Electronic Supplementary Material (ESI) for ChemComm.

This journal is © The Royal Society of Chemistry 2022

Supporting Information

Palladium-Catalyzed Acetalization/Cyclization of Enynones with Alcohols: Rapid Access to Functionalized Dihaloalkenyl Dihydrofurans

Ruize Ma,[‡a] Yang Chen,[‡a] Songjia Fang,[‡a] Huanfeng Jiang,[a] Shaorong Yang,[a] and Wanqing Wu*[,a]

[a] *School of Chemistry and Chemical Engineering, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China*

E-mail: cewuwq@scut.edu.cn; Fax: (+86) 20-87112906.

Table of Contents

A. General Information **S2**

B. General Procedure for the Synthesis of Starting Materials **S2**

C. Optimization of Reaction Conditions **S3**

D. Typical Procedure for the Synthesis of Haloalkyne **S7**

E. Mechanistic Studies **S9**

F. References **S13**

G. X-ray Crystallographic Analysis for Product 3k **S13**

H. Characterization Data for All Products **S14**

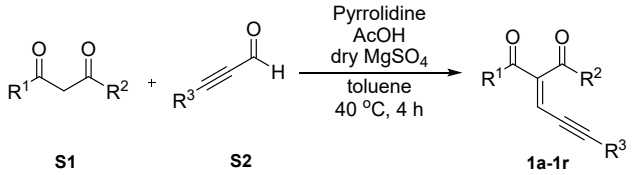
I. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra **S25**

A. General Information

^{1}H and ^{13}C NMR spectra were recorded using a Bruker DRX-400 spectrometer using CD_3CN、DMSO-d_6 or $CDCl_3$ as solvent and TMS as an internal standard. The chemical shifts are referenced to signals at 0.00 and 77.0 ppm, respectively. The multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. GC-MS data were obtained using electron ionization. HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). Melting points were measured using a melting point instrument and were uncorrected. TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). X-ray structural analyses were conducted on an X-ray analysis instrument. All the reaction temperatures reported are oil bath temperatures. All purchased reagents and solvents were used without further purification unless otherwise noted. The starting materials of enynones were synthesized in accordance with known procedures [1].

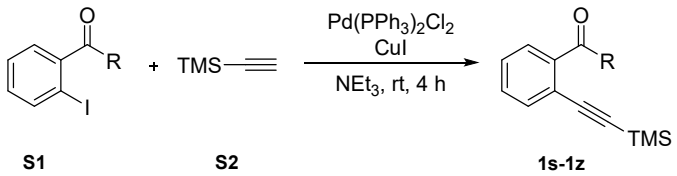
B. General Procedure for the Synthesis of Starting Materials

General Procedure for the Synthesis of 1a ~ 1r



To a 25 mL round bottom flask, a mixture of 1,3-diketone (**S1**, 0.5 mmol), AcOH (0.1 mmol, 6 mg), pyrrolidine (0.05 mmol, 3.6 mg) and dry $MgSO_4$ (0.5 mmol, 60 mg) was added to a solution of alkynyl aldehyde (**S2**, 0.6 mmol) in toluene. The reaction was stirred at 40 °C for 4 h and monitored by TLC analysis. After the completion of the reaction, the reaction mixture was filtered through celite and removed the solvent by rotary evaporation to give the crude product. The ene-yne-ketones **1a-1r** were purified by chromatography on silica gel with the appropriate mixture of petroleum ether and ethyl acetate in 60-90% yields.

General Procedure for the Synthesis of 1s ~ 1z

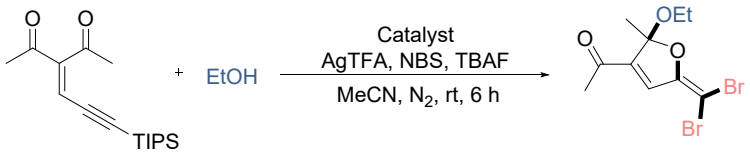


S1 **S2** **1s-1z**

To a 25 mL round bottom flask, a mixture of 2'-iodophenyl ketone (**S3**, 0.5 mmol), (trimethylsilyl)acetylene (**S4**, 0.6 mmol), Pd $(PPh_3)_2Cl_2$ (0.025 mmol, 3.6 mg) and CuI (0.05 mmol, 60 mg) was added to a solution of triethylamine (5 mL). The reaction was stirred at room temperature for 4 h and monitored by TLC analysis. After the completion of the reaction, the reaction mixture was filtered through *celite* and removed the solvent by rotary evaporation to give the crude product. **1s-1z** were then purified by chromatography on silica gel with the appropriate mixture of petroleum ether and ethyl acetate in 74-93% yields.

C. Optimization of Reaction Conditions

(a) Optimization of Catalyst [a]



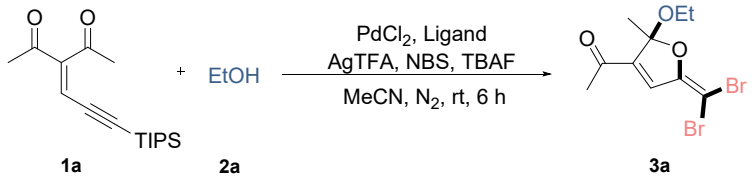
1a **2a** **3a**

Entry	Catalyst	Yield (%)
1	$Pd(dppp)Cl_2$	12
2	$PdBr_2$	15
3	$Pd(dppf)Cl_2$	19
4	$Pd(PPh_3)_4$	23
5	$Pd_2(dba)_3$	22
6	$Pd(OAc)_2$	26
7	$PdCl_2$	25
8	$Pd(PPh)_3Cl_2$	26
9	$Pd(Py)_2Cl_2$	20
10	$Pd_2(allyl)_2Cl_2$	trace
11	CuI	8
12	CuCl	trace
13	$Cu(MeCN)_4PF_6$	trace

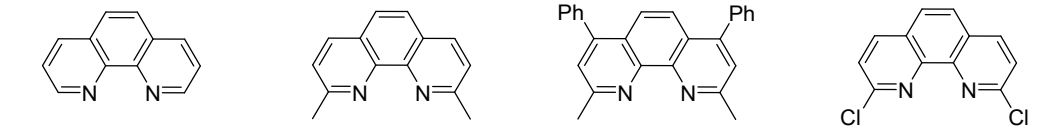
14	$CuCl_2$	trace

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (0.5 mmol), catalyst (20 mol %), AgTFA (20 mol %), NBS (2.0 equiv), TBAF (1.2 equiv), in dry MeCN (1.0 mL) under N_2 at room temperature for 6 h. Isolated yield. NBS = *N*-bromosuccinimide.

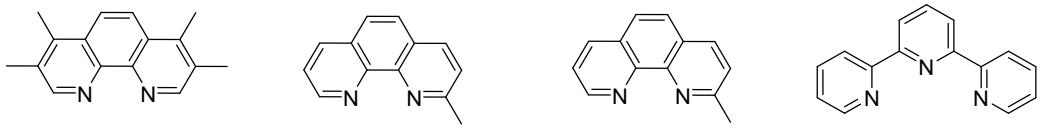
(b) Screening of Ligand [a]



1a **2a** **3a**



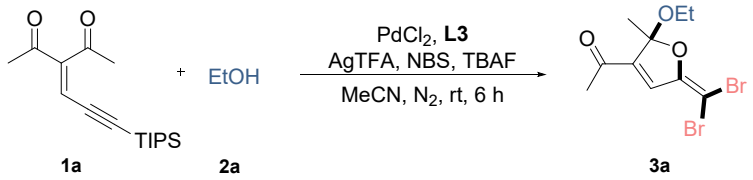
16% **L1** | 23% **L2** | 65% **L3** | 42% **L4**



26% **L5** | 40% **L6** | trace **L7** | 15% **L8**

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (0.5 mmol), $PdCl_2$ (20 mol %), Ligand (20 mol %), AgTFA (20 mol %), NBS (2.0 equiv), TBAF (1.2 equiv) in dry MeCN (1.0 mL) under N_2 at room temperature for 6 h. Isolated yield.

(c) Optimization of Amount of Silver Salt [a]

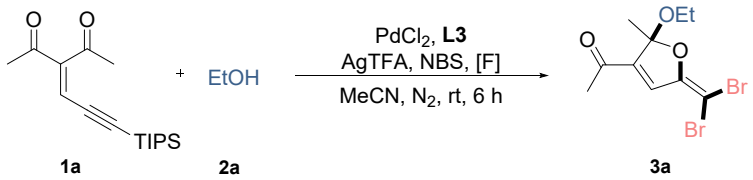


1a **2a** **3a**

Entry	[Ag] (x mol %)	Yield (%)
1	30	trace
2	20	trace
3	10	27
4	5	68

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (0.5 mmol), $PdCl_2$ (20 mol %), **L3** (20 mol %), AgTFA (x mol %), NBS (2.0 equiv), TBAF (1.2 equiv), in dry MeCN (1.0 mL) under N_2 at room temperature for 6 h. Isolated yield.

(d) Optimization of [F] Source [a]

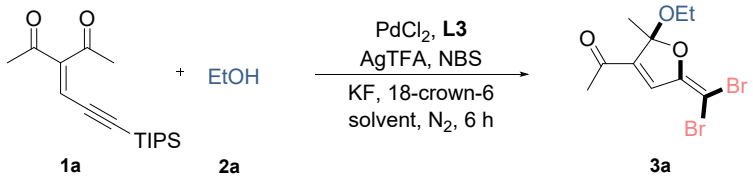


1a 2a 3a

Entry	[F] Source	Yield (%)
1	TBAF	65
2	KF	trace
3	NaF	n.d.
4	**KF + 18-crown-6**	**86**

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (0.5 mmol), $PdCl_2$ (20 mol %), **L3** (20 mol %), AgTFA (5 mol %), NBS (2.0 equiv), [F] (1.2 equiv), in dry MeCN (1.0 mL) under N_2 at room temperature for 6 h. Isolated yield.

(e) Optimization of Solvent and Temperature [a]

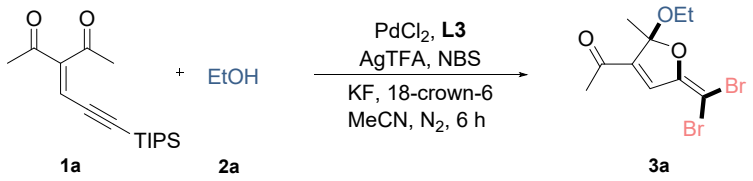


1a 2a 3a

Entry	Solvent	Temp. (°C)	Yield (%)
1	MeCN	r.t.	86
2	THF	r.t.	52
3	CH_2Cl_2	r.t.	trace
4	Toluene	r.t.	trace
5	MeCN	50	44
6	MeCN	80	19

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (0.5 mmol), $PdCl_2$ (20 mol %), **L3** (20 mol %), AgTFA (5 mol %), NBS (2.0 equiv), KF (1.2 equiv), 18-crown-6 (1.2 equiv) in dry solvent (1.0 mL) under N_2 for 6 h. Isolated yield.

(f) Optimization of Catalyst Loading [a]

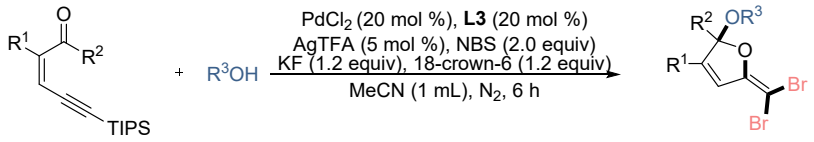


1a 2a 3a

Entry	$PdCl_2$ (X mol %)	Solvent	Yield (%)
1	20	MeCN	85
2	10	MeCN	66
3	5	MeCN	53

[a] Conditions: Unless otherwise noted, all reactions were performed with **1a** (0.1 mmol), **2a** (0.5 mmol), $PdCl_2$ (X mol %), **L3** (20 mol %), AgTFA (5 mol %), NBS (2.0 equiv), KF (1.2 equiv), 18-crown-6 (1.2 equiv) in dry MeCN (1.0 mL) under N_2 for 6 h. Isolated yield.

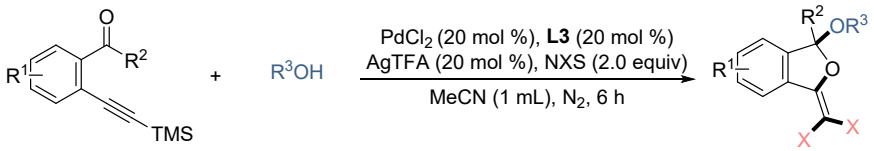
General Procedure for the Synthesis of 3a-3r



1 **2** **3**

A mixture of $PdCl_2$ (20 mol %), **L3** (20 mol %), AgTFA (5 mol %), NBS (2.0 equiv), KF (1.2 equiv), 18-crown-6 (1.2 equiv) was added to a 10 mL resealable Schlenk tube under air. Then enynones **1** (0.1 mmol), alcohol **2** (0.5 equiv) and 1.0 mL of dry MeCN were added through the syringe in the glove box filled with nitrogen. The mixture was stirred at room temperature under N_2 for 6 h. After the reaction was completed, it was filtered through silica gel with EtOAc (5 mL × 3). Then the mixture was concentrated under reduced pressure, and the crude product was purified by silica gel chromatography to give the products **3a-3r** in 63-88% yields. Among these products, compounds **3f**, **3g**, **3h**, **3i**, **3j**, **3l** and **3r** cannot be further purified through general purification methods involving chromatography on silica gel, recrystallization and preparative chromatography since it is mixed with some impurities with similar polarity to the corresponding product.

General Procedure for the Synthesis of 3s-3z

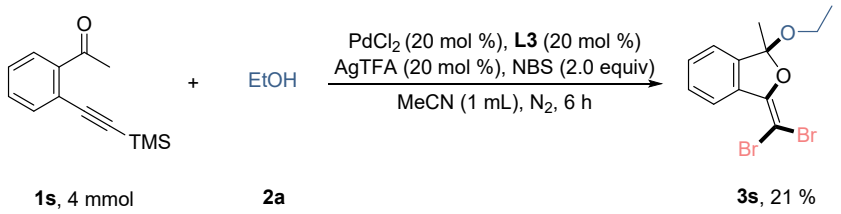


1 **2** **3**

A mixture of $PdCl_2$ (20 mol %), **L3** (20 mol %), AgTFA (20 mol %), NXS (2.0 equiv) was added to a 10 mL resealable Schlenk tube under air. Then enynones **1** (0.1 mmol), alcohol **2** (0.5 equiv) and 1.0 mL of dry MeCN were added through the syringe in the glove box filled with nitrogen.

The mixture was stirred at room temperature under N_2 for 6 h. After the reaction was completed, it was filtered through silica gel with EtOAc (5 mL × 3). Then the mixture was concentrated under reduced pressure, and the crude product was purified by silica gel chromatography to give the products **3s-3z** in 56-95% yields.

Scale-Up Reaction

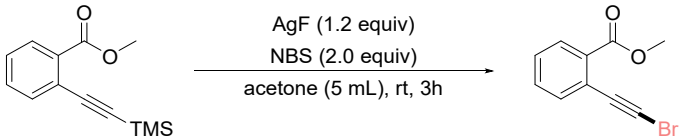


1s, 4 mmol **2a** **3s**, 21 %

To a 100 mL round bottom flask, a solid mixture of $PdCl_2$ (0.8 mmol, 141.9 mg), **L3** (0.8 mmol, 288.4 mg), AgTFA (0.2 mmol, 44.2 mg) and NBS (8 mmol, 1423.8 mg) were added under air. Then 1-(2-((trimethylsilyl)ethynyl)phenyl)ethan-1-one (**1s**, 4.0 mmol), ethanol (**2a**, 20.0 mmol, 921.4 mg) and 40 mL of dry MeCN were added through the syringe in the glove box filled with nitrogen. The mixture was stirred at room temperature under N_2 for 6 h. and the reaction was monitored by TLC. After the reaction was completed, it was filtered through silica gel with EtOAc (20 mL × 3). Then the mixture was concentrated under reduced pressure, and the crude product was purified by column chromatography to give the product **3s** in 21 % yield.

D. Typical Procedure for the Synthesis of Haloalkyne

Typical Procedure for the Synthesis of 4

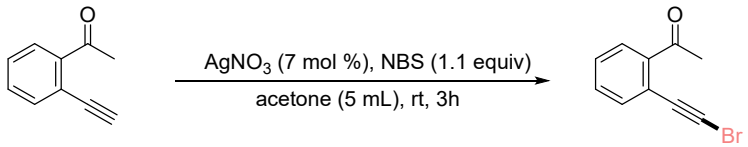


1y **4**, 91%

To a 25 mL round bottom flask, a mixture of AgF (0.6 mmol, 1.2 equiv) and NBS (1 mmol, 2.0 equiv) in acetone (5 mL) was added to a solution of methyl 2-((trimethylsilyl)ethynyl)benzoate (**1y**, 0.5 mmol). The reaction was stirred at room temperature for 3 h and monitored by TLC. After the completion of the reaction, the reaction mixture was filtered through *celite* and removed the solvent by rotary evaporation to give the crude product **4**, which was then purified by chromatography on silica gel with the appropriate mixture of petroleum ether and ethyl acetate in

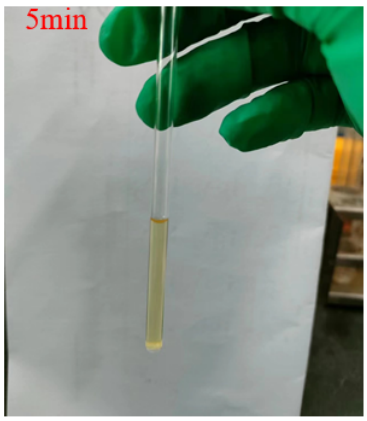
91% yield.

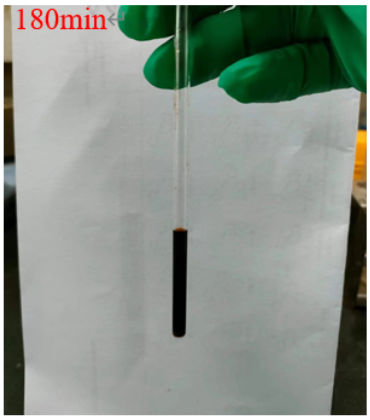
Failed examples

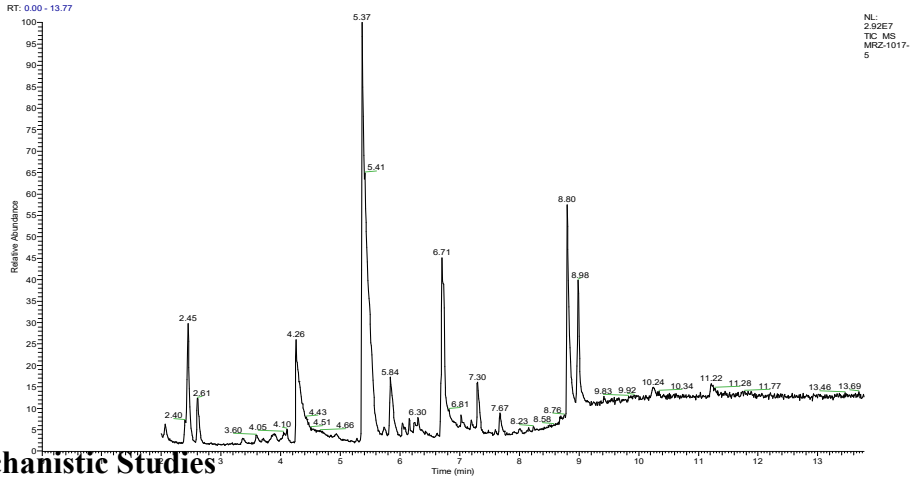


3 mmol not obtained

To a 25 mL round bottom flask, a mixture of $AgNO_3$ (7 mol %) and NBS (1.1 equiv) in acetone (5 mL) was added to a solution of *ortho*-ethynylacetophenones (3 mmol). The reaction was stirred at room temperature for 3 h and monitored by TLC. However, the color of the reaction mixture was changed to black after the completion of the reaction and a complicated GC-MS spectrum was obtained.





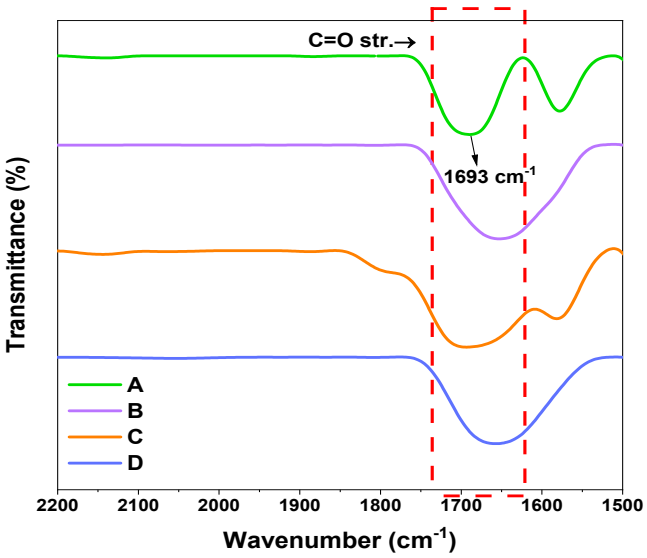


E. Mechanistic Studies

Typical Procedure for IR Spectrum Experiment for 1s

To a solution of 3-(3-(triisopropylsilyl)prop-2-yn-1-ylidene)pentane-2,4-dione (**1s**, 0.1 mmol, 21.6 mg) in MeCN (1.0 mL), was respectively added the following catalysts. (A) none, (B) $PdCl_2$ (20

mol %), (C) AgTFA (20 mol %), (D) $PdCl_2$ (20 mol %), AgTFA (20 mol %). After stirring for 20 min at room temperature, 0.2 mL of the solution was used for IR detection. The IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets.

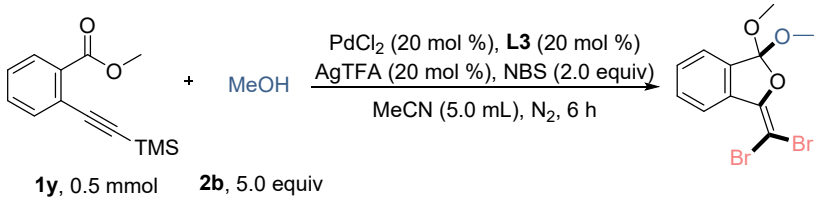


FT-IR spectra of A: the substrate **1s** (green), B: the mixture of **1s** and $PdCl_2$ (20 mol %) after 20 min (purple), C: the mixture of **1s** and AgTFA (20 mol %) after 20 min (orange), D: the mixture of **1s**, $PdCl_2$ (20 mol %) and AgTFA (20 mol %) after 20 min (blue).

The results showed that A exhibited a characteristic peak at 1693 cm^{-1} corresponding to ketone carbonyl stretching. When substrate **1s** was mixed with only palladium or silver salt, the carbonyl peak of B shifted obviously compared to C. Additionally, the result of D was consistent with the FT-IR spectrum of B, demonstrating that the carbonyl group of substrate **1s** preferentially coordinated with palladium salt at the initial reaction stage.

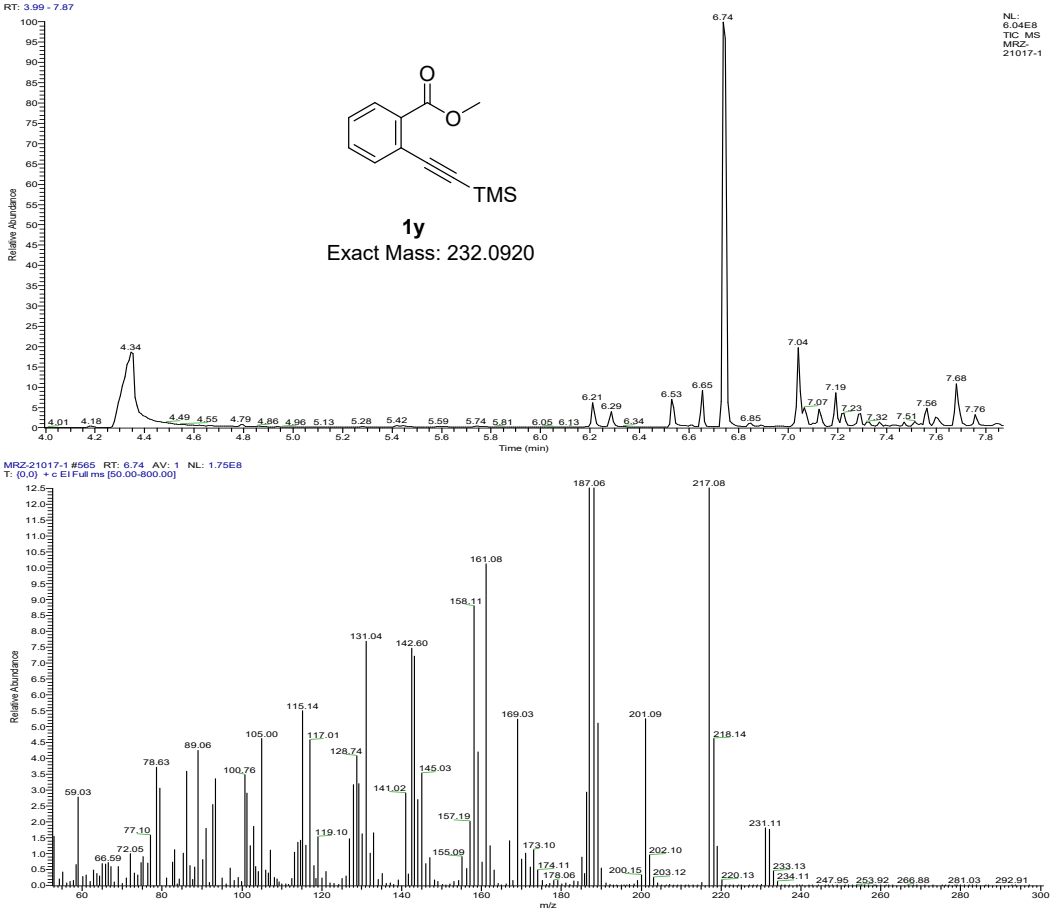
Reaction Process Monitored by GC-MS

A mixture of $PdCl_2$ (20 mol %), **L3** (20 mol %), AgTFA (20 mol %), NXS (2.0 equiv) were added to a 25 mL round bottom flask under air. Then enynones **1y** (0.5 mmol), methanol **2b** (0.5 equiv) and 5.0 mL of dry MeCN were added through the syringe in the glove box filled with nitrogen. The mixture was stirred at room temperature under N_2. Taking samples from the reaction mixture 30 min a time and monitoried by GC-MS.

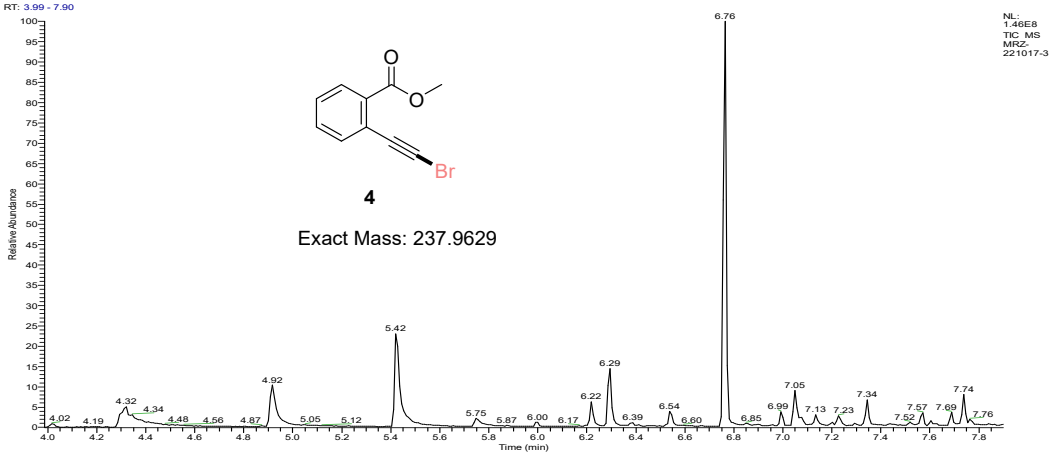


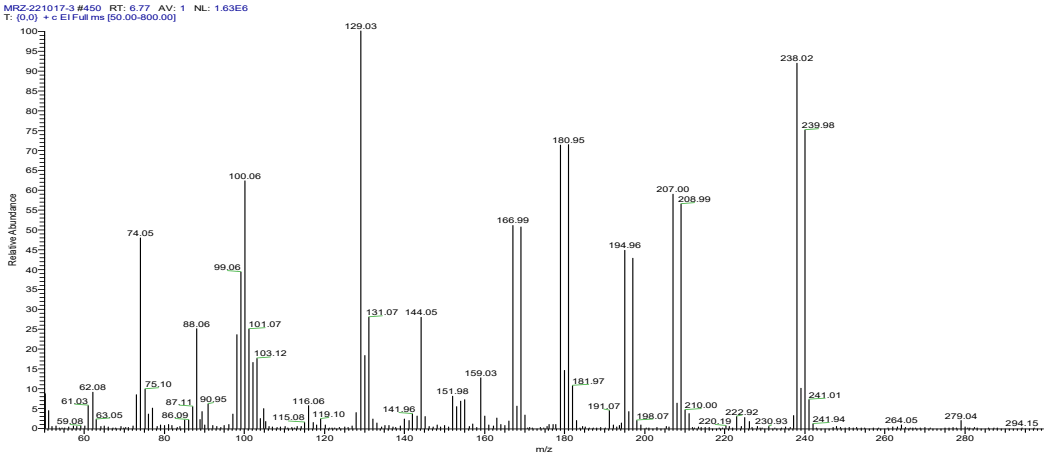
1y, 0.5 mmol **2b**, 5.0 equiv

Reaction Time (h)	Retention Time (min)	MW.	Peak Analysis
0.5	6.74	232.02	Substrate **1y**

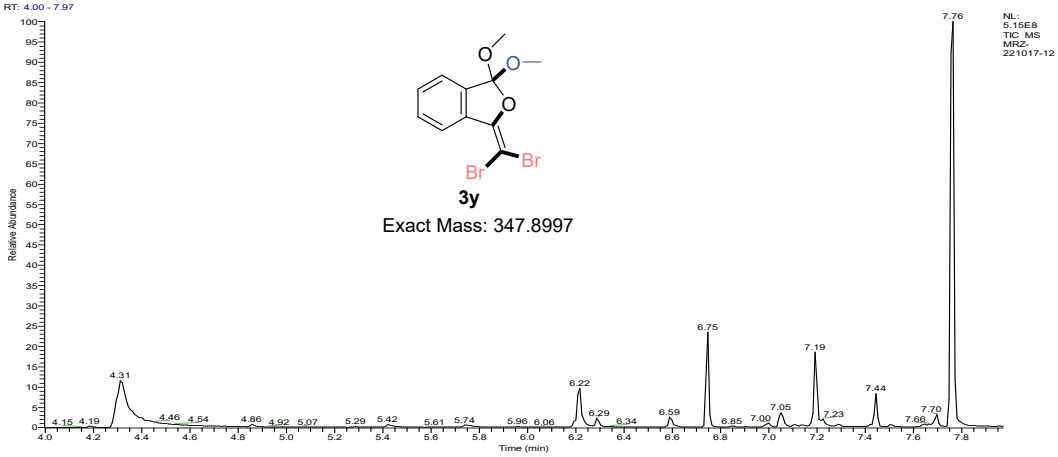


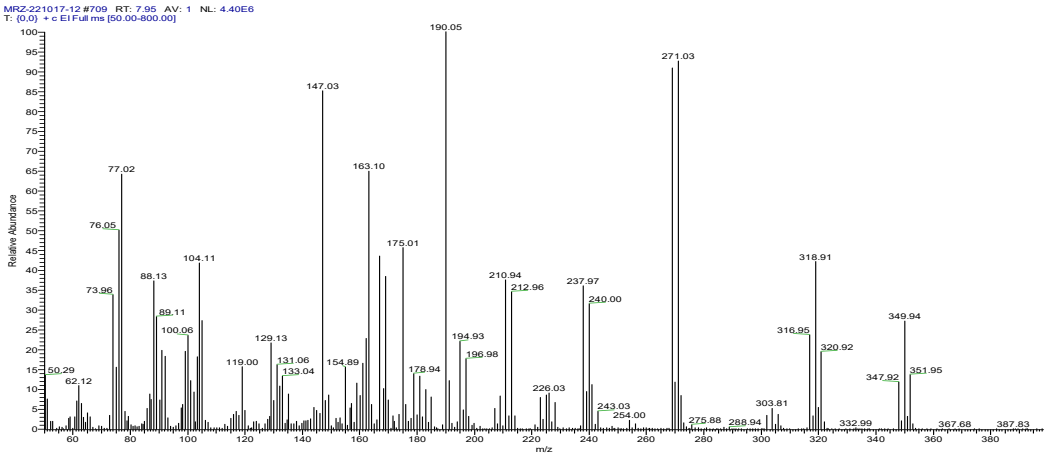
Reaction Time (h)	Retention Time (min)	MW.	Peak Analysis
1.5 h	6.76	238.02	Bromoalkyne **4**
	6.76	232.02	Substrate **1y**





Reaction Time (h)	Retention Time (min)	MW.	Peak Analysis
6.0	7.76	347.92	Product **3y**

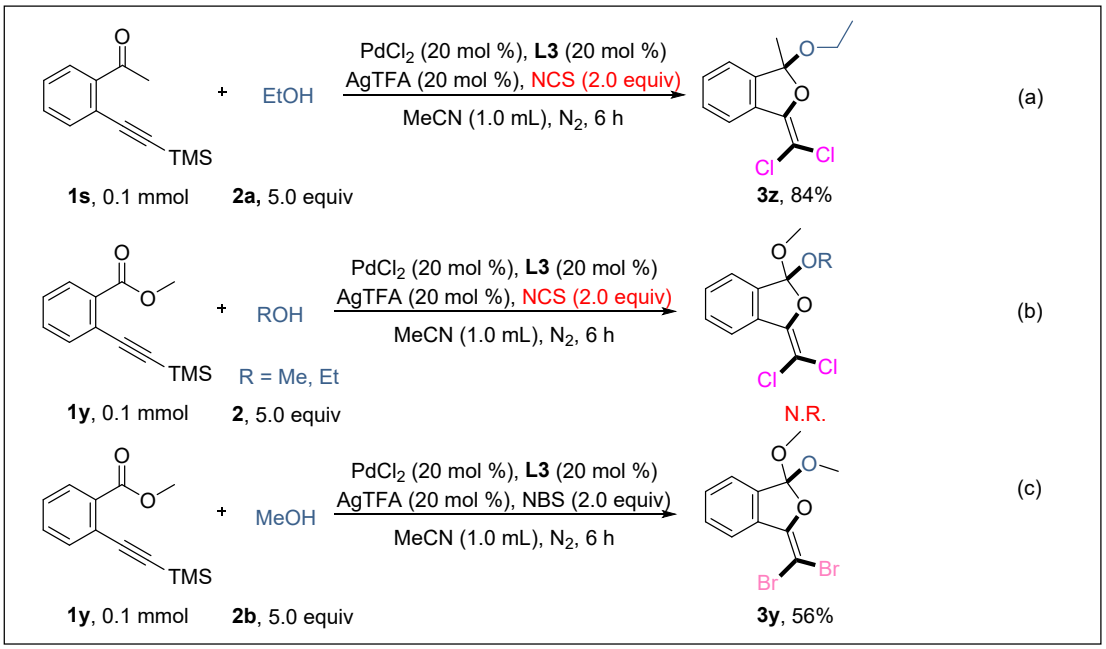




The result shows that the corresponding bromoalkyne (**4**) was found at reaction time of 1.5 h and it should be noted that the peak of substrate **1y** and bromoalkyne **4** overlapped at retention time of 6.74 min at reaction time of 1.5 h.

Control Experiments

Substrate **1s** reacted with NCS well to provide **3z** in 84% yield using ethanol as a nucleophile, while the reaction of substrate **1y** with NCS could not occur whether using ethanol or methanol, suggesting that NCS could react with the substrates with higher activity like TMS-protected *ortho*-alkynylketone. The reaction of **1y** with NBS was feasible but did not work with NCS, indicating the different reactivity between NBS and NCS.



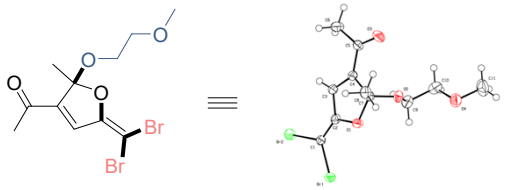
F. References

[1] (a) A. Ahrens, N. F. Heinrich, S. R. Kohl, M. Hokamop, M. Rudolph, F. Rominger and A. S. K. Hashmi, *Adv. Syn. & Cat.*, **2019**, *361*, 5605; (b) Y. Xia, S. Qu, Q. Xiao, Z. Wang, P. Qu, L. Chen, Z. Liu, L. Tian, Z. Huang, Y. Zhang and J. Wang, *J. Am. Chem. Soc.*, **2013**, *135*, 13502; (c) Y. M. Siu, R. James, M. J. Krische, *J. Am. Chem. Soc.*, **2021**, *143*, 10590.

[2] (a) C. M. Crawforth, S. Burling, I. J. S. Fairlamb, A. R. Kapdi, R. J. K. Taylor and A. C. Whitwood, *Tetrahedron*, **2005**, *61*, 9736; (b) G. Yin, X. Mu, and G. Liu, *Acc. Chem. Res.*, **2016**, *49*, 2413; (c) X. Li, J. Jin, P. Chen and G. Liu, *Nat. Chem.*, **2022**, *14*, 425.

G. X-ray Crystallographic Analysis for Product 3k

The X-ray crystallographic structures for **3k**. ORTEP representation with 50% probability thermal ellipsoids. Crystal data have been deposited to CCDC, number 2119937



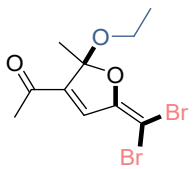
3k *x-ray of* **3k**

Empirical formula	$C_{11}H_{14}Br_2O_4$
Formula weight	367.93
Temperature	150.00 (10) K
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	7.7019(5)
b/Å	10.3698(7)
c/Å	25.1234(14)
α/°	90
β/°	90
γ/°	90

Volume/Å^3	2006.5(2)
Z	4
ρ_{calc}g/cm^3	1.260
μ/mm^{-1}	0.178
F(000)	816.0
Crystal size/mm^3	0.13 × 0.12 × 0.11
Radiation	MoKα (λ = 0.71073)
Final R indices [I>2sigma(I)]	R1 = 0.0428, wR2 = 0.1088
R indices (all data)	R1 = 0.0453, wR2 = 0.1069
Theta range for data collection/°	4.25 to 59.042
Index ranges	-10 ≤ h ≤ 9, -12 ≤ k ≤ 13, -33 ≤ l ≤ 33
Reflections collected	11893
Data/restraints/parameters	4700/0/246
Goodness-of-fit on F2	1.028
Final R indexes [I>=2σ (I)]	R1 = 0.0445, wR2 = 0.0940
Final R indexes [all data]	R1 = 0.0527, wR2 = 0.0988
Largest diff. peak/hole / e Å-3	0.46/-0.26

H. Characterization Data for All Products

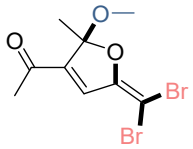
1-(5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3a)



Yellow oil (80%, 29 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 3.53-3.38 (m, 1H), 3.32-3.12 (m, 1H), 2.44 (s, 3H), 1.77 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

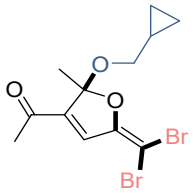
192.2, 154.3, 144.1, 131.6, 115.5, 71.0, 59.1, 27.5, 24.3, 14.8 ppm; ν_{max}(KBr)/cm^{-1} = 3595, 3387, 3114, 1702, 982, 561 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{10}H_{12}Br_2NaO_3$ $[M + Na]^+$: 360.9045, found 360.9043.

1-(5-(Dibromomethylene)-2-methoxy-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3b)



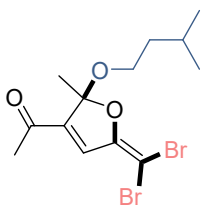
Yellow oil (74%, 24 mg); ^{1}H NMR (400 MHz, CD_3CN) δ 7.37 (s, 1H), 3.06 (s, 3H), 2.40 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 193.4, 155.3, 143.7, 132.7, 116.2, 69.9, 27.3, 23.7 ppm; ν_{max}(KBr)/cm^{-1} = 3391, 2927, 1676, 1234, 789 cm^{-1}; HRMS-ESI (m/z) calcd for $C_9H_{10}Br_2NaO_3$ $[M + Na]^+$: 346.8889, found 346.8894.

1-(2-(Cyclopropylmethoxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3c)



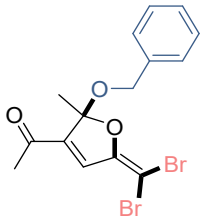
Yellow oil (72%, 28 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (s, 1H), 3.20 (dd, J = 9.8, 6.9 Hz, 1H), 2.97 (dd, J = 9.8, 7.0 Hz, 1H), 2.41 (s, 3H), 1.75 (s, 3H), 1.08-0.97 (m, 1H), 0.57-0.48 (m, 2H), 0.21-0.12 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 154.3, 138.6, 132.4, 115.0, 71.0, 70.3, 59.0, 27.4, 24.4, 18.7, 14.8 ppm; ν_{max}(KBr)/cm^{-1} = 3509, 1671, 1414, 1143, 1055, 628 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{14}Br_2NaO_3$ $[M + Na]^+$: 386.9202, found 386.9211.

1-(5-(Dibromomethylene)-2-isopentyloxy-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3d)



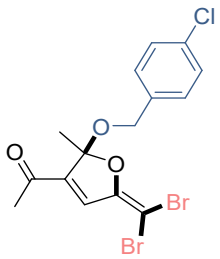
Yellow oil (85%, 31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 4.16-3.90 (m, 2H), 3.50-3.40 (m, 1H), 3.33-3.14 (m, 1H), 1.99 (m, 1H), 1.75 (s, 3H), 1.17 (t, J = 7.0 Hz, 3H), 0.96 (d, J = 6.7 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 154.6, 138.9, 132.8, 115.4, 71.4, 70.6, 59.4, 27.8, 24.7, 19.1, 15.1 ppm; ν_{max}(KBr)/cm^{-1} = 3447, 1672, 1413, 1237, 927, 628 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{13}H_{18}Br_2NaO_3$ [M + Na]$^+$: 402.9515, found 402.9517.

1-(2-(Benzyloxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3e)



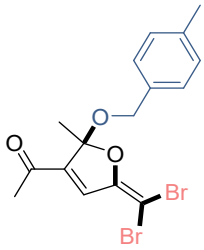
Yellow oil (84%, 34 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28-7.26 (m, 5H), 7.17 (s, 1H), 4.46 (d, J = 8.8 Hz, 1H), 4.26 (d, J = 9.2 Hz, 1H),)2.33 (s, 3H), 1.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 144.2, 136.8, 131.7, 128.1, 127.8, 127.5, 115.5, 71.5, 65.8, 29.4, 27.5, 24.4 ppm; ν_{max}(KBr)/cm^{-1} = 2927, 2044, 1691, 1390, 1162, 624 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{15}H_{14}Br_2NaO_3$ [M + Na]$^+$: 422.9202, found 422.9207.

1-(2-((4-Chlorobenzyl)oxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3f)



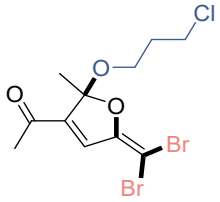
Yellow oil (85%, 39 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34-7.24 (m, 4H), 7.22 (s, 1H), 4.43 (d, J = 11.2 Hz, 1H), 4.24 (d, J = 11.2 Hz, 1H), 2.40 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 154.5, 144.1, 135.6, 133.6, 132.1, 129.3, 128.5, 115.7, 72.1, 65.2, 27.8, 24.6 ppm; ν_{max}(KBr)/cm^{-1} = 3407, 3094, 1682, 1575, 1164, 638 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{15}H_{13}Br_2ClNaO_3$ [M + Na]$^+$: 456.8812, found 456.8816.

1-(5-(Dibromomethylene)-2-methyl-2-((2-methylbenzyl)oxy)-2,5-dihydrofuran-3-yl)ethan-1-one (3g)



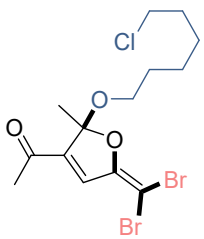
Yellow oil (88%, 38 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29-7.10 (m, 5H), 4.46 (d, J = 10.8 Hz, 1H), 4.25 (d, J = 10.8 Hz, 1H), 2.32 (s, 6H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.4, 154.8, 144.6, 137.4, 134.8, 131.8, 130.4, 128.3, 125.8, 115.7, 71.6, 64.5, 27.8, 24.6, 19.0 ppm; ν_{max}(KBr)/cm^{-1} = 3597, 1684, 1560, 1164, 962, 639 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{16}H_{16}Br_2NaO_3$ $[M + Na]^+$: 436.9358, found 436.9356.

1-(2-(3-Chloropropoxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3h)



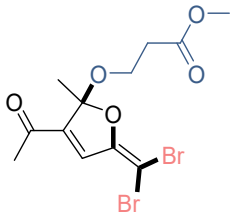
Yellow oil (64%, 27 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 3.61 (td, J = 5.8, 1.5 Hz, 2H), 3.51 (ddd, J = 9.5, 6.0, 4.7 Hz, 1H), 3.33-3.29 (m, 1H), 2.43 (s, 3H), 1.74 (s, 3H), 1.06 (s, 1H), 1.02 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.2, 154.2, 143.6, 131.7, 115.5, 71.4, 59.6, 41.4, 32.0, 27.5, 24.2 ppm; ν_{max}(KBr)/cm^{-1} = 3004, 1707, 1536, 1171, 976, 639, 531 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{11}H_{13}Br_2ClNaO_3$ $[M + Na]^+$: 408.8812, found 408.8820.

1-(2-((6-Chlorohexyl)oxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3i)



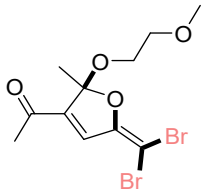
Yellow oil (83%, 37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (s, 1H), 3.35 (q, J = 6.8 Hz, 1H), 3.13 (q, J = 7.0 Hz, 1H), 2.41 (s, 3H), 1.74 (s, 2H), 1.59 (s, 2H), 1.32-1.25 (m, 6H), 0.88 (s, J = 6.5 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 154.7, 144.6, 131.8, 115.9, 71.2, 63.9, 31.5, 29.5, 27.8, 25.6, 24.6, 22.5, 14.0 ppm; ν_{max}(KBr)/cm^{-1} = 3413, 2926, 1679, 1399, 1239, 693, 627 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{14}H_{19}Br_2ClNaO_3$ [M + Na]$^+$: 450.9282, found 450.9291.

Methyl 3-((3-Acetyl-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-2-yl)oxy)propanoate (3j)



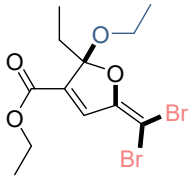
Yellow oil (78%, 32 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 3.67 (s, 3H), 3.61 (t, J = 7.6 Hz, 1H), 3.49 -3.41 (m, 1H), 2.58 (q, J = 7.2, 6.0 Hz, 2H), 2.42 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.45, 171.6, 154.5, 143.9, 132.0, 115.6, 71.8, 59.2, 51.8, 34.5, 27.9, 24.5 ppm; ν_{max}(KBr)/cm^{-1} = 3405, 2926, 1680, 1339, 1236, 625 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{14}Br_2NaO_5$ [M + Na]$^+$: 418.9100, found 418.9109.

1-(5-(Dibromomethylene)-2-(2-methoxyethoxy)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3k)



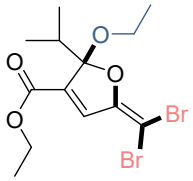
Yellow solid (69%, 26 mg); mp: 99.0-99.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (s, 1H), 3.50 (d, J = 7.1 Hz, 3H), 3.33 (m, 4H), 2.41 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 154.7, 144.5, 132.0, 115.8, 71.6, 71.1, 62.9, 58.9, 27.9, 24.5 ppm; ν_{max}(KBr)/cm^{-1} = 3400, 2925, 2855, 1678, 1236, 785, 626 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{11}H_{14}Br_2NaO_4$ [M + Na]$^+$: 390.9151, found 390.9156.

Ethyl 5-(Dibromomethylene)-2-ethoxy-2-ethyl-2,5-dihydrofuran-3-carboxylate (3l)



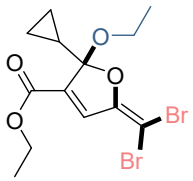
Yellow oil (70%, 40 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 4.28 (q, J = 7.1 Hz, 2H), 3.50-3.40 (m, 1H), 3.32-3.23 (m, 1H), 2.07 (m, 2H), 1.33 (t, J = 7.2 Hz, 3H), 1.18 (t, J = 7.0 Hz, 3H), 0.91 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3, 154.7, 137.5, 132.9, 117.3, 67.0, 61.0, 58.7, 39.0, 16.1, 14.8, 13.6 ppm; ν_{max}(KBr)/cm^{-1} = 2976, 1718, 1330, 1241, 1099, 903, 766 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{16}Br_2NaO_4$ $[M + Na]^+$: 404.9308, found 404.9302.

Ethyl 5-(Dibromomethylene)-2-ethoxy-2-isopropyl-2,5-dihydrofuran-3-carboxylate (3m)



Yellow oil (71%, 28 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 1H), 4.25 (q, J = 7.1 Hz, 2H), 3.42-3.32 (m, 1H), 3.27-3.18 (m, 1H), 2.43 (p, J = 6.8 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H), 1.09 (d, J = 6.8 Hz, 3H), 0.72 (d, J = 6.9 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.8, 155.4, 138.0, 133.1, 119.3, 69.9, 61.3, 59.2, 34.7, 16.9, 15.7, 15.2, 14.2 ppm; ν_{max}(KBr)/cm^{-1} = 2974, 1718, 1242, 1102, 901, 767 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{13}H_{18}Br_2NaO_4$ $[M + Na]^+$: 418.9464, found 418.9470.

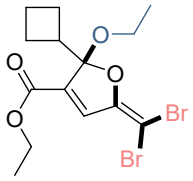
Ethyl 2-Cyclopropyl-5-(dibromomethylene)-2-ethoxy-2,5-dihydrofuran-3-carboxylate (3n)



Yellow oil (63%, 25 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (s, 1H), 4.30 (q, J = 7.2 Hz, 2H), 3.58-3.49 (m, 1H), 3.42-3.33 (m, 1H), 1.58 (m, ,1H), 1.34 (t, J = 7.2 Hz, 3H), 1.20 (t, J = 7.0 Hz, 3H), 0.93 (m, 1H), 0.65-0.56 (m, 1H), 0.45-0.36 (m, 1H), 0.21 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4, 154.6, 138.9, 131.6, 115.1, 69.9, 60.9, 59.4, 16.3, 14.9, 13.8, 2.2 ppm;

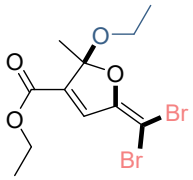
ν_{max}(KBr)/cm^{-1} = 2973, 1717, ,1242, 1101, 983, 901, 767, 623 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{13}H_{16}Br_2NaO_4$ $[M + Na]^+$: 416.9308, found 416.9314.

Ethyl 2-Cyclobutyl-5-(dibromomethylene)-2-ethoxy-2,5-dihydrofuran-3-carboxylate (3o)



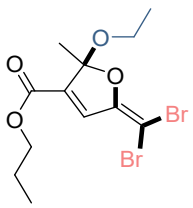
Yellow oil (76%, 31 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (s, 1H), 4.26 (q, J = 7.1 Hz, 2H), 3.44 (dq, J = 9.1, 7.1 Hz, 2H), 3.27 (dq, J = 9.1, 7.0 Hz, 2H), 3.09 (p, J = 8.3 Hz, 1H), 2.38-2.26 (m, 1H), 2.05 (m, 1H), 1.83-1.76 (m, 2H), 1.71-1.58 (m, 2H), 1.32 (t, J = 7.1 Hz, 3H), 1.17 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 155.2, 137.2, 133.3, 117.8, 70.0, 61.3, 59.5, 40.4, 22.45, 22.2, 17.8, 15.2, 14.2 ppm; ν_{max}(KBr)/cm^{-1} = 3394, 2980, 1721, 1528, 1236, 773, 682 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{14}H_{18}Br_2NaO_4$ $[M + Na]^+$: 430.9464, found 430.9472.

Ethyl 5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-carboxylate (3p)



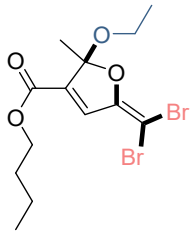
Yellow oil (79%, 29 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.56-3.42 (m, 1H), 3.37-3.22 (m, 1H), 1.79 (s, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.22 (t, J = 7.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.6, 154.6, 138.8, 132.6, 115.4, 70.6, 61.3, 59.4, 24.67, 15.2, 14.2 ppm; ν_{max}(KBr)/cm^{-1} = 3411, 2928, 1712, 1387, 1255, 1088, 955, 741 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{11}H_{14}Br_2NaO_4$ $[M + Na]^+$: 390.9151, found 390.9155.

Propyl 5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-carboxylate (3q)



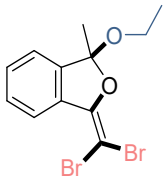
Yellow oil (79%, 29 mg); ^{1}H NMR (400 MHz, CD_3CN) δ 7.35-7.27 (m, 1H), 4.18 (t, J = 6.5 Hz, 2H), 3.41 (dq, J = 9.2, 7.1 Hz, 1H), 3.29 (dq, J = 9.1, 7.0 Hz, 1H), 1.75-1.70 (m, 5H), 1.14 (t, J = 7.0 Hz, 3H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 162.01, 155.6, 139.8, 132.8, 116.1, 70.0, 67.3, 59.9, 24.8, 22.3, 15.2, 10.4 ppm; ν_{max}(KBr)/cm^{-1} = 3403, 2926, 1712, 1387, 1254, 1161, 955, 740 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{16}Br_2NaO_4$ $[M + Na]^+$: 404.9308, found 404.9309.

Butyl 5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-carboxylate (3r)



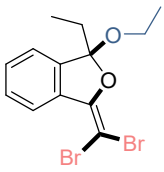
Yellow oil (81%, 33 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (s, 1H), 4.25 (m, 2H), 3.54-3.42 (m, 1H), 3.35-3.21 (m, 1H), 1.78 (s, 3H), 1.75-1.66 (m, 2H), 1.52-1.40 (m, 2H), 1.21 (t, J = 7.0 Hz, 3H), 0.98 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.7, 154.6, 138.8, 132.7, 115.4, 70.6, 65.2, 59.4, 30.6, 24.7, 19.1, 15.2, 13.7 ppm; ν_{max}(KBr)/cm^{-1} = 3416, 2927, 2929, 1712, 1388, 1254, 1088, 954 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{13}H_{18}Br_2NaO_4$ $[M + Na]^+$: 418.9464, found 418.9465.

3-(Dibromomethylene)-1-ethoxy-1-methyl-1,3-dihydroisobenzofuran (3s)



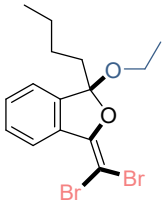
Yellow oil (84%, 31 mg); ^{1}H NMR (400 MHz, DMSO-*d6*) δ 8.24-8.18 (m, 1H), 7.66-7.50 (m, 3H), 3.21 (dq, J = 9.2, 7.1 Hz, 1H), 2.90 (dq, J = 9.3, 7.1 Hz, 1H), 1.72 (s, 3H), 1.04 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.8, 142.2, 131.3, 130.9, 130.6, 123.9, 123.3, 112.6, 97.0, 59.0, 26.4, 15.5 ppm; ν_{max}(KBr)/cm^{-1} = 3403, 2974, 1721, 1385, 1239, 1069, 857 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{12}Br_2NaO_2$ $[M + Na]^+$: 368.9096, found 368.9093.

3-(Dibromomethylene)-1-ethoxy-1-ethyl-1,3-dihydroisobenzofuran (3t)



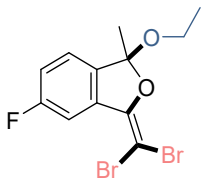
Yellow oil (95%, 34 mg); ^{1}H NMR (400 MHz, CD_3CN) δ 8.28 (dd, J = 6.4, 2.4 Hz, 1H), 7.60-7.55 (m, 2H), 7.43 (d, J = 6.3 Hz, 1H), 3.27 (dd, J = 9.3, 7.1 Hz, 1H), 2.97 (dd, J = 9.3, 7.1 Hz, 1H), 2.12-2.00 (m, 2H), 1.07 (d, J = 7.1 Hz, 3H), 0.76 (t, J = 7.5 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 153.0, 142.2, 132.7, 131.0, 130.5, 124.6, 123.5, 114.8, 64.1, 59.3, 32.6, 15.1, 7.4 ppm; ν_{max}(KBr)/cm^{-1} = 3411, 2975, 1722, 1239, 1080, 771 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{13}H_{14}Br_2NaO_2$ $[M + Na]^+$: 382.9258, found 382.9253.

1-Butyl-3-(dibromomethylene)-1-ethoxy-1,3-dihydroisobenzofuran (3u)



Yellow oil (79%, 32 mg); ^{1}H NMR (400 MHz, CD_3CN) δ 8.21-8.14 (m, 1H), 7.51-7.44 (m, 2H), 7.38-7.31 (m, 1H), 3.16 (dq, J = 9.4, 7.1 Hz, 1H), 2.86 (dq, J = 9.3, 7.0 Hz, 1H), 2.05-1.90 (m, 2H), 1.28-1.09 (m, 4H), 0.97 (t, J = 7.1 Hz, 3H), 0.74 (t, J = 14.4 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 152.4, 142.0, 132.0, 130.5, 130.0, 124.1, 123.0, 113.9, 63.6, 58.6, 38.7, 25.1, 22.2, 14.5, 13.2 ppm; ν_{max}(KBr)/cm^{-1} = 3115, 1694, 1597, 1487, 1282, 1225, 1009, 977 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{15}H_{18}Br_2NaO_2$ $[M + Na]^+$: 410.9566, found 410.9573.

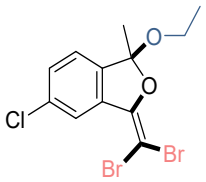
3-(Dibromomethylene)-1-ethoxy-5-fluoro-1-methyl-1,3-dihydroisobenzofuran (3v)



Yellow oil (86%, 28 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (dd, J = 8.7, 4.7 Hz, 1H), 7.17 (td, J = 8.7, 2.4 Hz, 1H), 7.05 (dd, J = 7.5, 2.4 Hz, 1H), 3.49-3.33 (m, 1H), 3.12-2.95 (m, 1H), 1.79 (s, 3H), 1.16 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 162.5, 151.2, 145.7, 127.7,

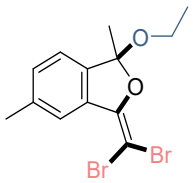
126.3 (d, $J_{C\text{-}F}$ = 8.9 Hz), 117.3 (d, $J_{C\text{-}F}$ = 23.2 Hz), 109.6 (d, $J_{C\text{-}F}$ = 23.7 Hz), 64.7, 59.1, 26.2, 15.1 ppm; ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.4 ppm; ν_{max}(KBr)/cm^{-1} = 2841, 2364, 1394, 1282, 1008, 876, 650 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{11}Br_2FNaO_2$ $[M + Na]^+$: 386.9002, found 386.9007.

5-Chloro-3-(dibromomethylene)-1-ethoxy-1-methyl-1,3-dihydroisobenzofuran (3w)



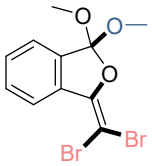
Yellow oil (84%, 34 mg); ^{1}H NMR (400 MHz, CD_3CN) δ 8.16 (d, J = 1.9 Hz, 1H), 7.49 (dd, J = 8.1, 1.8 Hz, 1H), 7.34 (d, J = 8.3 Hz, 1H), 3.20 (dq, J = 9.3, 7.1 Hz, 1H), 2.90 (dq, J = 9.3, 7.0 Hz, 1H), 1.64 (s, 3H), 0.99 (t, J = 7.1 Hz, 2H); ^{13}C NMR (100 MHz, CD_3CN) δ 150.9, 141.6, 135.3, 133.1, 130.6, 124.4, 123.9, 111.5, 65.5, 59.0, 25.4, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2972, 1692, 1437, 1099, 930, 694 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{11}Br_2ClNaO_2$ $[M + Na]^+$: 402.8707, found 402.8715.

3-(Dibromomethylene)-1-ethoxy-1,5-dimethyl-1,3-dihydroisobenzofuran (3x)



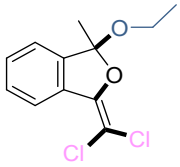
Yellow oil (71%, 27 mg); ^{1}H NMR (400 MHz, CD_3CN) δ 7.99 (s, 1H), 7.31 (d, J = 8.4 Hz, 1H), 7.23 (d, J = 7.8 Hz, 1H), 3.16 (dq, J = 9.3, 7.0 Hz, 1H), 2.86 (dq, J = 9.3, 7.1 Hz, 1H), 2.36 (s, 3H), 1.62 (s, 3H), 0.97 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CD_3CN) δ 152.2, 140.3, 140.3, 131.6, 131.5, 124.3, 122.5, 111.6, 63.5, 58.7, 25.6, 20.7, 14.5 ppm; ν_{max}(KBr)/cm^{-1} = 2973, 1696, 1438, 1314, 1098, 931, 691, 495 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{13}H_{14}Br_2NaO_2$ $[M + Na]^+$: 382.9253, found 382.9256.

3-(Dibromomethylene)-1,1-dimethoxy-1,3-dihydroisobenzofuran (3y)



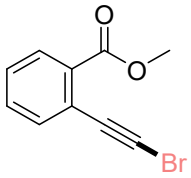
Yellow oil (56%, 20 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, J = 7.7 Hz, 1H), 7.65-7.61 (m, 1H), 7.56 (td, J = 7.7, 1.3 Hz, 1H), 7.46 (td, J = 7.5, 1.4 Hz, 1H), 3.22 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 135.3, 134.7, 130.2, 129.0, 128.1, 126.8, 114.4, 50.4, 42.8 ppm; ν_{max}(KBr)/cm^{-1} = 2256, 2129, 1650, 1170, 1005, 760, 688 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{11}H_{10}Br_2NaO_3$ $[M + Na]^+$: 370.8889, found 370.8893.

3-(Dichloromethylene)-1-ethoxy-1-methyl-1,3-dihydroisobenzofuran (3z)



Yellow oil (84%, 22 mg); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.40-8.20 (m, 1H), 7.94-7.77 (m, 3H), 3.61 (s, 3H), 3.53-3.43 (m, 1H), 3.22-3.13 (m, 1H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.9, 142.3, 131.2, 131.0, 130.6 124.0, 123.4, 112.7, 97.0, 59.1, 26.5, 15.6 ppm; ν_{max}(KBr)/cm^{-1} = 2256, 2130, 1650, 1289, 999, 764, 676 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{12}H_{12}Cl_2NaO_2$ $[M + Na]^+$: 281.0107, found 281.0112.

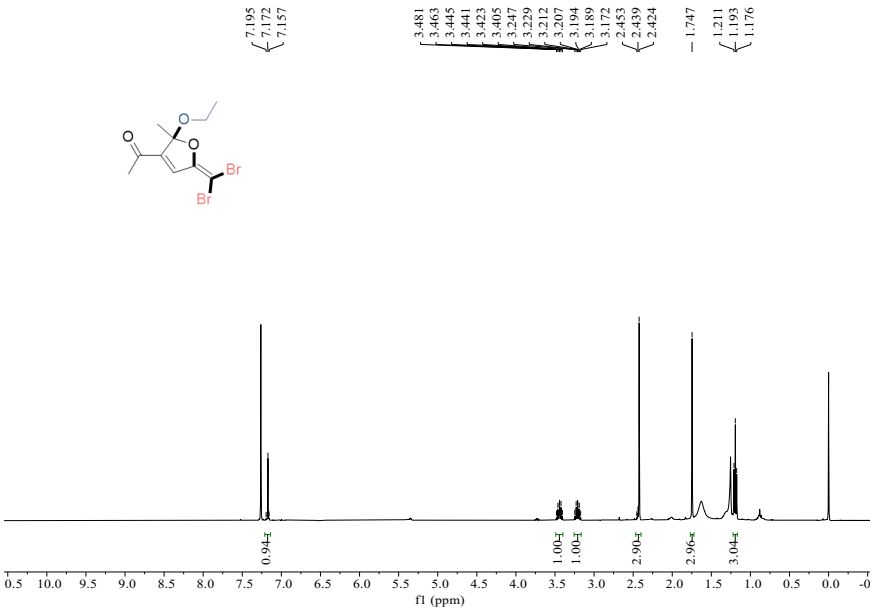
Methyl 2-(Bromoethynyl)benzoate (4)

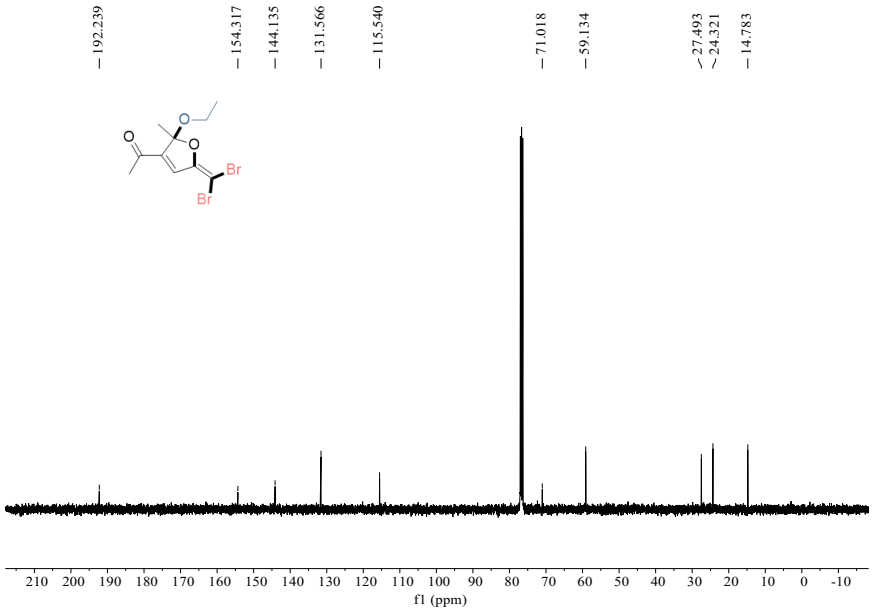


Yellow oil (91%, 22 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.8 Hz, 1H), 7.55 (d, J = 7.7 Hz, 1H), 7.48-7.42 (m, 1H), 7.41-7.34 (m, 1H), 3.92 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 134.7, 132.2, 131.7, 130.4, 128.2, 123.1, 78.5, 54.9, 52.2 ppm; ν_{max}(KBr)/cm^{-1} = 1792, 1723, 1291, 1041, 757, 693 cm^{-1}; HRMS-ESI (m/z) calcd for $C_{10}H_7BrNaO_2$ $[M + Na]^+$: 260.9522, found 260.9525.

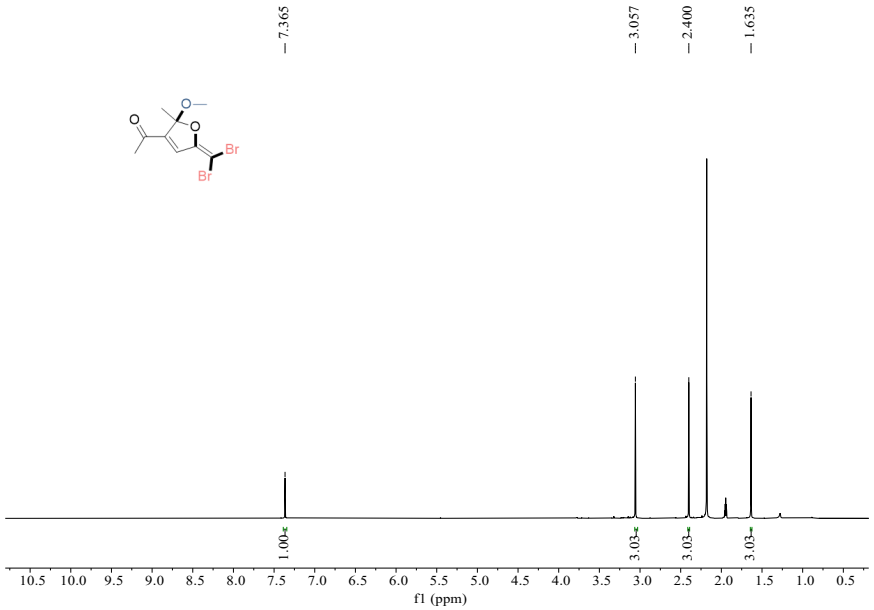
I. Copies of ^{1}H, ^{13}C and ^{19}F NMR Spectra

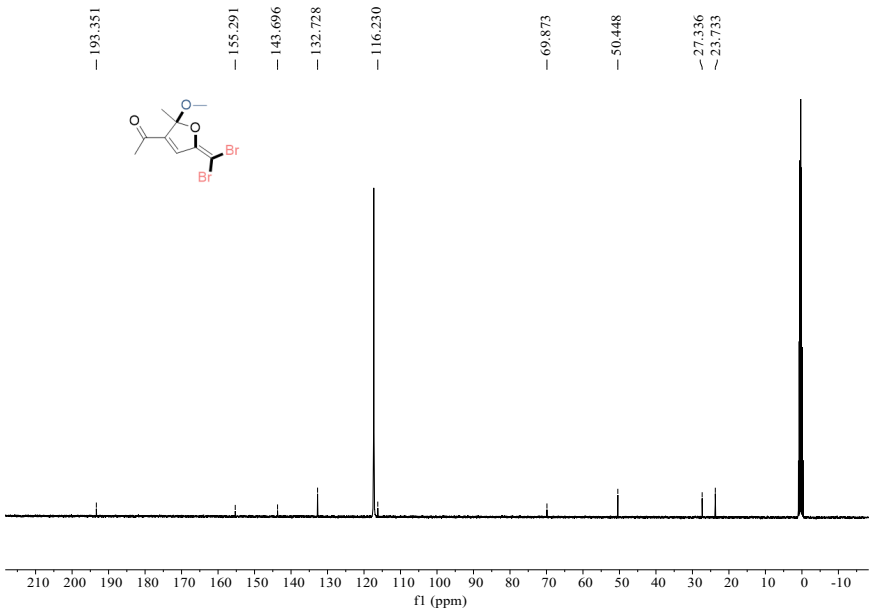
1-(5-(Dibromomethylene)-2-methoxy-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3a)



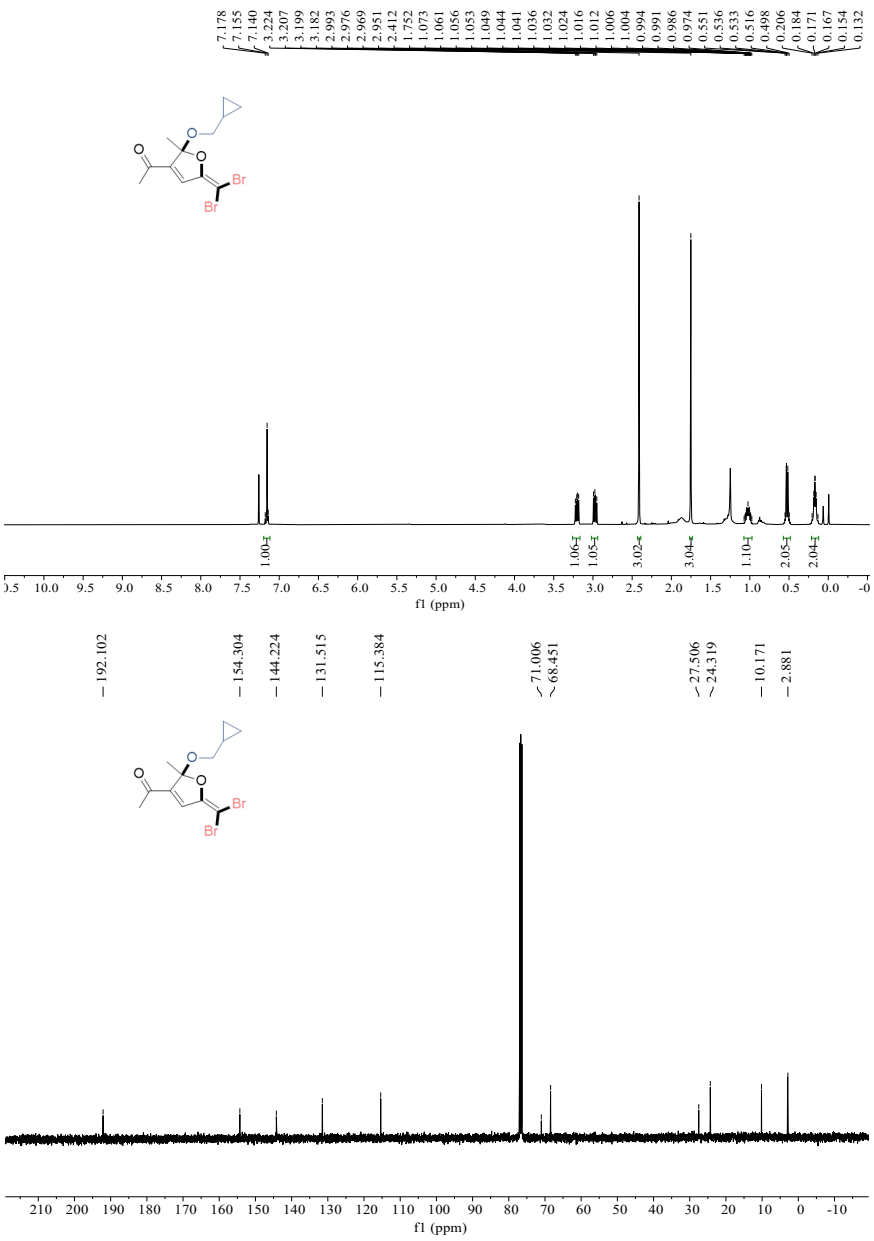


1-(5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3b)

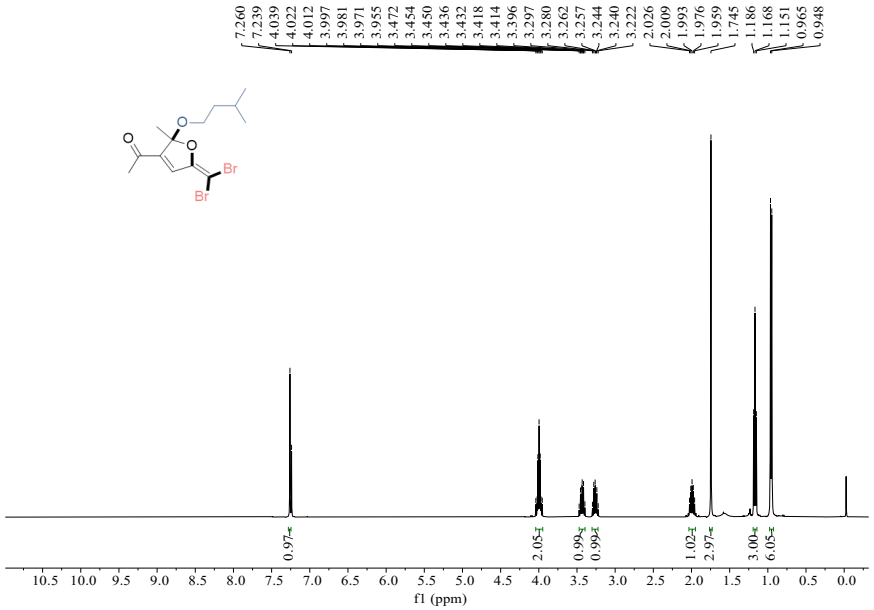


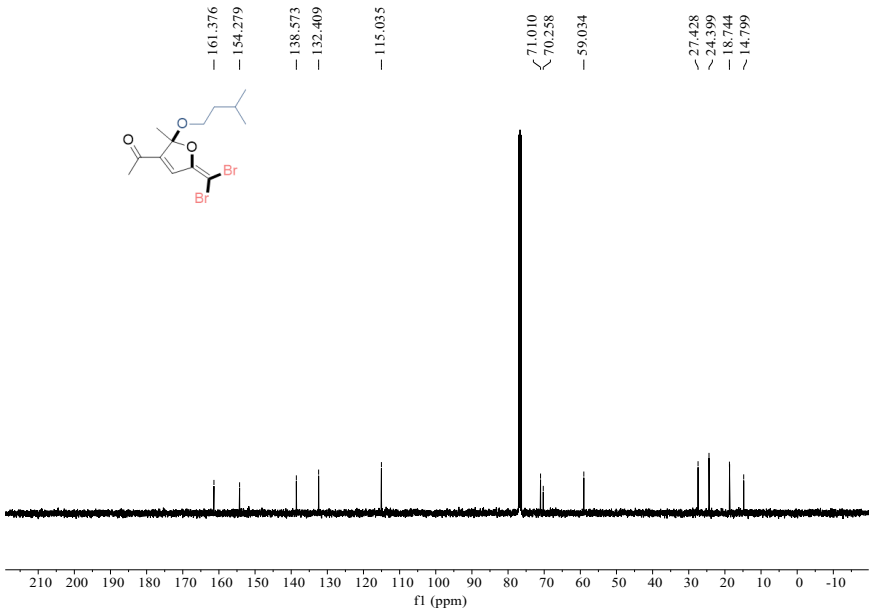


1-(2-(Cyclopropylmethoxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3c)

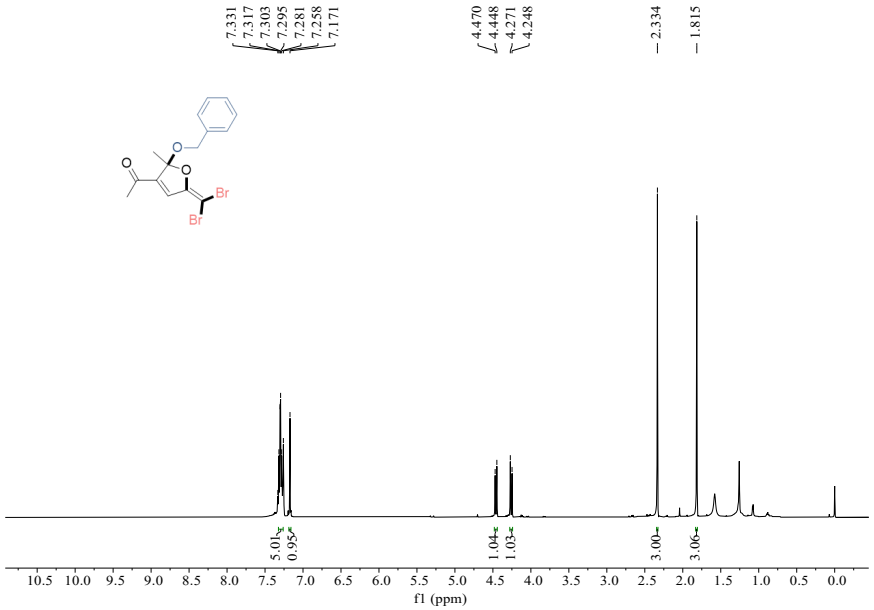


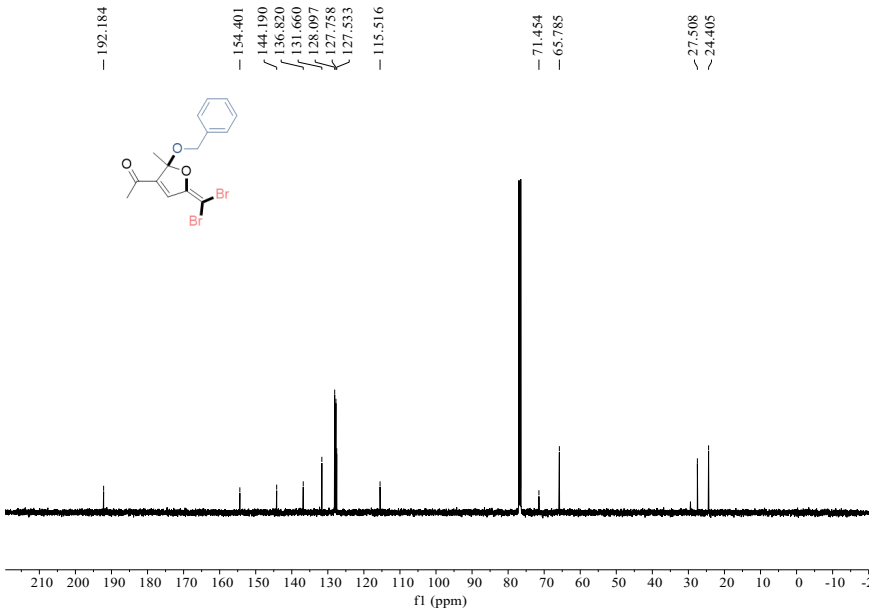
1-(5-(Dibromomethylene)-2-isopentyloxy-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3d)



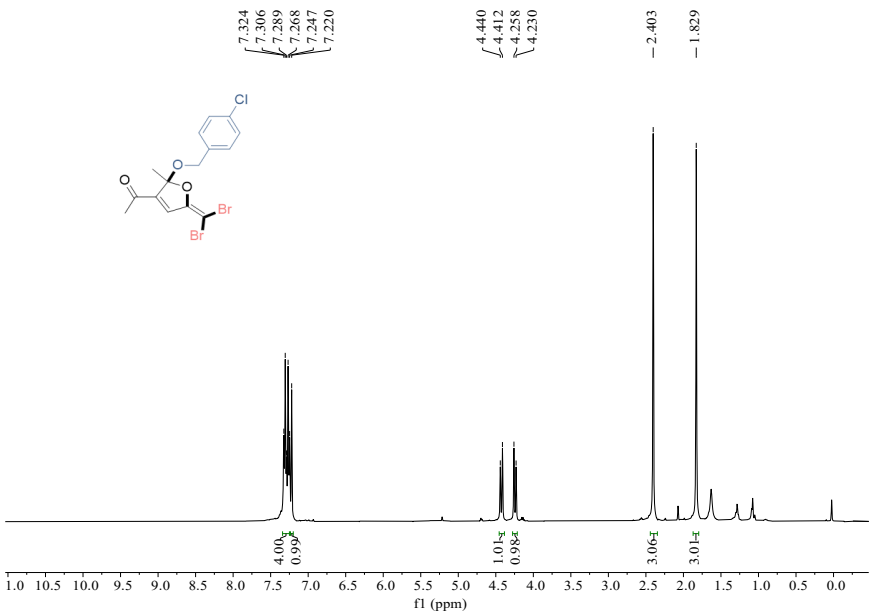


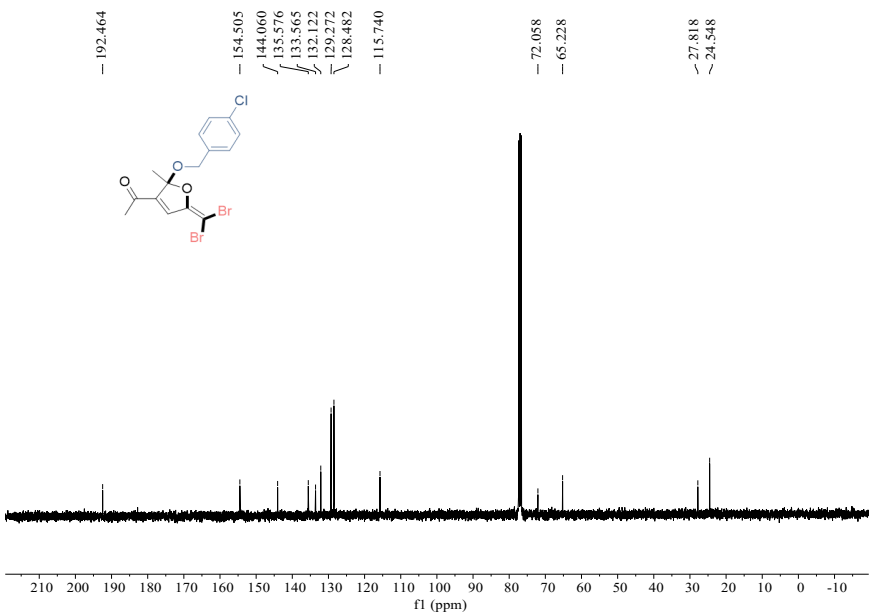
1-(2-(Benzyloxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3e)



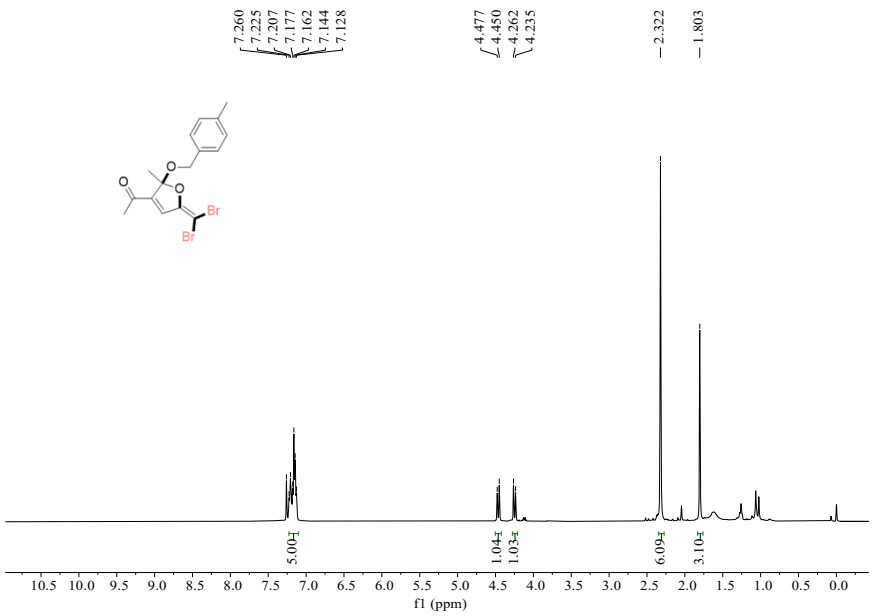


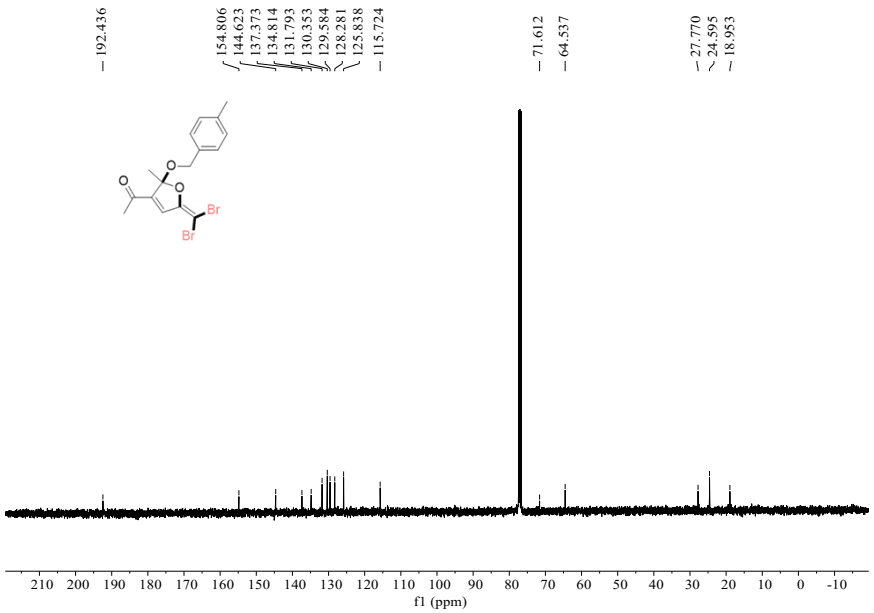
1-(2-((4-Chlorobenzyl)oxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3f)





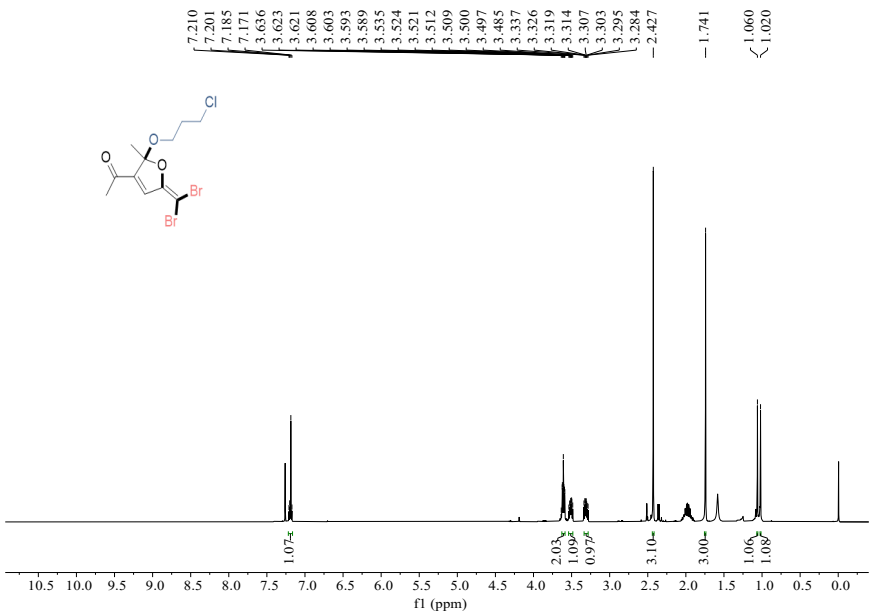
1-(5-(Dibromomethylene)-2-methyl-2-((2-methylbenzyl)oxy)-2,5-dihydrofuran-3-yl)ethan-1-one (3g)

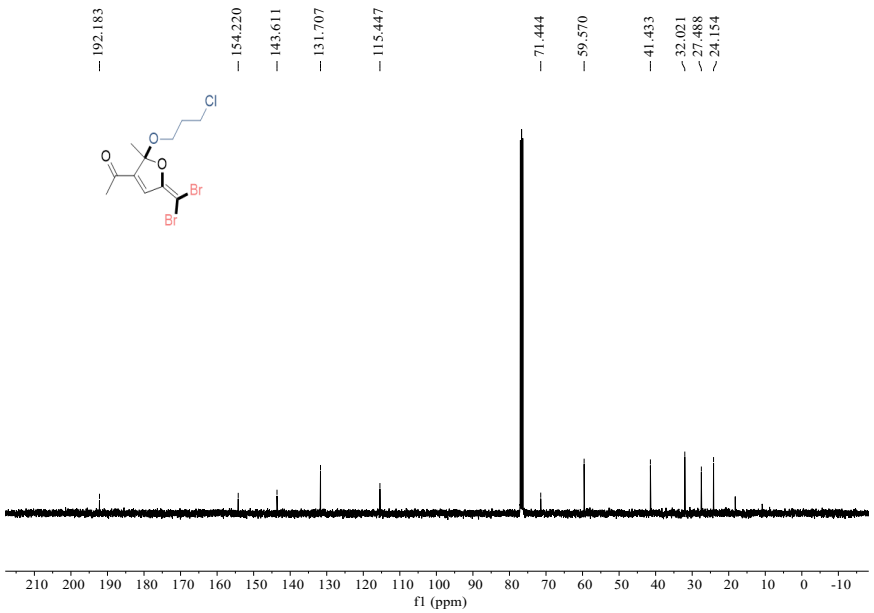




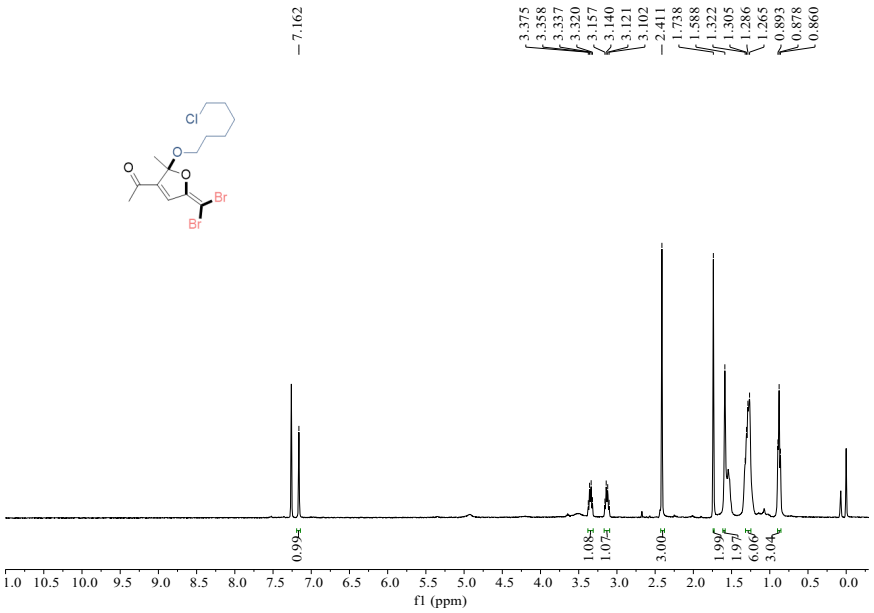
1-(2-(3-Chloropropoxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one

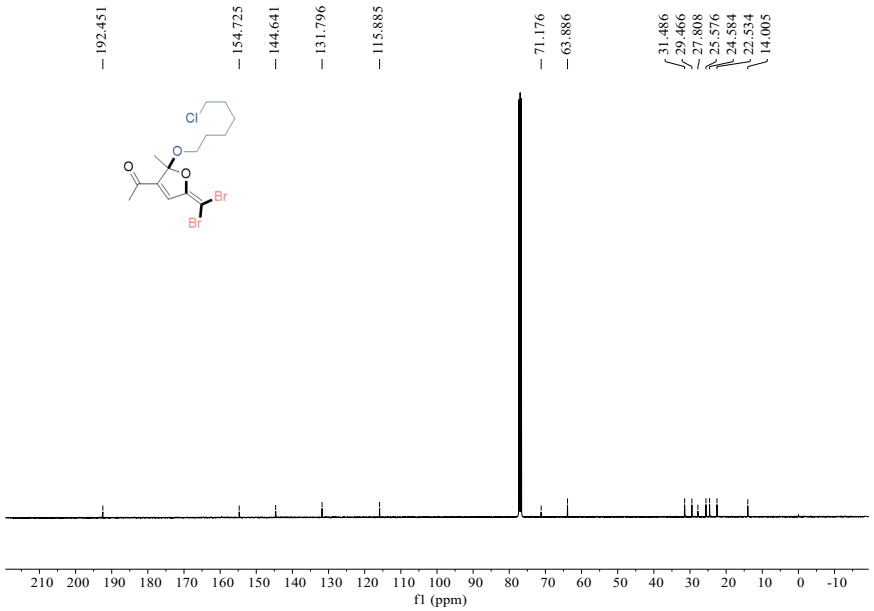
(3h)





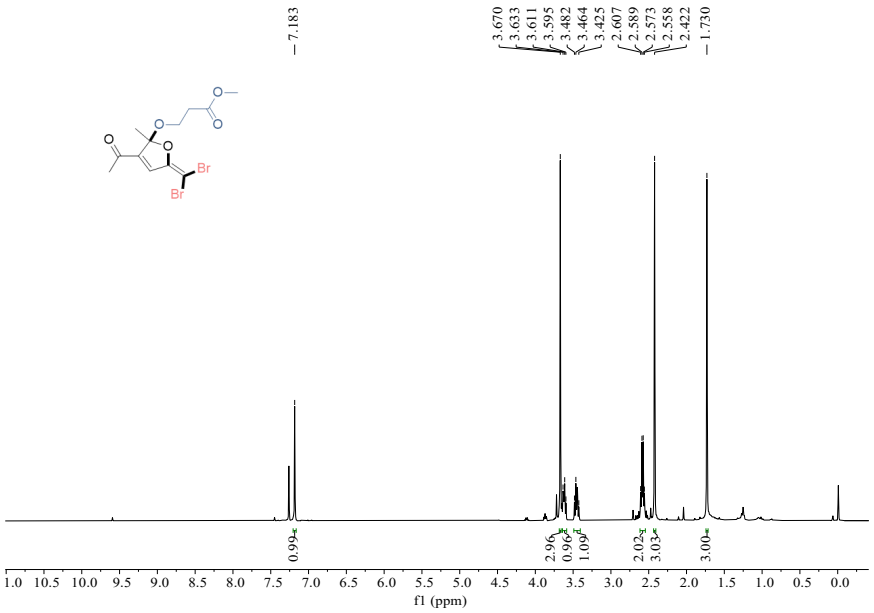
1-(2-((6-Chlorohexyl)oxy)-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one (3i)

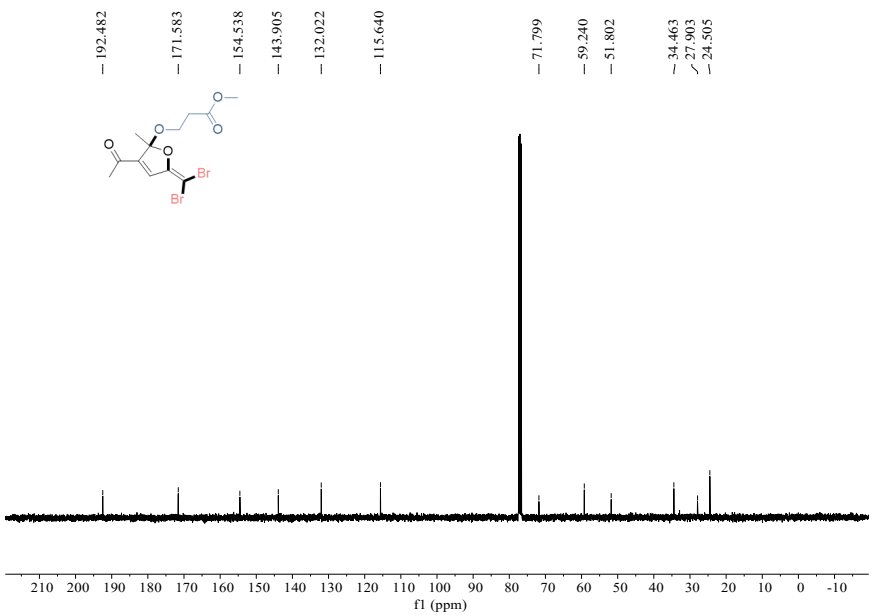




Methyl 3-((3-Acetyl-5-(dibromomethylene)-2-methyl-2,5-dihydrofuran-2-yl)oxy)propanoate

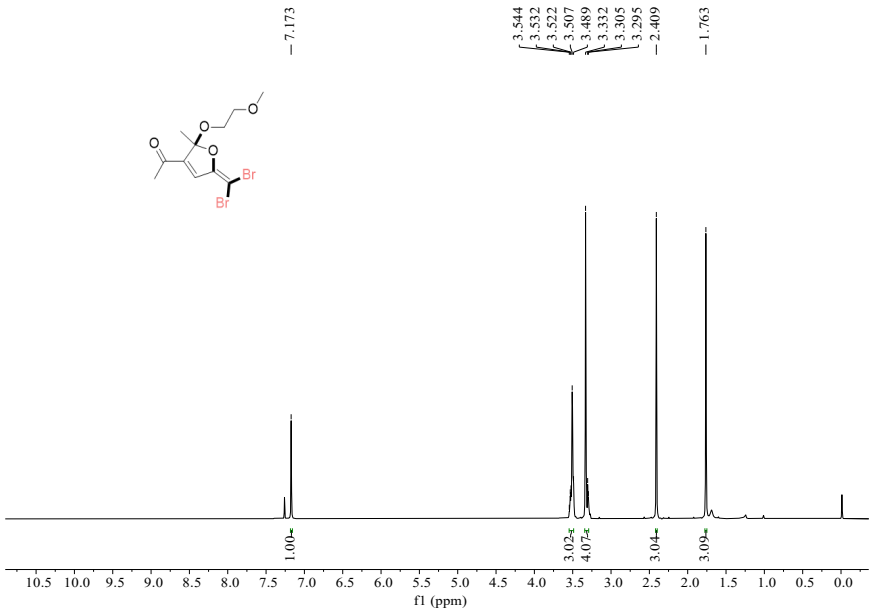
(3j)

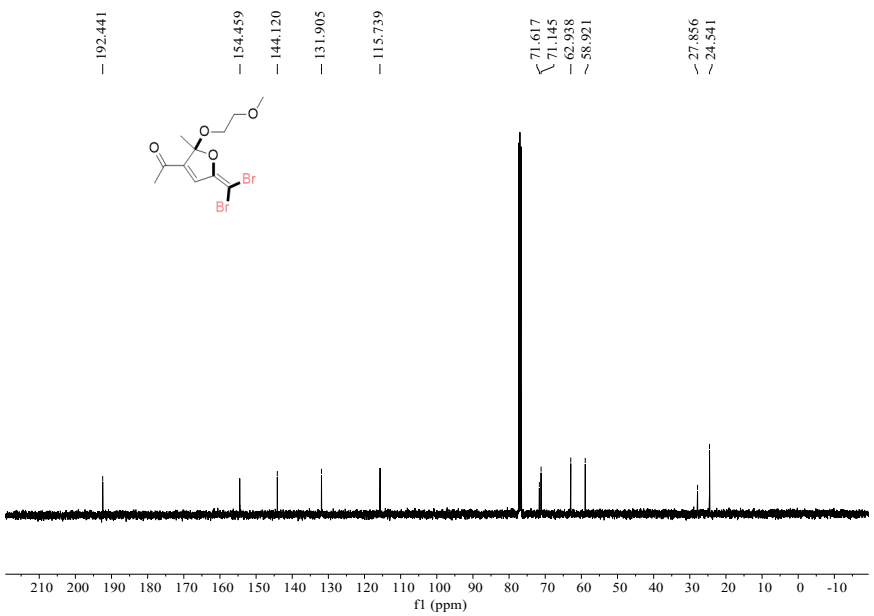




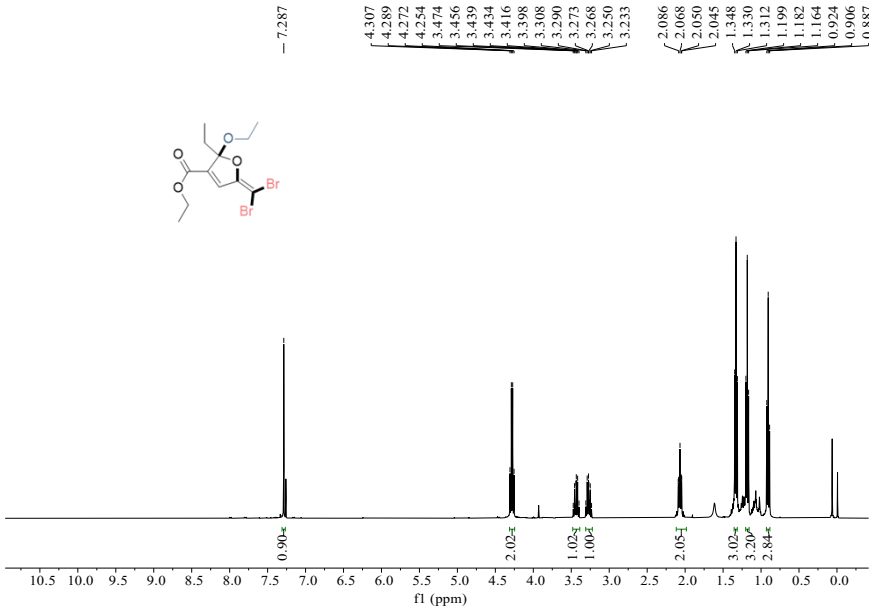
1-(5-(Dibromomethylene)-2-(2-methoxyethoxy)-2-methyl-2,5-dihydrofuran-3-yl)ethan-1-one

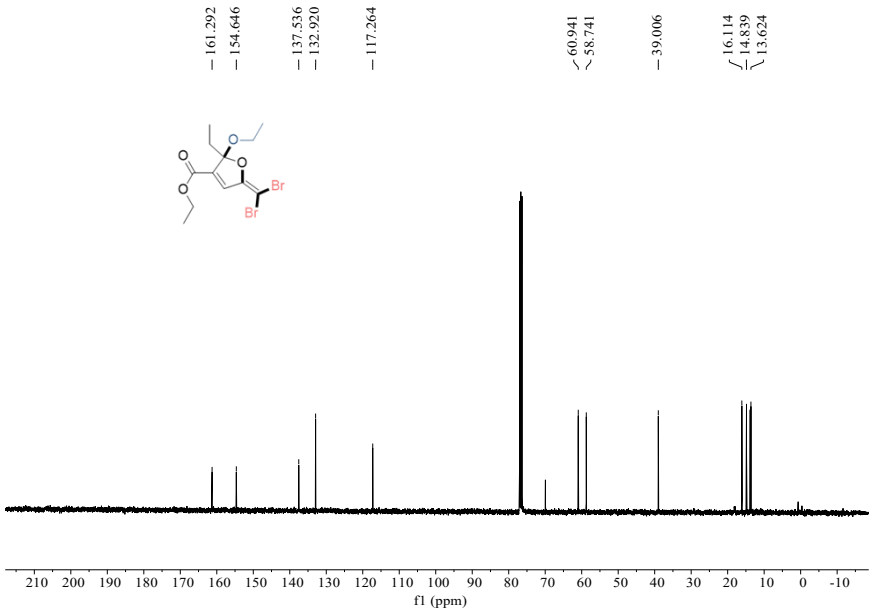
(3k)



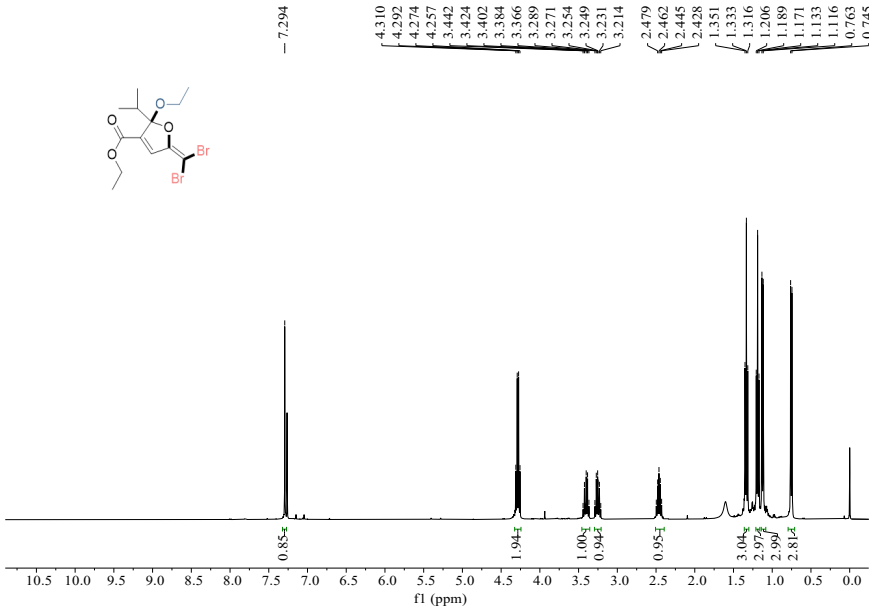


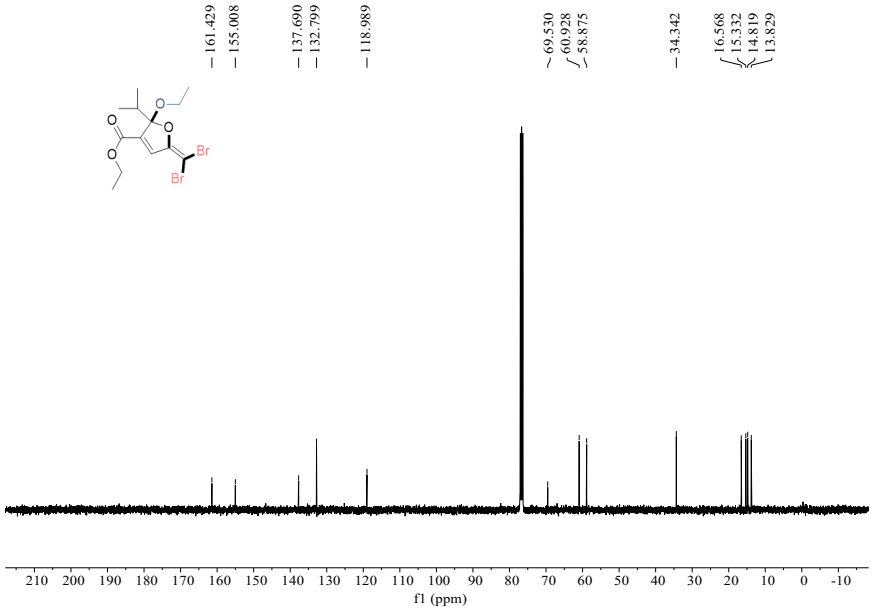
Ethyl 5-(Dibromomethylene)-2-ethoxy-2-propyl-2,5-dihydrofuran-3-carboxylate (3l)



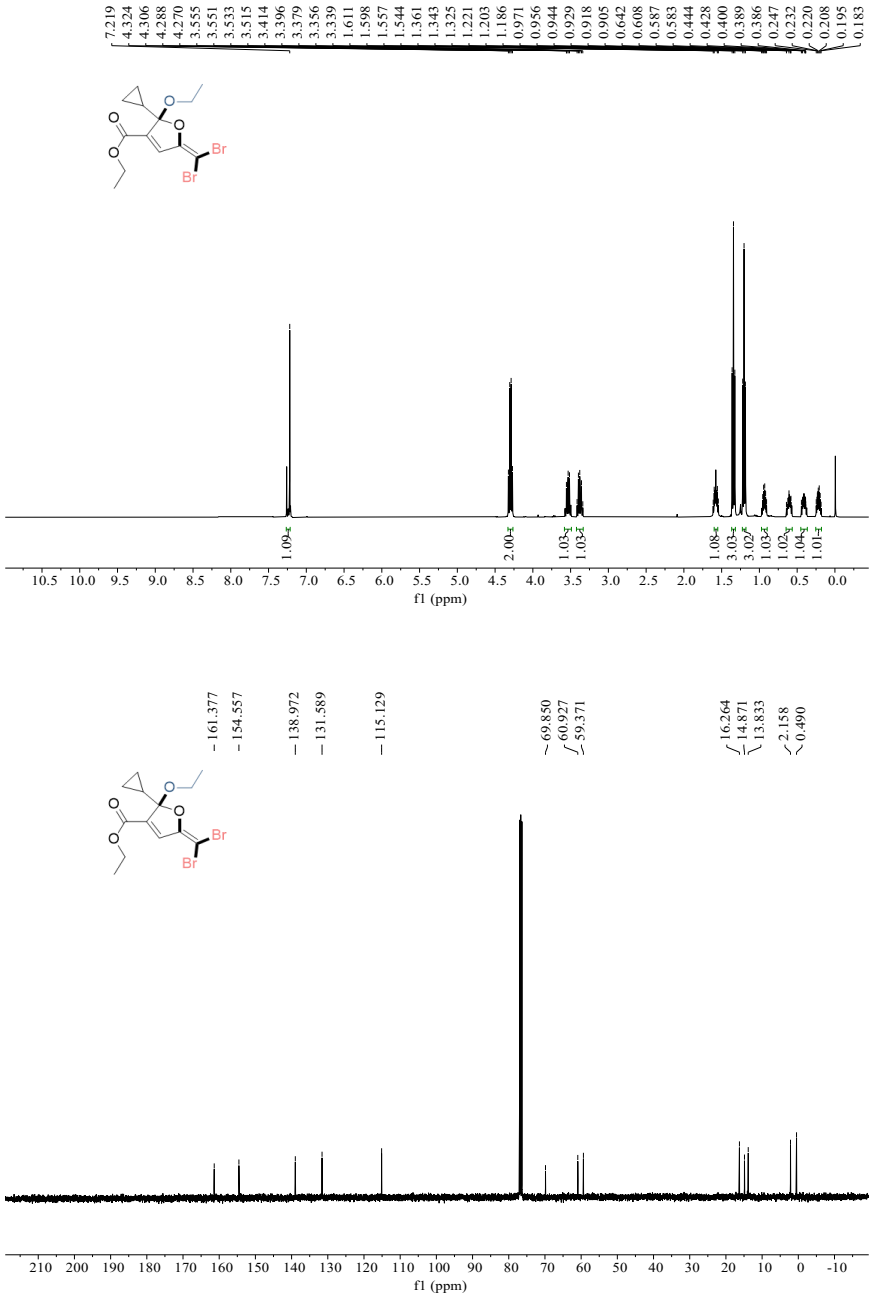


Ethyl 2-Cyclopropyl-5-(dibromomethylene)-2-ethoxy-2,5-dihydrofuran-3-carboxylate (3m)

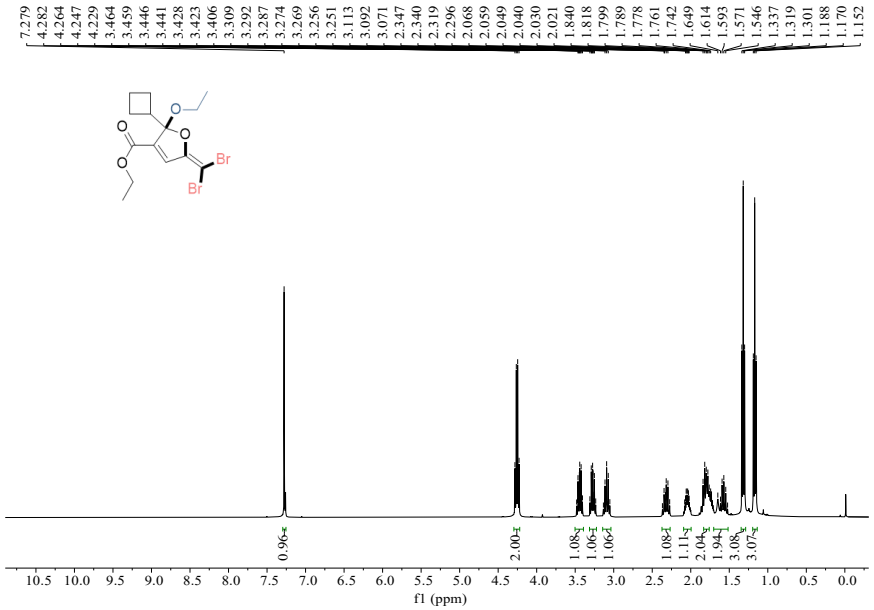


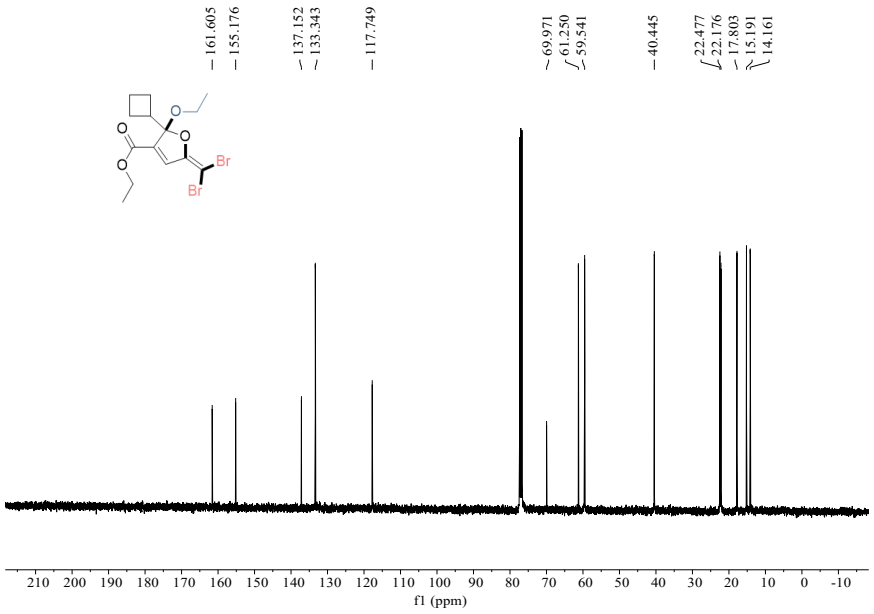


Ethyl 5-(Dibromomethylene)-2-ethoxy-2-isopropyl-2,5-dihydrofuran-3-carboxylate (3n)

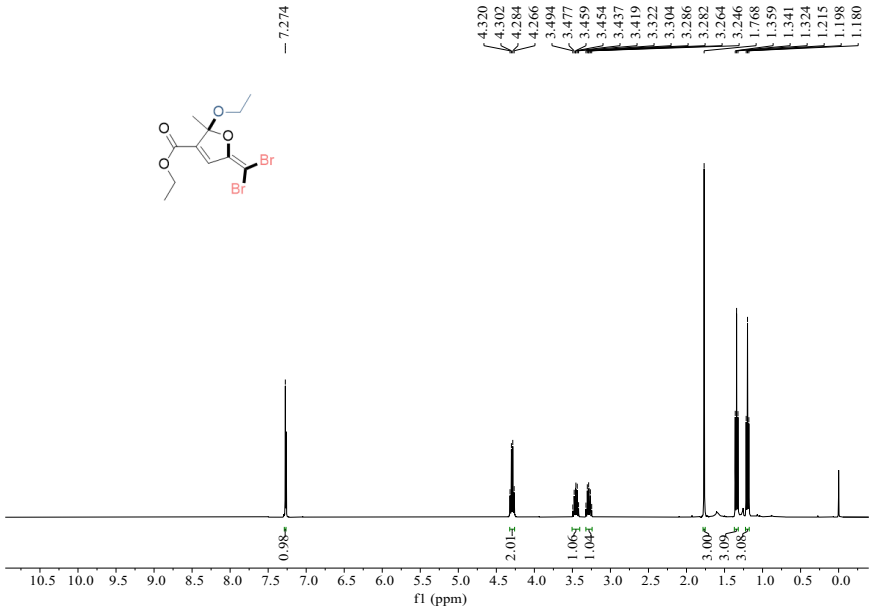


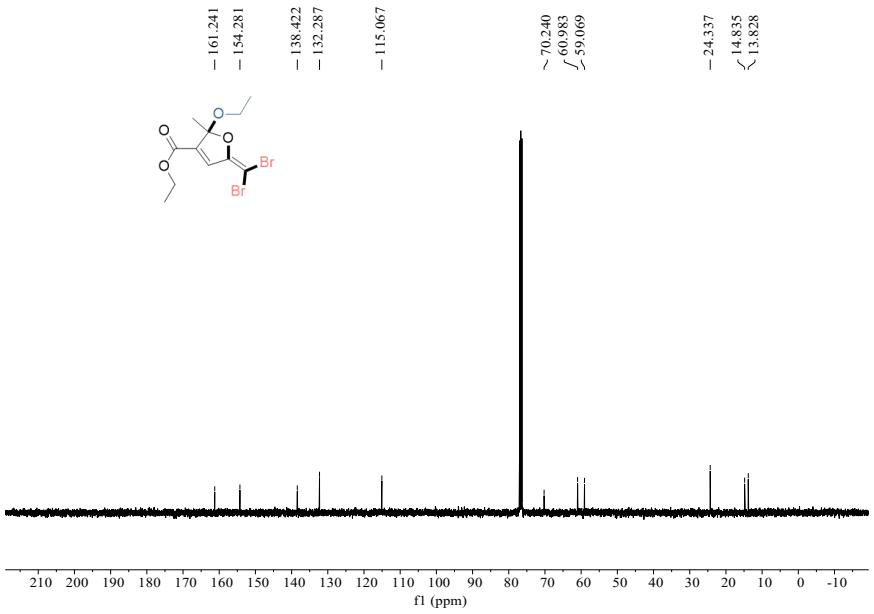
Ethyl 2-Cyclobutyl-5-(dibromomethylene)-2-ethoxy-2,5-dihydrofuran-3-carboxylate (3o)



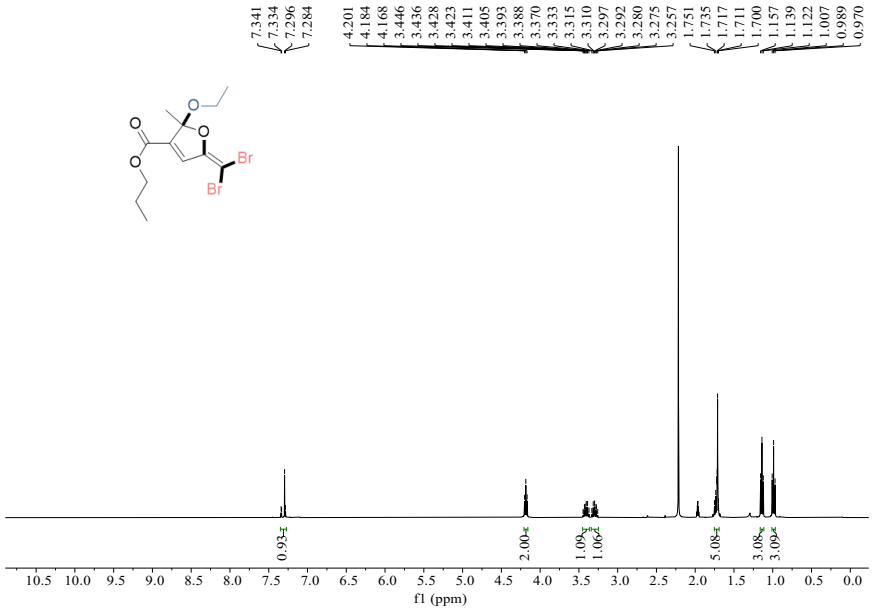


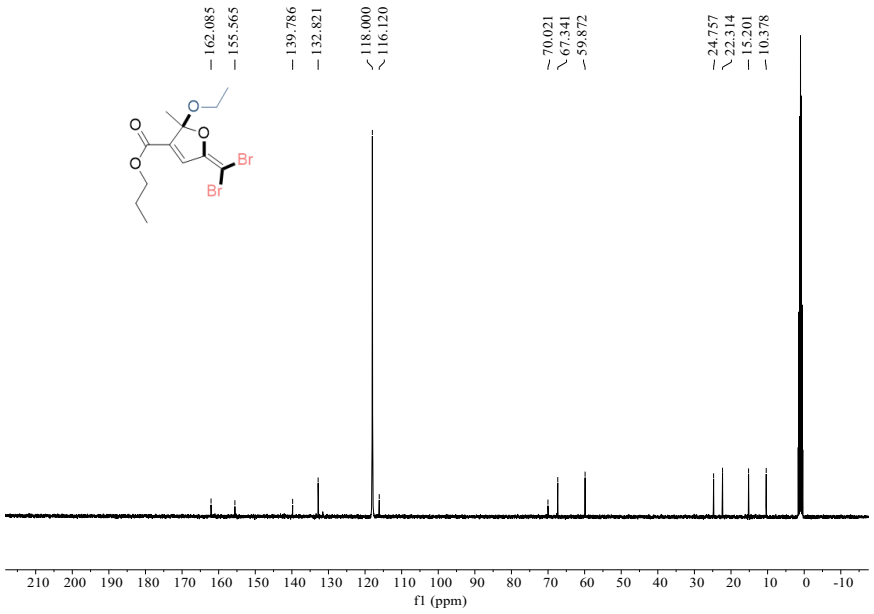
Ethyl 5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-carboxylate (3p)



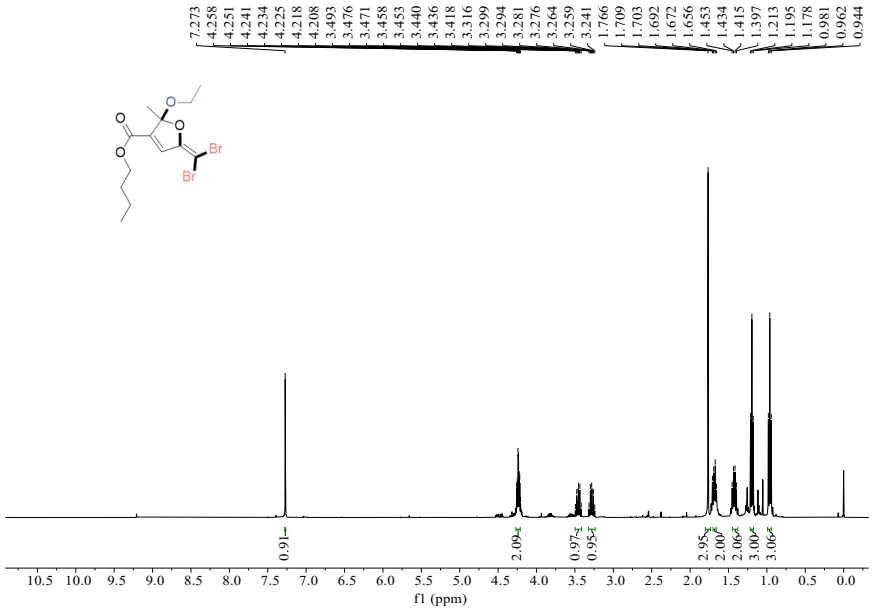


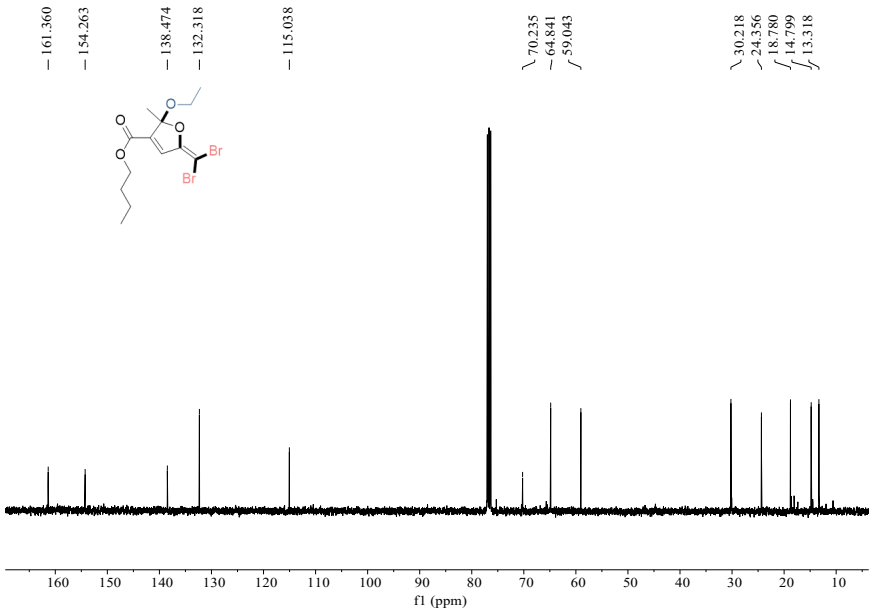
Propyl 5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-carboxylate (3q)



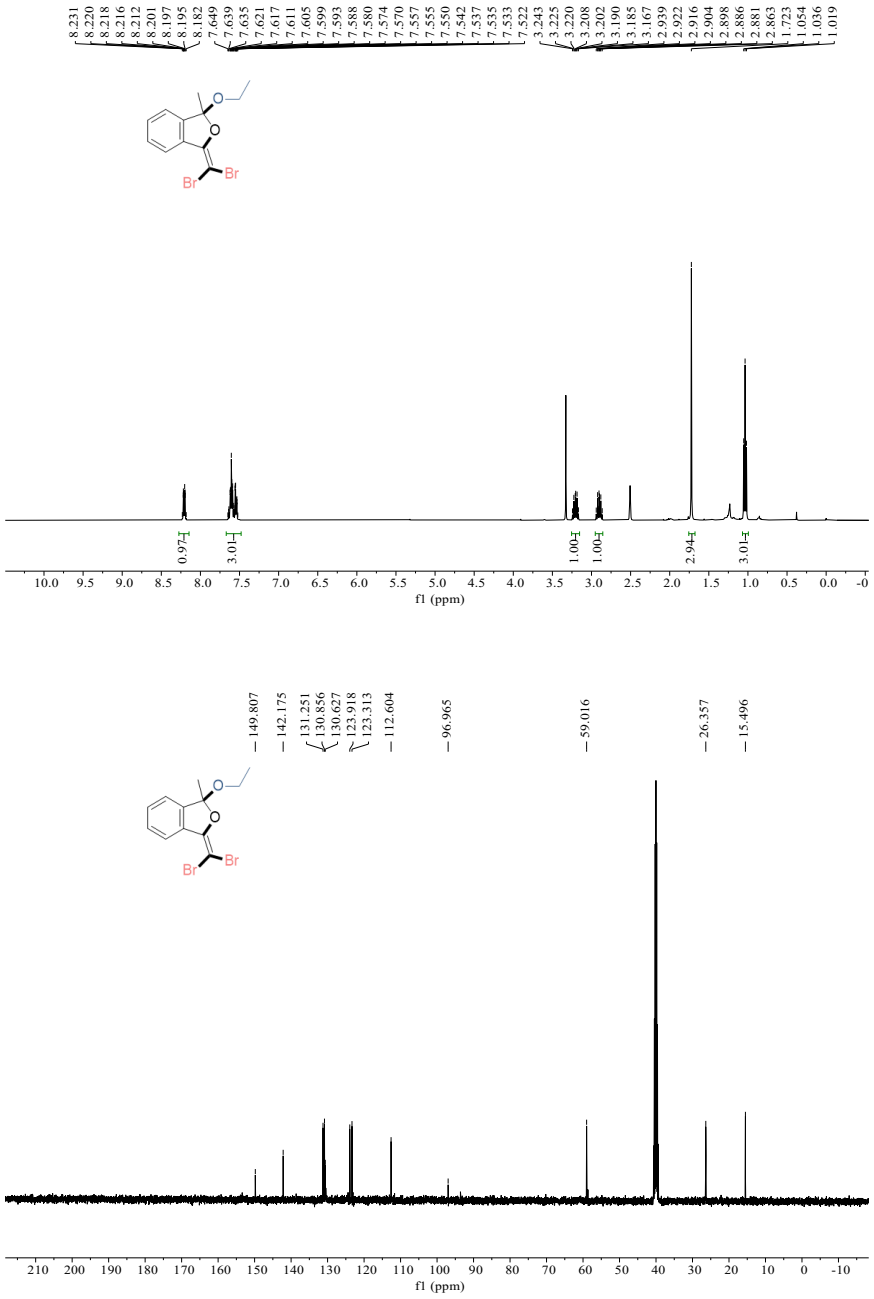


Butyl 5-(Dibromomethylene)-2-ethoxy-2-methyl-2,5-dihydrofuran-3-carboxylate (3r)

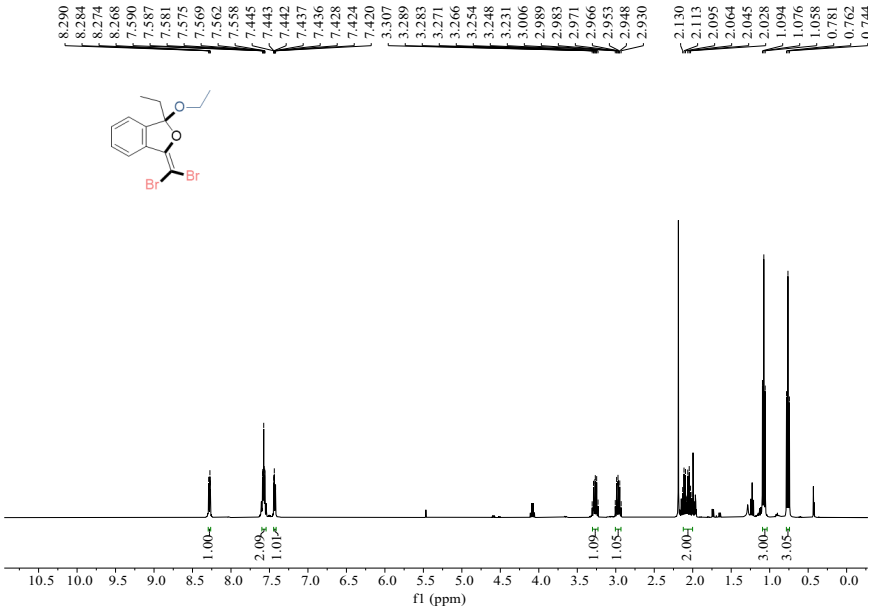


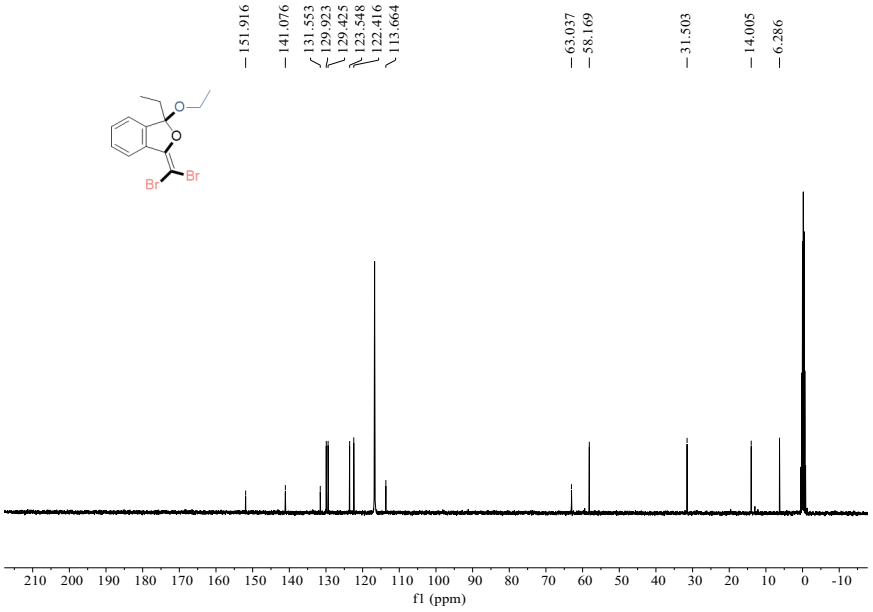


3-(Dibromomethylene)-1-ethoxy-1-methyl-1,3-dihydroisobenzofuran (3s)

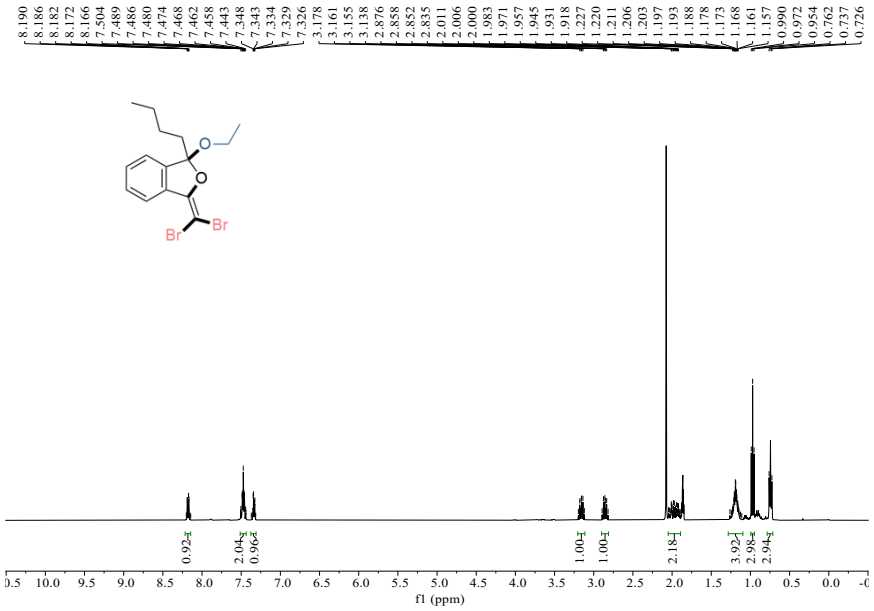


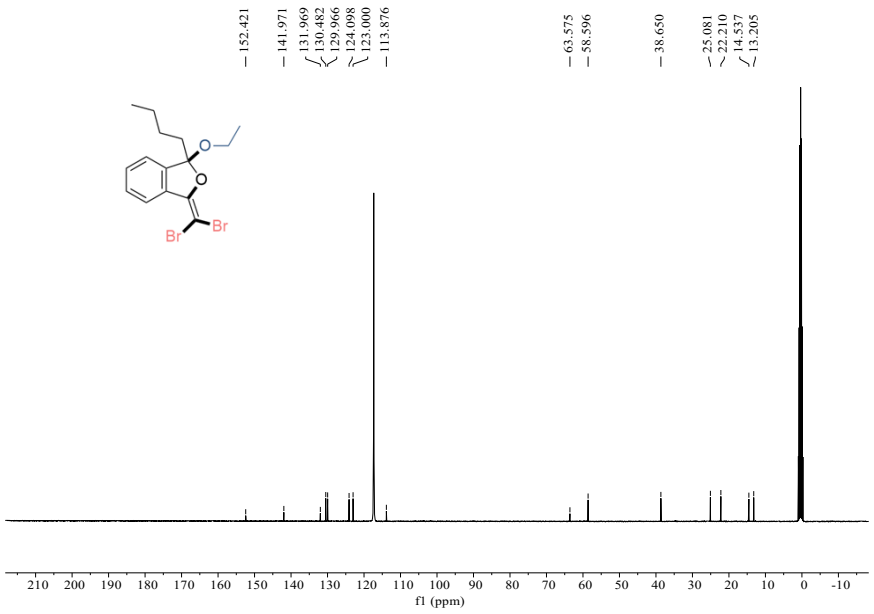
3-(Dibromomethylene)-1-ethoxy-1-ethyl-1,3-dihydroisobenzofuran (3t)



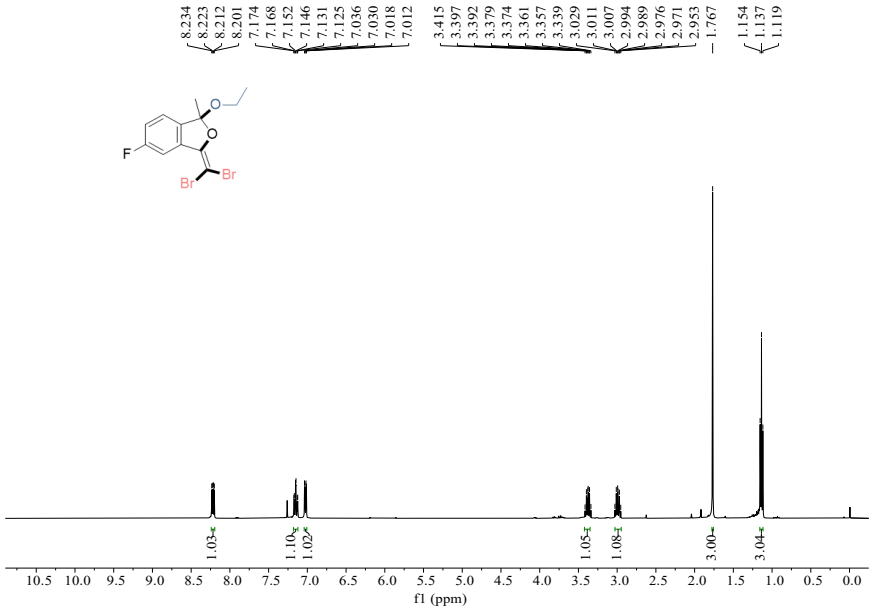


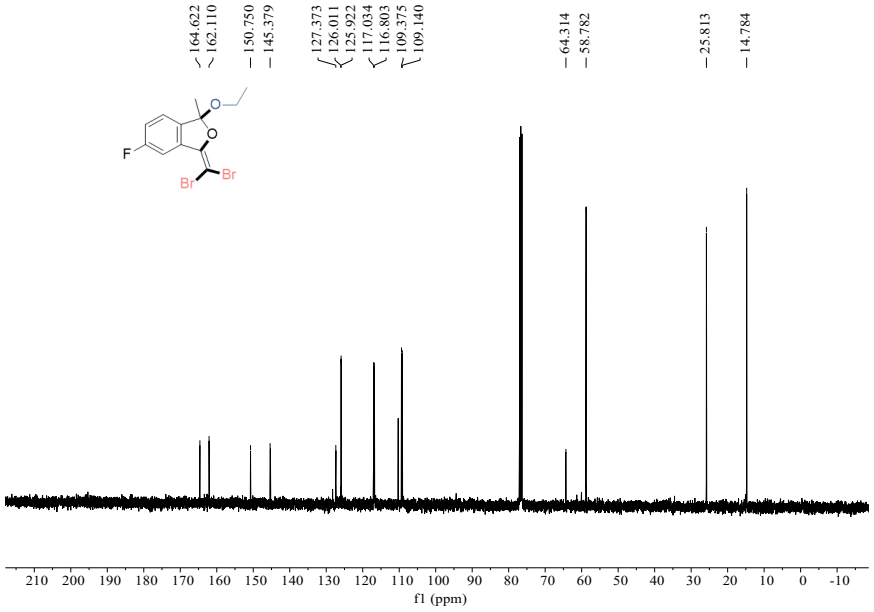
1-Butyl-3-(dibromomethylene)-1-ethoxy-1,3-dihydroisobenzofuran (3u)

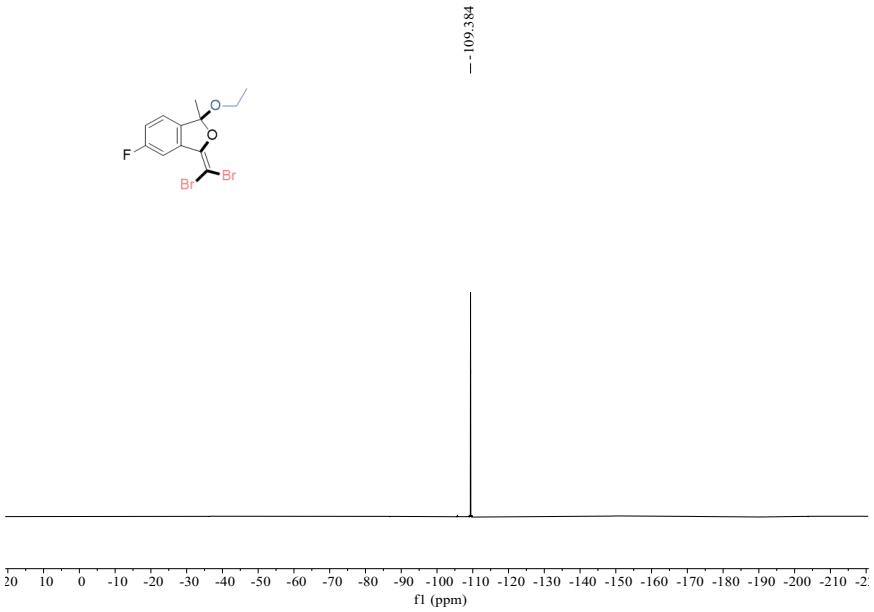




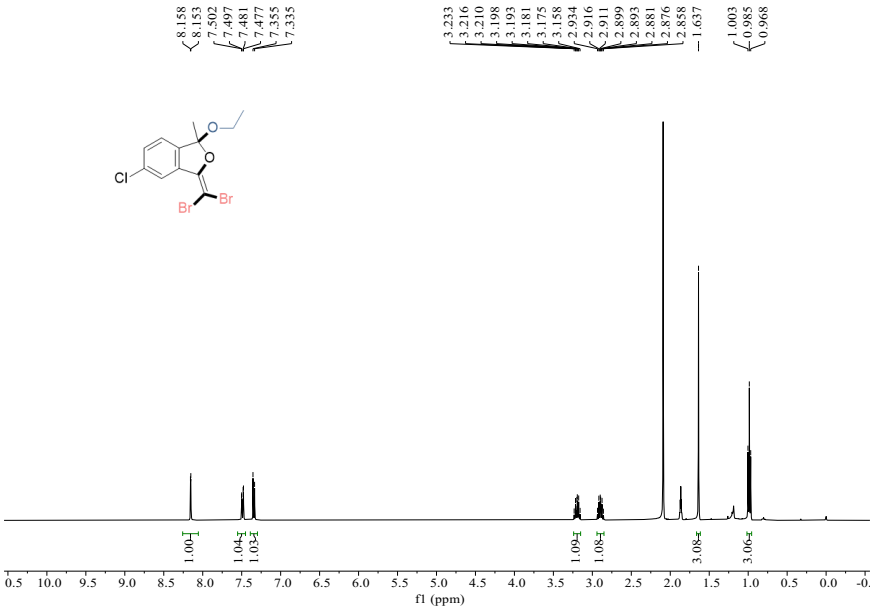
3-(Dibromomethylene)-1-ethoxy-5-fluoro-1-methyl-1,3-dihydroisobenzofuran (3v)

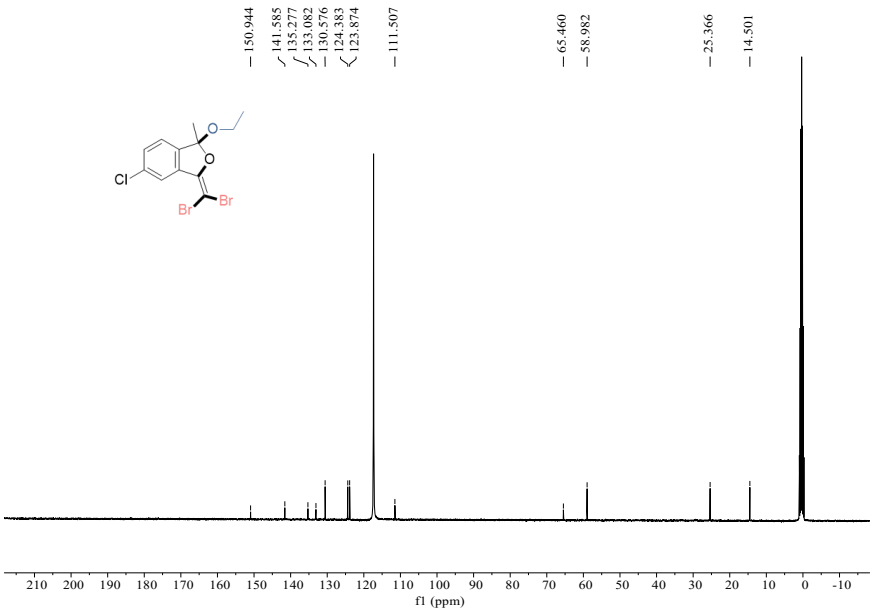




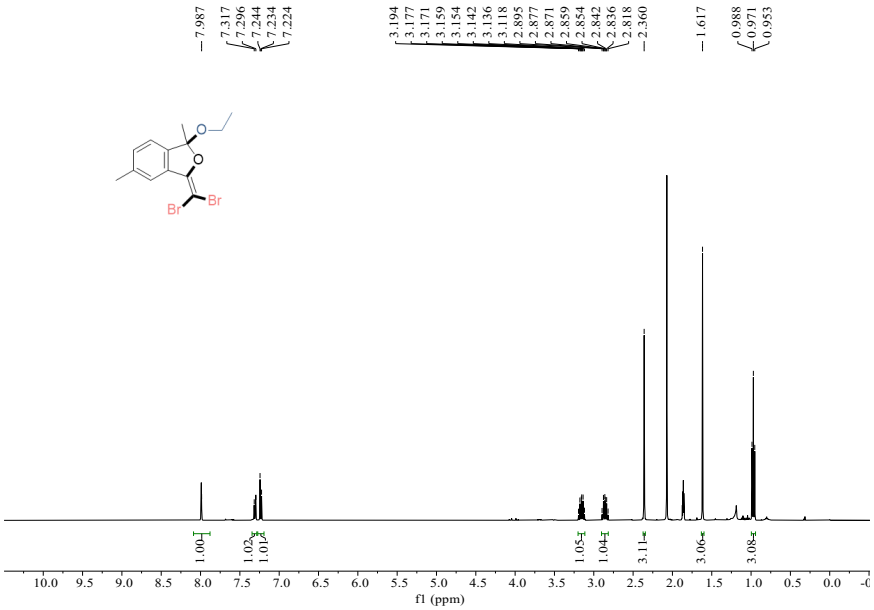

-109.384
F
O
O
Br
Br
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

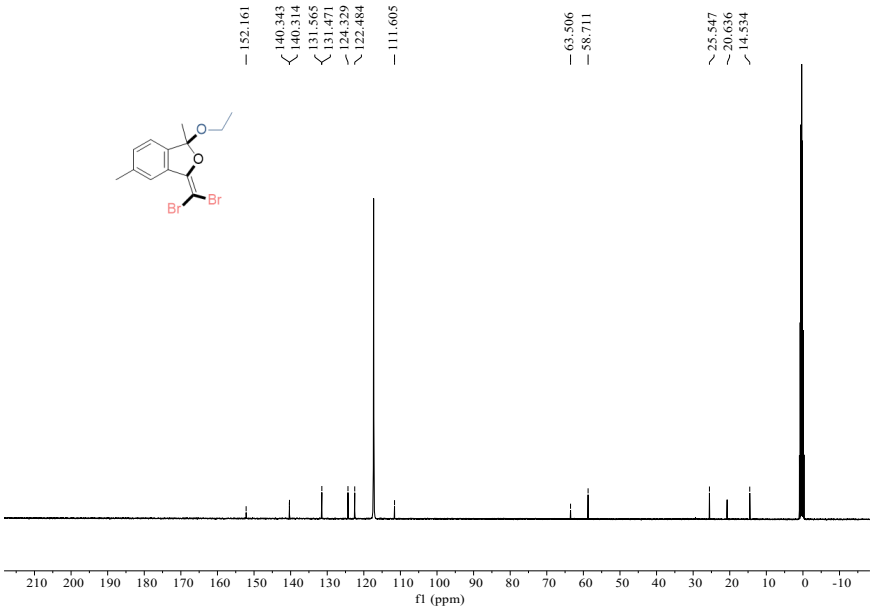
5-Chloro-3-(dibromomethylene)-1-ethoxy-1-methyl-1,3-dihydroisobenzofuran (3w)



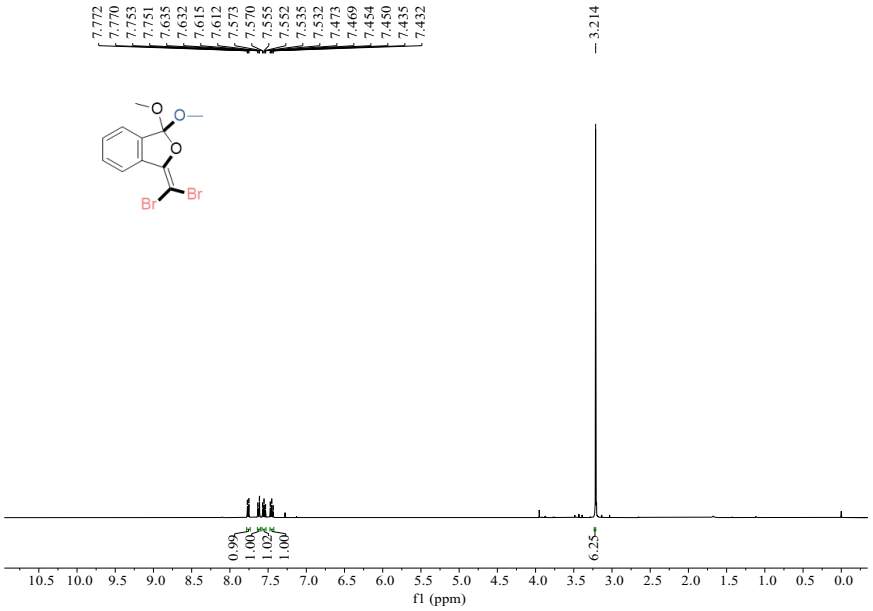


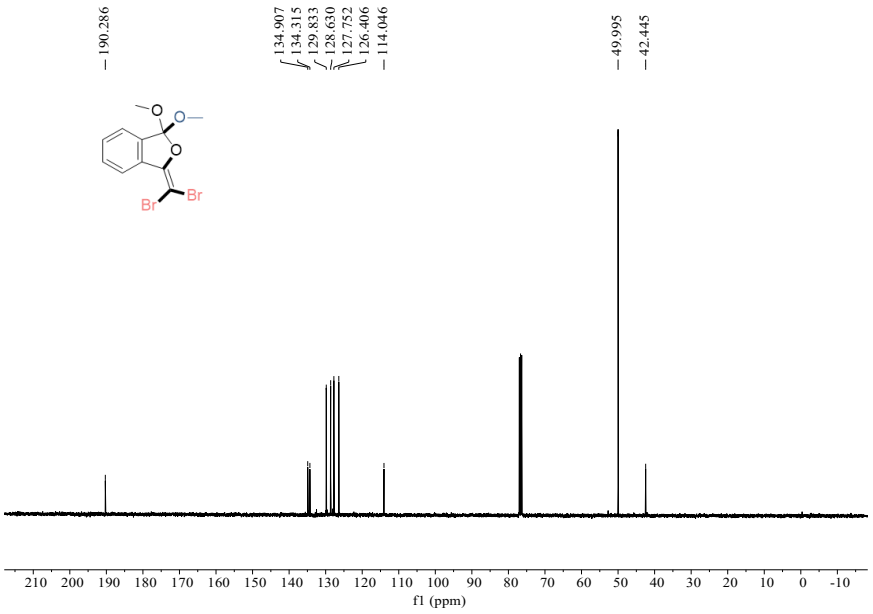
3-(Dibromomethylene)-1-ethoxy-1,5-dimethyl-1,3-dihydroisobenzofuran(3x)



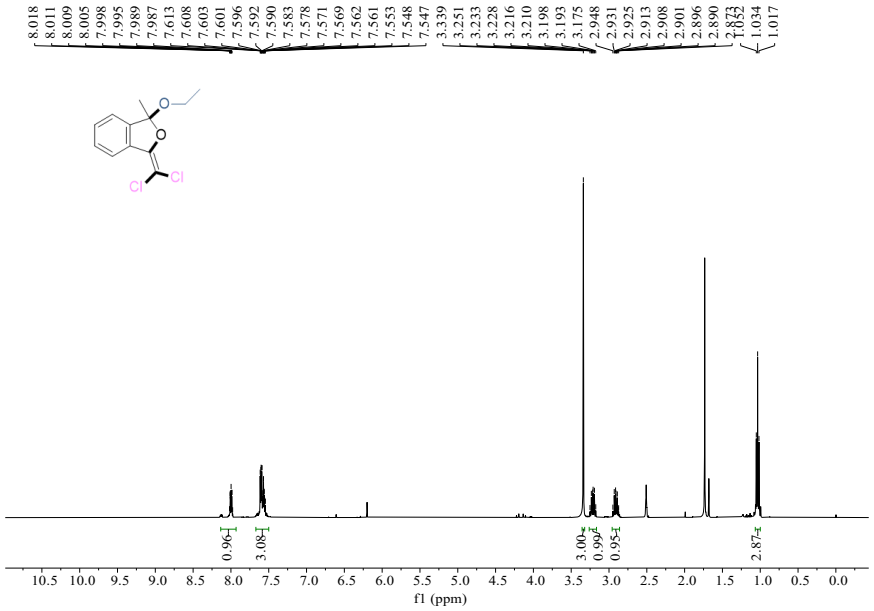


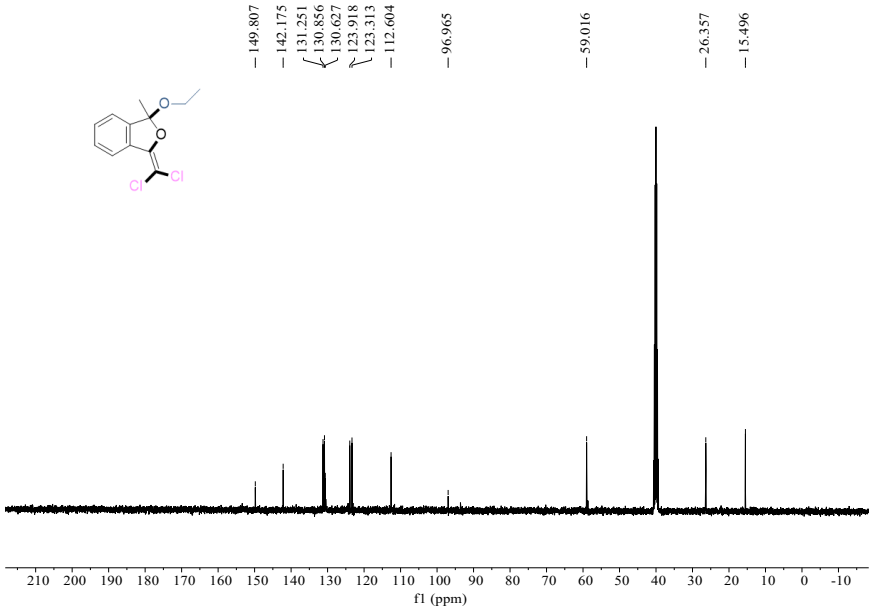
3-(Dibromomethylene)-1,1-dimethoxy-1,3-dihydroisobenzofuran (3y)



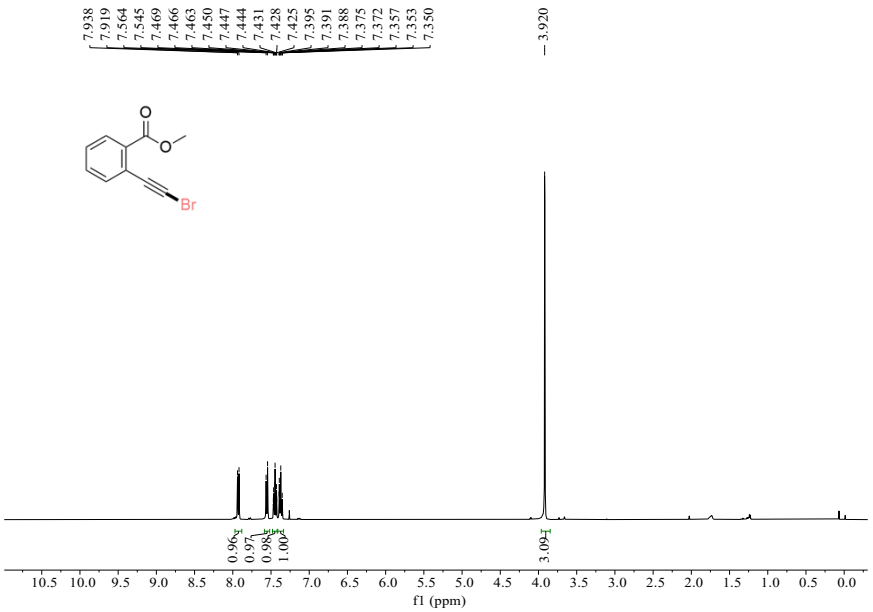


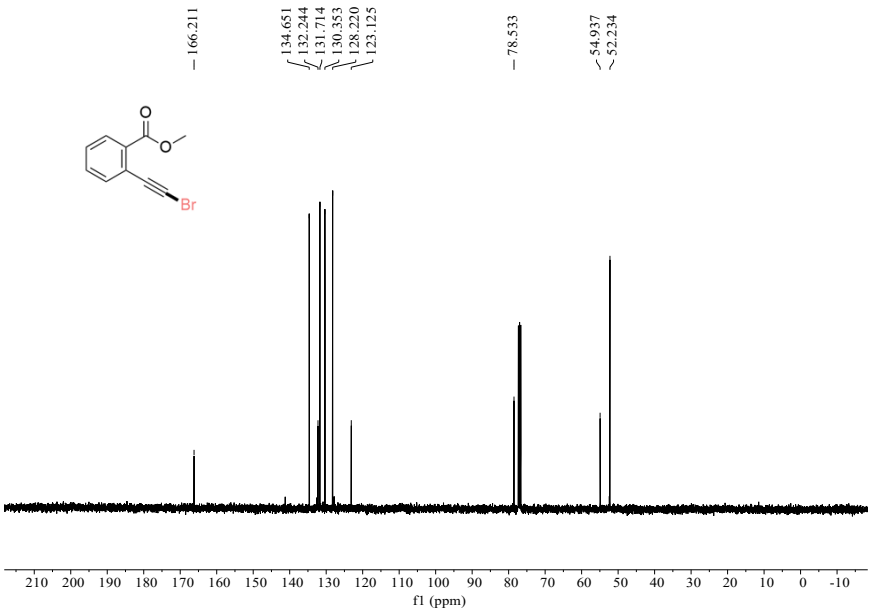
3-(Dichloromethylene)-1-ethoxy-1-methyl-1,3-dihydroisobenzofuran (3z)





Methyl 2-(Bromoethynyl)benzoate (4)





Methyl 2-(chloroethynyl)benzoate (5)