Supporting Information For:

Copper-catalyzed radical coupling of 1,3-dicarbonyl compounds with terminal alkenes for the synthesis of tetracarbonyl compounds

Mei-Na Zhang, Mi-Na Zhao, Ming Chen, Zhi-Hui Ren, Yao-Yu Wang, and Zheng-Hui Guan*

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, Department of Chemistry & Materials Science, Northwest University, Xi'an 710127, P. R. China

E-mail: guanzhh@nwu.edu.cn

CONTENTS

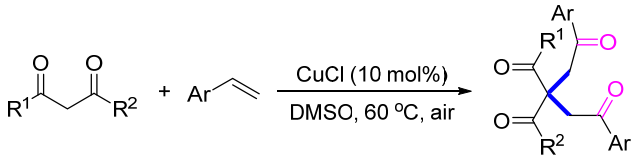
1. General information

Column chromatography was carried out on silica gel. ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. All new products were further characterized by HRMS; copies of their ^{1}H NMR and ^{13}C NMR spectra are provided. Unless otherwise stated, all reagents and solvents were purchased from commercial suppliers and used without further purification. *β*-diketone esters were synthesized by the following procedure.

2. Typical procedure for preparation of *β*-diketone esters

A homogeneous mixture of methyl acetoacetate (1.0 equiv.) and an alcohol (1.5 equiv.) was charged in a round bottomed flask and gently heated at 110 ^{o}C under solvent-free, catalyst-free conditions, for a certain period of time as required. The progress of the reaction was monitored by TLC. After completion, the resulting desired product was distilled out directly or separated by short column chromatography over silica gel using petroleum ether and ethyl acetate (80:20) to afford the pure product in 80-85% yield.

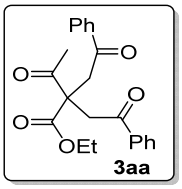
3. Typical procedure for the synthesis of target product



1 **2** **3**

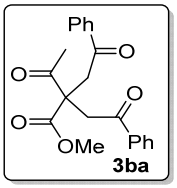
In a 25 mL round bottom flask, the ethyl acetoacetate **1** (0.2 mmol), styrene **2** (0.8 mmol) and CuCl (10 mol%, 1.98 mg) was stirred in DMSO (2 mL) at 60 °C. After completion of the reaction (detected by TLC), the reaction mixture was cooled to room temperature, extracted with ethyl acetate (20 mL) and washed with brine (20 mL). The organic layer was dried over by anhydrous Na_2SO_4 and evaporated in vacuo. The desired product **3** was obtained after purification by flash chromatography on silica gel with hexanes/ethyl acetate as the eluent.

4. Spectroscopic data for target product



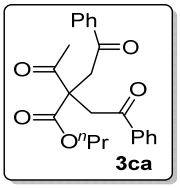
3aa

3aa: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, 4 H), 7.56 (t, *J* = 6.8 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 4.23-4.18 (m, 2 H), 4.12-3.99 (m, 4 H), 2.36 (s, 3 H), 1.20 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.1, 197.6, 170.3, 136.1, 133.5, 128.5, 128.0, 77.3, 77.0, 76.7, 61.9, 59.4, 42.2, 26.4, 13.8. HRMS Calcd (ESI) m/z for $C_{22}H_{22}NaO_5$: $[M+Na]^+$ 389.1359, found: 389.1352.



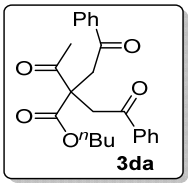
3ba

3ba: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, 4 H), 7.57 (t, *J* = 6.8 Hz, 2 H), 7.45 (t, *J* = 7.2 Hz, 4 H), 4.10-4.00 (m, 4 H), 3.74 (s, 3 H), 2.36 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.0, 197.5, 171.0, 136.0, 133.5, 128.6, 128.1, 77.3, 77.2, 77.0, 76.8, 76.7, 59.2, 53.0, 42.4, 26.5. HRMS Calcd (ESI) m/z for $C_{21}H_{20}NaO_5$: $[M+Na]^+$ 375.1203, found: 375.1202.

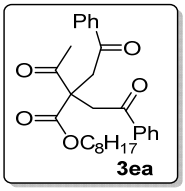


3ca

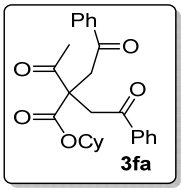
3ca: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* = 7.6 Hz, 4 H), 7.57 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 4.12-4.00 (m, 6 H), 2.36 (s, 3 H), 1.61-1.56 (m, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.2, 197.7, 170.5, 136.1, 133.5, 128.6, 128.1, 77.3, 77.0, 76.7, 67.6, 59.4, 42.3, 26.4, 21.6, 10.3. HRMS Calcd (ESI) m/z for $C_{23}H_{24}NaO_5$: $[M+Na]^+$ 403.1516, found: 403.1512.



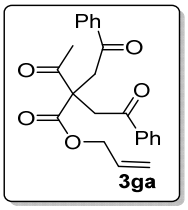
3da: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* = 7.6 Hz, 4 H), 7.57 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 4.15 (t, *J* = 6.8 Hz, 2 H),4.12-3.99 (m, 4 H), 2.36 (s, 3 H), 1.57-1.50 (m, 2 H), 1.30-1.20 (m, 2 H), 0.84 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.1, 197.6, 170.5, 136.1, 133.5, 128.6, 128.1, 77.3, 77.0, 76.7, 65.8, 59.4, 42.3, 26.4, 18.9, 13.5. HRMS Calcd (ESI) m/z for $C_{24}H_{26}NaO_5$: $[M+Na]^+$ 417.1672, found: 417.1671.



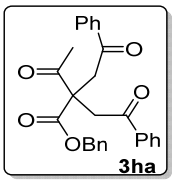
3ea: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* = 7.6 Hz, 4 H), 7.57 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* =7.6 Hz, 4 H), 4.14-3.99 (m, 6 H), 2.35 (s, 3 H), 1.54 (s, 2 H), 1.22-1.15 (m, 10 H) ,0.86 (t, *J* =6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.1, 197.6, 170.5, 136.1, 133.5, 128.6, 128.1, 77.3, 77.0, 76.7, 66.1, 59.4, 42.3, 31.6, 29.0, 28.2, 26.4, 25.8, 22.5, 14.0. HRMS Calcd (ESI) m/z for $C_{28}H_{34}NaO_5$: $[M+Na]^+$ 473.2298, found: 473.2296.



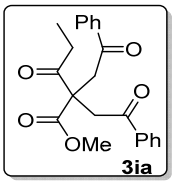
3fa: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.96 (d, *J* = 7.6 Hz, 4 H), 7.56 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 4.87 (s, 1H), 4.10-3.97 (m, 4 H), 2.36 (s, 3 H), 1.75 (s, 2 H), 1.59 (s, 2 H), 1.44-1.20 (m, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.3, 197.6, 169.7, 136.2, 133.5, 128.5, 128.0, 77.3, 77.0, 76.7, 74.1, 59.6, 42.3, 30.9, 26.4, 25.1, 23.3. HRMS Calcd (ESI) m/z for $C_{26}H_{28}NaO_5$: $[M+Na]^+$ 443.1829, found: 443.1830.



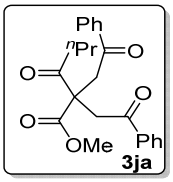
3ga: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (d, *J* = 7.6 Hz, 4 H), 7.57 (t, *J* =7.2 Hz, 2 H), 7.45 (t, *J* = 7.2 Hz, 4 H),5.86-5.78 (m, 1 H), 5.28-5.17 (m, 2 H), 4.64 (d, *J* = 5.6 Hz, 2 H), 4.12-4.01 (m, 4 H), 2.36 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.0, 197.6, 170.2, 136.1, 133.6, 131.3, 128.6, 128.1, 118.8, 77.3, 77.0, 76.7, 66.5, 59.4, 42.3, 26.5. HRMS Calcd (ESI) m/z for $C_{23}H_{22}NaO_5$: $[M+Na]^+$ 401.1359, found: 401.1349.



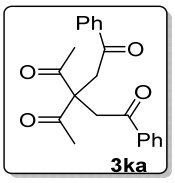
3ha: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 (d, *J* =7.6 Hz, 4 H), 7.56 (t, *J* = 7.2 Hz, 2 H),7.43 (t, *J* = 7.6 Hz, 4 H), 7.25 (d, *J* = 6.8 Hz, 5 H), 5.16 (s, 2 H), 4.12-4.00 (m, 4 H), 2.28 (s, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.9, 197.6, 170.3, 136.0, 135.1, 133.6, 128.6, 128.4, 128.2, 128.1, 128.1, 77.3, 77.0, 76.7, 67.7, 59.4, 42.4, 26.5. HRMS Calcd (ESI) m/z for $C_{27}H_{24}NaO_5$: $[M+Na]^+$ 451.1516, found:451.1501.



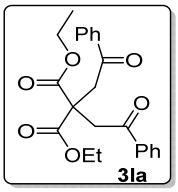
3ia: Yellow solid, mp 60-62 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (d, *J* = 7.6 Hz, 4 H), 7.57 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 7.6 Hz, 4 H), 4.09-3.99 (m, 4 H), 3.73 (s, 3 H), 2.74-2.69 (m, 2 H), 1.13 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 206.0, 197.6, 171.3, 136.1, 133.5, 128.6, 128.1, 77.3, 77.0, 76.7, 58.9, 52.9, 42.6, 32.0, 7.92. HRMS Calcd (ESI) m/z for $C_{22}H_{22}NaO_5$: $[M+Na]^+$ 389.1359, found: 389.1369.



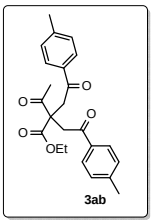
3ja: Yellow solid, mp 75-77 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ =7.96 (d, *J* = 7.6 Hz, 4 H), 7.56 (t, *J* = 7.2 Hz, 2 H), 7.45 (t, *J* = 6.8 Hz, 4 H), 4.06 (s, 4 H), 3.73 (s, 3 H), 2.66 (t, *J* = 6.8 Hz, 2 H), 1.70-1.64 (m, 2 H), 0.93 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.9, 197.6, 171.2, 136.1, 133.5, 128.6, 128.1, 77.3, 77.0, 76.7, 59.1, 52.9, 42.3, 40.1, 16.9, 13.4. HRMS Calcd (ESI) m/z for $C_{23}H_{24}NaO_5$: $[M+Na]^+$ 403.1516, found: 403.1505.



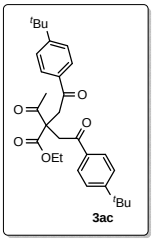
3ka: Yellow solid, mp 142-144 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.95 (d, *J* = 7.6 Hz, 4 H), 7.57 (t, *J* = 7.2 Hz, 2 H), 7.44 (t, *J* = 7.6 Hz, 4 H), 4.18 (s, 4 H), 2.20 (s, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.1, 198.1, 135.9, 133.7, 128.6, 128.1, 77.3, 77.0, 76.7, 66.9, 42.2, 25.9. HRMS Calcd (ESI) m/z for $C_{21}H_{21}O_4$: $[M+H]^+$ 337.1434, found: 337.1443.



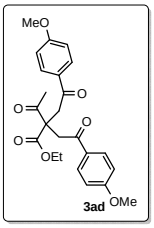
3la: Yellow solid, mp 82-84 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (d, *J* = 7.2 Hz, 4 H), 7.59 (t, *J* = 7.2 Hz, 2 H), 7.48 (t, *J* = 7.6 Hz, 4 H), 4.28-4.22 (m, 4 H), 4.11 (s, 4 H), 1.24 (t, *J* = 7.2 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 197.5, 169.8, 136.2, 133.4, 128.5, 128.0, 77.3, 77.0, 76.7, 62.0, 53.2, 41.7, 13.8. HRMS Calcd (ESI) m/z for $C_{23}H_{24}NaO_6$: $[M+Na]^+$ 419.1465, found: 419.1472.



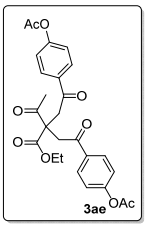
3ab: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.76 (d, *J* = 8.0 Hz, 4 H), 7.14 (d, *J* = 8.0 Hz, 4 H), 4.13-4.08 (m, 2 H), 3.99-3.86 (m, 4 H), 2.29 (s, 6 H), 2.26 (s, 3 H), 1.10 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.2, 197.2, 170.5, 144.3, 133.7, 129.2, 128.1, 77.3, 77.0, 76.7, 61.8, 59.4, 42.1, 26.3, 21.6, 13.7. HRMS Calcd (ESI) m/z for $C_{24}H_{26}NaO_5$: $[M+Na]^+$ 417.1672, found: 417.1671.



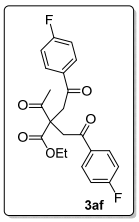
3ac: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.91 (d, *J* = 8.0 Hz, 4 H), 7.45 (d, *J* = 8.4 Hz, 4 H), 4.23-4.18 (m, 2 H), 4.11-3.97 (m, 4 H), 2.35 (s, 3 H), 1.32 (s, 18 H), 1.21 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.1, 197.3, 170.5, 157.3, 133.6, 128.1, 125.5, 77.3, 77.0, 76.7, 61.9, 59.4, 42.1, 35.1, 31.0, 26.3, 13.8. HRMS Calcd (ESI) m/z for $C_{30}H_{39}O_5$: $[M+H]^+$ 479.2792, found: 479.2798.



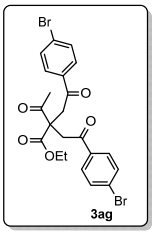
3ad: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.93 (d, *J* = 8.8 Hz, 4 H), 6.90 (d, *J* = 8.8 Hz, 4 H), 4.22-4.16 (m, 2 H), 4.05-3.91 (m, 4 H), 3.85 (s, 6 H), 2.33 (s, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.3, 196.1, 170.6, 163.7, 130.4, 129.3, 113.7, 77.3, 77.0, 76.7, 61.8, 59.5, 55.4, 41.9, 26.3, 13.8. HRMS Calcd (ESI) m/z for $C_{24}H_{26}NaO_7$: $[M+Na]^+$ 449.1571, found: 449.1556.



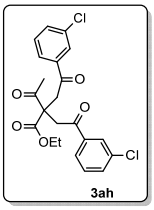
3ae: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (d, *J* = 8.4 Hz, 4 H), 7.18 (d, *J* = 8.0 Hz, 4 H), 4.22-4.17 (m, 2 H), 4.08-3.95 (m, 4 H), 2.32 (d, *J* = 9.6 Hz, 9 H), 1.19 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.9, 196.3, 170.2, 168.7, 154.6, 133.7, 129.7, 121.8, 121.6, 77.3, 77.0, 76.7, 62.0, 59.4, 42.1, 26.3, 21.0, 13.8. HRMS Calcd (ESI) m/z for $C_{26}H_{26}NaO_9$: $[M+Na]^+$ 505.1469, found: 505.1455.



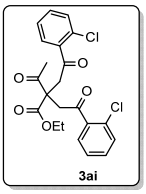
3af: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.00 (t, *J* = 5.6 Hz, 4 H), 7.13 (t, *J* = 8.4 Hz, 4 H), 4.23-4.18 (m, 2 H), 4.07-3.95 (m, 4 H), 2.35 (s, 3 H), 1.20 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.0, 196.1, 170.3, 166.0 (d, J_{CF} = 254.2 Hz), 132.6 (d, J_{CF} = 3.0 Hz), 130.8 (d, J_{CF} = 9.4 Hz), 115.8 (d, J_{CF} = 21.8 Hz), 77.3, 77.0, 76.7, 62.1, 59.5, 42.1, 26.4, 13.8. HRMS Calcd (ESI) m/z for $C_{22}H_{20}F_2NaO_5$: $[M+Na]^+$ 425.1171, found: 425.1158.



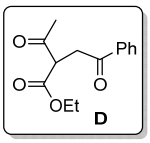
3ag: Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81 (d, *J* = 8.4 Hz, 4 H), 7.59 (d, *J* = 8.8 Hz, 4 H), 4.22-4.17 (m, 2 H), 4.03-3.91 (m, 4 H), 2.34 (s, 3 H), 1.19 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.8, 196.7, 170.2, 134.8, 132.0, 129.6, 128.9, 77.3, 77.2 77.0, 76.7, 62.1, 59.4, 42.1, 26.4, 13,8. HRMS Calcd (ESI) m/z for $C_{22}H_{20}Br_2KO_5$: $[M+K]^+$ 560.9309, found: 560.9308.



3ah: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.92 (s, 2 H), 7.84 (d, *J* = 7.6 Hz, 2 H), 7.54 (d, *J* = 7.6 Hz, 2 H), 7.41 (t, *J* = 7.6 Hz, 2 H), 4.23 (t, *J* = 6.8 Hz, 2 H), 4.05-3.94 (m, 4 H), 2.35 (s, 3 H), 1.21 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.8, 196.4, 170.1, 137.5, 135.0, 133.5, 130.0, 129.7, 128.1, 126.2, 77.3, 77.2 77.0, 76.7, 62.2, 59.3, 42.2, 26.4, 13,8. HRMS Calcd (ESI) m/z for $C_{22}H_{20}Cl_2NaO_5$: $[M+Na]^+$ 457.0580, found: 457.0565.

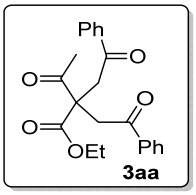


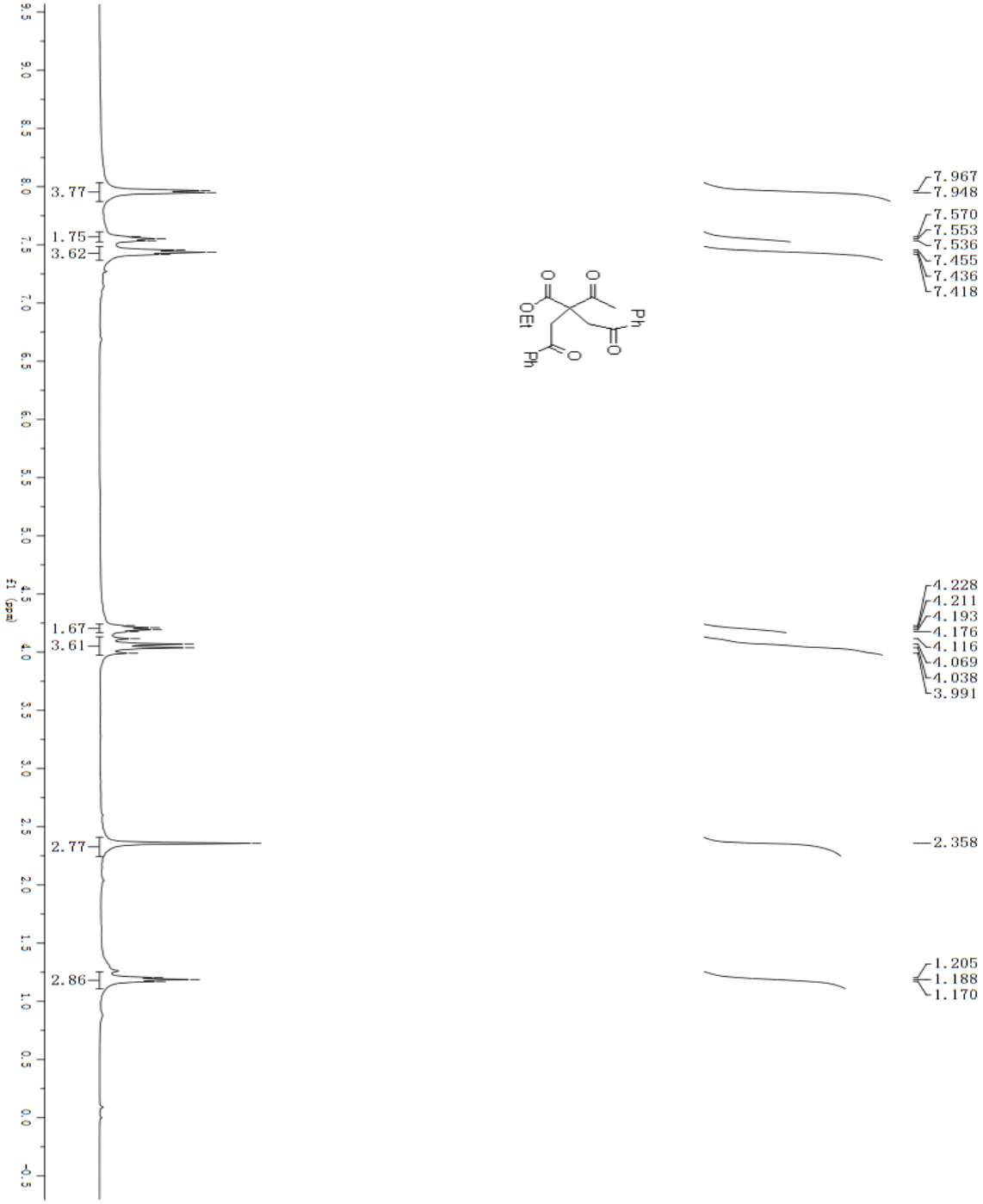
3ai: Yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.53 (d, *J* = 7.2 Hz, 2 H), 7.42 (s, 4 H), 7.35 (s, 2 H), 4.28-4.23 (m, 2 H), 4.03-3.93 (m, 4 H), 2.40 (s, 3 H), 1.29 (t, *J* = 6.8 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.7, 200.3, 170.0, 138.2, 132.1, 130.8, 130.6, 129.0, 126.9, 77.3, 77.0, 76.7, 62.2, 59.8, 46.2, 26.6, 13.9. HRMS Calcd (ESI) m/z for $C_{22}H_{20}Cl_2NaO_5$: $[M+Na]^+$ 457.0580, found: 457.0574.

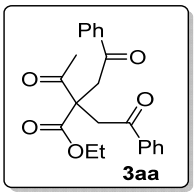


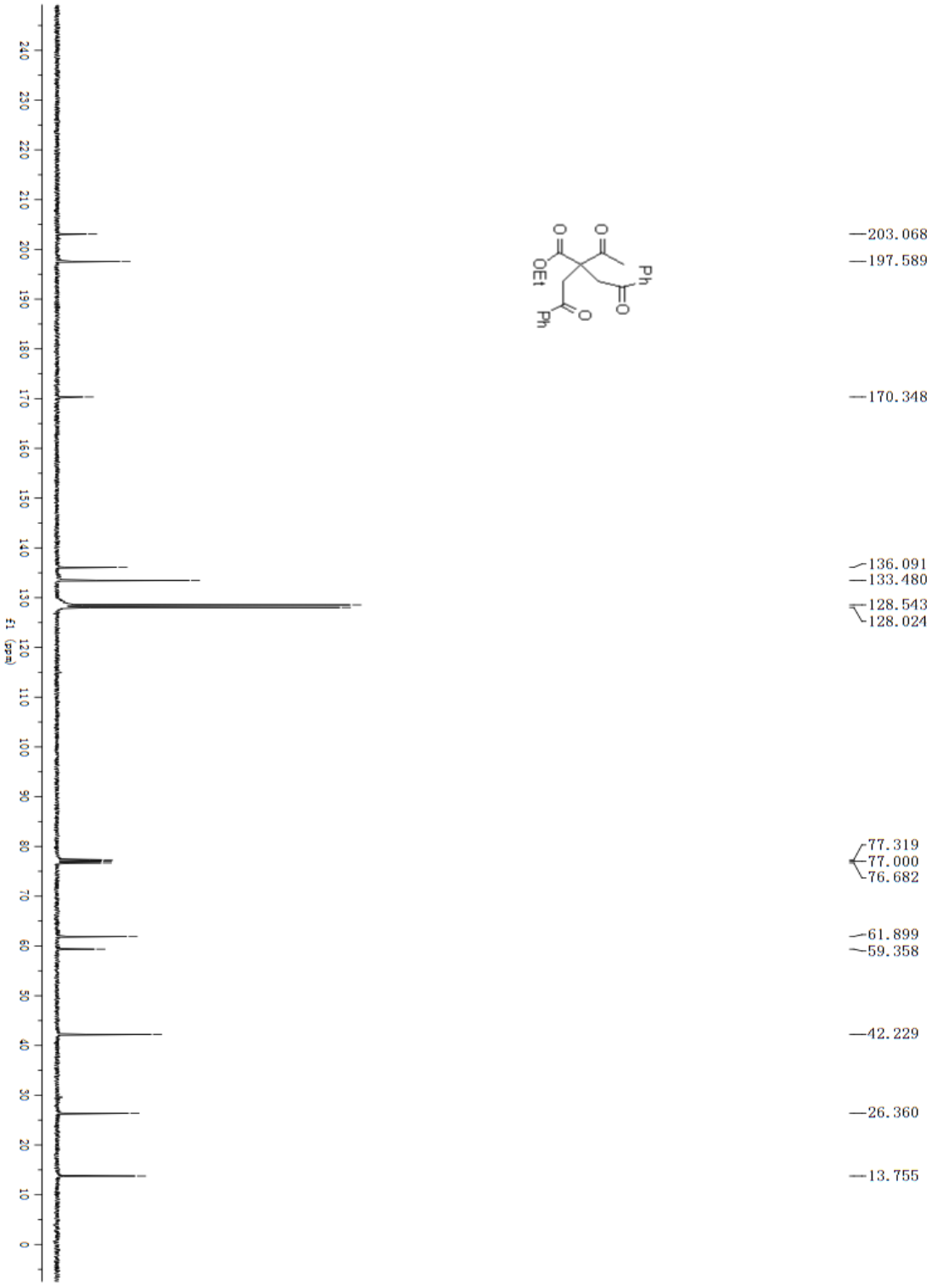
D: Colourless liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.98 (d, *J* = 7.2 Hz, 2 H), 7.59 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 4.26-4.20 (m, 3 H), 3.74 (dd, *J* = 18.4 Hz, 8.4 Hz, 1 H), 3.53 (dd, *J* = 18.4 Hz, 5.6 Hz, 1 H), 2.45 (s, 3 H), 1.30 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 202.4, 197.1, 168.9, 136.0, 133.5, 128.6, 128.1, 77.3, 77.2, 77.0, 76.7, 61.8, 53.8, 37.4, 30.3, 14.0. HRMS Calcd (ESI) m/z for $C_{14}H_{16}NaO_4$: $[M+Na]^+$ 271.0941, found: 271.0938.

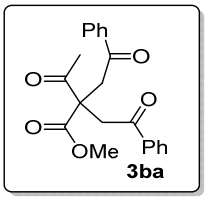
5. Appendix (copies of ^{1}H and ^{13}C NMR spectra)

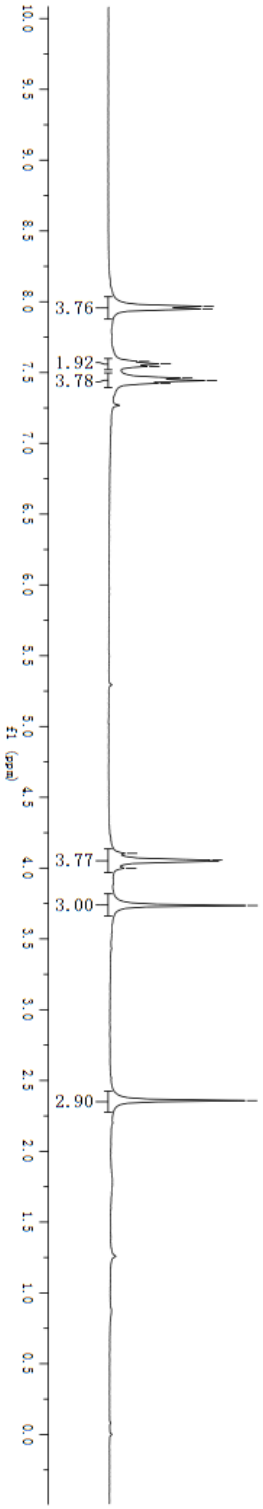


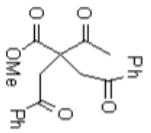


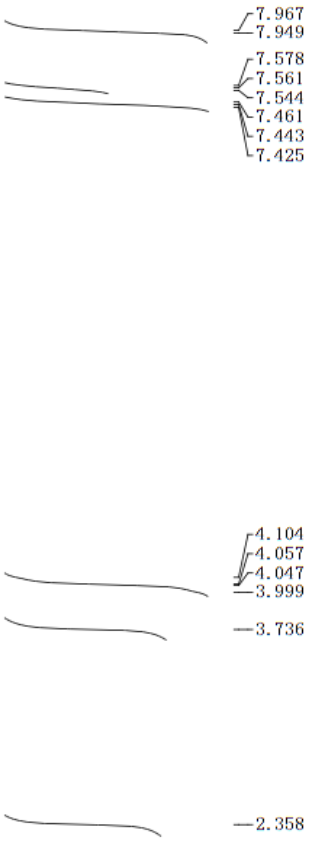

Ph
O
O
O
O
OEt
Ph
3aa

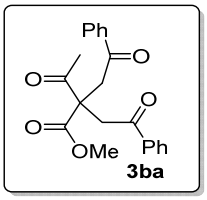

f1 (ppm)
203.068
197.589
170.348
136.091
133.480
128.543
128.024
77.319
77.000
76.682
61.899
59.358
42.229
26.360
13.755

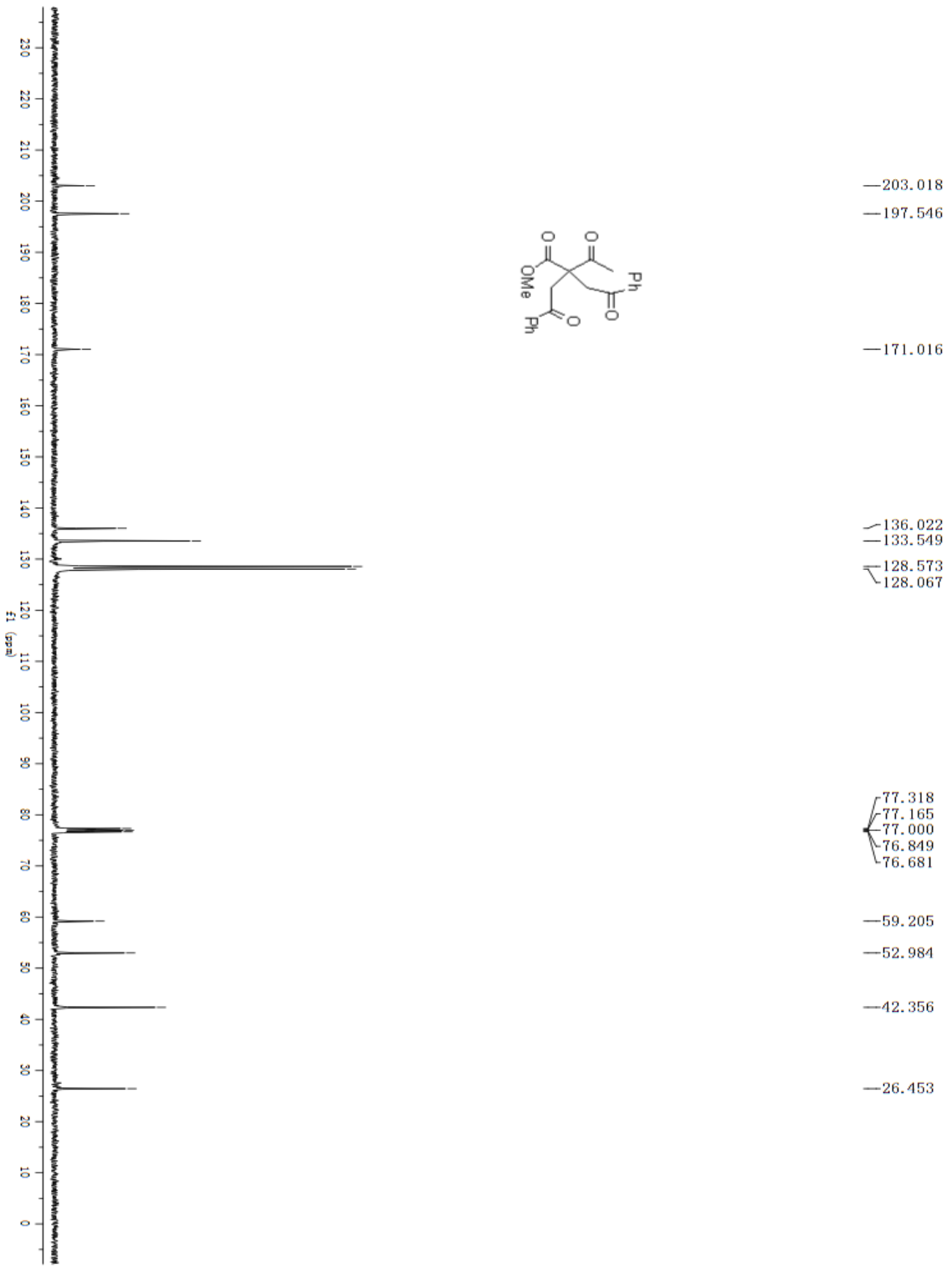

Ph
O
O
O
O
OMe
Ph
3ba

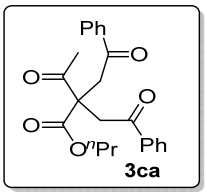

3.76
1.92
3.78
3.77
3.00
2.90
f1 (ppm)

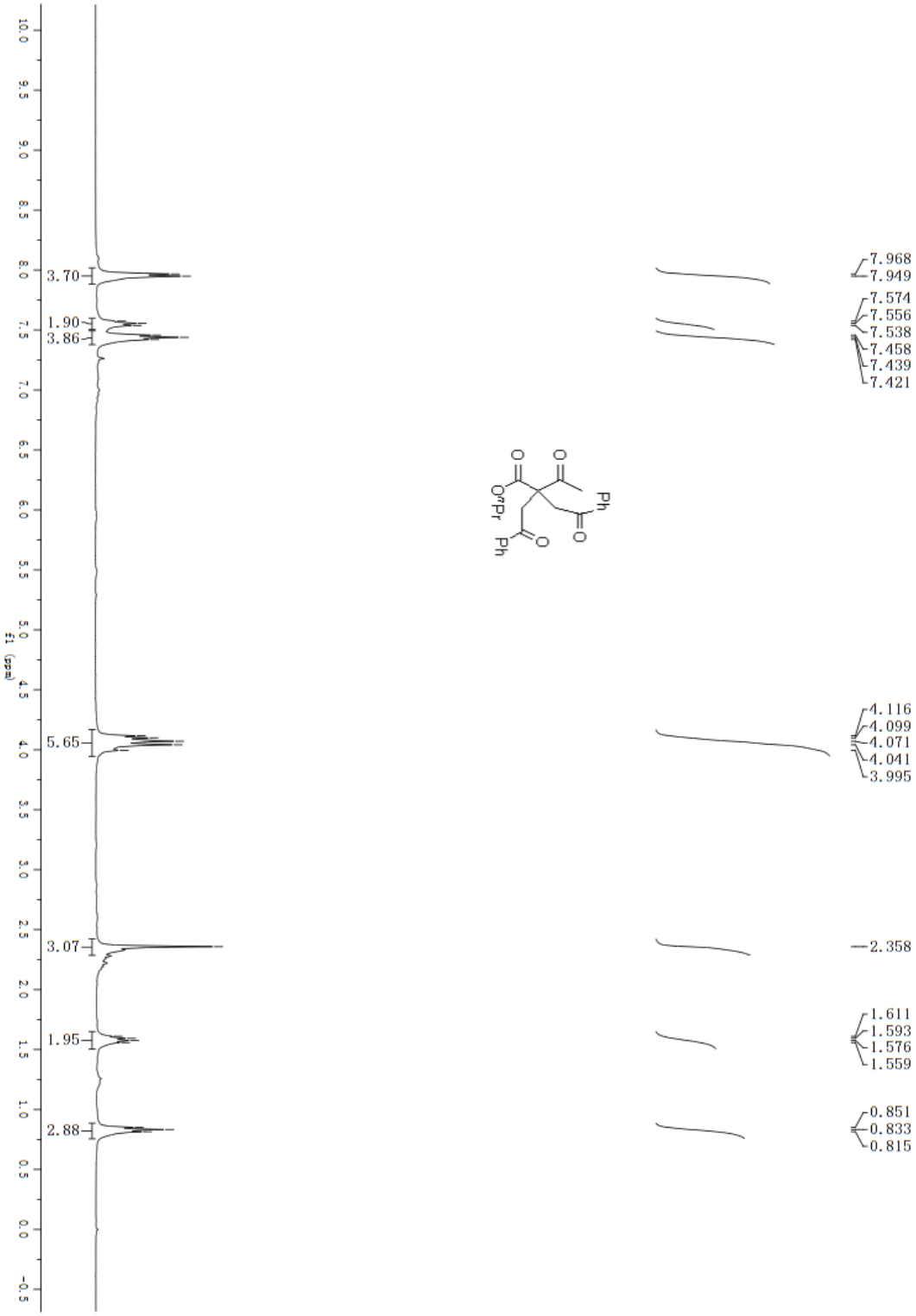

O
O
OMe
Ph
Ph
O

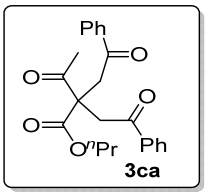

7.967
7.949
7.578
7.561
7.544
7.461
7.443
7.425
4.104
4.057
4.047
3.999
3.736
2.358


Ph
O
O
O
OMe
O
Ph
3ba

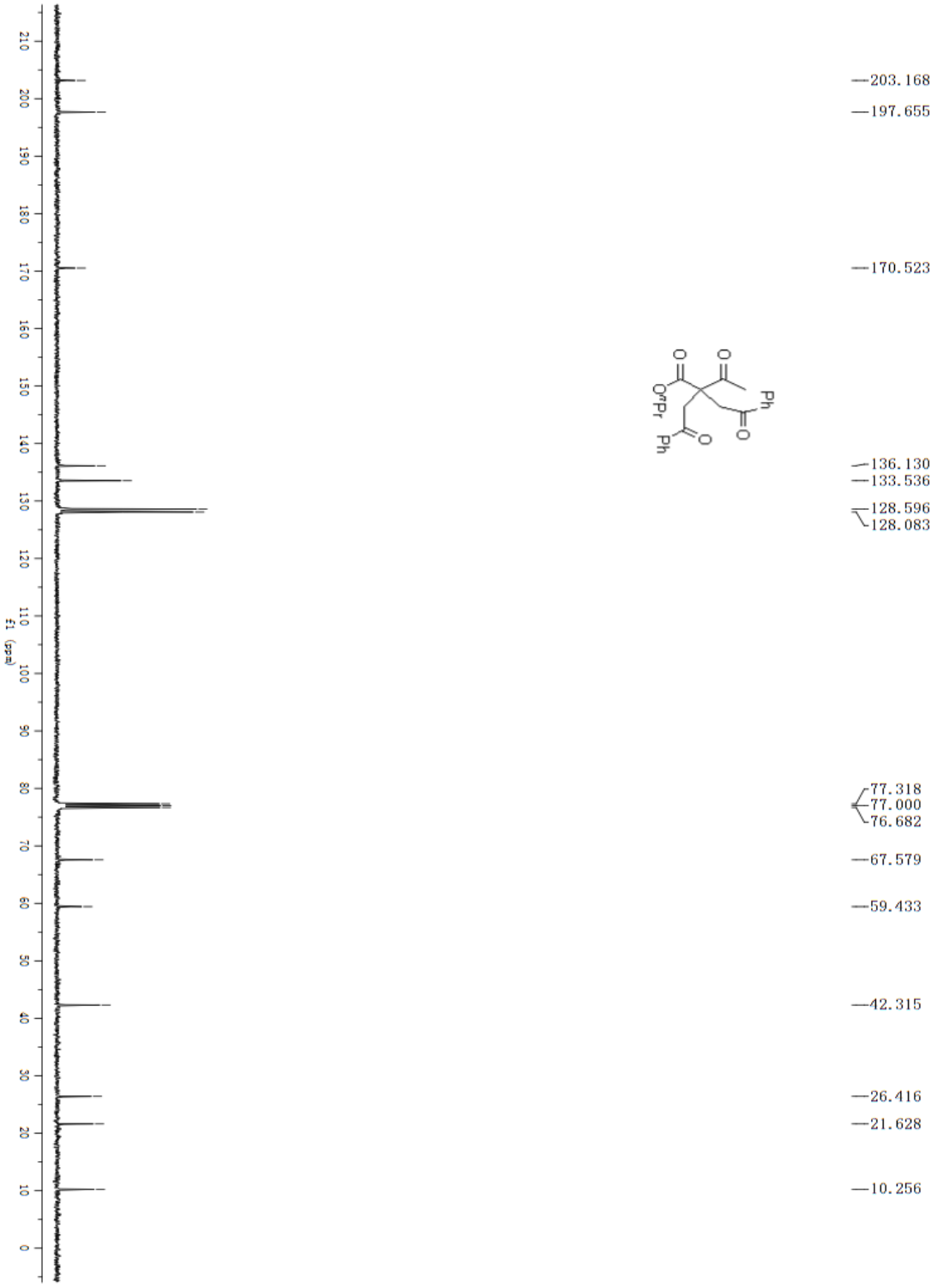

f1 (ppm)
203.018
197.546
171.016
136.022
133.549
128.573
128.067
77.318
77.165
77.000
76.849
76.681
59.205
52.984
42.356
26.453

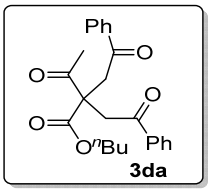

Ph
O
O
O
O
O^{n}Pr
Ph
3ca


3.70
1.90
3.86
5.65
3.07
1.95
2.88
7.968
7.949
7.574
7.556
7.538
7.458
7.439
7.421
4.116
4.099
4.071
4.041
3.995
2.358
1.611
1.593
1.576
1.559
0.851
0.833
0.815

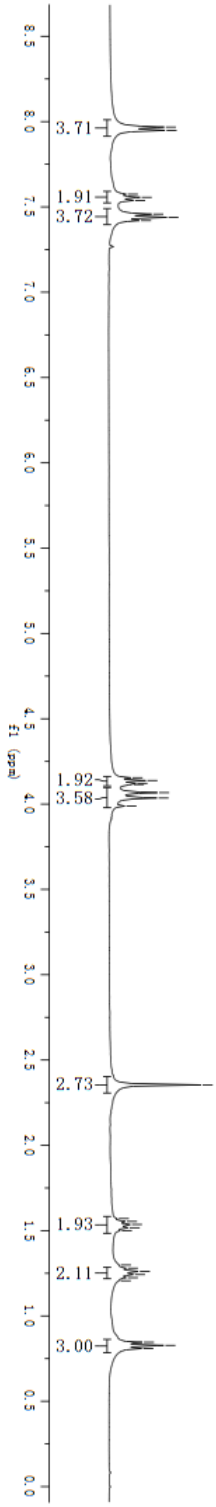

Ph
O
O
O
O
O^{n}Pr
Ph

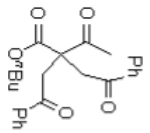
3ca

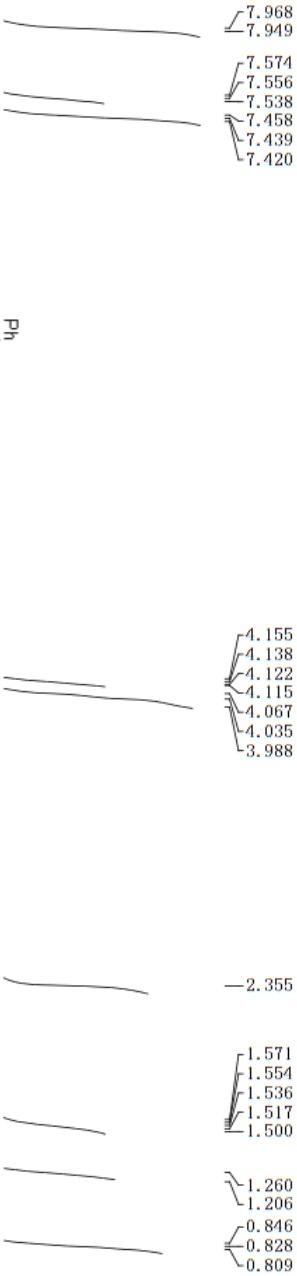

f1 (ppm)
203.168
197.655
170.523
136.130
133.536
128.596
128.083
77.318
77.000
76.682
67.579
59.433
42.315
26.416
21.628
10.256

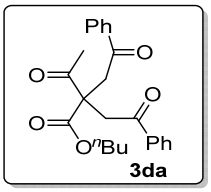

Ph
O
O
O
O
O
nBu
Ph

3da

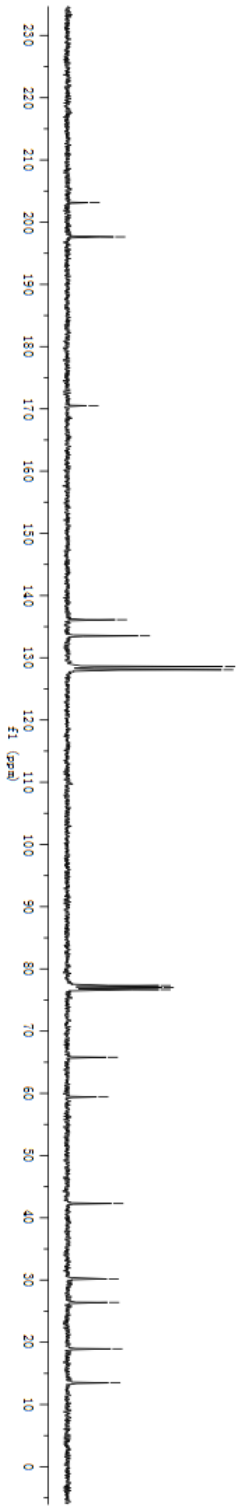

3.71
1.91
3.72
1.92
3.58
2.73
1.93
2.11
3.00
f1 (ppm)

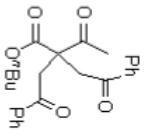

O
O
O
nBu
Ph
Ph
O


7.968
7.949
7.574
7.556
7.538
7.458
7.439
7.420
4.155
4.138
4.122
4.115
4.067
4.035
3.988
2.355
1.571
1.554
1.536
1.517
1.500
1.260
1.206
0.846
0.828
0.809

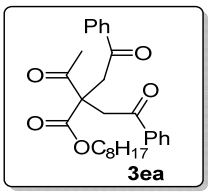


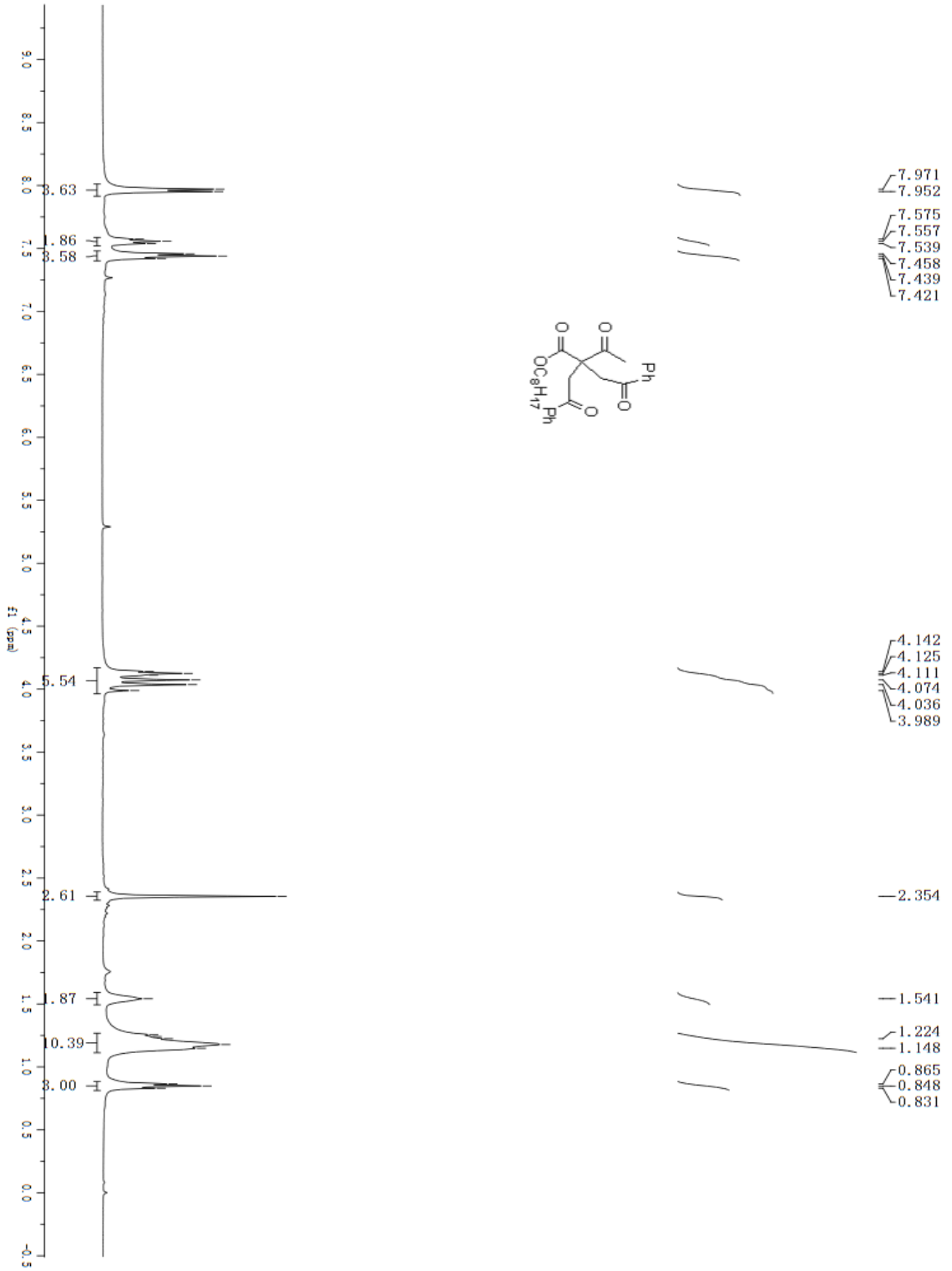
3da

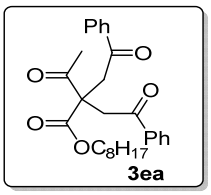




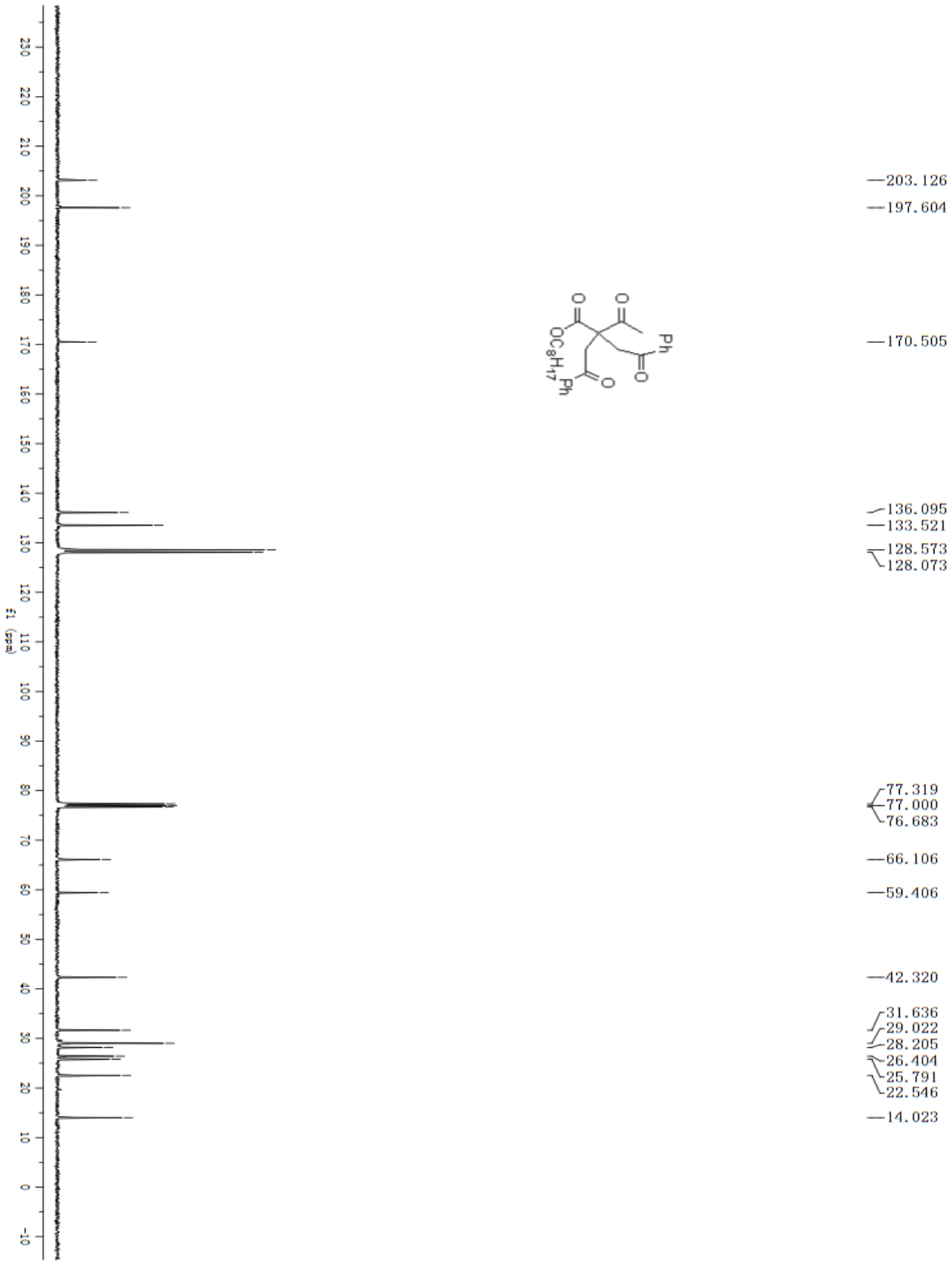
203.135
197.632
170.516
136.114
133.520
128.576
128.066
77.318
77.000
76.682
65.800
59.419
42.297
30.180
26.402
18.945
13.471

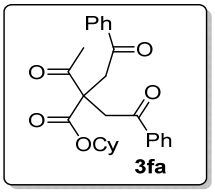

Ph
O
O
O
O
OC8H17
Ph
3ea

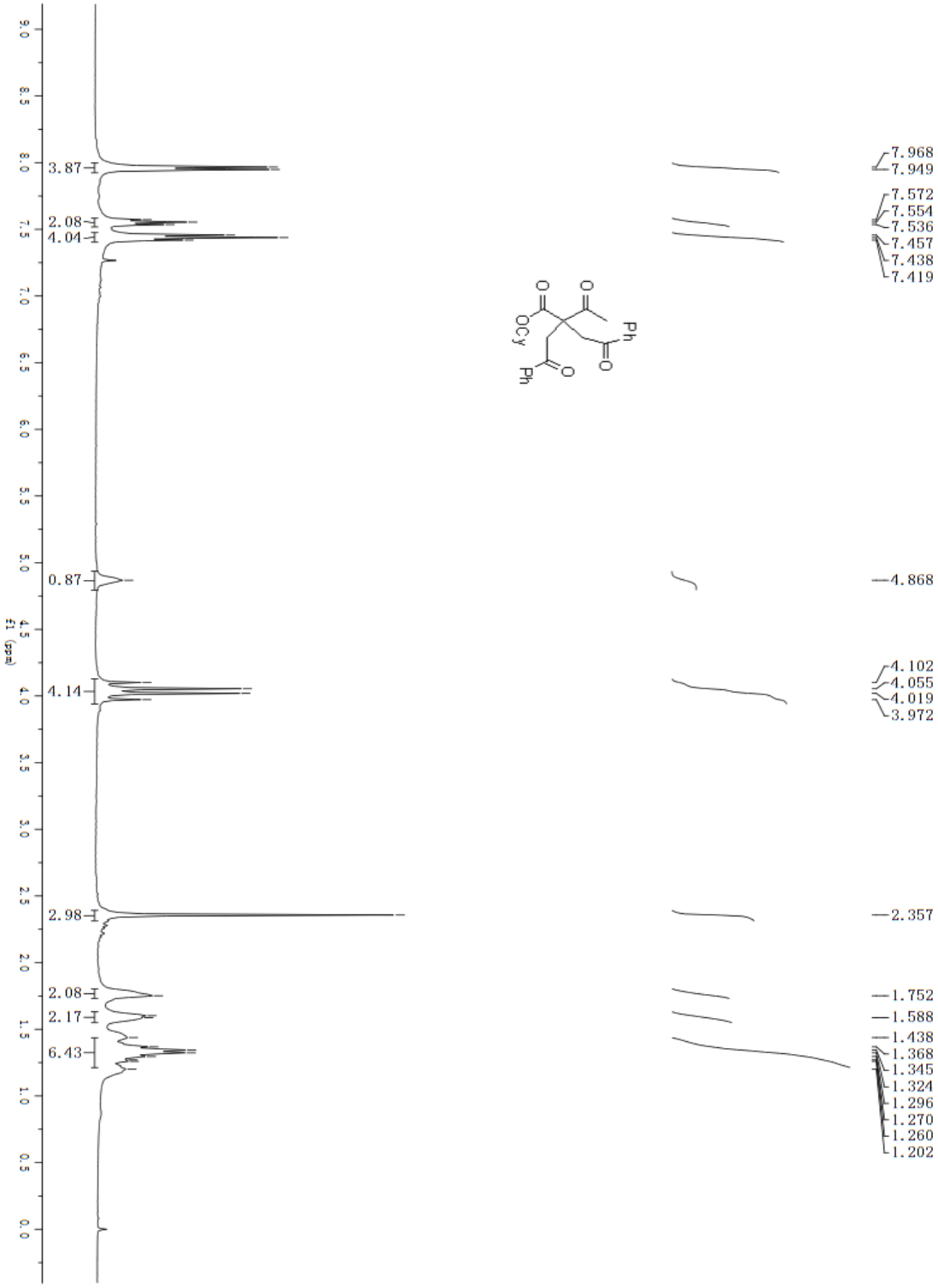

3.63
1.86
3.58
5.54
2.61
1.87
10.39
3.00
7.971
7.952
7.575
7.557
7.539
7.458
7.439
7.421
4.142
4.125
4.111
4.074
4.036
3.989
2.354
1.541
1.224
1.148
0.865
0.848
0.831

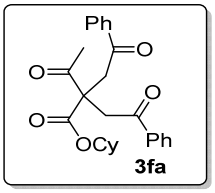

Ph
O
O
O
O
OC8H17
Ph

3ea

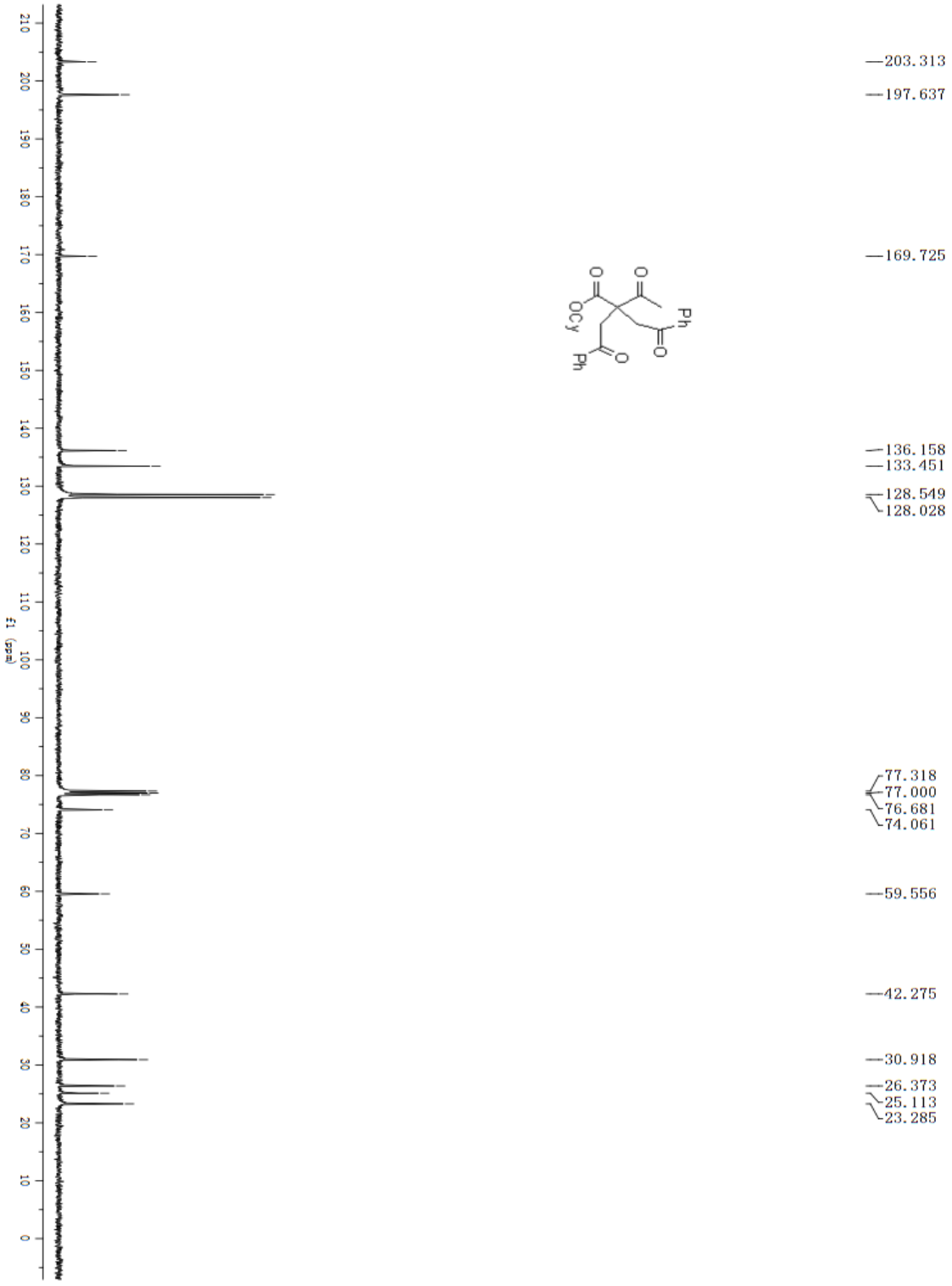

f1 (ppm)
203.126
197.604
170.505
136.095
133.521
128.573
128.073
77.319
77.000
76.683
66.106
59.406
42.320
31.636
29.022
28.205
26.404
25.791
22.546
14.023

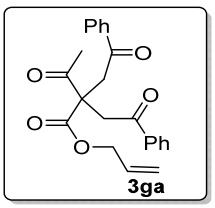

Ph
O
O
O
O
OCy
Ph
3fa

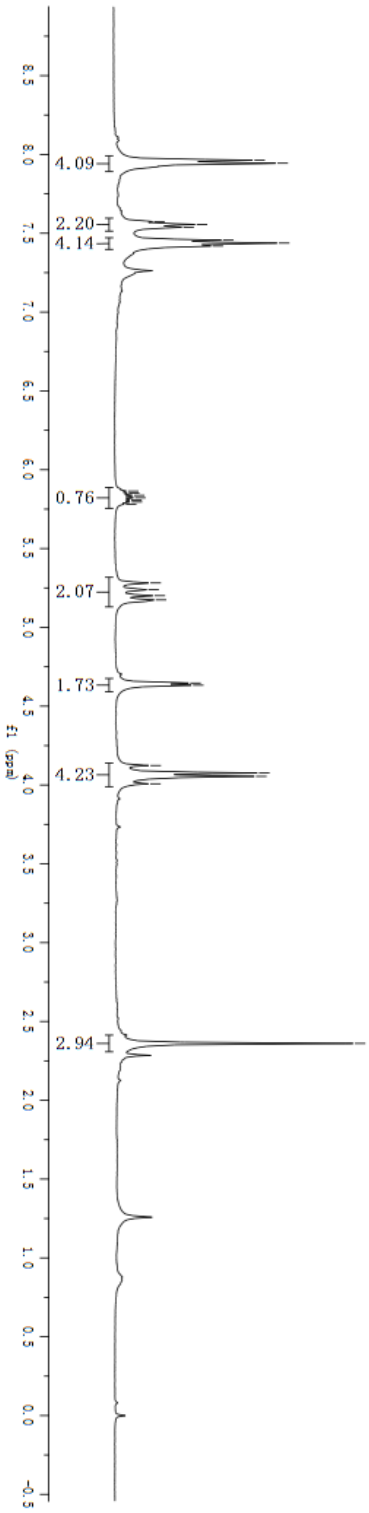

3.87
2.08
4.04
0.87
4.14
2.98
2.08
2.17
6.43
7.968
7.949
7.572
7.554
7.536
7.457
7.438
7.419
4.868
4.102
4.055
4.019
3.972
2.357
1.752
1.588
1.438
1.368
1.345
1.324
1.296
1.270
1.260
1.202

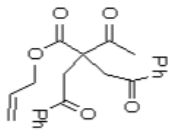

Ph
O
O
O
O
OCy
Ph

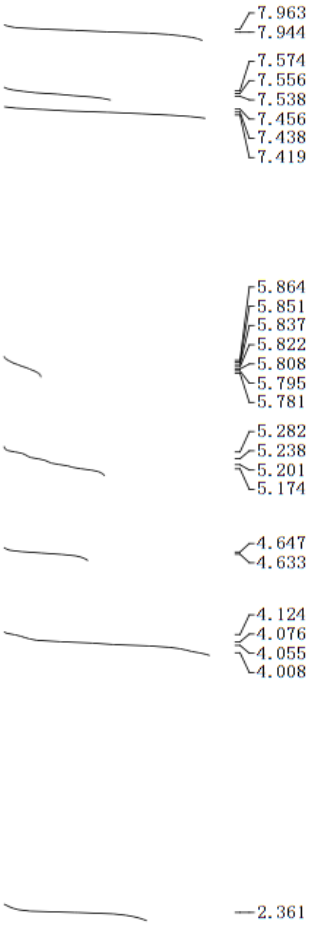
3fa

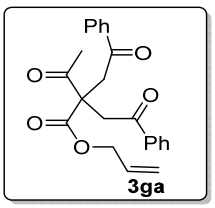

f1 (ppm)
203.313
197.637
169.725
136.158
133.451
128.549
128.028
77.318
77.000
76.681
74.061
59.556
42.275
30.918
26.373
25.113
23.285

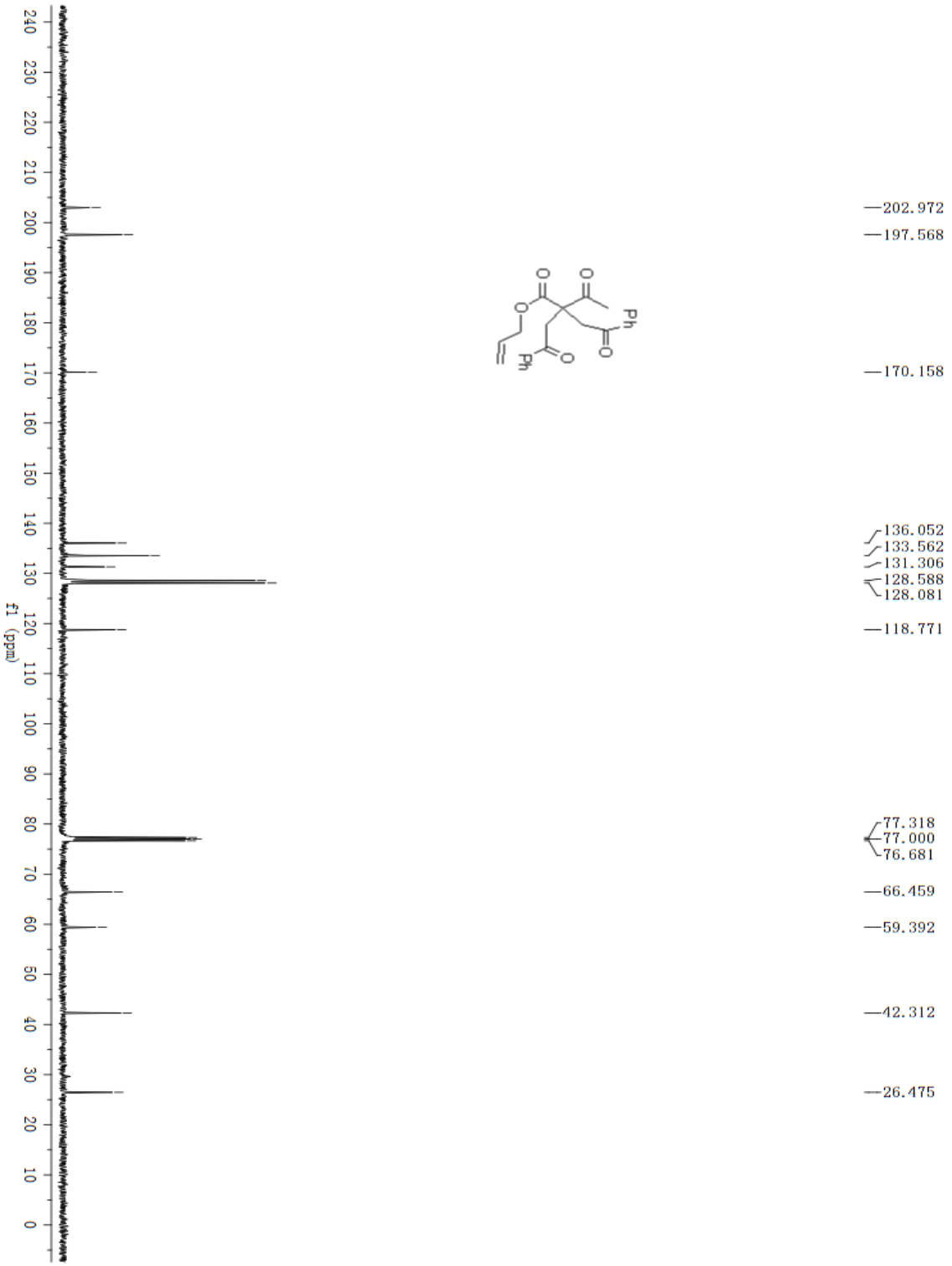

Ph
O
O
O
O
Ph
O
3ga

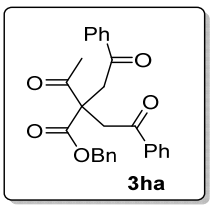

4.09
2.20
4.14
0.76
2.07
1.73
4.23
2.94
f1 (ppm)


O
O
O
Ph
O
Ph

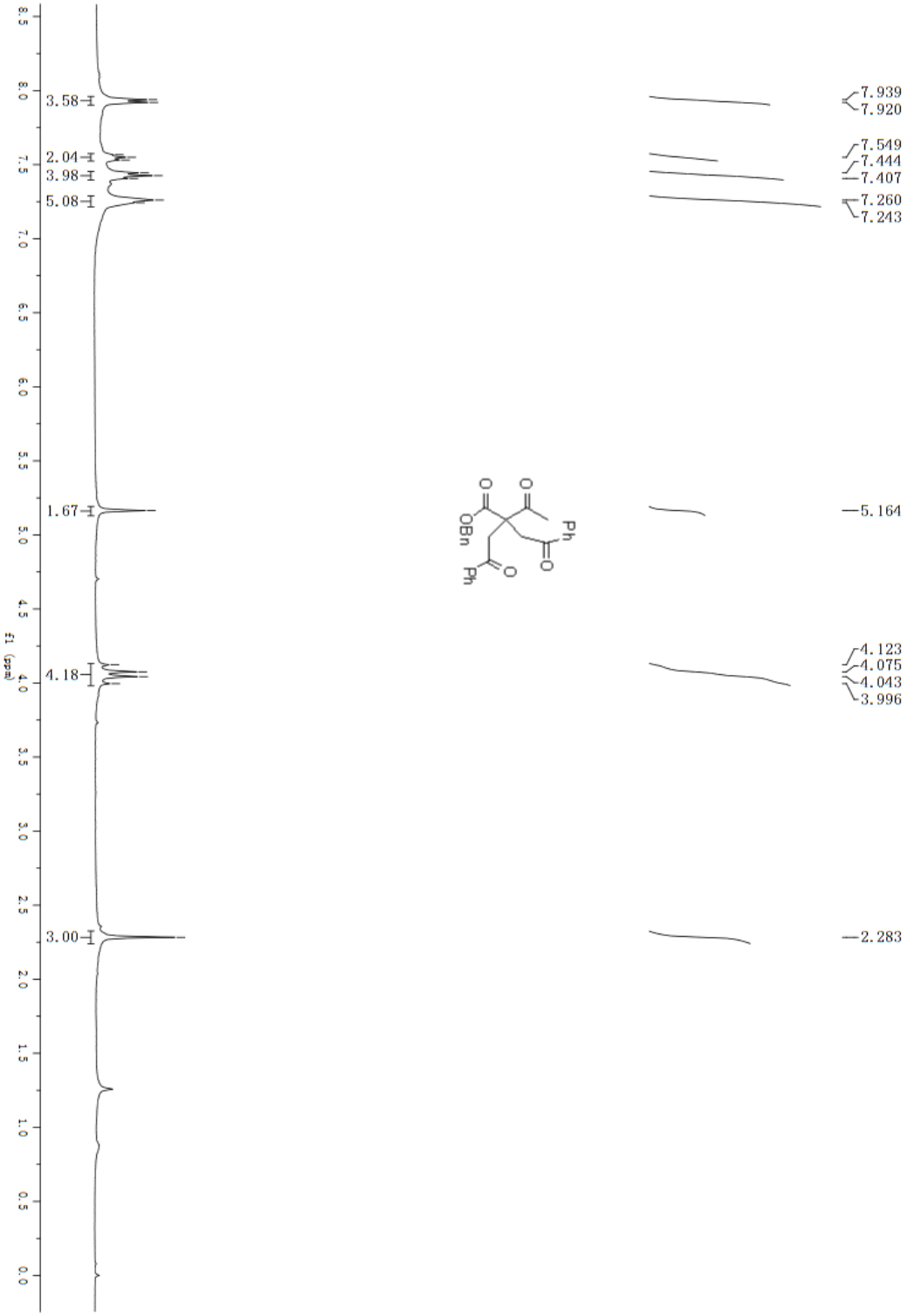

7.963
7.944
7.574
7.556
7.538
7.456
7.438
7.419
5.864
5.851
5.837
5.822
5.808
5.795
5.781
5.282
5.238
5.201
5.174
4.647
4.633
4.124
4.076
4.055
4.008
2.361

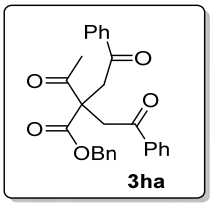

Ph
O
O
O
O
Ph
O
3ga


f1 (ppm)
202.972
197.568
170.158
136.052
133.562
131.306
128.588
128.081
118.771
77.318
77.000
76.681
66.459
59.392
42.312
26.475

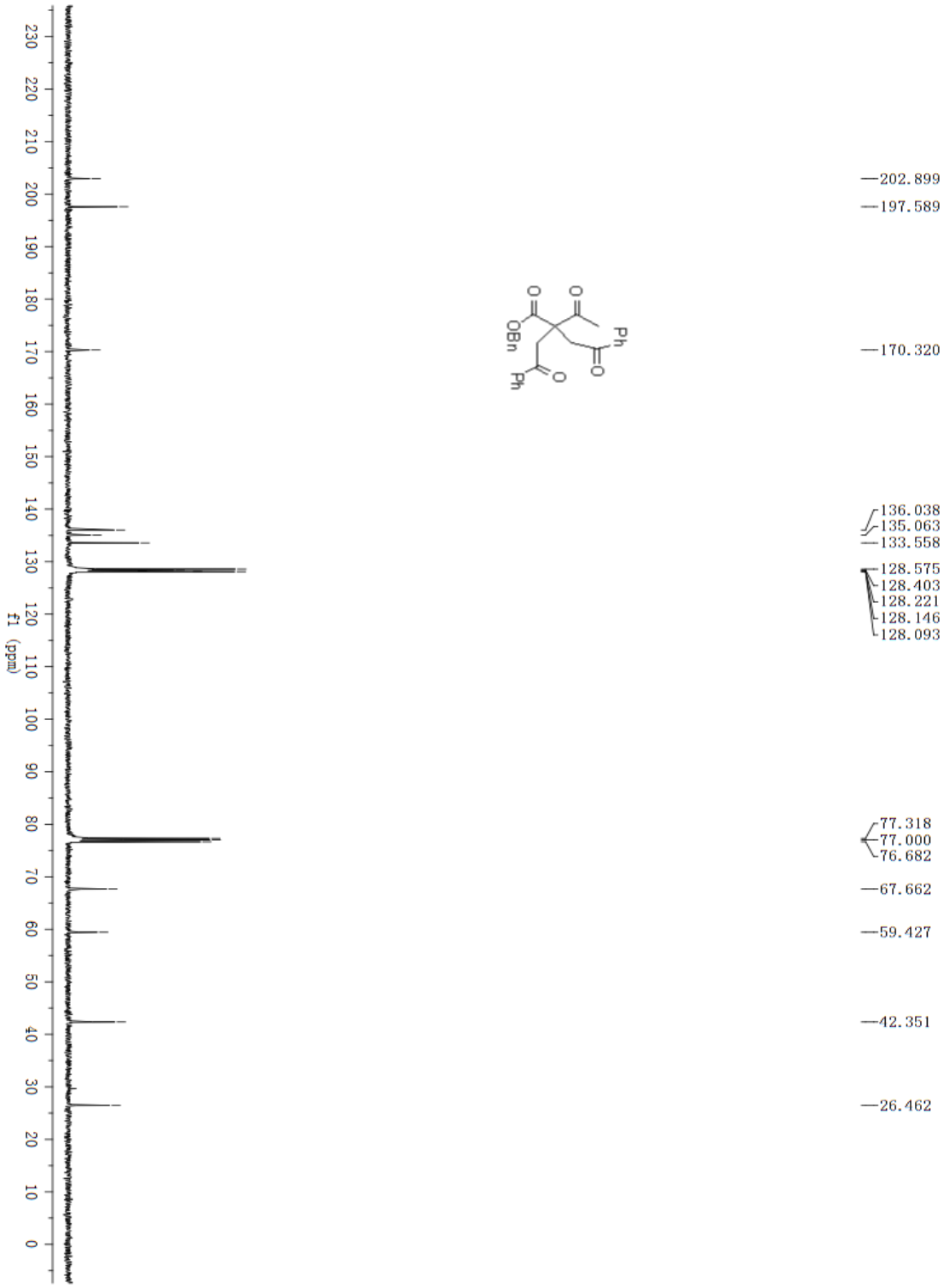

Ph
O
O
O
O
OBn
Ph

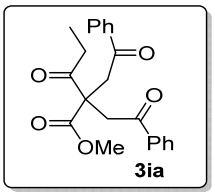
3ha


3.58
2.04
3.98
5.08
1.67
4.18
3.00
f1 (ppm)
7.939
7.920
7.549
7.444
7.407
7.260
7.243
5.164
4.123
4.075
4.043
3.996
2.283

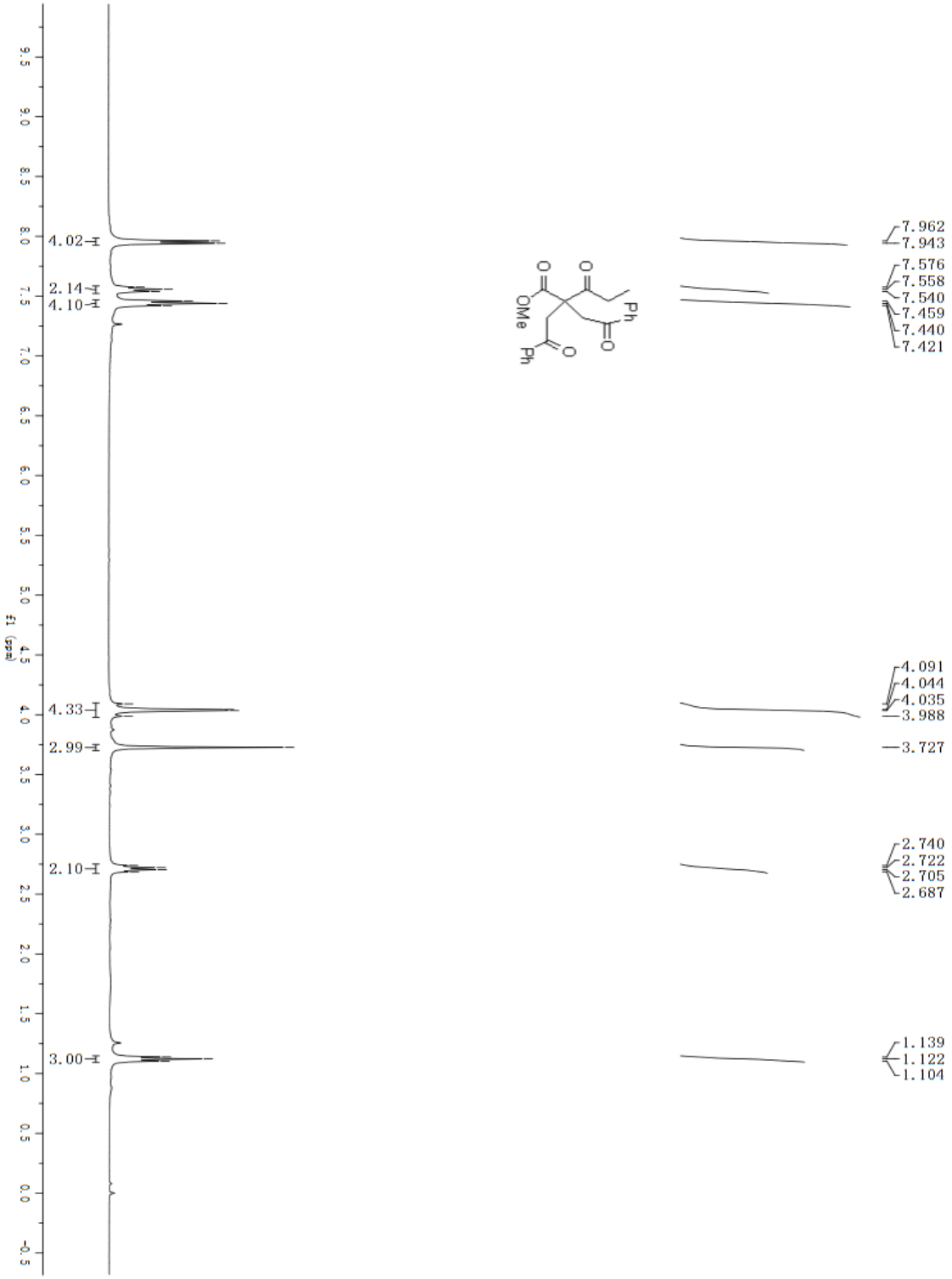

Ph
O
O
O
O
OBn
Ph

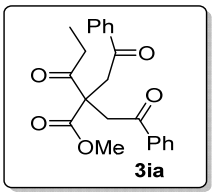
3ha


f1 (ppm)
202.899
197.589
170.320
136.038
135.063
133.558
128.575
128.403
128.221
128.146
128.093
77.318
77.000
76.682
67.662
59.427
42.351
26.462

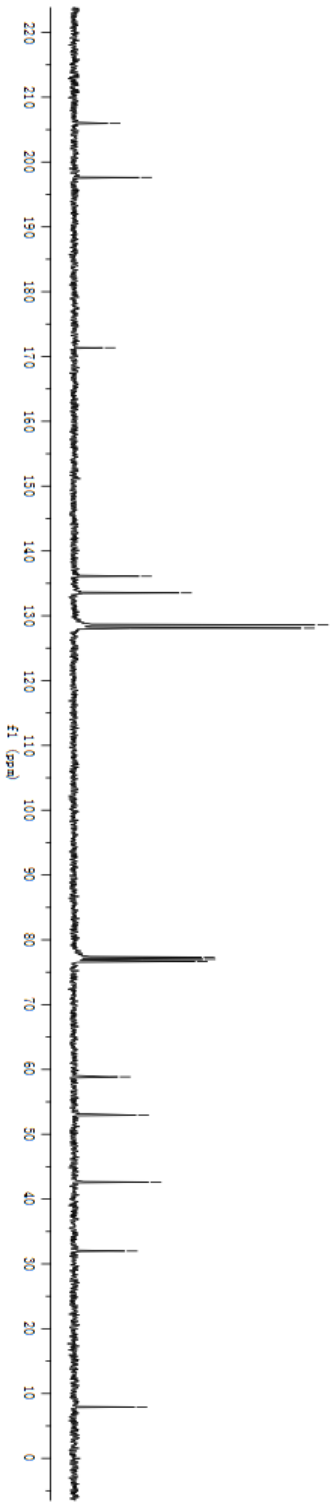

Ph
O
O
O
O
OMe
Ph

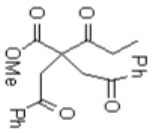
3ia


4.02
2.14
4.10
4.33
2.99
2.10
3.00
f1 (ppm)
7.962
7.943
7.576
7.558
7.540
7.459
7.440
7.421
4.091
4.044
4.035
3.988
3.727
2.740
2.722
2.705
2.687
1.139
1.122
1.104

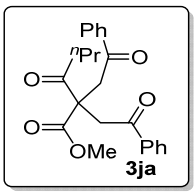


3ia

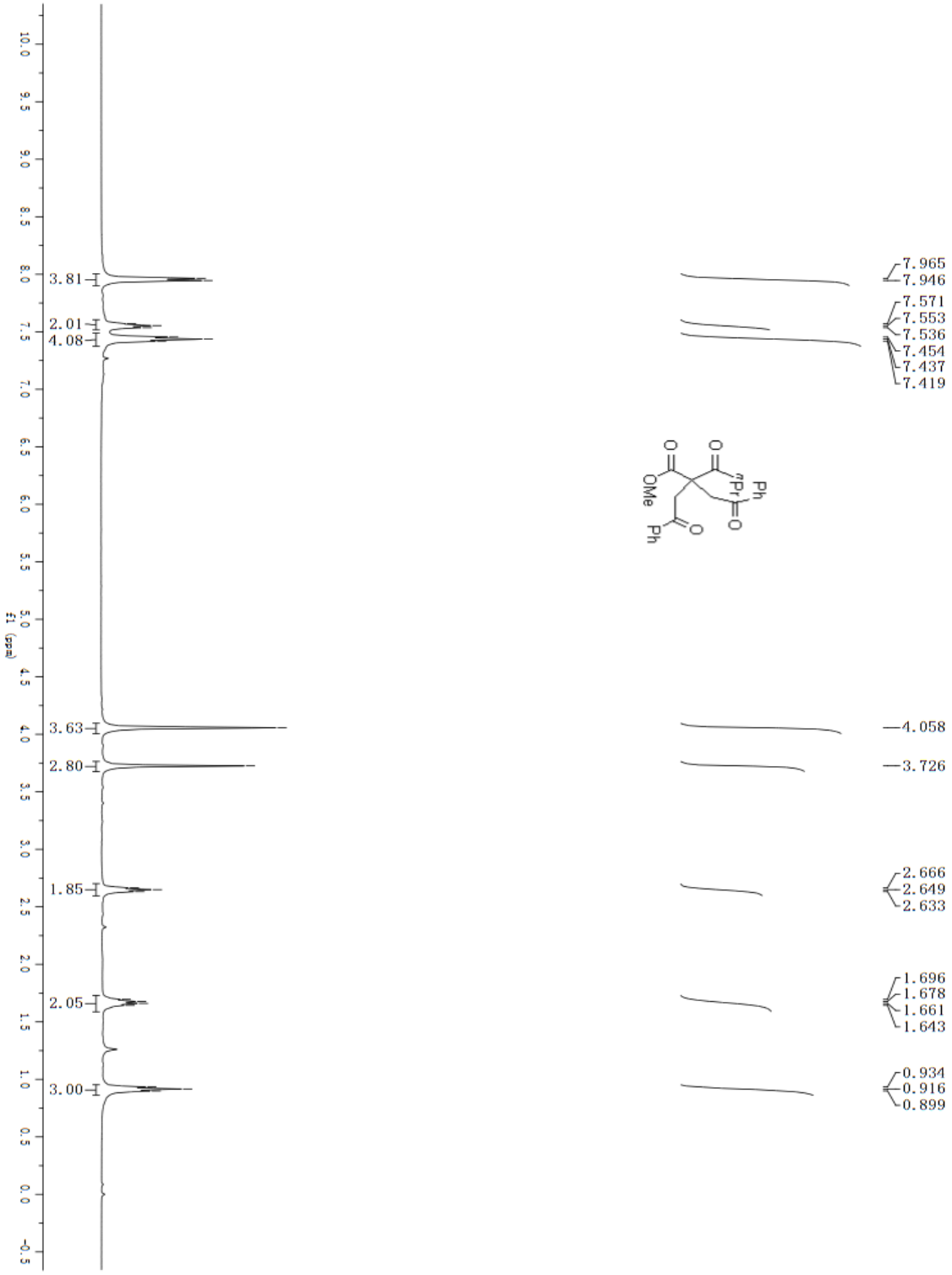


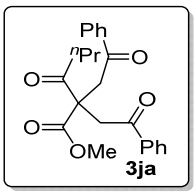


205.962
197.619
171.342
136.097
133.528
128.582
128.086
77.317
77.000
76.681
58.857
52.934
42.620
31.978
7.919

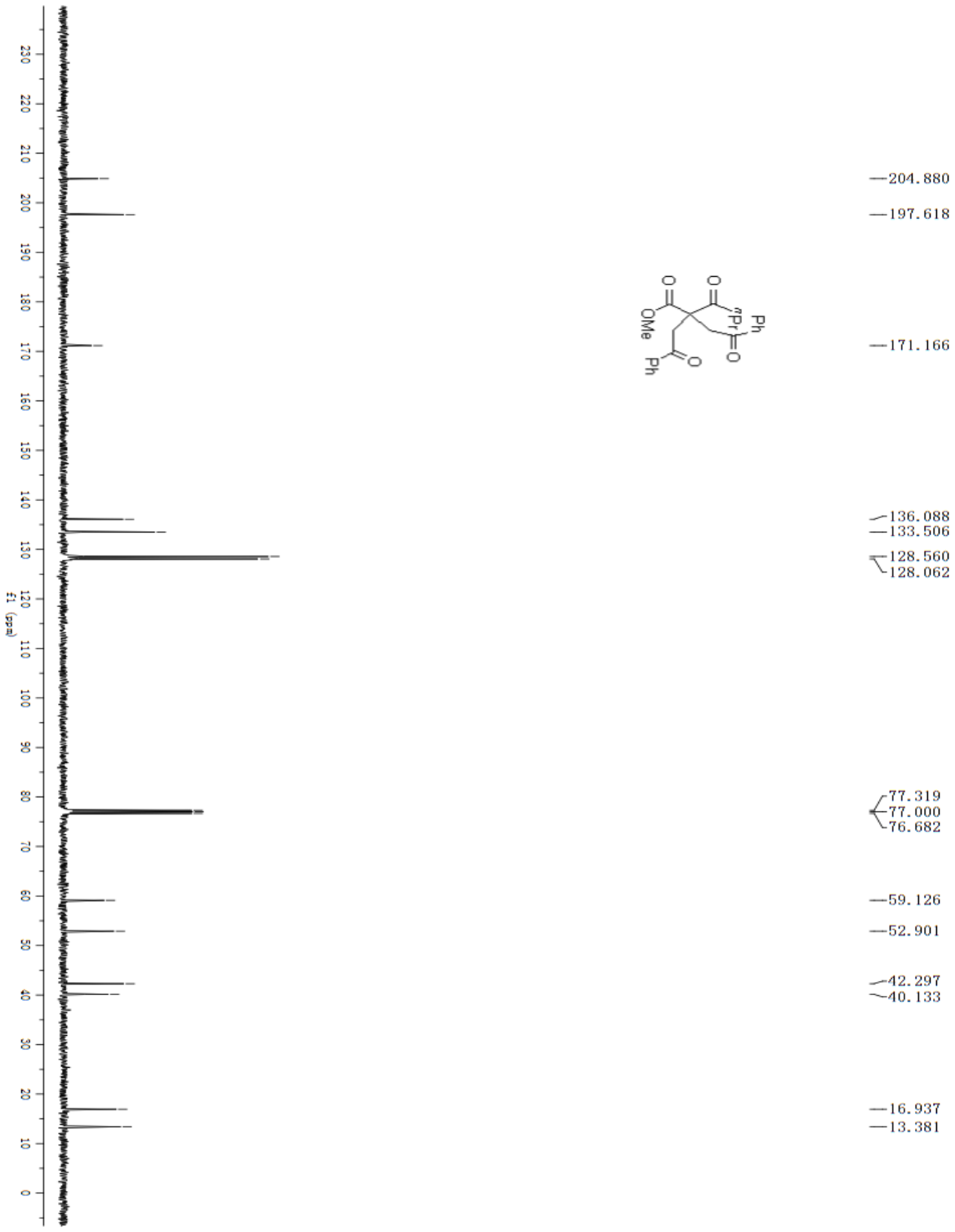

Ph
nPr
O
O
O
O
OMe
Ph

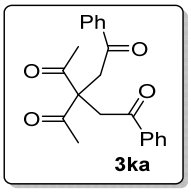
3ja


3.81
2.01
4.08
3.63
2.80
1.85
2.05
3.00
7.965
7.946
7.571
7.553
7.536
7.454
7.437
7.419
4.058
3.726
2.666
2.649
2.633
1.696
1.678
1.661
1.643
0.934
0.916
0.899

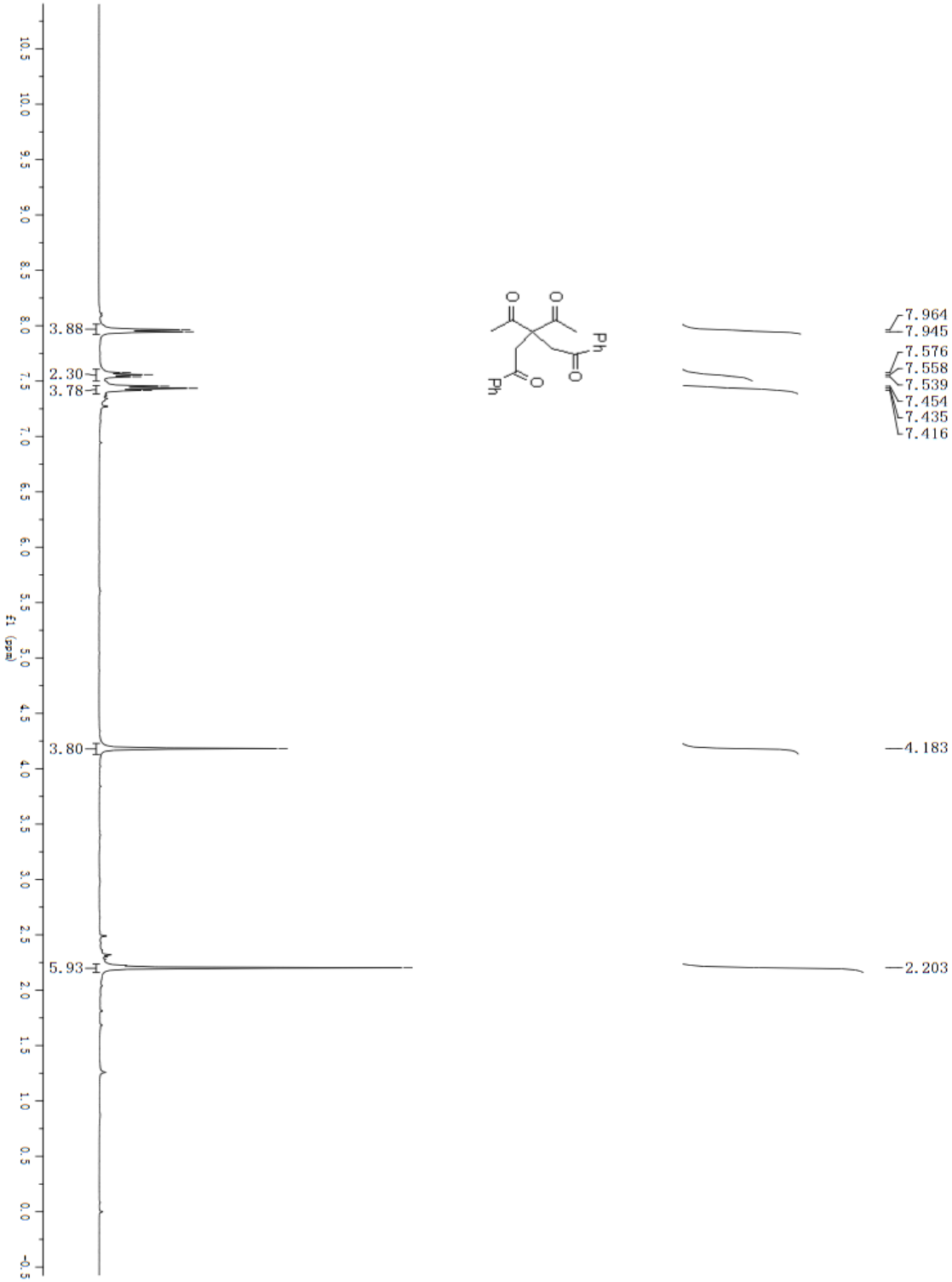

Ph
nPr
O
O
O
O
OMe
Ph

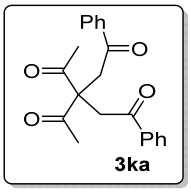
3ja


f1 (ppm)
204.880
197.618
171.166
136.088
133.506
128.560
128.062
77.319
77.000
76.682
59.126
52.901
42.297
40.133
16.937
13.381

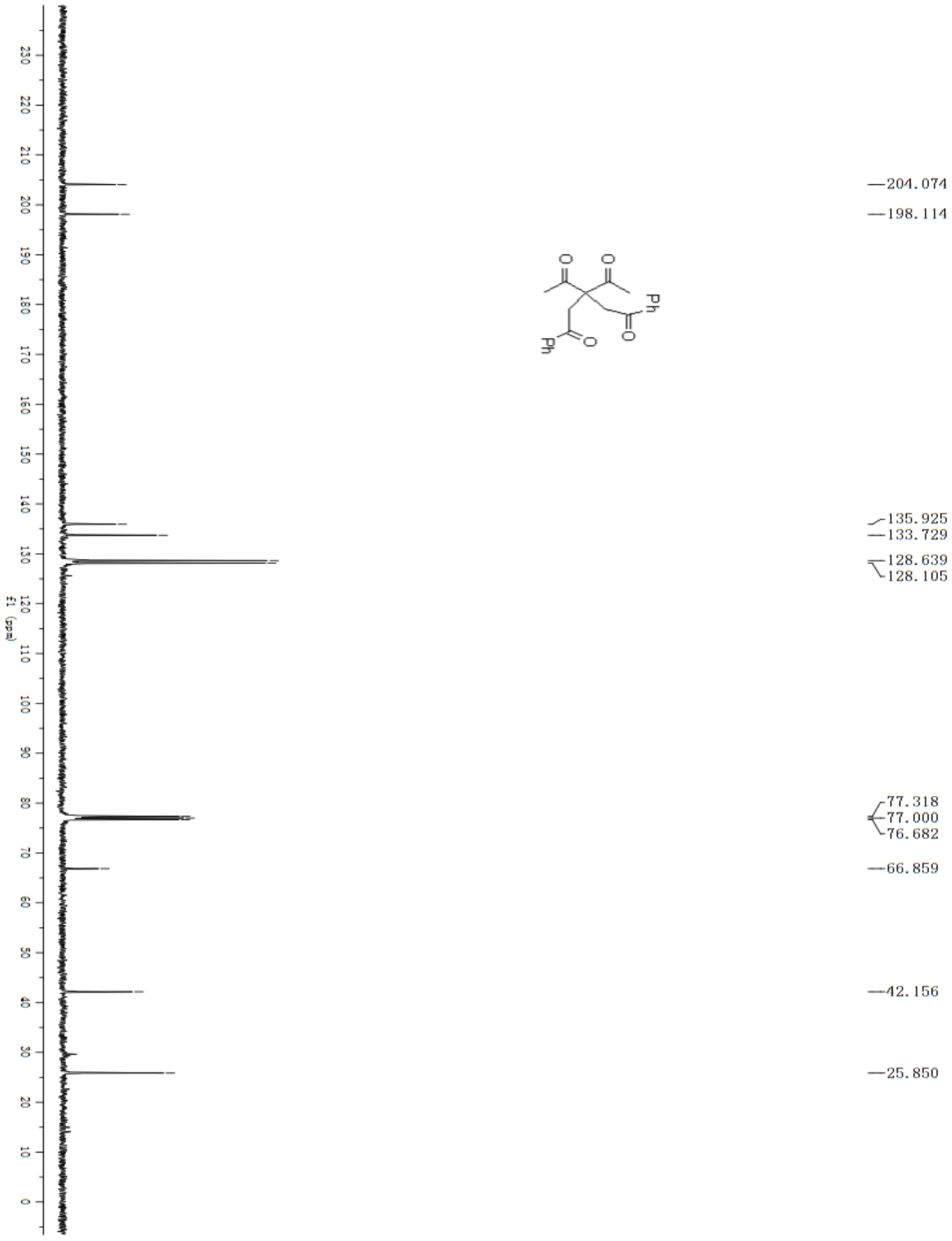

Ph
O
O
O
O
Ph

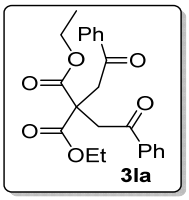
3ka


3.88
2.30
3.78
3.80
5.93
f1 (ppm)
7.964
7.945
7.576
7.558
7.539
7.454
7.435
7.416
4.183
2.203

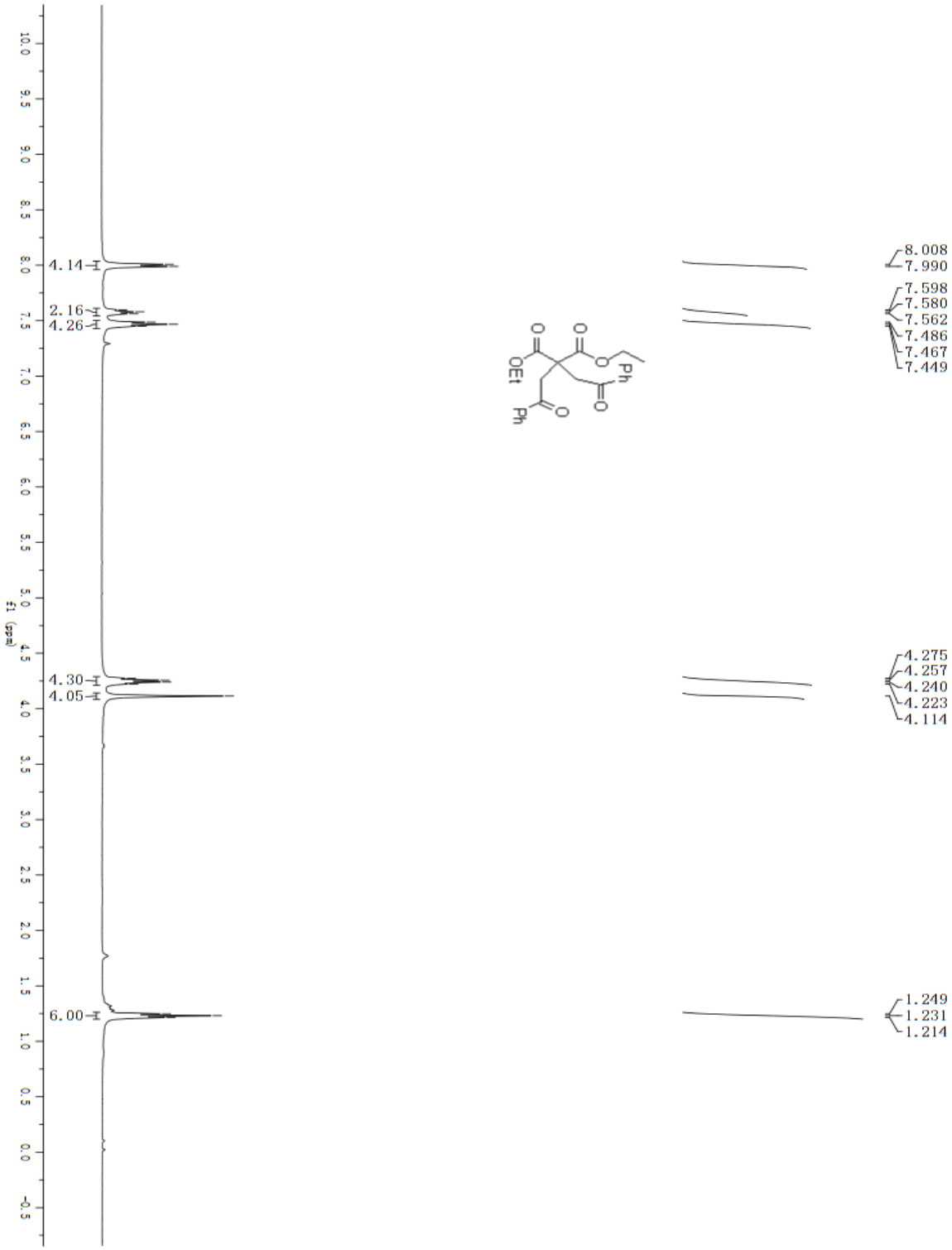

Ph
O
O
O
O
Ph

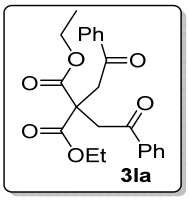
3ka


f1 (ppm)
204.074
198.114
135.925
133.729
128.639
128.105
77.318
77.000
76.682
66.859
42.156
25.850

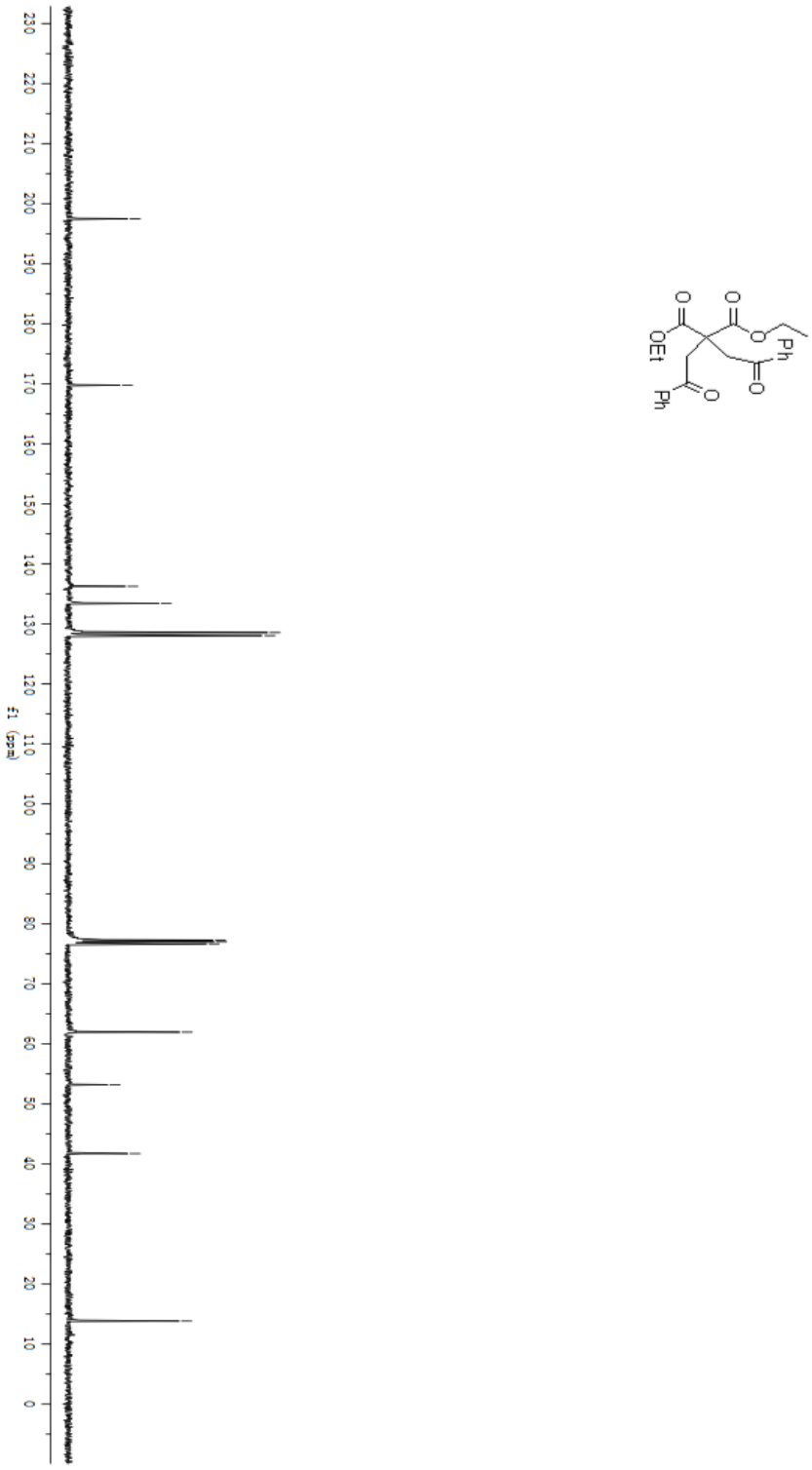

Ph
O
O
O
O
O
OEt
Ph

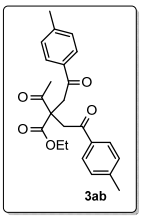
3la

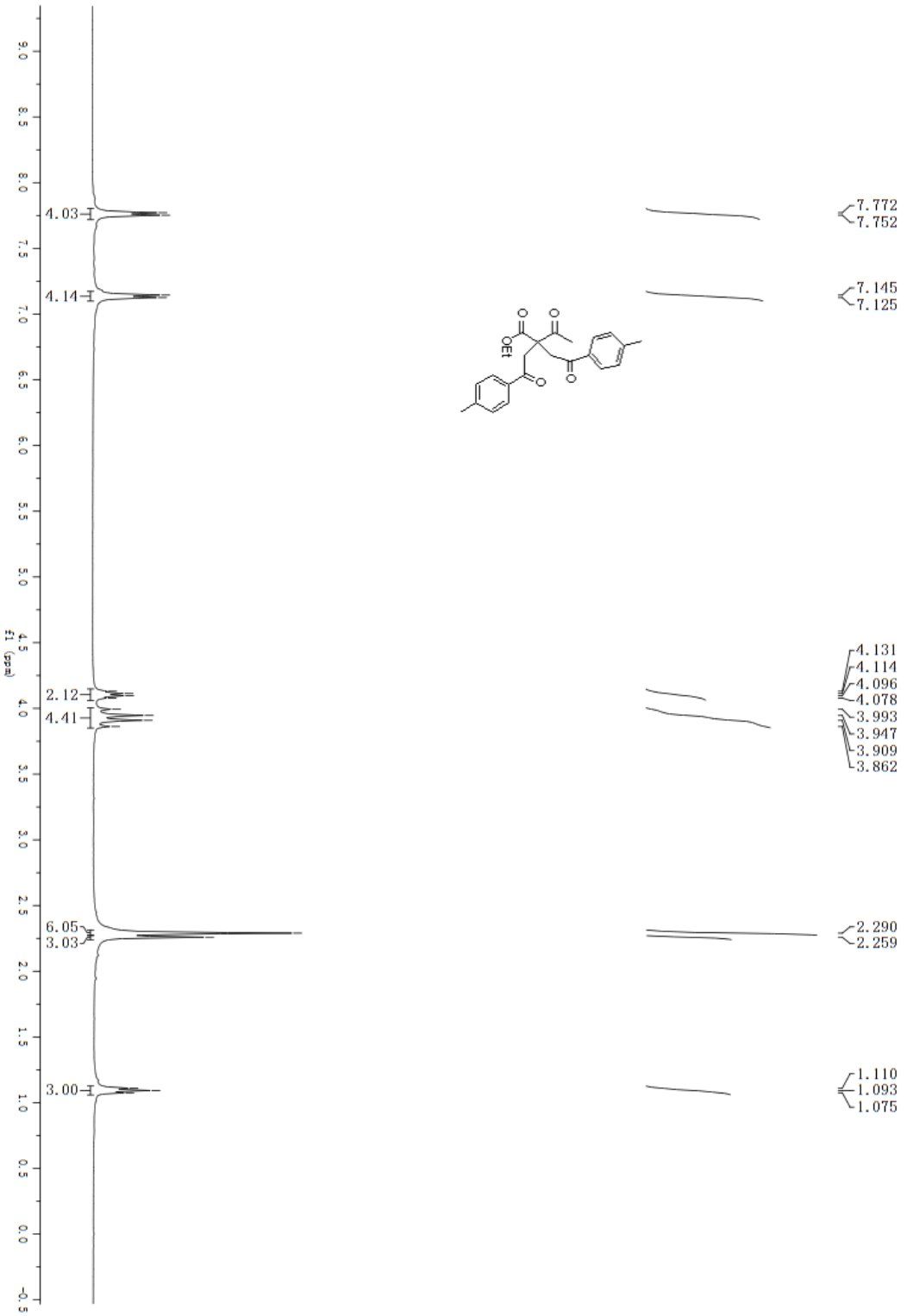

4.14
2.16
4.26
4.30
4.05
6.00
f1 (ppm)
8.008
7.990
7.598
7.580
7.562
7.486
7.467
7.449
4.275
4.257
4.240
4.223
4.114
1.249
1.231
1.214

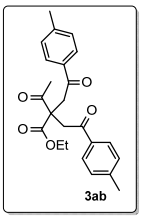

Ph
O
O
O
O
O
OEt
Ph

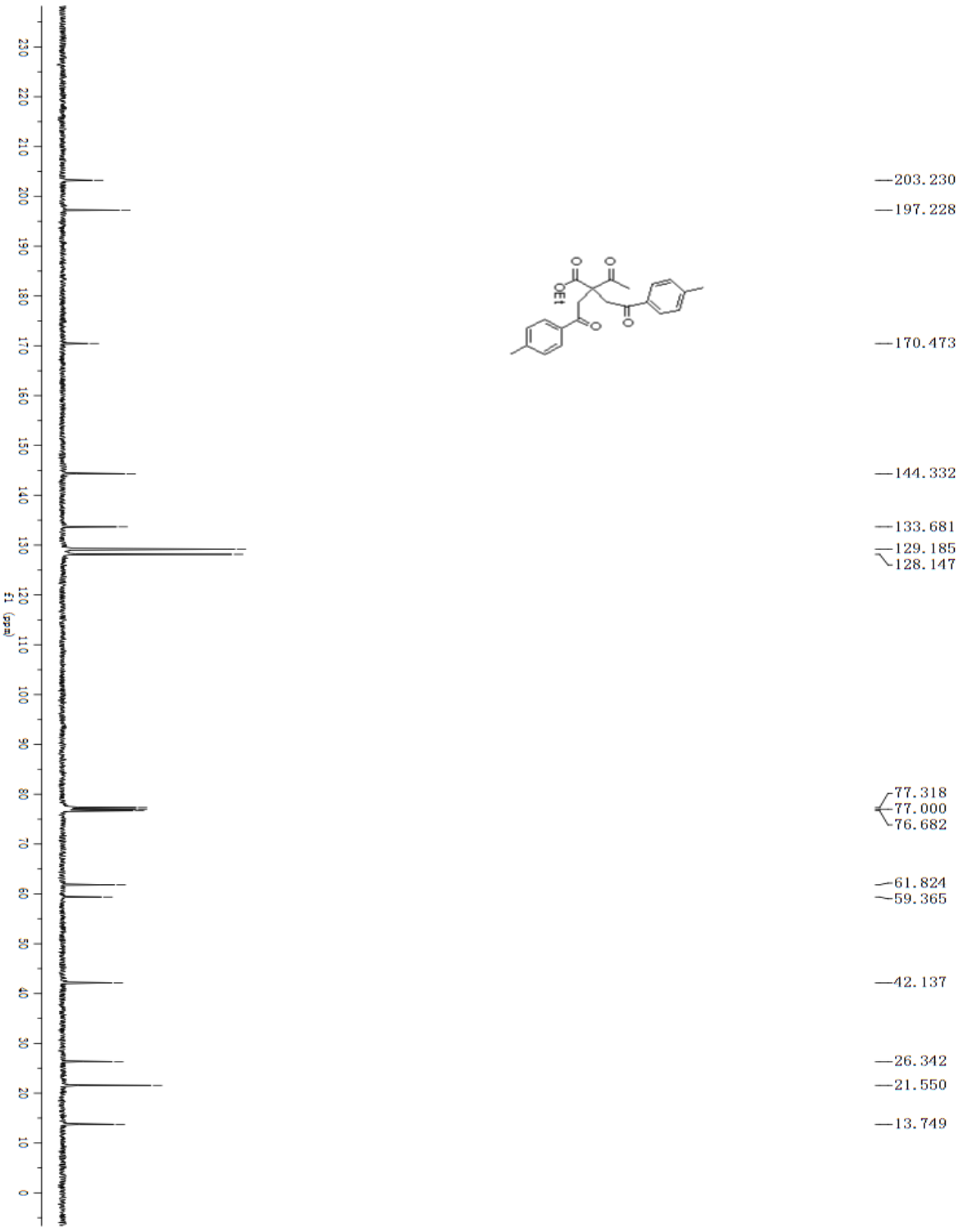
3la

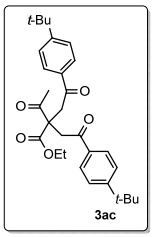

f1 (ppm)
197.486
169.763
136.248
133.413
128.544
128.039
77.318
77.000
76.682
61.978
53.229
41.740
13.846

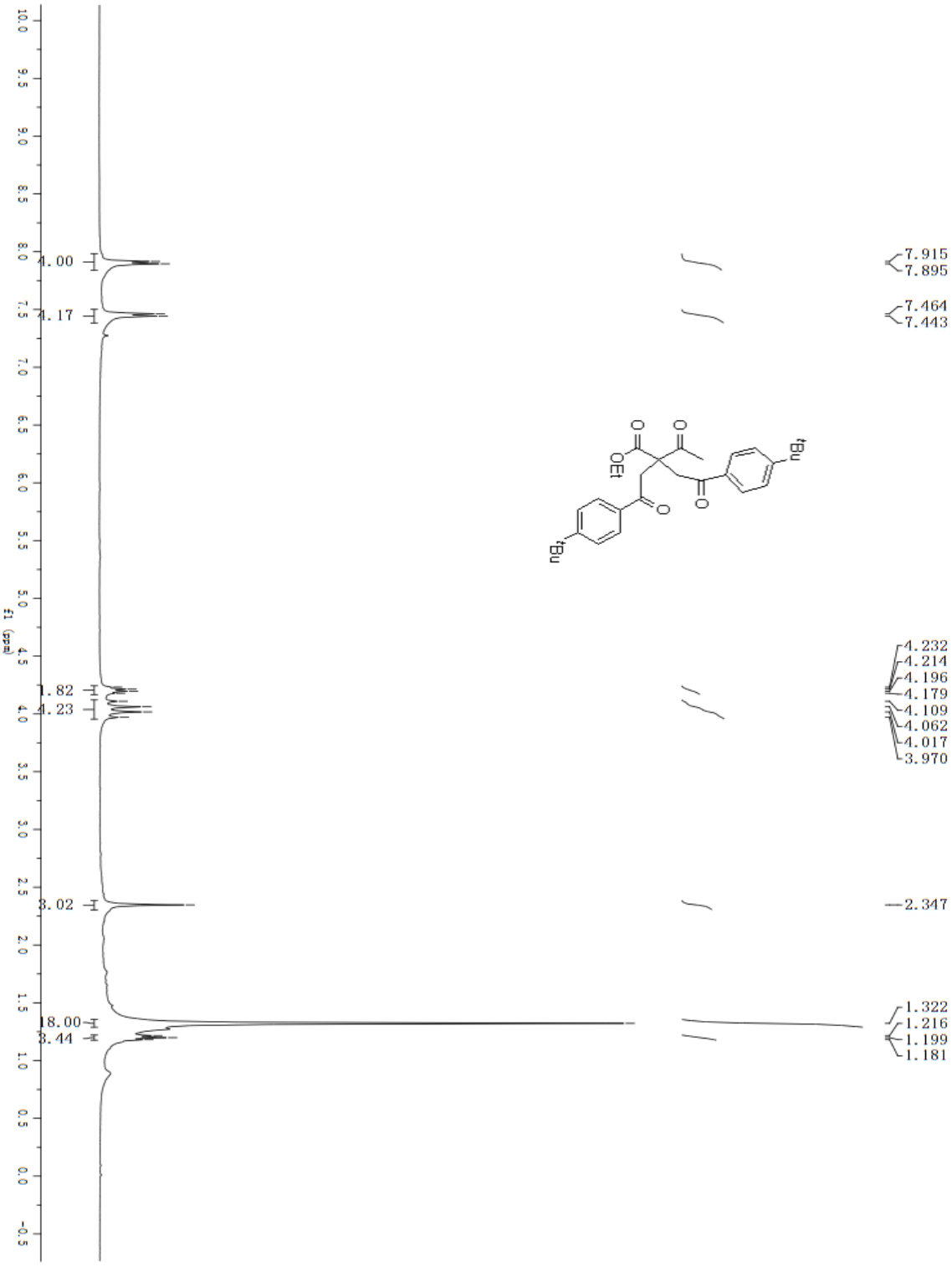

O
O
O
O
OEt
O
3ab

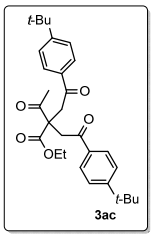

4.03
4.14
2.12
4.41
6.05
3.03
3.00
7.772
7.752
7.145
7.125
4.131
4.114
4.096
4.078
3.993
3.947
3.909
3.862
2.290
2.259
1.110
1.093
1.075
OEt
f1 (ppm)

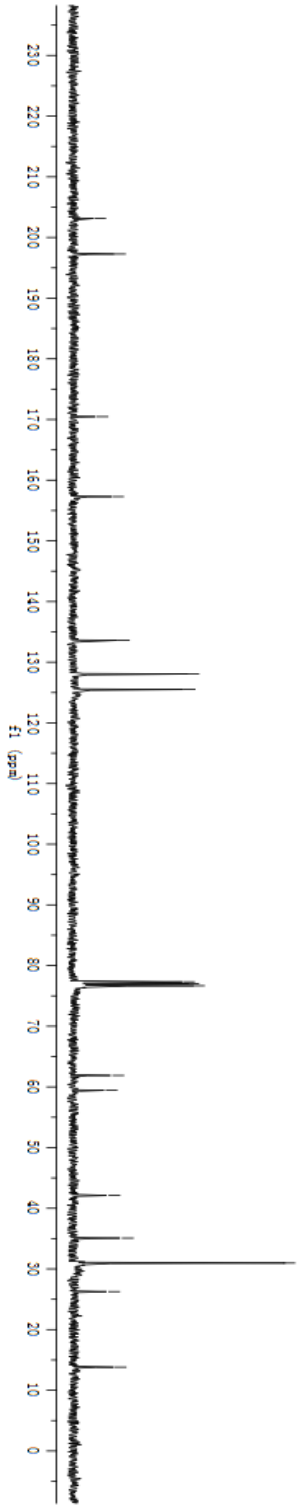

O
O
O
O
OEt
O
3ab

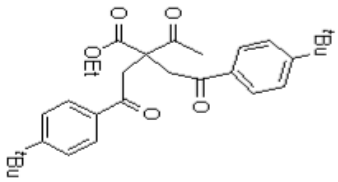

f1 (ppm)
203.230
197.228
170.473
144.332
133.681
129.185
128.147
77.318
77.000
76.682
61.824
59.365
42.137
26.342
21.550
13.749


t-Bu
OEt
t-Bu
3ac

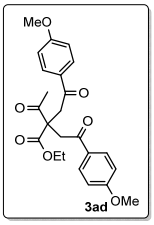

4.00
4.17
1.82
4.23
3.02
18.00
3.44
7.915
7.895
7.464
7.443
4.232
4.214
4.196
4.179
4.109
4.062
4.017
3.970
2.347
1.322
1.216
1.199
1.181
OEt
tBu
tBu
f1 (ppm)

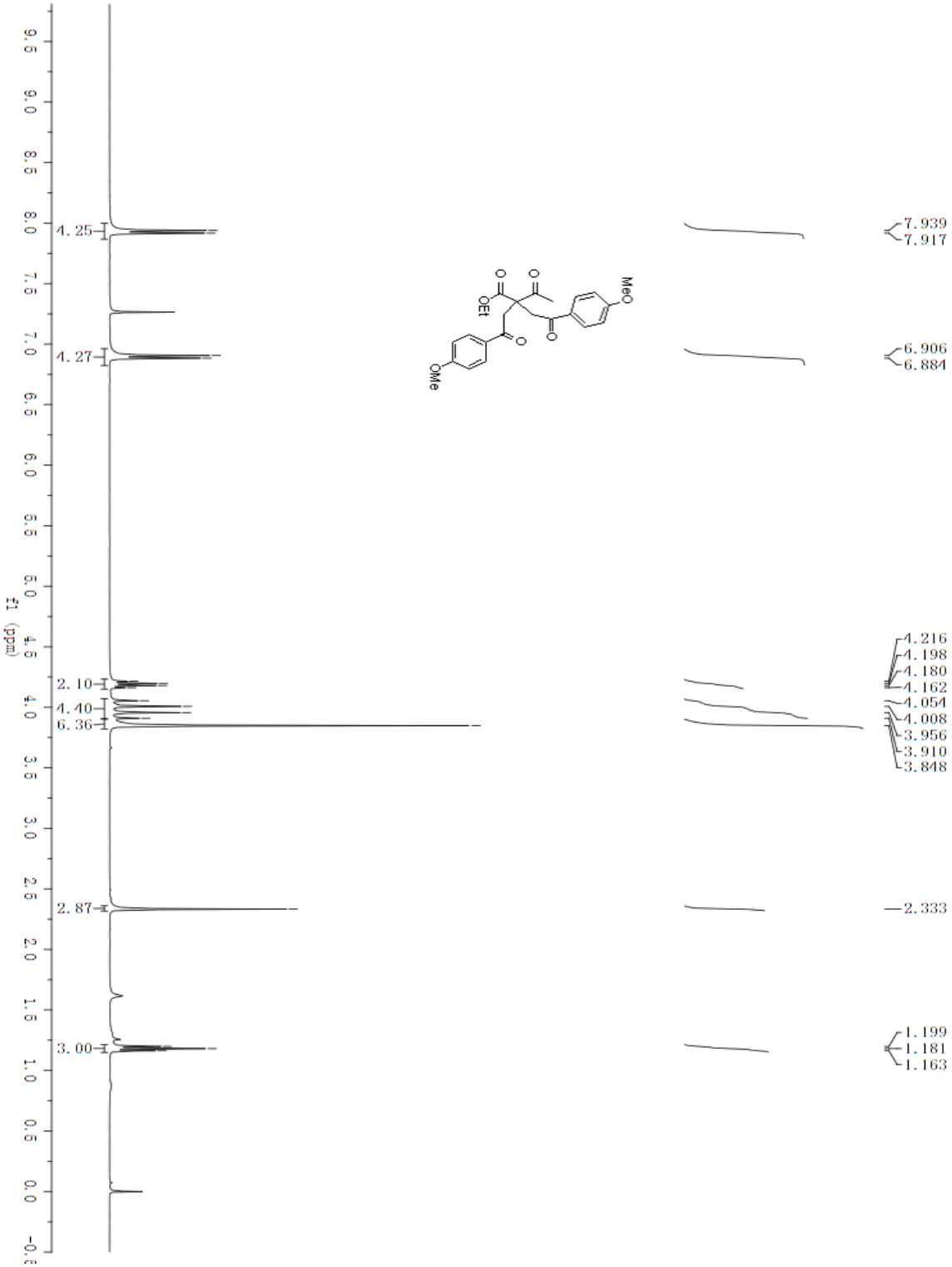


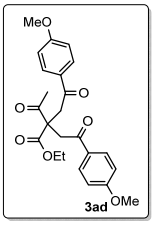


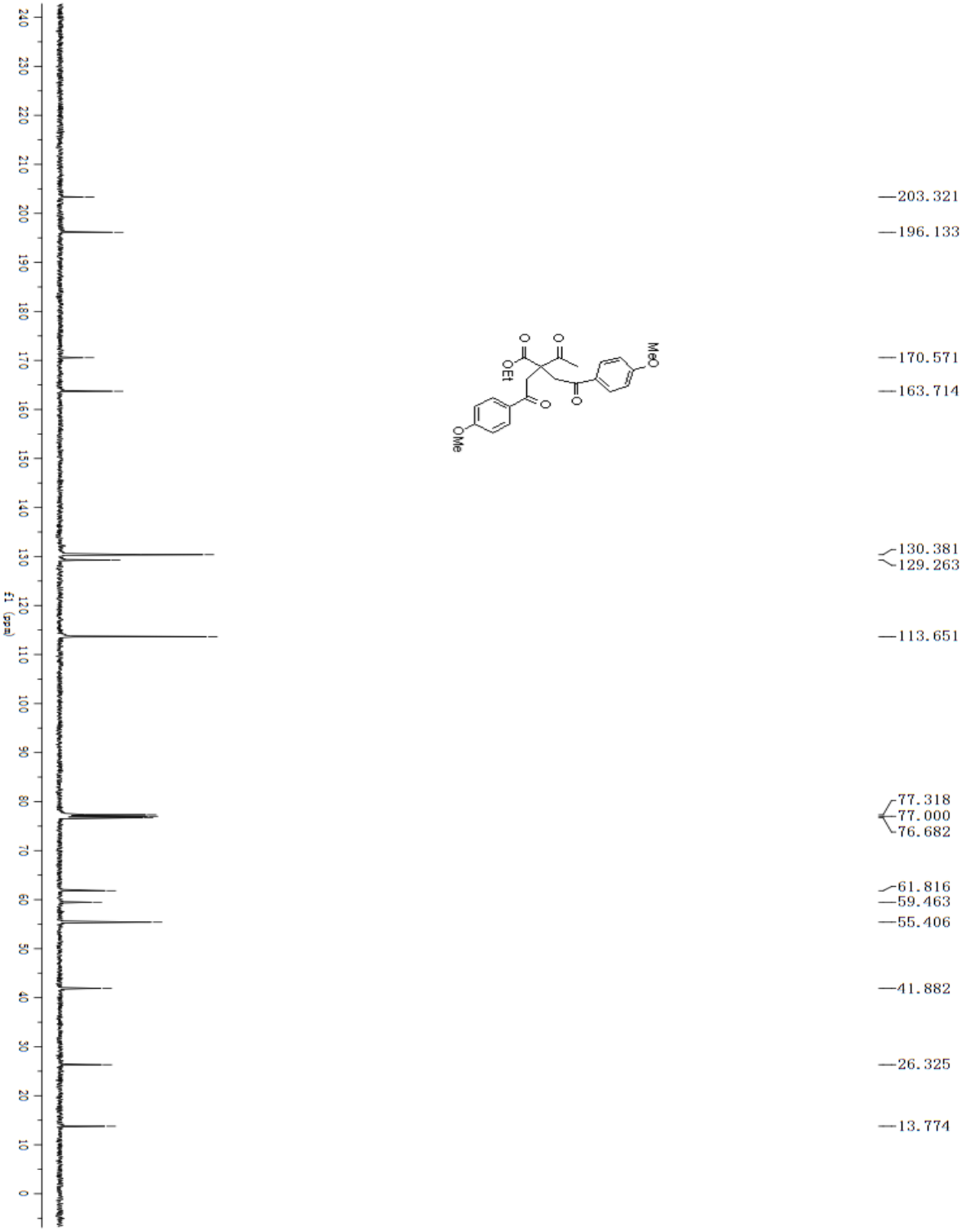


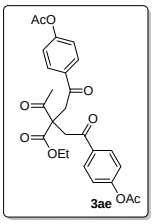
203.141
197.277
170.476
157.295
133.612
128.065
125.507
77.317
77.000
76.681
61.888
59.440
42.114
35.079
30.969
26.262
13.811

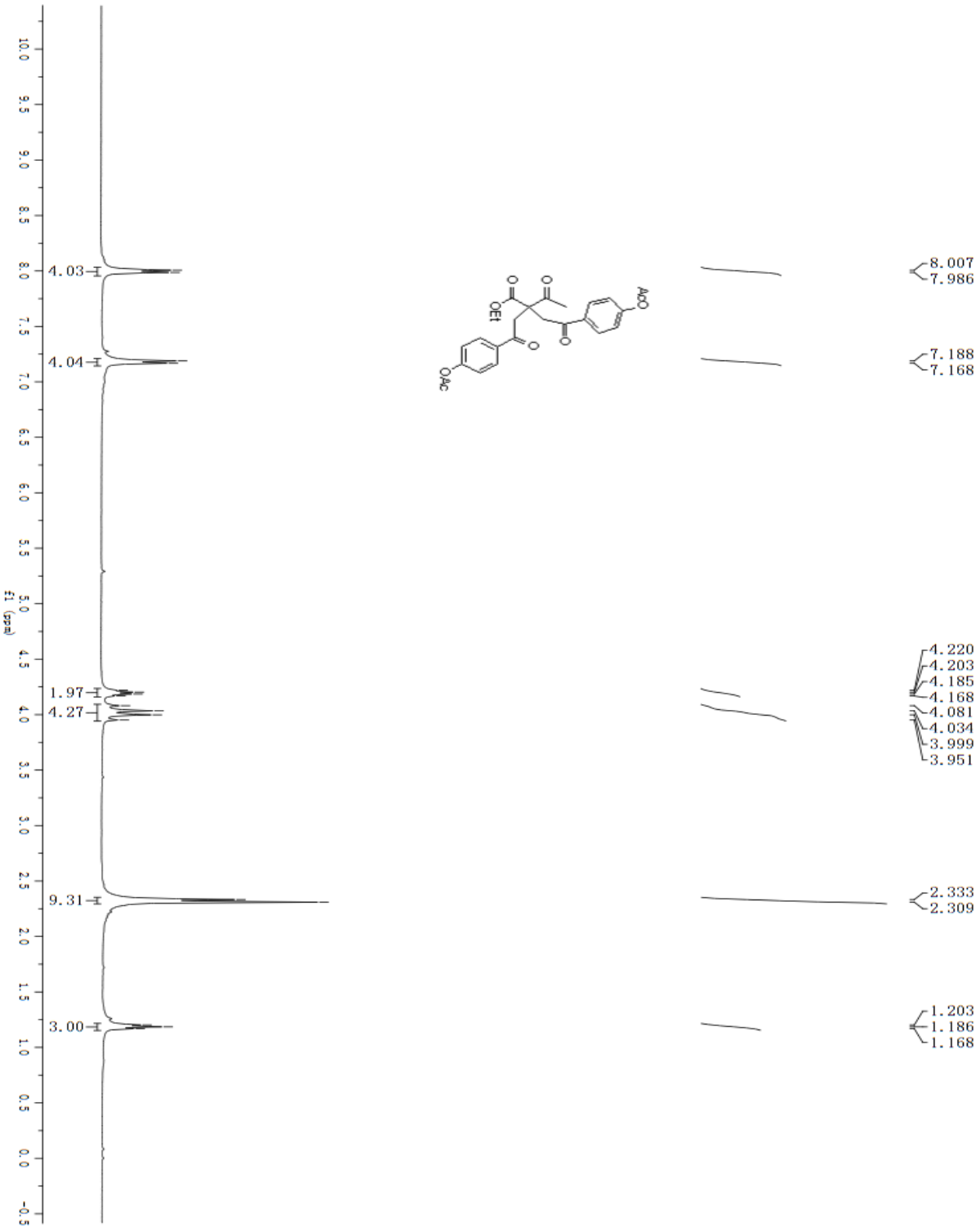

MeO
O
O
O
O
OEt
3ad
OMe

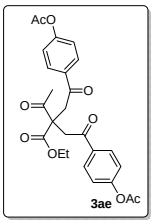

f1 (ppm)
4.25
4.27
2.10
4.40
6.36
2.87
3.00
OEt
MeO
OMe
7.939
7.917
6.906
6.884
4.216
4.198
4.180
4.162
4.054
4.008
3.956
3.910
3.848
2.333
1.199
1.181
1.163

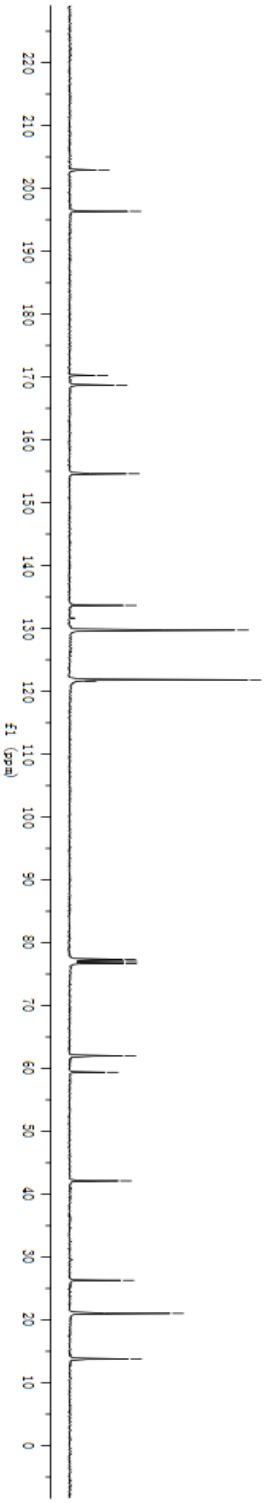

MeO
O
O
O
O
OEt
3ad
OMe

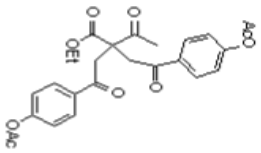

f1 (ppm)
203.321
196.133
170.571
163.714
130.381
129.263
113.651
77.318
77.000
76.682
61.816
59.463
55.406
41.882
26.325
13.774
OEt
MeO
OMe


AcO
O
O
O
OEt
O
OAc
3ae

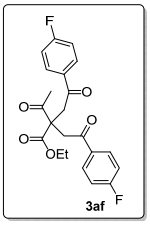

4.03
4.04
1.97
4.27
9.31
3.00
f1 (ppm)
8.007
7.986
7.188
7.168
4.220
4.203
4.185
4.168
4.081
4.034
3.999
3.951
2.333
2.309
1.203
1.186
1.168

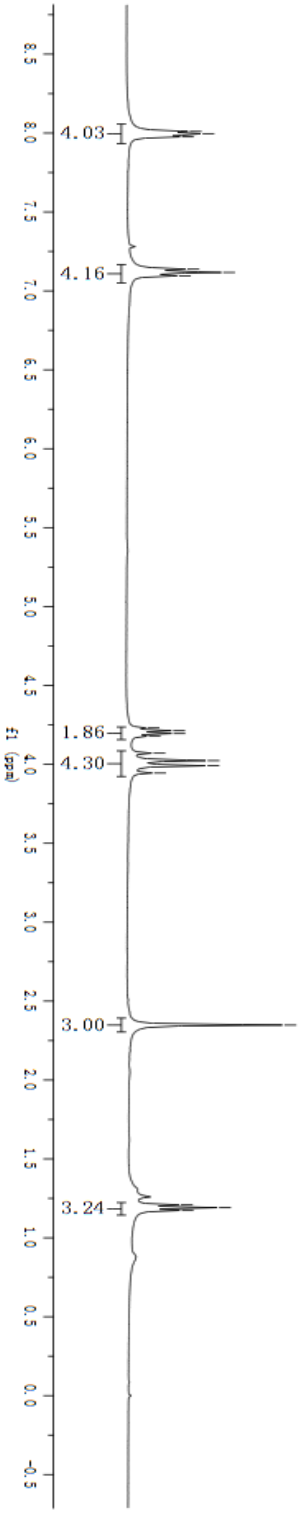


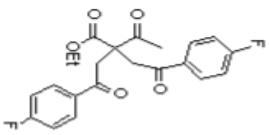


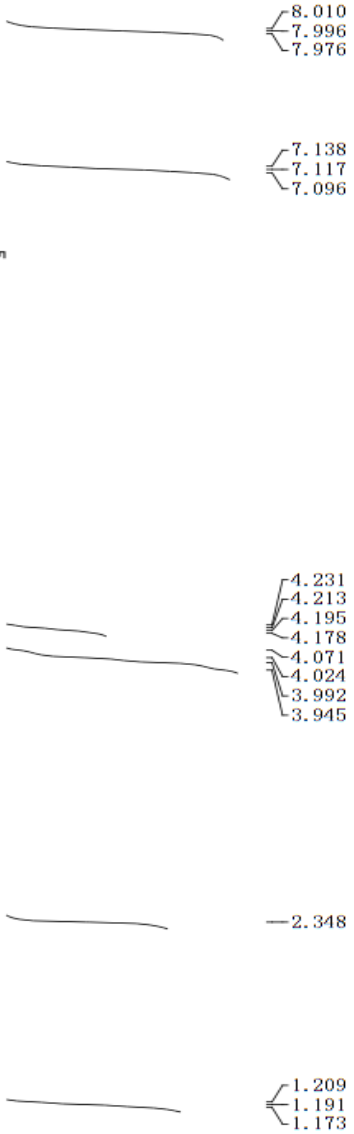


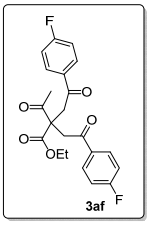
202.884
196.333
170.212
168.675
154.601
133.655
129.722
121.799
121.607
77.318
77.000
76.681
61.979
59.372
42.112
26.278
21.030
13.759

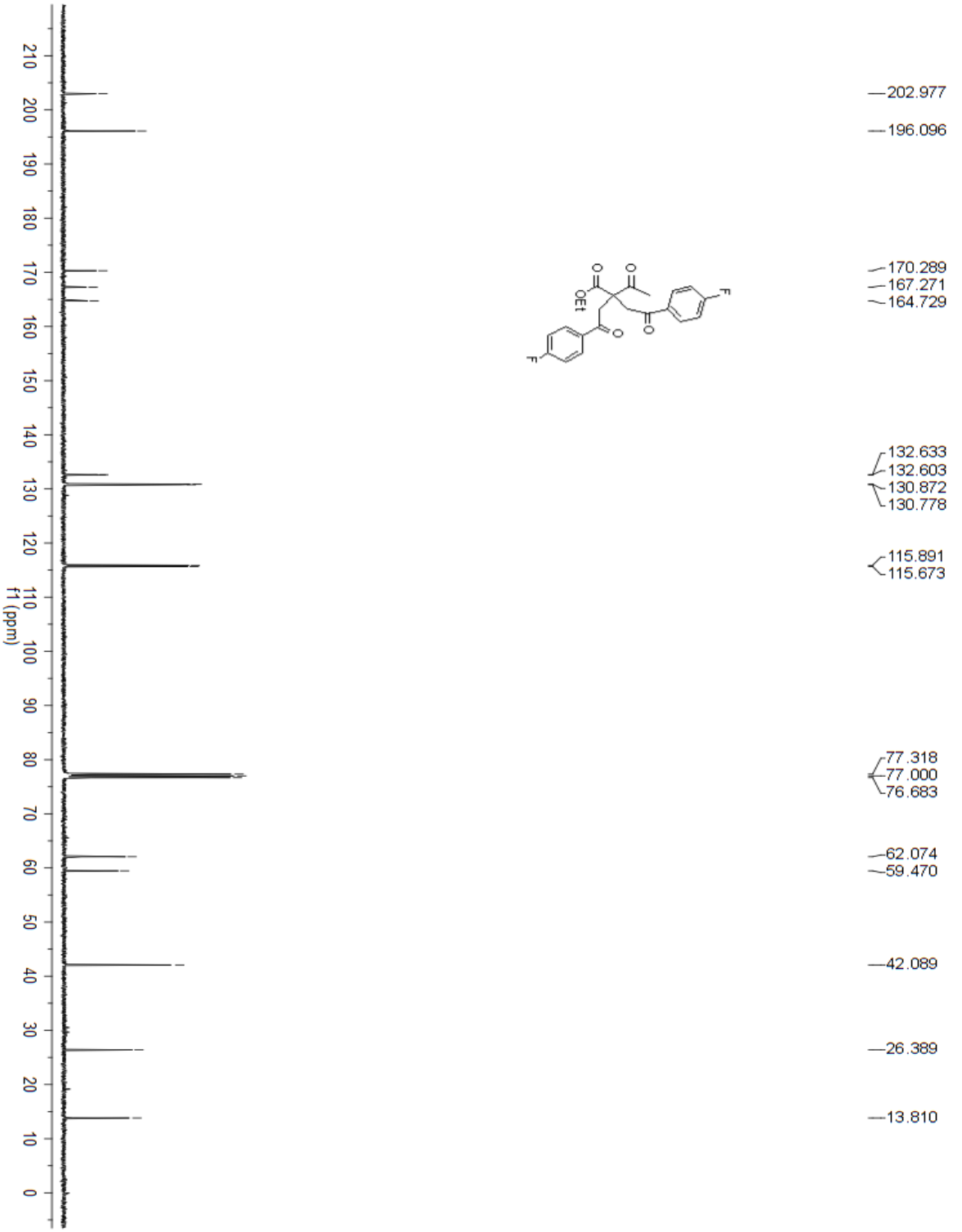

F
O
O
O
OEt
O
F
3af

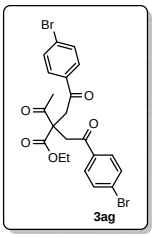

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
4.03
4.16
1.86
4.30
3.00
3.24

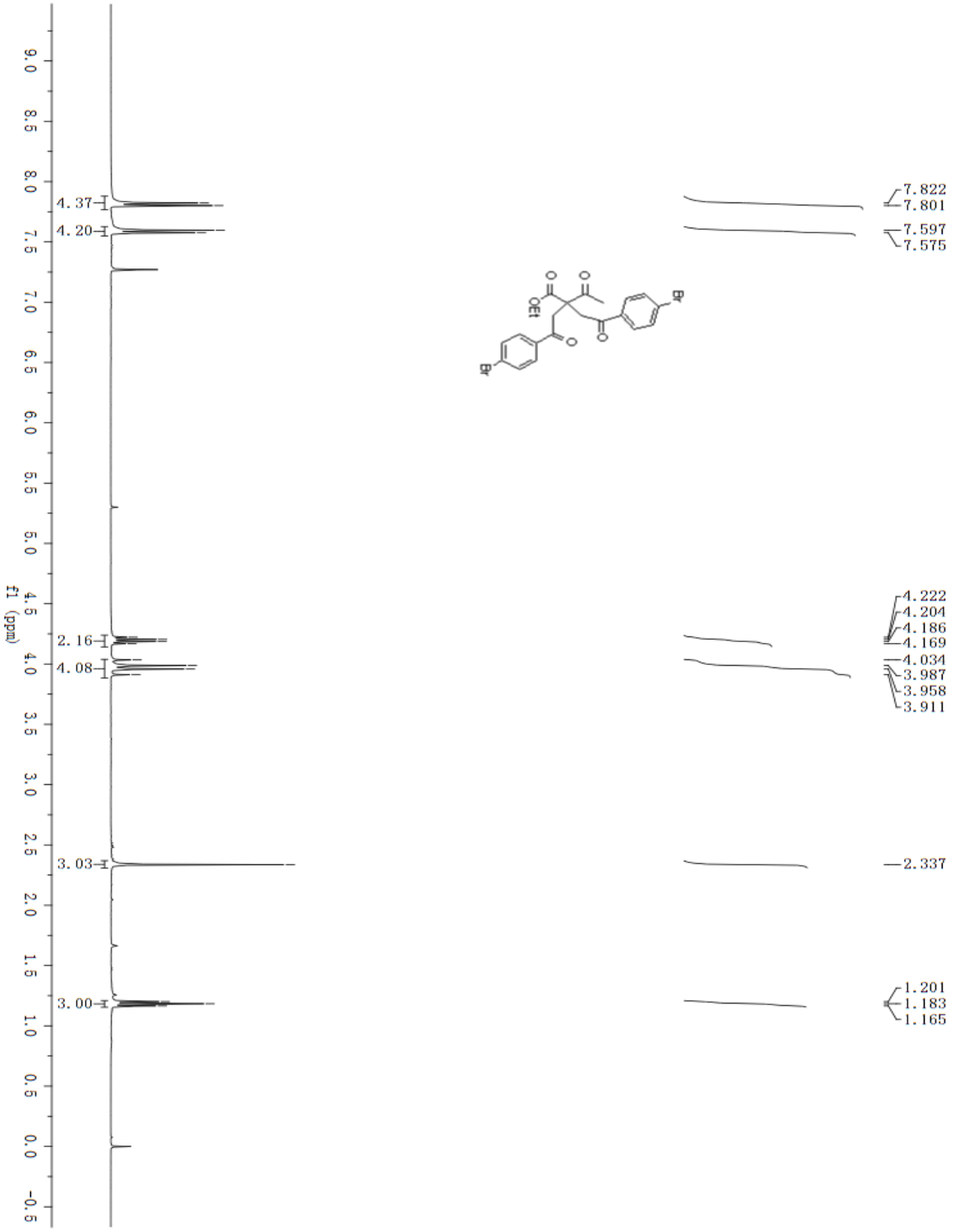

O
O
OEt
O
F
O
F

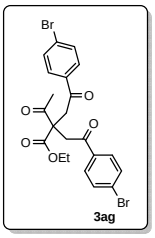

8.010
7.996
7.976
7.138
7.117
7.096
4.231
4.213
4.195
4.178
4.071
4.024
3.992
3.945
2.348
1.209
1.191
1.173

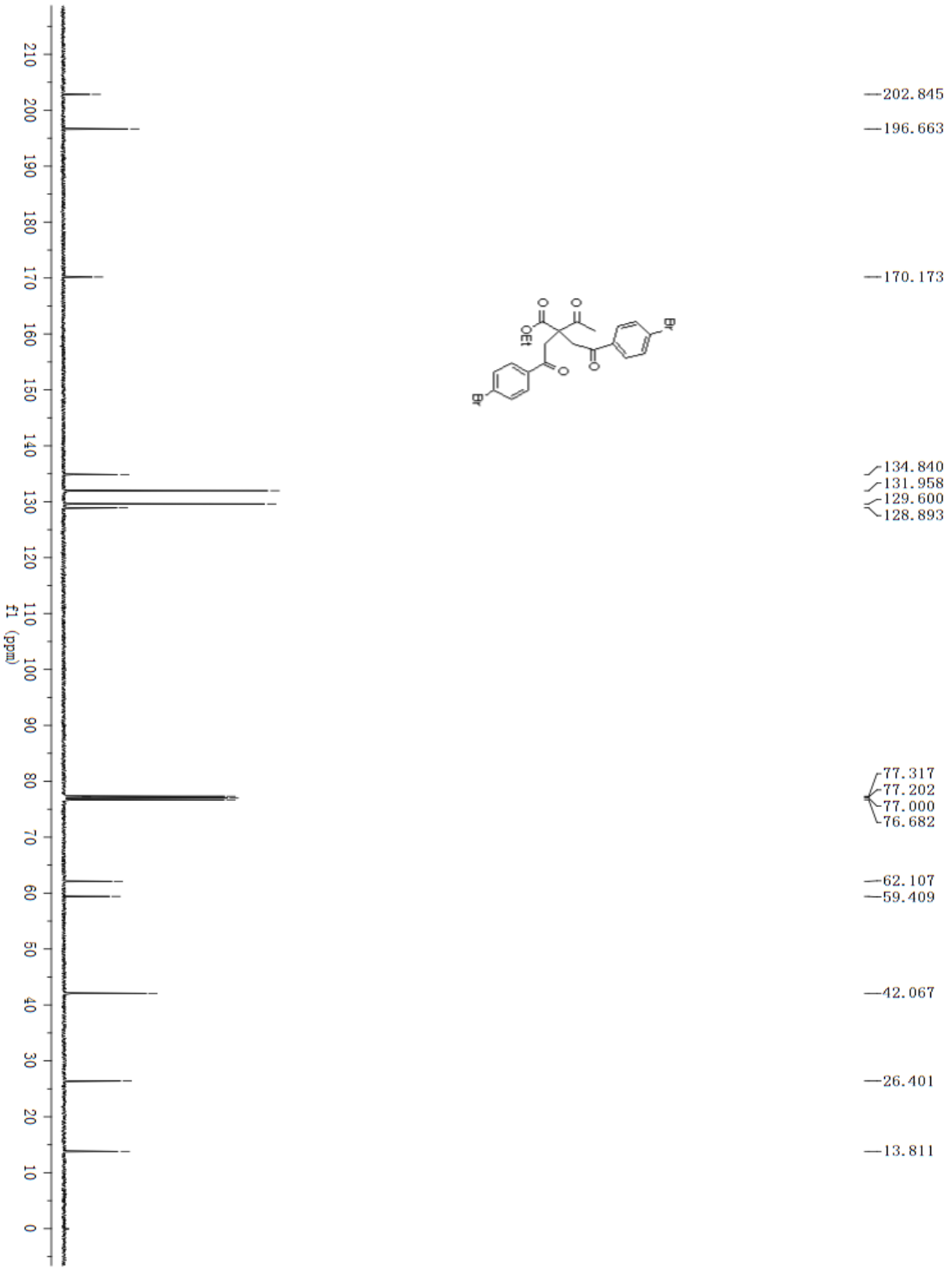

F
O
O
O
OEt
O
F
3af

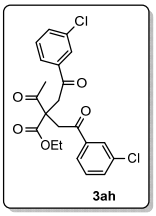

f1 (ppm)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
202.977
196.096
170.289
167.271
164.729
132.633
132.603
130.872
130.778
115.891
115.673
77.318
77.000
76.683
62.074
59.470
42.089
26.389
13.810
OEt
O
O
O
F
F

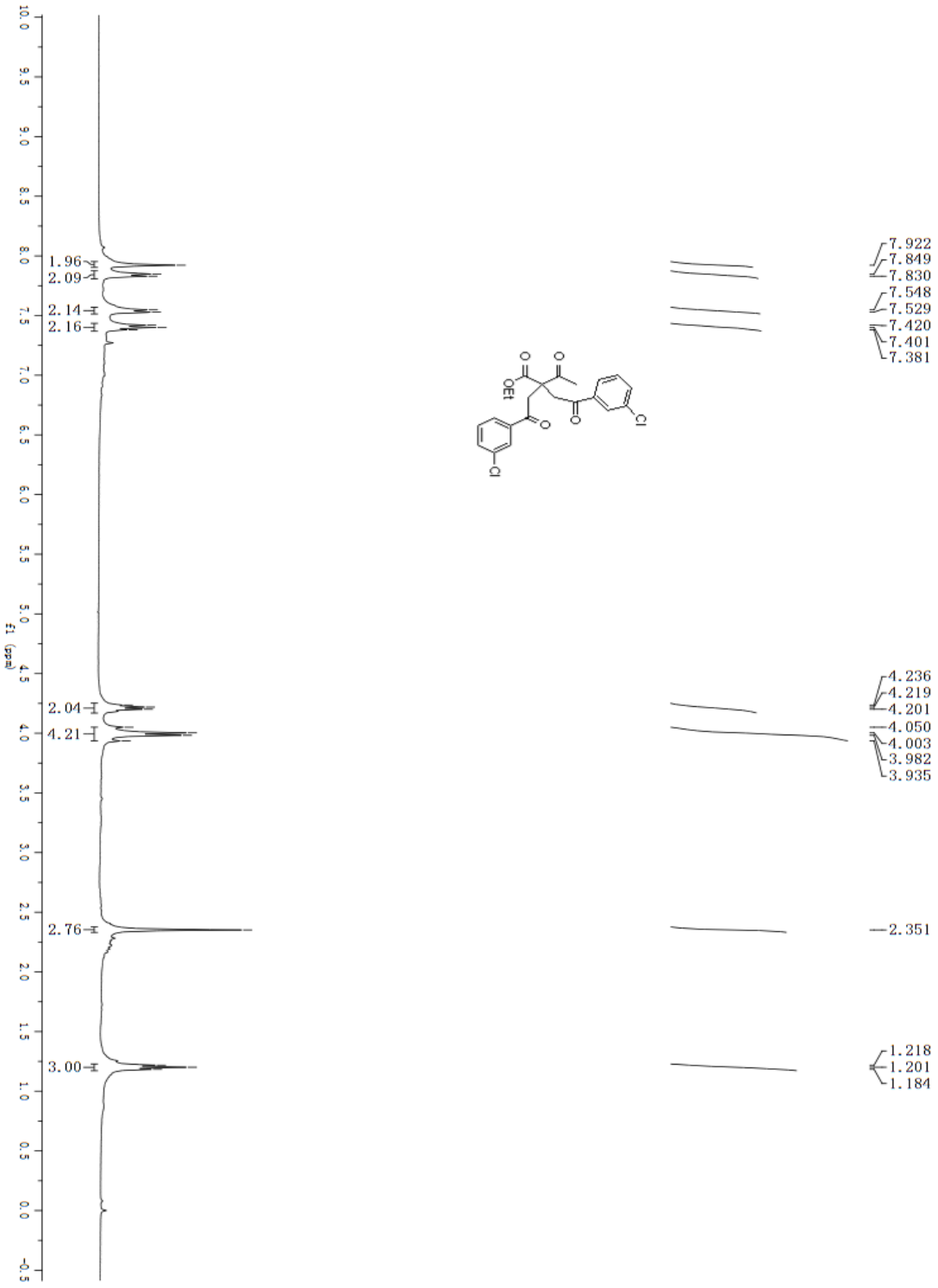

Br
O
O
O
O
OEt
Br
3ag

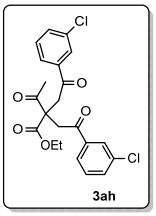

9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
4.37
4.20
2.16
4.08
3.03
3.00
7.822
7.801
7.597
7.575
4.222
4.204
4.186
4.169
4.034
3.987
3.958
3.911
2.337
1.201
1.183
1.165
OEt
Br
Br

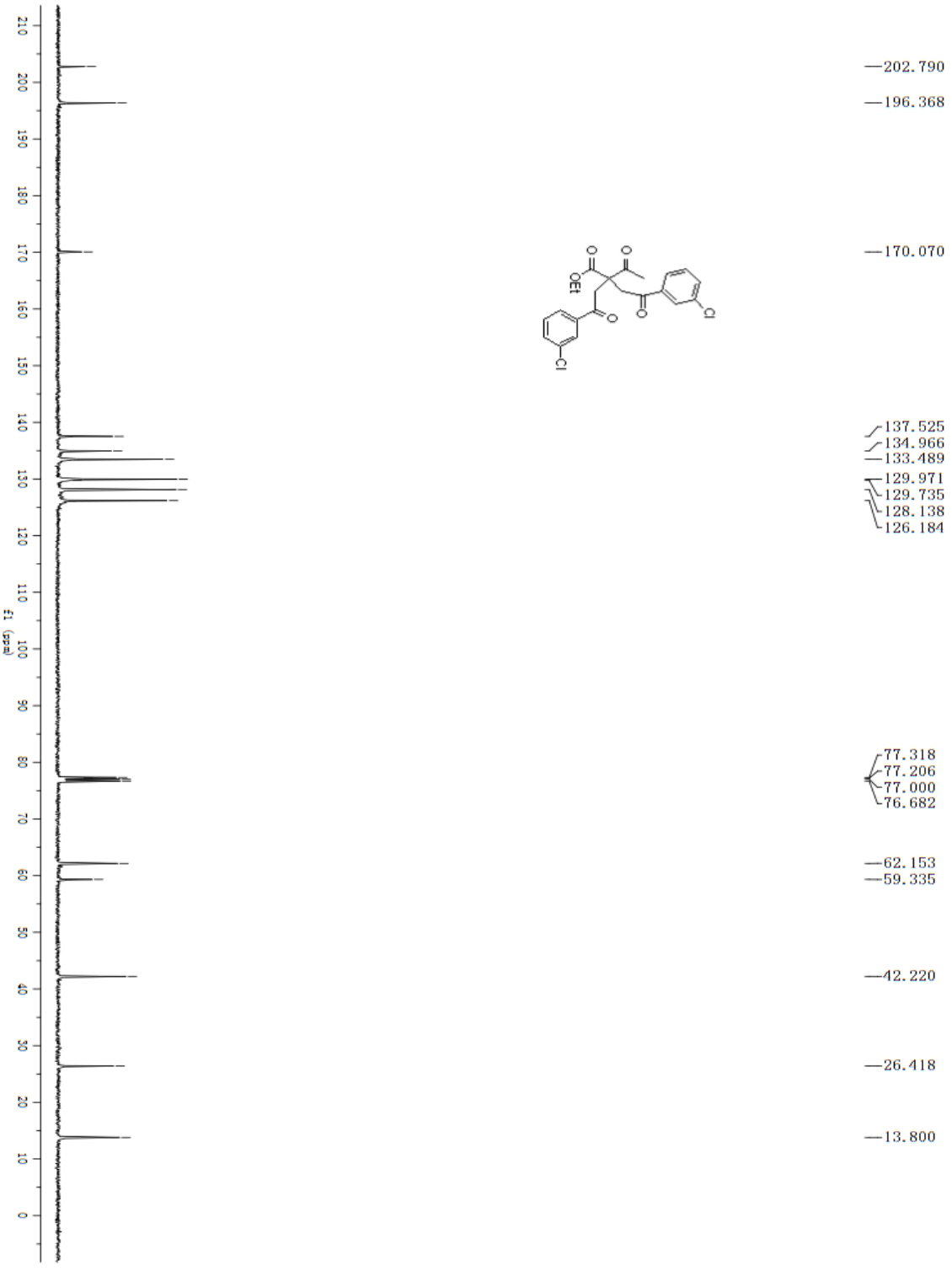

Br
O
O
O
O
OEt
Br
3ag

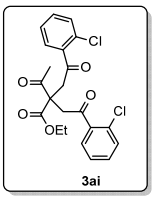

f1 (ppm)
202.845
196.663
170.173
134.840
131.958
129.600
128.893
77.317
77.202
77.000
76.682
62.107
59.409
42.067
26.401
13.811

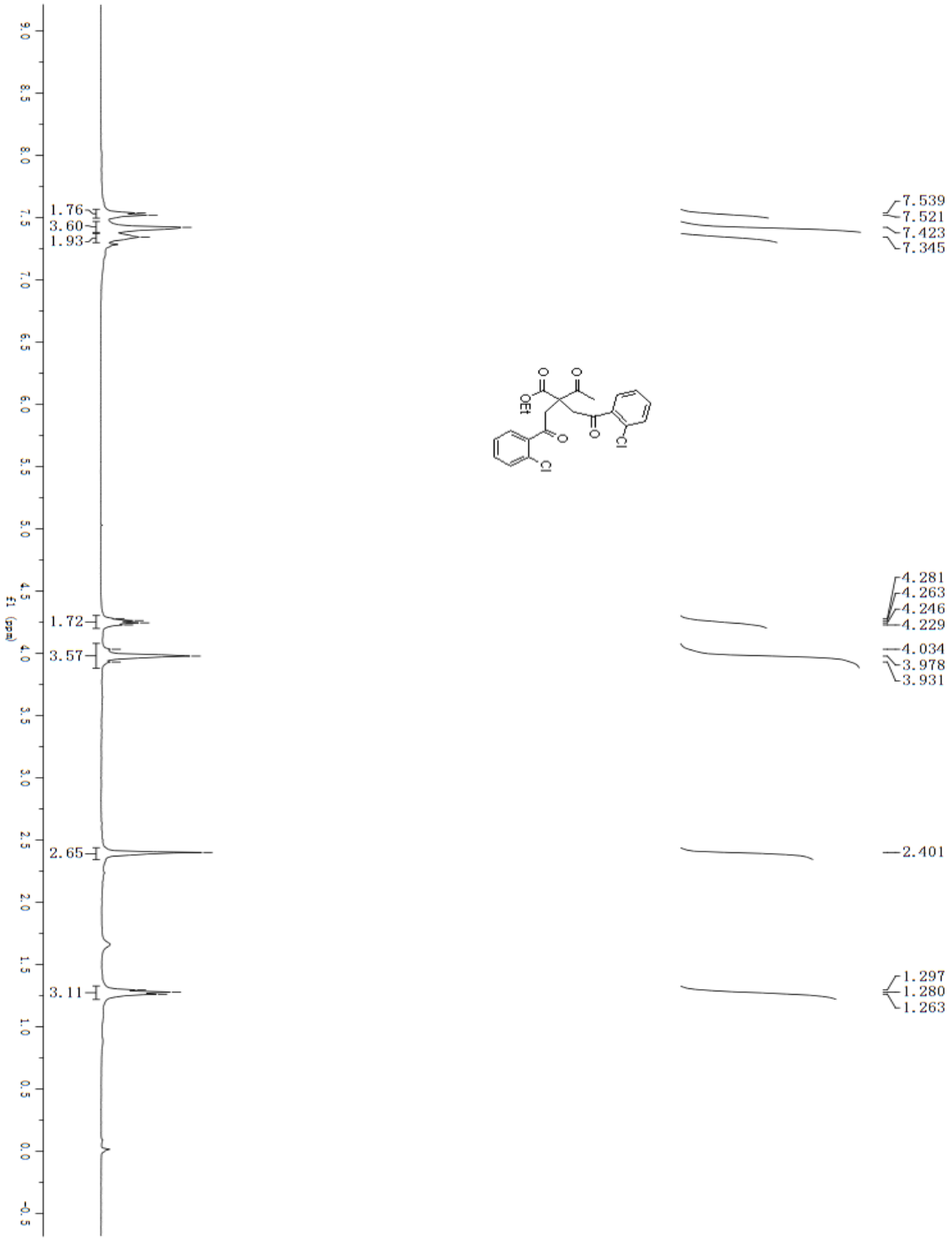

Cl
O
O
O
OEt
O
Cl
3ah

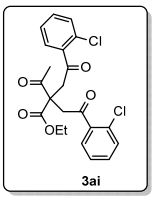

1.96
2.09
2.14
2.16
2.04
4.21
2.76
3.00
f1 (ppm)
7.922
7.849
7.830
7.548
7.529
7.420
7.401
7.381
4.236
4.219
4.201
4.050
4.003
3.982
3.935
2.351
1.218
1.201
1.184

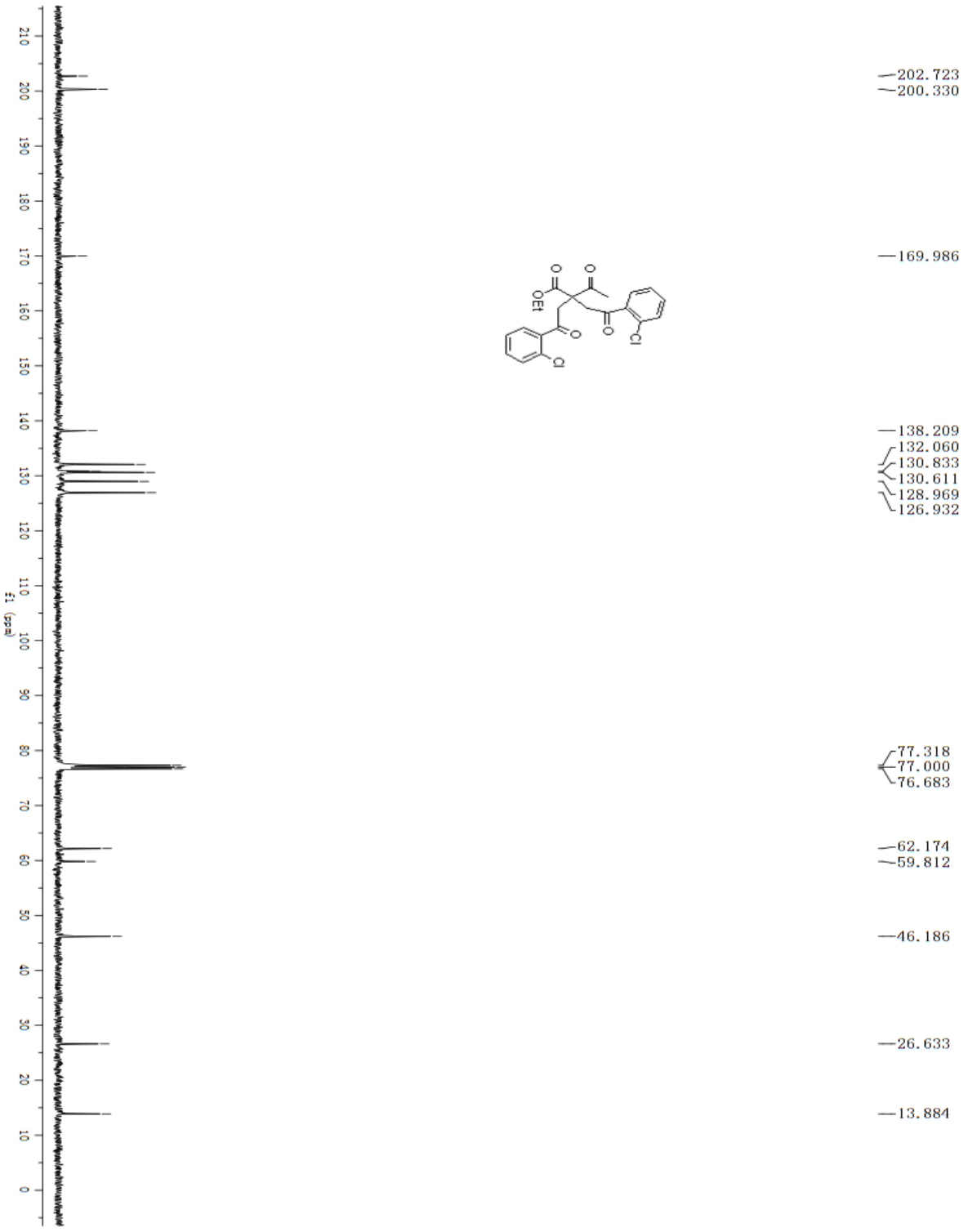

Cl
O
O
O
O
OEt
O
Cl
3ah

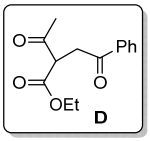

f1 (ppm)
202.790
196.368
170.070
137.525
134.966
133.489
129.971
129.735
128.138
126.184
77.318
77.206
77.000
76.682
62.153
59.335
42.220
26.418
13.800


Cl
O
O
O
OEt
O
Cl
3ai

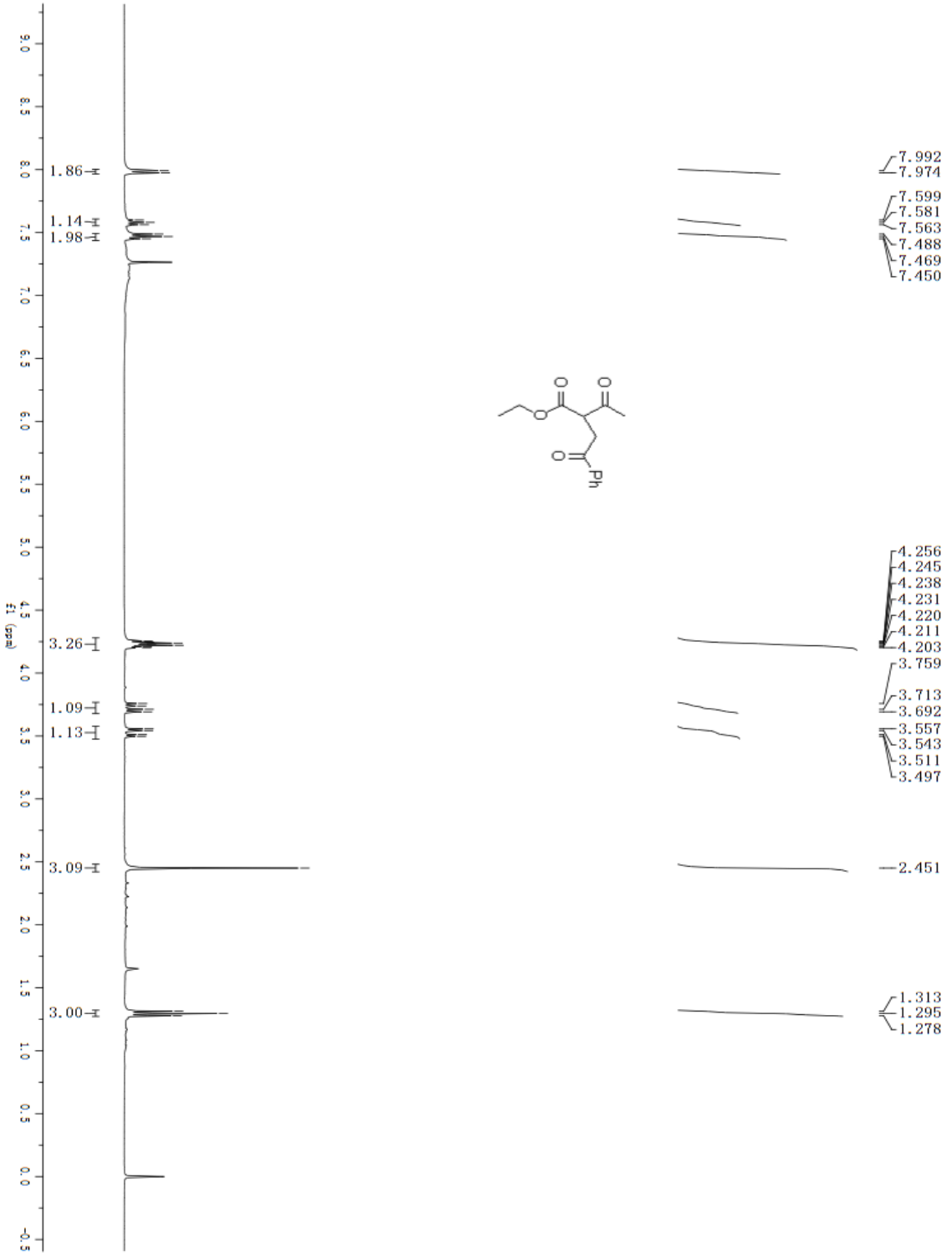

1.76
3.60
1.93
1.72
3.57
2.65
3.11
f1 (ppm)
7.539
7.521
7.423
7.345
4.281
4.263
4.246
4.229
4.034
3.978
3.931
2.401
1.297
1.280
1.263
OEt
O
O
O
Cl
Cl

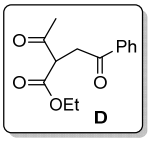

Cl
O
O
O
O
OEt
O
Cl
3ai


f1 (ppm)
202.723
200.330
169.986
138.209
132.060
130.833
130.611
128.969
126.932
77.318
77.000
76.683
62.174
59.812
46.186
26.633
13.884
OEt
Cl
Cl

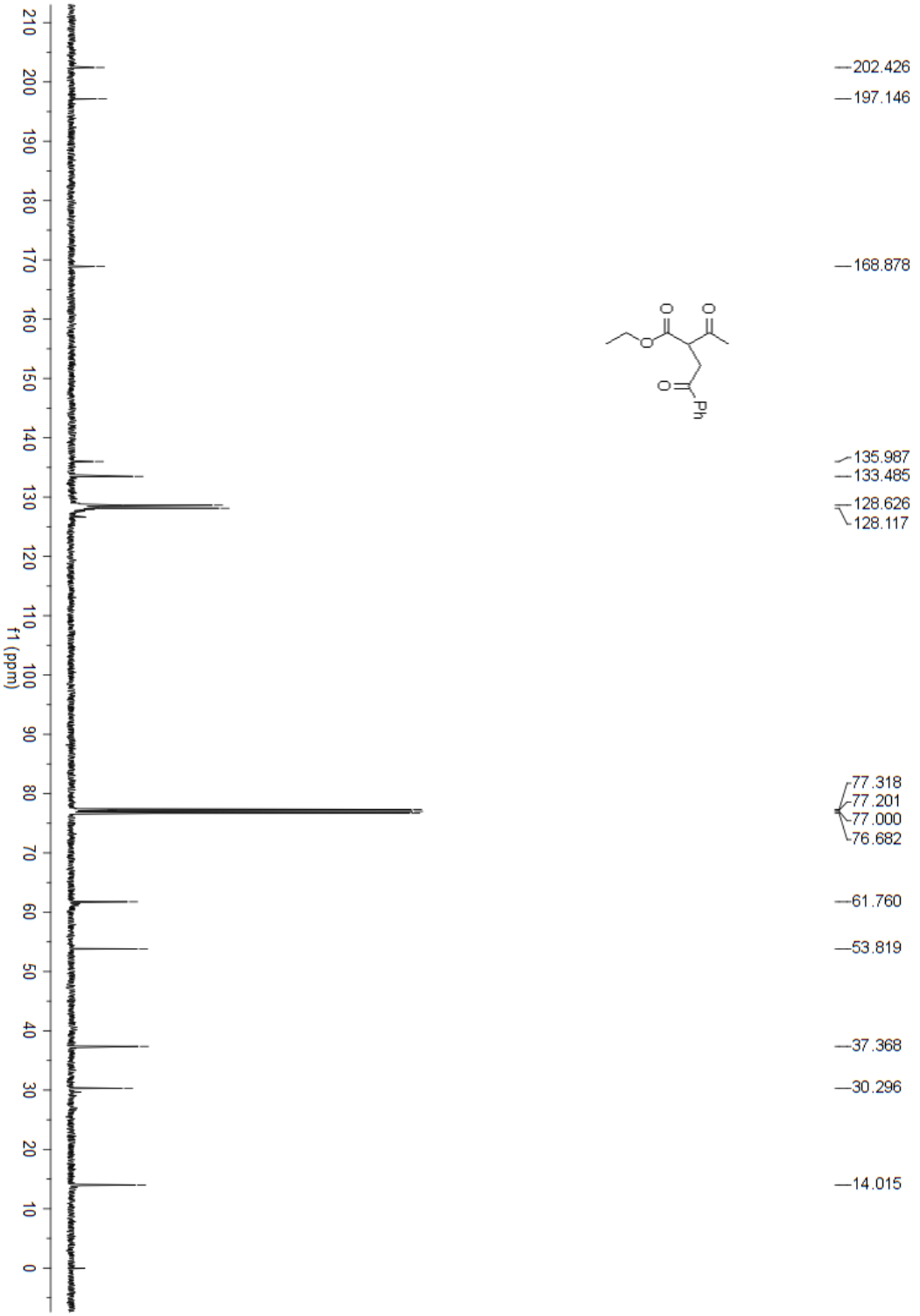

O
O
Ph
O
OEt

D


1.86
1.14
1.98
3.26
1.09
1.13
3.09
3.00
7.992
7.974
7.599
7.581
7.563
7.488
7.469
7.450
4.256
4.245
4.238
4.231
4.220
4.211
4.203
3.759
3.713
3.692
3.557
3.543
3.511
3.497
2.451
1.313
1.295
1.278
f1 (ppm)


O
Ph
O
O
OEt

D


f1 (ppm)
202.426
197.146
168.878
135.987
133.485
128.626
128.117
77.318
77.201
77.000
76.682
61.760
53.819
37.368
30.296
14.015