Supporting Information

Ferric Nitrene-Promoted anti-Markovnikov Ring-Opening of Epoxides and Nucleophilic Functionalization of Benzylic C-H Bonds under Photo-Irradiation

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# equal contribution to this paper

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1. General Information

Unless otherwise noted, all reactions were performed under air using flame-dried glassware. MeCN, DCE, 1,4-dioxane and DCM were purchased as reaction solvents without preprocessing. All new compounds were fully characterized. NMR-spectra were recorded on Bruker ARX-400 MHz spectrometer. ^{1}H NMR spectra data were reported as δ values in ppm relative to chloroform (δ7.26). ^{13}C NMR spectra data were reported as δ values in ppm relative to chloroform (δ 77.0) .^{1}H NMR coupling constants were reported in Hz, and multiplicity was indicated as follows: s (singlet); d (doublet); t (triplet); q (quartet); quint (quintet); m (multiplet); dd (doubletof doublets); ddd (doublet of doublet of doublets); dddd (doublet of doublet of doublet of doublets); dt (doublet of triplets); td (triplet of doublets); ddt (doublet of doublet of triplets); dq (doubletof quartets); app (apparent); br (broad). The reactor was 2.0 cm from 10W blue LED strips，the power density of the incident light was recorded on a HPS350j spectral irradiance colorimeter (Beijing Rogertech Co.ltd). Photoredox reactions were carried out in flame-dried 10 mL sealed tubes with Teflon screw caps under air. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. The puritfy of $FeCl_3$ used in the paper is > 99.9% metal basis.

2. The spectrum of our lamp and the visible-light irradiation instrument

All reactions have been studied in borosilicate glass vessels irradiated by a blue light LED strips purchased from Beijing Rogertech Co.ltd without using filters.

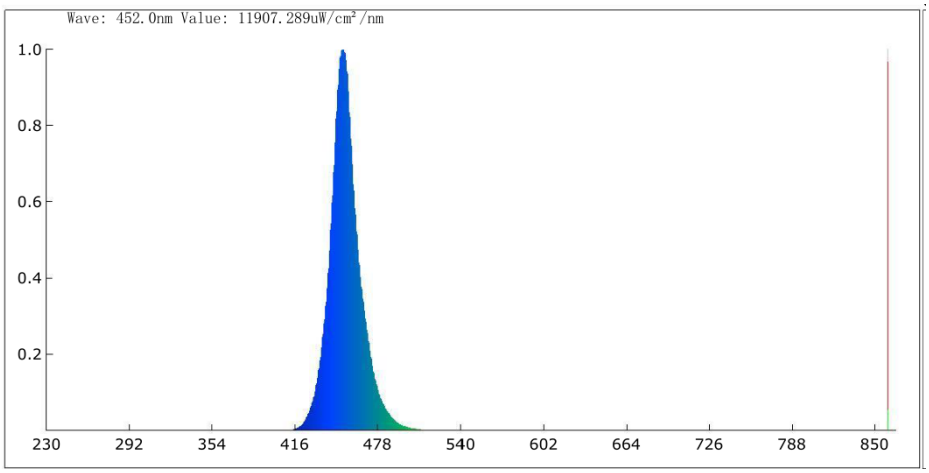
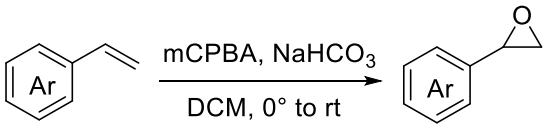


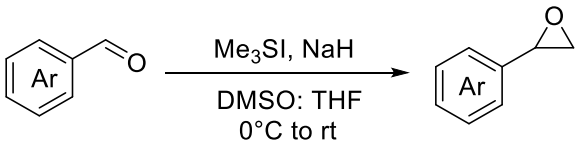
Figure S1. The spectrum of our blue LED. λ_{max} = 460 nm.

Figure S2. Photograph of the reaction setup

3. Experimental procedure for the synthesis of epoxides

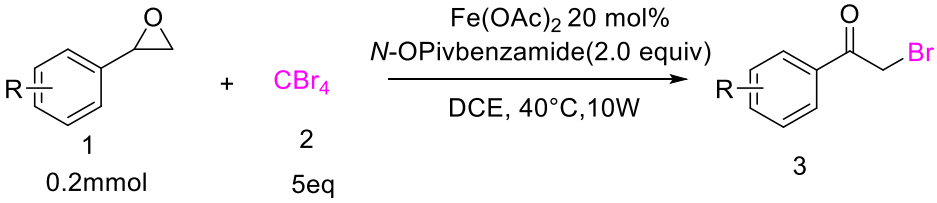


Unless otherwise mentioned in the following specific substrates, the general procedure is: to a 100 mL dried Schlenk flask was added alkene (1.0 equiv), $NaHCO_3$ (1.3 equiv) and CH_2Cl_2 (20 mL) under Ar atmosphere. The flask was then fitted with an addition funnel containing m-CPBA (73%, 1.2 equiv.) dissolved in CH_2Cl_2 (20 mL). The m-CPBA solution was added dropwise through the addition funnel over 20 minutes at 0 ºC. The reaction was then stirred for an additional 1 h and then allowed to warm to room temperature. After completion of the reaction (TLC monitoring), the reaction mixture is quenched with aqueous $Na_2S_2O_3$, and the aqueous phase is extracted with CH_2Cl_2. The combined organic layers are washed successively with a saturated solution of $NaHCO_3$ and brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (PE: EA) with Et_3N (1%) afforded the corresponding epoxides. [3]

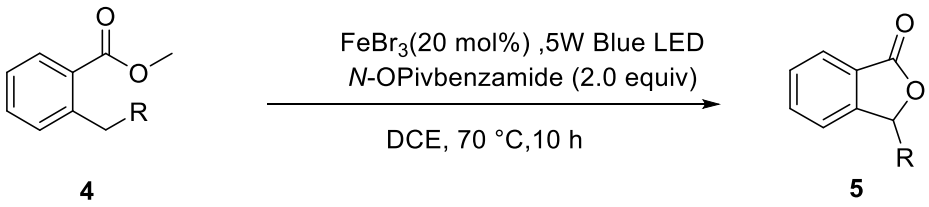


Unless otherwise mentioned in the following specific substrates, the general procedure is: to an oven dried Schlenk flask was added trimethylsulfonium iodide (1.6 equiv) and dry DMSO/THF (15 mL, 2/1), and then NaH (60% in mineral oil, 1.5 equiv) was added to the above mixture at 0 °C under argon, the reaction allowed to stir for 30 min at room temperature. Aldehyde (1.0 equiv) in THF was added to the reaction at 0 °C. The reaction mixture is maintained at 0 °C for 1 h and allowed to stir at room temperature for overnight. Then the reaction was quenched with H_2O, the aqueous layer was extracted with Et_2O. The combined organic extracts were washed with brine and dried over Na_2SO_4. The filtrate was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (PE: EA) with Et_3N (1%) afforded the corresponding epoxides. [3]

4. General procedure for the synthesis of 3, 5 and 8

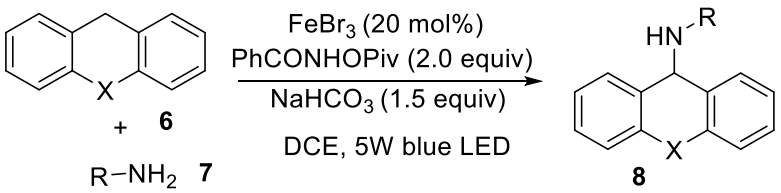


To a 10 mL sealed tube containing a magnetic stirrer and fitted with a Teflon cap, the epoxides **1** (0.2 mmol), **2** (5.0 equiv), *N*-pivaloyloxybenzamide (2.0 eq), PPh_3 (0.3 eq), $Fe(OAc)_2$ (0.2 equiv), and DCE (1.0 mL) were added. The tube was screwed and the mixture was stirred at 40℃ under blue light irradiation（10W）with a cooling fan. After 4 h, the mixture was diluted with EA (5.0 mL) and the aqueous phase was separated and discarded. The organic phase was vacuumed to remove the solvent and the crude mixture was purified through silica gel column with ethyl acetate/petroleum ether as the eluent.



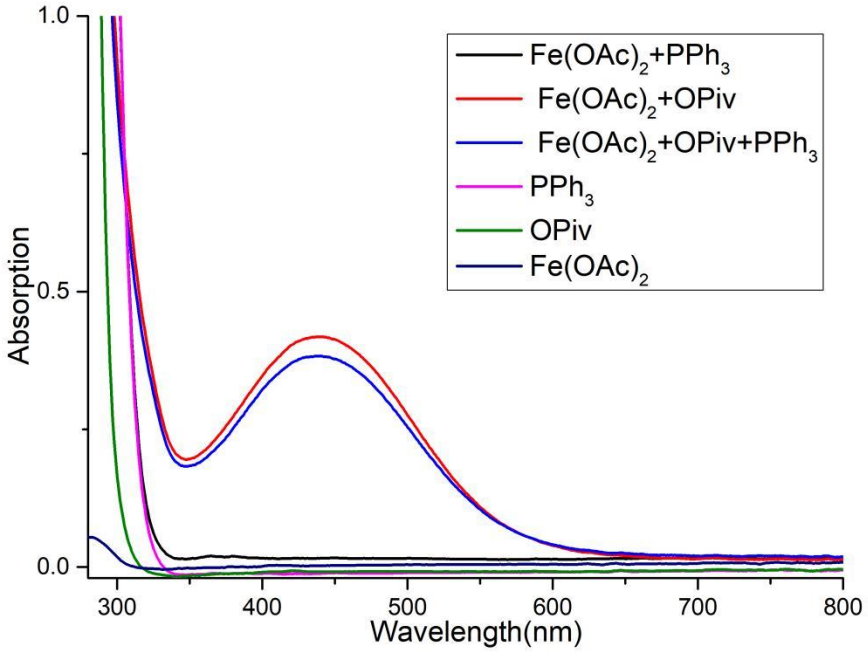
To the test tube was added 2-ethylbenzoic ester (0.4 mmol, 1.0 equiv.), $FeBr_3$ (0.08 mmol, 0.2 equiv.), *N*-pivaloyloxybenzamide (0.8 mmol, 2.0 equiv), and then 1, 2-Dichloroethane (2 mL) was

added to the mixture. The mixture was then stirred under blue light at 70°C for 5W until the substrate was completely consumed, and the resulting mixture was cooled to room temperature. Extract the mixture with EA (2 mL x 3). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by silica gel chromatography using a petroleum ether/ethyl acetate mixture to give the desired product.



To was added a mixture of oxanthene **6** (0.2mmol, 1.0 equiv), *N*-pivaloyloxybenzamide (0.4 mmol, 2.0 equiv), $NaHCO_3$ (1.5 equiv), amine **7** (0.3 mmol, 1.5 equiv) and $FeBr_3$ (0.2 equiv) in DCE (2 mL) was added into a 10 mL vial equipped with a stir bar. The vial was placed in a blue 5 W LED 30℃ photoreactor until the reaction is complete. The reaction solution was transferred to a 25 mL round bottom bottle and added into water (3 mL). The resulting mixture was extracted by DCM (3×3 mL). The combined organic layers were dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash chromatography (eluent: Petroleum ether/dichloromethane = 2/1) provided the target product **8**.

5. UV-visible absorption experiment



Calculation details

DFT calculations were employed to optimize structures under B3LYP/6-31+G(d,p) with tight criteria, with frequency calculations ensuring that all optimized structures and transition states had zero or one imaginary frequency, respectively. It is worthy of noticing that the multiplicity of iron atom is estimated at sextet state. All calculations results were carried out with Gaussian 09 program.

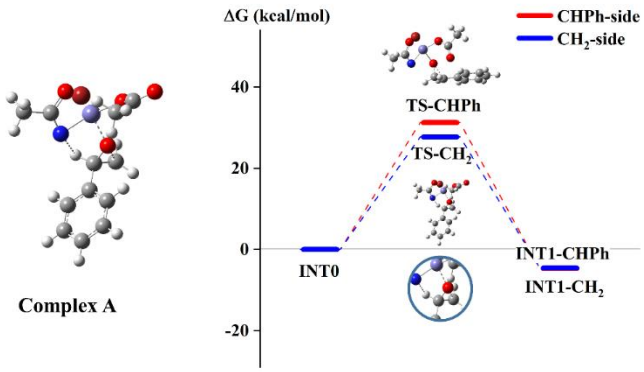


Figure 1. The whole profile of calculated reaction pathways of different ring-opening side (CH_2 side (blue line, ΔG = 27.7 kcal/mol) and CHPh side (red line, ΔG = 31.3 kcal/mol)), with 3D structure of critical transition states. A 3D figure of N-CH interaction of INT0 is included.

According to DFT calculations, the selective ring-opening pathways of epoxides catalyzed by iron-catalyst were elucidated as depicted in the figure. Initially, the iron catalyst coordinates with the oxygen atom of the epoxide, followed by the induced ring-opening upon the attack of bromide anion. According to the computational results, the energy barrier for the bromide anion attacking the unsubstituted side is significantly lower than that for attacking the substituted aromatic ring side. This energy barrier difference suggests that the ring-opening occurs preferentially and specifically on the unsubstituted side. Additionally, thermodynamic analysis of the ring-opened product (INT1) further confirms that the product derived from the ring-opening on the unsubstituted side is more stable.

Cartesian coordination of intermediates and transition states

INT0

Fe	1.333938	0.370514	0.426270
N	1.105979	1.640466	1.846433
C	0.333646	2.410581	1.127391
C	-0.230604	3.733275	1.612089
H	-1.327206	3.706621	1.567699
H	0.089774	3.942224	2.637372
H	0.103622	4.544128	0.951603
O	0.004939	2.025662	-0.084930
O	2.836880	1.024192	-0.823967
C	-1.517883	-0.627048	-0.765382
C	-0.793306	-1.890842	-0.503041
O	-0.651116	-0.764779	0.385750
H	-1.099438	0.028859	-1.524250
H	0.104274	-2.118279	-1.070372
H	-1.328938	-2.728743	-0.058056
Br	2.384722	-1.787115	0.999970
C	-2.973832	-0.474186	-0.482597
C	-3.516121	-0.798031	0.769472
C	-3.827708	-0.013476	-1.494380
C	-4.889143	-0.682439	0.995373
H	-2.848885	-1.117713	1.564972
C	-5.202351	0.097248	-1.270371
H	-3.409130	0.264780	-2.459297
C	-5.738790	-0.238264	-0.023608
H	-5.295819	-0.929356	1.973657
H	-5.851638	0.457260	-2.065554
H	-6.807657	-0.145338	0.155774
C	2.390898	0.503478	-1.905183
C	3.207373	0.689938	-3.171217
H	3.524701	1.733973	-3.264370
H	4.112645	0.073287	-3.107392
H	2.629866	0.389268	-4.049408
O	1.316954	-0.151324	-1.925687

(three lowest vibration frequency: 23.15, 26.70, 28.35)

INT1-CH2

Fe	-1.430912	0.677165	0.146462
N	-2.601086	1.569990	-1.168540
C	-2.765599	2.498615	-0.286343
C	-3.660317	3.711124	-0.438301
H	-3.068510	4.629531	-0.329837
H	-4.152563	3.705410	-1.415312
H	-4.418318	3.715692	0.355808
O	-2.108123	2.404220	0.889197
O	-2.274763	-0.817422	1.057523
C	1.351511	-0.273344	-0.039283
C	1.425621	-1.115143	-1.324669
O	0.410819	0.737197	-0.171422
H	1.101587	-0.944857	0.796142
H	2.137767	-1.938968	-1.255270
H	1.642147	-0.488468	-2.191370
Br	-0.333151	-1.946634	-1.705252
C	2.754529	0.292130	0.194507
C	3.035386	1.637968	-0.072768
C	3.782468	-0.526583	0.685874
C	4.313393	2.156026	0.157017
H	2.224109	2.269226	-0.422071
C	5.061499	-0.012035	0.913371
H	3.570468	-1.568372	0.921801
C	5.334207	1.333425	0.643971
H	4.511807	3.207749	-0.041251
H	5.842900	-0.658745	1.308271
H	6.327031	1.739122	0.828013
C	-1.750143	-1.750057	1.801254
C	-2.772771	-2.760703	2.316845
H	-3.582266	-2.240295	2.841755
H	-3.224535	-3.288132	1.467783
H	-2.296747	-3.482939	2.985203
O	-0.553182	-1.857559	2.086836

(three lowest vibration frequency: 19.93, 31.73, 35.32)

INT1-CHPh

Fe	-1.238085	0.060678	-0.076991
N	-1.202133	-0.902713	1.670374
C	-2.010843	-0.048499	2.223718
C	-2.446883	-0.085833	3.660150
H	-2.134023	0.840808	4.155334
H	-3.540849	-0.144939	3.708674
H	-2.009299	-0.944498	4.179316
O	-2.413163	0.902491	1.426154
O	-1.082971	1.767370	-0.986977
C	0.807064	-1.980498	-0.306677
C	2.301672	-2.136560	-0.302148
O	0.332945	-0.706144	-0.617875
H	0.391875	-2.711060	-1.027065
H	2.630596	-3.171947	-0.412326
Br	-2.965467	-1.193237	-1.197229

C	3.321644	-1.174522	-0.109962
C	4.689353	-1.596117	-0.151329
C	3.078777	0.212947	0.139747
C	5.733832	-0.703293	0.043497
H	4.904995	-2.646869	-0.340143
C	4.136159	1.093723	0.333736
H	2.060161	0.579237	0.174461
C	5.469237	0.654658	0.288950
H	6.762047	-1.059858	0.005519
H	3.911367	2.140701	0.524425
H	6.287323	1.355307	0.441924
C	-0.260621	2.689312	-0.570091
C	-0.323948	3.980694	-1.379678
H	-0.116718	3.767579	-2.434970
H	-1.335668	4.400143	-1.325670
H	0.398670	4.706814	-0.998578
O	0.512425	2.567460	0.385808
H	0.419454	-2.292258	0.684888

(three lowest vibration frequency: 16.94, 27.41, 33.83)

TS-CH2

Fe	-1.138402	-0.002039	-0.014990
N	-0.104416	-0.167766	1.620285
C	-1.206038	-0.135401	2.315538
C	-1.259100	-0.342328	3.809233
H	-1.836958	-1.248711	4.029097
H	-0.252237	-0.440170	4.225647
H	-1.774811	0.503628	4.280481
O	-2.330441	0.077821	1.665004
O	-1.993520	1.392754	-0.993707
C	1.556270	-0.817095	-0.867460
C	1.532036	-1.110483	-2.322517
O	0.493646	0.098197	-1.057866
H	1.254631	-1.670545	-0.251674
H	0.773629	-1.786743	-2.702496
H	2.039950	-0.440410	-3.008861
Br	-1.709562	-2.277487	-0.687278
C	2.833827	-0.200656	-0.339264
C	3.170177	1.125782	-0.639086
C	3.723497	-0.969787	0.420262
C	4.382126	1.666080	-0.202520
H	2.461832	1.731390	-1.197630
C	4.943440	-0.437353	0.846253
H	3.456176	-1.991987	0.680560
C	5.276402	0.885111	0.537743
H	4.626633	2.700616	-0.434819
H	5.624537	-1.048401	1.435160
H	6.220143	1.306220	0.878066
C	-2.239778	2.671686	-0.835341
O	-2.810574	3.358741	-1.680412
C	-1.771256	3.275816	0.487325
H	-0.684273	3.164963	0.587607
H	-2.035459	4.335597	0.534087
H	-2.232250	2.735630	1.322105

(imaginary frequency: -630.00)
(three lowest vibration frequency: 12.74, 17.97, 27.45)

TS-CHPh

Fe	-1.437410	-0.037055	-0.037697
N	-2.064618	0.145358	1.795623
C	-3.153982	0.712742	1.361876
C	-4.269326	1.195393	2.262083
H	-4.445640	2.264612	2.088940
H	-5.197175	0.662964	2.016878
H	-4.018189	1.029238	3.313972
O	-3.290515	0.872449	0.061702
O	-0.697900	1.367287	-1.181072
C	0.825421	-0.289646	1.883766
C	1.979474	-1.129011	1.502293
O	0.289358	-0.689988	0.643541
H	0.238837	-0.643431	2.737406
H	1.873083	-2.195101	1.685135
Br	-2.049169	-2.005356	-1.290690
C	3.169393	-0.693571	0.829521
C	4.194343	-1.636853	0.564853
C	3.378529	0.654660	0.440698
C	5.391807	-1.248492	-0.027289
H	4.035469	-2.678130	0.837833
C	4.575269	1.029595	-0.162180
H	2.583784	1.385157	0.567706
C	5.590216	0.089843	-0.392333
H	6.168015	-1.987085	-0.215234
H	4.713905	2.064408	-0.466290
H	6.521945	0.394802	-0.863523
C	0.126442	2.343398	-0.972126
C	0.309087	3.249581	-2.191092
H	0.676925	2.659004	-3.038652
H	-0.659816	3.668677	-2.486979
H	1.010788	4.058605	-1.970287
O	0.741912	2.574703	0.079342
H	1.001094	0.788222	1.949488

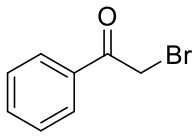
(imaginary frequency: -542.45)
(three lowest vibration frequency: 13.61, 23.11, 30.94)

The Gibbs free energy of transition states complex TS-CH_2 (original "**A**") in doublet, quartet, sextet, octet and dectet, as shown in the Table R1, and we set the Gibbs free energy of TS-CH_2 in doublet as 0.

Multiplicity	Relative Gibbs free energy (kcal/mol)
Doublet (II)	22.6
Quartet (IV)	8.1
Sextet (VI)	0.0
Octet (VIII)	37.4
Dectet (X)	136.8

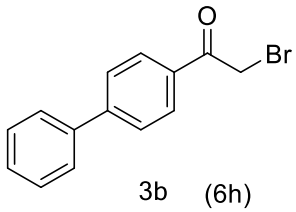
According to DFT calculations, the A in sextet has the lowest Gibbs free energy, which means the sextet is the most stable spin configuration among the five cases.

6. Characterization Data of All Products



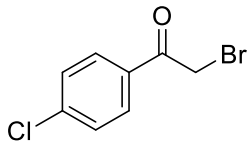
3a

2-bromo-1-phenylethan-1-one (3a)[1]: Prepared according to general procedure from 5. Yellow solid (30mg, 75% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.99-7.97 (m, 2H), 7.62-7.58 (m, 1H), 7.50-7.47 (m, 2H), 4.45 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 191.3, 134.0, 133.9, 128.9, 128.9, 31.0.



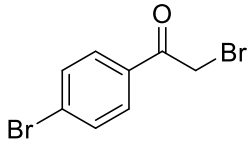
3b (6h)

1-([1,1'-biphenyl]-4-yl)-2-bromoethan-1-one (3b)[1]: Prepared according to general procedure from 5. Yellow solid (32mg, 59% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.06-8.04 (m, 2H), 7.71-7.69 (m, 2H), 7.63-7.62 (m, 2H), 7.48-7.41 (m, 3H), 4.47 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.9, 146.6, 139.5, 132.6, 129.6, 129.0, 128.5, 127.5, 127.3, 30.9.



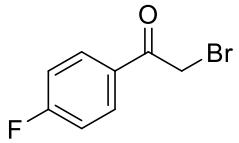
3c

2-bromo-1-(4-chlorophenyl)ethan-1-one (3c)[2]: Prepared according to general procedure from 5. Yellow solid (33mg, 70% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.93-7.91 (m, 2H), 7.47-7.45 (m, 2H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.2, 140.5, 132.2, 130.4, 129.2, 30.4.



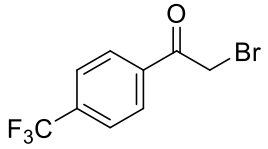
3d

2-bromo-1-(4-bromophenyl)ethan-1-one (3d)[2]: Prepared according to general procedure from 5. Yellow solid (40mg, 73% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.82-7.80 (m, 2H), 7.61-7.60 (m, 2H), 4.38 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.4, 132.6, 132.2, 130.4, 130.0, 30.5.



3e

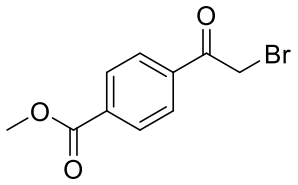
2-bromo-1-(4-fluorophenyl)ethan-1-one (3e)[2]: Prepared according to general procedure from 5. Yellow solid (30mg, 69% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.02-8.00 (m, 2H), 7.99-7.12 (m, 2H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 189.82, 166.1 (d, *J*= 255Hz), 131.7 (d, *J*= 9Hz), 130.3 (d, *J*= 3Hz), 116.1 (d, *J*= 22Hz), 30.5.



3f

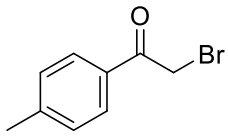
2-bromo-1-(4-(trifluoromethyl)phenyl)ethan-1-one (3f)[3]: Prepared according to general procedure from 5. Yellow solid (34mg, 64% yield).^{1}H NMR (400 MHz,

$CDCl_3$): δ= 8.09-8.07 (m, 2H), 7.75-7.74 (m, 2H), 4.44 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.4, 136.5, 129.3, 128.9, 125.9, 122.0, 30.4.



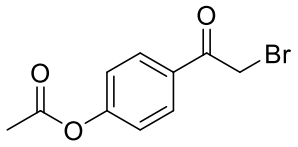
3g

methyl 4-(2-bromoacetyl)benzoate (3g)[4]: Prepared according to general procedure from 5. Yellow solid (30mg, 59% yield).^1H NMR (400 MHz, $CDCl_3$): δ= 8.13-8.11 (m, 2H), 8.02-8.00 (m, 2H), 4.45 (s, 2H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.8, 165.9, 137.1, 134.6, 130.1, 128.8, 52.6, 30.7.



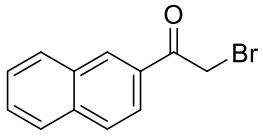
3h

2-bromo-1-(p-tolyl)ethan-1-one (3h)[2]: Prepared according to general procedure from 5. Yellow solid (29mg, 67% yield).^1H NMR (400 MHz, $CDCl_3$): δ= 7.88-7.86 (m, 2H), 7.28-7.27 (m, 2H), 4.42 (s, 2H), 2.41 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 191.0, 145.0, 131.4, 129.6, 129.0, 31.0, 21.8.



3i

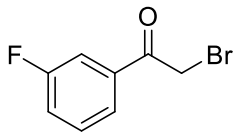
4-(2-bromoacetyl)phenyl acetate (3i)[4]: Prepared according to general procedure from 5. Yellow solid (33mg, 65% yield).^1H NMR (400 MHz, $CDCl_3$): δ= 8.02-8.00 (m, 2H), 7.23-7.21 (m, 2H), 4.42 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.1, 168.7, 154.9, 131.4, 130.6, 122.1, 30.7, 21.2.



3j (6h)

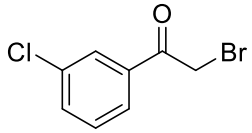
2-bromo-1-(naphthalen-2-yl)ethan-1-one (3j)[1]: Prepared according to general procedure from 5. Yellow solid (30mg, 60% yield).^1H NMR (400 MHz, $CDCl_3$): δ= 8.50-8.49 (m, 1H), 8.02-7.87 (m, 4H), 7.64-7.57 (m, 2H), 4.57 (s, 2H). ^{13}C NMR (101

MHz, $CDCl_3$): δ= 191.3, 135.9, 132.4, 131.2, 131.0, 129.7, 129.0, 128.8, 127.8, 127.1, 124.1, 31.0.



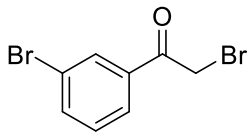
3k

2-bromo-1-(3-fluorophenyl)ethan-1-one (3k)[5]: Prepared according to general procedure from 5. Yellow solid (30mg, 68% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.83-7.78 (m, 2H), 7.46-736 (m, 3H), 4.98 (s, 1H), 3.51 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.1, 162.8 (d, *J*= 248Hz), 135.87 (d, *J*= 6Hz), 130.6 (d, *J*= 8Hz), 124.7 (d, *J*= 3Hz), 121.1 (d, *J*= 22Hz), 115.6 (d, *J*= 22Hz), 30.6.



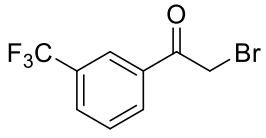
3l

2-bromo-1-(3-chlorophenyl)ethan-1-one (3l)[5]: Prepared according to general procedure from 5. Yellow solid (30mg, 64% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.95-7.92 (m, 1H), 7.85-7.84 (m, 1H), 7.59-7.57 (m, 1H), 7.46-7.42 (m, 1H), 4.42 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.1, 135.4, 135.2, 133.9, 130.2, 128.9, 127.0, 30.5.



3m

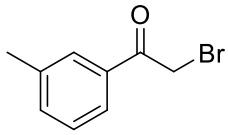
2-bromo-1-(3-bromophenyl)ethan-1-one (3m)[3]: Prepared according to general procedure from 5. Yellow solid (36mg, 65% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.09 (s, 1H), 7.89-7.87 (m, 1H), 7.73-7.71 (m, 1H), 7.38-7.34 (m, 1H), 4.40 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.0, 136.8, 135.6, 131.9, 130.4, 127.5, 123.2, 30.5.



3n

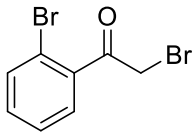
2-bromo-1-(3-(trifluoromethyl)phenyl)ethan-1-one (3n)[6]: Prepared according to general procedure from 5. Yellow solid (28mg, 53% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.24-8.23 (m, 1H), 8.19-8.17 (m, 1H), 7.88-7.86 (m, 1H), 7.68-7.64 (m, 1H), 4.46 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.1, 134.4, 132.1, 130.3, 129.6,

128.4, 128.1, 125.8, 30.2.



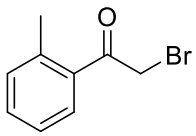
3o

2-bromo-1-(m-tolyl)ethan-1-one (3o)[3]: Prepared according to general procedure from 5. Yellow solid (23mg, 53% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.77-7.76 (m, 2H), 7.40-7.36 (m, 2H), 4.43 (s, 2H), 2.40 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 191.5, 138.8, 134.7, 134.0, 129.3, 128.7, 126.1, 31.1, 21.3.



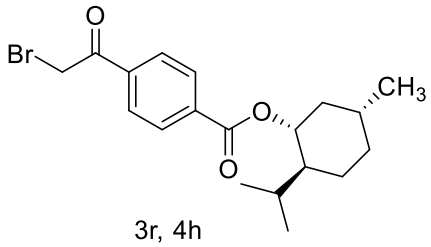
3p

2-bromo-1-(2-bromophenyl)ethan-1-one (3p)[3]: Prepared according to general procedure from 5. Yellow solid (23mg, 36% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.63-7.61 (m, 1H), 7.47-7.45 (m, 1H), 7.41-7.34 (m, 2H), 4.48 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 194.9, 138.6, 133.7, 132.49, 129.7, 127.6, 119.1, 33.9.



3q

2-bromo-1-(o-tolyl)ethan-1-one (3q)[6]: Prepared according to general procedure from 5. Yellow solid (14mg, 27% yield).^{1}H NMR (400 MHz, $CDCl_3$): δ= 7.66-7.64 (m, 1H), 7.41-7.39 (m, 1H), 7.29-7.25 (m, 2H), 4.40 (m, 2H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 194.2, 139.7, 134.4, 132.3, 132.3, 129.0, 125.8, 33.7, 21.4.

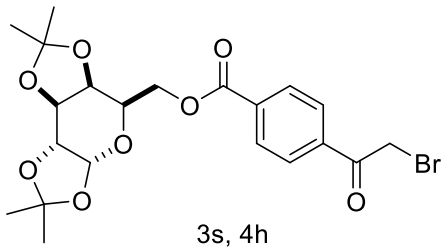


3r, 4h

from DL-Menthol

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-(2-bromoacetyl)benzoate (3r):

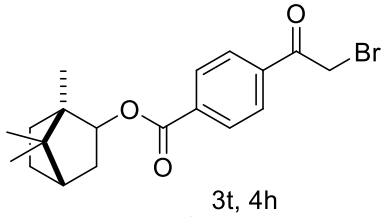
Prepared according to general procedure from 5. Yellow solid (37mg, 44% yiel d).[1]H NMR (400 MHz, $CDCl_3$): δ= 8.14-8.12 (m, 2H), 8.03-8.01 (m, 2H), 4.9 7-4.91 (m, 1H), 4.45 (s, 2H), 2.12-2.09 (m, 1H), 1.92 (m, 1H), 1.73-1.71 (m, 2H), 1.58-1.53 (m, 2H), 1.14-1.09 (m, 2H), 0.91 (m, 7H), 0.78-0.77 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.9, 164.9, 136.9, 135.3, 130.0, 128.8, 7 5.6, 47.2, 40.8, 34.2, 31.4, 30.7, 26.5, 23.6, 22.0, 20.7, 16.5.



3s, 4h

from Diacetonefructose

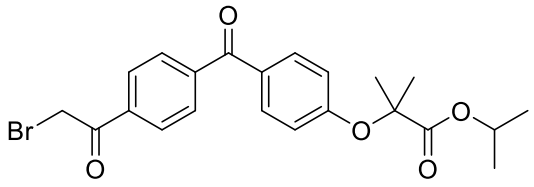
((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b: 4',5'-d]pyran-5-yl)methyl 4-(2-bromoacetyl)benzoate (3s): Prepared according to general procedure from 5. Yellow solid (39mg, 45% yield).[1]H NMR (400 MHz, $CDCl_3$): δ= 8.17-8.15 (m, 2H), 8.03-8.01 (m, 2H), 4.70-4.61 (m, 2H), 4.45 (s, 2H), 4.42-4.41 (m, 1H), 4.34-4.32 (m, 1H), 4.25-4.23 (m, 1H), 3.94-3.91 (m, 1H), 3.79-3.76 (m, 1H), 1.52 (s, 3H), 1.43 (s, 3H), 1.33-1.32 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.8, 164.8, 137.2, 134.3, 130.2, 128.9, 109.1, 108.9, 101.5, 70.7, 70.6, 70.0, 65.9, 61.3, 30.7, 26.5, 25.9, 25.4, 24.0.



3t, 4h

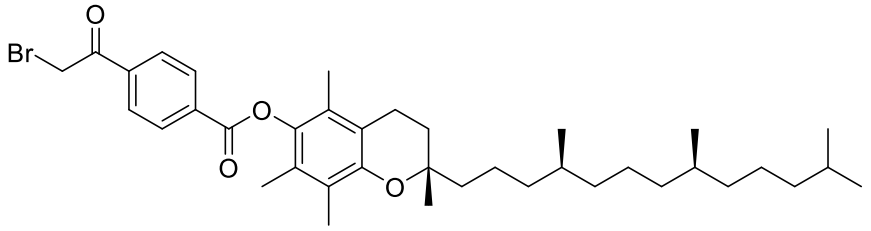
from Borneol

(1S,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 4-(2-bromoacetyl)benzoate (3t): Prepared according to general procedure from 5. Yellow solid (40mg, 48% yield).[1]H NMR (400 MHz, $CDCl_3$): δ= 8.16-8.14 (m, 2H), 8.05-8.02 (m, 2H), 5.13-5.11 (m, 1H), 4.45 (s, 2H), 2.50-2.45 (m, 2H), 2.11-2.07 (m, 1H), 1.84-1.74 (m, 2H), 1.44-1.26 (m, 3H), 1.13-1.07 (m, 1H), 0.95 (s, 3H), 0.90 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.8, 165.6, 137.0, 135.32, 129.9, 128.9, 81.3, 49.1, 47.9, 44.9, 36.9, 30.7, 28.1, 27.4, 19.7, 18.9, 13.6.



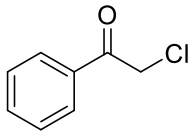
3u, 3h
from Fenofibrate

isopropyl 2-(4-(4-(2-bromoacetyl)benzoyl)phenoxy)-2-methylpropanoate (3u): Prepared according to general procedure from 5. Yellow solid (31mg, 35% yield).[1]H NMR (400 MHz, $CDCl_3$): δ= 8.07-8.02 (m, 2H), 7.82-7.73 (m, 4H), 6.86-6.84 (m, 2H), 5.10-5.04 (m, 1H), 4.47 (s, 2H), 1.65 (s, 6H), 1.19 (d, *J*= 4Hz,6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 194.3, 190.8, 173.0, 160.1, 142.7, 136.0, 132.1, 129.8, 128.8, 128.4, 117.2, 79.5, 69.4, 30.7, 25.3, 21.5.



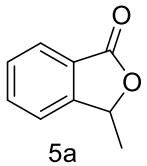
3v, 2h from D-Tocopherol

(S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl 4-(2-bromoacetyl)benzoate (3v): Prepared according to general procedure from 5. Yellow solid (40mg, 30% yield).[1]H NMR (400 MHz, $CDCl_3$): δ= 8.36-8.34 (m, 2H), 8.12-8.10 (m, 2H), 4.48 (s, 2H), 2.61-2.60 (m, 2H), 2.11-2.00 (m, 8H), 1.82-1.79 (m, 1H), 1.70-1.08 (m, 24H), 0.86-0.84 (m, 11H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 190.8, 164.1, 161.4, 140.4, 137.5, 134.1, 133.4, 130.5, 129.1, 124.9, 123.3, 117.6, 75.2, 39.4, 37.4, 37.3, 32.8, 30.6, 29.7, 28.0, 26.5, 24.8, 24.4, 22.7, 22.6, 21.0, 20.6, 19.7, 19.7, 13.1, 12.2, 11.9.



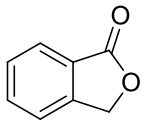
3w

2-chloro-1-phenylethan-1-one (3w)[3]: Prepared according to general procedure from 5. Yellow solid (16mg, 51% yield).[1]H NMR (400 MHz, $CDCl_3$): δ= 7.96-7.94 (m, 1H), 7.61-7.59 (m, 1H), 7.51-7.47 (m, 2H), 4.71 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ= 191.1, 134.2, 134.0, 128.9, 128.5, 46.0.



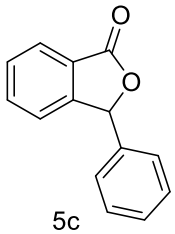
5a

3-methylisobenzofuran-1(3H)-one (5a)[6]: The title compound was prepared according to the general procedure A, Colorless oil (38.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.85 (m, 1H), 7.71-7.62 (m, 1H), 7.56-.39 (m, 2H), 5.56 (q, J = 6.3 Hz, 1H), 1.63 (d, J = 6.7 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 170.5, 151.2, 134.1, 129.0, 125.5, 125.4, 121.7, 77.8, 20.3; IR (cm^{-1}): 3063, 2982 1760, 1467, 1347, 1287, 1045, 763; HRMS (ESI-TOF): ($[M+H]^+$) calcd for $C_{10}H_{11}O_2^+$: 149.0603, found: 149.0609.



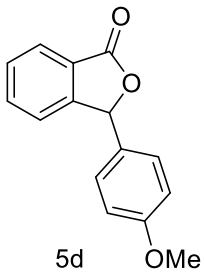
5b

isobenzofuran-1(3H)-one (5b) [6]: The title compound was prepared according to the general procedure A. White solid (32.3 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93-7.84 (m, 1H), 7.72-7.63 (m, 1H), 7.55-7.44 (m, 2H), 5.29 (s, 2H); ^{13}C{^{1}H}NMR (100 MHz, $CDCl_3$) δ 171.1, 146.5, 134.0, 129.0, 125.7, 125.6, 122.0, 69.7; IR (cm_{-1}):1758, 1623, 1599, 1469, 1439, 1357, 1310, 1280, 1227, 1050, 1033, 997, 737; HRMS (ESI-TOF): ($[M+H]^+$) calcd for $C_8H_7O_2^+$: 135.0446; found: 135.0445.



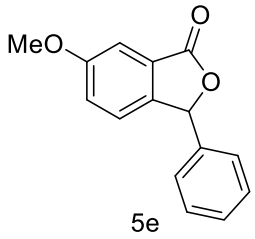
5c

3-phenylisobenzofuran-1(3H)-one (5c)[6]: The title compound was prepared according to the general procedure. Yellow solid (57.4 mg, 68% yield). ^{1}H NMR (400 MHz, CDCl3) δ 8.04-7.93 (m, 1H), 7.73-7.61 (m, 1H), 7.61-7.51 (m, 1H), 7.43-7.16 (m, 7H), 6.41 (s, 1H); ^{13}C{^{1}H}NMR (100 MHz, CDCl3) δ 170.5, 149.7, 136.4, 134.3, 129.4, 129.3, 129.0, 127.0, 125.7, 125.56, 122.9, 82.7; IR (cm^{-1}): 2963, 1734, 1640, 1599, 1457, 1292, 1068, 967, 725; HRMS (ESI-TOF): ($[M+H]^+$) calcd for $C_{14}H_{11}O_2^+$: 211.0759; found: 211.0756.



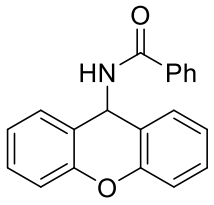
5d

3-(4-methoxyphenyl)isobenzofuran-1(3H)-one(5d)[6]: The title compound was prepared according to the general procedure. Yellow solid (75.0 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31-7.26 (m, 4H), 7.22-7.14 (m, 2H), 7.14-7.10 (m, 2H), 6.27 (s, 1H), 3.79 (s, 1H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 170.7, 160.8, 142.2, 136.6, 129.3, 129.0, 127.0, 123.8, 123.3, 107.3, 82.7, 55.8.



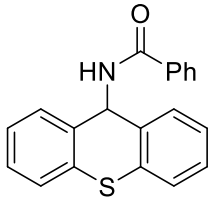
5e

6-methoxy-3-phenylisobenzofuran-1(3H)-one(5e)[7]: The title compound was prepared according to the general procedure. Yellow solid (70.1 mg, 73% yield). ^{1}H NMR (400 MHz, CDCl3) δ 7.91-7.84 (m, 1H), 7.61-7.54 (m, 1H), 7.53-7.45 (m, 1H), 7.27-7.21 (m, 1H), 7.11-7.05 (m, 2H), 6.84-6.78 (m, 2H), 6.29 (s, 1H), 3.72 (s, 3H); $^{13}C\{^{1}H\}$NMR (100 MHz, $CDCl_3$) δ 170.6, 160.4, 149.8, 134.3, 129.3, 128.8, 128.3, 125.9, 125.6, 123.0, 114.3, 82.8, 55.4.



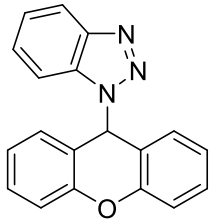
8a

***N*-(9H-xanthen-9-yl)benzamide (8a)[8]**: The title compound was prepared according to the general procedure. White Solid.(53.01 mg, 88%; eluent: 25%-50% Dichloromethane/ Petroleum ether); m.p. = 235-237 °C; ^{1}H NMR (400 MHz, DMSO) δ (ppm) = 9.47 (d, *J* = 8.5 Hz, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.0 Hz, 1H), 7.45 (d, *J* = 7.4 Hz, 2H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 7.13 (t, *J* = 7.4 Hz, 2H), 6.56 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, DMSO) δ (ppm) = 166.26, 151.05, 134.31, 131.92, 129.45, 129.39, 128.73, 127.97, 123.92, 122.20, 116.59, 43.51; IR(KBr): 3446, 3328, 1629, 1578, 1518, 1481, 1458,1333, 1259,1212, 751 cm^{-1}; HRMS (ESI) for $C_{20}H_{15}NO_2Na[M+Na]^+$ calcd. 324.1000, found 324.1013.



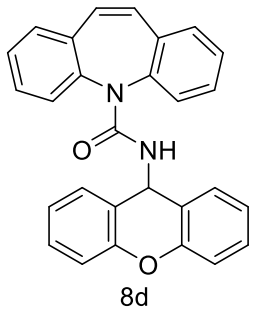
8b

***N*-(9H-thioxanthen-9-yl)benzamide (8b)[8]**: The title compound was prepared according to the general procedure. Yellow Solid.(50.7 mg, 80%; eluent: 25%-50% Dichloromethane/ Petroleum ether); m.p. = 180-181 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.66 (d, *J* = 6.7 Hz, 2H), 7.62 (s, 2H), 7.44-7.49(m, 2H), 7.39 (d, *J* = 5.8 Hz, 1H), 7.29-7.34 (m, 2H), 7.22-7.28 (m, 4H), 7.03 (d, *J* = 6.9 Hz, 1H), 6.45 (d, *J* = 7.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 166.36, 134.85, 134.00, 132.90, 131.58, 129.26, 128.46, 127.83, 127.14, 127.03, 127.01, 53.74; IR(KBr): 3448, 1641, 1530, 1458, 1384, 731,696 cm^{-1}; HRMS (ESI) for $C_{20}H_{15}NSONa[M+Na]^+$ calcd. 340.0772, found 340.0770.



8c

1-(9*H*-xanthen-9-yl)-1*H*-benzo[d][1,2,3]triazole (8c)[9]: The title compound was prepared according to the general procedure. White Solid.(43.66 mg,73%; eluent: 25%-50% Dichloromethane/ Petroleum ether); m.p.=215-216 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.97 (d, *J* = 7.6 Hz, 1H), 7.58 (s, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 4.4 Hz, 3H), 7.13 (d, *J* = 6.6 Hz, 1H), 7.00 (d, *J* = 5.6 Hz, 2H), 6.82 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 150.97, 146.87, 130.44, 129.30, 127.35, 123.96 (d, *J* = 8.1 Hz), 119.97, 117.02, 116.80, 110.10, 55.36; HRMS (ESI) for $C_{19}H_{13}N_3ONa[M+Na]^+$ calcd. 322.0956, found 322.0970.



8d

***N*-(9H-xanthen-9-yl)-5H-dibenzo[b,f]azepine-5-carboxamide (8d)[10]**: The title compound was prepared according to the general procedure. Yellow Solid.(62.42 mg, 75%; eluent: 25%-50% Dichloromethane/ Petroleum ether); m.p.=209-210 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.47-7.55 (m, 4H), 7.39-7.43 (m, 2H), 7.34-7.37 (m, 2H), 7.27-7.32 (m, 2H), 7.22-7.26 (m, 2H), 7.09-7.15 (m, 2H), 7.0-7.05 (m, 2H), 6.93-6.99 (m, 2H), 6.41 (d, *J* = 8.7 Hz, 1H), 4.87 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) = 156.47, 150.69, 139.78, 135.22, 130.45,129.67, 129.55, 129.15, 129.06, 128.89, 127.85, 123.35, 121.76, 116.37, 44.79; IR(KBr): 3652, 3397, 1655, 1637, 1483, 1457, 1435, 1336, 1257, 1210, 744 cm^{-1}; HRMS (ESI) for $C_{16}H_{15}NO_3SNa[M+Na]^+$ calcd. 439.1244, found 439.1435.

7. Reference

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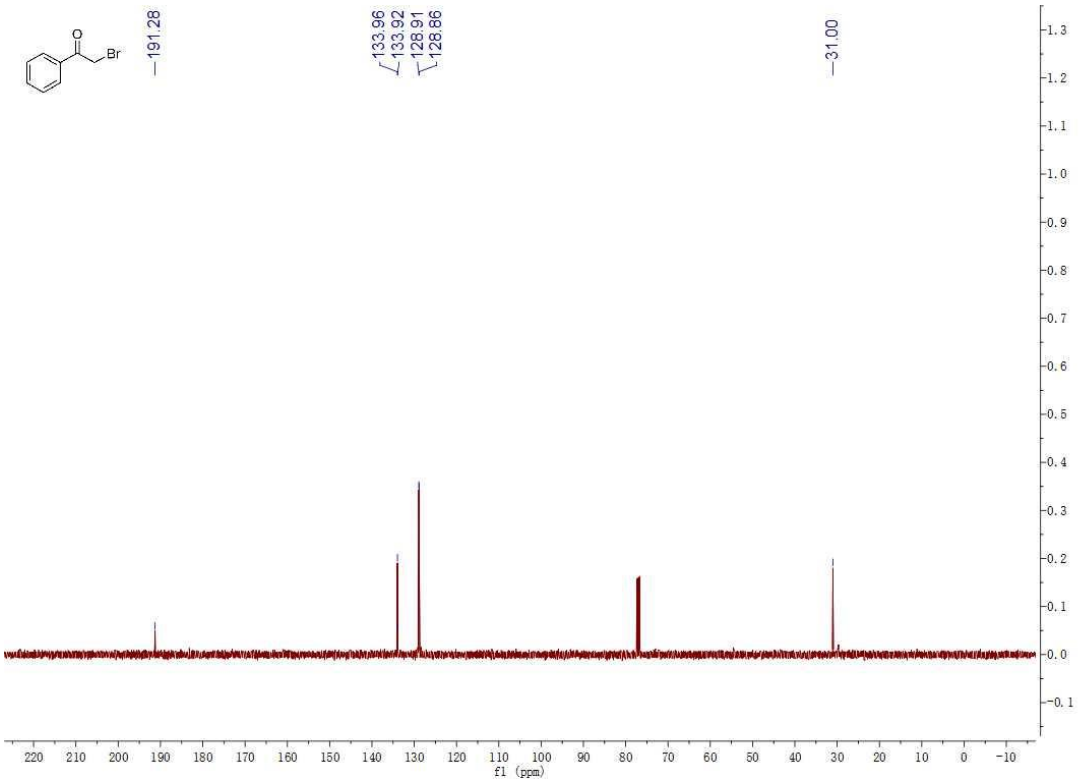
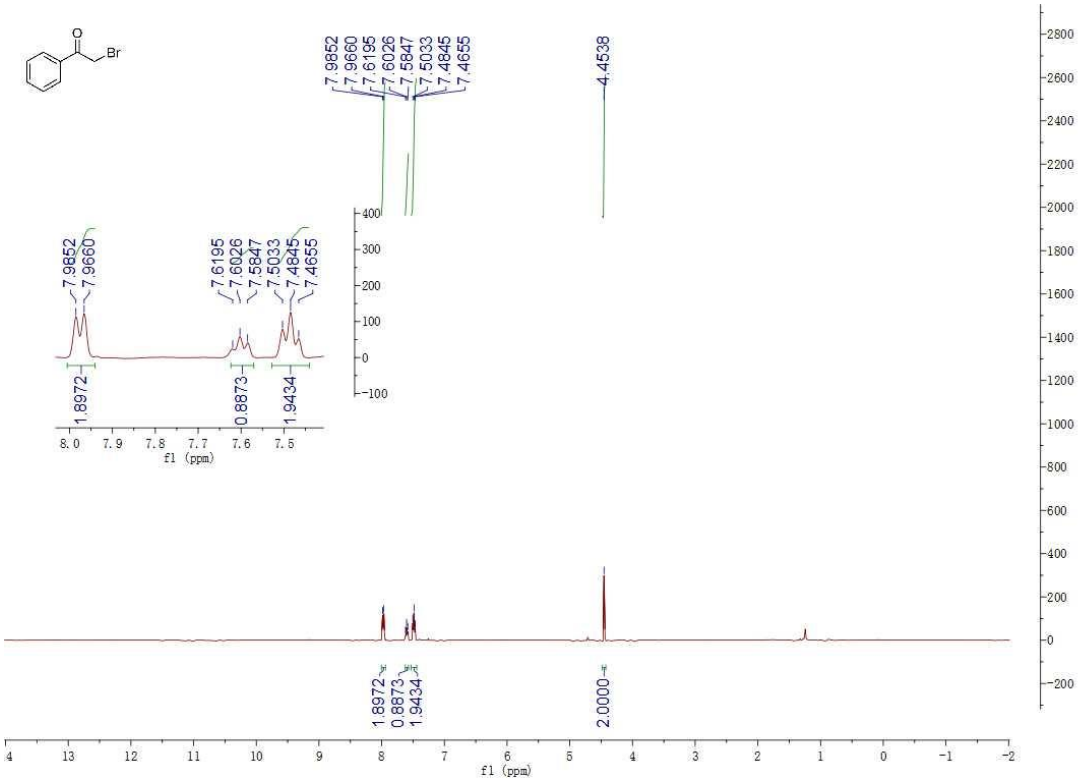
8. Spectra of All Products

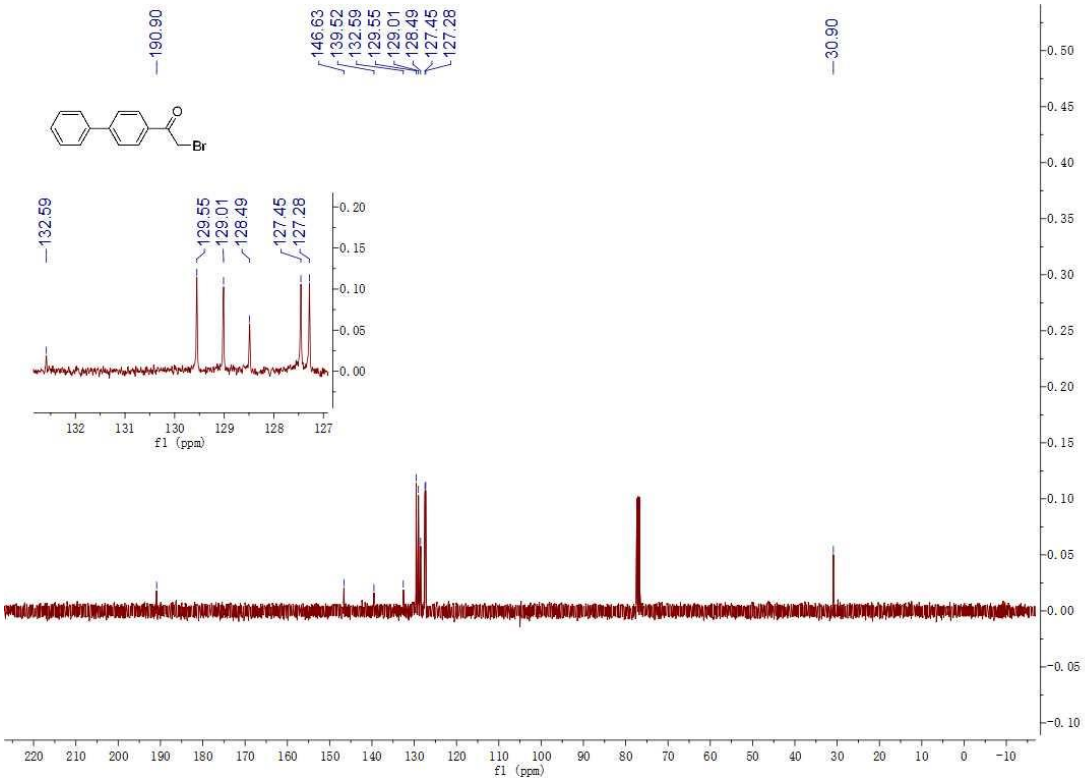
^{13}C NMR (101 MHz, $CDCl_3$) 3a



^{1}H NMR (400 MHz, $CDCl_3$) 3a



^{13}C NMR (101 MHz, $CDCl_3$) 3b



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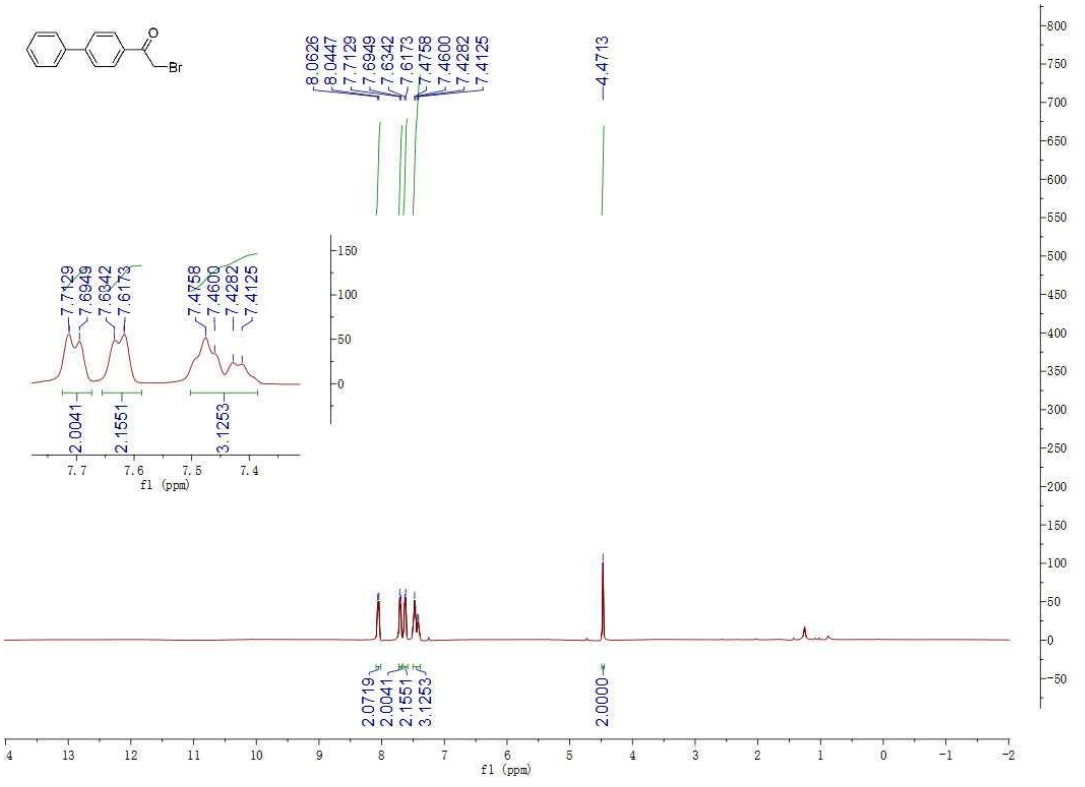
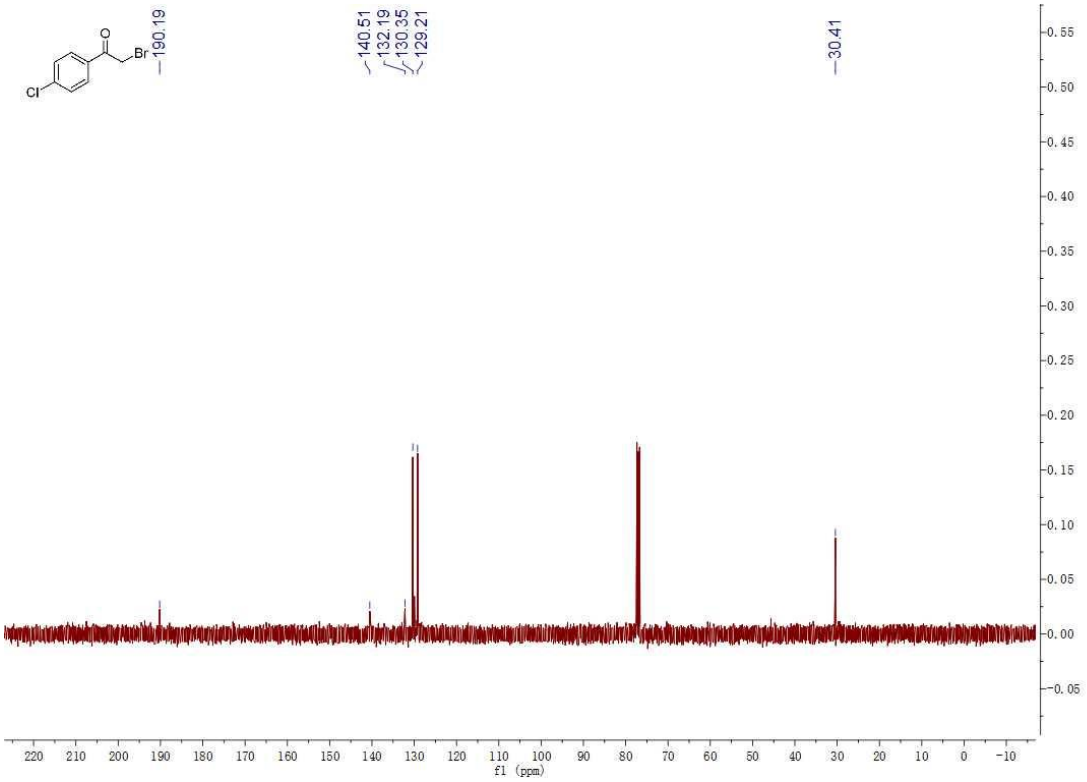


^{13}C NMR (101 MHz, $CDCl_3$) 3c



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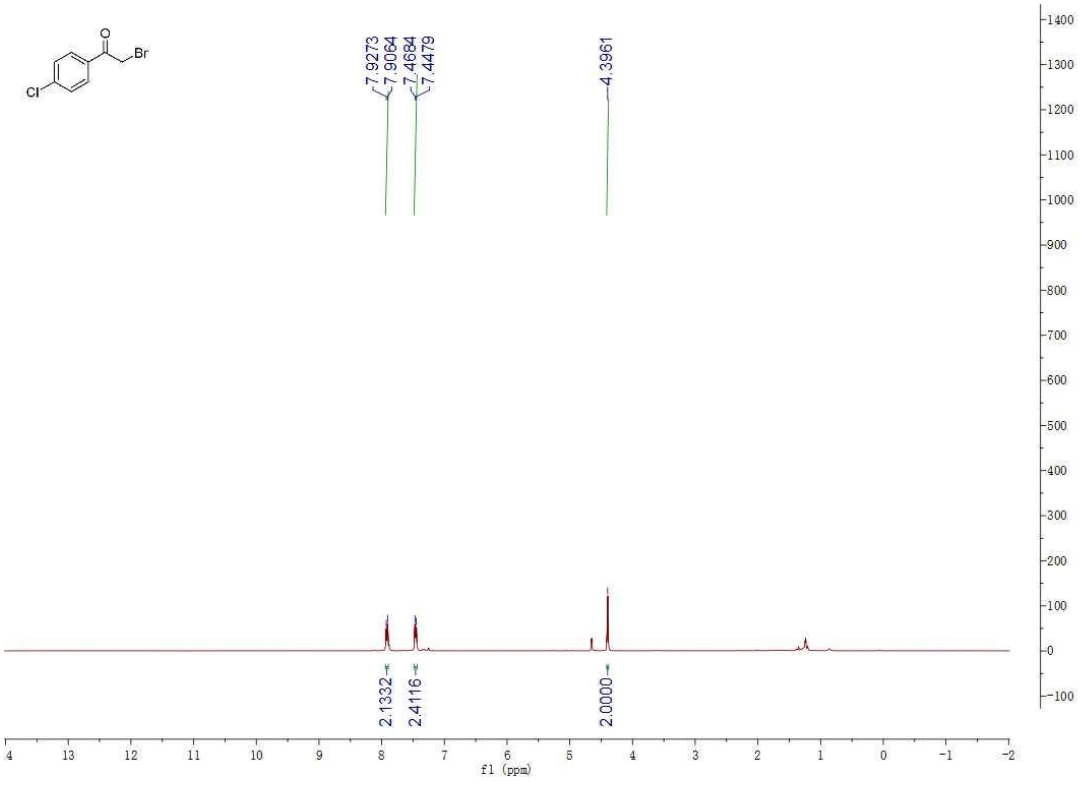
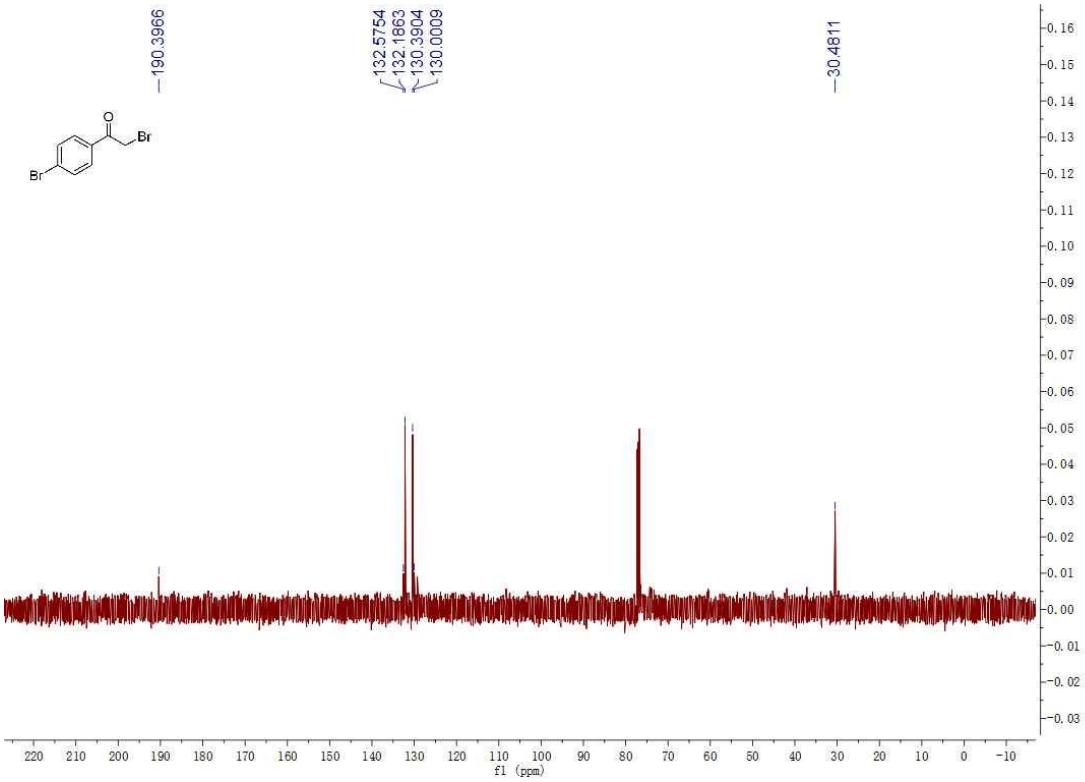
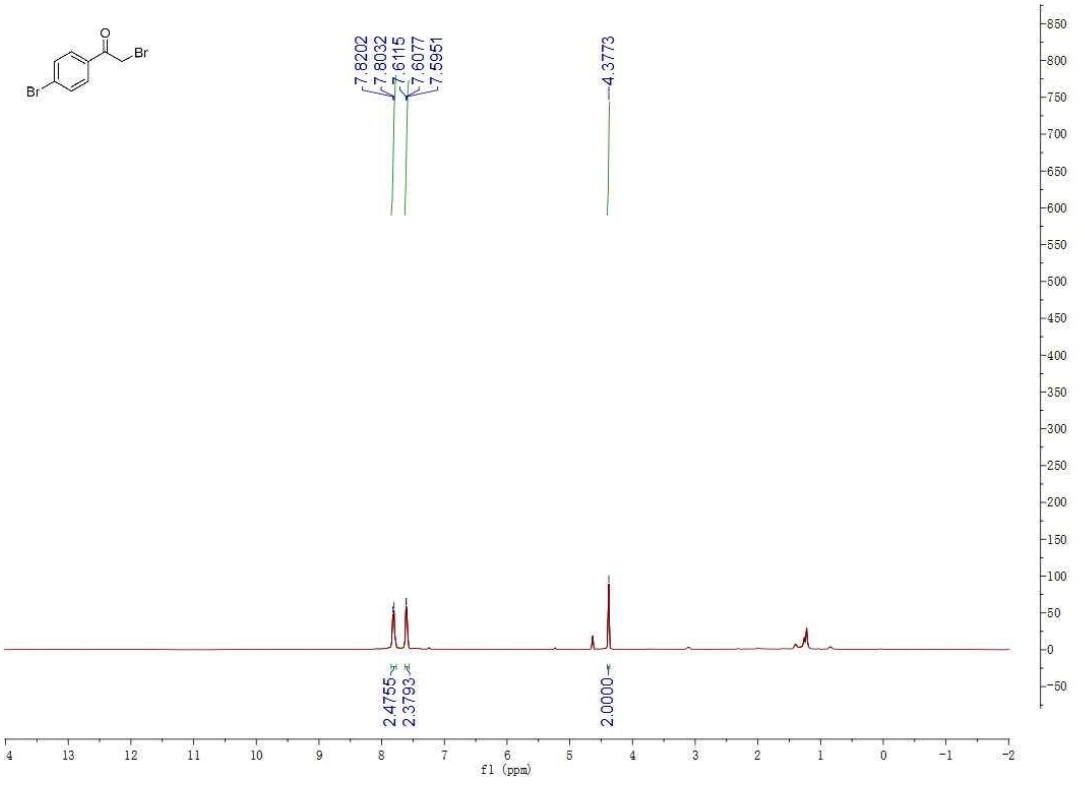


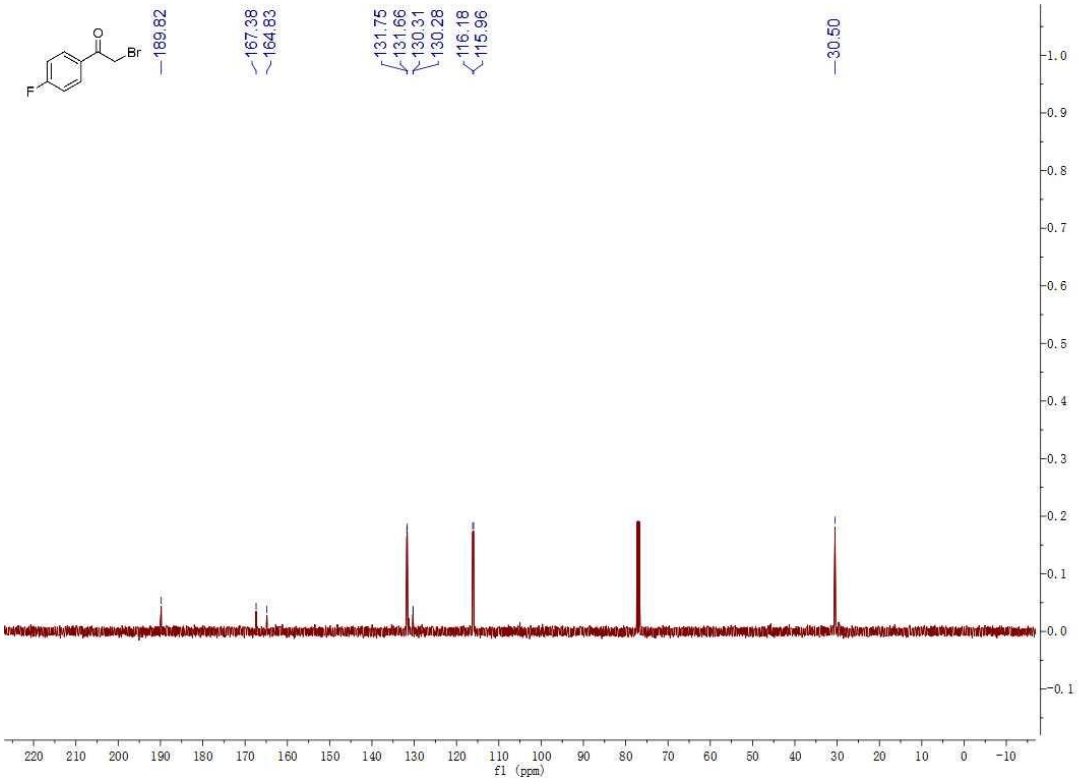
^{13}C NMR (101 MHz, $CDCl_3$) 3d

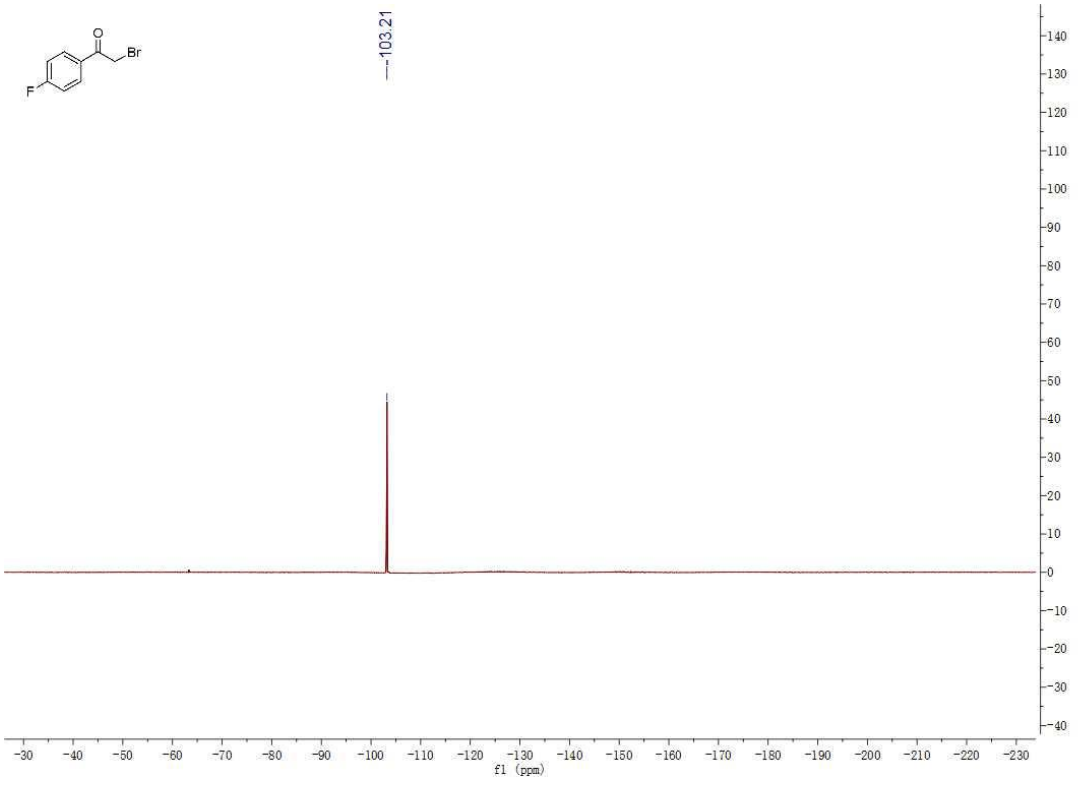


^{1}H NMR (400 MHz, $CDCl_3$) 3d

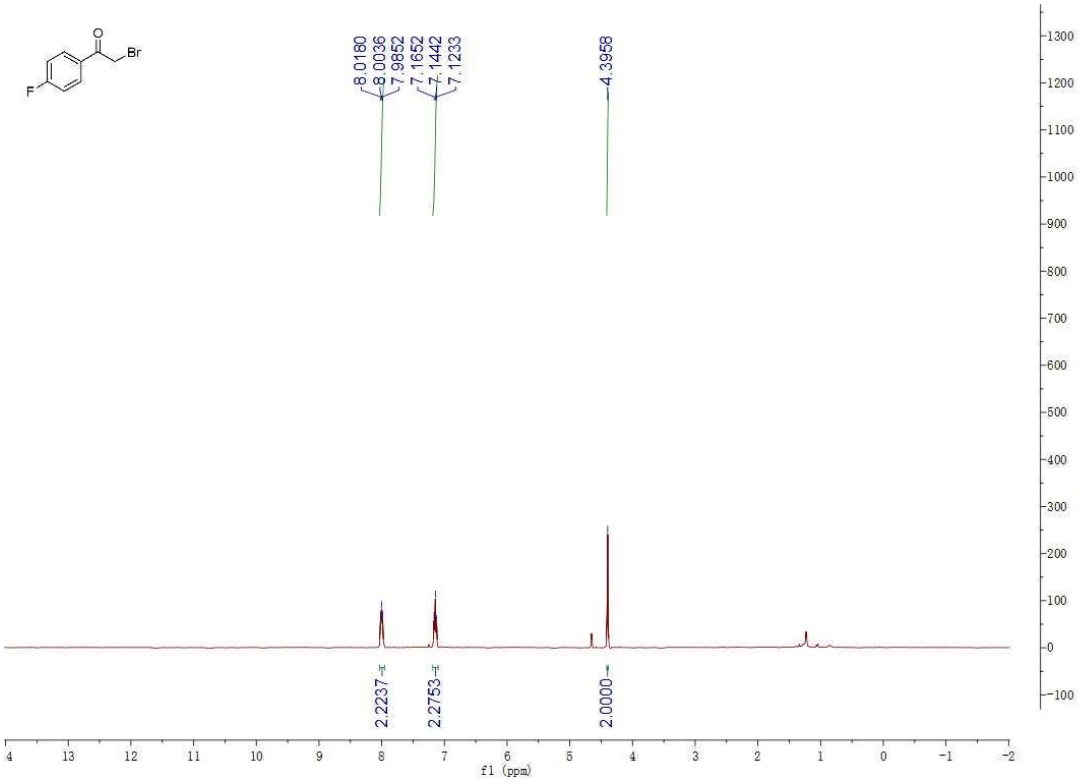


^{13}C NMR (101 MHz, $CDCl_3$) 3e

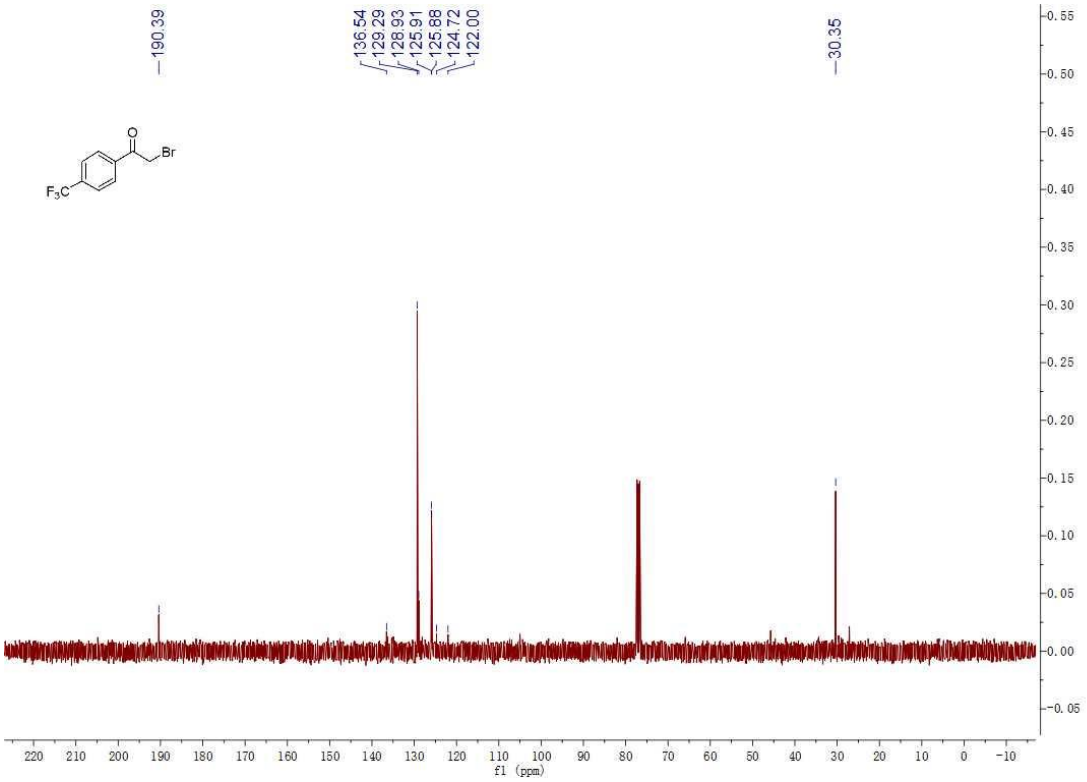


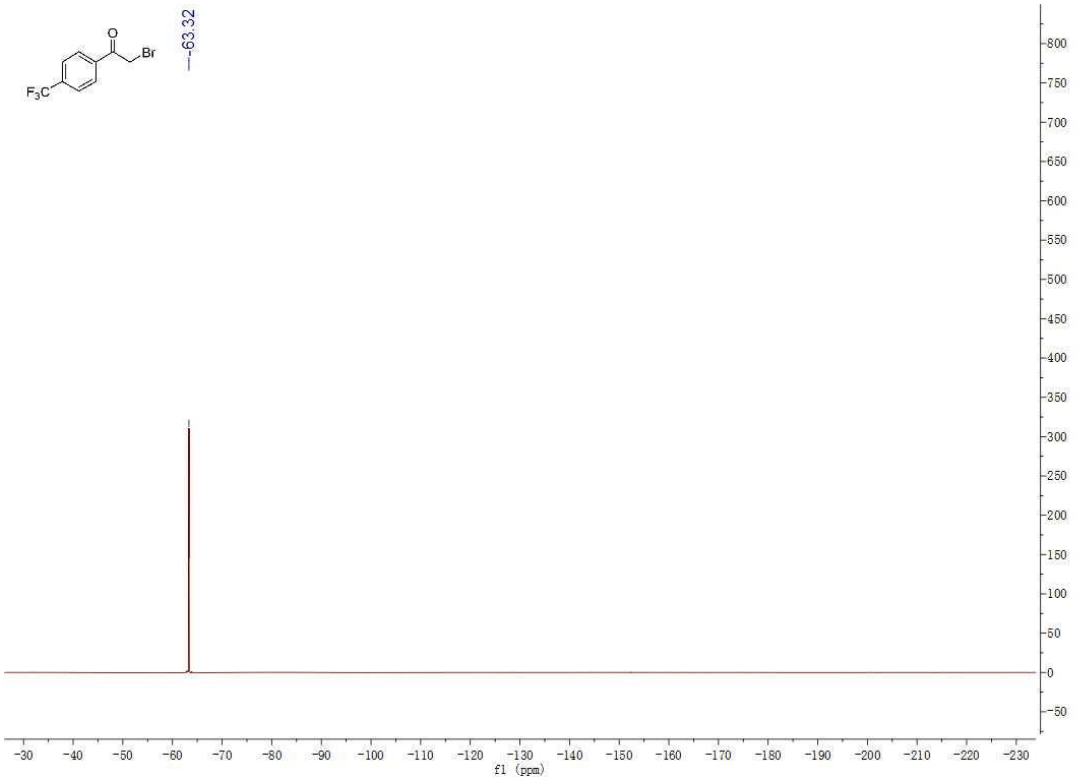


^{1}H NMR (400 MHz, $CDCl_3$) 3e

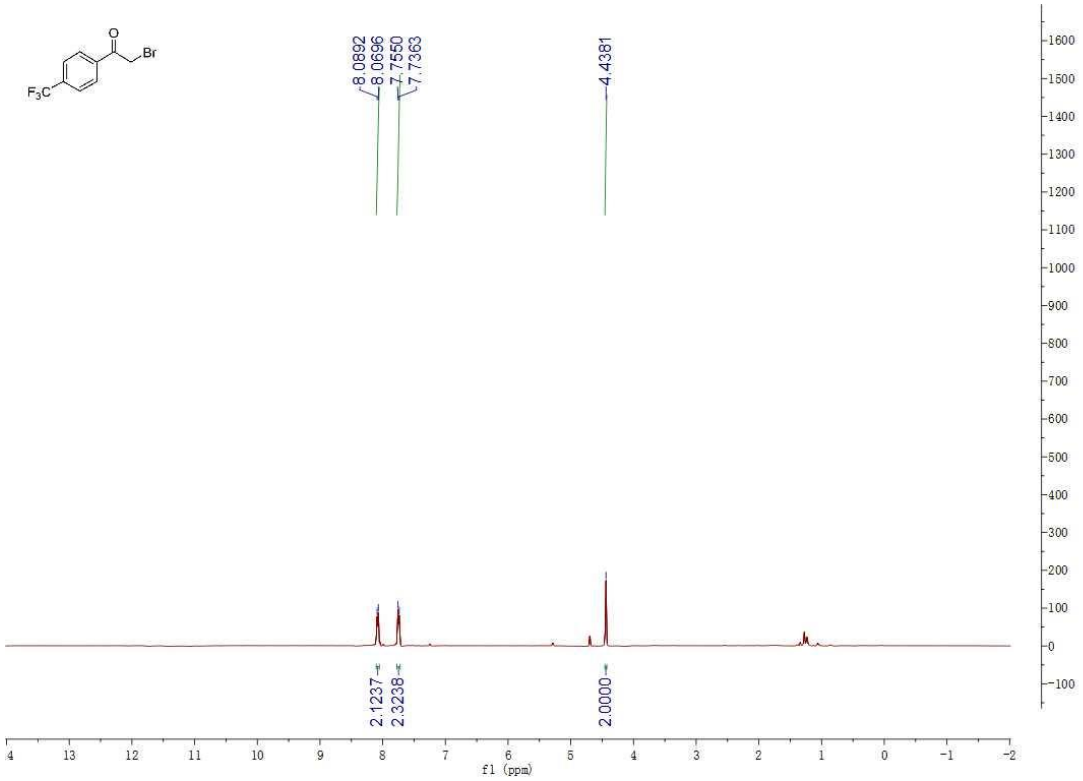


^{13}C NMR (101 MHz, $CDCl_3$) 3f





^{1}H NMR (400 MHz, $CDCl_3$) 3f


O
Br
F3C
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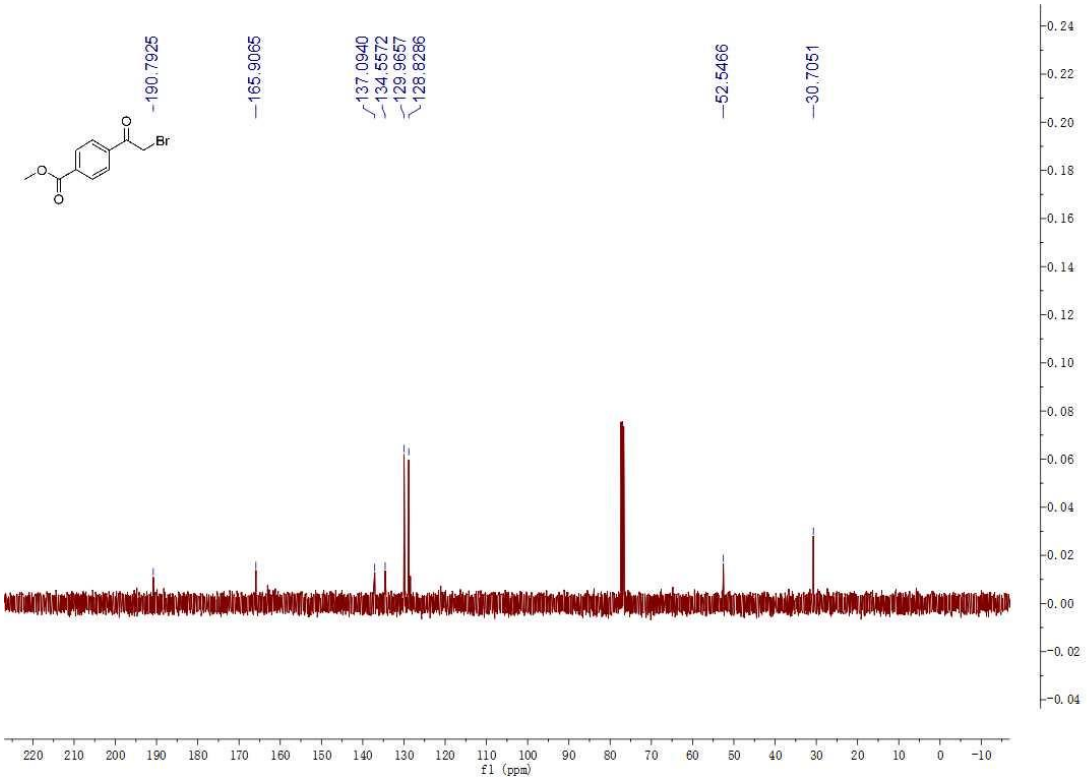
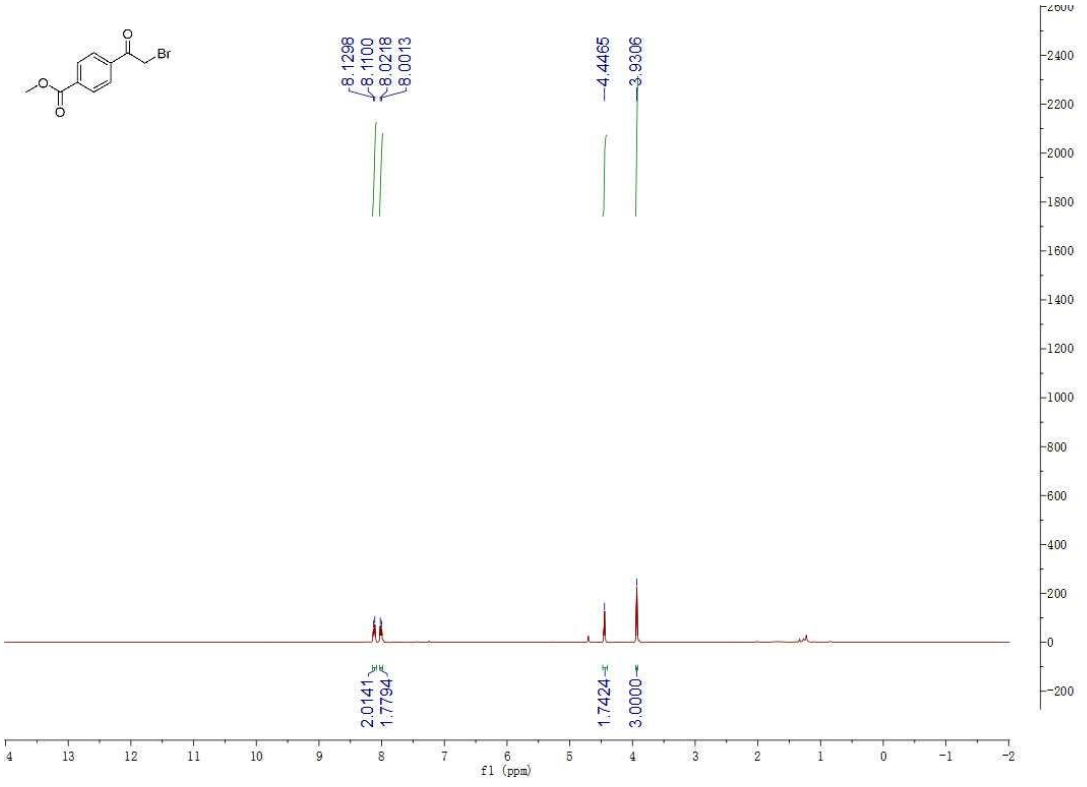
8.0696
7.7550
7.7363
4.4381
2.1237
2.3238
2.0000
f1 (ppm)

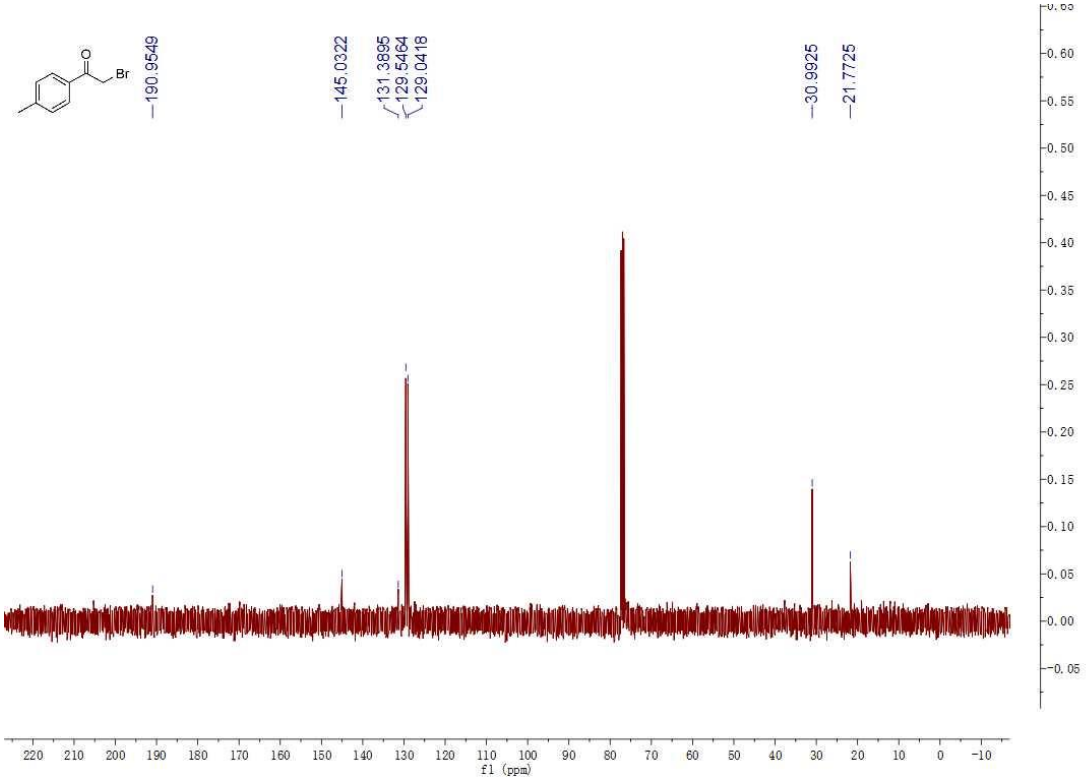
^{13}C NMR (101 MHz, $CDCl_3$) 3g



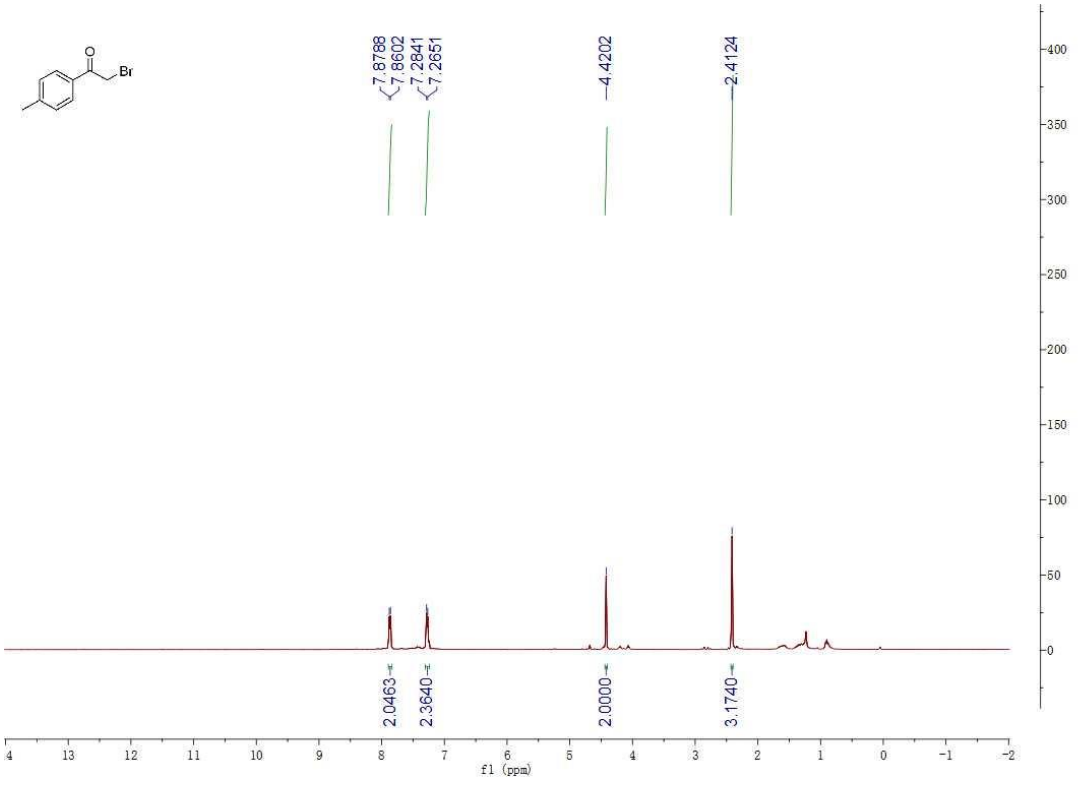
^{1}H NMR (400 MHz, $CDCl_3$) 3g



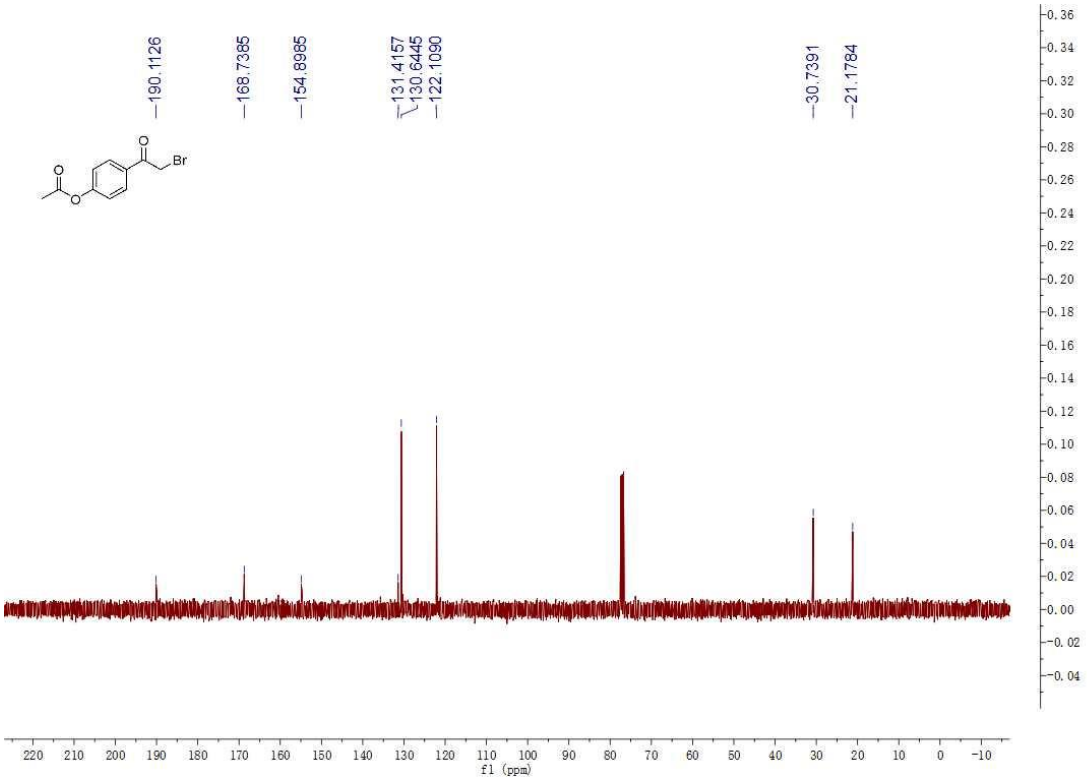
^{13}C NMR (101 MHz, $CDCl_3$) 3h



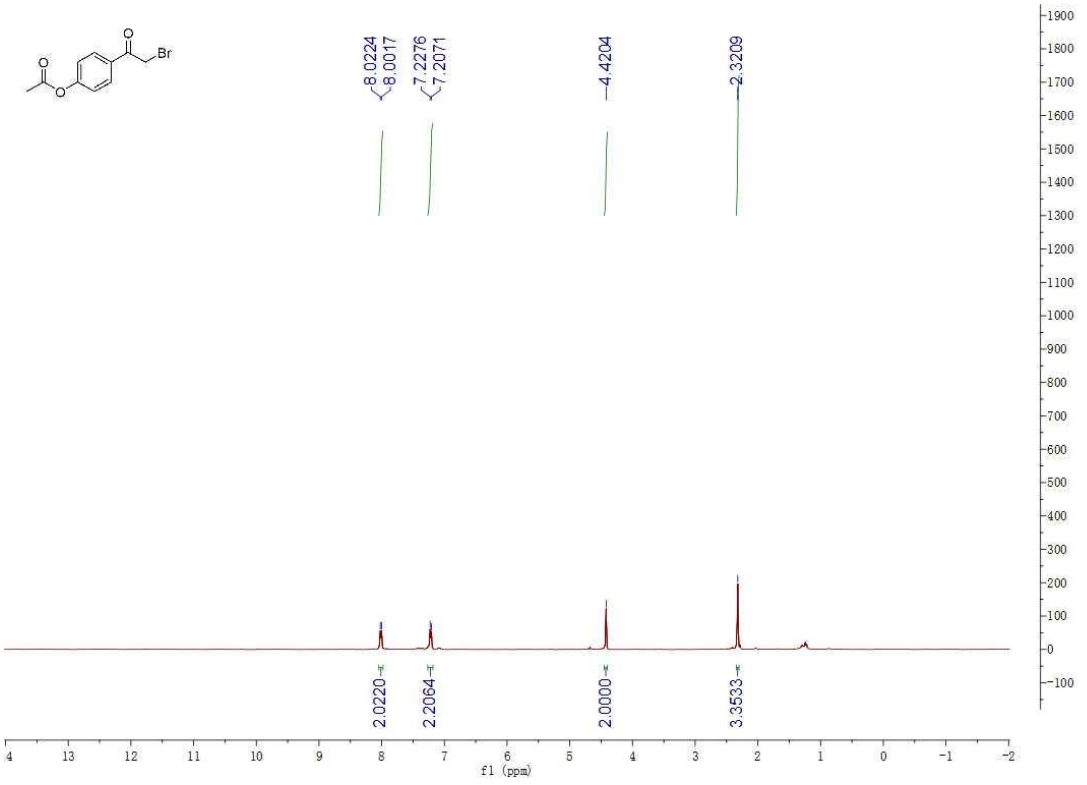
^{1}H NMR (400 MHz, $CDCl_3$) 3h



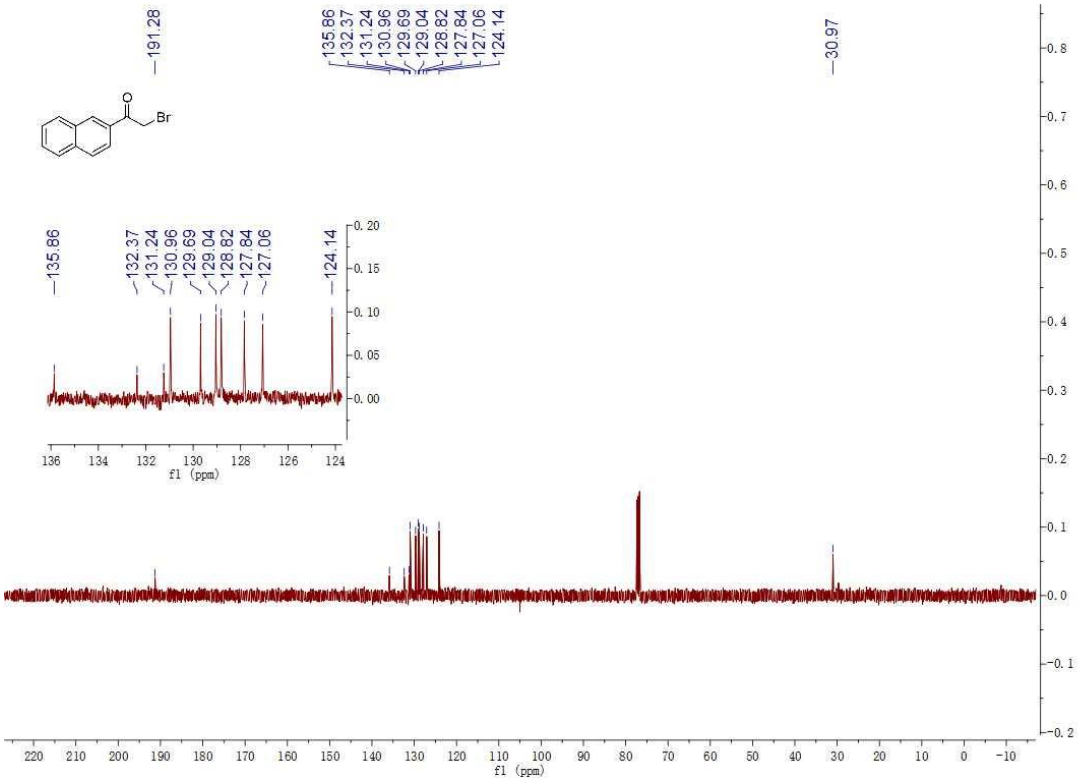
^{13}C NMR (101 MHz, $CDCl_3$) 3i



^{1}H NMR (400 MHz, $CDCl_3$) 3i



^{13}C NMR (101 MHz, $CDCl_3$) 3j



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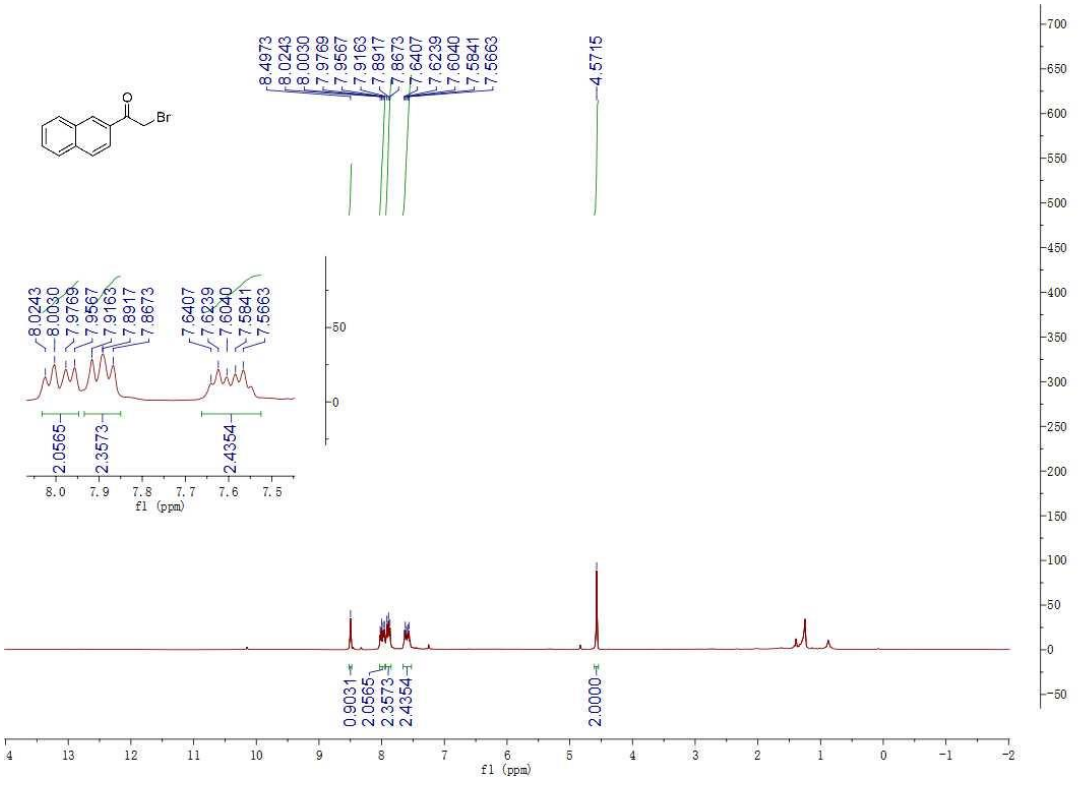
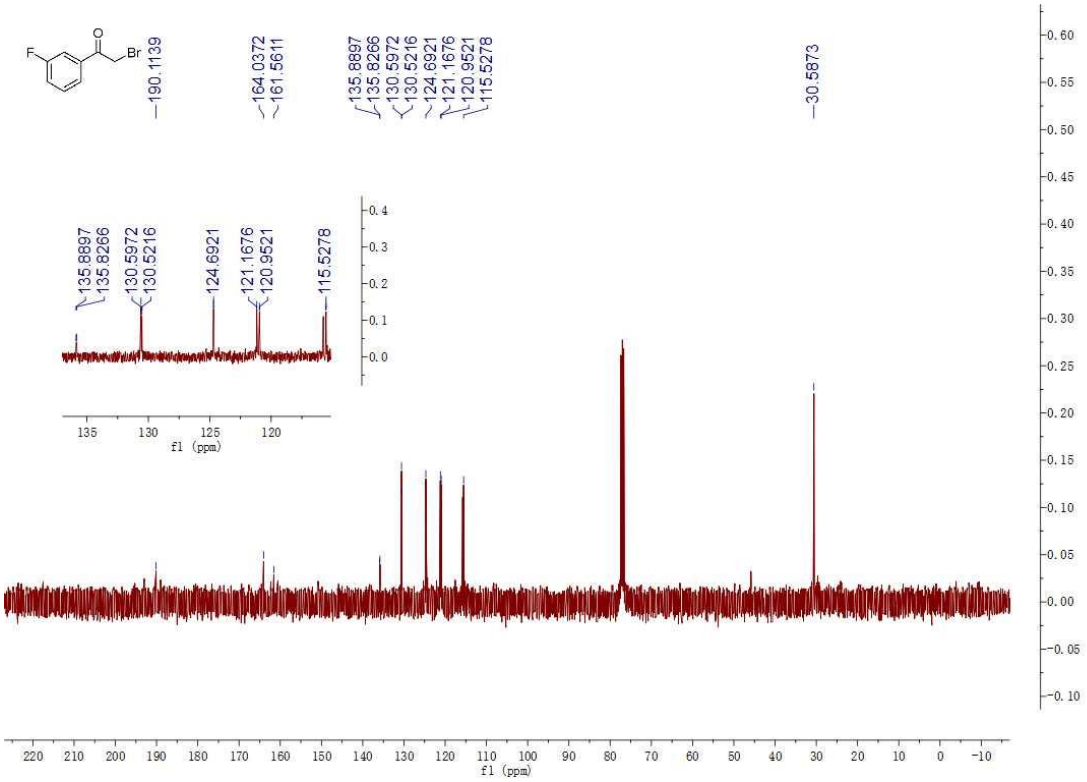
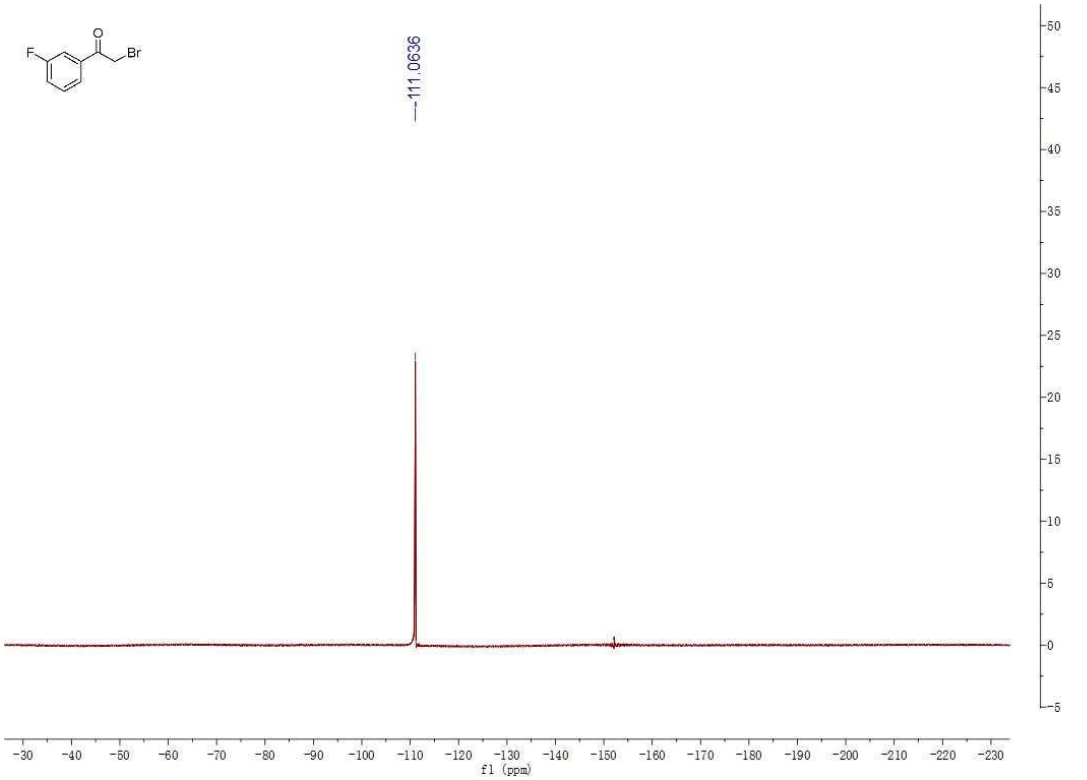
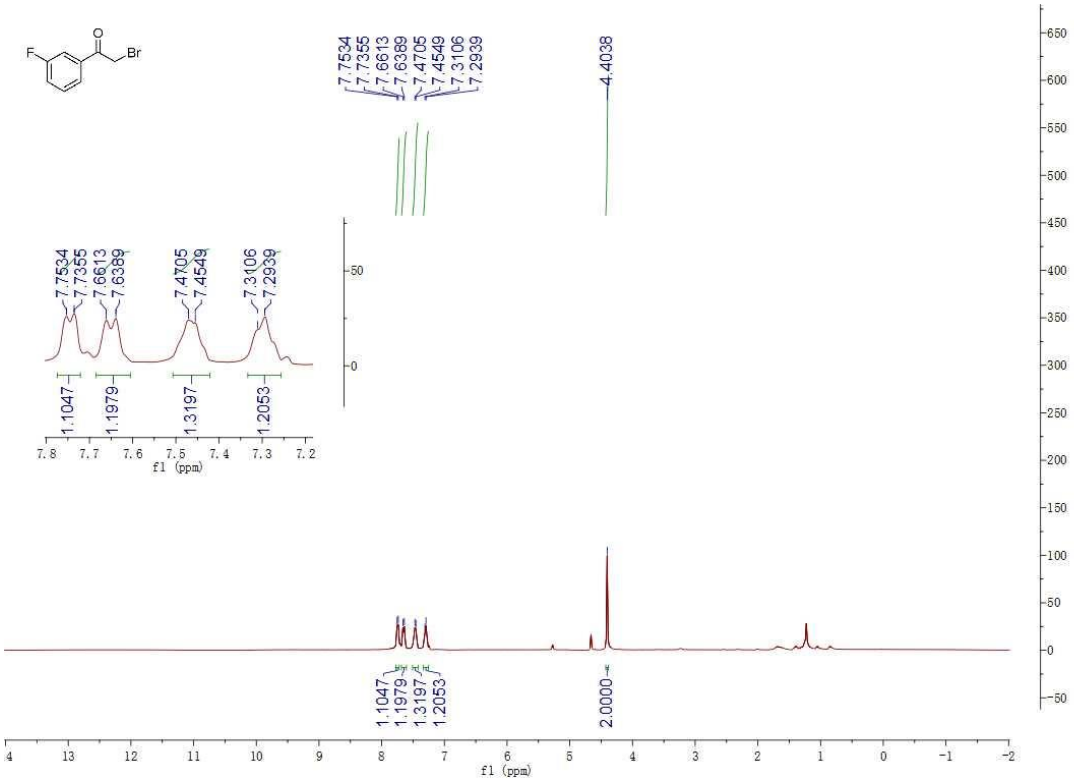


^{13}C NMR (101 MHz, $CDCl_3$) 3k

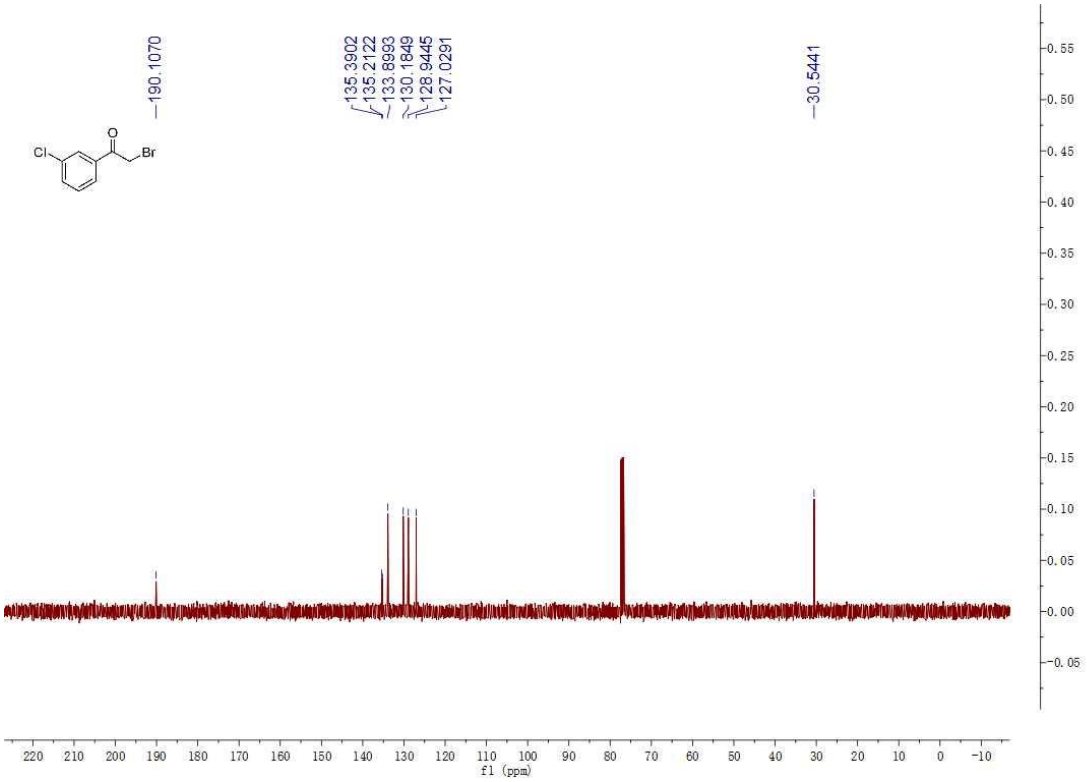




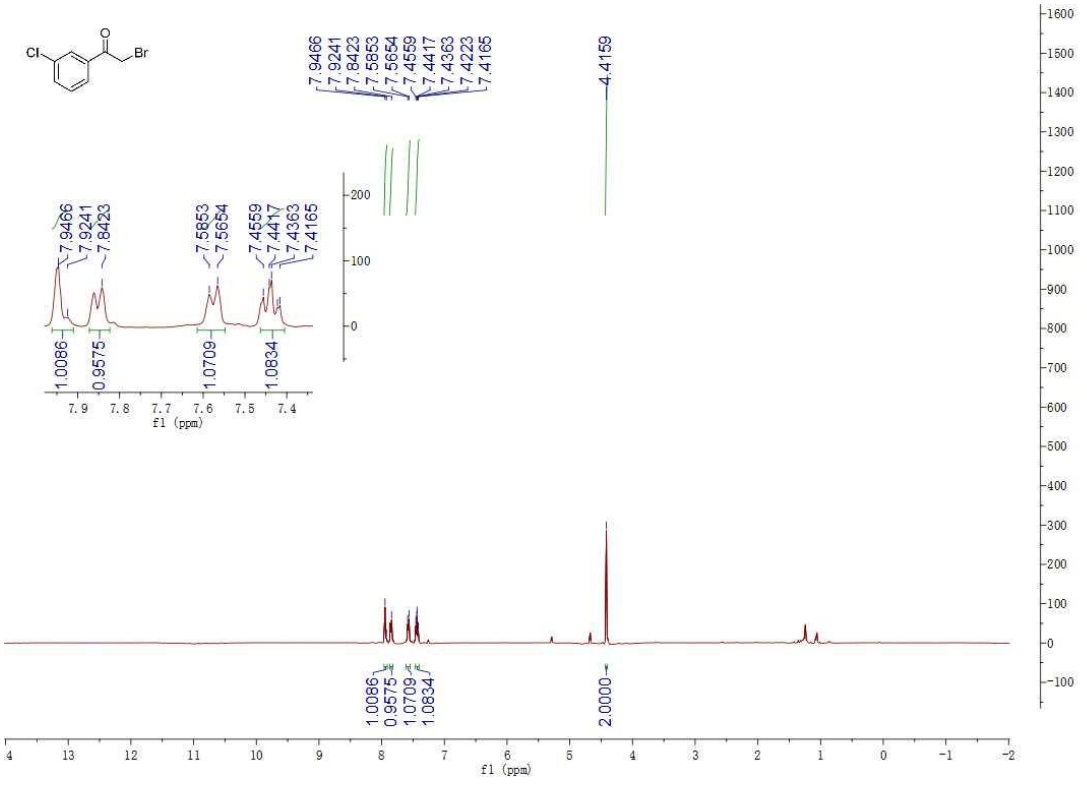
^{1}H NMR (400 MHz, $CDCl_3$) 3k



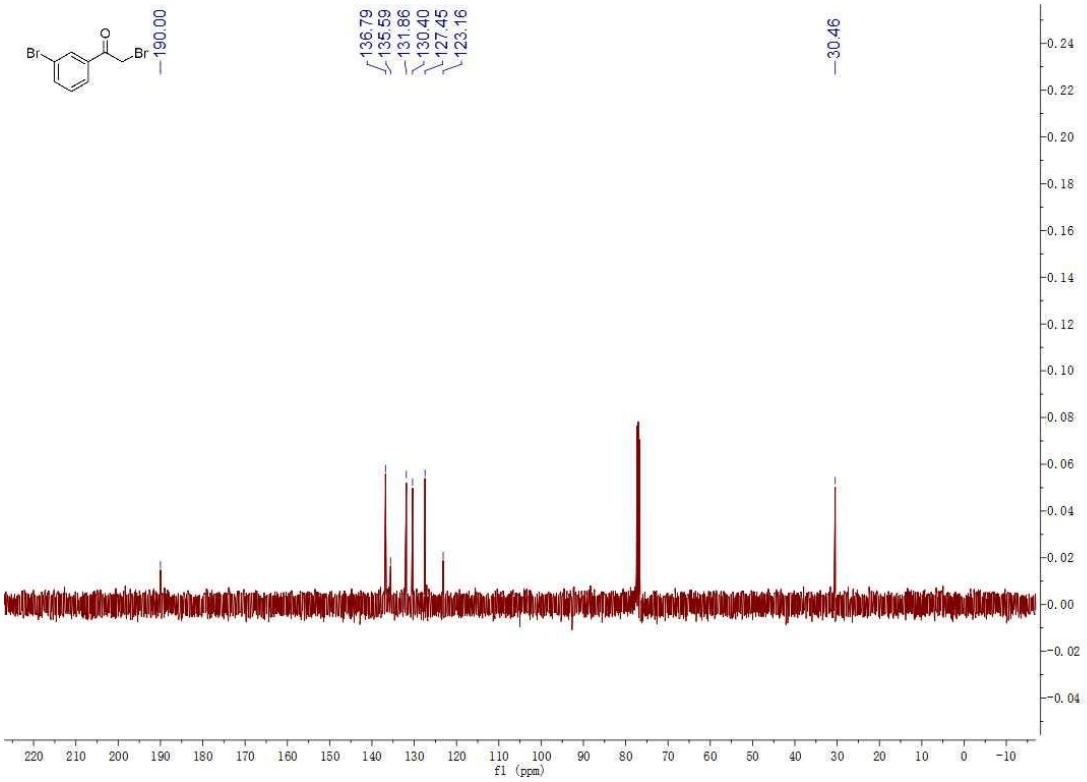
^{13}C NMR (101 MHz, $CDCl_3$) 3l



^{1}H NMR (400 MHz, $CDCl_3$) 3l



^{13}C NMR (101 MHz, $CDCl_3$) 3m



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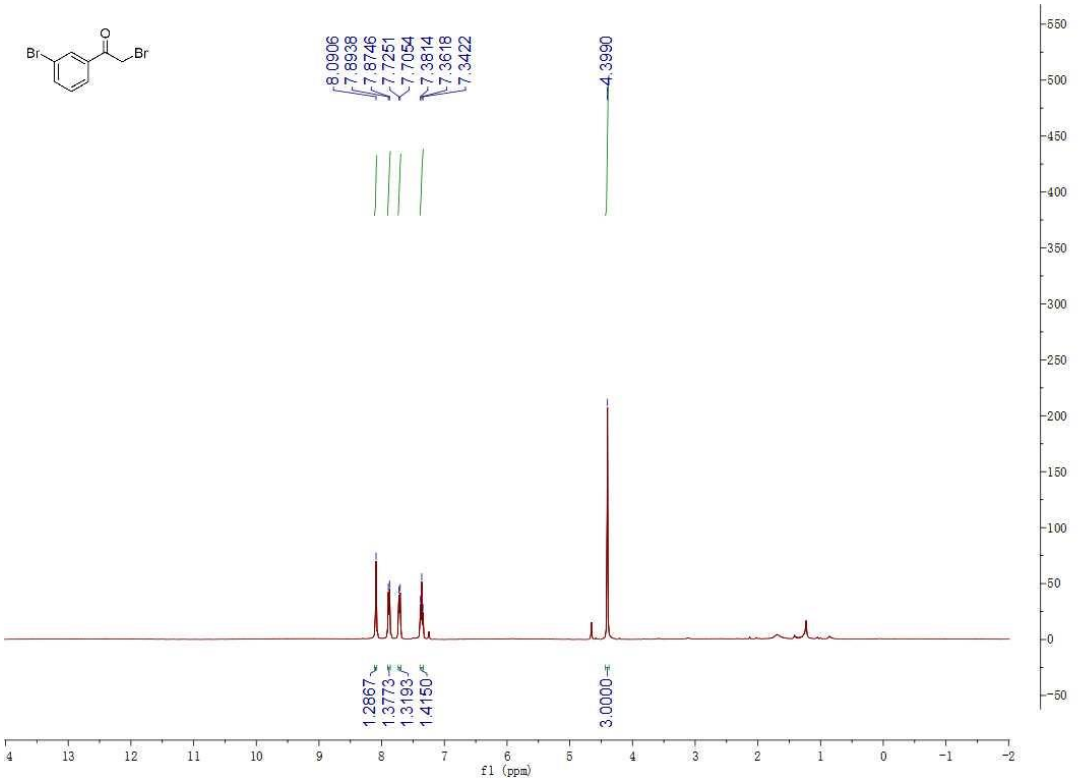

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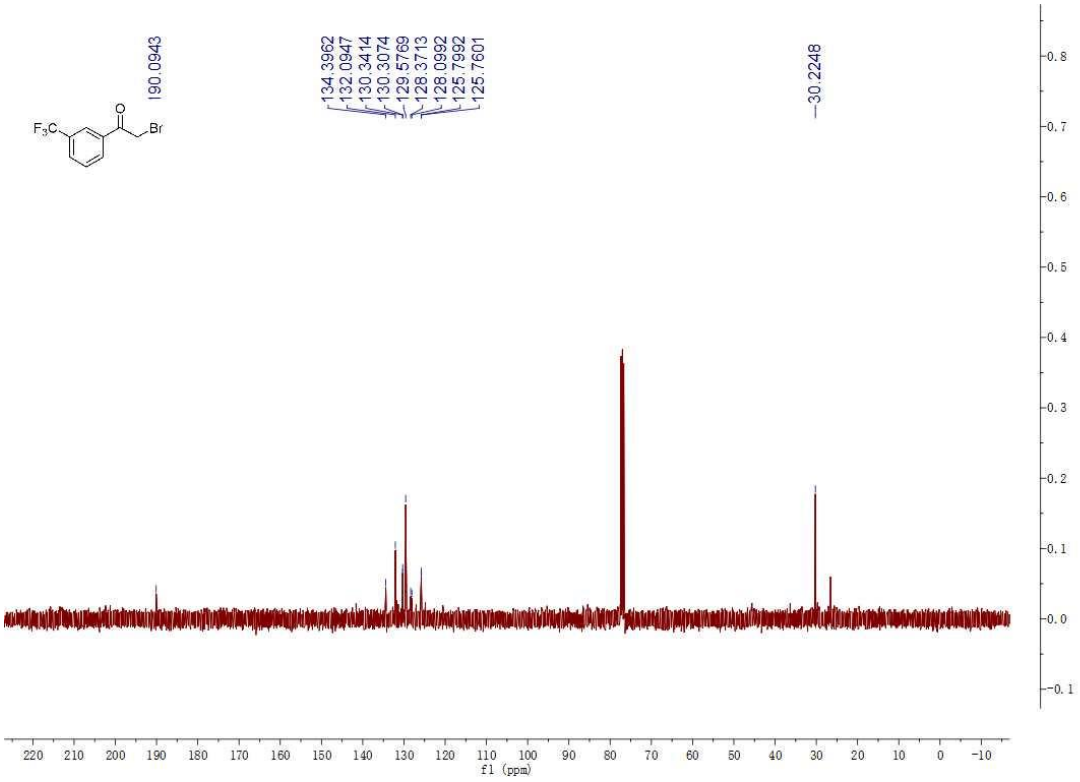

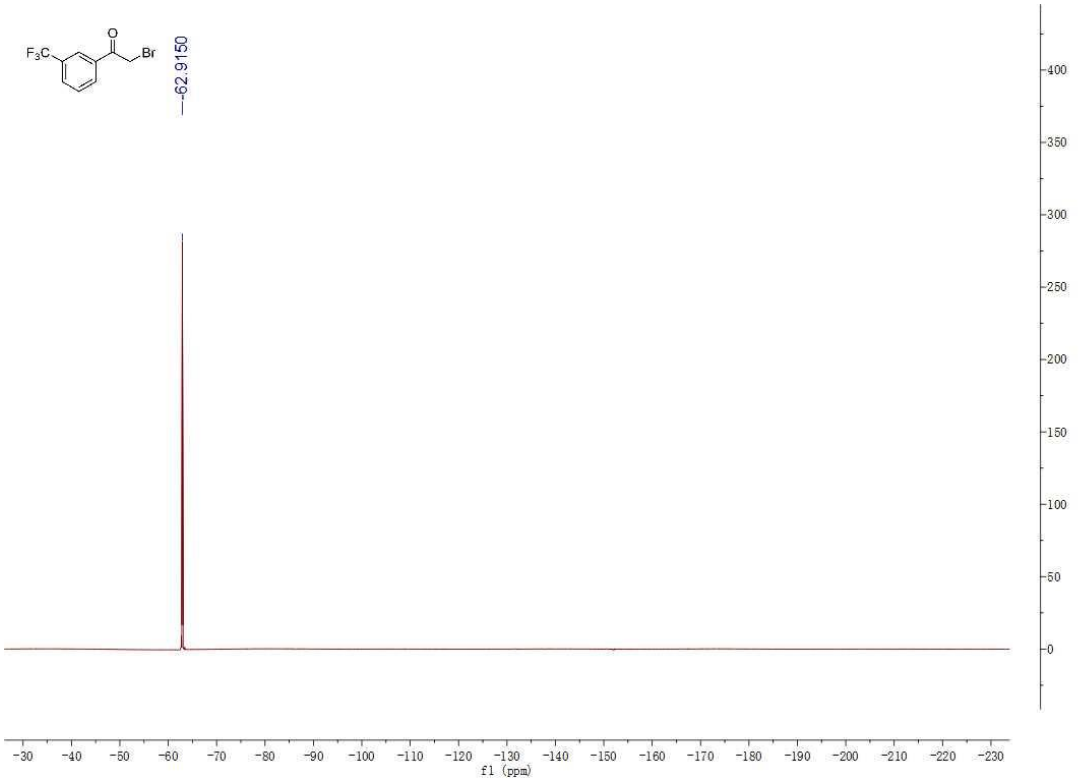

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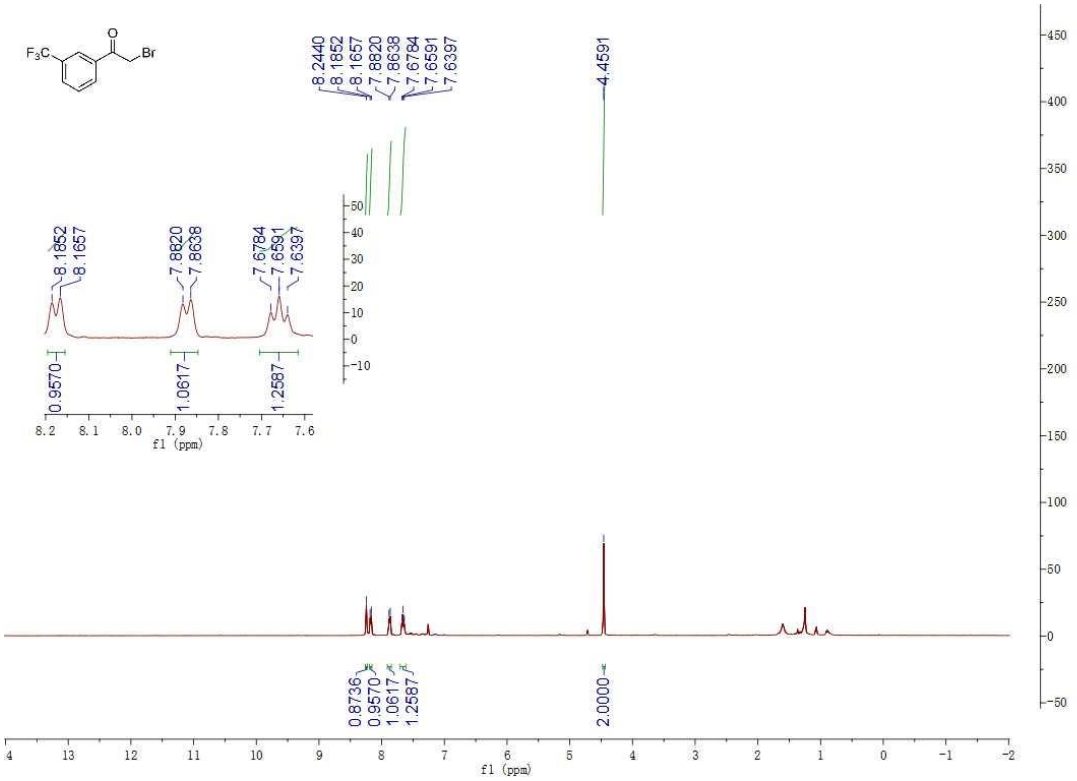
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Br
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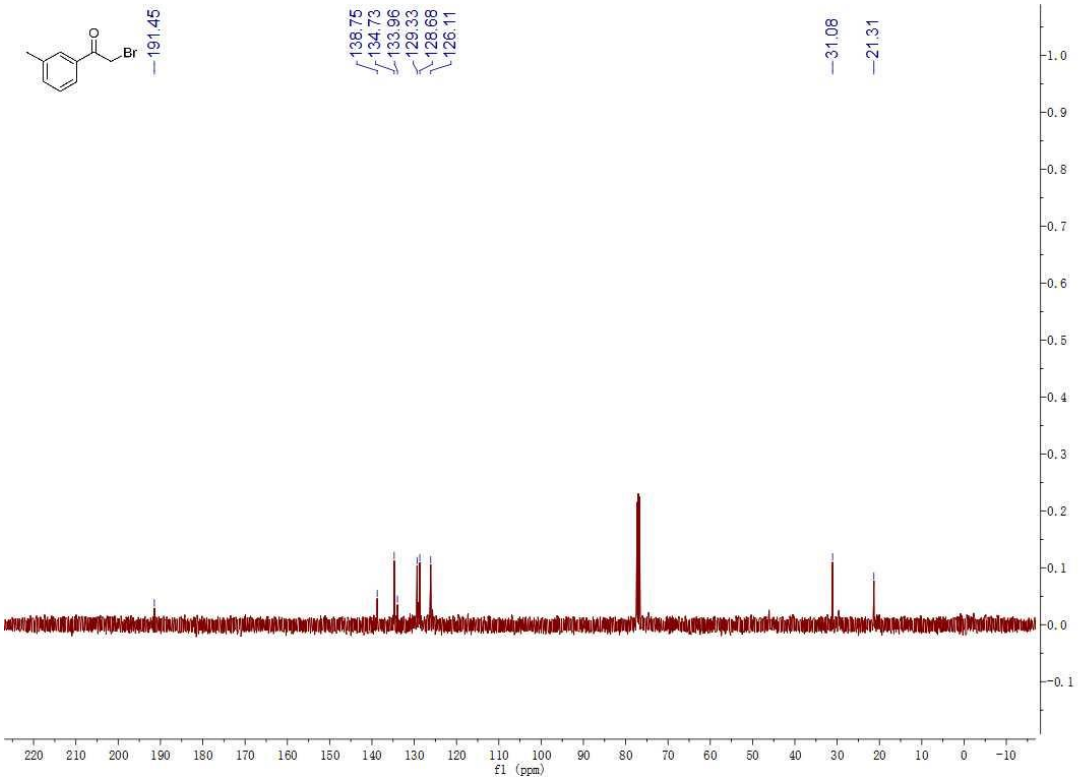
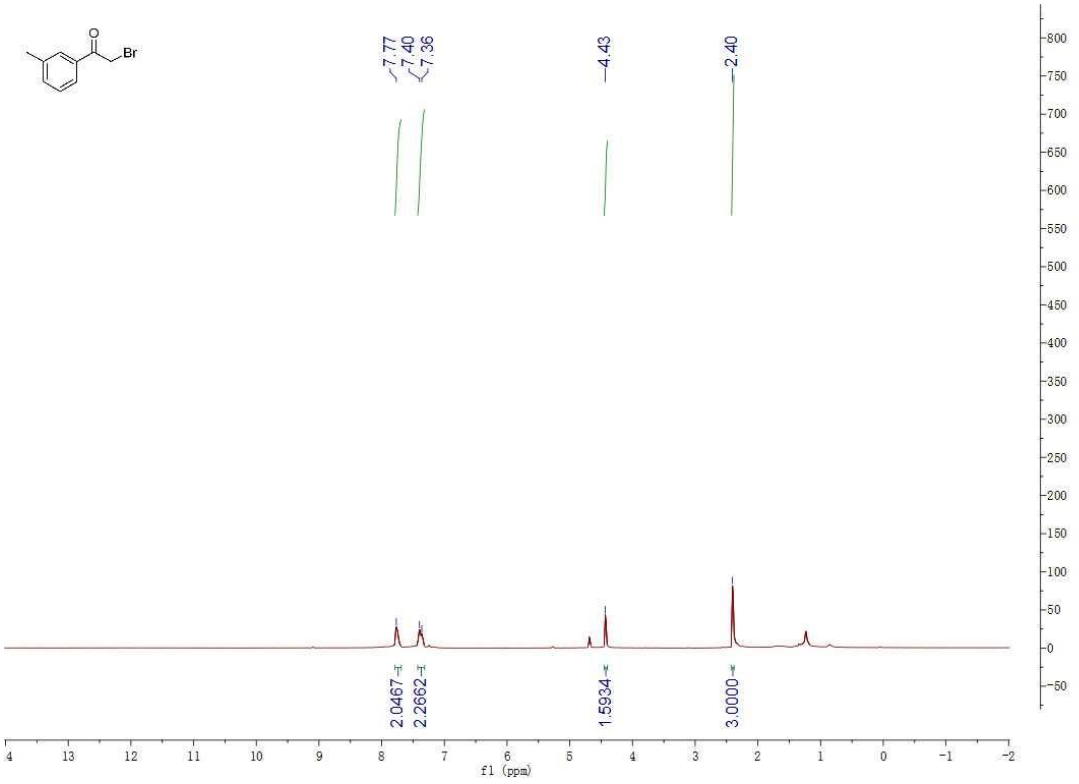
7.6397
4.4591
0.9570
1.0617
1.2587
f1 (ppm)
0.8736
2.0000

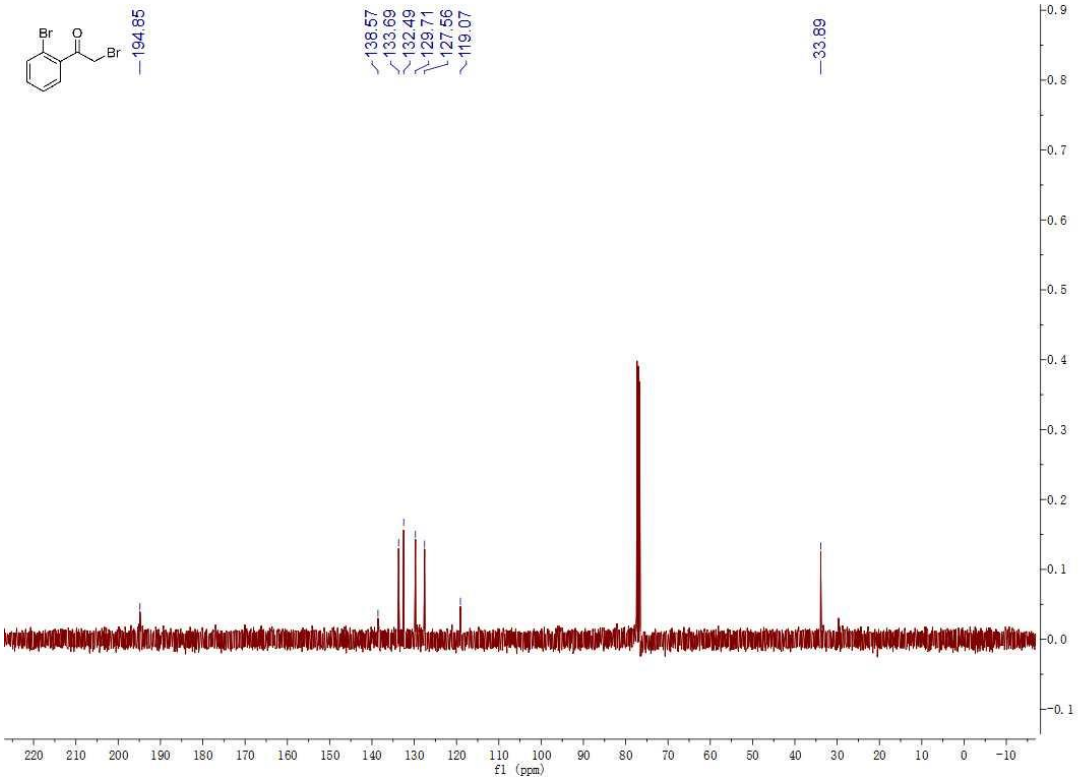
^{13}C NMR (101 MHz, $CDCl_3$) 3o



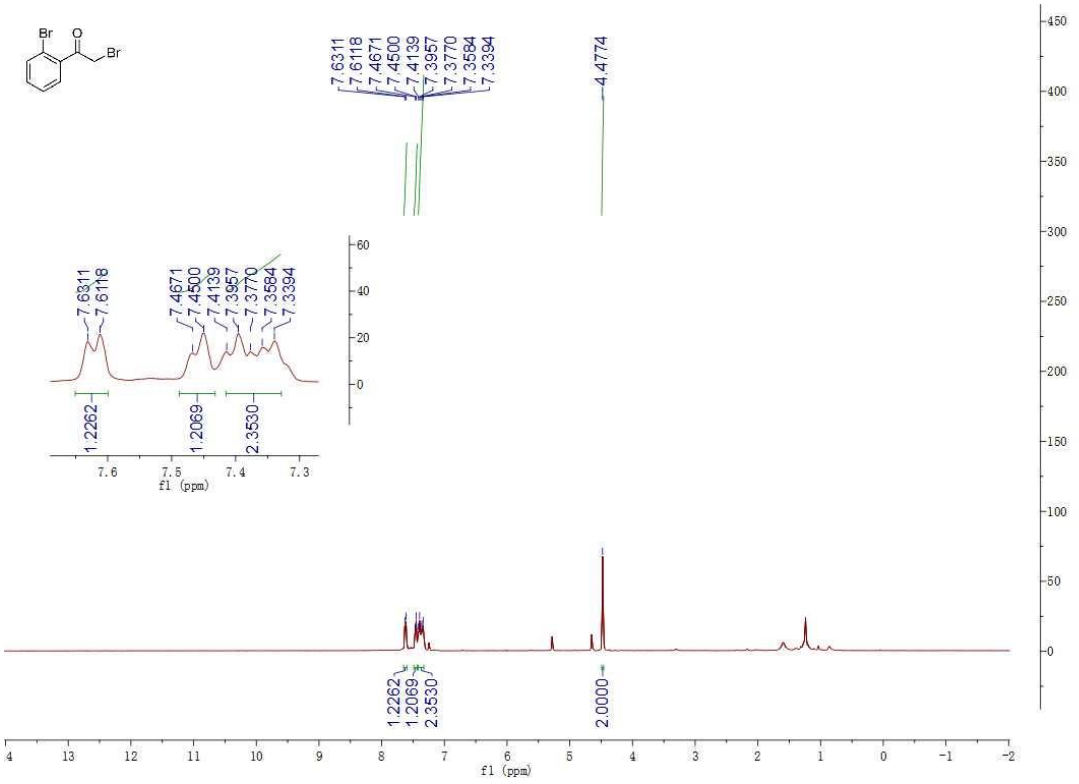
^{1}H NMR (400 MHz, $CDCl_3$) 3o



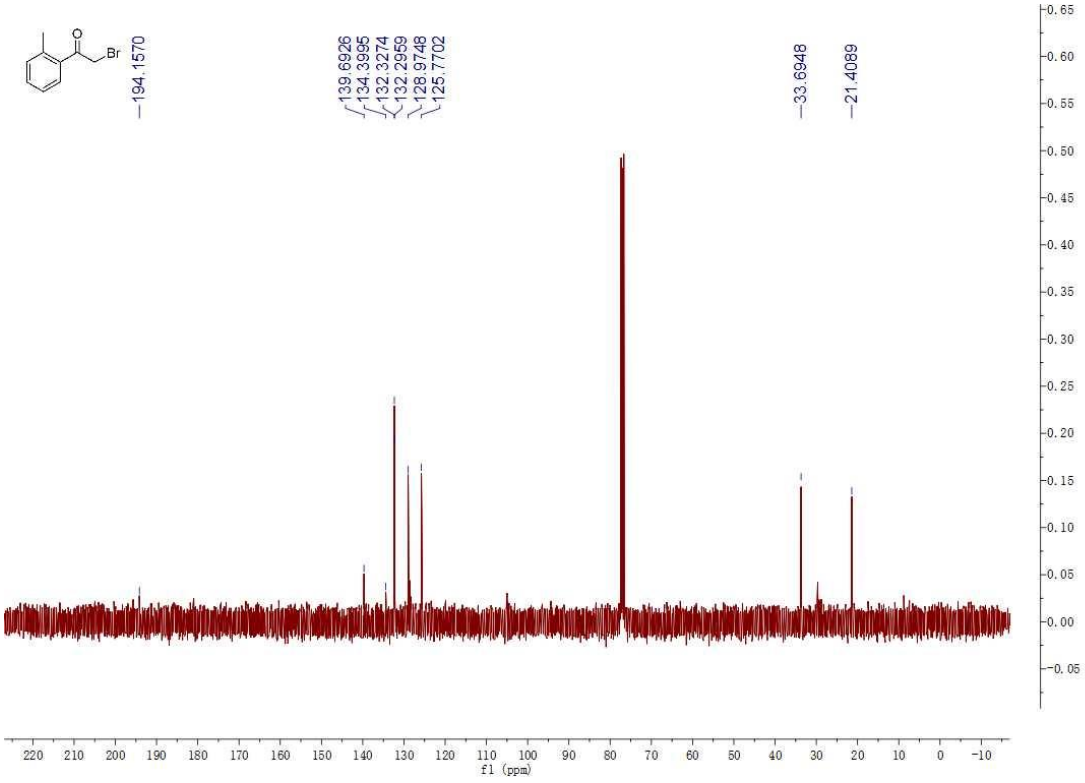
^{13}C NMR (101 MHz, $CDCl_3$) 3p



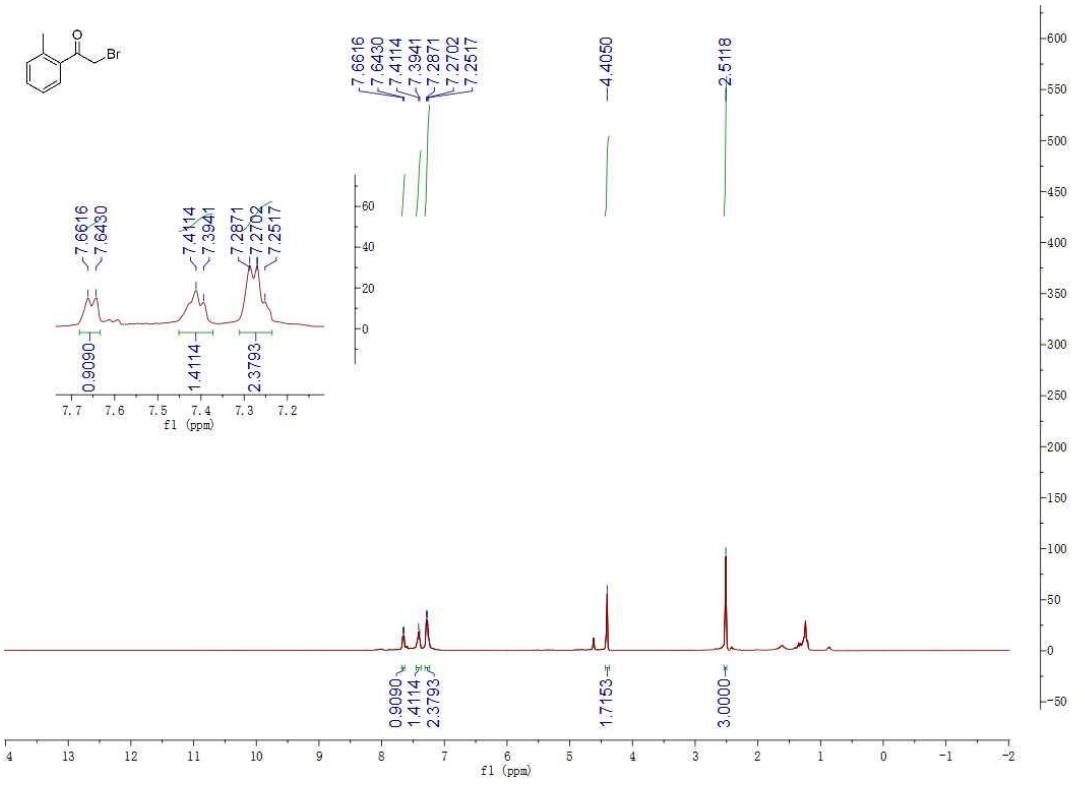
1H NMR (400 MHz, CDCl3) 3p



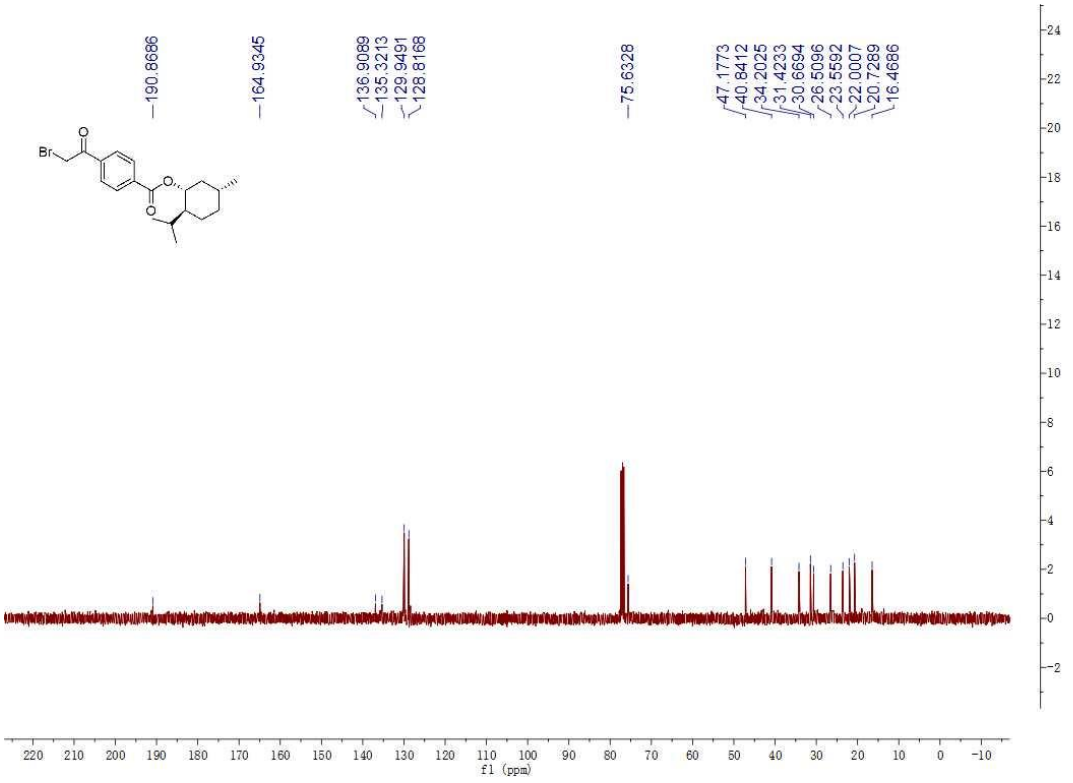
^{13}C NMR (101 MHz, $CDCl_3$) 3q



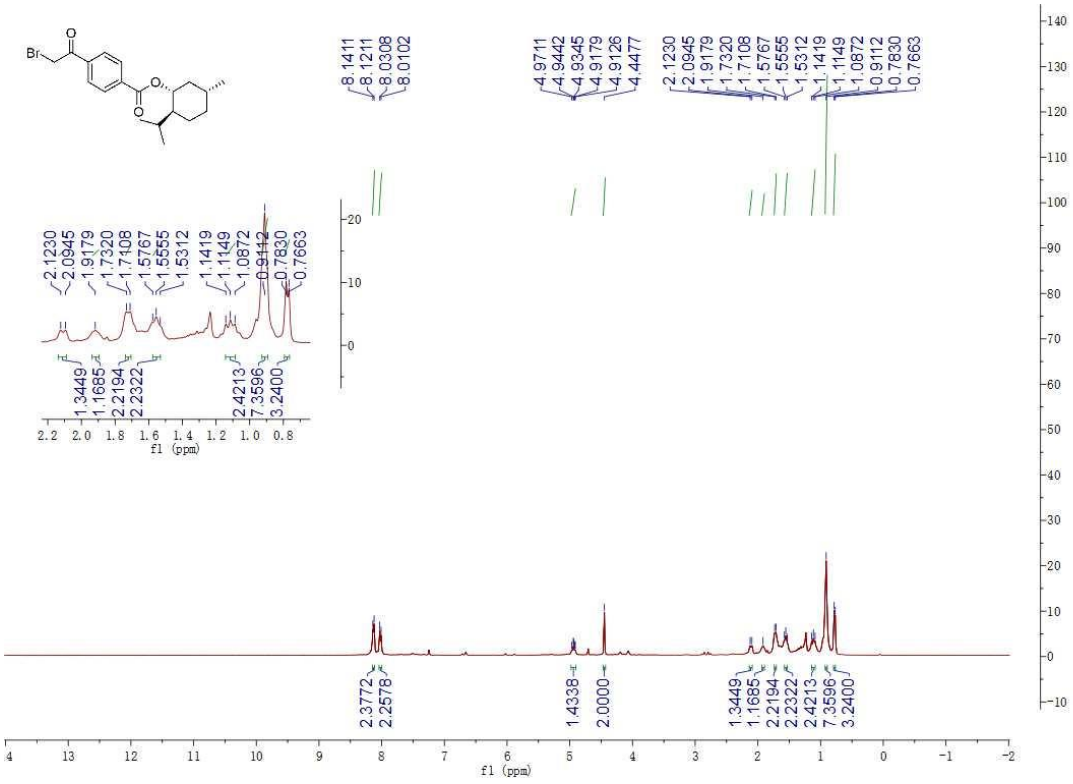
^{1}H NMR (400 MHz, $CDCl_3$) 3q



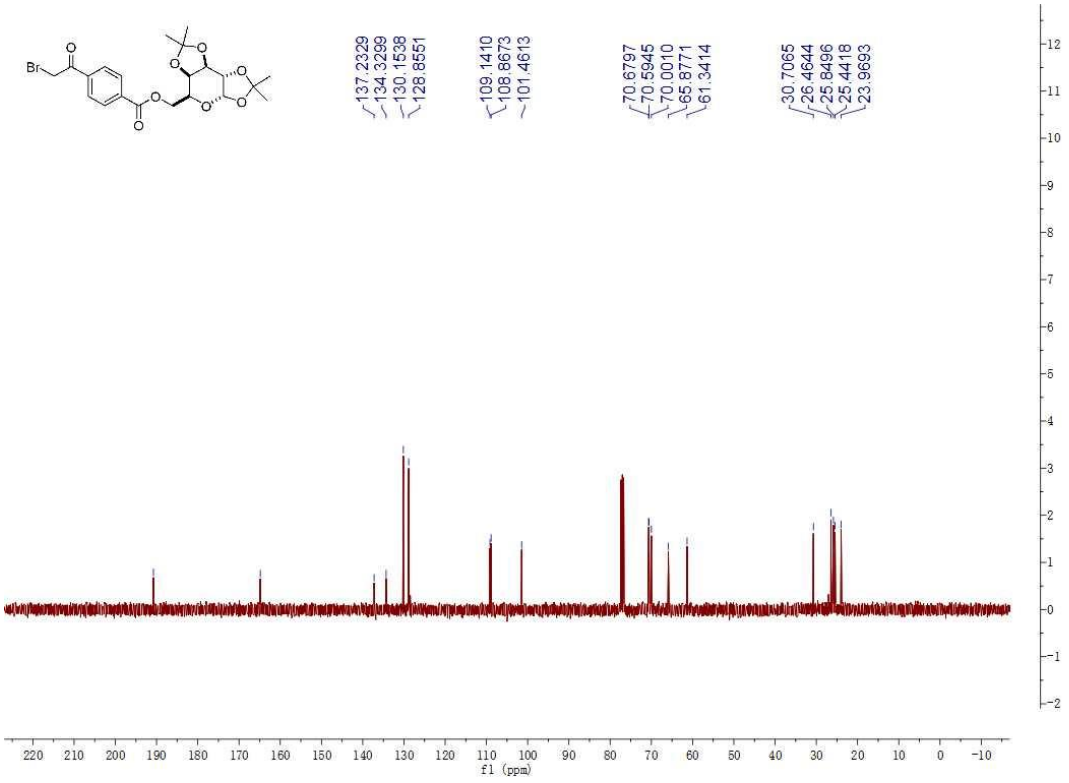
^{13}C NMR (101 MHz, $CDCl_3$) 3r



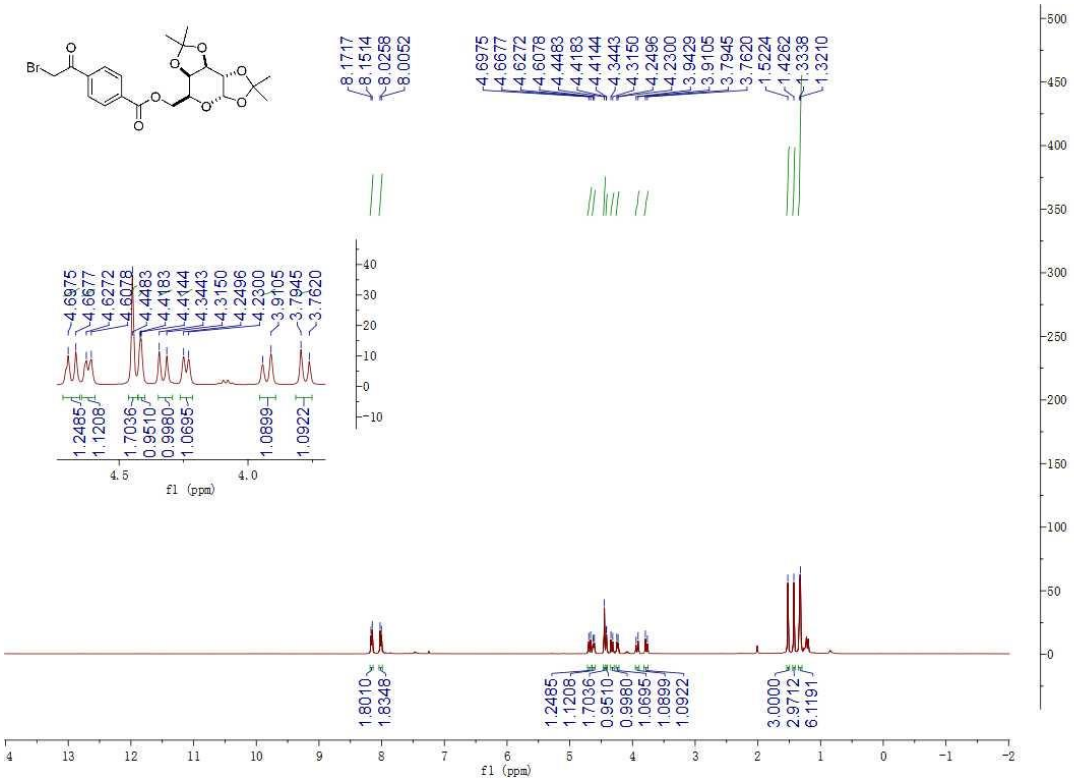
^{1}H NMR (400 MHz, $CDCl_3$) 3r



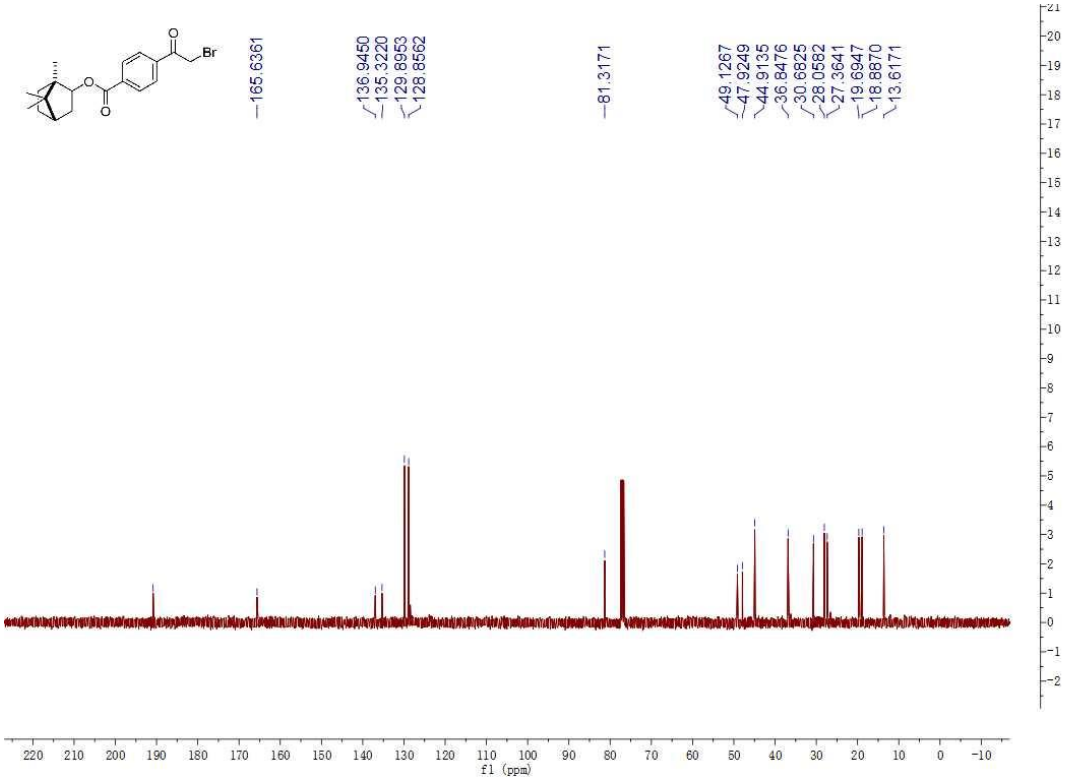
^{13}C NMR (101 MHz, $CDCl_3$) 3s



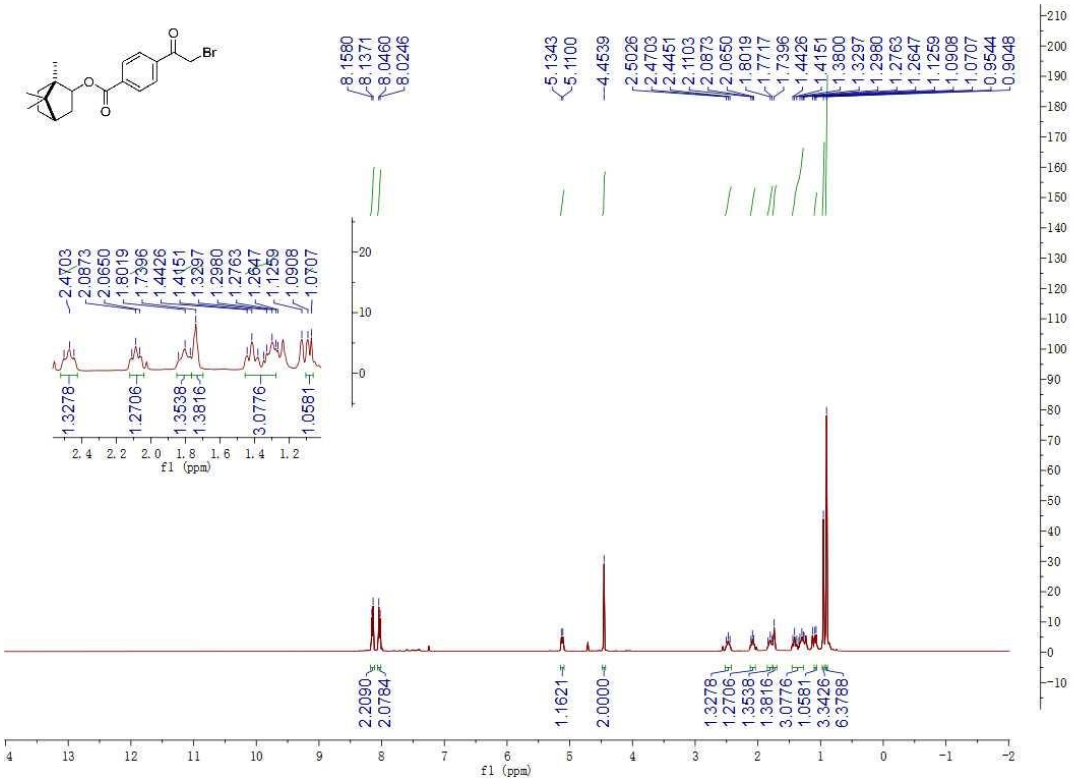
^{1}H NMR (400 MHz, $CDCl_3$) 3s



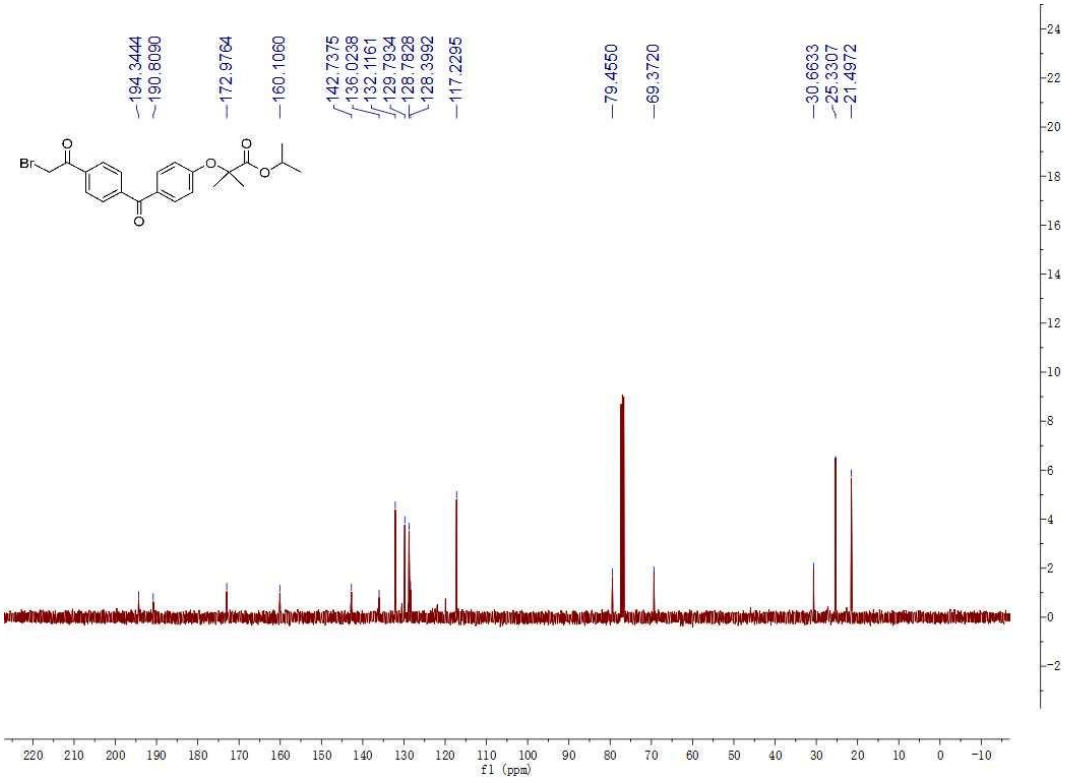
^{13}C NMR (101 MHz, $CDCl_3$) 3t



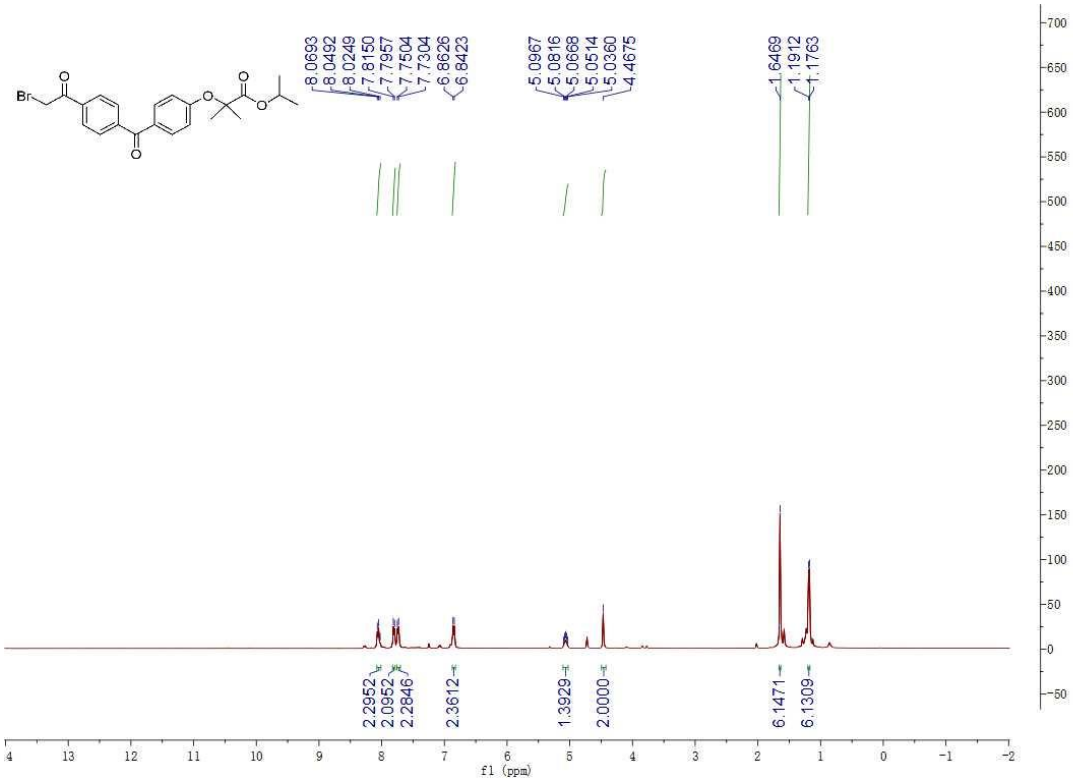
^{1}H NMR (400 MHz, $CDCl_3$) 3t



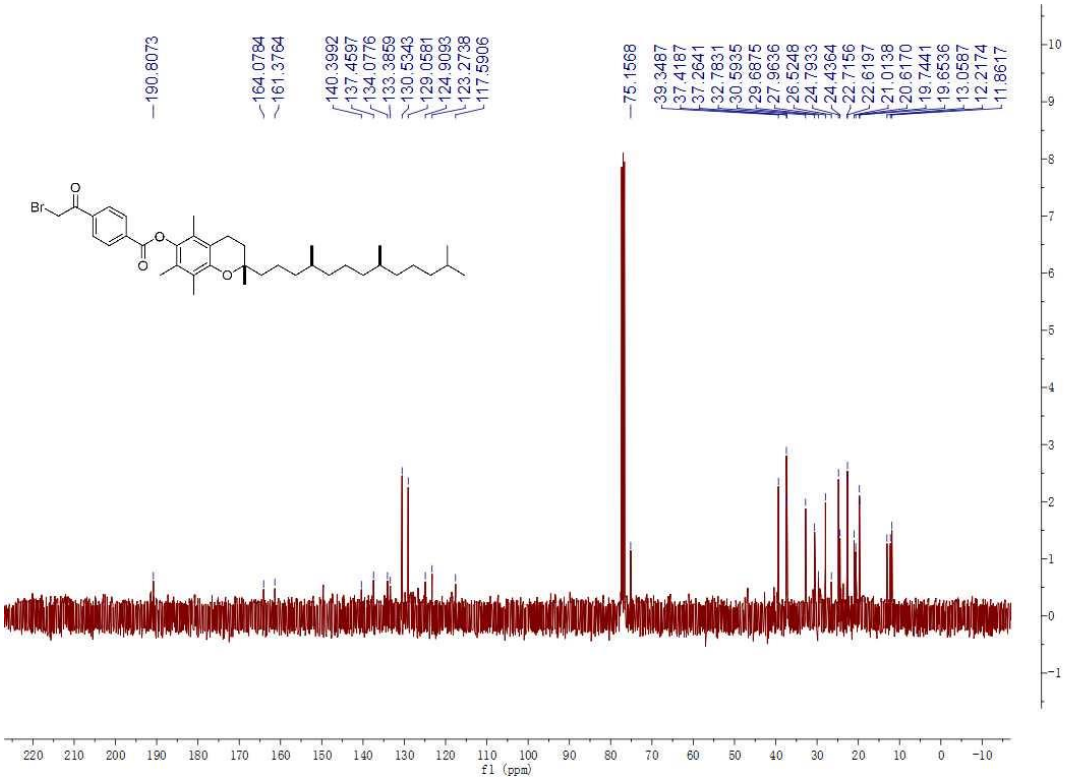
^{13}C NMR (101 MHz, $CDCl_3$) 3u



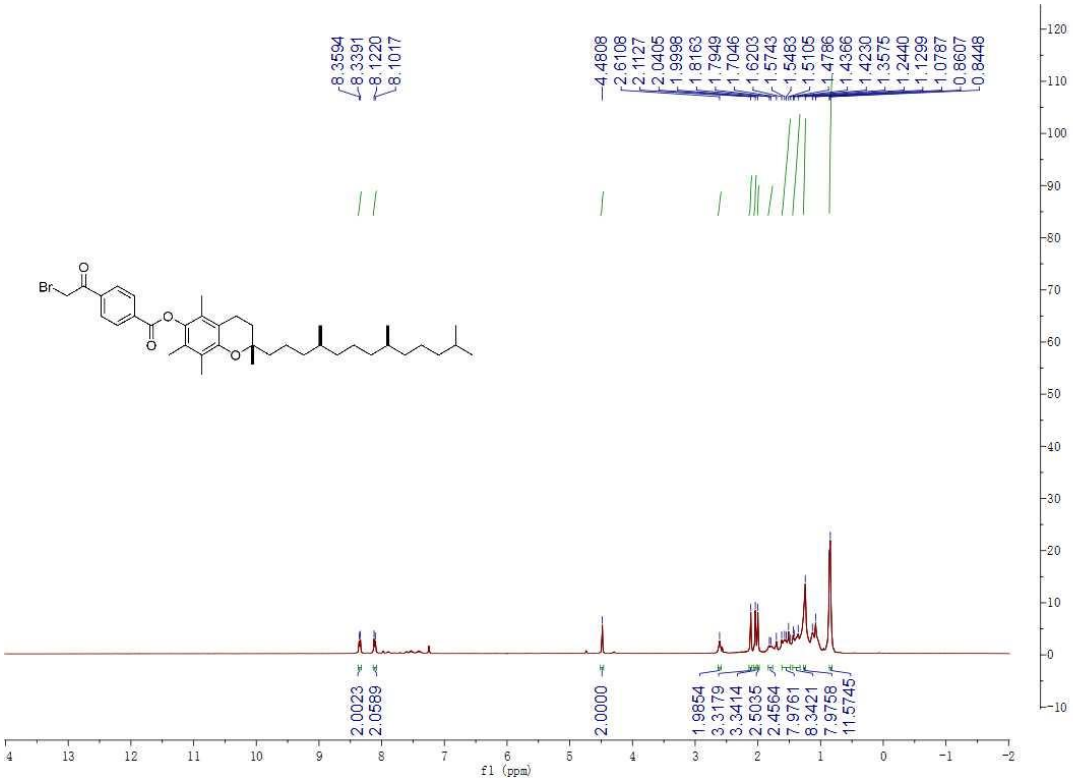
^{1}H NMR (400 MHz, $CDCl_3$) 3u



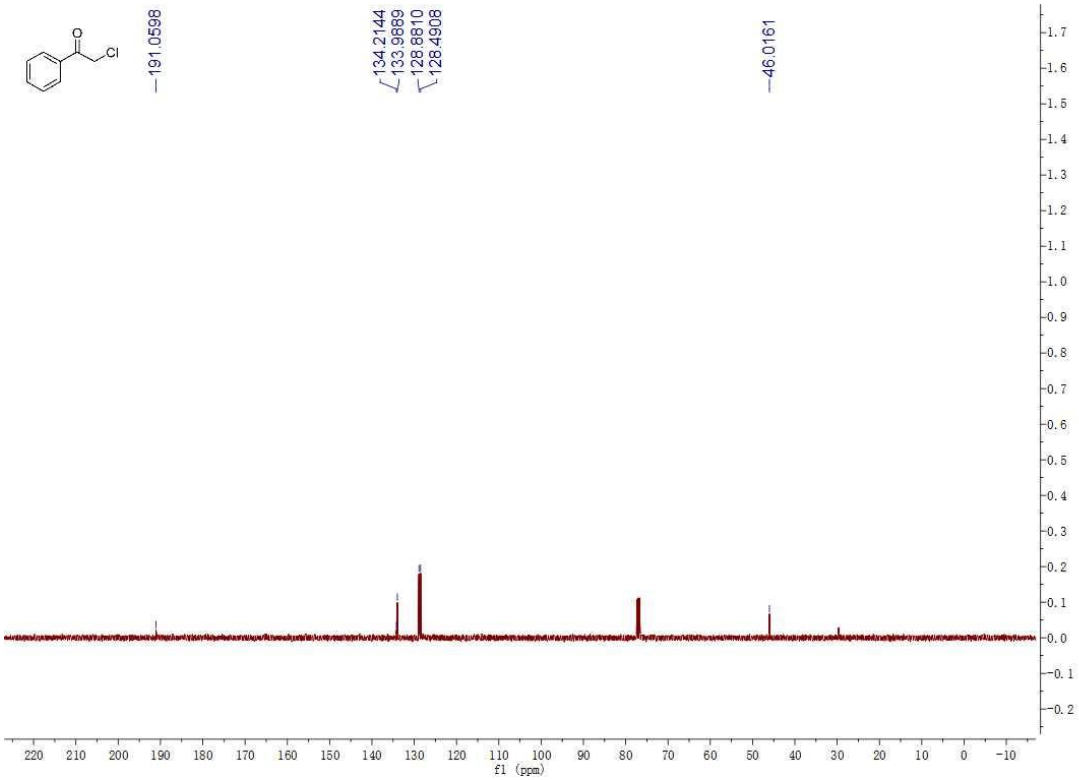
^{13}C NMR (101 MHz, $CDCl_3$) 3v



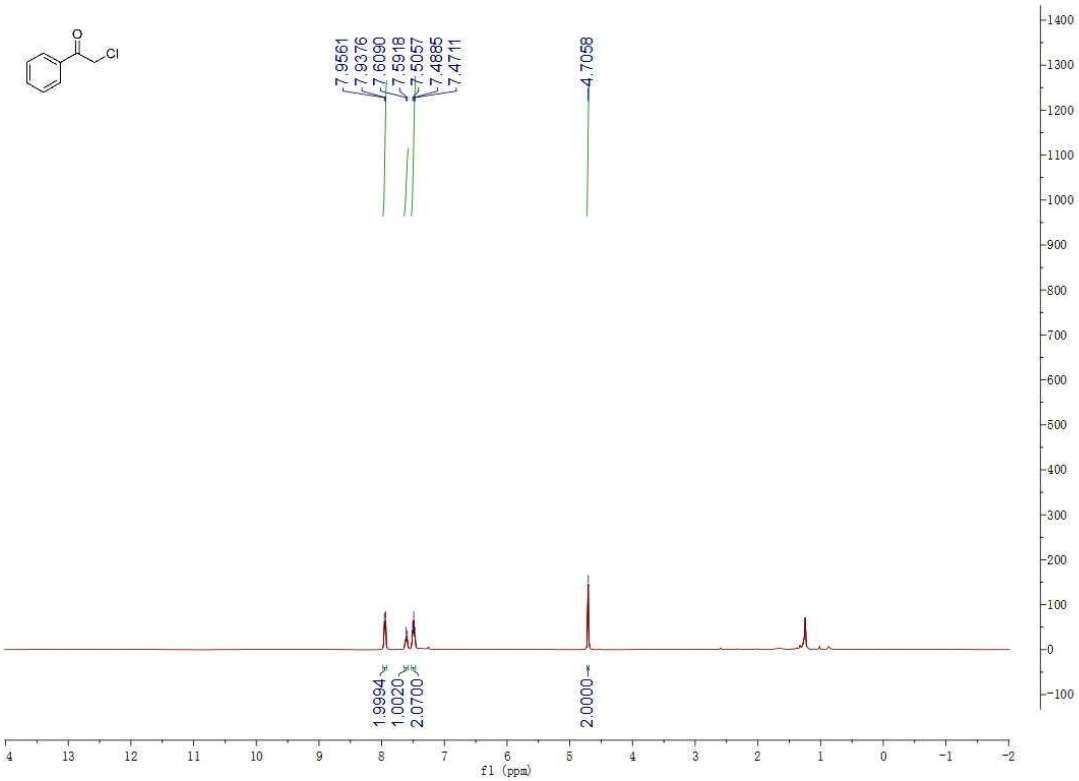
^{1}H NMR (400 MHz, $CDCl_3$) 3v



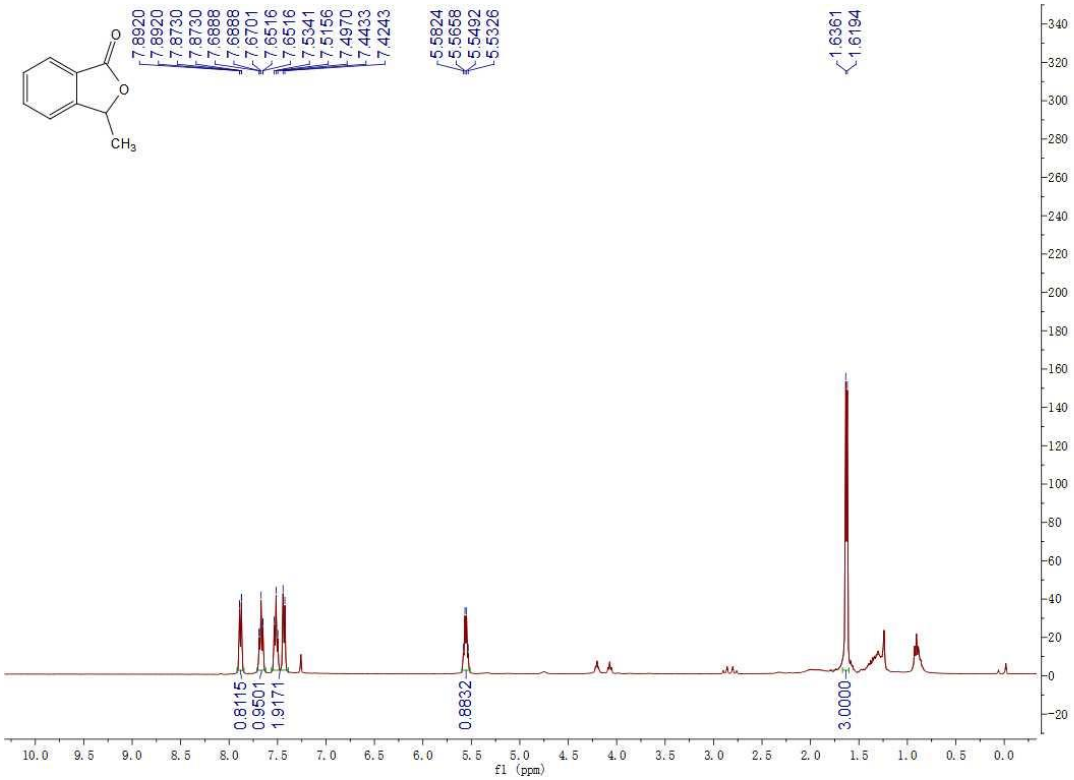
^{13}C NMR (101 MHz, $CDCl_3$) 3w



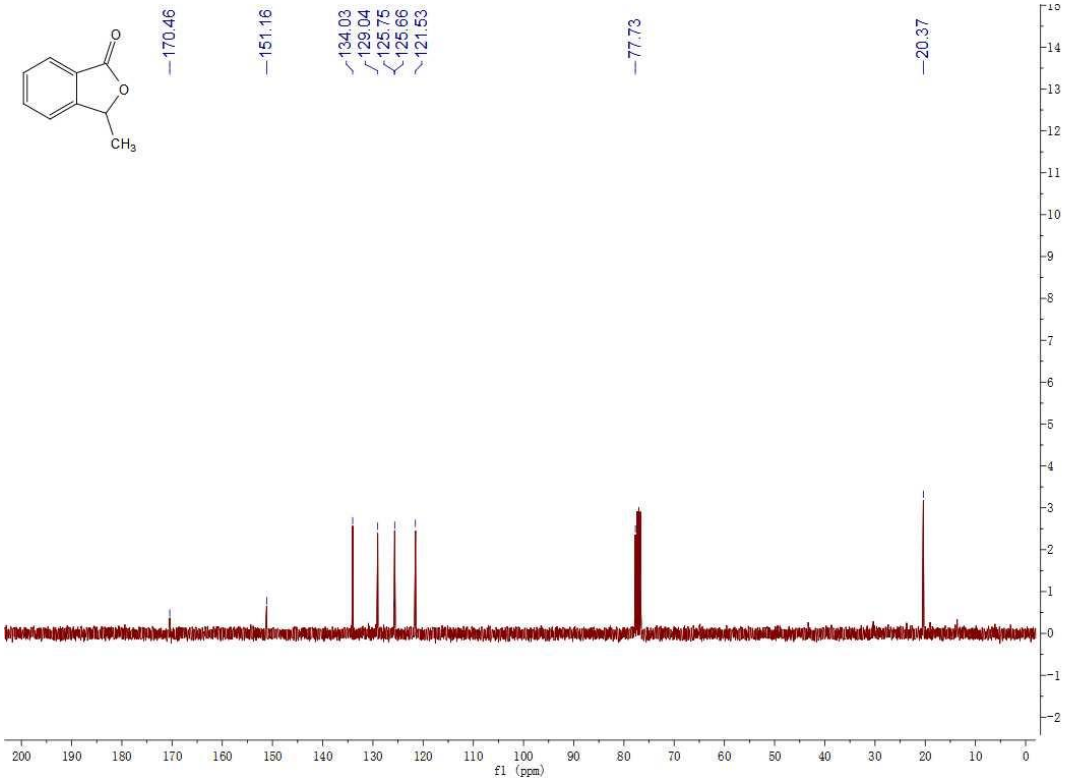
^{1}H NMR (400 MHz, $CDCl_3$) 3w



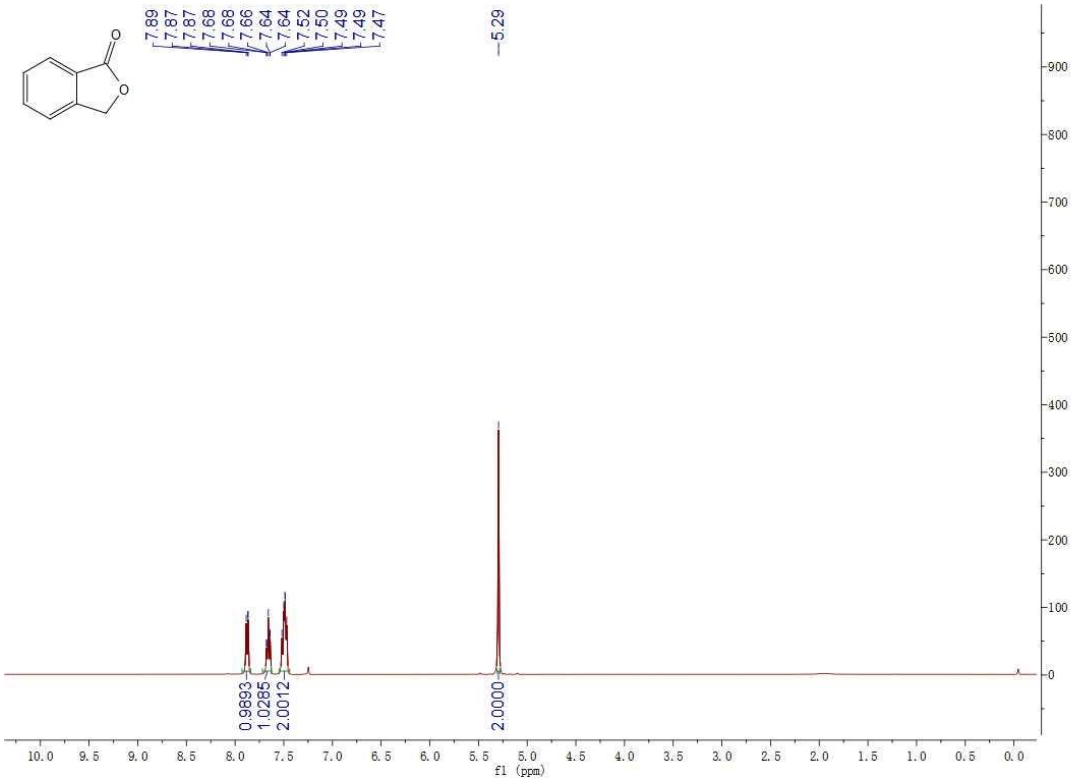
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5a**



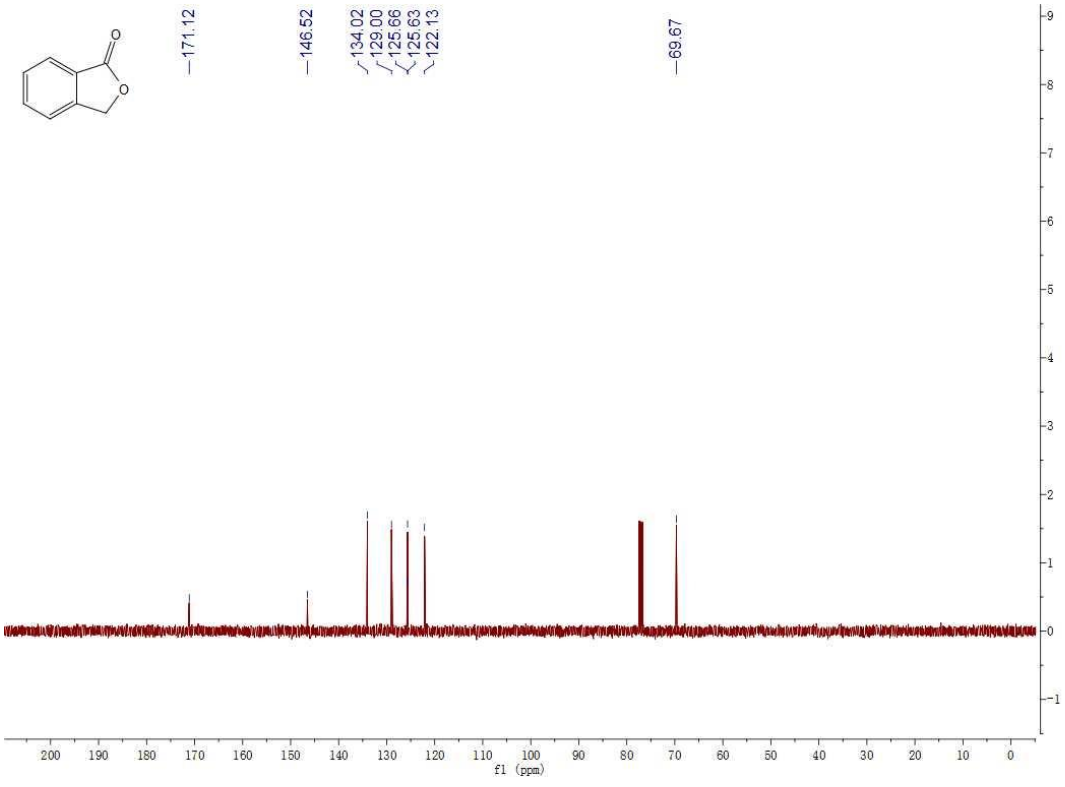
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5a**



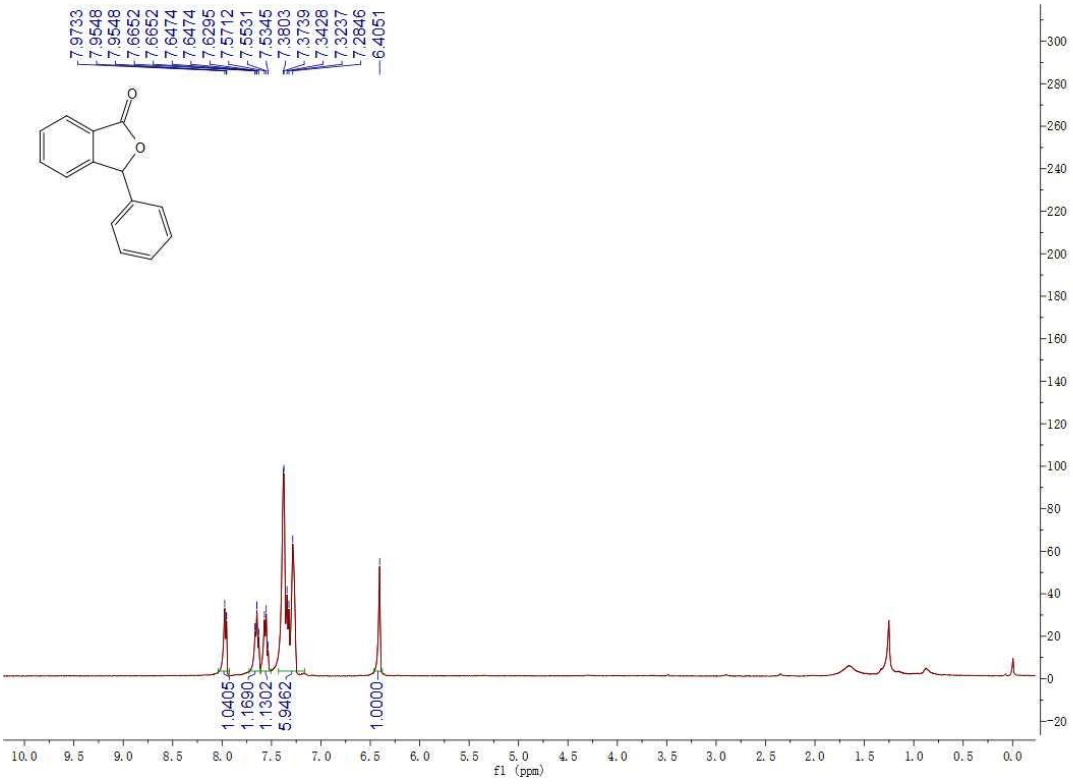
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5b**



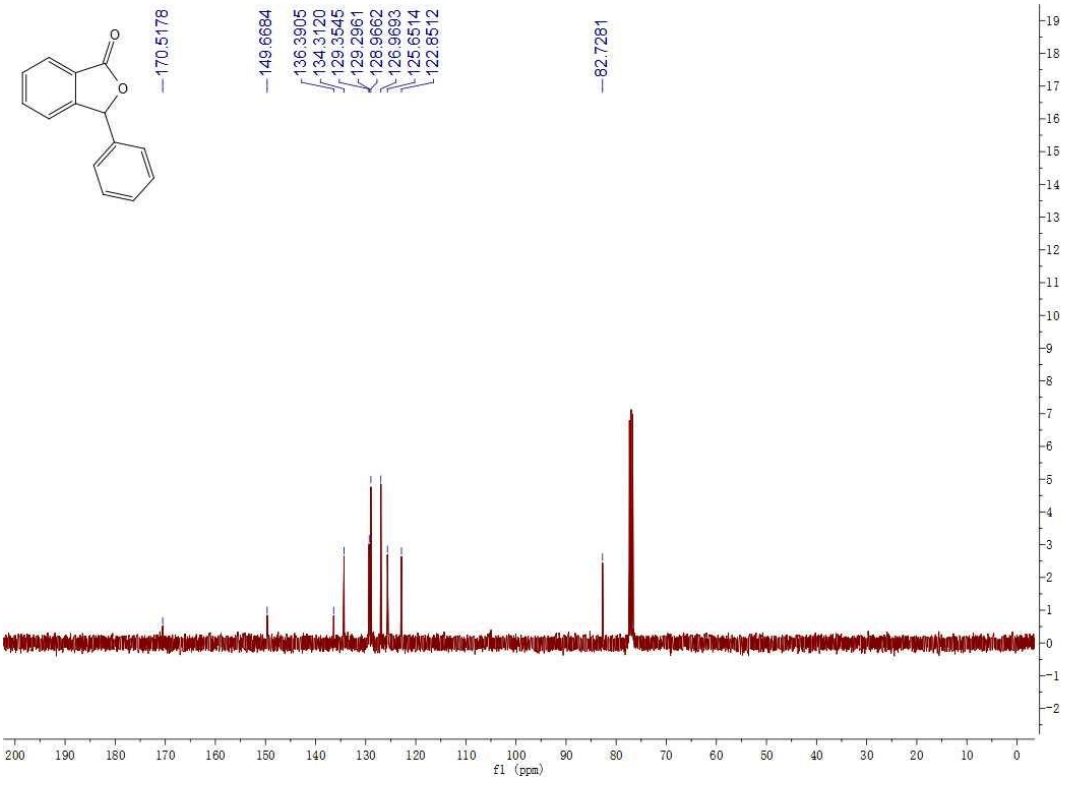
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5b**



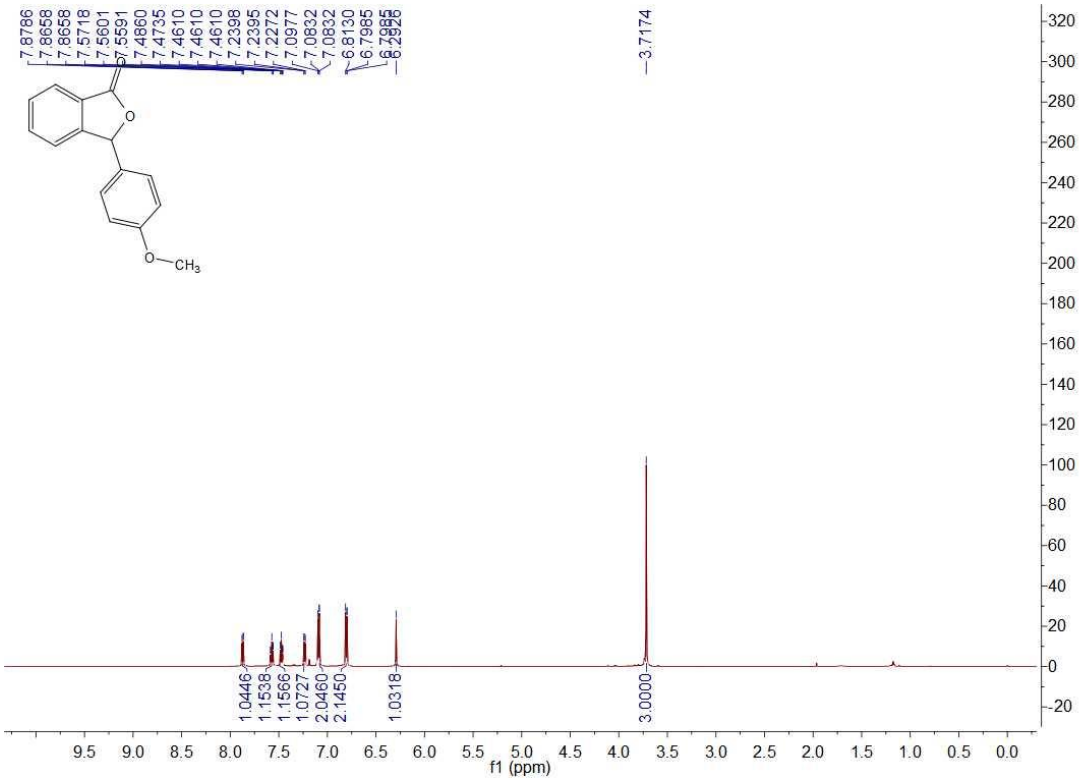
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5c**



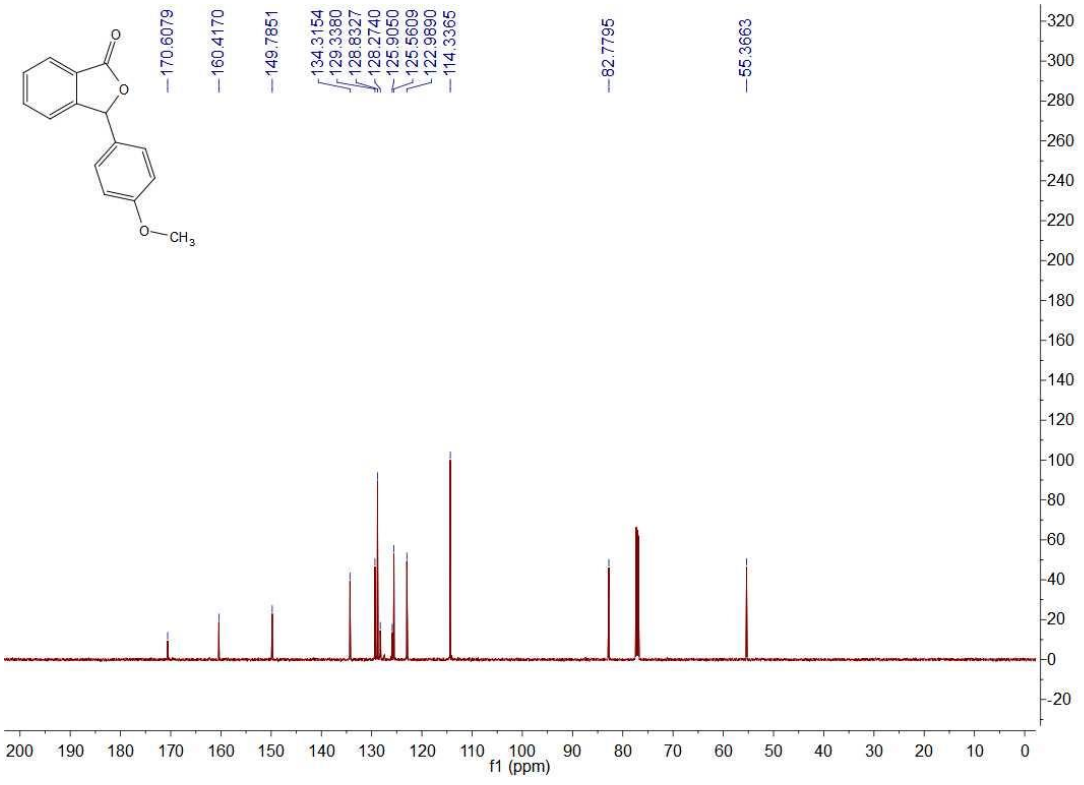
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5c**



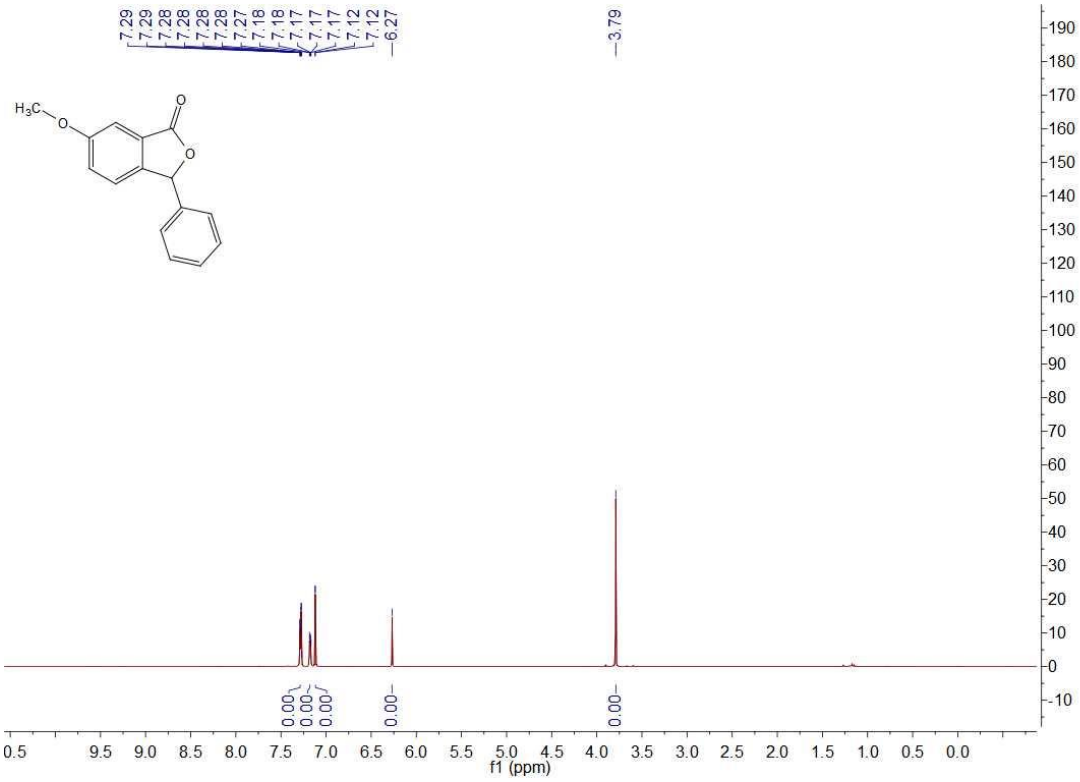
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5d**



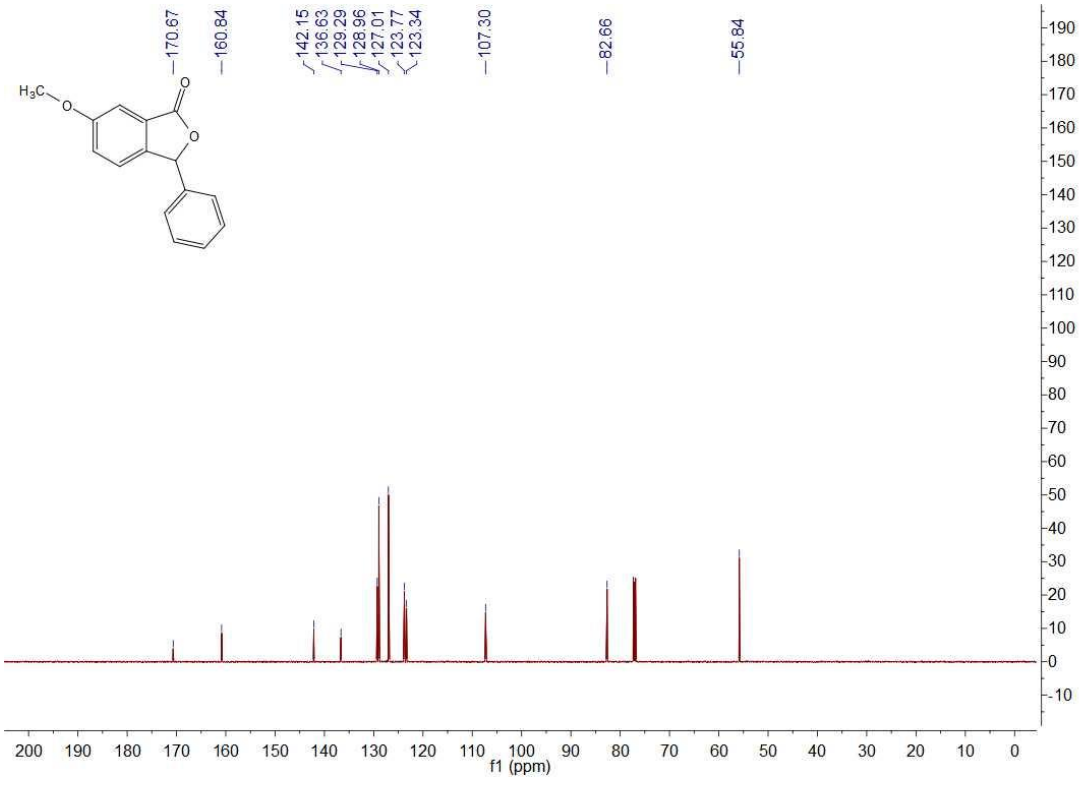
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5d**



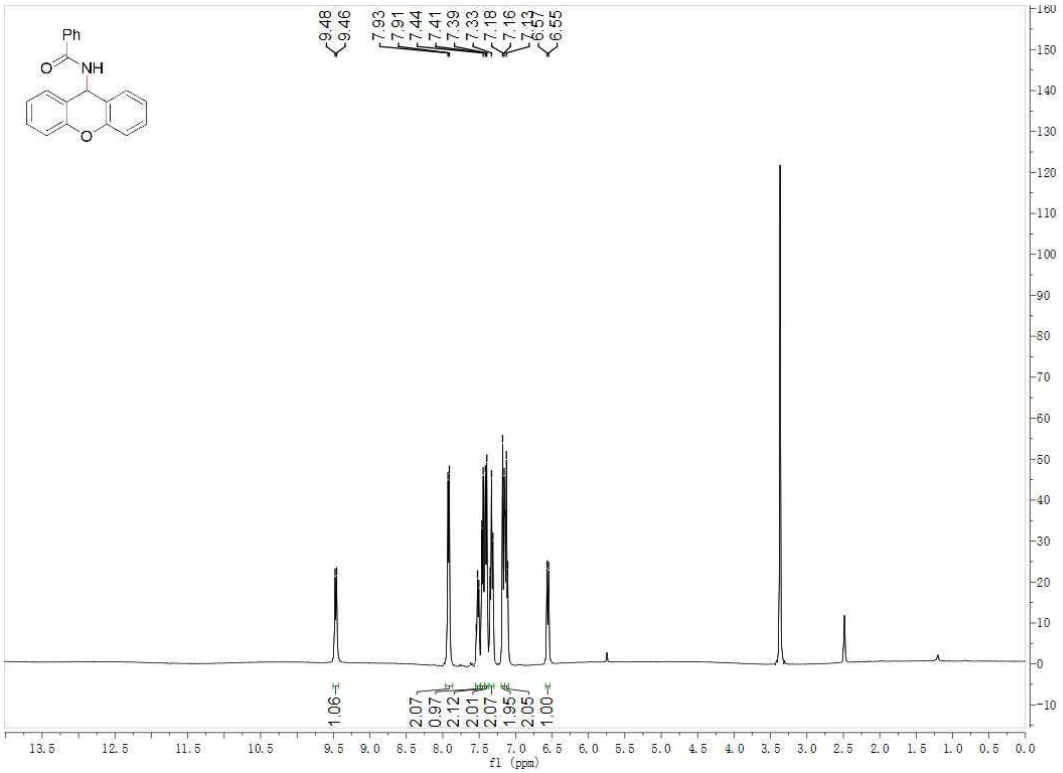
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **5e**



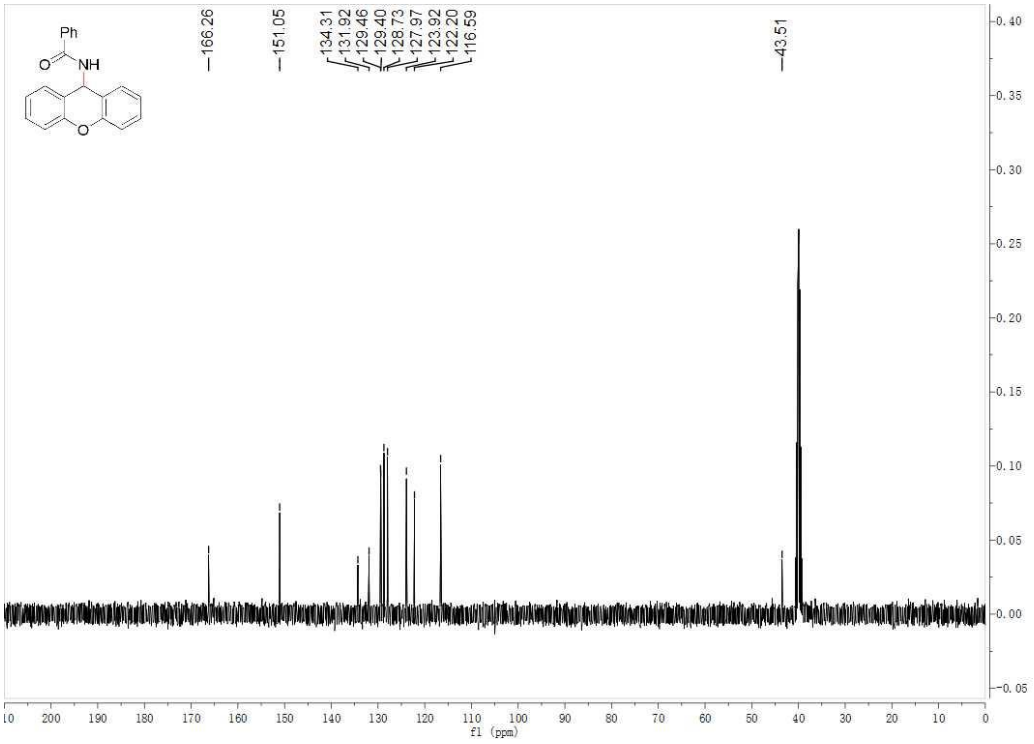
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **5e**



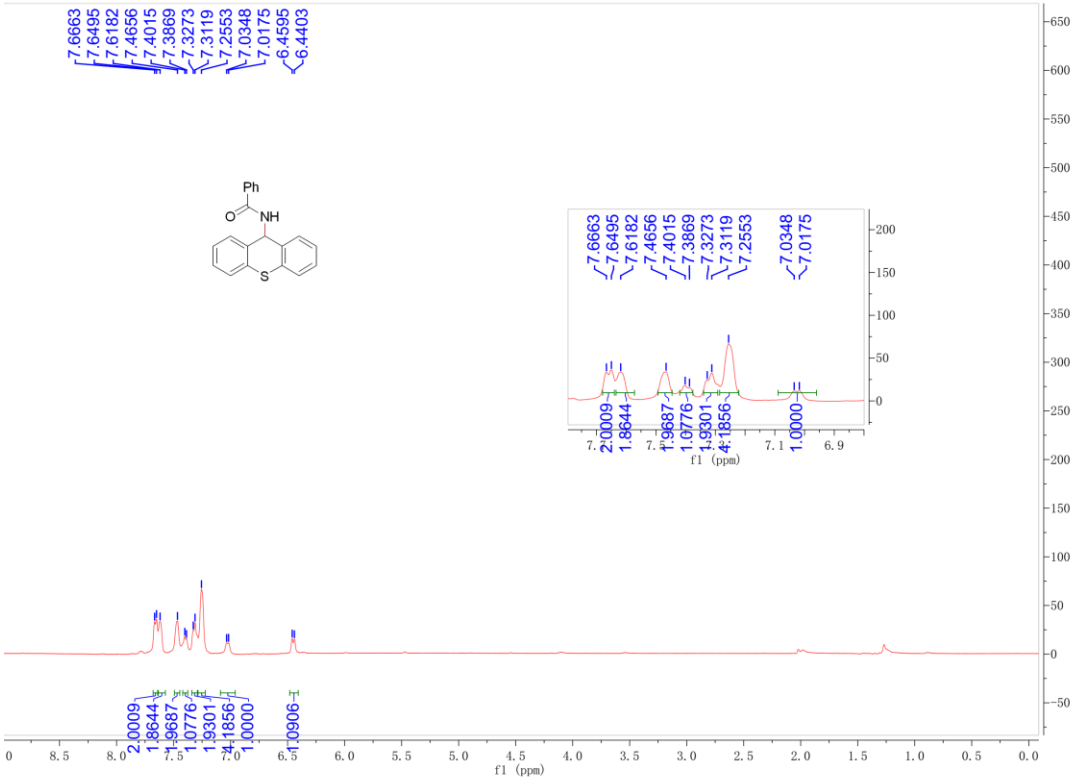
^{1}H NMR spectrum (400 MHz, DMSO) of compound **8a**



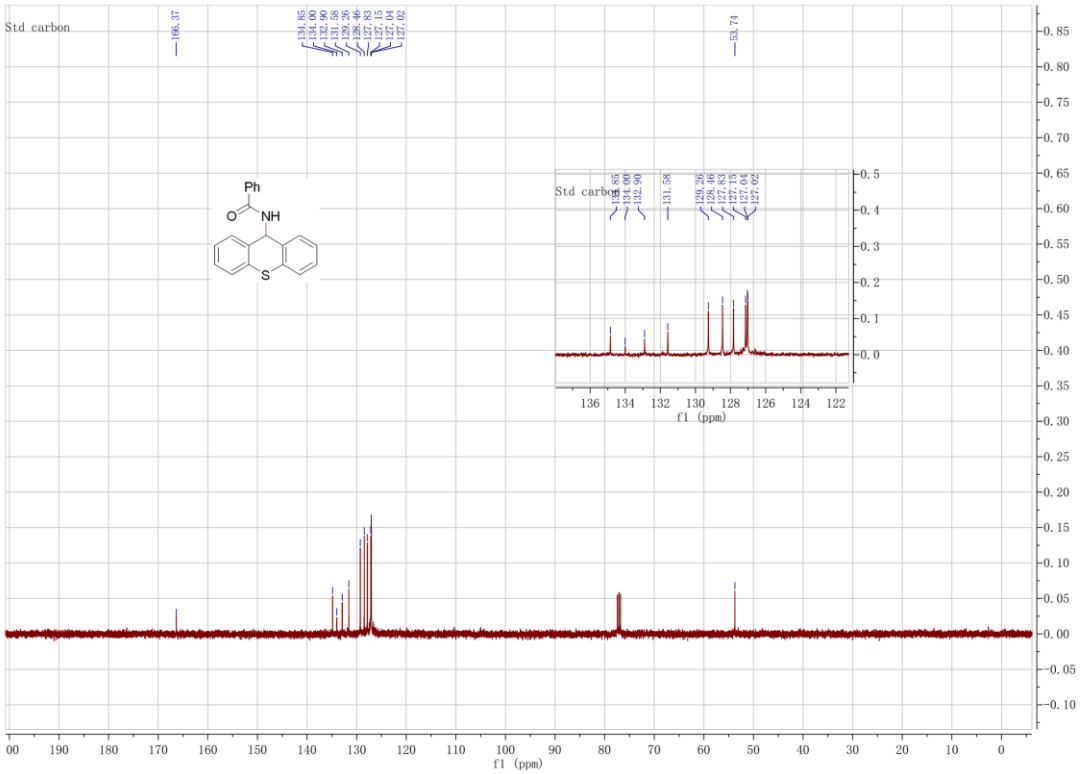
^{13}C NMR spectrum (100 MHz, DMSO) of compound **8a**



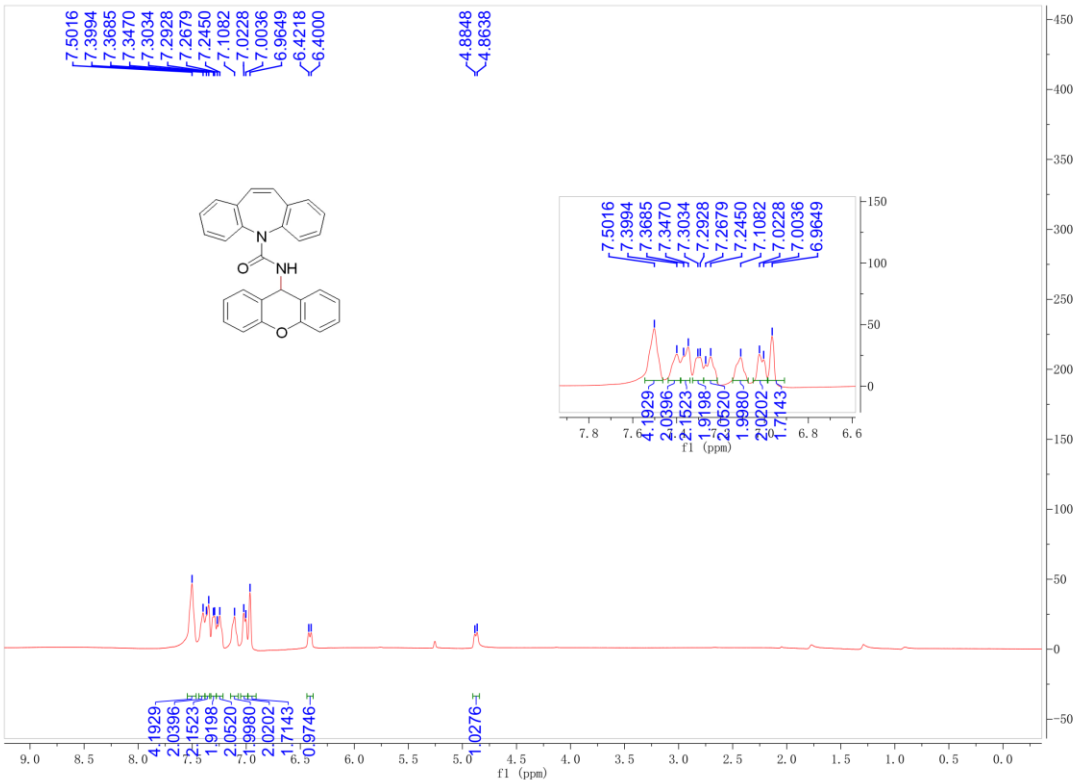
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8b**



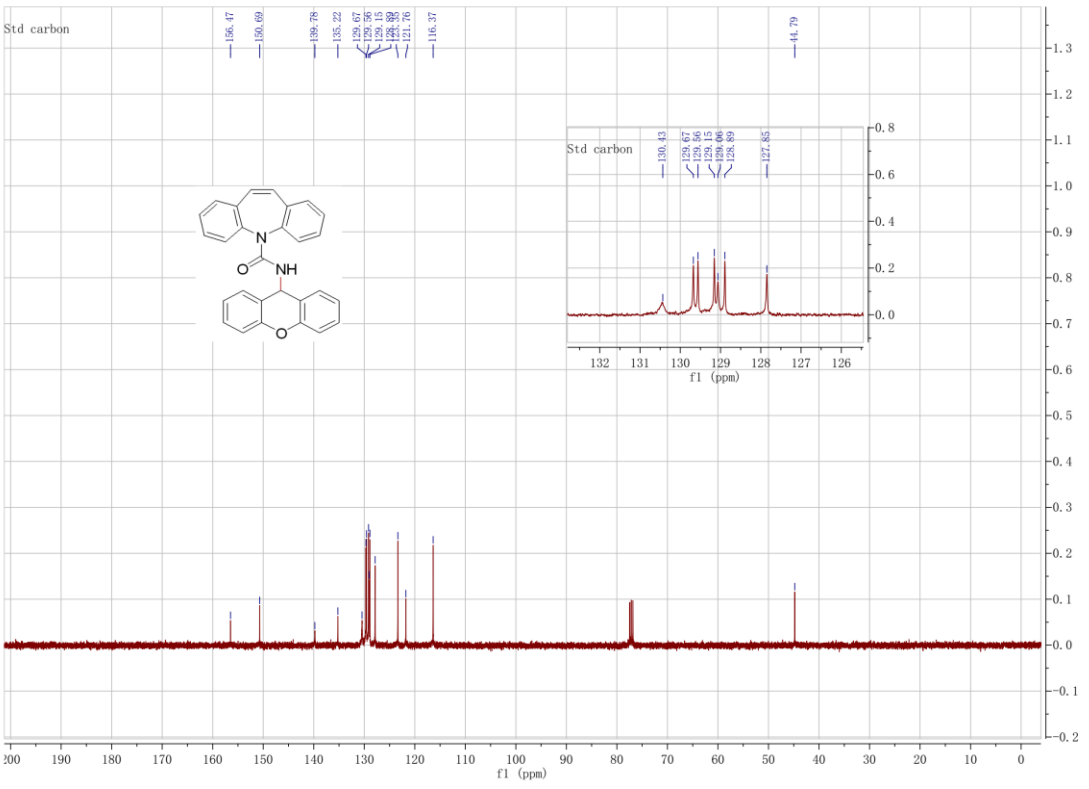
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8b**



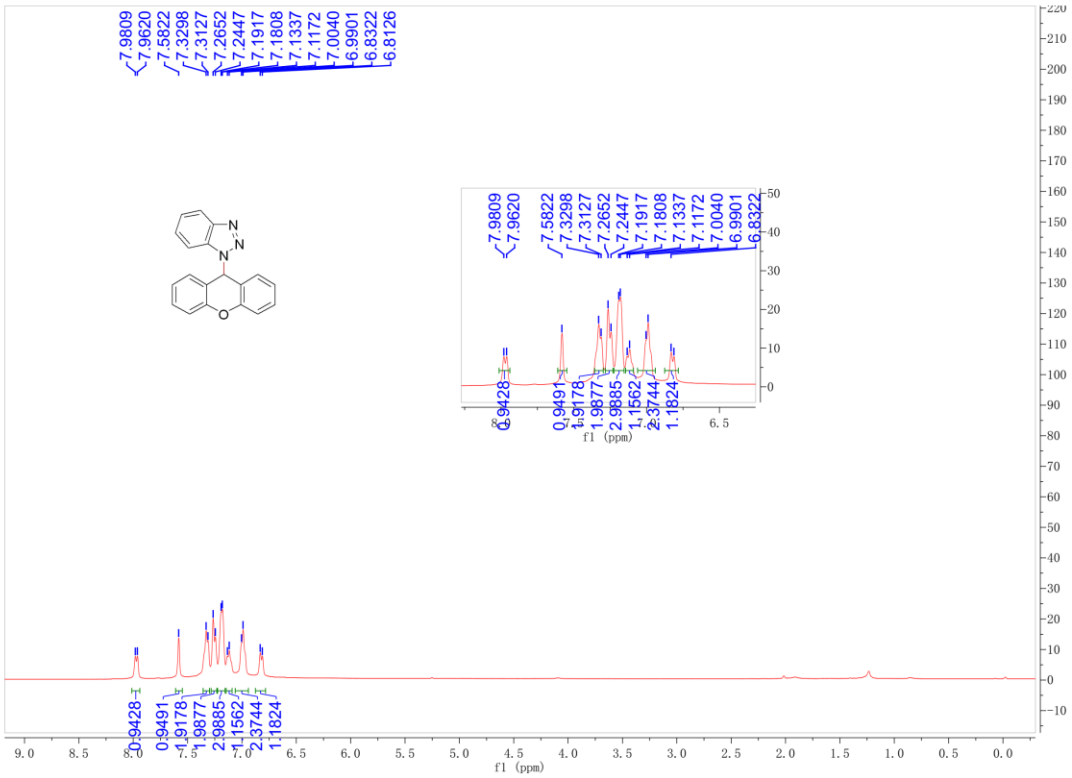
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8c**



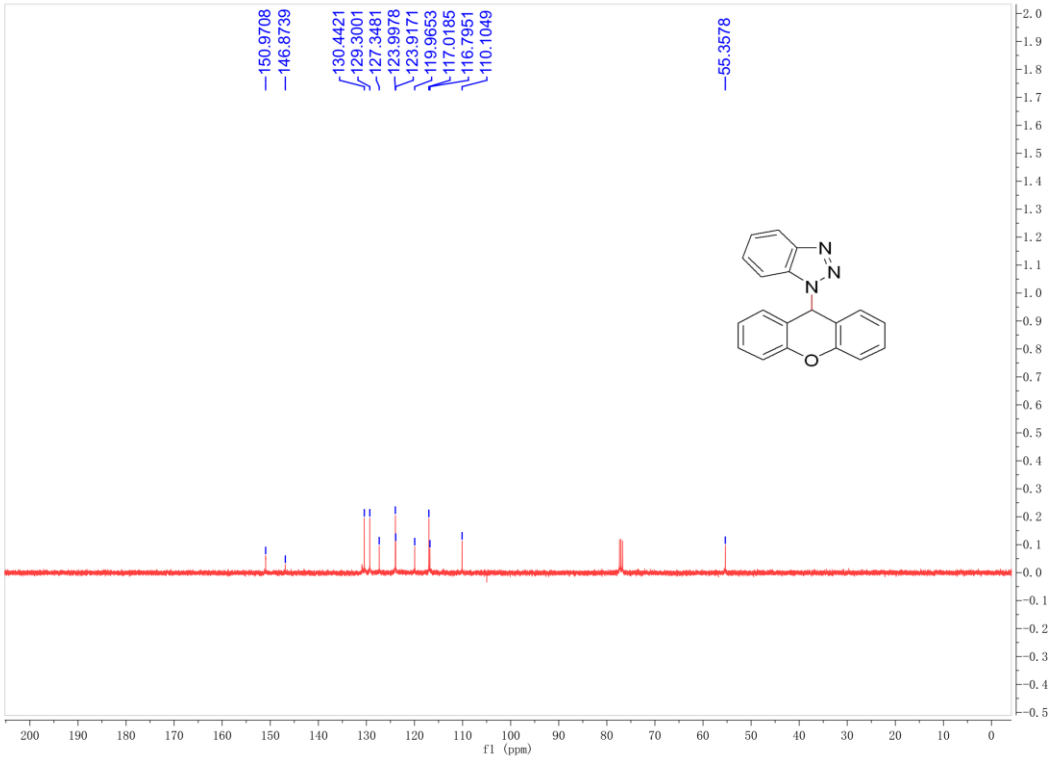
^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8c**



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **8d**



^{13}C NMR spectrum (100 MHz, $CDCl_3$) of compound **8d**



9. Crystallographic data

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                  alpha=90          beta=90           gamma=90
Temperature:      293 K

                 Calculated                Reported
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Hall group       P 2c -2ac                 P 2c -2ac
Moiety formula   C10 H9 Br O3              2(C10 H9 Br O3)
Sum formula      C10 H9 Br O3              C20 H18 Br2 O6
Mr               257.07                    514.16
Dx,g cm-3        1.708                     1.708
Z                8                         4
Mu (mm-1)        5.449                     5.449
F000             1024.0                    1024.0
F000'            1021.15
h,k,lmax         13,17,16                  12,17,16
Nref             3955[ 2072]               2352
Tmin,Tmax                                  0.340,1.000
Tmin'

Correction method= # Reported T Limits: Tmin=0.340 Tmax=1.000
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Data completeness= 1.14/0.59        Theta(max)= 72.153

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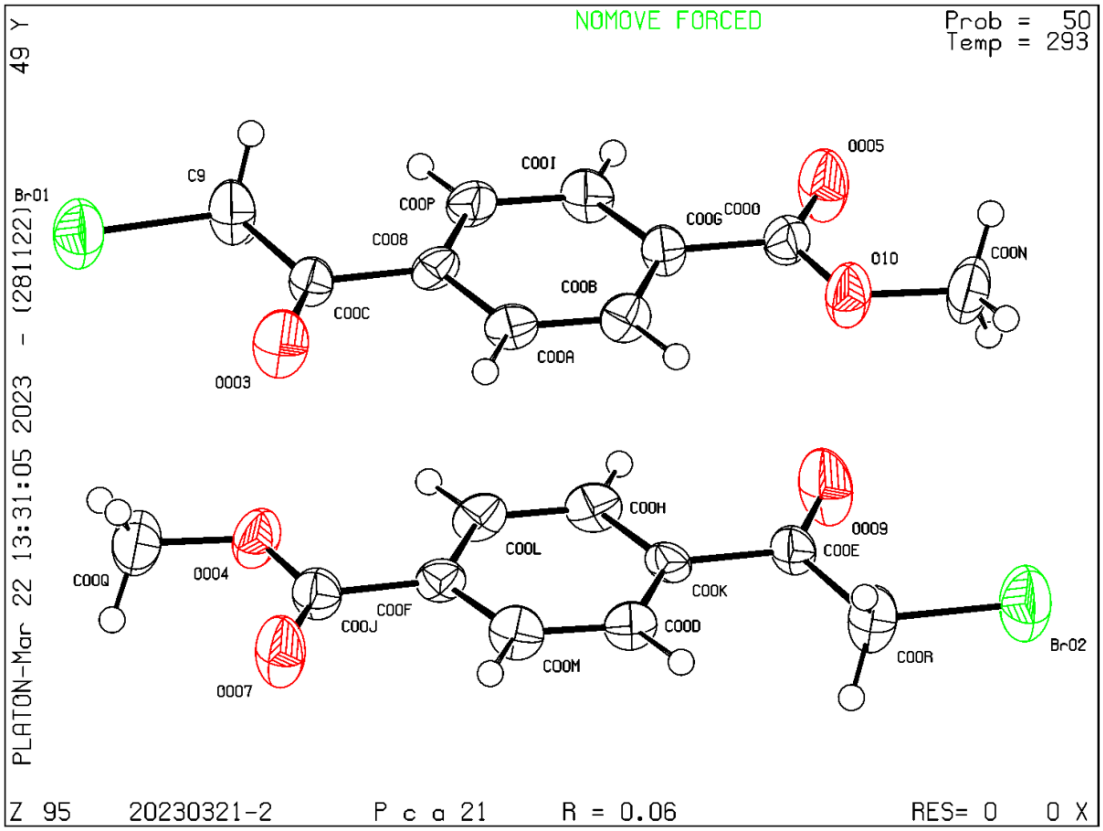
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010
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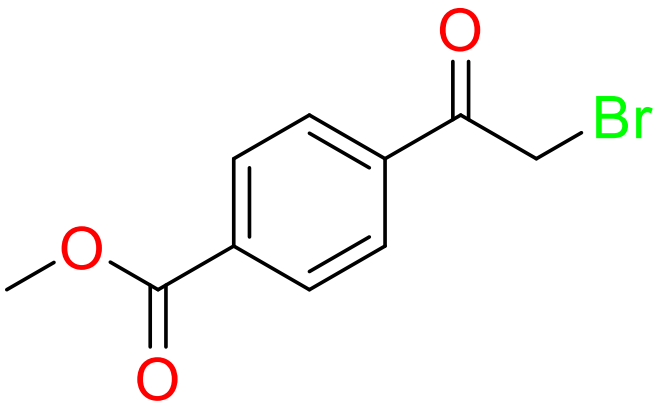
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Br
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