Supporting Information

Hypervalent-iodine Promoted Selective Cleavage of C(sp^3)–C(sp^3) Bonds in Ethers

Yaxin Wang,*[a,b] Qin He,[a] Zehui Cao,[a] Peng Wang,[b] Gong Chen[c] and Matthias Beller*[b]

[a] College of Pharmacy, Nanjing University of Chinese Medicine, Nanjing 210023 (China).
Email: 300500@njucm.edu.cn, Yaxin.Wang@catalysis.de

[b] Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein Straße 29a, 18059 Rostock (Germany).
E-mail: Matthias.Beller@catalysis.de

[c] State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071 (China).

Content

1. Reagents

All commercial materials were used as received unless otherwise noted. Superdry solvents (DCM, EtOAc, CH_3OH, EtOH, ethers, and HFIP) and deuterated solvents were purchased from *J&K* Chemical. Hypervalent iodine (III) reagents (BIN_3 **1**, BIOH, BIOAc, BICl) were synthesized according to reported procedures[1-4] and used as freshly prepared. Starting materials for this study were purchased from TCI or were synthesized according to reported procedures. $Ru(bpy)_3Cl_2$ (98%, Ru＞15.75%, Energy Chemical), LiCl (≥99%, Aladdin), and Bu_4NBr (99%, Energy Chemical) were used for studying the deconstructive oxygenation and esterification reactions of ethers. TLC were performed on silica gel Huanghai HSGF254 plates and visualization of the developed chromatogram was performed by fluorescence quenching (λ_{max} = 254 nm). Flash chromatography was performed using silica gel (200-300 mesh) purchased from Qingdao Haiyang Chemical Co., China.

2. Instruments

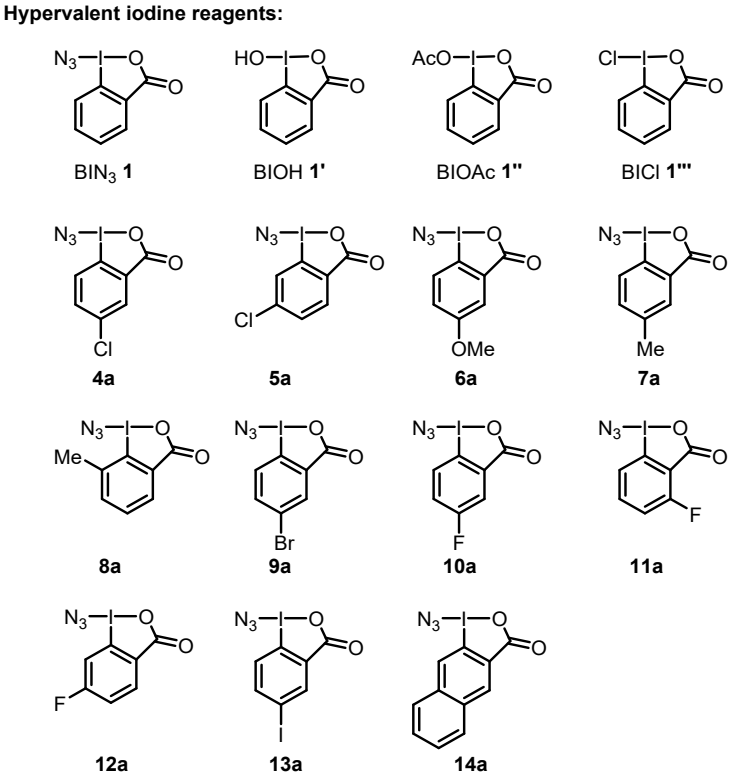
NMR spectra were recorded on Bruker AVANCE AV 500 or 300 instruments and all NMR experiments were reported in units, parts per million (ppm), using residual solvent peaks as internal reference. Multiplicities are recorded as: s = singlet, d = doublet, t = triplet, dd = doublet of doublets, br = broad singlet, m = multiplet. High resolution ESI mass experiments were operated on a Waters LCT Premier instrument. All reactions were carried out in a 20 mL glass vial (Thermo SCIENTIFIC National B7999-2, made from superior quality 33 expansion borosilicate clear glass), sealed with a PTEF cap on bench top if necessay.

Lights: PHILIPS TORNADO 24W CFL and Cnlight blue LED lights 24 W were used for photo-promoted reactions.

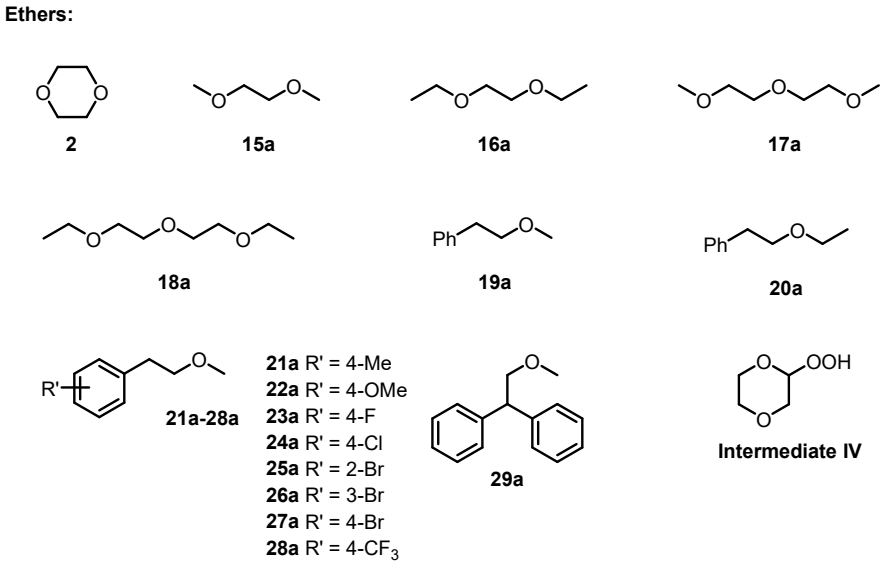
Note： All reactions and subsequent workup were performed behind a blast shield with the sash positioned as low as possible. While we did not encounter any issues

during their synthesis, proper precautions were taken.

3. Synthesis of substrates



Scheme S1. List of hypervalent iodines reagents used in this study[1-4]

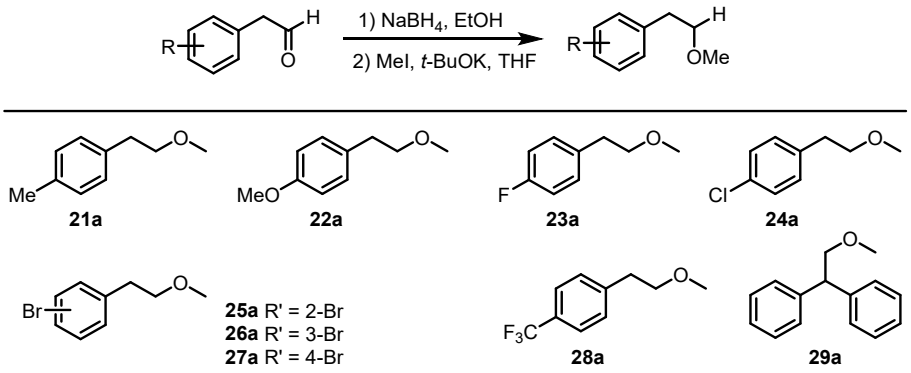


Scheme S2. Ether substrates used in this study

Hypervalent iodine (III) reagents in Scheme **S1** were synthesized according to

reported procedures and used as freshly prepared.[1-4] Ethers for this study were purchased from TCI or were synthesized according to reported procedures.[5-6]

3.1 Synthesis of compounds arenethyl alkyl ethers



Scheme S3. Synthesis of arenethyl alkyl ethers

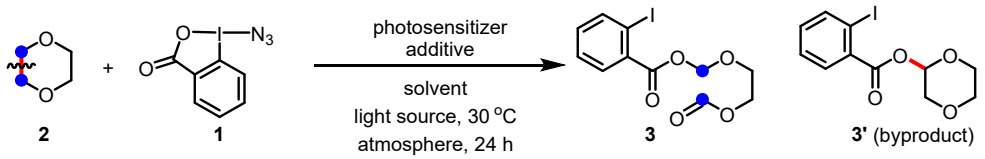
The preparation of alcohols: To a solution of phenylacetone (5 mmol, 1 equiv) in 5 mL EtOH, $NaBH_4$ (5 mmol, 1.0 equiv) was added slowly at 0 °C. After After stirring at room temperature for two hours, saturated NH_4Cl was added slowly and the EtOH was removed *in vacuo*. Ether was added and aqueous layer was removed. The organic layer was washed with water, brine, and dried over Na_2SO_4. The solvent was removed *in vacuo* to afford pure alcohol.

The preparation of ether: The pure alcohol (5 mmol, 1.0 equiv) was taken up in THF (10 mL) and KO*t*Bu (5 mmol, 1.0 equiv) was added. The reaction mixture was sonicated for 5 mins and MeI (5 mmol, 1.0 equiv) was added dropwise at 0 °C. The reaction was stirred over night and the solvent was removed. EtOAc was added and washed with water. The organic layer was dried over Na_2SO_4 and filtered through a short plug of silica gel to afford pure ether. The ^{1}H-NMR spectroscopic data of compounds **21a-29a** were consistent with those previously reported in the literature.[5-6]

4. Reaction optimization for C(sp^3)-C(sp^3) bond esterification of dioxane

All screening reactions were carried out at a 0.5 mmol scale in a 20 mL glass vial (Thermo Scientific, National B7999-2) sealed with PTEF cap and stirred on bench top. A 24 W blue-led light or 24 W white Compact Fluorescent Lamp (24 W white CFL) was positioned 5 cm aside from the reaction vials if necessary.

Dioxane **2** and other specified reagents were first dispersed in specific solvent and stirred for 5 min at rt. Reagent **1** BIN_3 was then added, and the resulting mixture was vigorously stirred at 30 °C with or without light irradiation for 24 h. After removal of the solvent *in vacuo*, the resulting residue was dissolved in 1 mL of $CDCl_3$ along with $Cl_2CHCHCl_2$ (20 uL) as an internal standard for ^{1}H-NMR analysis. The composition of reaction mixture was analyzed based on the methylene peak at δ 5.57 (s, 2H) for compound **3**, and the methyne δ 6.11 (s, 1H) for compound **3'**.



Entry	**2** (mL)	**1** (mmol)	Catalyst (equiv.)	Additive (equiv.)	Solvent (mL)	Light source	Atmosphere	Yield **3** (%)	Yield **3'** (%)
1	0.2 mmol	1.0	$Ru(bpy)_3Cl_2$ (0.01)	No	HFIP (1)	White CFL	Air	13	16
2	1	0.5	$Ru(bpy)_3Cl_2$ (0.01)	No	HFIP (1)	White CFL	Air	33	31
3	2	0.5	$Ru(bpy)_3Cl_2$ (0.01)	No	HFIP (2)	White CFL	Air	38	29
4	3	0.5	$Ru(bpy)_3Cl_2$ (0.01)	No	HFIP (3)	White CFL	Air	40	27
5	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	No	HFIP (5)	White CFL	Air	51	20

6	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	NaCl (0.1)	HFIP (5)	White CFL	Air	50	20
7	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	LiCl (0.1)	HFIP (5)	White CFL	Air	51	19
8	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	NaBr (0.1)	HFIP (5)	White CFL	Air	48	20
9	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	Na_2SO_4 (0.1)	HFIP (5)	White CFL	Air	50	19
10	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	Cs_2CO_3 (0.1)	HFIP (5)	White CFL	Air	69	14
11	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	Na_2CO_3 (0.1)	HFIP (5)	White CFL	Air	70	13
12	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	$NaHCO_3$ (0.1)	HFIP (5)	White CFL	Air	65	15
13	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	NaOAc (0.1)	HFIP (5)	White CFL	Air	55	28
14	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	KH_2PO_4 (0.1)	HFIP (5)	White CFL	Air	20	<10
15	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	75(71[b])	13(7[b])
16	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.01)	HFIP (5)	White CFL	Air	58	13
17	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.05)	HFIP (5)	White CFL	Air	66	13
18	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.2)	HFIP (5)	White CFL	Air	40	38
19	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.4)	HFIP (5)	White CFL	Air	35	52
20	5	0.5	$Ru(bpy)_3Cl_2$	K_2CO_3	HFIP	White	Air	<10	61

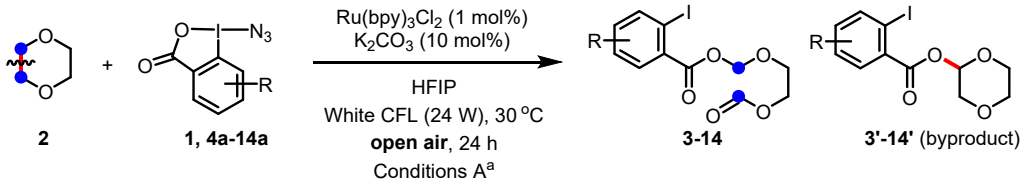
			(0.01)	(0.8)	(5)	CFL			
21	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (1.0)	HFIP (5)	White CFL	Air	<10	63
22	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (2.0)	HFIP (5)	White CFL	Air	<10	65
23	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (5.0)	HFIP (5)	White CFL	Air	<10	62
24	5	0.5	No	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	<10	<10
25	5	0.5	$Ru(bpy)_3Cl_2$ (0.005)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	65	11
26	5	0.5	$Ru(bpy)_3Cl_2$ (0.05)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	60	18
27	5	0.5	$Ru(bpy)_3Cl_2$ (0.1)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	51	23
28	5	0.5	$Ru(phen)_3Cl_2$ (0.002)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	61	11
29	5	0.5	$Ru(phen)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	65	11
30	5	0.5	$Ru(phen)_3Cl_2$ (0.1)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	30	35
31	5	0.5	Acid red 91 (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	<10	<10
32	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	Blue LED	Air	70	12
33	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	Darkness	Air	<10	<10
34	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	O_2	72	12

35	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Ar	<10	53
36	10	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	No	White CFL	Air	48	16
37	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	DCM (5)	White CFL	Air	31	13
38	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	EtOAc (5)	White CFL	Air	<10	<10
39	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	CH_3OH (5)	White CFL	Air	<10	<10
40	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	EtOH (5)	White CFL	Air	<10	<10
41	5	BIOH instead of BIN_3	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	<10	<10
42	5	BIOAc instead of BIN_3	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	<10	<10
43	5	BICl instead of BIN_3	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1)	HFIP (5)	White CFL	Air	<10	<10
44	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1), LiCl (0.1)	HFIP (5)	White CFL	Air	<10	65
45	5	0.5	$Ru(bpy)_3Cl_2$ (0.01)	K_2CO_3 (0.1), Bu_4NBr (0.1)	HFIP (5)	White CFL	Air	<10	60

a) Yields are based on ^{1}H-NMR analysis of reaction mixture on a 0.5 mmol scale using ACS grade solvents under air atmosphere unless specified otherwise. Source of VL source: 24 W blue LEDs or 24 W white CFL. t = 24 h. T = 30 °C. HFIP is 1,1,1,3,3,3-hexafluoropropan-2-ol solvent. Reaction mixture is under air atmosphere (air bubbling reaction) if necessary. b) Isolated yield.

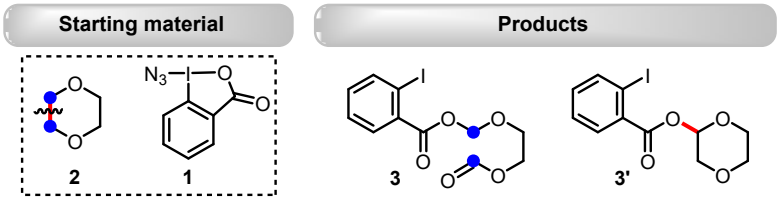
Table S1. Reaction optimization for C(sp^3)- C(sp^3) bond esterification of dioxane

5. C(sp^3)-C(sp^3) bond esterification of dioxane with hypervalent iodine (III) azide reagents



Scheme S4. C(sp^3)-C(sp^3) bond esterification of dioxane with hypervalent iodine (III) azides reagents

General conditions A: $Ru(bpy)_3Cl_2$ (0.005 mmol, 1 mol%) and K_2CO_3 (0.05 mmol, 10 mol%) were first dispersed in 5 mL dioxane **2** and 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). Hypervalent iodine (III) azide reagents (0.5 mmol, 1.0 equiv) was then added. The reaction mixture vigorously stirred at air (air bubbling) and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. After completion as detected by TLC, the solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air (air was bubbled into the reaction system by an air pump) during C(sp^3)-C(sp^3) bonds cleavage reactions.



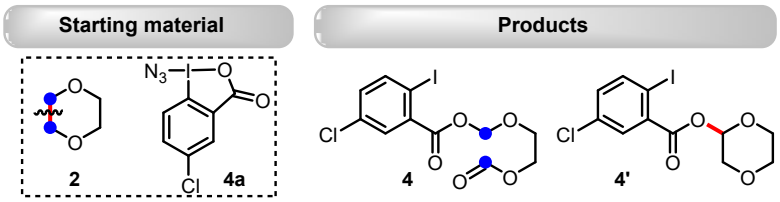
R_f = 0.5, 10% acetone in hexane (**3**)

R_f = 0.6, 10% acetone in hexane (**3'**)

Compound **3** as a colorless oil was isolated in 71% yield (^{1}H NMR yield: 75%) and side product compound **3'** as a colorless oil was isolated in 7% yield (^{1}H NMR yield: 13%) following the general conditions **A**.

Compound 3: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.02 (d, J = 7.9 Hz, 1H), 7.87 (dd, J = 7.8, 1.5 Hz, 1H), 7.45 – 7.40 (m, 1H), 7.21 – 7.15 (m, 1H), 5.57 (s, 2H), 4.40 – 4.34 (m, 2H), 4.04 – 3.99 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.85, 160.88, 141.71, 134.36, 133.22, 131.38, 128.13, 94.39, 90.31, 68.52, 62.74. **HRMS** Calcd for $C_{11}H_{11}INaO_5$ [M+Na$^+$]: 372.9543; Found: 372.9547.

Compound 3': ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J = 7.9 Hz, 1H), 7.94 (dd, J = 7.8, 1.4 Hz, 1H), 7.43 (t, J = 7.6 Hz, 1H), 7.18 (t, J = 7.7 Hz, 1H), 6.11 (s, 1H), 4.30 – 4.21 (m, 1H), 3.96 – 3.89 (m, 2H), 3.88 – 3.80 (m, 2H), 3.73 – 3.65 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.12, 141.70, 134.31, 133.19, 131.58, 128.09, 94.45, 90.77, 67.77, 66.21, 61.98. **HRMS** Calcd for $C_{11}H_{11}INaO_4$ [M+Na$^+$]: 356.9594; Found: 356.9593.



R_f = 0.4, 10% acetone in hexane (**4**)

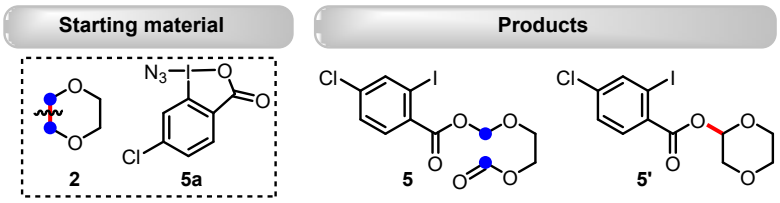
R_f = 0.5, 10% acetone in hexane (**4'**)

Compound **4** as a colorless oil was isolated in 75% yield and side product compound **4'** as a colorless oil was isolated in 8% yield following the general conditions **A**.

Compound 4: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.84 (d, J = 2.5 Hz, 1H), 7.17 (dd, J = 8.4, 2.6 Hz, 1H), 5.57 (s, 2H), 4.41 – 4.32 (m, 2H), 4.05 – 3.96 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.68, 160.83, 142.79, 135.69, 134.76, 133.31, 131.42, 91.54, 90.62, 68.67, 62.67. **HRMS** Calcd for $C_{11}H_{10}ClINaO_5$ [M+Na$^+$]: 406.9154; Found: 406.9150.

Compound 4': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 1H), 7.89 (d, J = 2.5 Hz, 1H), 7.18 (dd, J = 8.4, 2.6 Hz, 1H), 6.10 (m, 1H), 4.29 – 4.21 (m, 1H), 3.95 –

3.90 (m, 2H), 3.88 – 3.83 (m, 2H), 3.71 (dt, *J* = 11.8, 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.06, 142.80, 135.77, 134.76, 133.30, 131.51, 91.61, 91.23, 67.70, 66.21, 62.05. **HRMS** Calcd for $C_{11}H_{10}ClINaO_4$ [M+Na$^+$]: 390.9205; Found: 390.9201.



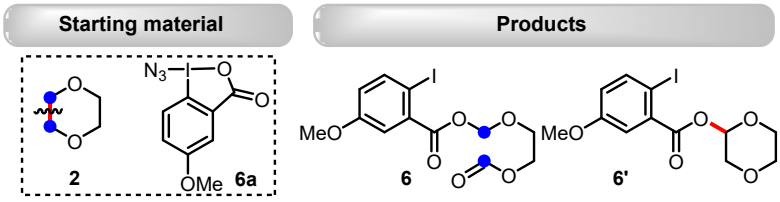
R_f = 0.5, 10% acetone in hexane (**5**)

R_f = 0.6, 10% acetone in hexane (**5'**)

Compound **5** as a colorless oil was isolated in 74% yield and side product compound **5'** as a colorless oil was isolated in 8% yield following the general conditions **A**.

Compound 5: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 8.04 (d, *J* = 2.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 1H), 7.41 (dd, *J* = 8.4, 2.0 Hz, 1H), 5.56 (s, 2H), 4.39 – 4.31 (m, 2H), 4.05 – 3.95 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.92, 160.85, 141.34, 138.86, 132.42, 132.19, 128.46, 94.88, 90.48, 68.62, 62.69. **HRMS** Calcd for $C_{11}H_{10}ClINaO_5$ [M+Na$^+$]: 406.9154; Found: 406.9150.

Compound 5': ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, *J* = 2.0 Hz, 1H), 7.91 (d, *J* = 8.4 Hz, 1H), 7.42 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.10 (m, 1H), 4.27 – 4.20 (m, 1H), 3.95 – 3.81 (m, 4H), 3.70 (dt, *J* = 11.8, 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.20, 141.36, 138.83, 132.40, 128.42, 94.95, 91.01, 67.76, 66.23, 62.03. **HRMS** Calcd for $C_{11}H_{10}ClINaO_4$ [M+Na$^+$]: 390.9205; Found: 390.9199.



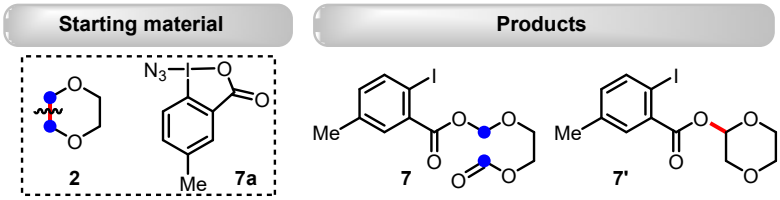
R_f = 0.3, 10% acetone in hexane (**6**)

R_f = 0.4, 10% acetone in hexane (**6'**)

Compound **6** as a colorless oil was isolated in 85% yield and side product compound **6'** as a colorless oil was isolated in 8% yield following the general conditions **A**.

Compound 6: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.40 (d, *J* = 3.1 Hz, 1H), 6.78 (dd, *J* = 8.7, 3.1 Hz, 1H), 5.57 (s, 2H), 4.41 – 4.32 (m, 2H), 4.05 – 3.98 (m, 2H), 3.82 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.71, 160.87, 159.67, 142.26, 135.21, 119.74, 117.03, 90.37, 82.63, 68.59, 62.74, 55.74. **HRMS** Calcd for $C_{12}H_{13}INaO_6$ [M+Na$^+$]: 402.9649; Found: 402.9657.

Compound 6': **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.46 (d, *J* = 3.1 Hz, 1H), 6.78 (dd, *J* = 8.7, 3.1 Hz, 1H), 6.10 (t, *J* = 1.7 Hz, 1H), 4.30 – 4.22 (m, 1H), 3.96 – 3.86 (m, 2H), 3.85 – 3.81 (m, 5H), 3.70 (dt, *J* = 11.7, 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.11, 159.64, 142.22, 135.36, 119.53, 117.32, 90.95, 82.62, 67.74, 66.20, 62.08, 55.74. **HRMS** Calcd for $C_{12}H_{13}INaO_5$ [M+Na$^+$]: 386.9700; Found: 386.9701.



R_f = 0.4, 10% acetone in hexane (**7**)

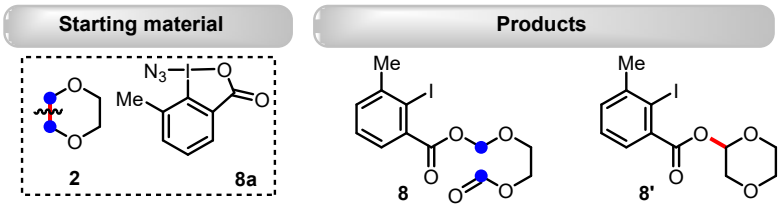
R_f = 0.5, 10% acetone in hexane (**7'**)

Compound **7** as a colorless oil was isolated in 80% yield and side product compound **7'** as a colorless oil was isolated in 10% yield following the general conditions **A**.

Compound 7: **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.67 (d, *J* = 1.9 Hz, 1H), 7.03 – 6.96 (m, 1H), 5.56 (s, 2H), 4.46 – 4.28 (m, 2H), 4.16 – 3.89 (m, 2H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.99, 160.86, 141.42, 138.34, 134.24, 134.16, 132.10, 90.24, 68.51, 62.74, 20.94. **HRMS** Calcd for $C_{12}H_{13}INaO_5$ [M+Na$^+$]: 386.9700; Found: 386.9696.

Compound 7': **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.72 (d, *J* = 2.0 Hz, 1H), 6.99 (dd, *J* = 8.1, 2.1 Hz, 1H), 6.09 (s, 1H), 4.25 (dt, *J* = 11.9, 6.6 Hz, 1H), 3.95 – 3.89 (m, 2H), 3.88 – 3.80 (m, 2H), 3.69 (dt, *J* = 11.8, 2.5 Hz, 1H), 2.34 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.28, 141.41, 138.28, 134.21, 134.15, 132.19,

90.73, 90.32, 67.78, 66.19, 62.04, 20.96. **HRMS** Calcd for $C_{12}H_{13}INaO_4$ [M+Na^+]: 370.9751; Found: 370.9745.



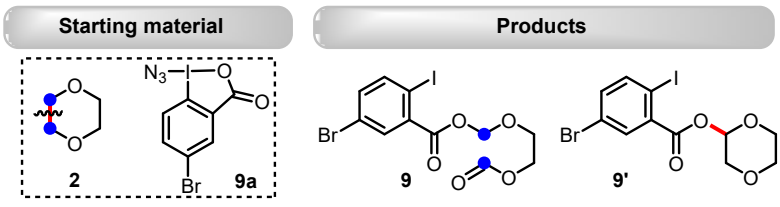
R_f = 0.4, 10% acetone in hexane (**8**)

R_f = 0.5, 10% acetone in hexane (**8'**)

Compound **8** as a colorless oil was isolated in 55% yield and side product compound **8'** as a colorless oil was isolated in 8% yield following the general conditions **A**.

Compound 8: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.42 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 5.57 (s, 2H), 4.39 – 4.36 (m, 2H), 4.03 – 4.00 (m, 2H), 2.53 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.68, 160.89, 143.77, 137.70, 132.34, 127.98, 127.47, 100.16, 90.42, 68.51, 62.76, 29.89. **HRMS** Calcd for $C_{12}H_{13}INaO_5$ [M+Na^+]: 386.9700; Found: 386.9704.

Compound 8': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.38 – 7.35 (m, 1H), 7.29 (t, *J* = 7.6 Hz, 1H), 6.11 (s, 1H), 4.28 – 4.23 (m, 1H), 3.96 – 3.84 (m, 2H), 3.85 – 3.81 (m, 2H), 3.69 (dt, *J* = 11.8, 2.5 Hz, 1H), 2.53 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.02, 143.70, 137.68, 132.28, 127.95, 127.64, 100.22, 90.85, 67.77, 66.23, 62.01, 29.88. **HRMS** Calcd for $C_{12}H_{13}INaO_4$ [M+Na^+]: 370.9751; Found: 370.9745.



R_f = 0.5, 10% acetone in hexane (**9**)

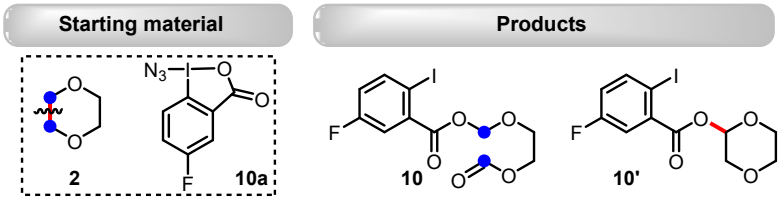
R_f = 0.6, 10% acetone in hexane (**9'**)

Compound **9** as a colorless oil was isolated in 75% yield and side product compound

9' as a colorless oil was isolated in 10% yield following the general conditions **A**.

Compound 9: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.99 (d, *J* = 2.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.5 Hz, 1H), 5.57 (s, 2H), 4.41 – 4.35 (m, 2H), 4.04 – 3.99 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.59, 160.85, 143.02, 136.24, 135.95, 134.27, 122.47, 92.42, 90.63, 68.69, 62.69. **HRMS** Calcd for $C_{11}H_{10}BrINaO_5$ [M+Na^+]: 450.8649; Found: 450.8646.

Compound 9': ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 2.4 Hz, 1H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.31 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.10 (s, 1H), 4.28 – 4.22 (m, 1H), 3.96 – 3.89 (m, 2H), 3.88 – 3.82 (m, 2H), 3.71 (dt, *J* = 11.9, 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.97, 143.00, 136.21, 136.06, 134.30, 122.46, 92.46, 91.26, 67.69, 66.20, 62.07. **HRMS** Calcd for $C_{11}H_{10}BrINaO_4$ [M+Na^+]: 434.8699; Found: 434.8700.



R_f = 0.3, 10% acetone in hexane (**10**)

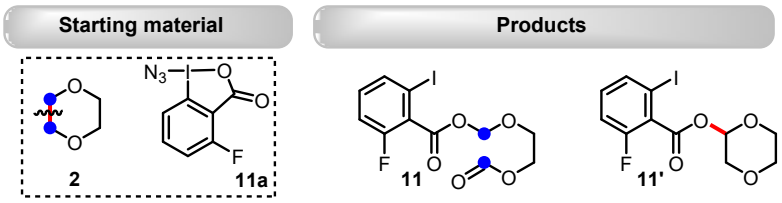
R_f = 0.4, 10% acetone in hexane (**10'**)

Compound **10** as a colorless oil was isolated in 78% yield and side product compound **10'** as a colorless oil was isolated in 10% yield following the general conditions **A**.

Compound 10: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (s, 1H), 7.97 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.61 (dd, *J* = 9.0, 3.1 Hz, 1H), 7.01 – 6.91 (m, 1H), 5.57 (s, 2H), 4.40 – 4.35 (m, 2H), 4.04 – 3.98 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.69, 164.67, 163.50, 161.52, 160.83, 143.16, 143.11, 135.90, 135.84, 120.96, 120.79, 118.94, 118.75, 90.61, 87.45, 87.42, 68.65, 62.67. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.94 – -112.99 (m). **HRMS** Calcd for $C_{11}H_{10}FINaO_5$ [M+Na^+]: 390.9449; Found: 390.9447.

Compound 10': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.67 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.99 – 6.93 (m, 1H), 6.10 (s, 1H), 4.29 – 4.21 (m, 1H), 3.95 – 3.89 (m, 2H), 3.88 – 3.83 (m, 2H), 3.70 (dt, *J* = 11.8, 2.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.01, 163.99, 163.51, 161.53, 143.16, 143.10, 135.92, 135.86,

120.93, 120.76, 119.09, 118.90, 91.18, 87.51, 87.48, 67.70, 66.20, 62.01. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -113.04 – -113.08 (m). **HRMS** Calcd for $C_{11}H_{10}FINaO_4$ [M+Na^+]: 374.9500; Found: 374.9497.



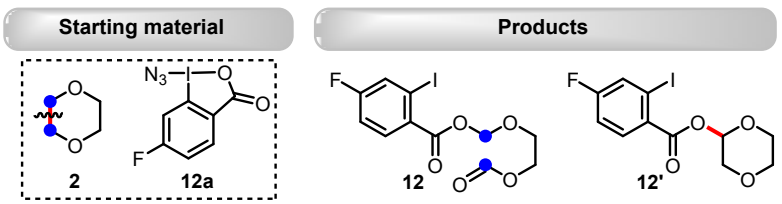
R_f = 0.3, 10% acetone in hexane (**11**)

R_f = 0.4, 10% acetone in hexane (**11'**)

Compound **11** as a colorless oil was isolated in 62% yield and side product compound **11'** as a colorless oil was isolated in 9% yield following the general conditions **A**.

Compound 11: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (s, 1H), 7.66 (dd, *J* = 5.3, 3.6 Hz, 1H), 7.16 – 7.10 (m, 2H), 5.59 (s, 2H), 4.41 – 4.34 (m, 2H), 4.06 – 3.98 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.65, 160.88, 160.17, 158.14, 135.34, 135.31, 132.79, 132.72, 128.09, 127.93, 116.07, 115.90, 92.45, 92.43, 90.79, 68.46, 62.65. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.53 (t, *J* = 7.4 Hz). **HRMS** Calcd for $C_{11}H_{10}FINaO_5$ [M+Na^+]: 390.9449; Found: 390.9439.

Compound 11': ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 – 7.62 (m, 1H), 7.17 – 7.09 (m, 2H), 6.15 (s, 1H), 4.33 – 4.24 (m, 1H), 3.95 – 3.81 (m, 4H), 3.68 (dt, *J* = 11.8, 2.1 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.15, 160.21, 158.18, 135.23, 135.20, 132.70, 132.63, 128.19, 128.03, 116.04, 115.87, 92.48, 92.46, 91.27, 67.62, 66.20, 61.72. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -110.52 – -110.60 (m). **HRMS** Calcd for $C_{11}H_{10}FINaO_4$ [M+Na^+]: 374.9500; Found: 374.9500.



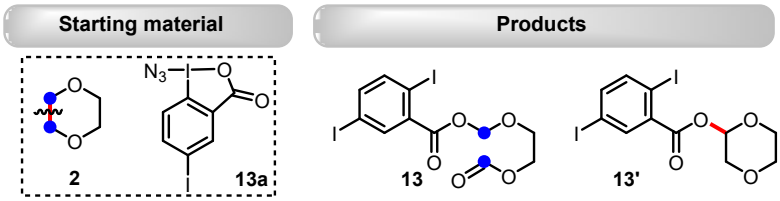
R_f = 0.3, 10% acetone in hexane (**12**)

R_f = 0.4, 10% acetone in hexane (**12'**)

Compound **12** as a colorless oil was isolated in 78% yield and side product compound **12'** as a colorless oil was isolated in 11% yield following the general conditions **A**.

Compound 12: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.07 (s, 1H), 7.94 (dd, *J* = 8.8, 5.9 Hz, 1H), 7.75 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.17 – 7.11 (m, 1H), 5.56 (s, 2H), 4.40 – 4.33 (m, 2H), 4.03 – 3.96 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.86, 164.70, 162.80, 160.84, 133.25, 133.18, 130.06, 130.03, 129.21, 129.02, 115.50, 115.33, 95.09, 95.02, 90.36, 68.56, 62.70. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.45 – -105.53 (m). **HRMS** Calcd for $C_{11}H_{10}FINaO_5$ [M+Na$^+$]: 390.9449; Found: 390.9451.

Compound 12': ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.8, 5.9 Hz, 1H), 7.76 (dd, *J* = 8.1, 2.5 Hz, 1H), 7.17 – 7.09 (m, 1H), 6.09 (t, *J* = 1.6 Hz, 1H), 4.27 – 4.20 (m, 1H), 3.94 – 3.88 (m, 2H), 3.87 – 3.81 (m, 2H), 3.69 (dt, *J* = 11.8, 2.5 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.88, 163.97, 162.82, 133.47, 133.40, 130.05, 130.02, 129.23, 129.04, 115.46, 115.29, 95.17, 95.10, 90.88, 67.78, 66.22, 62.01. **^{19}F NMR** (471 MHz, $CDCl_3$) δ -105.54 – -105.62 (m). **HRMS** Calcd for $C_{11}H_{10}FINaO_4$ [M+Na$^+$]: 374.9500; Found: 374.9498.



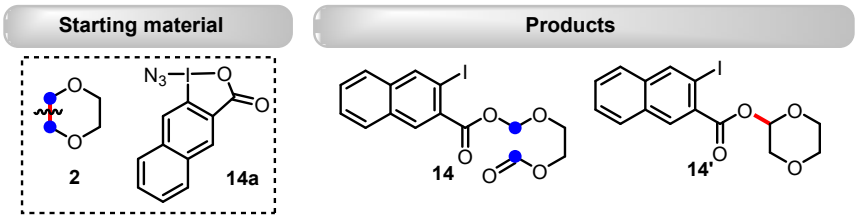
R_f = 0.4, 10% acetone in hexane (**13**)

R_f = 0.5, 10% acetone in hexane (**13'**)

Compound **13** as a colorless oil was isolated in 79% yield and side product compound **13'** as a colorless oil was isolated in 10% yield following the general conditions **A**.

Compound 13: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 2.1 Hz, 1H), 8.08 (s, 1H), 7.70 (d, *J* = 8.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.56 (s, 2H), 4.39 – 4.32 (m, 2H), 4.05 – 3.94 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.41, 160.82, 143.06, 142.03, 139.93, 136.06, 93.66, 93.22, 90.56, 68.65, 62.66. **HRMS** Calcd for $C_{11}H_{10}I_2NaO_5$ [M+Na$^+$]: 498.8510; Found: 498.8512.

Compound 13': ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.2 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.47 (dd, *J* = 8.3, 2.2 Hz, 1H), 6.08 (t, *J* = 8.9 Hz, 1H), 4.28 – 4.21 (m, 1H), 3.95 – 3.88 (m, 2H), 3.88 – 3.83 (m, 2H), 3.70 (dt, *J* = 11.9, 2.4 Hz, 1H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 163.84, 143.05, 142.03, 139.93, 136.26, 93.67, 93.24, 91.23, 67.66, 66.17, 62.06. **HRMS** Calcd for $C_{11}H_{10}I_2NaO_4$ [M+Na$^+$]: 482.8561; Found: 482.8564.



R_f = 0.4, 10% acetone in hexane (**14**)

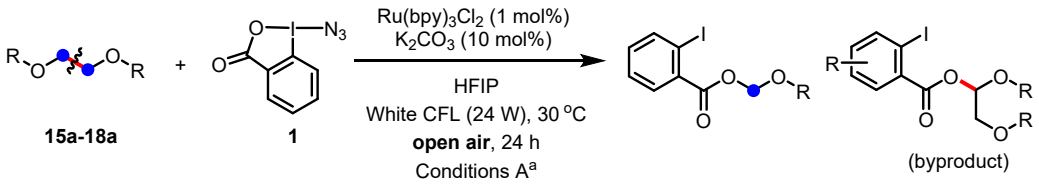
R_f = 0.5, 10% acetone in hexane (**14'**)

Compound **14** as a colorless oil was isolated in 80% yield and side product compound **14'** as a colorless oil was isolated in 8% yield following the general conditions **A**.

Compound 14: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.44 (s, 1H), 8.09 (s, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 1H), 7.65 – 7.55 (m, 2H), 5.64 (s, 2H), 4.43 – 4.36 (m, 2H), 4.09 – 4.04 (m, 2H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.90, 160.90, 141.15, 136.05, 132.38, 131.66, 130.37, 129.28, 128.99, 127.65, 126.79, 90.38, 88.50, 68.61, 62.80. **HRMS** Calcd for $C_{15}H_{11}IO_5$ [M+H$^+$]: 400.9880; Found: 400.9876.

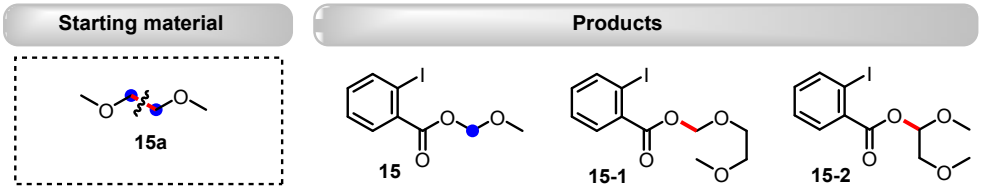
Compound 14': ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.49 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.54 (m, 2H), 6.17 (s, 1H), 4.36 – 4.28 (m, 1H), 4.03 – 3.92 (m, 2H), 3.87 (dd, *J* = 6.8, 2.4 Hz, 2H), 3.74 (dt, *J* = 11.8, 2.4 Hz, 1H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.06, 141.05, 135.94, 132.39, 131.55, 130.25, 129.14, 128.94, 127.49, 126.68, 90.78, 88.55, 67.81, 66.19, 62.05. **HRMS** Calcd for $C_{15}H_{13}INaO_4$ [M+Na$^+$]: 406.9751; Found: 406.9750.

6. C(sp^3)-C(sp^3) bond esterification of acyclic glycol ethers with BIN_3



Scheme S5. C(sp^3)-C(sp^3) bond esterification of acyclic glycol ethers

General conditions A: $Ru(bpy)_3Cl_2$ (0.005 mmol, 1 mol%) and K_2CO_3 (0.05 mmol, 10 mol%) were first dispersed in 5 mL acyclic glycol ether and 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). BIN_3 (0.5 mmol, 1.0 equiv) was then added. The reaction mixture vigorously stirred at air (air bubbling) and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. After completion as detected by TLC, the solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air (air was bubbled into the reaction system by an air pump) during C(sp^3)-C(sp^3) bonds cleavage reactions.



R_f = 0.7, 10% acetone in hexane (**15**)

R_f = 0.4, 10% acetone in hexane (**15-1**)

R_f = 0.3, 10% acetone in hexane (**15-2**)

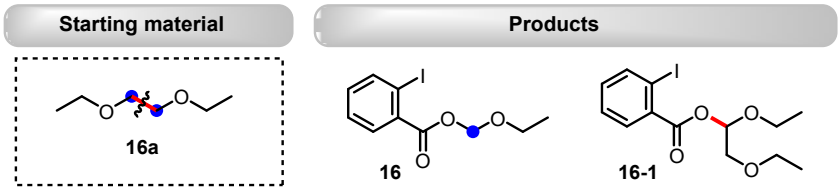
Compound **15** as a colorless oil was isolated in 73% yield following the general conditions **A**. And side product compound **15-1** as a colorless oil was isolated in 6% yield and side product compound **15-2** as a colorless oil was isolated in 5% yield following the general conditions **A**.

Compound 15: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.87 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.21 – 7.13 (m, 1H), 5.50 (s, 2H), 3.59 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.00, 141.66, 134.73, 133.05, 131.32,

128.08, 94.29, 91.80, 58.35. **HRMS** Calcd for $C_9H_9INaO_3$ [M+Na$^+$]: 314.9489; Found: 314.9483.

Compound 15-1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.14 (m, 1H), 5.59 (s, 2H), 3.95 – 3.90 (m, 2H), 3.62 – 3.57 (m, 2H), 3.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.95, 141.65, 134.65, 133.07, 131.40, 128.08, 94.35, 90.78, 71.63, 70.18, 59.26. **HRMS** Calcd for $C_{11}H_{13}INaO_4$ [M+Na$^+$]: 358.9751; Found: 358.9741.

Compound 15-2: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 6.14 (t, *J* = 4.9 Hz, 1H), 3.64 (d, *J* = 4.7 Hz, 2H), 3.60 (s, 3H), 3.44 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.07, 141.69, 134.47, 133.14, 131.37, 128.11, 98.31, 94.47, 72.74, 59.72, 57.79. **HRMS** Calcd for $C_{11}H_{13}INaO_4$ [M+Na$^+$]: 358.9751; Found: 358.9747.



R_f = 0.7, 10% acetone in hexane (**16**)

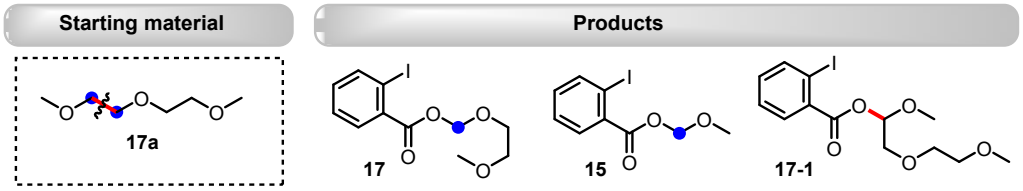
R_f = 0.4, 10% acetone in hexane (**16-1**)

Compound **16** as a colorless oil was isolated in 70% yield and side product compound **16-1** as a colorless oil was isolated in 8% yield following the general conditions **A**.

Compound 16: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 5.55 (s, 2H), 3.82 (q, *J* = 7.1 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.09, 141.64, 134.86, 133.01, 131.30, 128.08, 94.28, 90.58, 66.66, 15.25. **HRMS** Calcd for $C_{10}H_{11}INaO_3$ [M+Na$^+$]: 328.9645; Found: 328.9634.

Compound 16-1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.86 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.22 (t, *J* = 5.1 Hz, 1H), 3.95 – 3.88 (m, 1H), 3.79 – 3.73 (m, 1H), 3.69 – 3.66 (m, 2H), 3.64 – 3.55 (m, 2H), 1.27 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz,

$CDCl_3$) δ 166.20, 141.59, 134.83, 132.99, 131.30, 128.07, 97.36, 94.38, 71.01, 67.32, 66.04, 15.30, 15.25. **HRMS** Calcd for $C_{13}H_{17}INaO_4$ [M+Na^+]: 387.0064; Found: 387.0065.



R_f = 0.4, 10% acetone in hexane (**17**)

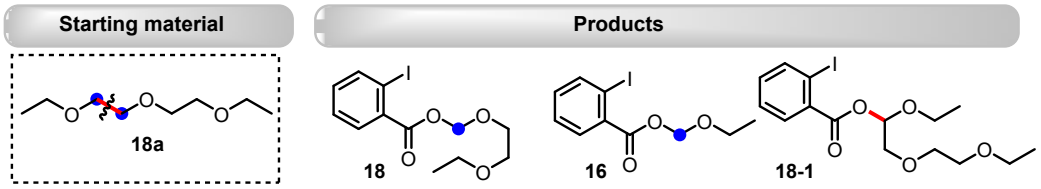
R_f = 0.7, 10% acetone in hexane (**15**)

R_f = 0.3, 10% acetone in hexane (**17-1**)

Compound **17** as a colorless oil was isolated in 45% yield and compound **15** as a colorless oil was isolated in 10% yield following the general conditions **A**. And side product compound **17-1** as a colorless oil was isolated in 10% yield following the general conditions **A**.

Compound 17 (Compound 15-1): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.19 – 7.14 (m, 1H), 5.59 (s, 2H), 3.95 – 3.90 (m, 2H), 3.62 – 3.57 (m, 2H), 3.40 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.95, 141.65, 134.65, 133.07, 131.40, 128.08, 94.35, 90.78, 71.63, 70.18, 59.26. **HRMS** Calcd for $C_{11}H_{13}INaO_4$ [M+Na^+]: 358.9751; Found: 358.9741.

Compound 17-1: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 1H), 7.88 (t, *J* = 7.9 Hz, 1H), 7.44 – 7.38 (m, 1H), 7.17 (t, *J* = 6.8 Hz, 1H), 6.27 – 6.11 (m, 1H), 4.03 – 3.87 (m, 1H), 3.76 – 3.66 (m, 3H), 3.61 – 3.53 (m, 4H), 3.43 (s, 1H), 3.37 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.05, 141.65, 133.11, 131.49, 131.35, 128.08, 98.45, 97.40, 72.81, 71.63, 69.72, 59.66, 57.76. **HRMS** Calcd for $C_{13}H_{17}INaO_5$ [M+Na^+]: 403.0013; Found: 403.0013.



R_f = 0.4, 10% acetone in hexane (**18**)

R_f = 0.7, 10% acetone in hexane (**16**)

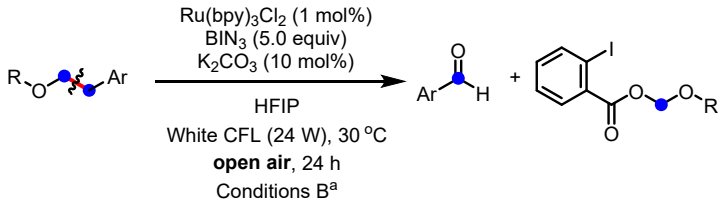
R_f = 0.3, 10% acetone in hexane (**18-1**)

Compound **18** as a colorless oil was isolated in 43% yield and compound **16** as a colorless oil was isolated in 10% yield following the general conditions **A**. And side product compound **18-1** as a colorless oil was isolated in 10% yield following the general conditions **A**.

Compound 18: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.88 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.17 (t, *J* = 7.7 Hz, 1H), 5.59 (s, 2H), 3.93 (dd, *J* = 5.5, 3.9 Hz, 2H), 3.64 (dd, *J* = 5.5, 3.9 Hz, 2H), 3.54 (q, *J* = 7.0 Hz, 2H), 1.21 (t, *J* = 7.0 Hz, 3H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 165.97, 141.65, 134.68, 133.06, 131.41, 128.07, 94.35, 90.83, 70.34, 69.57, 66.93, 15.27. **HRMS** Calcd for $C_{12}H_{15}INaO_4$ [M+Na^+]: 372.9907; Found: 372.9906.

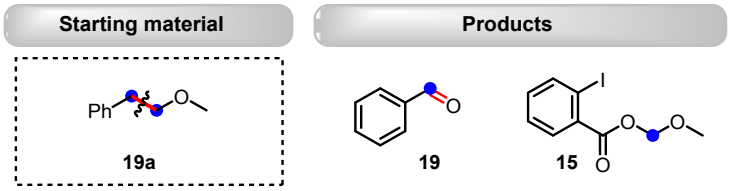
Compound 18-1: ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 1H), 6.24 (t, *J* = 5.1 Hz, 1H), 4.02 – 3.96 (m, 1H), 3.94 – 3.88 (m, 1H), 3.80 – 3.47 (m, 8H), 1.24 – 1.15 (m, 6H). ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 166.11, 141.60, 134.64, 133.03, 131.43, 128.06, 97.75, 94.46, 70.85, 69.84, 69.52, 67.28, 66.81, 15.32, 15.27. **HRMS** Calcd for $C_{15}H_{21}INaO_5$ [M+Na^+]: 431.0326; Found: 431.0329.

7. Deconstructive oxygenation and esterification of arenethyl alkyl ethers by C(sp^3)-C(sp^3) cleavage



Scheme S6. Deconstructive oxygenation and esterification of arenethyl alkyl ethers by C(sp^3)-C(sp^3) cleavage

General conditions B: Substrate arenethyl alkyl ether (0.5 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.005 mmol, 1 mol%) and K_2CO_3 (0.05 mmol, 10 mol%) were first dispersed in 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). BIN_3 (2.5 mmol, 5.0 equiv) was then added. The reaction mixture vigorously stirred at air (air bubbling) and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. After completion as detected by TLC, the solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products. It is worth noting that the reaction mixture always opened to air (air was bubbled into the reaction system by an air pump) during C(sp^3)-C(sp^3) bonds cleavage reactions.

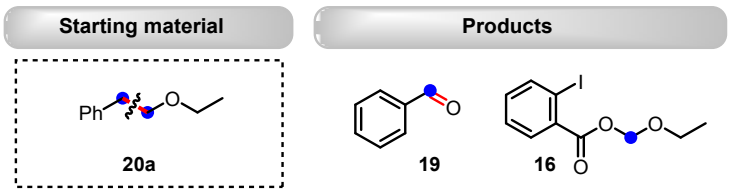


R_f = 0.8, 5% acetone in hexane (**19**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **19** as a colorless oil was isolated in 35% yield (^{1}H NMR yield: 75%) and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

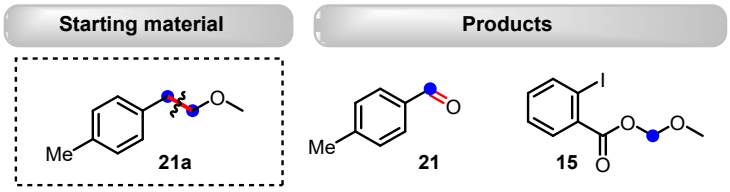
Compound 19: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.02 (s, 1H), 7.91 – 7.84 (m, 2H), 7.65 – 7.60 (m, 1H), 7.56 – 7.50 (m, 2H).[7]



R_f = 0.8, 5% acetone in hexane (**19**)

R_f = 0.7, 10% acetone in hexane (**16**)

Compound **19** as a colorless oil was isolated in 30% yield (^{1}H NMR yield: 70%) and compound **16** as a colorless oil was isolated in 56% yield following the general conditions **B**.

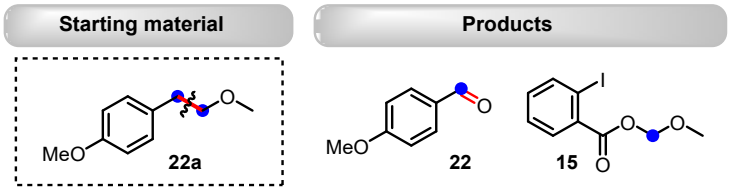


R_f = 0.7, 5% acetone in hexane (**21**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **21** as a colorless oil was isolated in 37% yield (^{1}H NMR yield: 80%) and compound **15** as a colorless oil was isolated in 55% yield following the general conditions **B**.

Compound 21: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.96 (s, 1H), 7.77 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.43 (s, 3H).[7]

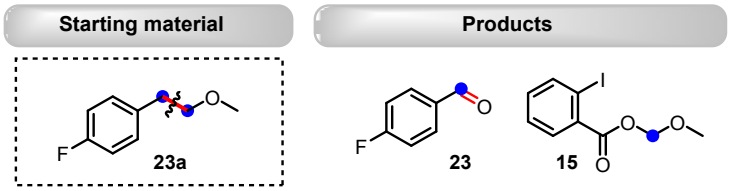


R_f = 0.7, 5% acetone in hexane (**22**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **22** as a colorless oil was isolated in 39% yield (^{1}H NMR yield: 85%) and compound **15** as a colorless oil was isolated in 57% yield following the general conditions **B**.

Compound 22: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (s, 1H), 7.82 (d, *J* = 8.9 Hz, 2H), 6.98 (d, *J* = 8.7 Hz, 2H), 3.87 (s, 3H).[7]

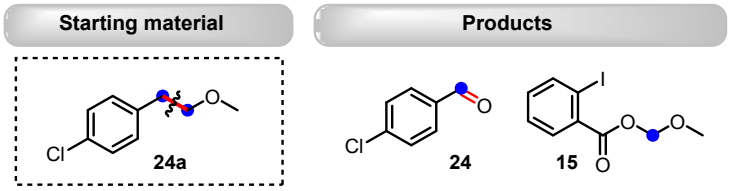


R_f = 0.8, 5% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **23** as a colorless oil was isolated in 35% yield (^{1}H NMR yield: 76%) and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

Compound 23: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 – 9.91 (m, 1H), 7.97 – 7.85 (m, 2H), 7.24 – 7.14 (m, 2H).[7]

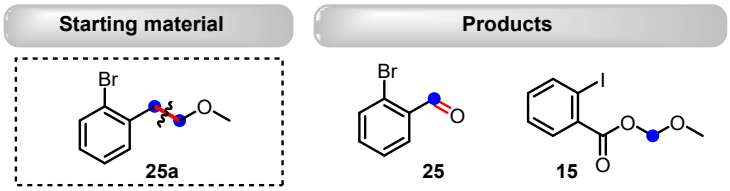


R_f = 0.8, 5% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **24** as a colorless oil was isolated in 36% yield (^{1}H NMR yield: 78%) and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

Compound 24: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.99 (s, 1H), 7.83 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H).[7]

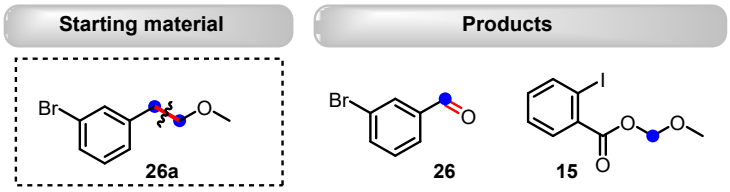


R_f = 0.8, 5% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **25** as a white solid was isolated in 35% yield (^{1}H NMR yield: 78%) and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

Compound 25: ^{1}H NMR (300 MHz, $CDCl_3$) δ 10.35 (s, 1H), 7.94 – 7.85 (m, 1H), 7.68 – 7.57 (m, 1H), 7.47 – 7.37 (m, 2H).[7]

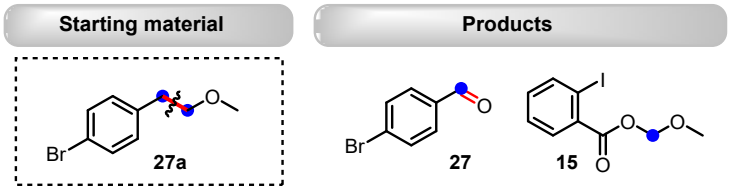


R_f = 0.8, 5% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **26** as a white solid was isolated in 35% yield (^{1}H NMR yield: 78%) and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

Compound 26: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.95 (s, 1H), 8.03 – 7.94 (m, 1H), 7.83 – 7.63 (m, 2H), 7.47 – 7.36 (m, 1H).[8]

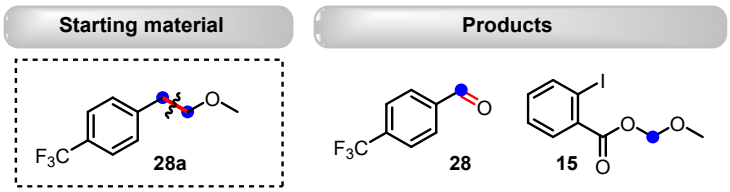


R_f = 0.8, 5% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **27** as a white solid was isolated in 36% yield (^{1}H NMR yield: 80%) and compound **15** as a colorless oil was isolated in 51% yield following the general conditions **B**.

Compound 27: ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.97 (s, 1H), 7.77 – 7.72 (m, 2H), 7.71 – 7.65 (m, 2H).[7]

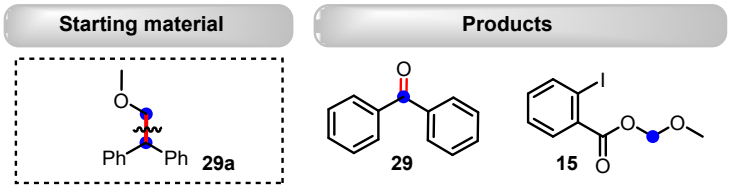


R_f = 0.8, 5% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

Compound **28** as a colorless oil was isolated in 31% yield (^{1}H NMR yield: 68%) and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

Compound 28: ^{1}H NMR (500 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.80 (d, J = 8.2 Hz, 2H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -63.22.[9]

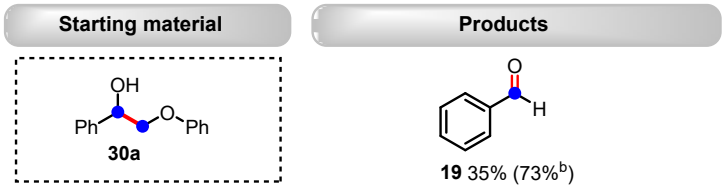


R_f = 0.6, 3% acetone in hexane (**23**)

R_f = 0.7, 10% acetone in hexane (**15**)

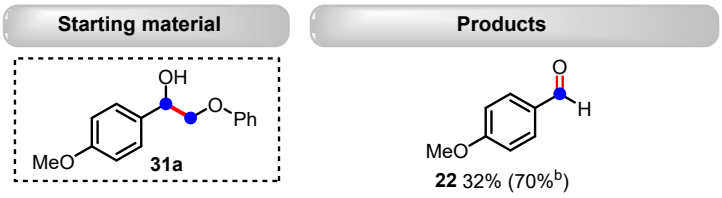
Compound **29** as a white solid was isolated in 85% yield and compound **15** as a colorless oil was isolated in 50% yield following the general conditions **B**.

Compound 29: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 – 7.75 (m, 4H), 7.62 – 7.55 (m, 2H), 7.52 – 7.43 (m, 4H).[7]



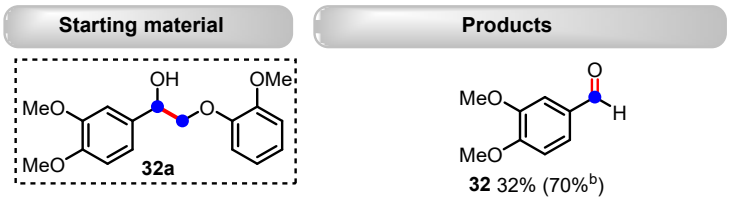
R_f = 0.8, 5% acetone in hexane (**19**)

Compound **19** as a colorless oil was isolated in 35% yield (^{1}H NMR yield: 73%) and following the general conditions **B**.



R_f = 0.7, 5% acetone in hexane (**22**)

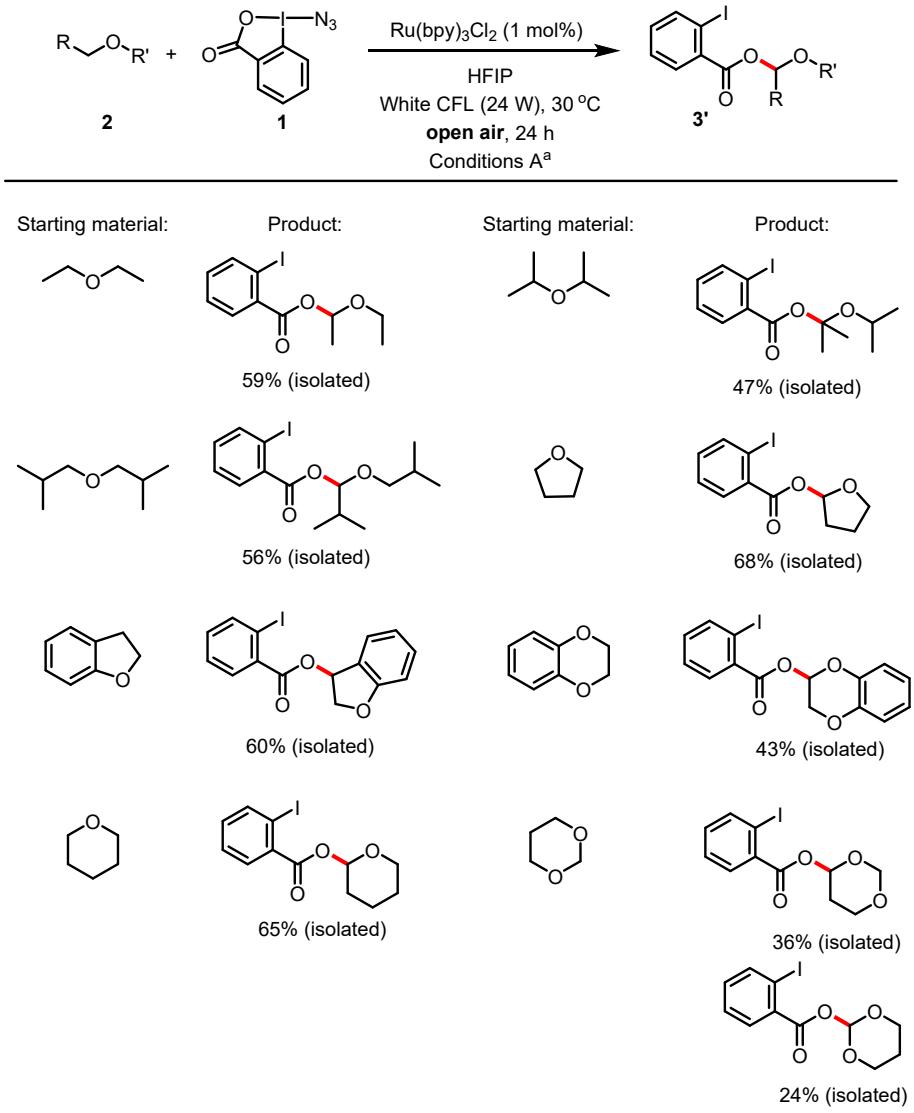
Compound **22** as a colorless oil was isolated in 32% yield (^{1}H NMR yield: 70%) and following the general conditions **B**.



R_f = 0.7, 5% acetone in hexane (**32**)

Compound **32** as a colorless oil was isolated in 32% yield (^{1}H NMR yield: 70%) and following the general conditions **B**.

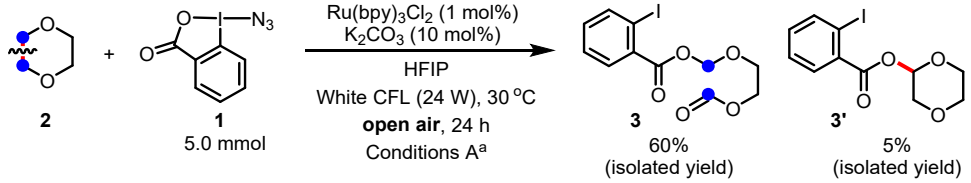
8. The limitation of C(sp^3)-C(sp^3) bond esterification of ethers



Scheme S7. The limitation of C(sp^3)-C(sp^3) esterification of ethers

As shown in Scheme **S7**, this reaction system is not applicable to alkyl alkyl ethers such as diethyl ether, di-isopropyl ether, di-iso-butyl ether, and tetrahydrofuran.

9. Gram-scale C(sp^3)-C(sp^3) bond esterification of dioxane

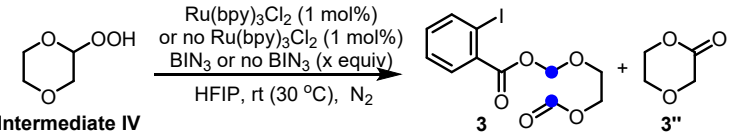


Scheme S8. Gram-scale C(sp^3)-C(sp^3) bond esterification of dioxane

$Ru(bpy)_3Cl_2$ (0.05 mmol, 1 mol%) and K_2CO_3 (0.5 mmol, 10 mol%) were first dispersed in 50 mL dioxane **2** and 50 mL 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). BIN_3 (5.0 mmol, 1.0 equiv) was then added. The reaction mixture vigorously stirred at air (air bubbling) and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 48 h. After completion as detected by TLC, the solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography (eluted with hexane/acetone (v/v 15:1)) to give the major product **3** in the isolated yield of 60% and the byproduct **3'** in the isolated yield of 5%.

10. Mechanistic studies

10.1 The mechanism investigation of the peroxide intermediate IV transformation



Intermediate IV **3** **3"**

Entry	Reagent (equiv), light sources, time, atmosphere	**3** (%)	**3"** (%)	**RSM** (%)
1	No additives, darkness	0	0	90
2	BIN_3 (5), darkness	0	0	90
3[b]	No additives, white CFL (24 W)	0	7	21
4[b]	BIN_3 (5), white CFL (24 W)	8	6	20
5	BIN_3 (5), $Ru(bpy)_3Cl_2$ (0.01), white CFL (24 W)	35	10	20
6	BIN_3 (5), $Ru(bpy)_3Cl_2$ (0.01), K_2CO_3 (0.1) white CFL (24 W)	53	5	10
7[b]	2-Iodobenzoic acid (5), $Ru(bpy)_3Cl_2$ (0.01), white CFL (24 W)	20	7	10
8	2-Iodobenzoic acid (5), $Ru(bpy)_3Cl_2$ (0.01), K_2CO_3 (0.1), white CFL (24 W)	50	5	10
9[b]	2-Iodobenzoic acid (5), K_2CO_3 (0.1), white CFL (24 W)	8	5	10

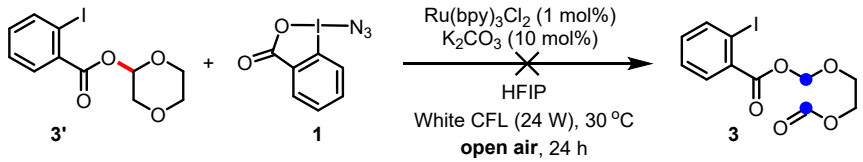
[a] Yields are based on isolated yield of reaction mixture on a 0.5 mmol scale at a 0.1 M concentration. Source of light: 24 W white Compact Fluorescent Lamp (white CFL). RSM is short for recovery of starting material. [b] The reaction system is messy, and many homolysis byproducts were formed.

Table S2. Control experiments of conversion of the intermediate **IV**

The mechanism investigation of the peroxide intermediate IV transformation: Plausible intermediate **IV** for this study was synthesized according to reported procedures.[10, 11] Intermediate **IV** (0.5 mmol, 1.0 equiv) and other specified reagents were first dispersed in 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). BIN_3 (2.5 mmol, 5.0 equiv) was then added if necessary. The reaction mixture vigorously stirred at N_2 atmosphere and room temperature (30 °C) with or without the compact fluorescent light (24 W) irradiation for 24 h. After completion as detected by TLC, the solvents were removed *in vacuo* and the residue was purified by silica gel flash chromatography to give the desired products.

A series of control experiments were performed to reveal the mechanism of conversion of the intermediate **IV** into a major product **3**. As shown in Table S2, Hydroperoxy dioxane intermediate **IV** is stable and could not undergo homolysis in the darkness over a long time (entry 1 and 2). Visible light irradiation could promote the homolysis of intermediate **IV** (entry 3). Visible light irradiation in the presence of BIN_3 could gave a small amount of **3** (entry 4), because the weak "I-N" bond of BIN_3 could be homolyzed by light irradiation. Photosensitizer $Ru(bpy)_3Cl_2$ and K_2CO_3 could accelerate the conversion of peroxide **IV** to obtain target molecular **3** (entry 4 vs entry 5 vs entry 6). When BIN_3 was replaced by 2-iodobenzoic acid, giving similar results (entry 5 vs entry 7 and entry 6 vs entry 8).

10.2 The mechanism investigation of the compound 3' transformation

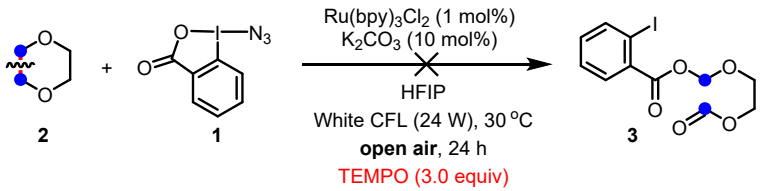


Scheme S9. The compound **3'** transformation

Compound **3'** (0.5 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.005 mmol, 1 mol%) and K_2CO_3 (0.05 mmol, 10 mol%) were first dispersed in 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol

(HFIP). BIN_3 (0.5 mmol, 1.0 equiv) was then added. The reaction mixture vigorously stirred at air (air bubbling) and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. The result showed that none of the desired product **3** was detected by crude ^{1}H-NMR. Recovery of starting material **3'** is 87%.

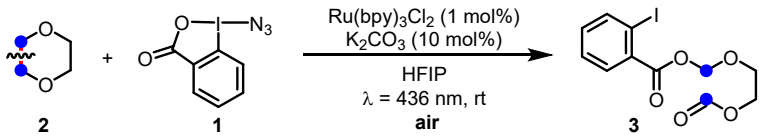
10.3 The experiment of trapping the radical intermediate



Scheme S10. The experiment of trapping the radical intermediate

TEMPO (1.5 mmol, 3.0 equiv), $Ru(bpy)_3Cl_2$ (0.005 mmol, 1 mol%) and K_2CO_3 (0.05 mmol, 10 mol%) were first dispersed in 5 mL dioxane **2** and 5 mL 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP). BIN_3 (0.5 mmol, 1.0 equiv) was then added. The reaction mixture vigorously stirred at air (air bubbling) and room temperature (30 °C) under the compact fluorescent light (24 W) irradiation for 24 h. The result showed that the reaction was stopped completely and none of the desired product was detected by crude ^{1}H-NMR. Recovery of starting material is 90%.

10.4 Measurement of quantum yield (Φ) for deconstructive esterification of dioxane.



Scheme S11. Measurement of quantum yield (Φ) for deconstructive esterification of dioxane

General information: All the experiments were carried out based on deconstructive esterification of dioxane following Yoon's procedure.[12] Solutions used were prepared in the dark and reactions were conducted in a 1 cm square quartz cuvette. A Hitachi F-4600 fluorescence spectrophotometer with a 150 W Xe lamp was used as the light source for the quantum yield measurements. A 24 W compact fluorescent light bulb was used for "light/dark" at a distance of 5 cm away from the reaction flask. UV-vis data were measured on a Hitachi U-3900 spectrophotometer.

The quantum yield can be calculated using eq 1:

$$\Phi = \frac{mols\ of\ \ product\ formed}{einsteins\ of\ light\ absorbed} = \frac{mols\ of\ starting\ material \cdot yield}{flux \cdot t \cdot f} \quad (1)$$

Where fluxl is the photon flux of the spectrophotometer, t is the reaction time and f is the light absorbance of catalyst.

A) Absorbance of catalyst:

The absorbance of $Ru(bpy)_3Cl_2$ in HFIP was measured at the reaction concentration of 1.0×10^{-2} M. The absorbance at 436 nm for a 1.0×10^{-2} M solution is >3 (**Figure S1**) indicating the fraction of light absorbed is >0.999.

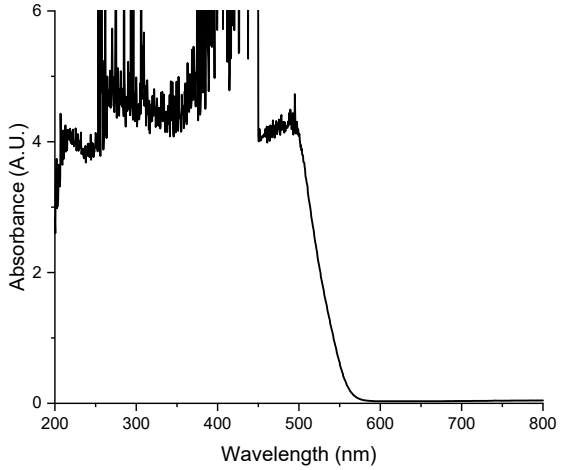


Figure S1. Absorbance of a 1.0×10^{-2} M solution of $Ru(bpy)_3Cl_2$ in HFIP.

B) Determination of the light intensity at 436 nm:

The photon flux of the spectrophotometer was determined by standard ferrioxalate actinometry. A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at $\lambda = 436$ nm with an emission slit width at 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the resulting solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Under light excitation the potassium ferrioxalate decomposes according to the following equations:

$$Fe(C_2O_4)_3^{3-} \xrightarrow{h\nu} Fe^{2+} + C_2O_4^{\bullet -} + 2C_2O_4^{2-}$$

$$Fe(C_2O_4)_3^{3-} + C_2O_4^{\bullet -} \longrightarrow Fe^{2+} + 2CO_2 + 3C_2O_4^{2-}$$

Scheme S12. The reaction of $Fe(C_2O_4)_3^{3-}$

The quantity of ferrous ions formed during an irradiatin period is monitored by conversion to the colored tris-phenanthroline complex. The original ferric ions are not appreciably complexed by phenanthroline and the complex does not absorb at 510 nm. The mols of ferrous ions formed in the irradiated volume are given by eq 2.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \quad (2)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity of phenanthroline complex at 510 nm (11,100 L mol^{-1} cm^{-1}).[13] The difference in absorbance at 510 nm between the irradiated and non-irradiated solutions was measured to be 0.328 (average of three experiments). The conversion was calculated using eq 2:

$$\text{mol } Fe^{2+} = \frac{0.00235\ L \cdot 0.328}{1.000 cm \cdot 11,100\ L\ mol^{-1}\ cm^{-1}} = 6.94 \times 10^{-8} \text{ mol}$$

The photon flux can be calculated using eq 3.

$$\text{photon flux} = \frac{mol\ Fe^{2+}}{\Phi \cdot t \cdot f} \quad (3)$$

Where mol Fe^{2+} is the mols of Fe^{2+} formed during irradiation (6.94×10^{-8} mol), Φ_{Fe} is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ = 436 nm), t is the time (90.0 s), and f_{Fe} is the fraction of light absorbed of the ferrioxalate solution at λ = 436 nm.

The fraction of light absorbed (f_{Fe}) by this solution was calculated using eq 4, where A is the measured absorbance at 436 nm.

$$f_{Fe} = 1\text{-}10^{-A} \quad (4)$$

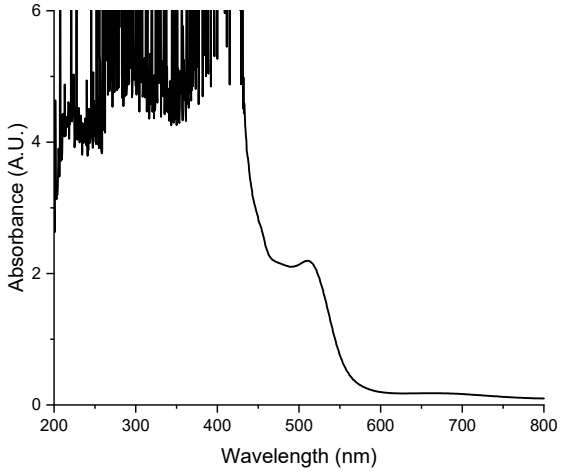


Figure S2. Absorbance of the ferrioxalate actinometer solution

The absorbance of the above ferrioxalate solution at 436 nm was measured to be 3.867 (average of three experiments). The light absorbed (f_{Fe}) was calculated using eq 4:

$$f = 1\text{-}10^{-3.867} = 0.99986$$

The photon flux was calculated using eq 3:

$$\text{photon flux} = \frac{6.94 \times 10^{-8}\, mol}{1.01 \cdot 90.0\, s \cdot 0.99986} = 7.64\times10^{-10} \text{ einstein s}^{-1}$$

C) Determination of quantum yield:

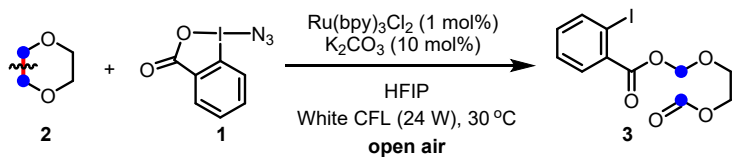
A clear vial was charged with azidoiodinane **1** (0.1 mmol, 1.0 equiv), $Ru(bpy)_3Cl_2$ (0.001 mmol, 1 mol%), and dioxane (1 mL) and HFIP (1 mL). The resulting mixture open air. The reaction mixture was irradiated (λ = 436 nm, slit width= 10.0 nm) for 10800 s (3 h). After irradiation, the solvent of the reaction mixture was removed under reduced pressure. The yield of was determined by ^{1}H NMR based on a

$Cl_2CHCHCl_2$ (20 μL) standard to be 7% (**3**). The quantum yield was calculated using eq 1:

$$\Phi = \frac{0.1 \times 10^{-3}\, mol \cdot 7\%}{7.64 \times 10^{-10}\, einstein\, s^{-1} \cdot 10800\, s \cdot 1.00} \approx 0.84$$

The quantum yield was calculated to be Φ (7%) = 0.84, indicating that a chain reaction mechanism can be excluded. (When quantum yield Φ >> 1, the radical reaction is a chain reaction mechanism).

10.5 Light/dark experiment of deconstructive esterification of dioxane



Scheme S13. Light/dark experiment of deconstructive esterification of dioxane

Six vials were equipped with a stir bar and charged with $Ru(bpy)_3Cl_2$ (0.005 mmol, 1 mol%), K_2CO_3 (0.05 mmol, 10 mol%), dioxane (5 mL) and HFIP (5 mL). Azidoiodinane **1** (0.5 mmol, 1.0 equiv) was then added and the reaction was stirred under air atmosphere. The reactions were alternatively irradiated with a 24 W white CFL bulb and kept in the dark in 2 h intervals. After each interval, one vial was taken out, the solvent was removed under reduced pressure, and the yield was determined by ^1H NMR based on a $Cl_2CHCHCl_2$ (20 μL) as an internal standard.

Vial	Time (h)/conditions						Yield (%)[a]
1	0-2/hv						6
2	0-2/hv	2-4/dark					6
3	0-2/hv	2-4/dark	4-6/hv				13

4	0-2/hv	2-4/dark	4-6/hv	6-8/dark			13
5	0-2/hv	2-4/dark	4-6/hv	6-8/dark	8-10/hv		20
6	0-2/hv	2-4/dark	4-6/hv	6-8/dark	8-10/hv	10-12/dark	20

a) NMR yield, average of three experiments.

Table S3. Yields of Light/Dark experiment

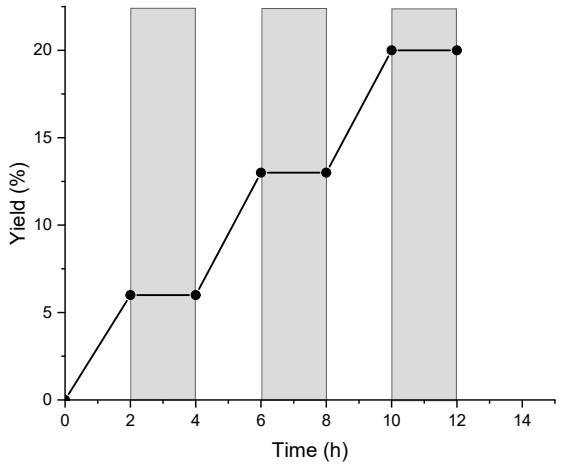


Figure S3. Light/dark experiment of deconstructive esterification of dioxane

10.6 Cyclic voltammetry (CV) experiment

Cyclic voltammetry was performed in a three-electrode cell connected to a schlenk line under nitrogen at room temperature. A cyclic voltammograms in CH_3CN (20 mL) by using Pt as the working electrode, Pt as the counter electrode and the saturated calomel electrode as the reference electrode. The scan rate was 50 mV/s, ranging from 0 V to 3.0 V. $[N(C_2H_5)_4](ClO_4)$ (0.1 mmol) was used as the electrolyte.

1) Blank experiment: A solution of $[N(C_2H_5)_4](ClO_4)$ (0.1 mmol) in 20 mL anhydrous CH_3CN was subject to cyclicvoltammetry experiment. Potential sweep rate was 50 mV/s.

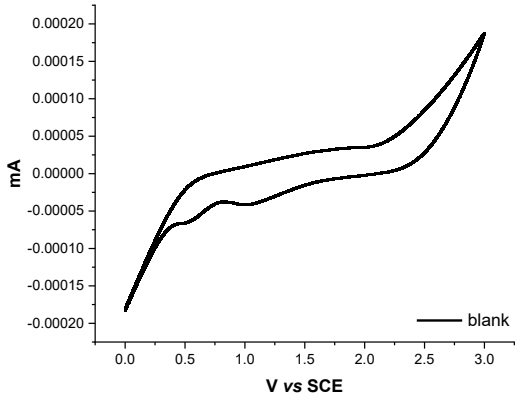


Figure S4. CV curve of blank

2) Cyclic voltammetry experiment of intermediate **IV**: A solution of intermediate **IV** (0.1 mmol) and $[N(C_2H_5)_4](ClO_4)$ (0.1 mmol) in 20 mL anhydrous CH_3CN was subject to cyclicvoltammetry experiment. Potential sweep rate was 50 mV/s.

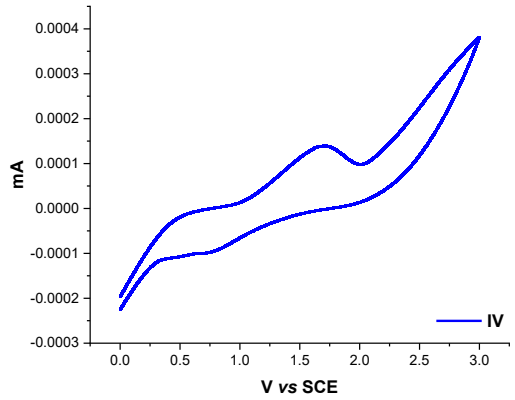


Figure S5. CV curve of intermediate **IV**

cyclic voltammetry experiment showed that the species **IV** has sufficiently oxidizing (**IV**, $E_{1/2}^{ox}$ = +1.70 V vs SCE) to accept an electron from Ru(II) ($E_{1/2}^{R(III)/R(II)}$ = +1.29 V vs SCE)[14], generating the radical cation $\mathbf{IV}^{\cdot-}$ and concurrently reducing the photocatalyst to Ru(III).

10.7 Stern-Volmer Experiment

To figure out how the excited state of $Ru(bpy)_3Cl_2$ interacts with BIN_3, luminescence quenching experiments were performed. The quenching of $Ru(bpy)_3Cl_2$ was conducted in HFIP, with a catalyst concentration of 0.003 mM in a quartz cell (4 mL) with a 1 cm path length and an excitation wavelength of 375 nm used. The emission of $Ru(bpy)_3Cl_2$ was measured with varying amounts of BIN_3. All spectra were corrected for small changes in volume upon addition of the substrates. As demonstrated in Supplementary Figure S6 and S7, the emission intensity decreased with increasing amounts of BIN_3, providing evidence for the direct BIN_3 reduction by photoexcited $Ru(bpy)_3Cl_2$*.

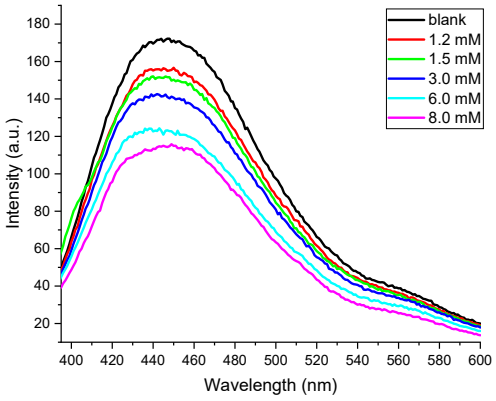


Figure S6. Fluorescence spectra of $Ru(bpy)_3Cl_2$

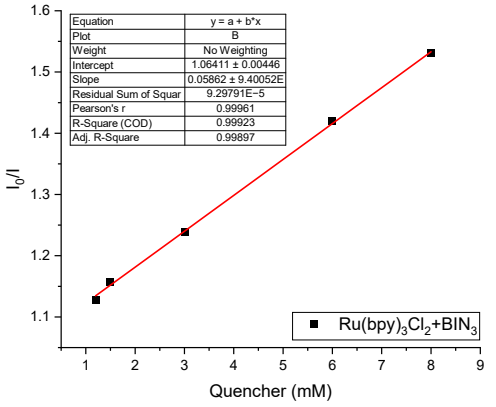


Figure S7. Stern-Volmer plot of $Ru(bpy)_3Cl_2$ (0.003Mm) in CH_3CN with varying BIN_3

11 Referance

[1] Zhdankin, V. V.; Krasutsky, A. P.; Kuehl, C. J.; Simonsen, A. J.; Woodward, J. K.; Mismash, B.; Bolz, J. T. Preparation, X-ray Crystal Structure, and Chemistry of Stable Azidoiodinanes Derivatives of Benziodoxole. *J. Am. Chem. Soc.* **1996**, *118*, 5192-5197.

[2] Akai, S.; Okuno, T.; Egi, M.; Takada, T.; Tohma, H.; Kita, Y. Preparation of Novel Cyclic Hypervalent Idoine(III) Compounds Having Azido, Cyano, and Nitrato Ligands. *Heterocycles*. **1996**, *42*, 47-51.

[3] Sharma, A.; Hartwig, J. F. Metal-catalysed azidation of tertiary C–H bonds suitable for late-stage functionalization. *Nature*. **2015**, *517*, 600-604.

[4] Matouš ek, V.; Pietrasiak, E.; Schwenk, R.; Togni, A. One-Pot Synthesis of Hypervalent Iodine Reagents for Ele- ctrophilic Trifluoromethylation. *J. Org. Chem*. **2013**, *78*, 6763-6768.

[5] Li, G.; Leow, D.; Wan, L.; Yu, J.-Q. Ether-Directed ortho-C–H Olefination with a Palladium(II)/Monoprotected Amino Acid Catalyst. *Angew. Chem. Int. Ed.* **2013**, *52*, 1245-1247.

[6] Shigeno, M.; Nakamura, R.; Hayashi, K.; Nozawa-Kumada, K.; Kondo, Y. Catalytic Amination of β-(Hetero)arylethyl Ethers by Phosphazene Base t-Bu-P4. *Org. Lett.* **2019**, *21*, 6695-6699.

[7] Wei, Z.; Ru, S.; Zhao, Q.; Yu, H.; Zhang, G.; Wei, Y. Highly efficient and practical aerobic oxidation of alcohols by inorganic-ligand supported copper catalysis. *Green Chemistry* **2019,** *21*, 4069-4075.

[8] Imada, Y.; Okada, Y.; Noguchi, K.; Chiba, K. Selective Functionalization of Styrenes with Oxygen Using Different Electrode Materials: Olefin Cleavage and Synthesis of Tetrahydrofuran Derivatives. *Angew. Chem. Int. Ed.* **2019,** *58*, 125-129.

[9] Meng, S.-S.; Lin, L.-R.; Luo, X.; Lv, H.-J.; Zhao, J.-L.; Chan, A. S. C. Aerobic oxidation of alcohols with air catalyzed by decacarbonyldimanganese. *Green Chemistry* **2019,** *21*, 6187-6193.

[10] Zhang, Y.; Yang, X.; Wu, J.; Huang, D. Aerobic C–H Functionalization Using Pyrenedione as the Photocatalyst. *Synthesis* **2020**, 52, 2512-2520.

[11] Sagadevan, A.; Hwang, K. C.; Su, M. D. Singlet oxygen-mediated selective C-H bond hydroperoxidation of ethereal hydrocarbons. *Nat. Commun.* **2017,** *8*, 1812-1819.

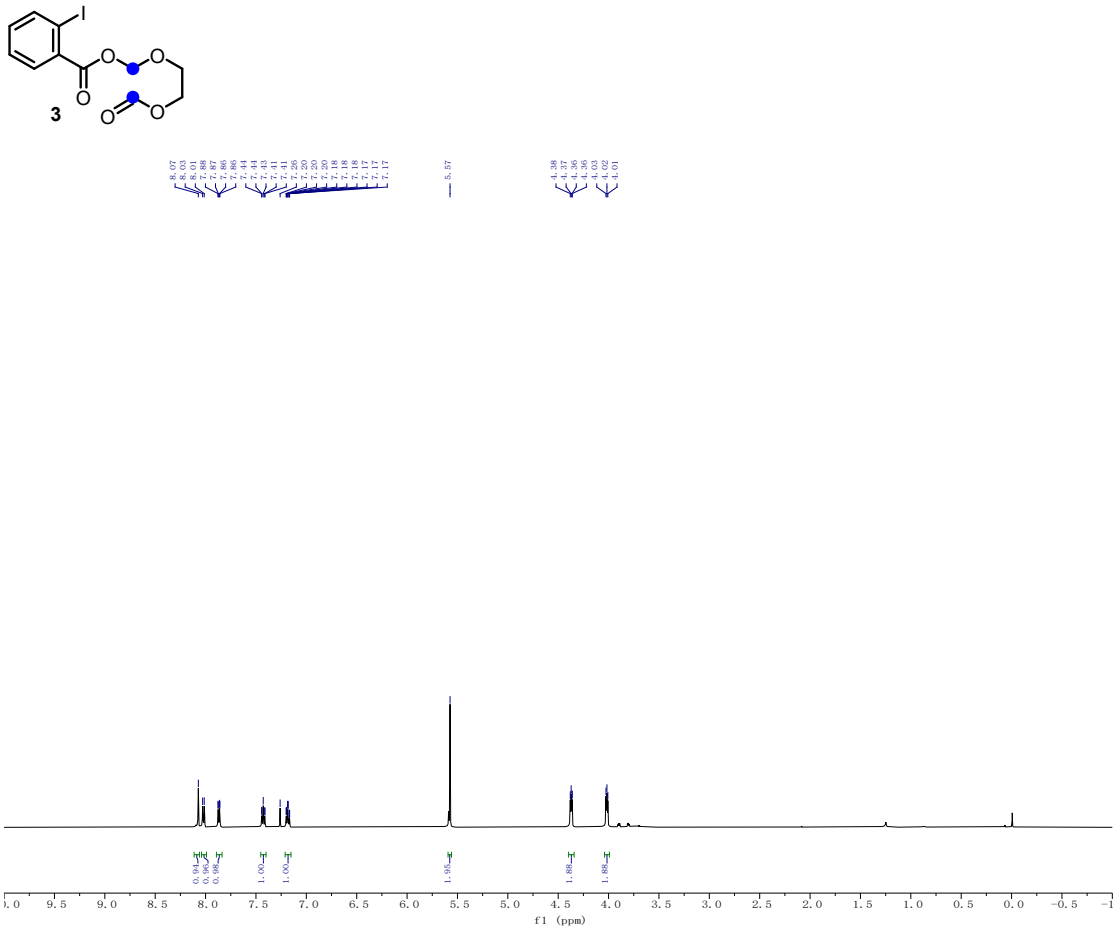
[12] Cismesia, M. A.; Yoon, T. P. Characterizing chain processes in visible light photoredox

catalysis. *Chem. Sci.* **2015**, *6*, 5426-5434.

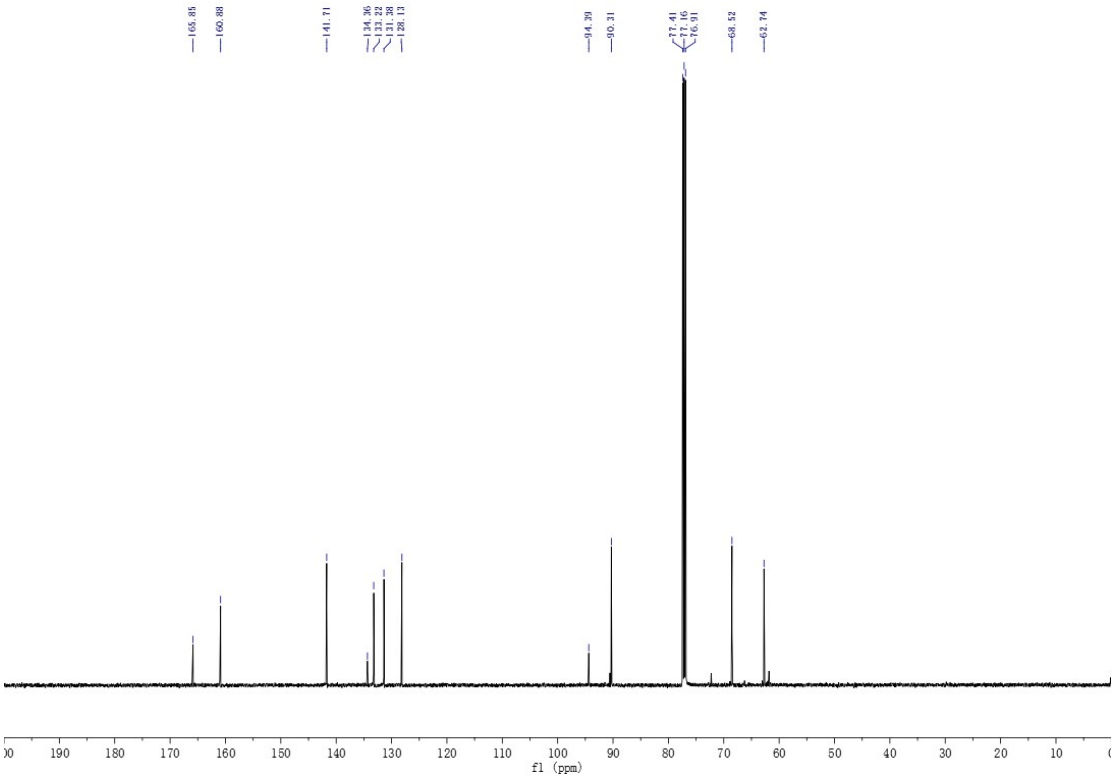
[13] Montalti, M.; Credi, A.; Prodi, L.; Gandolfi, M. T. Chemical Actinometry, *Handbook of Photochemistry*, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, 2006, 601.

[14] Prier, C. K. Rankic, D. A. MacMillan, D. W. C. *Chem. Rev.* **2013**, *113*, 5322-5363.

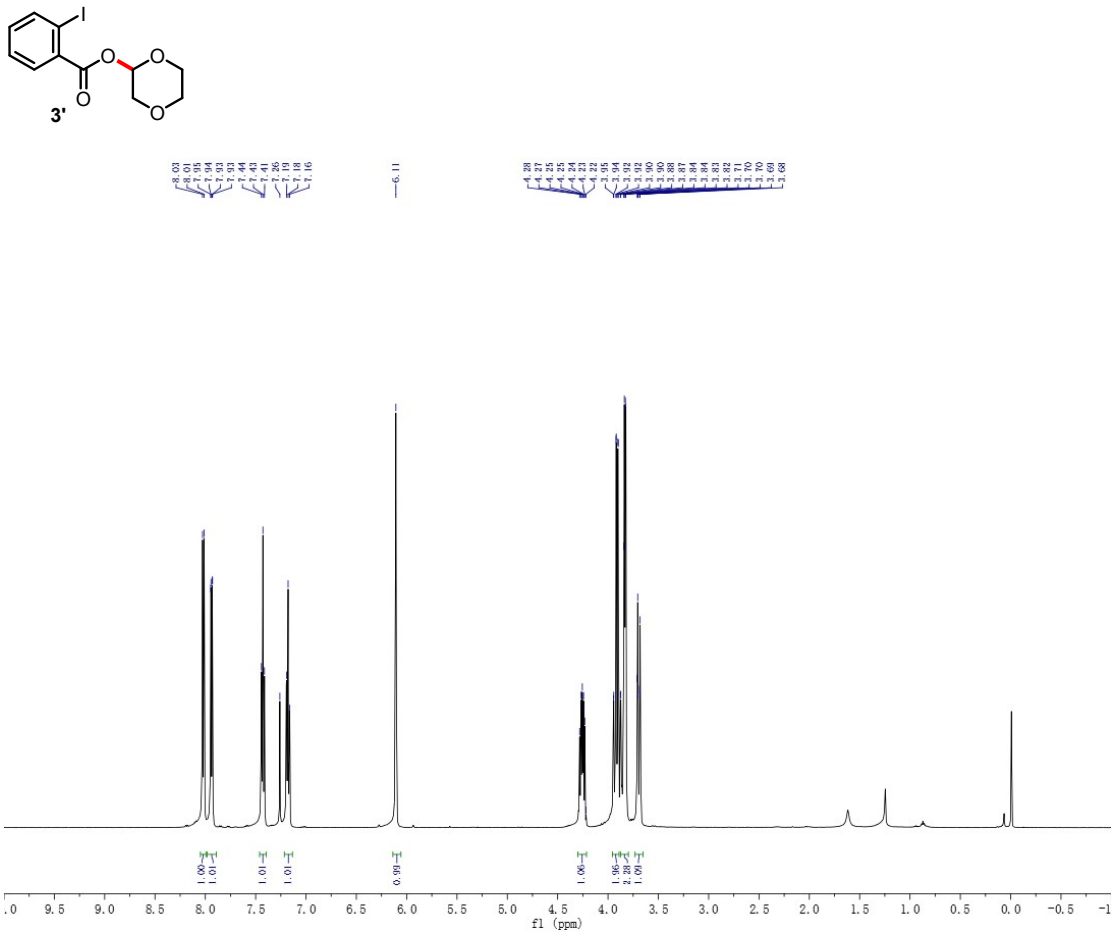
12 ^{1}H-NMR and ^{13}C-NMR spectra



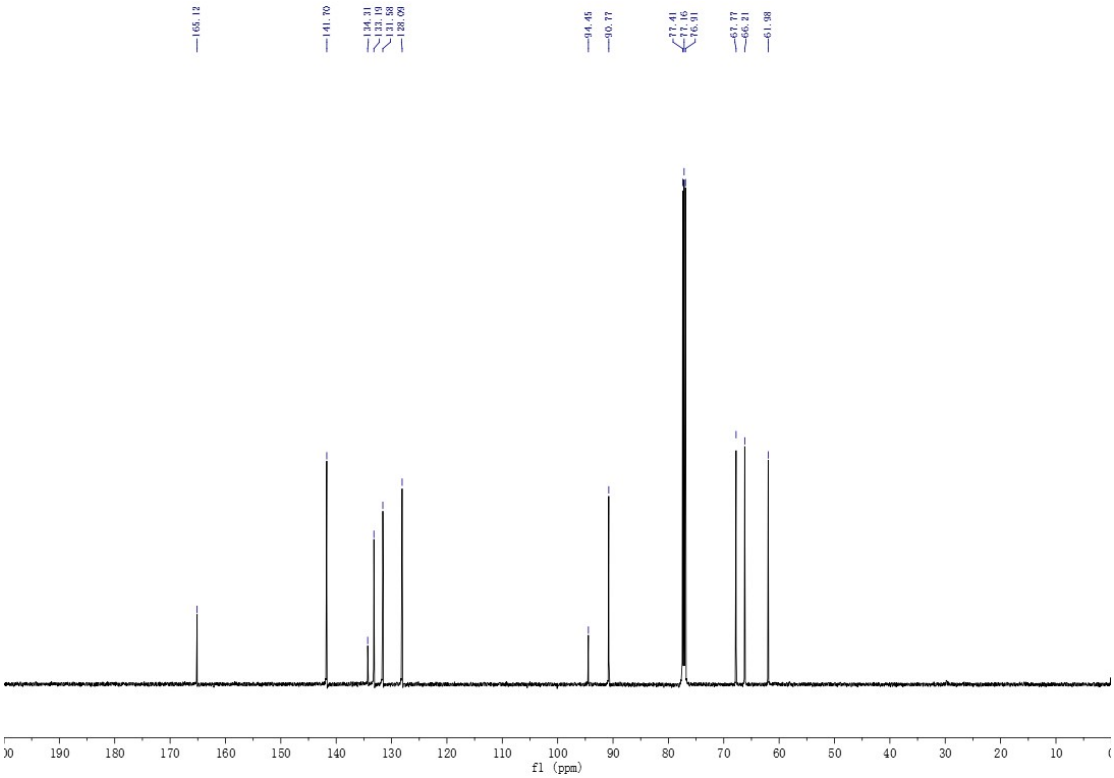
^{1}H NMR of compound **3**



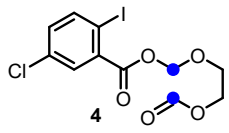
^{13}C NMR of compound **3**

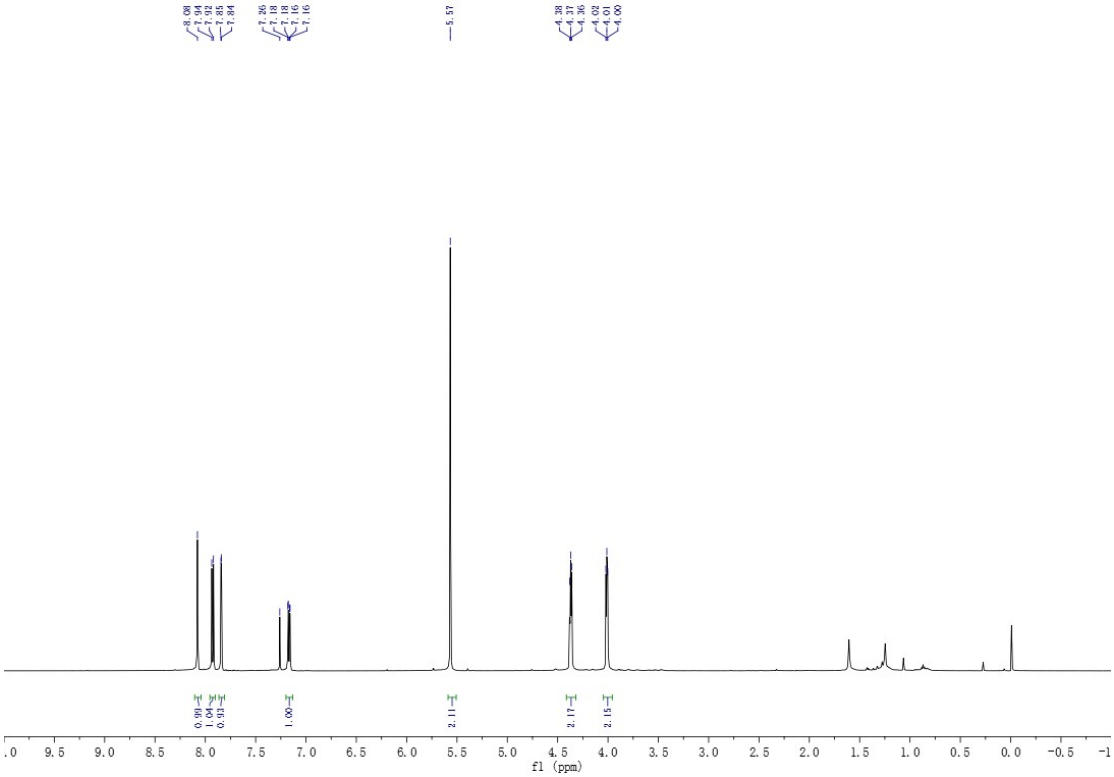


^{1}H NMR of compound **3'**

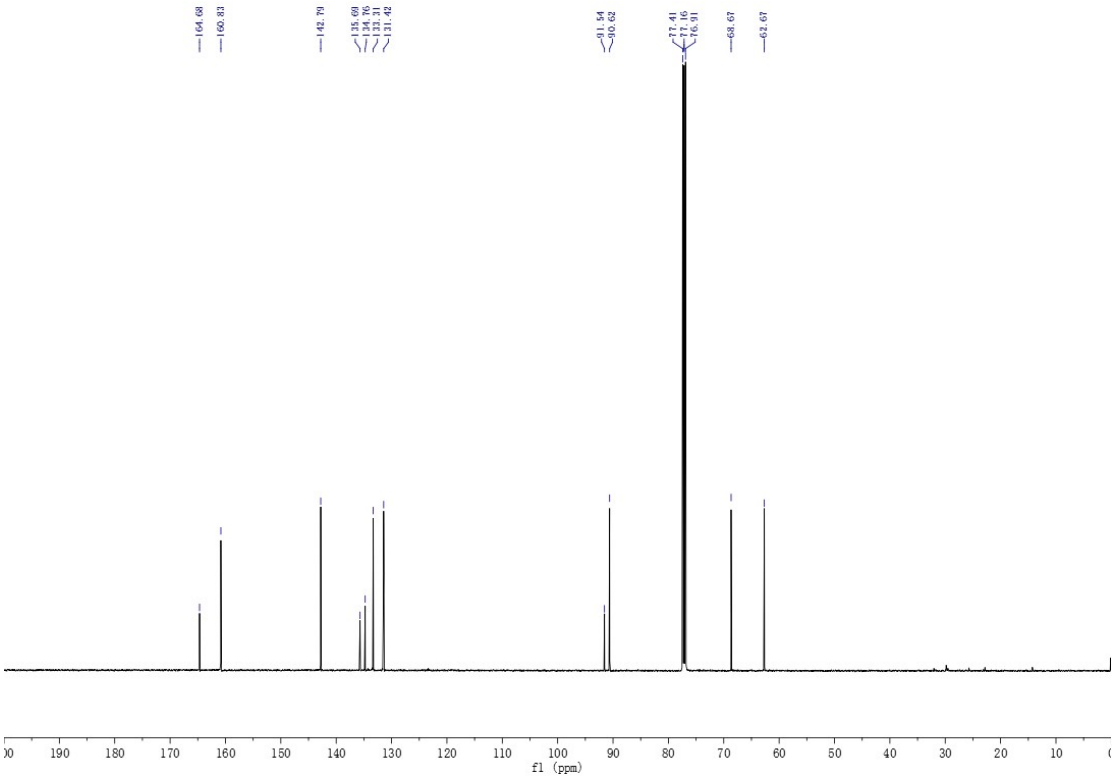


^{13}C NMR of compound **3'**

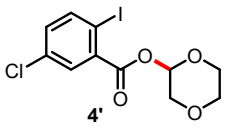


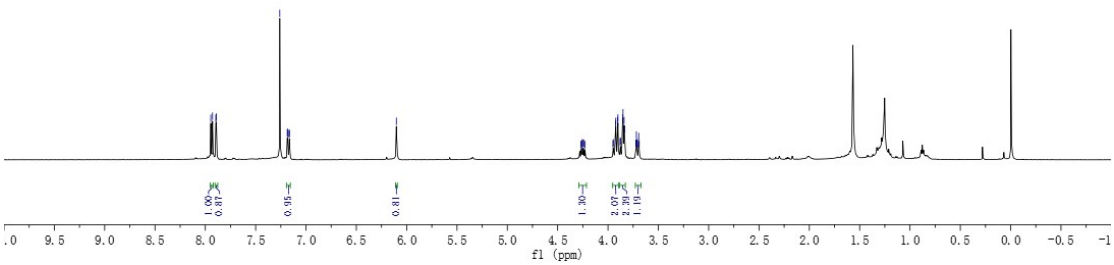


^{1}H NMR of compound **4**

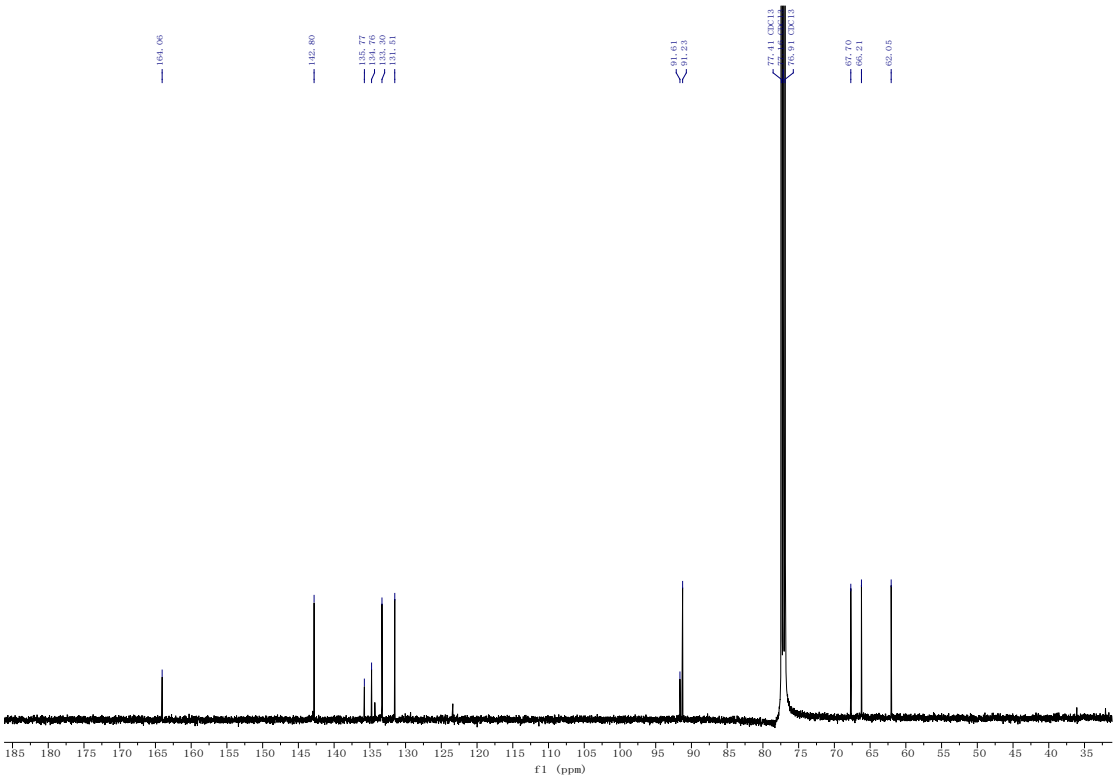


^{13}C NMR of compound **4**

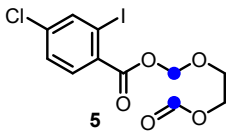




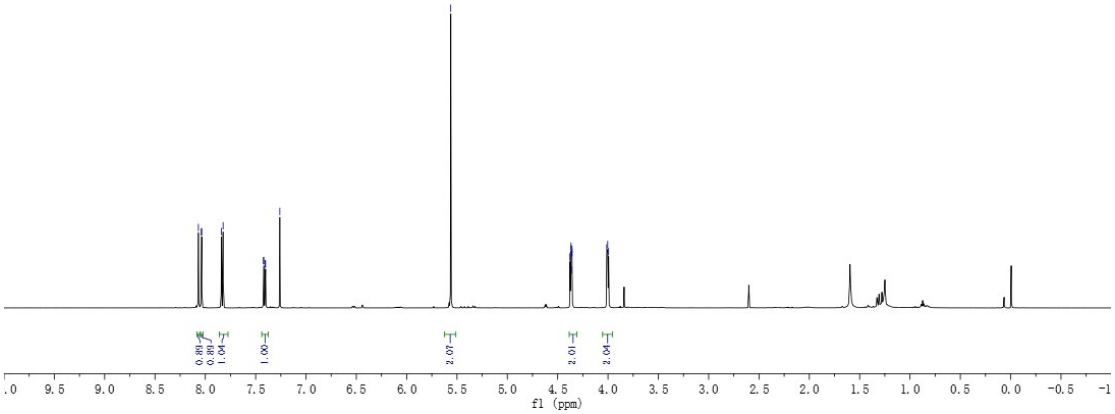
^{1}H NMR of compound **4'**



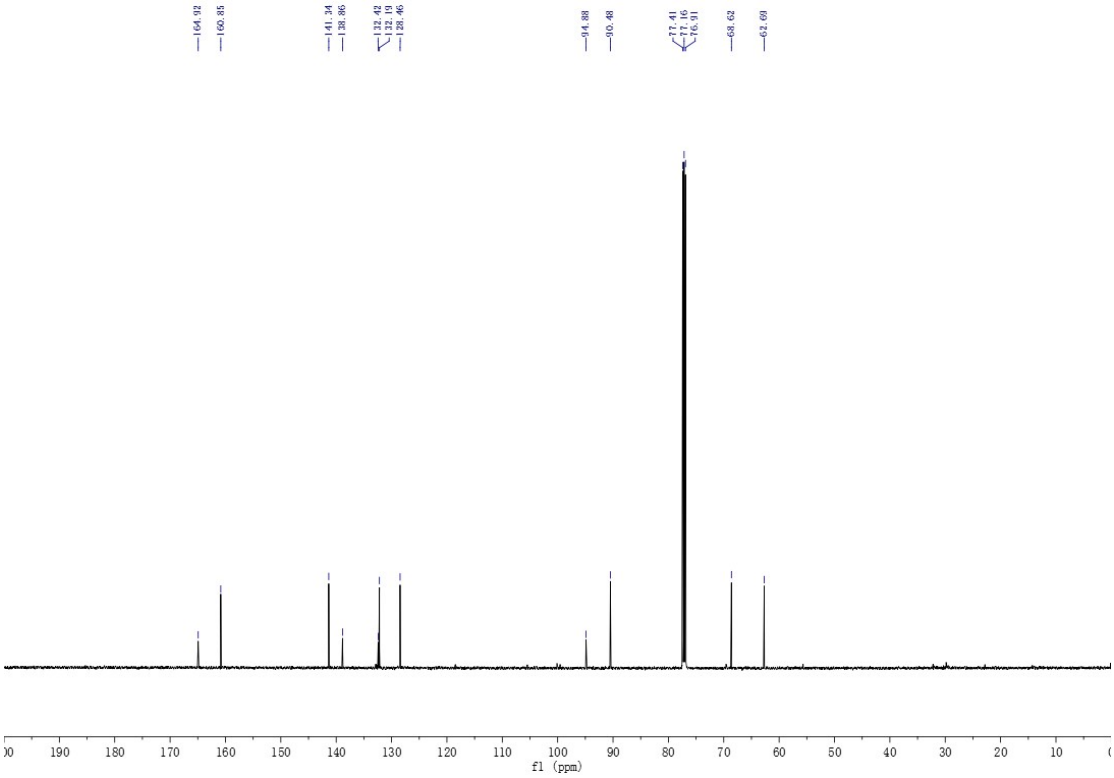
^{13}C NMR of compound **4'**



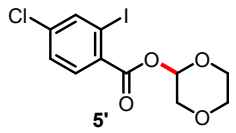
5

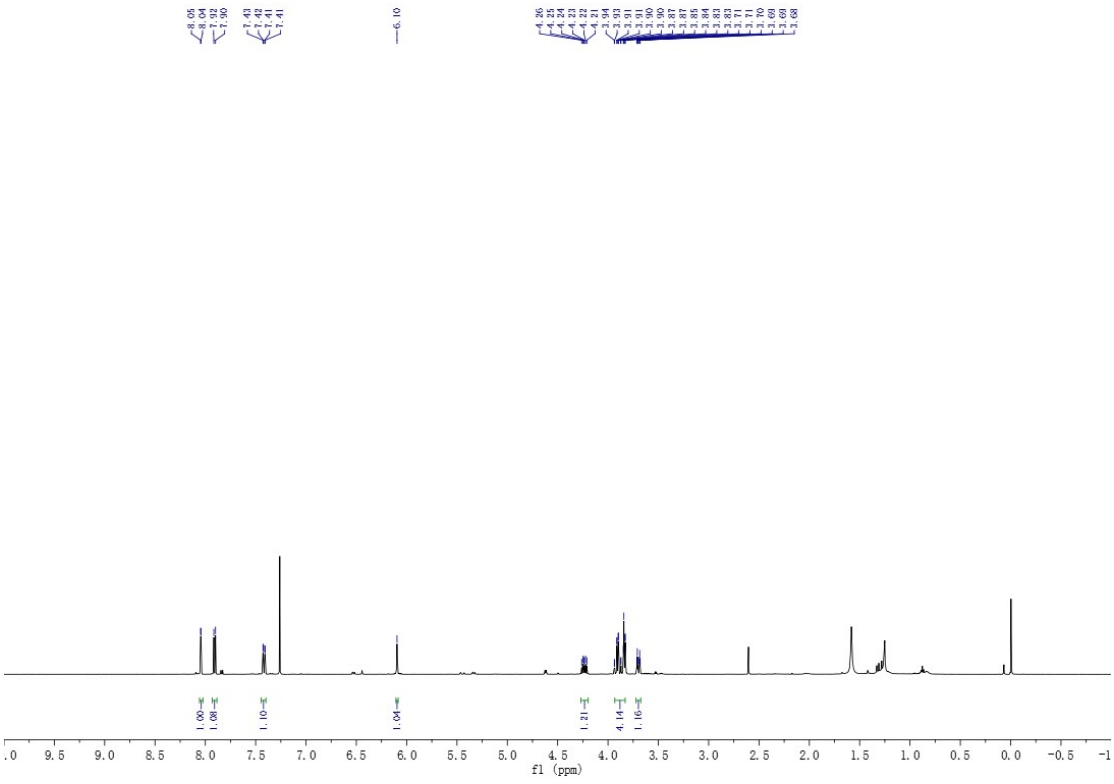


^{1}H NMR of compound **5**

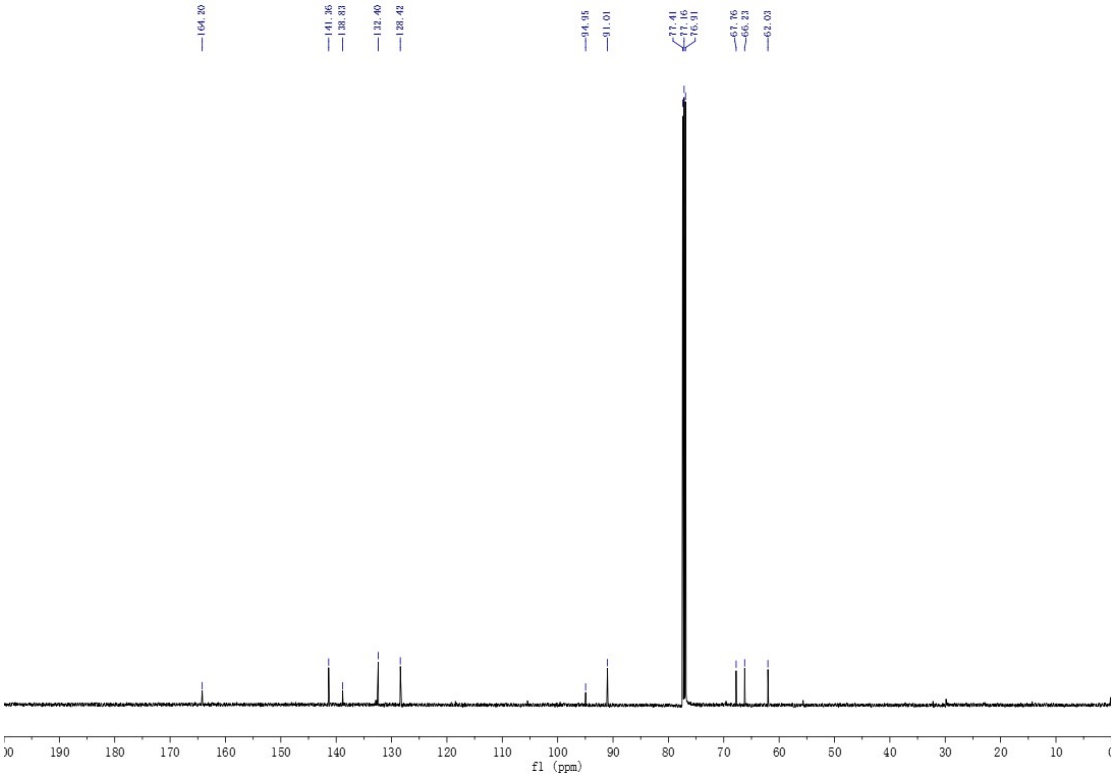


^{13}C NMR of compound **5**

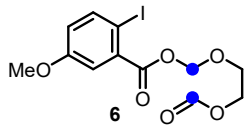




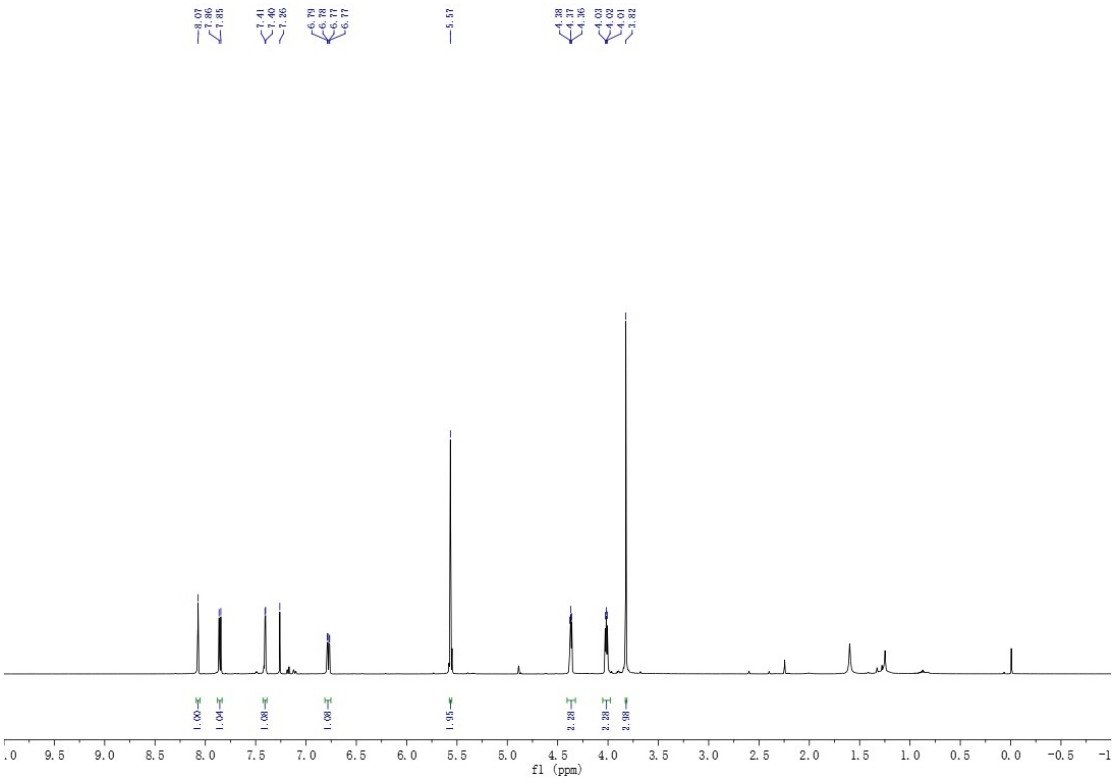
^{1}H NMR of compound **5'**



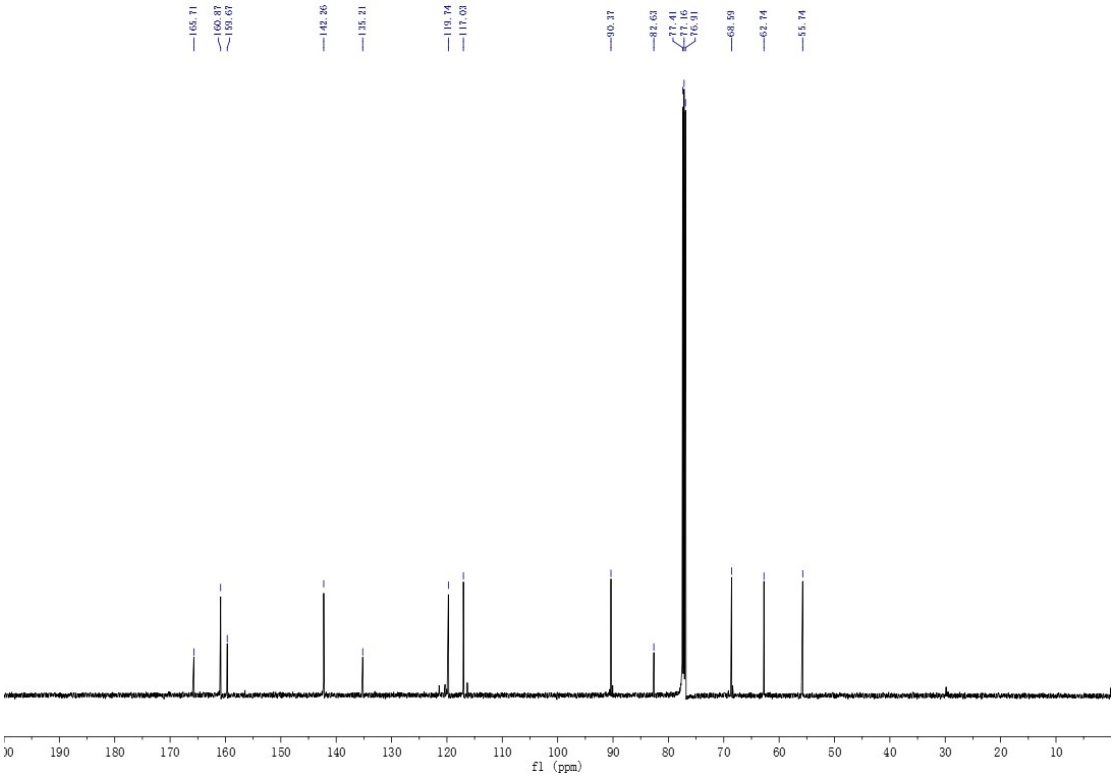
^{13}C NMR of compound **5'**



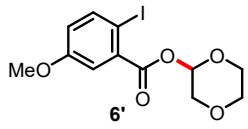
6

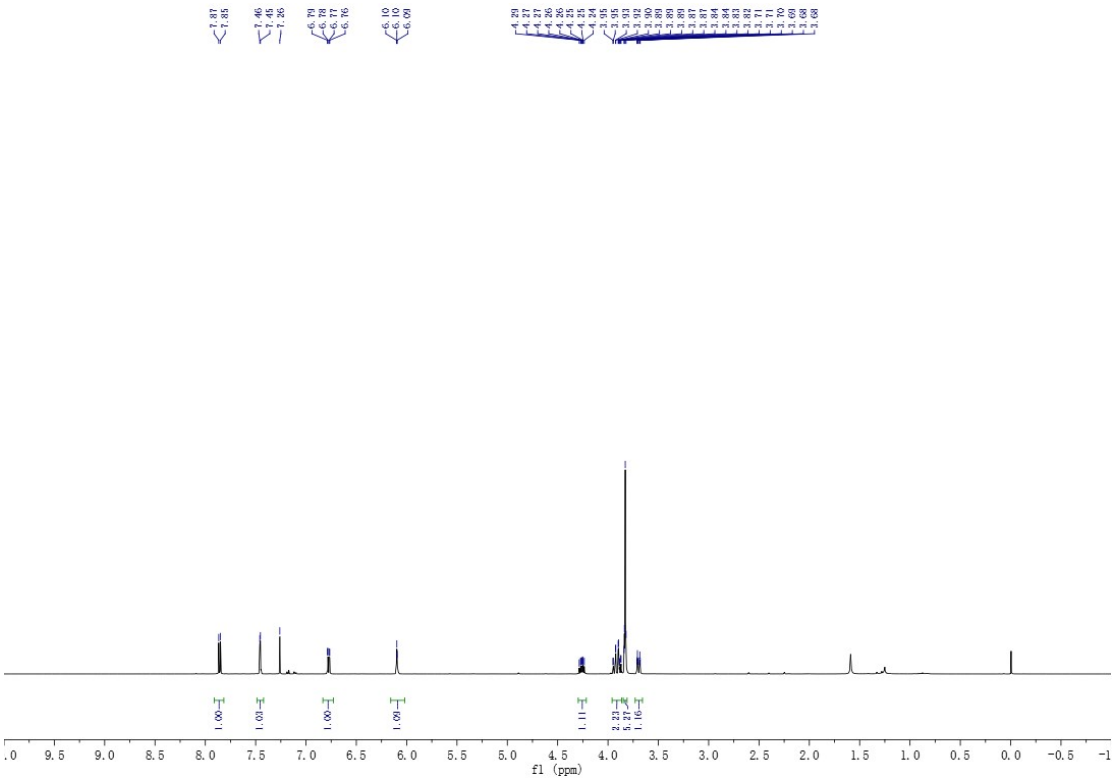


^{1}H NMR of compound **6**

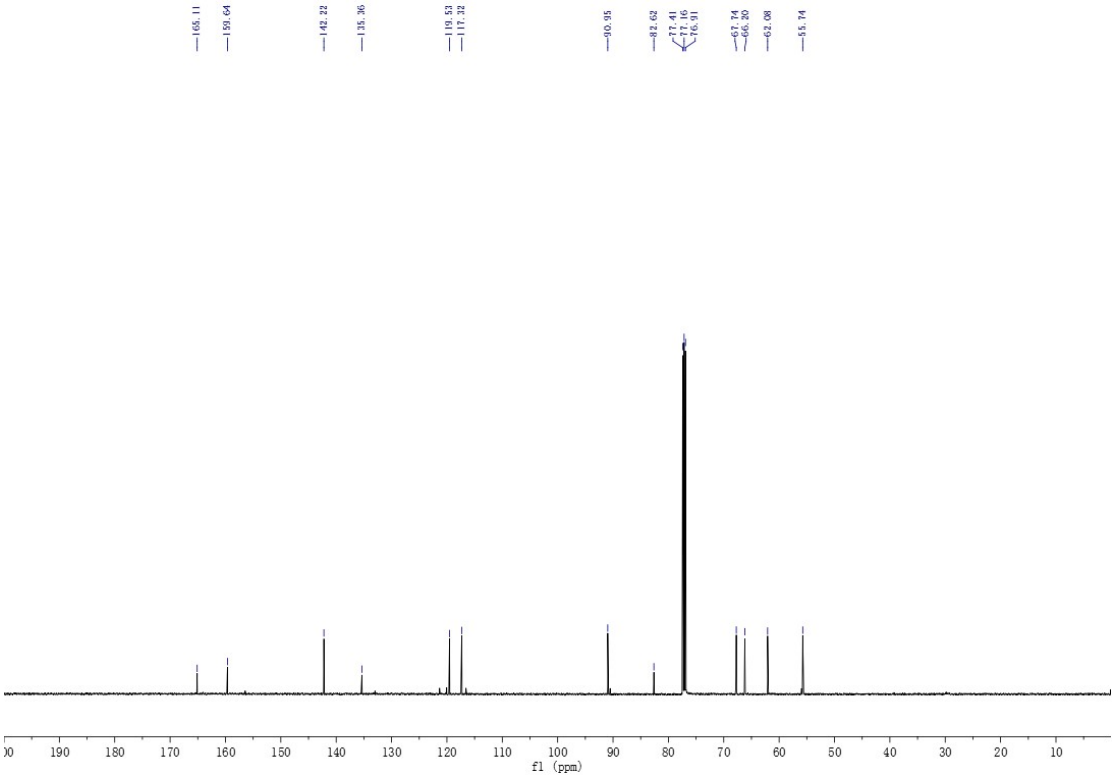


^{13}C NMR of compound **6**

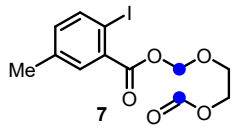




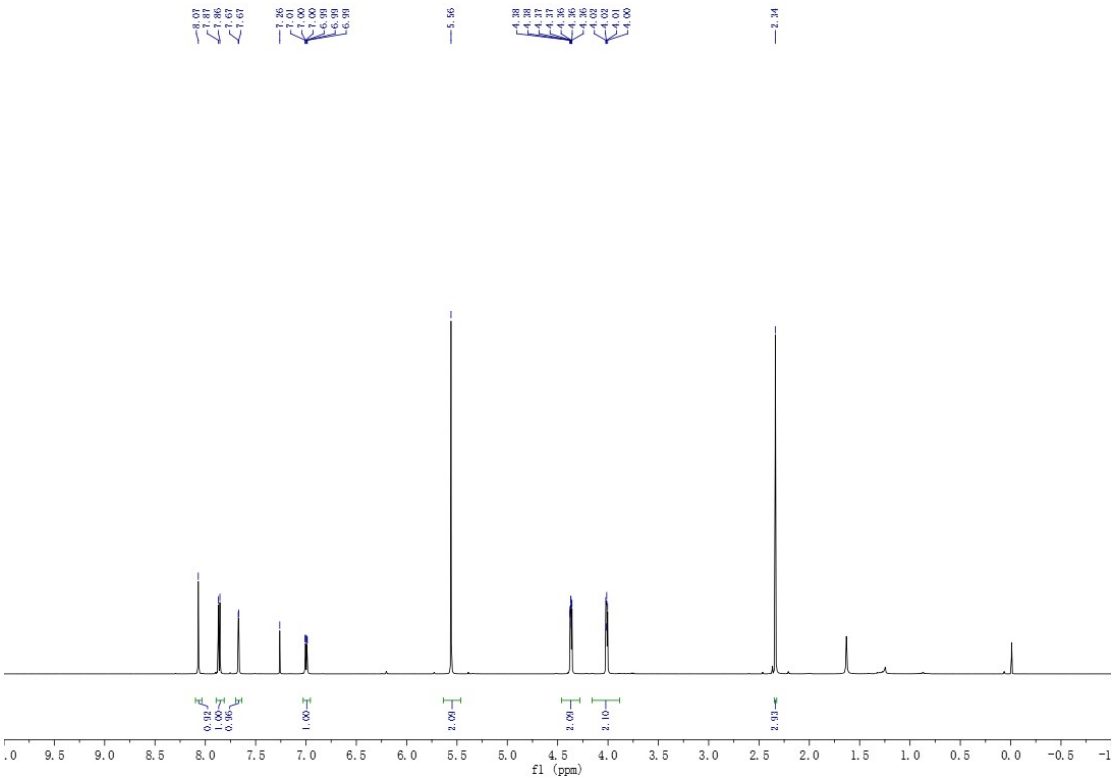
^{1}H NMR of compound **6'**



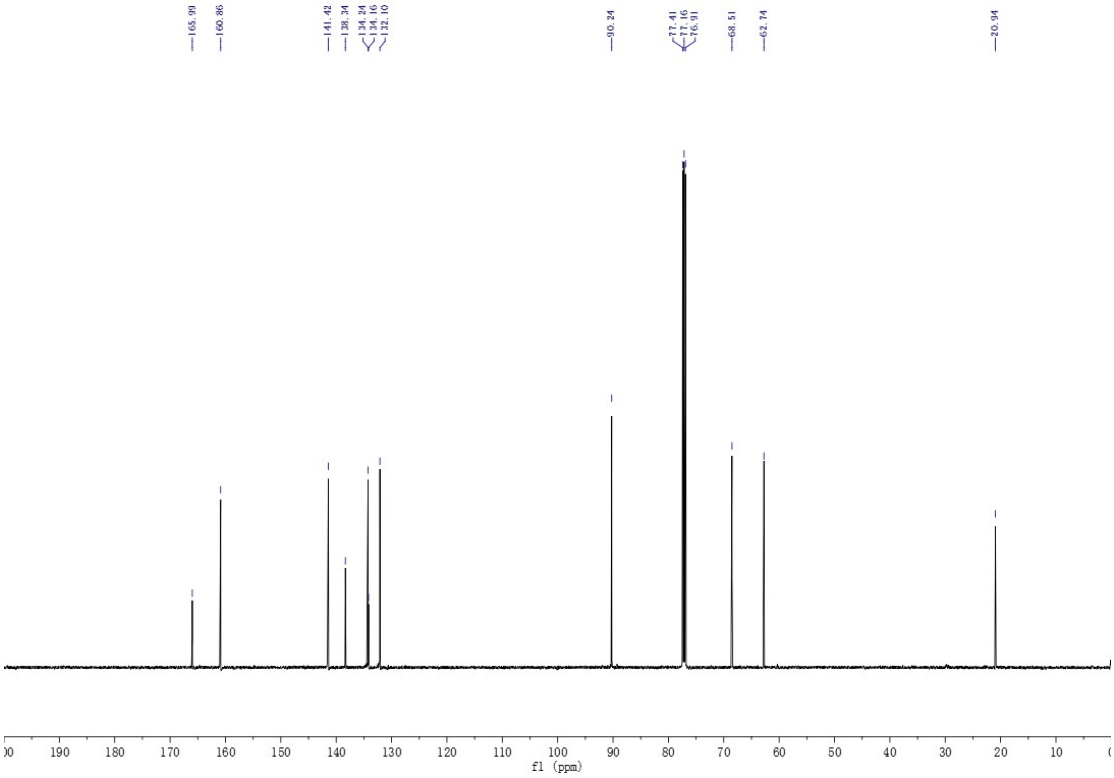
^{13}C NMR of compound **6'**



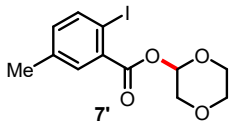
7



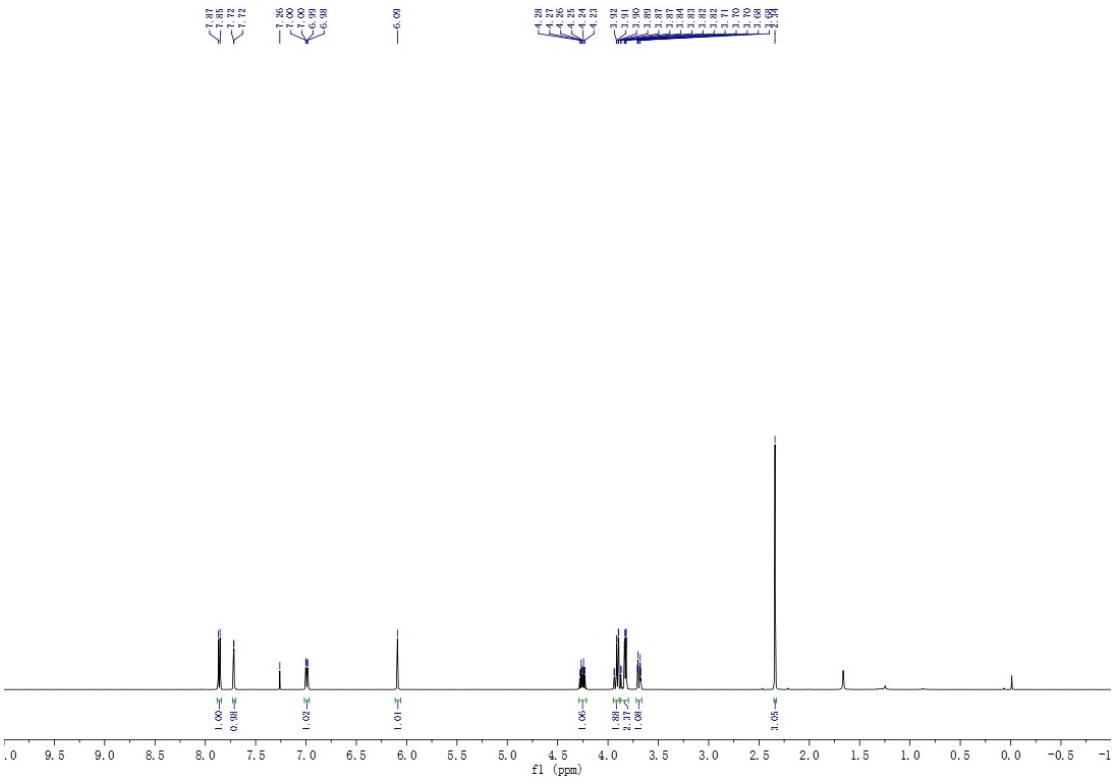
^{1}H NMR of compound **7**



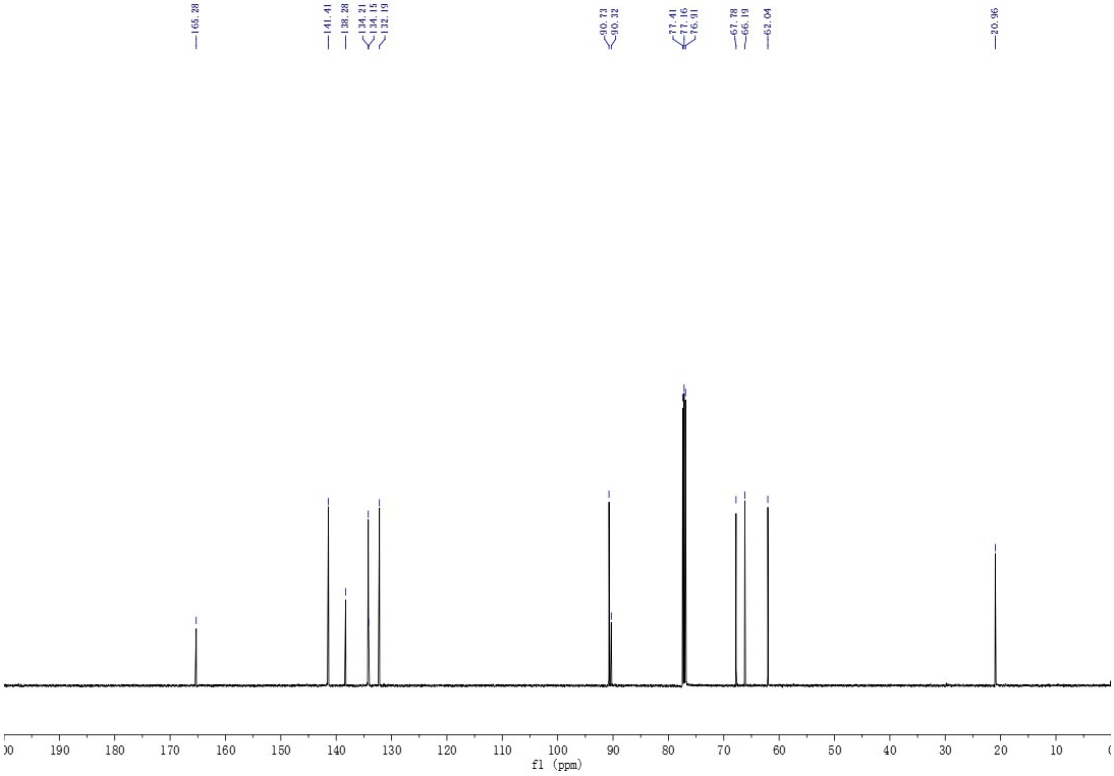
^{13}C NMR of compound **7**



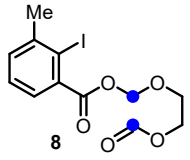
7'



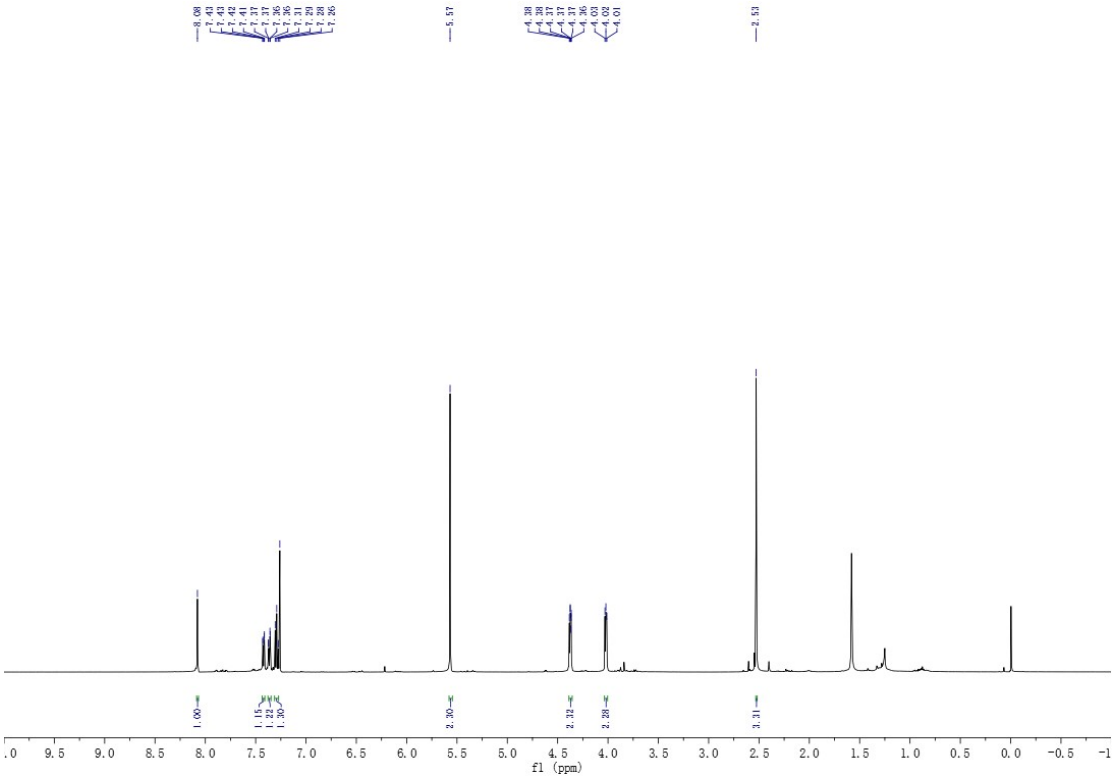
^{1}H NMR of compound **7'**



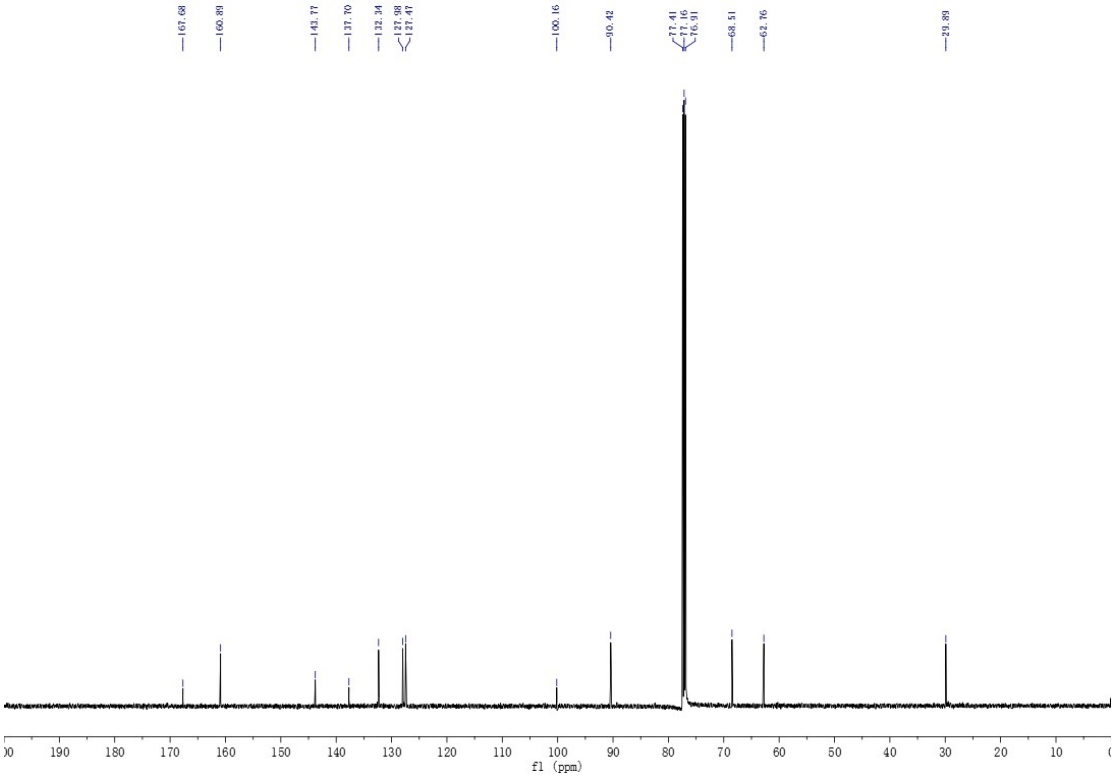
^{13}C NMR of compound **7'**



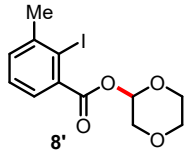
8

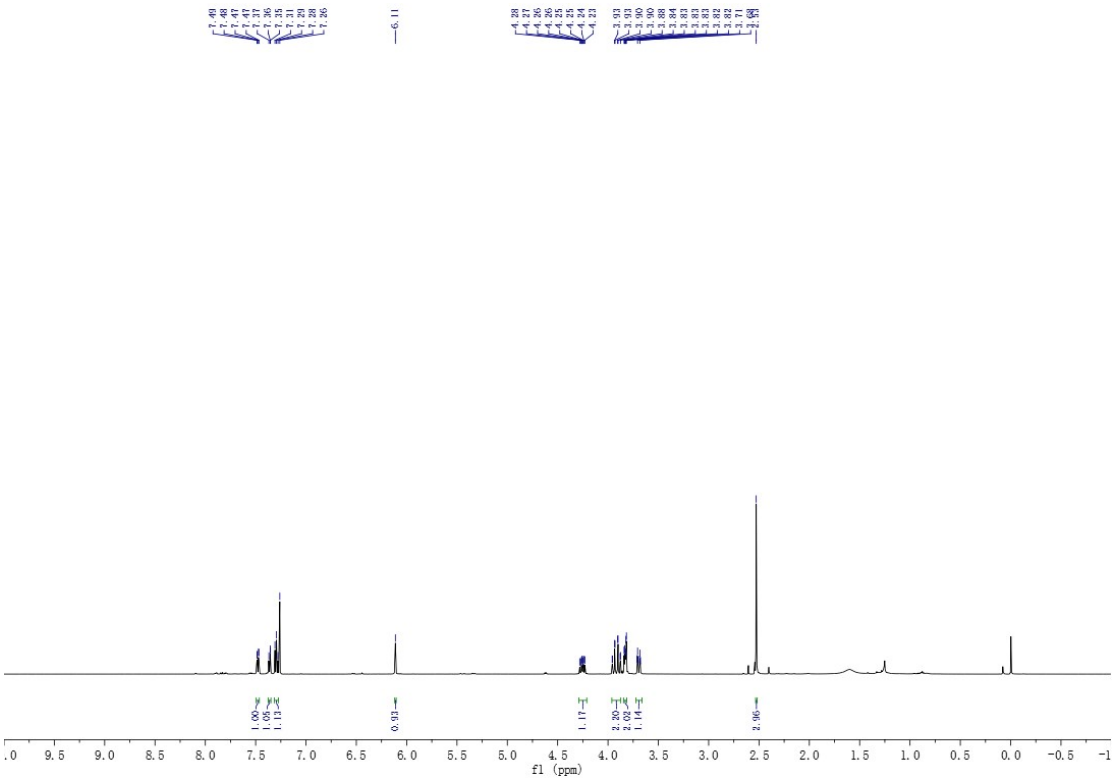


^{1}H NMR of compound **8**

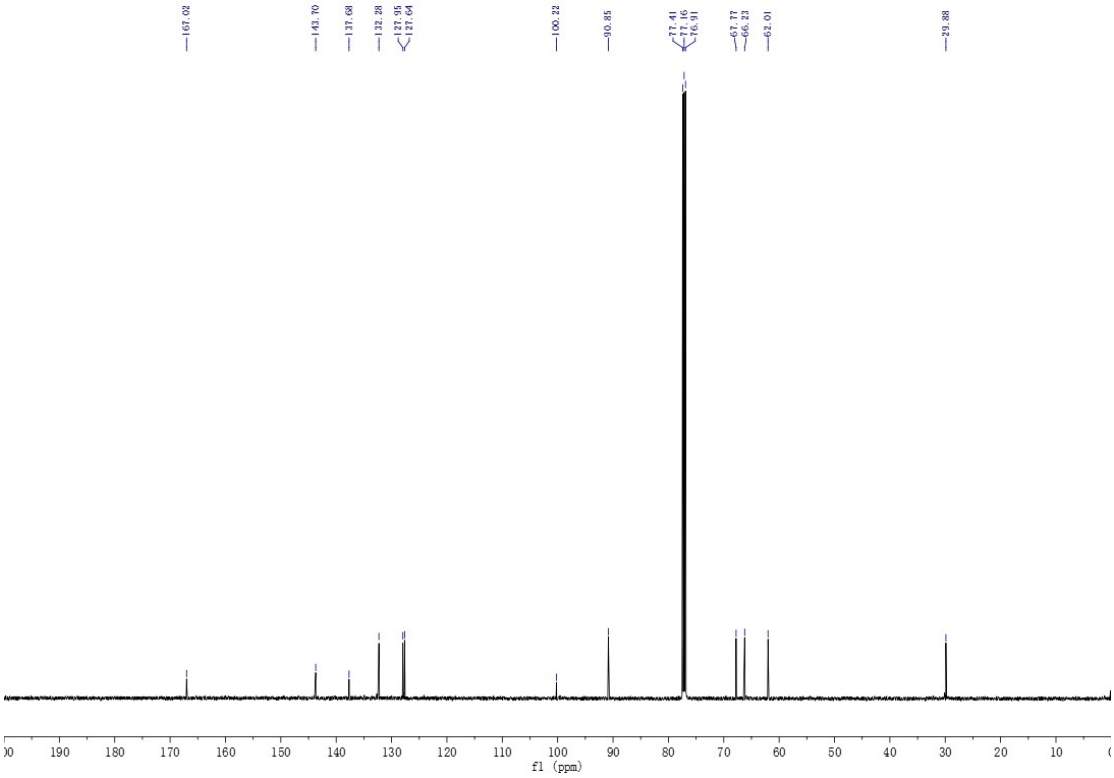


^{13}C NMR of compound **8**

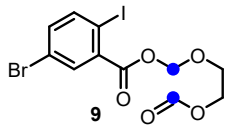


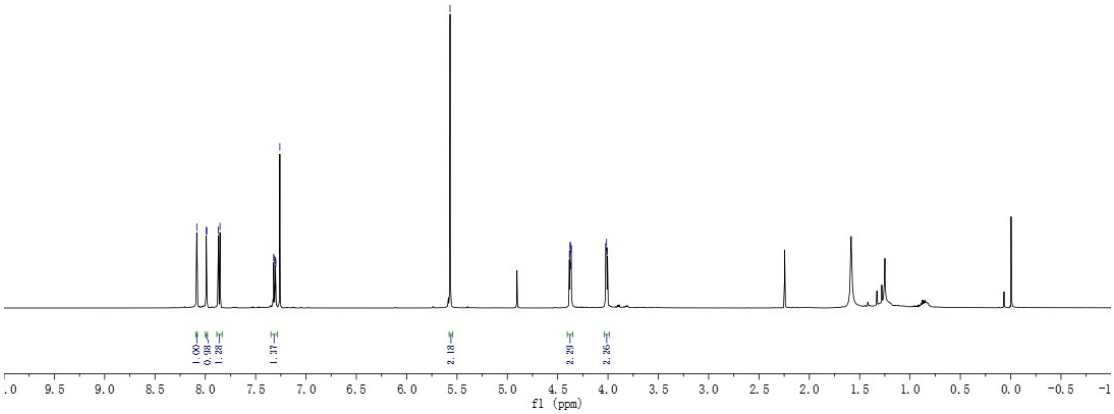


^{1}H NMR of compound **8'**

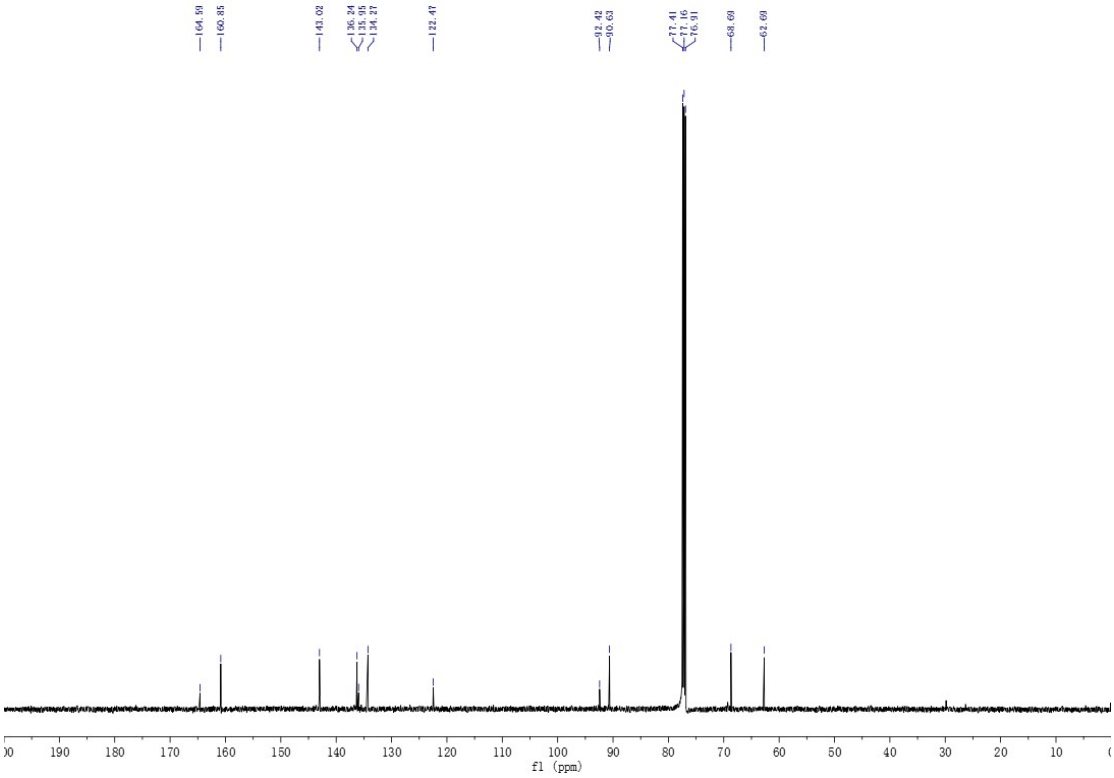


^{13}C NMR of compound **8'**

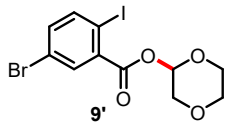


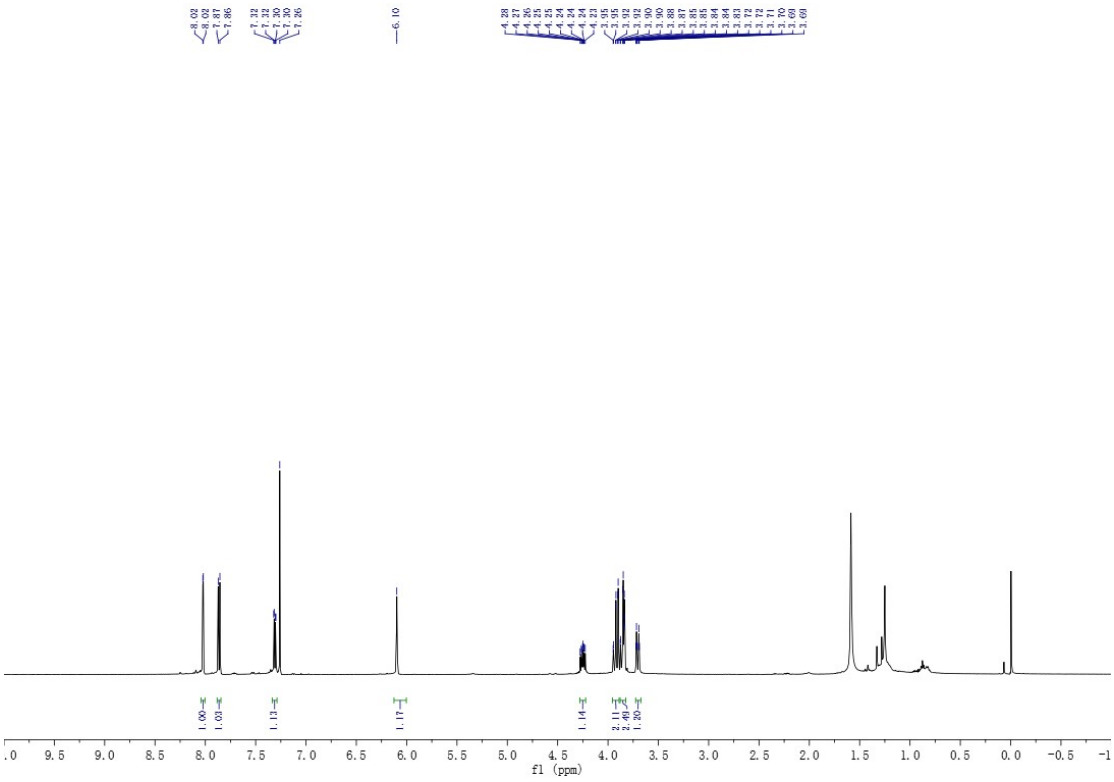


^{1}H NMR of compound **9**

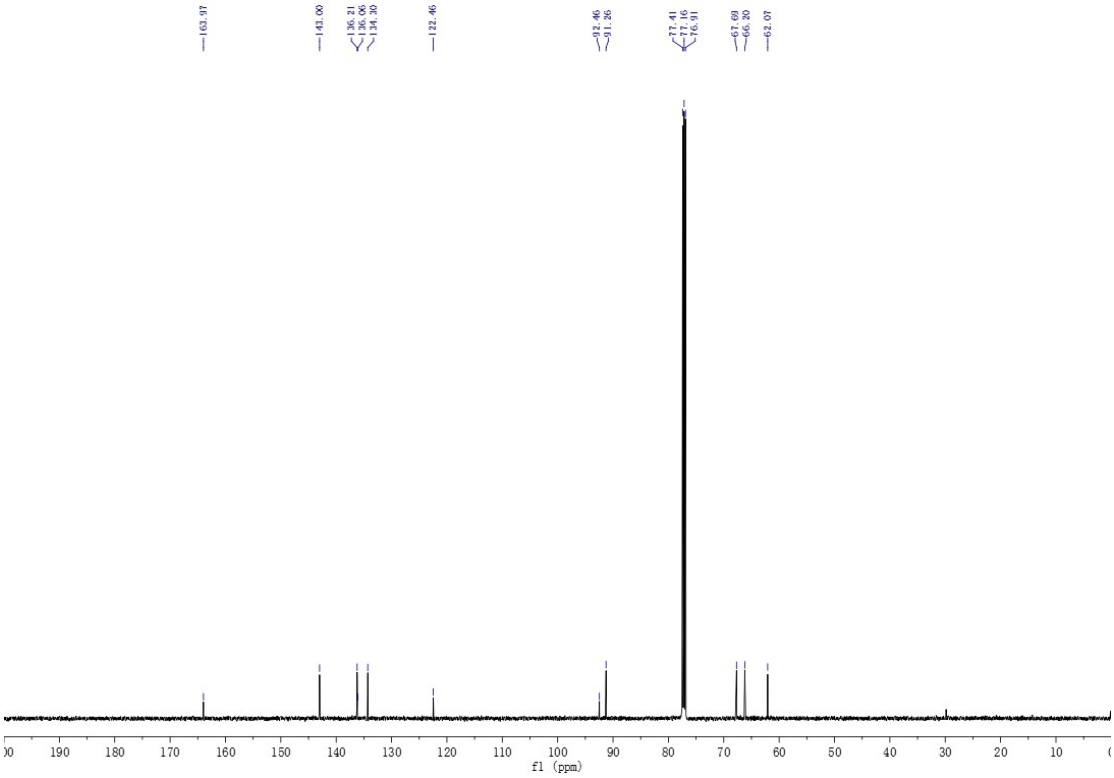


^{13}C NMR of compound **9**

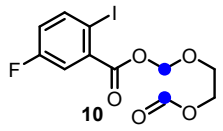


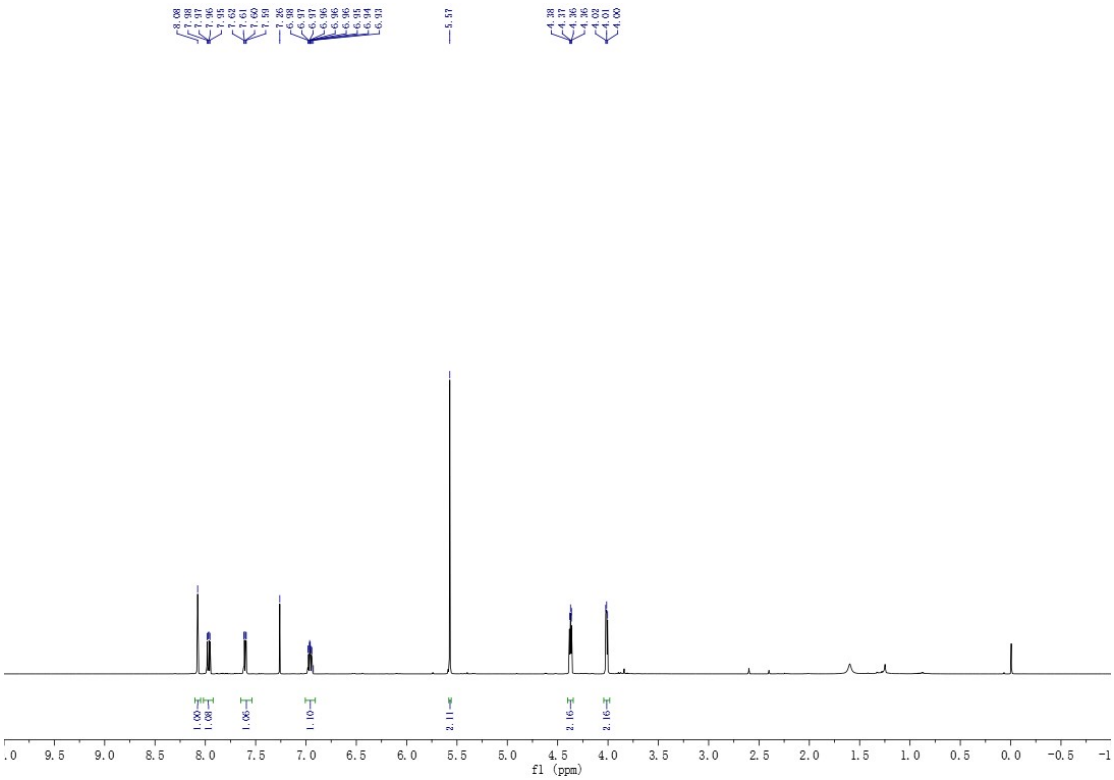


^{1}H NMR of compound **9'**

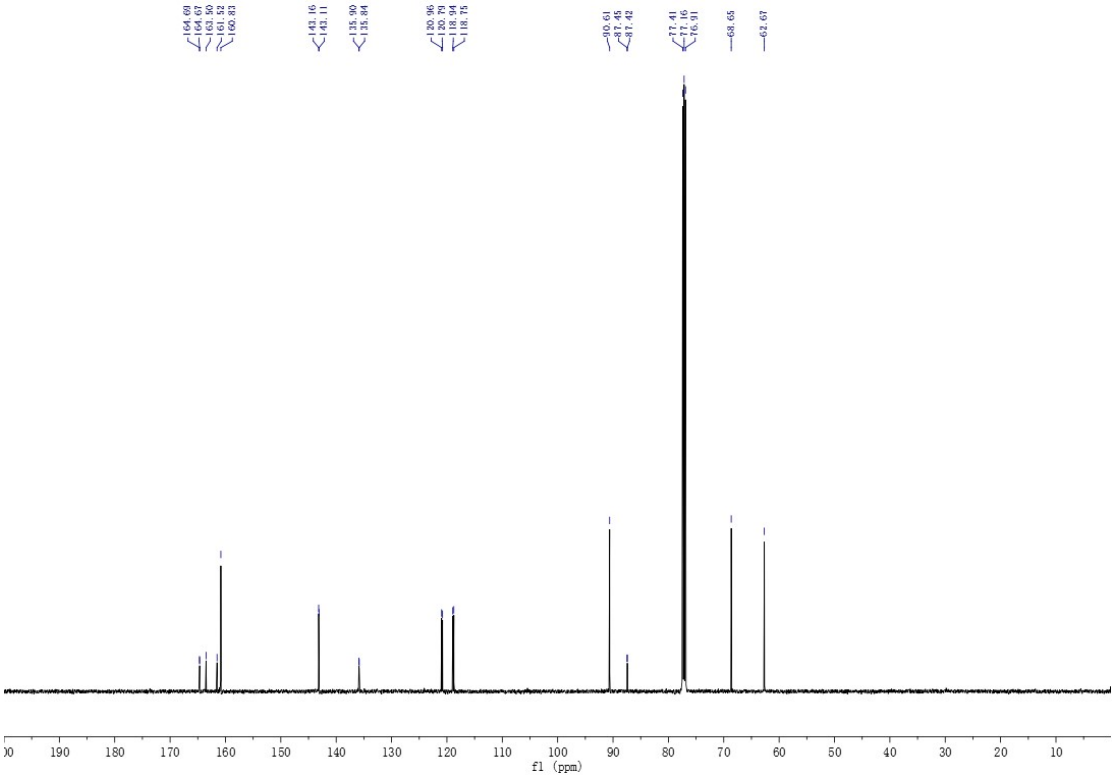


^{13}C NMR of compound **9'**

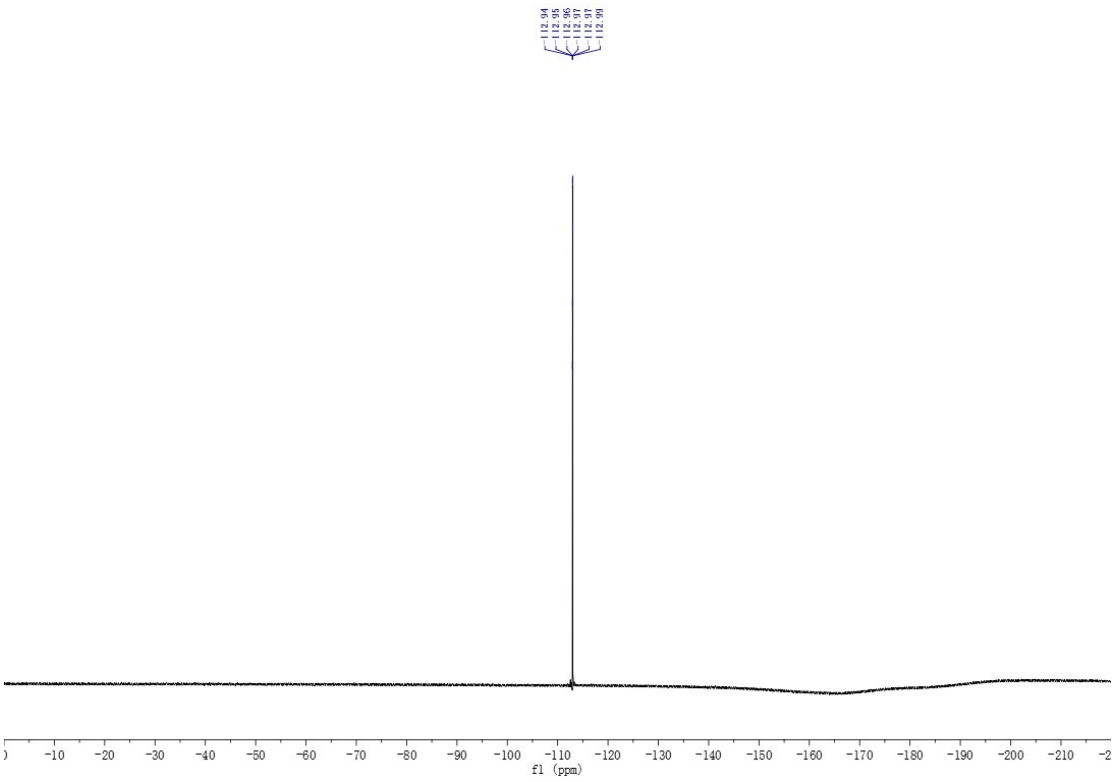




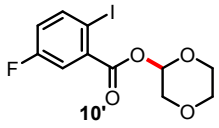
^{1}H NMR of compound **10**

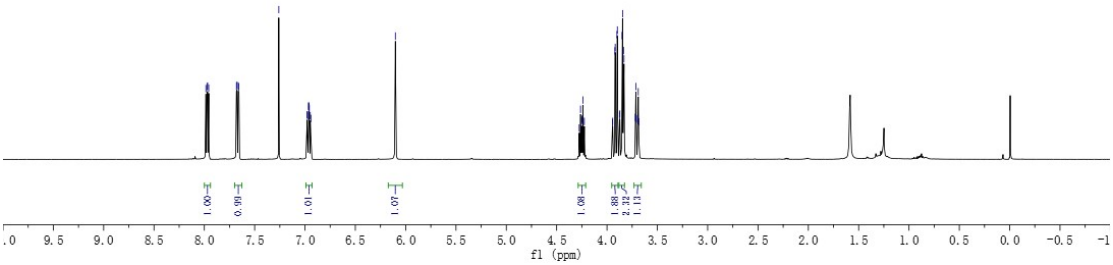


^{13}C NMR of compound **10**

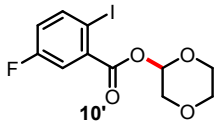


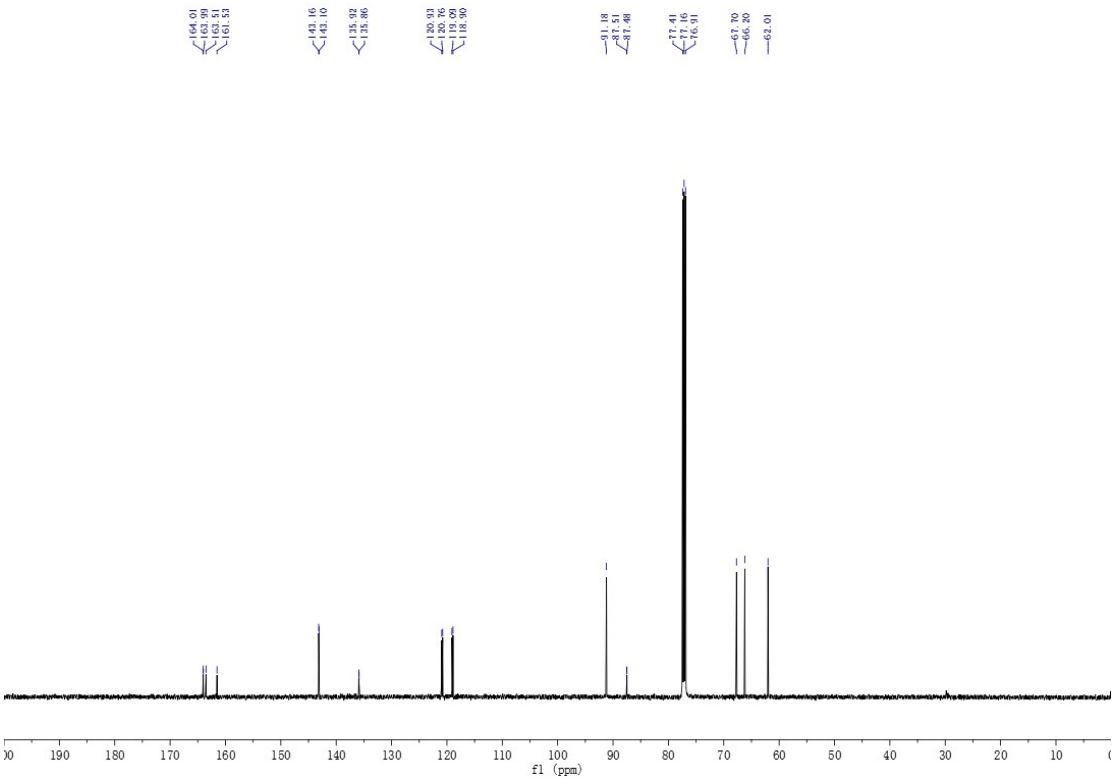
^{19}F NMR of compound **10**



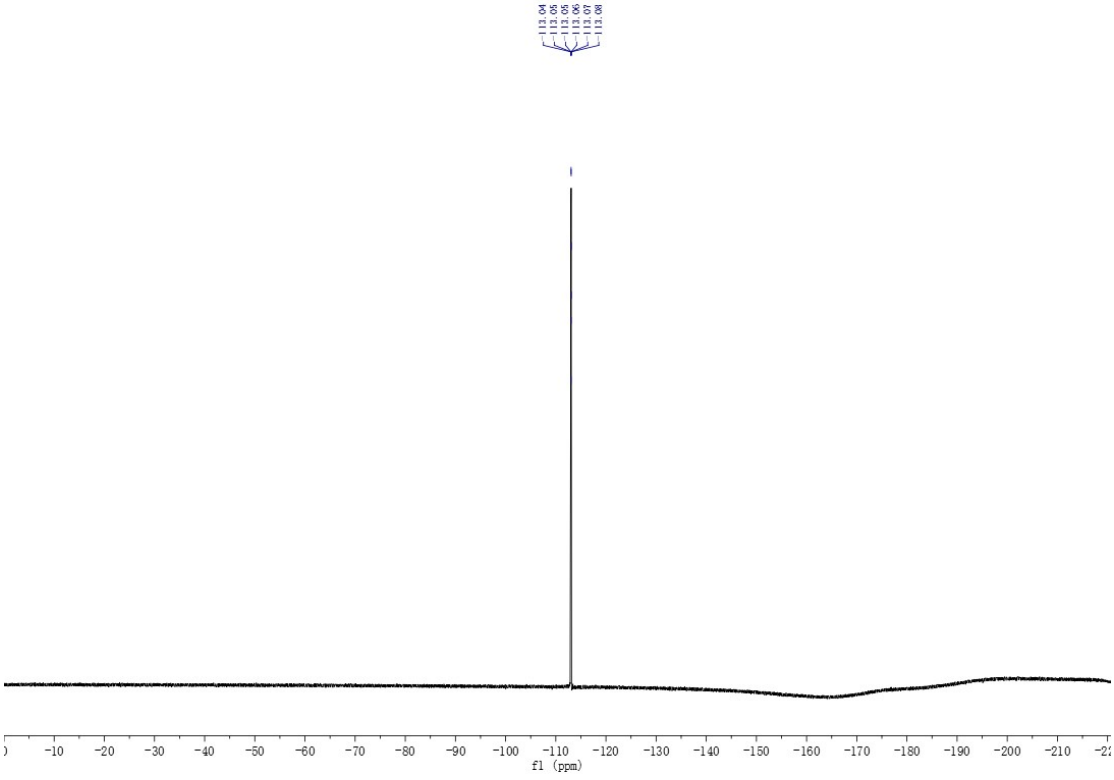


^{1}H NMR of compound **10'**

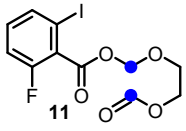




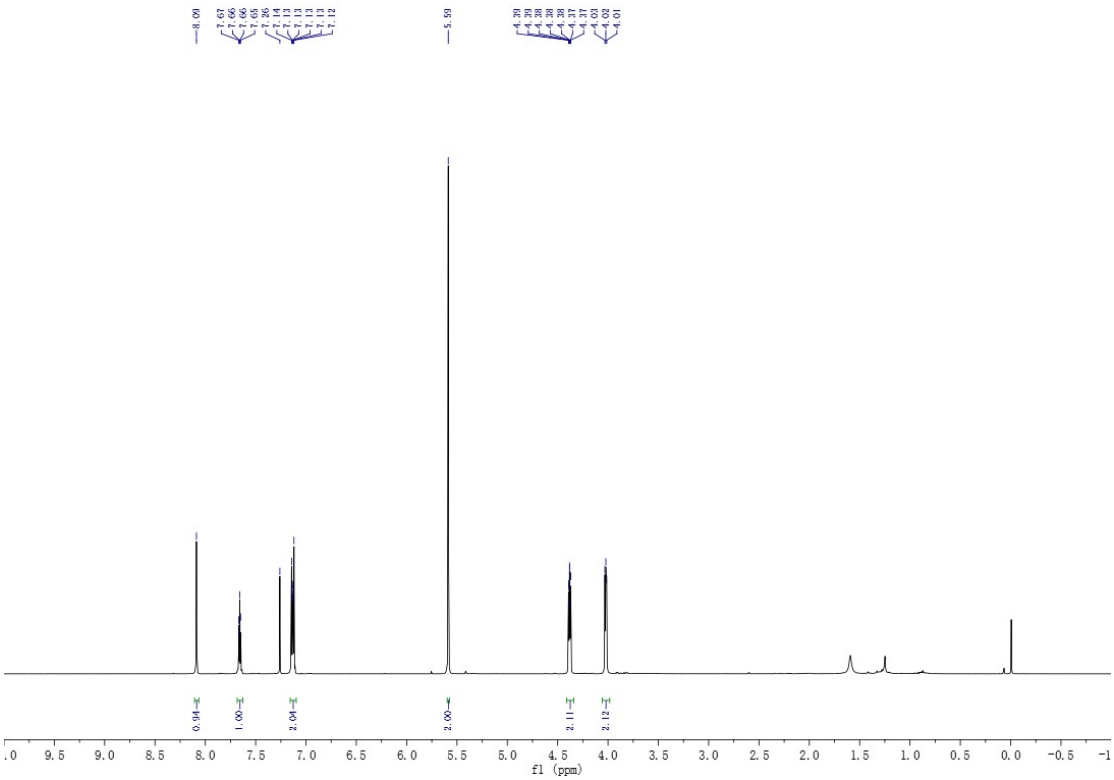
^{13}C NMR of compound **10'**



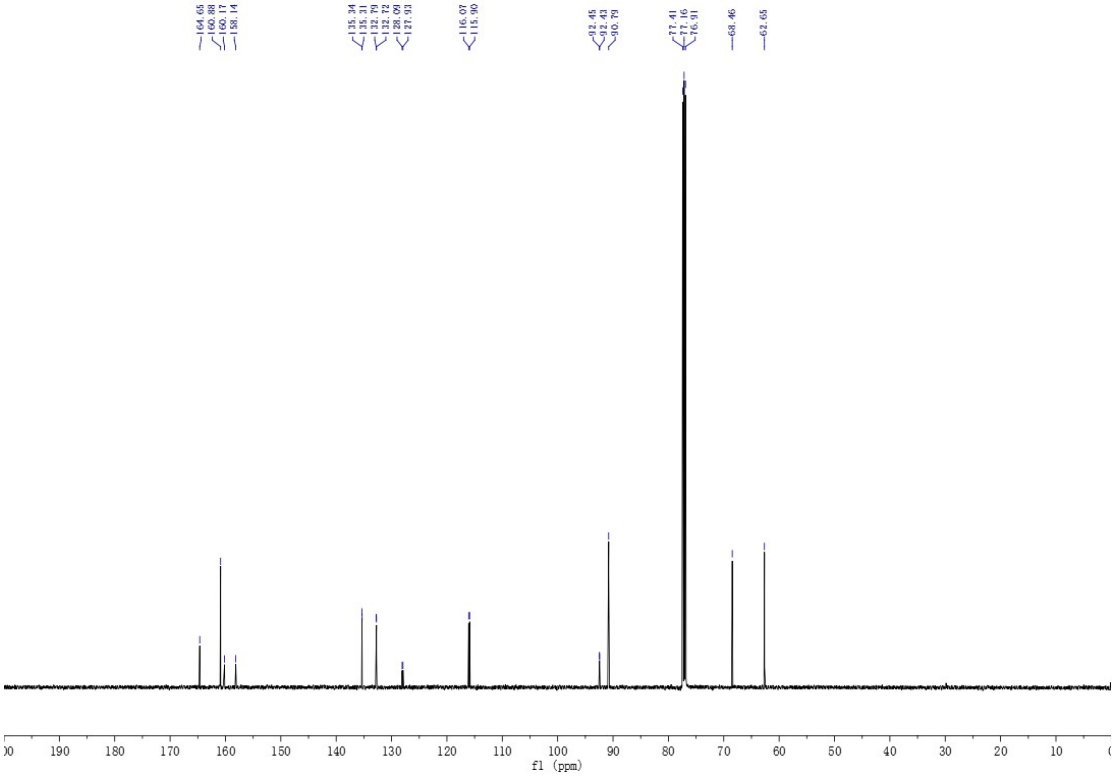
^{19}F NMR of compound **10'**



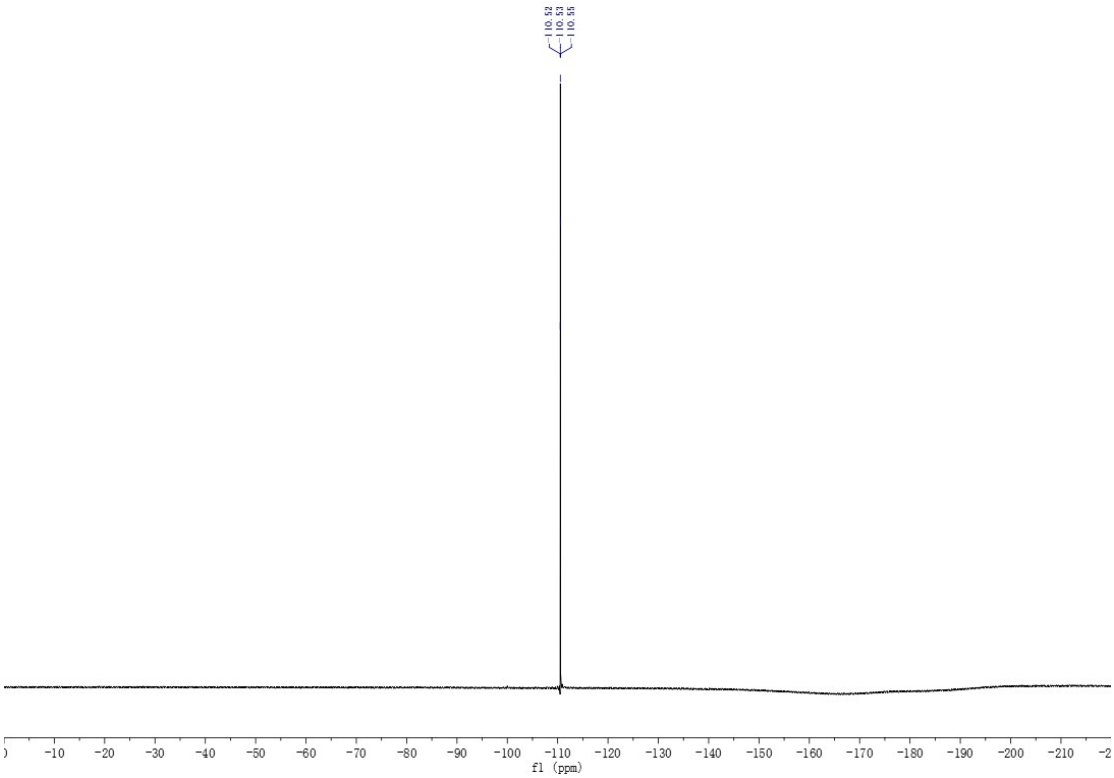
11



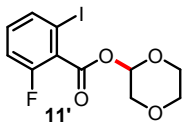
^{1}H NMR of compound **11**

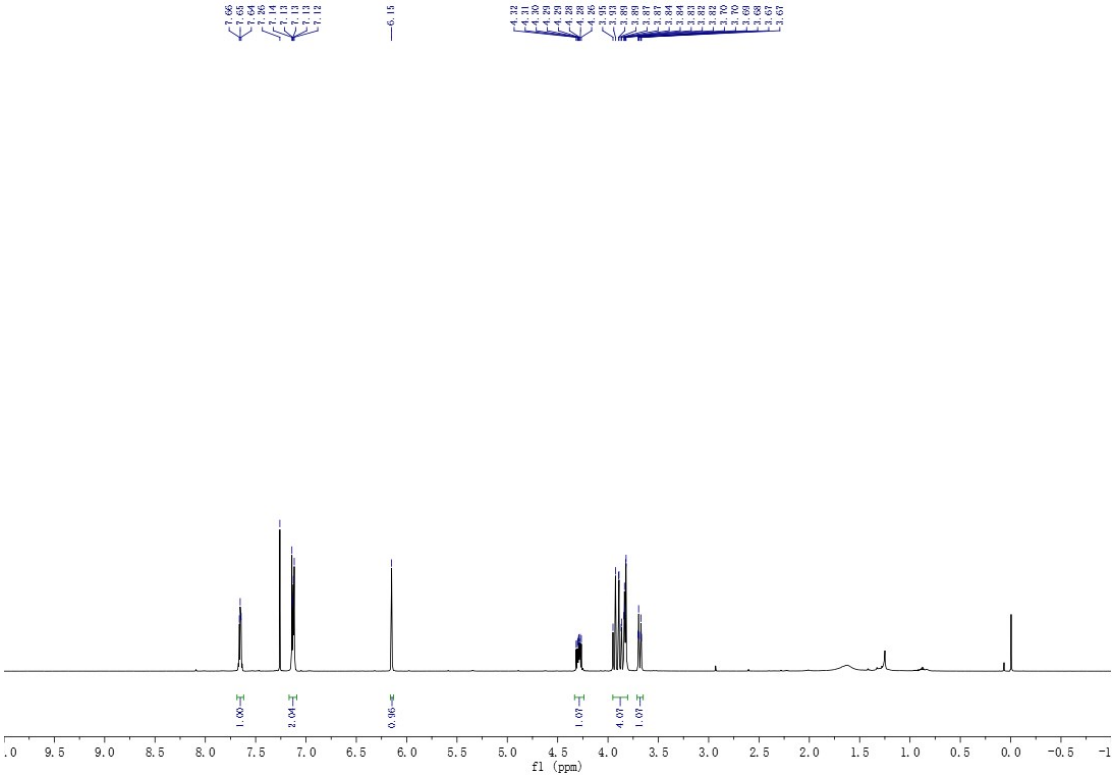


^{13}C NMR of compound **11**

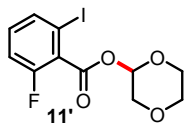


^{19}F NMR of compound **11**

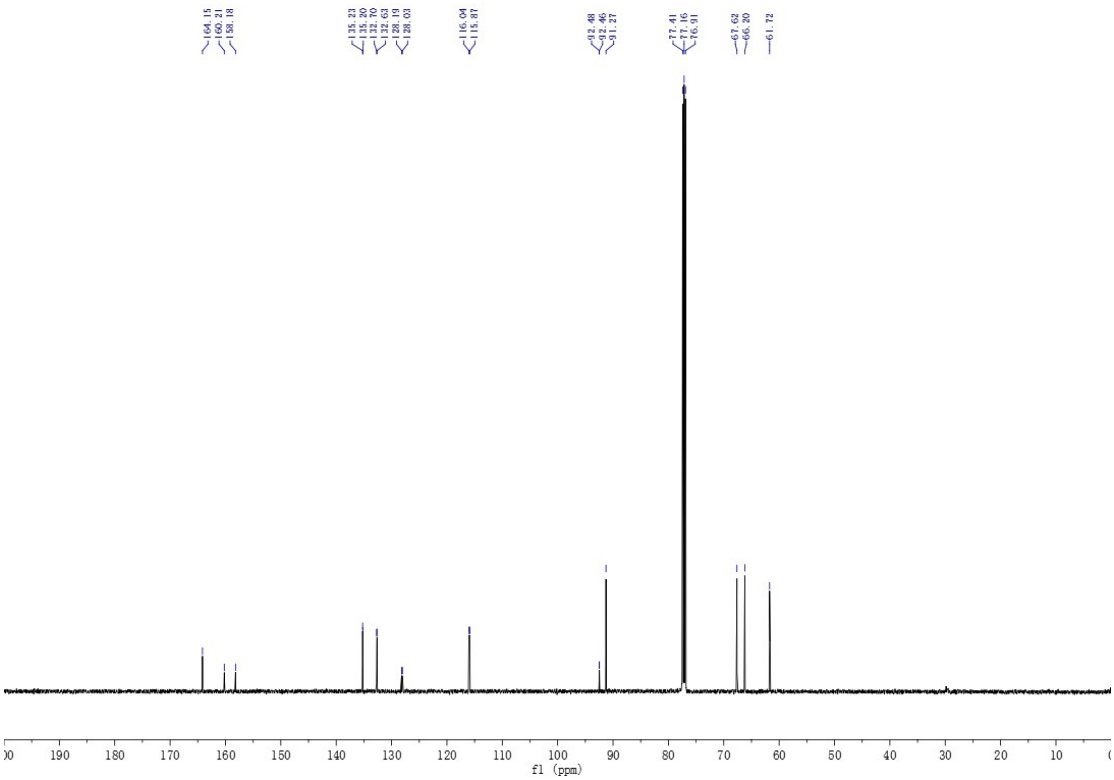




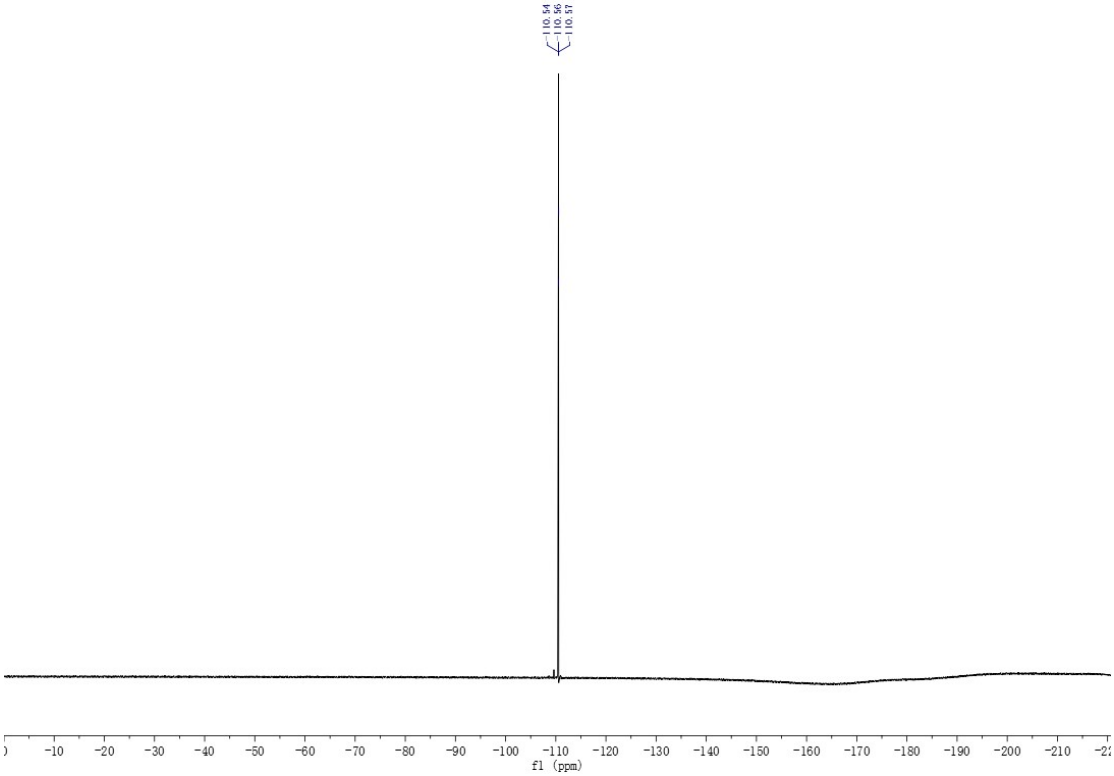
^{1}H NMR of compound **11'**



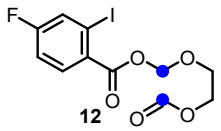
11'

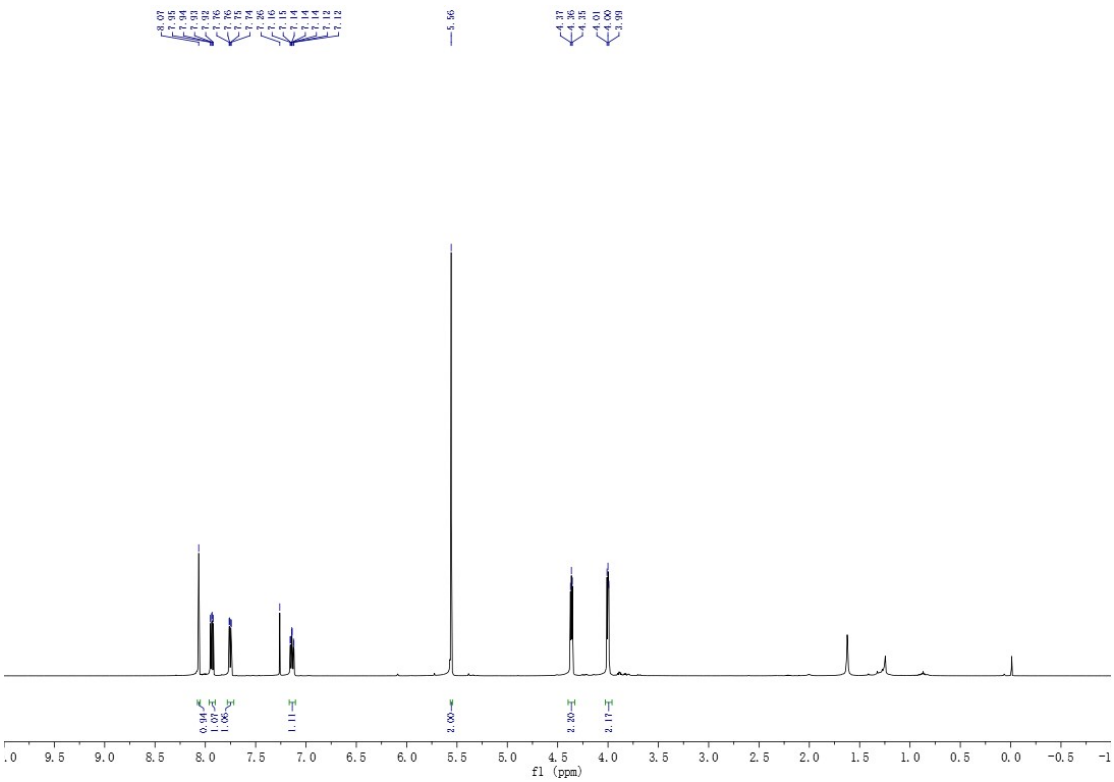


^{13}C NMR of compound **11'**

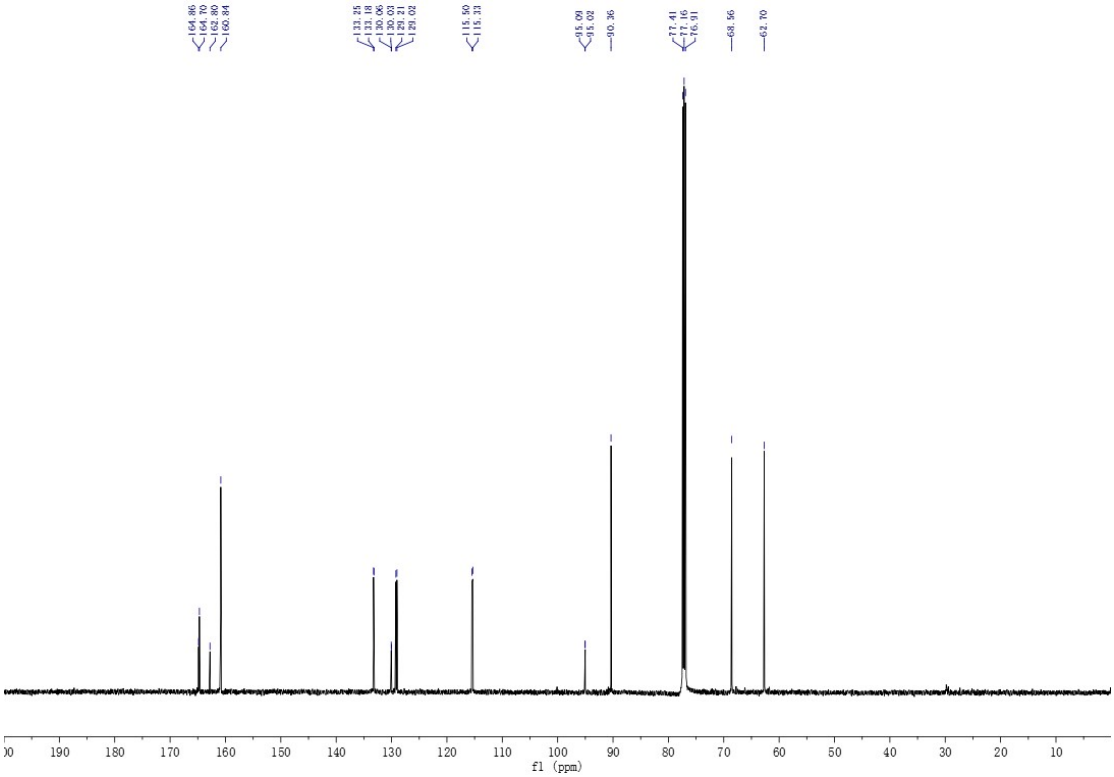


^{19}F NMR of compound **11'**

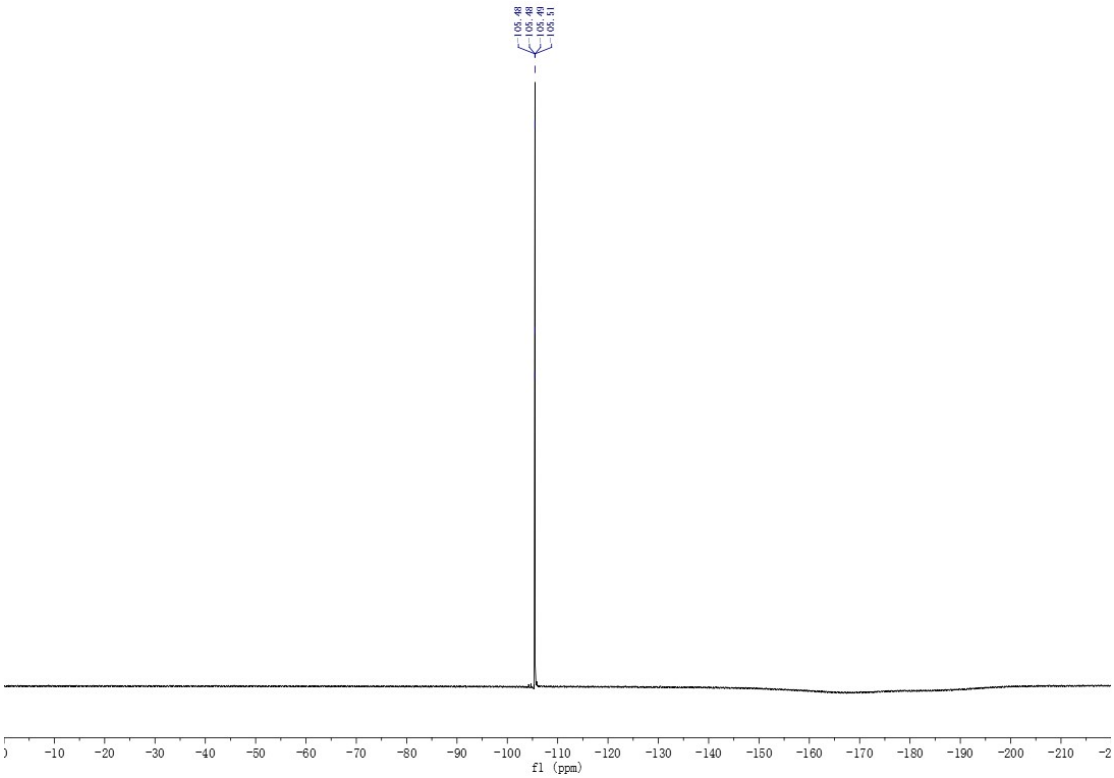




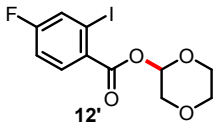
^{1}H NMR of compound **12**

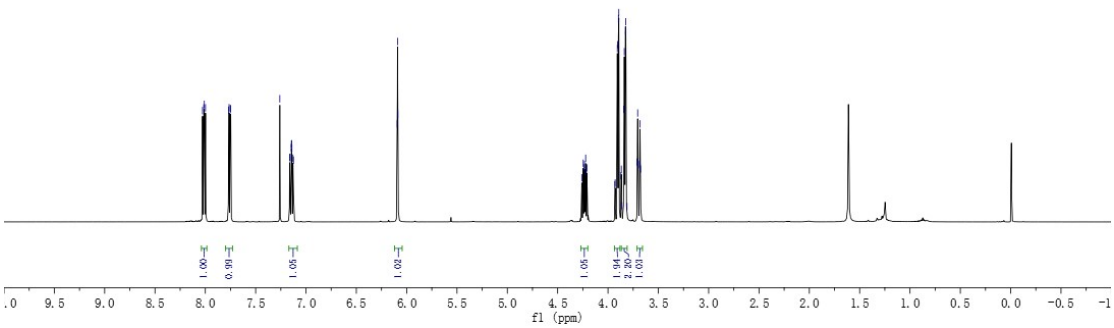


^{13}C NMR of compound **12**

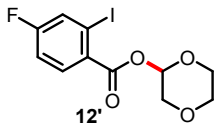


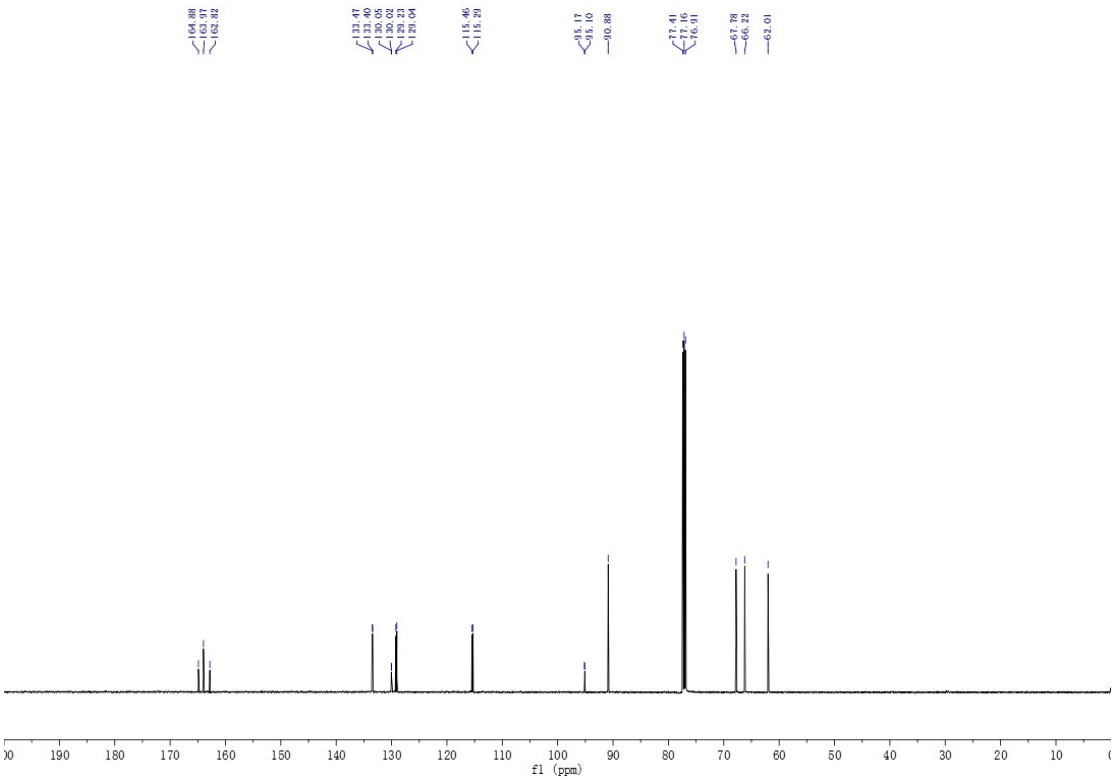
^{19}F NMR of compound **12**



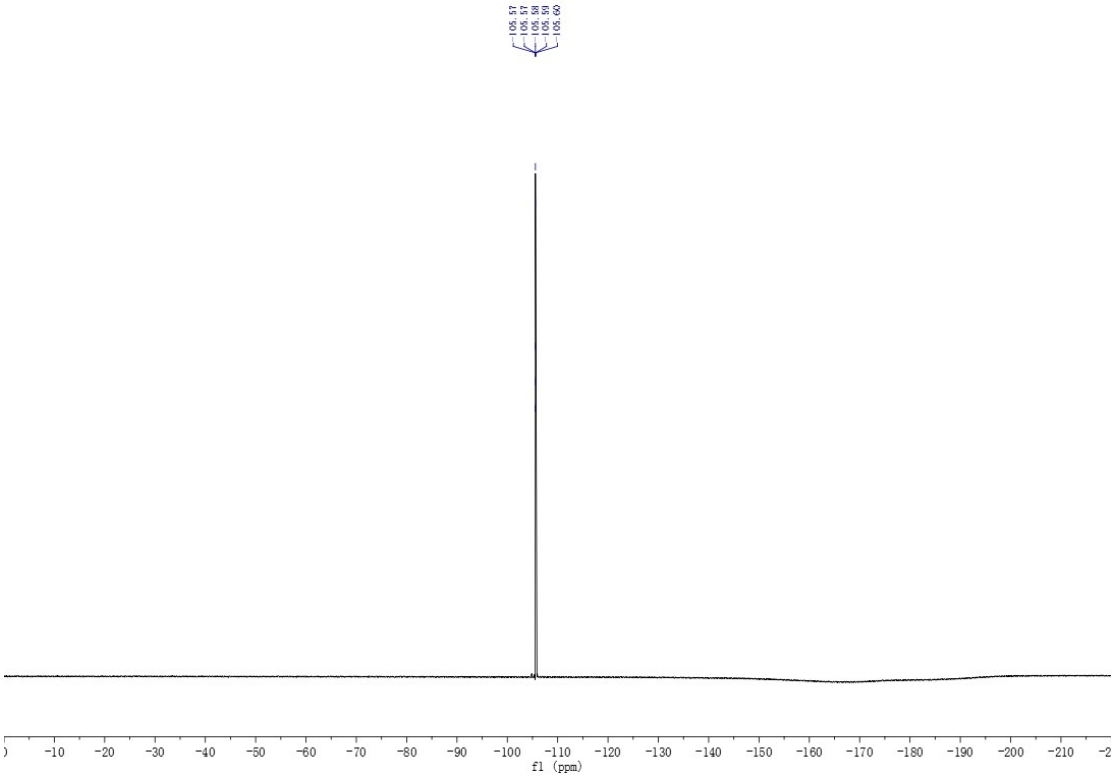


^{1}H NMR of compound **12'**

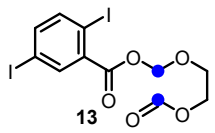


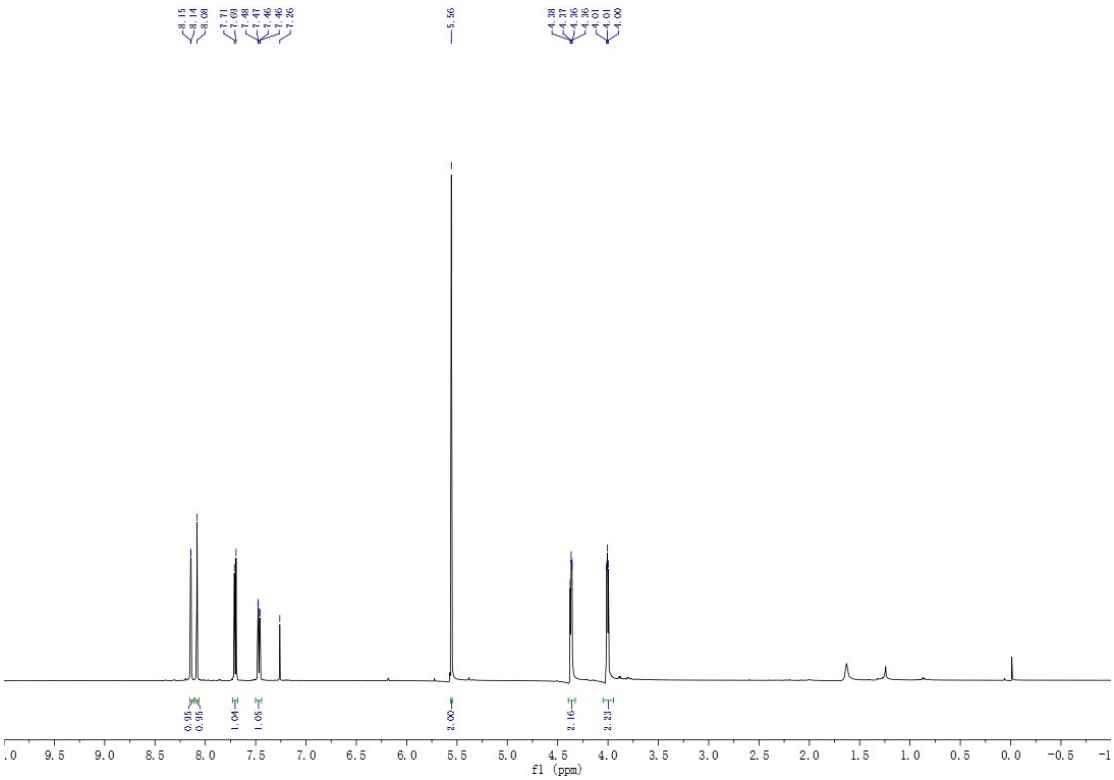


^{13}C NMR of compound **12'**

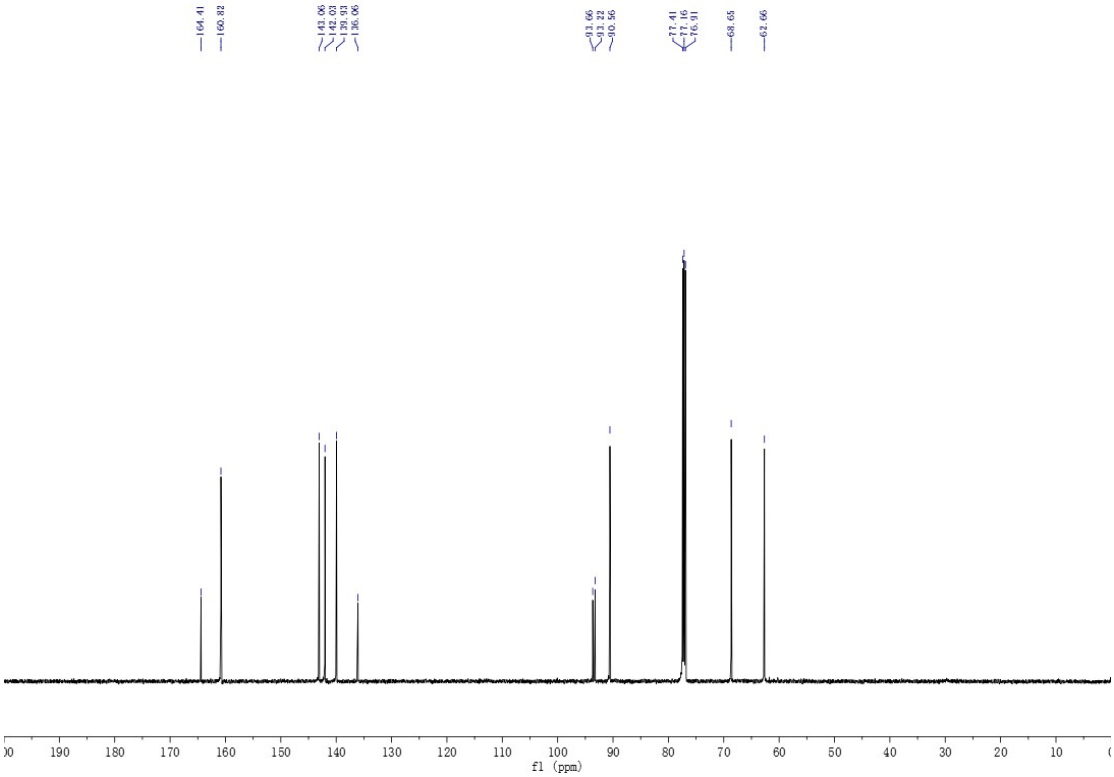


^{19}F NMR of compound **12'**

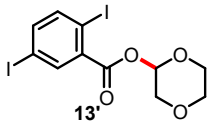


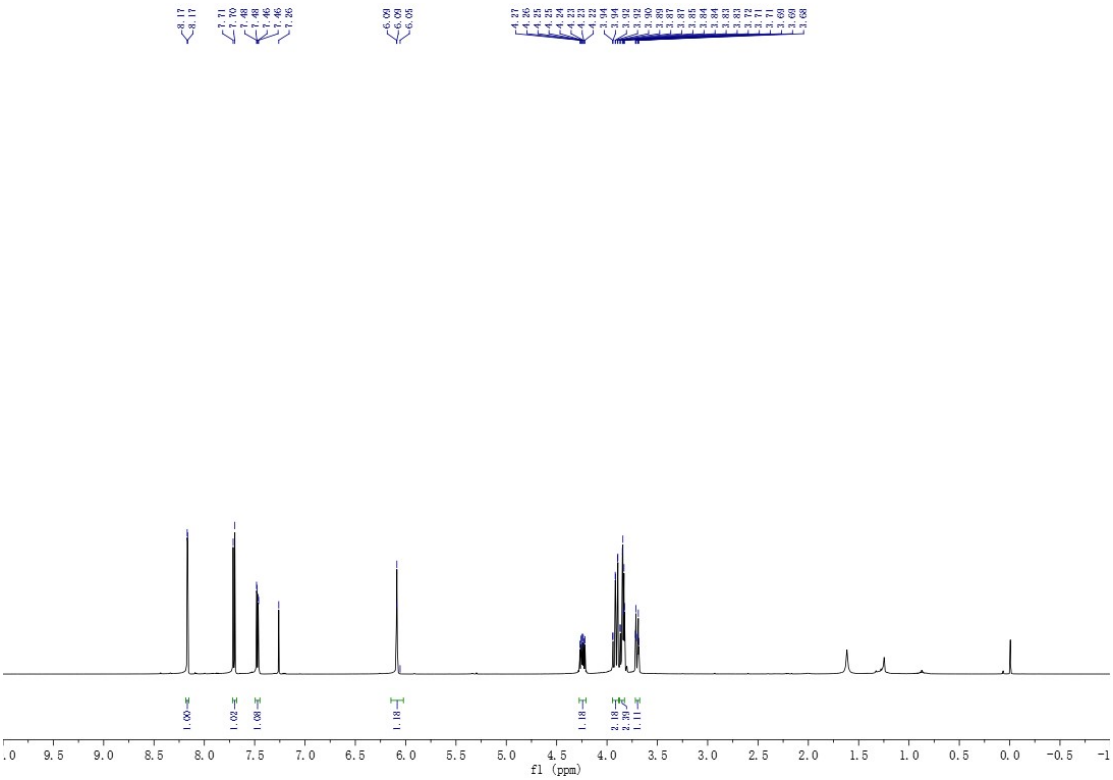


^{1}H NMR of compound **13**

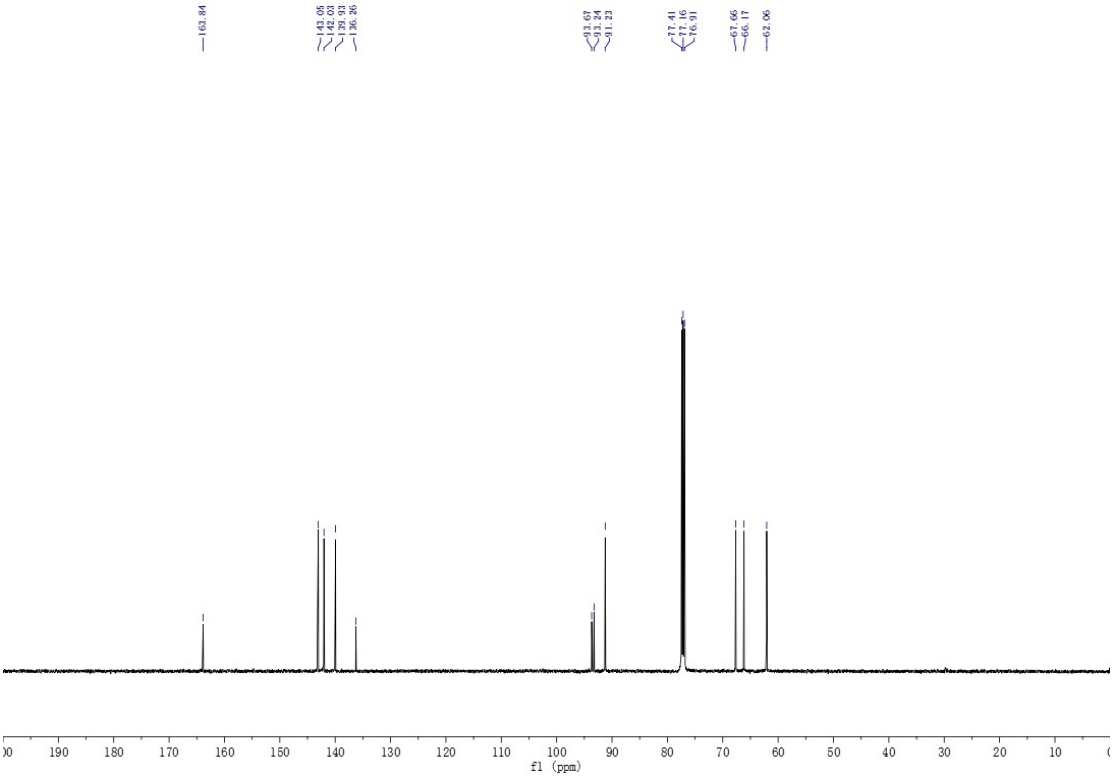


^{13}C NMR of compound **13**

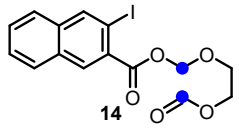


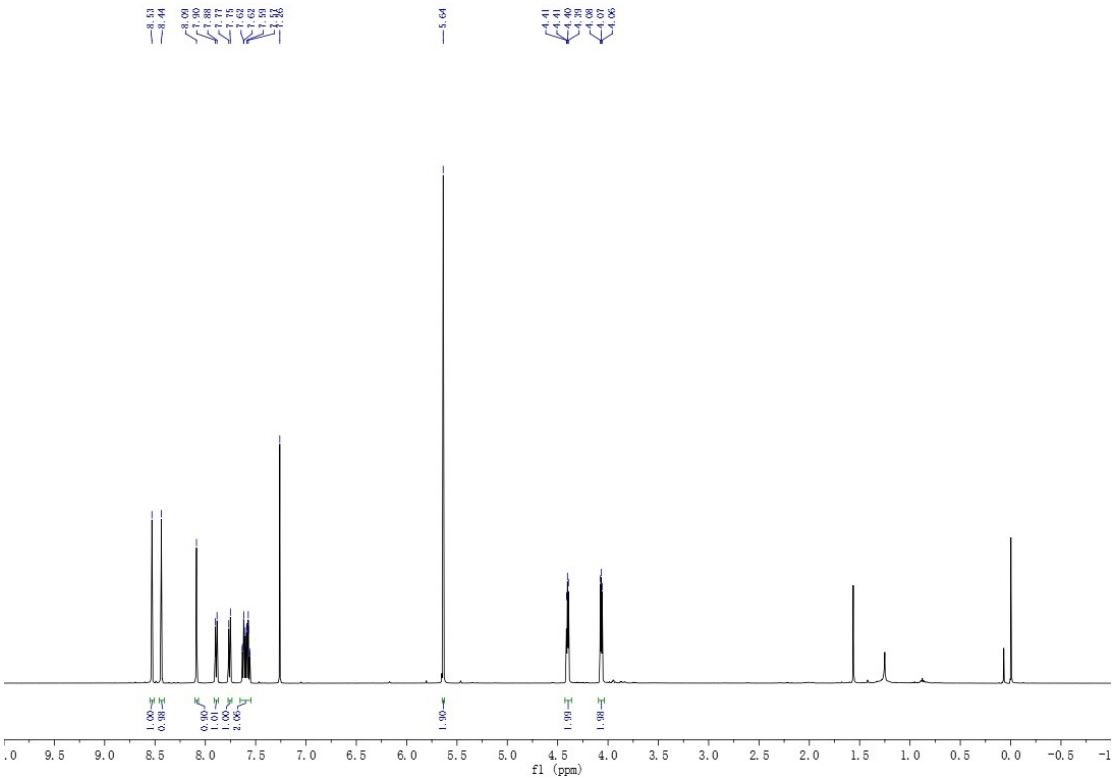


^{1}H NMR of compound **13'**

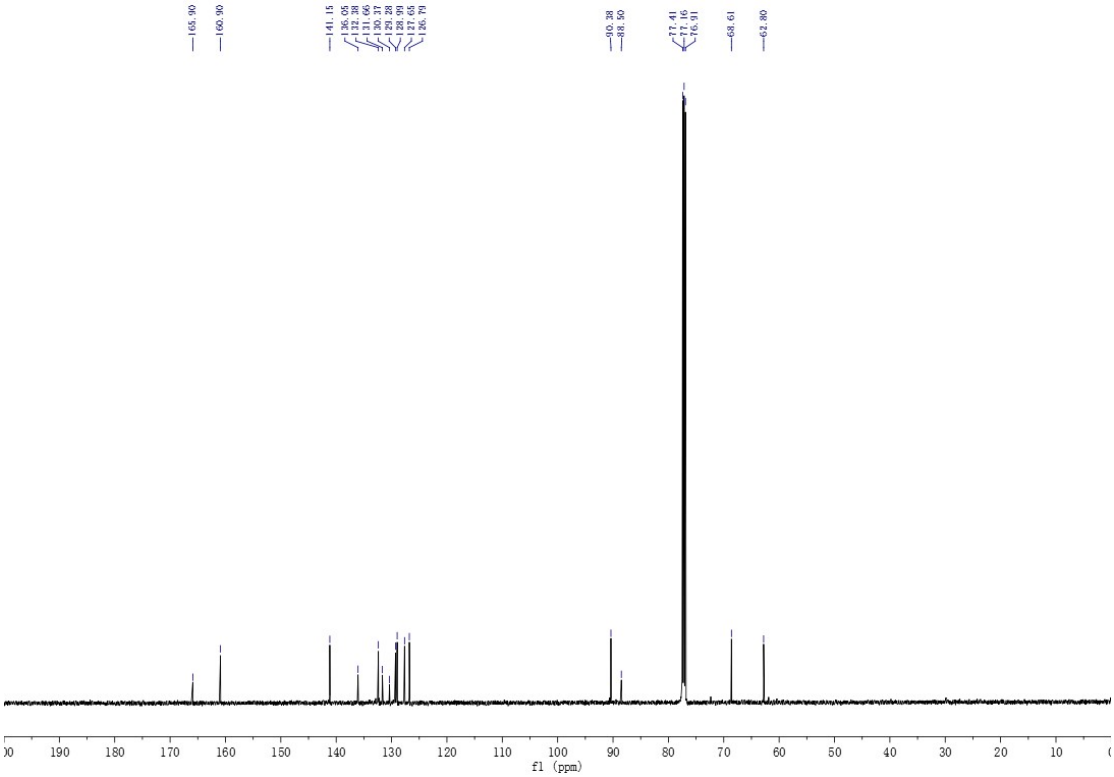


^{13}C NMR of compound **13'**

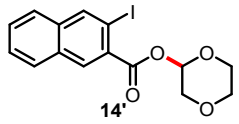


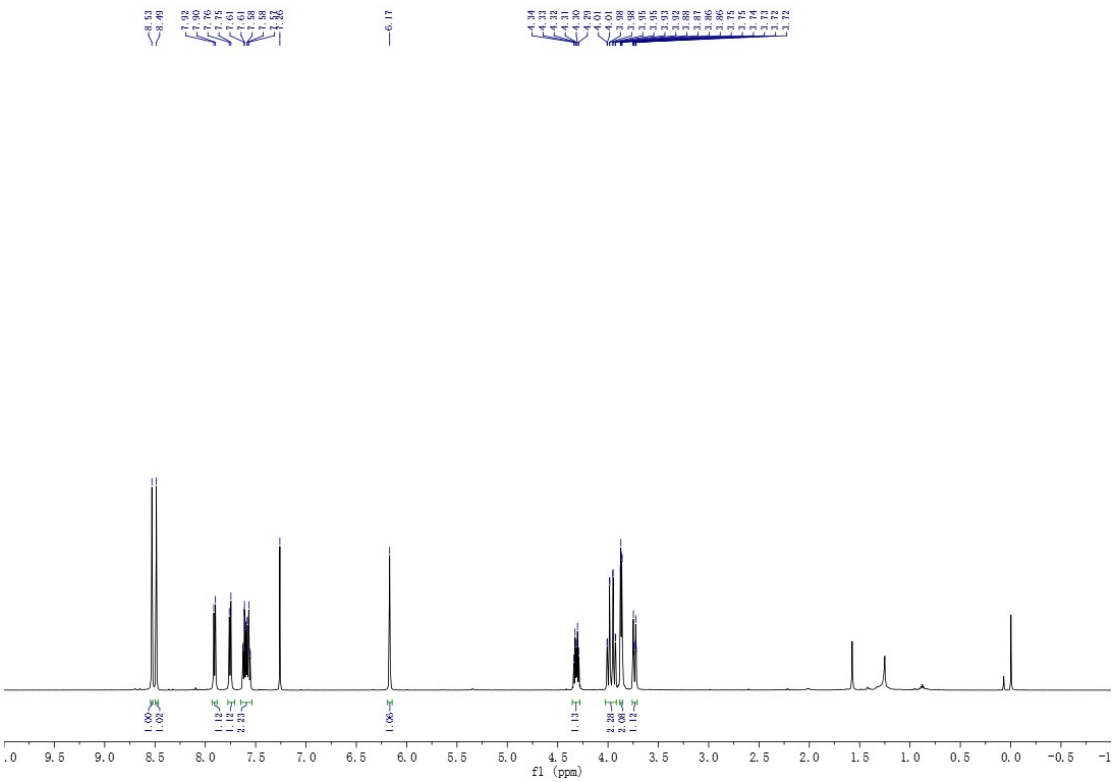


^{1}H NMR of compound **14**

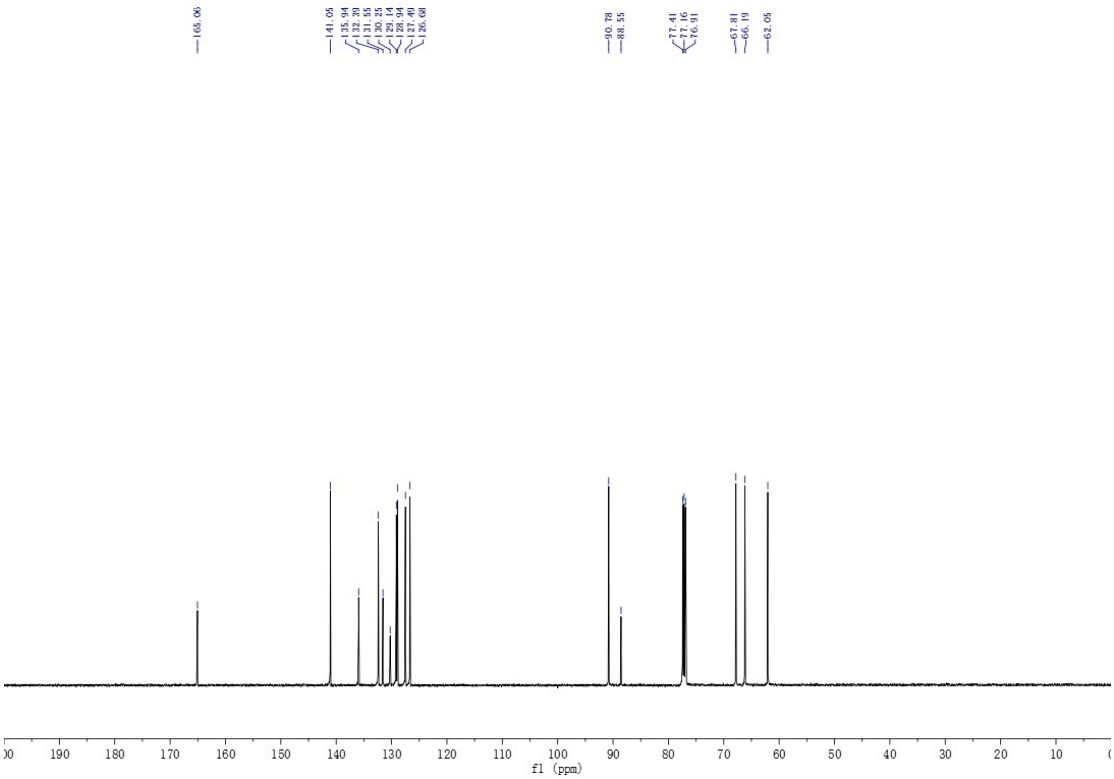


^{13}C NMR of compound **14**

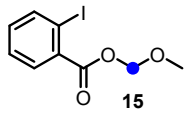


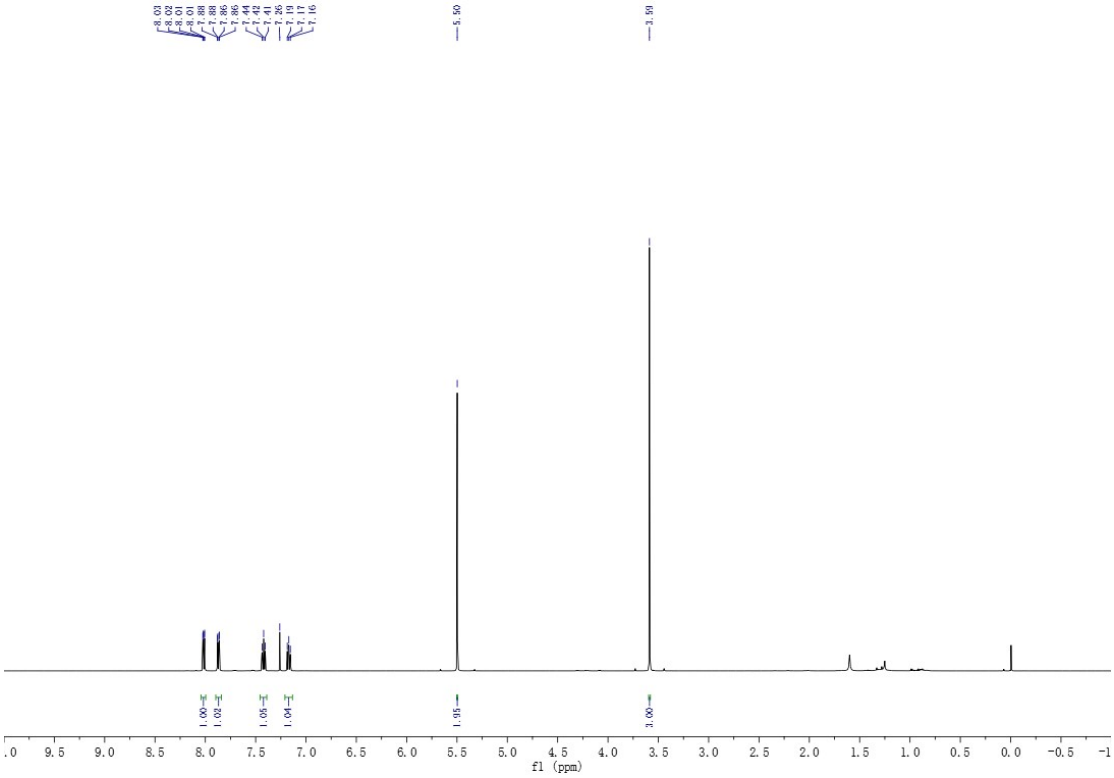


^{1}H NMR of compound **14'**

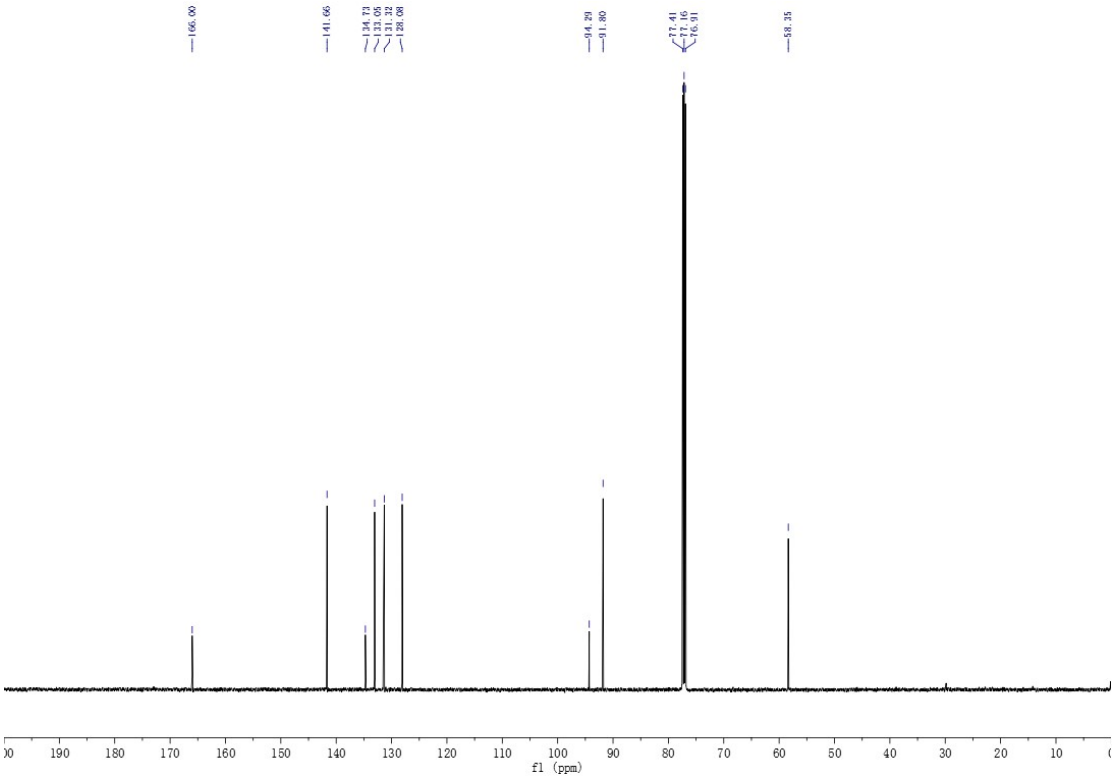


^{13}C NMR of compound **14'**

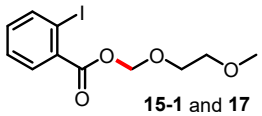




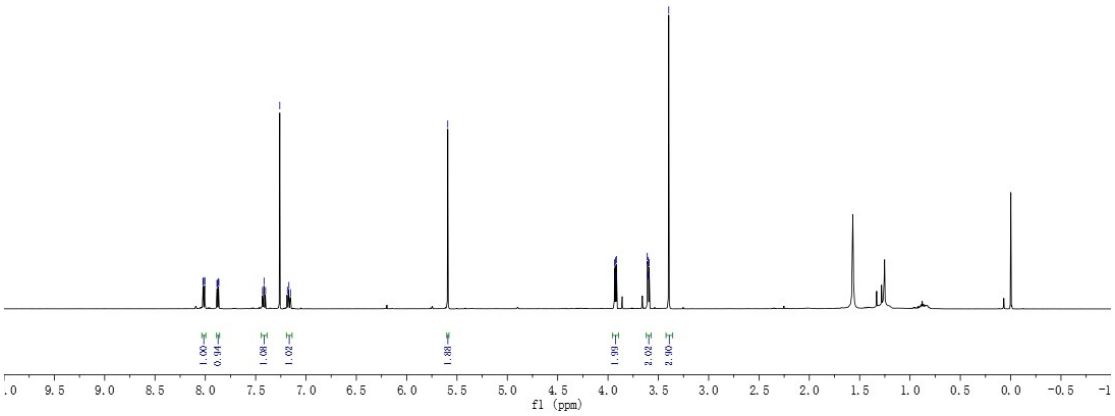
^{1}H NMR of compound **15**



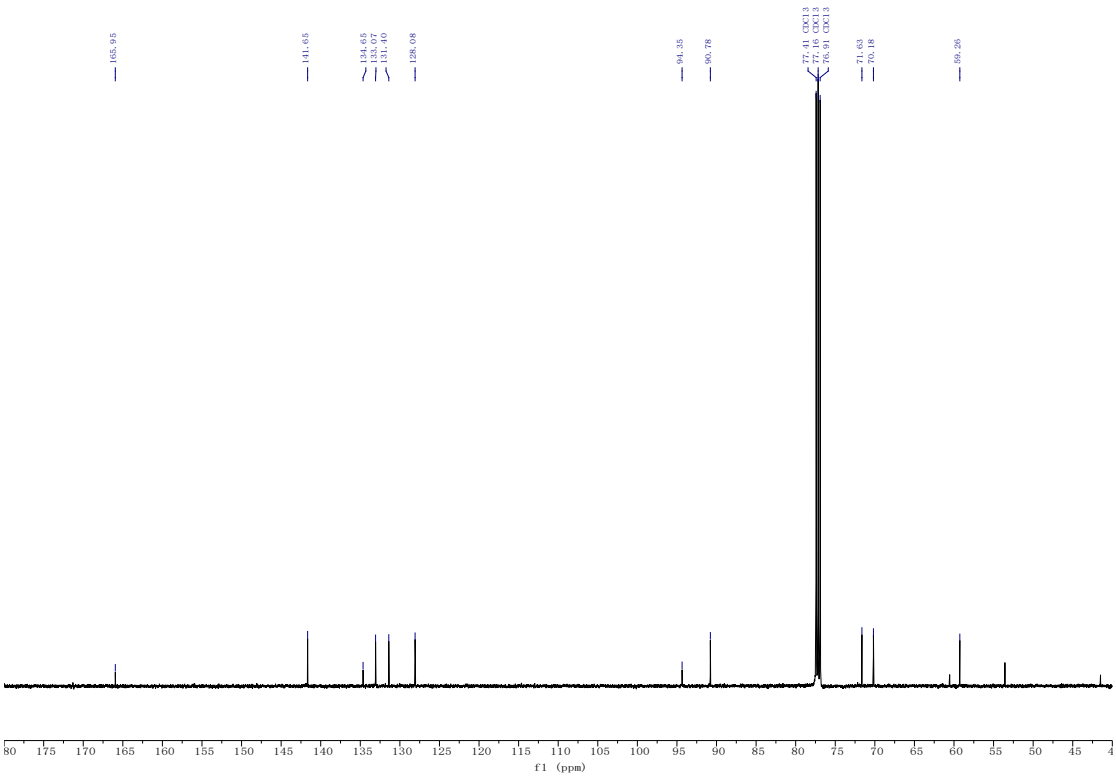
^{13}C NMR of compound **15**



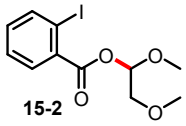
15-1 and **17**



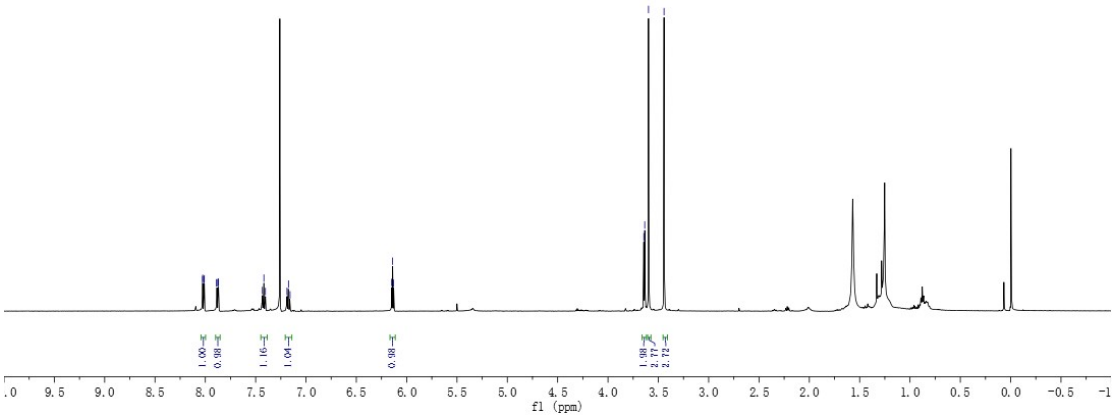
^{1}H NMR of compound **15-1**



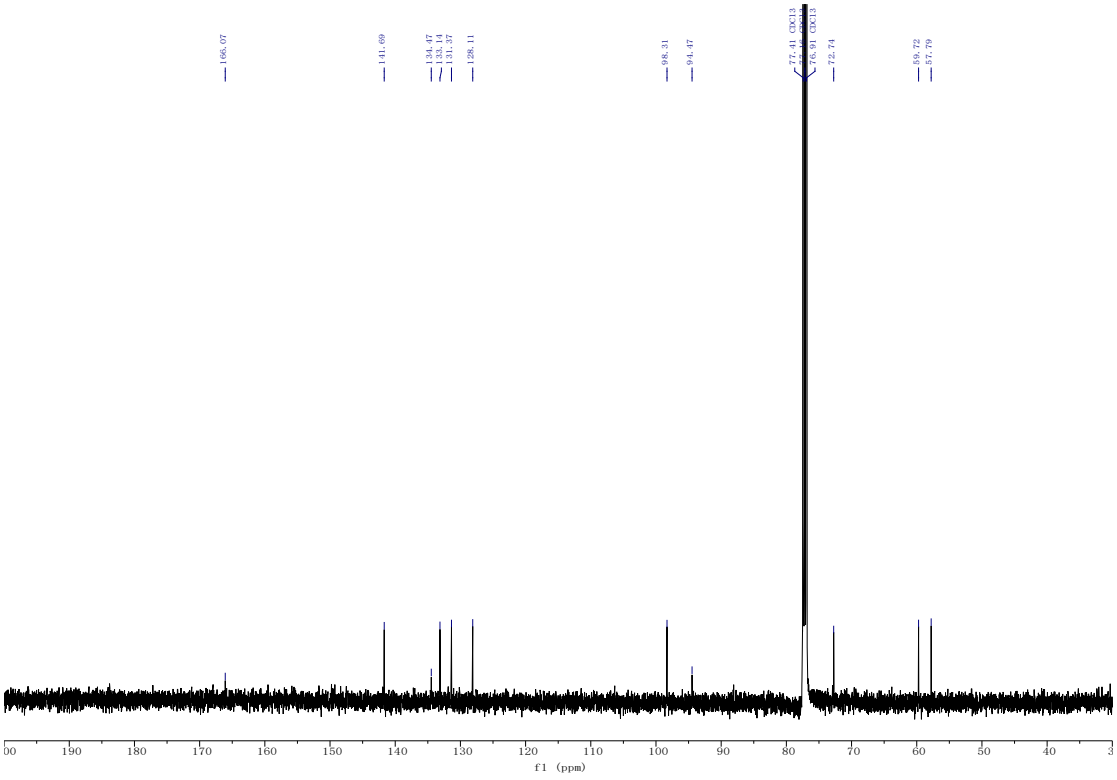
^{13}C NMR of compound **15-1**



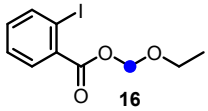
15-2

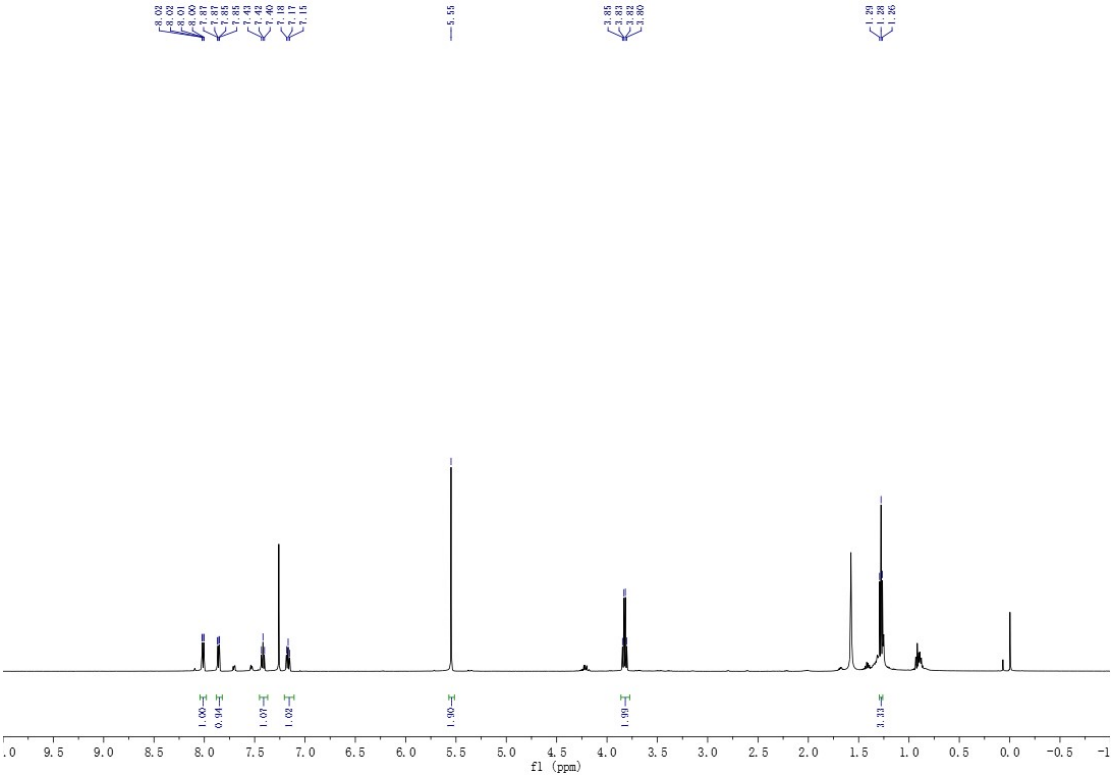


^{1}H NMR of compound **15-2**

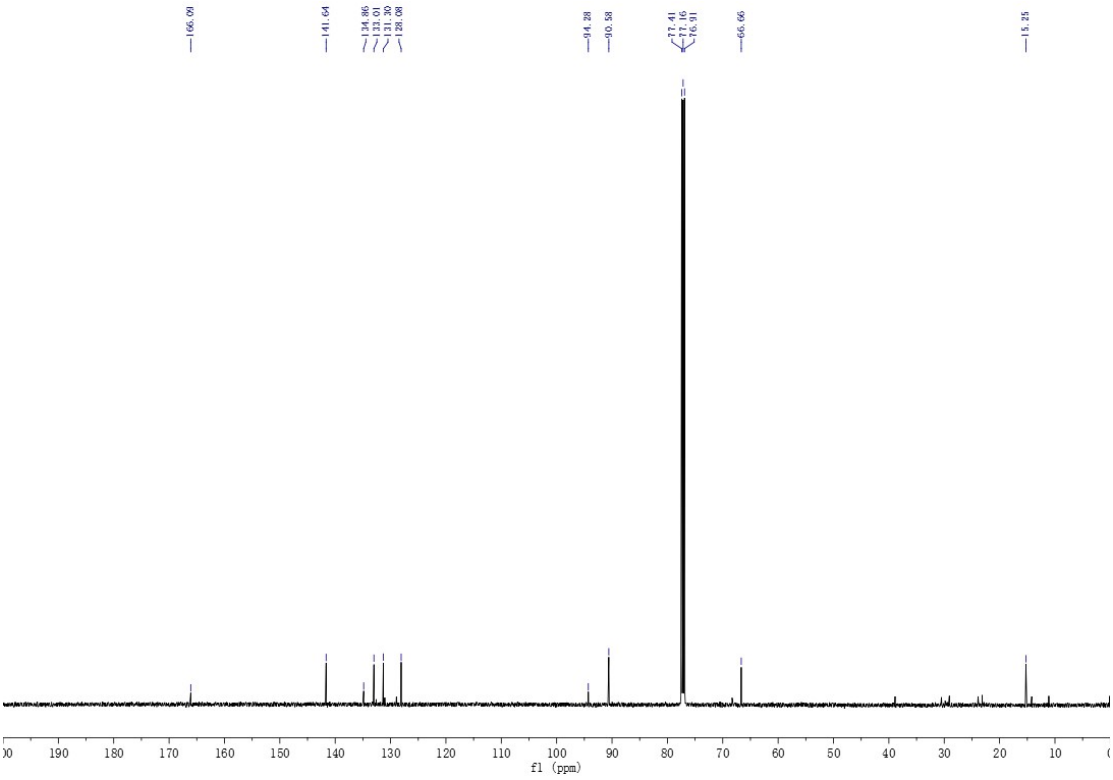


^{13}C NMR of compound **15-2**

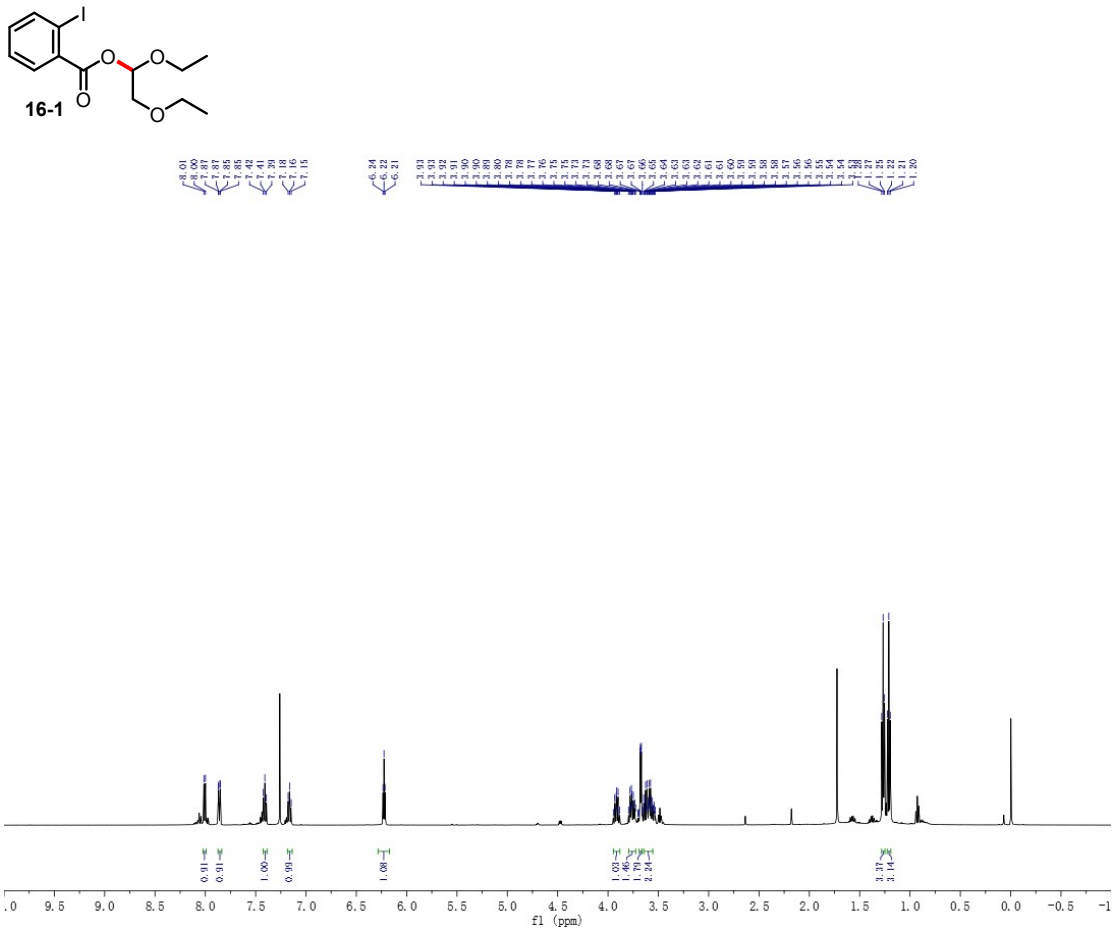




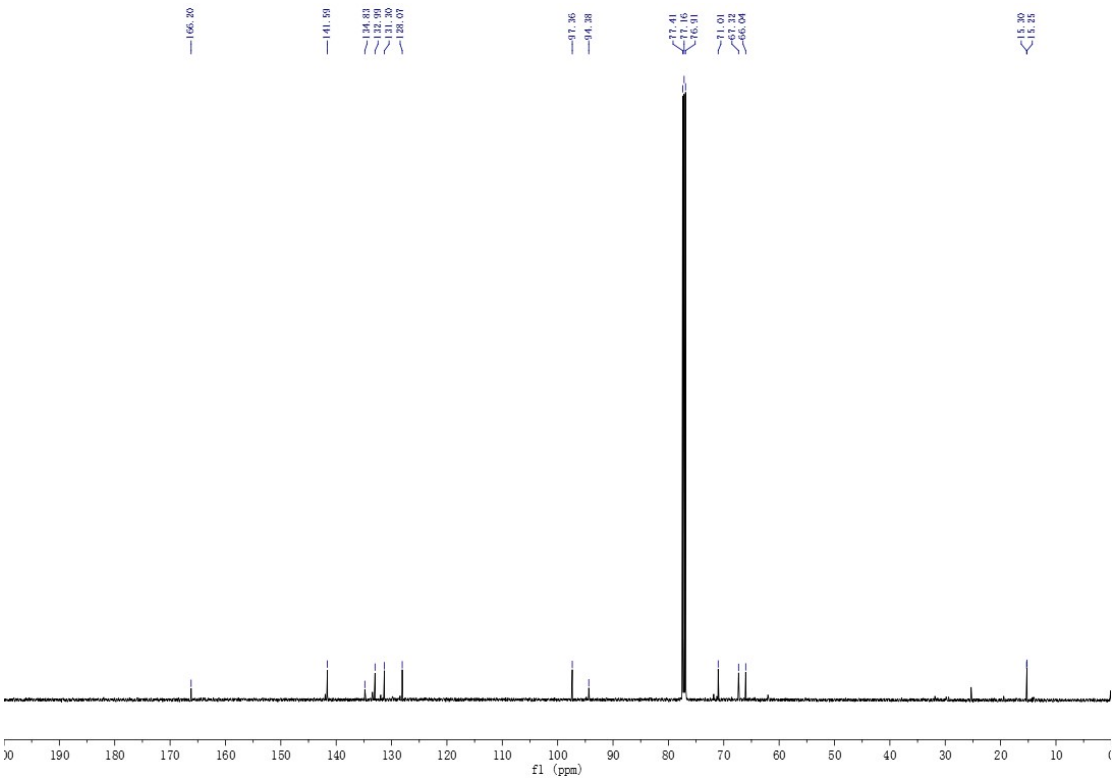
^{1}H NMR of compound **16**



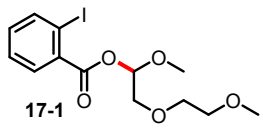
^{13}C NMR of compound **16**

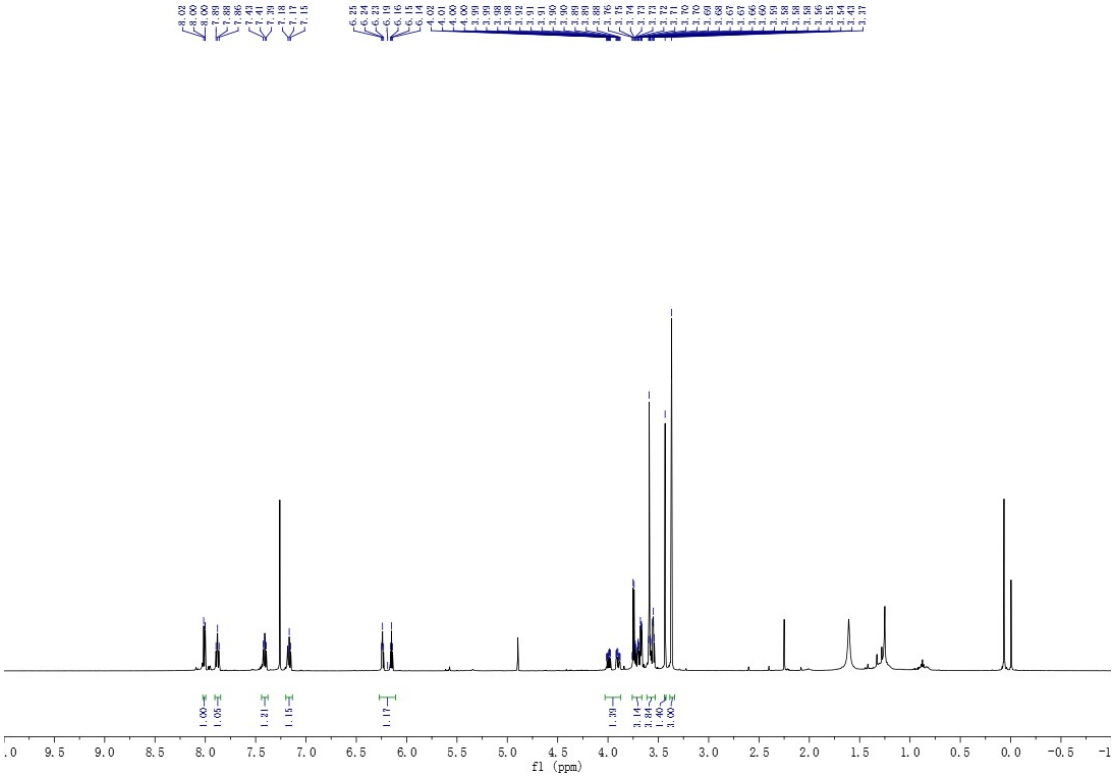


^{1}H NMR of compound **16-1**

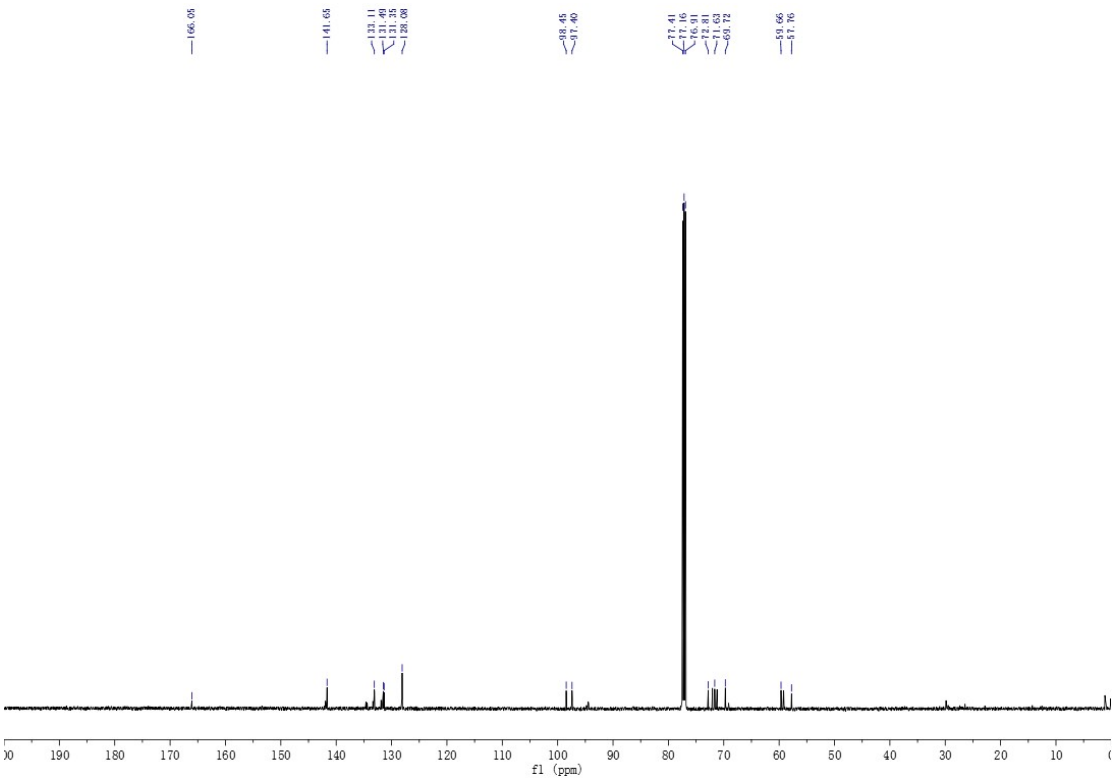


^{13}C NMR of compound **16-1**

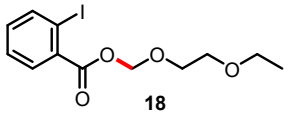




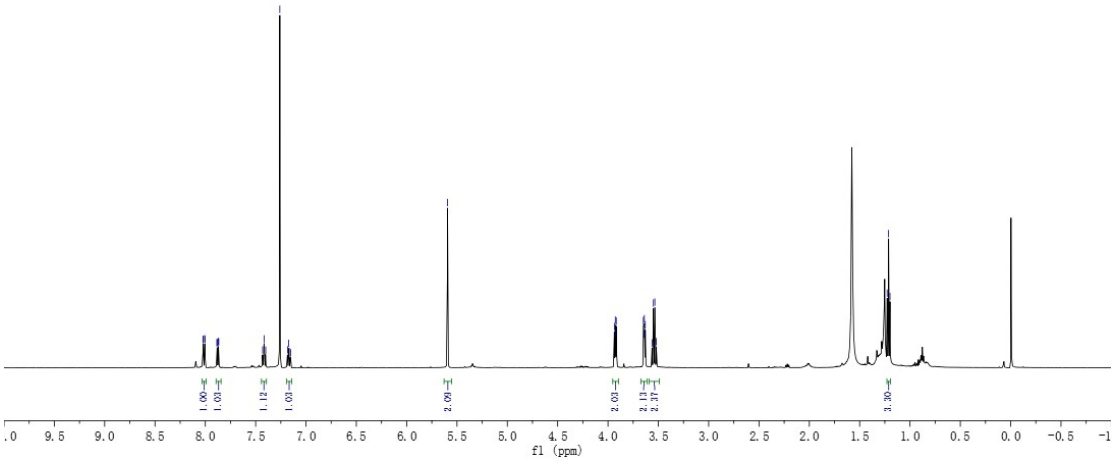
^{1}H NMR of compound **17-1**



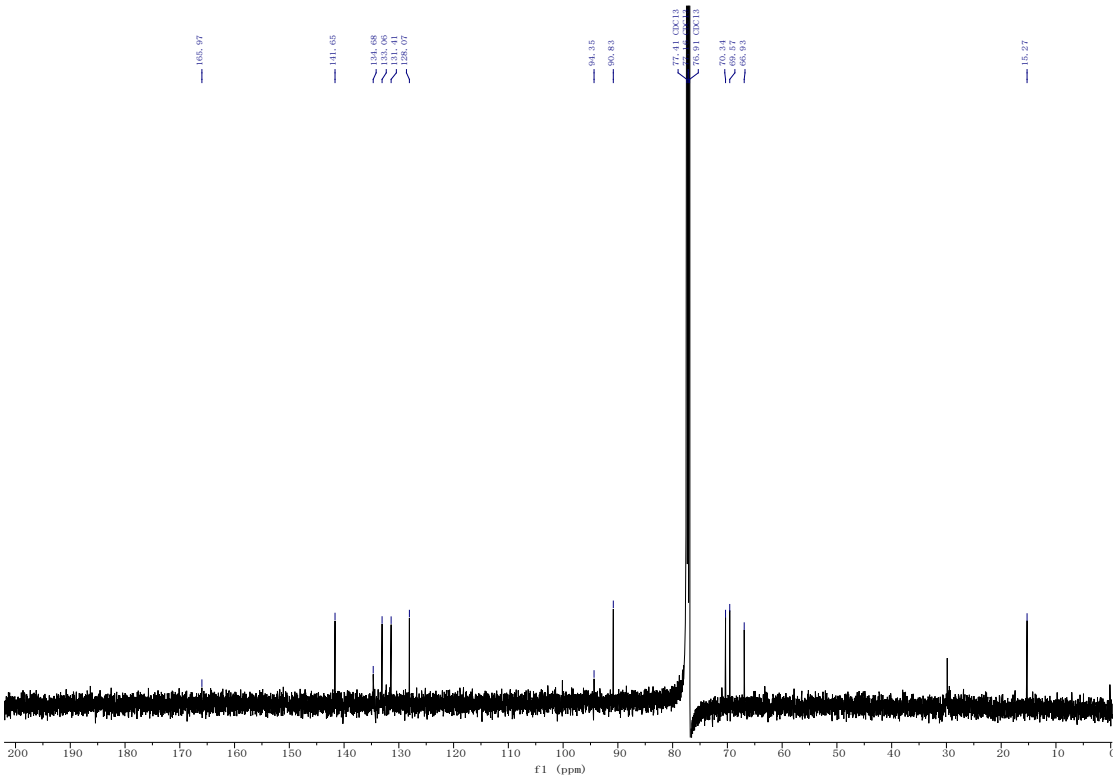
^{13}C NMR of compound **17-1**



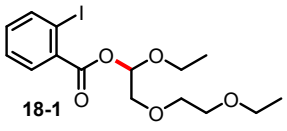
18



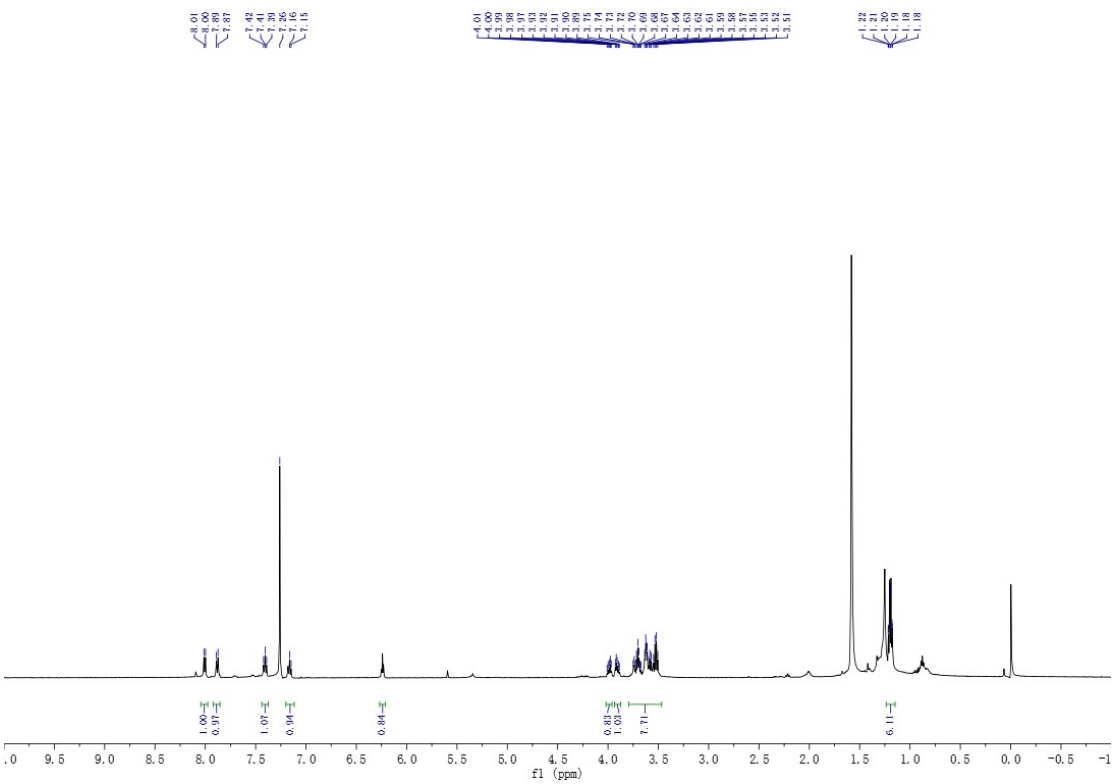
^{1}H NMR of compound **18**



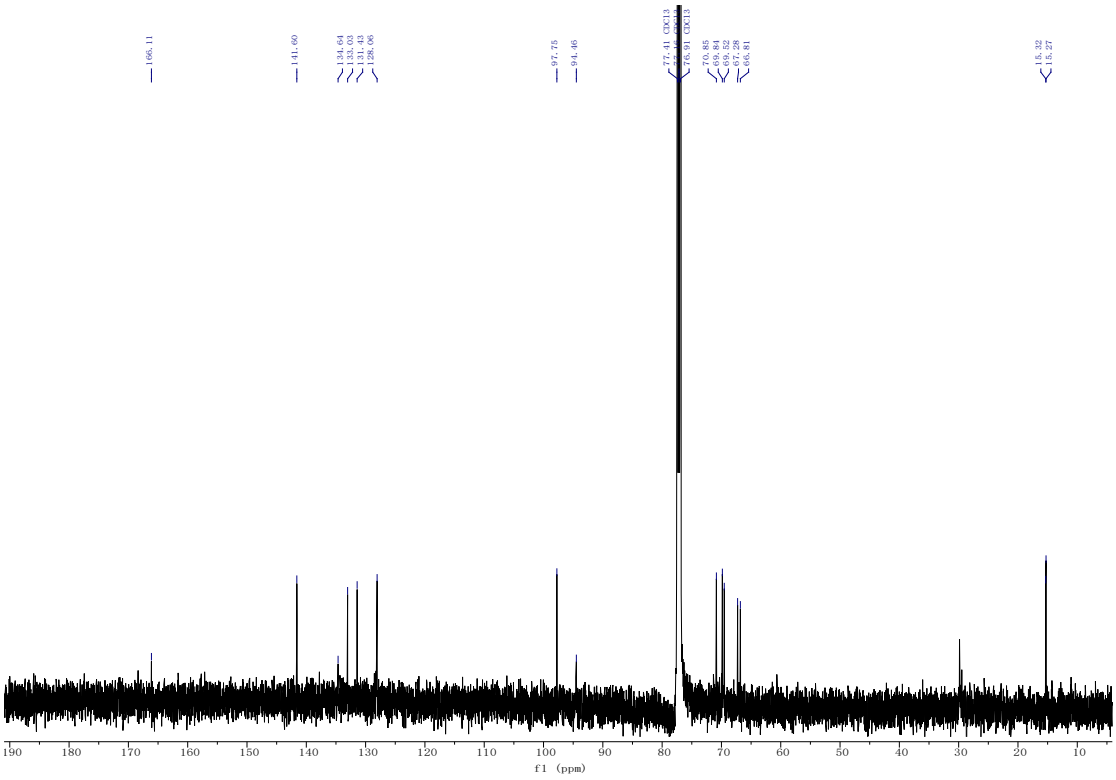
^{13}C NMR of compound **18**



18-1

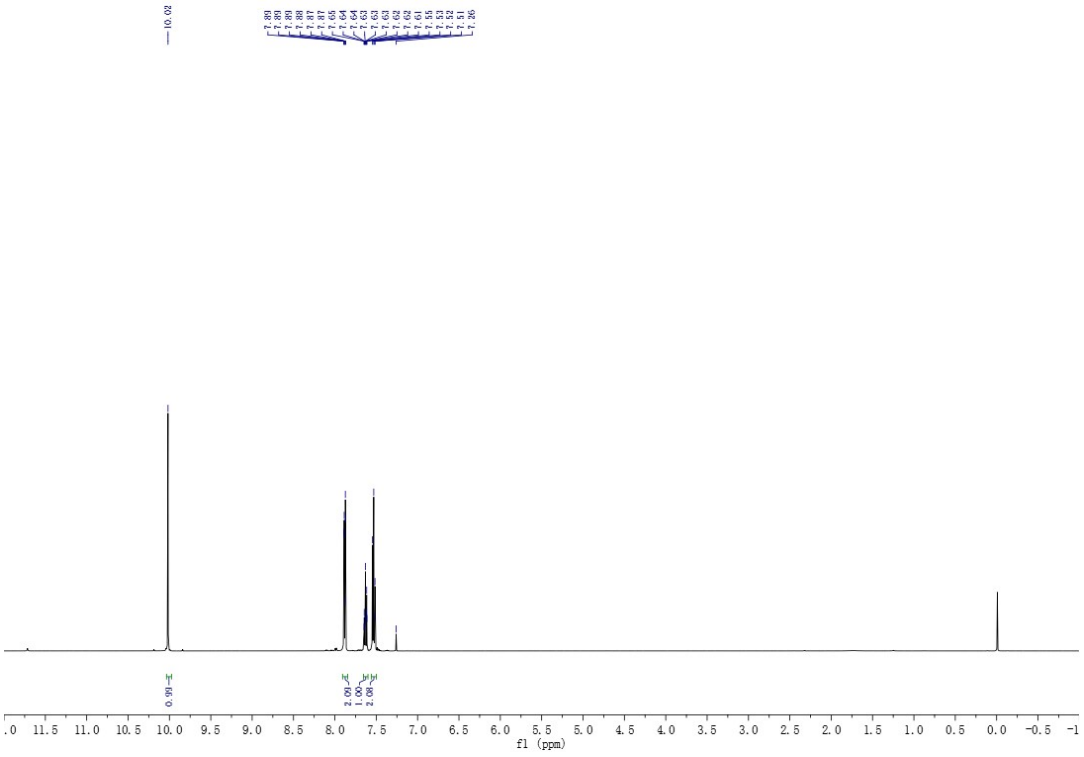


^{1}H NMR of compound **18-1**

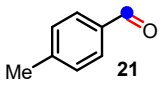


^{13}C NMR of compound **18-1**

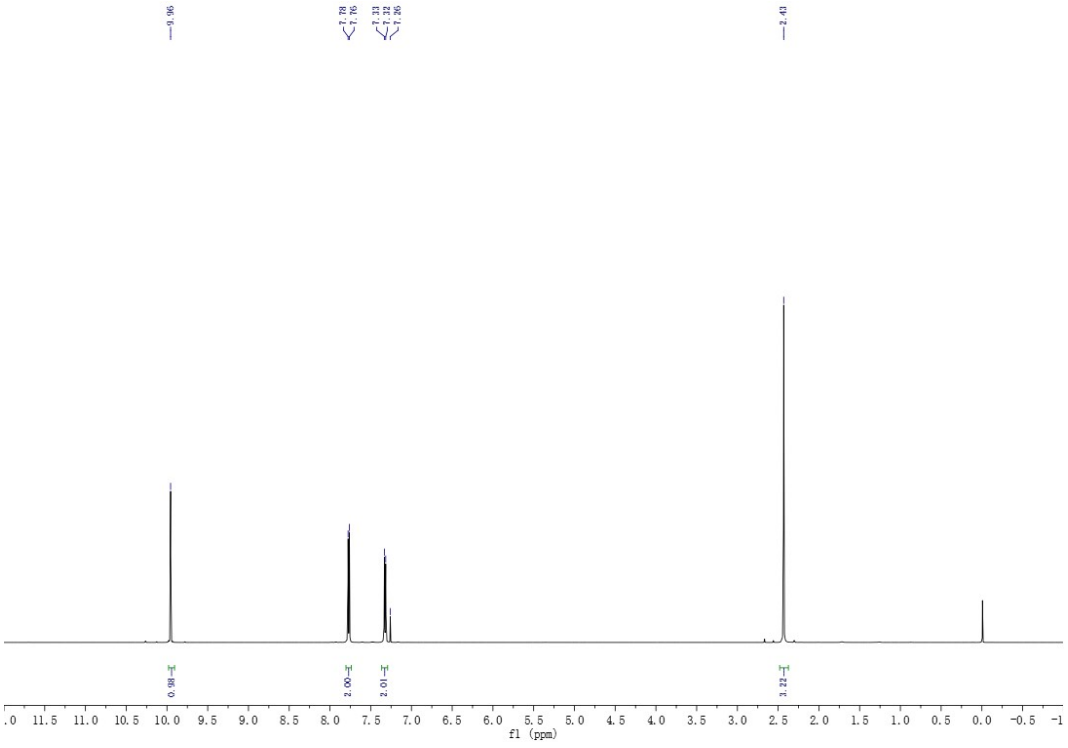
19



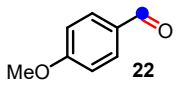
^{1}H NMR of compound **19**



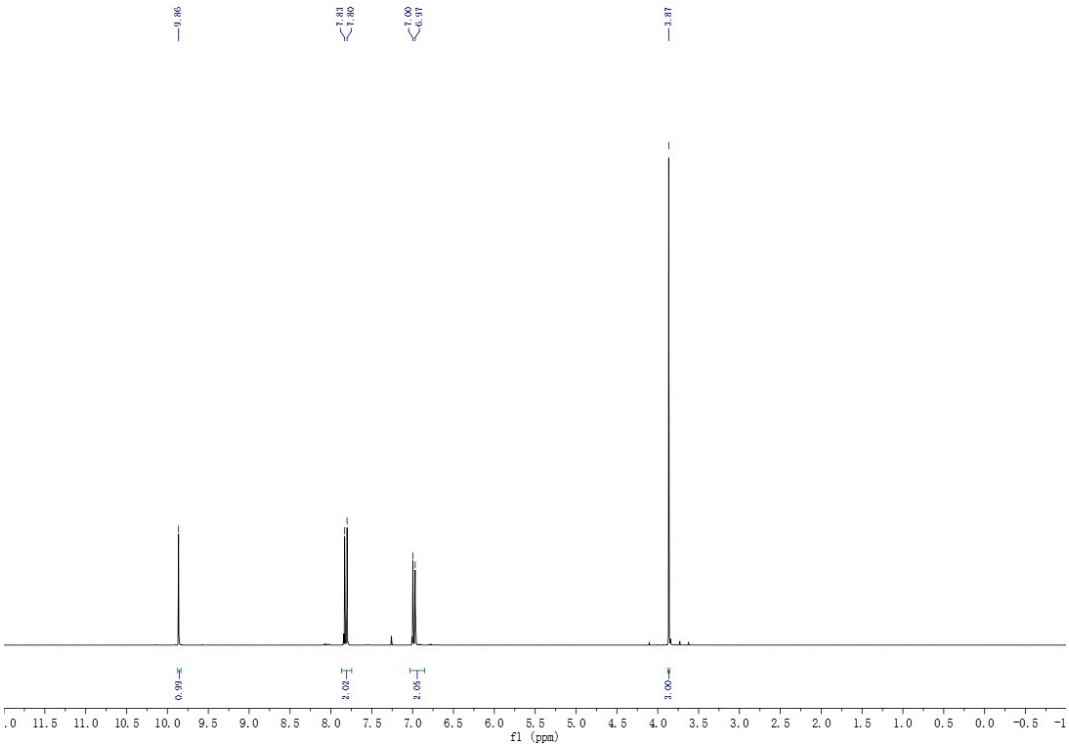
21



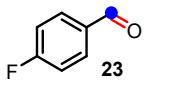
^{1}H NMR of compound **21**



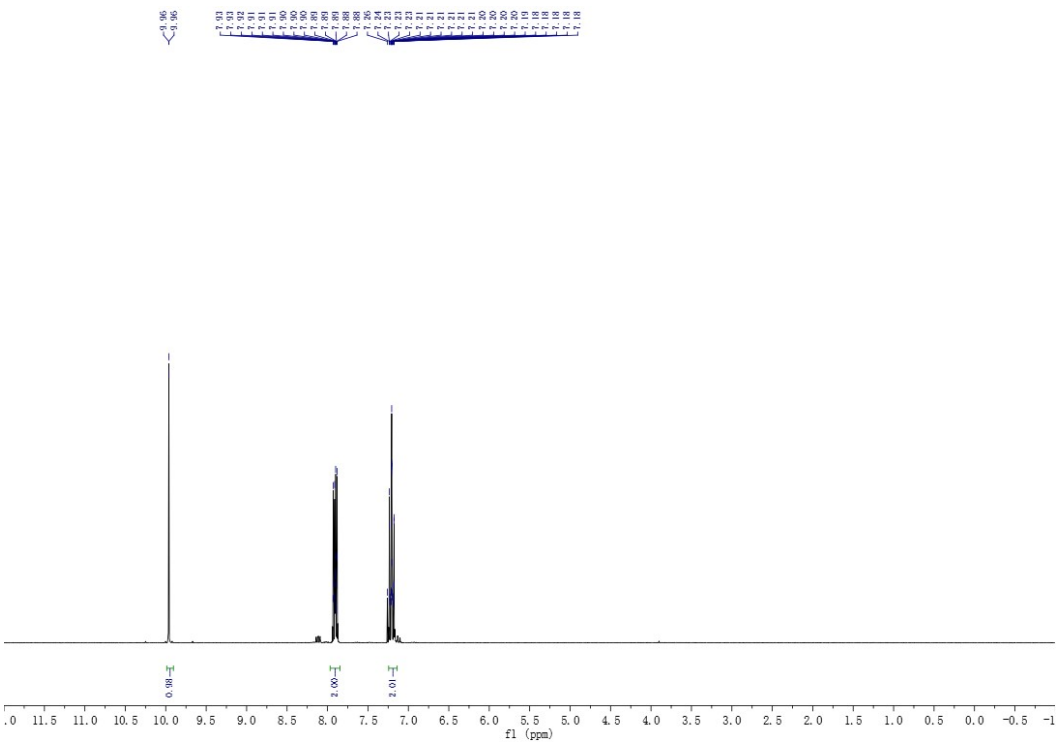
22



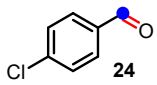
^{1}H NMR of compound **22**

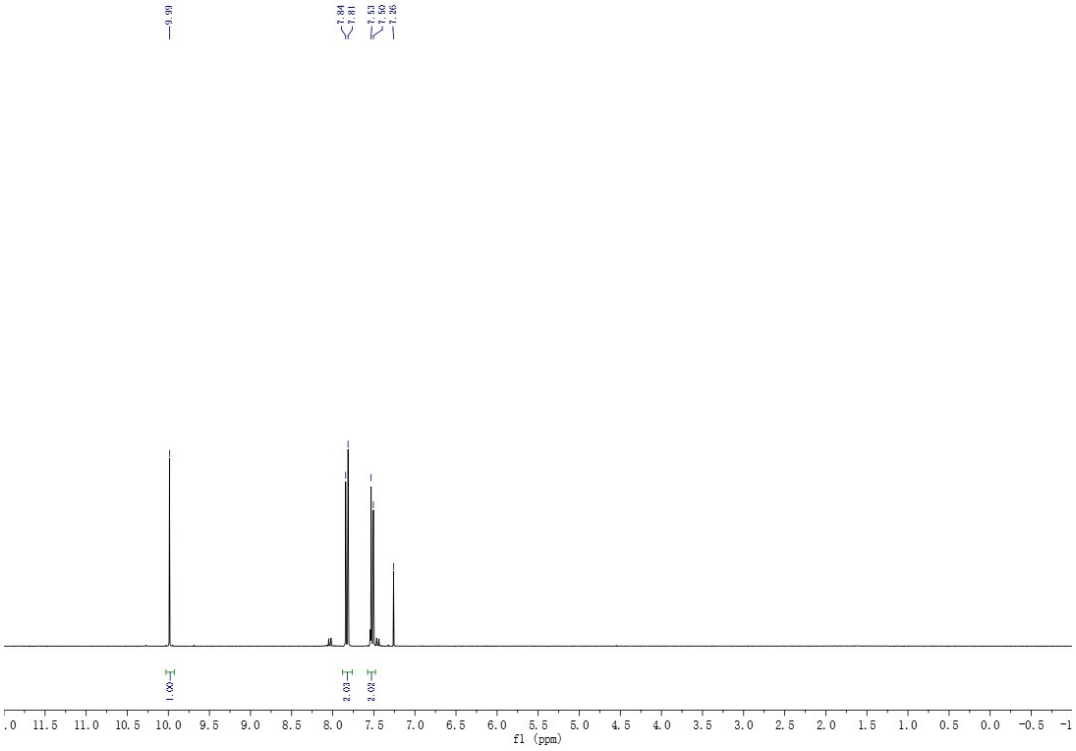


23

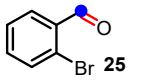


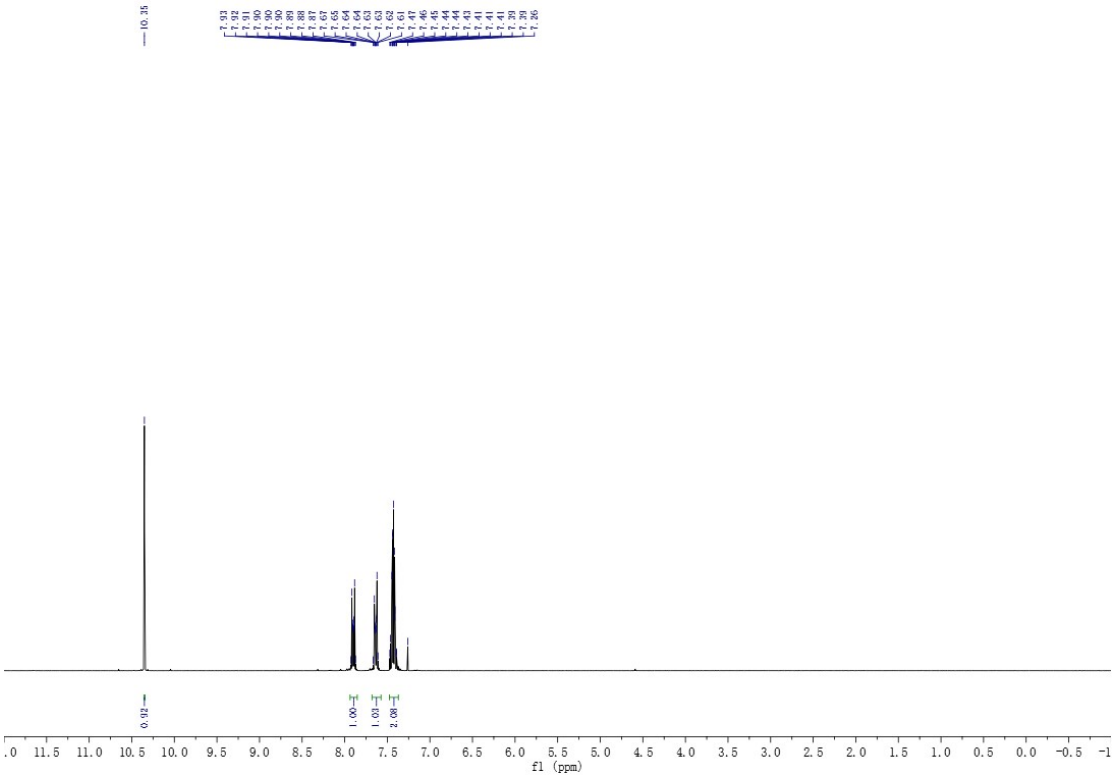
^{1}H NMR of compound **23**



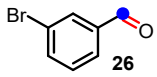


^{1}H NMR of compound **24**

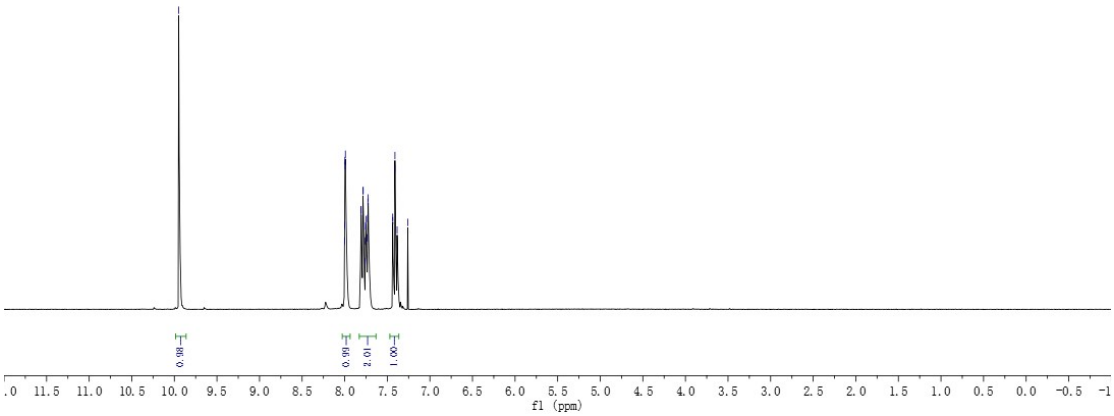




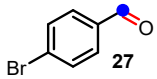
^{1}H NMR of compound **25**



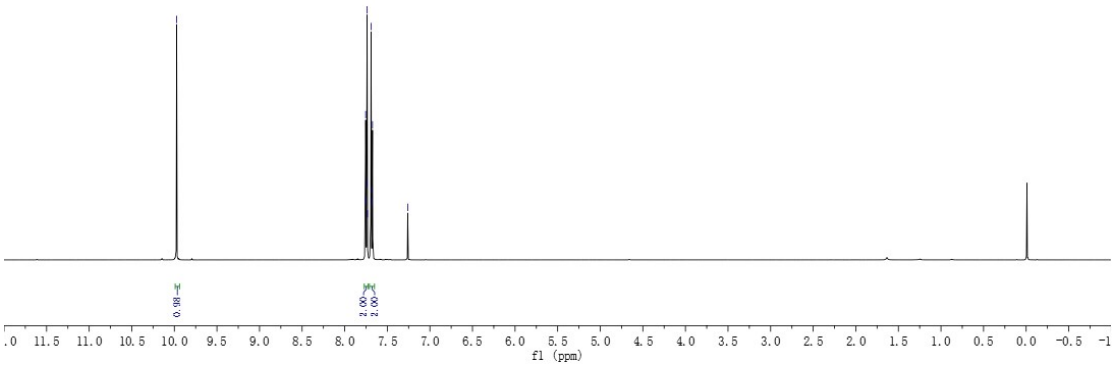
26



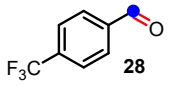
^{1}H NMR of compound **26**



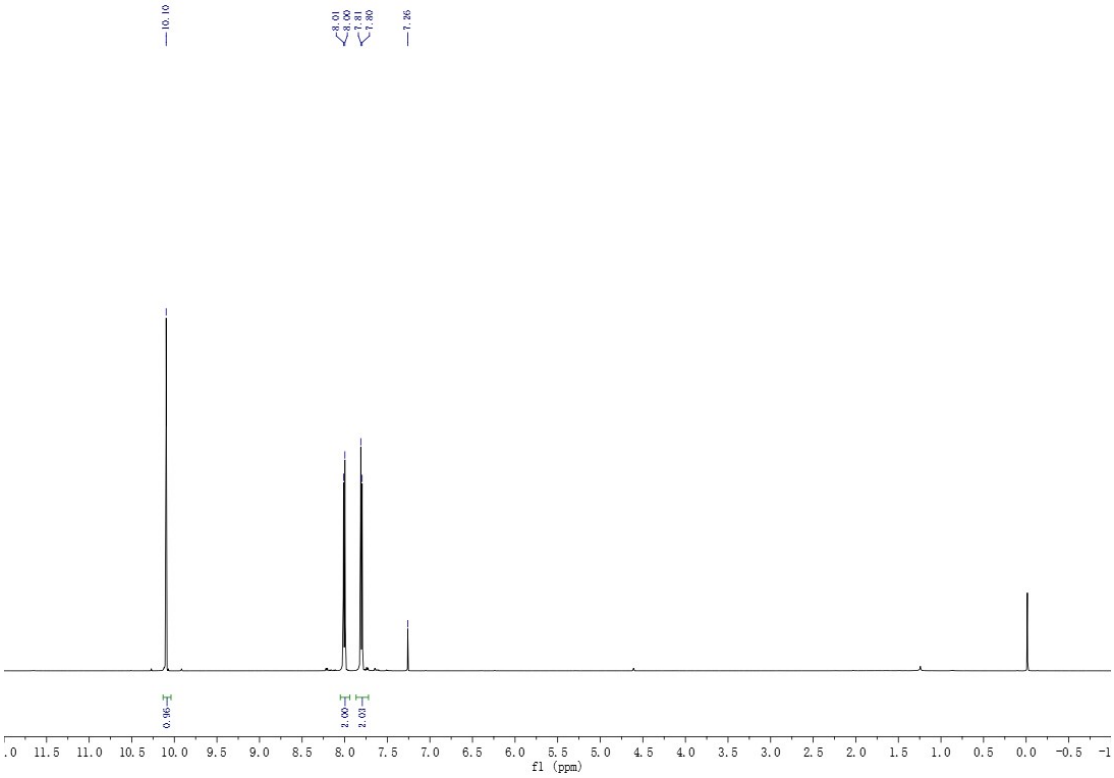
27



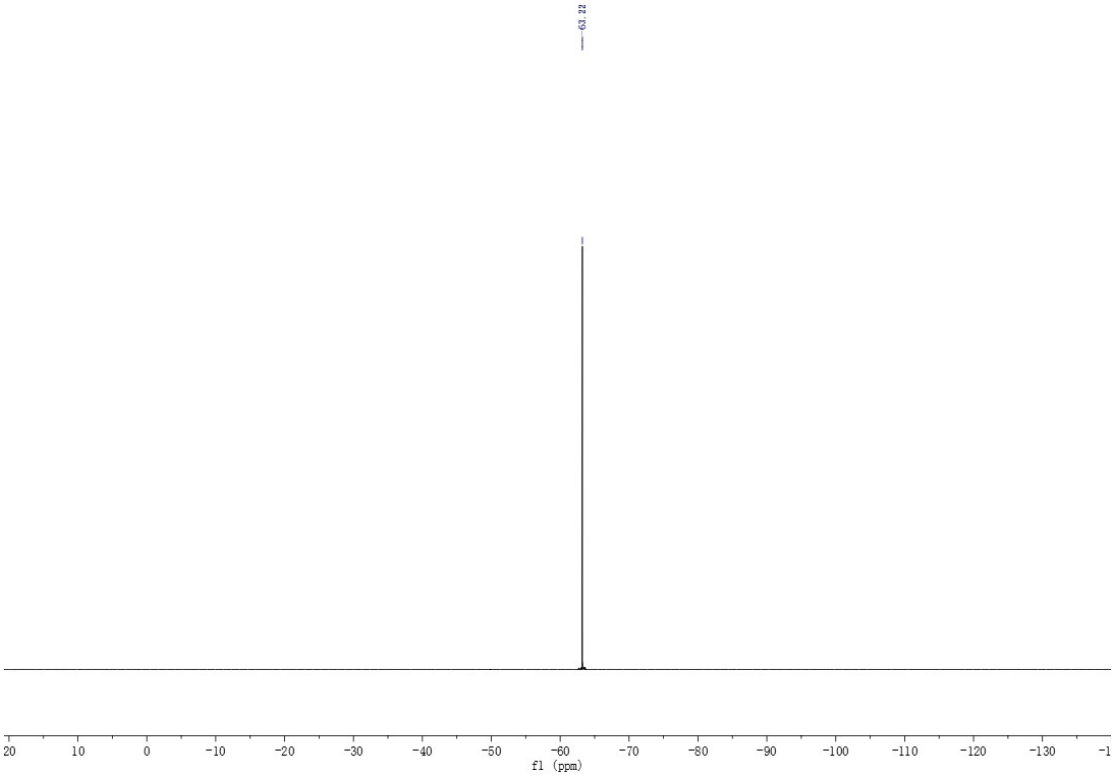
^{1}H NMR of compound **27**



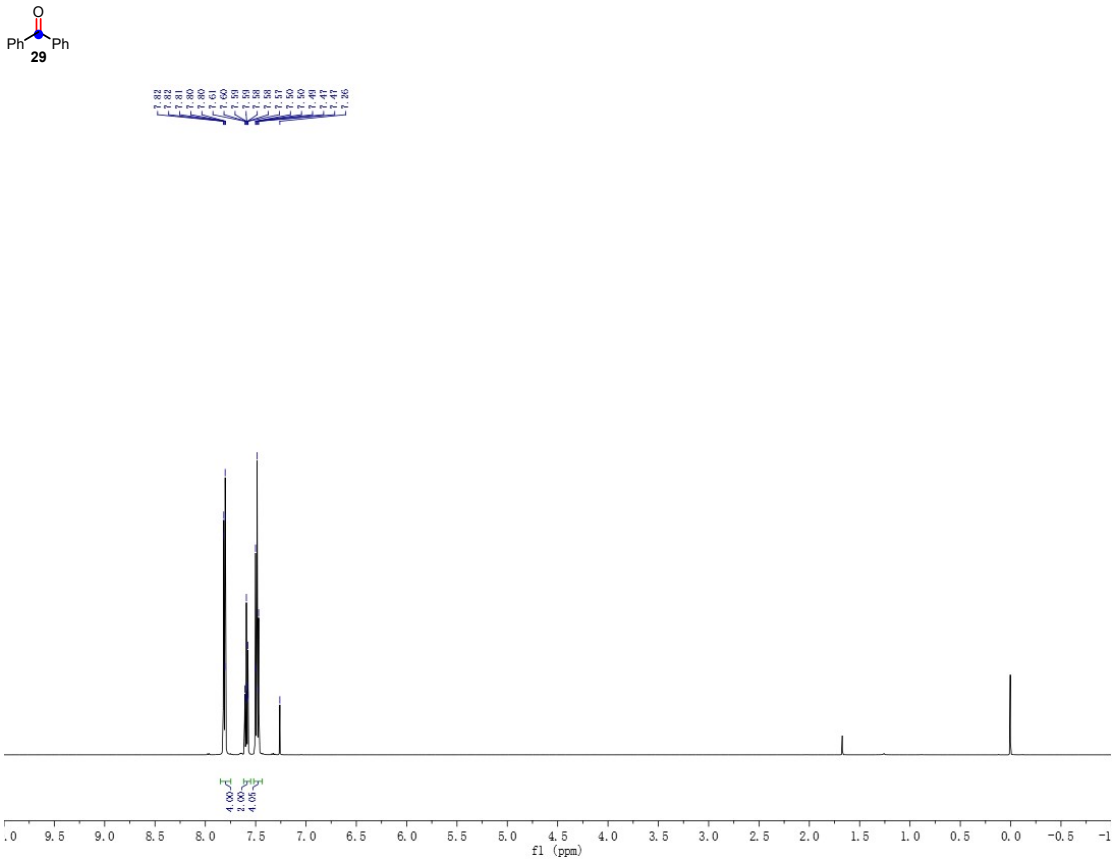
28



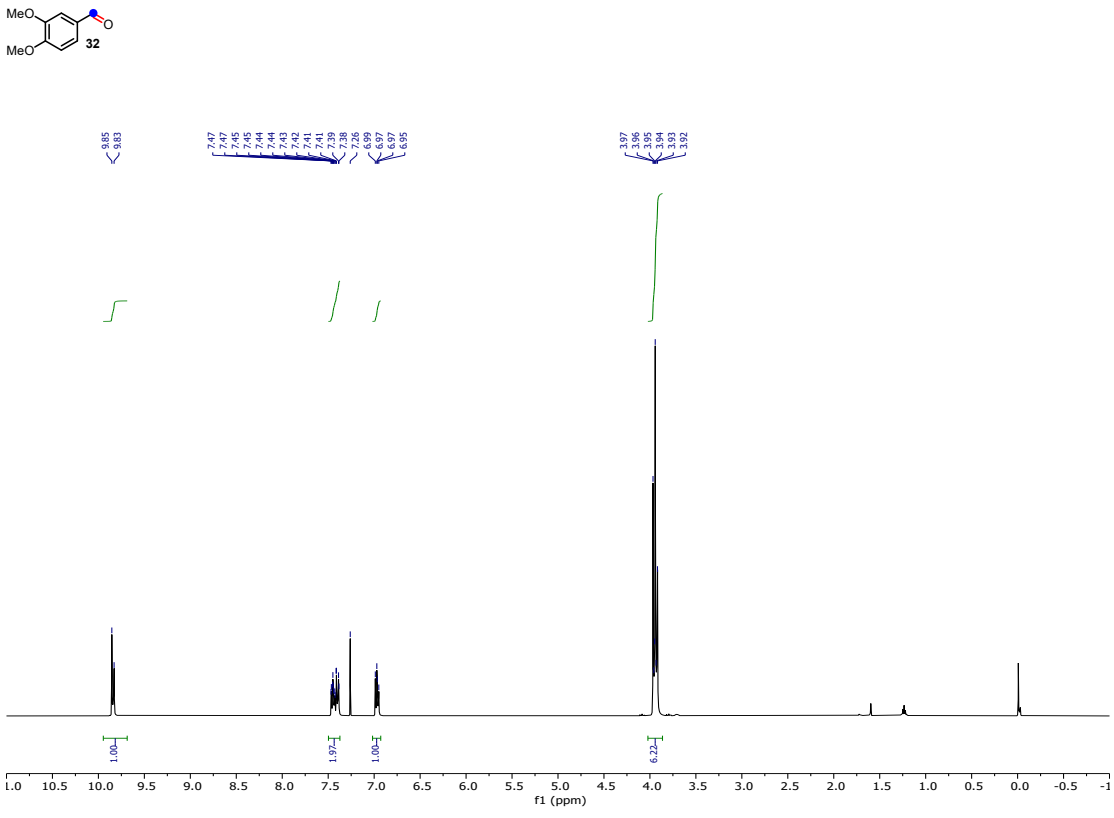
^{1}H NMR of compound **28**



^{19}F NMR of compound **28**



^{1}H NMR of compound **29**



^{1}H NMR of compound **32**