# Supporting Information

ACETAL ELIMINATION REACTION ACCOMPANIED WITH REGIOSELECTIVE RING OPENING OF 1,4-BISACETAL-1,4-EPOXY-1,4-DIHYDRONAPHTHALENES

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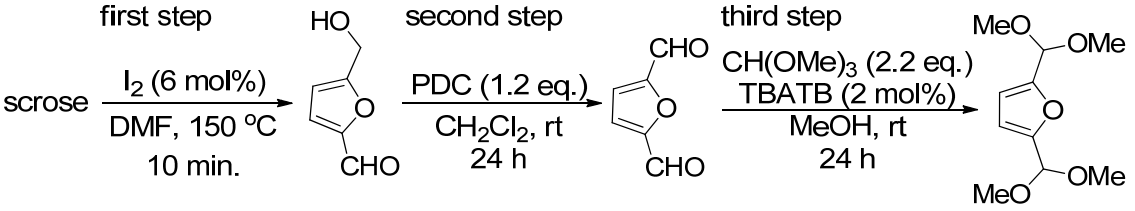
**Contents**

## 1. General Information.

All reactions were performed in oven-dried glassware under argon. Unless otherwise noted, substrates and anhydrous solvents were purchased from commercial sources and used without further purification. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 63–210 μm spherical, neutral). $^{1}H$ and $^{13}C$ NMR spectra were recorded on a JEOL ECA 500 spectrometer at room temperature in $CDCl_3$, $CD_3OD$ or $CD_3CN$ as a solvent and internal standard ($^{1}H$ NMR: δ= 7.26; $^{13}C$ NMR: δ= 77.0 for $CDCl_3$; $^{1}H$ NMR: δ = 3.31; $^{13}C$ NMR: δ = 49.0 for $CD_3OD$; $^{1}H$ NMR: δ= 1.94; $^{13}C$ NMR: δ= 1.32 for $CD_3CN$) with tetramethylsilane as an internal standard. IR spectra were recorded by a Brucker FT-IR ALPHA. ESI high resolution mass spectra (HRMS) were measured by a Shimazu hybrid IT-TOF mass spectrometer.

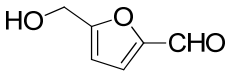
## 2. Preparation of the substrates.

### 2-1. Preparation of 2,5-bis(dimethoxymethyl)furan




First step was carried out according to reference [1]; To a solution of scrose (15 g, 45 mmol) in DMF (50 mL) were dropwised a solution of $I_2$ (350 mg, 2.7 mmol) in hexane (1 mL) at 170 °C under Ar. After stirring for 10 min., the reaction mixture was quenched with $H_2O$ (30 mL) at 0 °C and extracted with EtOAc (50 mL x 10). The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give 5-(hydroxymethyl)furan-2-carbaldehyde (5.1 g, 41 mmol) in 90% yield.

**5-(Hydroxymethyl)furan-2-carbaldehyde**

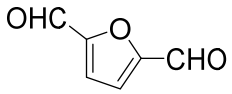



$^{1}H$ NMR (500 MHz, $CDCl_3$): δ 9.58 (s, 1H), 7.21 (d, 1H, *J* = 3.4 Hz), 6.51 (d, 1H, *J* = 3.4 Hz), 4.72 (d, 2H, *J* = 5.7 Hz), 2.57 (brs, 1H).
Spectroscopic data of $^{1}H$ NMR were identical to that of reference [2].

Second step; To a solution of 5-(hydroxymethyl)furan-2-carbaldehyde (5.0 g, 40 mmol) in $CH_2Cl_2$

(100 mL) were added PDC (16 g, 44 mmol) and celite (16 g) at room tepmerature under Ar. After stirring for 24 h, the reaction mixture was filtrated thorough a celite pad and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give furan-2,5-dicarbaldehyde (4.36 g, 35 mmol) in 88% yield.

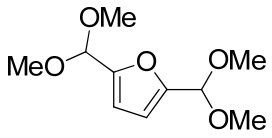
**Furan-2,5-dicarbaldehyde**



$^1$H NMR (500 MHz, $CDCl_3$): δ 9.86 (s, 2H), 7.34 (s, 2H).
Spectroscopic date of $^1$H NMR was identical to that of reference [3].

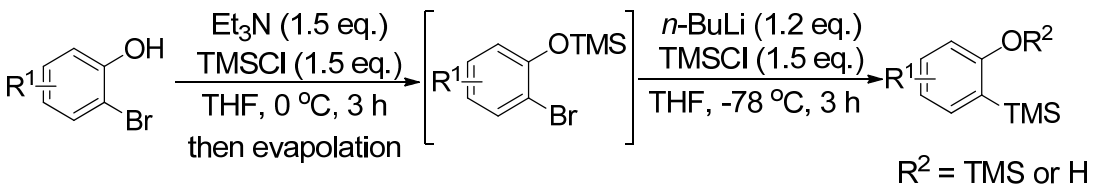
Third step; To a solution of furan-2,5-dicarbaldehyde (1.0 g, 8.7 mmol) in MeOH (20 mL) were added trimethyl orthoformate (2 mL, 19.2 mmol) and tetrabutylammonium tribromide (TBATB; 90 mg, 0.17 mmol) at room tepmerature under Ar. After stirring for 6 h, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (20 mL) and extracted with EtOAc (20 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc/$Et_3N$ = 100/10/1) to give 2,5-bis(dimethoxymethyl)furan in 89% yield (1.68 g, 7.8 mmol).

**2,5-Bis(dimethoxymethyl)furan**



Colorless oil; IR (ATR) cm$^{-1}$: 2937, 2831, 1444, 1356, 1190, 1102, 1051, 1017; $^1$H NMR (500 MHz, $CDCl_3$): δ 6.40 (s, 2H), 5.42 (s, 2H), 3.34 (s, 12H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 150.8, 108.9, 97.8, 52.8; ESI-HRMS m/z: 239.0878 ([M+Na]$^+$); Calcd for $C_{10}H_{16}O_5Na$: 239.0890.

**2-2. Preparation of trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivatives.**



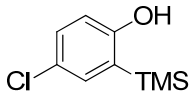

This preparation method was carried out according to reference [4].

First step; To a solution of 2-bromophenol derivative (5 mmol) in anhydrous THF (20 mL) were added $Et_3N$ (1 mL, 7.5 mmol) and TMSCl (1 mL, 7.5 mmol) at 0 °C under argon. After stirring

for 3 h, the reaction mixture was concentrated in vacuo. The residue was filtrated through a celite pad (washed with hexane) and the filtrate was concentrated in vacuo to provide 2-bromophenyl trimethylsilyl ether derivative which was used in next step without further purification.

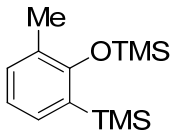
Socond step; To a solution of the obtained silyl ether in anhydrous THF (20 mL) was dropwised 2.6 M solution of *n*-BuLi in hexane (3.75 mL, 6 mmol) at -78 ºC under Ar. After stirring for 1 h, TMSCl (1 mL, 7.5 mmol) was added to the reaction mixture at -78 ºC and the reaction mixture was further stirred for 3 h. The reaction mixture was quenched with sat. $NaHCO_3$ aq. (10 mL) at 0 ºC and extracted with hexane (10 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/$Et_3N$ = 100/1) to give a trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivative .

**4-Chloro-2-(trimethylsilyl)phenol**



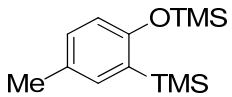

Colorless oil; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.27―7.26 (m, 1H), 7.16 (dd, 1H, *J* = 8.3, 2.9 Hz), 6.60 (d, 1H, *J* = 8.3 Hz) 0.30 (s, 9H).
Spectroscopic date of $^1$H NMR was identical to that of reference [5].

**Trimethyl(3-methyl-2-((trimethylsilyl)oxy)phenyl)silane**




Colorless oil; IR (ATR) cm$^{-1}$: 2954, 1449, 1403, 1254, 1222, 1190, 1148; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.24 (dd, 1H, *J* = 7.5, 1.5 Hz), 7.14 (dd, 1H, *J* = 6.9, 1.5 Hz), 6.90 (dd, 1H, *J* = 7.5, 6.9 Hz), 2.25 (s, 3H), 0.30 (s, 9H), 0.29 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 158.9, 133.2, 132.8, 130.2, 127.0, 121.3, 19.3, 1.9, -0.1; ESI-HRMS m/z: 275.1288 ([M+Na]$^+$); Calcd for $C_{13}H_{24}OSi_2Na$: 275.1258.

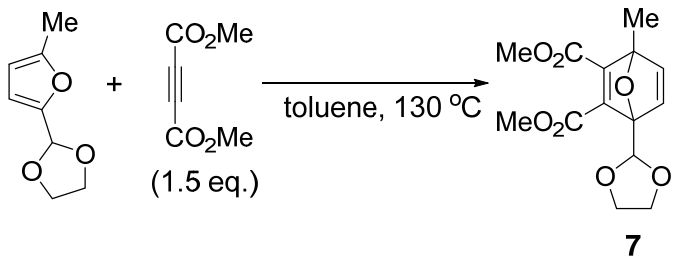
**Trimethyl(5-methyl-2-((trimethylsilyl)oxy)phenyl)silane**




Colorless oil; IR (ATR) cm$^{-1}$: 2956, 1474, 1386, 1275, 1235, 1140, 1079; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.16 (s, 1H), 7.04 (d, 1H, *J* = 8.0 Hz), 6.67 (d, 1H, *J* = 8.0 Hz), 2.28 (s, 3H), 0.32 (s, 9H), 0.26 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 158.1, 135.8, 130.9, 129.6, 129.4, 116.2, 20.6,

0.6, -0.9; ESI-HRMS m/z: 253.1430 ([M+H]$^+$); Calcd for $C_{13}H_{24}OSi_2$: 253.1438.

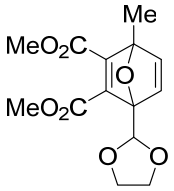
**2-3. Preparation of dimethyl-1-(1,3-dioxolan-2-yl)-4-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7)**




**7**

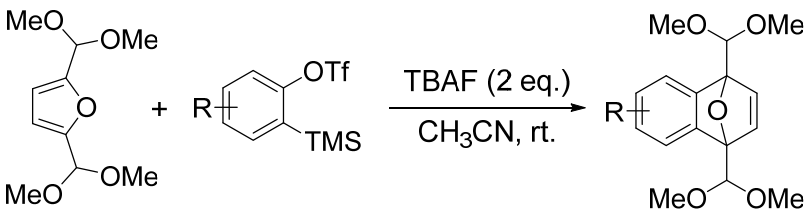
To a solution of 2-(5-methylfuran-2-yl)-1,3-dioxolane (470.0 mg, 3.0 mmol) in toluene (2 mL) was added dimethyl but-2-ynedioate (0.6 mL, 4.5 mmol) and the reaction mixture was stirred at 130 °C under Ar. After stirring for 24 h, the reaction mixture was concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 2/1) to give dimethyl 1-(1,3-dioxolan-2-yl)-4-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**3**; 799.4 mg, 2.7 mmol) in 90% yield.

**Dimethyl-1-(1,3-dioxolan-2-yl)-4-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (7)**




Yellow oil; IR (ATR) cm$^{-1}$: 2955, 1713, 1633, 1435, 1306, 1242, 1138, 1095, 1038; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.11 (d, 1H, *J* = 5.2 Hz), 7.00 (d, 1H, *J* = 5.2 Hz), 5.74 (s, 1H), 4.12—4.05 (m, 2H), 4.00—3.94 (m ,2H), 3.80 (s, 3H), 3.78 (s, 3H), 1.84 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 164.2, 163.8, 154.0, 152.9, 147.4, 142.9, 100.0, 95.8, 93.1, 65.9, 65.9, 52.3, 52.2, 15.4; ESI-HRMS m/z: 319.0815 ([M+Na]$^+$); Calcd for $C_{14}H_{16}O_7Na$: 319.0788.

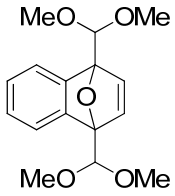
**2-4. Preparation of trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivative (1a, 1c an 1d)**




**1**

To a solution of 2,5-bis(dimethoxymethyl)furan (252.5 mg, 1.0 mmol) in $CH_3CN$ (15 mL) were added trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivative (324.3 mg, 1.5 mmol) and a solution of tetrabutylammonium fluoride in THF (TBAF: 2 mL, 2.0 mmol) and the reaction mixture was stirred at room temperature under Ar. After stirring for 24 h, the reaction mixture was quenched with $H_2O$ (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 3/1) to give trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivative.

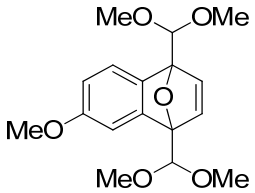
**1,4-Bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (1a)**




2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (1.68 g, 7.8 mmol) was used and 1,4-bis(dimethoxymethyl)-1,4-dihydro-1,4-epoxynaphthalene (**1a**: 1.85 g, 6.3 mmol) was obtained in 81% yield after purification by silica-gel column chromatography (Hex/EtOAc = 3/1).

Colorless oil; IR (ATR) $cm^{-1}$: 2936, 2832, 1447, 1383, 1288, 1191, 1141, 1104, 1065, 1034; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.33 (dd, 1H, *J* = 5.2, 3.0 Hz), 7.01 (s, 2H), 6.96 (dd, 2H, *J* = 5.2, 3.0 Hz), 5.01 (s, 2H), 3.63 (s, 6H), 3.62 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 149.1, 142.9, 124.9, 120.6, 103.3, 93.1, 56.5, 56.2; ESI-HRMS m/z: 315.1175 ($[M+Na]^+$); Calcd for $C_{16}H_{20}O_5Na$: 315.1203.

**1,4-Bis(dimethoxymethyl)-6-methoxy-1,4-epoxy-1,4-dihydronaphthalene (1c)**

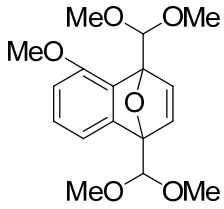



4-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (492.6 mg, 1.5 mmol) was used and 1,4-bis(dimethoxymethyl)-6-methoxy-1,4-dihydro-1,4-epoxynaphthalene (**1c**: 23.8 mg, 0.45 mmol) was obtained in 30% yield after purification by silica-gel column chromatography (Hex/EtOAc = 3/1).

Yellow oil; IR (ATR) $cm^{-1}$: 2939, 2833, 1598, 1465, 1382, 1346, 1272, 1207, 1190, 1107, 1068, 1038, 1025; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.20 (d, 1H, J = 8.0 Hz), 7.01—6.96 (m, 3H), 6.42 (d, 1H, *J* = 8.0 Hz), 4.99 (s, 1H), 4.97 (s, 1H), 3.76 (s, 3H), 3.62 (s, 6H), 3.61 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 157.3, 151.1, 143.3, 142.2, 140.7, 120.7, 109.9, 107.3, 103.3, 103.2, 92.9,

92.9, 56.6, 56.5, 56.2, 56.2, 55.5; ESI-HRMS m/z: 345.1298 ([M+Na]$^+$); Calcd for $C_{17}H_{22}O_6Na$: 345.1309.

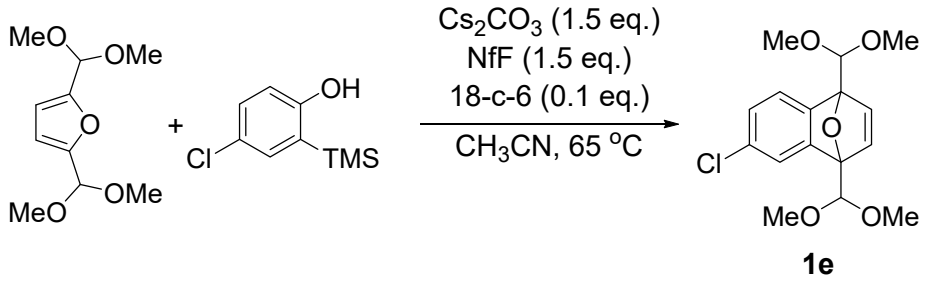
**1,4-Bis(dimethoxymethyl)-5-methoxy-1,4-epoxy-1,4-dihydronaphthalene (1d)**



2-Methoxy-6-(trimethylsilyl)phenyl trifluoromethanesulfonate (1.82 g, 5.56 mmol) was used and 1,4-bis(dimethoxymethyl)-5-methoxy-1,4-dihydro-1,4-epoxynaphthalene (**1d**: 207.9 mg, 0.65 mmol) was obtained in 16% yield after purification by silica-gel column chromatography (Hex/EtOAc = 3/1).

Colorless oil; IR (ATR) cm$^{-1}$: 2936, 2834, 1607, 1477, 1441, 1381, 1355, 1287, 1260, 1231, 1192, 1103, 1078, 1036; $^1$H NMR (500 MHz, $CDCl_3$): δ 7.01—6.99 (m, 3H), 6.95 (t, 1H, *J* = 7.5 Hz), 6.59 (d, 1H, *J* = 8.5 Hz), 5.58 (s, 1H), 4.97 (s, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 3.59 (s, 3H), 3.56 (s, 3H), 3.55 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 152.7, 151.8, 143.1, 142.3, 135.6, 127.1, 114.1, 110.2, 103.3, 99.9, 94.3, 93.5, 56.5, 56.2, 55.6, 55.5, 54.2; ESI-HRMS m/z: 345.1306 ([M+Na]$^+$); Calcd for $C_{17}H_{22}O_6Na$: 345.1309.

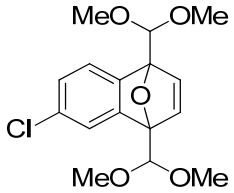
**2-5. Preparation of 6-chloro-1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (1e)**




This step was carried out according to reference [5]; To a solution of 2,5-bis(dimethoxymethyl)furan (233.5 mg, 1.5 mmol) in $CH_3CN$ (4 mL) were added 4-chloro-2-(trimethylsilyl)phenol (162.3 mg, 0.9 mmol), $Cs_2CO_3$ (450 mg, 1.4 mmol), nonafluorobutanesulfonyl fluoride (NfF: 243 μL, 1.4 mmol) and 18-crown-6 (132 mg, 0.1 mmol) and the reaction mixture was stirred at 65 °C under Ar. After stirring for 20 h, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (10 mL) and extracted with EtOAc (10 mL x 3). The combined organic layers were dried over $Na_2SO_4$ and concentrated in vacuo. The residue was

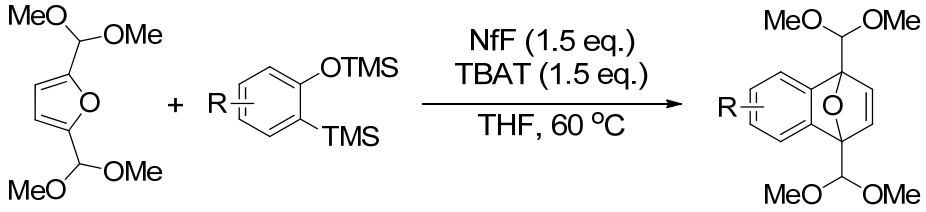
purified by silica-gel column chromatography (Hex/acetone = 5/1) to give 6-chloro-1,4-bis(dimethoxymethyl)-1,4-dihydro-1,4-epoxynaphthalene (**1e**; 83.3 mg, 0.27 mmol) in 28% yield.

**6-Chloro-1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (1e)**



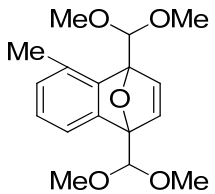

Colorless oil; IR (ATR) $cm^{-1}$: 2935, 2834, 1442, 1380, 1287, 1191, 1108, 1072, 1033; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.31 (d, 1H, *J* = 1.7 Hz), 7.23 (d, 1H, *J* = 7.8 Hz), 7.00 (d, 1H, *J* = 5.7 Hz), 6.98 (d, 1H, *J* = 5.7 Hz), 6.94 (dd, 1H, *J* = 7.8 , 1.7 Hz), 4.96 (s, 1H), 4.95 (s, 1H), 3.63 (s, 3H), 3.61 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 151.4, 147.7, 143.2, 142.7, 130.8, 124.6, 121.7, 121.4, 103.2, 93.1, 93.0, 56.8, 56.7, 56.4, 56.3; ESI-HRMS m/z: 349.0806 ($[M+Na]^+$); Calcd for $C_{16}H_{19}O_5ClNa$: 349.0813.

**2-6. Preparation of trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivative (1f or 1g)**




This step was carried out according to reference [4]; To a solution of 2,5-bis(dimethoxymethyl)furan (252.5 mg, 1.0 mmol) in THF (3 mL) were added trimethyl(2-((trimethylsilyl)oxy)phenyl)silane derivative (324.3 mg, 1.5 mmol), nonafluorobutanesulfonyl fluoride (NfF: 263 μL, 1.5 mmol) and tetrabutylammonium triphenyldifluorisilicate (TBAT: 809.8 mg, 1.5 mmol) and the reaction mixture was stirred at 60 °C under Ar. After stirring for 24 h, the reaction mixture was filtered through a short pad of silica gel and concentrated in vacuo. The residue was purified by silica-gel column chromatography to give **1f** (R = 5-Me) or **1g** (R = 6-Me).

**1,4-Bis(dimethoxymethyl)-5-methyl-1,4-epoxy-1,4-dihydronaphthalene (1f)**

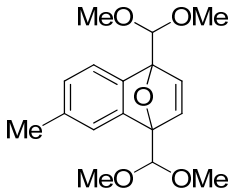



(5-Methoxy-2-((trimethylsilyl)oxy)phenyl)trimethylsilane (252.5 mg, 1.0 mmol) was used and 1,4-bis(dimethoxymethyl)-5-methoxy-1,4-dihydro-1,4-epoxynaphthalene (**1f**: 115.8 mg, 0.38

mmol) was obtained in 38% yield after purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Colorless oil; IR (ATR) $cm^{-1}$: 2934, 2832, 1470, 1378, 1285, 1192, 1158, 1081; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.17 (d, 1H, *J* = 7.2 Hz), 6.97 (d, 1H, *J* = 12.6 Hz), 6.98 (d, 1H, *J* = 12.6 Hz), 6.86 (dd, 1H, *J* = 7.5, 7.2 Hz), 6.75 (d, 1H, *J* = 7.5 Hz), 5.18 (s, 1H), 4.99 (s, 1H), 3.63 (s, 3H), 3.60 (s, 3H), 3.57 (s, 6H), 2.36 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 149.4, 146.9, 143.1, 142.6, 131.0, 128.2, 125.0, 118.0, 103.3, 102.2, 95.0, 92.7, 56.3, 56.2, 55.7, 55.6, 19.5; ESI-HRMS m/z: 329.1362 ($[M+Na]^+$); Calcd for $C_{17}H_{22}O_5Na$: 329.1359.

**1,4-Bis(dimethoxymethyl)-6-methyl-1,4-epoxy-1,4-dihydronaphthalene (1g)**




(6-Methoxy-2-((trimethylsilyl)oxy)phenyl)trimethylsilane (252.3 mg, 1.0 mmol) was used and 1,4-bis(dimethoxymethyl)-6-methoxy-1,4-dihydro-1,4-epoxynaphthalene (**1g**: 130.4 mg, 0.43 mmol) was obtained in 43% yield after purification by silica-gel column chromatography (Hex/EtOAc = 4/1).

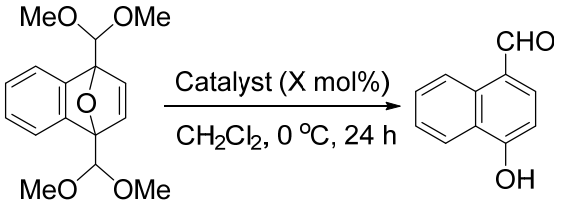
Colorless oil; IR (ATR) $cm^{-1}$: 2934, 2832, 1447, 1381, 1356, 1289, 1192, 1107, 1076, 1034; $^1H$ NMR (500 MHz, $CDCl_3$): δ 7.20 (d, 1H, *J* = 7.5 Hz), 7.17 (s, 1H), 6.99 (d, 1H, *J* = 12.6 Hz), 6.98 (d, 1H, *J* = 12.6 Hz), 6.76 (d, 1H, *J* = 7.5 Hz), 4.99 (s, 2H), 3.64 (s, 3H), 3.62 (s, 3H), 3.62 (s, 3H), 3.60 (s, 3H), 2.29 (s, 3H); $^{13}C$ NMR (125 MHz, $CDCl_3$): δ 149.3, 146.2, 143.2, 142.7, 134.7, 125.0, 121.8, 120.2, 103.4, 103.3, 93.0, 56.6, 56.4, 56.3, 56.2, 21.3; ESI-HRMS m/z: 329.1354 ($[M+Na]^+$); Calcd for $C_{17}H_{22}O_5Na$: 329.1359.

## 3. General procedure of key reactions.

To a solution of the substrate (**1**, **4**, **5** or **7**: 0.15 mmol) in $CH_2Cl_2$ (0.75 mL) was added $FeX_3$ (0.0075 mmol) [and TMSCl (27 μL, 0.15 mmol)] at room temperature. After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. and the mixture was extracted with $CH_2Cl_2$ (5 mL x 2). The combined organic layers were dried over $Na_2SO_4$, concentrated in vacuo and purified by silica-gel column chromatography to give the product.

## 4. Screening of catalysts.

Table S1. Catalyst efficiency using 1,4-diacetal-1,4-epoxy-1,4-dihydronaphthalene as a substrate.

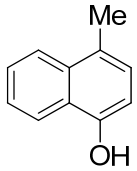



**1a** **2a**

| Entry | catalyst | X (mol%) | additive (1 equive.) | Yield (%) |
|---|---|---|---|---|
| 1 | $FeCl_3$ | 5 | — | 47 |
| 2 | $FeCl_3$ | 20 | — | 61 |
| 3 | $FeCl_3$ | 5 | TMSCl | 42 |
| 4 | $FeBr_3$ | 5 | — | 49 |
| 5 | $FeBr_3$ | 20 | — | 70 |
| 6 | $FeBr_3$ | 5 | TMSCl | 42 |
| 7 | $AuCl_3$ | 5 | TMSCl | 15 |
| 8 | TMSOTf | 5 | — | 19 |
| 9 | $BF_3$ $Et_2O$ | 5 | — | 11 |
| 10 | $B(C_6F_5)_3$ | 5 | — | 0 |
| 11 | TFA | 5 | — | trace |
| 12 | TFAA | 5 | — | 0 |

## 5. Spectroscopic data.

**4-Methylnaphthalen-1-ol (6).**

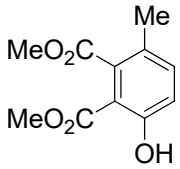



1-(Dimethoxymethyl)-4-methyl-1,4-dihydro-1,4-epoxynaphthalene (**5a**: 15.2 mg, 0.15 mmol) and $FeCl_3$ (1.2 mg, 0.0075 mmol) were used according to the typical procedure and 4-methylnaphthalen-1-ol (**6**: 43.2 mg, 0.12 mmol) was obtained in 82% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

$^1$H NMR (500 MHz, $CD_3OD$): δ 8.22 (d, 1H, *J* = 8.6 Hz), 7.95 (d, 1H, *J* = 8.0 Hz), 7.57—7.50 (m, 2H), 7.14 (d, 1H, *J* = 7.5 Hz), 6.73 (d, 1H, *J* = 8.0 Hz), 5.20 (brs, 1H), 2.62 (s, 3H).

Spectroscopic date of $^1$H NMR was identical to that of reference [6].

**Dimethyl 3-hydroxy-6-methylphthalate (8).**

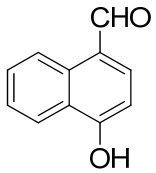



Dimethyl 1-(1,3-dioxolan-2-yl)-4-methyl-7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**7**: 30.3 mg, 0.10 mmol) and $FeCl_3$ (0.8 mg, 0.005 mmol) were used according to the typical procedure and dimethyl 3-hydroxy-6-methylphthalate (**8**: 19.2 mg, 0.09 mmol) was obtained in 87% yield after 18 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 3/1).

$^1$H NMR (500 MHz, $CD_3OD$): δ 10.76 (s, 1H), 7.29 (d, 1H, *J* = 8.6 Hz), 6.96 (d, 1H, *J* = 8.6 Hz), 3.91 (s, 3H), 3.89 (s, 3H), 2.21 (s, 3H).

Spectroscopic date of $^1$H NMR was identical to that of reference [7].

**4-Hydroxy-1-naphthaldehyde (2a) in eq. 5.**



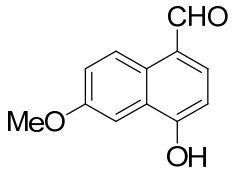

1,4-Bis(dimethoxymethyl)-1,4-dihydro-1,4-epoxynaphthalene (**1a**: 19.2 mg, 0.10 mmol) and $FeBr_3$ (5.9 mg, 0.02 mmol) were used according to the typical procedure and 4-hydroxy-1-naphthaldehyde (**2a**: 12.1 mg, 0.07 mmol) was obtained in 70% yield after 24 h stirring and

purification by silica-gel column chromatography (Hex/EtOAc = 2/1) (30% of starting material was recovered).

$^1$H NMR (500 MHz, $CD_3OD$): δ 10.10 (s, 1H), 9.27 (d, 1H, *J* = 8.6 Hz), 8.36 (d, 1H, *J* = 8.0 Hz), 7.95 (d, 1H, *J* = 8.0 Hz), 7.69 (dt, 1H, *J* = 7.5, 1.2 Hz), 7.57 (t, 1H, *J* = 7.5 Hz), 6.99 (d, 1H, *J* = 8.0 Hz).

Spectroscopic date of $^1$H NMR was identical to that of reference [8].

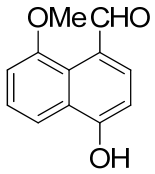
**4-Hydroxy-6-methoxy-1-naphthaldehyde (2c)**




1,4-Bis(dimethoxymethyl)-6-methoxy-1,4-dihydro-1,4-epoxynaphthalene (**2c**: 6.0 mg, 0.02 mmol), $FeCl_3$ (0.16 mg, 0.001 mmol) and TMSCl (2.5 μL, 0.02 mmol) were used according to the typical procedure and 4-hydroxy-6-methoxy-1-naphthaldehyde (**6c**: 4.7 mg, 0.02 mmol) was obtained in quantitative yield after 6 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Brown solid; M. p. 159.0—161.0 ºC; IR (ATR) cm$^{-1}$: 3175, 2957, 2925, 2853, 1675, 1652, 1625, 1567, 1520, 1491, 1464, 1436, 1395, 1364, 1293, 1261, 1224, 1208, 1182, 1150, 1111, 1067, 1031; $^1$H NMR (500 MHz, $CD_3CN$): δ 10.08 (s, 1H), 9.18 (d, 1H, *J* = 9.0 Hz), 7.78 (d, 1H, *J* = 7.5 Hz), 7.59 (d, 1H, *J* = 2.5 Hz), 7.34 (dd, 1H, *J* = 9.0, 2.5 Hz), 7.13 (d, 1H, *J* = 7.5 Hz), 3.92 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$): δ 193.3, 158.9, 158.6, 138.7, 128.2, 127.2, 126.9, 125.3, 122.2, 108.9, 101.9, 55.9; ESI-HRMS m/z: 201.0553 ([M-H]$^-$); Calcd for $C_{12}H_{10}O_3$: 201.0557.

**4-Hydroxy-8-methoxy-1-naphthaldehyde (2d)**

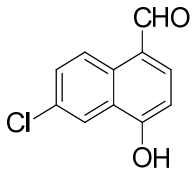



1,4-Bis(dimethoxymethyl)-5-methoxy-1,4-dihydro-1,4-epoxynaphthalene (**1d**: 14.6 mg, 0.05 mmol), $FeCl_3$ (0.4 mg, 0.0025 mmol) and TMSCl (6.3 μL, 0.05 mmol) were used according to the typical procedure and 4-hydroxy-8-methoxy-1-naphthaldehyde (**2d**; 4.6 mg, 0.02 mmol) was obtained in 42% yield after 3 h stirring and purification by silica-gel column chromatography (Hex/acetone = 3/1) (35% of starting material was recovered).

Yellow solid; M. p. 122.0—124.2 ºC; IR (ATR) cm$^{-1}$: 3351, 2496,1638, 1561, 1542, 1354, 1327, 1262, 1222, 1179, 1084, 1049; $^1$H NMR (500 MHz, $CD_3OD$): δ 11.00 (s, 1H), 7.97 (d, 1H, *J* =

8.6 Hz), 7.94 (d, 1H, *J* = 7.5 Hz), 7.43 (t, 1H, *J* = 7.5 Hz), 7.15 (d, 1H, *J* = 7.5 Hz), 6.89 (d, 1H, *J* = 8.6 Hz), 4.02 (s, 3H)); $^{13}$C NMR (125 MHz, $CD_3OD$): δ 196.2, 160.7,157.7, 130.9, 127.7, 127.3, 126.6, 126.4, 116.9, 109.2, 109.0, 56.1; ESI-HRMS m/z: 225.0546 ($[M+Na]^+$); Calcd for $C_{12}H_{10}O_3Na$: 225.0522.

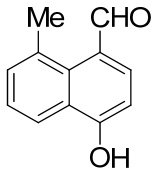
**6-Chloro-4-hydroxy-1-naphthaldehyde (2e)**




6-Chloro-1,4-bis(dimethoxymethyl)-1,4-dihydro-1,4-epoxynaphthalene (**1e**: 82.0 mg, 0.25 mmol), $FeCl_3$ (4.0 mg, 0.025 mmol) and TMSCl (27 μL, 0.25 mmol) was used according to the typical procedure and 6-chloro-4-hydroxy-1-naphthaldehyde (**2e**: 12.0 mg, 0.06 mmol) was obtained in 23% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 2/1) (50% of starting material was recovered).

Colorless solid; M. p. 63.1—64.7 °C; IR (ATR) $cm^{-1}$: 3089, 2924, 1652, 1562, 1505, 1464, 1389, 1354, 1324, 1210, 1157, 1055; $^1$H NMR (500 MHz, $CD_3OD$): δ 9.95 (s, 1H), 9.16 (d, 1H, *J* = 9.2 Hz), 8.17 (d, 1H, *J* = 2.3 Hz), 7.84 (d, 1H, *J* = 8.0 Hz), 7.52 (dd, 1H, *J* = 9.2, 2.3 Hz), 6.90 (d, 1H, *J* = 8.0 Hz); $^{13}$C NMR (125 MHz, $CD_3OD$): δ 193.8, 160.9, 142.1, 132.9, 131.9, 130.8, 127.9, 127.3, 124.9, 123.0, 109.2; ESI-HRMS m/z: 207.0235 ($[M+H]^+$); Calcd for $C_{11}H_7O_2Cl$: 207.0207.

**4-Hydroxy-8-methyl-1-naphthaldehyde (2fa)**

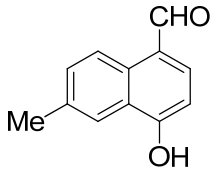



1,4-Bis(dimethoxymethyl)-5-methyl-1,4-dihydro-1,4-epoxynaphthalene (**1f**: 31.8 mg, 0.10 mmol) and $FeBr_3$ (3.0 mg, 0.01 mmol) was used according to the typical procedure and 4-hydroxy-8-methyl-1-naphthaldehyde (**2fa** and **2fb**: 4.1 mg, 0.02 mmol) was obtained in 22% (major/minor = 92/8) yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 3/1) (68% of starting material was recovered).

Colorless solid; M. p. 78.1—78.9 °C; IR (ATR) $cm^{-1}$: 3353, 2500, 1640, 1563, 1515, 1450, 1421, 1324, 1217, 1101; $^1$H NMR (500 MHz, $CD_3OD$): major: δ 10.53 (s, 1H), 8.23 (d, 1H, *J* = 8.0 Hz), 7.96 (d, 1H, *J* = 8.0 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), 7.40 (dd, 1H, *J* = 8.0, 7.5 Hz), 6.87 (d, 1H, *J* = 8.0 Hz), 2.71 (s, 3H); minor: δ 10.02 (s, 1H), 9.15 (d, 1H, *J* = 8.0 Hz), 7.82 (d, 1H, *J* = 8.0 Hz), 7.44 (overrupped on the peaks of major isomer, 1H), 7.26 (d, 1H, *J* = 7.5 Hz), 6.89 (d, 1H, *J* = 8.0

Hz), 2.91 (s, 3H); $^{13}$C NMR (125 MHz, $CD_3OD$) of major isomer: δ 193.7, 161.6, 135.0, 134.9, 134.1, 133.0, 128.7, 127.4, 126.2, 122.6, 107.8, 26.2; ESI-HRMS m/z: 209.0576 ([M+Na]$^+$); Calcd for $C_{12}H_{10}O_2Na$: 209.0573.

**4-Hydroxy-6-methyl-1-naphthaldehyde (2g)**




1,4-Bis(dimethoxymethyl)-6-methyl-1,4-dihydro-1,4-epoxynaphthalene (**1g**: 30.8 mg, 0.10 mmol) and $FeBr_3$ (1.5 mg, 0.005 mmol) was used according to the typical procedure and 4-hydroxy-6-methyl-1-naphthaldehyde (**2g**: 4.2 mg, 0.02 mmol) was obtained in 22% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 3/1) (49% of starting material was recovered).

Colorless solid; M. p. 80.0—81.5 °C; IR (ATR) cm$^{-1}$: 3346, 2497, 1650, 1563, 1517, 1397, 1256, 1218, 1060; $^1$H NMR (500 MHz, $CD_3OD$): δ 10.00 (s, 1H), 9.10 (d, 1H, $J$ = 8.6 Hz), 8.07 (s, 1H), 7.81 (d, 1H, $J$ = 7.8 Hz), 7.48 (d, 1H, $J$ = 8.6 Hz), 6.89 (d, 1H, $J$ = 7.8 Hz); $^{13}$C NMR (125 MHz, $CD_3OD$): δ 194.1, 161.7, 141.3, 136.8, 132.4, 132.6, 126.5, 125.7, 124.9, 122.9, 108.4, 21.8; ESI-HRMS m/z: 187.0768 ([M+H]$^+$); Calcd for $C_{12}H_{10}O_2$: 187.0754.

## 6. References.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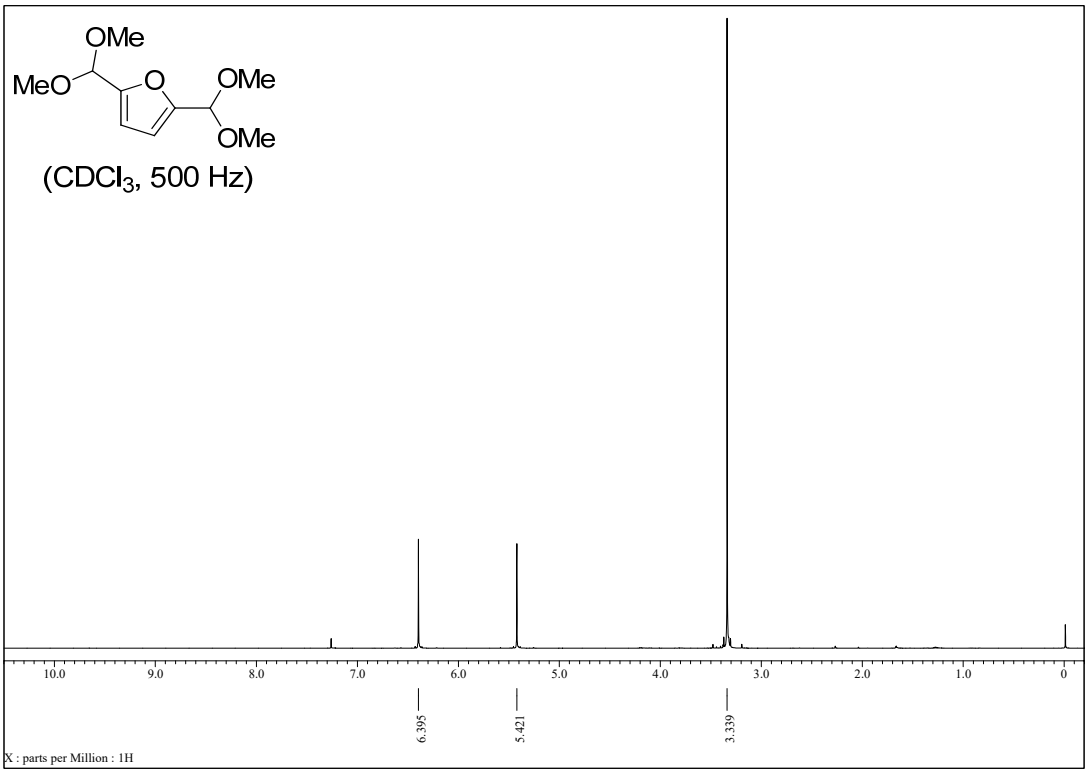
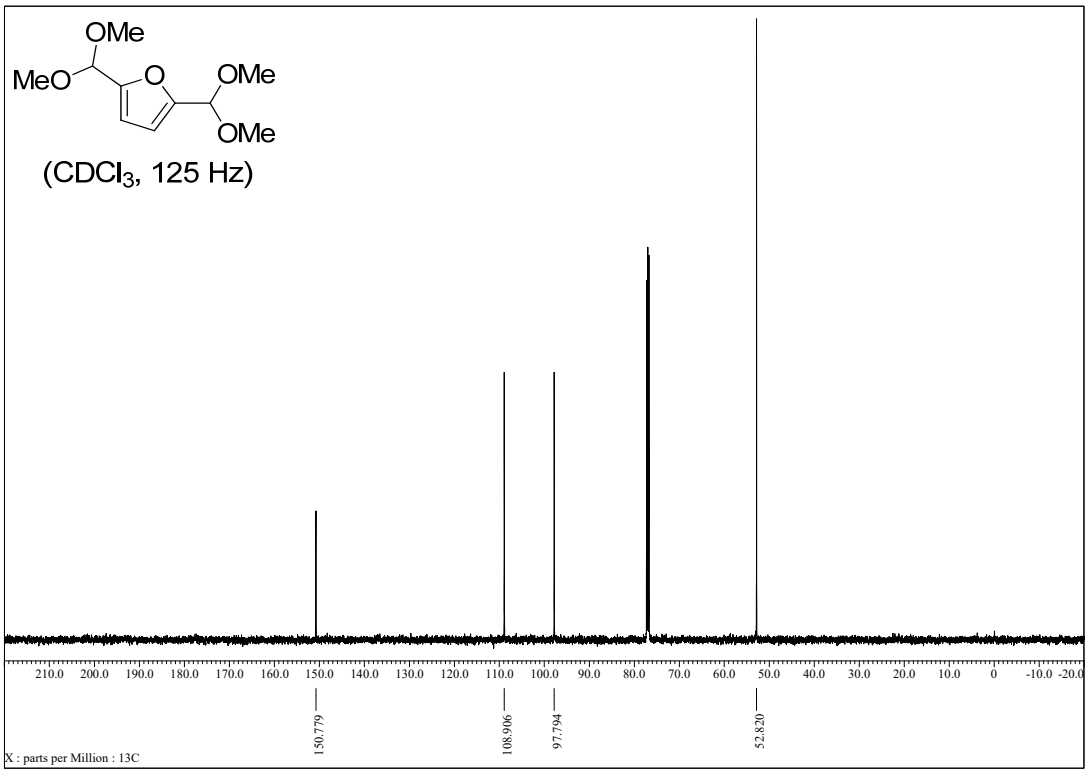
## 7. $^{1}H$ and $^{13}C$ NMR spectra of the newly synthesized substrates and products.

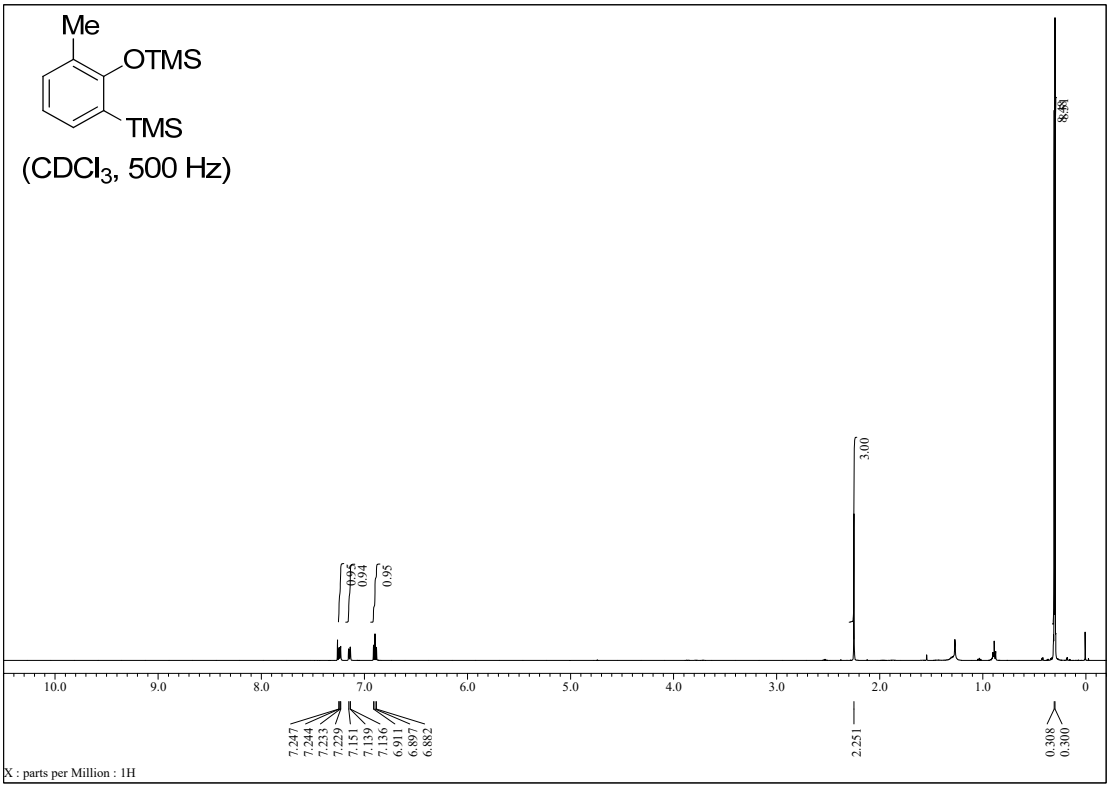
$^{1}H$ NMR of 2,5-bis(dimethoxymethyl)furan



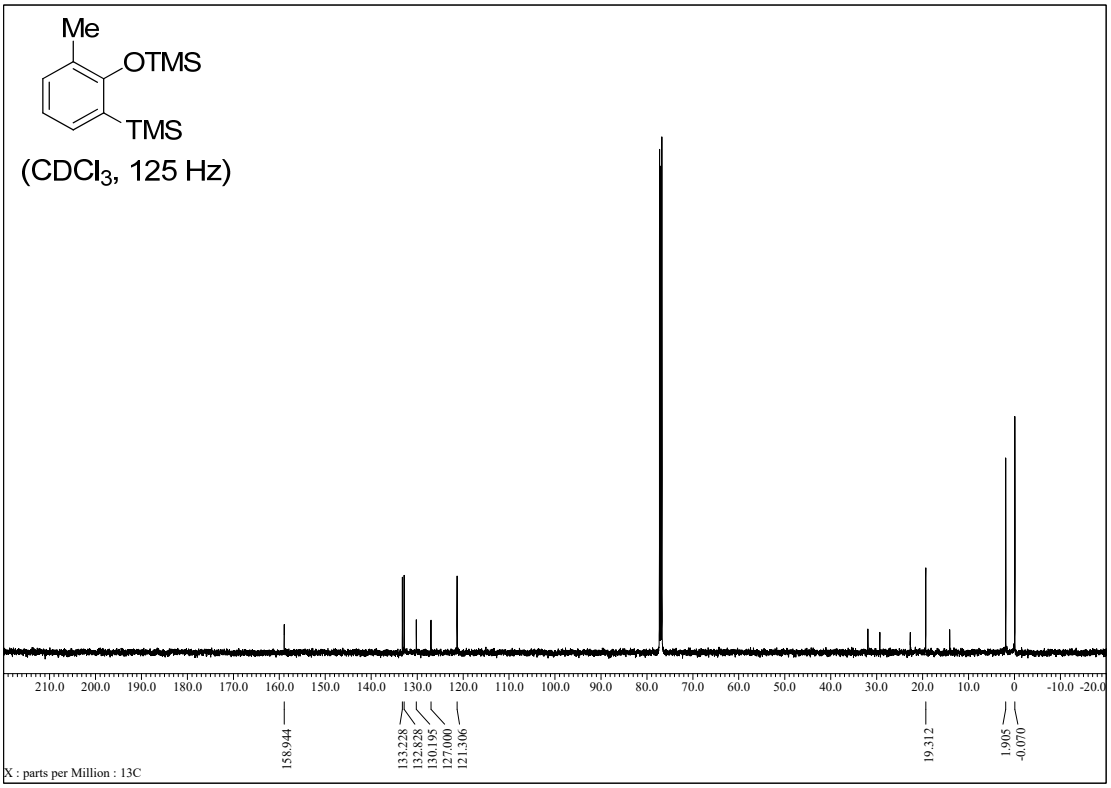

$^{13}C$ NMR of 2,5-bis(dimethoxymethyl)furan



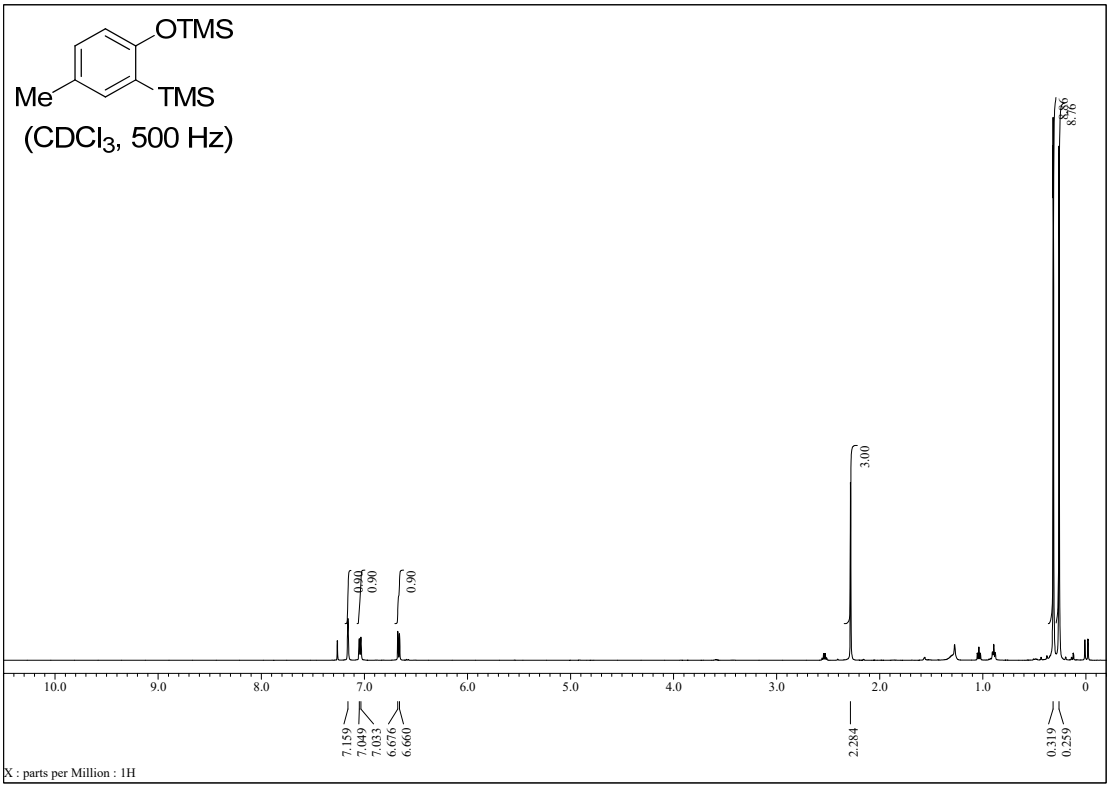
$^{1}$H NMR of trimethyl(3-methyl-2-((trimethylsilyl)oxy)phenyl)silane



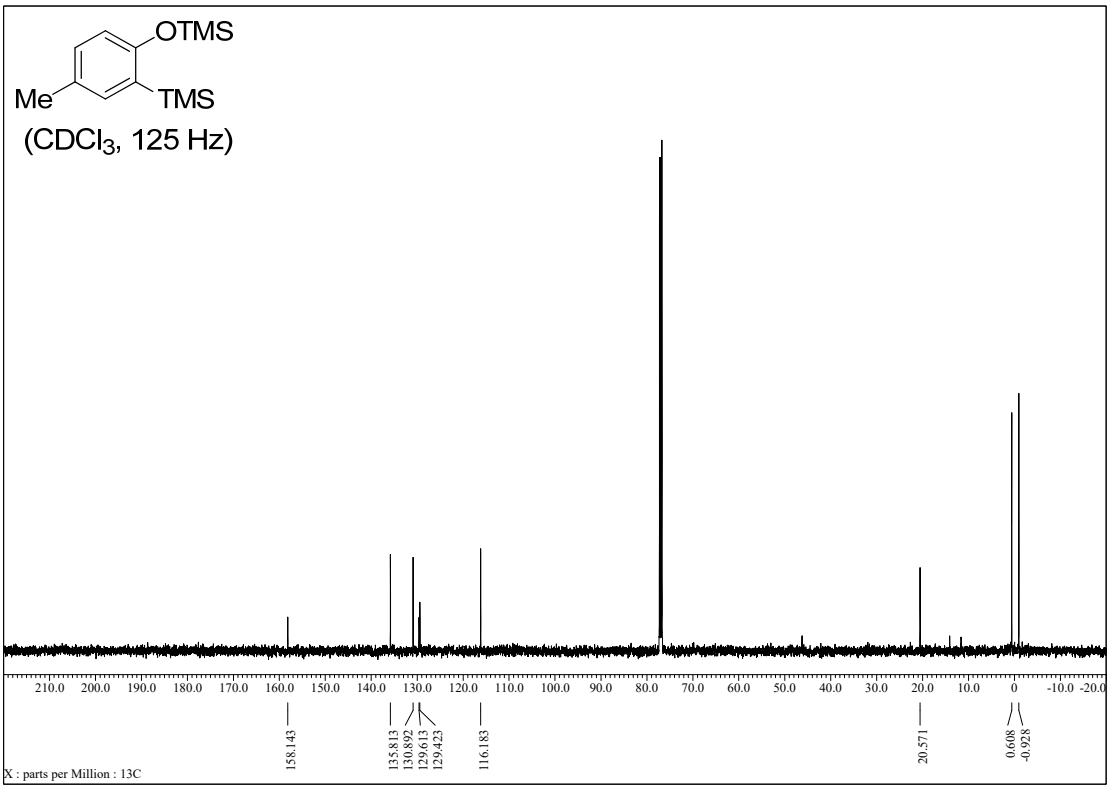

$^{13}$C NMR of trimethyl(3-methyl-2-((trimethylsilyl)oxy)phenyl)silane



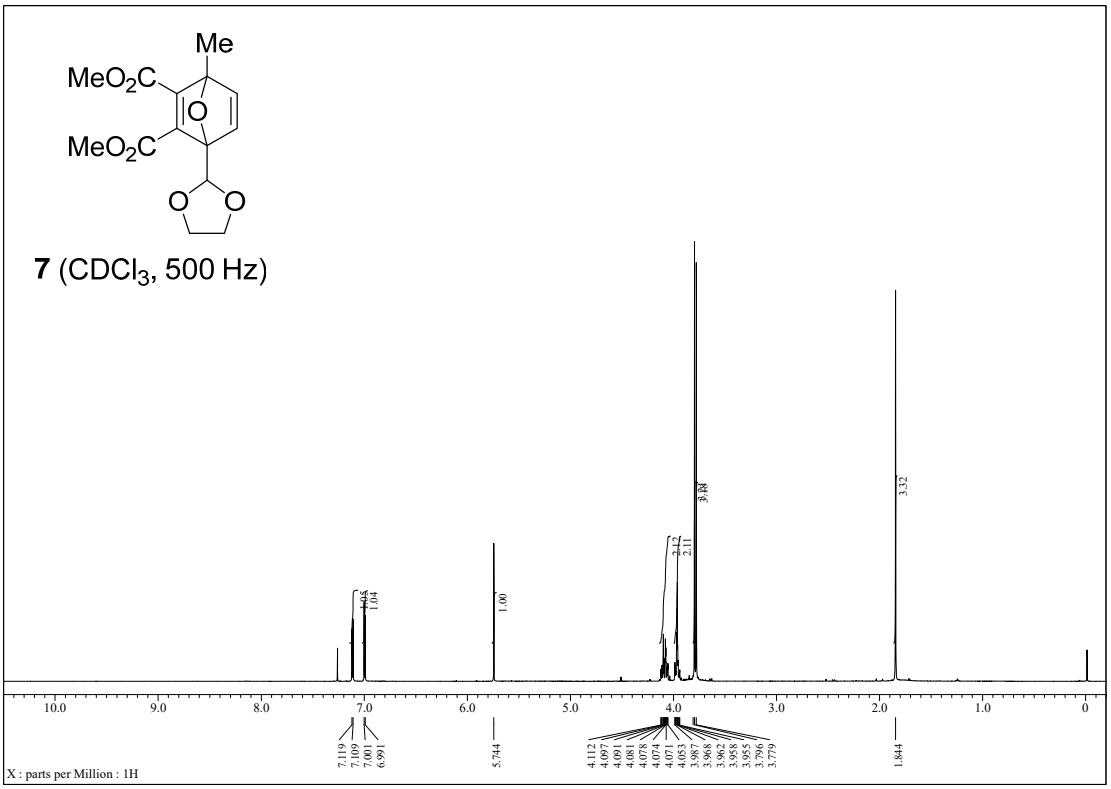
$^{1}$H NMR of trimethyl(5-methyl-2-((trimethylsilyl)oxy)phenyl)silane



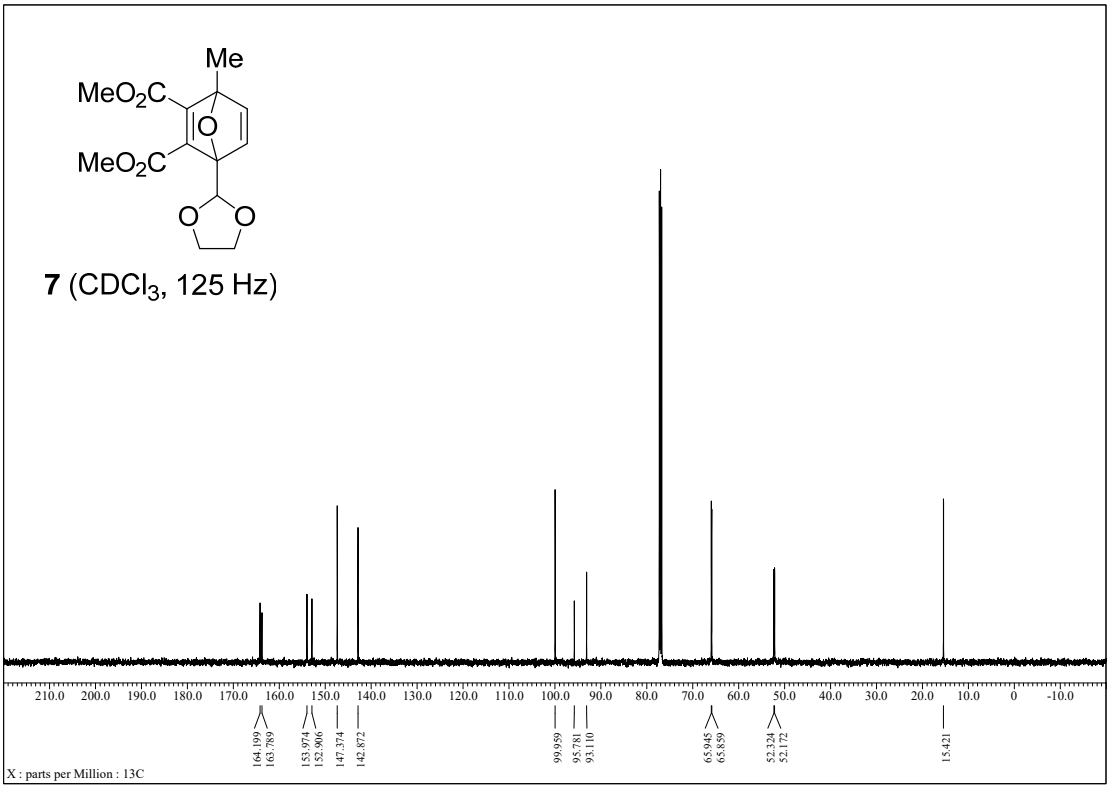

$^{13}$C NMR of trimethyl(5-methyl-2-((trimethylsilyl)oxy)phenyl)silane



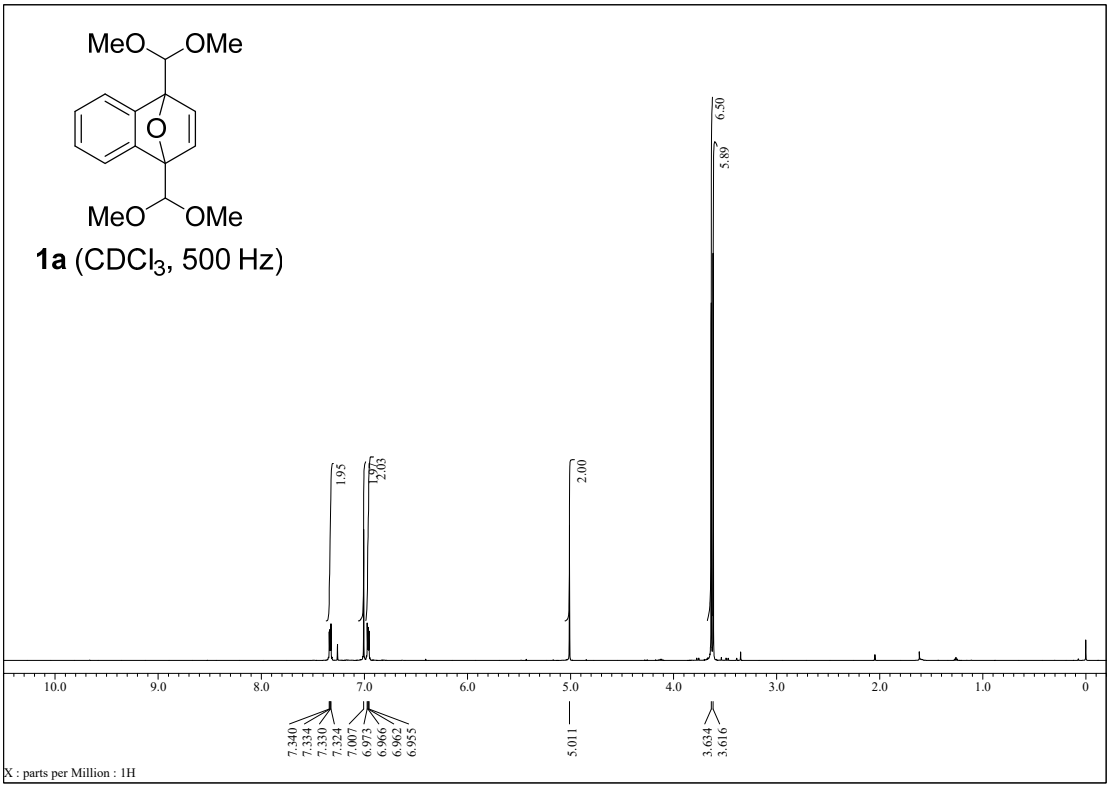
$^{1}$H NMR of 1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (**7**)



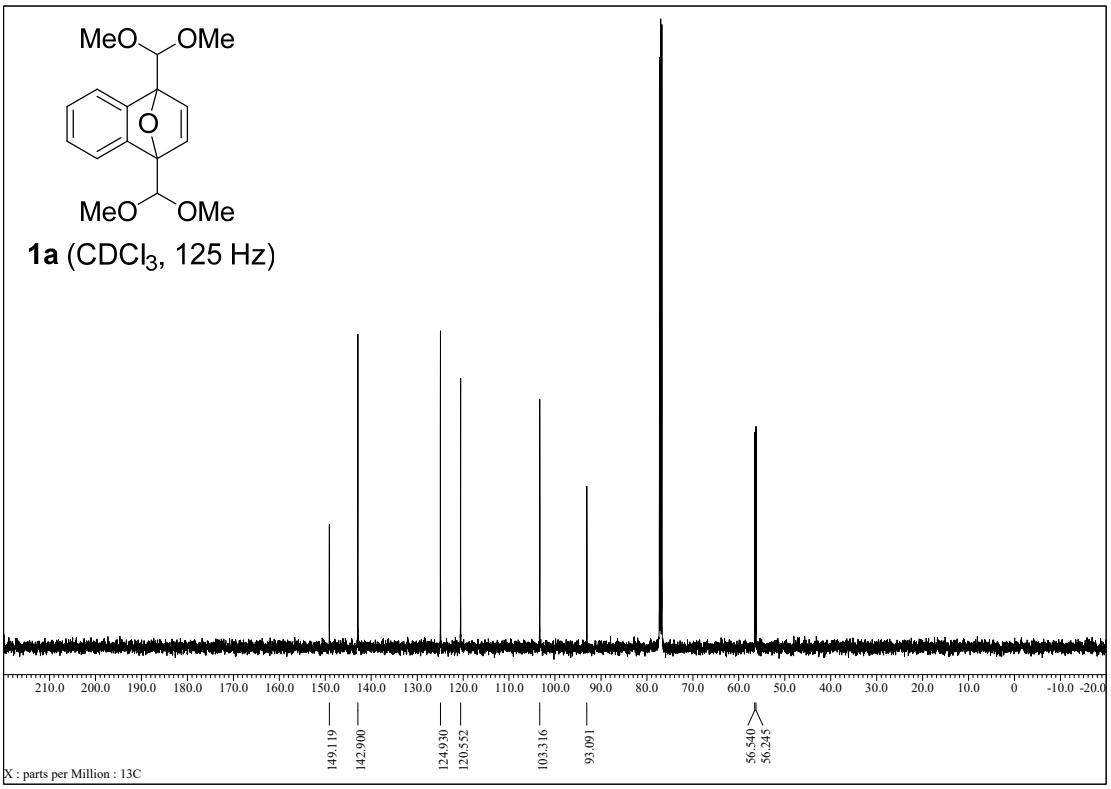

$^{13}$C NMR of 1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (**7**)



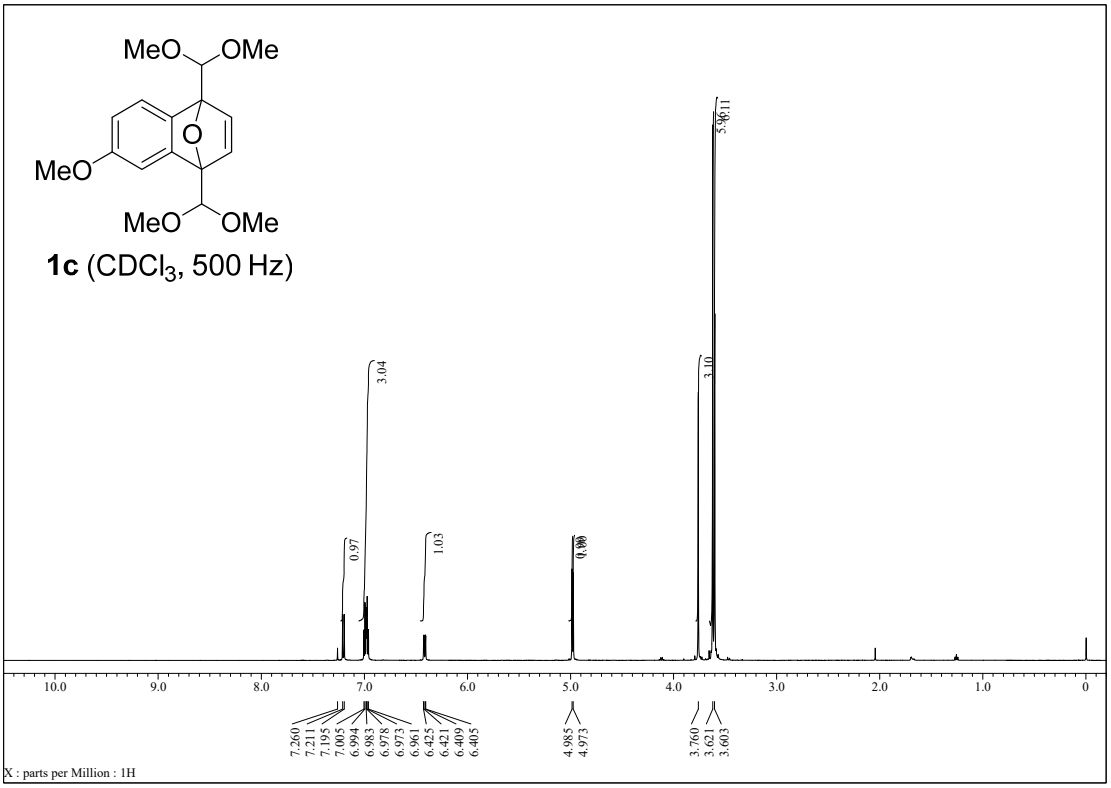
$^{1}$H NMR of 1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (**1a**)



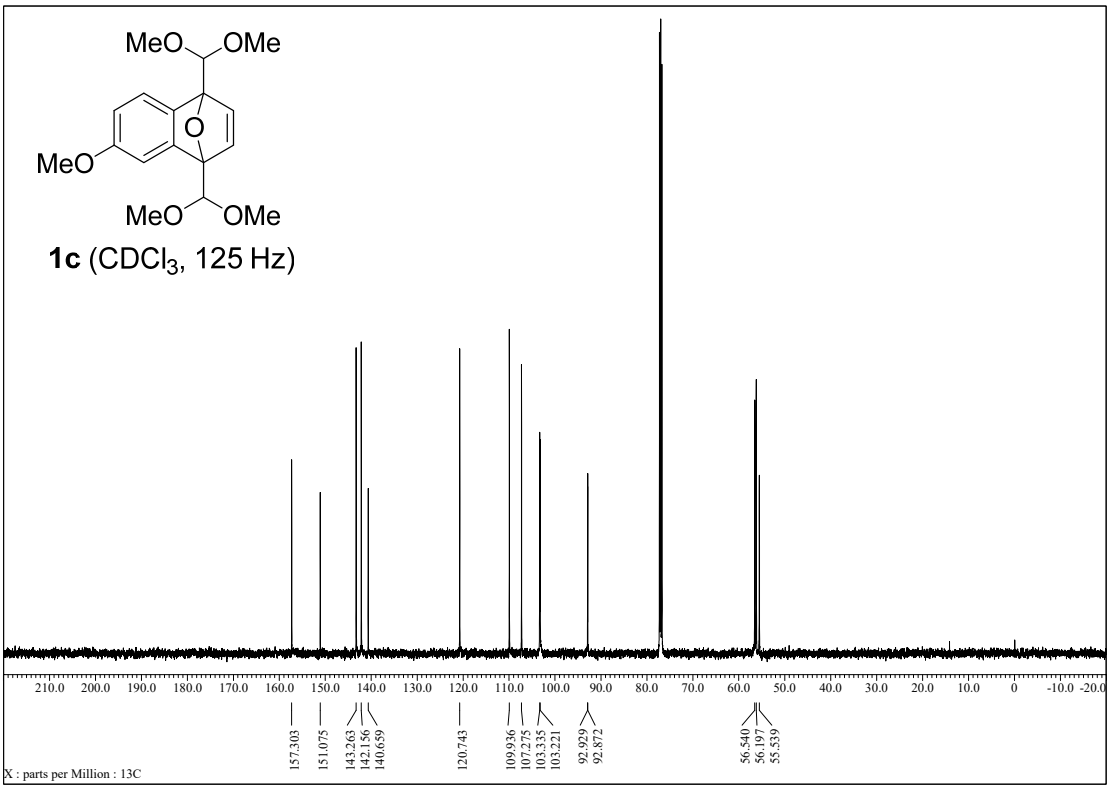

$^{13}$C NMR of 1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (**1a**)



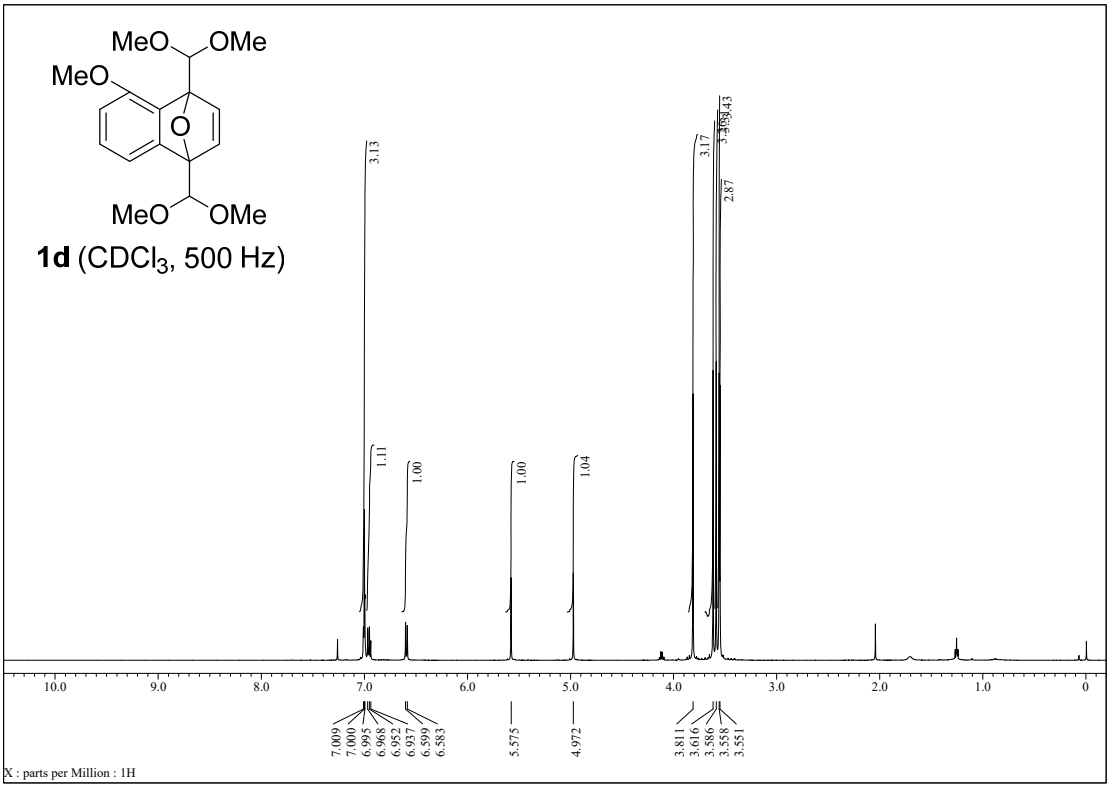
$^{1}$H NMR of 1,4-bis(dimethoxymethyl)-6-methoxy-1,4-epoxy-1,4-dihydronaphthalene (**1c**)



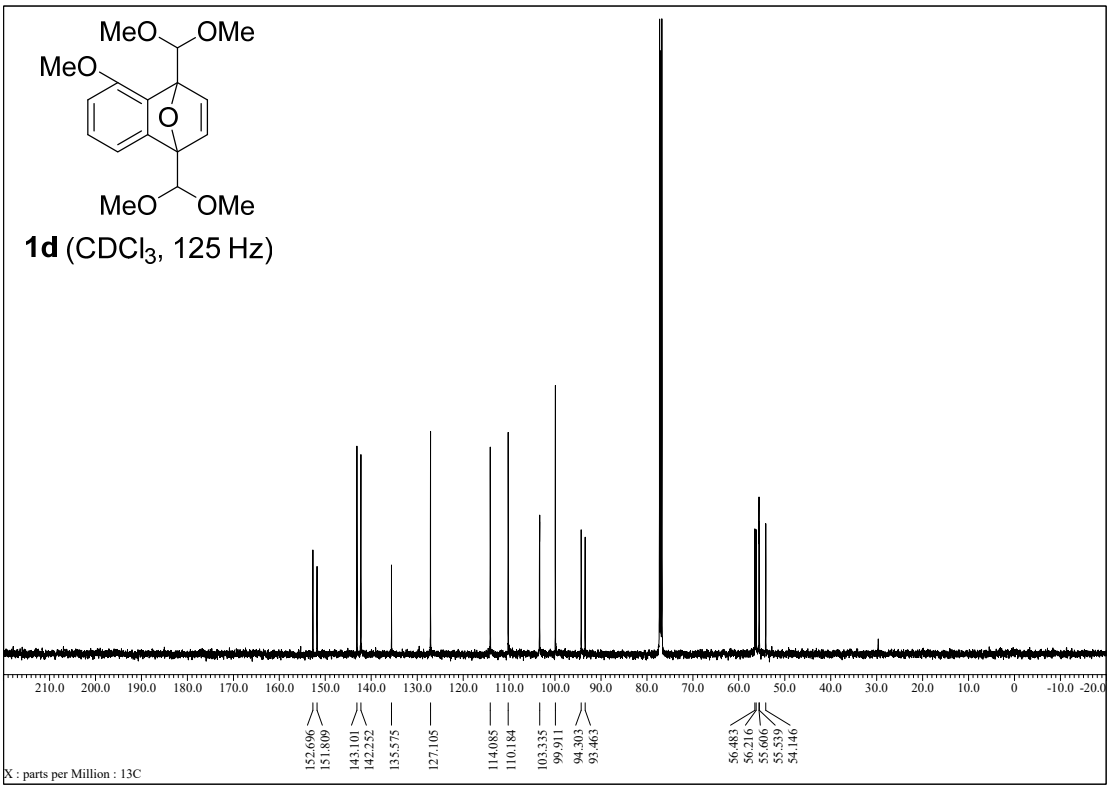

$^{13}$C NMR of 1,4-bis(dimethoxymethyl)-6-methoxy-1,4-epoxy-1,4-dihydronaphthalene (**1c**)



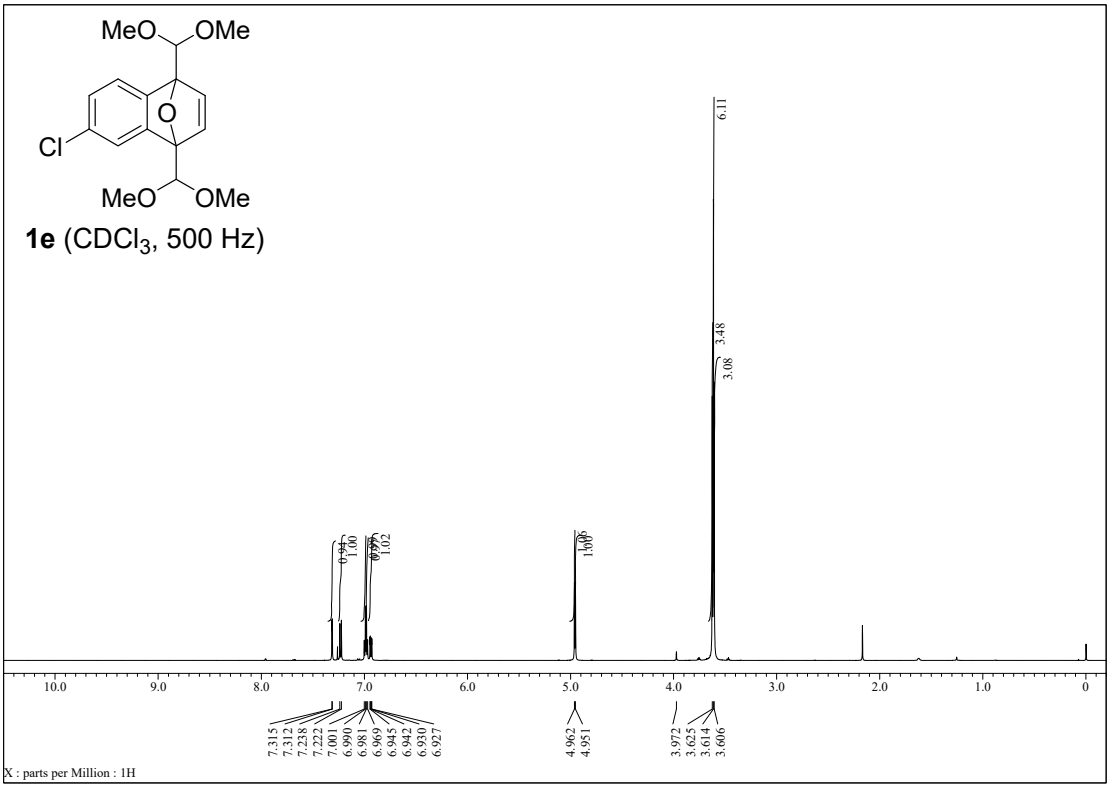
$^{1}$H NMR of 1,4-bis(dimethoxymethyl)-5-methoxy-1,4-epoxy-1,4-dihydronaphthalene (**1d**)



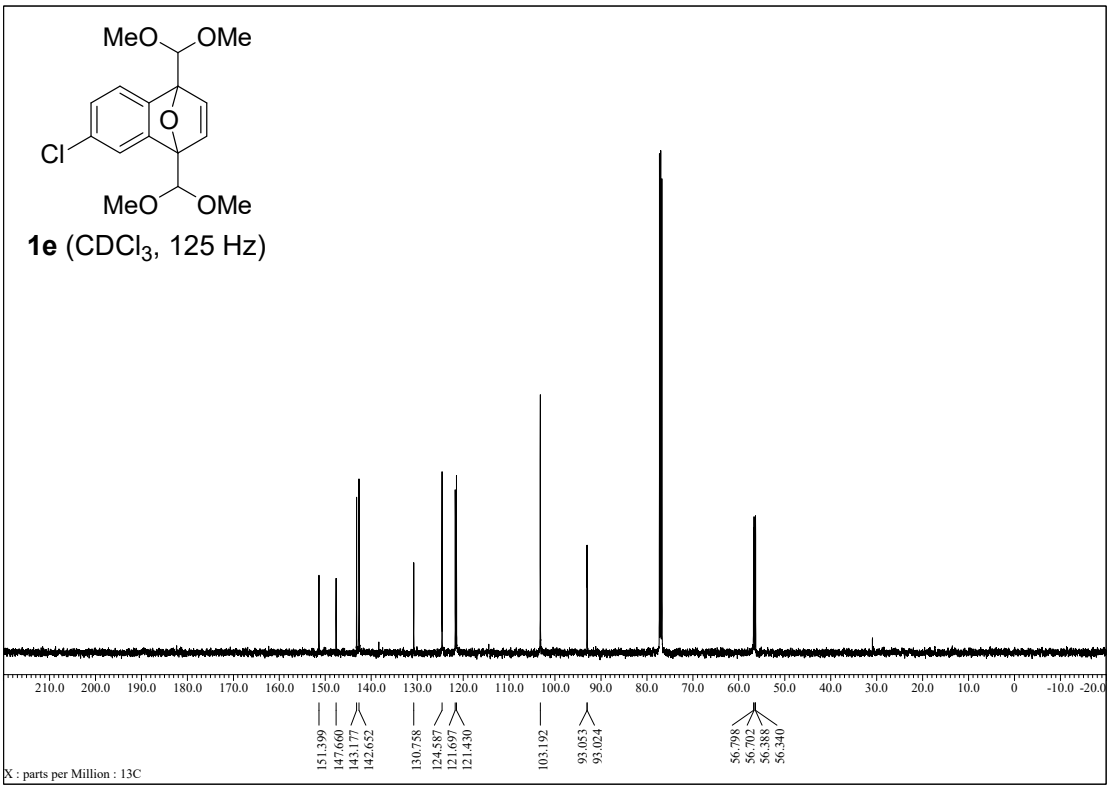

$^{13}$C NMR of 1,4-bis(dimethoxymethyl)-5-methoxy-1,4-epoxy-1,4-dihydronaphthalene (**1d**)



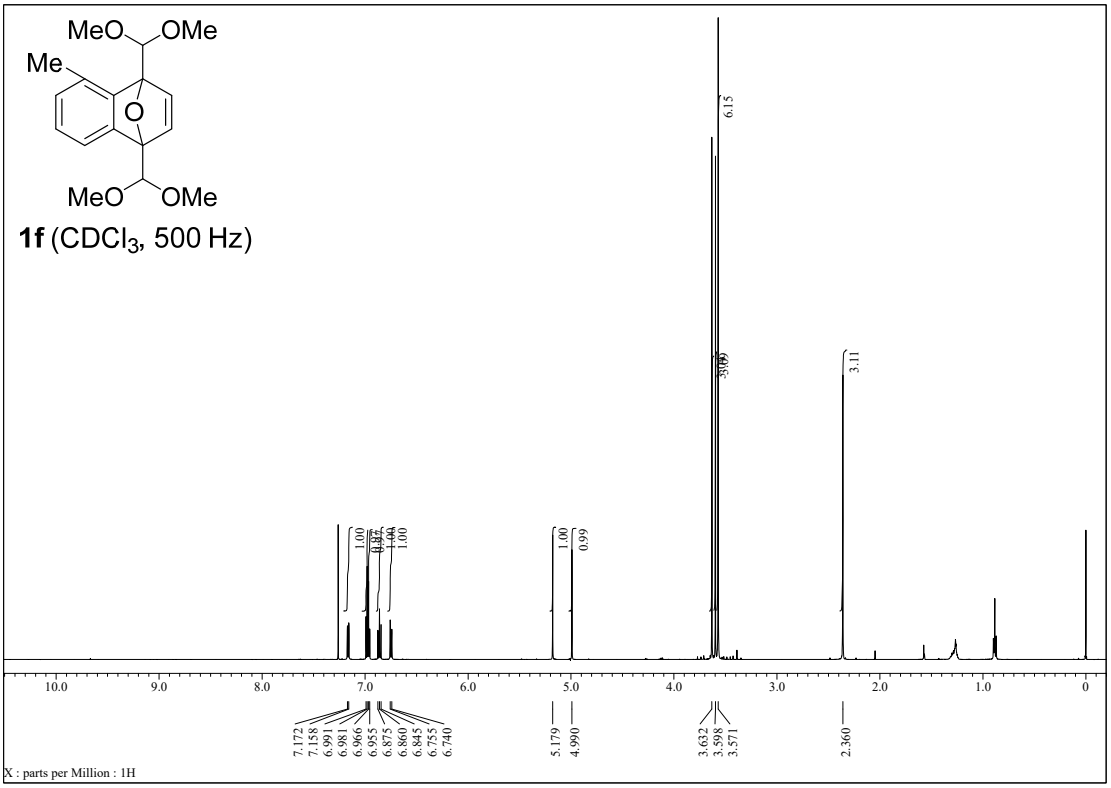
$^{1}$H NMR of 6-chloro-1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (**1e**)



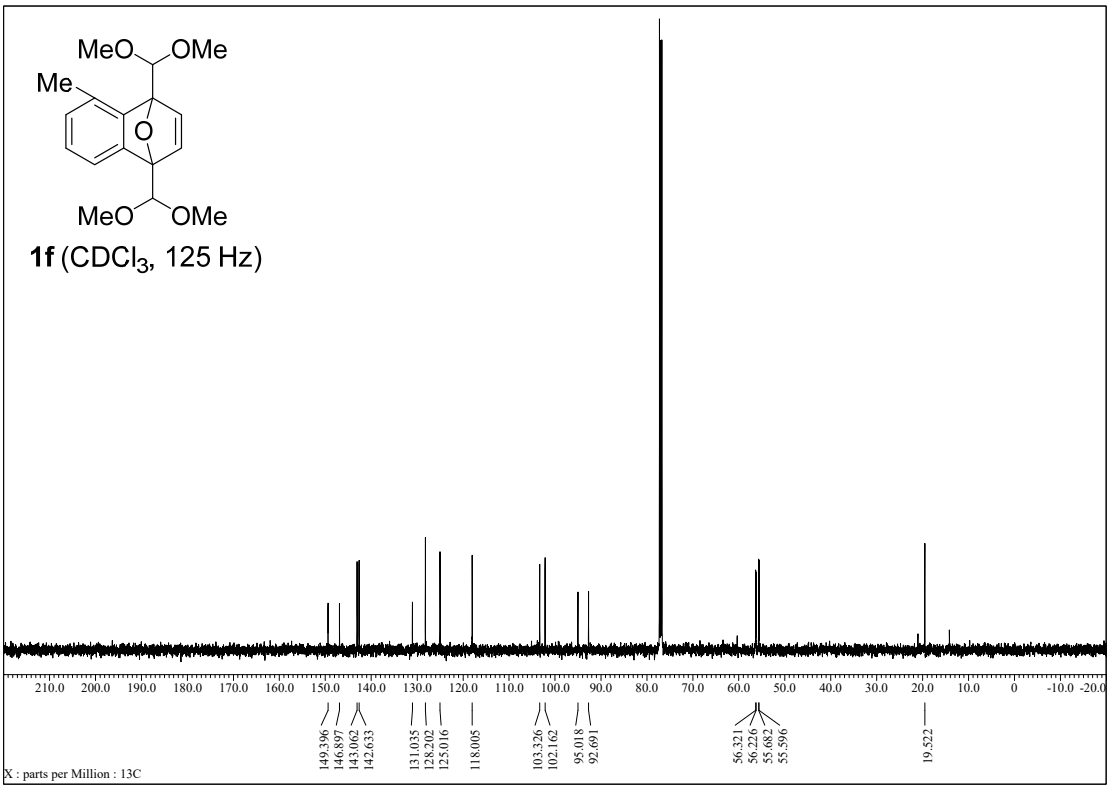

$^{13}$C NMR of 6-chloro-1,4-bis(dimethoxymethyl)-1,4-epoxy-1,4-dihydronaphthalene (**1e**)



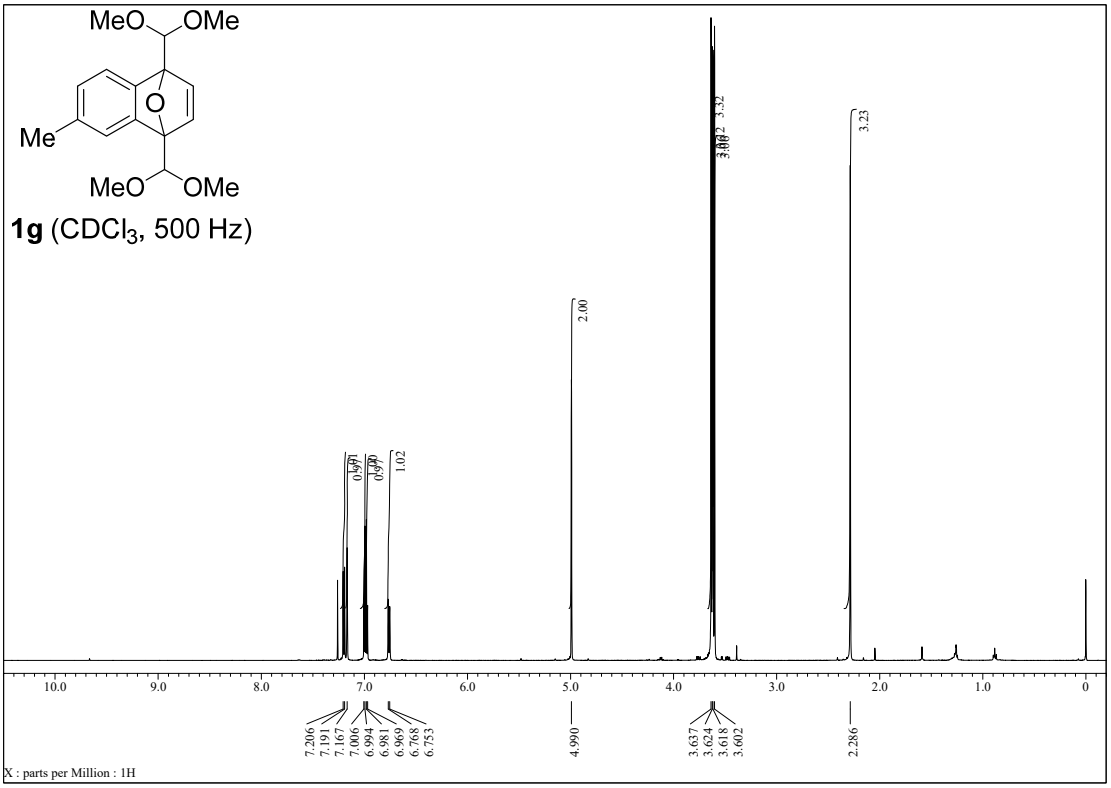
$^{1}$H NMR of 1,4-bis(dimethoxymethyl)-5-methyl-1,4-epoxy-1,4-dihydronaphthalene (**1f**)



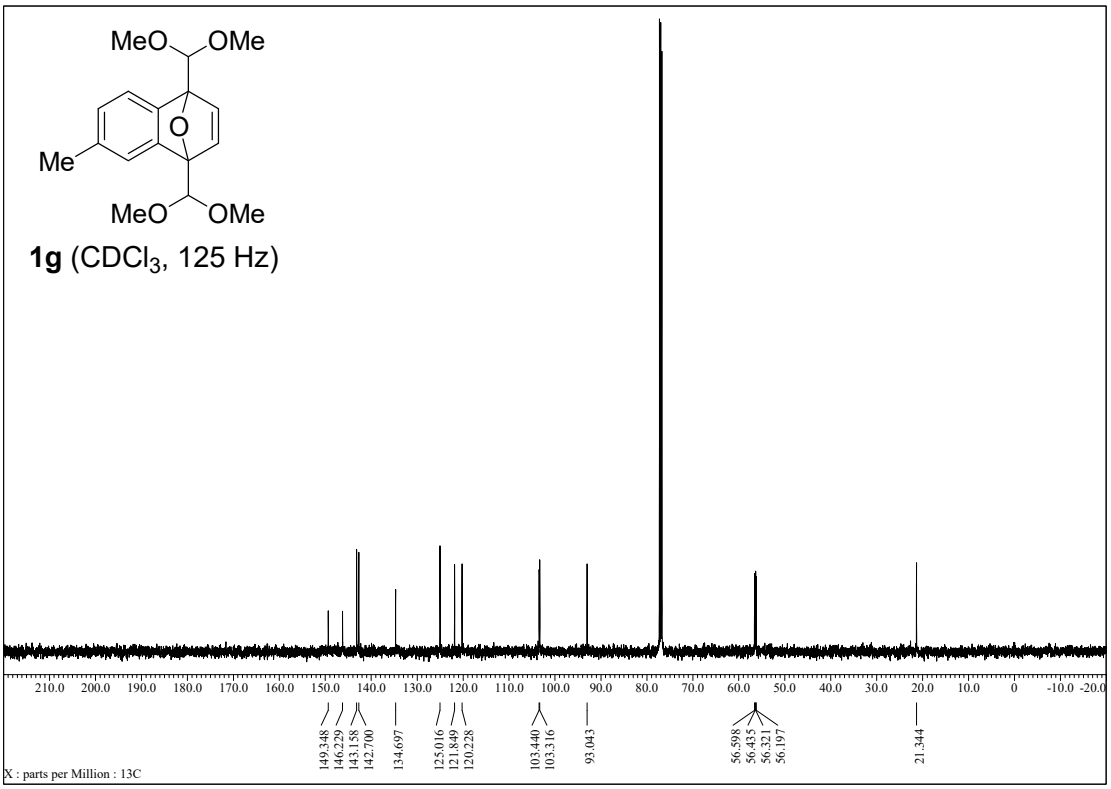

$^{13}$C NMR of 1,4-bis(dimethoxymethyl)-5-methyl-1,4-epoxy-1,4-dihydronaphthalene (**1f**)



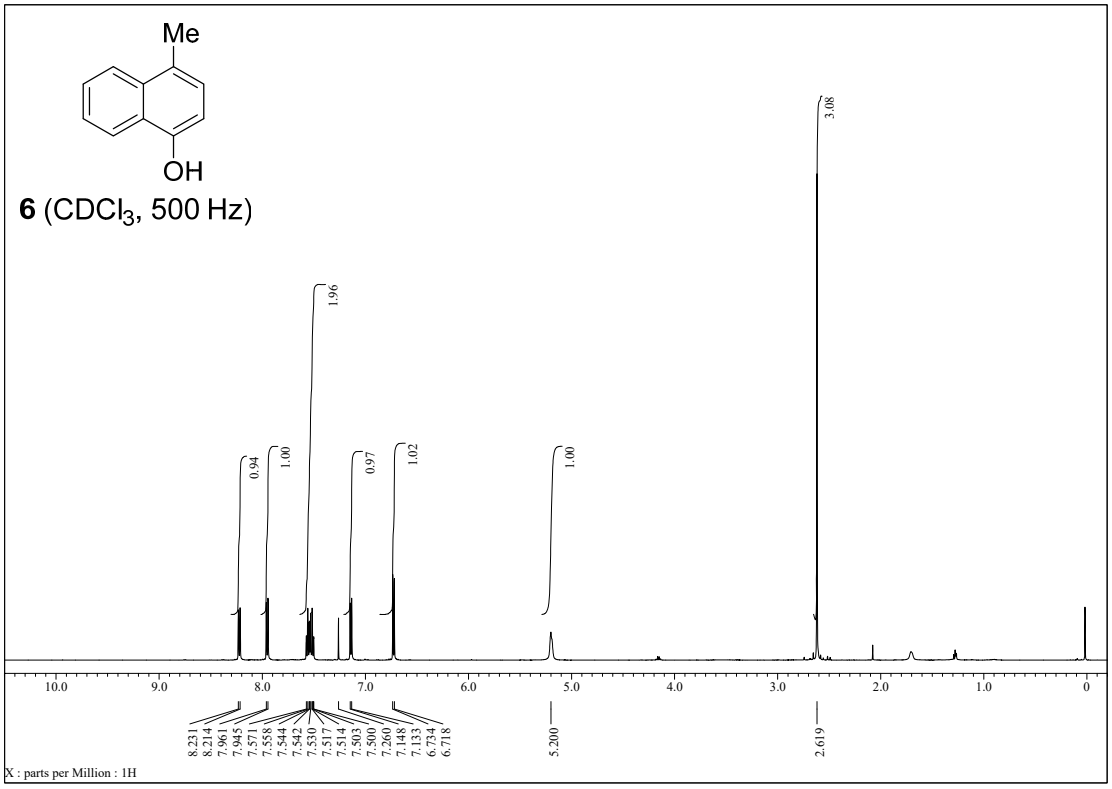
$^{1}$H NMR of 1,4-bis(dimethoxymethyl)-6-methyl-1,4-epoxy-1,4-dihydronaphthalene (**1g**)



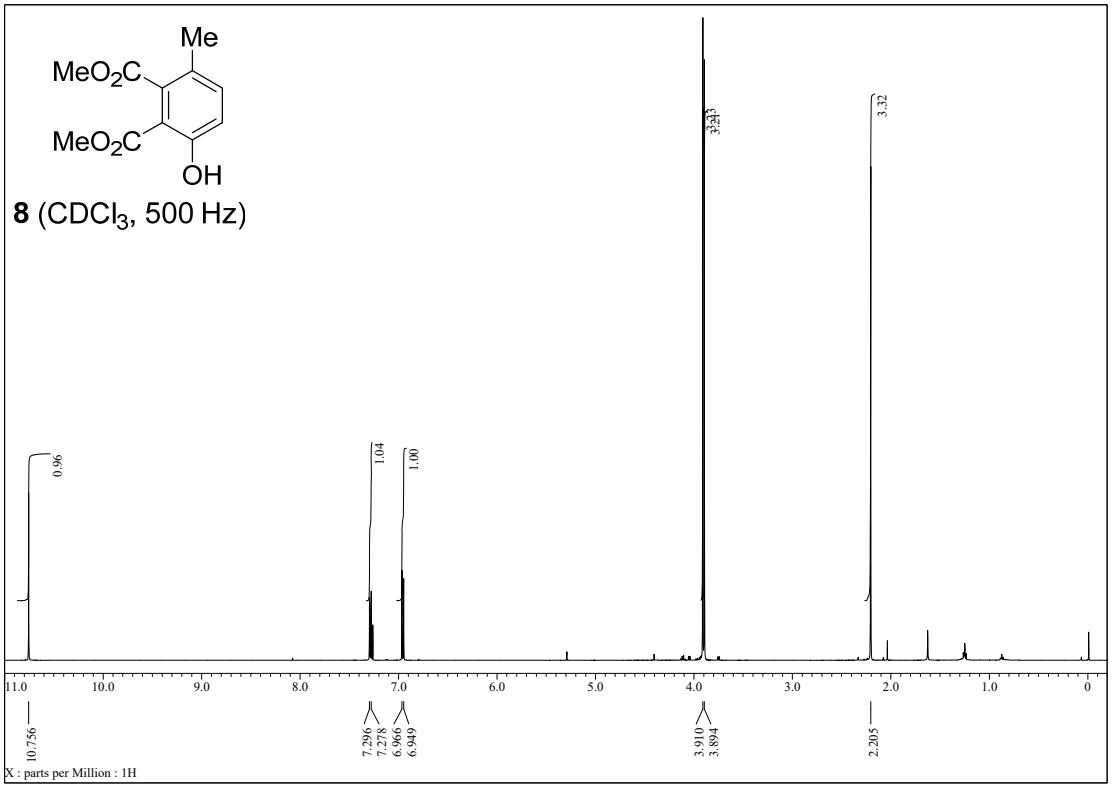

$^{13}$C NMR of 1,4-bis(dimethoxymethyl)-6-methyl-1,4-epoxy-1,4-dihydronaphthalene (**1g**)



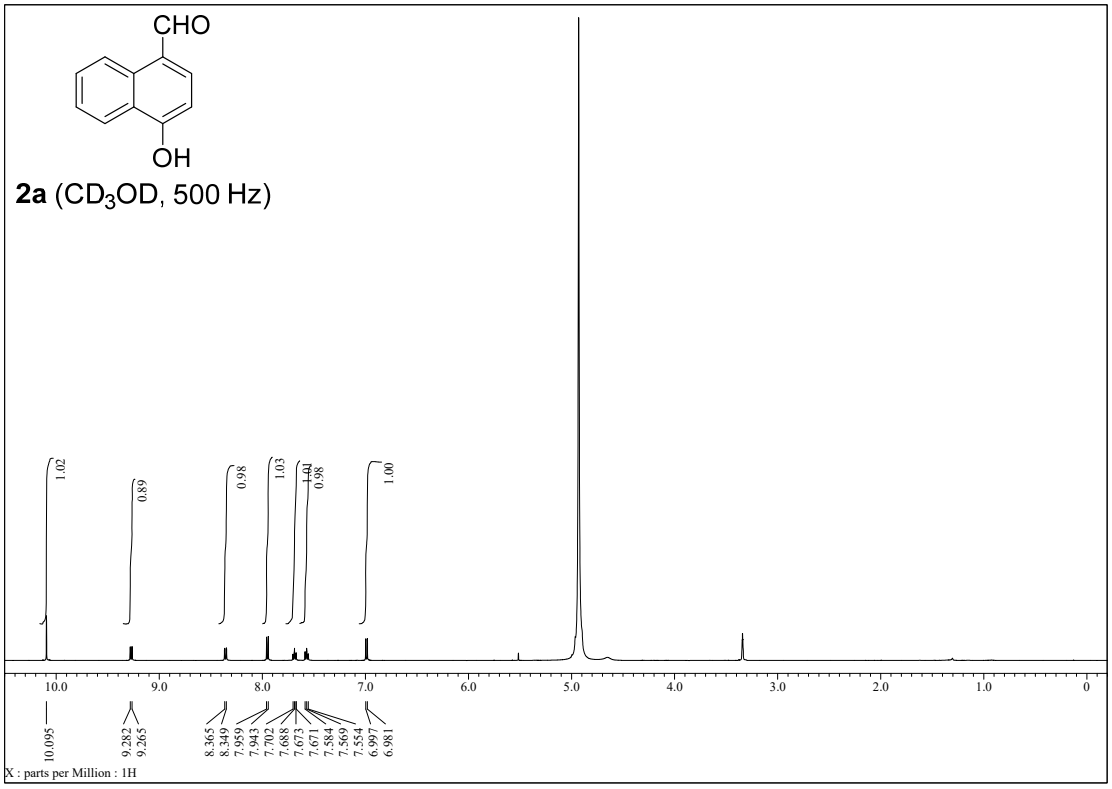
$^{1}$H NMR of 4-methylnaphthalen-1-ol (**6**)



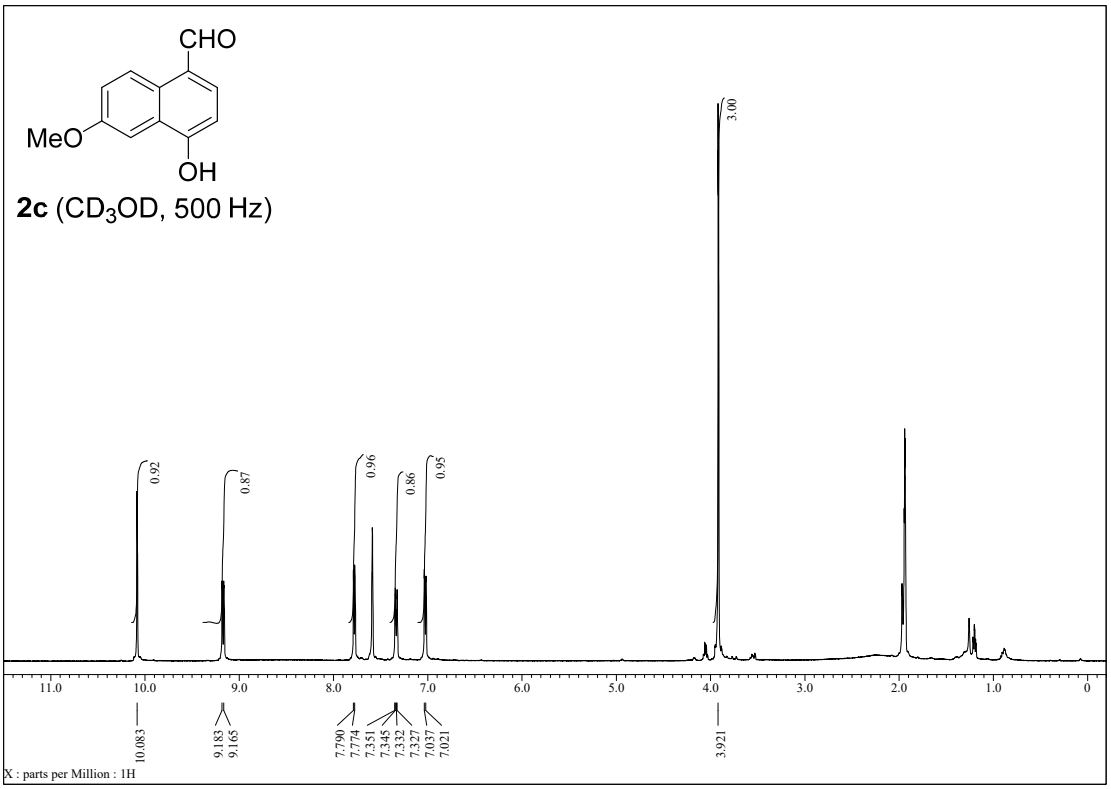
$^{1}$H NMR of dimethyl 3-hydroxy-6-methylphthalate (**8**)



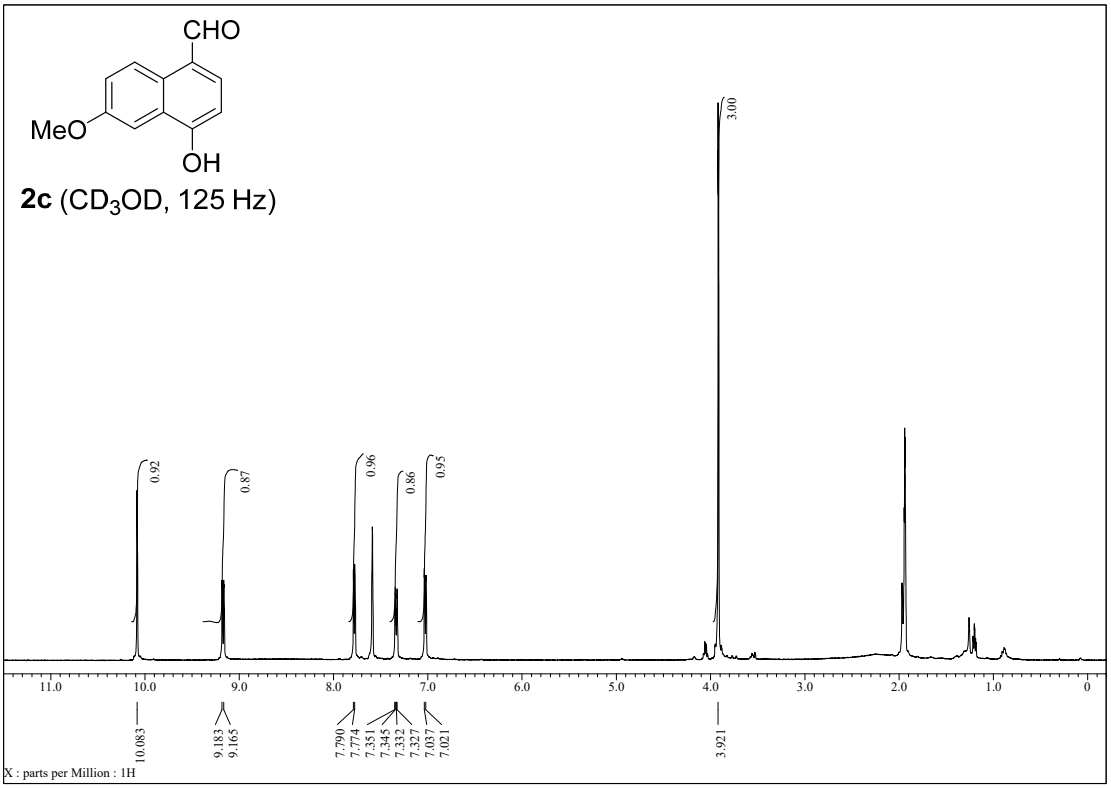
$^{1}$H NMR of 4-hydroxy-1-naphthaldehyde (**2a**)



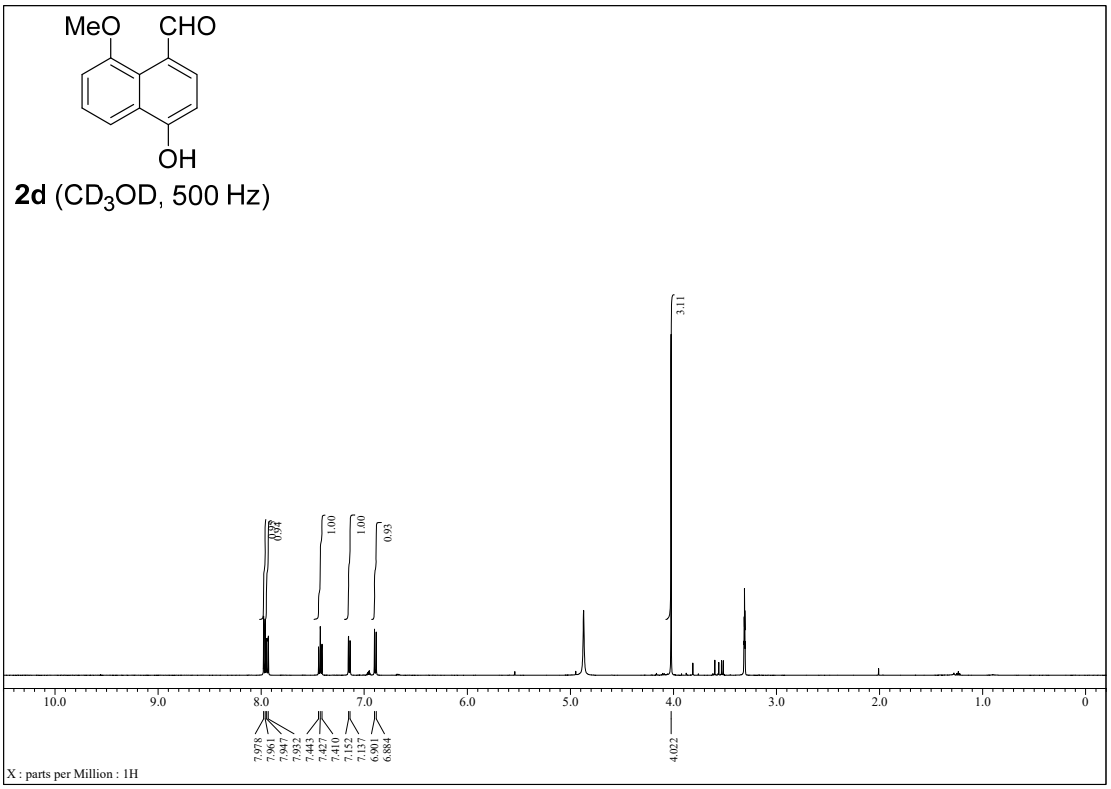
$^{1}$H NMR of 4-hydroxy-6-methoxy-1-naphthaldehyde (**2c**)



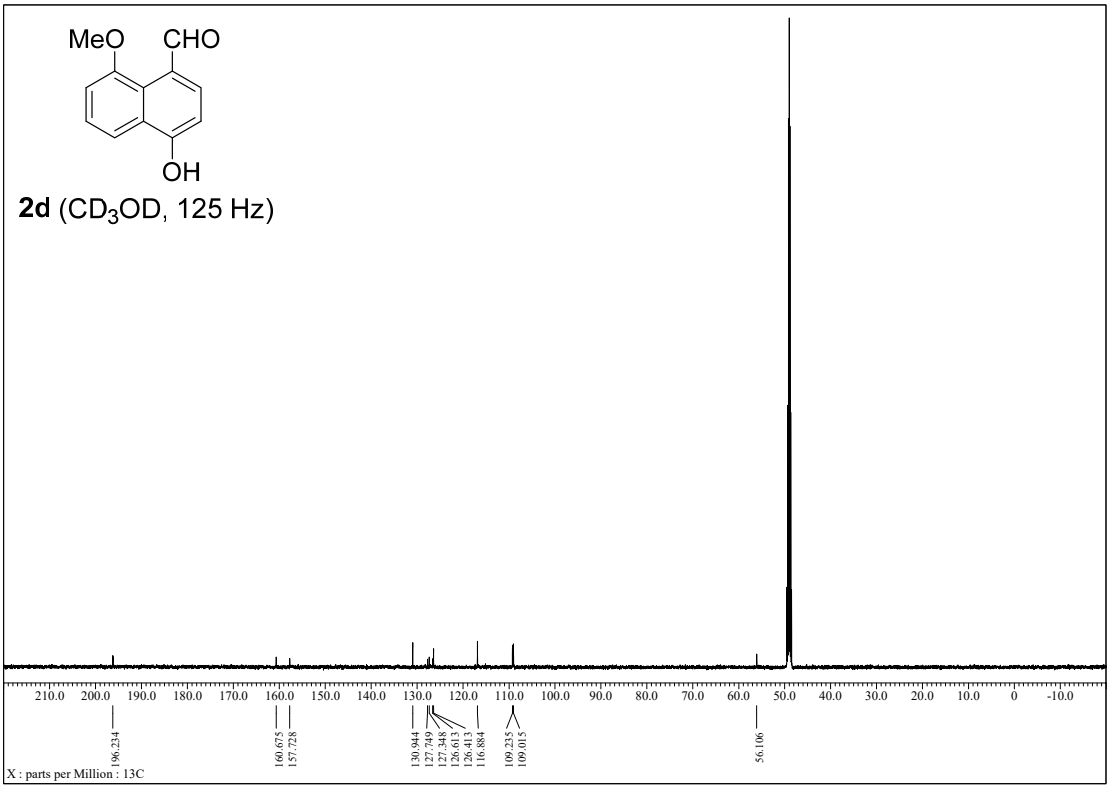

$^{13}$C NMR of 4-hydroxy-6-methoxy-1-naphthaldehyde (**2c**)



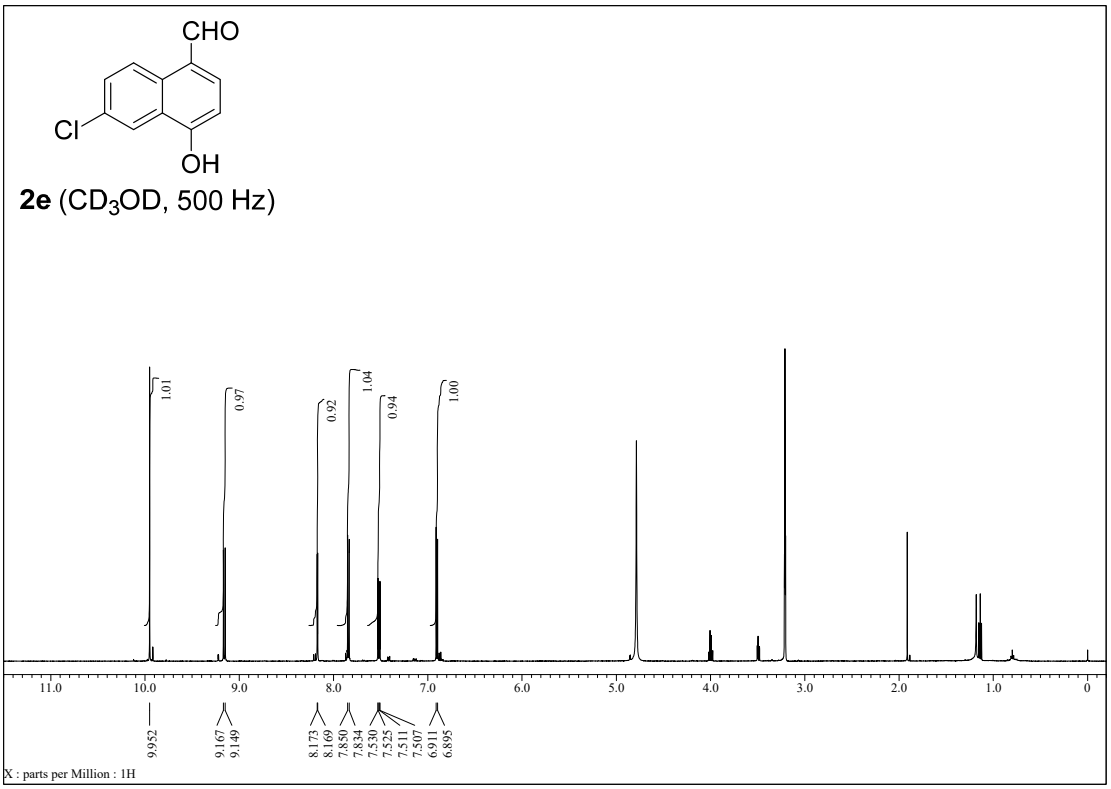
$^{1}$H NMR of 4-hydroxy-8-methoxy-1-naphthaldehyde (**2d**)



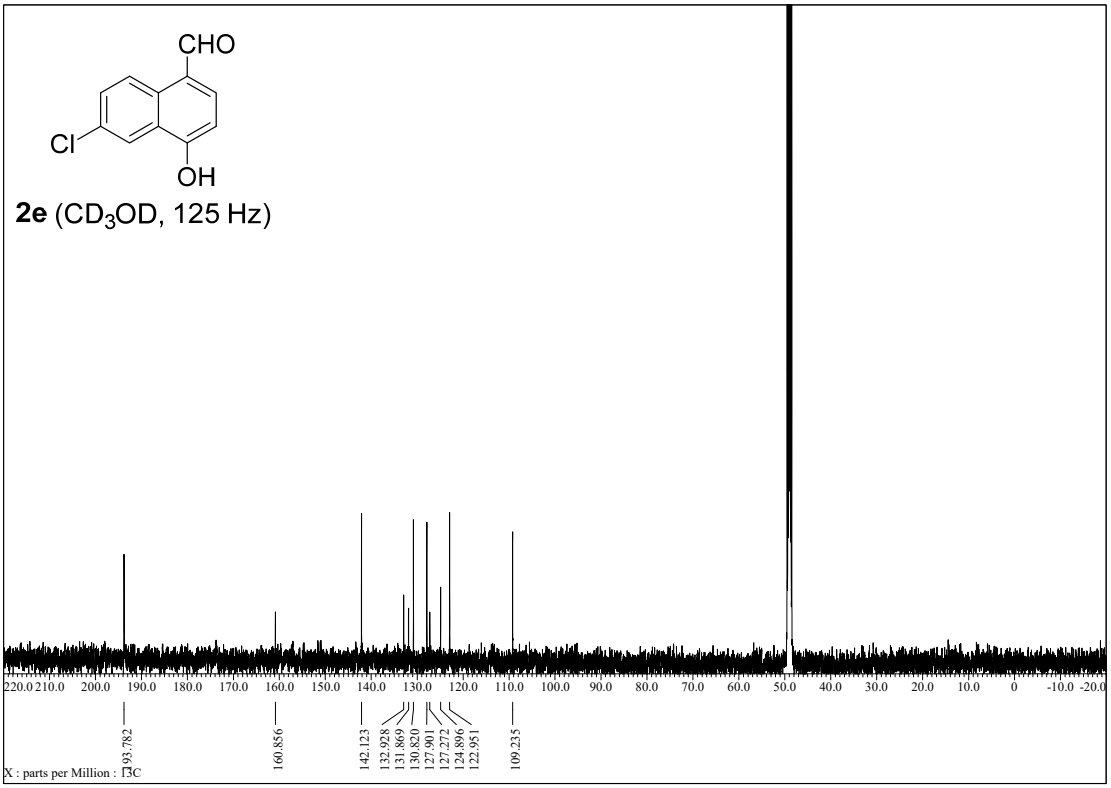

$^{13}$C NMR of 4-hydroxy-8-methoxy-1-naphthaldehyde (**2d**)



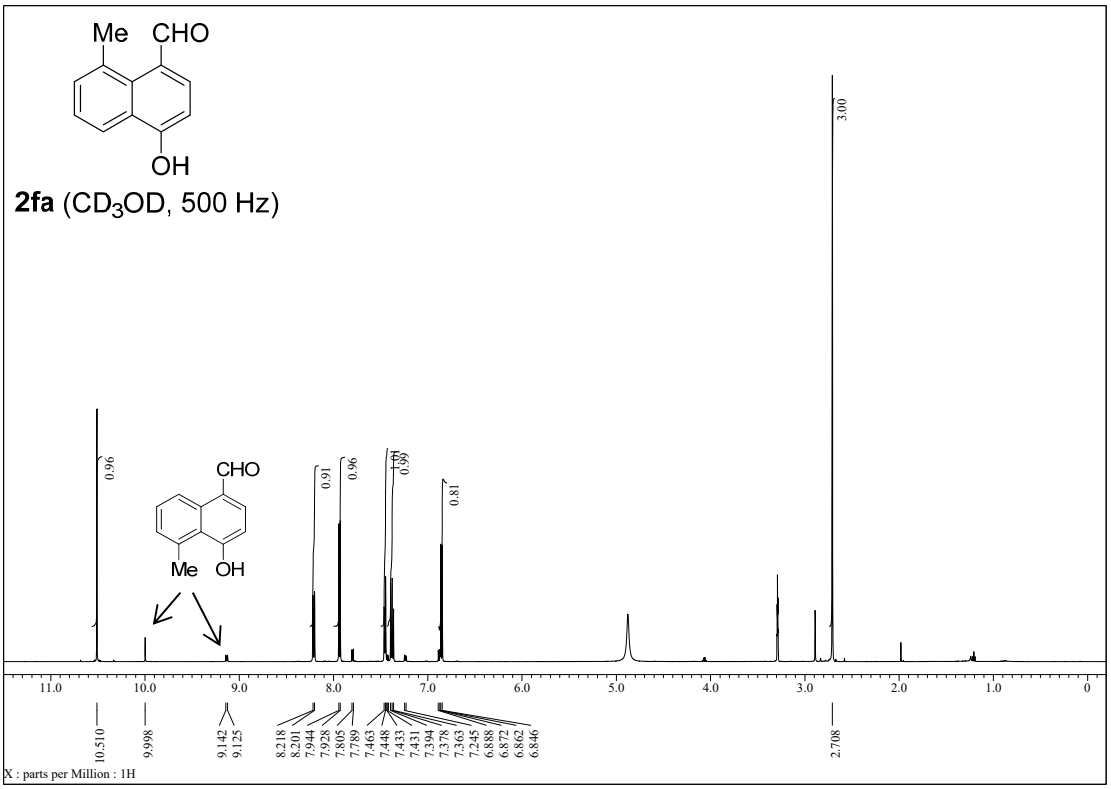
$^{1}$H NMR of 6-Chloro-4-hydroxy-1-naphthaldehyde (**2e**)



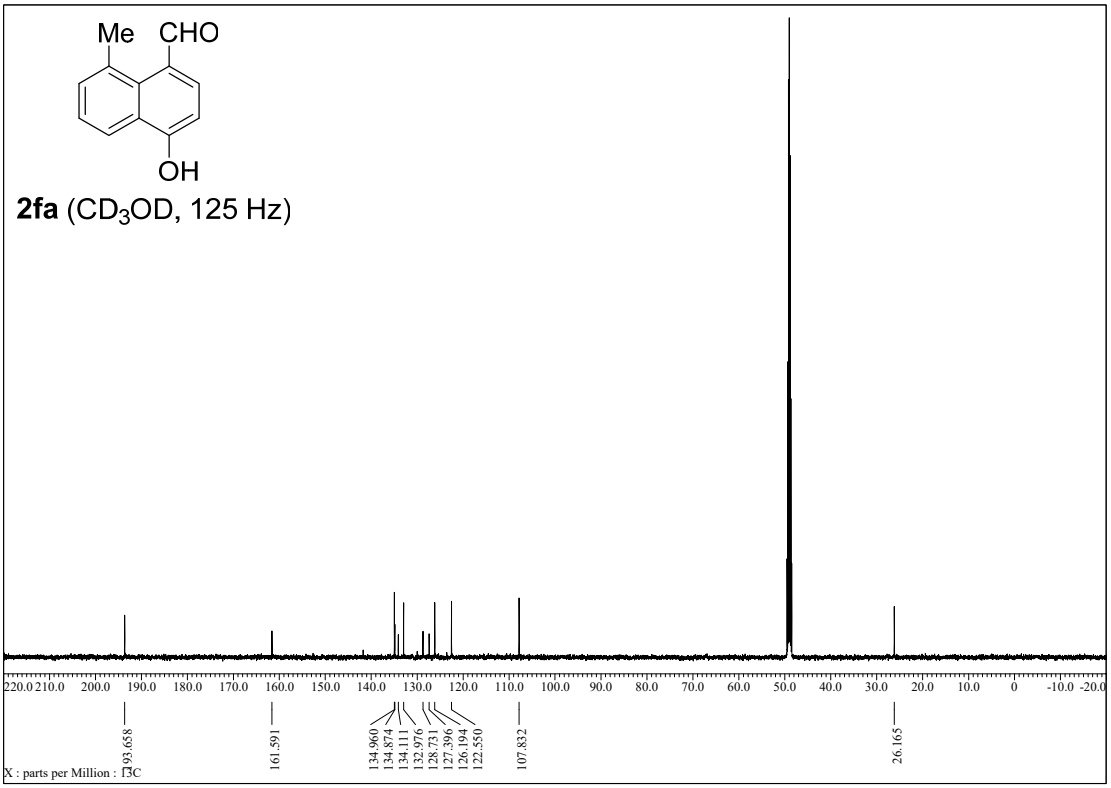

$^{13}$C NMR of 6-chloro-4-hydroxy-1-naphthaldehyde (**2e**)



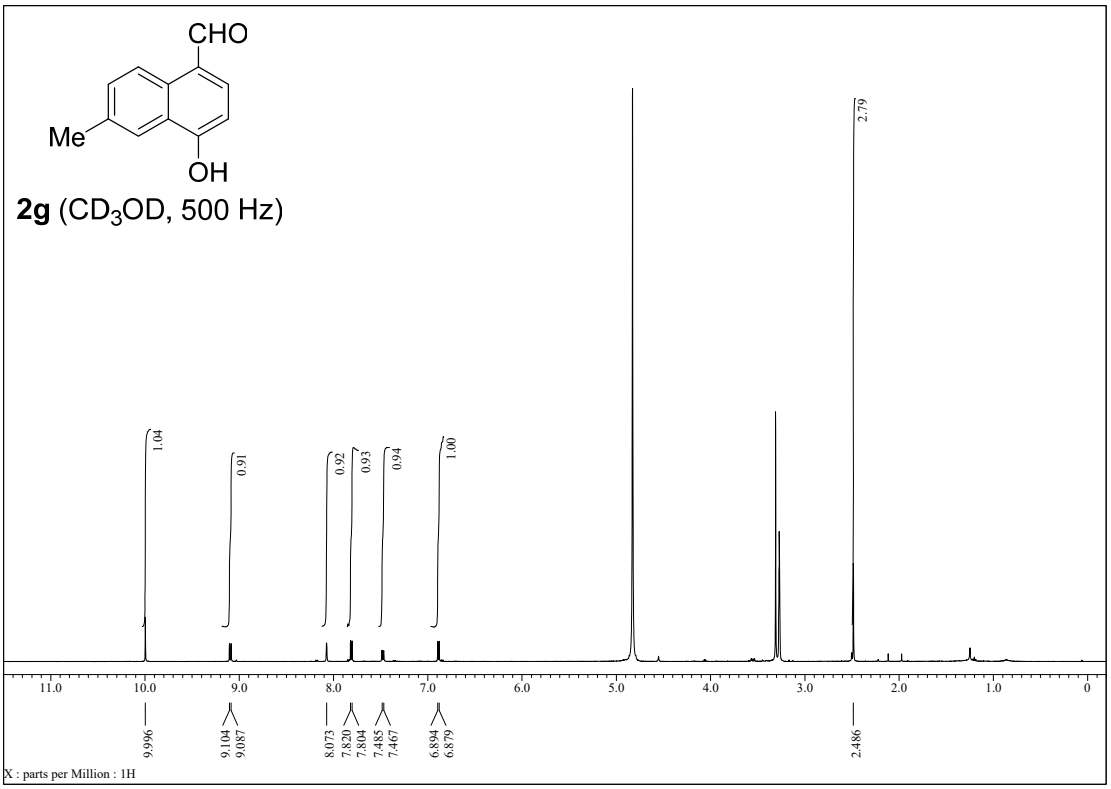
$^{1}$H NMR of 4-hydroxy-8-methyl-1-naphthaldehyde (**2fa**)




$^{13}$C NMR of 4-hydroxy-8-methyl-1-naphthaldehyde (**2fa**)



$^{1}$H NMR of 4-hydroxy-6-methyl-1-naphthaldehyde (**2g**)




$^{13}$C NMR of 4-hydroxy-6-methyl-1-naphthaldehyde (**2g**)