Electronic Supplementary Material (ESI) for Green Chemistry.

Supplementary Information

Direct synthesis of oxaspirolactones in batch, photoflow, and silica gel-supported solvent-free conditions *via* visible-light photo- and heterogeneous Brønsted acid relay catalysis

Shinje Miñoza,‡ Wei-Cheng Ke,‡ Yin-Yin Yu,‡ Prem Kumar Keerthipati, Kuei-Chen Chang, Wei-Cheng Kao, Zong-Nan Tsai, and Hsuan-Hung Liao*

Department of Chemistry, National Sun Yat-sen University, Kaohsiung 80424, Taiwan
*Email: hsuan-hung.liao@mail.nsysu.edu.tw

Back to contents

1. General Information

1.1. Experiment and pre-treatment of solvents and reagents

Glassware. All glassware were oven-dried after washing with cleaning machine Steelco LAB 500CL.

Experiment. Otherwise specified, air- and water-sensitive reactions were carried out in a nitrogen-filled glovebox (Vigor SG1200/750TS-F) or via standard Schlenk techniques.

Chemicals. TMSCl was distilled according to the Purification of Laboratory Chemicals prior to use. To maintain the activity, highly sensitive compounds such as metal reagents were opened and stored in the glovebox. Other chemicals were directly used as received and were always filled with nitrogen and twined with parafilm carefully before storage. See Section S1.4. for the complete list of suppliers for each chemical. All the names of the chemicals listed herein were generated from ChemDraw.

Solvents. All solvents were purchased from suppliers (Table S2 to Table S4). Unless otherwise stated, ACS grade solvents (Acetonitrile, 1,4-Dioxane, Diethyl Ether, DCM, DMF, THF, Toluene) were stored over microwave-activated 3Å molecular sieves for at least one night before transferring into our anhydrous engineering alumina column drying system (*Vigor* Gas Purification Technologies Co., Ltf, VSPS-7) prior to use.

Experiment Except as specified, air- and water-sensitive reactions were carried out in nitrogen-filled glovebox or standard Schlenk techniques.

1.2. Chromatography, data analysis and collection

Thin-layer Chromatography (TLC). Merck aluminium backed sheets coated with $60F_{254}$ silica gel. Visualization of the silica plates was achieved using a UV lamp (λ_{max} = 254 nm), and/or PMA stain (10% PMA in 95% EtOH), CAM stain (2.5% Ammonium molybdate tetrahydrate, aqueous solution $KMnO_4$, phosphomolybdic acid (PMA), or *p*-anisaldehyde solution followed by heating.

Column Chromatography. Column chromatography was carried out using KM3 scientific silica gel (45 – 75 μm) purchased from KM3 scientific or Merck silica gel 60 GF254 (5—40 μm, Catalogue Number: 1.07730.9025).

Automated Flash Column Chromatography. Automated flash column chromatography was carried out Biotage® Selekt.

1.3. Instrument catalogue

Nuclear Magnetic Resonance (NMR) ^{1}H-, and ^{13}C-Nuclear Magnetic Resonance (NMR) spectra were used to identify the structure of starting materials and products by using Bruker Avance 300 MHz, Jeol ECZS 400 MHz, Bruker Avance 500 MHz and Jeol ECZR 600 MHz. Coupling constants are abridged as following: s = singlet, br.s = broad singlet, d = doublet, br. d = broad doublet, t = triplet, q = quartet, quin = quintet, sext = sextet, sept = septet, m = multiplet, dd = doublet of doublet.

Back to contents

High Resolution Mass Spectra (HRMS) Jeol AccuTOF GCx-plus / Shimadzu QP2020

Gas Chromatography–Mass Spectrometry (GC-MS) The operation method was set as following: 1.0 mL sample was injected by auto-sampler in a split mode (100:1) with 0.5 mL air gap into the GC-MS system consisting of an Agilent 8860 gas chromatograph, an Agilent 5977B mass selective detector, and Agilent 7693A autoinjector. Gas chromatography was performed on a 30 m HP-5MS with 0.25 mm inner diameter (I.D.) and 0.25 mm film thickness with an initial injection temperature of 50 ℃ to 300 ℃, MSD transfer line of 280 ℃, and the ion source adjusted to 230 ℃. The helium carrier gas was set at a constant flow rate of 1.197 ml min^{-1}. The mass spectrometer was operated in positive electron impact mode (EI), ionization energy in *m/z* 50 – 550 scan range. The spectra of all chromatogram peaks were evaluated using the MSD Chemstation.

Fourier Transform-Infrared (FT-IR) Spectrophotometer PerkinElmer Spectrum Two FT-IR spectrometer equipped with Attenuated Total Reflectance (ATR) accessory.

Melting Point Apparatus Tianjin Tianguang New Optical Instrument Technology Co., Ltd. RY-1G Melting Point Apparatus.

Table S1. Supplier of equipment and instruments.

Equipment	Supplier
Electronic balance	*Shimadzu* UW2200H/ ATX224
Hot plate stirrer	*Corning* PC-420D
Immersion cooler	*Panchum* IC-9090
Pump of rotary evaporator	*KNF Laboport* N820.3FT.18
Rotary evaporator	*Heidolph* Hei-Vap Core HL G3
Refrigerated circulator bath	*Panchum* CC-300
Ultra-low temp. reaction bath	*Panchum* UR-8500
Vacuum pump	*Edwards* RV5
Light Sources	*Kessil* PR160L-456 nm *Kessil* PR160L-525 nm
Shutter controller	*Thorlabs* SC10
Solvent purification systems	*Vigor* VSPS-7
Instruments	**Supplier**
Flash chromatography instrument	*Biotage* Biotage® Selekt
Glovebox	*Vigor* SG1200/750TS-F
GC-MS (Gas Chromatograph Mass Spectrometer)	*Agilent* 5977B
HPLC (High Performance Liquid Chromatography)	*Agilent* 1260 Infinity II
UV-Vis	*Agilent* Cary 8454

Back to contents

1.4. Purchased solvents and reagents

Table S2. Supplier of solvents.

Solvent	Supplier	Solvent	Supplier
ACS Acetone	Duksan	HPLC Acetonitrile	J.T. Baker
ACS Acetonitrile	J.T. Baker	HPLC DMF	Macron
ACS Benzene	Echo	HPLC Ethyl acetate	Merck
ACS Chloroform	Acros	HPLC Hexane	Echo
ACS Dimethyl sulfoxide	UR	HPLC Isopropanol	Echo
ACS Diethyl ether	Duksan	ACS Hexane	Duksan
ACS Dichloromethane	Macron /Duksan	ACS Methanol	Macron
ACS Ethanol	J.T. Baker	ACS THF	Macron
ACS Ethyl acetate	Macron	ACS Toluene	Echo

Table S3. Supplier of solvents in solvent purification systems.

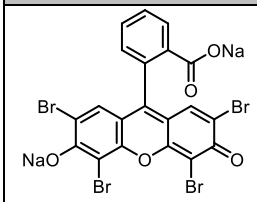
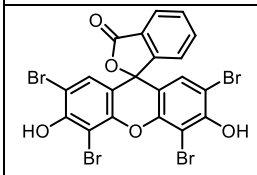
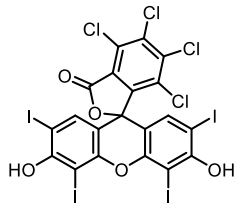
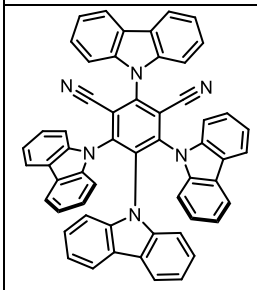
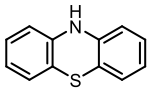
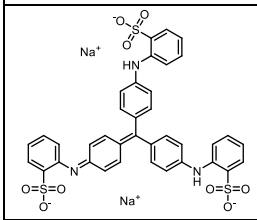
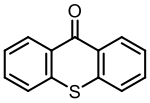
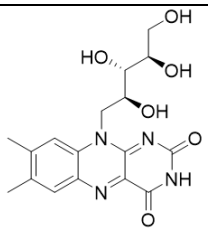
Solvent	Supplier	Solvent	Supplier
Acetonitrile	J.T. Baker	Dichloromethane	Macron
DMF	Macron	THF	Macron
1,4-Dioxane	J.T. Baker	Toluene	J.T. Baker
Diethyl ether	Echo		

Table S4. Supplier of deuterated solvents.

Solvent	Supplier	Solvent	Supplier
Acetonitrile-d_3	Sigma-Aldrich	DMSO-d_6	Sigma-Aldrich
Benzene-d_6	Sigma-Aldrich	Dichloromethane-d_2	Sigma-Aldrich
Chloroform-d_1	Merck	Methanol-d_4	Sigma-Aldrich

Back to contents

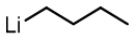
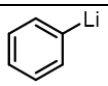
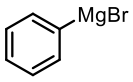
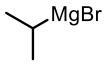
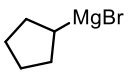
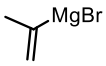
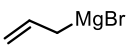
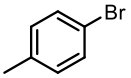
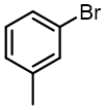
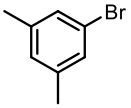
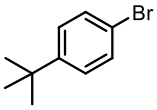
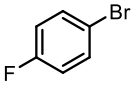
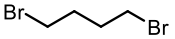
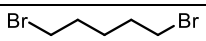
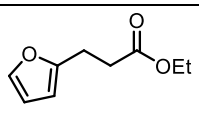
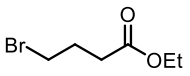
Table S5. Catalogue of photocatalysts.

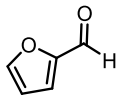
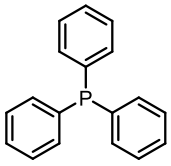
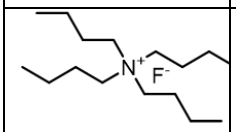
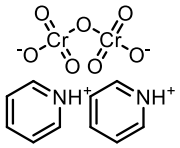
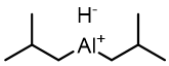
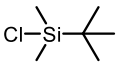
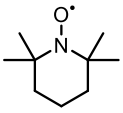
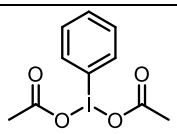
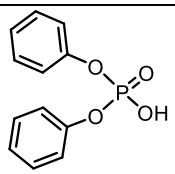
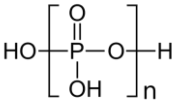
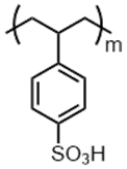
Structure	Name	CAS Number	Supplier
	Na_2-Eosin Y (Acid Red 87)	17372-87-1	TCI
	Eosin Y (Tetrabromofluorescein)	15086-94-9	TCI
	Rose Bengal	632-69-9	Alfa Aesar
	4CzIPN*	1416881-52-1	---[1]
	10*H*-Phenothiazine	92-84-2	Alfa Aesar
	Methyl blue	28983-56-4	Acros
	9*H*-Thioxanthen-9-one	492-22-8	Fluorochem
	Riboflavin	83-88-5	Acros

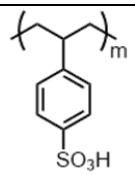
*Synthesized in the laboratory using a literature method.[1]

Back to contents

Table S6. Catalogue of commercial reagents

Structure	Name	CAS Number	Supplier
MeLi	Methyl lithium (3.1 M solution in diethoxymethane)	917-54-4	Sigma Aldrich
	*n*-Butyl lithium** (2.5 M solution in hexane)	10031-90-0	Alfa Aesar/ Sigma-Aldrich
	*tert*-Butyl lithium (1.9 M solution in pentane)	594-19-4	Acros
	Phenyl lithium (20% solution in dibutyl ether)	591-51-5	Rockwood
	Phenylmagnesium bromide (1 M solution in THF)	100-58-3	TCI
EtMgBr	Ethylmagnesium bromide (3.0 M solution in diethyl ether)	925-90-6	Acros
	Isopropylmagnesium chloride (2.0 M solution in THF)	1068-55-9	Acros
	Cyclopentylmagnesium bromide (2.0M solution in diethyl ether)	33240-34-5	Acros
	Isopropenylmagnesium bromide (0.5 M solution in THF)	13291-18-4	Acros
	Allylmagnesium bromide (1.0 M solution in diethyl ether)	1730-25-2	Acros
	4-Bromotoluene	106-38-7	TCI
	1-Bromo-3-methylbenzene	591-17-3	TCI
	1-Bromo-3,5-dimethylbenzene	556-96-7	BLDpharm
	1-Bromo-4-*tert*-butylbenzene	3972-65-4	Fluorochem
	4-Bromofluorobenzene	460-00-4	Alfa Aesar
	1,4-Dibromobutane	110-52-1	Alfa Aesar
	1,5-Dibromopentane	111-24-0	Alfa Aesar
	Ethyl 3-(furan-2-yl)propionate	10031-90-0	Alfa Aesar
	Ethyl 4-bromobutyrate	2969-81-5	Alfa Aesar

	Furfural	98-01-1	Aldrich
	Furan*	110-00-9	Alfa-Aesar
	1*H*-imidazole	288-32-4	Merck
	Triphenylphosphine	603-35-0	Alfa Aesar
	Potassium *tert*-butoxide	865-47-4	Aldrich
MeI	Iodomethane	74-88-4	Showa
	Tetrabutylammonium fluoride	429-41-4	Acros
	Pyridinium dichromate	20039-37-6	Acros
	Diisobutylaluminum hydride (1 M solution in hexane)	1191-15-7	Alfa Aesar
	Chlorotrimethylsilane	75-77-4	Merck
	*tert*-Butyldimethylsilane chloride	18162-48-6	TCI/ Nova-Matls
	(2,2,6,6-Tetramethylpiperidin-1-yl)oxyl	2564-83-2	Alfa Aesar
	Phenyl-λ^3-iodanediyl diacetate	3240-34-4	Alfa Aesar
	Diphenyl phosphate	838-85-7	Acros
	Polyphosphoric acid (83% P_2O_5)	8017-16-1	Showa
	Amberlyst® 15 hydrogen form	39389-20-3	Sigma Aldrich

	Dowex 50X8-200	11119-67-8	JANSSEN
$NaBH_4$	Sodium borohydride	16940-66-2	Aldrich
$LiAlH_4$	Lithium Aluminium Hydride	16853-85-3	Merck
CuO	Copper oxide	1317-38-0	Sigma-Aldrich
I_2	Iodine	7553-56-2	TCI
Cs_2CO_3	Cesium carbonate	534-17-8	BLDpharm
Pd/C	Palladium on carbon	7440-05-3	Merck
Mg	Magnesium turnings	7439-95-4	SCHARLAU
O_2	Oxygen	7782-44-7	JING SHANG
H_2	Hydrogen	1333-74-0	JING SHANG

*The reagent was purified by distillation before using.

**The concentration of the reagent was confirmed by titration before using.

Back to contents

1.5. Home-made LED photoreactors

1.5.1 Details on the construction of photoreactors

Using a 24 cm x 25 cm pre-cut aluminum sheet, a roll with a 14-15 cm diameter was made enough to house a 4 x 5 metal test-tube rack. A 2.3 m LED strip was then pasted inside the bottom part of the aluminum roll using a double-sided tape starting from a 1 cm allowance. A computer fan is then placed at the top of the roll for every reaction to avoid overheating of the aluminum sheet.

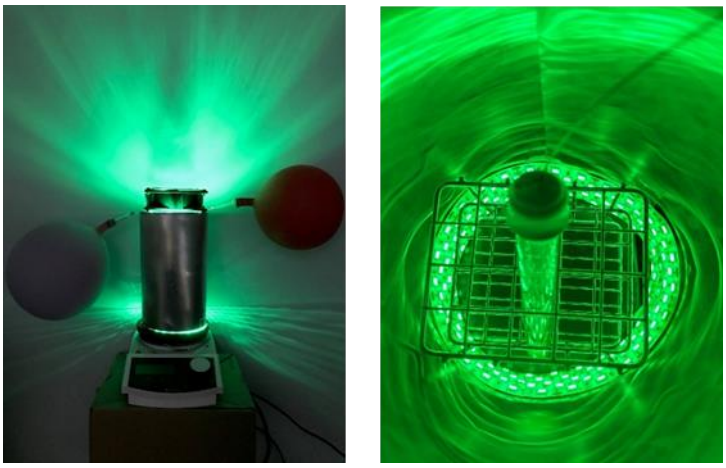


Figure S1. Actual reaction setup for light irradiation using LED strip.

Back to contents

1.5.2 Wavelength of distribution for the purchased LEDs

1. Green LED strip, purchased from Centenary Materials, SMD3528-60-G, 518.34 nm (detected with Ocean Optics USB2000 Optic Spectrometer), 60 LED per meter, 4.8 W per meter, 120° beam angle.

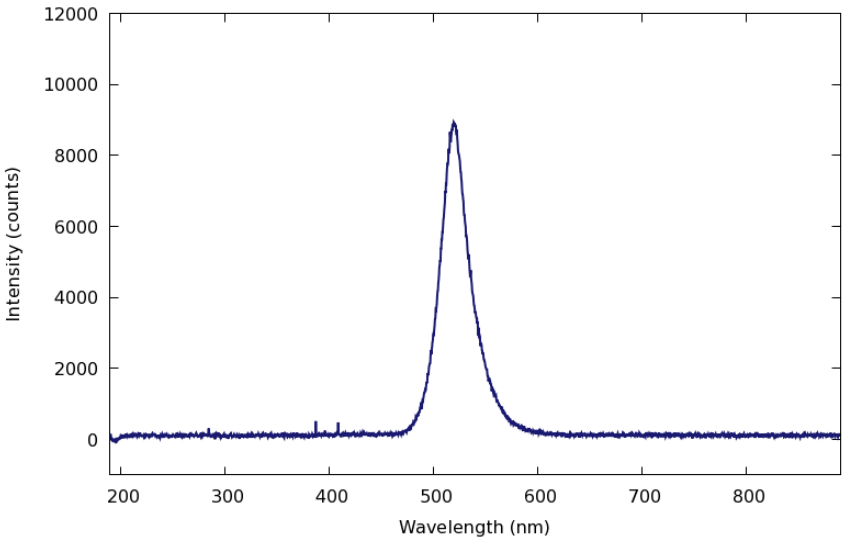


Figure S2. Measured wavelength of distribution for green LED strip.

2. White LED strip, purchased from Centenary Materials, SMD3528-60-W, 60 LED per meter, 4.8 W per meter, 120° beam angle.

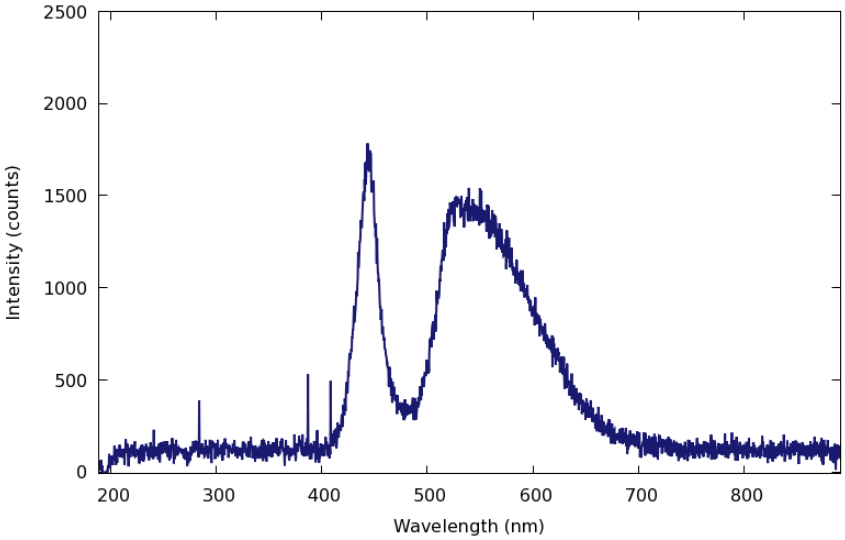


Figure S3. Measured wavelength of distribution for white LED strip.

Back to contents

3. Neutral white LED strip, purchased from Centenary Materials, 5050-60-W-IP67, 60 LED per meter, 12 W per meter, 120° beam angle.

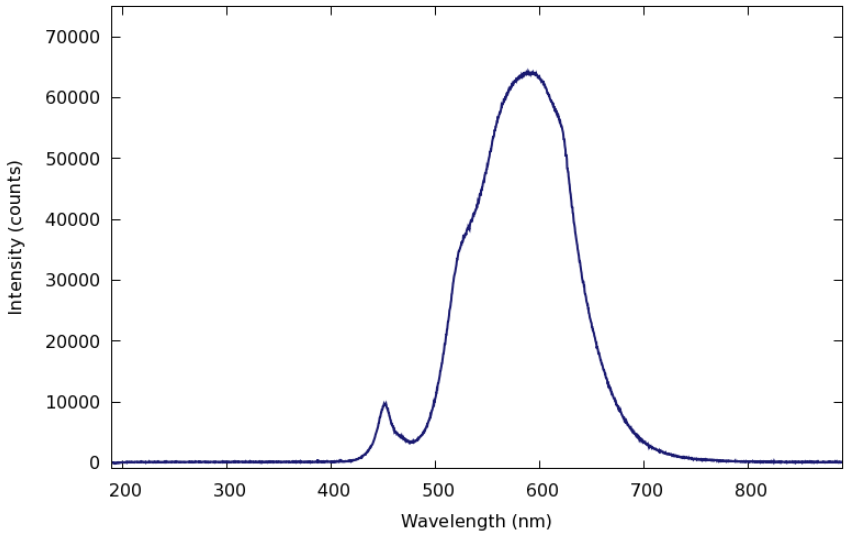


Figure S4. Measured wavelength of distribution for neutral white LED strip.

4. Pure white LED strip, purchased from Centenary Materials, 5 SMD3528-60-W, 60 LED per meter, 12 W per meter, 120° beam angle.

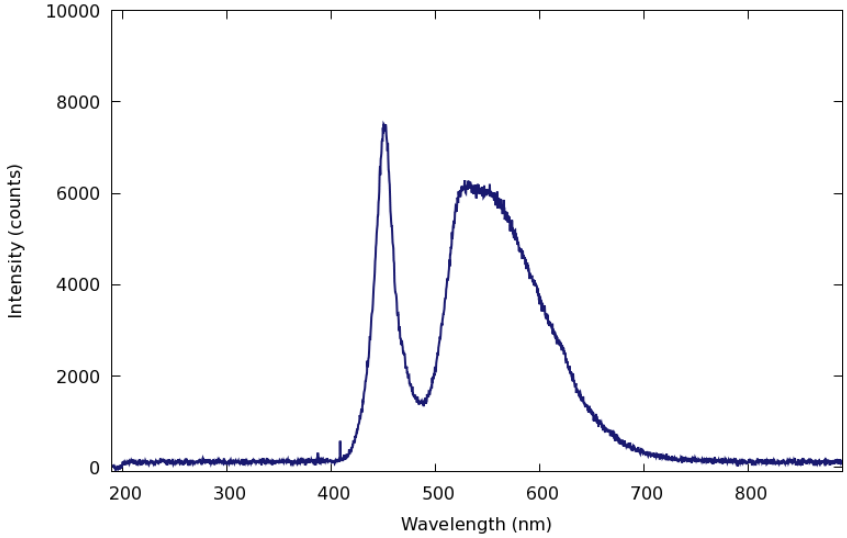


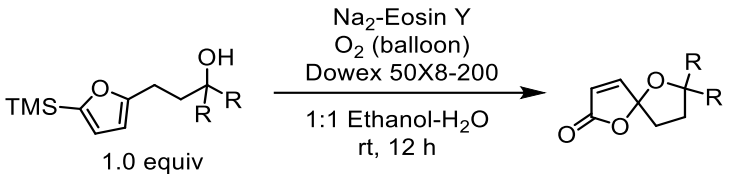
Figure S5. Measured wavelength of distribution for pure white LED strip.

Back to contents

2. Experimental Procedures

2.1. General method for the synthesis of oxaspirolactones (2 and 4)

General procedure A:



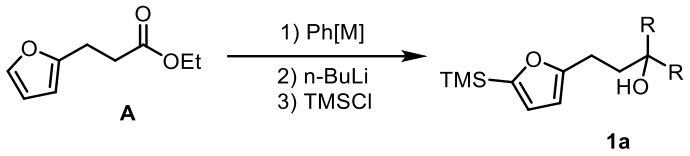
Scheme S1. Synthesis of oxaspirolactones in batch conditions.

To a 25-mL test tube equipped with a magnetic stirring bar, hydroxyalkyl furan (**1** or **3**) (1.0 equiv), Na_2-Eosin Y (0.01 equiv), and Dowex 50X8-200 (0.1 equiv) were added and sealed with a rubber septum. The system is then purged with oxygen for at least three times and was added with a pre-treated solvent (EtOH/H_2O = 1/1), gently bubbled with oxygen for an hour. The reaction mixture was then placed into an aluminium coil equipped with green LED strip and stirred vigorously under constant irradiation for 12 h. After completion of the reaction, the mixture was extracted with ethyl acetate and the combined organic layer was dried with magnesium sulfate and concentrated in vacuo. The crude product was then filtered through a short pad of silica placed in a Pasteur pipette and was eluted with diethyl ether to give the desired oxaspirolactone (**2** or **4**).

Back to contents

2.2. General method for the synthesis of hydroxyalkyl furans (1 and 3)

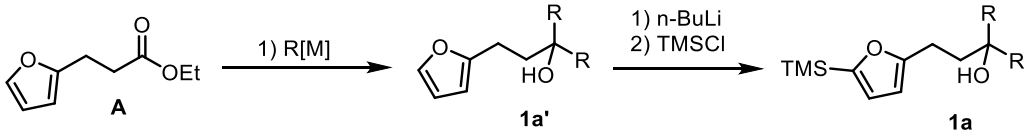
General procedure B:



Scheme S2. Synthesis of disubstituted starting materials in one-pot conditions.

To a heat gun-dried Schlenk tube under nitrogen atmosphere, ethyl 3-(2-furyl)propionate **A** (1.0 equiv) in dry diethyl ether (0.1 M) was added and cooled to -78 ℃. An appropriate organolithium reagent (2.5 equiv) was then slowly added dropwise, and the resulting mixture was stirred for 3 h at room temperature before it was recooled to -78 ℃. A previously titrated *n*-BuLi (2.8 equiv, titrated against diphenylacetic acid) was slowly added dropwise and the mixture was stirred for an hour at room temperature before it was recooled again at 0 ℃. Distilled trimethylsilyl chloride (3.0 equiv) was then added dropwise and the reaction was stirred for further 3 hours at room temperature before being quenched with saturated $NH_4Cl_{(aq)}$ and 1 M $HCl_{(aq)}$. The layers were then separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography to give pure hydroxyalkyl furan **1**.

General procedure C:



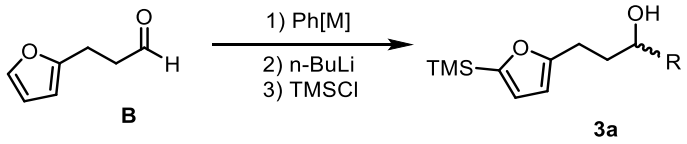
Scheme S3. Synthesis of disubstituted starting materials in two-step.

To a heat gun-dried Schlenk tube under nitrogen atmosphere, ethyl 3-(2-furyl)propionate **A** (1.0 equiv) in dry THF (0.1 M) was added and cooled to 0 ℃. An appropriate Grignard reagent (2.5 equiv) was then slowly added dropwise, and the resulting mixture was refluxed for 3 h before being quenched with water. The mixture was then extracted with ethyl acetate for three times and the combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude alcohol **1a'** was directly used for the next reaction.

To a heat gun-dried Schlenk tube under nitrogen atmosphere, the above crude alcohol in dry diethyl ether (0.6 M) was added and cooled to -78 ℃. A previously titrated *n*-BuLi (2.8 equiv, titrated against diphenylacetic acid) was slowly added dropwise and the mixture was stirred for an hour at room temperature before it was recooled again at 0 ℃. Distilled trimethylsilyl chloride (3.0 equiv) was then added dropwise and the reaction was stirred for further 3 hours at room temperature before being quenched with saturated $NH_4Cl_{(aq)}$ and 1 M

$HCl_{(aq)}$. The layers were then separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography to give pure hydroxyalkyl furan **1**.

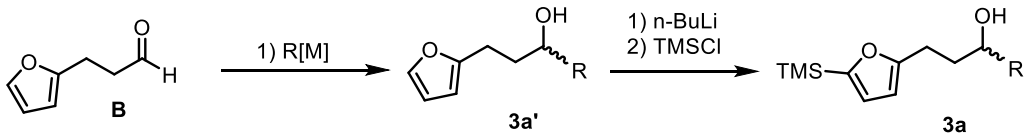
General procedure D:



Scheme S4. Synthesis of mono-substituted starting materials in one-pot conditions.

To a heat gun-dried Schlenk tube under nitrogen atmosphere, 3-(furan-2-yl)propanal **B** (1.0 equiv) in dry diethyl ether (0.1 M) was added and cooled to -78 ℃. An appropriate organolithium reagent (2.5 equiv) was then slowly added dropwise, and the resulting mixture was stirred for 3 h at room temperature before it was recooled to -78 ℃. A previously titrated n-BuLi (2.8 equiv, titrated against diphenylacetic acid) was slowly added dropwise and the mixture was stirred for an hour at room temperature before it was recooled again at 0 ℃. Distilled trimethylsilyl chloride (3.0 equiv) was then added dropwise and the reaction was stirred for further 3 hours at room temperature before being quenched with saturated $NH_4Cl_{(aq)}$ and 1 M $HCl_{(aq)}$. The layers were then separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography to give pure hydroxyalkyl furan **3**.

General procedure E:



Scheme S5. Synthesis of monosubstituted starting materials in two-step.

To a heat gun-dried Schlenk tube under nitrogen atmosphere, 3-(furan-2-yl)propanal **B** (1.0 equiv) in dry THF (0.1 M) was added and cooled to 0 ℃. An appropriate Grignard reagent (2.5 equiv) was then slowly added dropwise, and the resulting mixture was refluxed for 3 h before being quenched with water. The mixture was then extracted with ethyl acetate for three times and the combined organic layers were washed with brine, dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude alcohol **3a'** was directly used for the next reaction.

Back to contents

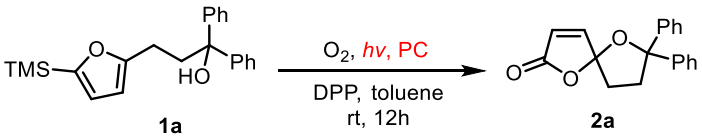
To a heat gun-dried Schlenk tube under nitrogen atmosphere, the above crude alcohol in dry diethyl ether (0.6 M) was added and cooled to -78 ℃. A previously titrated n-BuLi (2.8 equiv, titrated against diphenylacetic acid) was slowly added dropwise and the mixture was stirred for an hour at room temperature before it was recooled again at 0 ℃. Distilled trimethylsilyl chloride (3.0 equiv) was then added dropwise and the reaction was stirred for further 3 hours at room temperature before being quenched with saturated $NH_4Cl_{(aq)}$ and 1 M $HCl_{(aq)}$. The layers were then separated, and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was then purified by column chromatography to give pure hydroxyalkyl furan **3**.

Back to contents

3. Optimization Studies

3.1. Oxaspirolactone synthesis

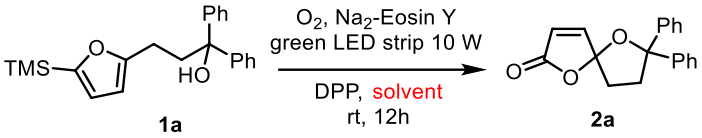
Table S7. Optimization of photocatalyst and light source



Entry	Photo cat.	h*v*	Yield (%)
1	Eosin Y	Kessil lamp 456 nm 20 W	72
2	4Czipn	Kessil lamp 456 nm 20 W	68
3	9*H*-thioxanthen-9-one	Kessil lamp 456 nm 20 W	17
4	Riboflavin	Kessil lamp 525 nm 20 W	34
5	Rose Bengal	Kessil lamp 525 nm 20 W	46
6	Methyl blue	LED neutral white 36 W	5
7	10*H*-phenothiazine	LED neutral white 36 W	77
8	Na_2-Eosin Y	Kessil lamp 525 nm 20 W	75
9	Na_2-Eosin Y	LED white 12.5 W	83
10	Na_2-Eosin Y	Green LED strip 10 W	84 (trace)[a]
11	Na_2-Eosin Y	LED pure white 30 W	94
12	Na_2-Eosin Y	LED neutral white 36 W	99

Based on General procedure A, but the reaction conditions were changed accordingly as specified in the table. [a]When no DPP is added.

Table S8. Optimization of solvent

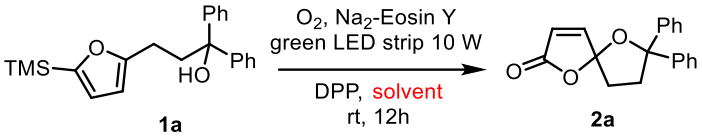


Entry	Solvent	Yield (%)
1	Toluene	83
2	DCM	50
3	EA	79
4	1,4-Dioxane	47
5	MeCN	36
6	THF	87
7	H_2O	52
8	IPA	74
9	MeOH	74
10	EtOH	81

Based on General procedure A, but the reaction conditions were changed accordingly as specified in the table.

Back to contents

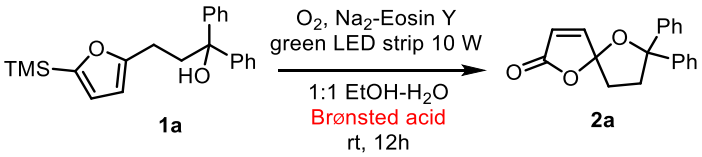
Table S9. Optimization of cosolvent



Entry	Solvent	Yield (%)
1	THF：H_2O = 1：1	91
2	THF：H_2O = 1：10	72
3	EtOH：H_2O = 1：1	93
4	EtOH：H_2O = 1：3	43
5	THF：EtOH：H_2O = 1：1：2	88

Based on General procedure A, but the reaction conditions were changed accordingly as specified in the table.

Table S10. Optimization of Brønsted acid



Entry	Amount of [H^+]	Brønsted Acid	Yield (%)
1	10 mol%	Polyphosphoric acid	18
2	15 mg	KM3 Silica gel	90
3	10 mol%	Amberlyst 15	80
4	1 eq.	Amberlyst 15	95
5	10 mol%	Dowex 50X8-200	99

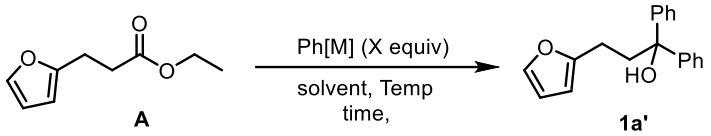
Based on General procedure A, but the reaction conditions were changed accordingly as specified in the table.

Back to contents

3.2. Synthesis of starting material 1a

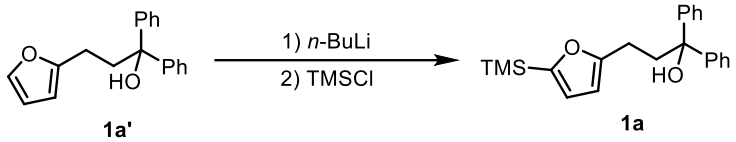
3.2.1 Optimization of two-step synthesis of starting material 1a

Table S11. Phenyl Addition for the synthesis of **1a'**.



Entry	[M]	Ph[M] (eq.)	Solvent	Temp	Time	Yield (%)
1	Li	2.0	Ether	0 °C	2.5 h	49
2	MgBr	2.0	Ether	rt	4.0 h	42
3	MgBr	2.2	Ether	Reflux	4.0 h	57
4	MgBr	2.6	Ether	Reflux	4.0 h	70
5	MgBr	2.6	THF	Reflux	3.0 h	88

Table S12. Silylation of **1a'** for the synthesis of **1a**.



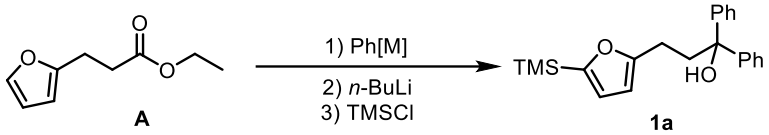
Entry	*n*-BuLi (eq.)	Condition of *n*-BuLi	TMSCl (eq.)	Condition of TMSCl	Solvent	Yield (%)
1	2.3	-78 °C (1h)→rt (1h)	2.5	-78 °C→rt (1h)	THF	45
2	2.3	-78 °C→rt (1h)	2.5	-78 °C→rt (1h)	Ether	70
3	2.8	-78 °C→rt (1h)	3	0 °C→rt (3h)	Ether	78

Based on the second part of General procedure C, but the reaction conditions were changed accordingly as specified in the table.

Back to contents

3.2.2 Optimization of one-pot synthesis of starting material 1a

Table S13. Optimization for the synthesis of **1a** in one-pot reaction.



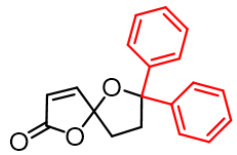
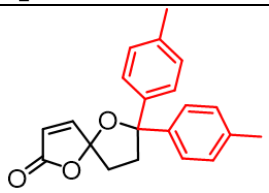
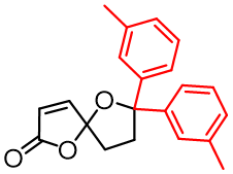
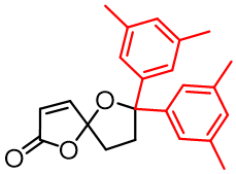
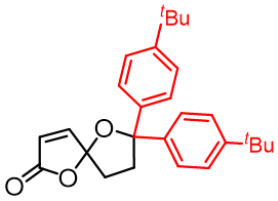
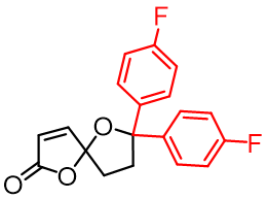
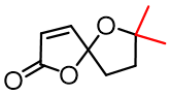
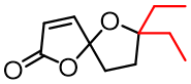
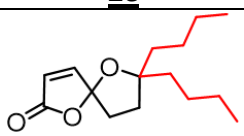
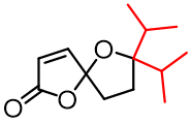
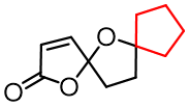
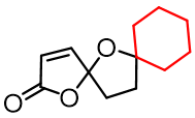
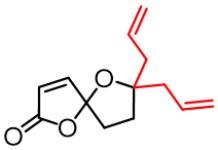
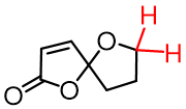
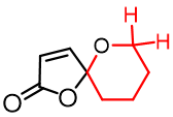
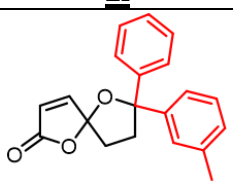
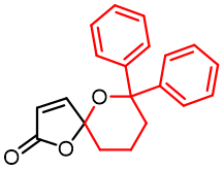
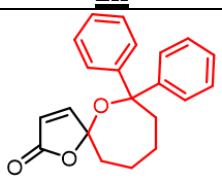
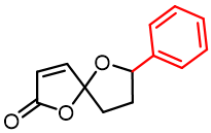
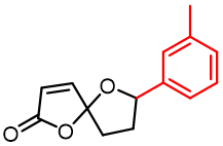
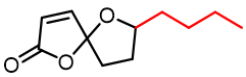
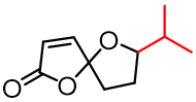
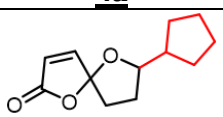
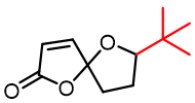
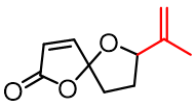
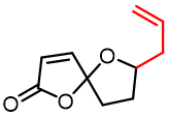
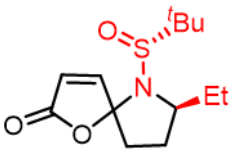
Entry	[M]	Solvent	*n*-BuLi (eq.)	Condition of *n*-BuLi	TMSCl (eq.)	Condition of TMSCl	Yield (%)
1	MgBr	THF	1.1	-78 °C→rt (1h)	3.0	0 °C→rt (3h)	0
2	MgBr	THF	2.5	-78 °C (0.5h)→rt (2.5h)	5.2	-78 °C→rt (1h)	0
3	Li	THF	2.5	-78 °C (0.5h)→rt (2.5h)	5.2	-78 °C→rt (1h)	60
4	Li	THF	2.5	-78 °C (0.5h)→rt (2.5h)	5.2	-78 °C→rt (3h)	68
5	Li	Ether	2.5	-78 °C (0.5h)→rt (2.5h)	5.2	-78 °C→rt (3h)	40
6	Li	THF	2.5	-78 °C (1h)→rt (1h)	5.2	-78 °C→rt (3h)	44
7	Li	THF	2.5	-78 °C→rt (1h)	3.0	0 °C→rt (3h)	71

Based on the second part of General procedure B, but the reaction conditions were changed accordingly as specified in the table.

Back to contents

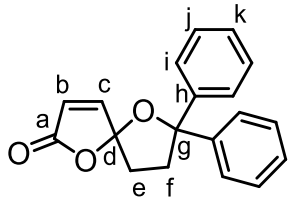
4. Substrate Scope

4.1. Summary of oxaspirolactones

 **2a**	 **2b**	 **2c**	 **2d**
 **2e**	 **2f**	 **2g**	 **2h**
 **2i**	 **2j**	 **2k**	 **2l**
 **2m**	 **2n**	 **2o**	 **2p**
 **2q**	 **2r**	 **4a**	 **4b**
 **4c**	 **4d**	 **4e**	 **4f**
 **4g**	 **4h**	 **7**	

Back to table of substrate scope

7,7-Diphenyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2a



The title compound was prepared according to General procedure A from **1a** (15.0 mg, 0.04 mmol) to give **2a** (12.4 mg, 0.042 mmol, 99%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ ($CDCl_3$, 400 MHz) δ 7.47 — 7.20 (10H, m, aryl-*H*), 7.15 (1H, d, *J* = 5.5 Hz, C_cH), 6.19 (1H, d, *J* = 5.5 Hz, C_bH), 3.00 — 2.85 (2H, m, C_eH), 2.34 — 2.19 (2H, m, C_fH).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.9 (C_a), 152.4 (C_c), 144.8 (C_h), 144.0 (C_h), 128.4 (C_j), 128.2 (C_j), 127.5 (C_k), 127.4 (C_k), 126.2 (C_i), 125.7 (C_i), 124.2 (C_b), 114.2 (C_d), 92.6 (C_g), 38.0 (C_e), 35.8 (C_f).

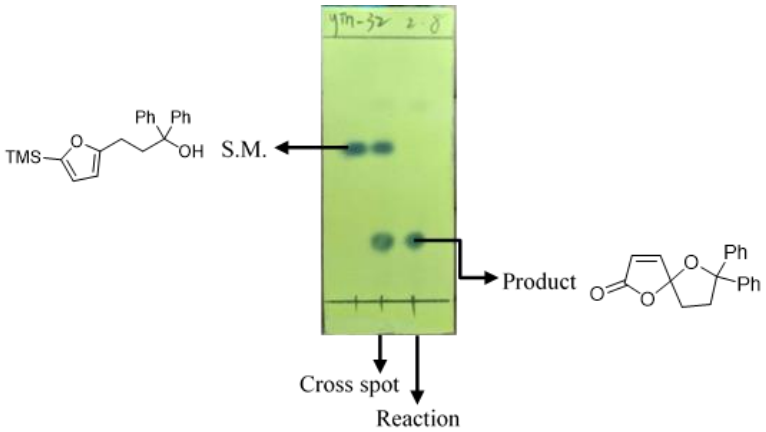
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{19}H_{16}O_3$ $[M]^+$ 292.1094, found 292.1094

IR (ATR) ν_{max}: 3088, 2955, 2923, 2852, 1758, 1093, 926, 915, 898, 829, 756, 702, 693, 529 cm^{-1}

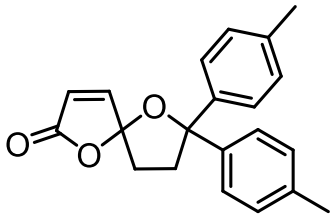
MP: 127±1 °C

TLC: R_f = 0.25 (1:4 EtOAc/Hexane)



Back to table of substrate scope

7,7-Di-*p*-tolyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2b



The title compound was prepared according to General procedure A from **1b** (26.5 mg, 0.07 mmol) to give **2b** (22.2 mg, 0.07 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, 2H, J = 8.2 Hz), 7.24 (d, 2H, J = 8.2 Hz), 7.17 (d, 2H, J = 8.0 Hz), 7.13 (d, 1H, J = 5.5 Hz), 7.08 (d, 2H, J = 8.0 Hz), 6.17 (d, 1H, J = 5.5 Hz), 2.99 — 2.80 (m, 2H), 2.35 (s, 3H), 2.29 (s, 3H), 2.32 — 2.18 (m, 2H).

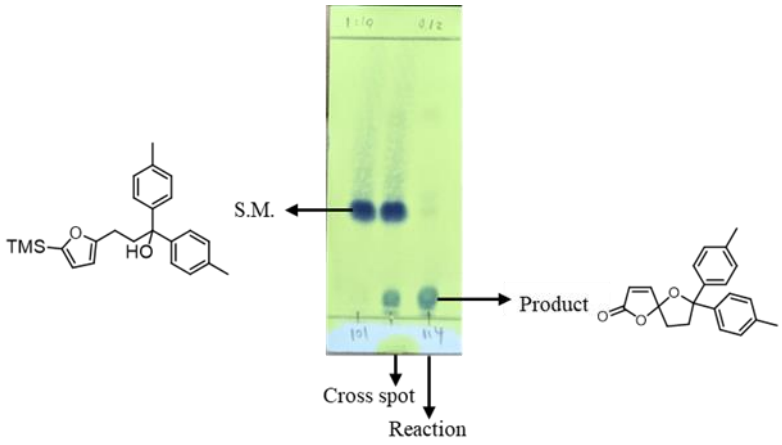
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.9, 152.5, 142.1, 141.2, 137.1, 137.0, 129.0, 128.8, 126.1, 125.7, 124.0, 114.3, 92.6, 38.0, 35.8, 21.0.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{21}H_{20}O_3$ $[M]^+$ 320.1407, found 320.1407

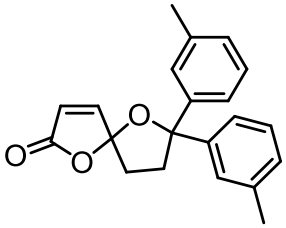
IR (ATR) ν_{max}: 3087, 2920, 1767, 1078, 922, 892, 810, 751 cm^{-1}

TLC: R_f = 0.12 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7-Di-*m*-tolyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2c



The title compound was prepared according to General procedure A from **1c** (26.5 mg, 0.07 mmol) to give **2c** (22.2 mg, 0.07 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 — 7.02 (m, 9H), 6.18 (d, 1H, J = 5.5 Hz), 2.97 — 2.81 (m, 2H), 2.31 (s, 3H), 2.35 (s, 3H), 2.30 — 2.18 (m, 2H).

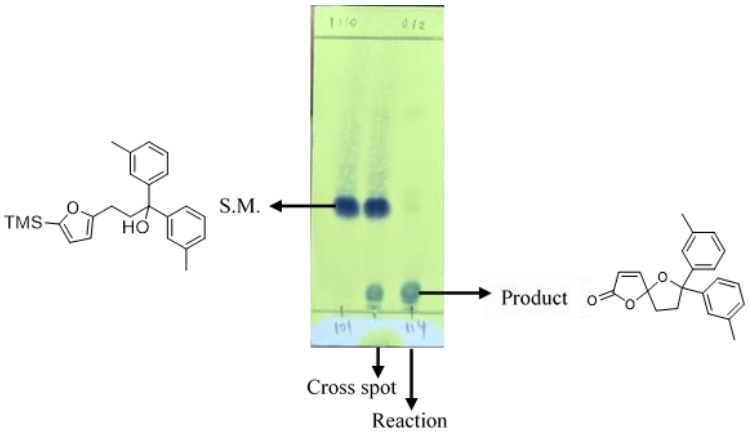
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.9, 152.5, 144.9, 144.2, 138.0, 137.8, 128.2, 128.1, 128.1, 128.1, 126.7, 126.4, 124.1, 123.2, 122.7, 114.2, 92.7, 37.8, 35.7, 21.6, 21.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{21}H_{20}O_3$ $[M]^+$ 320.1407, found 320.1404

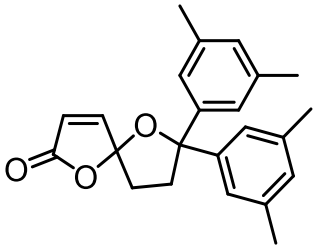
IR (ATR) ν_{max}: 3024, 2922, 2859, 1764, 1085, 921, 887, 696 cm^{-1}

TLC: R_f = 0.12 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7,7-Bis(3,5-dimethylphenyl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 2d



The title compound was prepared according to General procedure A from **1d** (28.5 mg, 0.07 mmol) to give **2d** (24.3 mg, 0.07 mmol, 99%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, 1H, J = 5.5), 7.04 (s, 2H), 6.98 (s, 2H), 6.91 (s, 1H), 6.85 (s, 1H), 6.18 (d, 1H, J = 5.5 Hz), 2.94 — 2.82 (m, 2H), 2.32 — 2.19 (m, 14H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 152.6, 144.9, 144.3, 137.7, 137.6, 129.0, 128.9, 124.0, 123.7, 123.4, 114.2, 92.7, 37.5, 35.7, 21.5, 21.4.

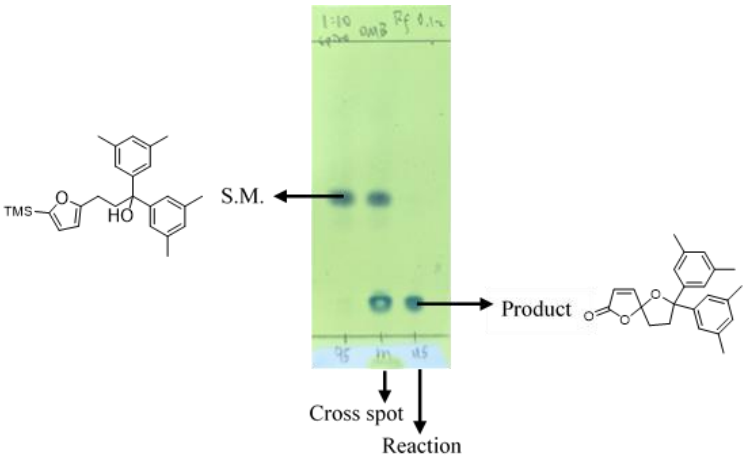
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{23}H_{24}O_3$ $[M]^+$ 348.1720, found 348.1721

IR (ATR) ν_{max}: 3116, 2918, 2860, 1759, 1095, 921, 849, 823, 742, 722, 667 cm^{-1}

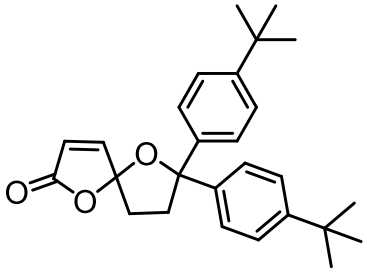
MP: 154 ±1 °C

TLC: R_f = 0.12 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7,7-Bis(4-(tert-butyl)phenyl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 2e



The title compound was prepared based on General procedure A from **1e** (18.5 mg, 0.04 mmol) but solvent was ethanol to give **2e** (16.2 mg, 0.04 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 — 7.30 (m, 8H), 7.16 (d, J = 5.5 Hz, 1H), 6.17 (d, 1H, J = 5.5 Hz), 2.95 — 2.84 (m, 2H), 2.31 — 2.19 (m, 2H), 1.32 (s, 9H), 1.28 (s, 9H).

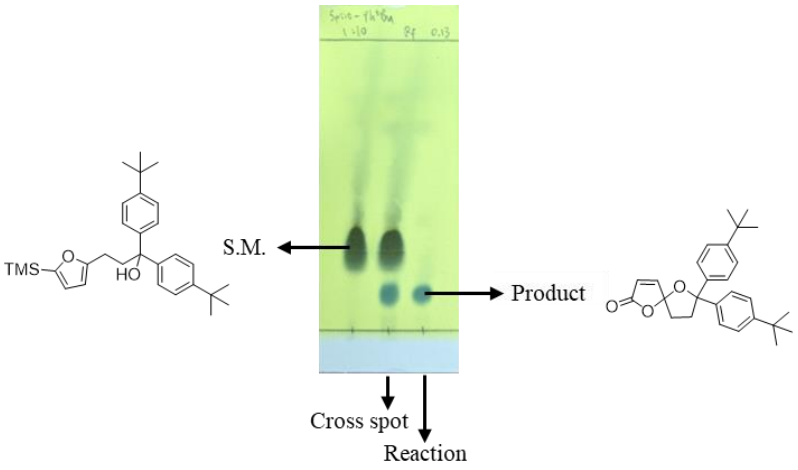
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 152.5, 150.2, 150.1, 141.9, 141.0, 126.0, 125.5, 125.2, 125.1, 124.0, 114.3, 92.7, 38.3, 35.8, 34.4, 34.4, 31.3, 31.3.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{27}H_{32}O_3$ $[M]^+$ 404.2346, found 404.2343

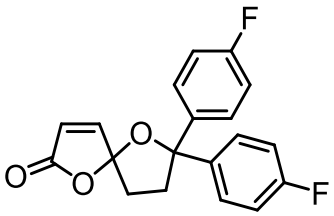
IR (ATR) ν_{max}: 2962, 2868, 1759, 921, 897, 815 cm^{-1}

TLC: R_f = 0.13 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7,7-bis(4-fluorophenyl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 2f



The title compound was prepared according to General procedure A from **1f** (27.1 mg, 0.07 mmol) to give **2f** (22.8 mg, 0.07 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 — 7.29 (m, 4H), 7.12 (d, 1H, J = 5.5 Hz), 7.08 — 6.95 (m, 4H), 6.20 (d, 1H, J = 5.6 Hz), 2.94 — 2.80 (m, 2H), 2.34 — 2.18 (m, 2H).

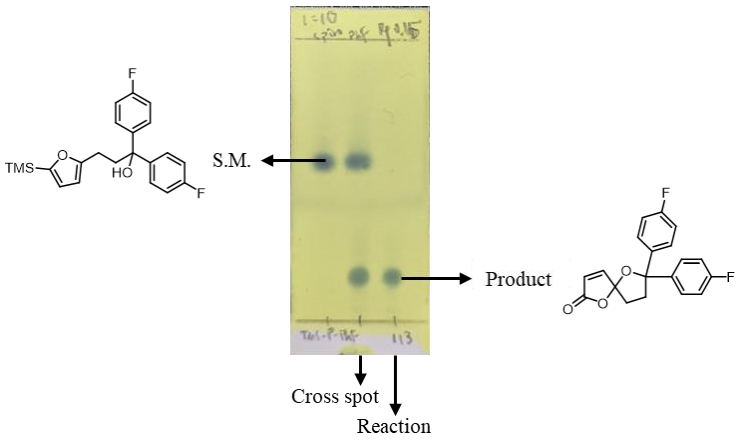
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 169.6, 162.1 (d, J = 248.2 Hz), 162.0 (d, J = 247.8 Hz), 152.1, 140.6 (d, J = 4.0 Hz), 139.6 (d, J = 3.4 Hz), 127.9 (d, J = 8.3 Hz), 127.5 (d, J = 8.3 Hz), 124.3, 115.3 (d, J = 25.9 Hz), 115.1 (d, J = 25.2 Hz), 114.1, 91.8, 38.3, 35.8.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{19}H_{14}O_3F_2$ $[M]^+$ 328.0906, found 328.0903

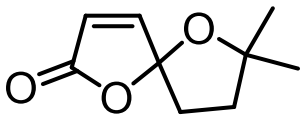
IR (ATR) ν_{max}: 2960, 1771, 1504, 1226, 1085, 839 cm^{-1}

TLC: R_f = 0.15 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7,7-Dimethyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2g



The title compound was prepared according to General procedure A from **1g** (29.6 mg, 0.13 mmol) to give **2g** (13.1 mg, 0.08 mmol, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, 1H, J = 5.6 Hz), 6.11 (d, 1H, J = 5.6 Hz), 2.37 — 1.95 (m, 4H), 1.46 (s, 3H), 1.30 (s, 3H).

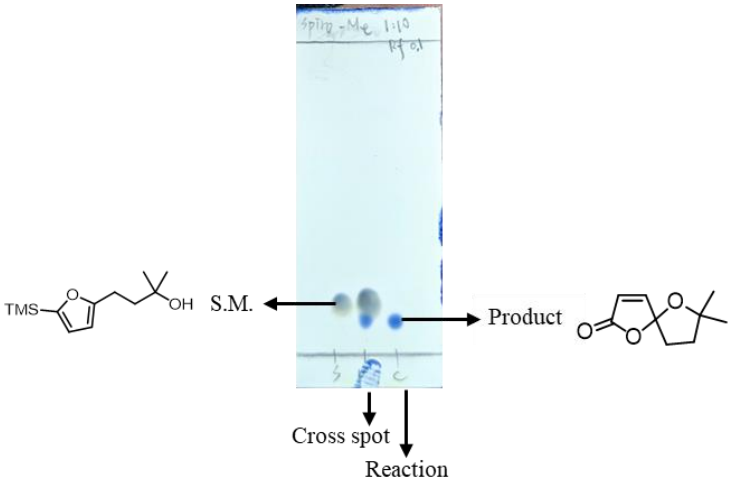
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 152.4, 124.0, 114.7, 86.6, 36.8, 36.0, 29.2, 28.1.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_9H_{12}O_3$ $[M]^+$ 168.0781, found 168.0778

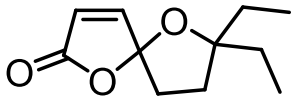
IR (ATR) ν_{max}: 2973, 2867, 1760, 1234, 1118, 917, 816 cm^{-1}

TLC: R_f = 0.10 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7,7-Diethyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2h



The title compound was prepared according to General procedure A from **1h** (17.8 mg, 0.07 mmol) to give 2h (11.6 mg, 0.06 mmol, 84%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, 1H, J = 5.6 Hz), 6.11 (d, 1H, J = 5.6 Hz), 2.31 — 1.92 (m, 4H), 1.82 — 1.55 (m, 4H), 0.91 (t, 3H, J = 7.5 Hz), 0.89 (t, 3H, J = 7.5 Hz).

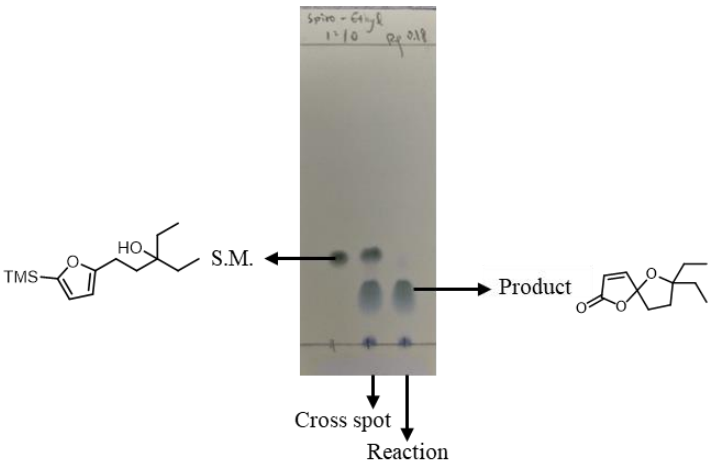
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.3, 152.3, 124.0, 114.8, 92.1, 36.0, 32.9, 31.8, 30.0, 8.6, 8.4.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{11}H_{16}O_3$ $[M]^+$ 196.1094, found 196.1095

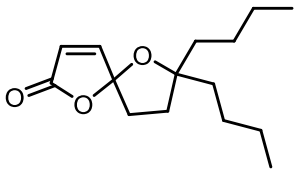
IR (ATR) ν_{max}: 2964, 2883, 1763, 1110, 914, 821 cm^{-1}

TLC: R_f = 0.18 (1:4 EtOAc/Hexane)



Back to table of substrate scope

7,7-Dibutyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2i



The title compound was prepared according to General procedure A from **1i** (21.7 mg, 0.07 mmol) to give **2i** (14.6 mg, 0.06 mmol, 83%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.06 (d, 1H, J = 5.6 Hz), 6.11 (d, 1H, J = 5.6 Hz), 2.31 — 1.93 (m, 4H), 1.76 — 1.16 (m, 12H), 0.91 (t, 3H, J = 7.0 Hz), 0.91 (t, 3H, J = 7.0 Hz).

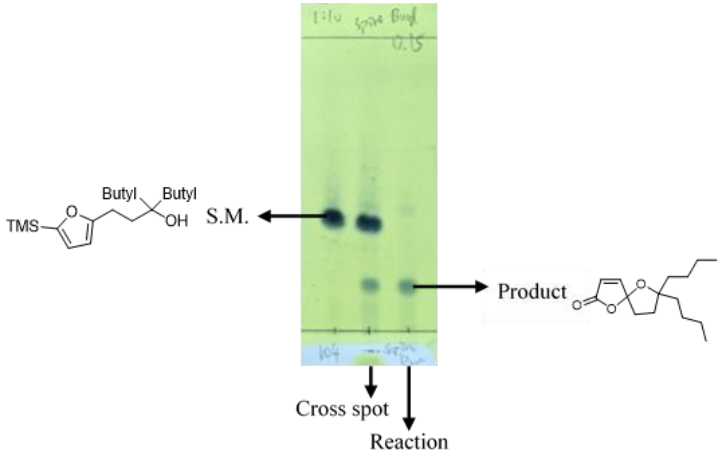
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.3, 152.4, 124.0, 114.7, 91.6, 39.5, 37.8, 36.0, 33.9, 26.5, 26.3, 23.1, 23.1, 14.0, 14.0.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{15}H_{24}O_3$ $[M]^+$ 252.1720, found 252.1719

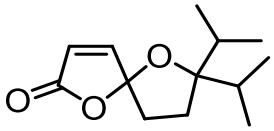
IR (ATR) ν_{max}: 2930, 2866, 1761, 1120, 913, 822 cm^{-1}

TLC: R_f = 0.15 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7,7-Diisopropyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2j



The title compound was prepared according to General procedure A from **1j** (19.8 mg, 0.07 mmol) to give **2j** (15.2 mg, 0.07 mmol, 97%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ($CDCl_3$, 400 MHz) δ 7.10 (d, 1H, J = 5.5 Hz), 6.09 (d, 1H, J = 5.5 Hz), 2.36 — 2.22 (m, 2H), 2.21 — 2.14 (m, 2H), 2.14 — 1.97 (m, 2H, 1.03 — 0.91 (m, 12H).

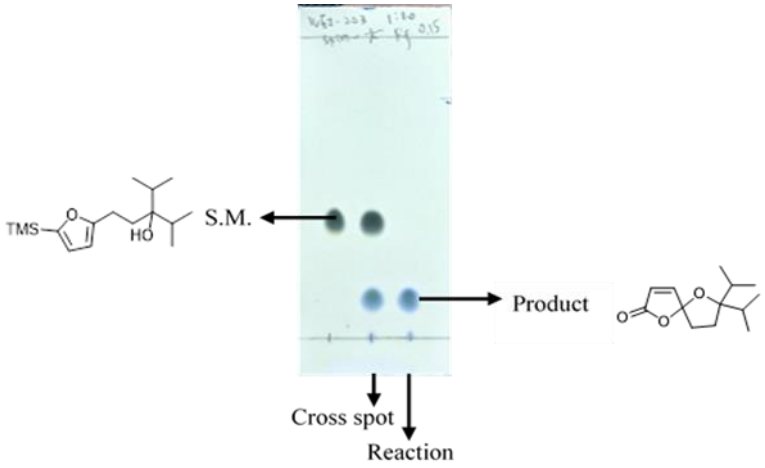
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.3, 152.4, 123.6, 115.3, 97.1, 36.8, 34.1, 33.6, 27.2, 18.3, 18.3, 17.7, 17.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{20}O_3$ $[M]^+$ 224.1407, found 224.1406

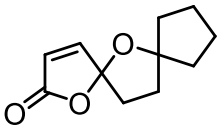
IR (ATR) ν_{max}: 2962, 2878, 1762, 1095, 976, 914, 817 cm^{-1}

TLC: R_f = 0.15 (1:10 EtOAc/Hexane)



Back to table of substrate scope

1,6-Dioxadispiro[4.1.4^{7}.2^{5}]tridec-3-en-2-one, 2k



The title compound was prepared according to General procedure A from **1k** (17.7 mg, 0.07 mmol) to give **2k** (12.2 mg, 0.07 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ ($CDCl_3$, 400 MHz) δ 7.06 (d, J = 5.5 Hz, 1H), 6.10 (d, J = 5.6 Hz, 1H), 2.36 – 2.20 (m, 3H), 2.15 – 2.02 (m, 2H), 1.90 – 1.53 (m, 8H).

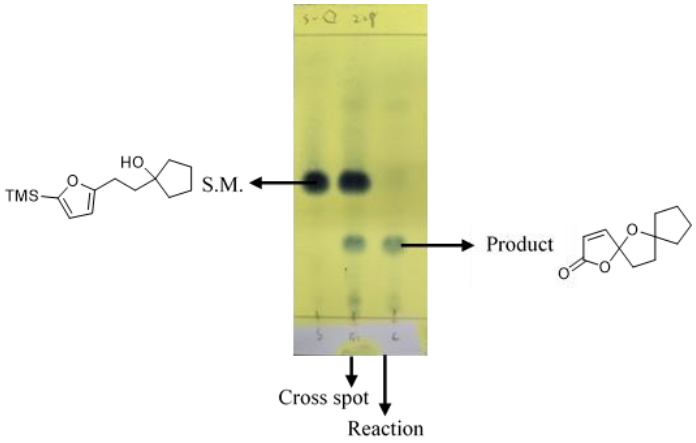
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.3, 152.6, 123.8, 114.5, 96.6, 39.1, 39.0, 36.2, 34.8, 24.0, 23.7.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{11}H_{14}O_3$ $[M]^+$ 194.0938, found 194.0934

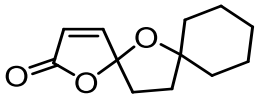
IR (ATR) ν_{max}: 2956, 2875, 1756, 1116, 915, 812 cm^{-1}

TLC: R_f = 0.25 (1:4 EtOAc/Hexane)



Back to table of substrate scope

1,6-Dioxadispiro[4.1.5^{7}.2^{5}]tetradec-3-en-2-one, 2l



The title compound was prepared according to General procedure A from **1l** (18.7 mg, 0.07 mmol) to give **2l** (14.5 mg, 0.07 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, 1H, *J* = 5.6 Hz), 6.11 (d, 1H, *J* = 5.6 Hz), 2.31 — 2.15 (m, 2H), 2.09 — 1.97 (m, 2H), 1.80 — 1.40 (m, 10H).

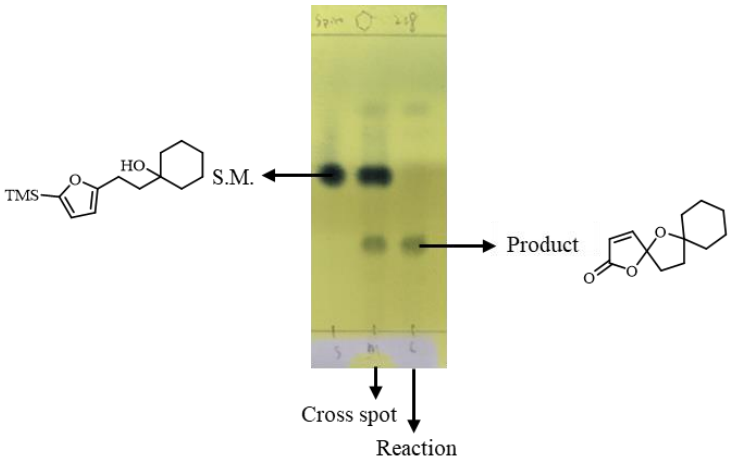
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.3, 152.5, 124.0, 114.4, 88.6, 38.6, 37.0, 35.4, 25.1, 23.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{12}H_{16}O_3$ $[M]^+$ 208.1094, found 208.1096

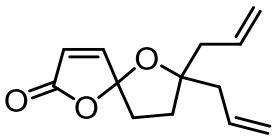
IR (ATR) ν_{max}: 2932, 2859, 1756, 1124, 918, 814 cm^{-1}

TLC: R_f = 0.29 (1:4 EtOAc/Hexane)



Back to table of substrate scope

7,7-Diallyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 2m



The title compound was prepared according to General procedure A from **1m** (19.5 mg, 0.07 mmol) to give **2m** (15.4 mg, 0.07 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, 1H, J = 5.6 Hz), 6.12 (d, 1H, J = 5.6 Hz), 5.88 — 5.74 (m, 2H), 5.15 — 5.10 (m, 4H), 2.56 — 2.43 (m, 2H), 2.34 — 2.13 (m, 4H), 2.02 — 1.97 (m, 2H).

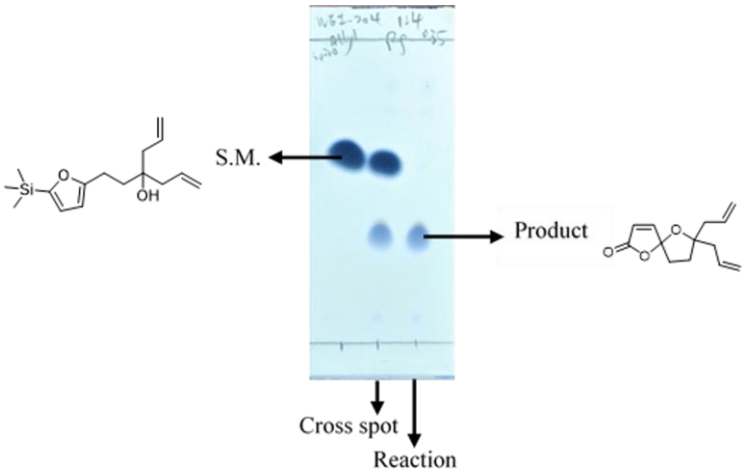
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.1, 152.0, 133.4, 133.2, 124.1, 118.9, 118.6, 114.7, 89.9, 45.0, 43.0, 35.9, 32.7.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{16}O_3$ $[M]^+$ 220.1094, found 220.1095

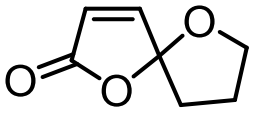
IR (ATR) ν_{max}: 3076, 2923, 2851, 1760, 1121, 917, 815, 750 cm^{-1}

TLC: R_f = 0.35 (1:4 EtOAc/Hexane)



Back to table of substrate scope

1,6-Dioxaspiro[4.4]non-3-en-2-one, 2n



The title compound was prepared according to General procedure A from **1n** (23.8 mg, 0.12 mmol) but solvent was ethanol to give **2n** (16.8 mg, 0.12 mmol, 99%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, 1H, J = 5.6 Hz), 6.14 (d, 1H, J = 5.6 Hz), 4.28 — 4.22 (m, 1H), 4.11 — 4.05 (m, 1H), 2.38 — 2.10 (m, 4H).

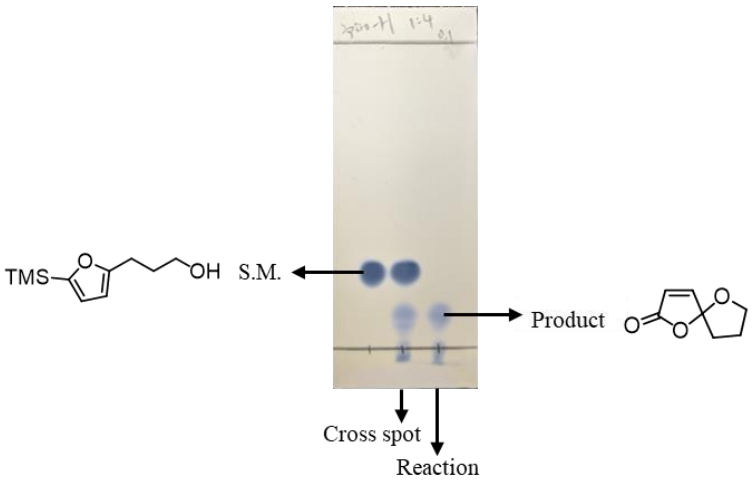
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.1, 151.9, 124.3, 114.5, 70.6, 35.3, 24.2.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_7H_8O_3$ $[M]^+$ 140.0468, found 140.0466

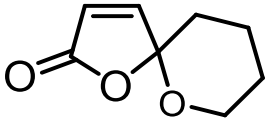
IR (ATR) ν_{max}: 3094, 2958, 2927, 2895, 1768, 1100, 917 cm^{-1}

TLC: R_f = 0.10 (1:4 EtOAc/Hexane)



Back to table of substrate scope

1,6-Dioxaspiro[4.5]dec-3-en-2-one, 2o



The title compound was prepared according to General procedure A from **1o** (14.4 mg, 0.06 mmol) but solvent was ethanol to give **2o** (9.6 mg, 0.0623 mmol, 92%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, 1H, J = 5.6 Hz), 6.10 (d, 1H, J = 5.6 Hz), 4.06 — 4.00 (m, 1H), 3.94 — 3.89 (m, 1H), 2.00 — 1.67 (m, 6H).

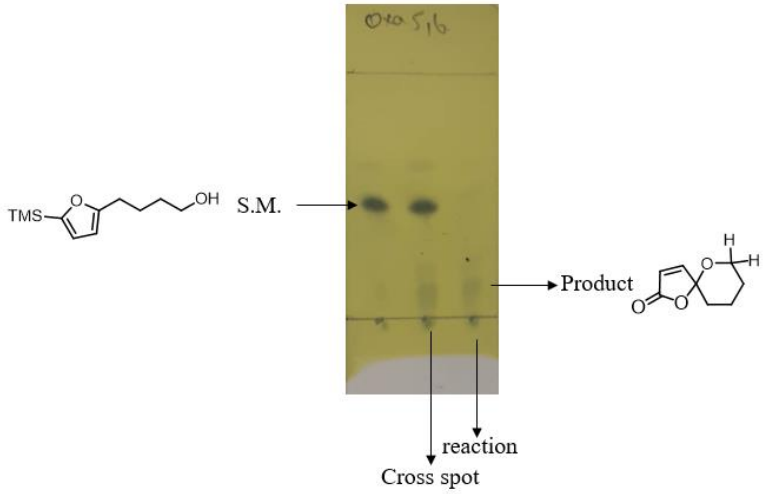
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.5, 154.3, 123.0, 106.9, 65.0, 32.1, 24.0, 19.0.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_8H_{10}O_3$ $[M]^+$ 154.0625, found 154.0623

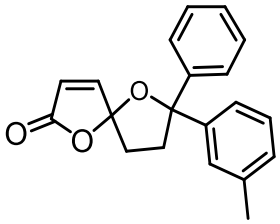
IR (ATR) ν_{max}: 2927, 1755, 1463, 905 cm^{-1}

TLC: R_f = 0.10 (1:5 EtOAc/Hexane)



Back to table of substrate scope

7-Phenyl-7-(*m*-tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 2p



The title compound was prepared according to General procedure A from **1p** (20.2 mg, 0.06 mmol) to give **2p** (16.3 mg, 0.06 mmol, 96%) as a colourless oil.

Diastereomer A:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 4H), 7.26 – 7.00 (m, 6H), 6.18 (d, 1H, *J* = 5.5 Hz), 3.00 – 2.81 (m, 2H), 2.36 (s, 3H), 2.29 – 2.16 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 152.6, 145.1, 144.4, 138.2, 128.5, 128.4, 128.3, 127.5, 126.9, 126.3, 124.3, 123.4, 114.4, 92.8, 38.1, 35.9, 21.8.

Diastereomer B:

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.28 (m, 4H), 7.26 – 7.00 (m, 6H), 6.18 (d, 1H, *J* = 5.5 Hz), 3.00 – 2.81 (m, 2H), 2.31 (s, 3H), 2.29 – 2.16 (m, 2H).

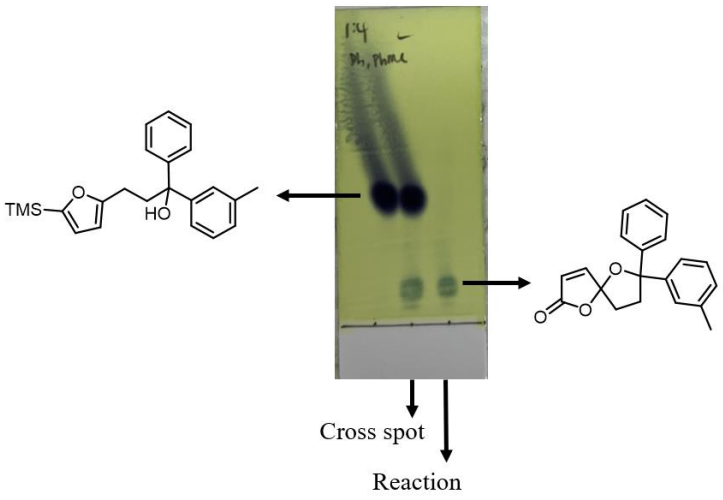
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.0, 152.6, 145.0, 144.1, 138.0, 128.5, 128.3, 128.2, 127.5, 126.7, 125.8, 124.2, 122.9, 114.4, 92.8, 38.0, 35.9, 21.7.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{20}H_{18}O_3$ $[M]^+$ 306.1251, found 306.1248

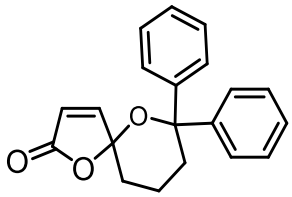
IR (ATR) ν_{max}: 3303, 3249, 3185, 3114, 2921, 2238, 1051 cm^{-1}

TLC: R_f = 0.14 (1:4 EtOAc/Hexane)



Back to table of substrate scope

17,7-Diphenyl-1,6-dioxaspiro[4.5]dec-3-en-2-one, 2q



The title compound was prepared according to General procedure A from **1q** (25.5 mg, 0.07 mmol) to give **2q** (16.1 mg, 0.05 mmol, 75%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.28 (m, 8H), 7.24 – 7.20 (m, 2H), 7.19 (d, 1H, J = 5.6 Hz), 6.10 (d, 1H, J = 5.6 Hz), 2.33 – 2.09 (m, 3H), 1.95 – 1.75 (m, 3H).

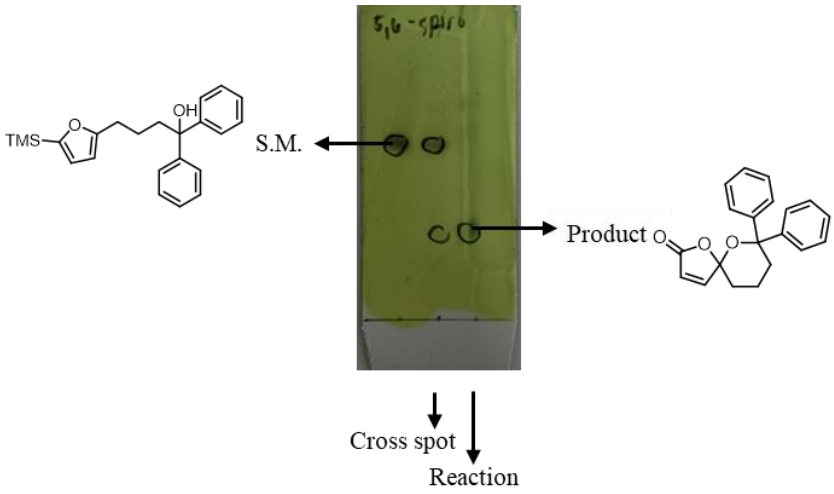
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 154.6, 146.7, 144.5, 128.2, 127.9, 127.2, 127.0, 126.7, 125.6, 122.9, 107.7, 81.7, 33.3, 30.6, 16.3.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{20}H_{18}O_3$ $[M]^+$ 306.1251, found 306.1253

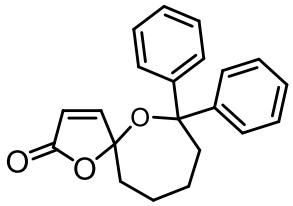
IR (ATR) ν_{max}: 2926, 1770, 1244, 1118,1045, 912 cm^{-1}

TLC: R_f = 0.30 (1:4 EtOAc/Hexane)



Back to table of substrate scope

7,7-diphenyl-1,6-dioxaspiro[4.6]undec-3-en-2-one, 2r



The title compound was prepared according to General procedure A from **1r** (20.0 mg, 0.053 mmol) to give **2r** (16.9 mg, 0.052 mmol, 99%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.36 (m, 5H), 7.34 – 7.28 (m, 5H), 7.16 (d, 1H J = 5.6 Hz), 6.10 (d, 1H, J = 5.6 Hz), 2.32 – 2.25 (m, 2H), 1.95 – 1.86 (m, 2H), 1.47 – 1.31 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.75, 154.45, 146.94, 128.28, 128.25, 128.19, 126.98, 126.97, 126.93, 126.07, 123.12, 123.11, 108.28, 78.32, 41.60, 37.38, 23.76, 23.66.

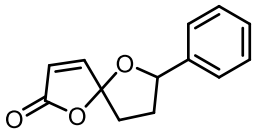
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{21}H_{20}O_3$ $[M]^+$ 320.1407, found 306.1406

IR (ATR) ν_{max}: 3055, 2927, 2853, 1722, 1265, 736, 704 cm^{-1}

Back to table of substrate scope

7-Phenyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 4a



The title compound was prepared according to General procedure A from **3a** (20.9 mg, 0.08 mmol) to give **4a** (16.4 mg, 0.08 mmol, 99%, 1.67:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.39 – 7.27 (m, 3H), 7.25 – 7.19 (m, 2H), 7.16 – 7.11 (m, 1H), 6.14 – 6.11 (m, 1H), 5.18 – 5.14 (m, 1H), 2.72 – 1.95 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 169.9, 152.0, 140.7, 128.6, 128.2, 126.3, 124.5, 114.5, 85.3, 37.2, 34.0.

Minor Diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.39 – 7.27 (m, 3H), 7.25 – 7.19 (m, 2H), 7.16 – 7.11 (m, 1H), 6.14 – 6.11 (m, 1H), 5.41 – 5.37 m, 1H), 2.72 – 1.95 (m, 4H).

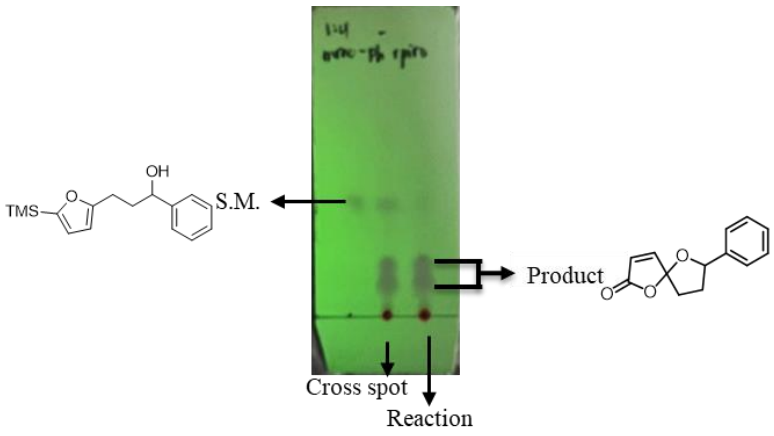
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 169.9, 151.7, 141.0, 128.6, 127.9, 125.5, 124.3, 114.6, 82.8, 34.5, 32.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{12}O_3$ $[M]^+$ 216.0781, found 216.0781

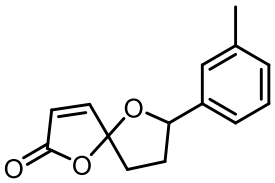
IR (ATR) ν_{max}: 3090, 2934, 1769, 193, 980, 920, 890, 700 cm^{-1}

TLC: R_f = 0.15; 0.09 (1:4 EtOAc/Hexane)



Back to table of substrate scope

7-(*m*-Tolyl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 4b



The title compound was prepared according to General procedure A from **3b** (12.0 mg, 0.05 mmol) to give **4b** (12 mg, 0.05 mmol, 96.4%, 1.38:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.46 – 7.11 (m, 5H), 6.22 – 6.17 (m, 1H), 5.29 – 5.14 (m, 1H), 2.79 – 2.37 (m, 2H), 2.36 (s, 3H), 2.34 – 2.06 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.0, 152.0, 140.5, 129.0, 128.5, 126.9, 126.2, 124.4, 123.4, 122.5, 114.5, 85.4, 37.2, 33.9, 21.4.

Minor Diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.46 – 7.11 (m, 5H), 6.22 – 6.17 (m, 1H), 5.51 – 5.38 (m, 1H), 2.79 – 2.37 (m, 2H), 2.36 (s, 3H), 2.34 – 2.06 (m, 2H).

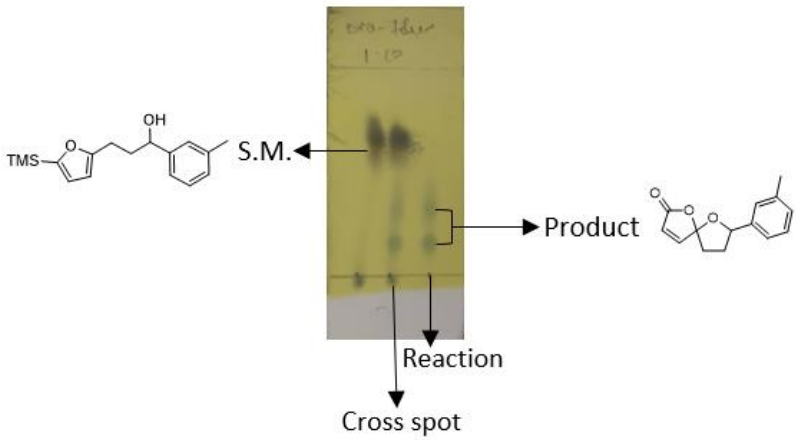
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.0, 151.8, 140.8, 138.3, 128.7, 127.1, 126.3, 124.2, 122.6, 114.6, 82.9, 34.6, 32.5, 29.7.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{14}H_{14}O_3$ $[M]^+$ 230.0938, found 230.0940

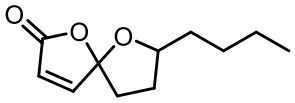
IR (ATR) ν_{max}: 3030, 2923, 2859, 1758, 1248, 917, 731 cm^{-1}

TLC: R_f = 0.33; 0.16 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7-Butyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 4c



The title compound was prepared according to General procedure A from **3c** (17.8 mg, 0.07 mmol) to give **4c** (12 mg, 0.05 mmol, 76%, 1.19:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.09 (d, 1H, J = 5.6 Hz), 6.13 (d, 1H, *J* = 5.6 Hz), 4.23 — 4.28 (m, 1H), 2.41 — 1.72 (m, 7H), 1.42 — 1.28 (m, 3H), 0.90 (t, 3H, *J* = 6.9 Hz).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.2, 152.1, 124.2, 114.4, 84.0, 36.5, 34.5, 30.3, 29.5, 28.1, 22.6.

Minor Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.11 (d, 1H, *J* = 5.6 Hz), 6.13 (d, 1H, *J* = 5.6 Hz), 4.39 — 4.44 (m,1H), 2.41 — 1.72 (m, 7H), 1.42 — 1.28 (m, 3H), 0.91 (t, 3H, *J* = 6.9 Hz).

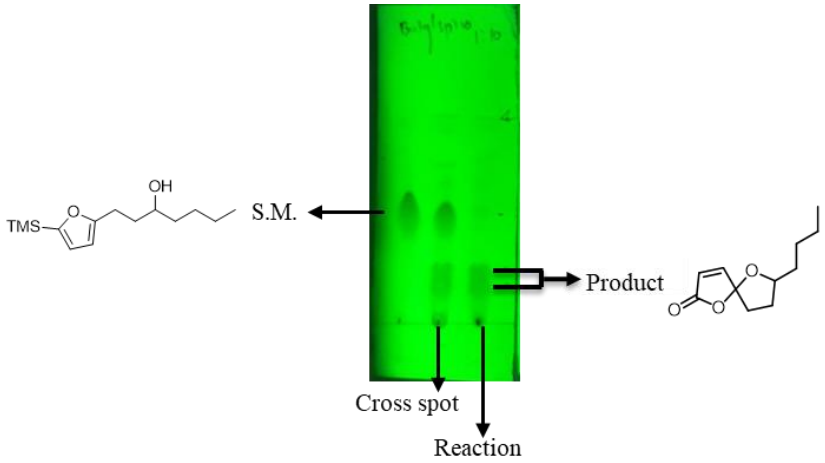
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.2, 152.2, 123.9, 114.5, 82.4, 36.1, 35.2, 30.3, 29.7, 27.8, 14.0.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{11}H_{16}O_3$ $[M]^+$ 196.1094, found 196.1091

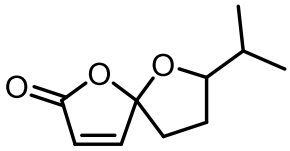
IR (ATR) ν_{max}: 2931, 2872, 1763, 1461, 1116, 921 cm^{-1}

TLC: R_f = 0.26; 0.23 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7-Isopropyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 4d



The title compound was prepared according to General procedure A from **3d** (16.8 mg, 0.07 mmol) to give **4d** (10.9 mg, 0.06 mmol, 86%, 1.22:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.09 (d, 1H, J = 5.6 Hz), 6.12 (d, 1H, J = 5.6 Hz), 3.95 — 3.90 (m, 1H), 2.33 — 1.96 (m, 4H), 1.88 — 1.72 (m, 1H), 0.99 (d, 3H, J = 6.6 Hz), 0.90 (d, 3H, J = 6.8 Hz).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.0, 152.2, 124.2, 114.3, 89.4, 36.7, 33.7, 28.1, 19.3, 18.1.

Minor Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.11 (d, 1H, J = 5.6 Hz), 6.13 (d, 1H, J = 5.6 Hz), 4.18 — 4.14 (m, 1H), 2.33 — 1.96 (m, 4H), 1.88 — 1.72 (m, 1H), 0.95 (d, 3H, J =6.7 Hz), 0.91 (d, 3H, J =6.8 Hz).

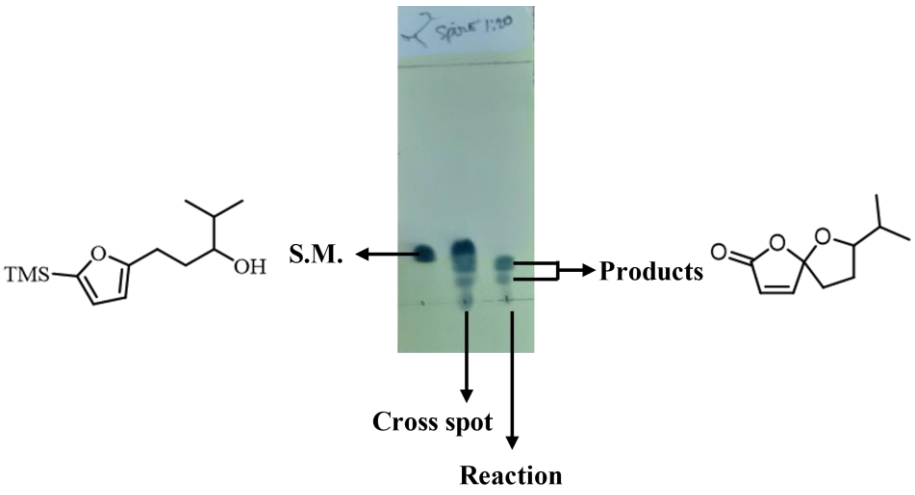
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.2, 152.0, 124.0, 114.6, 87.3, 34.8, 32.6, 26.9, 18.5, 18.1.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{10}H_{14}O_3$ $[M]^+$ 182.0938, found 182.0940

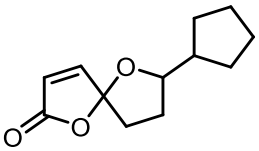
IR (ATR) ν_{max}: 3099, 2963, 1766, 1118, 917 cm^{-1}

TLC: R_f = 0.28; 0.19 (1:20 EtOAc/Hexane)



Back to table of substrate scope

7-Cyclopentyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 4e



The title compound was prepared according to General procedure A from **3e** (21.3 mg, 0.08 mmol) to give 4e (14.7mg, 0.07 mmol, 71%, 1.17:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.09 (d, 1H, J = 5.6 Hz), 6.12 (d, 1H, J = 5.6 Hz), 4.09 — 4.04 (m, 1H), 2.36 — 2.17 (m, 4H), 2.30 — 1.53 (m, 9H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.1, 152.2, 124.2, 114.5, 88.2, 45.6, 36.6, 29.9, 29.4, 28.6, 25.4, 25.4.

Minor Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.11 (d, 1H, J = 5.6 Hz), 6.12 (d, 1H, J = 5.6 Hz), 4.26 — 4.22 (m, 1H), 2.36 — 2.17 (m, 4H), 2.30 — 1.53 (m, 9H)

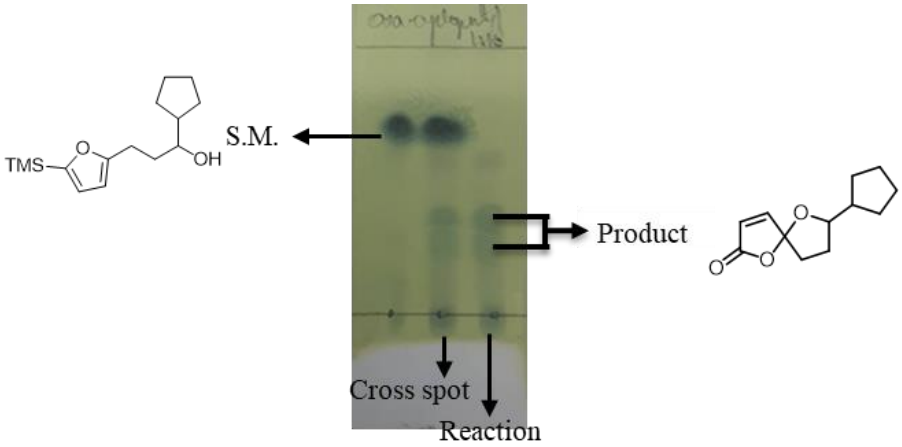
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 170.2, 152.1, 123.9, 114.6, 86.4, 44.7, 34.7, 29.4, 28.9, 28.6, 25.5, 25.4.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{12}H_{16}O_3$ $[M]^+$ 208.1094, found 208.1096

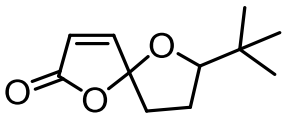
IR (ATR) ν_{max}: 2951, 2865, 1761, 1454. 1137, 920, 816, 748 cm^{-1}

TLC: R_f = 0.37; 0.31 (1:10 EtOAc/Hexane)



Back to table of substrate scope

7-(tert-Butyl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 4f



The title compound was prepared according to General procedure A from **3f** (15.0 mg, 0.06 mmol) to give **4f** (7.8 mg, 0.04 mmol, 67%, 1.42:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.09 (d, 1H, J = 5.6 Hz), 6.11 (d, 1H, J = 5.6 Hz), 3.97 — 3.93 (m, 1H), 2.21 — 2.16 (m, 2H), 2.14 — 2.08 (m, 2H) 0.94 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 152.5, 124.1, 114.3, 92.1, 36.8, 33.5, 25.7, 25.4.

Minor Diastereomer:

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.09 (d, 1H, J = 5.6 Hz), 6.11 (d, 1H, J = 5.6 Hz), 3.97 — 3.93 (m, 1H), 2.21 — 2.16 (m, 2H), 2.14 — 2.08 (m, 2H) 0.94 (s, 9H).

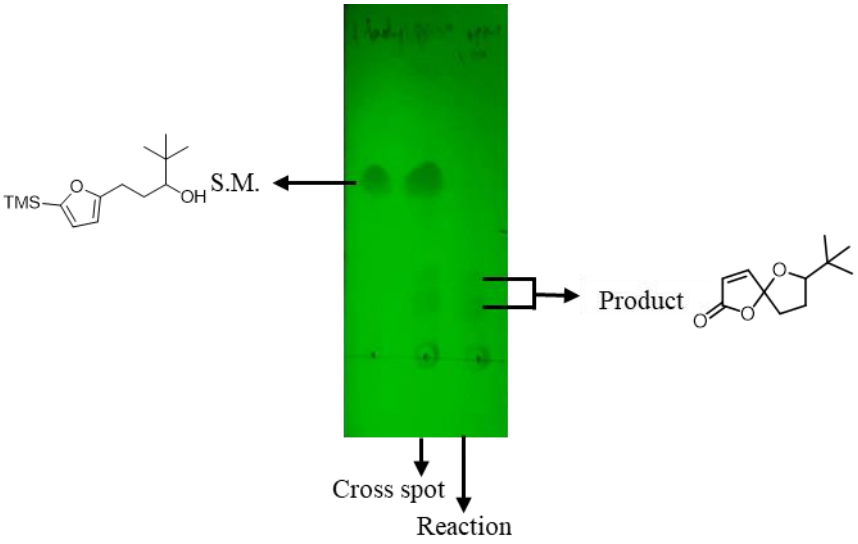
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170.2, 151.8, 124.1, 114.8, 89.9, 35.1, 33.9, 25.3, 24.9.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{11}H_{16}O_3$ $[M]^+$ 196.1094, found 196.1097

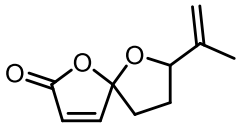
IR (ATR) ν_{max}: 2958, 2871, 2927, 1765, 1463, 1087, 920 cm^{-1}

TLC: R_f = 0.27; 0.23 (1:5 EtOAc/Hexane)



Back to table of substrate scope

7-(Prop-1-en-2-yl)-1,6-dioxaspiro[4.4]non-3-en-2-one, 4g



The title compound was prepared according to General procedure A from **3g** (16.7 mg, 0.07 mmol) to give **4g** (10.0 mg, 0.06 mmol, 79%, 1.37:1 *d.r.*) as a yellow oil.

Major Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.05 (d, 1H, J = 5.6 Hz), 6.08 (d, 1H, J = 5.6 Hz), 4.99 (s, 1H), 4.84 (s, 1H), 4.62 — 4.59 (m, 1H), 2.44 — 1.86 (m, 4H), 1.72 (s, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170, 152.0, 143.5, 124.3, 114.3, 112.9, 86.8, 36.6, 29.4, 17.1.

Minor Diastereomer:

^{1}H NMR (500 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.10 (d, 1H, J = 5.6 Hz), 6.10 (d, 1H, J = 5.6 Hz), 4.93 (s, 1H), 4.81 (s, 1H), 4.75 (dd, 1H, J = 8.2, 5.1 Hz), 2.44 — 1.86 (m, 4H), 1.67 (s, 3H).

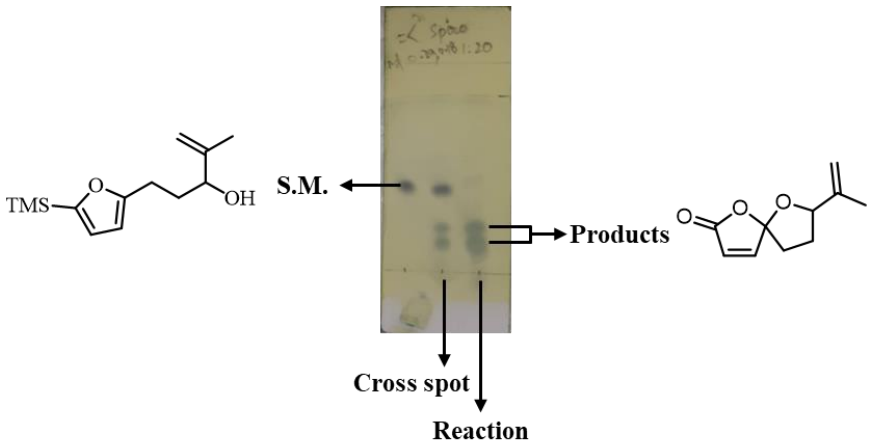
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 170, 151.7, 129.7, 124.3, 114.5, 111.4, 84.4, 34.4, 28.7, 18.0.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{10}H_{12}O_3$ $[M]^+$ 180.0781, found 180.0779

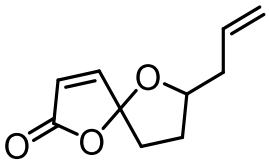
IR (ATR) ν_{max}: 3090, 2972, 1085, 1764, 915 cm^{-1}

TLC: R_f = 0.29; 0.18 (1:20 EtOAc/Hexane)



Back to table of substrate scope

7-Allyl-1,6-dioxaspiro[4.4]non-3-en-2-one, 4h



The title compound was prepared according to General procedure A from 3h (16.7 mg, 0.07 mmol) to give 4h (6.5 mg, 0.04 mmol, 52%, 1.19:1 d.r.) as a yellow oil.

Major Diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.09 (d, 1H, J = 5.6 Hz), 6.14 (d, 1H, J = 5.6 Hz), 5.85 — 5.75 (m, 1H), 5.16 — 5.09 (m, 2H), 4.35 — 4.30 (m, 1H), 2.57 — 1.81 (m, 6H).

^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.9, 133.8, 124.3, 117.7, 114.3, 82.9, 40.6, 36.4, 29.9, 28.7.

Minor Diastereomer:

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, 1H, J = 5.6 Hz), 6.13 (d, 1H, J = 5.6 Hz), 5.85 — 5.75 (m, 1H), 5.16 — 5.09 (m, 2H), 4.54 — 4.49 (m, 1H), 2.57 — 1.81 (m, 6H).

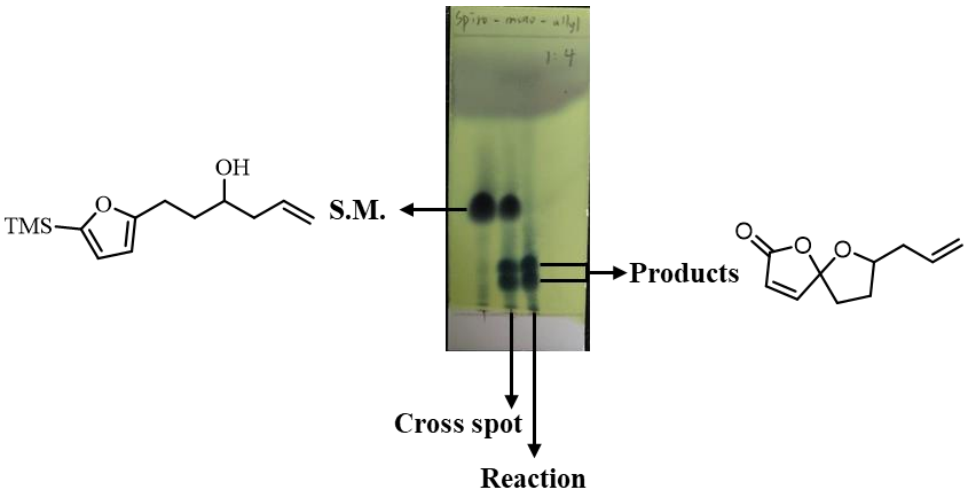
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) δ 151.9, 133.4, 124.1, 118.0, 114.6, 81.3, 39.6, 34.5, 29.7, 28.7.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{10}H_{12}O_3$ $[M]^+$ 180.0781, found 180.0780

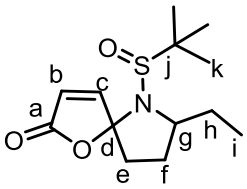
IR (ATR) ν_{max}: 3078, 2922, 1762, 1087, 815 cm^{-1}

TLC: R_f = 0.18; 0.13 (1:4 EtOAc/Hexane)



Back to table of substrate scope

(5S,7S)-6-((*R*)-*Tert*-butylsulfinyl)-7-ethyl-1-oxa-6-azaspiro[4.4]non-3-en-2-one, 7



The title compound was prepared according to General procedure A from 6 (60 mg, 0.18 mmol) to give 7 (10 mg, 0.04 mmol, 20%, single diastereomer) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.44 (1H, d, J = 5.6 Hz, C_cH), 6.15 (1H, d, J = 5.6 Hz, C_bH), 4.07 – 3.83 (1H, m, C_gH), 2.47 – 2.19 (2H, m, C_eH), 2.11 – 1.91 (2H, m, C_fH), 1.86 – 1.67 (2H, m, C_hH), 1.17 (9H, d, J = 7.8 Hz, C_kH), 0.93 (3H, td, J = 7.4, 4.7 Hz, C*i*H).

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 170.2 (C_a), 153.7 (C_c), 122.3 (C_b), 107.3 (C_d), 57.7 (C_j), 56.1 (C_g), 35.4 (C_e), 29.9 (C_f), 28.2 (C_h), 23.0 (C_k), 11.1 (C_i).

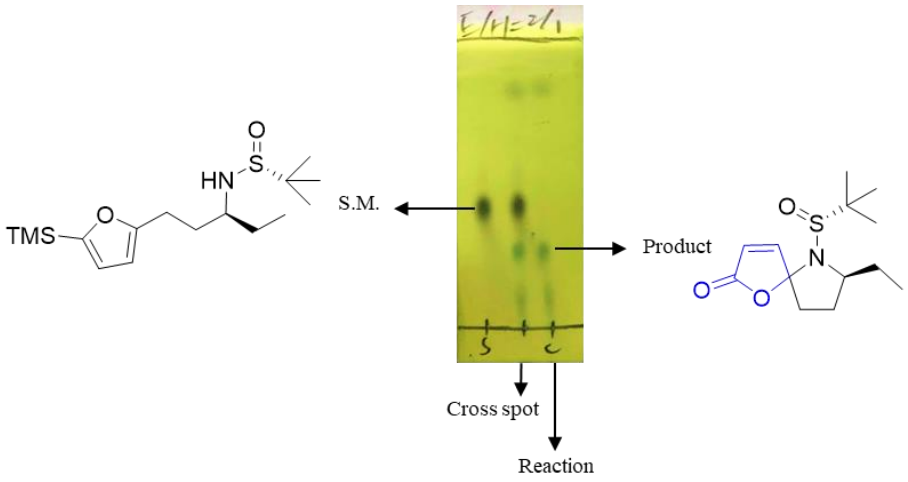
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{21}NO_3S$ $[M]^+$ 271.1236, found 271.1237

IR (ATR) ν_{max}: 2926, 2857, 1729, 1365, 1245, 1122, 1074, 913 cm^{-1}

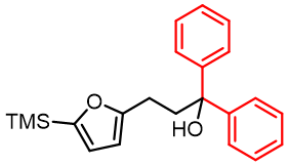
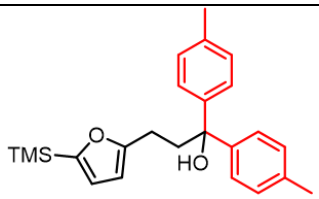
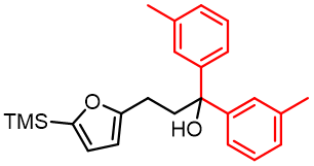
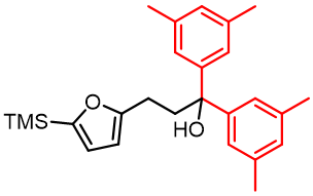
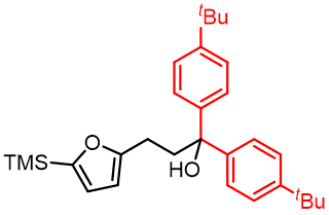
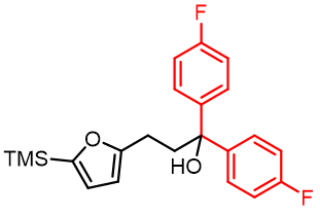
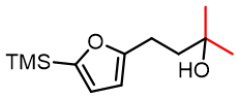
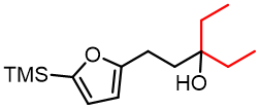
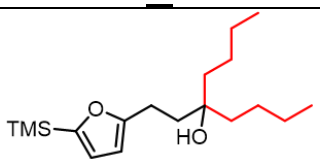
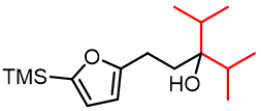
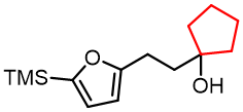
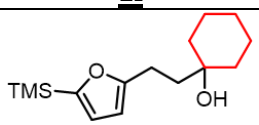
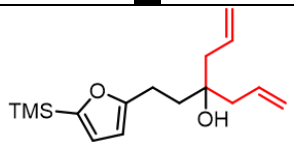
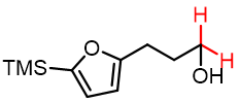
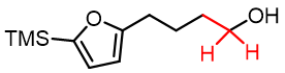
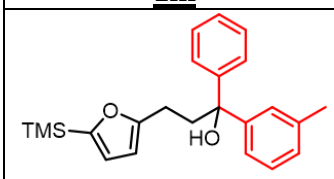
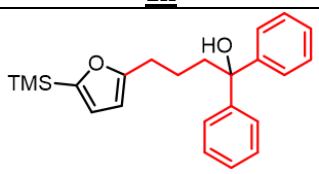
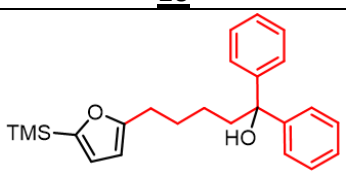
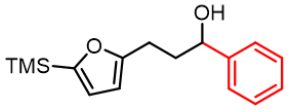
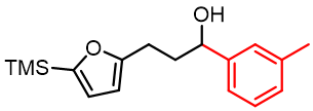
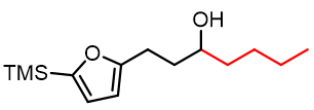
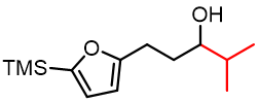
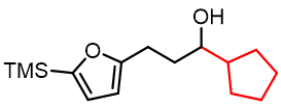
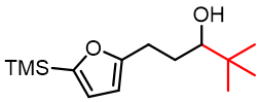
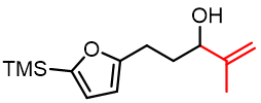
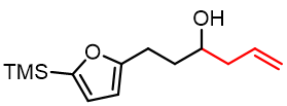
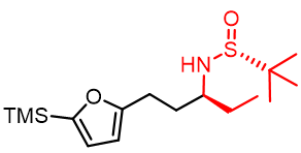
TLC: R_f = 0.3 (2:1 EtOAc/Hexane)

Due to the instability of the title compound, we are not able to measure the [α]D value and sufficient NOE experiments.



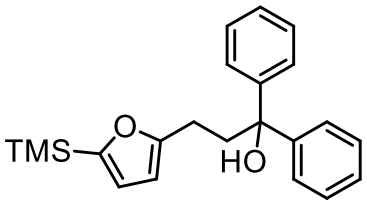
Back to contents

4.1. Summary of starting materials

 **1a**	 **1b**	 **1c**
 **1d**	 **1e**	 **1f**
 **1g**	 **1h**	 **1i**
 **1j**	 **1k**	 **1l**
 **1m**	 **1n**	 **1o**
 **1p**	 **1q**	 **1r**
 **3a**	 **3b**	 **3c**
 **3d**	 **3e**	 **3f**
 **3g**	 **3h**	 **6**

Back to table of starting materials

1,1-Diphenyl-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 1a



The title compound was prepared according to General procedure C to give **1a** (295.0 mg, 0.84 mmol, 69% (two step yield)) as a pale-yellow solid. The title compound can also be directly prepared according to General procedure B from ethyl 3-(2-furyl)propionate (0.2 mL, 1.25 mmol) to give **1a** (312.9 mg, 0.89 mmol, 71%) as a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 — 7.44 (m, 4H), 7.34 — 7.31 (m, 4H), 7.25 — 7.22 (m, 2H), 6.49 (d, 1H, J = 3.1 Hz), 5.95 (d, 1H, J = 3.1 Hz), 2.66 (s, 2H), 2.66 (s, 2H), 0.23 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.2, 158.6, 146.6, 128.2, 127.0, 126.0, 120.4, 104.8, 78.0, 39.9, 23.0, -1.5.

See NMR Spectra

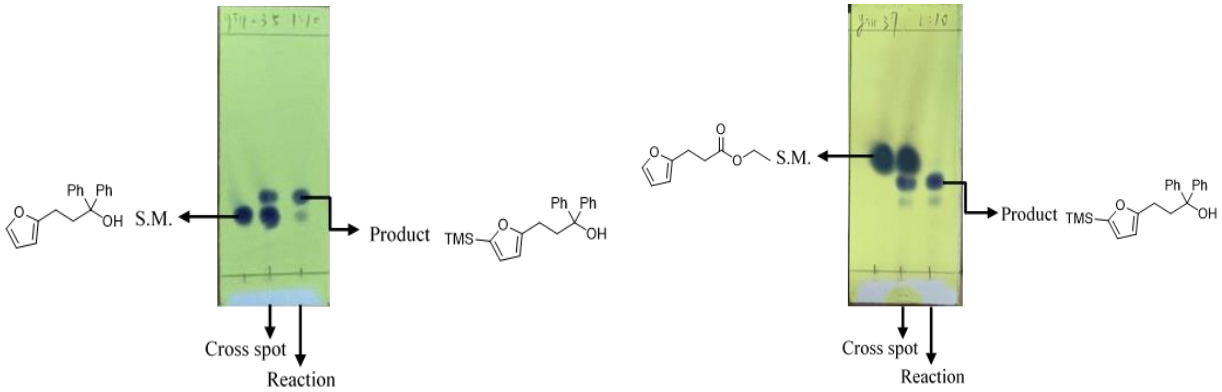
HRMS (*m/z*): (EI) calc'd for $C_{22}H_{26}O_2Si$ $[M]^+$ 350.1696, found 350.1697

IR (ATR) ν_{max}: 3599, 3569, 3059, 3024, 2963, 2953, 2897, 1588, 1492, 1247, 837, 787, 757, 746, 693 and 594 cm^{-1}

MP: 63±1 °C

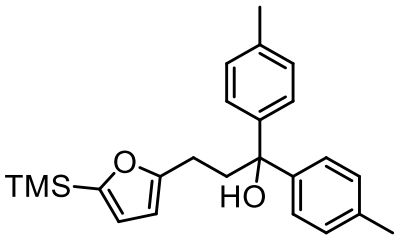
TLC (two steps reaction procedure/ one pot reaction procedure):

R_f = 0.35 (1:10 EtOAc/Hexane)



Back to table of starting materials

1,1-Di-p-tolyl-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 1b



The title compound was prepared according to General procedure C but use 3.0 eq. Grignard reagent to give **1b** (196.9 mg, 0.52 mmol, 21%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (d, 4H, J = 8.2 Hz), 7.12 (d, 4H, J = 8.0 Hz), 6.50 (d, 1H, J = 3.1 Hz), 5.95 (d, 1H, J = 3.1 Hz), 2.70 — 2.58 (m, 4H), 2.32 (s, 6H), 0.23 (s, 9H).

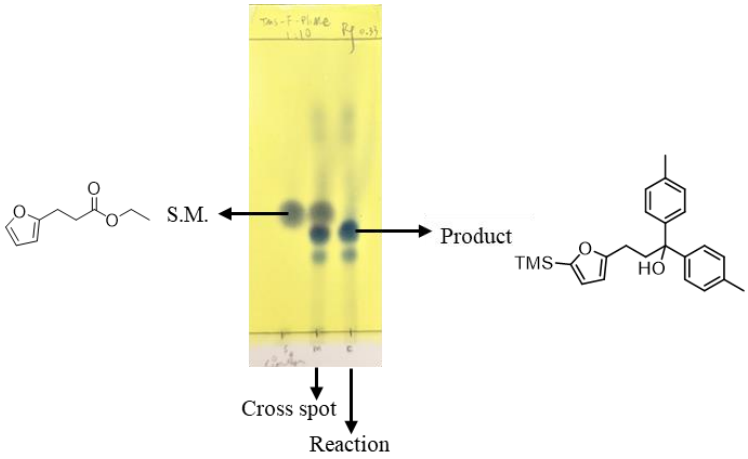
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.5, 143.9, 136.5, 128.9, 125.9, 120.4, 104.7, 77.7, 39.9, 23.1, 21.0, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{24}H_{30}O_2Si$ $[M]^+$ 378.2009, found 378.2007

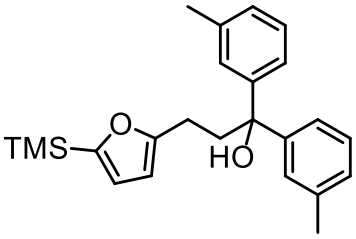
IR (ATR) ν_{max}: 3548, 3020, 2960, 1246, 834, 754 cm^{-1}

TLC: R_f = 0.21 (1:20 EtOAc/Hexane)



Back to table of starting materials

1,1-Di-m-tolyl-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 1c



The title compound was prepared according to General procedure C but use 3.0 eq. Grignard reagent to give **1c** (248.4 mg, 0.66 mmol, 17%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (m, 2H), 7.22 — 7.20 (m, 4H), 7.06 — 7.03 (m, 2H), 6.51 (d, 1H, J = 3.1 Hz), 5.97 (d, 1H, J = 3.1 Hz), 2.69 — 2.59 (m, 4H), 2.34 (s, 6H), 0.23 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.5, 146.6, 137.8, 128.1, 127.7, 126.6, 123.1, 120.4, 104.7, 77.9, 40.0, 23.1, 21.7, -1.5.

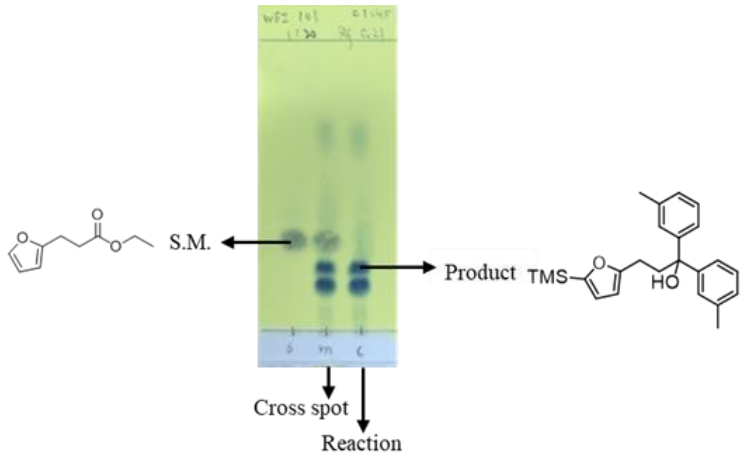
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{24}H_{30}O_2Si$ $[M]^+$ 378.2009, found 378.2010

IR (ATR) ν_{max}: 3543, 3028, 2952, 2859, 1251, 837, 775, 704 cm^{-1}

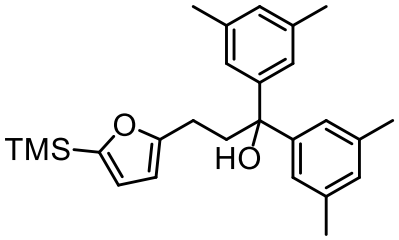
MP: 53±1 °C

TLC: R_f = 0.21 (1:20 EtOAc/Hexane)



Back to table of starting materials

1,1-Bis(3,5-dimethylphenyl)-3-(furan-2-yl)propan-1-ol, 1d



The title compound was prepared according to General procedure C but use 3.0 eq. Grignard reagent to give **1d** (241.0 mg, 0.59 mmol, 15%) as a white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 4H), 6.87 (s, 2H), 6.51 (d, 1H, J = 3.1 Hz), 5.97 (d, 1H, J = 3.1 Hz), 2.67 — 2.56 (m, 4H), 2.29 (s, 12H), 0.23 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.6, 158.5, 146.7, 137.6, 128.5, 123.7, 120.4, 104.7, 77.8, 40.0, 23.1, 21.5, -1.5.

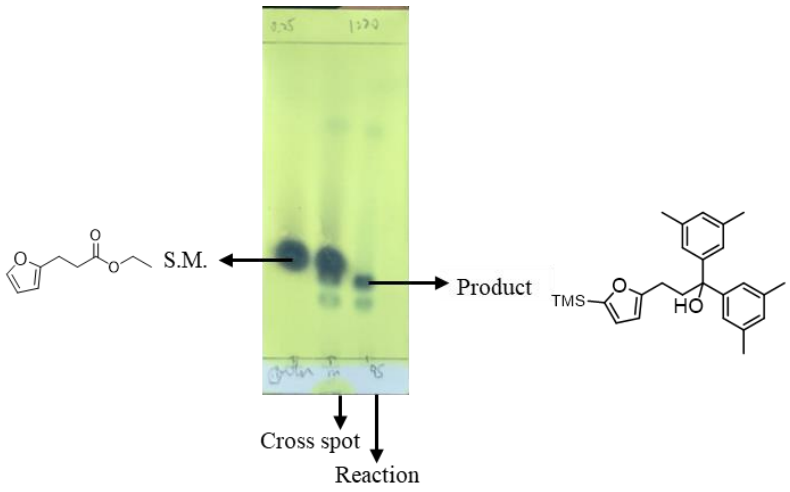
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{26}H_{34}O_2Si$ $[M]^+$ 406.2322, found 406.2324

IR (ATR) ν_{max}: 3543, 2953, 2864, 1249, 837, 751 cm^{-1}

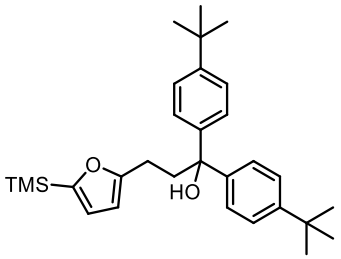
MP: 92±1 °C

TLC: R_f = 0.25 (1:20 EtOAc/Hexane)



Back to table of starting materials

1,1-Bis(4-(tert-butyl)phenyl)-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 1e



The title compound was prepared according to General procedure C but use 3.0 eq. Grignard reagent to give **1e** (739.8 mg, 1.60 mmol, 40%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 — 7.32 (m, 8H), 6.50 (d, 1H, J = 3.1 Hz), 5.96 (d, 1H, J = 3.1 Hz), 2.70 — 2.60 (m, 4H), 1.30 (s, 18H), 0.23 (s, 9H).

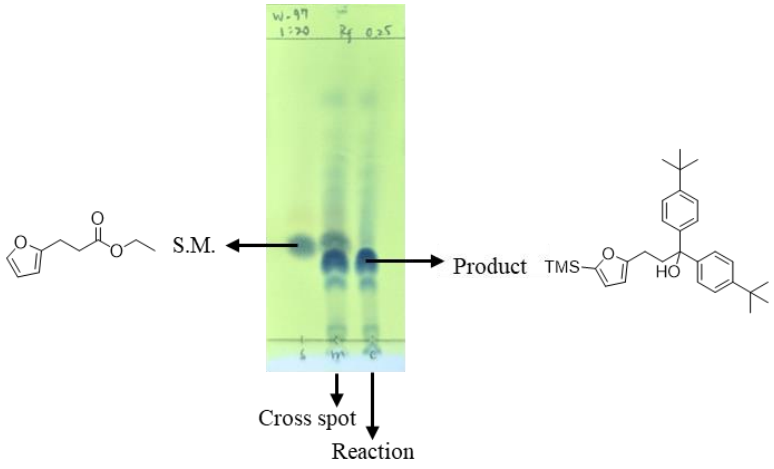
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 158.4, 149.6, 143.6, 125.7, 125.1, 120.4, 104.65, 77.7, 40.0, 34.4, 31.3, 23.1, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{30}H_{42}O_2Si$ $[M]^+$ 462.2948, found 462.2947

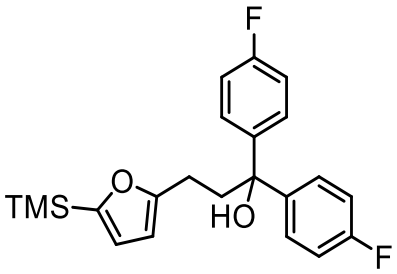
IR (ATR) ν_{max}: 3555, 2959, 2865, 1247, 838, 756 cm^{-1}

TLC: R_f = 0.25 (1:20 EtOAc/Hexane)



Back to table of starting materials

1,1-Bis(4-fluorophenyl)-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 1f



The title compound was prepared according to General procedure C but use 3.0 eq. Grignard reagent to give **1f** (48.9 mg, 0.13 mmol, 7%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 — 7.36 (m, 4H), 7.04 — 6.98 (m, 4H), 6.50 (d, 1H, J = 4.1 Hz), 5.95 (d, 1H, J = 4.1 Hz), 2.63 (m, 4H), 0.23 (s, 9H).

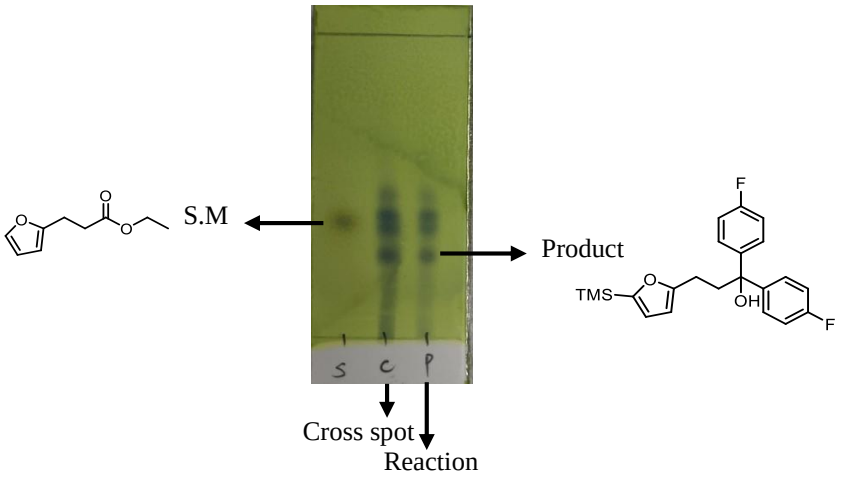
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.8 (d, J = 247.3 Hz), 159.7, 158.8, 142.3 (d, J = 3.1 Hz), 127.7 (d, J = 8.0 Hz), 120.4, 115.1 (d, J = 21.3 Hz), 105.0, 65.8, 40.1, 22.9, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{22}H_{26}O_2Si$ $[M]^+$ 386.1508, found 386.1510

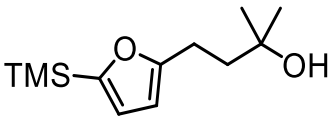
IR (ATR) ν_{max}: 3467, 2956, 1502, 1224, 1160, 832, 574 cm^{-1}

TLC: R_f = 0.25 (1:10 EtOAc/Hexane)



Back to table of starting materials

2-Methyl-4-(5-(trimethylsilyl)furan-2-yl)butan-2-ol, 1g



The title compound was prepared according to General procedure B from ethyl 3-(2-furyl)propionate (0.48 mL, 3.0 mmol) but use 2.2 eq. MeLi, 2.2 eq. n-BuLi and 2.5 eq. TMSCl to give **1g** (301.4 mg, 1.33 mmol, 44%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.98 (d, 1H, J = 3.1 Hz), 2.80 — 2.74 (m, 2H), 1.88 — 1.82 (m, 2H), 1.27 (s, 6H), 0.24 (s, 9H).

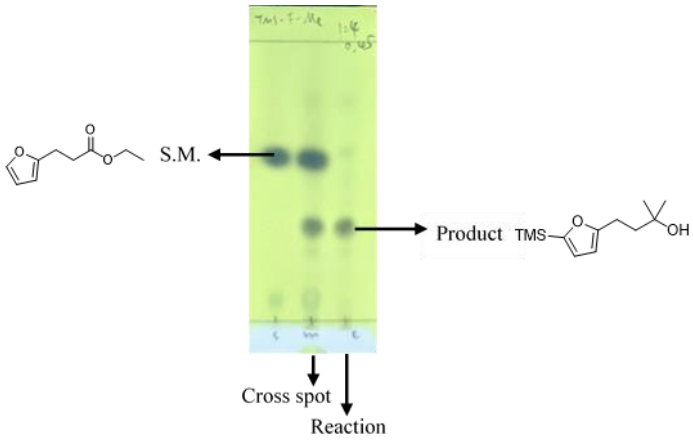
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.4, 120.4, 104.7, 70.6, 41.6, 29.2, 23.3, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{12}H_{22}O_2Si$ $[M]^+$ 226.1383, found 226.1381

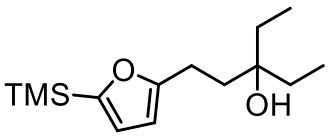
IR (ATR) ν_{max}: 3423, 2970, 1755, 1119, 928, 839 cm^{-1}

TLC: R_f = 0.45 (1:4 EtOAc/Hexane)



Back to table of starting materials

3-Ethyl-1-(5-(trimethylsilyl)furan-2-yl)pentan-3-ol, 1h



The title compound was prepared according to General procedure C to give **1h** (146.4 mg, 1.74 mmol, 24%) as a yellow oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (d, 1H, *J* = 3.1 Hz), 5.98 (d, 1H, *J* = 3.1 Hz), 2.75 — 2.66 (m, 2H), 1.84 — 1.75 (m, 2H), 1.51 (q, 4H, *J* = 7.5 Hz), 0.89 (t, 6H, *J* = 7.5 Hz), 0.24 (s, 9H).

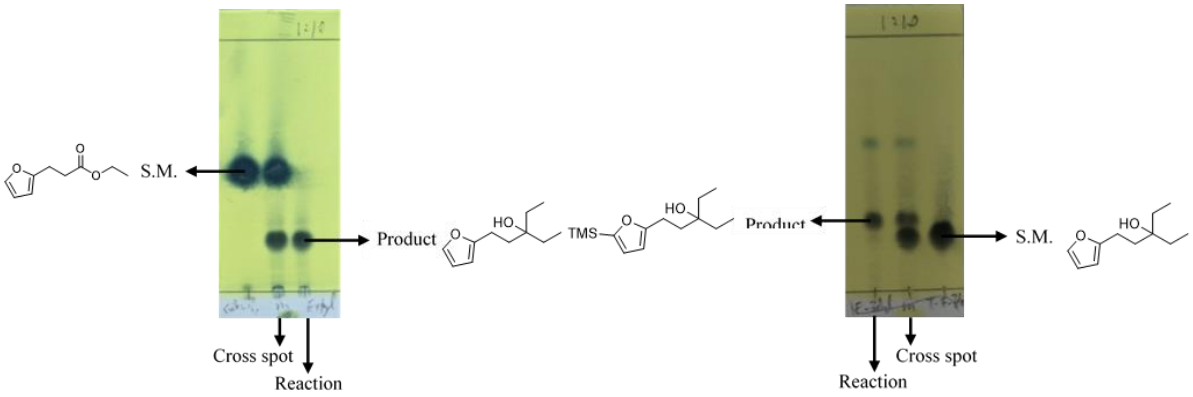
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.8, 158.5, 120.5, 104.7, 74.4, 36.2, 31.0, 22.6, 7.9, -1.4.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{14}H_{26}O_2Si$ $[M]^+$ 254.1696, found 254.1698

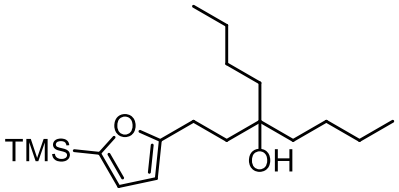
IR (ATR) ν_{max}: 3453, 2968, 2878, 1760, 926, 841 cm^{-1}

TLC: R_f = 0.28 (1:10 EtOAc/Hexane)



Back to table of starting materials

5-(2-(5-(Trimethylsilyl)furan-2-yl)ethyl)nonan-5-ol, 1i



The title compound was prepared according to General procedure B to give **1i** (653.5 mg, 2.1 mmol, 60%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.98 (d, 1H, J = 3.1 Hz), 2.72 — 2.68 (m, 2H), 1.82 — 1.78 (m, 2H), 1.49 — 1.45 (m, 4H), 1.35 — 1.25 (m, 9H), 0.92 (t, 6H, J = 6.7 Hz), 0.24 (s, 9H).

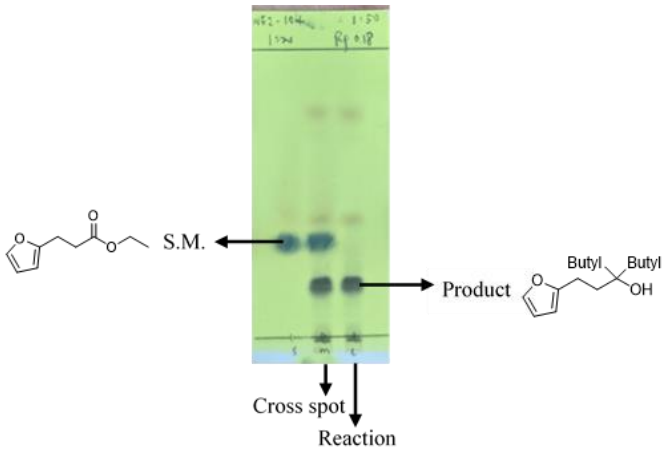
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.7, 158.4, 120.4, 104.6, 74.1, 38.8, 37.1, 25.7, 23.3, 22.5, 14.1, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{18}H_{34}O_2Si$ $[M]^+$ 310.2323, found 310.2323

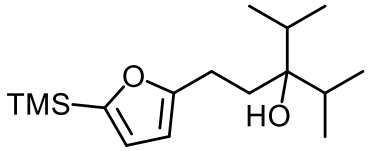
IR (ATR) ν_{max}: 3423, 2956, 2863, 1247, 837, 780, 755 cm^{-1}

TLC: R_f = 0.18 (1:20 EtOAc/Hexane)



Back to table of starting materials

3-Isopropyl-4-methyl-1-(5-(trimethylsilyl)furan-2-yl)pentan-3-ol, 1j



The title compound was prepared according to General procedure C to give **1j** (174.6 mg, 0.62 mmol, 31%) as an orange oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.98 (d, 1H, J = 3.1 Hz), 2.75 — 2.71 (m, 2H), 2.01 — 1.91 (m, 2H), 1.89 — 1.84 (m, 2H), 0.98 (d, 6H, J = 7.0 Hz), 0.96 (d, 6H, J = 7.0 Hz), 0.24 (s, 9H).

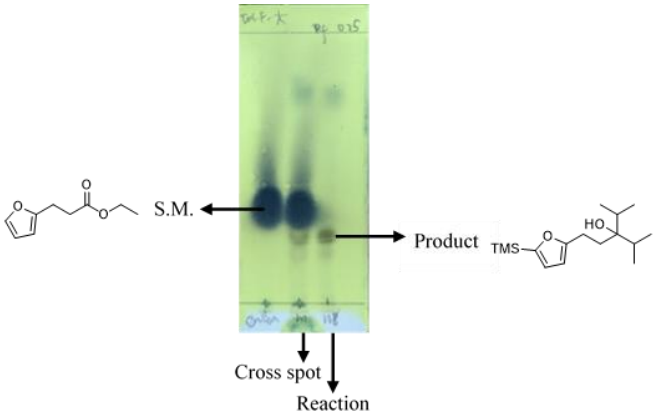
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.9, 158.4, 120.4, 104.4, 34.2, 31.5, 23.4, 17.5, 17.2, -1.5. (Hydroxyl carbon peak not observed: 50-90 ppm)

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{16}H_{30}O_2Si$ $[M]^+$ 282.2009, found 282.2008

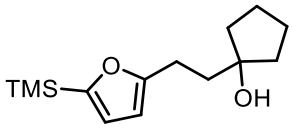
IR (ATR) ν_{max}: 3494, 2959, 1248, 1007, 837, 755 cm^{-1}

TLC: R_f = 0.25 (1:15 EtOAc/Hexane)



Back to table of starting materials

1-(2-(5-(Trimethylsilyl)furan-2-yl)ethyl)cyclopentan-1-ol, 1k



The title compound was prepared according to General procedure C but use 6.0 eq. Grignard reagent, 2.2 eq. n-BuLi and 2.3 eq. TMSCl to give **1k** (467.5 mg, 1.85 mmol, 53%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.98 (d, 1H, J = 3.1 Hz), 2.88 – 2.76 (m, 2H), 1.97 — 1.93 (m, 2H), 1.83 — 1.57 (m, 8H, overlapped with H_2O), 0.24 (s, 9H).

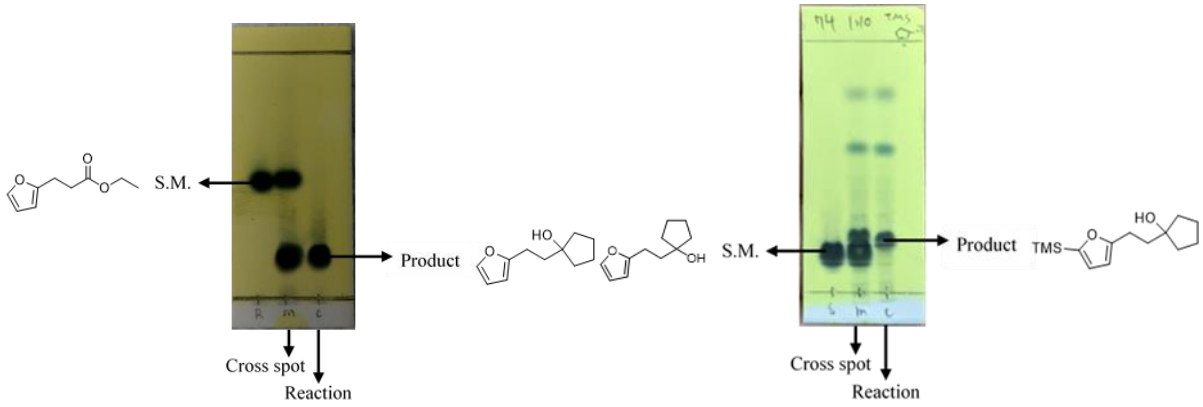
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.6, 158.4, 120.4, 104.7, 82.1, 39.7, 39.5, 23.8, 23.7, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{14}H_{24}O_2Si$ $[M]^+$ 252.1540, found 252.1539

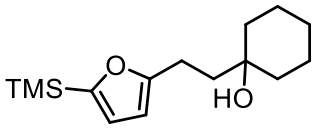
IR (ATR) ν_{max}: 3434, 2952, 1750, 1102, 984, 846 cm^{-1}

TLC: R_f = 0.20 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-(2-(5-(Trimethylsilyl)furan-2-yl)ethyl)cyclopentan-1-ol, 1l



The title compound was prepared according to General procedure C but use 6.0 eq. Grignard reagent, 2.2 eq. n-BuLi and 2.3 eq. TMSCl to give **1l** (312.9 mg, 1.17 mmol, 20%) as a yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.51 (d, 1H, J = 3.1 Hz), 5.97 (d, 1H, J = 3.1 Hz), 2.78 — 2.74 (m, 2H), 1.83 — 1.79 (m, 2H), 1.64 — 1.42 (m, 10H, overlapped with H_2O), 0.24 (s, 9H).

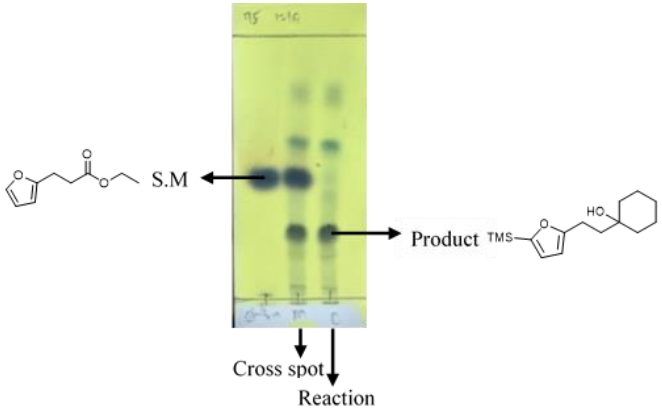
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.8, 158.4, 120.4, 104.6, 71.1, 37.4, 25.8, 22.2, 22.0, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{15}H_{26}O_2Si$ $[M]^+$ 266.1696, found 266.1699

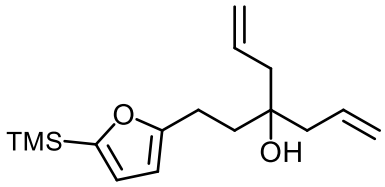
IR (ATR) ν_{max}: 3269, 2932, 2861, 1246, 833, 786, 758 cm^{-1}

TLC: R_f = 0.25 (1:10 EtOAc/Hexane)



Back to table of starting materials

4-(2-(5-(Trimethylsilyl)furan-2-yl)ethyl)hepta-1,6-dien-4-ol, 1m



The title compound was prepared according to General procedure C to give **1m** (721.6 mg, 2.59 mmol, 78%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.97 (d, 1H, J = 3.1 Hz), 5.92 — 5.81 (m, 2H), 5.18 — 5.12 (m, 4H), 2.79 — 2.74 (m, 2H), 2.33 — 2.23 (m, 4H), 1.86 — 1.82 (m, 2H), 0.24 (s, 9H).

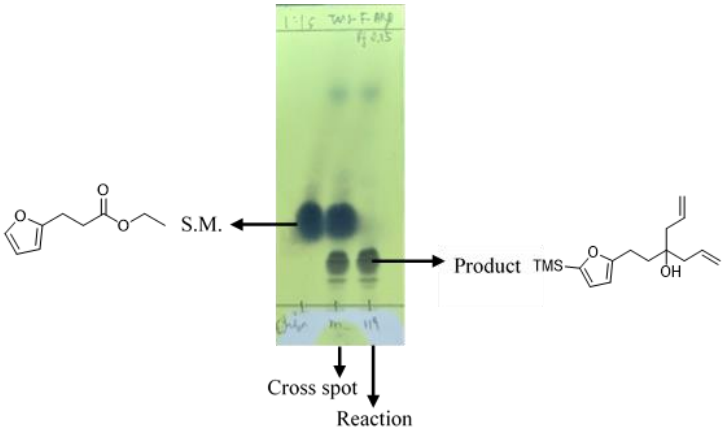
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.3, 158.5, 133.4, 120.4, 119.0, 104.7, 73.1, 43.6, 37.0, 22.4, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{16}H_{26}O_2Si$ $[M]^+$ 278.1696, found 278.1697

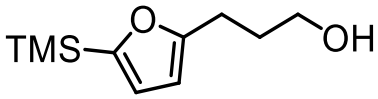
IR (ATR) ν_{max}: 3457, 3075, 2955, 1757, 1247, 918, 840, 757 cm^{-1}

TLC: R_f = 0.15 (1:15 EtOAc/Hexane)



Back to table of starting materials

3-(5-(Trimethylsilyl)furan-2-yl)propan-1-ol, 1n



The title compound was prepared based on a literature method,[2] to afford the pure alcohol (580.1 mg, 4.60 mmol, 98%) as a colorless oil. Then, according to the second step of General procedure C to **1p** (448.4 mg, 2.26 mmol, 45%) as a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.2 Hz), 6.00 (d, 1H, J = 3.2 Hz), 3.70 (t, 2H, J = 6.5 Hz), 2.76 (t, 2H, J = 8.0 Hz), 1.92 — 1.89 (m, 2H), 0.24 (s, 9H).

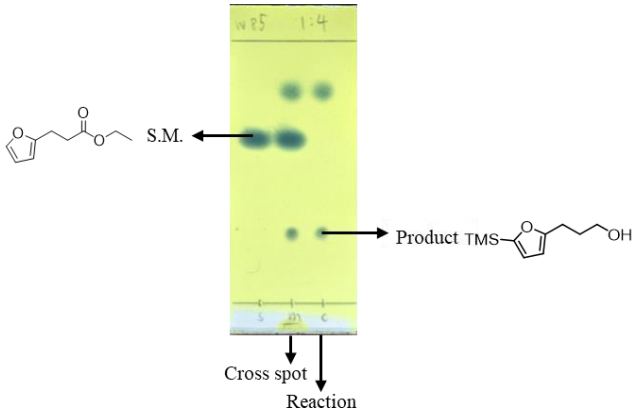
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.9, 158.6, 120.4, 105.1, 62.3, 31.1, 24.5, -1.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{10}H_{18}O_2Si$ $[M]^+$ 198.1070, found 198.1070

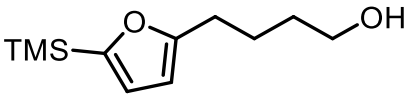
IR (ATR) ν_{max}: 2335, 2595, 1248, 835, 755 cm^{-1}

TLC: R_f = 0.28 (1:4 EtOAc/Hexane)



Back to table of starting materials

3-(5-(Trimethylsilyl)furan-2-yl)propan-1-ol, 1o



The title compound was prepared based on a literature method,[3] to afford the pure alcohol. Then, according to the second step of General procedure D but from 4-(furan-2-yl)butan-1-ol (616 mg, 4.39 mmol) to give **1q** (90mg, 0.424 mmol, 42.4 %) as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.50 (d, J = 3.0 Hz, 1H), 5.96 (d, J = 2.8 Hz, 1H), 4.68 — 4.64 (m, 1H), 3.62 — 3.57 (m, 1H), 3.45 — 3.40 (m, 1H), 2.67 (t, J = 7.2 Hz, 2H), 1.76 —1.61 (m, 4H), 0.23 (s, 9H).

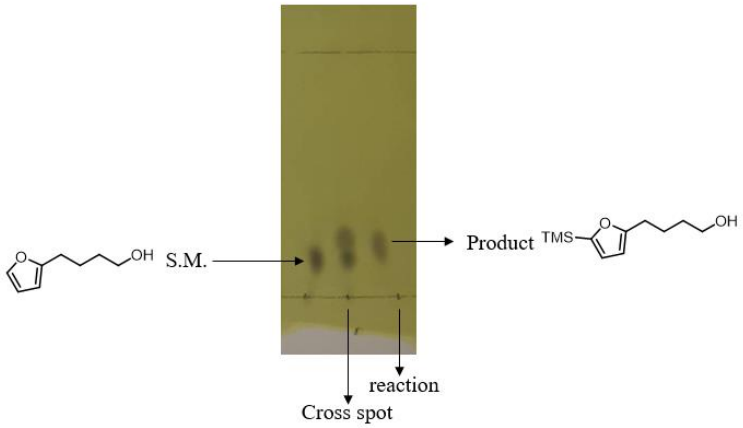
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 160.6, 158.5, 120.5, 105.1, 62.9, 32.4, 28.1, 24.5, -1.4.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{11}H_{20}O_2Si$ $[M]^+$ 212.1227, found 212.1227

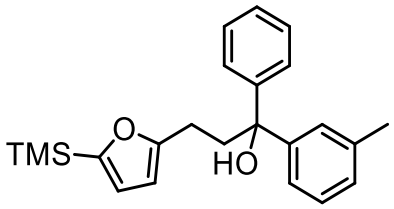
IR (ATR) ν_{max}: 3393, 2926, 2160, 1714, 1495, 841 cm^{-1}

TLC: R_f = 0.26 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-Phenyl-1-(m-tolyl)-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 1p



The title compound was prepared according to General procedure C to give **1n** (159 mg, 0.44 mmol, 43%) as a yellow oil, and the reactant used is 3-(furan-2-yl)-1-phenylpropan-1-one. The preparation of 3-(furan-2-yl)-1-phenylpropan-1-one from furfural was according to a previous literature.[4]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 6H), 7.26 – 7.19 (m, 3H), 7.07 – 7.05 (m, 1H), 6.51 (dd, 1H, *J* = 3.1, 1.9 Hz), 5.97 (dd, 1H, *J* = 2.5 Hz), 2.66 – 2.64 (m, 4H), 2.34 (d, 3H, *J* = 1.8 Hz), 0.24 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.5, 158.7, 146.8, 146.7, 138.0, 128.4, 128.3, 127.9, 127.1, 126.9, 126.2, 123.3, 120.6, 104.9, 78.1, 40.1, 23.2, 21.8, -1.4.

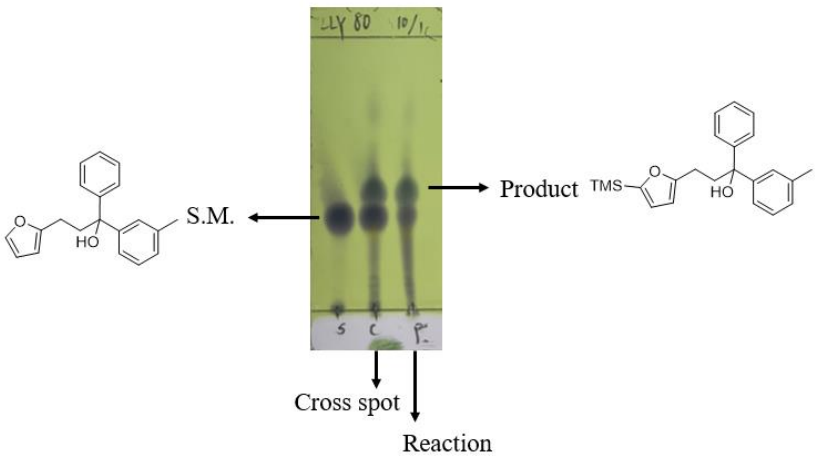
See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{16}H_{26}O_2Si$ $[M]^+$ 364.1853, found 364.1855

IR (ATR) ν_{max}: 3304, 3209, 3164, 3075, 2988, 2752, 2554, 2506, 2414, 1045, 461 cm^{-1}

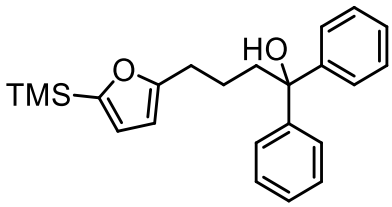
MP: 67-68 ^{o}C

TLC: R_f = 0.43 (1:10 EtOAc/Hexane)



Back to table of starting materials

1,1-Diphenyl-4-(5-(trimethylsilyl)furan-2-yl)butan-1-ol, 1q



The title compound was prepared according to General procedure C to give **1o** (159 mg, 0.44 mmol, 43%) as a yellow oil using methyl 4-(furan-2-yl)butanoate. The preparation of methyl 4-(furan-2-yl)butanoate from furan was according to a previous literature.[3,5]

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 — 7.38 (m, 4H), 7.31 — 7.28 (m, 4H), 7.23 — 7.20 (m, 2H), 6.50 (d, 1H, J = 3.1 Hz), 5.92 (d, 1H, J = 3.0 Hz), 2.68 (t, 2H, J = 7.3 Hz), 2.34 — 2.31 (m, 2H), 1.69 — 1.63 (m, 2H), 0.23 (s, 9H).

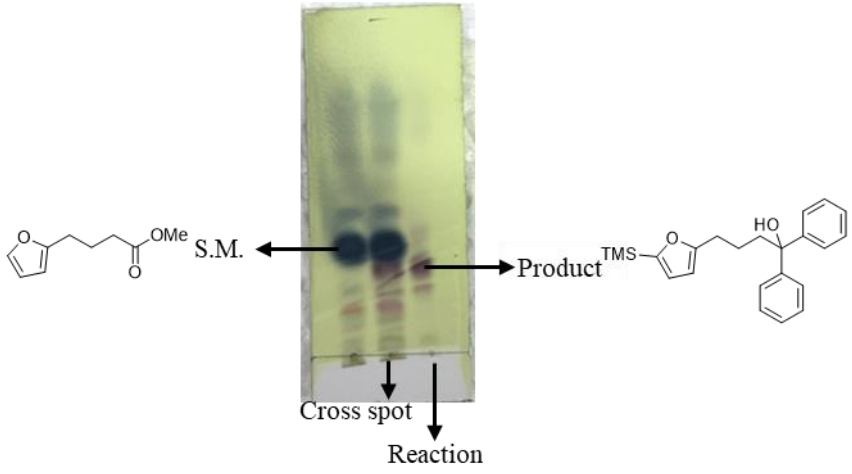
^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 160.2, 158.4, 146.9, 128.1, 126.8, 126.0, 120.4, 105.1, 78.2, 41.3, 28.2, 22.4, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{23}H_{28}O_2Si$ $[M]^+$ 364.1853, found 364.1850

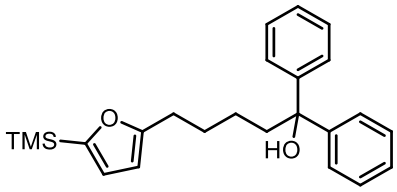
IR (ATR) ν_{max}: 3565, 3453, 2960, 1492, 1448, 1250, 841, 754, 700 cm^{-1}

TLC: R_f = 0.25 (1:10 EtOAc/Hexane)



Back to table of starting materials

1,1-Diphenyl-5-(5-(trimethylsilyl)furan-2-yl)pentan-1-ol, 1r



The title compound was prepared according to General procedure C to give **1r** (184 mg, 0.49 mmol, 39%) as a yellow oil using ethyl 5-(furan-2-yl)pentanoate. The preparation of ethyl 5-(furan-2-yl)pentanoate from ethyl 4-bromobutyrate was according to a previous literature.[6]

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.38 (m, 5H), 7.30 (td, 5H, J = 6.9, 1.7 Hz), 7.24 – 7.19 (m, 2H), 6.49 (d, 1H, J = 3.0 Hz), 5.91 (dd, 1H, J = 3.0, 0.9 Hz), 2.62 (t, 2H, J = 7.7 Hz), 2.33 – 2.27 (m, 2H), 1.68 (quint, 2H, J = 7.6 Hz), 1.42 – 1.32 (m, 2H), 0.22 (s, 9H).

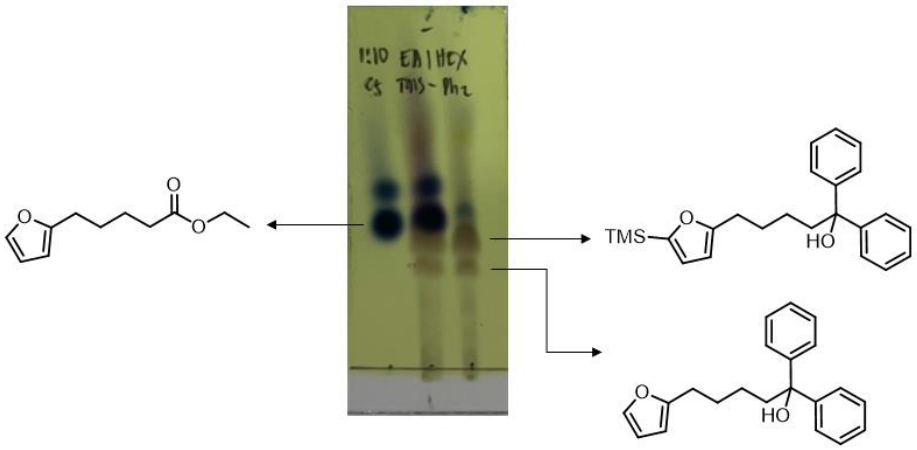
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.75, 158.39, 147.21, 128.29, 126.94, 126.15, 120.49, 104.87, 78.36, 41.85, 28.56, 28.25, 23.63, -1.38.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{24}H_{30}O_2Si$ $[M]^+$ 378.2010, found 378.2006

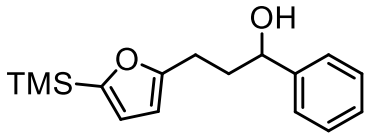
IR (ATR) ν_{max}: 3440, 2955, 2932, 2861, 1465, 1249, 1010, 931, 841, 756 cm^{-1}

TLC: R_f = 0.39 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-Phenyl-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 3a



The title compound was prepared according to General procedure D from 3-(furan-2-yl)propanal[7] (300 mg, 2.42 mmol) to give **3a** (21.9 mg, 0.11 mmol, 4.4 %) as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 — 7.28 (m, 5H), 6.52 (d, 1H, J = 3.0 Hz), 5.99 (d, 1H, J = 3.1 Hz), 4.75 — 4.71 (m, 1H), 2.82 — 2.66 (m, 2H), 2.19 — 2.03 (m, 2H), 0.24 (s, 9H).

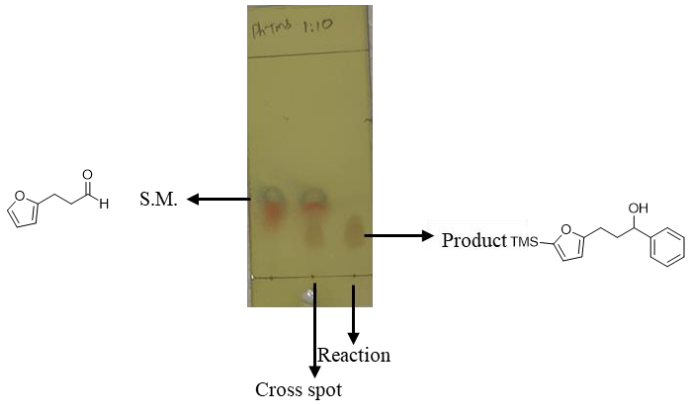
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.8, 158.6, 144.4, 128.5, 127.7, 125.9, 120.4, 105.1, 73.8, 37.2, 24.6, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{16}H_{22}O_2Si$ $[M]^+$ 274.1383, found 274.1386

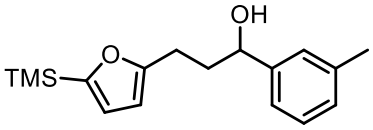
IR (ATR) ν_{max}: 3370, 3027, 2953, 1253, 845, 724 cm^{-1}

TLC: R_f = 0.33 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-(*p*-Tolyl)-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 3b



The title compound was prepared according to General procedure E from 3-(furan-2-yl)propanal[7] (400 mg, 3.23 mmol) to give **3b** (30 mg, 0.104 mmol, 3.2 %) as a yellowish. oil.

^{1}H NMR (300 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 7.43 — 7.09 (m, 4H), 6.52 (d, 1H, J = 3.1 Hz), 6.00 (d, 1H, J = 3.1 Hz), 4.69 (t, 1H, J = 6.1 Hz), 2.79 — 2.72 (m, 2H), 2.37 (s, 3H), 2.20 — 2.04 (m, 2H), 0.24 (s, 9H).

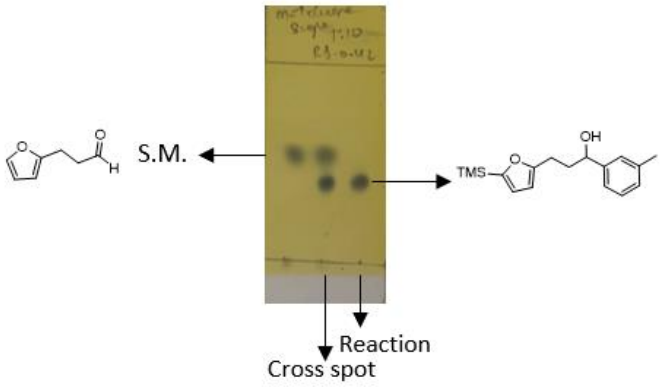
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 160.1, 158.7, 138.4, 128.6, 128.1, 127.3, 126.7, 123.1, 120.5, 105.3, 74.0, 37.3, 24.8, 21.6, -1.4.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{17}H_{24}O_2Si$ $[M]^+$ 288.1540, found 288.1537

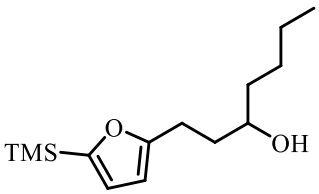
IR (ATR) ν_{max}: 3364, 3030, 2966, 1720, 1009, 838 cm^{-1}

TLC: R_f = 0.42 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-(5-(Trimethylsilyl)furan-2-yl)heptan-3-ol, 3c



The title compound was prepared according to General procedure D from 3-(furan-2-yl)propanal[7] (400 mg, 3.23 mmol) to give **3c** (199.0 mg, 0.781 mmol, 32.3 %) as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.98 (d, 1H, J = 3.1 Hz), 3.67 — 3.60 (m, 1H), 2.86 — 2.71 (m, 2H), 1.93 — 1.69 (m, 2H), 1.50 — 1.30 (m, 6H), 0.93 — 0.89 (m, 3H), 0.24 (s, 9H).

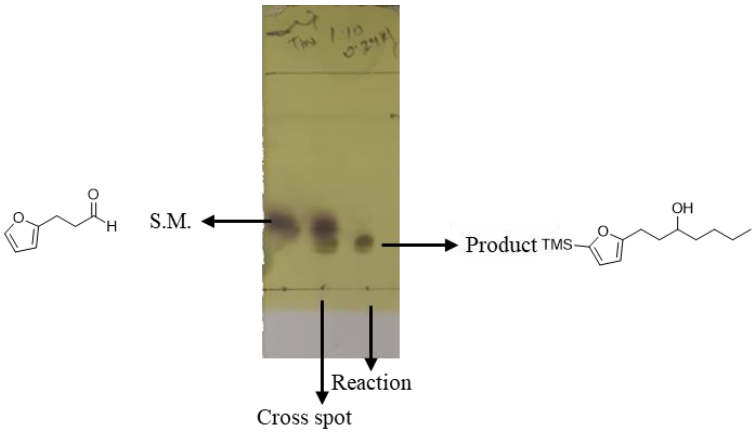
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 160.2, 158.5, 120.4, 105.0, 71.3, 37.1, 35.6, 27.8, 24.5, 22.7, 14.0, -1.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{14}H_{26}O_2Si$ $[M]^+$ 254.1696, found 254.1693

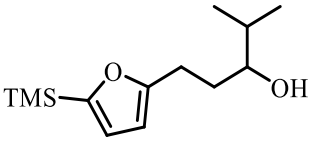
IR (ATR) ν_{max}: 3361, 2957, 2932, 2858, 1250, 1005, 840, 725 cm^{-1}

TLC: R_f = 0.29 (1:10 EtOAc/Hexane)



Back to table of starting materials

4-Methyl-1-(5-(trimethylsilyl)furan-2-yl)pentan-3-ol, 3d



The title compound was prepared according to General procedure E from 3-(furan-2-yl)propanal[7] (300 mg, 2.42 mmol) but used 2.5 eq. *n*-BuLi to give **3d** (121.6 mg, 0.51 mmol, 20.9 %) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (d, J = 3.0 Hz, 1H), 5.99 (d, J = 3.0 Hz, 1H), 3.41 — 3.37 (m, 1H), 2.89 — 2.83 (m, 1H), 2.77 — 2.71 (m, 1H), 1.90 — 1.83 (m, 1H), 1.73 — 1.65 (m, 2H), 0.92 (d, J = 6.9 Hz, 6H), 0.24 (s, 9H).

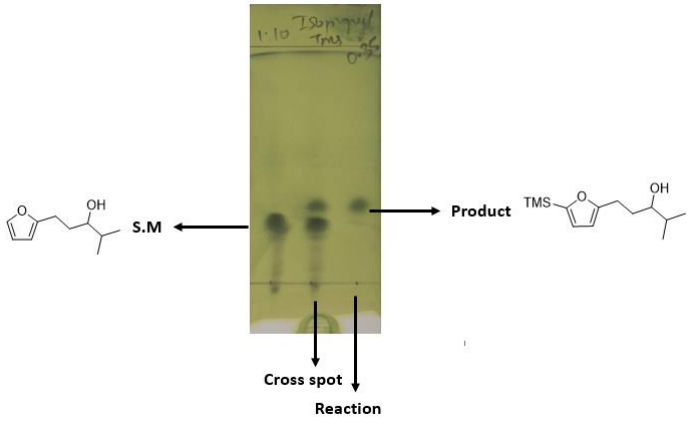
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) δ 160.3, 158.5, 120.4, 105.0, 76.1, 33.6, 32.5, 24.8, 18.7, 17.2, -1.5.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{24}O_2Si$ $[M]^+$ 240.1540, found 240.1540

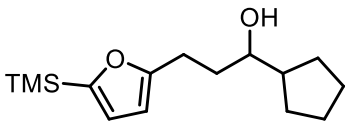
IR (ATR) ν_{max}: 3354, 3110, 2962, 1594, 1250, 843 cm^{-1}

TLC: R_f = 0.35 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-Cyclopentyl-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 3e



The title compound was prepared according to General procedure E from 3-(furan-2-yl)propanal[7] (400 mg, 3.23 mmol) but used 1.3 eq. Grignard reagent and 2.5 eq. *n*-BuLi to give **3e** (55.0 mg, 0.21 mmol, 6.41 %) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.99 (d, 1H, J = 2.9 Hz), 3.45 – 3.39 (m, 1H), 2.90 – 2.72 (m, 2H), 1.95 – 1.59 (m, 8H), 1.38 – 1.17 (m, 3H), 0.24 (s, 9H).

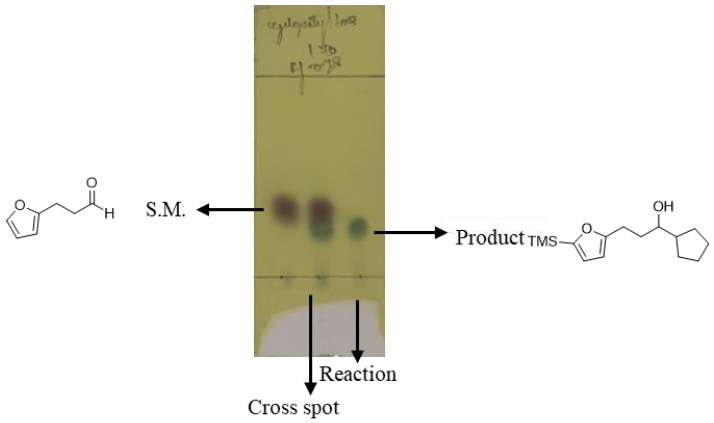
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.5, 120.4, 105.0, 75.3, 46.4, 34.4, 29.1, 28.6, 25.7, 25.6, 24.6, -1.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{15}H_{26}O_2Si$ $[M]^+$ 266.1696, found 266.1697

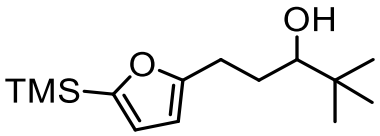
IR (ATR) ν_{max}: 3370, 2959, 2869, 1253, 1008, 835, 758 cm^{-1}

TLC: R_f = 0.28 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-Cyclopentyl-3-(5-(trimethylsilyl)furan-2-yl)propan-1-ol, 3f



The title compound was prepared according to General procedure D from 3-(furan-2-yl)propanal[7] (300 mg, 2.42 mmol) but used 2.5 eq. n-BuLi to give **3f** (40.2 mg, 0.16 mmol, 6.5 %) as a yellowish oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.52 (d, 1H, *J* = 3.1 Hz), 5.99 (d, 1H, *J* = 3.1 Hz), 3.21 (dd, 1H, *J* = 10.6, 1.8 Hz), 2.92 (ddd, 1H, *J* = 14.3, 8.6, 4.8 Hz), 2.73 (dt, 1H, *J* = 15.6, 8.1 Hz), 1.98 — 1.87 (m, 1H), 1.64 — 1.51 (m, 1H), 0.90 (s, 9H), 0.24 (s, 9H).

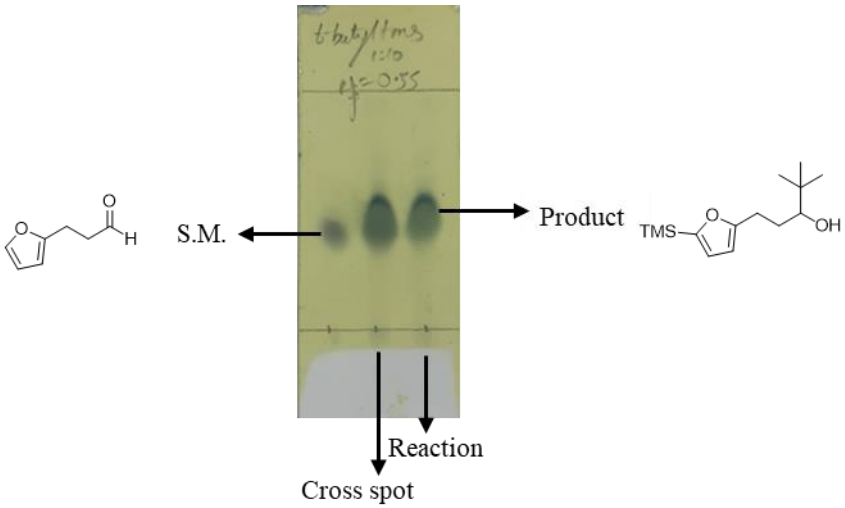
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.4, 158.5, 120.4, 105.1, 79.1, 34.9, 30.0, 25.6, -1.5. (Quaternary carbon peak was not observed)

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{14}H_{26}O_2Si$ $[M]^+$ 254.1696, found 254.1693

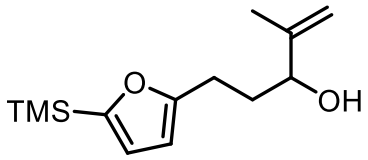
IR (ATR) ν_{max}: 3417, 2956, 2906, 2870, 1763, 1250, 844 cm^{-1}

TLC: R_f = 0.55 (1:10 EtOAc/Hexane)



Back to table of starting materials

2-Methyl-5-(5-(trimethylsilyl)furan-2-yl)pent-1-en-3-ol, 3g



The title compound was prepared according to General procedure E from 3-(furan-2-yl)propanal[7] (300 mg, 2.42 mmol) but used 2.5 eq. n-BuLi to give **3g** (53.7 mg, 0.23 mmol, 9.3 %) as a yellowish oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 6.51 (d, 1H, J = 3.1 Hz), 5.99 (d, 1H, J = 3.1 Hz), 4.98 — 4.97 (m, 1H), 4.87 — 4.87 (m, 1H), 4.12 — 4.10 (m, 1H), 2.79 — 2.67 (m, 2H), 1.98 — 1.83 (m, 2H), 1.74 (s, 3H), 0.24 (s, 9H).

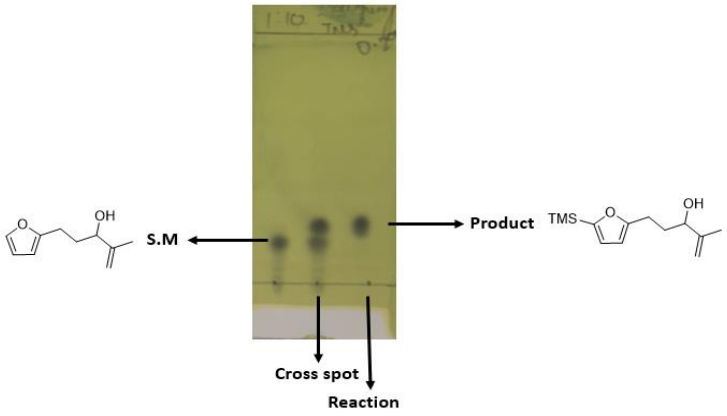
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.0, 160.0, 147.2, 120.4, 111.2, 105.0, 75.1, 33.1, 24.4, 17.6, -1.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{22}O_2Si$ $[M]^+$ 238.1383, found 238.1382

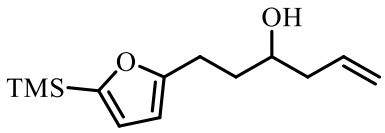
IR (ATR) ν_{max}: 3354, 3074, 2957, 1591, 1252, 842 cm^{-1}

TLC: R_f = 0.29 (1:10 EtOAc/Hexane)



Back to table of starting materials

1-(5-(Trimethylsilyl)furan-2-yl)hex-5-en-3-ol, 3h



The title compound was prepared according to General procedure E from 3-(furan-2-yl)propanal[7] (248 mg, 2.00 mmol) but reflux when the first step to give **3h** (60.9 mg, 0.26 mmol, 13 %) as a yellowish oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.52 (d, 1H, J = 3.1 Hz), 5.99 (d, 1H, J = 3.1 Hz), 5.88 — 5.77 (m, 1H), 5.17 — 5.16 (m, 1H), 5.13 — 5.12 (m, 1H), 3.73 — 3.66 (m, 1H, J = 8.0, 4.3 Hz), 2.88 — 2.72 (m, 2H), 2.36 — 2.15 (m, 2H), 1.91 — 1.74 (m, 2H), 0.24 (s, 9H).

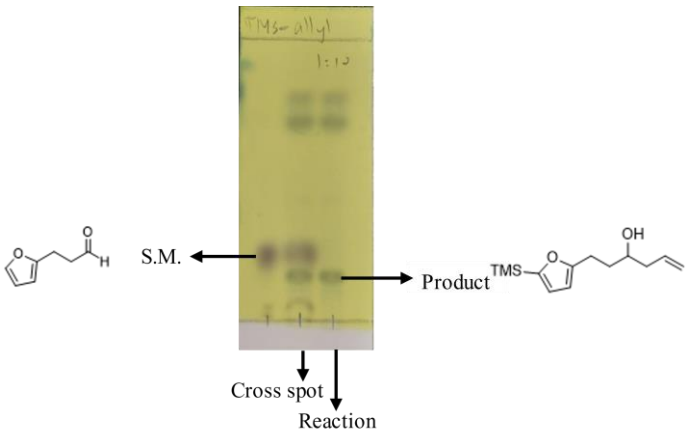
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 160.0, 158.5, 134.6, 120.4, 118.3, 105.0, 70.0, 41.9, 35.0, 24.5, -1.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{13}H_{22}O_2Si$ $[M]^+$ 238.1383, found 238.1381

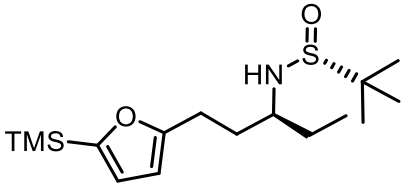
IR (ATR) ν_{max}: 3357, 2956, 1248, 1008, 837, 755 cm^{-1}

TLC: R_f = 0.15 (1:10 EtOAc/Hexane)



Back to table of starting materials

(*R*)-2-Methyl-N-((*S*)-1-(5-(trimethylsilyl)furan-2-yl)pentan-3-yl)propane-2-sulfinamide, 6



The title compound was prepared according to a modified General procedure E. In the first step,[8] 6 equiv. of Grignard reagent was added at -50 °C and warmed to rt to stir overnight. In the second step, 6.0 equiv. *n*-BuLi and 4.0 equiv TMSCl were added. Product **6** (112 mg, 0.435 mmol, 99%) was obtained as a yellowish oil.

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.51 (d, J = 3.0 Hz, 1H), 5.98 – 5.96 (m, 1H), 3.22 – 3.01 (m, 2H), 2.78 – 2.71 (m, 2H), 1.98 – 1.63 (m, 4H), 1.22 (s, 9H), 0.98 – 0.93 (m, 3H), 0.24 (s, 9H).

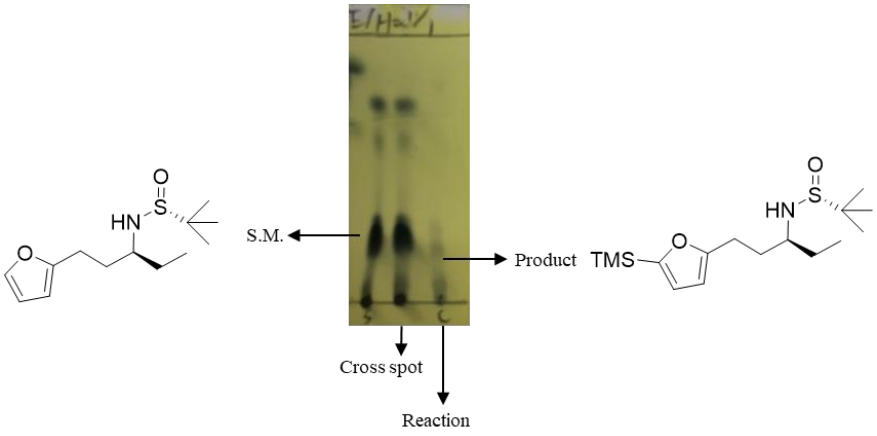
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 159.9, 158.6, 120.4, 105.0, 57.7, 55.9, 33.3, 29.2, 24.2, 22.7, 10.1, -1.6.

See NMR Spectra

HRMS (*m/z*): (EI) calc'd for $C_{16}H_{31}NO_2SiS$ $[M]^+$ 329.1839, found 329.1839

IR (ATR) ν_{max}: 3217, 2957, 1589, 1496, 1363, 1249, 1052, 840 cm^{-1}

TLC: R_f = 0.20 (1:1 EtOAc/Hexane)



Back to contents

5. Applications

5.1. Photoflow reaction

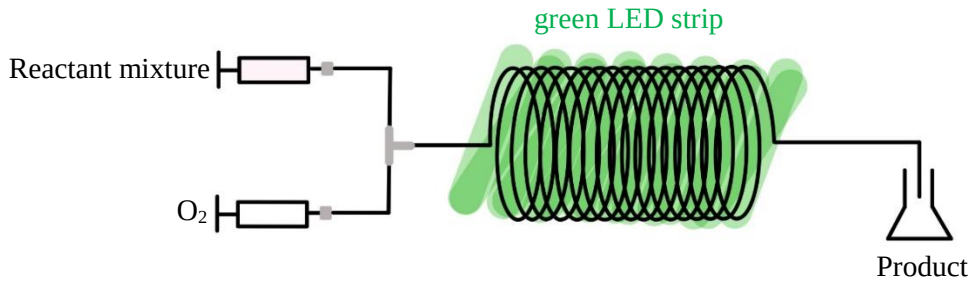


Figure S6. Schematic diagram for the photoflow reactor setup.

Starting material **1a** (351 mg, 1 mmol), Na_2-Eosin Y (6.9 mg, 1 mol%), and diphenyl phosphate (25 mg) were added to a vial, to which a pre-treated ethanol (15 mL), pre-treated by gently bubbling with oxygen for an hour, was added. Subsequently, the resulting solution was transferred to a syringe, where it was pumped to the T-mixer, connected to the inlet of the photoreactor, at 6.5 ml/h through a syringe pump. Simultaneously, oxygen was withdrawn from a balloon using a syringe and an O_2 gas flow of 365 μL/min was maintained to the T-mixer using a syringe pump. The green LEDs were turned on as well as the cooling machine to ensure a consistent reaction temperature. After the reaction mixture were all pumped, the inlet was then connected to and HPLC pump with a flow rate of 0.3 ml/min. The photoflow reactor was allowed to continue to flow until all reaction mixture had been collected in a round bottom flask. After completion, the mixture is concentrated in vacuo and the crude product was purified by filtration over a short pad of silica (KM3 scientific silica gel 45 — 75 μm, diethyl ether) to give **2a** (291 mg, 0.99 mmol, 99%) as a yellow solid.

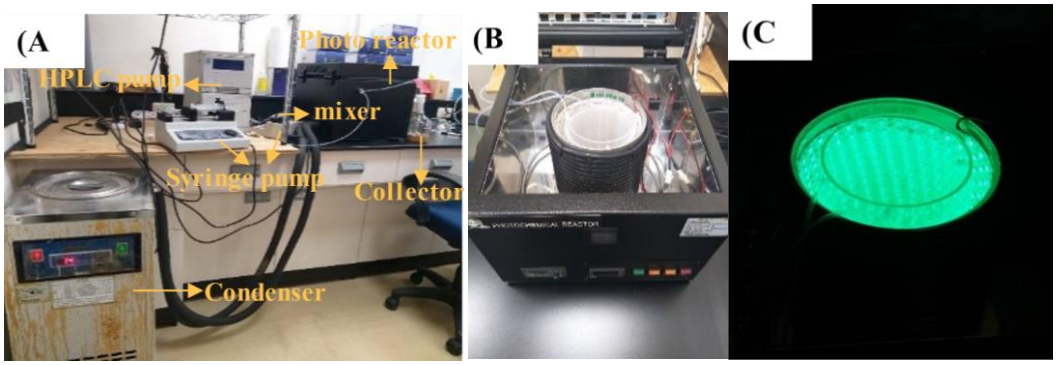


Figure S7. Reaction setup using the photoflow system: (A) full system; (B) photoflow reactor; and (C) “turned on” light source

Photo reactor:	PANCHUM, FLPR-1000
Syringe pump:	LongerPump, LSP01-1A
	KD Scientific, KDS100
HPLC pump:	DIONEX, IP-25 Isocratic Pump
Mixer:	INPAC, U-428
Tube:	PFA, 1/16 (for injection) and 1/8 (after mix)

Back to contents

5.1.1 Calculation of Productivity

Productivity $= Yield \times Flow\ rate \times Concentration$

$$= 0.99 \times 0.3\ \frac{mL}{min} \times 0.067\ \frac{mmol}{mL}$$

$$= 0.02\ \frac{mmol}{min}$$

5.1.2 Calculation of Residence Time

Residence time (t_r) $= \frac{Reaction\ scale\ in\ mmol}{Productivity}$

$$= \frac{1\ mmol}{0.02\ \frac{mmol}{min}}$$

$$= 50\ min$$

Back to contents

5.2. Solvent-free reaction

5.2.1 Procedure for TLC glass plate setup for irradiation under green LED

1a (15 mg, 0.0428 mmol) and Na_2-Eosin Y (0.3 mg, 1 mol%) were dissolved in ethanol in a sample vial. Then, the solution was loaded on the glass TLC plate. After ethanol volatilized, the reaction was placed into an aluminium coil equipped with the green LED strip. After completion of the reaction, the crude product was purified by flash column chromatography (KM3 scientific silica gel 45 — 75 μ m, diethyl ether) to give 2a (12.1, 0.041, 97%) as a yellow solid.

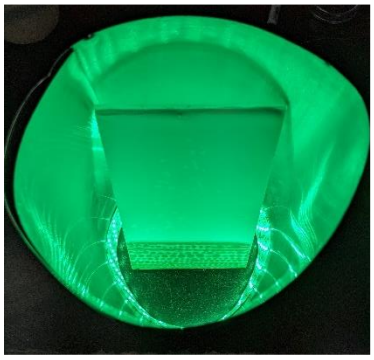


Figure S8. Reaction setup for TLC glass plate irradiation using green LED.

5.2.2. Procedure of TLC glass plate setup for sunlight exposure

1a (15 mg, 0.0428 mmol) and Na_2-Eosin Y (0.3 mg, 1 mol%) were dissolved with ethanol in sample vial. Then the solution was dropped on glass TLC. After ethanol volatilize, the reaction was under sunlight for 10 h. After completion of the reaction, the crude product was purified by flash column chromatography (KM3 scientific silica gel 45 — 75 μm, diethyl ether) to give **2a** (11.5 mg, 0.039 mmol, 92%) as a yellow solid.

Figure S9. Reaction setup of TLC glass plate for sunlight exposure.

Back to contents

5.2.3. Procedure of silica coated setup for sunlight exposure

1a (15 mg, 0.0428 mmol), Na_2-Eosin Y (0.3 mg, 1 mol%) and silica (100 mg) were added to a vial. The solvent ethanol was added to the vial, then concentrated in vacuo. The reactants mixture was spread out on a petri dish. The reaction was placed under sunlight for 12 h (2021/08/22 06:30 – 18:30). After completion of the reaction, the crude product was purified by flash column chromatography (KM3 scientific silica gel 45 — 75 μm, diethyl ether) to give **2a** (12.5 mg, 0.043 mmol, 99%) as a yellow solid.

Figure S10. Reaction setup for solvent-free silica-supported sunlight exposure.

Table S14. Weather during solvent-free sunlight irradiation

	Press		temperature	dew point	RH	WD/WS				Precp		SunShine		visibility	UVI	Cloud
觀測時間 (hour)	測站氣壓 (hPa)	海平面氣壓 (hPa)	氣溫 (°C)	露點溫度 (°C)	相對溼度 (%)	風速 (m/s)	風向 (360degree)	最大陣風 (m/s)	最大陣風風向 (360degree)	降水量 (mm)	降水時數 (h)	日照時數 (h)	全天空日射量 (MJ/m^2)	能見度 (km)	紫外線指數	總雲量 (0~10)
ObsTime	StnPres	SeaPres	Temperature	Td dew point	RH	WS	WD	WSGust	WDGust	Precp	PrecpHour	SunShine	GloblRad	Visb	UVI	Cloud Amount
01	1007.8	1008.6	26.7	22.8	79	0.5	40	4.3	90	0.0	0.0	...	0.00	...	0	...
02	1007.3	1008.1	26.3	22.4	79	0.6	110	3.7	80	0.0	0.0	...	0.00	...	0	...
03	1007.1	1007.9	26.3	21.5	75	1.3	90	3.0	80	0.0	0.0	...	0.00	...	0	...
04	1007.1	1007.9	26.2	21.9	77	1.9	80	3.3	80	0.0	0.0	...	0.00	...	0	...
05	1007.0	1007.8	26.2	21.6	76	1.2	90	3.9	80	0.0	0.0	...	0.00	...	0	...
06	1007.5	1008.3	26.1	21.3	75	0.5	80	2.6	70	0.0	0.0	0.1	0.02	...	0	...
07	1007.9	1008.7	27.0	21.1	70	0.3	320	3.3	80	0.0	0.0	1.0	0.50	...	0	...
08	1008.4	1009.2	29.1	21.6	64	0.8	90	3.0	110	0.0	0.0	1.0	1.39	10.0	1	2.0
09	1008.3	1009.1	30.9	23.6	65	1.8	290	3.6	270	0.0	0.0	1.0	2.18	11.0	4	4.0
10	1008.2	1009.0	30.8	24.7	70	2.3	290	4.3	290	0.0	0.0	1.0	3.03	...	7	...
11	1008.2	1009.0	30.8	25.2	72	2.9	300	5.6	290	0.0	0.0	1.0	3.52	11.0	10	3.0
12	1008.0	1008.8	30.9	25.0	71	2.2	290	6.1	280	0.0	0.0	1.0	3.71	...	11	...
13	1007.7	1008.5	31.0	25.4	72	1.7	280	6.2	290	0.0	0.0	1.0	3.74	...	11	...
14	1006.9	1007.7	31.0	25.6	73	1.0	300	6.3	290	0.0	0.0	1.0	3.28	10.0	9	3.0
15	1006.3	1007.1	31.4	24.6	67	1.6	290	5.0	300	0.0	0.0	1.0	2.98	...	7	...
16	1006.1	1006.9	31.1	25.0	70	2.4	300	5.6	270	0.0	0.0	1.0	2.24	...	4	...
17	1005.5	1006.3	30.8	24.9	71	2.7	290	5.9	300	0.0	0.0	1.0	1.73	10.0	1	5.0
18	1006.0	1006.8	29.9	24.1	71	2.1	280	5.6	300	0.0	0.0	0.5	0.46	...	0	...
19	1006.5	1007.3	29.6	24.3	73	1.0	300	3.5	270	0.0	0.0	0.0	0.04	...	0	...

Back to contents

5.2.4. Silica loaded reaction mixture under normal household light irradiation

1a (1000 mg, 2.85 mmol), Na_2-Eosin Y (19.7 mg, 1 mol%) and silica (2000 mg) were added to a flask. The solvent ethanol was added to the flask, then concentrated in vacuo. The reactants mixture was spread out on a PET box. The reaction was placed under room lamp for 24 h. After completion of the reaction, the crude product was purified by flash column chromatography (KM3 scientific silica gel 45 − 75 μm, diethyl ether) to give **2a** (798.8 mg, 2.73 mmol, 95.8%) as a yellow solid.

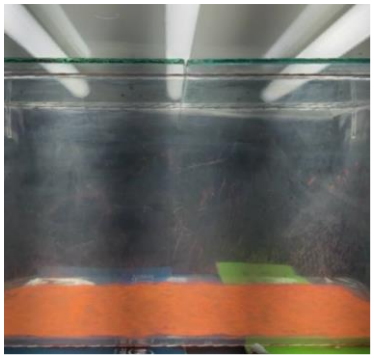


Figure S11. Reaction setup for solvent-free silica-supported household light irradiation.

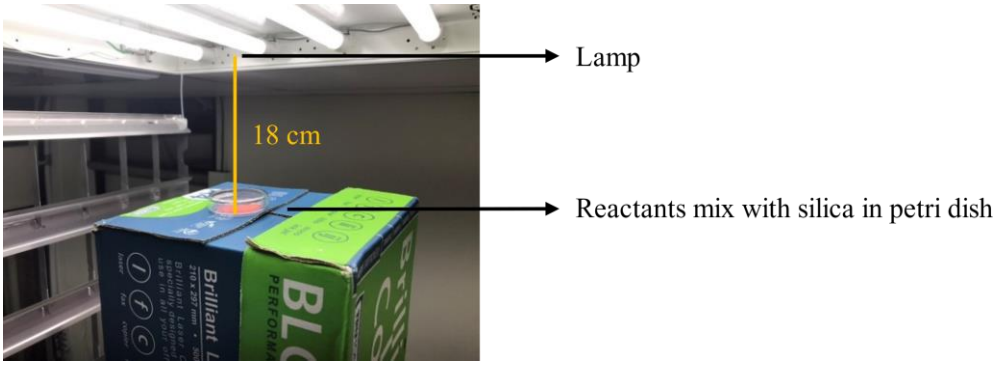


Figure S12. Reaction setup for solvent-free silica-supported lamp irradiation

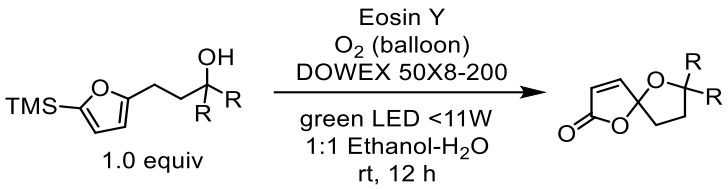
Room lamp:	TLW, FOE-T8-2-65K-9W
Petri dish diameter:	5.5 (cm)
PP box:	LocknLock, HPL826, 248 X 180 X 93 mm
PET box:	SHUEI SHUN INDUSTRIAL, 336 X 165 X 150 mm

Back to contents

6. Preliminary Mechanism Studies

6.1. Control reactions

Table S15. Control reactions performed

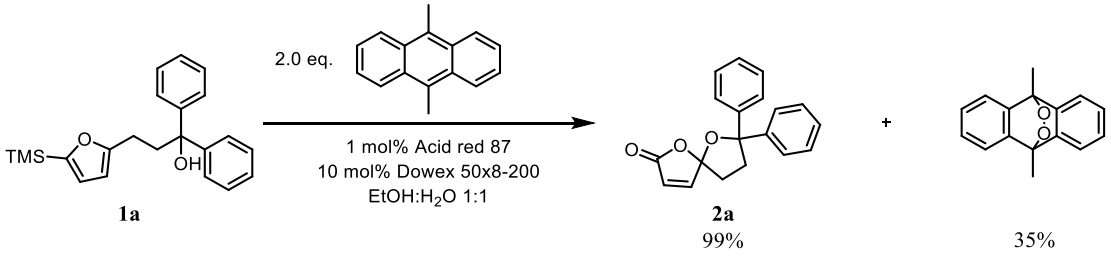


Entry	Condition	Yield (%)
1	without light	N.R.
2	without photocatalyst	N.R.
3	without oxygen	N.R.
4	without silyl group	15
5	air bubble (stir for 12 h)	77
6	air bubble (stir for 18 h)	99
7	water as solvent	47

Based on General procedure A, but the reaction conditions were changed accordingly as specified in the table.

6.2. Detection of formed singlet oxygen

9,10-Dimethylanthracene was known as a singlet oxygen trap. According to the General procedure A but added 2.0 eq. 9,10-dimethylanthracene(DMA). The cycloaddition product was 35% yield which was added 1, 3, 5-trimethoxybenzene as internal standard for NMR yield determination. This result clearly verify the formation of singlet oxygen and the NMR spectra correspond with Wang's group.[9]



Scheme S6. Using DMA as singlet oxygen trap

Back to contents

6.3. Light on/off experiment

To investigate what character does the light source play in this reaction, we tried to switch the light on and off to observe how the yield changes.

1a (1.0 eq.), Na_2-Eosin Y (1 mol%) and Dowex 50X8-200 (10 mol%) were added to a test tube, followed by purging with O2 for three times. The solvent (EtOH/H2O = 1/1) was added to the test tube before pretreament of oxygen gently bubbled for 1 h. The reaction was placed into an aluminum coil equipped with green LED strip. The mixture was stirred vigorously under irradiation for different times but total reaction time was fixed for 12 h. After completion of the reaction, the solution was extracted with EtOAc and dried with MgSO4, then concentrated in vacuo. The crude product was purified by flash column chromatography (KM3 scientific silica gel 45 — 75 μ m, diethyl ether) to give oxaspirolactone. And 4.55 μL of 1, 1, 2, 2-tetrachloroethane was added to the vial as internal standard for NMR yield determination.

Table S16. Light on/off experiment

Entry	Irradiation time (min)	Total reaction time (h)	2a yield (%)
1	10	12	14
2	30	12	56
3	60	12	82
4	180	12	99
5	360	12	99
6	540	12	99
	720	12	99

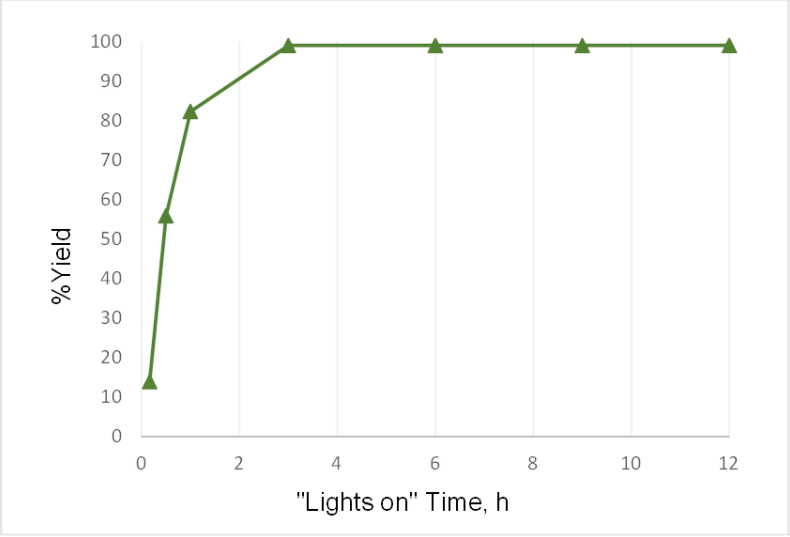


Figure S13. Yields obtained from varying irradiation time.

Back to contents

6.3. Reaction monitoring

1a (1.0 eq.), Na_2-Eosin Y (1 mol%) and Dowex 50X8-200 (10 mol%) were added to a test tube, followed by purging with O2 for three times. The solvent (EtOH/H2O = 1/1) was added to the test tube, which was pre-treated with oxygen by bubbling gently for 1 h. The reaction was placed into an aluminium coil equipped with green LED strip. The mixture was stirred vigorously under continuous irradiation. After completion of the reaction, the solution was extracted with EtOAc and dried with MgSO4, then concentrated in vacuo. The crude product was purified by flash column chromatography (KM3 scientific silica gel 45 – 75 μm, diethyl ether) to give oxaspirolactone 2a. Lastly, 4.55 µL of 1,1,2,2-tetrachloroethane was added to the vial as internal standard for NMR yield determination.

Table S17. Lights on/off experiment.

Entry	Lights on (min)	Lights off (min)	**1a** residual content (%)	**2a** yield (%)
1	0	0	100	0
2	10	0	72	28
3	30	0	56	37
4	60	0	24	76
5	120	0	13	85
6	180	0	0	94

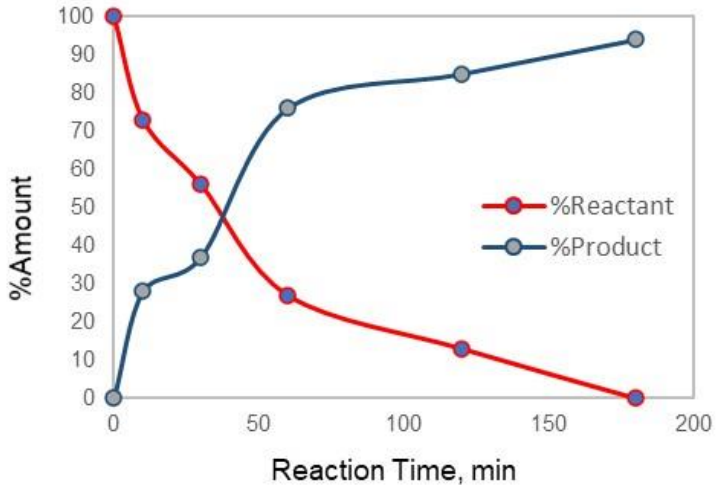


Figure S14. Yields of product and recovery of starting materials in varying reaction times.

Back to contents

6.4. Plausible mechanism

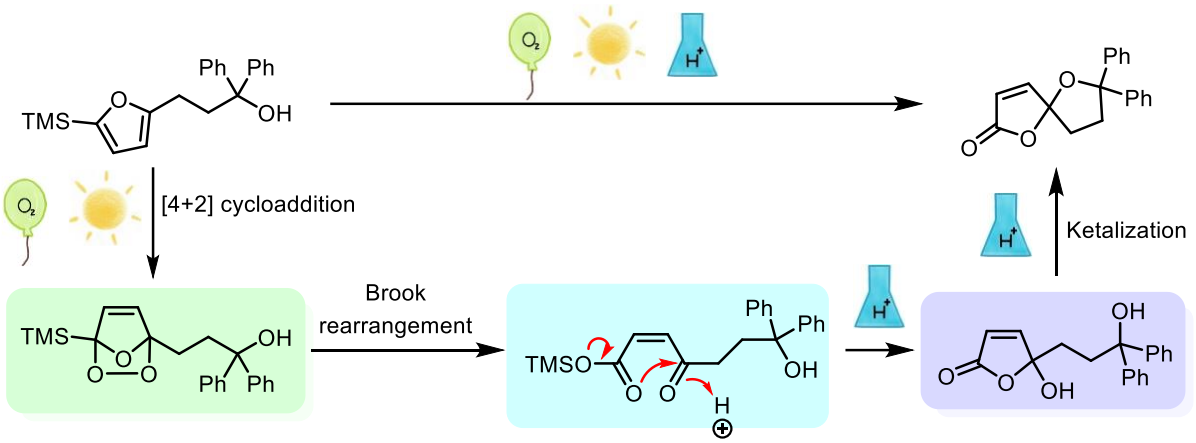


Figure S15. Plausible mechanism for the synthesis of oxaspirolactones.

Back to contents

7. EcoScale and Green Metrics

7.1. EcoScale

7.1.1. EcoScale[10] price calculation (for item 2)

To project the price of compound **1a**, the price was calculated from the prices of the reagents used for its preparation.

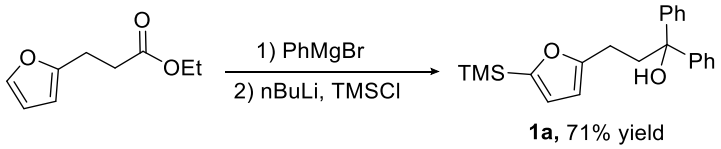
Total mmol of compound **1a** needed to prepare 10 mmol of product **2a**
= 10 mmol product **2a**/Yield = 10 mmol **2a**/0.99 = 10.10 mmol **2a**

Table S18. Calculation of Price(USD)/mol for each reagent.

Reagent	Price (USD)/bottle[a]	MW (g/mol)	Total mmol of bottle	Price (USD)/mmol
Ethyl 3-(2-furanyl)propanoate	131.97/25 g	168.19	148.64	0.89
Trimethylsilane chloride	125.53/500 mL	108.64	3958.03	0.03
n-Butyl lithium (2.5 M in hexanes)	428.11/1000 mL	64.06	2500.00	0.17
Phenyl magnesium bromide (1 M in THF)	189.91/800 mL	181.31	800.00	0.24
Na_2-Eosin Y	74.03/25 g	691.85	36.14	2.05
Dowex 50X8-200 (4.83 mmol/g)	489.26/100 g	---	483.00	1.01

[a]Prices are based on the Sigma-Aldrich website, accessed on September 14, 2022.

Price for each reagent needed to prepare 10.10 mmol of compound **1a**



1a, 71% yield

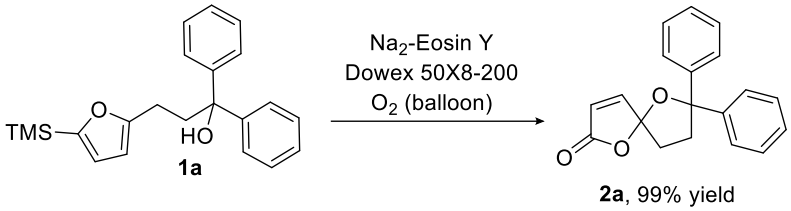
Scheme S7. Synthesis of starting materials **1a**.

Table S19. Calculation of Price(USD)/reaction for each reagent to prepare 10.10 mmol of **1a**.

Reagent	Reaction Equiv.	Yield for **1a**	Amount (mmol) in reaction	Price (USD) for the reaction
Ethyl 3-(2-furanyl)propanoate	1.00	0.71	14.23	12.63
Trimethylsilane chloride	3.00	0.71	42.68	1.35
n-Butyl lithium	2.80	0.71	39.83	6.82
Phenyl magnesium bromide	2.50	0.71	35.56	8.44
Total price to prepare 10.10 mmol of compound **1a** =				29.25

Back to contents

Price for each reagent need to prepare 10 mmol of compound **2a**



Scheme S8. Synthesis of oxaspirolactone **2a**.

Table S20. Calculation of Price(USD)/reaction for each reagent to prepare 10.0 mmol of **2a**

Reagent	Reaction Equiv.	Yield for **1a**	Amount (mmol) in reaction	Price (USD) for the reaction
Compound **1a**	1.00	0.99	10.10	29.25
Na_2-Eosin Y	0.01	0.99	0.10	0.21
Dowex 50-X8	0.10	0.99	1.02	1.03
Total price to prepare 10 mmol of compound **2a** =				30.49

Note: Oxygen is excluded in the calculations.

Back to contents

7.1.2. Screenshots of Prices from Sigma-Aldrich Website (accessed September 14, 2022)

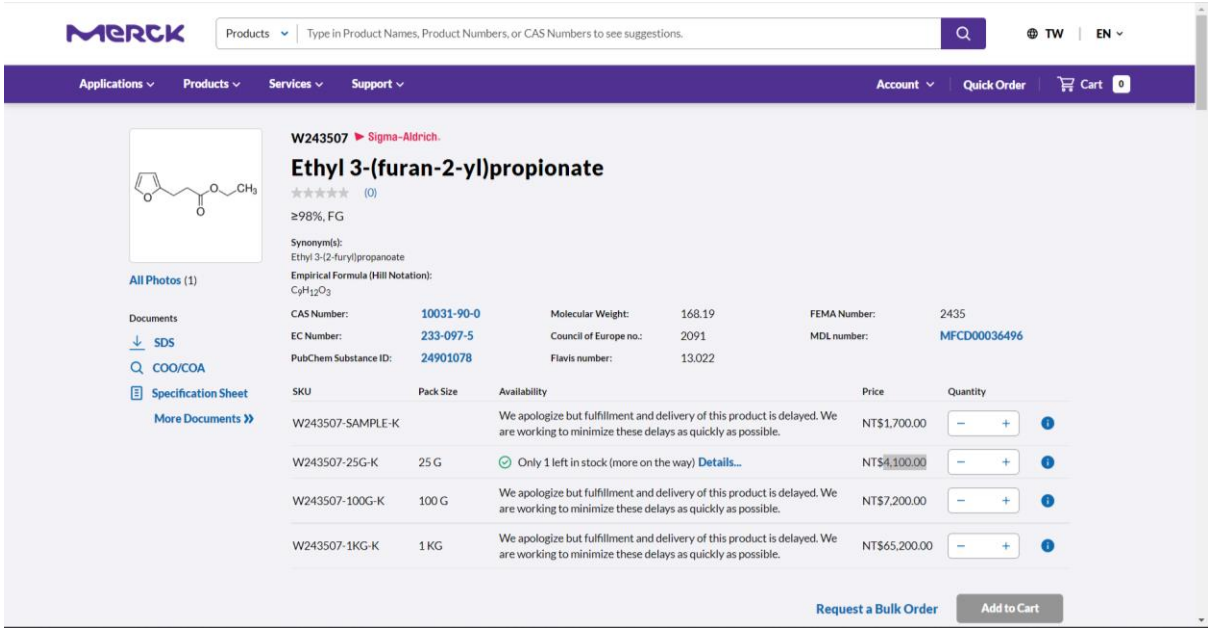


Figure S16. Screenshot of the Sigma-Alrich website for the price of ethyl 3-(furan-2-yl)propionate.

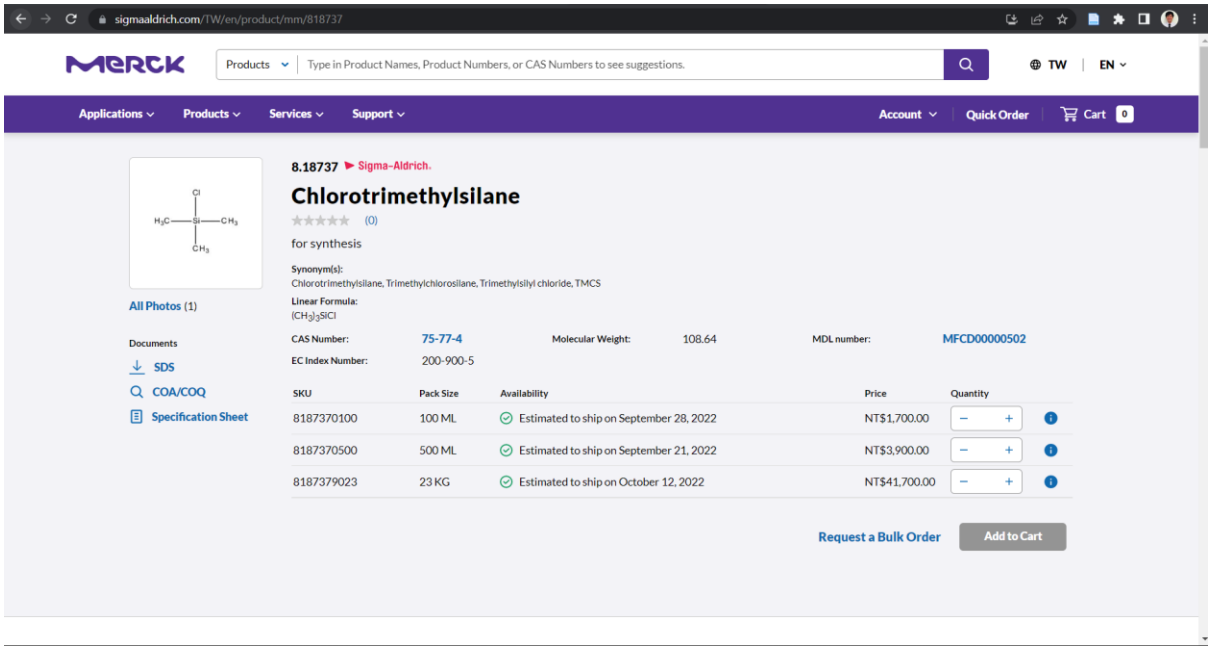


Figure S17. Screenshot of the Sigma-Alrich website for the price of chlorotrimethylsilane.

Back to contents

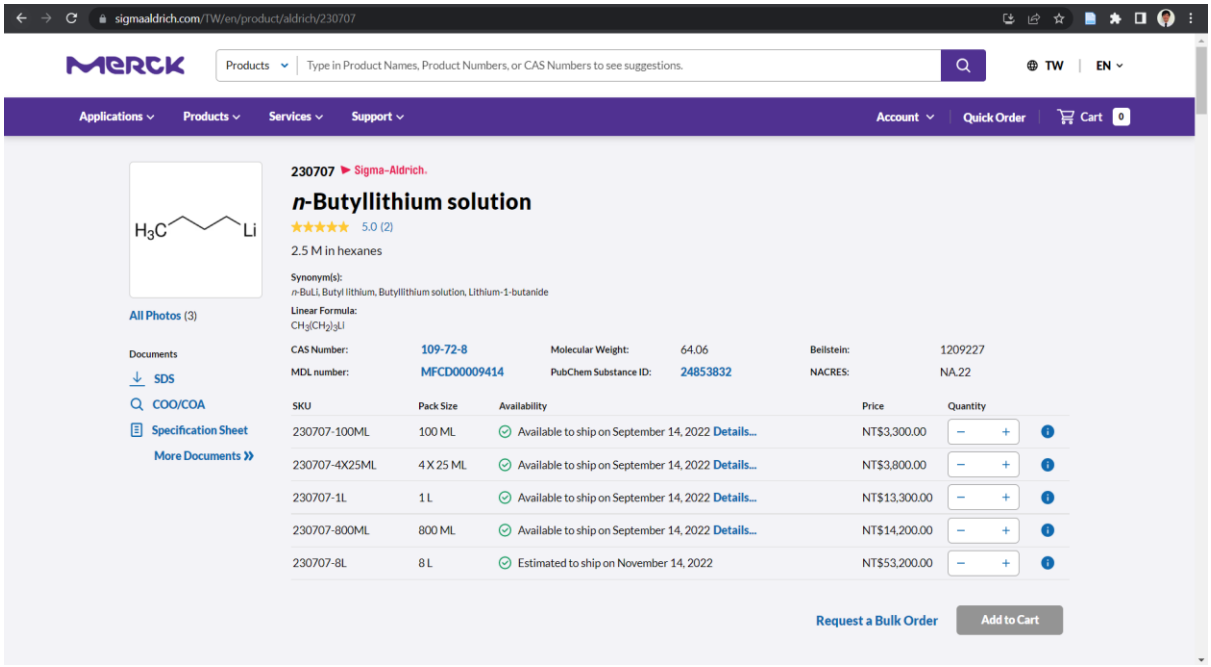


Figure S18. Screenshot of the Sigma-Alrich website for the price of *n*-butyllithium solution.

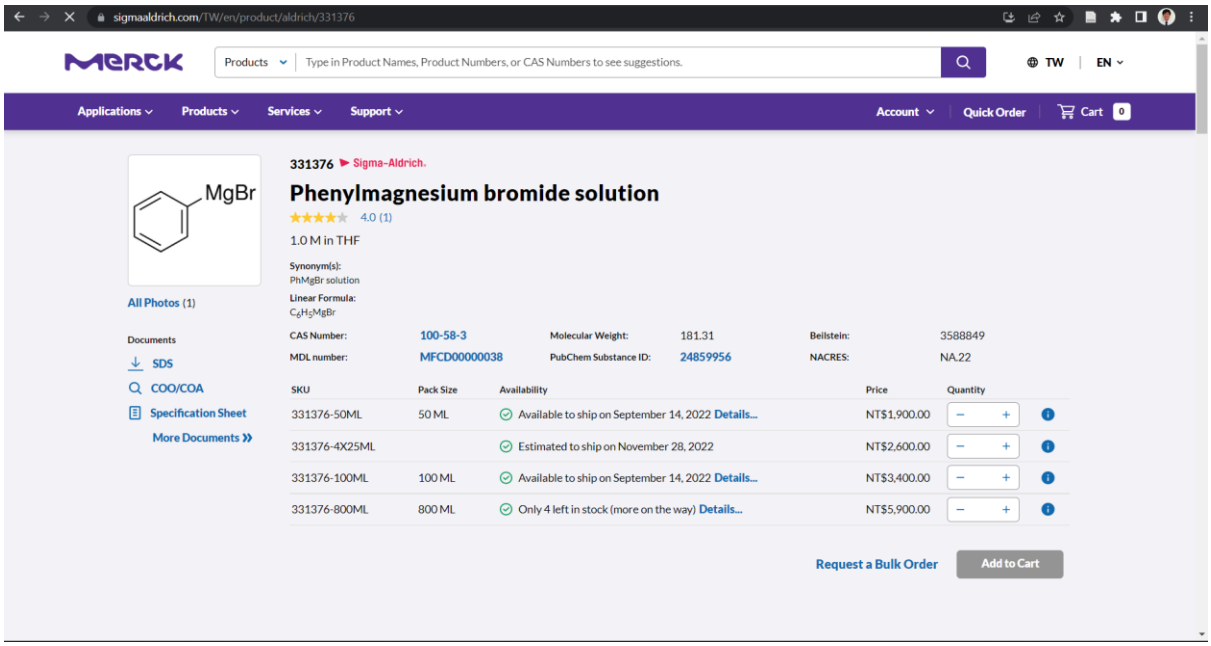


Figure S19. Screenshot of the Sigma-Alrich website for the price of phenyl magnesium bromide.

Back to contents

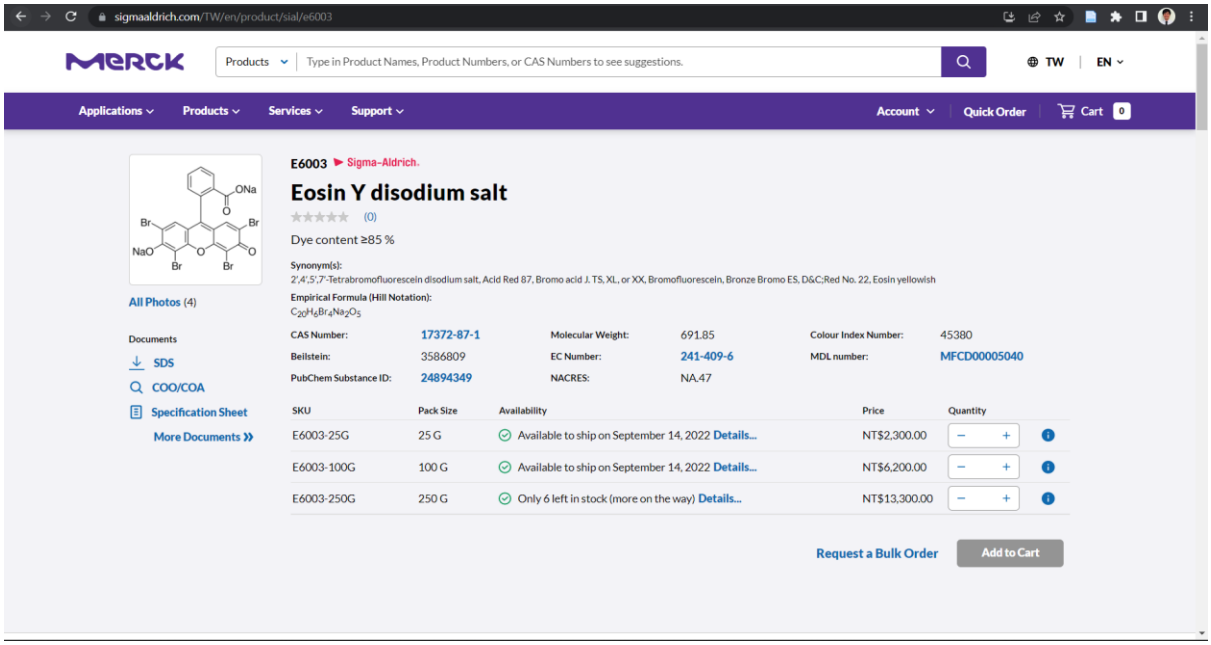


Figure S20. Screenshot of the Sigma-Alrich website for the price of Eosin Y disodium salt.

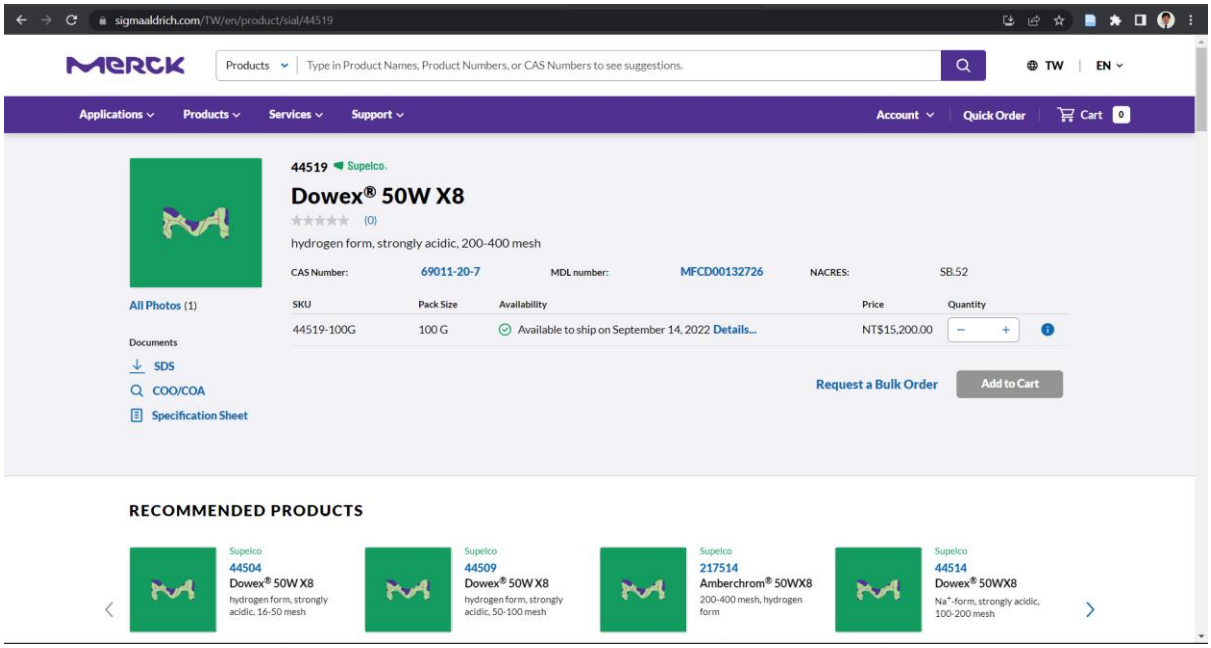


Figure S21. Screenshot of the Sigma-Alrich website for the price of Dowex 50W X8.

Back to contents

7.1.3. Conversion of prices in New Taiwan Dollar (NTD) to US Dollar (USD)

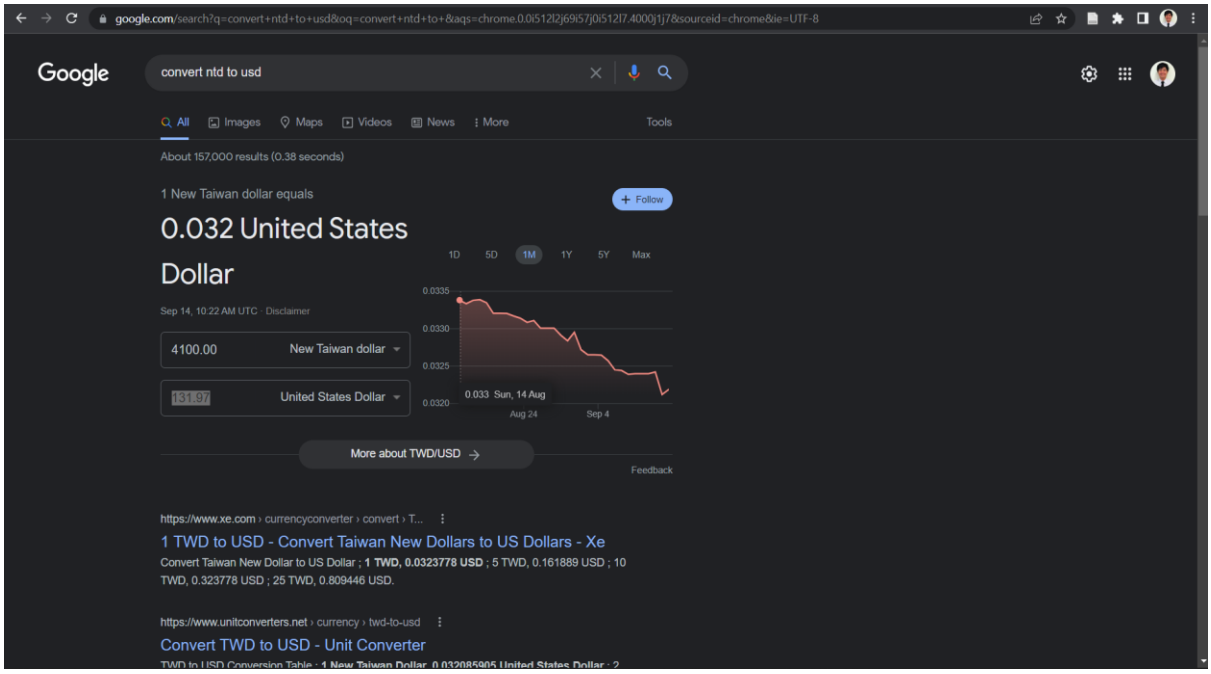


Figure S22. Conversion for the price of ethyl 3-(furan-2-yl)propionate in NTD to USD.

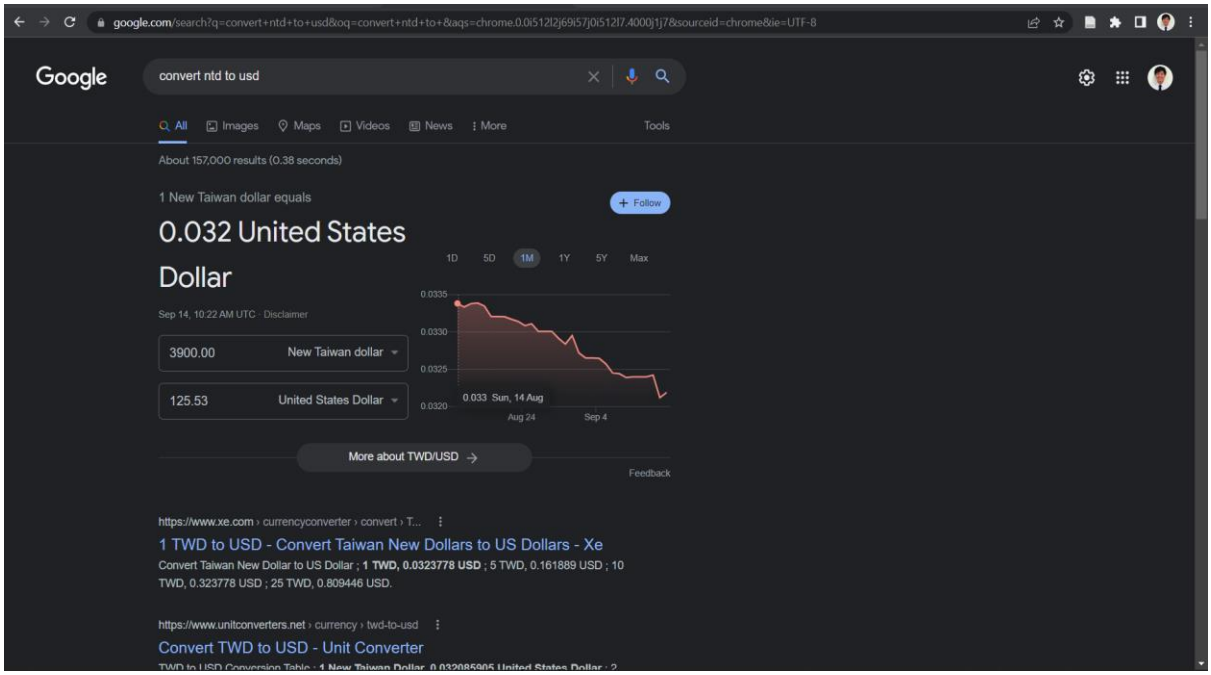


Figure S23. Conversion for the price of chlorotrimethylsilane in NTD to USD.

Back to contents

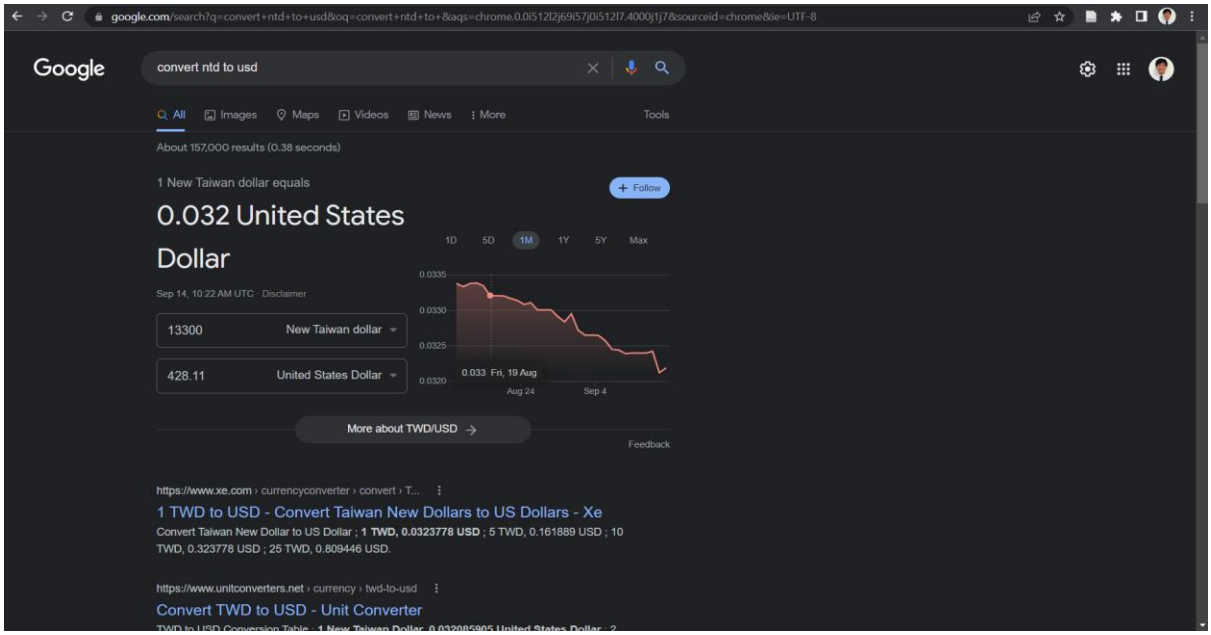


Figure S24. Conversion for the price of *n*-butyllithium solution in NTD to USD.

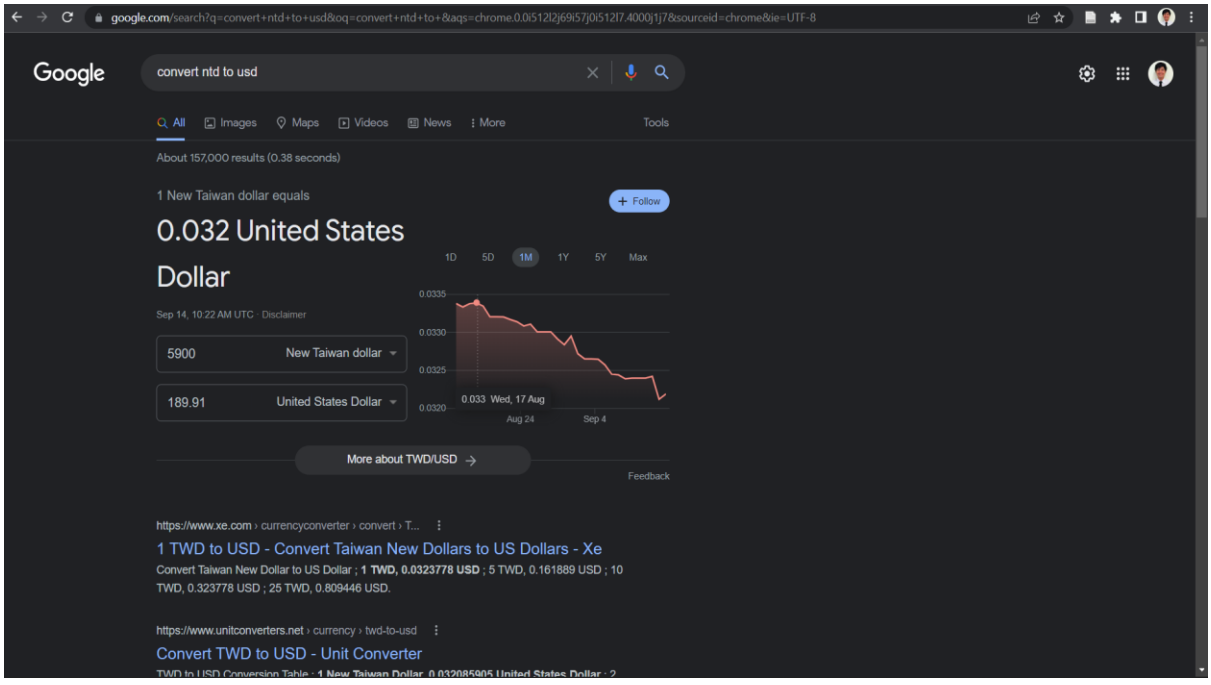


Figure S25. Conversion for the price of phenyl magnesium bromide in NTD to USD.

Back to contents

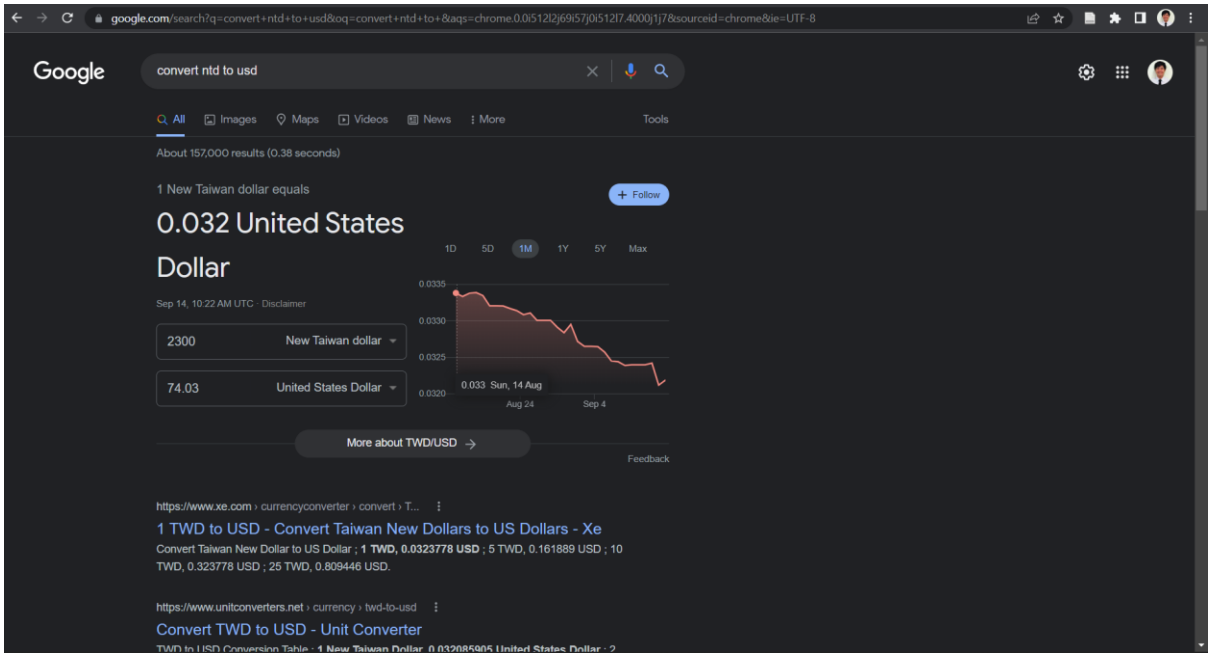


Figure S26. Conversion for the price of Eosin Y disodium salt in NTD to USD.

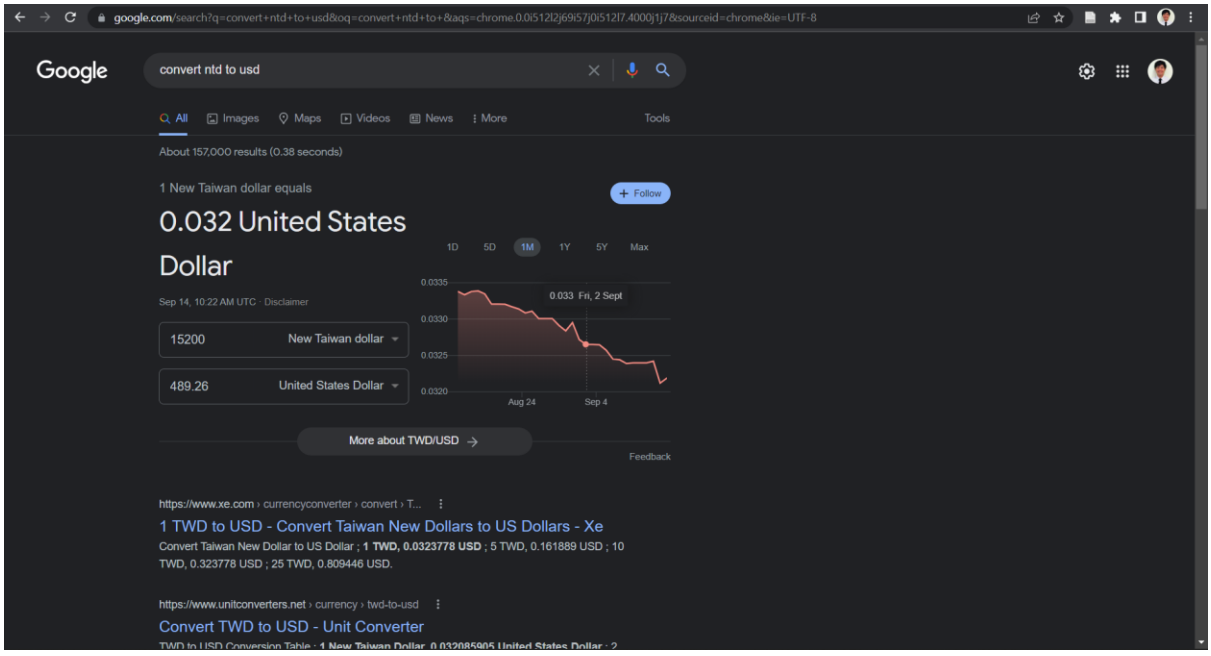


Figure S27. Conversion for the price of Dowex 50W X8 in NTD to USD.

Back to contents

7.1.4. EcoScale Penalty Point Calculation

Table S21. Penalty Calculation for the synthesis of **2a** in batch, flow, and solvent-free conditions.

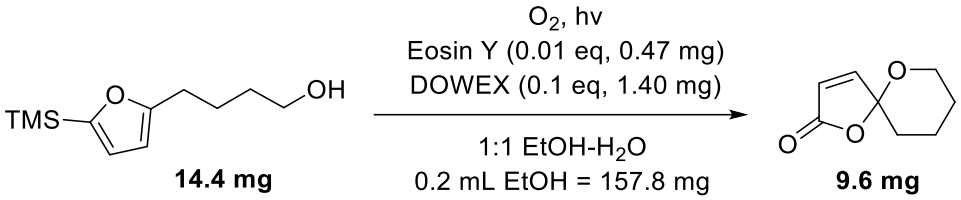
Parameters	Penalty Points		
	Batch	Flow	Solvent-free
1. Yield: (100-%Yield)/2	0.5	0.5	1.5
2. Price of reaction components (to obtain 10 mmol of end product) a)Starting material **1a** = USD 29.25 b) Na_2-Eosin Y = USD 0.21 c)Dowex 50X8-200 = USD 1.03 Total price = USD 30.49 Thus, inexpensive (<USD 10)	0	0	0
3. Safety Ethanol: F (highly flammable)	5	5	0
4. Technical Setup Unconventional activation technique	2	2	0
5. Temperature/Time Room temperature, <24 h	1	1	1
6. Work-up and Purification Ethyl acetate: adding solvent Liquid-liquid extraction Simple filtration	 0 3 0	 0 3 0	 0 3 0
Total Penalty Points =	11.5	11.5	5.5
B. EcoScale Calculation EcoScale = 100 – Total Penalty Points	88.5	88.5	94.5
C. Conclusion	>75 = excellent synthesis		

See Reference 10 for complete list of penalty points.

Back to contents

7.2. Green metrics

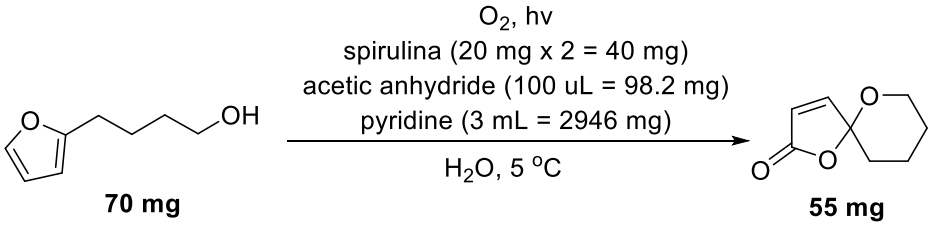
Path A



Scheme S9. Synthesis of **2o** from 2-silylated hydroxyalkylfuran **1o**.

1. Isolated Yield (%) = 92%
2. E-factor = $\frac{14.4\ mg + 0.47\ mg + 1.40\ mg\ - 9.6\ mg}{9.6\ mg} = 0.7$
3. Atom Economy (%) = $\frac{154.1650\ g/mol}{212.3640\ g/mol + 32\ g/mol\ (O_2)} \times 100 = 63.1\%$
4. Reaction Mass Efficiency (%) = $\frac{9.6\ mg}{14.4\ mg} \times 100 = 66.7\%$
5. Process Mass Intensity = $\frac{14.4\ mg + 0.47\ mg + 1.4\ mg}{9.6\ mg} = 1.7$

Path B[11]

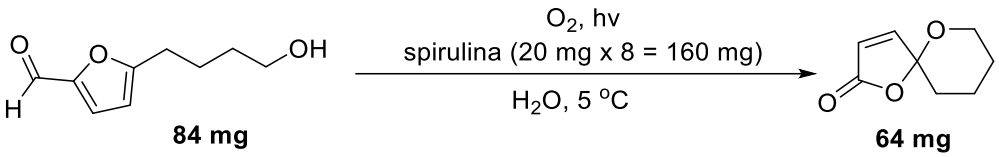


Scheme S10. Reported synthesis of **2o** from 4-(furan-2-yl)butan-1-ol.

1. Isolated Yield (%) = 71%
2. E-factor = $\frac{70\ mg + 40\ mg + 98.2\ mg + 2946\ mg - 55\ mg}{55\ mg} = 56.3$
3. Atom Economy (%) = $\frac{154.1650\ g/mol}{140.1820\ g/mol + 32\ g/mol\ (O_2)} \times 100 = 89.5\%$
4. Reaction Mass Efficiency (%) = $\frac{55\ mg}{70\ mg} \times 100 = 78.6\%$
5. Process Mass Intensity = $\frac{70\ mg + 40\ mg + 98.2\ mg + 2946\ mg}{55\ mg} = 57.3$

Back to contents

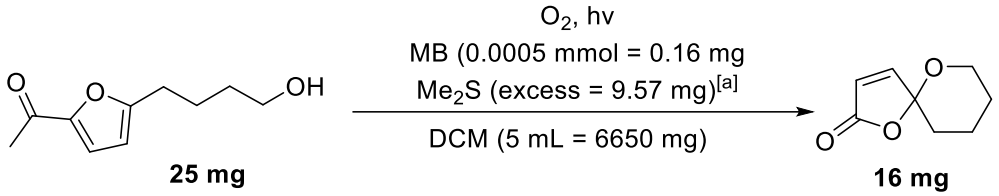
Path C[11]



Scheme S11. Reported synthesis of **2o** from 5-(4-hydroxybutyl)furan-2-carbaldehyde.

1. Isolated Yield (%) = 83%
2. E-factor = $\frac{84\ mg + 160\ mg - 64\ mg}{64\ mg} = 2.8$
3. Atom Economy (%) = $\frac{154.1650\ g/mol}{168.1920\ g/mol + 32\ g/mol\ (O_2)} \times 100 = 77.0\%$
4. Reaction Mass Efficiency (%) = $\frac{64\ mg}{84\ mg} \times 100 = 76.2\%$
5. Process Mass Intensity = $\frac{84\ mg + 160\ mg}{64\ mg} = 3.8$

Path D[12]



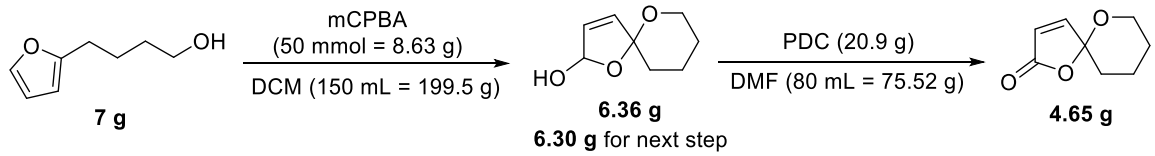
Scheme S12. Reported synthesis of **2o** from 1-(5-(4-hydroxybutyl)furan-2-yl)ethan-1-one.

1. Isolated Yield (%) = 75%
2. E-factor = $\frac{25\ mg + 0.16\ mg + 9.57\ mg + 6650\ mg - 16\ mg}{16\ mg} = 416.8$
3. Atom Economy (%) = $\frac{154.1650\ g/mol}{182.2190\ g/mol + 32\ g/mol\ (O_2)} \times 100 = 72.0\%$
4. Reaction Mass Efficiency (%) = $\frac{16\ mg}{25\ mg} \times 100 = 64.0\%$
5. Process Mass Intensity = $\frac{25\ mg + 0.16\ mg + 9.57\ mg + 6650\ mg}{16\ mg} = 417.8$

[a]Assuming that the excess Me_2S added is in 1.1 equivalence to the starting material.

Back to contents

Path E[13]



Scheme S13. Reported two-step synthesis of **2o** from 4-(furan-2-yl)butan-1-ol.

1. Isolated Yield (%) = 0.8155 × 0.7851 = 64.0%
2. E-factor = $\frac{7\ g + 8.63\ g + 199.5\ g - 6.36\ g}{6.36\ g} + \frac{6.30\ g + 20.9\ g + 75.52\ g - 4.65\ g}{4.65\ g} = 32.8 + 21.1 = 53.9$
3. Atom Economy (%) = $\frac{156.1810\ g/mol}{140.1820\ g/mol + 172.5640\ g/mol\ (mCPBA)} \times \frac{154.1650\ g/mol}{156.1810\ g/mol} \times 100 = 49.3\%$
4. Reaction Mass Efficiency (%) = $\frac{6.36\ g}{7\ g} \times \frac{4.65\ g}{6.30\ g} \times 100 = 67.1\%$
5. Process Mass Intensity = $\frac{7\ g + 8.63\ g + 199.5\ g}{6.36\ g} + \frac{6.30\ g + 20.9\ g + 75.52\ g}{4.65\ g}$
$= 33.8 + 22.1 = 55.9$

Back to contents

8. References

(1) S. Engle, *Org. Synth.*, 2019, **96**, 455–473.

(2) C. B. Kelly, M. A. Mercadante, R. J. Wiles, N. E. Leadbeater, *Org. Lett.*, 2013, **15**, 2222– 2225

(3) M. Sun, Y. Deng, E. Batyreva, W. Sha, R. G. Salomon, *J. Org. Chem*., 2002, **67**, 3575−3584.

(4) M. Rehan, S. Maity, L. K. Morya, K. Pal, P. Ghorai, *Angew. Chem. Int. Ed.*, 2016, **55**, 7728–7732.

(5) D. Drikermann, V. Kerndl, H. Görls, I. Vilotijevic, *Synlett*, 2020, **31**, 1158–1162.

(6) K. Wei, H.-T. Gao, W.-D. Z. *J.* Li, *Org. Chem.*, 2004, **69**, 5763-5765.

(7) A. Zúñiga, G. Pazos, P. Besada, Y. Fall, *Tetrahedron Lett.*, 2012, **53**, 4293–4295.

(8) a) L. Nielsen, K. B. Lindsay, J. Faber, N. C. Nielsen, T. Skrydstrup, *J. Org. Chem.*, 2007, **72**, 10035–10044. b) G. Liu, D. A. Cogan, J. A. Ellman, *J. Am. Chem. Soc.*, 1997, **119**, 9913–9914.

(9) X. Zhang, Y. Han, G. Liu, F. Wang, *Chin. Chem. Lett.*, 2019, **30**, 1927– 1930.

(10) K. Van Aken, L. Strekowski, L. Patiny, *Beilstein J. Org. Chem.*, 2006, 2.

(11) D. Noutsias, I. Alexopoulou, T. Montagnon, G. Vassilikogiannakis, *Green Chem.*, 2012, **14**, 601–604.

(12) M. Tofi, T. Montagnon, T. Georgiou, G. Vassilikogiannakis, *Org. Biomol. Chem.*, 2007, **5**, 772–777.

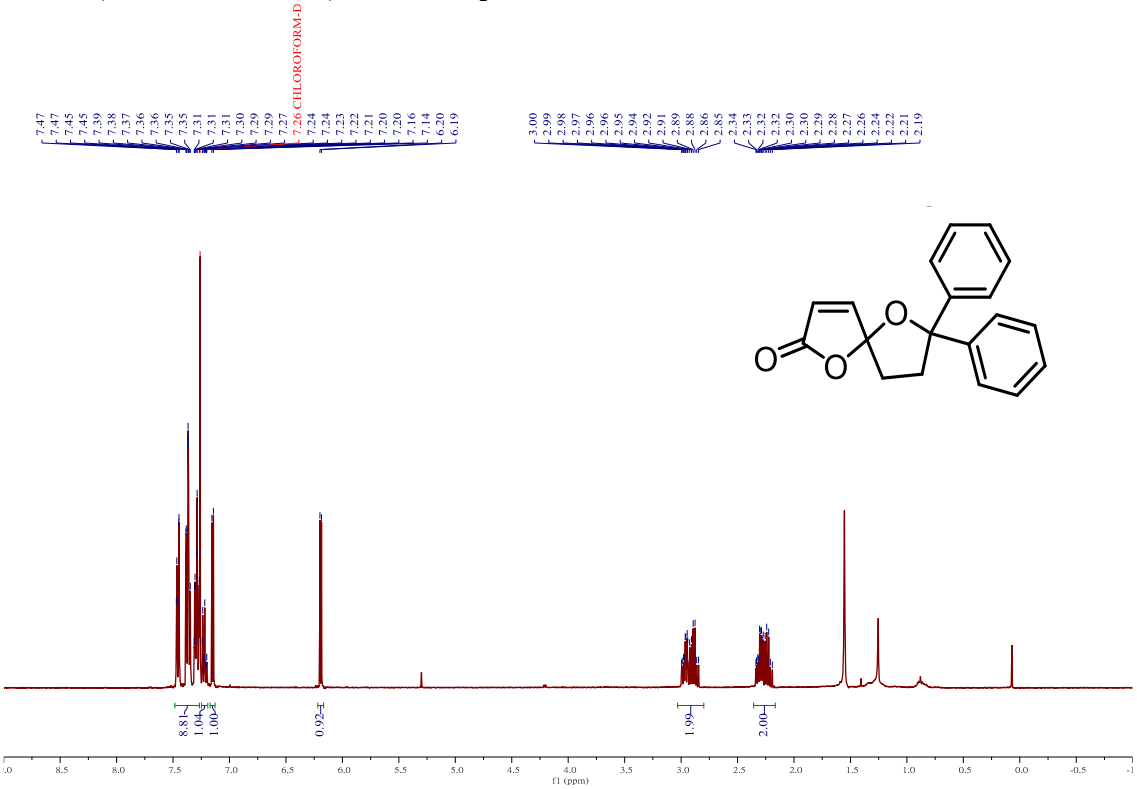
(13) J. Robertson, P. Meo, J. W. P. Dallimore, B. M. Doyle, C. Hoarau, *Org. Lett.*, 2004, **6**, 3861.

Back to contents

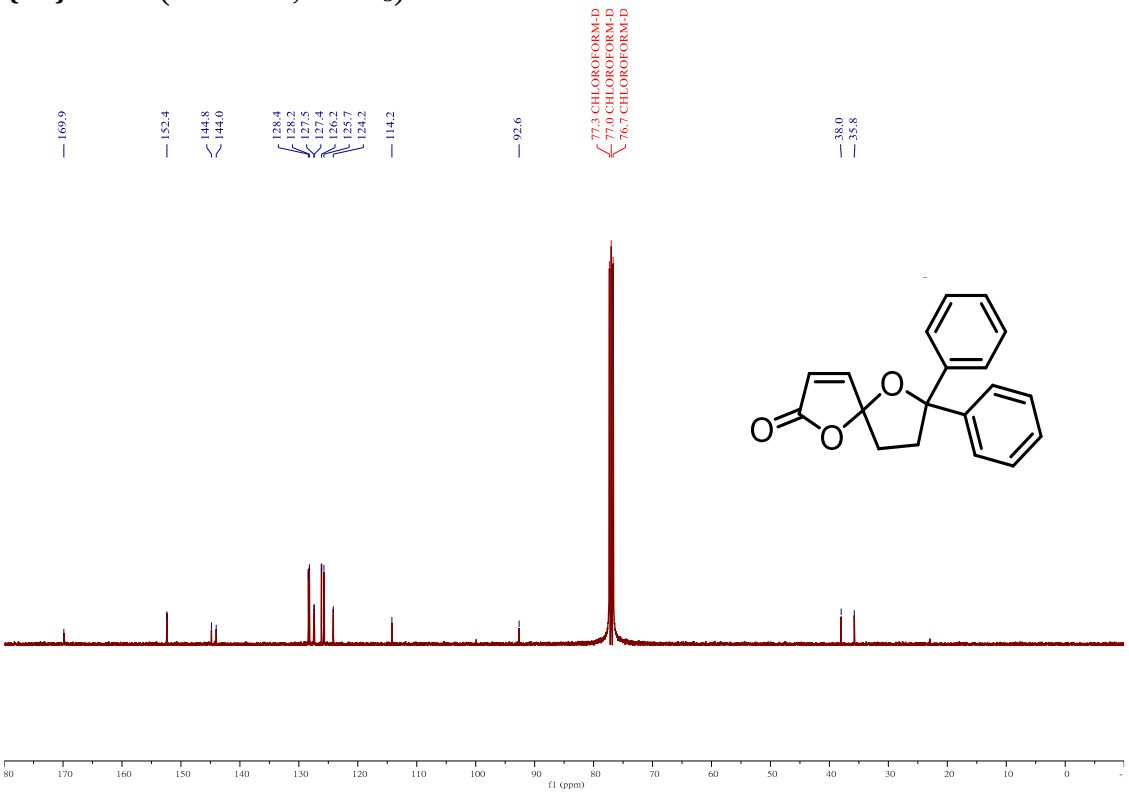
9. NMR Spectra

9.1. Oxaspirolactone substrate scope

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

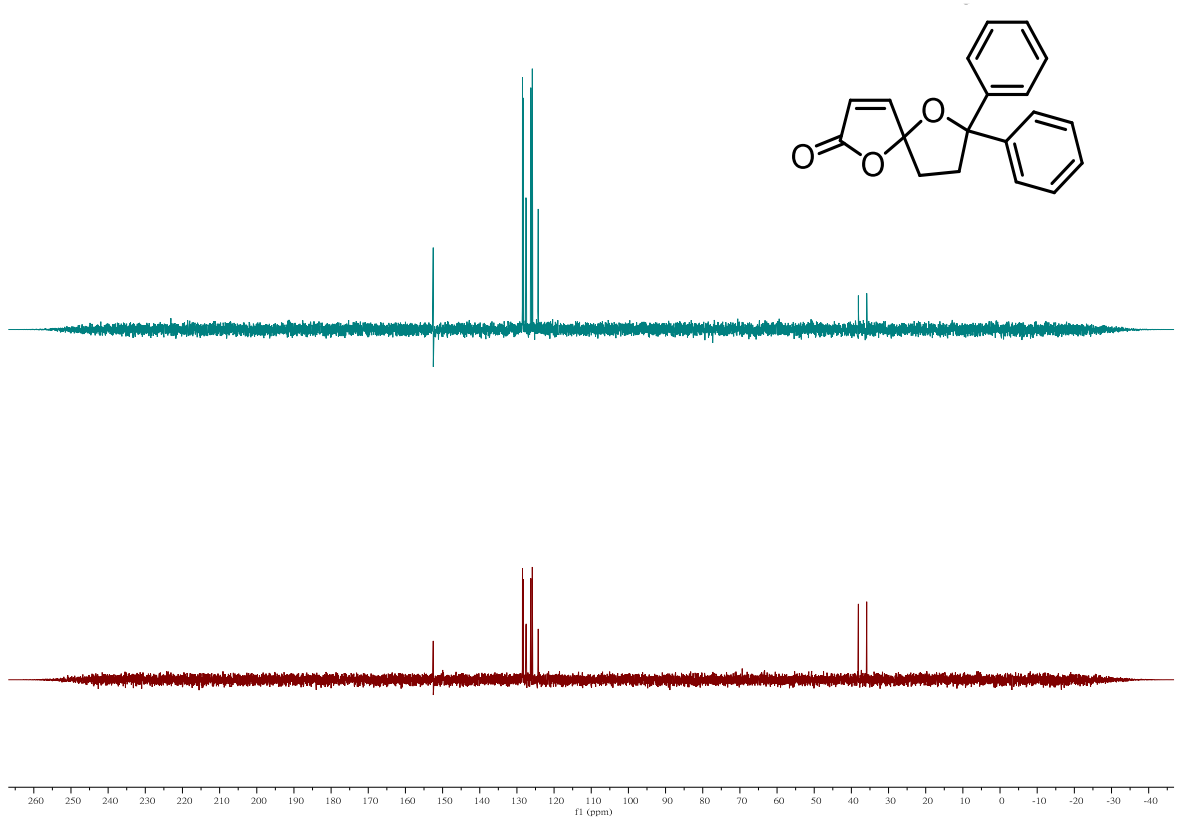


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2a**

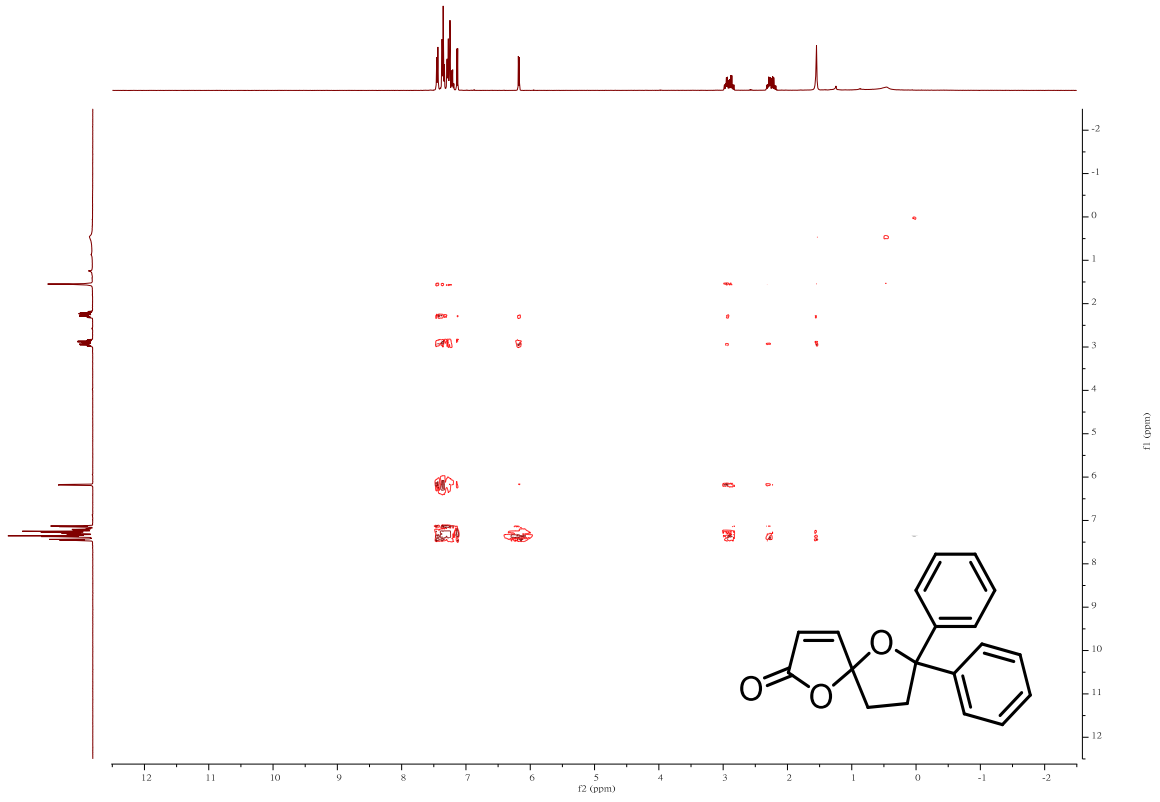


Back to contents

DEPT (400 MHz, $CDCl_3$) spectra of **2a**

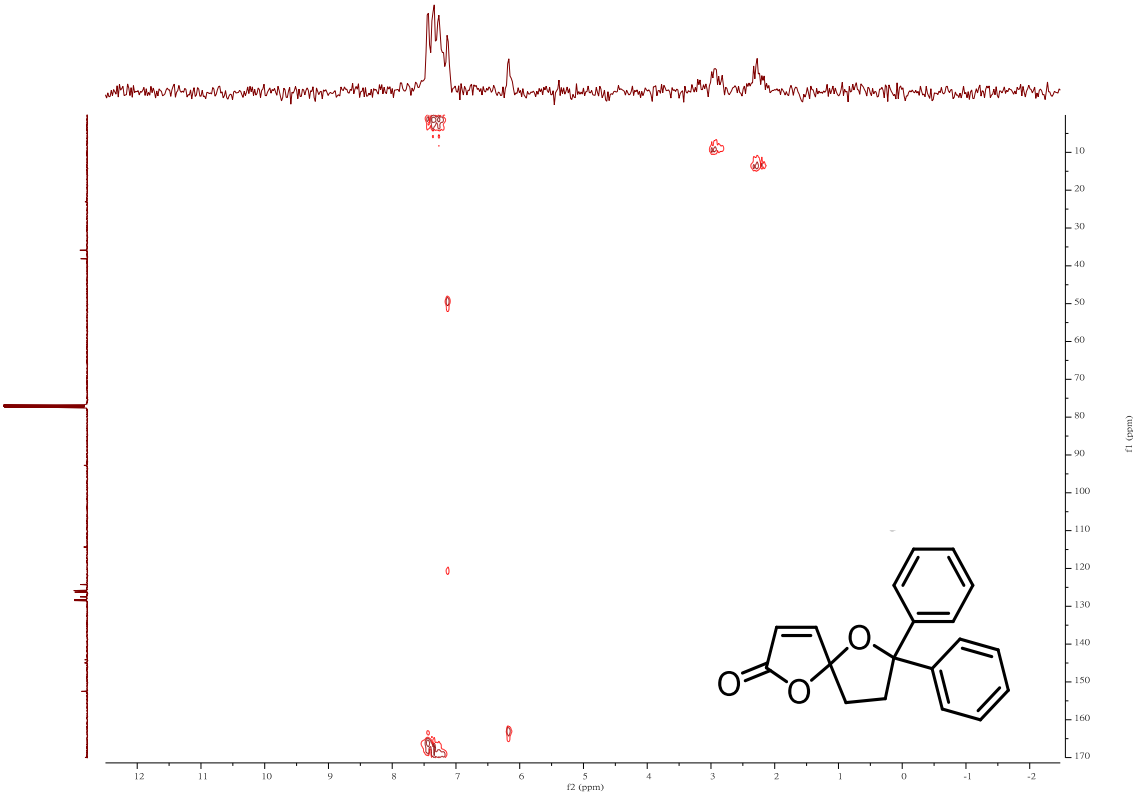


COSY (400 MHz, $CDCl_3$) of **2a**

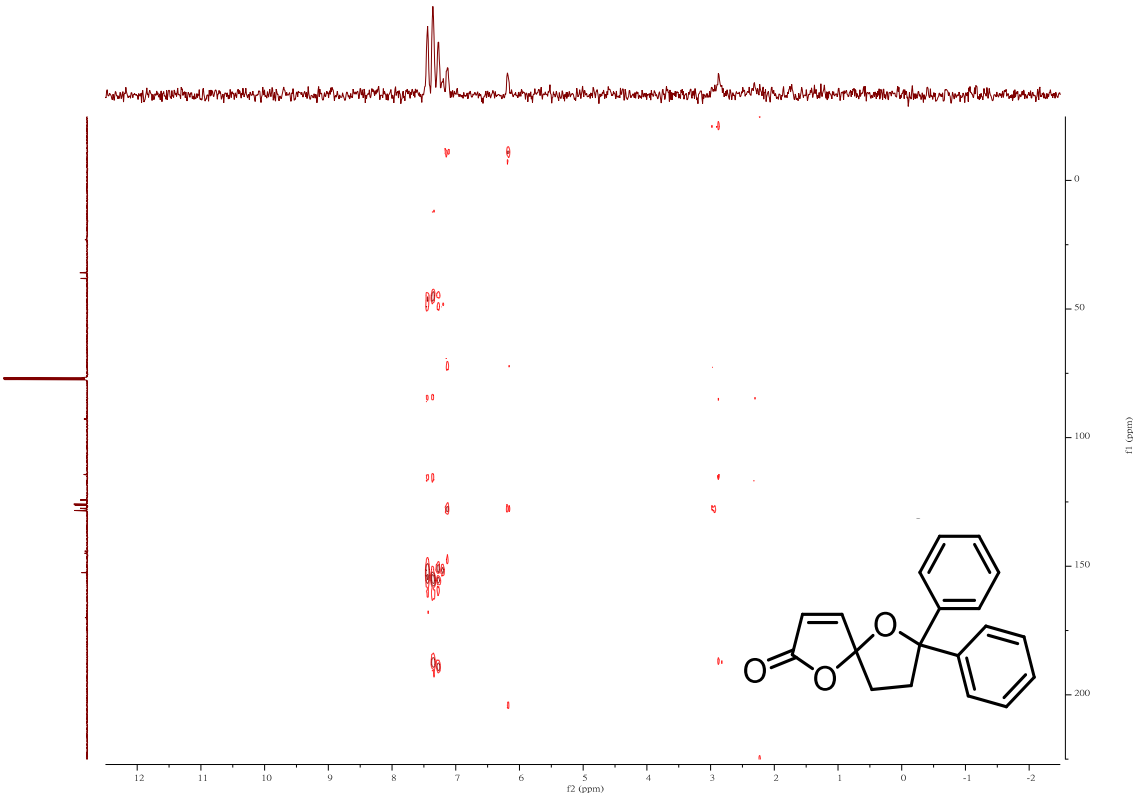


Back to contents

HMQC (400 MHz, CDC_3) of **2a**

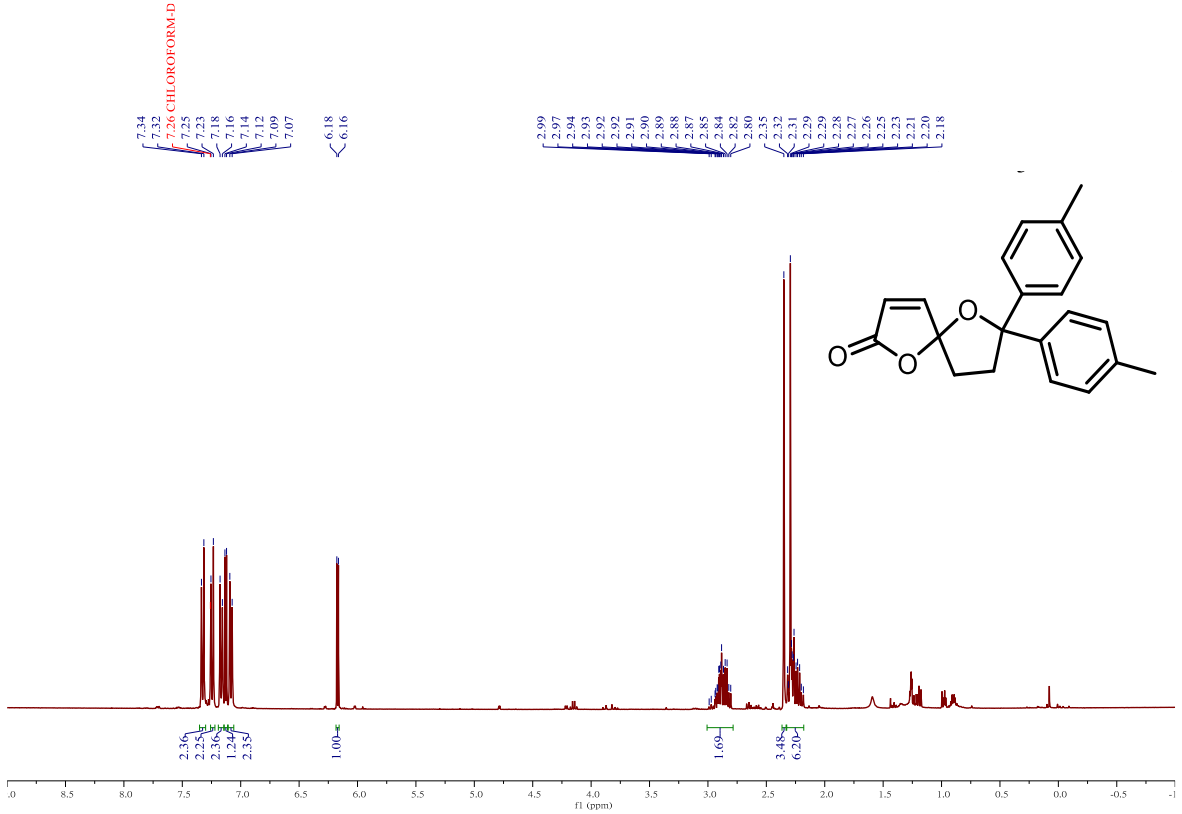


HMBC (400 MHz, $CDCl_3$) of **2a**

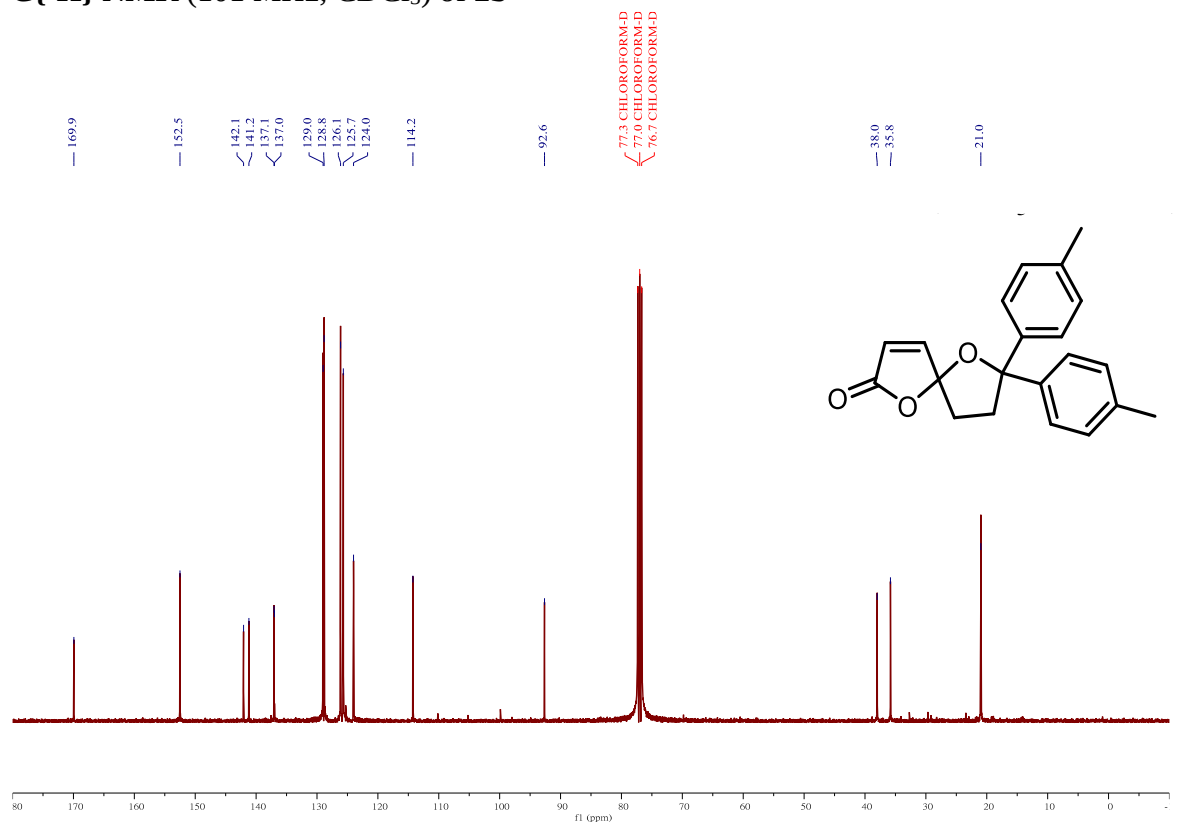


Back to contents

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

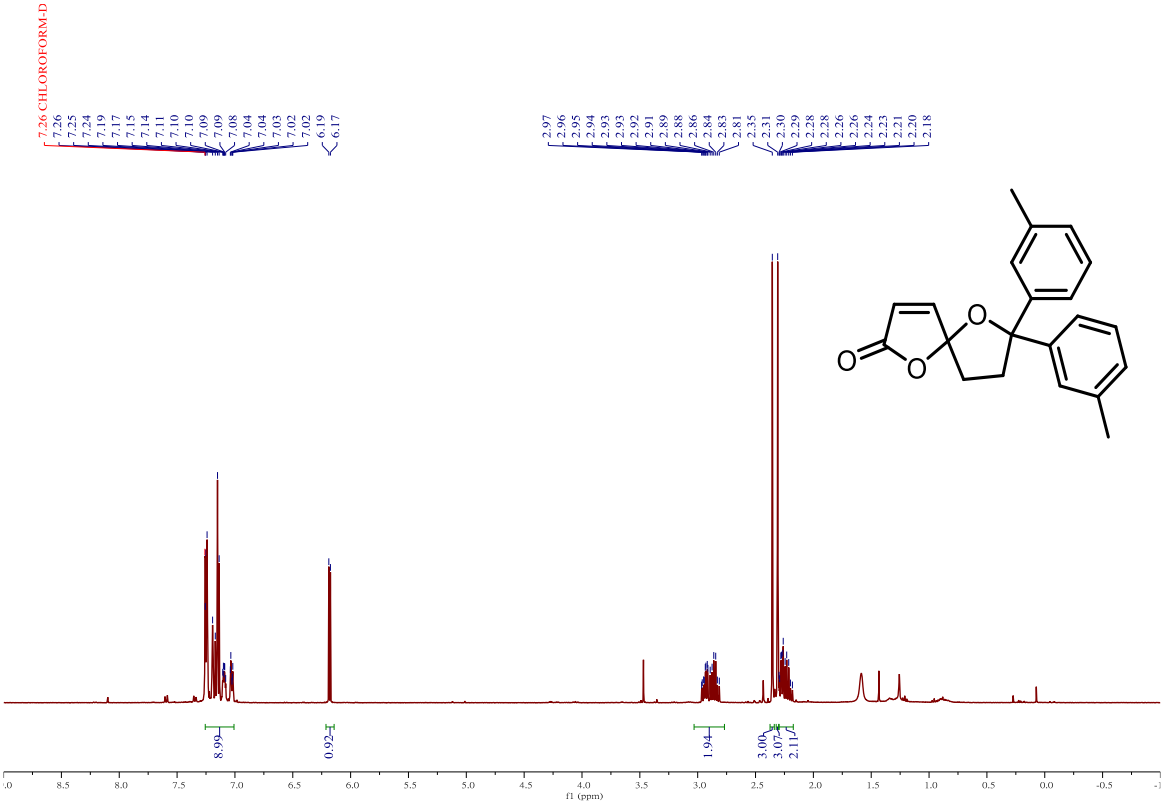


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2b**

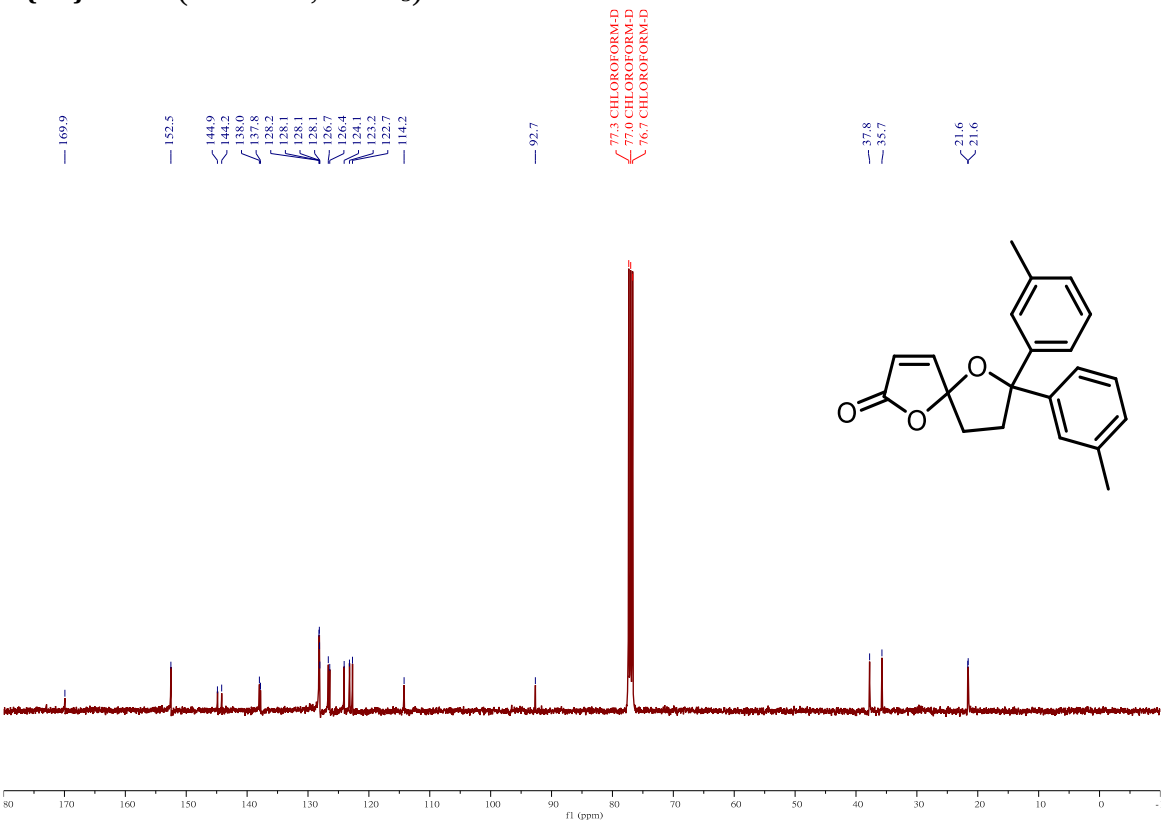


Back to contents

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

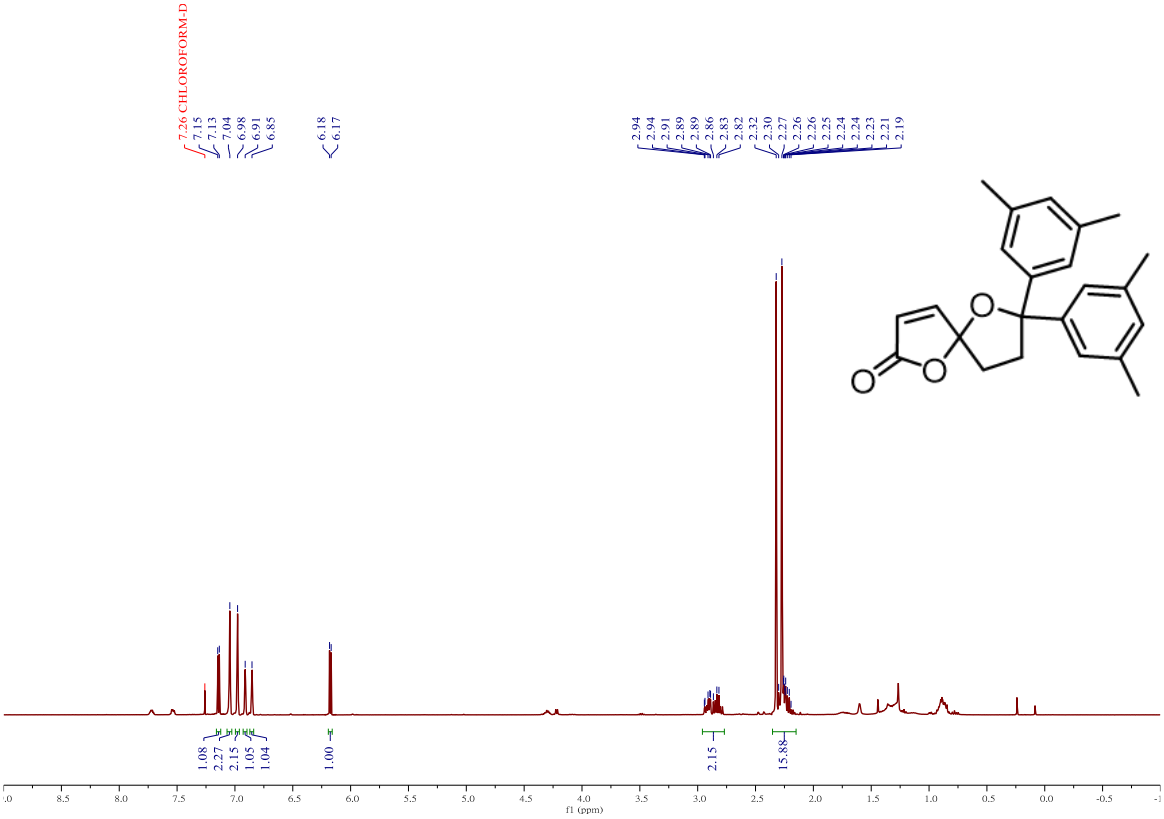


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2c**

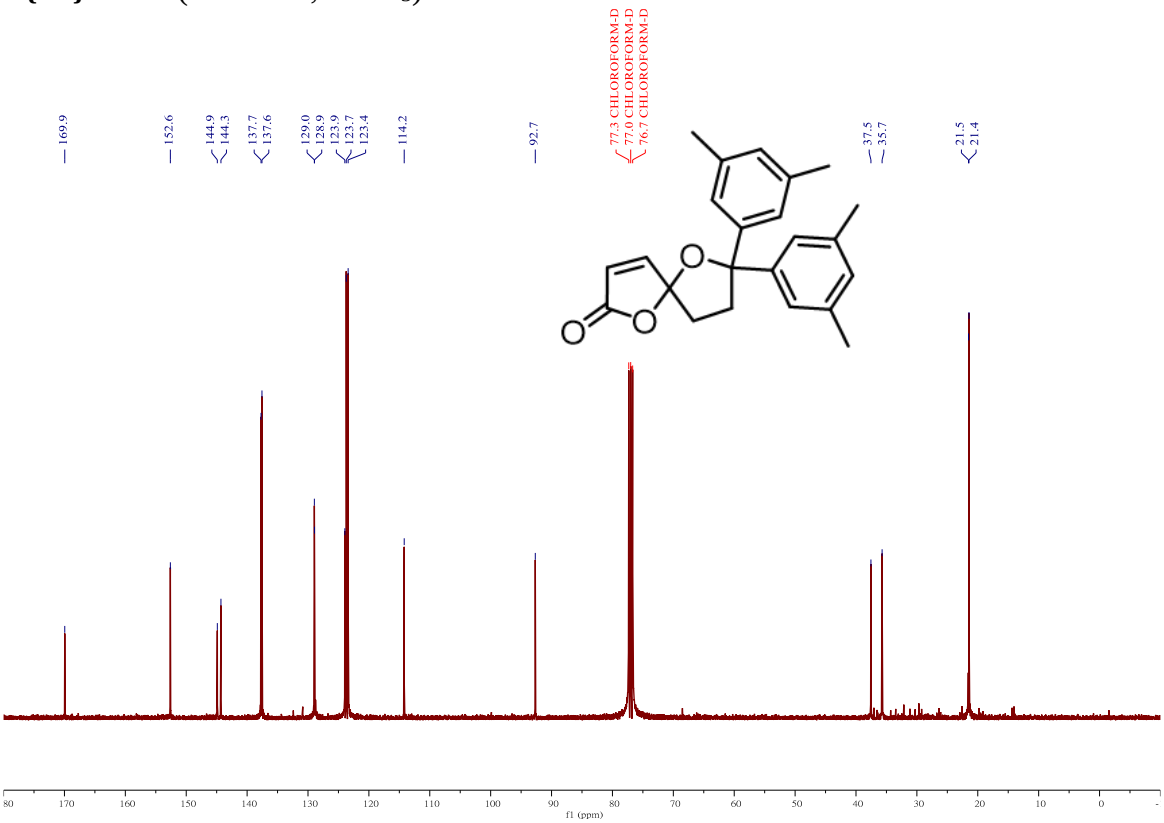


Back to contents

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

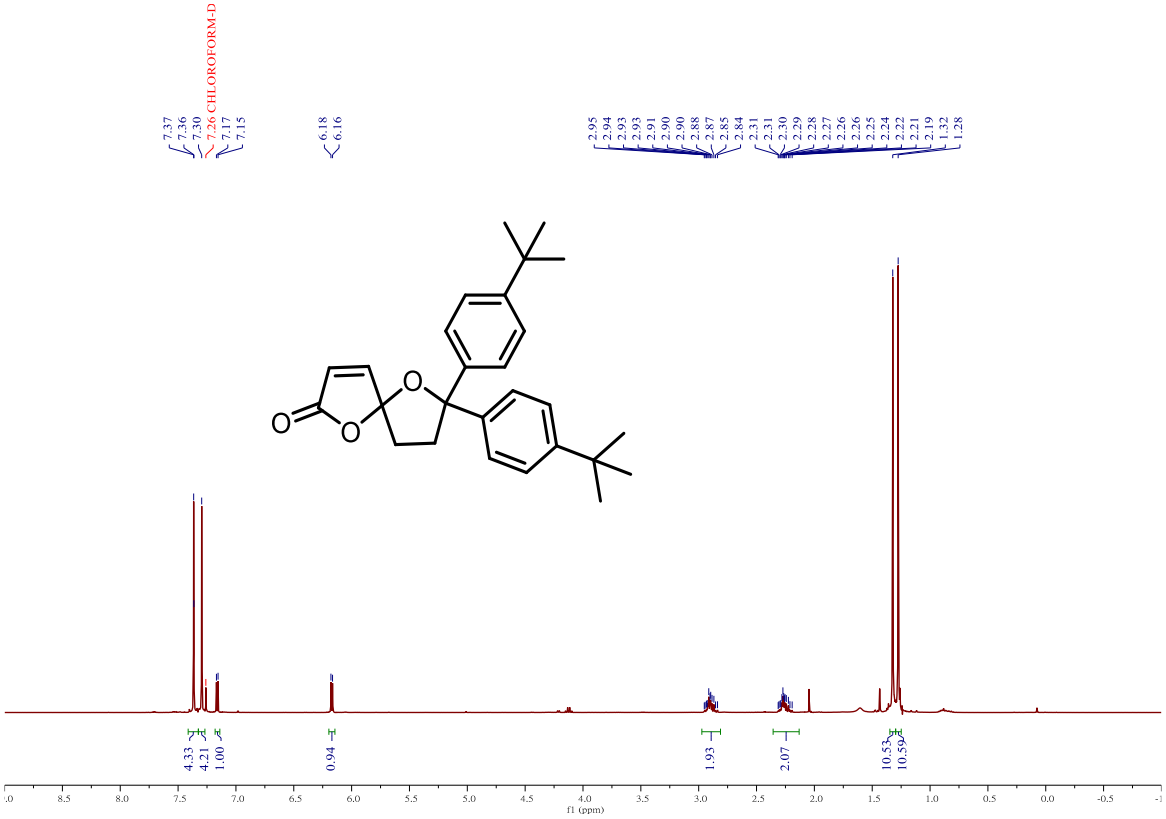


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2d**

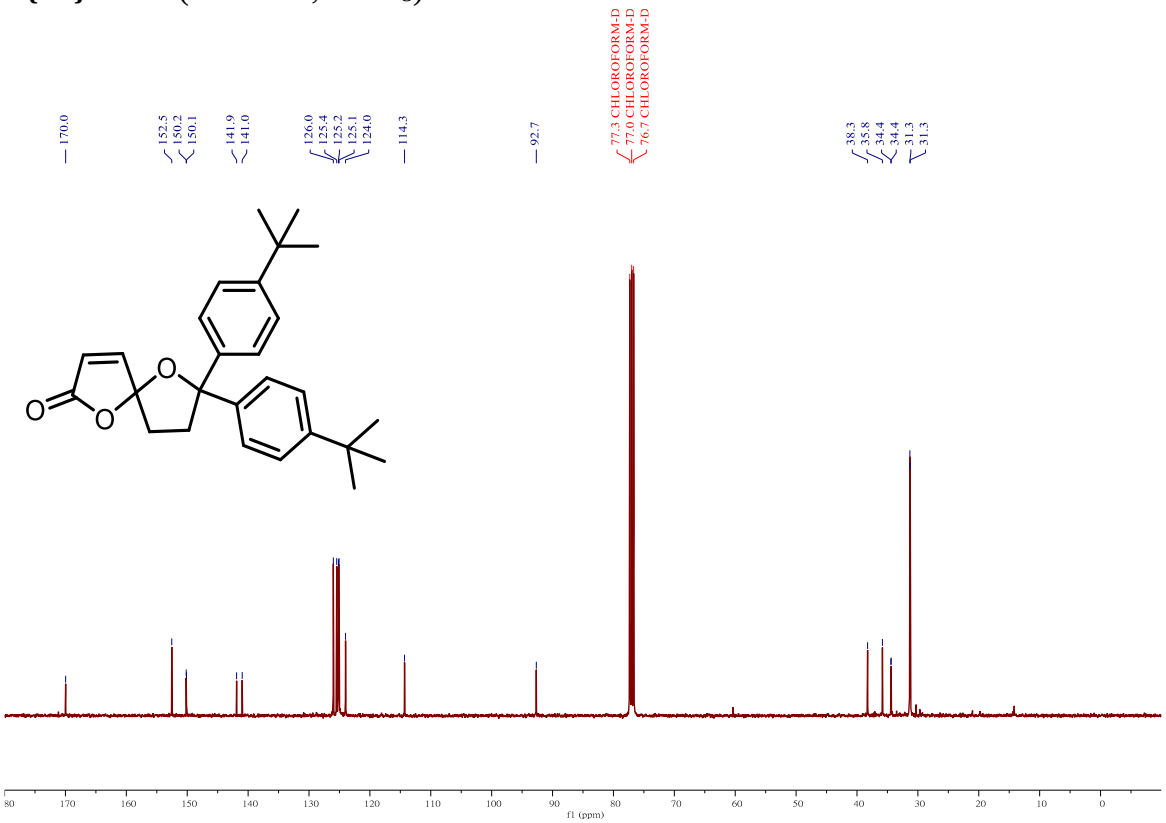


Back to contents

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

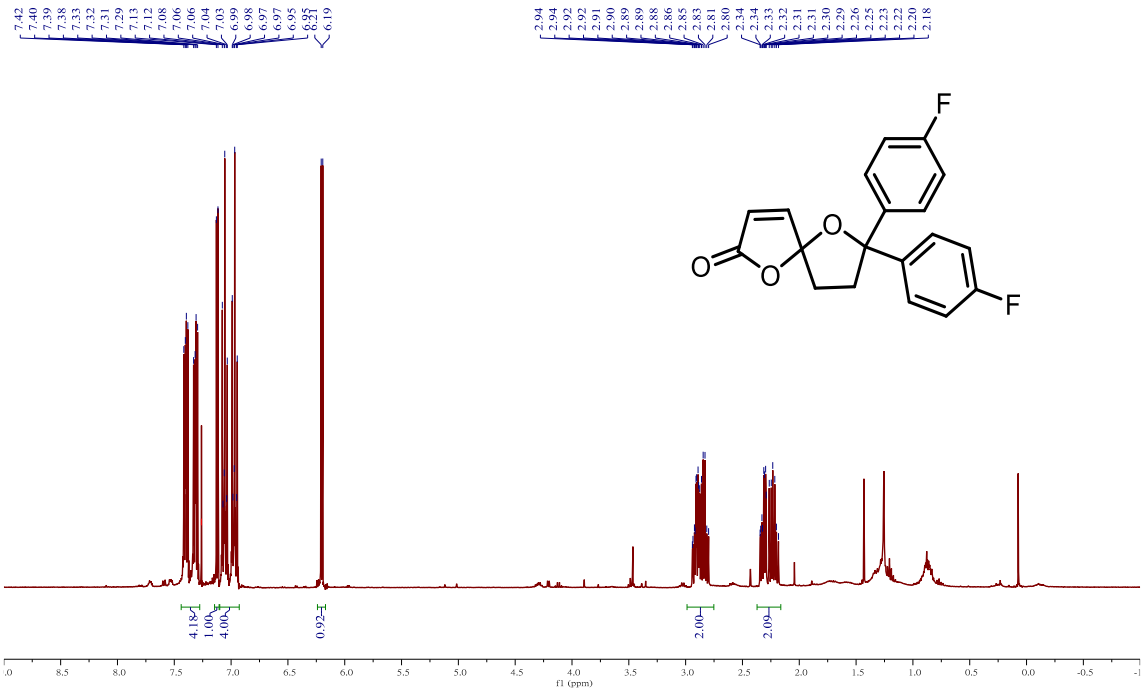


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2e**

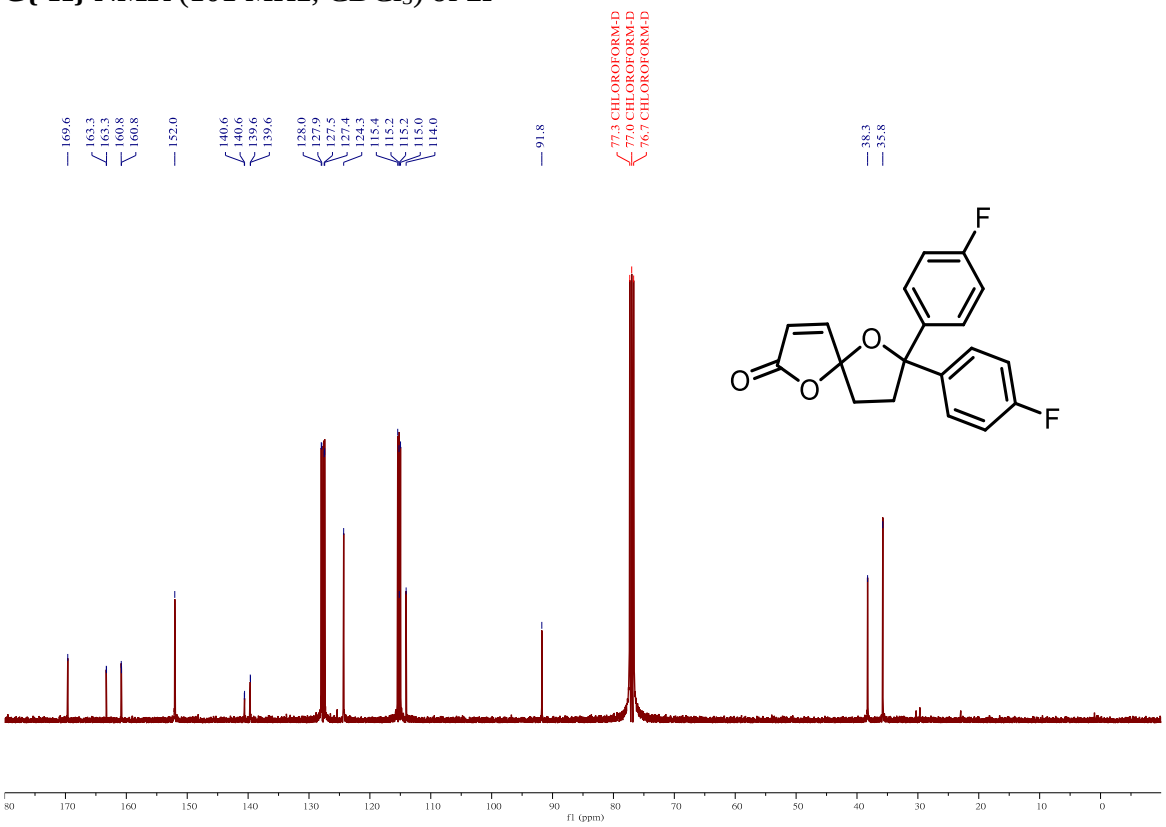


Back to contents

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

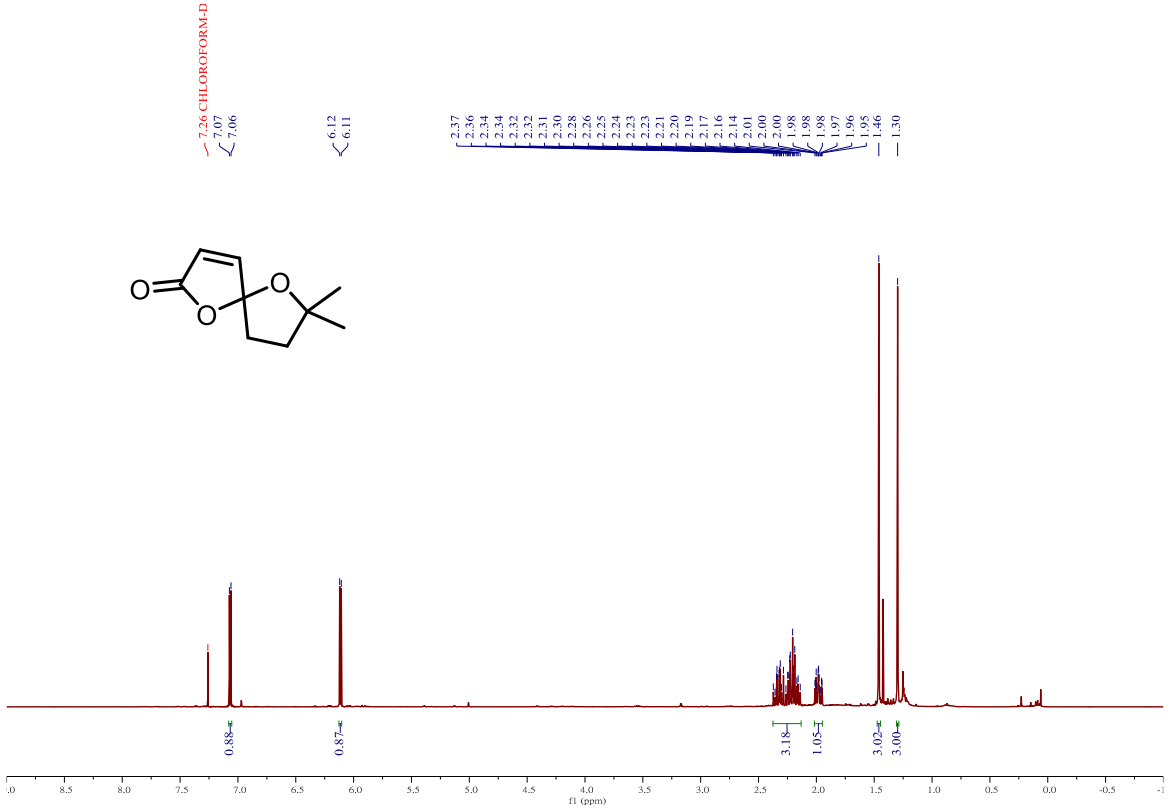


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2f**

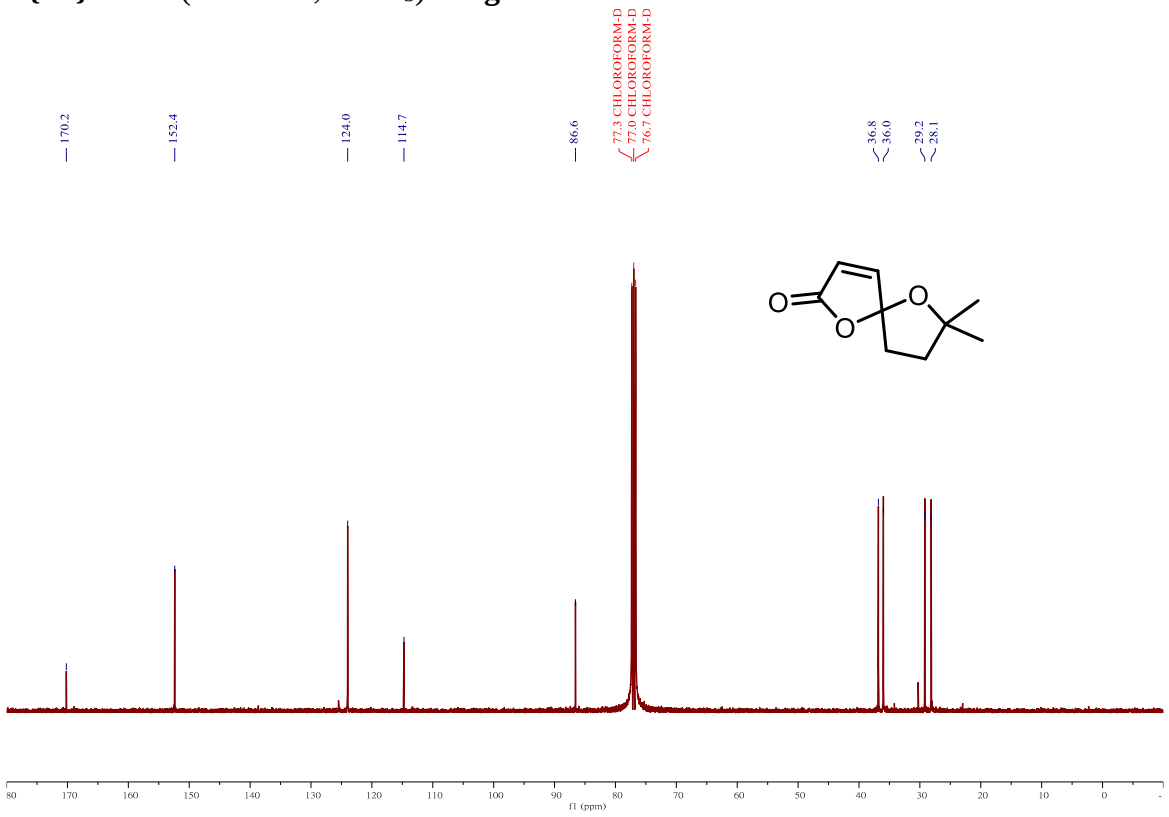


Back to contents

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

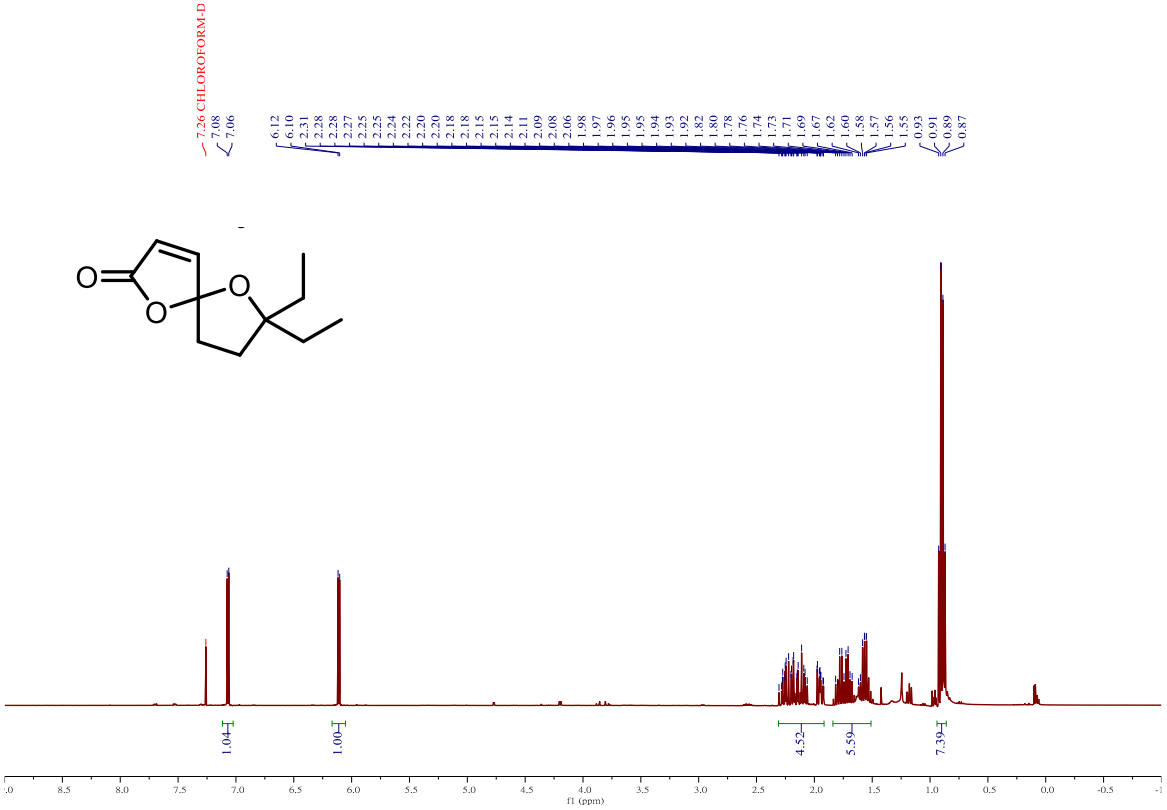


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2g**

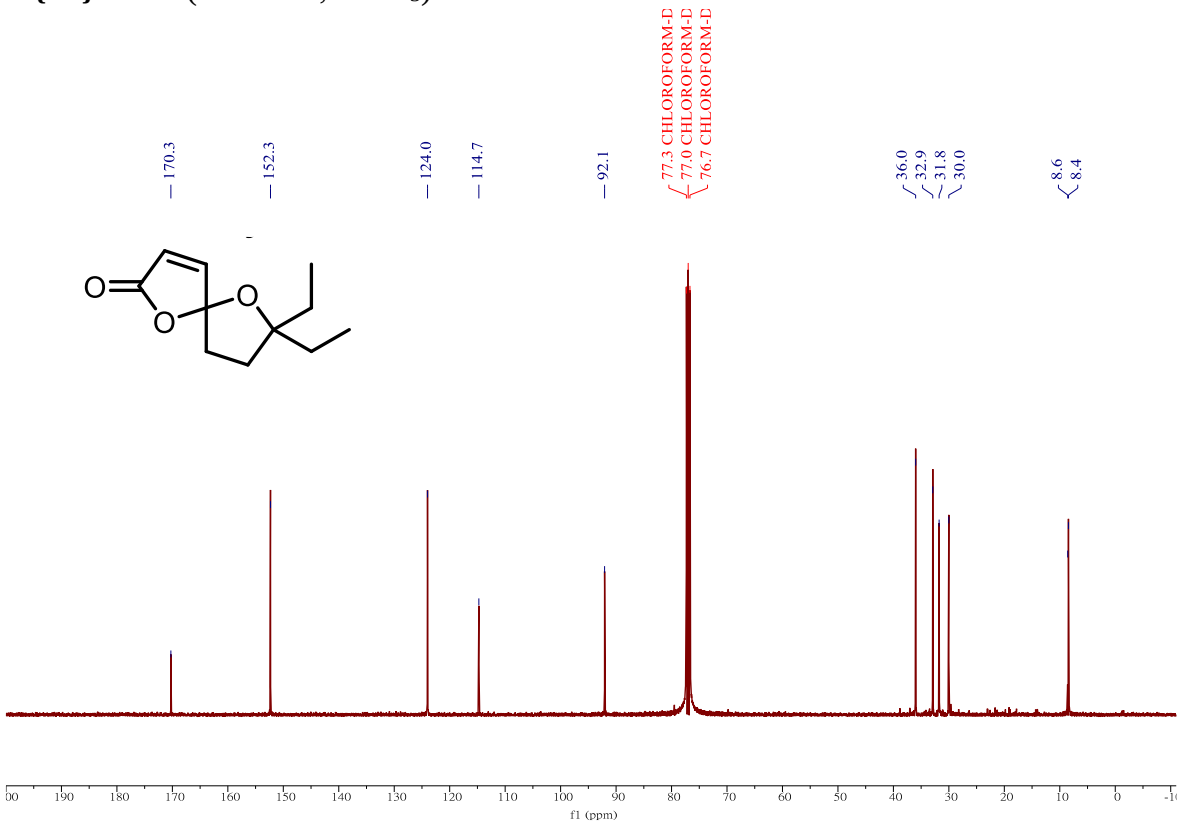


Back to contents

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

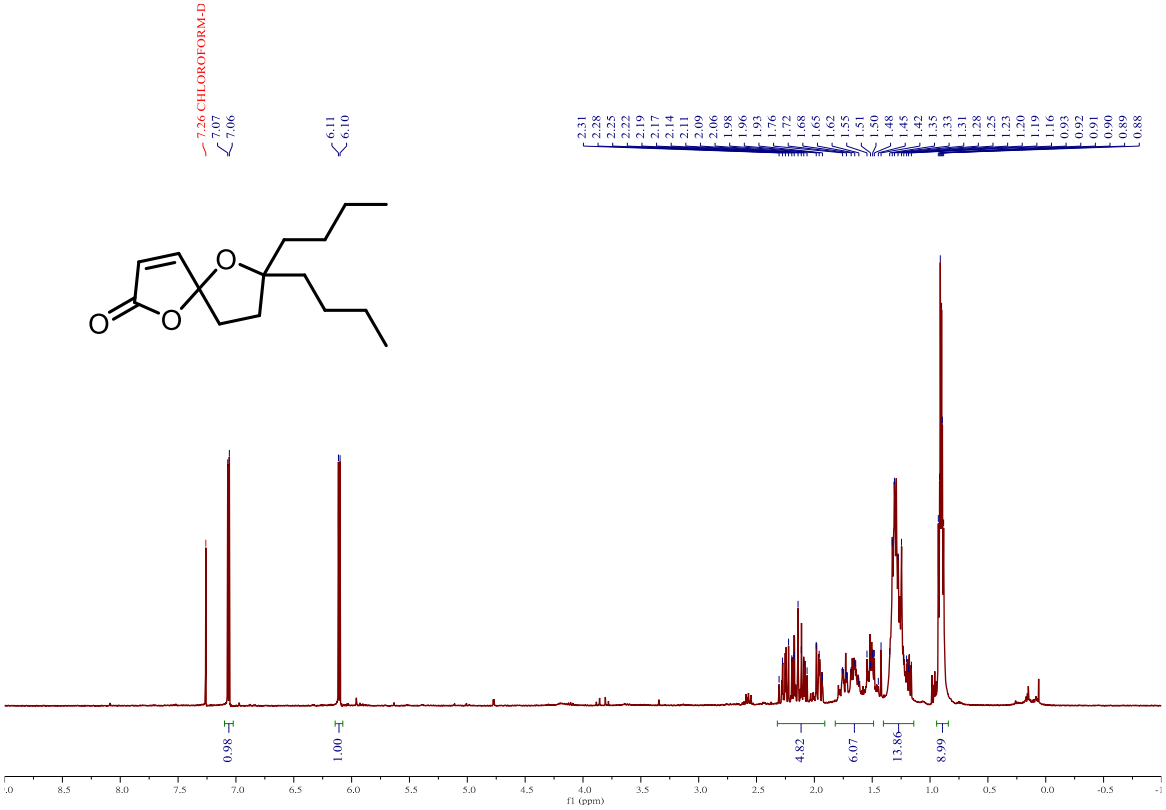


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2h**

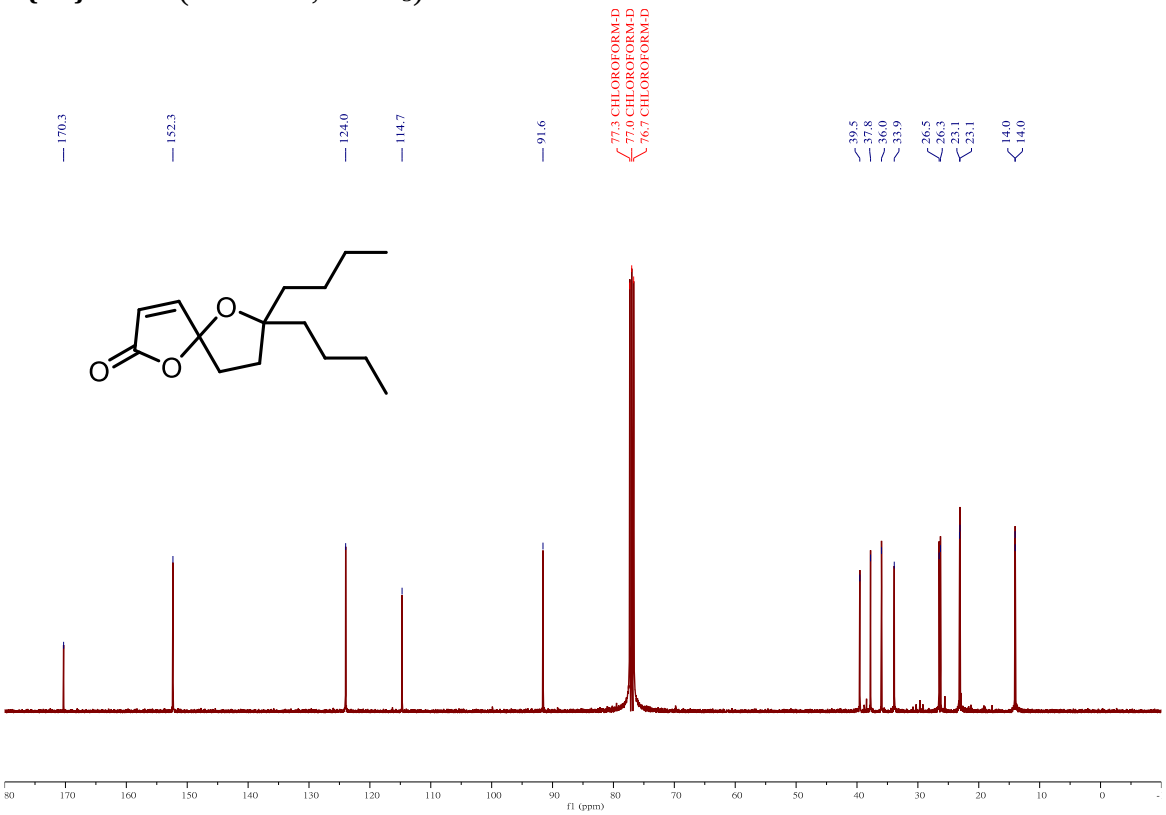


Back to contents

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

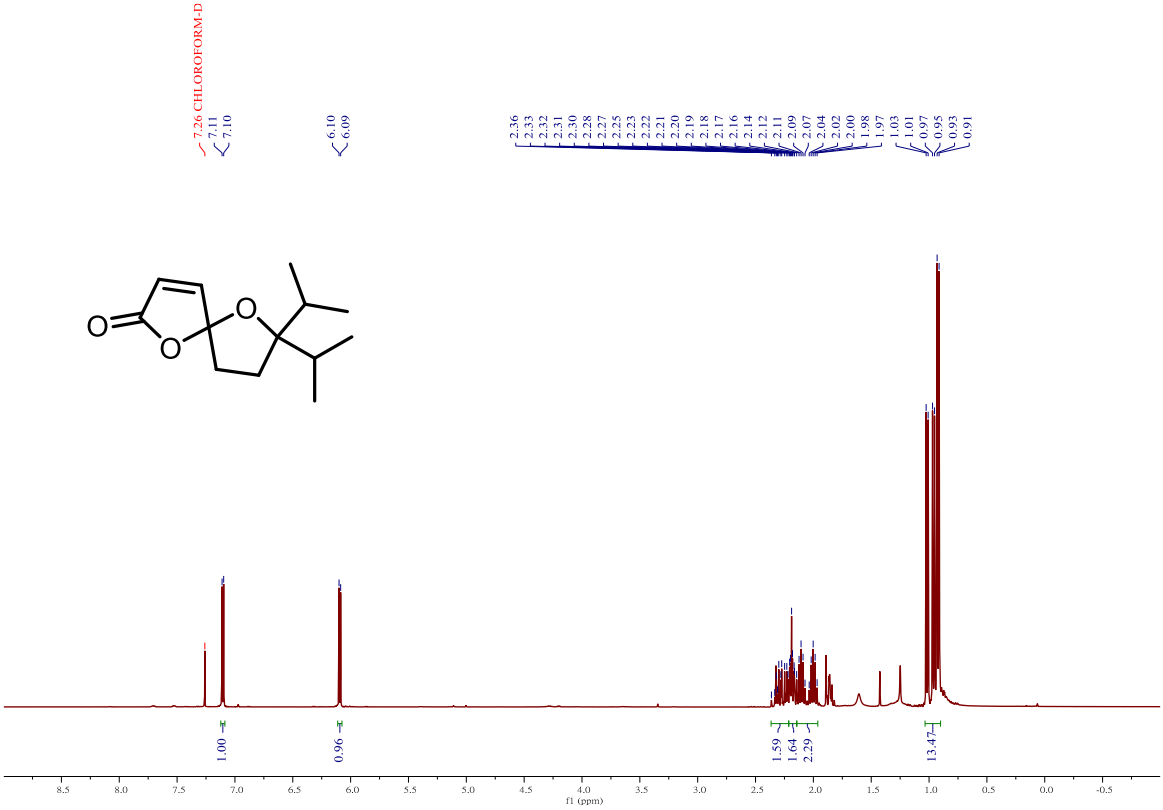


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2i**

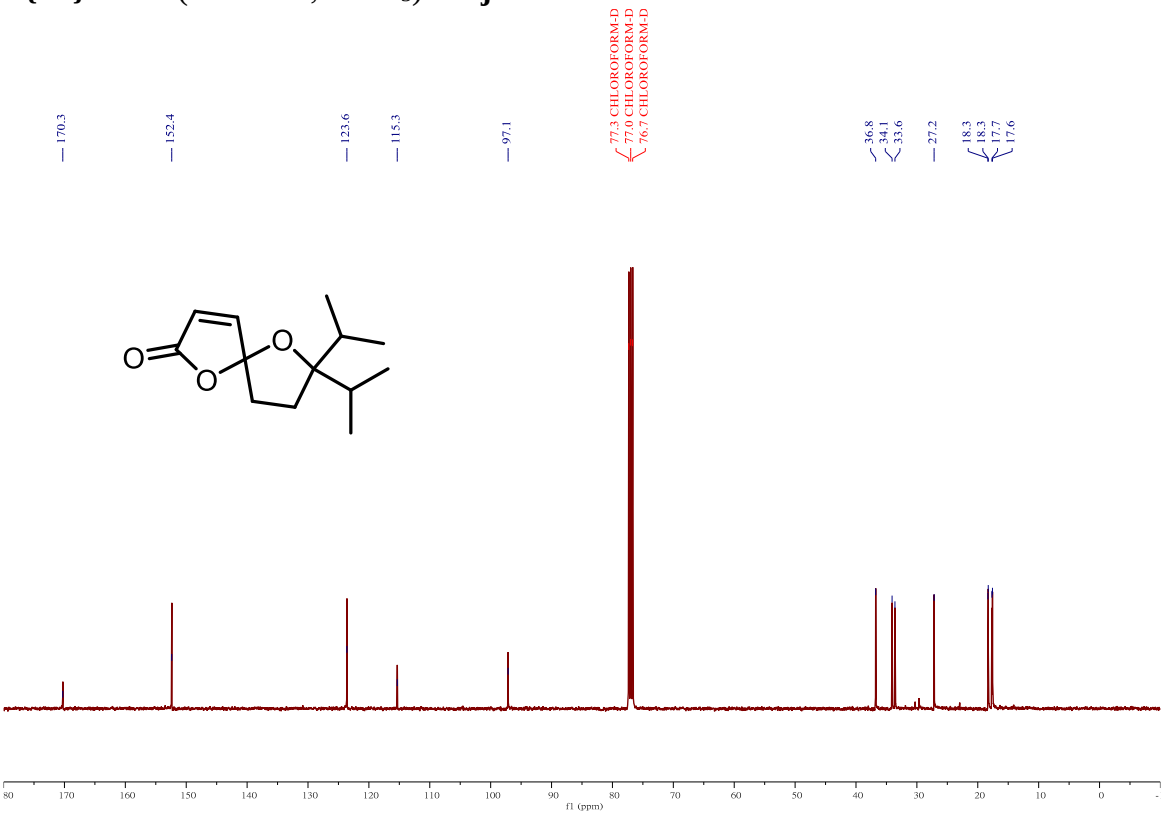


Back to contents

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

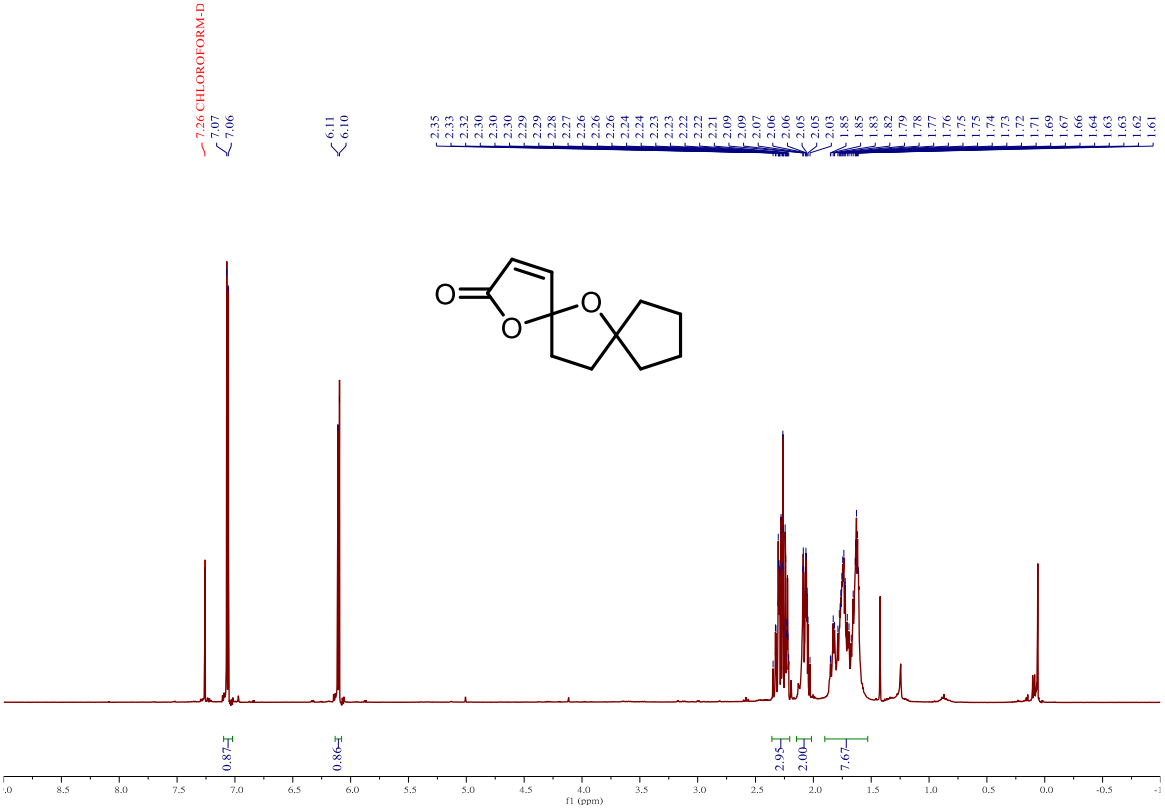


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2j**

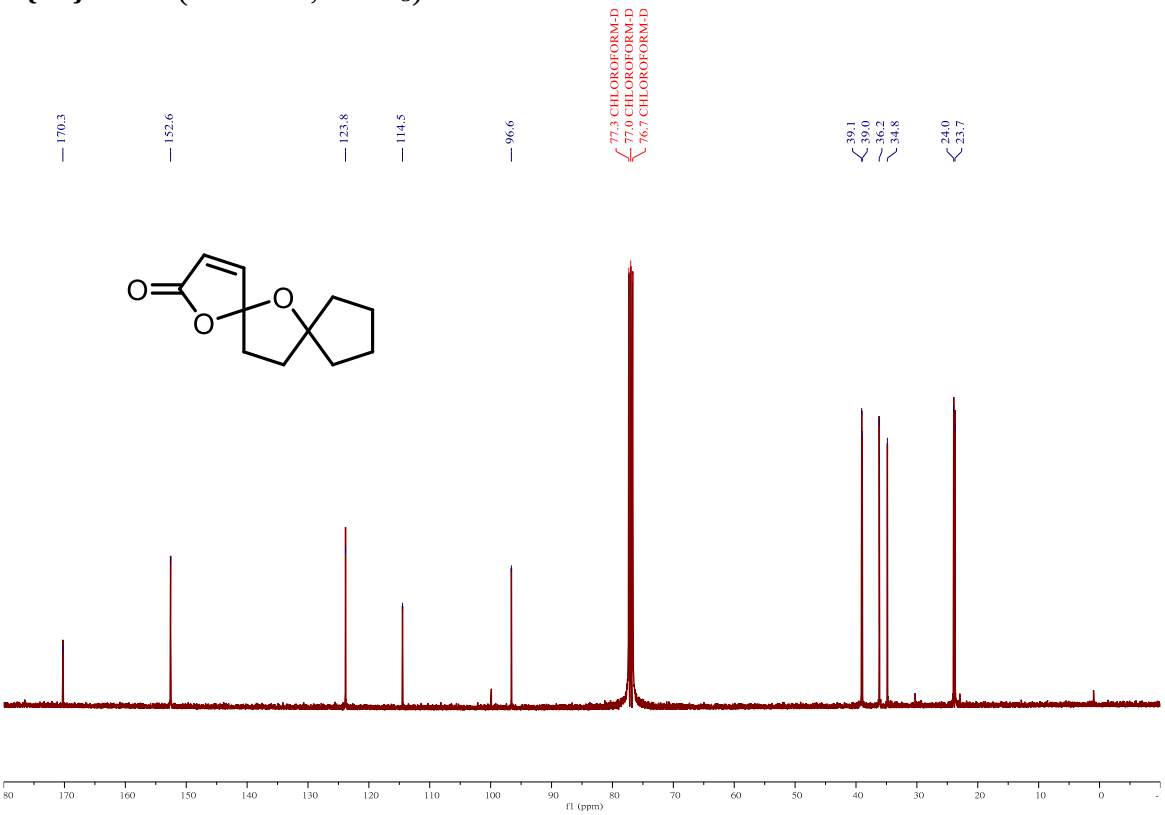


Back to contents

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

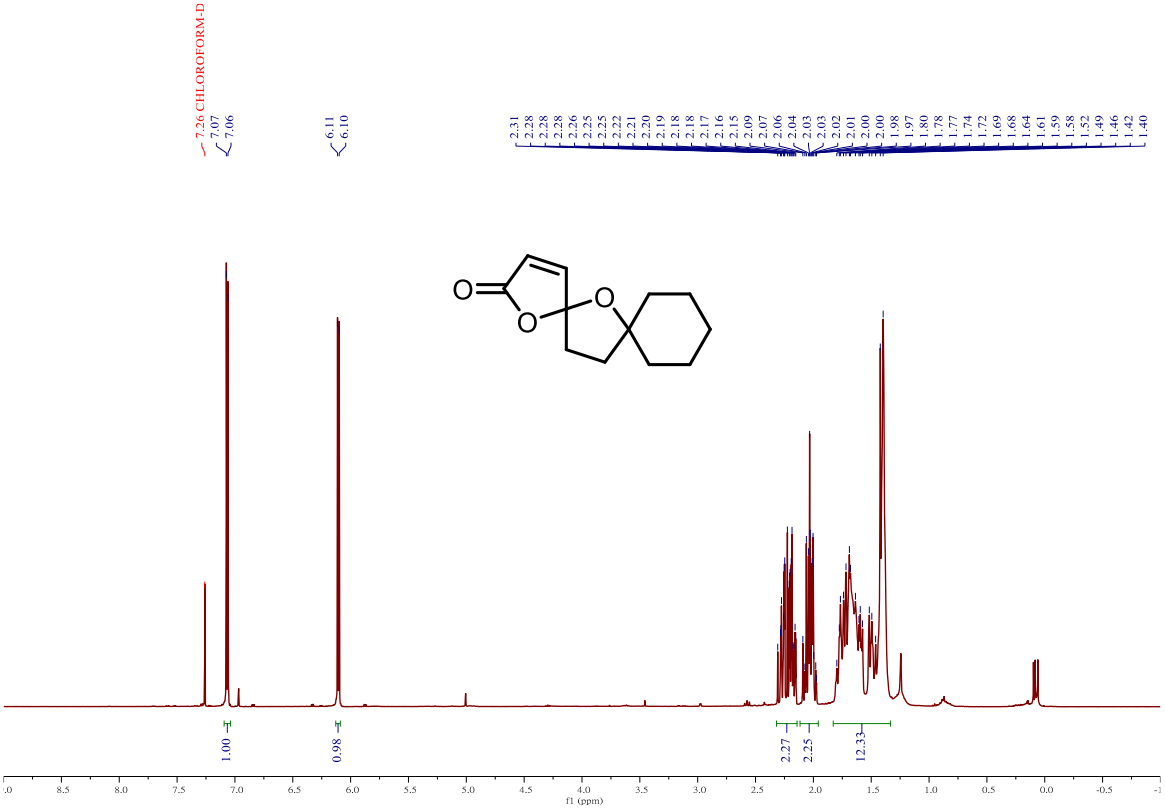


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2k**

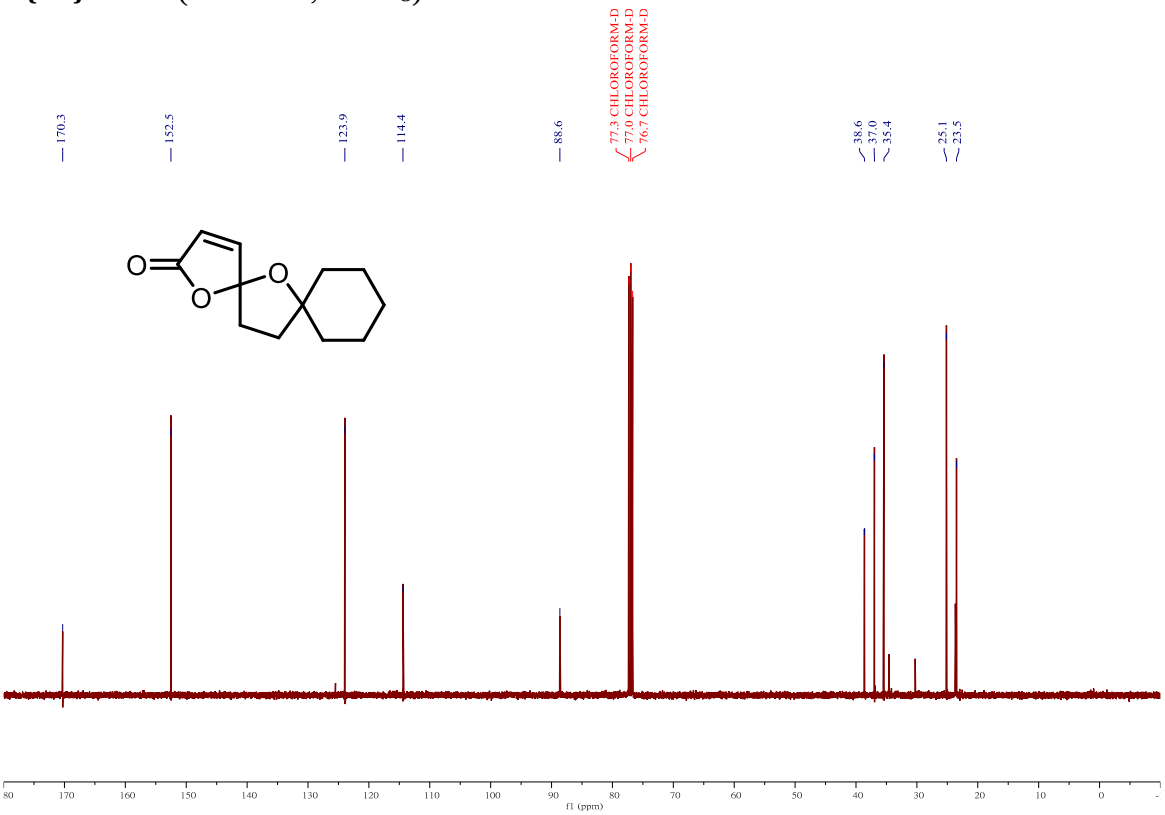


Back to contents

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

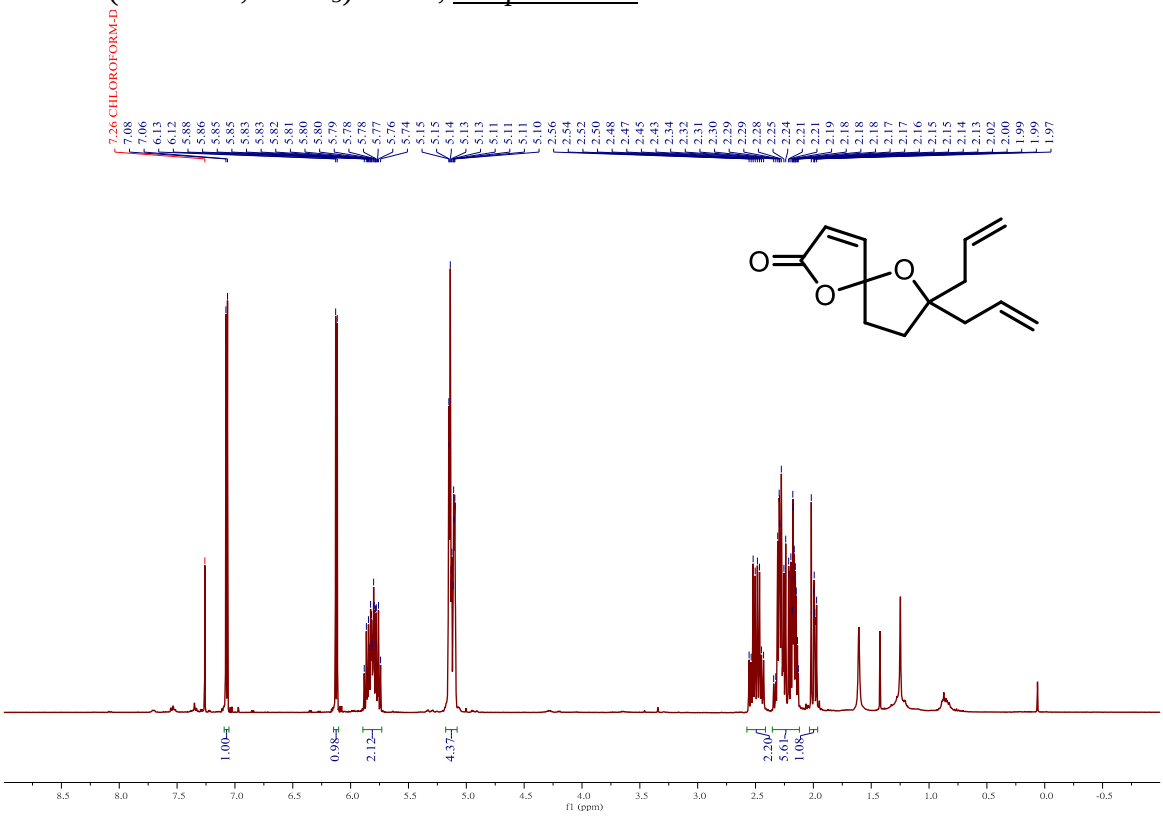


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2l**

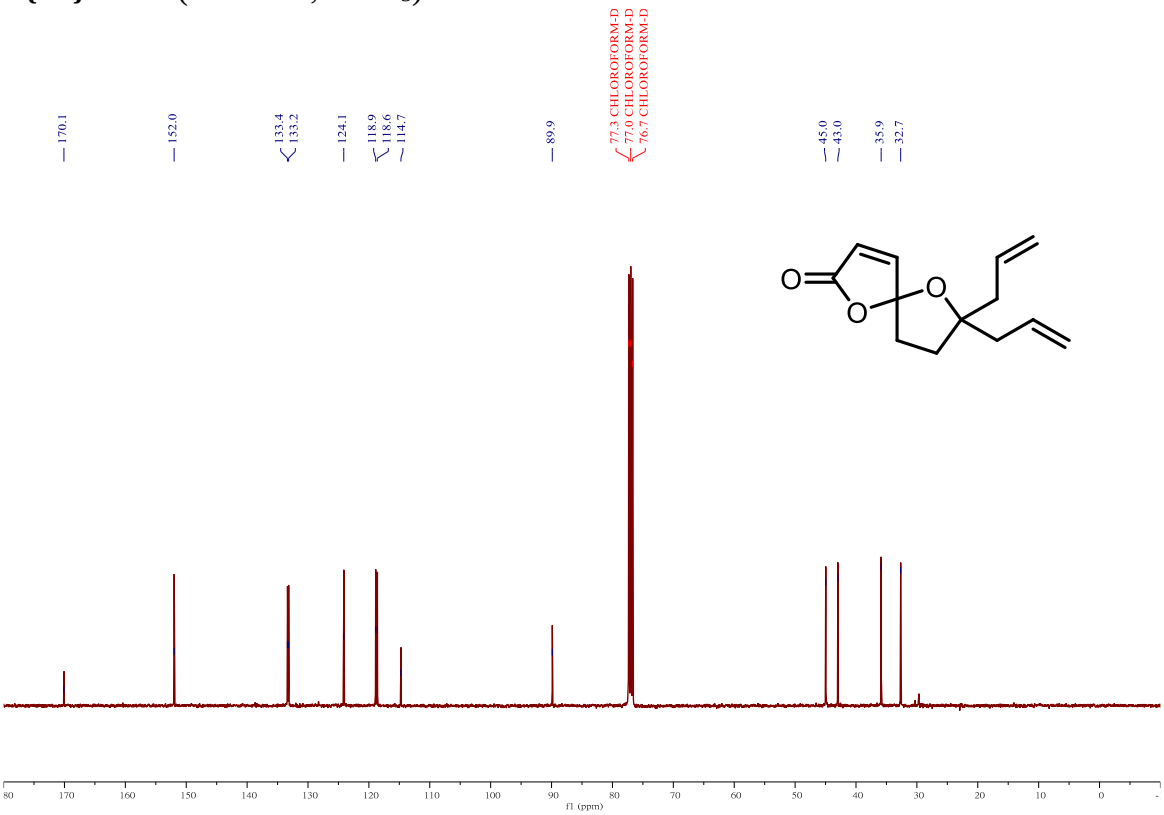


Back to contents

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

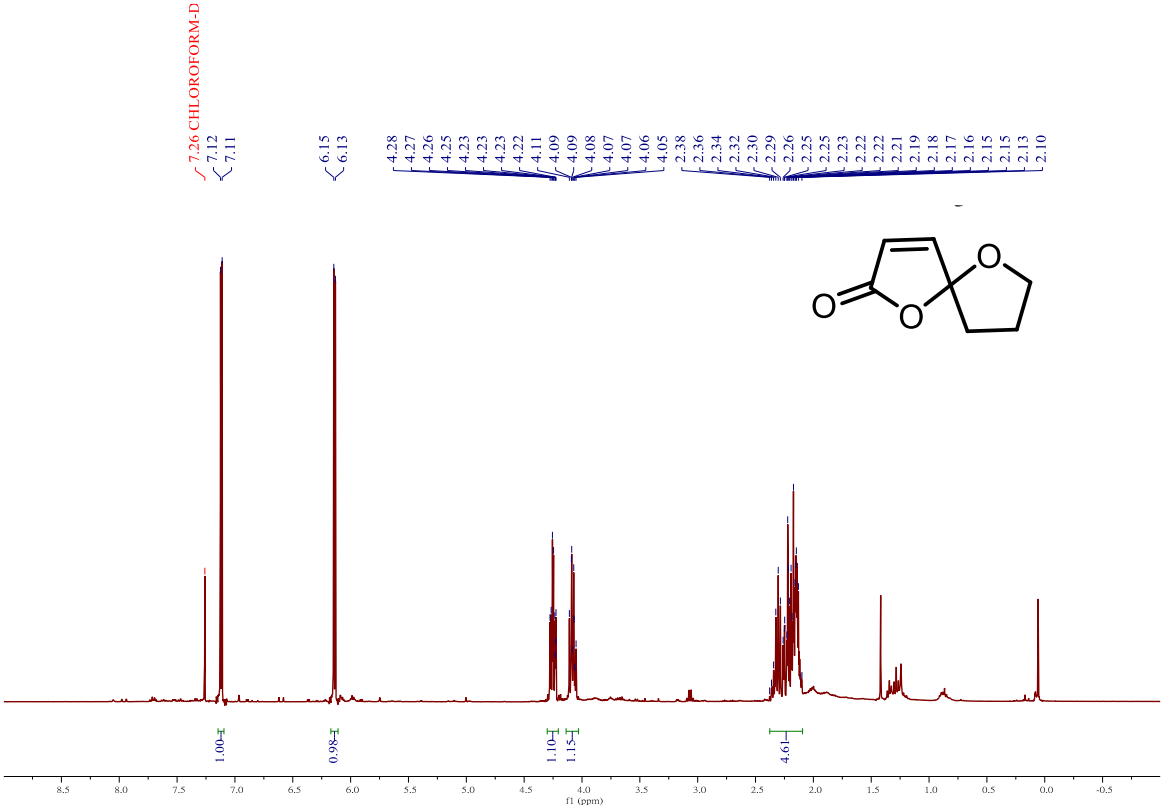


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2m**

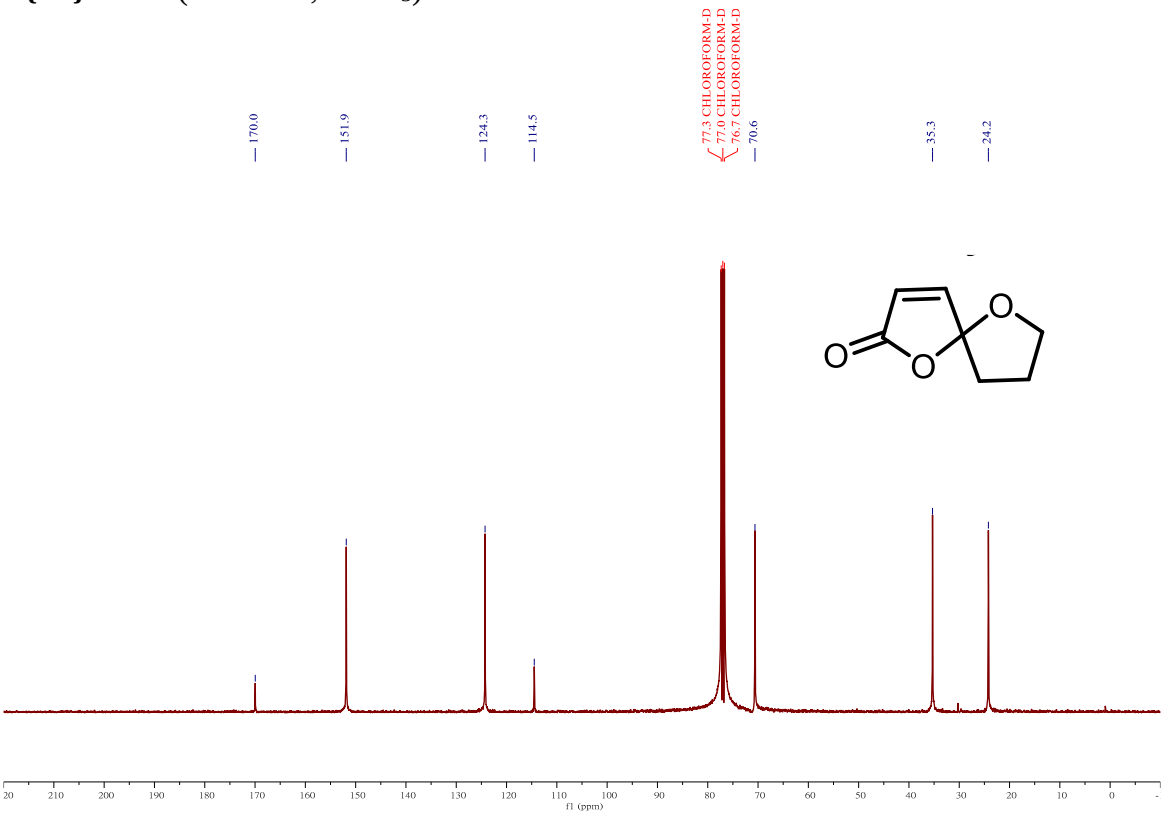


Back to contents

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

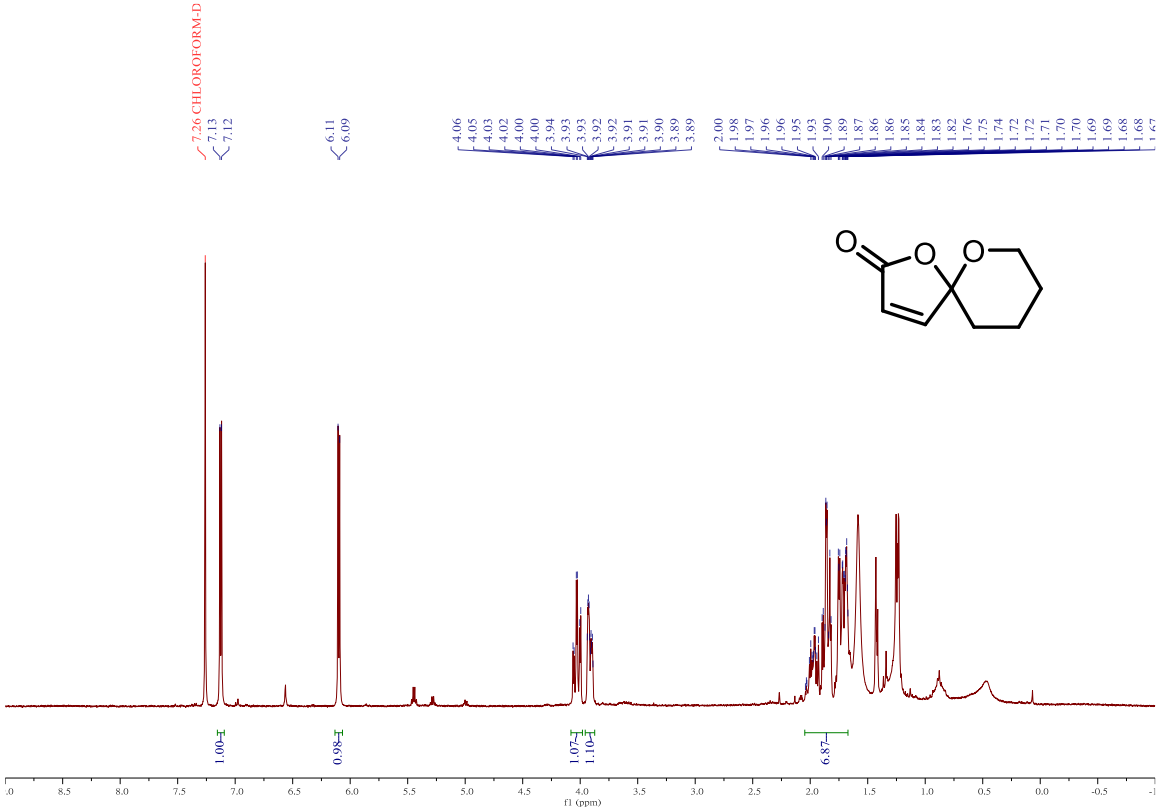


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2n**

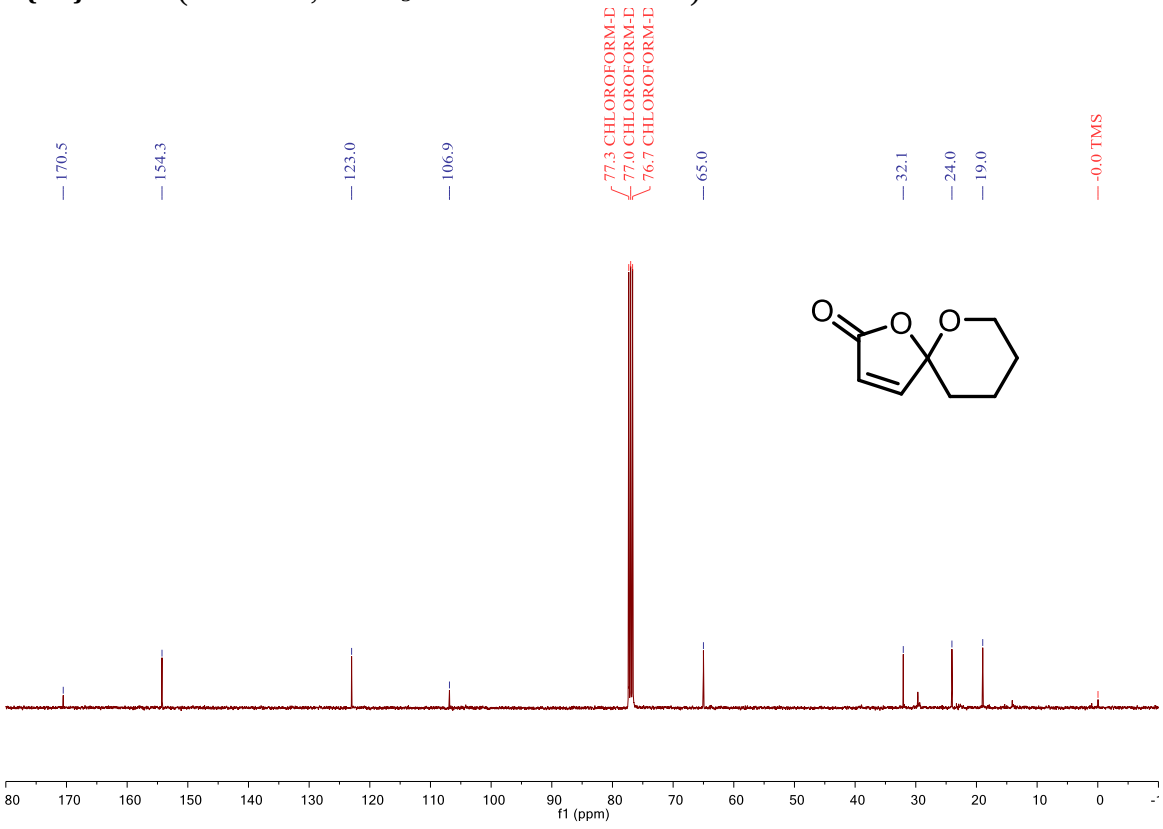


Back to contents

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

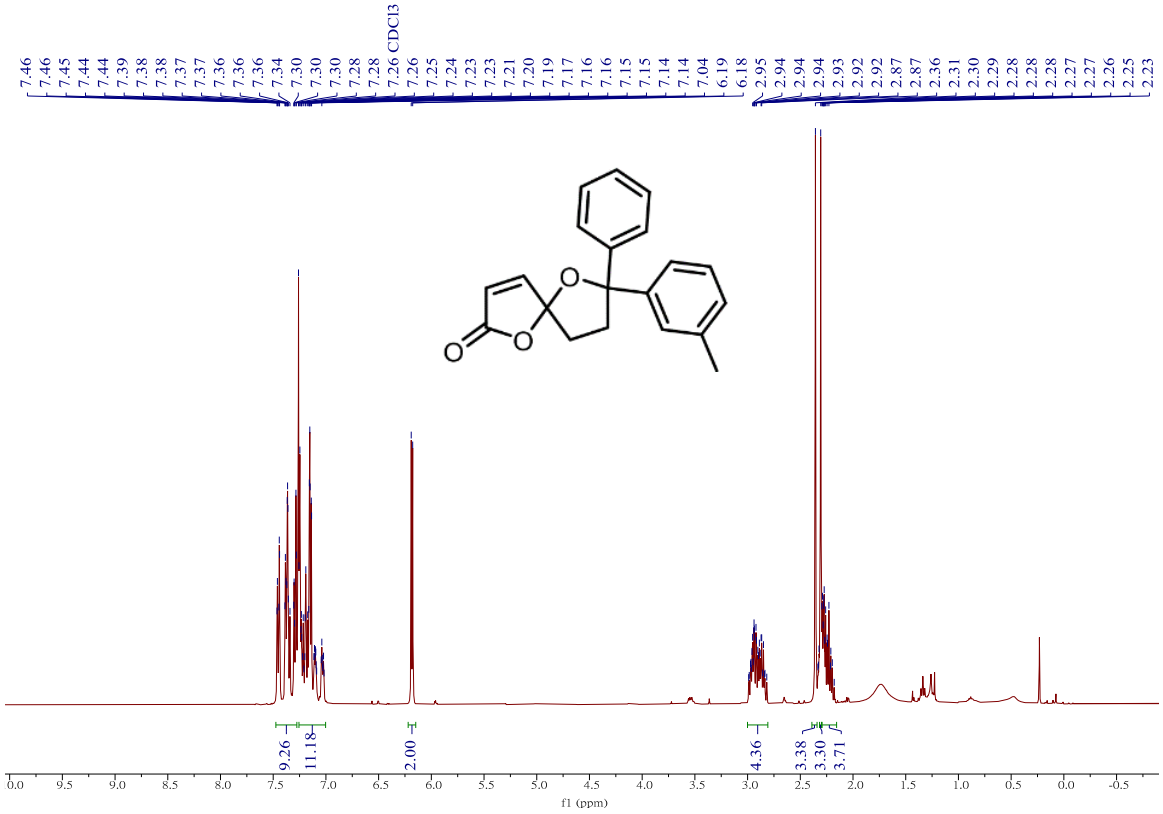


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) of **2o**

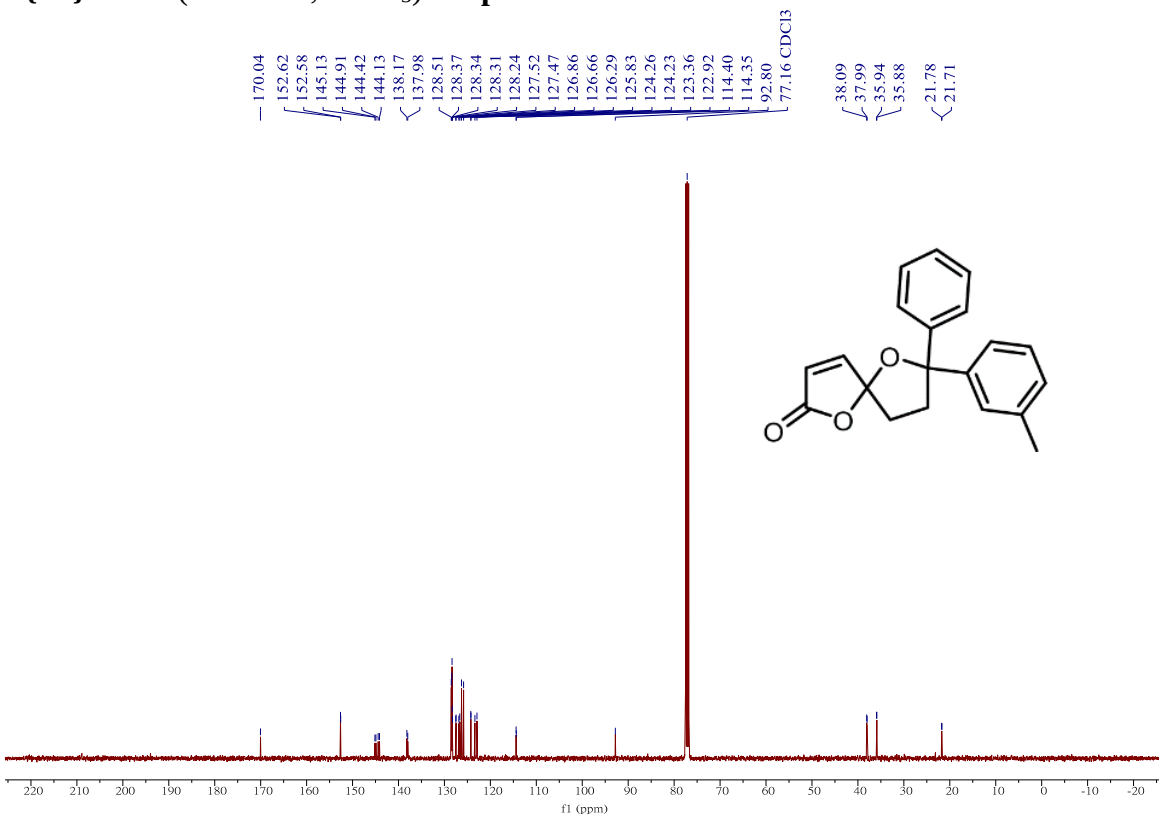


Back to contents

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

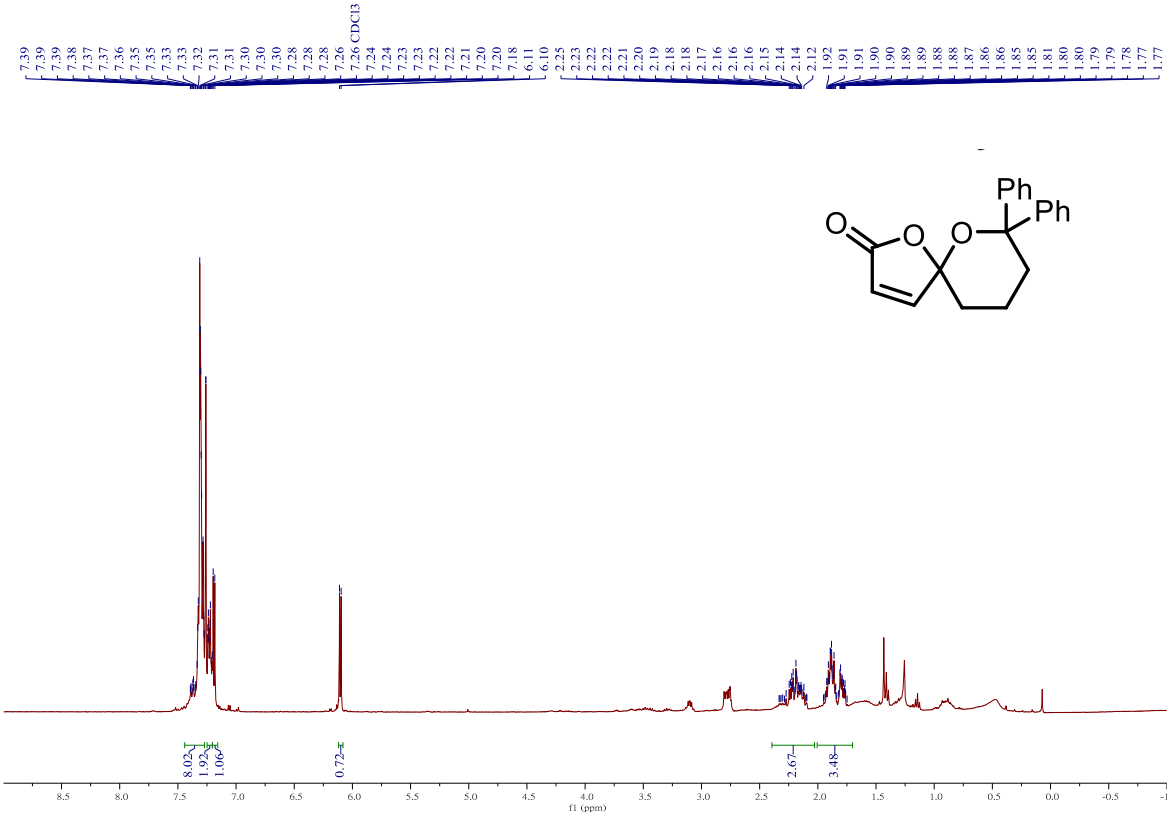


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2p**

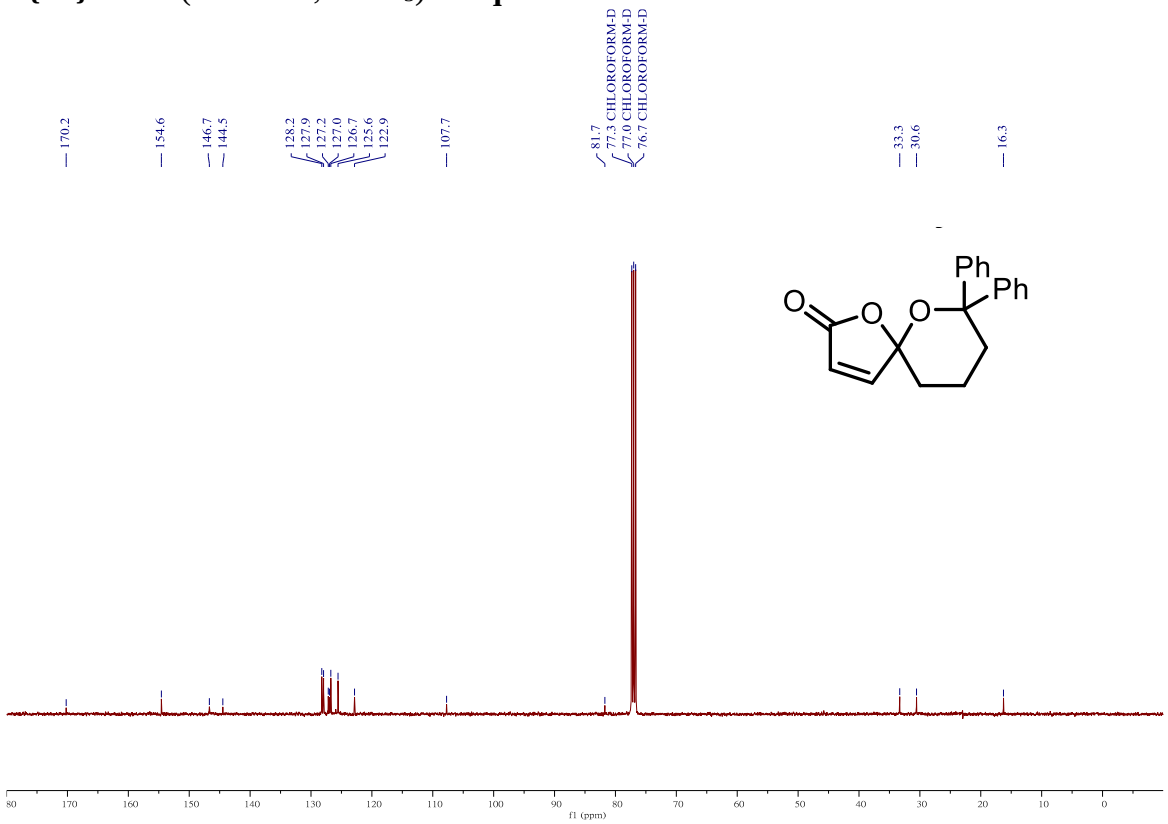


Back to contents

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

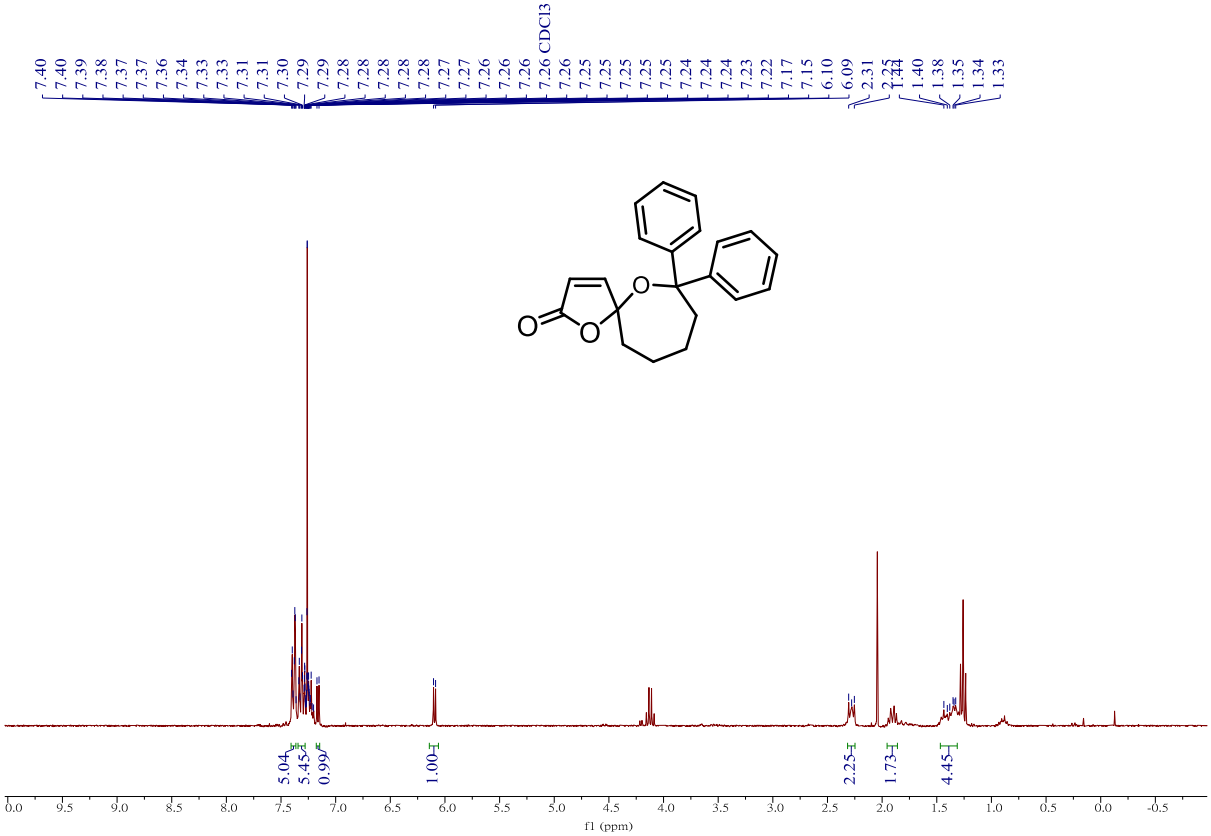


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2q**

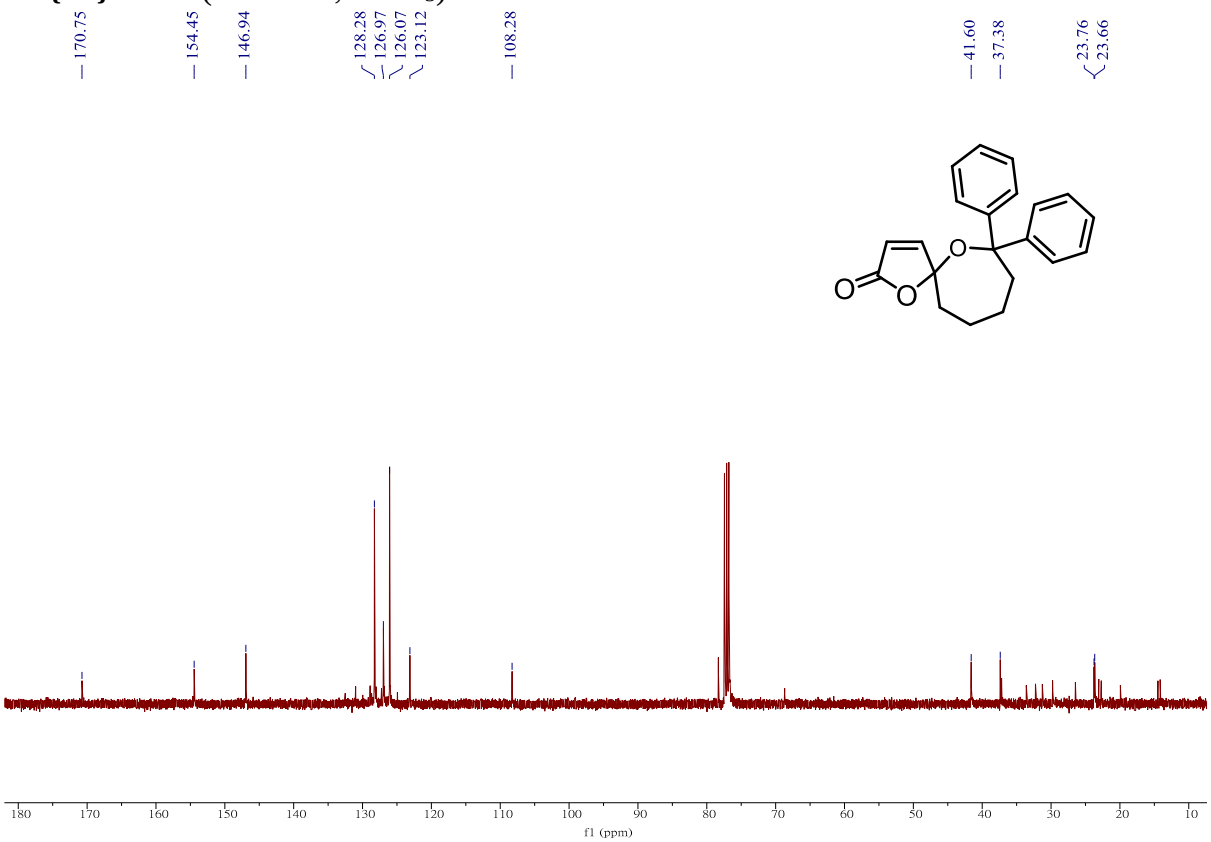


Back to contents

^{1}H NMR (300 MHz, $CDCl_3$) of **2r**, *See procedure*

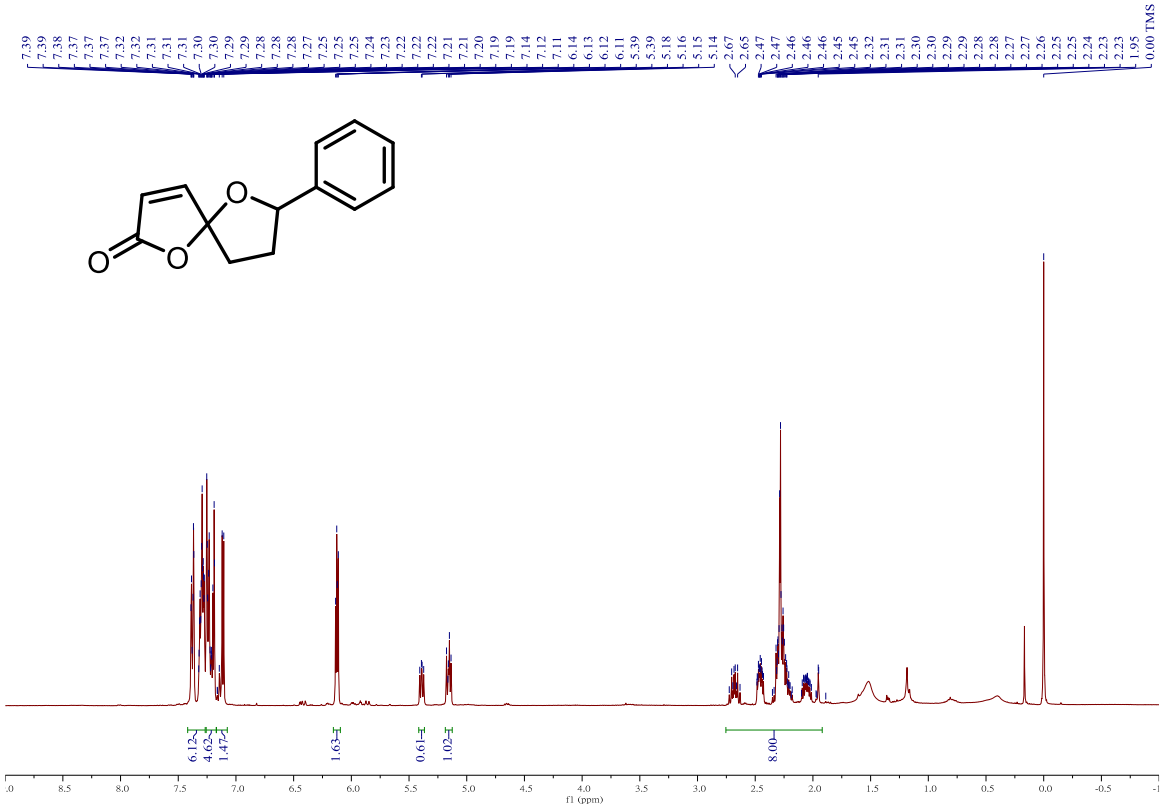


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **2r**

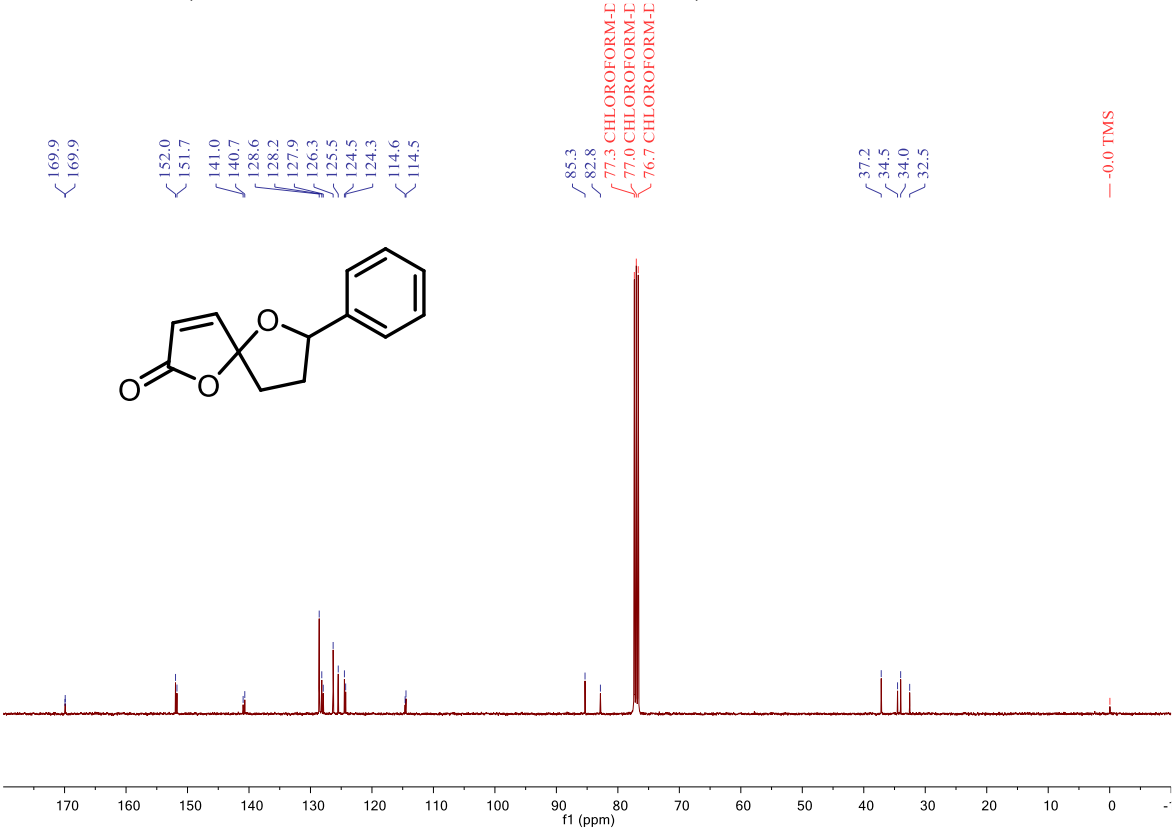


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$ with 0.05% v/v TMS) of **4a**, *See procedure*

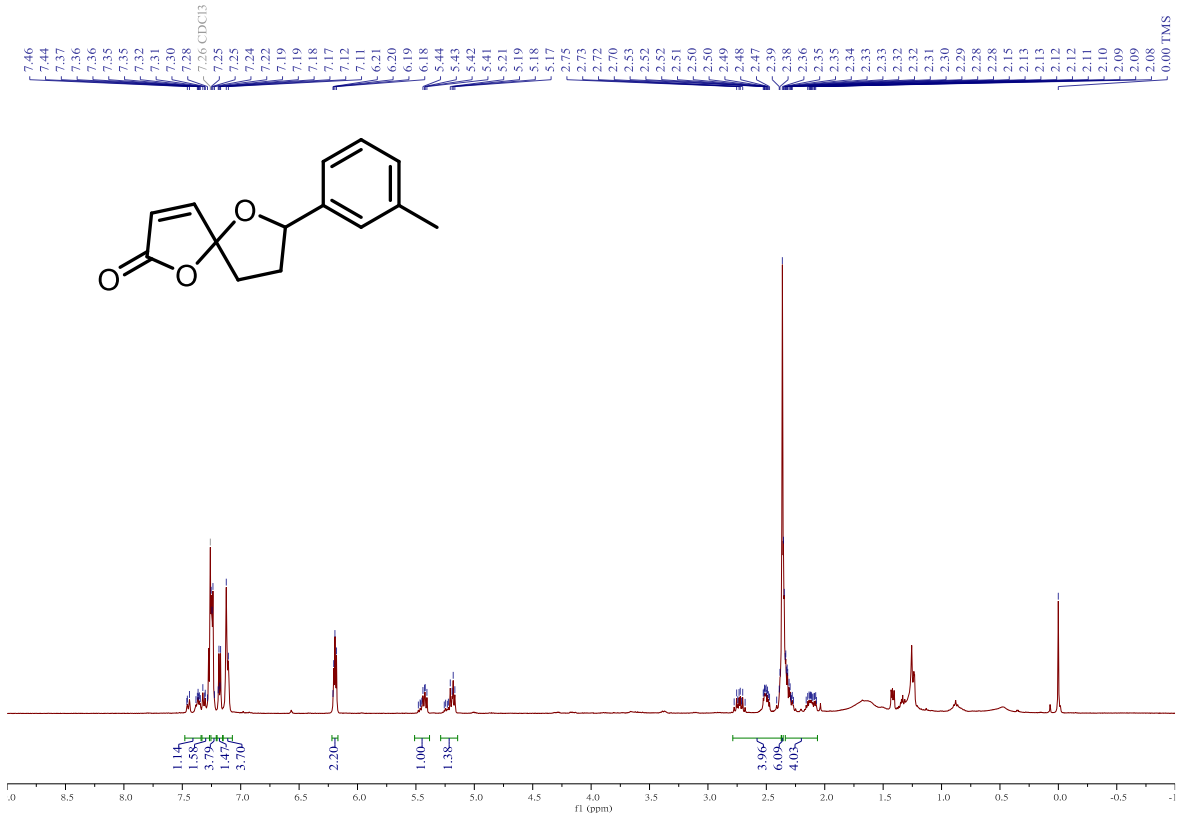


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) of **4a**

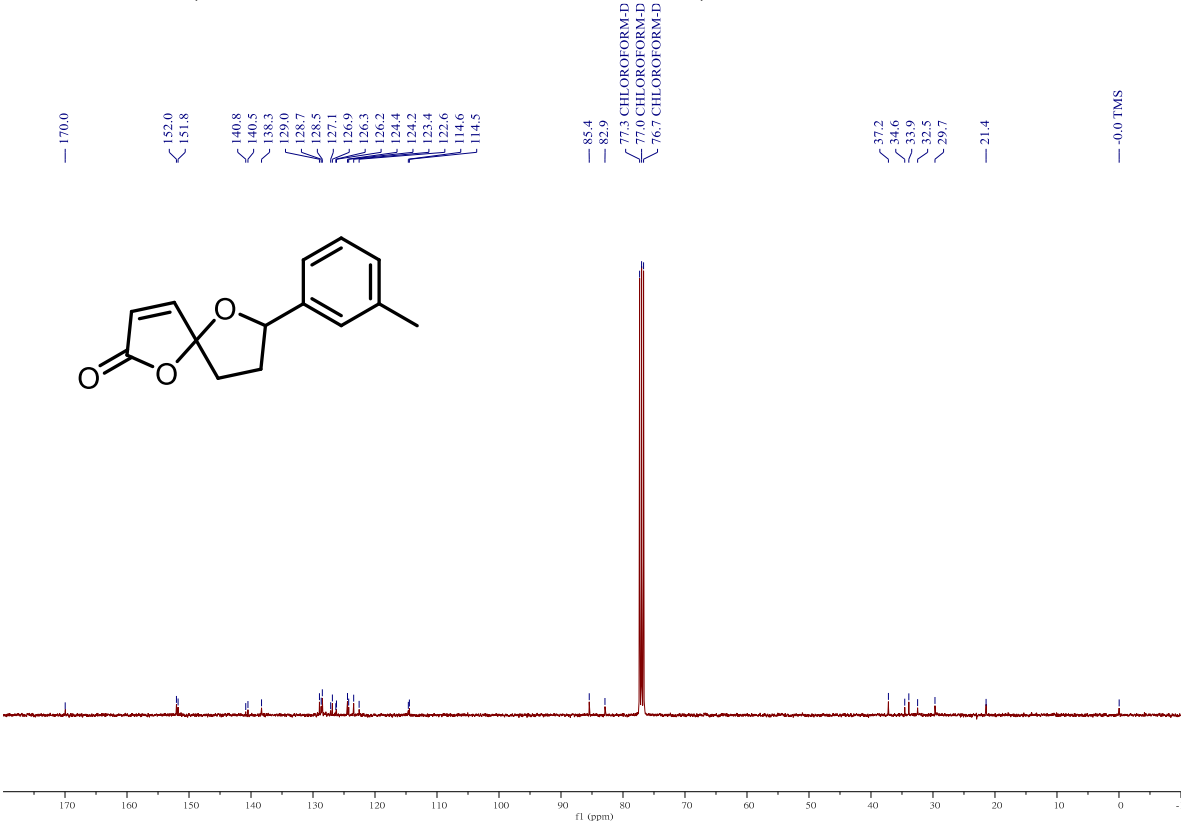


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **4b**, *See procedure*

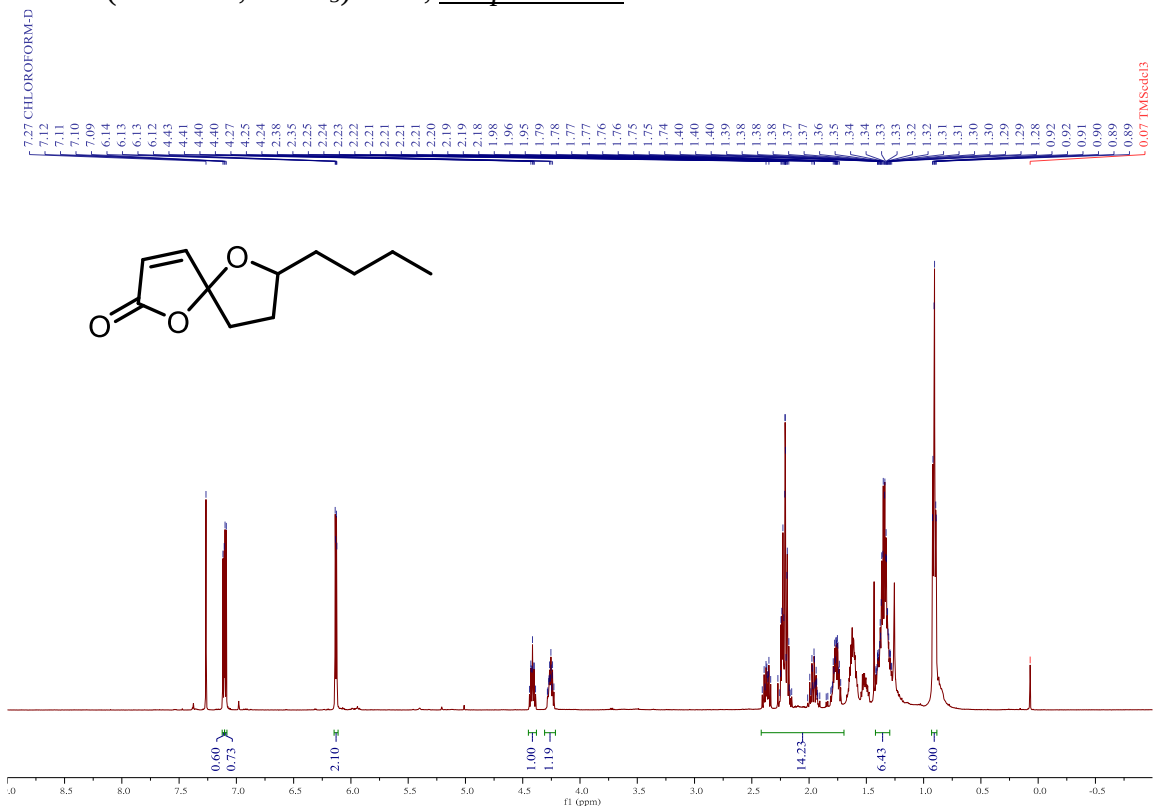


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) of **4b**

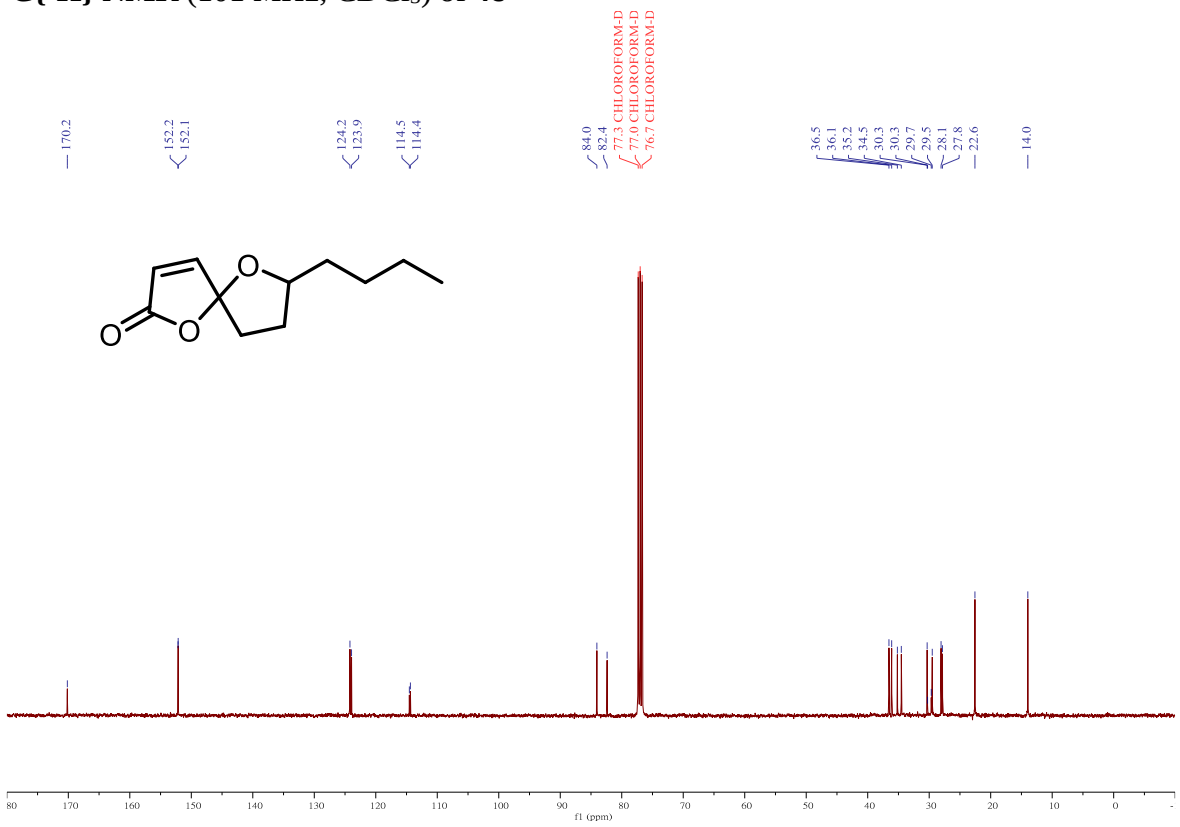


Back to contents

^{1}H NMR (500 MHz, $CDCl_3$) of **4c**, *See procedure*

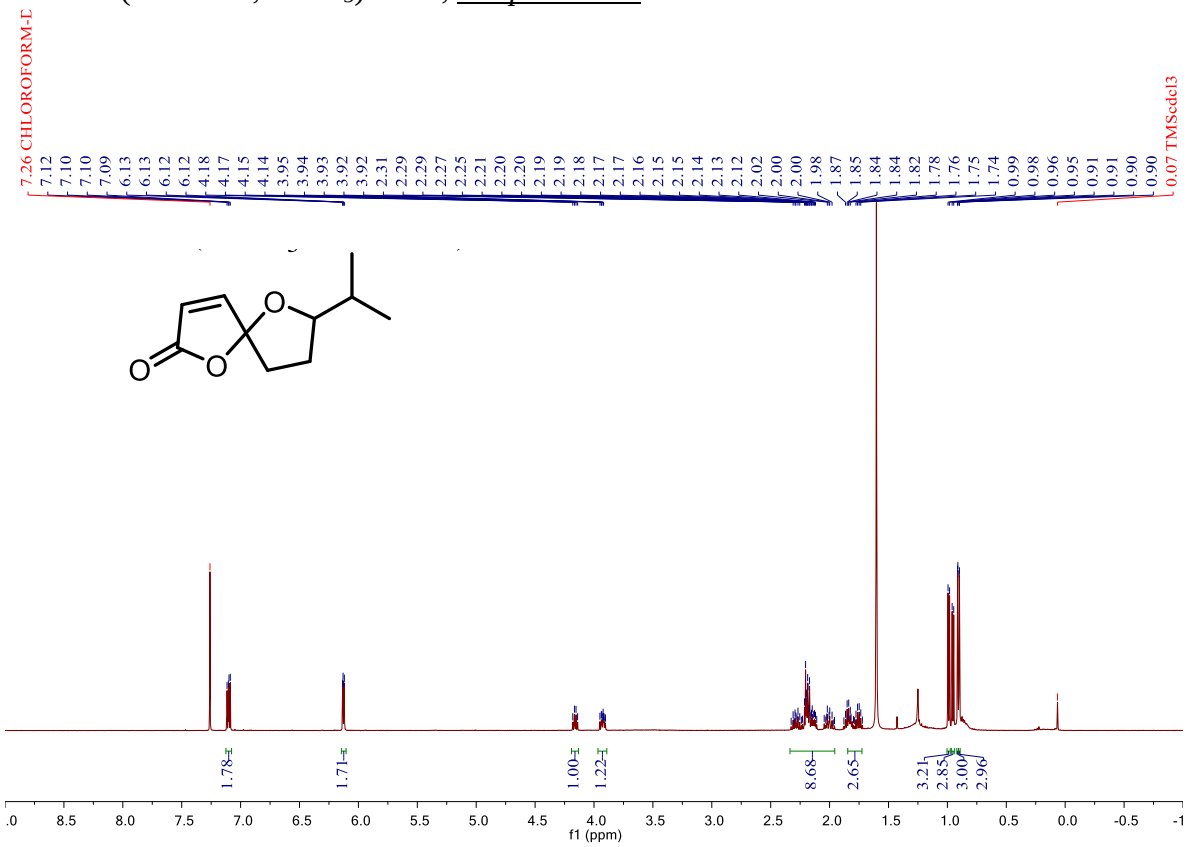


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **4c**

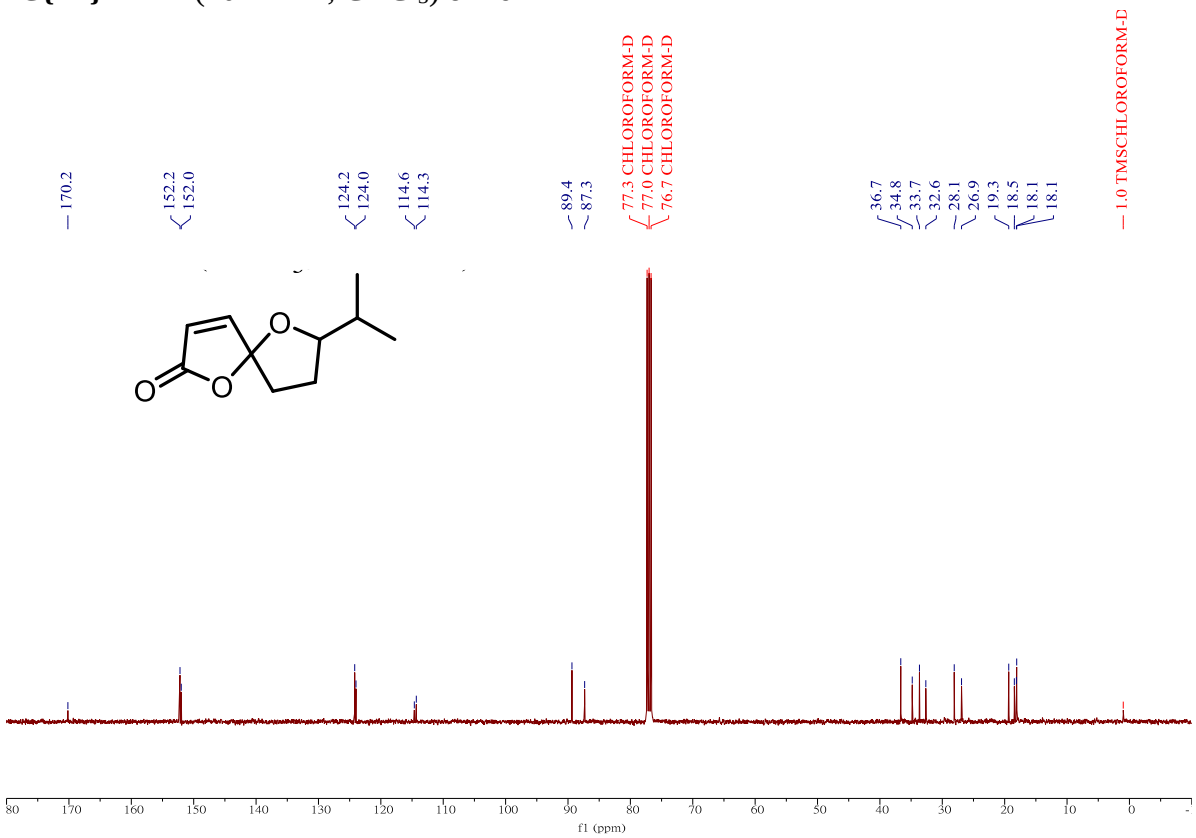


Back to contents

^{1}H NMR (500 MHz, $CDCl_3$) of **4d**, *See procedure*

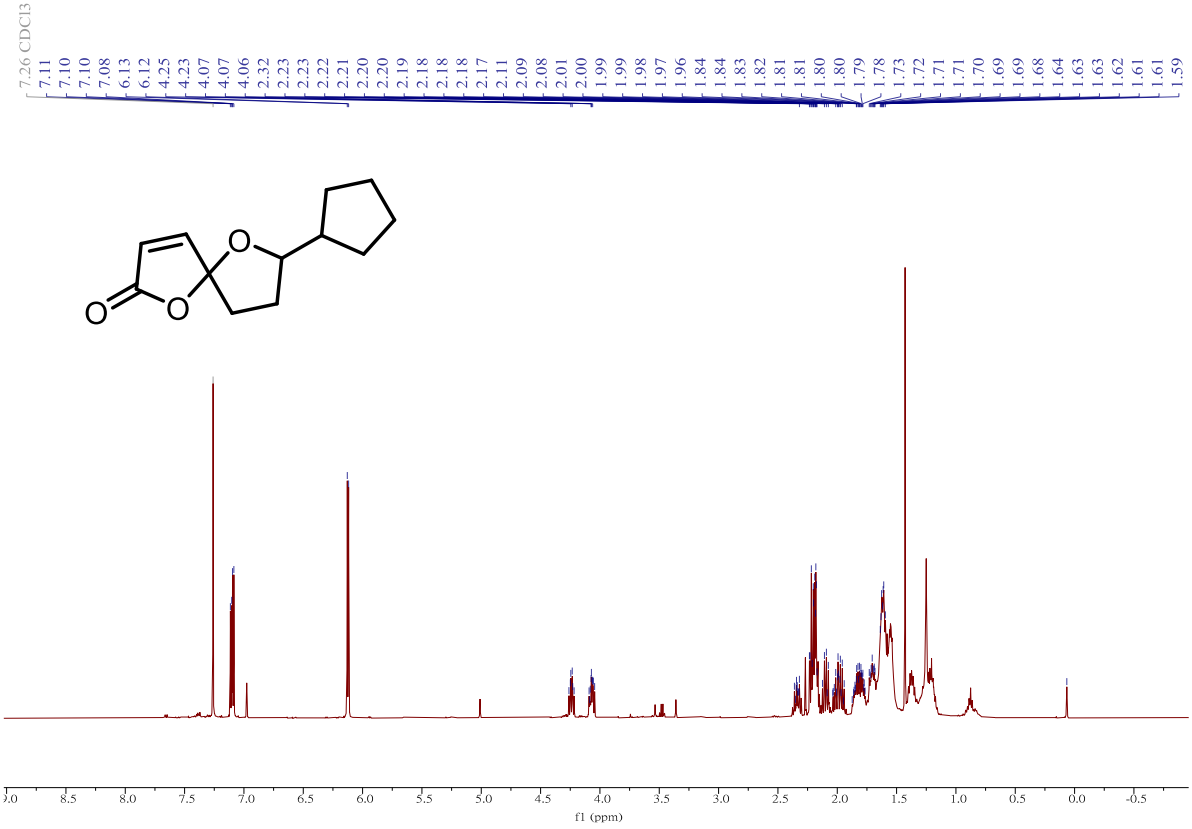


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **4d**

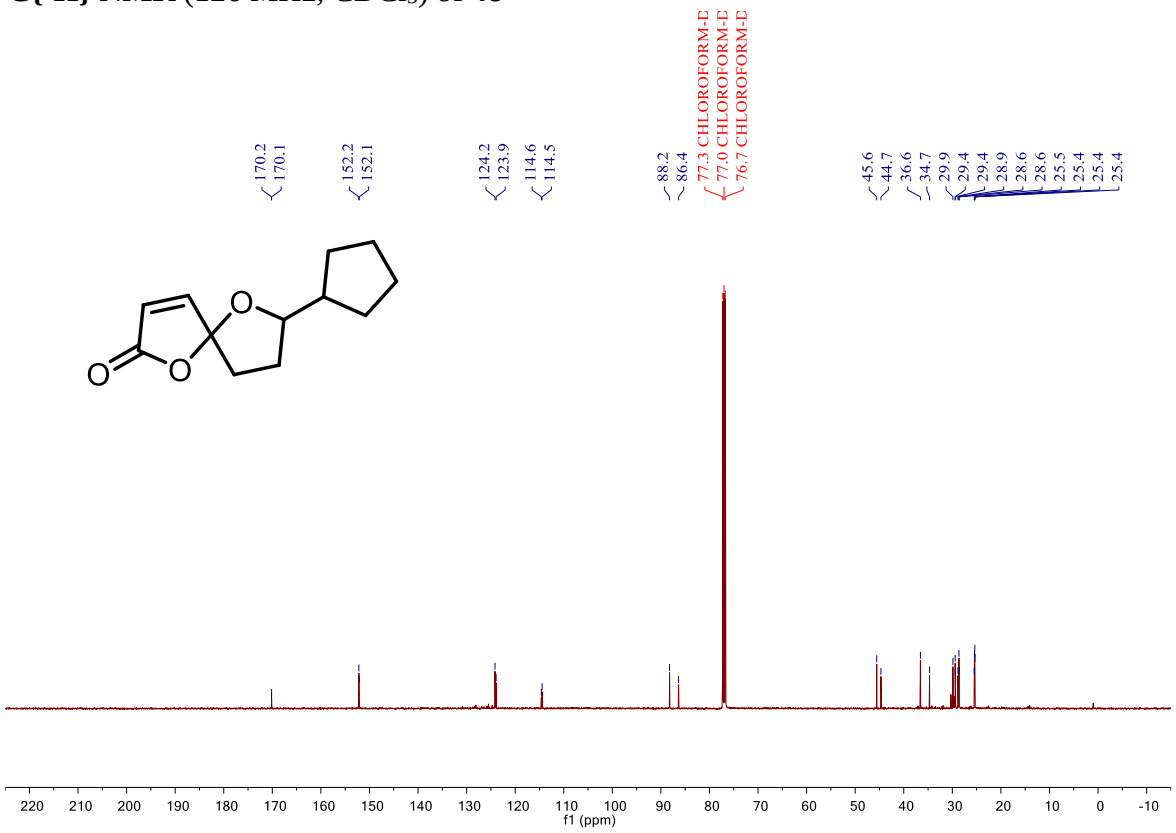


Back to contents

^{1}H NMR (500 MHz, $CDCl_3$) of **4e**, *See procedure*

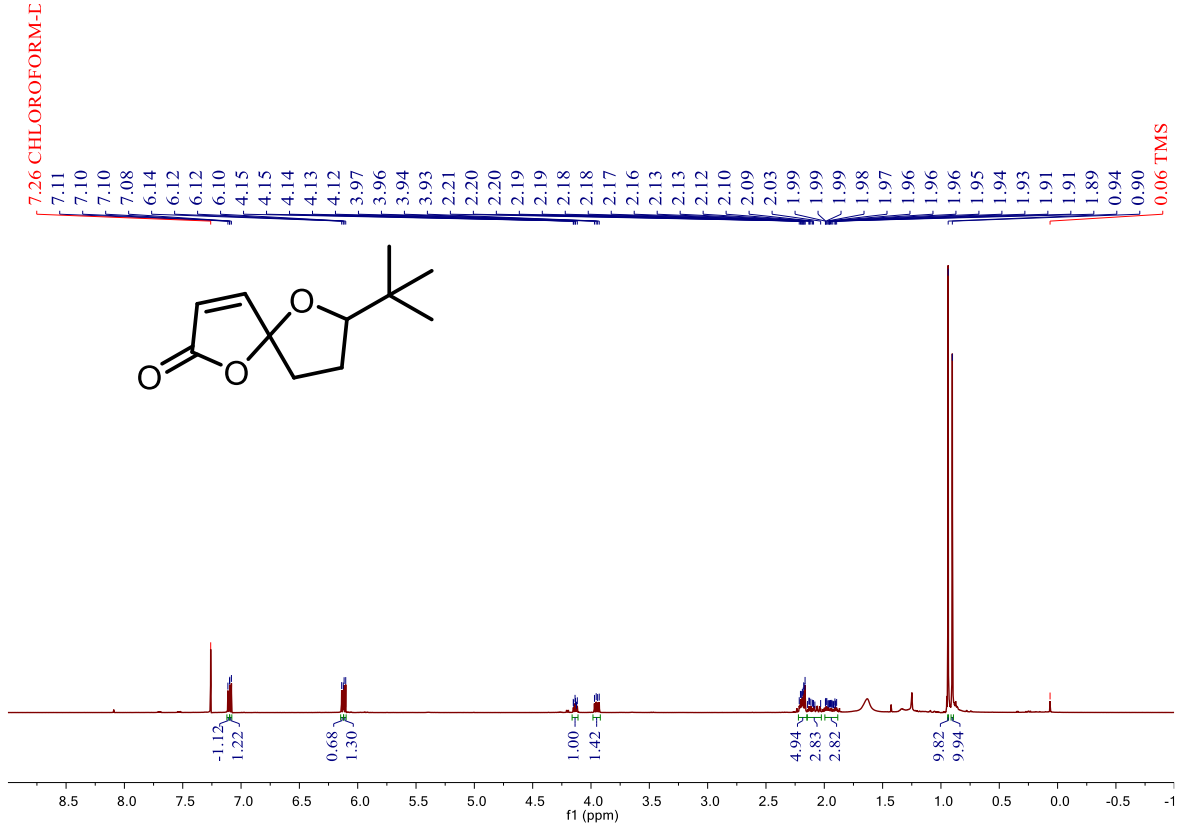


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of **4e**

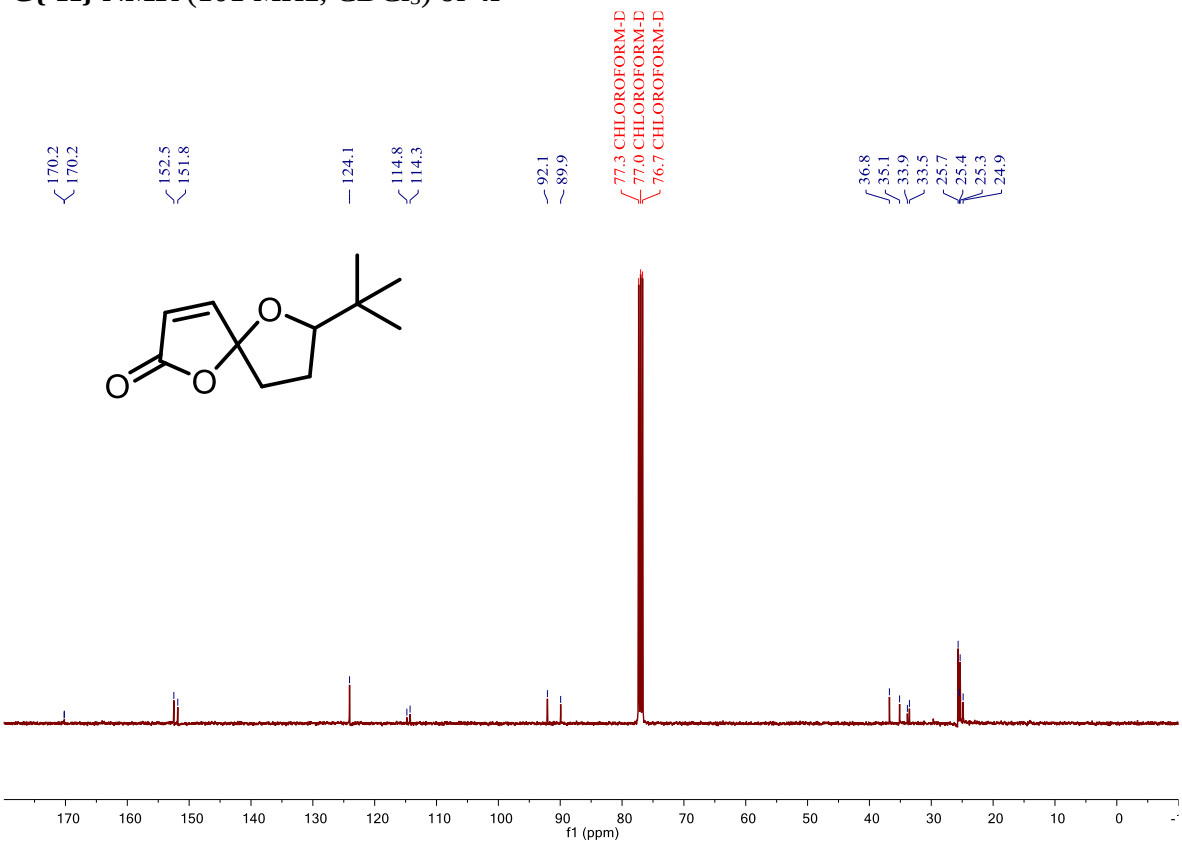


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **4f**, *See procedure*

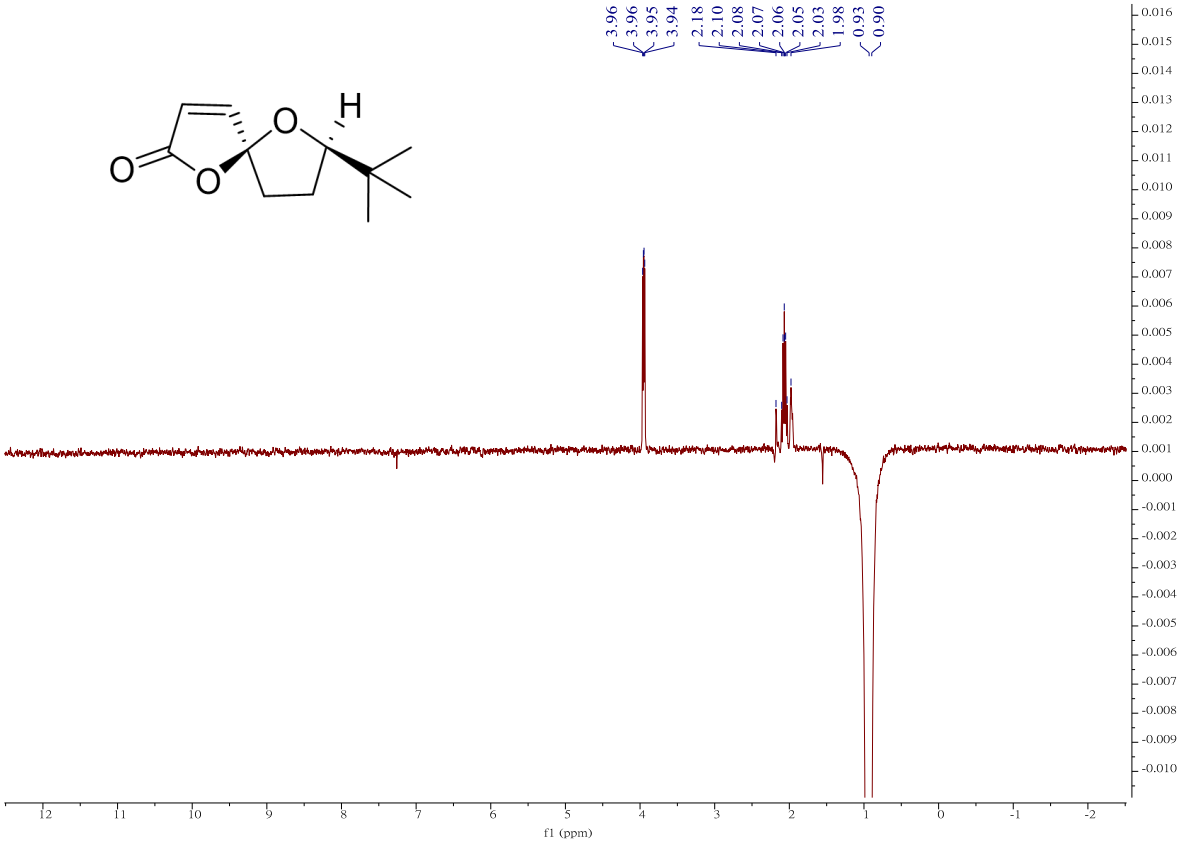


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **4f**

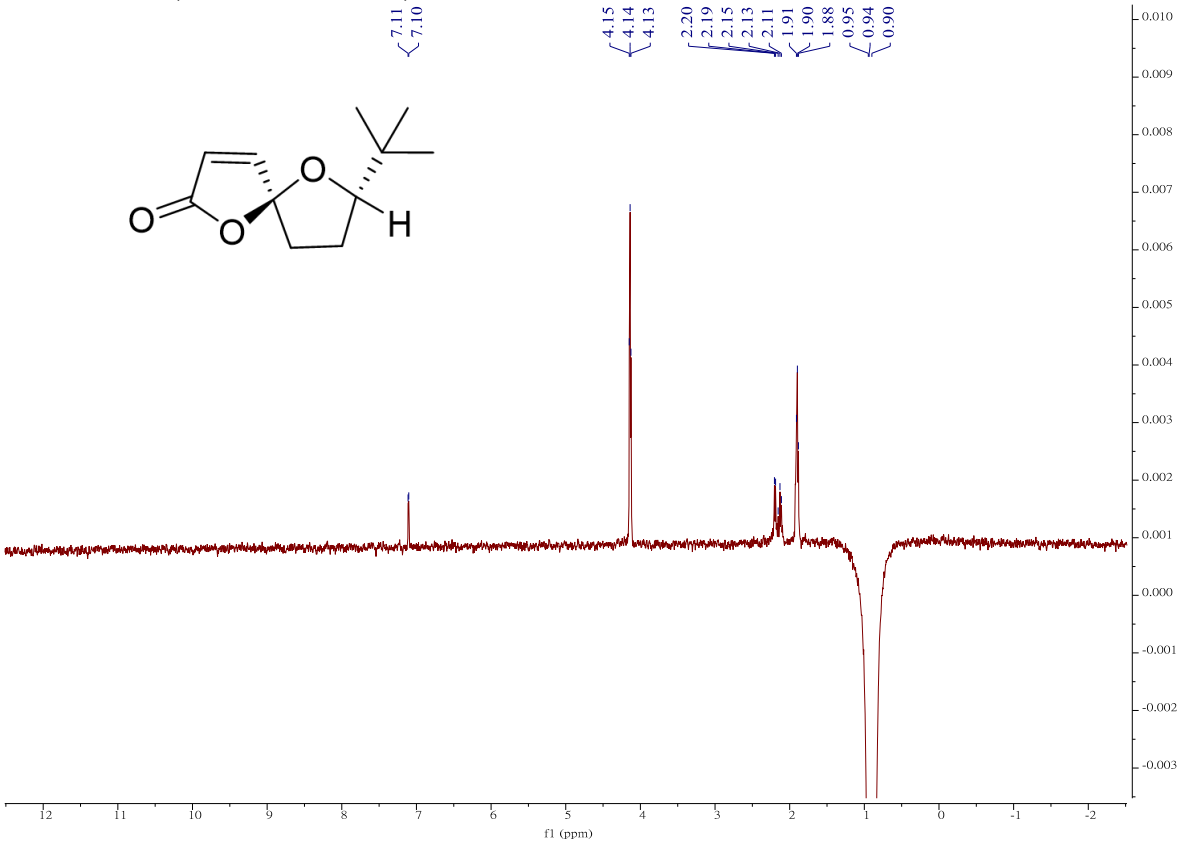


Back to contents

1D NOESY (600 MHz, $CDCl_3$) of **4f**-major diastereomer

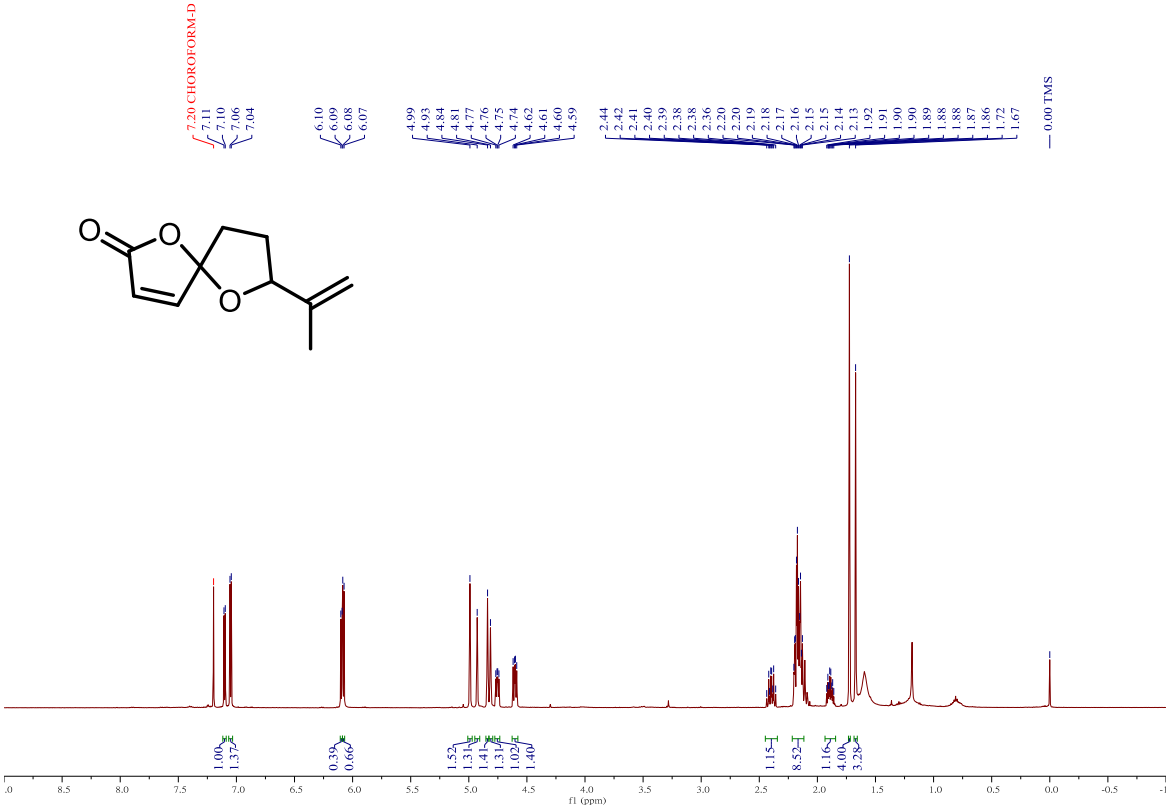


1D NOESY (600 MHz, $CDCl_3$) of **4f**-minor diastereomer

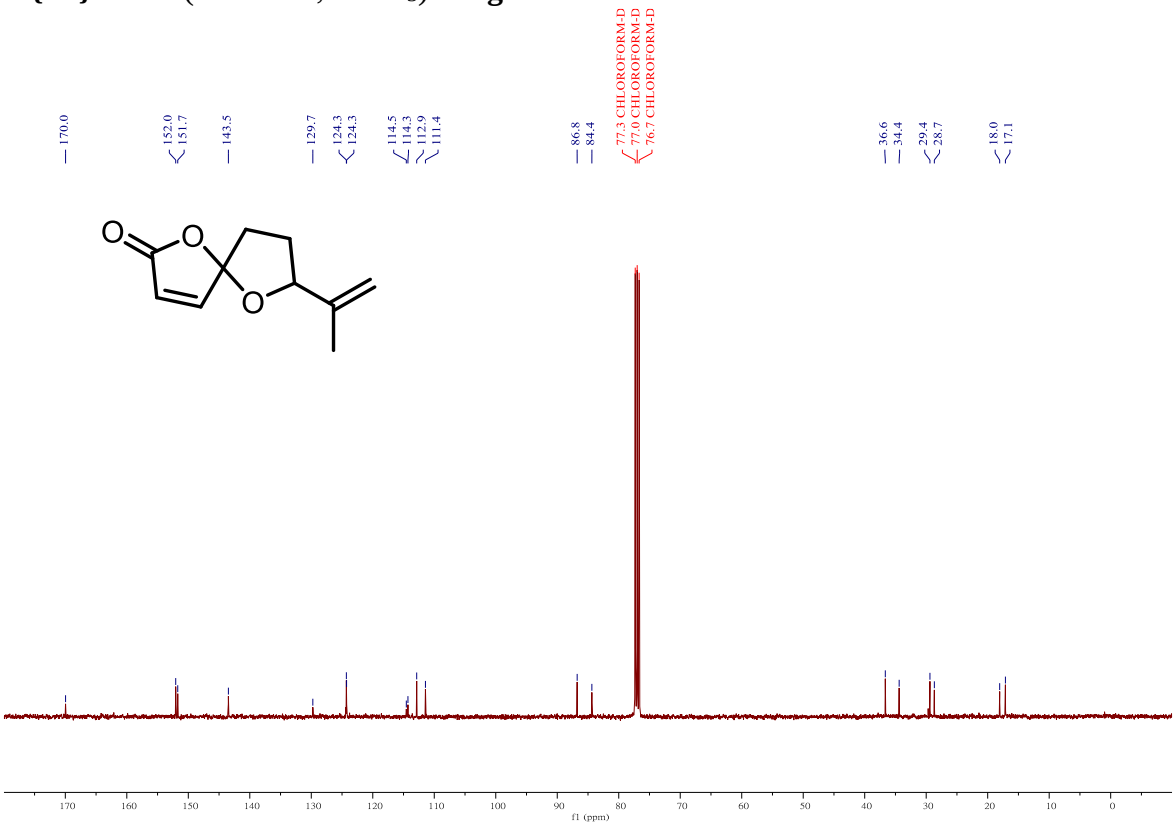


Back to contents

^{1}H NMR (500 MHz, $CDCl_3$) of **4g**, *See procedure*

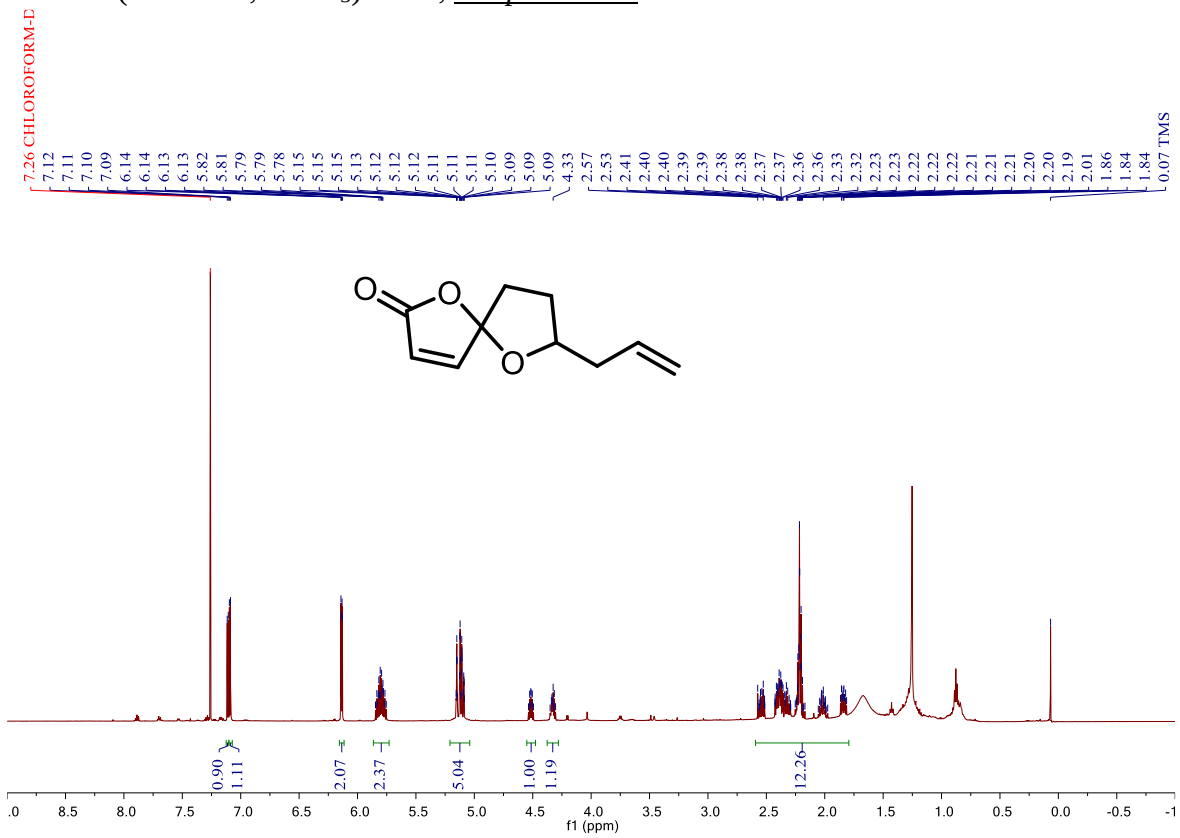


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **4g**

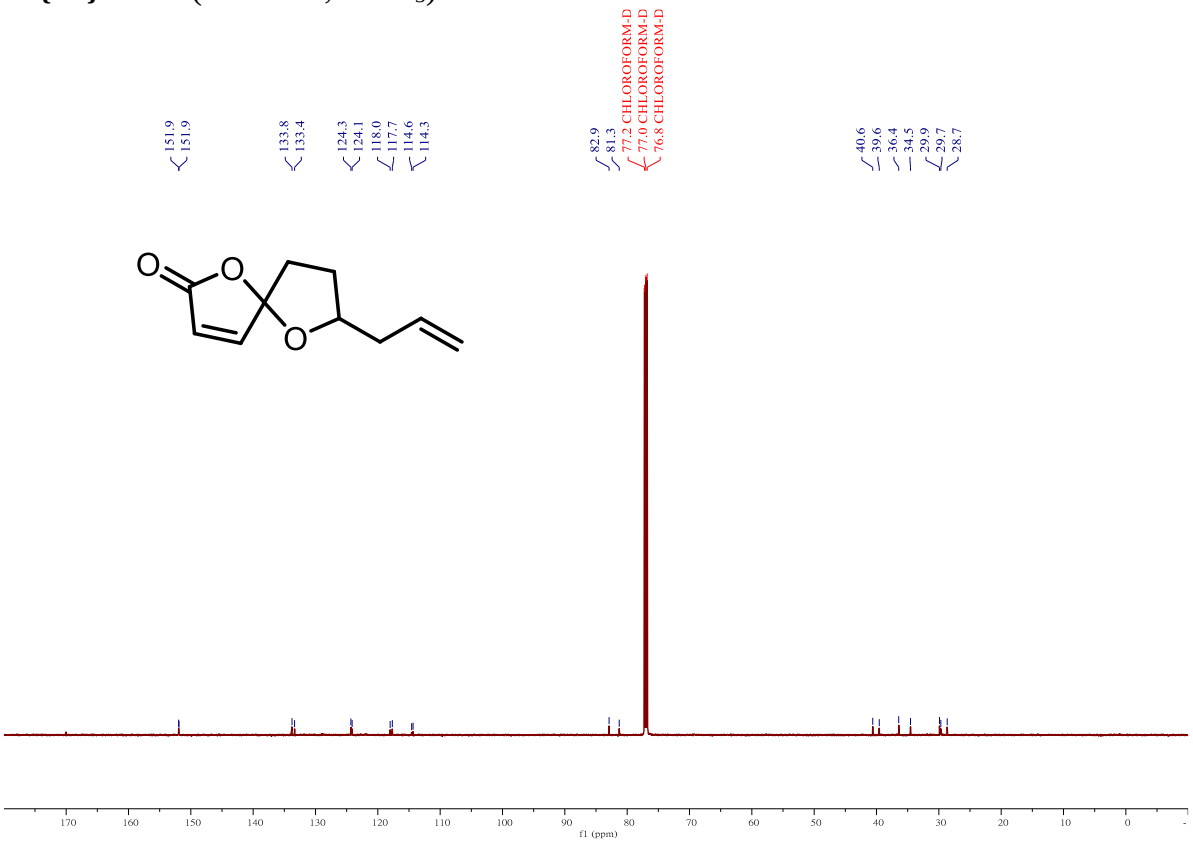


Back to contents

^{1}H NMR (600 MHz, $CDCl_3$) of **4h**, *See procedure*

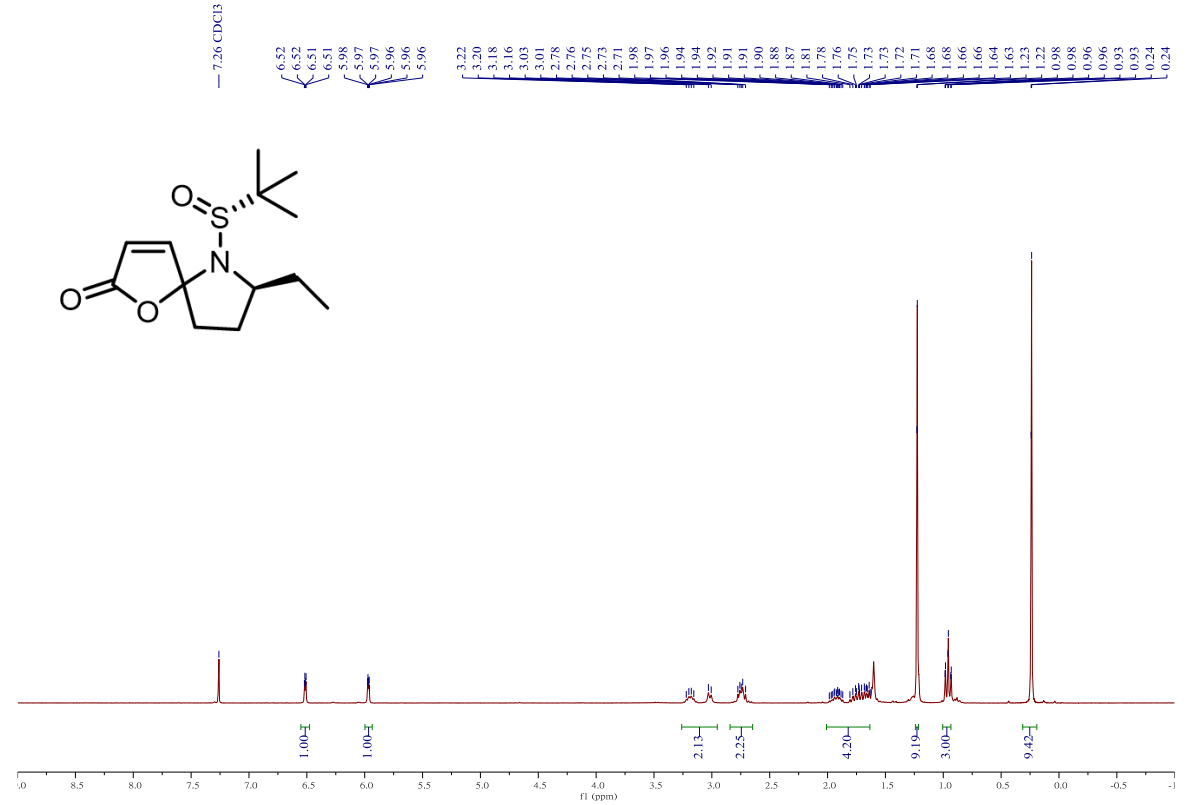


$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) of **4h**



Back to contents

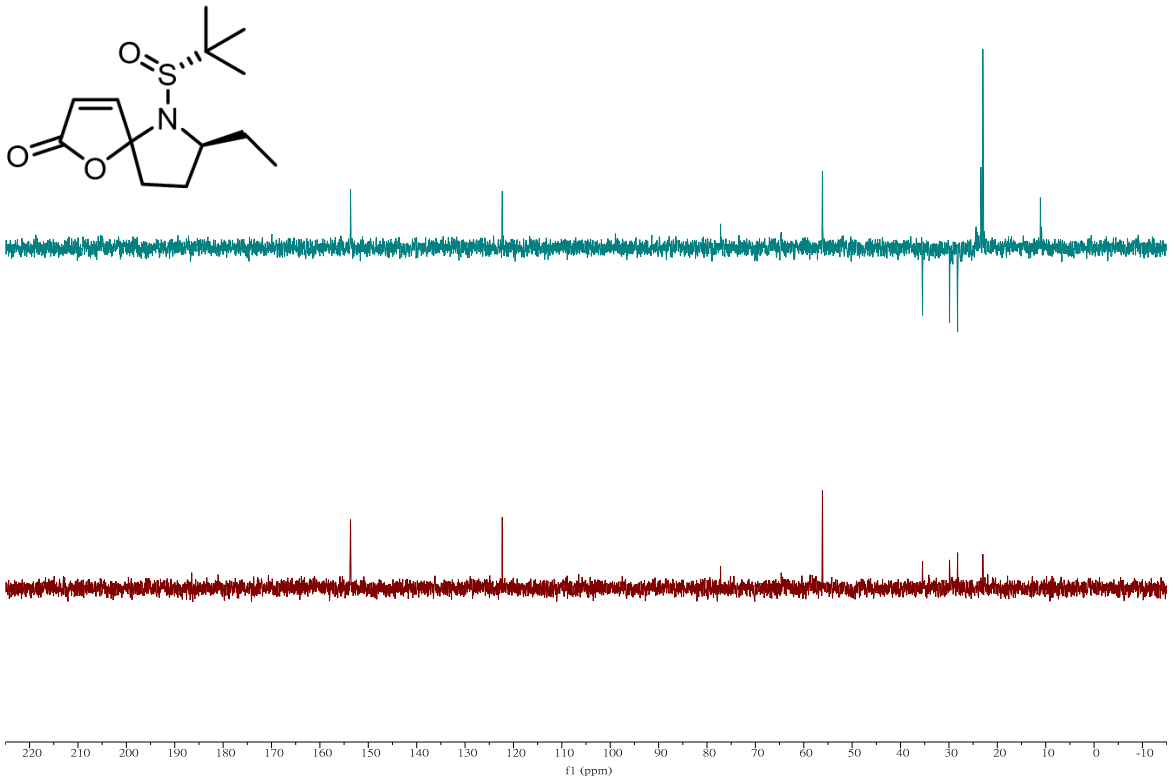
^{1}H NMR (300 MHz, $CDCl_3$) of **7**, *See procedure*



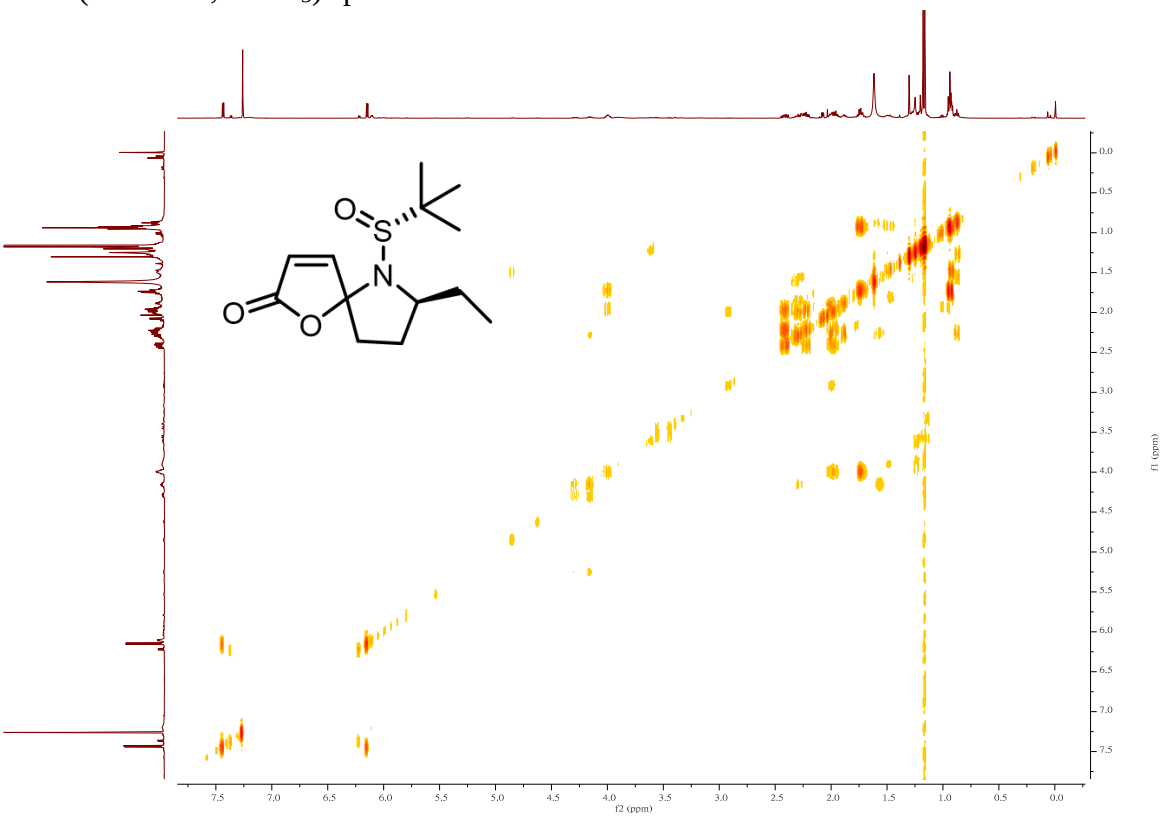
$^{13}C\{^{1}H\}$ NMR (126 MHz, $CDCl_3$) of **7**

Back to contents

DEPT (500 MHz, $CDCl_3$**)** spectra of **7**

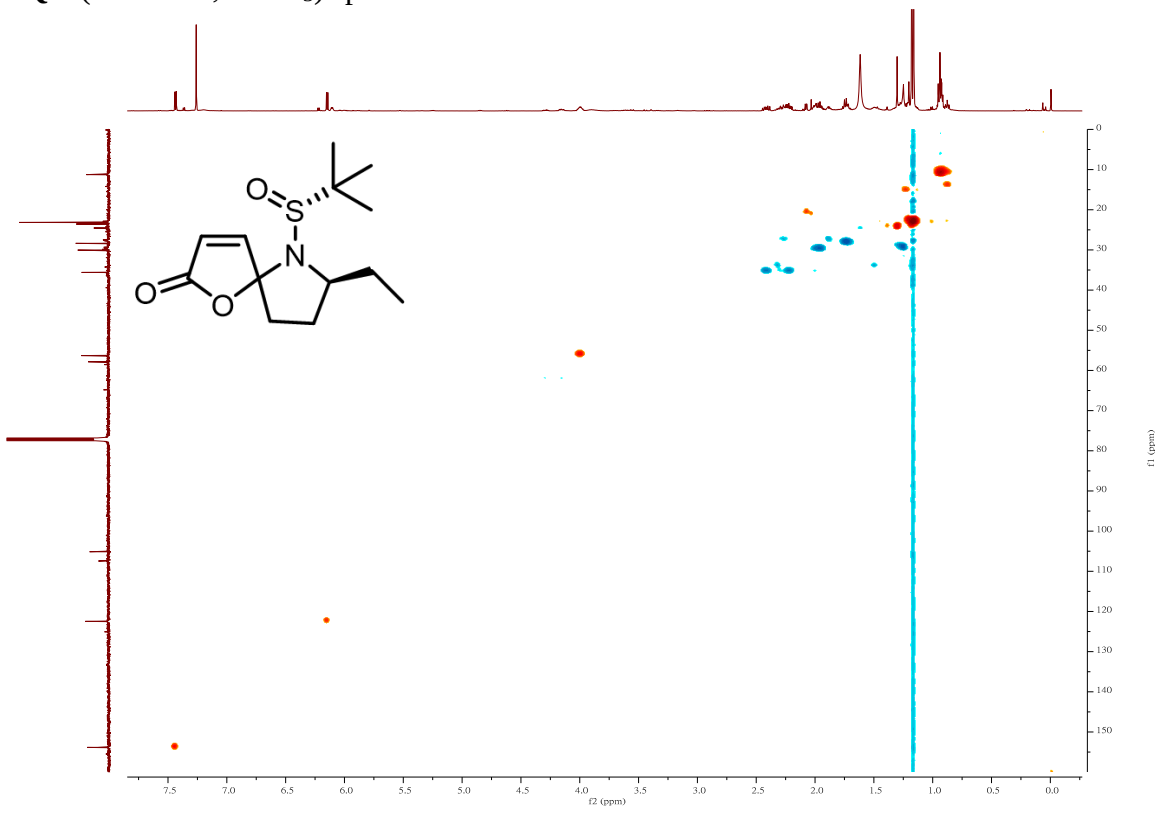


COSY (500 MHz, $CDCl_3$) spectrum of **7**

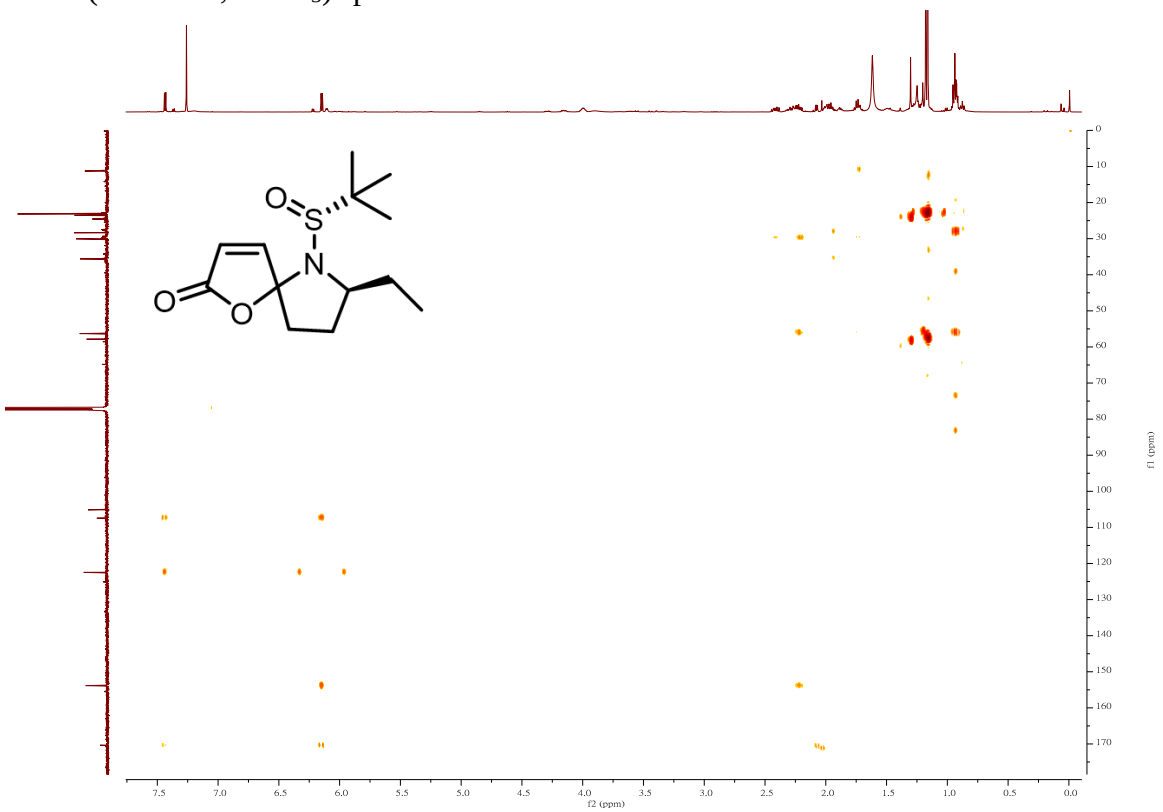


Back to contents

HSQC (500 MHz, $CDCl_3$) spectrum of **7**



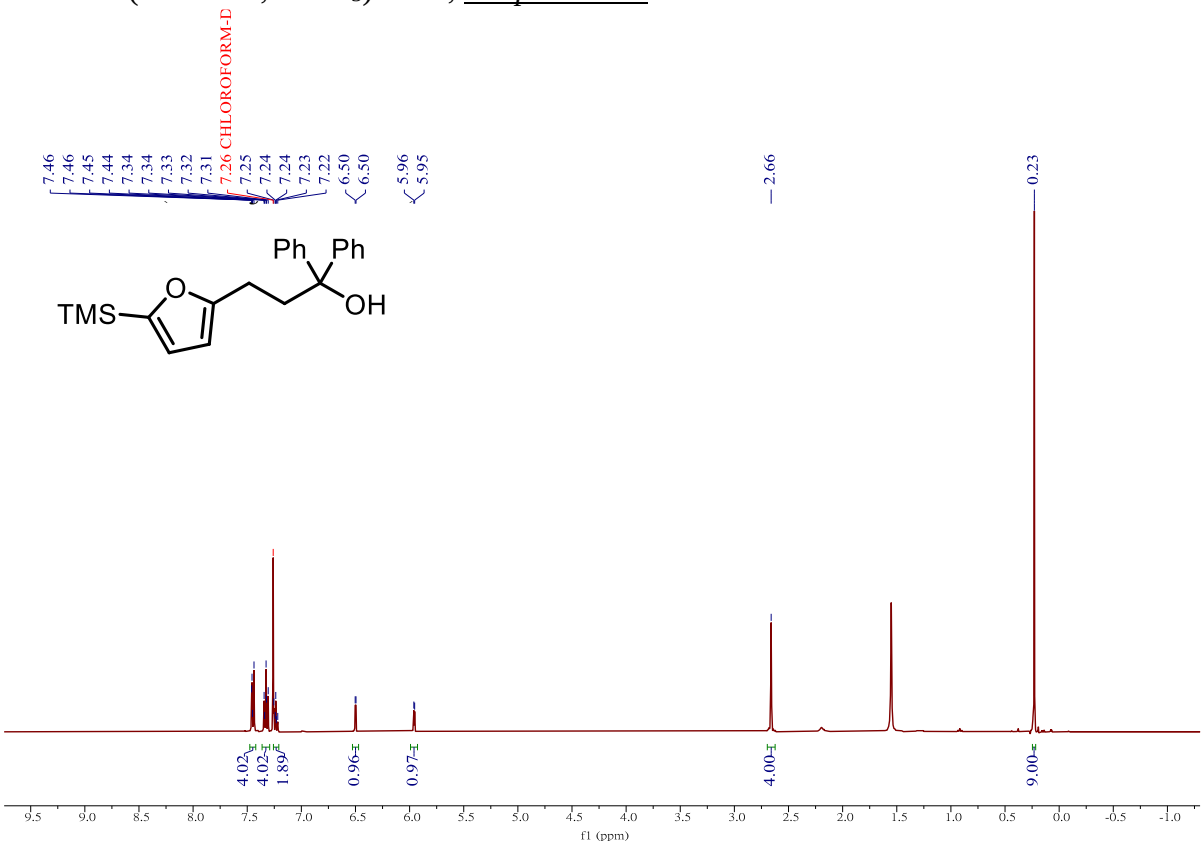
HMBC (500 MHz, $CDCl_3$) spectrum of **7**



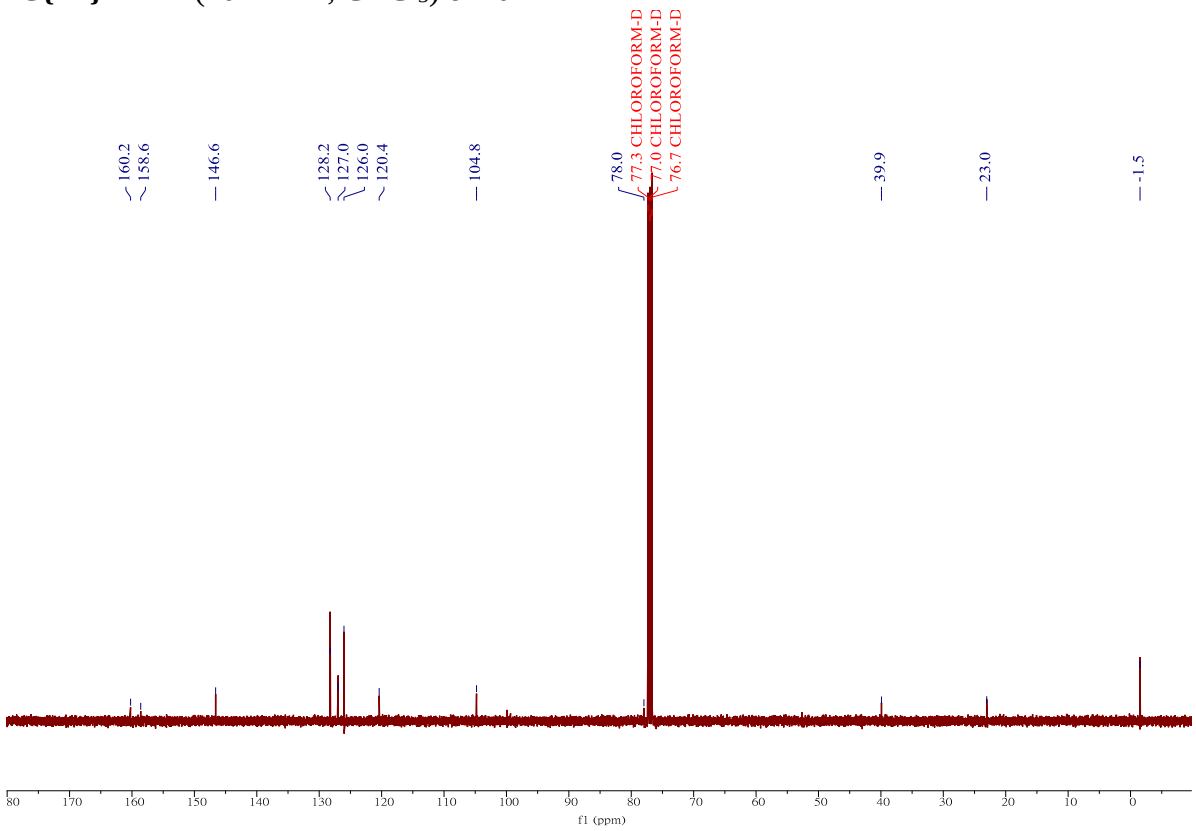
Back to contents

9.2. Starting material scope

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

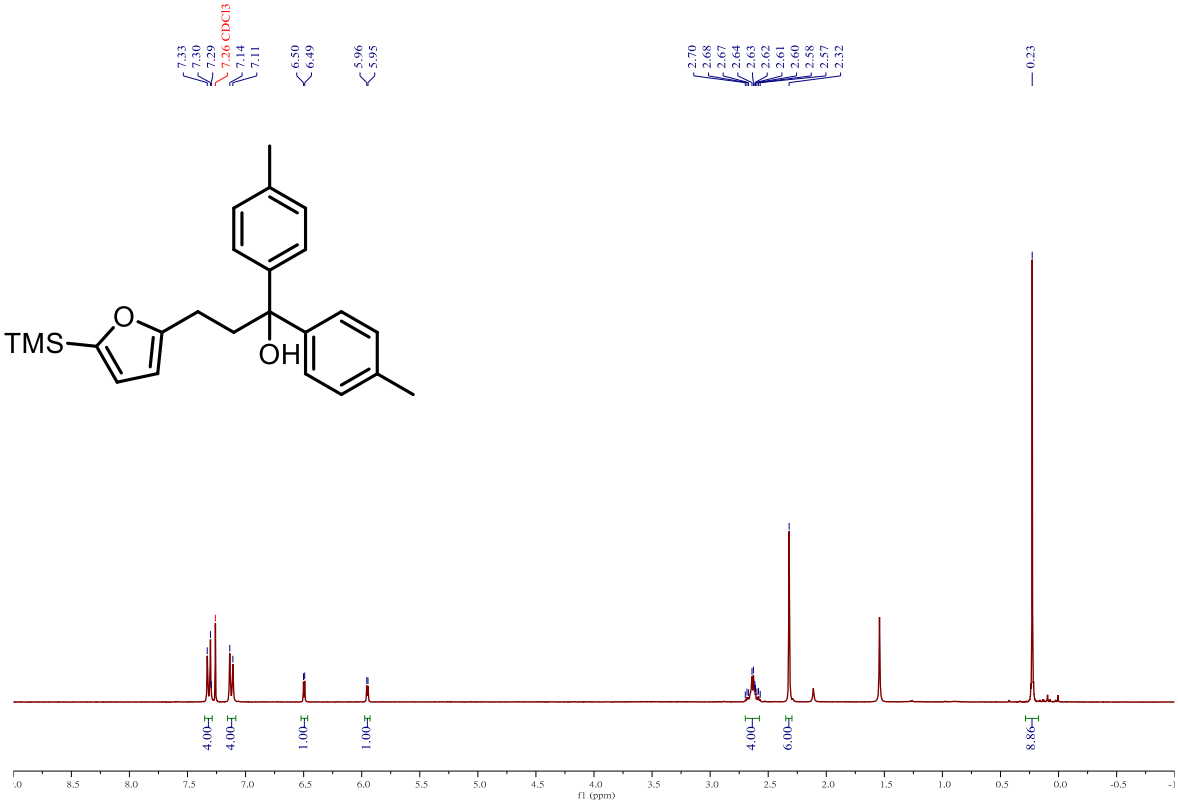


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1a**

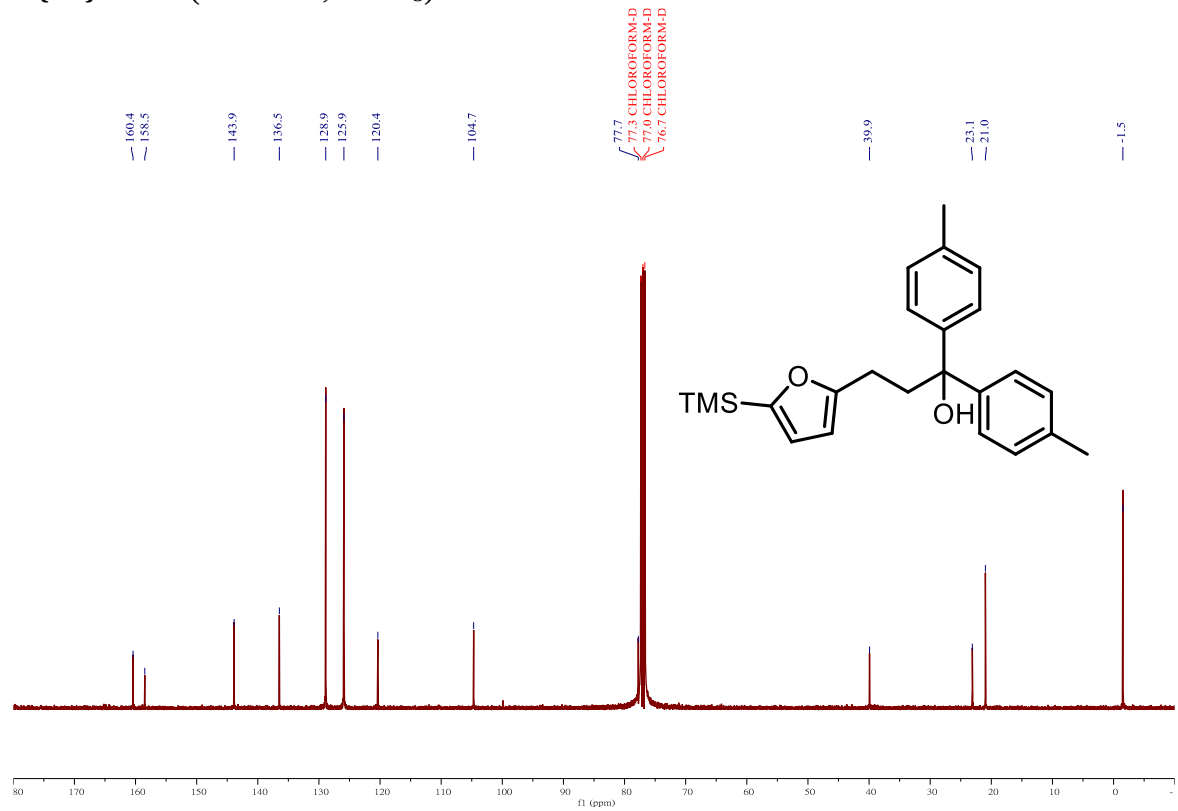


Back to contents

^{1}H NMR (300 MHz, $CDCl_3$) of **1b**, *See procedure*

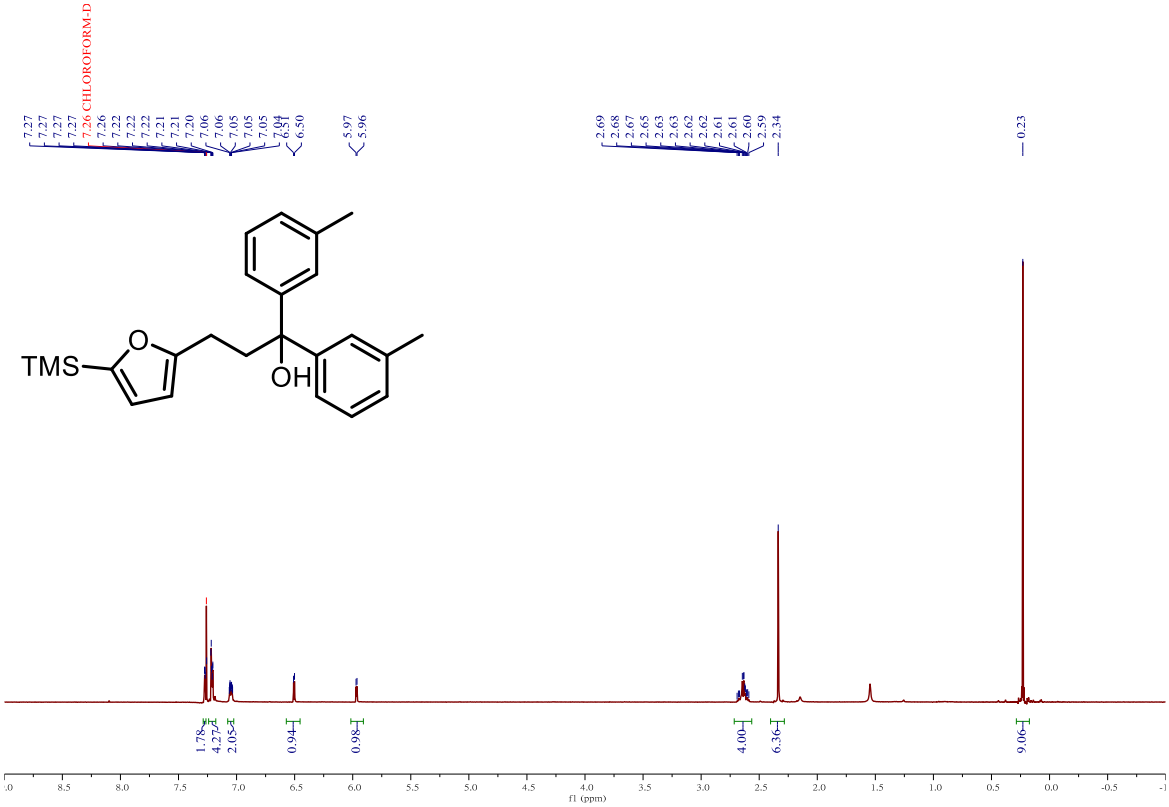


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1b**

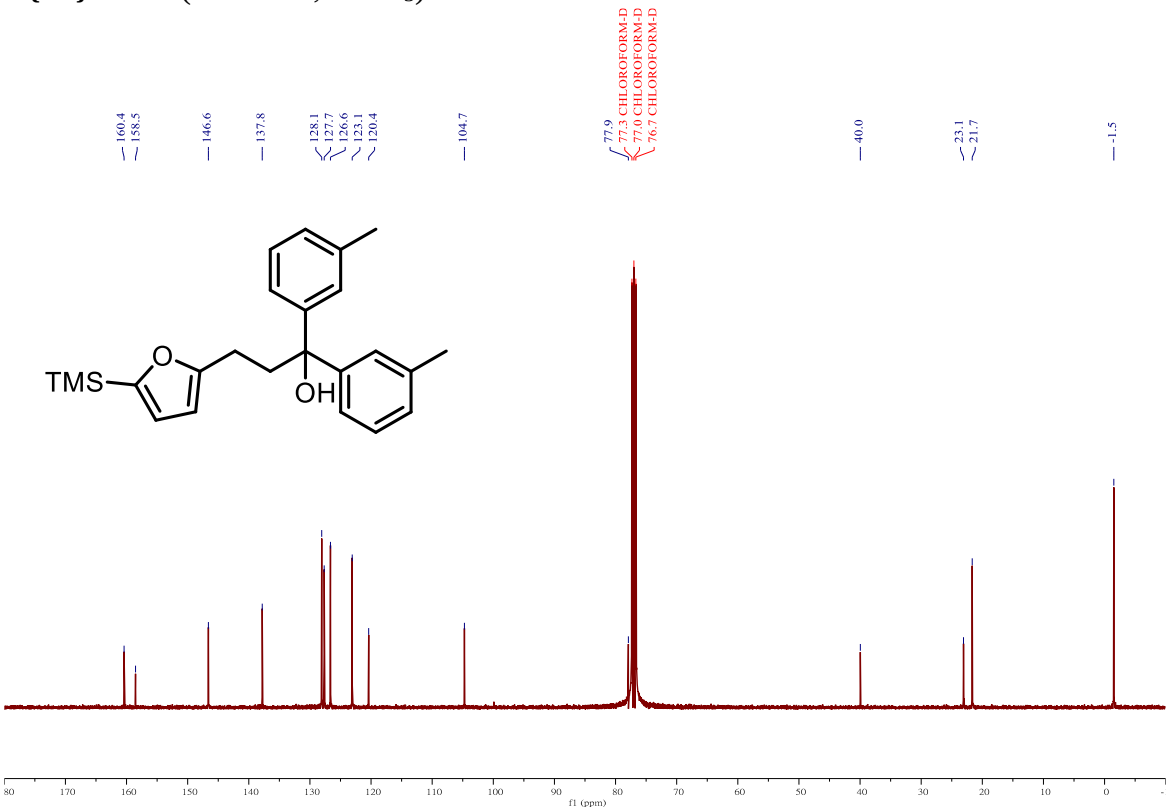


Back to contents

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

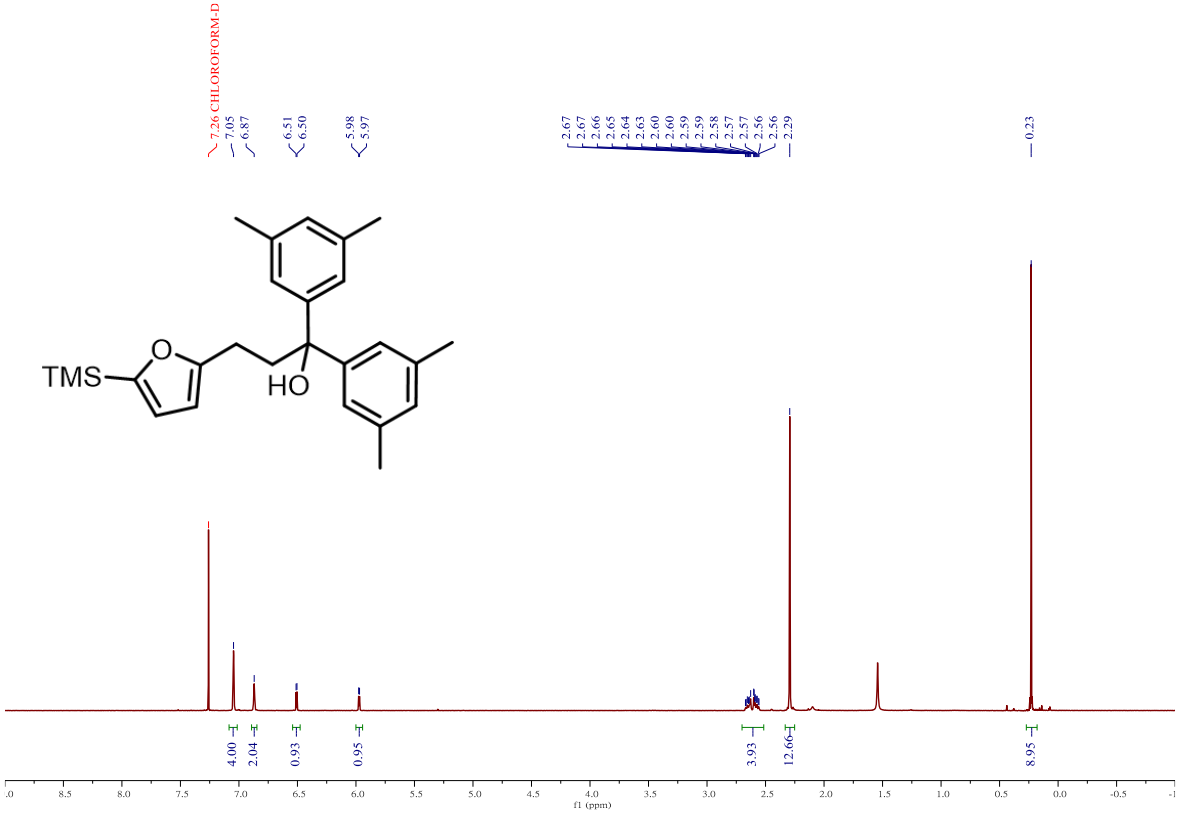


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1c**

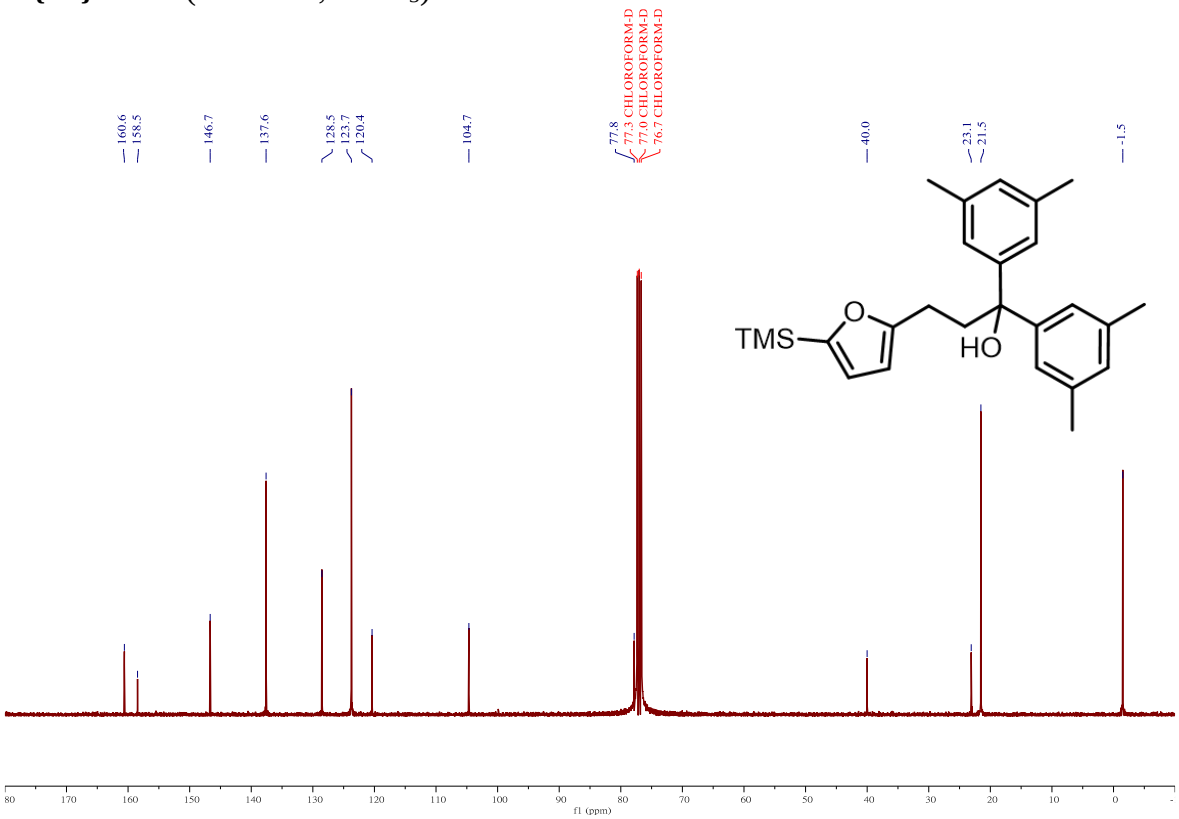


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **1d**, *See procedure*

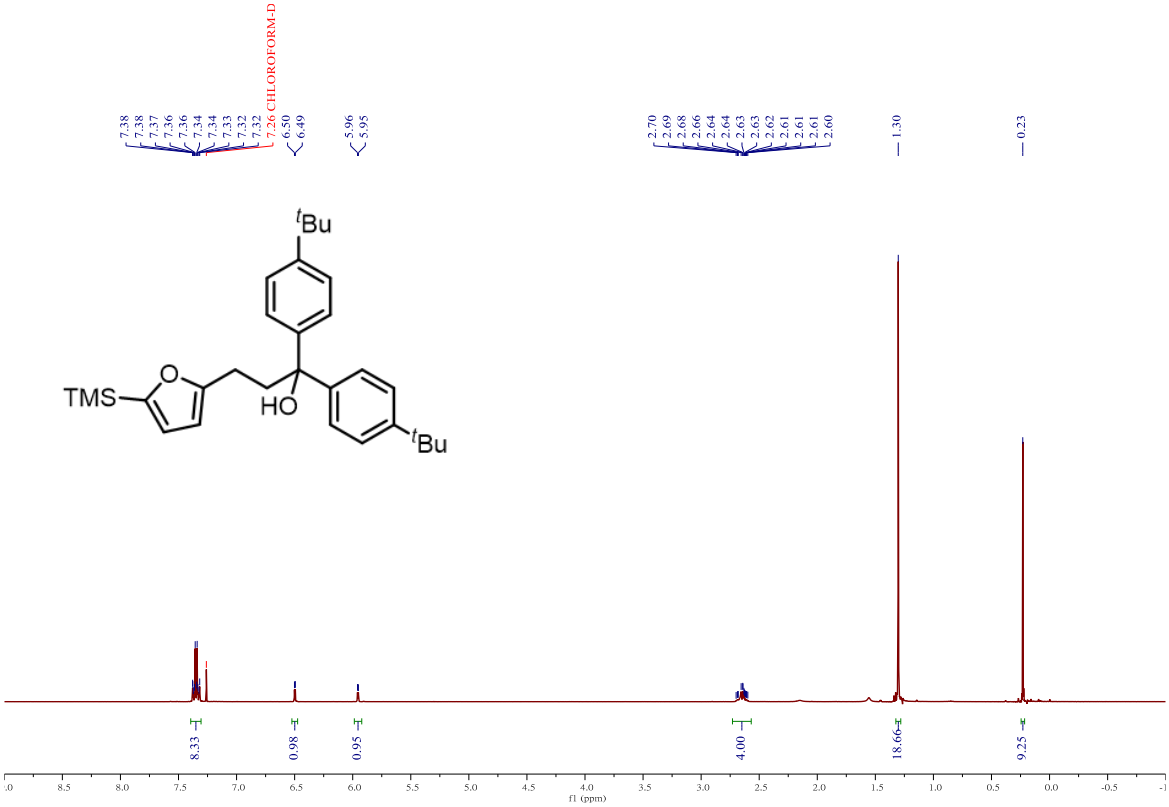


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1d**

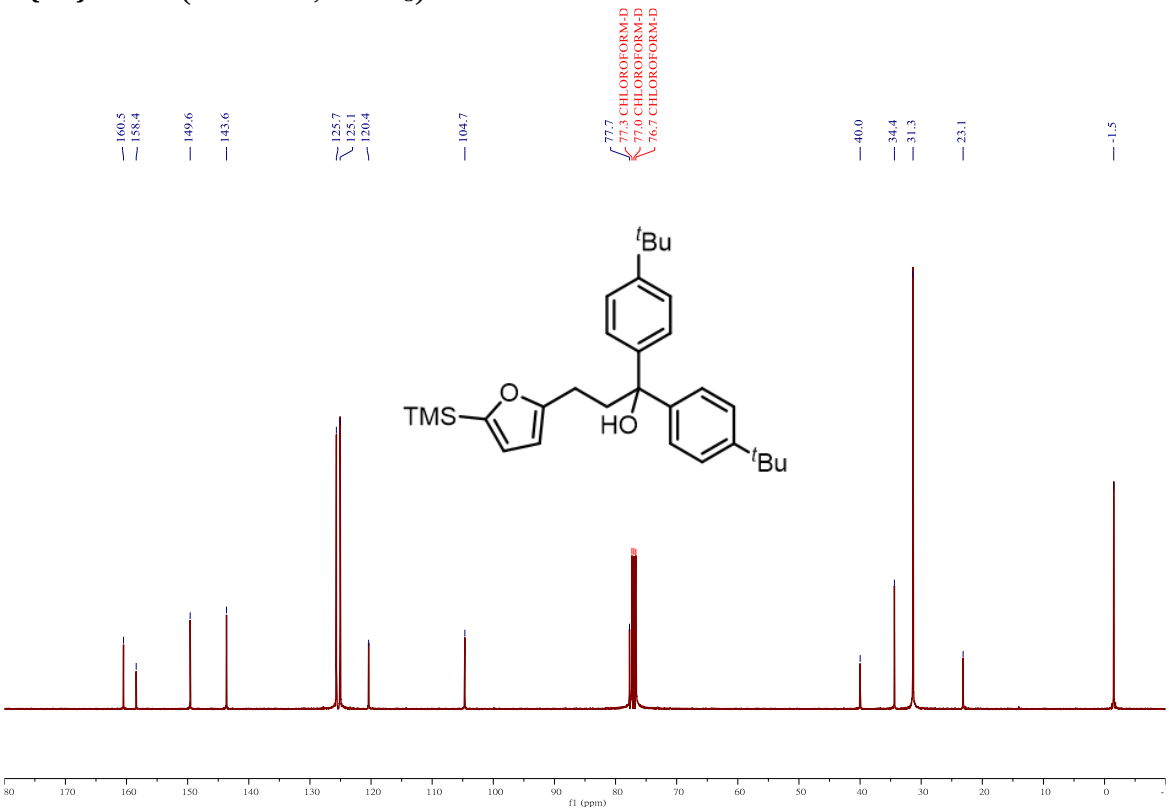


Back to contents

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

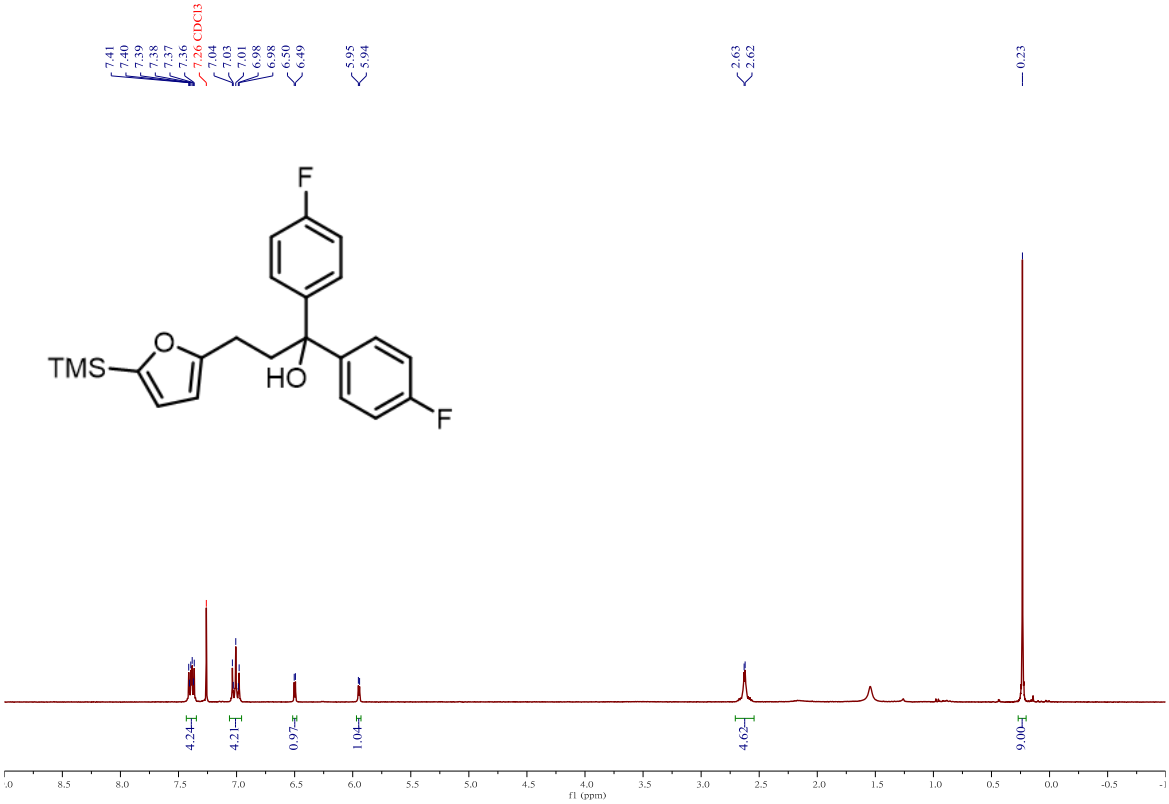


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1e**

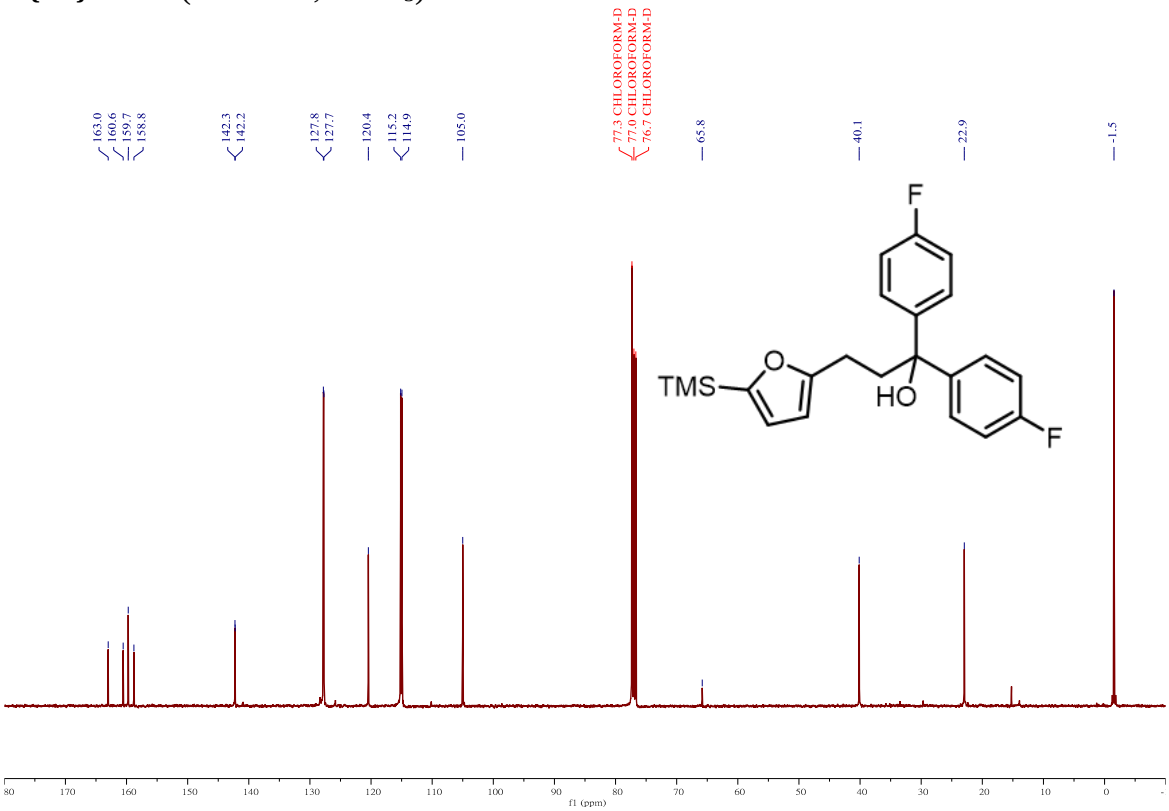


Back to contents

^{1}H NMR (300 MHz, $CDCl_3$) of **1f**, *See procedure*

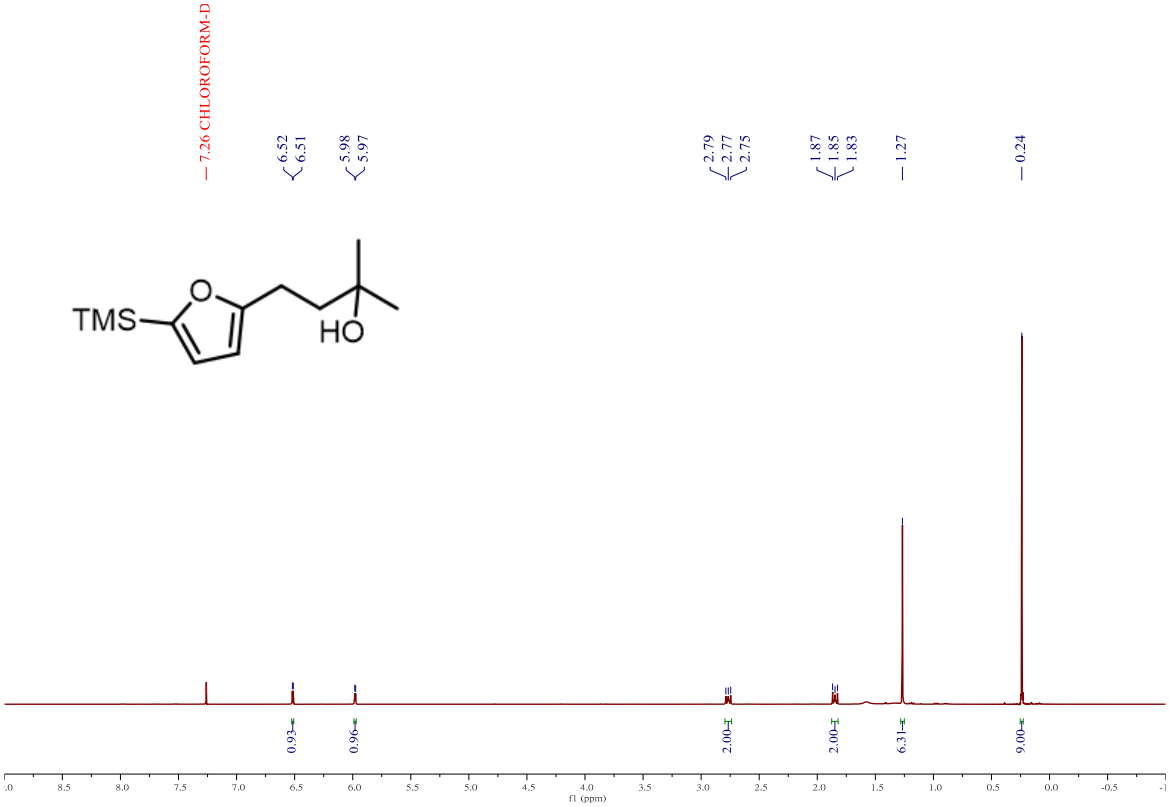


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1f**

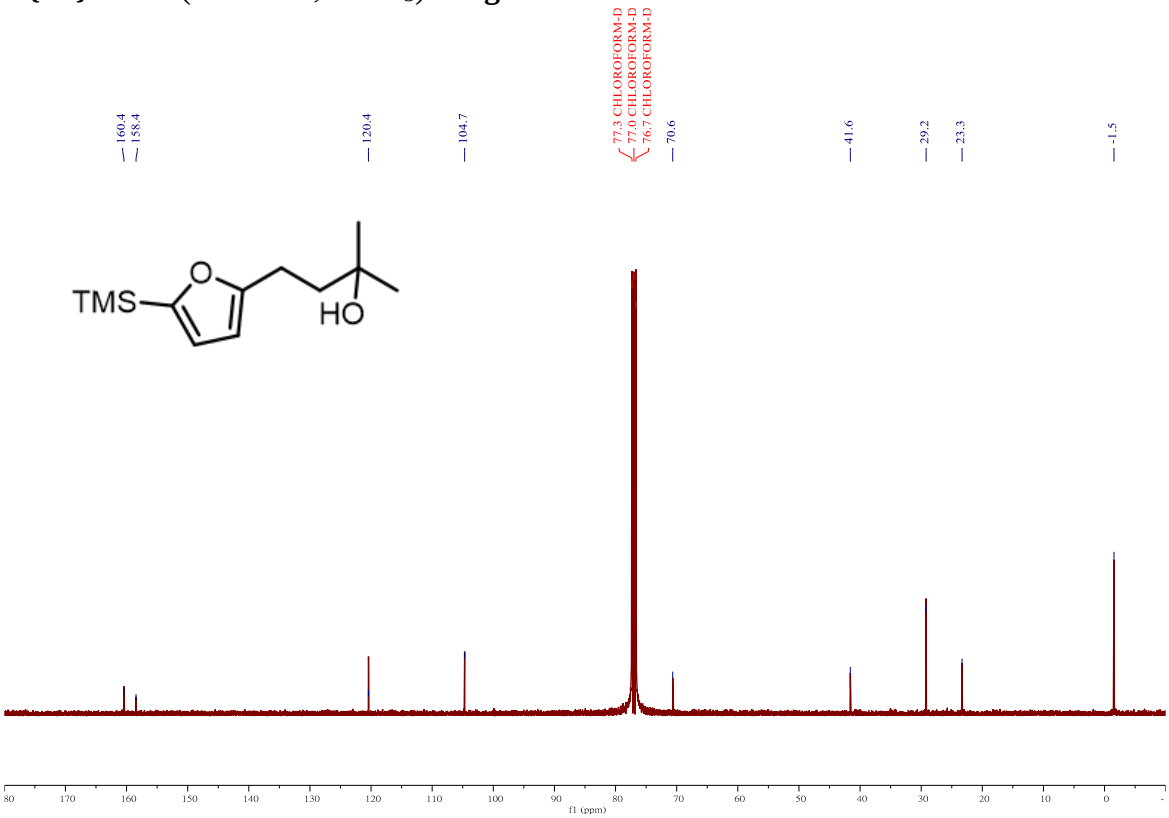


Back to contents

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

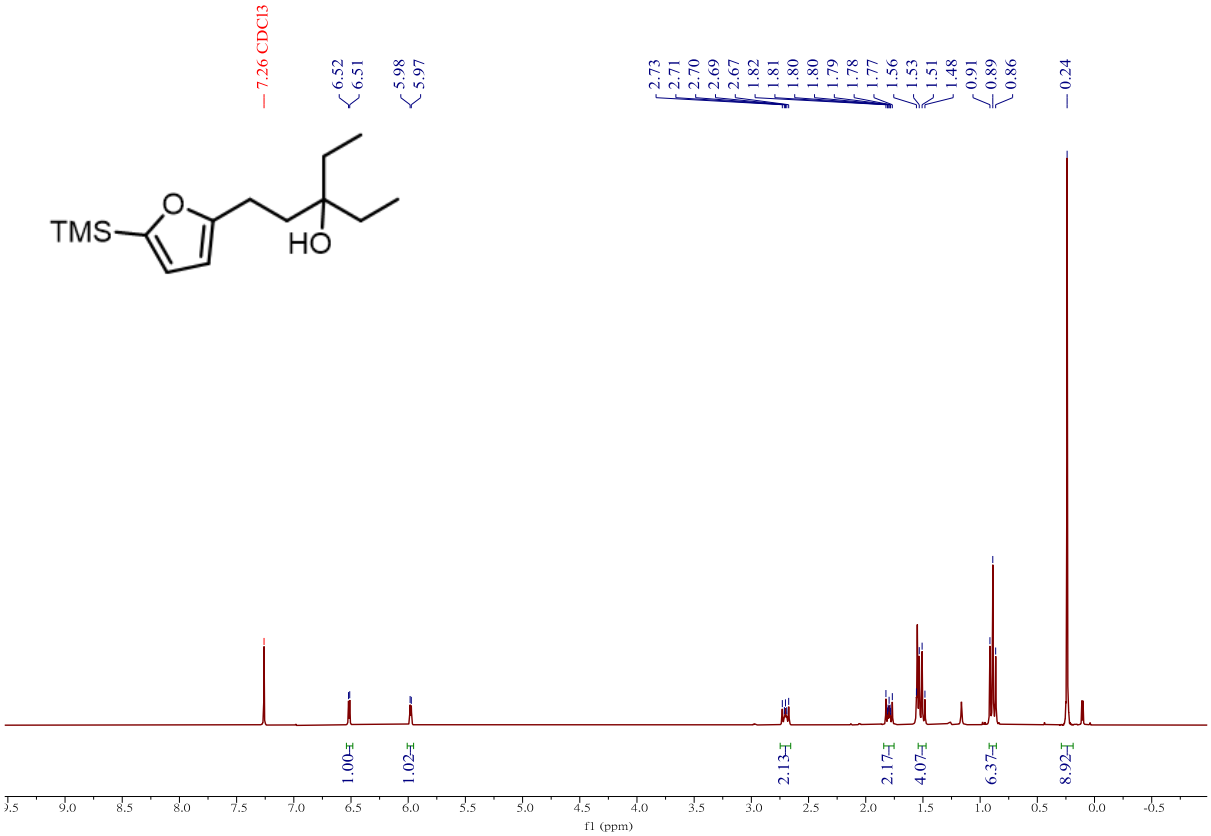


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1g**

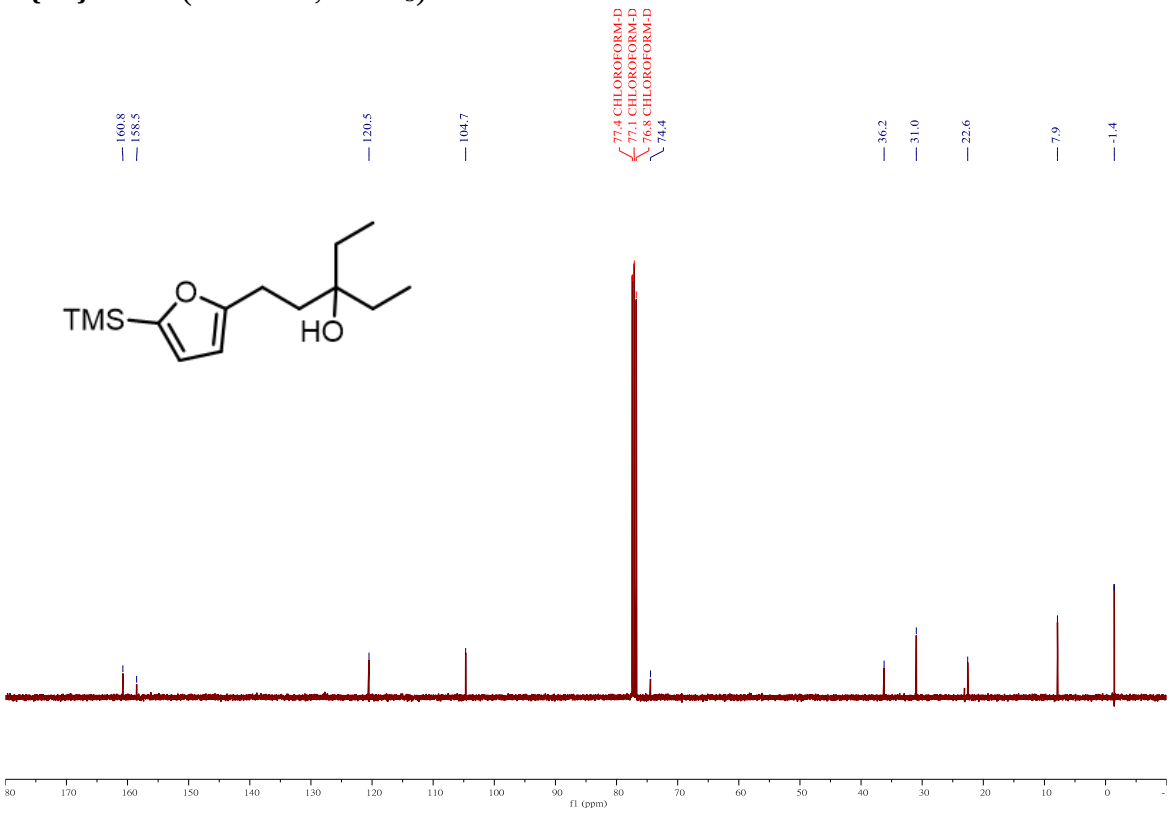


Back to contents

^{1}H NMR (300 MHz, $CDCl_3$) of **1h**, *See procedure*

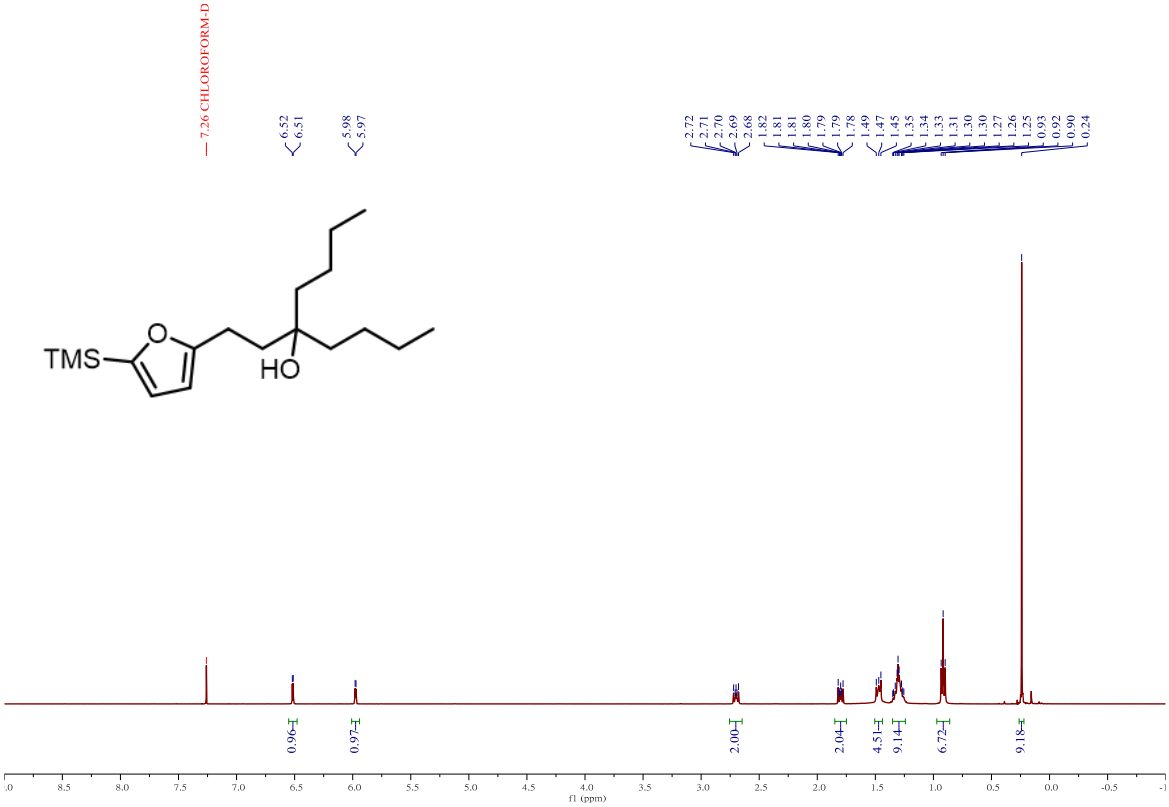


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1h**

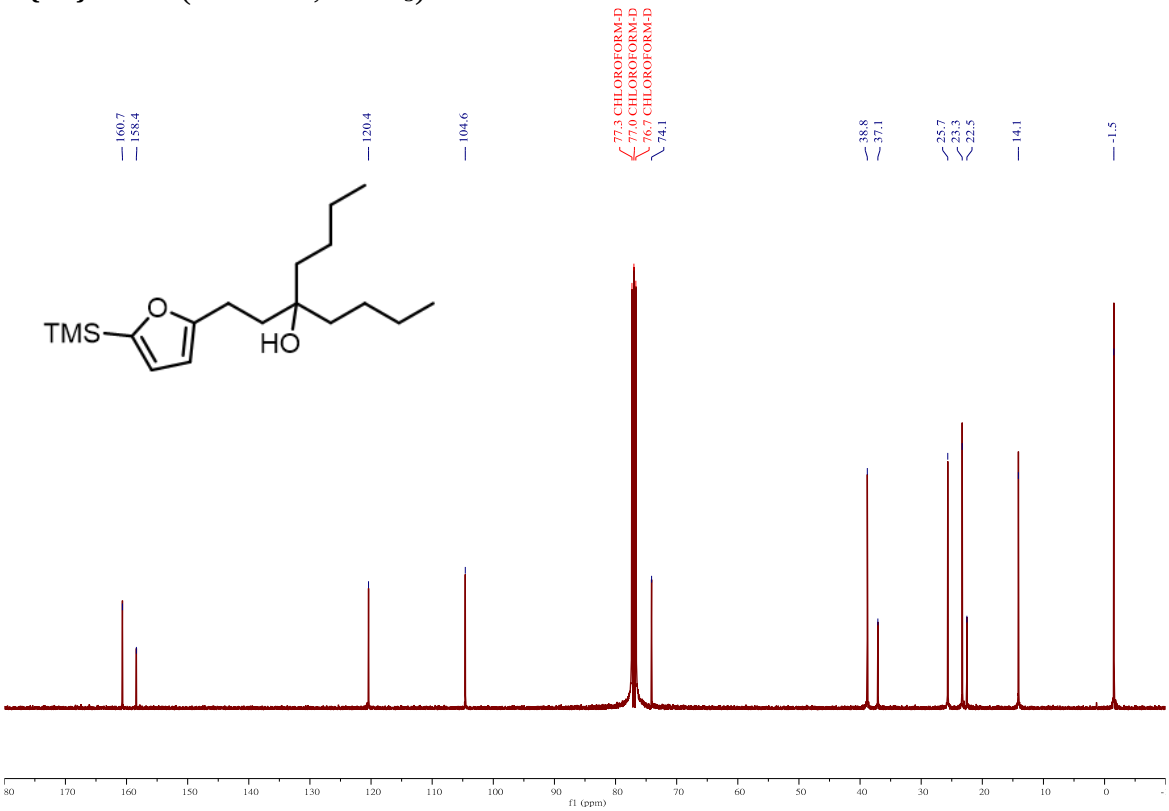


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **1i**, *See procedure*

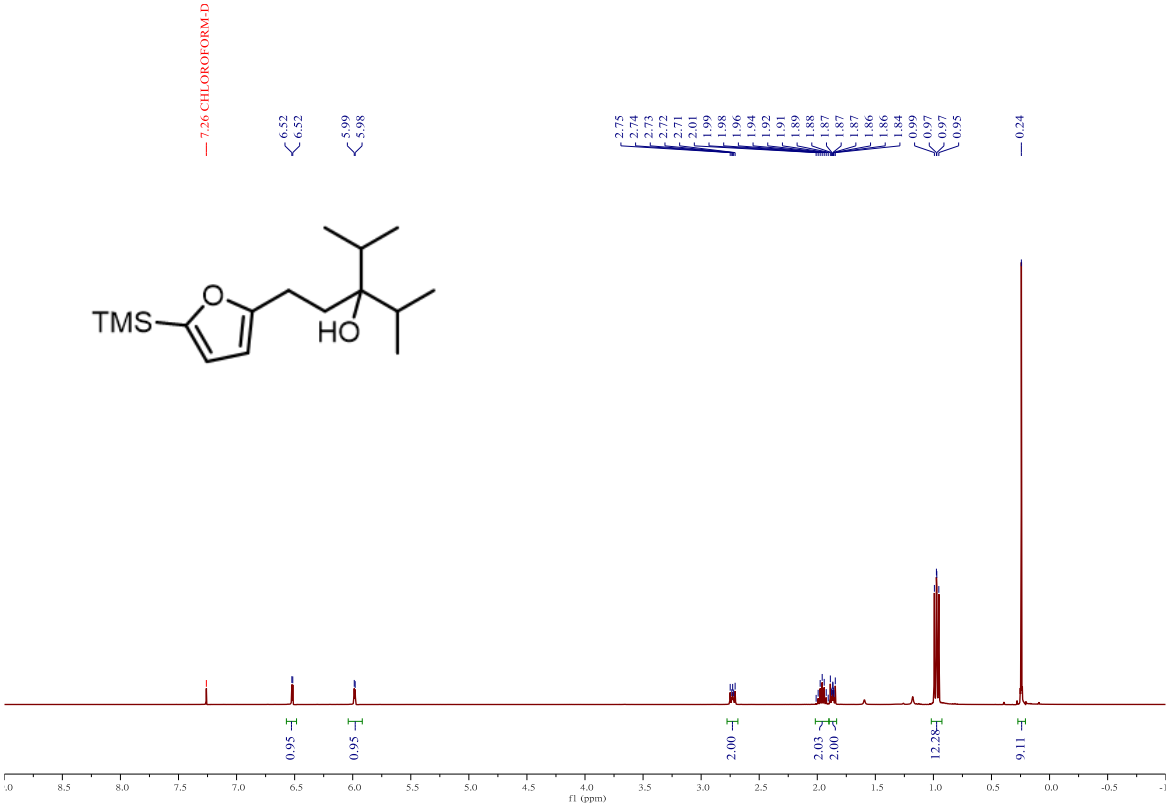


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1i**



Back to contents

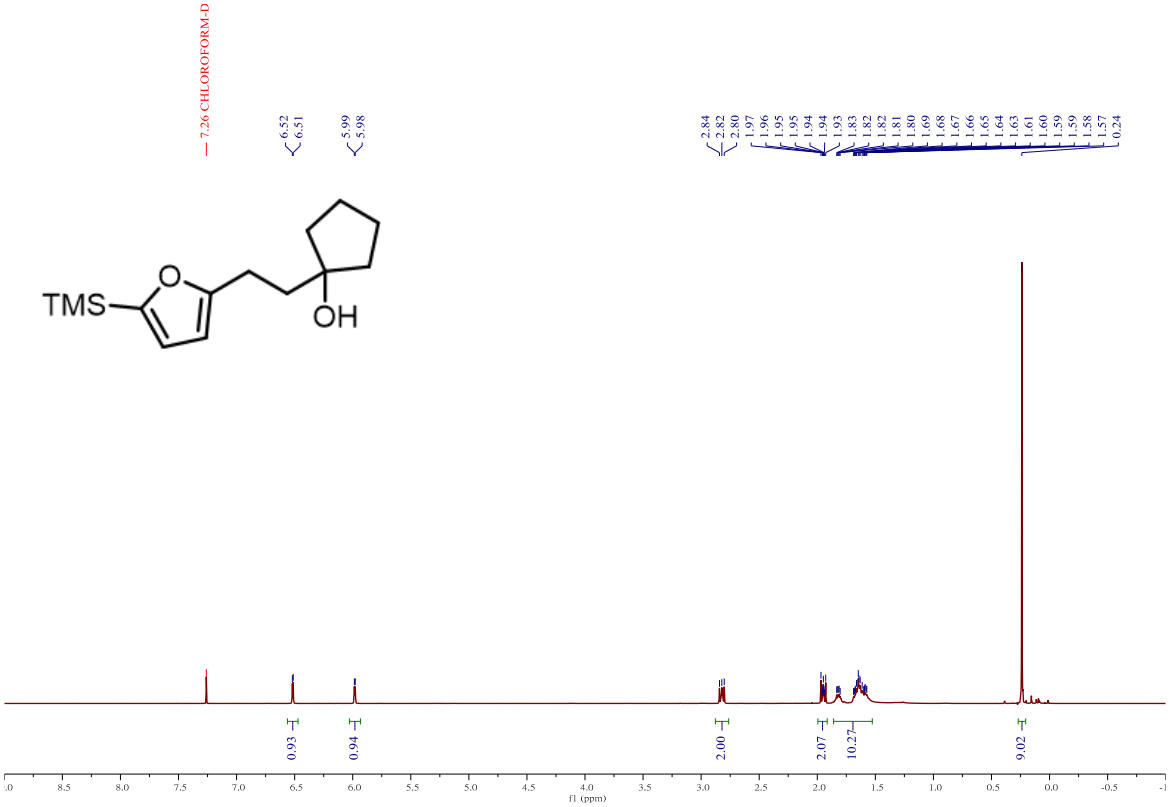
^{1}H NMR (400 MHz, $CDCl_3$) of **1j**, *See procedure*



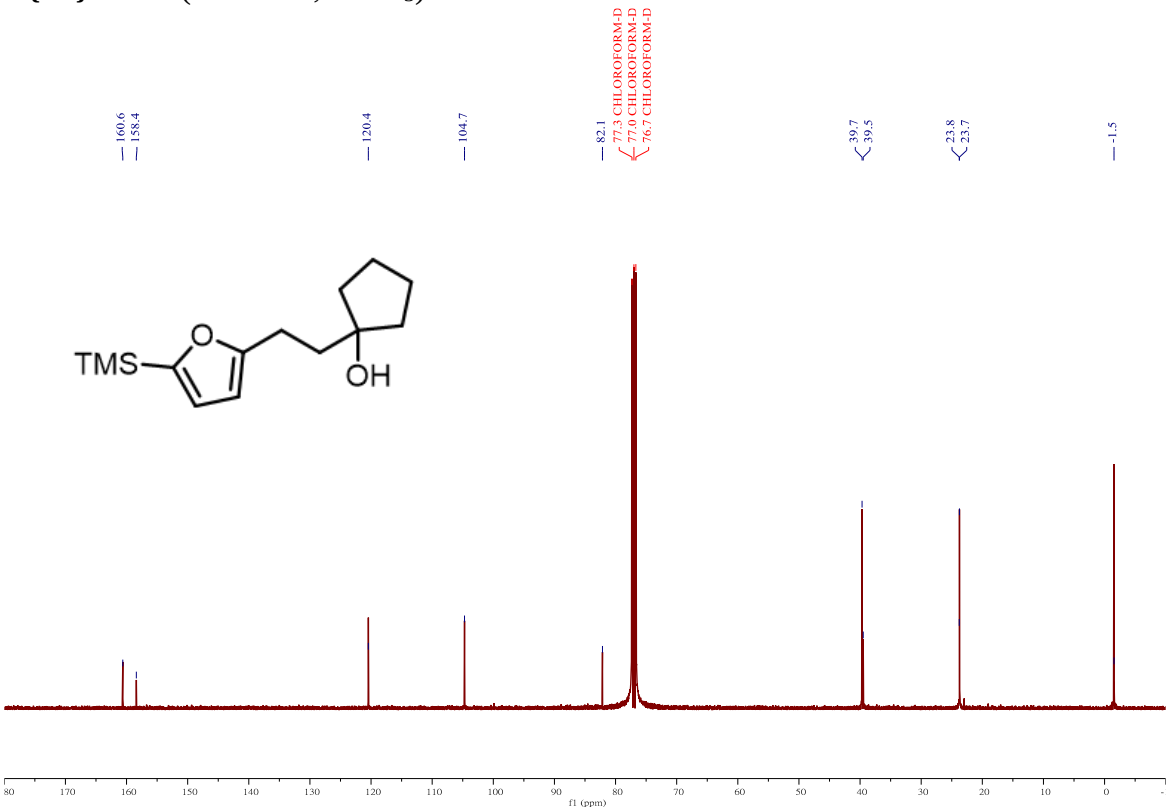
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1j**

Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **1k**, *See procedure*

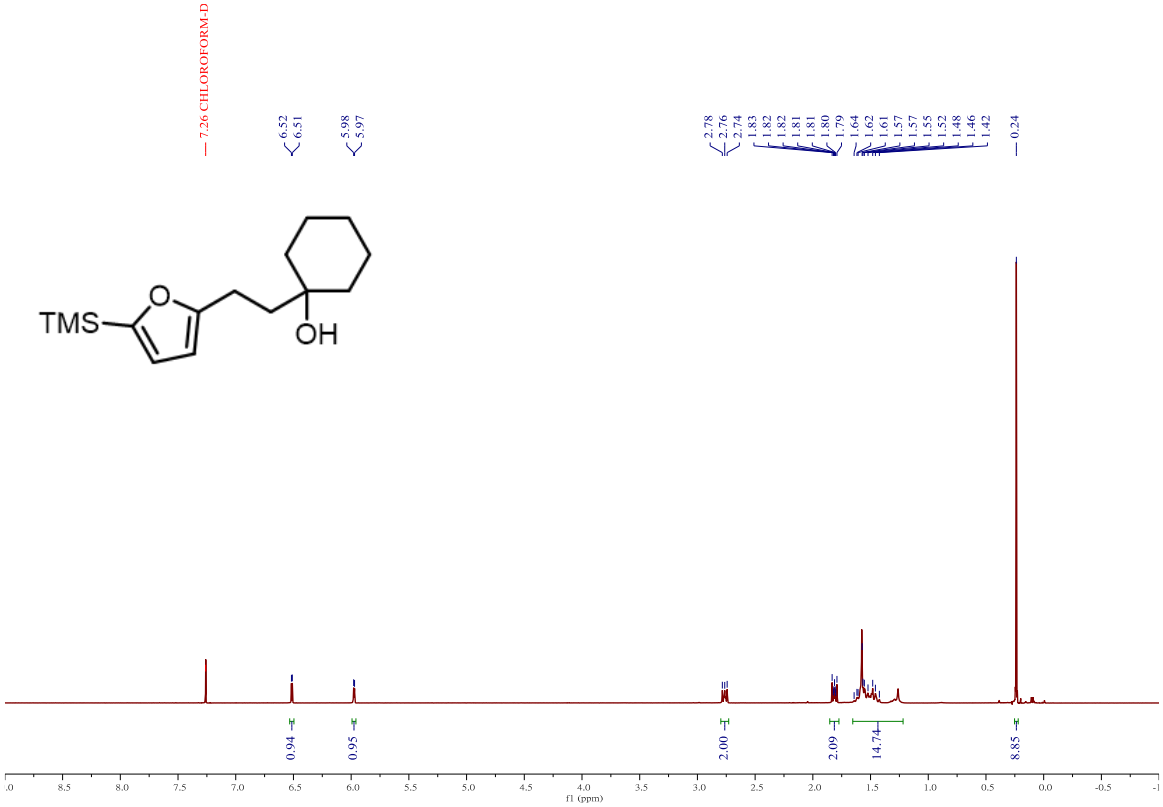


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1k**

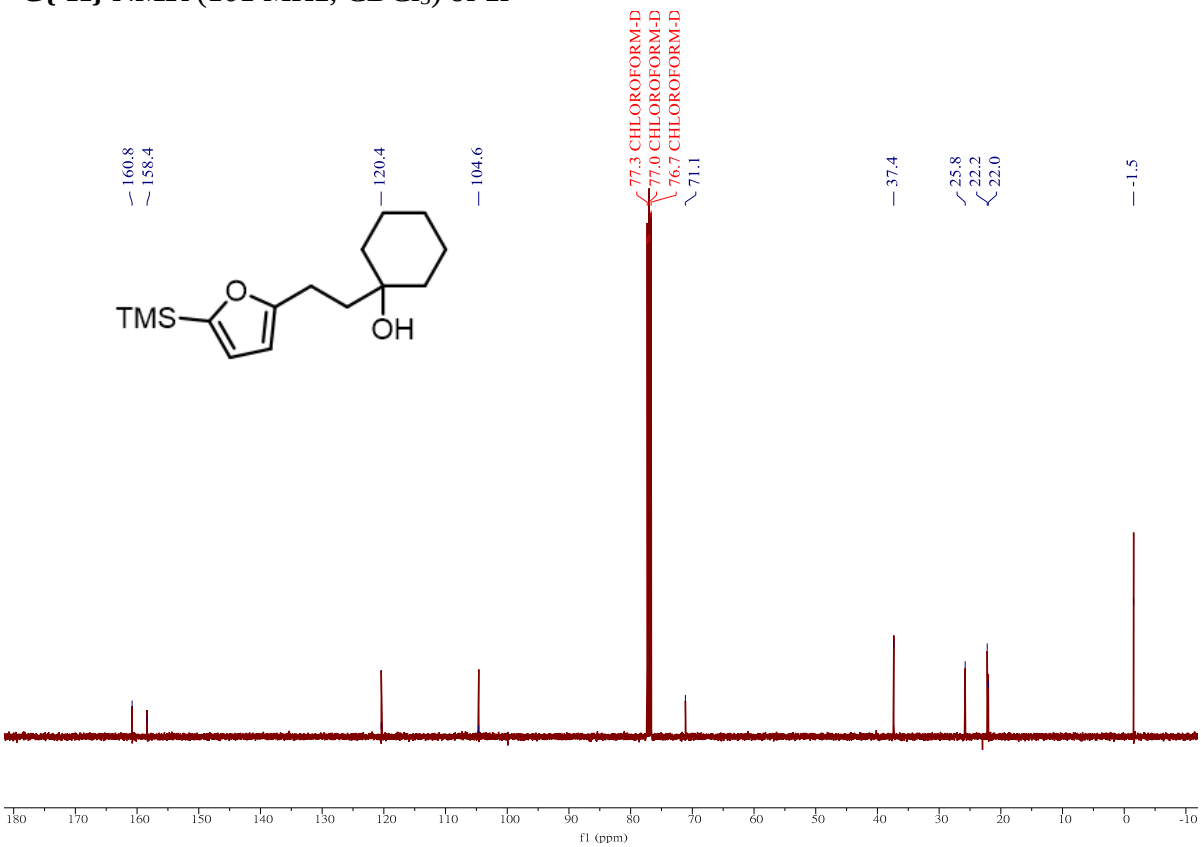


Back to contents

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

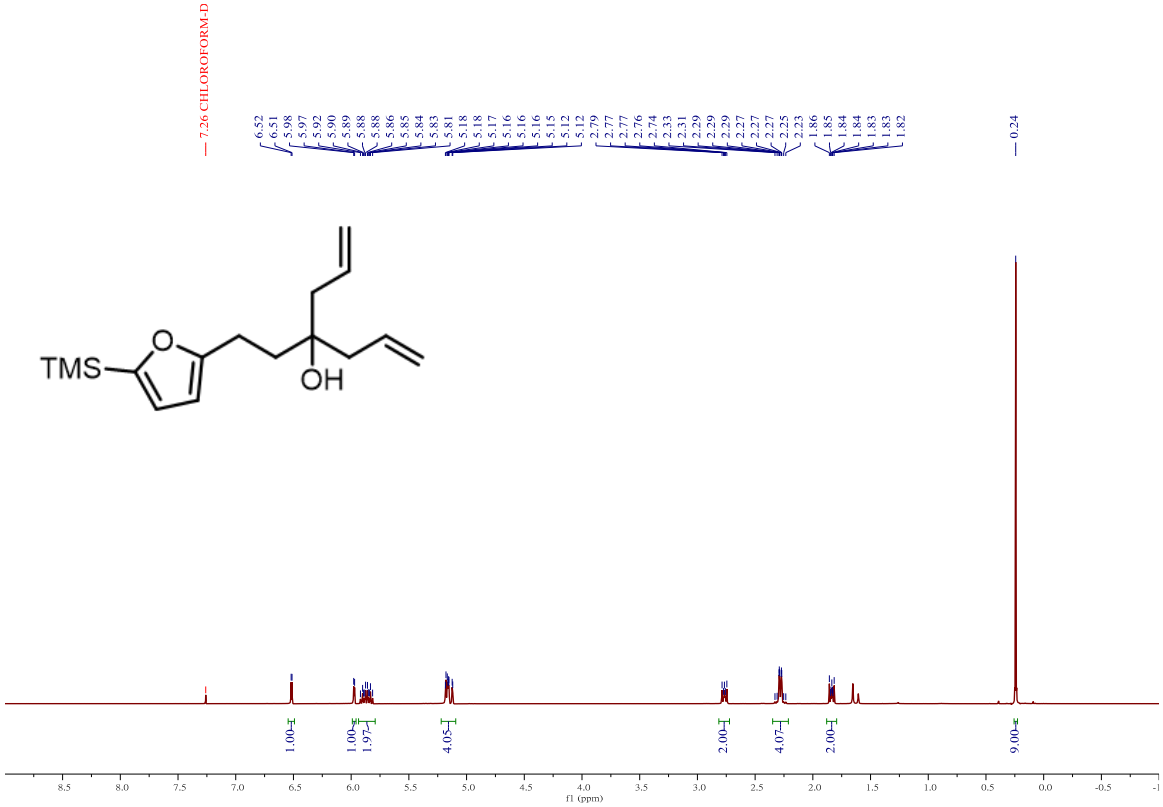


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1l**

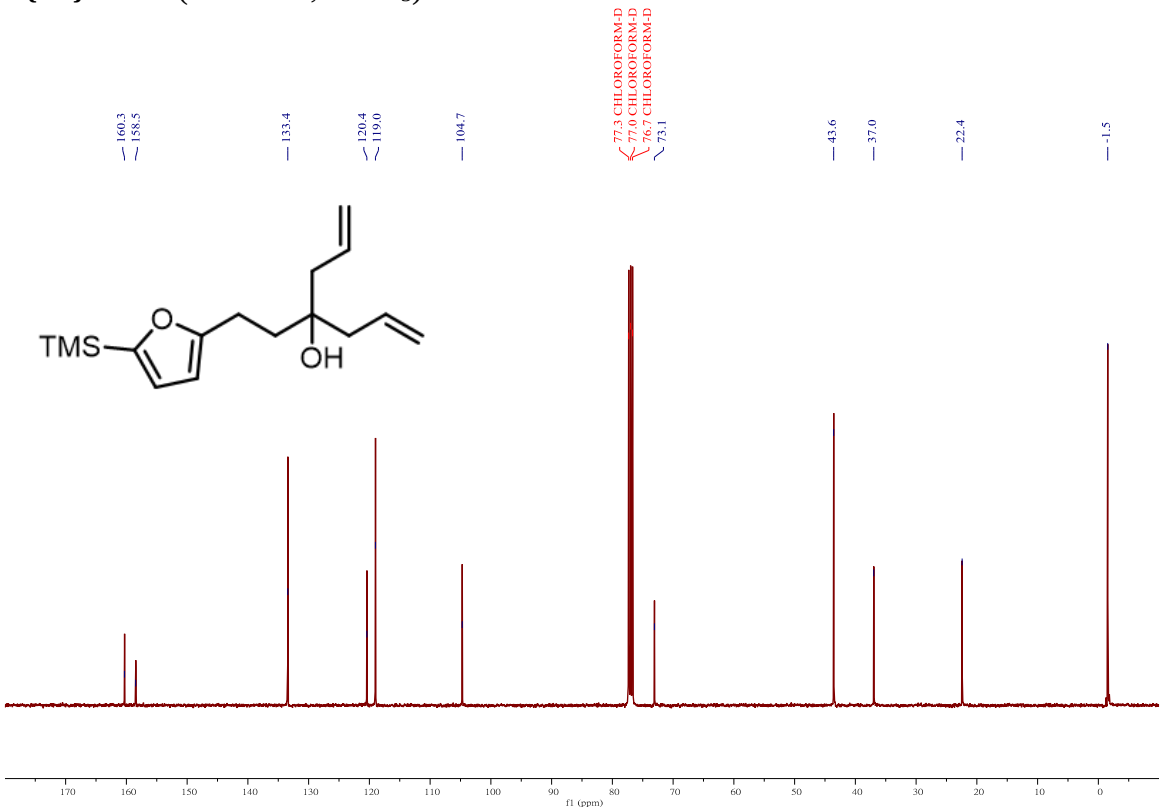


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **1m**, *See procedure*

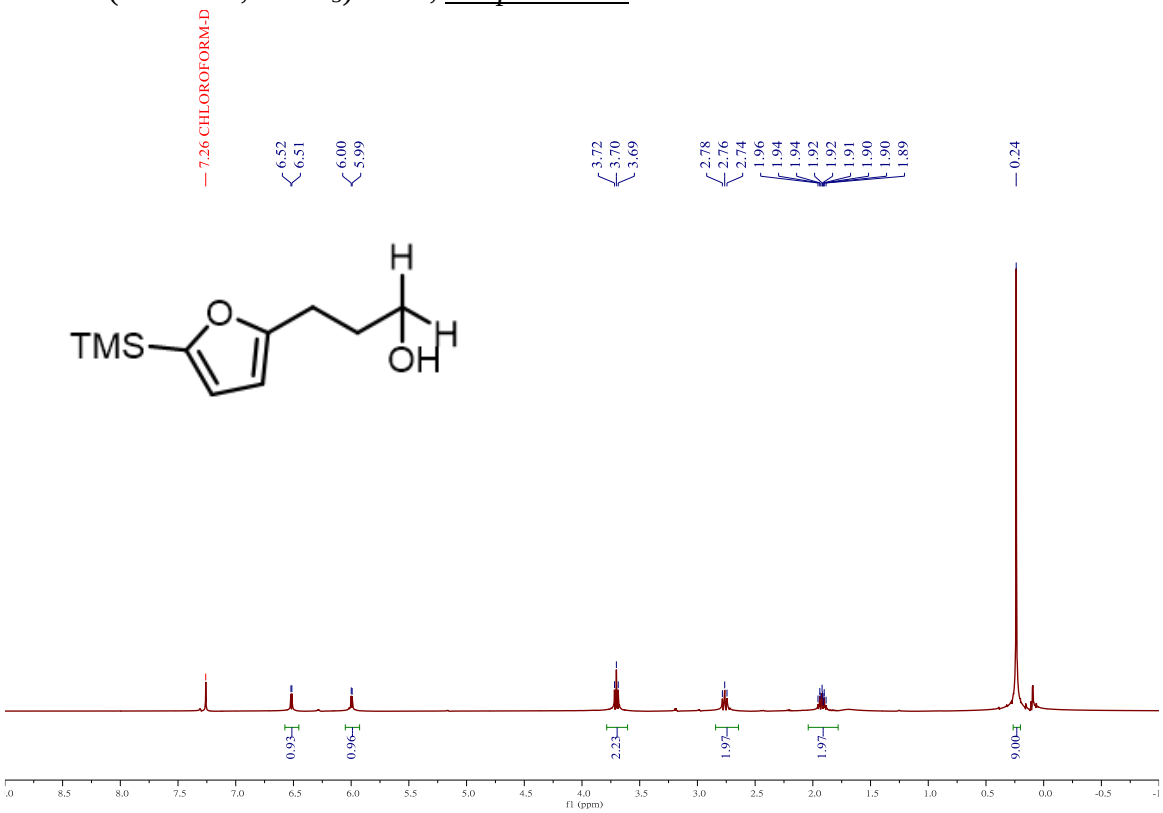


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1m**

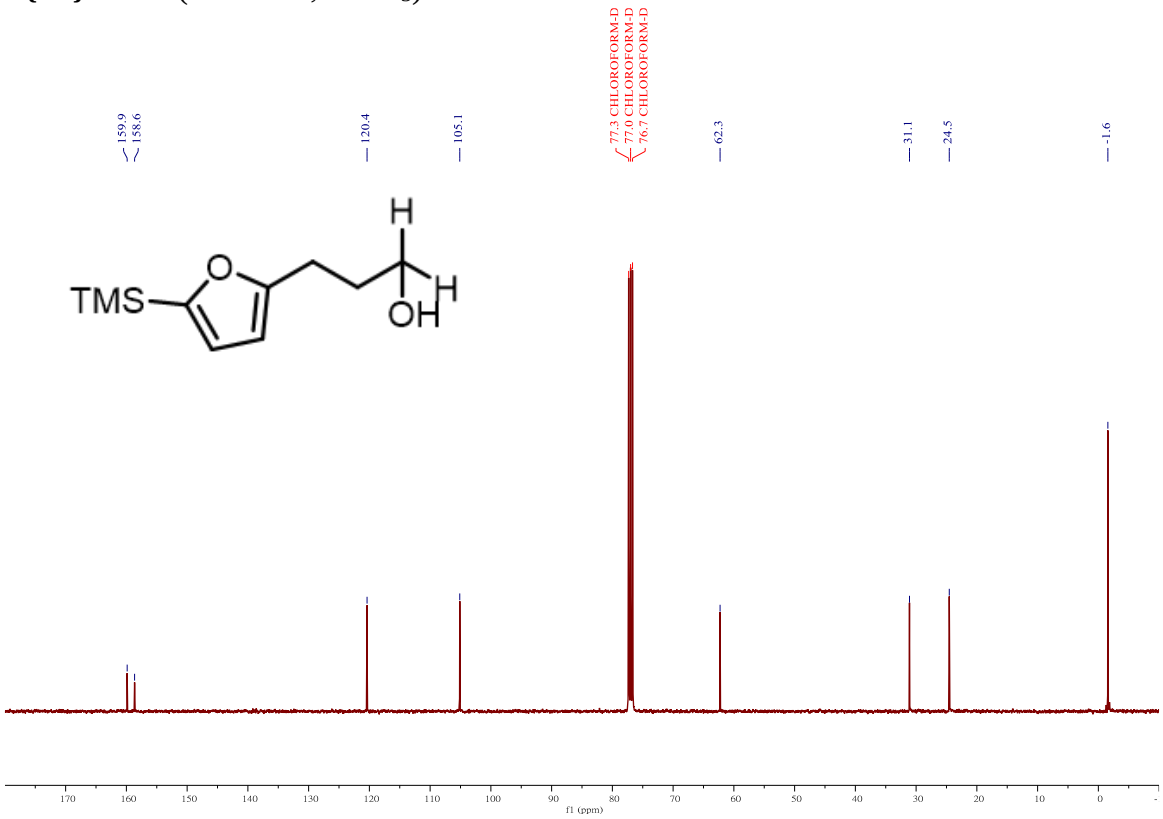


Back to contents

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

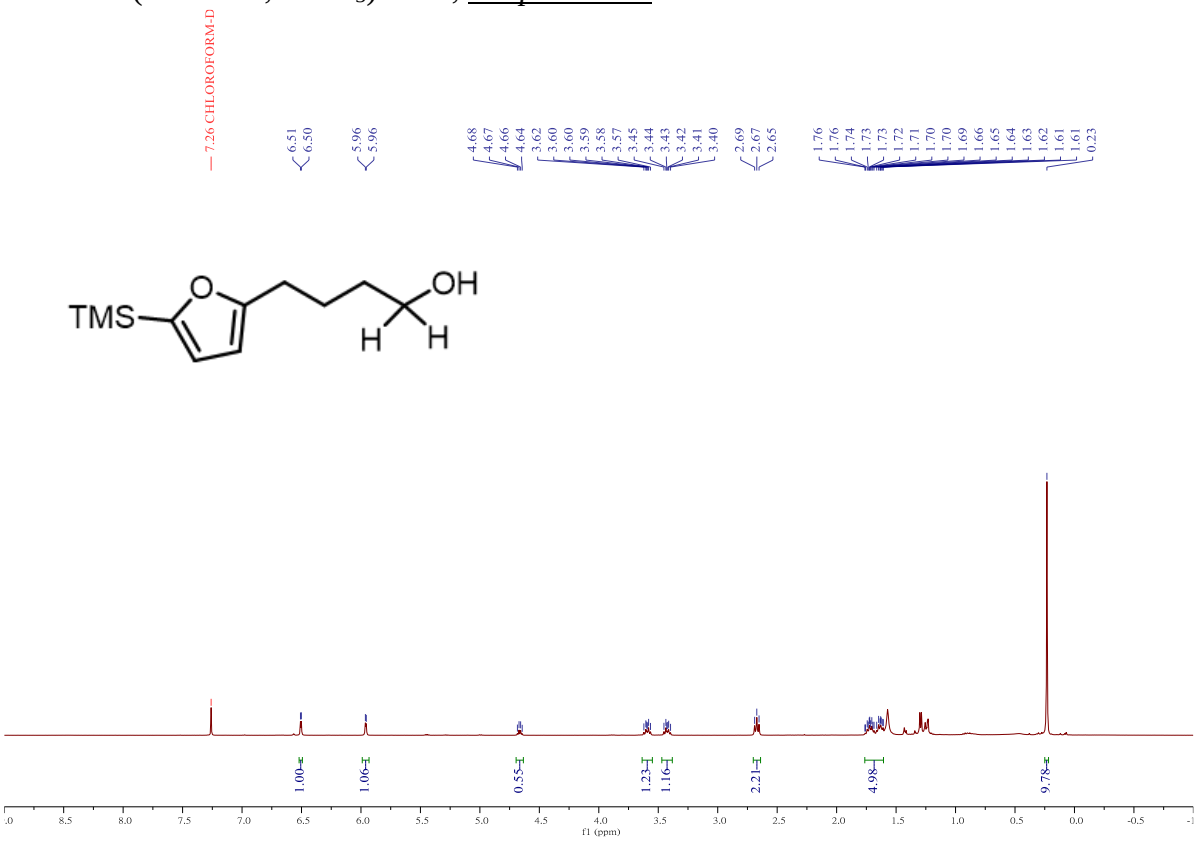


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1n**

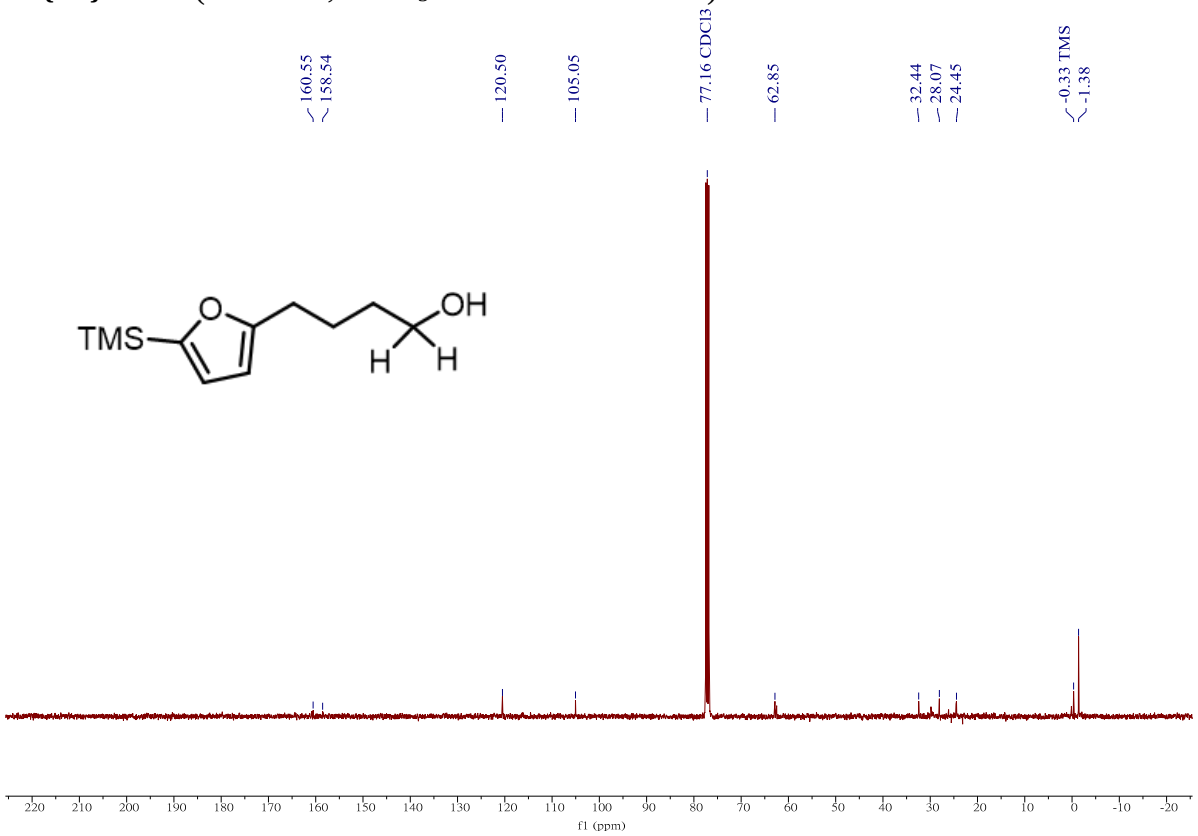


Back to contents

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

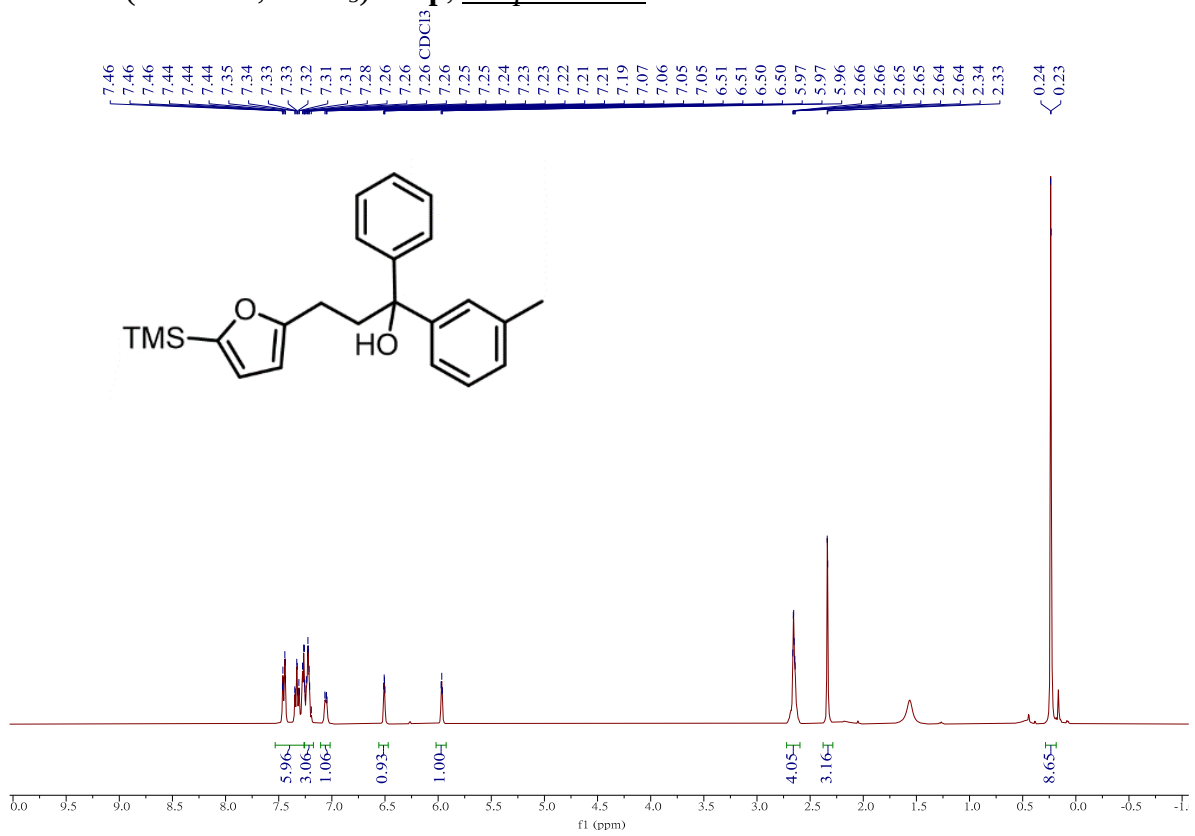


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) of **1o**

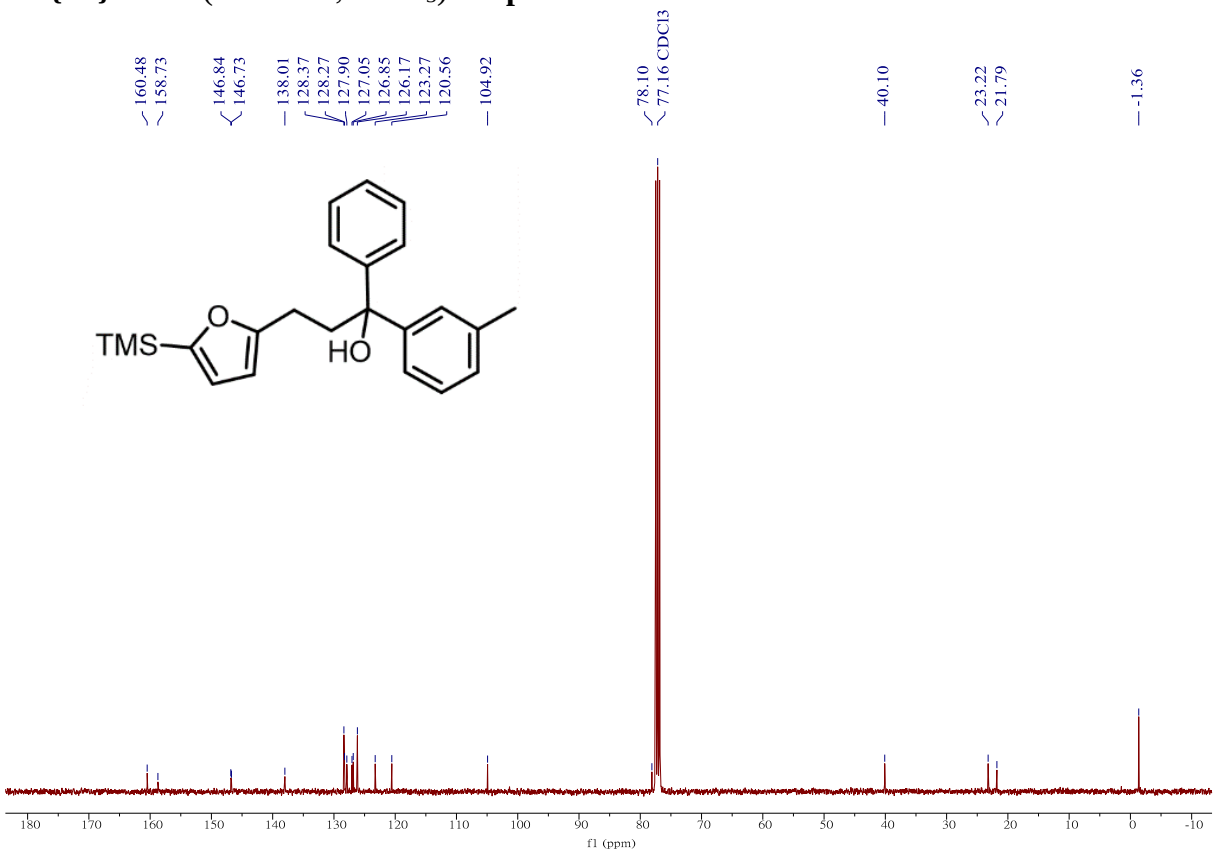


Back to contents

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

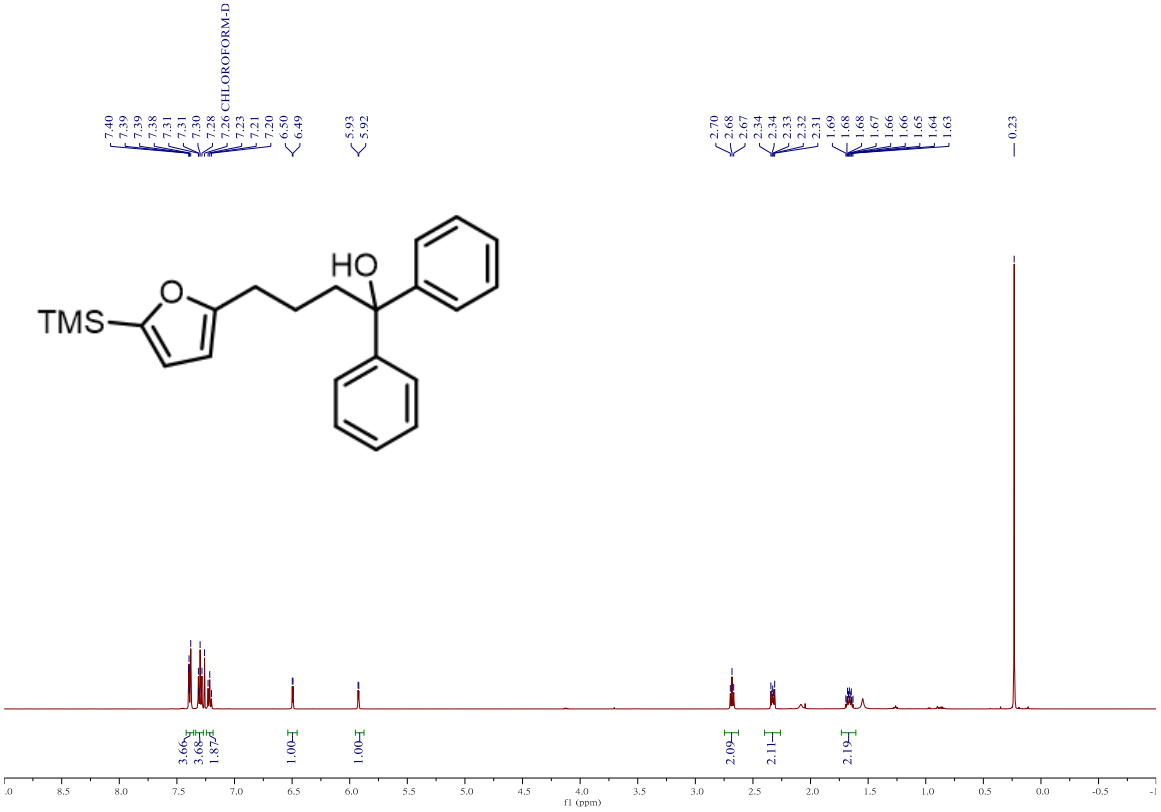


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1p**

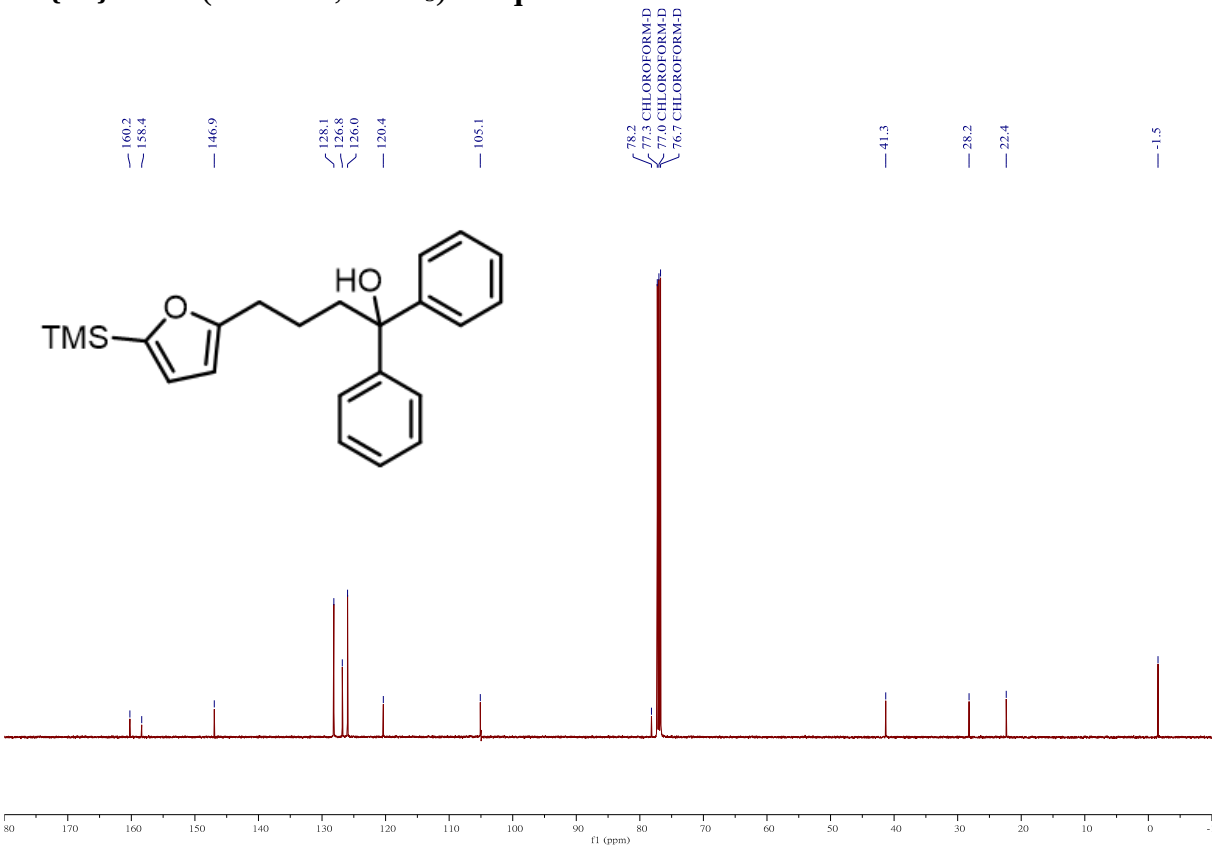


Back to contents

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

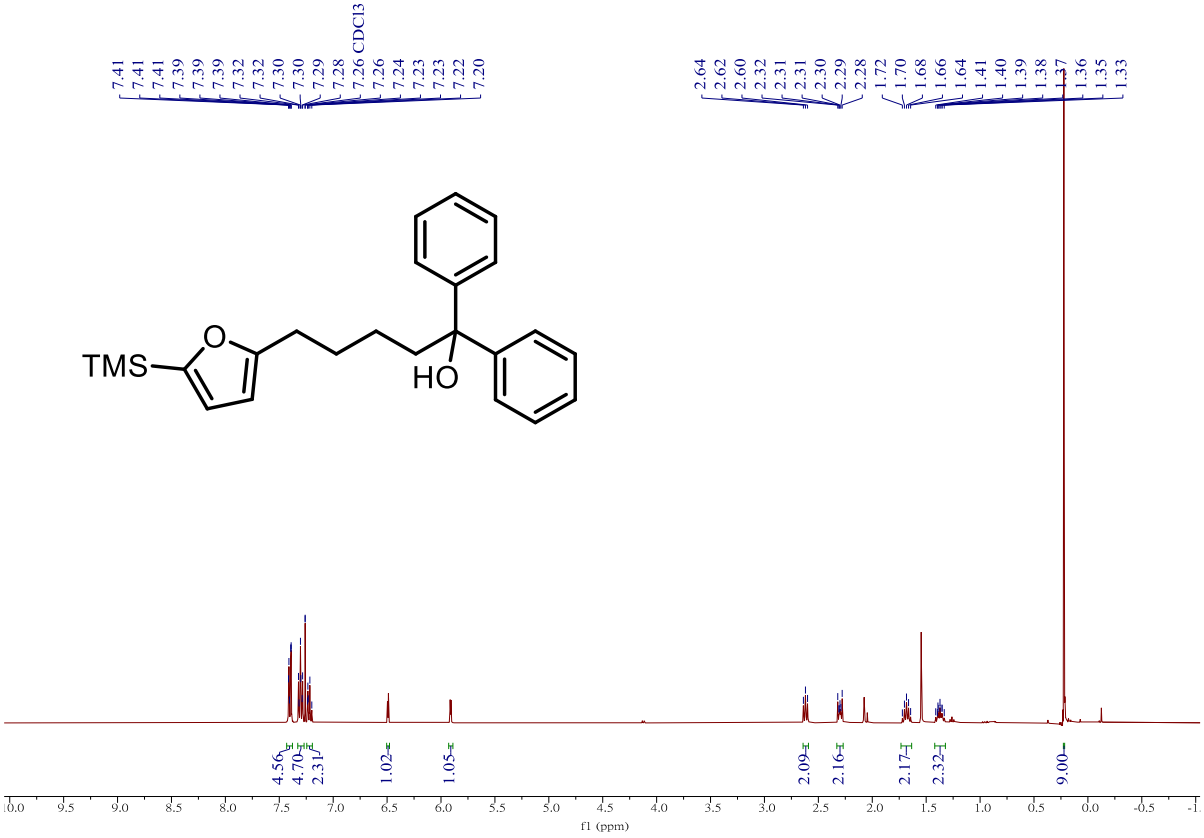


^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) of **1q**

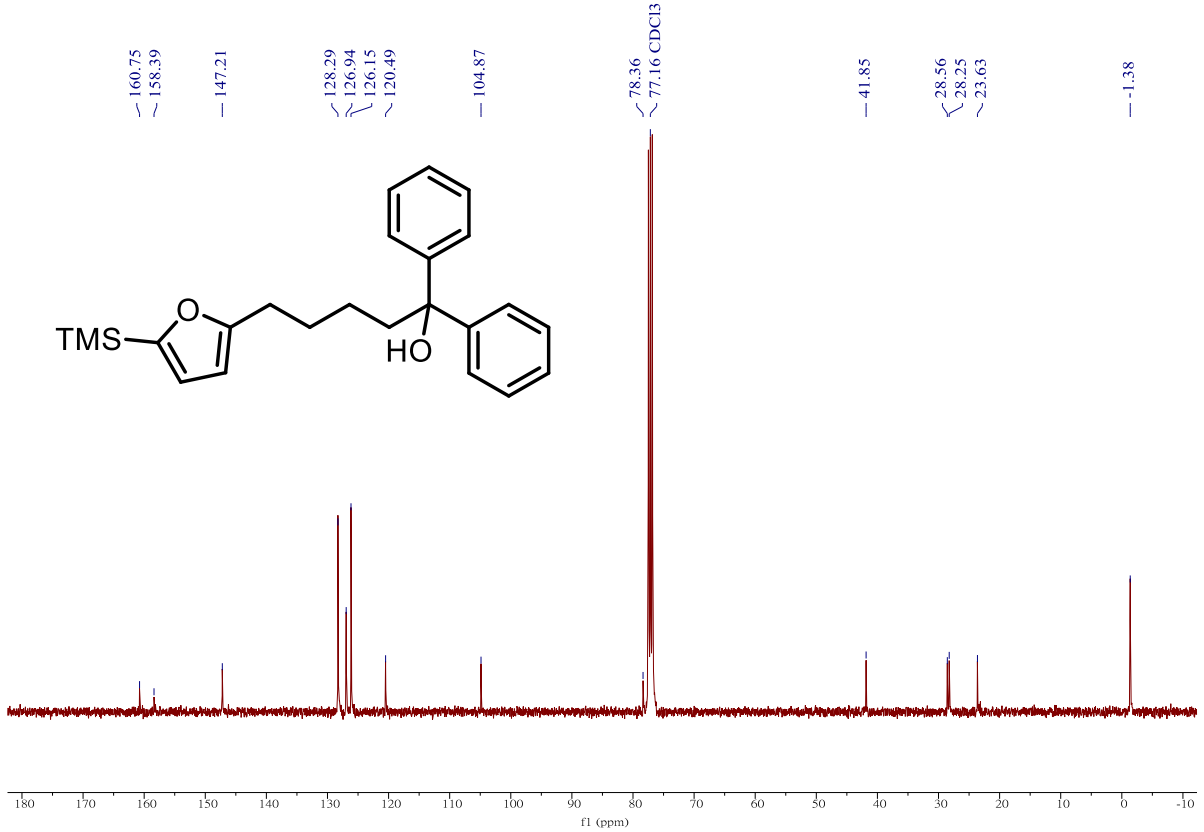


Back to contents

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

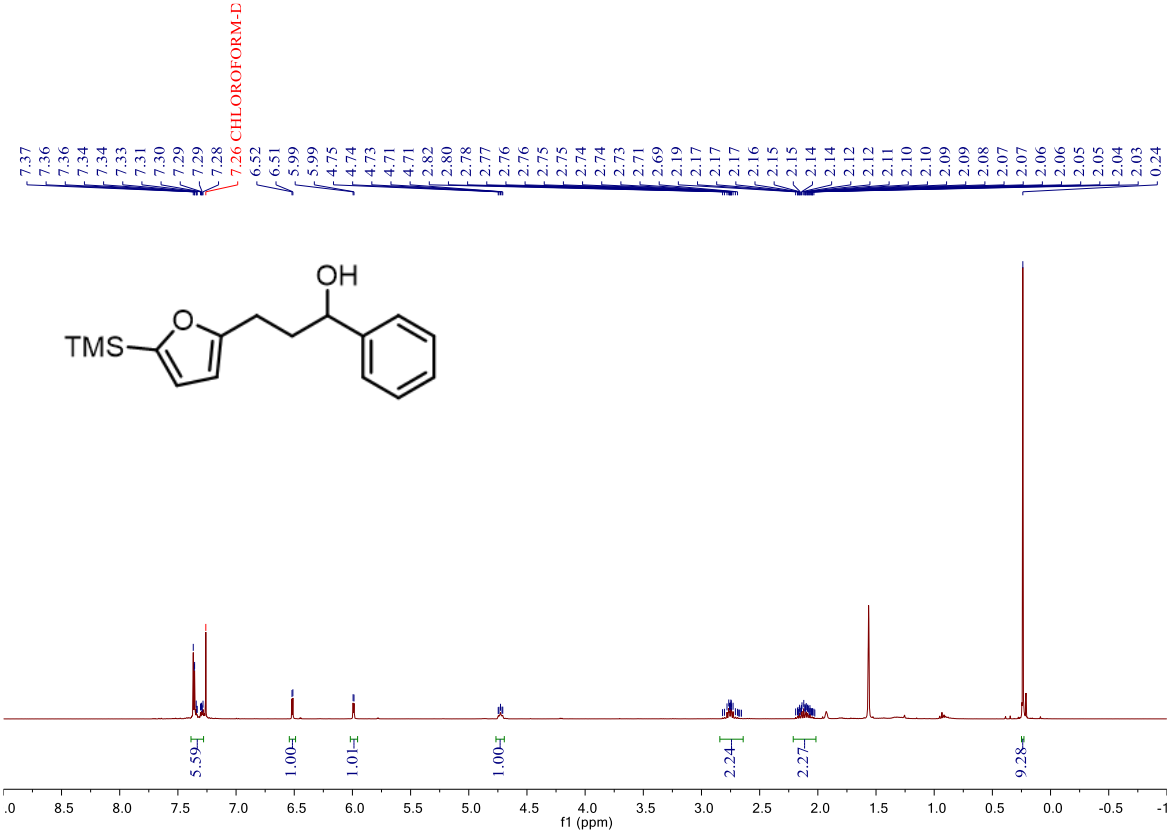


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **1r**

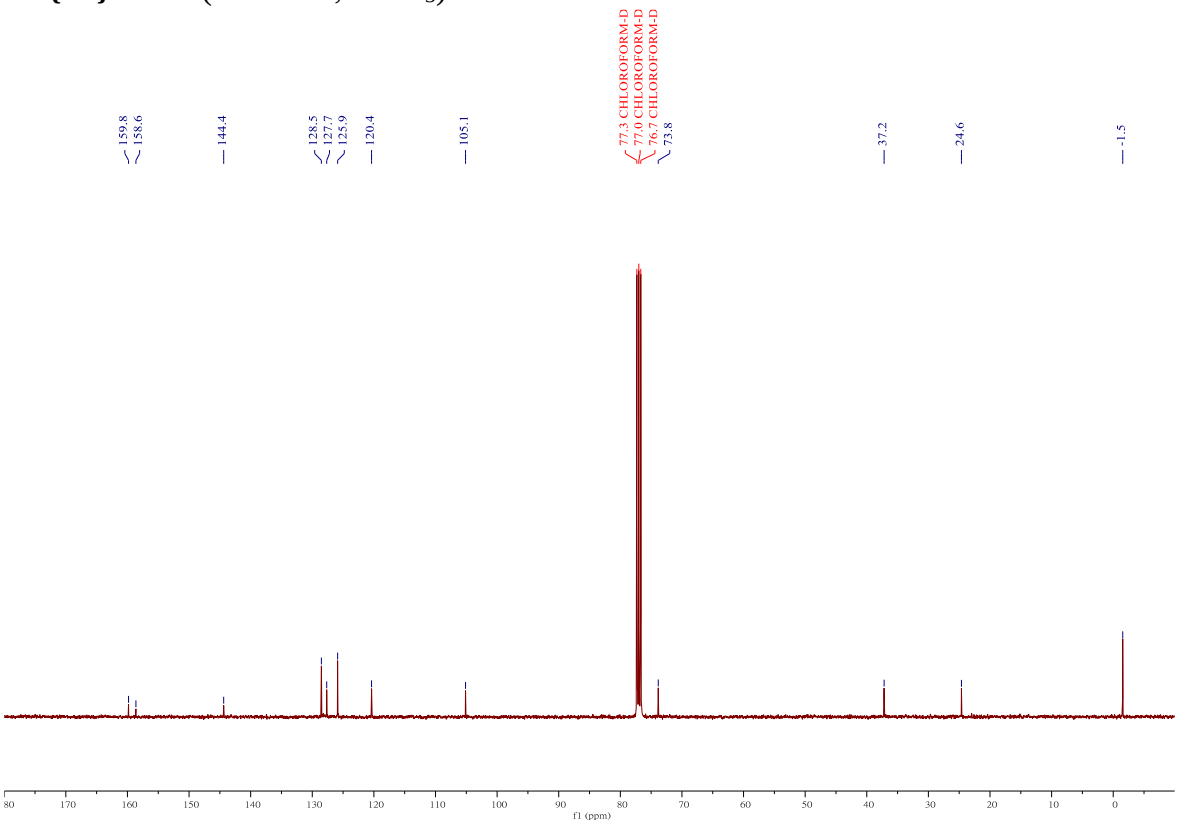


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **3a**, *See procedure*

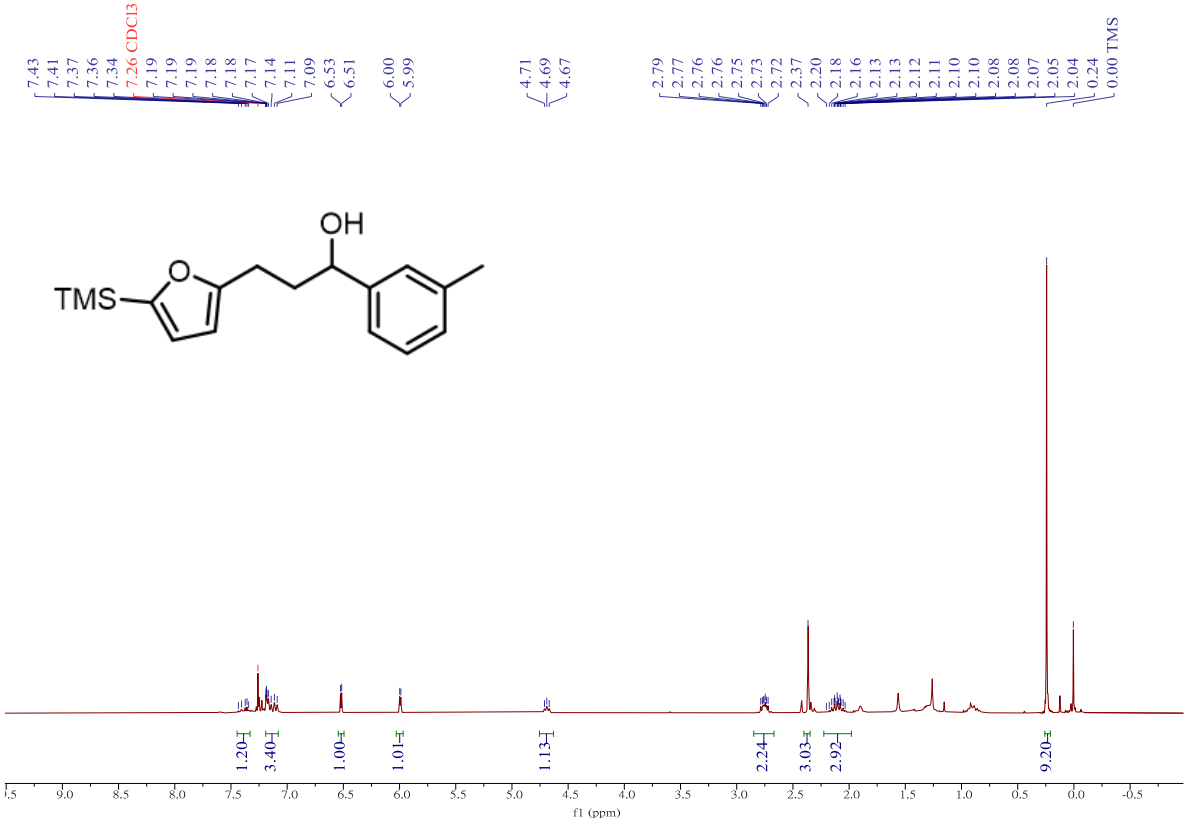


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3a**

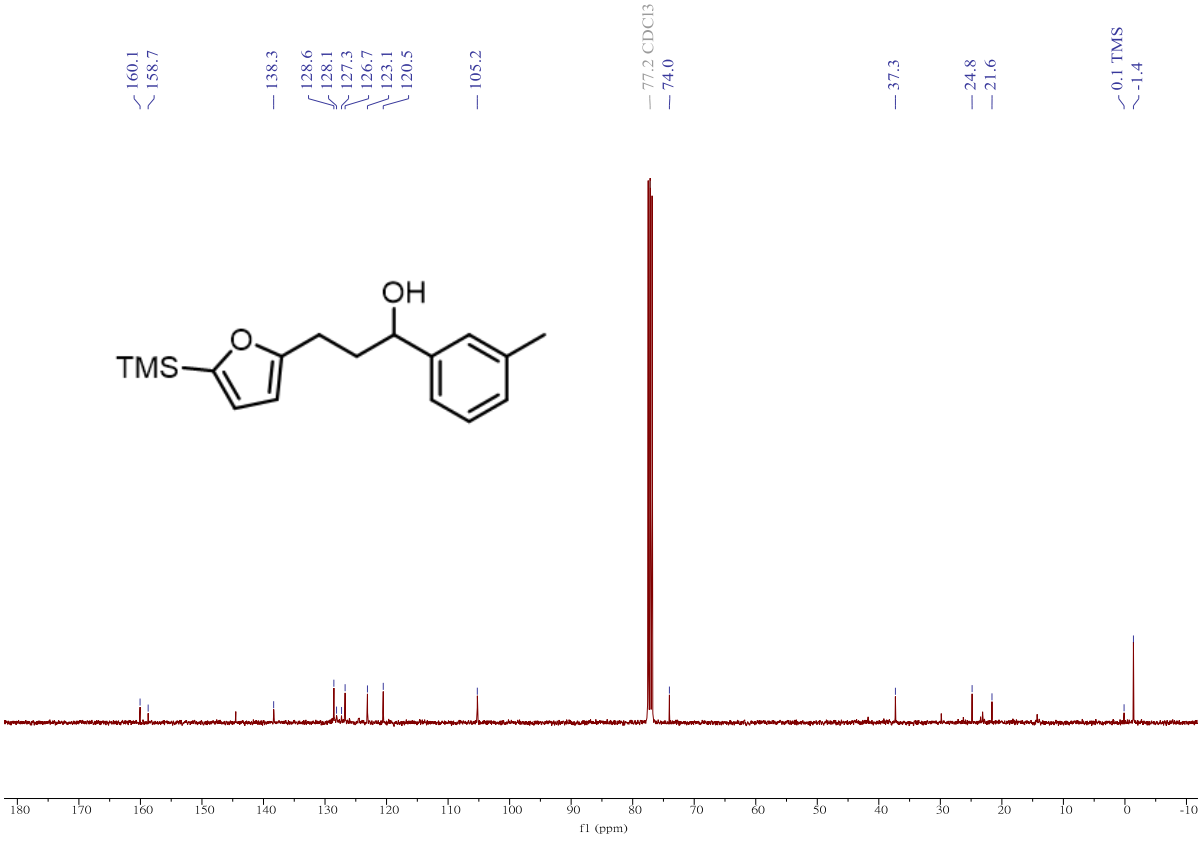


Back to contents

^{1}H NMR (300 MHz, $CDCl_3$ with 0.05% v/v TMS) of **3b**, *See procedure*

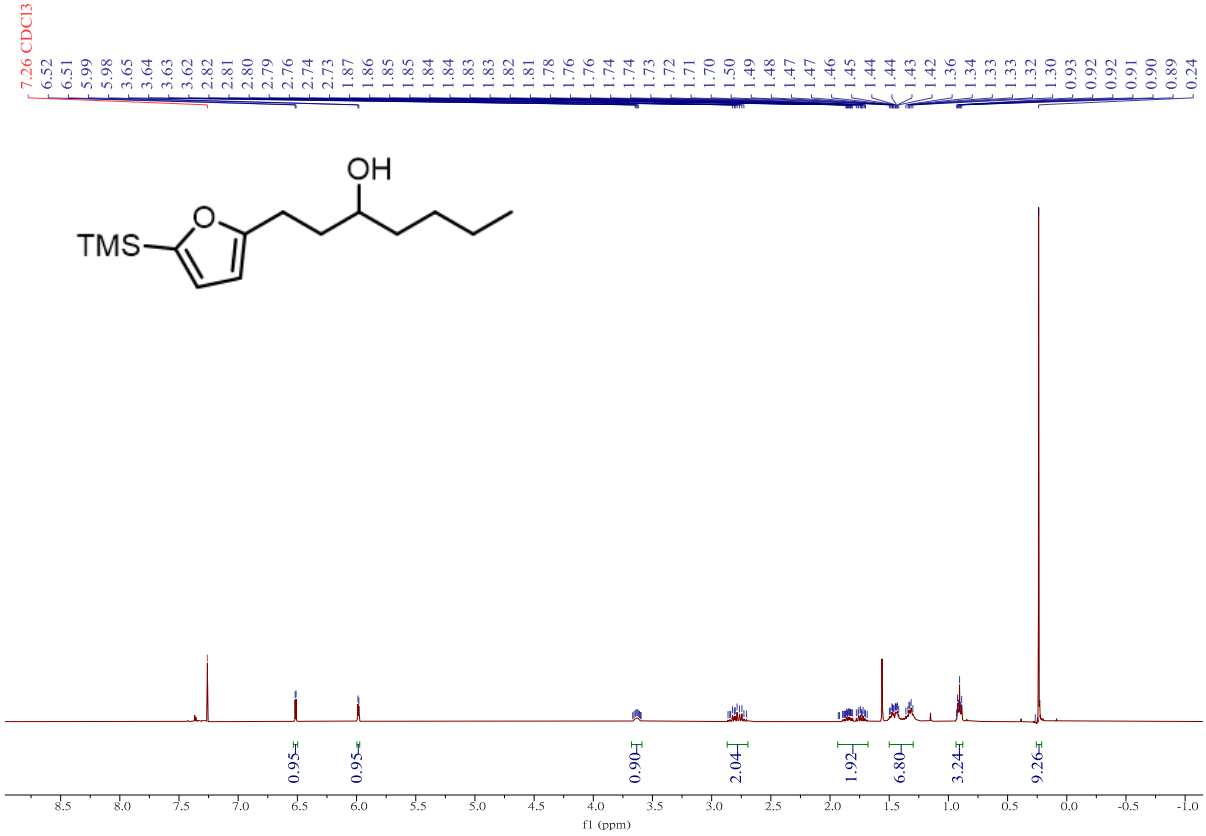


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$ with 0.05% v/v TMS) of **3b**

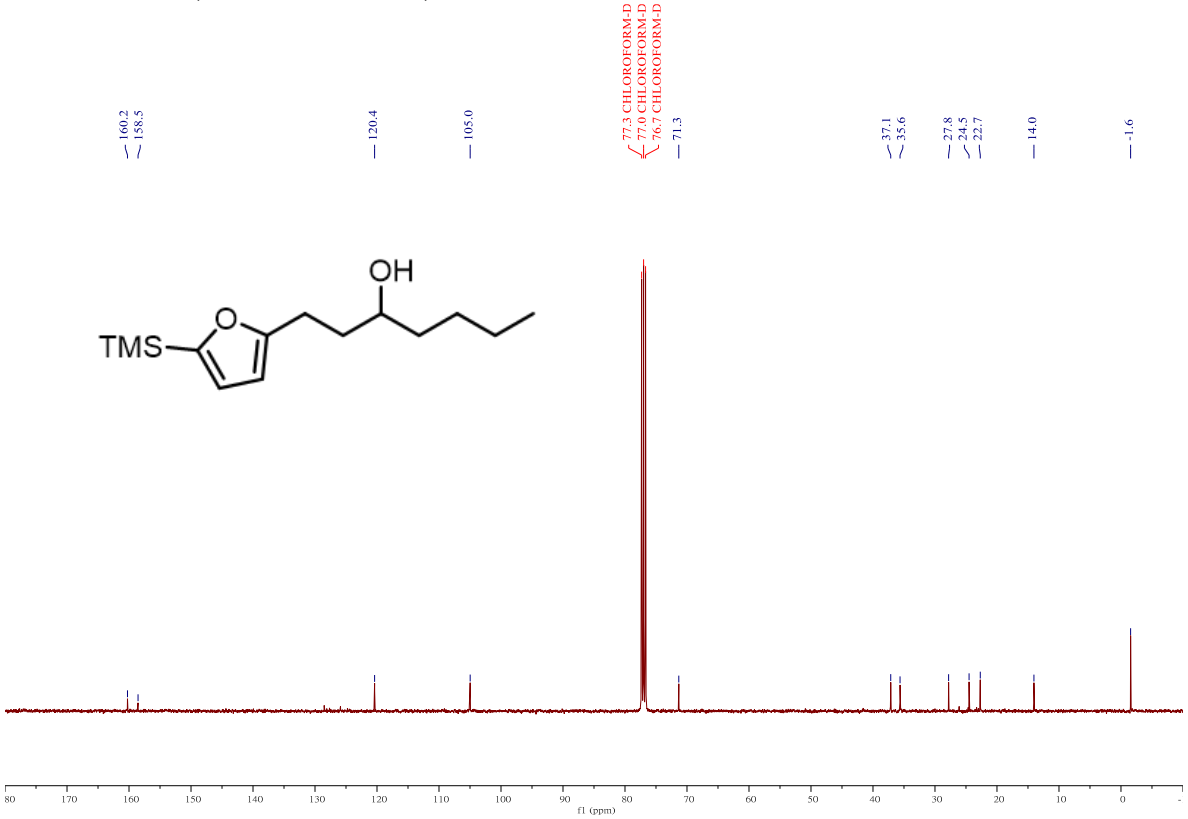


Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **3c**, *See procedure*

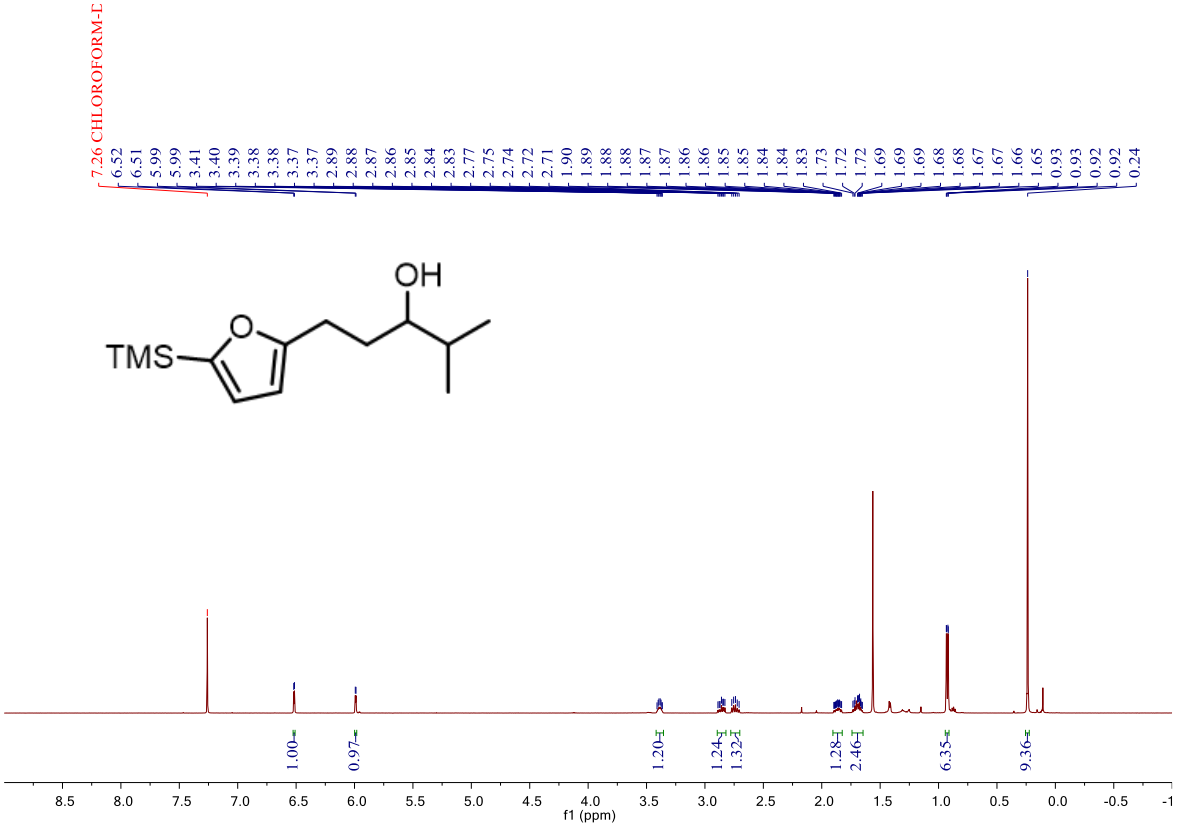


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3c**

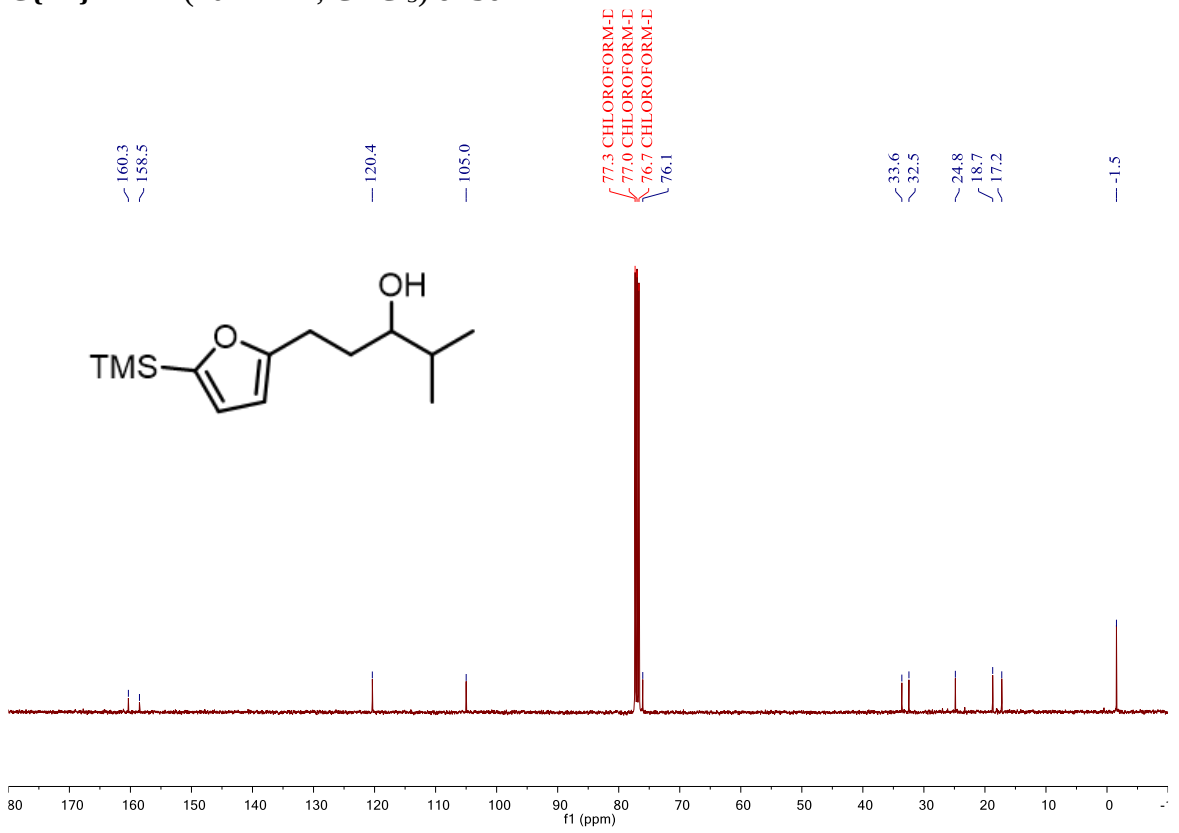


Back to contents

^{1}H NMR (500 MHz, $CDCl_3$) of **3d**, *See procedure*

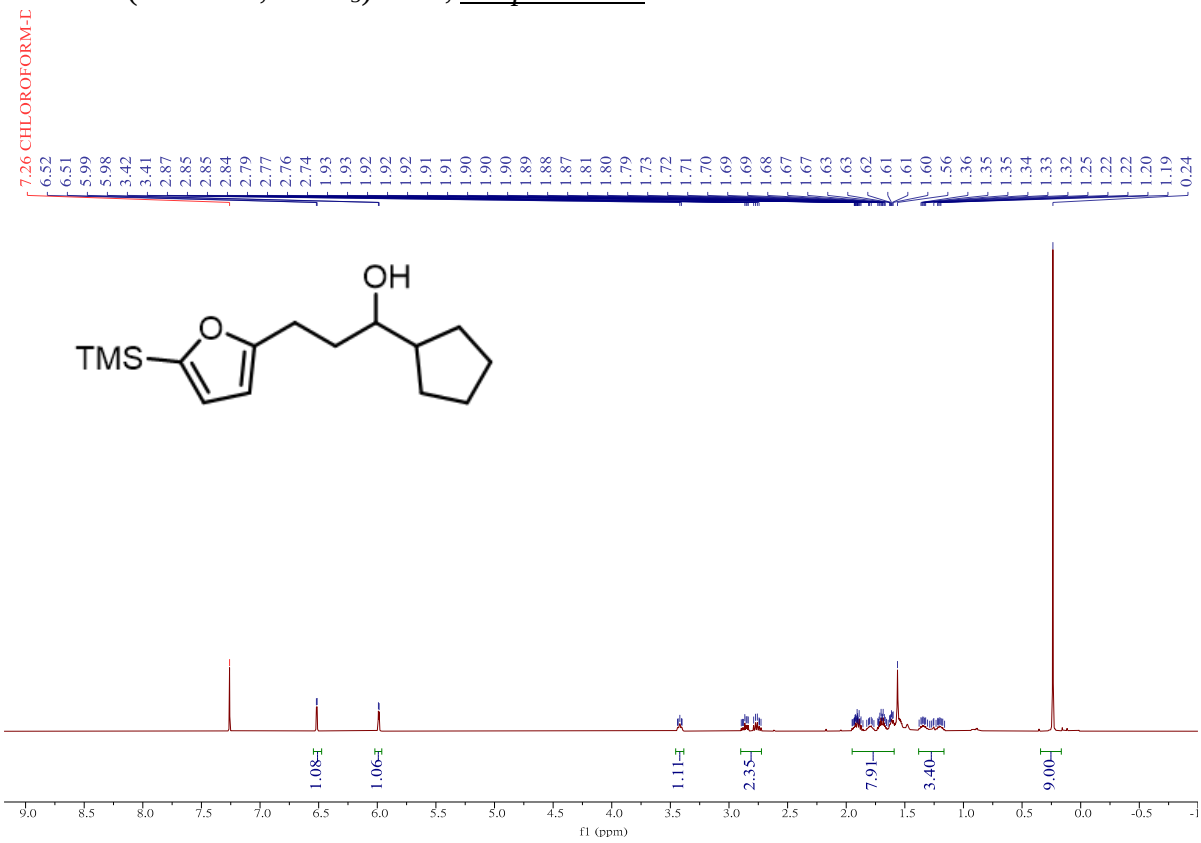


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3d**

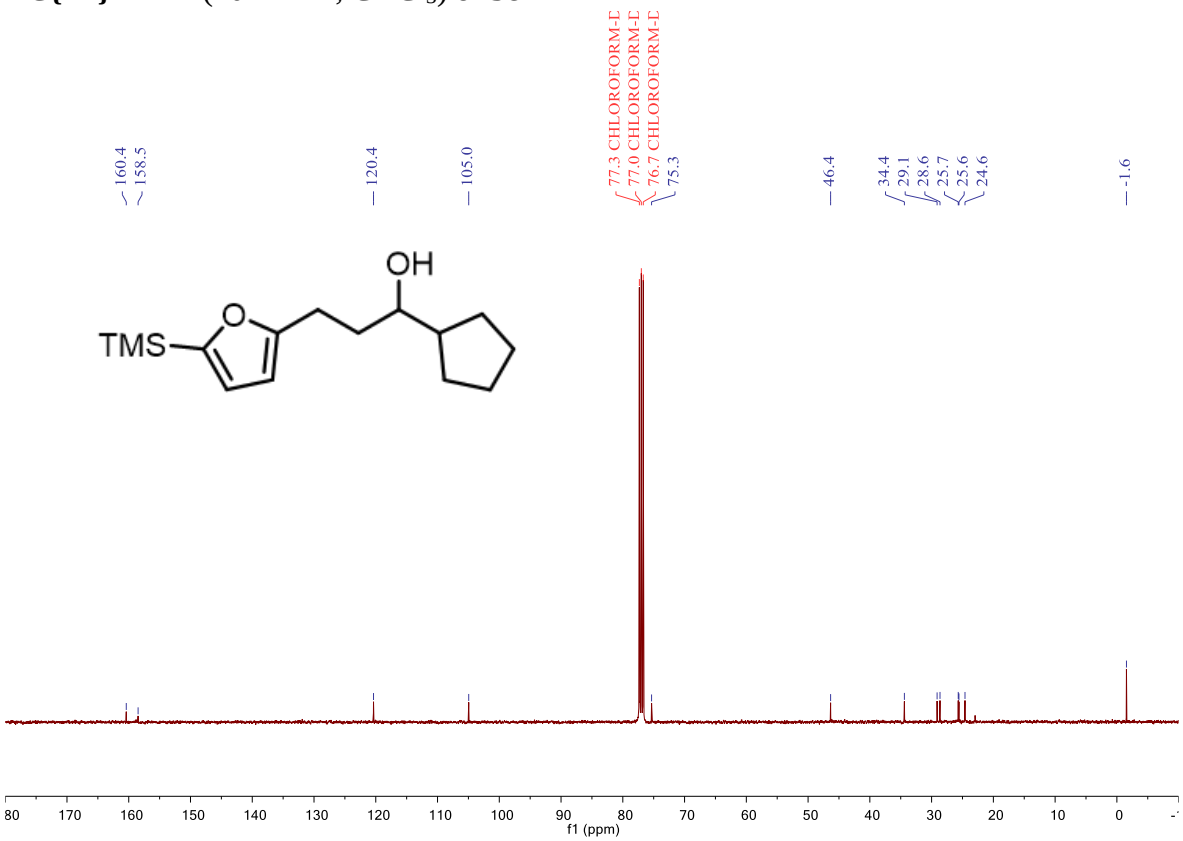


Back to contents

^{1}H NMR (500 MHz, $CDCl_3$) of **3e**, *See procedure*

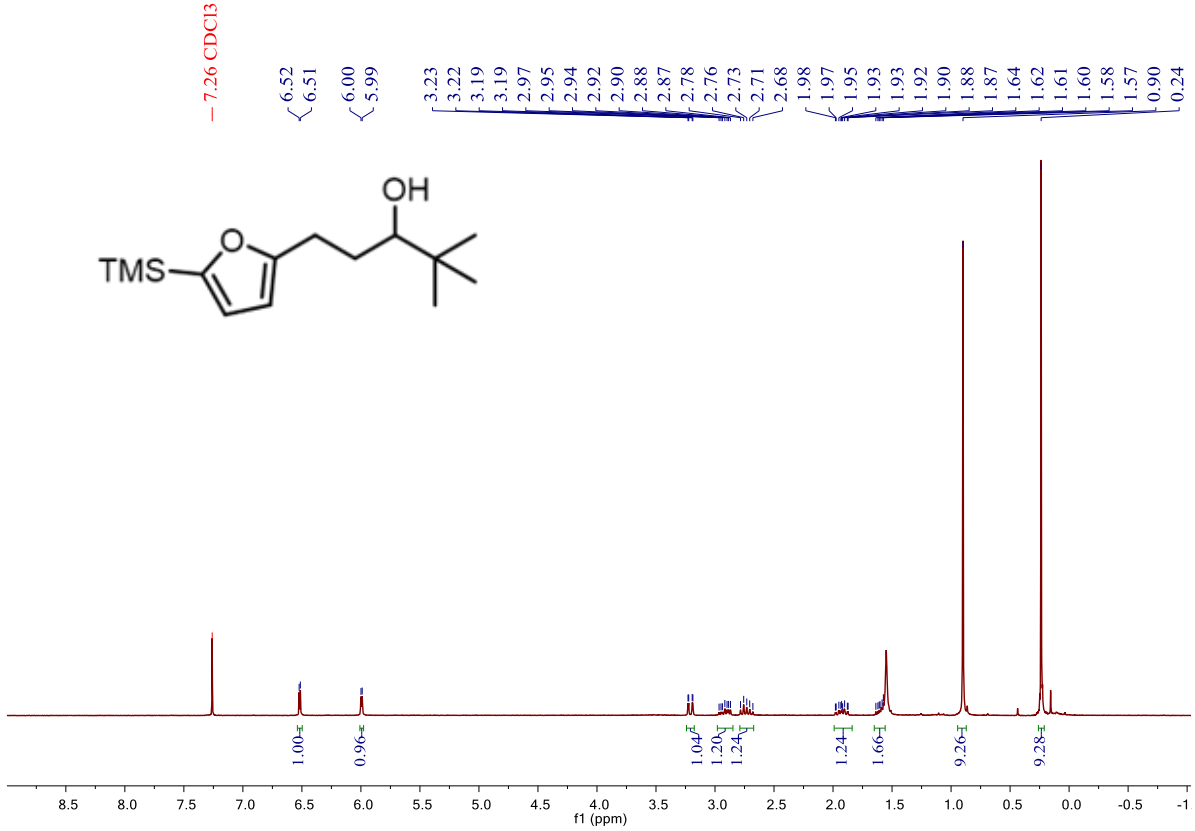


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3e**

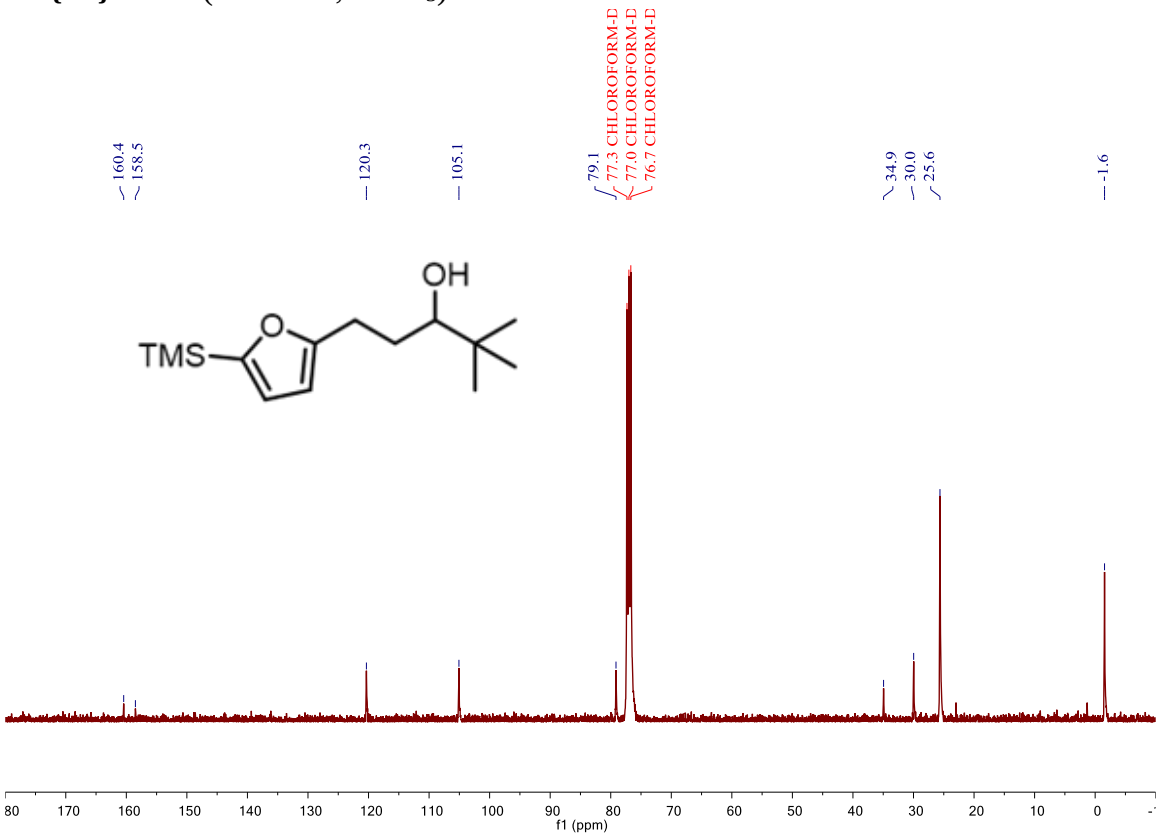


Back to contents

^{1}H NMR (300 MHz, $CDCl_3$) of **3f**, *See procedure*

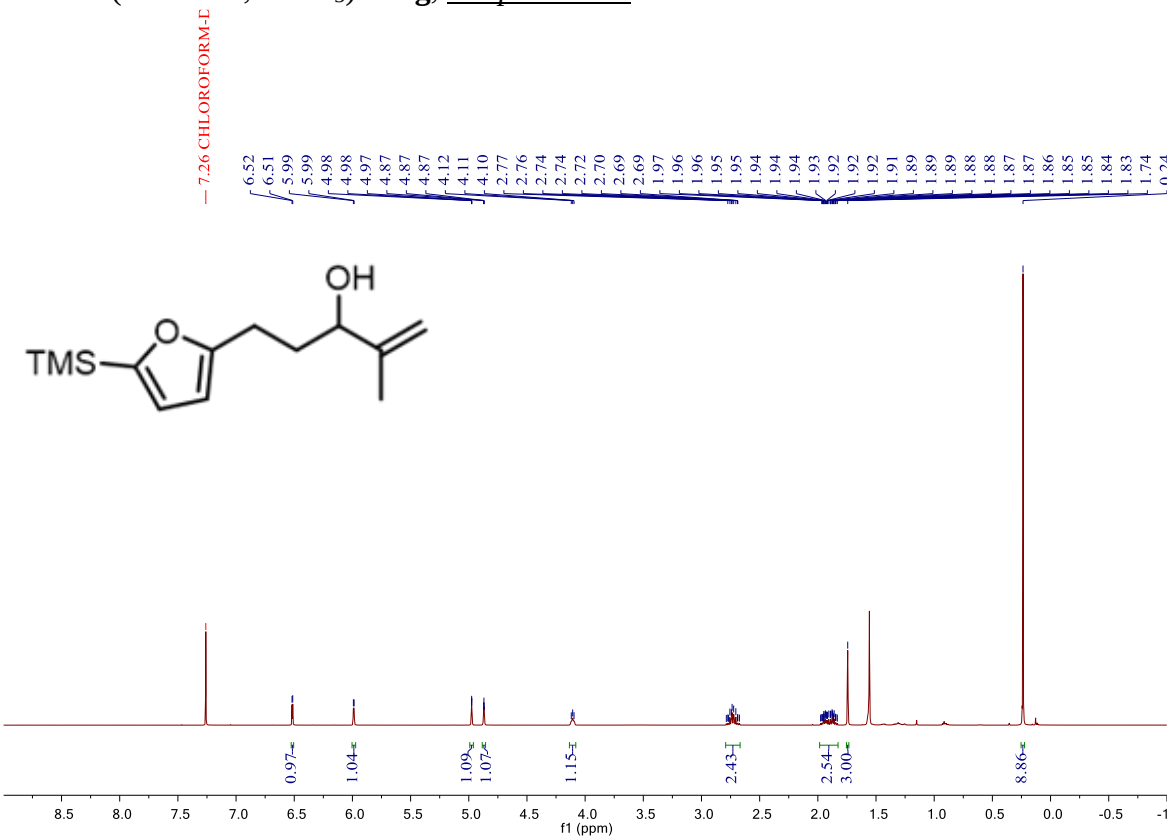


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3f**



Back to contents

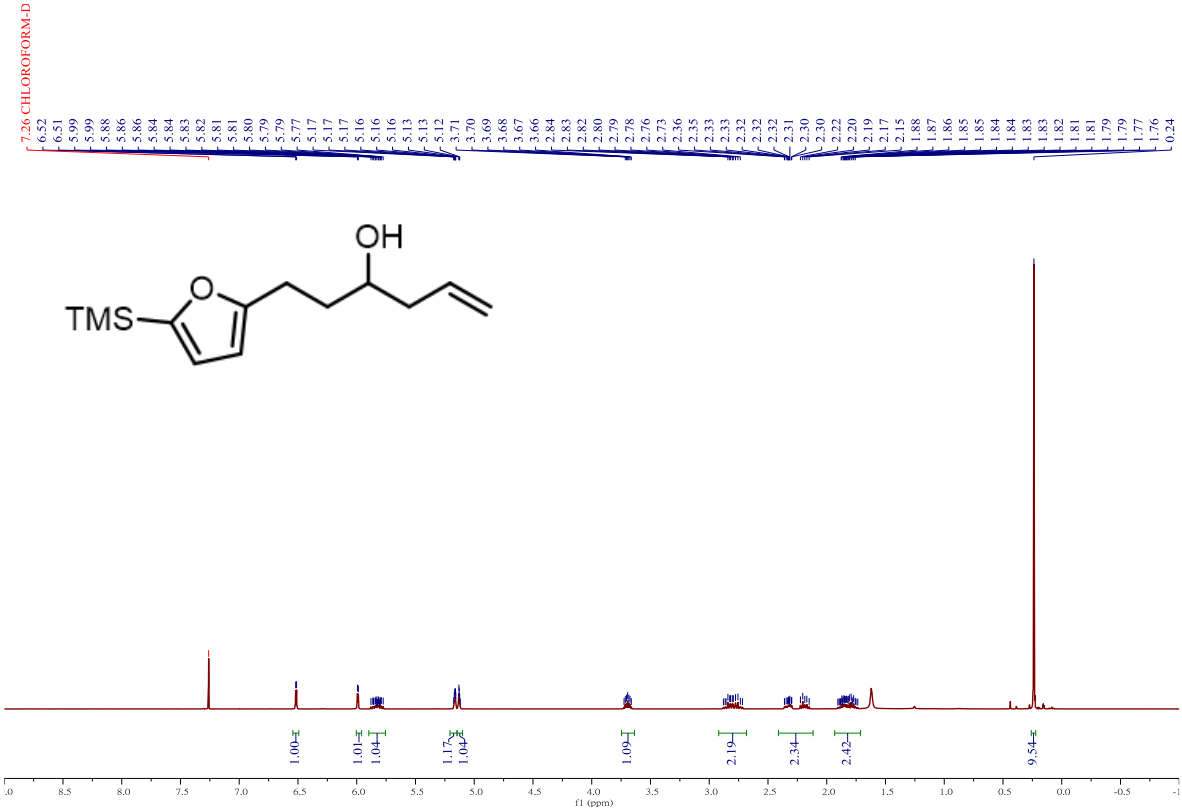
^{1}H NMR (500 MHz, $CDCl_3$) of **3g**, *See procedure*



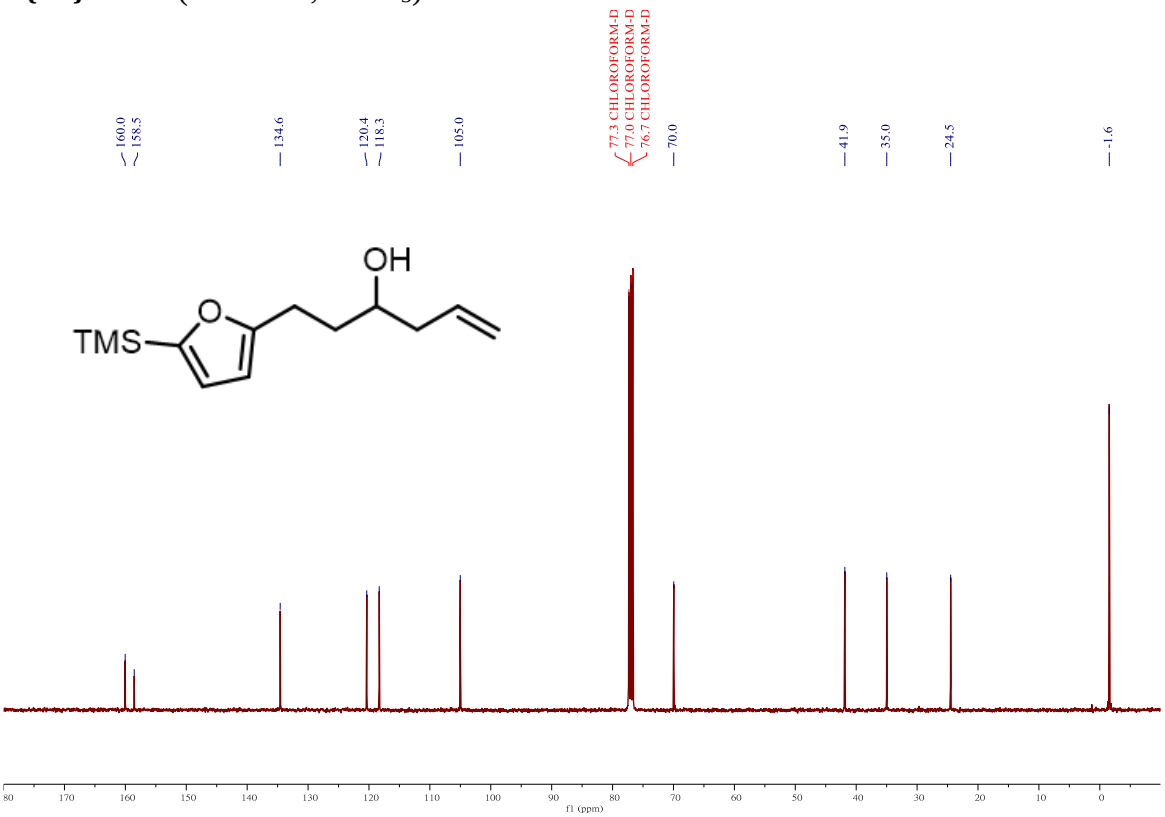
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3g**

Back to contents

^{1}H NMR (400 MHz, $CDCl_3$) of **3h**, *See procedure*

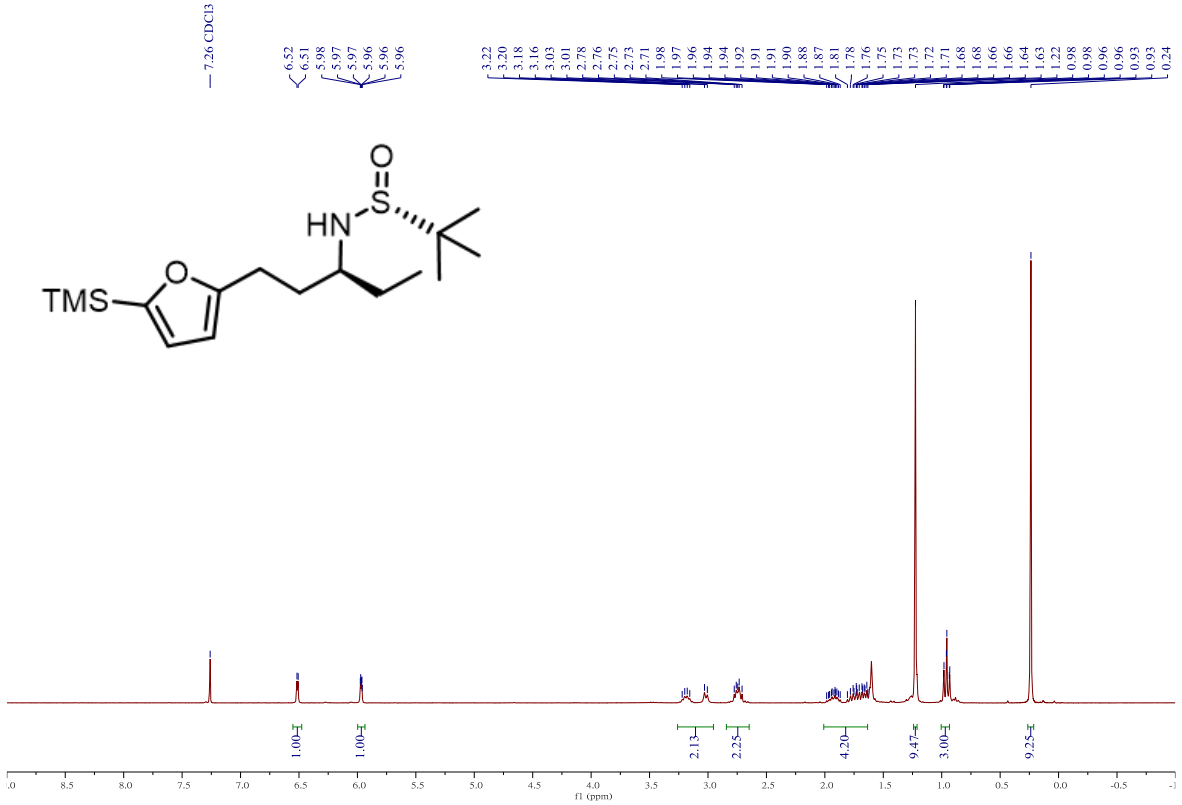


^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **3h**



Back to contents

^{1}H NMR (300 MHz, $CDCl_3$) of **6**, *See procedure*



^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) of **6**