Supporting Information

KI-Catalyzed α-Acyloxylation of Acetone with Carboxylic Acids

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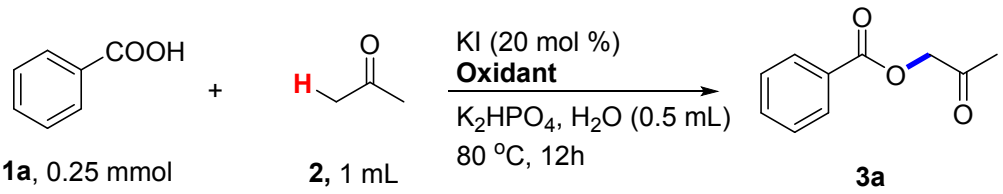
1. General

All reagents were used as received from commercial sources unless specified otherwise. Acetone was purchased from Sinopharm and used without any purification. Potassium iodide was purchased from Sigma-Aldrich.

^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker Avance 600 or 400 spectrometer at ambient temperature. Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, dt = doublet of triplet, etc.), coupling constant (Hz), and integration. Gas chromatographic (GC) analyses were performed on a GC equipped with a flame-ionization detector and an Rtx@-65 (30 m × 0.32 mm ID × 0.25 μ mdf) column using diphenyl as an internal standard, added duringreaction workup. GC-MS analyses were performed on a GC-MS with an EI mode. High resolution mass spectra were obtained on an HRMS-TOF spectrometer. Analytical thin layer chromatography (TLC) was performed on precoated silica gel plates. After elution, the plate was visualized under UV illumination at 254 nm for UV active materials. Column chromatography was performed on silica gel (200−300 mesh) by standard techniques eluting with solvents as indicated.

2. Optimization of Oxidant

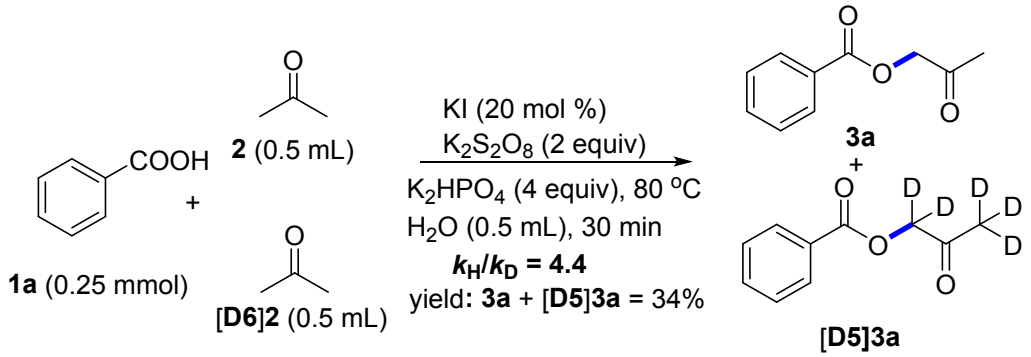


1a, 0.25 mmol **2,** 1 mL **3a**

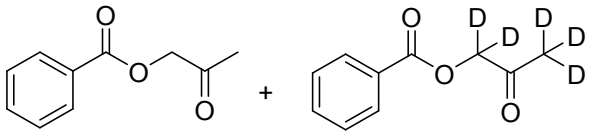
Entry	Oxidant (equiv)	K_2HPO_4	Yield (%)[a]
1	$K_2S_2O_8$ (1)	1 equiv	22
2	TBHP (1)	1 equiv	7
3	H_2O_2 (1)	1 equiv	0
4	CHP (1)	1 equiv	13
5	UHP (1)	1 equiv	5
6	**$K_2S_2O_8$ (2)**	**4 equiv**	**93 (91)**
7	TBHP (2)	4 equiv	51
8	H_2O_2 (2)	4 equiv	43
9	CHP (2)	4 equiv	60
10	UHP (2)	4 equiv	39

[a]Yield determined by GC diphenyl as the internal standard, isolated yield in parentheses.

3. Intermolecular Kinetic Isotope Effect (KIE)

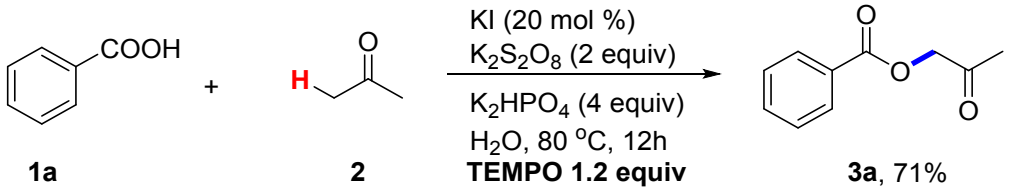


A 15 mL oven-dried Schlenk tube equipped with a magnetic stirrer was charged with KI (20 mol%), benzoic acid (0.25 mmol), $K_2S_2O_8$ (2 equiv) and K_2HPO_4 (4 equiv). Then acetone **2** (0.5 mL), **[D6]2**(0.5 mL) and H_2O (0.5 mL) were added by syringe respectively under air atmosphere. The reaction mixture was stirred at 80 °C for 30 min. The reaction tube was cooled to room temperature and the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether). This KIE value was determined by ^{1}H NMR analysis.



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, J = 7.1 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 4.88 (s, 2H), 2.24 (s, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 201.79 (s), 165.81 (s), 133.43 (s), 129.84 (s), 129.11 (s), 128.46 (s), 68.69 (s), 26.19 (s).

3. Radical Capturing Experiments



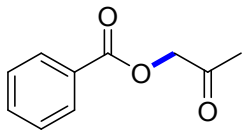
A 15 mL oven-dried Schlenk tube equipped with a magnetic stirrer was charged with KI (20 mol%), benzoic acid (0.25 mmol), $K_2S_2O_8$ (2 equiv), K_2HPO_4 (4 equiv) and TEMPO (1.2 equiv). Then acetone (1 mL) and H_2O (0.5 mL) were added by

syringe respectively under air atmosphere. The reaction mixture was stirred at 80 °C for 12 h. After 12 h, the reaction tube was cooled to room temperature and the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether).

4. Experimental Procedures

A 15 mL oven-dried Schlenk tube equipped with a magnetic stirrer was charged with KI (20 mol%), carboxylic acids (0.25 mmol), $K_2S_2O_8$ (2 equiv) and K_2HPO_4 (4 equiv). Then acetone (1 mL) and H_2O (0.5 mL) were added by syringe respectively under air atmosphere. The reaction mixture was stirred at 80 °C for 12h. After 12 h, the reaction tube was cooled to room temperature and the mixture was quenched with water and extracted with ethyl acetate (3 x 10 mL). The organic layers were combined and concentrated under vacuo. The product was purified by flash column chromatography on silica gel (ethyl acetate : petroleum ether).

5. Spectral Data

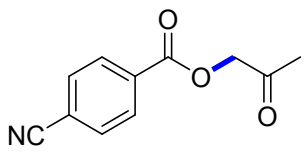


2-oxopropyl benzoate (**3a**)

White solid, 40.5 mg (91% from 30.5 mg of benzoic acid **1a**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.6 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 4.88 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.78 (s), 165.83 (s), 133.44 (s), 129.85 (d, *J* = 4.0 Hz), 129.17 (s), 128.47 (s), 68.72 (s), 26.20 (s). GCMS (EI) *m*/*z* 178 $(M)^+$.

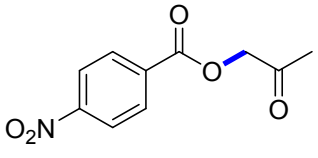
Reference: Cadierno, V.; Francos, J.; Gimeno, J.; *Green Chem.* **2010**, *12*, 135.



2-oxopropyl 4-cyanobenzoate (**3b**)

Light yellow solid, 35 mg (69% from 36.8 mg of 4-cyanobenzoic acid **1b**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.3 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 2H), 4.92 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.34 (s), 164.14 (s), 132.96 (s), 132.23 (s), 130.29 (s), 117.76 (s), 116.75 (s), 69.00 (s), 26.01 (s). HRMS calcd for $C_{11}H_9NO_3$ [M^+]: 203.0582; found: 203.0584.

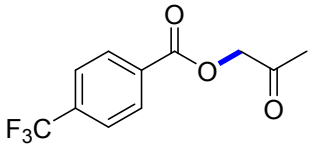


2-oxopropyl 4-nitrobenzoate (**3c**)

Colourless solid, 45.2 mg (81% from 41.8 mg of 4-nitrobenzoic acid **1c**)

^{1}H NMR (600 MHz,$CDCl_3$) δ 8.29 (d, *J* = 8.8 Hz, 2H), 8.24 (d, *J* = 8.7 Hz, 2H), 4.95 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.23 (s), 163.90 (s), 150.73 (s), 134.55 (s), 130.96 (s), 123.55 (s), 69.09 (s), 26.01 (s). GCMS (EI) *m*/*z* 223 $(M)^+$.

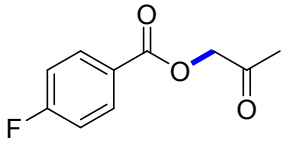
Reference: Fernandes, R. A.;Chaudhari, D. A. *J. Org. Chem.* **2014**, *79*, 5787.



2-oxopropyl 4-(trifluoromethyl)benzoate (**3d**)

Light yellow solid, 46.8 mg (76% from 47.5 mg of 4-(trifluoromethyl)benzoic acid hydrate **1d**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.1 Hz, 2H), 7.73 (d, *J* = 8.2 Hz, 2H), 4.92 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, CDCl3) δ 200.75 (s), 164.62 (s), 134.86 (q, *J* = 32.8 Hz), 132.43 (s), 125.50 (q, *J* = 3.7 Hz), 124.22 (s), 123.53 (q, *J* = 272.8 Hz), 68.94 (s), 26.07 (s). ^{19}F NMR (564 MHz, $CDCl_3$) δ -63.24 (s). HRMS calcd for $C_{11}H_9F_3O_3$ [M^+]: 246.0504; found: 246.0506.

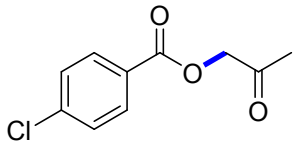


2-oxopropyl 4-fluorobenzoate (**3e**)

White solid, 42.6 mg (87% from 35 mg of 4-fluorobenzoic acid **1e**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 8.6, 5.6 Hz, 2H), 7.13 (t, *J* = 8.6 Hz, 2H),

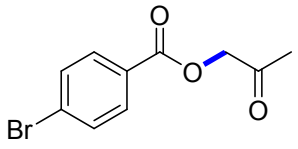
4.87 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.37 (s), 166.87 (s), 165.18 (s), 164.81 (s), 132.46 (d, J = 9.4 Hz), 125.42 (d, J = 3.0 Hz), 115.66 (d, J = 22.1 Hz), 68.71 (s), 26.11 (s). ^{19}F NMR (564 MHz, $CDCl_3$) δ -104.76 (dq, J = 8.3, 5.5 Hz). HRMS calcd for $C_{10}H_9FO_3$ [M^+]: 196.0536; found: 196.0539.



2-oxopropyl 4-chlorobenzoate (**3f**)

White solid, 52 mg (98% from 40 mg of 4-chlorobenzoic acid **1f**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (d, J = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 4.87 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.19 (s), 164.92 (s), 139.91 (s), 131.21 (s), 128.81 (s), 127.60 (s), 68.75 (s), 26.09 (s). HRMS calcd for $C_{10}H_9ClO_3$ [M^+]: 212.0240; found: 212.0244.

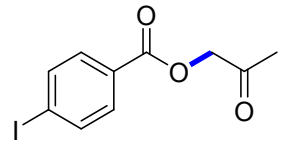


2-oxopropyl 4-bromobenzoate (**3g**)

White solid, 62.7 mg (98% from 50 mg of 4-bromobenzoic acid **1g**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, J = 8.4 Hz, 2H), 7.60 (d, J = 8.4 Hz, 2H), 4.87 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.16 (s), 165.07 (s), 131.82 (s), 131.34 (s), 128.62 (s), 128.06 (s), 68.77 (s), 26.11 (s). GCMS (EI) m/z 256 $(M)^+$.

Reference: Ali, R.; Yavar, A.; Nasrabadi, F. Z.; Morteza, R. *J. Heterocycl. Chem.* **2013**, *50*, 1294.

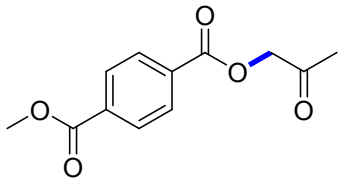


2-oxopropyl 4-iodobenzoate (**3h**)

Light yellow solid, 66.9 mg (88% from 62 mg of 4-iodobenzoic acid **1h**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (d, J = 8.1 Hz, 2H), 7.77 (d, J = 8.0 Hz, 2H), 4.86 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.15 (s), 165.28 (s), 137.80 (s),

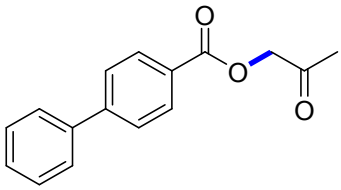
131.18 (s), 128.59 (s), 101.34 (s), 68.73 (s), 26.09 (s). HRMS calcd for $C_{10}H_9IO_3$ [M^+]: 303.9596; found: 303.9596.



methyl (2-oxopropyl) terephthalate (**3i**)

White solid, 38 mg (65% from 45 mg of 4-(methoxycarbonyl)benzoic acid **1i**)

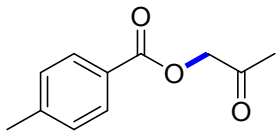
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 8.4 Hz, 2H), 8.10 (d, J = 8.2 Hz, 2H), 4.90 (s, 2H), 3.93 (s, 3H), 2.22 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.01 (s), 166.08 (s), 164.97 (s), 134.31 (s), 132.89 (s), 129.79 (s), 129.57 (s), 68.87 (s), 52.41 (s), 26.10 (s). HRMS calcd for $C_{12}H_{12}O_5$ [M^+]: 236.0685; found: 236.0684.



2-oxopropyl [1,1'-biphenyl]-4-carboxylate (**3j**)

White solid, 49.5 mg (78% from 49.5 mg of [1,1'-biphenyl]-4-carboxylic acid **1j**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 8.1 Hz, 2H), 7.69 (d, J = 8.2 Hz, 2H), 7.63 (d, J = 7.5 Hz, 2H), 7.48 (t, J = 7.6 Hz, 2H), 7.41 (t, J = 7.3 Hz, 1H), 4.90 (s, 2H), 2.25 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.78 (s), 165.69 (s), 146.18 (s), 139.84 (s), 130.38 (s), 128.92 (s), 128.22 (s), 127.86 (s), 127.20 (d, J = 18.2 Hz), 68.72 (s), 26.19 (s). HRMS calcd for $C_{16}H_{14}O_3$ [M^+]: 254.0943; found: 254.0940.

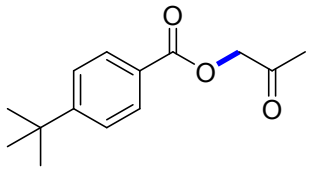


2-oxopropyl 4-methylbenzoate (**3k**)

White solid, 44 mg (91% from 34mg of 4-methylbenzoic acid **1k**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.98, 7.97, 7.26, 7.24, 4.84, 2.41, 2.22. ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.02 (s), 165.84 (s), 144.19 (s), 129.86 (s), 129.15 (s), 126.39 (s), 68.58 (s), 26.16 (s), 21.65 (s). GCMS (EI) m/z 192 $(M)^+$.

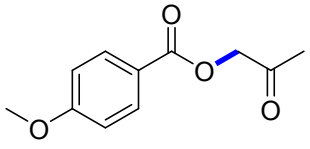
Reference: Fernandes, R. A.; Chaudhari, D. A. *J. Org. Chem.* **2014**, *79*, 5787.



2-oxopropyl 4-(*tert*-butyl)benzoate (**3l**)

Colourless oil, 37.4 mg (64% from 44.5 mg of 4-(*tert*-butyl)benzoic acid **1l**)

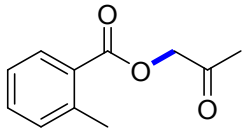
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 4.86 (s, 2H), 2.23 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.09 (s), 165.83 (s), 157.20 (s), 129.75 (s), 126.35 (s), 125.46 (s), 68.61 (s), 35.12 (s), 31.06 (s), 26.19 (s). HRMS calcd for $C_{14}H_{18}O_3$ [M^+]: 234.1256; found: 234.1256.



2-oxopropyl 4-methoxybenzoate (**3m**)

Colourless oil, 48.9 mg (94% from 38 mg of 4-methoxybenzoic acid **1m**)

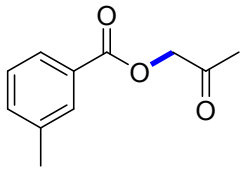
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.7 Hz, 2H), 6.92 (d, *J* = 8.7 Hz, 2H), 4.82 (s, 2H), 3.84 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 202.13 (s), 165.44 (s), 163.69 (s), 131.87 (s), 121.43 (s), 113.68 (s), 68.46 (s), 55.37 (s), 26.10 (s). HRMS calcd for $C_{11}H_{12}O_4$ [M^+]: 208.0736; found: 208.0734.



2-oxopropyl 2-methylbenzoate (**3n**)

Colourless oil, 41.3 mg (86% from 34 mg of 2-methylbenzoic acid **1n**)

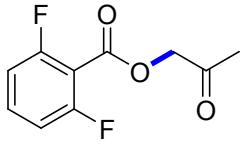
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 7.27 (dd, *J* = 7.0, 3.7 Hz, 2H), 4.85 (s, 2H), 2.61 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.74 (s), 166.61 (s), 140.71 (s), 132.43 (s), 131.73 (s), 130.81 (s), 128.50 (s), 125.77 (s), 68.52 (s), 26.17 (s), 21.67 (s). HRMS calcd for $C_{11}H_{12}O_3$ [M^+]: 192.0786; found: 192.0786.



2-oxopropyl 3-methylbenzoate (**3o**)

Colourless oil, 44.6 mg (93% from 34 mg of 3-methylbenzoic acid **1o**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 – 7.86 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.34 (t, *J* = 7.6 Hz, 1H), 4.86 (s, 2H), 2.40 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.86 (s), 165.97 (s), 138.27 (s), 134.18 (s), 130.35 (s), 129.06 (s), 128.35 (s), 126.99 (s), 68.65 (s), 26.16 (s), 21.21 (s). HRMS calcd for $C_{11}H_{12}O_3$ [M^+]: 192.0786; found: 192.0783.

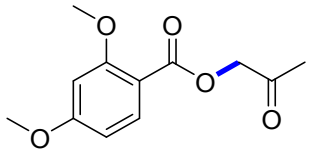


2-oxopropyl 2,6-difluorobenzoate (**3p**)

Light yellow oil, 53 mg (99% from 39.5 mg of 2,6-difluorobenzoic acid **1p**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51 – 7.41 (m, 1H), 6.97 (t, *J* = 8.4 Hz, 2H), 4.87 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.12 (s), 161.82 (d, *J* = 5.7 Hz), 160.71 (s), 160.11 (d, *J* = 5.7 Hz), 133.45 (t, *J* = 10.6 Hz), 112.14 (dd, *J* = 21.7, 3.9 Hz), 69.20 (s), 26.17 (s). GCMS (EI) *m*/*z* 214 $(M)^+$.

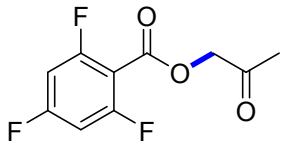
Reference: Bruneau, C.; Kabouche, Z.; Neveux, M.; Seiller, B.; Dixneuf, P. H. *Inorg. Chim. Acta* **1994**, *222*, 155.



2-oxopropyl 2,4-dimethoxybenzoate (**3q**)

Light yellow oil, 54.1 mg (91% from 45.5 mg of 2,4-dimethoxybenzoic acid **1q**)

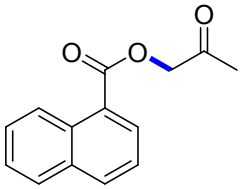
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 – 7.38 (m, 1H), 7.13 – 7.06 (m, 2H), 4.85 (s, 2H), 3.91 (s, 3H), 3.88 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.86 (s), 165.26 (s), 153.53 (s), 149.48 (s), 124.91 (s), 123.84 (s), 122.48 (s), 116.35 (s), 68.72 (s), 61.57 (s), 56.06 (s), 26.18 (s). HRMS calcd for $C_{12}H_{14}O_5$ [M^+]: 238.0841; found: 238.0837.



2-oxopropyl 2,4,6-trifluorobenzoate (**3r**)

Colourless oil, 51 mg (88% from 44 mg of 2,4,6-trifluorobenzoic acid **1r**)

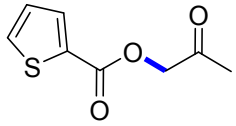
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.75 (t, *J* = 8.5 Hz, 2H), 4.88 (s, 2H), 2.24 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 200.76 (s), 165.56 (t, *J* = 15.4 Hz), 163.86 (t, *J* = 15.4 Hz), 162.95 (dd, *J* = 15.2, 8.3 Hz), 161.23 (dd, *J* = 15.2, 8.3 Hz), 159.97 (t, *J* = 2.1 Hz), 101.47 (d, *J* = 4.5 Hz), 101.30 (d, *J* = 4.8 Hz), 101.13 (d, *J* = 4.4 Hz), 69.22 (s), 26.17 (s). ^{19}F NMR (564 MHz, $CDCl_3$) δ -100.42 – -100.55 (m), -104.79 (t, *J* = 9.1 Hz). HRMS calcd for $C_{10}H_7F_3O_3$ [M^+]: 232.0347; found: 232.0347.



2-oxopropyl 1-naphthoate (**3s**)

Colourless oil, 45.2 mg (79% from 43 mg of 1-naphthoic acid **3s**)

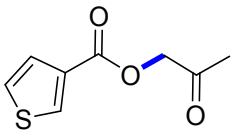
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.94 (d, *J* = 8.7 Hz, 1H), 8.30 (d, *J* = 7.2 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.58 – 7.48 (m, 2H), 4.96 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.66 (s), 166.58 (s), 133.79 (d, *J* = 12.8 Hz), 131.35 (s), 130.61 (s), 128.50 (s), 127.90 (s), 126.26 (s), 125.99 (s), 125.65 (s), 124.43 (s), 68.67 (s), 26.15 (s). HRMS calcd for $C_{14}H_{12}O_3$ [M^+]: 228.0786; found: 228.0784.



2-oxopropyl thiophene-2-carboxylate (**3t**)

White solid, 39.1 mg (85% from 32mg of thiophene-2-carboxylic acid **1t**)

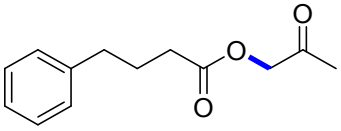
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.8 Hz, 1H), 7.60 (d, *J* = 4.6 Hz, 1H), 7.15 – 7.08 (m, 1H), 4.82 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.57 (s), 161.28 (s), 134.26 (s), 133.14 (s), 132.34 (s), 127.87 (s), 68.60 (s), 26.09 (s). HRMS calcd for $C_8H_8O_3S$ [M^+]: 184.0194; found: 184.0194.



2-oxopropyl thiophene-3-carboxylate (**3u**)

Colourless oil, 33.9 mg (74% from 32mg of thiophene-3-carboxylic acid **1u**)

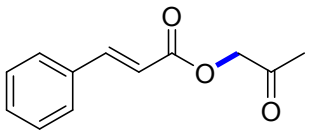
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 4.4, 3.3 Hz, 1H), 7.33 (dt, *J* = 4.9, 2.5 Hz, 1H), 4.83 (d, *J* = 1.2 Hz, 2H), 2.22 (d, *J* = 3.0 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.74 (s), 161.77 (s), 133.63 (s), 132.40 (s), 127.94 (s), 126.25 (s), 68.42 (s), 26.15 (s). HRMS calcd for $C_8H_8O_3S$ [M^+]: 184.0194; found: 184.0191.



2-oxopropyl 4-phenylbutanoate (**5a**)

White solid, 36.9 mg (67% from 41mg of 4-phenylbutanoic acid **4a**)

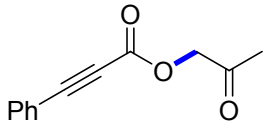
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.20 (d, J = 6.7 Hz, 3H), 4.65 (s, 2H), 2.70 (t, J = 7.6 Hz, 2H), 2.45 (t, J = 7.4 Hz, 2H), 2.16 (s, 3H), 2.05 – 1.97 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.74 (s), 161.77 (s), 133.63 (s), 132.40 (s), 127.94 (s), 126.25 (s), 68.42 (s), 26.15 (s). HRMS calcd for $C_{13}H_{16}O_3$ [M^+]: 220.1099; found: 220.1094.



2-oxopropyl cinnamate (**5b**)

White solid, 41.8mg (82% from 37mg of cinnamic acid **4b**)

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.44 – 7.31 (m, 3H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.77 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.82 (s), 165.99 (s), 146.17 (s), 134.06 (s), 130.53 (s), 128.86 (s), 128.16 (s), 116.71 (s), 68.32 (s), 26.06 (s). HRMS calcd for $C_{12}H_{12}O_3$ [M^+]: 204.0786; found: 204.0786.

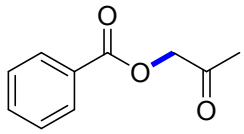


2-oxopropyl 3-phenylpropiolate (**5c**)

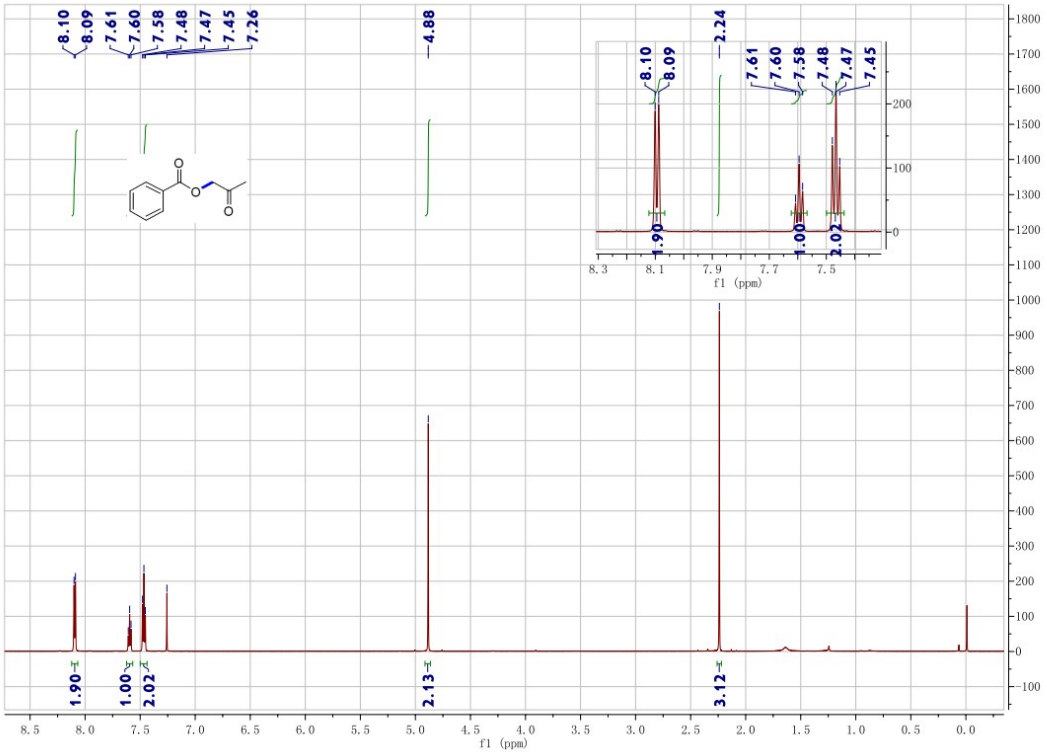
White solid, 35.5mg (70% from 36.5mg of cinnamic acid **4c**)

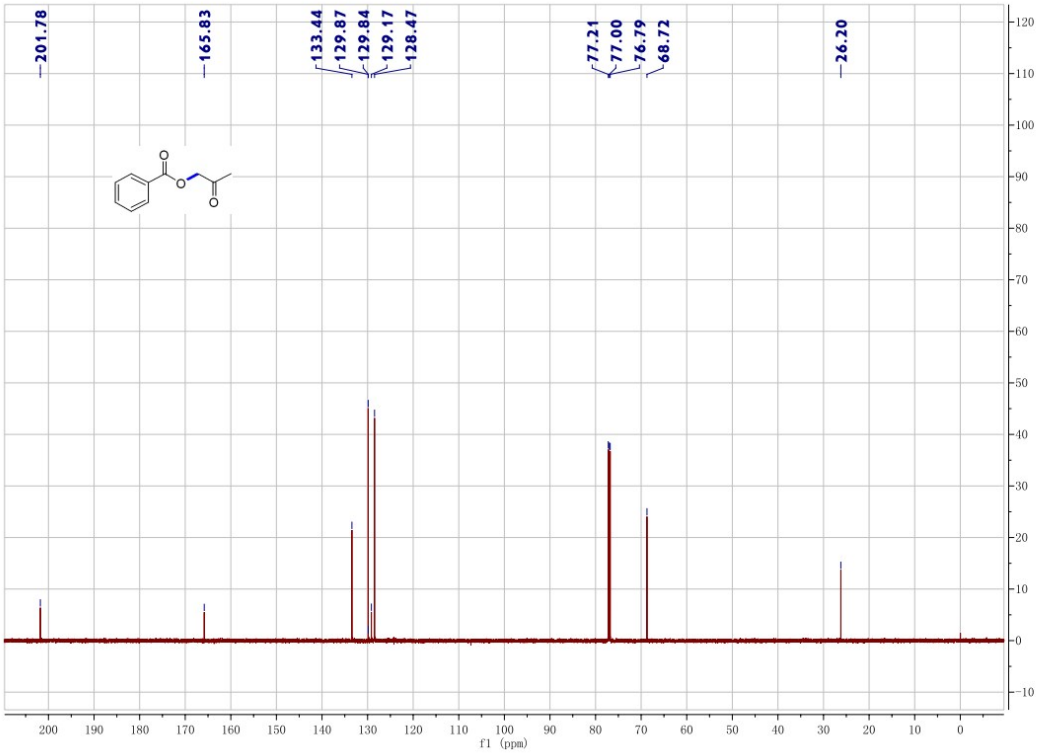
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 16.0 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.44 – 7.31 (m, 3H), 6.53 (d, *J* = 16.0 Hz, 1H), 4.77 (s, 2H), 2.20 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 201.82 (s), 165.99 (s), 146.17 (s), 134.06 (s), 130.53 (s), 128.86 (s), 128.16 (s), 116.71 (s), 68.32 (s), 26.06 (s). HRMS calcd for $C_{12}H_{10}O_3$ [M^+]: 202.0630; found: 202.0627.

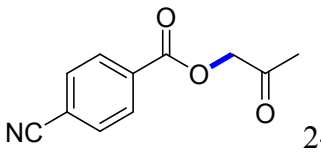
6. NMR spectra



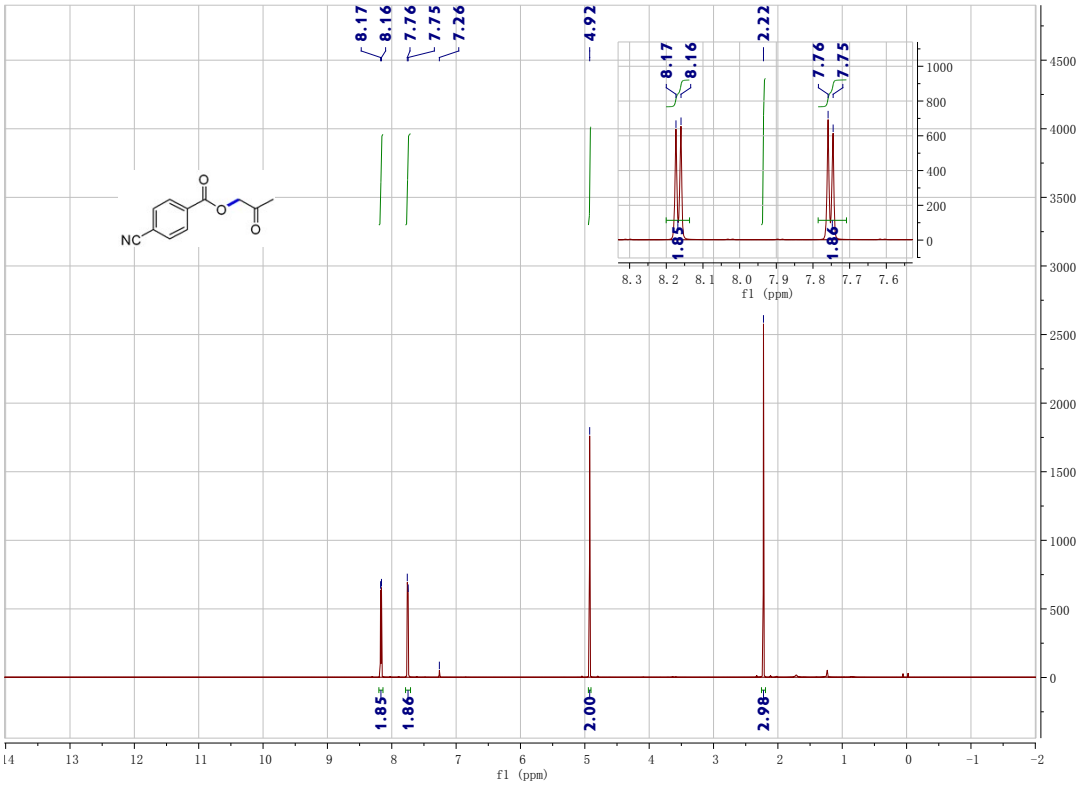
2-oxopropyl benzoate (**3a**)

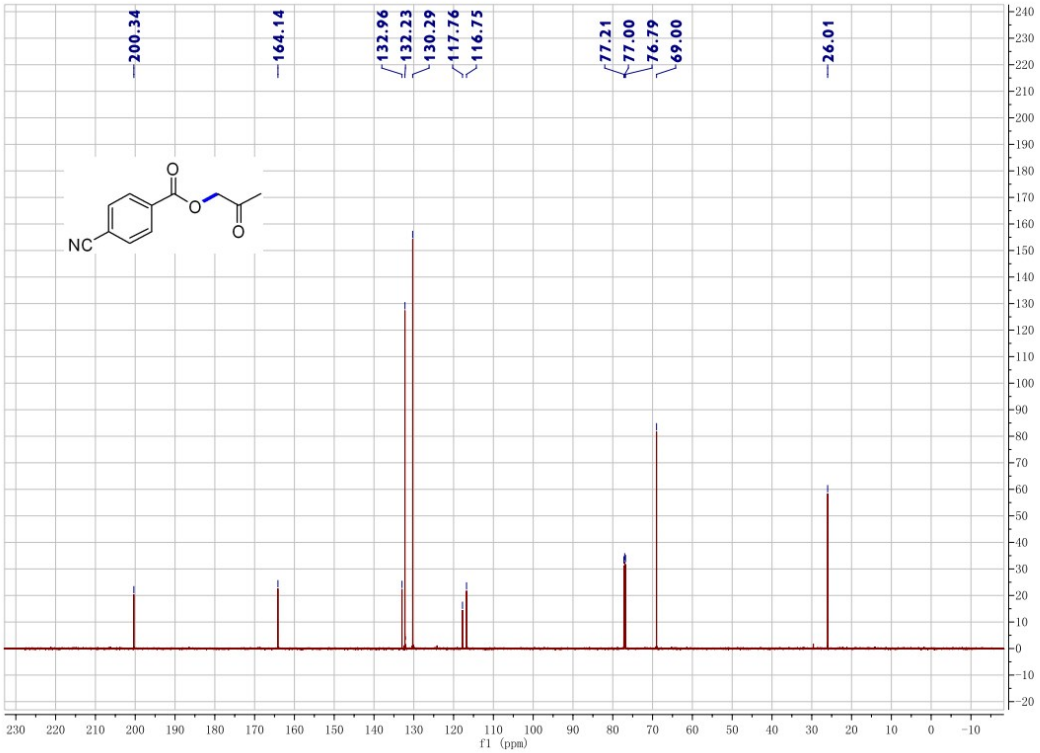


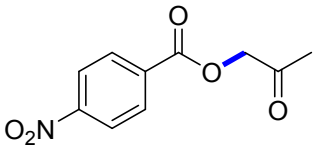




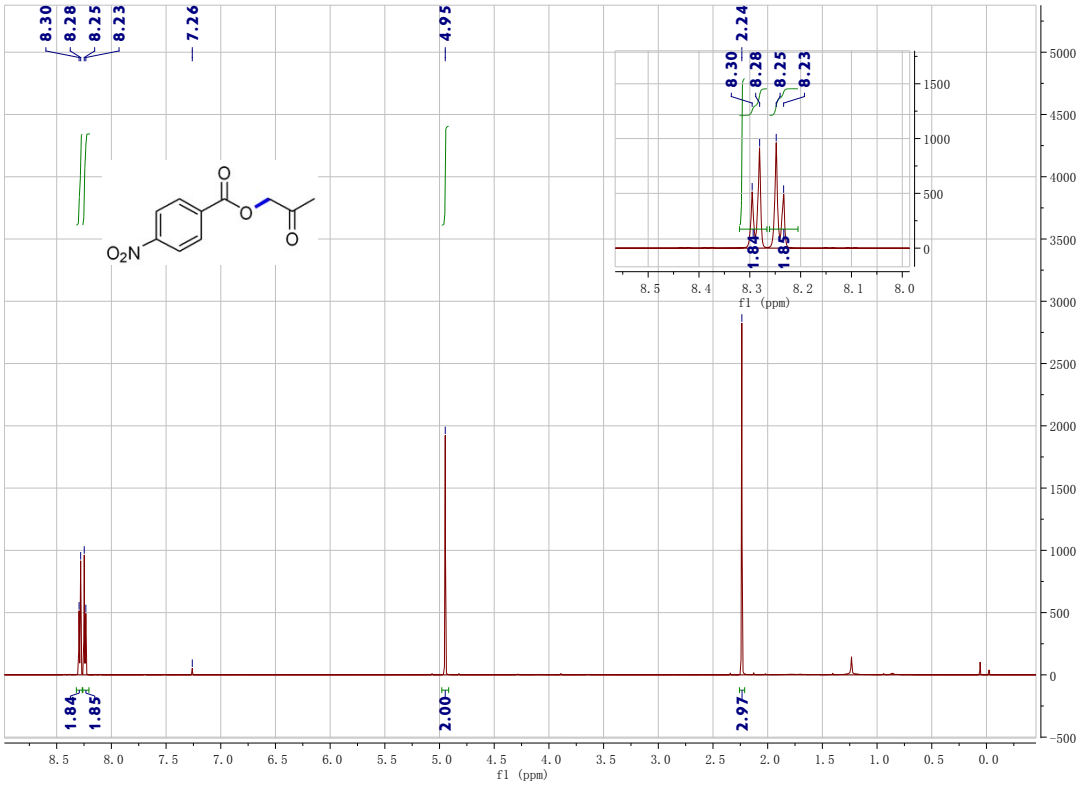
2-oxopropyl 4-cyanobenzoate (**3b**)

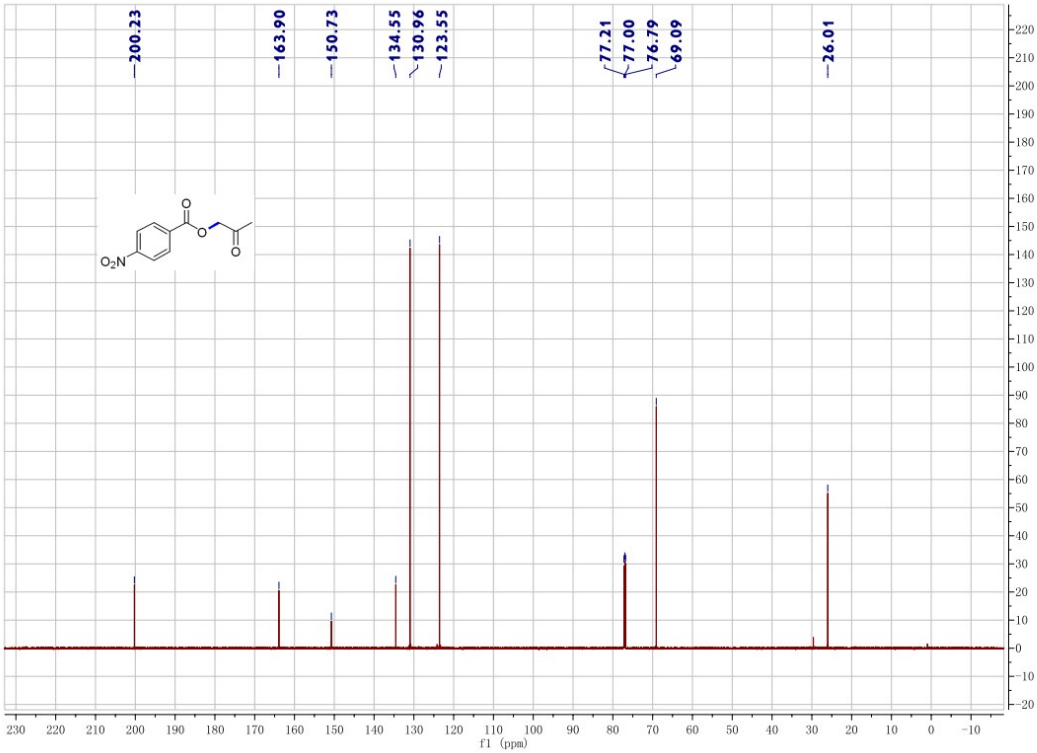


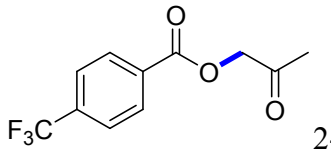




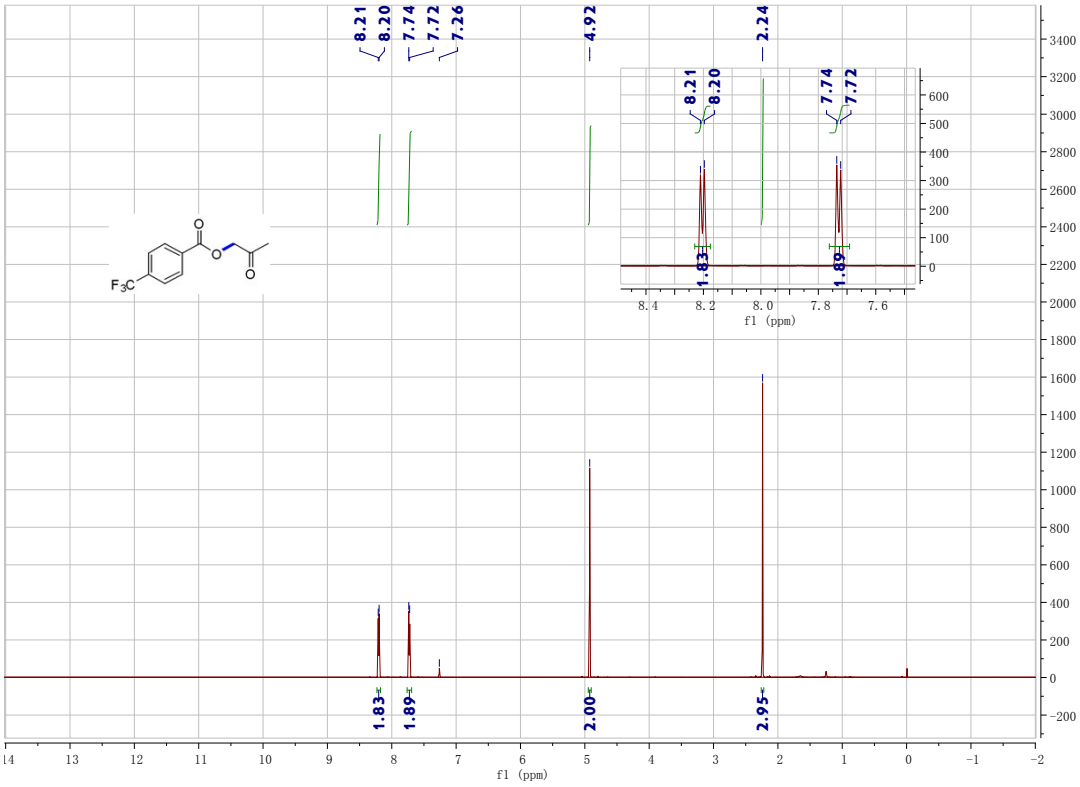
2-oxopropyl 4-nitrobenzoate (**3c**)

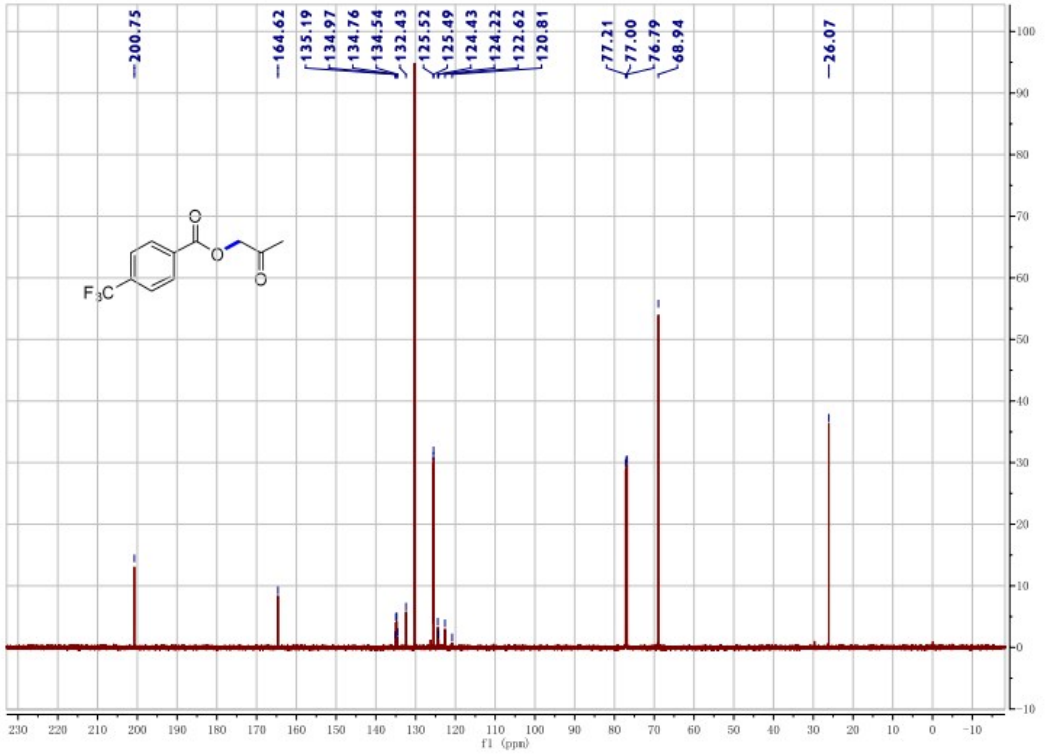


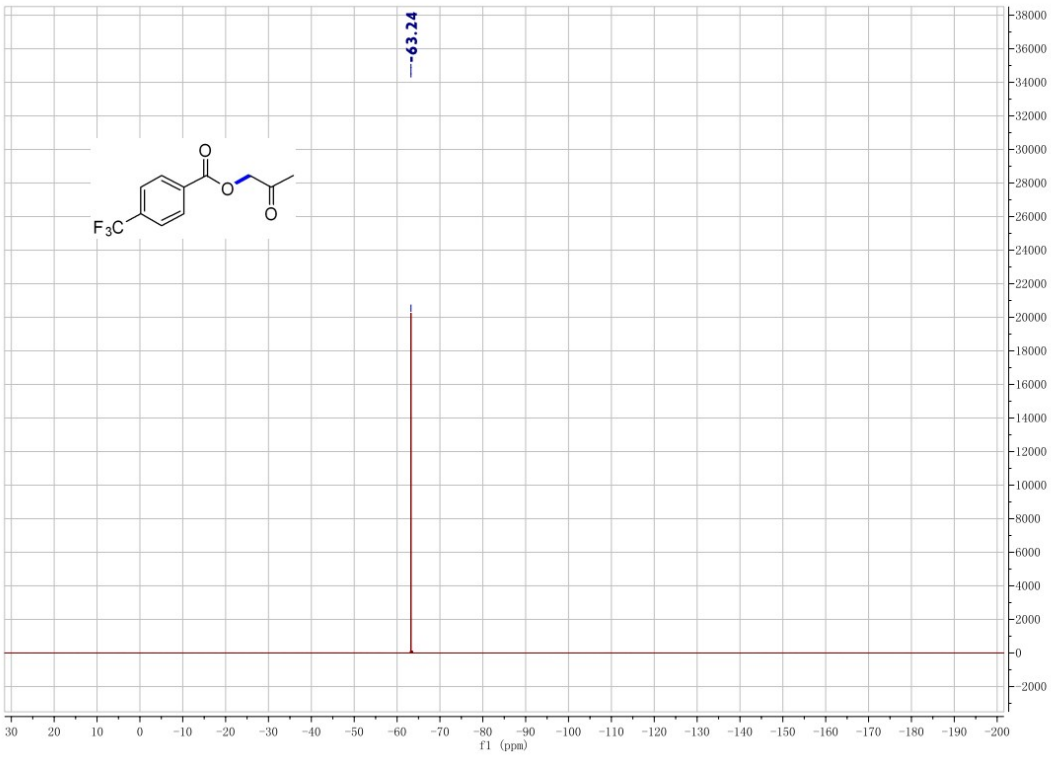




2-oxopropyl 4-(trifluoromethyl)benzoate (**3d**)



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O
O
O
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36000
34000
32000
30000
28000
26000
24000
22000
20000
18000
16000
14000
12000
10000
8000
6000
4000
2000
0
-2000
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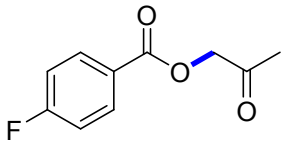
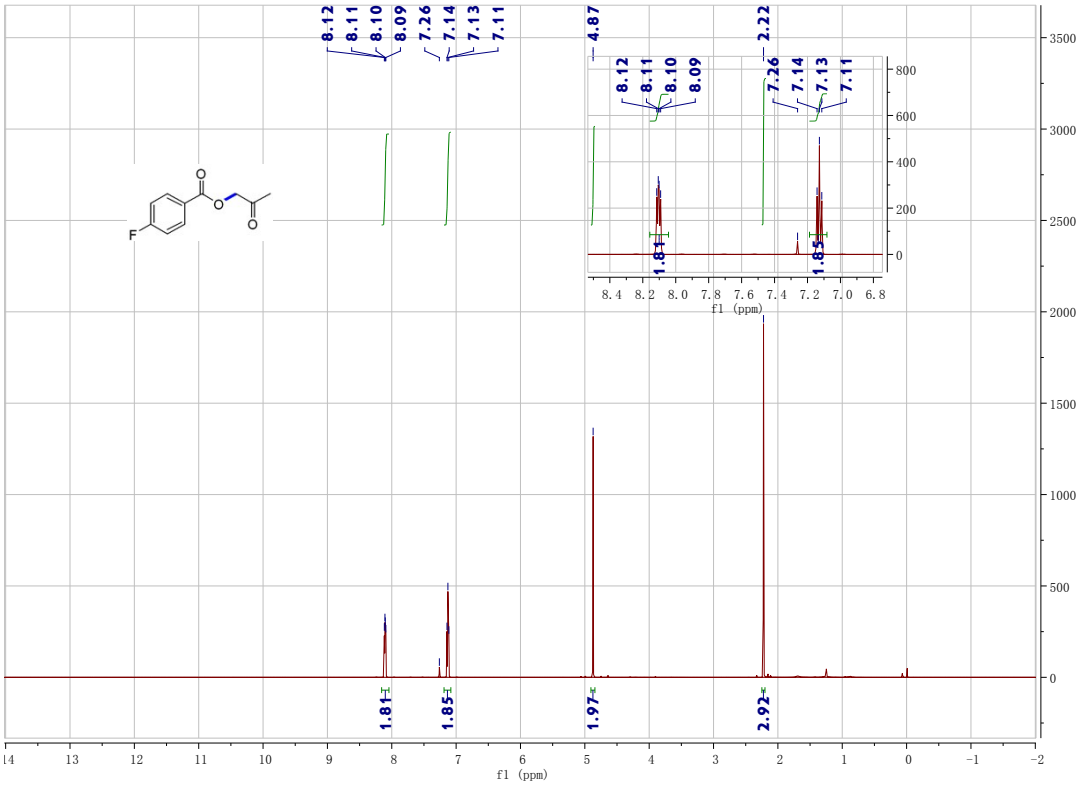
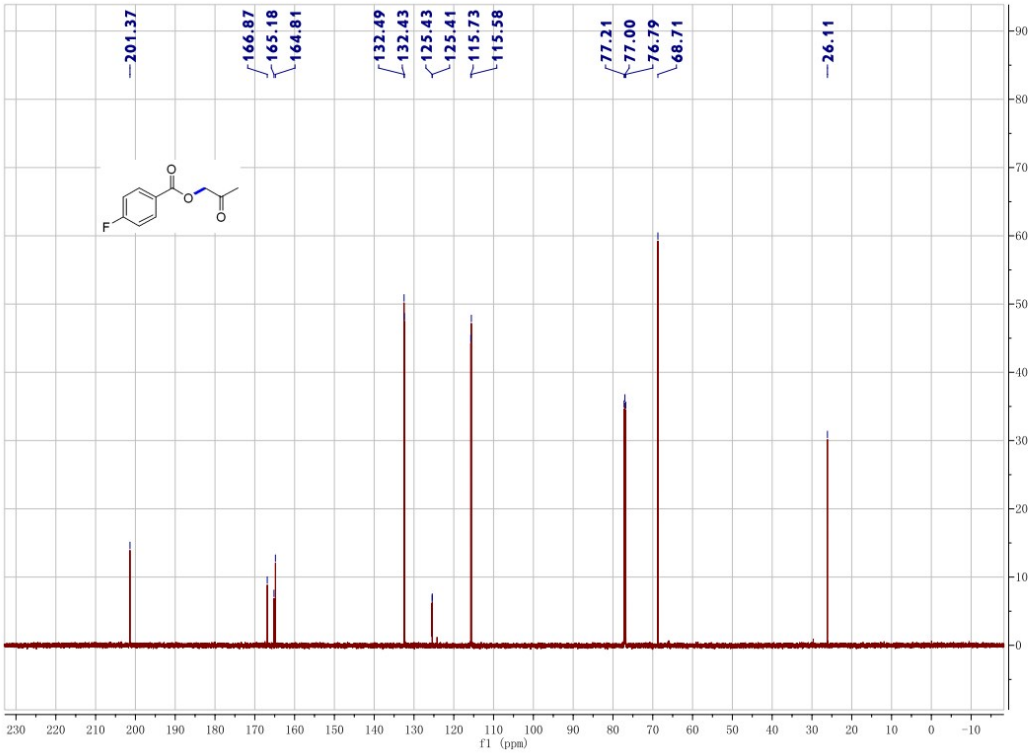
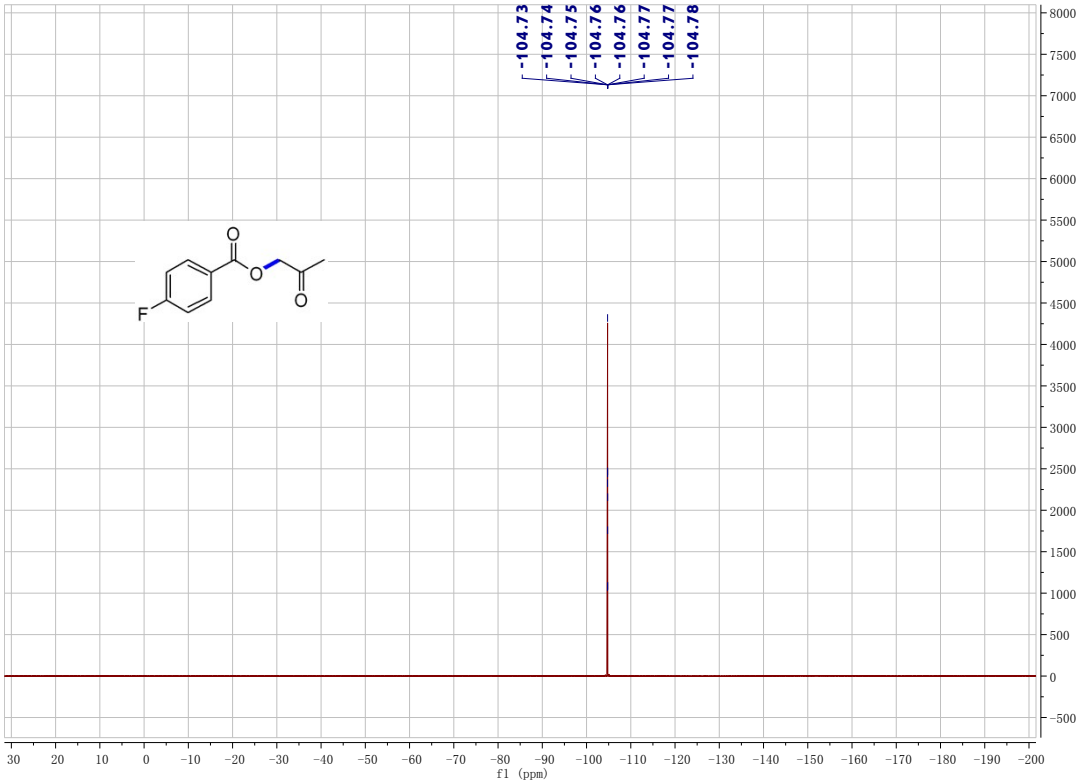
f1 (ppm)



2-oxopropyl 4-fluorobenzoate (**3e**)






-104.73
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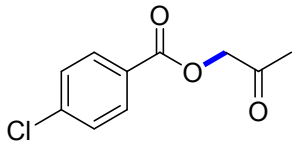
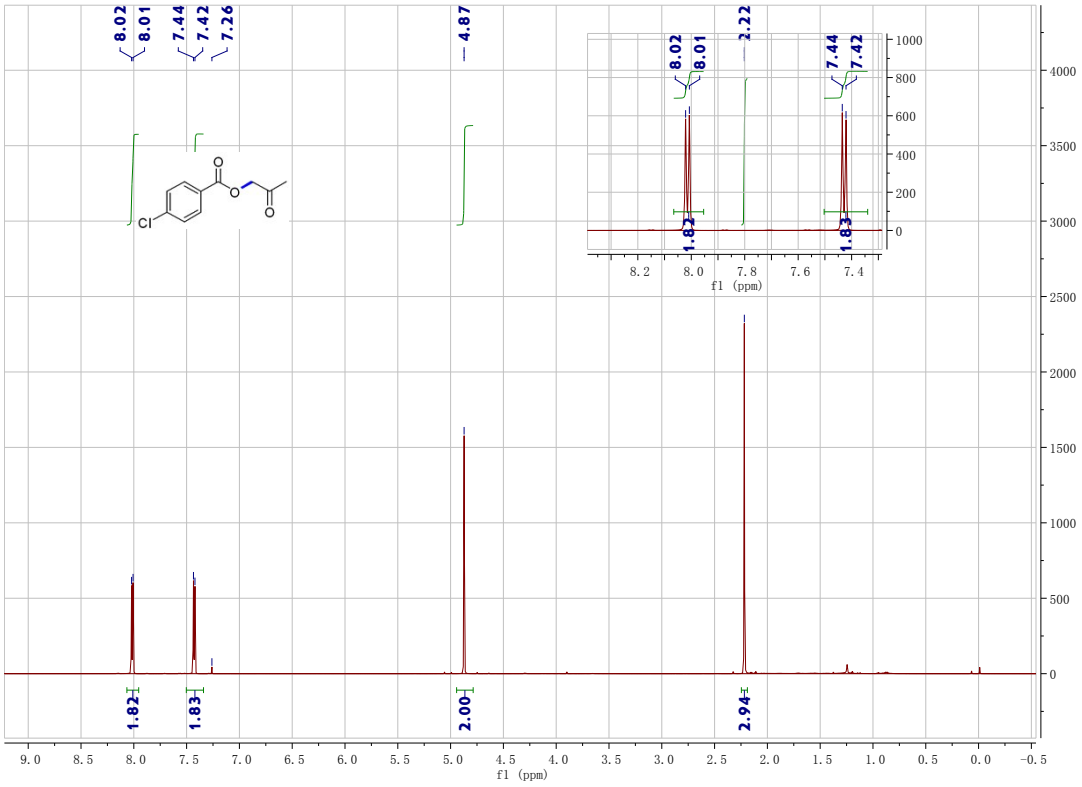
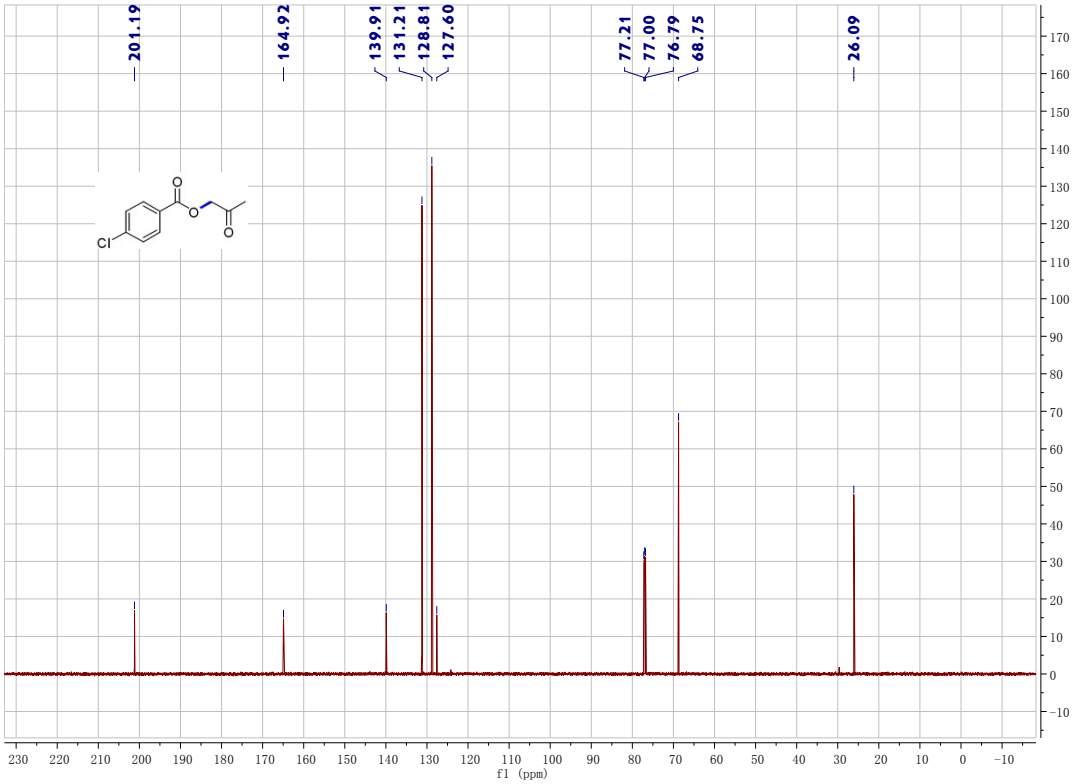
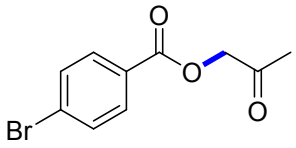
-104.76
-104.76
-104.77
-104.77
-104.78
O
O
O
F
f1 (ppm)



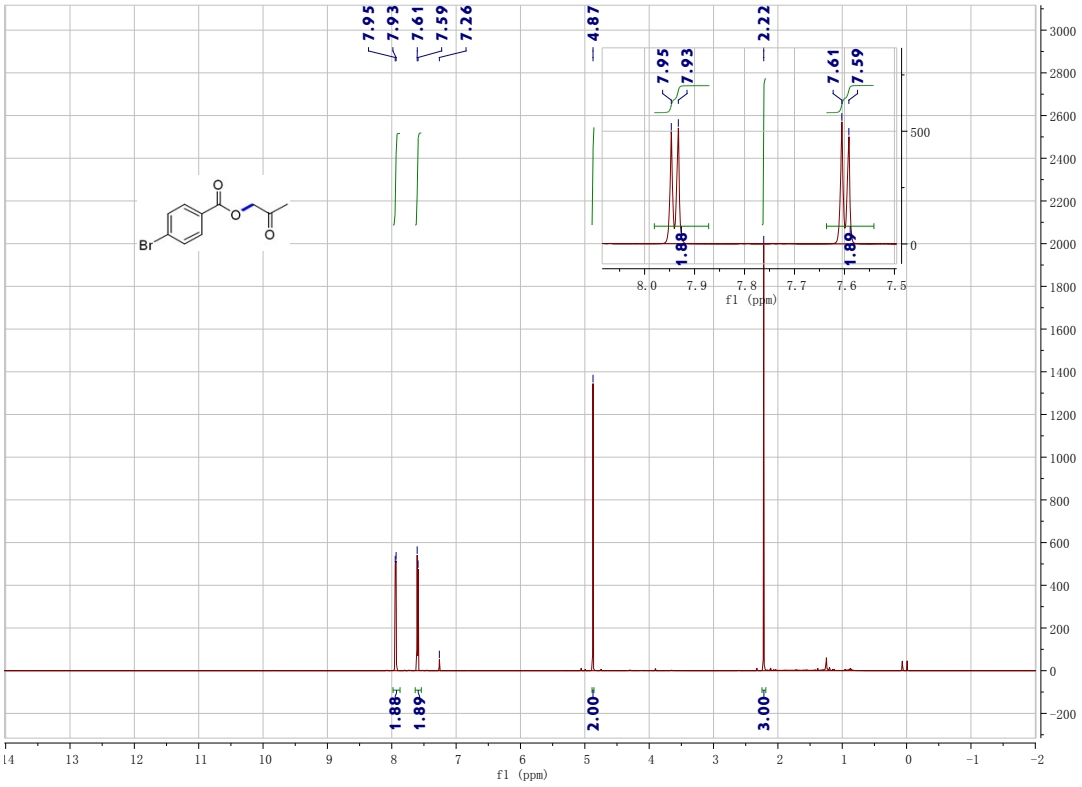
2-oxopropyl 4-chlorobenzoate (**3f**)

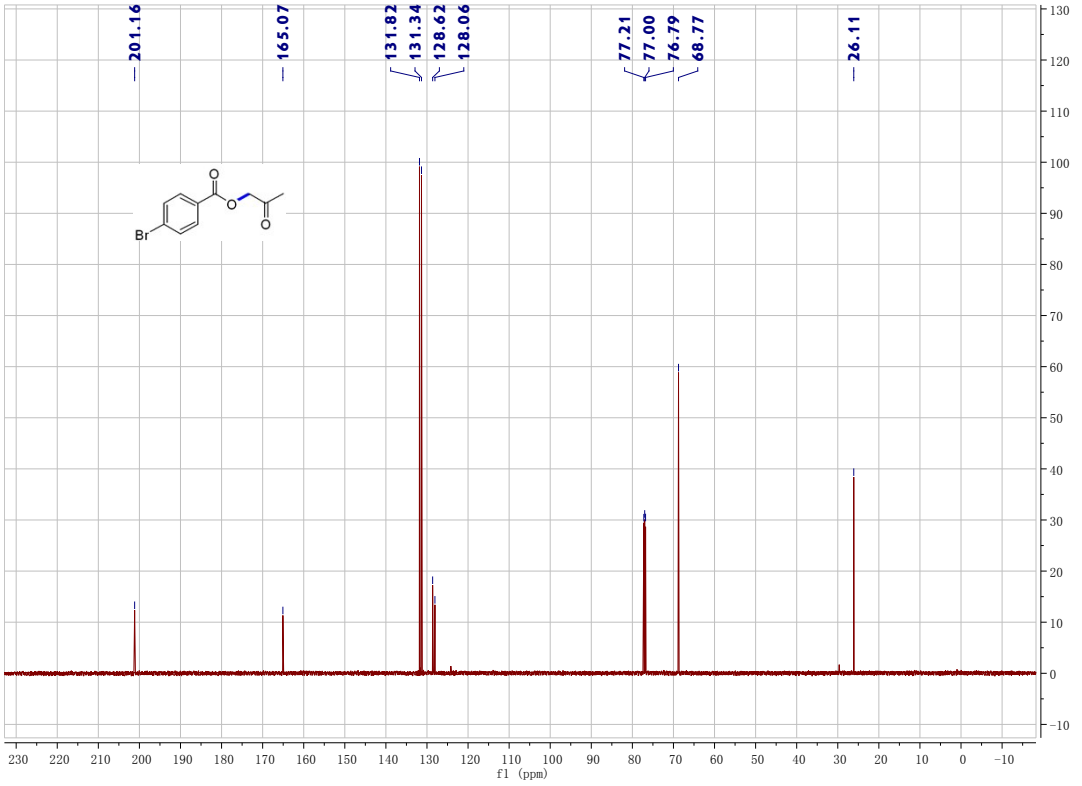


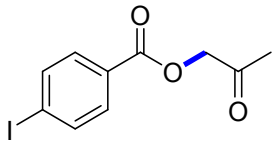




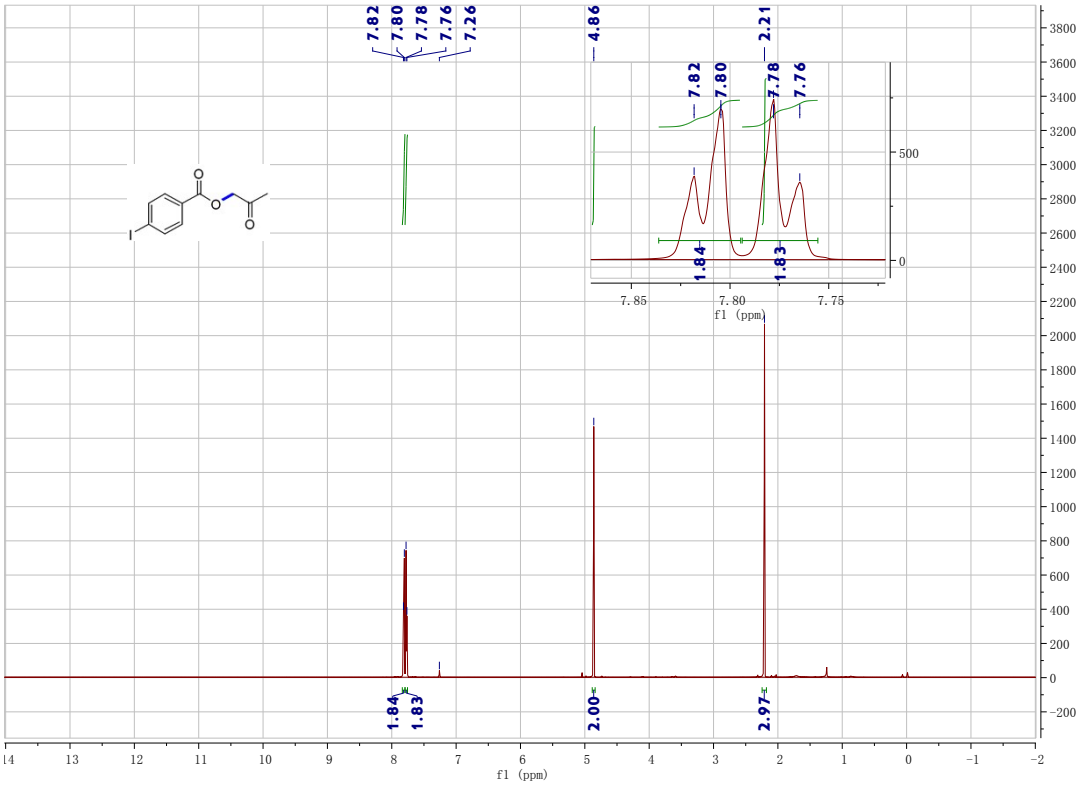
2-oxopropyl 4-bromobenzoate (**3g**)

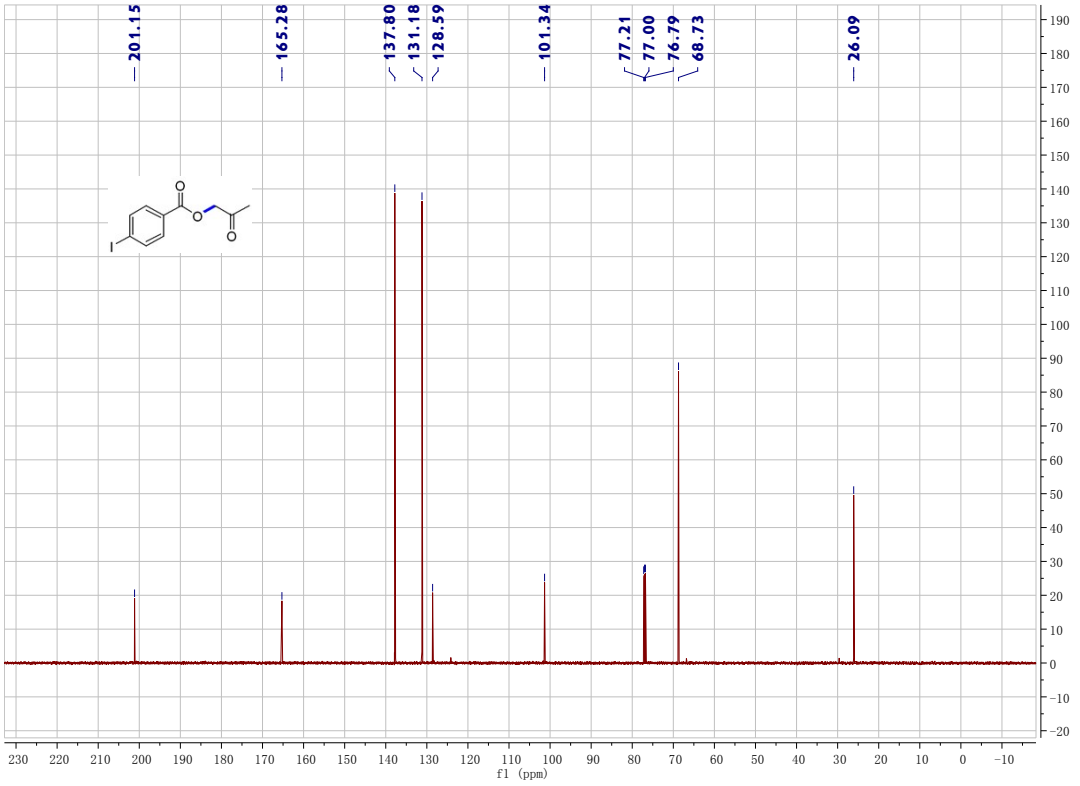


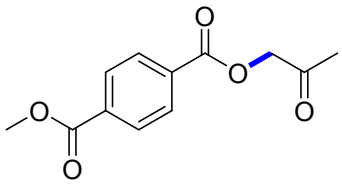




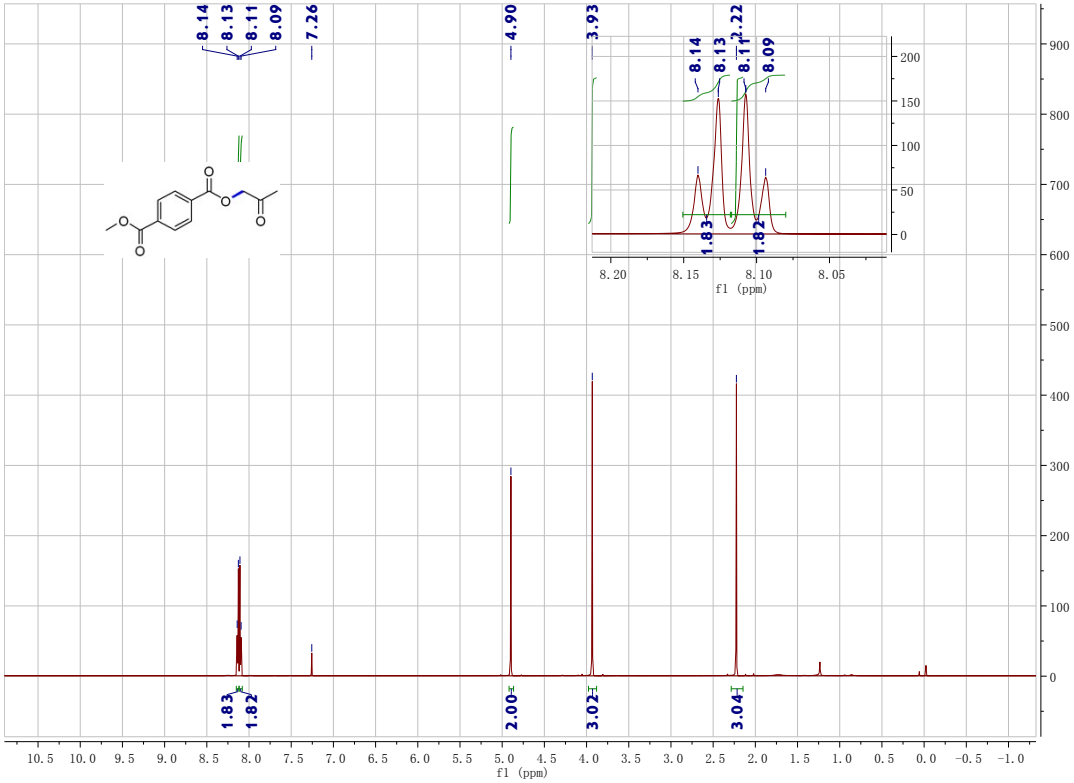
2-oxopropyl 4-iodobenzoate (**3h**)

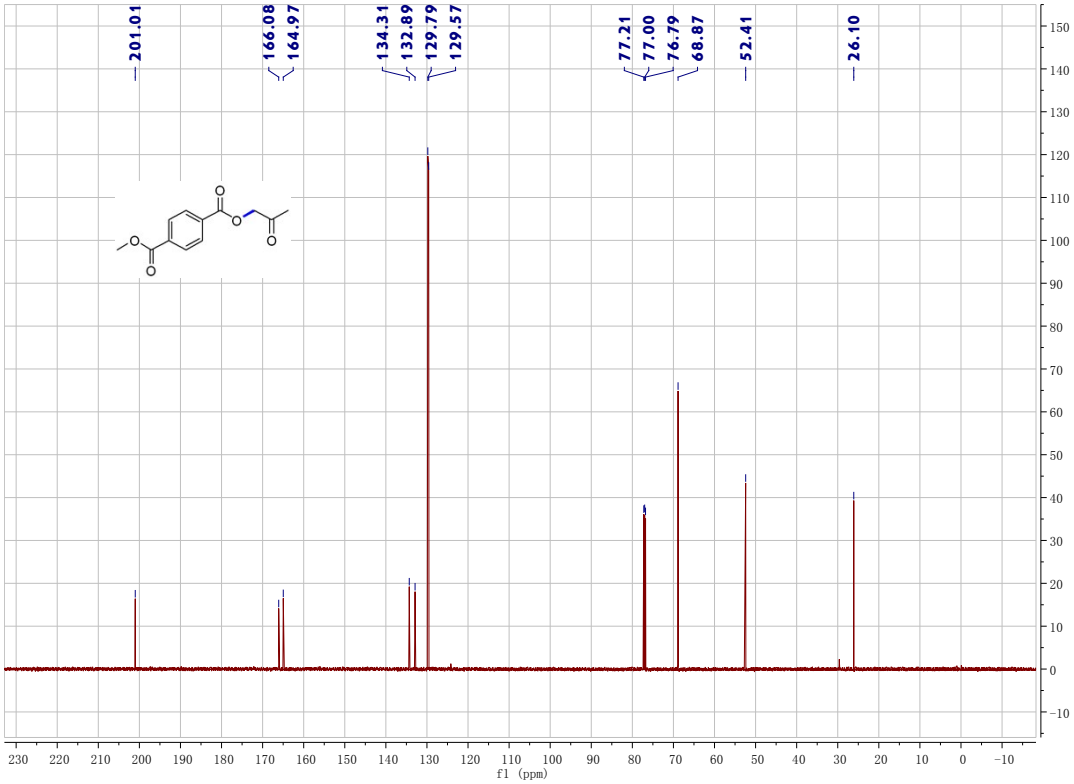


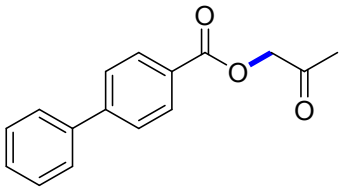




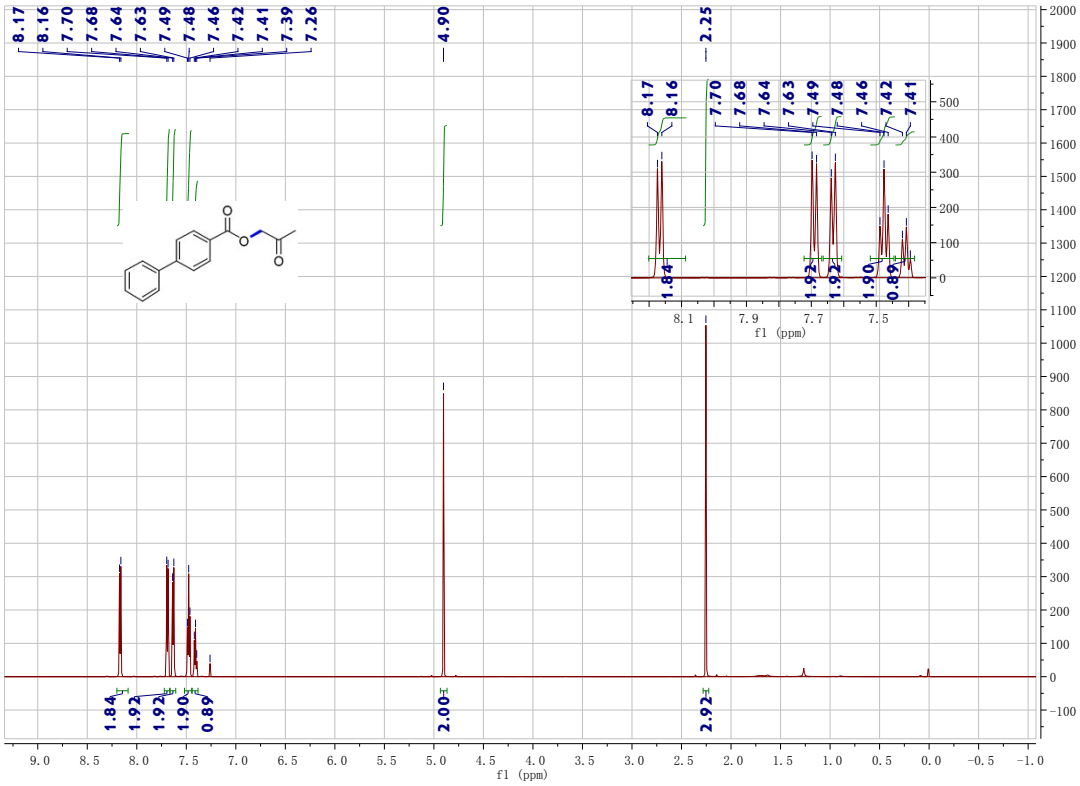
methyl (2-oxopropyl) terephthalate (**3i**)

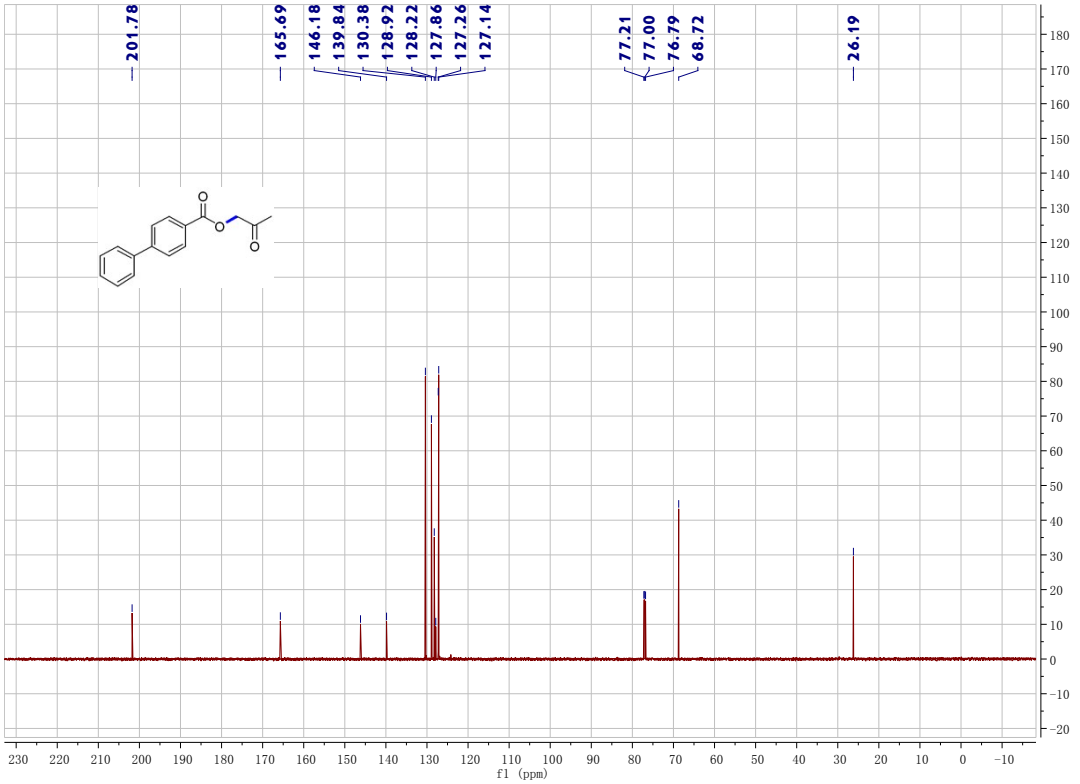


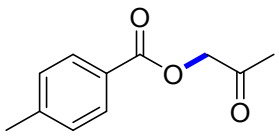




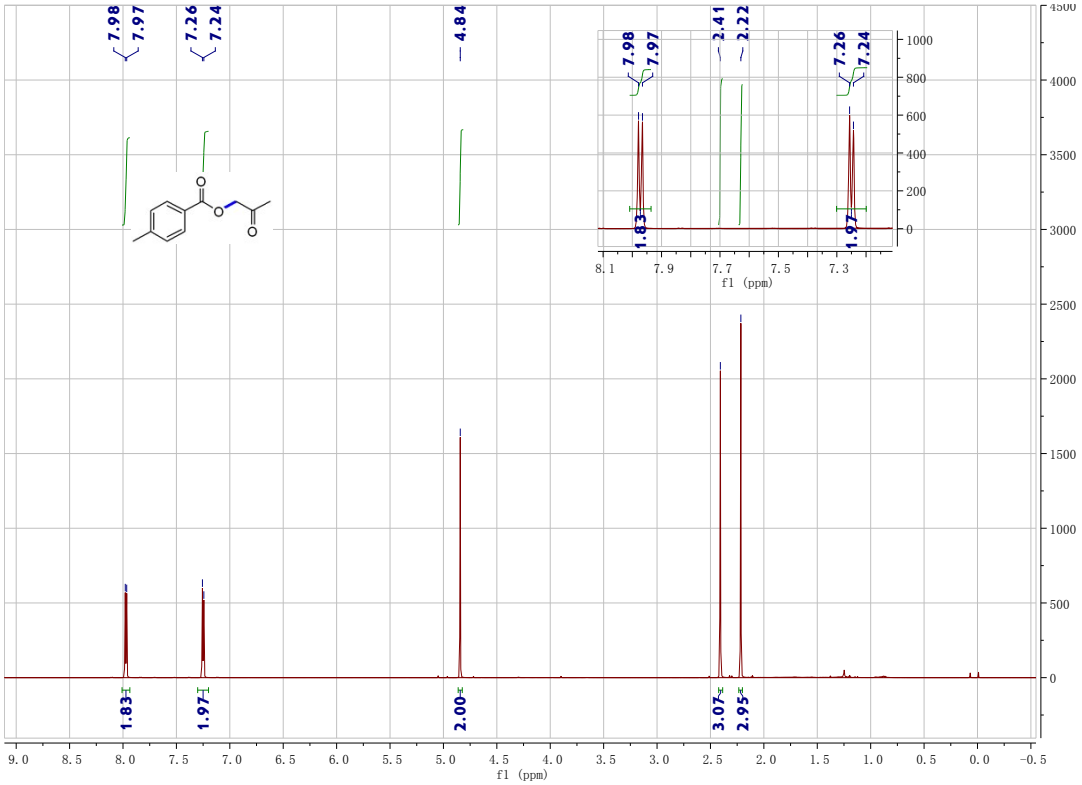
2-oxopropyl [1,1'-biphenyl]-4-carboxylate (**3j**)

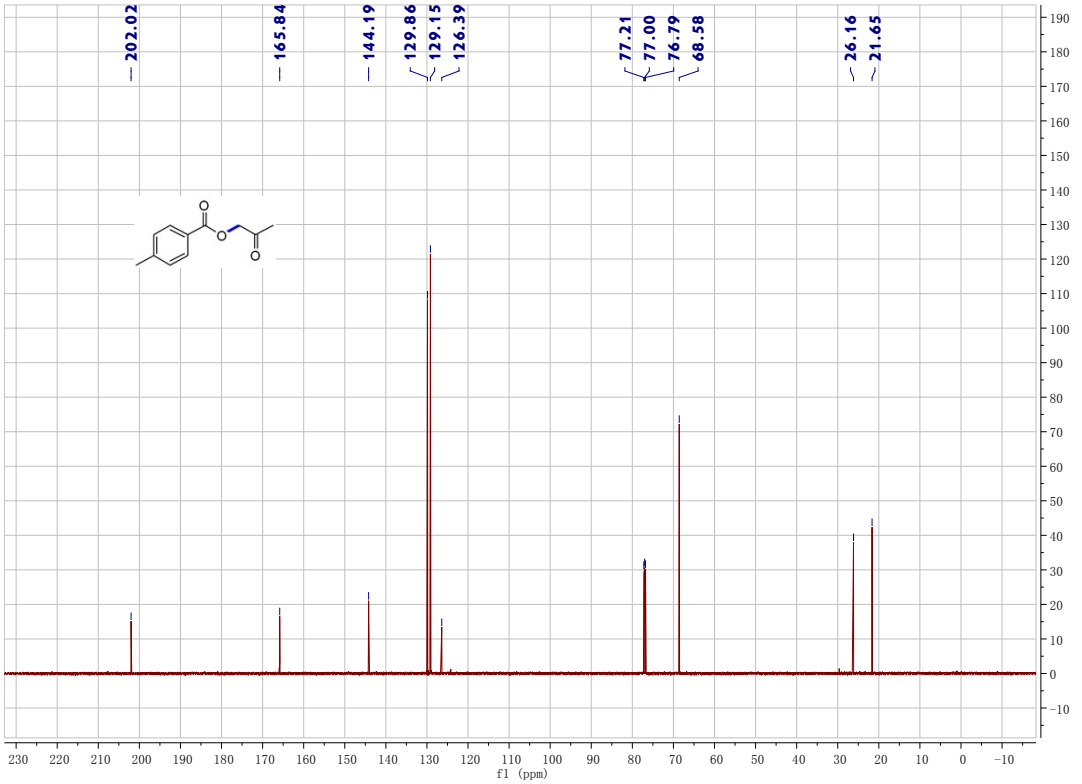


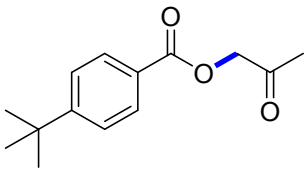




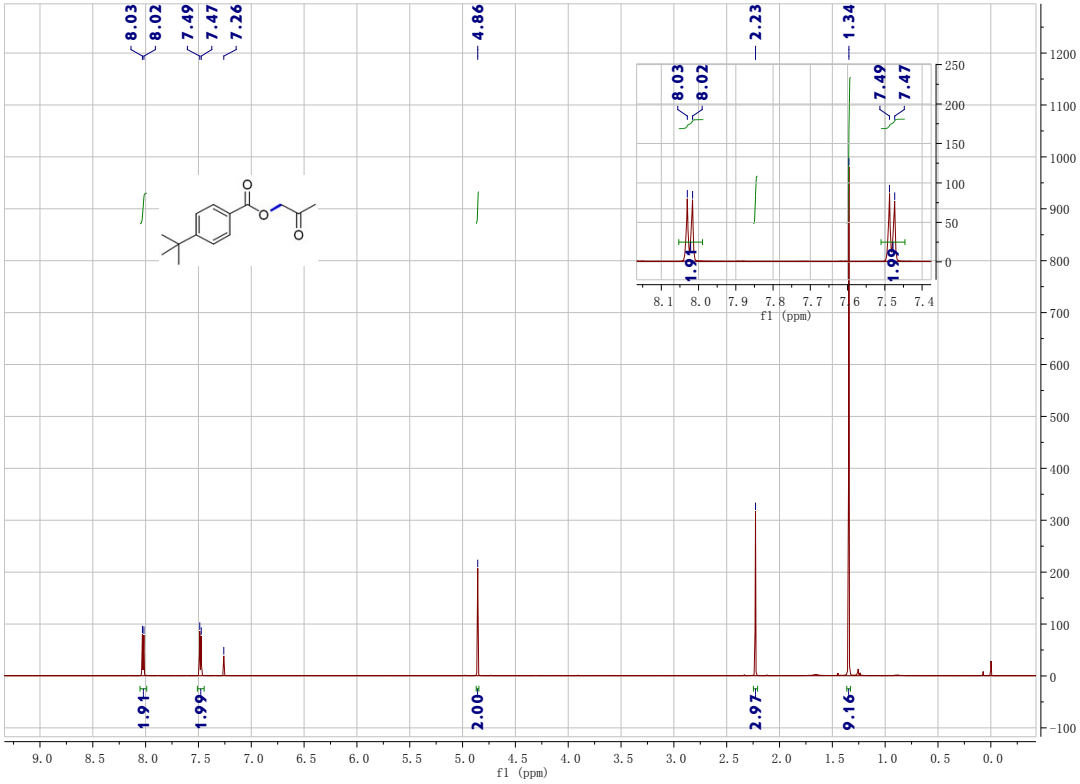
2-oxopropyl 4-methylbenzoate (**3k**)

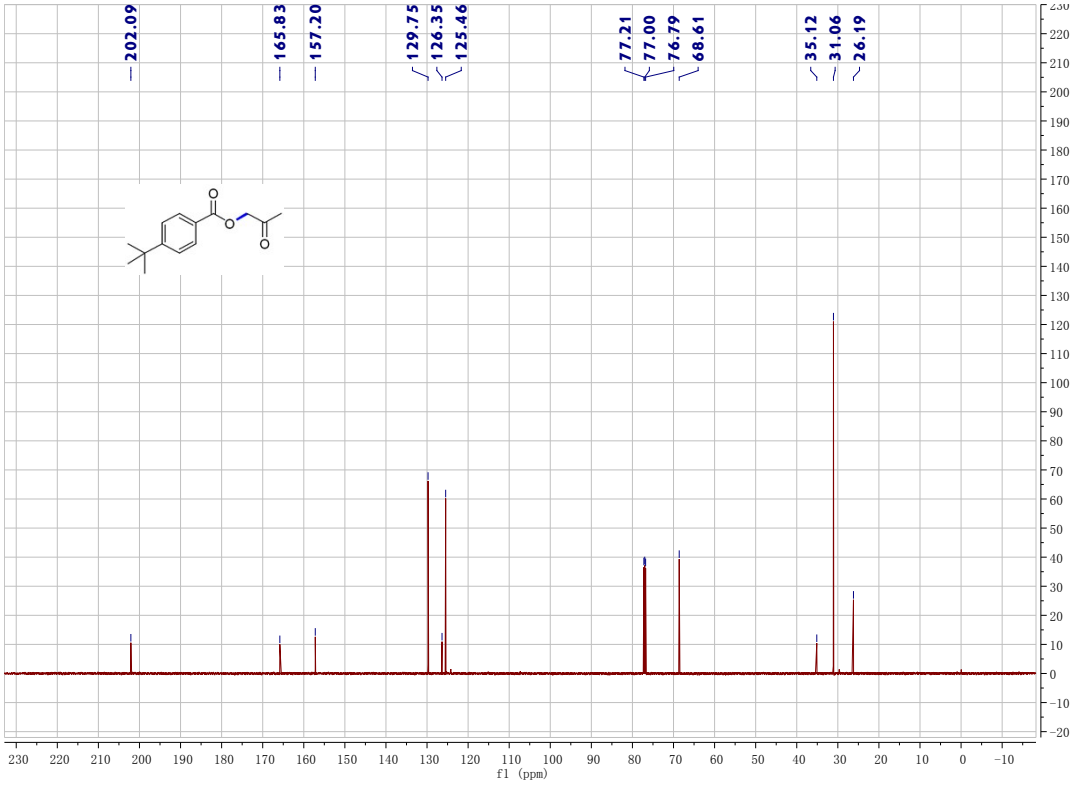


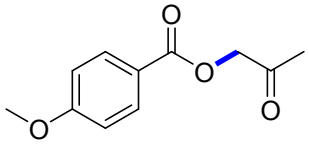




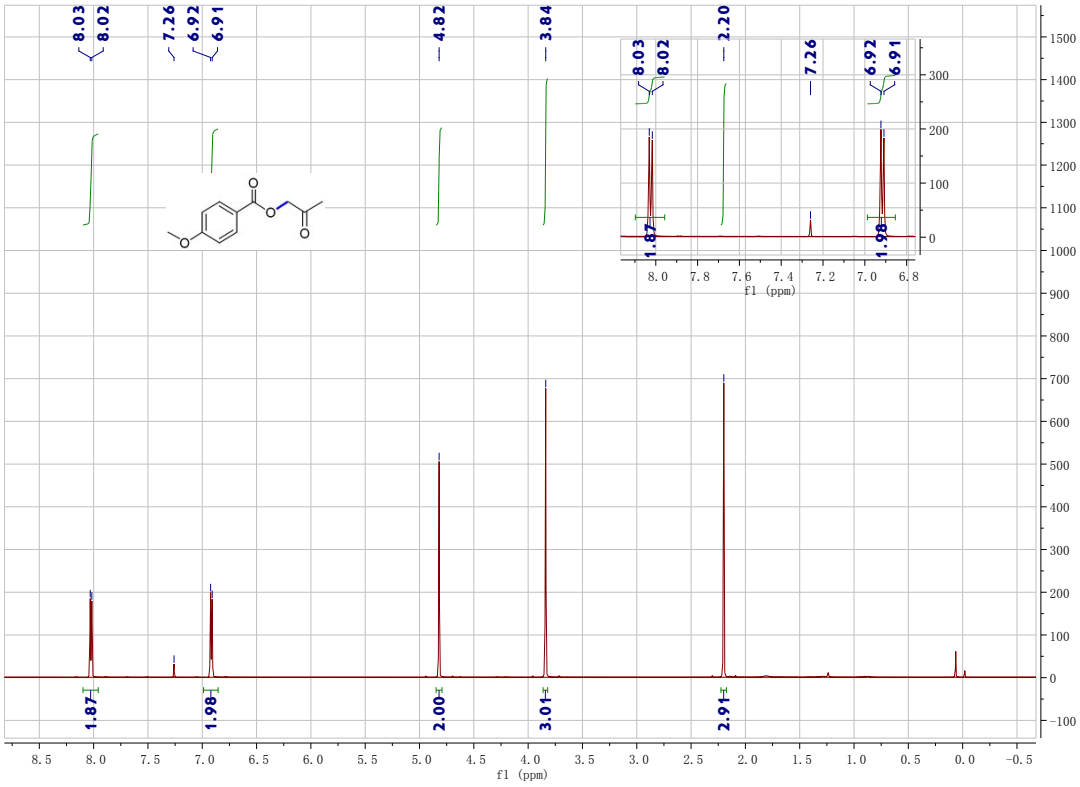
2-oxopropyl 4-(*tert*-butyl)benzoate (**3l**)

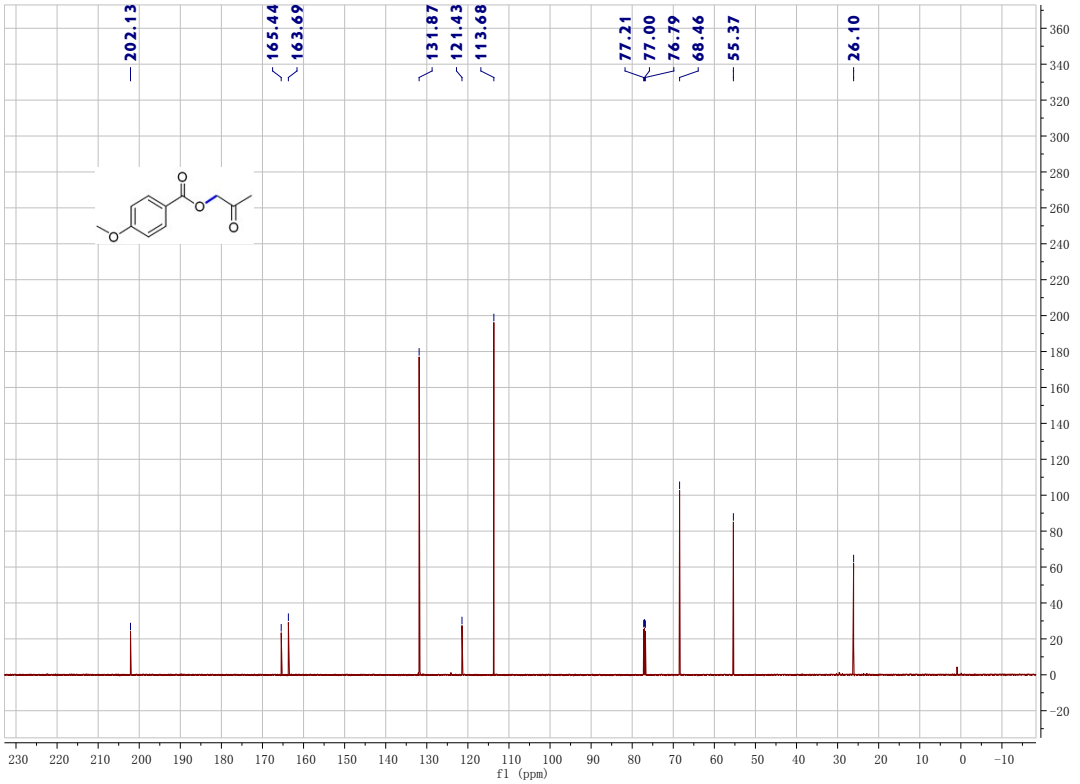


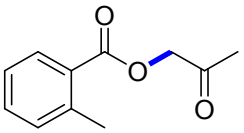




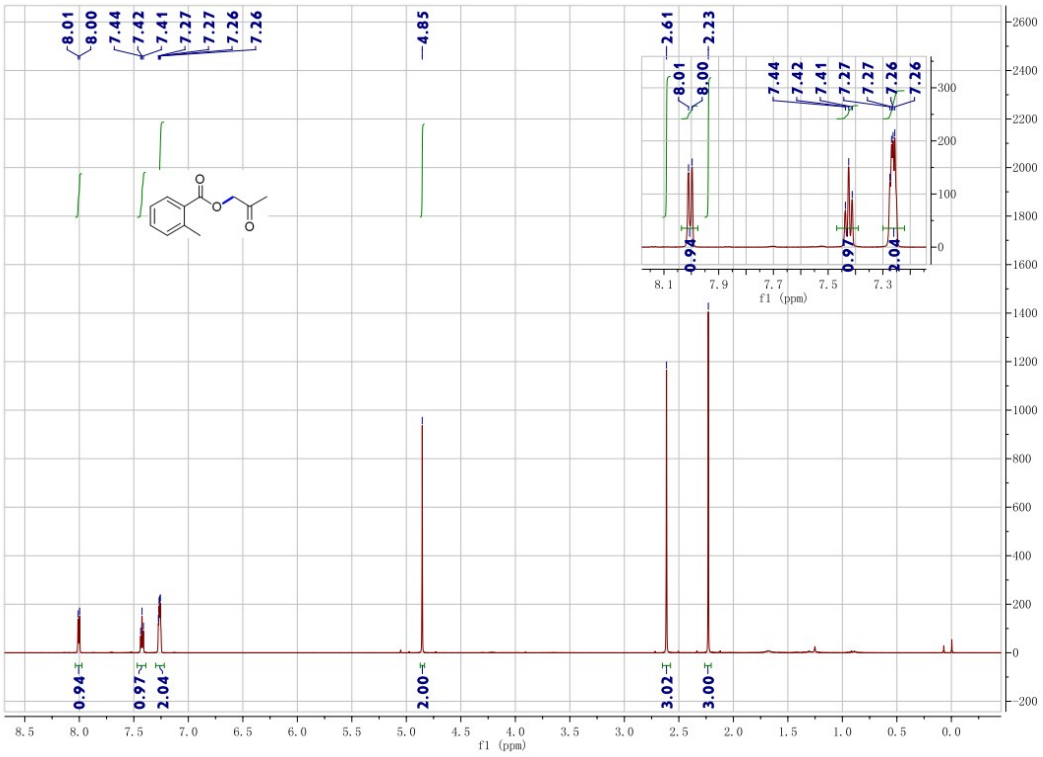
2-oxopropyl 4-methoxybenzoate (**3m**)

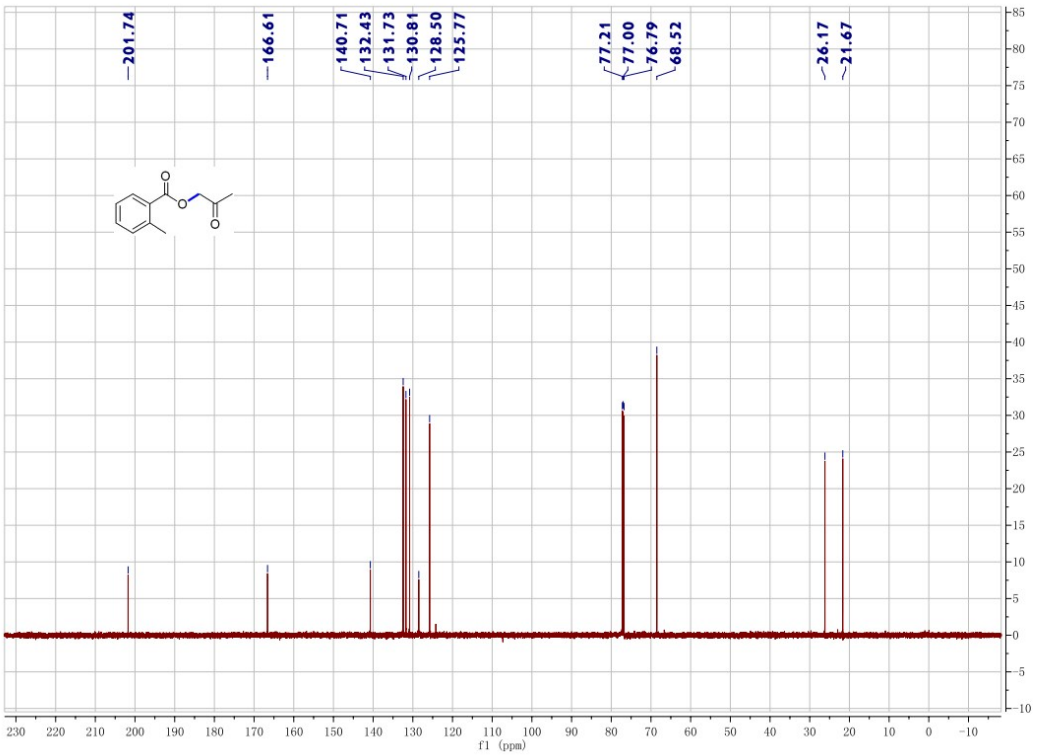


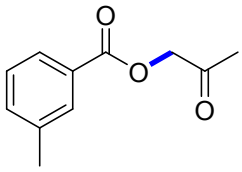




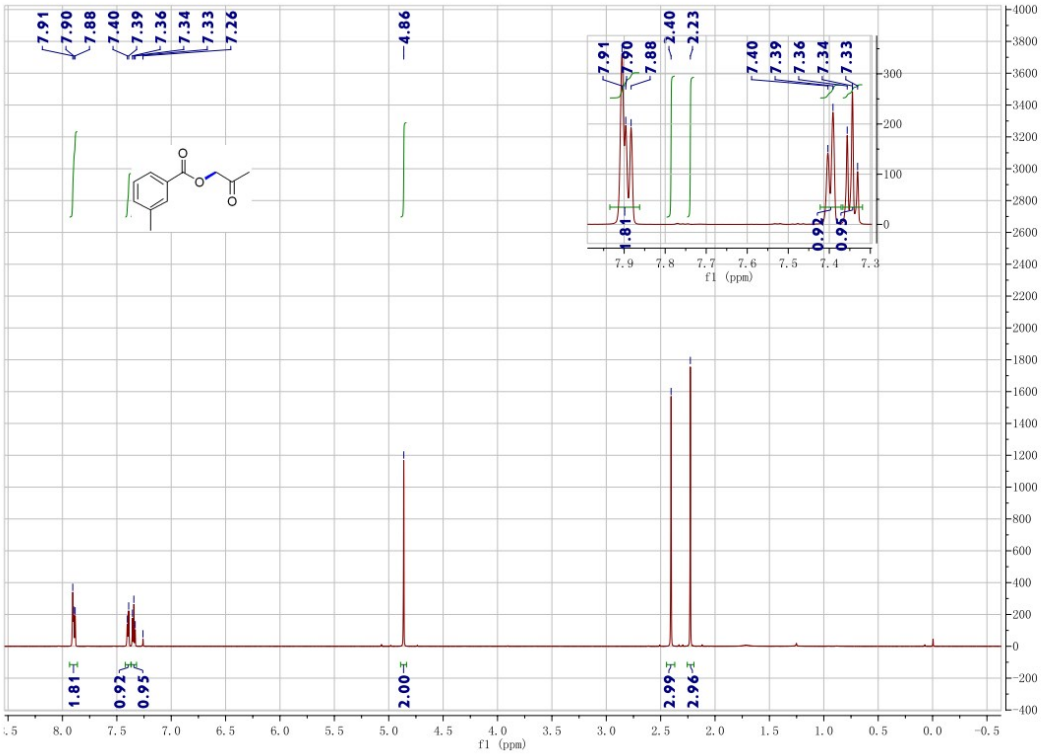
2-oxopropyl 2-methylbenzoate (**3n**)

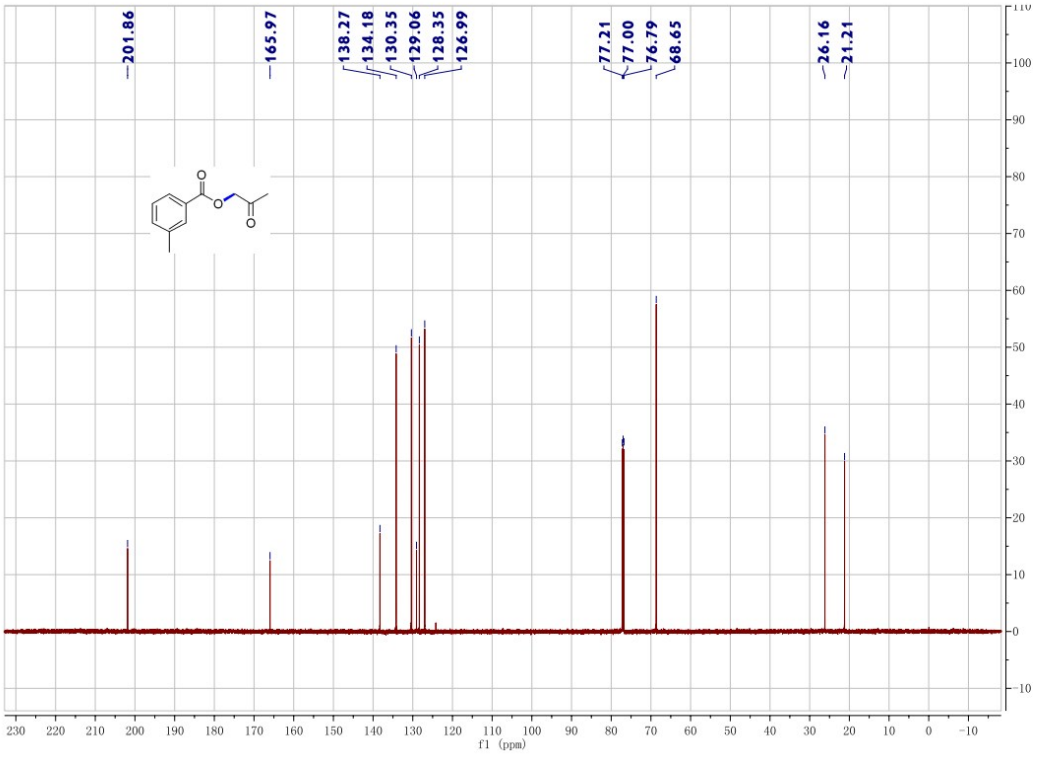


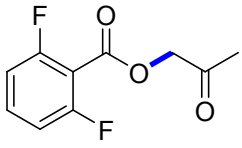




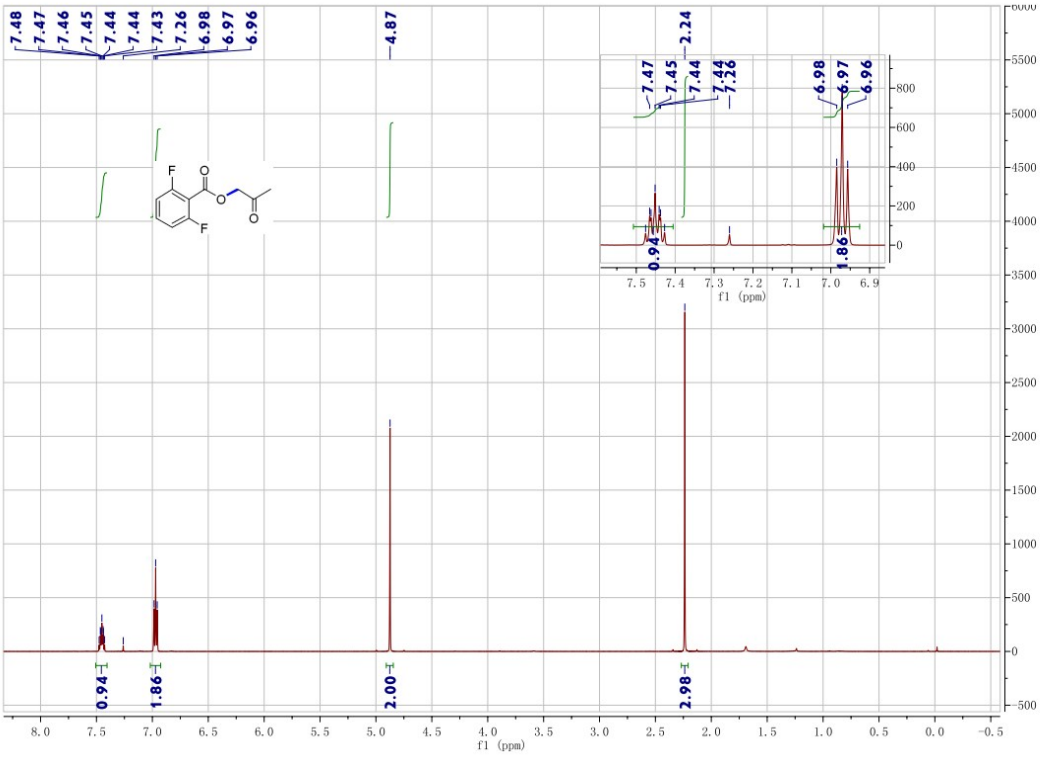
2-oxopropyl 3-methylbenzoate (**3o**)

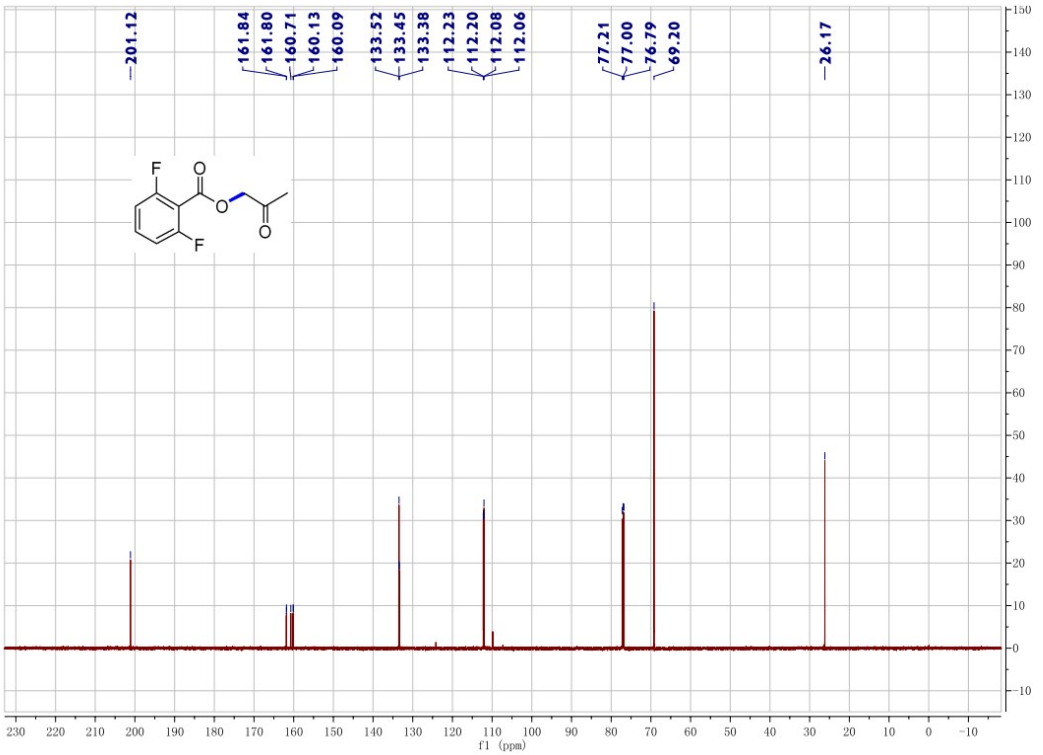


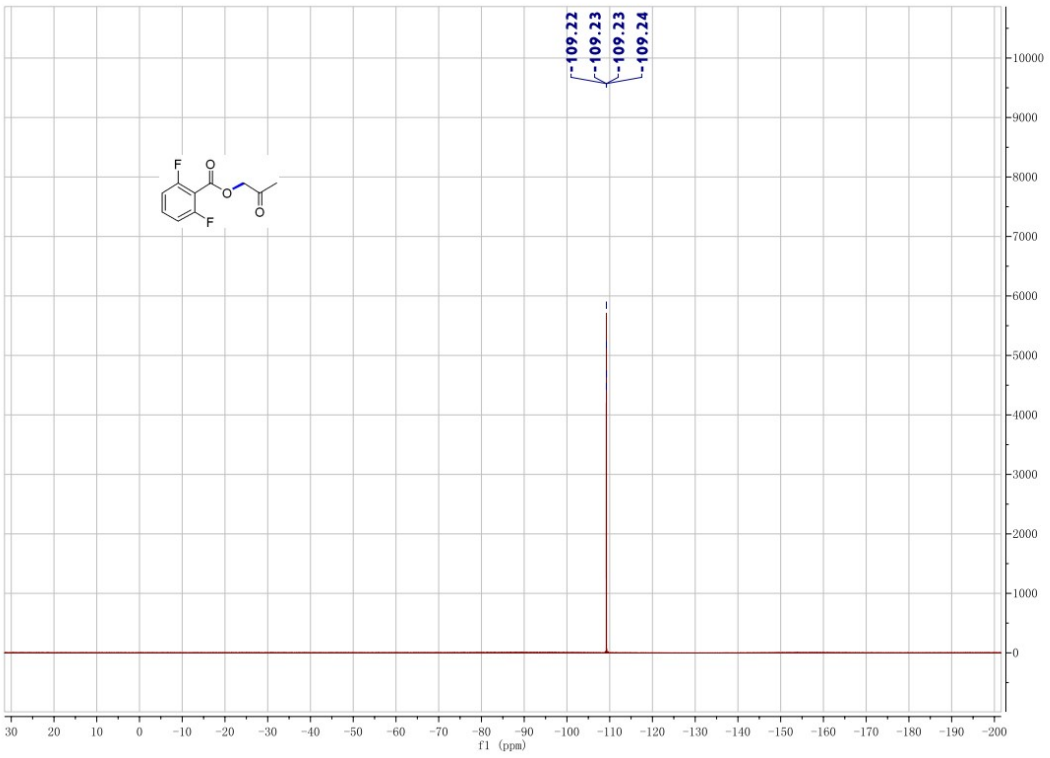




2-oxopropyl 2,6-difluorobenzoate (**3p**)



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-109.23
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F
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6000
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3000
2000
1000
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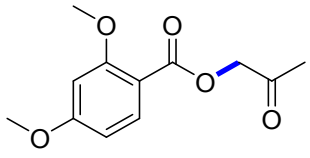
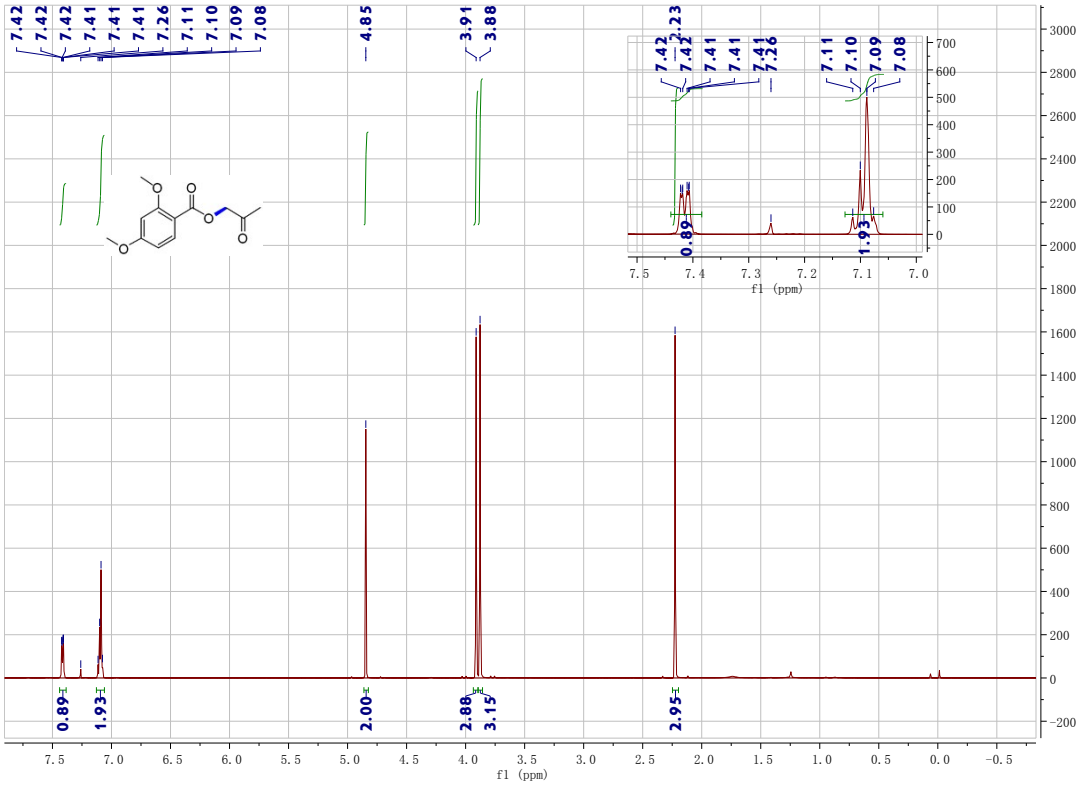
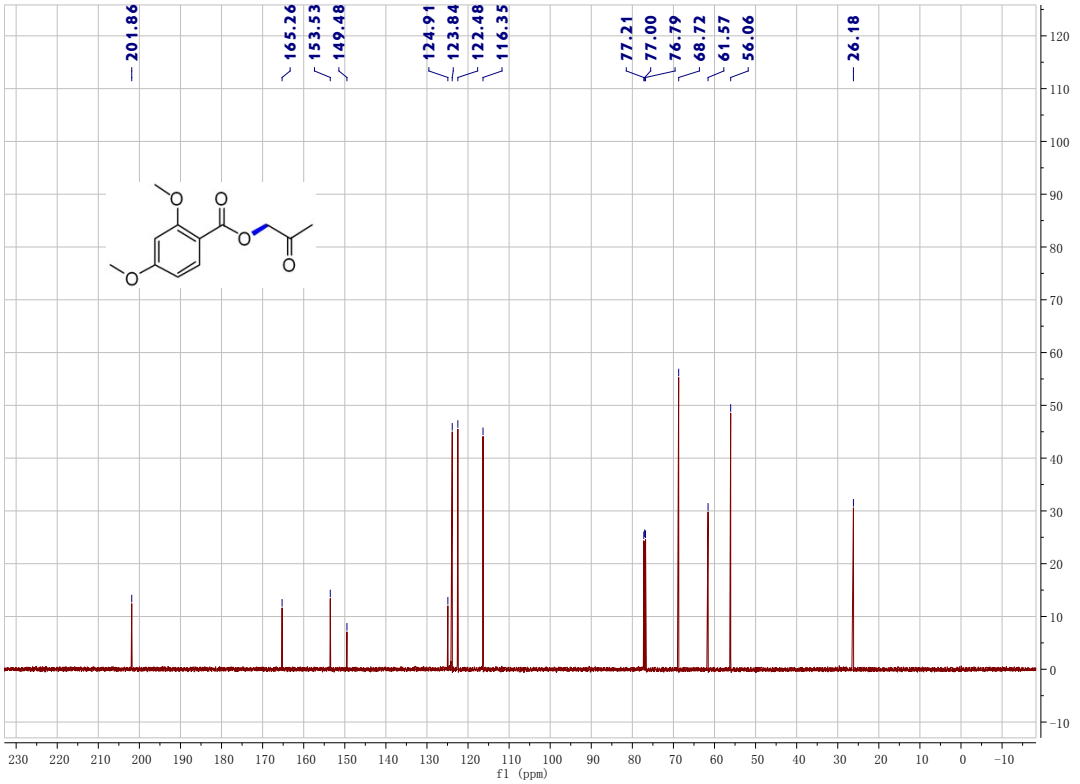
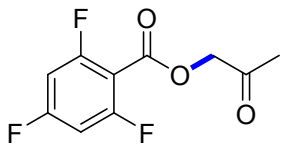
f1 (ppm)



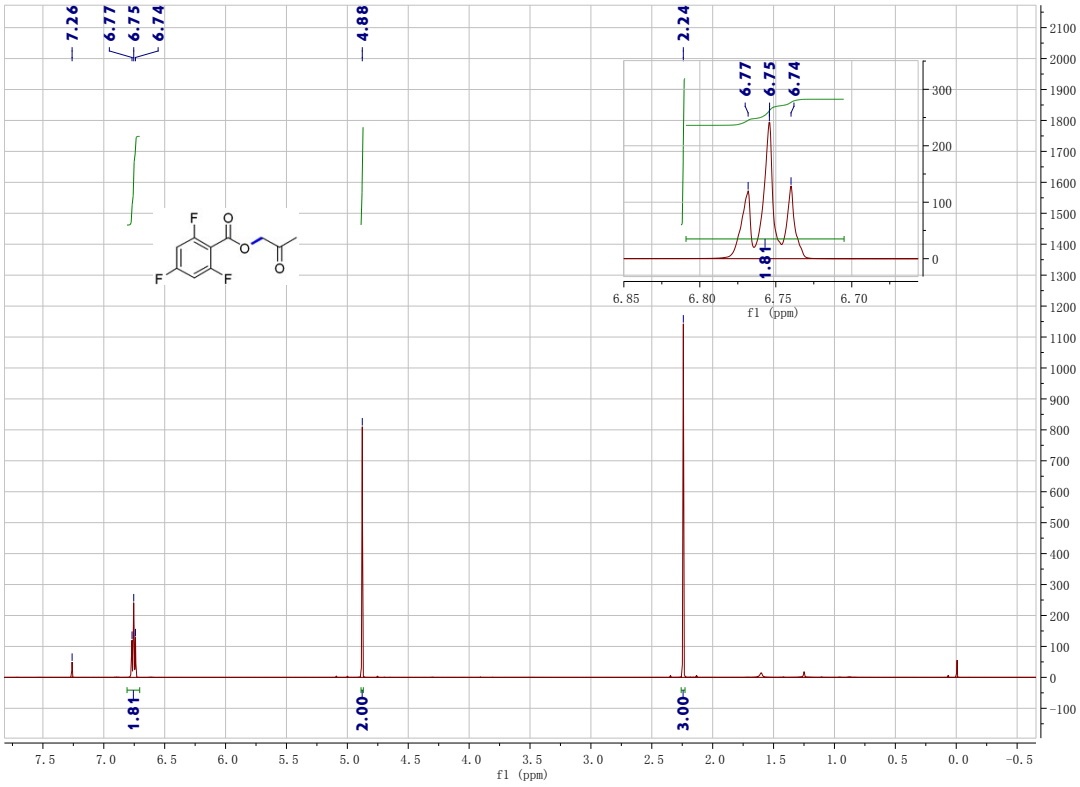
2-oxopropyl 2,4-dimethoxybenzoate (3q)

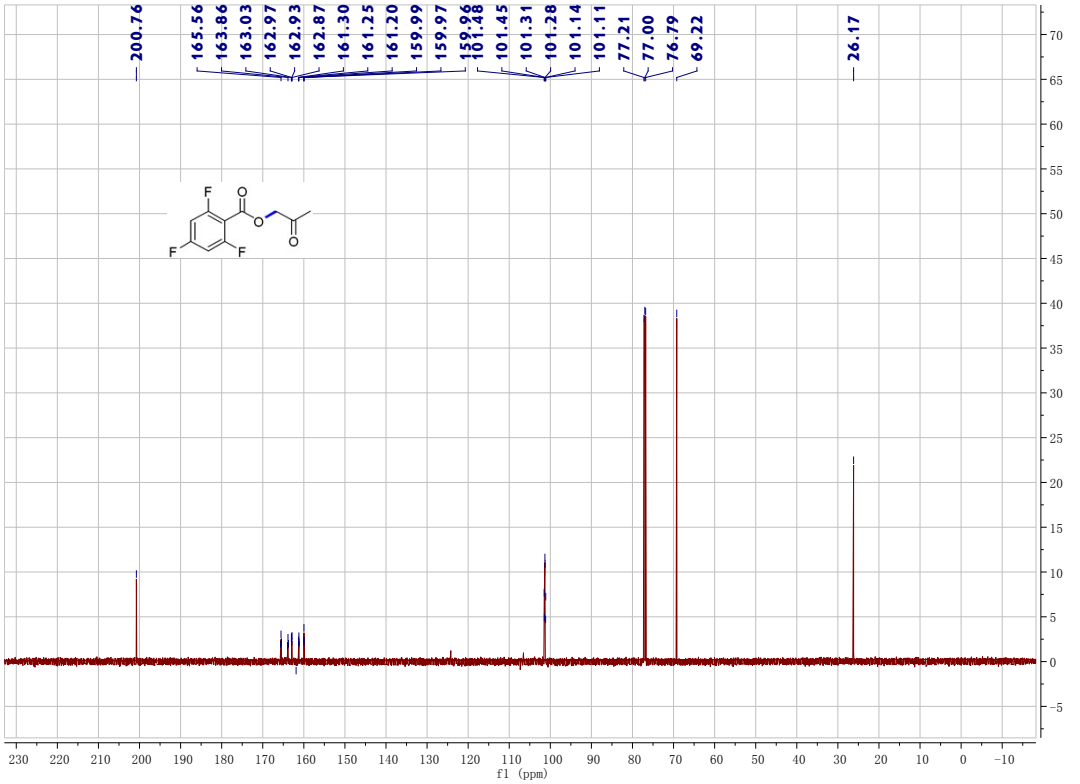


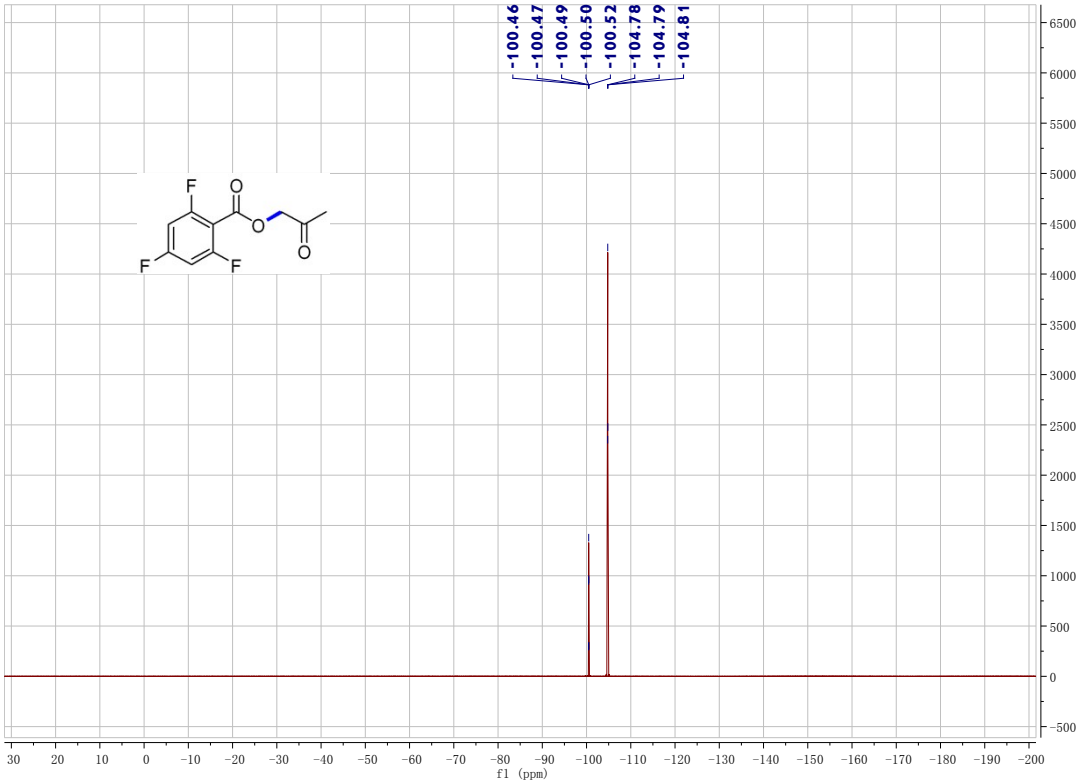




2-oxopropyl 2,4,6-trifluorobenzoate (**3r**)



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5000
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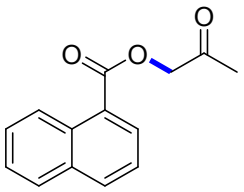
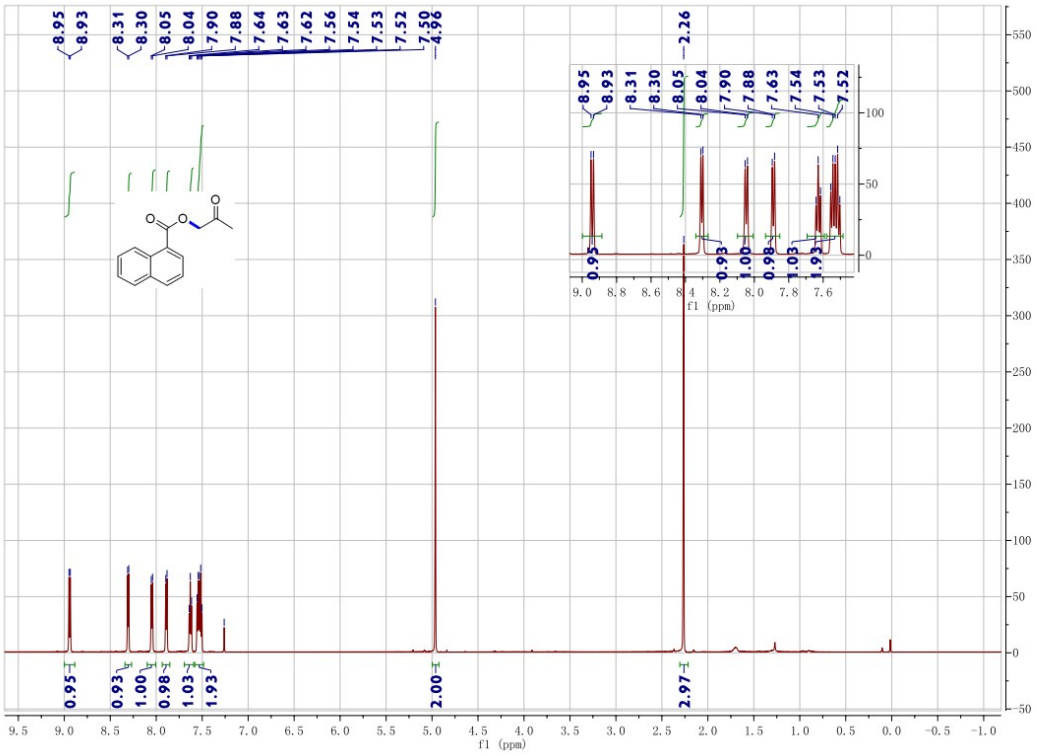
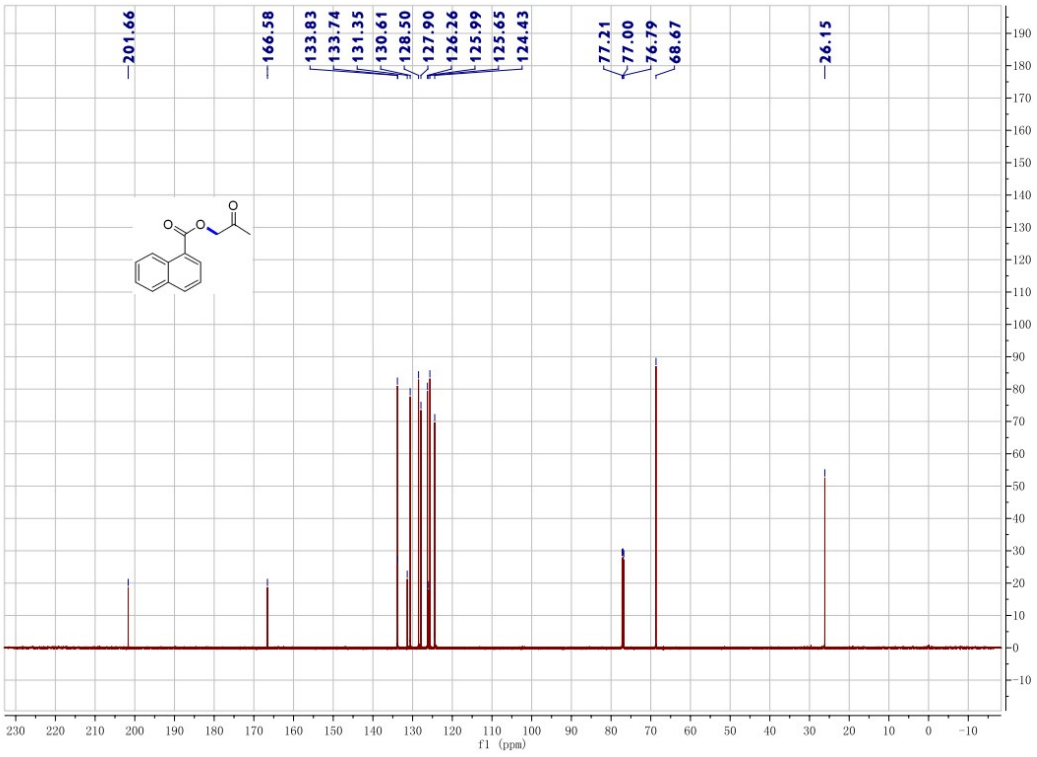
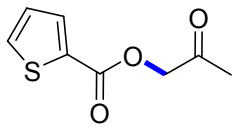
f1 (ppm)



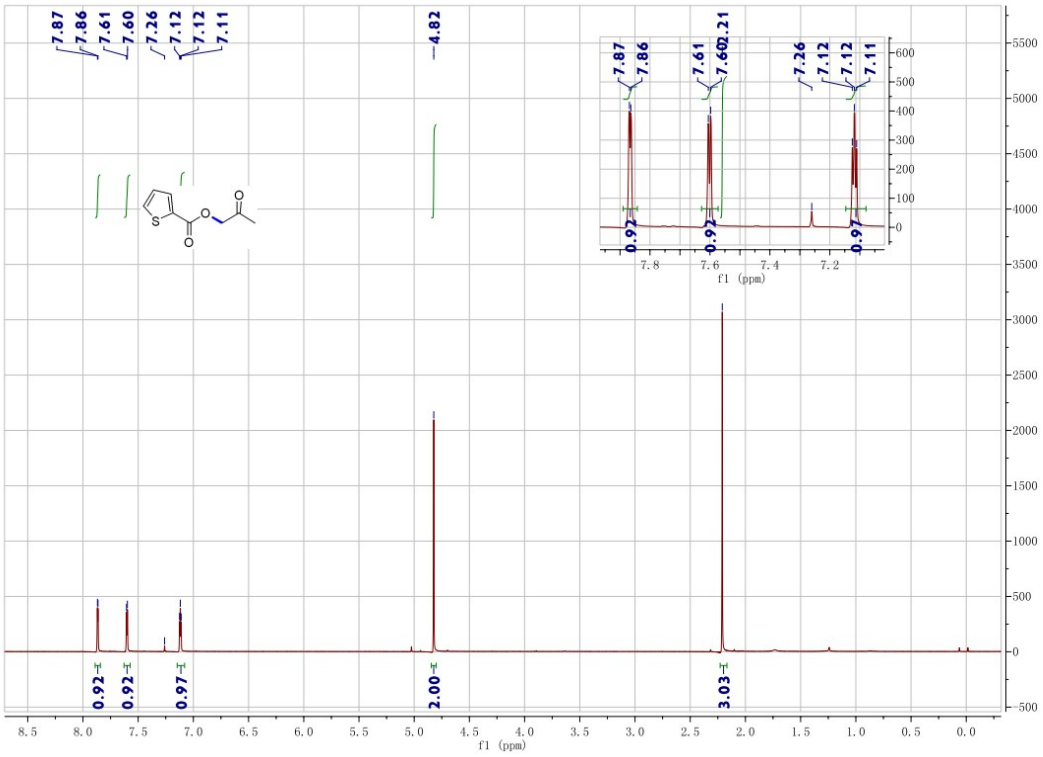
2-oxopropyl 1-naphthoate (**3s**)

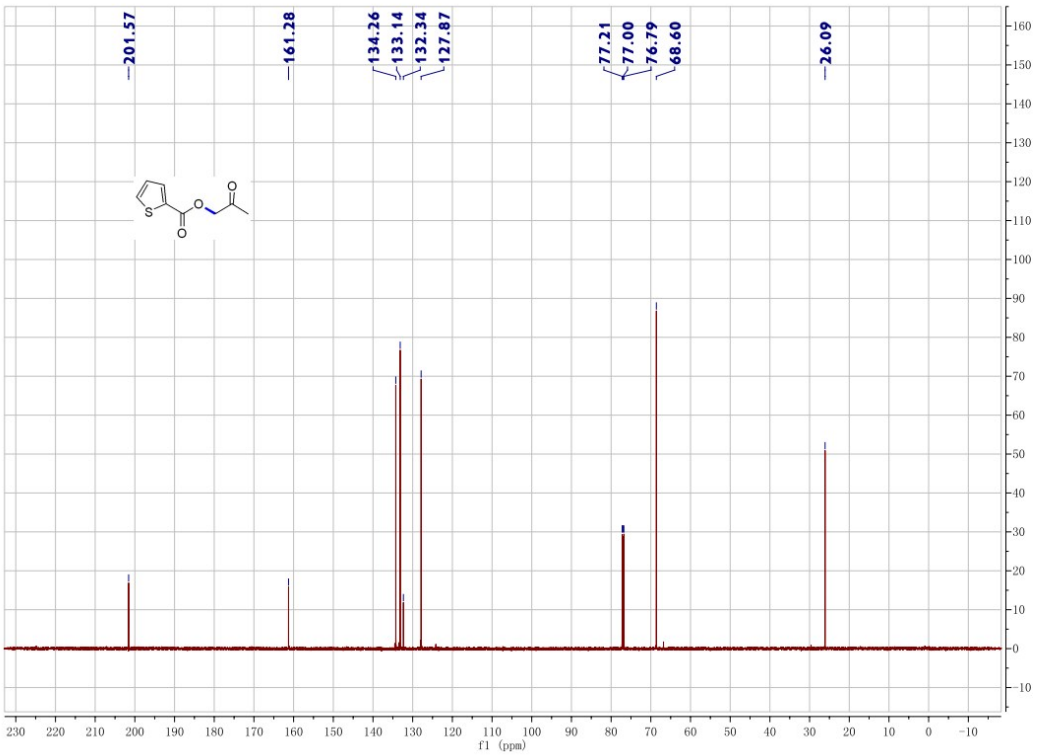


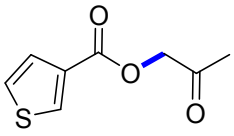




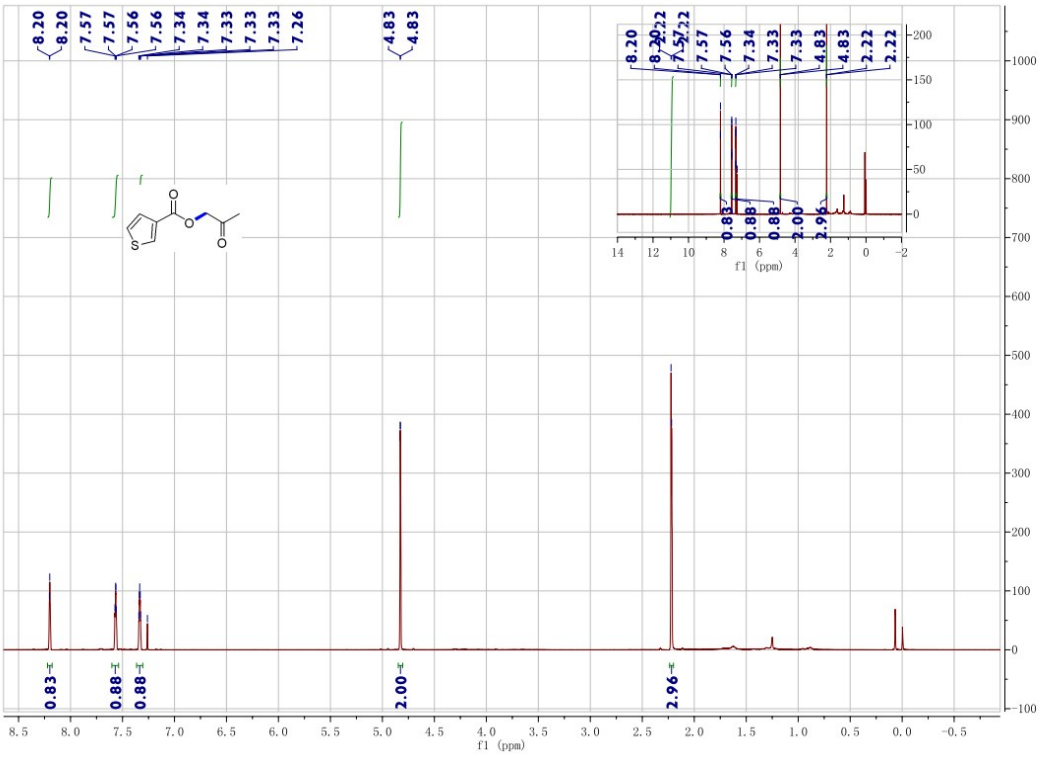
2-oxopropyl thiophene-2-carboxylate (**3t**)

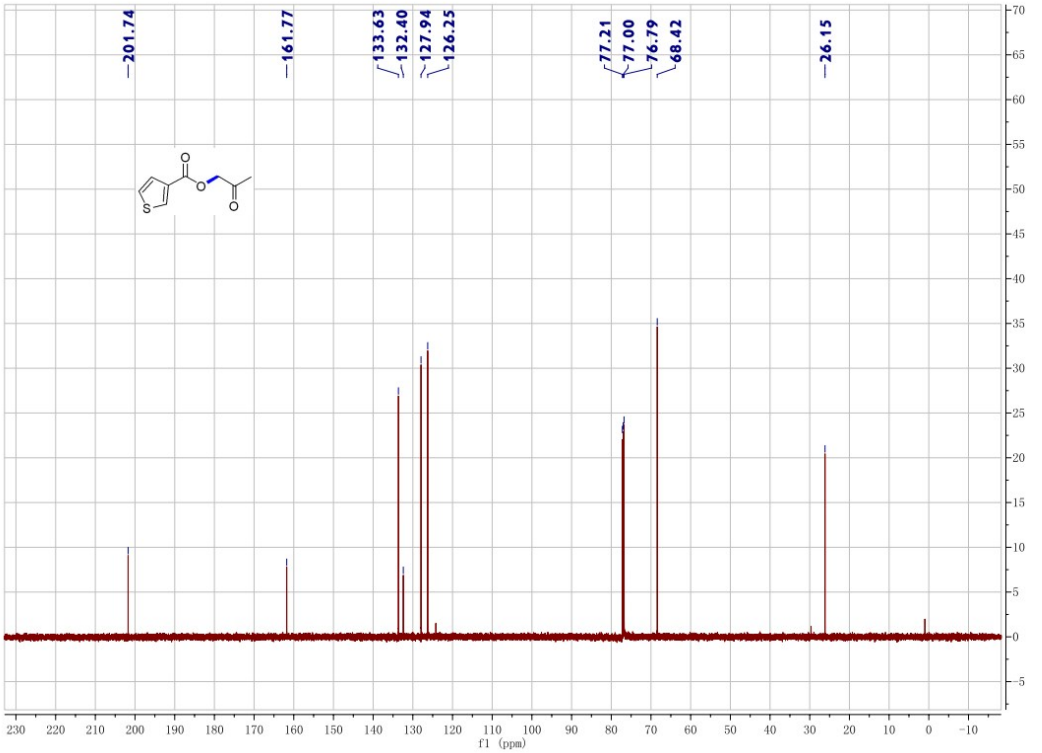


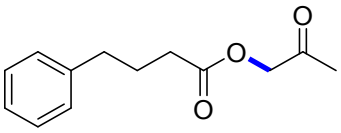




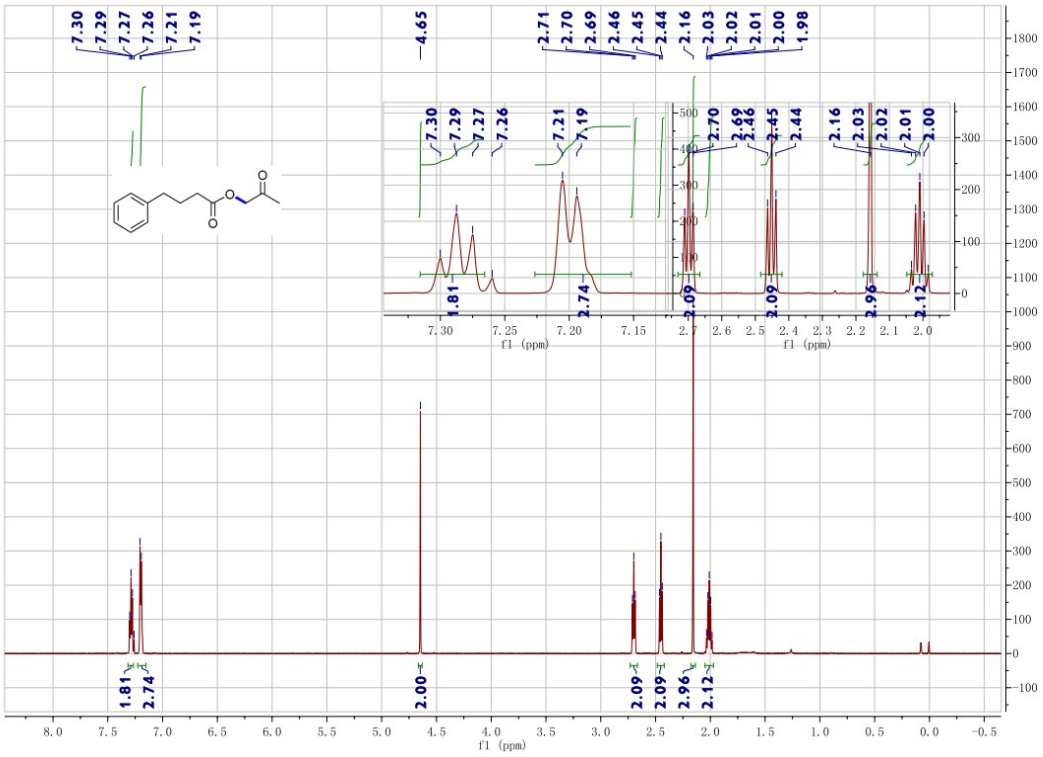
2-oxopropyl thiophene-3-carboxylate (**3u**)

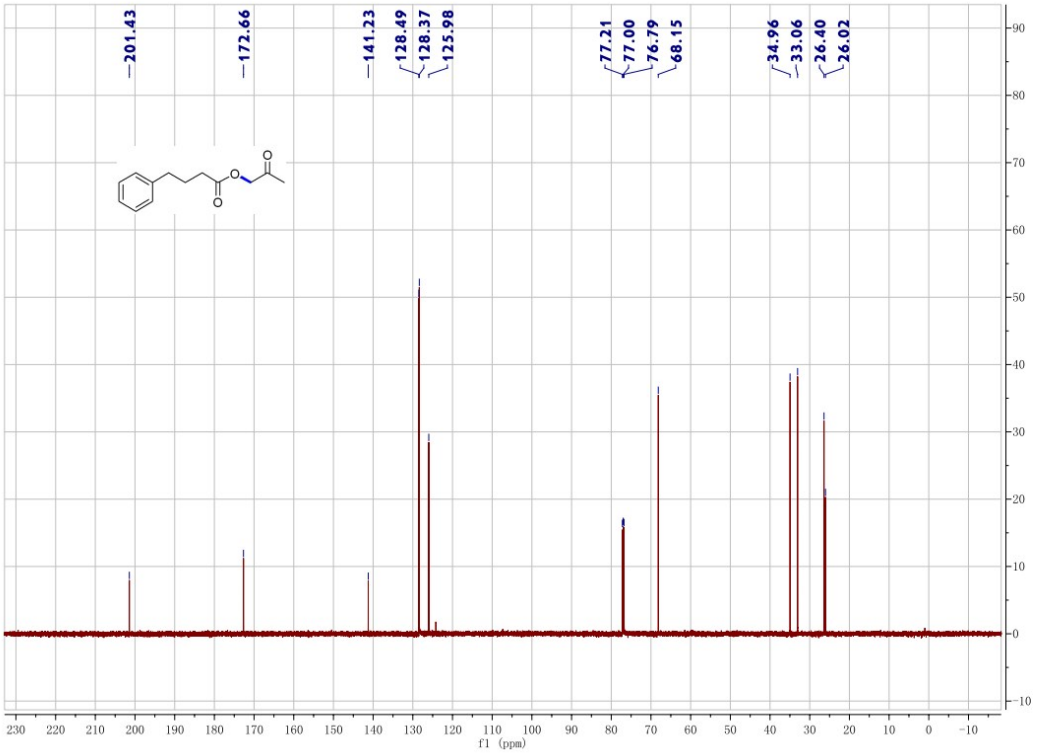


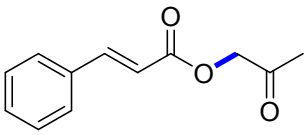




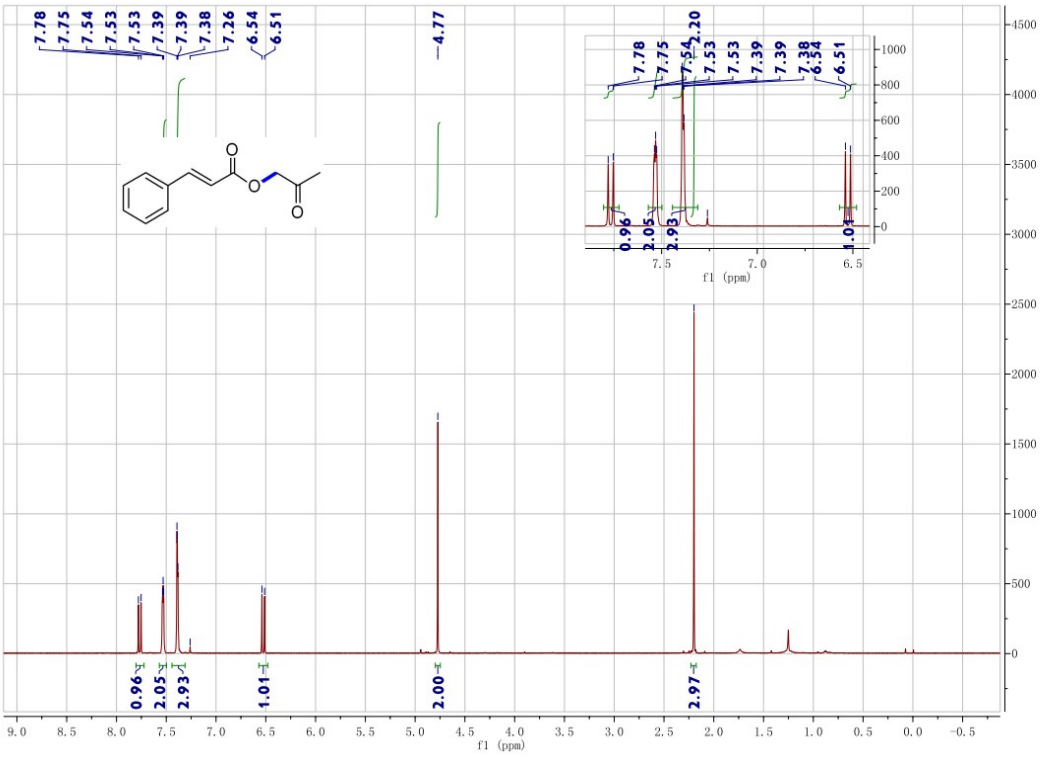
2-oxopropyl 4-phenylbutanoate (**5a**)

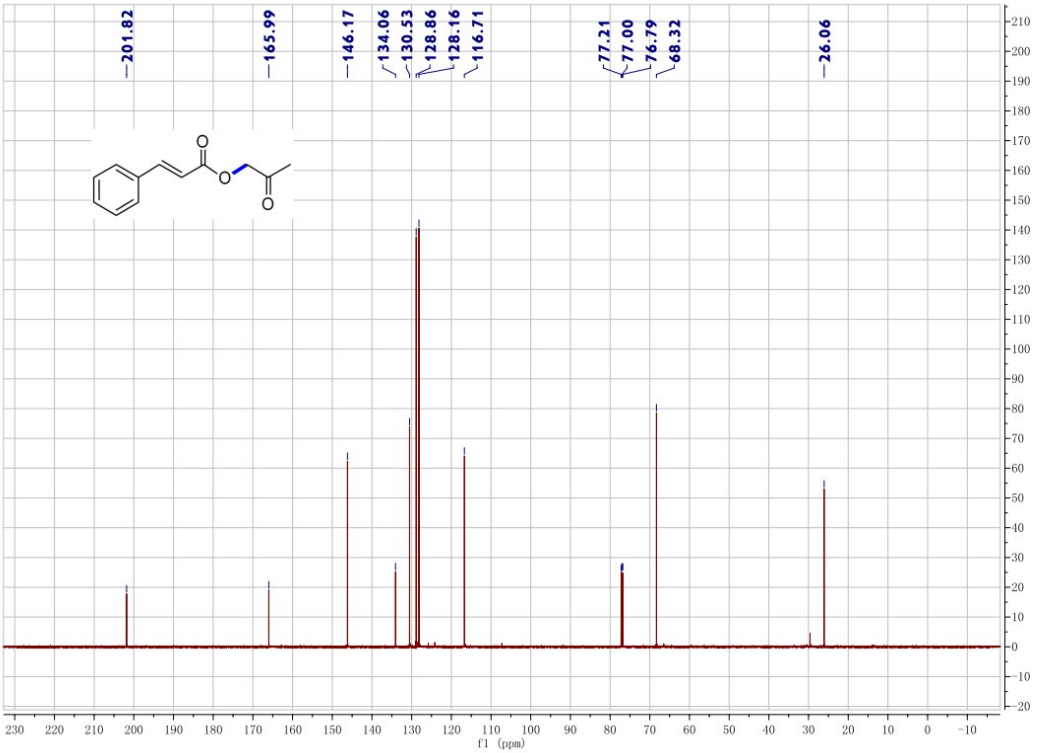


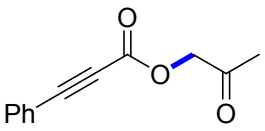




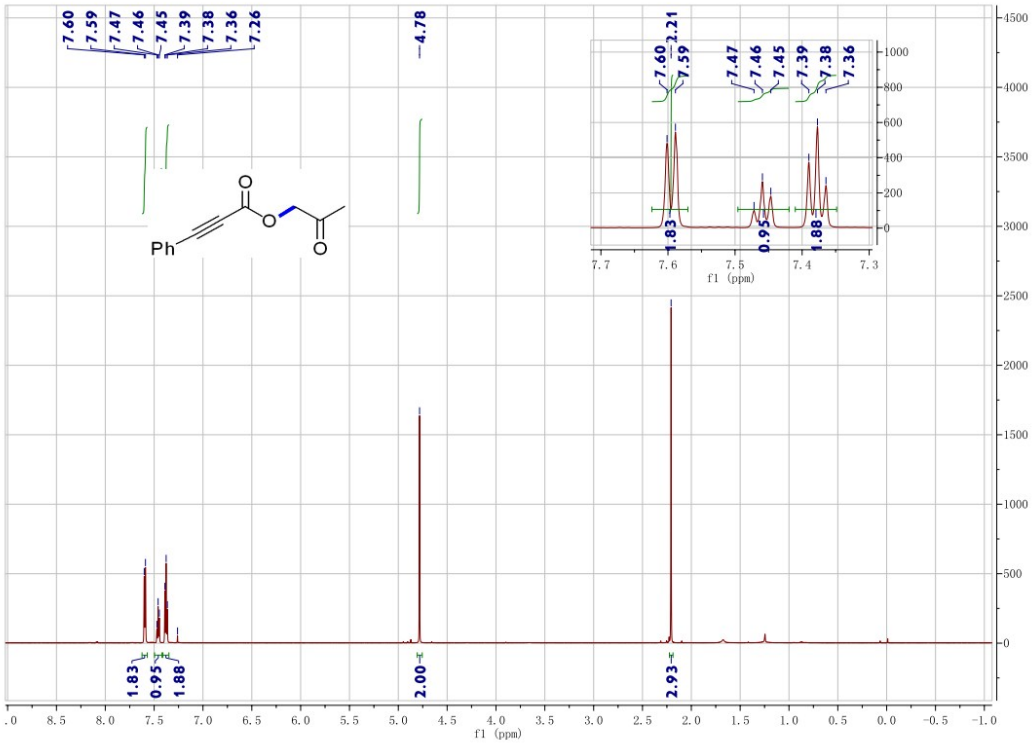
2-oxopropyl cinnamate (**5b**)

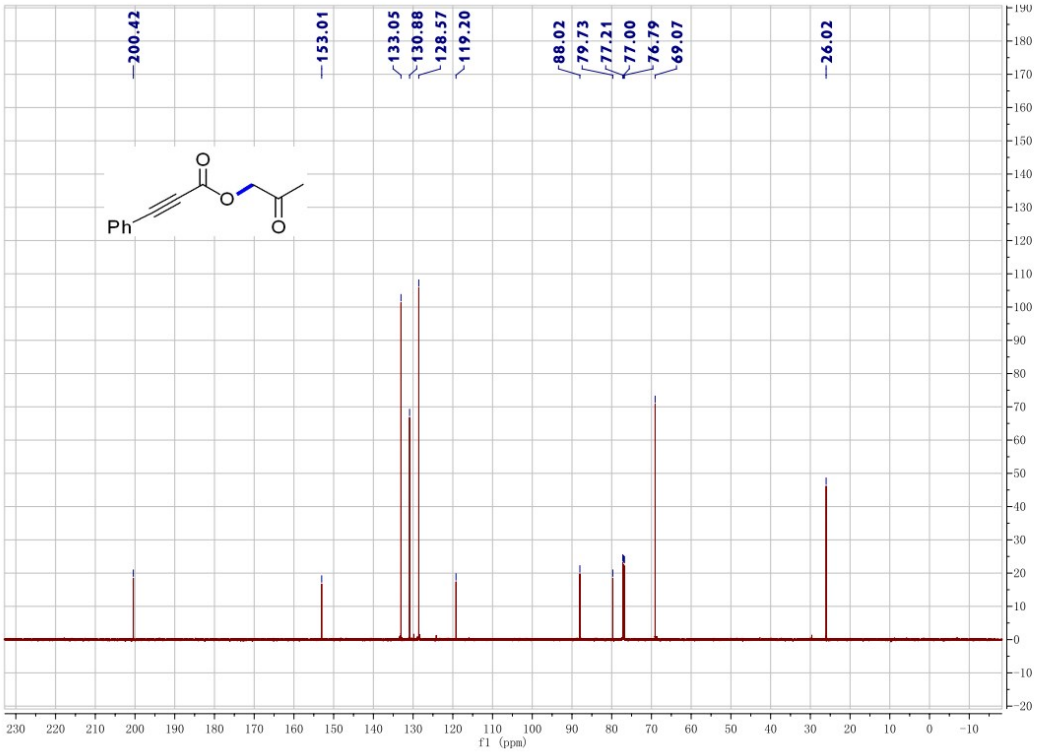


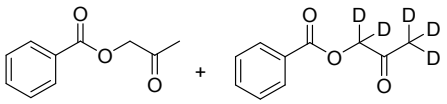




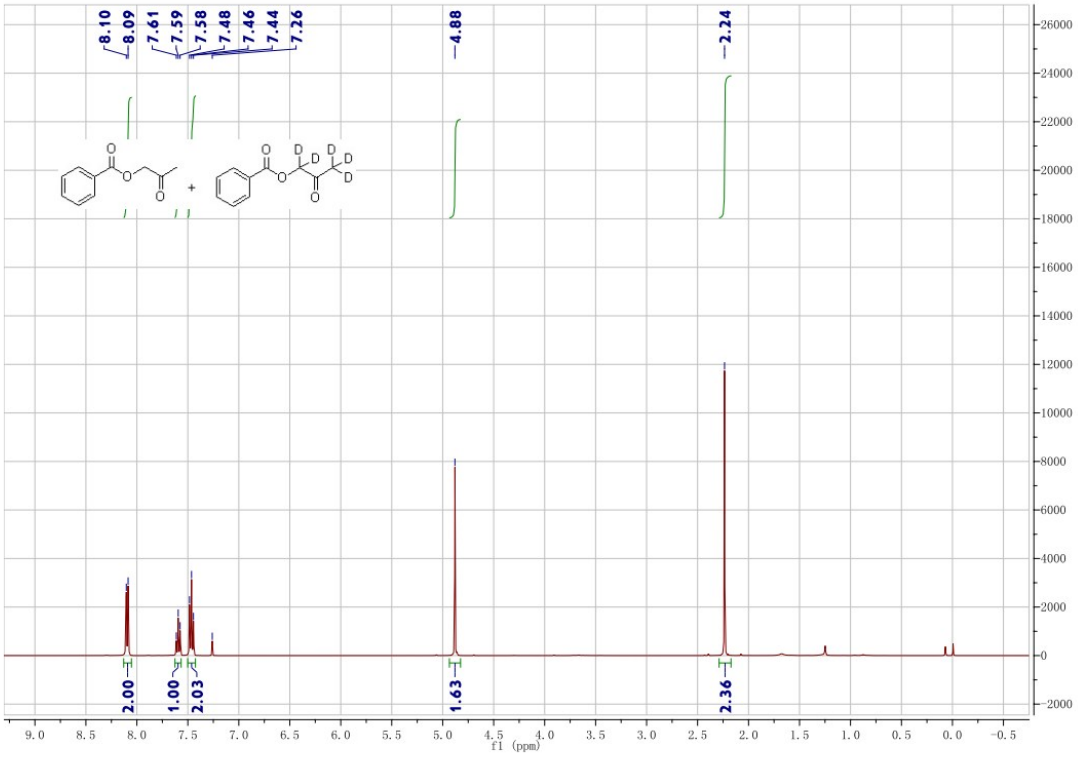
2-oxopropyl 3-phenylpropiolate (**5c**)







3a + **[D5]3a**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2.00
1.00
2.03
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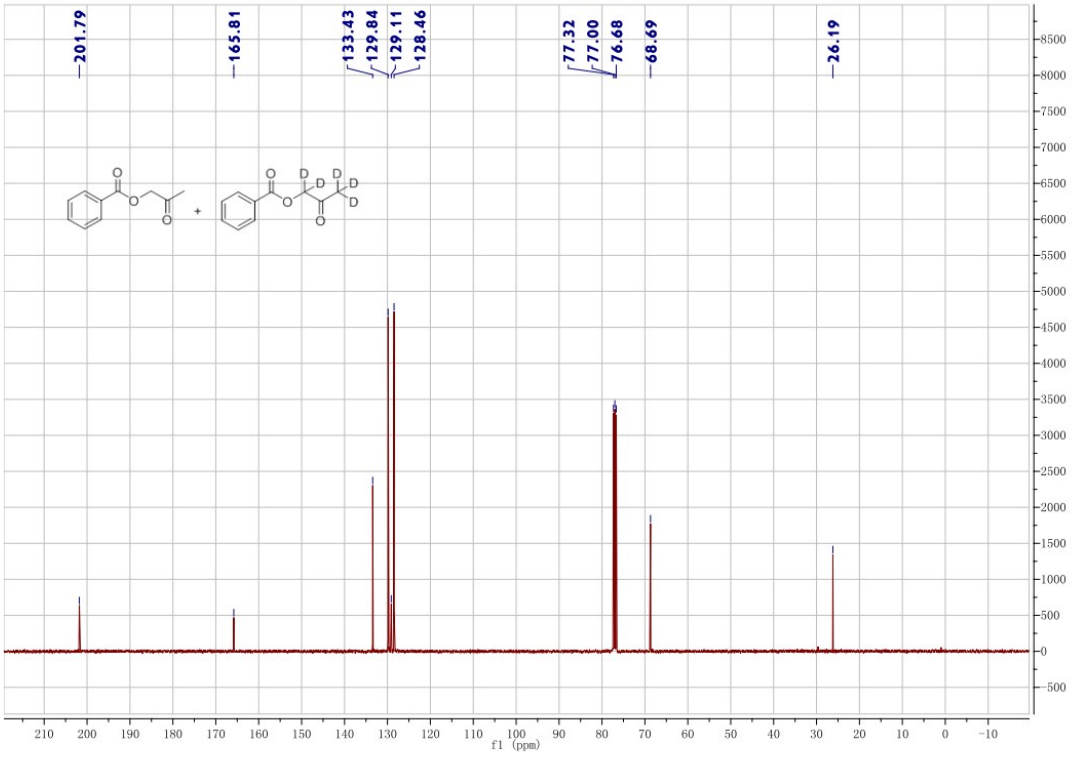
2.36
f1 (ppm)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77.00
76.68
68.69
26.19
f1 (ppm)