Supporting Information

Metal-free $PhI(OAc)_2$-oxidized decarboxylation of propiolic acids towards synthesis of α-acetoxy ketones and insights into general decarboxylation with DFT calculations

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Content

1. Experimental Section

General Information.

The product was characterized via ^{1}H and ^{13}C NMR using 500/126 MHz NMR spectrometer and 400/101 MHz NMR spectrometer at 20–25 °C, and $CDCl_3$ was used as the solvent. ^{1}H NMR spectra was reported in parts per million using tetramethyl silane (δ = 0.000 ppm) or DMSO-d_6 (δ = 2.500 ppm) as an internal standard. The data of ^{1}H NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, and m = multiplet), coupling constants (*J*, Hz), and integration. ^{13}C NMR spectra was reported in parts per million using solvent $CDCl_3$ (δ = 77.20 ppm) or DMSO-d_6 (δ = 39.50 ppm) as an internal standard. The data of ^{13}C NMR are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet), and coupling constants (*J*, Hz). High-resolution mass spectroscopy (HRMS) spectra were obtained using a quadrupole time-of-flight (Q-TOF) MS spectrometer. Thin layer chromatography was performed on a glass plate coated with GF-254 silica gel and observed under 254 nm UV light. Reactions were monitored by TLC and column chromatography was performed using silica gel. Commercially available reagents are analytically pure and used without further purification unless otherwise specified. Acetic acid was HPLC grade and added with molecular sieves for more than two weeks. All solvents were dried with molecular sieves over two weeks. All reactions were performed at atmospheric pressure, and all reagents were weighing at room temperature in air.

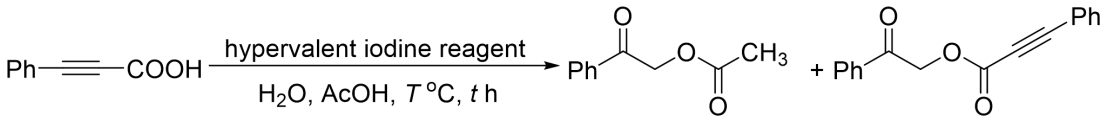
Typical Procedure for the Synthesis of 1b−1x.[1]

(i) To a solution of boronic acid (2.4 mmol, 1.2 equivalents), $Pd(OAc)_2$ (0.1 mmol, 5 mmol %), Ag_2O(3.0 mmol, 1.5 equivalents) and K_2CO_3(4.0 mmol, 2.0 equivalents) in ACN (6 mL) was added methyl propiolate (2.0 mmol) under argon. After stirring and reacting at 70°C for 12 hours, the solvent was removed by vacuum and the boronic acid was removed by the silica-gel column chromatography (petroleum ether / ethyl acetate = 10:1) to give a liquid or solid mixture. (ii) To the solution of mixture in MeOH (10 mL) was added 1 N NaOH (10 mL) and stirred overnight at room temperature. The MeOH was removed by vacuum, the aqueous phase was extracted with ethyl acetate (20 mL × 3). Then added 2 N HCl until the pH reached 2, and extracted with ethyl acetate (20 mL × 3). The organic layers were dried over anhydrous $MgSO_4$ and the solvents were removed in vacuo to give the pure solid propiolic acids in 34% to 73% yield.

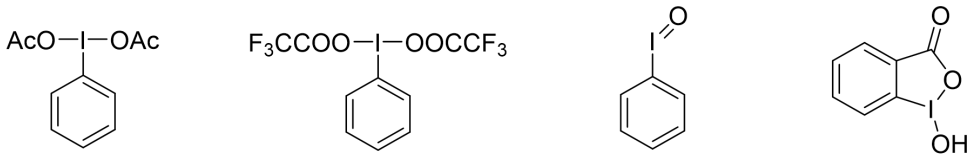
General Procedure for the Synthesis of α-acyloxy ketones 2a−2za.

Propiolic acid **1** (0.50 mmol, 1.0 equivalents), H_2O (22 μL, 1.25 mmol, 2.5 equivalents), 8 mL AcOH and $PhI(OAc)_2$ (483 mg, 1.5 mmol, 3.0 equivalents) were added in a round-bottom flask. The mixture was allowed to stir at 80 °C (oil bath temperature) under air for 1 h. After cooling to room temperature, the mixture was concentrated by rotary evaporation and the resulting residue was purified using a column chromatography (petroleum ether / ethyl acetate = 10:1) to give product **2**.

Investigation on hypervalent iodine reagents [a]



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

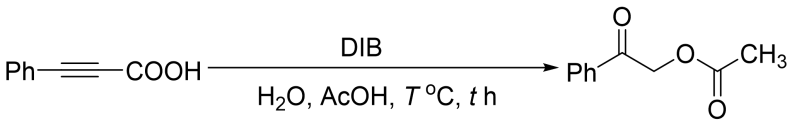


DIB PIFA PhIO ABX

entry	hypervalent iodine reagent	yield of **2a** (%) [b]	yield of **3a** (%) [b]
1	PIFA (3.0 equiv)	3	-
2	PhIO (3.0 equiv)	23	trace
3	ABX (3.0 equiv)	18	2
4	**DIB (3.0 equiv)**	**81**	**trace**
5	DIB (2.0 equiv)	76	trace
6	DIB (2.5 equiv)	77	trace
7	DIB (2.8 equiv)	78	trace
8	DIB (3.5 equiv)	72	trace
9	DIB (3.3 equiv)	79	trace

[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equivalent), hypervalent iodine reagents, H_2O (1.0 mmol, 2.0 equivalents) and acetic acid (2 mL) were refluxed at 80°C for 3 hours. [b] Yields were determined by ^1H NMR using mesitylene as a standard.

Investigation on water and solvent, temperature and time [a],[b]



1a **2a**

entry	H_2O (equiv)	AcOH (mL)	*T* (℃)	*t* (h)	yield (%) [c]
1	2.0	2.0	80	3	81
2	2.0	2.0	70	3	73
3	2.0	2.0	75	3	77
4	2.0	2.0	85	3	79
5	2.0	2.0	90	3	76
6	1.5	2.0	80	3	78
7	2.5	2.0	80	3	83
8	3.0	2.0	80	3	80
9	2.5	1.0	80	3	76
10	2.5	4.0	80	3	84
11	2.5	6.0	80	3	87
12	2.5	8.0	80	3	96
13	2.5	9.0	80	3	95
14	2.5	8.0	80	5	96

entry	H_2O (equiv)	AcOH (mL)	*T* (℃)	*t* (h)	yield (%) [c]
15	2.5	8.0	80	4	95
16	2.5	8.0	80	2	96
17	**2.5**	**8.0**	**80**	**1**	**97**
18	2.5	8.0	80	0.5	79
19[d]	2.5	8.0	80	1	96

[a] Reaction conditions: **1a** (0.5 mmol, 1.0 equivalent), DIB (1.5 mmol, 3.0 equivalents), H_2O (specified) and acetic acid (specified) were refluxed at *T* °C for *t* hours. [b] Using mesitylene as the standard, the yield of the by-product **3a** was determined by ^{1}H NMR as **trace**. [c] Yield of **2a** by ^{1}H NMR using mesitylene as an intnernal standard. [d] Argon atmosphere.

2. Standard orientations of A, TS, B, C and CO_2

Intermediate A

Zero-point correction= 0.255354 (Hartree/Particle)
Thermal correction to Energy= 0.277572
Thermal correction to Enthalpy= 0.278516
Thermal correction to Gibbs Free Energy= 0.198222
Sum of electronic and zero-point Energies= -967.603222
Sum of electronic and thermal Energies= -967.581004
Sum of electronic and thermal Enthalpies= -967.580059
Sum of electronic and thermal Free Energies= -967.660353

6	0	1.577476	-2.012478	-0.067759
6	0	2.618978	-1.380897	-0.057164
6	0	0.357031	-2.801554	-0.073283
8	0	-0.793776	-2.125384	-0.044433
8	0	0.369880	-4.020968	-0.098962
53	0	-0.824409	0.083323	0.013840
8	0	-1.377667	2.255379	0.081974
6	0	-0.276370	2.974506	0.142300
8	0	0.850242	2.474758	0.147347
6	0	-0.523574	4.469210	0.199565
1	0	-1.198407	4.705258	1.027061
1	0	0.424632	4.992840	0.324202
1	0	-1.008188	4.796455	-0.725591
6	0	-2.979275	-0.210537	-0.013775
6	0	-3.496781	-1.304491	0.670000
6	0	-3.764682	0.692161	-0.721775
6	0	-4.882667	-1.496534	0.635757
1	0	-2.850129	-2.006154	1.181779
6	0	-5.148122	0.481818	-0.734477
1	0	-3.327729	1.542521	-1.229561
6	0	-5.705277	-0.607566	-0.060082
1	0	-5.309340	-2.348100	1.157025
1	0	-5.782896	1.173996	-1.279603

1	0	-6.779459	-0.765153	-0.079461
6	0	3.855975	-0.668784	-0.045055
6	0	5.072526	-1.381087	-0.099198
6	0	3.875761	0.740102	0.021817
6	0	6.284851	-0.694220	-0.086885
1	0	5.051071	-2.465010	-0.150156
6	0	5.096314	1.414541	0.033919
1	0	2.943148	1.293591	0.064496
6	0	6.299724	0.703538	-0.020190
1	0	7.217921	-1.248442	-0.129010
1	0	5.105789	2.499292	0.085904
1	0	7.246485	1.236168	-0.010325

TS

Frequencies -- -167.1923

Zero-point correction= 0.253040 (Hartree/Particle)

Thermal correction to Energy= 0.275263

Thermal correction to Enthalpy= 0.276207

Thermal correction to Gibbs Free Energy= 0.194051

Sum of electronic and zero-point Energies= -967.562493

Sum of electronic and thermal Energies= -967.540270

Sum of electronic and thermal Enthalpies= -967.539326

Sum of electronic and thermal Free Energies= -967.621482

6	0	-1.165037	-1.317159	-1.351982
6	0	-2.123311	-0.887115	-0.698409
6	0	-0.293646	-2.146820	-2.319228
8	0	0.899345	-1.746410	-2.390245
8	0	-0.893382	-3.073719	-2.865994
53	0	0.683458	0.533371	-0.516739
8	0	2.128062	1.998478	0.280322
6	0	1.807137	3.192498	-0.191872
8	0	0.839801	3.383415	-0.921805
6	0	2.770797	4.281532	0.239696
1	0	3.655683	4.235837	-0.403615
1	0	2.289323	5.252364	0.117427
1	0	3.093917	4.133417	1.271828
6	0	1.749781	-0.872535	0.718831
6	0	2.504371	-1.870349	0.110326
6	0	1.647332	-0.715884	2.100636
6	0	3.201394	-2.749753	0.946989
1	0	2.501744	-1.985341	-0.968422
6	0	2.359538	-1.602656	2.912244
1	0	1.046497	0.073032	2.538555
6	0	3.132989	-2.615892	2.336128
1	0	3.792094	-3.543656	0.500307

1	0	2.301871	-1.500793	3.991771
1	0	3.677258	-3.306712	2.973261
6	0	-3.182209	-0.353850	0.074665
6	0	-3.502412	-0.918764	1.331563
6	0	-3.943166	0.736656	-0.407658
6	0	-4.552856	-0.399362	2.082542
1	0	-2.926092	-1.763866	1.693989
6	0	-4.990133	1.247721	0.354031
1	0	-3.702590	1.163849	-1.375782
6	0	-5.297227	0.683379	1.598123
1	0	-4.796647	-0.840041	3.044598
1	0	-5.570244	2.084927	-0.022092
1	0	-6.116732	1.084317	2.187354

Intermediate B

Zero-point correction=	0.253783 (Hartree/Particle)
Thermal correction to Energy=	0.277609
Thermal correction to Enthalpy=	0.278554
Thermal correction to Gibbs Free Energy=	0.189822
Sum of electronic and zero-point Energies=	-967.612957
Sum of electronic and thermal Energies=	-967.589130
Sum of electronic and thermal Enthalpies=	-967.588186
Sum of electronic and thermal Free Energies=	-967.676917

6	0	-0.979256	-0.628373	-0.210041
6	0	-2.198579	-0.662239	-0.251950
6	0	-1.105566	1.780524	2.793800
8	0	0.042327	1.559753	2.788802
8	0	-2.253600	2.007281	2.805641
53	0	1.149646	-0.865255	-0.093063
8	0	3.503475	-0.763449	-0.066937
6	0	3.935643	-1.941683	0.294887
8	0	3.185974	-2.892740	0.558695
6	0	5.448867	-2.068097	0.376934
1	0	5.726116	-3.097670	0.607881
1	0	5.902348	-1.758762	-0.569627
1	0	5.831338	-1.400836	1.156551
6	0	1.399996	1.216891	-0.734240
6	0	0.480096	1.747422	-1.629378
6	0	2.472844	1.937838	-0.225254
6	0	0.646562	3.078544	-2.029826
1	0	-0.352038	1.160506	-2.001034
6	0	2.617023	3.268025	-0.637895
1	0	3.185120	1.478375	0.447228
6	0	1.710141	3.837310	-1.535185
1	0	-0.060031	3.512279	-2.731359

1	0	3.446502	3.852426	-0.250773
1	0	1.832658	4.869395	-1.849946
6	0	-3.626542	-0.710761	-0.315960
6	0	-4.265983	-1.570325	-1.232676
6	0	-4.412944	0.094440	0.532822
6	0	-5.657722	-1.621444	-1.294951
1	0	-3.662737	-2.192892	-1.885836
6	0	-5.804400	0.038891	0.460377
1	0	-3.926049	0.756202	1.241242
6	0	-6.430970	-0.817452	-0.450675
1	0	-6.139512	-2.289443	-2.003026
1	0	-6.400490	0.664111	1.118805
1	0	-7.515123	-0.859022	-0.502080

Intermediate C

Zero-point correction= 0.241680 (Hartree/Particle)
Thermal correction to Energy= 0.259114
Thermal correction to Enthalpy= 0.260058
Thermal correction to Gibbs Free Energy= 0.191860
Sum of electronic and zero-point Energies= -779.035768
Sum of electronic and thermal Energies= -779.018333
Sum of electronic and thermal Enthalpies= -779.017389
Sum of electronic and thermal Free Energies= -779.085588

6	0	1.124781	-0.353442	-0.000022
6	0	2.345019	-0.362433	-0.000003
53	0	-0.985693	-0.668191	-0.000100
8	0	-3.353081	-0.801004	-0.000316
6	0	-3.666026	-2.069580	0.000149
8	0	-2.827281	-2.981436	0.000631
6	0	-5.159833	-2.356486	0.000060
1	0	-5.624847	-1.904330	0.882006
1	0	-5.624581	-1.905120	-0.882432
1	0	-5.333696	-3.433507	0.000512
6	0	-1.346306	1.523910	-0.000052
6	0	-0.247079	2.371267	-0.000204
6	0	-2.660845	1.976129	0.000131
6	0	-0.483264	3.751761	-0.000174
1	0	0.765515	1.984898	-0.000335
6	0	-2.867838	3.361877	0.000163
1	0	-3.491727	1.283186	0.000225
6	0	-1.788418	4.247616	0.000012
1	0	0.364719	4.430481	-0.000295
1	0	-3.886859	3.737749	0.000306
1	0	-1.962940	5.319445	0.000038
6	0	3.773945	-0.378446	0.000026

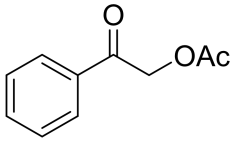
6	0	4.488163	-0.388485	1.215505
6	0	4.488206	-0.389200	-1.215421
6	0	5.882098	-0.407950	1.210871
1	0	3.940284	-0.383633	2.152417
6	0	5.882141	-0.408661	-1.210726
1	0	3.940361	-0.384900	-2.152355
6	0	6.582649	-0.418003	0.000088
1	0	6.422647	-0.417198	2.152847
1	0	6.422723	-0.418461	-2.152678
1	0	7.668661	-0.434223	0.000112

CO_2

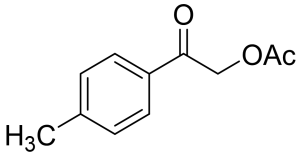
Zero-point correction= 0.011565 (Hartree/Particle)
Thermal correction to Energy= 0.014202
Thermal correction to Enthalpy= 0.015146
Thermal correction to Gibbs Free Energy= -0.009149
Sum of electronic and zero-point Energies= -188.578828
Sum of electronic and thermal Energies= -188.576191
Sum of electronic and thermal Enthalpies= -188.575246
Sum of electronic and thermal Free Energies= -188.599542

6	0	0.000000	0.000000	0.000000
8	0	0.000000	0.000000	1.169356
8	0	0.000000	0.000000	-1.169356

3. ^{1}H and ^{13}C -NMR Analytical Date

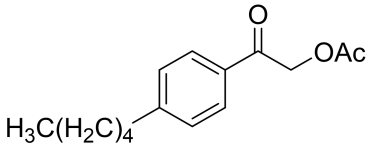


2-Oxo-2-phenylethyl Acetate (**2a**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 84 mg (94%) of **2a**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J = 7.5 Hz, 2H), 7.59 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.0 Hz, 2H), 5.33 (s, 2H), 2.21 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 192.3, 170.5, 134.3, 133.9, 128.9, 127.8, 66.1, 20.6. For the high-resolution mass spectrometry data please refer to [2].

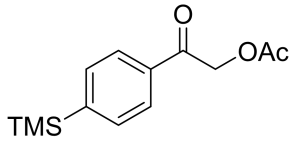


2-Oxo-2-(*p*-tolyl)ethyl Acetate (**2b**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 44 mg (46%) of **2b**.

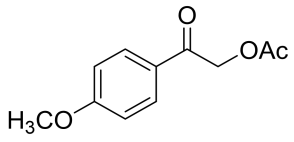
Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, J = 7.5 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 5.32 (s, 2H), 2.42 (s, 3H), 2.23 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.9, 170.6, 145.0, 131.9, 129.7, 128.0, 66.1, 21.9, 20.7. For the high-resolution mass spectrometry data please refer to [2].



2-Oxo-2-(4-pentylphenyl)ethyl Acetate (**2c**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 104 mg (84%) of **2c**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 7.5 Hz, 2H), 7.28 (d, J = 7.5 Hz, 2H), 5.32 (s, 2H), 2.66 (t, J = 7.5 Hz, 2H), 2.22 (s, 3H), 1.66 – 1.60 (m, 2H), 1.36 – 1.30 (m, 4H), 0.89 (t, J = 6.5 Hz, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.9, 170.5, 149.9, 132.1, 129.0, 128.0, 66.1, 36.1, 31.5, 30.8, 22.6, 20.7, 14.1. HRMS (ESI-TOF) *m/z*: calcd for $C_{15}H_{20}O_3$ $[M + H]^+$ 249.1486, found 249.1491.

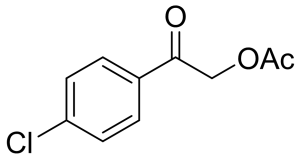


2-Oxo-2-(4-(trimethylsilyl)phenyl)ethyl Acetate (**2d**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 59 mg (47%) of **2d**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.0 Hz, 2H), 5.33 (s, 2H), 2.22 (s, 3H), 0.29 (s, 9H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 192.5, 170.5, 148.6, 134.4, 133.9, 126.8, 66.2, 20.7, -1.3. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{18}O_3Si$ $[M + H]^+$ 251.1098, found 251.1104.

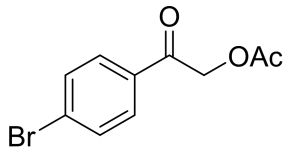


2-(4-Methoxyphenyl)-2-oxoethyl Acetate (**2e**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 58 mg (56%) of **2e**. Lightyellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 7.5 Hz, 2H), 6.94 (d, J = 8.0 Hz, 2H), 5.29 (s, 2H), 3.86 (s, 3H), 2.21 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 190.7, 170.5, 164.1, 130.1, 127.3, 114.1, 65.8, 55.6, 20.6. For the

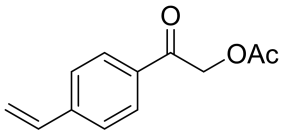
high-resolution mass spectrometry data please refer to [2].



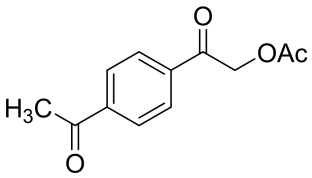
2-(4-Chlorophenyl)-2-oxoethyl Acetate (**2f**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 51 mg (48%) of **2f**. White solid, mp: 57–60 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, J = 7.5 Hz, 2H), 7.46 (d, J = 7.5 Hz, 2H), 5.29 (s, 2H), 2.22 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.3, 170.5, 140.6, 132.7, 129.4, 129.3, 66.0, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_9ClO_3$ $[M + H]^+$ 213.0313, found 213.0308.



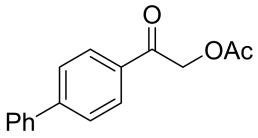
2-(4-Bromophenyl)-2-oxoethyl Acetate (**2g**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 39 mg (30%) of **2g**. White solid, mp: 77–79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, J = 7.5 Hz, 2H), 7.64 (d, J = 7.5 Hz, 2H), 5.29 (s, 2H), 2.23 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.5, 170.5, 133.1, 132.4, 129.4, 129.3, 66.0, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_9BrO_3$ $[M + H]^+$ 256.9808, found 256.9802.



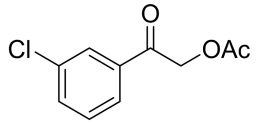
2-Oxo-2-(4-vinylphenyl)ethyl Acetate (**2h**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 85 mg (83%) of **2h**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.5 Hz, 2H), 6.75 (dd, J = 17.5, 10.5 Hz, 1H), 5.89 (d, J = 17.5 Hz, 1H), 5.43 (d, J = 11.0 Hz, 1H), 5.33 (s, 2H), 2.24 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.7, 170.6, 143.0, 135.9, 133.4, 128.3, 126.7, 117.5, 66.2, 20.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{12}O_3$ $[M + H]^+$ 205.0860, found 205.0854.



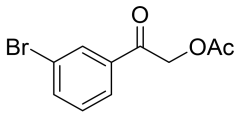
2-(4-Acetylphenyl)-2-oxoethyl Acetate (**2i**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 50 mg (45%) of **2i**. White solid, mp: 65–68 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (d, J = 7.5 Hz, 2H), 7.99 (d, J = 7.5 Hz, 2H), 5.34 (s, 2H), 2.65 (s, 3H), 2.34 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 197.4, 192.0, 170.5, 141.0, 137.5, 128.9, 128.2, 66.3, 27.0, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{14}O_3$ $[M + H]^+$ 221.0809, found 221.0801.



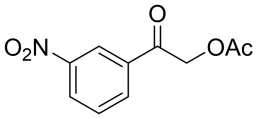
2-([1,1'-Biphenyl]-4-yl)-2-oxoethyl Acetate (**2j**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 103 mg (81%) of **2j**. White solid, mp: 102–105 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, J = 7.5 Hz, 2H), 7.71 (d, J = 7.5 Hz, 2H), 7.62 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.0 Hz, 2H), 7.41 (t, J = 7.5 Hz, 1H), 5.337 (s, 2H), 2.25 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 192.0, 170.6, 146.8, 139.8, 133.1, 129.2, 128.63, 128.55, 127.7, 127.5, 66.2, 20.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{14}O_3$ $[M + H]^+$ 255.1016, found 255.1013.



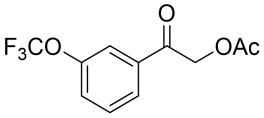
2-(3-Chlorophenyl)-2-oxoethyl Acetate (**2k**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 84 mg (79%) of **2k**. Khaki oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (s, 1H), 7.79 (d, J = 7.5 Hz, 1H), 7.58 (d, J = 7.5 Hz, 1H), 7.44 (t, J = 7.5 Hz, 1H), 5.30 (s, 2H), 2.23 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.3, 170.5, 135.8, 135.4, 134.0, 130.4, 128.1, 126.0, 66.1, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_9ClO_3$ $[M + H]^+$ 213.0313, found 213.0315.



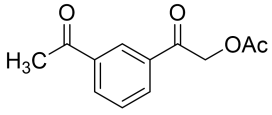
2-(3-Bromophenyl)-2-oxoethyl Acetate (**2l**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 75 mg (58%) of **2l**. Khaki oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 1H), 5.30 (s, 2H), 2.24 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.2, 170.5, 136.9, 136.0, 131.0, 130.6, 126.4, 123.4, 66.1, 20.7. For the high-resolution mass spectrometry data please refer to [2].



2-(3-Nitrophenyl)-2-oxoethyl Acetate (**2m**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 26 mg (23%) of **2m**. Gold oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.48 (d, J = 8.5 Hz, 1H), 8.26 (d, J = 7.5 Hz, 1H), 7.74 (t, J = 8.5 Hz, 1H), 5.37 (s, 2H), 2.25 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 190.6, 170.5, 148.6, 135.5, 133.5, 130.5, 128.3, 122.9, 66.1, 20.7. For the mass spectrometry data please refer to [3].

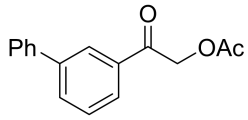


2-Oxo-2-(3-(trifluoromethoxy)phenyl)ethyl Acetate (**2n**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 52 mg (40%) of **2n**. Lightgoldenrodyellow solid, mp: 43–45 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, J = 7.5 Hz, 1H), 7.77 (s, 1H), 7.55 (t, J = 7.5 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 5.31 (s, 2H), 2.23 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 191.1, 170.5, 149.8, 136.1, 130.7, 126.4, 126.2, 120.5 (d, J = 259.6 Hz), 120.4, 66.1, 20.6. HRMS (ESI-TOF) *m/z*: calcd for $C_{11}H_9F_3O_4$ $[M + Na]^+$ 285.0346, found 285.0345.

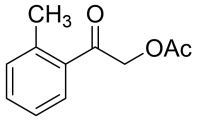


2-(3-Acetylphenyl)-2-oxoethyl Acetate (**2o**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 74 mg (67%) of **2o**. Colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (s, 1H), 8.20 (d, J = 7.5 Hz, 1H),

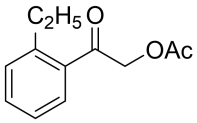
8.12 (d, J = 8.0 Hz, 1H), 7.63 (t, J = 8.0 Hz, 1H), 5.38 (s, 2H), 2.67 (s, 3H), 2.25 (s, 3H). $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 197.1, 191.9, 170.6, 137.7, 134.7, 133.4, 132.1, 129.6, 127.6, 66.2, 26.9, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_{13}H_{14}O_3$ $[M + H]^+$ 221.0809, found 221.0812.



2-([1,1'-Biphenyl]-3-yl)-2-oxoethyl Acetate (**2p**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 95 mg (75%) of **2p**. White solid, mp: 88–91 °C. ^1H NMR (500 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.88 (d, J = 7.5 Hz, 1H), 7.83 (d, J = 7.5 Hz, 1H), 7.60 (d, J = 7.0 Hz, 2H), 7.56 (t, J = 8.0 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 7.40 (t, J = 7.5 Hz, 1H), 5.39 (s, 2H), 2.25 (s, 3H). $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 192.3, 170.6, 142.3, 140.0, 134.9, 132.7, 129.5, 129.2, 128.2, 127.4, 126.7, 126.6, 66.3, 20.8. HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{14}O_3$ $[M + H]^+$ 255.1016, found 255.1008.

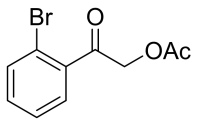


2-Oxo-2-(*o*-tolyl)ethyl Acetate (**2q**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 40 mg (41%) of **2q**. Colorless oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, J = 8.0 Hz, 1H), 7.42 (t, J = 7.5 Hz, 1H), 7.28 (d, J = 7.5 Hz, 2H), 5.18 (s, 2H), 2.52 (s, 3H), 2.21 (s, 3H). $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 195.9, 170.6, 139.2, 134.4, 132.4, 132.3, 128.2, 125.9, 67.4, 21.3, 20.7. For the mass spectrometry data please refer to [4].

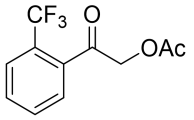


2-(2-Ethylphenyl)-2-oxoethyl Acetate (**2r**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 64 mg (62%) of **2r**. Lightgoldenrodyellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, J = 7.5 Hz, 1H), 7.45 (t, J = 14.5, 7.5 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.27 (t, J = 7.5 Hz, 1H), 5.15 (s, 2H), 2.84 (q, J = 7.5 Hz, 2H), 2.21 (s, 3H), 1.22 (t, J = 7.5 Hz, 3H). $^{13}C\{H\}$ NMR (126 MHz, $CDCl_3$) δ 196.4, 170.5, 145.0, 134.6, 132.3, 130.8, 128.0, 125.8, 67.6, 27.0,

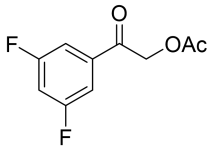
20.7, 16.0. HRMS (ESI-TOF) *m/z*: calcd for $C_{12}H_{14}O_3$ $[M + H]^+$ 207.1016, found 207.1019.



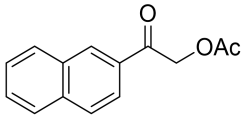
2-(2-Bromophenyl)-2-oxoethyl Acetate (**2s**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 61 mg (47%) of **2s**. Lightyellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.0 Hz, 1H), 7.41 (t, J = 7.5 Hz, 1H), 7.36 (t, J = 7.5 Hz, 1H), 5.16 (s, 2H), 2.18 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 196.6, 170.5, 138.4, 134.0, 132.7, 129.5, 127.7, 119.3, 67.8, 20.6. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_9BrO_3$ $[M + H]^+$ 256.9808, found 256.9808.



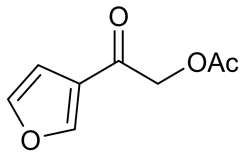
2-Oxo-2-(2-(trifluoromethyl)phenyl)ethyl Acetate (**2t**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 86 mg (70%) of **2t**. Lightyellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (dd, J = 7.2, 2.0 Hz, 1H), 7.64 (td, J = 6.8, 2.4, 2H), 7.57 – 7.55(m, 1H), 5.04 (s, 2H), 2.18 (s, 3H). ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 197.3, 170.4, 136.6, 132.1, 131.1, 127.8, 127.0 (q, J = 4.6 Hz), 123.5 (q, J = 275.7), 67.9, 20.5. For the high-resolution mass spectrometry data please refer to [4].



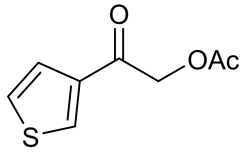
2-(3,5-Difluorophenyl)-2-oxoethyl Acetate (**2u**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 23 mg (21%) of **2u**. White solid, mp: 79–81 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (d, J = 4.0 Hz, 2H), 7.07 (t, J = 8.0 Hz, 1H), 5.25 (s, 2H), 2.23 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 190.2, 170.4, 163.4 (dd, J = 252, 11.3 Hz), 137.1 (t, J = 7.6 Hz), 111.1 (dd, J = 20.2, 6.3 Hz), 109.4 (t, J = 25.2 Hz), 66.0, 20.6. HRMS (ESI-TOF) *m/z*: calcd for $C_{10}H_8F_2O_3$ $[M + H]^+$ 215.0515, found 215.0510.



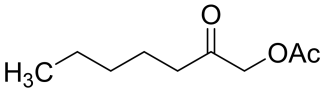
2-(Naphthalen-2-yl)-2-oxoethyl Acetate (**2v**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 74 mg (65%) of **2v**. Lightyellow solid, mp: 77–79 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (s, 1H), 7.95 (t, J = 8.5 Hz, 2H), 7.88 (dd, J = 14.5, 8.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 1H), 7.56 (t, J = 7.0 Hz, 1H), 5.47 (s, 2H), 2.26 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 192.2, 170.7, 136.0, 132.5, 131.6, 129.7, 129.6, 129.02, 128.96, 128.0, 127.2, 123.4, 66.2, 20.8. For the high-resolution mass spectrometry data please refer to [2].



2-(Furan-3-yl)-2-oxoethyl Acetate (**2w**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 56 mg (66%) of **2w**. Lightyellow oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.49 (s, 1H), 6.79 (s, 1H), 5.04 (s, 2H), 2.21 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 187.7, 170.5, 147.3, 144.5, 124.5, 108.5, 66.6, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_8H_8O_4$ [M + H]$^+$ 169.0496, found 169.0501.

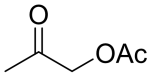


2-Oxo-2-(thiophen-3-yl)ethyl Acetate (**2x**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 10 / 1) to afford 58 mg (63%) of **2x**. Goldenrod oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.12 (s, 1H), 7.59 (d, J = 4.0 Hz, 1H), 7.37 (t, J = 3.0 Hz, 1H), 5.21 (s, 2H), 2.22 (s, 3H). ^{13}C{H} NMR (126 MHz, $CDCl_3$) δ 186.9, 170.6, 138.8, 132.4, 127.0, 126.6, 66.4, 20.7. HRMS (ESI-TOF) *m/z*: calcd for $C_8H_8O_3S$ [M + H]$^+$ 185.0267, found 185.0270.

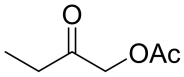


2-Oxoheptyl Acetate (**2y**). Purification was performed by column chromatography

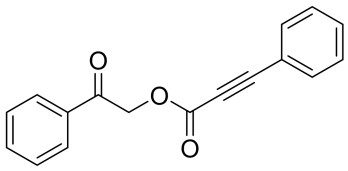
(petroleum ether / ethyl acetate = 4 / 1) to afford 34 mg (40%) of **2y**. White solid, mp: 17– 19 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.73 (s, 2H), 2.40 (t, J = 7.2 Hz, 2H), 2.08 (s, 3H), 1.51 – 1.43 (m, 2H), 1.29 – 1.19 (m, 4H), 0.85 (t, J = 7.2 Hz, 3H). ^{13}C{H} NMR (101 MHz, DMSO-d_6) δ 202.4, 172.6, 67.8, 37.7, 30.7, 22.4, 21.4, 20.2, 13.8. HRMS (ESI-TOF) *m/z*: calcd for $C_9H_{16}O_3$ [M + Na]$^+$ 195.0992, found 195.0992.



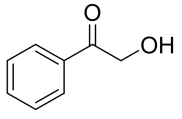
2-Oxopropyl Acetate (**2z**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 20 / 1) to afford 52 mg (45%) of **2z**. Amber liquid. ^{1}H NMR (400 MHz, DMSO-d_6) δ 4.71 (s, 2H), 2.18 (s, 3H), 2.03 (s, 3H). For the ^{13}C{H} NMR data please refer to [4], and for the high-resolution mass spectrometry data please refer to [8].



2-Oxobutyl Acetate (**2za**). Purification was performed by column chromatography (petroleum ether / ethyl acetate = 20 / 1) to afford 17 mg (26%) of **2za**. Amber liquid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.66 (s, 2H), 2.48-2.42 (q, J = 7.2 Hz, 2H), 2.17 (s, 3H), 1.10 (t, J = 7.4 Hz, 3H).



2-Oxo-2-phenylethyl 3-phenylpropiolate (**3a**). Purification was performed by column chromatography (petroleum ether/ ethyl acetate = 10/1) to afford 17 mg (35%) of **3a**. White solid, mp: 83–85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 7.2 Hz, 2H), 7.65 – 7.61 (m, 3H), 7.53 – 7.45 (m, 3H), 7.40 (t, J = 7.6 Hz, 2H), 5.50 (s, 2H). ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 191.1, 153.5, 134.3, 134.1, 133.3, 131.1, 129.1, 128.8, 128.0, 119.6, 88.2, 80.1, 67.2. For the high-resolution mass spectrometry data please refer to [5].



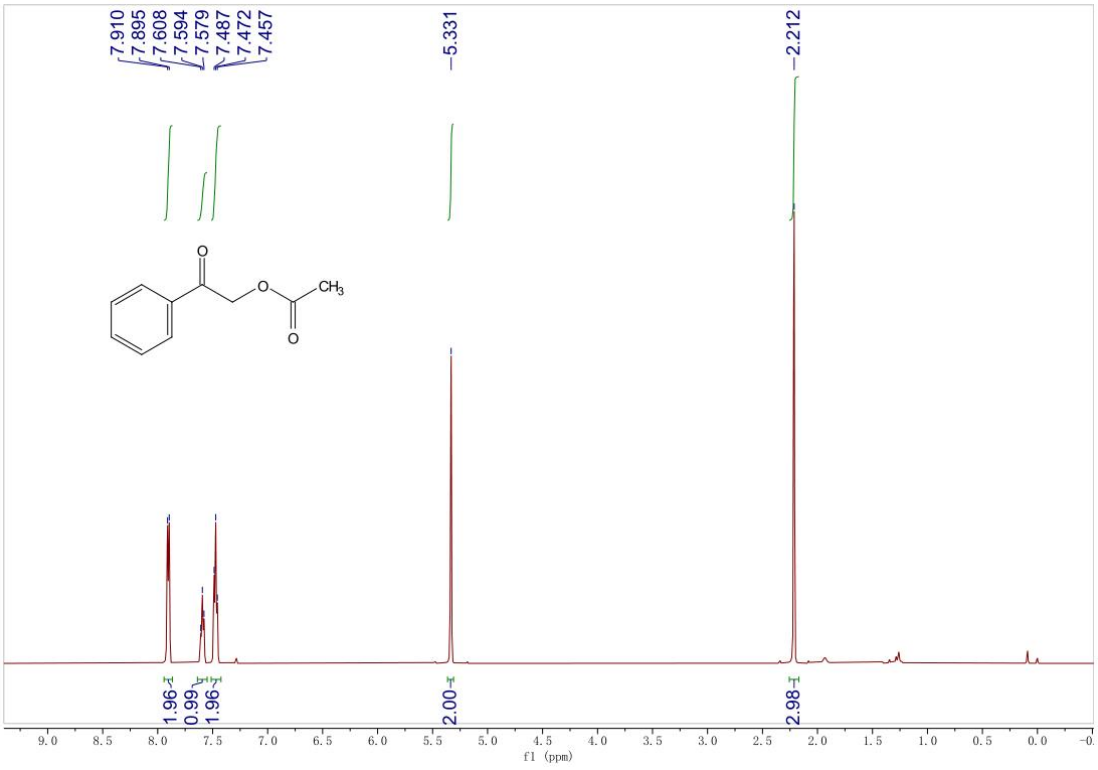
2-Hydroxy-1-phenylethan-1-one (**4**). Purification was performed by column

chromatography (petroleum ether/ ethyl acetate = 10/1) to afford 7 mg (10%) of **4**. White solid, mp: 79–81 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 7.6 Hz, 2H), 7.64 (t, J = 7.2 Hz, 1H), 7.51 (t, J = 8.0 Hz, 2H), 4.89 (s, 2H), 3.52 (s, 1H). ^{13}C{H} NMR (101 MHz, $CDCl_3$) δ 198.6, 134.5, 133.5, 129.2, 127.9, 65.6. For the high-resolution mass spectrometry data please refer to [6].

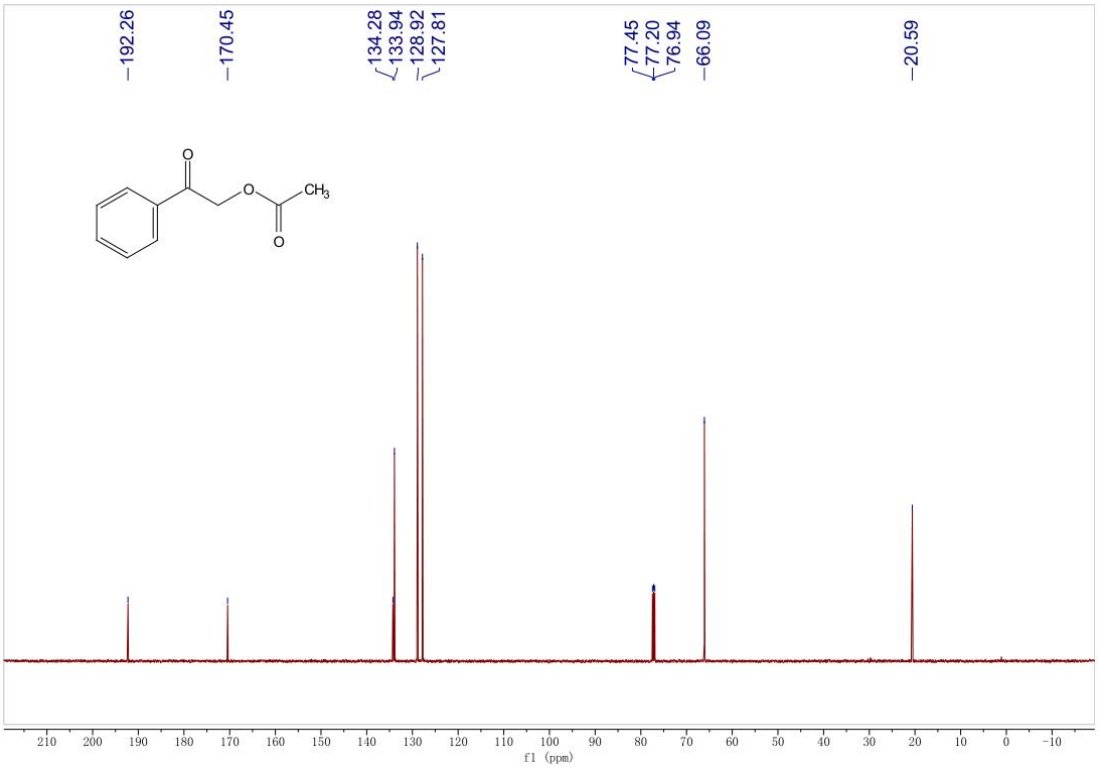
4. Copies of ^{1}H- and ^{13}C-NMR spectra of products

2-oxo-2-phenylethyl acetate (2a)

^{1}H NMR (500 MHz, $CDCl_3$)

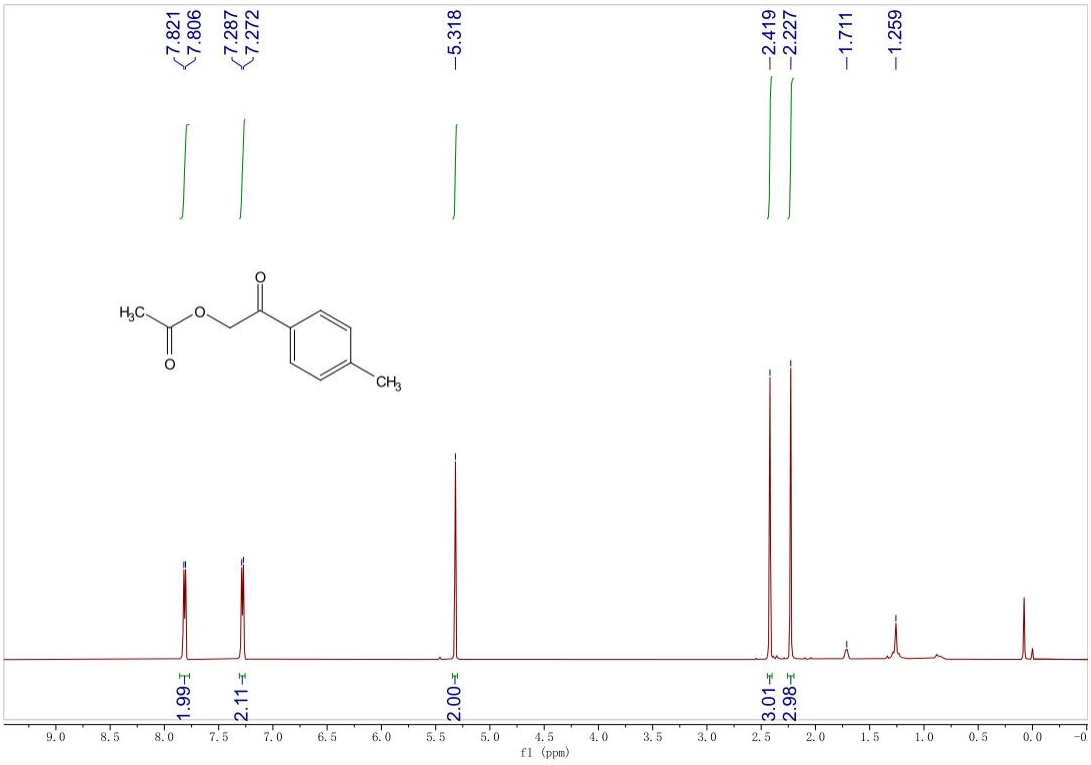


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

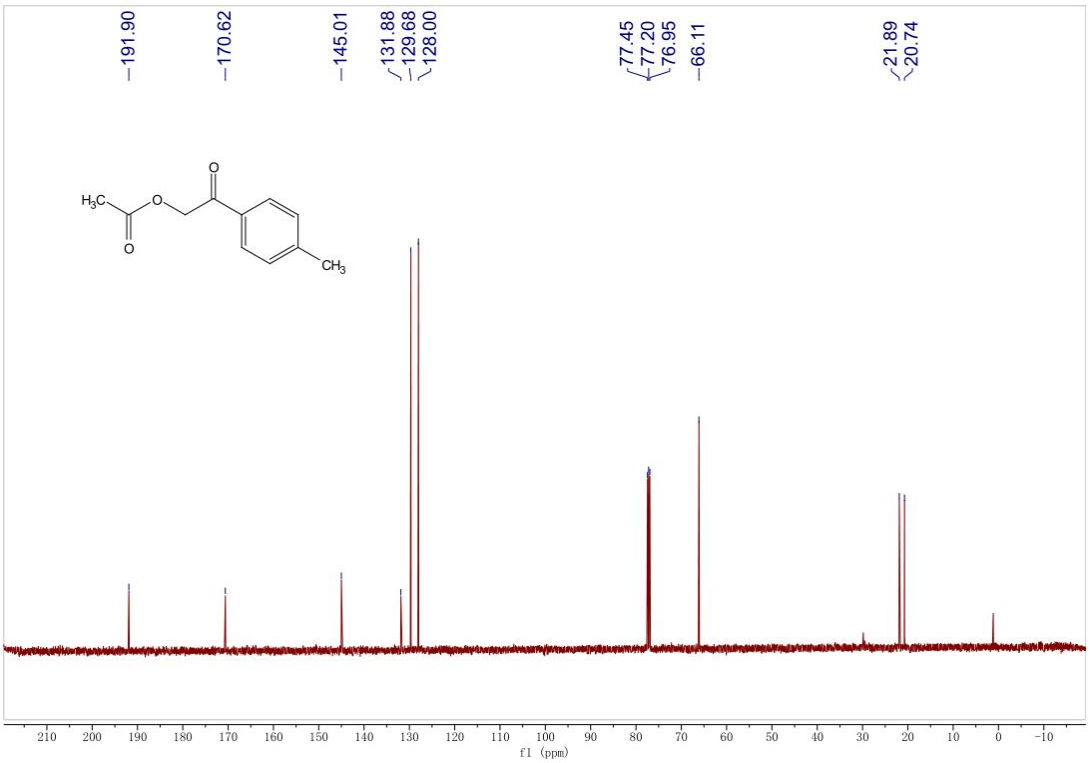


2-oxo-2-(*p*-tolyl)ethyl acetate (2b)

^{1}H NMR (500 MHz, $CDCl_3$)

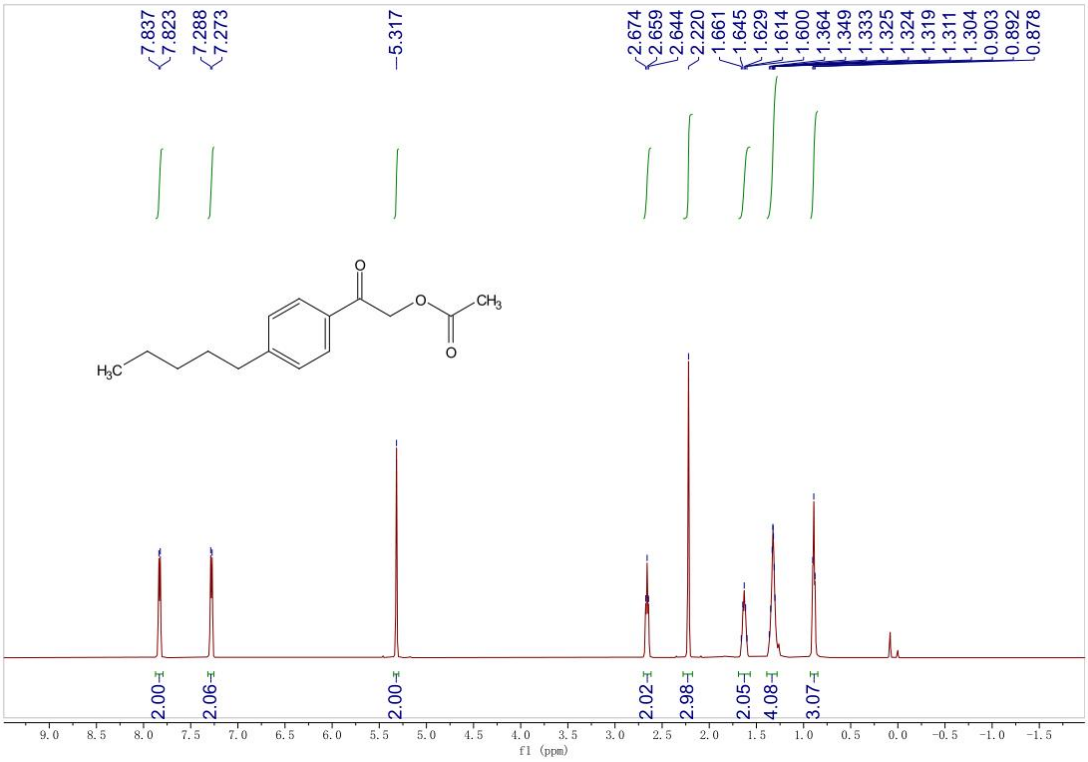


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

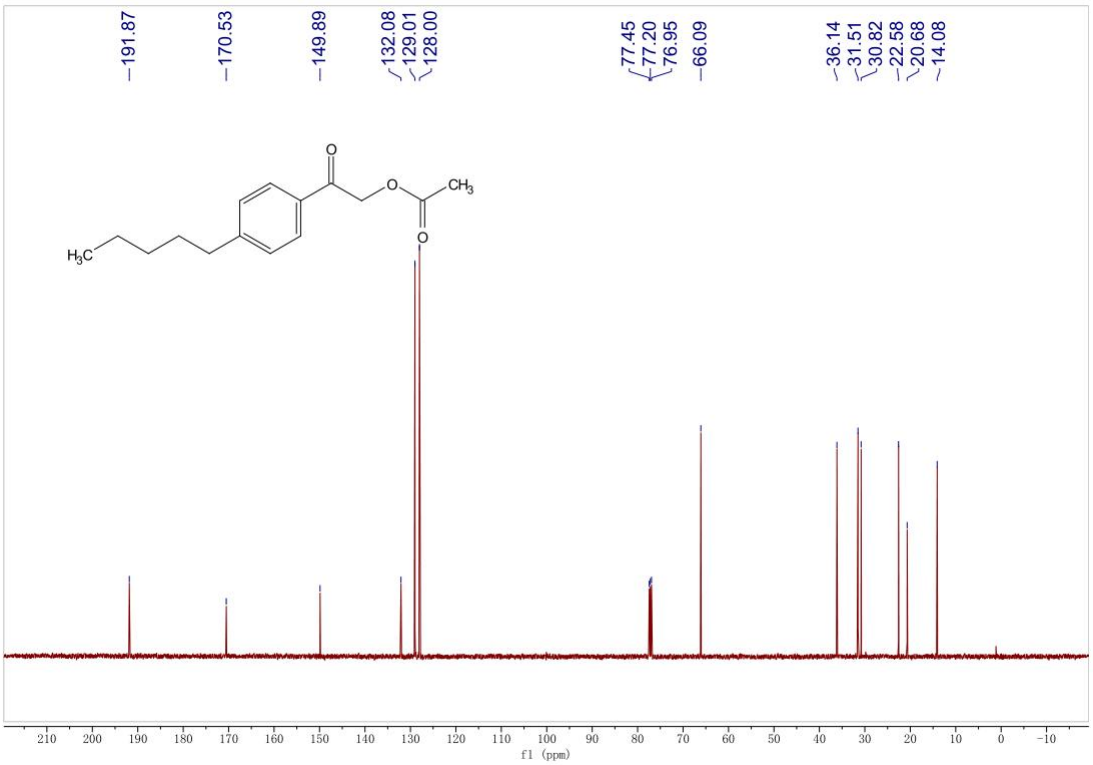


2-oxo-2-(4-pentylphenyl)ethyl acetate (2c)

^{1}H NMR (500 MHz, $CDCl_3$)

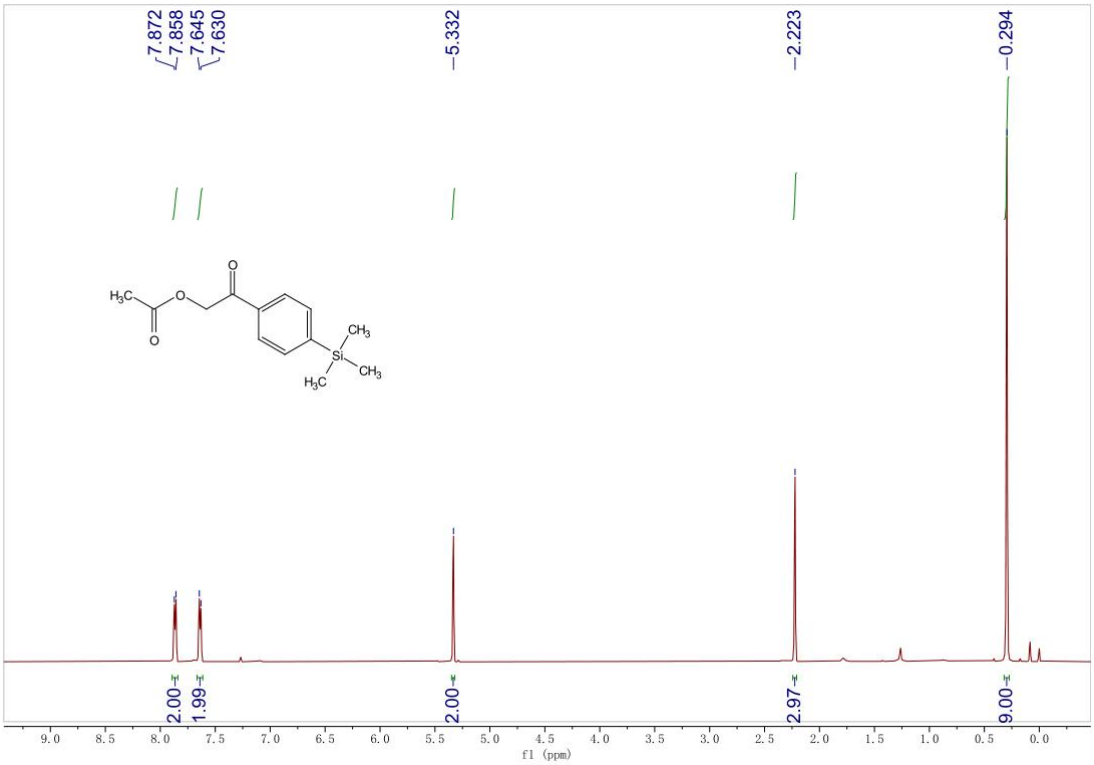


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

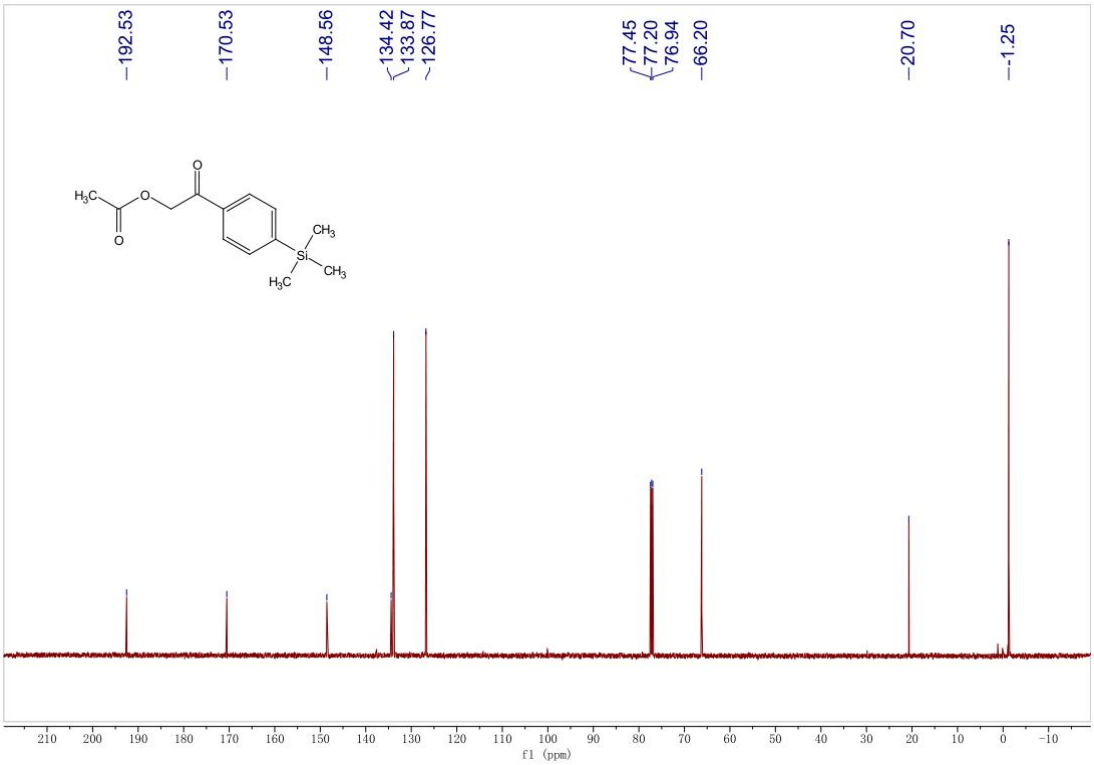


2-oxo-2-(4-(trimethylsilyl)phenyl)ethyl acetate (2d)

^{1}H NMR (500 MHz, $CDCl_3$)

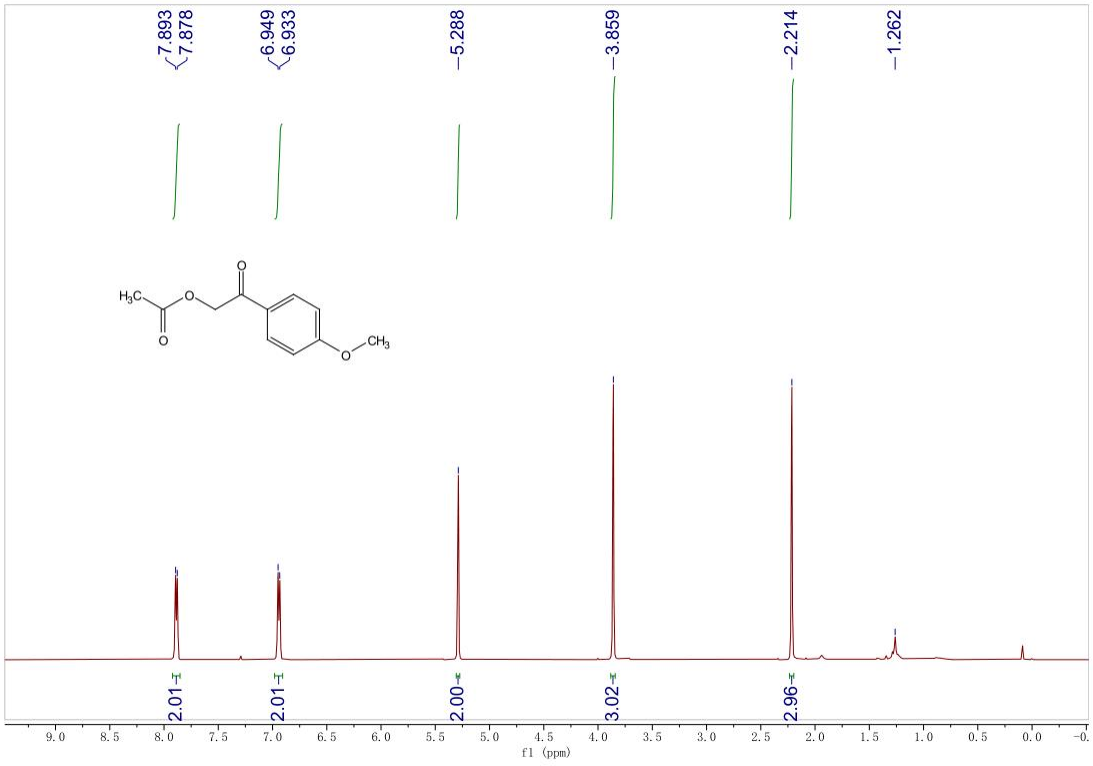


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

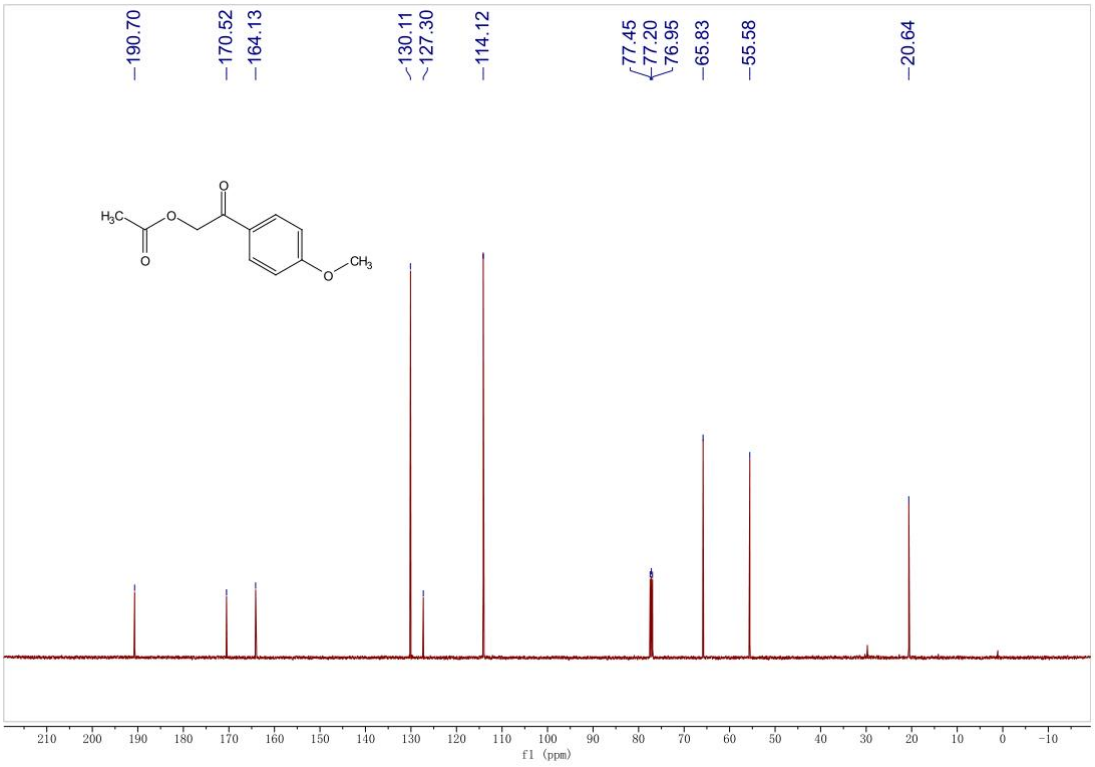


2-(4-methoxyphenyl)-2-oxoethyl acetate (2e)

^{1}H NMR (500 MHz, $CDCl_3$)

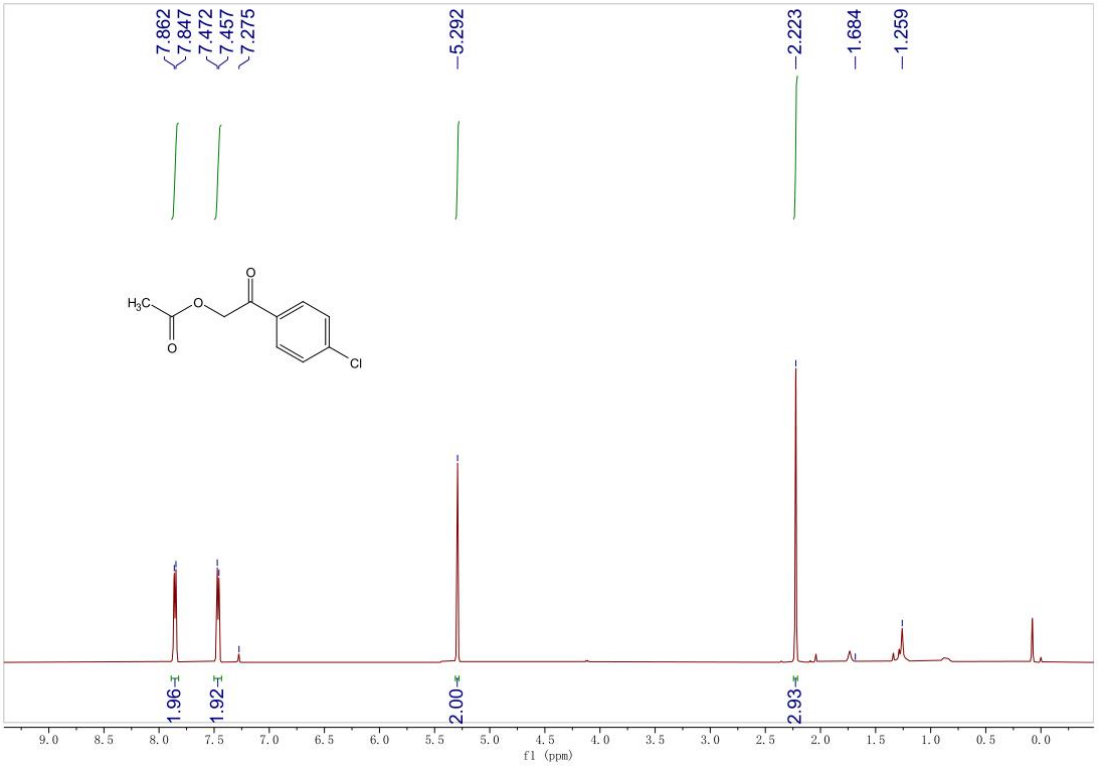


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

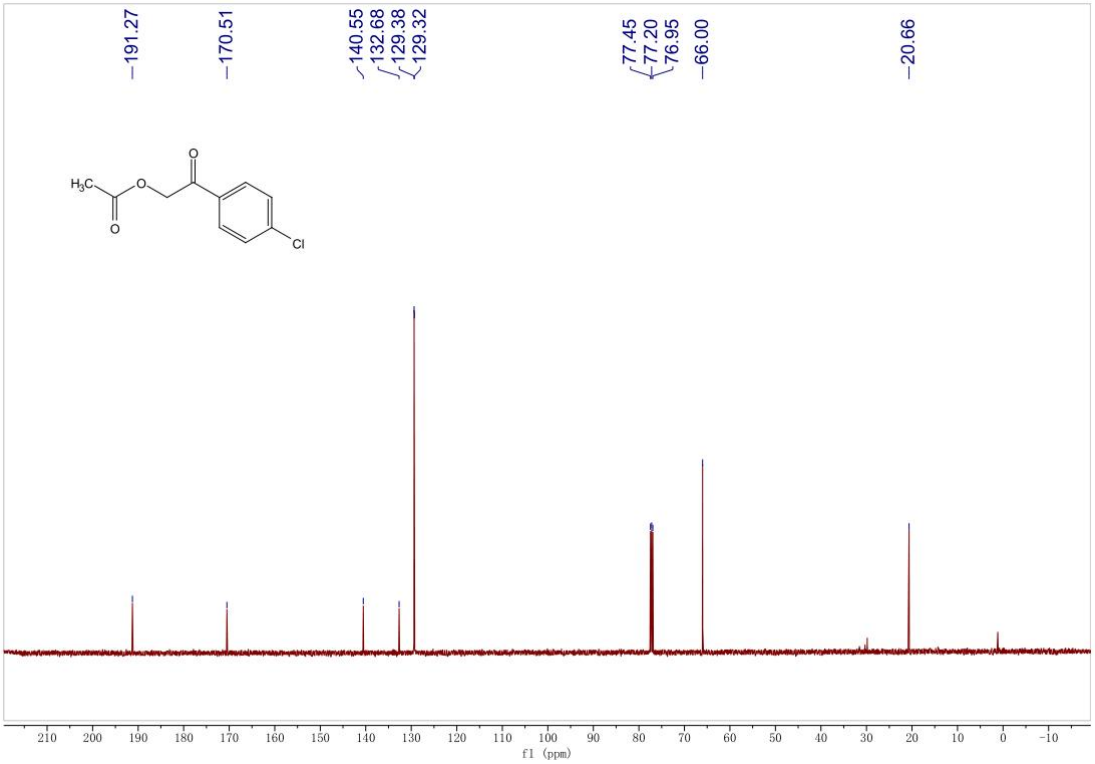


2-(4-chlorophenyl)-2-oxoethyl acetate (2f)

^{1}H NMR (500 MHz, $CDCl_3$)

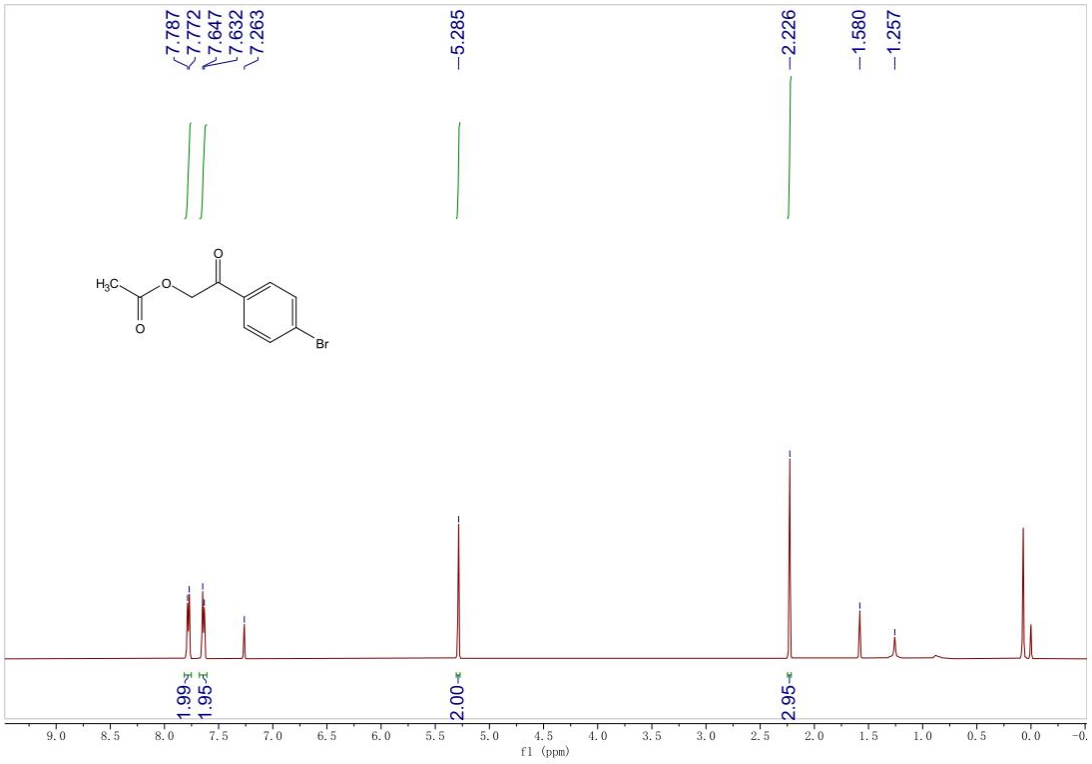


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

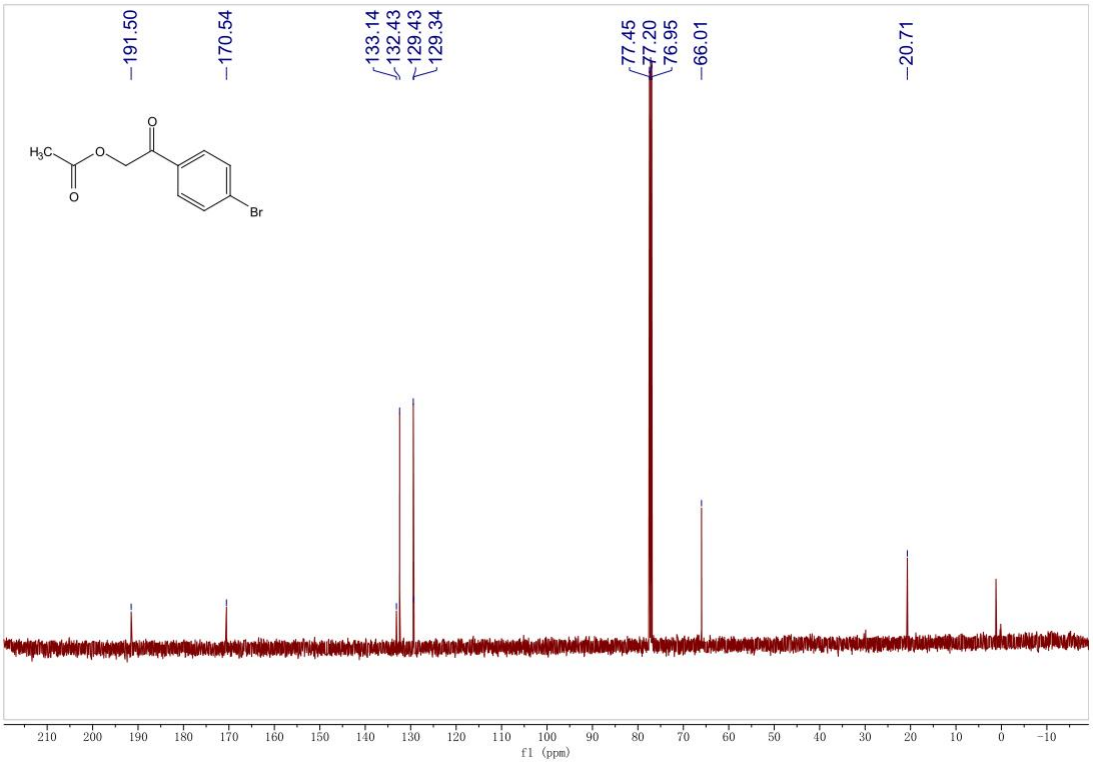


2-(4-bromophenyl)-2-oxoethyl acetate (2g)

^{1}H NMR (500 MHz, $CDCl_3$)

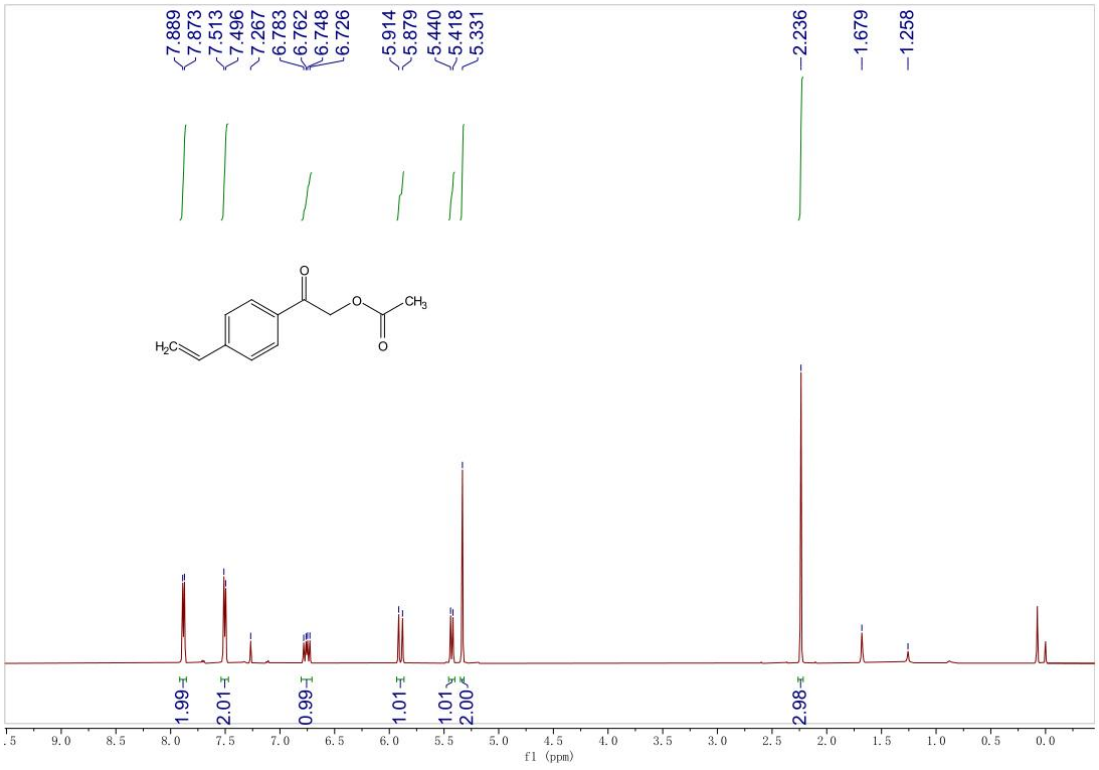


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

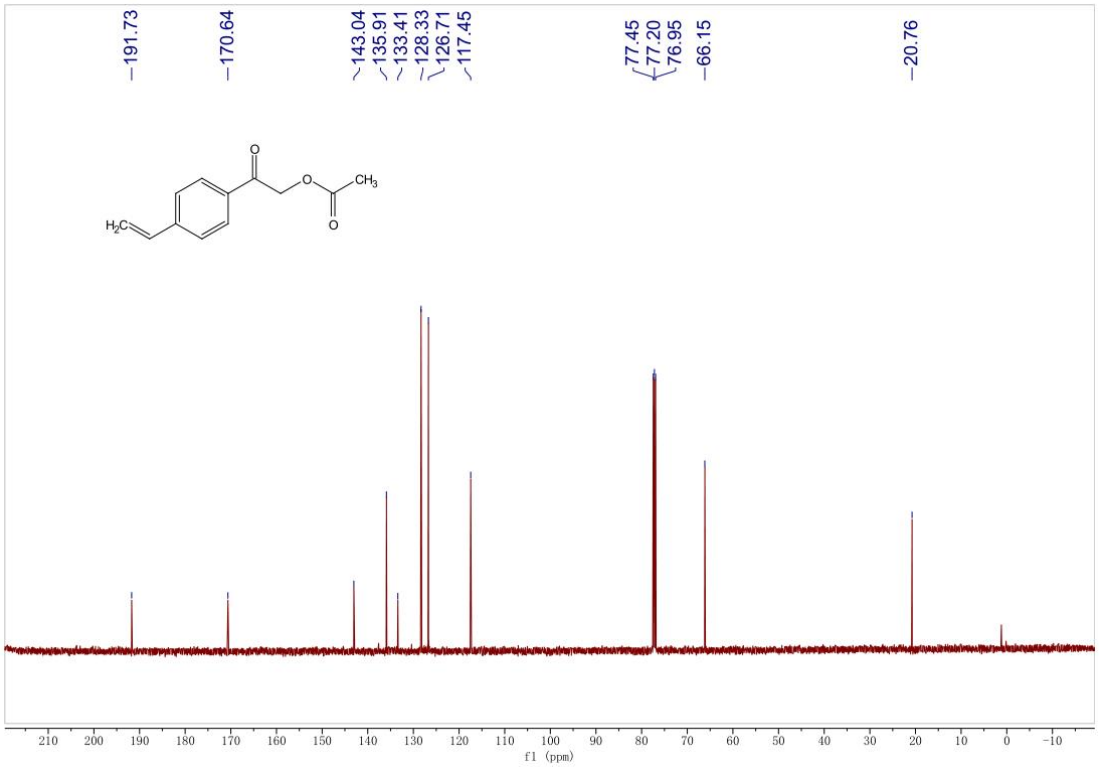


2-oxo-2-(4-vinylphenyl)ethyl acetate (2h)

^{1}H NMR (500 MHz, $CDCl_3$)

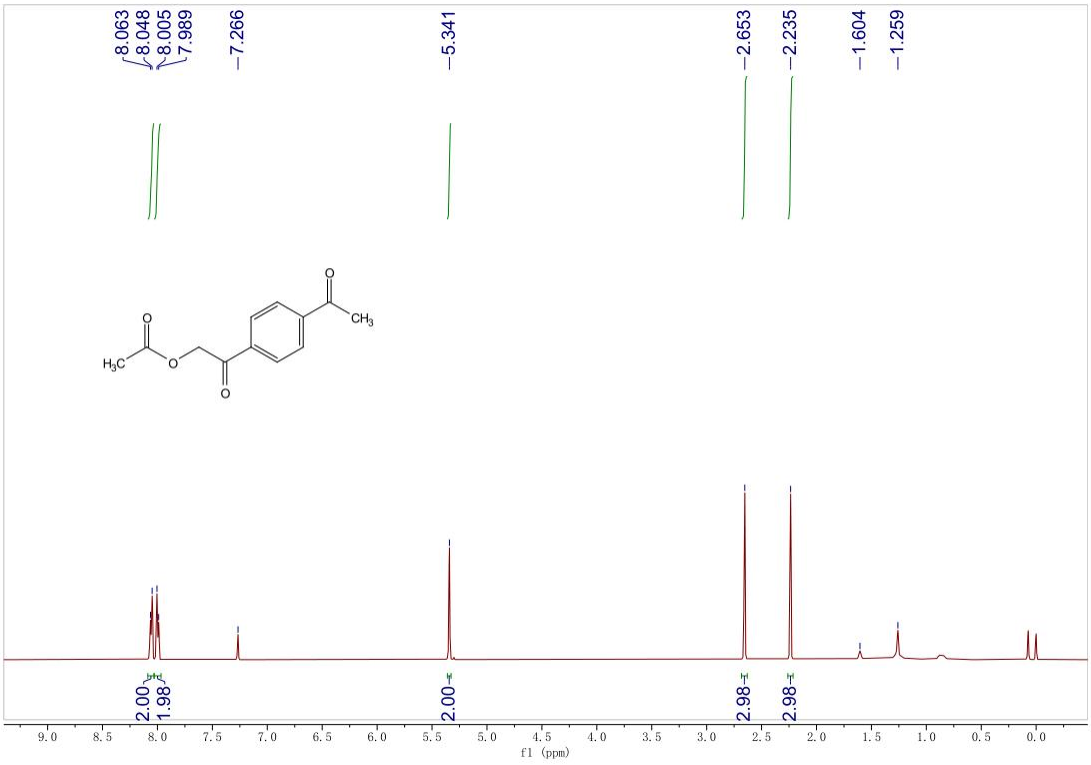


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

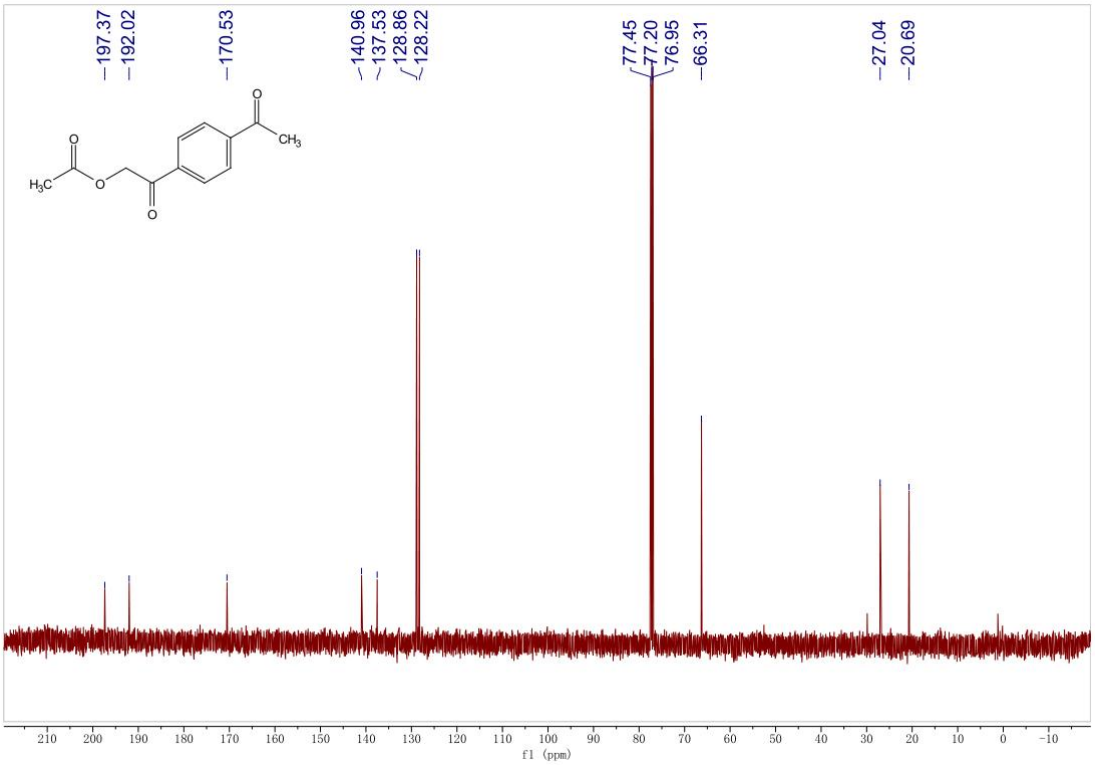


2-(4-acetylphenyl)-2-oxoethyl acetate (2i)

^{1}H NMR (500 MHz, $CDCl_3$)

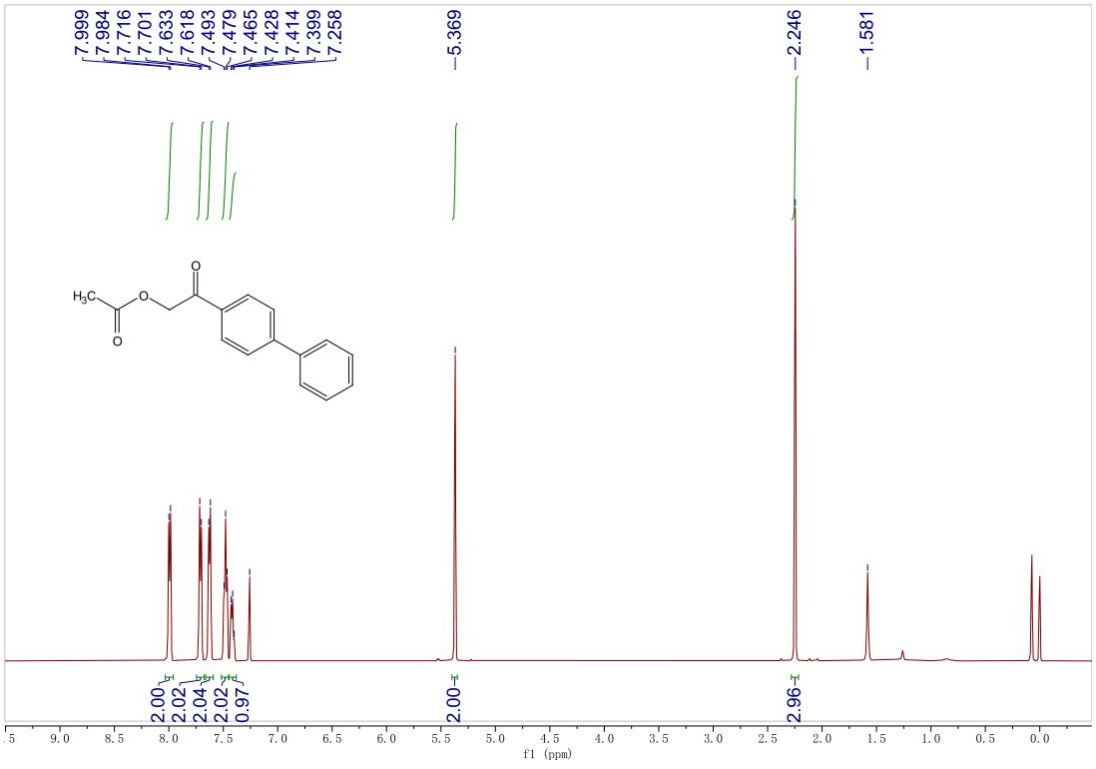


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

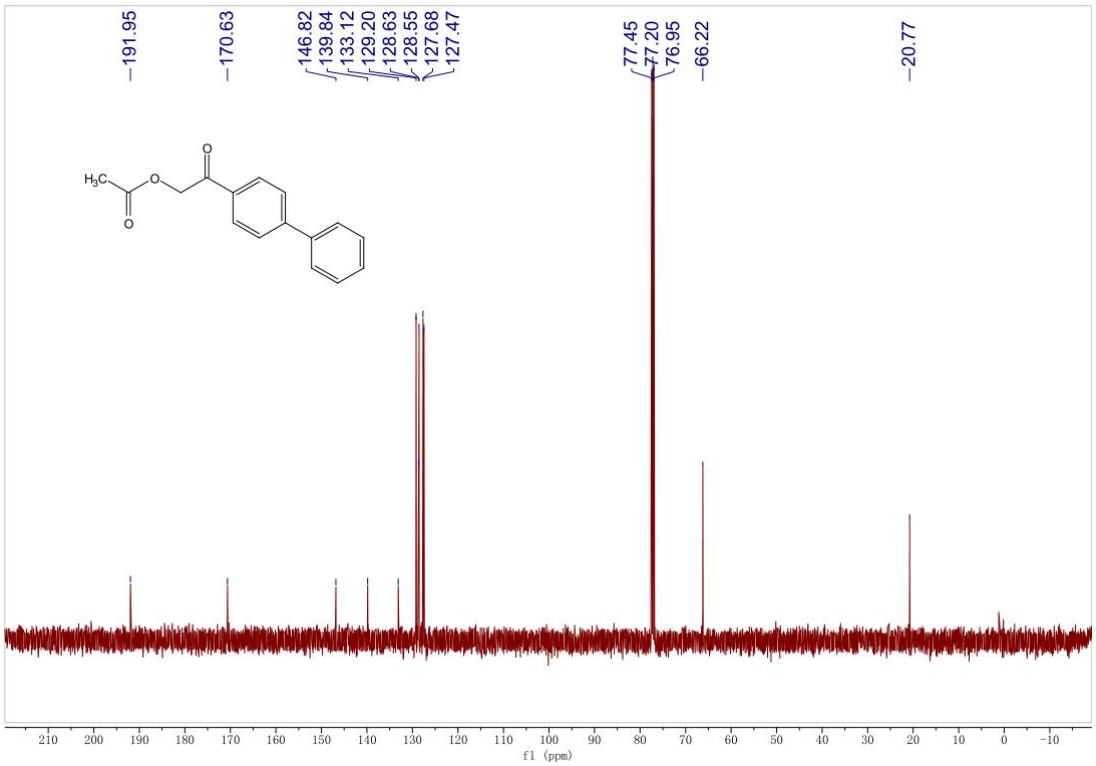


2-([1,1'-biphenyl]-4-yl)-2-oxoethyl acetate (2j)

^{1}H NMR (500 MHz, $CDCl_3$)

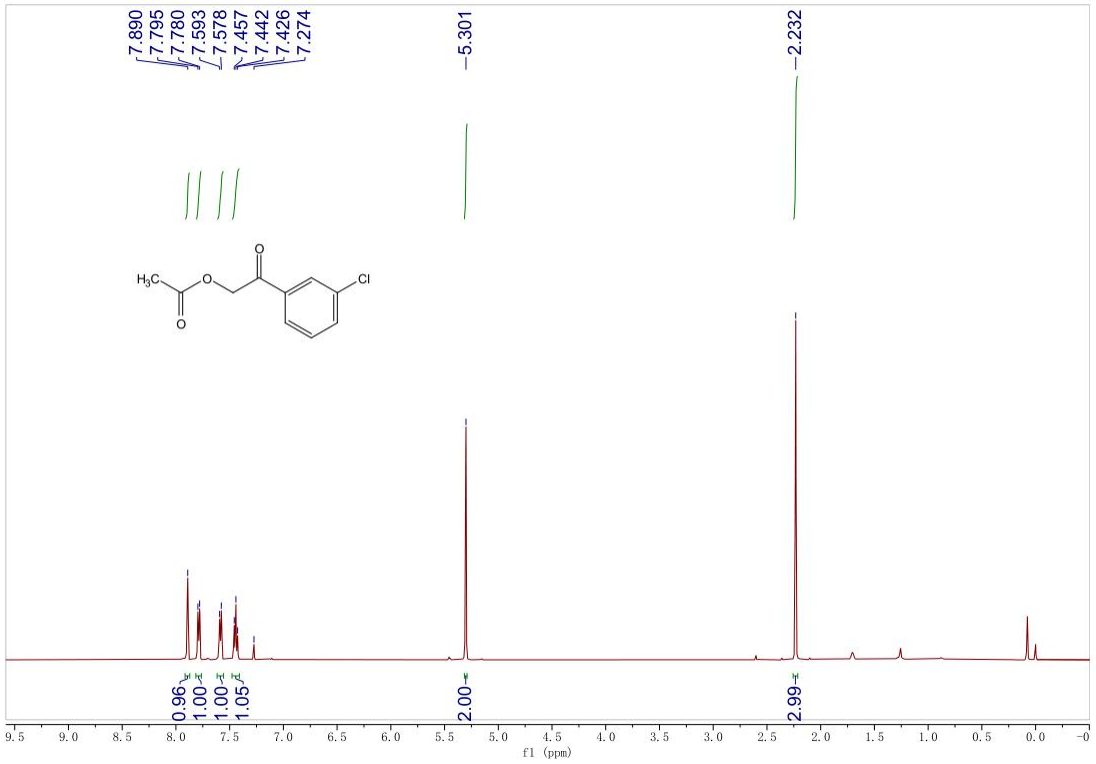


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

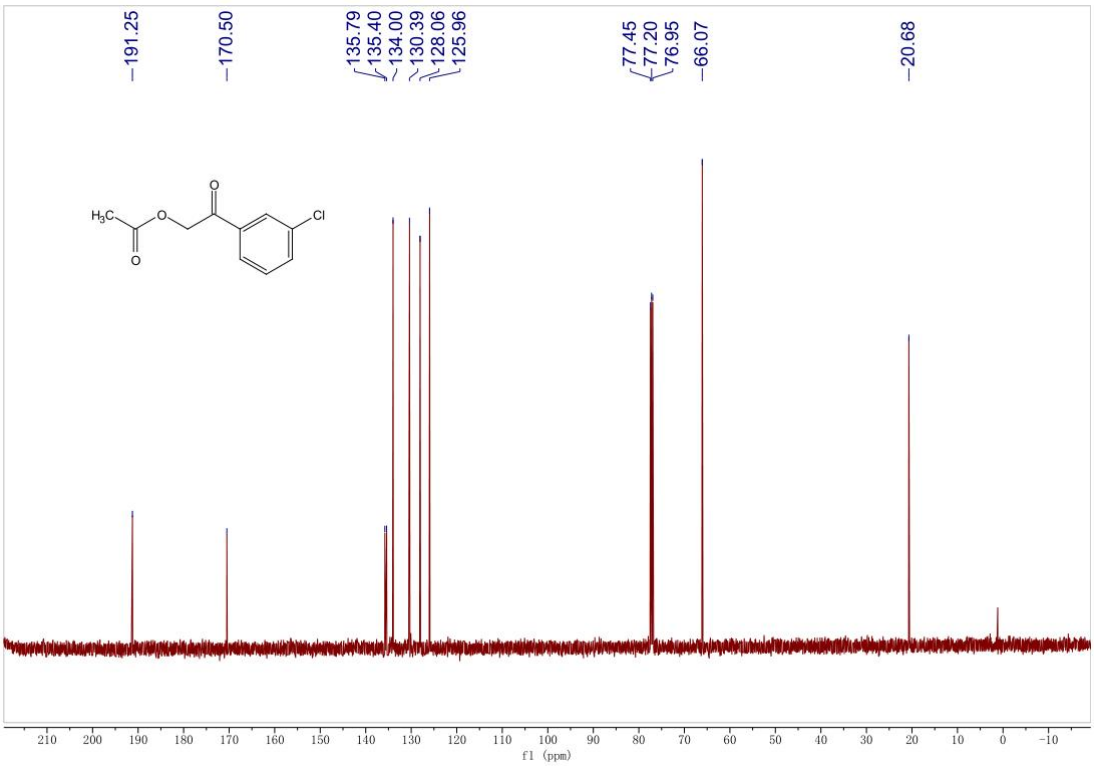


2-(3-chlorophenyl)-2-oxoethyl acetate (2k)

^{1}H NMR (500 MHz, $CDCl_3$)

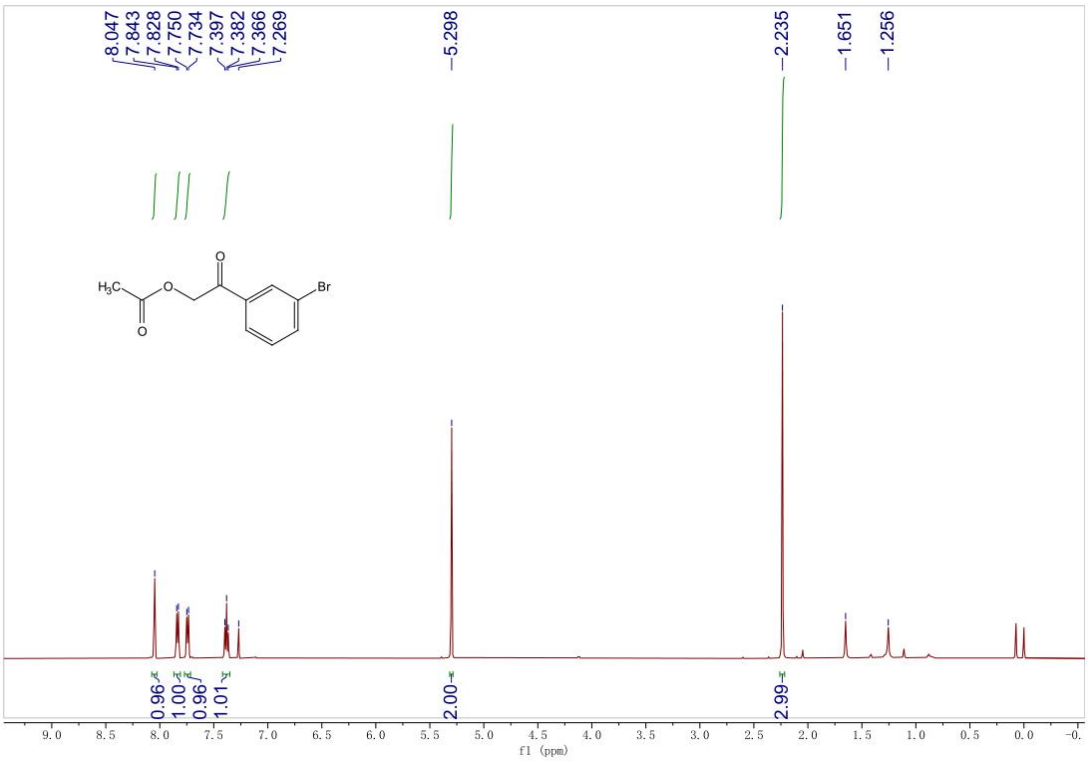


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

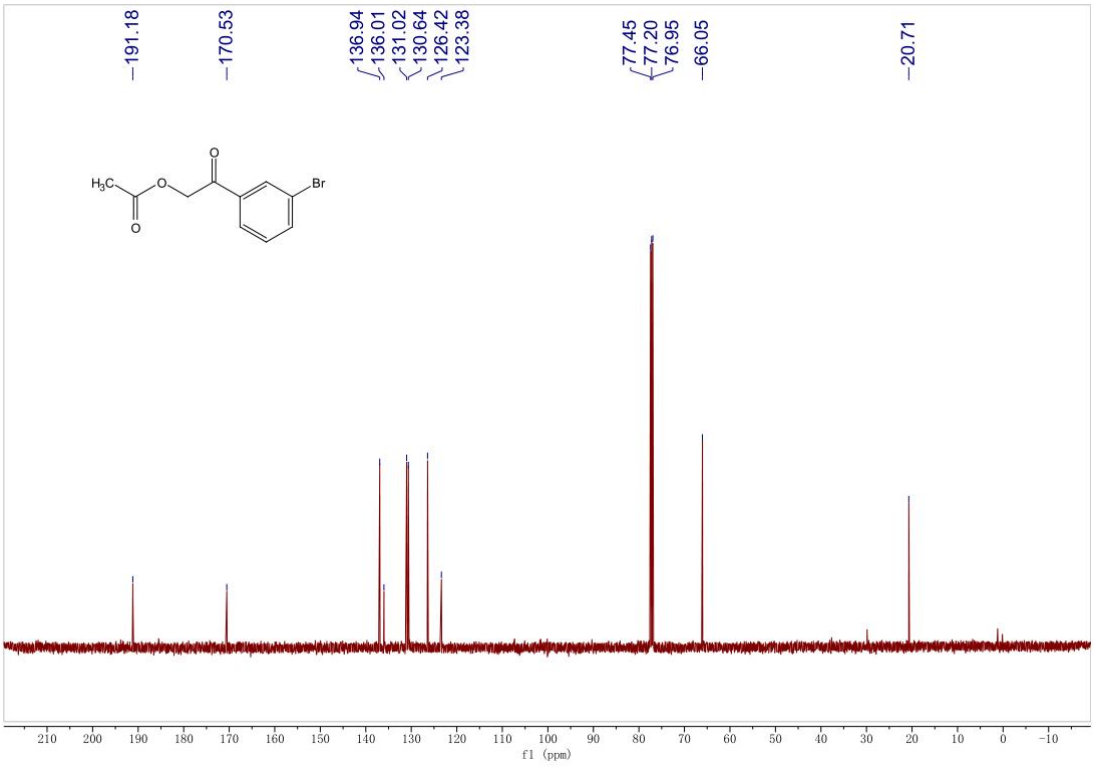


2-(3-bromophenyl)-2-oxoethyl acetate (2l)

^{1}H NMR (500 MHz, $CDCl_3$)

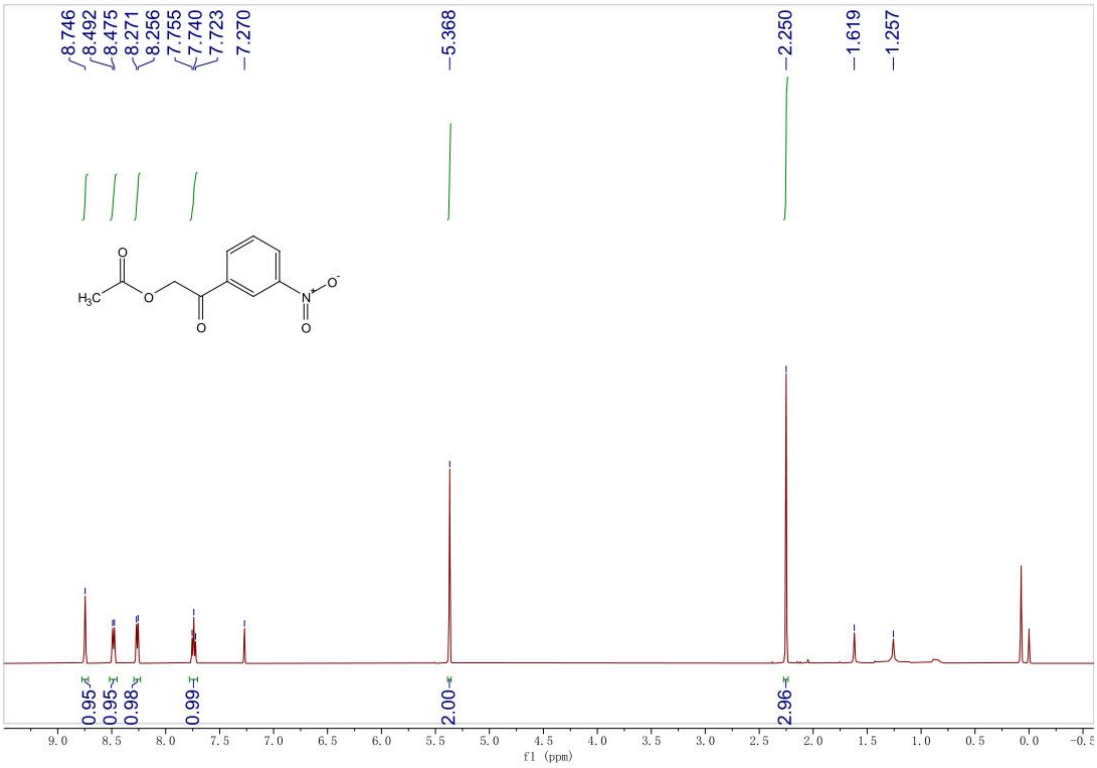


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

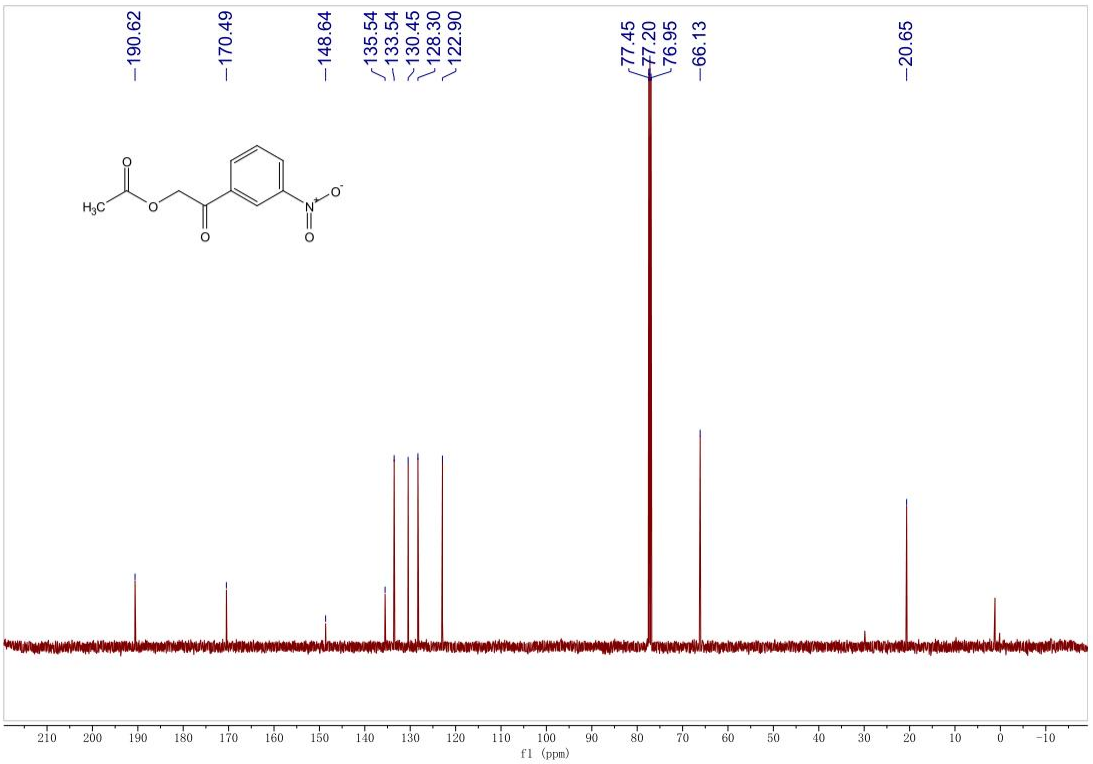


2-(3-nitrophenyl)-2-oxoethyl acetate (2m)

^{1}H NMR (500 MHz, $CDCl_3$)

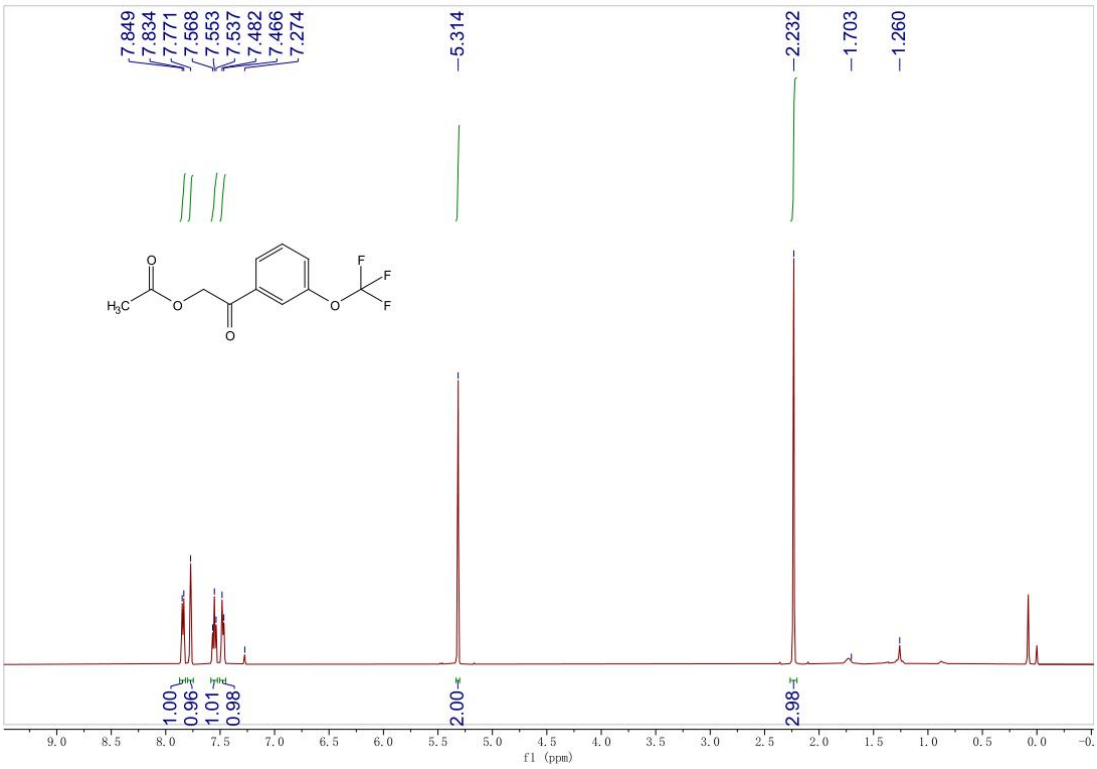


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

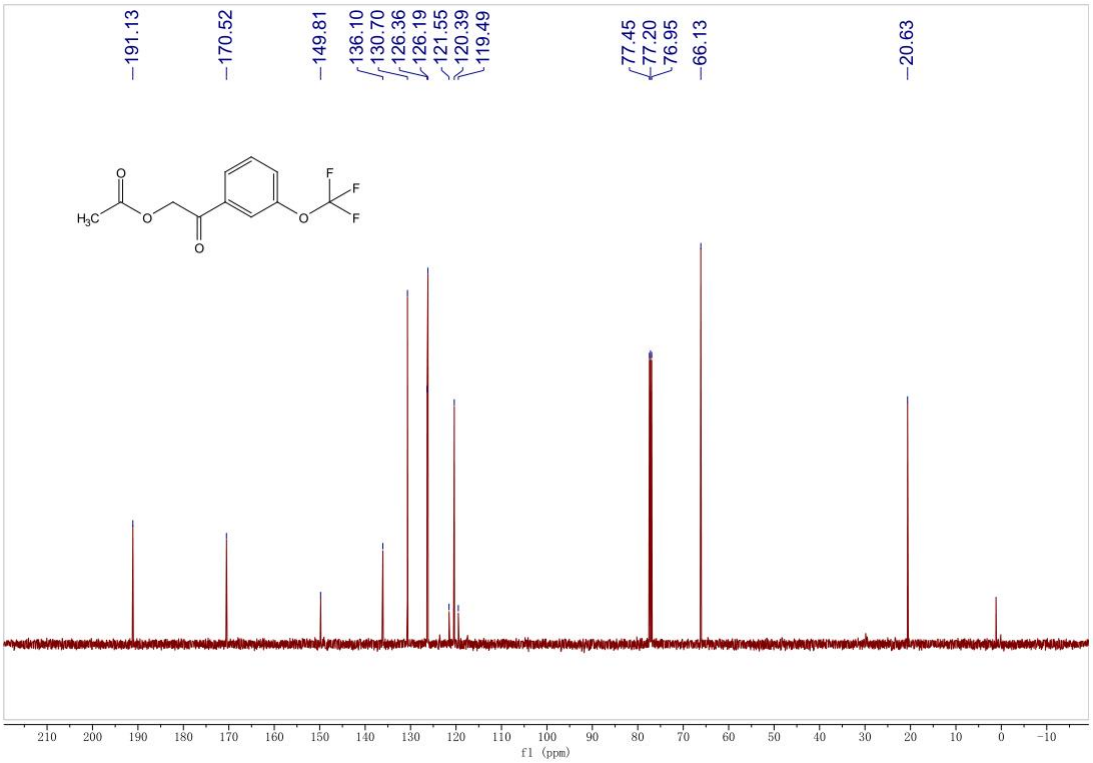


2-oxo-2-(3-(trifluoromethoxy)phenyl)ethyl acetate (2n)

^{1}H NMR (500 MHz, $CDCl_3$)

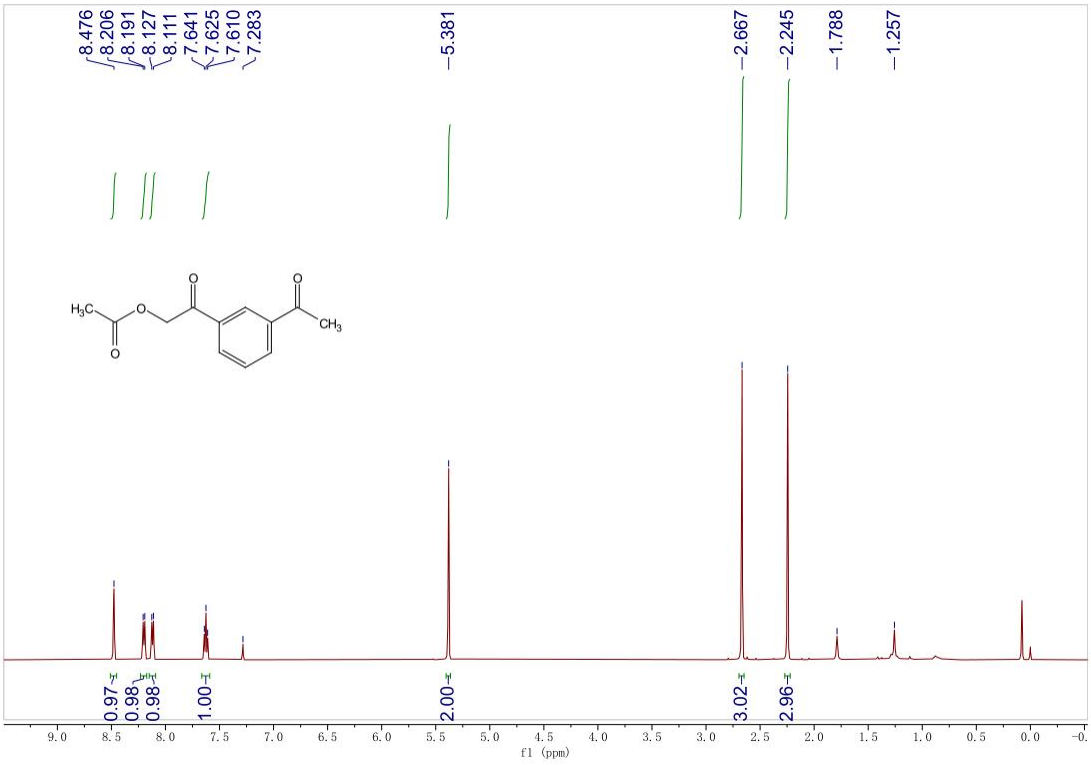


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

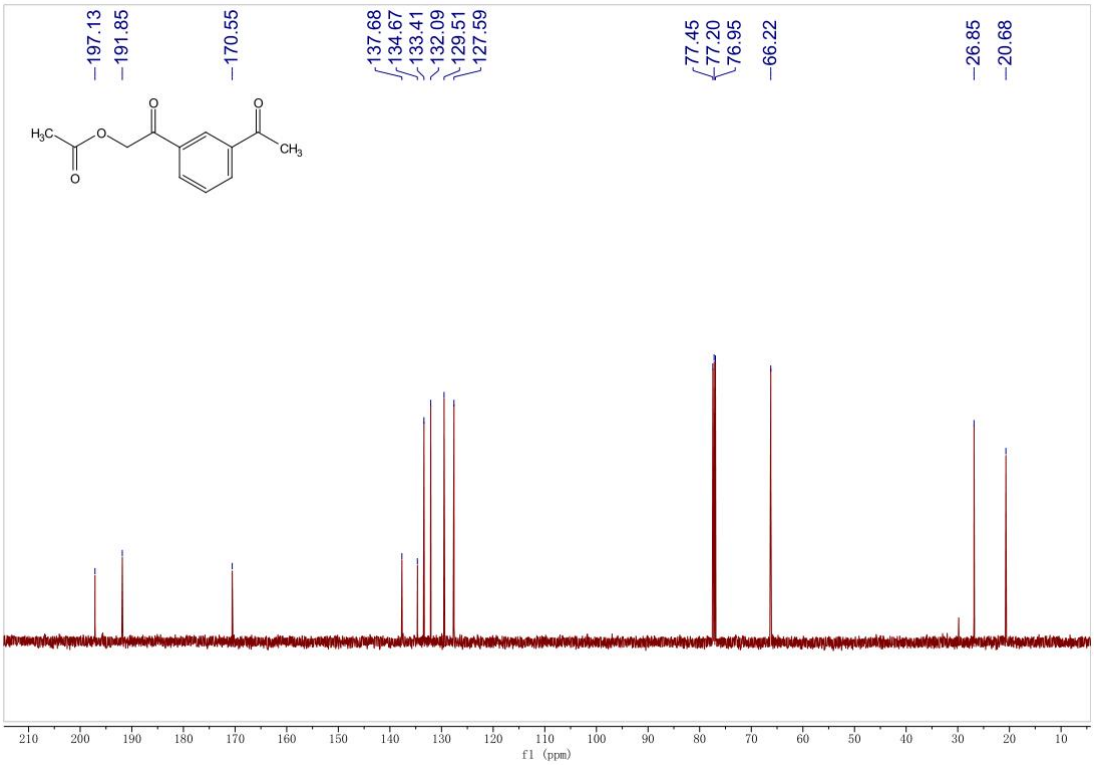


2-(3-acetylphenyl)-2-oxoethyl acetate (2o)

^{1}H NMR (500 MHz, $CDCl_3$)

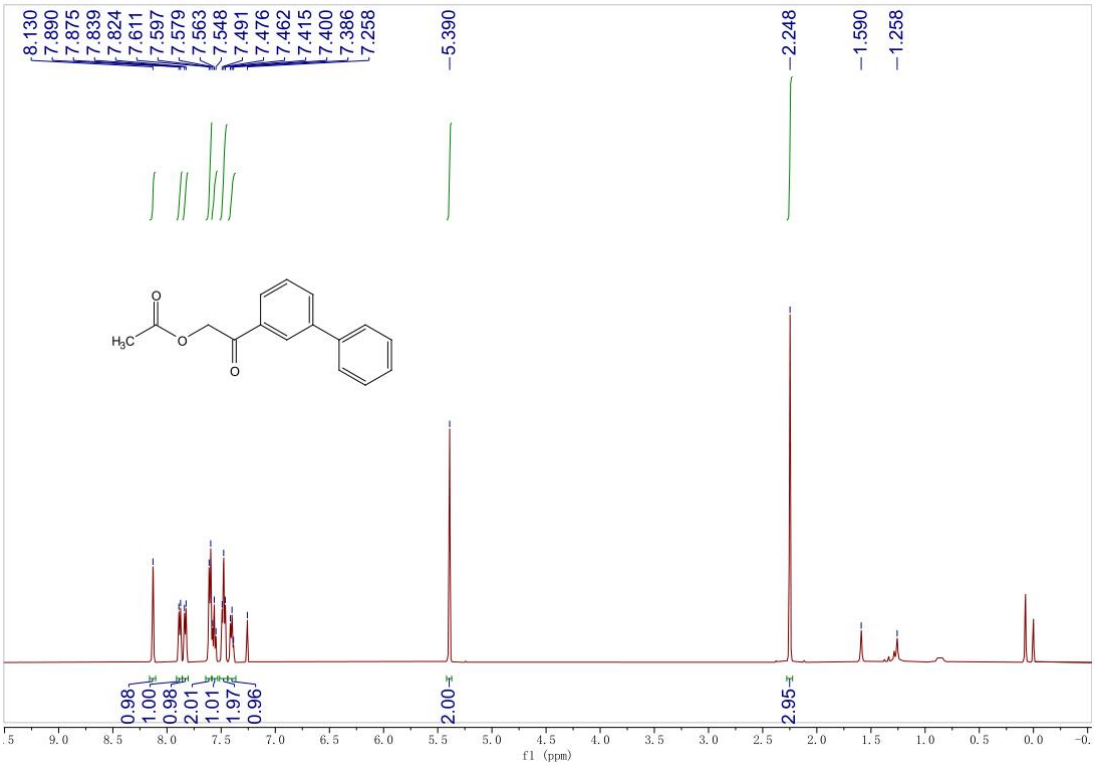


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

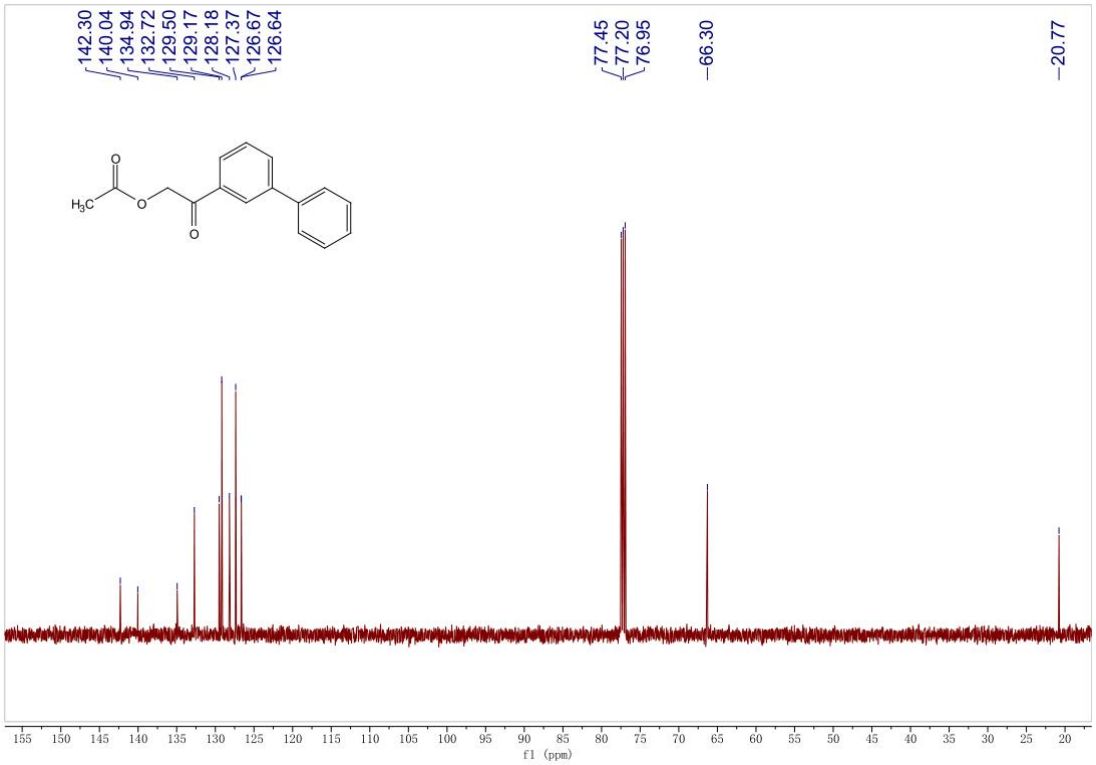


2-([1,1'-biphenyl]-3-yl)-2-oxoethyl acetate (2p)

^{1}H NMR (500 MHz, $CDCl_3$)

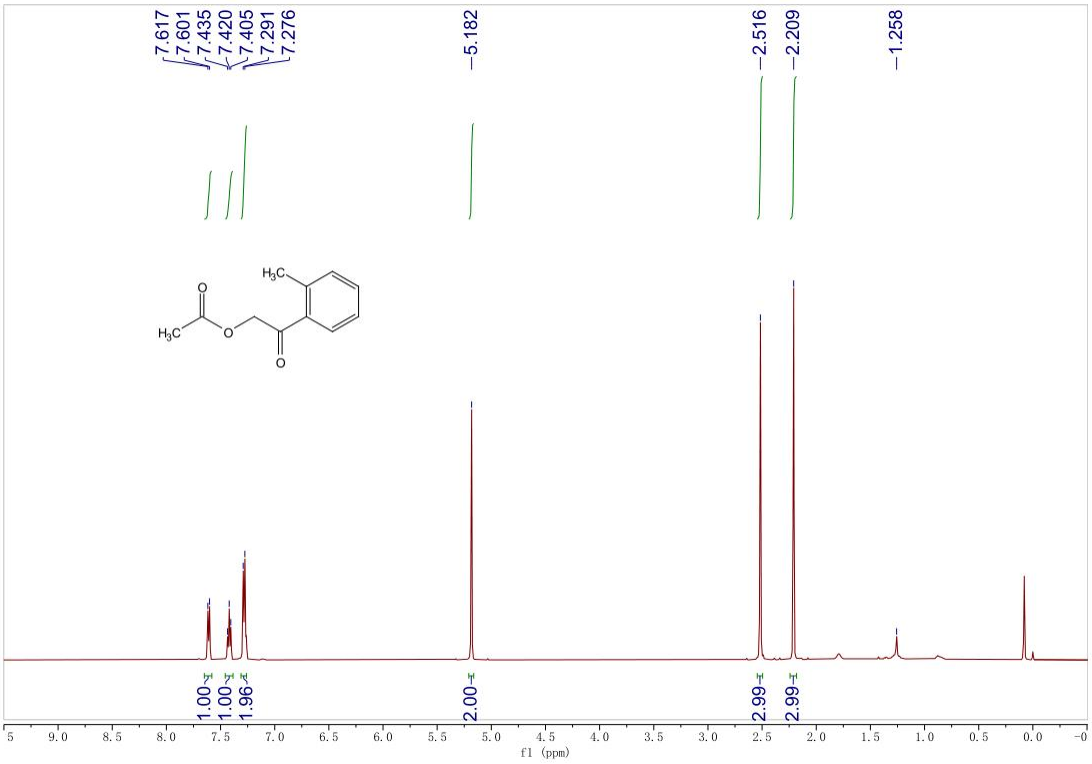


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

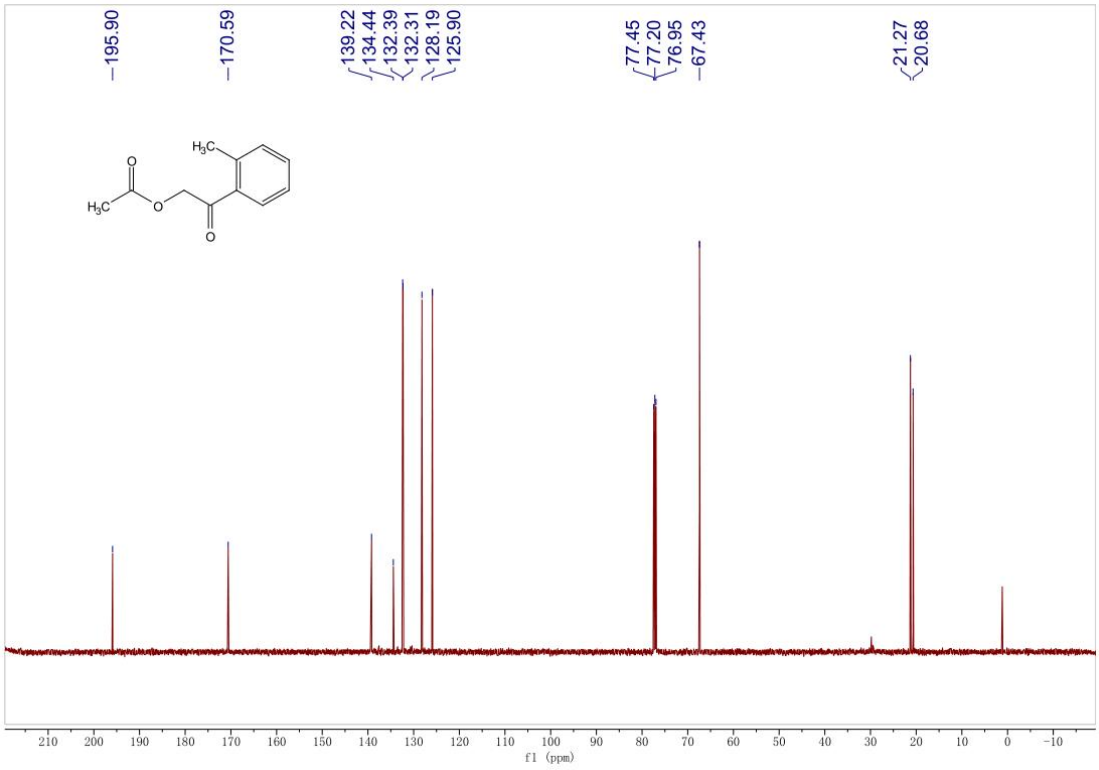


2-oxo-2-(*o*-tolyl)ethyl acetate (2q)

^{1}H NMR (500 MHz, $CDCl_3$)

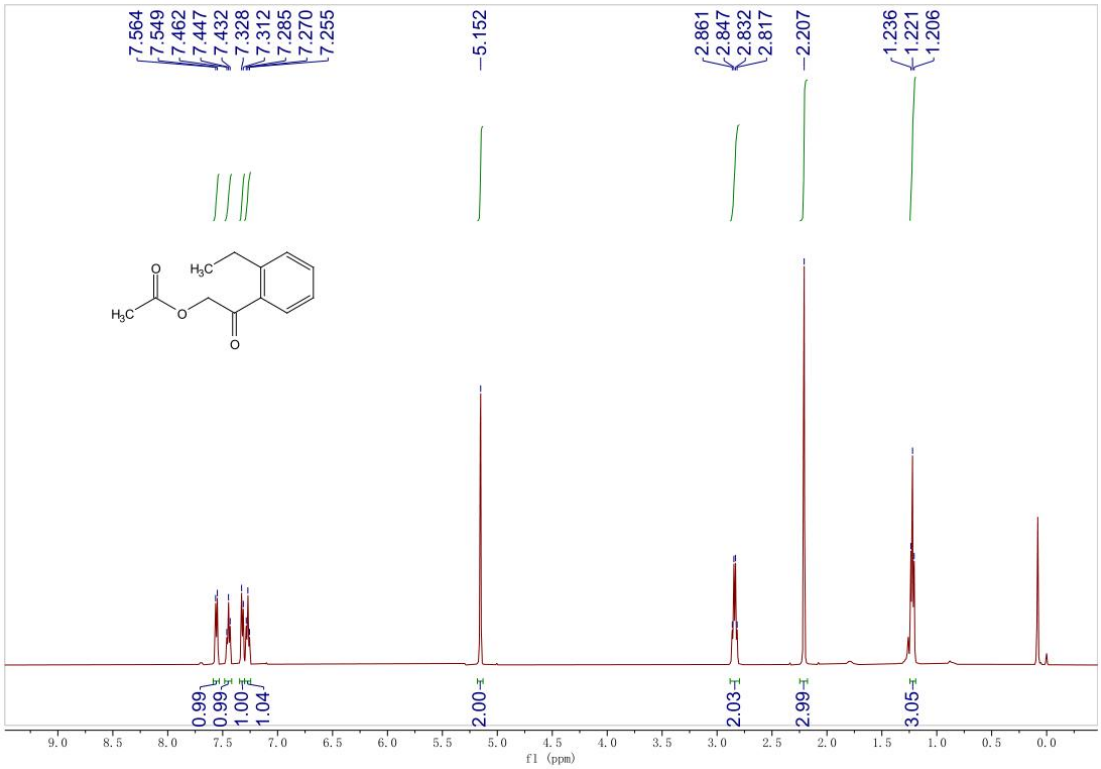


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

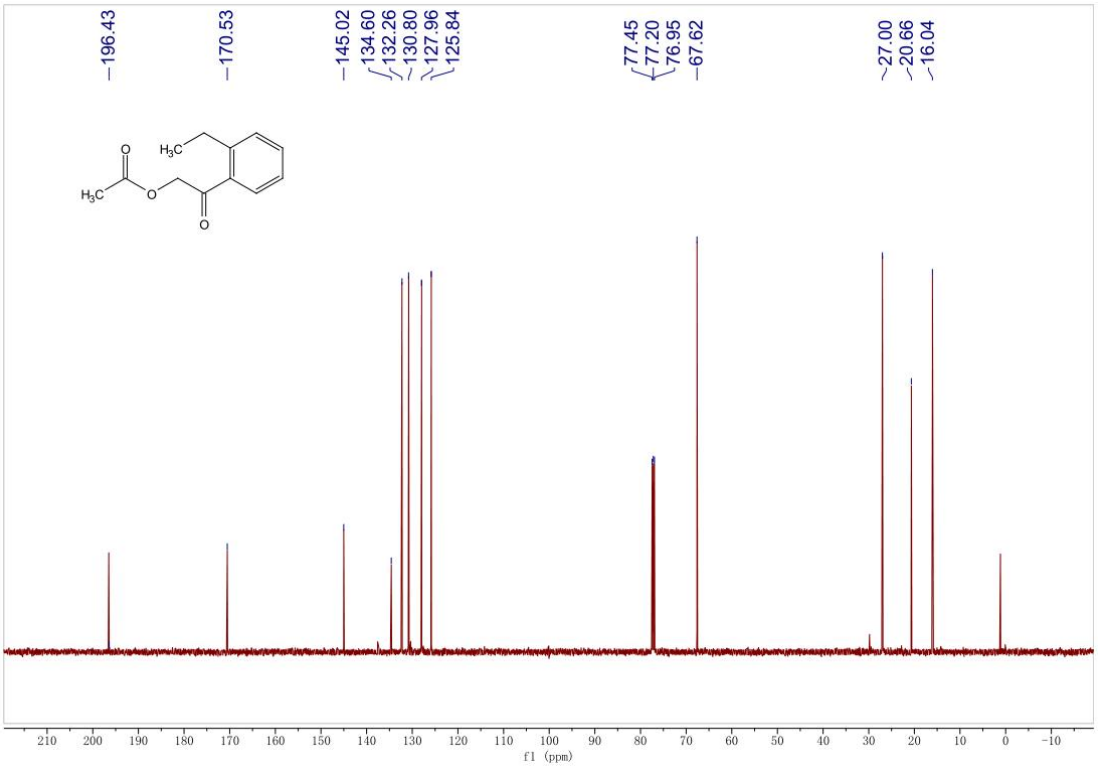


2-oxo-2-(*o*-tolyl)ethyl acetate (2r)

^{1}H NMR (500 MHz, $CDCl_3$)

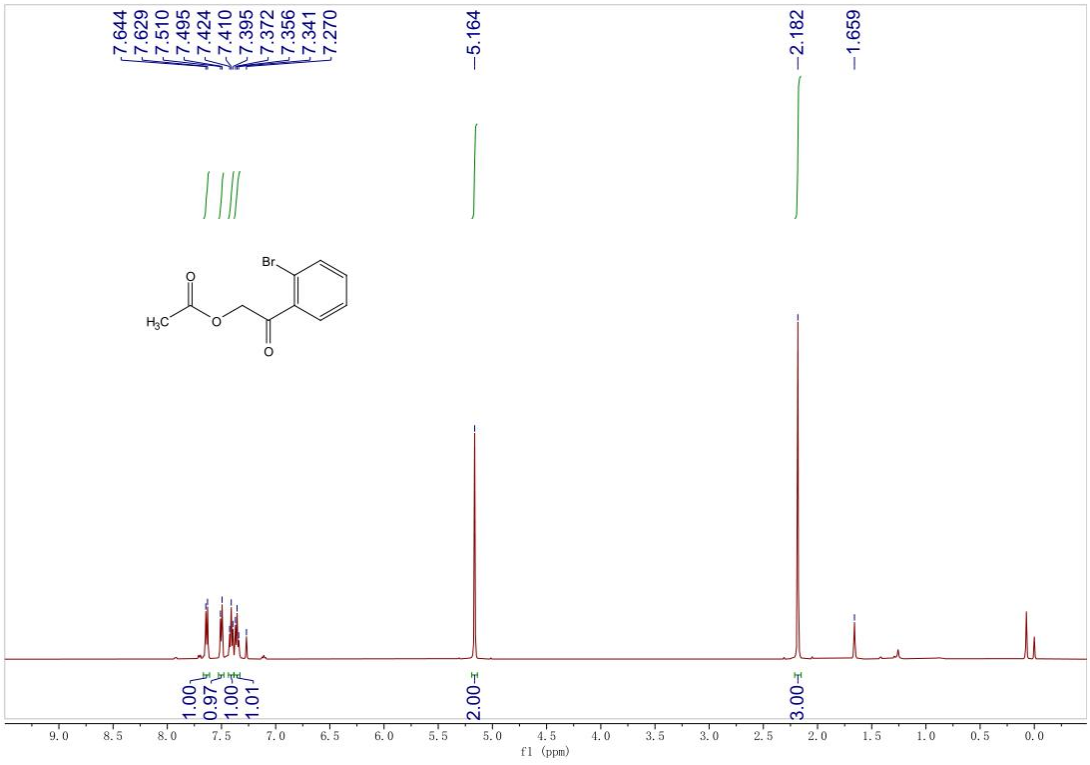


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

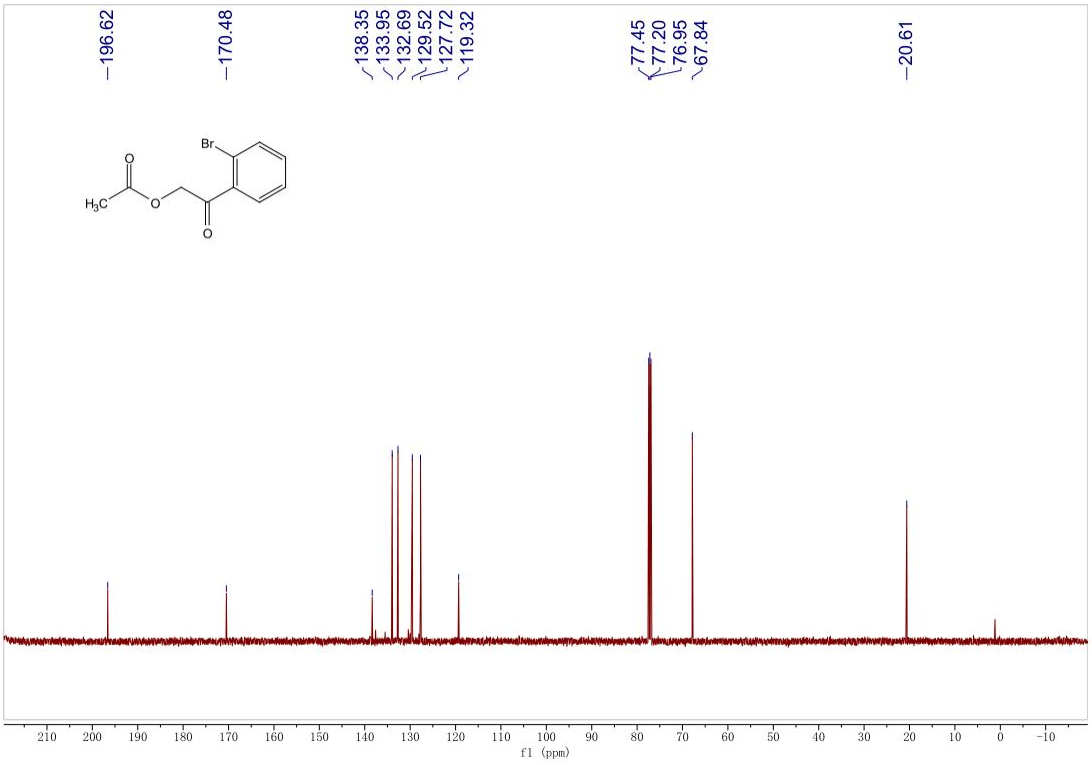


2-(2-bromophenyl)-2-oxoethyl acetate (2s)

^{1}H NMR (500 MHz, $CDCl_3$)

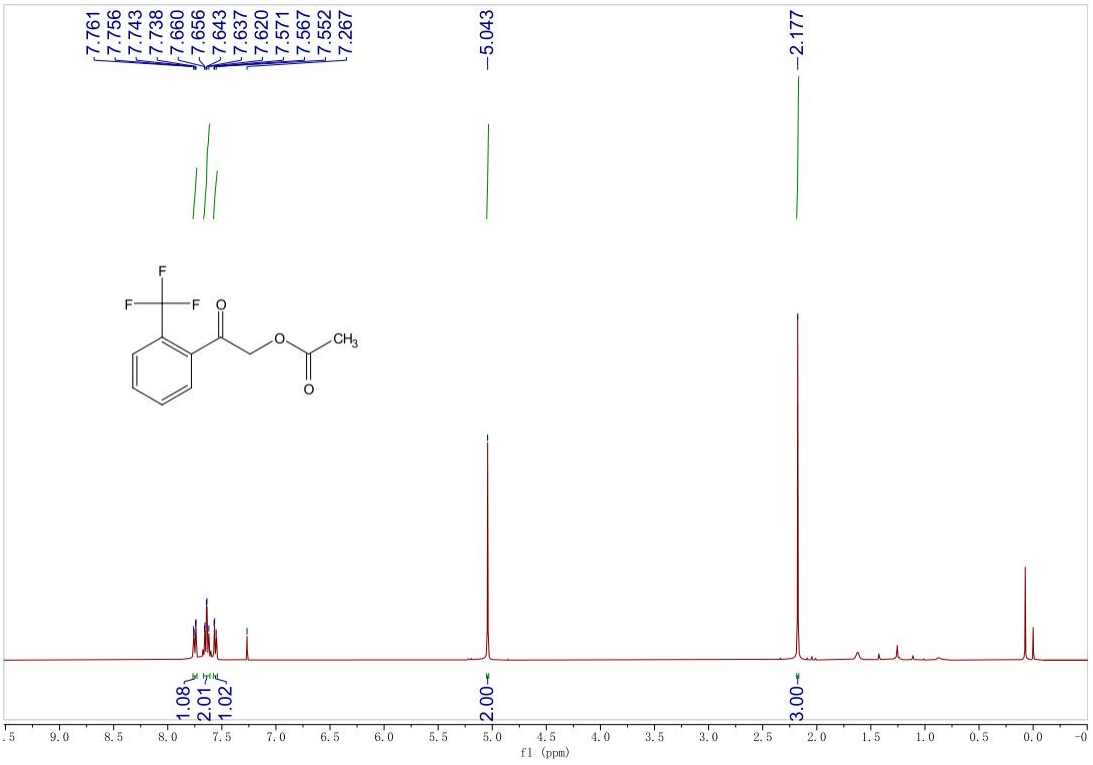


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

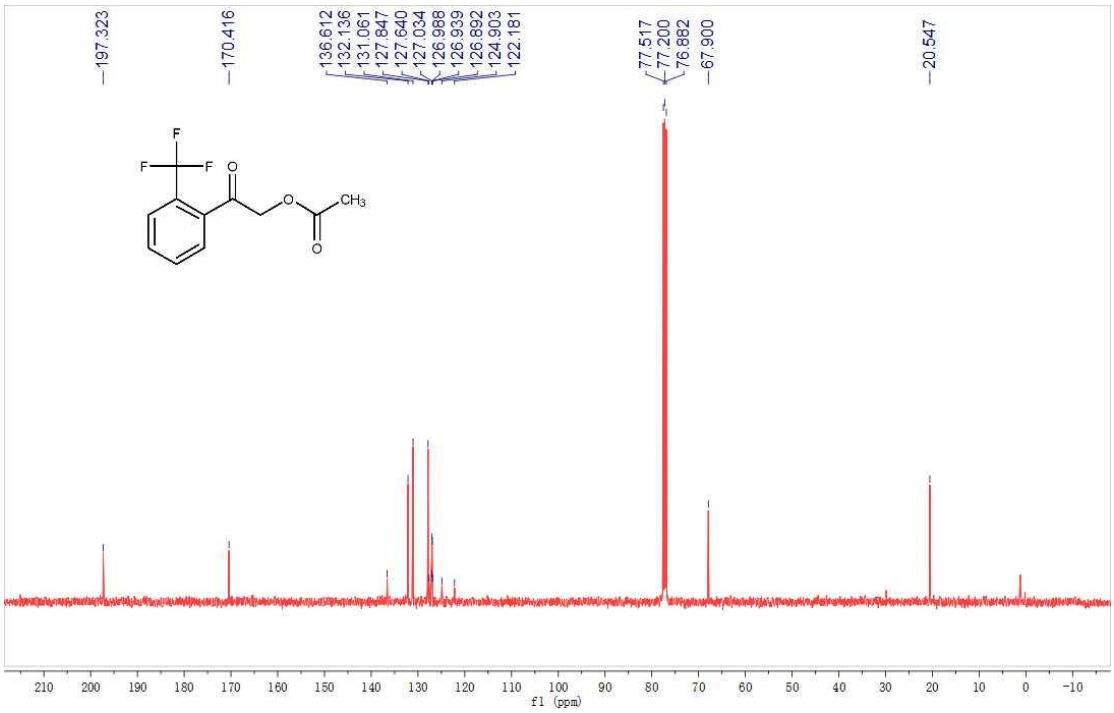


2-oxo-2-(2-(trifluoromethyl)phenyl)ethyl acetate (2t)

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

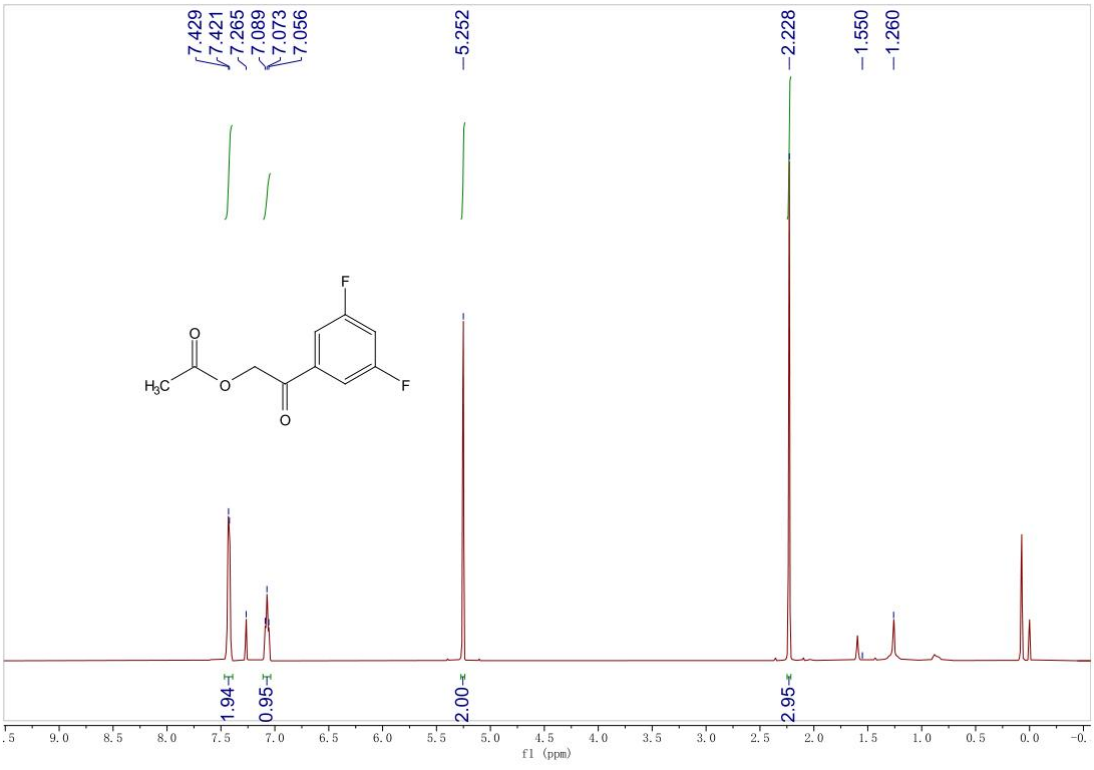


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)

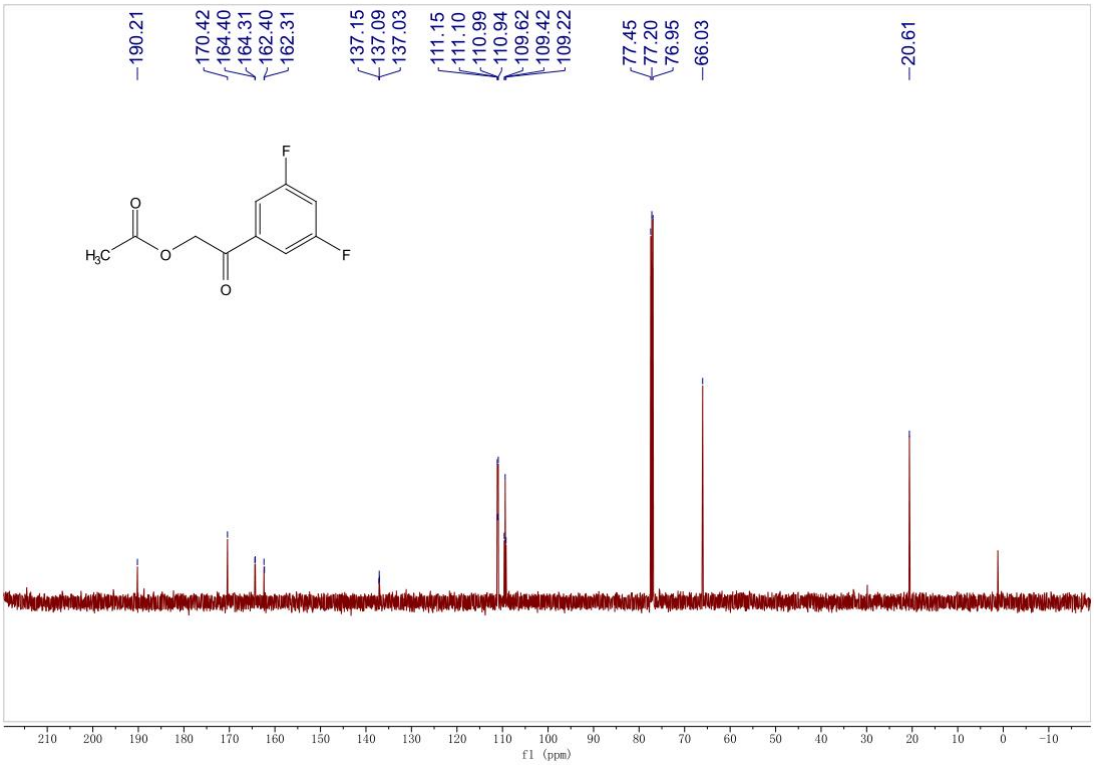


2-(3,5-difluorophenyl)-2-oxoethyl acetate (2u)

^{1}H NMR (500 MHz, $CDCl_3$)

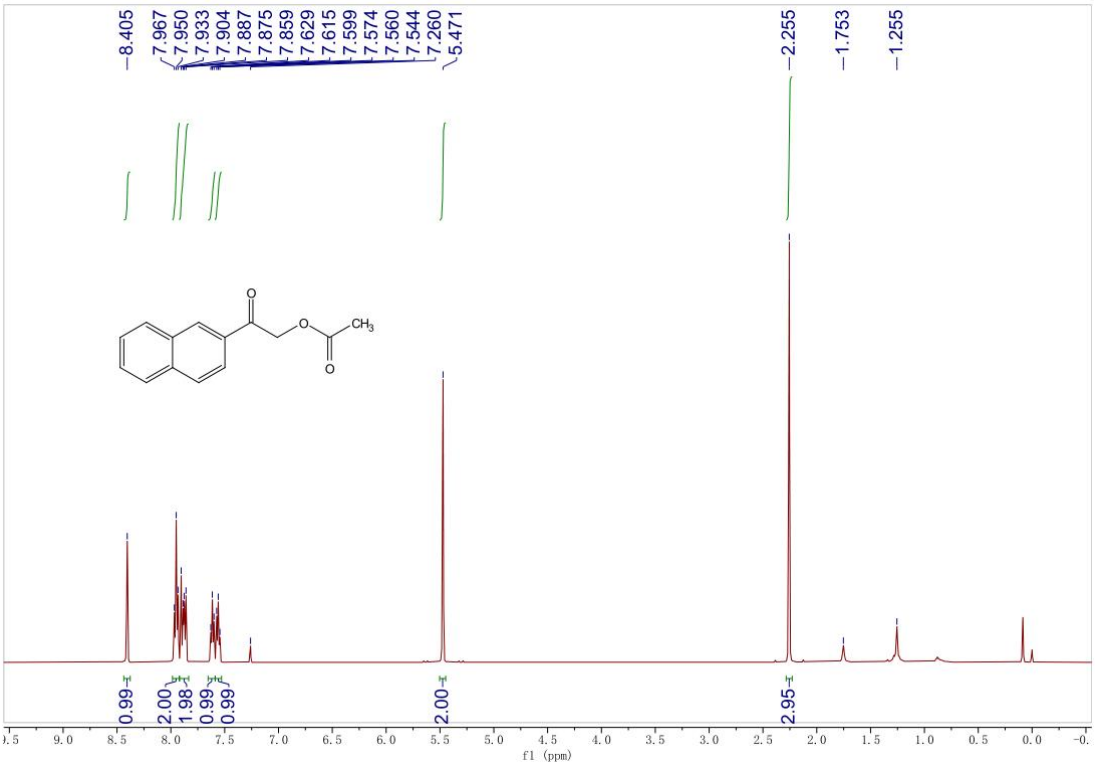


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

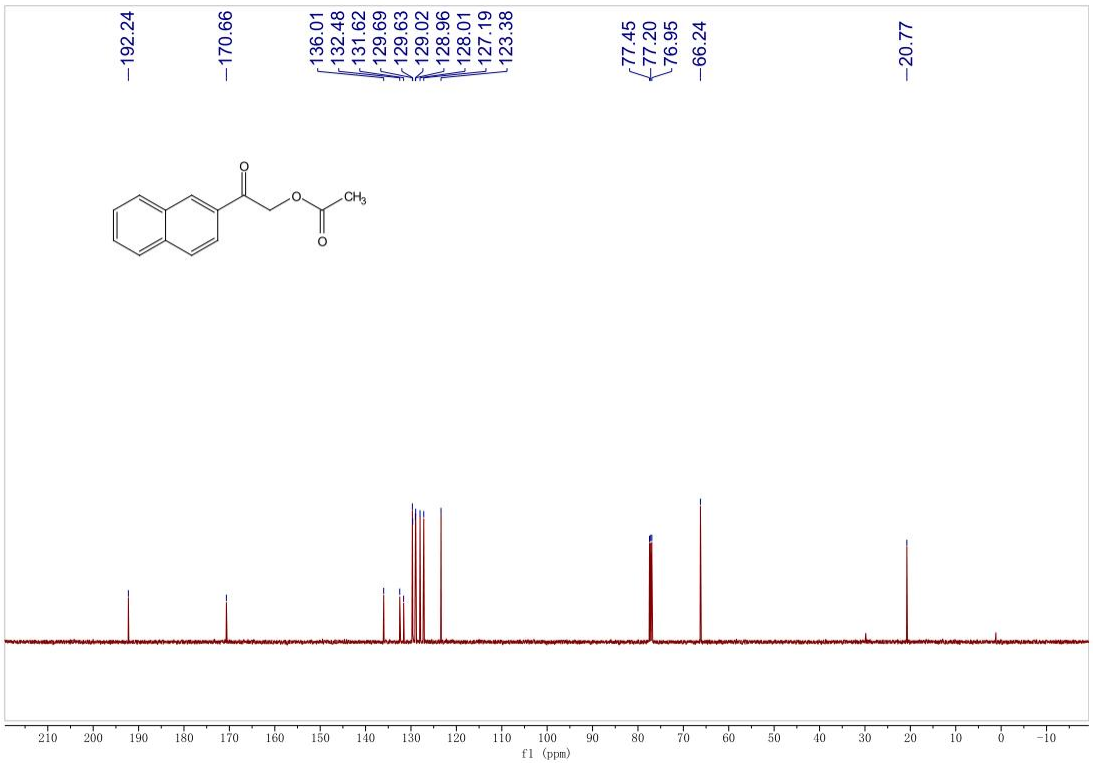


2-(naphthalen-2-yl)-2-oxoethyl acetate (2v)

^{1}H NMR (500 MHz, $CDCl_3$)

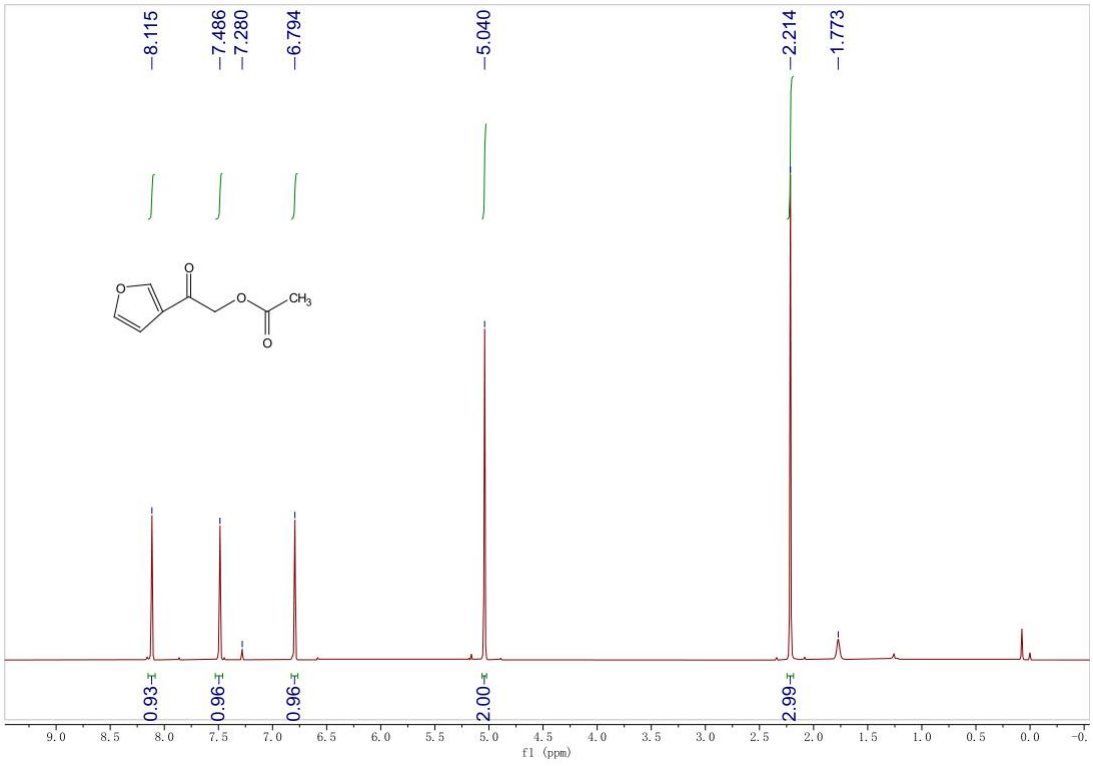


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

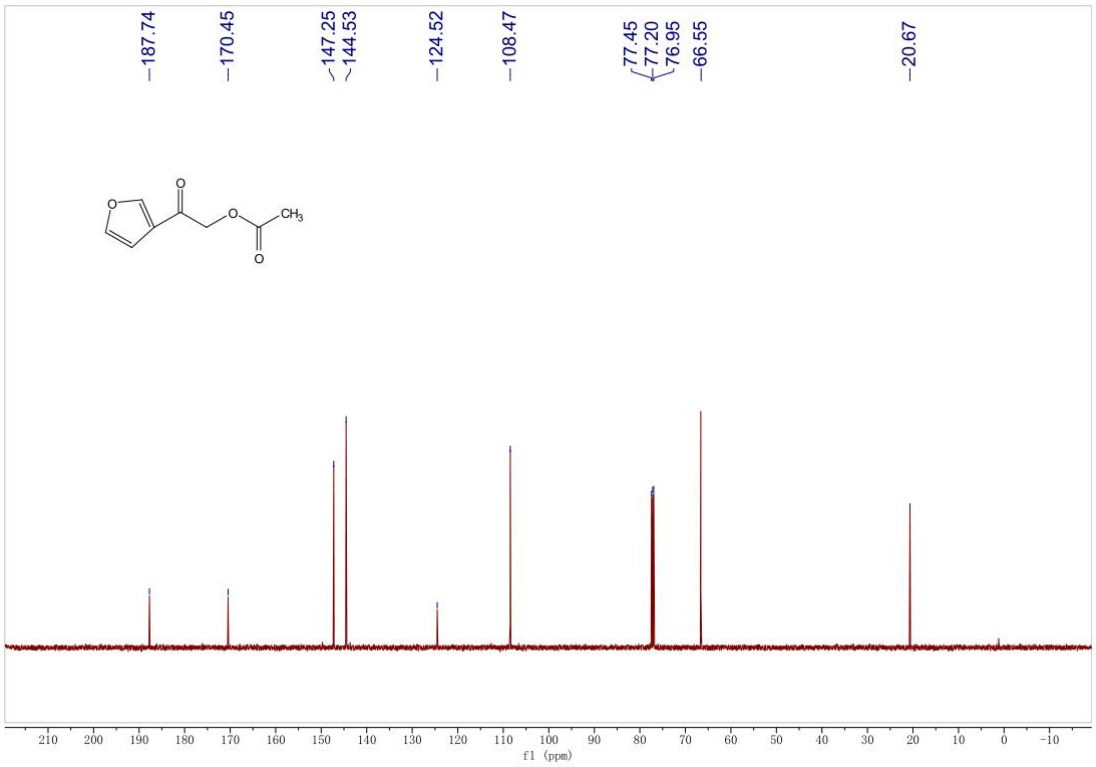


2-(furan-3-yl)-2-oxoethyl acetate (2w)

^{1}H NMR (500 MHz, $CDCl_3$)

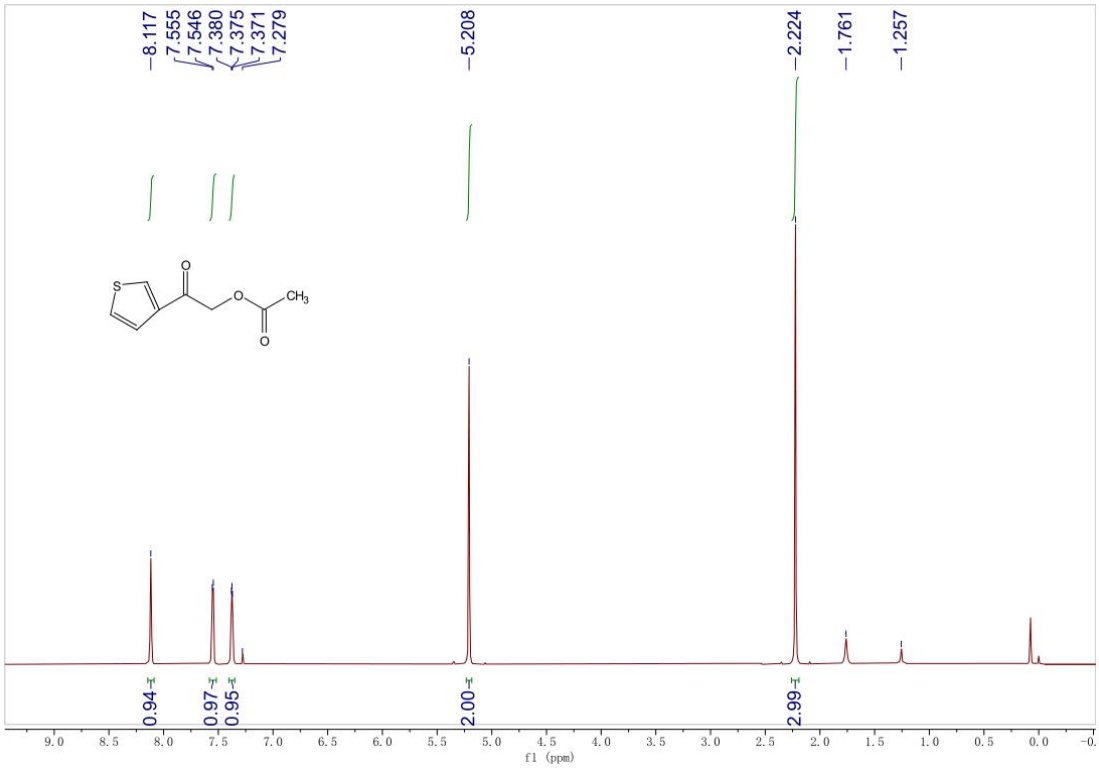


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

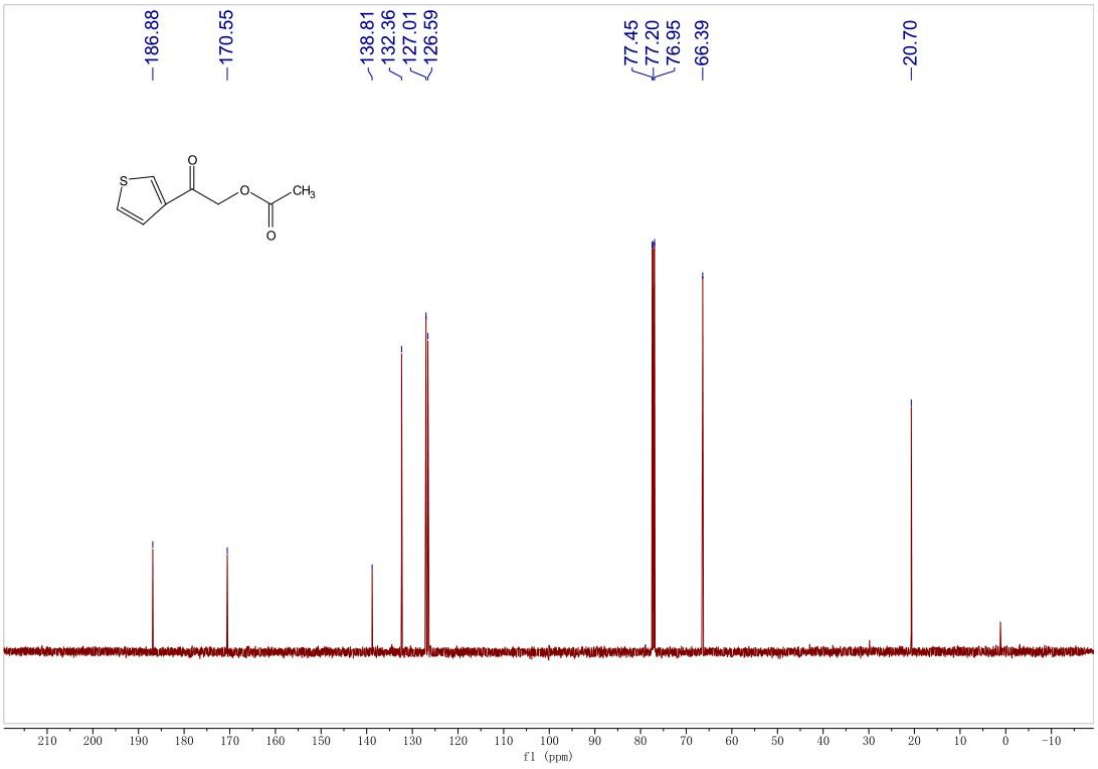


2-oxo-2-(thiophen-3-yl)ethyl acetate (2x)

^{1}H NMR (500 MHz, $CDCl_3$)

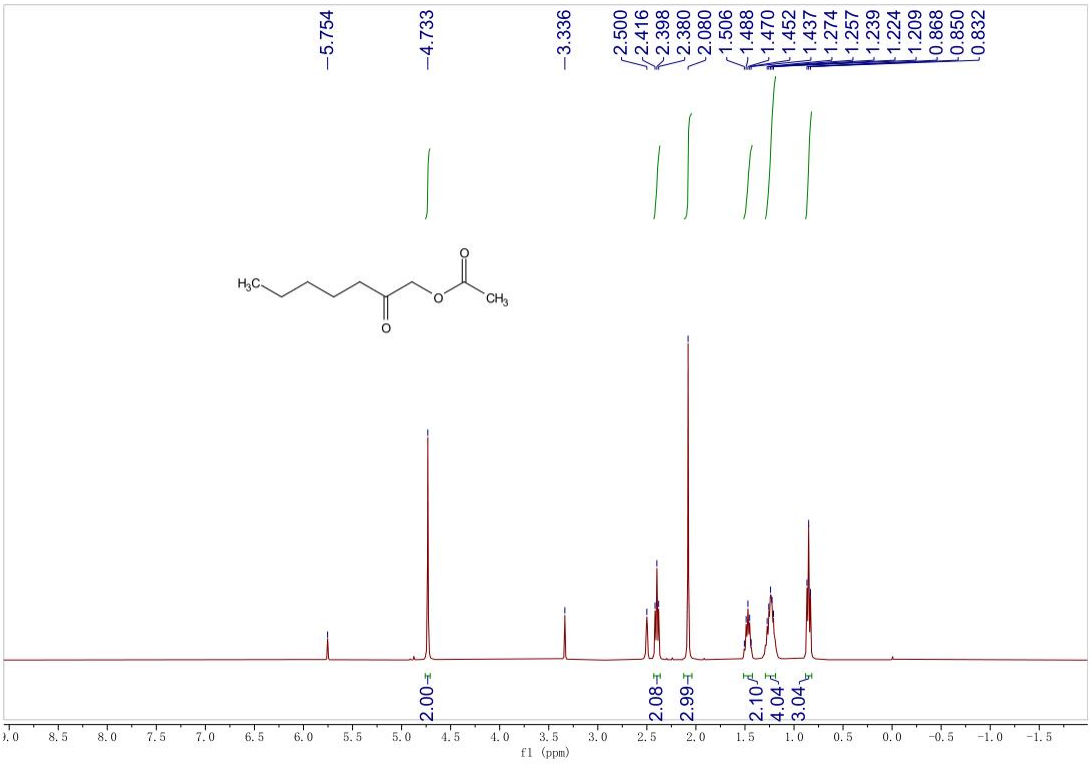


^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$)

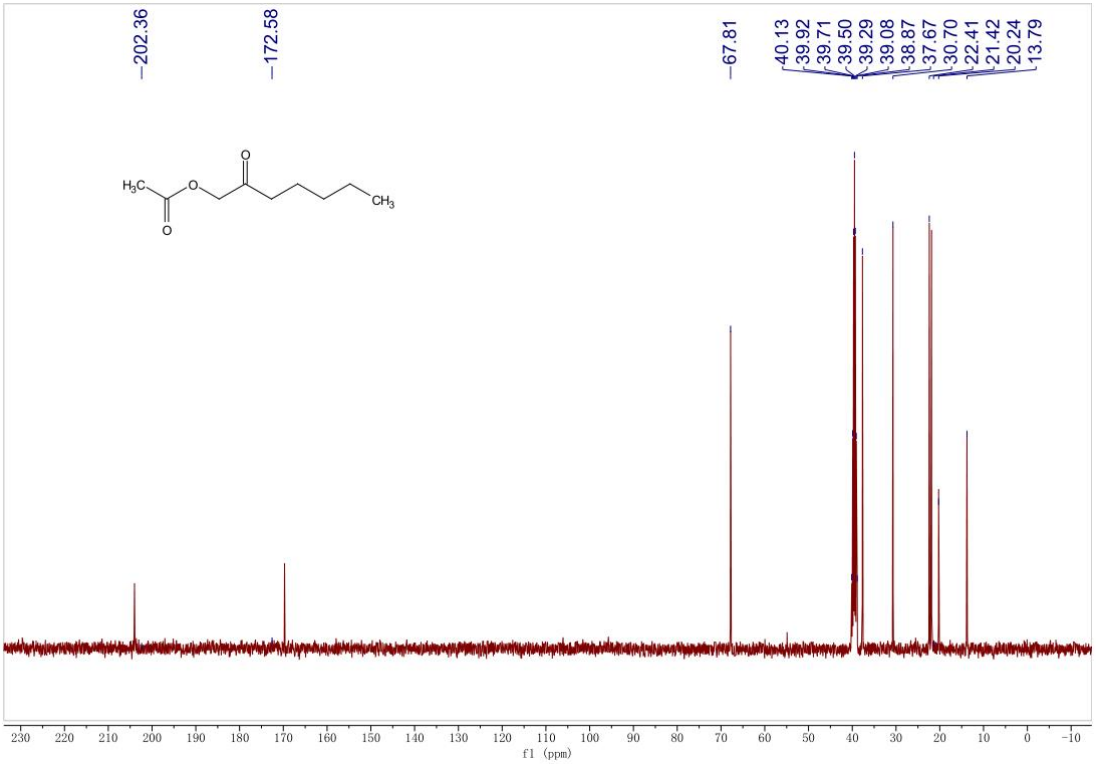


2-oxoheptyl acetate (2y)

^{1}H NMR (400 MHz, DMSO-*d*$_6$)

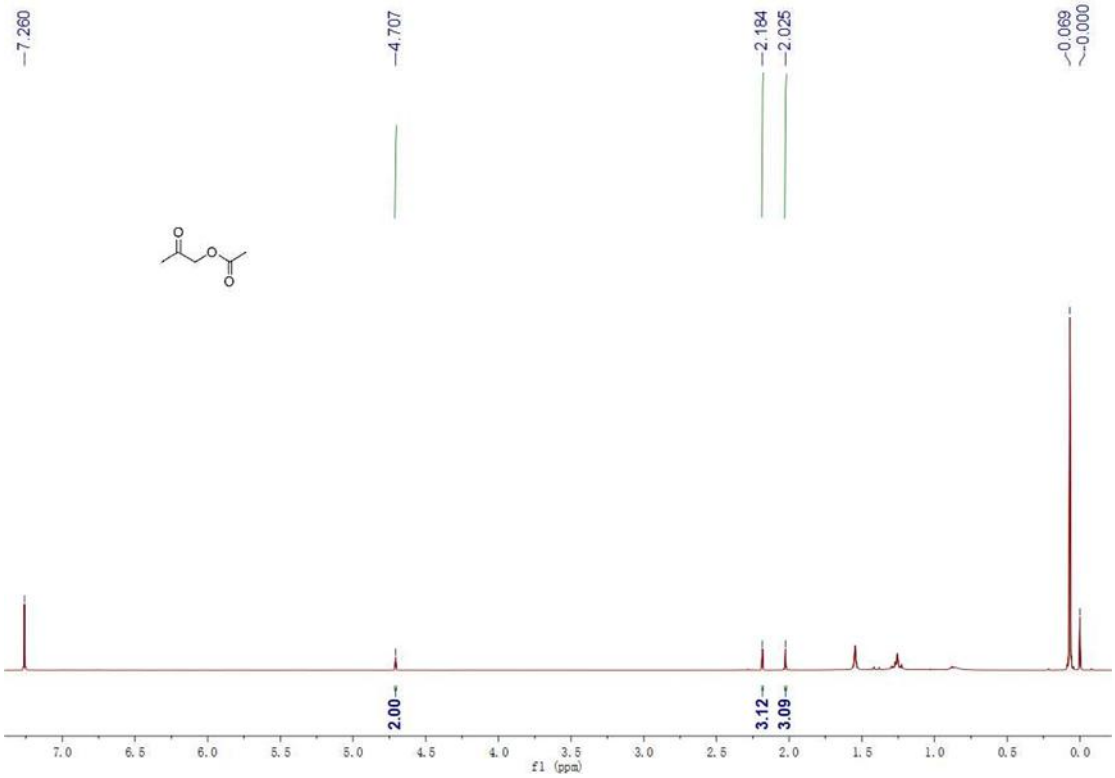


^{13}C {^{1}H} NMR (101 MHz, DMSO-*d*$_6$)



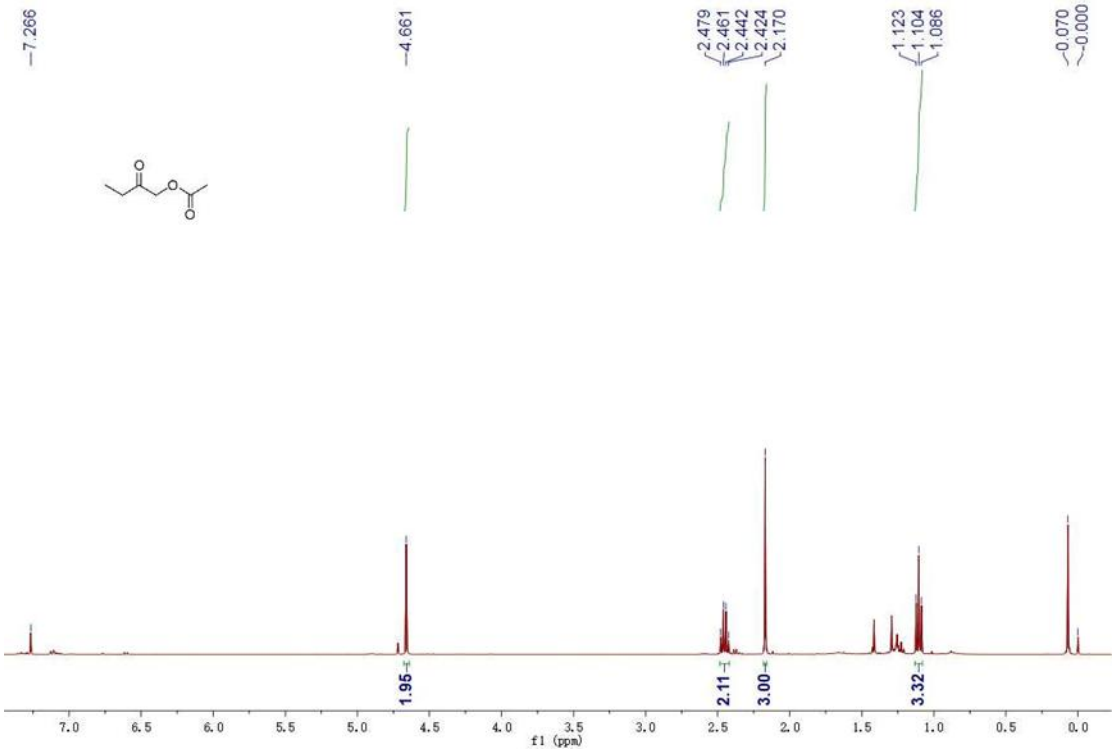
2-Oxopropyl Acetate (2z)

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



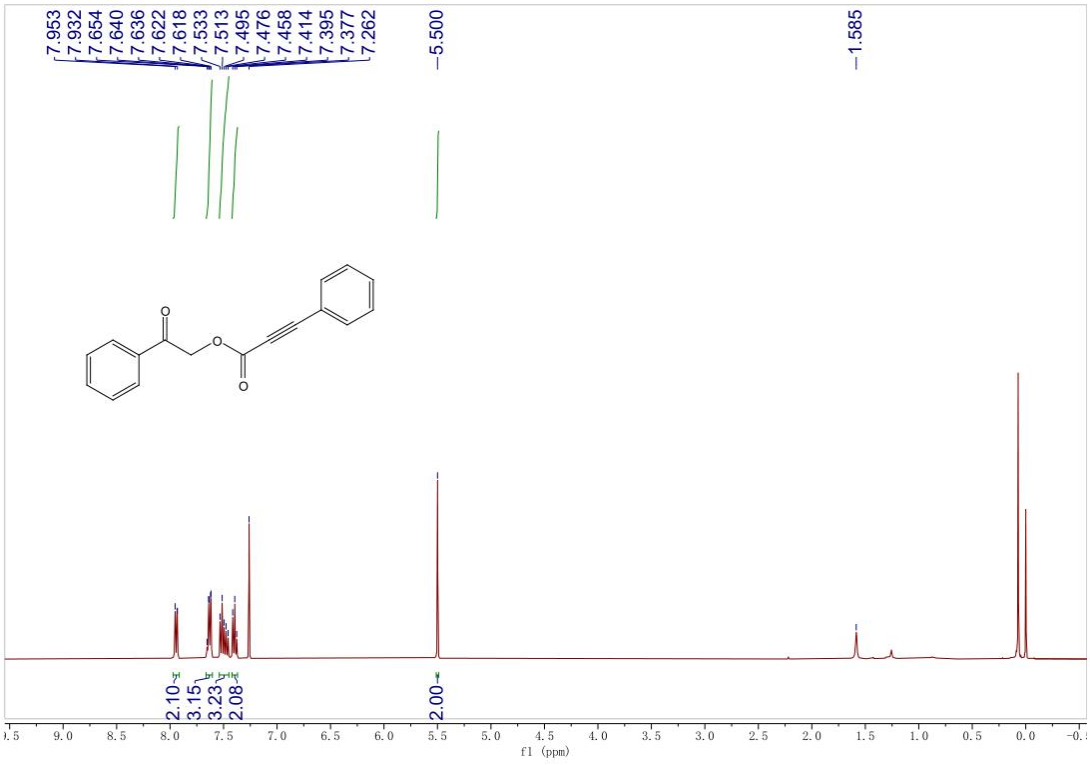
2-Oxobutyl Acetate (2za)

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

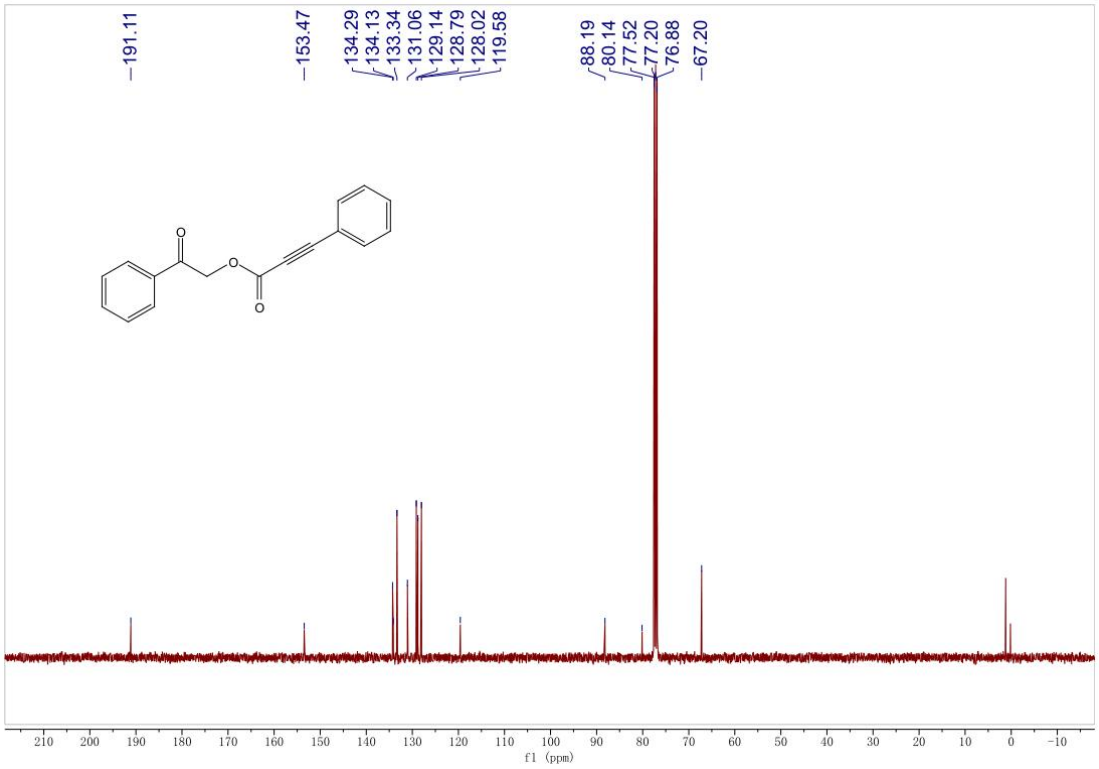


2-oxo-2-phenylethyl 3-phenylpropiolate (3a)

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

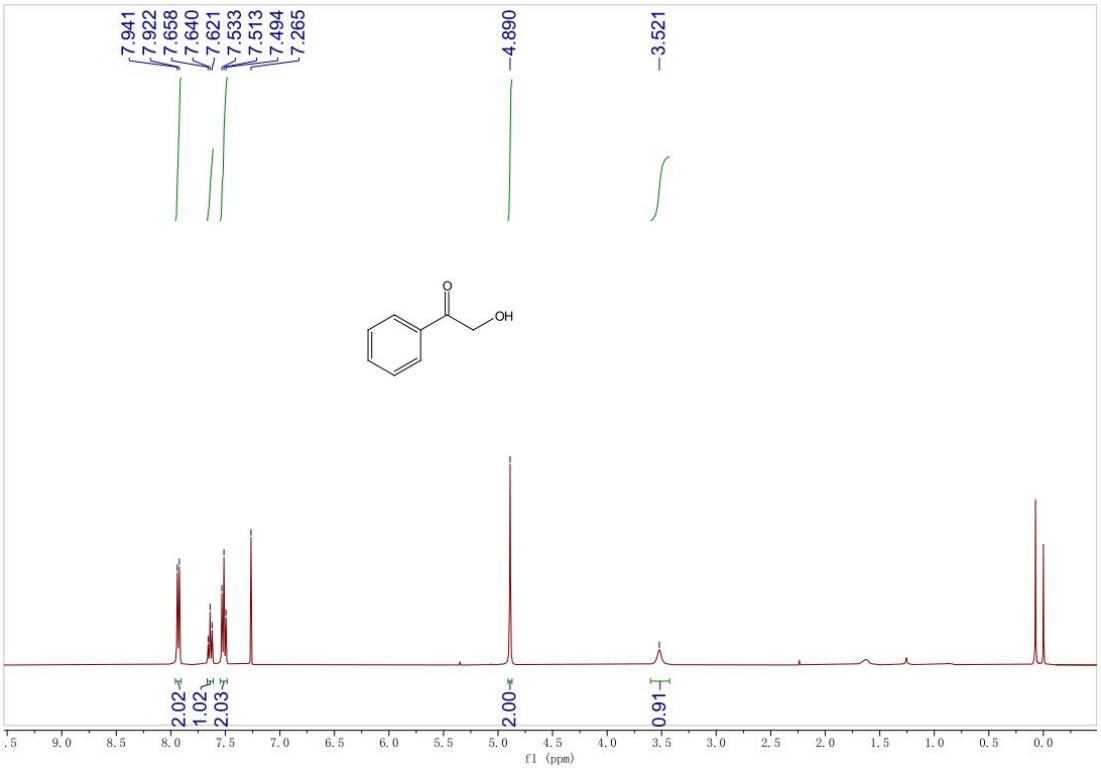


^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$)

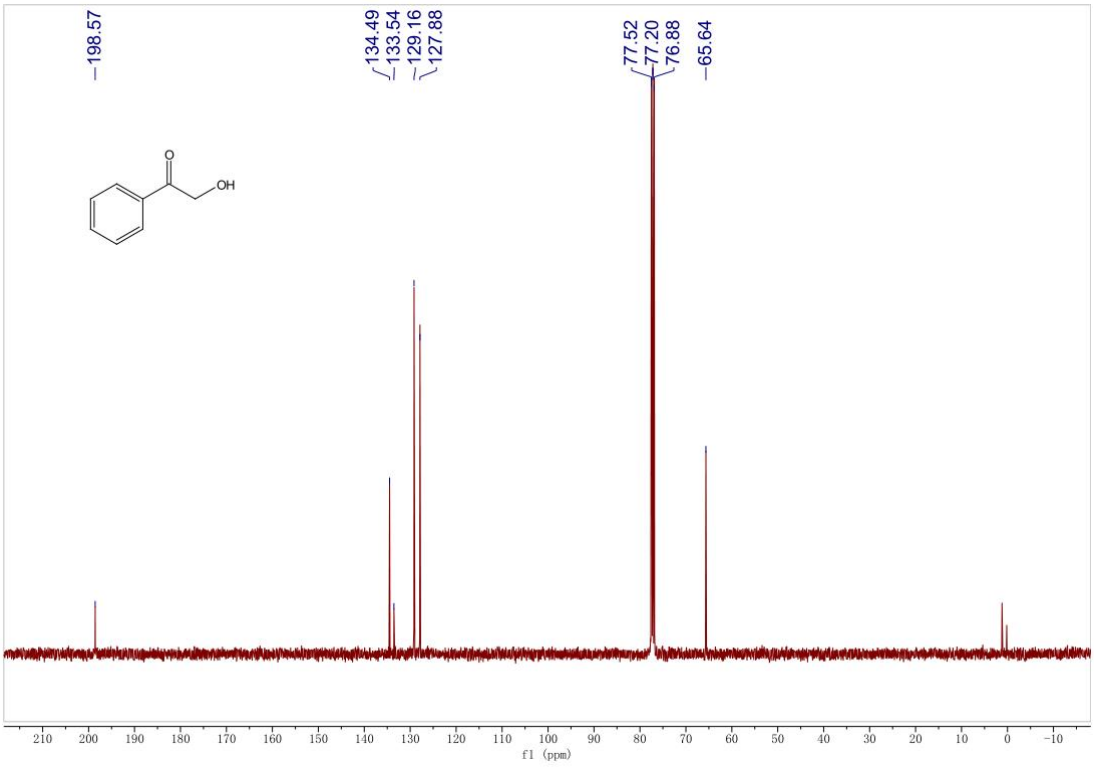


2-hydroxy-1-phenylethan-1-one (4)

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



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


198.57
134.49
133.54
129.16
127.88
77.52
77.20
76.88
65.64
O
OH
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

5. Mass spectrometry for mechanism study

Propiolic acid **1a** (0.50 mmol, 1.0 equivalent), H_2O (22 μL, 1.25 mmol, 2.5 equivalent), $PhI(OAc)_2$ (483 mg, 1.5 mmol, 3.0 equivalent) and 8 mL AcOH were added in a round-bottom flask. The mixture was allowed to stir at 80 °C (oil bath temperature) under air for 0.5 h. After cooling to room temperature, the mixture was characterized by high resolution mass spectroscopy and intermediate **C** was detected.

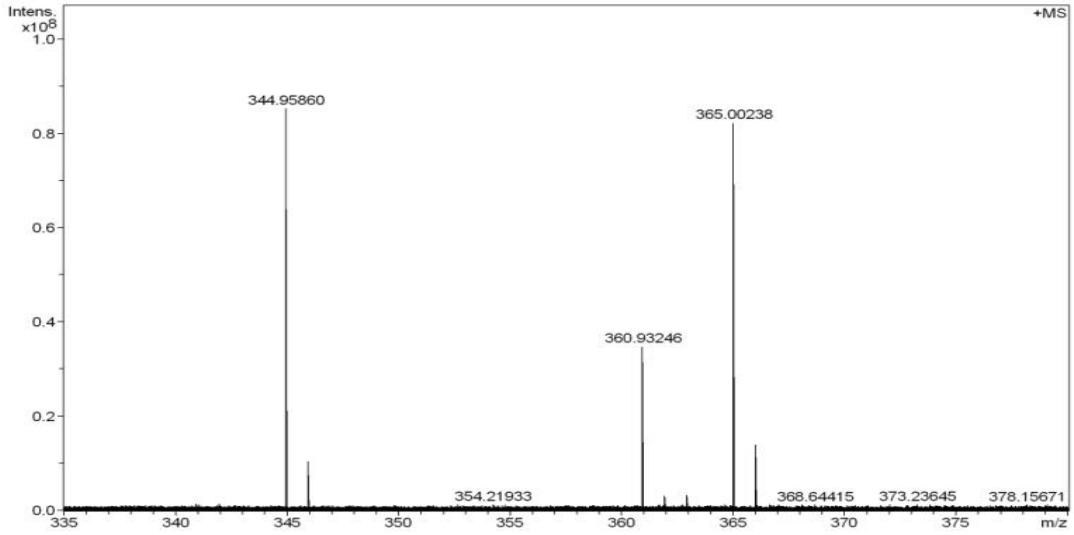
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\202112\GTY-16_000004.d	Acquisition Date	12/13/2021 3:30:52 PM
Method	4_17_Mass_range_pos_7T	Operator	
Sample Name	GTY-16	Instrument	solariX
Comment			

Acquisition Parameter

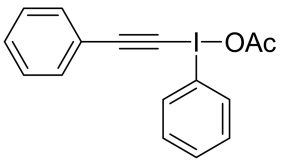
Polarity	Positive	n/a	n/a	No. of Laser Shots	200
n/a	n/a	No. of Cell Fills	1	Laser Power	20.0 lp
Broadband Low Mass	200.7 m/z	n/a	n/a	n/a	n/a
Broadband High Mass	1000.0 m/z	n/a	n/a	n/a	n/a
Acquisition Mode	Single MS	n/a	n/a		
Pulse Program	basic	n/a	n/a	Calibration Date	Wed Nov 17 04:29:35
Source Accumulation	0.500 sec	n/a	n/a	Data Acquisition Size	4194576
Ion Accumulation Time	0.200 sec	n/a	n/a	Apodization	Sine-Bell Multiplication
Flight Time to Acq. Cell	0.001 sec				



Meas. m/z	#	Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSig ma	rdb	e⁻ Conf	N-R ule
344.95860	1	C 10 H 11 I Na O 4	100.00	344.95942	2.39	2.39	12.0	4.5	even	ok
365.00238	1	C 16 H 14 I O 2	100.00	365.00330	2.51	2.49	10.6	9.5	even	ok

Bruker Compass DataAnalysis 4.0 printed: 4/29/2022 4:28:09 PM Page 1 of 1

Intermediate **C**



HRMS (ESI-TOF) *m/z*: calcd for $C_{16}H_{13}IO_2$ $[M+H]^+$ 365.0033, found 365.0024.

6. References

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