3, 1593.3, 1506.3, 1451.6, 1422.6, 1356.3, 1243.1, 1006.0, 826.9, 757.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{15}H_{15}O_2$ [M+H]⁺ 227.1067; found 227.1066.

4'-Acetyloxyacetophenone (4e)



4e³⁰ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (142.55 mg, 80%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.00–7.95 (m, 2H), 7.20–7.15 (m, 2H), 2.58 (s, 3H), 2.31 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 196.9, 168.9, 154.4, 134.8, 130.0, 121.9, 26.7, 21.2. IR 3071.8, 1749.0, 1670.8, 1591.3, 1503.6, 1418.0, 1265.5, 1161.4, 1007.5, 850.3 cm⁻¹; HRMS (ESI⁺)

(m/z) calcd. for $C_{10}H_{11}O_3 [M+H]^+$ 179.0703; found 179.0700.

4'-Fluoroacetophenone (4f)



4f³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (117 mg, 85%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.01–7.94 (m, 2H), 7.15–7.08 (m, 2H), 2.58 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 196.6, 164.6 (d, J = 253 Hz), 133.7 (d, J = 2.9 Hz), 131.0 (d, J = 9.2 Hz), 115.7 (d, J = 21.6 Hz), 26.6.

IR 3073.3, 1682.2, 1594.3, 1504.5, 1408.4, 1357.5, 1227.6, 1155.1, 835.0 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_8FO [M+H]^+$ 139.0554; found 139.0549.

4'-Chloroacetophenone (4g)



4g³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (139 mg, 90%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.89–7.84 (m, 2H), 7.43–7.38 (m, 2H), 2.56 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 196.9, 139.6, 135.5, 129.8, 129.0, 26.6. IR 3066.7, 1682.3, 1585.2, 1485.8, 1395.4, 1356.5,

1255.6, 1092.3, 1011.7, 823.6, 758.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_8ClO [M+H]^+$ 155.0258; found 155.0254.

4'-Bromoacetophenone (4h)



4h³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (175 mg, 88%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.83–7.78 (m, 2H), 7.61–7.57 (m, 2H), 2.57 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 197.1, 135.9, 132.0, 130.0, 128.4, 26.6. IR 1666.1, 1576.2, 1390.4, 1258.7, 1171.7, 1068.0,

818.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_8BrO [M+H]^+$ 198.9753; found 198.9747.

4'-Iodoacetophenone (4i)



4i²⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a brown solid (224 mg, 91%). M.P. 80–82 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.84–7.80 (m, 2H), 7.67–7.63 (m, 2H), 2.56 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 197.4, 138.0, 136.5, 129.8, 101.2, 26.6. IR 1668.1, 1573.4, 1417.8, 1386.4, 1354.0, 1171.5,

813.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₈IO [M+H]⁺ 246.9614; found 246.9611.

4'-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)acetophenone (4j)



4j³² was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light-yellow oil (172 mg, 70%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.88 (q, *J* = 8.0 Hz, 4H), 2.61 (s, 3H), 1.35 (s, 12H). ¹³C-NMR (100 MHz, CDCl₃) δ : 198.6, 139.1, 135.0, 127.4, 84.3, 26.9, 25.0. IR 1678.1, 1506.6, 1393.8, 1353.7, 1261.5,

1140.3, 1090.4, 854.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₄H₂₀BO₃ [M+H]⁺ 247.1500; found 247.1498.

4-Methoxycarbonylbenzaldehyde (4k)



MeCN (10 mL) was used as the solvent instead of EtOH. $4k^{31}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (148 mg, 90%). ¹H-NMR (400 MHz, CDCl₃) δ : 10.10 (s, 1H), 8.21–8.17 (m, 2H), 7.97–7.93 (m, 2H), 3.96 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 191.8, 166.2,

139.3, 135.2, 130.3, 129.7, 52.7. IR 1720.7, 1682.2, 1572.2, 1500.4, 1432.6, 1387.8, 1193.9, 1102.3, 1007.8, 849.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_9H_9O_3$ [M+H]⁺ 165.0546; found 165.0542.

3,4-Dimethoxybenzaldehyde (4l)



MeCN (10 mL) was used as the solvent instead of EtOH. **4I**³³ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (143 mg, 86%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.81 (s, 1H), 7.41 (dd, J = 8.2, 1.9 Hz, 1H), 7.37 (d, J = 1.9 Hz, 1H), 6.93 (d, J = 8.2 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H). ¹³C-NMR

(100 MHz, CDCl₃) δ : 191.0, 154.5, 149.6, 130.1, 126.9, 110.4, 108.9, 56.2, 56.0. IR 3072.97, 2943.76, 2839.54, 2764.68, 1675.23, 1583.70, 1505.70, 1463.02, 1419.78, 1129.93, 1011.43, 869.50 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₁₁O₃ [M+H]⁺ 167.0703; found 167.0700.

2,3-Dihydrobenzofuran-5-carboxaldehdye (4m)



MeCN (10 mL) was used as the solvent instead of EtOH. $4m^{34}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (120 mg, 81%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.80 (s, 1H), 7.73–7.70 (m, 1H), 7.66–7.62 (m, 1H), 6.84 (d, J = 8.2 Hz, 1H), 4.64 (t, J = 8.8 Hz, 2H), 3.22 (t, J = 9.2 Hz, 2H).

¹³C-NMR (100 MHz, CDCl₃) δ: 190.7, 165.7, 133.1, 130.5, 128.5, 126.0, 109.7, 72.5, 28.8. IR 2906.3, 2833.3, 2742.8, 1677.6, 1596.9, 1486.1, 1441.2, 1327.5, 1239.7, 1091.9, 816.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₉O₂ [M+H]⁺ 149.0597; found 149.0592.

trans-Cinnamaldehyde (4n)



MeCN (10 mL) was used as the solvent instead of EtOH. **4n**³³ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (104 mg, 79%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.69 (d, J = 7.7 Hz, 1H), 7.58–7.52 (m, 2H), 7.49–7.40 (m, 4H), 6.68 (dd, J = 16.0, 7.7 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 193.7,

152.8, 134.1, 131.3, 129.2, 128.64, 128.55. IR 3057.9, 2813.5, 2741.8, 1668.6, 1621.7, 1448.8, 1296.4, 1247.8, 1118.7, 744.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₉O [M+H]⁺ 133.0648; found 133.0647.

2-Ethynylbenzaldehyde (40)



MeCN (10 mL) was used as the solvent instead of EtOH. **40**³⁵ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (107 mg, 82%). ¹H-NMR (400 MHz, CDCl₃) δ : 10.53 (s, 1H), 7.91 (dd, J = 7.7, 1.4 Hz, 1H), 7.60 (dd, J = 7.8, 1.5 Hz, 1H), 7.54 (td, J = 7.3, 1.5 Hz, 1H), 7.50–7.44 (m, 1H), 3.46 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 191.5, 136.7, 134.0, 133.8, 129.3, 127.4, 125.6, 84.4, 79.3. IR 3345.2,

2847.6, 2753.7, 2091.9, 1681.6, 1584.3, 1445.5, 1388.2, 1342.0, 1264.4, 1195.3, 726.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C_9H_7O [M+H]⁺ 131.0491; found 131.0490.

Benzophenone (4p)



4p³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (175 mg, 96%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.83–7.78 (m, 4H), 7.62–7.56 (m, 2H), 7.51–7.45 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ : 196.8, 137.7, 132.5, 130.2, 128.4. IR 3056.8, 1653.2, 1594.7, 1444.4, 1361.8, 1273.0, 756.5

 cm^{-1} ; HRMS (ESI⁺) (m/z) calcd. for $C_{13}H_{11}O$ [M+H]⁺ 183.0804; found 183.0797.

3,4-Dihydronaphthalen-1(2H)-one (4q)



4q³⁶ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (118 mg, 81%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.02 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.44 (td, *J* = 7.4, 1.5 Hz, 1H), 7.33–7.22 (m, 2H), 2.95 (t, *J* = 6.1 Hz, 2H), 2.64 (t, *J* = 6.3 Hz, 2H), 2.11 (p, *J* = 6.6 Hz, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 198.5, 144.6, 133.5, 132.7, 128.9, 127.3, 126.7, 39.3, 29.8, 23.4. IR 3025.1, 2941.2, 2871.7, 1678.7, 1599.1,

1452.1, 1323.3, 1186.2, 1024.3, 762.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{10}H_{11}O [M+H]^+$ 147.0804; found 147.0797.

2-Naphthaldehyde (4r)



MeCN (10 mL) was used as the solvent instead of EtOH. $4r^{31}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (131 mg, 84%). ¹H-NMR (400 MHz, CDCl₃) δ : 10.13 (s, 1H), 8.28 (s, 1H), 7.99–7.84 (m, 4H), 7.65–7.53 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 192.2, 136.5, 134.6, 134.1,

132.7, 129.6, 129.14, 129.10, 128.1, 127.1, 122.8. IR 2825.3, 1683.0, 1458.0, 1339.6, 1158.4, 870.0, 745.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{11}H_9O$ [M+H]⁺ 157.0648; found 157.0646.

2-Acetonaphthone (4s)



4s²⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (141 mg, 83%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.46 (s, 1H), 8.02 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.91–7.85 (m, 2H), 7.63–7.52 (m, 2H), 2.72 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 198.2, 135.7,

134.6, 132.6, 130.3, 129.7, 128.6, 128.5, 127.9, 126.9, 124.0, 26.8. IR 3057.5, 1668.7, 1460.1, 1425.8, 1360.4, 1274.9, 1186.0, 1123.0, 867.0, 751.0 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{12}H_{11}O$ [M+H]⁺ 171.0804; found 171.0800.

Fluorenone (4t)



4t³⁷ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a yellow solid (175 mg, 97%). M.P. 81–83 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 7.64 (d, J = 7.4 Hz, 2H), 7.53–7.44 (m, 4H), 7.32–7.24 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 194.0, 144.6, 134.8, 134.3, 129.2, 124.4, 120.4. IR 3054.2, 1706.1, 1596.8, 1443.0, 1291.6, 1185.2, 1088.9, 726.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₉O

 $[M+H]^+$ 181.0648; found 181.0641.

2-Acetylthiophene (4u)



4u³⁸ was purified by flash column chromatography (dichloromethane/hexane = 1:1 to 3:1) as a light-yellow oil (105 mg, 83%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.69 (dd, J = 3.8, 1.2 Hz, 1H), 7.63 (dd, J = 4.9, 1.1 Hz, 1H), 7.12 (dd, J = 5.0, 3.8 Hz, 1H), 2.57 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 190.9, 144.7, 133.9, 132.6, 128.2, 27.1. IR 3094.1, 1655.9,

1516.1, 1410.9, 1355.6, 1267.9, 1028.9, 852.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C_6H_7OS [M+H]⁺ 127.0212; found 127.0211.

2-Benzoylthiophene (4v)



 $4v^{39}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (166 mg, 88%). ¹H-NMR (400 MHz, CDCl₃) δ: 7.88–7.84 (m, 2H), 7.70 (dd, J = 4.9, 1.2 Hz, 1H), 7.63 (dd, J = 3.8, 1.2 Hz, 1H), 7.61–7.55 (m, 1H), 7.52– 7.46 (m, 2H), 7.14 (dd, J = 5.0, 3.8 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 188.3, 143.7, 138.2, 134.9, 134.3, 132.4, 129.2, 128.5, 128.1. IR 3099.1, 1623.7, 1588.8, 1511.9, 1447.3, 1409.2,

 $1049.4, 708.0 \text{ cm}^{-1}$; HRMS (ESI⁺) (m/z) calcd. for C₁₁H₉OS [M+H]⁺ 189.0369; found 189.0368.

Benzofuran-2-carboxaldehyde (4w)



MeCN (10 mL) was used as the solvent instead of EtOH. $4w^{40}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (120) mg, 82%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.84 (s, 1H), 7.71 (dt, J = 7.9, 1.0 Hz, 1H),

7.60-7.53 (m, 2H), 7.52-7.46 (m, 1H), 7.34-7.29 (m, 1H).¹³C-NMR (100 MHz, CDCl₃) δ: 179.8, 156.3, 152.8, 129.3, 126.7, 124.3, 123.7, 117.9, 112.7. IR 3089.8, 2835.9, 2726.2, 1675.7, 1609.3, 1552.3, 1476.2, 1445.9, 1323.6, 1286.7, 1117.9, 735.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₇O₂ [M+H]⁺ 147.0441; found 147.0445.

Indole-3-carboxaldehyde (4x)



MeCN (10 mL) was used as the solvent instead of EtOH. 4x⁴⁰ was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1) as a brown solid (123 mg, 85%). M.P. 196-198 °C. ¹H-NMR (400 MHz, DMSO) δ: 12.13 (s, 1H), 9.93 (s, 1H), 8.30–8.25 (m, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.50 (d, *J* = 6.9 Hz, 1H), 7.29–7.18 (m, 2H).

¹³C-NMR (100 MHz, DMSO) δ: 184.9, 138.4, 137.0, 124.1, 123.4, 122.1, 120.8, 118.1, 112.4. IR 3103.9, 3041.4, 2815.6, 2737.4, 1627.1, 1571.4, 1518.6, 1436.7, 1385.6, 1237.8, 1122.7, 1078.5, 756.0 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_9H_8NO [M+H]^+$ 146.0600; found 146.0600.

1-Phenylpentan-1-one (4y)



 $4y^{39}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (140 mg, 86%). ¹H-NMR (400 MHz, CDCl₃) δ: 7.98–7.94 (m, 2H), 7.57–7.52 (m, 1H), 7.48–7.42 (m, 2H), 2.94 (t, *J* = 7.4 Hz, 2H), 1.69 (p, *J* = 7.3 Hz, 2H), 1.37 (h, J = 7.4 Hz, 2H), 0.93 (t, J = 7.4 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 200.7,

137.2, 133.0, 128.7, 128.2, 38.4, 26.6, 22.6, 14.1. IR 3061.9, 2932.3, 2868.8, 1682.4, 1593.2, 1450.3, 1353.1, 1263.4, 1207.6, 1010.6, 747.4 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₁H₁₅O [M+H]⁺ 163.1117; found 163.1114.

Undecan-6-one (4z)



 $4z^{41}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (160 mg, 94%). ¹H-NMR (400 MHz, CDCl₃) δ : 2.35 (t, J = 7.4 Hz, 4H), 1.52 (p, J = 7.5 Hz, 4H), 1.36–1.19 (m, 8H), 0.86 (t, J = 6.9 Hz, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 211.8, 42.9, 31.6, 23.7, 22.6, 14.0. IR 2928.7, 2863.7, 1712.4, 1460.6, 1411.1, 1371.7, 1131.7, 729.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₁H₂₃O [M+H]⁺ 171.1743; found 171.1737.

4-Phenylcyclohexanone (4aa)

4aa⁴² was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to **4aa**(m, 2H), 7.27–7.19 (m, 3H), 2.98 (tt, J = 12.1, 3.5 Hz, 1H), 2.57–2.46 (m, 4H), 2.26–2.17 (m, 2H), 2.01–1.87 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 211.2, 144.9, 128.7, 126.8, 126.7, 42.8, 41.5, 34.1. IR 3026.3, 2937.1, 2866.9, 1698.4, 1599.6, 1489.8, 1450.2, 1416.9, 1163.6, 755.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₅O [M+H]⁺ 175.1117; found 175.1114.

4-tert-Butylcyclohexanone (4ab)

t-Bu4ab³⁶ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to
1:5) as a light-yellow oil (119 mg, 77%). ¹H-NMR (400 MHz, CDCl₃) δ : 2.41–2.23 (m,
4H), 2.10–2.02 (m, 2H), 1.51–1.36 (m, 3H), 0.89 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃)
 δ : 212.6, 46.8, 41.4, 32.6, 27.7. IR 2945.7, 2868.3, 1719.2, 1460.4, 1420.3, 1362.1, 1218.3, 1160.8 cm⁻¹;
HRMS (ESI⁺) (m/z) calcd. for C₁₀H₁₉O [M+H]⁺ 155.1430; found 155.1432.

(5*S*)-17-Acetyl-4,5-dihydrotestosterone (4ac)



MeCN/AcOH (50/1, 10 mL) was used as the solvent instead of EtOH, and additional CeBr₃ (19 mg, 0.05 mmol) and H₂O₂ (204 μ L, 2 mmol) were needed. **4ac⁴³** was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a white solid (206 mg, 62%). M.P. 159–161 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 4.62–4.56 (m, 1H), 2.42–2.09 (m, 5H), 2.03 (s, 3H), 1.77–1.24 (m, 14H), 1.20–1.12 (m, 1H), 1.01 (s, 3H), 0.96–0.85

(m, 1H), 0.80 (s, 3H), 0.78–0.71 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 212.0, 171.3, 82.9, 53.9, 50.7, 46.7, 44.8, 42.8, 38.6, 38.2, 37.0, 35.9, 35.3, 31.4, 28.9, 27.7, 23.7, 21.3, 21.0, 12.3, 11.6. IR 2929.7, 2848.3, 1730.7, 1710.5, 1436.6, 1371.2, 1241.9, 1029.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₂₁H₃₃O₃ [M+H]⁺ 333.2424; found 333.2416. [α]_D²⁵ = +29 (*c* 1, CHCl₃).

1-Indanone (4ad)



4ad³⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (83.3 mg, 63%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.74 (d, *J* = 7.7 Hz, 1H), 7.60–7.55 (m, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 1H), 3.12 (t, *J* = 5.8 Hz, 2H),

4ad 2.71–2.66 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ: 207.2, 155.3, 137.2, 134.7, 127.4, 126.8, 123.8, 36.3, 25.9. IR 3049.6, 2943.9, 2893.5, 1704.0, 1601.8, 1471.1, 1439.6, 1274.8, 1195.5, 1033.3, 756.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₉O [M+H]⁺ 133.0648; found 133.0644.

4-*tert*-Butylbenzaldehyde (4ae)



MeCN (10 mL) was used as the solvent instead of EtOH. **4ae³¹** was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (146 mg, 90%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.98 (s, 1H), 7.81 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 1.36 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 192.2, 158.6,

134.2, 129.8, 126.1, 35.5, 31.2. IR 2906.5, 2870.8, 2823.3, 2726.9, 1697.1, 1604.4, 1467.6, 1414.1, 1368.9, 1217.2, 1105.6, 825.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{11}H_{15}O[M+H]^+$ 163.1117; found 163.1112.

4-Methoxybenzaldehyde (4af)



MeCN (10 mL) was used as the solvent instead of EtOH. **4af**³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (128 mg, 94%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.88 (s, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 6.99 (d, *J* = 8.4 Hz, 2H), 3.88 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 190.9, 164.7, 132.1,

130.1, 114.4, 55.7. IR 3009.5, 2837.6, 2738.7, 1681.7, 1596.0, 1508.3, 1460.3, 1253.1, 1213.5, 1154.8, 1021.2, 827.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_9O_2$ [M+H]⁺ 137.0597; found 137.0597.

4-Phenylbenzaldehyde (4ag)



MeCN (10 mL) was used as the solvent instead of EtOH. **4ag³¹** was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (162 mg, 89%). ¹H-NMR (400 MHz, CDCl₃) δ : 10.06 (s, 1H), 7.98–7.93 (m, 2H), 7.78–7.74 (m, 2H), 7.66–7.62 (m, 2H), 7.52–7.46 (m, 2H), 7.45–7.40 (m, 1H). ¹³C-NMR (100

MHz, CDCl₃) δ : 192.0, 147.3, 139.8, 135.3, 130.4, 129.1, 128.6, 127.8, 127.5. IR 3025.1, 2833.8, 2742.7, 1687.7, 1598.2, 1560.8, 1382.7, 1213.0, 1166.7, 830.3, 758.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₁O [M+H]⁺ 183.0804; found 183.0810.

1-Pyrenecarboxaldehyde (4ah)



MeCN (10 mL) was used as the solvent instead of EtOH. **4ah**⁴⁴ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a yellow solid (200 mg, 87%). M.P. 124–126 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 10.77 (s, 1H), 9.39 (d, *J* = 5.3 Hz, 1H), 8.41 (d, *J* = 4.5 Hz, 1H), 8.31–8.27 (m, 3H), 8.20 (dd, *J* = 7.7, 4.5 Hz, 2H), 8.10–8.06 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 193.2, 135.7, 131.5, 131.2, 131.1,

131.0, 130.8, 130.5, 127.5, 127.3, 127.2, 127.0, 126.7, 124.8, 124.7, 124.2, 123.1. IR 2705.2, 1675.1, 1577.8, 1498.3, 1370.5, 1174.1, 1051.6, 778.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{17}H_{11}O[M+H]^+$ 231.0804; found 231.0797.

Cyclododecanone (4ai)



 $4ai^{37}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:5) as a light-yellow oil (168 mg, 92%). ¹H-NMR (400 MHz, CDCl₃) δ: 2.47–2.42 (m, 4H), 1.74–1.65 (m, 4H), 1.35–1.20 (m, 14H). ¹³C-NMR (100 MHz, CDCl₃) δ: 212.7, 40.4, 24.8, 24.6, 24.2, 22.6, 22.4. IR 2926.0, 2856.4, 1702.1, 1468.0, 1435.4, 1362.4, 1129.8, 1019.2, 722.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₂₃O [M+H]⁺ 183.1743; found

183.1741.

Ethyl levulinate (4aj)



 $4aj^{45}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (123 mg, 85%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.06 (q, J =7.1 Hz, 2H), 2.69 (t, J = 6.5 Hz, 2H), 2.51 (t, J = 6.7 Hz, 2H), 2.15 (s, 3H), 1.19 (t, J = 7.2 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ: 206.8, 172.8, 60.7, 38.0, 29.9, 28.1, 14.2. IR 2934.7, 1717.1,

1363.6, 1204.9, 1185.2, 1155.2, 1029.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₇H₁₃O₃ [M+H]⁺ 145.0859; found 145.0854.

2,4-Dichlorobenzaldehyde (4ak)



MeCN (10 mL) was used as the solvent instead of EtOH. 4ak⁴⁶ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (154 mg, 88%). ¹H-NMR (400 MHz, CDCl₃) δ : 10.38 (s, 1H), 7.83 (d, J = 8.4 Hz, 1H), 7.44 (s, 1H), 7.33 (d, J = 8.4 Hz, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 188.5, 141.2, 138.6,

131.0, 130.5, 130.4, 128.0. IR 3081.5, 2884.8, 2639.7, 1683.1, 1576.9, 1461.3, 1412.3, 1248.9, 1043.4, 820.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_7H_5Cl_2O [M+H]^+$ 174.9712; found 174.9719.

4'-Trifluoromethylacetophenone (4al)



MeCN (10 mL) was used as the solvent instead of EtOH. 4al³⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (175 mg, 93%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.02 (d, J = 5.0 Hz, 2H), 7.69 (d, J = 4.8 Hz, 2H), 2.62 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 197.0, 139.8, 134.2 (q, J =

18.5 Hz), 128.7, 125.7 (q, J = 2.2 Hz), 121.4 (q, J = 155 Hz), 26.8. IR 3010.9, 1690.9, 1409.6, 1320.2, 1258.6, 1165.8, 1116.9, 1058.8, 1013.0, 837.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₈F₃O [M+H]⁺ 189.0522; found 189.0516.

3-Chlorobenzaldehyde (4am)



MeCN (10 mL) was used as the solvent instead of EtOH. 4am³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (128 mg, 91%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.97 (s, 1H), 7.84 (t, J = 1.1 Hz, 1H), 7.75 (dt, *J* = 4.3, 0.7 Hz, 1H), 7.58 (ddd, *J* = 4.6, 1.3, 0.6 Hz, 1H), 7.47 (t, *J* = 4.4 Hz, 1H).

¹³C-NMR (100 MHz, CDCl₃) δ: 191.0, 137.9, 135.6, 134.5, 130.5, 129.4, 128.1. IR 3070.5, 2830.1, 2729.5,

1695.6, 1572.4, 1470.1, 1432.1, 1191.0, 1070.9, 785.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_7H_6ClO [M+H]^+$ 141.0102; found 141.0099.

1-(6-methoxynaphthalen-2-yl)-propan-1-one (4an)



4an⁴⁷ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a brown solid (201 mg, 94%). M.P. 110–112 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 8.38 (s, 1H), 7.99 (dd, *J* = 4.9, 1.0 Hz, 1H), 7.81 (d, *J* = 5.1 Hz, 1H), 7.73 (d, *J* = 4.9 Hz, 1H), 7.17 (dd, *J* = 5.1, 1.5 Hz, 1H), 7.12 (d, *J* = 1.5 Hz,

1H), 3.92 (s, 3H), 3.07 (q, J = 4.1 Hz, 2H), 1.26 (t, J = 4.1 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 200.6, 159.7, 137.2, 132.4, 131.2, 129.5, 127.9, 127.1, 124.7, 119.7, 105.8, 55.5, 31.7, 8.6. IR 3059.5, 1674.9, 1618.2, 1474.8, 1383.1, 1344.9, 1185.4, 1017.3, 860.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₄H₁₅O₂ [M+H]⁺ 215.1067; found 215.1060.

Anthracene-9-carbaldehyde (4ao)



MeCN (10 mL) was used as the solvent instead of EtOH. **4ao**³³ was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow solid (134 mg, 65%). M.P. 103–105 °C; ¹H-NMR (400 MHz, CDCl₃) δ : 11.53 (s, 1H), 8.98 (dd, J = 9.0, 1.0 Hz, 2H), 8.70 (s, 1H), 8.06 (d, J = 8.4 Hz, 2H), 7.71–7.66 (m, 2H), 7.58–7.53 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 193.2, 135.4, 132.3, 131.2, 129.4,

129.3, 125.8, 124.9, 123.7. IR 1659.8, 1547.3, 1515.4, 1437.8, 1242.5, 1155.0, 1041.6, 843.8, 723.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{15}H_{11}O$ [M+H]⁺ 207.0804; found 207.0808.

Octanal (4ap)



MeCN (10 mL) was used as the solvent instead of EtOH. **4ap**⁴⁸ was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (64.1 mg, 50%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.76 (t, J = 1.9 Hz, 1H), 2.39 (td, J = 7.4, 1.9 Hz, 2H), 1.67–1.59 (m, 2H), 1.34–1.24 (m, 8H), 0.86 (t, J = 7.0 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 203.2, 44.1, 31.8, 29.3, 29.2, 22.7, 22.2, 14.2. IR 2925.5, 2857.5, 2715.6, 1725.1,

1461.0, 1383.9, 1140.4, 724.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_{17}O$ [M+H]⁺ 129.1274; found 129.1275.

3'-Bromo-4'-fluoroacetophenone (4aq)



MeCN (10 mL) was used as the solvent instead of EtOH. **4aq** was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (176 mg, 81%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.15 (dd, J = 6.6, 2.2 Hz, 1H), 7.88 (ddd, J = 8.6, 4.6, 2.2 Hz, 1H), 7.17 (t, J = 8.3 Hz, 1H), 2.58 (s, 3H). ¹³C-NMR (100

MHz, CDCl₃) δ: 195.4, 160.9 (d, J = 254 Hz), 134.7 (d, J = 3.4 Hz), 134.3 (d, J = 1.8 Hz), 129.6 (d, J = 8.5

Hz), 116.7 (d, J = 22.8 Hz), 109.7 (d, J = 21.5 Hz), 26.6. IR 3088.9, 1677.3, 1583.0, 1484.9, 1391.0, 1351.1, 1248.8, 1040.3, 899.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₇BrFO [M+H]⁺ 216.9659; found 216.9668.

1-(3-Fluorophenyl)-propan-1-one (4ar)



MeCN (10 mL) was used as the solvent instead of EtOH. **4ar**⁴⁹ was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (126 mg, 83%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.73 (d, *J* = 7.8 Hz, 1H), 7.67–7.62 (m, 1H), 7.48–7.41 (m, 1H), 7.29–7.22 (m, 1H), 2.96 (q, *J* = 7.2 Hz, 2H), 1.21 (t, *J* = 7.4 Hz,

3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 199.6 (d, J = 2.1 Hz), 161.8 (d, J = 246 Hz), 139.1 (d, J = 6.0 Hz), 130.3 (d, J = 7.6 Hz), 123.8 (d, J = 3.0 Hz), 119.9 (d, J = 21.3 Hz), 114.8 (d, J = 21.9 Hz), 32.1, 8.2. IR 2940.6, 1687.8, 1586.4, 1439.3, 1350.4, 1244.9, 1165.4, 780.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₉H₁₀FO [M+H]⁺ 153.0710; found 153.0713.

4-Bromobenzaldehyde (4as)



MeCN (10 mL) was used as the solvent instead of EtOH. **4as**³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (124 mg, 67%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.97 (s, 1H), 7.76–7.71 (m, 2H), 7.70–7.65 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 191.2, 135.2, 132.6, 131.1, 129.9. IR 1685.5,

1576.3, 1473.0, 1379.3, 1198.1, 1147.2, 1058.3, 806.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_7H_6BrO [M+H]^+$ 184.9597; found 184.9590.

2-Acetyl-6-methoxy naphthalene (4at)



4at⁵⁰ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a white solid (170 mg, 85%). M.P. 109–111 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 8.38 (s, 1H), 7.98 (dd, J = 8.6, 1.8 Hz, 1H), 7.83 (d, J = 8.9 Hz, 1H), 7.74 (d, J = 8.6 Hz, 1H), 7.18 (dd, J = 8.9, 2.5 Hz, 1H), 7.14 (d, J =

2.5 Hz, 1H), 3.94 (s, 3H), 2.69 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 197.9, 159.9, 137.4, 132.8, 131.2, 130.2, 128.0, 127.2, 124.8, 119.8, 105.9, 55.5, 26.6. IR 1669.45, 1614.38, 1468.06, 1355.57, 1267.16, 1194.54, 1014.38, 857.77 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₃H₁₃O₂ [M+H]⁺ 201.0910; found 201.0904.

4-Methylbenzaldehyde (4au)



MeCN (10 mL) was used as the solvent instead of EtOH. **4au**³³ was purified by flash column chromatography (ethyl acetate/hexane = 1:20 to 1:5) as a light-yellow oil (76.9 mg, 64%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.95 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 192.1, 145.6, 134.3,

129.9, 129.8, 22.0. IR 2824.6, 2733.2, 1691.5, 1602.8, 1386.5, 1301.7, 1208.8, 1109.2, 1040.0, 844.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_9O[M+H]^+$ 121.0648; found 121.0654.

2-Fluorobenzaldehyde (4av)



MeCN (10 mL) was used as the solvent instead of EtOH. **4av**³¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (62.1 mg, 50%). ¹H-NMR (400 MHz, CDCl₃) δ : 10.33 (s, 1H), 7.82 (td, *J* = 7.4, 2.0 Hz, 1H), 7.64–7.57 (m, 1H), 7.29–7.23 (m, 1H), 7.19–7.12 (m, 1H). ¹³C-NMR (100 MHz, CDCl₃)

δ: 186.8 (d, J = 6.6 Hz), 163.2 (d, J = 257 Hz), 136.2 (d, J = 9.1 Hz), 128.5 (d, J = 1.9 Hz), 124.5 (d, J = 3.8 Hz), 124.0 (d, J = 7.8 Hz), 116.2 (d, J = 20.3 Hz). IR 1693.7, 1609.6, 1583.1, 1481.5, 1457.5, 1400.5, 1273.1, 1188.0, 1095.9, 758.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₇H₆FO [M+H]⁺ 125.0397; found 125.0398.

3-Methoxybenzaldehyde (4aw)



MeCN (10 mL) was used as the solvent instead of EtOH. **4aw**⁵¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:5) as a light-yellow oil (84.4 mg, 62%). ¹H-NMR (400 MHz, CDCl₃) δ : 9.97 (s, 1H), 7.47–7.43 (m, 2H), 7.40–7.38 (m, 1H), 7.19–7.15 (m, 1H), 3.86 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ :

192.3, 160.3, 137.9, 130.2, 123.7, 121.7, 112.2, 55.6. IR 2837.8, 2730.0, 1697.0, 1589.8, 1482.7, 1459.9, 1389.1, 1146.2, 1038.2, 778.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_8H_9O_2$ [M+H]⁺ 137.0597; found 137.0601.

$$R \xrightarrow{O} S \xrightarrow{Me} \frac{H_2O_2, CeBr_3}{MeCN, 1 h} R \xrightarrow{OH} 6$$

General Procedure IV: To a stirred solution of compound **5** (1 mmol) in MeCN (5 mL) were added CeBr₃ (19.0 mg, 0.05 mmol) and 30% H₂O₂ (100 μ L, 1 mmol) at rt. After completion of the addition, the resulting mixture was allowed to stir at room temperature for 1 h. Then the mixture was quenched by aqueous Na₂S₂O₃ (0.1 M, 20 mL) and ethyl acetate (20 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (3 × 20 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography to give compound **6**.

2-Phenylethanol (6a)

6a

.OH

6a⁵² was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (85.5 mg, 70%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.35–7.31 (m, 2H), 7.27–7.23 (m, 3H), 3.81 (t, *J* = 6.7 Hz, 2H), 2.85 (t, *J* = 6.6 Hz, 2H), 1.98 (brs, 1H).

¹³C-NMR (100 MHz, CDCl₃) δ: 138.6, 129.1, 128.6, 126.5, 63.7, 39.2. IR 3323.1, 3027.4, 2939.0, 2872.9, 1601.6, 1494.2, 1450.5, 1174.6, 1042.0, 907.3, 854.1, 742.1, 695.5, 570.2, 491.9 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₁₁O [M+H]⁺ 123.0804; found 123.0809.

2-Cyanoethanol (6b)



Solid Na₂S₂O₃ (316 mg, 2 mmol) was used to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly. **6b**⁵³ was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light-yellow oil (59.7 mg,

84%). ¹H-NMR (400 MHz, CDCl₃) δ : 3.84 (t, *J* = 6.0 Hz, 2H), 3.18 (s, 1H), 2.59 (t, *J* = 6.0 Hz, 2H). ¹³C-NMR (101 MHz, CDCl₃) δ : 118.5, 57.7, 21.5. IR 3417.4, 2899.2, 2254.3, 1723.4, 1638.2, 1414.3, 1326.5, 1171.0, 1119.1, 1051.1, 852.1, 576.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₃H₆NO [M+H]⁺ 72.0444; found 72.0447.

2-Phenoxyethanol (6c)

О_ОН

6c⁵⁴ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (98.1 mg, 71%). ¹H-NMR (400 MHz, CDCl₃) δ : 7.28 (t, *J* = 7.4 Hz, 2H), 7.00-6.92 (m, 3H), 4.06 (t, *J* = 4.2 Hz, 2H), 3.94 (t, *J* = 4.2 Hz, 2H),

2.53 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 158.7, 129.6, 121.2, 114.6, 69.2, 61.5. IR 3385.3, 2930.7, 1721.9, 1594.2, 1492.3, 1455.4, 1327.8, 1298.3, 1239.6, 1169.0, 1128.0, 1078.0, 1042.7, 957.2, 913.3, 791.7, 751.0, 690.3, 604.3, 554.6, 509.1, 482.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₁₁O₂ [M+H]⁺ 139.0754; found 139.0751.

Cyclohexylmethanol (6d)

Solid Na₂S₂O₃ (316 mg, 2 mmol) was used to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly. $6d^{55}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (74.2 mg, 65%). ¹H-NMR (400 MHz, CDCl₃) δ : 3.37 (d, J = 6.4 Hz, 2H), 2.26 (s, 1H), 1.73–1.61 (m, 5H), 1.47–1.39 (m, 1H), 1.26–1.11 (m, 3H), 0.93–0.83 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 69.0, 40.7, 29.7, 26.7, 26.0. IR 3334.1, 2922.1, 2851.7, 1718.9, 1448.9, 1338.8, 1171.1, 1089.1, 1019.2, 973.0, 943.1, 891.7, 835.9, 778.5, 744.9, 554.1, 524.5, 486.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₇H₁₅O [M+H]⁺ 115.1117; found 115.1121.

Cyclopentylmethanol (6e)

1-Undecanol (6f)

 $Me \swarrow_{11}^{OH} 6f$

6f⁵⁷ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (123 mg, 66%). ¹H-NMR (400 MHz, CDCl₃) δ : 3.61 (t, *J* = 6.6 Hz,

2H), 1.56–1.51 (m, 2H), 1.27–1.23 (m, 18H), 0.84 (t, J = 6.3 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 63.3, 32.7, 32.1, 29.8, 29.77, 29.74, 29.6, 29.5, 25.9, 22.8, 14.2. IR 3353.3, 2921.8, 2853.4, 1461.6, 1350.9, 1173.6, 1046.6, 720.5, 528.6 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₂₇O [M+H]⁺ 187.2056; found 187.2065.

3-[(tert-Butyloxycarbonyl)amino]propanol (6g)

BocHN Gg Solid Na₂S₂O₃ (316 mg, 2 mmol) was used to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly. $6g^{58}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:2) as a light-yellow oil (123 mg, 70%). ¹H-NMR (400 MHz, CDCl₃) δ : 4.91 (s, 1H), 3.61 (t, J = 5.3 Hz, 2H), 3.29–3.24 (m, 2H), 1.67–1.64 (m, 2H), 1.41 (s, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 157.2, 79.6, 59.3, 37.1, 32.9, 28.5. IR 3348.7, 2974.1, 1682.7, 1519.6, 1452.0, 1393.9, 1365.4, 1163.9, 1046.1, 866.8, 777.9, 596.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₈H₁₈NO₃[M+H]⁺ 176.1281; found 176.1283.

3-(3-Trifluoromethylphenyl)propanol (6h)

6h⁵⁹ was purified by flash column chromatography (ethyl acetate/hexane =OH1:10 to 1:3) as a light-yellow oil (167 mg, 82%). ¹H-NMR (400 MHz, CDCl₃)6h δ : 7.45–7.38 (m, 4H), 3.67 (t, J = 6.3 Hz, 2H), 2.76 (t, J = 7.8 Hz, 2H), 1.94–

1.87 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 142.9, 132.0, 130.7 (q, J = 32.0 Hz), 128.9, 125.2 (q, J = 4.0 Hz), 122.8 (q, J = 4.0 Hz), 120.3 (q, J = 271.0 Hz), 62.0, 34.1, 32.0. IR 3325.8, 2941.1, 1448.4, 1325.3, 1160.5, 1118.6, 1067.8, 903.7, 798.8, 740.0, 700.5, 658.7, 516.0 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₀H₁₂F₃O [M+H]⁺ 205.0835; found 205.0839.

2-Naphthaleneethanol (6i)



F₃C

6i⁶⁰ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (127 mg, 74%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.05 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.56–7.48 (m, 2H), 7.45–7.38 (m, 2H), 3.98 (t, *J* = 6.6 Hz, 2H), 3.34 (t, *J* = 6.6 Hz, 2H). ¹³C-NMR (100 MHz, 100 MHz)

CDCl₃) δ : 134.5, 134.1, 132.2, 129.0, 127.5, 127.3, 126.2, 125.8, 125.6, 123.8, 63.2, 36.3. IR 3327.4, 3046.4, 2943.2, 2875.6, 1716.1, 1593.9, 1509.5, 1391.4, 1164.1, 1034.7, 865.7, 772.7, 732.7, 597.7, 551.5, 422.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₁₂NaO [M+Na]⁺ 195.0780; found 195.0781.

Cyclohexanol (6j)

OH Gj Gj $Solid Na_2S_2O_3$ (316 mg, 2 mmol) was used to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly. $6j^{61}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (90.1 mg, 90%). ¹H-NMR (400 MHz, CDCl₃) δ : 3.62–3.59 (m, 1H), 1.92–1.87 (m, 1H), 1.77–1.70 (m, 2H), 1.57–1.45 (m, 3H), 1.31–1.14 (m, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ : 70.3, 35.6, 25.5, 24.1. IR 3341.3, 2997.5, 2855.4, 1715.5, 1449.6, 1367.0, 1174.8, 1059.1, 964.0, 889.9, 841.5, 781.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₆H₁₃O [M+H]⁺ 101.0961; found 101.0956.

Tetrahydro-4-pyranol (6k)

Solid Na₂S₂O₃ (316 mg, 2 mmol) was used to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly. $6k^{62}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 2:1) as a light-yellow oil (87.8 mg, 86%). ¹H-NMR (400 MHz, CDCl₃) δ : 3.92 (dt, J = 11.7, 4.4 Hz, 2H), 3.88–3.81 (m, 1H), 3.46–3.40 (m, 2H), 1.91–1.87 (m, 2H), 1.74 (s, 1H), 1.60–1.51 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 67.1, 65.8, 35.6. IR 3382.2, 2945.2, 2854.8, 1652.8, 1450.3, 1368.0, 1285.3, 1227.1, 1133.0, 1077.0, 1032.7, 1004.5, 984.6, 857.2, 813.7, 611.6, 517.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₅H₁₁O₂ [M+H]⁺ 103.0754; found 103.0756.

trans-4-[(tert-Butyloxycarbonyl)amino]cyclohexan-1-ol (6l)



Solid Na₂S₂O₃ (316 mg, 2 mmol) was used to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly. **61**⁶³ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:2) as a white solid (129 mg, 60%). M.P. 172–174 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 4.38

(s, 1H), 3.60–3.55 (m, 1H), 3.40 (s, 1H), 2.00–1.94 (m, 4H), 1.77 (s, 1H), 1.42 (s, 9H), 1.37–1.34 (m, 2H), 1.16–1.12 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 155.4, 79.4, 69.9, 49.0, 34.1, 31.3, 28.5. IR 3340.1, 2978.6, 2933.5, 2858.7, 2280.5, 2114.4, 1678.5, 1523.4, 1451.4, 1363.5, 1312.0, 1263.3, 1228.1, 1063.7, 948.5, 895.1, 782.9, 740.2, 619.0, 521.6, 461.4, 427.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₁H₂₂NO₃ [M+H]⁺ 216.1594; found 216.1592.

(1*R*,2*S*,5*R*) (-)-Menthol (6m)

 $\begin{array}{l} & \mathbf{6m^{64}} \text{ was purified by flash column chromatography (ethyl acetate/hexane} = 1:10 to \\ 1:3) \text{ as a light-yellow oil (127 mg, 81%). }^{1}\text{H-NMR} (400 \text{ MHz, CDCl}_3) \delta: 3.37 (td, J = \\ 10.4, 4.3 \text{ Hz}, 1\text{H}), 2.19-2.14 (m, 1\text{H}), 1.98-1.93 (m, 1\text{H}), 1.68-1.58 (m, 2\text{H}), 1.43-\\ 1.41 (m, 1\text{H}), 1.13-1.07 (m, 1\text{H}), 0.96-0.90 (m, 8\text{H}), 0.87-0.82 (m, 1\text{H}), 0.80 (d, J = \\ 1.5 \text{ Hz}, 3\text{H}). \, ^{13}\text{C-NMR} (100 \text{ MHz, CDCl}_3) \delta: 71.7, 50.3, 45.2, 34.7, 31.8, 26.0, 23.3, 22.4, 21.2, 16.2. IR \\ 3359.0, 2952.5, 2921.3, 2867.8, 1723.4, 1454.6, 1368.9, 1176.1, 1099.4, 1027.0, 985.3, 914.5, 874.4, 842.6, \\ 771.2, 545.3 \text{ cm}^{-1}; \text{ HRMS (ESI^+) (m/z) calcd. for C}_{10}\text{H}_{20}\text{NaO} [\text{M+Na}]^+ 179.1406; found 179.1407. } [\alpha]_{\text{D}}^{25} = \\ -51 (c \ 0.1, \text{ EtOH}) \end{array}$

1,2:3,4-Di-O-isopropylidene-α-D-galactopyranose (6n)



 $6n^{65}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:5) to 2:1) as a light-yellow oil (195 mg, 75%). ¹H-NMR (400 MHz, CDCl₃) δ: 5.56 (d, J = 5.0 Hz, 1H), 4.60 (d, J = 7.9 Hz, 1H), 4.34–4.26 (m, 2H), 3.87– 3.83 (m, 2H), 3.77-3.73 (m, 1H), 1.53 (s, 3H), 1.46 (s, 3H), 1.33 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ: 109.6, 108.8, 96.4, 71.8, 70.9, 70.7, 68.2, 62.5, 26.2, 26.1, 25.1, 24.4. IR 3493.7, 2986.0, 2932.9, 1723.5, 1457.1, 1377.8,

1253.2, 1209.7, 1168.7, 1063.3, 997.7, 890.8, 858.7, 802.4, 769.0, 644.2, 552.8, 509.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₂H₂₁O₆ $[M+H]^+$ 261.1333; found 261.1335. $[\alpha]_D^{25} = -59$ (c 0.1, CHCl₃)

(-)-Borneol (60)



 60^{66} was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a white solid (128 mg, 83%). M.P. 207-210 °C. ¹H-NMR (400 MHz, CDCl₃) δ: 4.01 (ddd, J = 10.0, 3.3, 1.6 Hz, 1H), 2.30-2.23 (m, 1H), 1.91-1.84 (m, 1H), 1.75-1.69 (m, 1H), 1.91-1.84 (m, 11H), 1.60 (t, J = 4.6 Hz, 1H), 1.27–1.20 (m, 2H), 0.91 (dd, J = 13.4, 3.4 Hz, 1H), 0.86– 0.84 (m, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ: 77.5, 49.6, 48.2, 45.2, 39.2, 28.4, 26.0,

20.3, 18.8, 13.5. IR 3299.0, 2945.2, 2874.9, 1451.8, 1380.2, 1303.0, 1232.1, 1139.3, 1107.5, 1053.4, 1023.0, 941.3, 828.4, 656.6. 528.1, 461.2 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₀H₁₈KO [M+K]⁺ 193.0989; found 193.0980. $[\alpha]_D^{25} = -34$ (*c* 0.1, EtOH).

2-Methyl-1-phenylpropan-2-ol (6p)



OHC

 $6p^{64}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (116 mg, 77%). ¹H-NMR (400 MHz, CDCl₃) δ: 7.32-7.20 (m, 5H), 2.76 (s, 2H), 1.22 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ: 137.9, 130.6, 128.3, 126.6, 70.9, 49.9, 29.3. IR 3389.7, 3028.6, 2971.0, 2927.6, 1709.0, 1493.1, 1455.1, 1373.1, 1306.5, 1207.1, 1146.6, 1031.3, 974.3. 900.0, 777.7, 725.4, 698.2, 608.2, 516.3, 466.3 cm⁻¹; HRMS

7-Hydroxy-3,7-dimethyloctanal (6q)

(ESI⁺) (m/z) calcd. for $C_{10}H_{14}NaO [M+Na]^+$ 173.0937; found 173.0938.

 $6q^{67}$ was purified by flash column chromatography (ethyl acetate/hexane = Me Me ↓∠OH 1:10 to 1:2) as a light-yellow oil (141 mg, 82%). ¹H-NMR (400 MHz, CDCl₃) δ: 9.69 (t, J = 2.3 Hz, 1H), 2.36–2.32 (m, 1H), 2.22–2.15 (m, 1H), 2.04–1.99 6a

(m, 1H), 1.45–1.30 (m, 6H), 1.19–1.15 (m, 6H), 0.90 (d, J = 6.7 Hz, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ : 203.2, 71.1, 51.1, 43.9, 37.4, 29.34, 29.25, 28.2, 21.7, 20.0. IR 3382.7, 2935.4, 1718.7, 1462.9, 1372.5, 1134.7, 937.1, 905.9, 761.9, 553.6, 482.7 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₀H₂₀NaO₂ [M+Na]⁺ 195.1356; found 195.1352.

3,7-Dimethyloctan-3-ol (6r)



 $6r^{68}$ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (125 mg, 79%). ¹H-NMR (400 MHz, CDCl₃) δ : 1.58–1.51 (m, 1H), 1.50–1.35 (m, 5H), 1.34–1.26 (m, 2H), 1.20–1.15 (m, 2H), 1.14 (s, 3H),

0.90–0.86 (m, 9H). ¹³C-NMR (100 MHz, CDCl₃) δ : 73.1, 41.7, 39.7, 34.4, 28.1, 26.5, 22.8, 21.7, 8.3. IR 3382.6, 2956.4, 1461.9, 1373.7, 1152.8, 1081.9, 972.8, 899.2, 840.1, 738.7, 612.3 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₁₀H₂₂KO [M+K]⁺ 197.1302; found 197.1301.

1-Adamantanol (6s)



6s⁶⁴ was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a white solid (129 mg, 85%). M.P. 246–249 °C. ¹H-NMR (400 MHz, CDCl₃) δ : 2.13 (s, 3H), 1.70 (d, J = 2.6 Hz, 6H), 1.64–1.56 (m, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 68.4, 45.5, 36.2, 30.8. IR 3272.9, 2891.8, 2843.9, 1722.7, 1446.5, 1345.8, 1299.3, 1223.7, 1174.7,

1109.6, 1081.5, 976.6, 923.2, 809.3, 651.4, 548.4, 464.6, 432.5 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{10}H_{16}NaO [M+Na]^+$ 175.1093; found 175.1090.

1-[4-[2-(tert-Butyldimethylsilyloxy)ethoxy]phenyl]-2-hydroxy-2-methylpropan-1-one (6t)



THF (5 mL) was used as the solvent instead of MeCN. **6t** was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) as a light-yellow oil (244 mg, 72%). ¹H-NMR (400 MHz, CDCl₃) δ : 8.03 (d, *J* = 8.5 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 4.30 (s, 1H), 4.10 (t, *J* = 4.8 Hz, 2H), 3.97 (t, *J* = 4.8 Hz, 2H), 1.62 (s, 6H), 0.90 (s, 9H), 0.09 (s, 6H). ¹³C-NMR (100 MHz, CDCl₃) δ : 202.7,

163.0, 132.5, 126.0, 114.3, 75.9, 69.7, 61.9, 28.8, 26.0, 18.5, -5.1. IR 3454.2, 2931.6, 2858.5, 1736.9, 1663.6, 1598.3, 1571.8, 1507.4, 1463.8, 1416.8, 1368.4, 1306.8, 1252.4, 1161.5, 1128.4, 1053.9, 954.9, 832.0, 773.1, 728.5, 667.1, 586.8, 565.7, 510.9, 426.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{18}H_{31}O_4Si [M+H]^+$ 339.1986; found 339.1998.

Thiophen-2-ylethanol (6u)

6u



3.06 (t, J = 6.4 Hz, 2H), 1.89 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ : 140.9, 127.1, 125.7, 124.1, 63.6, 33.4. IR 3327.40, 2936.70, 1433.76, 1239.20, 1132.01, 1041.30, 845.97, 821.23, 690.27, 494.72 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for C₆H₉OS [M+H]⁺ 129.0369; found 129.0370.

6. Gram-scale dethioacetalization of 3a and 5j under open-air condition



Gram-scale synthesis of 4a: To a stirred solution of compound **3a** (6.5 g, 30.9 mmol) in EtOH (150 mL) were added CeBr₃ (285 mg, 0.75 mmol) and H₂O₂ (30%, 6.2 mL, 60 mmol). After completion of the addition, the resulting mixture was allowed to stir at 40 °C for additional 1 h. Then the reaction was quenched by solid Na₂S₂O₃ (9.5 g, 60 mmol), and stirred for 30 min followed by filtration. The resulting filtrate was evaporated and purified by vacuum distillation (131-139 °C/~80 Torr) to give compound **4a** (2.97 g, 80%).

Gram-scale synthesis of 6j: To a stirred solution of compound **5j** (6.0 g, 37.4 mmol) in MeCN (90 mL) were added CeBr₃ (300 mg, 0.79 mmol) and H₂O₂ (30%, 3.9 mL, 37.4 mmol). After completion of the addition, the resulting mixture was allowed to stir at rt for additional 1 h. Then the reaction was quenched by solid Na₂S₂O₃ (5.9 g, 37.4 mmol), and stirred for 30 min followed by filtration. The resulting filtrate was evaporated and purified by vacuum distillation (107-113 °C/~80 Torr) to give compound **6j** (3.07 g, 82%).

7. Controlled experiments of bromide and cerium catalysts for dethioacetalization.


To a stirred solution of compound **3a** (21.0 mg, 0.1 mmol) in EtOH (1 mL) or **5j** (16.0 mg, 0.1 mmol) in MeCN (1 mL) were added KBr (with or without, 3.6 mg, 0.03 mmol), metal catalyst (0.01 mmol) and H₂O₂ (30%, 20 μ L, 0.2 mmol for **3a**; 10 μ L, 0.1 mmol for **5j**). After completion of the addition, the reaction mixture was allowed to stir at rt for 1.5 h. The reaction was quenched by dilute aqueous Na₂S₂O₃ solution (0.1 M, 4 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (2 × 10 mL). The combined organic fractions were washed with H₂O, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Yield was determined by ¹H-NMR of the crude reaction mixture using CH₂Br₂ as the internal reference. For compound **6j**, solid Na₂S₂O₃ (63.2 mg, 0.4 mmol) was added directly to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly.

8. Radical trapping (ABTS) experiments.



To a stirred solution of compound **3a** (21.0 mg, 0.1 mmol) in EtOH/H₂O (10/1, 1.1 mL) or compound **5j** (16.0 mg, 0.1 mmol) in MeCN/H₂O (10/1, 1.1 mL) were added ABTS (with or without, 110 mg, 0.2 mmol), and the mixture was stirred for 5 min. Then H₂O₂ (30%, 20 μ L, 0.2 mmol for **3a**; 10 μ L, 0.1 mmol for **5j**) and CeBr₃ (3.8 mg, 0.01 mmol) were added, and the resulting solution was stirred at rt for 1.5 h. The reaction was quenched by dilute aqueous Na₂S₂O₃ solution (0.1 M, 4 mL) and ethyl acetate (10 mL). The organic fractions

were collected, and the aqueous phase was extracted with ethyl acetate (2×4 mL). The combined organic fractions were washed with H₂O, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. Yield was determined by ¹H-NMR of the crude reaction mixture using CH₂Br₂ as the internal reference. For compound **6j**, solid Na₂S₂O₃ (63.2 mg, 0.4 mmol) was added to quench the reaction instead of an aqueous solution, and the resulting mixture was evaporated directly.

9. Isotopic labeling experiment.



To a stirred solution of compound **3s** (13.0 mg, 0.05 mmol) in ethanol (1 mL) and H₂¹⁸O (0.2 mL) were added CeBr₃ (1.9 mg, 0.005 mmol) and 30% H₂O₂ (10 μ L, 0.1 mmol). After completion of the addition, the resulting mixture was allowed to stir at rt for 1.5 h. Then the mixture was quenched by aqueous Na₂S₂O₃ solution (0.1 M, 10 mL) and ethyl acetate (10 mL). The organic fractions were collected, and the aqueous phase was extracted with ethyl acetate (3 × 10 mL). The combined organic fractions were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography (ethyl acetate/hexane = 1:10 to 1:3) to give compound **4s** (6.0 mg, 70%). MS = 173.1 for ¹⁸O-4s, while MS = 171.2 for ¹⁶O-4s.



10. The isolation and confirmation of related side products.



Disulfide 7-12 were isolated by flash column chromatography following the above General Procedure III-IV and confirmed by GC-MS, HRMS and NMR (¹H and ¹³C).

1,2-Dithiolane (7)



The purification of compound 7 always led to polymeric material⁷⁰, so the reaction mixture of **3w** was passed through millipore filter (0.45 μ m) directly after 5 min at rt and analyzed by GC-MS directly. Mass spectrum and retrieval results were listed below respectively, and compound 7 (m/z = 106.0) was identified as 1,3-dithiolane.



Bis(4-methylphenyl) disulfide (8)



8⁷¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:20) as a light-yellow oil (207 mg, 84%) following the deprotection of **3ag** (1 mmol). ¹H-NMR (400 MHz, DMSO) δ : 7.37 (d, *J* = 8.3 Hz, 4H), 7.16 (d, *J* = 8.0 Hz, 4H), 2.27 (s, 6H). ¹³C-NMR (100 MHz, DMSO) δ : 137.4, 132.6, 130.0, 128.1, 20.5. IR 1591.2, 1481.9, 1397.8, 1301.6, 1177.9, 1112.6, 1072.8, 1010.0, 794.3,

478.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{14}H_{15}S_2$ [M+H]⁺ 247.0610; found 247.0609.

Dibenzyl disulfide (9)



9⁷¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:40 to 1:20) as a light-yellow oil (123 mg, 50%) following the deprotection of **3ad** (1 mmol). ¹H-NMR (400 MHz, CDCl₃) δ : 7.24–7.11 (m, 10H), 3.49 (s, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ : 137.5, 129.5, 128.6, 127.5, 43.3. IR 3024.6, 2918.8, 1594.9, 1488.0, 1449.7, 1407.6, 1222.8, 1192.7, 1066.2, 1023.4, 758.7, 465.1 cm⁻¹; HRMS (ESI⁺) (m/z) calcd.

for $C_{14}H_{15}S_2 [M+H]^+ 247.0610$; found 247.0604.

Bis(2-hydroxyphenyl) disulfide (10)



10⁷² was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1) as a light-yellow oil (173 mg, 69%) following the deprotection of **3ar** (1 mmol). ¹H-NMR (400 MHz, CDCl₃) δ : 7.37–7.32 (m, 2H), 7.22 (dd, *J* = 7.8, 1.7 Hz, 2H), 7.00 (dd, *J* = 8.2, 1.3 Hz, 2H), 6.81 (td, *J* = 7.6, 1.3 Hz, 2H), 6.29 (s, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ : 157.0, 136.3, 133.3, 121.2, 120.1, 115.9. IR 3449.7, 3399.5,

 $1566.5, 1459.4, 1331.8, 1291.5, 1236.4, 1174.4, 1021.1, 829.1, 749.4, 496.4, 428.1 \ cm^{-1}; \ HRMS \ (ESI^+) \ (m/z) \ calcd. \ for \ C_{12}H_{11}O_2S_2 \ [M+H]^+ \ 251.0195; \ found \ 251.0189.$

Bis(2-aminophenyl) disulfide (11)



11⁷¹ was purified by flash column chromatography (ethyl acetate/hexane = 1:5 to 1:1) as a light-yellow oil (109 mg, 44%) following the deprotection of **3as** (1 mmol). ¹H-NMR (400 MHz, CDCl₃) δ : 7.18–7.13 (m, 4H), 6.70 (dd, *J* = 8.4, 1.2 Hz, 2H), 6.57 (td, *J* = 7.4, 1.3 Hz, 2H), 4.22 (s, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ : 148.8, 137.0, 131.7, 118.9, 118.4, 115.4. IR 3375.1, 3061.7, 1611.8, 1580.3,

1468.2, 1441.1, 1299.5, 1242.9, 1151.1, 1020.8, 856.4, 745.5, 451.8 cm⁻¹; HRMS (ESI⁺) (m/z) calcd. for $C_{12}H_{13}N_2S_2$ [M+H]⁺ 249.0515; found 249.0525.

Dimethyl disulfide (12)

S—S Me Compound 12 was too volatile to be isolated, so the reaction mixture of 5j was passed through millipore filter (0.45 μm) directly after 10 min and analyzed by GC-MS directly. 12

Mass spectrum and retrieval results were listed below respectively, and compound 12 (m/z = 94.0) was identified as dimethyl disulfide.



11. Green chemistry metrics analysis.

E-Factor for 3a and 3p using H₂O₂/CeBr₃:



Amount of final product: 175 mg

Amount of waste: 359 mg - 175 mg = 184 mg

E-Factor = Amount of waste/Amount of product = 184/175 = 1.05

AE for 3a and 3p using H₂O₂/CeBr₃:



Molecular weight of product: 120

Sum of molecular weight of reagent: 210 + 34 = 244

Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 120/244 = 49.2%



Molecular weight of product: 182

Sum of molecular weight of reagent: 272 + 34 = 306

Atom economy = Molecular weight of product/Sum of molecular weight of reagent = 182/306 = 59.5%

RME for 3a and 3p using H₂O₂/CeBr₃:



Mass of product: 103 mg

Total mass of reagent: 210 mg + 68 mg = 278 mg

RME = Mass of product/Total mass of reagent = 103/278 = 37.1%



Mass of product: 175 mg

Total mass of reagent: 272 mg + 68 mg = 340 mg

RME = Mass of product/Total mass of reagent = 175/340 = 51.5%

PMI for 3a and 3p using H₂O₂/CeBr₃:



Mass of product: 175 mg

PMI = Total mass in process/Mass of product = 359/175 = 2.05

Green chemistry metrics for **3a** and **3p** using other protocols (SDS-I₂/H₂O₂⁷³, TBHP⁷⁴, NBS⁷⁵, IBX⁷⁶, DDQ⁷⁷ and Oxone⁷⁸) were calculated according to the published literatures, and the results were listed below:

			Ave	3p												
Reagent	CeBr ₃	IBX	DDQ	TBHP	NBS	Oxone	SDS, I_2/H_2O_2	CeBr ₃	IBX	DDQ		TBHP	TBHP NBS			
E-Factor	1.47	3.90	4.11	2.16	2.65	14.2	2.05	1.05	3.09	3.11		1.70 2.07				
AE	54.4%	28.8%	32.0%	45.2%	35.7%	23.2%	54.4%	59.5%	33.0%	36.5%		50.3%	50.3% 40.5%			
RME	44.3%	21.0%	20.4%	32.4%	28.2%	6.6%	39.7%	51.5%	24.5%	24.4%		37.0%				
PMI	2.47	4.90	5.11	3.16	3.65	15.2	3.05	2.05	4.09	4.11		2.70	2.70 3.07			
				3a												
Reagent	CeBr ₃	IBX	DDQ	TBHP	NBS	Oxone	SDS, I_2/H_2O_2									
E-Factor	1.88	4.70	5.11	2.61	3.22	14.2	2.47									
AE	49.2%	24.5%	27.5%	40.0%	30.9%	23.2%	49.2%									
RME	37.1%	17.5%	16.4%	27.7%	23.7%	6.6%	34.70%									
DMI	200	5 70	6.11	2.61	4 22	15.2	2 47									

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f1 (ppm)





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)





S – 53





210 200 -10 Ó fl (ppm)

















7.6700 7.6669 7.6502 7.6470 7.4974 7.4778 7.4778 7.4778 7.4778 7.3772 7.3772 7.3772 7.3589 7.3589	2553 2553 2553 2553 2553 2553 2553 2553	2.8801 2.8704 2.1797 2.1687 2.1689 2.1580 2.1580 2.1580 2.1593 2.1335 2.13555 2.13555 2.13555 2.13555 2.13555 2.135555 2.135555 2.1355555 2.13555555555555555555555555555555555555















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f1 (ppm)
























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f1 (ppm)







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

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>=-{ S、_NH 3ao Title SN-2-YL.1.fid Origin Bruker BioSpin GmbH Owner nmrsu Spectrometer spect Solvent CDC13 Temperature 298.9 Pulse Sequence zg30 Experiment 1DNumber of Scans 16 Receiver Gain 64 1.0000 Relaxation Delay Pulse Width 9.7800 4.0894 Acquisition Time Acquisition Date 2021-09-15T05:52:19 2021-09-15T05:52:20 Modification Date Spectrometer Frequency 400.15 Spectral Width 8012.8 Lowest Frequency -1545.7 1HNucleus 32768 Acquired Size Spectral Size 65536





210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)









S – 99























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	~73.99	-37.92 $\int 30.24$ $\int 26.69$		
<pre></pre>			Parameter Title Comment Origin Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time Acquisition Time Acquisition Date Spectrometer Frequency Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	Value CR-B-54. 4. fid CR-B-54-C Bruker BioSpin GmbH nmrsu Avance NEO CDC13 297. 5 zgpg30 1D 1024 101 2.0000 8.0000 1.3763 2021-10-17T16:11:46 2021-10-17T16:11:66 100. 62 23809. 5 -1831. 7 13C 32768 65536
210 200 190 180 170 160 150 140 130 120 110 100	90 80 70 60		- <u>10</u> 0 -10	

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-1	5	4	-	00	5	3	2	0	0	-	-	9	4	4	3	3	2	-	0	6	4	2	-	0	6
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~75.36 -29.75 -25.56 -39.27 -13.93Parameter Value Title CR-B-62.6.fid CR-B-62-C Comment Origin Bruker BioSpin GmbH └__O__S_`Me 5e Owner nmrsu Site Spectrometer Avance NEO Author CDC13 Solvent Temperature 299.5 Pulse Sequence zgpg30 Experiment 1D Number of Scans 1024 Receiver Gain 101 Relaxation Delay 2.0000 Pulse Width 8.0000 Acquisition Time 1.3763 Acquisition Date 2021-09-27T18:11:06 Modification Date 2021-09-27T18:11:24 Spectrometer Frequency 100.62 Spectral Width 23809.5 Lowest Frequency -1831.4 Nucleus 13C Acquired Size 32768 Spectral Size 65536 190 50 -10 210 200 180 170 160 150 140 130 120 110 100 90 80 70 60 40 30 20 10 Ó fl (ppm)



















	~74.47 ~72.00	-32.14 $\int 25.86$ -24.25	- 13.88
$\underbrace{\bigcirc}_{5j} \overset{O \smile S}{5j} Me$			ParameterValueTitleCR-B-11.8.fidCommentCR-B-11-COriginBruker BioSpin GmbHOwnernmrsuSiteSSpectrometerAvance NEOAuthorSolventSolventCDC13Temperature299.5Pulse Sequencezgpg30Experiment1DNumber of Scans1024Receiver Gain101Relaxation Delay2.0000Pulse Width8.0000Acquisition Time1.3763Acquisition Date2021-09-27T19:16:41Modification Date2021-09-27T19:17:00Spectral Width23809.5Lowest Frequency-1829.2Nucleus13CAcquired Size32768Spectral Size65536
		- <u>-</u>	

S – 127



~71.78 ~70.73 ~65.72

-32.21 -13.78

	Parameter Title Comment Origin Owner Site	Value CR-B-58.6.fid CR-B-58-C Bruker BioSpin GmbH nmrsu
5k 5k	Spectrometer Author Solvent Temperature Fulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Fulse Width Acquisition Time Acquisition Date Spectrometer Frequency Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	Avance NEO CDC13 297.5 zgpg30 1D 1024 101 2.0000 8.0000 1.3763 2021-10-17T17:16:24 2021-10-17T17:15:44 100.62 23809.5 -1838.3 13C 32768 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 f1 (ppm)	20 10 0 -10	-

	4.6419 7.3.6187 7.3.6187 7.3.6086 7.3.5984 7.3.5921 7.3.5524 7.3.5559 7.3.5556	2.1487 f2.0469 f2.0360 f2.0246 72.0103 c1.9877 t1.9774	T1.9733 1.19659 1.14395 1.13895 1.13895 1.13812 1.364 1.1364	-1.1940 -1.1857 -1.1816 -1.1816 -1.1816 -1.1629 -1.1571 -1.1536
			Parameter Title Comment Origin Owner	Value CR-B-78 Bruker BioSpin GmbH nmrsu
			Site Spectrometer Author	spect
BocHN ^{VV} (±) 5I			Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time Acquisition Date Modification Date Spectrometer Frequen Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	CDC13 298.0 zg30 1D 16 31 1.0000 9.7800 4.0894 2021-09-16T08:50:58 2021-09-16T08:51:00 hey 400.15 8012.8 -1533.4 1H 32768 65536
			Min Min	
	2.00- 1.00-] 1.00-4 1.00-4	3.02~ 4.00-4	2.00 Å	
8.5 8.0 7.5 7.0 6.5 6.0 5.5	5.0 4.5 4.0 3.5 3.0 f1 (ppm)	0 2.5 2.0 1.	5 1.0 0.5 0.0	-0.5 -1.0

9.0





40	3	400014000
0 0	4	0 5 5 5 1 4 1 8 5
in a	00	04-1000-104
L L	4	4000000
11	1	5-5-1-1-

	Parameter Title Comment	Value CR-B-82.3.fid
Me Me	Origin Owner Site	Bruker BioSpin GmbH nmrsu
····/ <i>i</i> -Pr 5m	Spectrometer Author	spect
	Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Date Modification Date Spectrometer Frequenc Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	CDC13 298.0 2gpg30 1D 600 202 2.0000 10.5800 1.3631 2021-09-26T01:09:52 2021-09-26T01:09:54 y 100.63 24038.5 -1946.4 13C 32768 65536
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 f1 (ppm)	10 0 -10	

-



9.0



-81.64











9.0

-78.90 -66.22 -66.22 -38.14 -30.78 -38.14 -23.75 -38.14 -22.75 -28.04 -22.75 -28.04 -22.75 -28.04 -22.75 -28.04 -22.75 -28.04 -22.75 -28.04 -22.75 -28.04 -22.75 -28.04 -27.75 -28.04 -2





-4.5769










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f1 (ppm)





















-191.75	—1 <mark>66</mark> .19	人139.29 人135.23 人130.33 人129.65	-52.71	
Me	eO ₂ C	4k	Title Origin Owner Spectrometer Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width	WYX-51.2.1 Bruker BioSpin GmbH nmrsu spect CDC13 298.0 zgpg30 1D 1024 202 2.0000 10.5800
			Acquisition Time Acquisition Date Modification Date Spectrometer Frequ Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	1. 3631 2021-04-30T07:11:30 2021-04-30T07:11:32 ency 100. 62 24038. 5 -1945. 1 13C 32768 65536









f1 (ppm)


























f1 (ppm)







		-27.08	
S 4u		Title Origin Owner Spectro Solvent Tempera Pulse S Experin Number Receive Relaxat Pulse W Acquisi Acquisi Modific Spectro Spectra	2-Yixianjisaifen. 2. 1 Bruker BioSpin GmbH nmrsu ometer spect : CDC13 iture 298.0 Sequence zgpg30 ment 1D of Scans 1024 er Gain 202 tion Delay 2.0000 Width 10.5800 ition Time 1.3631 ition Date 2021-01-11T21:29:50 cation Date 2021-01-11T21:29:52 ometer Frequency 100.62 al Width 24038.5
		Nucleus Acquire Spectra	1364.1 ; 13C ed Size 32768 al Size 65536
210 200 190 180 170	160 150 140 130 120 110 10 f1 (р	0 90 80 70 60 50 40 30 20 10 om)	0 0 -10









-179.80	~156.29 ~152.75	129.27 7126.71 7124.26 1123.73 1117.90 1112.73		
		N	Title Origin Owner Spectrometer Solvent Temperature	WYX-21.2.1 Bruker BioSpin GmbH nmrsu spect CDC13 298.0
			Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Date Modification Date Spectrometer Frequent Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	zgpg30 1D 1024 202 2.0000 10.5800 1.3631 2021-04-24T13:52:58 2021-04-24T13:53:00 ncy 100.62 24038.5 -1953.9 13c 32768 65536
		<i>L</i> LM	 L	



		Titl	le	WYX-25YD.2.fid
		Orig	<i>ş</i> in	Bruker BioSpin GmbH
		Owne	r	nmrsu
		Spec	trometer	spect
	\cap	Solv	vent	DMSO
		Temp	erature	298.0
	J	Puls	e Sequence	zgpg30
	\checkmark	Expe	riment	10
\prec		Num	er of Scans	700
		Rece	viver Gain	202
HIN	48	Puls	.xacion Deray	10 5800
		Acm	isition Time	1 3631
		Acqu	isition Date	2021-11-11702.02.49
		Modi	fication Date	2021-11-11102.02.43
		Spec	trometer Frequer	100 63
		Spec	tral Width	24038. 5
		Lowe	est Frequency	-2008. 4
		Nucl	leus	13C
		Acqu	ired Size	32768
		Spec	stral Size	65536









9.0



-42.90

58 59 04 31

4







9.0

t-BuO 4ab		Title Origin Owner Spectrometer Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Date Modification Date Spectrometer Frequent Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	WYX-11.2.fid Bruker BioSpin Gmb nmrsu spect CDC13 298.0 zgpg30 1D 800 202 2.0000 10.5800 1.3631 2021-03-25T21:37:1 2021-03-25T21:37:1 ncy 100.63 24038.5 -1947.8 13C 32768 65536
		<u> </u>	

-212.61

0	9		S		8	N	4	S	2	σ	4	-	4	0	9	S	σ	S	S	N	- r	$\sim c$. ГО	N	0	MU	M	0		~	0	4 r	1 4	8	S	N	-	S	N	N	σ	σ	0	o (J N	
σ	5	9	9	σ	N	5	σ	4	2	0	0	4	8	5	9	-	9	-	8	00 1	5 5	4 U	co	00	-	S	00 -	- 4	MI	> 0	0	N	MF	· 0	σ	0	S	0	4	2	9	S	σ		5	D 00	NC
0	8	00	9	~	9	4	N	-	0	0	σ	S	-	4	0	0	σ	σ	N	NI	5 0	X N	N	-	-	9	LO N	N	0 0	ח ת	9	4	MP	. LO	M	N	0	σ	~	4	9	5	0	M	5 1	D 4	4
9	S	5	LO	M	M	N	M	M	M	M	0	01	N	-	_	-	0	0	0		0 1	0 10	0 10	10	10	10	10 10	10	10 1	t st	ST.	5	ST N	N M	N	M	M	N	N	01	-	-	0	G	00 0	nN	
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					1.1				1.1								<u> </u>	<u> </u>	<u> </u>		- ·	.		-	.						1000	1.0									0.00		~.				
4	4	4	4	N	N	N	N	N	N	N	2	N	N	N	N	N	5	N	5.0	2,	- ,			-	1.6	1		-			2	-		_	1	-	-	-	2	1	-	-	-	0	0 0	5 0	0



-212.01 -171.32 53.85 (46.74 (44.78 (44.78 (44.78 (44.78 (44.78 (54.75 (54.75 (54.75)) (53.65) 82.85 Title Origin Bruker BioSpin GmbH QAc Owner nmrsu Spectrometer spect Solvent CDC13 Η 298.0 Temperature Pulse Sequence zgpg30 Ĥ Ē Experiment 1D Number of Scans 28 188 Receiver Gain \cap Ē 4ac Relaxation Delay 2.0000 Pulse Width 12.0000 Acquisition Time 0.7690 Acquisition Date 2021-06-20108:43:21 Modification Date 2021-06-20T08:43:30 Spectrometer Frequency 176.05 42613.6 Spectral Width Lowest Frequency -3680.7 Nucleus 13C 32768 Acquired Size 65536 Spectral Size 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



-207.17	-155.27	√137.20 −134.70 √127.39 √126.81 √123.82		36.33	-2 <mark>5.9</mark> 1		
$\begin{array}{c} & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & \\ & $						Title Origin Owner Spectrometer Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Date Modification Date Spectrometer Frequent Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	WYX-71-chanwu. 2. 1 Bruker BioSpin GmbH nmrsu spect CDC13 296.9 zgpg30 1D 1024 202 2.0000 10.5800 1.3631 2021-05-28T02:54:29 2021-05-28T02:54:30 cy 100.62 24038.5 -1947.9 13C 32768 65536
210 200 190 180 170	160 150	140 130 120 110 f1	100 90 80 70 (ppm)	60 <mark>50 4</mark> 0 3	30 20	0 10 0 -10	_

S – 207









12									5 C		1.0										- N	
210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	0	-10
										f	1 (ppm)										










~			Title Origin	WYX-81chanwu, 2, f Bruker BioSpin G
			Owner Spectrometer Solvent	nmrsu spect CDC13
$\left[\right]$			Temperature	299.9
			Experiment	zgpg30 1D
4ai		I	Number of Scans	1024
i di			Receiver Gain Relaxation Delay	2.0000
			Pulse Width	10.5800
			Acquisition Time	1.3631
			Acquisition Date	2021-07-15121:2
			Spectrometer Freque	ncy 100, 63
			Spectral Width	24038.5
			Lowest Frequency	-1951.9
			Nucleus Accuired Size	13C 32768
			Spectral Size	65536
			- 372-0-0016559-0004039 - 2427-2490-091	
	1			
			11	

M















































0	Title	SN-1.2.fid Bruker BicSpin (mb
	Owner	nmrsu
\sim $^{\prime}$	Spectrometer	spect
	Solvent	CDC13
	Temperature	302.4
\downarrow \downarrow	Pulse Sequence	zgpg30
Br 4 as	Experiment	1D
-405	Number of Scans	507
	Receiver Gain	202
	Relaxation Delay	2.0000
	Pulse Width	10.5800
	Acquisition Time	1.3631
	Acquisition Date	2021-08-02T15:11:5
	Modification Date	2021-08-02T15:12:0
	Spectrometer Frequer	ncy 100.63
	Spectral Width	24038.5
	Lowest Frequency	-1945.2
	Nucleus	13C
	Acquired Size	32768
	Spectral Size	65536

f1 (ppm)















	-160.28	<pre>\137.94 /130.15 /123.67 /121.65</pre>	-112.16	55.59		
	MeO	4aw			Title Origin Owner Spectrometer Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Date Modification Date Spectrometer Frequent Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	L-cys-2-YL. 2. fid Bruker BioSpin GmbH nmrsu spect CDC13 298.0 zgpg30 1D 1024 202 2.0000 10.5800 1.3631 2021-09-22T23:32:24 2021-09-22T23:32:24 ccy100.63 24038.5 -1946.7 13C 32768 65536
nanan na mandana			sheren and a second	ىدىراي م ىرىدىيەرمىيەر	49499999999999999999999999999999999999	





-10 ó fl (ppm)











		12	· · ·	1 T T			0 10 20	10 10		10 N		1 I I				1 1					10 21		17 1	-
2	210	200	190	180	170	160	150	140	130	120	110	100	90	80	70	60	50	40	30	20	10	Ó	 io	
												f1 (ppm)												




210 200 190 180 170 180 150 140 150 120 110 100 90 80 70 80 50 40 50 20 10 0 -10 fl (ppm)



	-67.49	-42.24	-29.18	Title Comment	6e.2.fid
				Origin	Bruker BioSpin GmbH
				Owner	nmrsu
				Site	
				Instrument	spect
				Author	
				Solvent	CDC13
^				Temperature	298.0
			Ĩ	Pulse Sequence	zgpg30
				Experiment	
				Probe	Z116098_0436 (PA BBO 400S1 BBF-H-D-05 Z SP)
6e				Number of Scans	1024
				Receiver Gam	202.1
				Pulse Width	10.5800
				Preseturation Frequency	10.5800
				A convisition Time	1 2621
				Acquisition Data	2022 02 18704-25-28
				Modification Date	2022-05-18104-25-38
ĩ				Class	2022-05-10104.25.56
				Spoatromator Fraguard	100.63
				Spectral Width	24038 5
				Lowest Frequency	-1945.2
				Nucleus	13C
				Acquired Size	32768
		ñ		Spectral Size	65536
				Digital Resolution	0.37
				9	

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



	-63.14	732.94 729.82 729.79 729.78 729.78	29.50 25.90 22.83 	Title Comment Origin Owner Site Instrument Author Solvent Temperature Pulea Sequence	6f.2.fid Bruker BioSpin GmbH nmrsu spect CDCl3 298.0 zonn30
Me H 6f				Experiment Probe Number of Scans Receiver Gain Relaxation Delay Pulse Width Presaturation Frequency Acquisition Time Acquisition Date Modification Date Class Spectrometer Frequency Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size Digital Resolution	1D Z116098_0436 (PA BBO 400S1 BBF-H-D-05 Z SP) 1024 202.1 2.0000 10.5800 1.3631 2022-03-17T21:38:27 2022-03-17T21:38:26 100.63 24038.5 -1944.9 13C 32768 65536 0.37

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)













-10 Ò fl (ppm)



		-35.56	~24.13	
UUG	-70.3		Title Comment Origin Owner Site Spectrometer Author Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time Acquisition Date Modification Date Spectral Width Lowest Frequency Nucleus	CR-B-12.30.fid CR-B-12-C Bruker BioSpin GmbH nmrsu Avance NEO CDCl3 299.5 zgpg30 1D 1024 101 2.0000 8.0000 1.3763 2021-09-28T19:00:46 2021-09-28T19:01:06 ney 100.62 23809.5 -1828.9 13C 32768
ĸĸŧĸĸŶġĸĸŧŔġĸġĸĸŢĸĸĸŔĬġĿŎĴġĸŶġĸŎĸŎĸġŎţijġġĸĸĸŎĸĸŎĸĸŎĸĸŎĸĸġĸĸġĸĸġŎŎŎĸĸţŎĬĸŎġĸĸŢĸġŎĸŶſĊĬĸġĸĸĸġŎġĸġĸġĸġĸġŎĸġŎĸġŎŎĸġ		an a	Spectral Size	65536

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



-67.08 -65.77 -35.62

1		
1	9	
	1	
3	1	
t	1	
	1	

	Parameter	Value
	Title	CR-B-59.12.fid
	Comment	CR-B-59-C
	Origin	Bruker BioSpin GmbH
	Owner	nmrsu
	Site	
,OH	Spectrometer Author	Avance NEO
$\langle \cdot \rangle$	Solvent	CDC13
	Temperature	299.5
	Pulse Sequence	zgpg30
6K	Experiment	1D
	Number of Scans	1024
	Receiver Gain	101
	Relaxation Delay	2.0000
	Pulse Width	8.0000
	Acquisition Time	1.3763
	Acquisition Date	2021-09-27721:28:27
	Modification Date	2021-09-27721:28:46
	Spectrometer Frequenc	y 100.62
	Spectral Width	23809.5
	Lowest Frequency	-1830. 3
	Nucleus	13C
	Acquired Size	32768
	Spectral Size	65536
	and the second	

70 50 40 110 100 90 80 fl (ppm) 0 -10 210 200 140 130 120 30 20 10 190 180 170 160 150 60







-71.70

-50.29 -45.20 34.68 31.78 25.99 25.99 22.35 21.15 21.15 16.24









9.0

~49.61 ~48.15 ~48.15 ~39.15 ~39.15 ~39.15 ~39.18 ~18.81 ~13.46



-77.50







-10 ò fl (ppm)





-71.07-51.11-43.89 $f^{37.40}$ $f^{37.40}$ $f^{29.25}$ $f^{29.25}$ $f^{28.18}$ $f^{21.72}$ $f^{20.02}$

111e CR-059-C Origin Bruker Biopin Gab 0HC Me 6q Batvent 0HC 6q 0HC 6q 0HC 0000 6q Batvent 0DHC 0000 0HC 0HC 0HC 0HC 0HC 0HC 0HC 0HC 0HC 0HC				Parameter	Value
Comment CR-0-59-C Origin Bruker BioSpin Cabl Over narrss Site DHC Gq HC Gq HC Gq HC Gq HC Gq HC HC Gq HC HC HC HC HC HC HC HC HC HC				Title	CR-B-89. 14. fid
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				Comment	CR-B-89-C
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				Origin	Bruker BioSpin GmbH
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				Owner	nmrsu
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				Site	
Me Me Me Author Solvent CDC13 Temperature 297.4 Pulse Sequence app30 Experient 10 Number of Scans 1024 Relaxation Delay 2.0000 Acquisition Time 1.3763 Acquisition Date 2021-10-1811:47:23 Modification Date 2021-10-1811:47:46:40 Spectrometer Prequency -183.9 Modification Date 32768 Spectral Width 23800.5 Lowest Prequency -183.9 Acquired Size 32768 Spectral Size 65336				Spectrometer	Avance NEO
OHC CHC CHC Solvent CDC13 6q Bogeriment 10 Nuber of Scans 1024 Receiver Gain 101 Relaxation Delay 2.0000 Pulse Width 8.0000 Acquisition Time 1.3783 Acquisition Date 2021-10-10T11:47:20 Modification Date 2021-10-10T11:47:20 Modification Date 2021-10-10T11:47:20 Modification Date 2020:00T0	Me Me			Author	
OHC				Solvent	CDC13
6q Pulse Sequence zgp30 6q Experiment 10 Number of Scans 1024 Receiver Gain 101 Relaxation Delay 2.0000 Pulse Width 8.0000 Acquisition Date 2021-10-19711:47.21 Modification Date 2021-0-19711:47.21 Modification Date 20210 Modification Date				Temperature	297.4
6q Experiment 10 Number of Scans 1024 Receiver Gain 101 Relaxation Delay 2.0000 Acquisition Time 1.3763 Acquisition Date 2021-10-18711:47:22 Modification Date 2021-10-18711:46:40 Spectrometer Prequency -1833.9 Nucleus 13C Spectral Size 65536 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 80 20 10 0 -10	∽ ∽ ∽ Me			Pulse Sequence	zgpg30
Number of Scans 1024 Receiver Gain 101 Relaxation Delay 2.0000 Pulse Width 1.3763 Acquisition Date 2021-10-18711147:20 Modification Date 2021-10-18711147:20 Modification Date 2021-10-18711147:20 Modification Date 2021-10-18711146:40 Spectral Width 23809.5 Lowest Frequency 106.2 Spectral Width 23809.5 Lowest Frequency 1.83.9 Nucleus 13C Acquired Size 32788 Spectral Size 65536 65536 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10	6g			Experiment	1D
Receiver Gain 101 Relexation Dalay 2.0000 Pulse Width 8.0000 Acquisition Time 1.3763 Acquisition Date 2021-10-16711:47:27 Modification Date 2021-10-16711:46:40 Spectral Width 23809.5 Lowest Frequency -1633.9 Nucleus 120 Acquired Size 32768 Spectral Size 65336	~ 4			Number of Scans	1024
Relaxation Delay 2.0000 Pulse Width 8.0000 Acquisition Time 1.3763 Acquisition Date 2021-10-18711:47:27 Modification Date 2021-10-18711:46:40 Spectrometer Prequency 100.62 Spectral Width 23009.5 Lowest Prequency				Receiver Gain	101
Pulse Width 8.0000 Acquisition Time 1.3763 Acquisition Date 2021-10-18711:46:40 Spectral Width 23809.5 Lowest Prequency 0.1833.9 Nucleus 13C Acquired Size 32765 Spectral Size 65536 				Relaxation Delay	2,0000
Acquisition Time 1 3763 Acquisition Date 2021-10-18711:47:21 Modification Date 2021-10-18711:46:44 Spectrometer Frequency 100.62 Spectral With 23809.5 Lowest Frequency -1833.9 Nucleus 13C Acquired Size 32766 Spectral Size 65536				Pulse Width	8.0000
Acquisition Date 2021-10-1811:47:21 Modification Date 2021-10-1811:47:22 Modification Date 2021-10-1811:46:41 Spectral Width 23809.5 Lowest Frequency -1833.9 Nucleus 13C Acquired Size 32768 Spectral Size 65536 				Acquisition Time	1.3763
Modification Date 2021-10-18111:46:4 Spectral Width 23809.5 Lowest Frequency -1833.9 Nucleus 13C Acquired Size 32768 Spectral Size 65536				Acquisition Date	2021-10-18T11:47:20
Spectrometer Frequency 100.62 Spectral Width 23809.5 Lowest Frequency -1833.9 Nucleus 130 Acquired Size 32768 Spectral Size 65536				Modification Date	2021-10-18T11:46:40
Spetral With 23809.5 Lowest Frequency -1833.9 Nucleus 13C Acquired Size 32768 Spectral Size 65536				Spectrometer Freq	uency 100.62
Lowest Prequency -1833.9 Nucleus 13C Acquired Size 32768 Spectral Size 65536				Spectral Width	23809.5
Nucleus 13C Acquired Size 32768 Spectral Size 65536			5	Lowest Frequency	-1833. 9
Acquired Size 52768 Spectral Size 65536				Nucleus	130
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10			1	Acquired Size	32708
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (mm)				Spectral Size	00000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (mm)					
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (mm)		0			
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (mm)		1			
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (mm)					
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (mm)					
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (nom)					
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (nom)					
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (nom)					
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10					
210 200 190 100 110 100 120 140 130 120 110 100 90 80 (0 του 50 40 30 20 10 0 -10 f1 (πασ		· · · · · · ·			
1.1. 310.007	tin 200 120 120 120 120 120 120 120 120 120	80 (0 6)	v 50 40 30	20 10 0 -10	



-73.1041.71
-39.71
-39.71
-34.38
-34.38
-22.76
-22.76
-21.74 -8.34Parameter Value Title CR-B-81 Comment Origin Bruker BioSpin GmbH Owner nmrsu Site Spectrometer spect Author CDC13 Solvent Me Et Temperature 299.3 Pulse Sequence zgpg30 *i-*Pr Experiment 1D OH Number of Scans 198 (±) 6r Receiver Gain 202 Relaxation Delay 2.0000 Pulse Width 10.5800 Acquisition Time 1.3631 Acquisition Date 2021-09-15T08:12:50 Modification Date 2021-09-15T08:12:52 Spectrometer Frequency 100.62 Spectral Width 24038.5 Lowest Frequency -1943.9 Nucleus 13C Acquired Size 32768 Spectral Size 65536 110 50 20 10 -10 210 200 190 180 170 160 150 140 130 120 100 90 80 70 60 40 30 Ó fl (ppm)





-68.36

-45.45 -36.20 -30.84

	Parameter	Value
	Title Comment	CR-B-77
6s	Origin Owner Site	Bruker BioSpin GmbH nmrsu
	Spectrometer Author	spect
	Solvent Temperature Pulse Sequence Experiment Number of Scans Receiver Gain Relaxation Delay Pulse Width Acquisition Time Acquisition Date Modification Date Spectrometer Freque Spectral Width Lowest Frequency Nucleus Acquired Size Spectral Size	CDC13 298.2 zgpg30 1D 500 202 2.0000 10.5800 1.3631 2021-09-16T02:49:55 2021-09-16T02:49:55 100.62 24038.5 -1946.5 13C 32768 65536

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)

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-10 ò fl (ppm)




210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



S - 290



210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)



S - 292

						Title	Fu-OH.2.fid
						Origin	Bruker BioSpin GmbH
						Owner	nmrsu
						Spectrometer	spect
						Solvent	CDC13
HÓ S—S ÒH			а			Temperature	298.0
		L L	100			Pulse Sequence	zgpg30
10						Experiment	1D
10						Number of Scans	700
						Receiver Gain	202
						Relaxation Delay	2.0000
						Pulse Width	10.5800
						Acquisition Time	1.3631
						Acquisition Date	2021-10-12T02:10:45
						Modification Date	2021-10-12T02:10:46
						Spectrometer Frequer	юу 100. 63
						Spectral Width	24038. 5
						Lowest Frequency	-1950. 4
	1					Nucleus	130
						Acquired Size	32768
				1		Spectral Size	65536
				1	1		







210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 f1 (ppm)