Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Direct Synthesis β-Acyloxy Substitued Aldehydes from Linear Allylic Esters Using O_2 as Sole Oxidant

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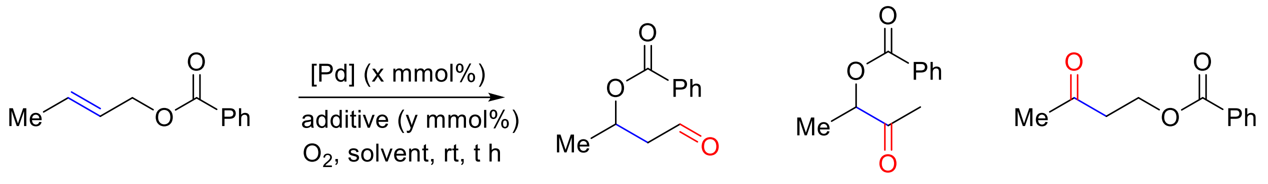
Contents

1. General Information

Unless otherwise specified, Analytical thin layer chromatography (TLC) was performed on HSGF 254 (0.17mm-0.23 thickness), visualized by irradiation with UV light (254 nm). Column chromatography was performed on silica gel FCP 200-400 using ethyl acetate (EA)/petroleum ether (PE)/ dichloromethane (DCM). all the reactions were carried out in a glassware under an oxygen atmosphere. $Pd(PhCN)_2Cl_2$ was commercially available and used without purification. *tert*-Butanol was purified by distillation over CaH under a nitrogen atmosphere. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 or JEOL 400 spectrometer. Chemical shifts are reported in δ units relative to $CDCl_3$ [^1H δ = 7.260, ^{13}C δ = 77.160]. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), and broad (br). High-resolution mass spectra (HRMS) were measured on Acquity UPLC/XEVO G2-XS QTOF.

2. Optimization for the Synthesis of 2a

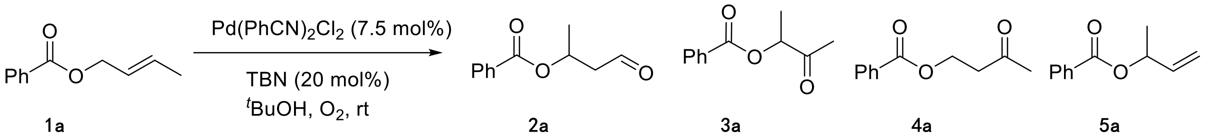


1a 2a 3a 4a

entry	[Pd]	x	solvent	additive	y	t/h	**2a**[d]	**3a**[d]	**4a**[d]	**1a**[d]
1	Pd(CH$_3$CN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	12	68	10	17	-
2	Pd(PPh$_3$)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	12	n.r.	-	-	97
3	PdCl$_2$	7.5	^{t}BuOH	TBN	20	12	trace	10	12	45
4	Pd(OAc)$_2$	7.5	^{t}BuOH	TBN	20	12	trace	10	10	74
5	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	5	78(77[e])	5	12	0
6[b]	Pd(PhCN)$_2$Cl$_2$	10	^{t}BuOH	TBN	20	5	68	12	15	0
7[c]	Pd(PhCN)$_2$Cl$_2$	5	^{t}BuOH	TBN	20	5	70	9	15	0
8	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	BQ	20	12	trace	5	5	40
9	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	DDQ	20	12	11	3	3	39
10	Pd(PhCN)$_2$Cl$_2$	7.5	MeOH	TBN	20	20	0	13	20	35
11	Pd(PhCN)$_2$Cl$_2$	7.5	EtOH	TBN	20	20	0	15	33	29
12	Pd(PhCN)$_2$Cl$_2$	7.5	THF	TBN	20	20	trace	40	15	3
13	Pd(PhCN)$_2$Cl$_2$	7.5	DMF	TBN	20	20	n.d.	-	-	75
14	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH:acetone = 24:1	TBN	20	5	65	11	15	0
15	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH:MeNO$_2$ = 24:1	TBN	20	5	72	9	17	0
16	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	10	5	66	12	15	0

[a] Reaction conditions: **1a** (0.5 mmol), [Pd] (7.5 mol%), additive (20 mol%), O$_2$ (1 atm), solvent (2 mL), rt., t h. [b] [Pd] (10 mol%), [c] [Pd] (5 mol%), [d] Yield was determined by ^{1}H NMR analysis of crude products. [e] Isolated yield.

3. Time Dependence of the Components for Reactions of 1a



Pd(PhCN)$_2$Cl$_2$ (14.4 mg, 0.0375 mmol) was weighed directly into a 25 mL flask and dried under high vacuum for 15 mins, purge oxygen 3 times. Under an atmosphere of oxygen (1 atm, balloon), ^{t}BuOH (2 mL) and ^{t}BuONO (10.3 mg, 0.1 mmol) were added and stirred at 25 ˚C. **1a** (0.5 mmol) was added. Taken samples with a micro-injector at 0.08 h, 0.17 h, 0.5 h, 0.67h, 1 h, 2 h, 3 h, 4 h, 5 h, and then filtered, filtrate concentrated under reduced pressure. Added internal standard in crude product, which was examined on ^{1}H NMR spectrometer to determine the yields.

entry[a]	[Pd]	x	solvent	additive	y	t/h	**2a**[b]	3**a**[b]	**4a**[b]	**5a**[b]	**1a**[b]
1	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	0.08	0	0	0	36	50
2	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	0.17	2	1	1	35	49
3	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	0.5	7	4	3	30	43
4	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	0.67	18	9	3	27	39
5	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	1	35	11	8	27	33
6	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	2	52	16	8	17	24
7	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	3	64	19	8	14	22
8	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	4	76	21	11	15	14
9	Pd(PhCN)$_2$Cl$_2$	7.5	^{t}BuOH	TBN	20	5	79	19	12	15	8

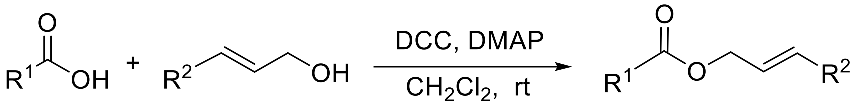
[a]Reaction conditions: **1a** (0.5 mmol), Pd(PhCN)$_2$Cl$_2$ (7.5 mol%), additive (20 mol%), O$_2$ (1 atm), solvent (2 mL), rt., t h. [b]yield was determined by ^{1}H NMR analysis of crude products.

4. Synthesis of 1a

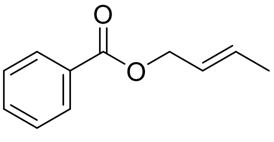
a）General procedure A

1a-1M was prepared according to the following method. Under nitrogen atmosphere, to a dry and clean Schlenk flask charged with CH_2Cl_2 (2 mL), allyl alcohol (2 mmol, 1 equiv.) and pyridine (4 mmol, 2 equiv.) was added acid chloride (2 mmol, 1 equiv.) at 0 °C slowly. The reaction mixture was then stirred overnight at room temperature. After the completion of reaction, the reaction mixture was diluted with EtOAc (2 mL), and washed with saturated sodium chloride, extracted by EtOAc, dried with anhydrous Na_2SO_4, and then concentrated. The crude product was purified by flash chromatography on silica gel.

b）General procedure B

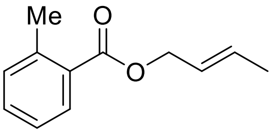


To a solution of alcohol (10.0 mmol, 1.0 equiv.), DCC (15.0 mmol, 1.5 equiv.) and DMAP (3.0 mmol, 30 mol%) in CH_2Cl_2 (30 mL) was added the acid. The reaction was monitored by TLC. After the completion of reaction, the crude product was filtered through celite and washed with CH_2Cl_2. The organic layers were then concentrated and purified by flash chromatography on silica gel.



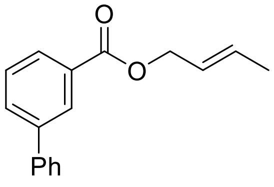
1a

***(E)*-but-2-en-1-yl benzoate (1a)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel [PE (petroleum ether)/EA (ethyl acetate) = 100:1] affording a colorless oil. (0.2467, 70%). ^1H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.01 (m, 2 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.7 Hz, 2 H), 5.94 – 5.80 (m, 1 H), 5.71 (dddd, *J* = 15.2, 7.9, 4.0, 1.5 Hz, 1 H), 4.75 (d, *J* = 6.4 Hz, 2 H), 1.79 – 1.69 (m, 3 H).[1]



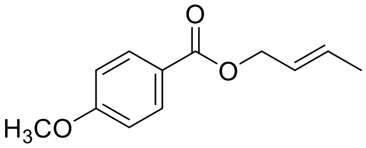
1b

***(E)*-but-2-en-1-yl 2-methylbenzoate (1b)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.3230 g, 85%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.83 (m, 1 H), 7.46 – 7.31 (m, 1 H), 7.23 (td, *J* = 7.1, 6.4, 3.7 Hz, 2 H), 5.95 – 5.80 (m, 1 H), 5.77 – 5.63 (m, 1 H), 4.72 (dd, *J* = 6.9, 1.5 Hz, 2 H), 2.59 (s, 3 H), 1.75 (s, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.47, 140.25, 131.98, 131.74, 131.34, 130.66, 129.82, 125.76, 125.36, 65.51, 21.85, 17.94. HRMS (ESI) calculated for $C_{12}H_{14}O_2H$ [M+H]$^+$ 191.1072, found 191.1064.



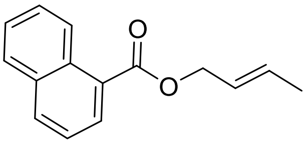
1c

***(E)*-but-2-en-1-yl [1,1'-biphenyl]-3-carboxylate (1c)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4693 g, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.32 (s, 1 H), 8.06 (d, *J* = 7.7 Hz, 1 H), 7.81 – 7.76 (m, 1 H), 7.67 – 7.61 (m, 2 H), 7.50 (dt, *J* = 16.7, 7.8 Hz, 3 H), 7.40 (d, *J* = 7.4 Hz, 1 H), 5.96-5.87 (m, 1 H), 5.81 – 5.71 (m, 1 H), 4.81 (d, *J* = 6.4 Hz, 2 H), 1.78 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.50, 141.55, 140.26, 131.63, 131.06 (d, *J* = 2.3 Hz), 129.02, 128.96, 128.54, 128.40, 127.86, 127.30, 65.93, 18.01. HRMS (ESI) calculated for $C_{17}H_{16}O_2H$ [M+H]$^+$ 253.1229, found 253.1221.



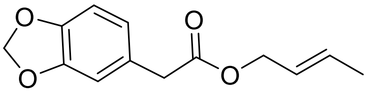
1d

***(E)*-but-2-en-1-yl 4-methoxybenzoate (1d)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.3712 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.15 – 7.90 (m, 2 H), 6.91 (d, *J* = 8.9 Hz, 2 H), 5.86 (dd, *J* = 15.3, 6.5 Hz, 1 H), 5.74 (s, 1 H), 4.72 (d, *J* = 6.4 Hz, 2 H), 3.85 (s, 3 H), 1.88 – 1.66 (m, 4 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.24, 163.37, 131.67, 131.10, 125.48, 122.86, 113.61, 65.42, 55.43, 17.89. HRMS (ESI) calculated for $C_{12}H_{15}O_3$ [M+H]$^+$ 207.1021, found 207.1019.



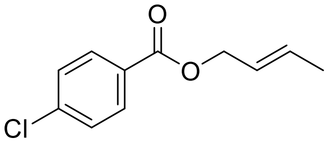
1e

***(E)*-but-2-en-1-yl-1-naphthoate （1e）** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a yellow oil. (0.3526 g, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.97 (d, *J* = 8.7 Hz, 1 H), 8.24 (d, *J* = 7.2 Hz, 1 H), 8.04 (d, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.65 (t, *J* = 7.4 Hz, 1 H), 7.54 (dt, *J* = 15.7, 7.8 Hz, 2 H), 6.02 – 5.91 (m, 1 H), 5.86 – 5.77 (m, 1 H), 4.89 (d, *J* = 6.4 Hz, 2 H), 1.81 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.48, 133.95, 133.40, 131.67, 131.49, 130.31, 128.64, 127.82, 127.40, 126.28, 125.95, 125.31, 124.60, 65.88, 17.99. HRMS (ESI) calculated for $C_{15}H_{14}O_2H$ $[M+H]^+$ 227.1072, found 227.1074.



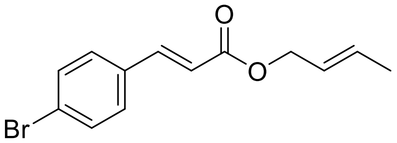
1f

***(E)*-but-2-en-1-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate (1f)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 30:1) affording a yellow oil. (0.4076 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.80 – 6.68 (m, 3 H), 5.93 (s, 2 H), 5.77 (tt, *J* = 14.8, 7.4 Hz, 1 H), 5.58 (dtd, *J* = 15.0, 6.5, 1.5 Hz, 1 H), 4.52 (d, *J* = 6.5 Hz, 2 H), 3.53 (s, 2 H), 1.75 – 1.69 (m, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.57, 147.82, 146.77, 131.63, 127.68, 125.07, 122.50, 109.83, 108.32, 101.10, 65.72, 40.98, 17.88. HRMS (ESI) calculated for $C_{13}H_{14}O_4H$ $[M+H]^+$ 235.0970, found 235.0964.



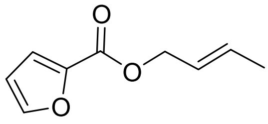
1g

***(E)*-but-2-en-1-yl 4-chlorobenzoate (1g)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (2.0223 g, 96%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.5 Hz, 2 H), 7.39 (d, *J* = 8.5 Hz, 2 H), 5.87 (dq, *J* = 12.9, 6.5 Hz, 1 H), 5.70 (dtd, *J* = 11.8, 6.4, 3.2 Hz, 1 H), 4.74 (d, *J* = 6.4 Hz, 2 H), 1.75 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.49, 139.31, 131.67, 131.04, 128.90, 128.68, 125.07, 65.92, 17.87. HRMS (ESI) calculated for $C_{11}H_{11}O_2ClH$ $[M+H]^+$ 211.0526, found 211.0523.

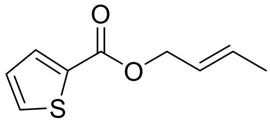


1h

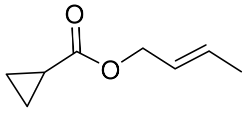
***(E)*-but-2-en-1-yl *(E)*-3-(4-bromophenyl) acrylate (1h)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a white solid. (0.4200 g, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 16.0 Hz, 1 H), 7.50 (d, *J* = 8.4 Hz, 2 H), 7.36 (d, *J* = 8.4 Hz, 2 H), 6.42 (d, *J* = 16.0 Hz, 1 H), 5.95 – 5.79 (m, 1 H), 5.72 – 5.60 (m, 1 H), 4.64 (d, *J* = 6.5 Hz, 2 H), 1.74 (d, *J* = 6.5 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.57, 143.48, 133.42, 132.21, 131.75, 129.51, 125.13, 124.59, 118.89, 65.50, 17.92. HRMS (ESI) calculated for $C_{13}H_{13}BrO_3H$ [M+H]$^+$ 281.0177, found 281.0177. MP:36 - 37 °C.


1 i

***(E)*-but-2-en-1-yl furan-2-carboxylate (1i)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (1.1632 g, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (s, 1 H), 7.14 (d, *J* = 3.2 Hz, 1 H), 6.46 (dd, *J* = 3.4, 1.6 Hz, 1 H), 5.89 – 5.77 (m, 1 H), 5.69 – 5.59 (m, 1 H), 4.69 (s, 2 H), 1.73 – 1.67 (m, 3 H). The spectroscopic data matched that previously report.[2]

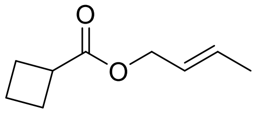

1 j

***(E)*-but-2-en-1-yl thiophene-2-carboxylate (1j)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (1.7313 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.79 (ddt, *J* = 3.7, 1.1, 0.5 Hz, 1 H), 7.53 (ddt, *J* = 5.0, 1.2, 0.5 Hz, 1 H), 7.08 (ddt, *J* = 4.9, 3.8, 0.8 Hz, 1 H), 5.93 – 5.80 (m, 1 H), 5.72 – 5.60 (m, 1 H), 4.71 (dq, *J* = 6.4, 1.0 Hz, 2 H), 1.76 – 1.71 (m, 3 H). The spectroscopic data matched that previously report.[2]


1k

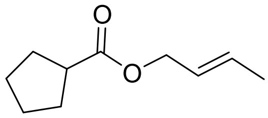
***(E)*-but-2-en-1-yl cyclopropanecarboxylate (1k)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.4696 g, 67%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.90 – 5.72 (m, 1 H), 5.69 – 5.51 (m, 1 H), 4.59 – 4.43 (m, 2 H), 1.73 (d, *J* = 6.5 Hz, 3 H), 1.61 (tq, *J* = 11.1, 6.4, 5.5 Hz, 1 H), 1.00 (p, *J* = 4.1 Hz, 2 H), 0.85 (dq, *J* = 7.4, 3.9 Hz, 2 H). ^{13}C

NMR (100 MHz, Chloroform-*d*) δ 174.84, 131.36, 125.28, 65.33, 17.88, 12.96, 8.51. HRMS (ESI) calculated for $C_8H_{12}O_2H$ $[M+H]^+$ 141.0916, found 141.0920.



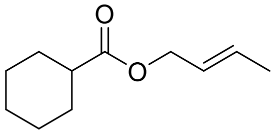
1l

***(E)*-but-2-en-1-yl cyclobutanecarboxylate (1l)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.2406 g, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.83 – 5.68 (m, 1 H), 5.56 (dtq, *J* = 13.0, 4.9, 1.5 Hz, 1 H), 4.48 (d, *J* = 6.4 Hz, 2 H), 3.12 (q, *J* = 8.5 Hz, 1 H), 2.33 – 2.10 (m, 4 H), 2.01 – 1.80 (m, 2 H), 1.73 – 1.65 (m, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.38, 131.25, 125.31, 65.12, 38.15, 25.31, 18.44, 17.86. HRMS (ESI) calculated for $C_9H_{14}O_2H$ $[M+H]^+$ 155.1072, found 155.1064.



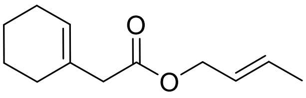
1m

***(E)*-but-2-en-1-yl cyclopentanecarboxylate (1m)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.2822 g, 84%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.78 (dq, *J* = 13.0, 6.5 Hz, 1 H), 5.64 – 5.54 (m, 1 H), 4.50 (d, *J* = 6.4 Hz, 2 H), 2.73 (p, *J* = 7.9 Hz, 1 H), 1.88 (qd, *J* = 11.5, 10.3, 5.1 Hz, 2 H), 1.83 – 1.76 (m, 2 H), 1.72 (p, *J* = 6.7 Hz, 6 H), 1.58 (qq, *J* = 8.8, 5.6, 4.7 Hz, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.68, 131.05, 125.38, 65.09, 43.87, 30.07, 25.87, 17.85. HRMS (ESI) calculated for $C_{10}H_{16}O_2H$ $[M+H]^+$ 169.1229, found 169.1230.



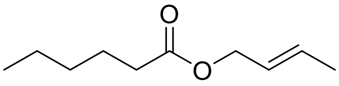
1n

***(E)*-but-2-en-1-yl cyclohexanecarboxylate (1n)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.3276 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.78 (dq, *J* = 13.0, 6.4 Hz, 1 H), 5.65 – 5.46 (m, 1 H), 4.49 (d, *J* = 6.4 Hz, 2 H), 2.30 (tt, *J* = 11.4, 3.6 Hz, 1 H), 1.90 (d, *J* = 13.1 Hz, 2 H), 1.80 – 1.59 (m, 6 H), 1.44 (q, *J* = 12.5, 12.1 Hz, 2 H), 1.34 – 1.18 (m, 3 H). The spectroscopic data matched that previously report.[3]



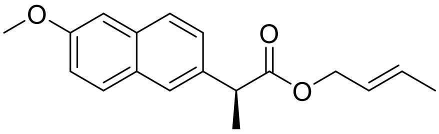
1o

***(E)*-but-2-en-1-yl 2-(cyclohex-1-en-1-yl) acetate (1o)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4867 g, 50%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.79 (dq, *J* = 13.0, 6.5 Hz, 1 H), 5.64 – 5.53 (m, 2 H), 4.51 (d, *J* = 6.5 Hz, 2 H), 2.95 (s, 2 H), 2.01 (d, *J* = 6.1 Hz, 5 H), 1.73 (d, *J* = 6.5 Hz, 4 H), 1.68 – 1.60 (m, 2 H), 1.60 – 1.52 (m, 3 H), 1.38 – 1.22 (m, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.94, 131.42, 131.19, 125.76, 125.19, 65.32, 43.69, 28.46, 25.36, 22.79, 22.05, 17.89. HRMS (ESI) calculated for $C_{12}H_{19}O_2$ [M+H]$^+$ 195.1385, found 195.1390.



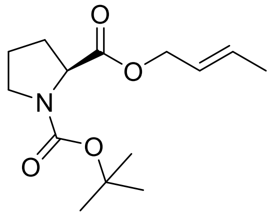
1p

***(E)*-but-2-en-1-yl hexanoate (1p)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.2554 g, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.73 (dq, *J* = 13.8, 6.4 Hz, 1 H), 5.59 – 5.48 (m, 1 H), 4.44 (d, *J* = 5.9 Hz, 2 H), 2.24 (t, *J* = 7.5 Hz, 2 H), 1.66 (d, *J* = 6.4 Hz, 3 H), 1.57 (p, *J* = 7.5 Hz, 2 H), 1.33 – 1.18 (m, 5 H), 0.84 (t, *J* = 6.7 Hz, 3 H). The spectroscopic data matched that previously report.[4]



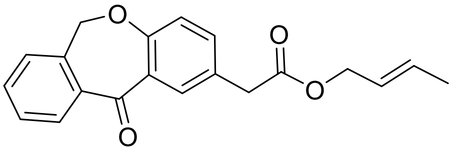
1q

***(E)*-but-2-en-1-yl (*S*)-2-(6-methoxynaphthalen-2-yl) propanoate (1q)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a yellow solid. (0.4970 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.74 – 7.64 (m, 3 H), 7.41 (dd, *J* = 8.4, 1.6 Hz, 1 H), 7.16 – 7.09 (m, 2 H), 5.78 – 5.66 (m, 1 H), 5.58 – 5.48 (m, 1 H), 4.54 (dd, *J* = 12.4, 6.4 Hz, 1 H), 4.46 (dd, *J* = 12.3, 6.4 Hz, 1 H), 3.91 (s, 3 H), 3.85 (q, *J* = 7.2 Hz, 1 H), 1.67 (d, *J* = 7.0 Hz, 3 H), 1.57 (d, *J* = 7.1 Hz, 4 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.60, 157.70, 135.84, 133.77, 131.34, 129.38, 129.02, 127.21, 126.37, 126.05, 125.12, 119.04, 65.62, 55.39, 45.58, 18.79, 17.86. HRMS (ESI) calculated for $C_{18}H_{20}O_3H$ $[M+H]^+$ 285.1491, found 285.1488. MP: 49 - 50 °C.



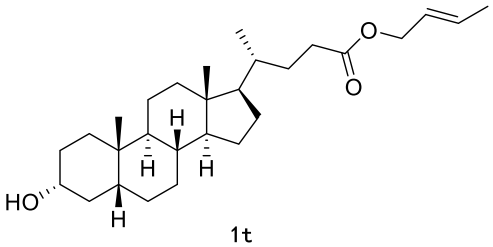
1r

***(E)*-2-(but-2-en-1-yl) 1-(tert-butyl) pyrrolidine-1,2-*d*icarboxylate (1r)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a yellow oil. (0.4848 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.77 (dt, *J* = 14.5, 7.6 Hz, 1 H), 5.64 – 5.47 (m, 1 H), 4.51 (d, *J* = 5.6 Hz, 2 H), 4.30 (dd, *J* = 8.5, 2.9 Hz, 0 H), 4.19 (dd, *J* = 8.5, 3.9 Hz, 1 H), 3.45 (dddd, *J* = 40.5, 23.4, 10.3, 5.4 Hz, 2 H), 2.18 (ddd, *J* = 20.8, 11.8, 9.0 Hz, 1 H), 2.01 – 1.79 (m, 3 H), 1.70 (d, *J* = 6.1 Hz, 3 H), 1.44 (s, 3 H), 1.39 (s, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 173.50, 173.20, 154.83, 154.27, 132.23, 131.72, 125.31 (d, *J* = 6.4 Hz), 80.29, 80.14, 66.02, 59.62, 59.29, 46.97, 46.74, 31.31, 30.33, 28.85, 28.69, 18.19. HRMS (ESI) calculated for $C_{14}H_{23}NO_4H$ $[M+H]^+$ 270.1705, found 270.1700.



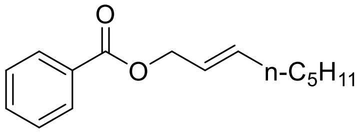
1s

***(E)*-but-2-en-1-yl 2-(11-oxo-6,11-*d*ihydrodibenzo[b,e]oxepin-2-yl)acetate (1s)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a yellow solid. (0.4970 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 (d, *J* = 2.2 Hz, 1 H), 7.89 (d, *J* = 7.5 Hz, 1 H), 7.56 (t, *J* = 7.3 Hz, 1 H), 7.51 – 7.40 (m, 2 H), 7.36 (d, *J* = 7.4 Hz, 1 H), 7.03 (d, *J* = 8.4 Hz, 1 H), 5.79 (dq, *J* = 12.9, 6.4 Hz, 1 H), 5.64 – 5.52 (m, 1 H), 5.19 (s, 2 H), 4.53 (d, *J* = 6.5 Hz, 2 H), 3.65 (s, 2 H), 1.72 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 190.93, 171.34, 160.54, 140.54, 136.48, 135.63, 132.84, 132.56, 131.82, 129.55, 129.34, 127.92, 127.89, 125.19, 124.96, 121.12, 73.69, 65.83, 40.27, 17.89. HRMS (ESI) calculated for $C_{20}H_{18}O_4H$ $[M+H]^+$ 323.1283, found 323.1279. MP: 69 – 70 °C.



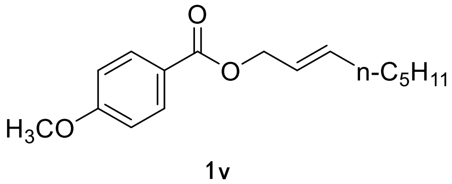
1t

***(E)*-but-2-en-1-yl(*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (1t)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 20:1) affording a colorless viscous oil. (0.6393 g, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.84 – 5.73 (m, 1 H), 5.63 – 5.54 (m, 1 H), 4.49 (d, *J* = 6.4 Hz, 2 H), 3.62 (tt, *J* = 10.1, 4.1 Hz, 1 H), 2.35 (ddd, *J* = 15.2, 10.1, 5.1 Hz, 1 H), 2.21 (ddd, *J* = 15.6, 9.5, 6.6 Hz, 1 H), 1.98 – 1.91 (m, 1 H), 1.89 – 1.63 (m, 11 H), 1.37 (td, *J* = 17.1, 16.1, 7.6 Hz, 9 H), 1.32 – 1.18 (m, 6 H), 1.18 – 0.95 (m, 8 H), 0.90 (d, *J* = 7.1 Hz, 7 H), 0.63 (s, 4 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 131.28, 125.23, 71.87, 65.03, 56.49, 55.96, 42.73, 42.10, 40.43, 40.17, 36.46, 35.85, 35.35, 34.58, 31.30, 30.98, 30.55, 28.20, 27.20, 26.42, 24.22, 20.82, 18.28, 17.81, 12.04. HRMS (ESI) calculated for $C_{28}H_{46}O_3H$ [M+H]$^+$ 431.3525, found 431.3521.



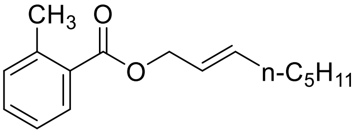
1u

***(E)*-oct-2-en-1-yl benzoate (1u)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4368 g, 94%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 (d, *J* = 7.5 Hz, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 5.86 (dt, *J* = 13.9, 6.7 Hz, 1 H), 5.69 (dt, *J* = 15.2, 6.4 Hz, 1 H), 4.77 (d, *J* = 6.4 Hz, 2 H), 2.08 (q, *J* = 7.1 Hz, 2 H), 1.47 – 1.23 (m, 6 H), 0.89 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.46, 136.74, 132.90, 130.52, 129.68, 128.37, 123.87, 65.82, 32.37, 31.47, 28.67, 22.59, 14.12. HRMS (ESI) calculated for $C_{15}H_{20}O_2H$ [M+H]$^+$ 233.1542, found 233.1540.



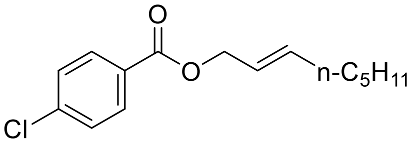
1v

***(E)*-oct-2-en-1-yl 4-methoxybenzoate (1v)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4827 g, 92%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.98 (m, 2 H), 6.94 – 6.88 (m, 2 H), 5.89 – 5.79 (m, 1 H), 5.69 (s, 1 H), 4.73 (d, *J* = 6.3 Hz, 2 H), 3.84 (d, *J* = 2.3 Hz, 3 H), 2.07 (q, *J* = 7.1 Hz, 2 H), 1.46 – 1.25 (m, 7 H), 0.89 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.25, 163.36, 136.48, 131.69, 124.06, 122.91, 113.61, 65.54, 55.45, 32.36, 31.47, 28.68, 22.59, 14.12. HRMS (ESI) calculated for $C_{16}H_{22}O_3H$ [M+H]$^+$ 263.1647, found 263.1645.



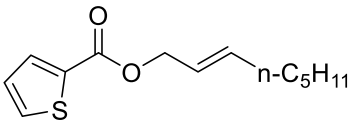
1w

***(E)*-oct-2-en-1-yl 2-methylbenzoate (1w)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.3892 g, 79%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.87 (m, 1 H), 7.38 (s, 1 H), 7.27 – 7.20 (m, 2 H), 5.85 (dt, *J* = 13.6, 6.7 Hz, 1 H), 5.75 – 5.62 (m, 1 H), 4.74 (d, *J* = 6.4 Hz, 2 H), 2.60 (s, 3 H), 2.08 (s, 2 H), 1.48 – 1.19 (m, 6 H), 0.89 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.50, 140.19, 136.72, 131.93, 131.71, 130.64, 129.93, 125.74, 123.97, 65.61, 32.37, 31.46, 28.69, 22.60, 21.81, 14.13. HRMS (ESI) calculated for $C_{16}H_{22}O_2H$ [M+H]$^+$ 247.1698, found 247.1693.



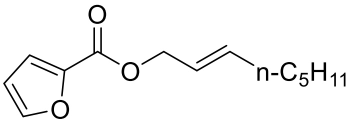
1x

***(E)*-oct-2-en-1-yl 4-chlorobenzoate (1x)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.5282 g, 99%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 (d, *J* = 8.4 Hz, 2 H), 7.41 (dd, *J* = 8.6, 1.9 Hz, 2 H), 5.93 – 5.80 (m, 1 H), 5.67 (dt, *J* = 15.2, 6.4 Hz, 1 H), 4.75 (d, *J* = 6.5 Hz, 2 H), 2.08 (q, *J* = 7.1 Hz, 2 H), 1.46 – 1.22 (m, 6 H), 0.89 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 165.54, 139.32, 137.04, 131.06, 128.94, 128.68 (d, *J* = 2.1 Hz), 123.64, 66.06, 32.34, 31.45, 28.63, 22.57, 14.10. HRMS (ESI) calculated for $C_{15}H_{19}ClO_2H$ [M+H]$^+$ 267.1152, found 267.1157.



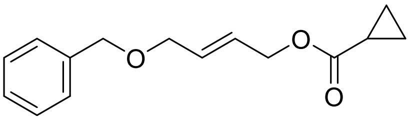
1y

***(E)*-oct-2-en-1-yl thiophene-2-carboxylate (1y)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4529 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 3.7 Hz, 1 H), 7.54 (d, *J* = 5.0 Hz, 1 H), 7.09 (t, *J* = 4.2 Hz, 1 H), 5.85 (dt, *J* = 13.7, 6.7 Hz, 1 H), 5.74 – 5.58 (m, 1 H), 4.73 (d, *J* = 6.4 Hz, 2 H), 2.07 (q, *J* = 7.1 Hz, 2 H), 1.40 (p, *J* = 7.2 Hz, 2 H), 1.30 (h, *J* = 6.5 Hz, 4 H), 0.89 (t, *J* = 6.8 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.12, 136.98, 134.07, 133.42, 132.33, 127.75, 123.64, 65.95, 32.33, 31.45, 28.62, 22.58, 14.11. HRMS (ESI) calculated for $C_{13}H_{18}O_2SH$ [M+H]$^+$ 239.1106, found 239.1098.



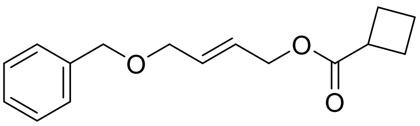
1z

***(E)*-oct-2-en-1-yl furan-2-carboxylate (1z**) was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4401 g, 99%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.56 (s, 1 H), 7.18 (d, *J* = 2.7 Hz, 1 H), 6.52 – 6.44 (m, 1 H), 5.92 – 5.78 (m, 1 H), 5.74 – 5.56 (m, 1 H), 4.73 (d, *J* = 6.5 Hz, 2 H), 2.05 (q, *J* = 7.0 Hz, 2 H), 1.44 – 1.20 (m, 6 H), 0.87 (dt, *J* = 7.1, 3.3 Hz, 3 H). The spectroscopic data matched that previously report.[2]



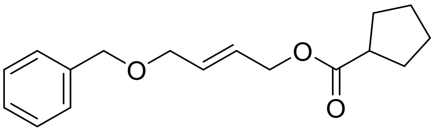
1A

***(E)*-4-(benzyloxy) but-2-en-1-yl cyclopropanecarboxylate (1A)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.4236 g, 86%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.26 (m, 5 H), 5.87 (s, 2 H), 4.60 (d, *J* = 4.3 Hz, 2 H), 4.53 (s, 2 H), 4.04 (d, *J* = 4.0 Hz, 2 H), 1.68 – 1.56 (m, 1 H), 1.09 – 0.98 (m, 3 H), 0.86 (dq, *J* = 7.5, 4.0 Hz, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.64, 138.21, 130.80, 128.50, 127.84, 127.76, 126.91, 72.44, 69.90, 64.34, 12.95, 8.60. HRMS (ESI) calculated for $C_{15}H_{18}O_3H$ [M+H]$^+$ 247.1334, found 247.1331.



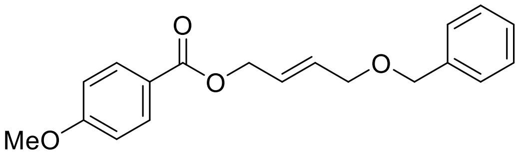
1B

***(E)*-4-(benzyloxy) but-2-en-1-yl-cyclobutanecarboxylate (1B)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.4426 g, 85%). ^{1}H NMR (401 MHz, Chloroform-*d*) δ 7.38 – 7.25 (m, 5 H), 5.92 – 5.79 (m, 2 H), 4.58 (dd, *J* = 4.7, 1.0 Hz, 2 H), 4.51 (s, 2 H), 4.03 (dd, *J* = 3.1, 2.1 Hz, 2 H), 3.23 – 3.05 (m, 1 H), 2.35 – 2.11 (m, 4 H), 2.04 – 1.82 (m, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 175.28, 138.16, 130.72, 128.50, 127.85, 127.77, 126.97, 72.43, 69.88, 64.17, 38.13, 25.36, 18.50. HRMS (ESI) calculated for $C_{15}H_{18}O_3H$ [M+H]$^+$ 261.1491, found 261.1488.



1C

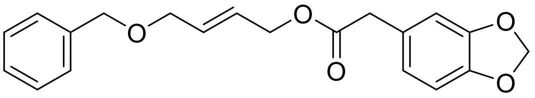
***(E)*-4-(benzyloxy) but-2-en-1-yl-cyclopentanecarboxylate (1C)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.5377 g, 98%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.29 (m, 5 H), 5.90 (q, *J* = 4.4 Hz, 2 H), 4.61 (d, *J* = 4.3 Hz, 2 H), 4.55 (s, 2 H), 4.07 (d, *J* = 3.8 Hz, 2 H), 2.77 (p, *J* = 8.0 Hz, 1 H), 2.00 – 1.52 (m, 8 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 176.42, 138.24, 130.59, 128.48, 127.83 (d, *J* = 2.3 Hz), 127.75 (d, *J* = 1.7 Hz), 127.05 (d, *J* = 3.6 Hz), 72.39, 69.90, 64.13, 43.87, 30.12, 25.92. HRMS (ESI) calculated for $C_{17}H_{22}O_3H$ [M+H]$^+$ 275.1647, found 275.1640.



1D

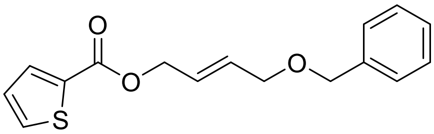
***(E)*-4-(benzyloxy) but-2-en-1-yl-4-methoxybenzoate (1D)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a white solid. (0.5335 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.98 (m, 2 H), 7.39 – 7.28 (m, 5 H), 6.96 – 6.89 (m, 2 H), 5.97 (t, *J* = 2.8 Hz, 2 H), 4.87 – 4.79 (m, 2 H), 4.54 (s, 2 H), 4.11 – 4.04 (m, 2 H), 3.86 (s, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.15, 163.48, 138.15, 131.79, 130.64, 128.53 (d, *J* = 0.9 Hz), 127.90, 127.80 (d, *J* =

0.9 Hz), 127.11 (d, *J* = 0.9 Hz), 122.60, 113.70, 72.51, 69.98, 64.51, 55.54. HRMS (ESI) calculated for $C_{19}H_{20}O_4H$ [M+H]$^+$ 313.1440, found 313.1437. MP: 32-33 ^{o}C.



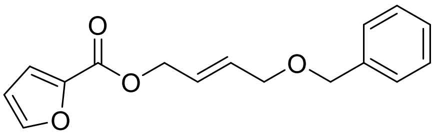
1E

***(E)*-4-(benzyloxy) but-2-en-1-yl-2-(benzo[d] [1,3] dioxol-5-yl) acetate (1E)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a yellow oil. (0.6807 g, 93%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.28 (m, 5 H), 6.85 – 6.70 (m, 3 H), 5.95 (s, 2 H), 5.94 – 5.83 (m, 2 H), 4.63 (d, *J* = 4.1 Hz, 2 H), 4.54 (s, 2 H), 4.06 (d, *J* = 3.6 Hz, 2 H), 3.58 (s, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 171.46, 147.88, 146.85, 138.19, 131.17, 128.53, 127.87, 127.80, 127.57 (d, *J* = 1.4 Hz), 126.54, 122.54, 109.86, 108.40, 101.13, 72.43, 69.82, 64.77, 40.99. HRMS (ESI) calculated for $C_{20}H_{20}O_5H$ [M+H]$^+$ 341.1389, found 341.1387.



1F

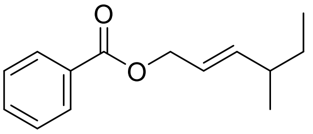
***(E)*-4-(benzyloxy) but-2-en-1-yl thiophene-2-carboxylate (1F)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.5479 g, 95%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 3.7, 1.1 Hz, 1 H), 7.58 (dd, *J* = 5.0, 1.1 Hz, 1 H), 7.43 – 7.28 (m, 5 H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1 H), 6.05 – 5.93 (m, 2 H), 4.84 (d, *J* = 4.2 Hz, 2 H), 4.57 (s, 2 H), 4.10 (d, *J* = 3.8 Hz, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.02, 138.17, 133.73, 133.69, 132.62, 131.19, 128.54, 127.89, 127.88 (d, *J* = 0.6 Hz), 127.81, 126.52, 72.53, 69.88, 64.91. HRMS (ESI) calculated for $C_{16}H_{16}O_3SH$ [M+H]$^+$ 289.0898, found 289.0892.



1G

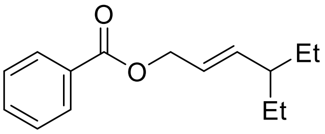
***(E)*-4-(benzyloxy) but-2-en-1-yl furan-2-carboxylate (1G)** was prepared according to general procedure A. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.4738 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.57 (m, 1 H), 7.41 – 7.27 (m, 5 H), 7.22 (d, *J* = 3.5 Hz, 1

H), 6.53 (dd, J = 3.5, 1.7 Hz, 1 H), 5.99 (q, J = 4.3 Hz, 2 H), 4.84 (d, J = 4.4 Hz, 2 H), 4.56 (s, 2 H), 4.09 (d, J = 3.7 Hz, 2 H). The spectroscopic data matched that previously report.[2]



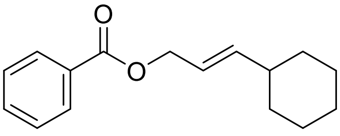
1H

***(E)*-4-methylhex-2-en-1-yl benzoate (1H)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.5688 g, 87%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11 – 8.02 (m, 2 H), 7.59 – 7.51 (m, 1 H), 7.44 (t, J = 7.7 Hz, 2 H), 5.74 (dd, J = 15.5, 7.2 Hz, 1 H), 5.64 (dt, J = 15.5, 6.0 Hz, 1 H), 4.78 (d, J = 5.9 Hz, 2 H), 2.09 (hept, J = 6.8 Hz, 1 H), 1.40 – 1.29 (m, 2 H), 1.01 (d, J = 6.7 Hz, 3 H), 0.87 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.51, 142.09, 132.91, 130.53, 129.69, 128.39, 122.34, 65.93, 38.16, 29.45, 19.79, 11.76. HRMS (ESI) calculated for $C_{14}H_{18}O_2H$ [M+H]$^+$ 219.1387, found 219.1385.



1J

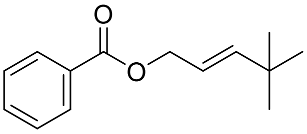
***(E)*-4-ethylhex-2-en-1-yl 2-methylbenzoate (1J)** was prepared according to general procedure B. The crude product was purified by chromatography on silica gel (PE/EA = 50:1) affording a colorless oil. (0.3485 g, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.08 – 8.04 (m, 2 H), 7.55 (t, J = 7.4 Hz, 1 H), 7.44 (t, J = 7.7 Hz, 2 H), 5.69 – 5.54 (m, 2 H), 4.79 (d, J = 5.9 Hz, 2 H), 1.89 – 1.79 (m, 1 H), 1.50 – 1.38 (m, 2 H), 1.27 (dp, J = 15.4, 7.5 Hz, 2 H), 0.86 (t, J = 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.47, 140.62, 132.89, 130.57, 129.67, 128.39, 124.09, 65.86, 46.05, 27.37, 11.76. HRMS (ESI) calculated for $C_{15}H_{20}O_2H$ [M+H]$^+$ 233.1542, found 233.1539.



1K

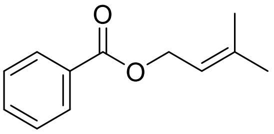
***(E)*-3-cyclohexylallyl benzoate (1K)** was prepared according to general procedure. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4374 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.14 – 8.05 (m, 2 H), 7.61 – 7.53 (m, 1 H), 7.46 (t, J = 7.7 Hz, 2 H), 5.83 (dd, J =

15.5, 6.5 Hz, 1 H), 5.72 – 5.60 (m, 1 H), 4.85 – 4.75 (m, 2 H), 2.03 (dtt, *J* = 10.1, 6.2, 3.1 Hz, 1 H), 1.85 – 1.63 (m, 6 H), 1.37 – 1.03 (m, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 166.47, 142.16, 132.90, 130.53, 129.70, 128.38, 121.47, 66.05, 40.47, 32.65, 26.21, 26.06. HRMS (ESI) calculated for $C_{16}H_{20}O_2H$ [M+H]$^+$ 245.1542, found 245.1533.



1L

***(E)*-4,4-*d*imethylpent-2-en-1-yl benzoate (1L)** was prepared according to general procedure. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.4799 g, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.04 (m, 2 H), 7.55 (t, *J* = 7.4 Hz, 1 H), 7.45 (d, *J* = 7.8 Hz, 3 H), 5.86 (d, *J* = 15.6 Hz, 1 H), 5.59 (dt, *J* = 15.6, 6.4 Hz, 1 H), 4.78 (dd, *J* = 6.4, 1.1 Hz, 2 H), 1.05 (s, 9 H). HRMS (ESI) calculated for $C_{14}H_{18}O_2H$ [M+H]$^+$ 219.1385, found 219.1386. The spectroscopic data matched that previously report.[5]

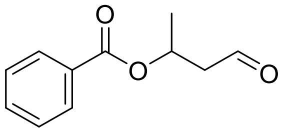


1M

3-methylbut-2-en-1-yl benzoate (1M) was prepared according to general procedure. The crude product was purified by chromatography on silica gel (PE/EA = 100:1) affording a colorless oil. (0.8561 g, 90%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 (dt, *J* = 8.5, 1.6 Hz, 2 H), 7.59 – 7.50 (m, 1 H), 7.48 – 7.37 (m, 2 H), 5.48 (dddt, *J* = 7.2, 5.8, 2.8, 1.4 Hz, 1 H), 4.82 (d, *J* = 7.2 Hz, 2 H), 1.78 (d, *J* = 6.5 Hz, 6 H). The spectroscopic data matched that previously report.[6]

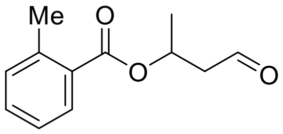
5. Synthesis of 2a

$Pd(PhCN)_2Cl_2$ (14.4 mg, 0.0375 mmol) was weighed directly into a 25 mL flask and dried under high vacuum for 15 mins, purge oxygen 3 times. Under an atmosphere of oxygen (1 atm, balloon), ^{t}BuOH (2 mL) and ^{t}BuONO (10.3 mg, 0.1 mmol) were added and stirred at 25 °C. *(E)*-but-2-en-1-yl benzoate (0.5 mmol) was then added and the resulting reaction mixture was monitored by TLC. After completion, the reaction was quenched by addition of water (5 mL) and extracted three times with CH_2Cl_2. The combined organic layers were subsequently washed with brine and dried over Na_2SO_4. The organic solvent was removed under reduced pressure then the crude mixture was examined on ^{1}H NMR spectrometer to determine the conversion and regioselectivity. The crude product was purified by chromatography on silica gel to affording the corresponding products.



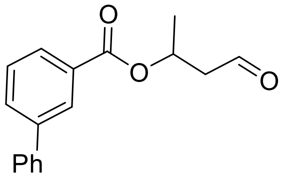
2a

4-oxobutan-2-yl benzoate (2a) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 30/1) as yellow oil (74.1 mg, 77%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 – 9.81 (m, 1 H), 8.07 – 7.99 (m, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.45 (t, *J* = 7.7 Hz, 2 H), 5.64 (h, *J* = 6.4 Hz, 1 H), 2.90 (ddd, *J* = 16.8, 7.1, 2.5 Hz, 1 H), 2.75 (ddd, *J* = 16.8, 5.3, 1.4 Hz, 1 H), 1.48 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.59, 165.93, 133.23, 130.09, 129.67, 128.49, 66.72, 49.73, 20.36. HRMS (ESI) calculated for $C_{11}H_{12}O_3H$ $[M+H]^+$ 193.0865, found 193.0861.



2b

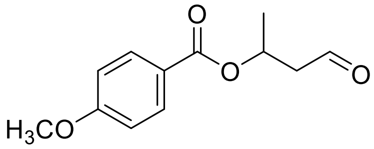
4-oxobutan-2-yl 2-methylbenzoate (2b) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (84.5 mg, 82%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (dd, *J* = 2.5, 1.5 Hz, 1 H), 7.85 (dd, *J* = 8.1, 1.3 Hz, 1 H), 7.40 (td, *J* = 7.5, 1.3 Hz, 1 H), 7.29 – 7.20 (m, 2 H), 5.64 (d, *J* = 6.4 Hz, 1 H), 2.88 (ddd, *J* = 16.8, 7.2, 2.5 Hz, 1 H), 2.73 (ddd, *J* = 16.7, 5.2, 1.5 Hz, 1 H), 2.58 (s, 3 H), 1.47 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.45, 166.84, 140.15, 131.72, 130.47, 129.48, 125.74, 66.33, 49.72, 21.77, 20.30. HRMS (ESI) calculated for $C_{14}H_{18}O_2H$ $[M+H]^+$ 219.1385, found 219.1386.



2c

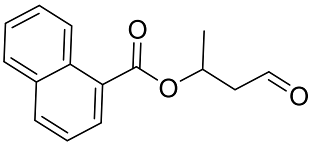
4-oxobutan-2-yl [1,1'-biphenyl]-3-carboxylate (2c) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (86.8mg, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.84 (dd, *J* = 2.4, 1.6 Hz, 1 H), 8.24 (t, *J* = 1.6 Hz, 1 H), 7.99 (dt, *J* = 7.8, 1.4 Hz, 1 H), 7.79

(ddd, *J* = 7.7, 1.9, 1.2 Hz, 1 H), 7.65 – 7.59 (m, 2 H), 7.55 – 7.44 (m, 3 H), 7.42 – 7.36 (m, 1 H), 5.71 – 5.62 (m, 1 H), 2.92 (ddd, *J* = 16.8, 7.1, 2.5 Hz, 1 H), 2.76 (ddd, *J* = 16.8, 5.4, 1.5 Hz, 1 H), 1.49 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.34, 165.79, 141.58, 140.09, 131.79, 130.61, 128.92, 128.89, 128.37, 128.28, 127.80, 127.20, 66.76, 49.69, 20.31. HRMS (ESI) calculated for $C_{17}H_{16}O_3H$ [M+H]$^+$ 269.1178, found 269.1175.



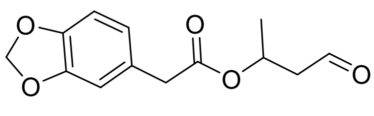
2d

4-oxobutan-2-yl 4-methoxybenzoate (2d) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (69.2 mg, 76%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.86 – 9.81 (m, 1 H), 8.01 – 7.95 (m, 2 H), 6.93 (d, *J* = 8.8 Hz, 2 H), 5.61 (h, *J* = 6.4 Hz, 1 H), 3.88 (s, 3 H), 2.88 (ddd, *J* = 16.7, 7.1, 2.6 Hz, 1 H), 2.74 (ddd, *J* = 16.7, 5.3, 1.4 Hz, 1 H), 1.47 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.61, 165.57, 163.49, 131.64, 122.42, 113.62, 66.29, 55.46, 49.74, 20.34. HRMS (ESI) calculated for $C_{12}H_{14}O_4H$ [M+H]$^+$ 223.0970, found 223.0968.



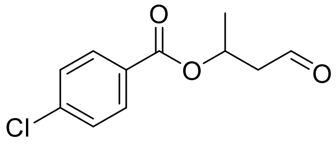
2e

4-oxobutan-2-yl 2-Naphthoate （2e） was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (83.4 mg, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.92 – 9.88 (m, 1 H), 8.91 (d, *J* = 8.7 Hz, 1 H), 8.15 (dd, *J* = 7.3, 1.0 Hz, 1 H), 8.05 (d, *J* = 8.2 Hz, 1 H), 7.91 (d, *J* = 8.1 Hz, 1 H), 7.65 (ddd, *J* = 8.5, 6.9, 1.3 Hz, 1 H), 7.60 – 7.48 (m, 2 H), 5.76 (h, *J* = 6.4 Hz, 1 H), 2.98 (ddd, *J* = 16.8, 7.2, 2.5 Hz, 1 H), 2.82 (ddd, *J* = 16.8, 5.3, 1.4 Hz, 1 H), 1.56 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.41, 166.76, 133.82, 133.53, 131.32, 130.12, 128.59, 126.97, 126.78, 125.65, 124.47, 66.64, 49.76, 20.36. HRMS (ESI) calculated for $C_{15}H_{14}O_3H$ [M+H]$^+$ 243.1021, found 243.1019.



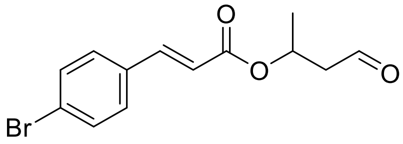
2f

4-oxobutan-2-yl 2-(benzo[d][1,3] dioxol-5-yl)acetate (2f) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (81.3 mg, 65%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.73 – 9.66 (m, 1 H), 6.75 (dd, *J* = 4.6, 3.2 Hz, 2 H), 6.69 (dd, *J* = 8.0, 1.5 Hz, 1 H), 5.94 (s, 2 H), 5.36 (h, *J* = 6.4 Hz, 1 H), 3.49 (s, 2 H), 2.72 (ddd, *J* = 16.8, 7.2, 2.4 Hz, 1 H), 2.59 (ddd, *J* = 16.8, 5.3, 1.4 Hz, 1 H), 1.31 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.42, 171.10, 147.84, 146.81, 127.39, 122.44, 109.71, 108.40, 101.14, 66.53, 49.54, 41.12, 20.18. HRMS (ESI) calculated for $C_{13}H_{14}O_5H$ [M+H]$^+$ 251.0919, found 251.0915.



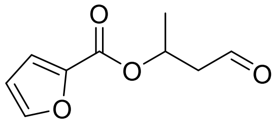
2g

4-oxobutan-2-yl 4-chlorobenzoate (2g) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (90.9 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 – 9.78 (m, 1 H), 8.03 – 7.89 (m, 2 H), 7.42 (d, *J* = 8.5 Hz, 2 H), 5.63 (h, *J* = 6.4 Hz, 1 H), 3.00 – 2.69 (m, 2 H), 1.48 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.14, 164.97, 139.58, 130.98, 128.74, 128.48, 66.91, 49.61, 20.24. HRMS (ESI) calculated for $C_{11}H_{11}ClO_3H$ [M+H]$^+$ 227.0475, found 227.0470.



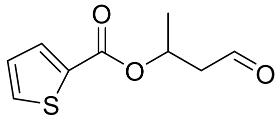
2h

4-oxobutan-2-yl *(E)*-3-(4-bromophenyl)acrylate (2h) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 5/1) as yellow oil (98.1 mg, 66%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.78 (dd, *J* = 2.5, 1.5 Hz, 1 H), 7.60 (d, *J* = 16.0 Hz, 1 H), 7.54 – 7.49 (m, 2 H), 7.41 – 7.34 (m, 2 H), 6.38 (d, *J* = 16.0 Hz, 1 H), 5.59 – 5.45 (m, 1 H), 2.81 (ddd, *J* = 16.8, 7.2, 2.5 Hz, 1 H), 2.68 (ddd, *J* = 16.8, 5.3, 1.5 Hz, 1 H), 1.40 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.40, 165.94, 143.84, 133.17, 132.17, 129.48, 124.69, 118.55, 66.21, 49.64, 20.26. HRMS (ESI) calculated for $C_{13}H_{13}BrO_3H$ [M+H]$^+$ 297.0126, found 297.0126.



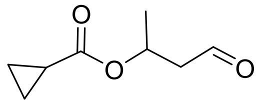
2i

4-oxobutan-2-yl furan-2-carboxylate (2i) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (91.1 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 – 9.79 (m, 1 H), 7.62 – 7.56 (m, 1 H), 7.18 (d, *J* = 3.4 Hz, 1 H), 6.52 (dd, *J* = 3.5, 1.7 Hz, 1 H), 5.61 (h, *J* = 6.5 Hz, 1 H), 2.90 (ddd, *J* = 17.0, 7.1, 2.3 Hz, 1 H), 2.73 (ddd, *J* = 17.0, 5.4, 1.4 Hz, 1 H), 1.46 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.11, 157.93, 146.47, 144.55, 118.22, 111.88, 66.68, 49.52, 20.24.



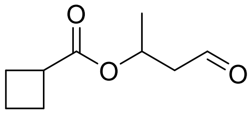
2j

4-oxobutan-2-yl thiophene-2-carboxylate (2j) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (72.7 mg, 73%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.96 – 9.69 (m, 1 H), 7.80 (d, *J* = 2.9 Hz, 1 H), 7.58 (d, *J* = 4.7 Hz, 1 H), 7.18 – 7.04 (m, 1 H), 5.59 (h, *J* = 6.4 Hz, 1 H), 2.98 – 2.67 (m, 2 H), 1.47 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.28, 161.48, 133.63, 133.58, 132.65, 127.80, 66.94, 49.56, 20.27.



2k

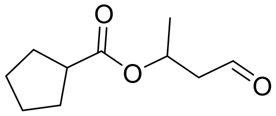
4-oxobutan-2-yl cyclopropanecarboxylate (2k) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 5/1) as yellow oil (45.3 mg, 58%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (dd, *J* = 2.5, 1.6 Hz, 1 H), 5.40 – 5.28 (m, 1 H), 2.71 (ddd, *J* = 16.7, 7.2, 2.6 Hz, 1 H), 2.58 (ddd, *J* = 16.7, 5.3, 1.6 Hz, 1 H), 1.54 (tt, *J* = 8.1, 4.6 Hz, 1 H), 1.31 (d, *J* = 6.4 Hz, 3 H), 0.96 (tdd, *J* = 5.2, 4.5, 3.8, 1.7 Hz, 2 H), 0.84 (ddd, *J* = 8.2, 4.7, 2.2 Hz, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.59, 174.23, 65.87, 49.64, 20.21, 12.97, 9.17. HRMS (ESI) calculated for $C_8H_{12}O_3H$ $[M+H]^+$ 157.0865, found 157.0872.



2l

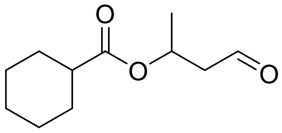
4-oxobutan-2-yl cyclobutanecarboxylate (2l) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil. (51.1 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.73 (dd, *J* = 2.5, 1.6 Hz, 1 H), 5.41 – 5.31 (m, 1 H), 3.15 – 3.01 (m, 1 H), 2.71 (ddd, *J* = 16.7, 7.4, 2.6 Hz, 1 H), 2.64 – 2.54 (m, 1 H), 2.33 – 2.10 (m, 4 H), 2.03 – 1.82 (m, 2 H), 1.31 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100

MHz, $CDCl_3$) δ 199.48, 174.78, 65.56, 49.63, 38.08, 25.08, 20.17, 18.35. HRMS (ESI) calculated for $C_9H_{14}O_3H$ $[M+H]^+$ 171.1021, found 171.1017.



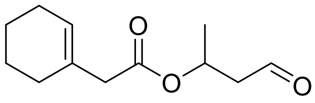
2m

4-oxobutan-2-yl cyclopentanecarboxylate (2m) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (61.3 mg, 66%). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.78 – 9.71 (m, 1 H), 5.36 (dt, *J* = 12.8, 6.4 Hz, 1 H), 2.76 – 2.57 (m, 3 H), 1.92 – 1.51 (m, 9 H), 1.32 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.52, 176.06, 65.53, 49.65, 43.81, 29.96, 25.77, 20.16. HRMS (ESI) calculated for $C_{10}H_{16}O_3H$ $[M+H]^+$ 185.1178, found 185.1170.



2n

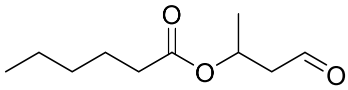
4-oxobutan-2-yl cyclohexanecarboxylate (2n) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (61.2 mg, 62%). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.83 – 9.62 (m, 1 H), 5.38 (h, *J* = 6.4 Hz, 1 H), 2.72 (ddd, *J* = 16.6, 7.4, 2.7 Hz, 1 H), 2.61 (ddd, *J* = 16.6, 5.1, 1.4 Hz, 1 H), 2.27 (tt, *J* = 11.2, 3.6 Hz, 1 H), 1.88 (d, *J* = 12.9 Hz, 2 H), 1.80 – 1.70 (m, 2 H), 1.70 – 1.61 (m, 1 H), 1.50 – 1.36 (m, 2 H), 1.33 (d, *J* = 6.4 Hz, 3 H), 1.31 – 1.15 (m, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.71, 175.52, 100.00, 65.46, 49.72, 43.24, 29.02, 28.91, 25.78, 25.46, 25.42, 20.26. HRMS (ESI) calculated for $C_{11}H_{18}O_3H$ $[M+H]^+$ 199.1334, found 199.1329.



2o

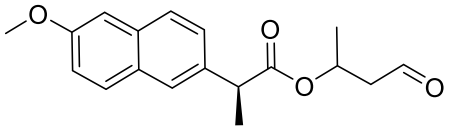
4-oxobutan-2-yl 2-(cyclohex-1-en-1-yl)acetate (2o) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (49.8 mg, 47%). ^1H NMR (400 MHz, Chloroform-*d*) δ 9.73 (dd, *J* = 2.5, 1.6 Hz, 1 H), 5.57 – 5.52 (m, 1 H), 5.40 (d, *J* = 6.4 Hz, 1 H), 2.90 (s, 2 H), 2.72 (ddd, *J* = 16.7, 7.3, 2.6 Hz, 1 H), 2.59 (ddd, *J* = 16.7, 5.2, 1.5 Hz, 1 H), 2.05 – 1.93 (m, 4 H), 1.62 (ddt, *J* =

12.2, 6.1, 3.1 Hz, 2 H), 1.55 (dd, *J* = 5.9, 2.1 Hz, 2 H), 1.32 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.40, 171.32, 130.85, 125.88, 65.96, 49.55, 43.69, 28.39, 25.28, 22,71, 21.96, 20.15. HRMS (ESI) calculated for $C_{12}H_{18}O_3H$ [M+H]$^+$ 211.1334, found 211.1327.



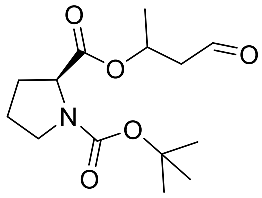
2p

4-oxobutan-2-yl hexanoate (2p) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (48.4 mg, 52%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.89 – 9.65 (m, 1 H), 5.40 (h, *J* = 6.4 Hz, 1 H), 2.74 (ddd, *J* = 16.7, 7.3, 2.6 Hz, 1 H), 2.62 (ddd, *J* = 16.7, 5.2, 1.5 Hz, 1 H), 2.29 (t, *J* = 7.6 Hz, 2 H), 1.63 (p, *J* = 7.5 Hz, 3 H), 1.39 – 1.25 (m, 8 H), 0.91 (t, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.43, 173.15, 65.62, 49.62, 34.41, 31.23, 24.60, 22.29, 20.19, 13.89. HRMS (ESI) calculated for $C_{10}H_{18}O_3H$ [M+H]$^+$ 187.1334, found 187.1337.



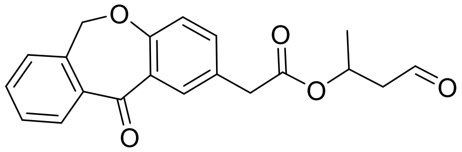
2q

4-oxobutan-2-yl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (2q) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 5/1) as yellow oil (99.1mg, 66%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (dd, *J* = 2.5, 1.5 Hz, 0.56 H), 9.50 (dd, *J* = 2.4, 1.7 Hz, 0.39 H), 7.70 (dd, *J* = 8.7, 1.7 Hz, 2 H), 7.67 – 7.60 (m, 1 H), 7.37 (ddd, *J* = 8.3, 6.2, 1.8 Hz, 1 H), 7.22 – 7.09 (m, 2 H), 5.42 – 5.31 (m, 1 H), 3.91 (s, 3 H), 3.81 (qd, *J* = 7.0, 5.0 Hz, 1 H), 2.75 – 2.43 (m, 2 H), 1.56 (dd, *J* = 7.2, 1.9 Hz, 3 H), 1.31 (d, *J* = 6.4 Hz, 1 H), 1.20 (d, *J* = 6.4 Hz, 2 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.55 (d, *J* = 8.2 Hz), 174.09 (d, *J* = 3.8 Hz), 157.72, 135.50 (d, *J* = 5.0 Hz), 133.75, 129.36, 129.10 – 128.76 (m), 127.26 (d, *J* = 2.9 Hz), 126.18 (d, *J* = 6.0 Hz), 126.00, 119.12 (d, *J* = 3.4 Hz), 105.65, 66.36 (d, *J* = 14.0 Hz), 55.41, 49.47 (d, *J* = 17.1 Hz), 45.57 (d, *J* = 4.9 Hz), 20.07 (d, *J* = 23.7 Hz), 18.48 (d, *J* = 18.9 Hz). HRMS (ESI) calculated for $C_{18}H_{20}O_4H$ [M+H]$^+$ 301.1440, found 301.1449.



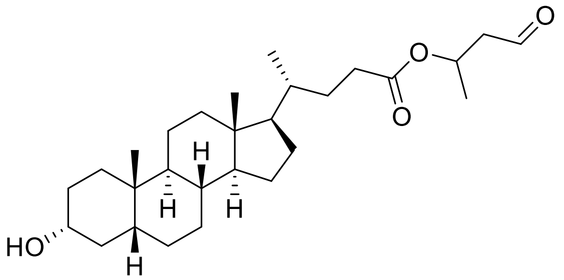
2r

1-(tert-butyl) 2-(4-oxobutan-2-yl) (2S)-pyrrolidine-1,2-dicarboxylate (2r) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil. (107.0 mg, 75%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.72 (s, 1 H), 5.37 (hept, *J* = 6.4 Hz, 1 H), 4.28 – 4.13 (m, 1 H), 3.58 – 3.30 (m, 2 H), 2.80 – 2.53 (m, 2 H), 2.17 (dqt, *J* = 20.4, 7.7, 4.4 Hz, 1 H), 1.99 – 1.80 (m, 3 H), 1.48 – 1.37 (m, 10 H), 1.36 – 1.26 (m, 3 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 198.85, 172.39, 153.78, 80.85 – 78.82 (m), 66.40 (t, *J* = 15.1 Hz), 59.69 – 56.86 (m), 50.46 – 48.61 (m), 46.43 (d, *J* = 23.5 Hz), 30.85 (d, *J* = 7.3 Hz), 29.83, 28.37 (d, *J* = 5.8 Hz), 24.32 (d, *J* = 7.1 Hz), 23.45, 20.08 (dd, *J* = 15.1, 9.8 Hz). HRMS (ESI) calculated for $C_{14}H_{23}NO_5H$ $[M+H]^+$ 286.1654, found 286.1651.



2s

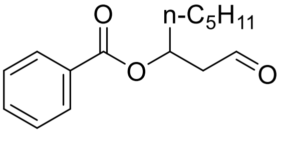
4-oxobutan-2-yl-2-(11-oxo-6,11-*d*ihydrodibenzo[b,e]oxepin-2-yl)acetate (2s) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 5/1) as yellow oil (113.4 mg, 67%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (dd, *J* = 2.3, 1.5 Hz, 1 H), 8.09 (d, *J* = 2.3 Hz, 1 H), 7.88 (dd, *J* = 7.7, 1.2 Hz, 1 H), 7.55 (td, *J* = 7.4, 1.4 Hz, 1 H), 7.46 (td, *J* = 7.6, 1.3 Hz, 1 H), 7.42 – 7.33 (m, 2 H), 7.02 (d, *J* = 8.4 Hz, 1 H), 5.41 (d, *J* = 6.4 Hz, 1 H), 5.18 (s, 2 H), 3.61 (s, 2 H), 2.74 (ddd, *J* = 16.9, 7.2, 2.4 Hz, 1 H), 2.60 (ddd, *J* = 16.9, 5.3, 1.5 Hz, 1 H), 1.32 (d, *J* = 6.4 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.23, 190.85, 70.13, 160.50, 140.41, 136.26, 135.53, 132.81, 132.39, 129.47, 129.28, 127.84, 127.56, 125.11, 121.11, 73.63, 66.60, 49.46, 40.29, 20.11. HRMS (ESI) calculated for $C_{20}H_{18}O_5H$ $[M+H]^+$ 339.1232, found 339.1236.



2t

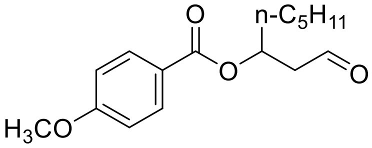
4-oxobutan-2-yl(4*R*)-4-((3*R*,5*R*,8*R*,9*S*,10*S*,13*R*,14*S*,17*R*)-3-hydroxy-10,13 dimethylhexadecahydro-1H-

cyclopenta[a]phenanthren-17-yl)pentanoate (2t) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 5/1) as white solid. (116.1 mg, 52%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.61 (tt, *J* = 11.0, 4.6 Hz, 1 H), 2.71 (ddd, *J* = 16.7, 7.3, 2.6 Hz, 1 H), 2.59 (ddd, *J* = 16.7, 5.2, 1.6 Hz, 1 H), 2.38 – 2.24 (m, 1 H), 2.24 – 2.11 (m, 1 H), 1.94 (dt, *J* = 12.3, 3.0 Hz, 1 H), 1.90 – 1.60 (m, 10 H), 1.53 (dddt, *J* = 21.2, 10.2, 4.4, 2.6 Hz, 3 H), 1.45 – 1.18 (m, 19 H), 1.18 – 0.98 (m, 7 H), 0.98 – 0.81 (m, 9 H), 0.63 (s, 4 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.52, 173.64, 71.81, 65.64, 56.48, 55.93, 49.60, 42.73, 42.08, 40.41, 40.16, 36.41, 35.83, 35.35, 35.30, 31.38, 30.91, 30.51, 28.19, 27.19, 26.42, 24.19, 23.38, 20.81, 20.19, 18.23, 12.03. HRMS (ESI) calculated for $C_{28}H_{46}O_4H$ [M+H]$^+$ 447.3474, found 447.3471. MP: 75- 76 °C.



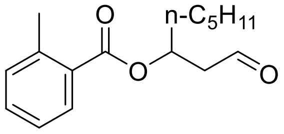
2u

1-oxooctan-3-yl benzoate (2u) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (89.4 mg, 72%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (dd, *J* = 2.6, 1.7 Hz, 1 H), 8.05 – 8.00 (m, 2 H), 7.57 (s, 1 H), 7.45 (d, *J* = 7.8 Hz, 2 H), 5.60 – 5.52 (m, 1 H), 2.90 – 2.72 (m, 2 H), 1.88 – 1.67 (m, 2 H), 1.50 – 1.24 (m, 7 H), 0.92 – 0.81 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.64, 166.03, 133.12, 130.02, 129.61, 128.41, 69.94, 48.24, 34.35, 31.49, 24.89, 22.47, 13.95. HRMS (ESI) calculated for $C_{15}H_{20}O_3H$ [M+H]$^+$ 249.1491, found 249.1494.



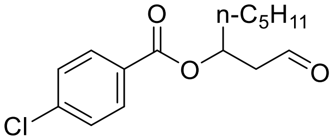
2v

1-oxooctan-3-yl 4-methoxybenzoate (2v) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (98.8mg, 71%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 – 9.79 (m, 1 H), 7.97 (dd, *J* = 9.3, 2.3 Hz, 2 H), 6.92 (dd, *J* = 9.3, 2.3 Hz, 2 H), 5.56 – 5.48 (m, 1 H), 3.86 (s, 3 H), 2.85 – 2.69 (m, 2 H), 1.86 – 1.65 (m, 2 H), 1.49 – 1.23 (m, 7 H), 0.94 – 0.82 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.86, 165.78, 163.50, 131.86, 122.38, 113.65, 69.58, 55.46, 48.32, 34.40, 31.50, 24.91, 22.48, 13.97. HRMS (ESI) calculated for $C_{16}H_{22}O_4H$ [M+H]$^+$ 279.1596, found 279.1590.



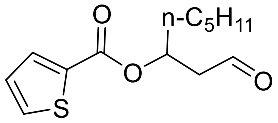
2w

1-oxooctan-3-yl 2-methylbenzoate (2w) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (91.8 mg, 70%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.87 – 9.83 (m, 1 H), 7.91 – 7.86 (m, 1 H), 7.45 – 7.39 (m, 1 H), 7.30 – 7.23 (m, 2 H), 5.57 (tt, *J* = 7.2, 5.4 Hz, 1 H), 2.92 – 2.72 (m, 2 H), 2.61 (s, 3 H), 1.91 – 1.68 (m, 2 H), 1.53 – 1.27 (m, 7 H), 0.96 – 0.87 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.65, 167.00, 140.22, 132.09, 131.73, 130.43, 129.48, 125.74, 69.61, 48.30, 34.38, 31.50, 24.97, 22.49,21.76, 13.96. HRMS (ESI) calculated for $C_{16}H_{22}O_3H$ [M+H]$^+$ 263.1647, found 263.1651.



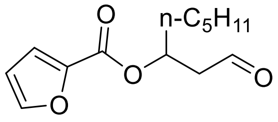
2x

1-oxooctan-3-yl 4-chlorobenzoate (2x) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 30/1) as yellow oil (96.1mg, 68%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.80 (dd, *J* = 2.6, 1.6 Hz, 1 H), 7.98 – 7.90 (m, 2 H), 7.45 – 7.37 (m, 2 H), 5.54 (tt, *J* = 7.3, 5.3 Hz, 1 H), 2.87 – 2.70 (m, 2 H), 1.87 – 1.65 (m, 2 H), 1.46 – 1.20 (m, 7 H), 0.88 (d, *J* = 6.9 Hz, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.63, 166.29, 139.70, 131.11, 128.87, 128.47, 70.26, 48.27, 34.37, 31.56, 24.99, 22.58, 14.10. HRMS (ESI) calculated for $C_{15}H_{19}ClO_3H$ [M+H]$^+$ 283.1101, found 283.1097.



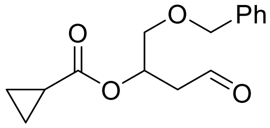
2y

1-oxooctan-3-yl thiophene-2-carboxylate (2y) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (76.3 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (dd, *J* = 2.6, 1.6 Hz, 1 H), 7.78 (dd, *J* = 3.8, 1.2 Hz, 1 H), 7.55 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.09 (dd, *J* = 5.0, 3.7 Hz, 1 H), 5.49 (tt, *J* = 7.3, 5.2 Hz, 1 H), 2.85 – 2.69 (m, 2 H), 1.83 – 1.64 (m, 2 H), 1.46 – 1.22 (m, 7 H), 0.91 – 0.82 (m, 3 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.72, 161.81, 133.76, 133.57, 132.78, 127.94, 70.29, 48.25, 34.37, 31.53, 24.93, 22.56, 14.07. HRMS (ESI) calculated for $C_{13}H_{18}O_3SH$ [M+H]$^+$ 250.1055, found 255.1049.



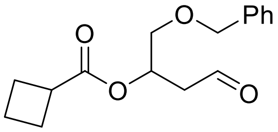
2z

1-oxobutan-3-ylfuran-2-carboxylate (2z) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (78.7mg, 66%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.80 (s, 1 H), 7.59 (s, 1 H), 7.17 (d, *J* = 4.1 Hz, 1 H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1 H), 5.59 – 5.50 (m, 1 H), 2.87 – 2.70 (m, 2 H), 1.85 – 1.58 (m, 3 H), 1.50 – 1.21 (m, 7 H), 0.99 – 0.80 (m, 3 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 199.41, 158.16, 146.51, 144.39, 118.24, 111.89, 69.94, 48.13, 34.28, 31.43, 24.83, 22.46, 13.96.



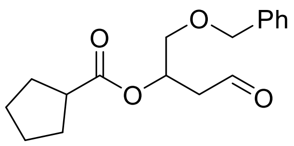
2A

1-(benzyloxy)-4-oxobutan-2-yl cyclopropanecarboxylate (2A) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (102.3 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.75 (t, *J* = 1.9 Hz, 1 H), 7.33 (d, *J* = 15.0 Hz, 6 H), 5.47 – 5.41 (m, 1 H), 4.60 – 4.49 (m, 2 H), 3.61 (qd, *J* = 10.4, 4.7 Hz, 2 H), 2.85 – 2.72 (m, 2 H), 1.61 (dt, *J* = 8.0, 3.9 Hz, 2 H), 1.00 (tt, *J* = 4.6, 2.5 Hz, 2 H), 0.88 (dq, *J* = 8.1, 3.2 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.17, 174.20, 137.65, 128.47, 127.85, 127.68, 73.35, 70.37, 67.88, 45.21, 12.90, 8.80. HRMS (ESI) calculated for $C_{15}H_{18}O_4H$ [M+H]$^+$ 263.1283, found 263.1280.



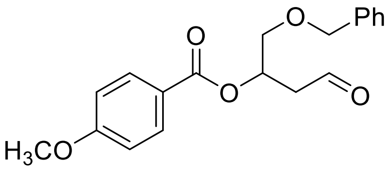
2B

1-(benzyloxy)-4-oxobutan-2-yl cyclobutanecarboxylate (2B) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (102.2 mg, 74%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.74 (t, *J* = 1.7 Hz, 1 H), 7.40 – 7.27 (m, 6 H), 5.45 (dt, *J* = 10.5, 5.0 Hz, 1 H), 4.61 – 4.49 (m, 2 H), 3.66 – 3.53 (m, 2 H), 3.13 (p, *J* = 8.5 Hz, 1 H), 2.85 – 2.70 (m, 2 H), 2.33 – 2.13 (m, 4 H), 2.03 – 1.83 (m, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.13, 174.76, 137.66, 128.46, 127.85, 127.67, 73.34, 70.42, 67.57, 45.23, 37.97, 25.20, 18.39. HRMS (ESI) calculated for $C_{16}H_{20}O_4H$ [M+H]$^+$ 277.1440, found 277.1437.



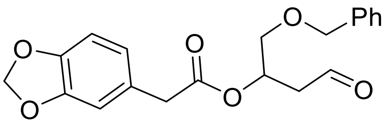
2C

1-(benzyloxy)-4-oxobutan-2-yl cyclopentanecarboxylate (2C) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (119.9 mg, 83%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (t, *J* = 1.7 Hz, 1 H), 7.41 – 7.29 (m, 6 H), 5.47 (dt, *J* = 10.5, 5.0 Hz, 1 H), 4.63 – 4.51 (m, 2 H), 3.69 – 3.56 (m, 2 H), 2.86 – 2.70 (m, 3 H), 1.95 – 1.51 (m, 9 H). ^{13}C NMR (400 MHz, CDCl$_3$) δ 199.19, 176.06, 137.67, 128.46, 127.84, 127.67, 73.34, 70.46, 67.54, 45.26, 43.69, 30.01, 25.81. HRMS (ESI) calculated for $C_{17}H_{22}O_4H$ [M+H]$^+$ 291.1596, found 291.1601.



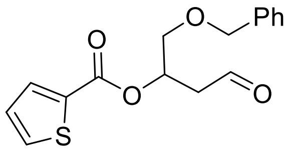
2D

1-(benzyloxy)-4-oxobutan-2-yl-4-methoxybenzoate (2D) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (131.3 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.76 (t, *J* = 1.7 Hz, 1 H), 7.41 – 7.29 (m, 6 H), 5.47 (dt, *J* = 10.5, 5.0 Hz, 1 H), 4.63 – 4.51 (m, 2 H), 3.69 – 3.56 (m, 2 H), 2.86 – 2.70 (m, 3 H), 1.95 – 1.51 (m, 9 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.26, 165.55, 163.64, 137.71, 131.83, 128.48, 127.84, 127.68, 122.10, 113.68, 73.40, 70.51, 68.32, 55.48. HRMS (ESI) calculated for $C_{19}H_{20}O_5H$ [M+H]$^+$ 329.1389, found 329.1383.



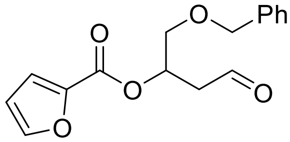
2E

1-(benzyloxy)-4-oxobutan-2-yl 2-(benzo[d][1,3]dioxol-5-yl)acetate (2E) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 5/1) as yellow oil (139.5mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.70 (t, *J* = 1.8 Hz, 1 H), 7.38 – 7.25 (m, 5 H), 6.79 – 6.67 (m, 4 H), 5.94 – 5.91 (m, 2 H), 5.45 (tt, *J* = 6.0, 4.6 Hz, 1 H), 4.56 – 4.43 (m, 2 H), 3.65 – 3.54 (m, 2 H), 3.52 (s, 2 H), 2.77 (dt, *J* = 6.6, 1.8 Hz, 2 H). ^{13}C NMR (100 MHz, CDCl$_3$) δ 198.92, 170.99, 147.78, 146.78, 137.60, 128.46, 127.86, 127.66, 127.15, 122.40, 109.67, 108.32, 101.05, 73.36, 70.29, 68.44, 44.98, 40.90. HRMS (ESI) calculated for $C_{20}H_{20}O_6H$ [M+H]$^+$ 357.1338, found 357.1342.



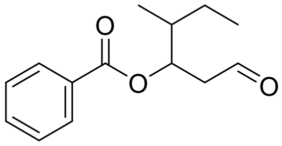
2F

1-(benzyloxy)-4-oxobutan-2-yl thiophene-2-carboxylate (2F) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 10/1) as yellow oil (122 mg, 80%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (t, *J* = 1.7 Hz, 1 H), 7.83 (dd, *J* = 3.7, 1.2 Hz, 1 H), 7.60 (dd, *J* = 5.0, 1.1 Hz, 1 H), 7.41 – 7.29 (m, 5 H), 7.13 (dd, *J* = 4.9, 3.8 Hz, 1 H), 5.68 (ddd, *J* = 10.8, 6.1, 4.7 Hz, 1 H), 4.67 – 4.54 (m, 2 H), 3.75 (qd, *J* = 10.6, 4.6 Hz, 2 H), 2.93 (dd, *J* = 6.2, 1.7 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 199.00, 161.44, 137.67, 133.99, 133.17, 132.98, 128.50, 127.90, 127.86, 73.38, 70.32, 68.88, 45.13. HRMS (ESI) calculated for $C_{16}H_{16}O_4SH$ [M+H]$^+$ 305.0848, found 305.0852.



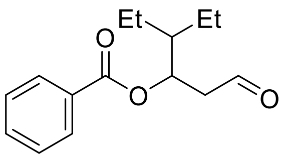
2G

1-(benzyloxy)-4-oxobutan-2-yl furan-2-carboxylate (2G) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (112.4 mg, 78%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.82 (t, *J* = 1.6 Hz, 1 H), 7.63 – 7.59 (m, 1 H), 7.41 – 7.27 (m, 6 H), 7.21 (d, *J* = 3.5 Hz, 1 H), 6.53 (dd, *J* = 3.5, 1.7 Hz, 1 H), 5.69 (ddd, *J* = 10.9, 6.1, 4.8 Hz, 1 H), 4.59 (q, *J* = 12.1 Hz, 2 H), 3.74 (qd, *J* = 10.5, 4.7 Hz, 2 H), 2.93 (dd, *J* = 6.2, 1.7 Hz, 2 H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 198.83, 157.86, 146.69, 144.14, 137.58, 128.47, 127.71, 118.64, 111.96, 73.37, 70.22, 68.52, 45.08.



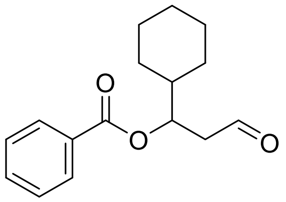
2H

4-methyl-1-oxohexan-3-yl benzoate (2H) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 60/1) as yellow oil (80.8 mg, 69%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.83 (dt, *J* = 3.0, 1.8 Hz, 1 H), 8.09 – 7.98 (m, 2 H), 7.58 (t, *J* = 7.4 Hz, 1 H), 7.46 (t, *J* = 7.7 Hz, 2 H), 5.65 – 5.51 (m, 1 H), 2.91 – 2.66 (m, 2 H), 1.98 – 1.75 (m, 1 H), 1.64 – 1.49 (m, 1 H), 1.29 (d, *J* = 7.6 Hz, 1 H), 1.08 – 0.94 (m, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 199.85, 133.15, 130.01, 129.63, 128.44, 72.34, 46.05, 45.00, 38.66, 38.19, 25.57, 25.07, 14.50, 14.24, 11.70, 11.50. HRMS (ESI) calculated for $C_{14}H_{18}O_3H$ [M+H]$^+$ 235.1334, found 235.1337.



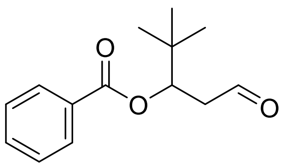
2J

4-ethyl-1-oxohexan-3-yl benzoate (2J) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 20/1) as yellow oil (74.5 mg, 60%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.81 (dd, *J* = 3.0, 1.5 Hz, 1 H), 8.05 – 7.97 (m, 2 H), 7.56 (d, *J* = 7.4 Hz, 1 H), 7.45 (d, *J* = 7.8 Hz, 2 H), 5.68 (dt, *J* = 8.5, 4.3 Hz, 1 H), 2.81 (ddd, *J* = 16.5, 8.4, 3.1 Hz, 1 H), 2.70 (ddd, *J* = 16.5, 4.1, 1.4 Hz, 1 H), 1.63 (dq, *J* = 12.5, 6.2 Hz, 1 H), 1.43 (ddt, *J* = 35.7, 14.1, 7.1 Hz, 4 H), 0.98 (dt, *J* = 11.1, 7.4 Hz, 6 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.99, 166.04, 133.14, 133.19, 129.99, 129.63, 128.43, 71.10, 45.62, 44.78, 22.16, 22.05, 11.72, 11.66. HRMS (ESI) calculated for $C_{15}H_{20}O_3H$ $[M+H]^+$ 249.1491, found 249.1486.



2K

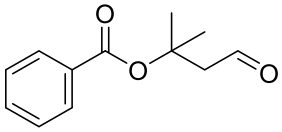
1-cyclohexyl-3-oxopropyl benzoate (2K) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 30/1) as yellow oil (98.9 mg, 76%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (dd, *J* = 2.7, 1.9 Hz, 1 H), 8.05 – 7.98 (m, 2 H), 7.55 (tt, *J* = 7.0, 1.3 Hz, 1 H), 7.43 (t, *J* = 7.7 Hz, 2 H), 5.44 (dt, *J* = 7.2, 5.4 Hz, 1 H), 2.83 – 2.69 (m, 2 H), 1.88 – 1.63 (m, 6 H), 1.32 – 1.03 (m, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.04, 133.15, 129.65, 128.44, 73.31, 45.83, 41.62, 28.79, 28.21, 26.21, 25.94, 25.89. HRMS (ESI) calculated for $C_{16}H_{20}O_3H$ $[M+H]^+$ 261.1491, found 261.1497.



2L

4,4-dimethyl-1-oxopentan-3-yl benzoate (2L) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 60/1) as yellow oil (65.3 mg, 56%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.79 (dd, *J* = 3.2, 1.6 Hz, 1 H), 8.05 – 7.99 (m, 2 H), 7.57 (d, *J* = 7.4 Hz, 1 H), 7.44 (t, *J* = 7.8 Hz, 2 H), 5.41 (dd, *J* = 8.6, 3.7 Hz, 1 H), 2.79 – 2.63 (m, 2 H), 1.03 (s, 9 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.14, 166.11, 133.19, 129.66, 128.46, 75.96, 44.97, 34.84, 25.85. HRMS (ESI) calculated for $C_{15}H_{20}O_3H$ $[M+H]^+$

235.1334, found 235.1337.



2M

2-methyl-4-oxobutan-2-yl benzoate (2M) was prepared according to the general procedure and purified by flash column chromatography (PE/EA = 60/1) as yellow oil (30.9 mg, 30%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.88 (t, *J* = 2.6 Hz, 1 H), 8.02 – 7.92 (m, 2 H), 7.59 – 7.51 (m, 1 H), 7.46 – 7.40 (m, 2 H), 3.01 (d, *J* = 2.6 Hz, 2 H), 1.72 (s, 6 H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 200.04, 165.68, 132.94, 131.06, 129.49, 128.36, 80.27, 53.61, 26.84. HRMS (ESI) calculated for $C_{12}H_{14}O_3H$ [M+H]$^+$ 207.1021, found 207.1014.

6 NMR Spectra of 1a

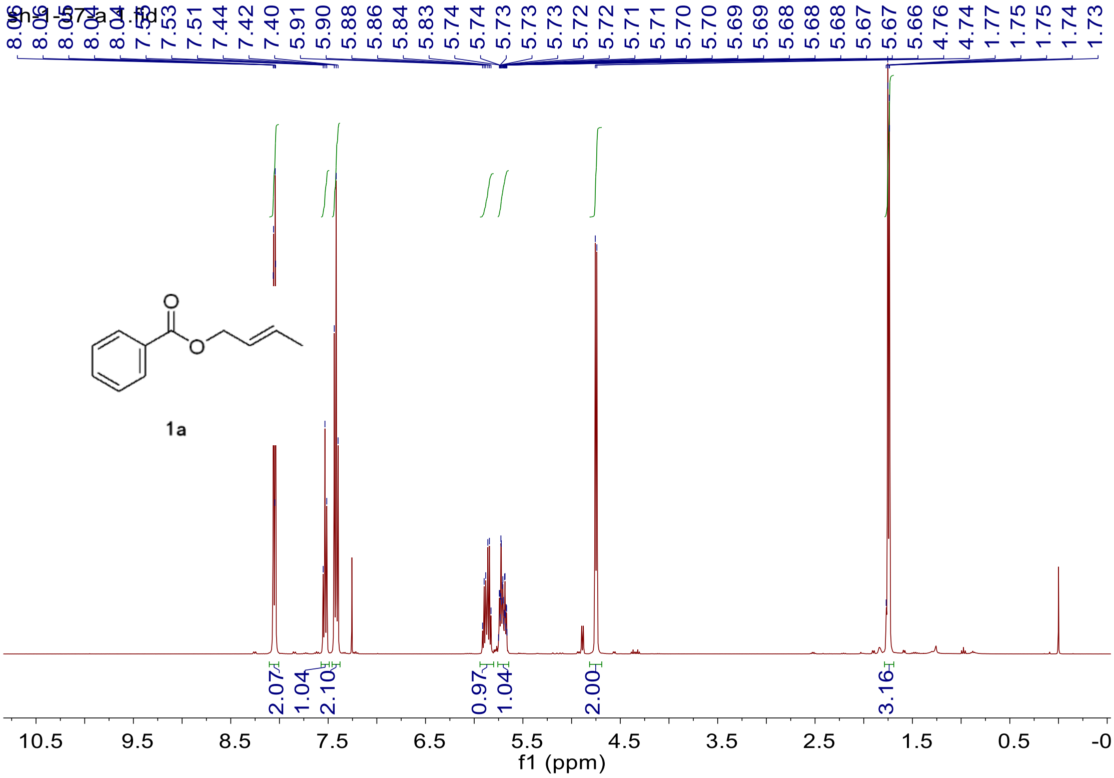


Figure 1. ^{1}H NMR of spectrum of **1a**

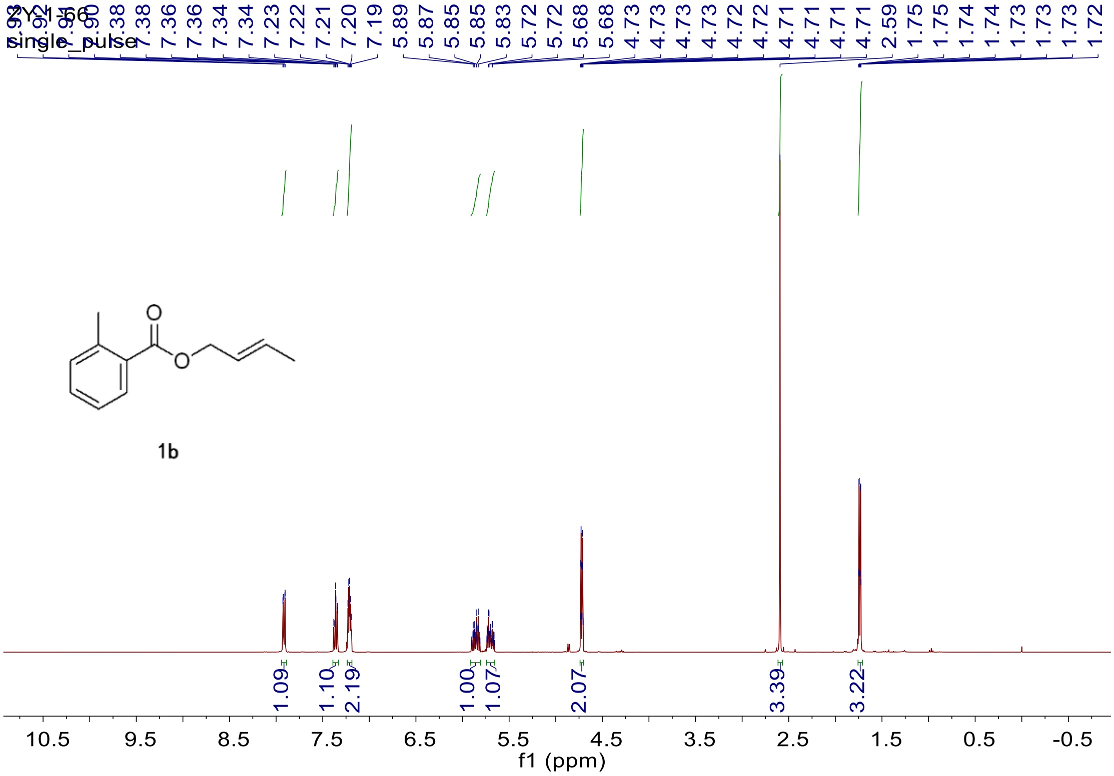


Figure 2. ^{1}H NMR of spectrum of **1b**

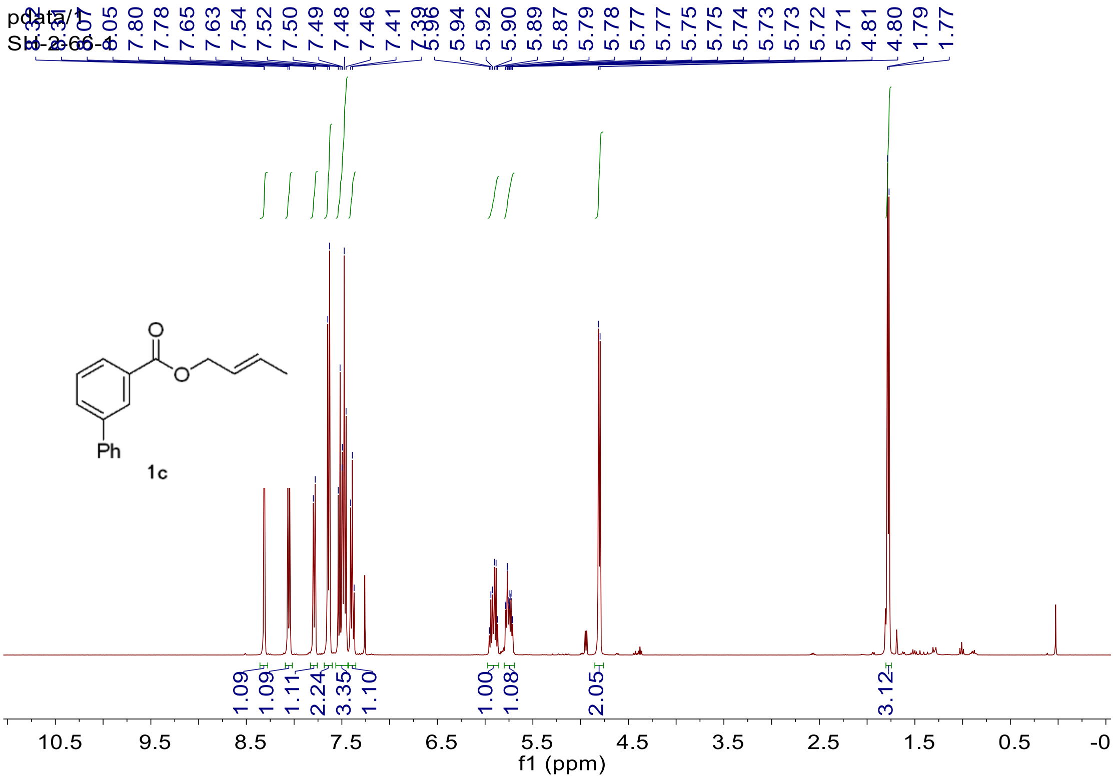


Figure 3. ^{1}H NMR of spectrum of **1c**

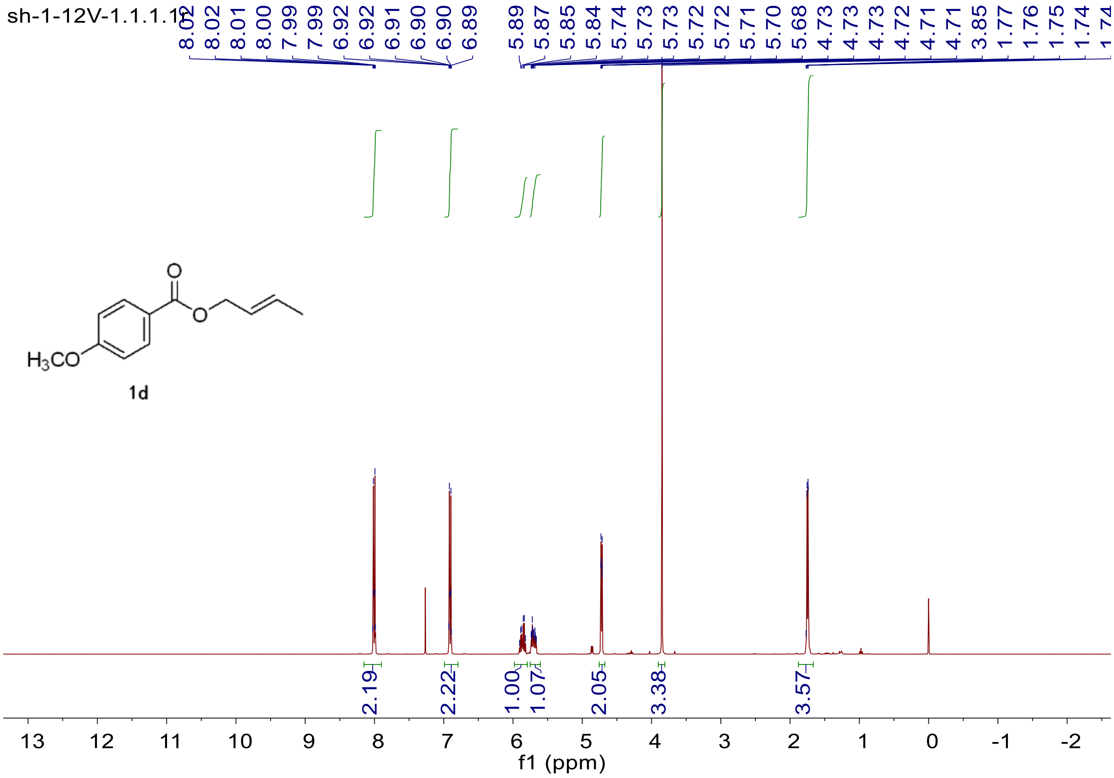


Figure 4 ^{1}H NMR of spectrum of **1d**

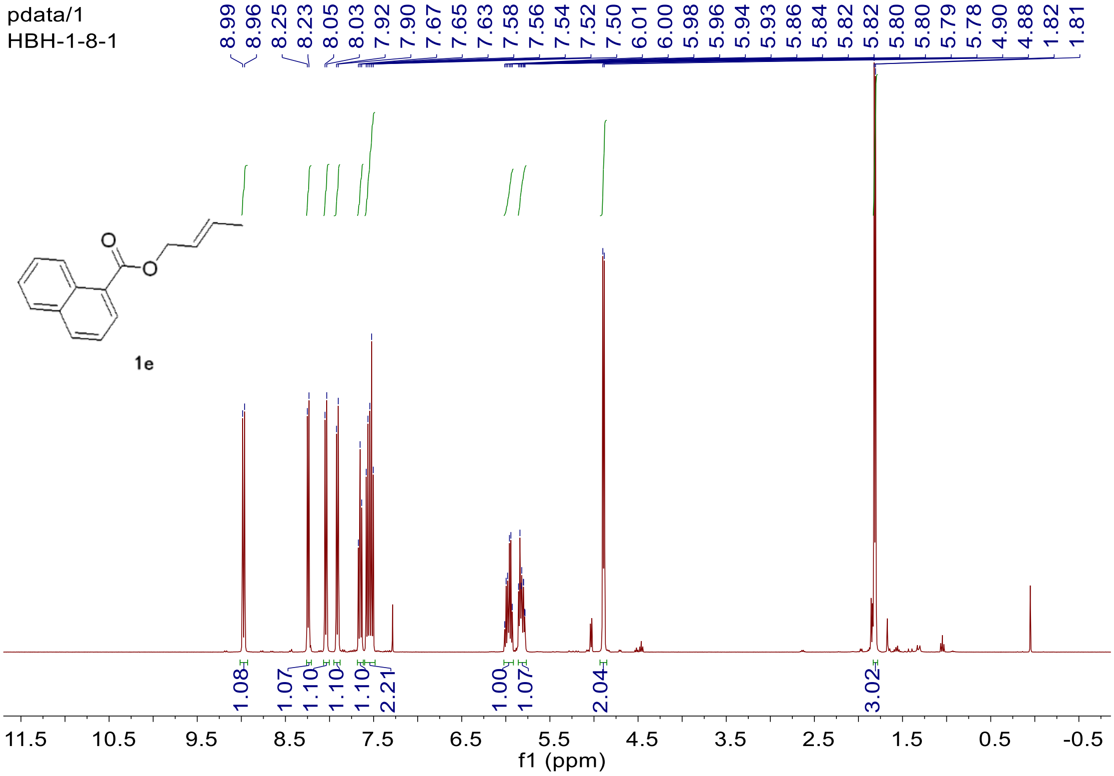


Figure 5 ^{1}H NMR of spectrum of **1e**

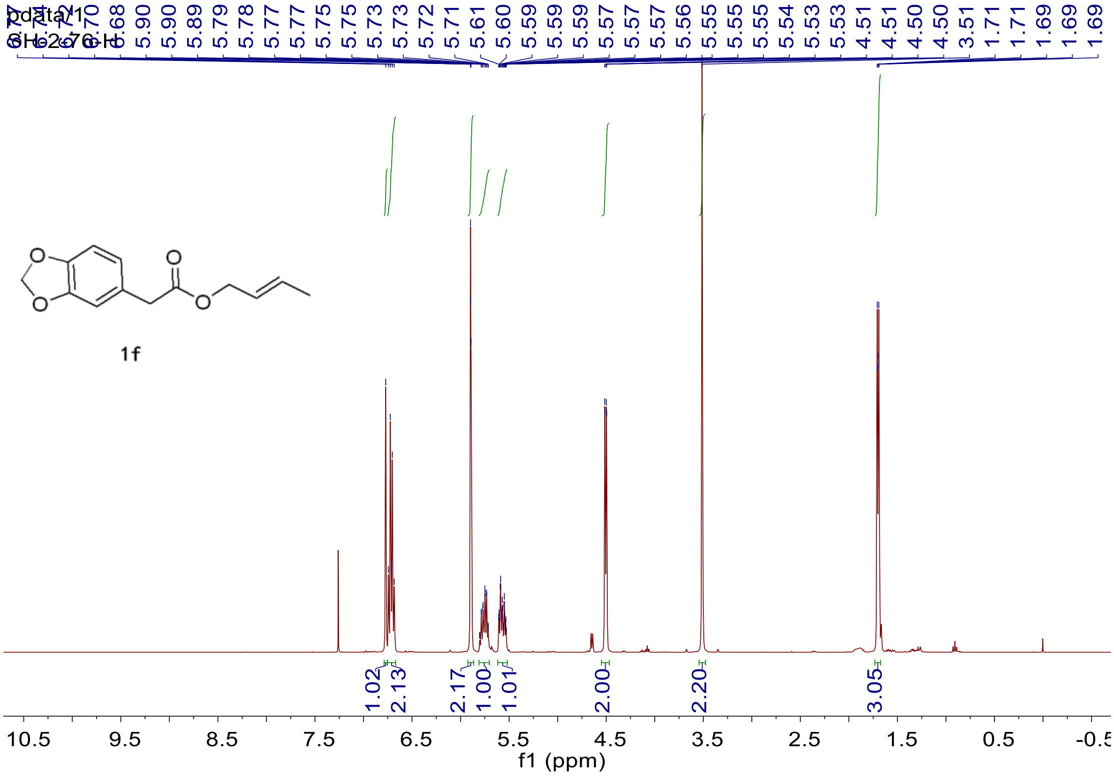


Figure 6 ^{1}H NMR of spectrum of **1f**

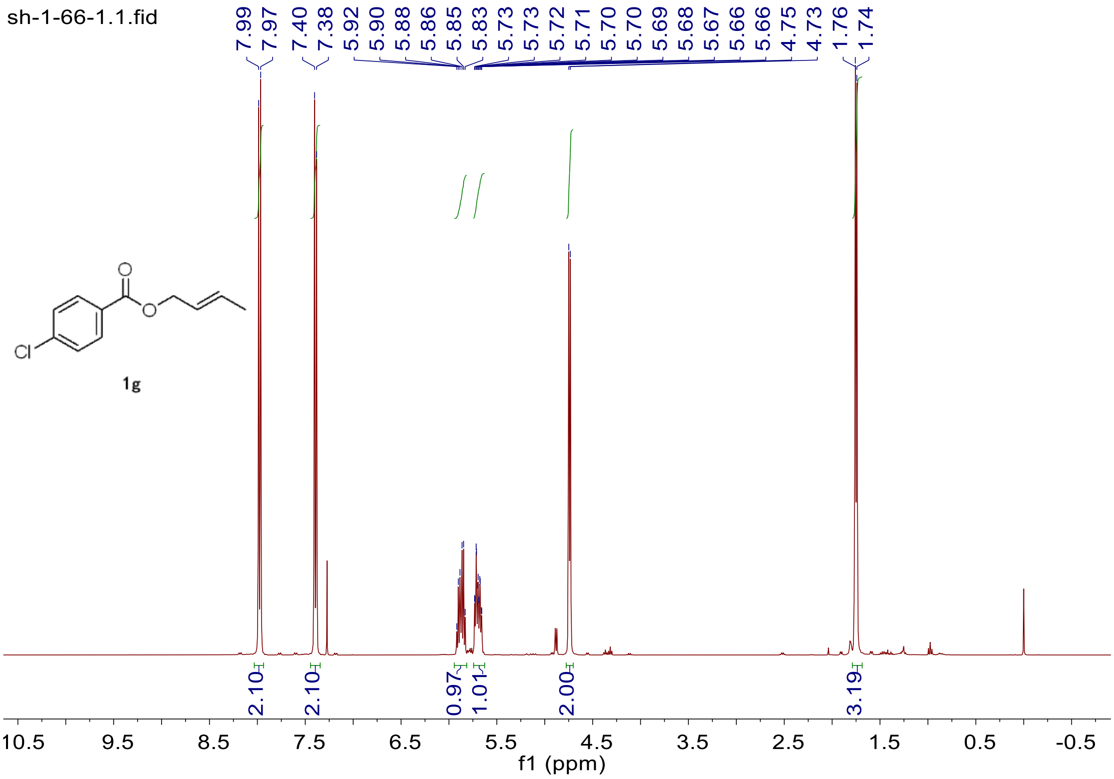


Figure 7 ^{1}H NMR of spectrum of **1g**

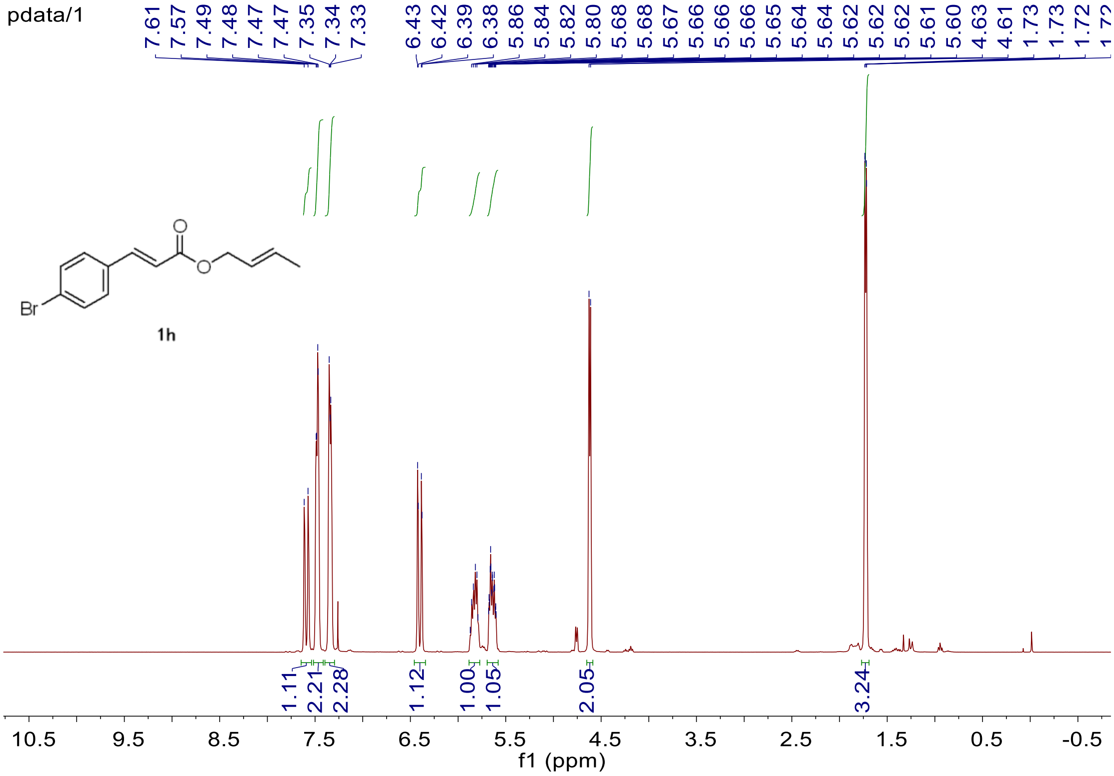


Figure 8 ^{1}H NMR of spectrum of **1h**

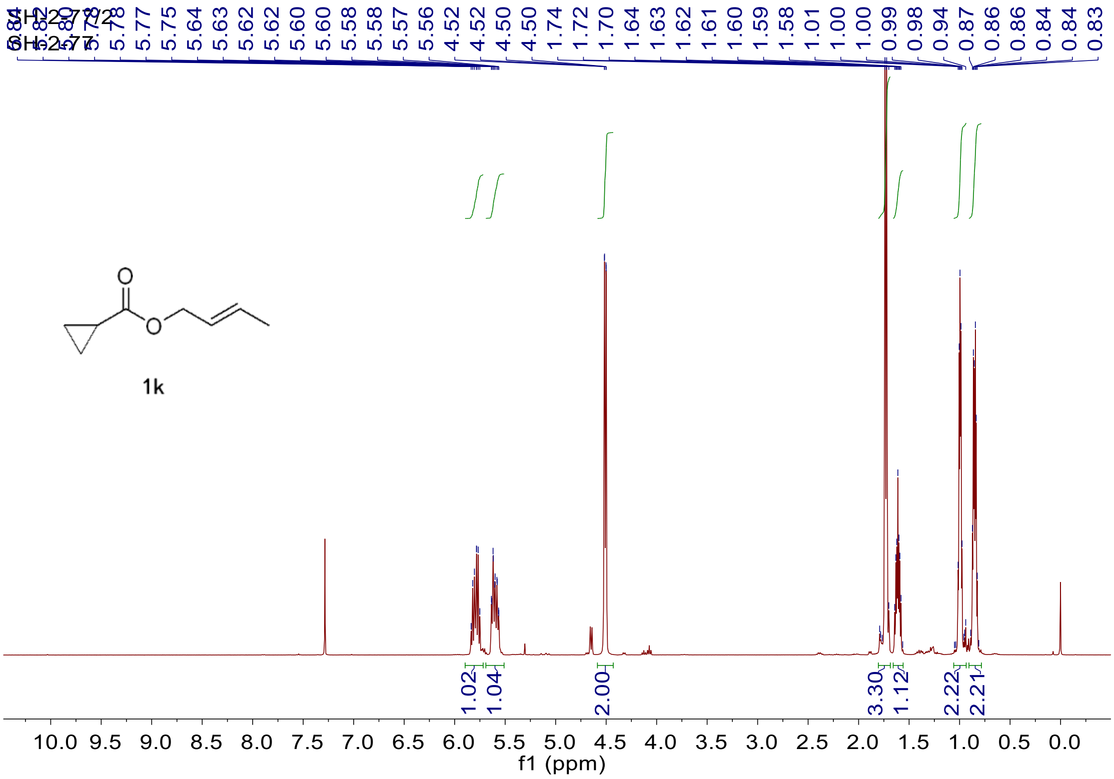


Figure 9 ^{1}H NMR of spectrum of **1k**

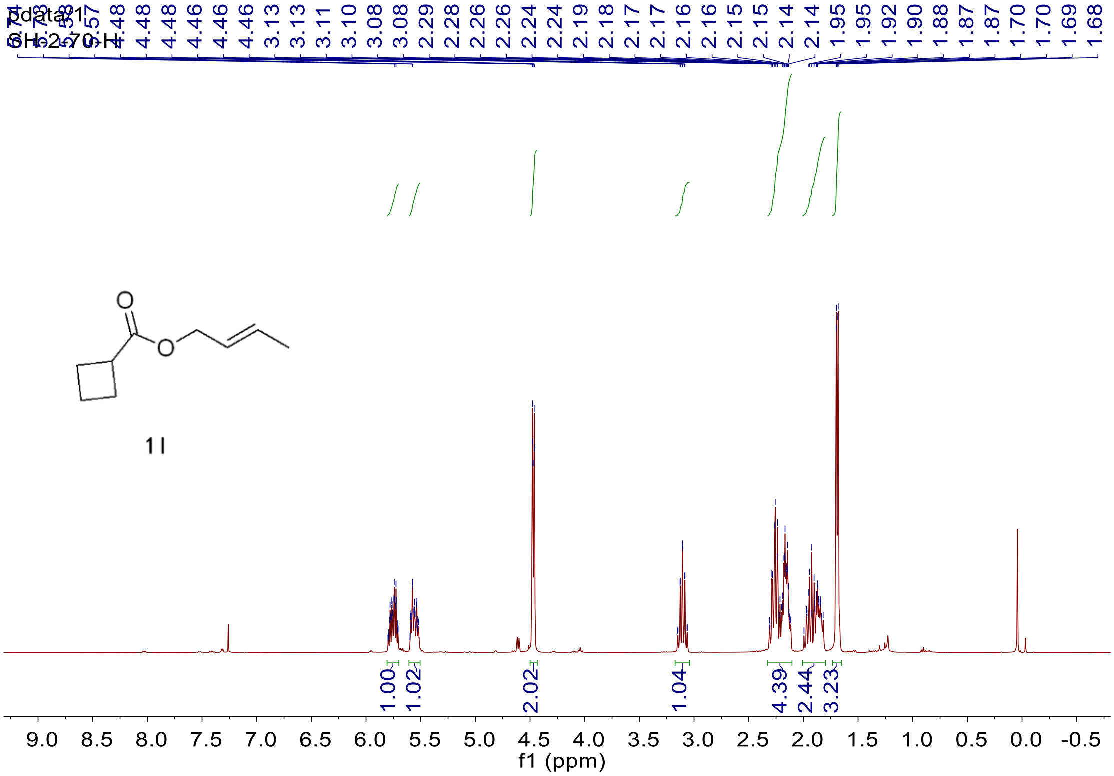


Figure 10 ^{1}H NMR of spectrum of **1l**

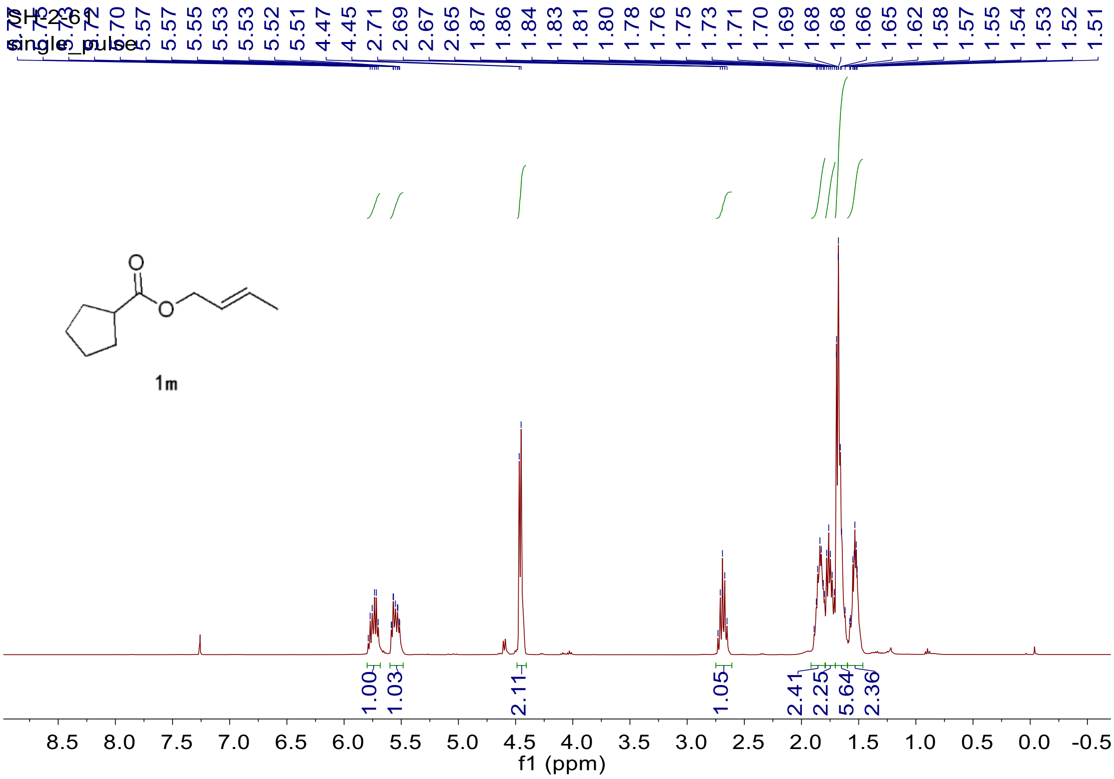


Figure 11 ^{1}H NMR of spectrum of **1m**

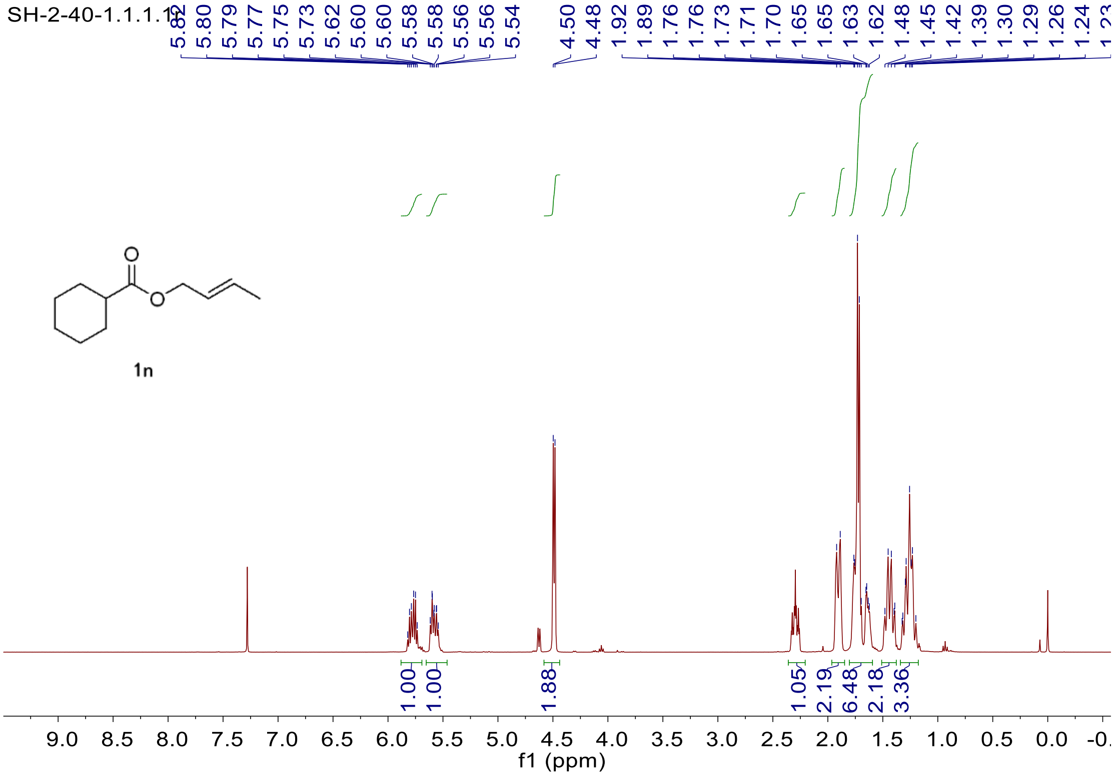


Figure 12 ^{1}H NMR of spectrum of **1n**

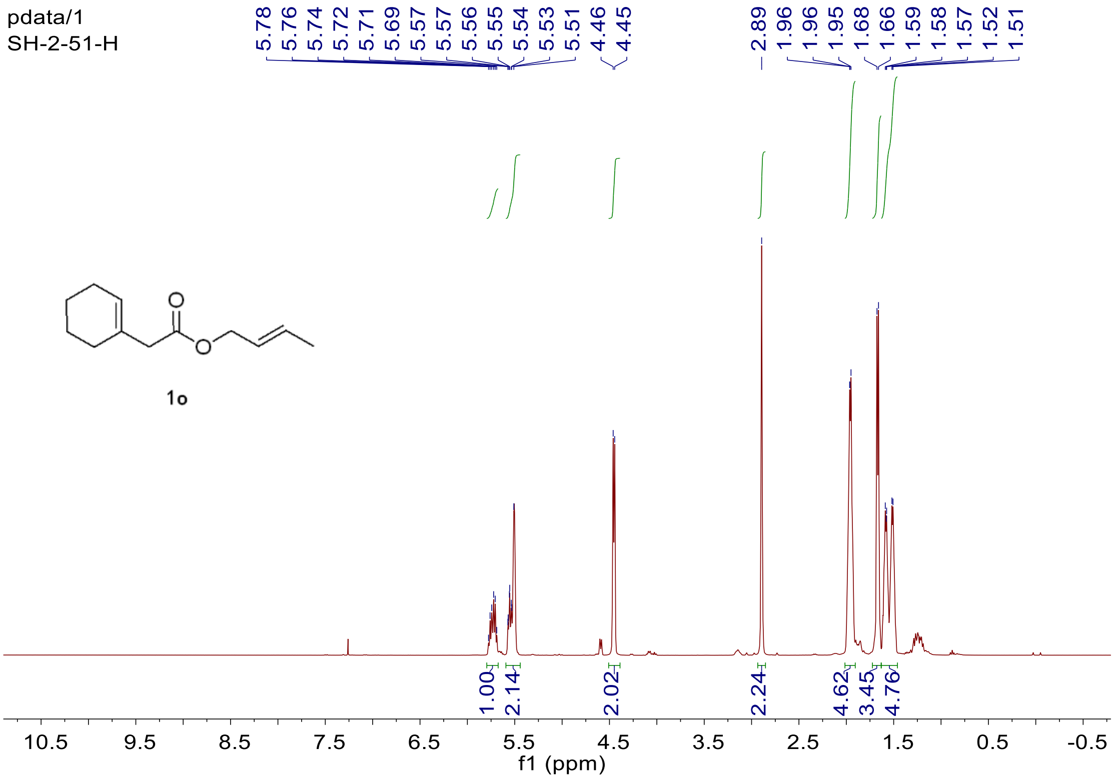


Figure 13 ^{1}H NMR of spectrum of **1o**

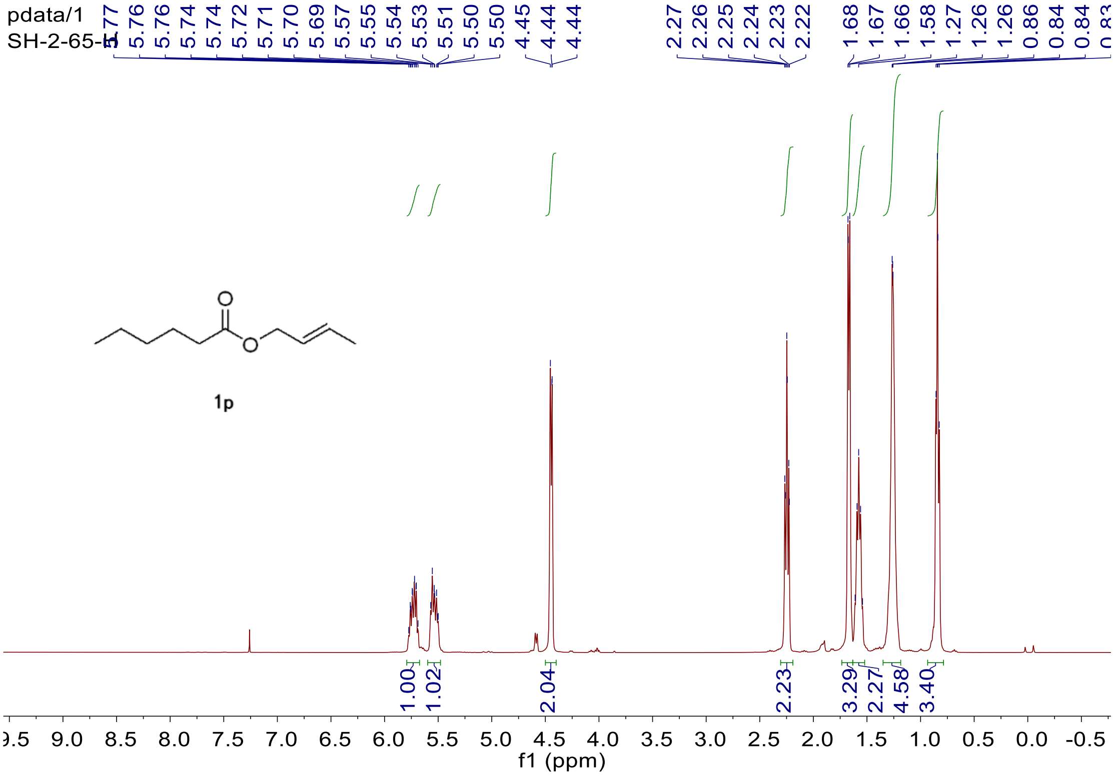


Figure 14 ^{1}H NMR of spectrum of **1p**

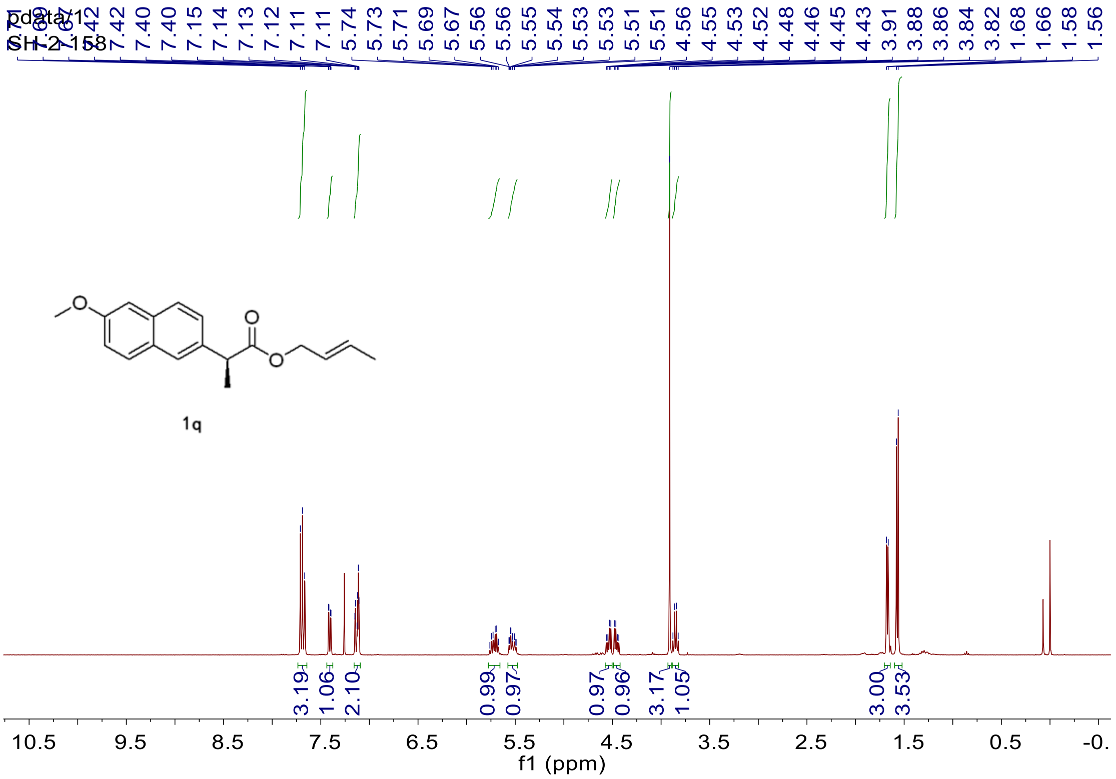


Figure 15 ^{1}H NMR of spectrum of **1q**

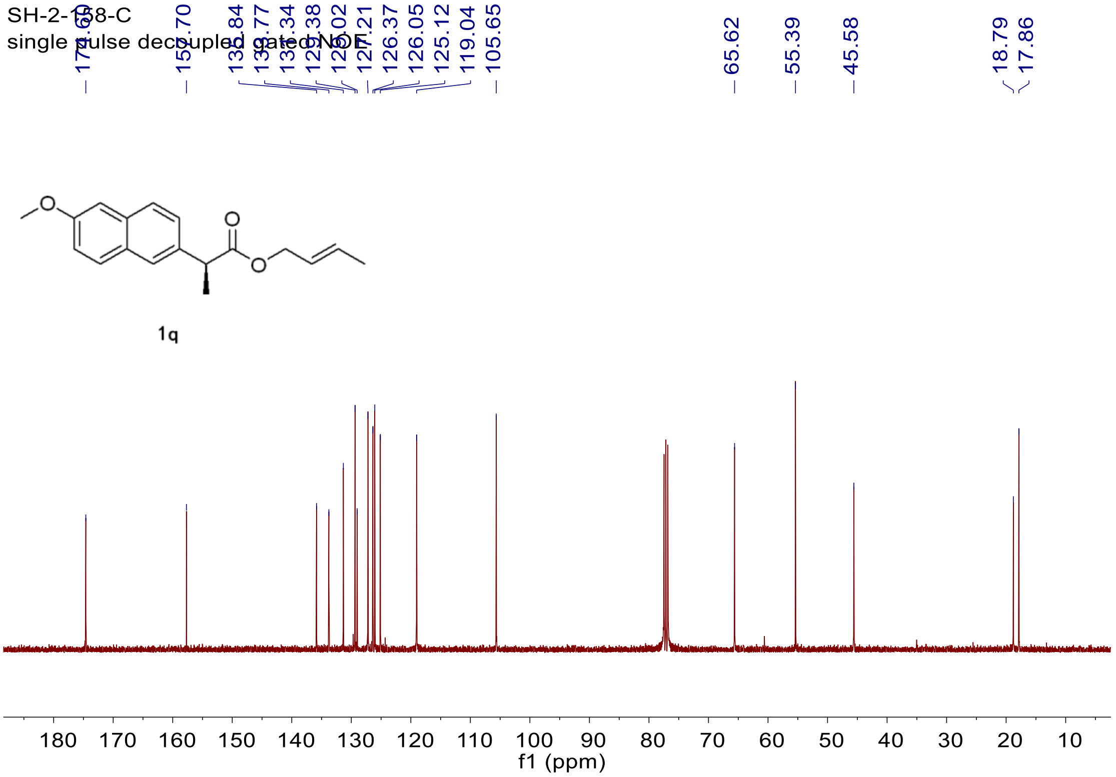


Figure 16 ^{13}C NMR of spectrum of **1q**

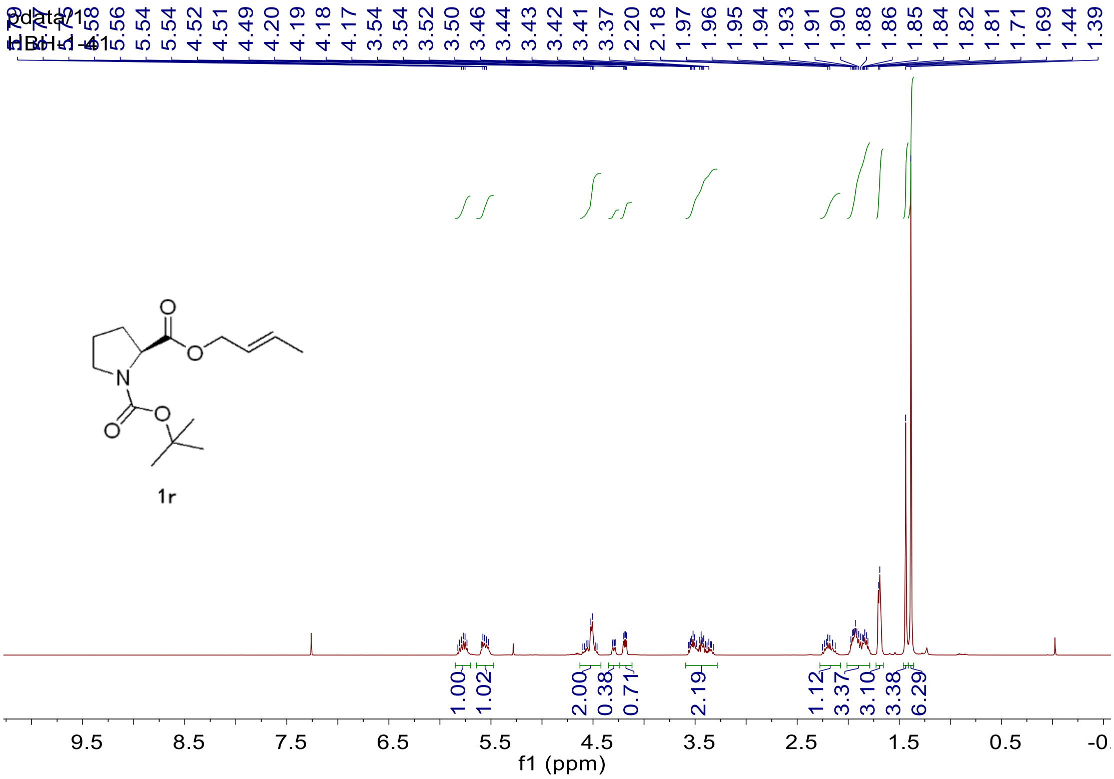


Figure 17 ^{1}H NMR of spectrum of **1r**

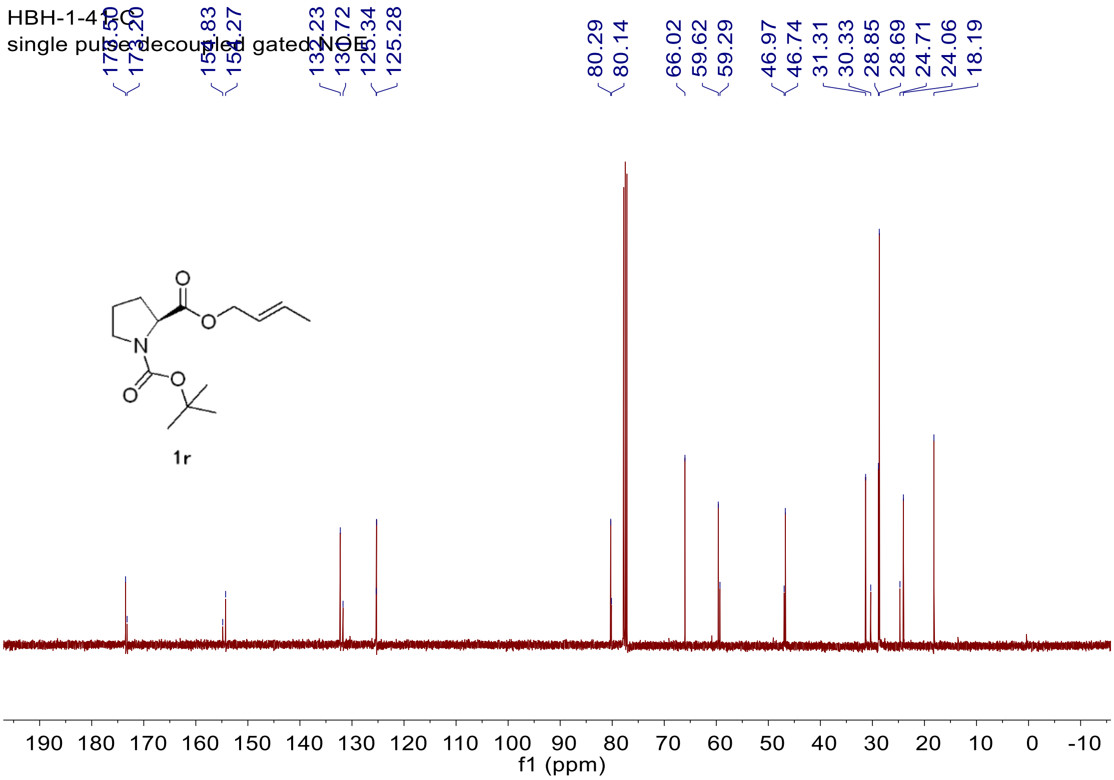


Figure 18 ^{13}C NMR of spectrum of **1r**

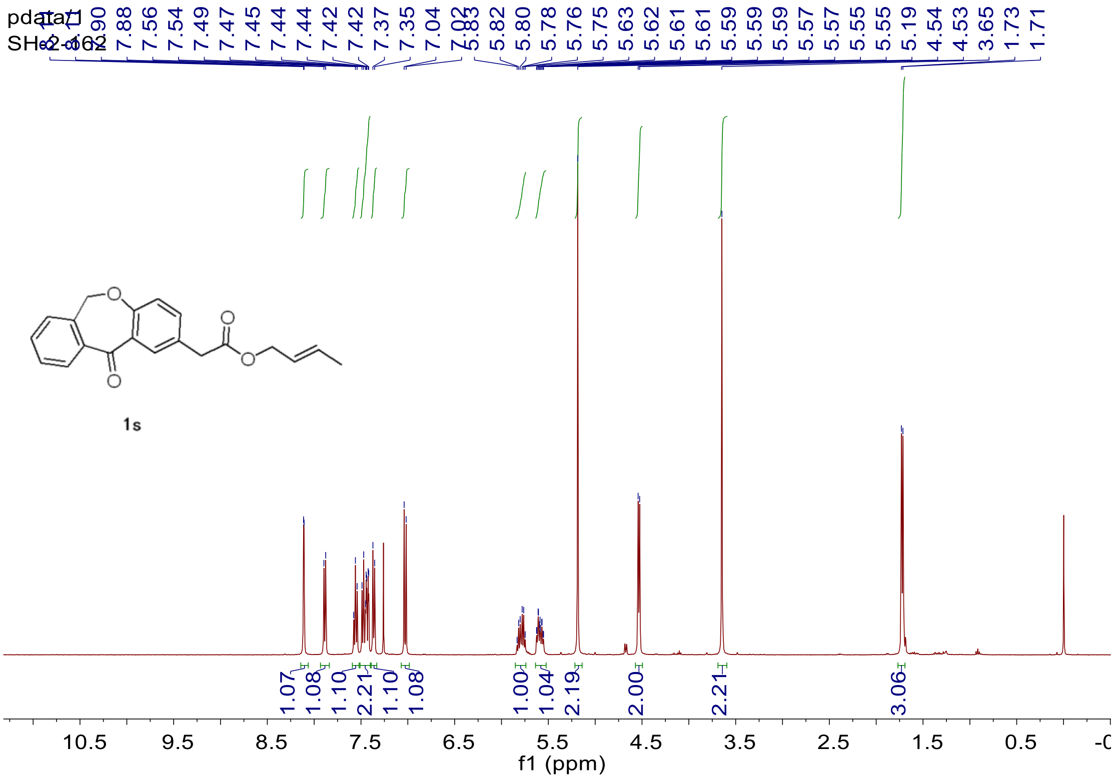


Figure 19 ^{1}H NMR of spectrum of **1s**

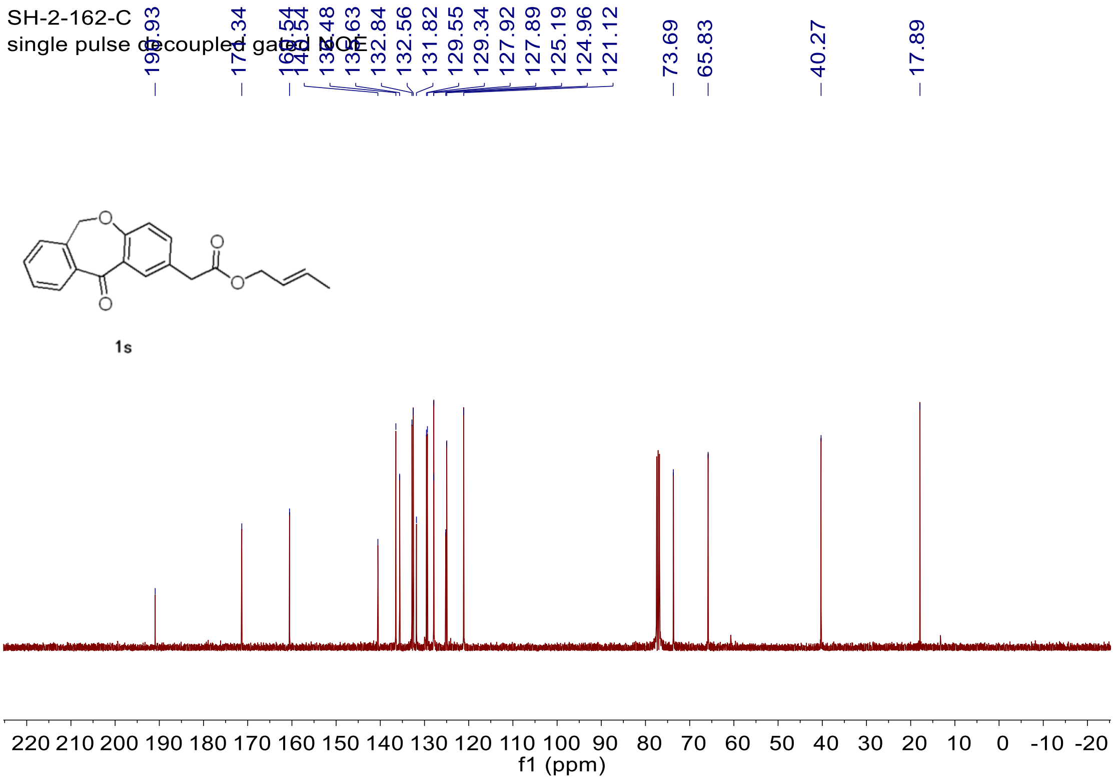


Figure 20 ^{13}C NMR of spectrum of **1s**

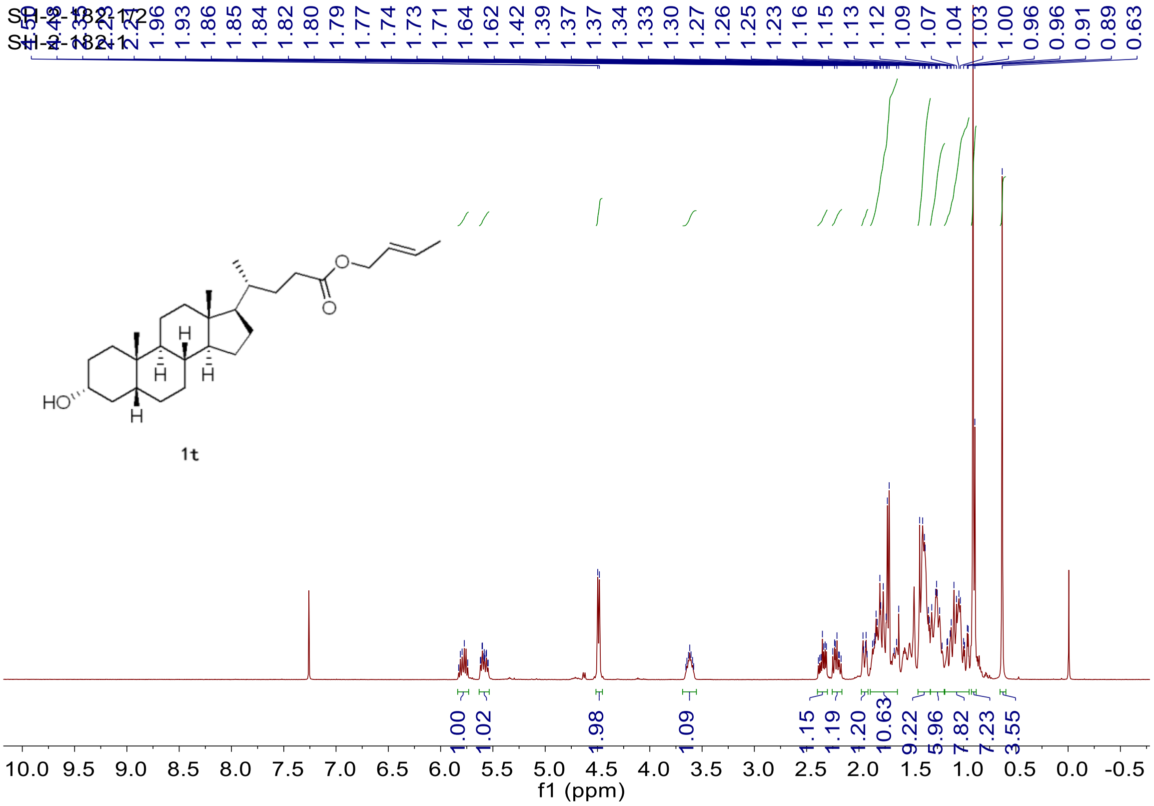


Figure 21 ^{1}H NMR of spectrum of **1t**

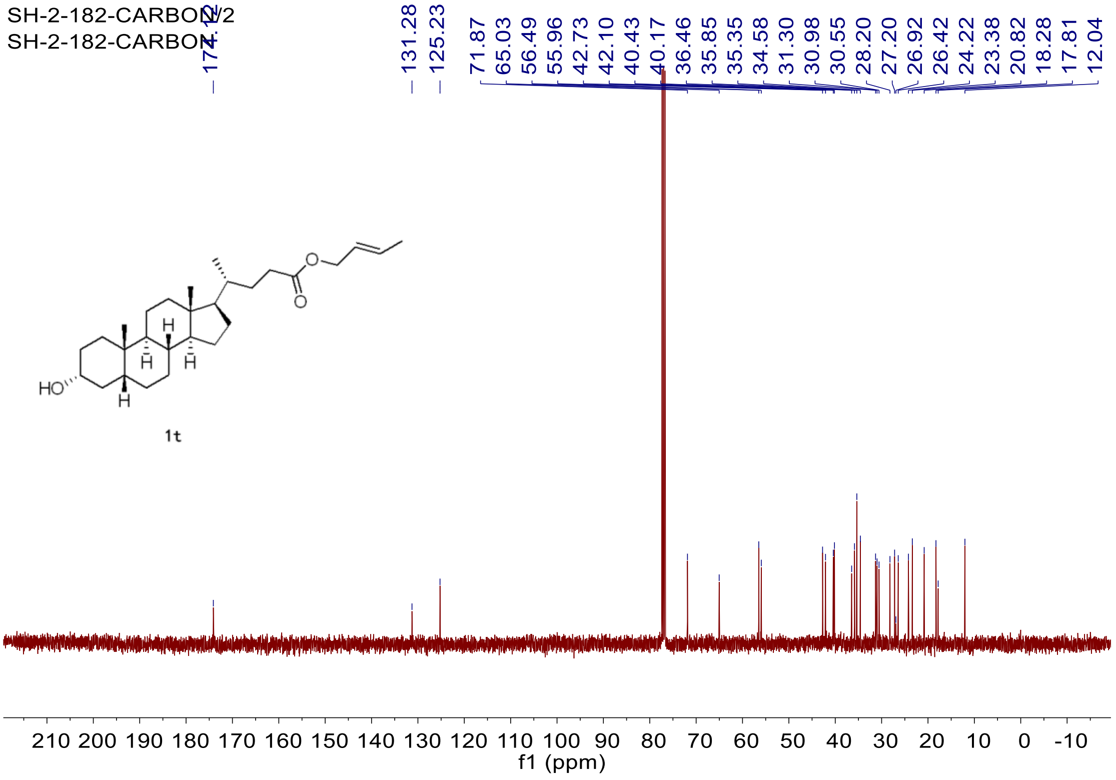


Figure 22 ^{13}C NMR of spectrum of **1t**

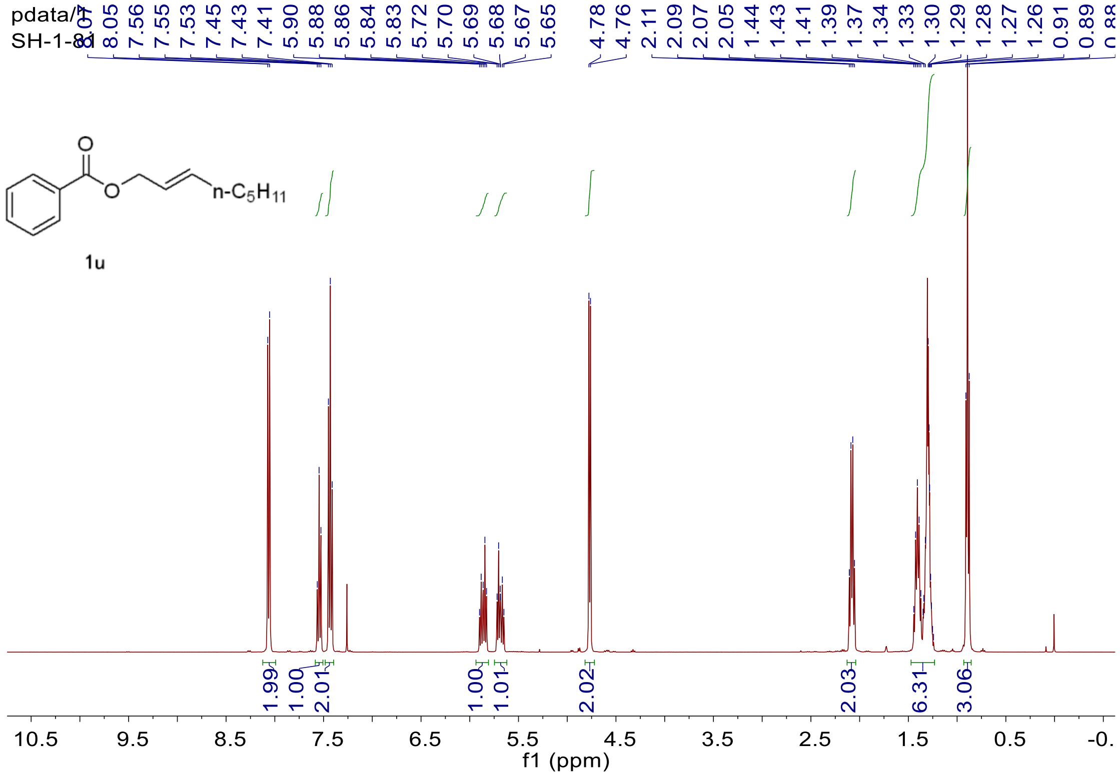


Figure 23 ^{1}H NMR of spectrum of **1u**

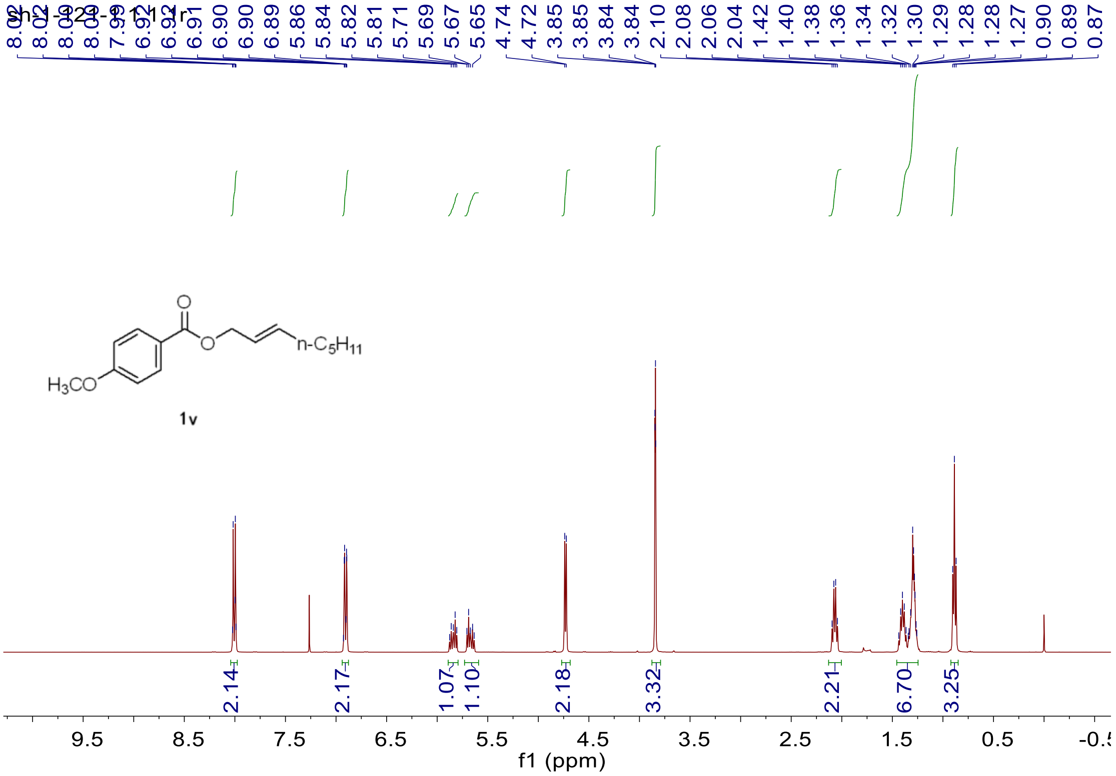


Figure 24 ^{1}H NMR of spectrum of **1v**

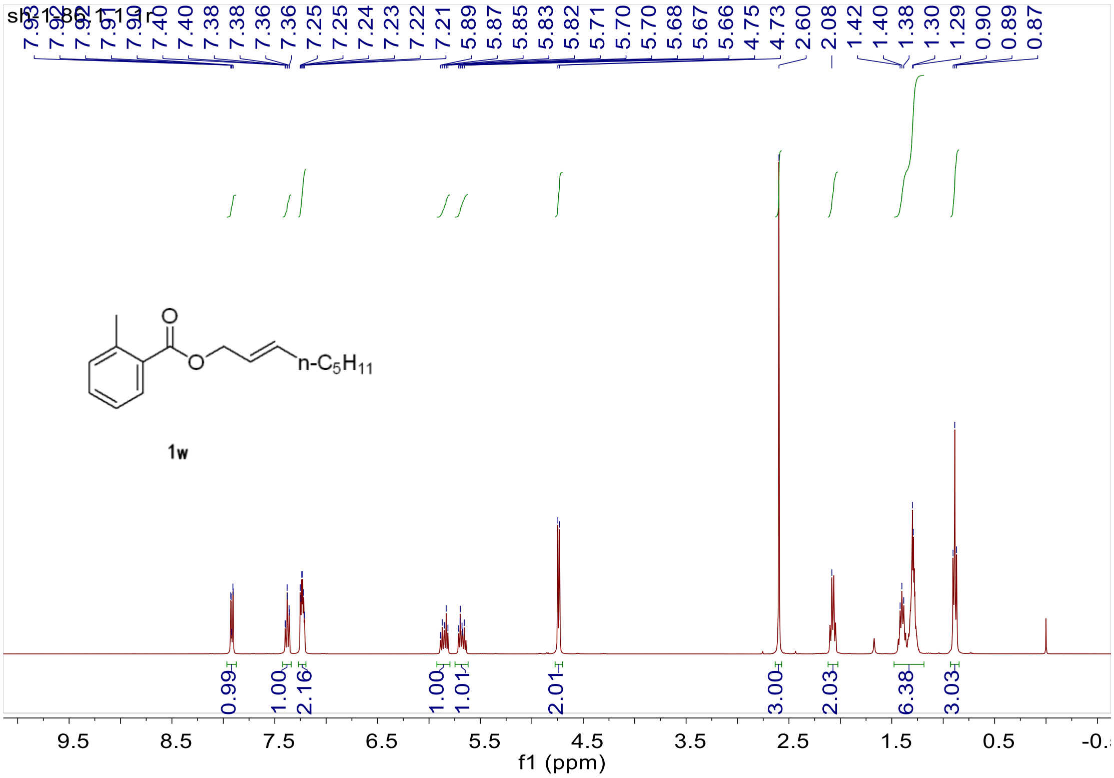


Figure 25 ^{1}H NMR of spectrum of **1w**

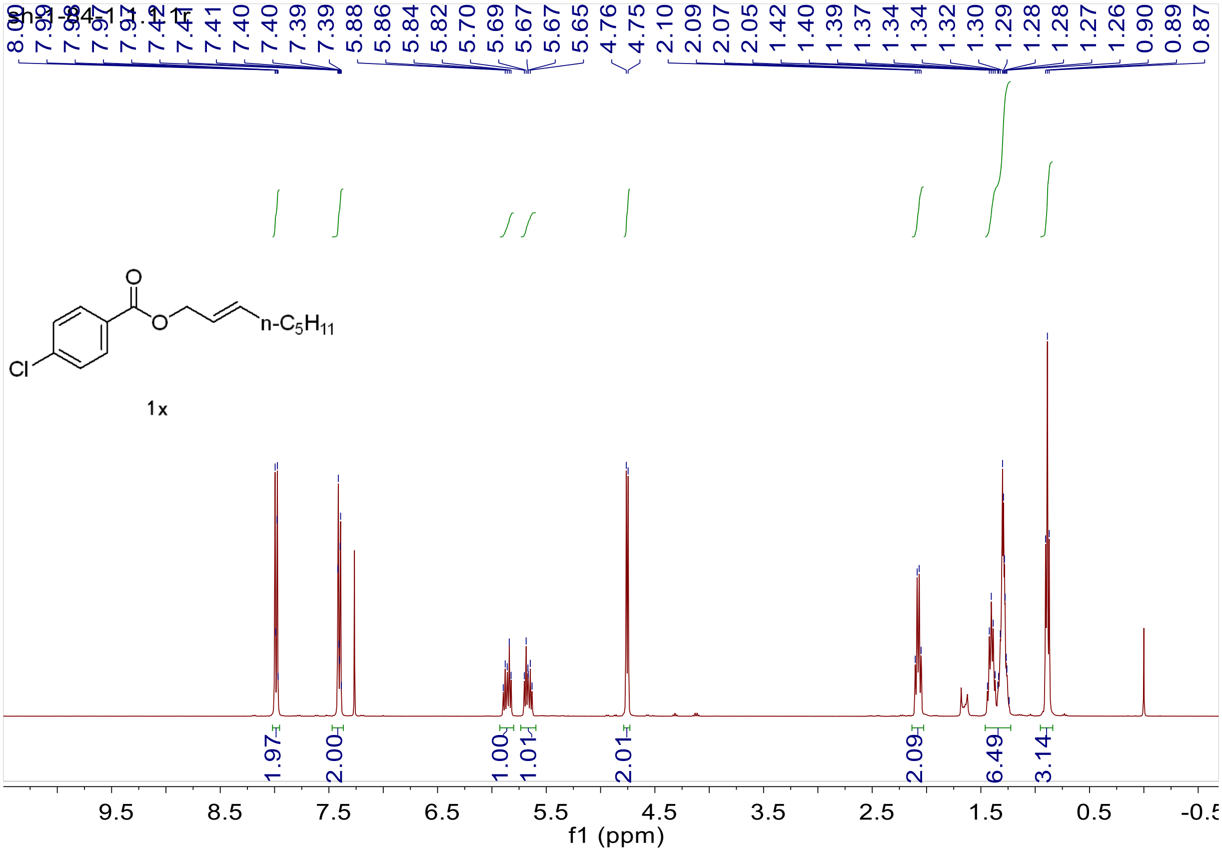


Figure 26 ^{1}H NMR of spectrum of **1x**

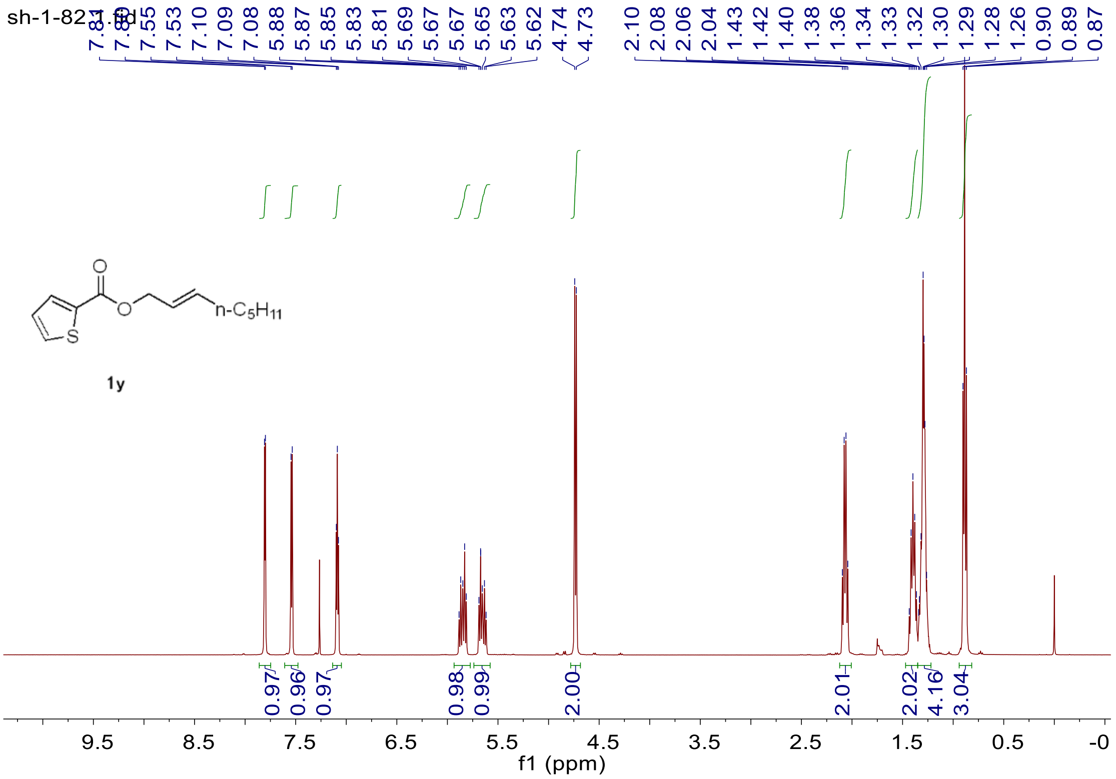


Figure 27 ^{1}H NMR of spectrum of **1y**

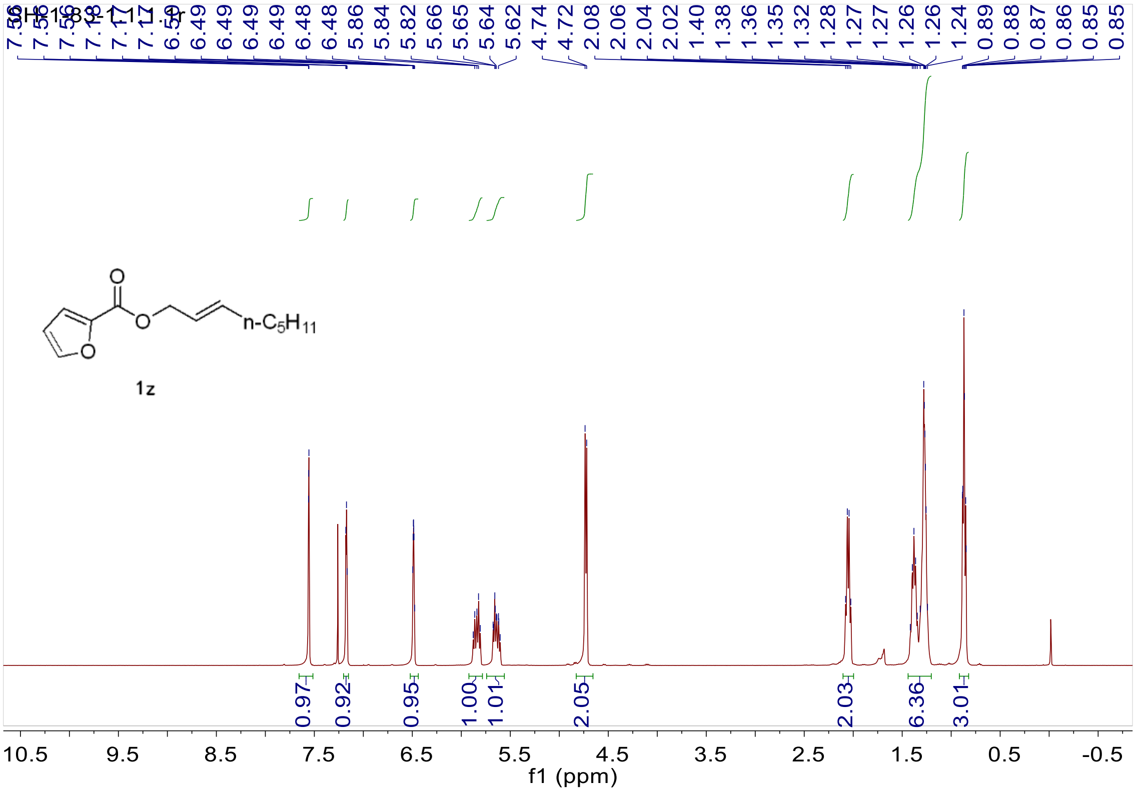


Figure 28 ^{1}H NMR of spectrum of **1z**

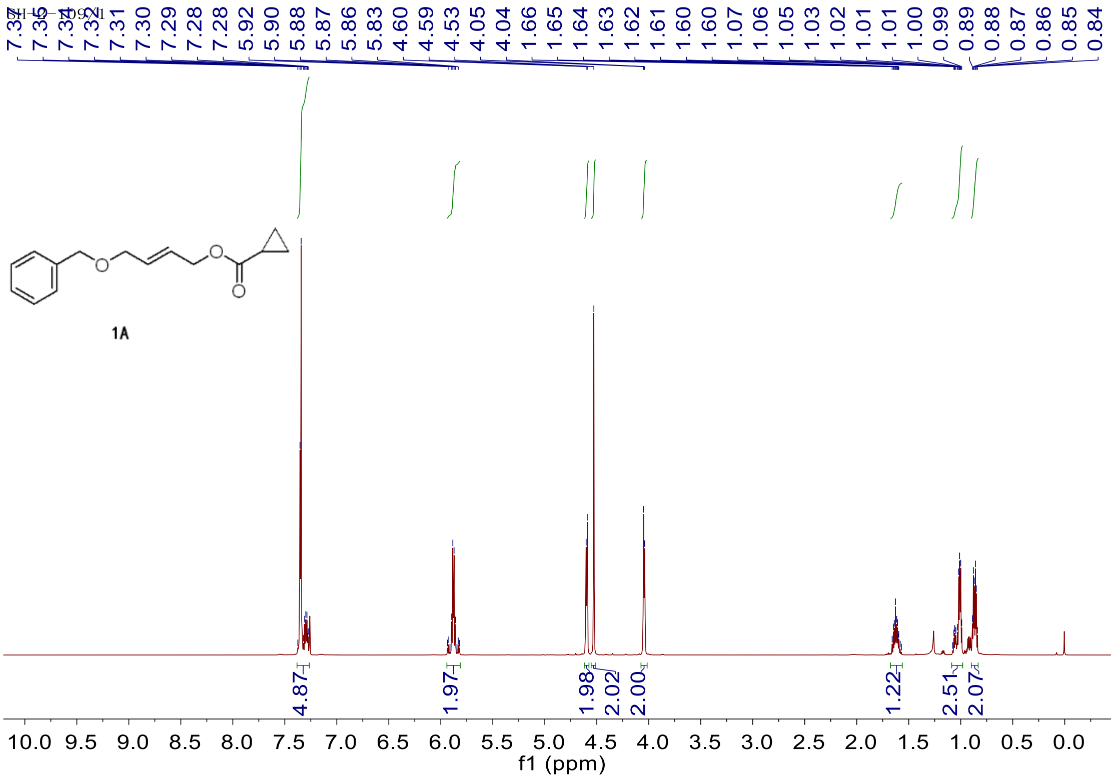


Figure 29 ^{1}H NMR of spectrum of **1A**

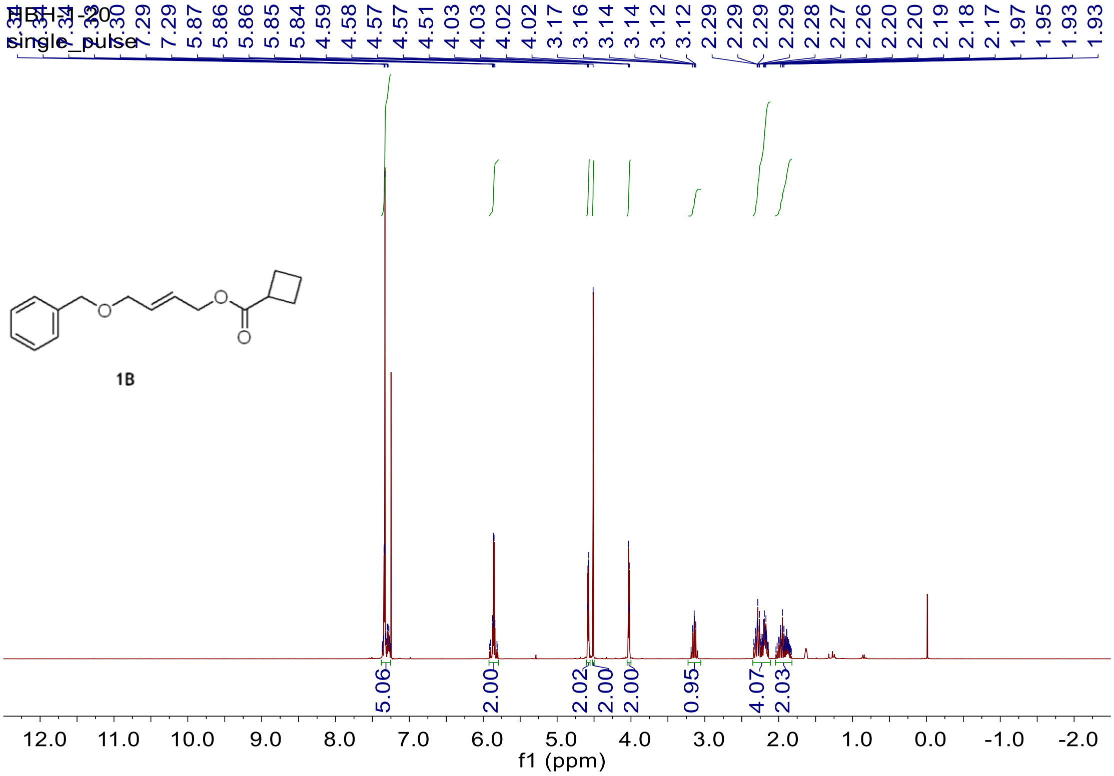


Figure 30 ^{1}H NMR of spectrum of **1B**

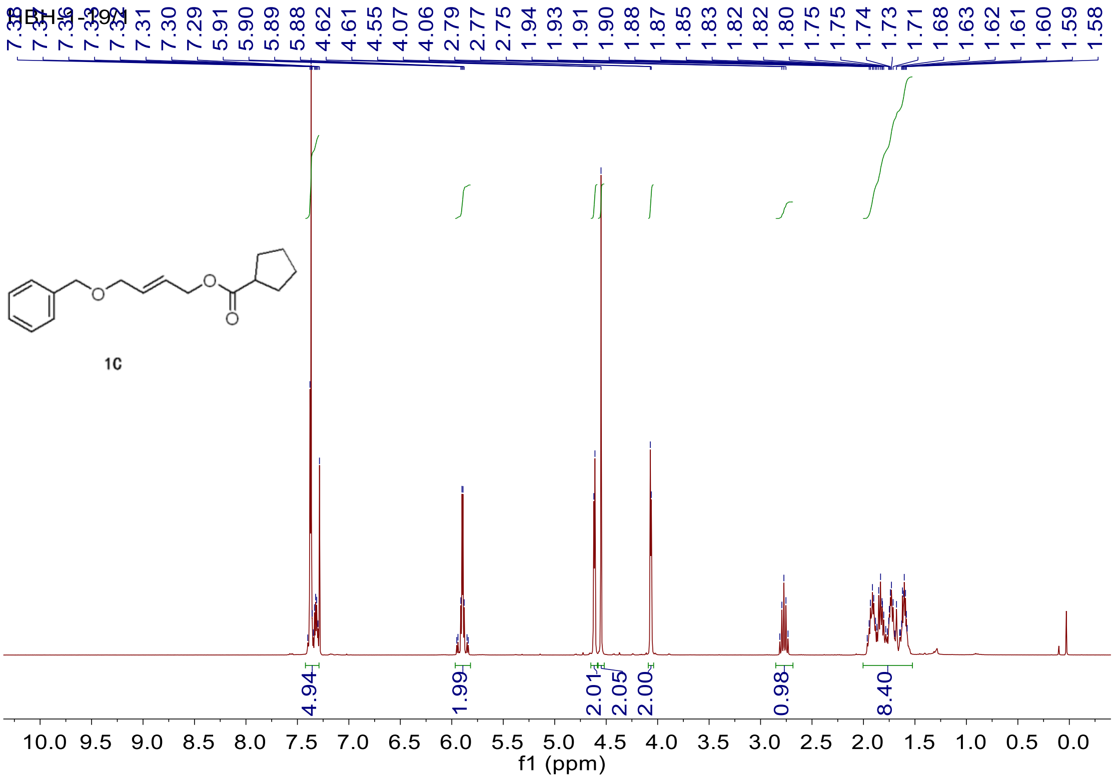


Figure 31 ^{1}H NMR of spectrum of **1C**

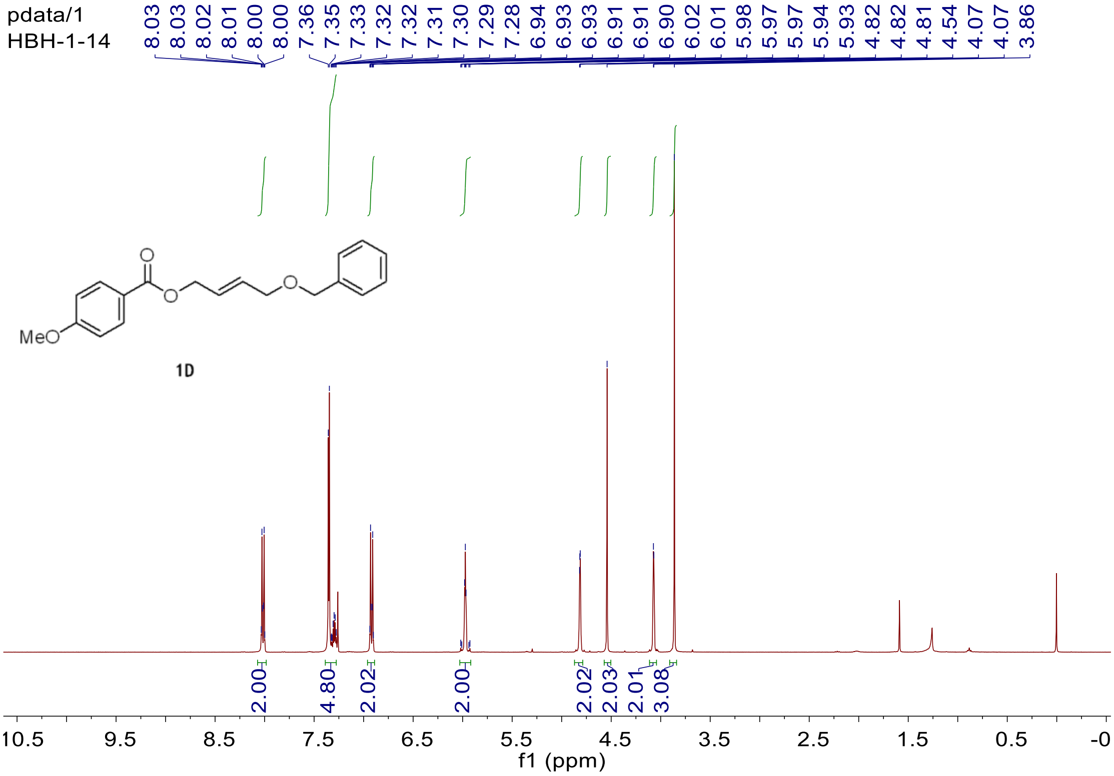


Figure 32 ^{1}H NMR of spectrum of **1D**

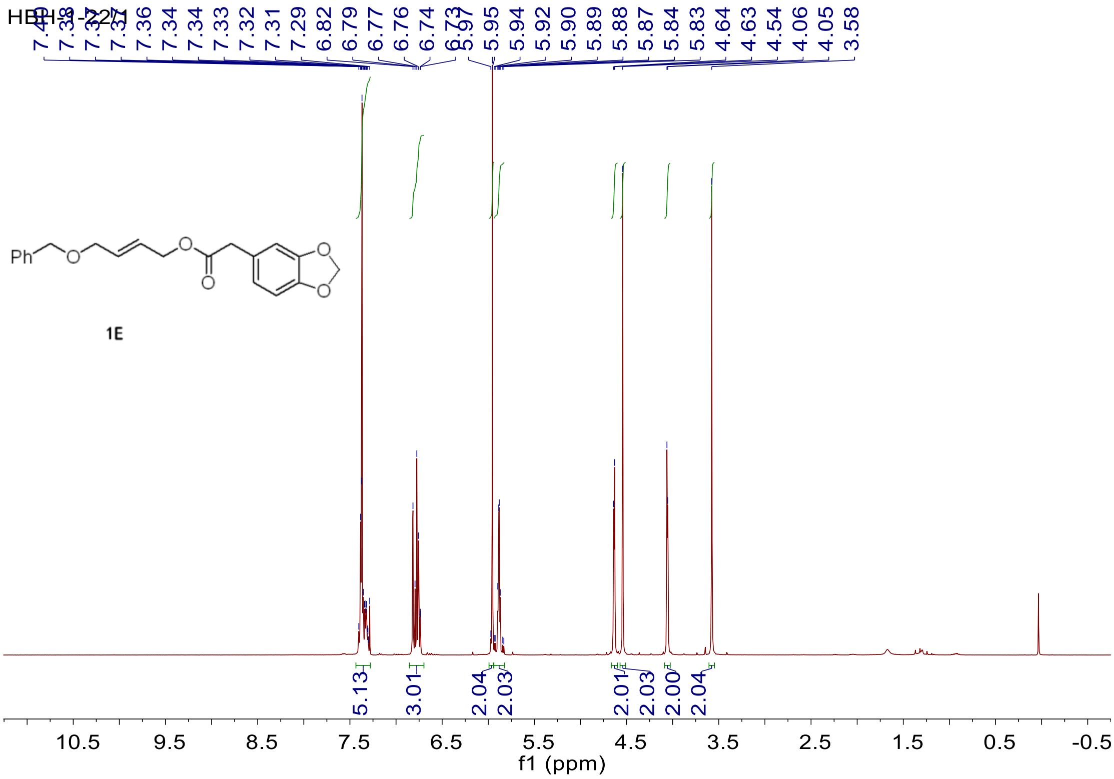


Figure 33 ^{1}H NMR of spectrum of **1E**

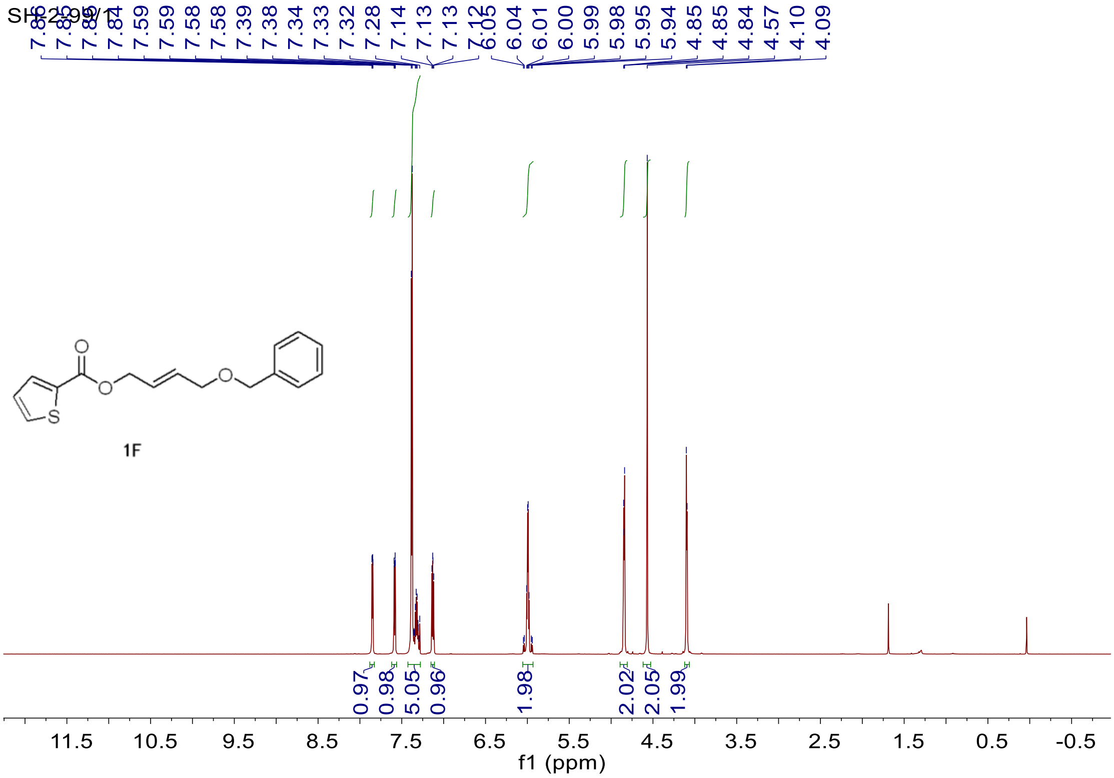


Figure 34 ^{1}H NMR of spectrum of **1F**

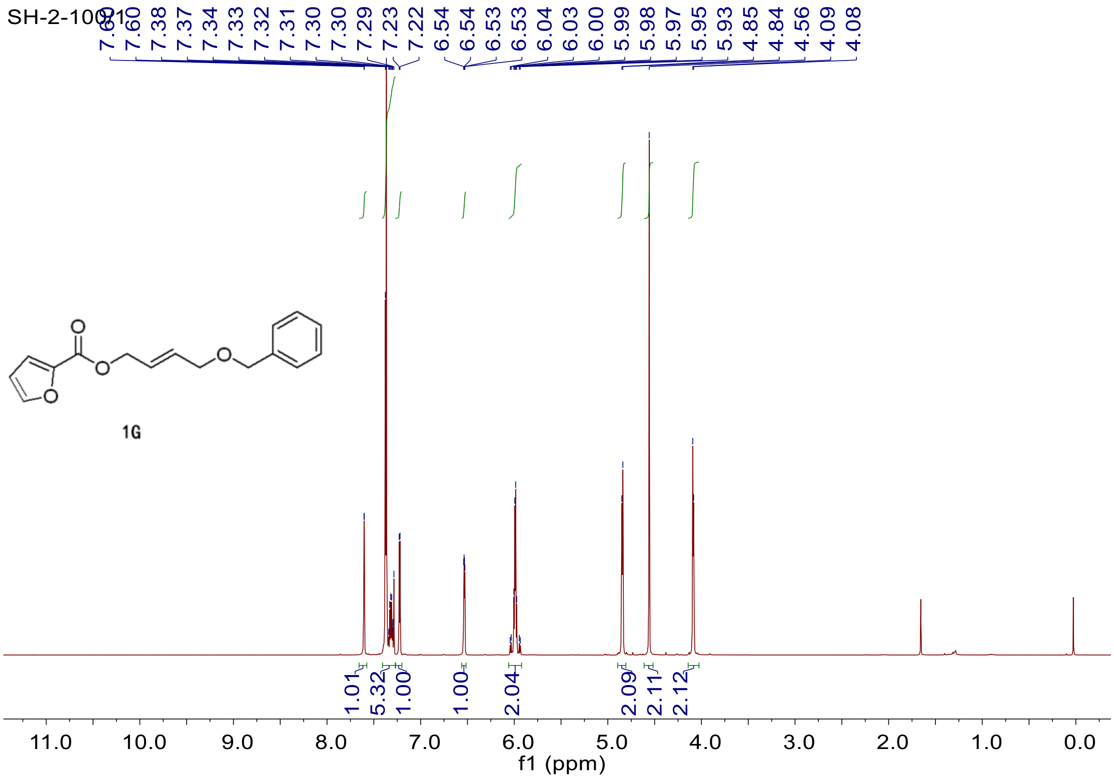


Figure 35 ^{1}H NMR of spectrum of **1G**

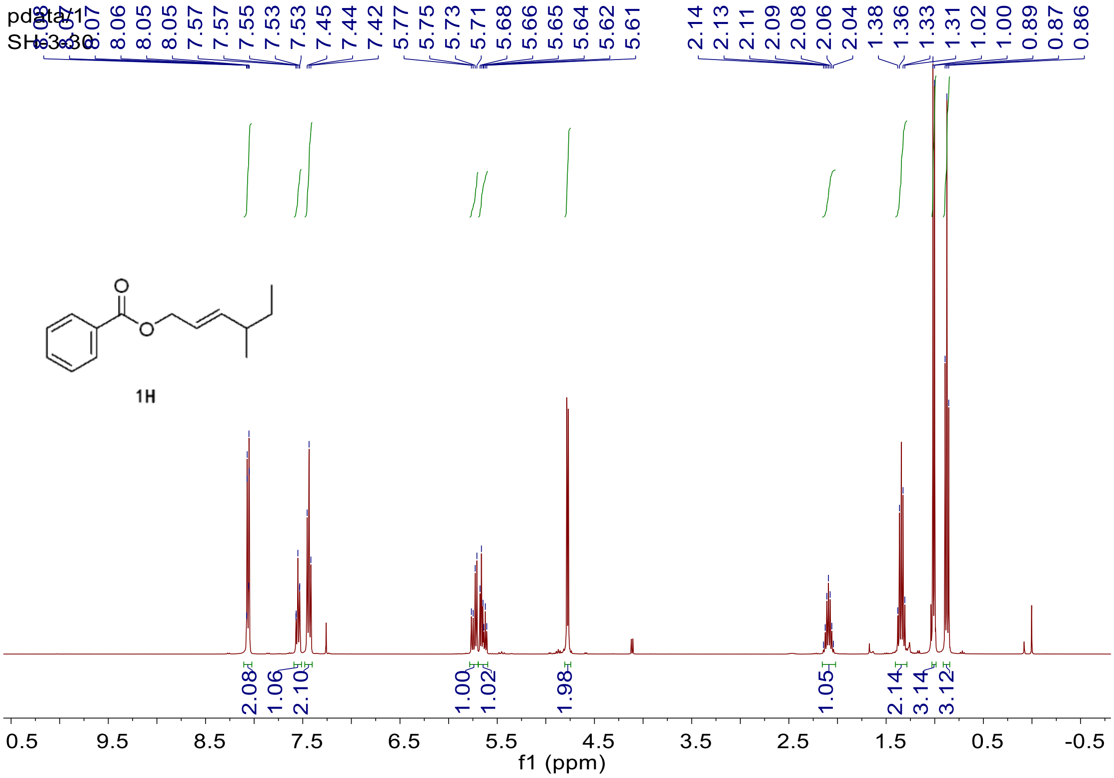


Figure 36 ^{1}H NMR of spectrum of **1H**

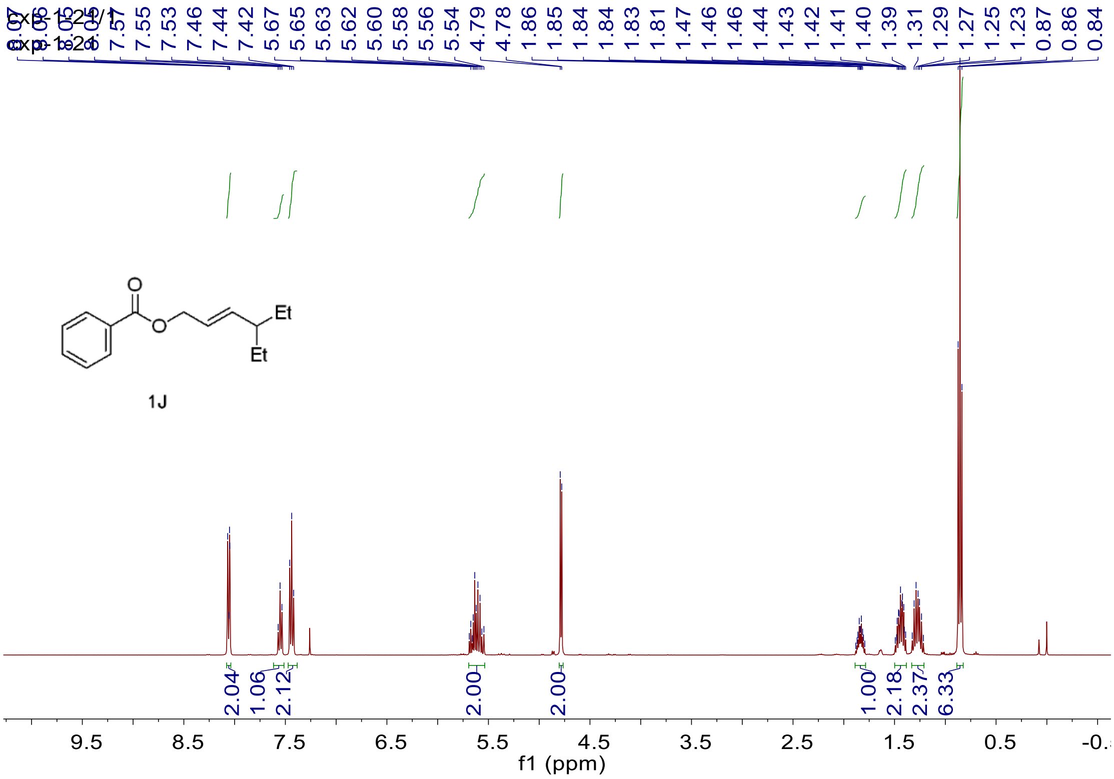


Figure 37 ^{1}H NMR of spectrum of **1J**

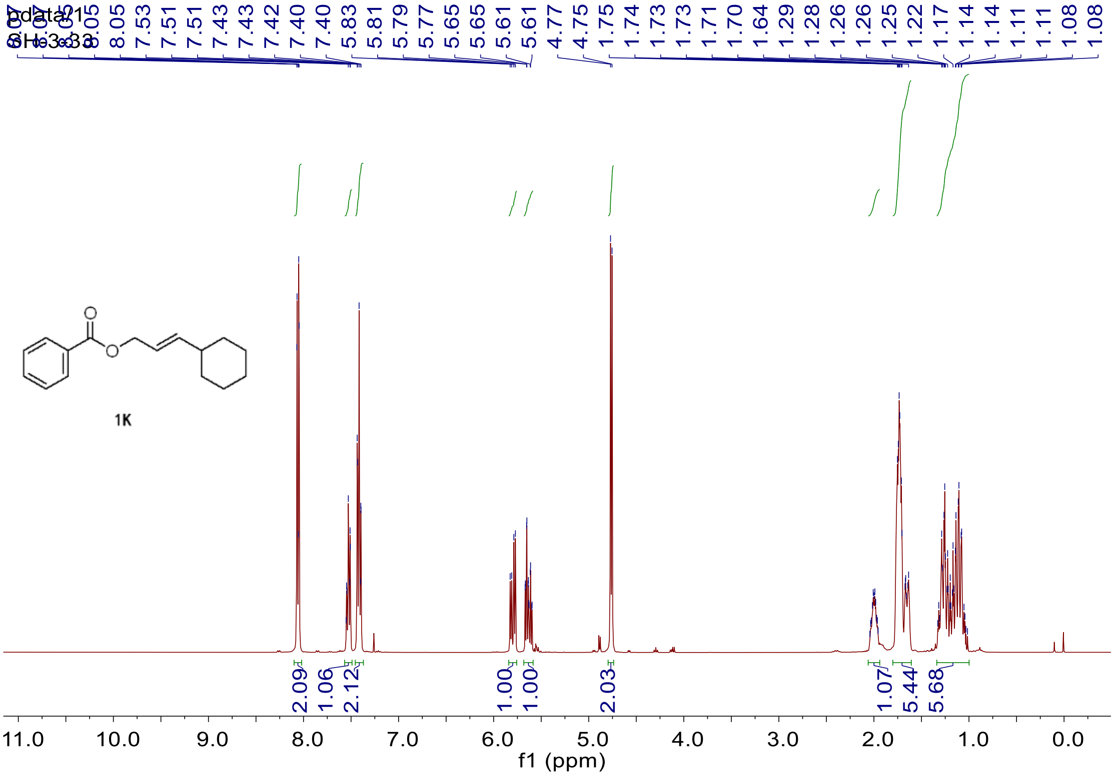


Figure 38 ^{1}H NMR of spectrum of **1K**

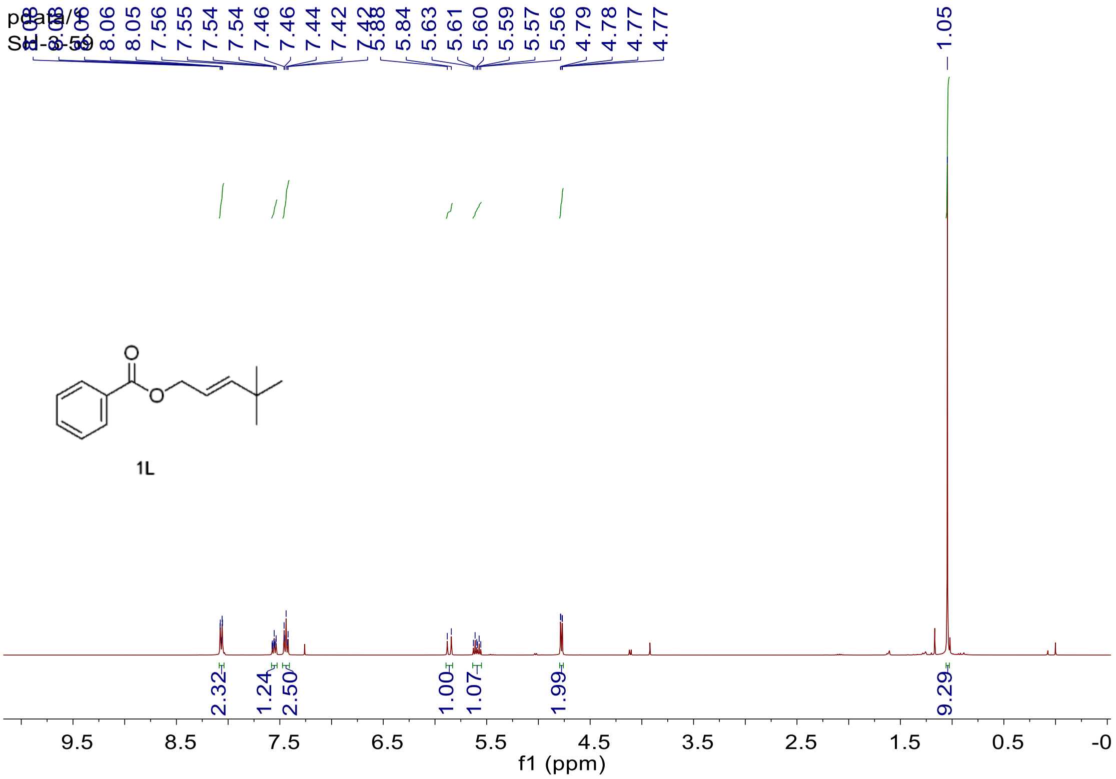


Figure 39 ^{1}H NMR of spectrum of **1L**

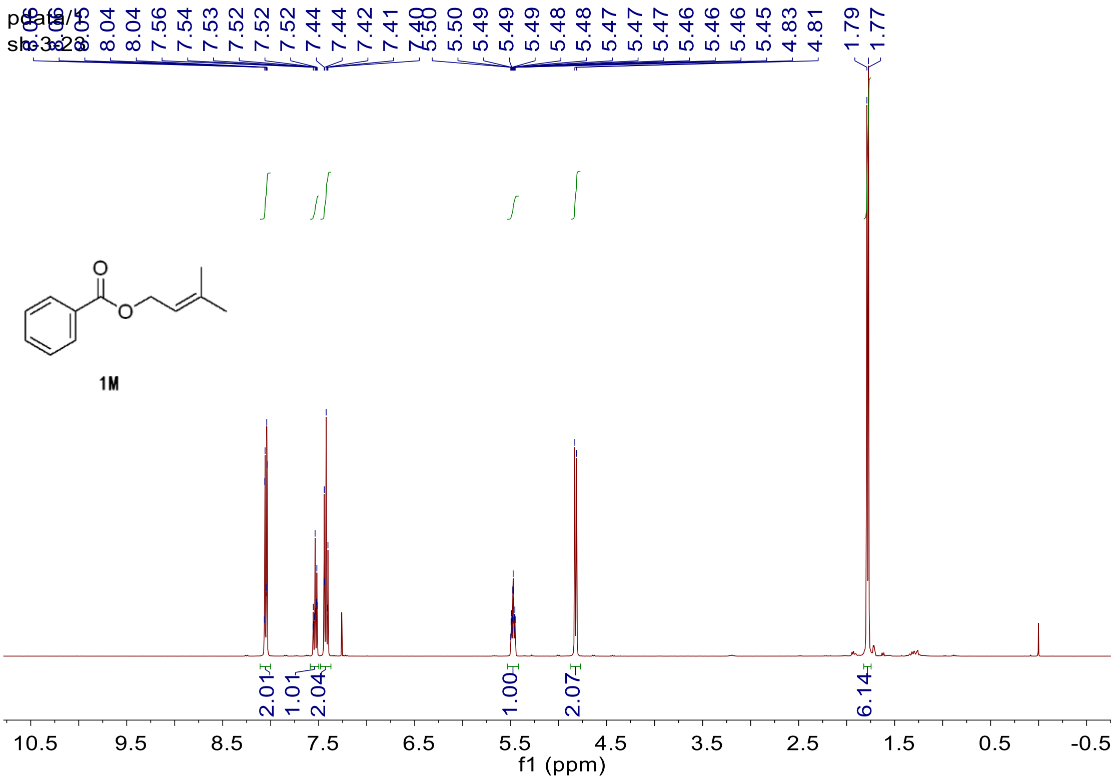


Figure 40 ^{1}H NMR of spectrum of **1M**

6 NMR Spectra of 2a

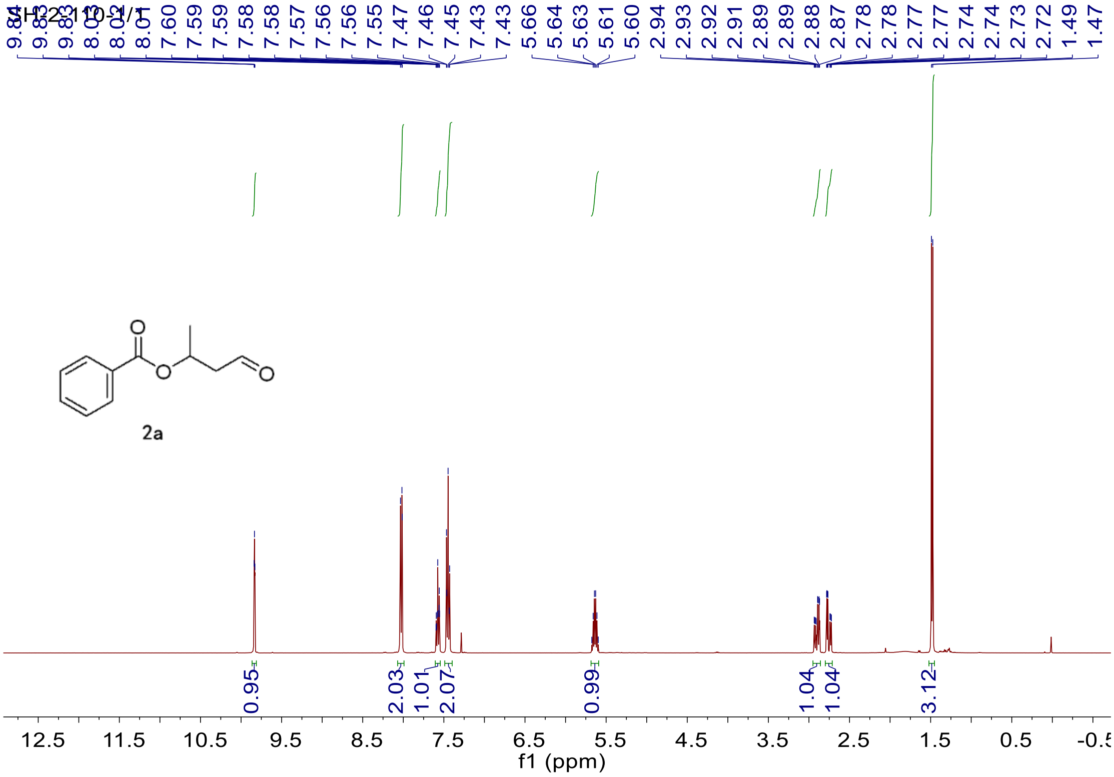


Figure 41 ^{1}H NMR of spectrum of **2a**

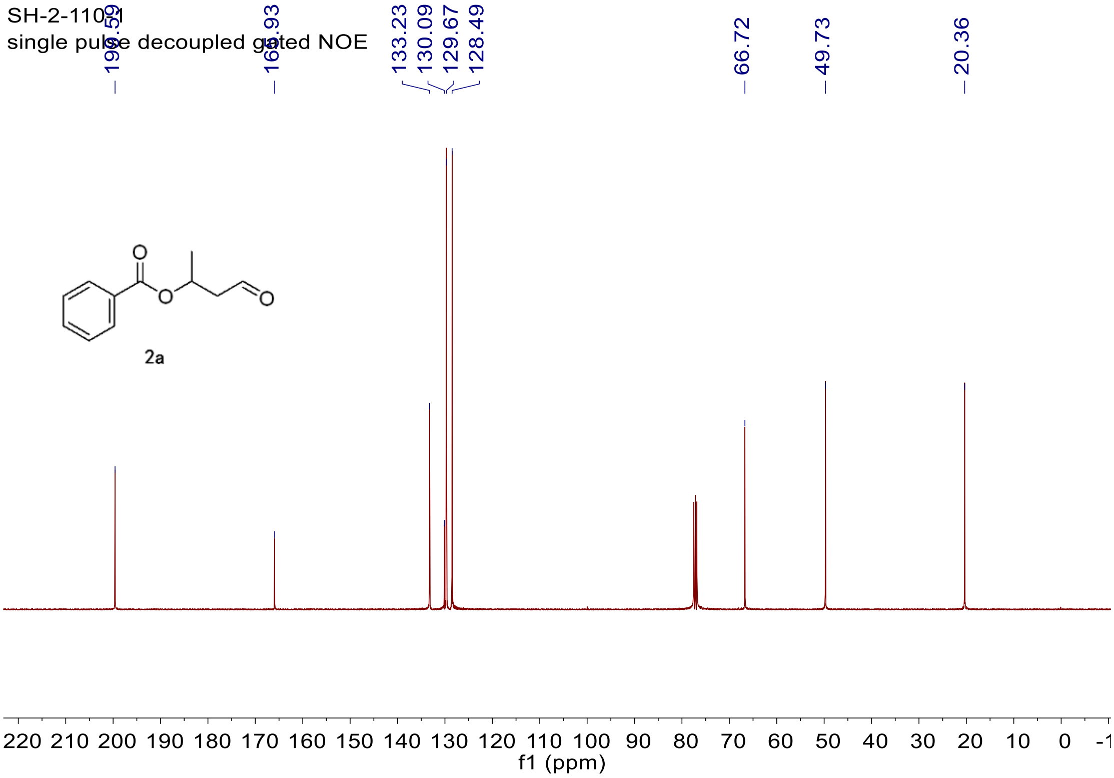


Figure 42 ^{13}C NMR of spectrum of **2a**

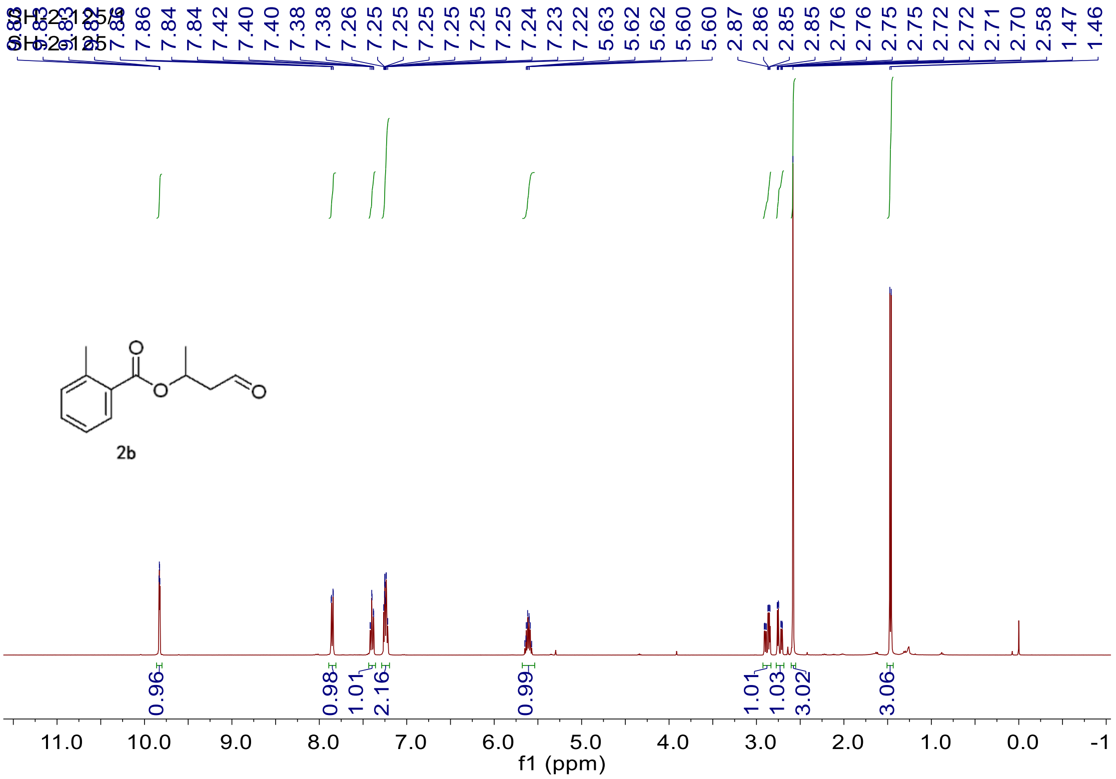


Figure 43 ^{1}H NMR of spectrum of **2b**

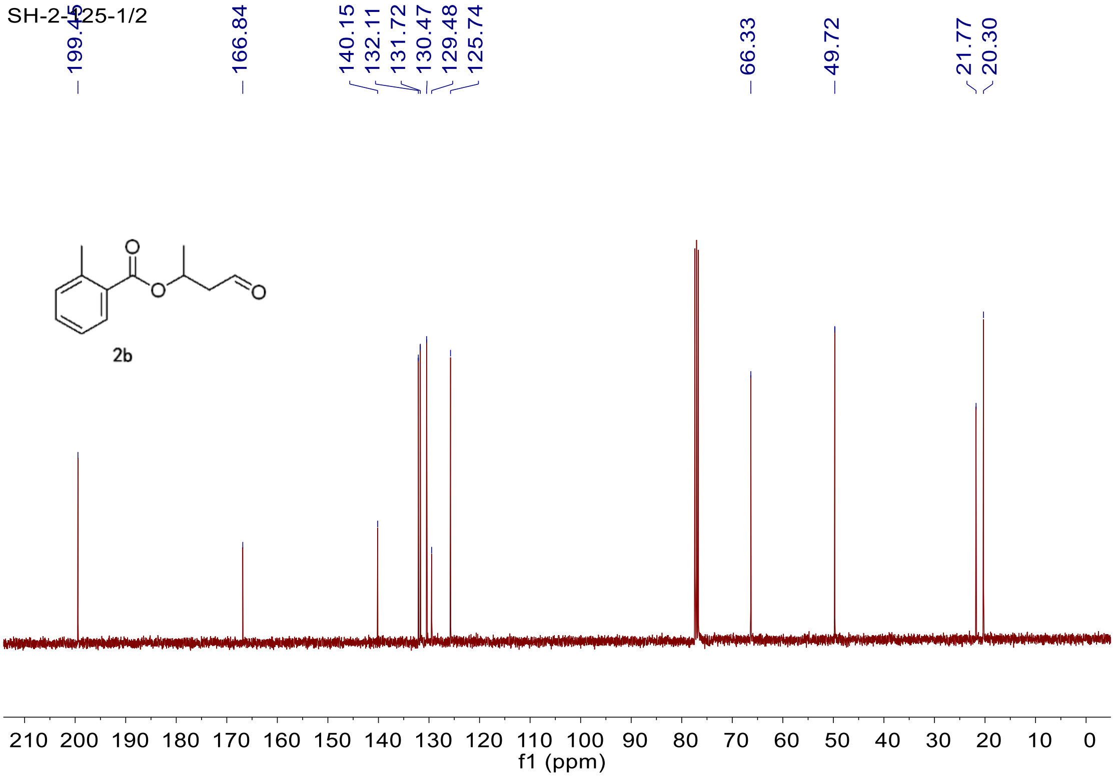


Figure 44 ^{13}C NMR of spectrum of **2b**

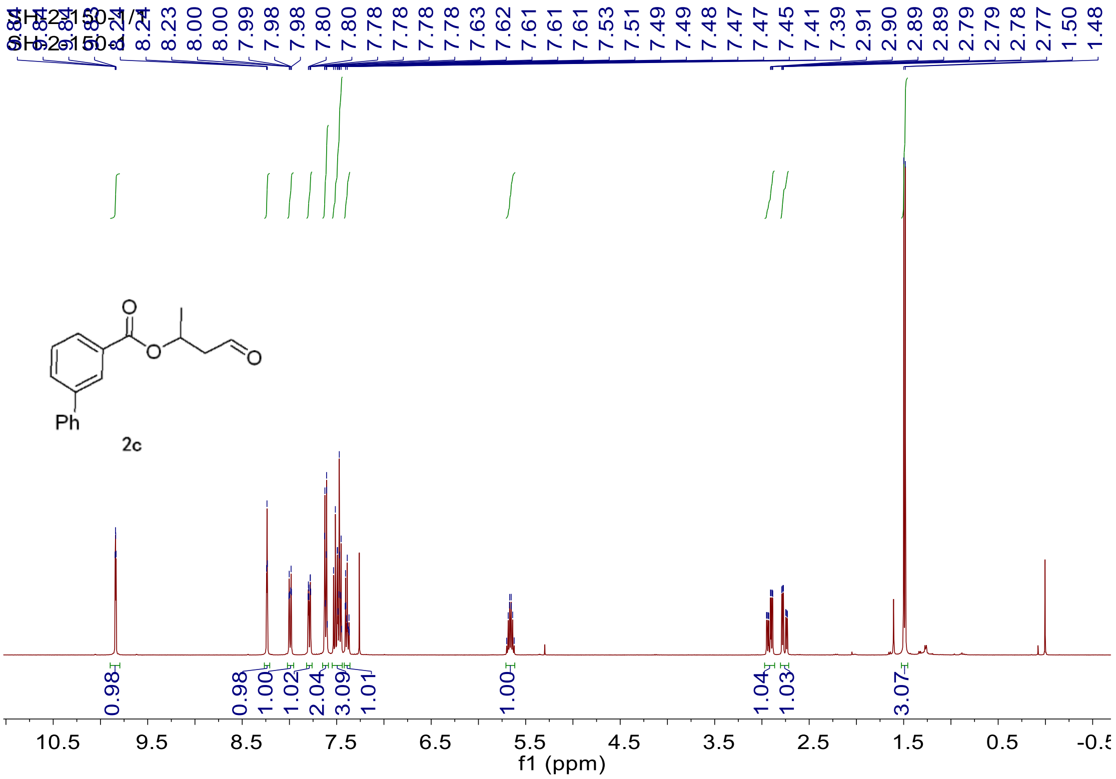


Figure 45 ^{1}H NMR of spectrum of **2c**

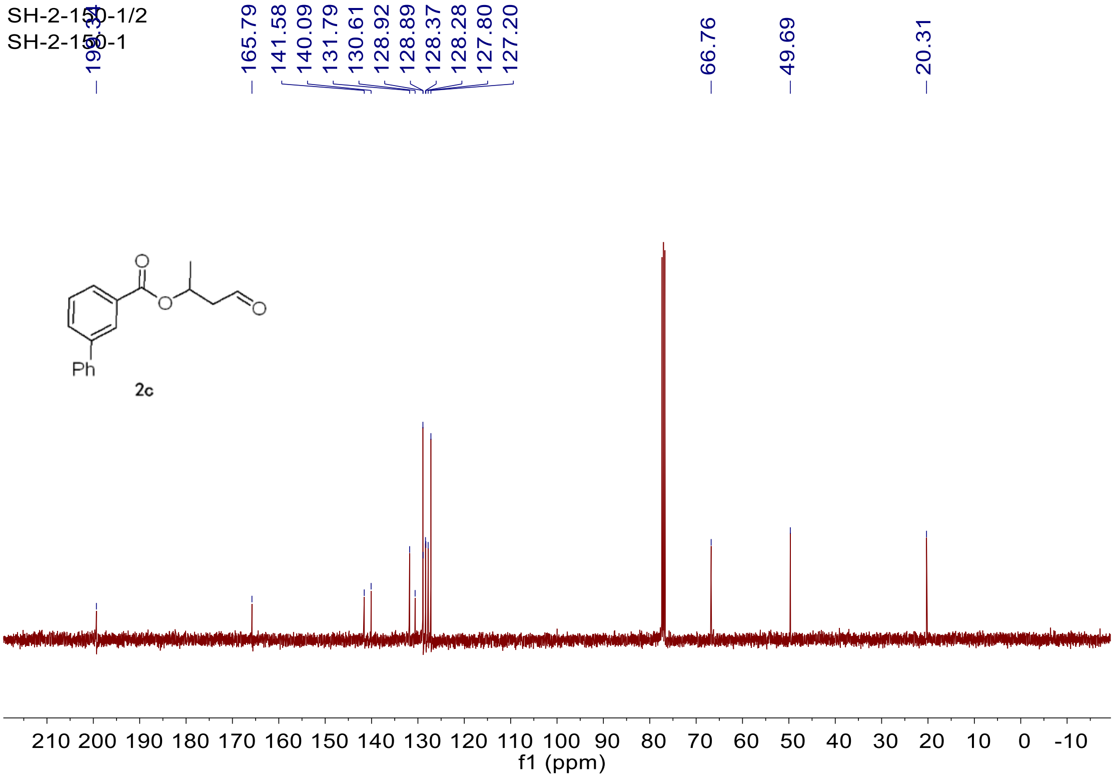


Figure 46 ^{13}C NMR of spectrum of **2c**

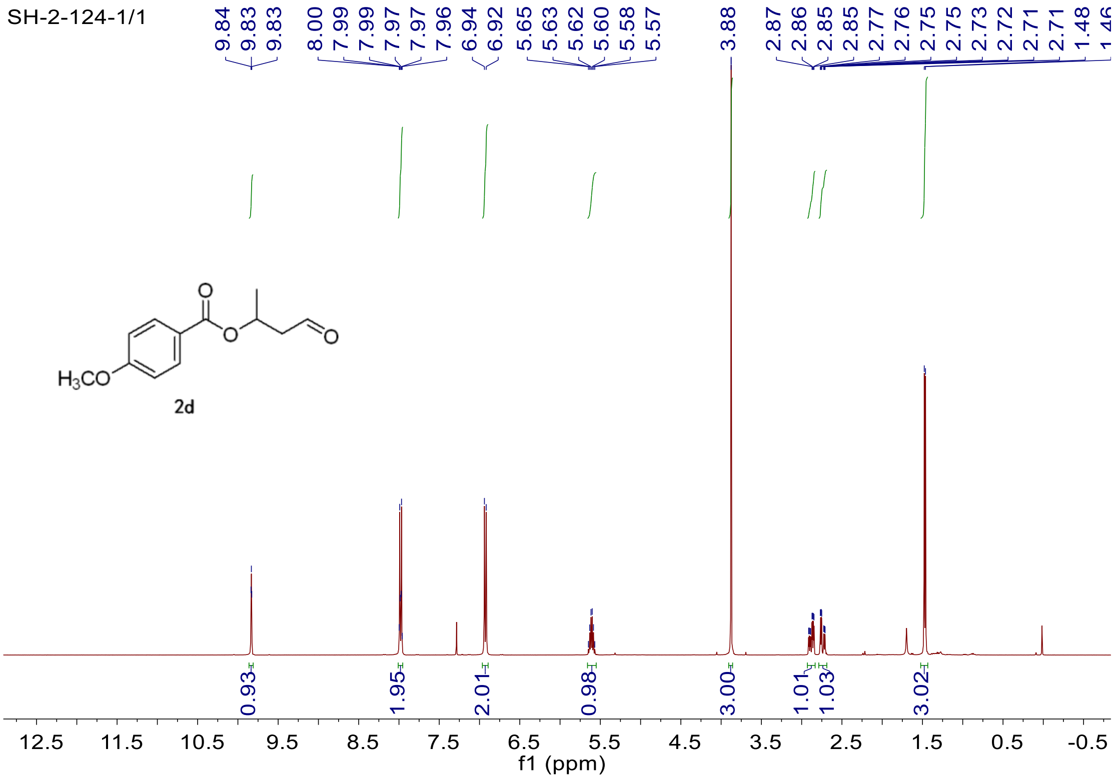


Figure 47 ^{1}H NMR of spectrum of **2d**

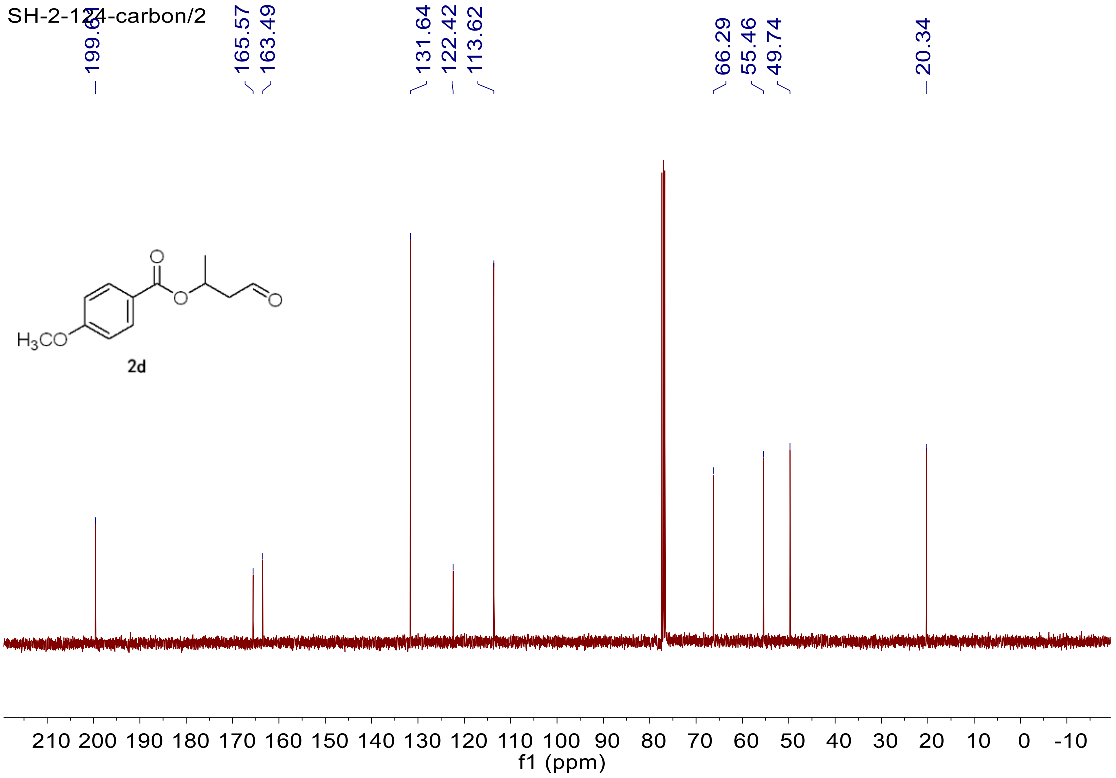


Figure 48 ^{13}C NMR of spectrum of **2d**

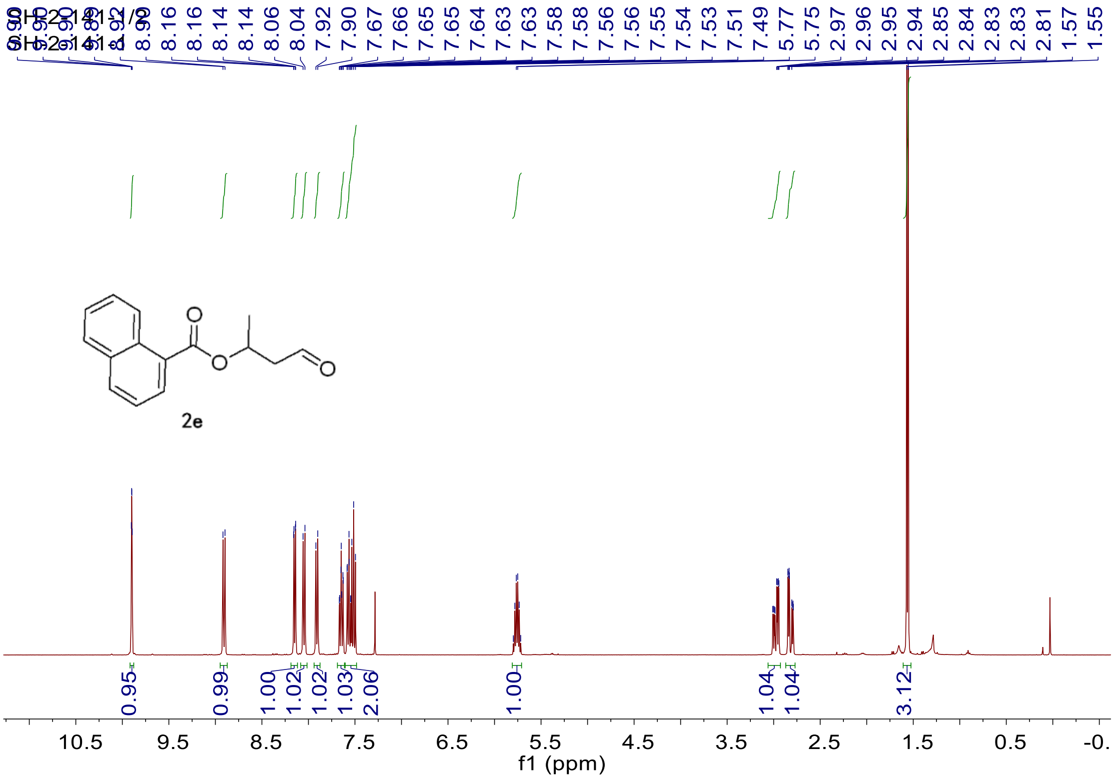


Figure 49 ^{1}H NMR of spectrum of **2e**

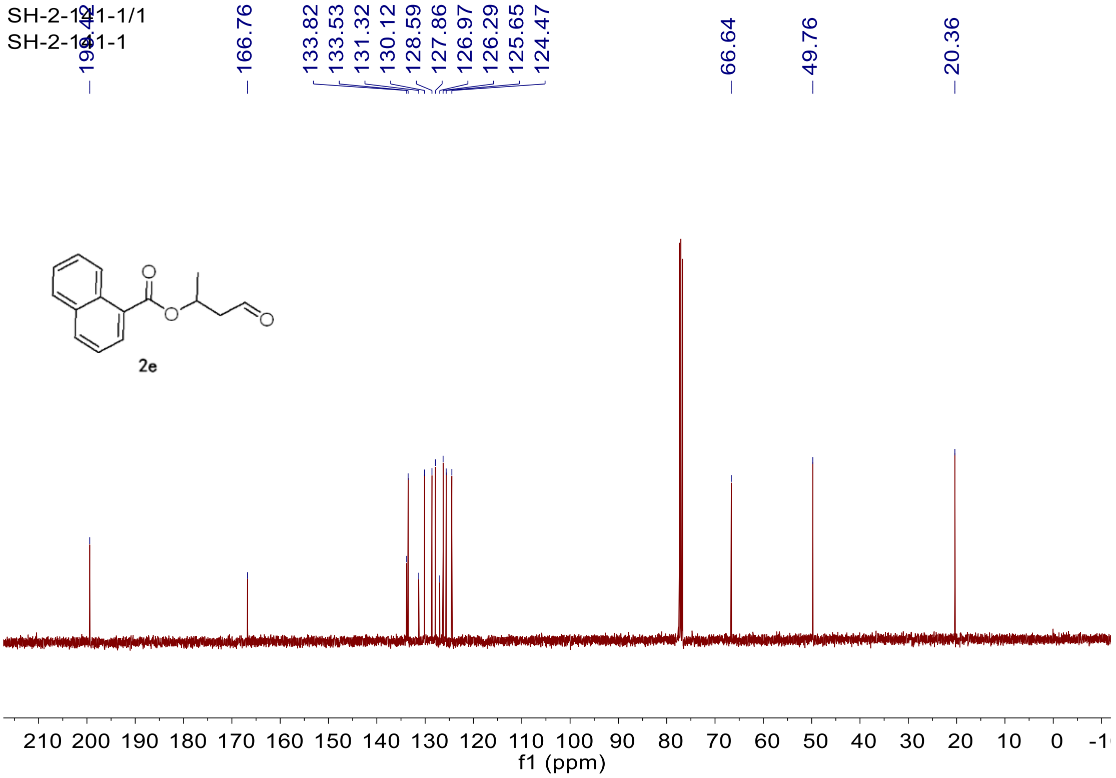


Figure 45 ^{13}C NMR of spectrum of **2e**

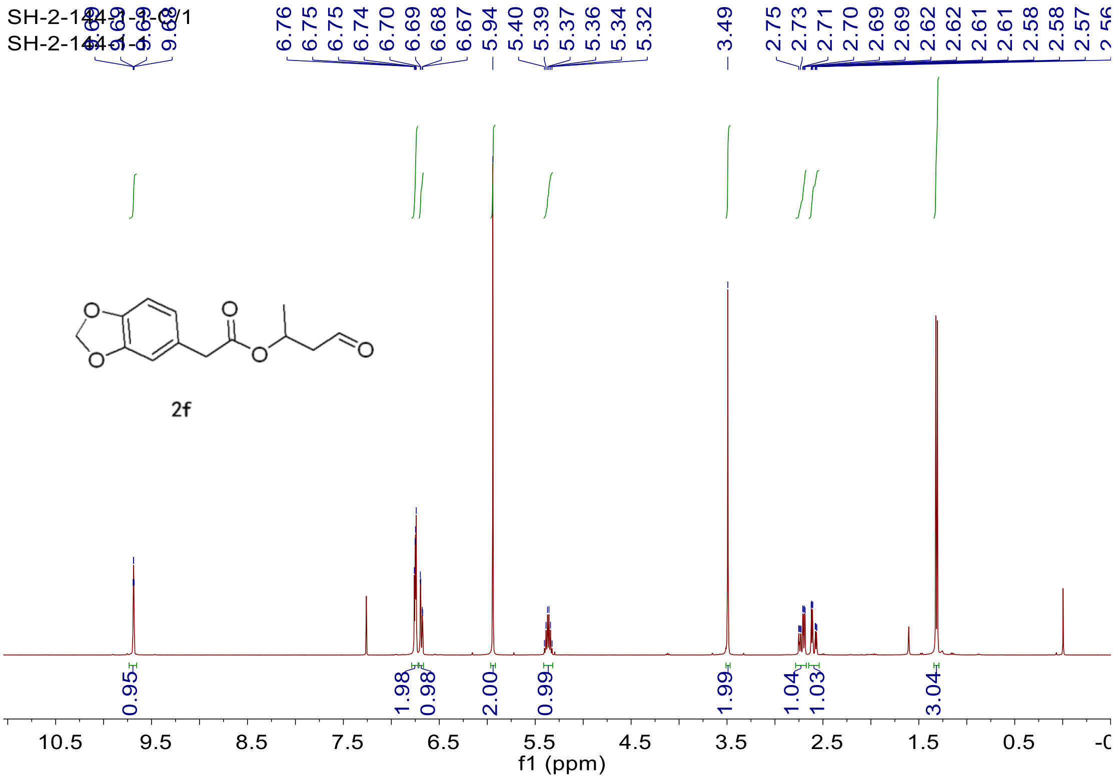


Figure 51 ^{1}H NMR of spectrum of **2f**

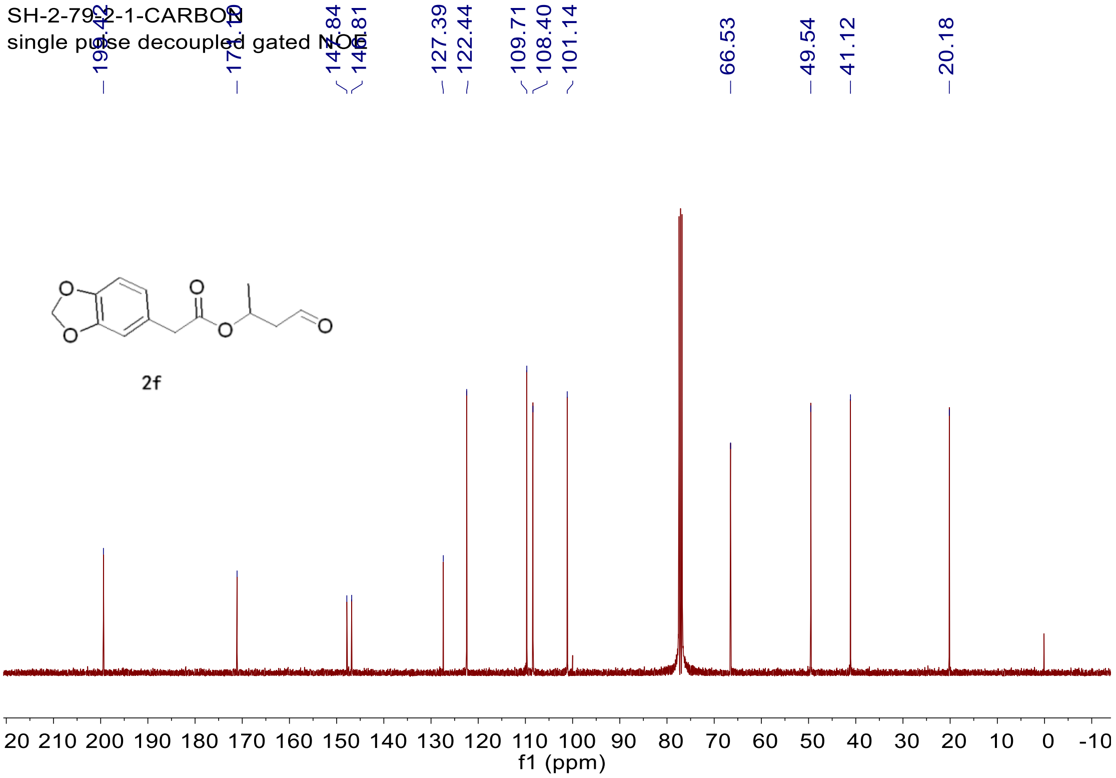


Figure 52 ^{13}C NMR of spectrum of **2f**

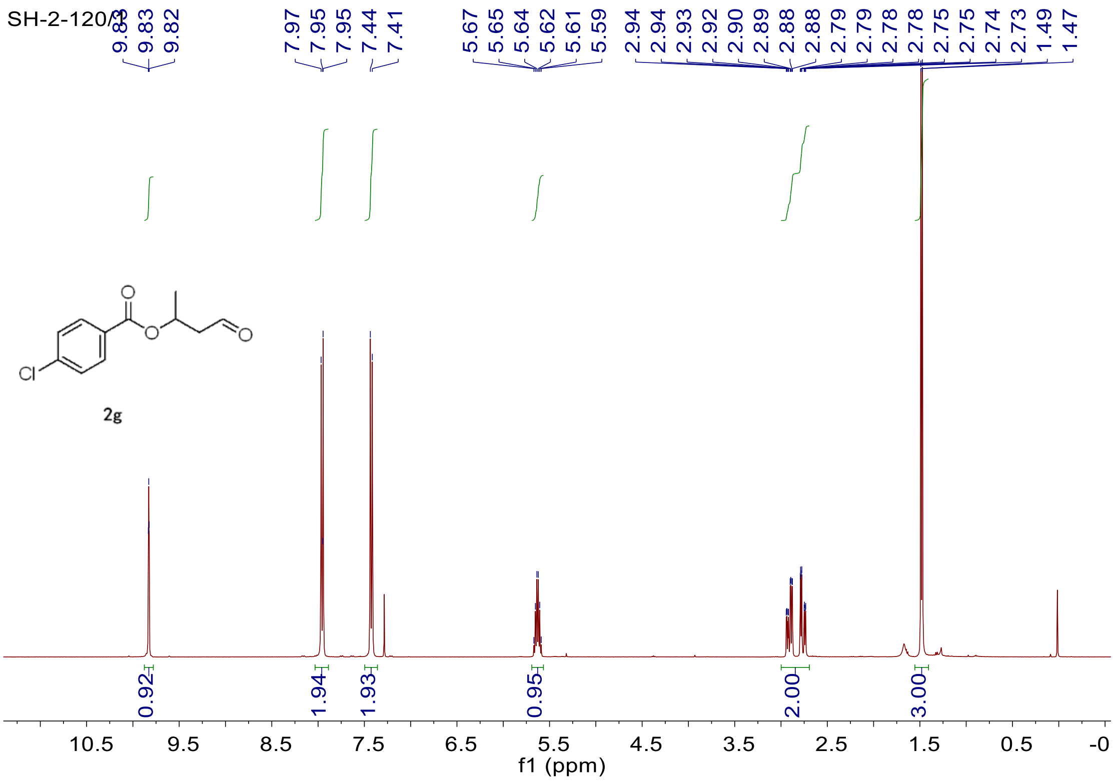


Figure 53 ^{1}H NMR of spectrum of **2g**

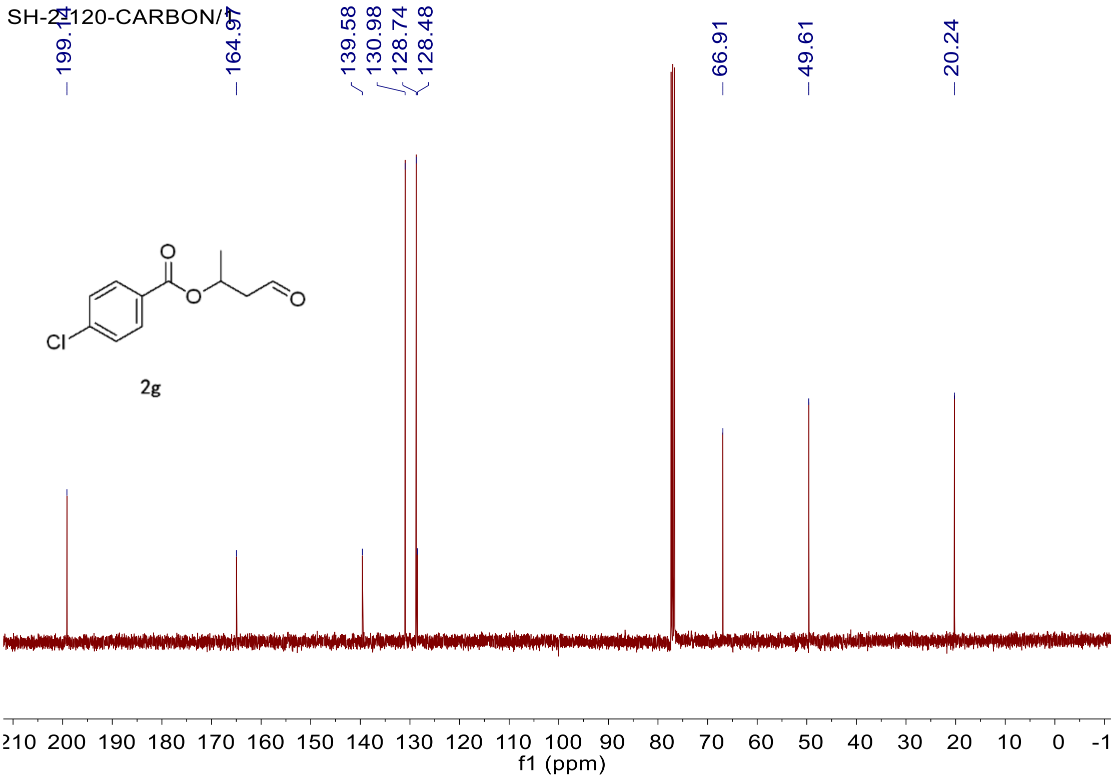


Figure 54 ^{13}C NMR of spectrum of **2g**

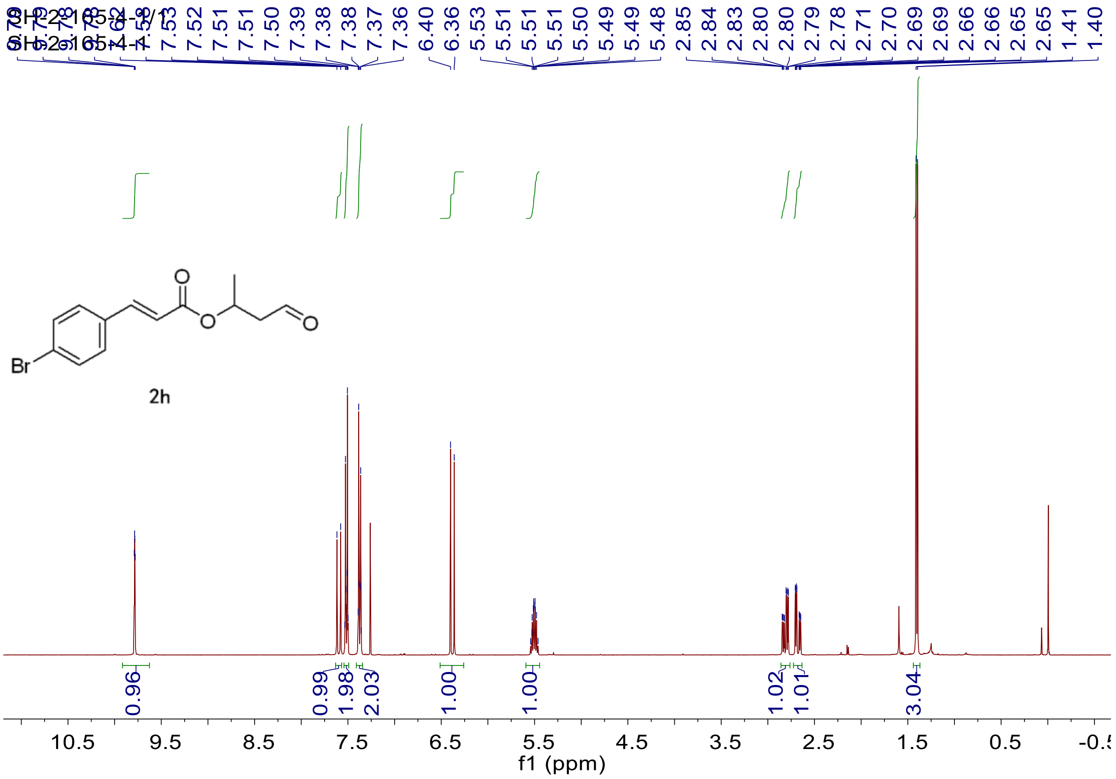


Figure 55 ^{1}H NMR of spectrum of **2h**

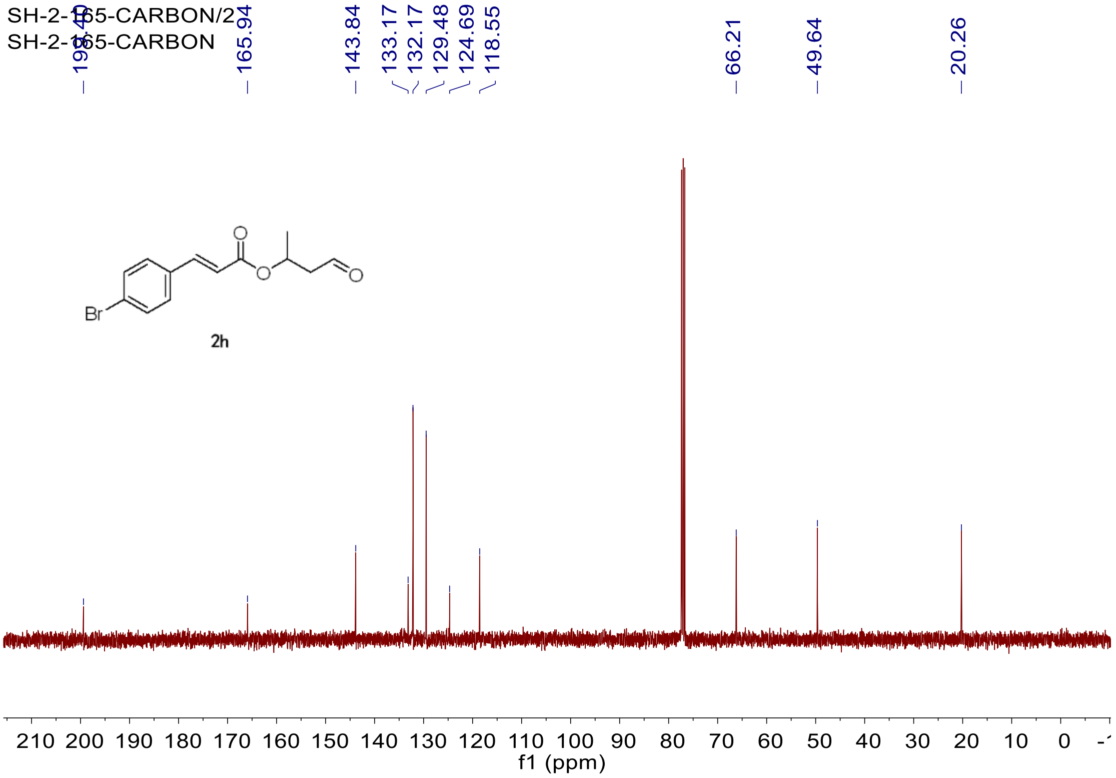


Figure 56 ^{13}C NMR of spectrum of **2h**

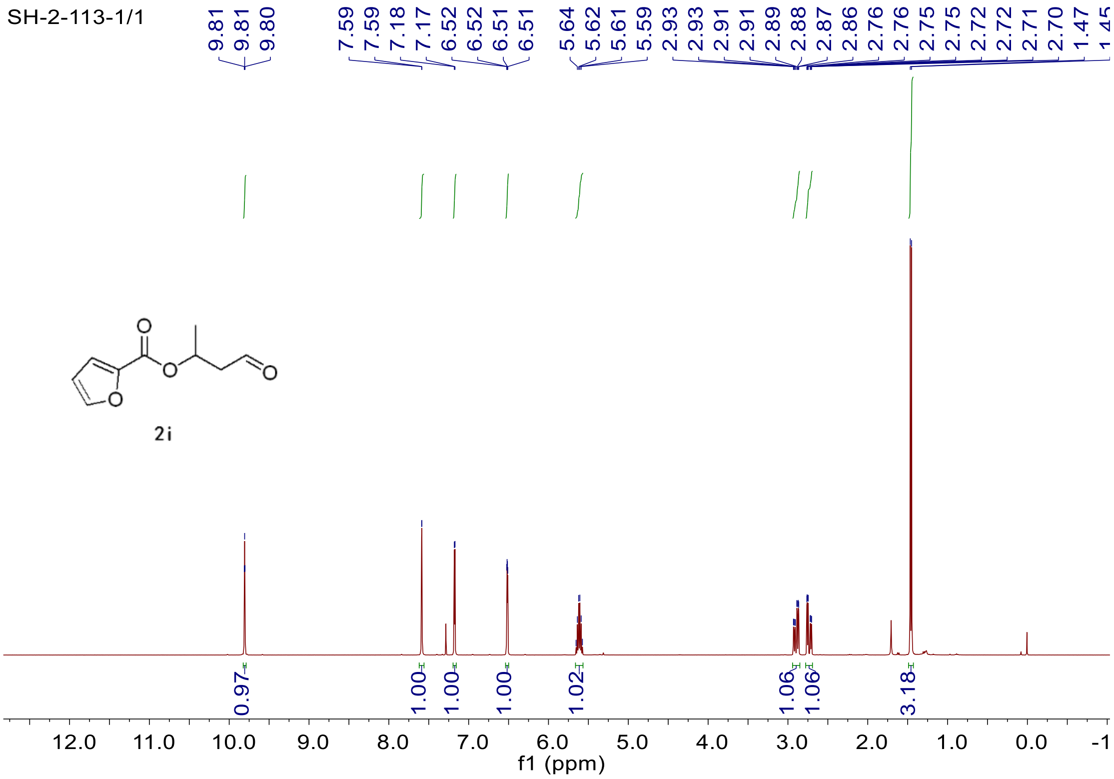


Figure 57 ^{1}H NMR of spectrum of **2i**

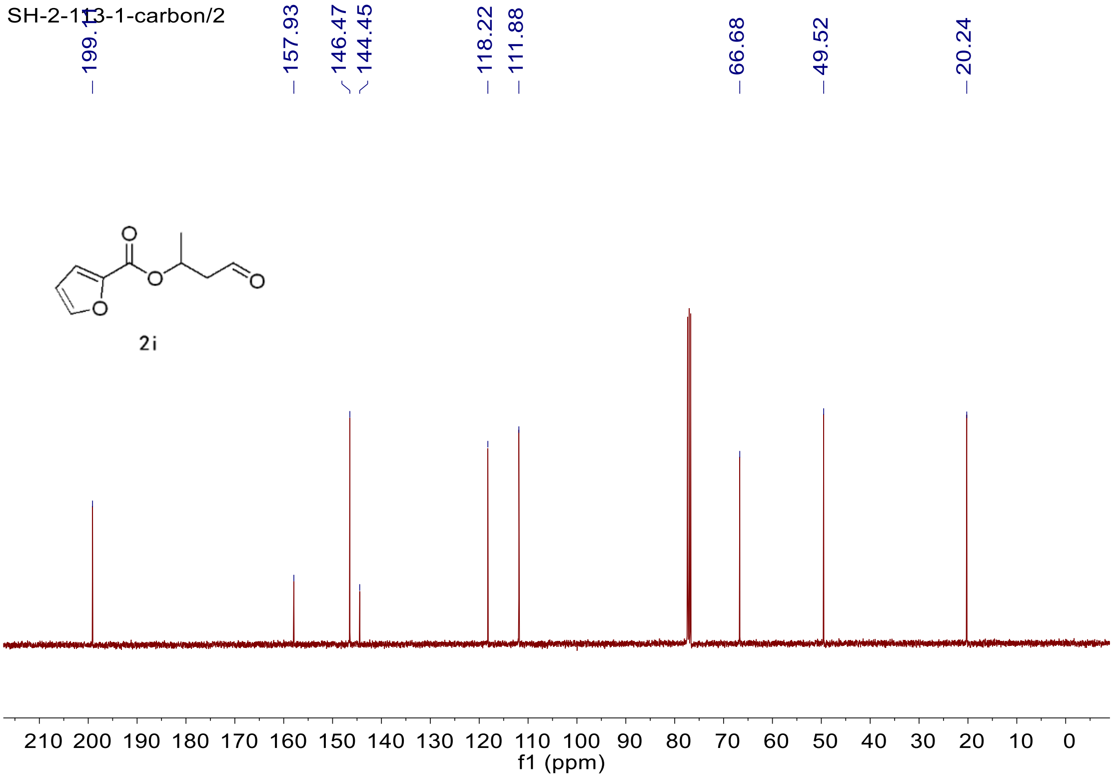


Figure 58 ^{13}C NMR of spectrum of **2i**

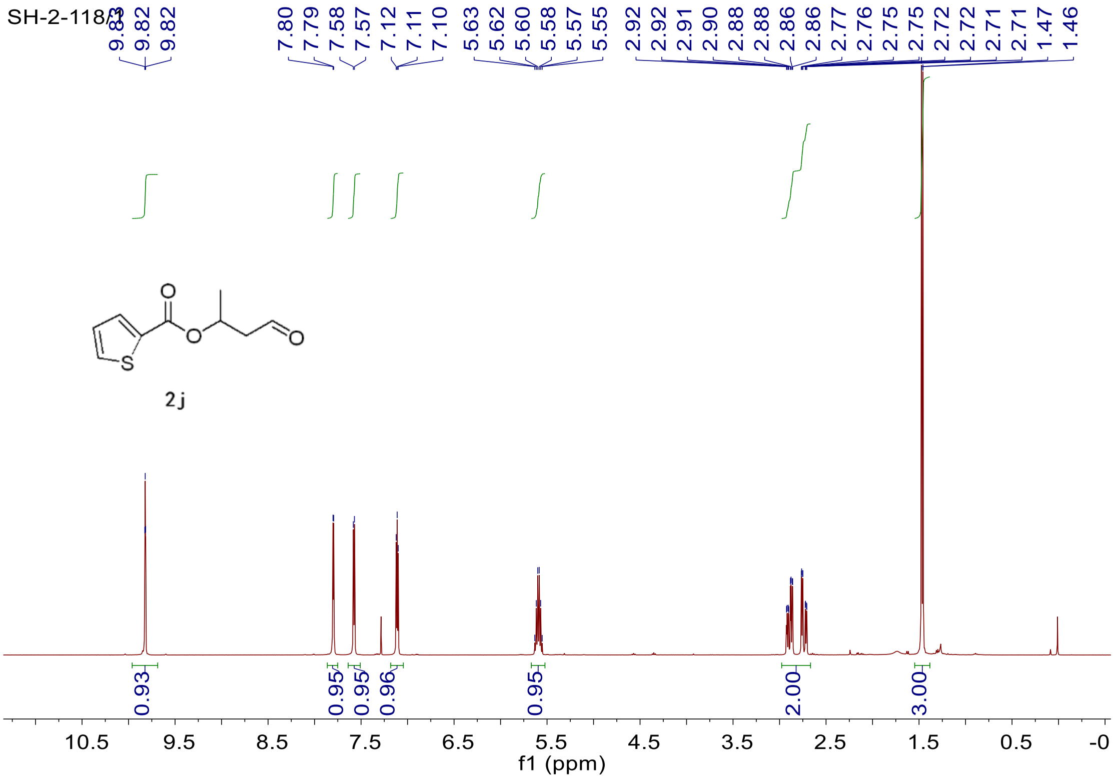


Figure 59 ^{1}H NMR of spectrum of **2j**

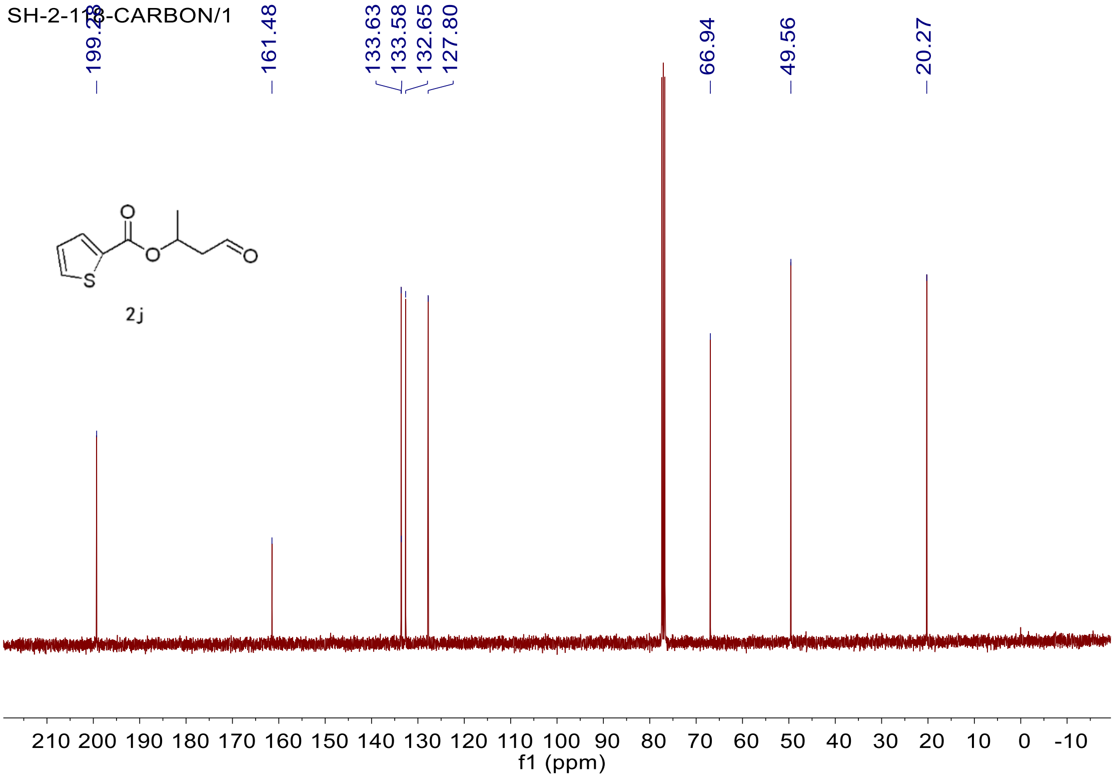


Figure 60 ^{13}C NMR of spectrum of **2j**

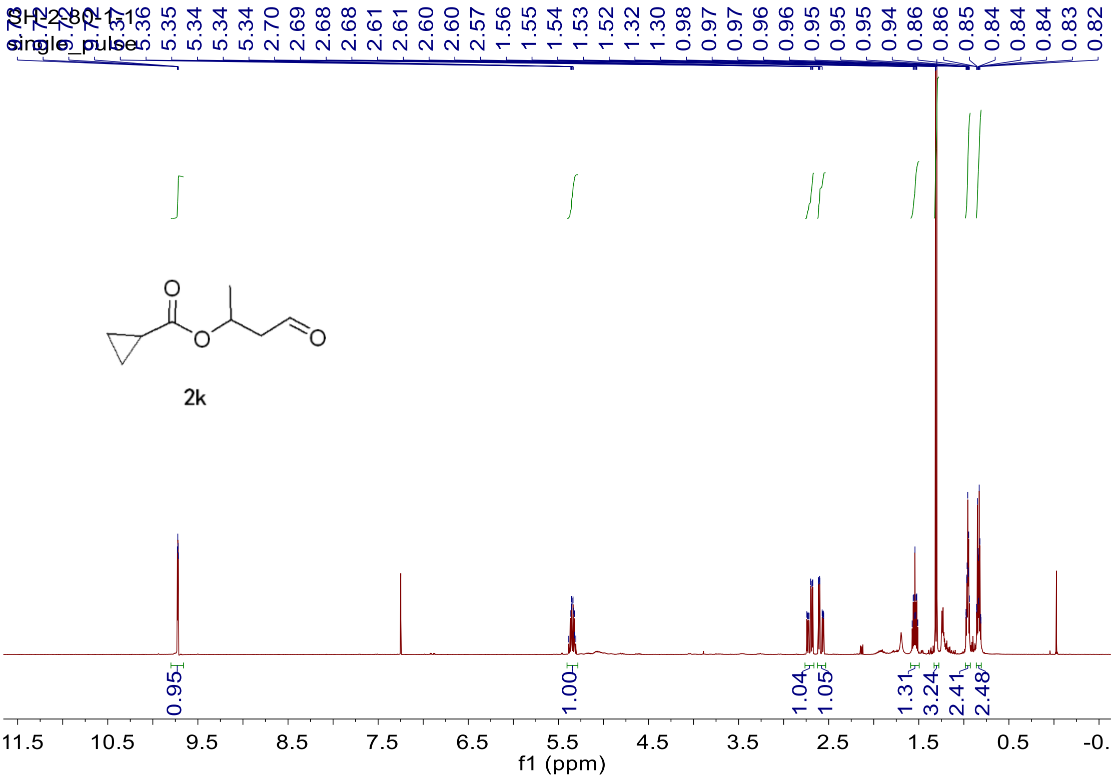


Figure 61 ^{1}H NMR of spectrum of **2k**

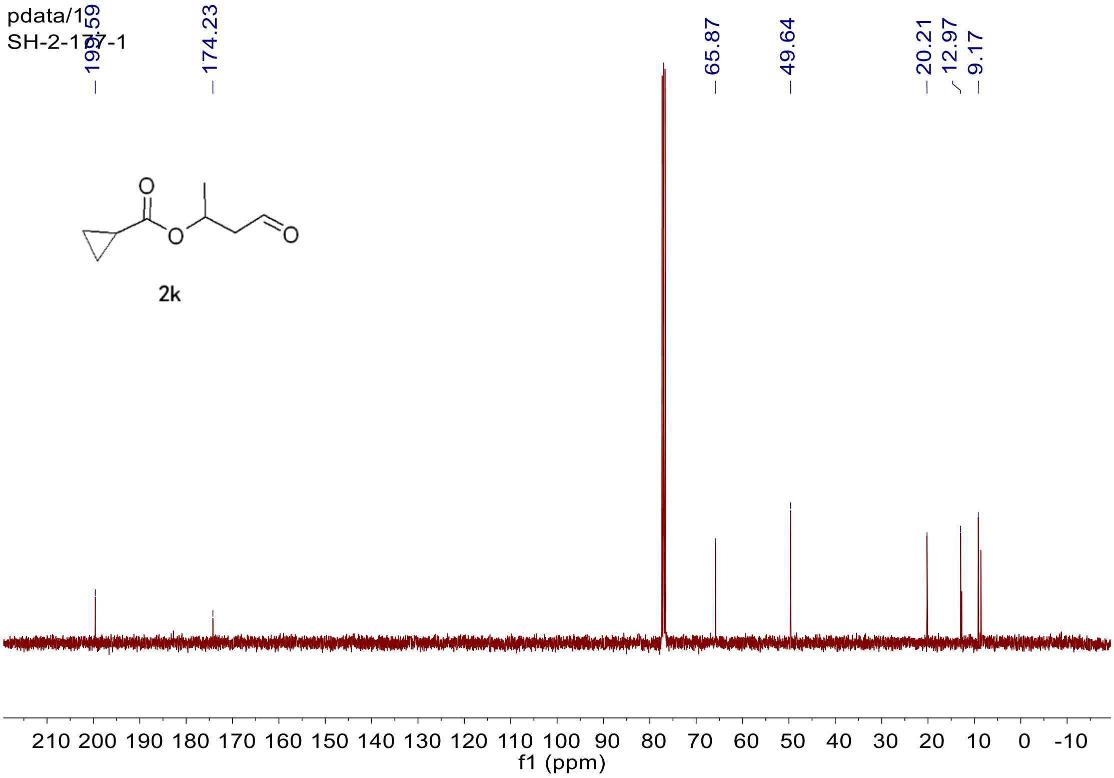


Figure 62 ^{13}C NMR of spectrum of **2k**

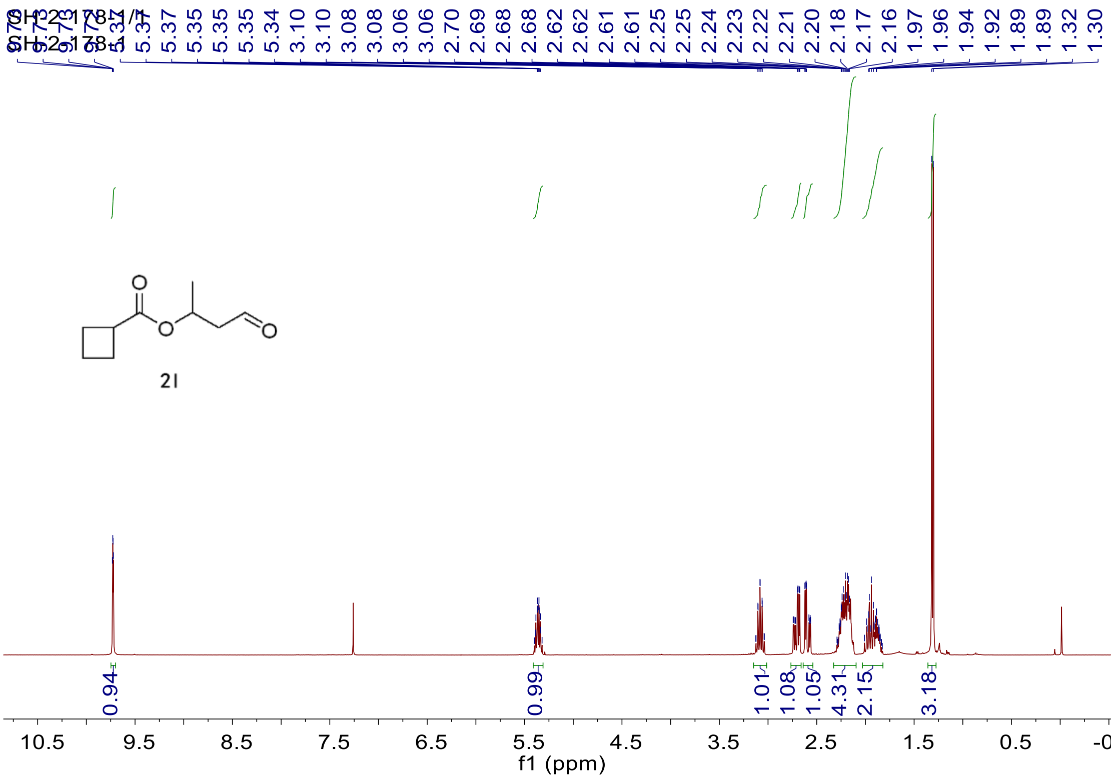


Figure 63 ^{1}H NMR of spectrum of **2l**

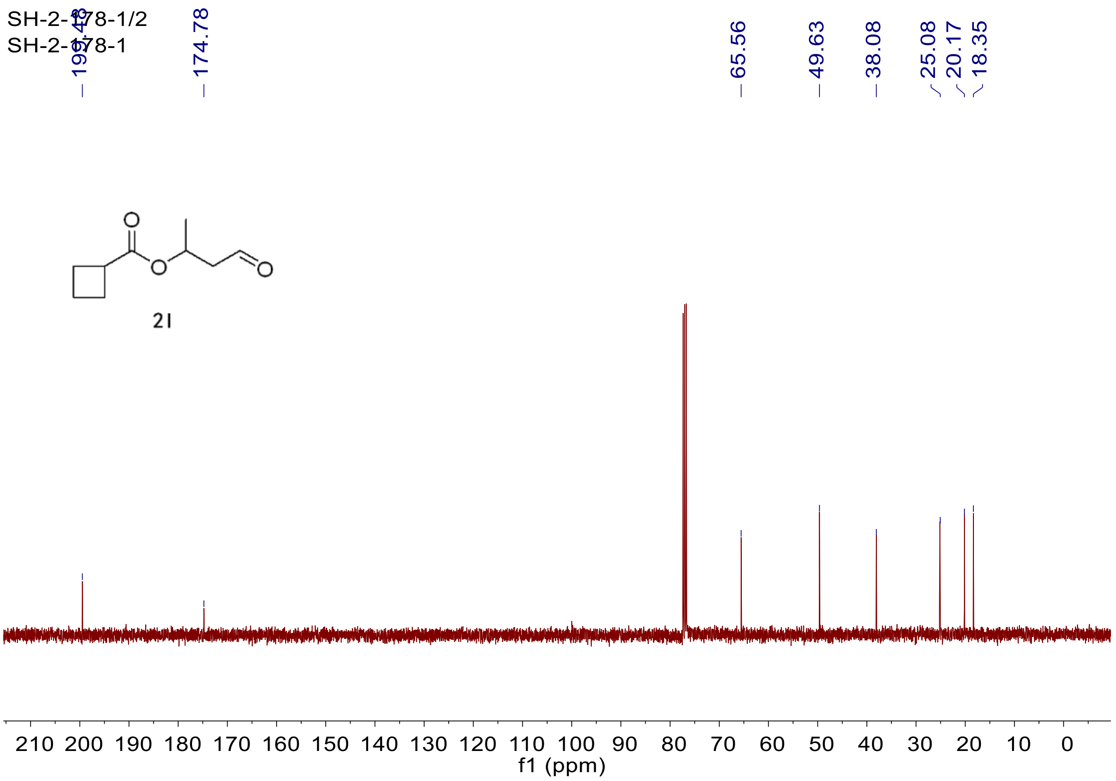


Figure 64 ^{13}C NMR of spectrum of **2l**

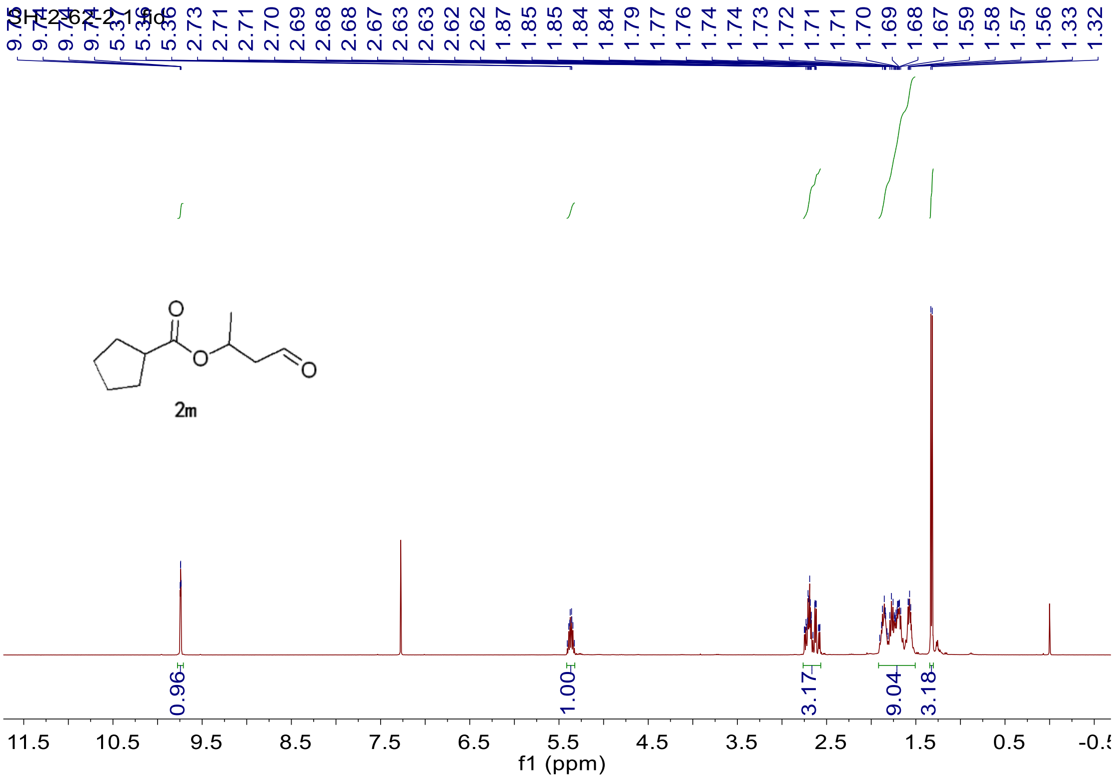


Figure 65 ^{1}H NMR of spectrum of **2m**

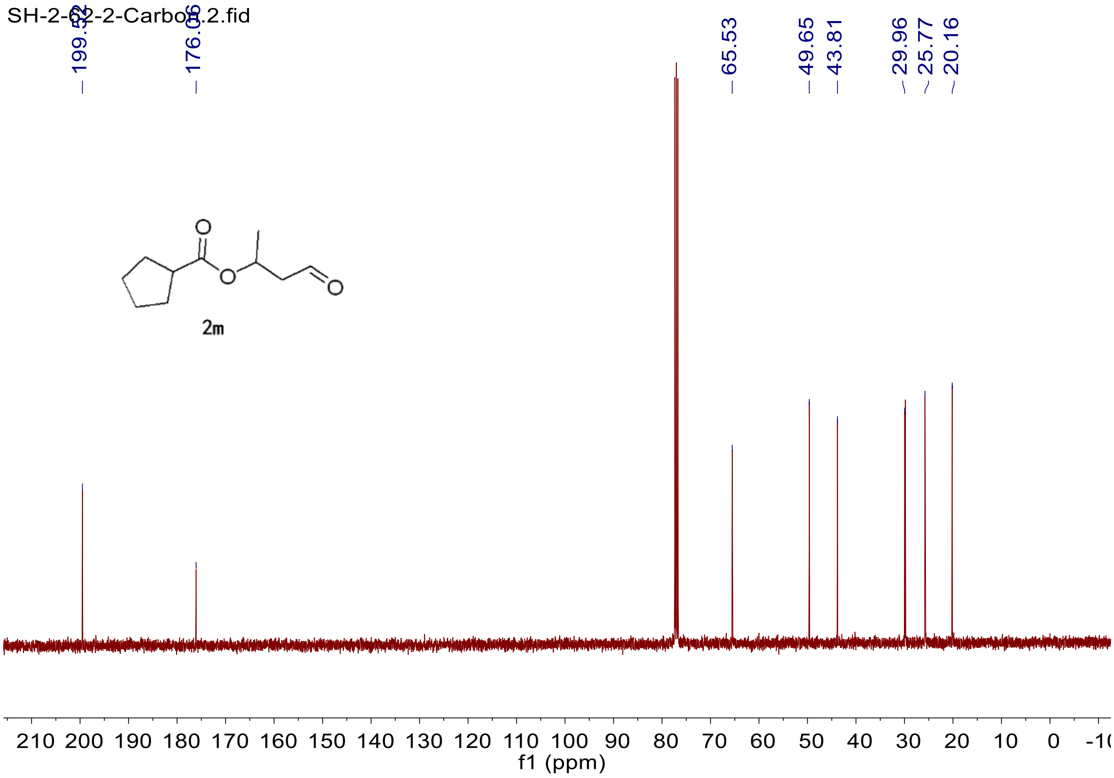


Figure 66 ^{13}C NMR of spectrum of **2m**

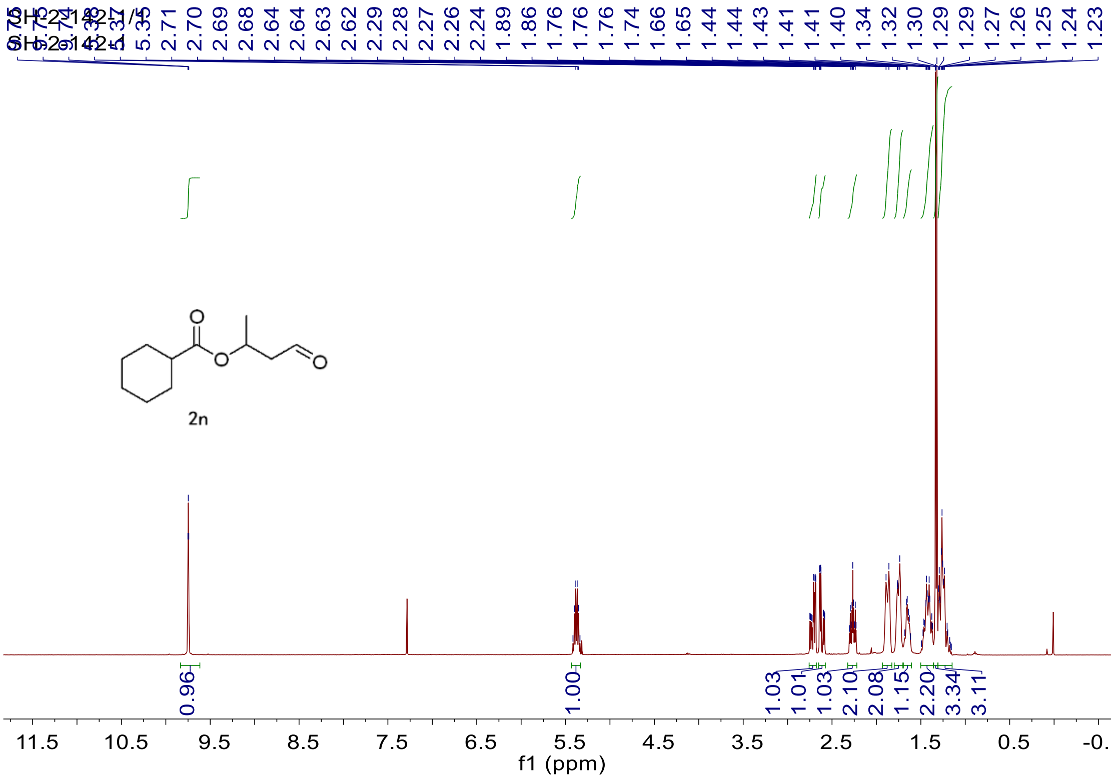


Figure 67 ^{1}H NMR of spectrum of **2n**

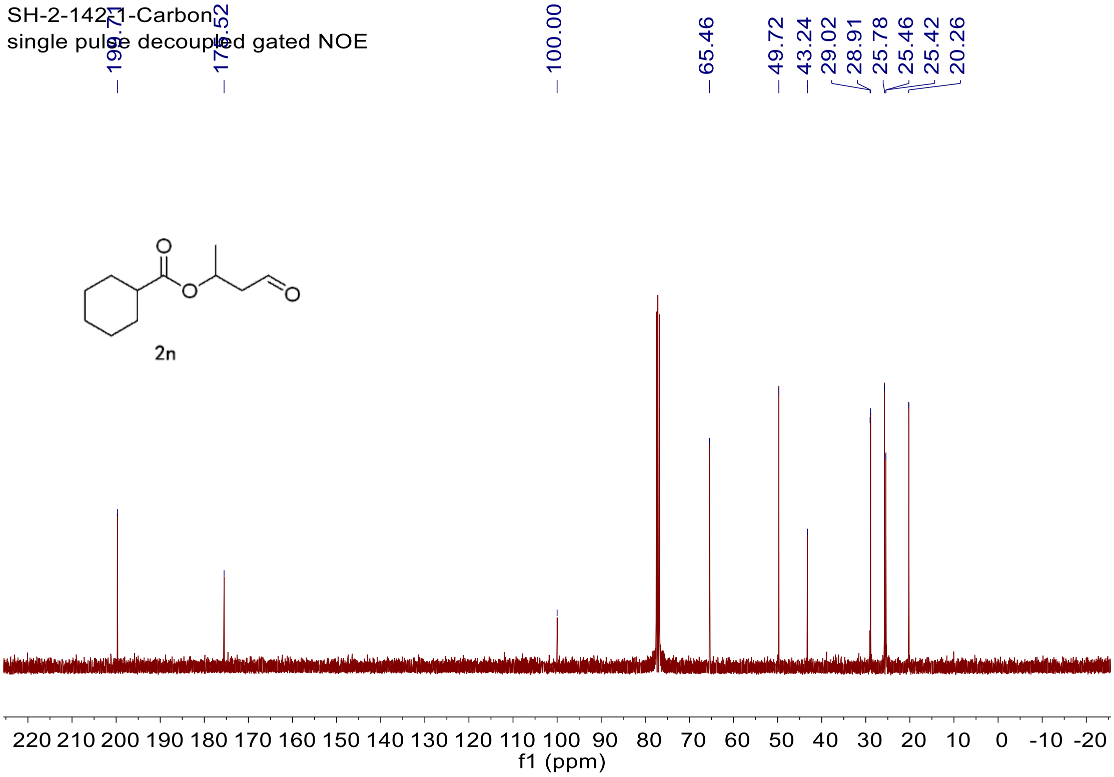


Figure 68 ^{13}C NMR of spectrum of **2n**

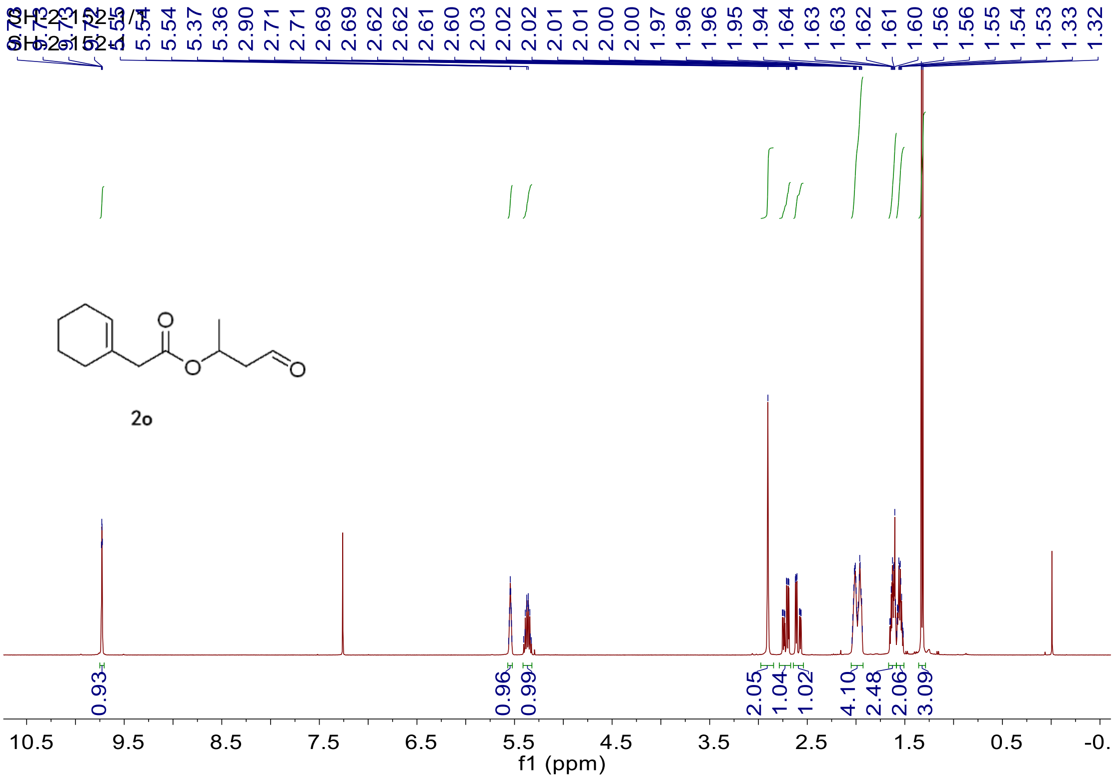


Figure 69 ^{1}H NMR of spectrum of **2o**

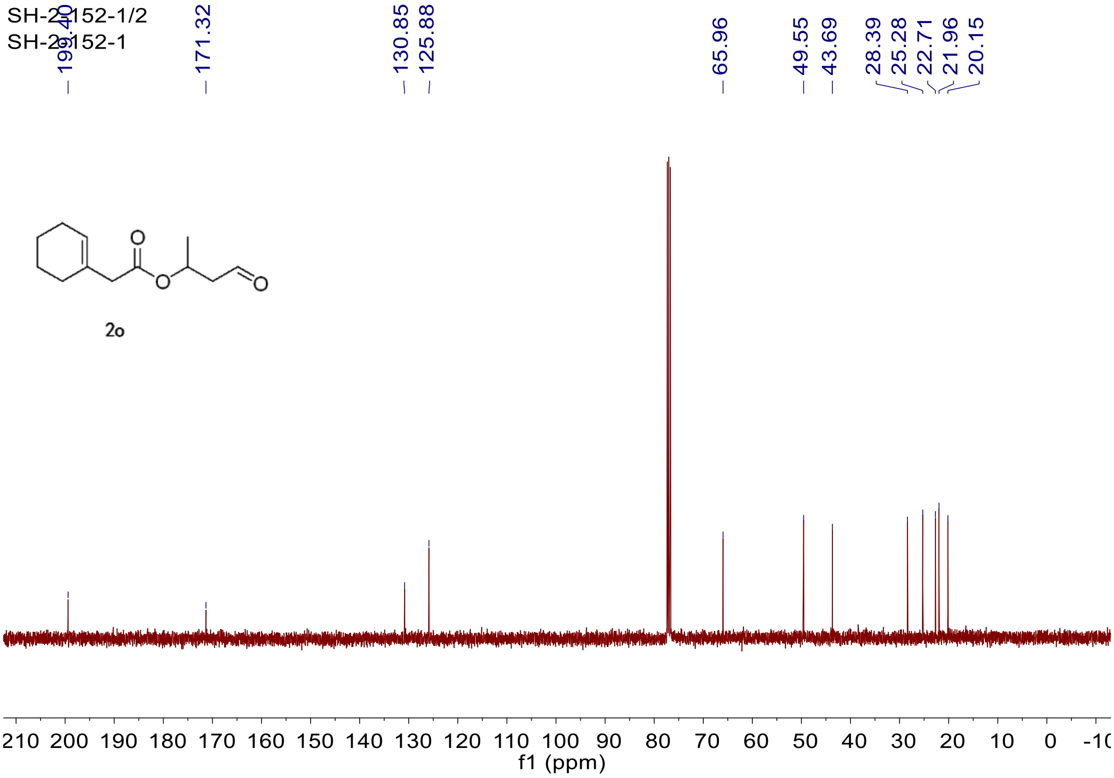


Figure 70 ^{13}C NMR of spectrum of **2o**

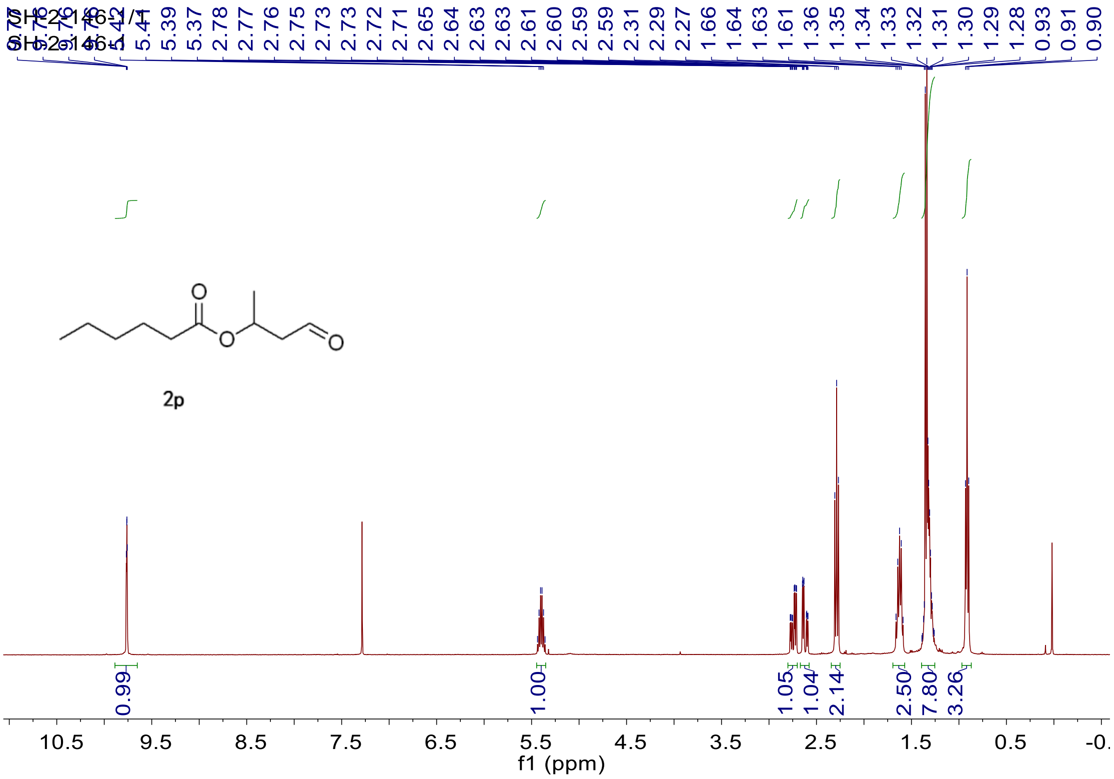


Figure 71 ^{1}H NMR of spectrum of **2p**

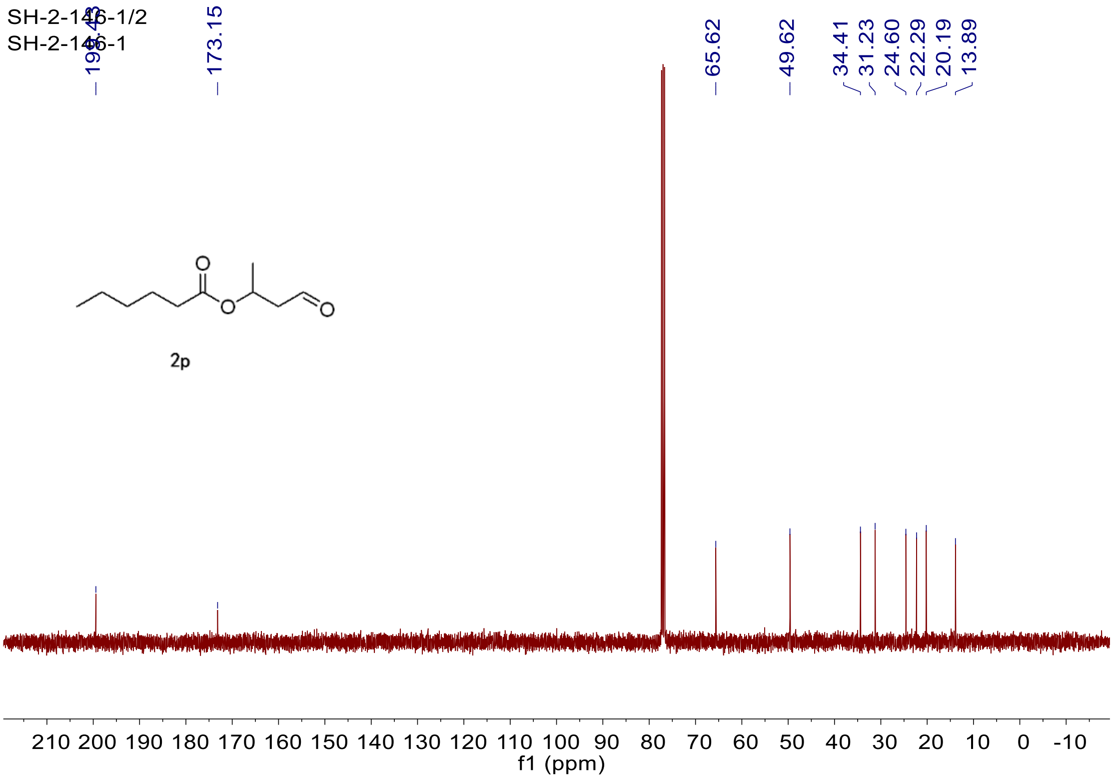


Figure 72 ^{13}C NMR of spectrum of **2p**

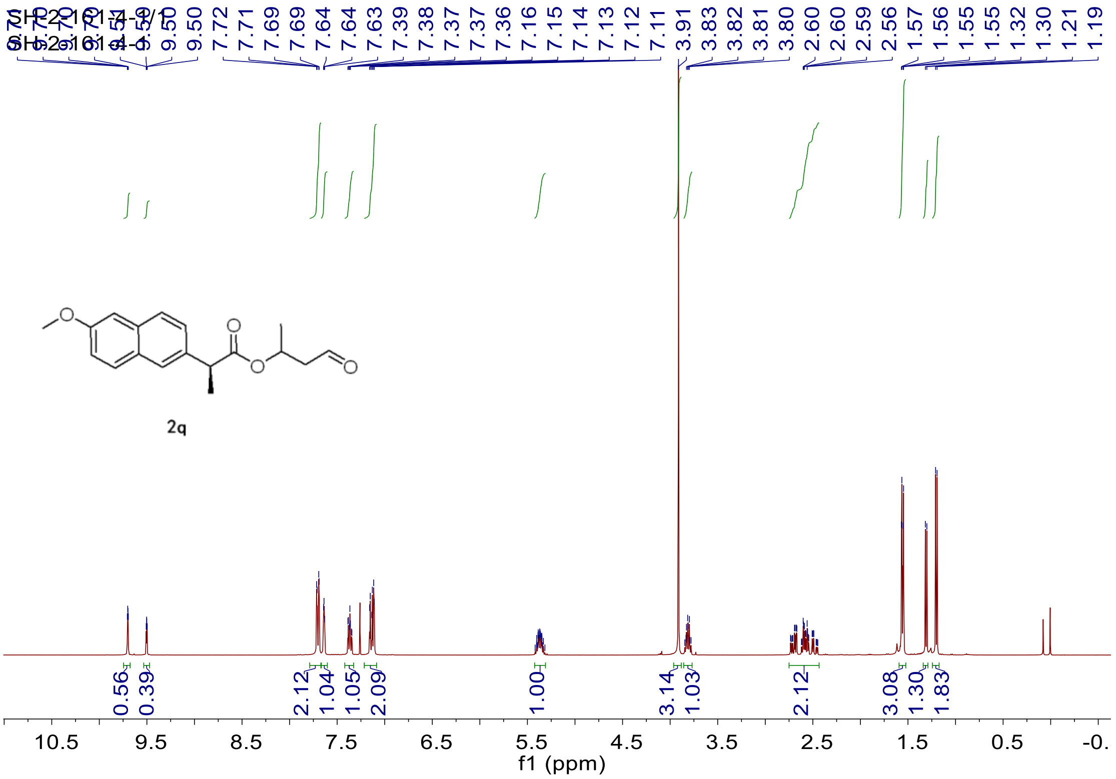


Figure 73 ^{1}H NMR of spectrum of **2q**

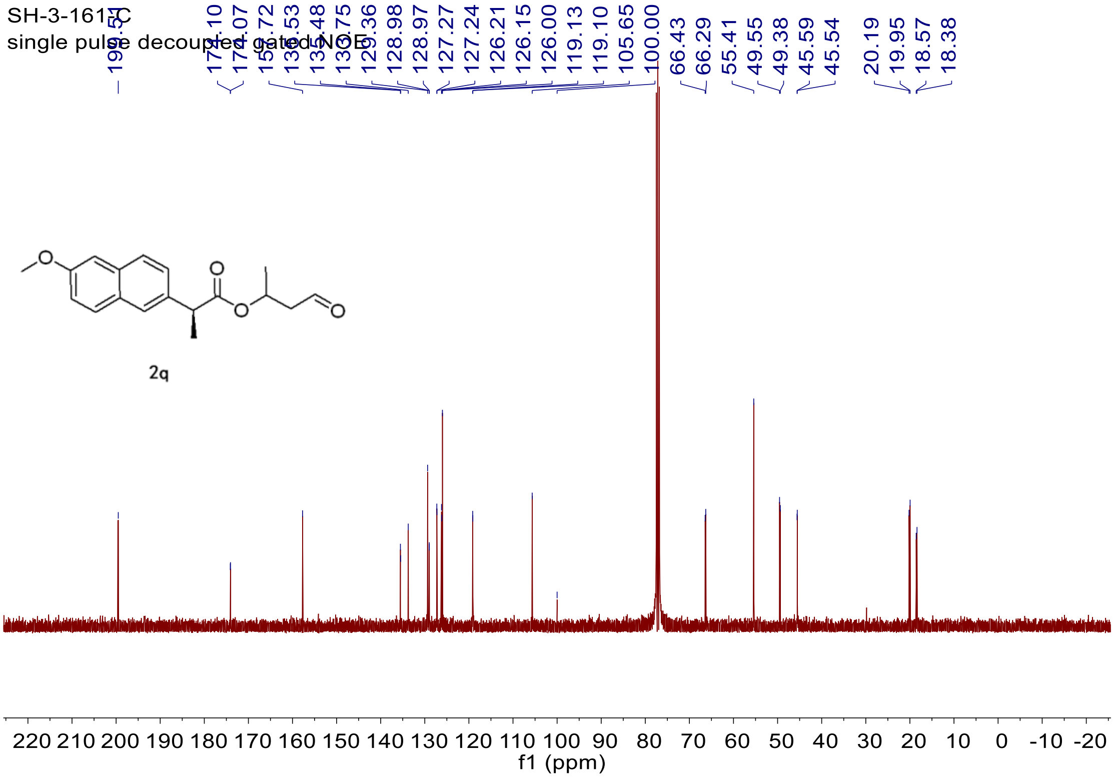


Figure 74 ^{13}C NMR of spectrum of **2q**

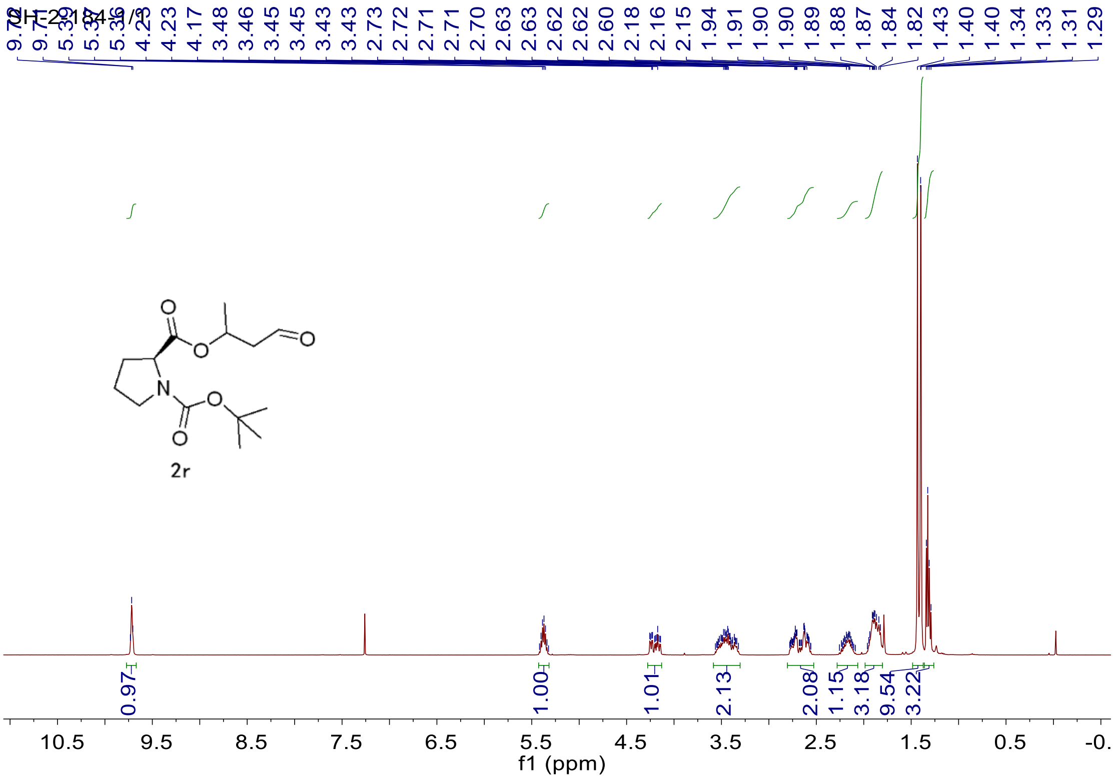


Figure 75 ^{1}H NMR of spectrum of **2r**

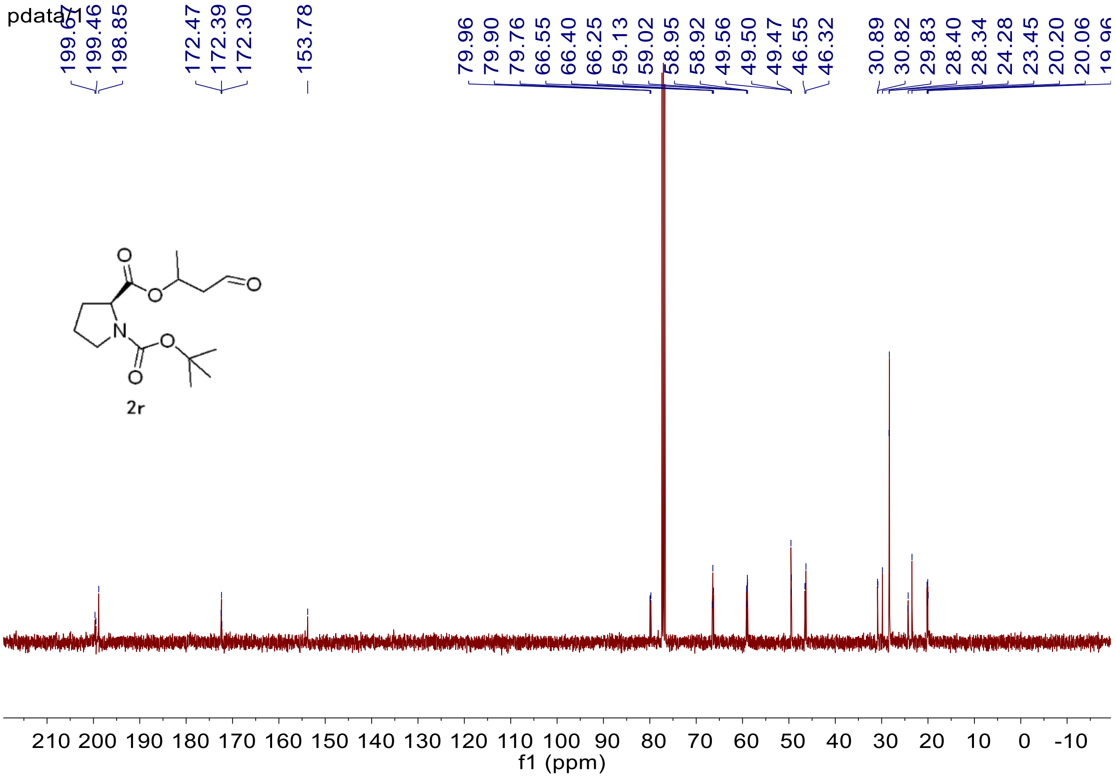


Figure 76 ^{13}C NMR of spectrum of **2r**

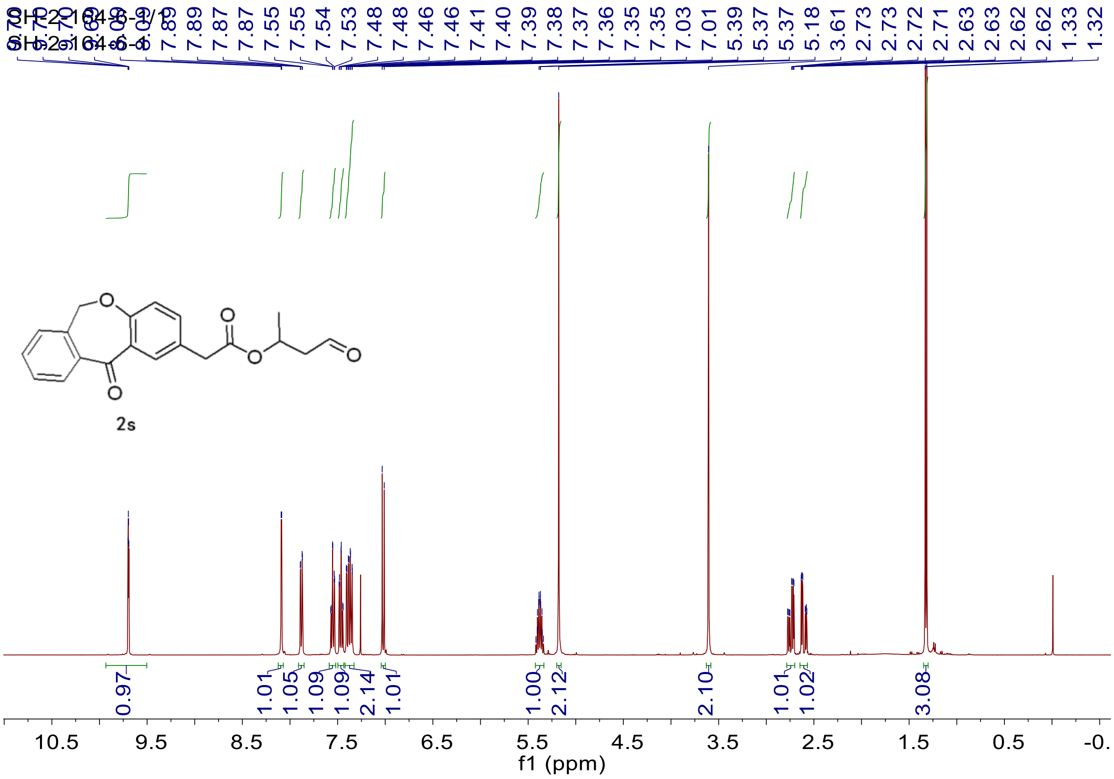


Figure 77 ^{1}H NMR of spectrum of **2s**

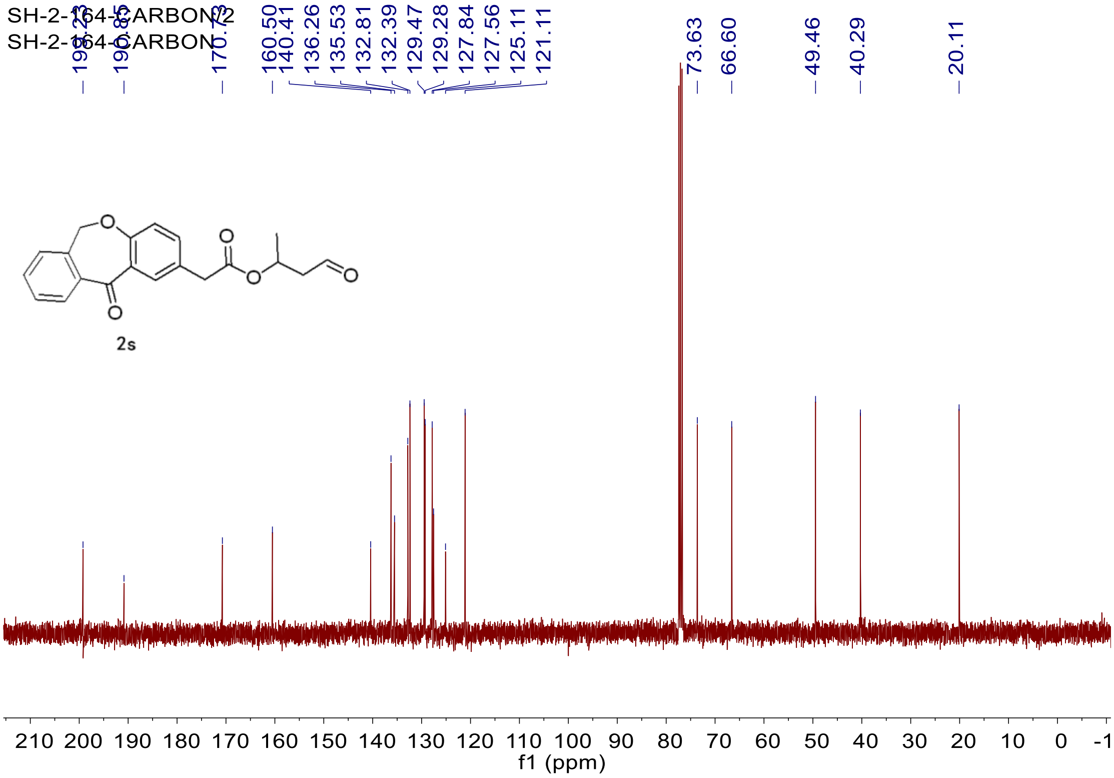


Figure 78 ^{13}C NMR of spectrum of **2s**

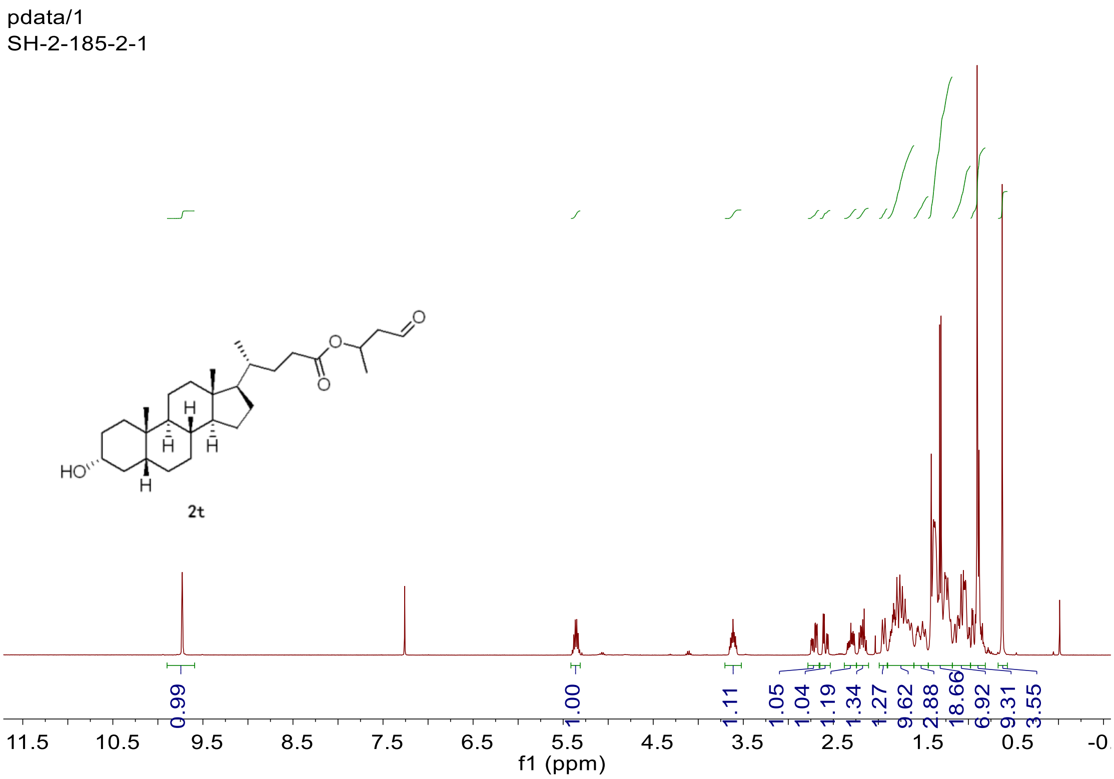


Figure 79 ^{1}H NMR of spectrum of **2t**

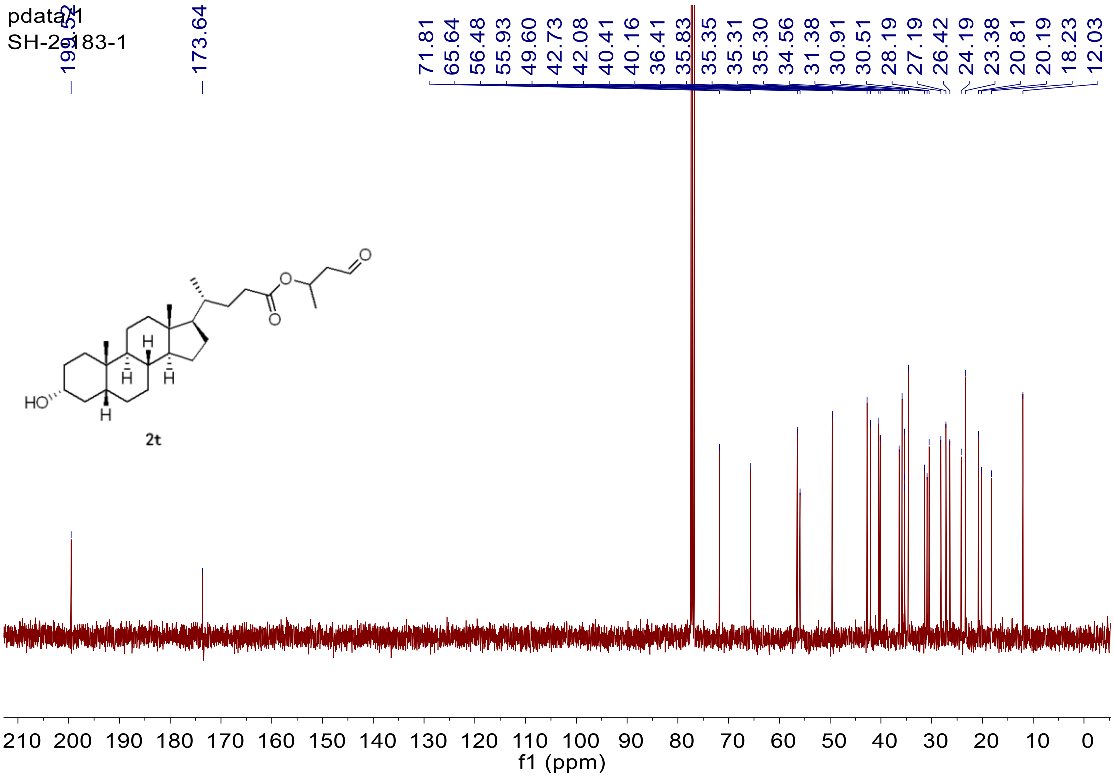


Figure 80 ^{1}H NMR of spectrum of **2t**

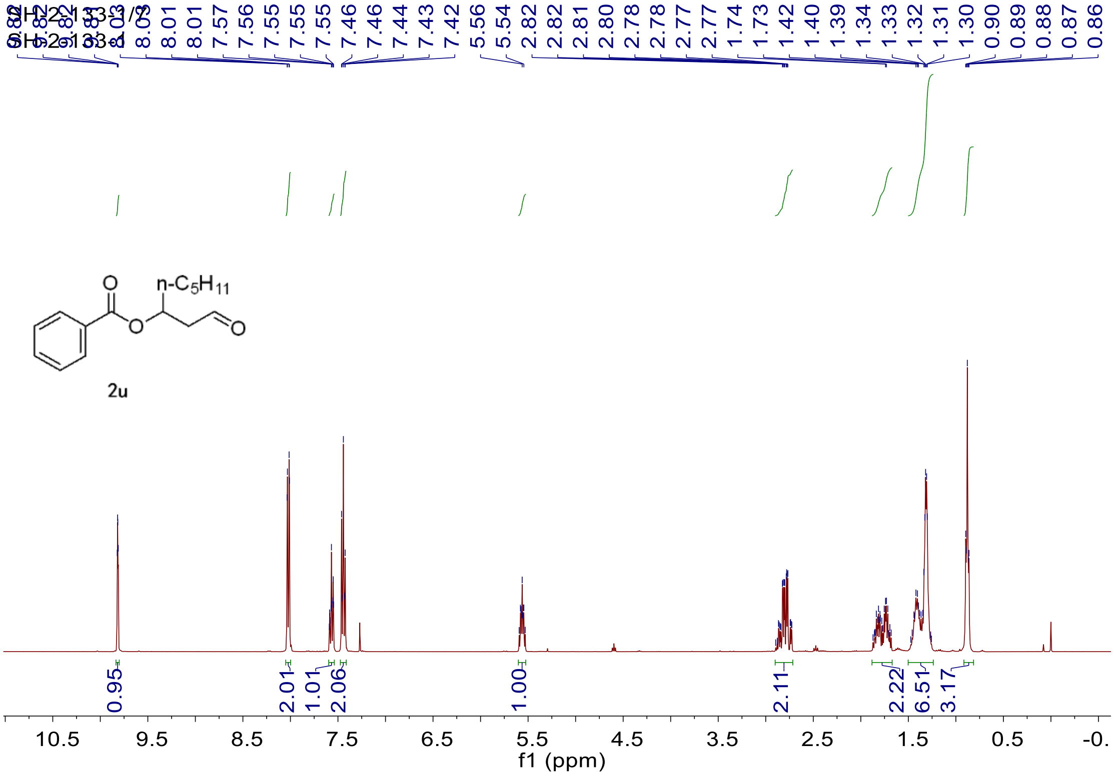


Figure 81 ^{1}H NMR of spectrum of **2u**

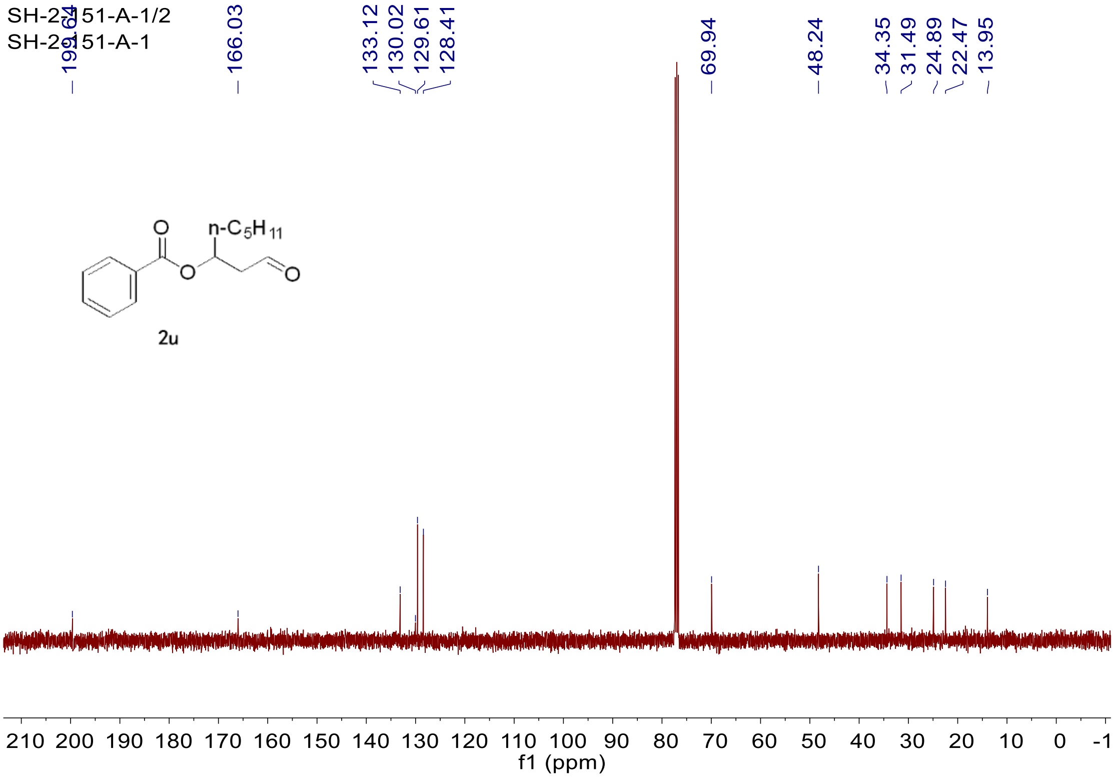


Figure 82 ^{13}C NMR of spectrum of **2u**

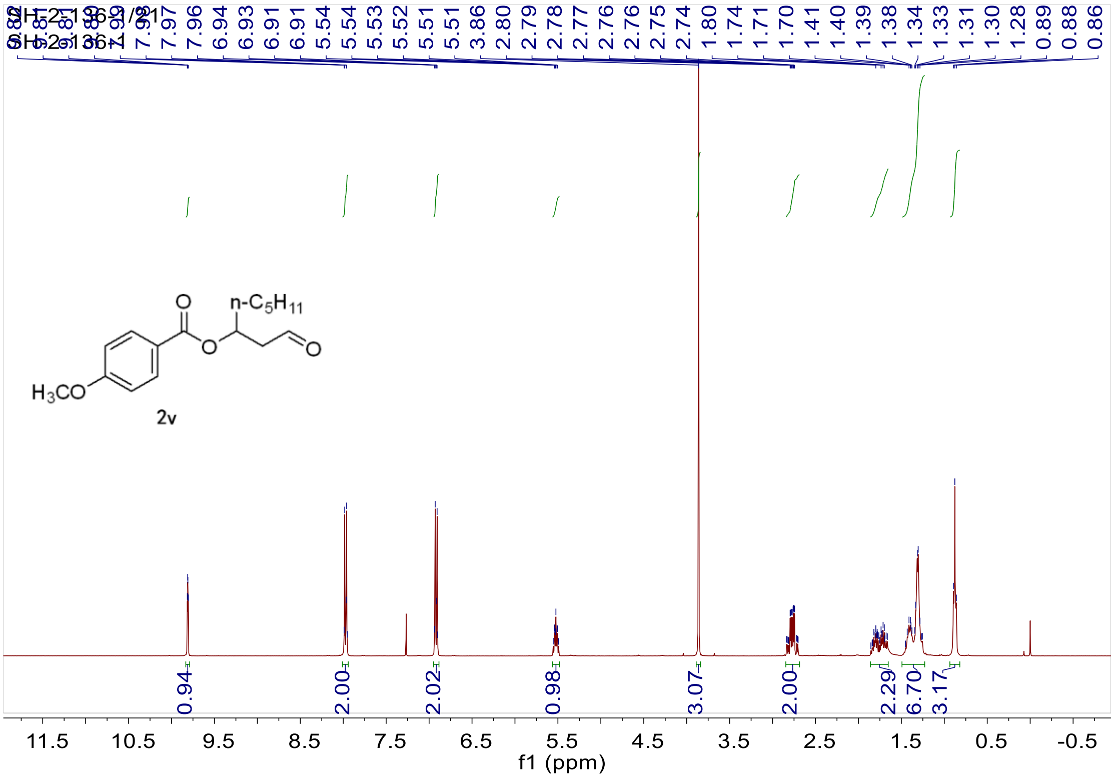


Figure 83 ^{1}H NMR of spectrum of **2v**

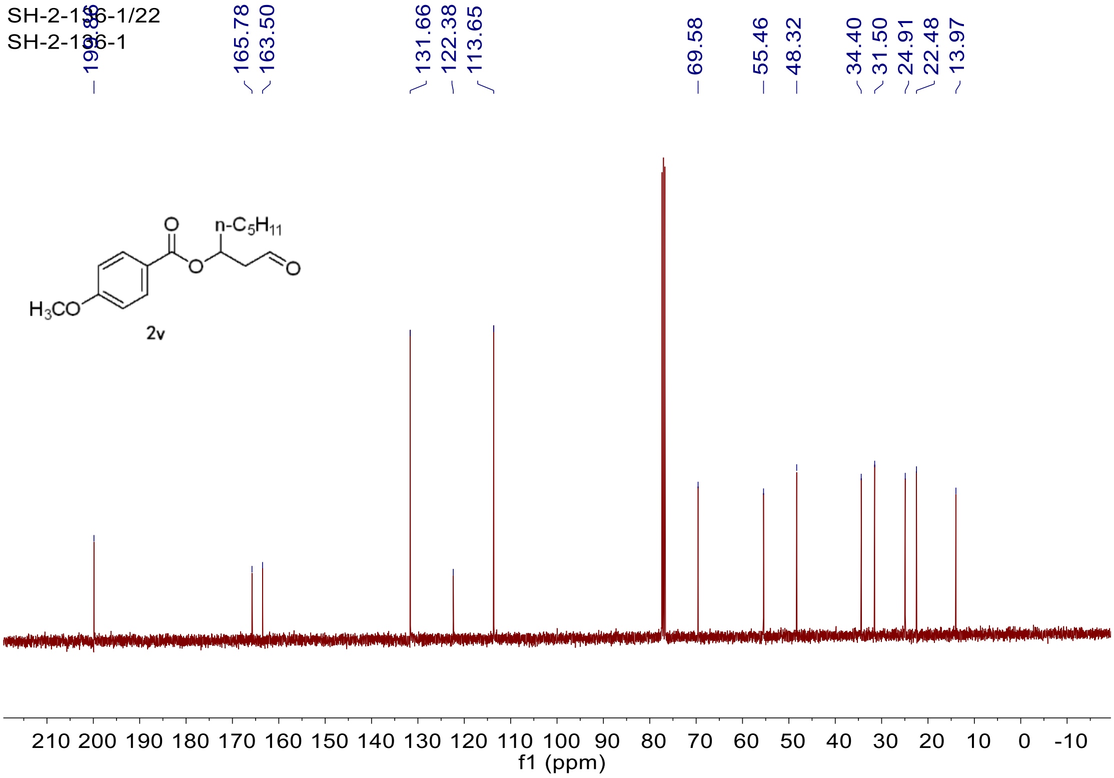


Figure 84 ^{13}C NMR of spectrum of **2v**

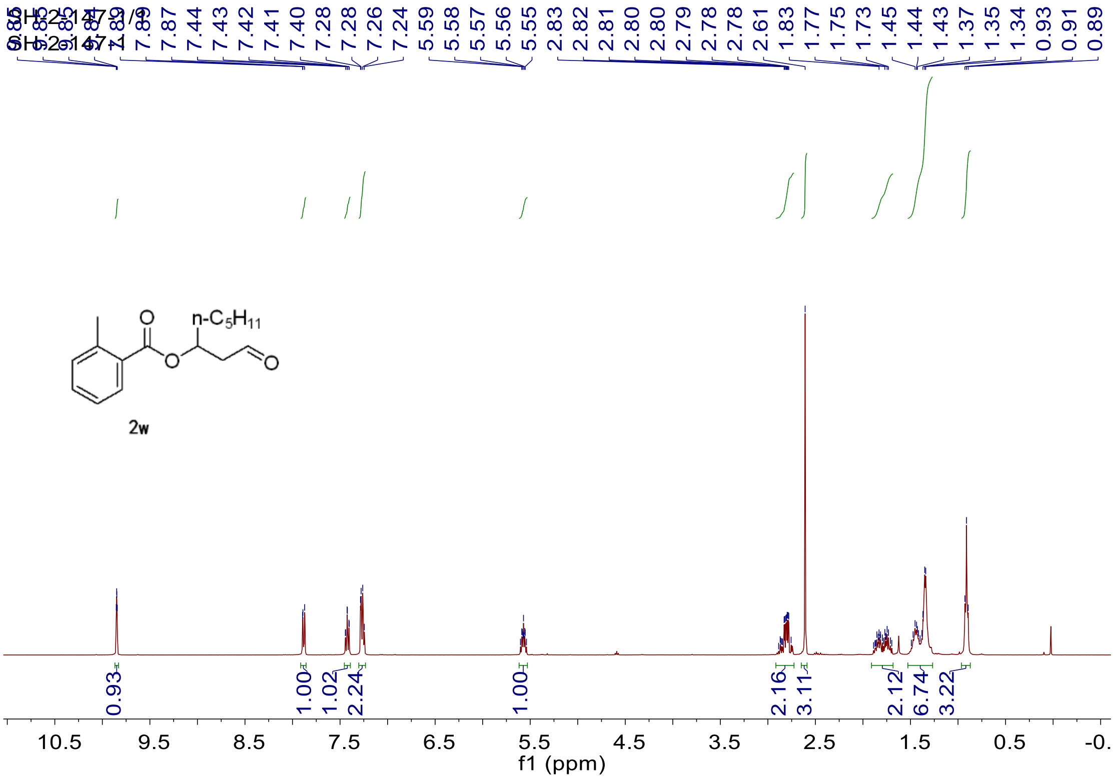


Figure 85 ^{1}H NMR of spectrum of **2w**

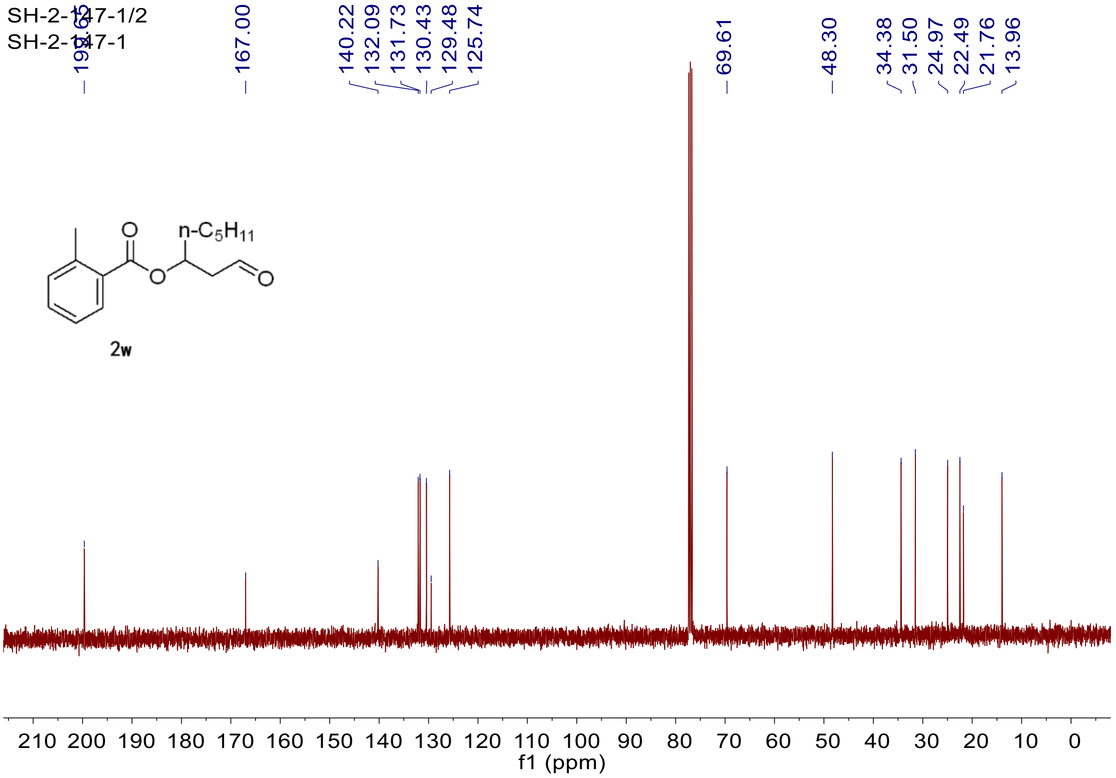


Figure 86 ^{13}C NMR of spectrum of **2w**

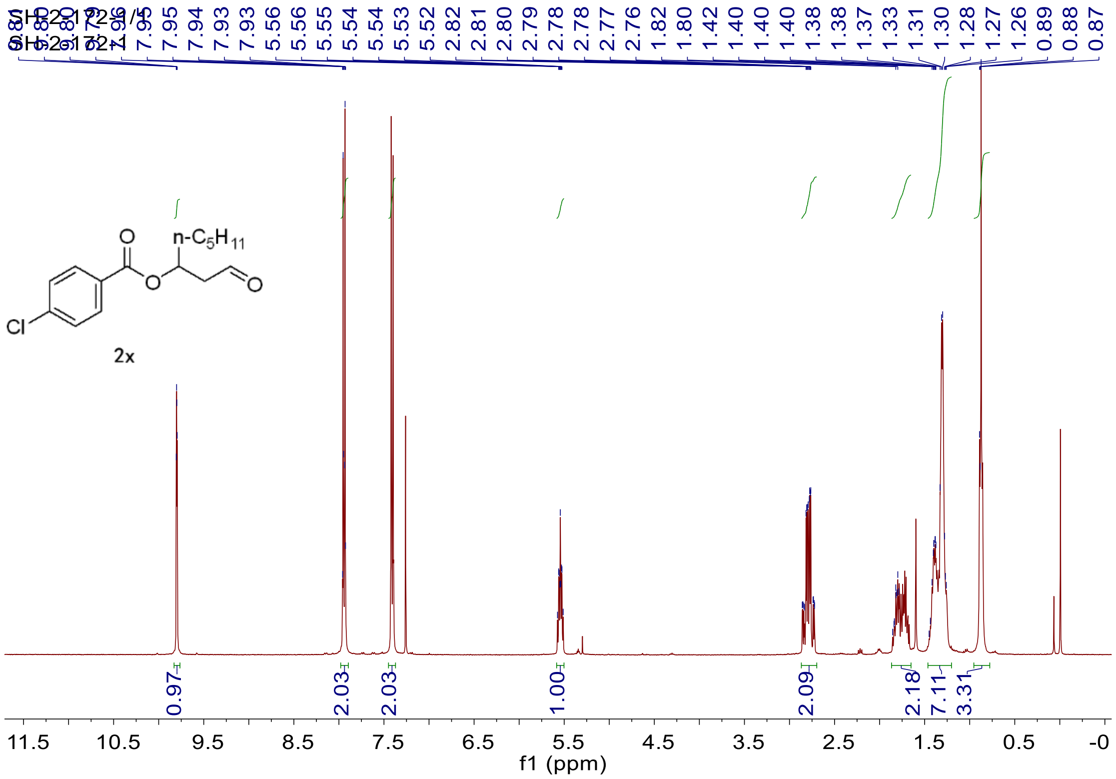


Figure 87 ^{1}H NMR of spectrum of **2x**

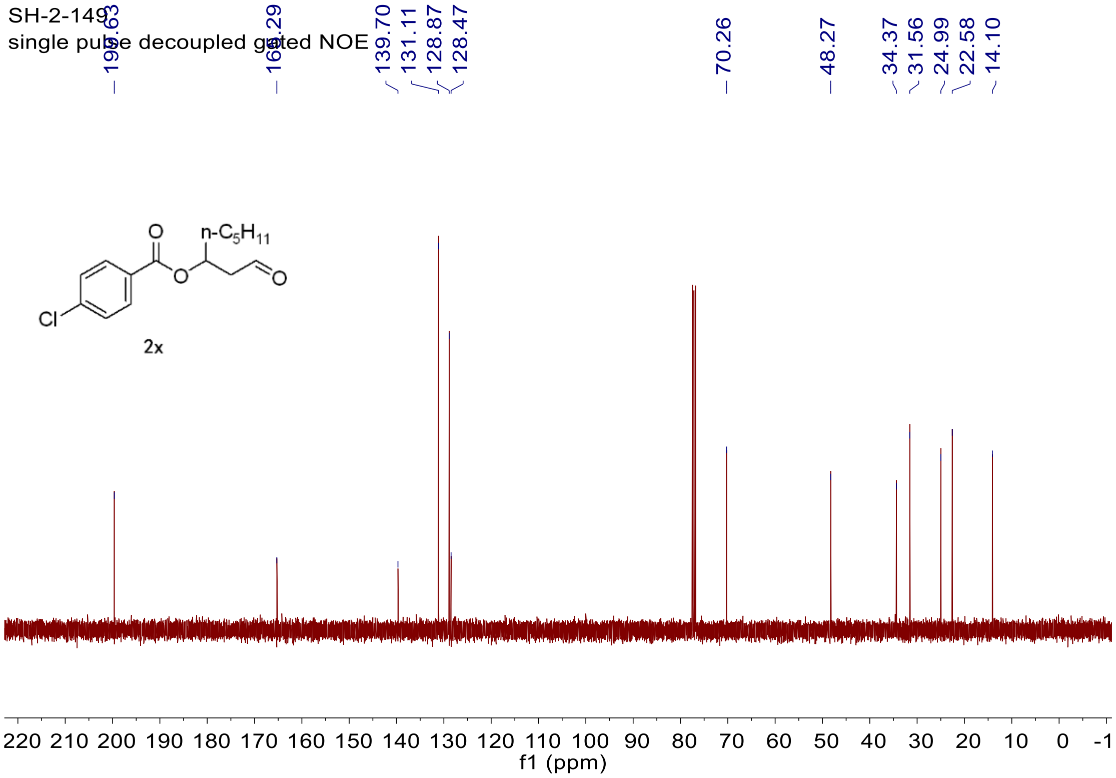


Figure 88 ^{13}C NMR of spectrum of **2x**

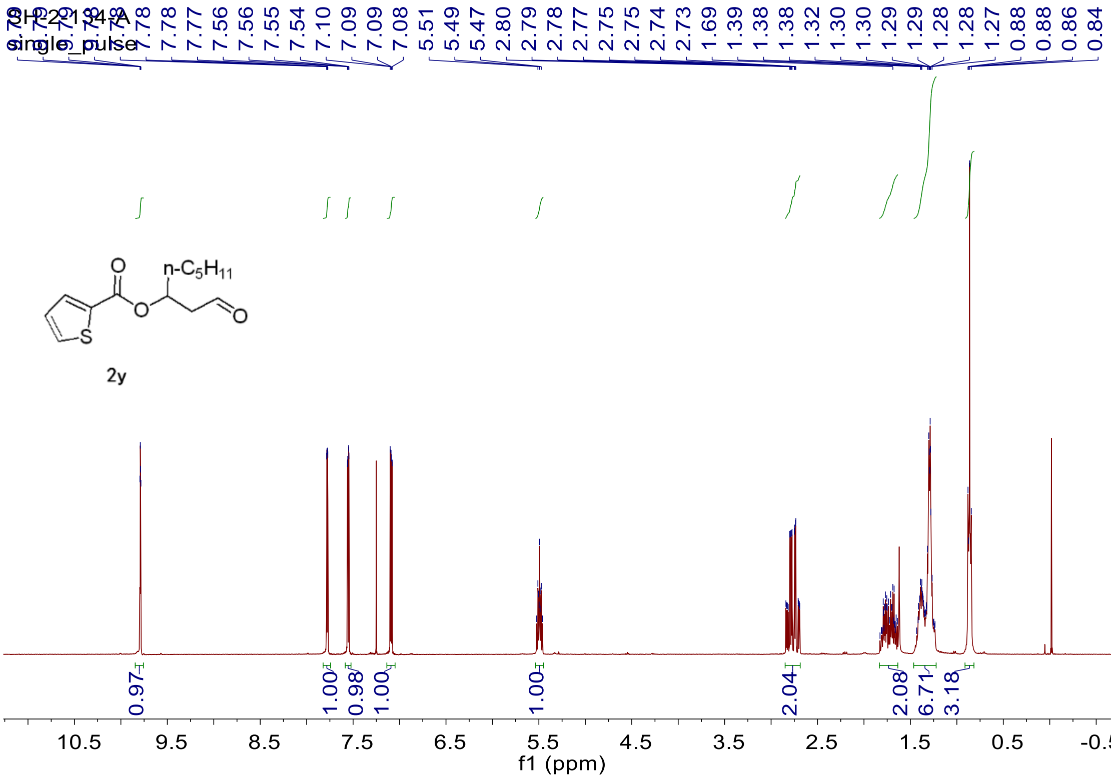


Figure 89 ^{1}H NMR of spectrum of **2y**

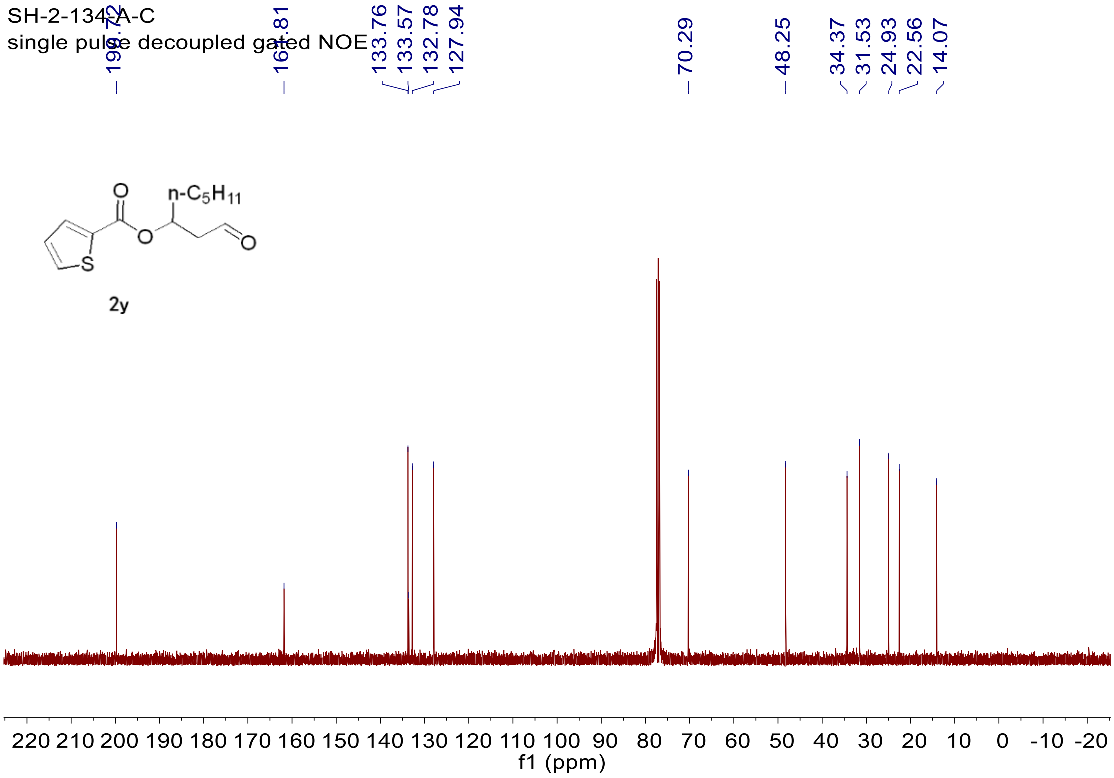


Figure 90 ^{13}C NMR of spectrum of **2y**

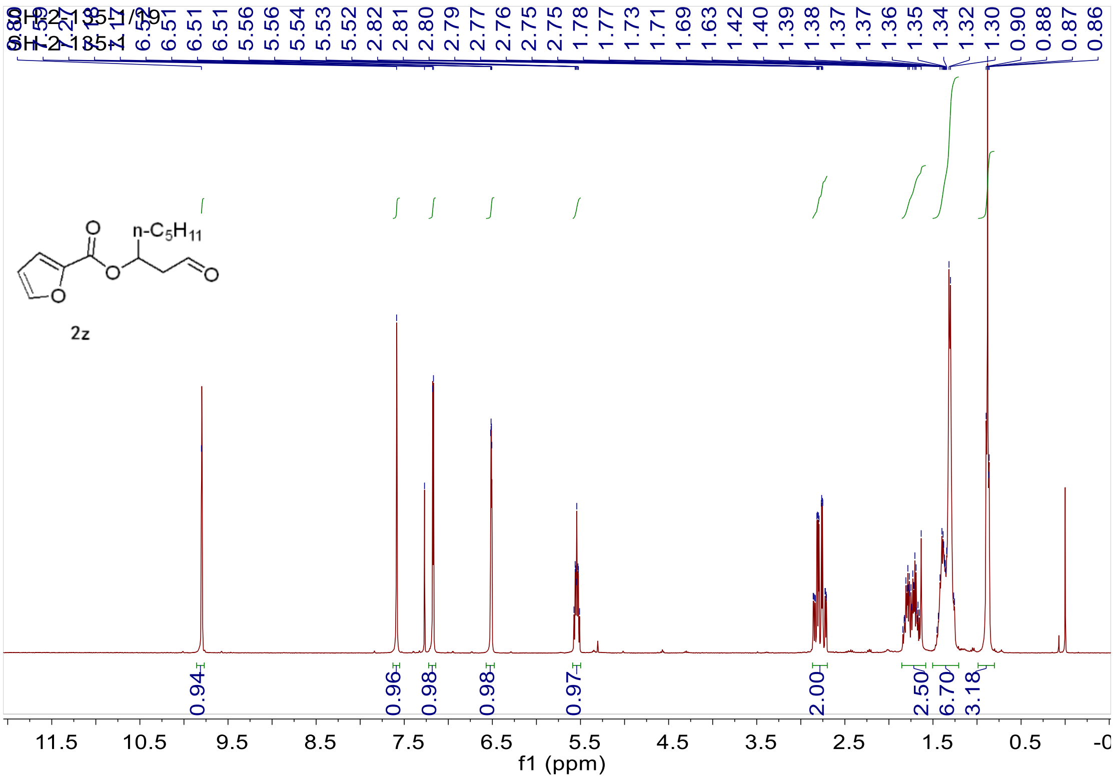


Figure 91 ^{1}H NMR of spectrum of **2z**

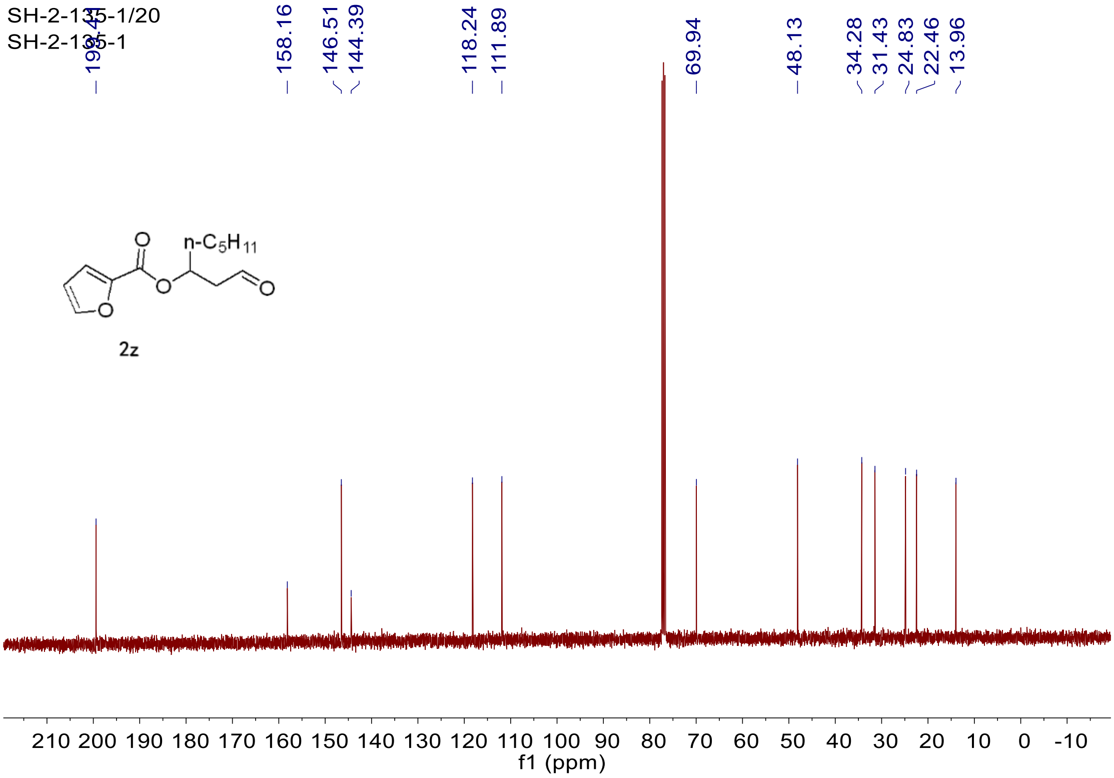


Figure 92 ^{13}C NMR of spectrum of **2z**

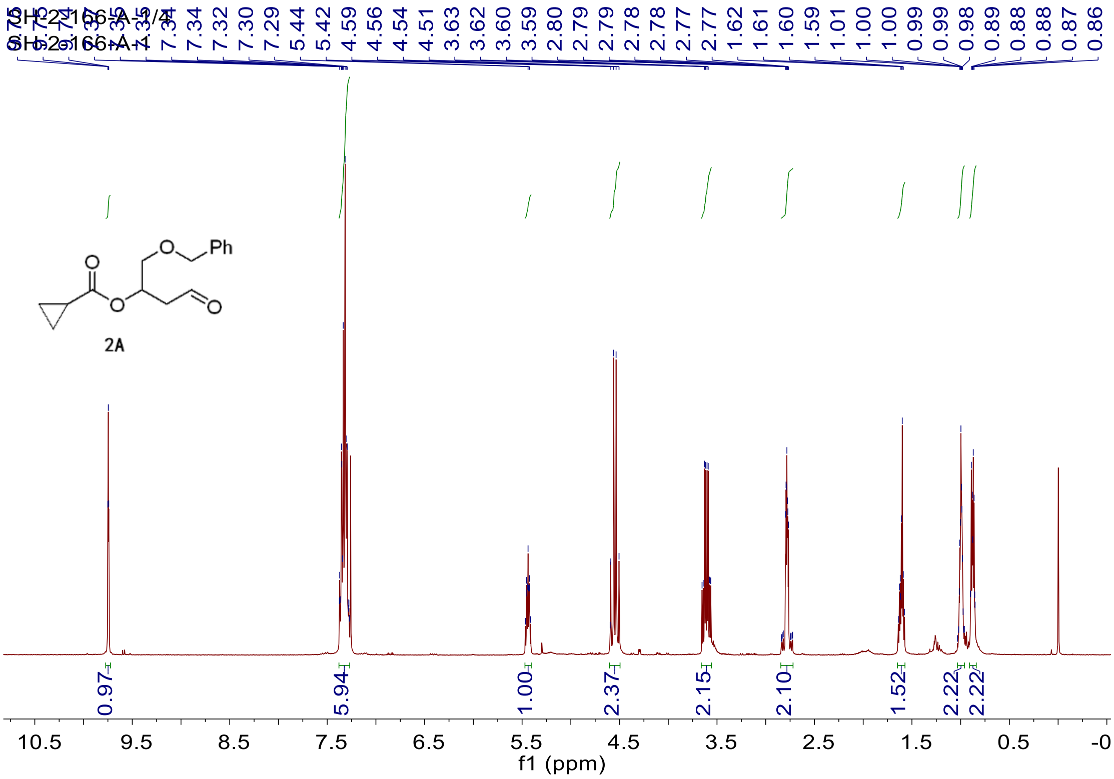


Figure 93 ^{1}H NMR of spectrum of **2A**

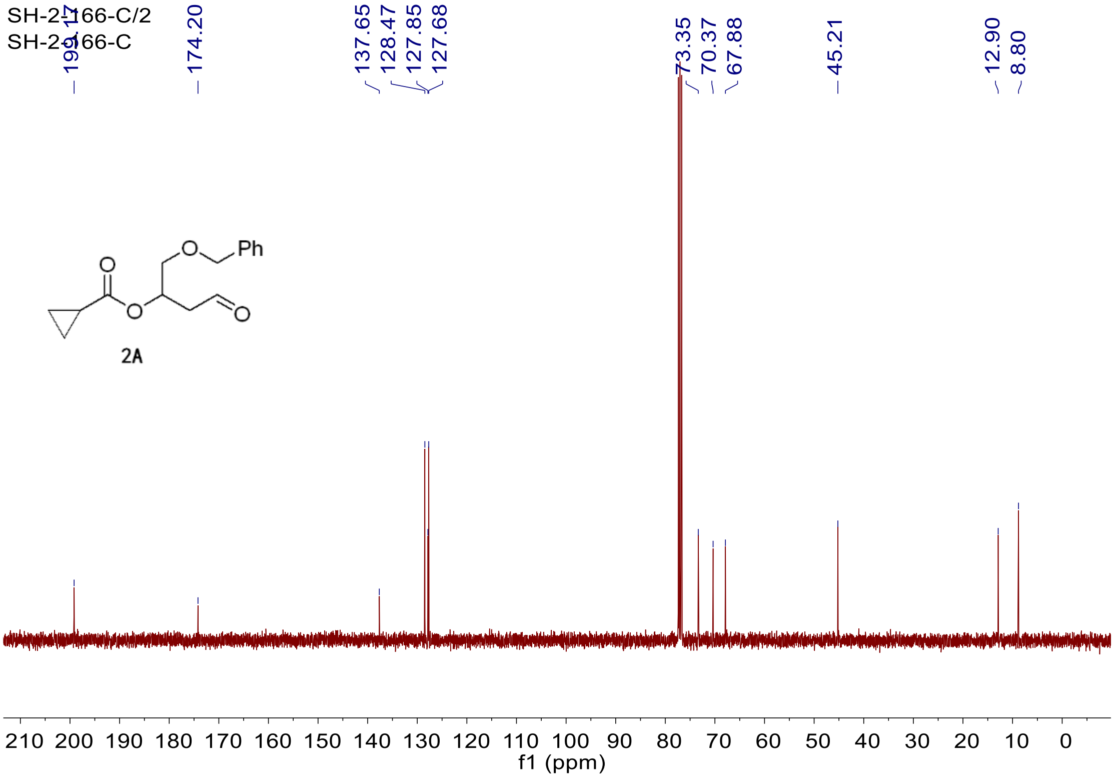


Figure 94 ^{13}C NMR of spectrum of **2A**

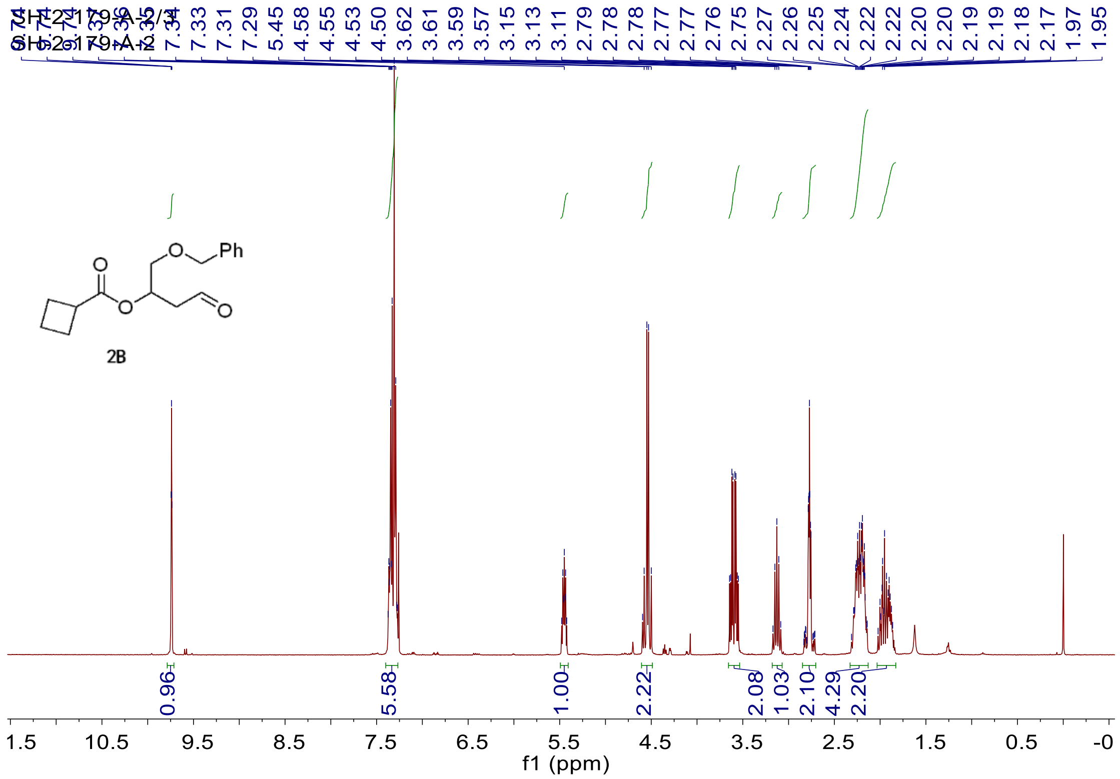


Figure 95 ^{1}H NMR of spectrum of **2B**

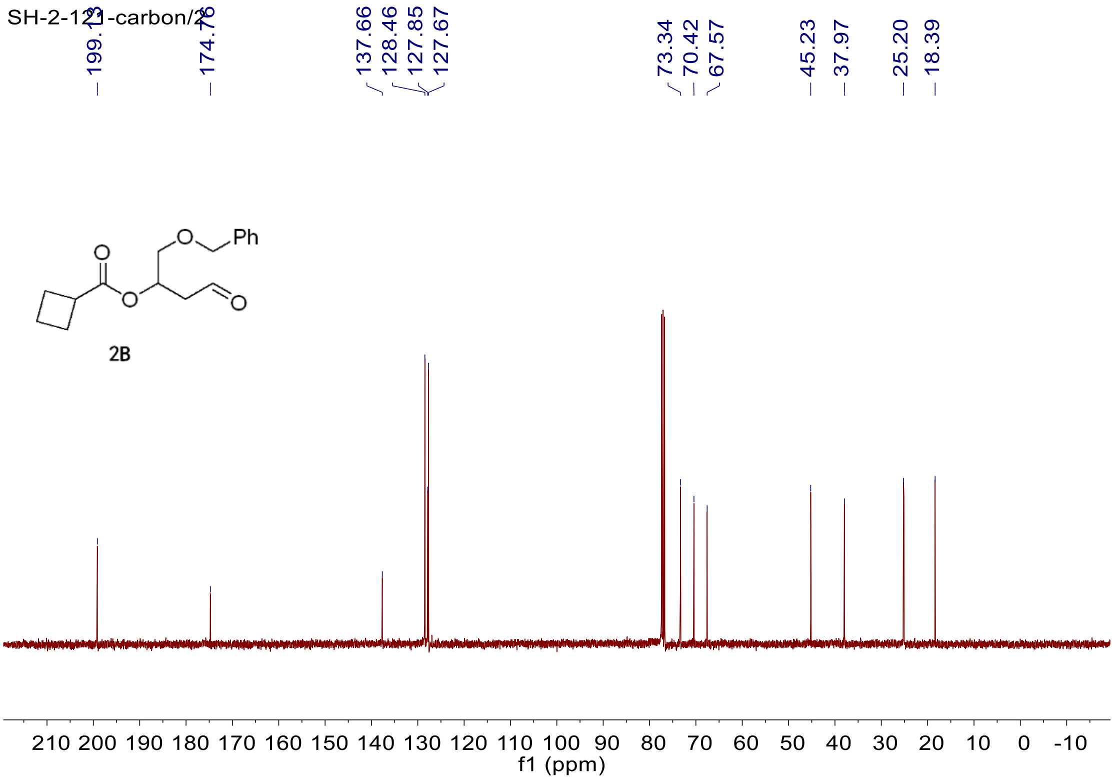


Figure 96 ^{13}C NMR of spectrum of **2B**

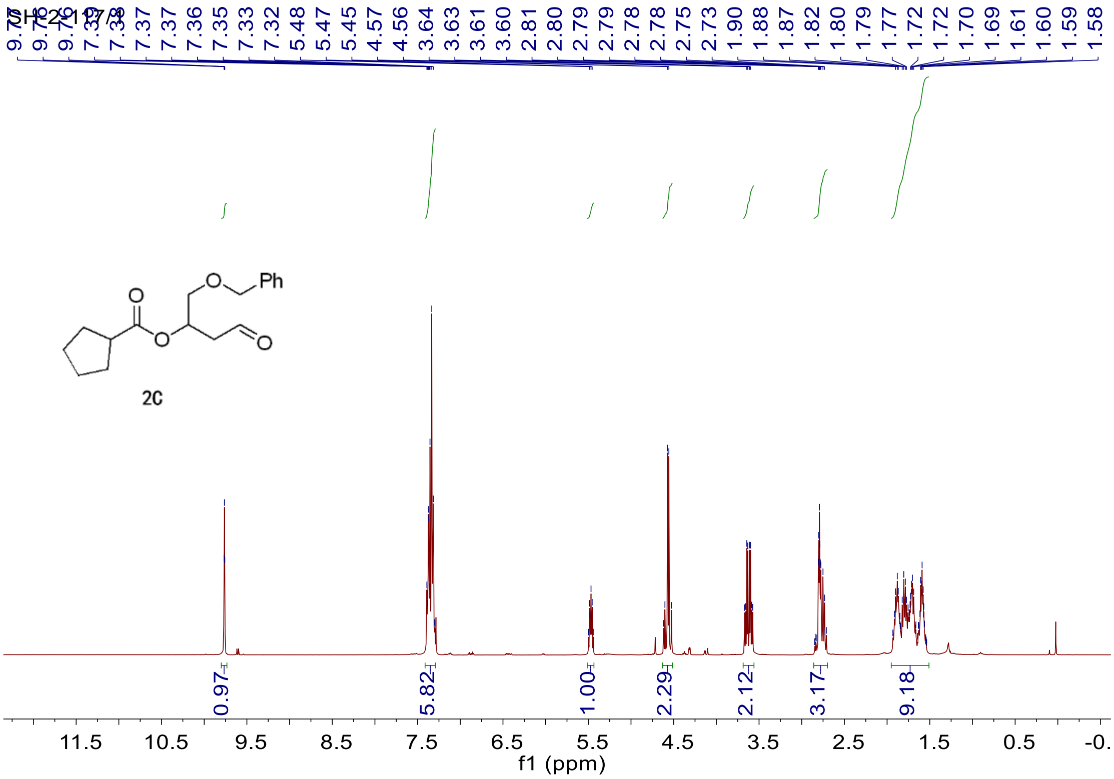


Figure 97 ^{1}H NMR of spectrum of **2C**

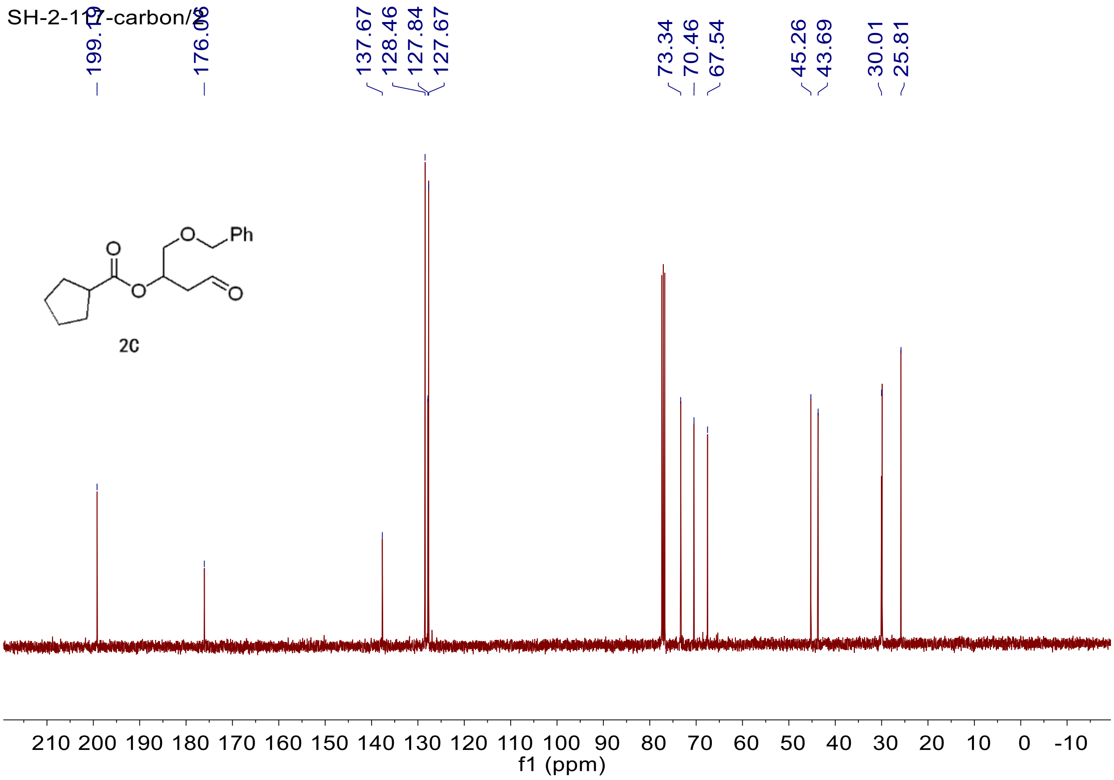


Figure 98 ^{13}C NMR of spectrum of **2C**

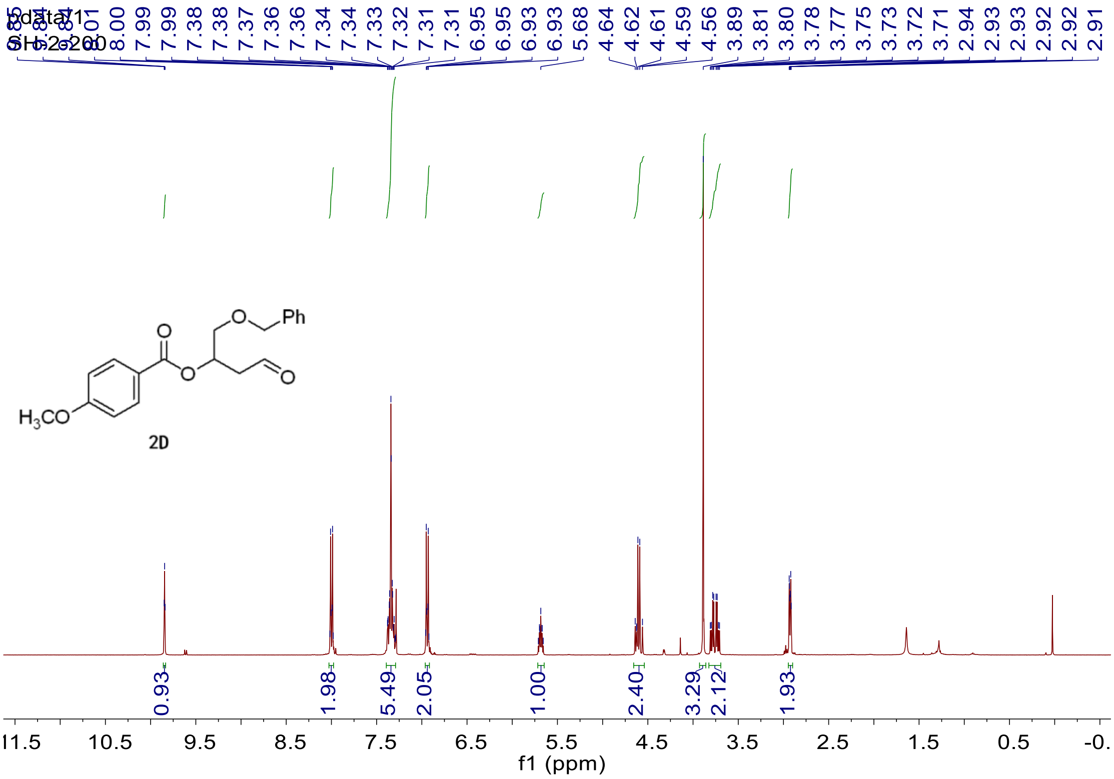


Figure 99 ^{1}H NMR of spectrum of **2D**

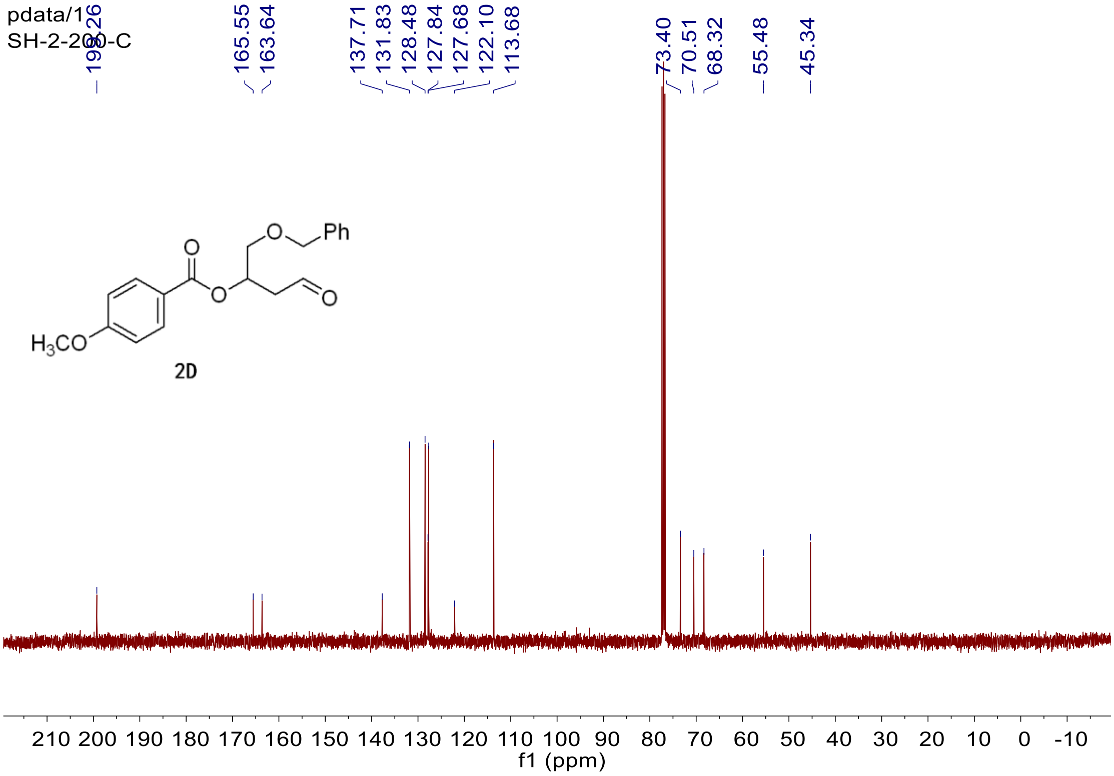


Figure 100 ^{13}C NMR of spectrum of **2D**

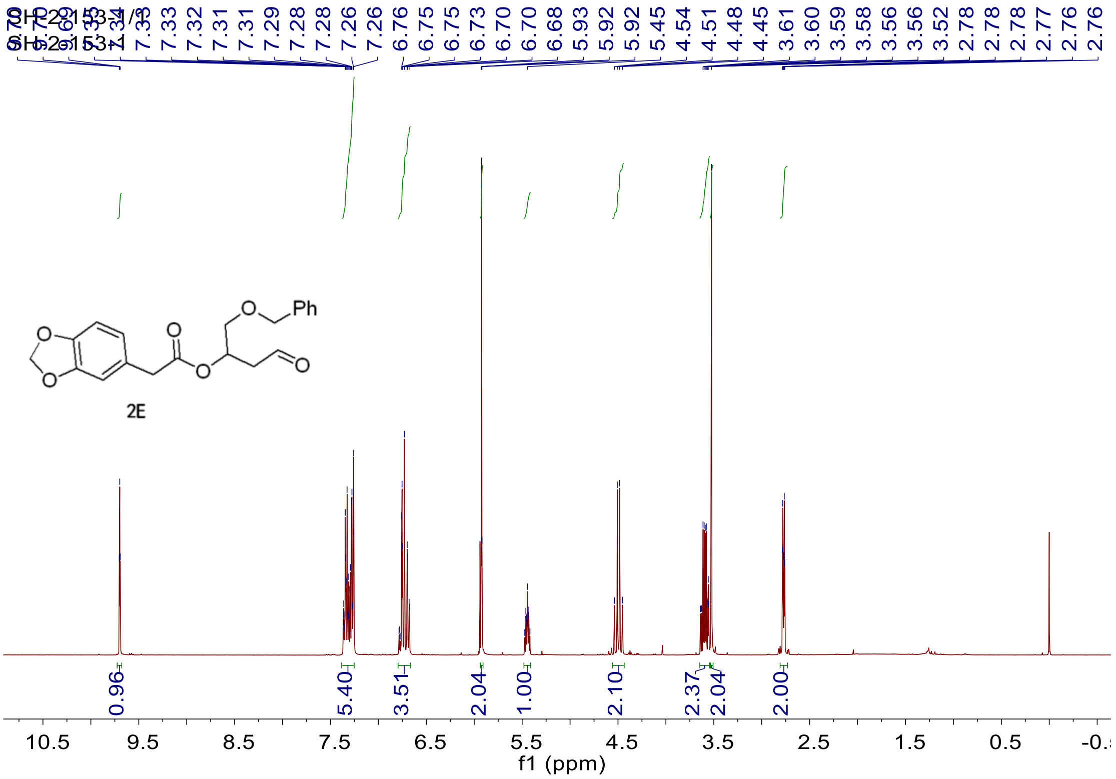


Figure 101 ^{1}H NMR of spectrum of **2E**

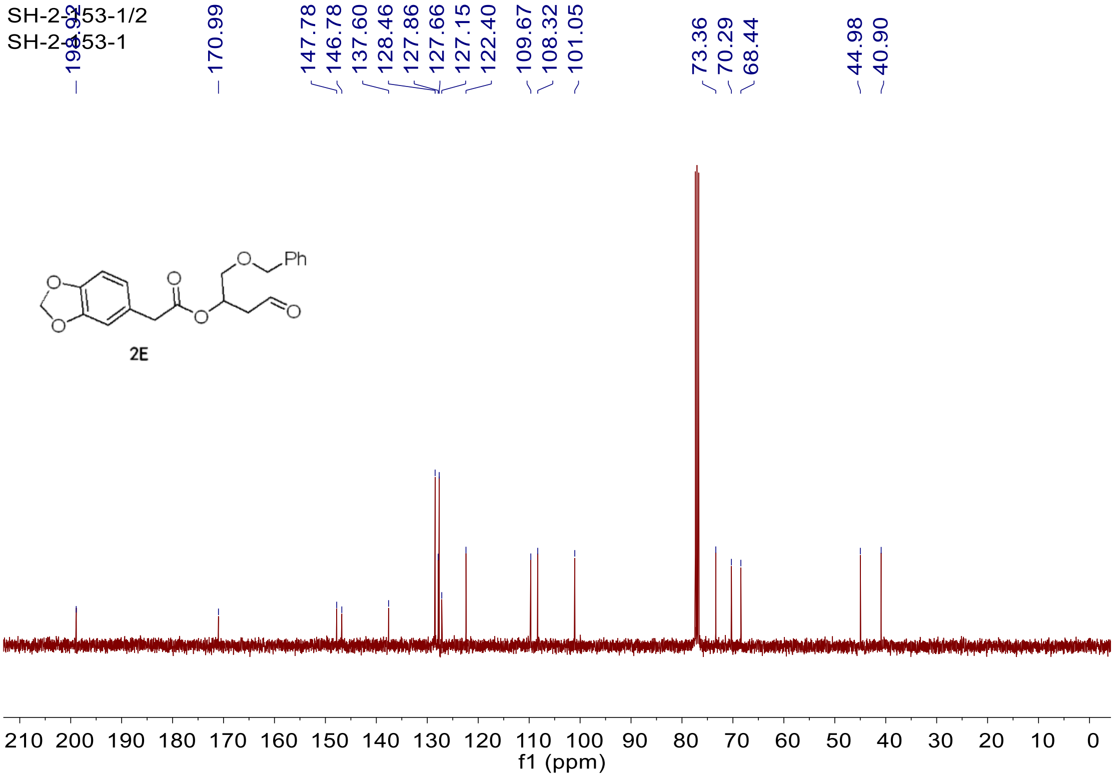


Figure 102 ^{13}C NMR of spectrum of **2E**

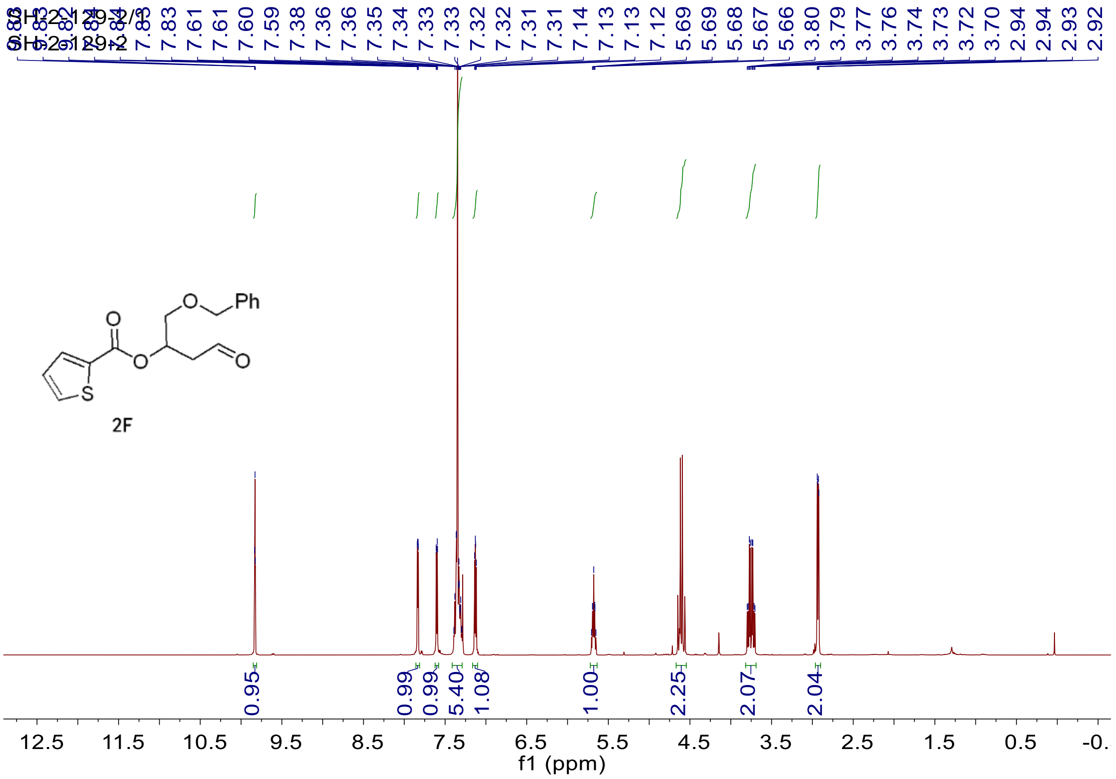


Figure 103 ^{1}H NMR of spectrum of **2F**

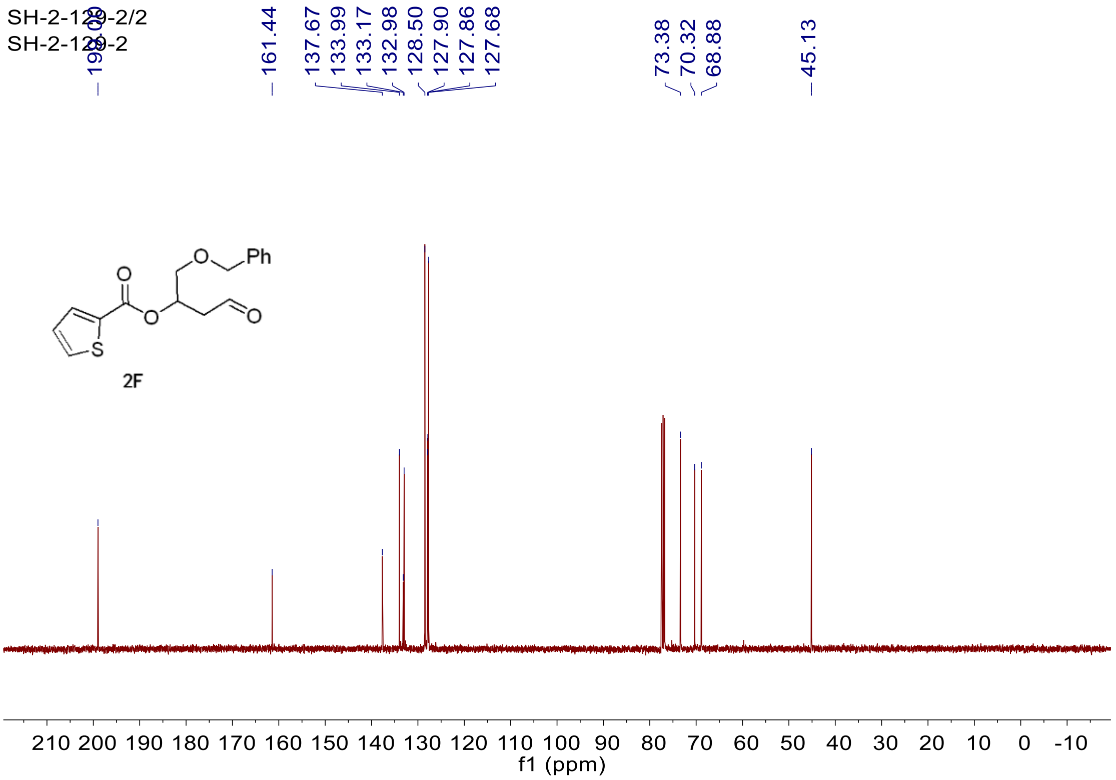


Figure 104 ^{13}C NMR of spectrum of **2F**

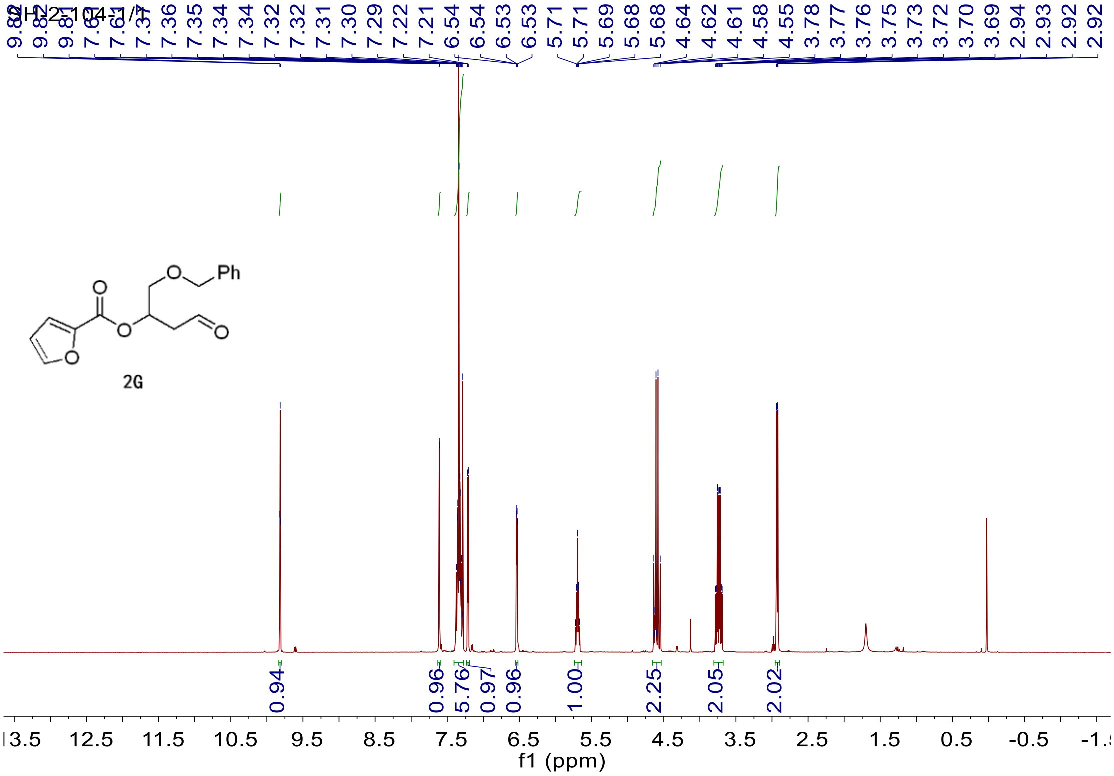


Figure 105 ^{1}H NMR of spectrum of **2G**

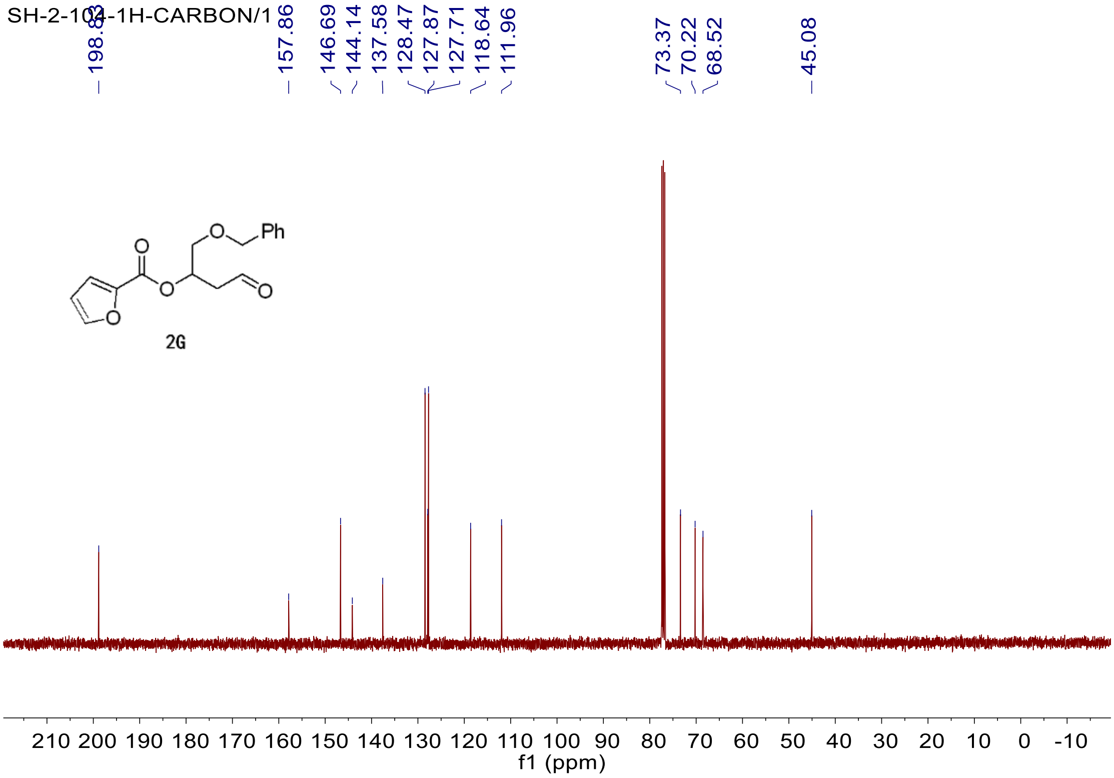


Figure 106 ^{13}C NMR of spectrum of **2G**

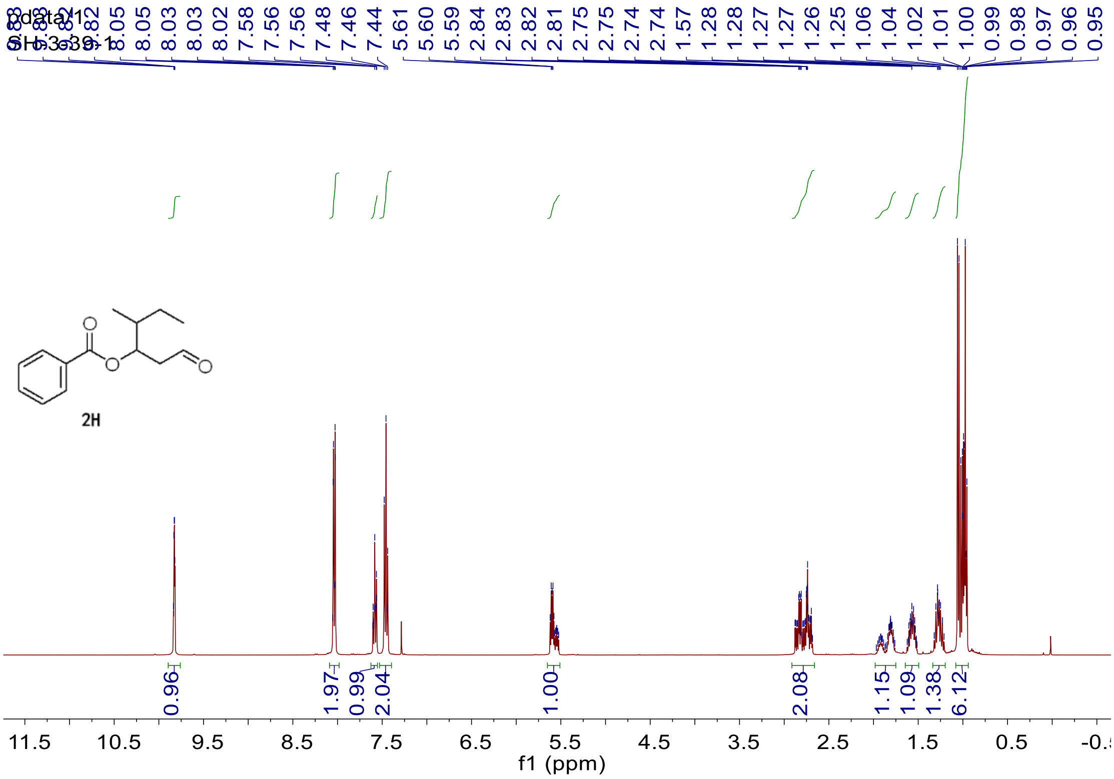


Figure 107 ^{1}H NMR of spectrum of **2H**

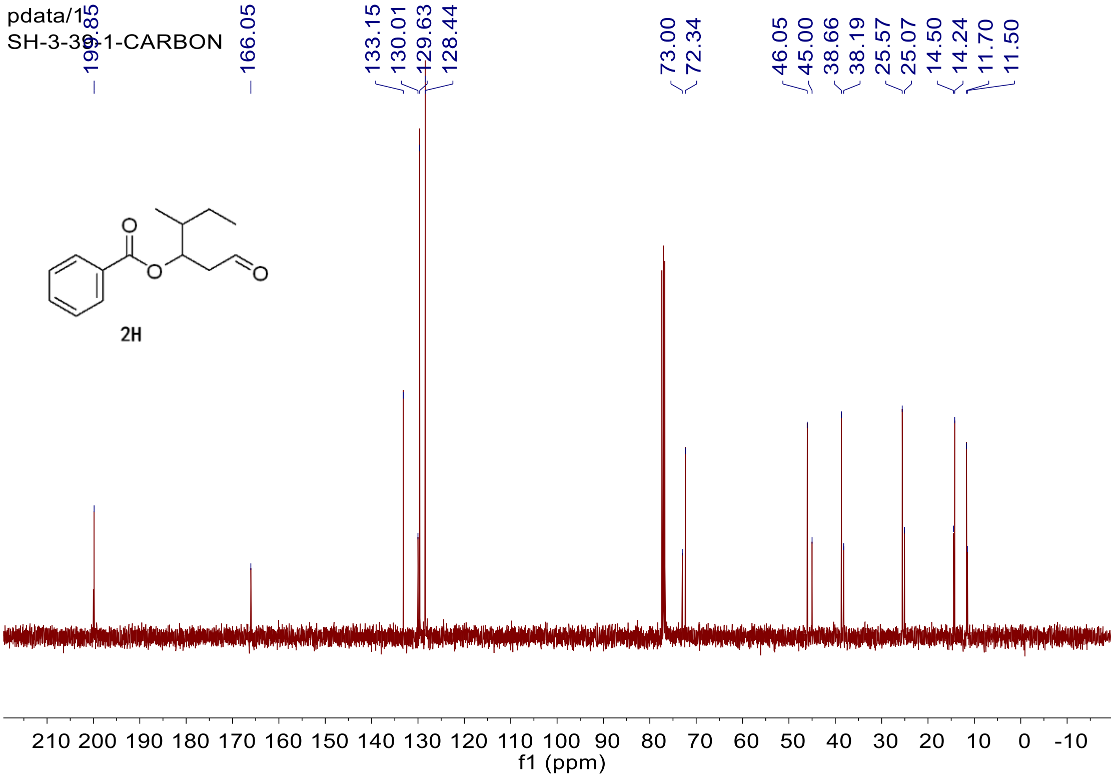


Figure 108 ^{13}C NMR of spectrum of **2H**

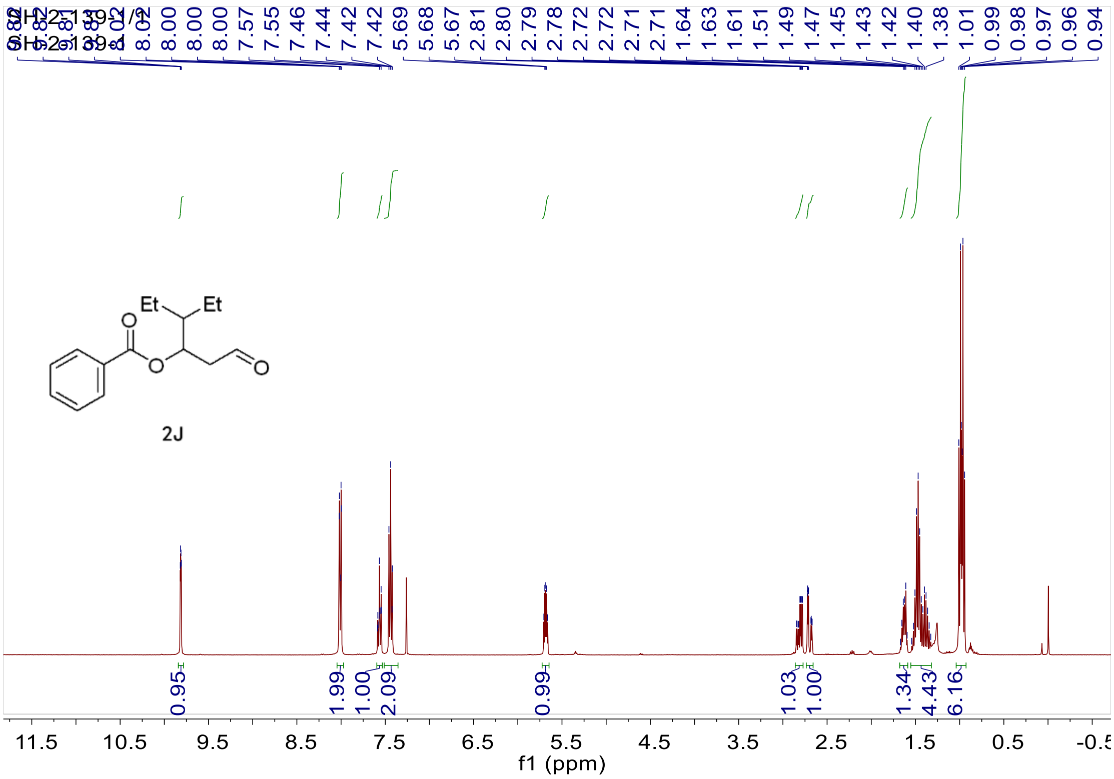


Figure 109 ^{1}H NMR of spectrum of **2J**

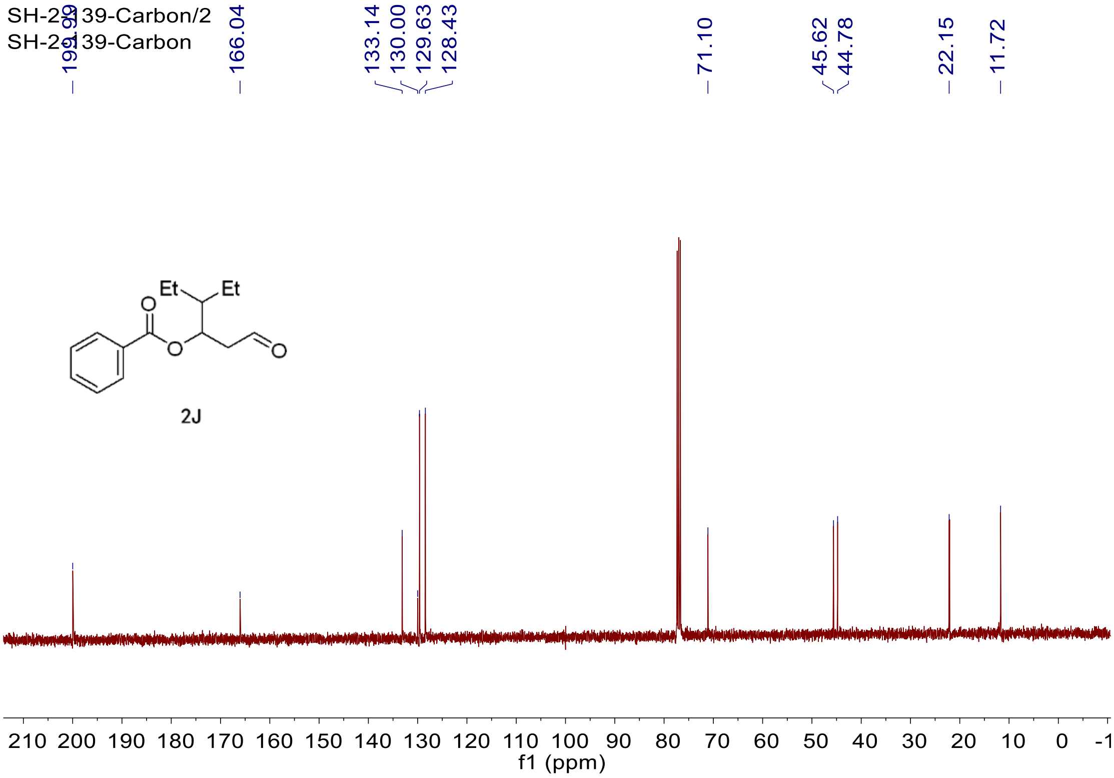


Figure 110 ^{13}C NMR of spectrum of **2J**

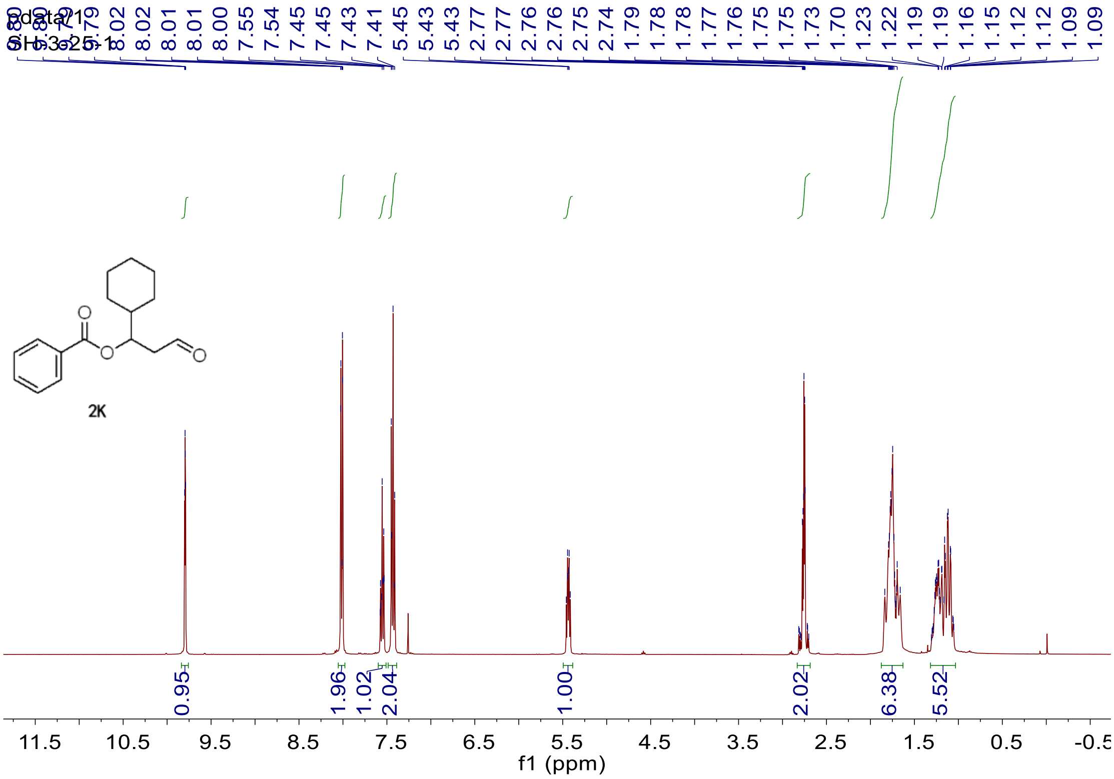


Figure 111 ^{1}H NMR of spectrum of **2K**

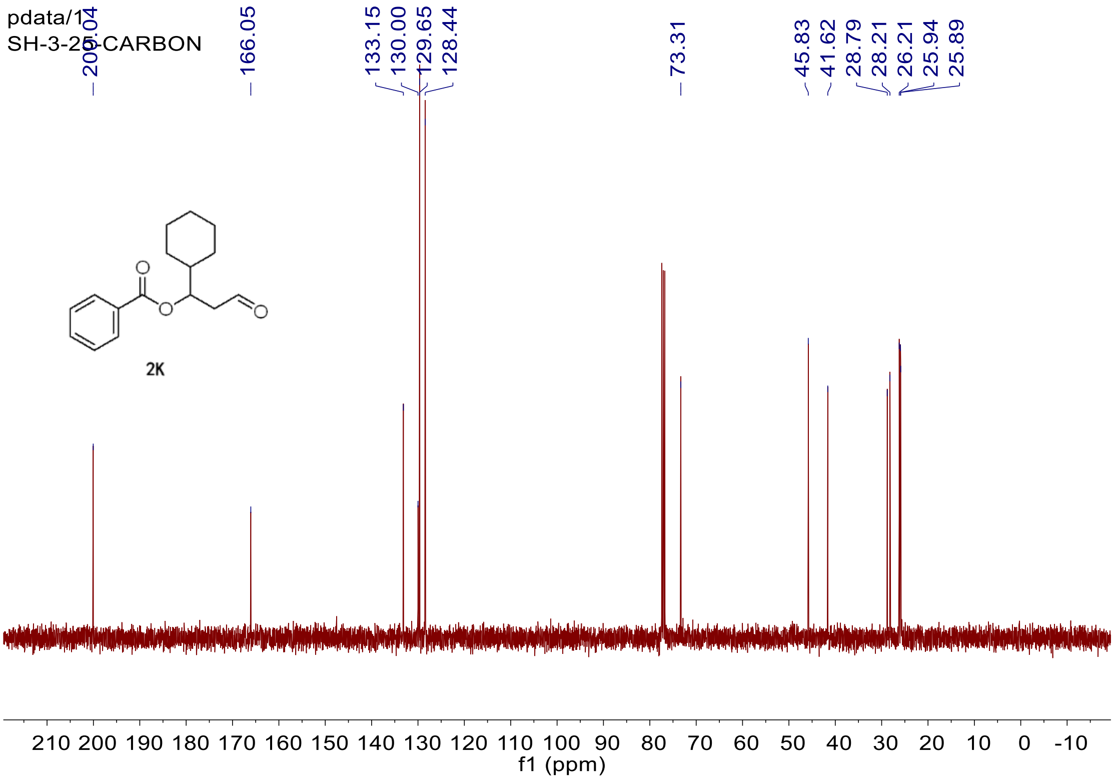


Figure 112 ^{13}C NMR of spectrum of **2K**

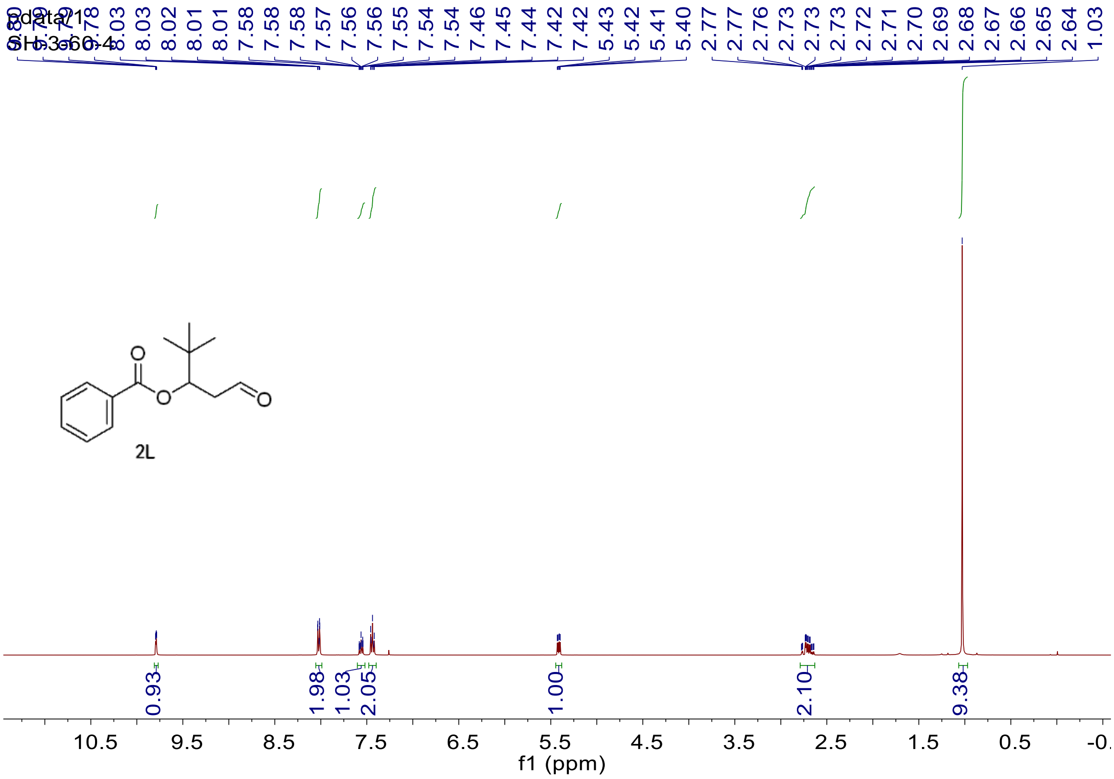


Figure 113 ^{1}H NMR of spectrum of **2L**

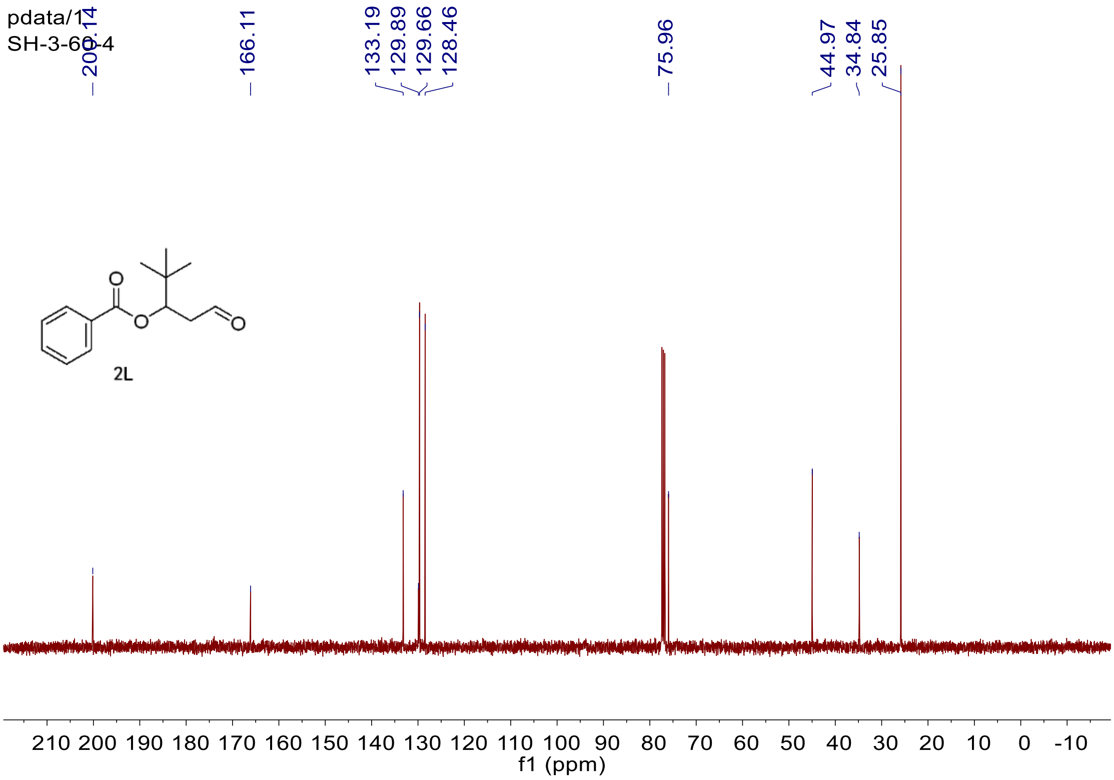


Figure 114 ^{13}C NMR of spectrum of **2L**

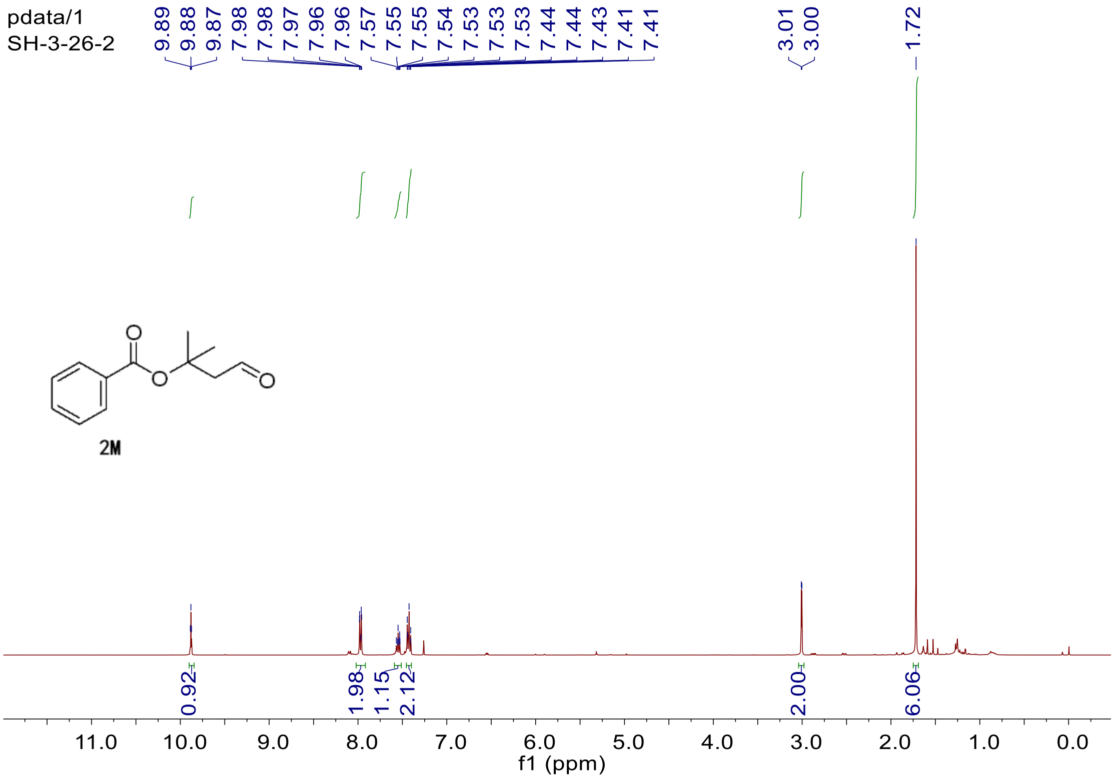


Figure 115 ^{1}H NMR of spectrum of **2M**

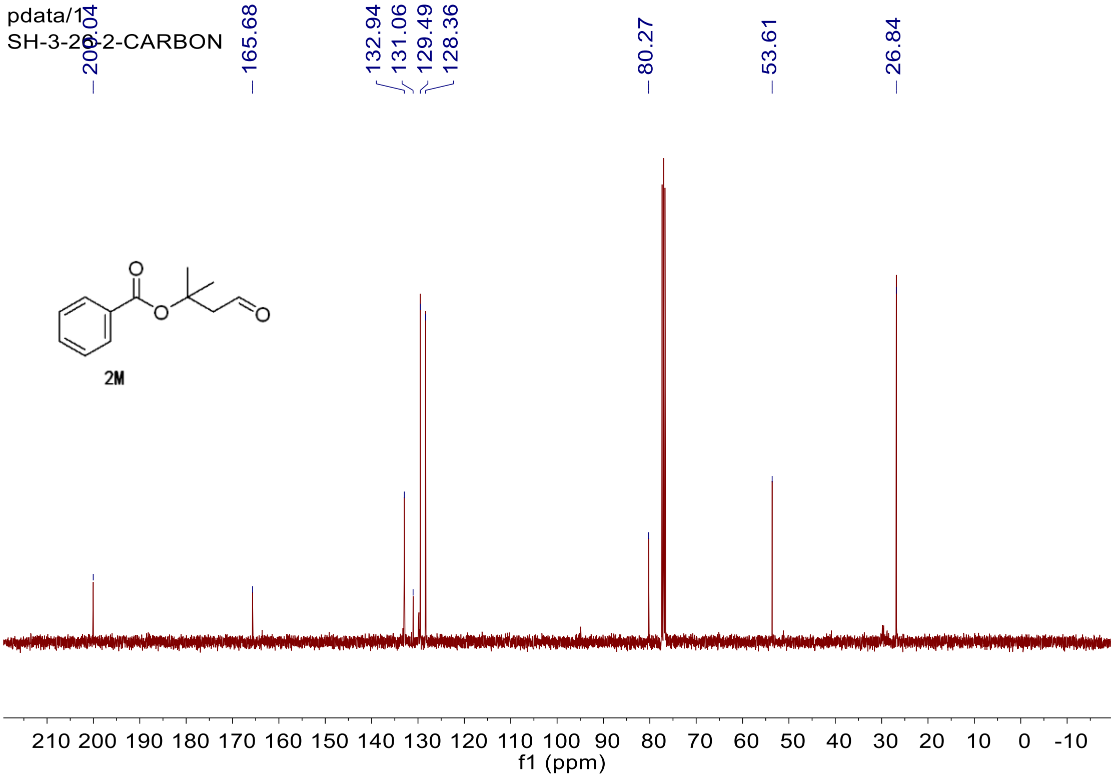


Figure 116 ^{13}C NMR of spectrum of **2M**

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