Supplementary Information

Electrochemically Assisted Deprotection of Acetals, Ketals, and Dithioacetals under Neutral Conditions

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1. General information

1.1 Instrumentation and Materials

All reagents and solvents were obtained from commercial sources and used without further purification unless otherwise noted. Flash column chromatography was performed with Silica Gel 60 N (Kanto Chemical Co., Inc., 40–50 μm spherical, neutral). ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECZ 400 (^{1}H: 400 MHz, ^{13}C: 100 MHz) or ECA 500 spectrometer (^{1}H: 500 MHz, ^{13}C: 125 MHz) at room temperature in $CDCl_3$ or CD_3CN as a solvent and the internal standard (^{1}H NMR: δ = 0.00 for TMS or 7.26 for $CDCl_3$, δ = 1.94 for CD_3CN; ^{13}C NMR: δ = 77.0 for $CDCl_3$, δ = 118.3 for CD_3CN). IR spectra were recorded by a Brucker FT-IR ALPHA. ESI-high-resolution mass spectra (HRMS) were measured by a JEOL AccuTOF (DART) mass spectrometer. Melting points were measured by a SANSYO SMP-300 melting point apparatus. ULVAC-PHI QuanteraSXM and PHI 5000 VersaProbe II were used for X-ray photoelectron spectroscopy (XPS). Electrochemical experiments were performed with IKA ElectraSyn 2.0. Cyclic vontanmetories were measured by ALS 1210C. SHIMADZU GC-2010 equipped with flame ionization detector (FID) and GL Science InertCap 5 capillary column (0.28 × 0.18 mm i.d., 20 m) was used for GC analysis. SHIMADZU HPLC system with a quaternary low-pressure LC-20 AD pump, an automatic SIL-20A HT injector, a CTO-10AS oven and a SPD-M20 with diode (DAD) equipped with GL Science chiral InertSustain® C18 column (4.6 × 150 mm, 5 μm) was used for HPLC analysis. Optical rotation was determined by ATAGO AP-300 automatic polarimeter.

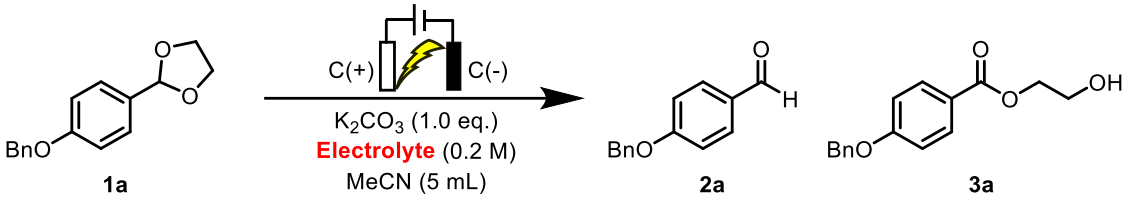
1.2 Method and preparation of electrolysis

Electrolysis experiments were performed in a 10 mL ElectraSyn vial on an IKA ElectraSyn 2.0. The magnetic stir bars and ElectraSyn vials were oven dried prior to use. All electrodes obtained from IKA were used repeatedly. Electrolysis under constant voltage were performed with a 0.05 M $Ag^{+/0}$ ($AgNO_3$) in CH_3CN non-aqueous reference electrode. To clean the graphite electrodes after use: the graphite electrode was sequentially washed with H_2O and CH_2Cl_2 and sonicated for 15 min in acetone. After that, the graphite was polished with 2000 grit sandpaper and dried in vacuum. To clean the Mg electrodes after use: the Mg electrodes were sequentially washed with water and CH_2Cl_2, and then sonicated for 15 min in acetone. After that, the Mg electrodes were rinsed with acetone and dried in vacuo.

2. Optimization of the reaction conditions

2.1 Optimization of electrolyte

Table S1 Optimization of electrolyte

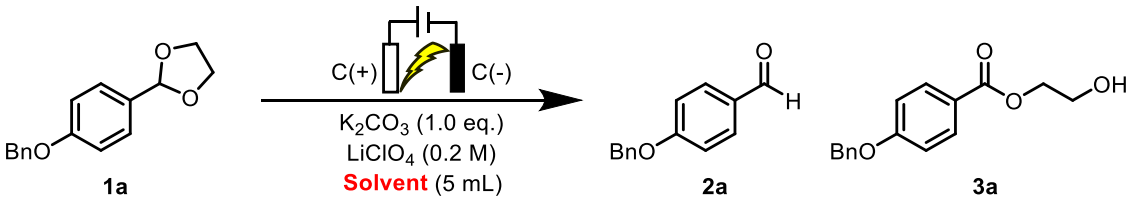


Entry	Electrolyte	^{1}H NMR yield (%)[a]		
		1a	**2a**	**3a**
1	$LiClO_4$	trace	98(95)[b]	trace
2	$NaClO_4$	11	78	7
3	$KClO_4$[c]	–	–	–
4	$Mg(ClO_4)_2$	0	94	4
5	$Mg(ClO_4)_2$[d]	–	–	–
6	$TBAClO_4$	52	9	0
7	$TBABF_4$	70	0	0
8	$TBABF_4$[e]	91	0	0
9	TBAI	15	0	0
10	TBACl	92	0	0
11	$LiClO_4$[f,g]	0	96(96)[b]	4

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard. [b] Isolated yields. [c] $KClO_4$ was not dissolved in MeCN. [d] 0.1 M of $Mg(ClO_4)_2$. [e] DMSO was used instead of MeCN. [f] Without K_2CO_3. [g] For 15 min.

2.2 Optimization of solvent

Table S2 Optimization of solvent



Entry	Solvent	^{1}H NMR yield (%)[a]		
		1a	**2a**	**3a**
1	MeCN	0	96(96)[b]	4
2	EtCN	0	94	4
3	$MeNO_2$	0	100	0
4	1-nitropropane[c]	–	–	–
5	2-nitropropane[c]	–	–	–
6	CH_2Cl_2[c]	–	–	–

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard. [b] Isolated yields. [c] $LiClO_4$ was not dissolved in the solvent.

Reaction conditions (Table S1 and S2):

The graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 0.2 mmol), K_2CO_3 (0.2 mmol, 1.0 eq.), and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried acetonitrile (MeCN, 5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with anode, cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15–60 min and stirring: 250 rpm). After electrolysis, the electrodes were washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixture was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The yield was determined by ^1H NMR using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

Results and discussion (Table S1 and S2):

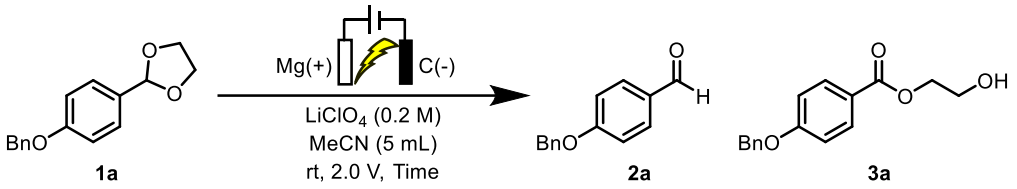
The reaction proceeded efficiently using $LiClO_4$, $NaClO_4$, and $Mg(ClO_4)_2$ as electrolytes. On the other hand, the reaction with $KClO_4$ did not proceed due to the low solubility of $KClO_4$ in MeCN. The reaction efficiency decreased when the counter cation of electrolyte was changed to TBA^+. Furthermore, the deprotection did not proceed when the counter anion was changed from ClO_4^- to BF_4^-, I^-, or Cl^-. This observation indicates that the combination of metal cation and ClO_4^- efficiently promotes the electrochemical deprotection reaction.

This deprotection reaction also proceeded when propionitrile (EtCN) or nitromethane ($MeNO_2$) was used as the solvent instead of MeCN. However, no current was observed with 1-nitropropane, 2-nitropropane, or dichloromethane (CH_2Cl_2) due to the low solubility of $LiClO_4$.

3. Control experiments

3.1 Investigation of the effect of Mg electrode

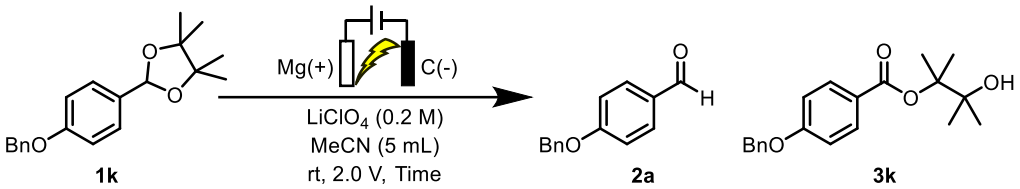
Table S3 Electrolysis of 1a using Mg as an anodic electrode



Time	^{1}H NMR yield (%)[a]			Current (mA)
	1a	**2a**	**3a**	
1 h	100	0	0	100.0 (start)→2.9 (end)

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Table S4 Electrolysis of 1k using Mg as an electrode



Time	^{1}H NMR yield (%)[a]			Current (mA)
	1k	**2a**	**3k**	
15 min	96	0	0	3.6 (start)→44.0 (max)→23.4 (end)
1 h	99	0	0	16.5 (start)→52.3 (max)→6.6 (end)

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Reaction conditions:

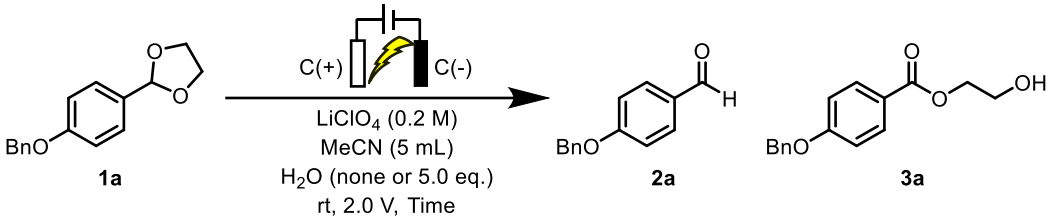
The graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a,** 0.2 mmol) or 2-(4-(benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**1k**, 0.2 mmol), and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried acetonitrile (MeCN, 5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with Mg anode, graphite cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 or 60 min and stirring: 250 rpm). After electrolysis, the electrodes were washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixture was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

Results and discussion (Table S3 and S4):

Under the optimized conditions, acetal **1a** and **1k** were electrolysed using a Mg electrode as the anode in place of graphite electrode. The deprotection reactions did not proceed in either case, and the substrates remained unchanged. The results suggest that the electrochemical deprotection reaction proceeds via anodic oxidation.

3.2 The effect of water

Table S5 Electrolysis of 1a under conditions with and without external addition of water



Entry	H_2O	Time	^{1}H NMR yield (%)[a]			Current (mA)
			1a	**2a**	**3a**	
1	none	15 min	0	99	trace	22.0 (start)→2.8 (end)
2	5.0 eq.	15 min	trace	98	2	12.9 (start)→2.3 (end)
3	none	1 h	2	88	8	22.9 (start)→1.8 (end)
4	5.0 eq.	1 h	0	94	6	13.5 (start)→1.4 (end)

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Reaction conditions:

The graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a,** 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried acetonitrile (MeCN, 5.0 mL) and H_2O (5.0 eq.) were then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with Mg anode, graphite cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 or 60 min and stirring: 250 rpm). After electrolysis, the electrodes were washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixture was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

Results and Discussion (Table S5):

1a was subject to electrolysis with and without the external addition of H_2O under the optimized conditions to investigate the effect of H_2O. While the addition of H_2O did not affect the deprotection efficiency, it slightly increased the yield of ester **3a** and decreased the initial current value during electrolysis.

4. Experimental procedure and analytical data for deprotection of acetal using a divided cell

The IKA pro-divided setup consists of two PTFE cells separated from each other by a glass frit (pore size 10–16 μm) equipped with an O-ring, and two specially designed stir bars were used (Figure S1-a and b). The pictures of the reaction solutions after the electrolysis under conditions A-1 and A-2 are shown in Figure S1-c (left) and c (right), respectively.

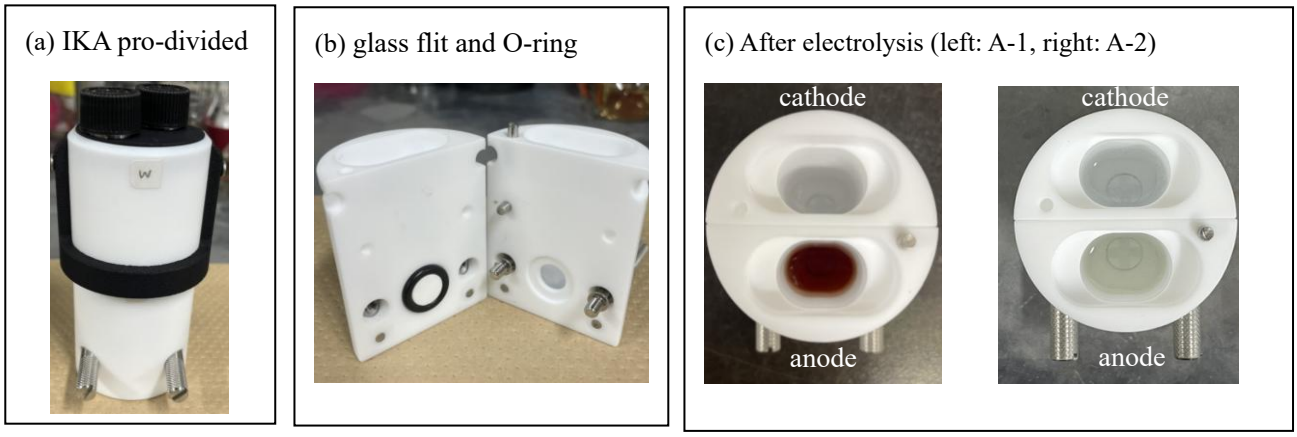
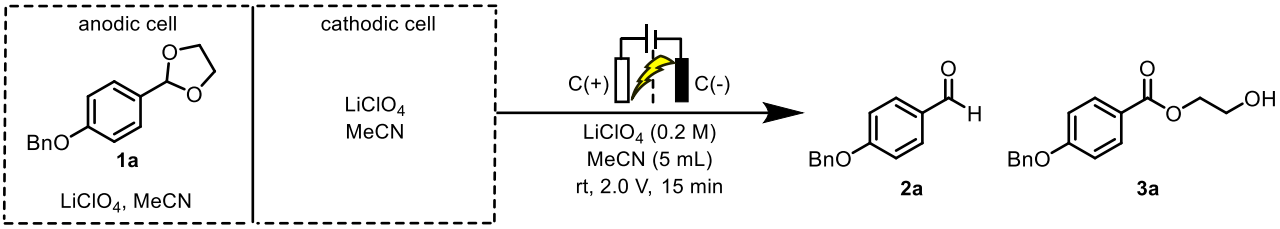


Figure S1 Divided cell and the picture of the reaction solution after electrolysis

Scheme S1 Deprotection of acetal using a divided cell (A-1)

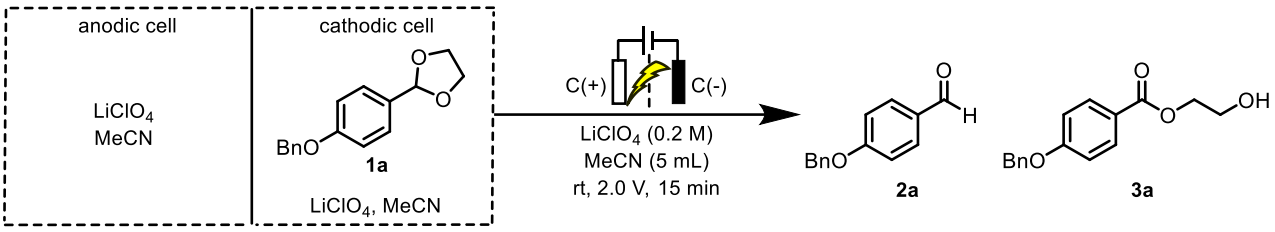


A-1	^{1}H NMR yield (%)[a]		
	1a	**2a**	**3a**
Anodic cell	0	89	5
Cathodic cell	0	0	0

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Condition A-1; 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were added into anodic chamber. To the cathodic chamber, $LiClO_4$ (1.0 mmol, 0.2 M) was added. MeCN (5.0 mL) was added into each chamber (10.0 mL in total). The chambers were capped with septa connected to the corresponding electrode before transferring out for electrolysis. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 min, total charge: 0.26 F/mol and stirring: 250 rpm). After electrolysis, each electrode was washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixtures were extracted with CH_2Cl_2 (20 mL×2), respectively. Each combined organic layer was dried over Na_2SO_4 and concentrated in vacuo to obtain the residues. The yield of **1a**, **2a**, and **3a** in each chamber were determined by ^{1}H NMR of the crude residue using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

Scheme S2 Deprotection of acetal using a divided cell (A-2)



A-2	^{1}H NMR yield (%)[a]		
	1a	**2a**	**3a**
Anodic cell	0	6	0
Cathodic cell	94	0	0

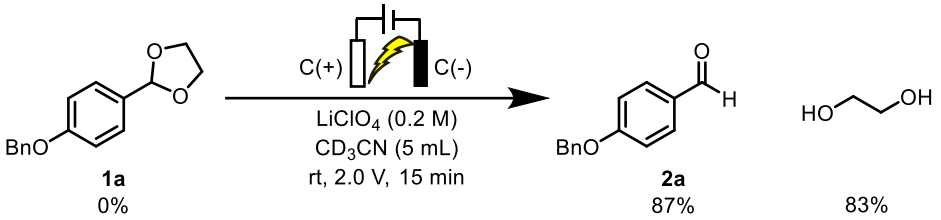
[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Condition A-2; 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were added into cathodic chamber. To the anodic chamber, $LiClO_4$ (1.0mmol, 0.2 M) was added. MeCN (5.0 mL) was added into each chamber (10.0 mL in total). The chambers were capped with septa connected to the corresponding electrode before transferring out for electrolysis. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 min, total charge: 0.10 F/mol and stirring: 250 rpm). After electrolysis, each electrode was washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixtures were extracted with CH_2Cl_2 (20 mL×2), respectively. Each combined organic layer was dried over Na_2SO_4 and concentrated in vacuo to obtain the residues. The yield of **1a**, **2a**, and **3a** in each chamber were determined by ^{1}H NMR of the crude residue using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

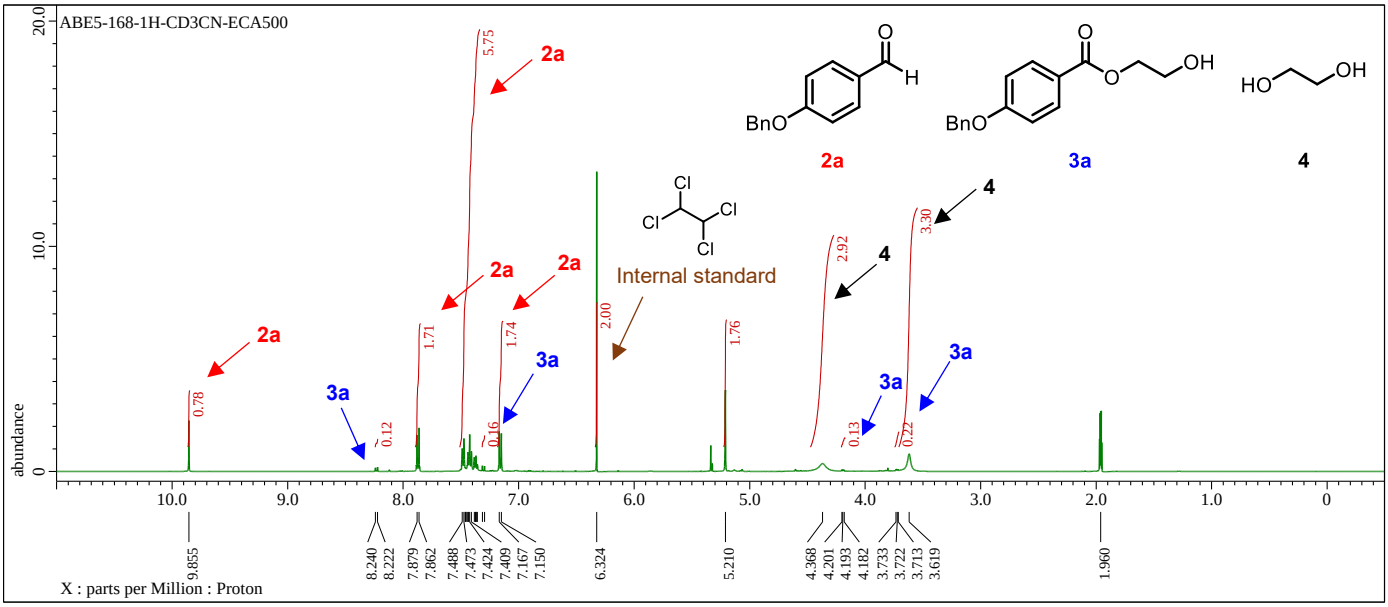
5. Experimental procedure and analytical data for the deprotection reaction in CD_3CN

Scheme S3 Deprotection of acetal in CD_3CN

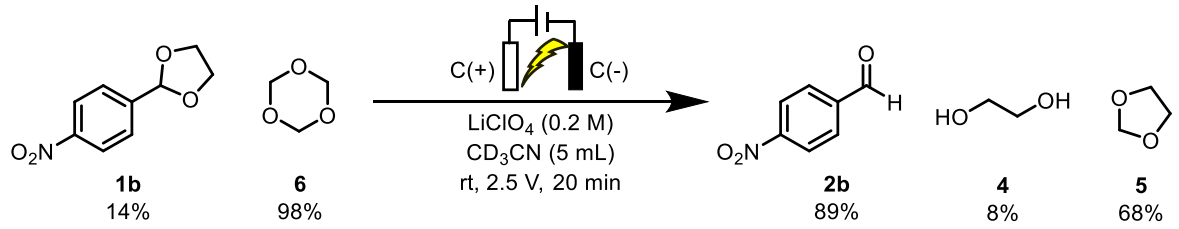
(a) Deprotection of **1a** in CD_3CN



Graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Acetonitrile-d_3 (CD_3CN, 5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with anode, cathode, and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 min, total charge: 0.41 F/mol and stirring: 250 rpm). After electrolysis, the 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) was added to the reaction mixture and yields of products were determined by ^{1}H NMR below.

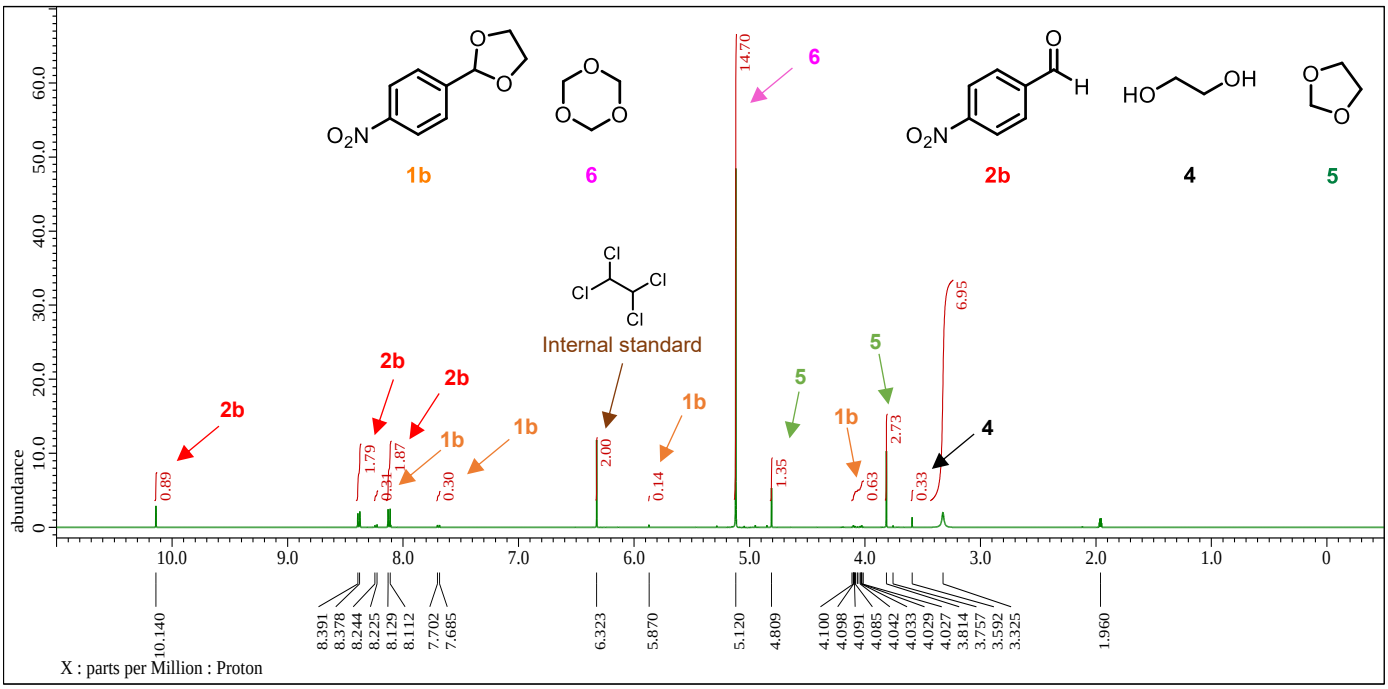


(b) Deprotection of **1b** in CD_3CN



Graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. 2-(4-Nitorophenyl)-1,3-dioxolane (**1b**, 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Acetonitrile-d_3 (CD_3CN, 5 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with anode, cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction

mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.28 F/mol and stirring: 250 rpm). After electrolysis, the 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) was added to the reaction mixture and yields of products were determined by ^{1}H NMR below.

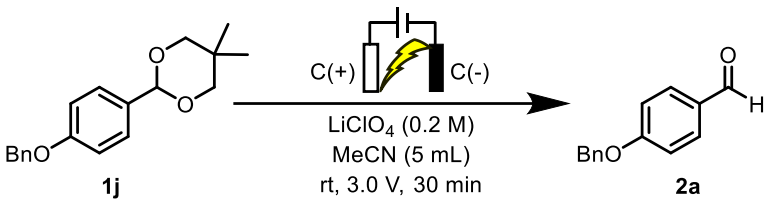


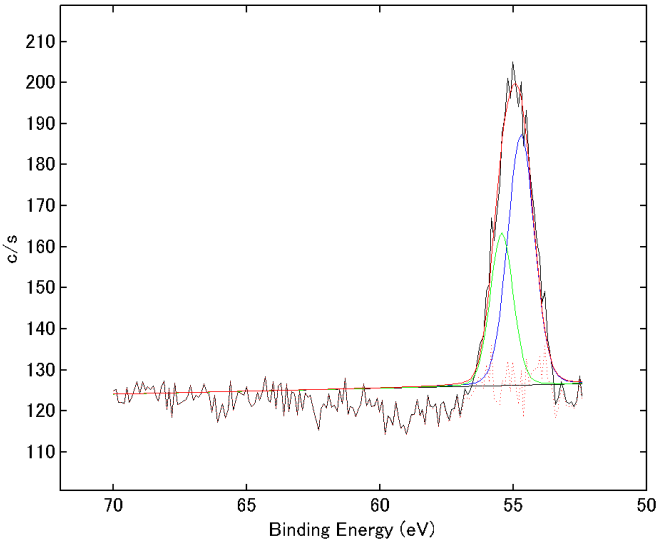
Results and Discussion (Scheme S3):

1,3-Dioxolane was detected by NMR after the deprotection reaction of **1b**. This result indicates that formaldehyde was generated from the partially decomposition of 1,3,5-trioxane during the reaction. The *in situ* generated formaldehyde would react with ethylene glycol to form 1,3-dioxolane through the electrogenerated acid (EGA) catalysis (please see Table S6 and reference 16). A decrease in the amount of ethylene glycol would suppress the regeneration of **1b** and accelerate the generation of **2b**.

6. Experimental procedure and XPS data of the generated salt on the cathode

(a) deprotection of acetal using an undivided cell



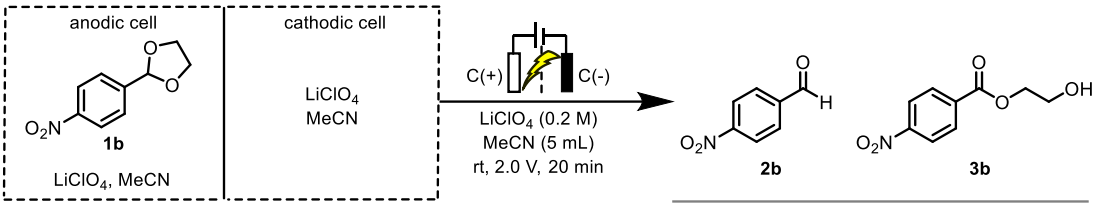


Binding energy (eV)	55.43	54.70
Species	$Li^{I}1s$ (from $LiClO_n$)	$Li^{I}1s$ (from LiCl)

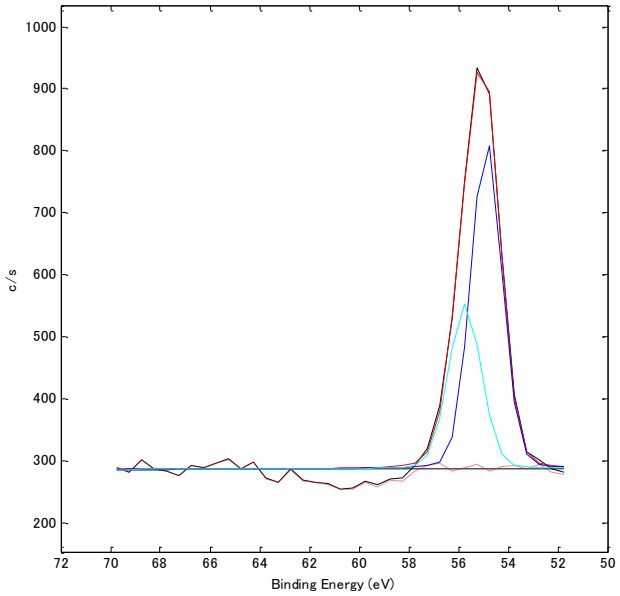
Figure S2 The XPS spectra of the Li in the generated salt on the cathode using an undivided cell

Graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were meticulously polished with 2000 grit sandpaper prior to utilisation. Subsequently, 2-(4-(benzyloxy)phenyl)-5,5-dimethyl-1,3-dioxolane (**1j**, 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried acetonitrile (MeCN, 5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with anode, cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 3.0 V, time: 30 min and stirring: 250 rpm). After electrolysis, the electrodes were washed with CH_2Cl_2 (10 mL), and then generated salt on the cathode was collected.

(b) deprotection of acetal using divided cell

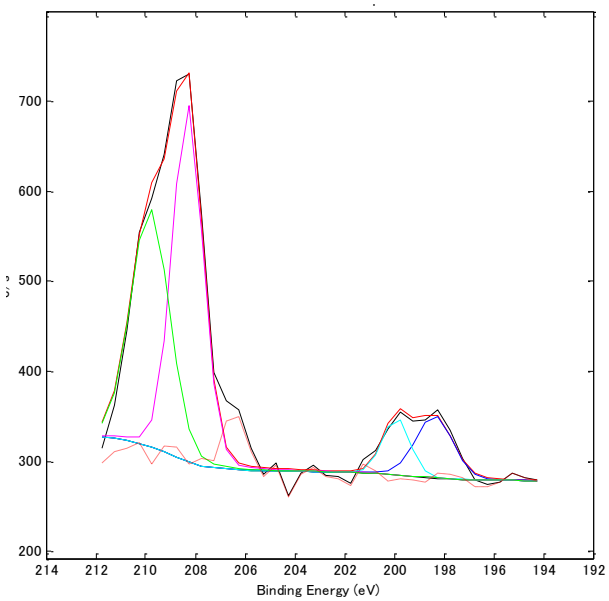


	1b	2b	3b
Anodic cell	56	39	4
Cathodic cell	1	0	0



Binding energy (eV)	55.75	54.89
Species	$Li^{I}1s$ (from $LiClO_n$)	$Li^{I}1s$ (from LiCl)

Figure S3 The XPS spectra of the Li in the generated salt on the cathode using a divided cell



Binding energy (eV)	209.83	208.32	199.93	198.40
Species	$Cl^{VII}2p^{1/2}$	$Cl^{VII}2p^{3/2}$	$Cl^{I}2p^{1/2}$	$Cl^{I}2p^{3/2}$

Figure S4 The XPS spectra of the Cl in the generated salt on the cathode using a divided cell

The graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were meticulously polished with 2000 grit sandpaper prior to utilisation. Subsequently, 2-(4-nitorophenyl)-1,3-dioxolane (**1b**, 0.2 mmol) and $LiClO_4$ (1.0 mmol, 0.2 M) were introduced into the anodic chamber. To the cathodic chamber, $LiClO_4$ (1.0 mmol, 0.2 M) was added. MeCN (5.0 mL) was added into each chamber (10.0 mL in total). The chambers were capped with septa connected to the corresponding electrode before transferring out for electrolysis. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.56 F/mol and stirring: 300 rpm). Subsequent to electrolysis, each electrode was washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixtures were extracted with CH_2Cl_2 (20 mL×2), respectively. Each combined organic layer was dried over Na_2SO_4 and concentrated in vacuo to obtain the residues. The yield of **1b**, **2b**, and **3b** in each chamber was determined by ^1H NMR of the crude residue using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

7. Experimental procedure and analytical data for time course study

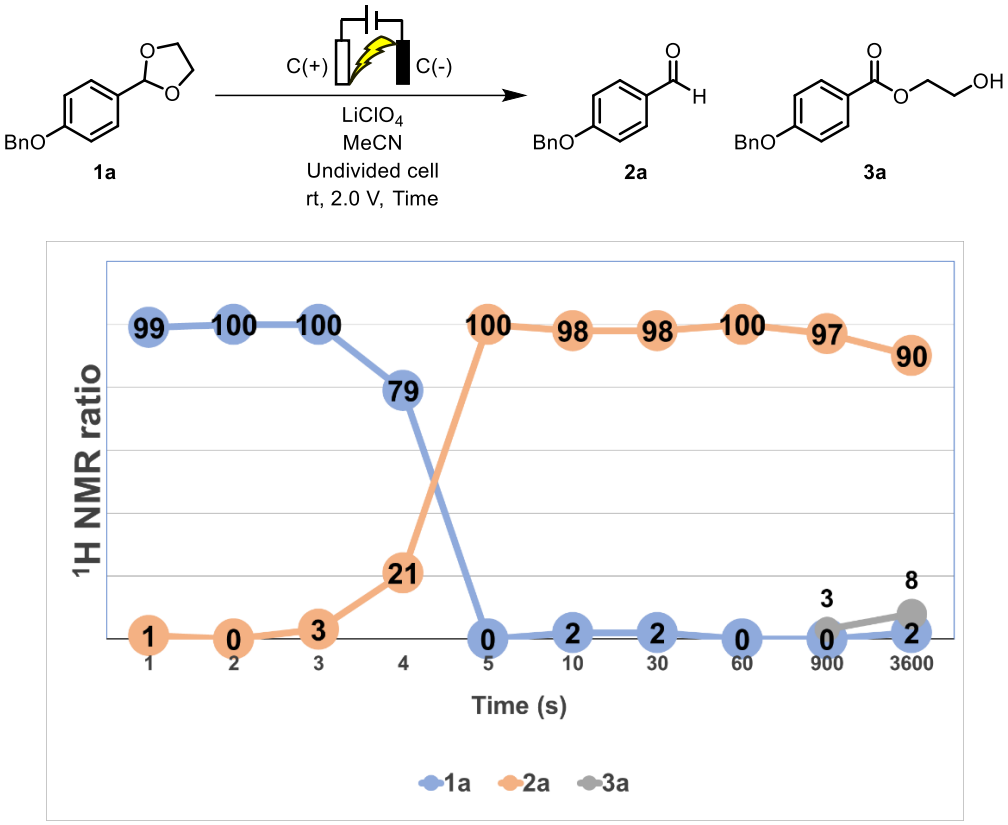
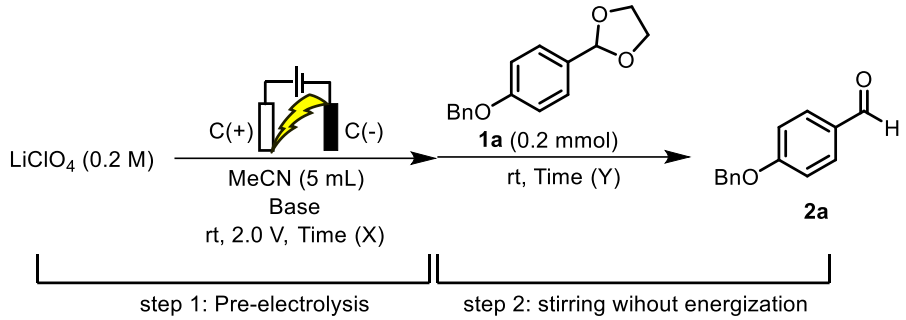


Figure S5 The time course study of electrochemical deprotection of 1a

Graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 0.2 mmol), and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried MeCN (5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with graphite anode, graphite cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 0–3600 sec and stirring: 250 rpm). After electrolysis, the electrodes were washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixture was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The ratio was determined by ^1H NMR using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

8. Pre-electrolysis experiments

Table S6 Effect of electrogenerated acid (EGA)



Entry	Time		Base	^{1}H NMR yield (%)[a]	
	X	Y		**1a**	**2a**
1	5 s	5 s	None	>99	trace
2	5 s	10 s	None	>99	trace
3	10 s	10 min	None	90	9
4	10 s	10 min	K_2CO_3 (1.0 eq.)	96	0

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard.

Reaction conditions (Table S6, Entry 4):

The graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. $LiClO_4$ (1.0 mmol, 0.2 M) and K_2CO_3 (0.2 mmol, 1.0 eq.) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried acetonitrile (MeCN, 5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with anode, cathode and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was pre-stirred for 10 min at room temperature. The reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 10 s and stirring: 400 rpm). After electrolysis was stopped, 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 0.2 mmol) was added into the reaction mixture, and then the reaction mixture was stirred at room temperature for a further 10 min. The solution was quenched with Et_3N (1.0 mL), the electrodes were washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixture was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (21.1 μL, 0.2 mmol) as the internal standard.

Results and Discussion (Table S6):

While the deprotection of **1a** did not proceed after pre-electrolysis of $LiClO_4$ in MeCN for 5 s (step 1) maintaining **1a** in quantitative yields (Table S6, Entries 1 and 2), extending step 1 (pre-electrolysis time: 10 s) and step 2 (stirring without energization time: 10 min) led to the formation of a small amount of **2a** in a 9% yield (Entry 3). Therefore, the EGA-catalysed deprotection was less effective compared to the electrochemical deprotection (Figure 1D or Figure S4). Furthermore, the pre-electrolysis in the presence of K_2CO_3 suppressed the deprotection of **1a** (Entry 4). These results suggest that deprotection of acetals **1** by EGA serves as a minor deprotection pathway with lower reaction efficiency compared to the electrochemical deprotection (Figure 1D or Figure S4) and activation of **1** through electrochemical one-electron oxidation is crucial for promoting the deprotection.

9. Cyclic voltammetry

All cyclic voltammetry studies were conducted with ALS 1210C. Measurements were performed in 0.1 M $TBAPF_6$ in MeCN using an undivided cell. All potentials referenced to Fc/Fc^+. The initial scan direction is oxidative (i.e., from relatively positive potentials to negative potentials)

Supporting Electrolyte: $TBAPF_6$

Solvent: super dehydrated MeCN (commercially available)

Working electrode: The working electrode is a diameter glassy carbon. Sonicated in distilled H_2O and acetone before drying.

Reference electrode: The reference electrode was washed with acetone before drying.

Counter electrode: The counter electrode is a platinum plate that was sonicated in distilled H_2O and acetone before drying.

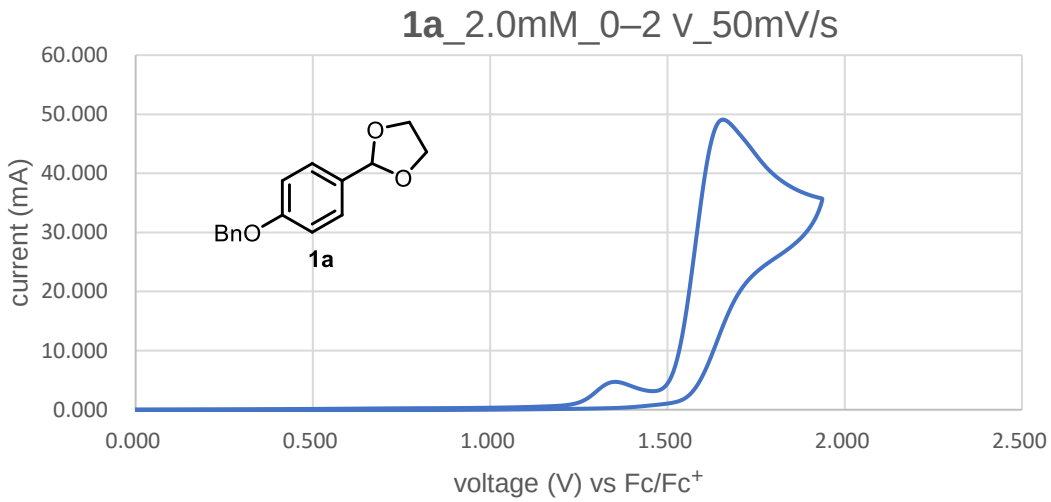


Figure S6 Cyclic voltammogram of 1a

CV of **1a** recorded in the presence of $TBAPF_6$ (1.0 mmol, 0.1 M) in MeCN (10.0 mL). The CV was recorded under argon from 0–2.0 V with scan rate of 50 mV/s.

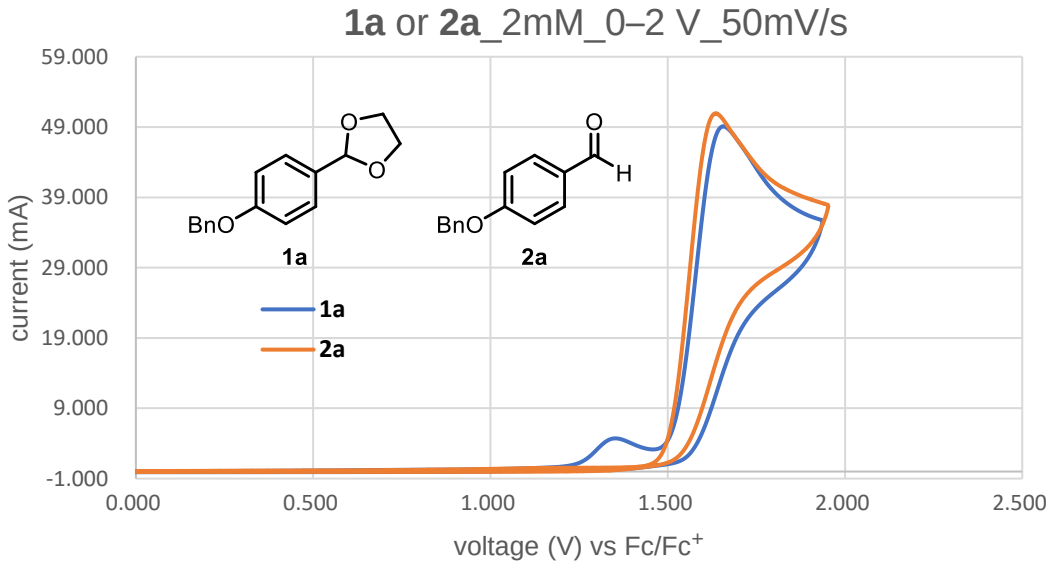


Figure S7 Cyclic voltammogram of 1a and 2a

CVs of **1a** and **2a** recorded in the presence of $TBAPF_6$ (1.0 mmol, 0.1 M) in MeCN (10 mL). The CV was recorded under argon from 0–2.0 V with scan rate of 50 mV/s.

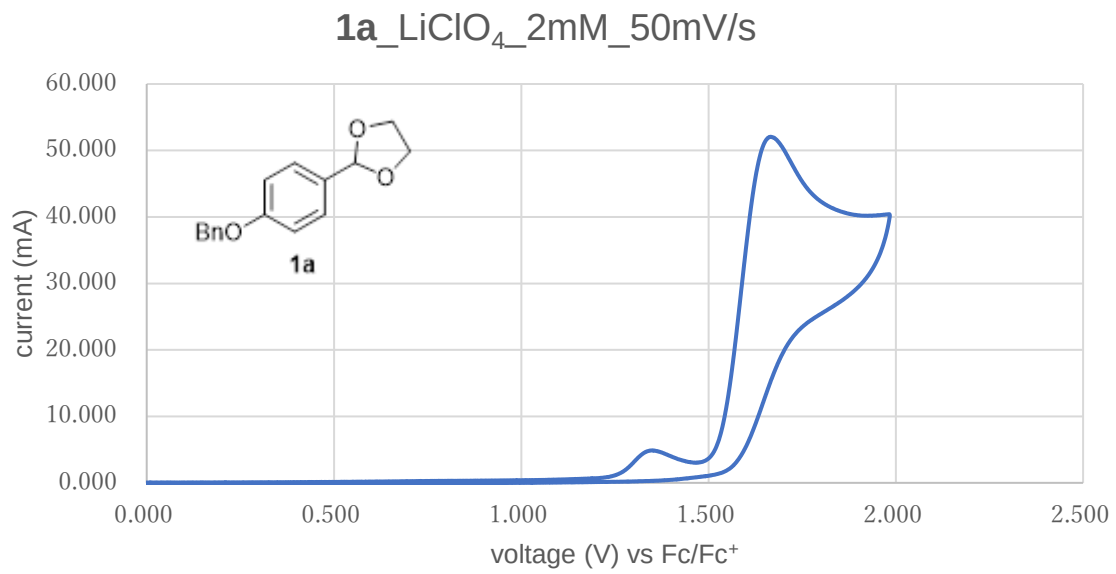


Figure S8 Cyclic voltammogram of 1a with $LiCO_4$

CV of **1a** (0.02 mmol, 2 mM) with $LiCO_4$ (0.1 mmol, 10 mM) recorded in the presence of $TBAPF_6$ (1.0 mmol, 0.1 M) in MeCN (10.0 mL). The CV was recorded under argon from 0–2.0 V with scan rate of 50 mV/s.

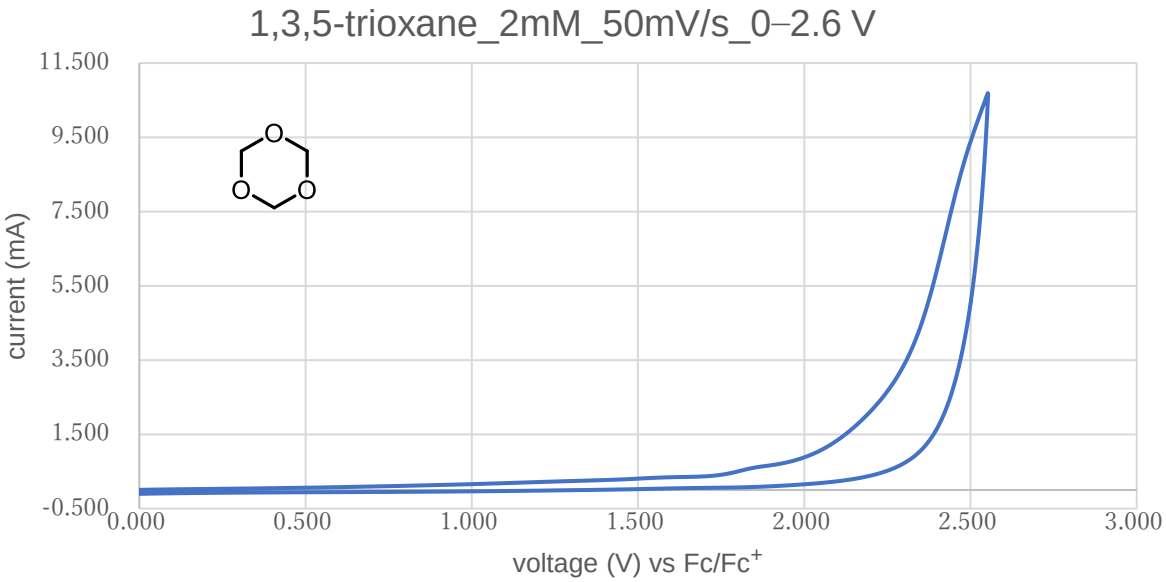
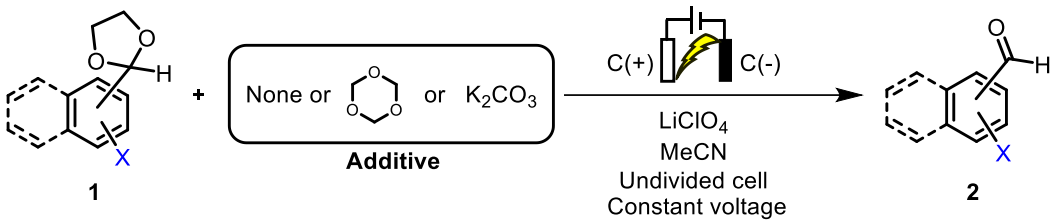


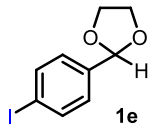
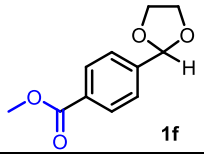
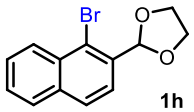
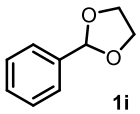
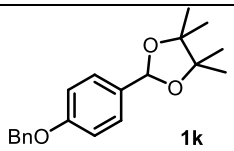
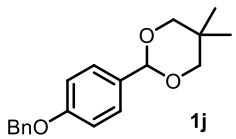
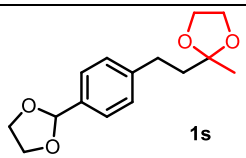
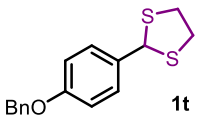
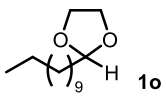
Figure S9 Cyclic voltammogram of 1,3,5-trioxane

CV of 1,3,5-trioxane recorded in the presence of $TBAPF_6$ (1.0 mmol, 0.1 M) in MeCN (10 mL). The CV was recorded under argon from 0–2.6 V with scan rate of 50 mV/s.

10. Effect of additive on substrate scope

Table S8 Control experiments for the deprotection reactions of 1 with or without additive



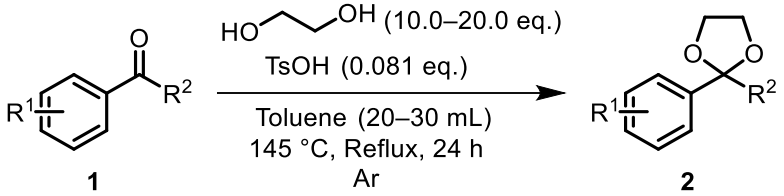
Substrate (**1**)	Additive	Conditions	Yield of **2** (%)[a]
 **1e**	K_2CO_3 (1.0 eq.)	2.8 V, 1.5 F/mol[b]	80
	1,3,5-trioxane (2.5 eq.)	2.8 V, 5 min, 0.40 F/mol	86[c]
 **1f**	K_2CO_3 (1.0 eq.)	3.0 V, 1.41 F/mol[b]	60
	1,3,5-trioxane (2.5 eq.)	2.5 V, 20 min, 0.43 F/mol	97[c]
 **1h**	K_2CO_3 (1.0 eq.)	2.0 V, 0.21 F/mol[b]	54
	1,3,5-trioxane (2.5 eq.)	1.5 V, 30 min, 0.30 F/mol	82[d]
 **1i**	None	2.0 V, 10 min, 0.16 F/mol	87[d]
	1,3,5-trioxane (2.5 eq.)	2.0 V, 10 min, 0.13 F/mol	quant.[d]
 **1k**	None	2.0 V, 15 min, 0.30 F/mol	62
	1,3,5-trioxane (2.5 eq.)	2.5 V, 20 min, 0.42 F/mol	84[c]
 **1j**	None	3.0 V, 15 min, 1.20 F/mol	57
	K_2CO_3 (1.0 eq.)	2.0 V, 0.23 F/mol[b]	55
	K_2CO_3 (1.0 eq.) and 1,3,5-trioxane (2.5 eq.)	2.0 V, 40 min, 0.59 F/mol	86[c]
 **1s**	None	2.0 V, 20 min, 0.32 F/mol	88
	1,3,5-trioxane (2.5 eq.)	2.0 V, 20 min, 0.22 F/mol	97[c]
 **1t**	K_2CO_3 (1.0 eq.)	4.0 V, 2.0 F/mol[b]	69
	1,3,5-trioxane (5.0 eq.)	2.5 V, 60 min, 1.73 F/mol	84[c]
 **1o**	K_2CO_3 (1.0 eq.)	2.0 V, 0.33 F/mol[b]	26
	1,3,5-trioxane (5.0 eq.)	2.0 V, 5 h, 1.88 F/mol	75[c]

*Reaction conditions: **1** (0.2 mmol), $LiClO_4$ (0.2 M), additive (K_2CO_3 1.0 eq. or 1,3,5-trioxane 2.5–5.0 eq.), and MeCN (5 mL) in an undivided cell with graphite carbon anode and cathode (both 10.0 mm × 8.0 mm × 1.0 mm) under Ar at rt.

[a] The yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane as the internal standard. [b] ElectraSyn was automatically stopped. [c] Isolated yields. [d] Determined by GC-FID.

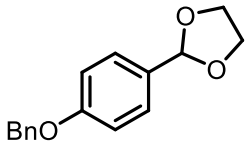
11. General procedures for the syntheses of substrates

General procedure A (GP A): protection of aldehydes and ketones



Aldehydes or ketones (**1**, 1.0–12.0 mmol, 1.0 eq.), ethylene glycol (10.0–20.0 eq.), *p*-toluenesulfonic acid (0.081 eq.), and toluene (20–30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. The solution was heated at 145 °C and refluxed for 24 h. After cooling to room temperature, the solution was quenched with sat. $NaHCO_3$ aq. (10 mL), extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL). The organic layer was dried over Na_2SO_4, concentrated in vacuo, and then the residue was purified by silica-gel column chromatography to obtain acetals or ketals (**2**).

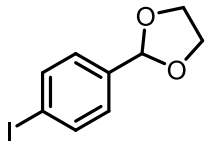
2-(4-Benzyloxyphenyl)-1,3-dioxolane (1a)



According to **GP A**, 4-benzyloxybenzaldehyde (**2a**, 212.0 mg, 1.0 mmol), ethylene glycol (3.4 mL, 10.0 eq.), *p*-toluenesulfonic acid (20.0 mg, 0.081 eq.), and toluene (25 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 7/1) to give 2-(4-benzyloxyphenyl)-1,3-dioxolane (**1a**, 253.0 mg, 0.99 mmol) in 99% yield as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.44–7.30 (m, 7H), 6.98 (d, J = 8.8 Hz, 2H), 5.75 (s, 1H), 5.07 (s, 2H), 4.17–3.97 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 136.8, 130.1, 128.5, 127.9, 127.9, 127.4, 114.6, 103.6, 69.9, 65.2. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **1**.

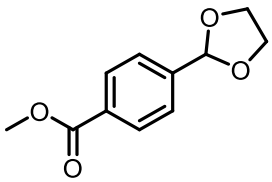
2-(4-Iodophenyl)-1,3-dioxolane (1e)



According to **GP A**, 4-iodobenzaldehyde (**2e**, 1.0 g, 4.3 mmol), ethylene glycol (2.7 mL, 10.0 eq.), *p*-toluenesulfonic acid (60 mg,0.081 eq.), and toluene (25 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 12/1) to give 2-(4-iodophenyl)-1,3-dioxolane (**1e**, 1.2 g, 4.3 mmol) in quantitative yield as a pale green solid.

^{1}H NMR (400 MHz, $CDCl_3$): 7.72 (d, J = 8.4 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 5.76 (s, 1H), 4.14–3.99 (m, 4H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.4, 128.3, 103.1, 95.1, 65.3. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **2**.

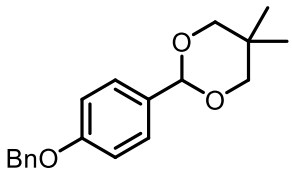
Methyl 4-(1,3-dioxolane-2-yl)benzoate (1f)



According to **GP A**, methyl 4-formylbenzoate (**2f**, 1.0 g, 6.1 mmol), ethylene glycol (3.4 mL, 10.0 eq.), *p*-toluenesulfonic acid (86.0 mg, 0.081 eq.), and toluene (25 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 12/1) to give methyl 4-(1,3-dioxolane-2-yl)benzoate (**1f**, 1.3 g, 6.1 mmol) in quantitative yield as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): 8.06 (d, J = 7.4 Hz, 2H), 7.55 (d, J = 7.4 Hz, 2H), 5.86 (s, 1H), 4.16–4.02 (m, 4H), 3.92 (s, 3H) ; ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.7, 142.7, 130.7, 129.6, 126.4, 103.0, 65.3, 52.2. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **3**.

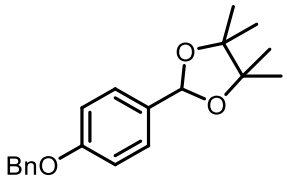
2-(4-(Benzyloxy)phenyl)-5,5-dimethyl-1,3-dioxolane (1j)



According to **GP A**, 4-benzyloxybenzaldehyde (**2a**, 1.1 g, 5.0 mmol), neopentyl glycol (5.2 g, 10.0 eq.), *p*-toluenesulfonic acid (69.7 mg, 0.081 eq.), and toluene (25 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 2-(4-(benzyloxy)phenyl)-5,5-dimethyl-1,3-dioxolane (**1j**, 802.8 mg, 2.7 mmol) in 54% yield as a colourless solid.

MP: 67 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 7.44–7.41 (m, 4H), 7.37 (t, J = 7.5 Hz, 2H), 7.31 (t, J = 7.3 Hz, 1H), 6.96 (d, J = 8.5 Hz, 2H), 5.35 (s, 1H), 5.07 (s, 2H), 3.75 (d, J = 10.8 Hz, 2H), 3.64 (d, J = 10.8 Hz, 2H), 1.29 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 136.9, 131.3, 128.5, 127.9, 127.4, 114.6, 101.6, 77.6, 69.9, 30.2, 23.0, 21.9; IR (ATR) cm^{-1}: 2950, 2862, 1614, 1515, 1454, 1387, 1304, 1248, 1216, 1172, 1104, 1013; DART-HRMS m/z: 299.1638 ($[M+H]^+$); Calcd. for $C_{19}H_{23}O_3$: 299.1647.

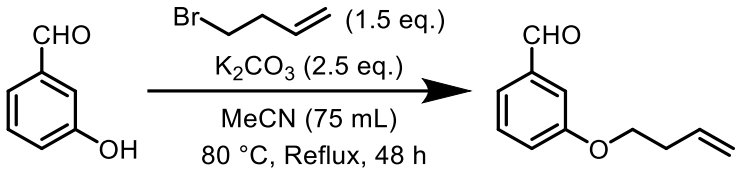
2-(4-(Benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (1k)



According to **GP A**, 4-benzyloxybenzaldehyde (**2a**, 679.0 mg, 3.0 mmol), pinacol (5.9 g, 10.0 eq.), *p*-toluenesulfonic acid (69.7 mg, 0.081 eq.), and toluene (20 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 7/1) to give 2-(4-(benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**1k**, 903.0 mg, 2.9 mmol) in 86% yield as a colourless solid.

MP: 77 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 7.43–7.30 (m, 7H), 6.96 (d, J = 7.5 Hz, 2H), 5.94 (s, 1H), 5.06 (s, 2H), 1.32 (s, 6H), 1.28 (s, 6H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.1, 136.9, 132.0, 128.5, 127.9, 127.7, 127.4, 114.6, 99.8, 82.5, 69.9, 24.4, 22.2; IR (ATR) cm^{-1}: 2977, 1612, 1512, 1454, 1378, 1302, 1222, 1151, 1111, 1072; DART-HRMS m/z: 313.1810 ($[M+H]^+$); Calcd. for $C_{20}H_{25}O_3$: 313.1804.

3-(But-3-enyloxy)benzaldehyde (2l)

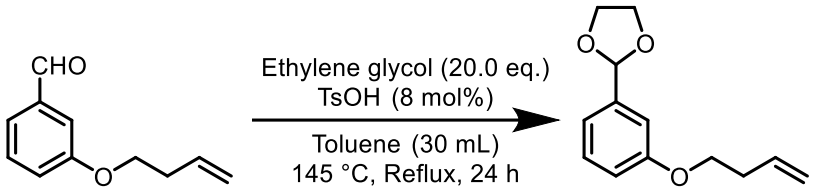


2l

To a solution of 3-hydroxybenzaldehyde (2.4g, 20.0 mmol) and K_2CO_3 (6.9 g, 2.5 eq.) in MeCN (75 mL), 4-bromo-1-butene (3.0 mL, 1.5 eq.) was added. The mixture was refluxed at 80 ℃ for 48 h. After cooling to room temperature, the solvent was removed under reduced pressure, and then poured into water. The residue was extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL), The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 15/1) to give 3-(but-3-enyloxy)benzaldehyde (**2l**, 1.8 g, 10.0 mmol) in 50% yield as a pale yellow oil .

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.47–7.38 (m, 3H), 7.21–7.15 (m, 1H), 5.96–5.86 (m, 1H), 5.21–5.16 (m, 1H), 5.15–5.11 (m, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 2.60–2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 159.4, 137.7, 134.1, 130.0, 123.4, 121.9, 117.2, 112.7, 67.4, 33.4. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **4**.

2-(3-(But-3-enyloxy)phenyl)-1.3-dioxolane (1l)

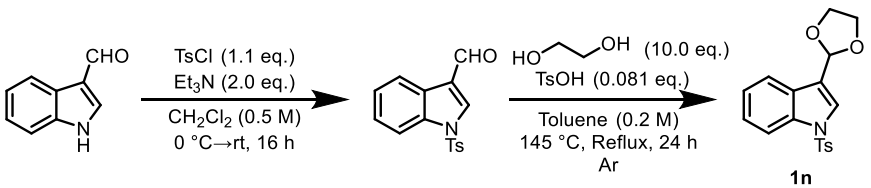


1l

3-(But-3-enyloxy)benzaldehyde (**2l**, 881.0 mg, 5.0 mmol), ethylene glycol (5.5 mL, 10.0 eq.), *p*-toluenesulfonic acid (11.4 mg, 0.081 eq.), and toluene (30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. The solution was heated to 145 ℃ and refluxed for 24 h. The solution was quenched with sat. $NaHCO_3$ aq. (10 mL), extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL), The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 2-(3-(but-3-enyloxy)phenyl)-1.3-dioxolane (**1l**, 963.0 mg, 4.4 mmol) in 88% yield as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (dd, *J* = 8.0, 2.8 Hz, 1H), 7.07–7.03 (m, 2H), 6.90 (ddd, *J* = 8.8, 2.6, 0.8 Hz, 1H), 5.96–5.85 (m , 1H), 5.79 (s, 1H), 5.20–5.14 (ddd, *J* = 17.2, 3.6, 2.0 Hz, 1H), 5.12–5.09 (ddd, *J* = 10.4, 3.2, 0.8, 1H), 4.16–3.99 (m, 6H), 2.57–2.51 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.0, 139.4, 134.4, 129.4, 118.8, 117.0, 115.6, 112.1, 103.5, 67.1, 65.2, 33.6; IR (ATR) cm^{-1}: 2882, 1603, 1490, 1452,1383, 1317, 1261, 1180, 1159, 1070, 1037; DART-HRMS m/z: 221.1170 ($[M+H]^+$); Calcd. for $C_{13}H_{17}O_3$: 221.1178.

3-(1,3-Dioxolane-2-yl)-1-((4-methylphenyl)sulfonyl)-1*H*-indol (1n)



1n

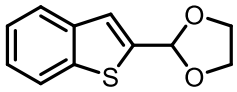
To a solution of 1*H*-indole-3-carboxaldehyde (1.45 g, 10.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added triethylamine (2.79 mL, 20.0 mmol). After stirring for 15 min, p-toluenesulfonyl chloride (2.10 g, 11.0 mmol) was added, and the reaction was stirred at room temperature for 16 h. Upon completion, the reaction solution was diluted with CH_2Cl_2 (20 mL) and washed

with sat. NH_4Cl aq. (50 mL), sat. $NaHCO_3$ aq. (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was used for the next reaction without further purification.

According to **GP A**, the residue, ethylene glycol (1.7 mL, 50.0 mmol), *p*-toluenesulfonic acid (69.7 mg, 0.41 mmol), and toluene (25 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 3-(1,3-Dioxolane-2-yl)-1-((4-methylphenyl)sulfonyl)-1*H*-indol (**1n**, 1.3 g, 3.8 mmol) in 38% (2 steps) yield as an orange solid

MP: 156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.97 (d, J = 8.4, 1H), 7.77 (d, J = 7.2, 2H), 7.68 (s, 1H), 7.66 (d, J = 7.6, 1H), 7.34–7.30 (m, 1H), 7.26–7.20 (m, 3H), 6.08 (s, 1H), 4.17–4.03 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.1, 135.4, 135.1, 129.9, 128.2, 126.9, 124.9, 124.8, 123.4, 120.6, 119.9, 113.5, 99.4, 65.1, 21.5; IR (ATR) cm^{-1}: 3350, 2951, 1678, 1446, 1377, 1176, 1125, 1087; DART-HRMS m/z: 344.0951 ([M+H]$^+$); Calcd. for $C_{18}H_{18}NO_4S$:344.0957.

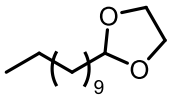
2-(Benzo[b]thiophen-2-yl)-1,3-dioxolane (1o)



According to **GP A,** benzo[b]thiophene-2-carbaldehyde (**2o**, 1.6 g, 10.0 mmol), ethylene glycol (10.0 mL, 20.0 eq.), *p*-toluenesulfonic acid (154.1 mg, 0.081 eq.), and toluene (30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/dichloromethane = 5/1) to give 2-(benzo[b]thiophen-2-yl)-1,3-dioxolane (**1o**, 2.0 g, 9.7 mmol) in 97% yield as a yellow oil.

MP: 67 °C; ^{1}H NMR (500 MHz, $CDCl_3$): 7.84–7.79 (m, 1H), 7.75–7.72 (m, 1H), 7.37 (s, 1H), 7.34–7.29 (m, 2H), 6.19 (s, 1H), 4.16–3.98 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 142.4, 139.9, 139.0, 124.7, 124.2, 123.9, 122.9, 122.5, 100.4, 65.3; IR (ATR) cm^{-1}: 2884, 1459, 1376, 1212, 1147, 1057; DART-HRMS m/z: 207.0467 ([M+H]$^+$); Calcd. for $C_{11}H_{11}O_2S$:207.0480.

2-Undecyl-1,3-dioxolane (1p)



According to **GP A**, *n*-dodecyl aldehyde (**2p**, 2.2 g, 12.0 mmol), ethylene glycol (6.9 mL, 10.0 eq.), *p*-toluenesulfonic acid (167.0 mg, 0.081 eq.), and toluene (20 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give 2-undecyl-1,3-dioxolane (**1p**, 2.6 g, 11.2 mmol) in 93% yield as a colourless oil.

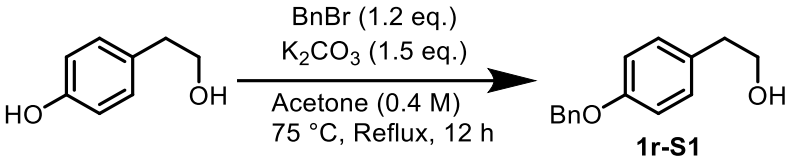
^{1}H NMR (400 MHz, $CDCl_3$): 4.84 (t, J = 4.2, 1H), 4.01–3.81 (m, 4H), 1.68–1.63 (m, 2H), 1.45–1.26 (m, 20H), 0.88 (t, J = 6.4, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 104.7, 64.8, 33.9, 31.9, 29.6, 29.6, 29.5 (2C), 29.3, 24.1, 22.7, 14.1. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **4**.

2-Methyl-2-tridecyl-1,3-dioxolane (1q)

According to **GP A**, pentadecane-2-one (**2q**, 2.2 g, 10.0 mmol), ethylene glycol (11.2 mL, 20.0 eq.), *p*-toluenesulfonic acid (140 mg, 0.081 eq.), and toluene (20 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give 2-methyl-2-tridecyl-1,3-dioxolane (**1q**, 2.4 g, 8.8 mmol) in 88% yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): 3.98–3.90 (m, 4H), 1.64–1.60 (m, 2H), 1.40–1.26 (m, 25H), 0.88 (t, J = 6.8, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 110.2, 64.6, 39.2, 31.9, 29.9, 29.7, 29.6 (2C), 29.6, 29.6, 29.4, 24.1, 23.7, 22.7, 14.1; IR (ATR) cm^{-1}: 2922, 2852, 1466, 1375, 1219, 1066; DART-HRMS m/z: 271.2625 ([M+H]$^+$); Calcd. for $C_{17}H_{35}O_2$: 271.2637.

2-(4-(Benzyloxy)phenyl)ethanol (1r-S1)

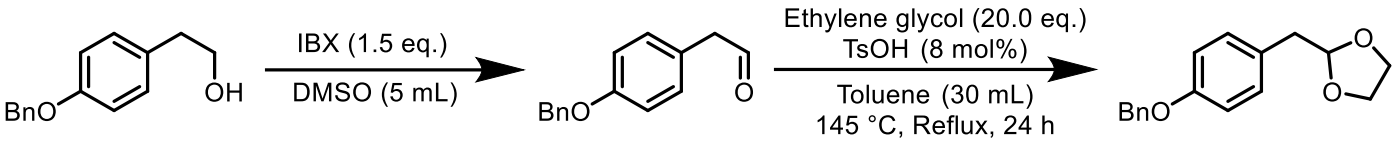


1r-S1

To a solution of 4-hydroxyphenylethanol (4.2 g, 30.0 mmol) in acetone (0.4 M, 75 mL) was added K_2CO_3 (6.2 g, 1.2 eq.), followed by dropwise addition of the benzyl bromide (4.4 mL, 1.2 eq.), and the mixture was heated at 75 ℃ for 12 h. After cooling to room temperature, the reaction mixture was poured into water and extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL). The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 2/1) to give 2-(4-(benzyloxy)phenyl)ethanol (**1r-S1**, 6.7 g, 29.5 mmol) in 98% yield as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44–7.37 (m, 5H), 7.15 (d, J = 8.5, 2H), 6.93 (d, J = 8.5, 2H), 5.05 (s, 1H), 3.82 (q, J = 6.3, 2H), 2.81 (t, J = 6.3, 2H), 1.39 (t, J = 6.3, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.5, 137.0, 130.6, 130.0, 128.6, 127.9, 127.4, 115.0, 70.0, 63.8, 38.2. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **5**.

2-(4-(Benzyloxy)phenyl)acetaldehyde (1r)



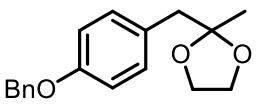
1r-S1 **1r**

To solution of 2-(4-(benzyloxy)phenyl)ethanol (**1r-S1**, 2.8 g, 10.0 mmol) in DMSO (5 mL), 2-iodoxybenzoic acid (IBX , 4.2 g, 15.0 mmol, 1.5 eq.) was added and suspension was stirred for 3 h at room temperature. Ethyl acetate (350 mL) was added to the reaction mixture. The insoluble solids were filtered off under suction. The organic layer was washed with H_2O (150 mL×3), brine (150 mL), and dried over Na_2SO_4. The organic layer was concentrated in vacuo and the residue was used for the next reaction without further purification.

According to **GP A**, the crude mixture, ethylene glycol (10.0 mL, 20.0 eq.), *p*-toluenesulfonic acid (29.4 mg, 0.081 eq.), and toluene (30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 7/1) to give 2-(4-(benzyloxy)benzyl)-1,3-dioxolane (**1r**, 1.8 g, 6.6 mmol) in 66% yield (2 steps) as a colourless solid.

MP: 72 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43–7.29 (m, 5H), 7.19 (d, J = 8.6 Hz, 2H), 6.92 (d, J = 8.6 Hz, 2H), 5.03–5.00 (m, 3H), 3.97–3.79 (m, 4H), 2.90 (d, J = 5.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.5, 137.1, 130.6, 128.5, 128.4, 127.9, 127.4, 114.7, 104.7, 69.9, 64.9, 39.8; IR (ATR) cm^{-1}: 2982, 2879, 1612, 1511, 1454, 1377, 1298, 1238, 1177, 1113, 1080, 1045; DART-HRMS m/z: 271.1335 ([M+H]$^+$); Calcd. for $C_{17}H_{19}O_3$: 271.1334.

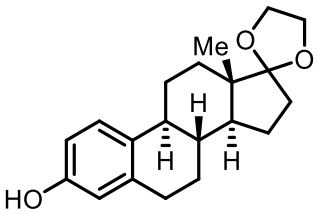
2-(4-(Benzyloxy)benzyl)-2-methyl-1,3-dioxolane (2s)



According to **GP A**, 1-(4-(benzyloxy)phenyl)propan-2-one (**2s**, 1.2 g, 5.2 mmol), ethylene glycol (5.8 mL, 20.0 eq.), *p*-toluenesulfonic acid (72.3 mg, 0.081 eq.), and toluene (25 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 7/1) to give 2-(4-(benzyloxy)benzyl)-2-methyl-1,3-dioxolane (**1s**, 1.3 g, 4.7 mmol) in 90% yield as a pale green solid.

MP: 66 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.30 (m, 5H), 7.18 (d, *J* = 8.5, 2H), 6.90 (d, *J* = 8.5, 2H), 5.03 (s, 2H), 3.92–3.72 (m, 4H), 2.86 (s, 2H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 157.4, 137.1, 131.3, 129.3, 128.5, 127.8, 127.4, 114.3, 109.7, 69.9, 64.8, 44.4, 24.2; IR (ATR) cm^{-1}: 2882, 1612, 1510, 1454, 1383, 1298, 1239, 1177, 1132, 1024; DART-HRMS m/z: 285.1494 ($[M+H]^+$); Calcd. for $C_{18}H_{21}O_3$: 285.1491.

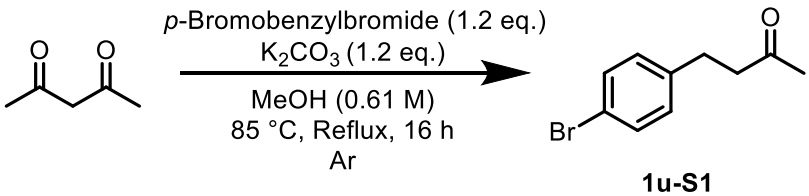
(8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (1t)



According to **GP A**, (8*R*,9*S*,13*S*,14*S*)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (estrone, **2t**, 810.9 mg, 3.0 mmol), ethylene glycol (3.4 mL, 20.0 eq.), *p*-toluenesulfonic acid (41.4 mg, 0.081 eq.), and toluene (30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (**1t**, 681.6 mg, 2.2 mmol) in 78% yield as a colourless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.5 Hz, 1H), 6.62 (dd, *J* = 8.5, 3.0 Hz, 1H), 6.56 (d, *J* = 3.0 Hz, 1H), 4.89 (s, 1H), 4.00–3.87 (m, 4H), 2.86–2.76 (m, 2H), 2.32–2.27 (m, 1H), 2.23–2.18 (m, 1H), 2.07–2.01 (m, 1H), 1.90–1.82 (m, 2H), 1.80–1.73 (m, 2H), 1.67–1.60 (m, 1H), 1.54 (ddd, *J* = 12.5, 3.3, 3.3 Hz, 1H), 1.49–1.36 (m, 4H), 0.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.3, .138.2, 132.6, 126.5, 119.5, 115.2, 112.6, 65.2, 64.5, 49.3, 46.1, 43.5, 38.9, 34.2, 30.7, 29.6, 26.8, 26.1, 22.3, 14.3. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **6**.

2-(4-Bromophenyl)butan-2-one (1u-S1)

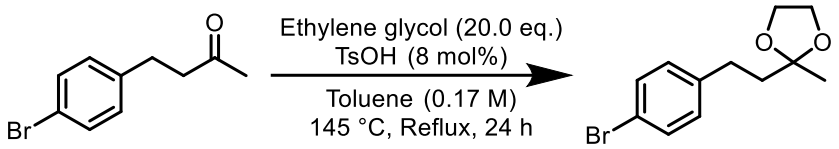


1u-S1

To a solution of acetylacetone (1.8 g, 18.3 mmol) and K_2CO_3 (2.8 g, 20.0 mmol, 1.2 eq.) in MeOH (30 mL) was added 4-bromobenzyl bromide (5.0 g, 1.2 eq., 20.0 mmol). The mixture was heated at 85 °C for 16 h and then diluted with H_2O. The resulting mixture was extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL), The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 8/1) to give 2-(4-bromophenyl)butan-2-one (**1u-S1**, 2.2 g, 9.8 mmol) in 49% yield as a colourless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 2H), 2.87–2.82 (m, 2H), 2.77–2.72 (m, 2H) , 2.14 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 140.0, 131.5, 130.1, 119.8, 44.8, 30.1, 29.0. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **7**.

2-(4-Bromophenethyl)-2-methyl-1,3-dioxolane (1u-S2)

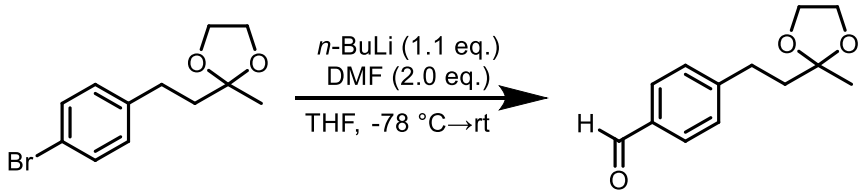


1u-S1 **1u-S2**

4-(4-bromophenyl)butan-2-one (**1u-S1**, 1.1 g, 5.0 mmol), ethylene glycol (5.5 mL, 20.0 eq.), *p*-toluenesulfonic acid (11.4 mg, 0.081 eq.), and toluene (30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. The solution was heated to 145 °C and refluxed for 24 h. The solution was quenched with sat. $NaHCO_3$ aq. (10 mL), extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL), The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (dichloromethane/hexane = 1/1) to give 2-(4-bromophenethyl)-2-methyl-1,3-dioxolane (**1u-S2**, 1.3 g, 4.9 mmol) in 97% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 4.02–3.94 (m, 4H), 2.69–2.65 (m, 2H), 1.96–1.91 (m, 2H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 131.4, 130.1, 119.4, 109.5, 64.8, 40.8, 29.6, 24.0; IR (ATR) cm^{-1}: 2981, 2953, 2878, 1488, 1374, 1252, 1218, 1137, 1071, 1053, 1010; DART-HRMS m/z: 271.0329 ($[M+H]^+$); Calcd. for $C_{12}H_{16}BrO_2$: 271.0334.

4-(2-(2-Methyl-1,3-dioxolan-2-yl)ethyl)benzaldehyde (1u-S3)

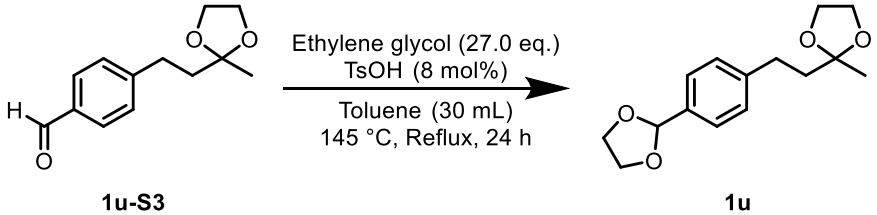


1u-S2 **1u-S3**

To a stirred solution of 2-(4-bromophenethyl)-2-methyl-1,3-dioxolane (**1u-S2**, 1.2 g, 4.4 mmol) in anhydrous THF (10 mL), a solution of *n*-BuLi in *n*-hexane (1.9 mL, 2.6 M, 1.1 eq.) was added dropwise at -78 ℃ for 5 min. The mixture was stirred at the same temperature for 30 min, and then *N,N*-dimethylformamide (0.76 mL, 2.0 eq.) was added to the mixture at -78 ℃ for 10 min. The mixture was allowed to warm to ambient temperature, quenched with H_2O (15 mL), extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL), The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 4-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)benzaldehyde (**1u-S3**, 811.0 mg, 3.7 mmol) in 84% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.80 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 4.03–3.95 (m, 4H), 2.83–2.78 (m, 2H), 2.02–1.97 (m, 2H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 149.8, 134.4, 130.0, 129.0, 109.4, 64.8, 40.5, 30.4, 24.1; IR (ATR) cm^{-1}: 2983, 2880, 1695, 1605, 1575, 1376, 1305, 1213, 1168, 1137, 1086, 1051; DART-HRMS m/z: 221.1163 ($[M+H]^+$); Calcd. for $C_{13}H_{17}O_3$: 221.1178.

2-(4-(1,3-Dioxolan-2-yl)phenethyl)-2-methyl-1,3-dioxolane (1u)

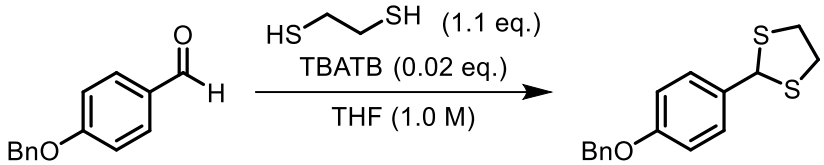


1u-S3 **1u**

4-(2-(2-methyl-1,3-dioxolan-2-yl)ethyl)benzaldehyde (**1u-S3**, 721.0 mg, 3.3 mmol), ethylene glycol (5.0 mL, 27.0 eq.), *p*-toluenesulfonic acid (11.4 mg, 0.081 eq.), and toluene (30 mL) were added into a round-bottomed flask equipped with a Dean–Stark trap with a condenser. The solution was heated to 145 °C and refluxed for 24 h. The solution was quenched with sat. $NaHCO_3$ aq. (10 mL), extracted with ethyl acetate (20 mL×3), and the combined organic layers were washed with brine (10 mL), The organic layer was concentrated in vacuo and the residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 2-(4-(1,3-dioxolan-2-yl)phenethyl)-2-methyl-1,3-dioxolane (**1u**, 812.0 mg, 3.1 mmol) in 93% yield as a yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39 (d, J = 8.3 Hz, 2H), 7.21 (d, J = 8.3 Hz, 2H), 5.78 (s, 1H), 4.15–4.00 (m, 4H), 4.00–3.93 (m, 4H), 2.74–2.70 (m, 2H), 1.96–1.93 (m, 2H), 1.36 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 143.3, 135.2, 128.2, 126.4, 109.5, 103.7, 65.2, 64.7, 40.9, 30.0, 23.9; IR (ATR) cm^{-1}: 2980, 2881, 1429, 1376, 1219, 1086, 1053; DART-HRMS m/z: 265.1435 ([M+H]$^+$); Calcd. for $C_{15}H_{21}O_4$: 265.1440.

2-(4-(Benzyloxy)phenyl)-1,3-dithiolane (1v)

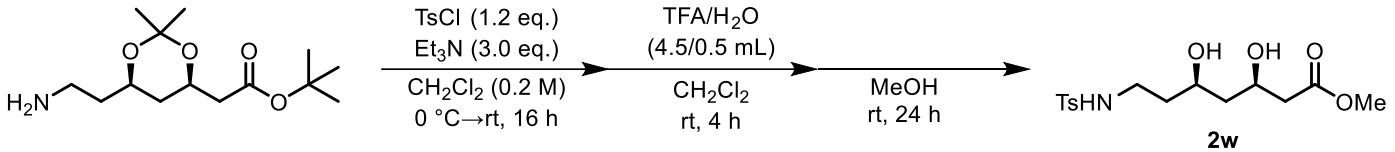


2a **1v**

To a solution of 4-benzyloxybenzaldehyde (**2a**, 1.1 g, 5.0 mmol) in THF (5 mL) and 1,2-ethanedithiol (0.5 mL, 1.1 eq.) was added tetrabutylammonium tribromide (TBATB, 48.0 mg, 0.02 eq.). The homogeneous reaction was stirred at room temperature and the progress of the reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was poured into sat. $NaHCO_3$ aq. (10 mL) and the product was extracted with ethyl acetate (2×25 mL). The combined organic layers were dried over Na_2SO_4 and concentrated. Further purification was achieved by a flash column chromatography (hexane/ethyl acetate = 10/1) to give 2-(4-(benzyloxy)phenyl)-1,3-dithiolane (**1v**, 1.4 g, 4.9 mmol) in 99% yield as a colourless solid.

^{1}H NMR (500 MHz, $CDCl_3$): 7.46–7.36 (m, 6H), 7.33–7.30 (m, 1H), 6.91 (d, J = 8.5 Hz, 2H), 5.63 (s, 1H), 5.05 (s, 2H), 3.52–3.30 (m, 4H) ; ^{13}C NMR (125 MHz, $CDCl_3$): δ 158.6, 136.8, 132.1, 129.1, 128.6, 128.0, 127.4, 114.7, 70.0, 56.0, 40.2. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **8**.

(3*R*, 5*R*)-Methyl 3,5-dihydroxy-7-(4-methylphenylsulfon amide)heptamoate (2w)



2w

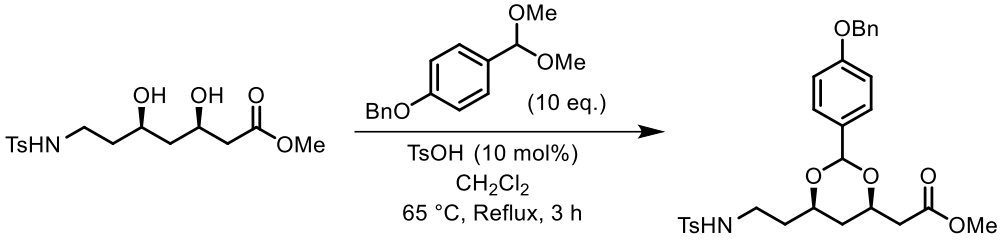
To a solution of tert-butyl 2-((4*R*, 6*R*)-6-(2-aminoethyl)-2,2-dimethyl-1,3-dioxan-4-yl)acetate (1.4 g, 5.0 mmol) in CH_2Cl_2 (20 mL) at 0 °C was added triethylamine (2.0 mL, 3.0 mmol). After stirring for 15 min, *p*-toluenesulfonyl chloride (1.1 g, 1.2 eq., 12.0 mmol) was added, and the reaction was stirred at room temperature for 16 h. Upon completion, the reaction solution was diluted with CH_2Cl_2 (30 mL) and washed with sat. NH_4Cl aq. (50 mL), sat. $NaHCO_3$ aq. (50 mL), and brine (50 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was used for the next reaction without further purification.

To a solution of the crude mixture in CH_2Cl_2 (3 mL) at 0 °C was added trifluoroacetic acid and H_2O (4.5/0.5 mL). The reaction was stirred at room temperature for 4 h, and then the reaction mixture was poured into brine, and extracted with *n*-butyl

alcohol (50 mL×3). The combined organic layers were concentrated in vacuo and the residue was used for the next reaction without further purification.

Methanol solution (20 mL) of the residue was stirred at room temperature for 24 h. The reaction was diluted with CH_2Cl_2 (30 mL) and washed brine (5 mL). The reaction mixture was poured into H_2O, extracted with CH_2Cl_2 (20 mL×3), and the combined organic layers were washed with brine (10 mL). The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 1/1) to give (3*R*,5*R*)-methyl 3,5-dihydroxy-7-(4-methylphenylsulfon amide)heptamoate (**2w**, 1.4 g, 4.2 mmol) in 42% yield (3 steps) as a colourless solid. MP: 124 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.43 (t, *J* = 5.2 Hz, 1H), 4.28–4.21 (m, 1H), 4.03–4.00 (m, 2H), 3.80 (s, 1H), 3.72 (s, 3H), 3.21–3.13 (m, 1H), 3.04–2.97 (m, 1H), 2.46 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.64–1.44 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ172.98, 143.21, 136.96, 129.65, 127.09, 70.98, 68.99, 51.91, 41.90, 41.21, 40.74, 35.93, 21.49; IR (ATR) cm^{-1}: 3467, 3281, 2951, 1722, 1598, 1438, 1322, 1203, 1156, 1092; DART-HRMS m/z: 328.1239 ([M-H_2O+H]$^+$); Calcd. for $C_{15}H_{24}NO_6S$: 328.1219; $[\alpha]_D^{25.8}$ = -16.77 (c 0.5, $CHCl_3$).

Methyl 2-((2*R*, 4*R*, 6*R*)-2-(4-(benzyloxy)phenyl)-6-(2-(4-methylphenylsulfon amide)ethyl)methyl)-1,3-dioxan-4-yl)acetate (1w)

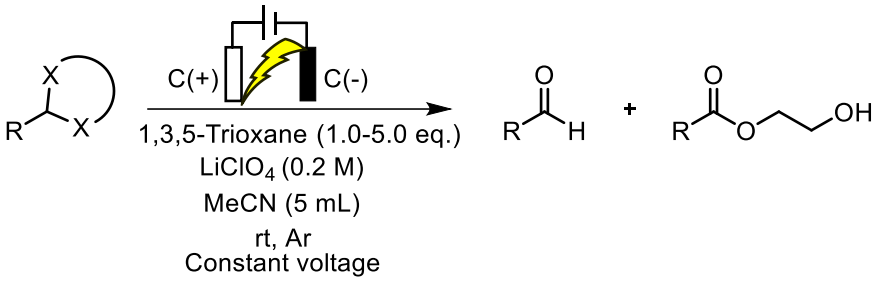


2w **1w**

1-(Benzyloxy)-4-(dimethoxymethyl)benzene (5.2 g, 10.0 eq., 20.0 mmol) was added to a solution of **2w** (813.4 mg, 2.4 mmol) and *p*-toluenesulfonic acid (44.9 mg, 0.1 eq.) in CH_2Cl_2 (15 mL). The solution was stirred for 3 h at 65 °C, and then sat. $NaHCO_3$ aq. (5 mL) was added to quench the reaction. The resulting mixture was extracted with CH_2Cl_2 (20 mL×3). The combined organic layers were washed with brine, dried over Na_2SO_4. and concentrated in vacuo. The residue was purified by silica-gel column chromatography (hexane/ethyl acetate = 1/1) to give methyl 2-((2*R*, 4*R*, 6*R*)-2-(4-(benzyloxy)phenyl)-6-(2-(4-methylphenylsulfon amide)ethyl)methyl)-1,3-dioxan-4-yl)acetate (**1w**, 1.0 g, 1.9 mmol) in 81% yield as a colourless solid. MP: 104 °C; ^{1}H NMR (400 MHz, $CDCl_3$): 7.67 (d, *J* = 8.6 Hz, 2H), 7.44–7.25 (m, 9H), 6.96 (d, *J* = 8.6 Hz, 2H), 5.42 (s, 1H), 5.08 (s, 2H), 4.93 (t, *J* = 5.6 Hz, 1H), 4.27–4.21 (m, 1H), 3.94–3.88 (m, 1H), 3.69 (s, 3H), 3.22–3.14 (m, 1H), 3.10–3.02 (m, 1H), 2.69 (dd, *J* = 15.6, 7.0 Hz, 1H), 2.47 (dd, *J* = 15.6, 6.2 Hz, 1H), 2.41 (s, 3H), 1.81–1.72 (m, 2H), 1.64–1.61 (m, 1H), 1.43–1.34 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ170.97, 159.11, 143.29, 136.82, 136.73, 130.67, 129.63, 128.54, 127.91, 127.39, 127.22, 127.04, 114.56, 100.53, 74.91, 72.89, 69.92, 51.77, 40.49, 40.08, 35.94, 34.70, 21.47; IR (ATR) cm^{-1}: 3283, 2950, 2873, 1737, 1614, 1515, 1436, 1327, 1242, 1159, 1120, 1092, 1060, 1011; DART-HRMS m/z: 540.2048([M+H]$^+$); Calcd. for $C_{29}H_{34}NO_7S$: 540.2056.

12. General procedure and analytical data for deprotection of acetals, ketals, and dithioacetal

General procedure B (GP B): deprotection of acetal or ketal by electrolysis



The graphite electrodes (10.0 mm×8.0 mm×1.0 mm) were polished with 2000 grit sandpaper before use. Substrate (0.2 mmol), 1,3,5-trioxane (1.0–5.0 eq.), and $LiClO_4$ (1.0 mmol, 0.2 M) were added into an oven dried ElectraSyn vial (10 mL) equipped with a magnetic stir bar. Dried acetonitrile (MeCN, 5.0 mL) was then added into the mixture. The vial was sealed with ElectraSyn vial cap equipped with graphite anode, graphite cathode, and reference electrode. An argon balloon was attached to the cap and the air inside the vial was replaced with argon using vacuum pump. The mixture was prestirred for 10 min at room temperature. The reaction mixture was subject to electrolysis. After electrolysis, the electrodes were washed with CH_2Cl_2 (5 mL×2) and H_2O (5 mL×1), and the reaction mixture was extracted with CH_2Cl_2 (20 mL×2). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica-gel column chromatography.

4-(Benzyloxy)benzaldehyde (2a)

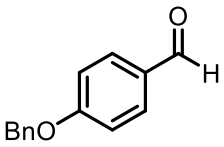


Table 1, Entry 1:

2-(4-Benzyloxyphenyl)-1,3-dioxolane (**1a**, 51.3 mg, 0.2 mmol), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 min, total charge: 0.16 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 7/1) to give 4-(benzyloxy)benzaldehyde (**2a**, 40.3 mg, 0.19 mmol) in 95% yield as a colourless solid.

Table 4 (deprotection of **1j**):

According to **GP B**, 2-(4-(benzyloxy)phenyl)-5,5-dimethyl-1,3-dioxolane (**1j**, 59.7 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), K_2CO_3 (27.6 mg, 0.2 mmol, 1.0 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 40 min, total charge: 0.59 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 4-(benzyloxy)benzaldehyde (**2a**, 37.0 mg, 0.17 mmol) in 86% yield as a colourless solid.

Table 4 (deprotection of **1k**):

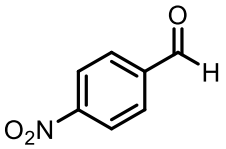
According to **GP B**, 2-(4-(benzyloxy)phenyl)-4,4,5,5-tetramethyl-1,3-dioxolane (**1k**, 62.5 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.42 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 4-(benzyloxy)benzaldehyde (**2a**, 35.7 mg, 0.17 mmol) in 84% yield as a colourless solid.

Table 4 (deprotection of **1t**):

According to **GP B**, 2-(4-(benzyloxy)phenyl)-1,3-dithiolane (**1t**, 57.7 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 60 min, total charge: 1.73 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 4-(benzyloxy)benzaldehyde (**2a**, 35.9 mg, 0.17 mmol) in 85% yield as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.88 (s , 1H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.45–7.33 (m, 5H), 7.07 (d, *J* = 8.6 Hz, 2H), 5.14 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.8, 163.7, 135.8, 132.0, 130.0, 128.7, 128.3, 127.5, 115.1, 70.2. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **9**.

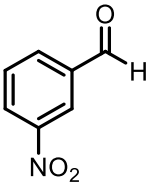
4-Nitrobenzaldehyde (2b)



According to **GP B**, 2-(4-nitorophenyl)-1,3-dioxolane (**1b**, 39.0 mg, 0.2 mmol), 1,3,5-trioxane (18.0 mg, 0.2 mmol, 1.0 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.63 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 4-nitrobenzaldehyde (**2b**, 29.4 mg, 0.19 mmol) in 94% yield as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.18 (s, 1H), 8.41 (d, *J* = 8.6 Hz, 2H), 8.10 (d, *J* = 8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 190.3, 151.1, 140.0, 130.5, 124.3. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **10**.

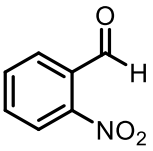
3-Nitrobenzaldehyde (2c)



According to **GP B**, 2-(3-nitorophenyl)-1,3-dioxolane (**1c**, 39.0 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.72 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 3-nitrobenzaldehyde (**2c**, 27.5 mg, 0.18 mmol) in 91% yield as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.73 (dd, *J* = 2.4, 2.4 Hz, 1H), 8.52–8.49 (m, 1H), 8.25 (ddd, *J* = 8.0, 2.4, 1.6 Hz , 1H), 7.79 (dd, *J* = 8.0, 8.0 Hz , 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 189.8, 148.7, 137.3, 134.6, 130.4, 128.6, 124.5. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **10**.

2-Nitrobenzaldehyde (2d)

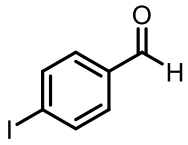


According to **GP B**, 2-(2-nitorophenyl)-1,3-dioxolane (**1d**, 39.0 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.),

$LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.31 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 2-nitrobenzaldehyde (**2d**, 27.1 mg, 0.18 mmol) in 90% yield as a yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 10.43 (s, 1H), 8.13 (d, *J* = 8.5 Hz, 1H), 7.97 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.84–7.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 188.2, 149.5, 134.1, 133.7, 131.3, 129.6, 124.5. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **10**.

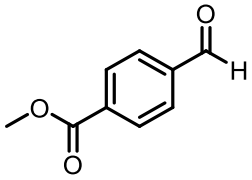
2-Iodobenzaldehyde (2e)



According to **GP B**, 2-(4-iodophenyl)-1,3-dioxolane (**1e**, 55.2 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.8 V, time: 5 min, total charge: 0.40 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 8/1) to give 2-iodobenzaldehyde (**2e**, 40.0 mg, 0.17 mmol) in 86% yield as a colourless solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.96 (s, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.60 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.5, 138.4, 135.5, 130.8, 102.9. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **11**.

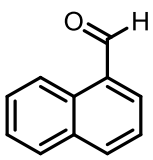
Methyl 4-formylbenzaldehyde (2f)



According to **GP B**, methyl 4-(1,3-dioxolane-2-yl)benzoate (**1f**, 41.6 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.43 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give methyl 4-formylbenzaldehyde (**2f**, 32.0 mg, 0.19 mmol) in 97% yield as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.20 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz , 2H), 3.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 191.6, 166.0, 139.1, 135.0, 130.1, 129.5, 52.6. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **12**.

1-Naphthaldehyde (2g)

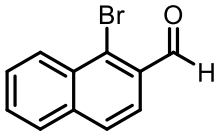


According to **GP B**, 2-(naphthalen-1-yl)-1,3-dioxolane (**1g**, 40.0 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the

reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 10 min, total charge: 0.59 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 1-naphthaldehyde (**2g**, 27.8 mg, 0.18 mmol) in 89% yield as a brown oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.40 (s, 1H), 9.26 (d, J = 8.6, 1H), 8.10 (d, J = 8.0 Hz , 1H), 7.99 (dd, J = 6.8, 1.6 Hz, 1H), 7.92 (d, J = 7.6 Hz , 1H), 7.72–7.67 (m, 1H), 7.65–7.56 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 193.6, 136.7, 135.3, 133.7, 131.3, 130.5, 129.1, 128.4, 126.9, 124.8 (2C). Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **13**.

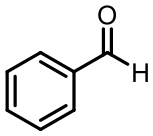
1-Bromo-2-naphthaldehyde (2h)



According to **GP B**, 2-(1-bromonaphthalen-2-yl)-1,3-dioxolane (**1h**, 55.6 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 1.5 V, time: 30 min, total charge: 0.30 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 1-bromo-2-naphthaldehyde (**2h**, 38.7 mg, 0.16 mmol) in 82% yield as a colourless solid.

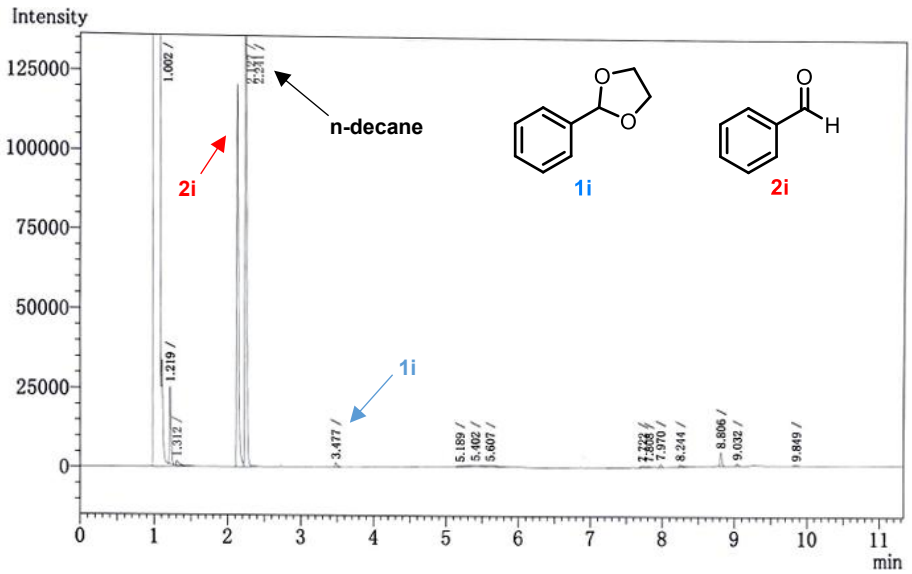
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.65 (s, 1H), 8.50–8.46 (m, 1H), 7.92 (d, J = 8.0 Hz, 1H), 7.88–7.82 (m, 2H), 7.70–7.65 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.8, 137.1, 132.0, 131.2, 129.7, 128.4, 128.2, 128.2, 128.0, 124.0. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **14**.

Benzaldehyde (2i)

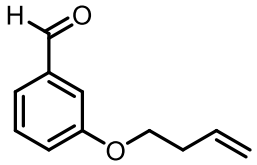


According to **GP B**, phenyl-1,3-dioxolane (**1i**, 30.0 mg, 0.2 mmol), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 20 min, total charge: 0.13 F/mol and stirring: 250 rpm) to give benzaldehyde (**2i**) quantitatively as GC yield. The yield of **2i** was determined by GC-FID of the crude residue using *n*-decane (39.0 μL, 0.2 mmol) as the internal standard. Retention time: 2.13 min (**2i**), 3.48 min (**1i**), and 2.24 min (*n*-decane).

GC-FID chart of **2i**



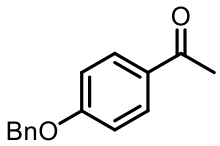
3-(But-3-enyloxy)benzaldehyde (2l)



According to **GP B**, 2-(3-(but-3-enyloxy)phenyl)-1.3-dioxolane (**1l**, 44.1 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 30 min, total charge: 0.26 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 10/1) to give 3-(but-3-enyloxy)benzaldehyde (**2l**, 33.8 mg, 0.19 mmol) in 96% yield as a pale yellow oil .

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.47–7.42 (m, 2H), 7.39–7.38 (m, 1H), 7.21–7.15 (m, 1H), 5.96–5.86 (m, 1H), 5.21–5.16 (m, 1H), 5.15–5.11 (m, 1H), 4.07 (t, *J* = 6.6 Hz, 2H), 2.60–2.54 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.1, 159.4, 137.7, 134.1, 130.0, 123.4, 121.9, 117.2, 112.7, 67.4, 33.4. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **15**.

1-(4-(benzyloxy)phenyl)ethanone (2m)

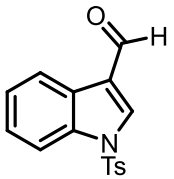


2-(4-(Benzyloxy)phenyl)-2-methyl-1,3-dioxolane (**1m**, 54.1 mg, 0.2 mmol), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 15 min, total charge: 0.16 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 7/1) to give 1-(4-(benzyloxy)phenyl)ethanone (**2m**, 40.9 mg, 0.18 mmol) in 90% yield as a colourless solid.

2-(4-(Benzyloxy)phenyl)-2-methyl-1,3-dioxolane (**1m**, 54.1 mg, 0.2 mmol), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant current: 5.0 mA, time: 1 h, total charge: 0.92 F/mol and stirring: 300 rpm) to give 1-(4-(benzyloxy)phenyl)ethanone (**2m**) in 87% ^{1}H NMR yield using 1,1,2,2-tetrachloroethane as the internal standard.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.93 (d, *J* = 9.0 Hz, 2H), 7.44–7.33 (m, 5H), 7.00 (d, *J* = 9.0 Hz, 2H), 5.12 (s, 1H), 2.55 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 196.7, 162.5, 136.1, 130.6, 130.4, 128.7, 128.2, 127.4, 114.5, 70.0, 26.3. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **16**.

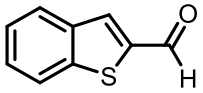
1-((4-Methylphenyl)sulfonyl)-1*H*-indol-3-carbaldehyde (2n)



According to **GP B**, 3-(1,3-dioxolane-2-yl)-1-tosyl-1*H*-indol (**1n**, 68.7 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 20 min, total charge: 0.15 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to

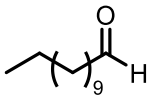
give 1-((4-methylphenyl)sulfonyl)-1*H*-indol-3-carbaldehyde (**2n**, 52.7 mg, 0.18 mmol) in 88% yield as a yellow solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 10.09 (s, 1H), 8.25 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.3 Hz, 2H), 7.43–7.34 (m, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 185.4, 146.1, 136.2, 135.1, 134.2, 130.3, 127.2, 126.3, 126.2, 125.0, 122.6, 122.3, 113.2, 21.6. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **17**.

Benzo[b]thiophene-2-carbaldehyde (2o)



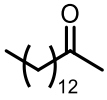
According to **GP B**, 2-(benzo[b]thiophen-2-yl)-1,3-dioxolane (**1o**, 41.3 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 30 min, total charge: 0.33 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give benzo[b]thiophene-2-carbaldehyde (**2o**, 29.2 mg, 0.18 mmol) in 90% yield as a yellow oil.
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.04 (s, 1H), 7.96–7.89 (m, 2H), 7.53–7.49 (m, 1H), 7.46–7.42 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 184.7, 143.3, 142.6, 138.5, 134.5, 128.2, 126.2, 125.2, 123.3. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **18**.

Decanal (2p)



According to **GP B**, 2-undecyl-1,3-dioxolane (**1p**, 45.7 mg, 0.2 mmol), 1,3,5-trioxane (90.0 mg, 1.0 mmol, 5.0 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 5 h, total charge: 1.88 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give decanal (**2p**, 27.5 mg, 0.15 mmol) in 75% yield as a colourless oil.
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.77 (t, *J* = 1.9 Hz, 1H), 2.42 (td, *J* = 7.0, 1.9 Hz, 2H), 1.66–1.60 (m, 2H), 1.33–1.26 (m, 16H), 0.88 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 203.0, 43.9, 31.9, 29.6 (2C), 29.4, 29.3, 29.3, 29.1, 22.7, 22.1, 14.1. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **19**.

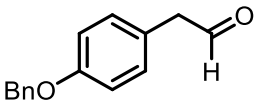
Pentadecane-2-one (2q)



According to **GP B**, 2-methyl-2-tridecyl-1,3-dioxolane (**1q**, 54.1 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 30 min, total charge: 0.16 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 20/1) to give pentadecane-2-one (**2q**, 43.3 mg, 0.19 mmol) in 96% yield as a colourless solid.
^{1}H NMR (500 MHz, $CDCl_3$): δ 2.42 (t, *J* = 7.5 Hz, 2H), 2.14 (s, 3H), 1.59–1.55 (m, 2H), 1.33–1.25 (m, 20H), 0.88 (t, *J* = 6.8

Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 209.4, 43.8, 31.9, 31.6, 29.8, 29.6, 29.6, 29.4, 29.4, 29.3, 29.1, 23.8, 22.7, 14.1. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **20**.

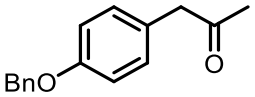
2-(4-(Benzyloxy)phenyl)acetaldehyde (2r)



According to **GP B**, 2-(4-(benzyloxy)benzyl)-1,3-dioxolane (**1r**, 54.1 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 60 min, total charge: 0.62 F/mol and stirring: 300 rpm). Purification by silica-gel column chromatography (dichloromethane/hexane = 1/1) to give 2-(4-(benzyloxy)phenyl)acetaldehyde (**2r**, 24.8 mg, 0.11 mmol) in 55% yield as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.72 (t, *J* = 2.5 Hz, 1H), 7.44–7.31 (m, 5H), 7.13 (d, *J* = 8.8 Hz, 2H), 6.98 (d, *J* = 8.8 Hz , 2H), 5.06 (s, 2H), 3.63 (d, *J* = 2.5 Hz, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.7, 158.1, 136.8, 130.7, 128.6, 128.0, 127.4, 123.9, 115.3, 70.0, 49.7. Spectroscopic data of ^{1}H and ^{13}C NMR were identical ro that of the reference **21**.

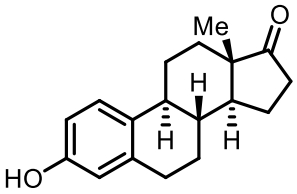
1-(4-(Benzyloxy)phenyl)propan-2-one (2s)



According to **GP B**, 2-(4-(benzyloxy)benzyl)-2-methyl-1,3-dioxolane (**1s**, 56.9 mg, 0.2 mmol), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M)), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 20 min, total charge: 0.38 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 1-(4-(benzyloxy)phenyl)propan-2-one (**2s**, 38.0 mg, 0.16 mmol) in 79% yield as a pale yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43–7.30 (m, 5H), 7.11 (d, *J* = 8.5 Hz, 2H), 6.94 (d, *J* = 8.5 Hz , 2H), 5.04 (s, 2H), 3.62 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 206.8, 157.8, 136.9, 130.4, 128.5, 127.9, 127.4, 126.5, 115.0, 69.9, 50.1, 29.1. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **22**.

(8*R*,9*S*,13*S*,14*S*)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[a]phenanthren-17-one (estrone, 2t)

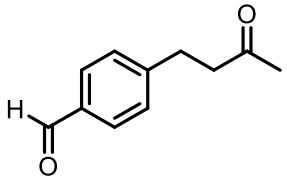


According to **GP B**, (8*R*,9*S*,13*S*,14*S*)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydrospiro[cyclopenta[*a*]phenanthrene-17,2'-[1,3]dioxolan]-3-ol (**1t**, 62.9 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.5 V, time: 9 min, total charge: 0.34 F/mol and stirring: 300 rpm). Purification by silica-gel column chromatography (hexane/acetone = 7/1) to give (8*R*,9*S*,13*S*,14*S*)-3-hydroxy-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (estrone, **2t**, 42.2 mg, 0.16 mmol) in 78% yield

as a colourless solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.0 Hz, 1H), 6.65 (dd, *J* = 8.0, 2.8 Hz, 1H), 6.59 (d, *J* = 2.8 Hz, 1H), 5.08 (s, 1H), 2.89–2.84 (m, 2H), 2.52 (dd, *J* = 18.8, 8.4 Hz, 1H), 2.43–2.33 (m, 1H), 2.26–2.20 (m 1H), 2.19–1.91 (m, 4H), 1.69–1.38 (m, 6H), 0.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 221.3, 153.5, 138.0, 132.0, 126.5, 115.3, 112.8, 50.3, 48.0, 43.9, 38.3, 35.9, 31.5, 29.5, 26.5, 25.9, 21.6, 13.8. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **23**.

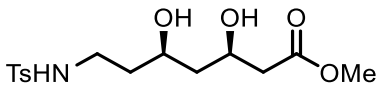
4-(3-Oxobutyl)benzaldehyde (2u)



According to **GP B**, 2-(4-(1,3-dioxolan-2-yl)phenethyl)-2-methyl-1,3-dioxolane (**1u**, 52.9 mg, 0.2 mmol), 1,3,5-trioxane (45.0 mg, 0.5 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 20 min, total charge: 0.22 F/mol and stirring: 250 rpm). Purification by silica-gel column chromatography (hexane/ethyl acetate = 5/1) to give 4-(3-oxobutyl)benzaldehyde (**2u**, 34.1 mg, 0.19 mmol) in 97% yield yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.97 (s, 1H), 7.81 (d, *J* = 7.8 Hz, 2H), 7.36 (d, *J* = 7.8 Hz, 2H), 2.98 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.1, 191.9, 148.4, 134.6, 130.0, 129.0, 44.3, 30.0, 29.6. Spectroscopic data of ^{1}H and ^{13}C NMR were identical to that of the reference **24**.

(3*R*, 5*R*)-Methyl 3,5-dihydroxy-7-(4-methylphenylsulfon amide)heptanoate (2w)



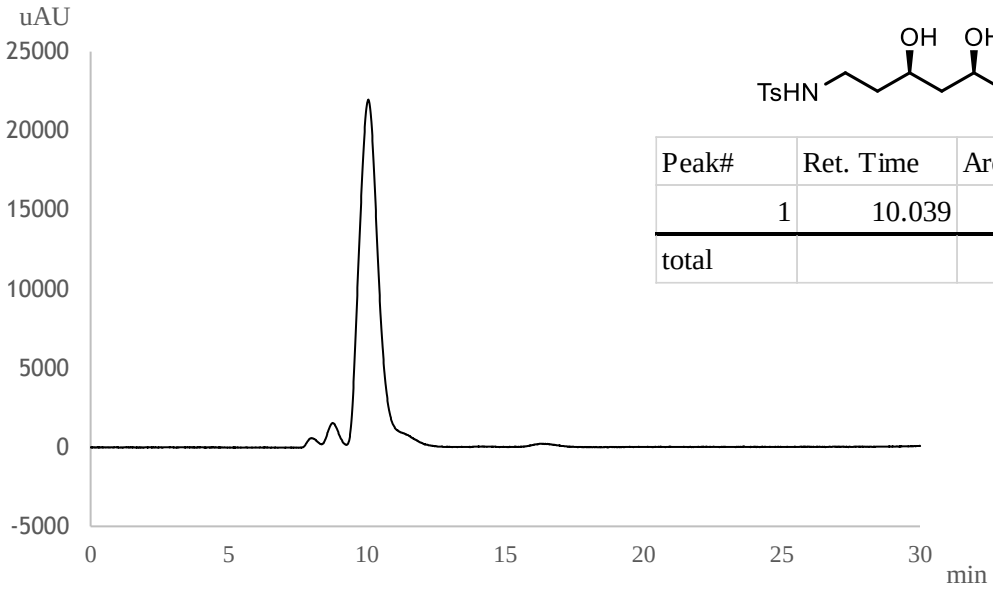
According to **GP B**, methyl 2-((2*R*, 4*R*, 6*R*)-2-(4-(benzyloxy)phenyl)-6-(2-(4-methylphenylsulfon amide)ethyl)methyl)-1,3-dioxan-4-yl)acetate (**1w**, 54.0 mg, 0.1 mmol), 1,3,5-trioxane (22.5 mg, 0.25 mmol, 2.5 eq.), $LiClO_4$ (106.4 mg, 1.0 mmol, 0.2 M), and MeCN (5.0 mL) were added into an ElectraSyn vial. After stirring for 10 min, the reaction mixture was subject to electrolysis (electrolysis parameters: constant voltage: 2.0 V, time: 2 min, total charge: 0.05 F/mol and stirring: 400 rpm). Purification by silica-gel column chromatography (ethyl acetate) to give (3*R*, 5*R*)-methyl 3,5-dihydroxy-7-(4-methylphenylsulfon amide)heptanoate (**2w**, 17.7 mg, 0.051 mmol) in 51% yield as a colourless solid. Rt: (GL Sciences Inertsustain® C18, IPA/H_2O = 1/1, 0.2 mL/min, 30 °C, 254 nm): 10.01 min (100%)

MP: 124 °C ; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.4 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.43 (t, *J* = 5.2 Hz, 1H), 4.28–4.21 (m, 1H), 4.03–4.00 (m, 2H), 3.80 (s, 1H), 3.72 (s, 3H), 3.21–3.13 (m, 1H), 3.04–2.97 (m, 1H), 2.46 (d, *J* = 6.4 Hz, 2H), 2.43 (s, 3H), 1.64–1.44 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ172.98, 143.21, 136.96, 129.65, 127.09, 70.98, 68.99, 51.91, 41.90, 41.21, 40.74, 35.93, 21.49; IR (ATR) cm^{-1}: 3467, 3281, 2951, 1722, 1598, 1438, 1322, 1203, 1156, 1092; DART-HRMS m/z: 328.1239 ([M-H_2O+H]$^+$); Calcd. for $C_{15}H_{24}NO_6S$: 328.1219; $[\alpha]_D^{26.2}$ = -17.57 (c 0.5, $CHCl_3$).

HPLC chart of **(3*R*, 5*R*)-Methyl 3,5-dihydroxy-7-(4-methylphenylsulfon amide)heptanoate (2u)**

【PDA chromatograms】

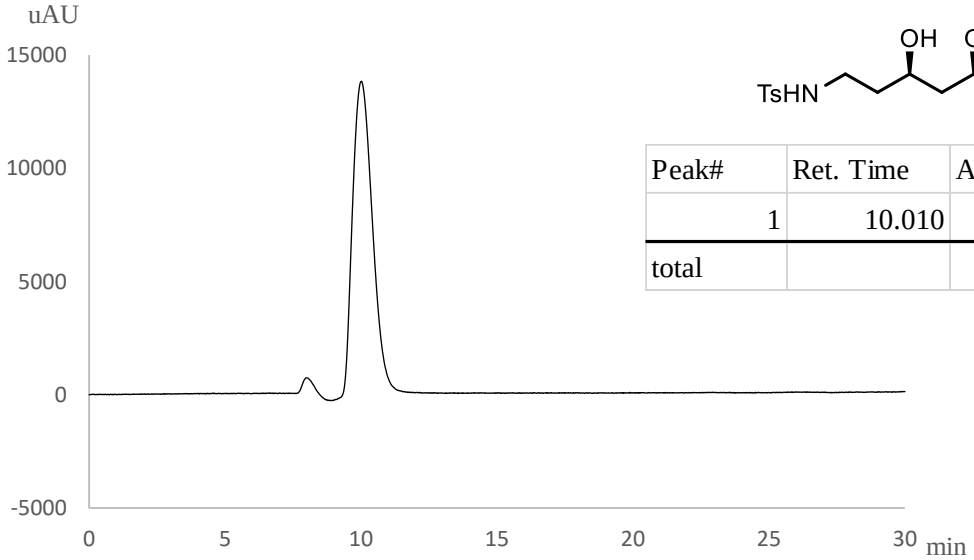
Synthesized **2u**



Peak#	Ret. Time	Area	Area%
1	10.039	1057327	100
total		1057327	100

Optical rotation: $[\alpha]_D^{25.8} = -16.77$ (c 0.5, $CHCl_3$)

2u obtained from electrolysis of **1u**

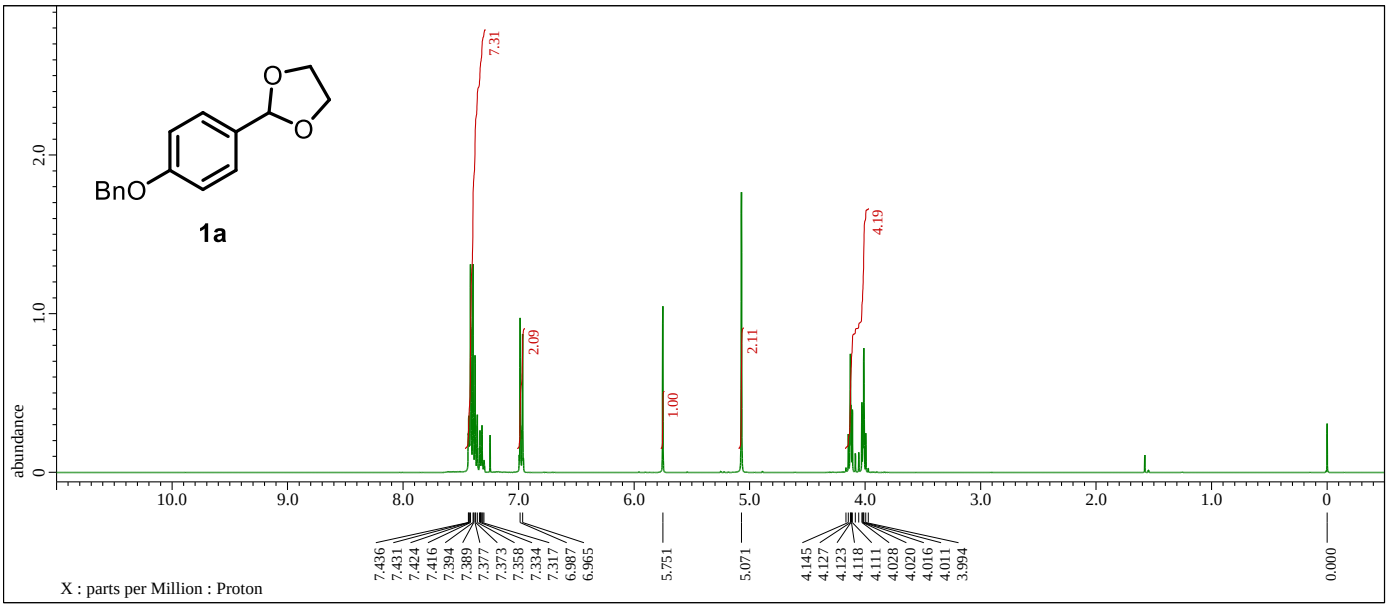


Peak#	Ret. Time	Area	Area%
1	10.010	699460	100
total		699460	100

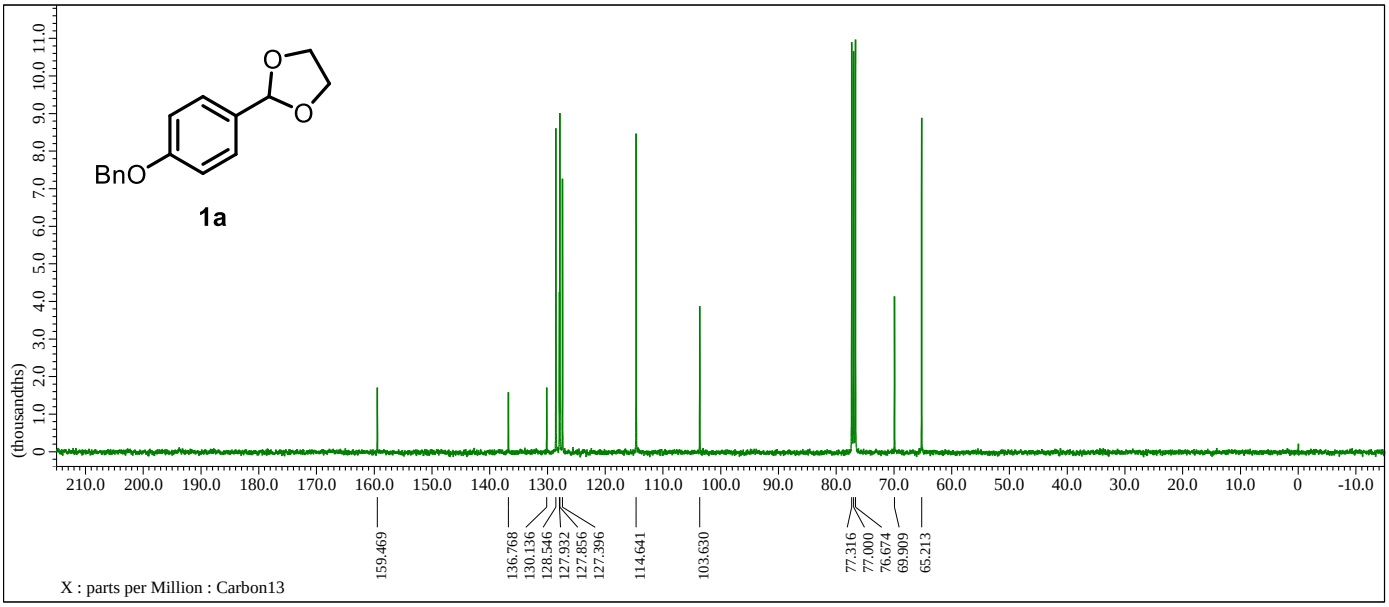
Optical rotation: $[\alpha]_D^{26.2} = -17.57$ (c 0.5, $CHCl_3$)

13. ^{1}H and ^{13}C NMR spectra

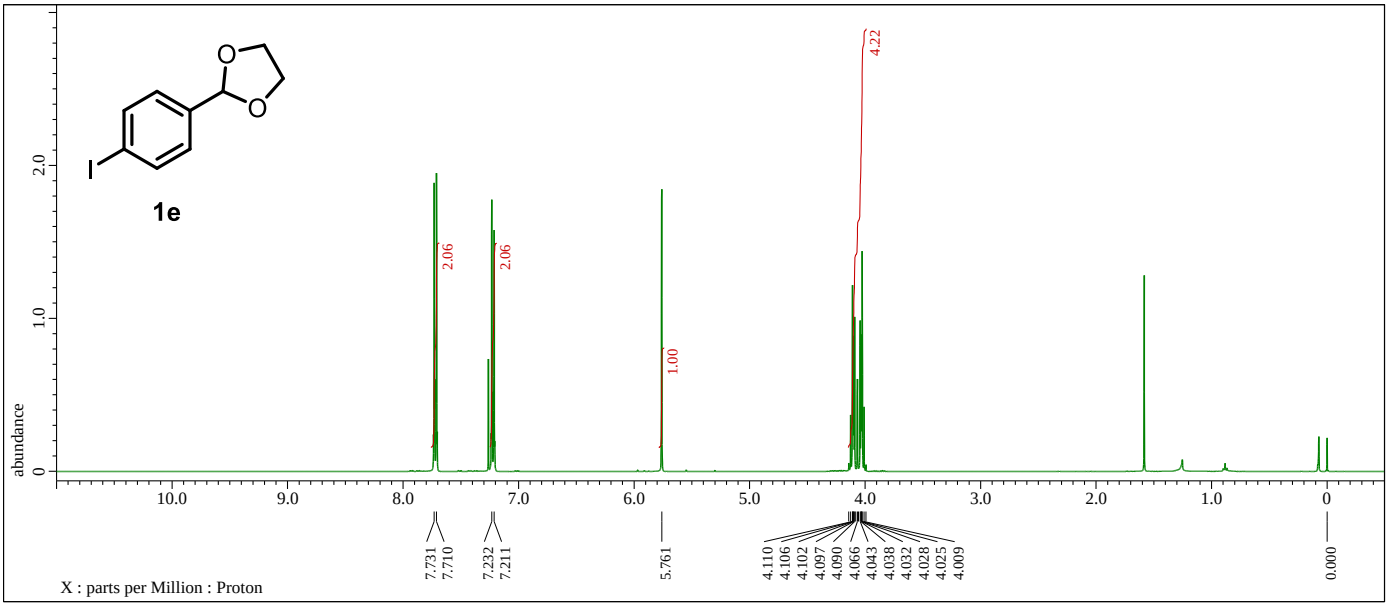
^{1}H NMR (400 MHz, $CDCl_3$) of **1a**



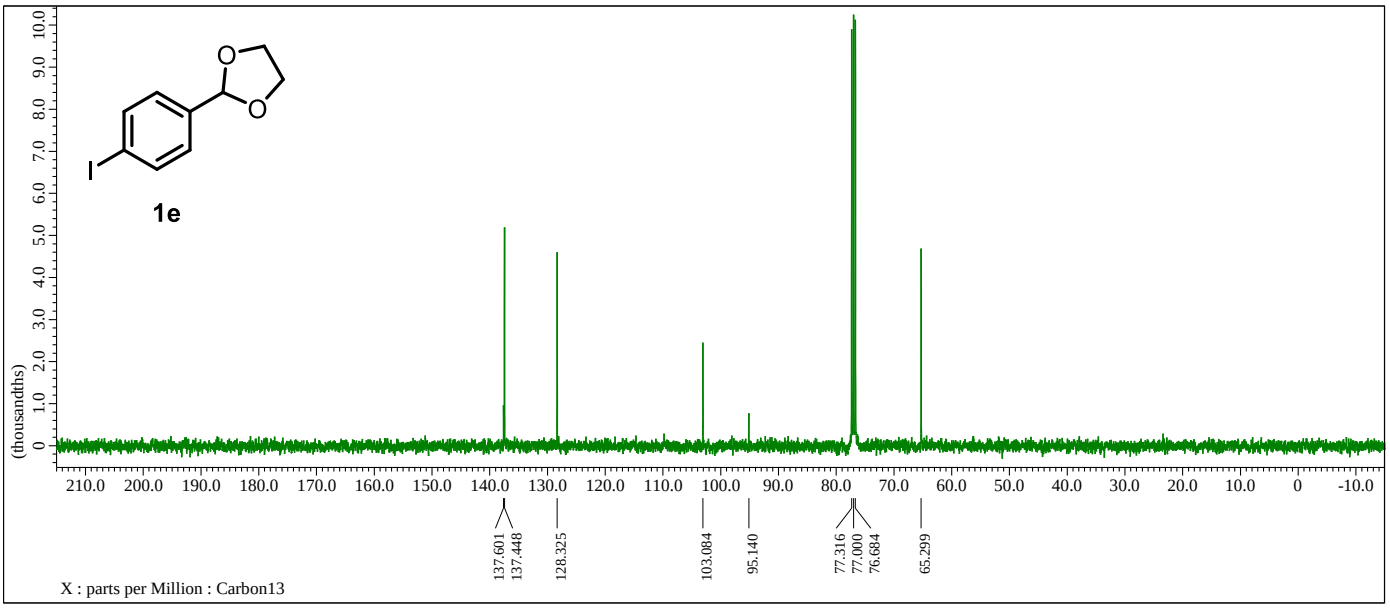
^{13}C NMR (100 MHz, $CDCl_3$) of **1a**



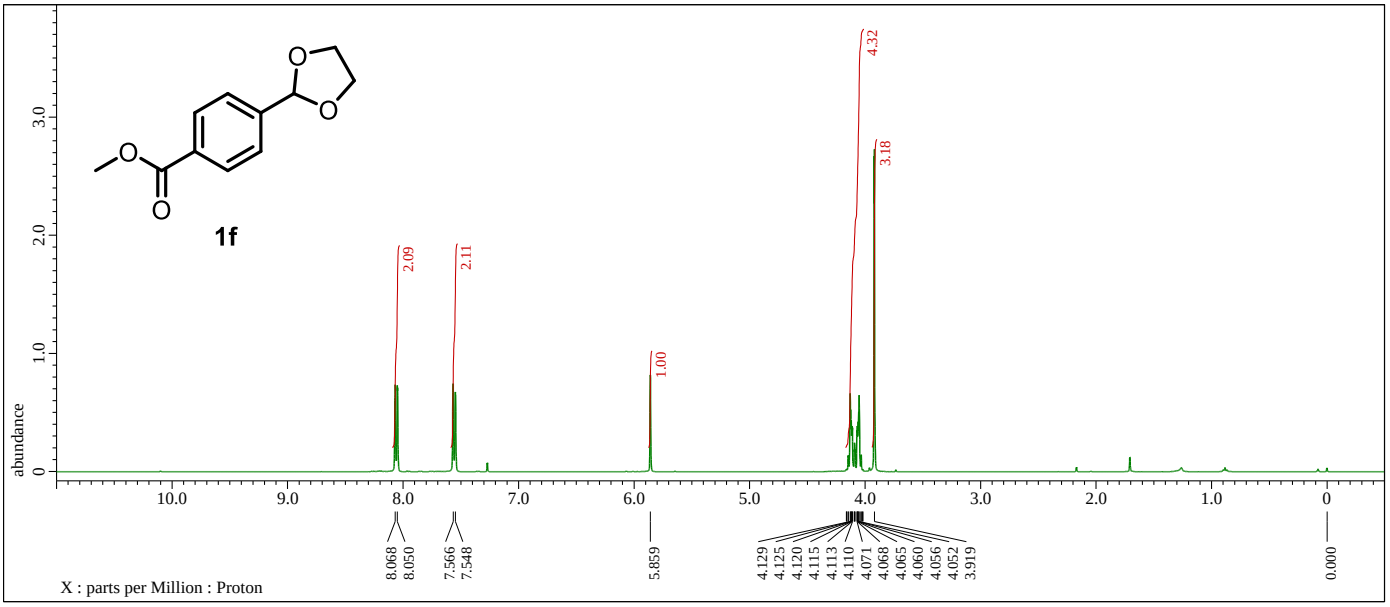
^{1}H NMR (400 MHz, $CDCl_3$) of **1e**



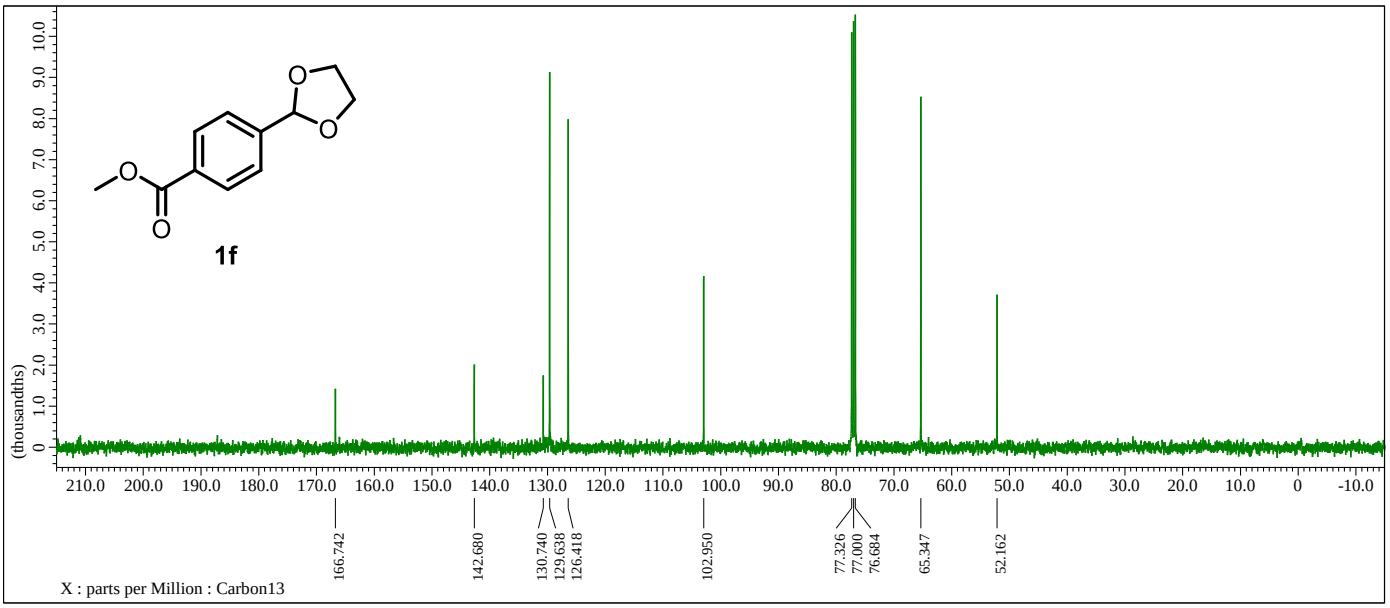
^{13}C NMR (100 MHz, $CDCl_3$) of **1e**



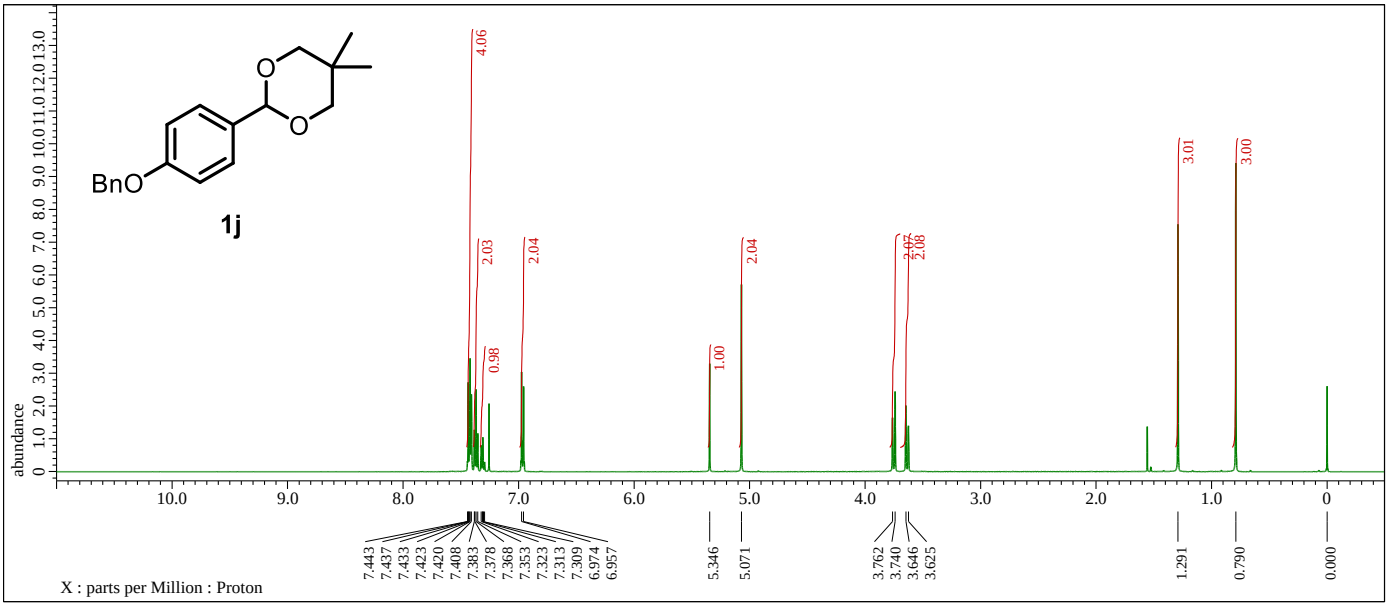
^{1}H NMR (400 MHz, $CDCl_3$) of **1f**



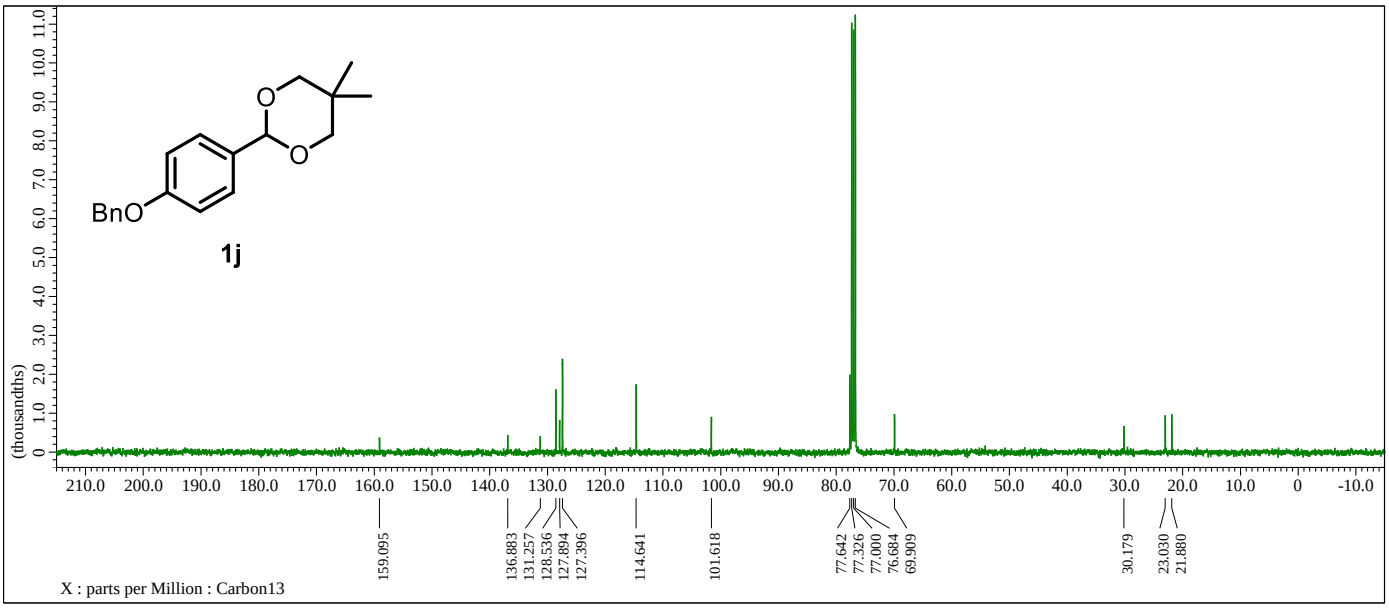
^{13}C NMR (100 MHz, $CDCl_3$) of **1f**



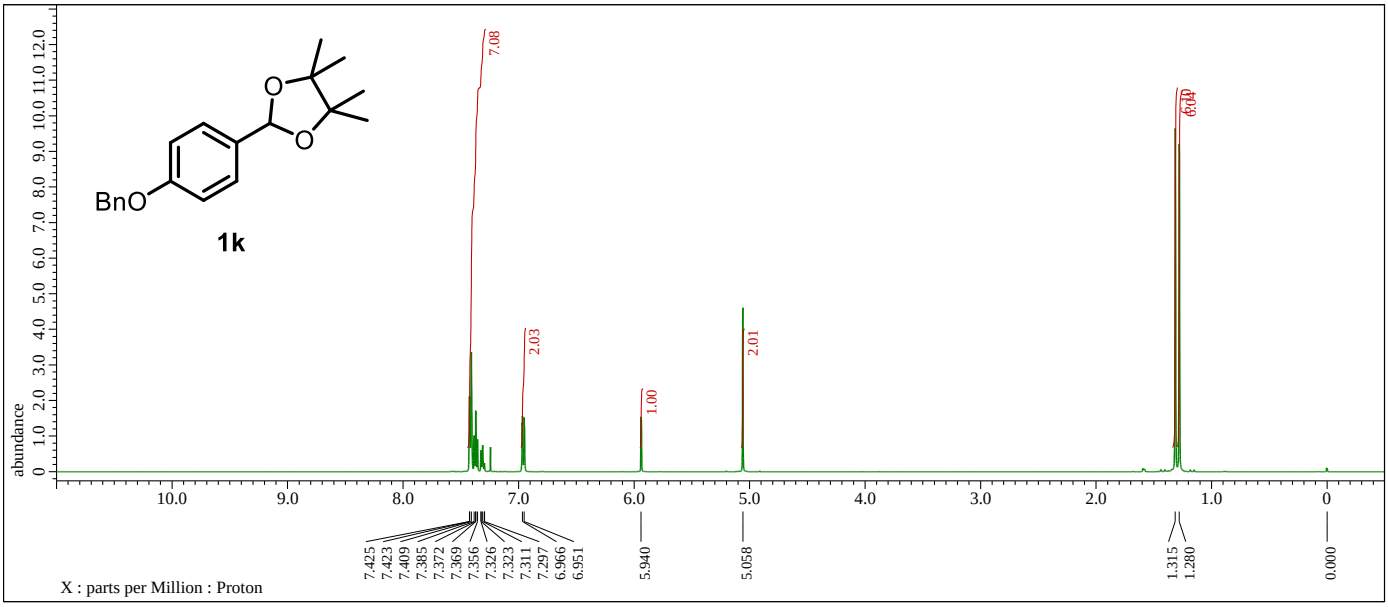
^{1}H NMR (500 MHz, $CDCl_3$) of **1j**



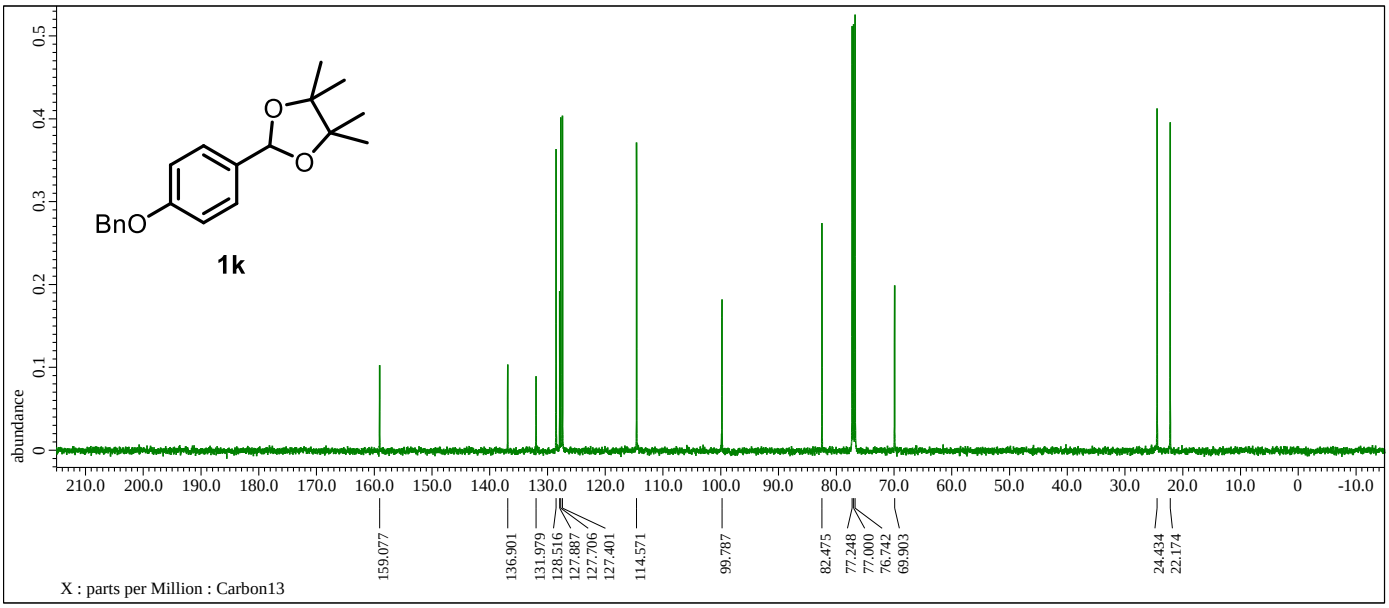
^{13}C NMR (100 MHz, $CDCl_3$) of **1j**



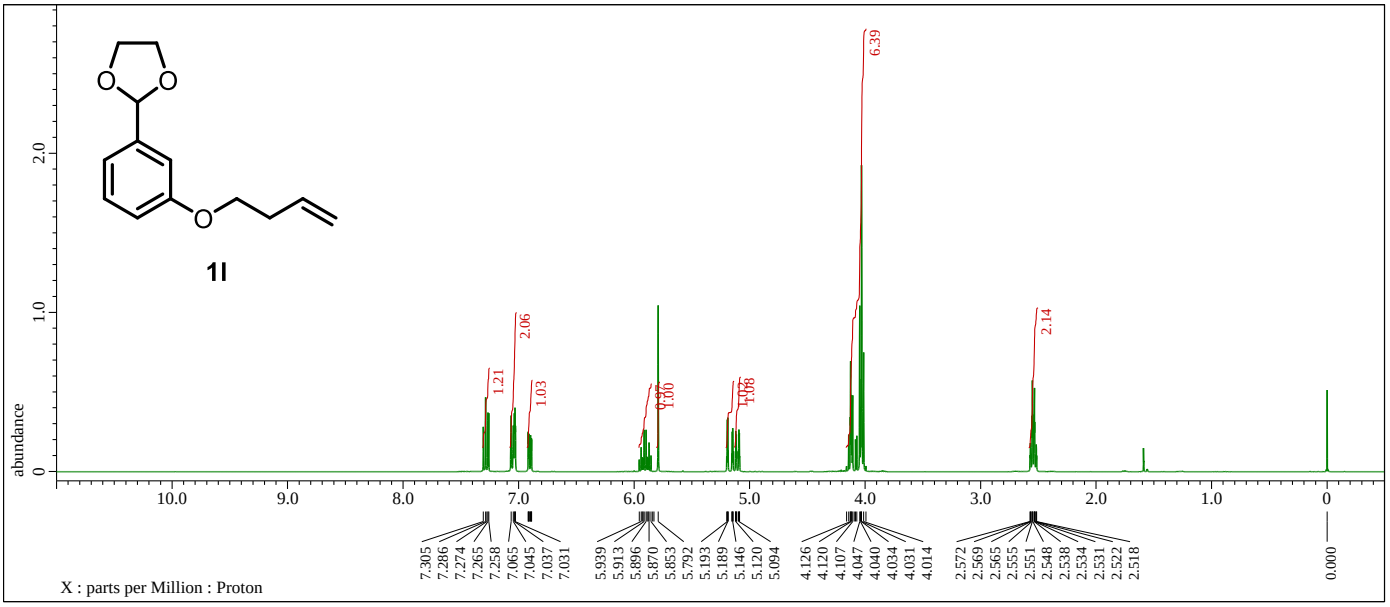
^{1}H NMR (500 MHz, $CDCl_3$) of **1k**



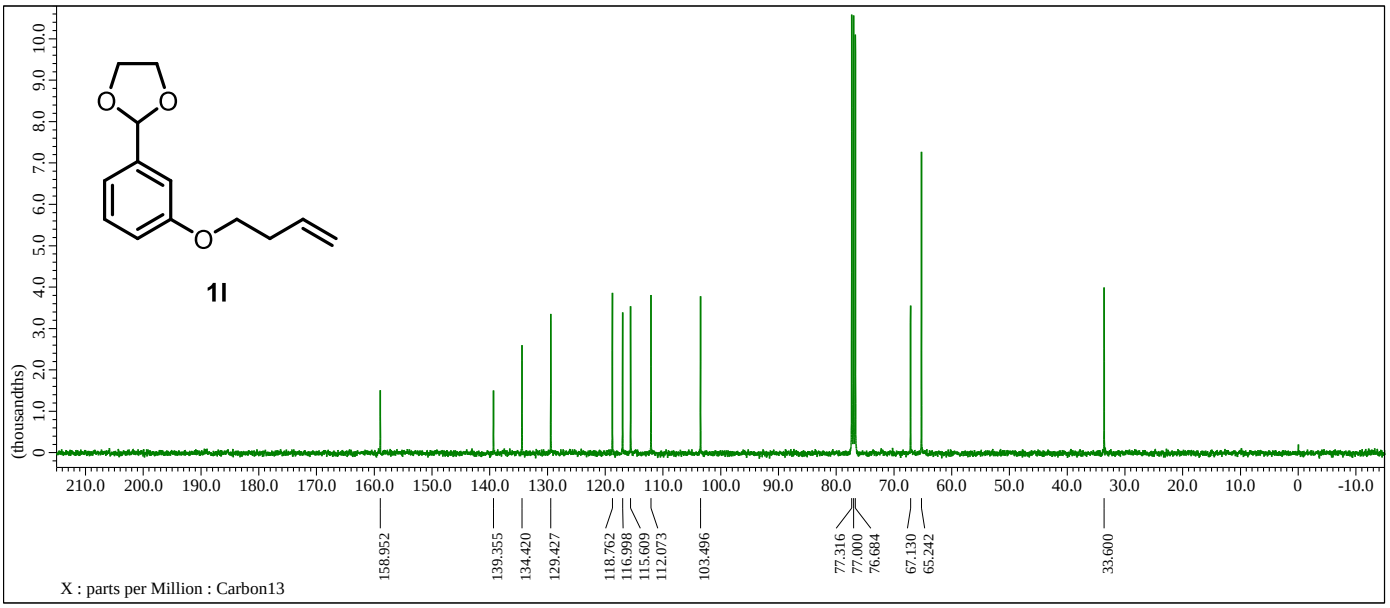
^{13}C NMR (125 MHz, $CDCl_3$) of **1k**



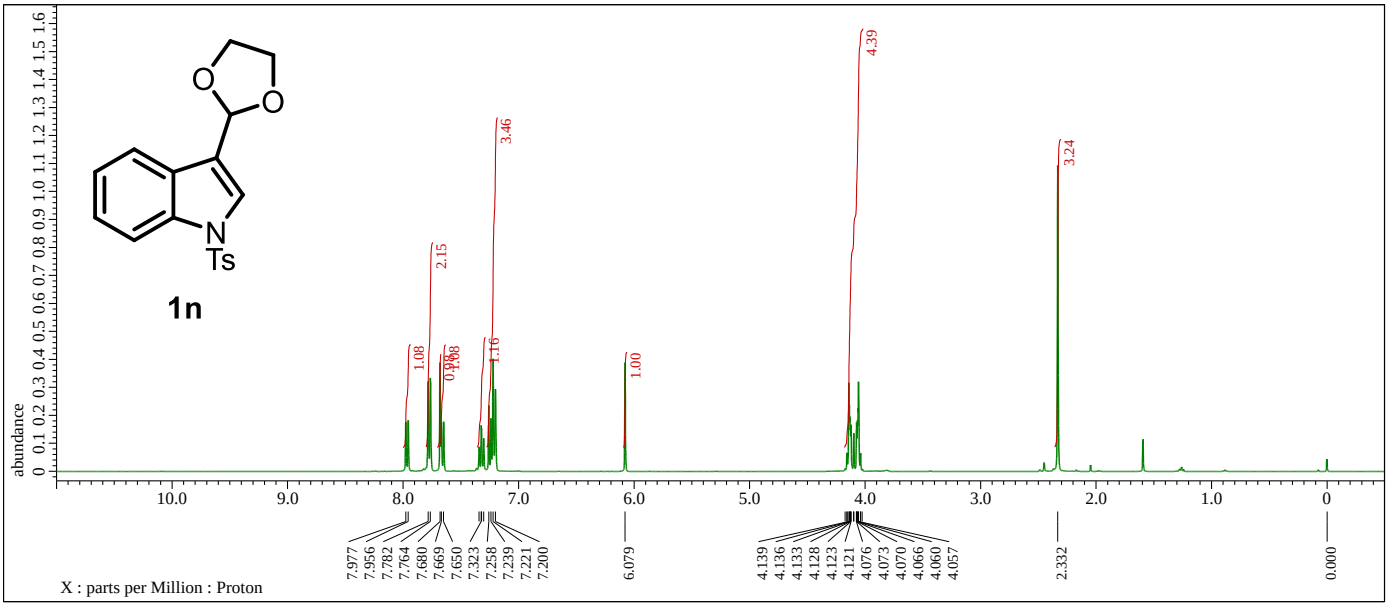
^{1}H NMR (400 MHz, $CDCl_3$) of **1l**



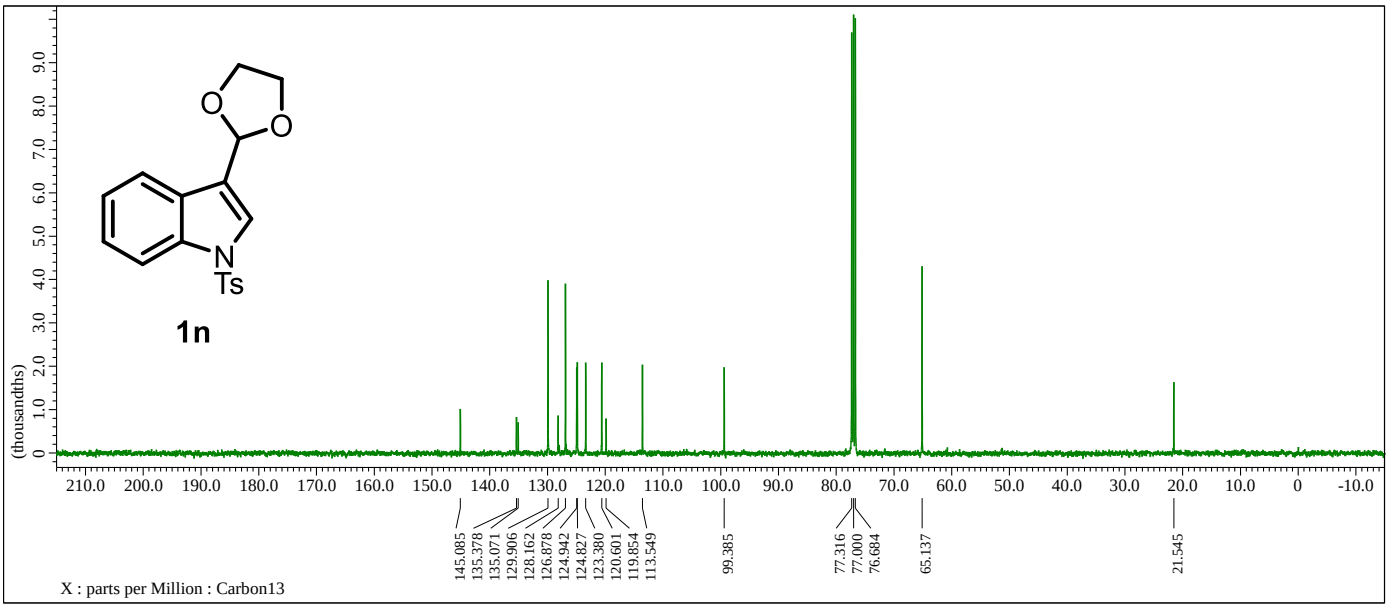
^{13}C NMR (100 MHz, $CDCl_3$) of **1l**



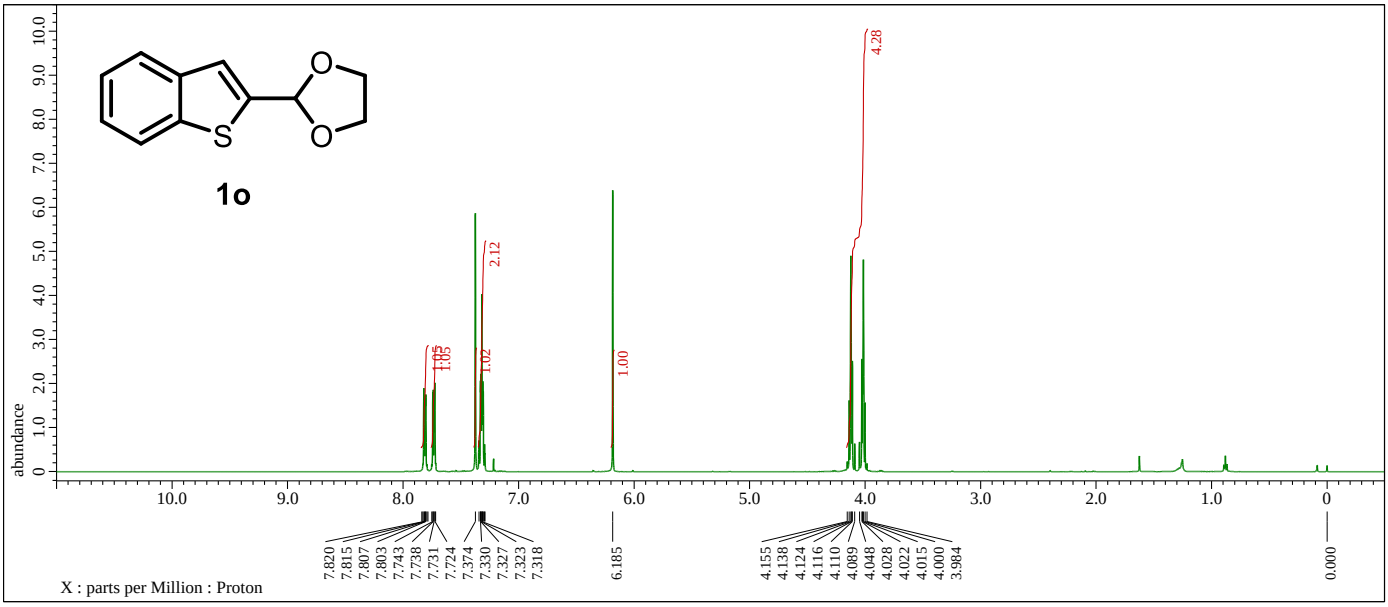
^{1}H NMR (400 MHz, $CDCl_3$) of **1n**



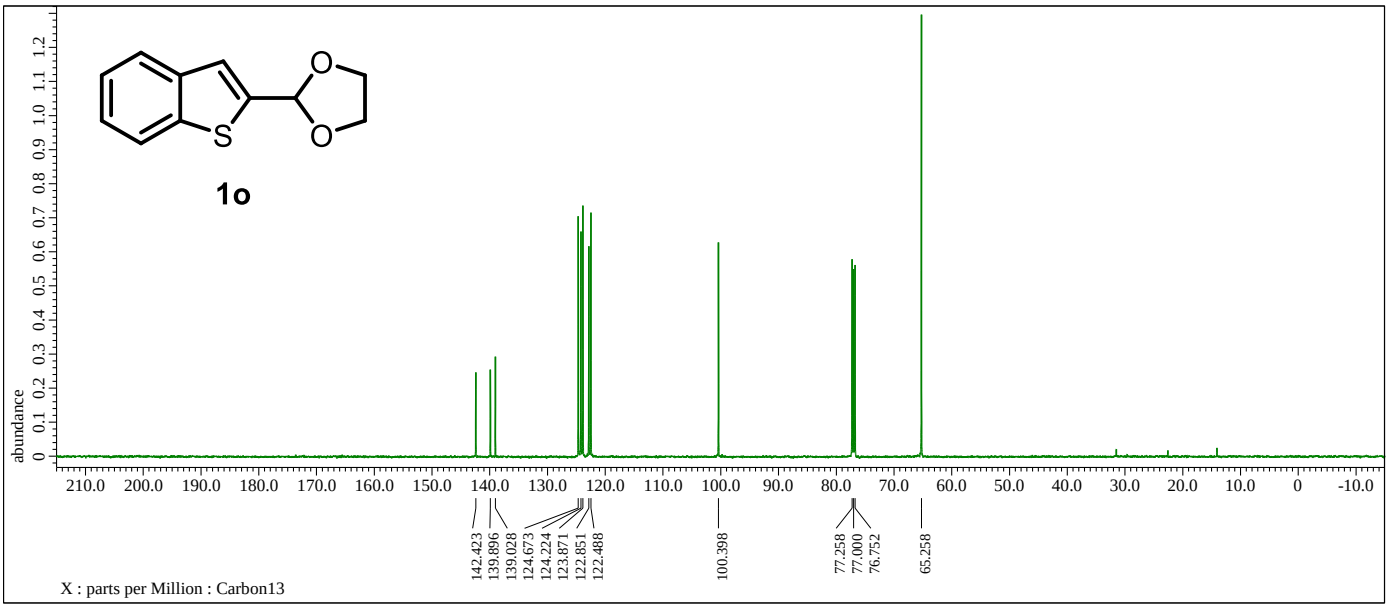
^{13}C NMR (100 MHz, $CDCl_3$) of **1n**



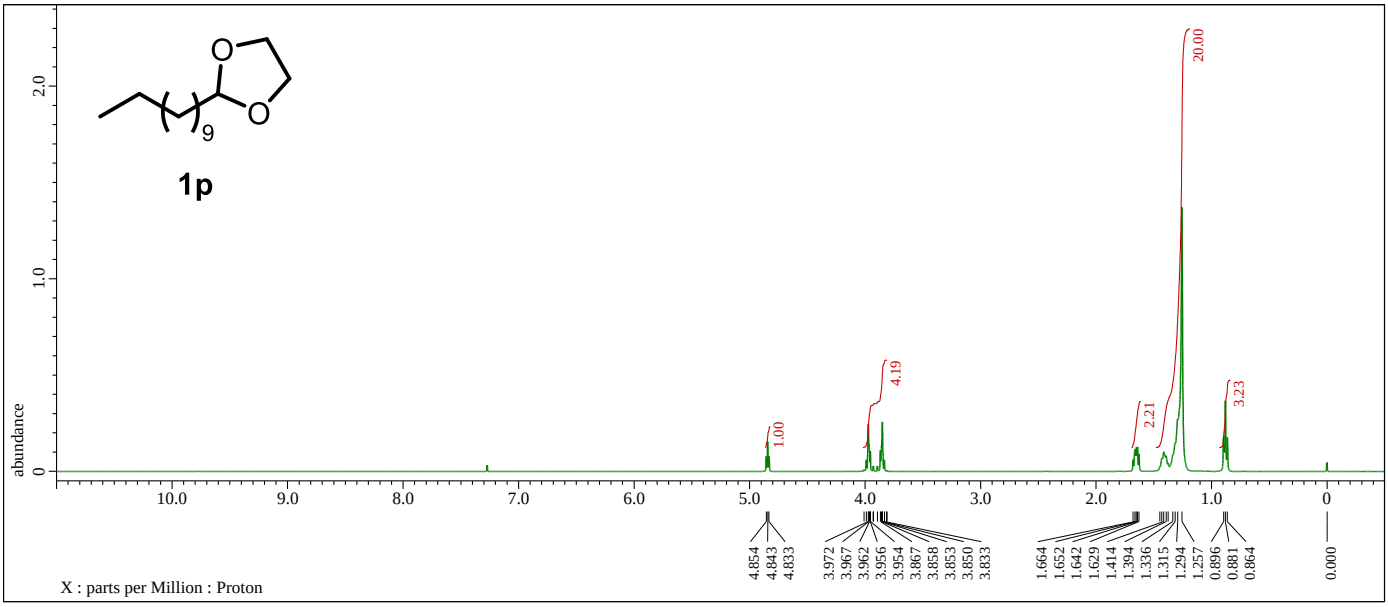
^{1}H NMR (500 MHz, $CDCl_3$) of **1o**



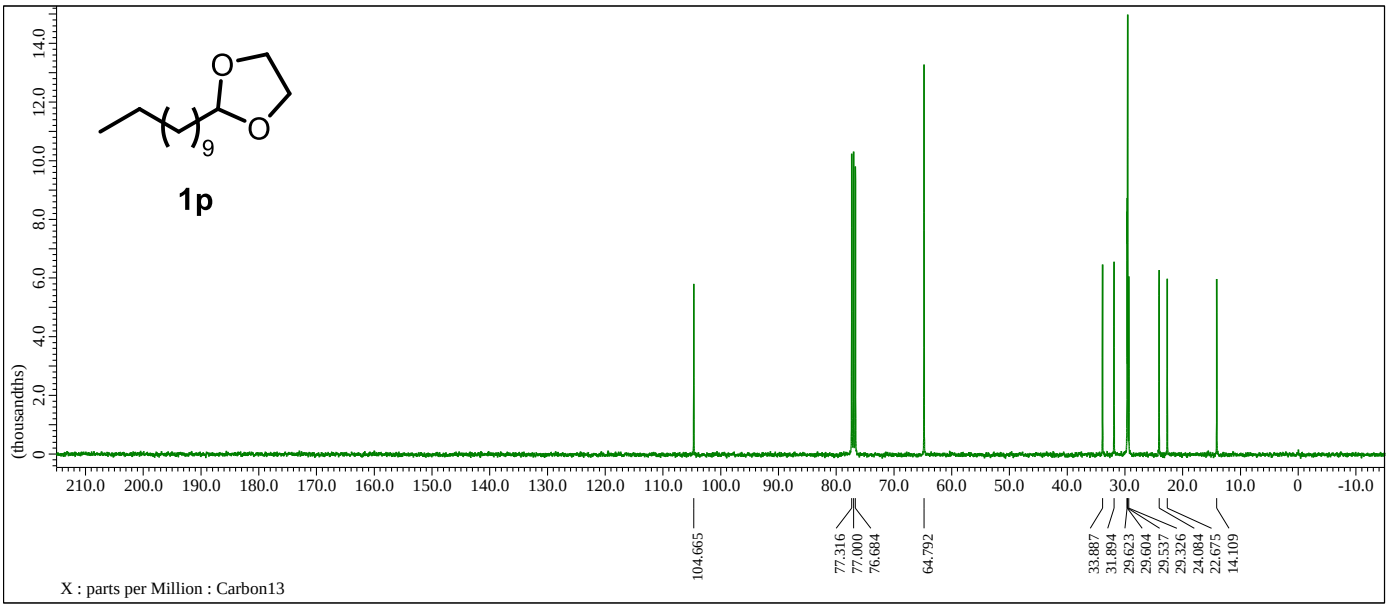
^{13}C NMR (125 MHz, $CDCl_3$) of **1o**



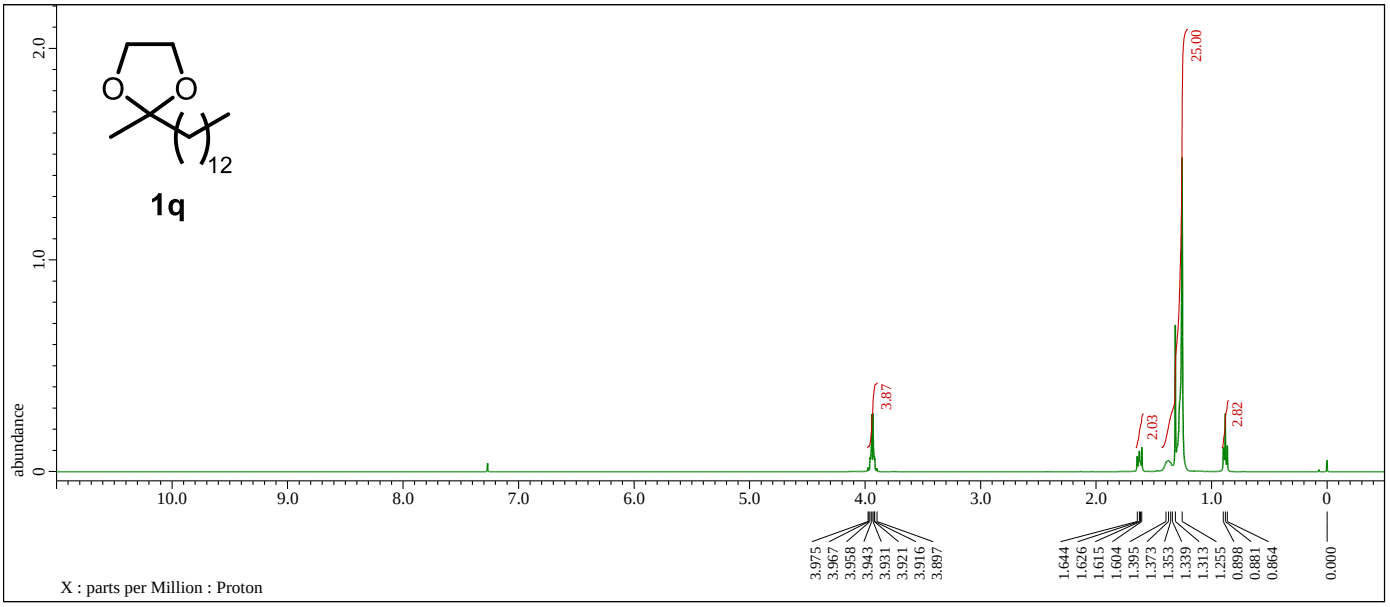
^{1}H NMR (400 MHz, $CDCl_3$) of **1p**



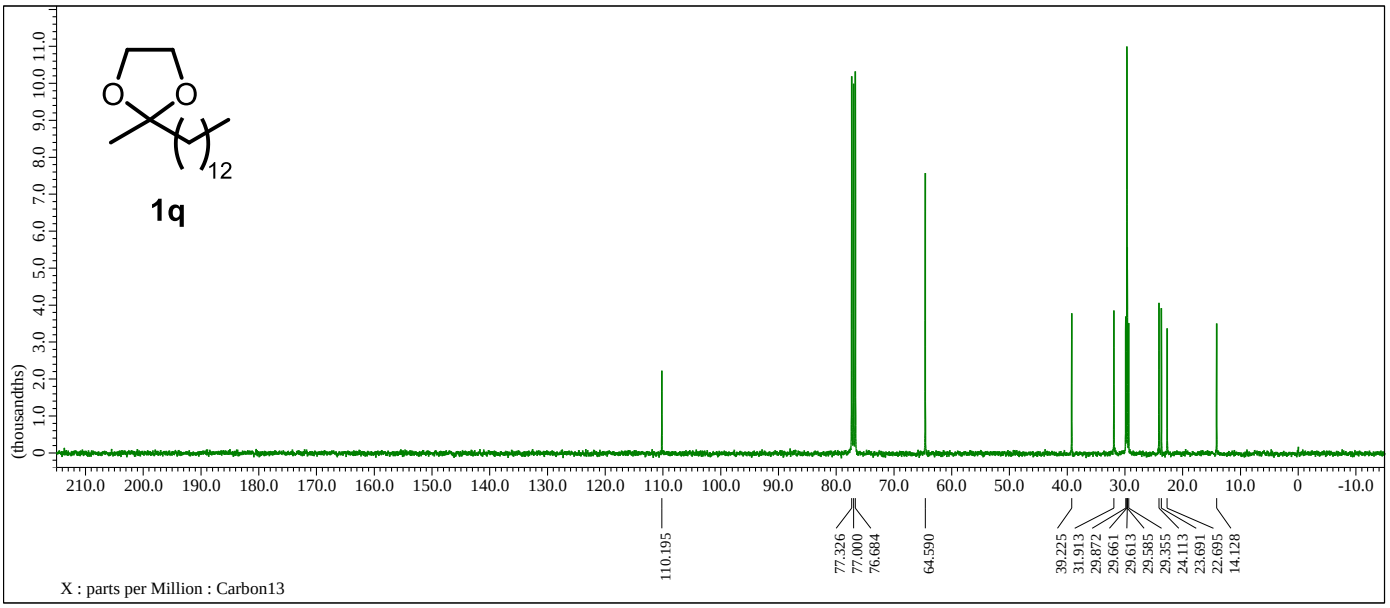
^{13}C NMR (100 MHz, $CDCl_3$) of **1p**



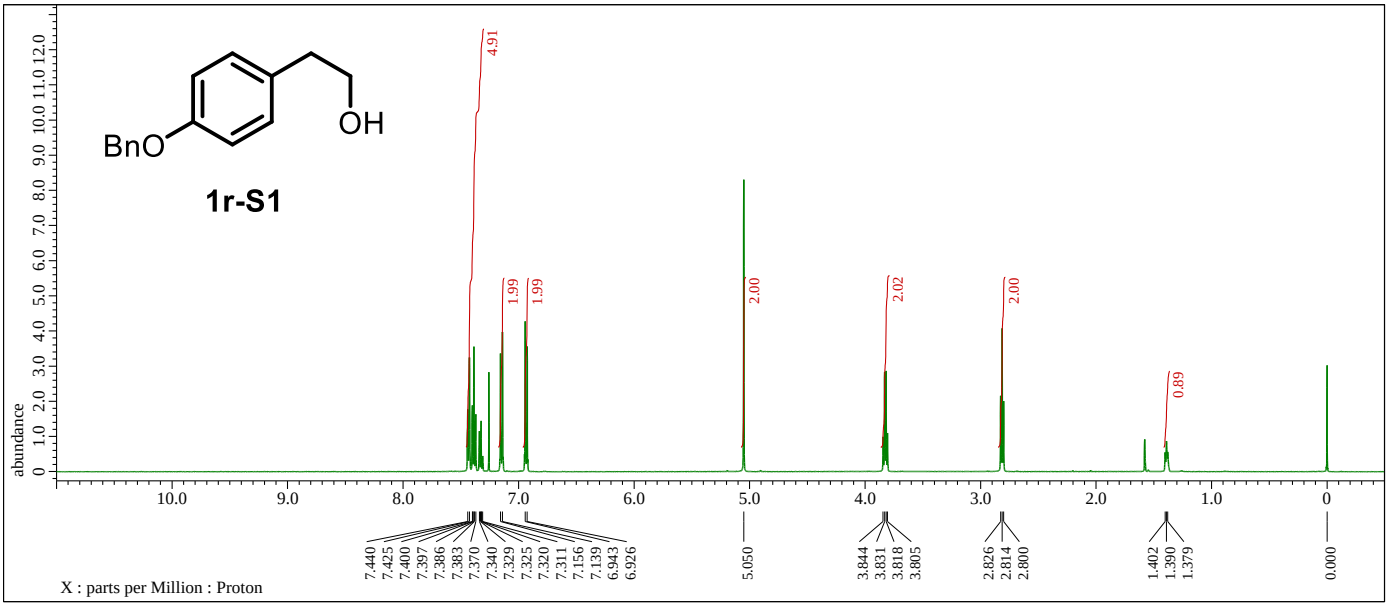
^{1}H NMR (400 MHz, $CDCl_3$) of **1q**



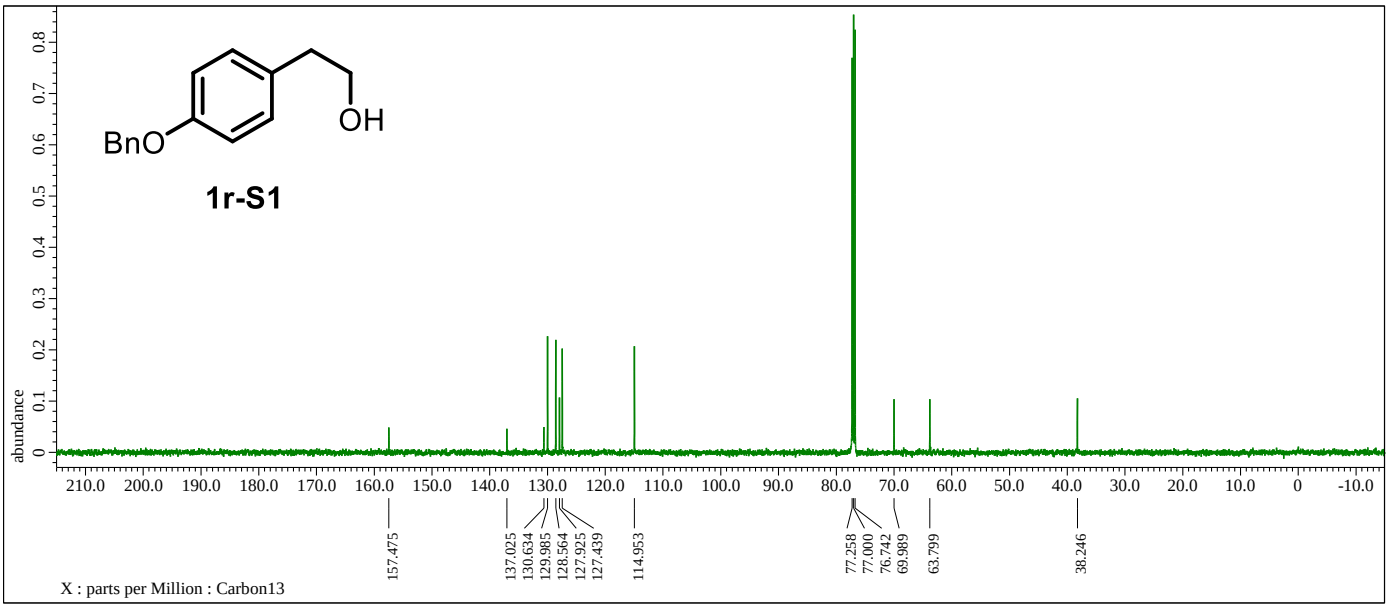
^{13}C NMR (100 MHz, $CDCl_3$) of **1q**



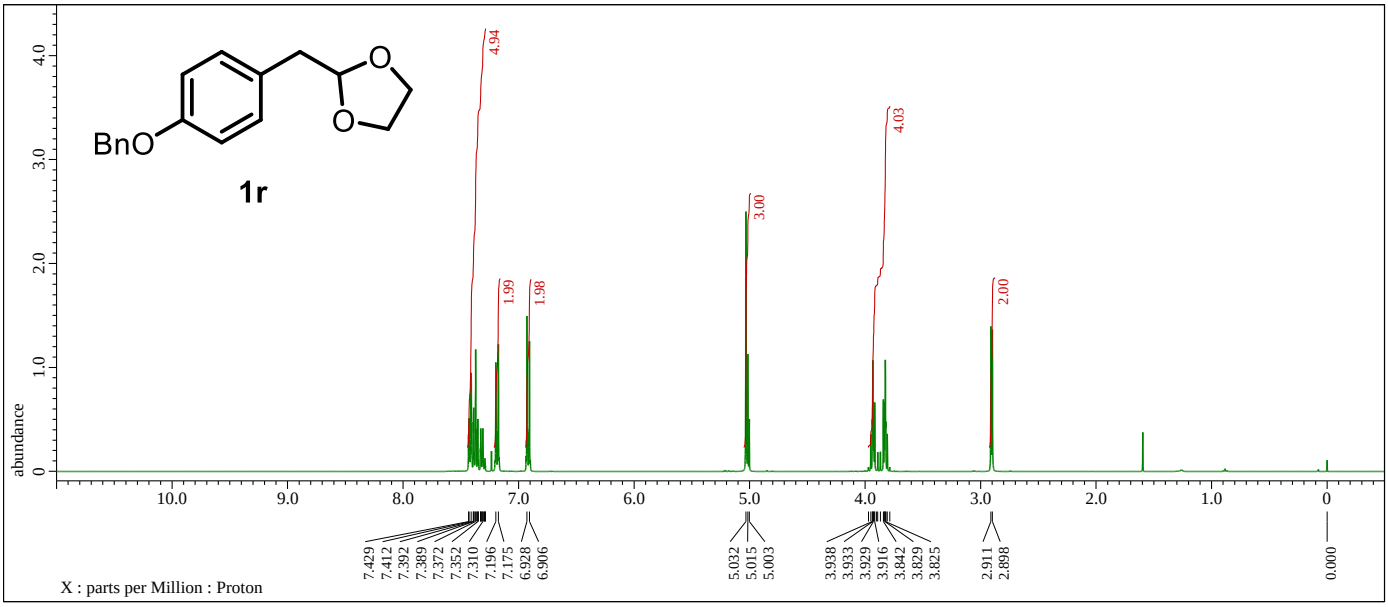
^{1}H NMR (400 MHz, $CDCl_3$) of **1r-S1**



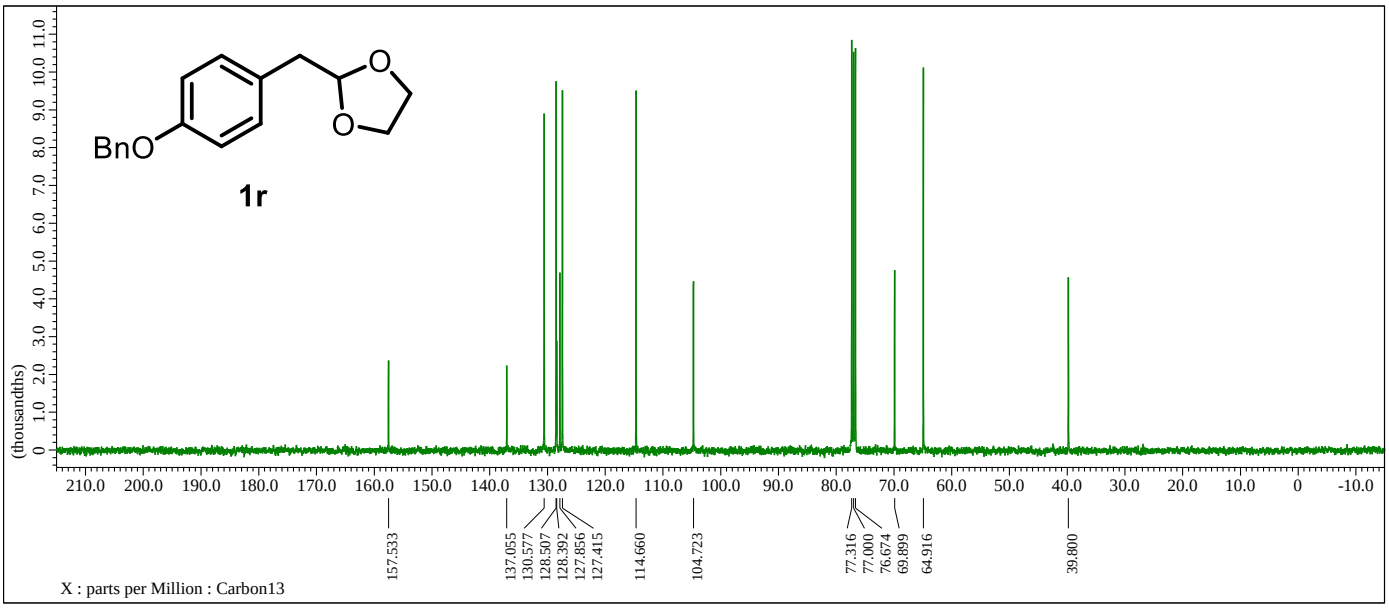
^{13}C NMR (125 MHz, $CDCl_3$) of **1r-S1**



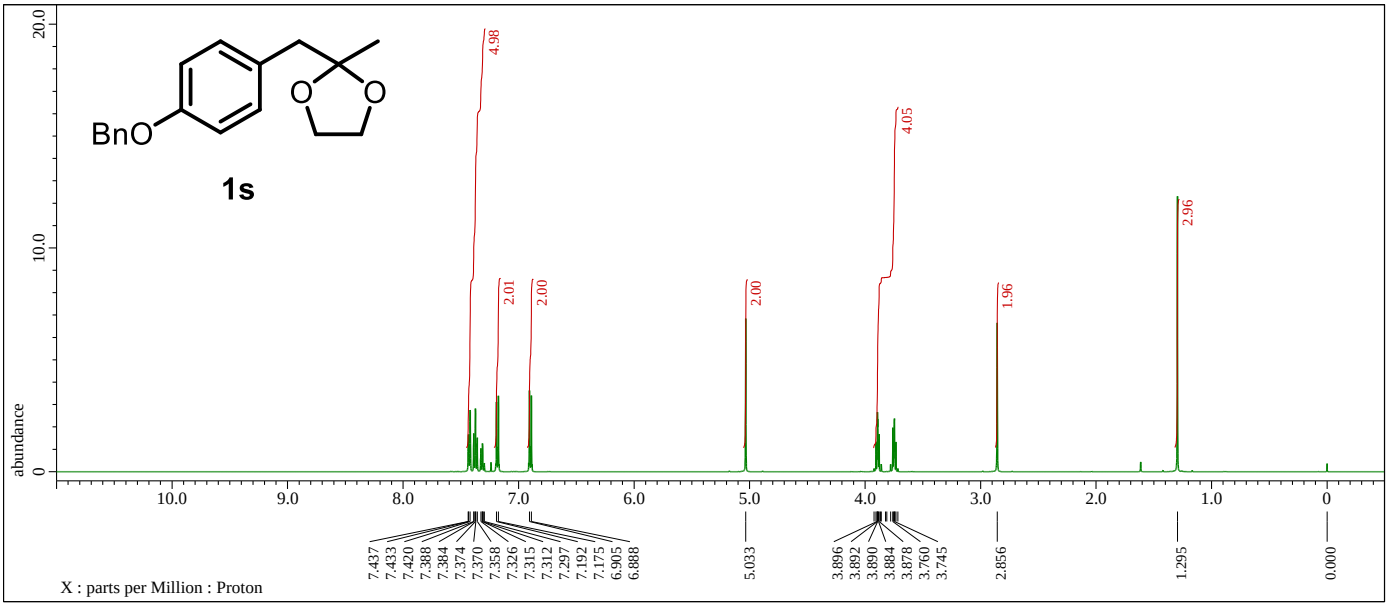
^{1}H NMR (400 MHz, $CDCl_3$) of **1r**



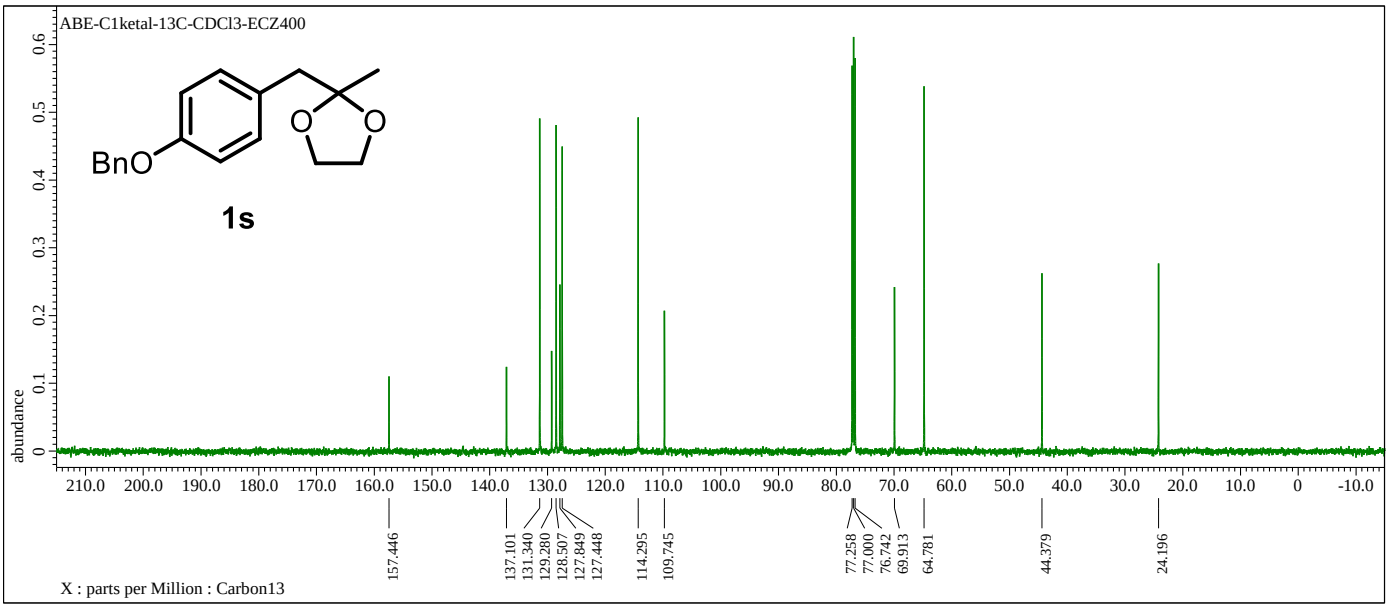
^{13}C NMR (100 MHz, $CDCl_3$) of **1r**



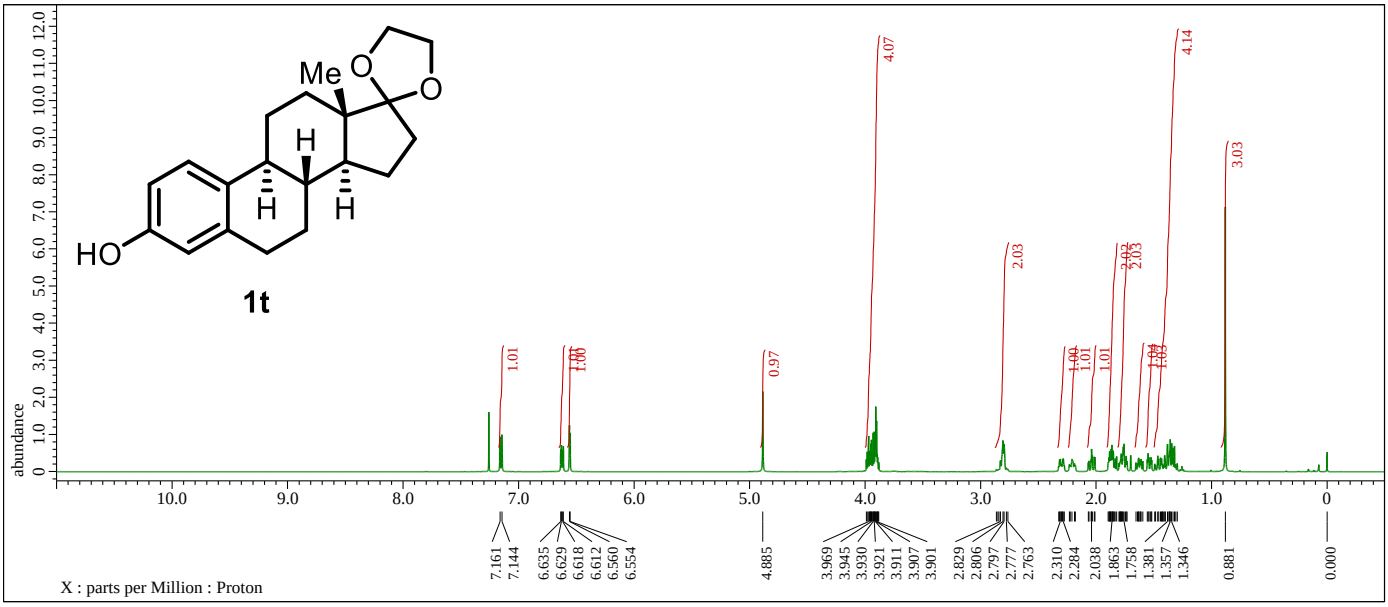
^{1}H NMR (500 MHz, $CDCl_3$) of **1s**



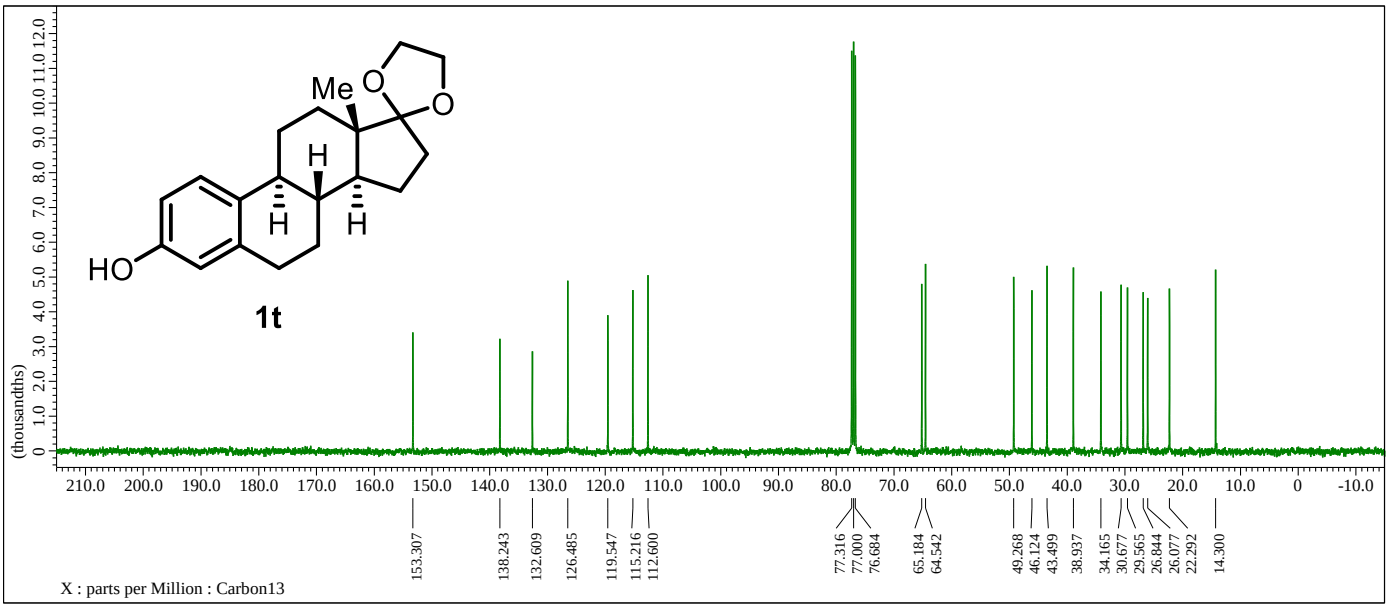
^{13}C NMR (125 MHz, $CDCl_3$) of **1s**



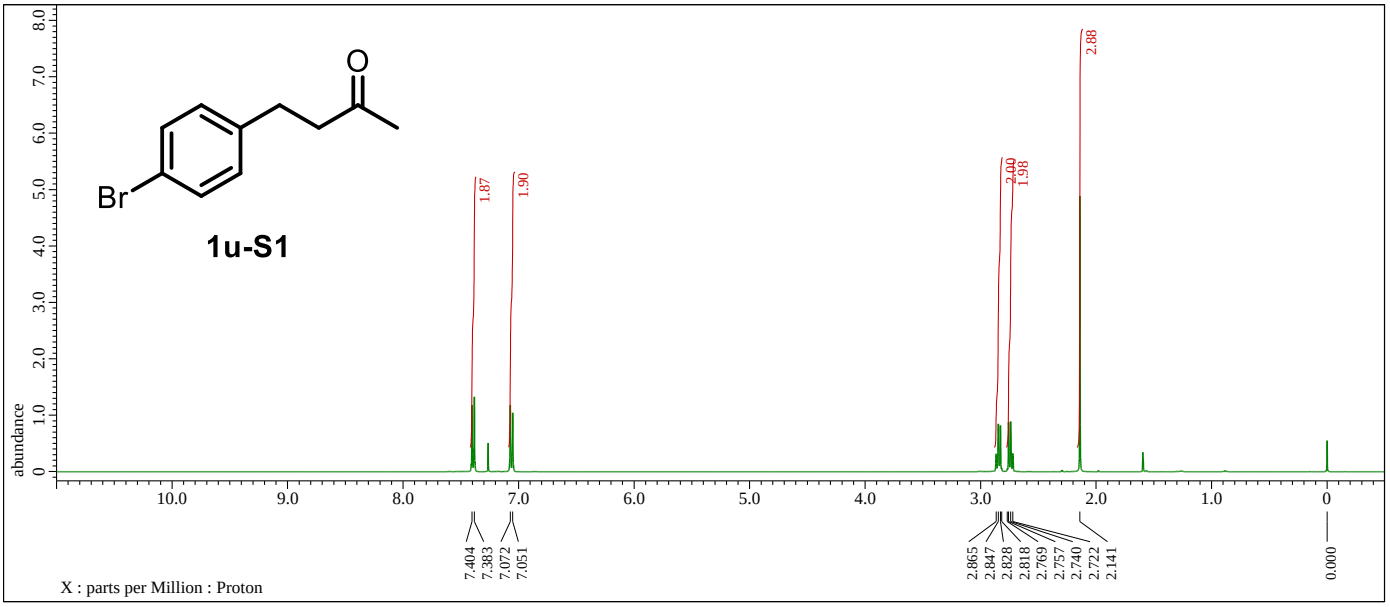
^{1}H NMR (400 MHz, $CDCl_3$) of **1t**



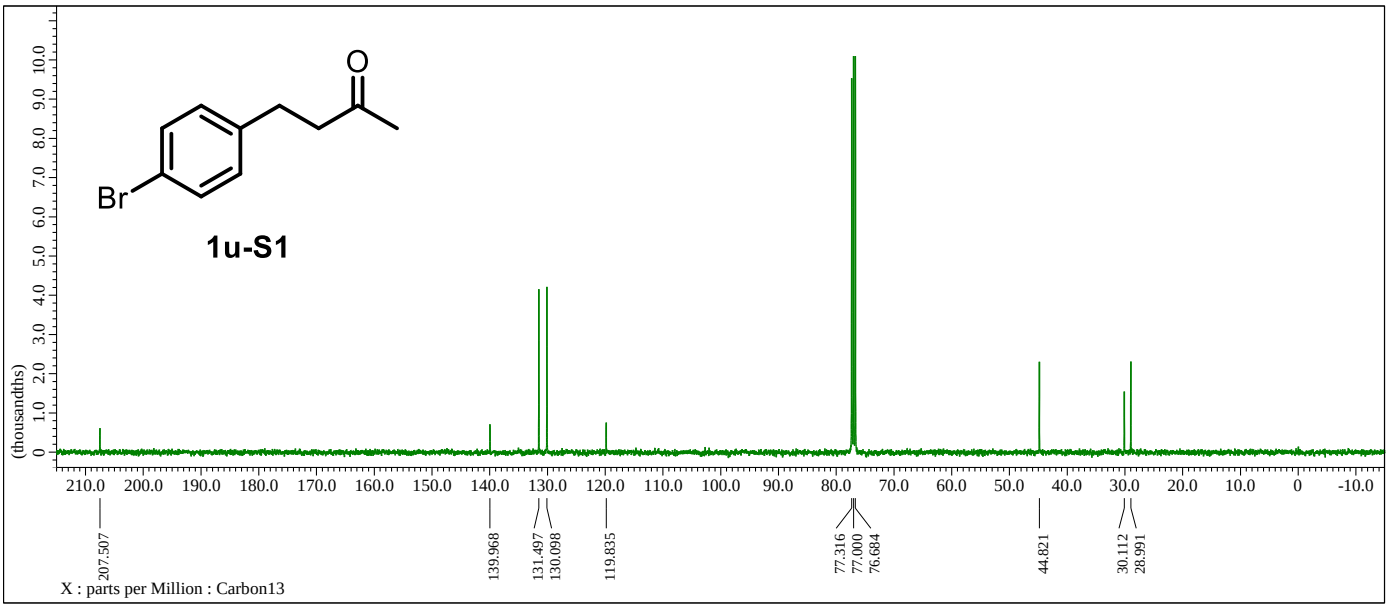
^{13}C NMR (100 MHz, $CDCl_3$) of **1t**



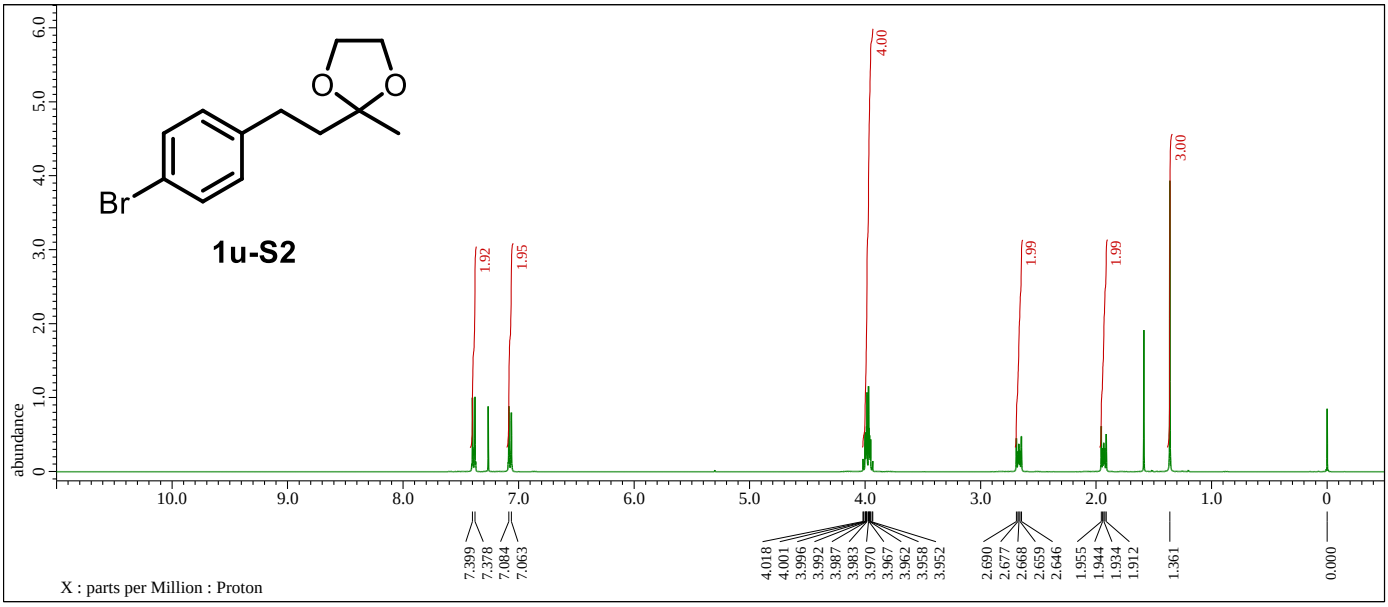
^{1}H NMR (400 MHz, $CDCl_3$) of **1u-S1**



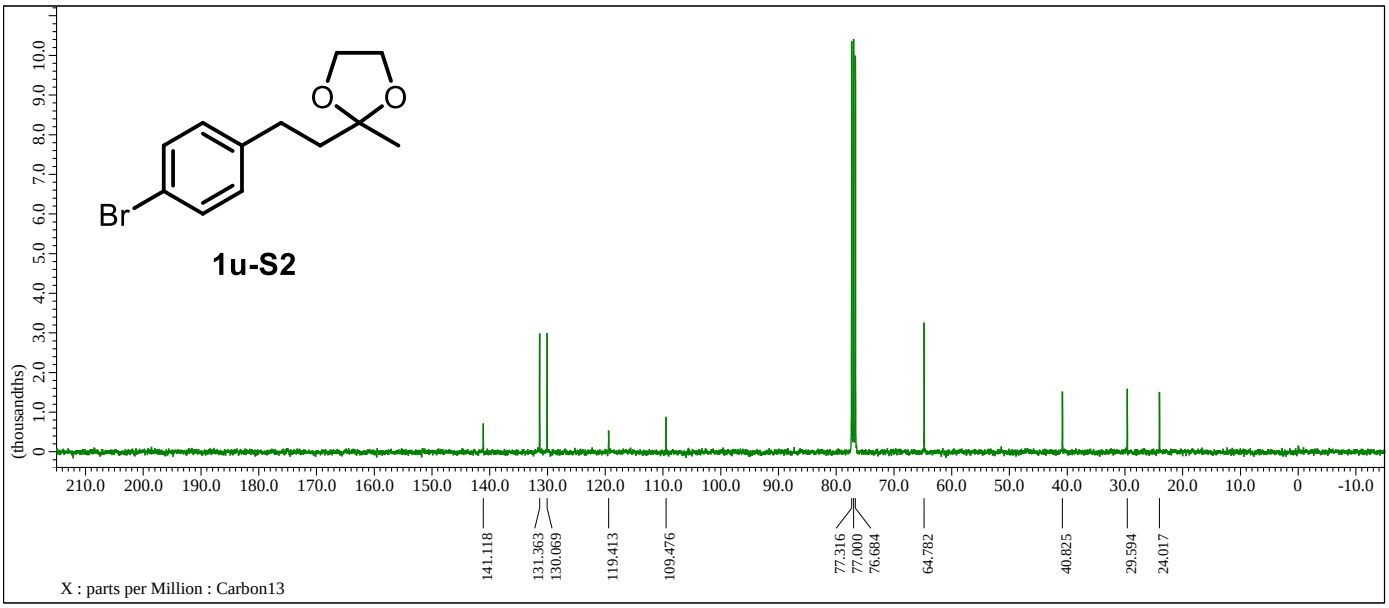
^{13}C NMR (100 MHz, $CDCl_3$) of **1u-S1**



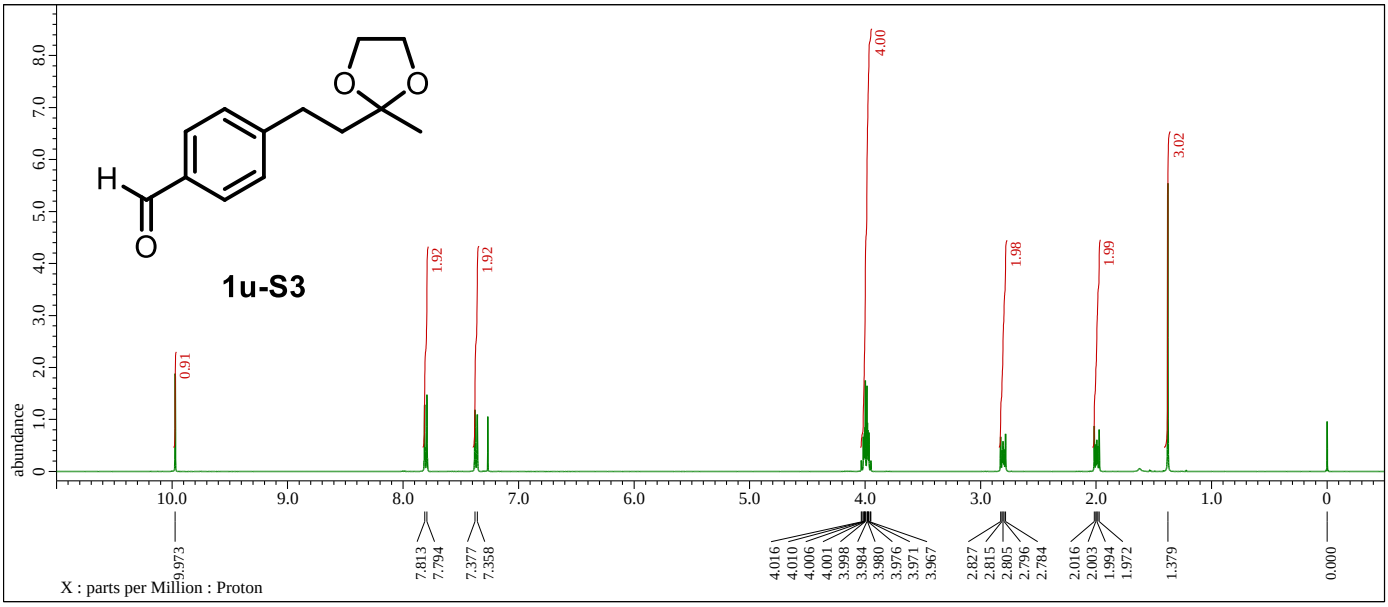
^{1}H NMR (400 MHz, $CDCl_3$) of **1u-S2**



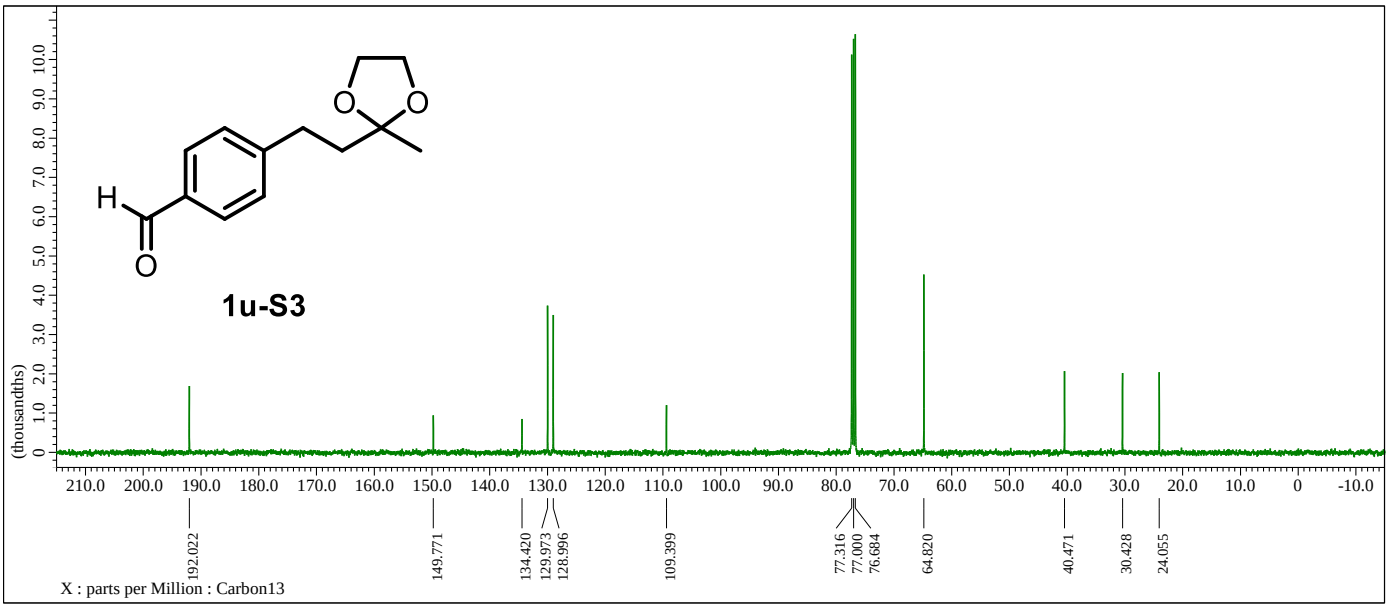
^{13}C NMR (100 MHz, $CDCl_3$) of **1u-S2**



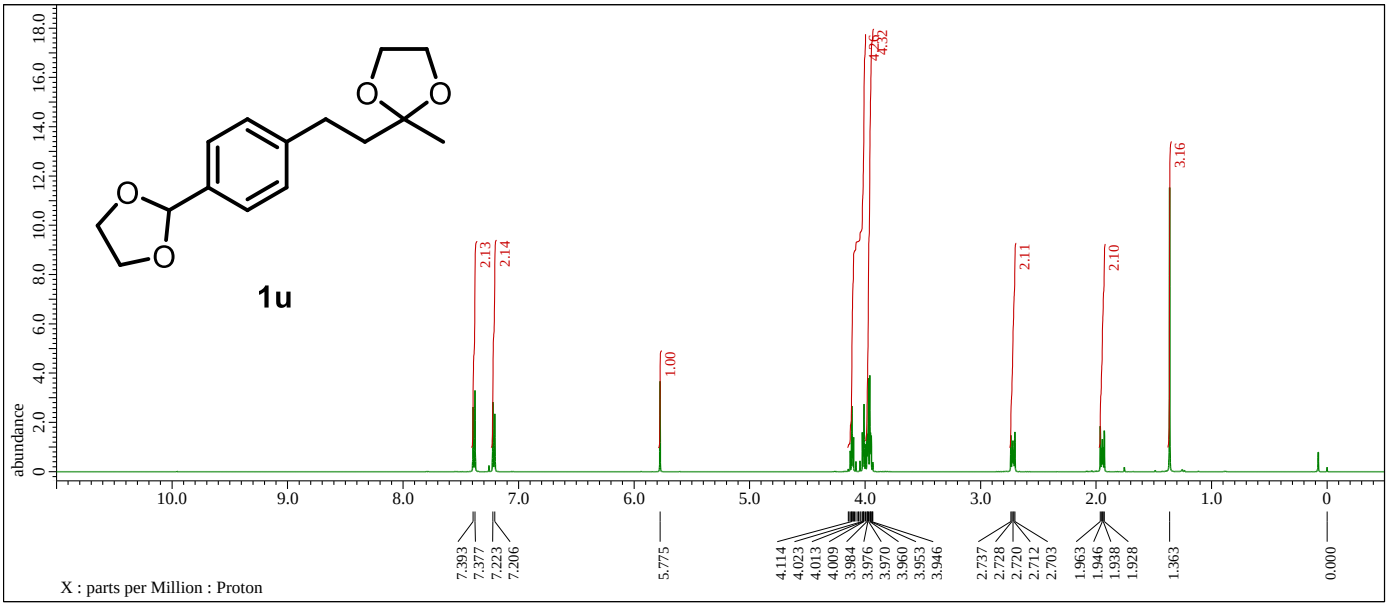
^{1}H NMR (400 MHz, $CDCl_3$) of **1u-S3**



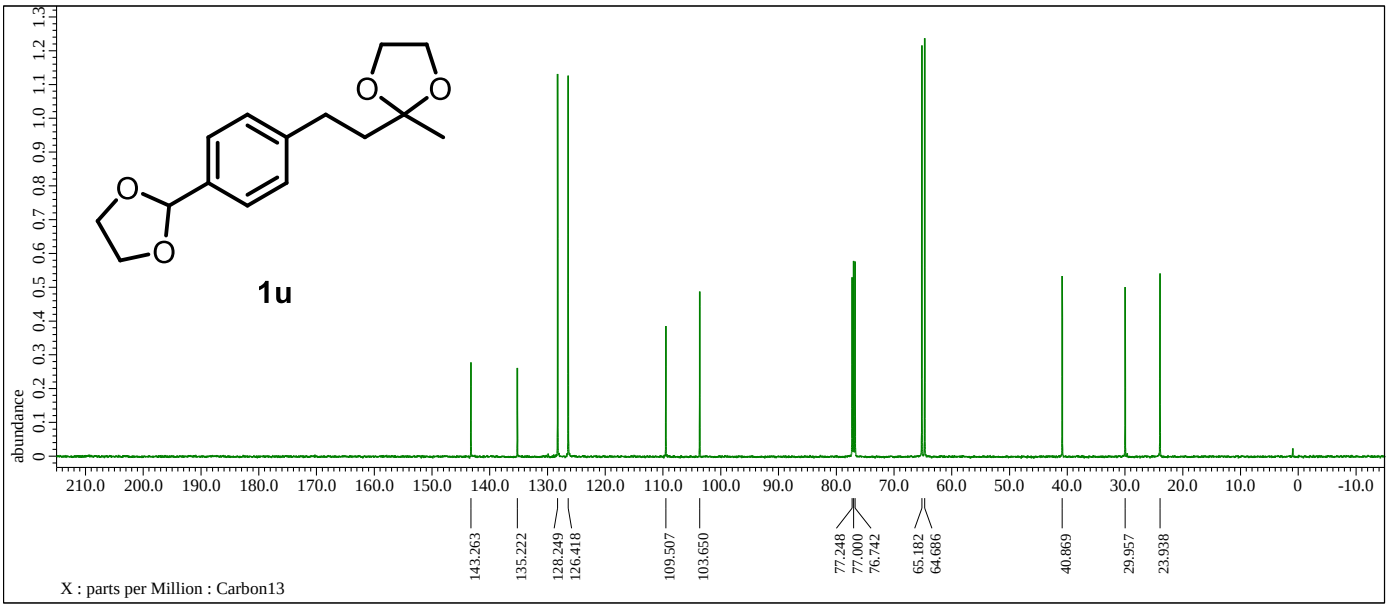
^{13}C NMR (100 MHz, $CDCl_3$) of **1u-S3**



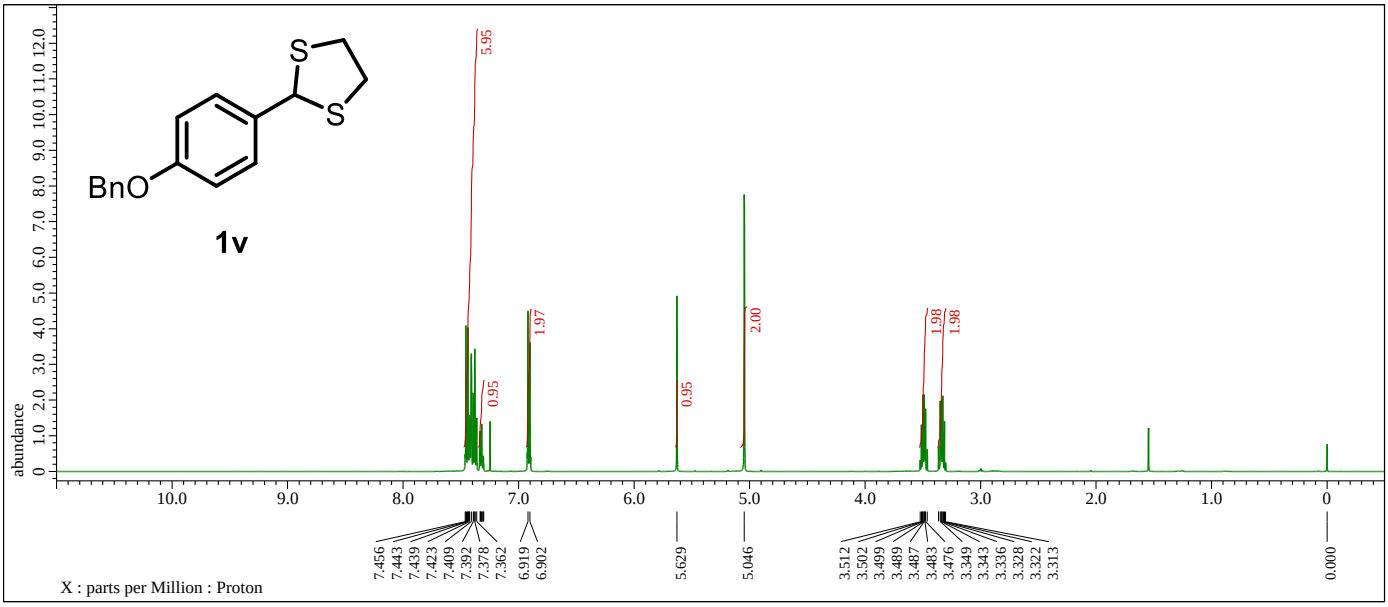
^{1}H NMR (500 MHz, $CDCl_3$) of **1u**



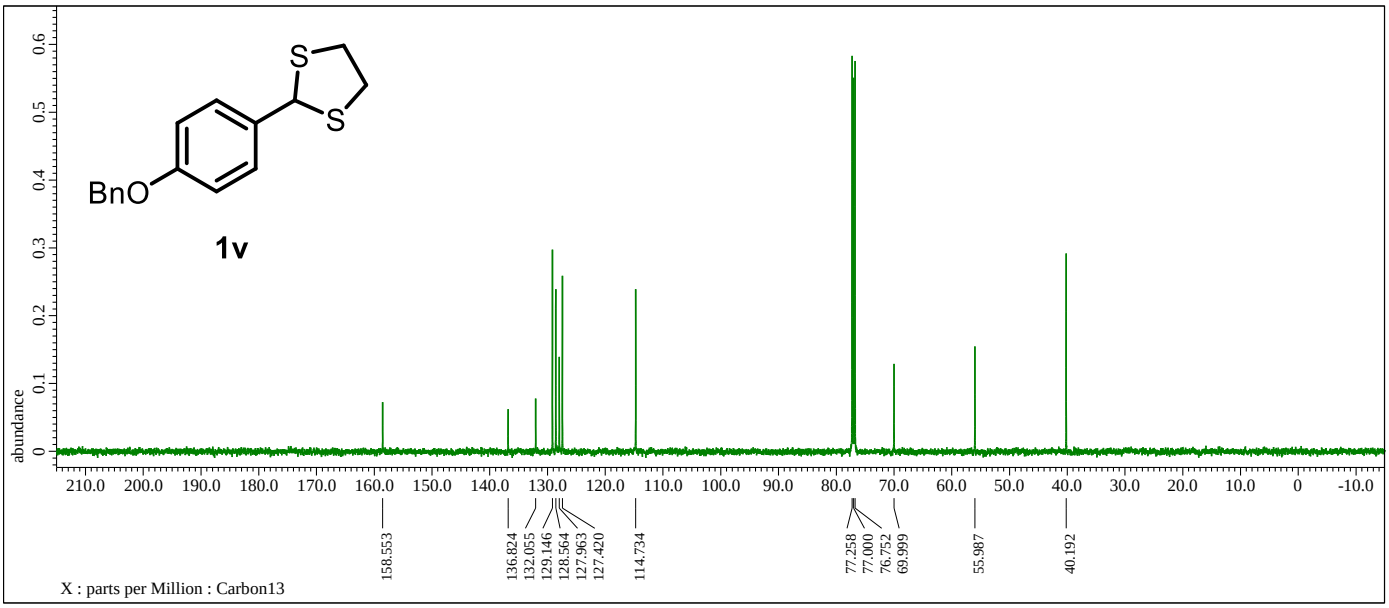
^{13}C NMR (125 MHz, $CDCl_3$) of **1u**



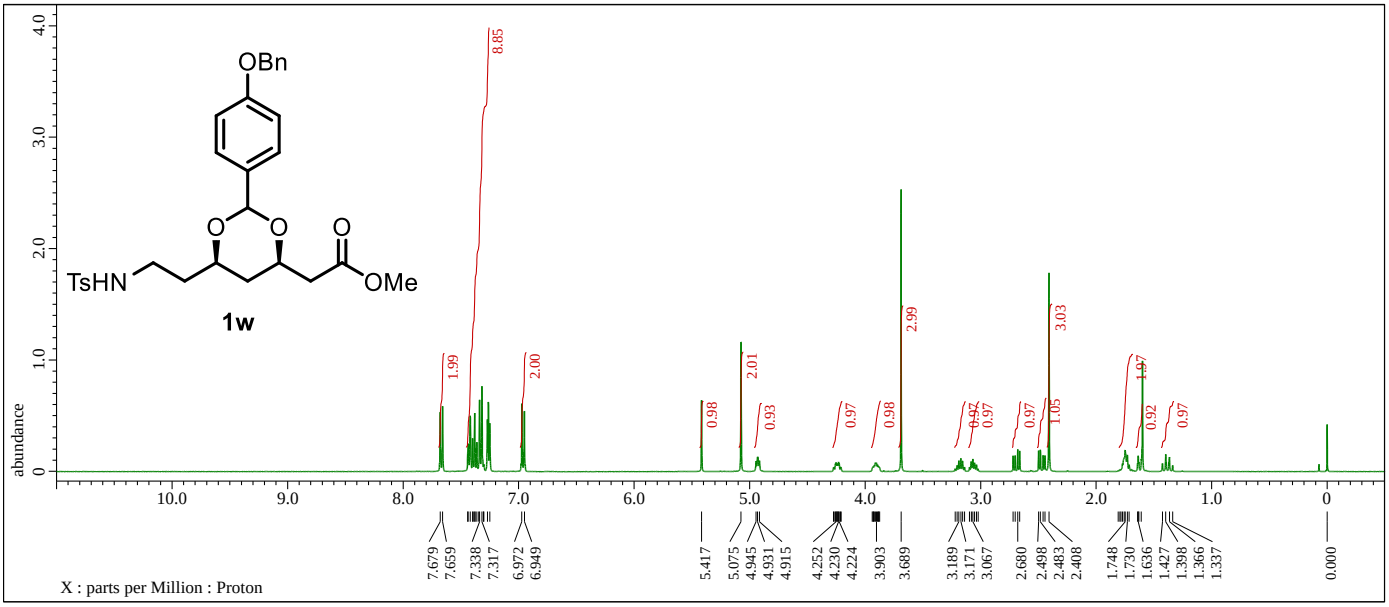
^{1}H NMR (500 MHz, $CDCl_3$) of **1v**



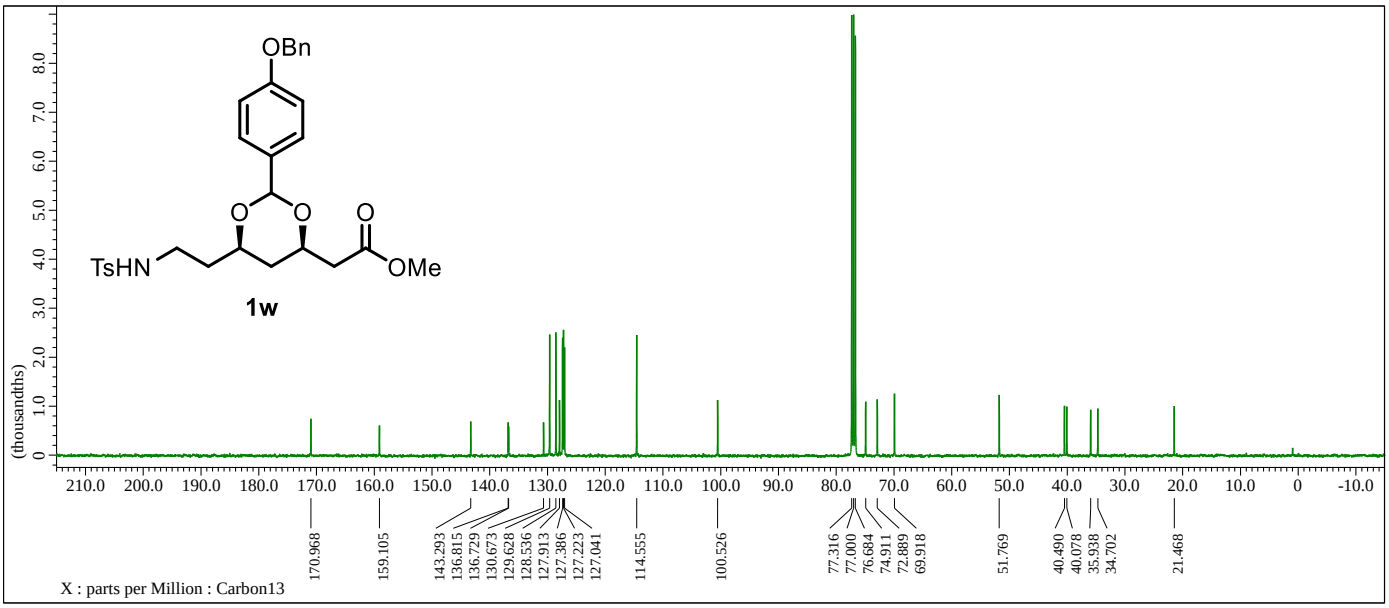
^{13}C NMR (125 MHz, $CDCl_3$) of **1v**



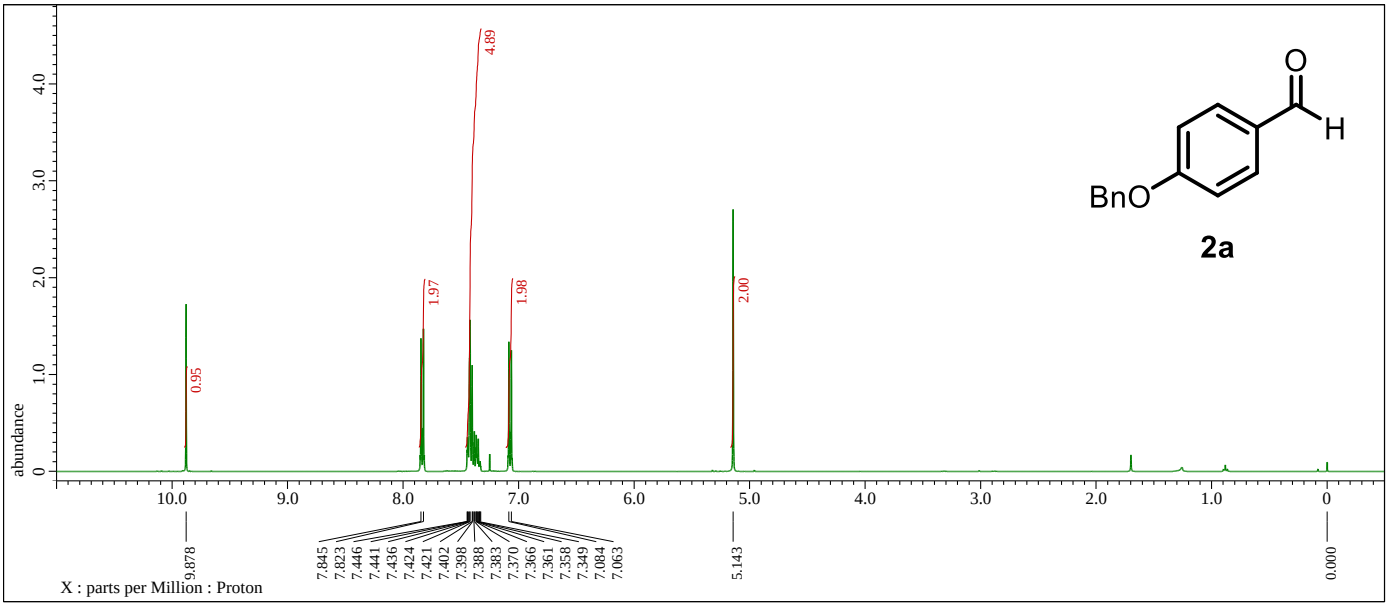
^{1}H NMR (400 MHz, $CDCl_3$) of **1w**



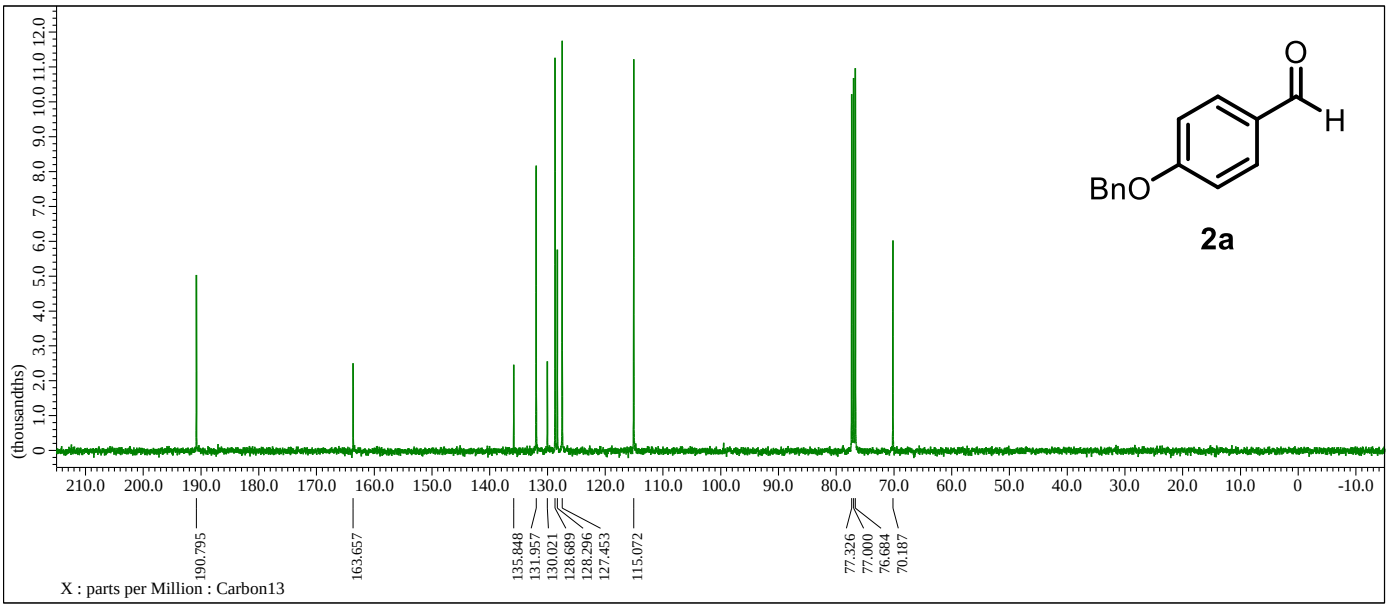
^{13}C NMR (100 MHz, $CDCl_3$) of **1w**



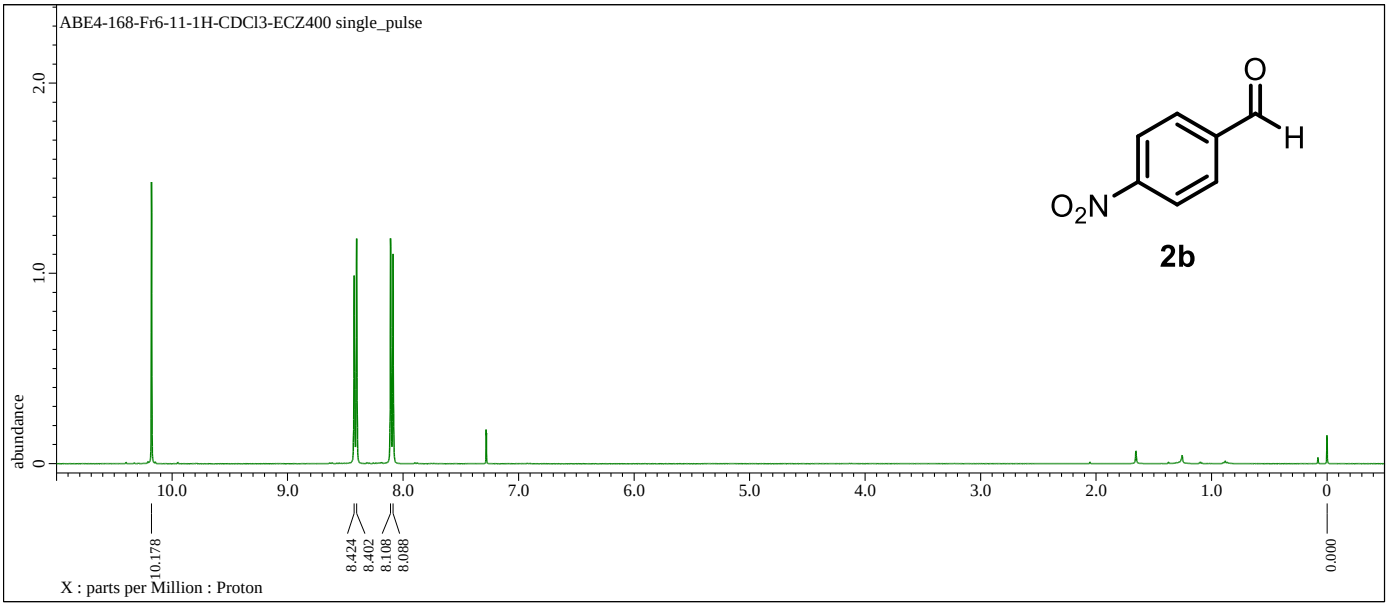
^{1}H NMR (400 MHz, $CDCl_3$) of **2a**



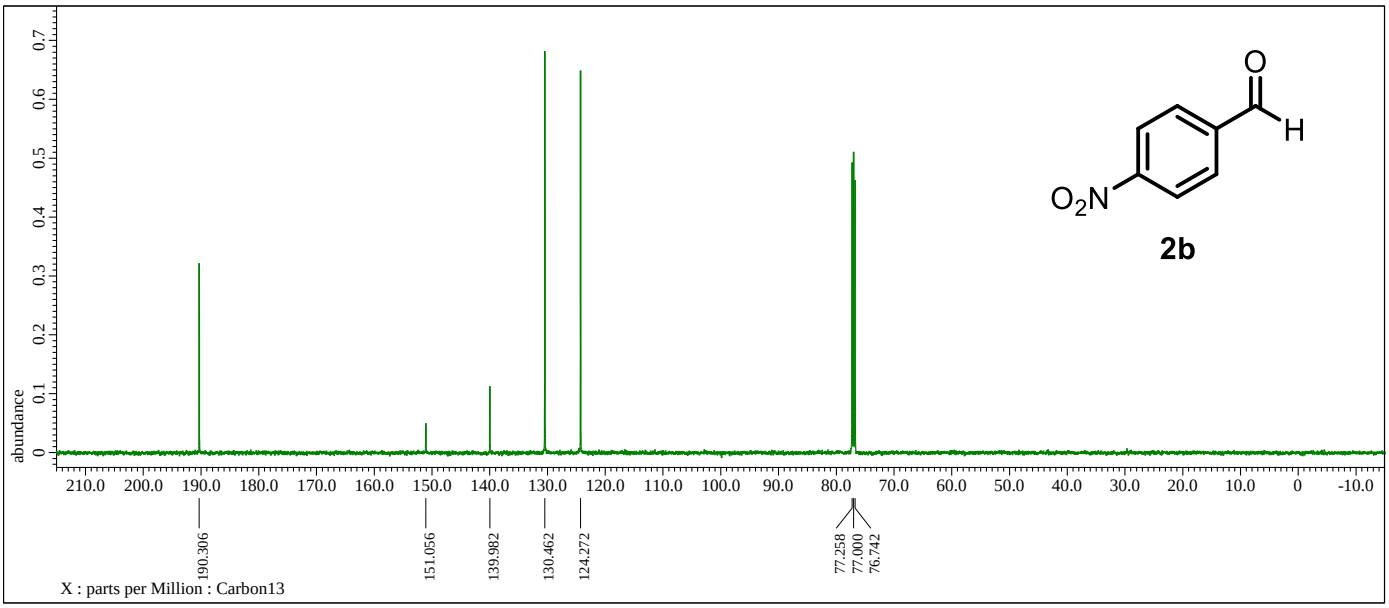
^{13}C NMR (100 MHz, $CDCl_3$) of **2a**



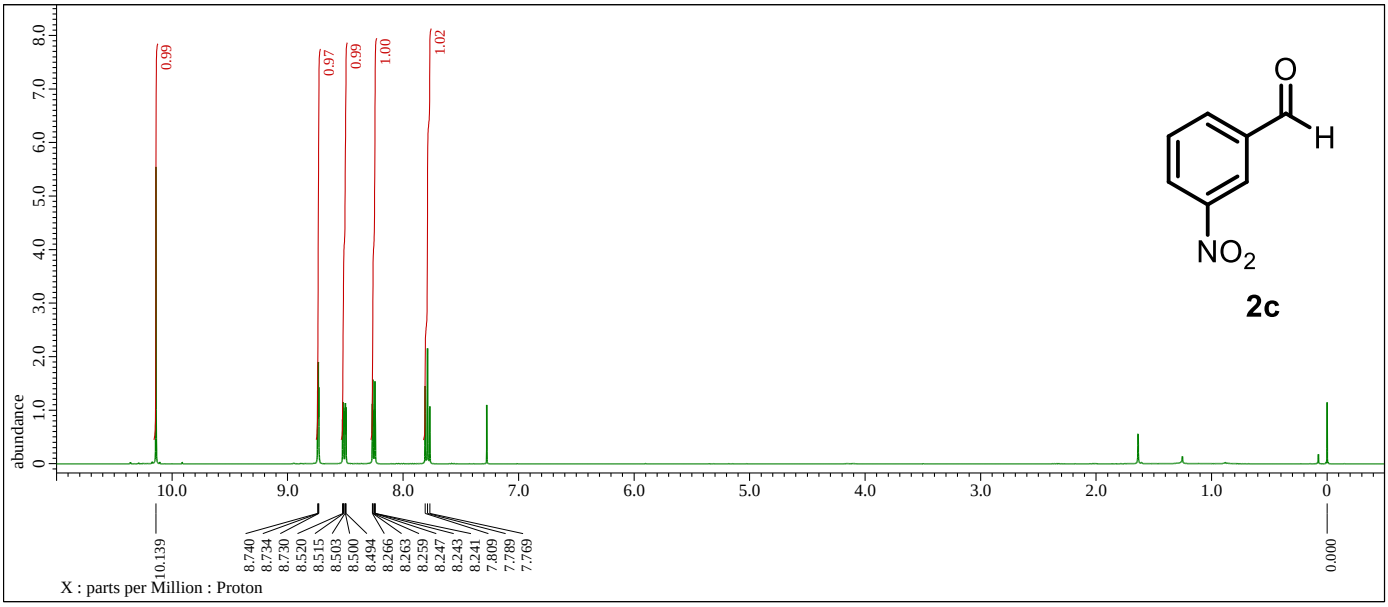
^{1}H NMR (400 MHz, $CDCl_3$) of **2b**



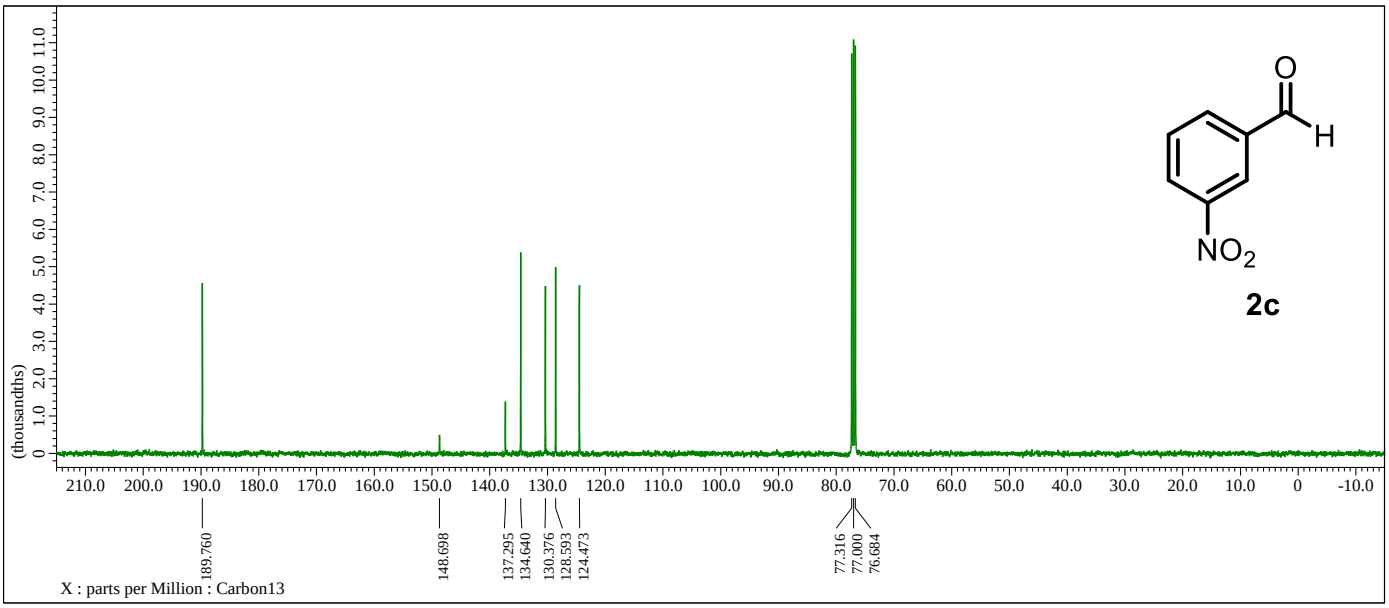
^{13}C NMR (125 MHz, $CDCl_3$) of **2b**



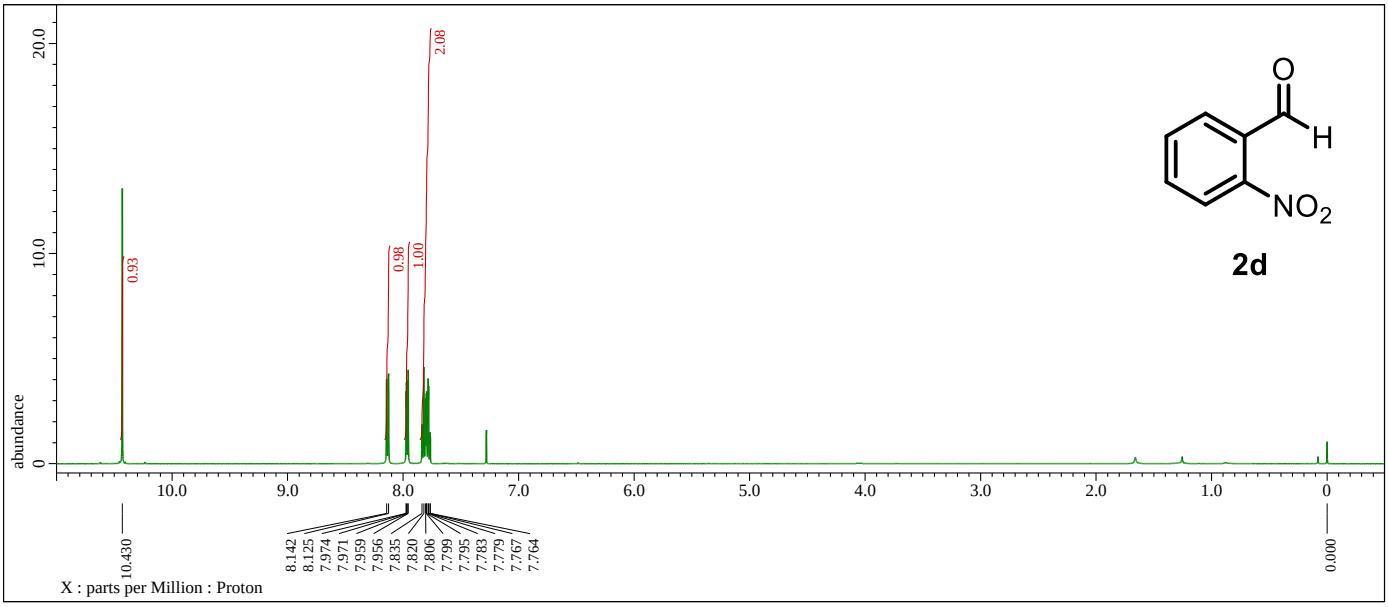
^{1}H NMR (400 MHz, $CDCl_3$) of **2c**



^{13}C NMR (100 MHz, $CDCl_3$) of **2c**



^{1}H NMR (500 MHz, $CDCl_3$) of **2d**



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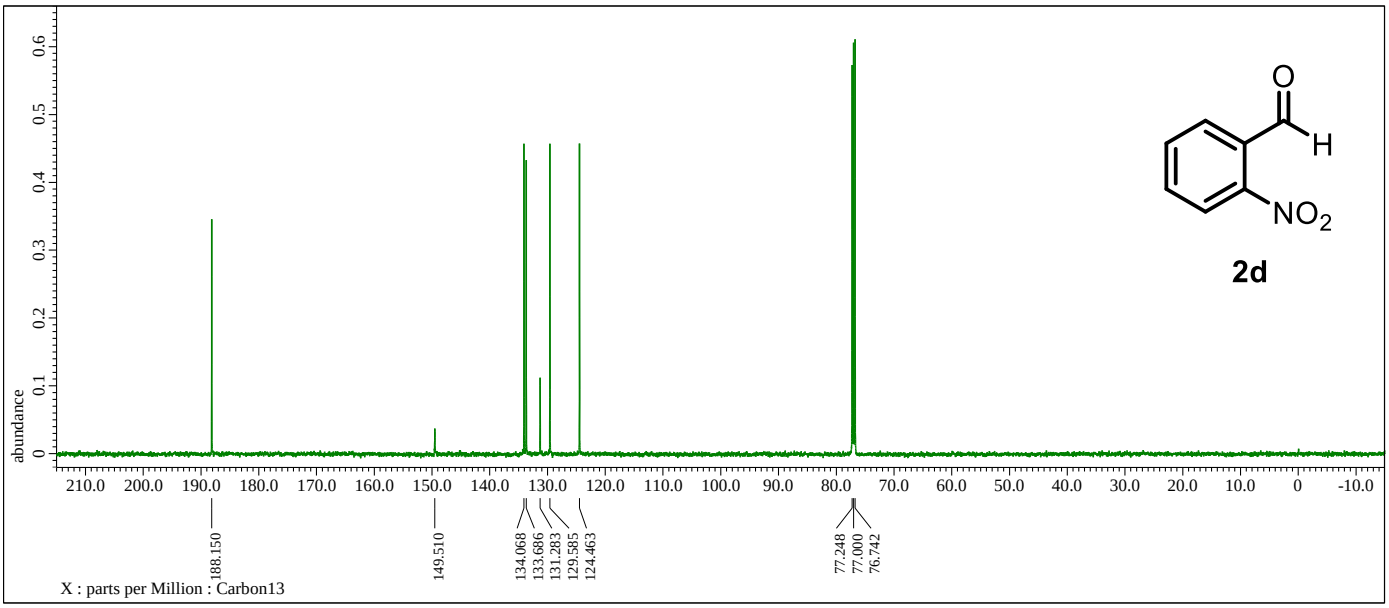

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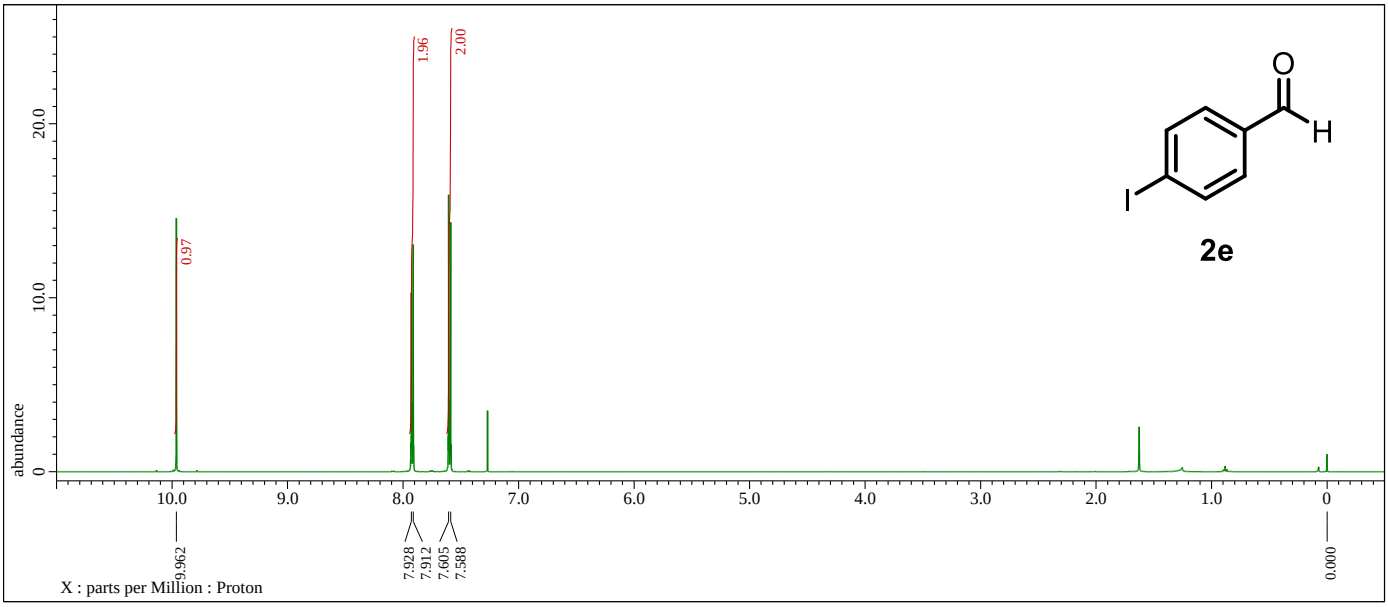

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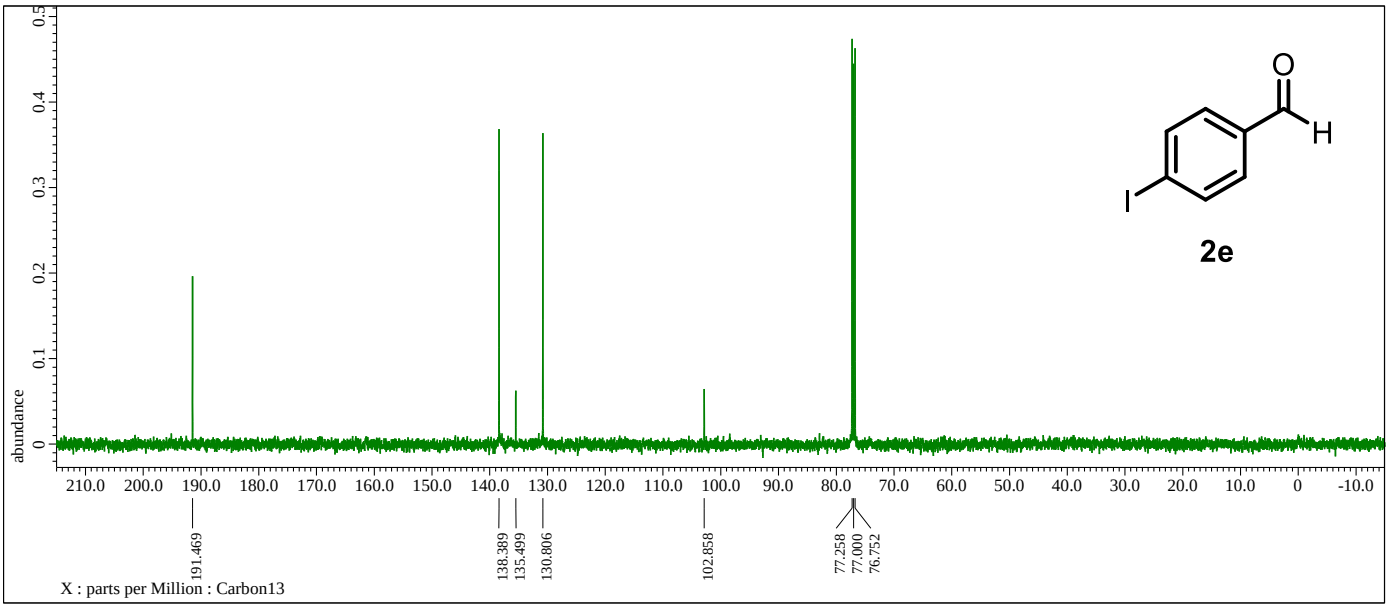
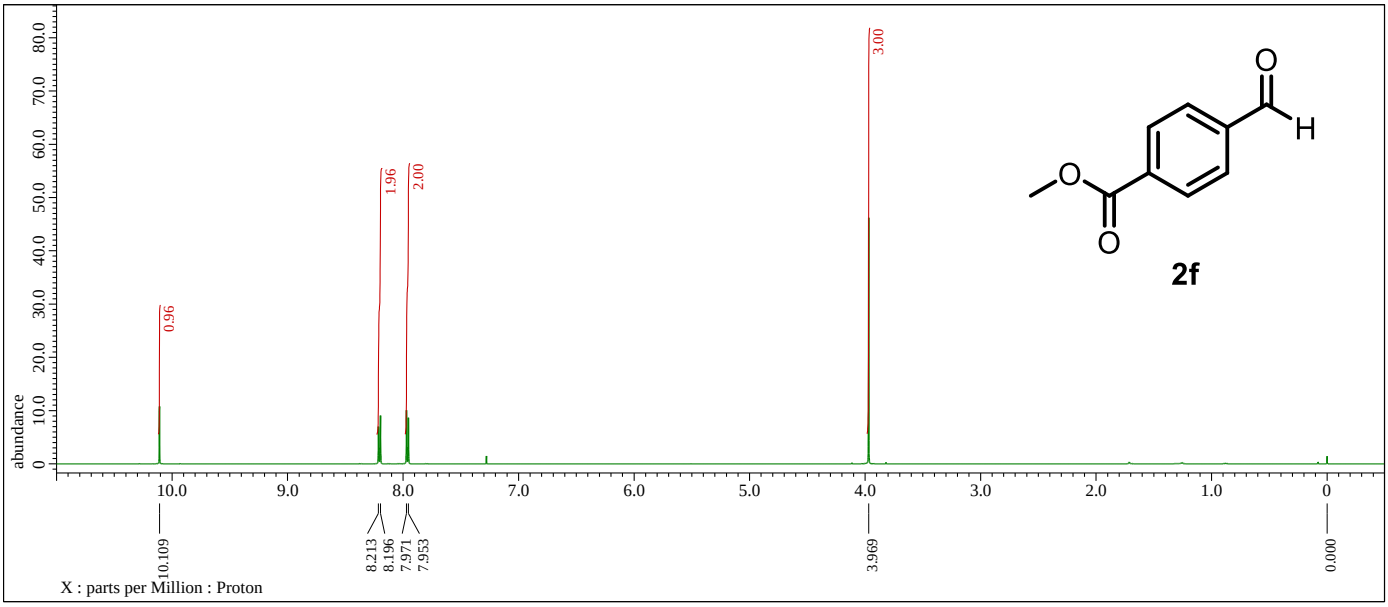
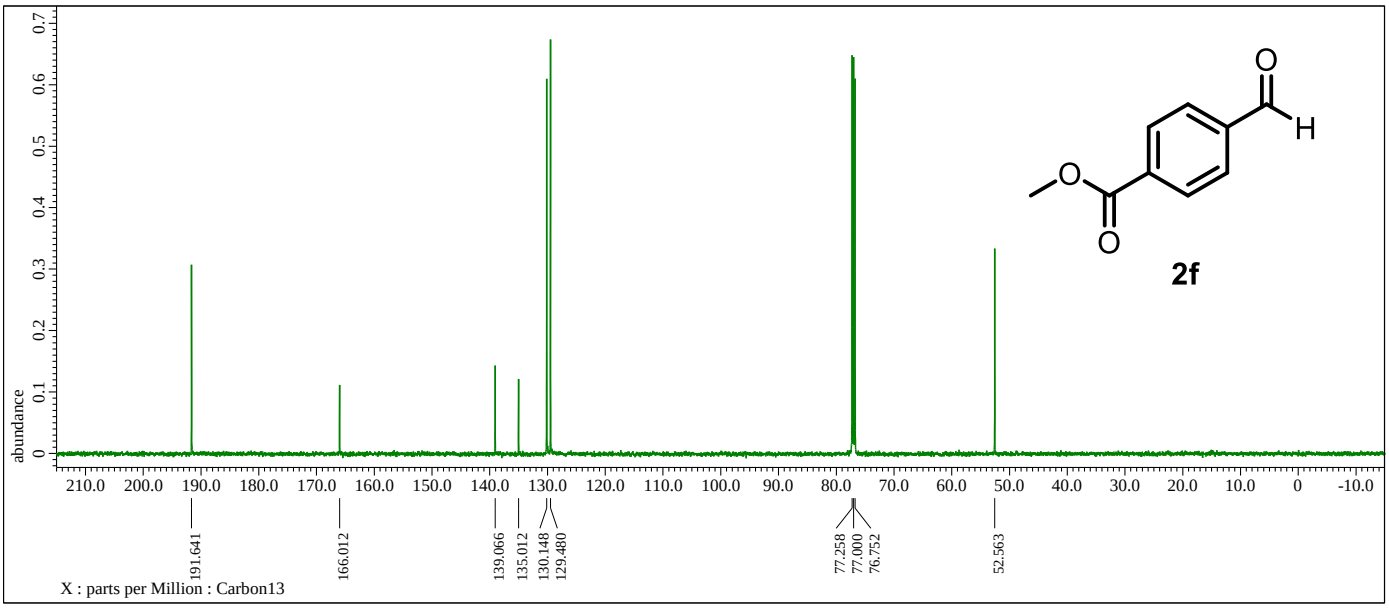


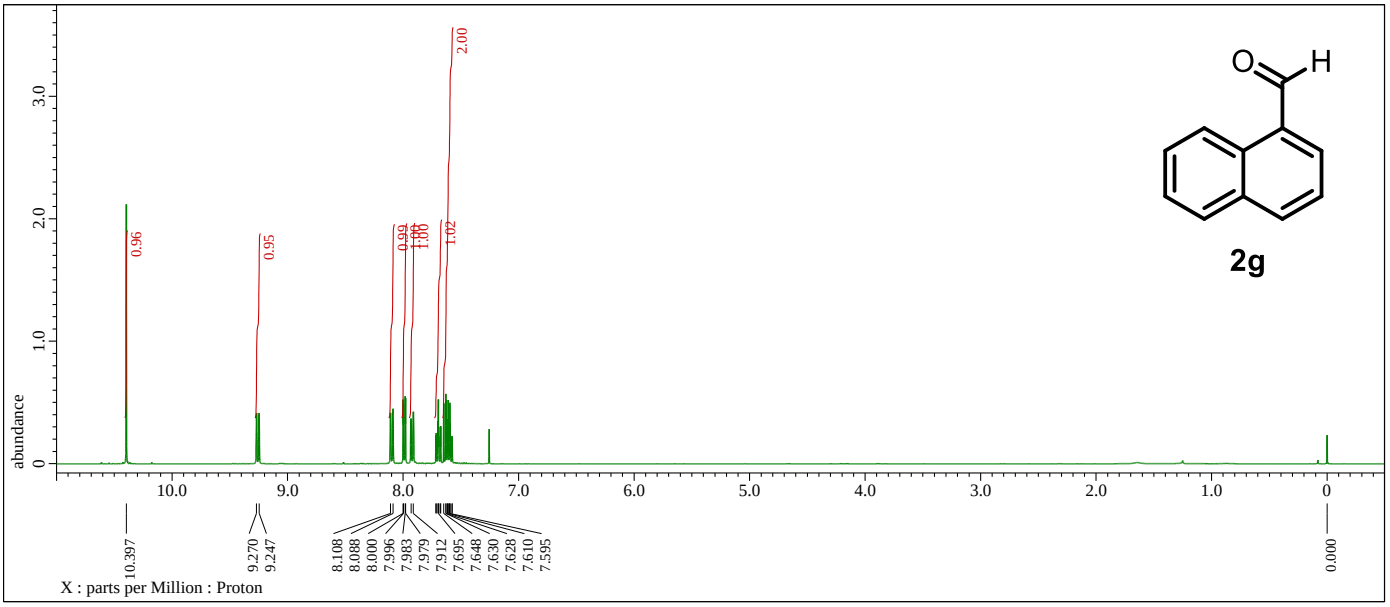
^{1}H NMR (400 MHz, $CDCl_3$) of **2f**



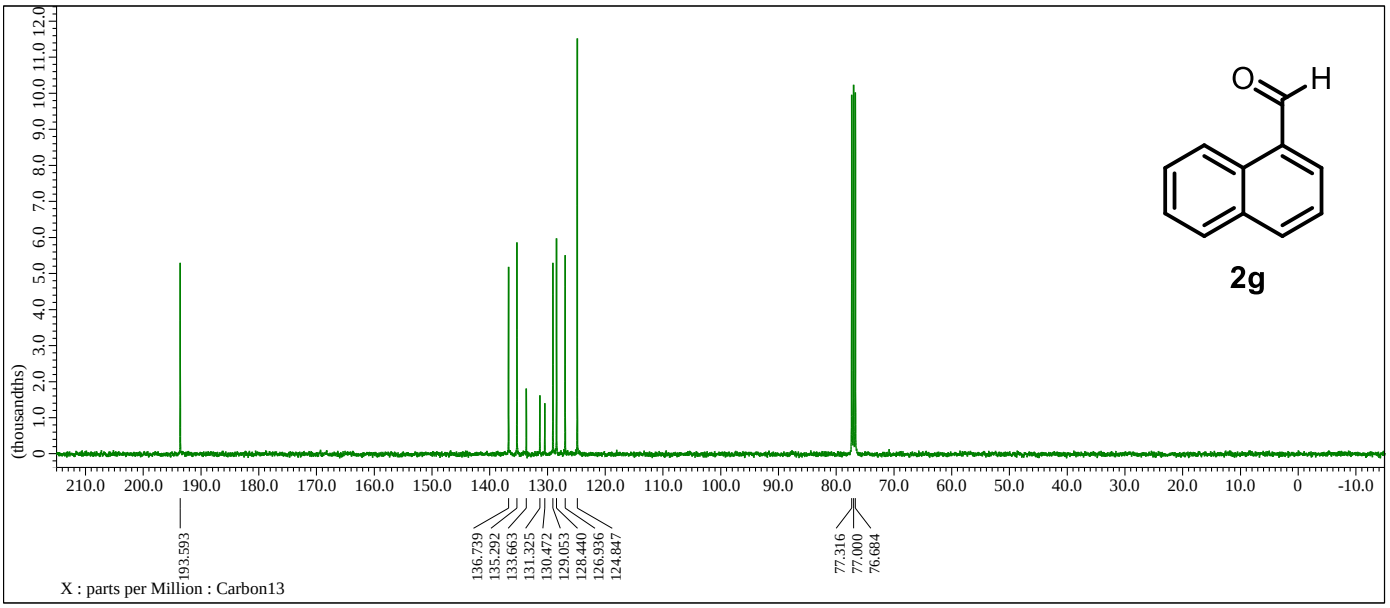
^{13}C NMR (125 MHz, $CDCl_3$) of **2f**



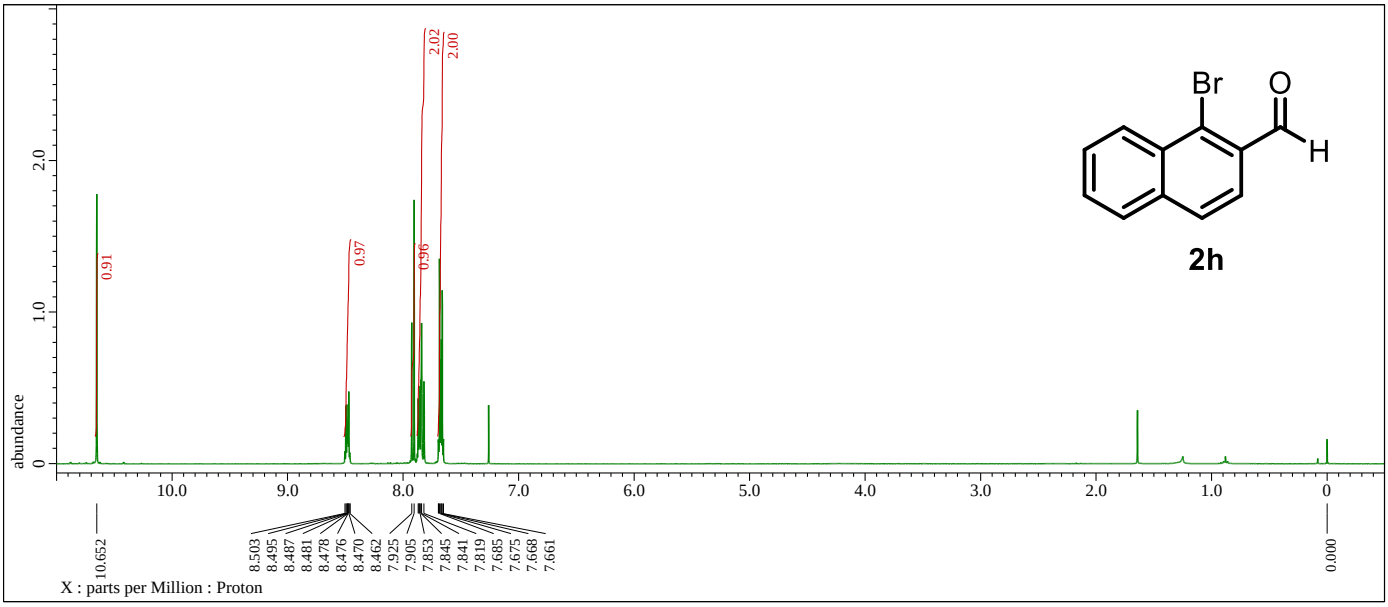
^{1}H NMR (400 MHz, $CDCl_3$) of **2g**



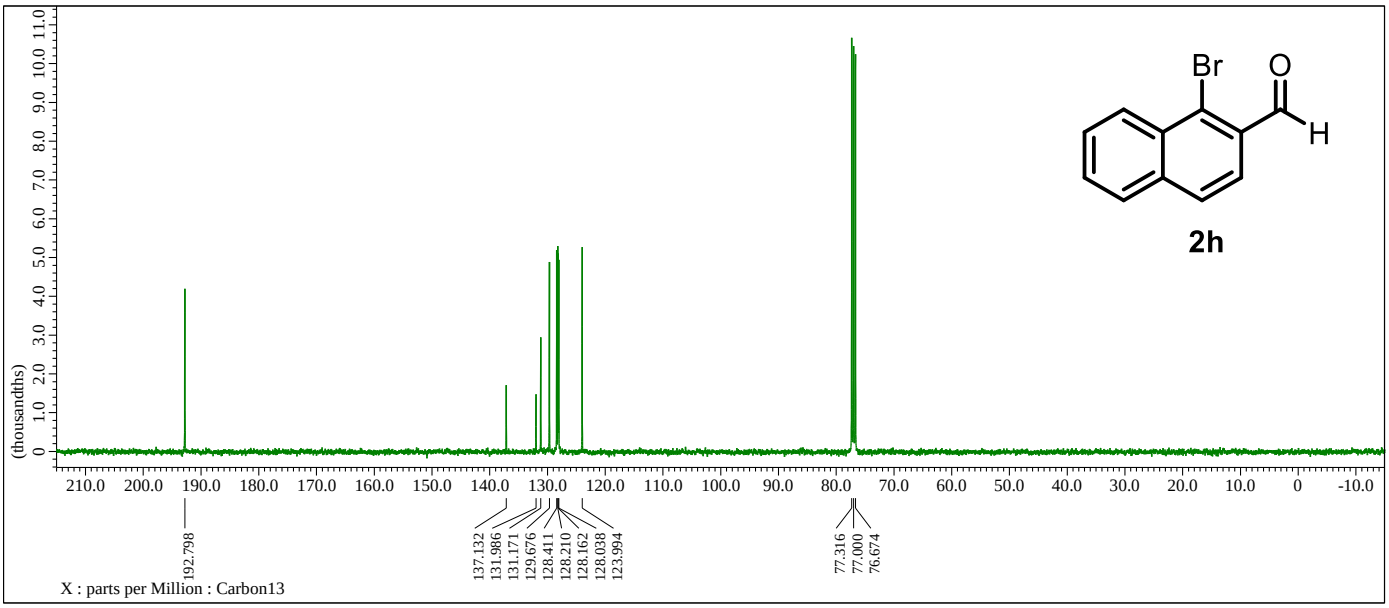
^{13}C NMR (100 MHz, $CDCl_3$) of **2g**



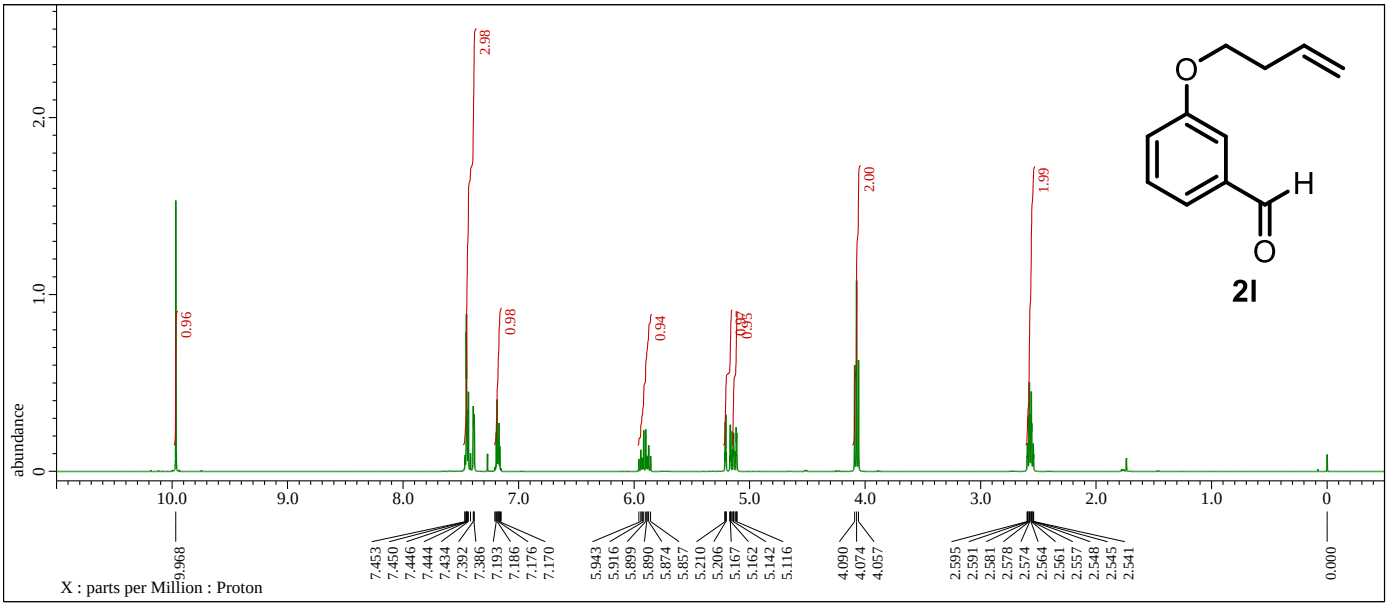
^{1}H NMR (400 MHz, $CDCl_3$) of **2h**



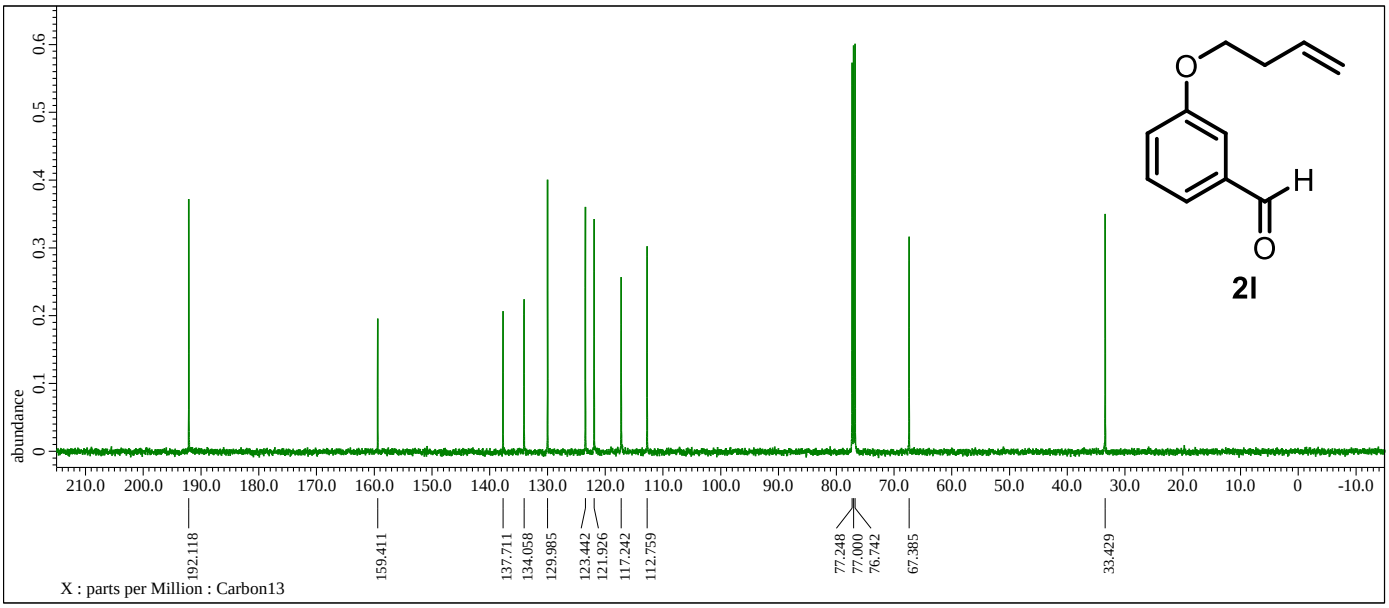
^{13}C NMR (100 MHz, $CDCl_3$) of **2h**



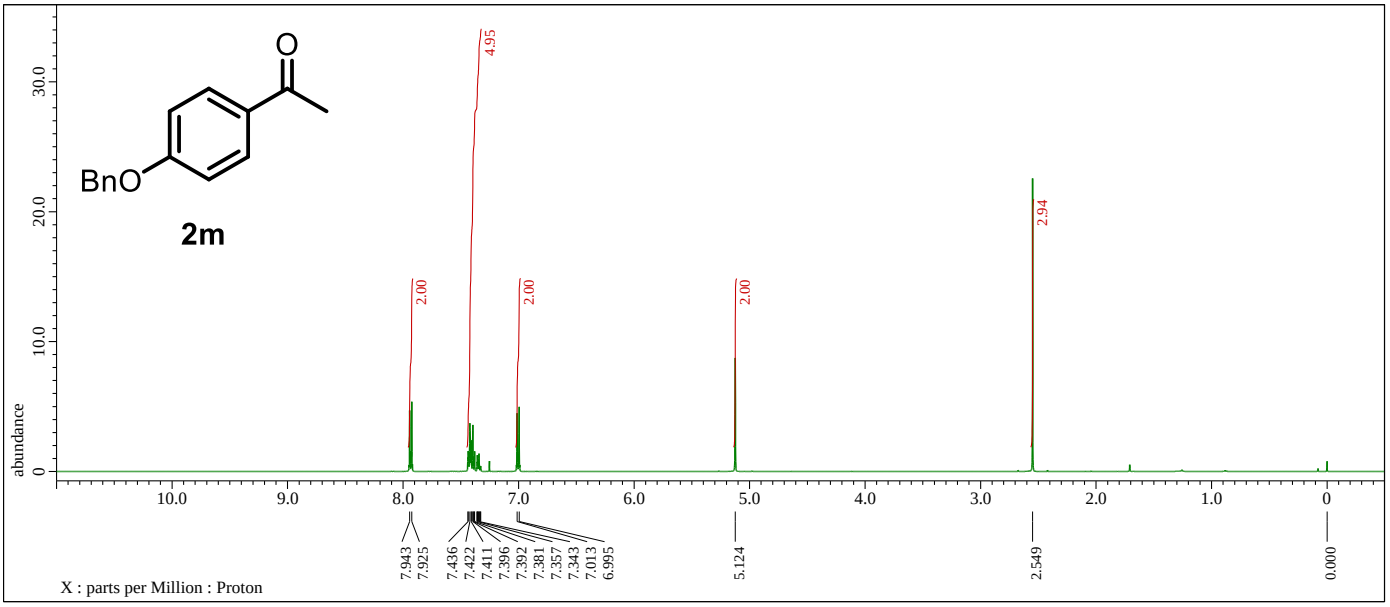
^{1}H NMR (500 MHz, $CDCl_3$) of **2l**



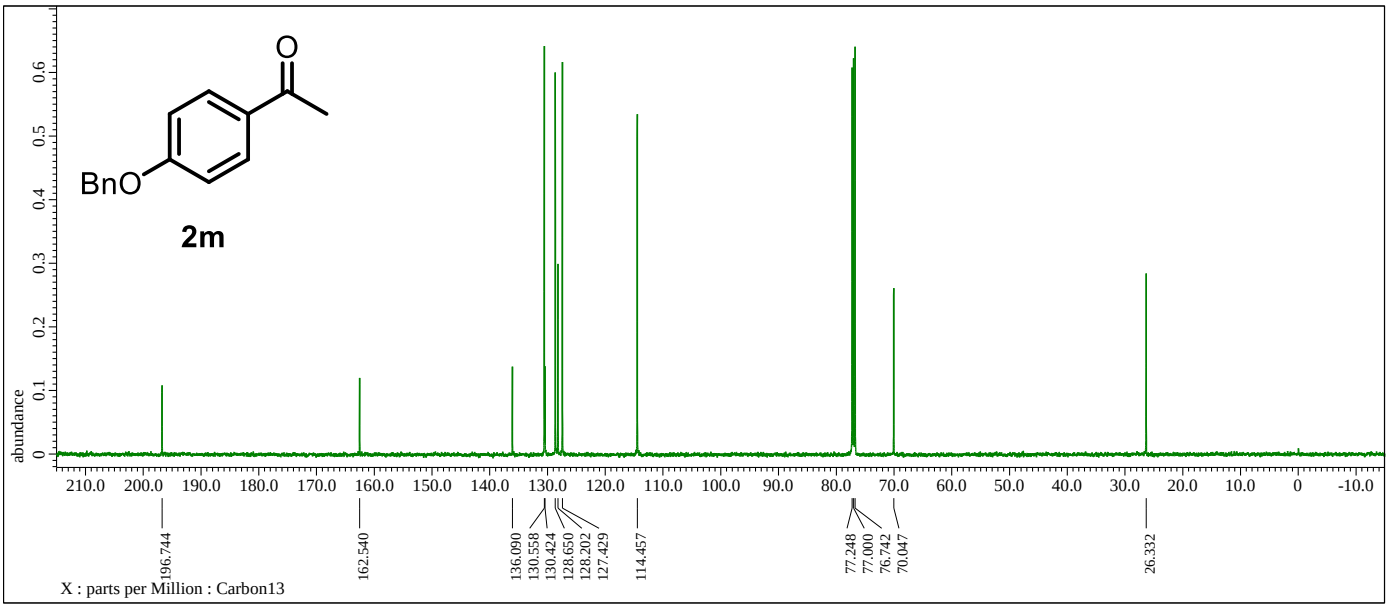
^{13}C NMR (125 MHz, $CDCl_3$) of **1l**



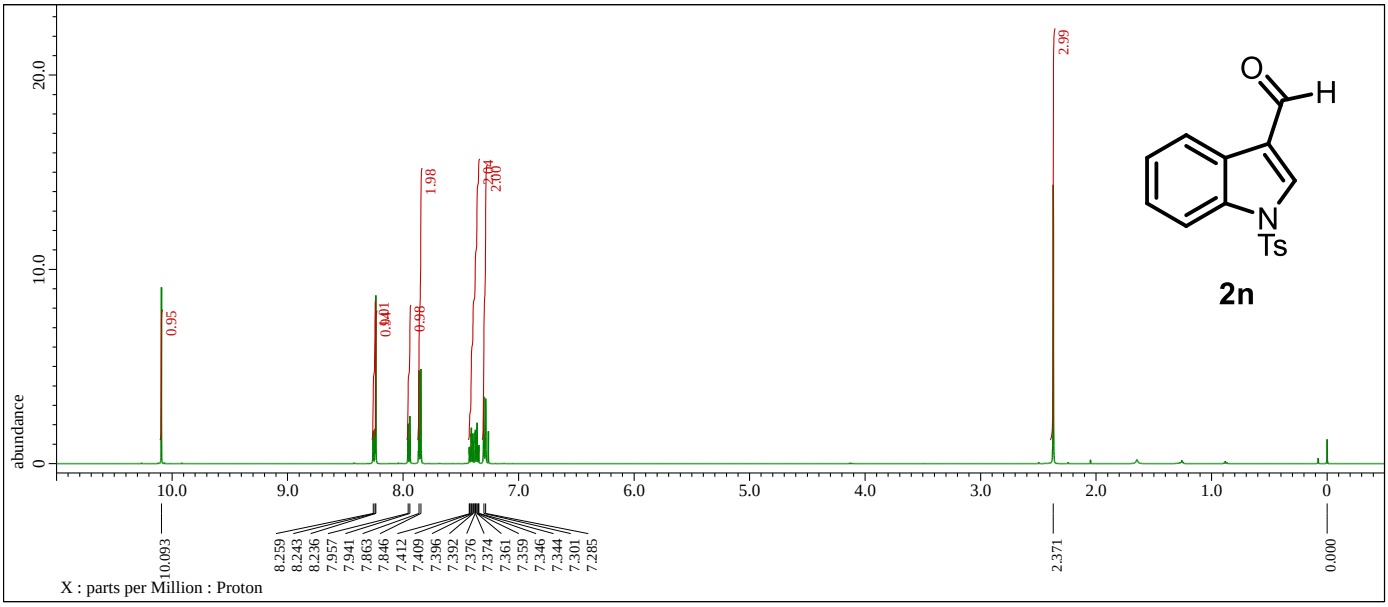
^{1}H NMR (500 MHz, $CDCl_3$) of **2m**



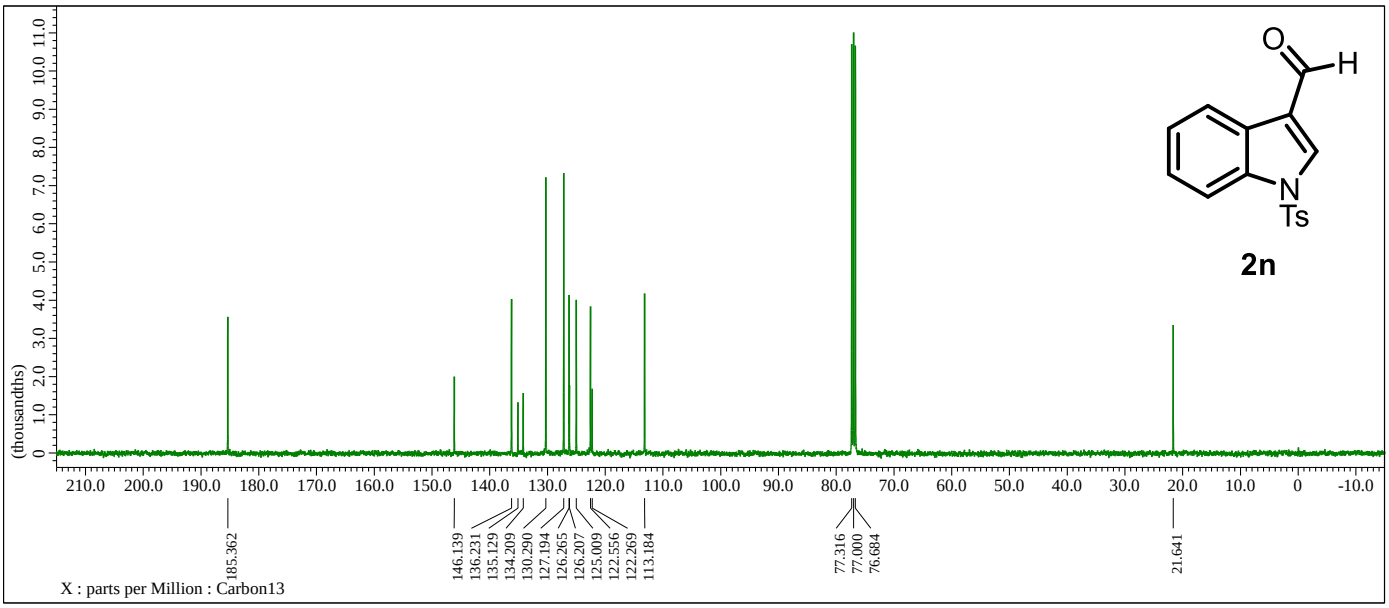
^{13}C NMR (125 MHz, $CDCl_3$) of **2m**



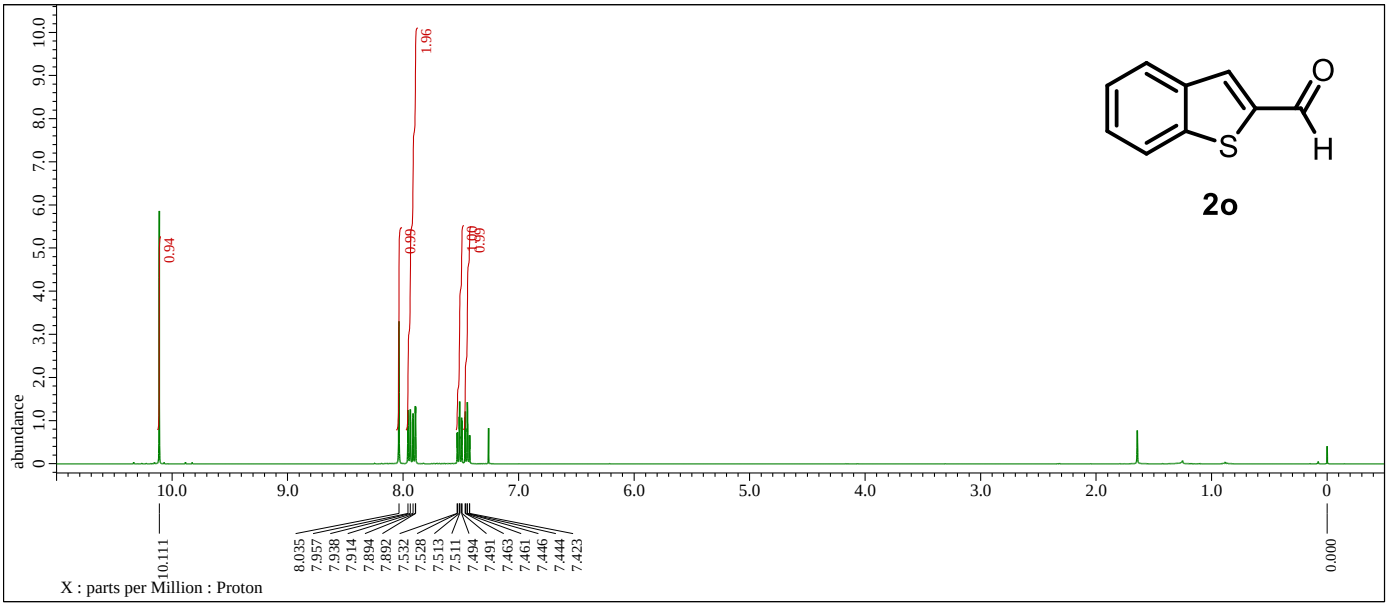
^{1}H NMR (500 MHz, $CDCl_3$) of **2n**



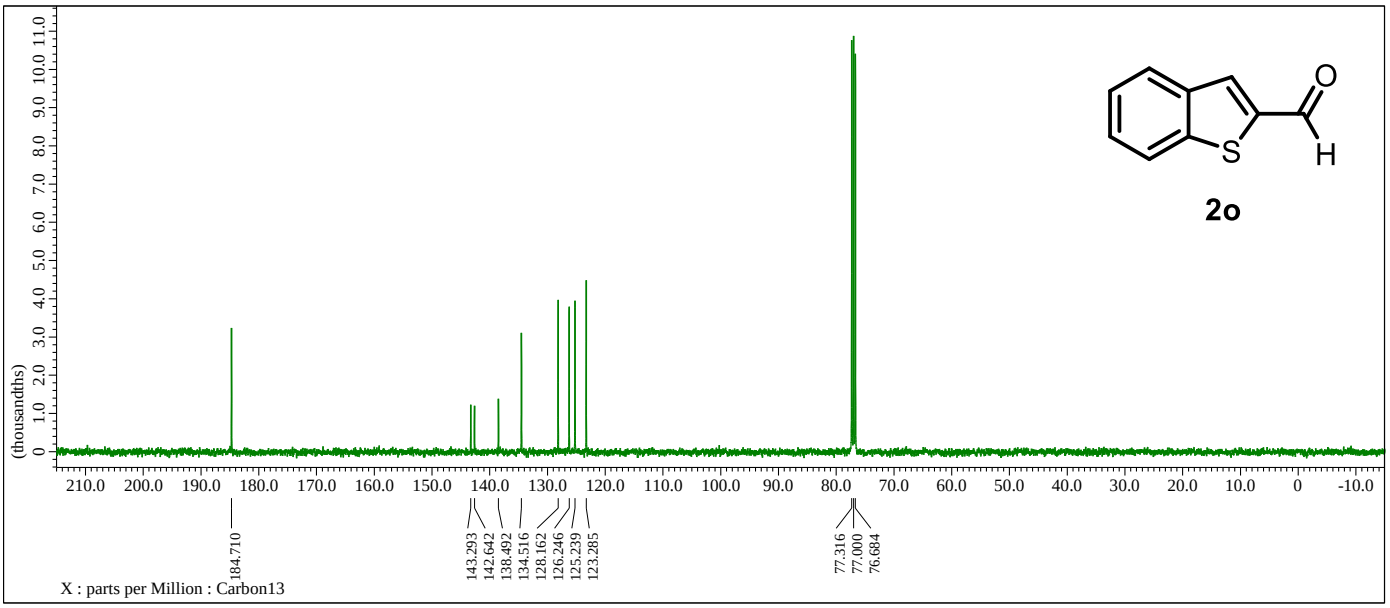
^{13}C NMR (100 MHz, $CDCl_3$) of **2n**



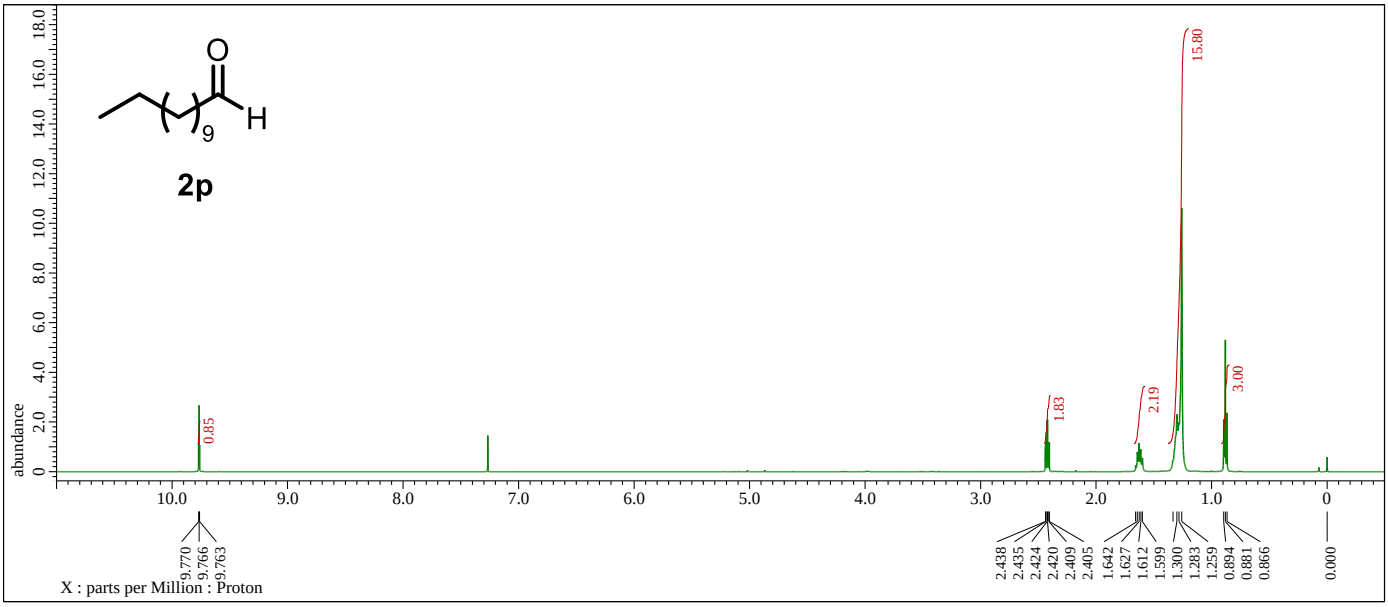
^{1}H NMR (400 MHz, $CDCl_3$) of **2o**



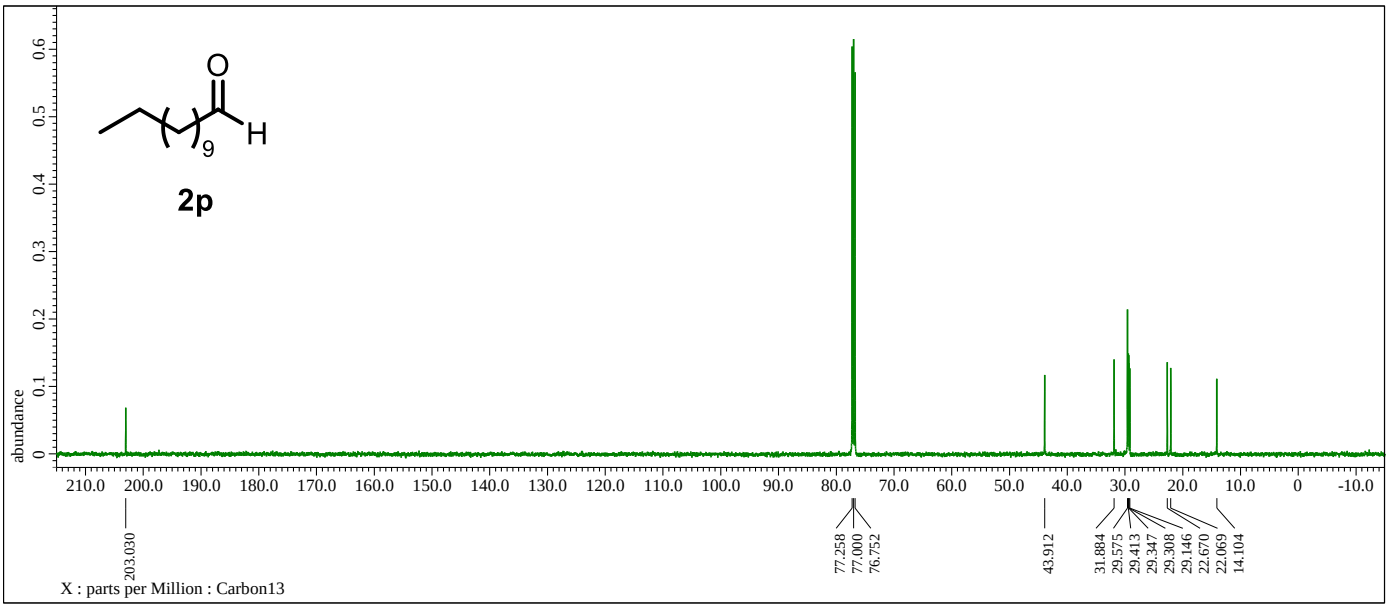
^{13}C NMR (100 MHz, $CDCl_3$) of **2o**



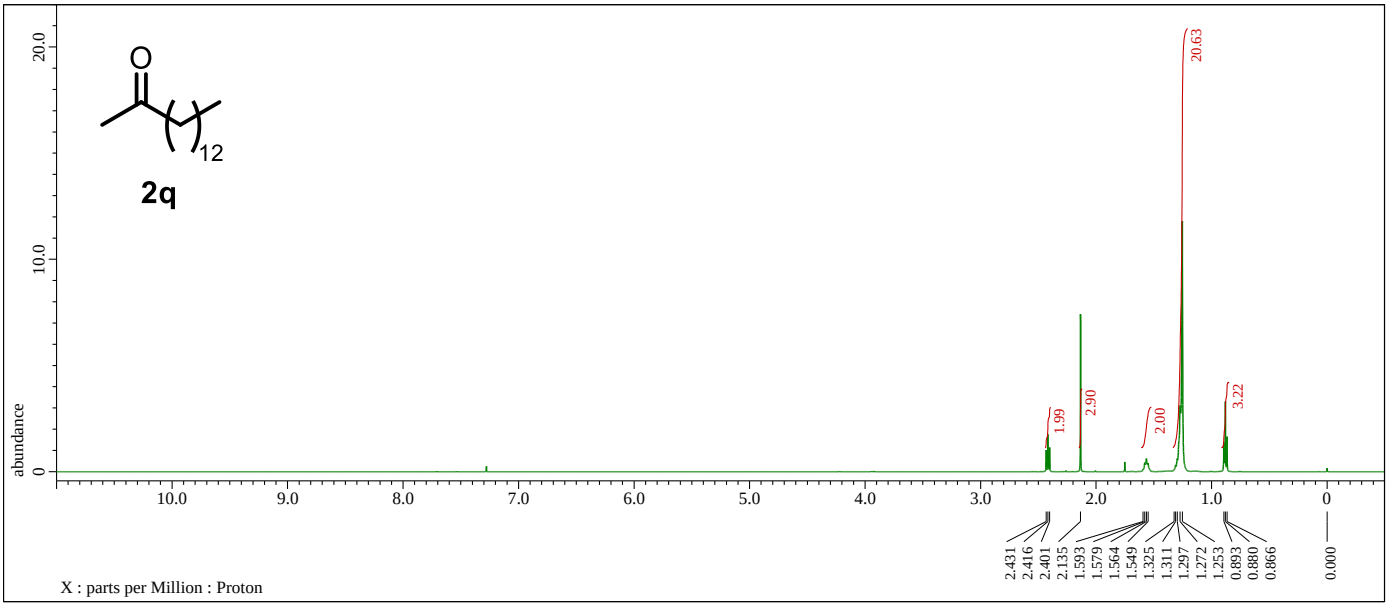
^{1}H NMR (400 MHz, $CDCl_3$) of **2p**



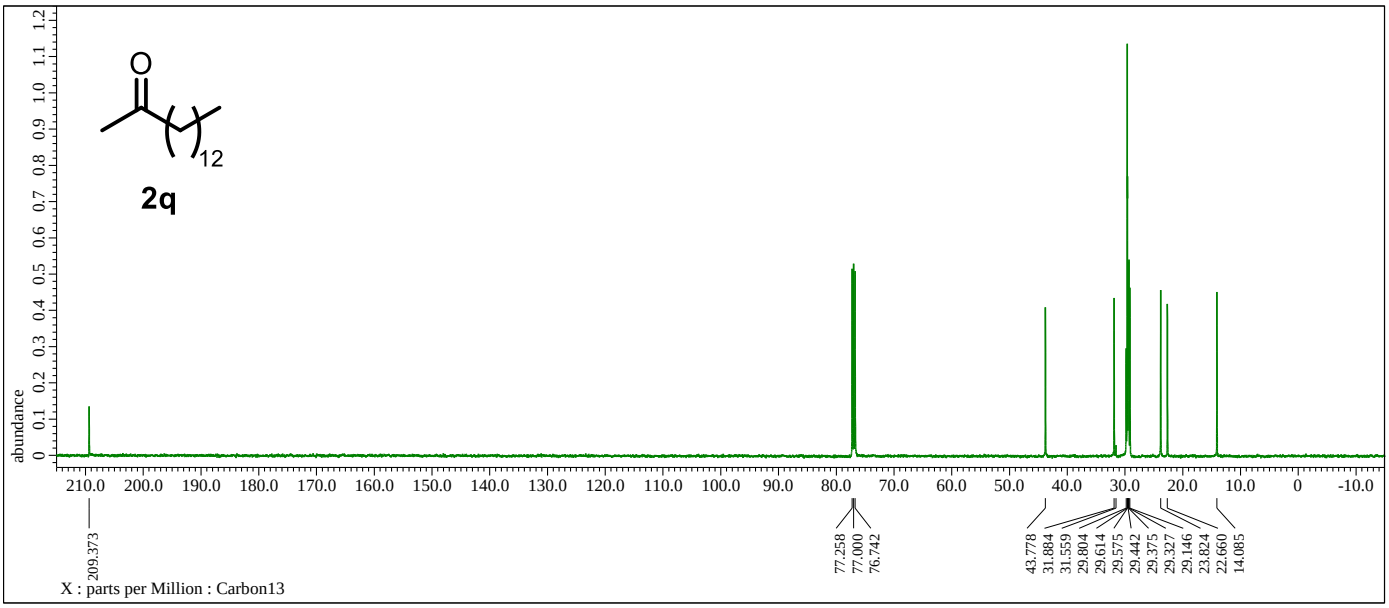
^{13}C NMR (100 MHz, $CDCl_3$) of **2p**



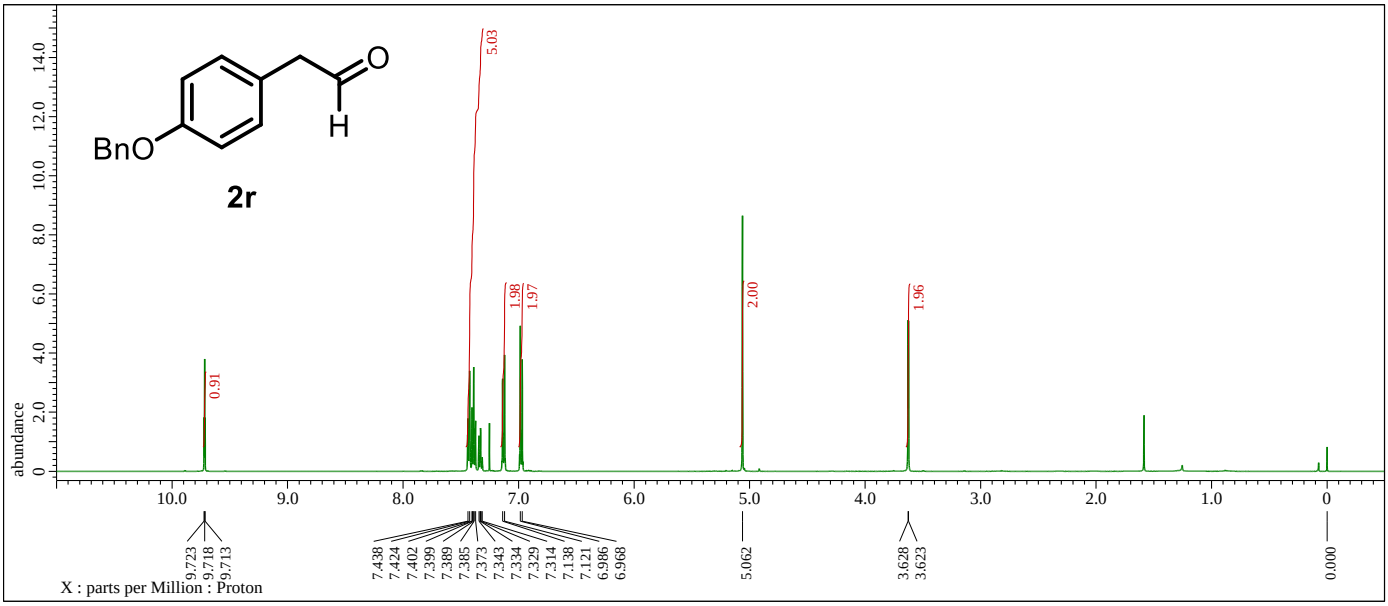
^{1}H NMR (500 MHz, $CDCl_3$) of **2q**



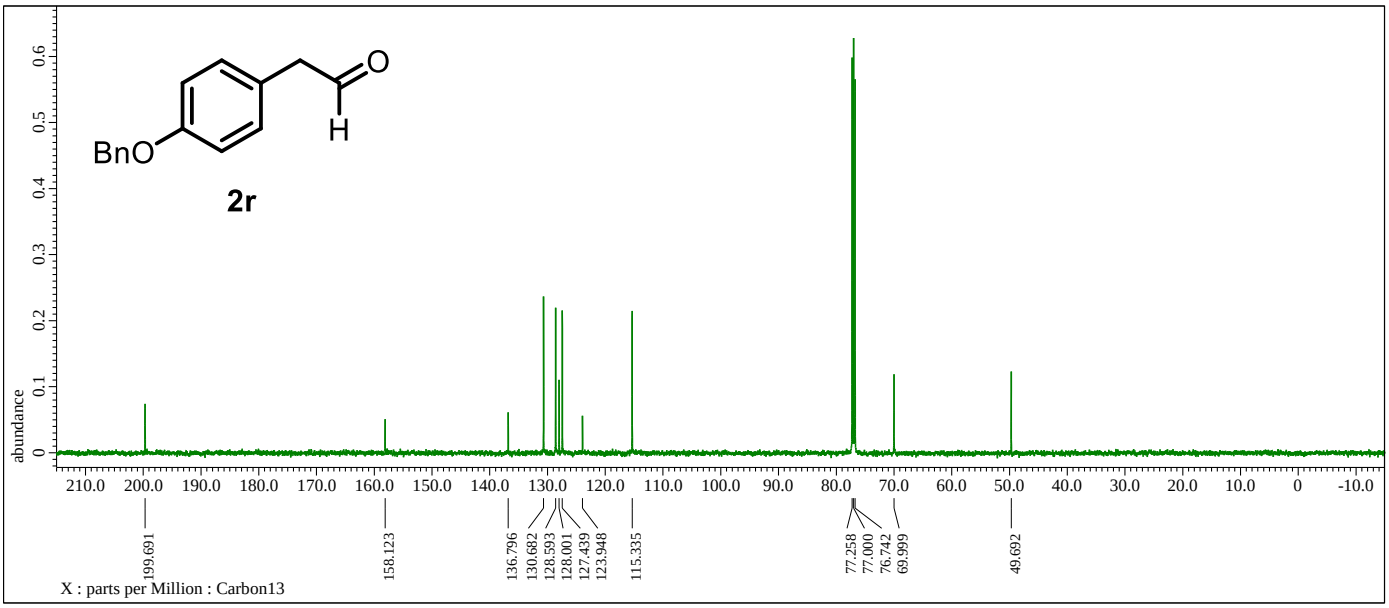
^{13}C NMR (125 MHz, $CDCl_3$) of **2q**



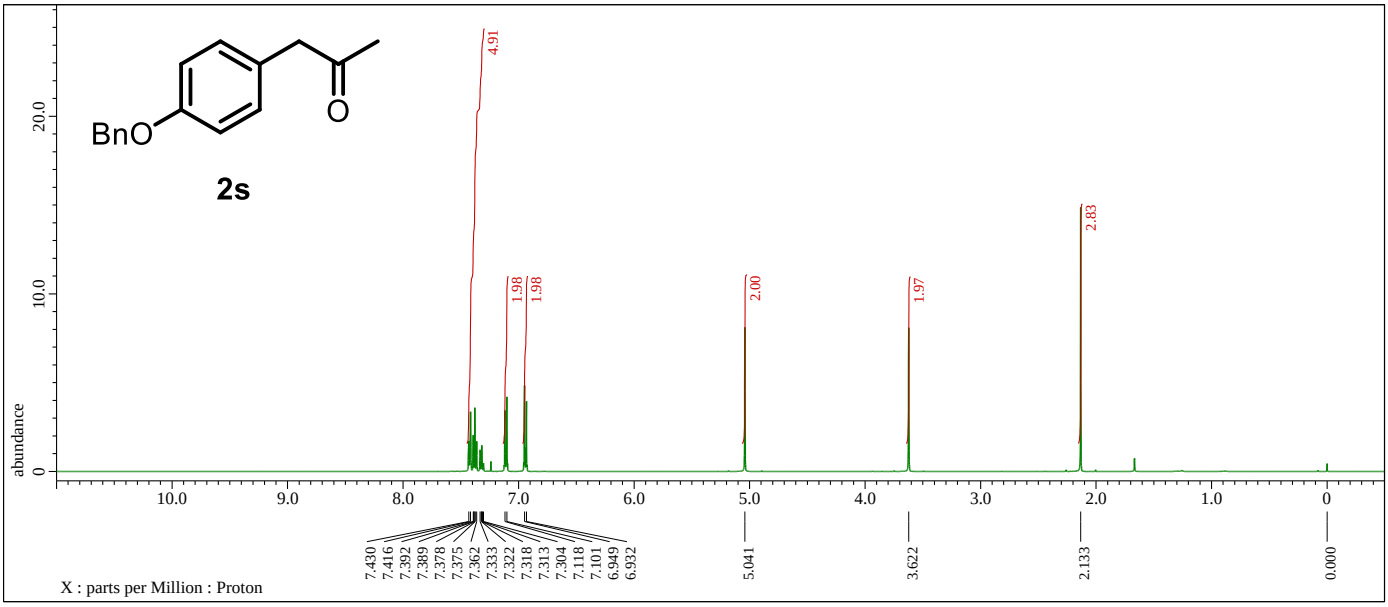
^{1}H NMR (500 MHz, $CDCl_3$) of **2r**



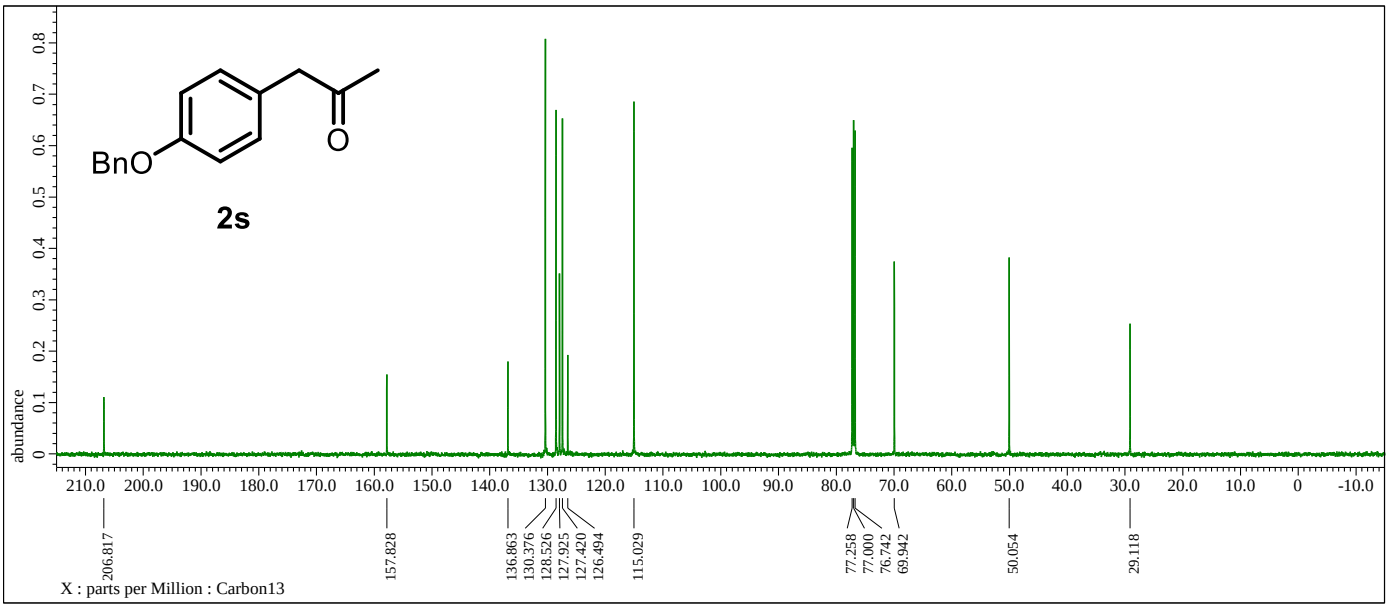
^{13}C NMR (125 MHz, $CDCl_3$) of **2r**



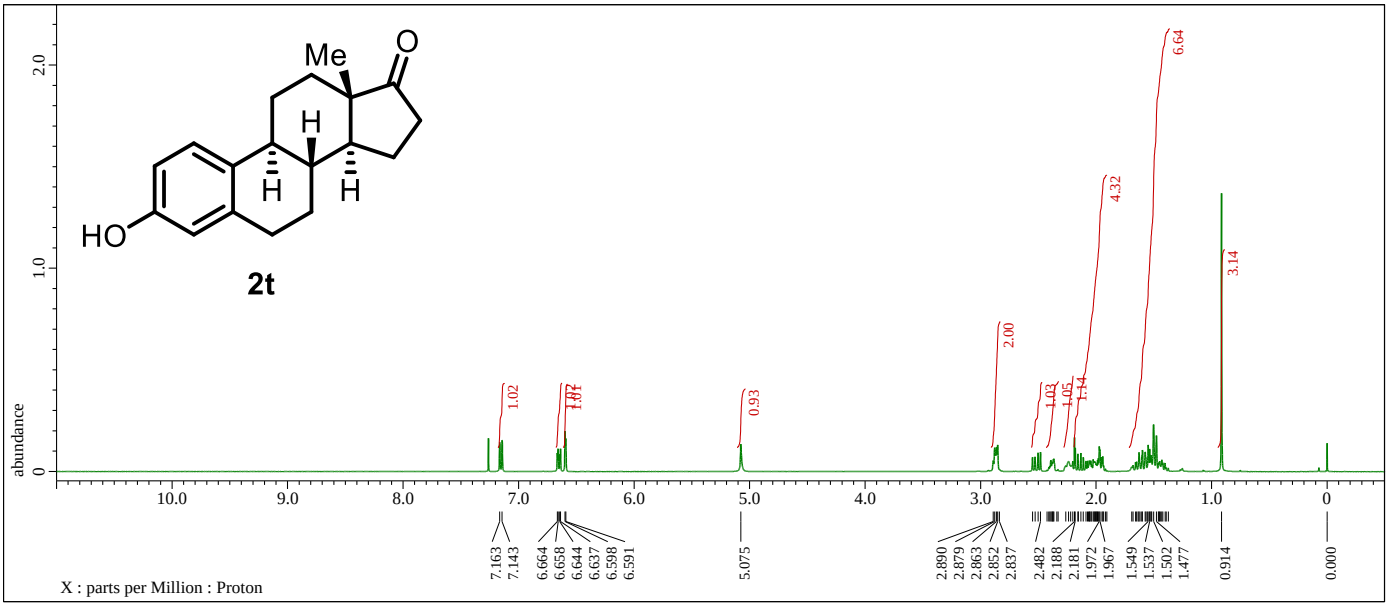
^{1}H NMR (500 MHz, $CDCl_3$) of **2s**



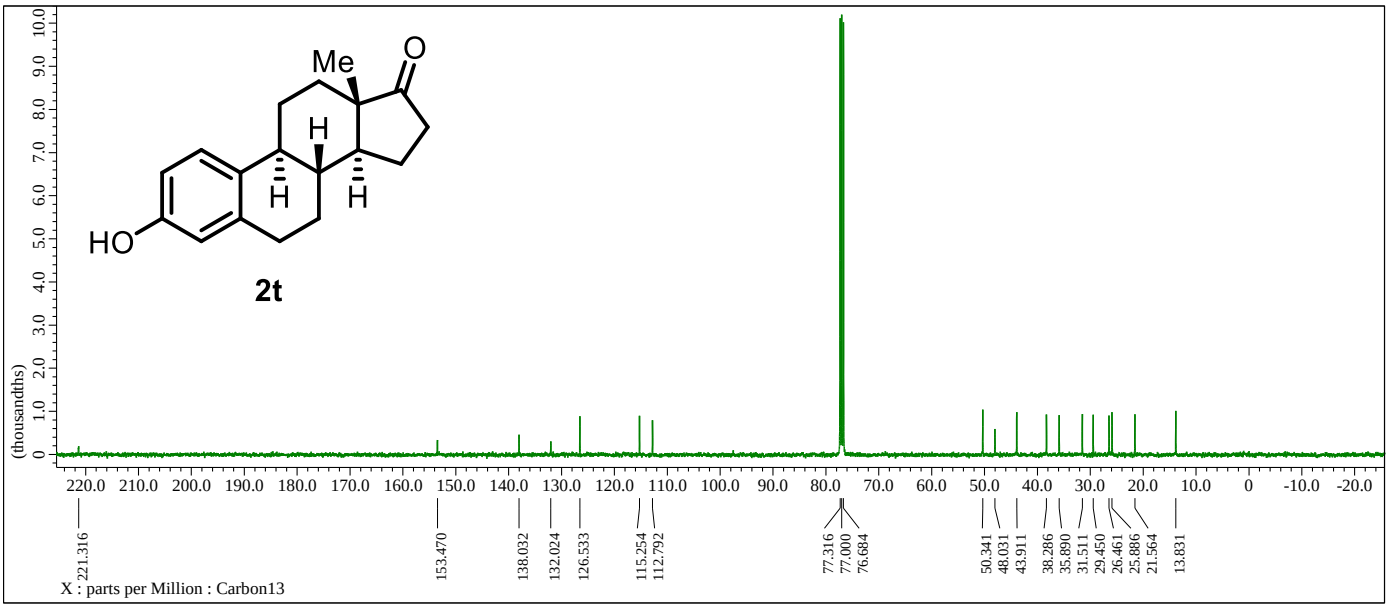
^{13}C NMR (125 MHz, $CDCl_3$) of **2s**



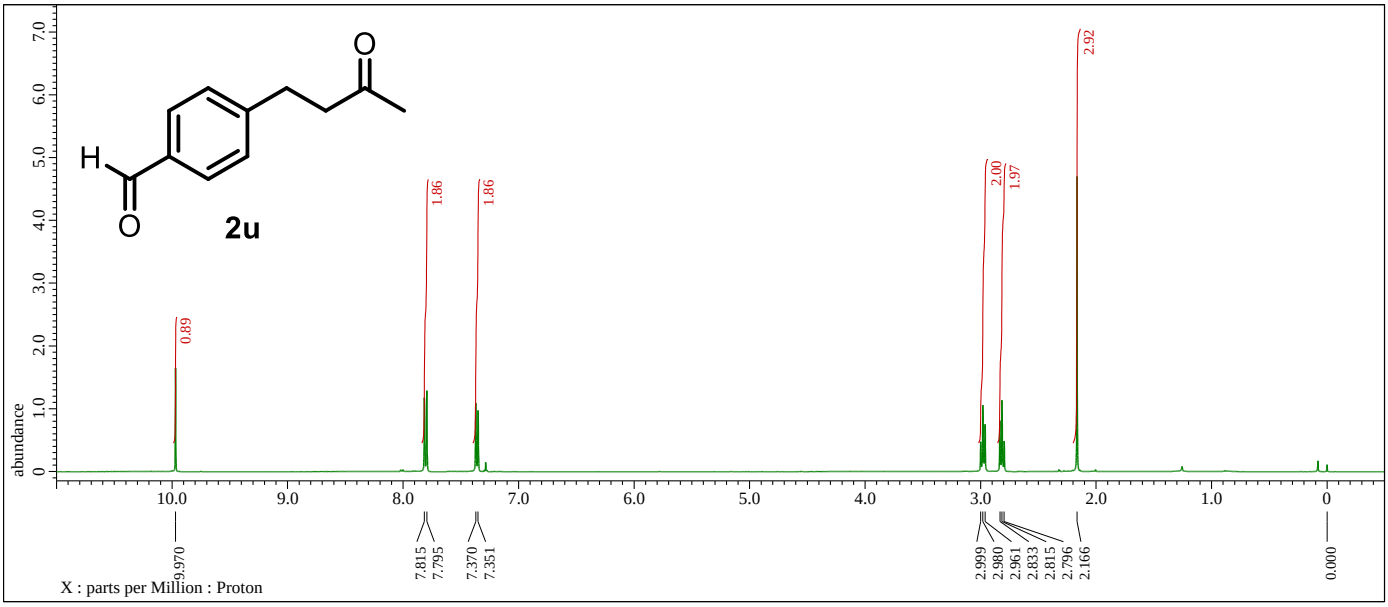
^{1}H NMR (400 MHz, $CDCl_3$) of **2t**



^{13}C NMR (100 MHz, $CDCl_3$) of **2t**



^{1}H NMR (400 MHz, $CDCl_3$) of **2u**



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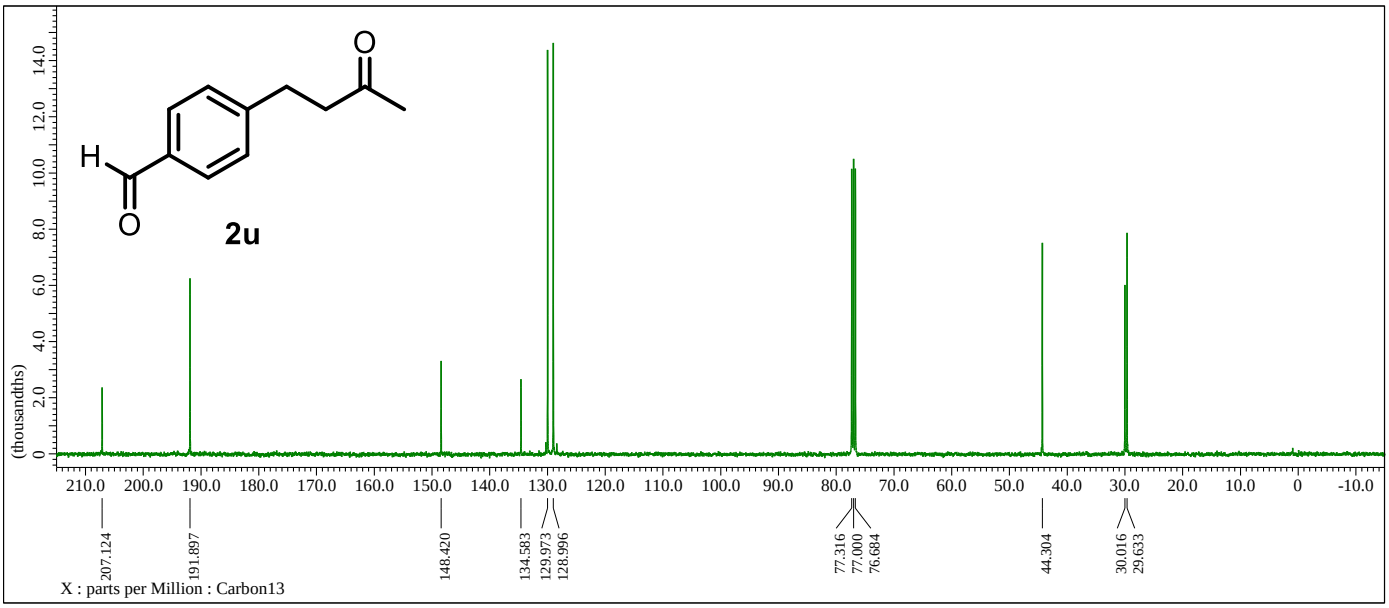
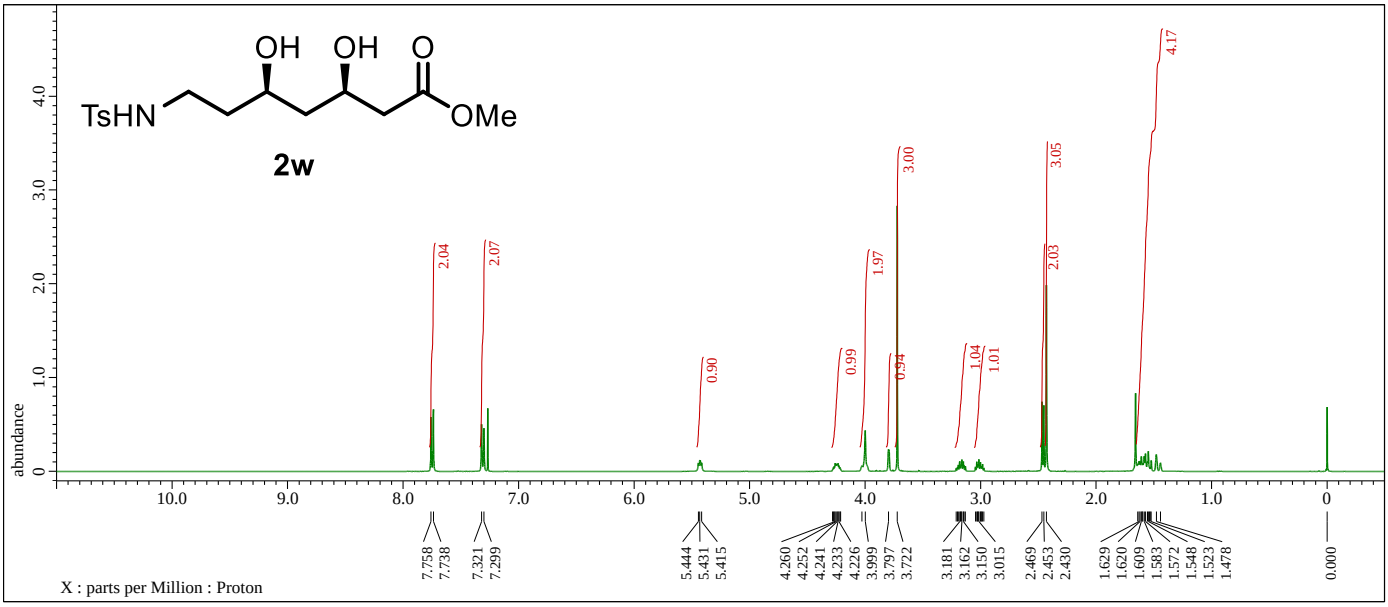
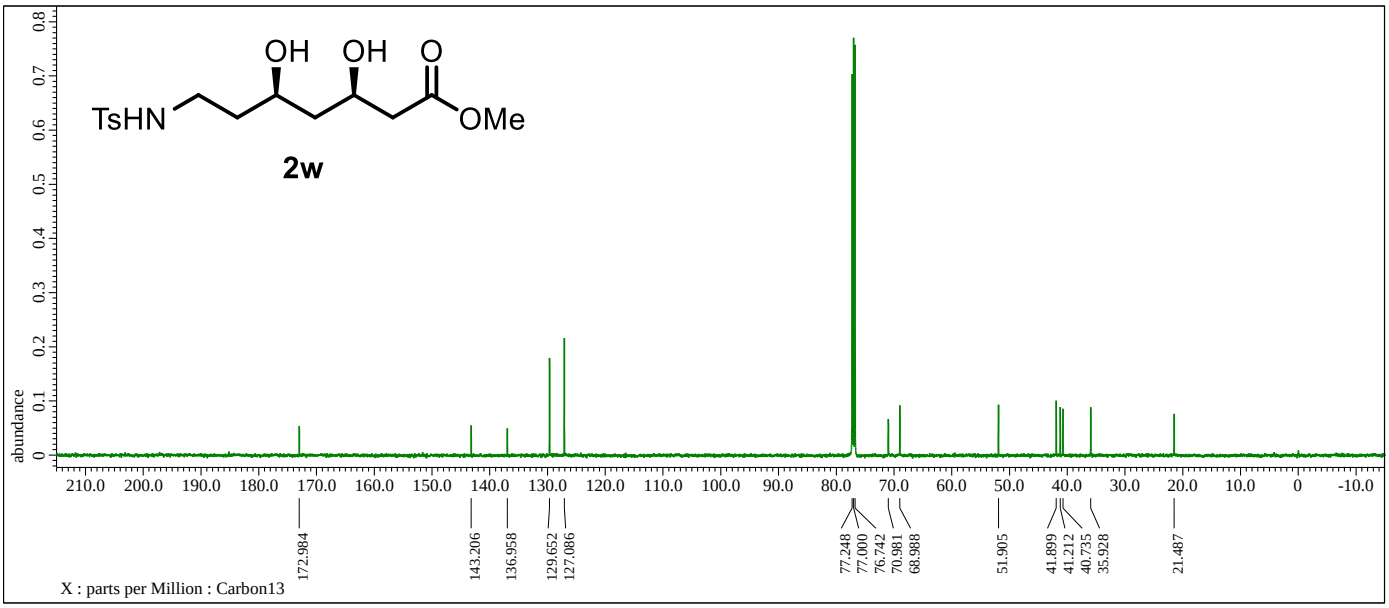


^{1}H NMR (500 MHz, $CDCl_3$) of **2w**



^{13}C NMR (125 MHz, $CDCl_3$) of **2w**



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