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Electronic Supplementary Information

Aromatic Aldehyde-Selective Aldol Addition with Aldehyde-Derived Silyl Enol Ethers

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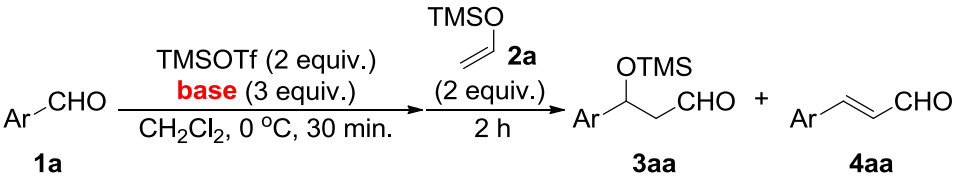
1. General Information.

All reactions were performed in oven-dried glassware under argon. Unless otherwise noted, the 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 $CDCl_3$ or CD_2Cl_2 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 = 5.32; ^{13}C NMR: δ = 53.5 for CD_2Cl_2) 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. Detailed optimization.

Table S1. Effect of base.



Ar = 4-MeOPh

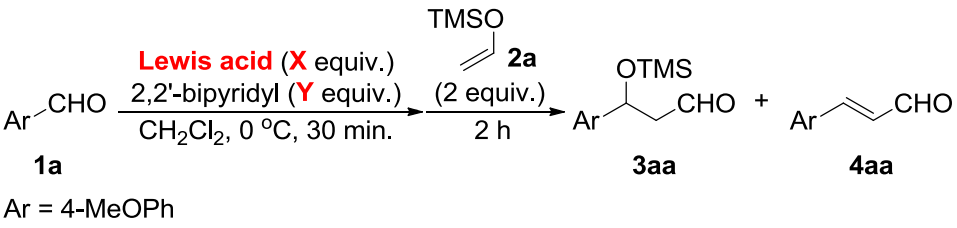
entry	base	Yield (%)[a]		
		1a	**3aa**	**4aa**
1	—	6	0	48
2	pyridine	98	0	0
3	DMAP	99	0	0
4	2-picoline	97	1	0
5	2,6-lutidine	40	57	0
6	2,4,6-collidine	46	45	0
7	2-phenylpyridine	2	94	0
8	2,2-bipyridyl	4	96 (90[b])	0
9	2,4-bipyridyl	90	0	0
10	2,2-biquinoline	0	0	13
11	1,10-phenanthroline	94	0	0
12	Et_3N	96	0	0
13	DIPEA	85	0	0
14	DABCO	95	0	0
15	NMM	89	0	0

[a] Yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as an internal standard.

[b] Isolated yield.

DIPEA = diisopropylethylamine. DABCO = 1,4-diazabicyclo[2.2.2]octane. NMM = *N*-methylmorphiline.

Table S2. Effect of ratio of TMSOTf/2,2'-bipyridyl and other Lewis acids.

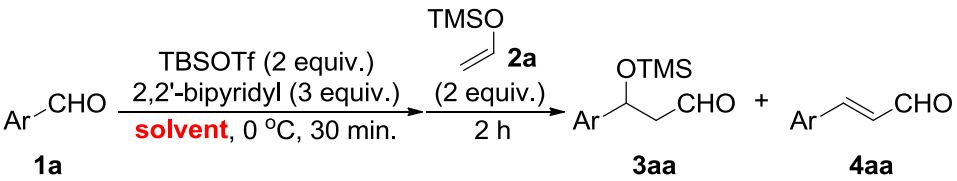


entry	Lewis acid	X equiv.	Y equiv.	Yield (%)[a]		
				1a	**3aa**	**4aa**
1	—	—	3	95	0	0
2[b]	TMSOTf	2	3	40[c]	57[c]	0
3	TMSOTf	2	3	4	96 (90[c])	0
4	TMSOTf	1	1.5	22	70	0
5	TMSOTf	0.2	0.3	82	12	0
6	TMSCl	2	3	78	0	0
7	TMSBr	2	3	86	0	0
8	TMSI	2	3	89	0	0

[a] Yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as an internal standard.

[b] 1 equiv. of **2a** was used and reaction was carried out for 12 h. [c] Isolated yield.

Table S3. Effect of solvents.



Ar = 4-MeOPh

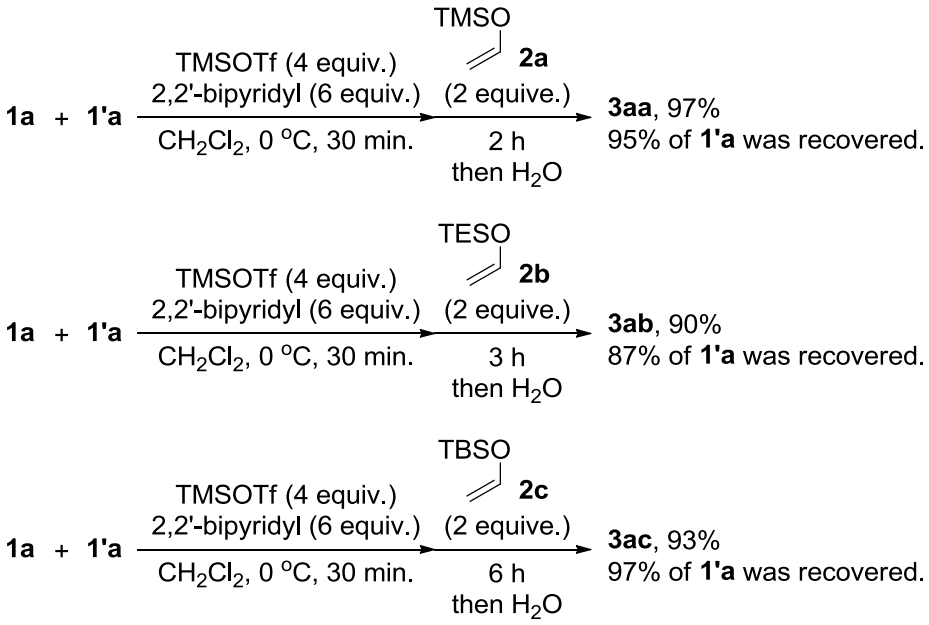
entry	solvent	Yield (%)[a]		
		1a	**3aa**	**4aa**
1	CH_2Cl_2	0	96 (90[b])	0
2	$(CH_2Cl)_2$	23	77	0
3	CH_3CN	9	38	0
4	toluene	18	77	0
5	Et_2O	27	52	0
6	THF	34	51	0
7	EtOAc	8	69	0

[a] Yield was determined by ^{1}H NMR using 1,2-methylenedioxybenzene as an internal standard.

[b] Isolated yield.

THF = tetrahydrofuran.

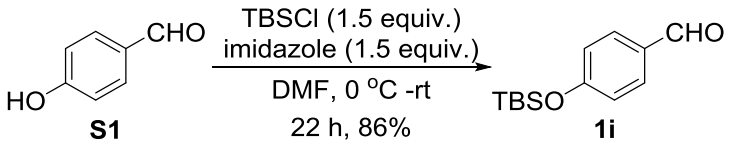
3. Chemoselective Mukaiyama aldol reaction.



When using a 1:1 mixture of aromatic aldehyde **1a** and aliphatic aldehyde **1'a** as substrates, **1a** was chemoselectively transformed into the coresponding products **3** in high yields and **1'a** remained unchanged. Triethylsilyl (TES) and *tert*-buthyldimethylsilyl (TBS) enol ethers (**2b** and **2c**) could be used as nucleophile, and chemoselectivity between **1a** and **1'a** was could be achieved as well.

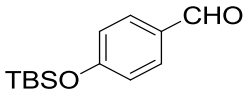
4. Procedures to prepare the substrates.

4-1. Preparation of 4-((*tert*-Butyldimethylsilyl)oxy)benzaldehyde (1i)



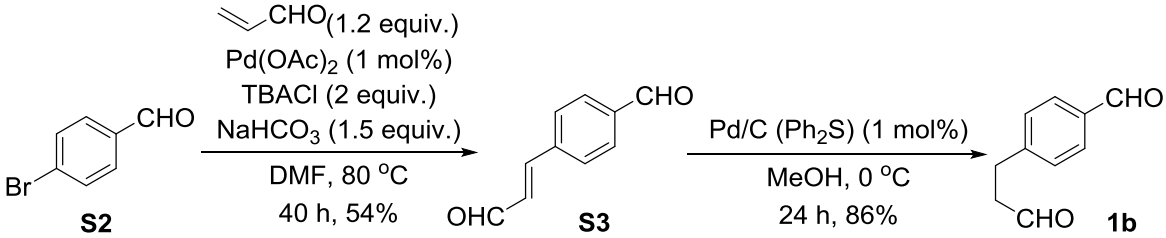
To a solution of 4-hydroxybenzaldehyde (**S1**: 2.40 g, 19.6 mmol) in anhydrous DMF (30 mL) were added imidazole (2.0 g, 29.3 mmol) and TBSCl (4.5 g, 29.8 mmol) at 0 °C under argon. After stirring for 22 h at room temperature, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (20 mL) and extracted with mixture solvent of hexane and AcOEt (Hex/EtOAc = 4/1, 20 mL × 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 = 15/1) to give **1i** (3.99 g, 16.9 mmol, 86% yield).

4-((*tert*-Butyldimethylsilyl)oxy)benzaldehyde (1i)[1]



Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.89 (s, 1H), 7.79 (d, *J* = 8.6 Hz, 2H), 6.94 (d, 2H, *J* = 8.6 Hz), 1.00 (s, 9H), 0.25 (s, 6H).
Spectroscopic date of ^{1}H NMR was identical to that of reference [1].

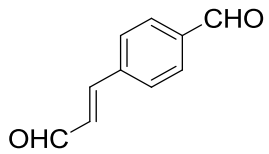
4-2. Preparation of 4-(3-oxopropyl)benzaldehyde (1b)



Step 1: To a solution of 4-bromobenzaldehyde (**S2**: 1.85 g, 10.0 mmol) in anhydrous DMF (50 mL) were added acrylic aldehyde (0.8 mL, 12.0 mmol), tetrabutyl-anmonium chloride (5.6 mL, 20.6 mmol), $NaHCO_3$ (1.26 g, 15.0 mmol) and $Pd(OAc)_2$ (22.4 mg, 0.10 mmol) under argon. After stirring for 40 h at 80 °C, the reaction mixture was passed through a celite pad. The filtrate was extracted with AcOEt (30 mL ×3) and 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 (*E*)-4-(3-oxoprop-1-en-1-yl)benzaldehyde (**S3**:

861 mg, 5.4 mmol, 54% yield).

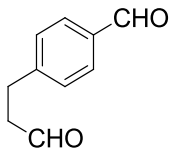
(*E*)-4-(3-Oxoprop-1-en-1-yl)benzaldehyde (S3)[2]



Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$): δ 10.06 (s, 1H), 9.77 (d, 1H, *J* = 7.5 Hz), 7.95 (d, 2H, *J* = 8.3 Hz), 7.73 (d, 2H, *J* = 8.3 Hz), 7.53 (d, 1H, *J* = 16.0 Hz), 6.81 (dd, 1H, *J* = 16.0, 7.5 Hz).
Spectroscopic date of ^{1}H NMR was identical to that of the reference [2].

Step 2 was followed a previous procedure in reference [3]: To a solution of a (*E*)-4-(3-oxoprop-1-en-1-yl)benzaldehyde (**S3**: 32.0 mg, 0.2 mmol) in methanol (1 mL) was added Pd/C(Ph_2S) (2.1 mg, 0.002 mmol) at 0 ^{o}C under H_2. After stirring for 3 h, the reaction mixture was passed through a membrane filter (Millipore, Millex-LH, 0.20 mm) to remove Pd/C(Ph_2S). The filtrate was concentrated in *vacuo*. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 5/1) to give 4-(3,3-dimethoxypropyl)benzaldehyde (24.9 mg). Then, this compound in CH_3CN (0.5 mL) was added 1N HCl (1 mL) at room temperature. After stirring for 42 h, the reaction mixture was extracted with CH_2Cl_2 (10 mL × 2) and the combined organic layers were dried over Na_2SO_4, and concentrated to give 4-(3-Oxopropyl)benzaldehyde (**1b**; 16.7 mg, 0.10 mmol, 49%).

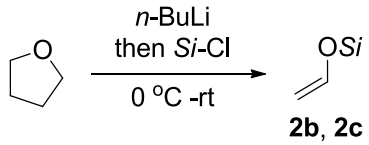
4-(3-Oxopropyl)benzaldehyde (1b)[4]



Colorless solid; ^{1}H NMR (500 MHz, $CDCl_3$); δ 9.98 (s, 1H), 9.84 (s, 1H), 7.82 (d, 2H, *J* = 8.0 Hz), 7.37 (d, 2H, *J* = 8.0 Hz), 3.04 (t, 2H, *J* = 7.5 Hz), 2.85 (t, 2H, *J* = 7.5 Hz).
Spectroscopic date of ^{1}H NMR was identical to that of the reference [4].

5. Procedures to prepare silyl enol ethers.

5-1. Preparation of trialkylsilyl vinyl ethers (2b and 2c)[5]



2b, **2c**

2.6 M Hexane solution of *n*-butyllithium (15 mL, 39.0 mmol) was mixed with anhydrous THF (25 mL) at 0 °C under argon. After stirring for 5 h at room temperature, trialkylsilyl chloride (30.0 mmol) was added to the reaction mixture at 0 °C, and reaction mixture was stirred for 24 h at room temperature under argon. The reaction mixture was concentrated under reduced pressure. The residue was treated with water (30 mL) at 0 °C, and the aqueous layers were extracted with diethylether (20 mL × 3). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by silica-gel column chromatography (Hex/Et_3N = 100/1) to give trialkylsilyl vinyl ethers (**2b** and **2c**).

Triethyl(vinyloxy)silane (2b)[6]

Triethylsilyl chloride (5.0 mL, 30.0 mmol) was used and triethyl(vinyloxy)silane (**2b**: 2.41 g, 15.2 mmol) was obtained in 51%.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$); δ 6.45 (dd, 1H, *J* = 13.1, 5.9 Hz), 4.44 (d, 1H, *J* = 13.1 Hz), 4.11 (d, 1H, *J* = 5.9 Hz), 0.98 (t, 9H, *J* = 8.0 Hz), 0.68 (q, 6H, *J* = 8.0 Hz).

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

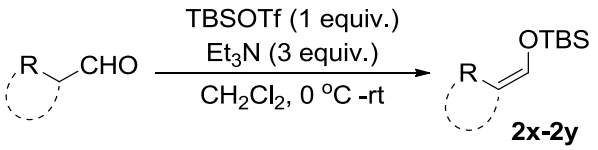
***tert*-Butyldimethyl(vinyloxy)silane (2c)[7]**

tert-Butyldimethyl silyl chloride (4.5 g, 30.0 mmol) was used and *tert*-butyldimethyl(vinyloxy)silane (**2c**: 772 mg, 4.88 mmol) was obtained in 16%.

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$); δ 6.43 (dd, 1H, J = 13.5, 5.7 Hz), 4.44 (d, 1H, J = 13.5 Hz), 4.11 (d, 1H, *J* = 5.7 Hz), 0.92 (s, 9H), 0.15 (s, 6H).

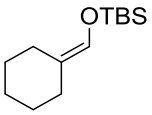
Spectroscopic date of ^{1}H NMR was identical to that of the reference [7].

5-2. Preparation of *ß*-substituted silyl enol ethers (2d–2y)



To a solution of the TBSOTf (0.7 mL, 3.0 mmol) in anhydrous CH_2Cl_2 (10 mL) was added a solution of an aldehyde (3.0 mmol) and Et_3N (0.7 mL, 9.0 mmol) in CH_2Cl_2 (5 mL) at 0 °C under argon. After stirring for adequate time at room temperature, the solvent was removed in *vacuo*, and the residue was purified by silica-gel column chromatography to give the desired ß-substituted silyl enol ethers (**2x**–**2y**).

***tert*-Butyl(cyclohexylidenemethoxy)dimethylsilane** (**2d**)[8]

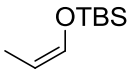


Cyclohexanecarbaldehyde (365 μL, 3.0 mmol) was used as a substrate and *tert*-butyl(cyclohexylidenemethoxy)dimethylsilane (**2d**: 415.3 mg, 1.83 mmol) was obtained in 61% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/Et_3N = 100/1).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.02 (s, 1H), 2.18 (t, 2H, *J* = 5.7 Hz), 1.93 (t, 2H, *J* = 5.7 Hz), 1.52—1.50 (m, 2H), 1.49—1.45 (m, 4H), 0.92 (s, 9H), 0.12 (s, 6H).

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

(*Z*)-*tert*-Butyldimethyl(prop-1-en-1-yloxy)silane (**2e**)[9]

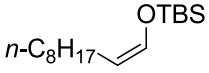


Propionaldehyde (210 μL, 3.0 mmol) was used as a substrate and (*Z*)-*tert*-butyldimethyl(prop-1-en-1-yloxy)silane (**2e**: 149.1 mg, 0.86 mmol) was obtained in 29% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/Et_3N = 100/1).

Colorless oil; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.19 (dq, 1H, *J* = 6.0, 1.7 Hz), 4.50 (dq, 1H, *J* = 6.9, 6.0 Hz), 1.57 (dd, 3H, *J* = 6.9, 1.7 Hz), 0.93 (s, 9H), 0.13 (s, 6H).

Spectroscopic date of ^{1}H NMR was identical to that of the reference [9].

(*Z*)-*tert*-Butyl(dec-1-en-1-yloxy)dimethylsilane (**2f**)



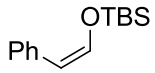
Decanal (564 μL, 3.0 mmol) was used as a substrate and (*Z*)-*tert*-butyl(dec-1-en-1-yloxy)dimethylsilane (**2f**: 629.0 mg, 2.30 mmol) was obtained in 78% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/Et_3N = 20/1).

Colorless oil; IR (ATR) cm^{-1}: 2956, 2925, 2855, 1655, 1463, 1400, 1362, 1255, 1133, 1092, 1005; ^1H NMR (500 MHz, $CDCl_3$): δ 6.17 (dt, 1H, *J* = 6.0, 1.7 Hz), 4.44 (dt, 1H, *J* = 7.5, 6.0 Hz), 2.09—2.05 (m, 2H), 1.31—1.27 (m, 12H), 0.92 (s, 9H), 0.88 (t, 3H), 0.12 (s, 6H); ^{13}C NMR (125 MHz, CDCl3): δ 138.3, 110.9, 31.9, 29.7, 29.5, 29.4, 29.3, 25.6, 23.6, 22.7, 18.3, 14.1, -5.4.

***tert*-Butyldimethyl(styryloxy)silane (2g and 2g')**

2-Phenylacetaldehyde (690 μL, 6.0 mmol) was used as a substrate and the reaction mixture was purified by silica-gel column chromatography (Hex/Et_3N = 100/1) to give (*Z*)-*tert*-butyldimethyl(styryloxy)silane (**2g**: 570.0 mg, 2.43 mmol) in 41% and (*E*)-*tert*-butyldimethyl(styryloxy)silane (**2g'**: 118.4 mg, 0.51 mmol) in 8%, respectively.

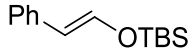
(*Z*)-*tert*-Butyldimethyl(styryloxy)silane (2g')[10]



Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.63 (d, 2H, *J* = 8.0 Hz), 7.29 (dd, 2H, *J* = 8.0, 7.5 Hz), 7.14 (t, 1H, *J* = 7.5 Hz), 6.43 (d, 1H, *J* = 6.3 Hz), 5.31 (d, 1H, *J* = 6.3 Hz), 0.99 (s, 9H), 0.23 (s, 6H).

Spectroscopic date of ^1H NMR was identical to that of the reference [10].

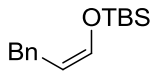
(*E*)-*tert*-Butyldimethyl(styryloxy)silane (2g')[11]



Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.25—7.22 (m, 4H), 7.15—7.12 (m, 1H), 7.01 (d, 1H, *J* = 12.0 Hz), 6.04 (d, 1H, *J* = 12.0 Hz), 0.96 (s, 9H), 0.22 (s, 6H).

Spectroscopic date of ^1H NMR was identical to that of the reference [11].

(*Z*)-*tert*-Butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (2h)[12]



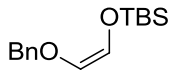
3-Phenylpropanal (396 μL, 3.0 mmol) was used as a substrate and (*Z*)-*tert*-butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (**2h**: 253.5 mg, 1.0 mmol) was

obtained in 34% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc/Et_3N = 100/2/1).

Colorless oil; ^1H NMR (500 MHz, $CDCl_3$): δ 7.29―7.26 (m, 2H), 7.23―7.22 (m, 2H), 7.19―7.16 (m, 1H), 6.31 (d, 1H, *J* = 6.0 Hz), 4.67 (dt, 1H, *J* = 6.9, 6.0 Hz), 3.45 (d, 2H, *J* = 6.9 Hz), 0.95 (s, 9H), 0.16 (s, 6H).

Spectroscopic date of ^1H NMR was identical to that of the reference [12].

(*Z*)-((2-(benzyloxy)vinyl)oxy)(*tert*-butyl)dimethylsilane (**2i**)



2-(Benzyloxy)acetaldehyde (425 μL, 3.0 mmol) was used as a substrate and (*Z*)-((2-(benzyloxy)vinyl)oxy)(*tert*-butyl)dimethylsilane (**2i**: 406.0 mg, 1.54 mmol) was obtained in 51% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/Et_3N = 100/1).

Colorless oil; IR (ATR) cm^{-1}: 2954, 2929, 2857, 1665, 1471, 1462, 1396, 1361, 1297, 1253, 1124, 1006; ^1H NMR (500 MHz, $CDCl_3$): δ 7.37―7.33 (m, 4H), 7.31―7.28 (m, 1H), 5.52 (d, 1H, *J* = 3.4 Hz),5.41 (d, 1H, *J* = 3.4 Hz), 4.81 (s, 2H), 0.94 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 137.7, 130.6, 128.3, 127.7, 127.4, 123.6, 73.7, 25.7, 18.5, -5.3.

6. General procedures to synthesize ß-siloxyaldehydes and modifications.

Typical procedure A (Tables 1, 2 and 3)

Aromatic aldehyde (**1**: 0.15 mmol) was stirred with 2,2'-bipyridyl (0.45 mmol) and *Si*OTf (0.30 mmol) in CH_2Cl_2 (0.75 mL) at 0 ^oC for 30 min., and then a silyl enol ether (**2**: 0.30 mmol) was added to the reaction mixture at 0 ^oC. After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. and 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 analytically pure *β*–siloxy aldehyde **3**.

Typical procedure B (Scheme 3)

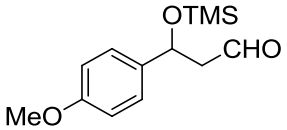
4-Methoxybenzaldehyde (**1a**: 0.15 mmol) was stirred with 2,2'-bipyridyl (0.45 mmol) and TMSOTf (0.30 mmol) in CH_2Cl_2 (0.75 mL) at 0 ^oC for 30 min., and then trimethylsilyl enol ether (**2a**: 0.30 mmol) was added to the reaction mixture at 0 ^oC. After stirring for 2 h, the nucleophile (0.75 mmol) was added at 0 ^oC. After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. and 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 analytically pure product **7**.

Typical procedure C (Scheme 5)

$TMSN_3$ (0.165 mmol) or allylTMS (0.225 mmol) and $FeCl_3$ or $FeBr_3$ (0.015 mmol) were added to a solution of the silyl ether derivative (**3aa** or **7a**: 0.15 mmol) in CH_2Cl_2 (0.75 mL) 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 analytically pure product **11**.

7. Spectroscopic data of newly synthesized products.

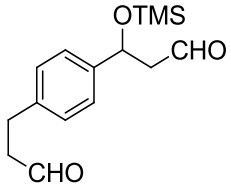
3-(4-Methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (3aa)



4-Methoxy benzaldehyde (**1a**: 1.09 g, 8.00 mmol) and trimethyl(vinyloxy)silane (**2a**: 2.4 mL, 16 mmol) were used according to the typical procedure A and 3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3aa**: 1.88 g, 7.46 mmol) was obtained in 93% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 2836, 1724, 1612, 1586, 1512, 1463, 1360, 1301, 1247, 1172, 1089, 1033; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (dd, 1H, *J* = 2.3, 2.3 Hz), 7.25 (d, 2H, *J* = 8.9 Hz), 6.87 (d, 2H, *J* = 8.9 Hz), 5.17 (dd, 1H, *J* = 8.6, 4.0 Hz), 3.80 (s, 3H), 2.86 (ddd, 1H, *J* = 15.9, 8.6, 2.3 Hz), 2.61 (ddd, 1H, *J* = 15.9, 4.0, 2.3 Hz), 0.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.6, 159.0, 135.7, 126.9, 113.8, 69.9, 55.2, 53.8, 0.0; ESI-HRMS m/z: 275.1074 ($[M+Na]^+$); Calcd for $C_{13}H_{20}O_3SiNa$: 275.1074.

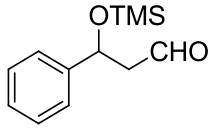
3-(4-(3-Oxopropyl)phenyl)-3-((trimethylsilyl)oxy)propanal (3ba)



4-(3-Oxopropyl)benzaldehyde (**1b**: 16.3 mg, 0.10 mmol) and trimethyl(vinyloxy)silane (**2a**: 24 μL, 0.20 mmol) were used according to the typical procedure A and 3-(4-(3-oxopropyl)phenyl)-3-((trimethylsilyl)oxy)propanal (**3ba**: 17.3 mg, 0.06 mmol) was obtained in 62% yield after 4 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 3/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 2923, 2850, 1721, 1513, 1048, 1359, 1251, 1091; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.82 (s, 1H), 9.76 (dd, 1H, *J* = 1.7 Hz), 7.26 (d, 2H, *J* = 7.5 Hz), 7.16 (d, 2H, *J* = 7.5 Hz), 5.19 (dd, 1H, *J* = 8.0, 4.0 Hz), 2.95 (t, 2H, *J* = 7.5 Hz), 2.85 (ddd, 1H, *J* = 16.0, 8.0, 1.7 Hz), 2.78 (t, 2H, *J* = 7.5 Hz), 2.61 (ddd, 1H, *J* = 16.0, 4.0, 1.7 Hz), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.5, 201.3, 141.7, 139.7, 128.4, 125.9, 70.0, 53.7, 45.2, 27.7, 0.0; ESI-HRMS m/z: 301.1247 ($[M+Na]^+$); Calcd for $C_{15}H_{22}O_3SiNa$: 301.1230.

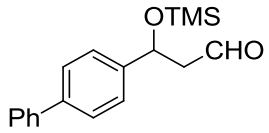
3-Phenyl-3-((trimethylsilyl)oxy)propanal (3ca)



Benzaldehyde (**1c**: 15.9 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-phenyl-3-((trimethylsilyl)oxy)propanal (**3ca** 30.6 mg, 0.14 mmol) was obtained in 92% yield after 2.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 1724, 1454, 1400, 1362, 1251, 1216, 1095, 1064, 1029; ^1H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.3, 1.7 Hz), 7.34―7.32 (m, 4H), 7.28―7.26 (m, 1H), 5.22 (dd, 1H, *J* = 8.6, 4.0 Hz), 2.87 (ddd, 1H, *J* = 16.0, 8.6, 2.3 Hz), 2.63 (ddd, 1H, *J* = 16.0, 4.0, 1.7 Hz), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.4, 143.6, 128.5, 127.6, 125.6, 70.2, 53.8, -0.0; ESI-HRMS m/z: 245.0953 ($[M+Na]^+$); Calcd for $C_{12}H_{18}O_2SiNa$: 245.0968.

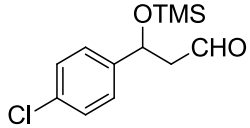
3-([1,1'-Biphenyl]-4-yl)-3-((trimethylsilyl)oxy)propanal (3da)



4-Phenylbenzaldehyde (**1d**: 27.3 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-([1,1'-biphenyl]-4-yl)-3-((trimethylsilyl)oxy)propanal (**3da**: 44.1 mg, 0.15 mmol) was obtained in 99% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 1725, 1487, 1405, 1353, 1251, 1092, 1031; ^1H NMR (500 MHz, $CDCl_3$): δ 9.81 (brs, 1H), 7.60―7.57 (m, 4H), 7.46―7.40 (m, 4H), 7.35 (t, 1H, *J* = 7.5 Hz), 5.28 (dd, 1H, *J* = 8.6, 4.0 Hz), 2.91 (dd, 1H, *J* = 16.0, 8.6, 2.3 Hz), 2.68 (dd, 1H, *J* = 16.0, 4.0), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.3, 142.7, 140.7, 140.5, 128.8, 127.3, 127.2, 127.0, 126.1, 70.0, 53.8, 0.1; ESI-HRMS m/z: 321.1281 ($[M+Na]^+$); Calcd for $C_{18}H_{22}O_2SiNa$: 321.1281.

3-(4-Chlorophenyl)-3-((trimethylsilyl)oxy)propanal (3ea)

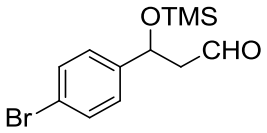


4-Chloro benzaldehyde (**1e**: 21.0 g, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and

3-(4-chlorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ea**: 34.1 mg, 0.13 mmol) was obtained in 89% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 1725, 1490, 1407, 1252, 1088, 1014; ^1H NMR (500 MHz, $CDCl_3$): δ 9.76 (dd, 1H, *J* = 2.3, 2.0 Hz), 7.31 (d, 2H, *J* = 8.6 Hz), 7.27 (d, 2H, *J* = 8.6 Hz), 5.20 (dd, 1H, *J* = 8.6, 4.0 Hz), 2.84 (ddd, 1H, *J* = 16.0, 8.6, 2.3 Hz), 2.61 (ddd, 1H, *J* = 16.0, 4.0, 2.0 Hz), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.8, 142.3, 133.2, 128.7, 127.0, 69.5, 53.7, -0.0; ESI-HRMS m/z: 279.0578 ($[M+Na]^+$); Calcd for $C_{12}H_{17}O_2SiClNa$: 279.0579.

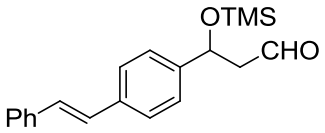
3-(4-Bromophenyl)-3-((trimethylsilyl)oxy)propanal (3fa)



4-Bromobenzaldehyde (**1f**: 27.7 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(4-bromophenyl)-3-((trimethylsilyl)oxy)propanal (**3fa**: 43.0 mg, 0.14 mmol) was obtained in 95% yield after 3 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 2723, 1724, 1592, 1486, 1403, 1347, 1298, 1250, 1089; ^1H NMR (500 MHz, $CDCl_3$): δ 9.75 (dd, 1H, *J* = 2.3, 1.7 Hz), 7.46 (d, 2H, *J* = 8.0 Hz), 7.22 (d, 2H, *J* = 8.0 Hz), 5.18 (dd, 1H, *J* = 8.7, 4.0 Hz), 2.84 (ddd, 1H, *J* = 16.5, 8.7, 2.3 Hz), 2.60 (ddd, 1H, *J* = 16.5, 4.0, 1.7 Hz), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.7, 142.8, 131.6, 127.3, 121.3, 69.5, 53.7, -0.0; ESI-HRMS m/z: 323.0091 ($[M+Na]^+$); Calcd for $C_{12}H_{17}O_2SiBrNa$: 323.0073.

(*E*)-3-(4-Styrylphenyl)-3-((trimethylsilyl)oxy)propanal (3ga)

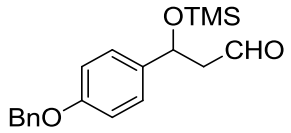


(*E*)-4-Styrylbenzaldehyde (**1g**: 31.2 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and (*E*)-3-(4-styrylphenyl)-3-((trimethylsilyl)oxy)propanal (**3ga**: 49.2 mg, 0.15 mmol) was obtained in quantitative yield after 3.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 6/1).

Colorless solid; Mp: 74.5―75.5 °C; IR (ATR) cm^{-1}: 3027, 2956, 2723, 1723, 1597, 1510, 1449, 1415, 1358, 1301, 1251, 1216, 1115, 1090, 1029; ^1H NMR (500 MHz, $CDCl_3$): δ 9.79 (dd, 1H,

J = 2.3, 1.7 Hz), 7.52—7.49 (m, 4H), 7.36 (t, 2H, *J* = 8.0 Hz), 7.33 (d, 1H, *J* = 8.0 Hz), 7.27 (t, 1H, *J* = 7.5 Hz), 7.14—7.07 (m, 2H), 5.23 (dd, 1H, *J* = 8.6, 4.0 Hz), 2.89 (ddd, 1H, *J* = 16.0, 8.6, 2.3 Hz), 2.64 (ddd, 1H, *J* = 16.0, 4.0, 1.7 Hz), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.2, 143.0, 137.2, 136.7, 128.8, 128.7, 127.7, 126.6, 126.5, 126.0, 70.0, 53.7, 0.0; ESI-HRMS m/z: 347.1440 ($[M+Na]^+$); Calcd for $C_{20}H_{24}O_2SiNa$: 347.1438.

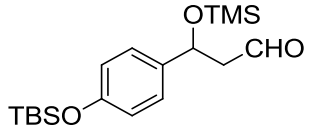
3-(4-Benzyloxyphenyl)-3-((trimethylsilyl)oxy)propanal (3ha)



4-Benzyloxybenzaldehyde (**1h**: 31.8 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(4-benzyloxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3ha**: 47.8 mg, 0.14 mmol) was obtained in 97% yield after 3.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless solid; Mp: 56.0—56.9 °C; IR (ATR) cm^{-1}: 2956, 1724, 1610, 1585, 1510, 1455, 1383, 1300, 1249, 1172, 1090, 1025; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (dd, 1H, *J* = 2.3, 2.3 Hz), 7.44 (d, 2H, *J* = 7.5 Hz), 7.39 (t, 2H, *J* = 7.5 Hz), 7.33 (t, 1H, *J* = 7.5 Hz), 7.26 (d, 2H, *J* = 8.8 Hz), 6.95 (d, 2H, *J* = 8.8 Hz), 5.17 (dd, 1H, *J* = 8.6, 4.0 Hz), 5.05 (s, 2H), 2.86 (ddd, 1H, *J* = 16.0, 8.6, 2.3 Hz), 2.61 (ddd, 1H, *J* = 16.0, 4.0, 2.3 Hz), 0.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.5, 158.3, 136.9, 136.0, 128.6, 128.0, 127.5, 126.9, 114.7, 70.0, 69.9, 53.8, 0.0; ESI-HRMS m/z: 351.1377 ($[M+Na]^+$); Calcd for $C_{19}H_{24}O_3SiNa$: 351.1387.

3-(4-((*tert*-Butyldimethylsilyl)oxy)phenyl)-3-((trimethylsilyl)oxy)propanal (3ia)

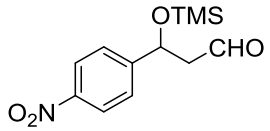


4-((*tert*-Butyldimethylsilyl)oxy)benzaldehyde (**1i**: 35.4 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-((trimethylsilyl)oxy)propanal (**3ia**: 48.1 mg, 0.14 mmol) was obtained in 91% yield after 4.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; IR (ATR) cm^{-1}:2956, 2931, 2859, 1726, 1608, 1509, 1472, 1362, 1251, 1167, 1089, 1030, 1000; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.76 (dd, 1H, *J* = 2.6, 1.7 Hz), 7.18 (d, 2H, *J* = 8.3 Hz), 6.79 (d, 2H, *J* = 8.3 Hz), 5.15 (dd, 1H, *J* = 8.6, 4.0 Hz), 2.85 (ddd, 1H, *J* = 16.0, 8.6, 2.6 Hz), 2.60 (ddd, 1H, *J* = 16.0, 4.0, 1.7 Hz), 0.98 (s, 9H), 0.19 (s, 6H), 0.01 (s, 9H); ^{13}C

NMR (125 MHz, $CDCl_3$): δ 201.6, 155.1, 136.3, 126.9, 120.0, 70.0, 53.7, 25.6, 18.2, 0.0, -4.4; ESI-HRMS m/z: 375.1790 ($[M+Na]^+$); Calcd for $C_{18}H_{32}O_3Si_2Na$: 375.1782.

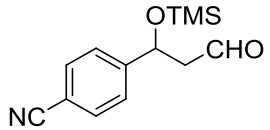
3-(4-Nitorophenyl)-3-((trimethylsilyl)oxy)propanal (3ja)



4-Nitorobenzaldehyde (**1j**: 30.2 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(4-nitorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ja**: 34.2 mg, 0.10 mmol) was obtained in 68% yield after 8 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

yellow oil; IR (ATR) cm^{-1}:2957, 2837, 2725, 1724, 1606, 1520, 1400, 1346, 1294, 1252, 1215, 1094, 1031, 1014; ^1H NMR (500 MHz, $CDCl_3$): δ 9.77 (dd, 1H, *J* = 2.0, 1.5 Hz), 8.21 (d, 2H, *J* = 8.6 Hz), 7.53 (d, 2H, *J* = 8.6 Hz), 5.34 (dd, 1H, *J* = 8.3, 4.0 Hz), 2.89 (ddd, 1H, *J* = 16.6, 8.3, 2.0 Hz), 2.66 (ddd, 1H, *J* = 16.6, 4.0, 1.5 Hz), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.7, 151.2, 147.4, 126.4, 123.8, 69.1, 53.5, -0.1; ESI-HRMS m/z: 268.1003 ($[M+H]^+$); Calcd for $C_{12}H_{18}NO_4Si$: 268.1000.

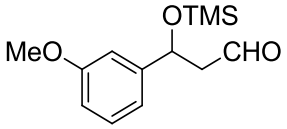
3-(4-Cyanophenyl)-3-((trimethylsilyl)oxy)propanal (3ka)



4-cyanobenzaldehyde (**1j**: 19.7 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(4-nitorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ja**: 16.9 mg, 0.07 mmol) was obtained in 45% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

yellow oil; IR (ATR) cm^{-1}: 2958, 2228, 1723, 1609, 1409, 1362, 1305, 1252, 1202, 1092; ^1H NMR (500 MHz, $CDCl_3$): δ 9.75 (brs, 1H), 7.63 (d, 2H, *J* = 8.6 Hz), 7.46 (d, 2H, *J* = 8.6 Hz), 5.27 (dd, 1H, *J* = 8.0, 4.0 Hz), 2.86 (ddd, 1H, *J* = 16.6, 8.0, 1.7 Hz), 2.63 (ddd, 1H, *J* = 16.6, 4.0, 1.2 Hz), 0.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 199.9, 149.1, 132.4, 126.3, 118.6, 111.4, 69.3, 53.4, -0.1; ESI-HRMS m/z: 248.1128 ($[M+H]^+$); Calcd for $C_{13}H_{18}NO_2Si$: 248.1101.

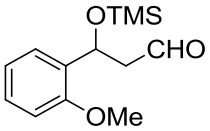
3-(3-Methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (3la)



3-Methoxybenzaldehyde (**1l**: 18 μL, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(3-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3la**: 37.4 mg, 0.14 mmol) was obtained in 93% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 2836, 1726, 1602, 1587, 1487, 1456, 1437, 1355, 1318, 1286, 1251, 1154, 1101, 1045; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (dd, 1H, *J* = 2.3, 1.7 Hz), 7.25, (t, 1H, *J* = 8.0 Hz), 6.91—6.89 (m, 2H), 6.82—6.79 (m, 1H), 5.20 (dd, 1H, *J* = 8.6, 4.0 Hz), 3.81 (s, 3H), 2.86 (ddd, 1H, *J* = 16.0, 8.6, 2.3 Hz), 2.62 (ddd, 1H, *J* = 16.0, 4.0, 1.7 Hz), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.3, 159.7, 145.3, 129.5, 117.9, 112.9, 111.2, 70.1, 55.2, 53.7, -0.0; ESI-HRMS m/z: 275.1068 ($[M+Na]^+$); Calcd for $C_{13}H_{20}O_3SiNa$: 275.1074.

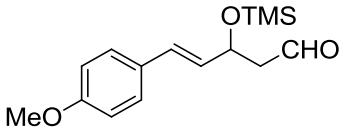
3-(2-Methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (3ma)



2-Methoxybenzaldehyde (**1m**: 18 μL, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(2-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3ma**: 41.0 mg, 0.15 mmol) was obtained in 99% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; IR (ATR) cm^{-1}: 2957, 1725, 1601, 1489, 1464, 1439, 1283, 1239, 1120, 1084, 1028; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.0, 2.0 Hz), 7.49 (dd, 1H, *J* = 7.5, 1.7 Hz), 7.24 (dt, 1H, *J* = 7.5, 1.7 Hz), 6.98 (t, 1H, *J* = 7.5 Hz), 6.84 (d, 1H, *J* = 7.5 Hz), 5.57 (dd, 1H, *J* = 7.2, 4.8 Hz), 3.83 (s, 3H), 2.73—2.66 (m, 2H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.2, 155.0, 131.7, 128.3, 126.4, 120.6, 109.9, 64.5, 55.1, 51.8, -0.1; ESI-HRMS m/z: 275.1070 ($[M+Na]^+$); Calcd for $C_{13}H_{20}O_3SiNa$: 275.1074.

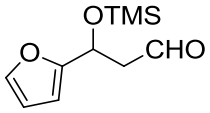
(*E*)-5-(4-Methoxyphenyl)-3-((triethylsilyl)oxy)pent-4-enal (3na)



(*E*)-3-(4-Methoxyphenyl)acrylaldehyde (**1n**: 25.9 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and (*E*)-5-(4-methoxyphenyl)-3-((triethylsilyl)oxy)pent-4-enal (**3na**: 44.1 mg, 0.15 mmol) was obtained in 99% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Yellow oil; IR (ATR) cm^{-1}: 2956, 2837, 1724, 1607, 1577, 1511, 1464, 1302, 1247, 1175, 1121, 1106, 1067, 1033; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.80 (dd, 1H, *J* = 2.3, 2.3 Hz), 7.31 (d, 2H, *J* = 8.6 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 6.51 (d, 1H, *J* = 16.0 Hz), 6.06 (dd, 1H, *J* = 16.0, 6.6 Hz), 4.83―4.80 (m, 1H), 3.81 (s, 3H), 2.73 (ddd, 1H, *J* = 15.9, 7.6, 2.3 Hz), 2.59 (ddd, 1H, *J* = 15.9, 4.6, 2.3 Hz), 0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.4, 159.4, 129.7, 129.1, 129.0, 127.7, 114.0, 69.2, 55.3, 51.7, 0.3; ESI-HRMS m/z: 301.1232 ($[M+Na]^+$); Calcd for $C_{15}H_{22}O_3SiNa$: 301.1230.

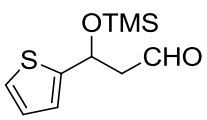
3-(Furan-2-yl)-3-((trimethylsilyl)oxy)propanal (3oa)



Furan-2-carbaldehyde (**1o**: 15 μL, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(furan-2-yl)-3-((trimethylsilyl)oxy)propanal (**3oa**: 38.4 mg, 0.15 mmol) was obtained in quantitative yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; IR (ATR) cm^{-1}: 2958, 1725, 1504, 1400, 1344, 1251, 1148, 1076, 1007; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.83 (dd, 1H, *J* = 2.0, 2.0 Hz), 7.37 (t, 1H, *J* = 1.7 Hz), 6.33―6.32 (m, 1H), 6.22 (d, 1H, *J* = 3.4 Hz), 5.24 (dd, 1H, *J* = 7.8, 4.8 Hz), 2.98 (ddd, 1H, *J* = 16.5, 7.8, 2.0 Hz), 2.79 (ddd, 1H, *J* = 16.5, 4.8, 2.0 Hz), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.6, 155.0, 142.1, 110.2, 106.6, 63.5, 49.8, -0.2; ESI-HRMS m/z: 235.0753 ($[M+Na]^+$); Calcd for $C_{10}H_{16}O_3SiNa$: 235.0761.

3-(Thiophen-2-yl)-3-((trimethylsilyl)oxy)propanal (3pa)

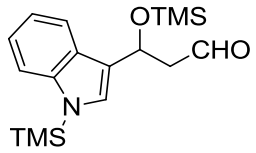


Thiophen-2-carbaldehyde (**1p**: 33.6 mg, 0.30 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)propanal (**3pa**: 71.2 mg, 0.30 mmol) was obtained in

quantitative yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Yelow oil; IR (ATR) cm^{-1}: 2957, 1724, 1439, 1370, 1321, 1251, 1176, 1088; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.3, 1.7 Hz), 7.23 (dd, 1H, *J* = 4.9, 1.7 Hz), 6.95―6.92 (m, 2H), 5.49 (dd, 1H, J = 8.0, 4.6 Hz), 2.98 (ddd, 1H, *J* = 16.0, 8.0, 2.3 Hz), 2.77 (ddd, 1H, 16.0, 4.6, 1.7 Hz), 0.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 200.6, 147.9, 126.6, 124.6, 123.3, 66.2, 53.8, -0.1; ESI-HRMS m/z: 251.0531 ($[M+Na]^+$); Calcd for $C_{10}H_{16}O_2SiSNa$: 251.0532.

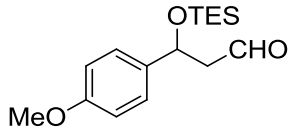
3-(1-(Trimethylsilyl)-1*H*-indol-3-yl)-3-((trimethylsilyl)oxy)propanal (3qa)



1*H*-Indole-3-carbaldehyde (**1q**: 21.8 mg, 0.15 mmol) and trimethyl(vinyloxy)silane (**2a**: 44 μL, 0.30 mmol) were used according to the typical procedure A and 3-(1-(trimethylsilyl)-1*H*-indol-3-yl)-3-((trimethylsilyl)oxy)propanal (**3qa**: 41.7 mg, 0.13 mmol) was obtained in 83% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 7/1).

Yellow oil; IR (ATR) cm^{-1}: 2957, 1724, 1555, 1452, 1304, 1304, 1251, 1164, 1145, 1131, 1066 ; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.84 (dd, 1H, *J* = 2.6, 2.3 Hz), 7.69 (d, 1H, *J* = 7.5 Hz), 7.49 (d, 1H, *J* = 8.6 Hz), 7.22 (dt, 1H, *J* = 7.5, 1.2 Hz), 7.16 (s, 1H), 7.10 (s, 1H), 5.89 (dd, 1H, *J* = 8.0, 4.3 Hz), 3.07 (ddd, 1H, *J* = 16.0, 8.0, 2.6 Hz), 2.86 (ddd, 1H, 16.0, 4.3, 2.3 Hz), 0.56 (s, 9H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.1, 140.9, 128.7, 127.0, 121.7, 120.6, 119.7, 119.5, 113.1, 64.8, 52.4, 0.1, -0.1; ESI-HRMS m/z: 356.1472 ($[M+Na]^+$); Calcd for $C_{17}H_{27}NO_2Si_2Na$: 356.1473.

3-(4-Methoxyphenyl)-3-((triethylsilyl)oxy)propanal (3ab)

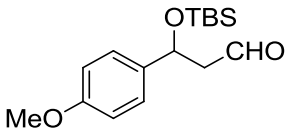


4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and triethyl(vinyloxy)silane (**2b**: 55 μL, 0.30 mmol) were used according to the typical procedure A and 3-(4-methoxyphenyl)-3-((triethylsilyl)oxy)propanal (**3ab**: 44.1 mg, 0.15 mmol) was obtained in 97% yield after 3 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 12/1).

Colorless oil; IR (ATR) cm^{-1}: 2954, 2910, 2876, 2836, 1725, 1612, 1512, 1460, 1414, 1359,

1302, 1247, 1173, 1090, 1035, 1004; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (dd, 1H, *J* = 2.3, 2.3 Hz), 7.26 (d, 2H, *J* = 8.6 Hz), 6.86 (d, 2H, *J* = 8.6 Hz), 5.17 (dd, 1H, *J* = 8.0, 4.5 Hz), 3.80 (s, 3H), 2.84 (ddd, 1H, *J* = 15.7, 8.0, 2.3 Hz), 2.61 (ddd, 1H, 15.7, 4.5, 2.3 Hz), 0.86 (t, 9H, *J* = 8.0 Hz), 0.55—0.46 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.7, 159.0, 136.0, 126.9, 113.7, 70.1, 55.2, 54.0, 6.9, 4.7; ESI-HRMS m/z: 317.1544 ($[M+Na]^+$); Calcd for $C_{16}H_{26}O_3SiNa$: 317.1543.

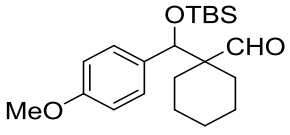
3-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (3ac)



4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and *tert*-butyldimethyl(vinyloxy)silane (**2c**: 50 μL, 0.30 mmol) were used according to the typical procedure A and 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ac**: 46.1 mg, 0.15 mmol) was obtained in 98% yield after 6 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Colorless oil; IR (ATR) cm^{-1}: 2955, 2930, 2856, 1725, 1612, 1512, 1463, 1301, 1248, 1173, 1088, 1035, 1004; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.78 (dd, 1H, *J* = 2.9, 1.7 Hz), 7.25 (d, 2H, *J* = 9.0 Hz), 6.87 (d, 2H, *J* = 9.0 Hz), 5.16 (dd, 1H, *J* = 8.3, 4.3 Hz), 3.80 (s, 3H), 2.83 (ddd, 1H, *J* = 15.6, 8.3, 2.9 Hz), 2.60 (ddd, 1H, 15.6, 4.3, 1.7 Hz), 0.85 (s, 9H), 0.03 (s, 3H), -0.16 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 201.8, 159.1, 136.0, 127.0, 113.9, 70.5, 55.3, 54.2, 25.8, 18.2, -4.5, -5.1; ESI-HRMS m/z: 317.1544 ($[M+Na]^+$); Calcd for $C_{16}H_{26}O_3SiNa$: 317.1543.

1-(((*tert*-Butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)cyclohexanecarbaldehyde (3ad)

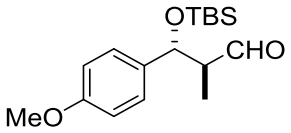


4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and *tert*-butyl(cyclohexylidenemethoxy)dimethylsilane (**2d**: 70 μL, 0.30 mmol) were used according to the typical procedure A and 1-(((*tert*-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)cyclohexanecarbaldehyde (**3ad**: 56.0 mg, 0.15 mmol) was obtained in quantitative yield after 5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 12/1).

Colorless oil; IR (ATR) cm^{-1}: 2930, 2855, 1720, 1612, 1512, 1463, 1248, 1174, 1077, 1064, 1037; ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.67 (s, 1H), 7.09 (d, 2H, *J* = 8.6 Hz), 6.82 (d, 2H, *J* =

8.6 Hz), 4.50 (s, 1H), 3.80 (s, 3H), 2.14 (d, 1H, *J* = 12.0 Hz), 1.90 (d, 1H, *J* = 12.0 Hz), 1.61—1.54 (m, 3H), 1.27—1.08 (m, 4H), 1.05—0.98 (m, 1H), 0.87 (s, 9H), -0.01 (s, 3H), -0.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 208.6, 159.0, 132.5, 128.8, 112.9, 80.7, 55.1, 55.0, 29.2, 27.4, 25.8, 25.7, 22.8, 22.4, 18.1, -4.6, -5.5; ESI-HRMS m/z: 385.2159 ($[M+Na]^+$); Calcd for $C_{21}H_{34}O_3SiNa$: 385.2169.

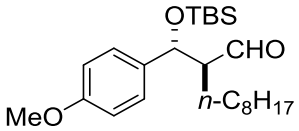
3-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-methylpropanal (3ae)



4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and (*Z*)-*tert*-butyldimethyl(prop-1-en-1-yloxy)silane (**2e**: 52 μL, 0.30 mmol) were used according to the typical procedure A and diastereomixture of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-methylpropanal (**3ae**: 42.5 mg, 0.14 mmol) was obtained in 92% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 8/1).

Colorless oil; *anti*:*syn* = 92:8; IR (ATR) cm^{-1}: 2955, 2930, 2857, 1725, 1612, 1512, 1462, 1302, 1248, 1173, 1067, 1035, 1006; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 9.80 (d, 0.92H, *J* = 2.9 Hz), 9.74 (brs, 0.08H), 7.21 (d, 2H, *J* = 8.3 Hz), 6.86 (d, 2H, *J* = 8.3 Hz), 5.07 (d, 0.08H, *J* = 5.0 Hz), 4.71 (d, 0.92H, *J* = 8.0 Hz), 3.81 (s, 2.76H), 3.80 (s, 0.24H), 2.69—2.63 (m, 0.92H), 2.60—2.54 (m, 0.08H), 1.03 (d, 0.24H, *J* = 6.9 Hz), 0.87 (d, 2.76H, *J* = 6.3 Hz), 0.85 (s, 0.72H), 0.84 (s, 8.28H), 0.02 (s, 0.24H), 0.00 (s, 2.76H), -0.18 (s, 0.24H), -0.26 (s, 3H); ^{13}C NMR of *anti* isomer (125 MHz, $CDCl_3$): δ 204.8, 159.1, 134.4, 127.8, 113.6, 76.4, 55.2, 54.7, 25.7, 18.0, 11.0, -4.5, -5.2; ESI-HRMS m/z: 331.1707 ($[M+Na]^+$); Calcd for $C_{17}H_{28}O_3SiNa$: 331.1700.

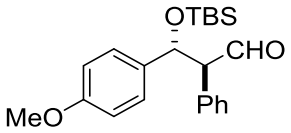
((tert-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)decanal (3af)



4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and (*Z*)-*tert*-butyl(dec-1-en-1-yloxy)dimethylsilane (**2f**: 81 μL, 0.30 mmol) were used according to the typical procedure A and diastereo mixture of ((*tert*-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)decanal (**3af**: 53.3 mg, 0.13 mmol) was obtained in 87% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 12/1).

Colorless oil; *anti*:*syn* = 87:13; IR (ATR) cm^{-1}: 2927, 2855, 1726, 1612, 1512, 1463, 1248, 1173, 1070, 1036; ^1H NMR of diasetereo mixture (500 MHz, $CDCl_3$): δ 9.69 (d, 0.87H, *J* = 4.0 Hz), 9.66 (d, 0.13H, *J* = 2.9Hz), 7.20 (d, 2H, *J* = 9.1 Hz), 6.86 (d, 2H, *J* = 9.1 Hz), 4.94 (d, 0.13H, *J* = 5.2 Hz), 4.76 (d, 0.87H, *J* = 8.0 Hz), 3.81 (s, 2.61H), 3.80 (s, 0.39H), 2.54—2.50 (m, 1H), 1.53—1.45 (m, 1H), 1.26—1.16 (m, 16H), 0.83 (s, 9H), 0.10 (s, 0.39H), -0.01 (s, 2.61H), -0.20 (s, 0.39H), -0.28 (s, 2.61H); ^{13}C NMR of *anti* isomer (125 MHz, $CDCl_3$): δ 204.7, 159.1, 134.5, 127.9, 113.6, 75.4, 60.6, 55.2, 31.8, 29.5, 29.2, 29.1, 26.9, 26.2, 25.7, 22.6, 18.0, 14.1, -4.5, -5.2; ESI-HRMS m/z: 429.2799 ($[M+Na]^+$); Calcd for $C_{24}H_{42}O_3SiNa$: 429.2795.

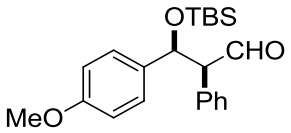
3-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (3ag)



4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and (*Z*)-*tert*-butyldimethyl(styryloxy)silane (**2g**: 72 μL, 0.30 mmol) were used according to the typical procedure A and diastereo mixture of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag**: 47.0 mg, 0.12 mmol) was obtained in 85% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 80:20; IR (ATR) cm^{-1}: 2954, 2929, 2856, 1725, 1612, 1511, 1463, 1302, 1247, 1173, 1073, 1034, 1005; ^1H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 9.98 (d, 0.8H, *J* = 3.4 Hz), 9.80 (d, 0.2H, *J* = 1.7 Hz), 7.32—7.28 (m, 0.6H), 7.22—7.16 (m, 2.4H), 7.04—6.98 (m, 4H), 6.75 (d, 0.4H, *J* = 8.6 Hz), 6.69 (d, 1.6H, *J* = 8.6 Hz), 5.31 (d, 0.2H, *J* = 5.7 Hz), 5.21 (d, 0.8H, *J* = 8.6 Hz), 3.83 (dd, 0.8H, *J* = 8.6, 3.4 Hz), 3.77 (s, 0.6H), 3.73 (s, 2.4H), 3.69 (dd, 0.2H, *J* = 5.7, 1.7 Hz), 0.85 (s, 7.2H), 0.75 (s, 1.8H), -0.02 (s, 2.4H), -0.14 (s, 0.6H), -0.26 (s, 2.4H), -0.31 (s, 0.6H); ^{13}C NMR of *anti* isomer (125 MHz, $CDCl_3$): δ 200.4, 158.8, 133.8, 130.6, 129.4, 128.5, 127.8, 127.4, 113.2, 76.1, 67.7, 55.1, 25.7, 18.1, -4.5, -5.3; ESI-HRMS m/z: 393.1880 ($[M+Na]^+$); Calcd for $C_{22}H_{30}O_3SiNa$: 393.1856.

3-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (3ag')

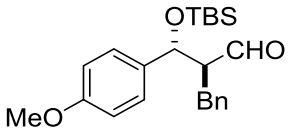


4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and (*E*)-*tert*-butyldimethyl(styryloxy)silane (**2g'**: 72 μL, 0.30 mmol) were used according to the typical procedure A and 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag'**: 38.0 mg, 0.11 mmol) was obtained in 68% yield after 24 h stirring and purification by silica-gel column

chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 15:85; IR (ATR) cm^{-1}: 2929, 2856, 1722, 1612, 1511, 1463, 1302, 1246, 1173, 1082, 1034, 1005; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 9.98 (d, 0.15H, *J* = 3.4 Hz), 9.81 (d, 0.85H, *J* = 2.3 Hz), 7.32—7.28 (m, 2H), 7.21—7.19 (m, 0.3H), 7.17—7.14 (m, 1.7H), 7.03 (d, 1.7H, *J* = 8.5 Hz), 7.00 (d, 0.3H, *J* = 9.2 Hz), 6.76 (d, 1.7H, *J* = 8.6 Hz), 6.69 (d, 0.3H, *J* = 8.6 Hz), 5.31 (d, 0.85H, *J* = 5.7 Hz), 5.21 (d, 0.15H, *J* = 8.6 Hz), 3.83 (dd, 0.15H, *J* = 8.6, 3.4 Hz), 3.77 (s, 2.55H), 3.73 (s, 0.45H), 3.70 (dd, 0.85H, *J* = 5.7, 1.7 Hz), 0.86 (s, 1.35H), 0.75 (s, 7.65H), -0.02 (s, 0.45H), -0.14 (s, 2.55H), -0.25 (s, 0.45H), -0.31 (s, 2.55H); ^{13}C NMR of *syn* isomer (125 MHz, $CDCl_3$): δ 201.0, 158.8, 134.5, 133.7, 130.6, 128.1, 127.8, 127.4, 113.2, 74.8, 67.5, 55.1, 25.6, 17.9, -4.7, -5.6; ESI-HRMS m/z: 393.1857 ($[M+Na]^+$); Calcd for $C_{22}H_{30}O_3SiNa$: 393.1856.

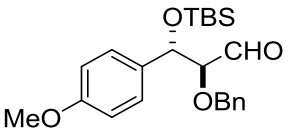
2-Benzyl-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (3ah)



4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and (*Z*)-*tert*-butyldimethyl((3-phenylprop-1-en-1-yl)oxy)silane (**2h**: 74 μL, 0.30 mmol) were used according to the typical procedure A and 2-benzyl-3-((tert-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ah**: 42.6 mg, 0.11 mmol) was obtained in 74% yield after 2.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 88:12; IR (ATR) cm^{-1}: 2954, 2930, 2857, 1726, 1612, 1511, 1463, 1303, 1248, 1173, 1063, 1035, 1005; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 9.78 (d, 0.88H, *J* = 3.2 Hz), 9.69 (d, 0.12H, *J* = 2.3 Hz), 7.27—7.21 (m, 4H), 7.15 (t, 0.88H, *J* = 7.2Hz), 7.09 (t, 0.12H, *J* = 8.0Hz), 7.04 (d, 2H, *J* = 6.9 Hz), 6.88 (d, 2H, *J* =8.6 Hz), 5.02 (d, 0.12H, *J* = 5.2 Hz), 4.86 (d, 0.88H, *J* = 6.9 Hz), 3.82 (s, 2.64H), 3.81 (s, 0.36H), 3.09—3.04 (m, 0.12H), 3.02—2.98 (m, 0.88H), 2.91 (dd, 0.88H, *J* = 13.8, 9.7 Hz), 2.81 (dd, 0.12H, *J* = 13.8, 4.0 Hz), 2.58 (dd, 1H, *J* = 13.9, 4.0 Hz), 2.48 (dd, 1H, *J* = 13.8, 6.3 Hz), 0.91 (s, 1.08H), 0.86 (s, 8.02H), 0.08 (s, 0.36H), 0.02 (s, 2.64H), -0.18 (s, 0.34H), -0.25 (s, 2.64H); ^{13}C NMR of *anti* isomer (125 MHz, $CDCl_3$): δ 204.1, 159.2, 138.8, 134.3, 128.8, 128.4, 127.8, 126.2, 113.7, 75.3, 61.7, 55.2, 32.4, 25.7, 18.1, -4.4, -5.2; ESI-HRMS m/z: 407.2017 ($[M+Na]^+$); Calcd for $C_{23}H_{32}O_3SiNa$: 407.2013.

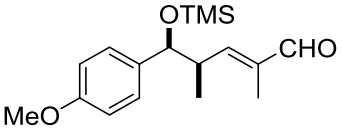
2-(Benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (3ai)



4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and (*Z*)-((2-(benzyloxy)vinyl)oxy)(*tert*-butyl)dimethylsilane (**2i**: 80 μL, 0.30 mmol) were used according to the typical procedure A and 2-(benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ai**: 20.1 mg, 0.05 mmol) was obtained in 33% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 83:17; IR (ATR) cm^{-1}: 2954, 2929, 2856, 1735, 1612, 1512, 1463, 1249, 1173, 1084, 1035, 1006; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 9.68 (d, 1H, *J* = 2.3 Hz), 9.60 (d, 1H, *J* = 1.7 Hz), 7.30—7.23 (m, 6H), 7.21—7.19 (m, 0.34H), 7.11—7.09 (m, 1.66H), 6.86 (d, 2H, *J* = 8.6 Hz), 4.96 (d, 0.17H, *J* = 5.2 Hz), 4.89 (d, 0.83H, *J* = 6.3 Hz), 4.57 (d, 0.17H, *J* = 12.6 Hz), 4.56 (d, 0.83H, *J* = 12.0 Hz), 4.46 (d, 0.17H, *J* = 12.6 Hz), 4.39 (d, 0.83H, *J* = 12.0 Hz), 3.82 (s, 2.49H), 3.81 (s, 0.51H), 3.79 (dd, 1H, *J* = 6.3, 2.3 Hz), 0.86 (s, 1.53H), 0.85 (s, 7.47H), 0.02 (s, 2.49H), -0.01 (s, 0.51H), -0.13 (s, 0.51H), -0.18 (s, 2.49H); ^{13}C NMR of *anti* isomer (125 MHz, $CDCl_3$): δ 201.6, 159.2, 137.2, 133.0, 128.3, 128.1, 128.0, 127.8, 113.5, 87.2, 74.8, 72.7, 55.2, 25.7, 18.1, -4.6, -5.2; ESI-HRMS m/z: 423.1965 ($[M+Na]^+$); Calcd for $C_{23}H_{32}O_4SiNa$: 423.1962.

(*E*)-5-(4-Methoxyphenyl)-2,4-dimethyl-5-((trimethylsilyl)oxy)pent-2-enal (3aj)

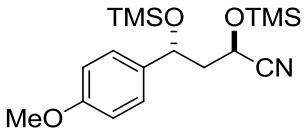


4-Methoxybenzaldehyde (**1a**: 20.0 mg, 0.15 mmol) and trimethyl(((1*E*,3*E*)-2-methylpenta-1,3-dien-1-yl)oxy)silane (**2j**: 65 μL, 0.30 mmol) were according to the typical procedure A and (*E*)-5-(4-methoxyphenyl)-2,4-dimethyl-5-((trimethylsilyl)oxy)pent-2-enal (**3aj**: 32.8 mg, 0.11 mmol) was obtained in 71% yield after 2 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 45:55; IR (ATR) cm^{-1}: 2958, 2836, 1686, 1642, 1612, 1586, 1511, 1457, 1364, 1302, 1248, 1173, 1072, 1033; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 9.39 (s, 0.45H), 9.30 (s, 0.55H), 7.16—7.14 (m, 2H), 6.82 (d, 1.1H, *J* = 8.6 Hz), 6.81 (d, 0.9H, *J* = 8.6 Hz), 6.42 (dd, 0.45H, *J* = 9.7, 1.2 Hz), 6.26 (dd, 0.55H, *J* = 10.3, 1.2 Hz), 4.53 (d, 0.45H, *J* = 5.7 Hz), 4.49 (d, 0.55H, *J* = 6.3 Hz), 3.79 (s, 1.35H), 3.79 (s, 1.65H), 2.98—2.87 (m, 1H), 1.57 (d, 1.65H, *J* = 1.2 Hz), 1.55 (d, 1.35H, *J* = 1.2 Hz), 1.07 (d, 1.65H, *J* = 6.3 Hz),

0.99 (d, 1.35H, *J* = 6.3 Hz), 0.01 (s, 4.95H), -0.01 (s, 4.05H); ^{13}C NMR of diastereo mixture (125 MHz, $CDCl_3$): δ 195.6, 195.5, 158.8, 157.0, 156.7, 139.5, 138.8, 135.3, 134.9, 127.5, 127.4, 113.3, 113.3, 78.1, 77.4, 55.2, 42.4, 42.4, 16.7, 15.4, 9.3, 9.3, 0.0; ESI-HRMS m/z: 329.1540 ($[M+Na]^+$); Calcd for $C_{17}H_{26}O_3SiNa$: 329.1543.

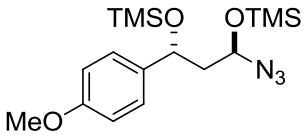
4-(4-Methoxyphenyl)-2,4-bis((trimethylsilyl)oxy)butanenitrile (7a)



TMSCN (95 μL, 0.75 mmol) was used according to the typical procedure B and 4-(4-methoxyphenyl)-2,4-bis((trimethylsilyl)oxy)butanenitrile (**7a**: 46.6 mg, 0.13 mmol) was obtained in 86% yield after 28 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 55:45; IR (ATR) cm^{-1}: 2957, 1612, 1512, 1249, 1173, 1095, 1037; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 7.22 (d, 2H, *J* = 8.6 Hz), 6.87 (d, 2H, *J* = 8.6 Hz), 4.81 (dd, 0.6H, J = 9.2, 4.0 Hz), 4.73 (dd, 0.4H, *J* = 10.0, 3.2 Hz), 4.61 (dd, 0.4H, *J* = 9.7, 3.4 Hz), 4.52 (dd, 0.6H, *J* = 8.6, 5.7 Hz), 3.81 (s, 3H), 2.20—2.11 (m, 1H), 2.06—2.00 (m, 1H), 0.25 (s, 3.6H), 0.20 (s, 5.4H), 0.02 (s, 5.4H), -0.04 (s, 3.6H); ^{13}C NMR of diastereo mixture (125 MHz, $CDCl_3$): δ 159.2, 159.1, 135.5, 135.5, 127.3, 127.1, 120.3, 120.0, 113.8, 113.7, 70.5, 69.8, 59.4, 58.1, 55.2, 76.8, 46.5, 0.2, 0.0, -0.1, -0.3; ESI-HRMS m/z: 374.1572 ($[M+Na]^+$); Calcd for $C_{17}H_{29}NO_3Si_2Na$: 374.1578.

4-Azido-6-(4-methoxyphenyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane (7b)

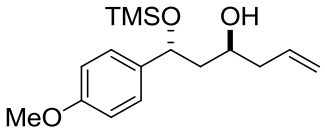


$TMSN_3$ (99 μL, 0.75 mmol) was used according to the typical procedure B and 4-azido-6-(4-methoxyphenyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane (**7b**: 23.0 mg, 0.08 mmol) was obtained in 52% yield after 24 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 67:33; IR (ATR) cm^{-1}: 2957, 2103, 1612, 1512, 1302, 1248, 1172, 1083, 1037; ^{1}H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 7.21 (d, 2H, *J* = 8.6 Hz), 6.87—6.83 (m, 2H), 4.84 (dd, 0.67H, *J* = 8.0, 4.6 Hz), 4.78 (dd, 0.33H, *J* = 8.0, 4.0 Hz), 4.72—4.69 (m, 1H), 3.81 (s, 0.99H), 3.80 (s, 2.01H), 2.12 (ddd, 0.33H, *J* = 13.5, 9.2, 4.0 Hz), 2.05 (ddd, 0.67H, *J* = 13.5, 9.2, 4.6 Hz), 1.93—1.87 (m, 1H), 0.21 (s, 2.97H), 0.18 (s, 7.03H), 0.01 (s, 7.03H), -0.03 (s, 2.97H); ^{13}C NMR of diastereo mixture (125 MHz, $CDCl_3$): δ 159.0,

158.8, 136.3, 136.3, 127.3, 127.0, 113.6, 113.6, 84.5, 84.0, 71.1, 71.0, 55.2, 47.8, 47.5, 0.2, 0.0, -0.0, -0.1; ESI-HRMS m/z: 391.1724 ($[M+H]^+$); Calcd for $C_{16}H_{29}N_3O_3Si_2$: 391.1718.

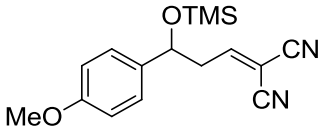
1-(4-Methoxyphenyl)-1-((trimethylsilyl)oxy)hex-5-en-3-ol (7c)



AllylBpin (50 μL, 0.30 mmol) was used according to the typical procedure B and 1-(4-methoxyphenyl)-1-((trimethylsilyl)oxy)hex-5-en-3-ol (**7c**: 40.0 mg, 0.14 mmol) was obtained in 94% yield after 6 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 64:36; IR (ATR) cm^{-1}: 3439, 2954, 2909, 2836, 1640, 1612, 1586, 1511, 1463, 1441, 1366, 1301, 1247, 1173, 1068; ^1H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 7.23 (d, 2H, *J* = 8.6 Hz), 7.22 (d, 2H, *J* = 8.6 Hz), 5.87—5.74 (m, 1H), 5.09—5.06 (m, 2H), 5.02 (dd, 0.64H, *J* = 4.0, 2.9 Hz), 4.83 (dd, 0.36H, *J* = 9.7, 4.0 Hz), 3.88—3.77 (m, 1H), 3.80 (s, 3H), 3.02 (d, 0.64H, *J* = 2.9 Hz), 2.28—2.16 (m, 2H), 1.88—1.69 (m, 2H), 1.62—1.59 (m, 2H), 0.05 (s, 5.76H), -0.01 (s, 3.24H); ^{13}C NMR of diastereo mixture (125 MHz, $CDCl_3$): δ 158.6, 136.4, 134.9, 134.7, 127.3, 126.8, 117.5, 117.4, 113.6, 113.5, 72.4, 67.5, 55.2, 46.0, 45.7, 42.1, 0.1, -0.1; ESI-HRMS m/z: 317.1533 ($[M+Na]^+$); Calcd for $C_{16}H_{26}O_3Si$: 317.1543.

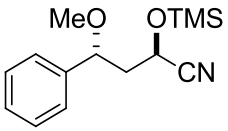
2-(3-(4-Methoxyphenyl)-3-((trimethylsilyl)oxy)propylidene)malononitrile (7d)



Malononitorile (56.1 mg, 0.75 mmol) was used according to the typical procedure B and 2-(3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)propylidene)malononitrile (**7d**: 33.8 mg, 0.12 mmol) was obtained in 77% yield after 12 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Yellow oil; IR (ATR) cm^{-1}: 2957, 2238, 1611, 1586, 1512, 1464, 1442, 1363, 1302, 1248, 1173, 1083, 1034; ^1H NMR (500 MHz, $CDCl_3$): δ 7.33 (t, 1H, *J* = 8.0 Hz), 7.20 (d, 2H, *J* = 8.6 Hz), 6.88 (d, 2H, *J* = 8.6 Hz), 4.87 (t, 1H, *J* = 5.4 Hz), 3.82 (s, 3H), 2.94—2.91 (m, 2H), 0.05 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.3, 159.4, 134.2, 126.6, 114.0, 112.1, 110.6, 91.1, 72.0, 55.3, 43.5, -0.1; ESI-HRMS m/z: 323.1183 ($[M+Na]^+$); Calcd for $C_{16}H_{20}N_2O_2SiNa$: 323.1186.

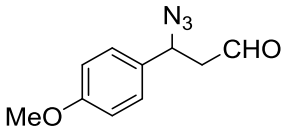
4-Methoxy-4-phenyl-2-((trimethylsilyl)oxy)butanenitrile (9)



Benzaldehyde dimethyl acetal (**8**: 22.8 mL, 0.15 mmol) was stirred with 2,2'-bipyridyl (71.9 mg, 0.45 mmol) and TMSOTf (55μL, 0.30 mmol) in CH_2Cl_2 (0.75 mL) at 0 ^oC for 30 min., and then trimethyl(vinyloxy)silane (**2a**: 0.30 mmol) was added to the reaction mixture at 0 ^oC for 2 h. Then, TMSCN (96 μL, 0.75 mmol) was added at 0 ^oC. After stirring for 24 h, 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 purification of the residue by silica-gel column chromatography (Hex/EtOAc = 10/1) to give 4-methoxy-4-phenyl-2-((trimethylsilyl)oxy)butanenitrile (**9**: 32.0 mg, 0.13 mmol).

Colorless oil; *anti*:*syn* = 60:40; IR (ATR) cm^{-1}: 2960, 2825, 1494, 1455, 1359, 1255, 1182, 1109, 1067, 1034, 1016; ^1H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 7.39―7.36 (m, 2H), 7.32―7.28 (m, 3H), 4.73 (dd, 0.4H, *J* = 10.0, 4.0 Hz), 4.62 (dd, 0.6H, *J* = 8.6, 6.3 Hz), 4.35 (dd, 0.6H, *J* = 9.7, 4.6 Hz), 4.24 (dd, 0.4H, *J* = 9.7, 3.4 Hz), 3.21 (s, 1.8H), 3.17 (s, 1.2H), 2.29―2.23 (m, 0.6H), 2.17―2.02 (m, 1.4H), 0.26 (s, 3.6H), 0.23 (s, 5.4); ^{13}C NMR of diastereo mixture (125 MHz, $CDCl_3$): δ 140.45, 140.2, 128.7, 128.2, 128. 1, 126.6, 126.5, 120.3, 119.9, 79.7, 78.0, 59.4, 57.8, 56.7, 56.5, 44.6, 44.4, -0.3, -0.5; ESI-HRMS m/z: 286.1239 ($[M+Na]^+$); Calcd for $C_{14}H_{21}NO_2SiNa$: 286.1234.

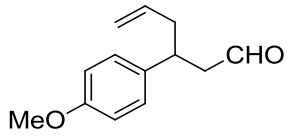
3-Azido-3-(4-methoxyphenyl)propanal (11a)



$TMSN_3$ (15 μL, 0.165 mmol) and $FeBr_3$ (2.6 mg, 10 mol%) were used according to typical procedure C and 3-azido-3-(4-methoxyphenyl)propanal (**11a**: 18.3 mg, 0.9 mmol) was obtained in 88% yield after 0.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 5/1).

Colorless oil; IR (ATR) cm^{-1}: 2936, 2838, 2095, 1722, 1670, 1603, 1513, 1463, 1306, 1249, 1177, 1128, 1031; ^1H NMR (500 MHz, $CDCl_3$): δ 9.75 (brs, 1H), 7.26 (d, 2H, *J* = 8.9 Hz), 6.92 (d, 2H, *J* = 8.9 Hz), 5.02 (dd, 1H, *J* = 8.6, 5.2 Hz), 3.81 (s, 3H), 2.96 (ddd, 1H, *J* = 18.1, 8.6, 1.7 Hz), 2.78 (dd, 1H, *J* = 18.1, 5.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 198.9, 159.8, 130.0, 128.1, 114.3, 59.6, 55.3, 49.5; ESI-HRMS m/z: 206.0924 ($[M+H]^+$); Calcd for $C_{10}H_{11}N_3O_2$: 206.0924.

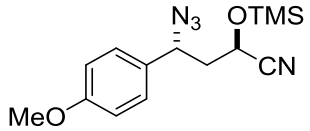
3-(4-Methoxyphenyl)hex-5-enal (11b)



AllylTMS (48 μL, 0.30 mmol) and $FeCl_3$ (1.6 mg, 5 mol%) were used according to the typical procedure C and 3-(4-methoxyphenyl)hex-5-enal (**11b**: 28.2 mg, 0.10 mmol) was obtained in 69% yield after 1 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; IR (ATR) cm^{-1}: 2911, 2836, 1721, 1639, 1611, 1512, 1464, 1442, 1417, 1301, 1247, 1179, 1107, 1034; ^1H NMR (500 MHz, $CDCl_3$): δ 9.66 (brs, 1H), 7.11 (d, 2H, *J* = 8.6 Hz), 6.84 (d, 2H, *J* = 8.6 Hz), 5.70—5.61 (m, 1H), 5.03—4.99 (m, 2H), 3.78 (s, 3H), 3.28—3.22 (m, 1H), 2.75 (ddd, 1H, *J* = 16.6, 6.3, 1.7 Hz), 2.68 (ddd, 1H, *J* = 16.6, 8.3, 1.7 Hz), 2.42—2.32 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 202.0, 158.2, 135.8, 135.3, 128.3, 117.1, 114.0, 55.2, 49.5, 41.1, 39.0; ESI-HRMS m/z: 227.1041 ($[M+Na]^+$); Calcd for $C_{13}H_{16}O_2Na$: 227.1043.

4-Azido-4-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)butanenitrile (11c)

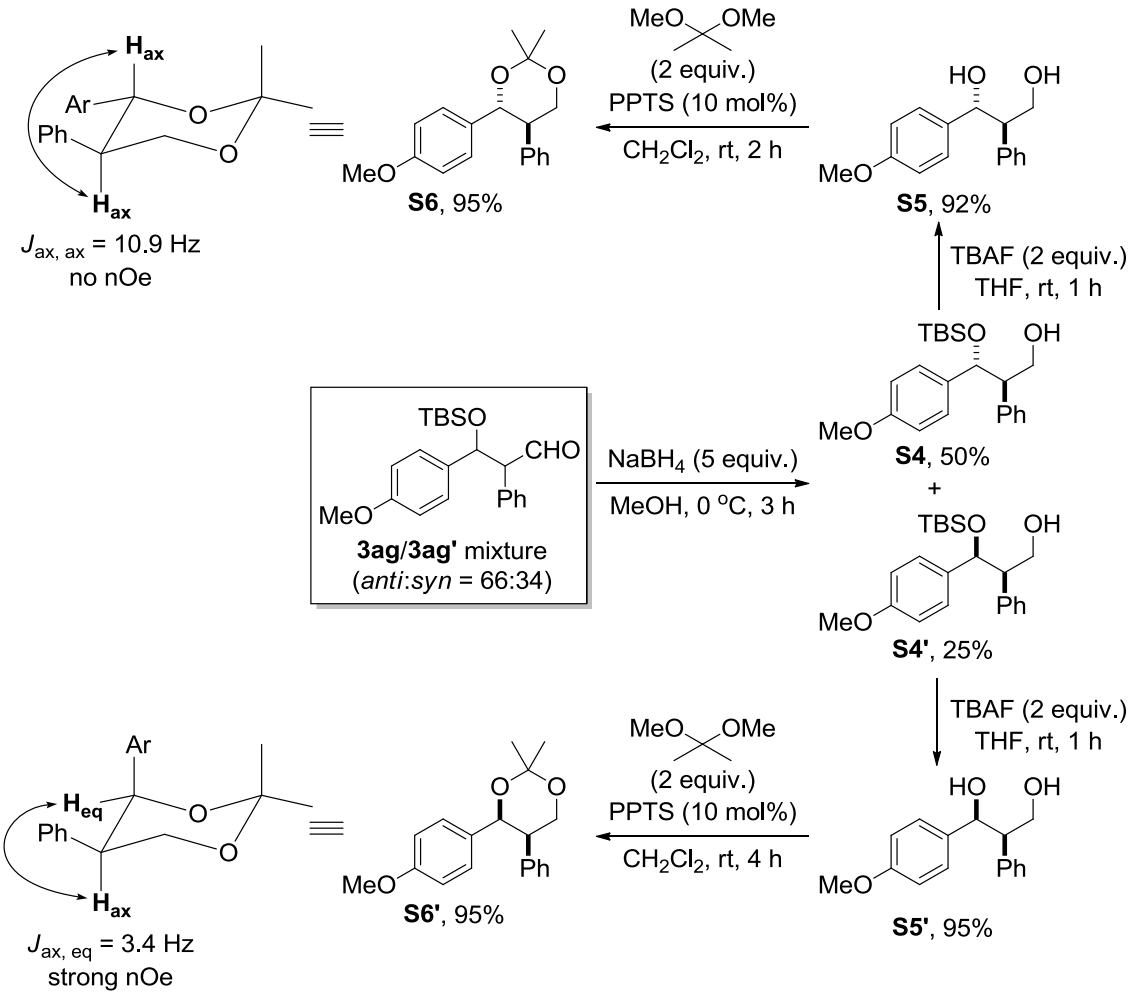


$TMSN_3$ (22 μL, 0.165 mmol) and $FeBr_3$ (4.4 mg, 10 mol%) were used according to the typical procedure C and 4-azido-4-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)butanenitrile (**11c**: 37.1 mg, 0.12 mmol) was obtained in 79% yield after 0.5 h stirring and purification by silica-gel column chromatography (Hex/EtOAc = 10/1).

Colorless oil; *anti*:*syn* = 63:37; IR (ATR) cm^{-1}: 2959, 2097, 1612, 1513, 1464, 1305, 1251, 1177, 1109, 1032; ^1H NMR of diastereo mixture (500 MHz, $CDCl_3$): δ 7.26—7.22 (m, 2H), 6.95—6.92 (m, 2H), 4.64—4.58 (m, 1.63H), 4.38 (dd, 0.37H, *J* = 6.9, 6.9 Hz), 3.83 (s, 3H), 2.33—2.27 (m, 0.37H), 2.16—2.10 (m, 1.63H), 0.27 (s, 5.67H), 0.19 (s, 3.33H); ^{13}C NMR of diastereo mixture (125 MHz, $CDCl_3$): δ 160.0, 159.9, 129.9, 129.3, 128.4, 128.2, 119.6, 119.4, 114.5, 114.4, 61.4, 60.8, 59.0, 58.1, 55.3, 42.3, 42.1, -0.4, -0.5; ESI-HRMS m/z: 327.1248 ($[M+Na]^+$); Calcd for $C_{14}H_{20}N_4O_2SiNa$: 327.1248.

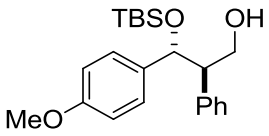
8. Consideration of stereochemistry.

8-1. Modification of 3ag and 3ag'[13]



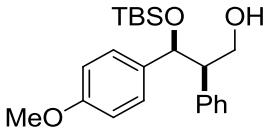
Step 1: To a solution of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag/3ag' mixture**: 120.0 mg, 0.30 mmol) in MeOH (3 mL) was added $NaBH_4$ (56.7 mg, 1.5 mmol) at 0 °C. After stirring for 3 h, the reaction mixture was extracted with CH_2Cl_2 (5 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 10/1) to give (*2R,3R*)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (**S4**; 56.0 mg, 0.15 mmol, 50% yield) and (*2R,3S*)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (**S4'**; 27.4 mg, 0.07 mmol, 25% yield), respectively.

(*2R,3R*)-3-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (S4)



Colorless oil; IR (ATR) cm^{-1}: 3441, 2953, 2929, 2856, 1612, 1510, 1463, 1361, 1302, 1246, 1172, 1065, 1033, 1004; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.21—7.13 (m, 3H), 7.03—6.99 (m, 4H), 6.71 (d, 2H, *J* = 9.2 Hz), 4.86 (d, 1H, *J* = 8.0 Hz), 4.17 (dd, 1H, *J* = 10.9, 6.9 Hz), 3.93—3.91 (m, 1H), 3.74 (s, 3H), 3.11—3.07 (m, 1H), 2.95 (brs, 1H), 0.90 (s, 9H), -0.04 (s, 3H), -0.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 139.7, 135.1, 128.6, 128.2, 127.7, 126.6, 113.1, 80.2, 65.3, 56.5, 55.0, 25.8, 18.0, -4.6, -5.3; ESI-HRMS m/z: 395.2031 ($[M+Na]^+$); Calcd for $C_{22}H_{32}O_3SiNa$: 395.2013.

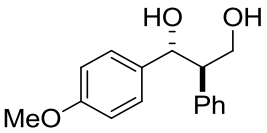
(*2R,3S*)-3-((*tert*-Butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (S4')



Colorless oil; IR (ATR) cm^{-1}: 3433, 2953, 2928, 2855, 1611, 1510, 1462, 1360, 1302, 1245, 1172, 1111, 1081, 1033, 1004; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.26—7.20 (m, 3H), 7.06 (dd, 2H, *J* = 7.7, 1.7 Hz), 6.99 (d, 2H, *J* = 8.6 Hz), 6.76 (d, 2H, *J* = 8.6 Hz), 4.90 (d, 1H, *J* = 5.7 Hz), 3.87 (dd, 1H, *J* = 10.6, 6.9 Hz), 3.78 (s, 3H), 3.76 (dd, 1H, *J* = 10.6, 6.9 Hz), 3.12 (dt, 1H, *J* = 6.9, 5.7 Hz), 1.95 (brs, 1H), 0.79 (s, 9H), -0.11 (s, 3H), -0.28 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.7, 139.1, 134.3, 129.3, 128.0, 127.9, 126.8, 113.0, 76.9, 63.7, 56.3, 55.1, 25.7, 18.0, -4.8, -5.5; ESI-HRMS m/z: 395.2019 ($[M+Na]^+$); Calcd for $C_{22}H_{32}O_3SiNa$: 395.2013.

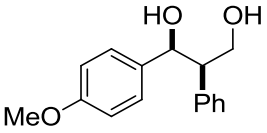
Step 2: To a solution of **S4** (56.0 mg, 0.15 mmol) in THF (1.5 mL) was added 1.0 M THF solution of TBAF (300 μL, 0.3 mmol) at room temperature. After stirring for 1 h, the reaction mixture was quenched with sat. NH_4Cl aq. (3 mL) and extracted with EtOAc (5 mL × 3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (Hex/EtOAc = 1/1) to give (*1R,2R*)-1-(4-methoxyphenyl)-2-phenylpropane-1,3-diol (**S5**; 33.1 mg, 0.13 mmol) in 92%.
S4' (27.4 mg, 0.07 mmol) was used as a substrate and (*1S,2R*)-1-(4-methoxyphenyl)-2-phenylpropane-1,3-diol (**S5'**: 17.2 mg, 0.07 mmol) was obtained in 95% in the above operation.

(*1R,2R*)-1-(4-Methoxyphenyl)-2-phenylpropane-1,3-diol (S5)



Colorless oil; IR (ATR) cm^{-1}: 3345, 2903, 1611, 1511, 1453, 1303, 1245, 1175, 1062, 1031; ^1H NMR (500 MHz, $CDCl_3$): δ 7.18―7.11 (m, 3H), 7.04 (d, 2H, *J* = 8.6 Hz), 6.97 (d, 2H, *J* = 6.9 Hz), 6.71 (d, 2H, *J* = 8.6 Hz), 4.95 (d, 1H, *J* = 9.1 Hz), 4.16 (dd, 1H, *J* = 10.9, 8.0 Hz), 3.91 (brd, 1H, *J* = 8.6 Hz), 3.72 (s, 3H), 3.35 (brs, 2H), 3.11 (ddd, 1H, *J* = 9.1, 8.6, 4.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.8, 139.2, 134.9, 128.4, 128.3, 127.7, 126.7, 113.4, 79.3, 66.6, 55.1, 54.7; ESI-HRMS m/z: 281.1157 ($[M+Na]^+$); Calcd for $C_{16}H_{18}O_3Na$: 281.1148.

(*1S*,*2R*)-1-(4-Methoxyphenyl)-2-phenylpropane-1,3-diol (S5')

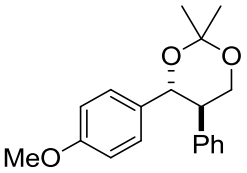


Colorless oil; IR (ATR) cm^{-1}: 3371, 2931, 1611, 1511, 1453, 1302, 1244, 1175, 1030; ^1H NMR (500 MHz, $CDCl_3$): δ 7.34 (dd, 2H, *J* = 7.5, 6.9 Hz), 7.29―7.27 (m, 1H), 7.23 (d, 2H, *J* = 6.9 Hz), 7.19 (d, 2H, *J* = 8.6 Hz), 6.85 (d, 2H, *J* = 8.6 Hz), 4.96 (d, 1H, *J* = 7.2 Hz), 3.80 (s, 3H), 3.75―3.73 (m, 2H), 3.14 (dt, 1H, *J* = 7.2 6.9 Hz), 2.18 (brs, 1H), 1.64 (brs, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.2, 138.7, 133.9, 129.0, 128.7, 127.8, 127.3, 113.7, 75.4, 64.1, 55.7, 55.2; ESI-HRMS m/z: 281.1157 ($[M+Na]^+$); Calcd for $C_{16}H_{18}O_3Na$: 281.1148.

Step 3: To a solution of **S5** (33.1 mg, 0.13 mmol) in CH_2Cl_2 (1.5 mL) was added 2,2-dimethoxypropane (37 μL, 0.3 mmol) and PPTS (3.8 mg, 0.013 mmol) at room temperature. After stirring for 2 h, the reaction mixture was quenched with sat. $NaHCO_3$ aq. (3 mL) and extracted with CH_2Cl_2 (5 mL × 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 = 20/4/1) to give (*4R*,*5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6**; 36.9 mg, 0.12 mmol) in 95%.

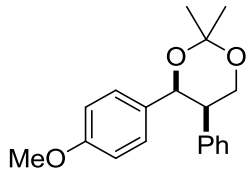
S5' (17.2 mg, 0.07 mmol) was used as a substrate and (*4S*,*5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6'**: 19.8 mg, 0.07 mmol) was obtained in 95% in the above operation.

(*4R*,*5R*)-4-(4-Methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (S6)



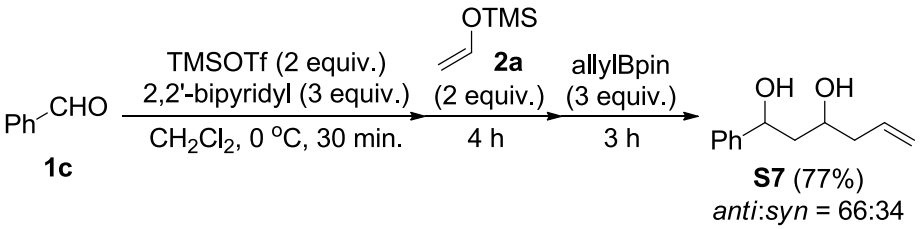
Colorless oil; IR (ATR) cm^{-1}: 2992, 1613, 1513, 1454, 1379, 1293, 1246, 1225, 1195, 1160, 1102, 1027; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.23—7.19 (m, 2H), 7.18—7.15 (m, 1H), 7.09 (d, 2H, *J* = 8.6 Hz), 7.04 (d, 2H, *J* = 8.6 Hz), 6.72 (d, 2H, *J* = 8.6 Hz), 4.99 (d, 1H, *J* = 10.9 Hz), 4.22 (dd, 1H, *J* = 11.5, 11.5 Hz), 3.98 (dd, 1H, *J* = 11.5, 5.2 Hz), 3.72 (s, 3H), 3.07 (ddd, 1H, *J* = 11.5, 10.9, 5.2 Hz), 1.72 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.0, 138.0, 132.2, 128.4, 128.2, 126.9, 113.4, 98.8, 76.5, 65.4, 55.1, 49.1, 29.8, 19.3; ESI-HRMS m/z: 321.1462 ($[M+Na]^+$); Calcd for $C_{19}H_{22}O_3Na$: 321.1461.

(*4S,5R*)-4-(4-Methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (S6')



Colorless oil; IR (ATR) cm^{-1}: 2991, 1613, 1513, 1453, 1380, 1302, 1246, 1195, 1161, 1098, 1034, 1019; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.28—7.26 (m, 2H), 7.13—7.11 (m, 3H), 6.93 (d, 2H, *J* = 8.6 Hz), 6.66 (d, 2H, *J* = 8.6 Hz), 5.38 (d, 1H, *J* = 3.4 Hz), 4.57 (dd, 1H, *J* = 11.8, 3.4 Hz), 4.10 (dd, 1H, *J* = 11.8, 1.2 Hz), 3.71 (s, 3H), 2.78 (dd, 1H, *J* = 3.4, 3.4 Hz), 1.67 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.3, 139.9, 132.5, 129.9, 127.5, 127.1, 126.1, 113.0, 99.4, 73.2, 65.3, 55.1, 45.6, 29.7, 18.9; ESI-HRMS m/z: 321.1465 ($[M+Na]^+$); Calcd for $C_{19}H_{22}O_3Na$: 321.1461.

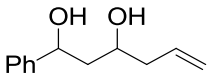
8-2. Consideration of stereochemistry of 1,3-diol (6a-6c, 8 and 10c; Scheme 3, 4 and 5)



After benzaldehyde (**1c**: 16.0 mg, 0.15 mmol) was treated with 2,2'-bipyridyl (71.9 mg, 0.45 mmol) and TMSOTf (55 μL, 0.30 mmol) in CH_2Cl_2 (0.75 mL) at 0 °C for 30 min., trimethyl(vilyloxy)silane (**2a**: 44 μL, 0.30 mmol) was added to the reaction mixture at 0 °C for 4 h. Then, allylBpin (86 μL, 0.45 mmol) was added at 0 °C. After stirring for 3 h, 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 (Hex/EtOAc = 6/1) to give the diastereomixture of 1-phenylhex-5-ene-1,3-diol (**S7**: 22.2 mg, 0.12 mmol).

The streochemistry of *syn*- and *anti*-**S7** has been already reported in the literature [14] and the diastereo ratio can be determined by ^{1}H NMR analysis. According to these results, the *anti*-isomer was preferentially obtianed in our method.

1-Phenylhex-5-ene-1,3-diol (S7)[14]



Colorless oil; *anti*:*syn* = 66:34; ^{1}H NMR of the diastereo mixture (500 MHz, $CDCl_3$): δ 7.37—7.33 (m, 4H), 7.29—7.25 (m, 1H), 5.83—5.74 (m, 1H), 5.15—5.10 (m, 2H), 5.05 (dd, 0.66H, *J* = 8.0, 3.4 Hz), 4.93 (dd, 0.34H, *J* = 9.5, 3.4 Hz), 3.99—3.97 (m, 0.34H), 3.94—3.89 (m, 0.66H), 2.78 (brs, 2H), 2.31—2.22 (m, 2H), 1.95—1.78 (m, 2H).

Spectroscopic date of ^{1}H NMR was identical to that of reference [14].

9. NMR study to detecte the pyridinium salts.

General procedure of NMR study

NMR experimets were performed in dry CD_2Cl_2 using a flame-dried NMR tube under argon.

An aldehyde **1** (0.075 mmol) was treated with the pyridine derivative (0.225 mmol) and TMSOTf (27 μL, 0.15 mmol) in CD_2Cl_2 (1.0 mL) at 0 ^oC for 30 min. (see NMR Charts J, M, P, Q, R and S) and the trimethyl(vinyloxy)silane **2a** (22 μL, 0.15 mmol) was added at 0 ^oC (see NMR Charts D, G, I and N).

After stirring for the adequate time, the mixture was quenched with sat. $NaHCO_3$ aq. (1.0 mL). CD_2Cl_2 layer was used for the NMR analysis (see NMR Charts E, H, K, O and T).

[1,1,2,2-Tetrachloroethane (10 μL, 0.095 mmol; 6.04 ppm in CD_2Cl_2) was added as an internal standard.]

Figure S1. The proton peak of aldehyde (9.87 ppm, **1a**) disappeared and the peaks corresponding to *N*,*O*-acetal (6.56/6.84 ppm, **B**) were observed (Chart D). **B** was worked up with H_2O to give the desired **3aa** (9.76 ppm for the aldehyde peak, Chart E).

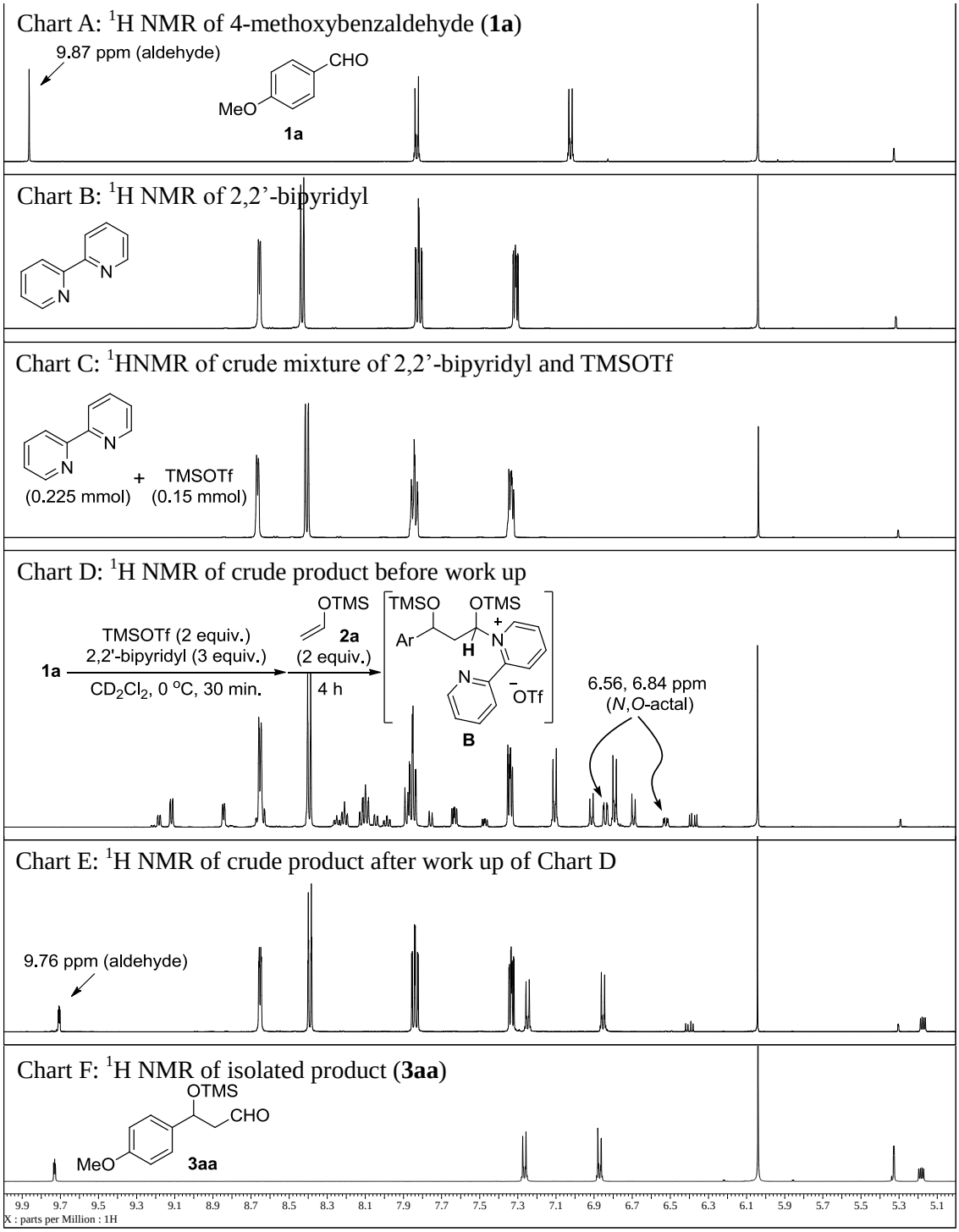


Figure S2. The carbon peak of aldehyde [201.6 ppm, **1a**] could not be observed and the peaks

of *N*,*O*-acetal [89.8/89.1 ppm] were confirmed (Chart G). After work up with H_2O of B, the peaks of *N*,*O*-acetal disappeared and aldehyde peak (201.6 ppm) was observed (Chart H).

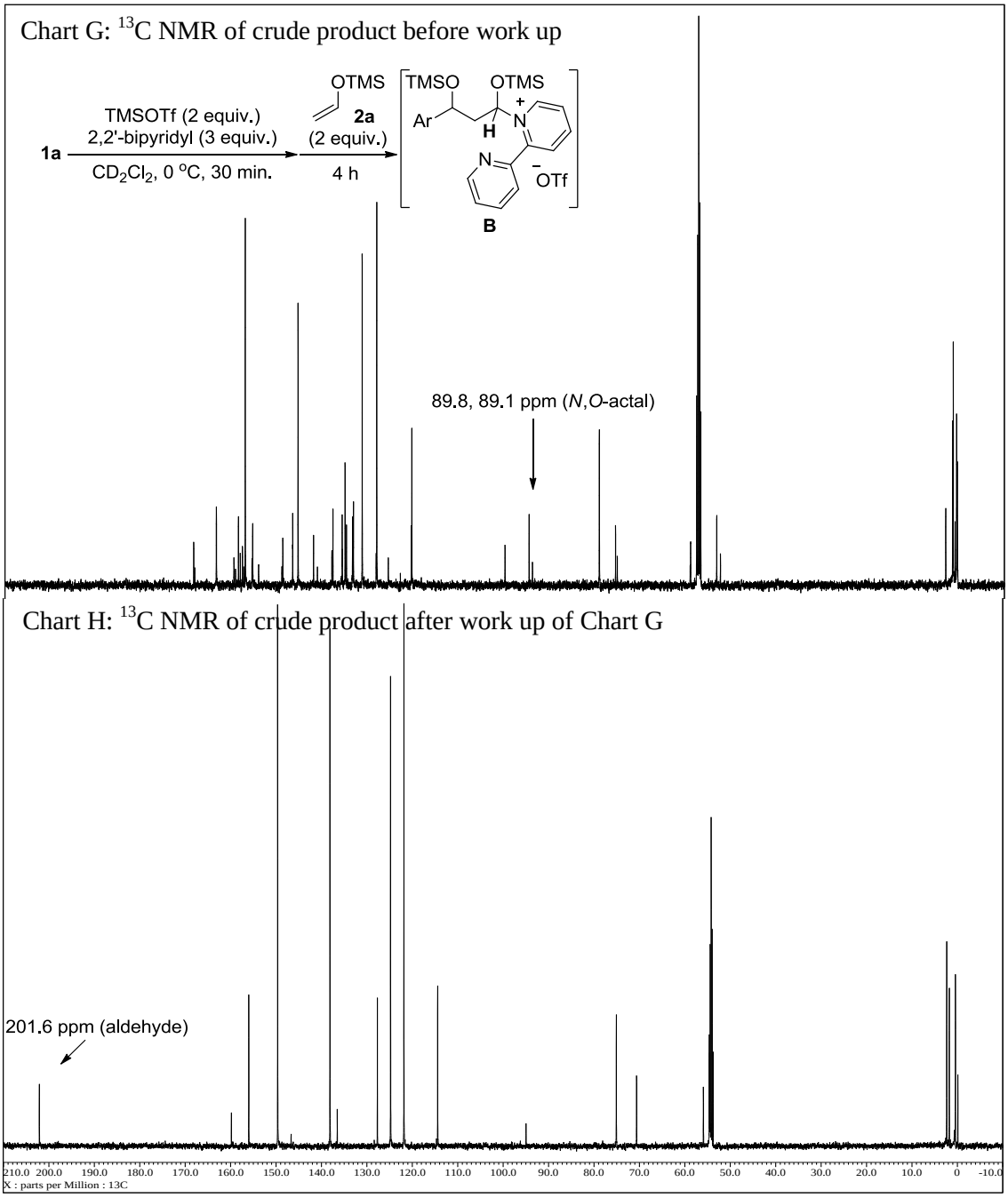


Figure S3. HMQC of pyridinium salt intermediate **B**.

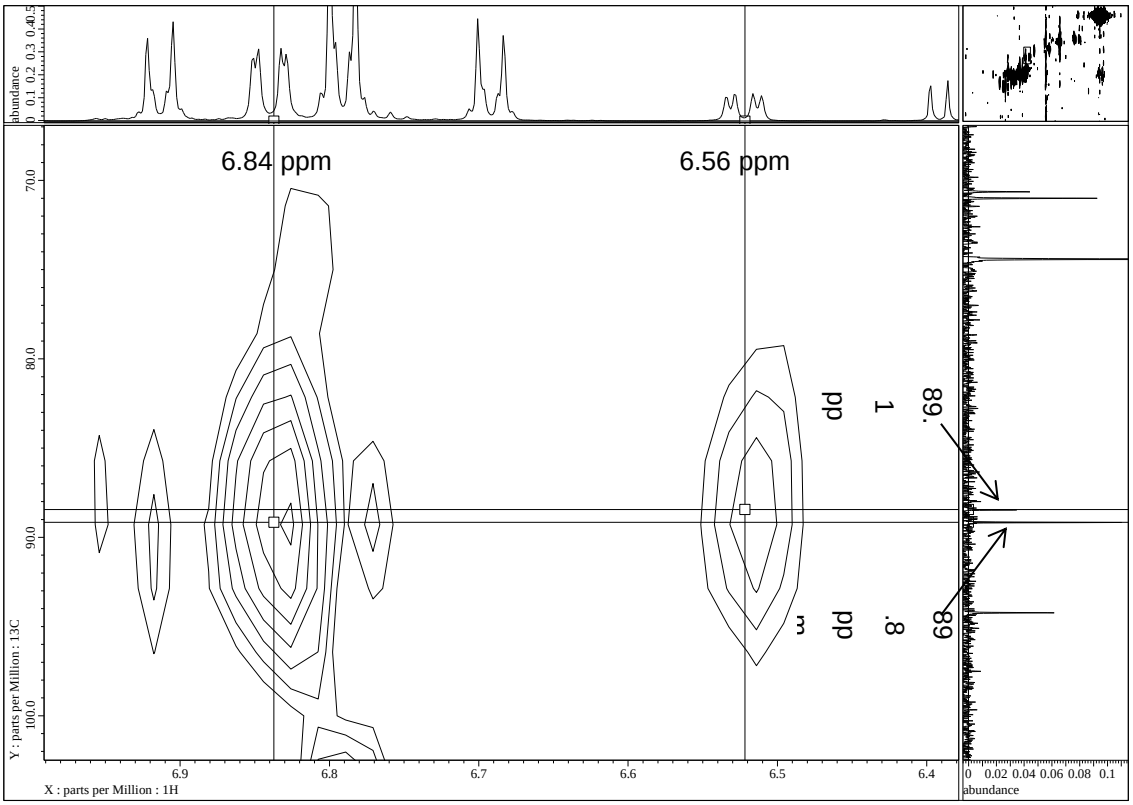


Figure S4. After the isolated product **3aa** was treated with TMSOTf and 2,2'-bipyridyl, ^{1}H NMR of crude mixture was measured. The obtained ^{1}H NMR spectra of Chart J was similar to that of Chart D. As shown in Chart K, **3aa** was regenerated by work up with H_2O (9.76 ppm for the aldehyde peak). Based on these results, the product **3** can be intermediate.

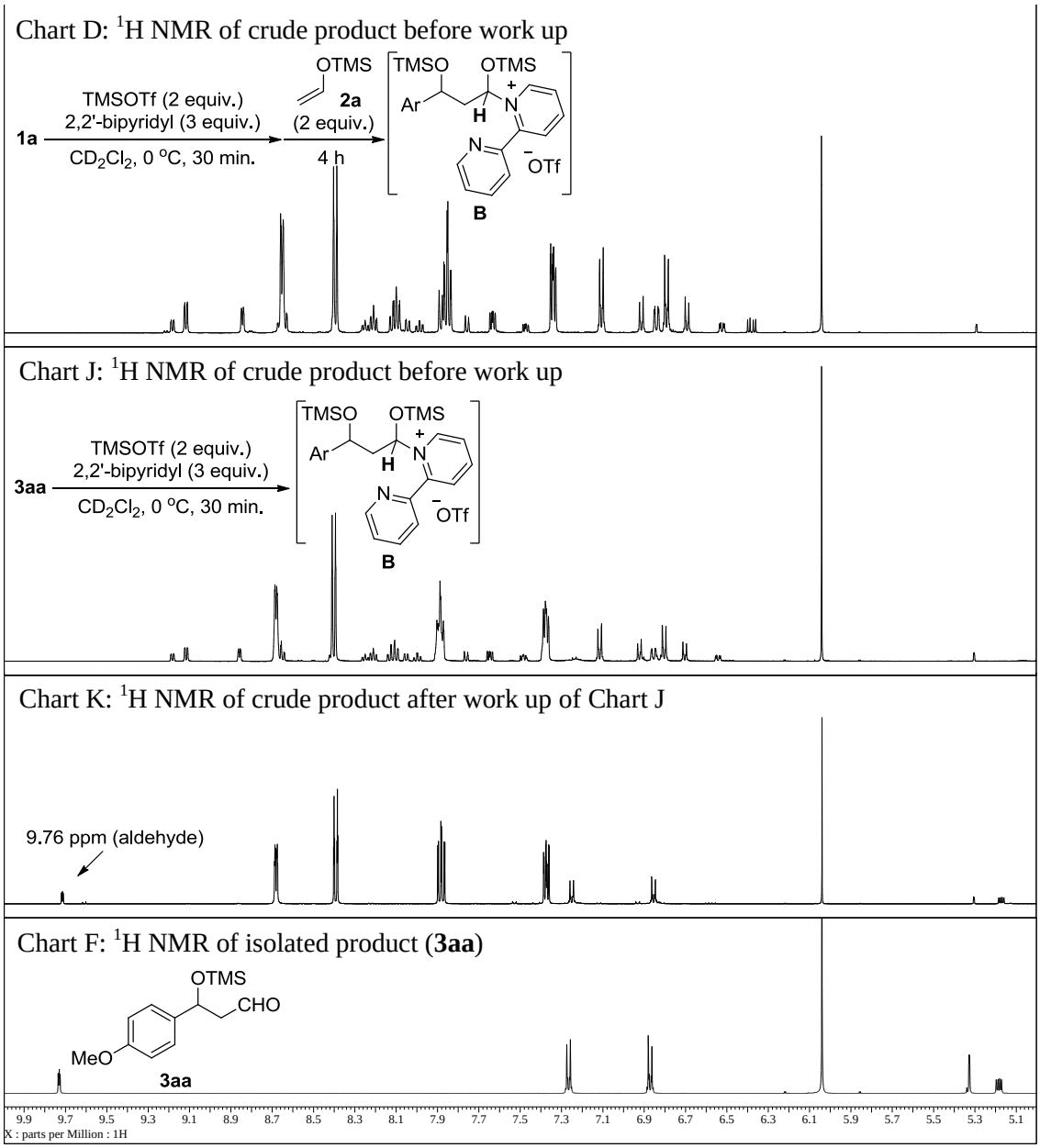


Figure S5. An aliphatic aldehyde **1'a** was transformed to intermediate **C** by TMSOTf and 2,2'-bipyridyl (Chart M). **C** was inert toward nucleophilic reaction of **2a** and the structure of *N,O*-acetal (Chart N) remained unchanged. **1'a** was reproduced after work up with H_2O (Chart M).

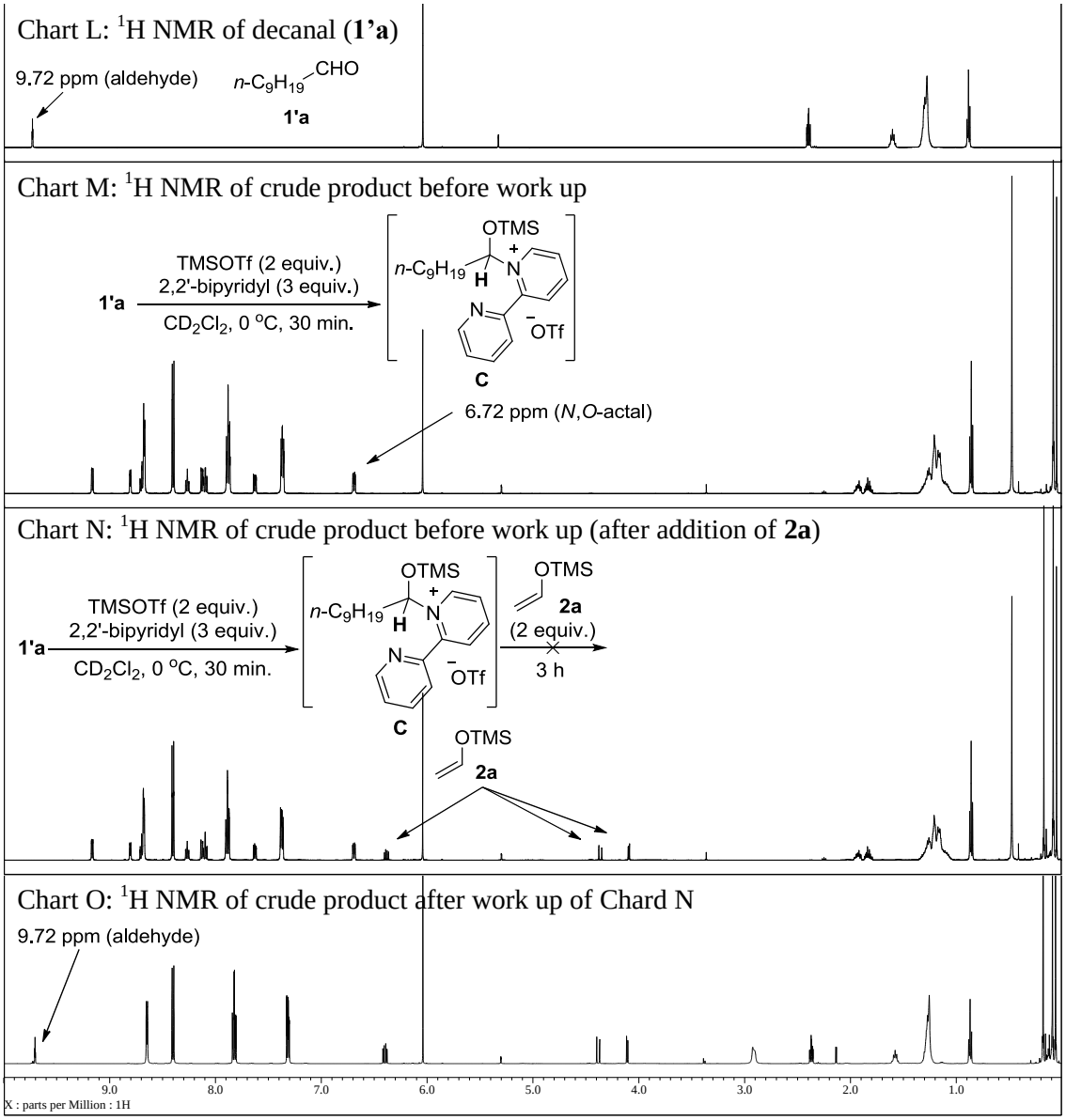


Figure S6. When aromatic aldehyde **1a** was treated with TMSOTf and 2,2'-bipyridyl, the proton peak of aldehyde (9.87 ppm, **1a**) disappeared and the peak corresponding to *N*,*O*-acetal (7.70 ppm, **B**) appeared (Chart P). However, the Chart P was unclear. The spectra of the pyridinium salt **A'** derived from 2-phenylpyridine instead of 2,2'-bipyridyl was also obscure (Chart Q). On the other hand, the pyridinium salt **A"** derived from pyridine showed a clear spectra (Chart R).

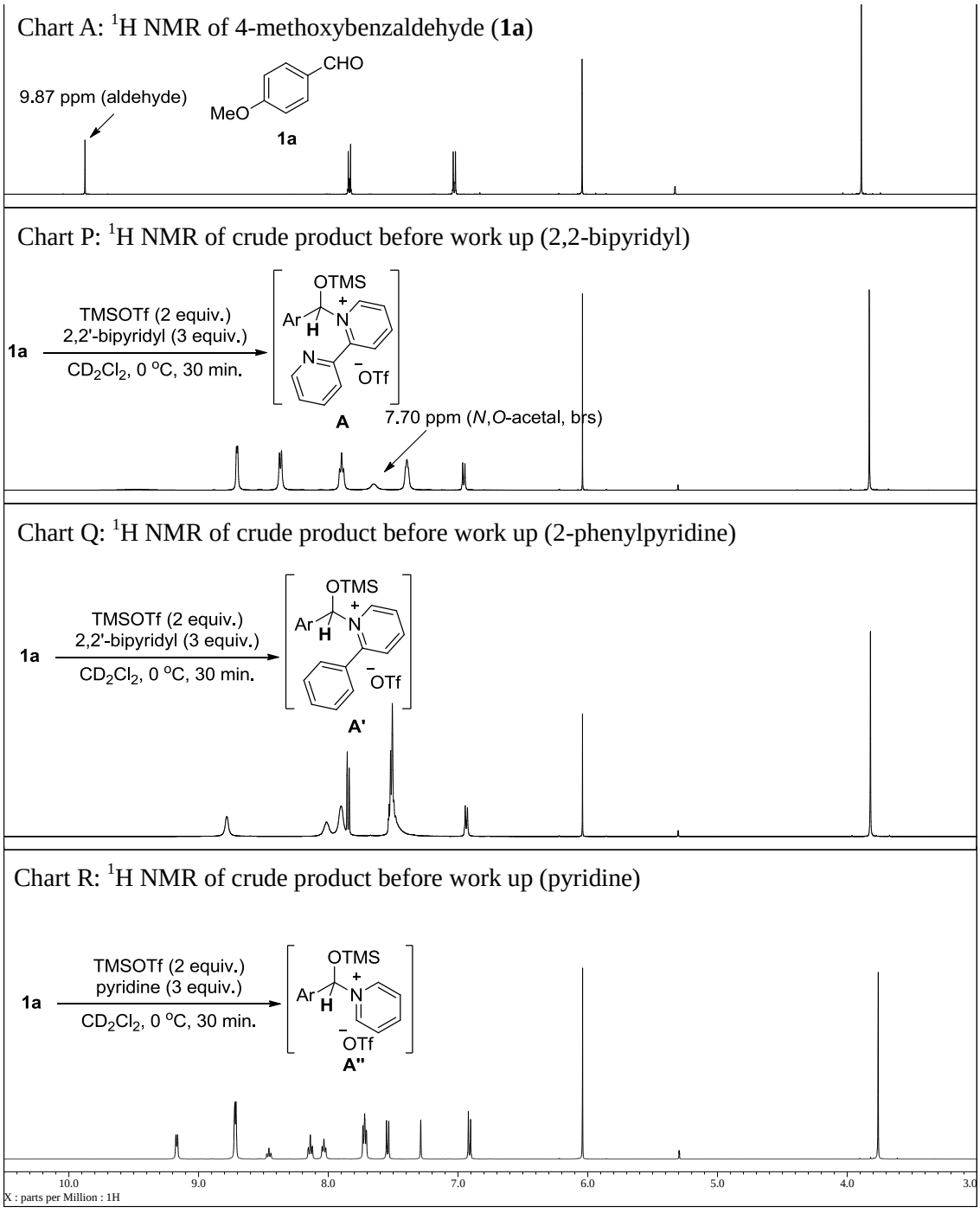


Figure S7. When benzaldehyde **1c** was treated with TMSOTf and 2,2'-bipyridyl, the carbon peak of aldehyde (196.2 ppm, **1c**) could not be observed, but the peak derived from *N*,*O*-actal did not appeared (Chart S). After work up with H_2O of **A'''**, the aldehyde peak (196.2 ppm) appeared (Chart T).

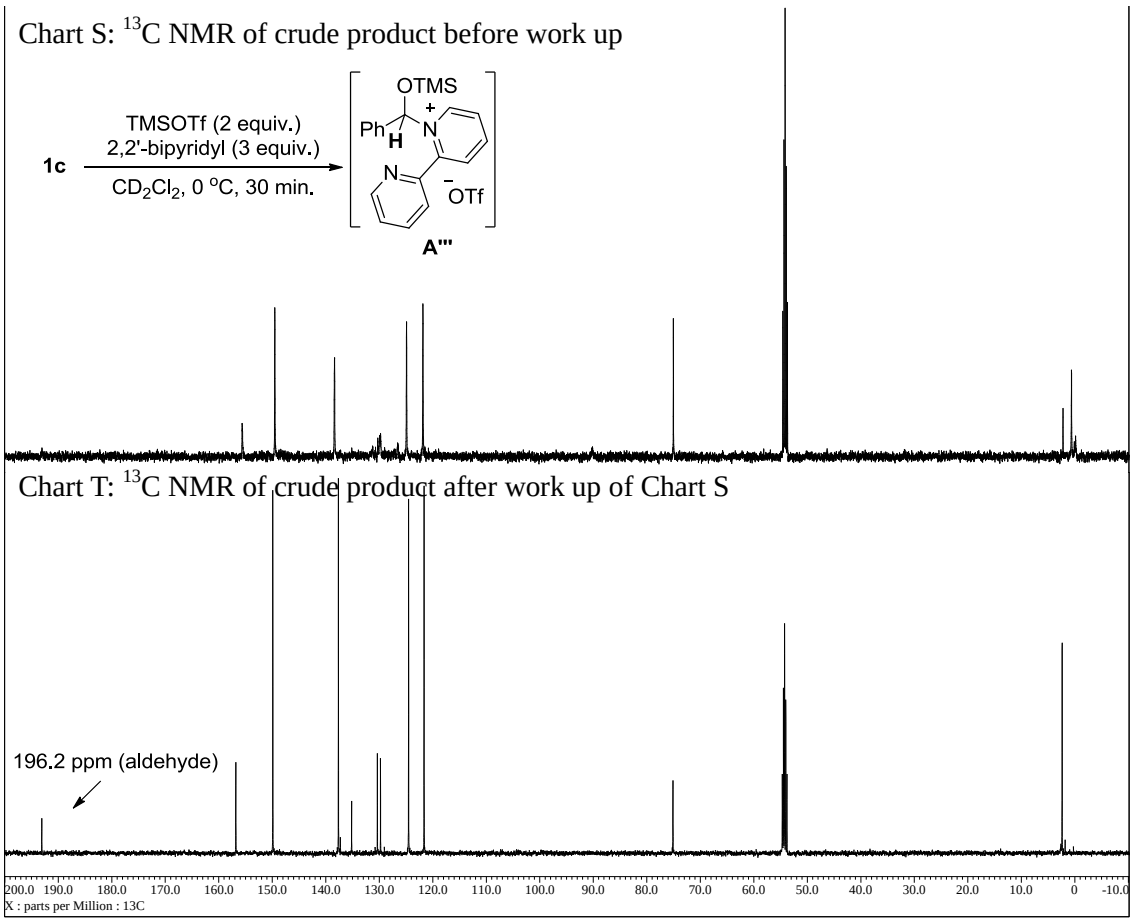


Chart D: ^{1}H NMR of crude product before work up

major	minor
g. 9.12 (1H, dd, *J* = 7.5, 1.2 Hz)	g. 9.19 (1H, dd, *J* = 7.0, 1.2 Hz)
k. 8.85 (1H, d, *J* = 4.6 Hz)	k. 8.70-8.63 (1H, overlapping)
i. 8.70-8.63 (1H, overlapping)	m. 8.40-8.39 (1H, overlapping)
m. 8.21 (1H, dt, *J* = 8.0, 1.2 Hz)	i. 8.25 (1H, dt, *J* = 7.7, 1.2 Hz)
h. 8.12 (1H, dt, *J* = 7.5, 1.7 Hz)	j. 8.05 (1H, dd, *J* = 7.7, 1.2 Hz)
j. 8.09 (1H, dd, *J* = 7.7, 1.7 Hz)	h. 7.99 (1H, dt, *J* = 7.0, 1.7 Hz)
n. 7.89 (1H, d, *J* = 8.0 Hz)	n. 7.76 (1H, d, *J* = 8.0 Hz)
l. 7.65-7.62 (1H, m)	l. 7.49-7.46 (1H, m)
c. 7.11 (2H, d, *J* = 8.6 Hz)	c. 6.91 (2H, d, *J* = 8.6 Hz)
f. 6.84 (1H, dd, *J* = 9.2, 1.7 Hz)	b. 6.69 (2H, d, *J* = 8.6 Hz)
b. 6.79 (2H, d, *J* = 8.6 Hz)	f. 6.56 (1H, dd, *J* = 8.6, 2.9 Hz)
d. 4.69 (1H, dd, *J* = 10.0, 2.0 Hz)	d. 4.69-4.66 (1H, m)
a. 3.73 (3H, s)	a. 3.77 (3H, s)
e. 2.42 (1H, ddd, *J* = 13.6, 10.0, 1.7 Hz)	e. 2.40-2.36 (1H, overlapping)
e. 1.98 (1H, ddd, *J* = 13.6, 9.2, 2.0 Hz)	e. 2.28 (1H, ddd, *J* = 13.8, 9.2, 2.9 Hz)

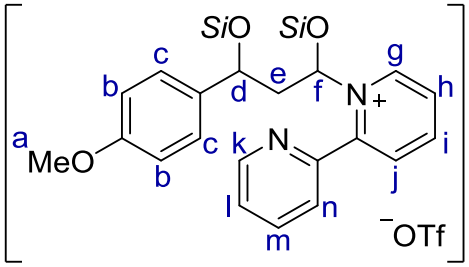


Chart L: ^{1}H NMR of crude product before work up

a. 9.17 (1H, dd, *J* = 7.5, 1.2 Hz)
h. 8.81 (1H, dd, *J* = 8.0, 1.7 Hz)
c. 8.70 (1H, dt, *J* = 7.5, 1.2 Hz)
f. 8.27 (1H, dt, *J* = 8.0, 1.7 Hz)
d. 8.13 (1H, dd, *J* = 7.5, 1.7 Hz)
b. 8.10 (1H, dt, *J* = 7.5, 1.7 Hz)
e. 7.90-7.86 (1H, overlapping)
g. 7.63 (1H, dt, *J* = 8.0, 1.2 Hz)
i. 6.69 (1H, dd, *J* = 8.6, 2.9 Hz)
j. 1.96-1.89 (1H, m)
j. 1.86-1.78 (1H, m)
j. 1.34-1.06 (14H, m)
j. 0.85 (3H, t, *J* = 6.9 Hz)
k. 0.07 (s, 9H)

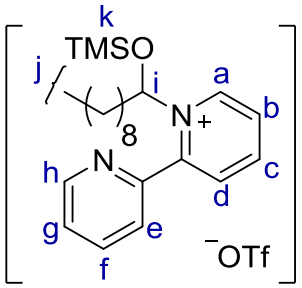
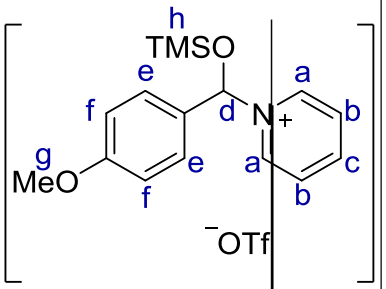


Chart O: ^{1}H NMR of crude product before work up

a. 9.17 (2H, d, *J* = 7.0 Hz)
c. 8.46 (1H, t, *J* = 7.0 Hz)
b. 8.03 (2H, dd, *J* = 7.0, 7.0 Hz)
f. 7.54 (2H, d, *J* = 9.0 Hz)
d. 7.29 (1H, s)
e. 6.91 (2H, d, *J* = 9.0 Hz)
g. 3.76 (3H, s)
h. 0.07 (9H, s)



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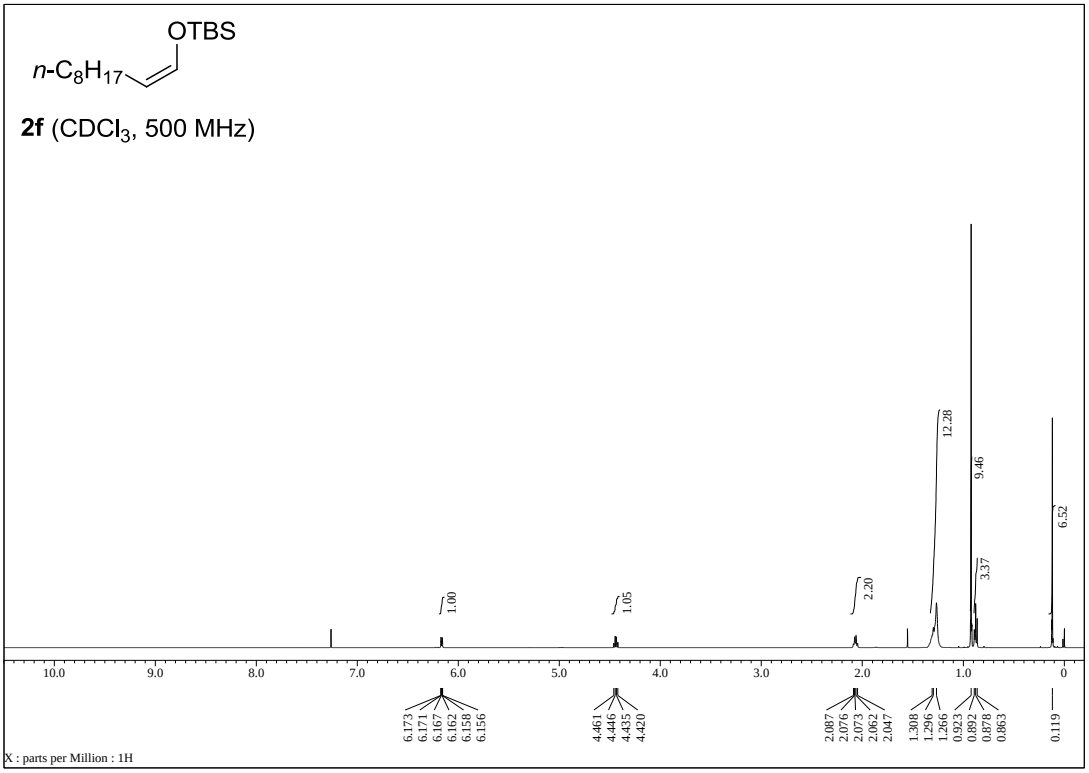
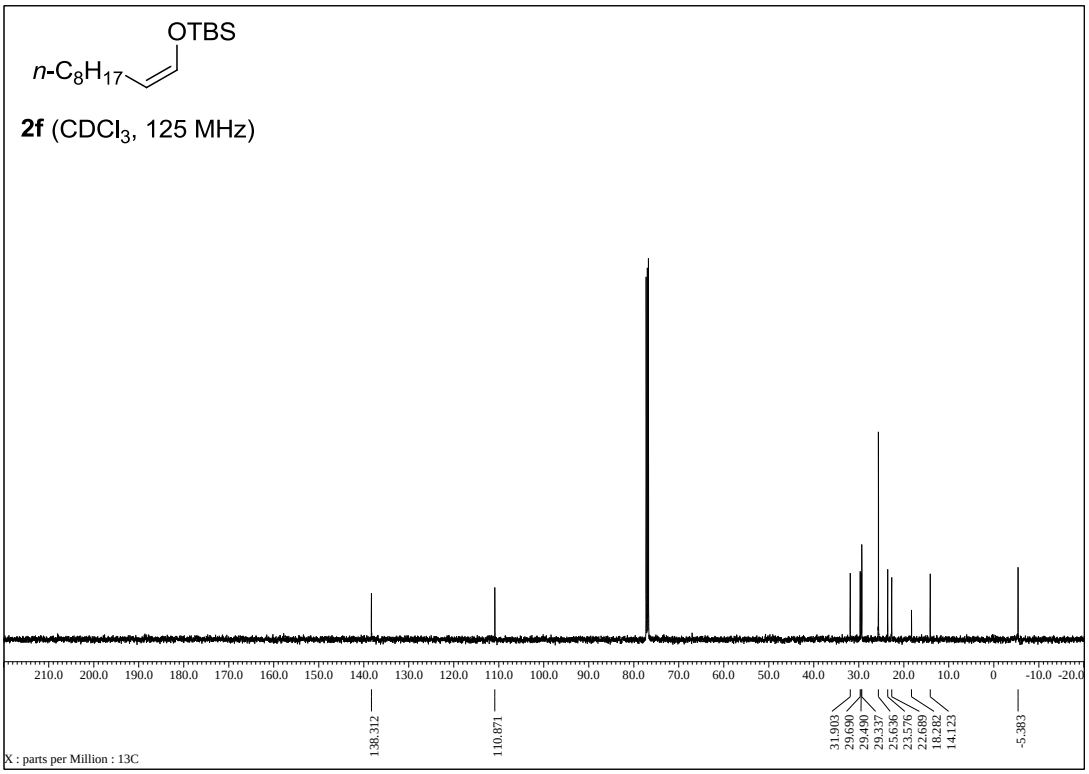
11. ^{1}H and ^{13}C NMR spectra of the newly synthesized substrates and products.

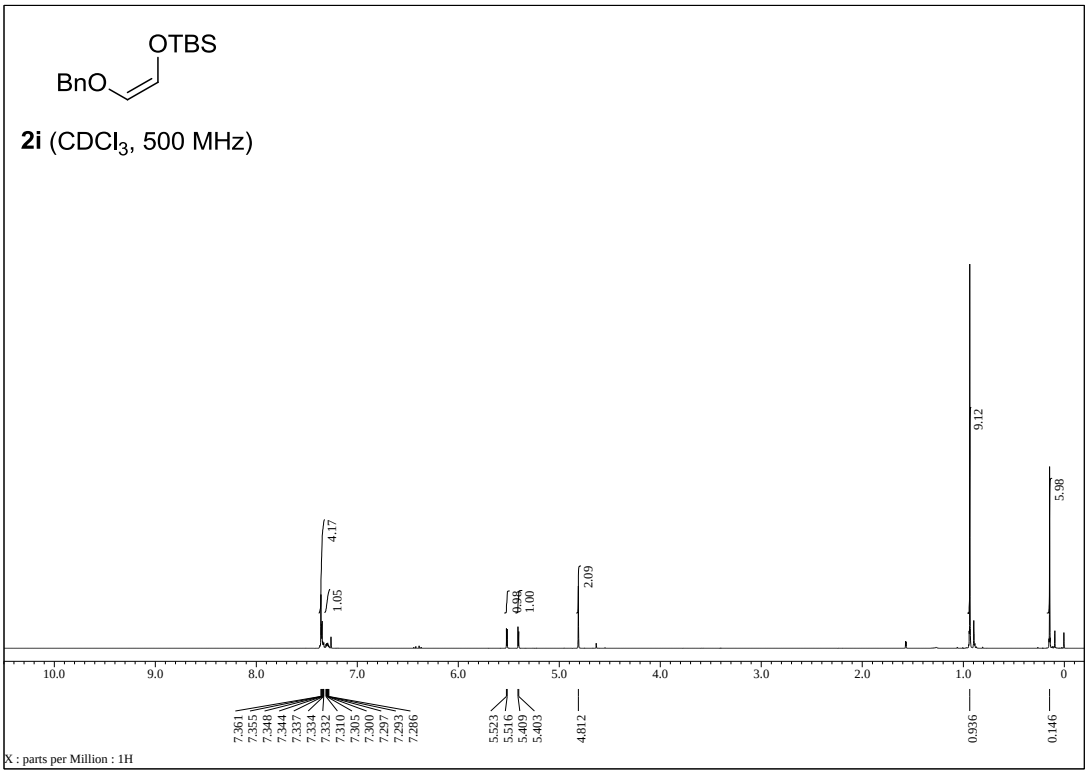
^{1}H NMR of (*Z*)-*tert*-Butyl(dec-1-en-1-yloxy)dimethylsilane (**2f**)



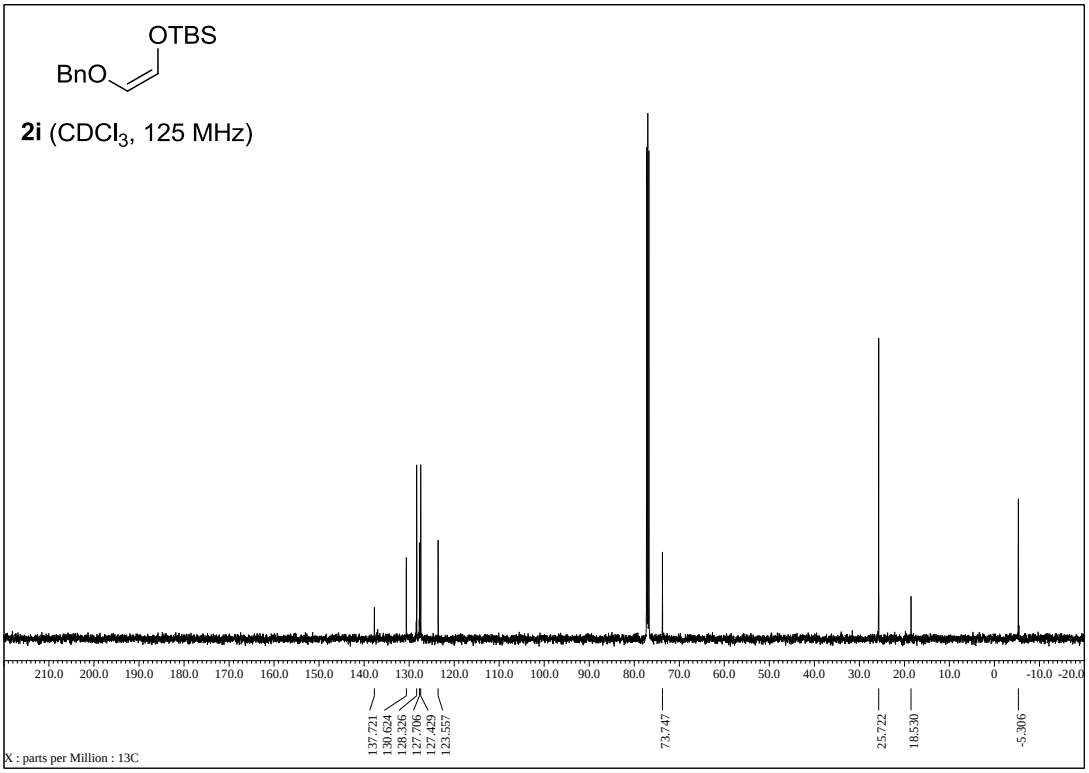
^{13}C NMR of (*Z*)-*tert*-Butyl(dec-1-en-1-yloxy)dimethylsilane (**2f**)



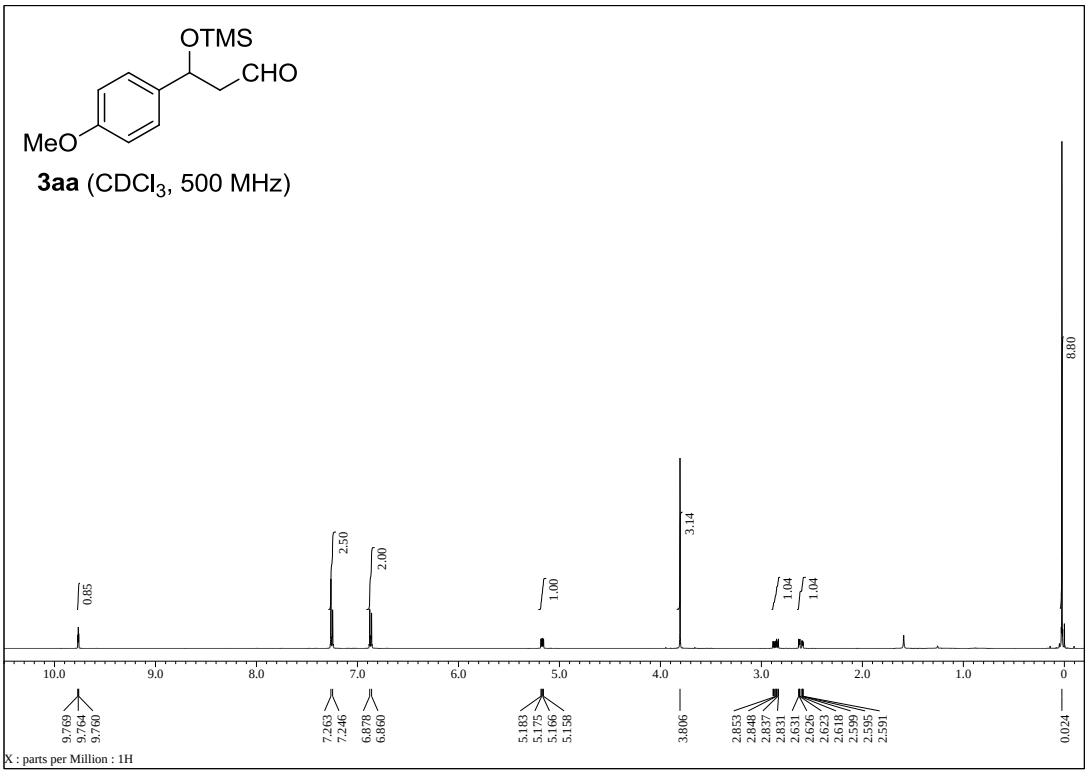
^{1}H NMR of (*Z*)-((2-(benzyloxy)vinyl)oxy)(*tert*-butyl)dimethylsilane (**2i**)



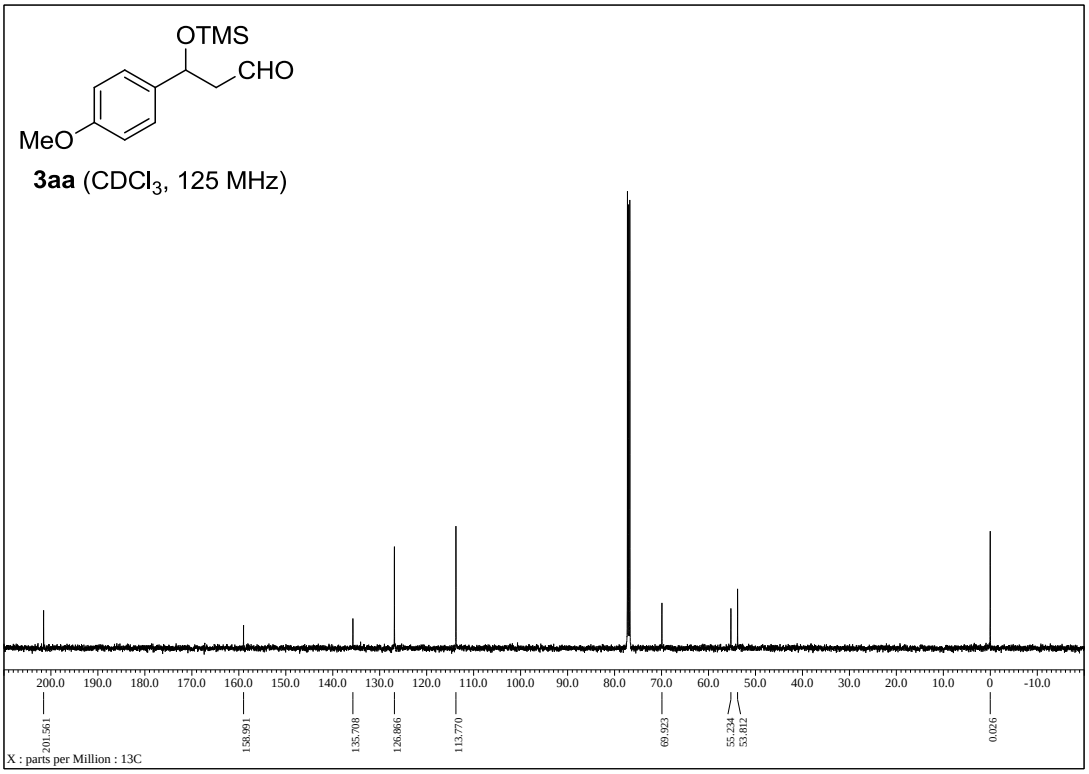
^{13}C NMR of (*Z*)-((2-(benzyloxy)vinyl)oxy)(*tert*-butyl)dimethylsilane (**2i**)



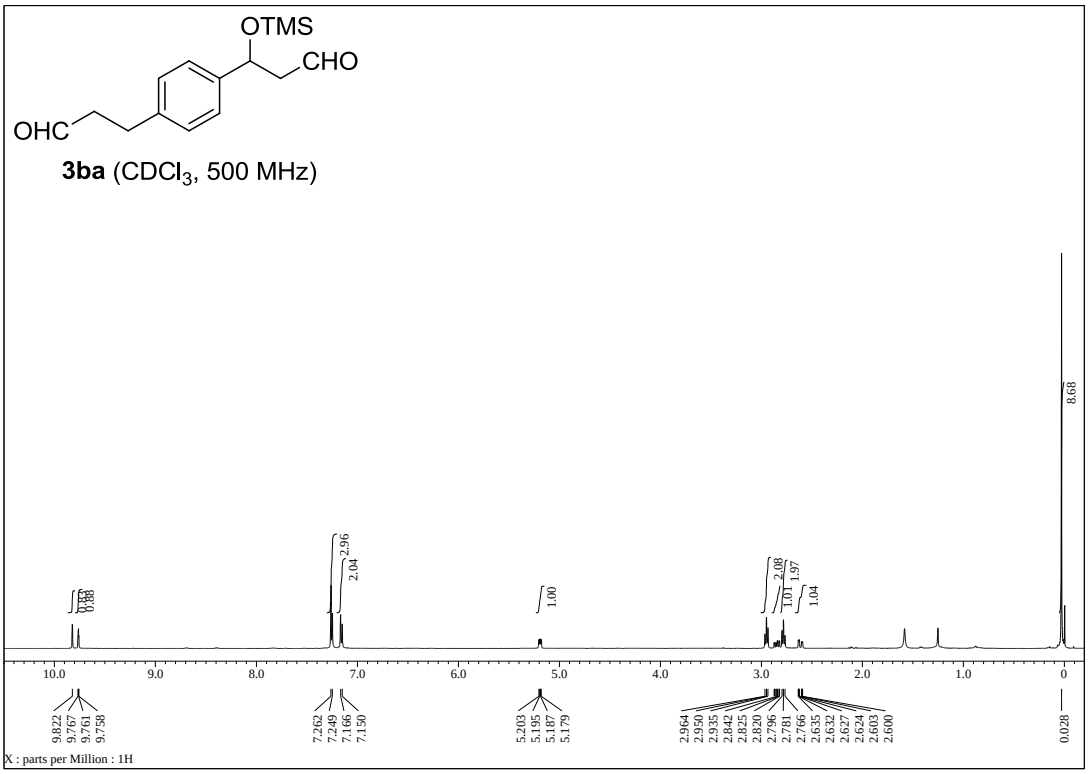
^{1}H NMR of 3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3aa**)



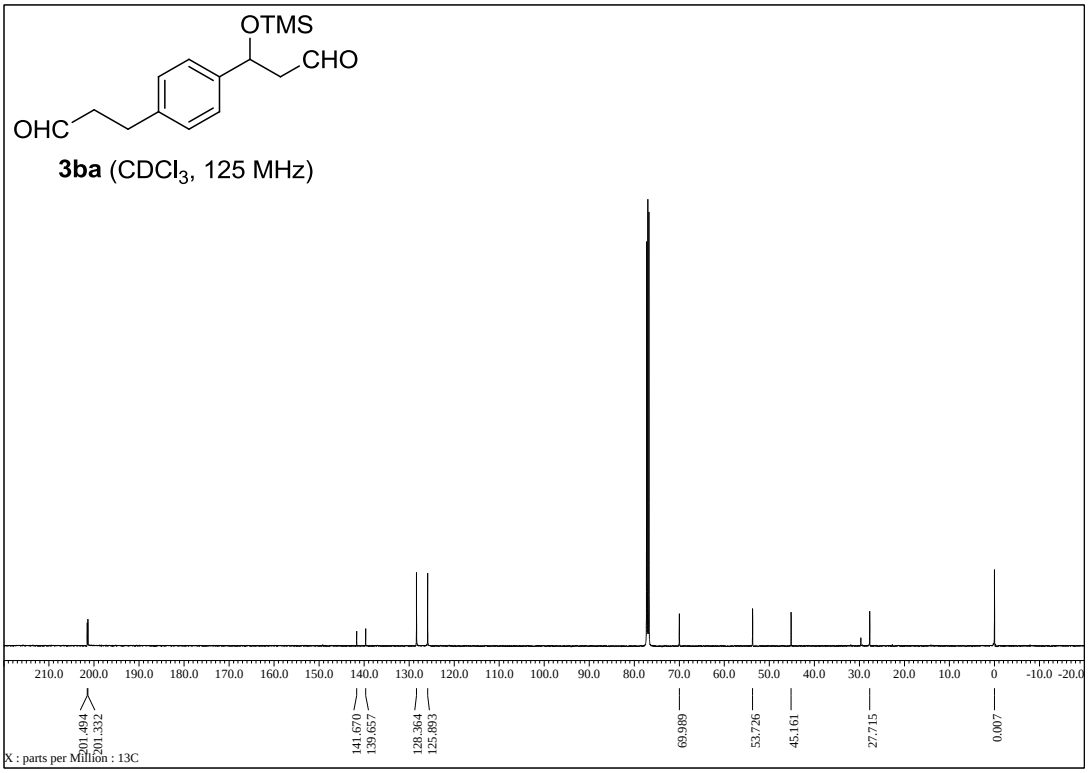
^{13}C NMR of 3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3aa**)



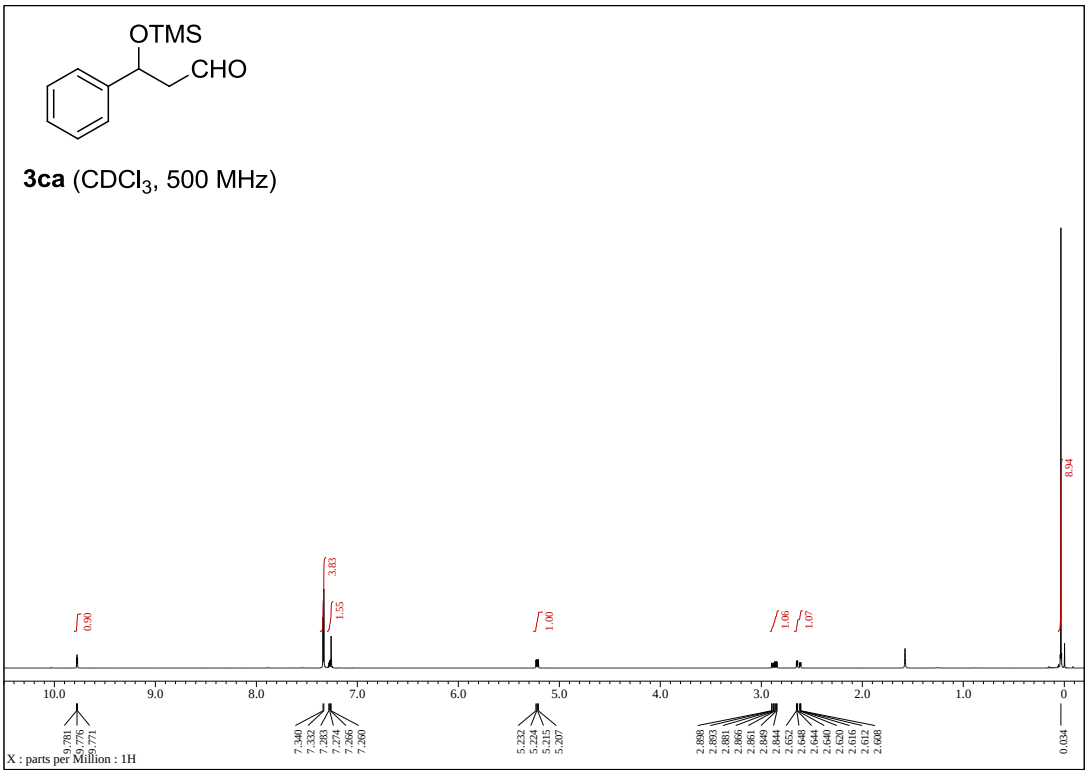
^{1}H NMR of 3-(4-(3-oxopropyl)phenyl)-3-((trimethylsilyl)oxy)propanal (**3ba**)



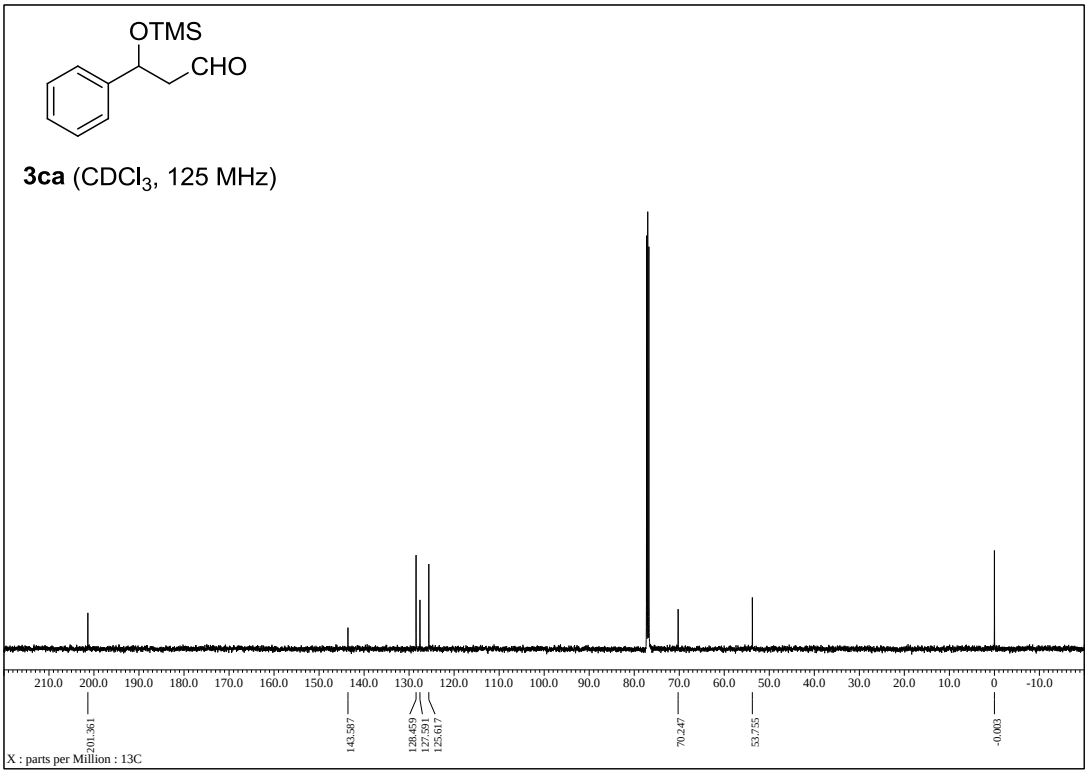
^{13}C NMR of 3-(4-(3-oxopropyl)phenyl)-3-((trimethylsilyl)oxy)propanal (**3ba**)



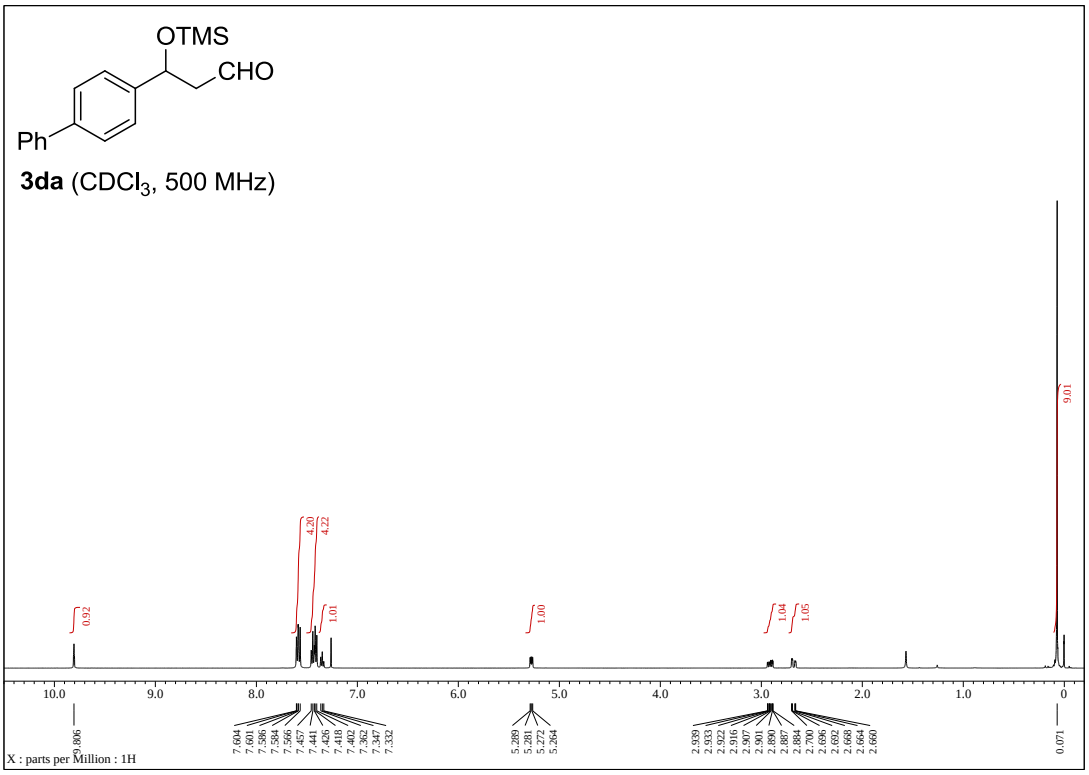
^{1}H NMR of 3-phenyl-3-((trimethylsilyl)oxy)propanal (**3ca**)



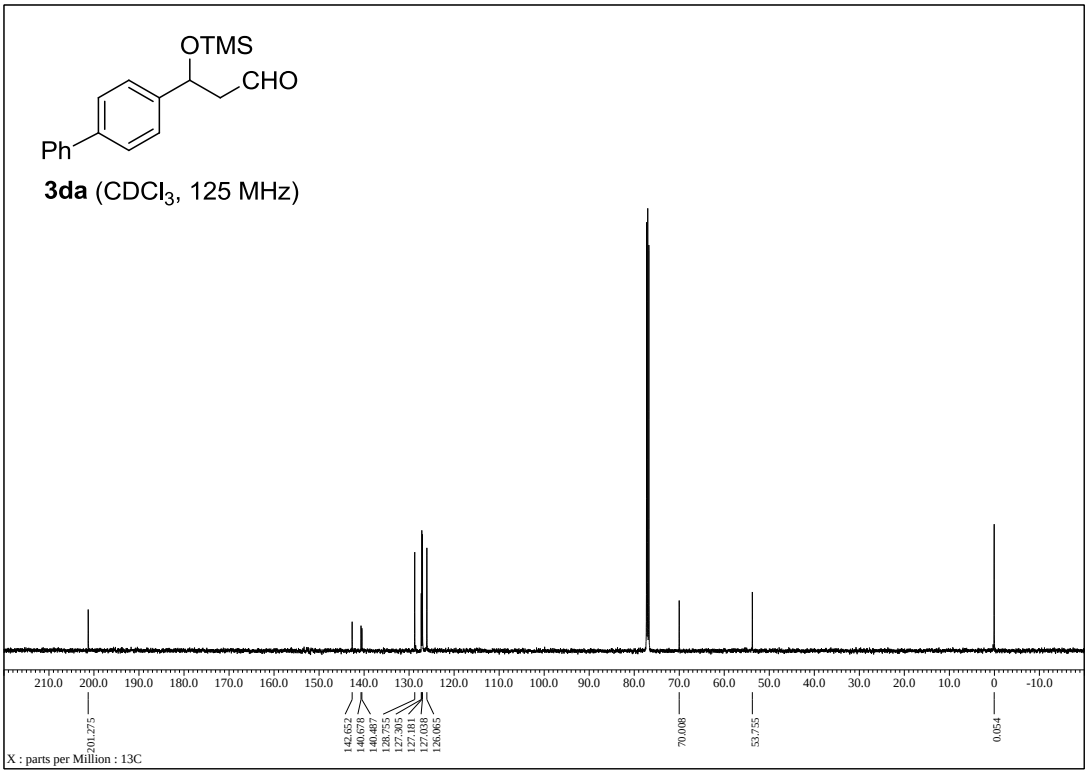
^{13}C NMR of 3-phenyl-3-((trimethylsilyl)oxy)propanal (**3ca**)



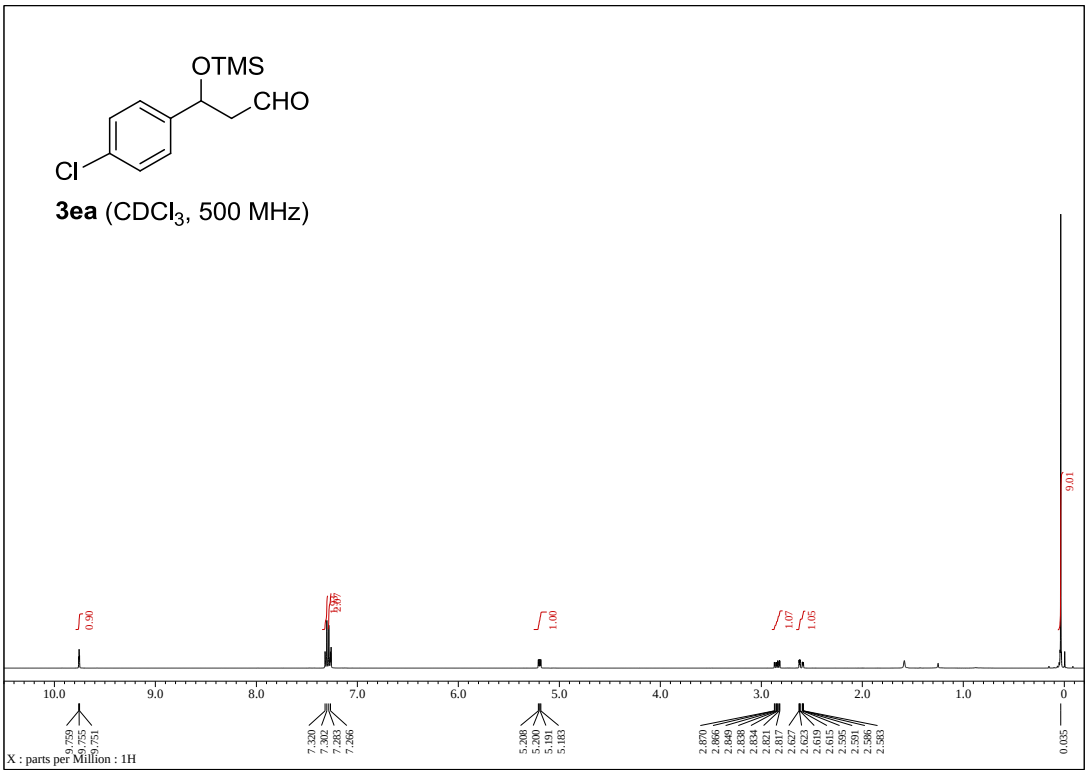
^{1}H NMR of 3-([1,1'-biphenyl]-4-yl)-3-((trimethylsilyl)oxy)propanal (**3da**)



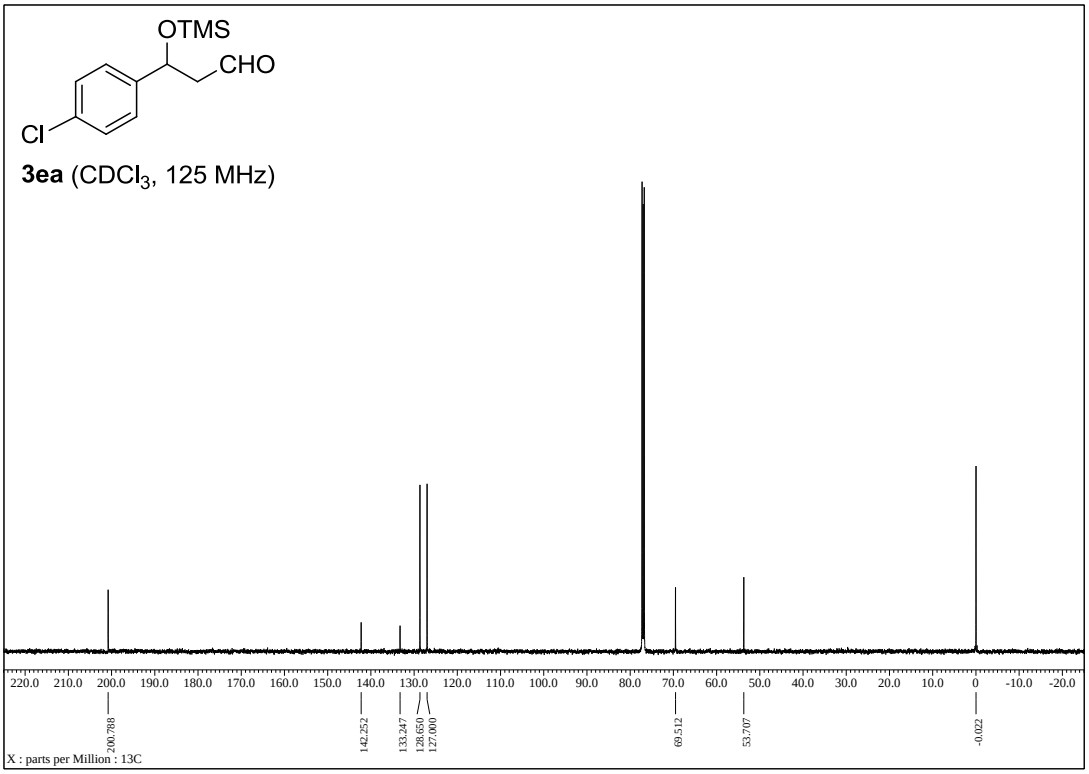
^{13}C NMR of 3-([1,1'-biphenyl]-4-yl)-3-((trimethylsilyl)oxy)propanal (**3da**)



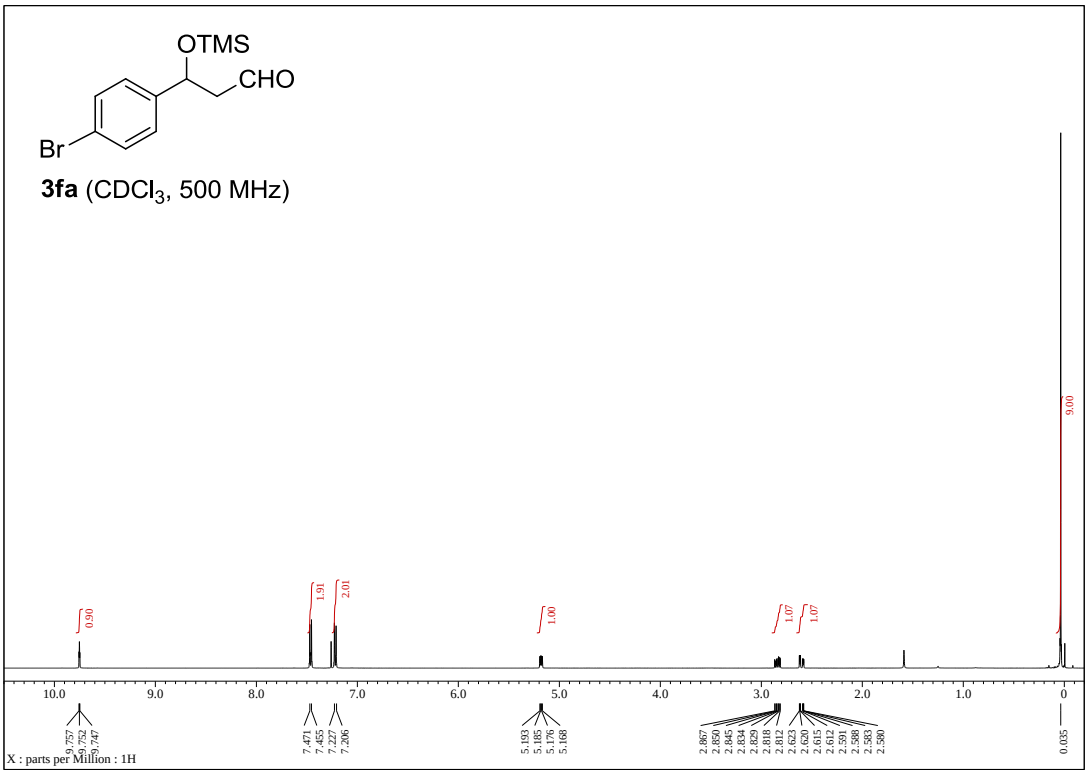
^{1}H NMR of 3-(4-chlorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ea**)



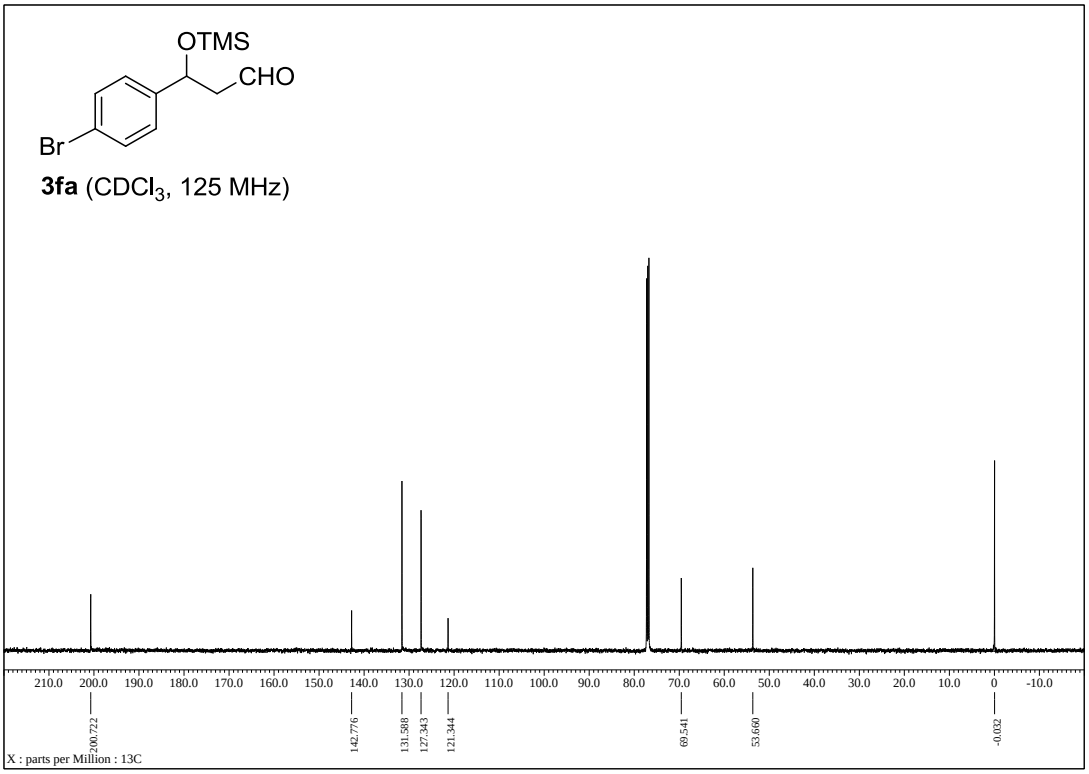
^{13}C NMR of 3-(4-chlorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ea**)



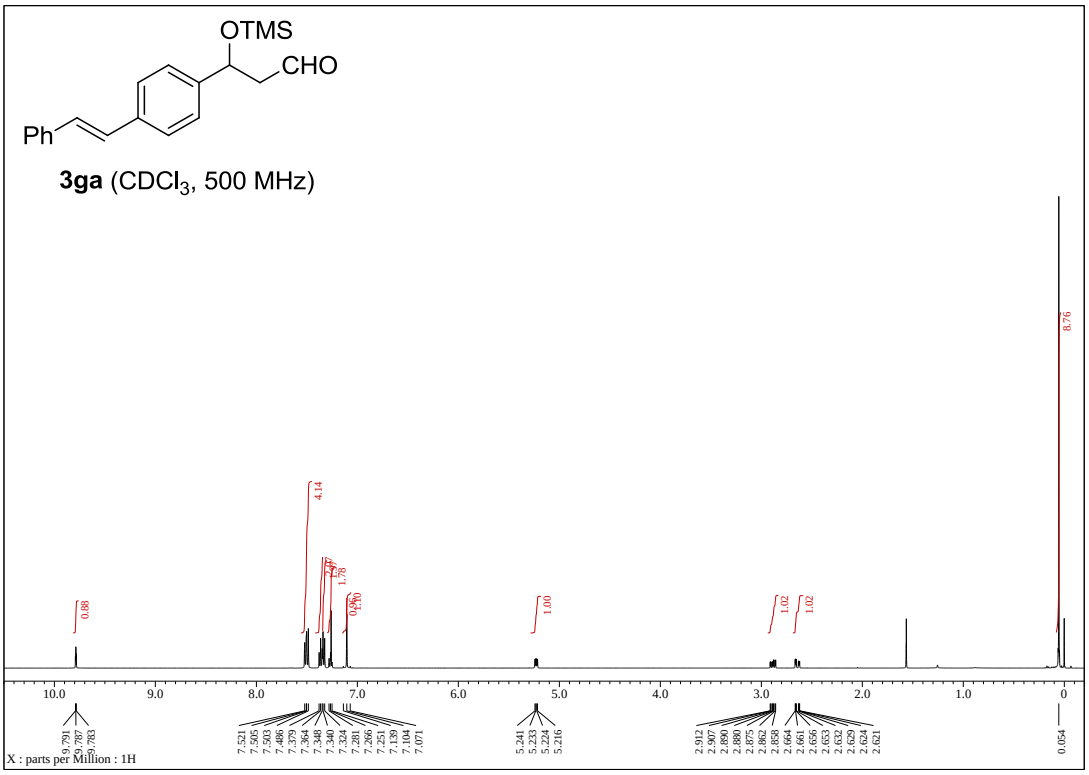
^{1}H NMR of 3-(4-bromophenyl)-3-((trimethylsilyl)oxy)propanal (**3fa**)



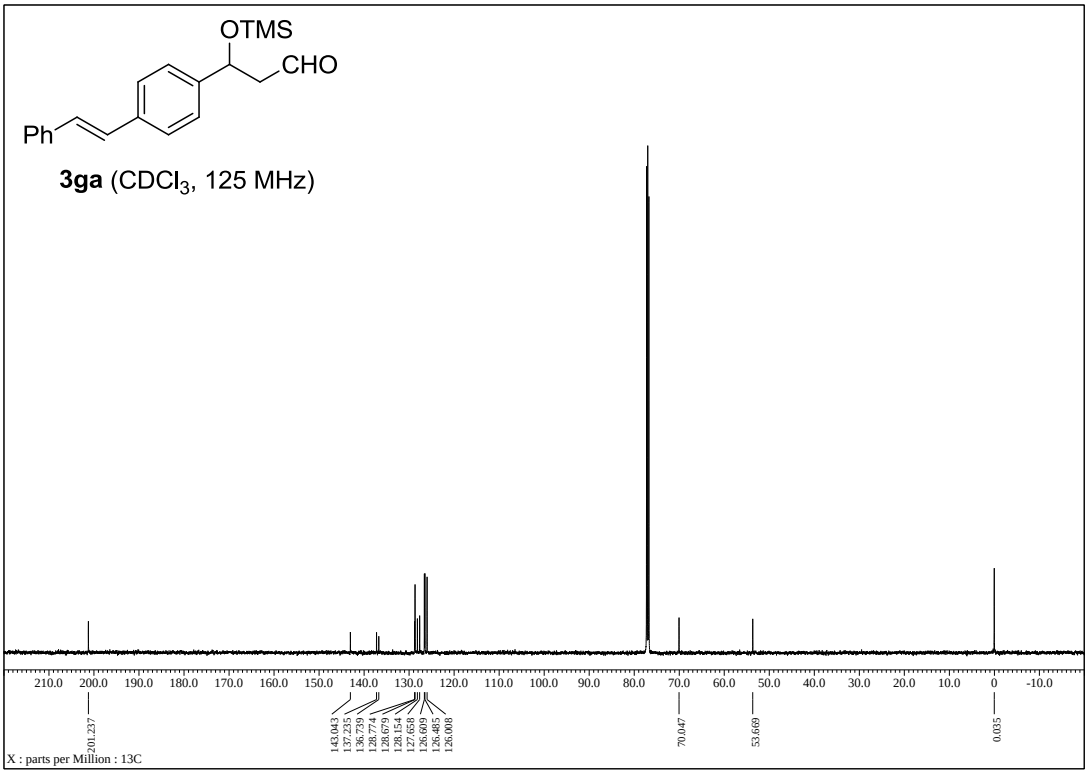
^{13}C NMR of 3-(4-bromophenyl)-3-((trimethylsilyl)oxy)propanal (**3fa**)



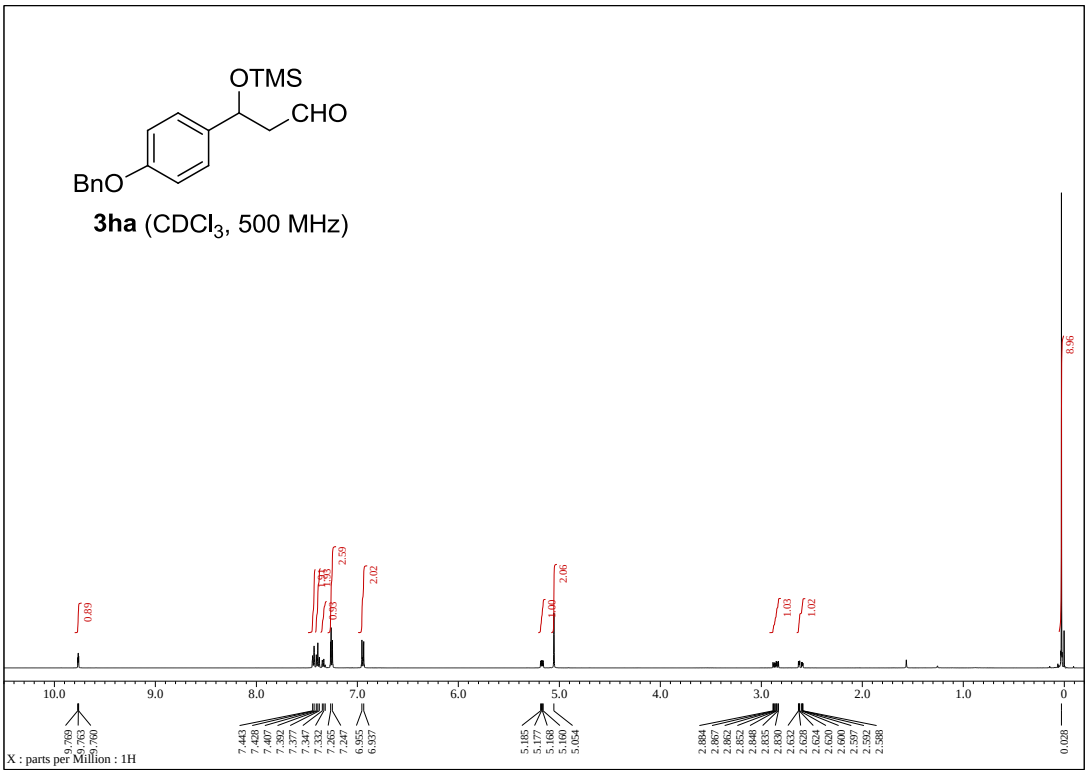
^{1}H NMR of (*E*)-3-(4-styrylphenyl)-3-((trimethylsilyl)oxy)propanal (**3ga**)



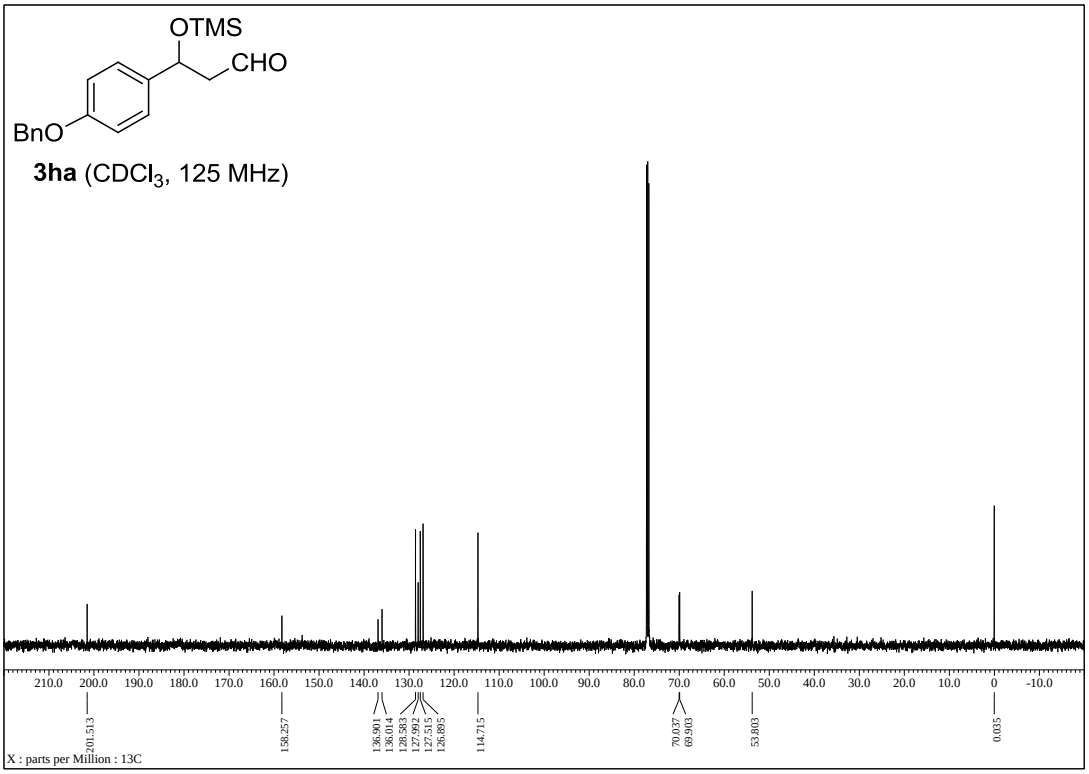
^{13}C NMR of (*E*)-3-(4-styrylphenyl)-3-((trimethylsilyl)oxy)propanal (**3ga**)



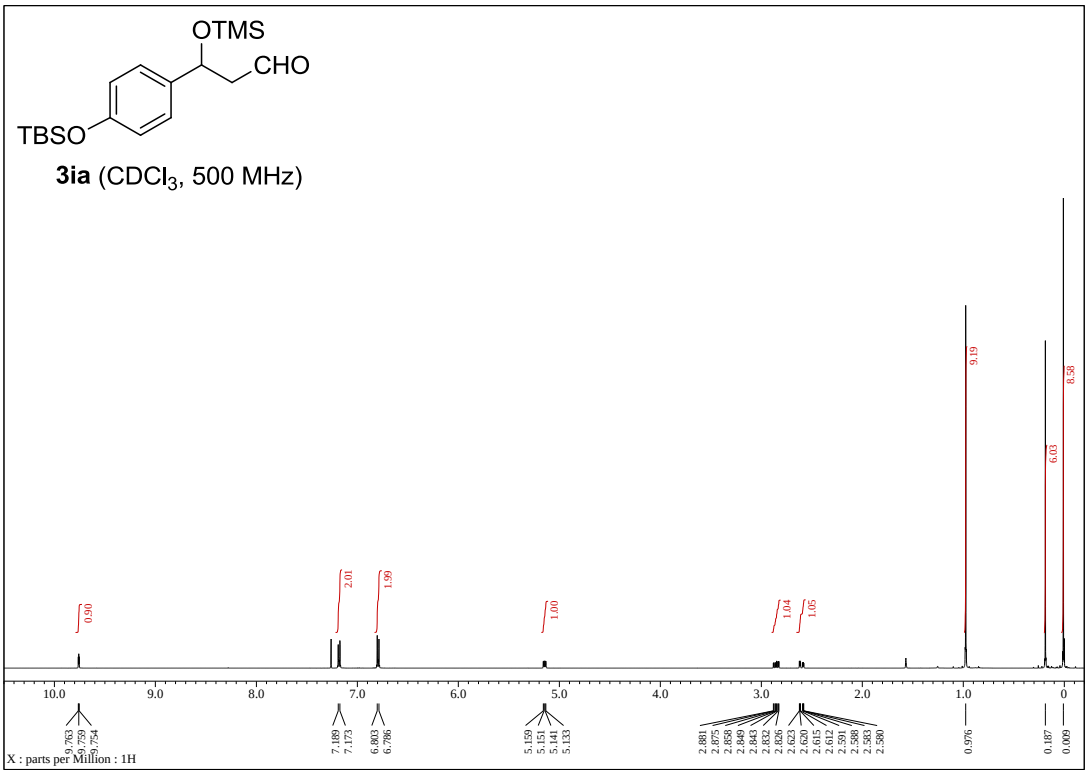
^{1}H NMR of 3-(4-benzyloxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3ha**)



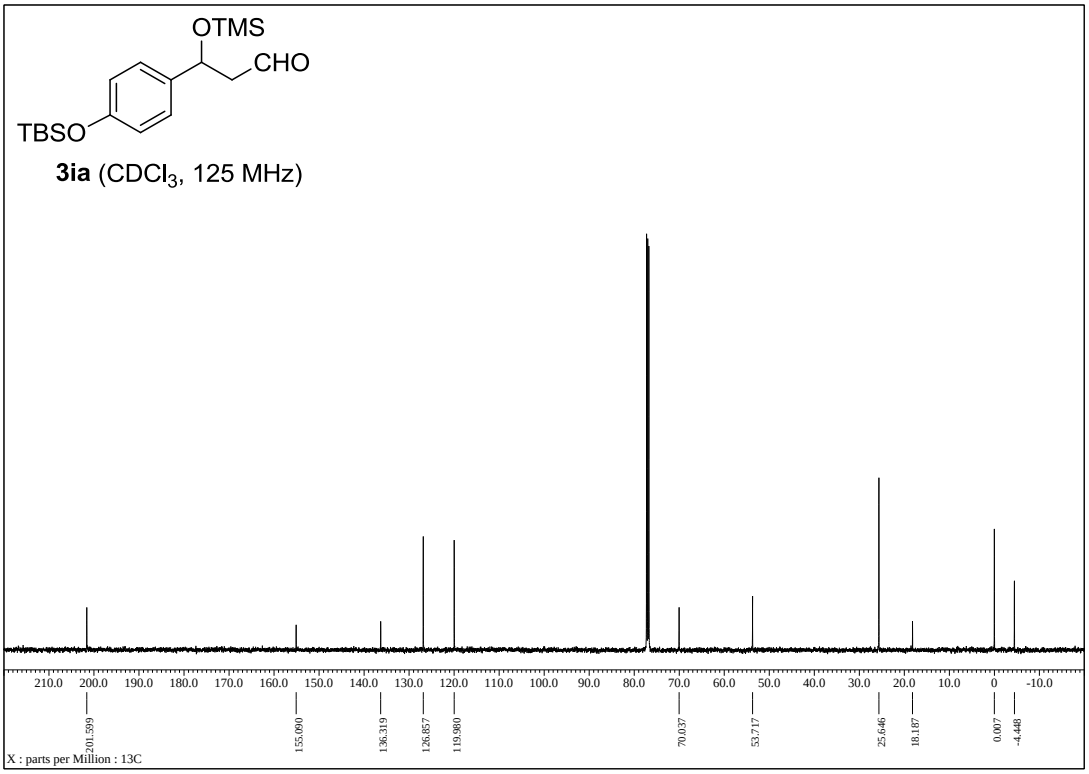
^{13}C NMR of 3-(4-benzyloxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3ha**)



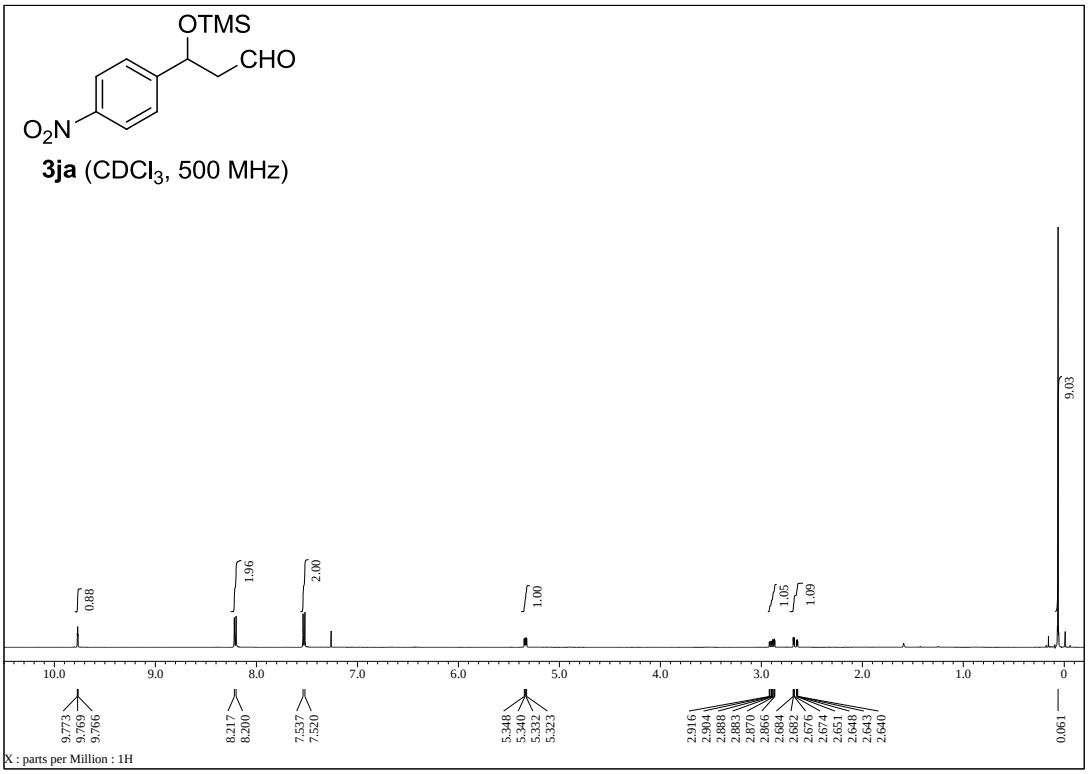
^{1}H NMR of 3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-((trimethylsilyl)oxy)propanal (**3ia**)



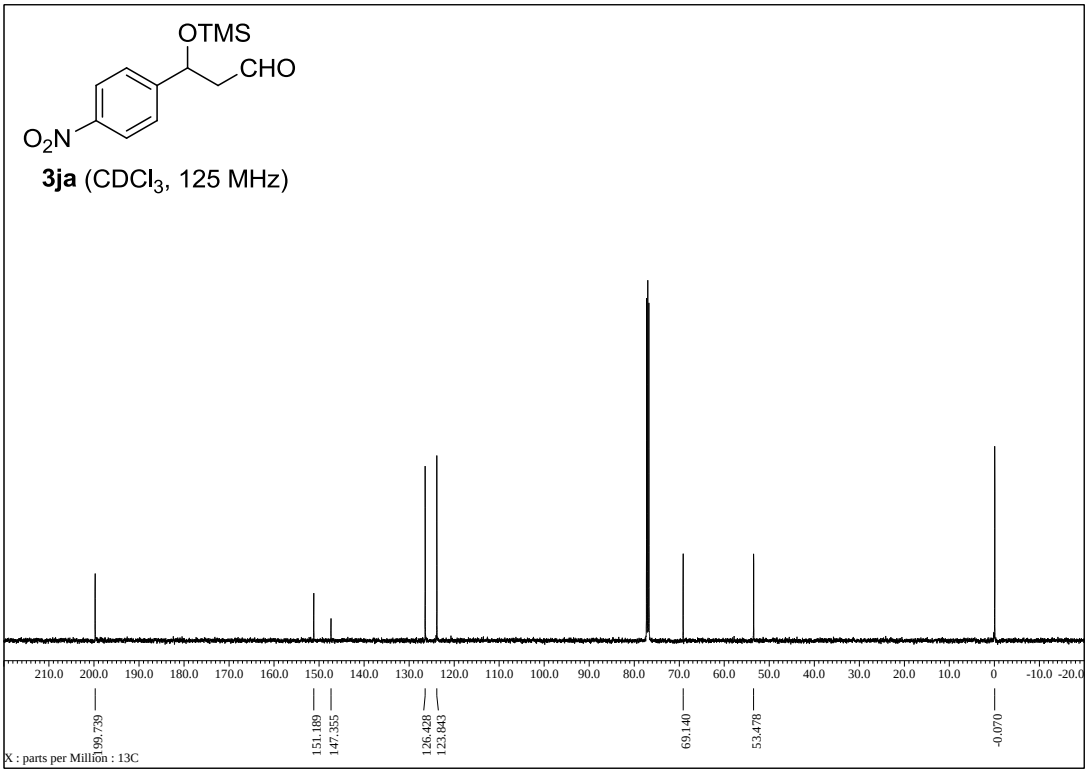
^{13}C NMR of 3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-3-((trimethylsilyl)oxy)propanal (**3ia**)



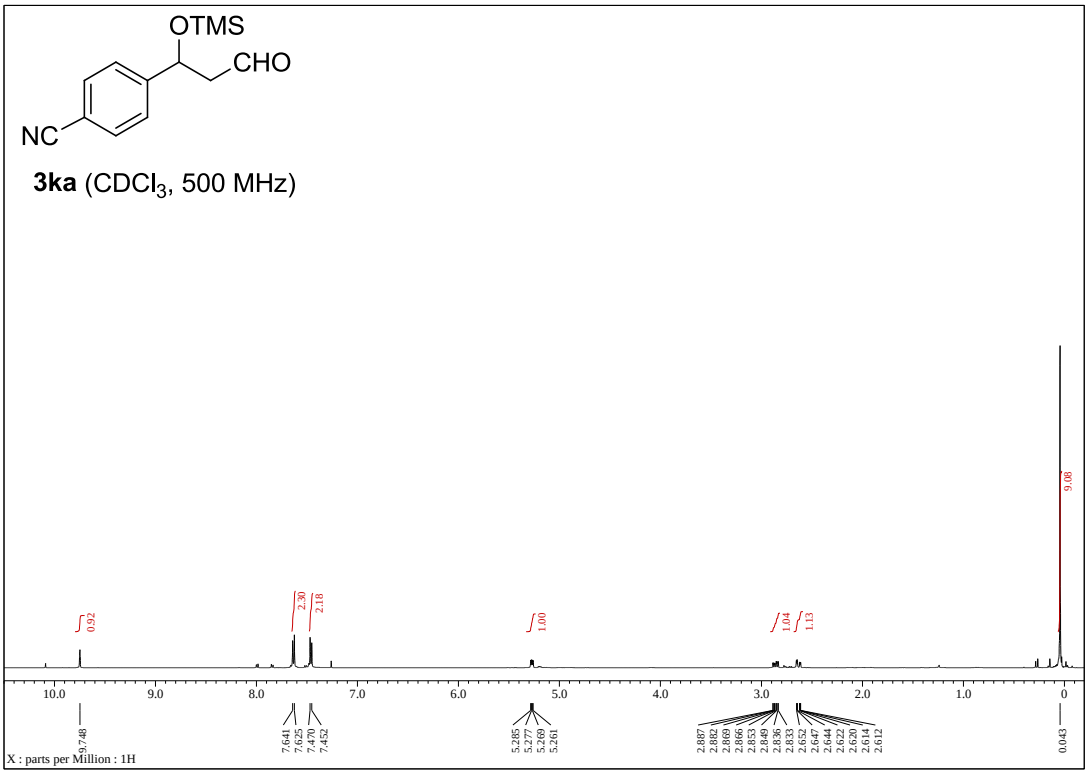
^{1}H NMR of 3-(4-nitorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ja**)



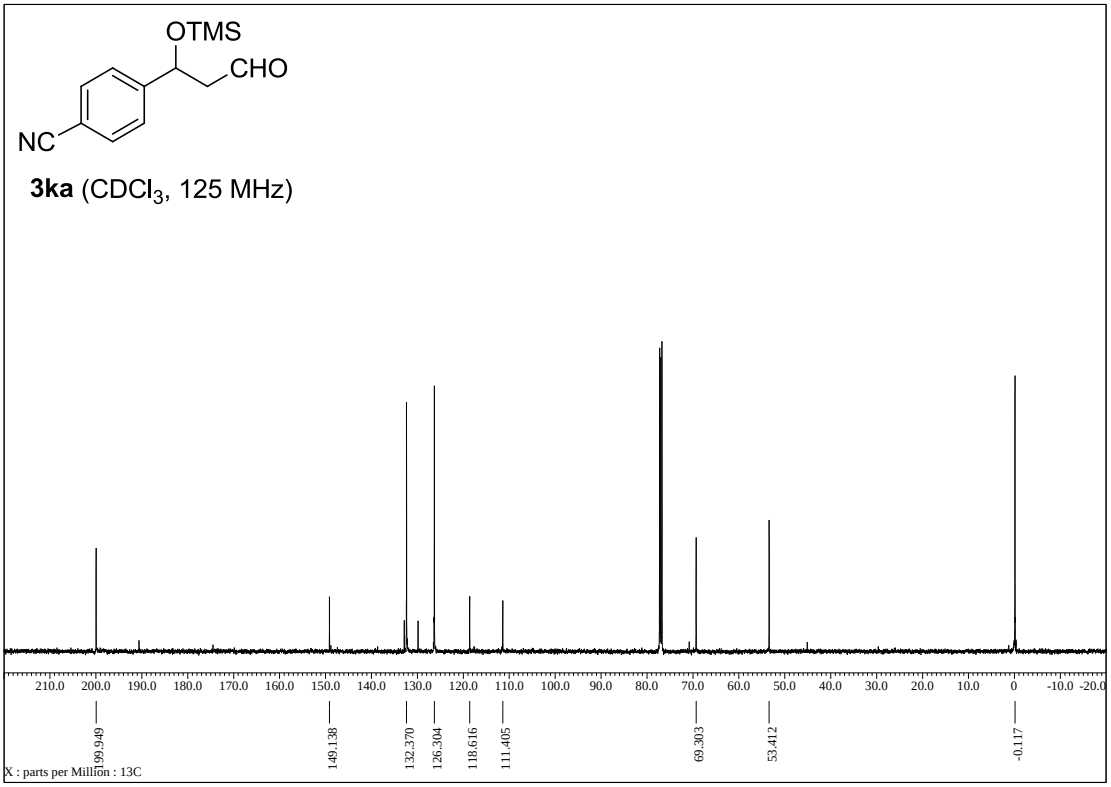
^{13}C NMR of 3-(4-nitorophenyl)-3-((trimethylsilyl)oxy)propanal (**3ja**)



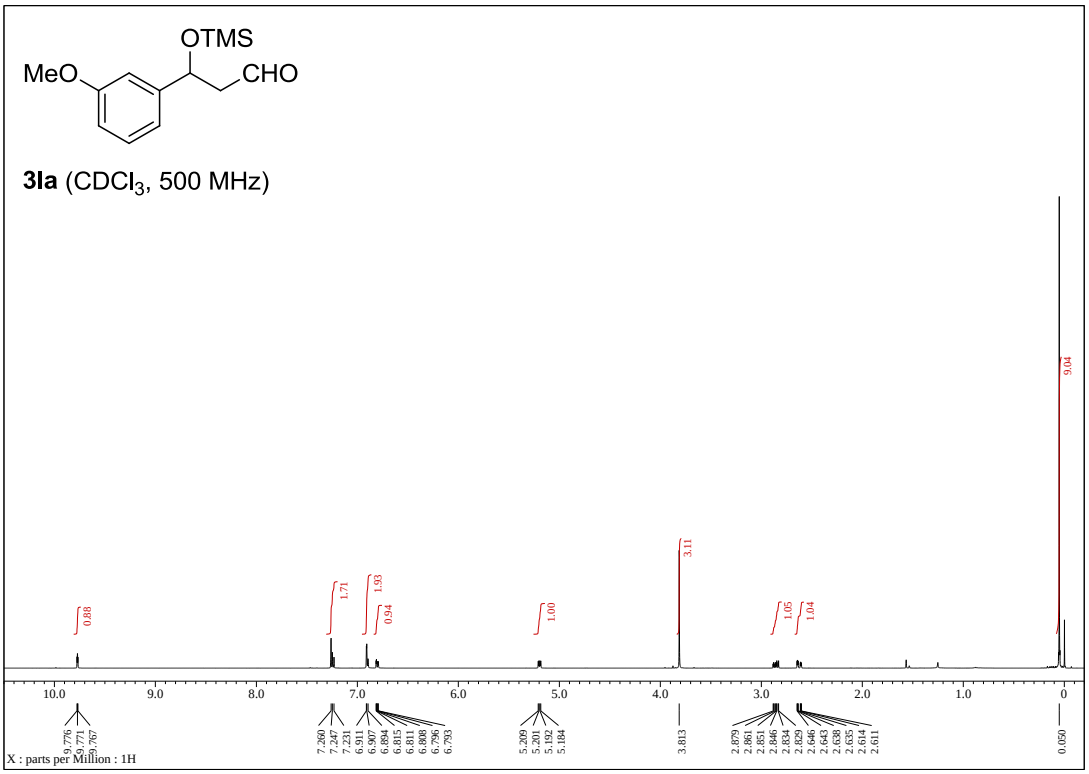
^{1}H NMR of 3-(4-cyanophenyl)-3-((trimethylsilyl)oxy)propanal (**3ka**)



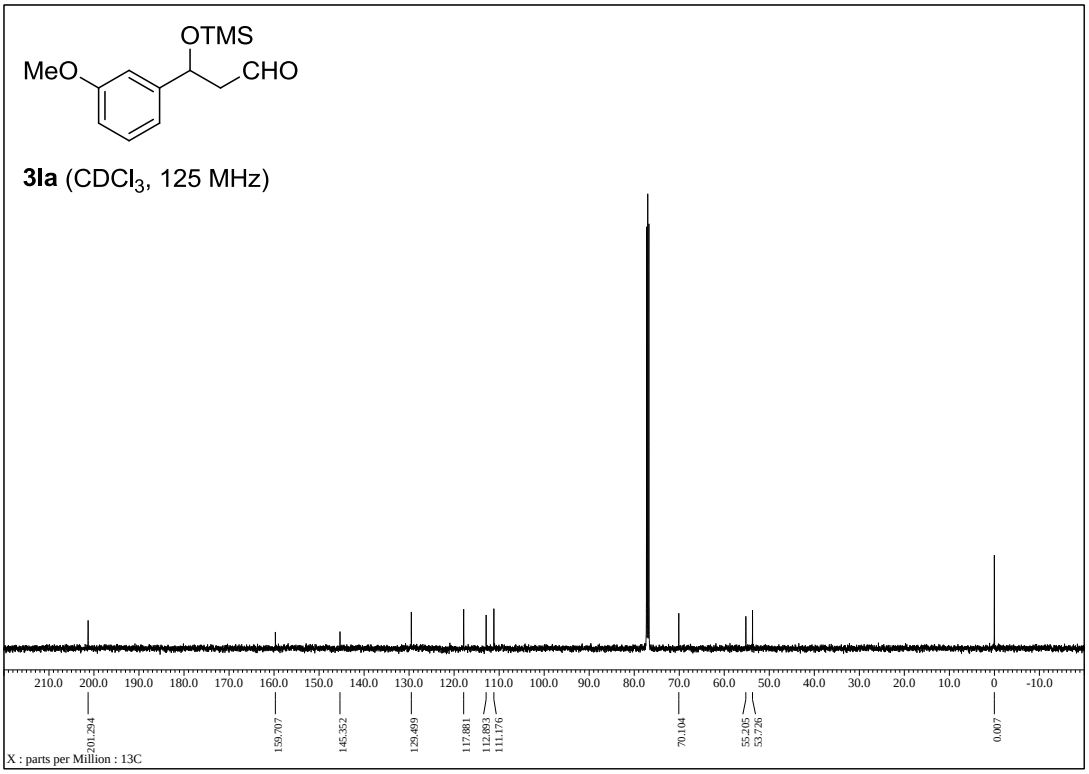
^{13}C NMR of 3-(4-cyanophenyl)-3-((trimethylsilyl)oxy)propanal (**3ka**)



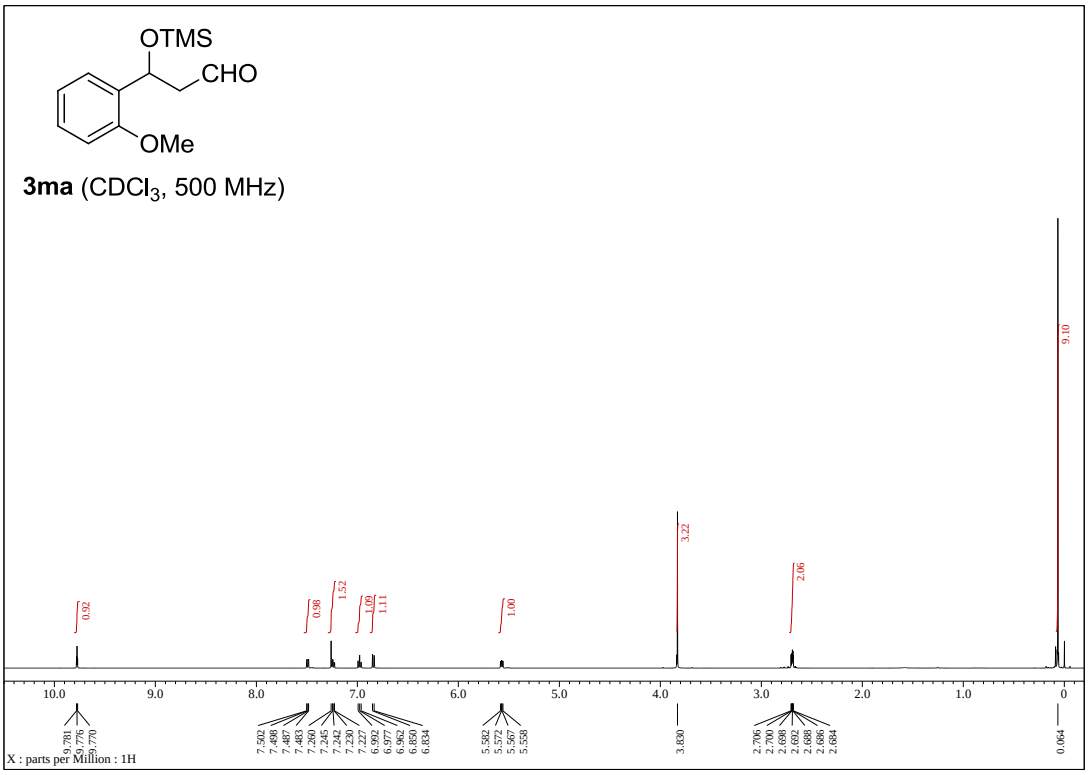
^{1}H NMR of 3-(3-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3la**)



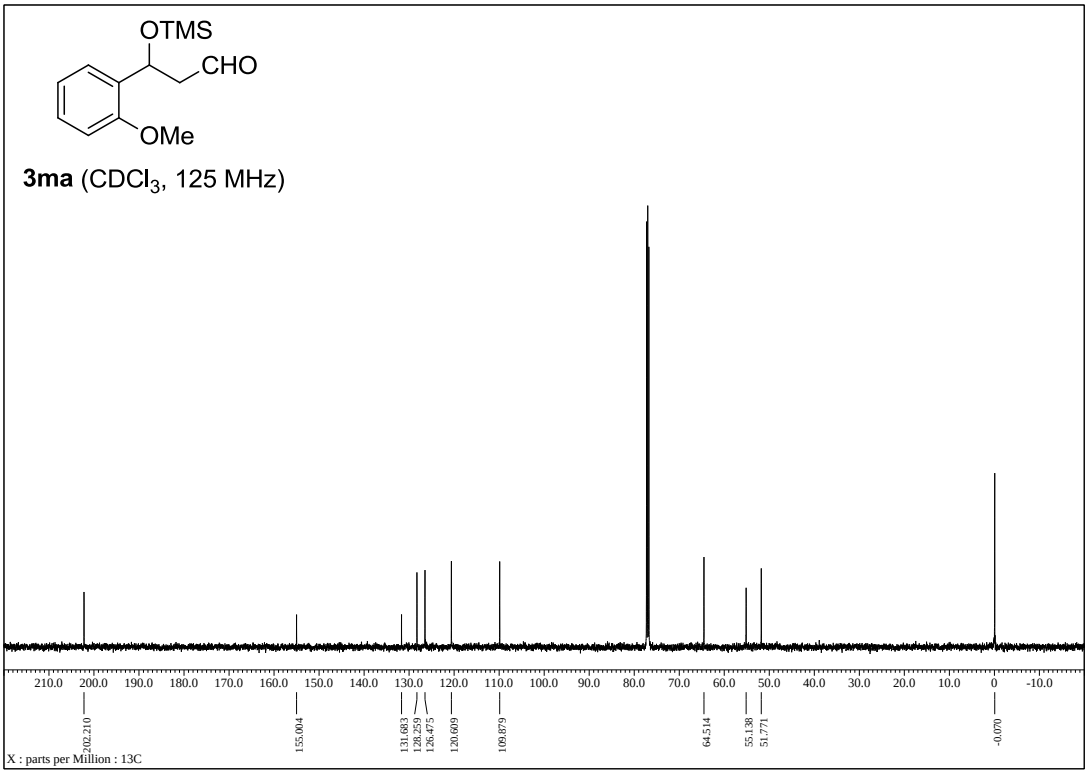
^{13}C NMR of 3-(3-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3la**)



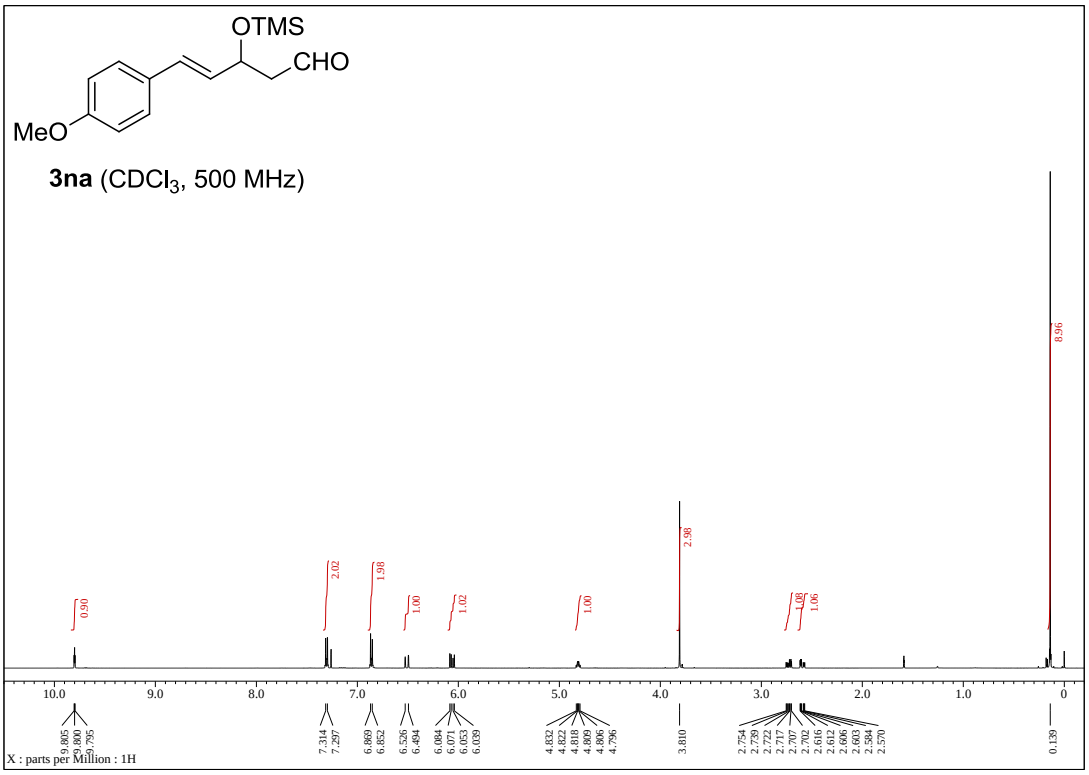
^{1}H NMR of 3-(2-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3ma**)



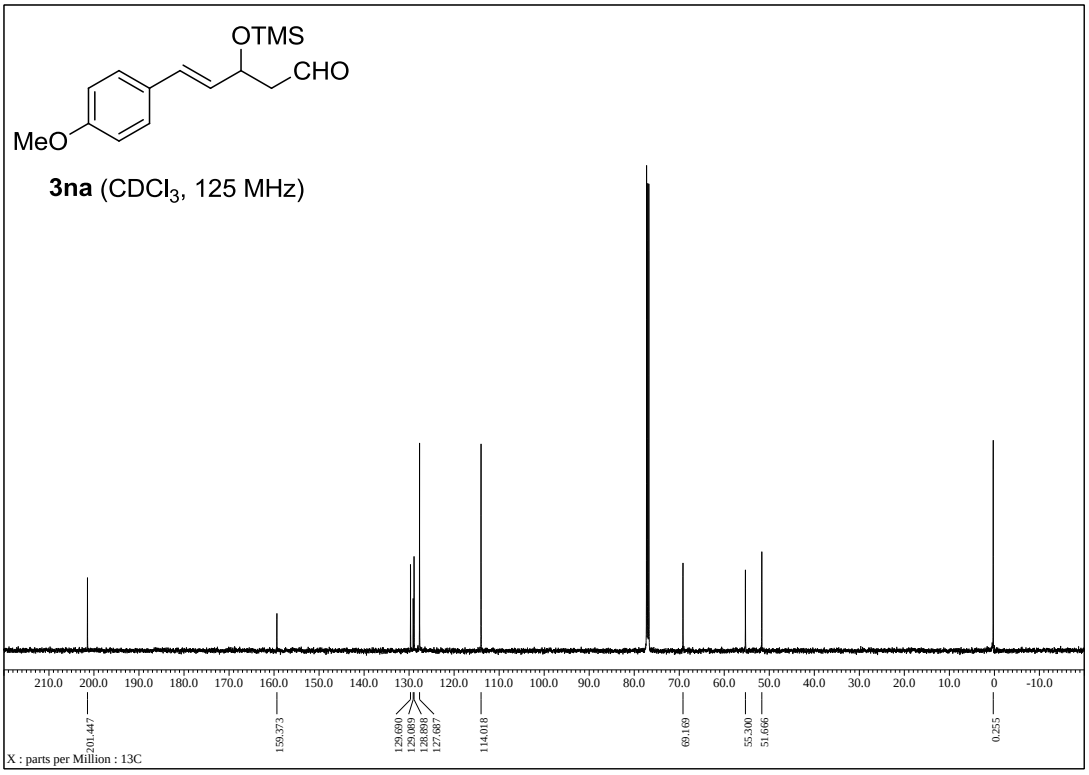
^{13}C NMR of 3-(2-methoxyphenyl)-3-((trimethylsilyl)oxy)propanal (**3ma**)



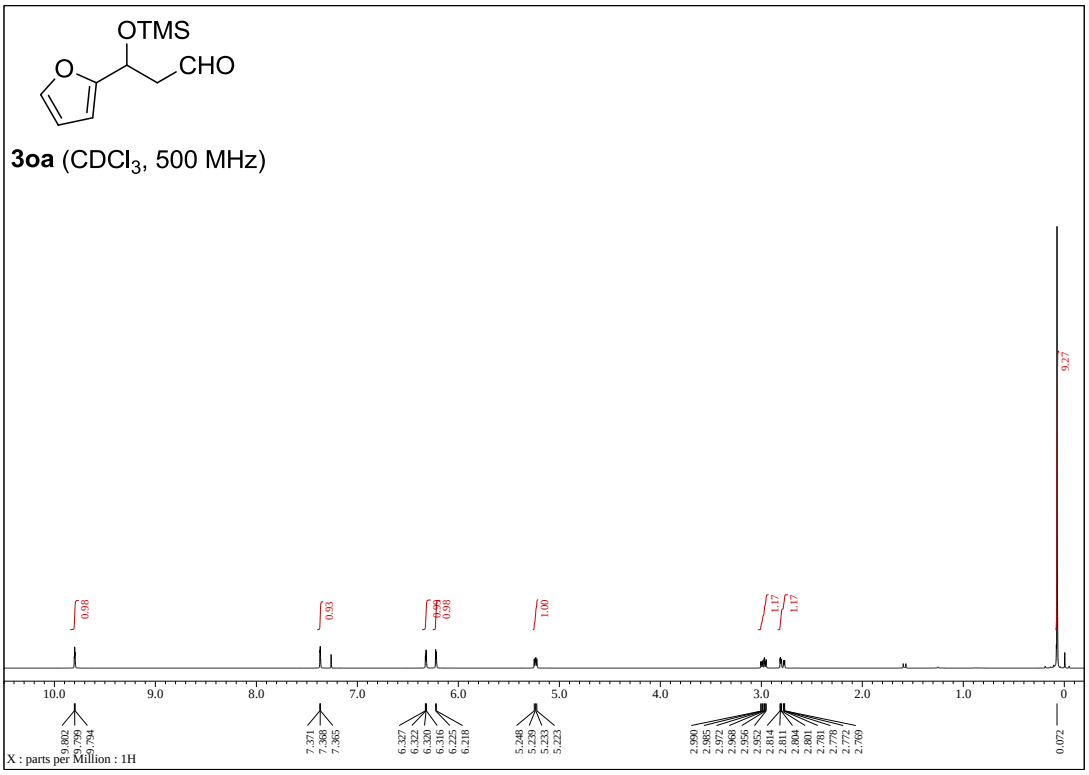
^{1}H NMR of (*E*)-5-(4-methoxyphenyl)-3-((triethylsilyl)oxy)pent-4-enal (**3na**)



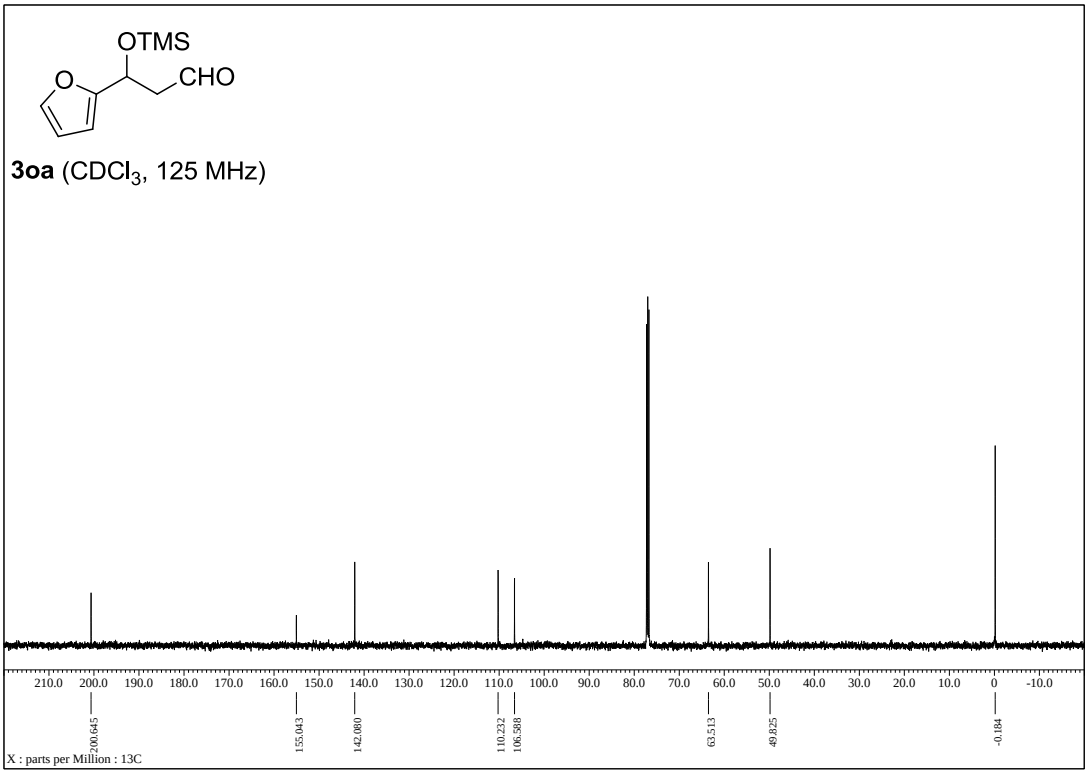
^{13}C NMR of (*E*)-5-(4-methoxyphenyl)-3-((triethylsilyl)oxy)pent-4-enal (**3na**)



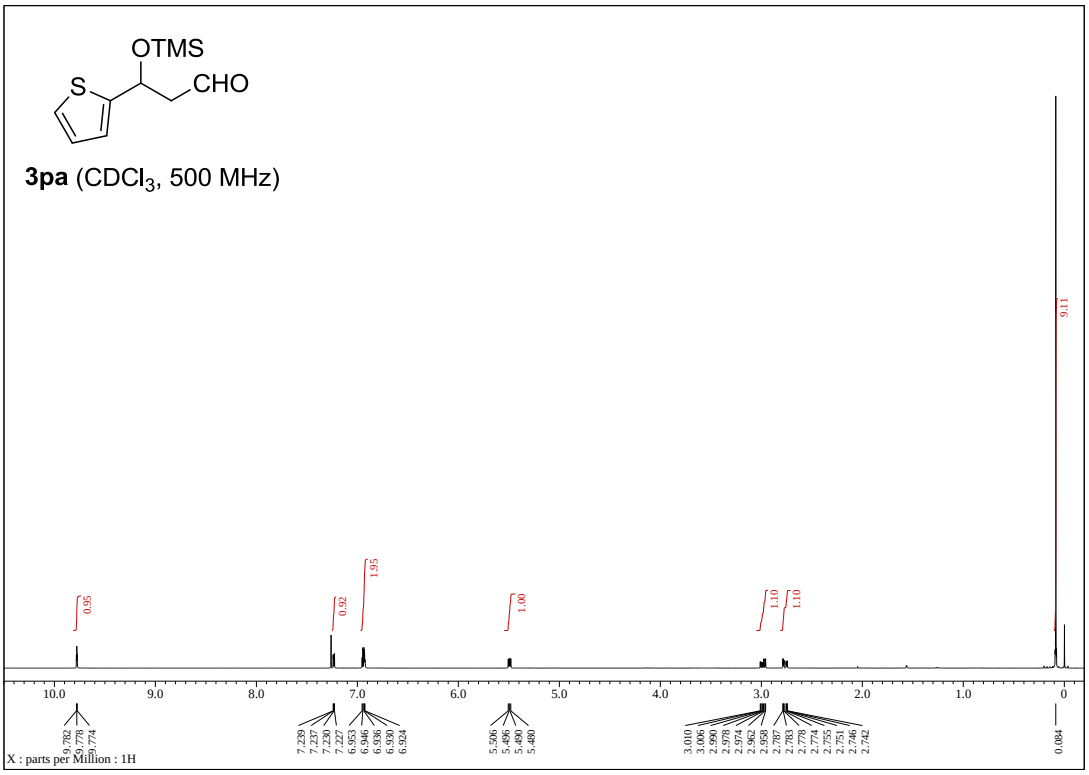
^{1}H NMR of 3-(furan-2-yl)-3-((trimethylsilyl)oxy)propanal (**3oa**)



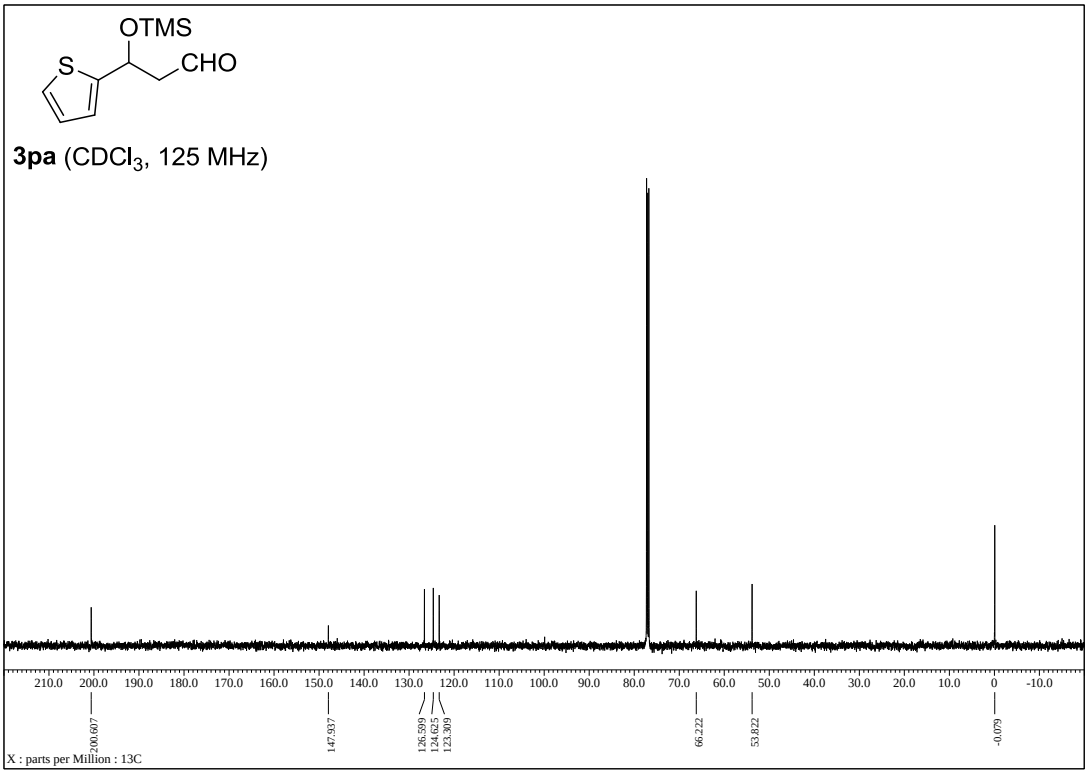
^{13}C NMR of 3-(furan-2-yl)-3-((trimethylsilyl)oxy)propanal (**3oa**)



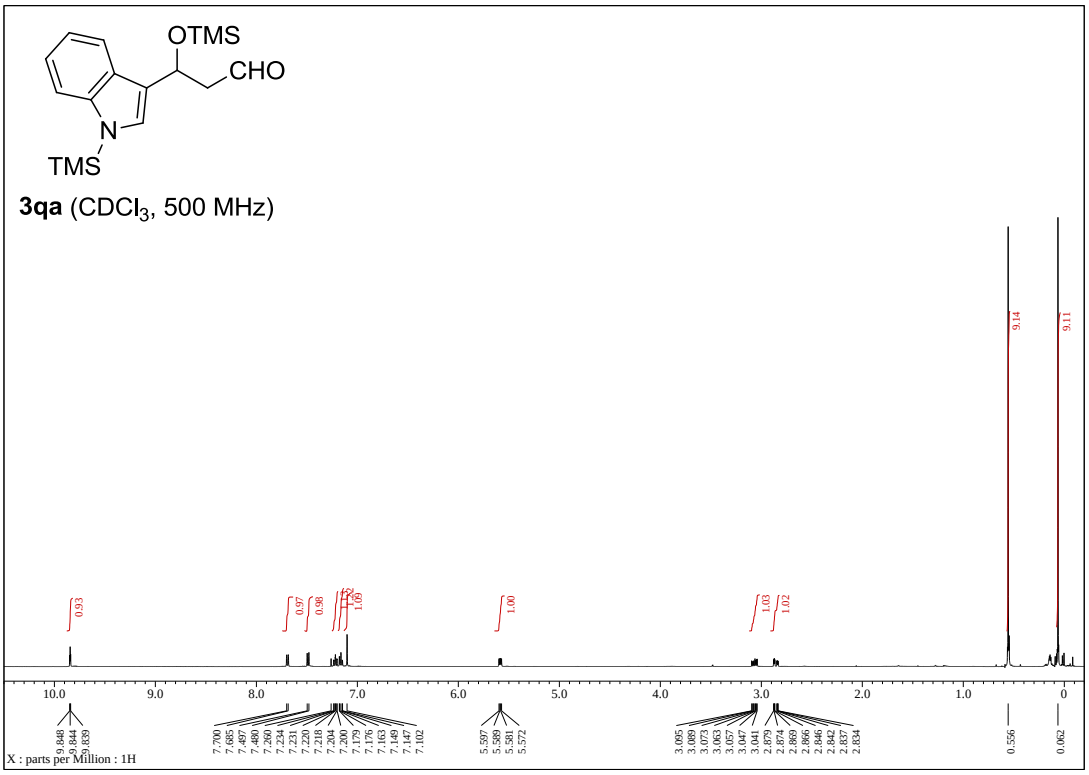
^{1}H NMR of 3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)propanal (**3pa**)



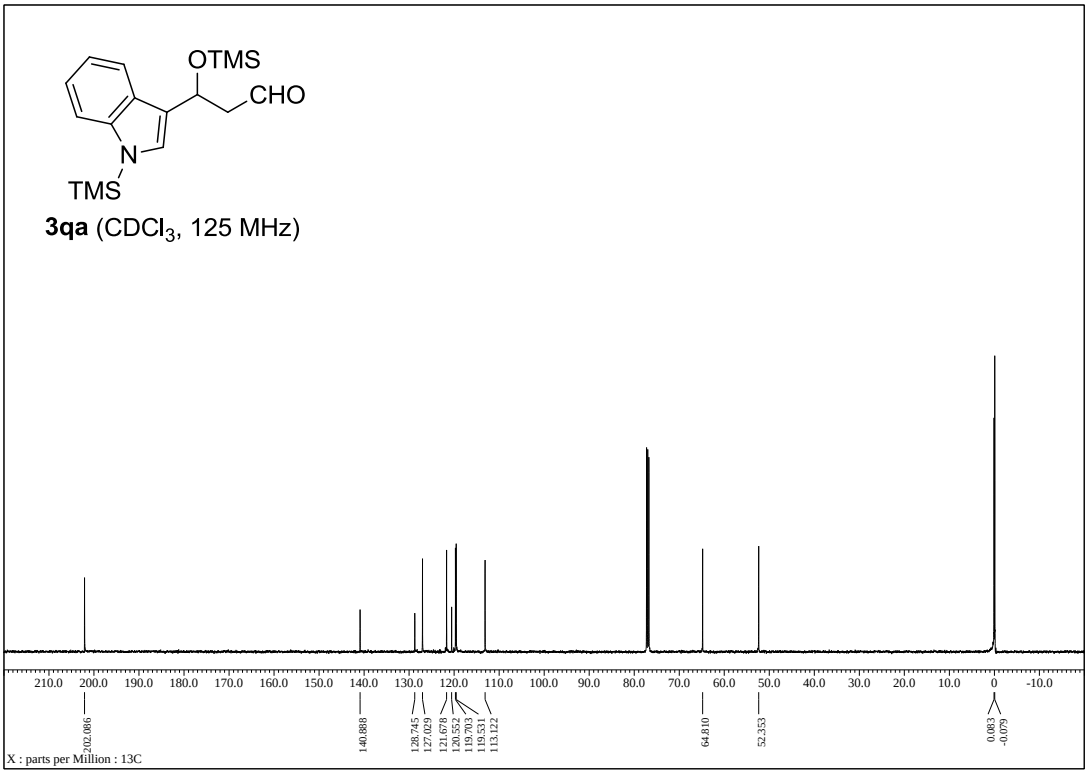
^{13}C NMR of 3-(thiophen-2-yl)-3-((trimethylsilyl)oxy)propanal (**3pa**)



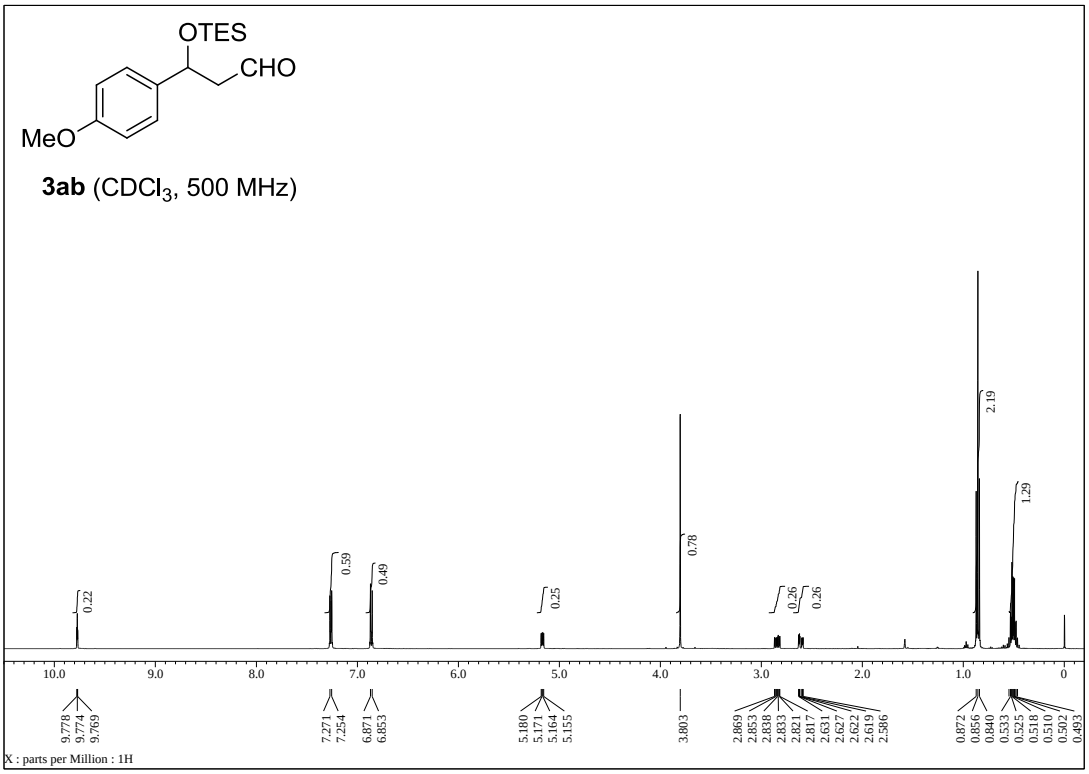
^{1}H NMR of 3-(1-(trimethylsilyl)-1*H*-indol-3-yl)-3-((trimethylsilyl)oxy)propanal (**3qa**)



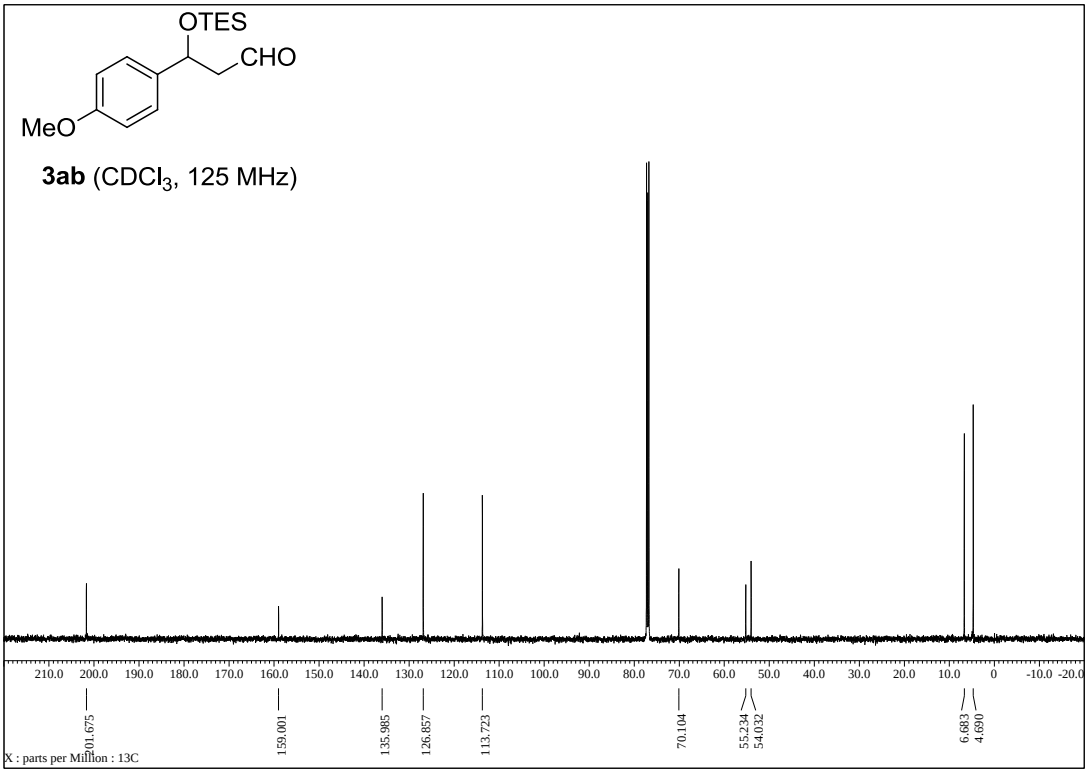
^{13}C NMR of 3-(1-(trimethylsilyl)-1*H*-indol-3-yl)-3-((trimethylsilyl)oxy)propanal (**3qa**)



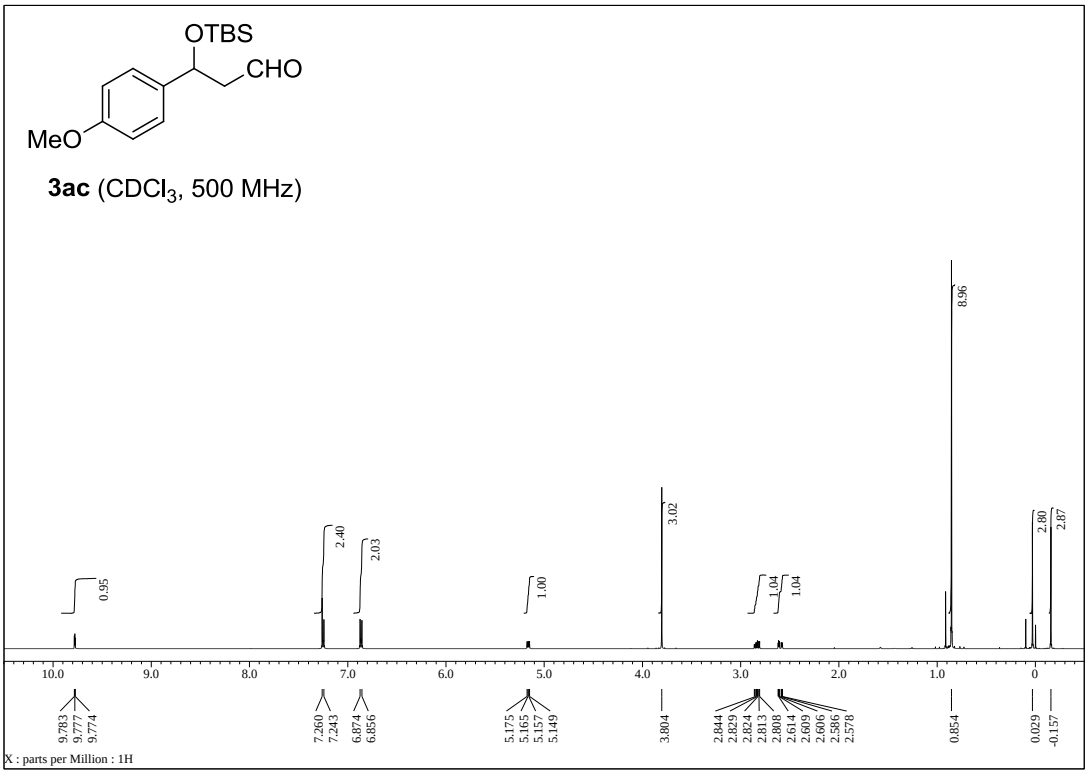
^{1}H NMR of 3-(4-methoxyphenyl)-3-((triethylsilyl)oxy)propanal (**3ab**)



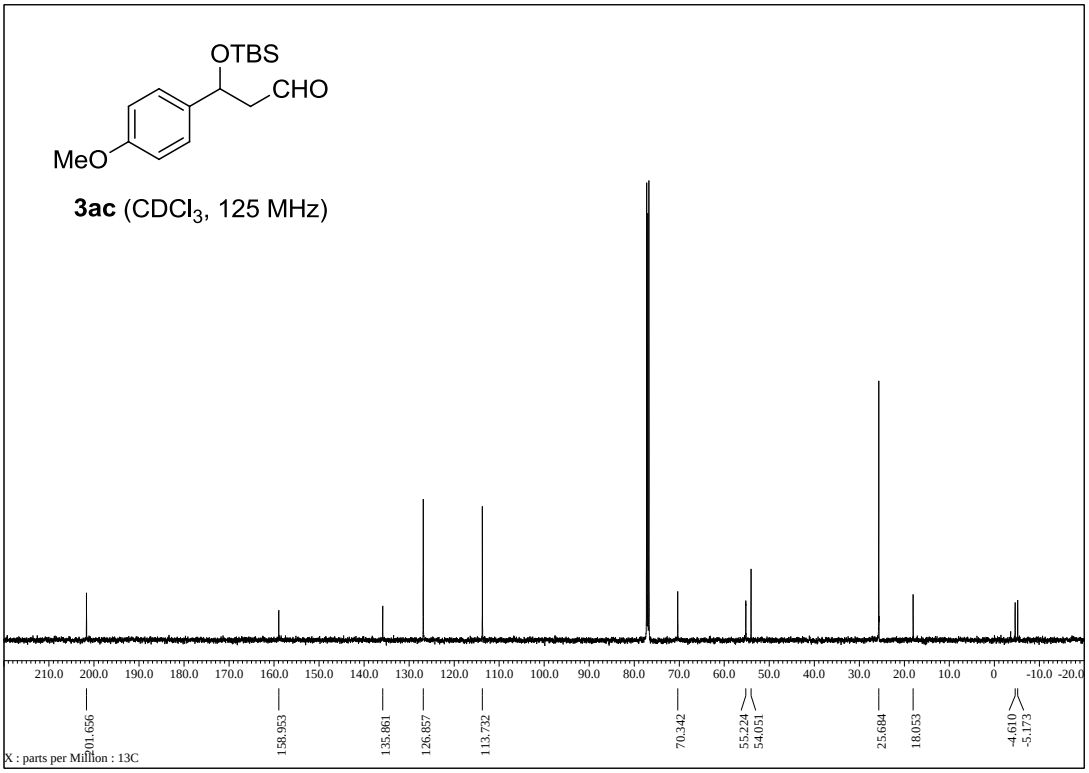
^{13}C NMR of 3-(4-methoxyphenyl)-3-((triethylsilyl)oxy)propanal (**3ab**)



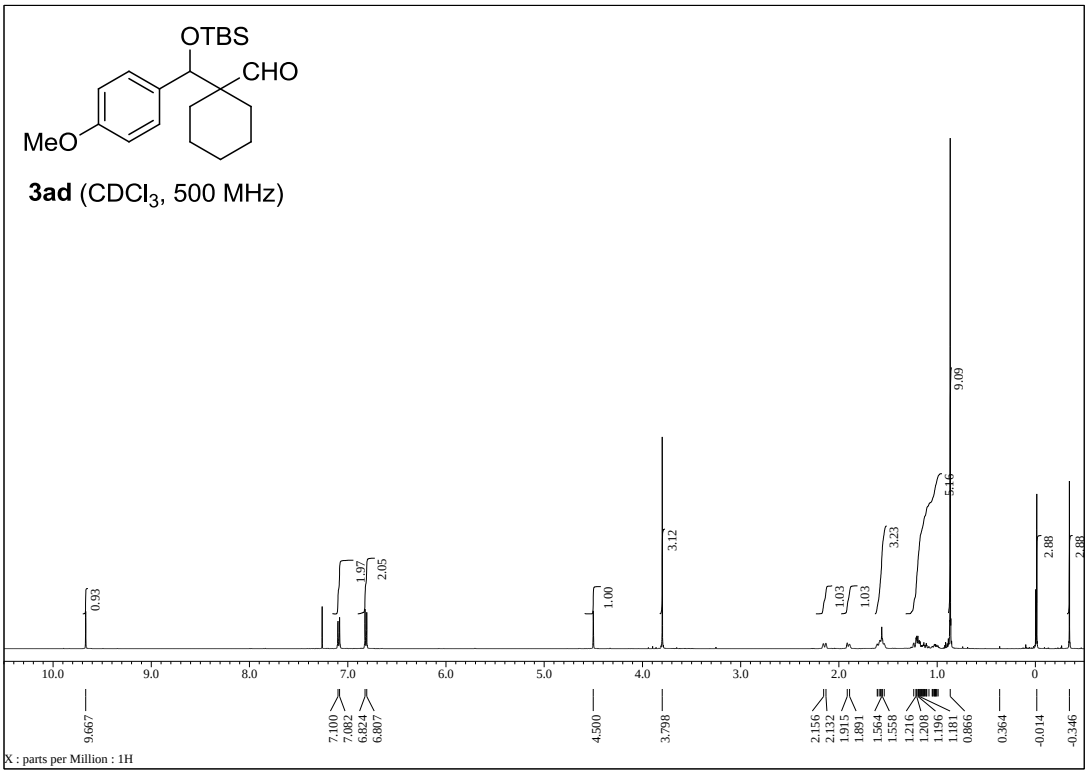
^{1}H NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ac**)



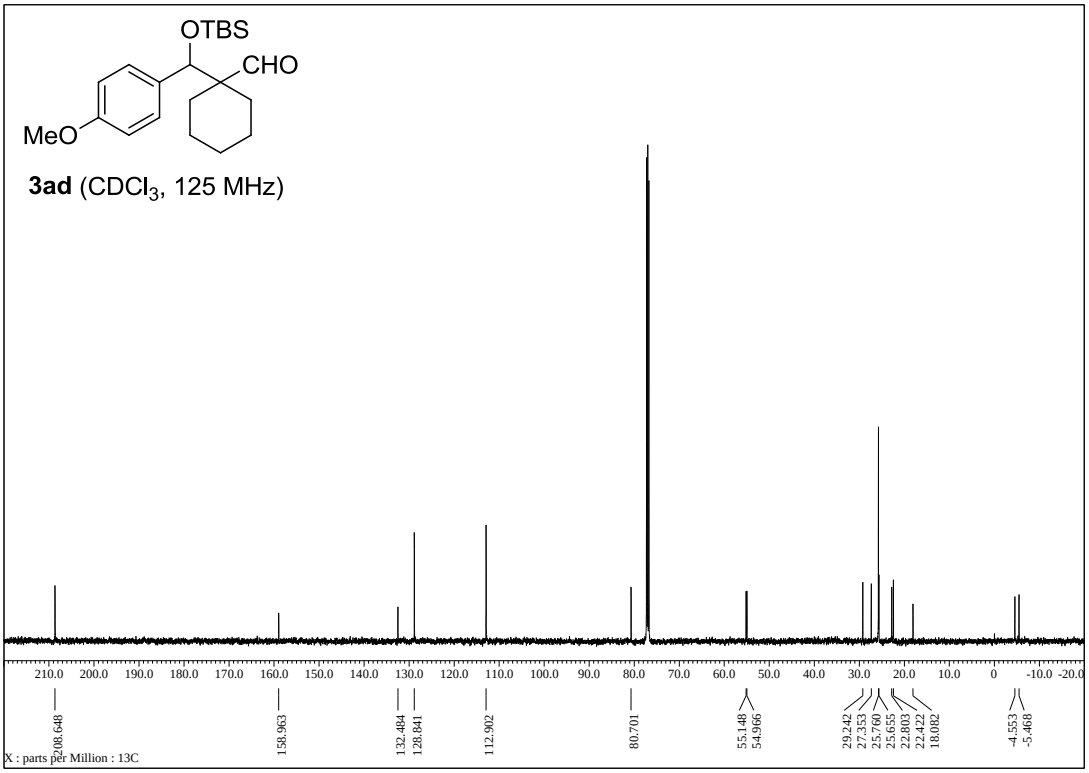
^{13}C NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ac**)



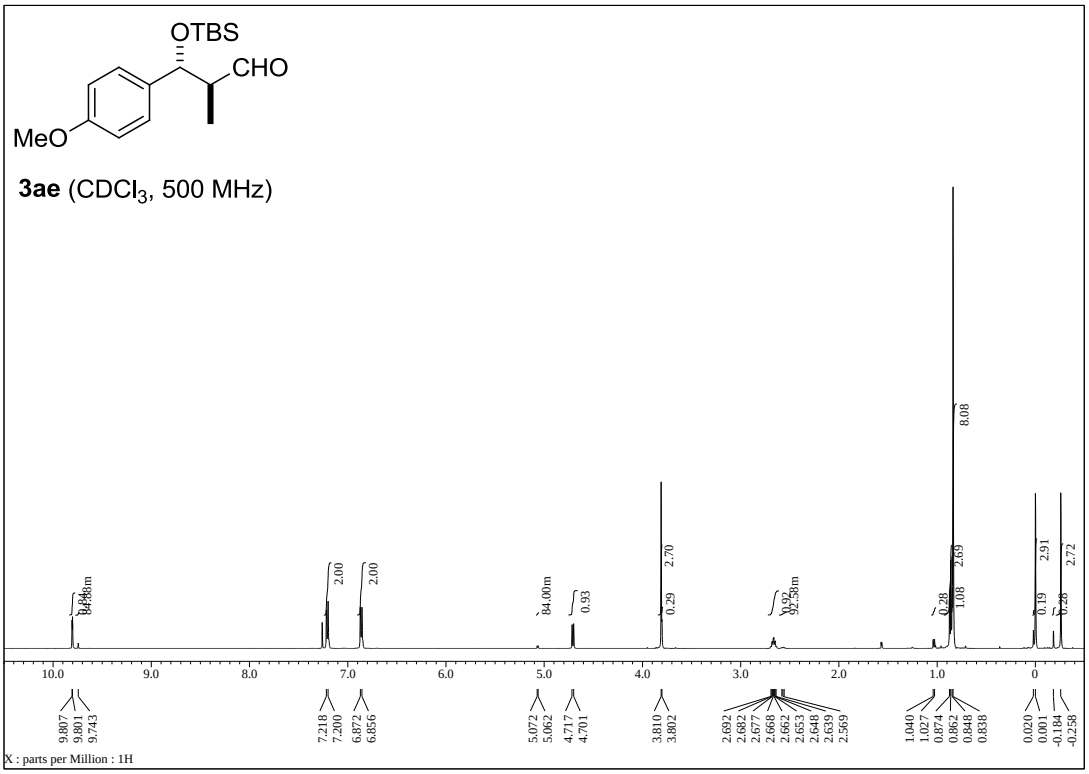
^{1}H NMR of 1-(((*tert*-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)cyclohexanecarbaldehyde (**3ad**)



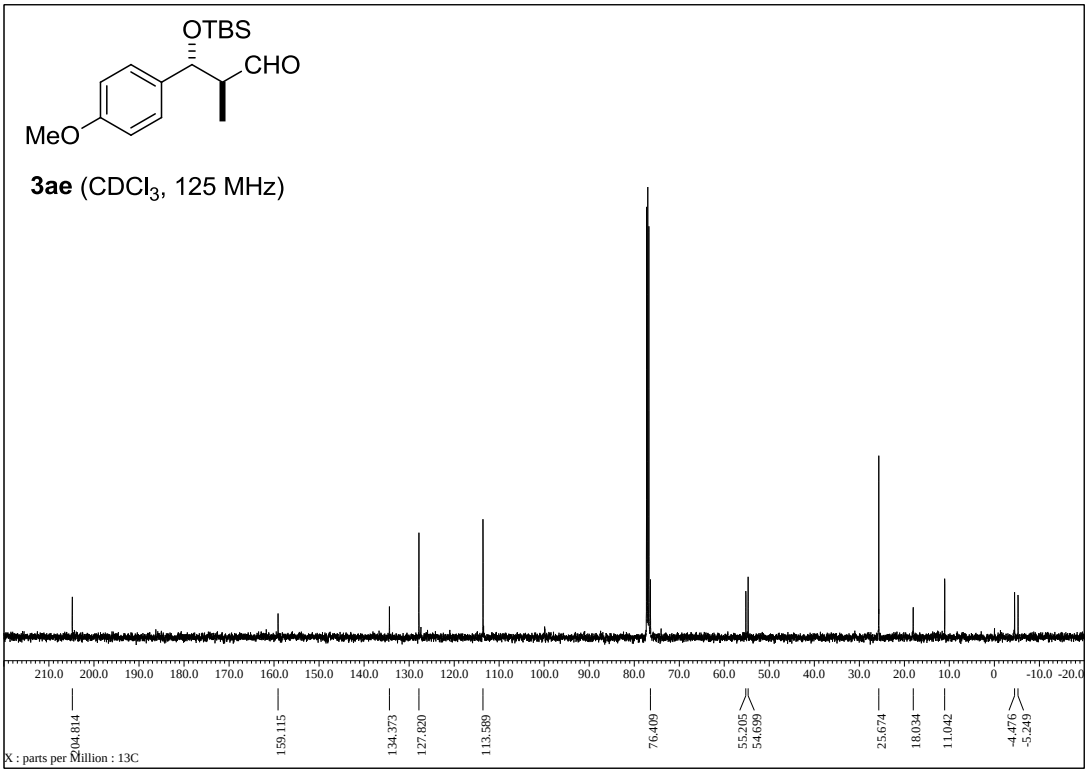
^{13}C NMR of 1-(((*tert*-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)cyclohexanecarbaldehyde (**3ad**)



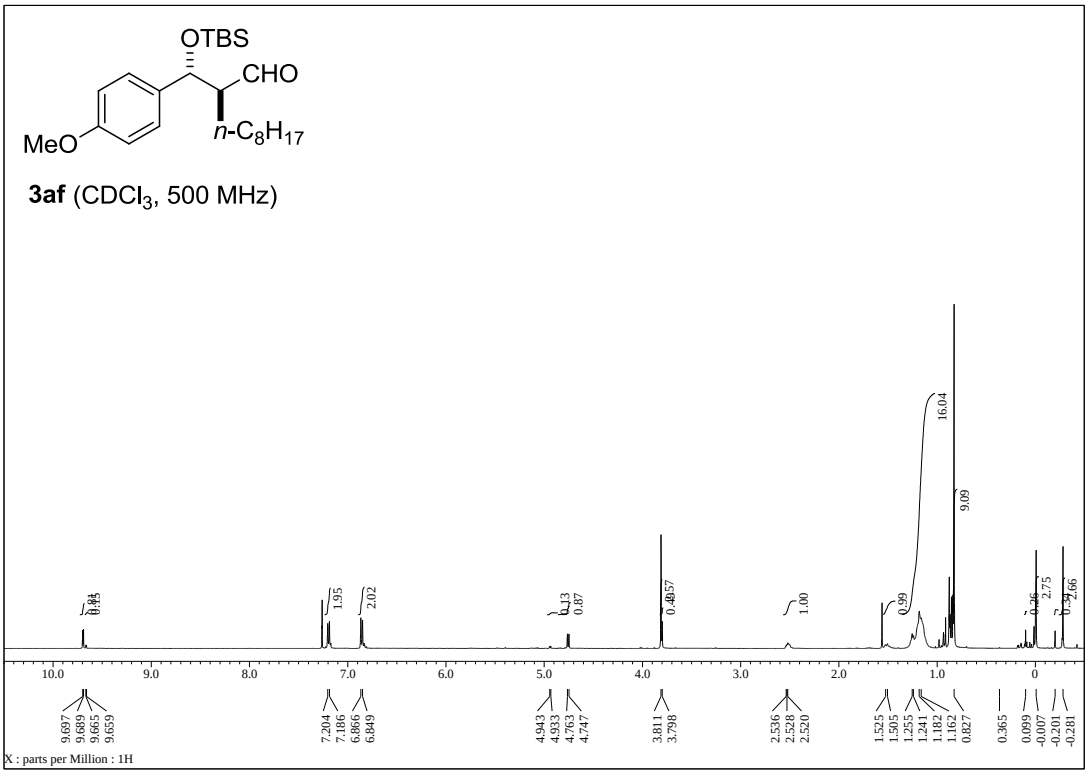
^{1}H NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-methylpropanal (**3ae**)



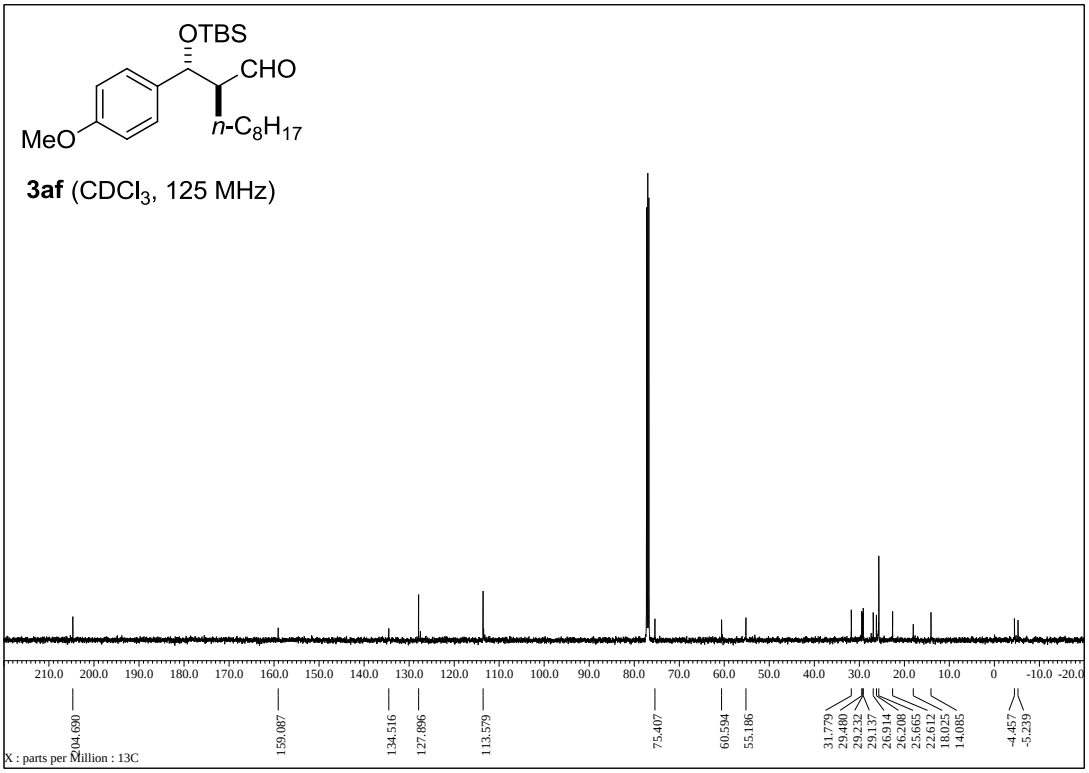
^{13}C NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-methylpropanal (**3ae**)



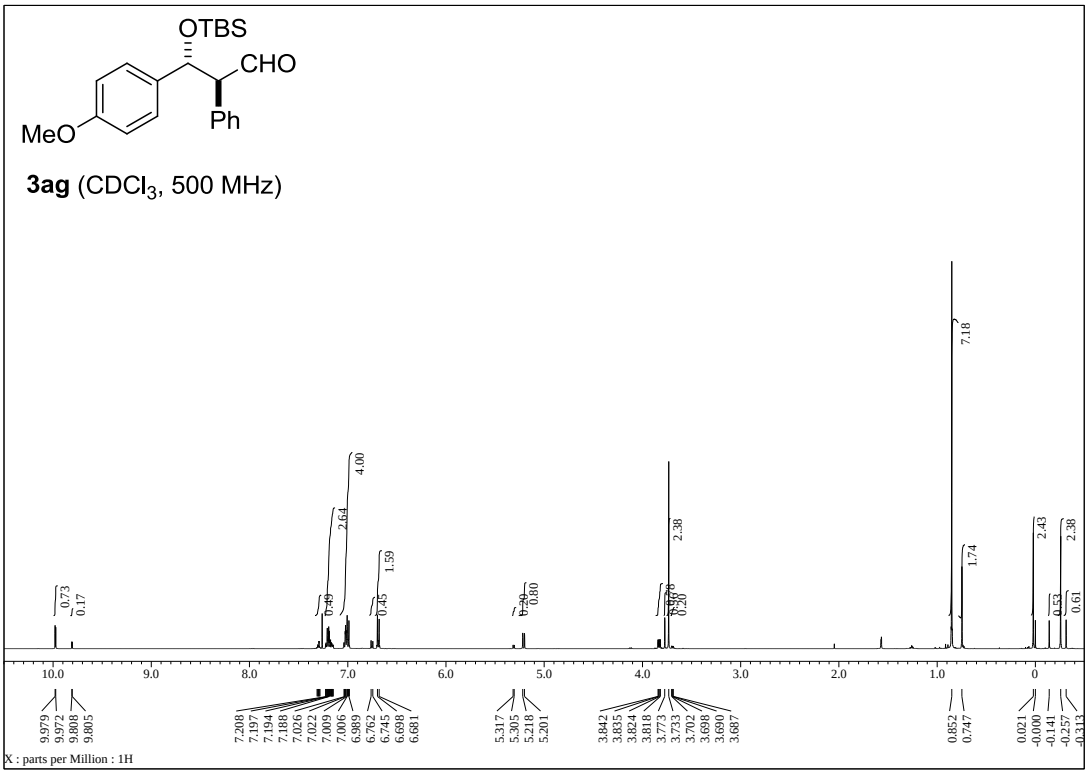
^{1}H NMR of ((tert-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)decanal (**3af**)



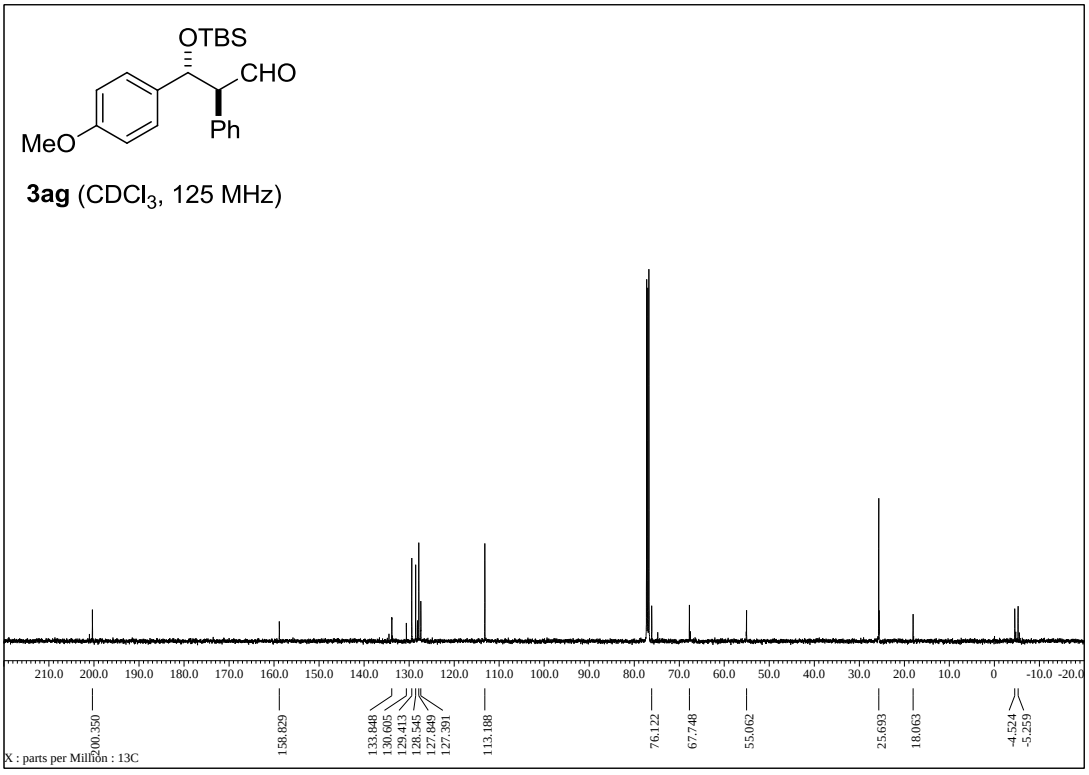
^{13}C NMR of ((tert-butyldimethylsilyl)oxy)(4-methoxyphenyl)methyl)decanal (**3af**)



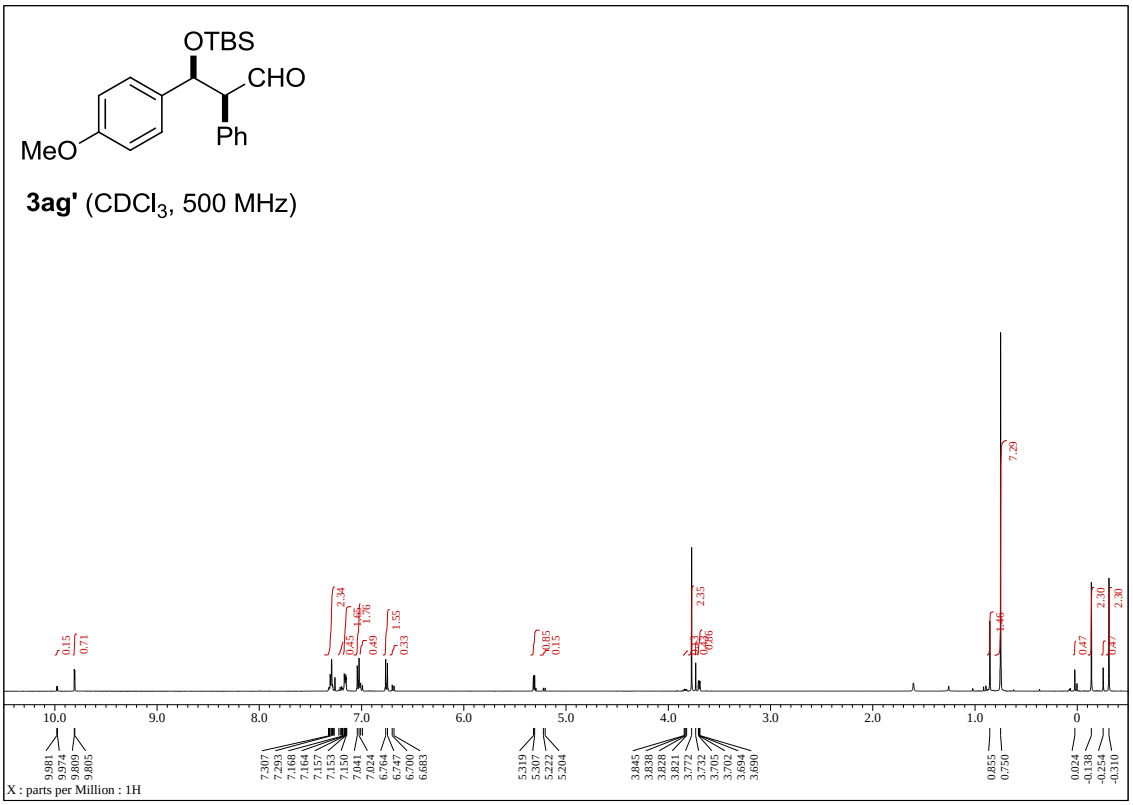
^{1}H NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag**)



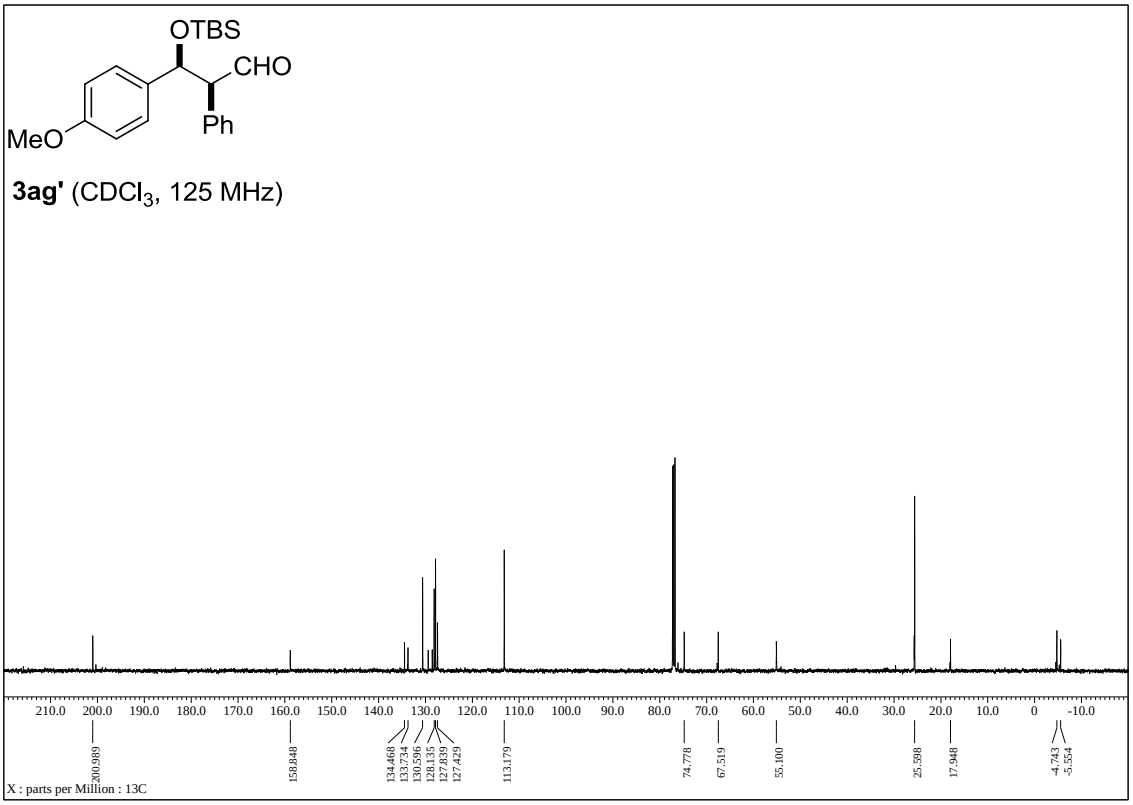
^{13}C NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag**)



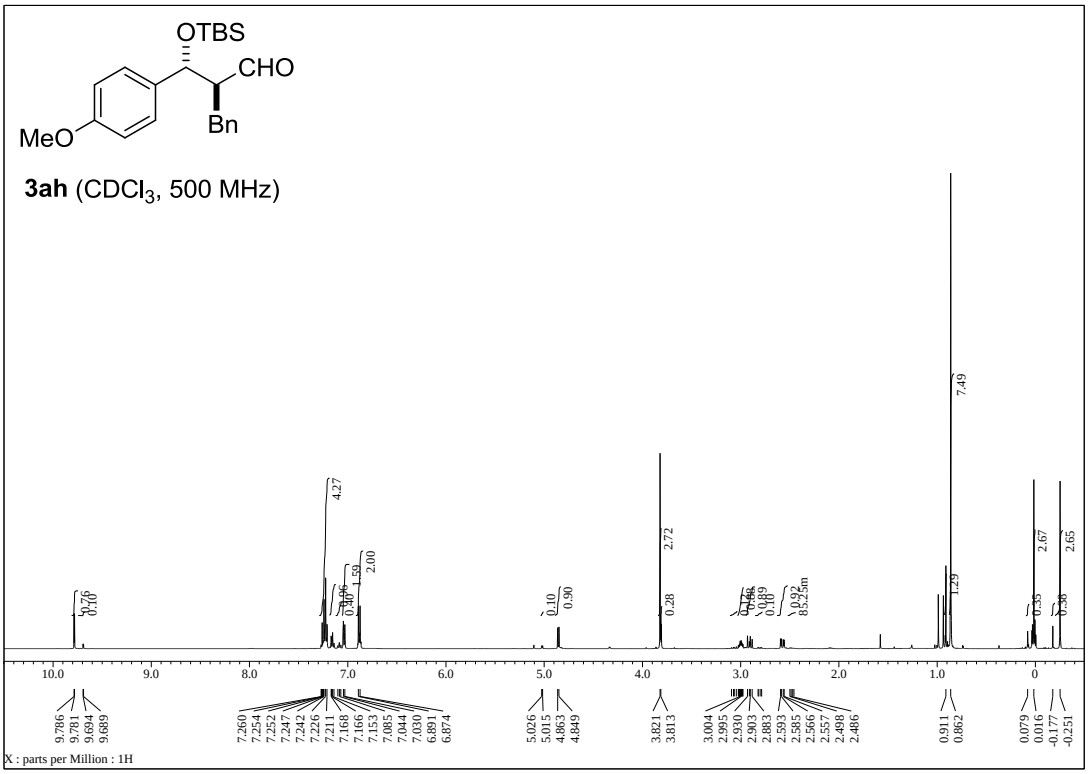
^{1}H NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag'**)



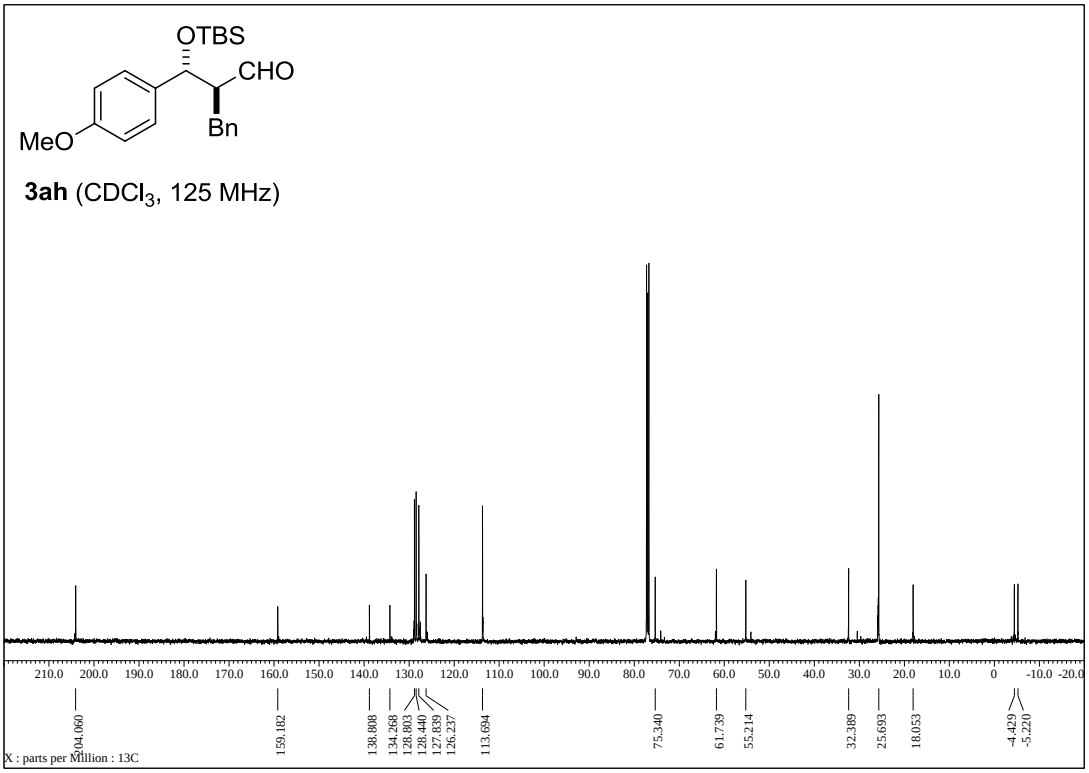
^{13}C NMR of 3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropanal (**3ag'**)



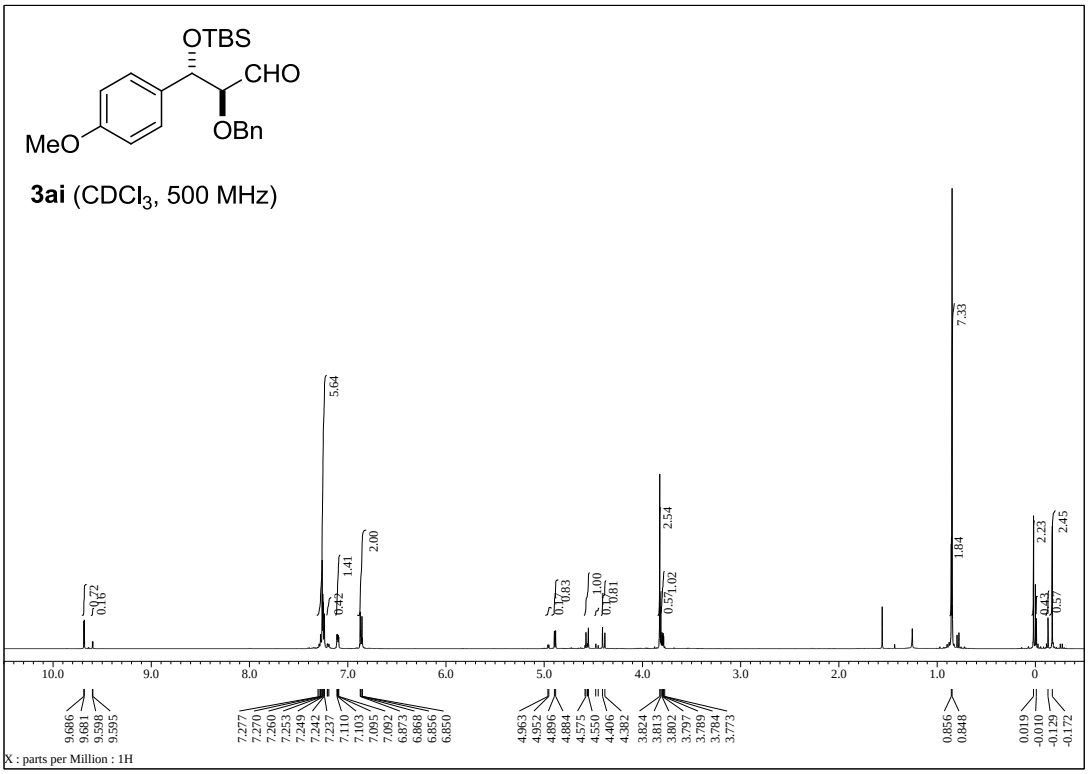
^{1}H NMR of 2-benzyl-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ah**)



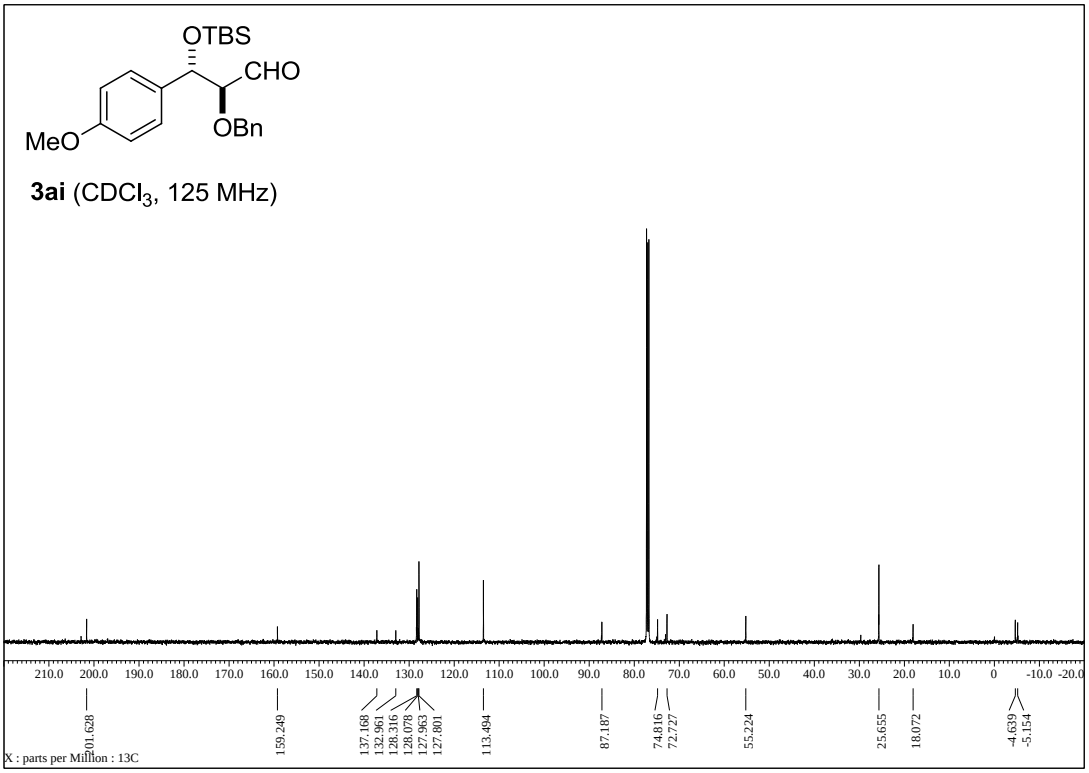
^{13}C NMR of 2-benzyl-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ah**)



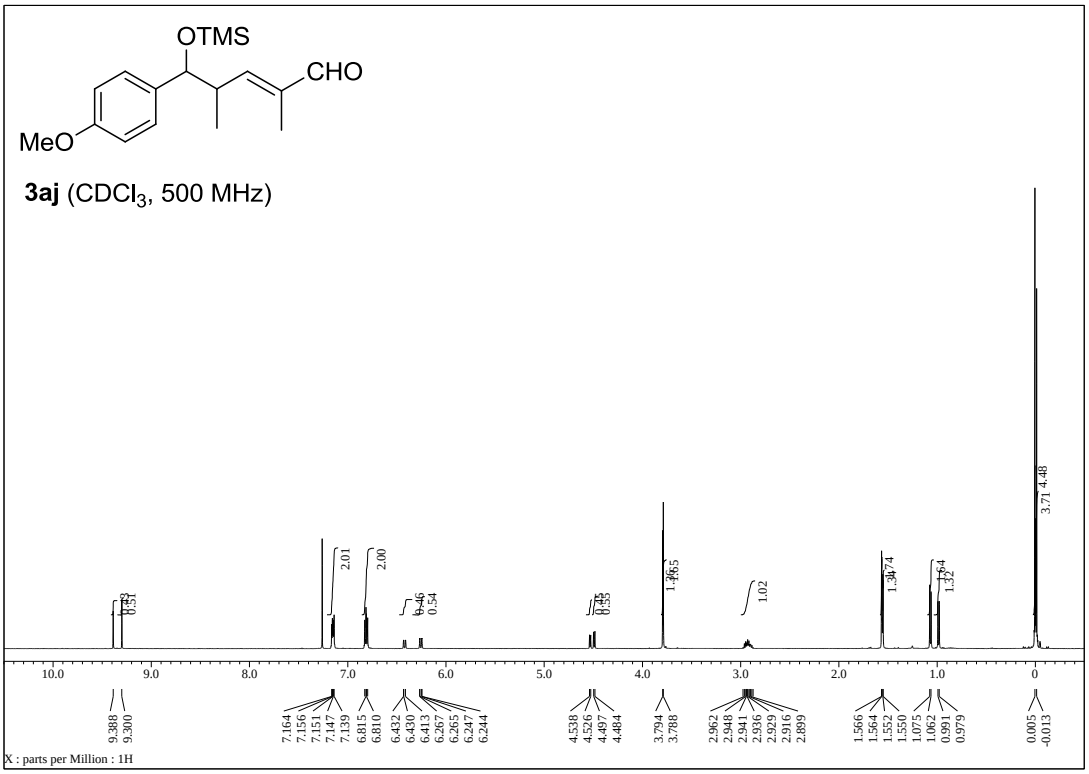
^{1}H NMR of 2-(benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ai**)



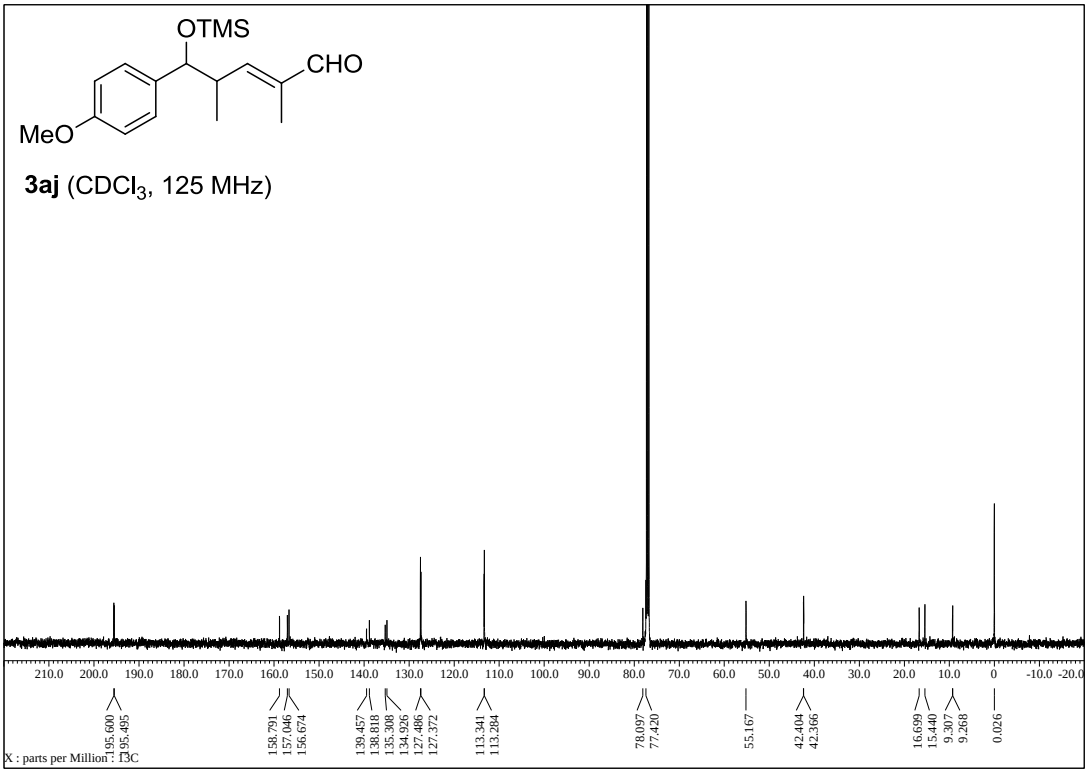
^{13}C NMR of 2-(benzyloxy)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)propanal (**3ai**)



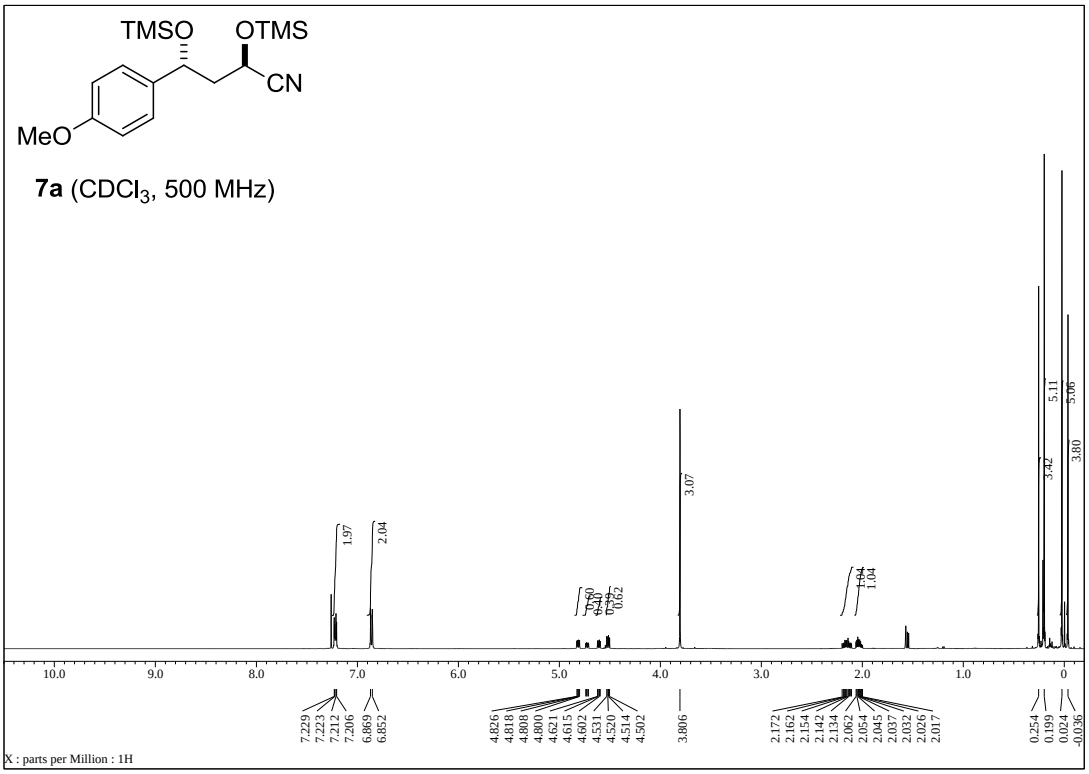
^{1}H NMR of (*E*)-5-(4-methoxyphenyl)-2,4-dimethyl-5-((trimethylsilyl)oxy)pent-2-enal (**3aj**)



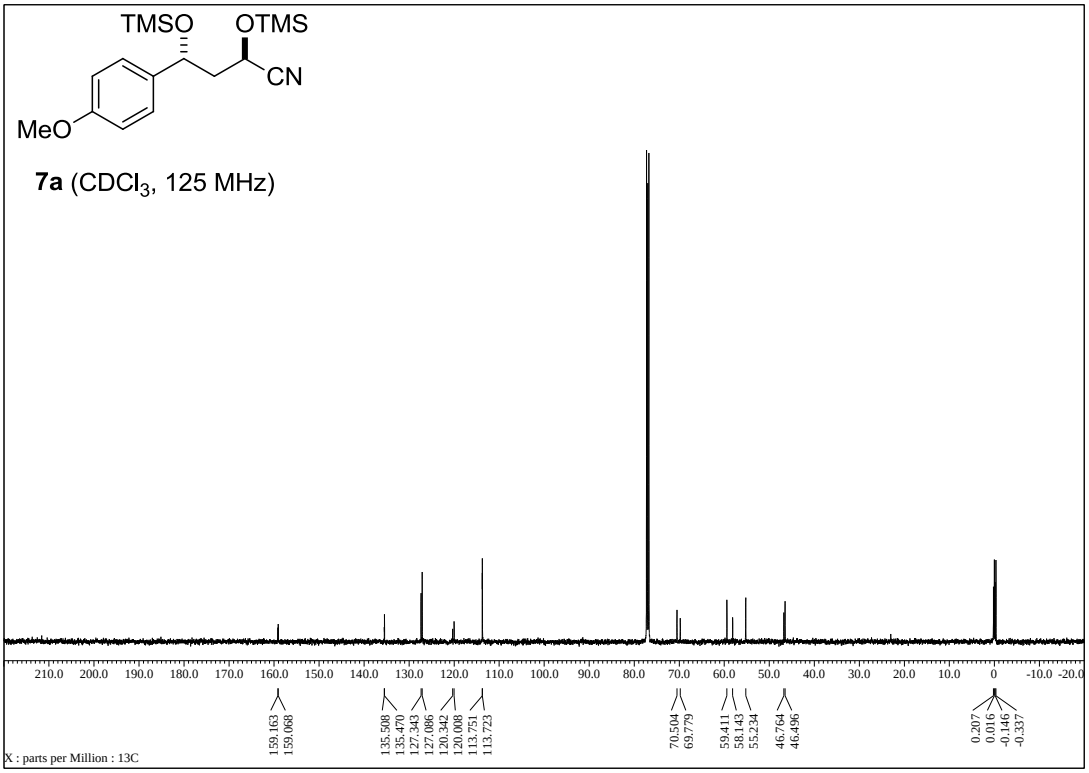
^{13}C NMR of (*E*)-5-(4-methoxyphenyl)-2,4-dimethyl-5-((trimethylsilyl)oxy)pent-2-enal (**3aj**)



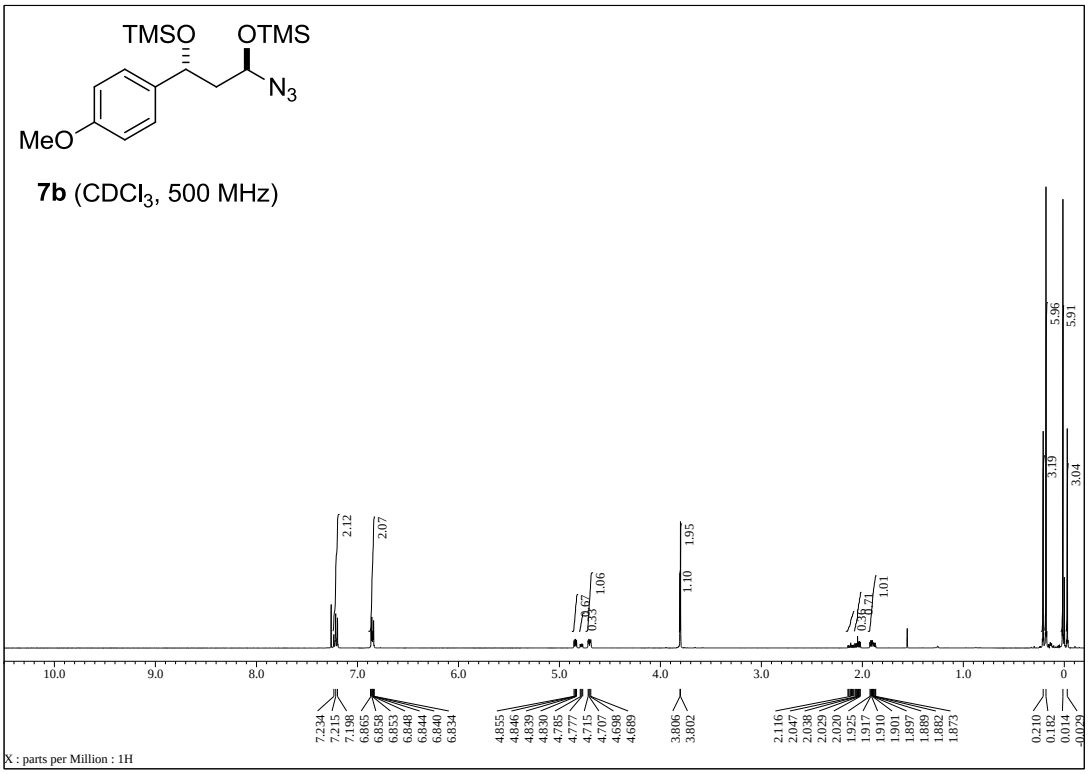
^{1}H NMR of 4-(4-methoxyphenyl)-2,4-bis((trimethylsilyl)oxy)butanenitrile (**7a**)



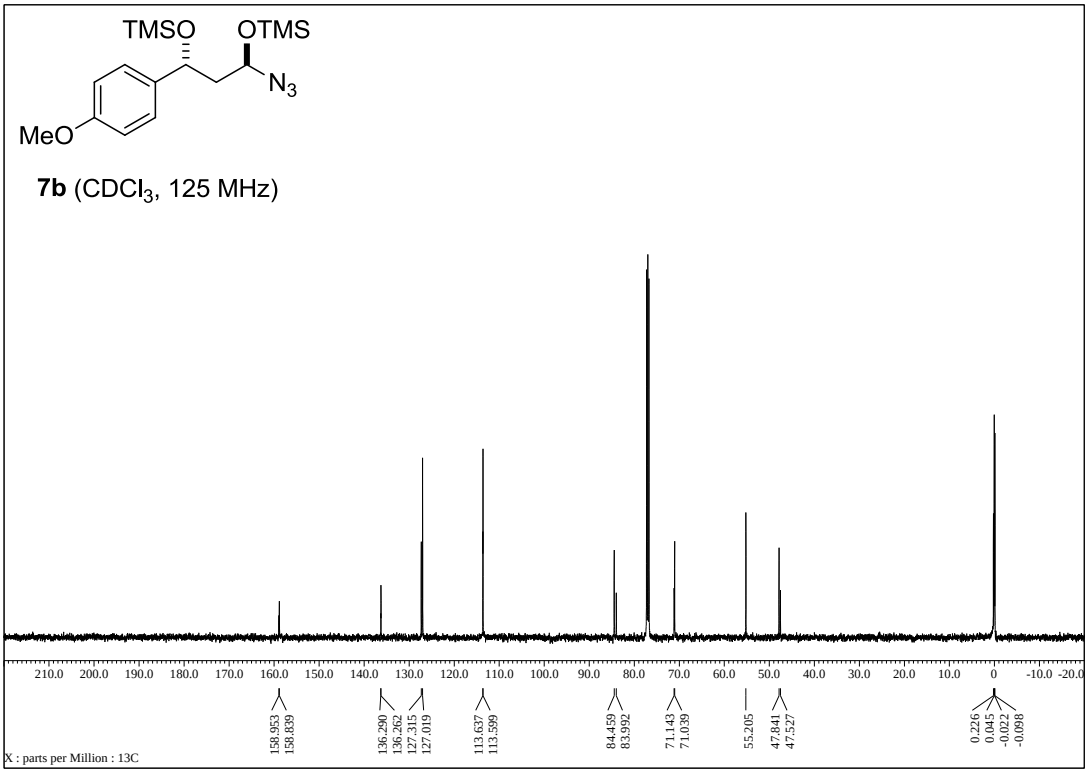
^{13}C NMR of 4-(4-methoxyphenyl)-2,4-bis((trimethylsilyl)oxy)butanenitrile (**7a**)



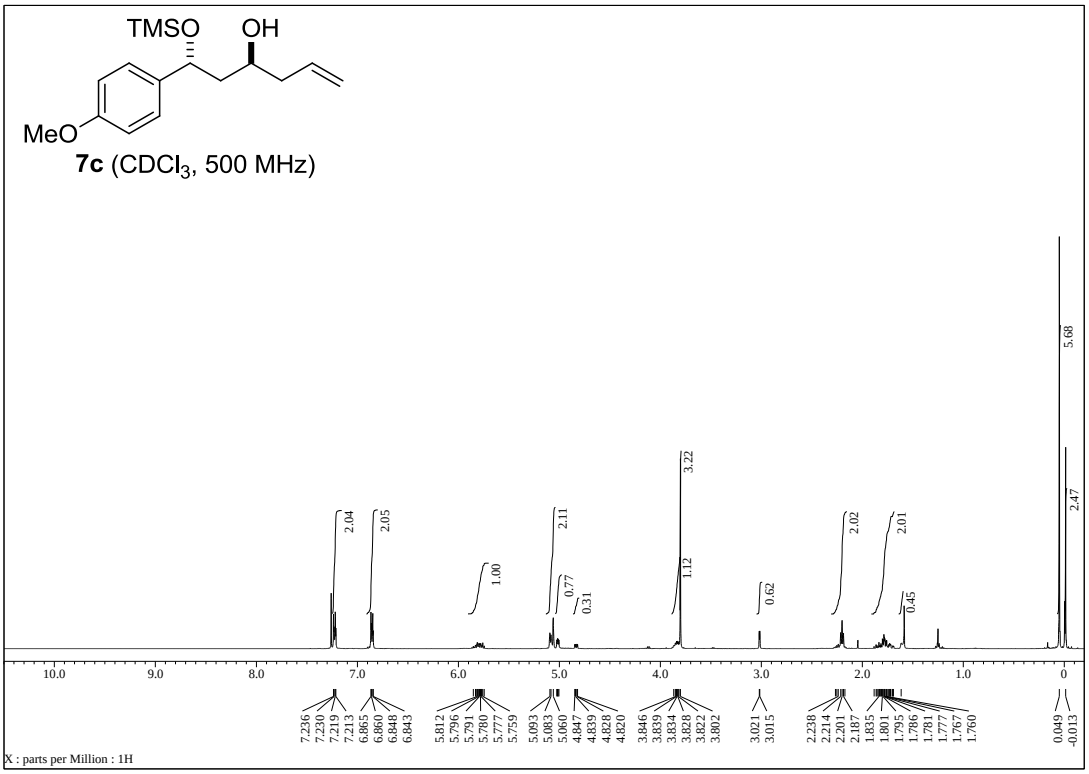
^{1}H NMR of 4-azido-6-(4-methoxyphenyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane (**7b**)



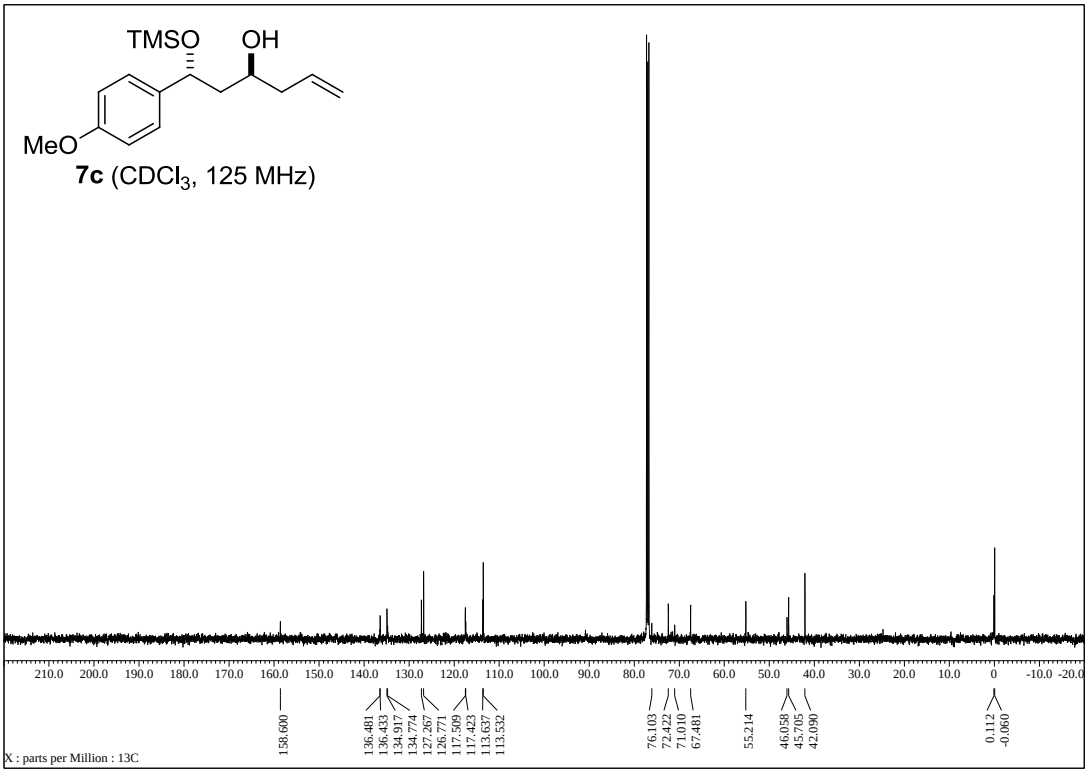
^{13}C NMR of 4-azido-6-(4-methoxyphenyl)-2,2,8,8-tetramethyl-3,7-dioxa-2,8-disilanonane (**7b**)



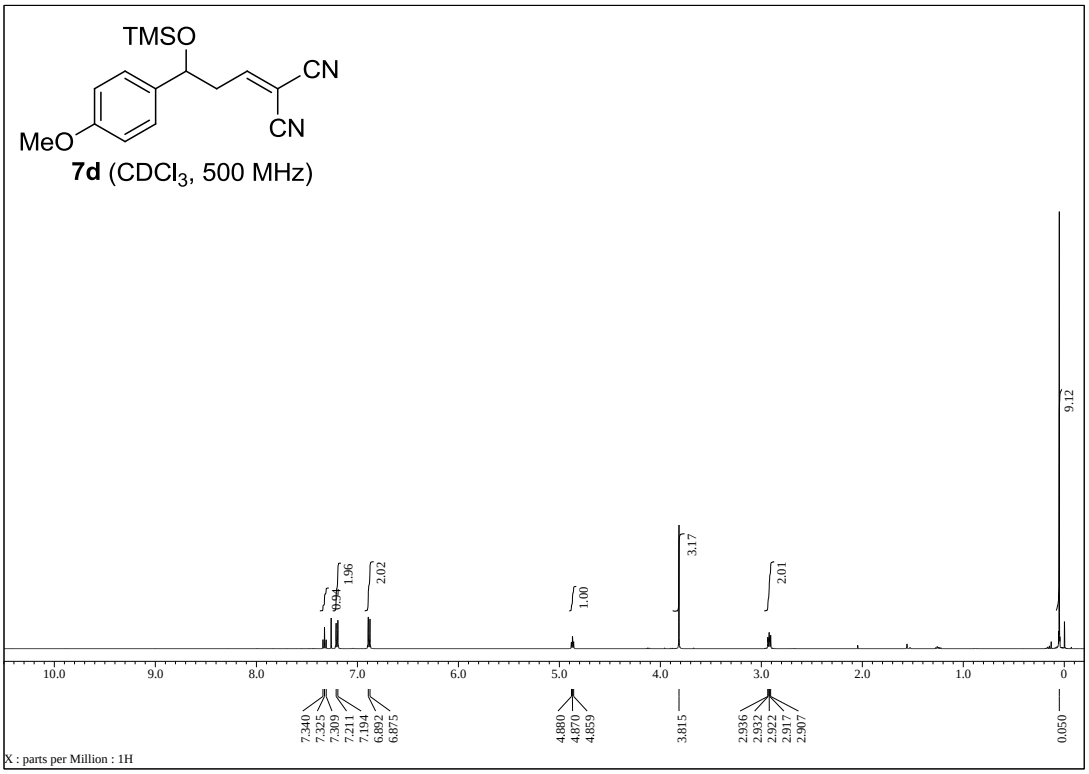
^{1}H NMR of 1-(4-methoxyphenyl)-1-((trimethylsilyl)oxy)hex-5-en-3-ol (**7c**)



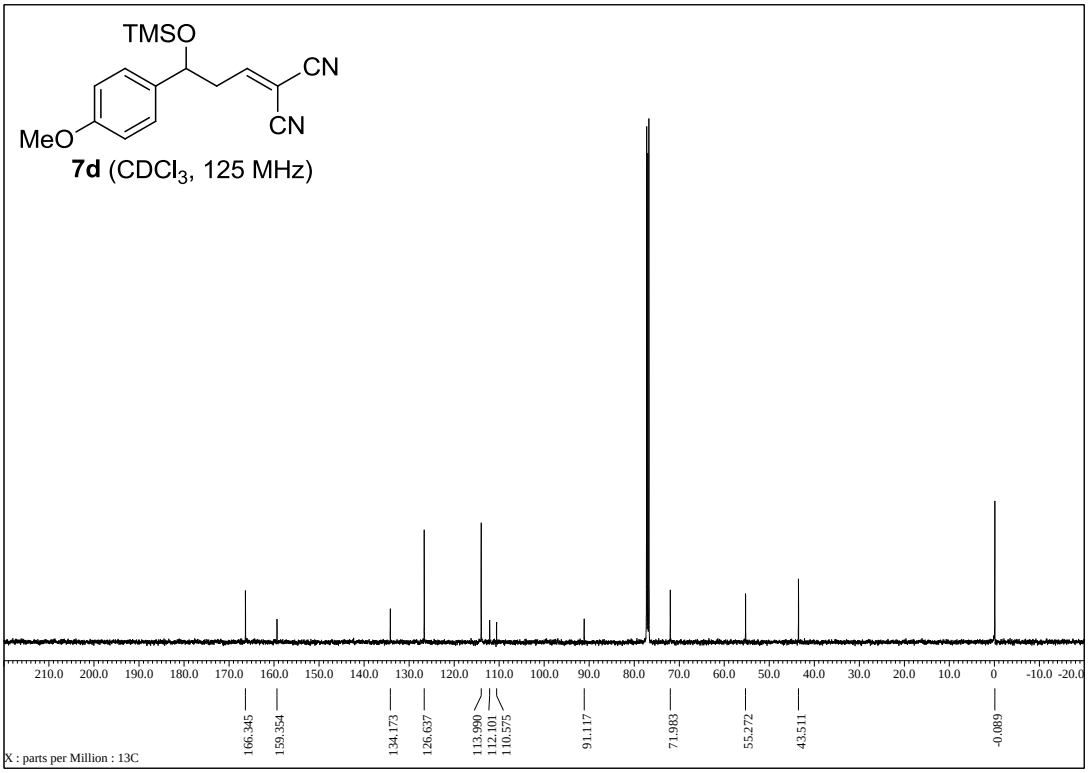
^{13}C NMR of 1-(4-methoxyphenyl)-1-((trimethylsilyl)oxy)hex-5-en-3-ol (**7c**)



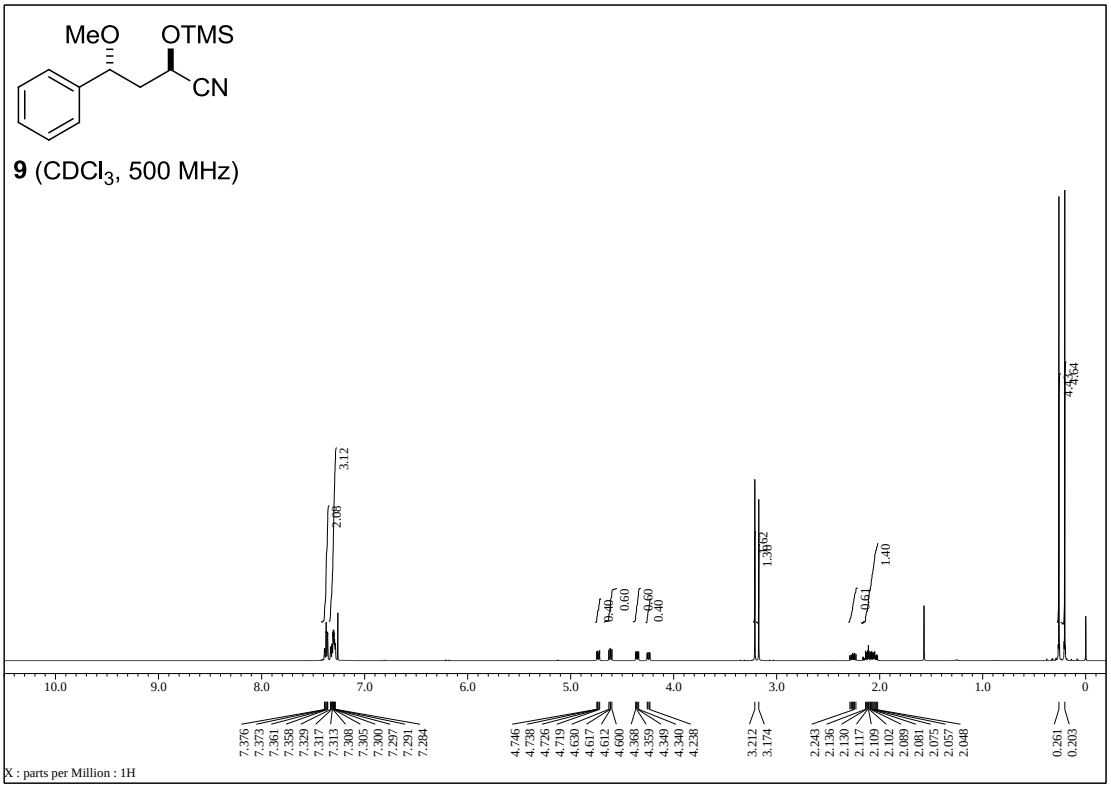
^{1}H NMR of 2-(3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)propylidene)malononitrile (**7d**)



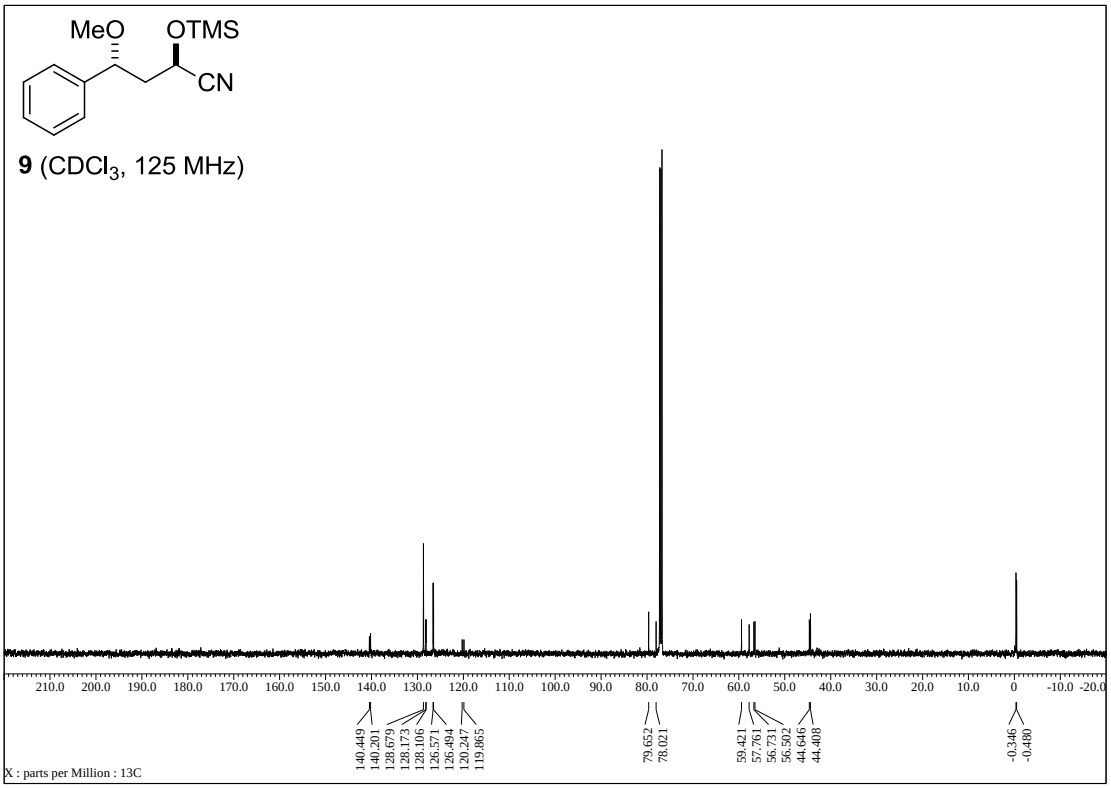
^{13}C NMR of 2-(3-(4-methoxyphenyl)-3-((trimethylsilyl)oxy)propylidene)malononitrile (**7d**)



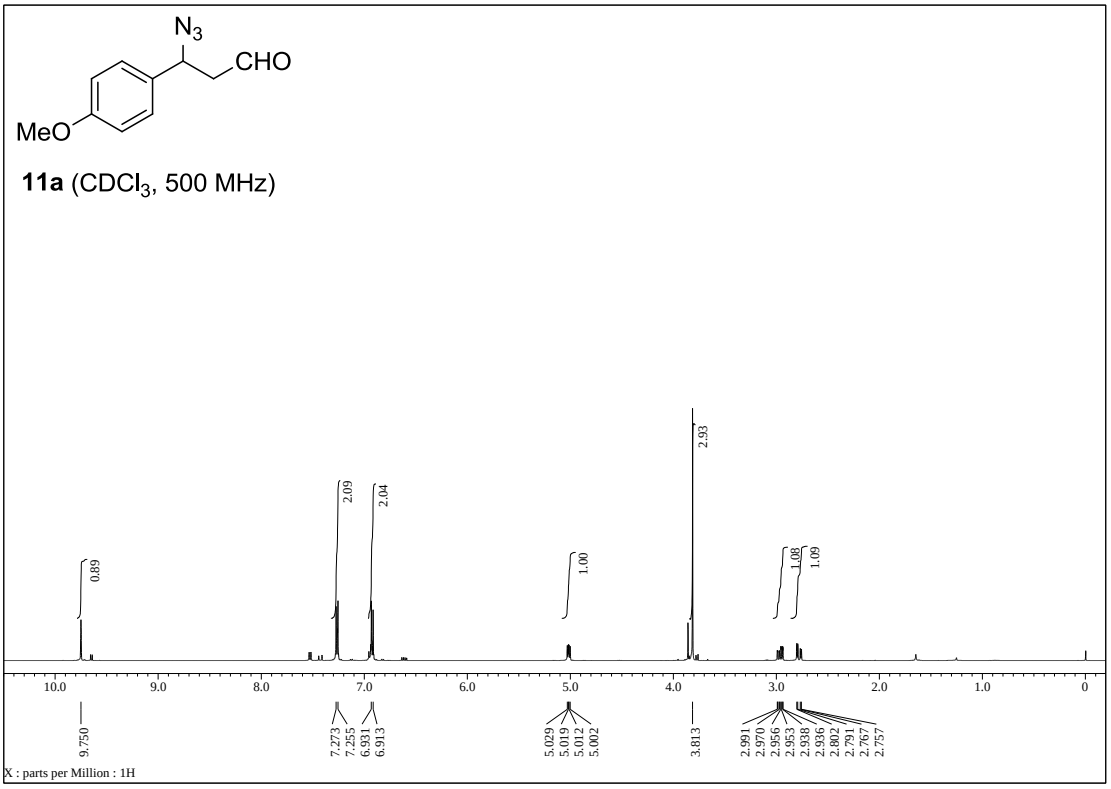
^{1}H NMR of 4-methoxy-4-phenyl-2-((trimethylsilyl)oxy)butanenitrile (**9**)



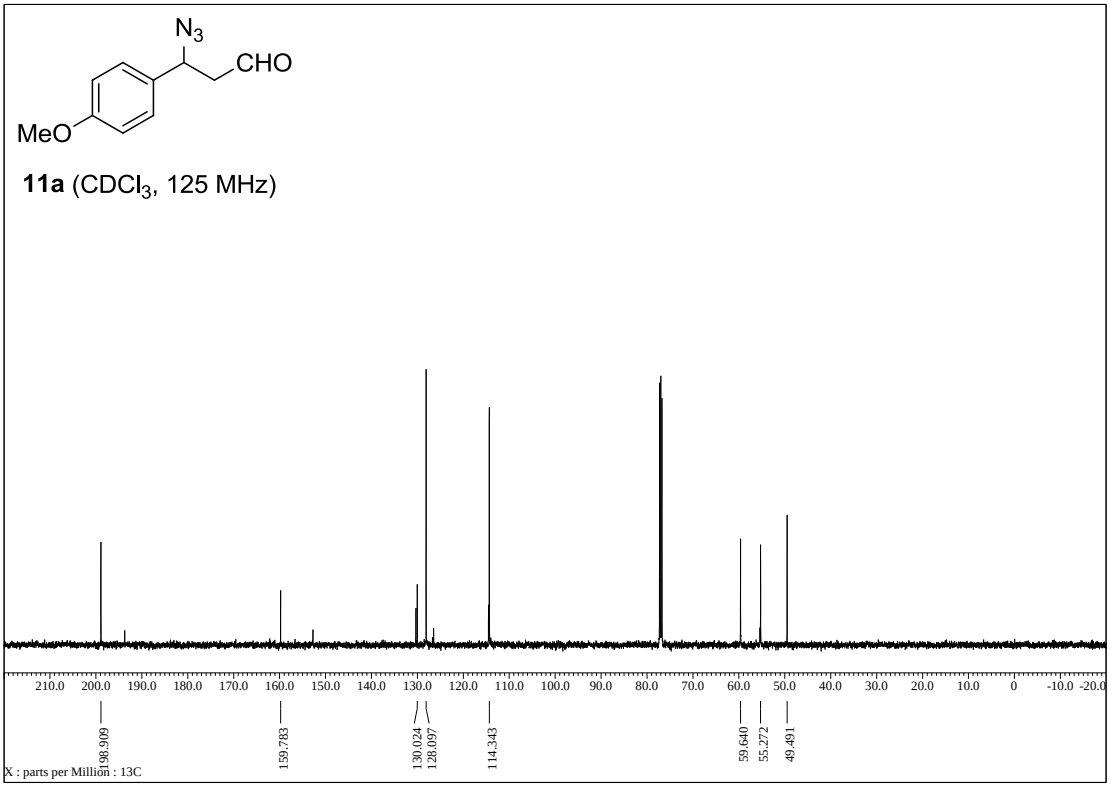
^{13}C NMR of 4-methoxy-4-phenyl-2-((trimethylsilyl)oxy)butanenitrile (**9**)



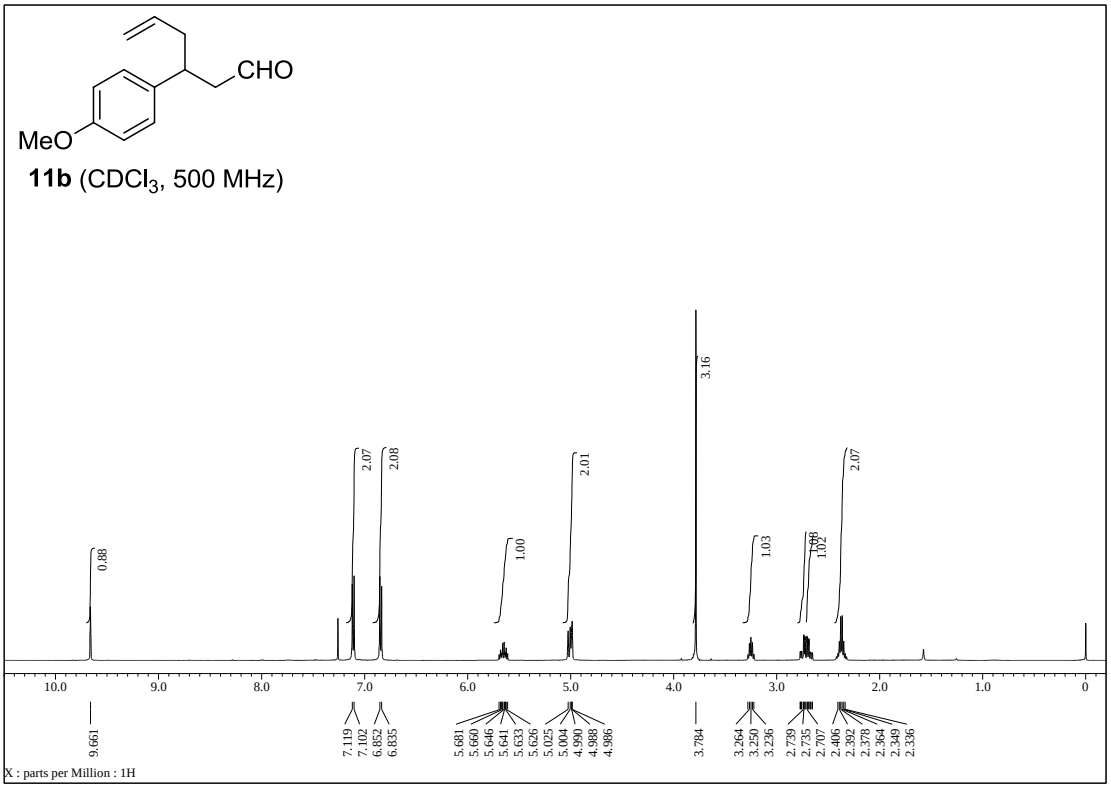
^{1}H NMR of 3-azido-3-(4-methoxyphenyl)propanal (**11a**)



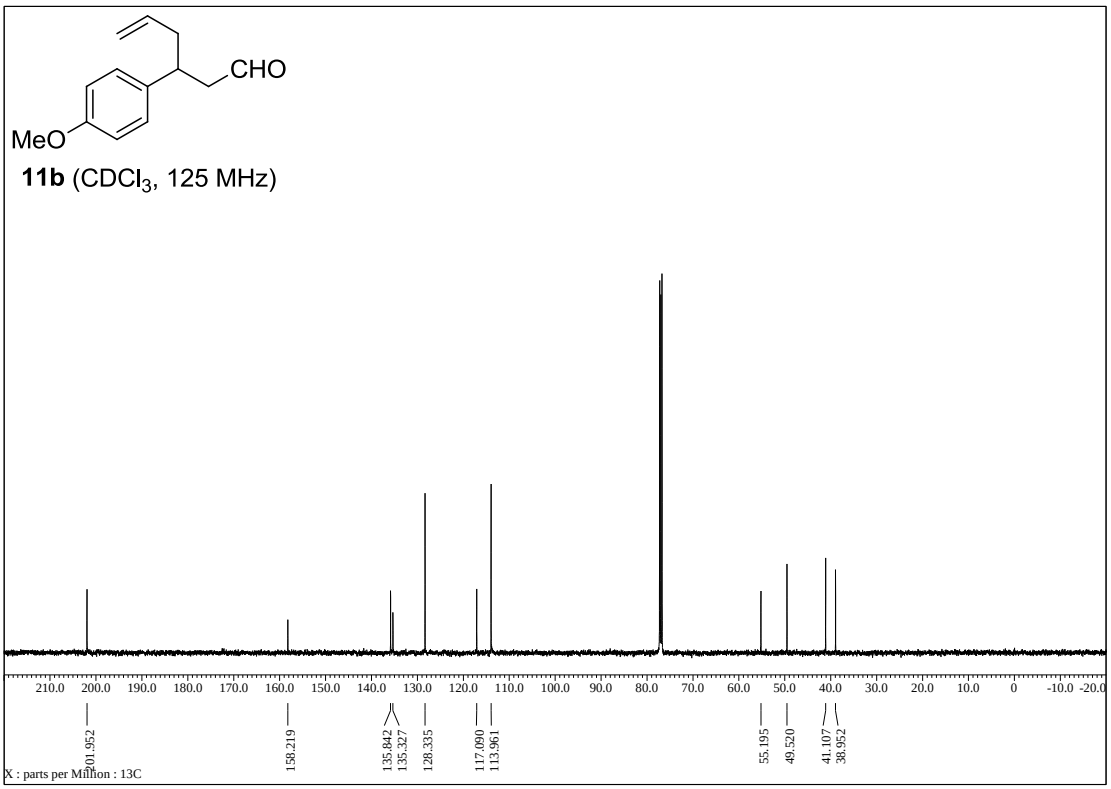
^{13}C NMR of 3-azido-3-(4-methoxyphenyl)propanal (**11a**)



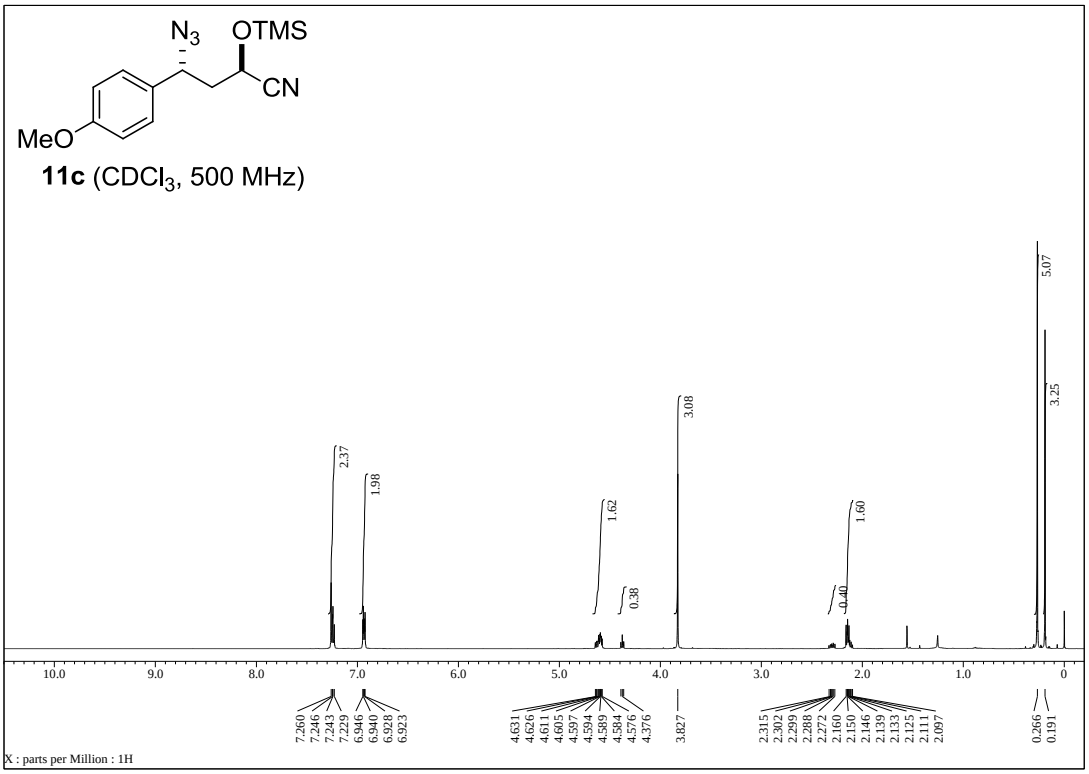
^{1}H NMR of 3-(4-methoxyphenyl)hex-5-enal (**11b**)



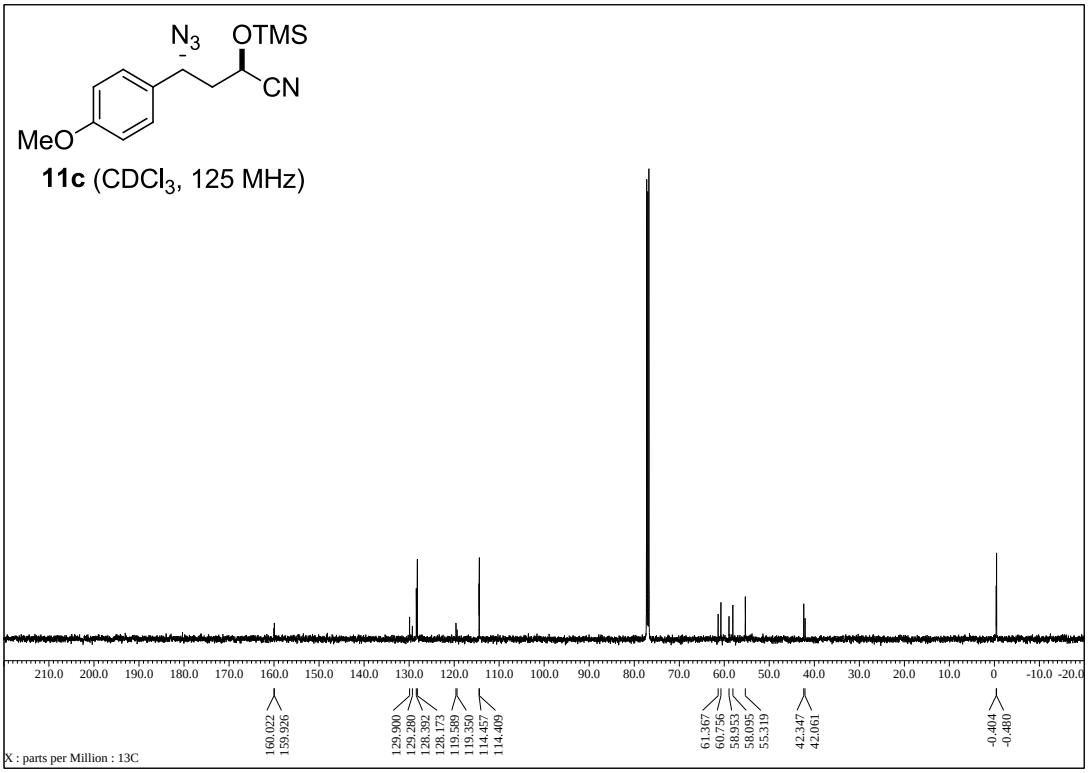
^{13}C NMR of 3-(4-methoxyphenyl)hex-5-enal (**11b**)



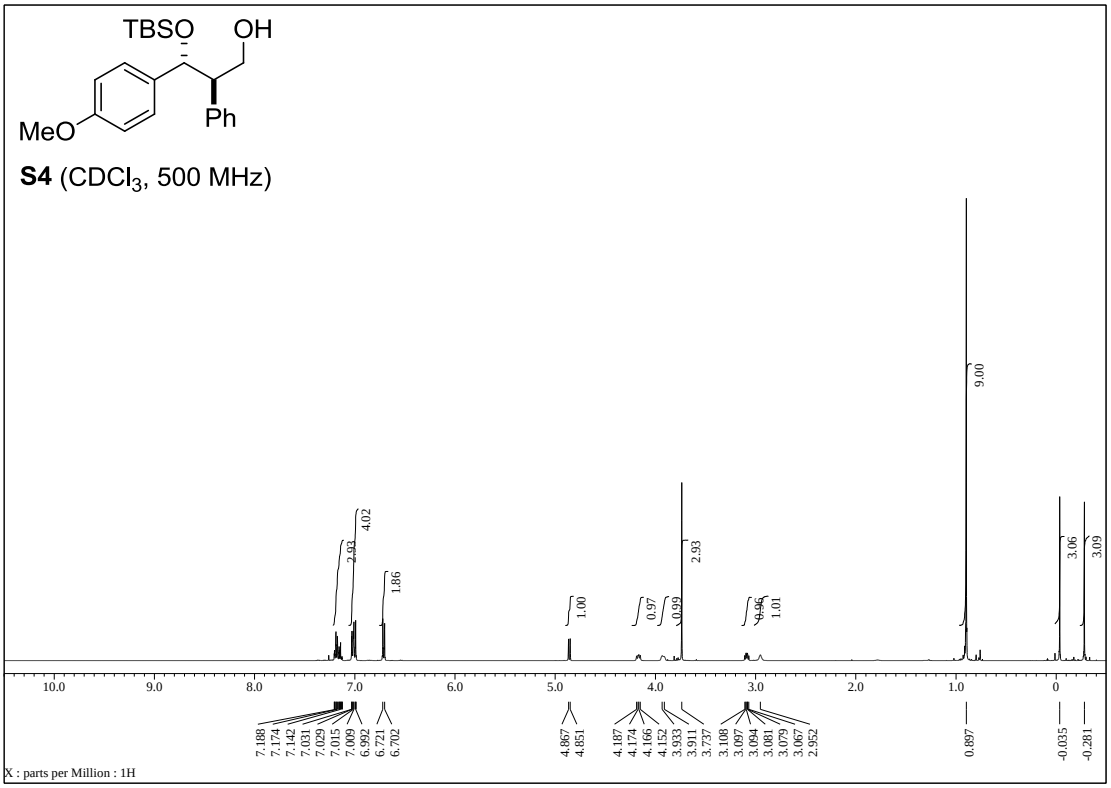
^{1}H NMR of 4-azido-4-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)butanenitrile (**11c**)



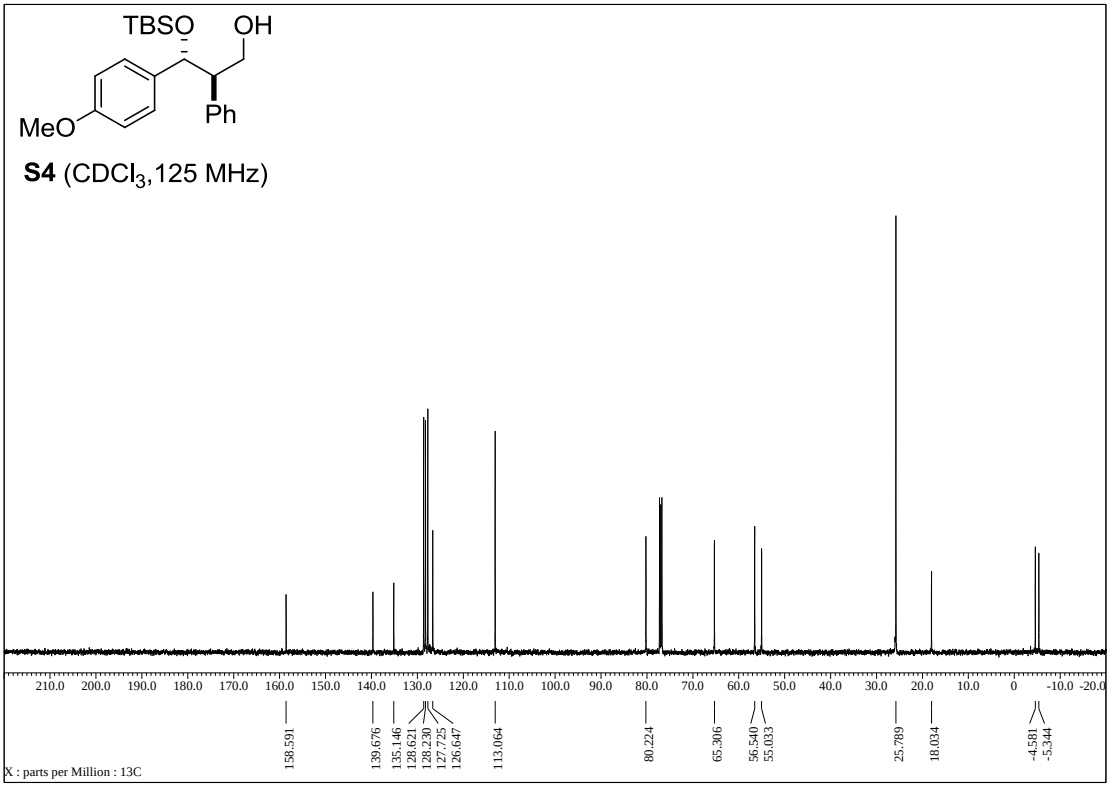
^{13}C NMR of 4-azido-4-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)butanenitrile (**11c**)



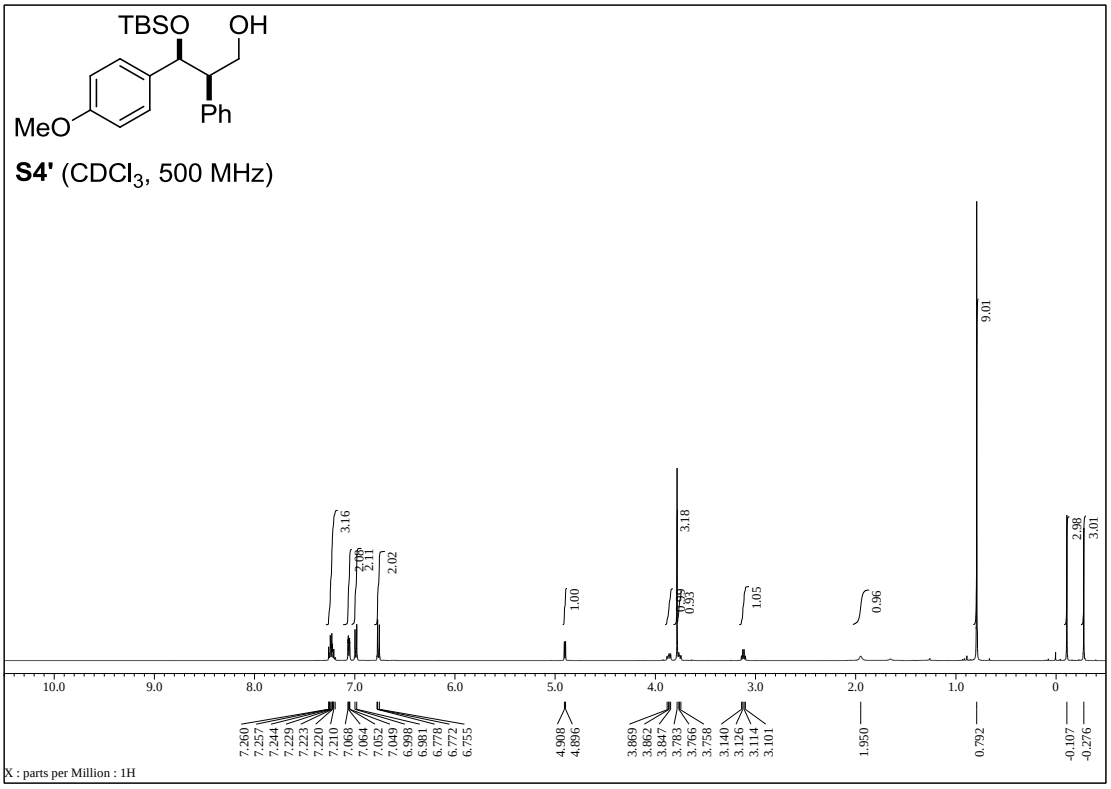
^{1}H NMR of (*2R,3R*)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (**S4**)



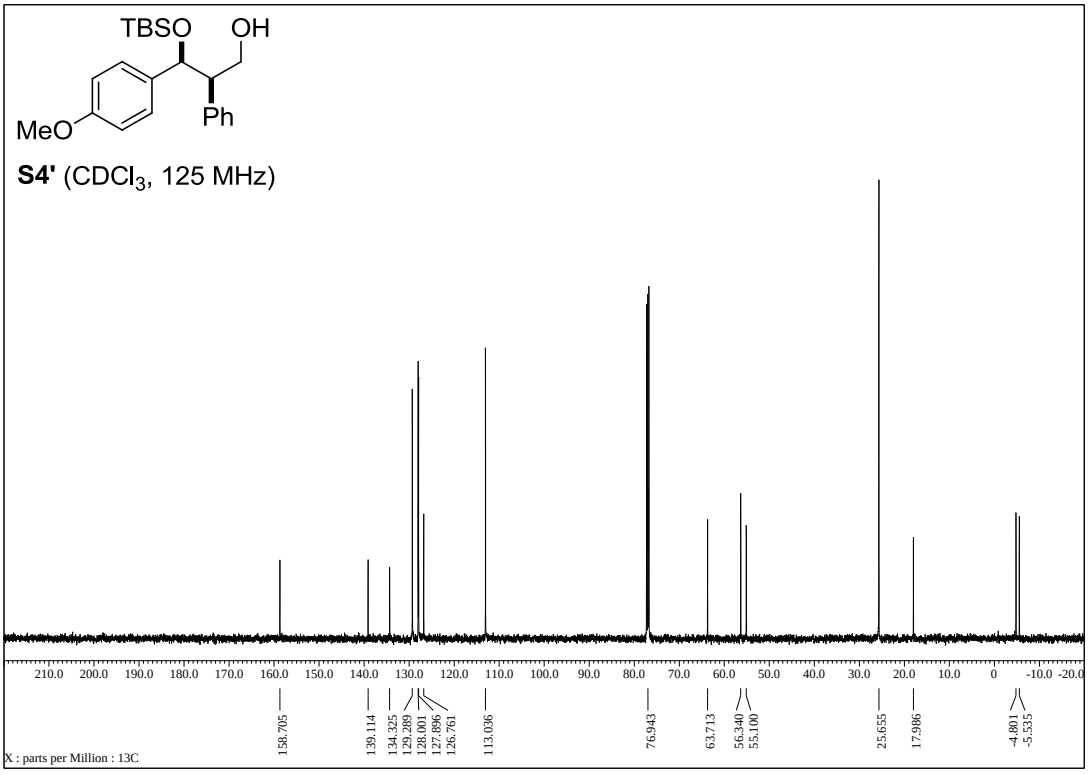
^{13}C NMR of (*2R,3R*)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (**S4**)



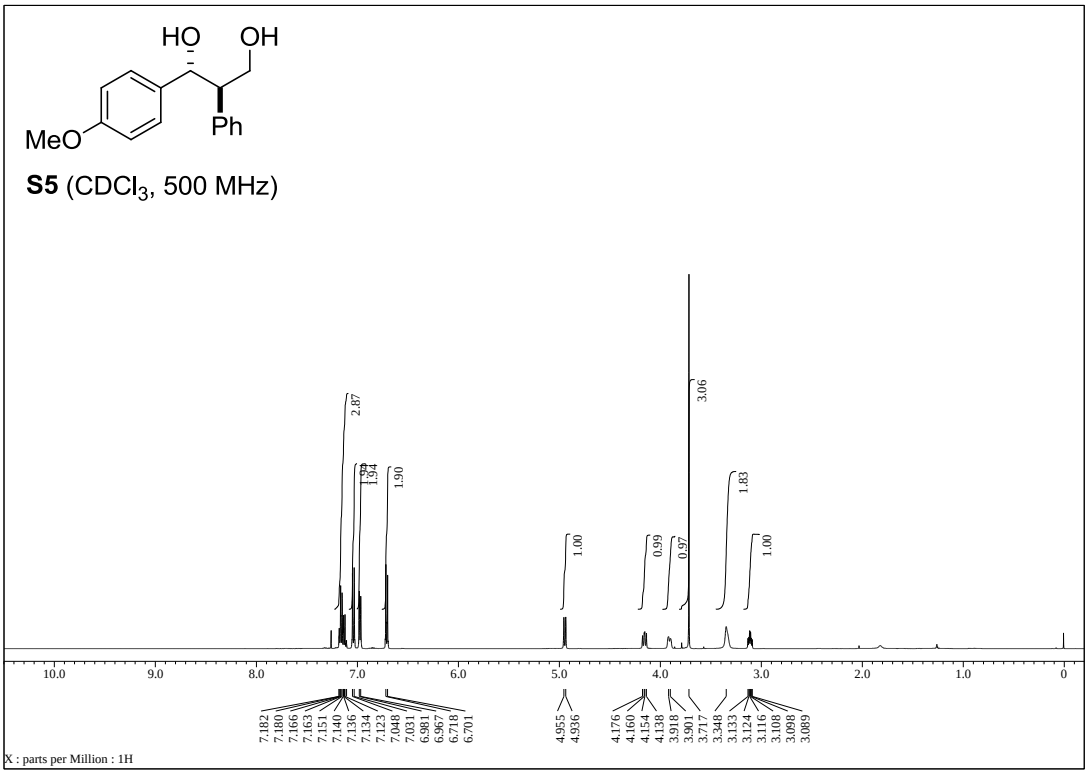
^{1}H NMR of (*2R,3S*)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (**S4'**)



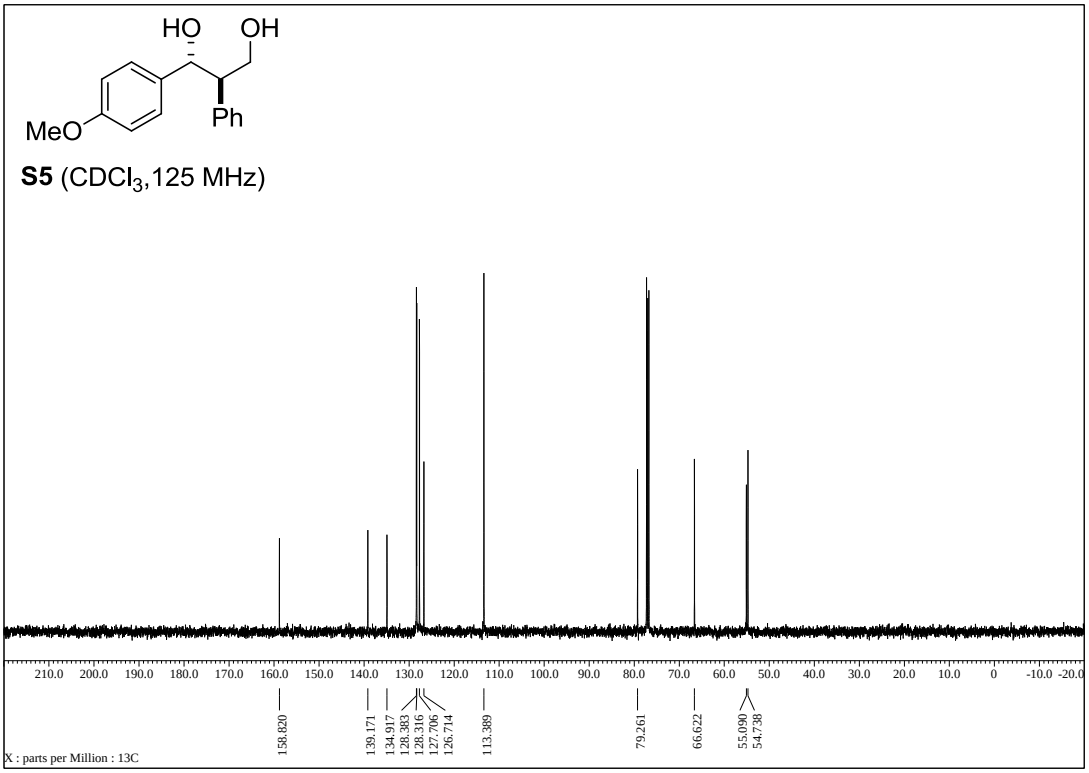
^{13}C NMR of (*2R,3S*)-3-((*tert*-butyldimethylsilyl)oxy)-3-(4-methoxyphenyl)-2-phenylpropan-1-ol (**S4'**)



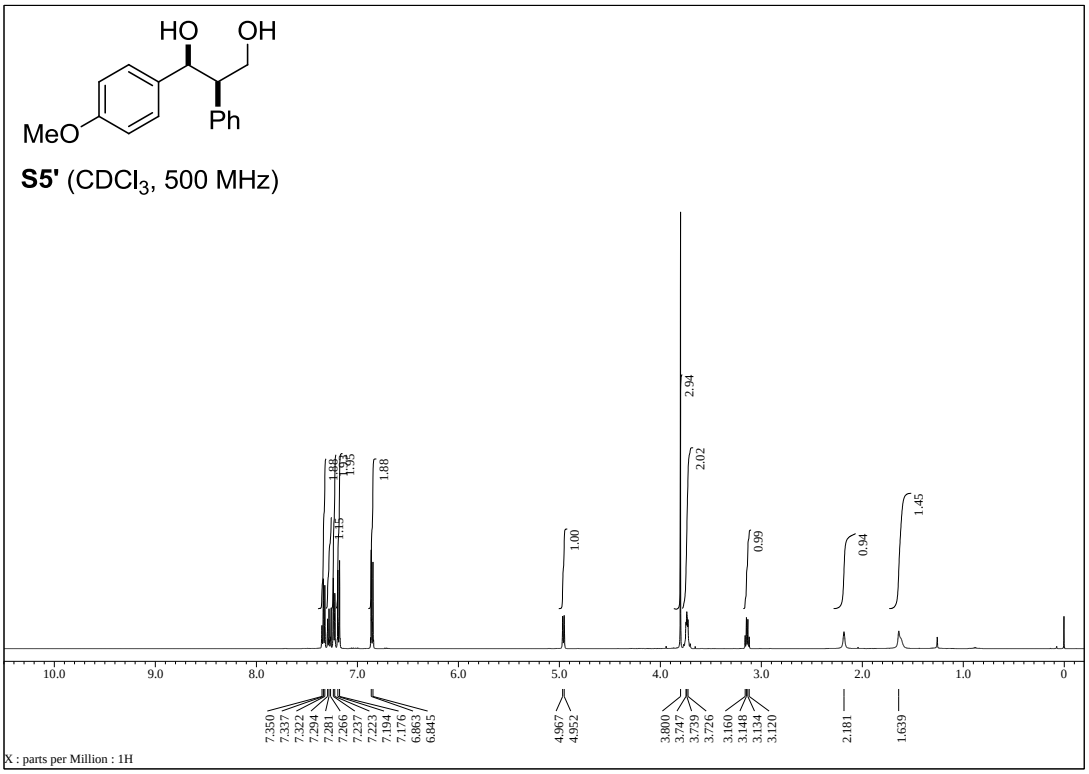
^{1}H NMR of (*1R,2R*)-1-(4-methoxyphenyl)-2-phenylpropane-1,3-diol (**S5**)



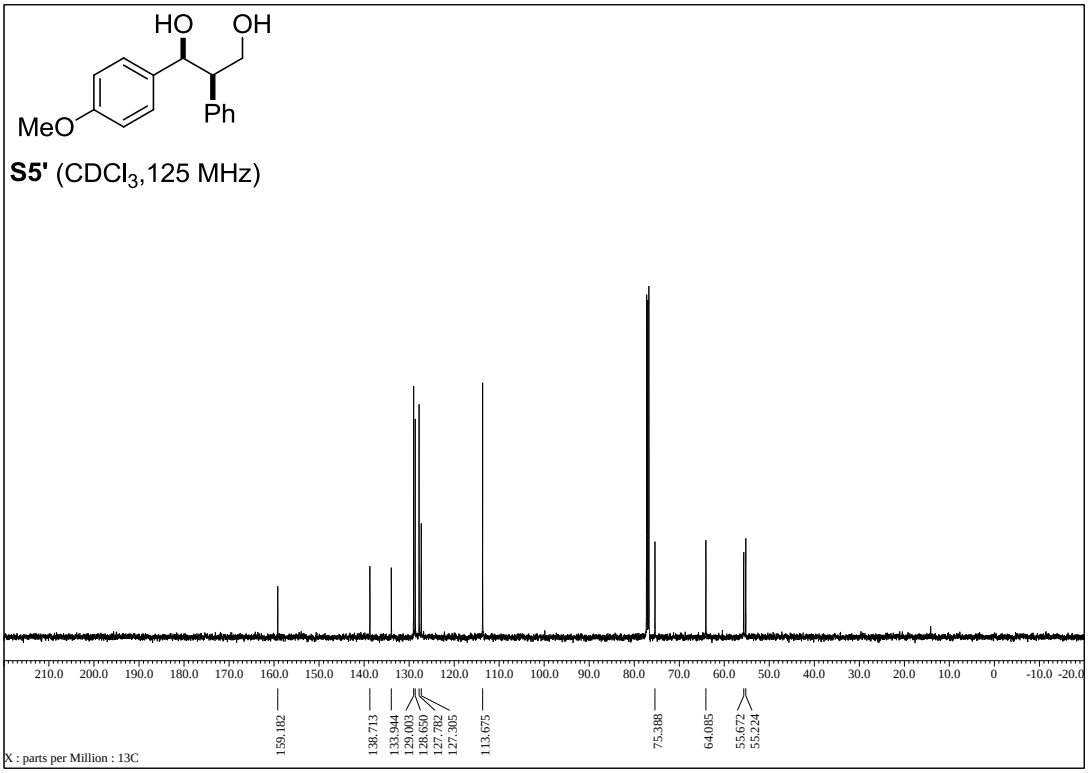
^{13}C NMR of (*1R,2R*)-1-(4-methoxyphenyl)-2-phenylpropane-1,3-diol (**S5**)



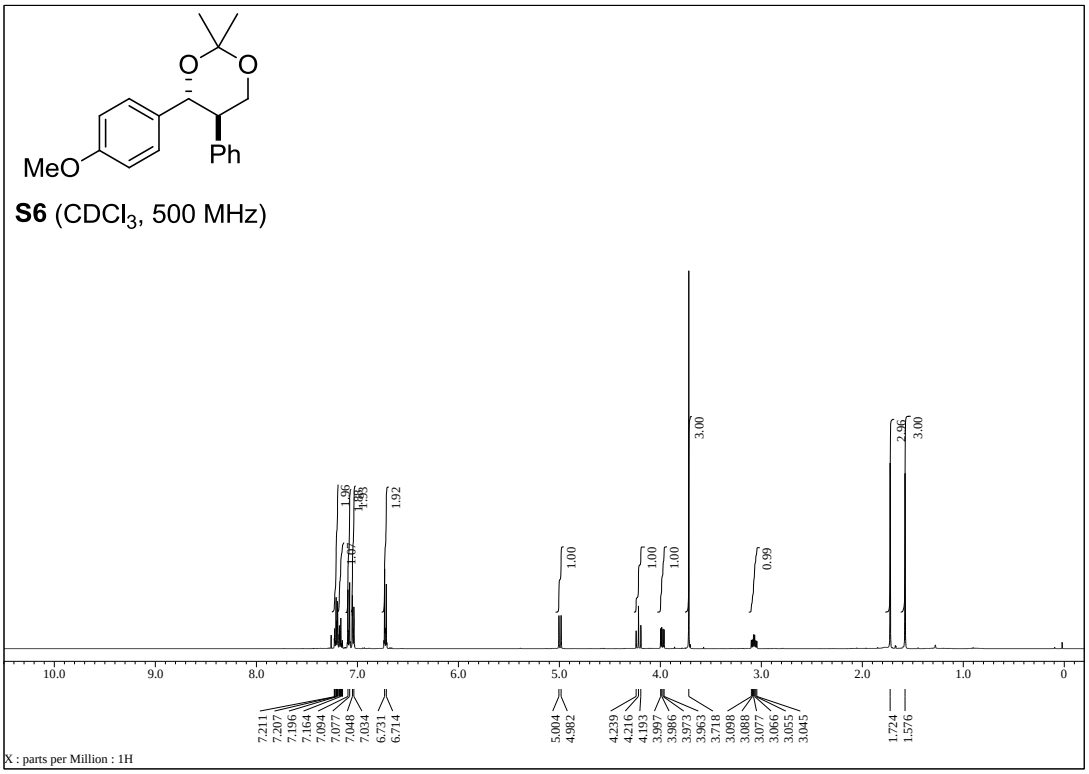
^{1}H NMR of (*1S,2R*)-1-(4-methoxyphenyl)-2-phenylpropane-1,3-diol (**S5'**)



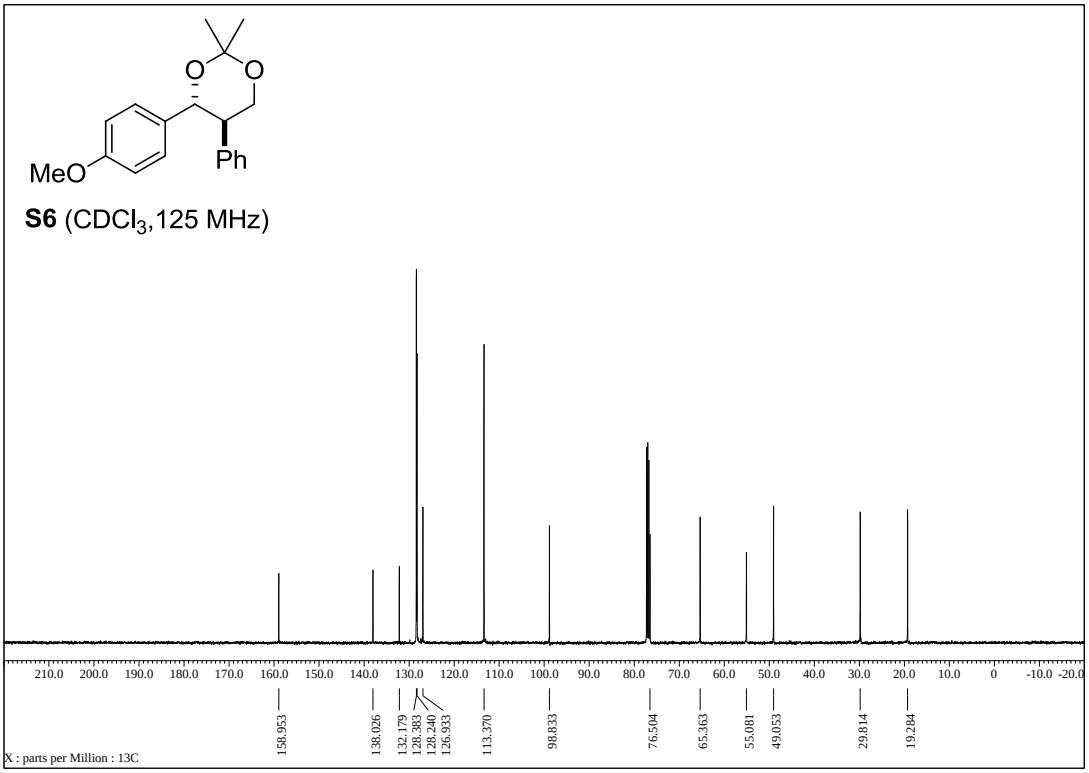
^{13}C NMR of (*1S,2R*)-1-(4-methoxyphenyl)-2-phenylpropane-1,3-diol (**S5'**)



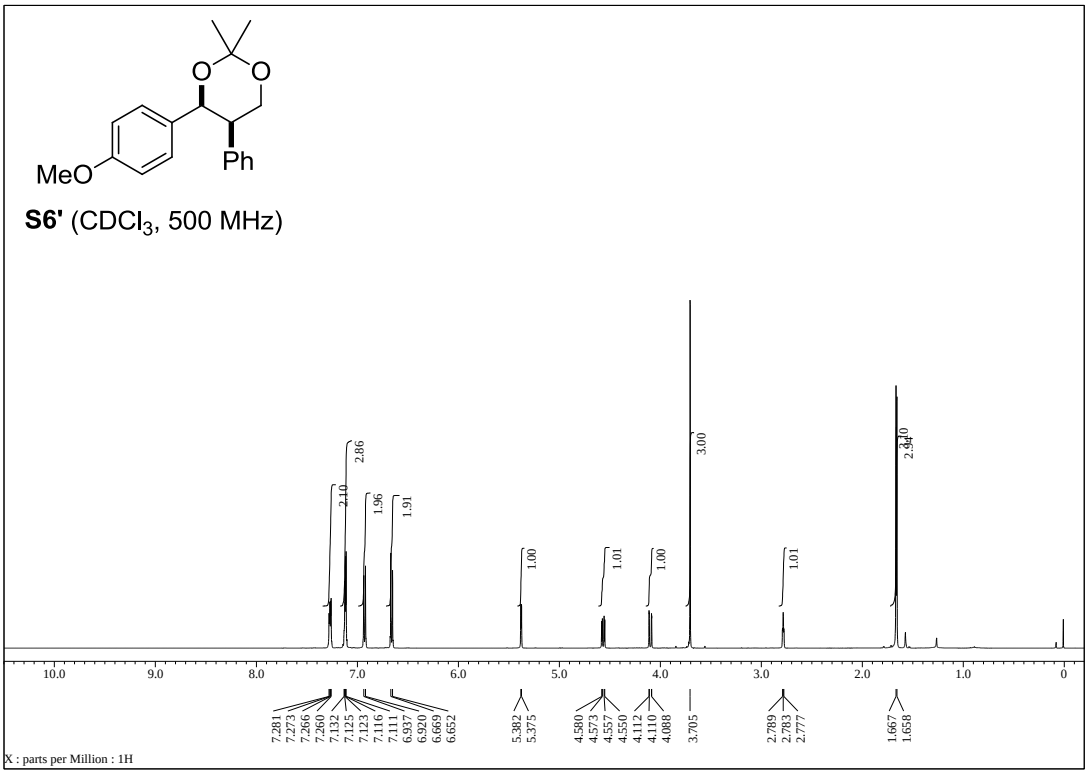
^{1}H NMR of (*4R,5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6**)



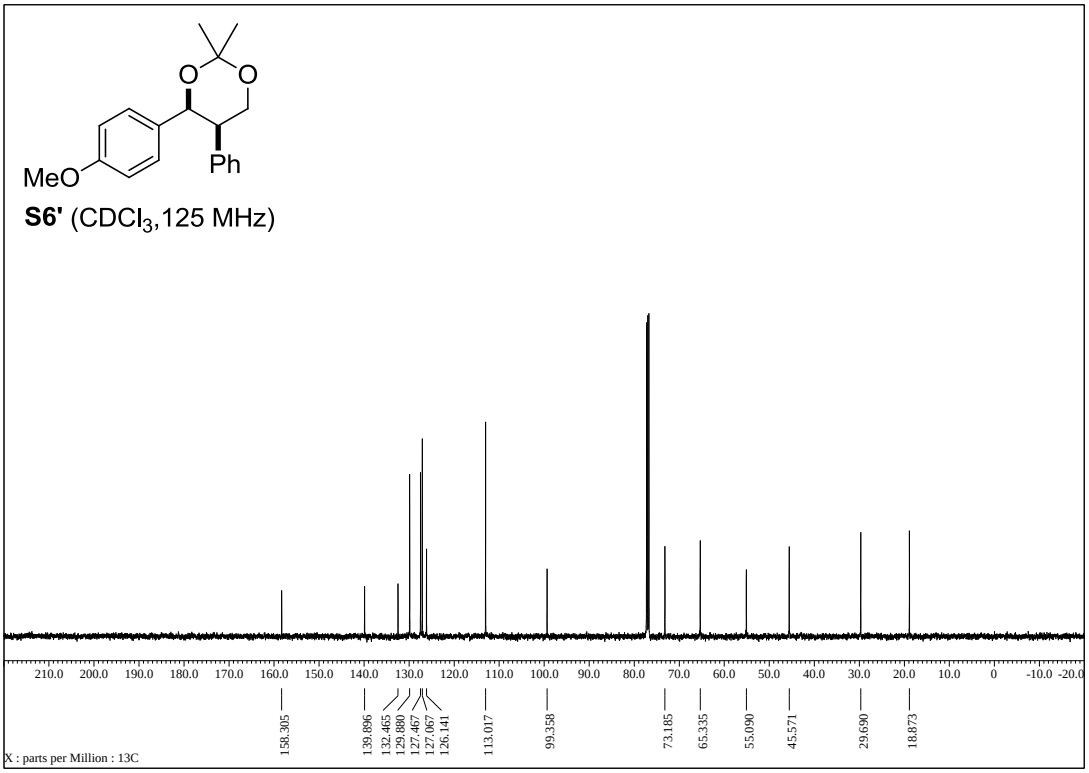
^{13}C NMR of (*4R,5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6**)



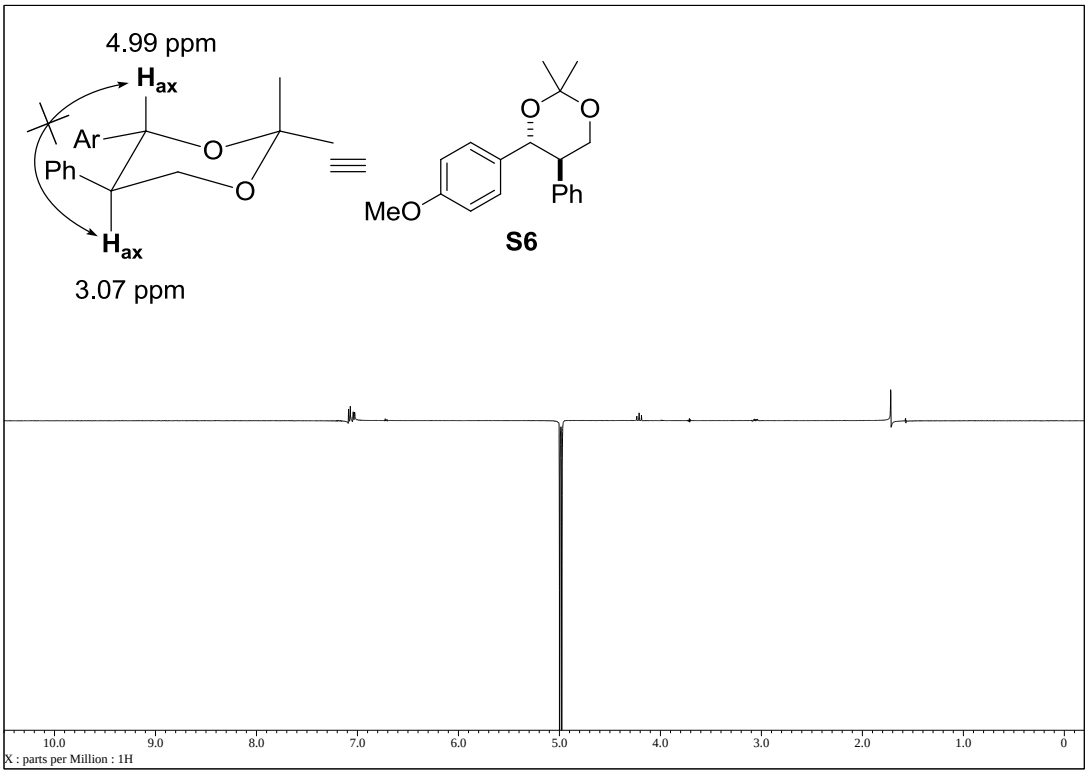
^{1}H NMR of (*4S,5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6'**)



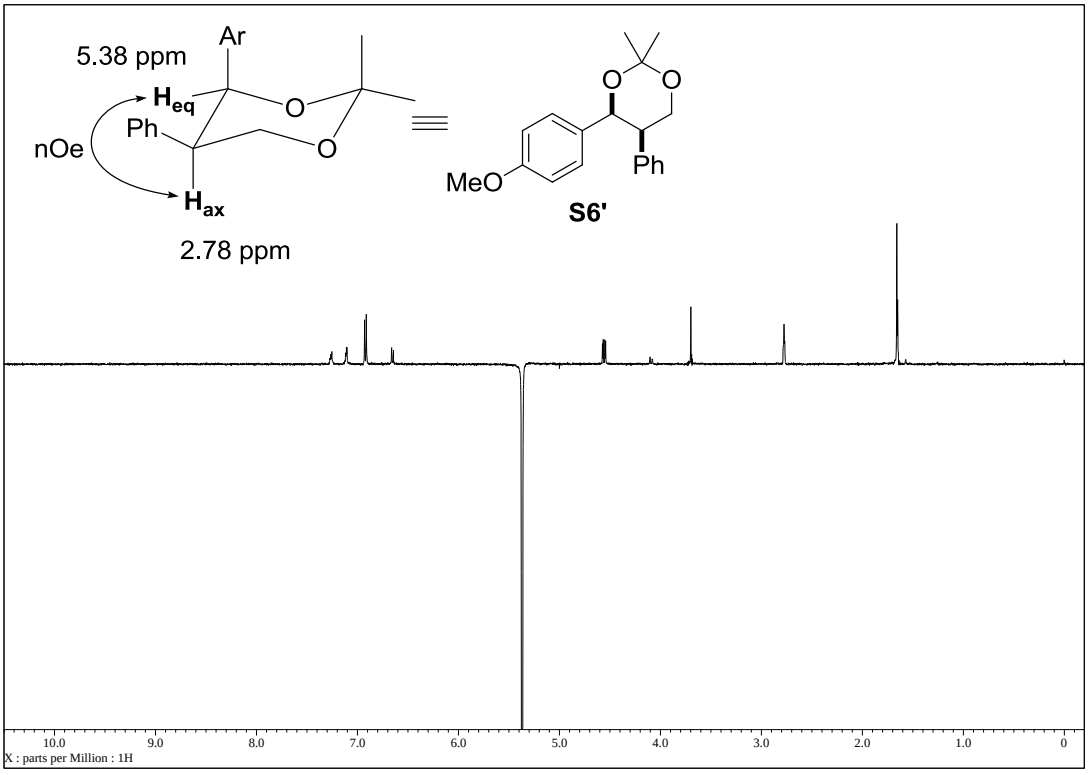
^{13}C NMR of (*4S,5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6'**)



nOe spectra of (*4R,5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6**)



nOe spectra of (*4S,5R*)-4-(4-methoxyphenyl)-2,2-dimethyl-5-phenyl-1,3-dioxane (**S6'**)



^{1}H NMR of 1-phenylhex-5-ene-1,3-diol (**S7**)