Supporting information

Metal-free oxidative esterification of acetophenones with alcohols: A facile one-pot approach to α-ketoesters

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General experimental

All general reagents and solvents were commercially available and used as received. ^{1}H and ^{13}C NMR spectra were measured on magnet system 400'54 ascend instrument purchased from Bruker Biospin AG. Chemical data for protons are reported in parts per million (ppm) downfield from tetramethylsilane and are referenced to the residual proton in the NMR solvent ($CDCl_3$, 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, p = penta, dd = doublet of doublets, dt = doublet of triplets, ddt = doublet of doublet of triplets, dtd = doublet of triplet of doublets, m = multiplet, br = broad), coupling constant (J) in Hertz (Hz), and integration. ^{13}C NMR were recorded at 125 MHz or 100 MHz and chemical data for carbons are reported in parts per million (ppm, δ scale) downfield from tetramethylsilane and are referenced to the carbon resonance of the solvent. Column chromatography was generally performed on Silicycle silica gel (200-300 mesh). Analytical thin-layer chromatography (TLC) was performed on 0.2 mm coated silica gel plates (HSGF 254) and visualized the course of the reactions using a UV light (254 nm or 365 nm).

Experimental procedures for synthesis of α-ketoesters

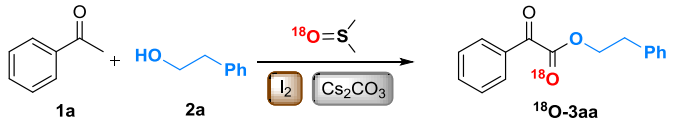
Acetophenones **1** (0.5 mmol), alcohols **2** (1.5 mmol), iodine (0.317 g, 1.25 mmol) and Cs_2CO_3 (0.407 g, 1.25 mmol) were dissolved in 3 ml of DMSO and stirred at 110℃ for 24h in the sealed tube. To determine the status of the reaction, it was monitored by TLC. After its completion, reaction mixture was cooled to room temperature then quenched with saturated $Na_2S_2O_3$ solution and extracted with ethyl acetate. Organic layer was washed with brine solution and dried over Na_2SO_4. Removal of the organic solvent in a vacuum rotavaper followed by flash silica gel column chromatographic purification (hexane/ethyl acetate 50:1) afforded the desired product **3** in good yields (60-89%).

Screening the equivalent of alcohols

Entry	Promoter(equiv.)	Base(equiv.)	Oxidant	Solvent	Alcohol(equiv.)	Temp(℃)	Yield(%)[b]
1	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	1.0	110	<20
2	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	1.5	110	47
3	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	2.0	110	70
4	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	2.5	110	83
5	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	3.0	110	89
6	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	3.5	110	84
7	I_2 (2.5)	Cs_2CO_3 (2.5)	DMSO	-	4.0	110	83

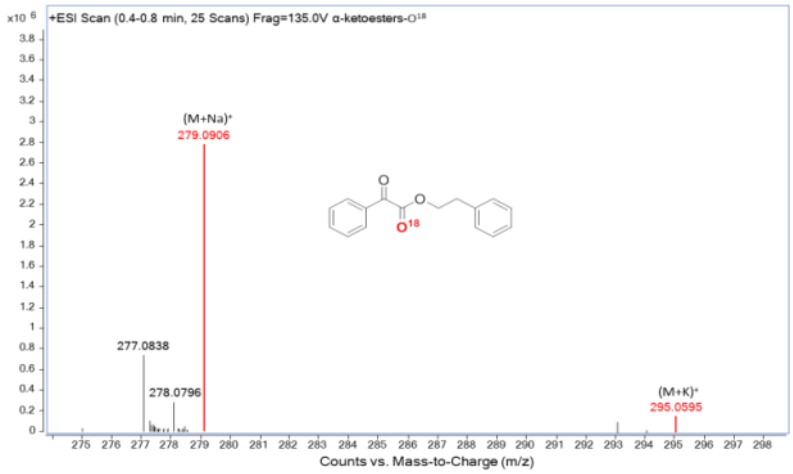
[a] Reaction conditions: 1a (0.5 mmol), 2a (1.5 mmol), promoter (2.5 equiv.), base (2.5 equiv.) were solved in 3 mL DMSO and stirred at 110℃ for 24h in the sealed tube. [b] Yields of the isolated product.

^{18}O Labeling experiment



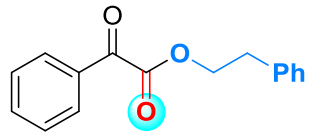
Method for preparation of ^{18}O-labeled DMSO:[1]

Solid dimethylsulfur dibromide (5.0 g, 22.5 mmoles) prepared as per known procedure[1] was added portionwise over 15 min to a vigorously stirred solution of triethylamine (6.3 ml, 45 mmoles, freshly distilled from potassium hydroxide) and ^{18}O-labeled water (0.20 ml, 11 mmoles) in 15 ml of tetrahydrofuran (freshly distilled from lithium aluminum hydride). The temperature of the reaction was maintained below 50℃ by occasional cooling in ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were distilled at room temperature (15 mm) to remove the solvent and the tan residue was distilled in a short-path apparatus (60-70℃ at 0.3 mm) giving 1.03 g of a pale yellow liquid. Without further purification the reaction was performed between acetophenones **1a** (60 mg, 0.5 mmol) and 2-phenylethanol **2a** (183 mg, 1.5 mmol) as per optimized procedure. After the reaction was completed, corresponding **^{18}O-3aa** product was obtained by column chromatography, which was analyzed by ESI-MS analysis. The results clearly assigned the presence of the signal $[M+Na]^+$ and $[M+K]^+$ at 279.0906 and 295.0595 (2 more than the one of **^{16}O-3aa** product) in noticeable detection (Scheme 1).



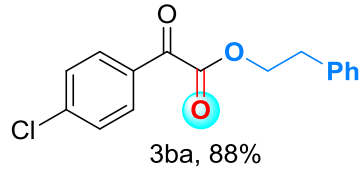
Scheme 1

Analytical data of α-ketoesters



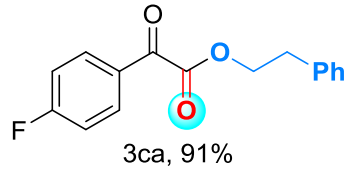
3aa, 89%

Product 3aa:[2] Light yellow oil (3aa, 113 mg, 89% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 1.2 Hz, 2H), 7.58 – 7.53 (m, 1H), 7.40 – 7.35 (m, 2H), 7.26 – 7.16 (m, 5H), 4.54 (t, *J* = 7.0 Hz, 2H), 3.01 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.41, 163.84, 137.06, 135.01, 132.41, 130.15, 129.14, 128.97, 128.81, 126.99, 66.54, 35.05; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{14}O_3$ 277.0835 found 277.0886.



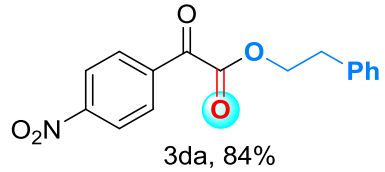
3ba, 88%

Product 3ba:[2] Light yellow oil (3ba, 124 mg, 91% yield); ^{1}H NMR (400 MHz, CDCl3) δ 7.80 (dd, J = 8.9, 5.4 Hz, 2H), 7.22 (dt, J = 23.2, 7.5 Hz, 5H), 7.03 (t, J = 8.6 Hz, 2H), 4.54 (t, J = 6.9 Hz, 2H), 3.01 (t, J = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 184.93, 163.23, 141.70, 136.99, 131.53, 130.83, 129.37, 129.14, 128.83, 127.03, 66.67, 35.01; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}O_3Cl$ 311.0445 found 311.0477.



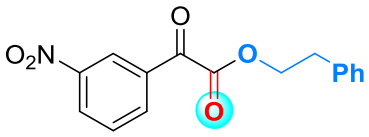
3ca, 91%

Product 3ca:[2] Light yellow oil (3ca, 124 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (dd, *J* = 8.9, 5.4 Hz, 2H), 7.28 – 7.17 (m, 5H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.55 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 184.60, 168.17, 165.61, 163.45, 137.04, 133.14 , 133.04, 129.16, 128.85, 127.04, 116.46, 116.24, 66.63, 35.05; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}O_3F$ 295.0741 found 295.0742.



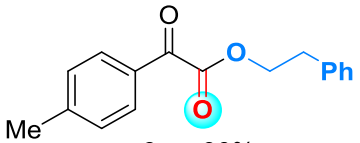
3da, 84%

Product 3da: Light yellow wax (3da, 126 mg, 84% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.13 (m, 2H), 8.13 – 8.02 (m, 2H), 7.28 – 7.17 (m, 5H), 4.51 (t, *J* = 6.9 Hz, 2H), 3.03 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 164.72, 150.64, 137.56, 135.76, 130.81, 129.04, 128.79, 126.94, 123.68, 66.45, 35.23; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}NO_5$ 322.0686 found 322.0691.



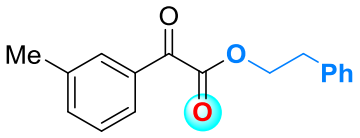
3ea, 81%

Product 3ea: Light yellow oil (3ea, 125 mg, 81% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 – 8.64 (m, 1H), 8.33 (ddd, *J* = 8.2, 2.2, 1.0 Hz, 1H), 8.28 – 8.18 (m, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.29 – 7.16 (m, 5H), 4.51 (t, *J* = 7.0 Hz, 2H), 3.04 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, CDCl3) δ 164.47, 148.36, 132.12, 129.75, 129.07, 128.78, 127.50, 126.92, 124.70, 66.43, 35.24; HRMS (TOF) m/z [M + Na]$^{+}$ Calcd for $C_{16}H_{13}NO_5$ 322.0686 found 322.0677.



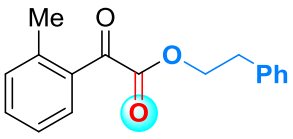
3ga, 90%

Product 3ga: Light yellow oil (3ga, 120.65 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.1 Hz, 2H), 7.24 – 7.14 (m, 7H), 4.51 (t, *J* = 6.9 Hz, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 2.33 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.04, 164.02, 146.32, 137.09, 130.24, 129.67, 129.10, 128.76, 126.93, 66.40, 35.03, 22.00; HRMS (TOF) m/z [M + Na]$^{+}$ Calcd for $C_{17}H_{16}O_3$ 291.0992 found 291.0988.



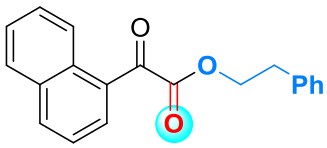
3ha, 93%

Product 3ha: Light yellow oil (3ha, 124.76 mg, 93% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.51 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.13 (m, 6H), 4.52 (t, *J* = 7.0 Hz, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.54, 163.91, 138.82, 137.00, 135.77, 132.36, 130.27, 129.01, 128.76, 128.69, 127.41, 126.87, 66.38, 34.97, 21.27; HRMS (TOF) m/z [M + Na]$^{+}$ Calcd for $C_{17}H_{16}O_3$ 291.0992 found 291.0998.



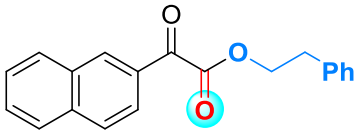
3ia, 91%

Product 3ia: Light yellow oil (3ia, 122.08 mg, 91% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (t, *J* = 8.1 Hz, 2H), 7.27-7.09 (m, 7H), 4.52 (t, *J* = 7.0 Hz, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.70, 164.61, 141.47, 137.10, 133.77, 132.50, 132.41, 131.15, 129.11, 128.77, 126.95, 126.02, 66.46, 35.03, 21.58; HRMS (TOF) m/z [M + Na]$^{+}$ Calcd for $C_{17}H_{16}O_3$ 291.0992 found 291.1016.



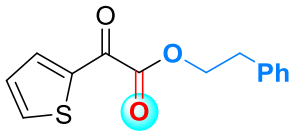
3ja, 90%

Product 3ja:[2] Light yellow wax (3ja, 136.96 mg, 90% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.95 (d, *J* = 8.6 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.59 (t, *J* = 7.3 Hz, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.34 (t, *J* = 7.7 Hz, 1H), 7.25 – 7.15 (m, 5H), 4.57 (t, *J* = 6.9 Hz, 2H), 3.02 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 188.79, 164.61, 137.18, 135.90, 134.28, 134.01, 131.06, 129.39, 129.17, 128.86, 128.81, 128.12, 127.15, 127.98, 125.73, 124.44, 66.54, 35.10; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{16}O_3$ 327.0992 found 327.1013.



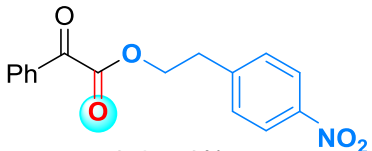
3ka, 82%

Product 3ka:[2] Light yellow oil (3ka, 124.78 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (s, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.83 – 7.75 (m, 3H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.26-7.15 (m, 5H), 4.59 (t, *J* = 7.0 Hz, 2H), 3.04 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.31, 163.94, 137.17, 136.49, 133.65, 132.36, 130.18, 129.84, 129.69, 129.15, 128.83, 128.02, 127.22, 127.02, 124.06, 66.62, 35.12; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{16}O_3$ 327.0992 found 327.1008.



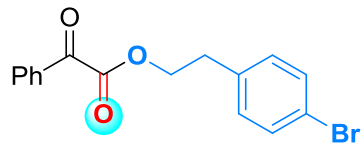
3la, 65%

Product 3la: Light yellow oil (3la, 84.60 mg, 65% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.26 – 7.14 (m, 5H), 7.06 (t, *J* = 4.4 Hz, 1H), 4.50 (t, *J* = 7.1 Hz, 2H), 3.02 (t, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.41, 161.69, 139.19, 137.55, 137.39, 137.02, 129.12, 128.80, 128.77, 126.99, 67.03, 34.98; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{14}H_{12}O_3S$ 283.0399 found 283.0391.



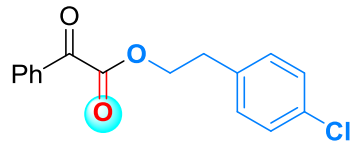
3ab, 70%

Product 3ab: Light yellow wax (3ab, 104.75 mg, 70% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.6 Hz, 2H), 7.88 (d, *J* = 8.1 Hz, 2H), 7.66 (t, *J* = 7.9 Hz, 1H), 7.46 (dd, *J* = 17.2, 8.2 Hz, 4H), 4.65 (t, *J* = 6.6 Hz, 2H), 3.21 (t, *J* = 6.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.90, 163.51, 147.22, 144.89, 135.23, 132.30, 130.05, 129.02, 123.97, 65.42, 34.86; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}O_5N$ 322.0686 found 322.0693.



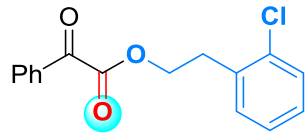
3ac, 77%

Product 3ac: Light yellow oil (3ac, 128.27 mg, 77% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.74 (m, 2H), 7.69 – 7.61 (m, 1H), 7.53 – 7.38 (m, 4H), 7.19 – 7.05 (m, 2H), 4.60 (ddd, *J* = 9.5, 5.9, 2.4 Hz, 2H), 3.04 (td, *J* = 6.6, 3.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.27, 163.75, 136.15, 135.12, 132.39, 131.93, 130.92, 130.13, 129.02, 120.96, 66.05, 34.5; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}O_3Br$ 354.9940 found 354.9964.



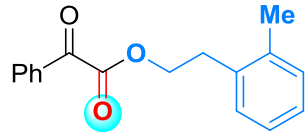
3ad, 72 %

Product 3ad: Light yellow oil (3ad, 103.94 mg, 72% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.20 (t, *J* = 6.7 Hz, 2H), 7.11 (d, *J* = 8.3 Hz, 2H), 4.52 (t, *J* = 6.8 Hz, 2H), 2.98 (t, *J* = 6.8 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.27, 163.74, 135.62, 135.11, 132.90, 132.38, 130.52, 130.11,129.00, 128.95, 66.13, 34.44; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}O_3Cl$ 311.0445 found 311.0454.



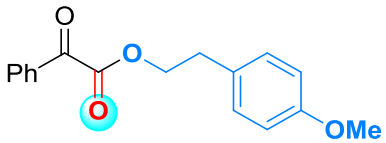
3ae, 73%

Product 3ae: Light yellow oil (3ae, 105.38 mg, 73% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.78 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.33 – 7.28 (m, 1H), 7.22 – 7.18 (m, 1H), 7.16 – 7.08 (m, 2H), 4.56 (t, *J* = 6.9 Hz, 2H), 3.16 (t, *J* = 6.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.20, 163.68, 135.02, 134.73, 134.37, 132.48, 131.48, 130.16, 129.84, 128.97, 128.59, 127.14, 64.86, 32.90; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{13}O_3Cl$ 311.0445 found 311.0460.



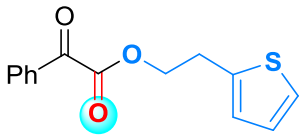
3af, 82%

Product 3af: Light yellow oil (3af, 112.69 mg, 82% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (t, *J* = 6.2 Hz, 2H), 7.65 (t, *J* = 6.9 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.17 (dd, *J* = 12.4, 5.1 Hz, 4H), 4.59 (t, *J* = 7.0 Hz, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.38 (d, *J* = 4.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.34, 163.79, 136.68, 135.08, 135.00, 132.50, 130.66, 130.18, 129.81, 128.98, 127.17, 126.38, 65.71, 32.35, 19.50; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{16}O_3$ 291.0992 found 291.1001.



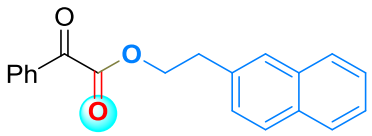
3ag, 88%

Product 3ag:[2] Light yellow oil (3ag, 125.10 mg, 88% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.68 – 7.58 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.24 – 7.10 (m, 2H), 6.94 – 6.78 (m, 2H), 4.59 (t, *J* = 7.0 Hz, 2H), 3.80 (s, 3H), 3.03 (t, *J* = 7.0 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.44, 163.86, 158.66, 134.98, 132.46, 130.14, 129.04, 128.94, 114.20 , 66.72, 55.36, 34.19; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{17}H_{16}O_4$ 307.0941 found 307.0949.



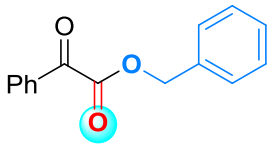
3ah, 66%

Product 3ah: Light yellow oil (3ah, 85.90 mg, 66% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 – 7.87 (m, 2H), 7.68 – 7.62 (m, 1H), 7.49 (td, *J* = 7.6, 1.7 Hz, 2H), 7.19 (dd, *J* = 5.1, 1.2 Hz, 1H), 7.01 – 6.88 (m, 2H), 4.62 (t, *J* = 6.8 Hz, 2H), 3.31 (t, *J* = 6.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.22, 163.70, 138.98, 135.04, 132.44, 130.17, 128.99, 127.18, 126.14, 124.43, 66.21, 29.22; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{14}H_{12}O_3S$ 283.0399 found 283.0417.



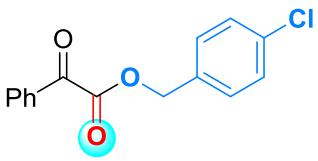
3ai, 76%

Product 3ai: Light yellow oil (3ai, 115.65 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.82 (m, 6H), 7.66-7.43 (m, 6H), 6.37 (p, *J* = 6.8 Hz, 1H), 1.81 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.37, 163.39, 137.66, 134.88, 133.28, 133.17, 132.50, 130.01, 128.90, 128.69, 128.15, 127.75, 126.46, 126.42, 123.90, 75.04, 22.18; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{20}H_{16}O_3$ 327.0992 found 327.1015.



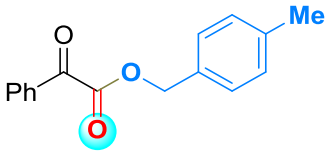
3aj, 80%

Product 3aj:[6] Colourless oil (3aj, 96.10 mg, 80% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.2 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.53 – 7.33 (m, 7H), 5.42 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.17, 163.77, 135.06, 134.67, 132.56, 130.15, 128.94, 128.87, 67.88; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{15}H_{12}O_3$ 263.0679 found 263.0685.



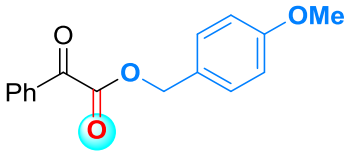
3ak, 69%

Product 3ak:[5] Light yellow solid (3ak, 94.77 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 13.8, 6.5 Hz, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.47 – 7.29 (m, 4H), 5.37 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 185.92, 163.56, 135.17, 134.94, 133.18, 132.48, 130.15, 130.11, 129.10, 129.07, 66.99; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{15}H_{11}O_3Cl$ 297.0829 found 297.0300.



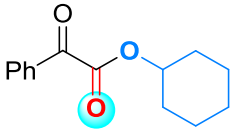
3al, 83%

Product 3al: Light yellow solid (3al, 105.53 mg, 83% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.89 (m, 2H), 7.68 – 7.59 (m, 1H), 7.53 – 7.44 (m, 2H), 7.33 (t, *J* = 10.6 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.38 (s, 2H), 2.37 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.27, 163.85, 138.91, 135.03, 132.61, 131.69, 130.16, 129.55, 129.02, 128.91, 67.92, 21.38; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{14}O_3$ 277.0835 found 277.0845.



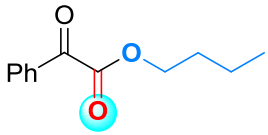
3am, 86%

Product 3am: Light yellow solid (3am, 116.22 mg, 86% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 2H), 6.85 – 6.81 (m, 2H), 5.27 (s, 2H), 3.73 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.30, 163.89, 160.20, 135.00 , 132.60, 130.72, 130.13, 129.00, 126.80, 114.24, 67.82, 55.4; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{16}H_{14}O_4$ 293.0784 found 293.0808.



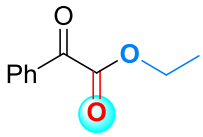
3an, 76%

Product 3an:[4] Light yellow liquid (3an, 88.27 mg, 76% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 – 7.76 (m, 2H), 7.74 – 7.56 (m, 1H), 7.54 – 7.40 (m, 2H), 5.09 (ddd, *J* = 13.2, 8.9, 4.0 Hz, 1H), 1.99 (d, *J* = 4.1 Hz, 2H), 1.78 (dd, *J* = 8.7, 4.2 Hz, 2H), 1.65 – 1.51 (m, 3H), 1.47 – 1.27 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.94, 163.80, 134.90, 132.71, 130.07, 129.00, 75.57, 31.57, 25.30, 23.76; HRMS (TOF) m/z [M + Na]$^+$ Calcd for $C_{14}H_{16}O_3$ 255.0992 found 255.0998.



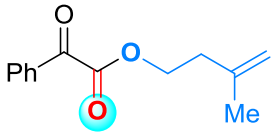
3ao, 71%

Product 3ao:[3] Colourless liquid (3ao, 73.22 mg, 71% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 4.32 (t, *J* = 6.7 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.43 – 1.32 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.62, 164.13, 134.99, 132.63, 130.11, 129.01, 66.21, 30.59, 19.15, 13.74; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{12}H_{14}O_3$ 229.0835 found 229.0841.



3ap, 69%

Product 3ap:[2] Light yellow liquid (3ap, 61.47 mg, 69% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 – 7.93 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.51 (t, *J* = 7.8 Hz, 2H), 4.45 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.56, 163.96, 135.02, 132.62, 130.15, 129.02, 62.46, 14.24; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{10}H_{10}O_3$ 201.0522 found 201.0523.

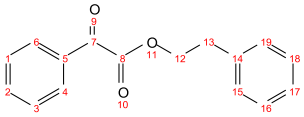


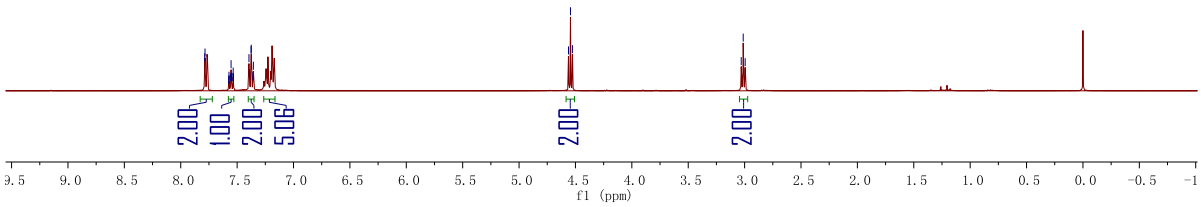
3aq, 60%

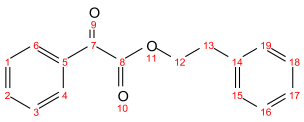
Product 3aq: Colourless liquid (3aq, 65.48 mg, 60% yield); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 4.78 (s, 1H), 4.72 (s, 1H), 4.44 (t, *J* = 6.9 Hz, 2H), 2.42 (t, *J* = 6.8 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.43, 163.92, 141.01, 135.01, 132.55, 130.16, 128.98, 113.13, 64.45, 36.66, 22.54; HRMS (TOF) m/z $[M + Na]^+$ Calcd for $C_{13}H_{14}O_3$ 241.0835 found 241.0834.

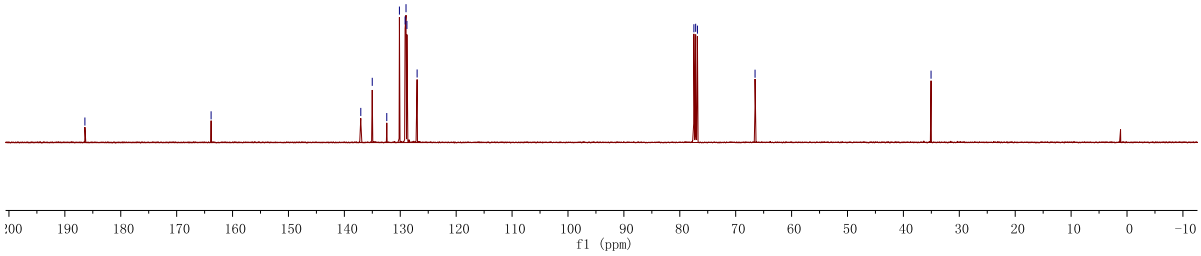
^{1}H NMR and ^{13}C NMR spectra of α-ketoesters 3

Product 3aa









Product 3ba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7.32
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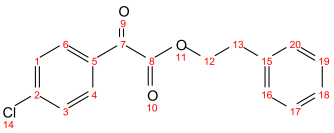
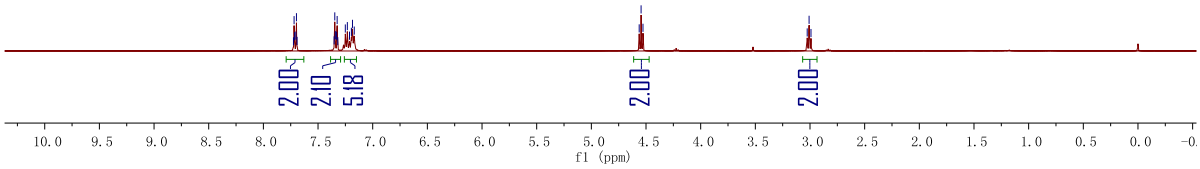
3.01
2.99

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127.03
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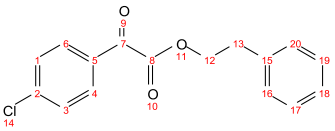
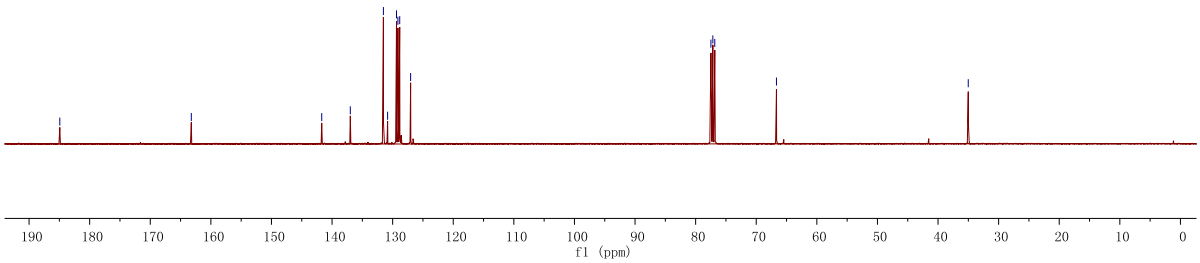
66.67
35.01




f1 (ppm)

Product 3ca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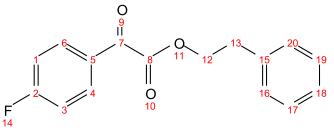

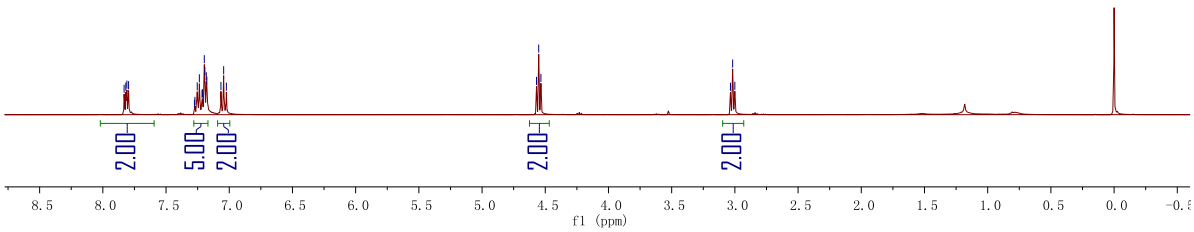
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f1 (ppm)


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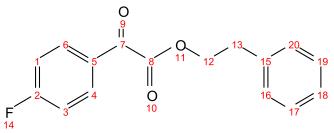

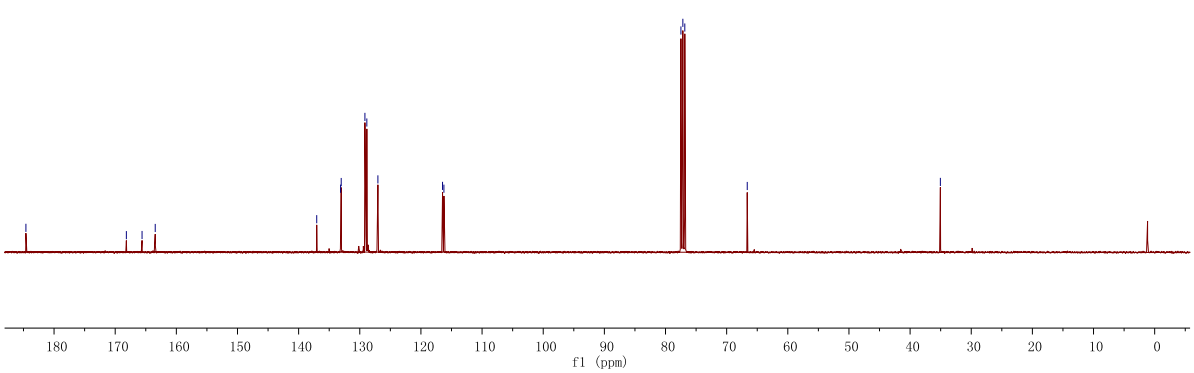
f1 (ppm)

Product 3da


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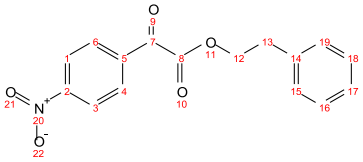
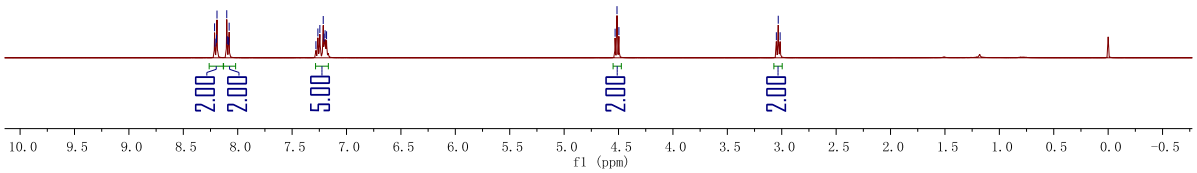
3.03
3.01

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f1 (ppm)


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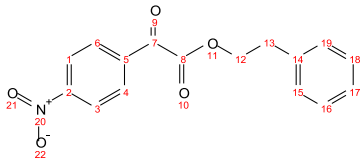
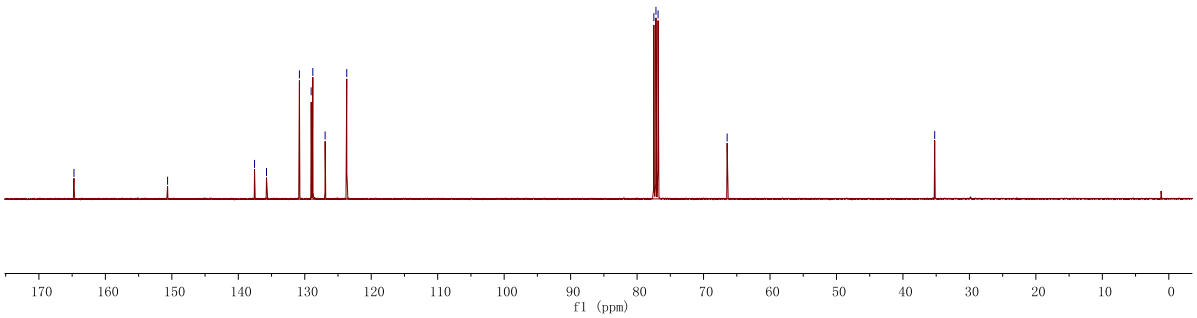
35.23




f1 (ppm)

Product 3ea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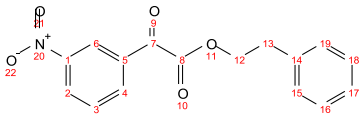
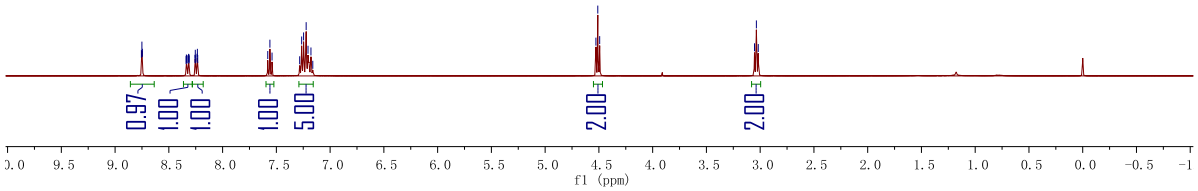
3.04
3.02

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f1 (ppm)


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127.50
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124.70
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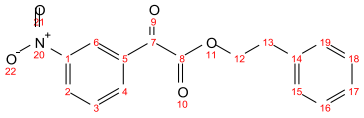
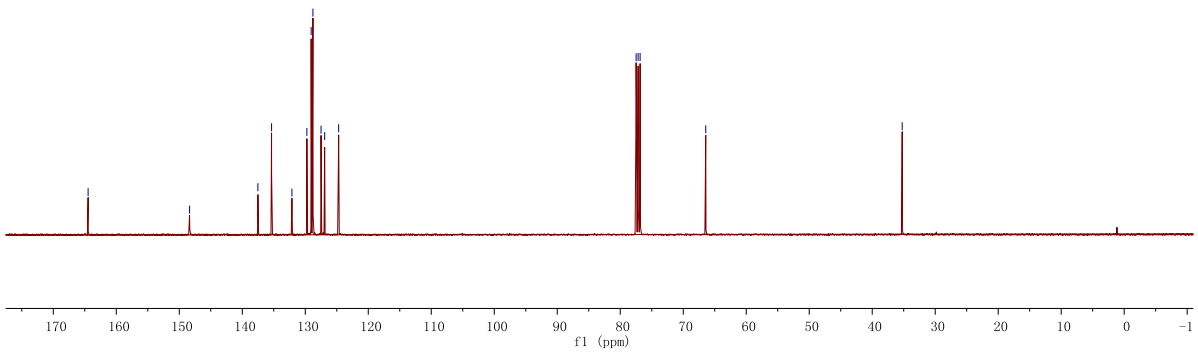
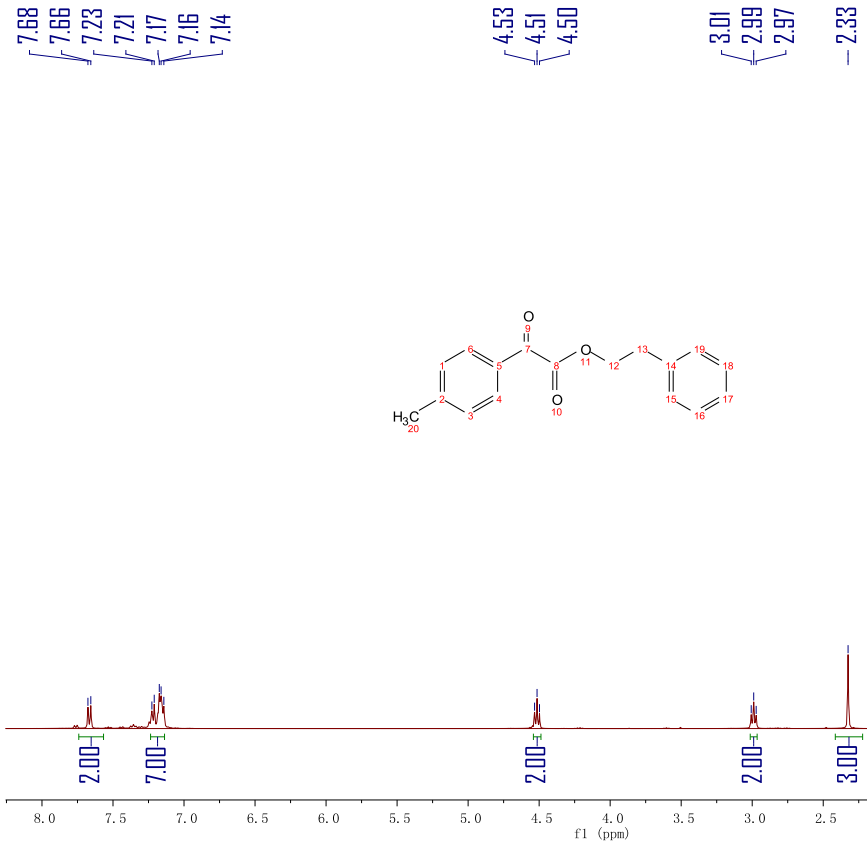
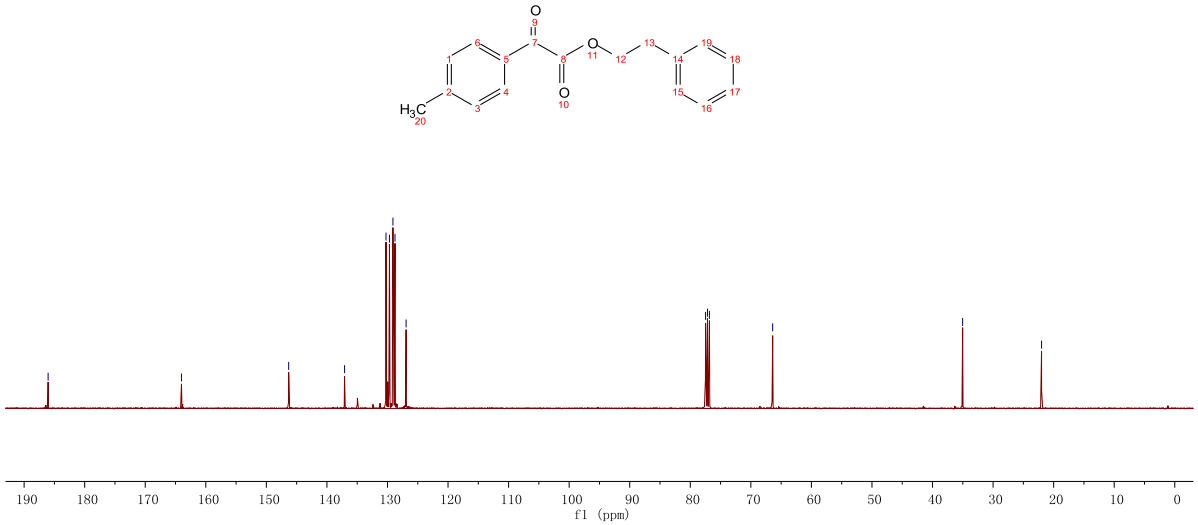
77.16
76.85
66.43
35.24




f1 (ppm)

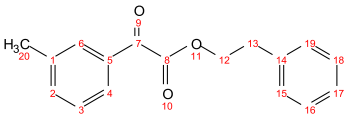
Product 3ga

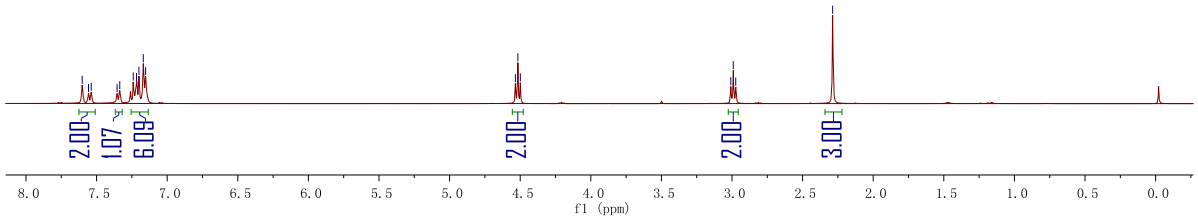

7.68
7.66
7.23
7.21
7.17
7.16
7.14
4.53
4.51
4.50
3.01
2.99
2.97
2.33
2.00
7.00
2.00
2.00
3.00
f1 (ppm)


166.04
164.02
146.32
137.09
130.24
129.67
129.10
128.76
126.93
77.48
77.16
76.84
66.40
35.03
22.00
f1 (ppm)

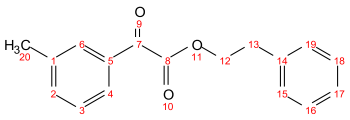
Product 3ha

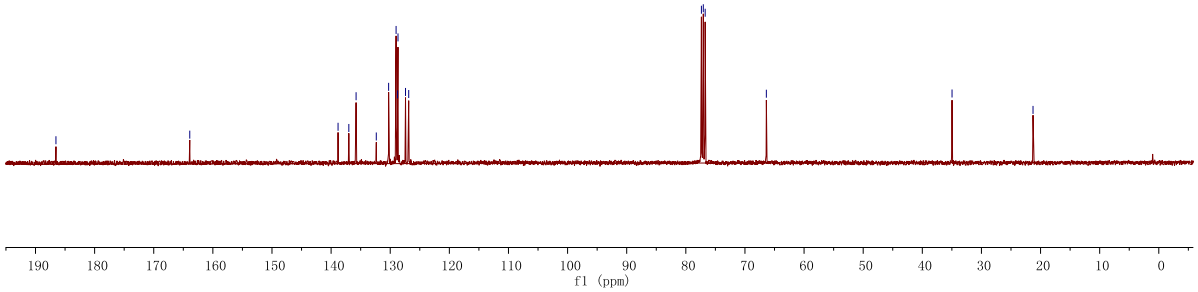

7.60
7.56
7.54
7.35
7.34
7.24
7.22
7.20
7.17
7.15
4.53
4.52
4.50
3.01
2.99
2.97
2.29




2.00
1.07
6.09
2.00
2.00
3.00
f1 (ppm)

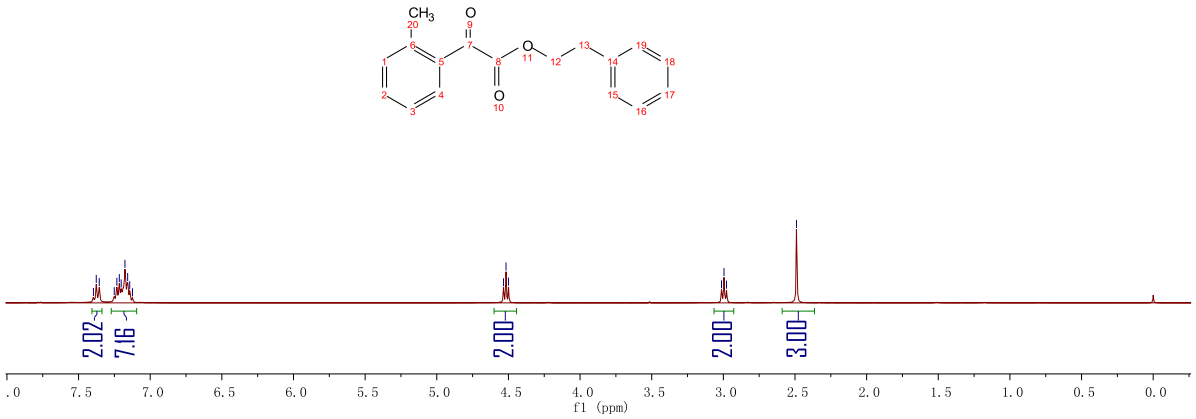

186.54
163.91
138.82
137.00
135.77
132.36
130.27
129.01
128.76
128.69
127.41
126.87
77.36
77.05
76.73
66.38
34.97
21.27



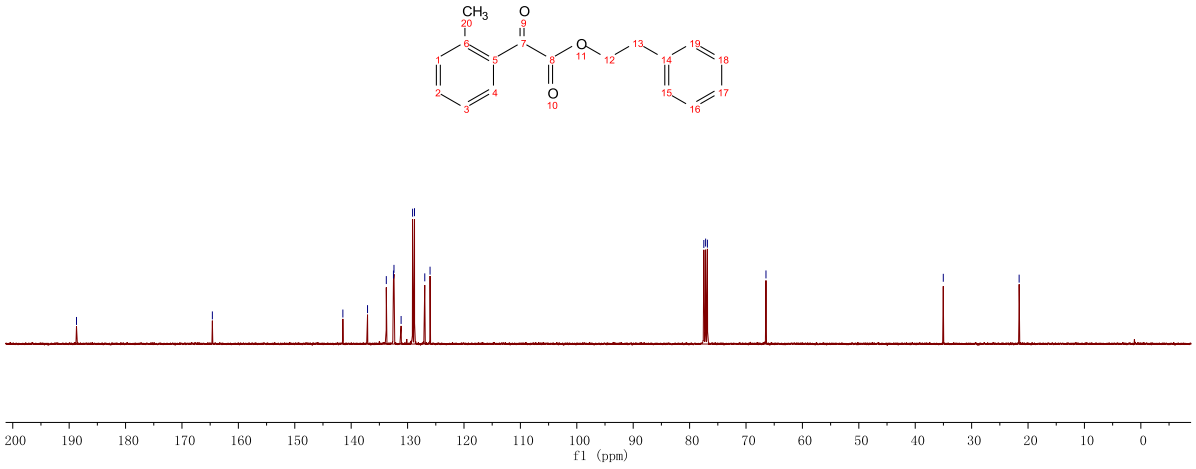

f1 (ppm)

Product 3ia


7.40
7.38
7.36
7.25
7.23
7.22
7.20
7.18
7.16
7.14
7.12
4.53
4.52
4.50
3.01
3.00
2.98
2.49

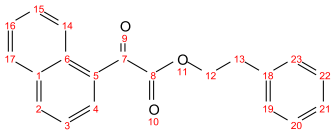

CH3
O
O
O
2.02
7.16
2.00
2.00
3.00
f1 (ppm)

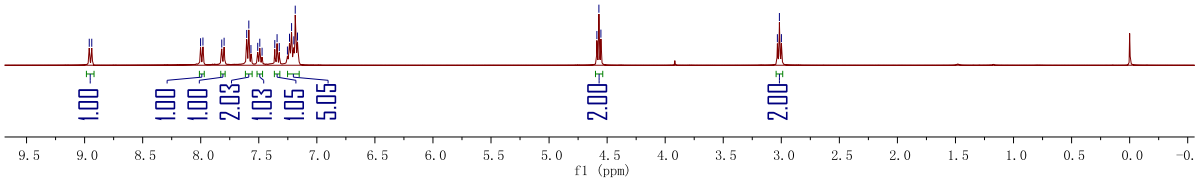

188.70
164.61
141.47
137.10
133.77
132.50
132.41
131.15
129.11
128.77
126.95
126.02
77.48
77.16
76.84
66.46
35.03
21.58


CH3
O
O
O
f1 (ppm)

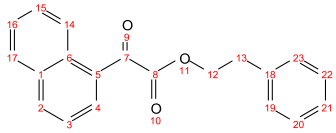
Product 3ja

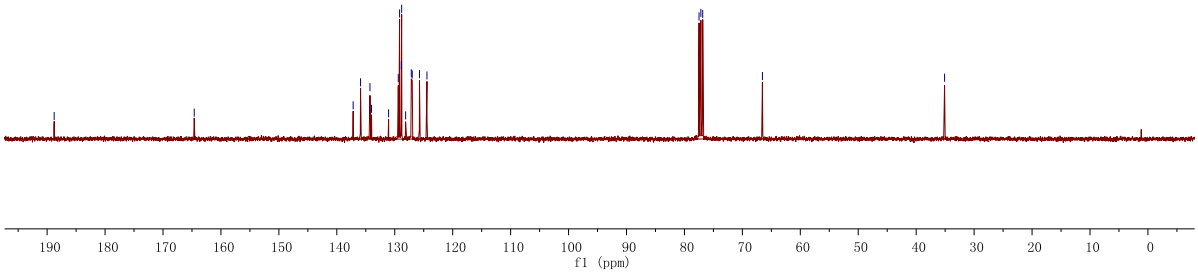

8.96
8.94
8.00
7.98
7.82
7.80
7.60
7.59
7.49
7.34
7.24
7.22
7.20
7.19
7.17
4.59
4.57
4.55
3.03
3.02
3.00




1.00
1.00
1.00
2.03
1.03
1.05
5.05
2.00
2.00
f1 (ppm)

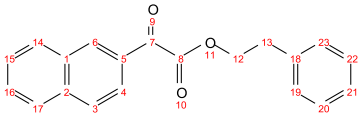

188.79
164.61
137.18
135.90
134.28
134.01
131.06
129.39
129.17
128.86
128.81
128.12
127.15
126.98
125.73
124.44
77.48
77.16
76.84
66.54
35.10

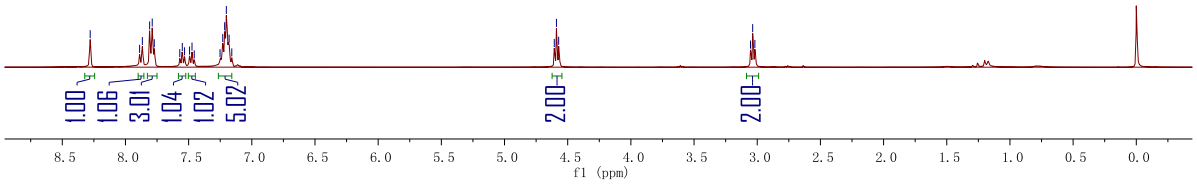



f1 (ppm)

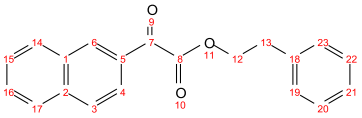
Product 3ka

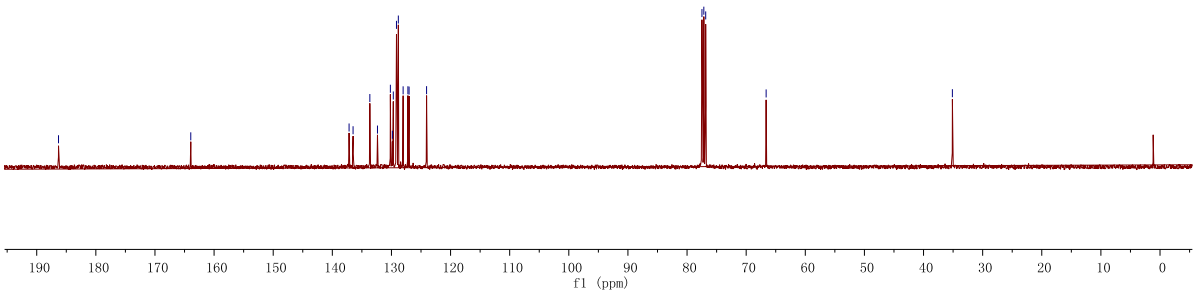

8.28
7.89
7.87
7.81
7.79
7.77
7.55
7.53
7.49
7.47
7.23
7.22
7.20
7.18
7.16
4.61
4.59
4.57
3.05
3.04
3.02




1.00
1.06
3.01
1.04
1.02
5.02
2.00
2.00
f1 (ppm)

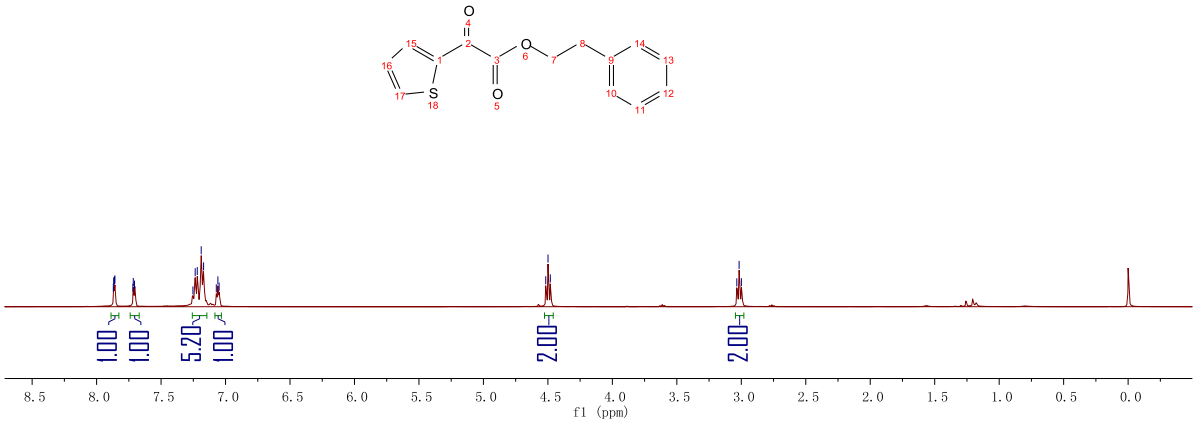

186.31
163.94
137.17
136.49
133.65
132.36
130.18
129.84
129.69
129.15
128.83
128.02
127.22
127.02
124.06
77.48
77.16
76.84
66.62
35.12

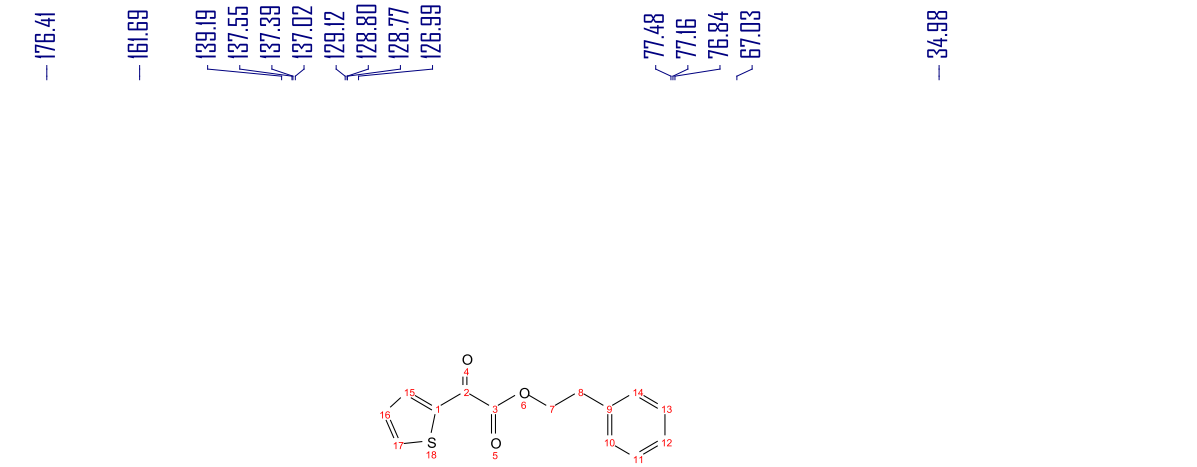


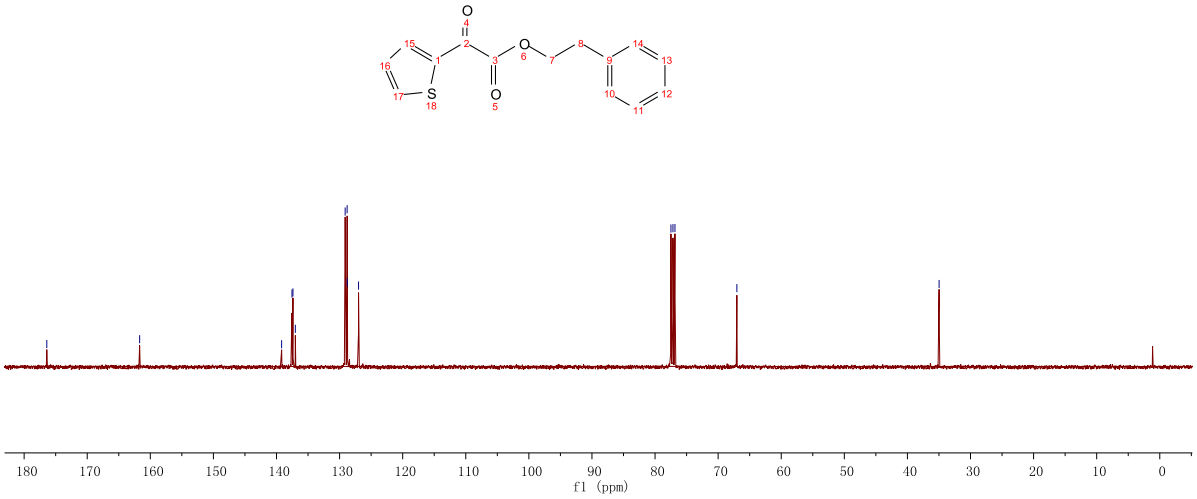

f1 (ppm)

Product 3la


7.87
7.87
7.86
7.86
7.72
7.72
7.71
7.25
7.24
7.22
7.19
7.17
7.07
7.06
7.05
4.52
4.50
4.48
3.03
3.02
3.00

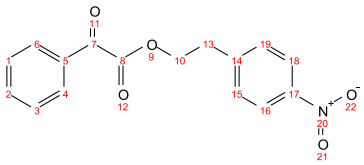

1.00
1.00
5.20
1.00
2.00
2.00
f1 (ppm)

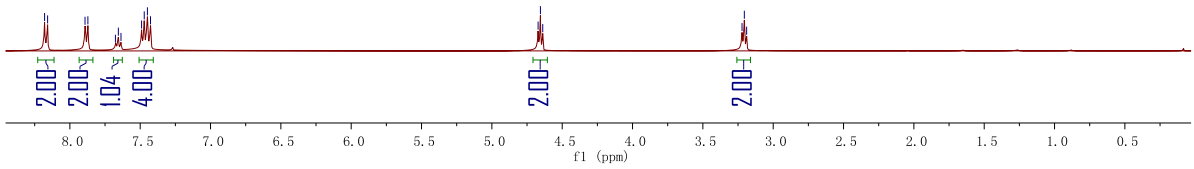

176.41
161.69
139.19
137.55
137.39
137.02
129.12
128.80
128.77
126.99
77.48
77.16
76.84
67.03
34.98


f1 (ppm)

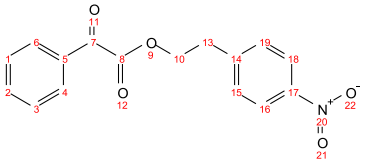
Product 3ab

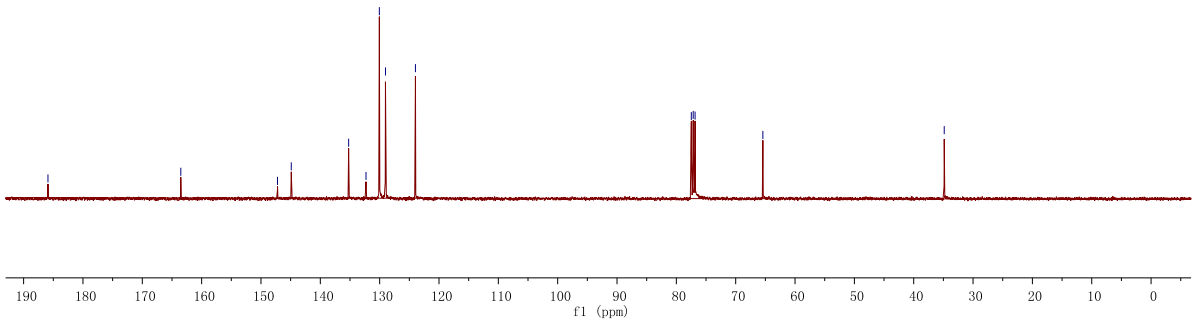

8.18
8.16
7.89
7.87
7.68
7.66
7.64
7.49
7.47
7.45
7.43
4.67
4.65
4.64
3.22
3.21
3.19




2.00
2.00
1.04
4.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

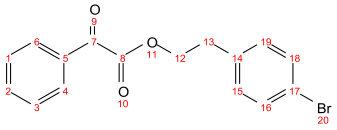

185.90
163.51
147.22
144.89
135.23
132.30
130.05
129.02
123.97
77.48
77.16
76.84
65.42
34.86

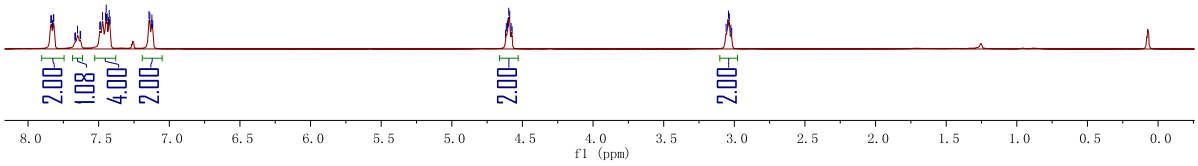



190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

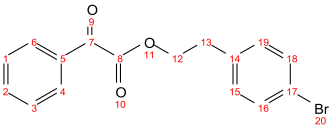
Product 3ac

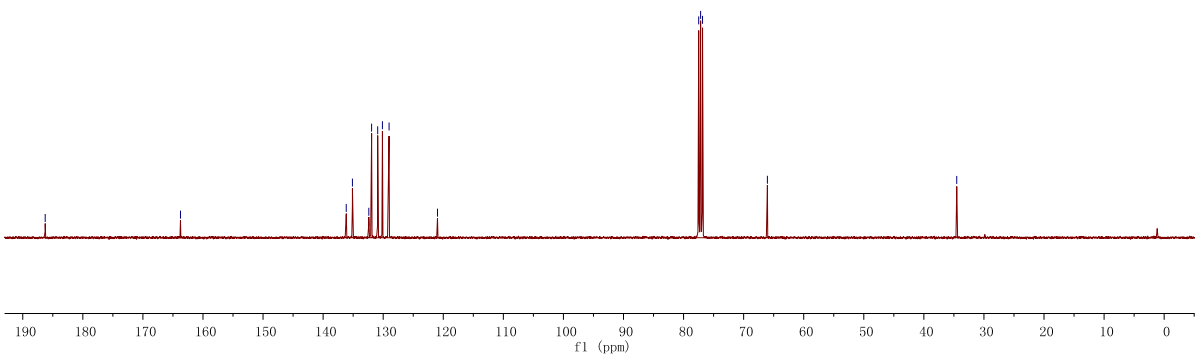

7.84
7.83
7.83
7.82
7.82
7.65
7.63
7.63
7.49
7.49
7.47
7.45
7.45
7.44
7.43
7.43
7.42
7.14
7.14
7.13
7.12
7.12
4.62
4.61
4.61
4.60
4.60
4.59
4.58
4.57
3.06
3.05
3.04
3.04
3.02
3.02


O
9
O
11
12
13
14
15
16
17
18
19
20
Br
O
10
1
2
3
4
5
6
7
8


2.00
1.08
4.00
2.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

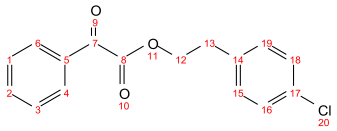

186.27
163.75
136.15
135.12
132.39
131.93
130.92
130.13
129.02
120.96
77.48
77.16
76.85
66.05
34.53

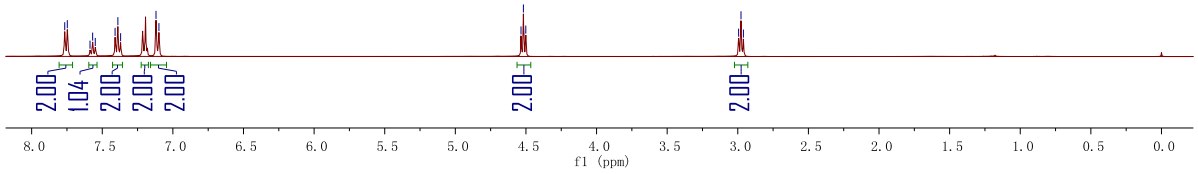

O
9
O
11
12
13
14
15
16
17
18
19
20
Br
O
10
1
2
3
4
5
6
7
8


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

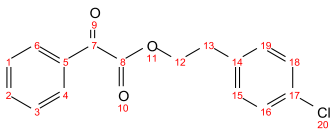
Product 3ad

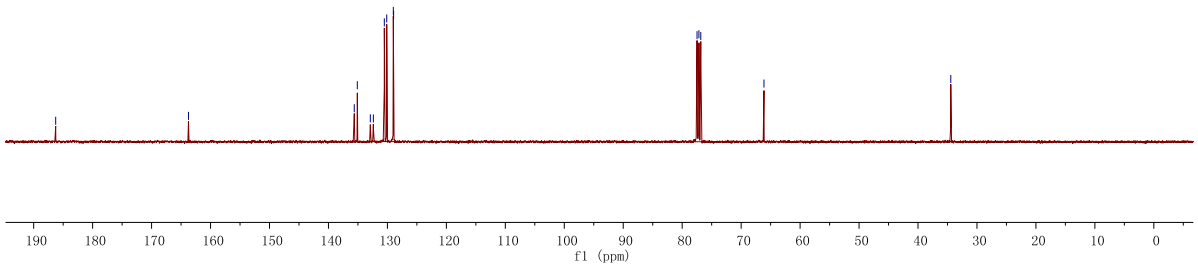

7.77
7.75
7.59
7.57
7.55
7.41
7.39
7.37
7.12
7.10
4.53
4.52
4.50
2.99
2.98
2.96


O
O
O
O
Cl

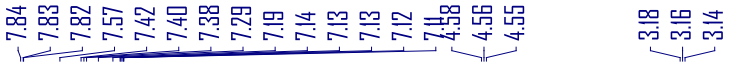

2.00
1.04
2.00
2.00
2.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

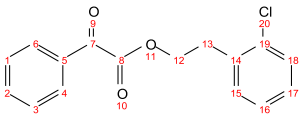

186.27
163.74
135.62
135.11
132.90
132.38
130.52
130.11
129.00
128.95
77.48
77.16
76.84
66.13
34.44

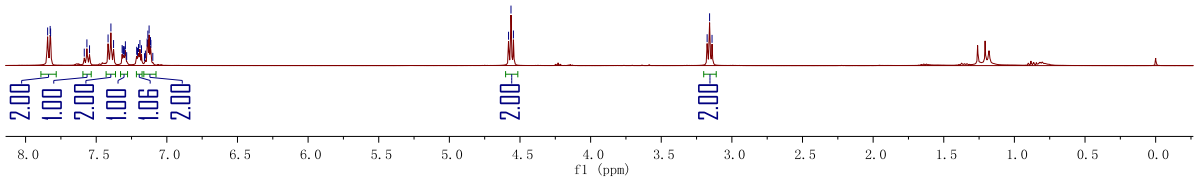

O
O
O
O
Cl

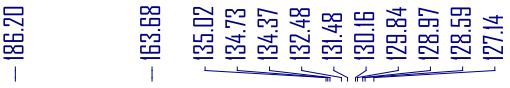

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

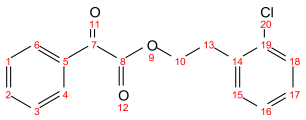
Product 3ae

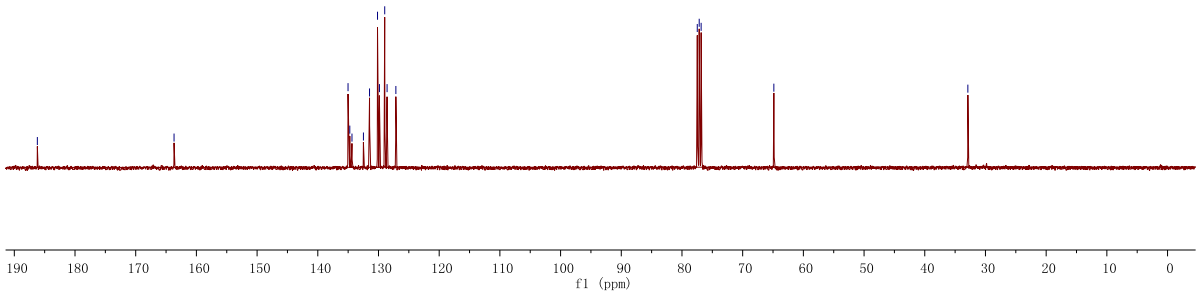

7.84
7.83
7.82
7.57
7.42
7.40
7.38
7.29
7.19
7.14
7.13
7.13
7.12
7.11
4.58
4.56
4.55
3.18
3.16
3.14


O
9
Cl
20
O
11
O
10


2.00
1.00
2.00
1.00
1.06
2.00
2.00
2.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

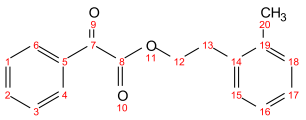

186.20
163.68
135.02
134.73
134.37
132.48
131.48
130.16
129.84
128.97
128.59
127.14
77.48
77.16
76.84
64.86
32.90

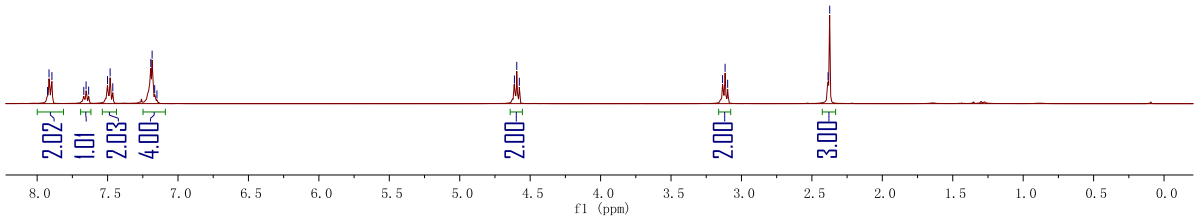

O
11
Cl
20
O
9
O
12


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

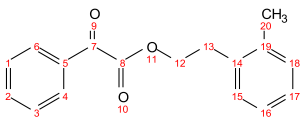
Product 3af

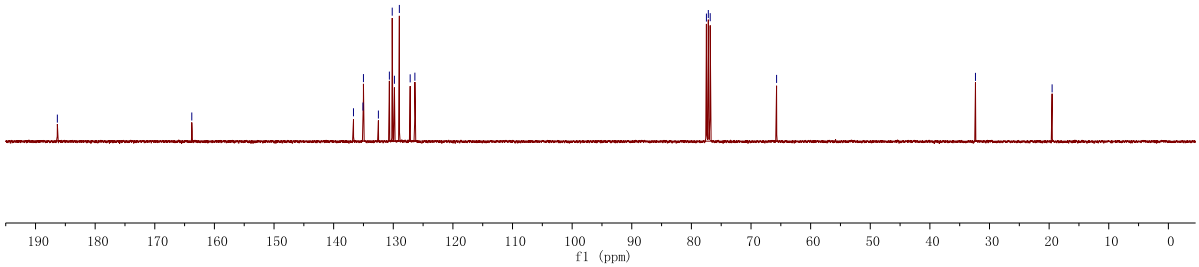

7.93
7.92
7.90
7.67
7.65
7.63
7.50
7.48
7.46
7.19
7.18
7.17
7.15
4.61
4.60
4.58
3.13
3.12
3.10
2.39
2.37


O
O
O
O
CH3


2.02
1.01
2.03
4.00
2.00
2.00
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

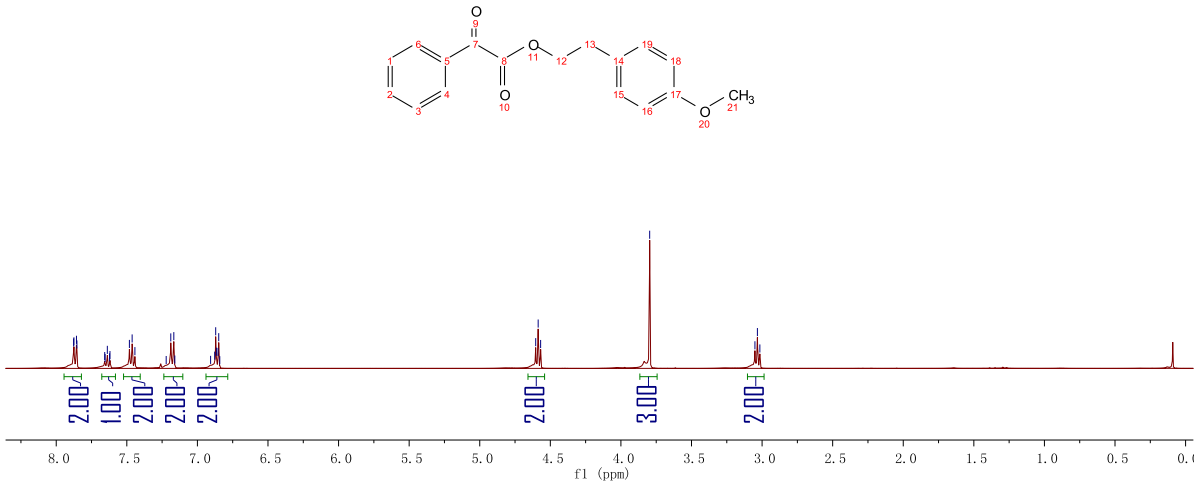

186.34
163.79
136.68
135.08
135.00
132.50
130.66
130.18
129.81
128.98
127.17
126.38
77.48
77.16
76.84
65.71
32.35
19.50

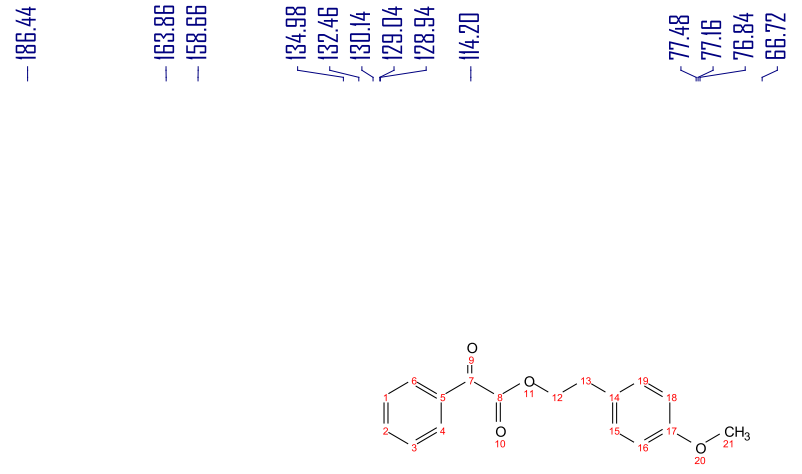

O
O
O
O
CH3


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Product 3ag


7.88
7.87
7.86
7.85
7.64
7.62
7.48
7.46
7.44
7.19
7.17
6.87
6.87
6.85
4.59
4.57
3.80
3.05
3.03
3.02


2.00
1.00
2.00
2.00
2.00
2.00
3.00
2.00
f1 (ppm)


186.44
163.86
158.66
134.98
132.46
130.14
129.04
128.94
114.20
77.48
77.16
76.84
66.72
55.36
34.19
f1 (ppm)

Product 3ah


7.94
7.93
7.92
7.91
7.91
7.67
7.65
7.65
7.65
7.63
7.63
7.63
7.50
7.50
7.49
7.48
7.47
7.47
7.20
7.19
7.18
7.18
6.97
6.96
6.95
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6.92
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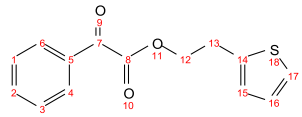
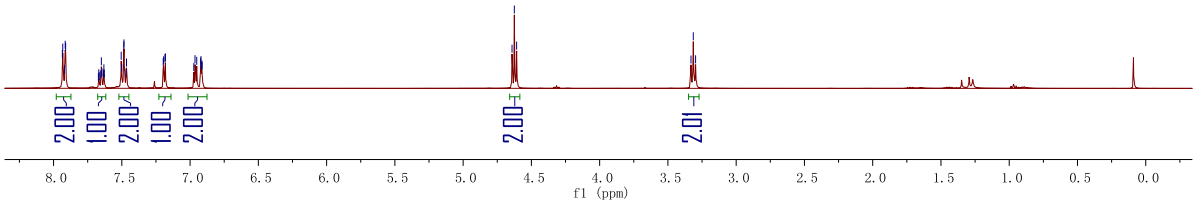
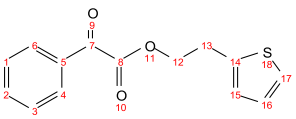
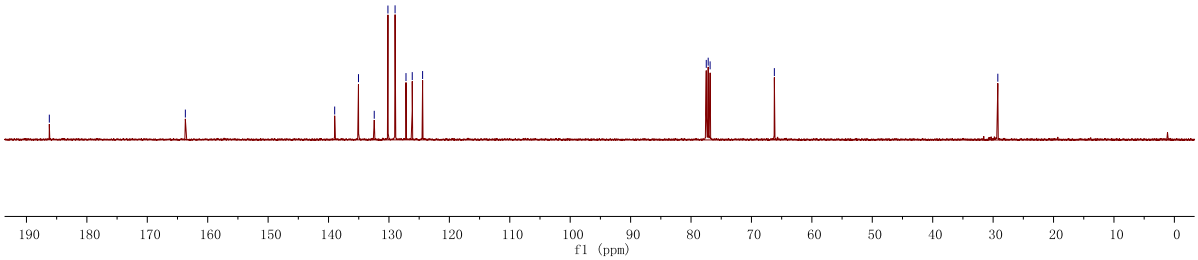
6.91
4.64
4.62
4.61
3.33
3.31
3.30



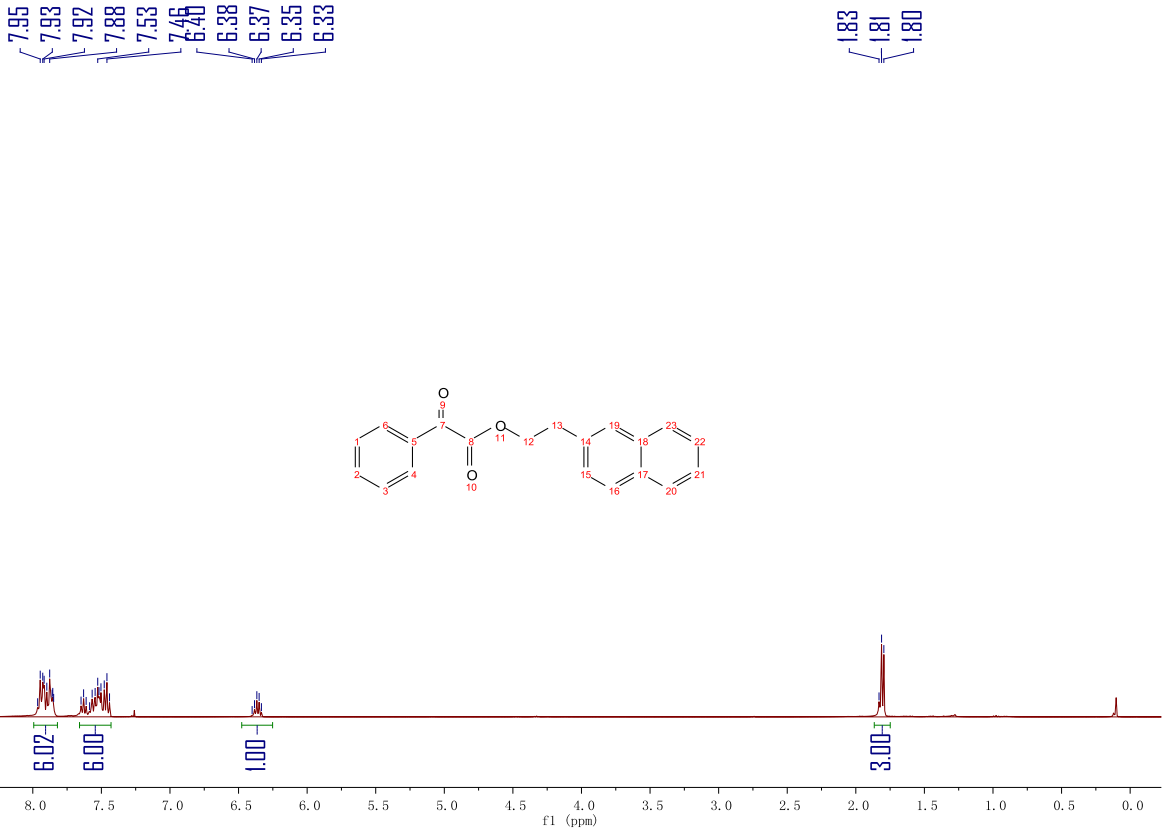

2.00
1.00
2.00
1.00
2.00
2.00
2.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

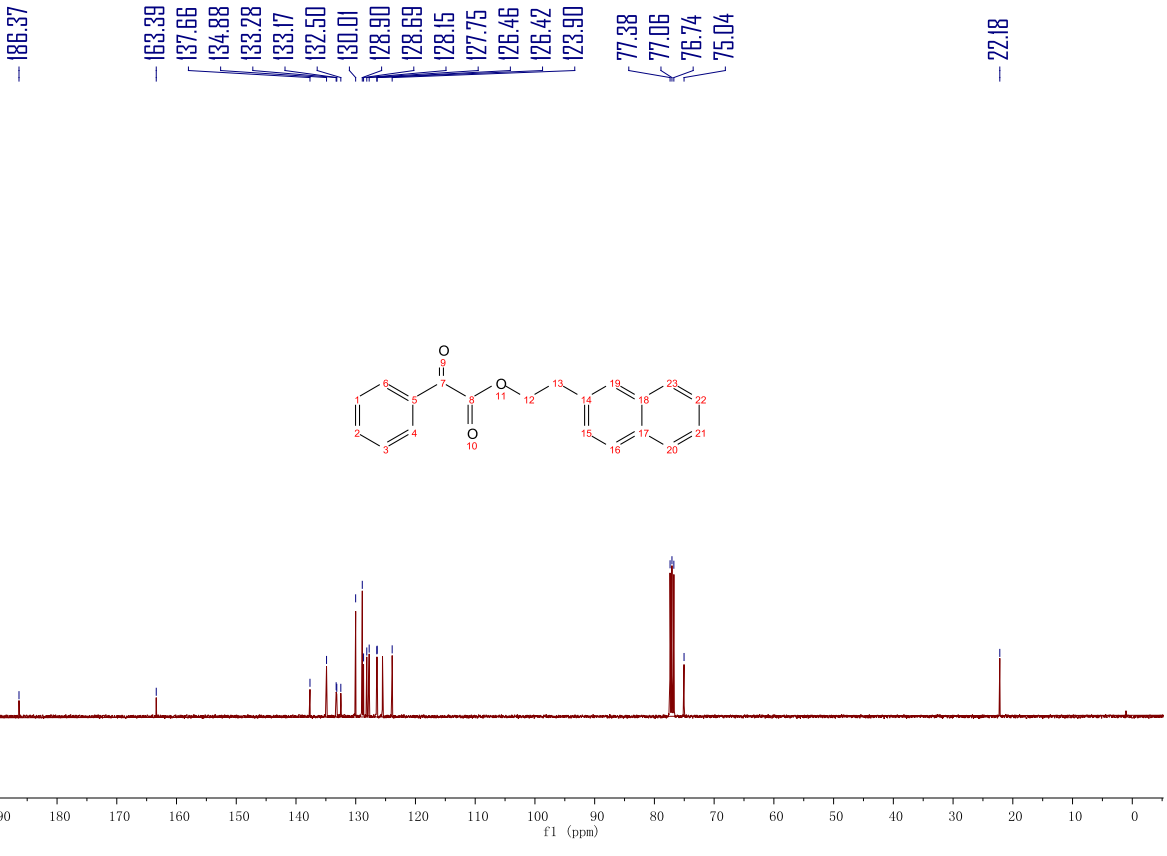

186.22
163.70
138.98
135.04
132.44
130.17
128.99
127.18
126.14
124.43
77.48
77.16
76.84
66.21
29.22



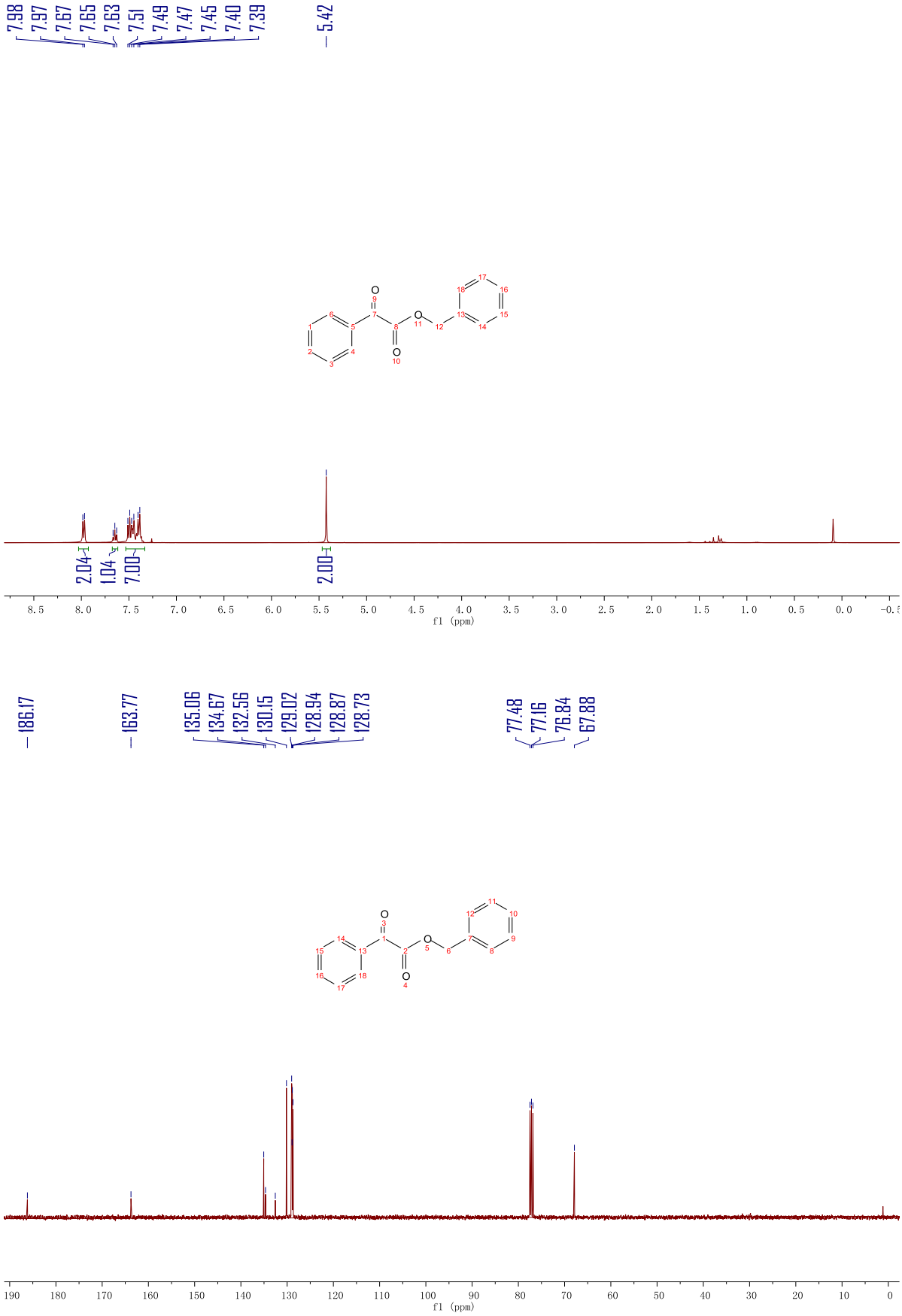

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Product 3ai


7.95
7.93
7.92
7.88
7.53
7.46
6.40
6.38
6.37
6.35
6.33
1.83
1.81
1.80
6.02
6.00
1.00
3.00
f1 (ppm)

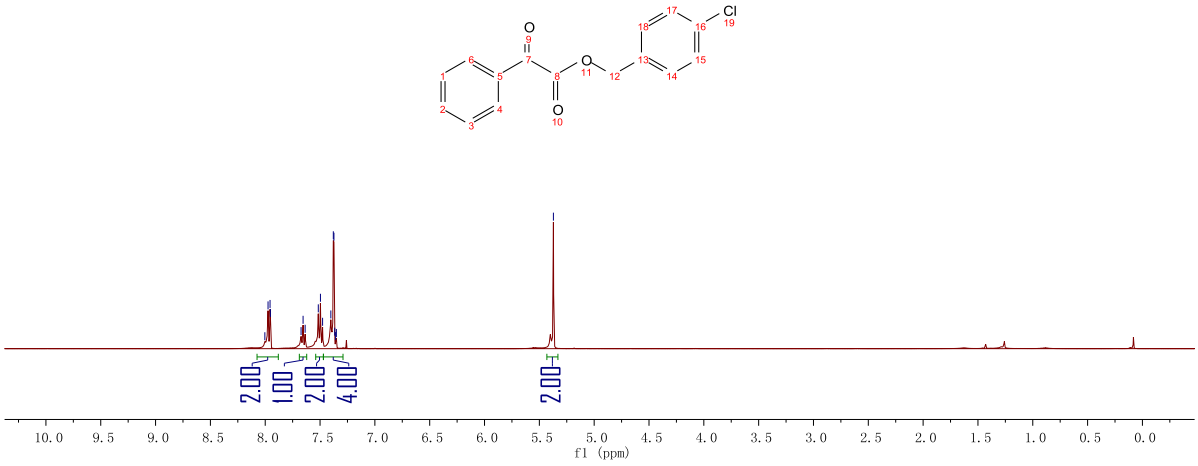

186.37
163.39
137.66
134.88
133.28
133.17
132.50
130.01
128.90
128.69
128.15
127.75
126.46
126.42
123.90
77.38
77.06
76.74
75.04
22.18
f1 (ppm)

Product 3aj

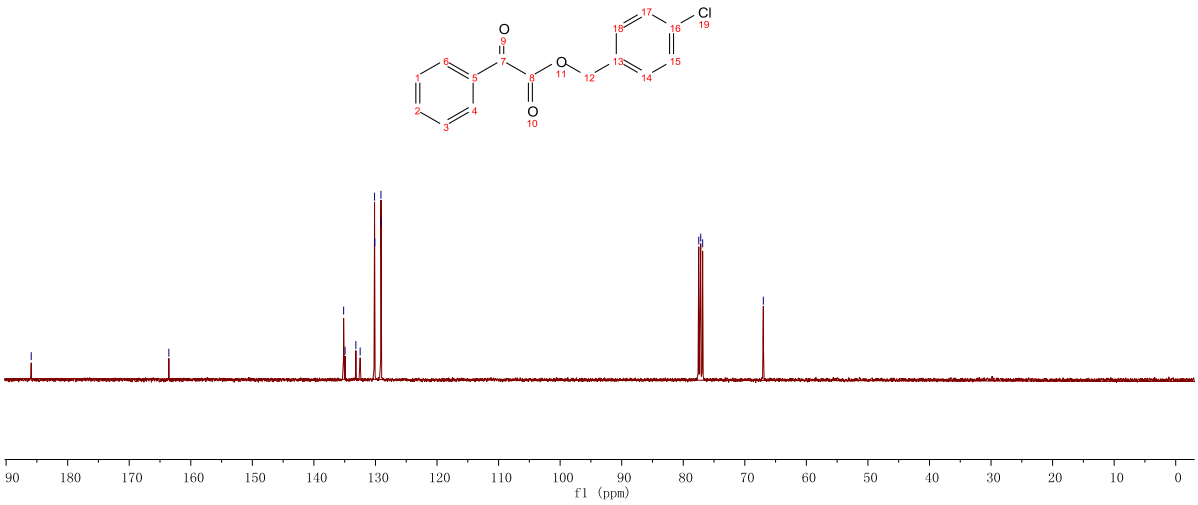

7.98
7.97
7.67
7.65
7.63
7.51
7.49
7.47
7.45
7.40
7.39
5.42
2.04
1.04
7.00
2.00
f1 (ppm)
166.17
163.77
135.06
134.67
132.56
130.15
129.02
128.94
128.87
128.73
77.48
77.16
76.84
67.88
f1 (ppm)

Product 3ak

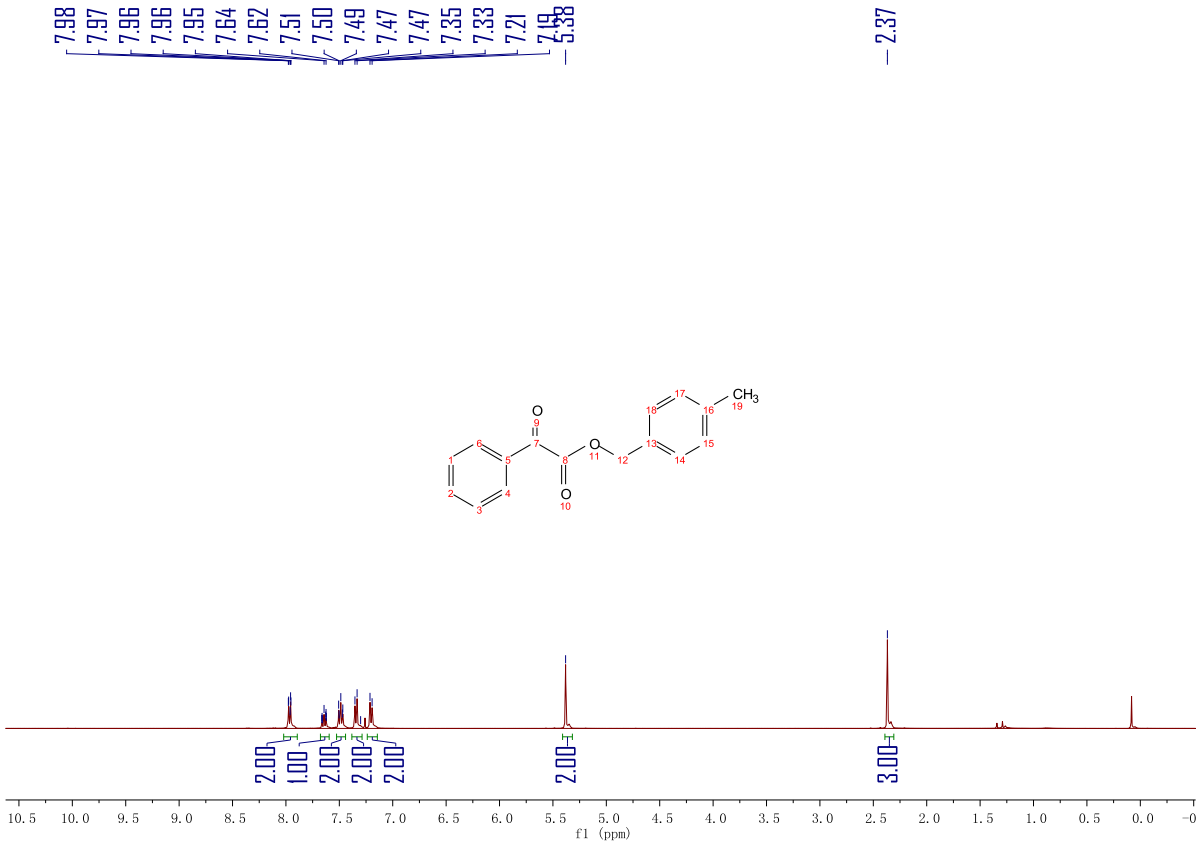

8.00
7.97
7.96
7.95
7.67
7.65
7.64
7.52
7.50
7.48
7.40
7.38
7.37
7.37
7.36
7.35
5.37

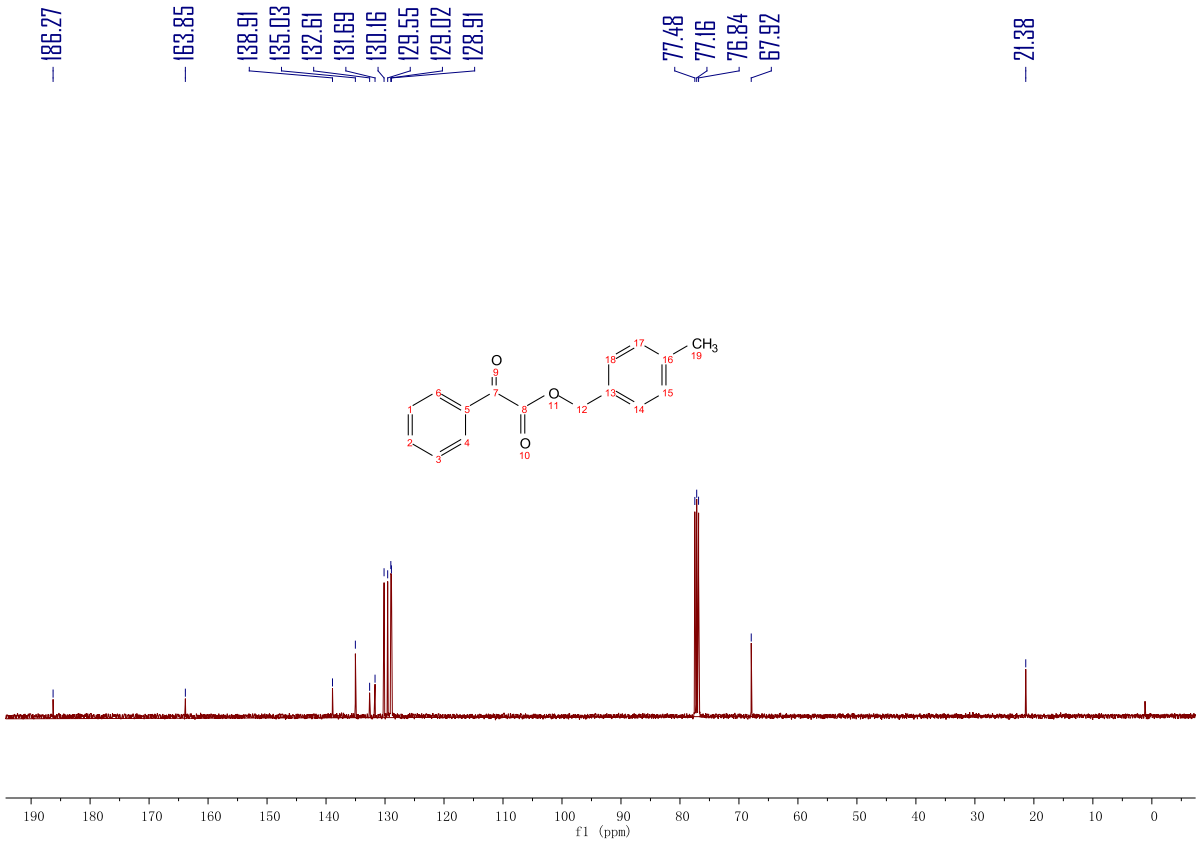

Cl
2.00
1.00
2.00
4.00
2.00
f1 (ppm)


185.92
163.56
135.17
134.94
133.18
132.48
130.15
130.11
129.10
129.07
77.48
77.16
76.85
66.99

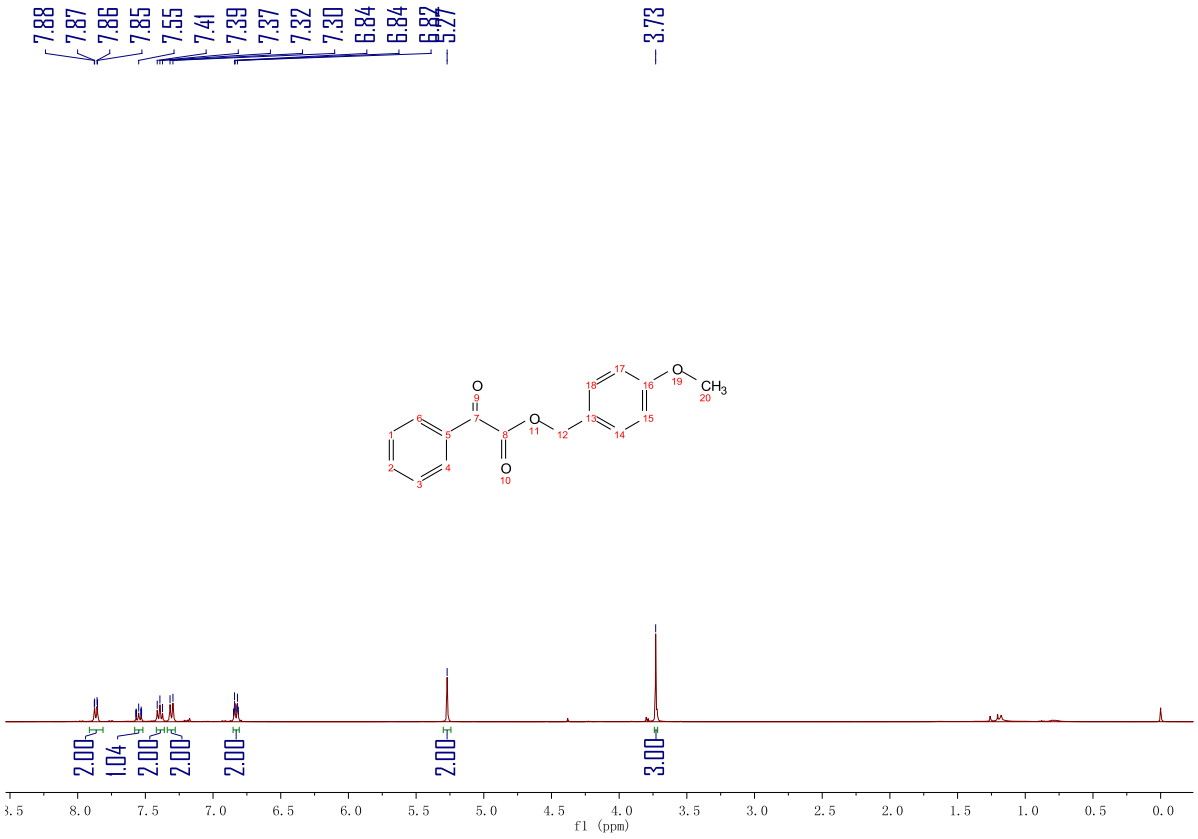

Cl
f1 (ppm)

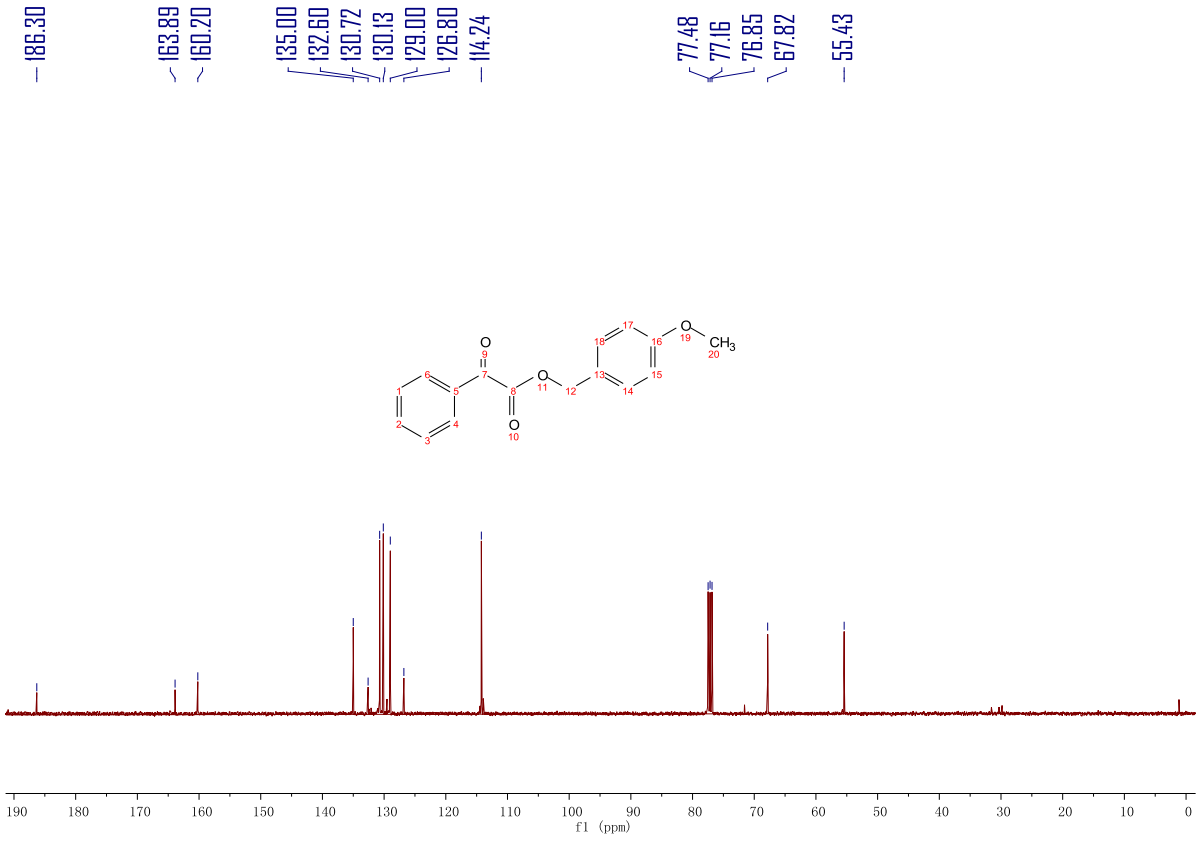
Product 3al


7.98
7.97
7.96
7.96
7.95
7.64
7.62
7.51
7.50
7.49
7.47
7.47
7.35
7.33
7.21
5.38
2.37
CH3
2.00
1.00
2.00
2.00
2.00
2.00
3.00
f1 (ppm)


186.27
163.85
138.91
135.03
132.61
131.69
130.16
129.55
129.02
128.91
77.48
77.16
76.84
67.92
21.38
CH3
f1 (ppm)

Product 3am


7.88
7.87
7.86
7.85
7.55
7.41
7.39
7.37
7.32
7.30
6.84
6.84
5.27
3.73
2.00
1.04
2.00
2.00
2.00
2.00
3.00
f1 (ppm)


186.30
163.89
160.20
135.00
132.60
130.72
130.13
129.00
126.80
114.24
77.48
77.16
76.85
67.82
55.43
f1 (ppm)

Product 3an


8.00
7.98
7.98
7.98
7.97
7.65
7.63
7.63
7.53
7.51
7.49
7.49
7.48
5.09
5.08
5.07
1.99
1.98
1.79
1.78
1.77
1.76
1.59
1.58
1.57
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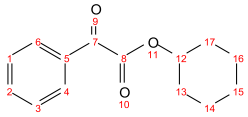
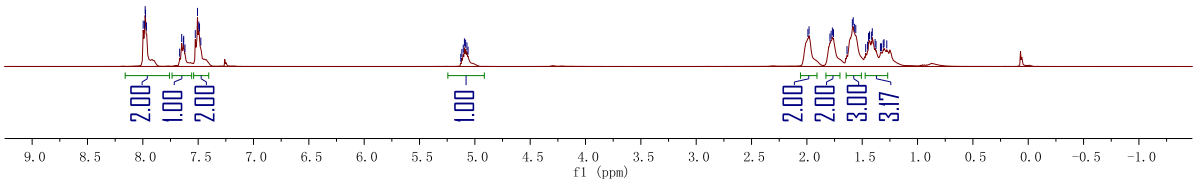
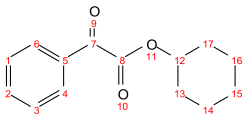
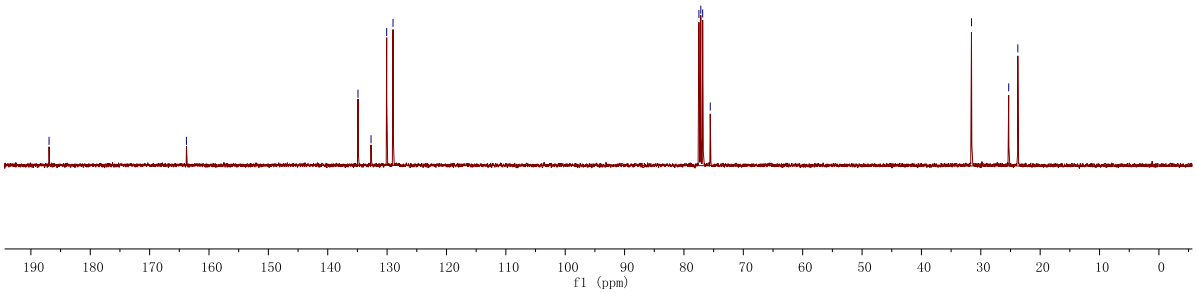
1.41
1.38
1.38
1.31
1.30
1.28



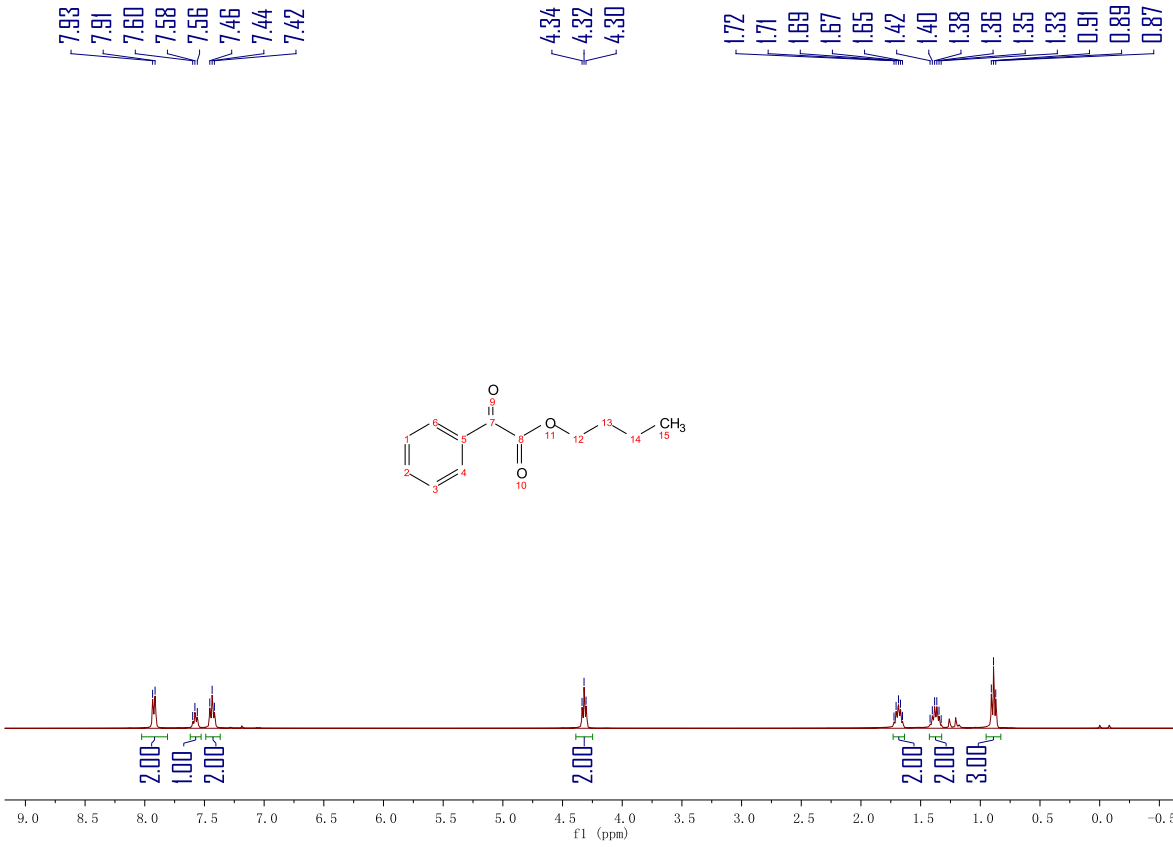

2.00
1.00
2.00
1.00
2.00
2.00
3.00
3.17
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
f1 (ppm)

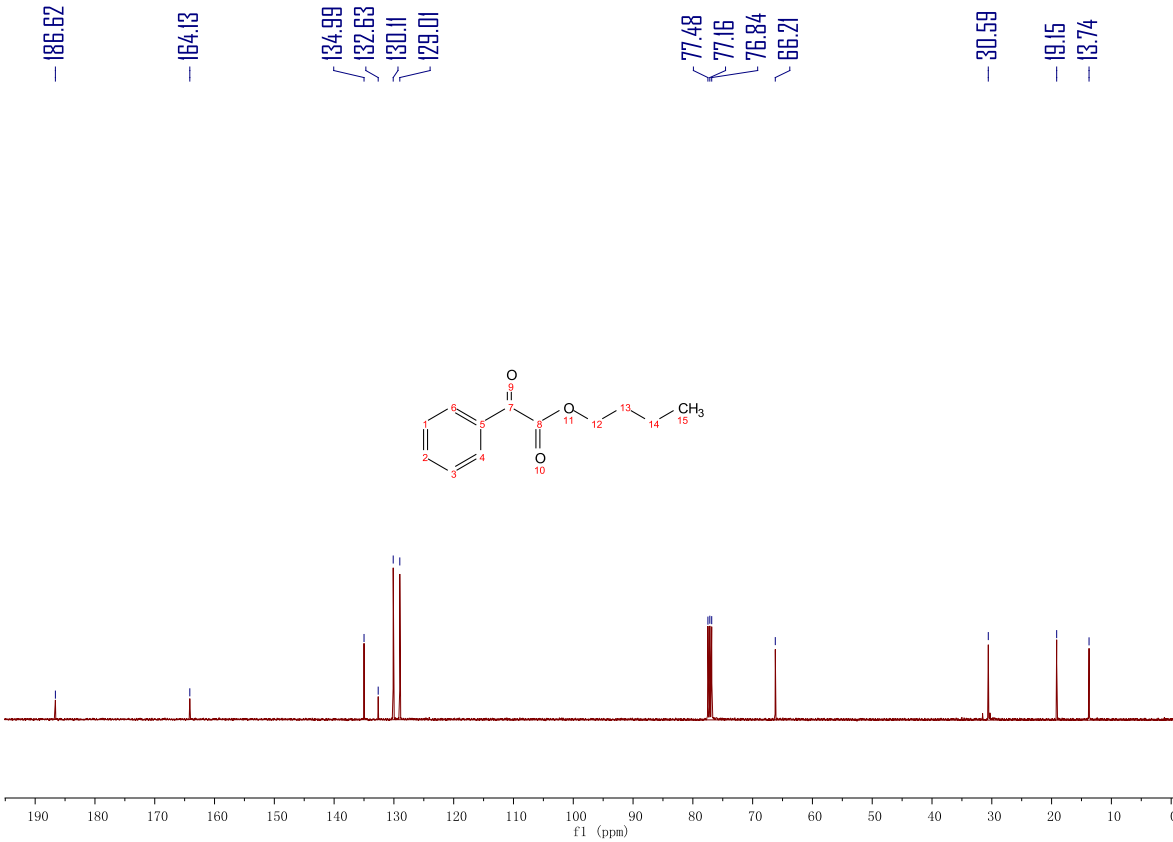

186.94
163.80
134.90
132.71
130.07
129.00
77.48
77.16
76.84
75.57
31.57
25.30
23.76



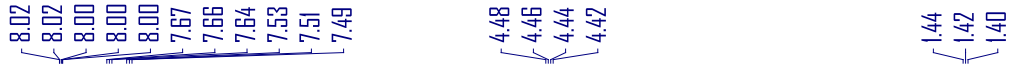

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

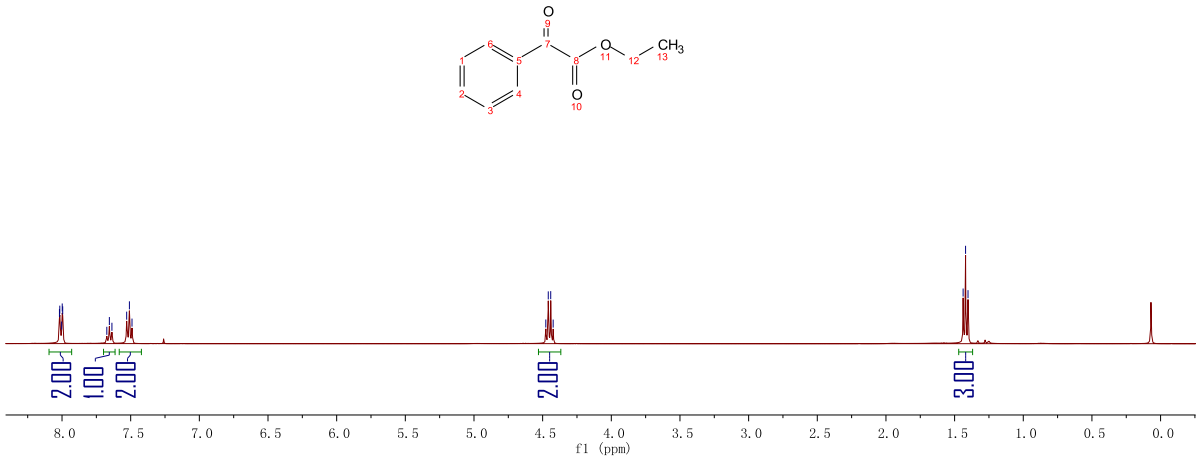
Product 3ao

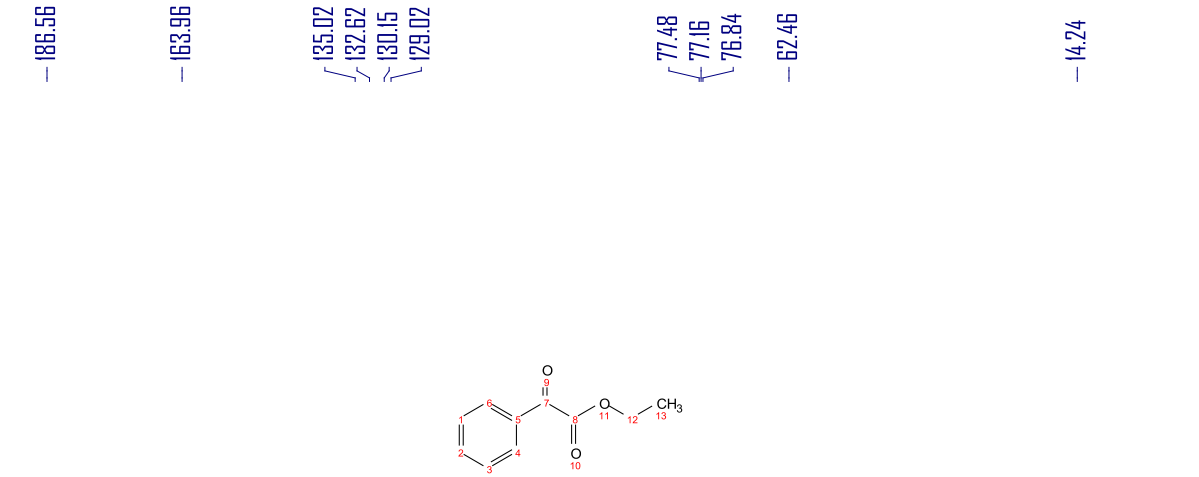

7.93
7.91
7.60
7.58
7.56
7.46
7.44
7.42
4.34
4.32
4.30
1.72
1.71
1.69
1.67
1.65
1.42
1.40
1.38
1.36
1.35
1.33
0.91
0.89
0.87
2.00
1.00
2.00
2.00
2.00
2.00
3.00
f1 (ppm)


186.62
164.13
134.99
132.63
130.11
129.01
77.48
77.16
76.84
66.21
30.59
19.15
13.74
f1 (ppm)

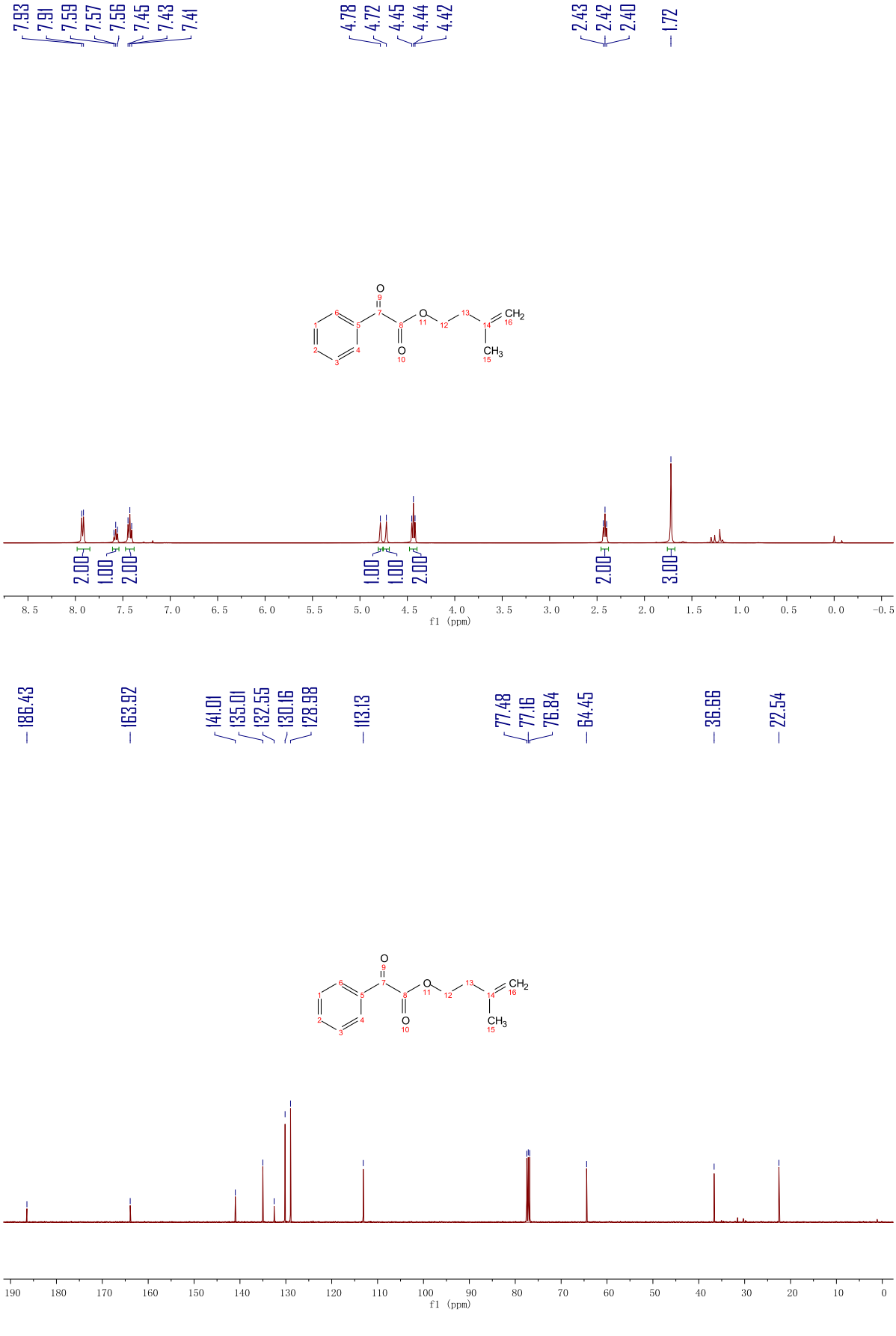
Product 3ap


8.02
8.02
8.00
8.00
8.00
7.67
7.66
7.64
7.53
7.51
7.49
4.48
4.46
4.44
4.42
1.44
1.42
1.40


2.00
1.00
2.00
2.00
3.00
f1 (ppm)


186.56
163.96
135.02
132.62
130.15
129.02
77.48
77.16
76.84
62.46
14.24
f1 (ppm)

Product 3aq


7.93
7.91
7.59
7.57
7.56
7.45
7.43
7.41
4.78
4.72
4.45
4.44
4.42
2.43
2.42
2.40
1.72
2.00
1.00
2.00
1.00
1.00
2.00
2.00
3.00
f1 (ppm)
186.43
163.92
141.01
135.01
132.55
130.16
128.98
113.13
77.48
77.16
76.84
64.45
36.66
22.54
f1 (ppm)

References

[1] A. H. Fenselau, J. G. Moffatt, *J. Am. Chem. Soc*., 1966, **88**, 1762.

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