Supplementary Information:

# Efficient Synthesis of Polysubstituted Isochromanones Via a Novel Photochemical Rearrangement Reaction

*Wujiong Xia,*[†,‡] Yutian Shao,[†] Weijun Gui,[†] and Chao Yang[†]*

[†]*State Key Lab of Urban Water Resource and Environment, the Academy of Fundamental and Interdisciplinary Sciences, Harbin Institute of Technology, Harbin 150080*

[‡] *State Key Lab of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, China*

xiawj@hit.edu.cn

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## 1. General and Materials

**General Procedures.** Reactions were carried out under an atmosphere of nitrogen and monitored by thin-layer chromatography (TLC) using UV light visualizing agent and ethanolic solution of sulfate acid. Melting point was determined on Büchi Melting Point B-540. NMR spectra were measured on Bruker AVANCE III 400M NMR in $CDCl_3$ with tetramethylsilane as the internal reference (7.262 for $^1H$, 77.01 for $^{13}C$). When peak multiplicities were reported, the following abbreviations were used: s-singlet, d-doublet, t-triplet, q-quartet, m-multiplet, br-broadened. IR absorption spectra results were obtained on Nicolet impact 400 FT-IR instrument and using as a film on NaCl single-crystal plate (SPECTRUM100). HRMS (ESI) was recorded using Agilent 6520 accurate-Mass Q-TOF LC/MS system (1200-6520/Agilent). Low-resolution Mass spectra were obtained from GC-MS system (7890A-5975C/Agilent). Silica gel (200-300 mesh, QingDao, China) was used for column chromatography and preparative thin-layer chromatography was performed on commercial available silica gel plates (GF254, QingDao, China).

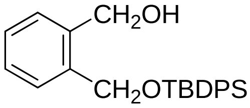
**Materials**. Anhydrous tetrehydrofuran (THF), benzene, diethyl ether ($Et_2O$), methanol (MeOH) and isopropanol (i-PrOH) were dried with sodium (Na). Anhydrous dichloromethane (DCM), N, N-dimethy formamide (DMF) and diisopropylethylamine (DIEA) were dealt with $CaH_2$. N-bromosuccinimide (NBS), azodiisobutyronitrile (AIBN). Reagents were purchased at the highest commercial quality and used without further purification.

## 2.Experimental Procedures

### 2.1 General procedure for Synthesis of Ester 3

In a 500 mL oven-dried, three-necked flask, equipped with mechanical stirrer, commercially available phthalate acids (50.0 g, 0.3 mol) and freshly dried THF (300 mL) were added, then $LiAlH_4$ (34.0 g, 0.9 mol) was added carefully in ice-water bath. Upon completion, saturated $NH_4Cl$ aqueous solution (40 mL) was added carefully to quench the reaction. The reaction mixture was filtered and the solid residue was washed with EtOH (3×100 mL). The solvent was evaporated *in vacuo* to yield 1, 2-benzenedimethanol (39.4 g, 94 %, primrose solid), which was used directly for next step without further purification.

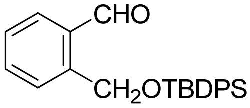
To a solution of 1, 2-benzenedimethanol (35.0 g, 0.25 mol) and redistilled DIEA (430.6 mL, 2.5 mol) in anhydrous DMF (150 mL) was added dropwise *tert*-butyldiphenylchlorosilane (TBDPSCl) (68.0 mL, 0.27 mol) under nitrogen at room temperature. After five hours, the reaction was quenched with addition of saturated $NH_4Cl$ aqueous solution (20 mL) and the organic layer was separated, washed with 2.0 M HCl (3×20 mL), saturated $NaHCO_3$ (3×40 mL), brine (2×30 mL) and dried ($MgSO_4$). The solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography to give a white solid (71.5 g, 75 %). [1]



1

**Compound 1**. Mp 73-75 ℃. **IR** (KBr) $\nu_{max}$: 3072, 2929, 2856, 1698, 1590, 1471, 1260, 1113, 701, 623 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.69 (d, $J$ = 7.6 Hz, 4H), 7.37-7.46 (m, 7H), 7.29 (t, $J$ = 7.2 Hz, 1H), 7.24 (d, $J$ = 7.2 Hz, 1H), 7.19 (t, $J$ = 7.6 Hz, 1H), 4.78 (s, 2H), 4.67 (s, 2H), 3.04 (br, 1H), 1.05 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 139.6, 138.2, 135.7, 132.8, 130.0, 129.0, 128.8, 128.2, 127.9, 127.9, 65.1, 63.7, 26.8, 19.2. **LRMS** (EI): 375 [M-1], 343, 319, 289, 199, 152, 122, 91, 75, 57, 41. **HRMS** (ESI): calcd for $C_{24}H_{29}O_2Si^+$ 377.1931 $[M+H]^+$, found 377.1938.

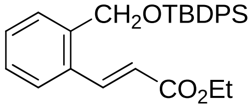
In a 250 mL round-bottomed flask, compound **1** (45.0 g, 0.12 mol) was dissolved in 150 mL of anhydrous $CH_2Cl_2$. To this solution, PCC (38.5 g, 0.18 mol) and Celite (77.0 g) were added and stirred for three hours at room temperature. 20 mL of $Et_2O$ was added to quench the reaction. The mixture was filtered on a pad of silica gel, and the solvent was removed under vacumn. The residue was purified by silica gel column chromatography to yield aldehyde **2**. [2]



2

**Compound 2.** Yield 89%. Mp 112-115 ℃. **IR** (KBr) $\nu_{max}$: 2958, 2645, 1767, 1695, 1589, 1437, 1219, 739, 609 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.15 (s, 1H), 7.82-7.88 (m, 2H), 7.64-7.70 (m, 4H), 7.62 (t, $J$ = 7.6 Hz, 1H), 7.36-7.48 (m, 7H), 5.21 (s, 2H), 1.12 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 192.9, 143.7, 135.5, 134.0, 133.3, 132.8, 132.7, 129.8, 127.8, 127.2, 126.9, 63.6, 26.9, 19.4. **LRMS** (EI): 374 [M], 318, 212, 167, 119, 91, 77, 57, 41. **HRMS** (ESI): calcd for $C_{24}H_{27}O_2Si^+$ 375.1775 $[M+H]^+$, found 375.1776.

In a 100 mL oven-dried flask, equipped with a constant pressure funnel, triethyl phosphonoacetate (5.74 g, 0.26 mmol) and 40 mL of anhydrous THF were added and cooled to -78 □, then *n*-butyl lithium (11.6 mL, 2.2 M in hexane, 25.5 mmol) was added with dropwise under nitrogen. After 15 minutes, compound **2** (8.0 g, 20.0 mmol) and HMPA (8.91 mL, 67.0 mmol) were slowly added. The mixture was warmed to room temperature gradually after two hours and stirred over night. The reaction was quenched by addition of 5 mL of water and the organic layer was separated, the aqueous layer was extracted with EtOAc (3× 30 mL). The combined organic layers were washed with brine (3×30 mL) and dried ($Na_2SO_4$). The solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography to give the ester **3**. [3]

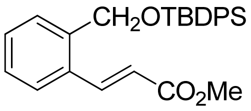


**3**

**Compound 3**. Yield 81 %, oil. **IR** (neat) $\nu_{max}$: 2958, 2740, 1959, 1714, 1635, 1428, 1176, 740, 623 cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.01 (dd, $J$ = 16.0, 1.6 Hz, 1H), 7.70 (t, $J$ = 8.0 Hz, 4H), 7.58 (d, $J$ = 7.6 Hz, 1H), 7.28-7.45 (m, 9H), 6.36 (dd, $J$ = 16.0, 1.6 Hz, 1H), 4.84 (s, 2H), 4.24 (q, $J$ = 7.0 Hz, 2H), 1.31 (t, $J$ = 7.2 Hz, 3H), 1.07 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.8, 141.7, 139.7, 135.6, 133.3, 132.9, 129.9, 129.8, 128.0, 127.8, 127.7, 126.6, 119.9, 64.0, 60.5, 26.8, 19.3, 14.3. **LRMS** (EI): 444 [M], 429, 384, 358, 342, 313, 297, 226, 184, 166, 138, 99, 75, 57, 29. **HRMS** (ESI): calcd for $C_{28}H_{33}O_3Si^+$ 445.2193 $[M+H]^+$, found 445.2201.

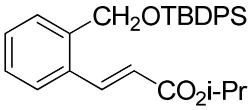
## 2.2 Synthesis of Esters 4 and 5

*n*-Butyl lithium (2.5 mL, 2.2 M in hexane, 5.5 mmol) was added to 5 mL of anhydrous MeOH or i-PrOH under nitrogen at -10℃. After 15 minutes, compound **3** (2.0 g, 5.34 mmol) dissolved in 10 mL of anhydrous THF was added with dropwise. After reaction, 5 ml of ice water was used to quench the reaction. The mixture was extracted with EtOAc (3×30 mL), and the combined organic phases was dried over $Na_2SO_4$. The solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography. [4]



4

**Compound 4**. Yield 98 %, oil. **IR** (neat) $v_{max}$: 2929, 2855, 1727, 1636, 1483, 1077, 687 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.01 (d, $J$ = 16.0 Hz, 1H), 7.76 (t, $J$ = 7.6 Hz, 4H), 7.57 (d, $J$ = 7.2 Hz, 1H), 7.27-7.45 (m, 9H), 6.36 (d, $J$ = 16.0 Hz, 1H), 4.85 (s, 2H), 3.77 (s, 3H), 1.07 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 167.3, 142.0, 139.7, 136.7, 135.6, 133.3, 132.8, 130.0, 129.8, 128.0, 127.8, 127.7, 126.6, 119.4, 64.0, 51.7, 26.8, 19.4. **LRMS** (EI): 431 [M+1], 415, 399, 372, 214, 183, 115, 91, 77, 57, 41, 15. **HRMS** (ESI): calcd for $C_{27}H_{31}O_3Si^+$ 431.2037 [M+H]$^+$, found 431.2041.



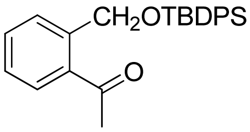
5

**Compound 5**. Yield 85 %, oil. **IR** (neat) $v_{max}$: 2930, 2856, 1711, 1635, 1471, 1274, 1109, 701, 604 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.96 (d, $J$ = 16.0 Hz, 1H), 7.69 (t, $J$ =7.6 Hz, 4H), 7.57 (d, $J$ = 7.2 Hz, 1H), 7.29-7.45 (m, 9H), 6.35 (d, $J$ = 15.6 Hz, 1H), 5.12 (m, $J$ = 6.2 Hz, 1H), 4.84(s, 2H), 1.28 (d, $J$ = 6.4 Hz, 6H), 1.07 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.4, 141.4, 139.6, 135.6, 133.3, 133.0, 129.8, 127.9, 127.8, 127.7, 127.6, 126.6, 120.5, 67.8, 64.0, 26.8, 22.0, 19.3. **LRMS** (EI): 458 [M], 414, 388, 361, 314, 279, 263, 206, 182, 134, 116, 91, 77, 43, 27. **HRMS** (ESI): calcd for $C_{29}H_{35}O_3Si^+$ 459.2350 [M+H]$^+$, found 459.2358.

### 2.3 General Procedure for Synthesis of Ketones 6 and 7 [5]

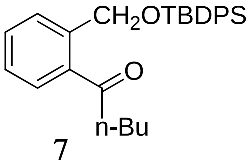
To an oven-dried, round-bottomed flask was added aldehyde **2** (2.0 g, 7.28 mmol) and 30 mL of anhydrous $Et_2O$ under nitrogen at 0 ℃. Then methylmagnesium iodide (2.8 mL, 3.12 M in $Et_2O$, 8.74 mmol) or n-butyl lithium (3.97 mL, 2.2 M in hexane, 8.74 mmol) solution was added with dropwise. The reaction was stirred until starting material consumed (detected by TLC). Saturated $NH_4Cl$ aqueous solution (5 mL) was added to quench the reaction. The separated organic layer was washed with brine (3×20 mL), dried ($Na_2SO_4$) and concentrated under vacuum to give the crude product which was used in next step without further purification.

To a solution of alcohol (6.0 mmol) prepared above in 40 mL of anhydrous $CH_2Cl_2$ was added a mixture of PCC (1.94 g, 9.0 mmol) and Celite (3.88 g) at room temperature and stirred over night. The mixture was diluted with 10 mL of $Et_2O$ and filtered on a pad of silica gel. The solvent was evaporated *in vacuo*, and the residue was purified by silica gel column chromatography to give the desired ketone **6** or **7**.



6

**Compound 6**. Yield 85 %, oil. **IR** (neat) $\nu_{max}$: 2930, 2778, 1718, 1681, 1589, 1428, 1252, 1067, 702, 616 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.04 (d, $J$ = 8.0 Hz, 1H), 7.74 (d, $J$ = 7.6 Hz, 1H), 7.68 (d, $J$ = 6.4 Hz, 4H), 7.57 (t, $J$ = 7.6 Hz, 2H), 7.29-7.41 (m, 6H), 5.13 (s, 2H), 2.50 (s, 3H), 1.13 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 200.7, 142.8, 135.5, 134.8, 133.5, 132.3, 129.7, 129.6, 127.7, 126.8, 126.3, 64.3, 28.8, 26.9, 19.4. **LRMS** (EI): 388 [M], 332, 287, 225, 200, 181, 165, 133, 105, 77, 57, 41. **HRMS** (ESI): calcd for $C_{25}H_{29}O_2Si^+$ 389.1931 $[M+H]^+$, found 389.1934.



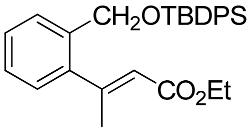
7

**Compound 7**. Yield 87 %, oil. **IR** (neat) $\nu_{max}$: 2931, 2858, 2740, 1770, 1682, 1471, 1260, 1076, 702, 615 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.04 (d, $J$ = 7.6 Hz, 1H), 7.71-7.71 (m, 5H), 7.60 (t, $J$ = 7.6 Hz, 1H), 7.36-7.46 (m, 7H), 5.13 (s, 2H), 2.88 (t, $J$ = 7.6 Hz, 2H), 1.63 (m, 2H), 1.34 (m, 2H), 1.16 (s, 9H), 0.93 (t, $J$ = 7.4 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 203.7, 142.4, 135.6, 135.4, 133.6, 131.9, 129.7, 128.6, 127.7, 127.0, 126.4, 64.2, 40.6, 27.0, 26.5, 22.5, 19.4, 13.9. **LRMS** (EI): 429 [M-1], 412, 396, 371, 352, 312, 295, 264, 211, 175, 156, 134, 118, 91, 77, 57, 41, 29. **HRMS** (ESI): calcd for $C_{28}H_{35}O_2Si^+$ 431.2401 $[M+H]^+$, found 431.2404.

### 2.4 General Methods for Synthesis of Esters (8) and (9) [6]

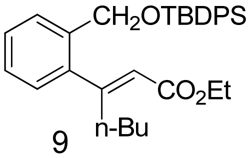
To an oven-dried, two-necked, round-bottomed flask, equipped with a condenser, was added Zn power (1.14 g, 17.5 mmol) and anhydrous benzene (40 mL) under nitrogen. Ketone **8** (1.36 g, 3.5 mmol) or **9** (1.5 g, 3.5 mmol) and ethyl bromoacetate (1.74 mL, 15.8 mmol) diluted in 15 mL of anhydrous benzene was then added with dropwise via a syringe as the reaction was maintaining under reflux. After addition, the reaction was refluxed for additional six hours. Saturated $NH_4Cl$ aqueous solution (10 mL) was slowly added to the mixture and stirred vigorously for one hour. The organic phase was separated and the water layer was extracted with EtOAc (3×30 mL), the combined organic layer was washed with brine (2×20 mL), dried over $Na_2SO_4$.

The solvent was removed *in vacuo* to give a dark residue which was then dissolved in 20 mL of pyridine and cooled to 0 ℃. To the mixture $POCl_3$ (0.84 g, 5.25 mmol) was slowly added under vigorously swirling. After addition, the reaction mixture was then warmed to room temperature gradually and stirred over night. The mixture was then poured into 50 mL of ice water, extracted with EtOAc (3×50 mL). The combined organic layer was washed with saturated $CuSO_4$ aqueous solution (5×30 mL), dried over $Na_2SO_4$ and concentrated under vacuum, the residue was then purified on a silica gel column.



8

**Compound 8**. Yield 57 % for two steps from **6**, oil. **IR** (neat) $\nu_{max}$: 2931, 1715, 1644, 1428, 1274, 1043, 879, 764 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.67 (t, $J$ = 7.2 Hz, 4H), 7.53 (d, $J$ = 7.6 Hz, 1H), 7.07-7.44 (m, 9H), 5.74 (s, 1H), 4.67 (s, 2H), 4.16 (q, $J$ = 7.2 Hz, 2H), 2.34 (s, 3H), 1.27 (t, $J$ = 7.0 Hz, 3H), 1.06 (s, 9H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.4, 156.8, 142.6, 136.8, 135.6, 133.4, 129.7, 128.1, 127.8, 127.7, 127.1, 127.1, 119.7, 63.5, 59.7, 26.8, 20.9, 19.3, 14.3. **LRMS** (EI): 460 [M+2], 443, 404, 355, 335, 311, 278, 222, 197, 181, 157, 129, 105, 91, 77, 57, 29. **HRMS** (ESI): calcd for $C_{29}H_{35}O_3Si^+$ 459.2350 [M+H]$^+$, found 459.2358.



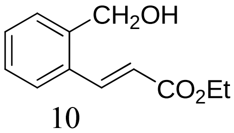
9

**Compound 9**. Yield 53 % for two steps from **7**, oil. **IR** (neat) $\nu_{max}$: 2978, 2928, 2850, 1715, 1633, 1469, 1171, 1038, 769 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.70 (t, $J$ = 8.0 Hz, 4H), 7.65 (d, $J$ = 7.6 Hz, 1H), 7.34-7.47 (m, 7H), 7.28 (t, $J$ = 7.2 Hz, 1H), 7.08 (d, $J$ = 7.6 Hz, 1H), 5.69 (s, 1H), 4.68 (s, 2H), 4.18 (q, *J* = 7.2 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 1.27 (m, 7H), 1.10 (s, 9H), 0.82 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.1, 161.2, 141.2, 137.3, 135.6, 133.4, 129.7, 127.9, 127.8, 127.7, 127.5, 126.8, 119.5, 63.4, 59.7, 33.5, 30.2, 26.9, 23.0, 19.3, 14.3, 13.8. **LRMS** (EI): 501 [M+1], 231, 187, 170, 143, 117, 91, 77, 55, 29. **HRMS** (ESI): calcd for $C_{32}H_{41}O_3Si^+$ 501.2819 $[M+H]^+$, found 501.2820.

### 2.5 General Method for Synthesis of Compounds 15-19

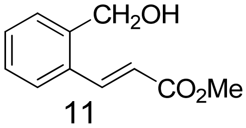
Acetyl chloride (15.8 mL) was added with dropwise to 100 mL of methanol, which was then cooled to room temperature. Ester (**3**, **4**, **5**, **8** or **9)** (2.67 mmol) prepared above was added and monitored by TLC. Upon completion, the reaction mixture was neutralized with 10 % NaOH, then concentrated *in vacuo* and the residue was purified by column chromatography to give alcohols **10-14**. [7]

Alcohol **10-14** (2.0 mmol) was dissolved in 20 mL of anhydrous $CH_2Cl_2$ and oxidized with a mixture of PCC (0.65 g, 3.0 mmol) and Celite (1.3 g) until no alcohol was detected by TLC. 5 mL of $Et_2O$ was added, the mixture was filtered on a pad of silica gel, and the solvent was removed under vacuum and the residue was purified by silica gel column chromatography to yield compounds **15-19**. [5]



10

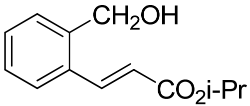
**Compound 10**. Yield 72 %, oil. **IR** (neat) $\nu_{max}$: 3434, 2980, 2929, 1715, 1634, 1368, 1031, 766, 610 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.04 (d, *J* = 16.0 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 1H), 7.33-7.45 (m, 3H), 6.39 (d, *J* = 16.0 Hz, 1H), 4.83 (s, 2H), 4.26 (q, *J* = 6.8 Hz, 2H), 2.17 (br, 1H), 1.34 (t, *J* = 7.0 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 167.0, 141.5, 139.8, 133.1, 130.1, 128.7, 128.1, 126.8, 120.1, 62.7, 60.6, 14.3. **LRMS** (EI): 206 [M], 188, 174, 162, 133, 89, 77, 65, 51, 39, 27. **HRMS** (ESI): calcd for $C_{12}H_{15}O_3^+$ 207.1016 $[M+H]^+$, found 207.1022.



11

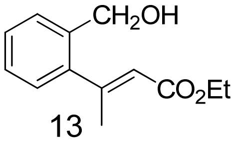
**Compound 11**. Yield 74 %, oil. **IR** (neat) $\nu_{max}$: 3340, 2930, 1697, 1631, 1427, 1315, 1169, 975, 764 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.02 (d, *J* = 15.6 Hz, 1H), 7.57 (d, *J* = 7.2 Hz, 1H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.28-7.38 (m, 2H), 6.37 (d, *J* = 15.6 Hz, 1H), 4.78 (s, 2H), 3.78 (s, 3H), 3.12

(br, 1H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): $\delta$ 167.6, 141.8, 139.7, 133.0, 130.2, 128.8, 128.2, 126.8, 119.6, 62.7, 51.8. **LRMS** (EI): 193 [M+1], 177, 159, 148, 130, 114, 103, 91, 77, 57, 27. **HRMS** (ESI): calcd for $C_{11}H_{13}O_3^+$ 193.0859 $[M+H]^+$, found 193.0868.



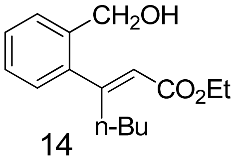
12

**Compound 12**. Yield 71 %, oil. **IR** (neat) $\nu_{max}$: 3436, 2927, 1709, 1634, 1454, 1312, 1017, 765 cm$^{-1}$. $^{1}$**H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.02 (d, $J$ = 16.0 Hz, 1H), 7.61 (d, $J$ = 7.6 Hz, 1H), 7.32-7.47 (m, 3H), 6.39 (d, $J$ = 15.6 Hz, 1H), 5.11-5.17 (m, J = 6.2 Hz, 1H), 4.82 (s, 2H), 2.19 (br, 1H), 1.31 (d, $J$ = 6.0 Hz, 6H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.5, 141.1, 139.5, 133.2, 130.1, 128.7, 128.2, 126.9, 120.8, 68.0, 62.9, 22.0. **LRMS** (EI): 220 [M], 202, 178, 161, 146, 133, 114, 102, 91, 77, 63, 51, 41, 27. **HRMS** (ESI): calcd for $C_{13}H_{17}O_3^+$ 221.1172 $[M+H]^+$, found 221.1181.



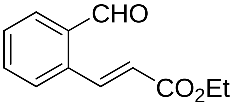
13

**Compound 13**. Yield 73 %, oil. **IR** (neat) $\nu_{max}$ : 3430, 2926, 1725, 1639, 1446, 1174, 1040, 879, 764 cm$^{-1}$. $^{1}$**H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.52 (d, $J$ = 7.6 Hz, 1H), 7.30-7.39 (m, 2H), 7.16 (d, $J$ = 7.6 Hz, 1H), 5.83 (s, 1H), 4.71 (s, 2H), 4.24 (q, $J$ = 7.2 Hz, 2H), 2.51 (s, 3H), 1.69 (br, 1H), 1.34 (t, $J$ = 7.2 Hz, 3H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.4, 156.7, 143.1, 136.7, 128.4, 128.1, 127.7, 127.4, 119.9, 62.8, 60.0, 29.7, 21.3, 14.3. **LRMS** (EI): 219 [M-1], 204, 188, 174, 160, 128, 115, 102, 91, 77, 63, 43, 29, 14. **HRMS** (ESI): calcd for $C_{13}H_{17}O_3^+$ 221.1172 $[M+H]^+$, found 221.1171.



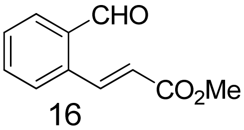
14

**Compound 14**. Yield 70 %, oil. **IR** (neat) $\nu_{max}$: 3381, 2930, 1725, 1637, 1442, 1101, 767, 620 cm$^{-1}$. $^{1}$**H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.53 (d, $J$ = 7.2 Hz, 1H), 7.35 (dt, $J$ = 7.6, 1.2 Hz, 1H), 7.28 (m, $J$ = 8.4 Hz, 1H), 7.11 (dd, $J$ = 7.6, 1.2 Hz, 1H), 5.75 (s, 1H), 4.66 (d, $J$ = 4.8 Hz, 2H), 4.21 (q, $J$ = 7.0 Hz, 2H), 3.75 (t, $J$ = 6.6 Hz, 2H), 2.96 (t, $J$ = 7.4 Hz, 2H), 2.14 (br, 1H), 1.87 (q, $J$ = 6.8 Hz, 2H), 1.32 (t, $J$ = 7.0 Hz, 3H), 0.87 (t, $J$ = 7.0 Hz, 3H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.2, 161.2, 141.6, 137.3, 128.2, 128.0, 127.7, 127.3, 119.7, 62.6, 60.0, 33.8, 30.2, 23.0, 14.3, 13.9. **LRMS** (EI): 262 [M], 2444, 218, 189, 146, 117, 91, 77, 57, 29. **HRMS** (ESI): calcd for $C_{16}H_{23}O_3^+$ 263.1642 $[M+H]^+$, found 263.1648.



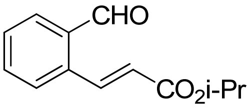
15

**Compound 15**. Yield 85%, oil. **IR** (neat) $v_{max}$: 2983, 2728, 1740, 1699, 1635, 1316, 1183, 774 cm$^{-1}$. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 10.31 (s, 1H), 8.51 (d, $J$ = 16.0 Hz, 1H), 7.88 (d, $J$ = 7.6 Hz, 1H), 7.54-7.64 (m, 3H), 6.38 (d, $J$ = 16.0 Hz, 1H), 4.29 (q, $J$ = 7.2 Hz, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 191.7, 166.2, 140.9, 136.7, 133.9, 133.9, 132.2, 129.9, 128.0, 123.3, 60.8, 14.3. **LRMS** (EI): 204 [M], 175, 158, 131, 103, 77, 51, 29. **HRMS** (ESI): calcd for $C_{12}H_{13}O_3^+$ 205.0859 $[M+H]^+$, found 205.0867.



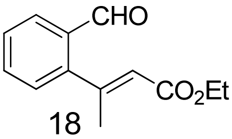
16

**Compound 16**. Yield 87%, oil. **IR** (neat) $v_{max}$: 2954, 1720, 1694, 1595, 1436, 1315, 1169, 974, 700 cm$^{-1}$. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 10.24 (s, 1H), 8.53 (d, $J$ = 16.0 Hz, 1H), 7.87 (d, $J$ = 7.2 Hz, 1H), 7.55-7.70 (m, 3H), 6.38 (d, $J$ = 16.0 Hz, 1H), 3.82 (s, 3H). **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 191.8, 166.6, 141.3, 136.4, 133.9, 133.8, 132.5, 130.0, 127.9, 122.6, 51.9. **LRMS** (EI): 190 [M], 176, 161, 105, 91, 75, 59, 15. **HRMS** (ESI): calcd for $C_{11}H_{11}O_3^+$ 191.0703 $[M+H]^+$, found 191.0709.



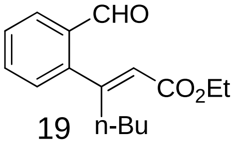
17

**Compound 17**. Yield 85 %, oil. **IR** (neat) $v_{max}$: 2936, 1715, 1635, 1595, 1268, 1108, 765, 660 cm$^{-1}$. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 10.31 (s, 1H), 8.49 (d, $J$ = 15.6 Hz, 1H), 7.88 (d, $J$ = 7.2 Hz, 1H), 7.53-7.65 (m, 3H), 6.36 (d, $J$ = 15.6 Hz, 1H), 5.11-5.21 (m, 1H), 1.33 (d, $J$ = 6.0 Hz, 6H). **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 191.7, 165.7, 140.6, 136.8, 133.9, 133.8, 132.0, 129.8, 128.0, 123.8, 68.2, 21.9. **LRMS** (EI): 218 [M], 175, 147, 129, 103, 75, 43, 27. **HRMS** (ESI): calcd for $C_{13}H_{15}O_3^+$ 219.1016 $[M+H]^+$, found 219.1018.



18

**Compound 18**. Yield 85 %, oil. **IR** (neat) $v_{max}$: 2928, 2853, 1708, 1634, 1385, 1162, 777, 670 cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.13 (s, 1H), 7.92 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.58-7.62 (m, 1H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.30 (d, *J* = 7.8, 0.8 Hz, 1H), 5.80 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 2.56 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 191.2, 165.8, 154.2, 147.1, 133.8, 133.0, 129.0, 128.4, 128.3, 121.9, 60.2, 21.7, 14.3. **LRMS** (EI): 218 [M], 199, 180, 159, 116, 91, 77, 57, 28, 14. **HRMS** (ESI): calcd for $C_{13}H_{15}O_3^+$ 219.1016 [M+H]$^+$, found 219.1017.



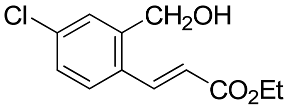
19

**Compound 19**. Yield 87 %, oil. **IR** (neat) $\nu_{max}$: 2958, 2931, 2860, 1715, 1633, 1447, 1171, 764, 609 cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.14 (s, 1H), 7.96 (d, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.30 (t, *J* = 7.6 Hz, 1H), 5.75 (s, 1H), 4.23 (q, *J* = 7.2 Hz, 2H), 3.05 (t, *J* = 7.6 Hz, 2H), 1.27-1.41 (m, 7H), 0.87 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 191.3, 165.5, 158.5, 146.2, 133.6, 133.5, 128.6, 128.6, 128.3, 121.8, 60.2, 34.3, 30.1, 22.9, 14.3, 13.8. **LRMS** (EI): 259 [M-1], 242, 216, 187, 144, 115, 91, 75, 51, 29. **HRMS** (ESI): calcd for $C_{16}H_{21}O_3$ 261.1485 [M+H]$^+$, found 261.1481.

### 2.6 General Procedure for Synthesis of Compounds 20-23

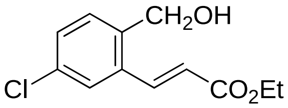
To a flame-dried, two-necked, round-bottomed flask were added NBS (4.27 g, 23.7 mmol), AIBN (0.89 g, 5.45 mmol) and 40 mL of anhydrous benzene. Then a mixture of (*E)*-ethyl 3-(2-methyl-4-chloro-phenyl) and 3-(2-methyl-5-chloro-phenyl) acrylates (4.9 g, 21.8 mmol) was added, and the reaction mixture was warmed to 80 ℃ and refluxed over night under nitrogen. The reaction was cooled down to room temperature and concentrated *in vacuo*. The residue was redissolved in 60 mL of dioxane/$H_2O$ (5:1 v/v), and then $CaCO_3$ (10.9 g, 0.11 mol) power were added. The mixture was refluxed for five hours and then cooled to room temperature. 50 mL of EtOAc was added, the mixture was filtered and the white solid was washed with EtOAc (3×30 mL). The organic layer was washed with brine (3×30 mL) before dried over $Na_2SO_4$. After removal of the solvent *in vacuo*, the residue was purified by silica gel column chromatography to yield compound **20** (1.3 g, 22%) and **21 (**1.5 g, 37 %). [8]

Alcohol **20** or **21**(1.0 g, 4.16 mmol) was dissolved in anhydrous $CH_2Cl_2$ and oxidized with a mixture of PCC (1.34g, 6.24 mmol) and Celite (2.7 g) at room temperature. After 3 hours, 5 mL of $Et_2O$ was added to diluted the mixture, which was then filtered on a pad of silica gel. The solvent was evaporated *in vacuo* and the residue was purified by silica gel column chromatography to give the desired product.



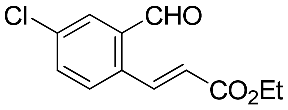
20

**Compound 20**. Yield 22 %, oil. **IR** (neat) $\nu_{max}$: 3441, 2955, 1727, 1636, 1595, 1483, 1292, 687 $cm^{-1}$. **$^1$H NMR**(400 MHz, $CDCl_3$): $\delta$ 7.93 (d, $J$ = 16.0 Hz, 1H), 7.56 (d, $J$ = 2.0 Hz, 1H), 7.40 (d, $J$ = 8.4 Hz, 1H), 7.34 (dd, $J$ = 8.4, 2.0 Hz, 1H), 6.39 (d, $J$ = 15.6 Hz, 1H), 4.79 (s, 2H), 4.27 (q, $J$ = 7.2 Hz, 2H ), 2.41 (br, 1H), 1.35 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 166.7, 140.0, 137.9, 134.7, 134.0, 130.0, 129.9, 126.7, 121.5, 62.2, 60.8, 14.3. **LRMS** (EI): 239 [M-1], 222, 219, 193, 181, 167, 151, 125, 103, 89, 77, 63, 51, 43, 29. **HRMS** (ESI): calcd for $C_{12}H_{14}ClO_3^+$ 241.0626 $[M+H]^+$, found 241.0628.



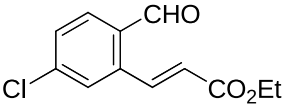
21

**Compound 21**. Yield 37 %, oil. **IR** (neat) $\nu_{max}$: 3430, 2924, 1715, 1685, 1366, 981, 698 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.87 (d, $J$ = 16.0 Hz, 1H), 7.46-7.49 (m, 2H), 7.26 (dd, $J$ = 8.8/8.4, 2.0/1.6 Hz, 1H), 6.33 (d, $J$ = 16.0 Hz, 1H), 4.78 (d, $J$ = 4.8 Hz, 2H), 4.24 (q, $J$ = 7.2 Hz, 2H), 2.96 (br, 1H), 1.32 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 167.0, 141.5, 140.1, 136.1, 131.1, 128.3, 128.1, 128.0, 120.4, 62.1, 60.8, 14.7. **LRMS** (EI): 239 [M-1], 221, 194, 168, 149, 131, 115, 103, 77, 51, 29. **HRMS** (ESI): calcd for $C_{12}H_{14}ClO_3^+$ 241.0626 $[M+H]^+$, found 241.0628.



22

**Compound 22**. Yield 94 %, oil. **IR** (neat) $\nu_{max}$: 2959, 1720, 1636, 1466, 1191, 823, 696 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.26 (s, 1H), 8.43 (d, $J$ = 16.0 Hz, 1H), 7.83 (d, $J$ = 8.4 Hz, 1H), 7.60 (d, $J$ = 2.0 Hz, 1H), 7.52 (dd, $J$ = 8.4, 2.0 Hz, 1H), 6.39 (d, $J$ = 15.6 Hz, 1H), 4.29 (q, $J$ = 7.2 Hz, 2H), 1.35 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 190.3, 165.8, 140.5, 139.4, 138.3, 133.3, 132.1, 129.9, 128.0, 124.4, 61.0, 14.3. **LRMS** (EI): 238 [M], 208, 192, 164, 135, 102, 75, 51, 43, 29. **HRMS** (ESI): calcd for $C_{12}H_{12}ClO_3^+$ 239.0478 $[M+H]^+$, found 239.0469.

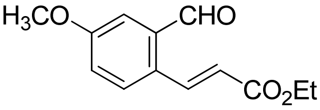


23

**Compound 23**. Yield 92 %, oil. **IR** (neat) $\nu_{max}$: 2926, 1715, 1638, 1556, 1365, 1033, 822, 692 cm$^{-1}$. $^{1}$**H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.27 (s, 1H), 8.41 (d, *J* = 16.0 Hz, 1H), 7.85 (s, 1H), 7.58 (d, J = 2.0 Hz, 2H), 6.37 (d, *J* = 16.0 Hz, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): $\delta$ 190.1, 165.9, 139.3, 136.3, 135.0, 134.9, 133.9, 131.3, 129.4, 123.9, 60.9, 14.3. **LRMS** (EI): 239 [M+1], 209, 193, 163, 136, 102, 75, 51, 43, 29, 14. **HRMS** (ESI): calcd for $C_{12}H_{12}ClO_3^+$ 239.0478 $[M+H]^+$, found 239.0469.

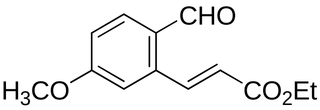
**2.7 General Method for Synthesis of Compound 24-25**.

A mixture of (*E*)-ethyl β-(2-$CH_2OH$-4-methyloxy-phenyl) or β-(2-$CH_2OH$-5-methyloxy-phenyl) acrylates (0.6 g, 2.54 mmol) dissolved in 30 mL of anhydrous $CH_2Cl_2$ was oxidized with a mixture of PCC (0.82 g, 3.81 mmol) and Celite (1.64 g) at room temperature. After three hours, $Et_2O$ (5 mL) was added. The mixture was filtered on a pad of silica gel, and the solvent was evaporated *in vacuo* and the residue was purified through a silica gel column to give the product.



24

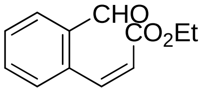
**Compound 24**. Yield 92 %, oil. **IR** (neat) $\nu_{max}$: 2924, 1712, 1631, 1601, 1497, 1028, 756, 668 cm$^{-1}$. $^{1}$**H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.38 (s, 1H), 8.46 (d, *J* = 16.0 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 7.40 (d, J = 2.8 Hz, 1H), 7.16 (dd, *J* = 8.8, 2.8 Hz, 1H), 6.34 (d, *J* = 16.0 Hz, 1H), 4.31 (q, *J* = 7.0 Hz, 2H), 3.92 (s, 3H), 1.37 (t, *J* = 7.2 Hz, 3H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): $\delta$ 191.0, 166.5, 161.0, 139.6, 135.1, 129.4, 129.4, 121.4, 120.8, 114.4, 60.7, 55.7, 14.3. **LRMS** (EI): 234 [M], 206, 177, 161, 134, 118, 89, 75, 63, 29. **HRMS** (ESI): calcd for $C_{13}H_{15}O_4^+$ 235.0965 $[M+H]^+$, found 235.0972.



25

**Compound 25.** Yield 89 %, oil. **IR** (neat) $\nu_{max}$: 2933, 1765, 1713, 1635, 1606, 1464, 1108, 737, 602 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.16 (s, 1H), 8.52 (d, $J$ = 16.0 Hz, 1H), 7.84 (d, $J$ = 8.8 Hz, 1H), 7.02-7.08 (m, 2H), 6.36 (d, $J$ = 16.0 Hz, 1H), 4.29 (q, $J$ = 7.2 Hz, 2H), 3.92 (s, 3H), 1.35 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 190.3, 166.2, 163.8, 141.1, 139.0, 134.8, 127.5, 123.3, 115.1, 113.1, 60.8, 55.7, 14.3. **LRMS** (EI): 233 [M-1], 219, 198, 175, 147, 105, 91, 77, 59, 28, 14. **HRMS** (ESI): calcd for $C_{13}H_{15}O_4^+$ 235.0965 $[M+H]^+$, found 235.0972.

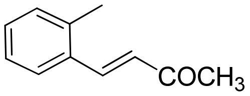
### 2.8 Synthesis of Compound 26 [9]



26

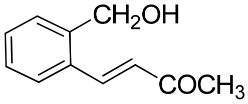
**Compound 26**. To an oven-dried, two-necked round-bottomed flask, commercially available (*Z*)-methyl-3-iodoacrylate (47.1 mg, 0.22 mmol), 2-formylphenylboronic acid (50.0 mg, 0.33 mmol), $Pd(PPh_3)_4$ (2.57 mg, 0.0022 mmol), $K_3PO_4.7H_2O$ (150.2 mg, 0.44 mmol) was added in anhydrous THF (4.0 mL) under nitrogen and the mixture was stirred at 40 ℃ for 10 hours. The reaction was diluted with 30 mL of $Et_2O$, the organic phase was separated and washed with brine (2×10 mL), dried over $Na_2SO_4$. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography to yield 23.1 mg (54 %) as a colorless oil. **IR** (neat) $v_{max}$: 2928, 2854, 1773, 1695, 1596, 1361, 1014, 755 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.14 (s, 1H), 7.89 (d, $J$ = 8.0 Hz, 1H), 7.57 (t, $J$ = 7.6 Hz, 1H), 7.47-7.52 (m, 2H), 7.37 (d, $J$ = 7.2 Hz, 1H), 6.18 (d, $J$ = 12.0 Hz, 1H), 4.04 (q, $J$ = 7.2 Hz, 2H), 1.11 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 191.9, 165.4, 142.1, 138.2, 133.2, 131.7, 131.0, 130.0, 128.5, 122.8, 60.3, 13.9. **LRMS** (EI): 204 [M], 175, 158, 131, 103, 77, 51, 29. **HRMS** (ESI): calcd for $C_{12}H_{13}O_3^+$ 205.0859 $[M+H]^+$, found 205.0867.

### 2.9 General Procedure for Synthesis of Compound 27-29



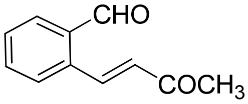
27

**Compound 27**. To a mixture of acetone (20 mL) and 10 % NaOH (3.86 mL, 11.0 mmol), 2-methylbenzaldehyde (1.1 g, 9.16 mmol) was added with dropwise and the reaction mixture was stirred at room temperature until the 2-methylbenzaldehyd was consumed (detected by TLC). The reaction was neutralized with 10 % HCl aqueous solution, and extracted with $Et_2O$ (3×30 mL). The combined organic layers was washed with brine (2 mL), dried over $Na_2SO_4$ and concentrated *in vacuo*. The crude product was purified through a silica gel column to yield a yellow oil (1.04 g, 71 %). [10] **IR** (neat) $\nu_{max}$: 2926, 1693, 1598, 1359, 1257, 975, 752 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.82 (d, $J$ = 16.0 Hz, 1H), 7.56 (d, $J$ = 7.6 Hz, 1H), 7.27-7.31 (m, 1H), 7.22 (t, $J$ = 7.0 Hz, 2H), 6.64 (d, $J$ = 16.0 Hz, 1H), 2.45 (s, 3H), 2.39 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 198.3, 140.9, 137.9, 133.4, 130.9, 130.3, 128.1, 126.5, 126.4, 27.8, 19.8. **LRMS** (EI): 160 [M], 144, 126, 117, 101, 89, 77, 57, 27. **HRMS** (ESI): calcd for $C_{11}H_{13}O^+$ 161.0961 [M+H$^+$], found 161.0961.



28

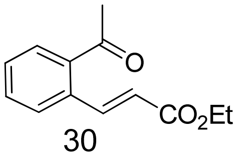
**Compound 28.** A mixture of compound **27** (0.9 g, 5.62 mmol), NBS (1.1 g, 6.18 mmol) and AIBN (0.23 g, 1.4 mmol) was dissolved in 50 mL of anhydrous benzene and refluxed at 80 ℃ under nitrogen protection for eight hours. Benzene was then evaporated *in vacuo*, the residue redissolved in 60 mL of dioxane/$H_2O$ (5:1, v/v) was refluxed with $CaCO_3$ (2.81 g, 28.1 mmol) over night. 40 mL of EtOAc was added and the reaction mixture was filtered. The organic layer was separated, washed with brine (2×20 mL) and dried over $Na_2SO_4$. After removal of the solvent, the resulted residue was purified through a silica gel column to give the desired alcohol **28** (0.63 g, 64 %). **IR** (neat) $\nu_{max}$: 3065, 2980, 2616, 1715, 1693, 1598, 1258, 1014, 755 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.95 (d, $J$ = 16.0 Hz, 1H), 7.65 (d, $J$ = 7.2 Hz, 1H), 7.35-7.46 (m, 3H), 6.70 (d, $J$ = 16.0 Hz, 1H), 4.86 (s, 2H), 2.42 (s, 3H), 2.00 (br, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 198.6, 140.2, 139.7, 133.4, 130.4, 129.0, 129.0, 128.5, 126.9, 63.3, 27.7. **LRMS** (EI): 177 [M+1], 157, 115, 89, 77, 63, 42. **HRMS** (ESI): calcd for $C_{12}H_{15}O_3^+$ 177.0910 $[M+H]^+$, found 177.0908.



29

**Compound 29.** A mixture of PCC (0.38 g, 1.77 mmol) and Celite (0.76 g) was added to a stirred solution of alcohol **28** (0.2 g, 1.14 mmol) in 20 mL of anhydrous $CH_2Cl_2$. The mixture was stirred over night. 10 mL of $Et_2O$ was added to dilute the reaction and the mixture was filtered on a pad of silica gel. The solvent was removed by rotary evaporation *in vacuo* and the residue was purified by silica gel column chromatography to give the product as a clear oil (0.17 g, 86 %). **IR** (neat) $\nu_{max}$: 2921, 1764, 1685, 1598, 1366, 1045, 737 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.24 (s, 1H), 8.49 (d, $J$ = 16.4 Hz, 1H), 7.87 (dd, $J$ = 7.2, 1.2 Hz, 1H), 7.58-7.69 (m, 3H), 6.60 (d, $J$ = 16.4 Hz, 1H), 2.46 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 198.7, 192.6, 140.6, 136.4, 134.0, 133.8, 131.8, 130.1, 127.9, 27.0. **LRMS** (EI): 175 [M+1], 158, 133, 104, 77, 51, 29. **HRMS** (ESI): calcd for $C_{11}H_{11}O_2^+$ 175.0754 [M+H$^+$], found 175.0761.

### 2.10 Synthesis of Compound 30 [2]

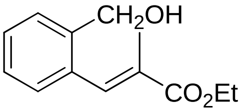


30

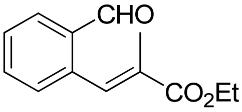
**Compound 30**. To a stirred solution of **15** (0.204 g, 1.0 mmol) in 10 mL of anhydrous $Et_2O$, Methylmagnesium iodide (0.5 mL, 3.12 M in $Et_2O$, 1.56 mmol) was added with dropwise through a syringe under nitrogen protection at -40 ℃. After one hour, saturated $NH_4Cl$ aqueous solution (5 mL) was slowly added to quench the reaction. The organic layer was separated, washed with brine (2×20 mL) and dried over $Na_2SO_4$. The solvent was evaporated *in vacuo* and the crude product was directly used for next step without further purification.

Alcohol (0.18 g, 0.82 mmol) obtained above was redissolved in 20 mL of anhydrous $CH_2Cl_2$, PCC (0.26 g, 1.23 mmol) and Celite (0.52 g) were then added. The mixture was stirred at room temperature for three hours. After reaction, $Et_2O$ (5 mL) was added and the mixture was filtered on a pad of silica gel. The solvent was removed *in vacuo*, the residue was purified by column chromatography to give the desired compound **30** (0.15 g, 86 % for two steps from compound **15**). **IR** (neat) $\nu_{max}$: 2982, 2850, 1714, 1682, 1566, 1359, 1251, 1178, 1041, 863, 768, 607 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.14 (d, $J$ = 16.0 Hz, 1H), 7.74 (d, $J$ = 7.6 Hz, 1H), 7.59 (d, $J$ = 7.6 Hz, 1H), 7.53 (t, $J$ = 7.4 Hz, 1H), 7.46 (q, $J$ = 7.6 Hz, 1H), 6.29 (d, $J$ = 16.0 Hz, 1H), 4.27 (d, $J$ = 7.2 Hz, 2H), 2.62 (s, 3H), 1.34 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 200.6, 166.3, 143.7, 138.0, 134.6, 131.8, 129.2, 129.1, 128.1, 120.7, 60.3, 29.1, 14.1. **LRMS** (EI): 218 [M], 190, 162, 134, 117, 91, 77, 29. **HRMS** (ESI): calcd for $C_{13}H_{15}O_3^+$ 219.1016 [M+H]$^+$, found 219.1017.

## 2.11 Synthesis of Compounds 31-32


31

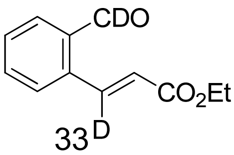
**Compound 31**. [11] Compound **2** (1.0 g, 2.67 mmol) was added to a solution of $PPh_3=C(CH_3)CO_2Et$ (1.06 g, 2.94 mmol) in 20 mL of anhydrous MeOH under nitrogen protection. After reaction, the solvent was removed *in vacuo*, and the residue was dissolved in EtOAc (50 mL), washed with brine (3×20 mL) and dried over $Na_2SO_4$. The solvent was evaporated *in vacuo* to give a colorless oil, which was directly used for next step without further purification. The protecting group was then removed by 3 % HCl-MeOH solution at room temperature to give the compound **31**. Yield, 54 % for two steps from **2**. **IR** (neat) $v_{max}$: 3331, 2936, 1713, 1592, 1367, 1101, 765, 601 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.80 (s, 1 H), 7.47 (t, $J$ = 8.8 Hz, 1H), 7.28-7.35 (m, 2 H), 7.21 (t, $J$ = 8.4 Hz, 1 H), 4.65 (s, 2H), 4.26 (q, $J$ = 7.0 Hz, 2 H), 2.26 (br, 1H), 1.93 (s, 3H), 1.34 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 168.4, 139.2, 136.8, 134.3, 130.4, 129.0, 128.4, 127.7, 127.4, 62.9, 61.0, 14.3, 14.0. **LRMS** (EI): 219 [M-1], 202, 189, 174, 161, 144, 131, 119, 105, 91, 77, 65, 51, 29. **HRMS** (ESI): calcd for $C_{13}H_{17}O_3^+$ 221.1172 $[M+H]^+$, found 221.1171.


32

**Compound 32**. Alcohol **31** (300 mg, 1.0 equiv) in 20 mL of anhydrous $CH_2Cl_2$ was oxidized with PCC (439 mg, 1.5 equiv) and Celite (880 mg, 3.0 equiv) at room temperature for three hours. Then $Et_2O$ (5 mL) was added and the mixture was filtered on a pad of silica gel. The solvent was removed *in vacuo* and the residue was purified by silica gel column chromatography to give the product **32** as a colorless oil (273 mg, 92 %). **IR** (neat) $v_{max}$: 2964, 2845, 1693, 1442, 1230, 1010, 869, 767 $cm^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 10.17 (s, 1H), 8.06 (s, 1H), 7.93 (dd, $J$ = 7.6, 1.0 Hz, 1H), 7.60-7.64 (m, 1H), 7.49 (t, $J$ = 7.4 Hz, 1H), 7.31 (d, $J$ = 7.6 Hz, 1H), 4.30 (q, $J$ = 7.0 Hz, 2H), 1.90 (d, $J$ = 1.6 Hz, 3H), 1.37 (t, $J$ = 7.2 Hz, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 191.6, 167.7, 138.8, 136.0, 133.8, 133.7, 132.0, 130.0, 129.9, 128.4, 61.1, 14.3, 14.0. **LRMS** (EI): 218 [M], 203, 189, 173, 161, 146, 131, 117, 102, 89, 77, 63, 51, 39, 29. **HRMS** (ESI): calcd for $C_{13}H_{15}O_3^+$ 219.1016 $[M+H]^+$, found 219.1017.

### 2.12 Synthesis of Compound 33

The synthesis route for compound **33** was similar to compound **15** except of LiAlD$_4$ used to reduce the phthalate in the first step.

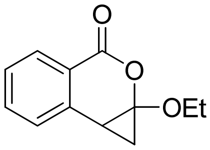


33

**Compound 33. IR** (neat) $\nu_{max}$: 2983, 2850, 1740, 1621, 1373, 1245, 1179, 1045, 847, 607 cm$^{-1}$. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 7.89 (d, $J$ = 7.6 Hz, 1H), 7.58-7.66 (m, 2H), 7.55 (t, $J$ = 8.4 Hz, 1H), 6.38 (s, 1H), 4.29 (q, $J$ = 7.2 Hz, 2H), 1.36 (t, $J$ = 7.2 Hz, 1H). **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 166.2, 136.6, 133.9, 133.8, 132.2, 129.9, 128.0, 123.2, 60.8, 14.3. **LRMS** (EI): 206 [M], 176, 160, 148, 133, 104, 79, 64, 43, 28, 14. **HRMS** (ESI): calcd for $C_{12}H_{10}D_2O_3^+$ $[M+H]^+$ 207.0985, found 207.0994.

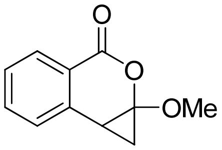
### 2.13 General Procedure for Irradiation of Compounds 15-19, 22-24, 26, 29, 30, 32, 33 in Benzene.

The reactant dissolved in benzene (2.0 mg/mL) was purged with nitrogen for 20 min then irradiated with a 500 W medium-pressure mercury lamp through a Pyrex filter. The reaction was monitored by TLC. After reaction, the solvent was removed *in vacuo* and the residue was purified by preparative thin layer chromatography to give the photoproduct. [2, 5]



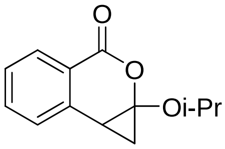
34

**Compound 34**. Yield 89 %. **IR** (neat): $\nu_{max}$ 2982, 2849, 1736, 1607, 1374, 1046, 737, 607 cm$^{-1}$. **$^1$H NMR** (400 MHz, CDCl$_3$): $\delta$ 8.16 (d, $J$ = 8.0 Hz, 1H), 7.56 (m, $J$ = 7.2 Hz, 1H), 7.42 (d, $J$ = 7.6 Hz, 1H), 7.37 (t, $J$ = 7.6 Hz, 1H), 3.88-3.94 (m, 2H), 2.60 (q, $J$ = 5.4 Hz, 1H), 1.83 (q, $J$ = 5.4 Hz, 1H), 1.29 (t, $J$ = 7.0 Hz, 3H), 0.81 (t, $J$ = 6.2 Hz, 1H). **$^{13}$C NMR** (100 MHz, CDCl$_3$): $\delta$ 161.8, 140.7, 134.2, 131.2, 127.9, 127.3, 120.4, 91.4, 64.4, 22.4, 21.4, 15.1. **LRMS** (EI): 204 [M], 175, 146, 131, 103, 77, 51, 29. **HRMS** (ESI): calcd for $C_{12}H_{13}O_3^+$ 205.0859 $[M+H]^+$, found 205.0867.



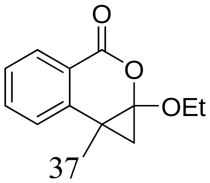
35

**Compound 35**. Yield 67.7%. **IR** (neat) $\nu_{max}$: 2952, 2834, 1716, 1608, 1476, 953, 826, 676 cm$^{-1}$. $^1$**H NMR** (400 MHz, $CDCl_3$): *δ* 8.16 (d, *J* = 8.0 Hz, 1H), 7.57 (m, *J* = 7.6 Hz, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 8.0 Hz, 1H), 3.62 (s, 3H), 2.61 (q, *J* = 7.0 Hz, 1H), 1.83 (q, *J* = 5.6 Hz, 1H), 0.82 (t, *J* = 5.4 Hz, 1H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): *δ* 161.8, 140.6, 134.3, 131.2, 127.9, 127.4, 120.3, 92.3, 55.7, 22.3, 21.2. **LRMS** (EI): 190 [M], 161, 130, 103, 77, 59, 28, 15. **HRMS** (ESI): calcd for $C_{11}H_{11}O_3$ 191.0703$^+$ [M+H]$^+$, found 191.0709.



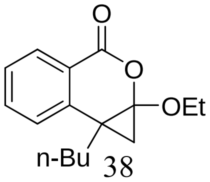
36

**Compound 36**. Yield 71%. **IR** (neat) $v_{max}$: 2923, 2779, 1724, 1606, 1463, 1108, 752, 688 cm$^{-1}$. $^1$**H NMR** (400 MHz, $CDCl_3$): *δ* 8.17 (d, *J* = 8.0 Hz, 1H), 7.57 (m, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 1H), 7.38 (m, *J* = 7.6 Hz, 1H), 4.30 (m, 1H), 2.59 (q, *J* = 5.4 Hz, 1H), 1.83 (q, *J* = 5.4 Hz, 1H), 1.30 (q, *J* = 6.0 Hz, 6H), 0.80 (t, *J* = 6.2 Hz, 1H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): *δ* 161.8, 140.7, 134.1, 131.2, 127.9, 127.3, 120.4, 90.7, 72.7, 23.4, 23.3, 22.3, 21.7. **LRMS** (EI): 218 [M], 191, 176, 162, 147, 130, 103, 91, 77, 59, 43, 28, 14. **HRMS** (ESI): calcd for $C_{13}H_{15}O_3^+$ 219.1016 [M+H]$^+$, found 219.1018.



37

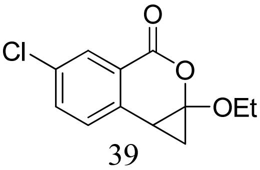
**Compound 37**. Yield 98 %. **IR** (neat) $v_{max}$: 2928, 2850, 1723, 1605, 1469, 1195, 770, 692 cm$^{-1}$. $^1$**H NMR** (400 MHz, $CDCl_3$): *δ* 8.19 (dd, *J* = 7.6, 0.8, 1.2 Hz, 1H), 7.56-7.63 (m, 2H), 7.36 (m, *J* = 8.0 Hz, 1H), 3.91 (q, *J* = 7.2, 2H), 1.66 (s, 3H), 1.48 (d, *J* = 6.0 Hz, 1H), 1.32 (t, *J* = 7.2 Hz, 3H), 0.86 (d, *J* = 6.4 Hz, 1H). $^{13}$**C NMR** (100 MHz, $CDCl_3$): *δ* 161.7, 144.4, 134.2, 131.0, 126.8, 125.5, 120.4, 94.6, 64.7, 27.4, 24.4, 16.1, 15.2. **LRMS** (EI): 218 [M], 189, 161, 145, 115, 91, 63, 45, 29, 14. **HRMS** (ESI): calcd for $C_{13}H_{15}O_3^+$ 219.1016 [M+H]$^+$, found 219.1024.



38

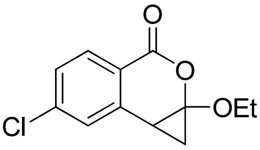
**Compound 38**. Yield 82 %. **IR** (neat) $v_{max}$: 2956, 2930, 2860, 1716, 1633, 1447, 1171, 764, 609 cm$^{-1}$. $^1$**H NMR** (400 MHz, $CDCl_3$): *δ* 8.19 (dd, *J* = 8.0, 0.6 Hz, 1H), 7.53-7.62 (m, 2H), 7.36

(m, *J* = 8.0 Hz, 1H), 4.08-4.16 (m, 1H), 3.80-3.87 (m, 1H), 2.32-2.38 (m, 1H), 1.56-1.64 (m, 3H), 1.44 (d, *J* = 6.0 Hz, 1H), 1.30-1.34 (m, 5H), 0.88 (t, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.8 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 161.6, 142.9, 133.9, 131.2, 126.6, 125.8, 121.3, 94.7, 64.8, 30.1, 29.3, 28.4, 27.0, 22.8, 15.3, 13.8. **LRMS** (EI): 260 [M], 242, 217, 189, 171, 156, 144, 131, 115, 103, 91, 77, 41, 29, 14. **HRMS** (ESI): calcd for $C_{16}H_{21}O_3^+$ 261.1485 $[M+H]^+$, found 261.1481.



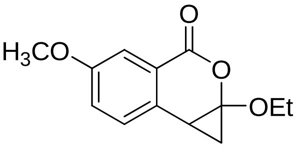
39

**Compound 39**. Yield 75 %. **IR** (neat) $\nu_{max}$: 2918, 2851, 1724, 1484, 1264, 1180, 1041, 953, 765 cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.10 (d, *J* = 8.4 Hz, 1H), 7.44 (d, J = 2.0 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.0 Hz, 1H), 3.87-3.93 (m, 2H), 2.58 (q, *J* = 5.4 Hz, 1H), 1.89 (q, *J* = 5.4 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H), 0.86 (t, *J* = 6.4 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 161.0, 142.3, 140.7, 132.8, 127.9, 127.9, 118.9, 91.4, 64.6, 22.6, 21.2, 15.1. **LRMS** (EI): 238 [M], 224, 210, 196, 183, 164, 158, 138, 131, 103, 89, 77, 63, 51, 43, 29. **HRMS** (ESI): calcd for $C_{12}H_{12}ClO_3^+$ 239.0478 $[M+H]^+$, found 239.0469.



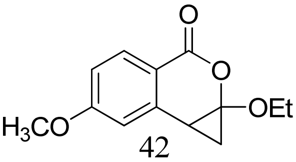
40

**Compound 40**. Yield 73 %. **IR** (neat) $\nu_{max}$: 2919, 2851, 1724, 1484, 1275, 1178, 953, 764 cm$^{-1}$. **$^{1}$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.14 (d, *J* = 2.0 Hz, 1H), 7.52 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 1H), 3.90 (m, 2H), 2.57 (q, *J* = 5.4 Hz, 1H), 1.85 (q, *J* = 5.4 Hz, 1H), 1.31 (t, *J* = 7.0 Hz, 3H), 0.82 (t, *J* = 6.2 Hz, 1H) . **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 160.6, 139.0, 134.3, 133.4, 130.9, 129.3, 121.9, 91.5, 64.6, 22.5, 20.9, 15.1. **LRMS** (EI): 239 [M+1], 209, 181, 165, 137, 102, 75, 51, 29. **HRMS** (ESI): calcd for $C_{12}H_{12}ClO_3^+$ 239.0478 $[M+H]^+$, found 239.0469.



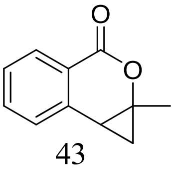
41

**Compound 41**. Yield 63 %. **IR** (neat) $\nu_{max}$: 2924, 2840, 1722, 1504, 1269, 1025, 679 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 7.66 (d, J = 2.8 Hz, 1H ), 7.35 (d, $J$ = 8.4 Hz, 1H), 7.16 (dd, $J$ = 8.4, 2.8 Hz, 1H), 3.89-3.96 (m, 2H), 3.86 (s, 3H), 2.57 (q, $J$ = 5.4 Hz, 1H), 1.78 (q, $J$ = 5.4 Hz, 1H), 1.31 (t, $J$ = 7.2 Hz, 3H), 0.76 (t, $J$ = 6.4 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 162.0, 158.8, 133.0, 129.0, 122.6, 121.2, 113.2, 91.5, 64.4, 55.7, 21.9, 20.8, 15.1. **LRMS** (EI): 234 [M], 205 176, 161, 117, 89, 77, 63, 29. **HRMS** (ESI): calcd for $C_{13}H_{15}O_4^+$ 235.0965 [M+H]$^+$, found 235.0972.



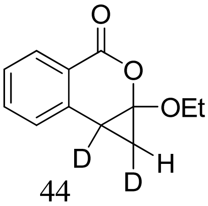
42

**Compound 42.** Yield 74 %. **IR** (neat) $v_{max}$: 2915, 2834, 1712, 1635, 1466, 1352, 1033, 679 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.13 (d, $J$ = 9.6 Hz, 1H), 6.88-6.90 (m, 2H), 3.90-3.95 (m, 5H), 2.56 (q, $J$ = 5.4 Hz, 1H), 1.83 (q, $J$ = 5.4 Hz, 1H), 1.31 (t, $J$ = 6.8 Hz, 3H), 0.85 (t, $J$ = 6.2 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 164.2, 161.7, 143.0, 133.6, 113.8, 113.0, 112.1, 91.2, 64.4, 55.6, 22.2, 21.7, 15.1. **LRMS** (EI): 234 [M], 206, 176, 161, 117, 89, 77, 63, 28. **HRMS** (ESI): calcd for $C_{13}H_{15}O_4^+$ 235.0965 [M+H]$^+$, found 235.0972.



43

**Compound 43**. Yield 48 %. **IR** (neat) $v_{max}$: 2928, 2854, 1715, 1608, 1488, 1308, 1128, 743, 645 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.14 (dd, $J$ = 8.0, 0.6 Hz, 1H), 7.54 (m, $J$ = 7.6 Hz, 1H), 7.41 (d, $J$ = 7.6 Hz, 1H), 7.33 (m, $J$ = 7.6 Hz, 1H), 2.16 (q, $J$ = 5.0 Hz, 1H), 1.72 (s, 3H), 1.43 (q, $J$ = 5.0 Hz, 1H), 0.69 (t, $J$ = 6.0 Hz, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 162.6, 142.0, 133.9, 131.0, 127.8, 126.8, 120.1, 63.0, 23.1, 22.9, 20.6. **LRMS** (EI): 173 [M-1], 131, 103, 77, 43, 15. **HRMS** (ESI): calcd for $C_{11}H_{11}O_2^+$ 175.0754 [M+H]$^+$, found 175.0763.



44

**Compound 44**. Yield 73 %. **IR** (neat) $v_{max}$: 2925, 2853, 1725, 1619, 1463, 1262, 1085, 747, 688 cm$^{-1}$. **$^1$H NMR** (400 MHz, $CDCl_3$): $\delta$ 8.17 (d, $J$ = 7.6 Hz, 1H), 7.57 (q, $J$ = 7.6 Hz, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 3.88-3.94 (m, 2H), 1.29 (t, *J* = 7.0 Hz, 3H), 0.81 (s, 1H). **$^{13}$C NMR** (100 MHz, $CDCl_3$): $\delta$ 161.8, 140.6, 134.2, 131.2, 127.9, 127.3, 120.4, 91.3, 64.5, 15.1. **LRMS** (EI): 206 [M], 176, 167, 133, 105, 78, 51, 29. **HRMS** (ESI): calcd for $C_{12}H_{10}D_2O_3^+$ $[M+H]^+$ 207.0985, found 207.0994.

**Quantum yields** for formation of products (lactones) were determined in dried benzene solutions containing 0.01 mol/L reactant and 1.000 g/mL tetradecane as internal standard. Equal volumes (3 mL) of each solution were placed in specially cleaned 1×10 cm Pyrex culture tubes, degassed 20 min and sealed. Irradiations were conducted at about 25 °C in a merry-go-round apparatus with a 500 W medium-pressure mercury lamp housed in an immersion well. The 313-nm mercury line was isolated by a glass tube which contained an aqueous solution of 0.002 mol/L $K_2CrO_4$/5% $K_2CO_3$. Quantum yields of photoproduct formation were determined by quantitative GC relative to acetophenone formation (<10%) from parallel runs on 0.1 mol/L valerophenone in benzene containing 1.000 g/mL of tetradecane as internal standard ($\Phi$= 0.32). Quantum yield for formation of lactones were determined at varying conversions. The experiment was repeated three times and average quantum yield for formation of lactone was 0.36.

## References

[1] Wan, X. B.; Dordot, G.; Joulié, M. M. *Org. Lett.* **2007**, 9, 977-980.

[2] Xia, W. J.; Yang, C.; Scheffer, J. R. *J. Am. Chem. Soc.* **2005**, 127, 2725-2730.

[3] Wang, Y.; West, F. G. *Synthesis* **2002**, 99-103.

[4] Cohn, O. M. *Org. Syn. Coll. Vol.* **1993**, 8, 350.

[5] Xia, W. J.; Scheffer, J. R.; Botoshansky, M. *Org. Lett.*, **2005**, 7, 1315-1318.

[6] Rinehar, K. L.; Jr. Perkins; Perkins, E.G. *Org. Syn. Coll. Vol.* **1963**, 4, 444.

[7] Wood, W. W.; Rashid, A. *Tetrahydron Lett.* **1987**, 28, 1933.

[8] Smith, J. G.; Dibble, P. W.; Sandborn, R. E. *J. Org. Chem.* **1986**, 51, 3762-3768.

[9] Bryan, C. S.; Lautens, M. *Org. Lett.* **2010**, 12, 2754-2757.

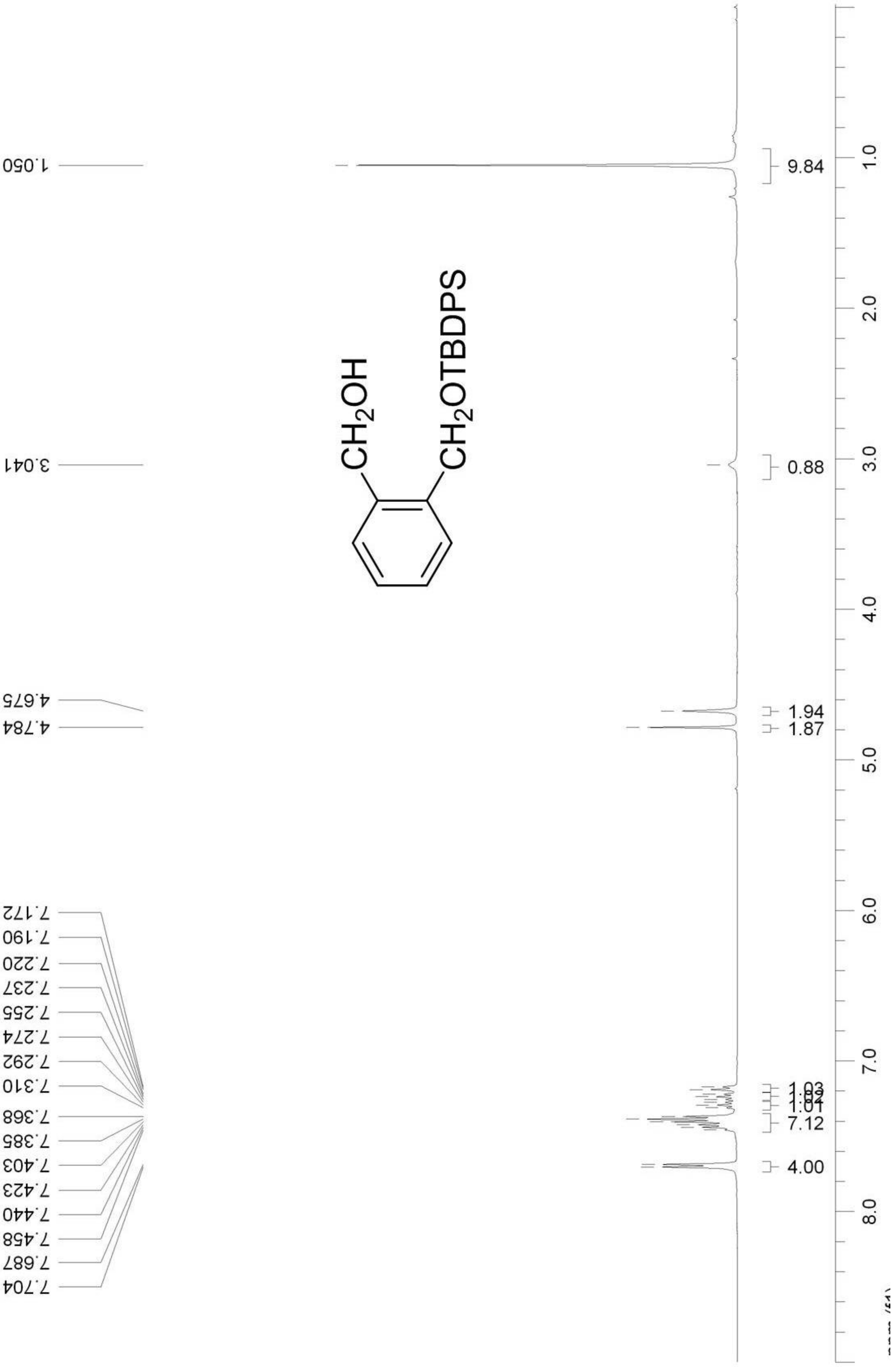
[10] Wang, Z. H.; Yin, G. D.; Qin, J. *Synthesis* **2008**, 3565-3568.

[11] Nakamura, M.; Mori, Y. Okuyama K. *Org. Biomol. Chem.* **2003**, 1, 3362-3376.

[12] Wagner, P. J., Kocheevar, I. E., Kemppainen, A. E. *J. Am. Chem. Soc.*, **1972**, 7489-7494.

[13] Leibovitch, M., Olovsson, G., Scheffer, J. R., Trotter, J. *J. Am. Chem. Soc.*, **1998**, 120, 12755-12769.

## Copies of NMR Spectra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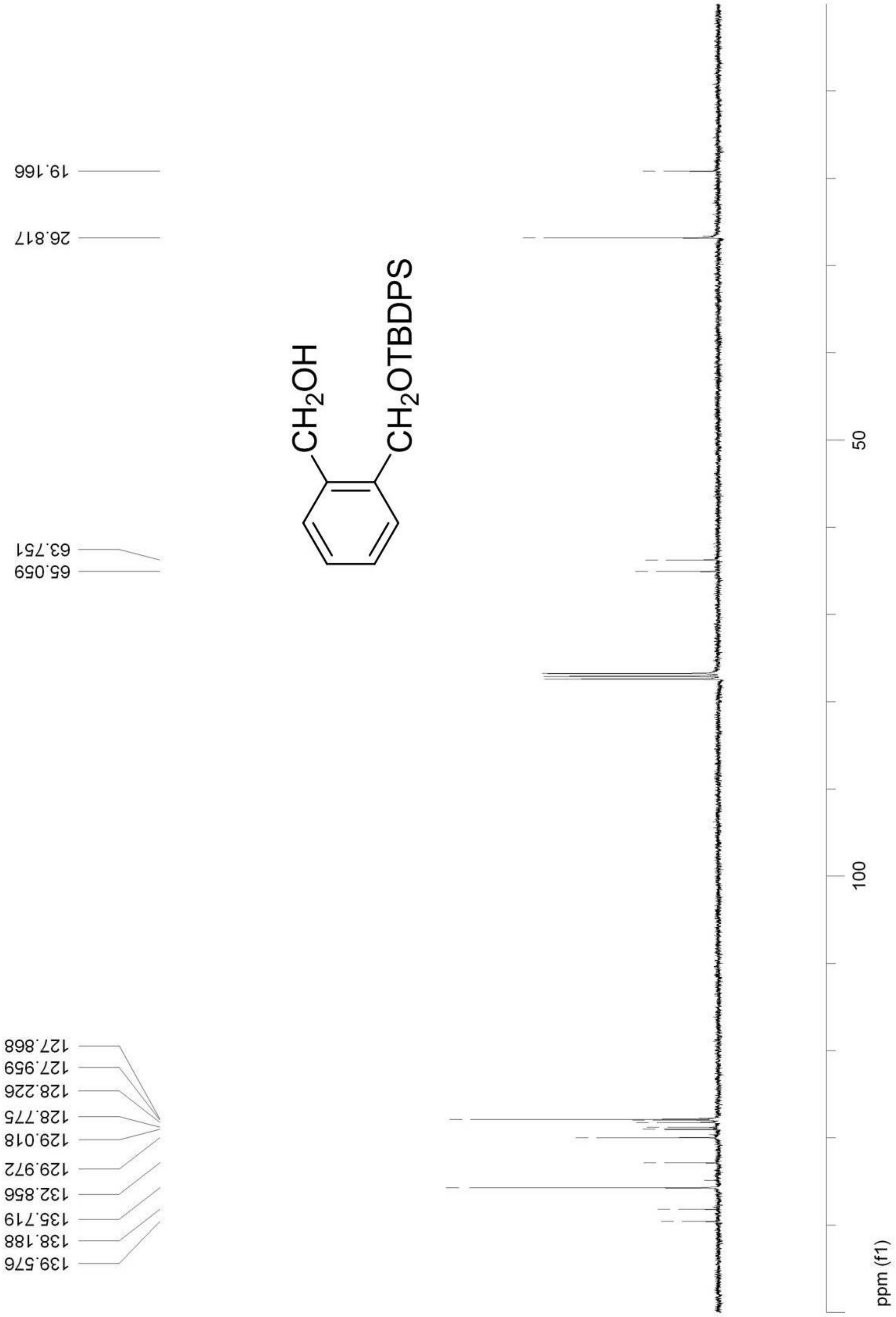
7.255
7.274
7.292
7.310
7.368
7.385
7.403
7.423
7.440
7.458
7.687
7.704
9.84
0.88
1.94
1.87
1.03
1.82
1.01
7.12
4.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0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138.188
139.576
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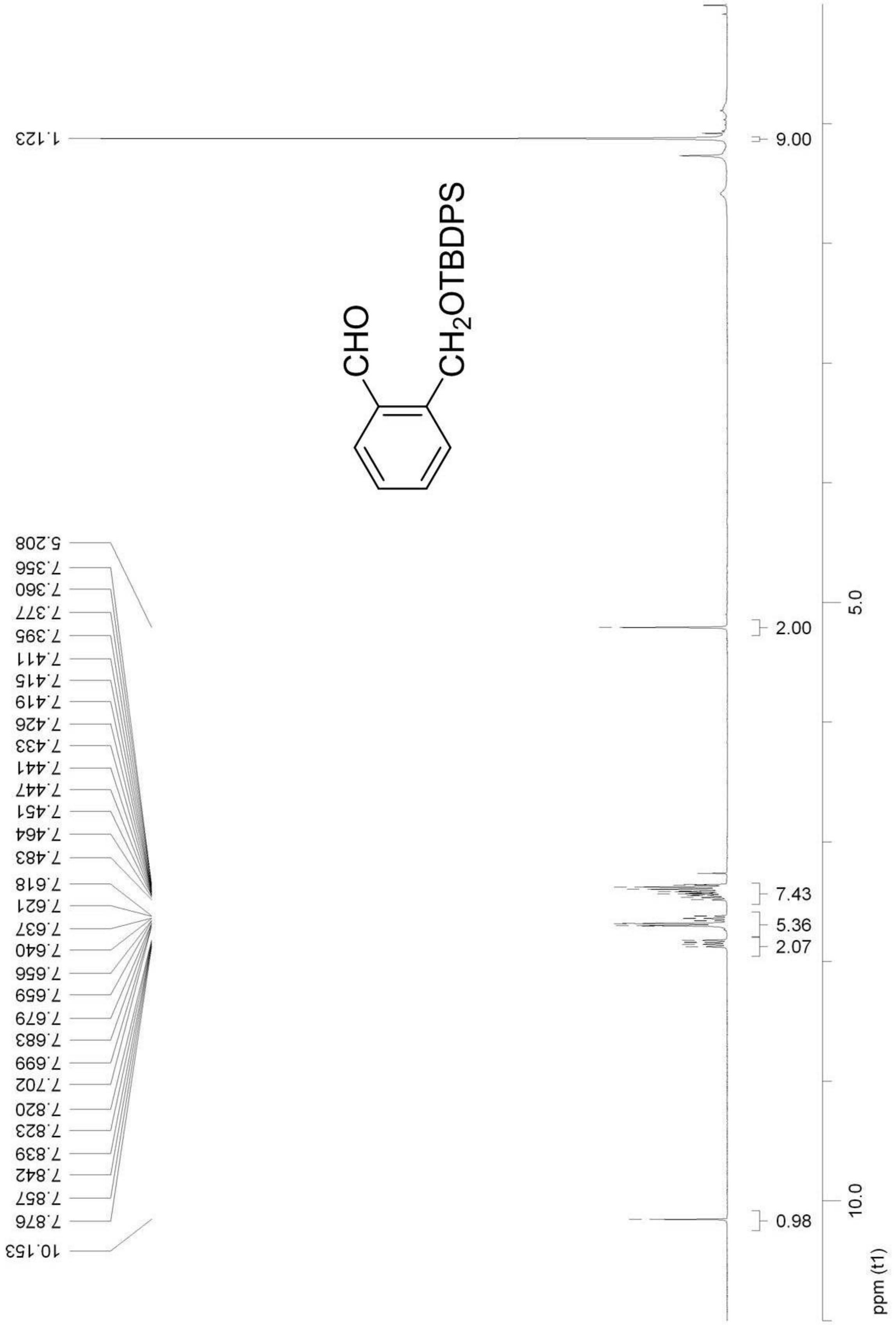
$CH_2OTBDPS$
50
100
ppm (f1)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7.360
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7.426
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7.441
7.447
7.451
7.464
7.483
7.618
7.621
7.637
7.640
7.656
7.659
7.679
7.683
7.699
7.702
7.820
7.823
7.839
7.842
7.857
7.876
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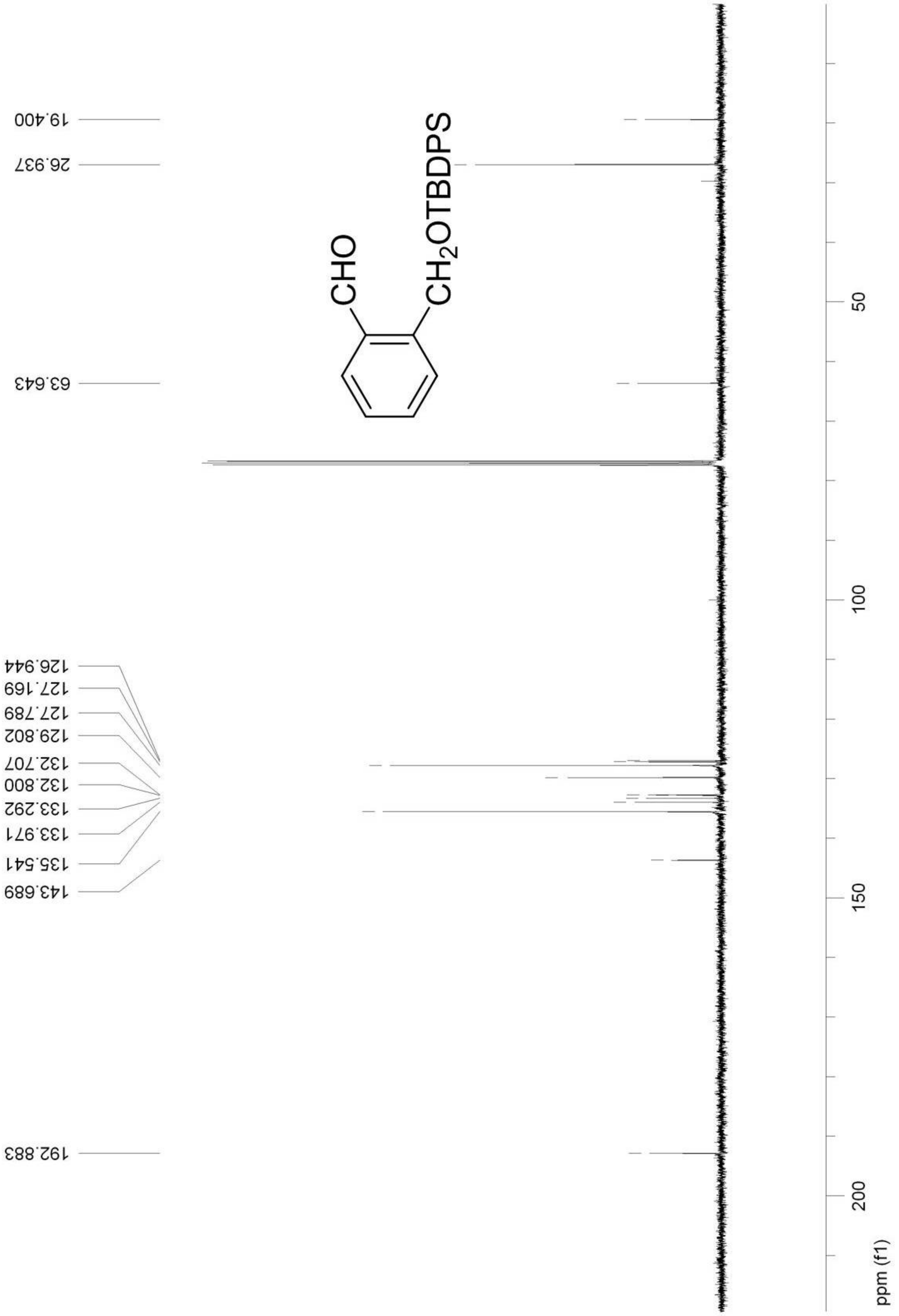
10.0
ppm (t1)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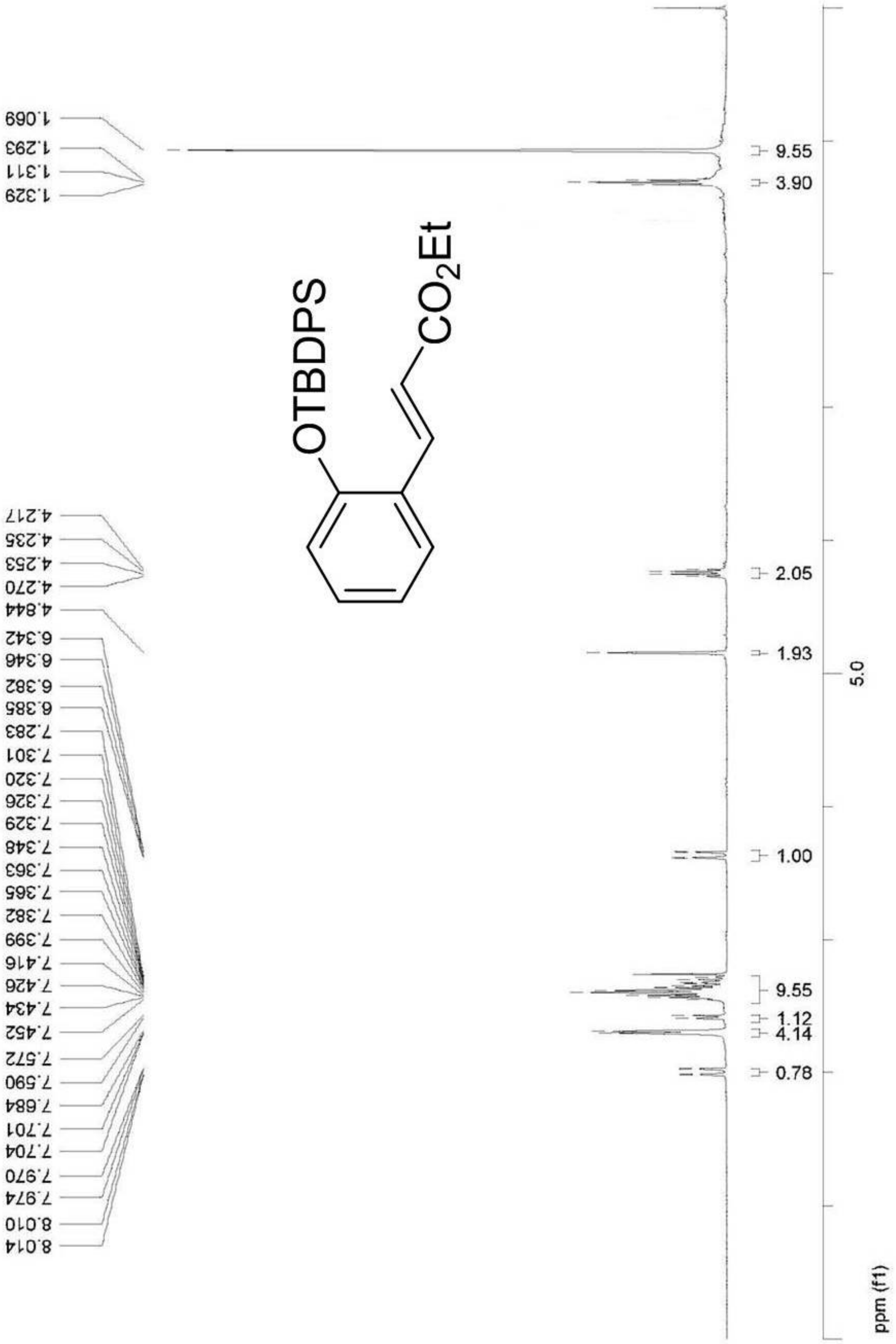
135.541
143.689
192.883
CHO
$CH_2OTBDPS$
50
100
150
200
ppm (f1)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6.385
7.283
7.301
7.320
7.326
7.329
7.348
7.363
7.365
7.382
7.399
7.416
7.426
7.434
7.452
7.572
7.590
7.684
7.701
7.704
7.970
7.974
8.010
8.014
OTBDPS
CO2Et
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2.05
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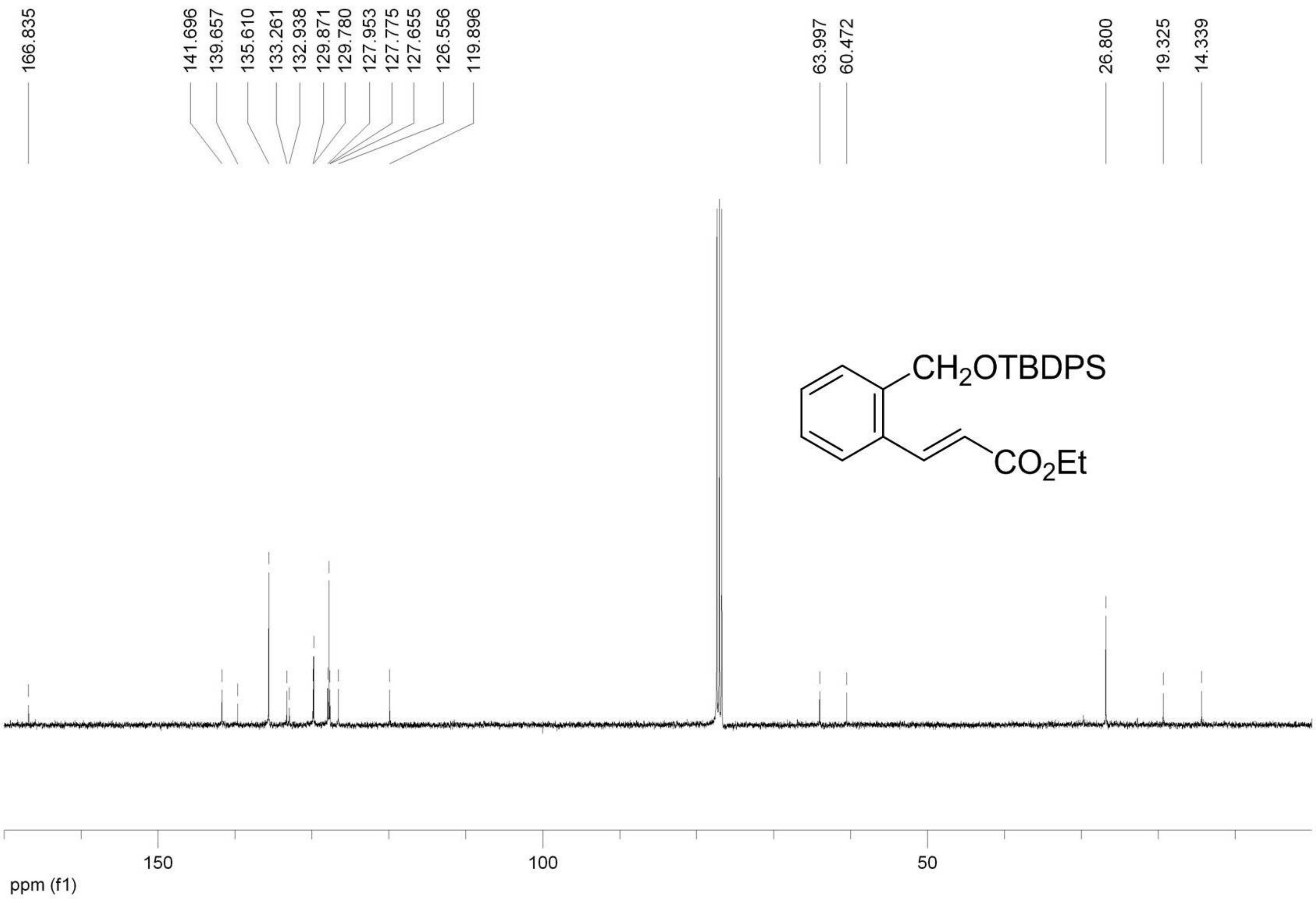
ppm (f1)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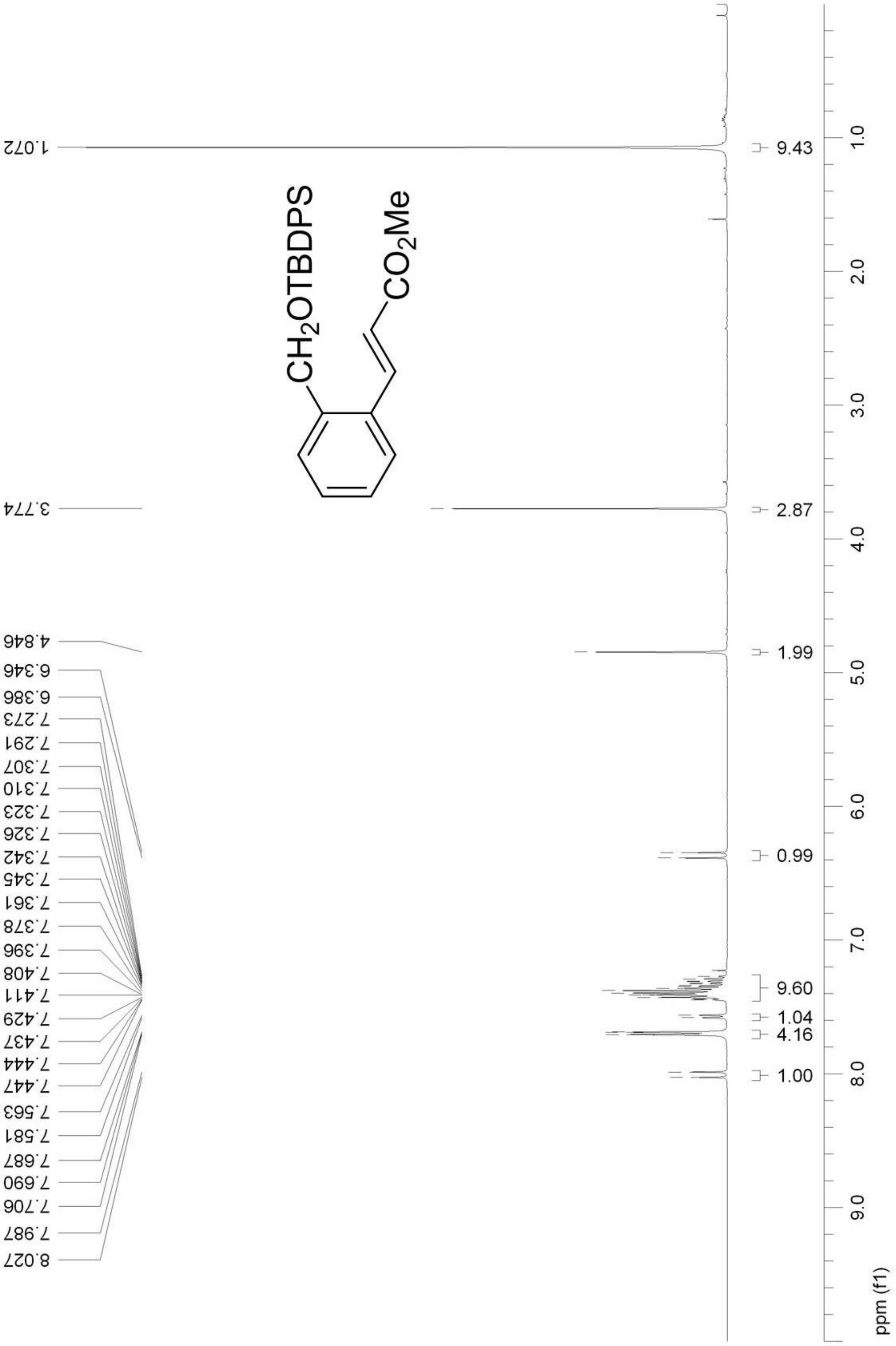
100
50
ppm (f1)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7.361
7.378
7.396
7.408
7.411
7.429
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7.444
7.447
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7.687
7.690
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CH2OTBDPS
CO2Me
9.43
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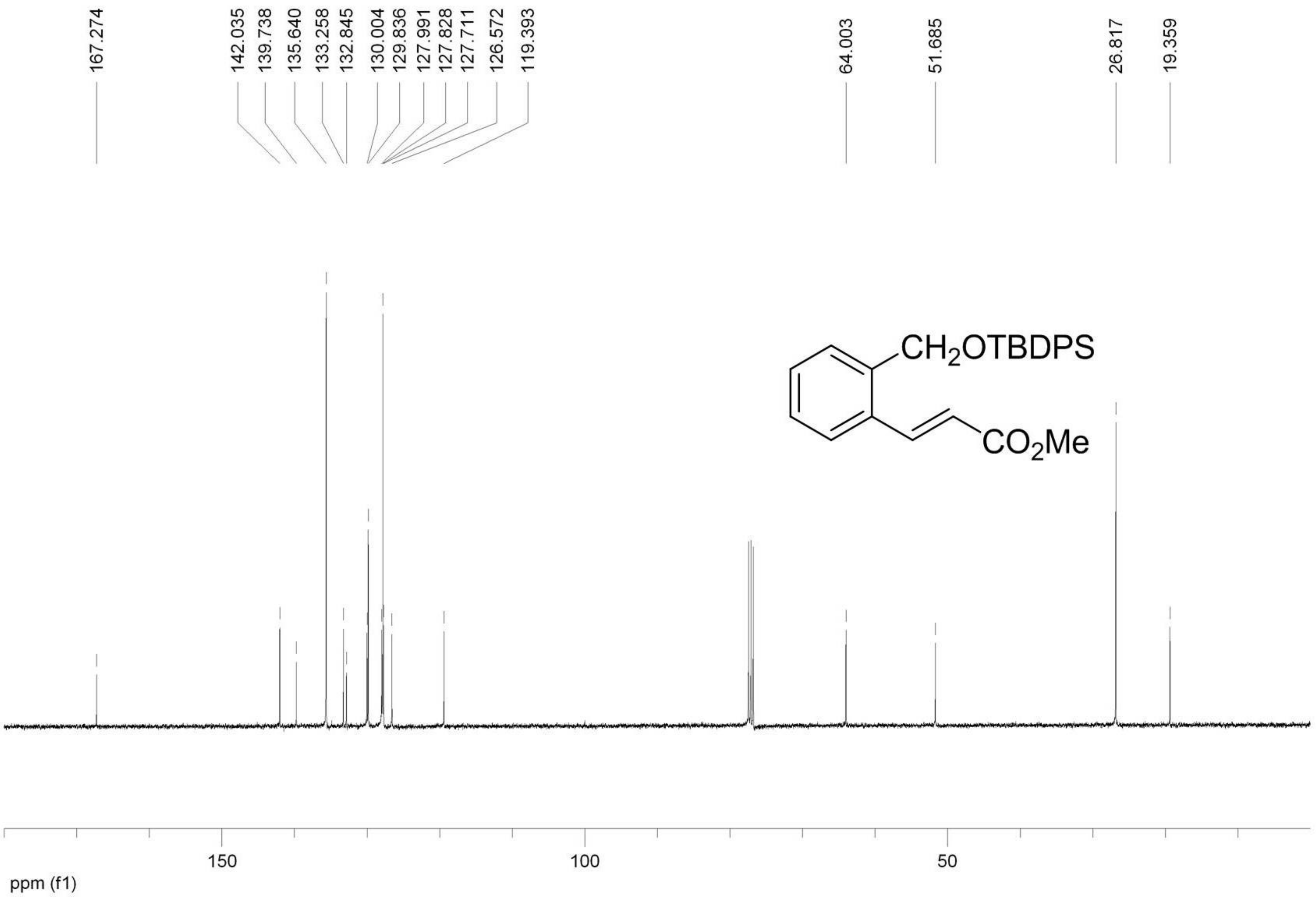
ppm (f1)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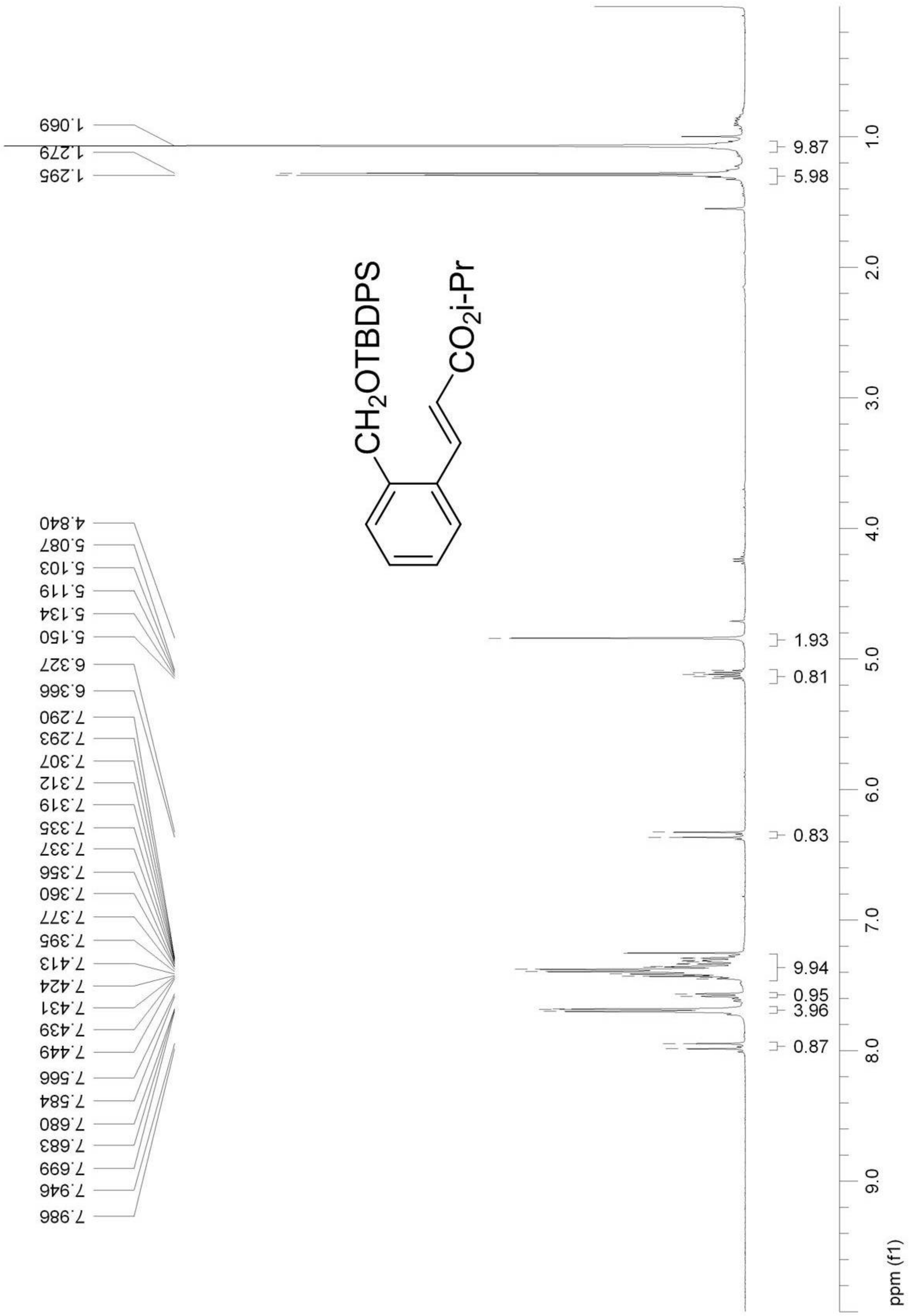
CO2Me
150
100
50
ppm (f1)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7.293
7.307
7.312
7.319
7.335
7.337
7.356
7.360
7.377
7.395
7.413
7.424
7.431
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7.680
7.683
7.699
7.946
7.986
CH2OTBDPS
CO2i-Pr
9.87
5.98
1.93
0.81
0.83
9.94
0.95
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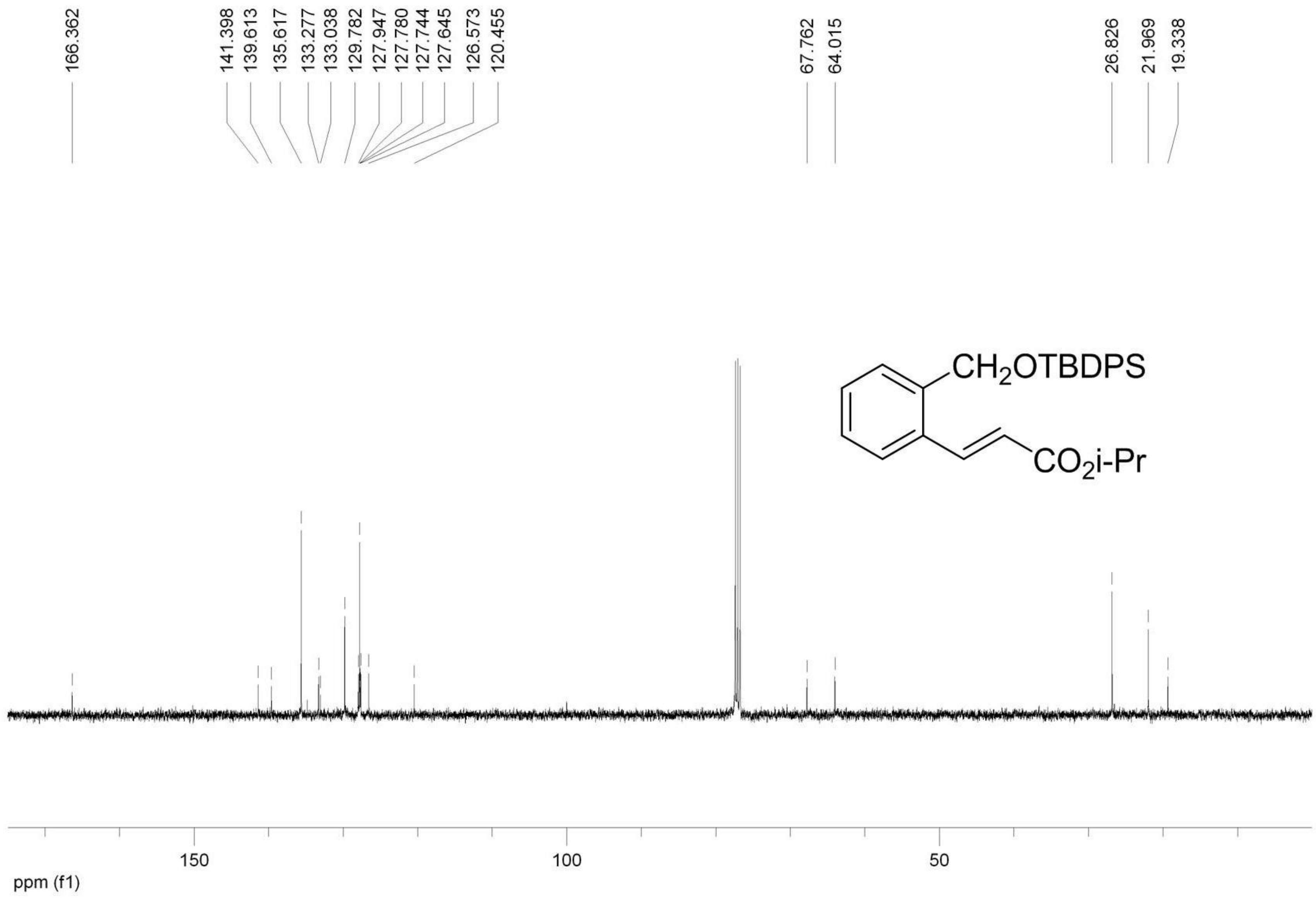
7.0
8.0
9.0
ppm (f1)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CO₂i-Pr
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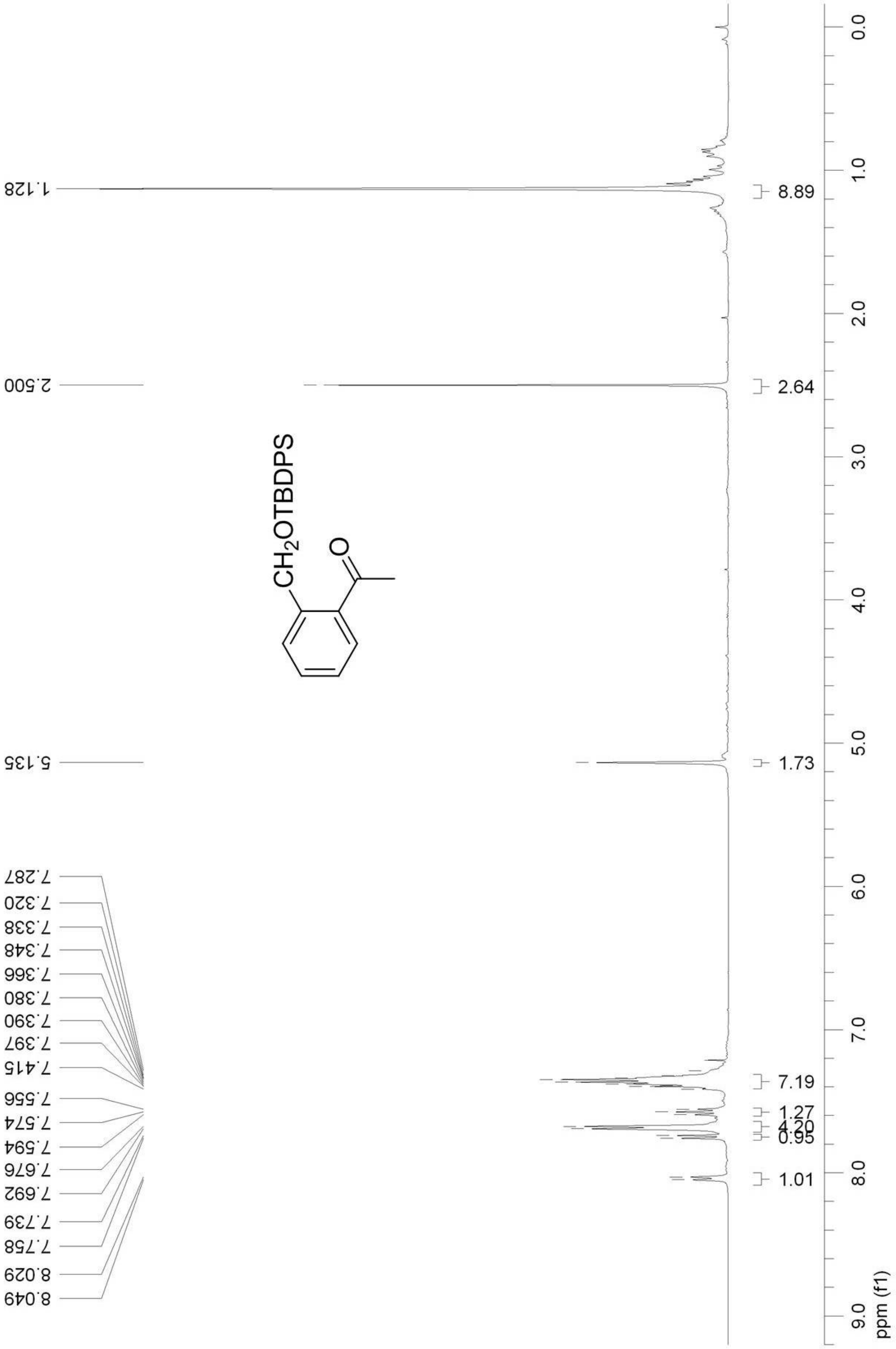
100
50
ppm (f1)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2.64
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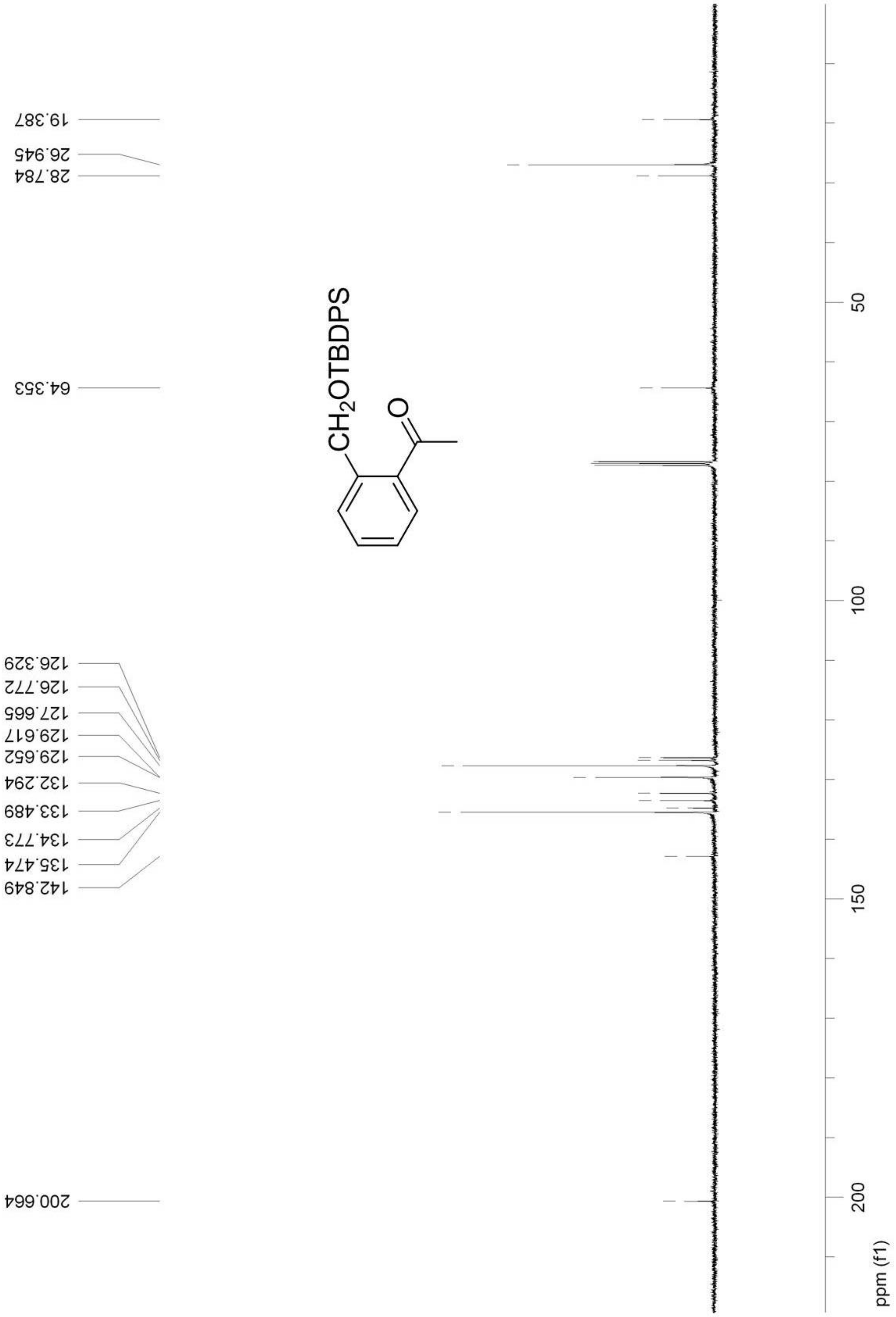
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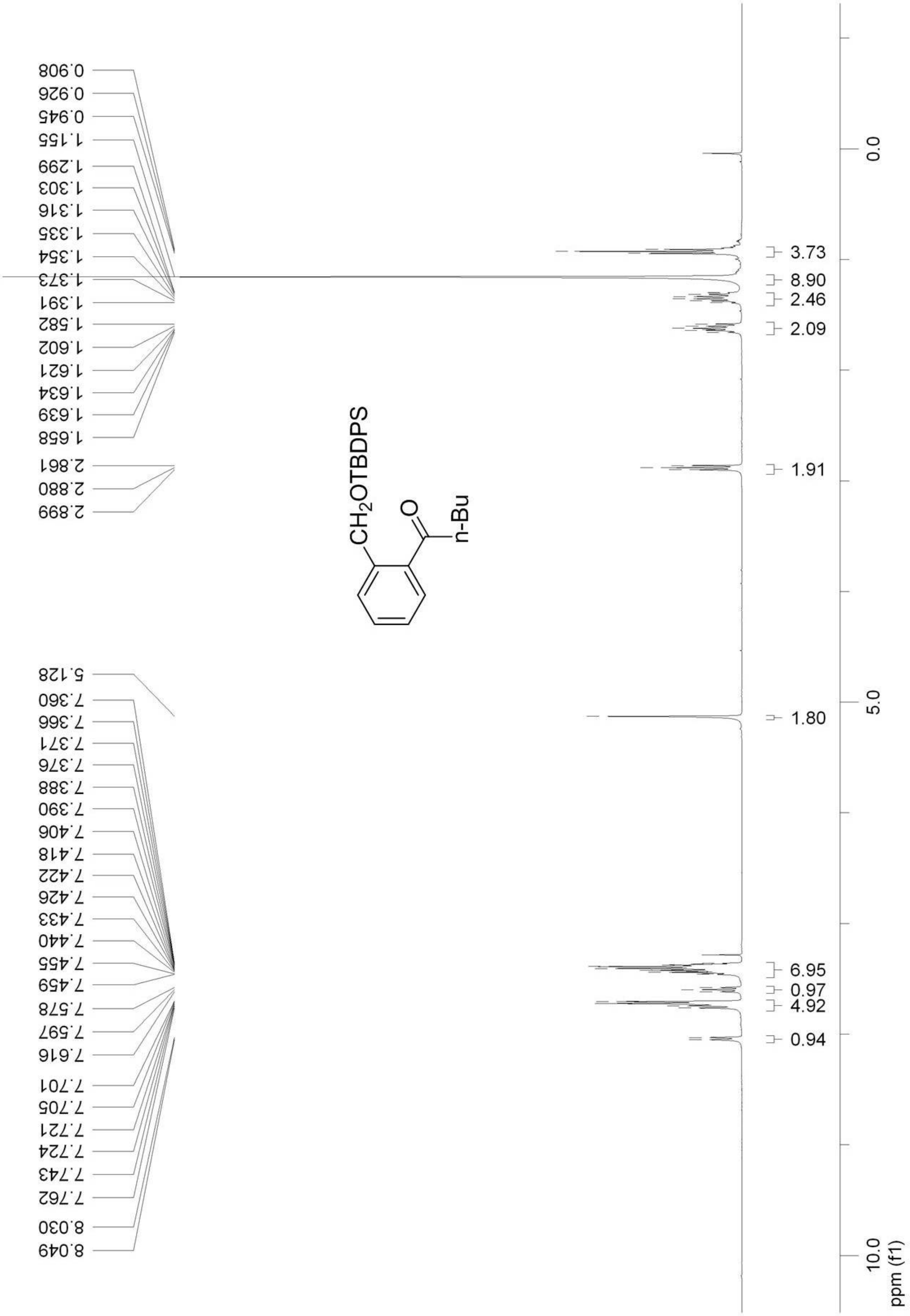
100
150
200
ppm (f1)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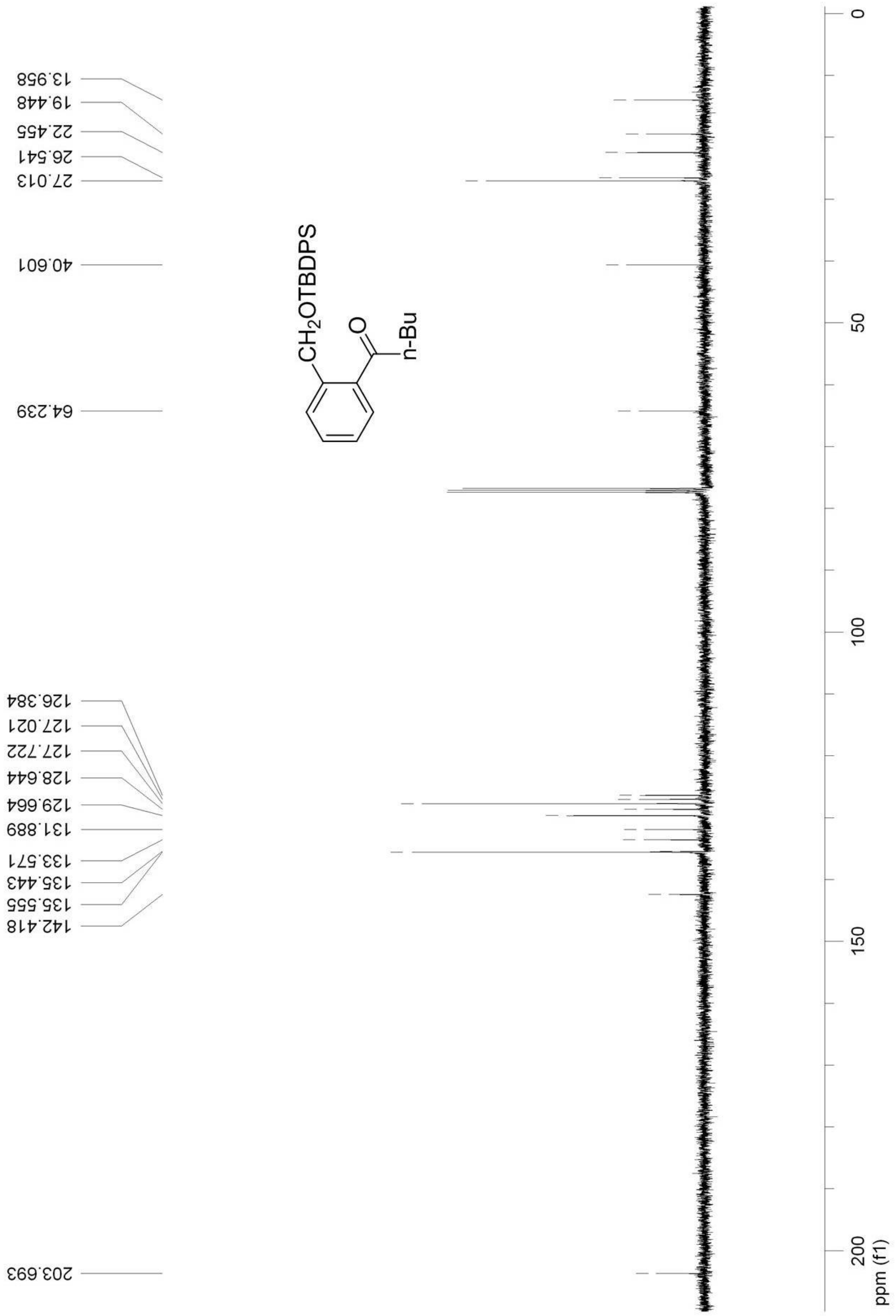
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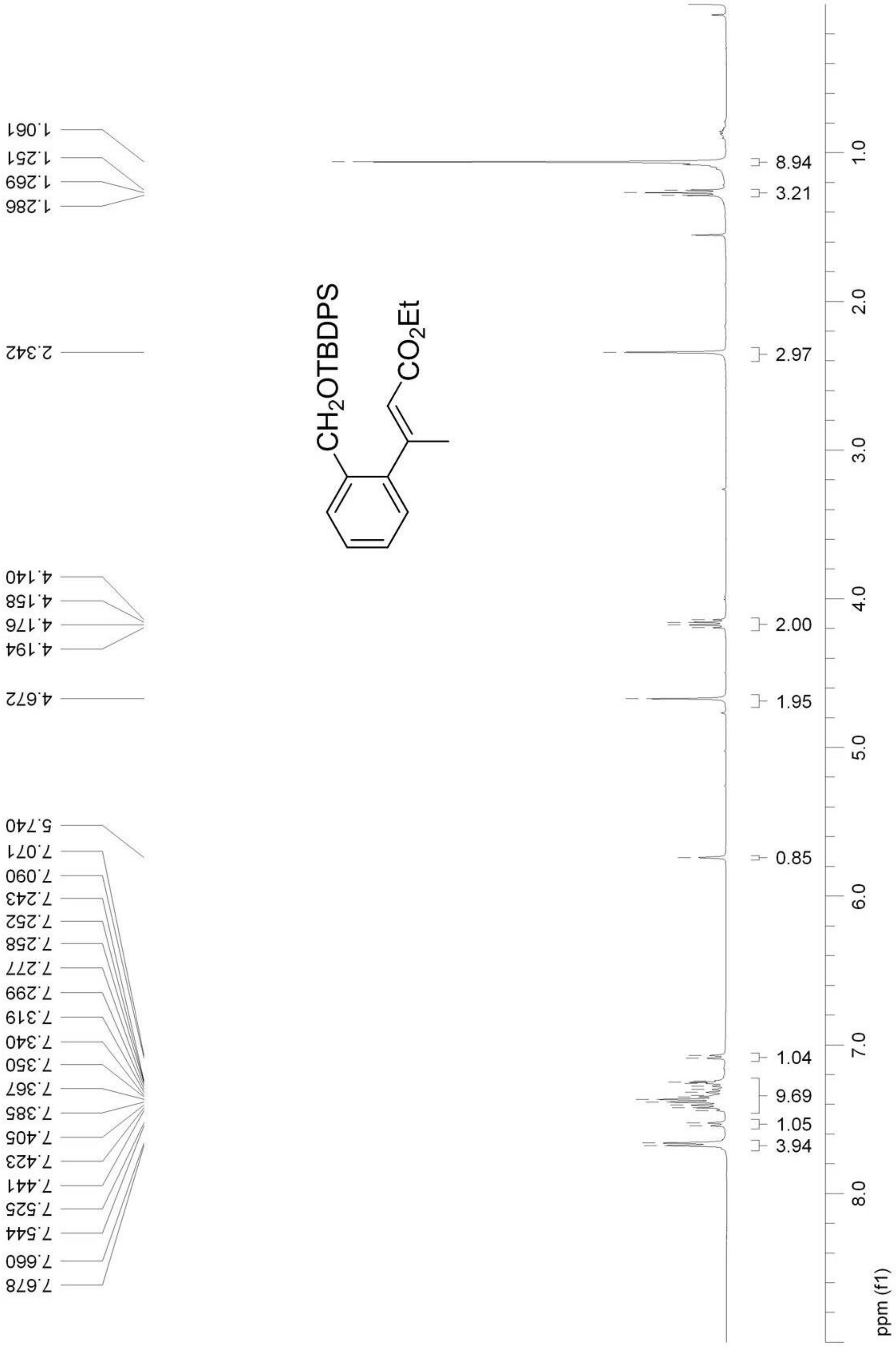
50
100
150
200
ppm (f1)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7.441
7.525
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CO2Et
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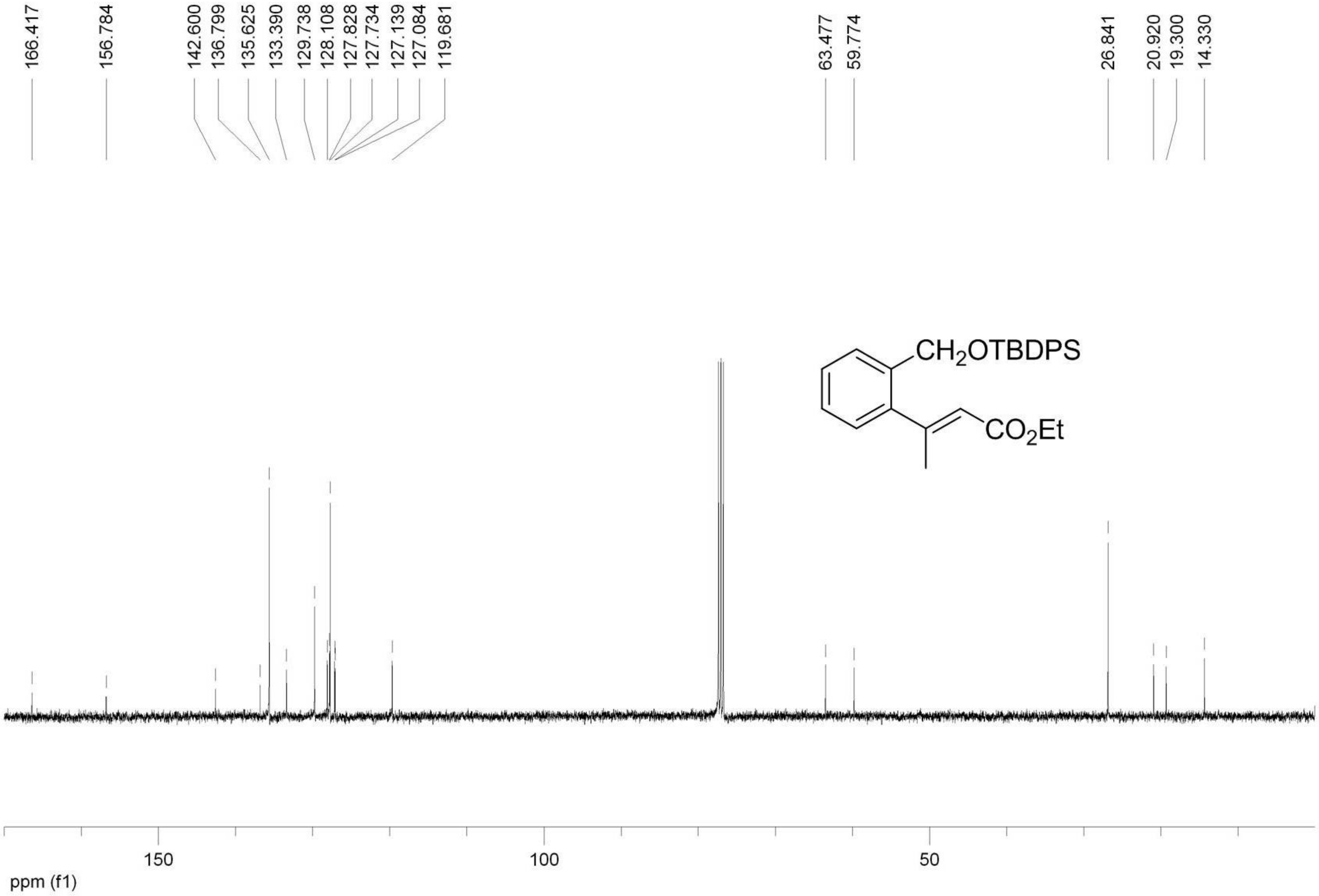
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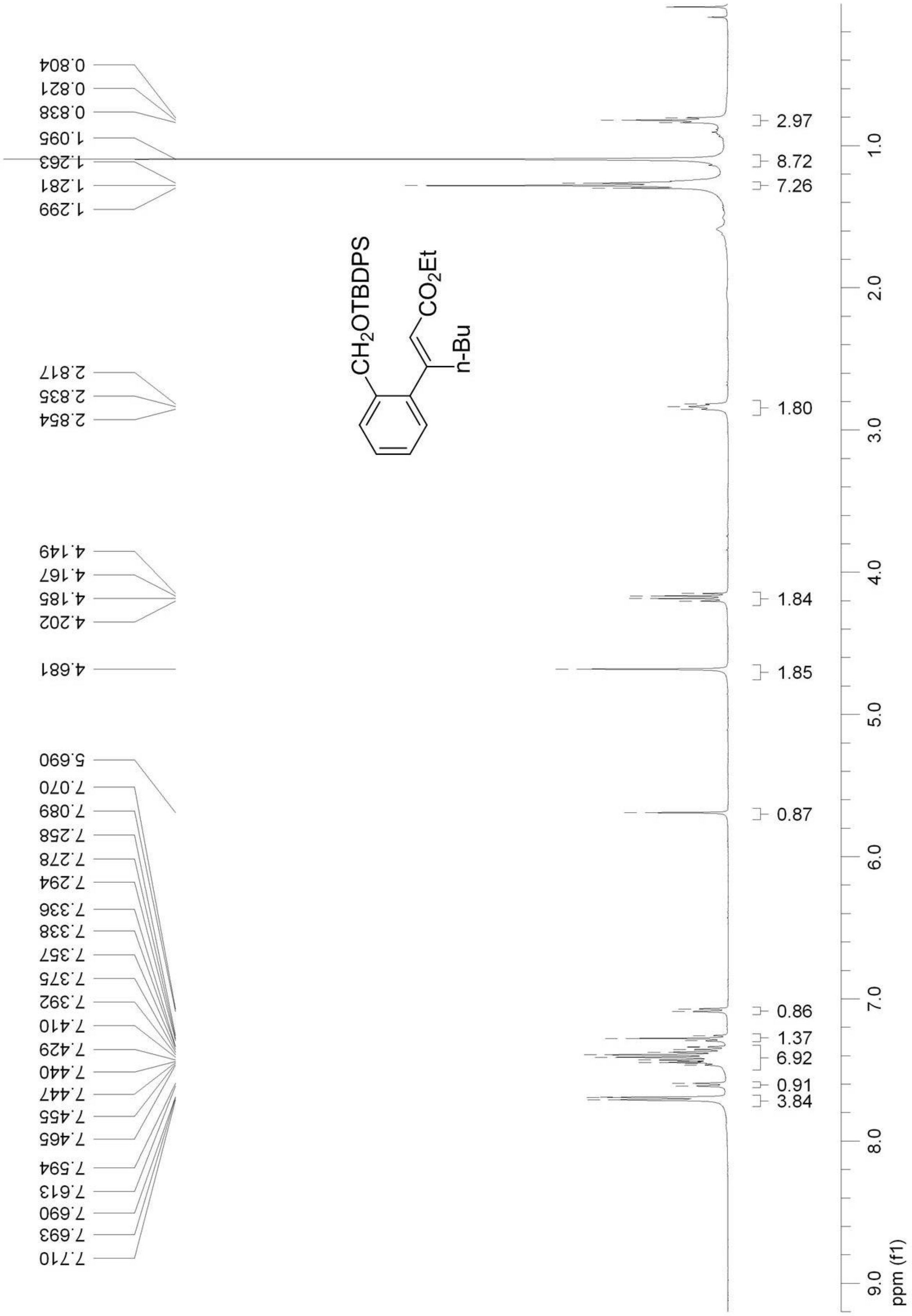
50
ppm (f1)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1.85
0.87
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1.37
6.92
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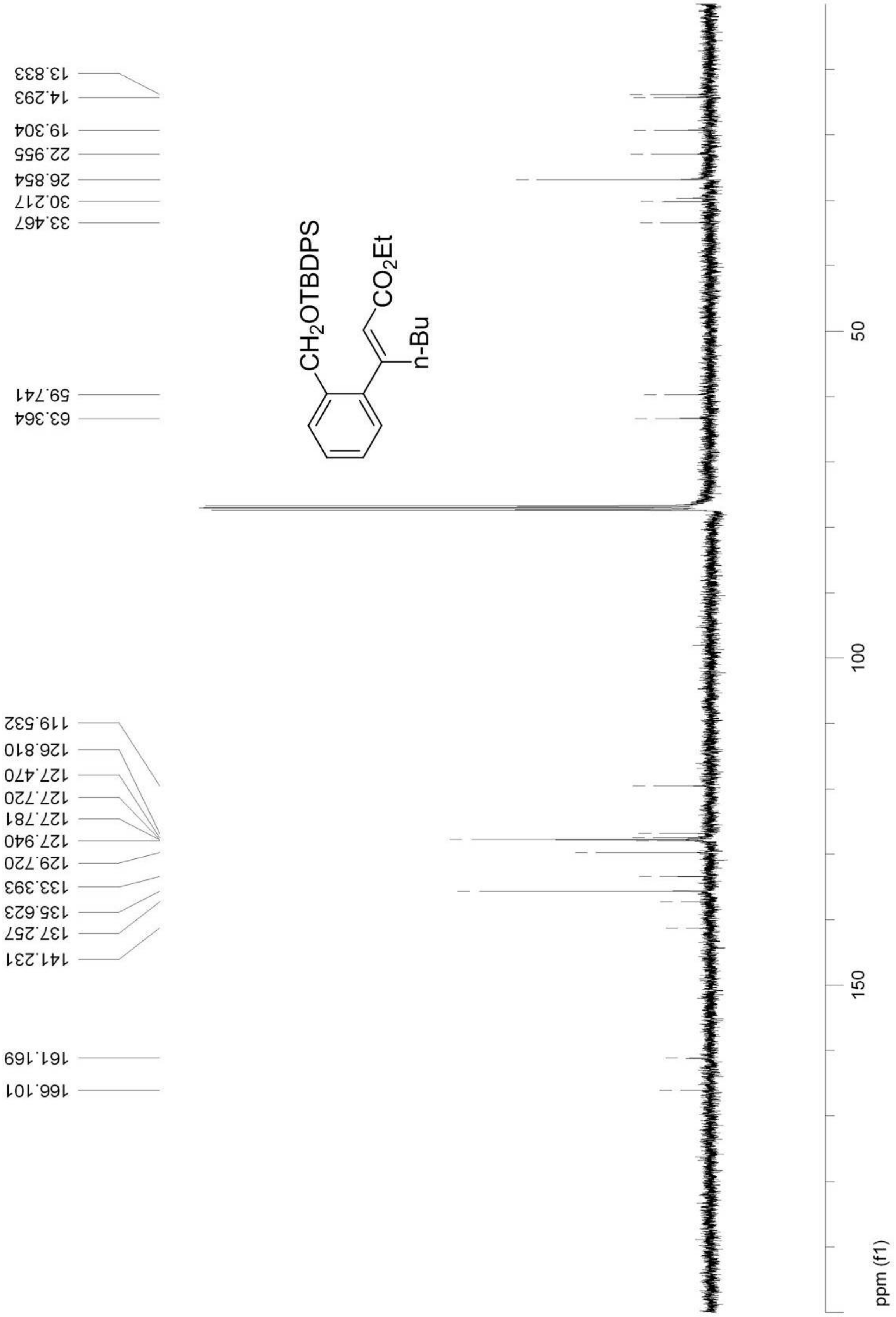
ppm (f1)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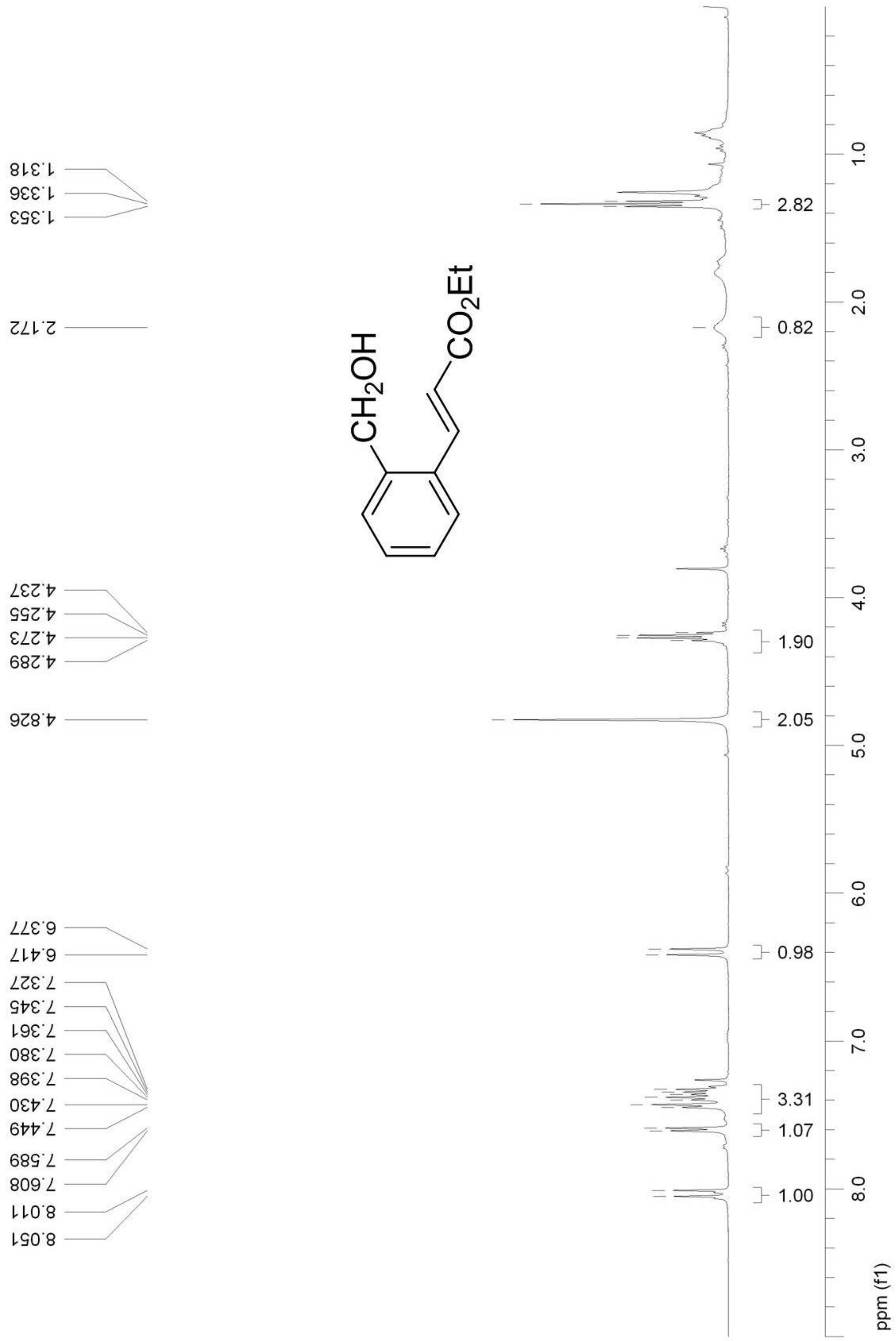
50
100
150
ppm (f1)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7.380
7.398
7.430
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7.589
7.608
8.011
8.051
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CO2Et
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2.05
0.98
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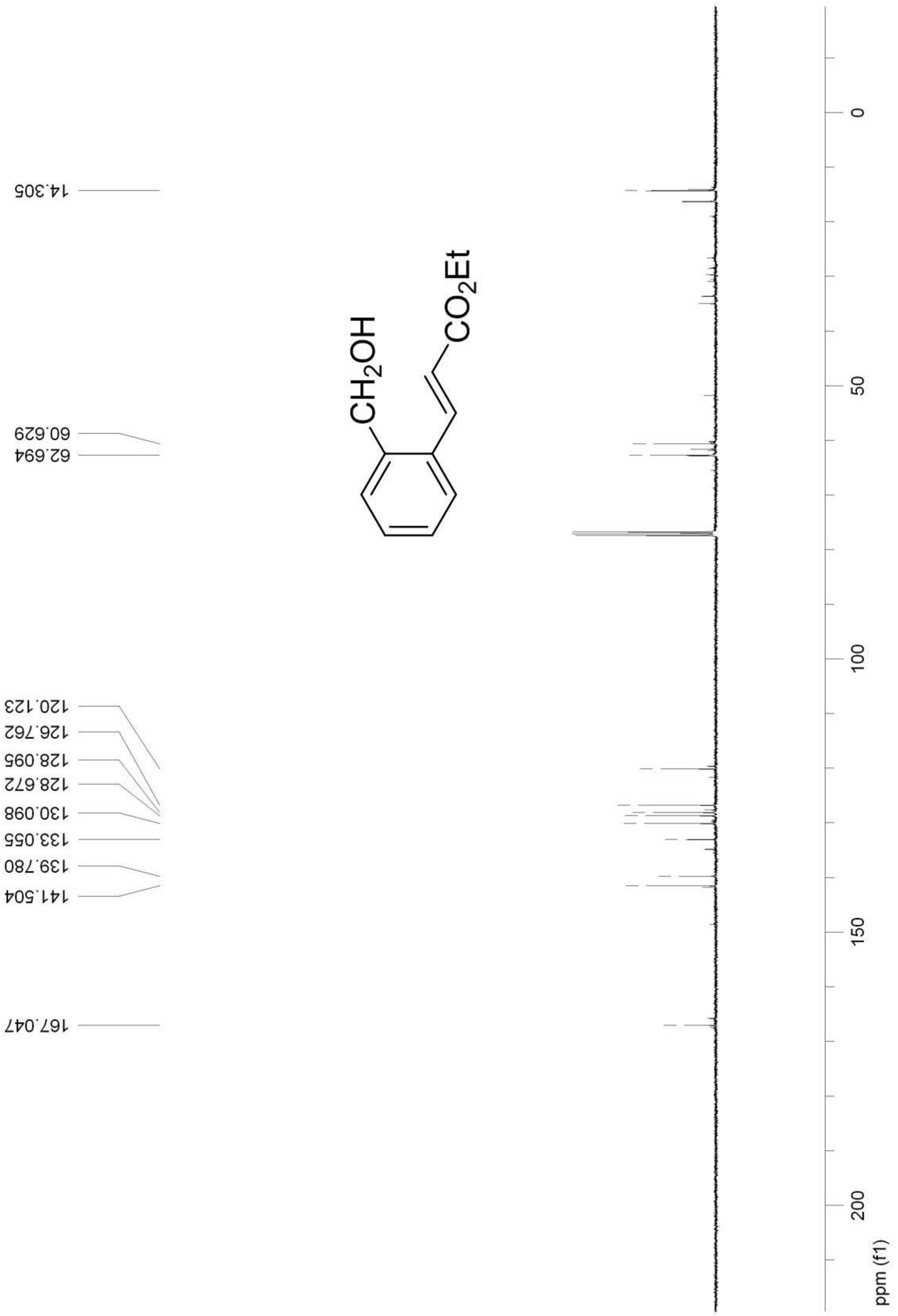
8.0
ppm (f1)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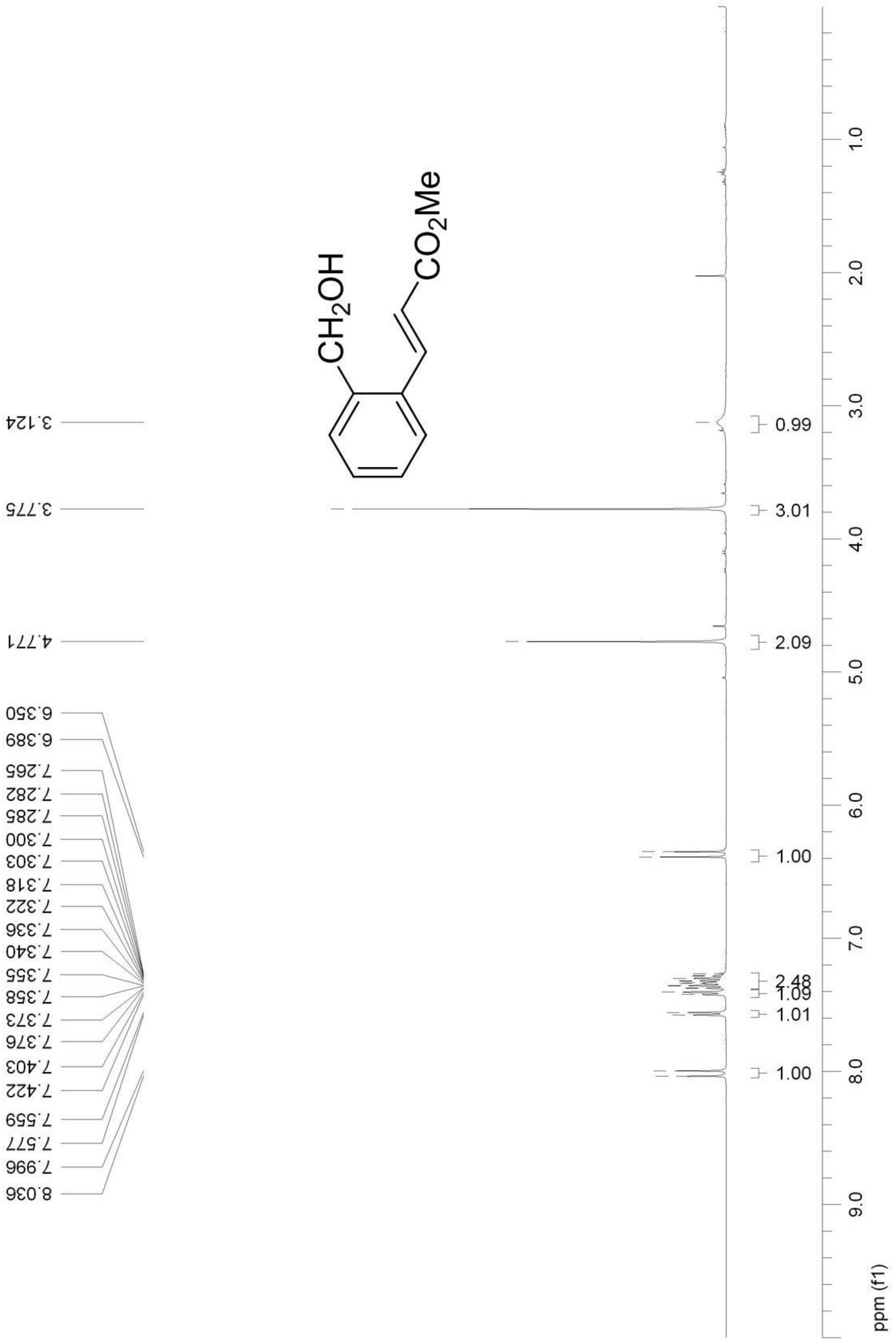
50
100
150
200
ppm (f1)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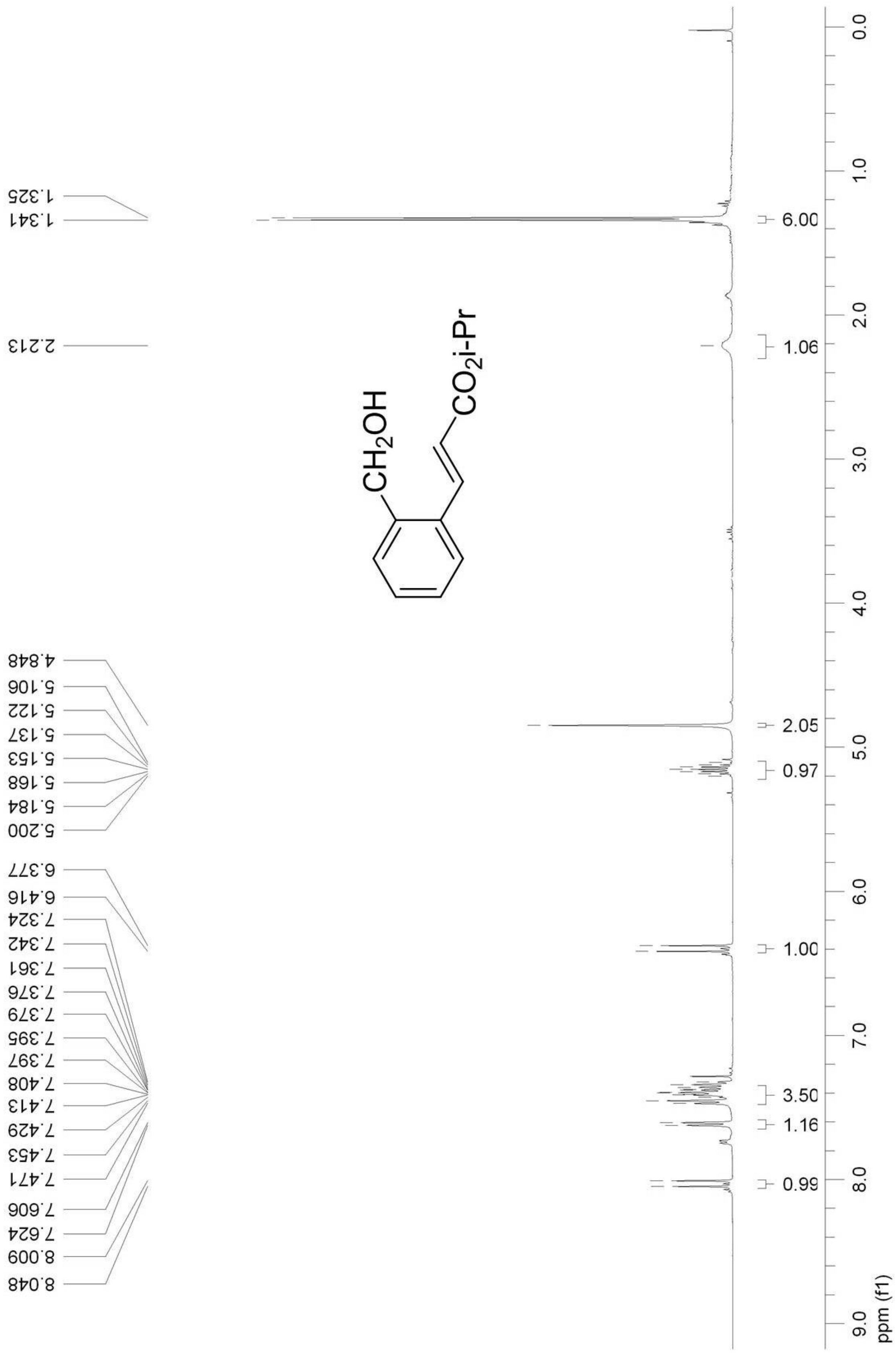
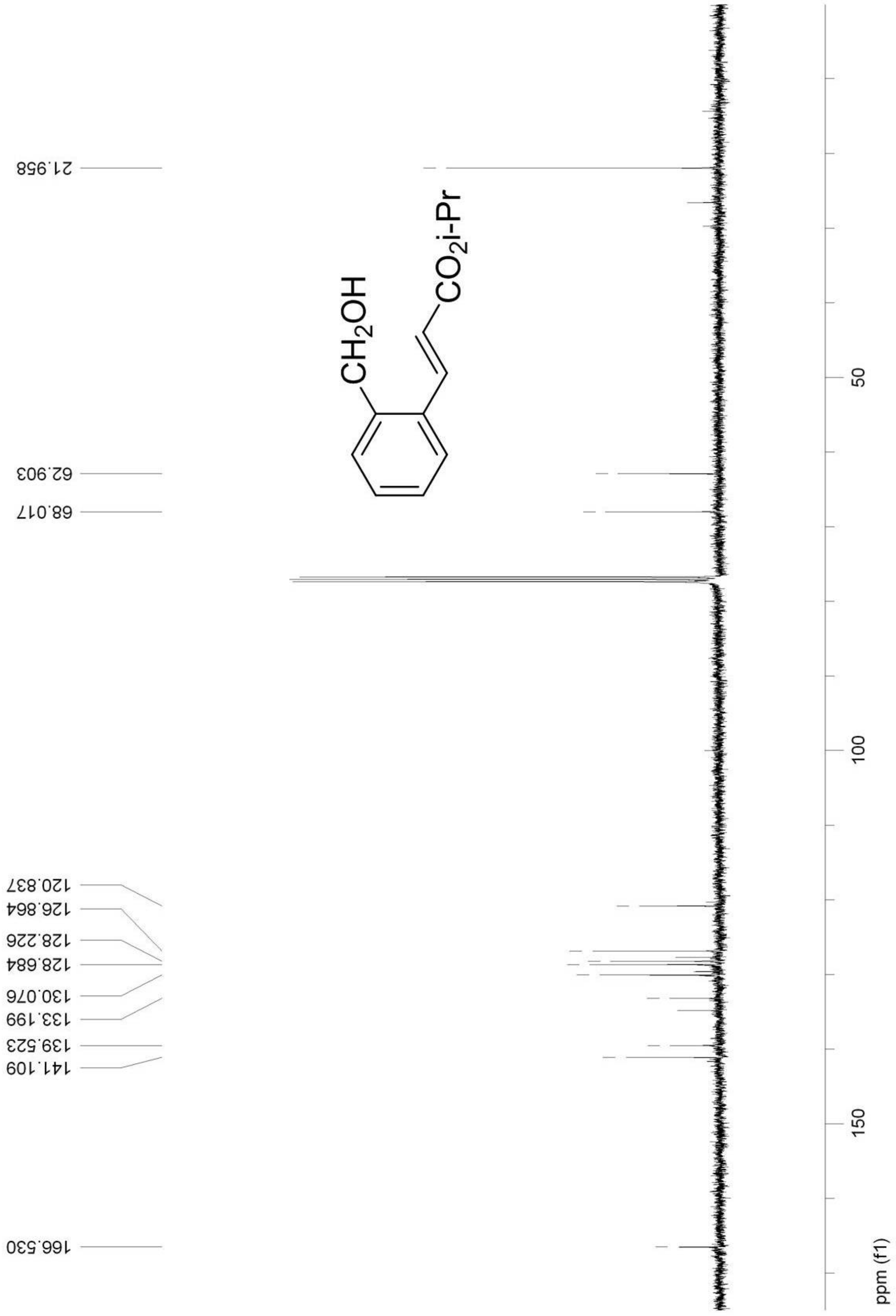
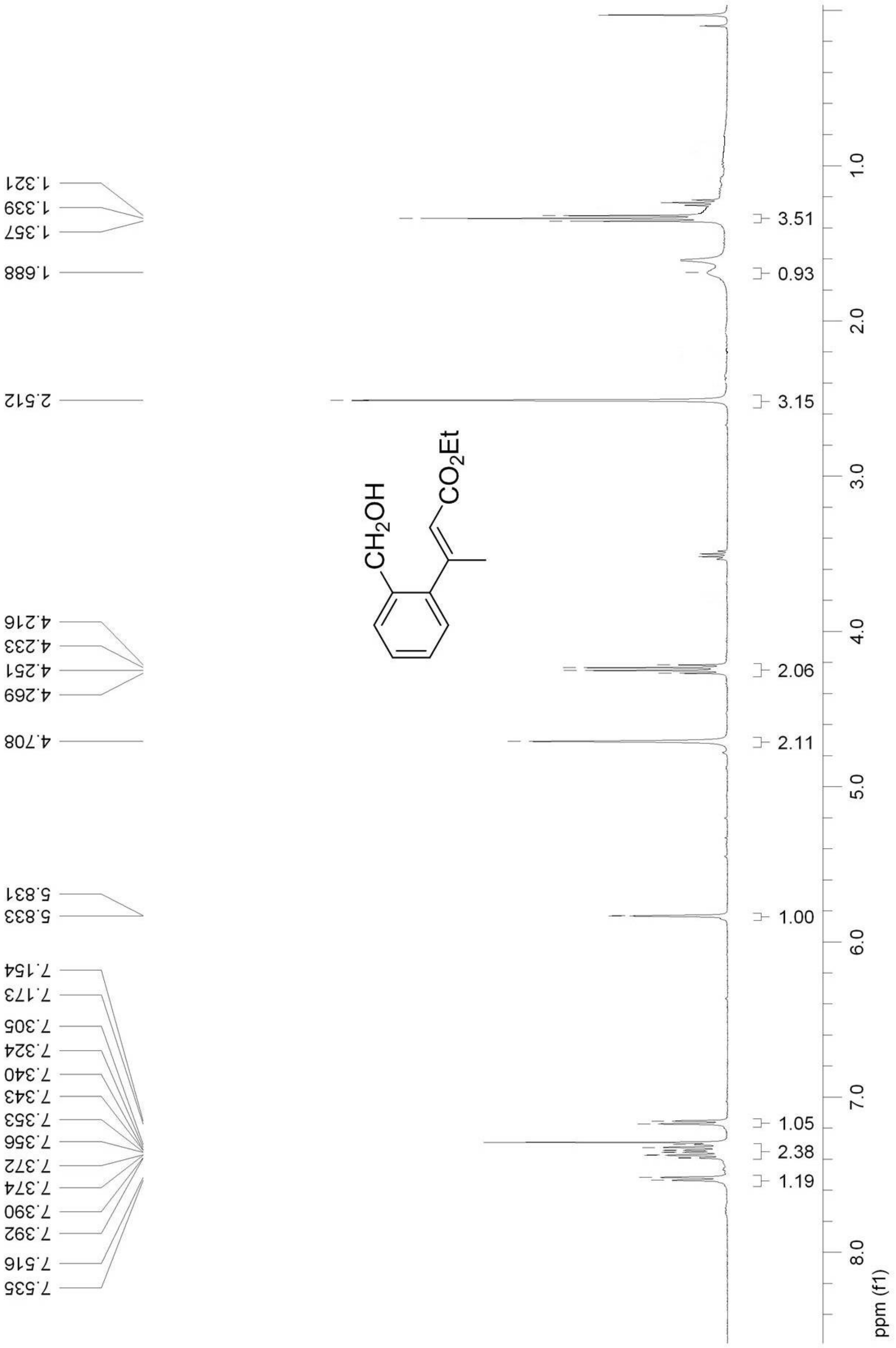
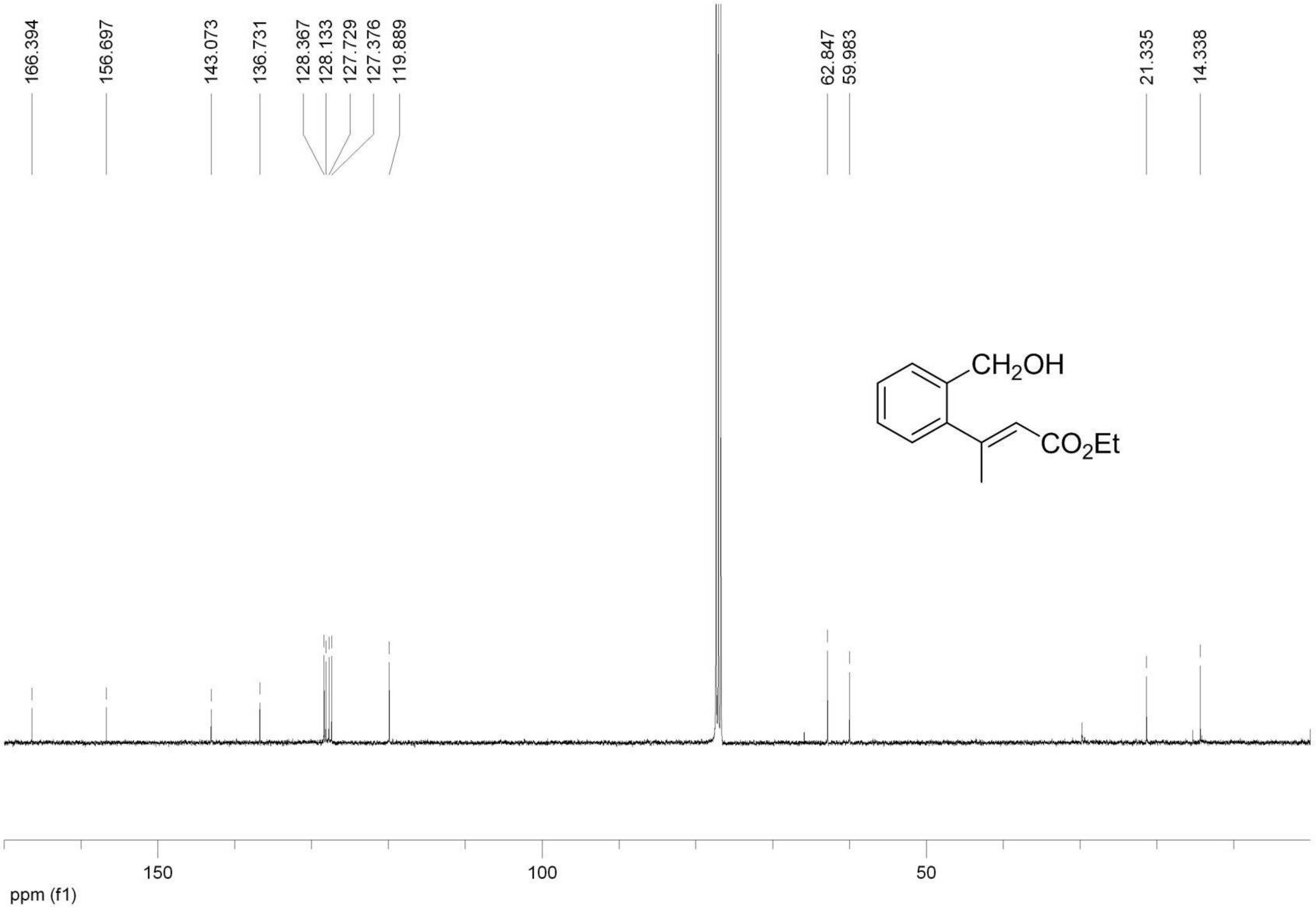
1.00
2.48
1.09
1.01
1.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)

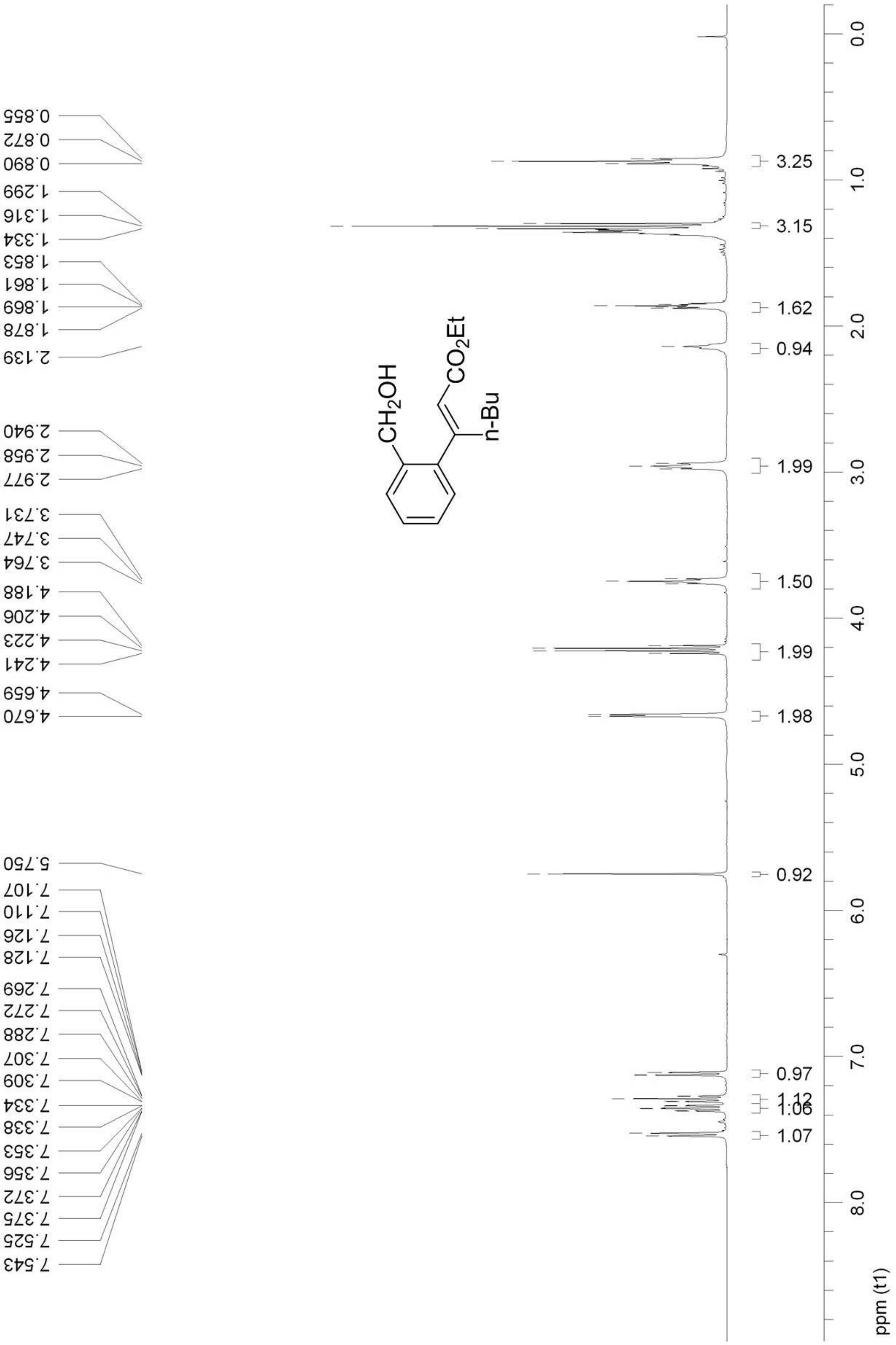

167.565
141.818
139.709
132.979
130.234
128.776
128.190
126.770
119.572
62.721
51.847
CH2OH
CO2Me
150
100
50
ppm (f1)

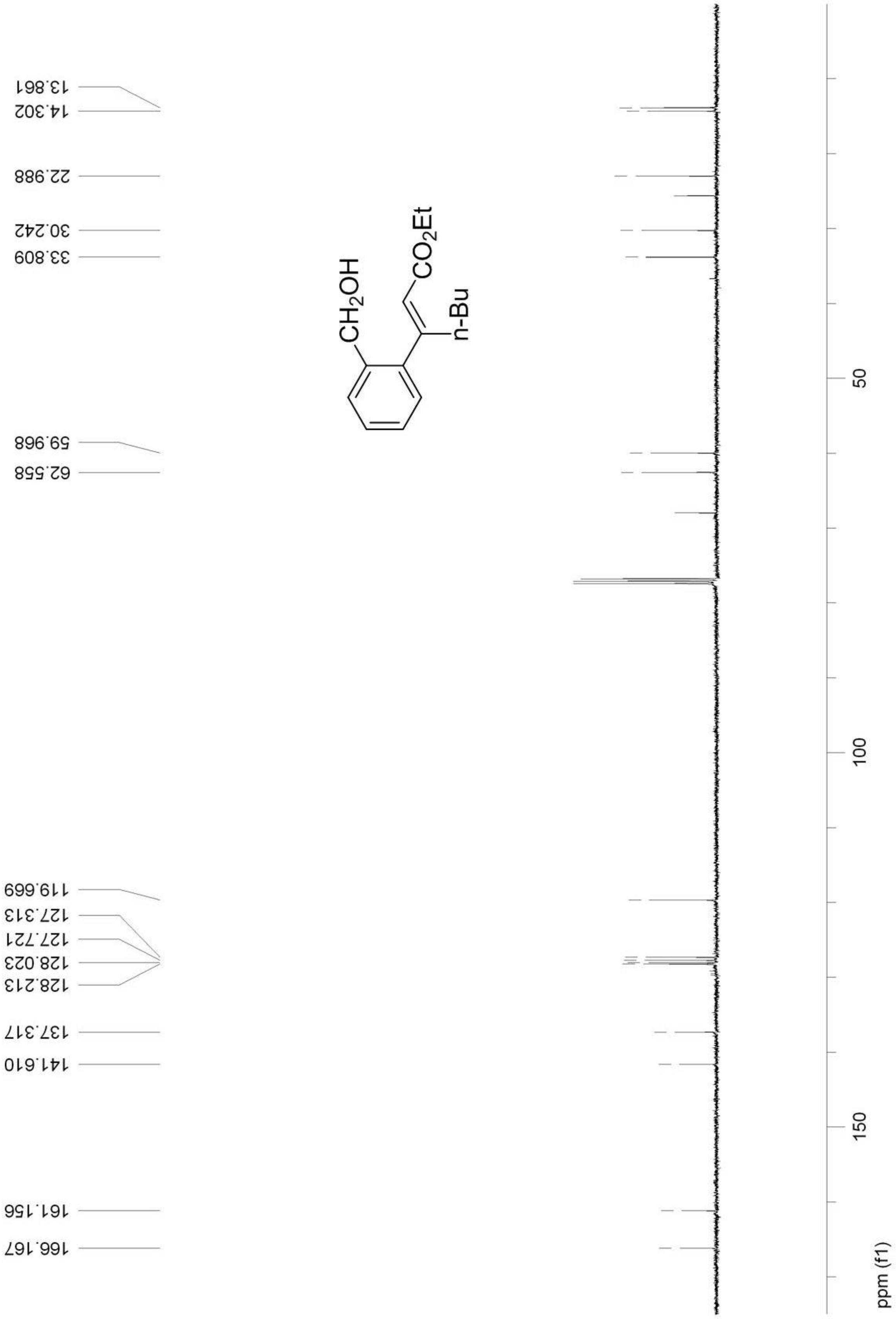

1.325
1.341
2.213
4.848
5.106
5.122
5.137
5.153
5.168
5.184
5.200
6.377
6.416
7.324
7.342
7.361
7.376
7.379
7.395
7.397
7.408
7.413
7.429
7.453
7.471
7.606
7.624
8.009
8.048
CH2OH
CO2i-Pr
6.00
1.06
2.05
0.97
1.00
3.50
1.16
0.99
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)

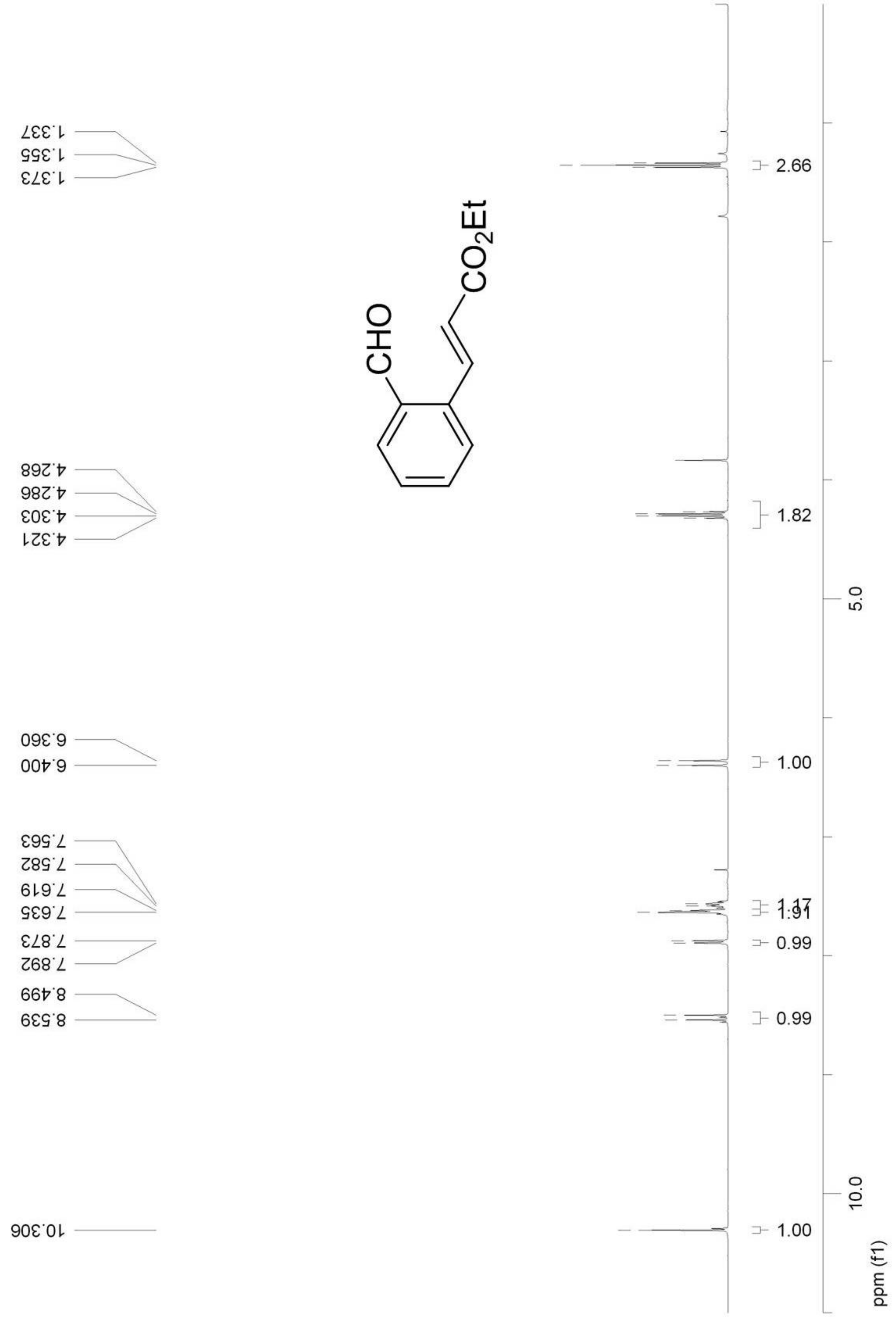

21.958
62.903
68.017
120.837
126.864
128.226
128.684
130.076
133.199
139.523
141.109
166.530
CH2OH
CO2i-Pr
50
100
150
ppm (f1)

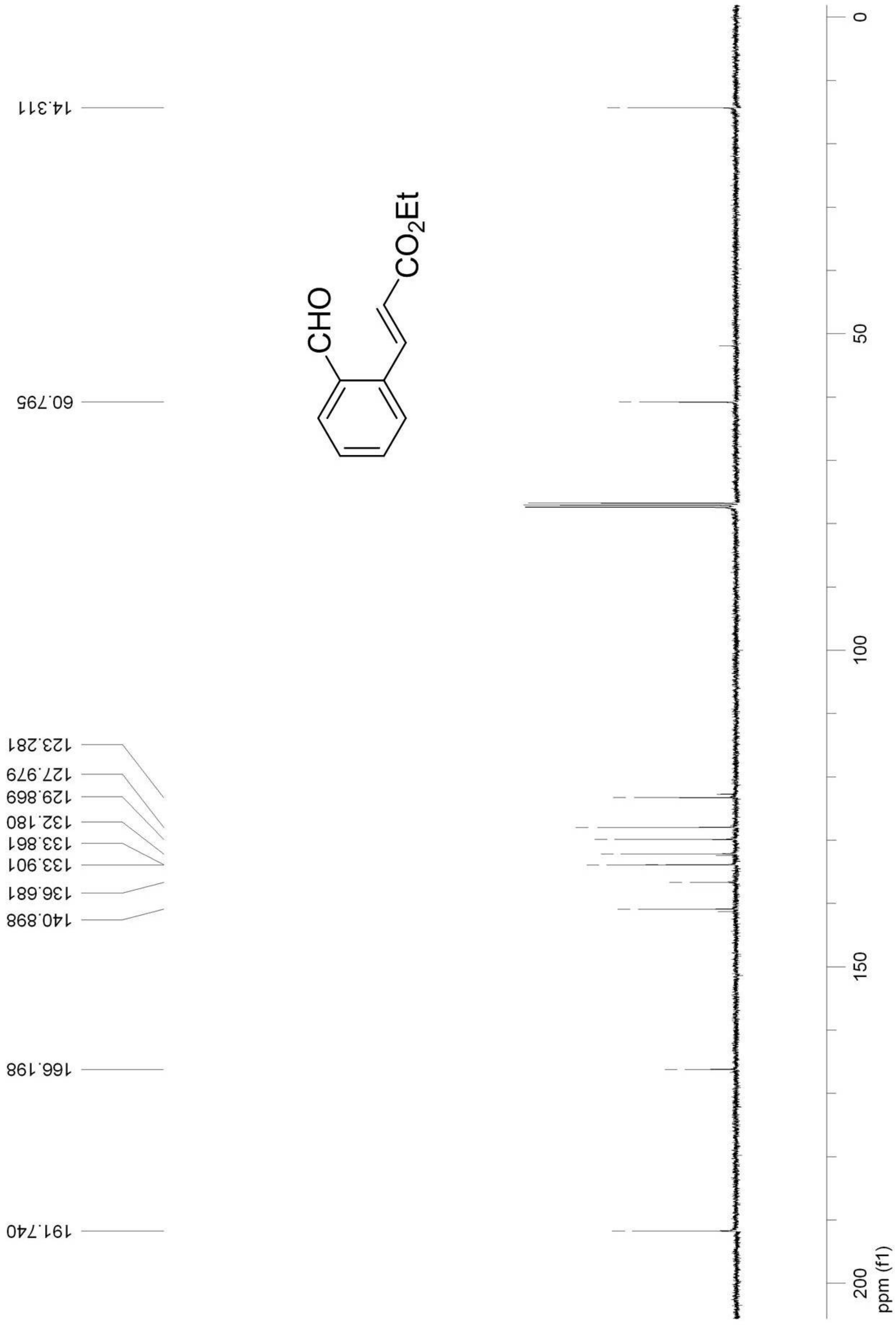

1.321
1.339
1.357
1.688
2.512
4.216
4.233
4.251
4.269
4.708
5.831
5.833
7.154
7.173
7.305
7.324
7.340
7.343
7.353
7.356
7.372
7.374
7.390
7.392
7.516
7.535
CH2OH
CO2Et
3.51
0.93
3.15
2.06
2.11
1.00
1.05
2.38
1.19
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

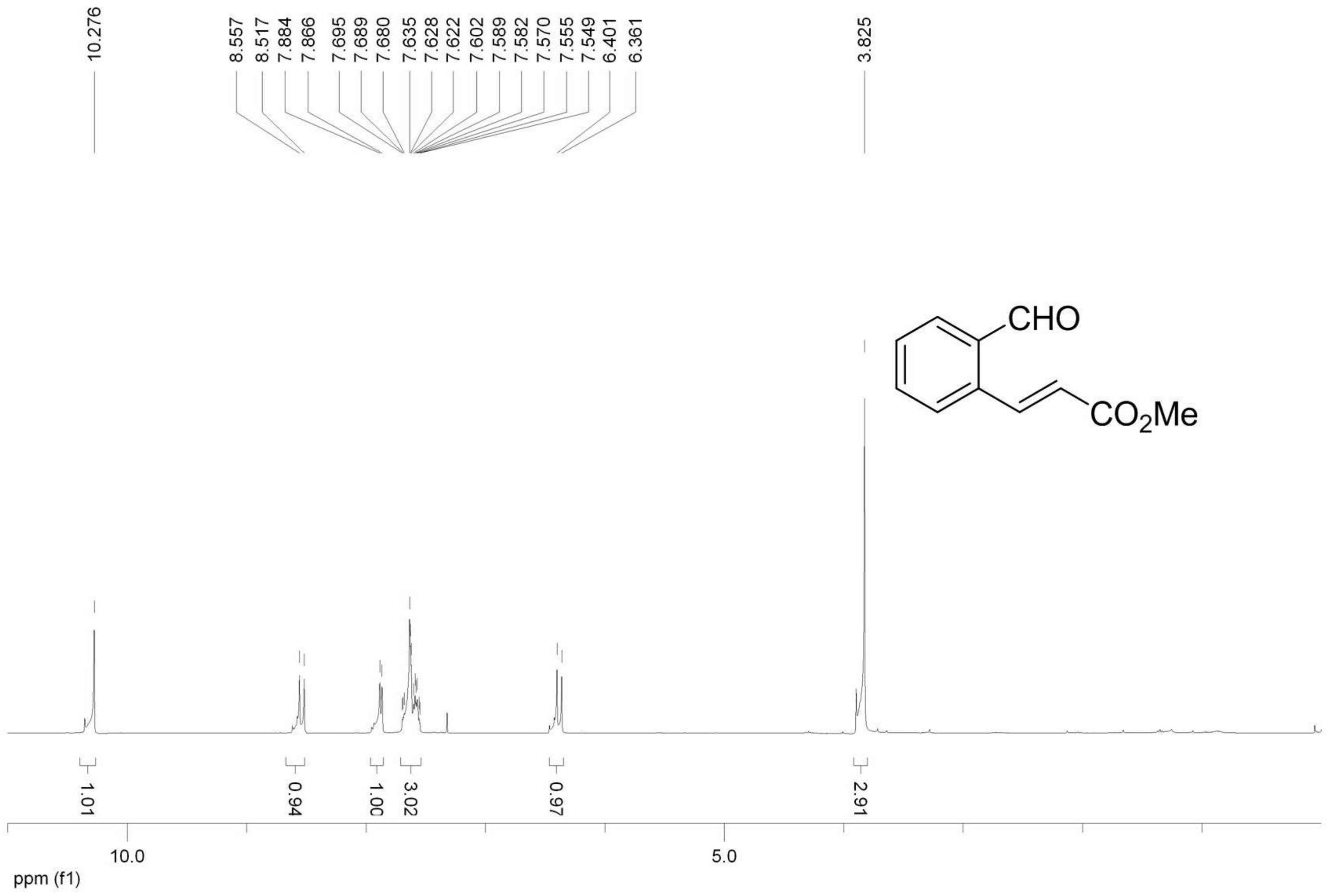

166.394
156.697
143.073
136.731
128.367
128.133
127.729
127.376
119.889
62.847
59.983
21.335
14.338
CH2OH
CO2Et
150
100
50
ppm (f1)

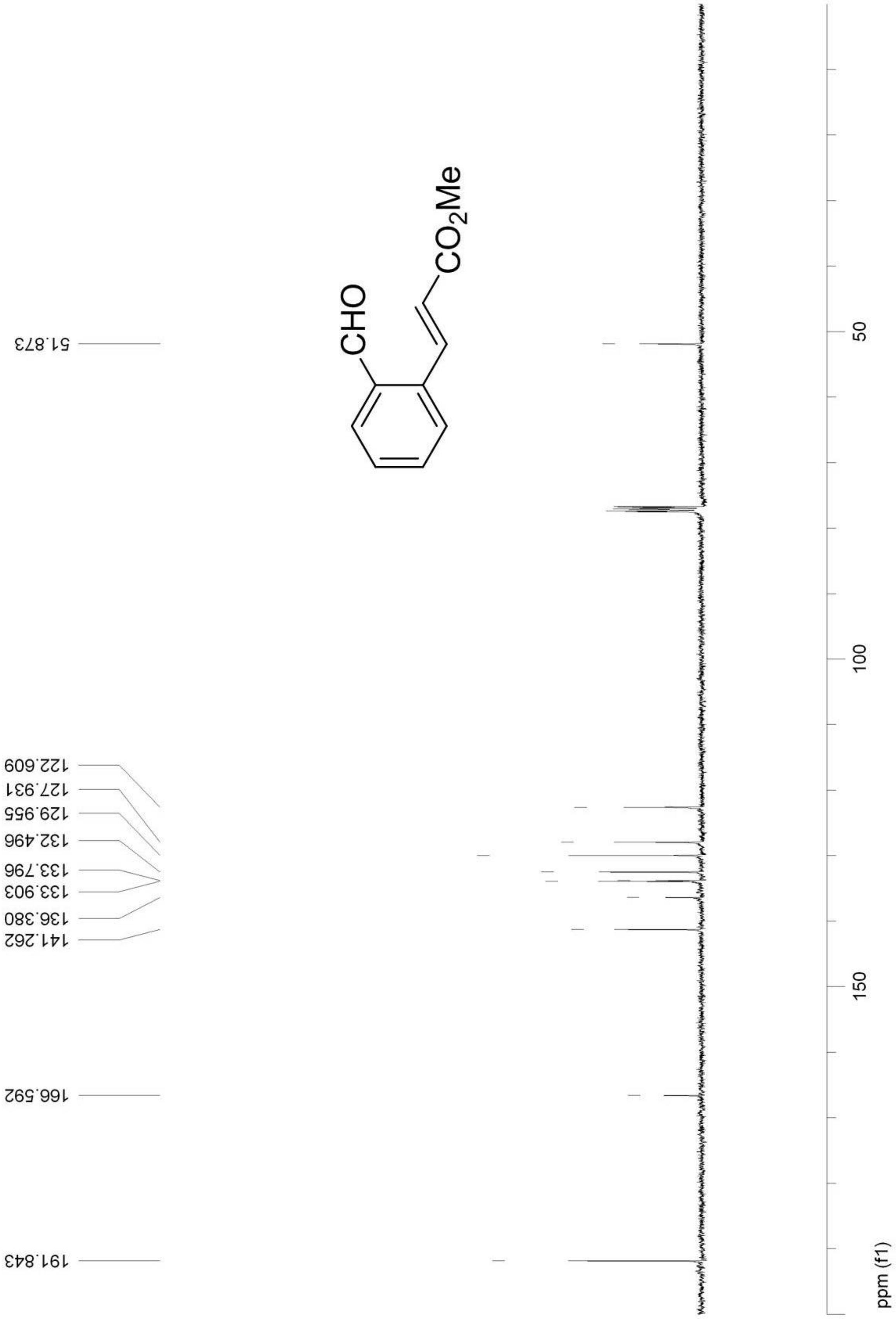

0.855
0.872
0.890
1.299
1.316
1.334
1.853
1.861
1.869
1.878
2.139
2.940
2.958
2.977
3.731
3.747
3.764
4.188
4.206
4.223
4.241
4.659
4.670
5.750
7.107
7.110
7.126
7.128
7.269
7.272
7.288
7.307
7.309
7.334
7.338
7.353
7.356
7.372
7.375
7.525
7.543
CH2OH
CO2Et
n-Bu
3.25
3.15
1.62
0.94
1.99
1.50
1.99
1.98
0.92
0.97
1.12
1.06
1.07
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)

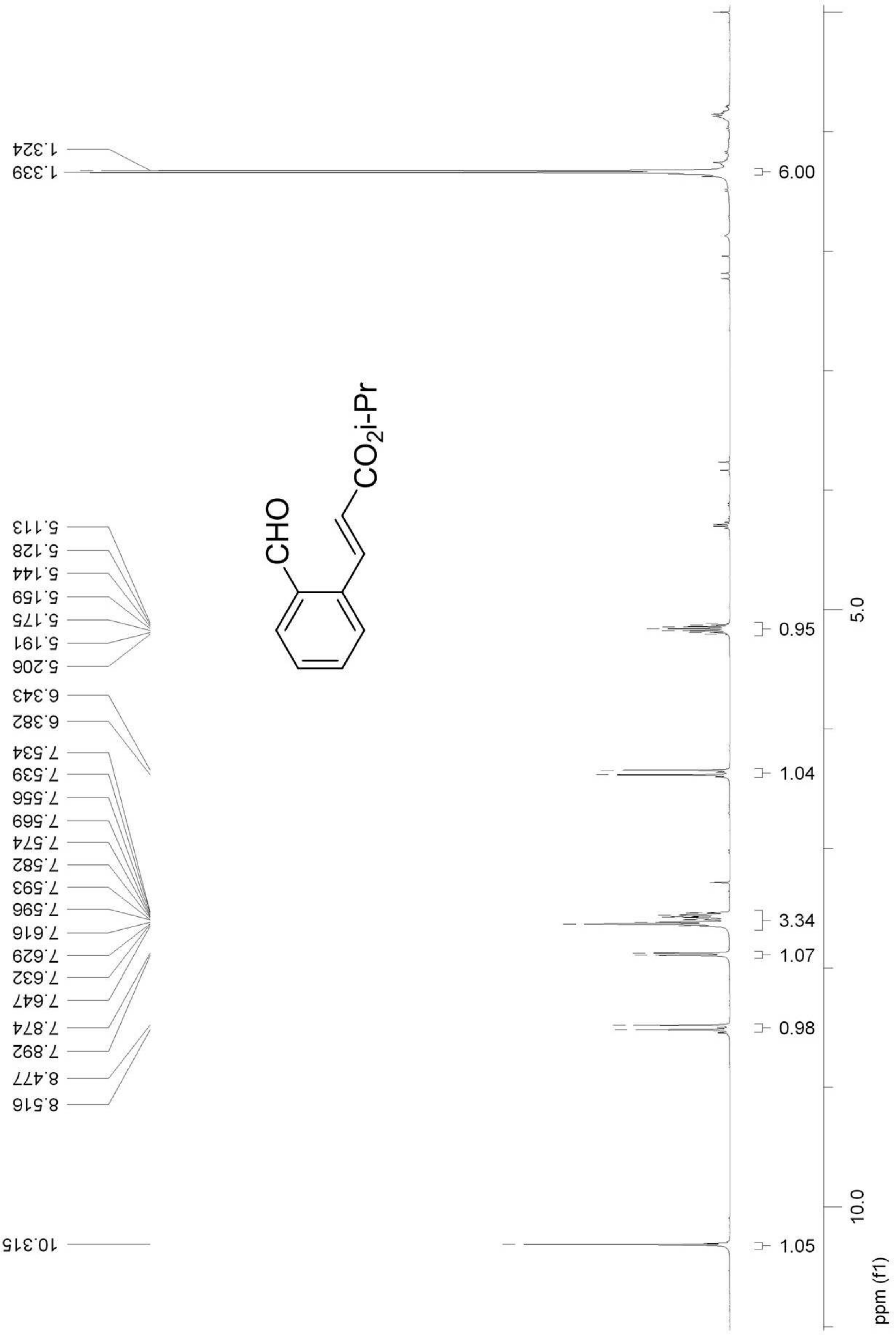

13.861
14.302
22.988
30.242
33.809
59.968
62.558
119.669
127.313
127.721
128.023
128.213
137.317
141.610
161.156
166.167
CH2OH
CO2Et
n-Bu
50
100
150
ppm (f1)

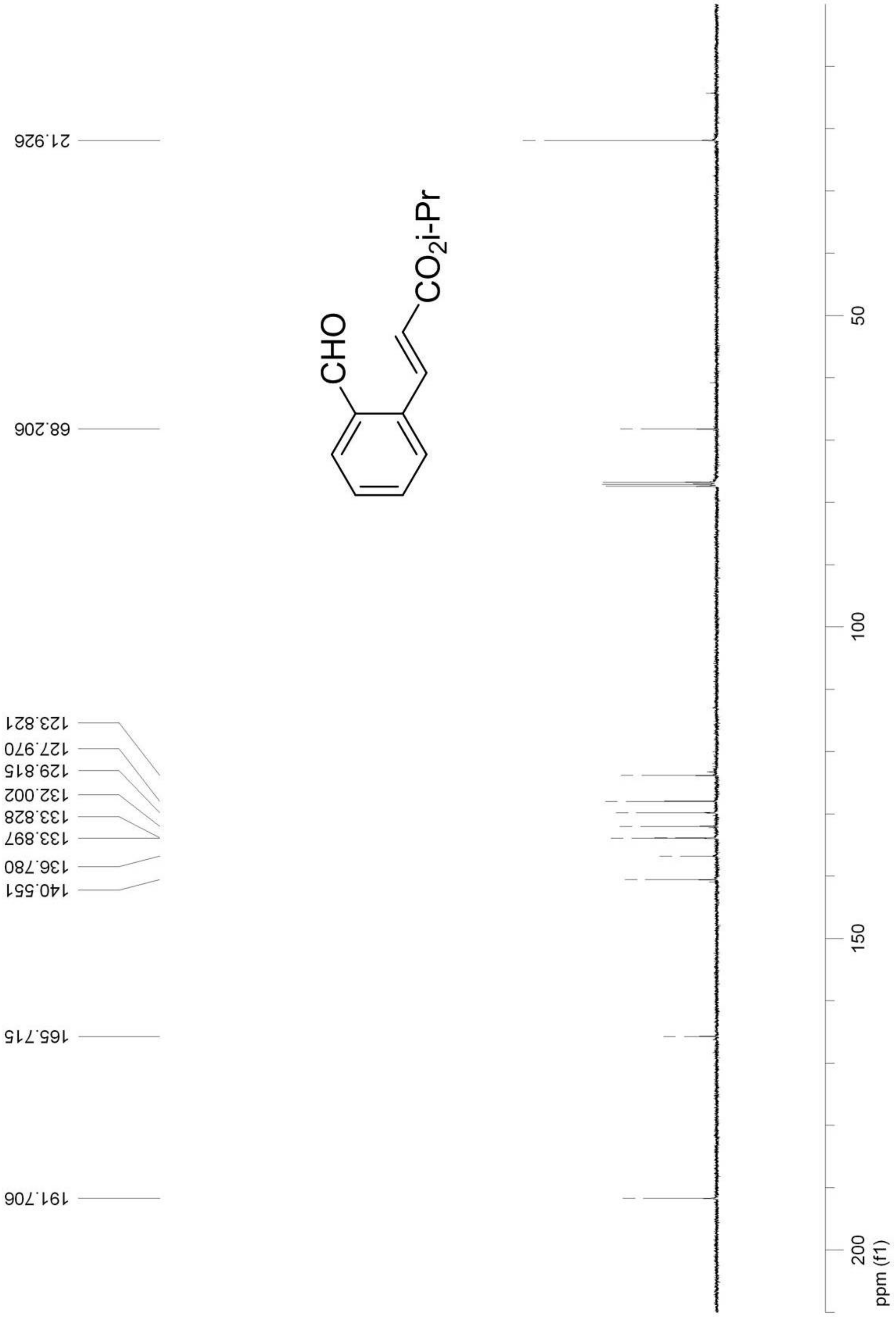

1.337
1.355
1.373
4.268
4.286
4.303
4.321
6.360
6.400
7.563
7.582
7.619
7.635
7.873
7.892
8.499
8.539
10.306
CHO
CO2Et
2.66
1.82
1.00
1.17
1.91
0.99
0.99
1.00
5.0
10.0
ppm (f1)

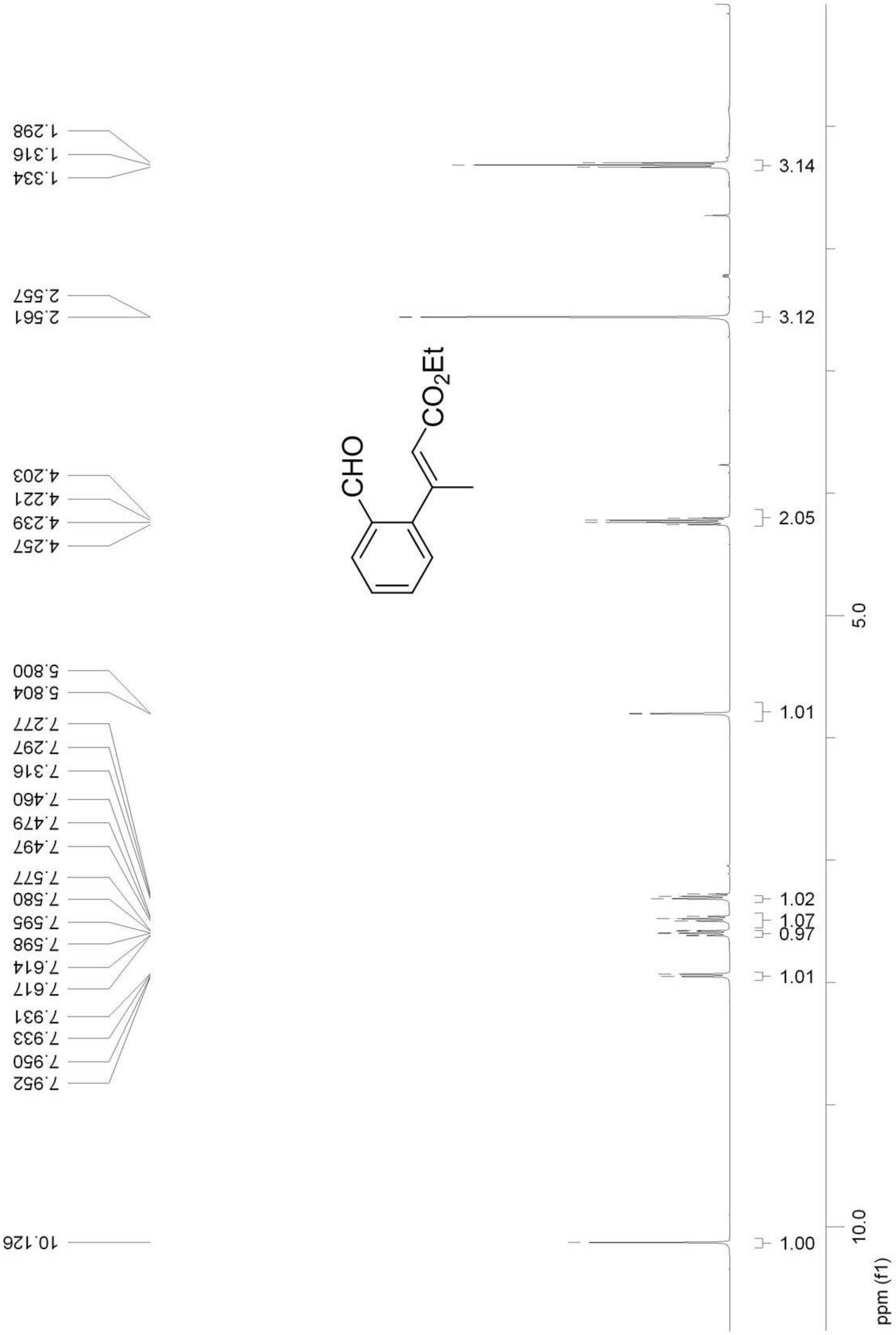

14.311
60.795
123.281
127.979
129.869
132.180
133.861
133.901
136.681
140.898
166.198
191.740
CHO
CO2Et
0
50
100
150
200
ppm (f1)

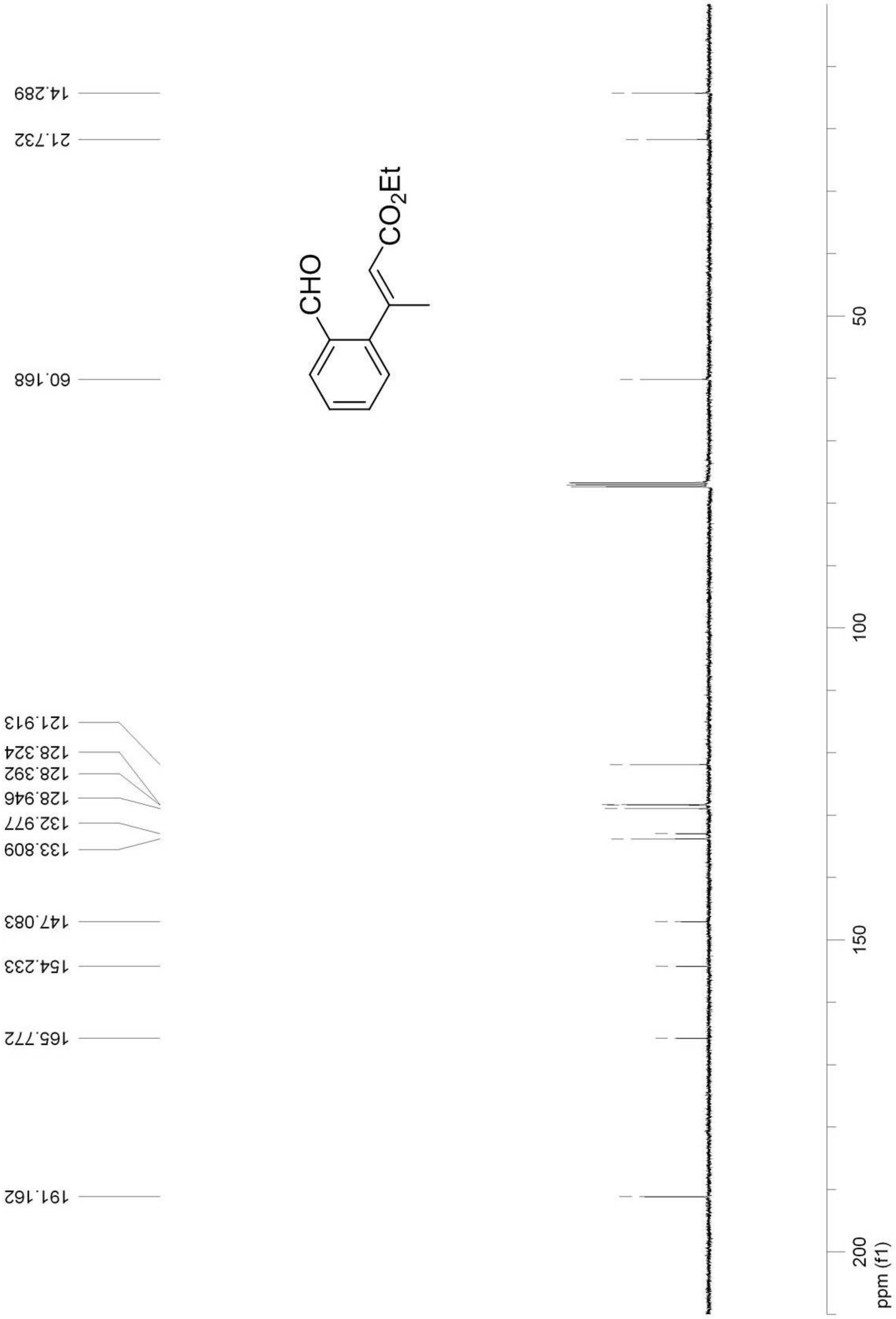

10.276
8.557
8.517
7.884
7.866
7.695
7.689
7.680
7.635
7.628
7.622
7.602
7.589
7.582
7.570
7.555
7.549
6.401
6.361
3.825
CHO
$CO_2Me$
1.01
0.94
1.00
3.02
0.97
2.91
10.0
5.0
ppm (f1)

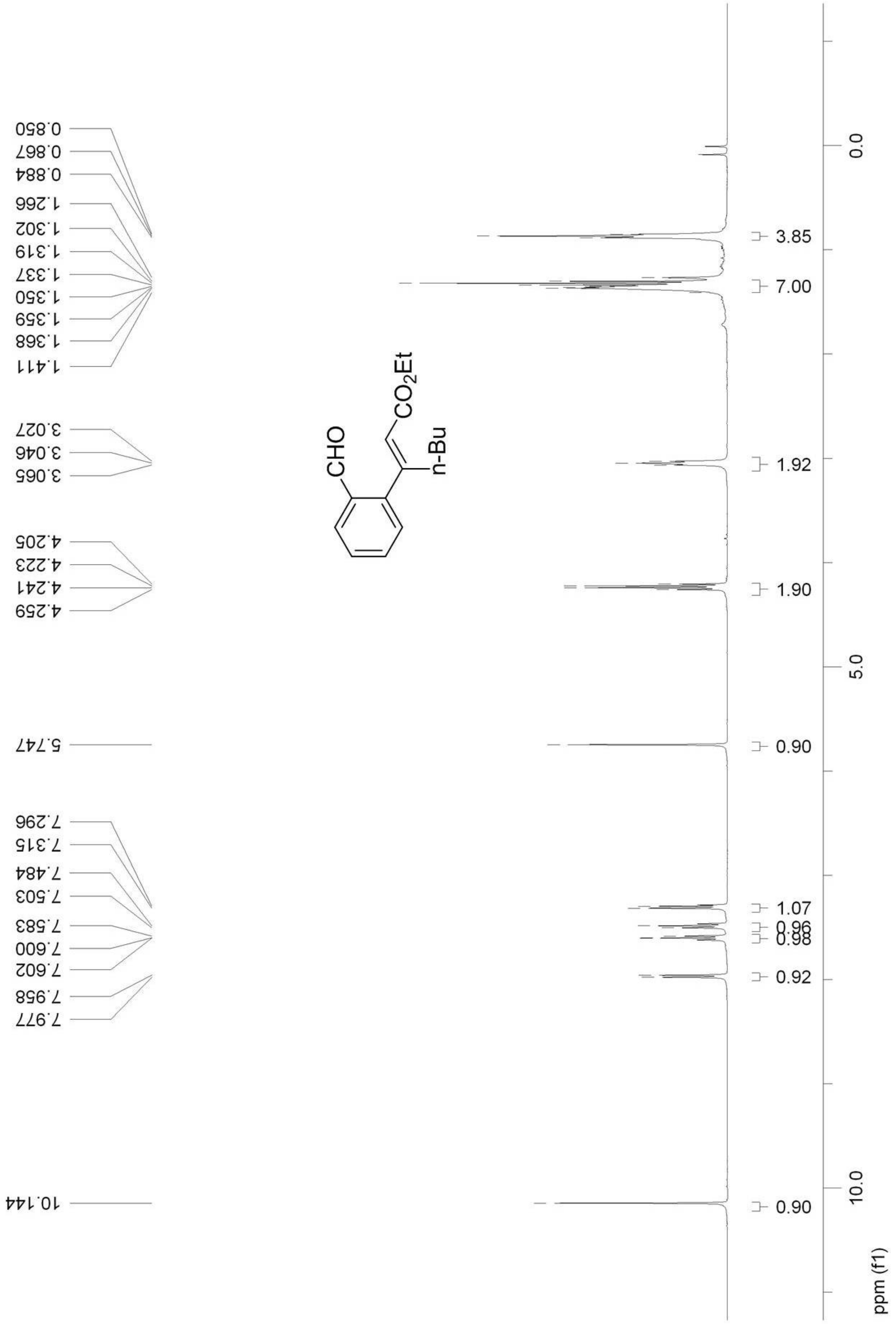

51.873
122.609
127.931
129.955
132.496
133.796
133.903
136.380
141.262
166.592
191.843
CHO
CO2Me
50
100
150
ppm (f1)

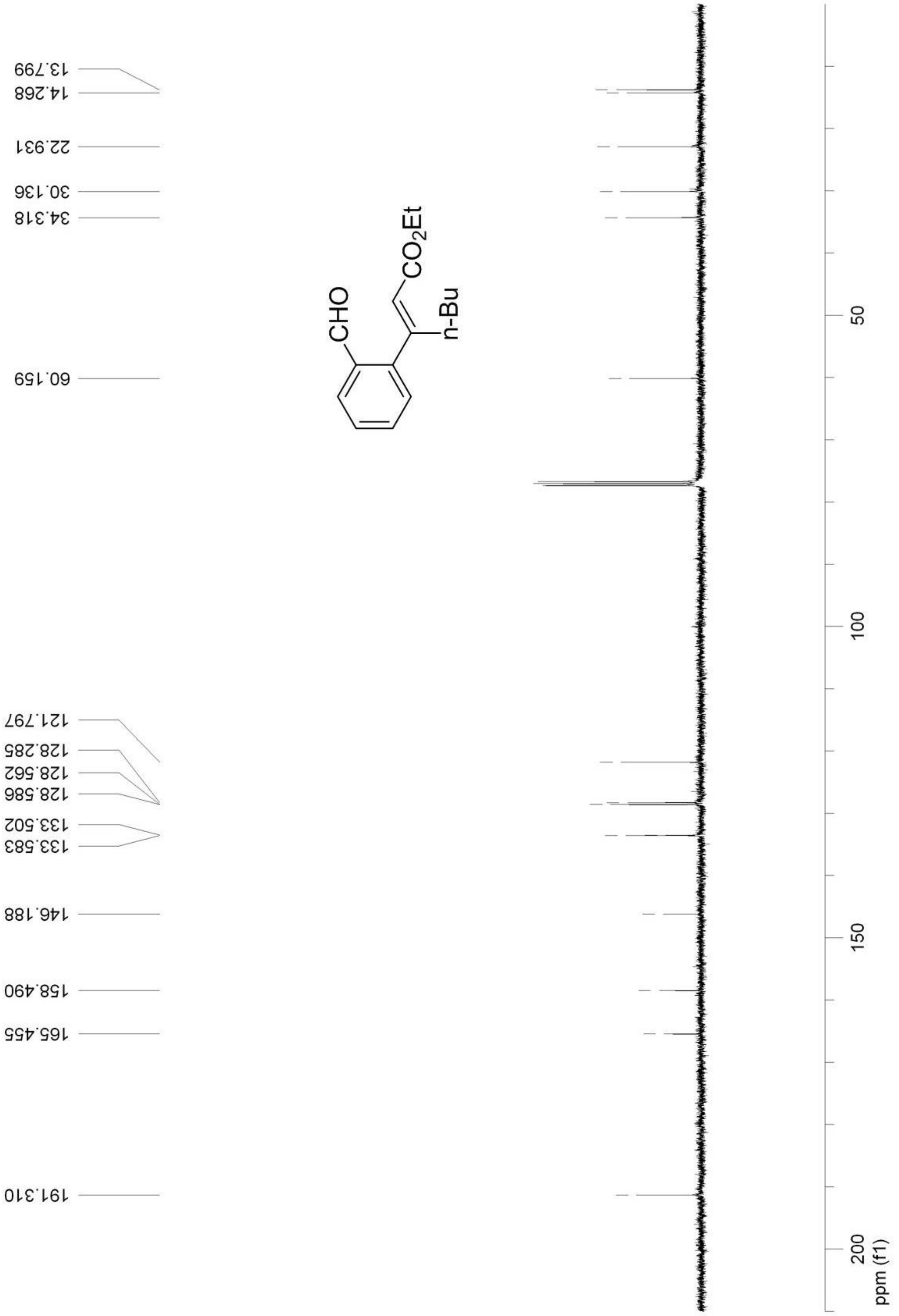

1.324
1.339
5.113
5.128
5.144
5.159
5.175
5.191
5.206
6.343
6.382
7.534
7.539
7.556
7.569
7.574
7.582
7.593
7.596
7.616
7.629
7.632
7.647
7.874
7.892
8.477
8.516
10.315
CHO
CO2i-Pr
6.00
0.95
1.04
3.34
1.07
0.98
1.05
5.0
10.0
ppm (f1)


21.926
68.206
123.821
127.970
129.815
132.002
133.828
133.897
136.780
140.551
165.715
191.706
CHO
CO2i-Pr
50
100
150
200
ppm (f1)

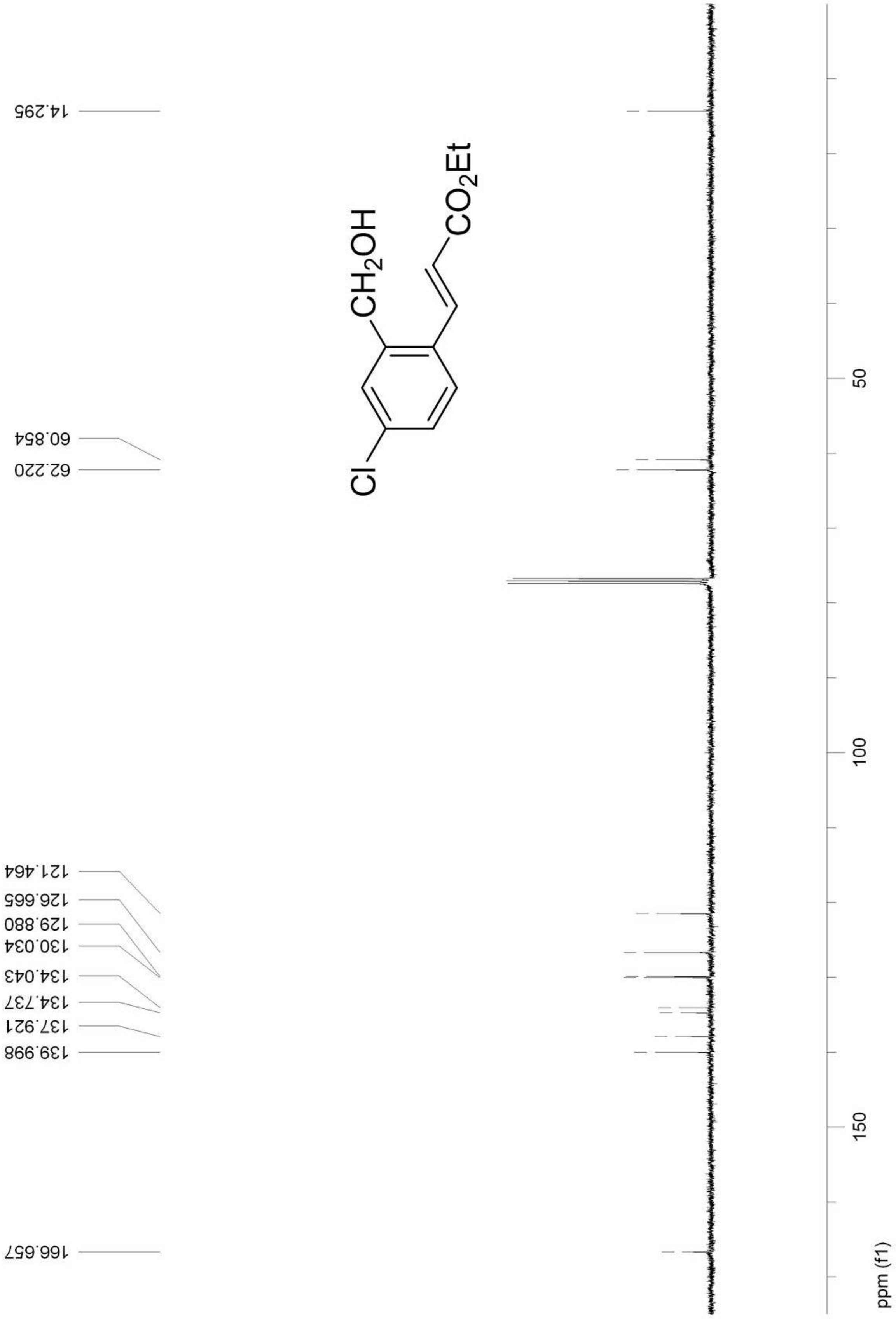

1.298
1.316
1.334
2.557
2.561
4.203
4.221
4.239
4.257
5.800
5.804
7.277
7.297
7.316
7.460
7.479
7.497
7.577
7.580
7.595
7.598
7.614
7.617
7.931
7.933
7.950
7.952
10.126
CHO
CO2Et
3.14
3.12
2.05
1.01
1.02
1.07
0.97
1.01
1.00
5.0
10.0
ppm (f1)

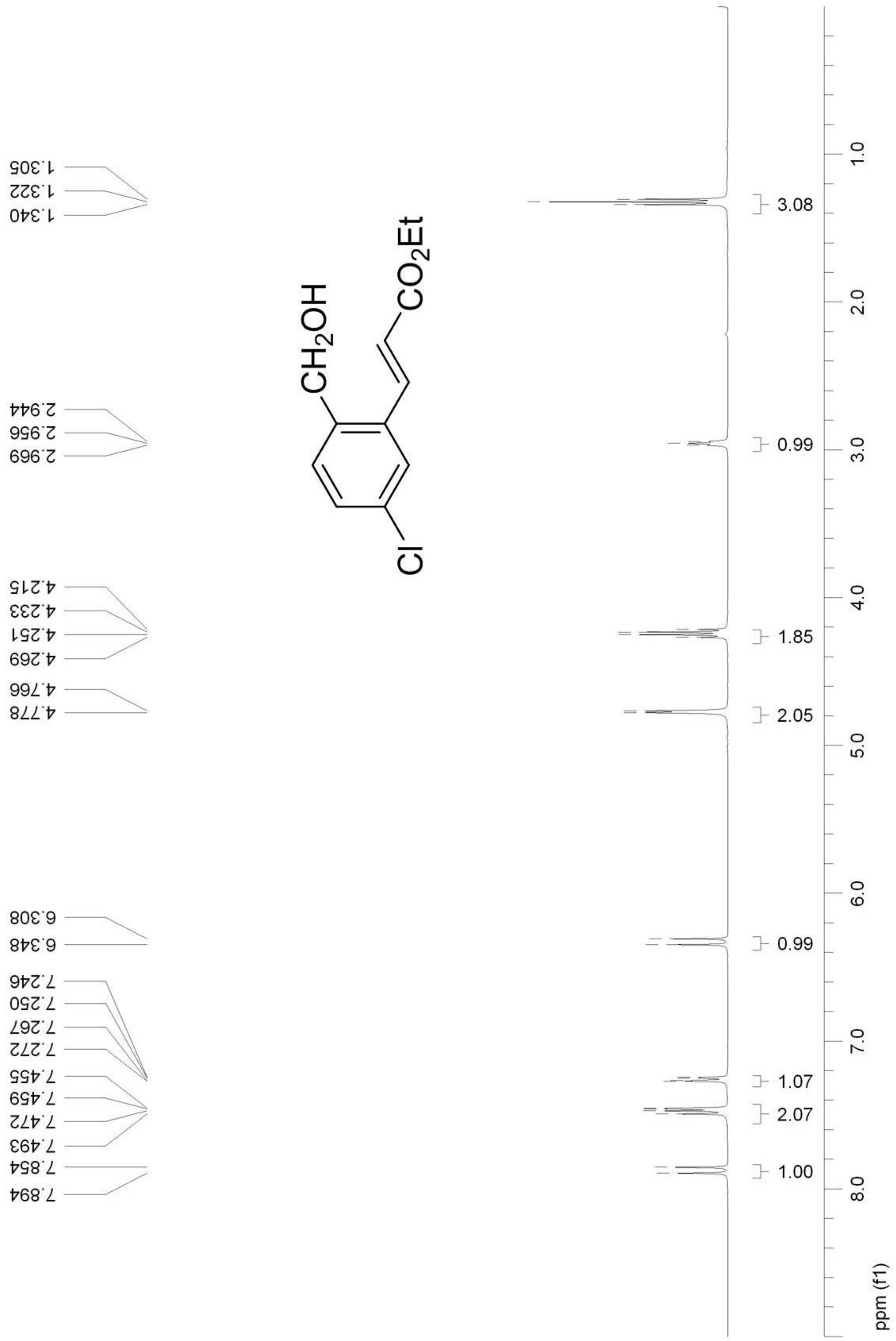

14.289
21.732
60.168
121.913
128.324
128.392
128.946
132.977
133.809
147.083
154.233
165.772
191.162
CHO
$CO_2Et$
50
100
150
200
ppm (f1)

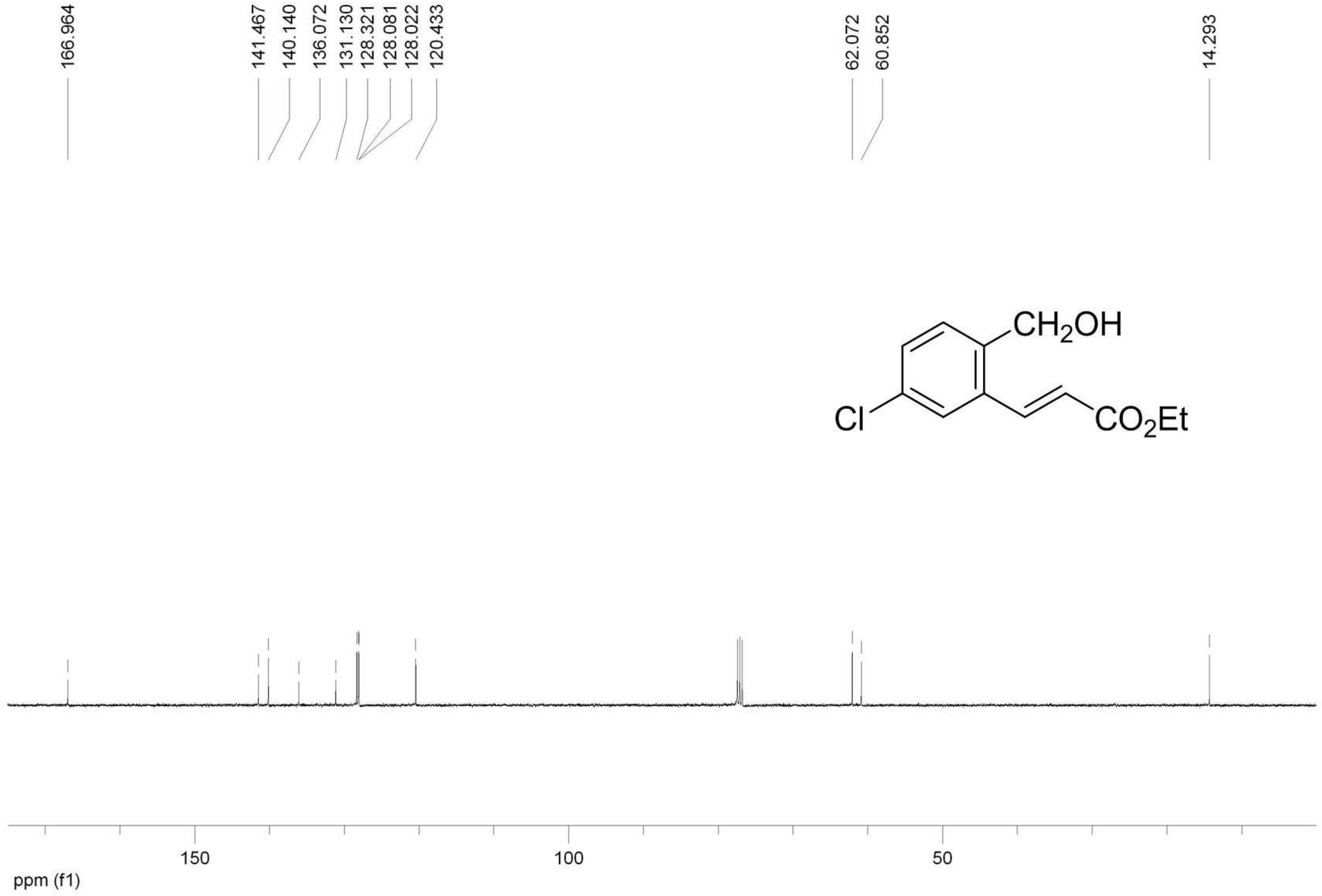

0.850
0.867
0.884
1.266
1.302
1.319
1.337
1.350
1.359
1.368
1.411
3.027
3.046
3.065
4.205
4.223
4.241
4.259
5.747
7.296
7.315
7.484
7.503
7.583
7.600
7.602
7.958
7.977
10.144
CHO
$CO_2Et$
n-Bu
3.85
7.00
1.92
1.90
0.90
1.07
0.96
0.98
0.92
0.90
0.0
5.0
10.0
ppm (f1)

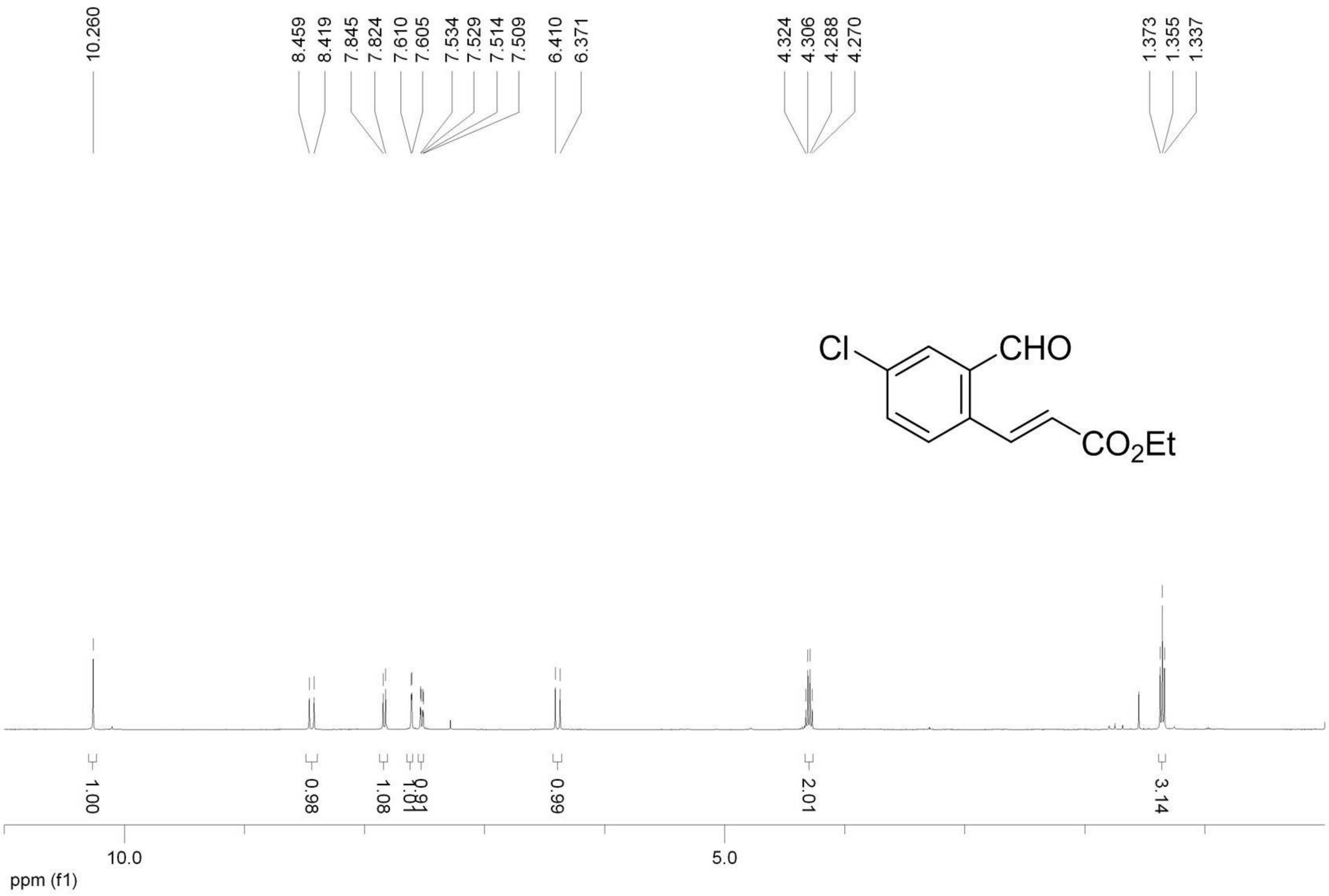

13.799
14.268
22.931
30.136
34.318
60.159
121.797
128.285
128.562
128.586
133.502
133.583
146.188
158.490
165.455
191.310
CHO
$CO_2Et$
n-Bu
50
100
150
200
ppm (f1)

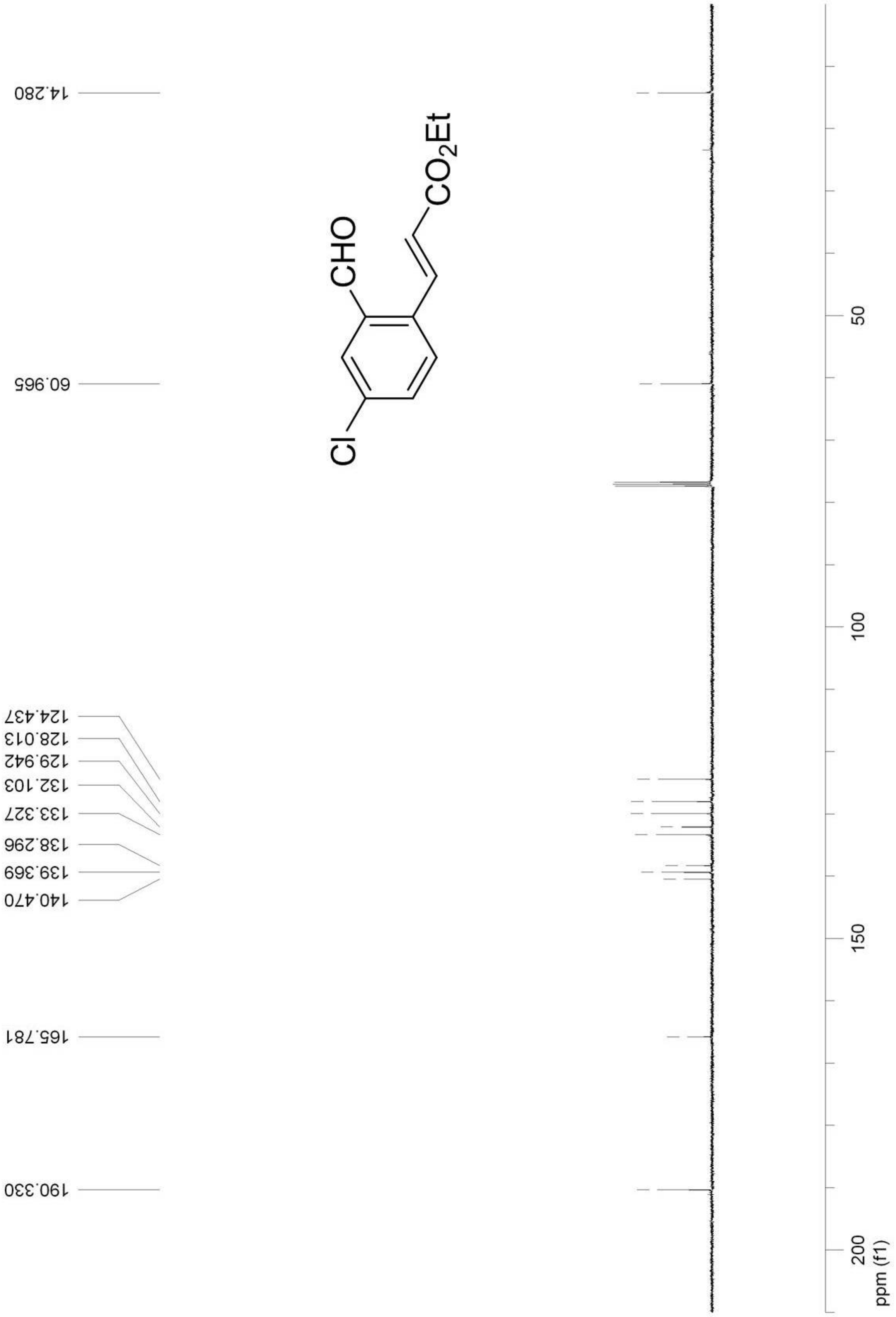

1.331
1.349
1.367
2.406
4.248
4.266
4.284
4.302
4.791
6.375
6.414
7.332
7.337
7.353
7.358
7.389
7.410
7.562
7.567
7.913
7.953
Cl
CH2OH
CO2Et
3.10
0.95
2.12
2.00
0.94
0.93
1.02
0.92
0.90
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

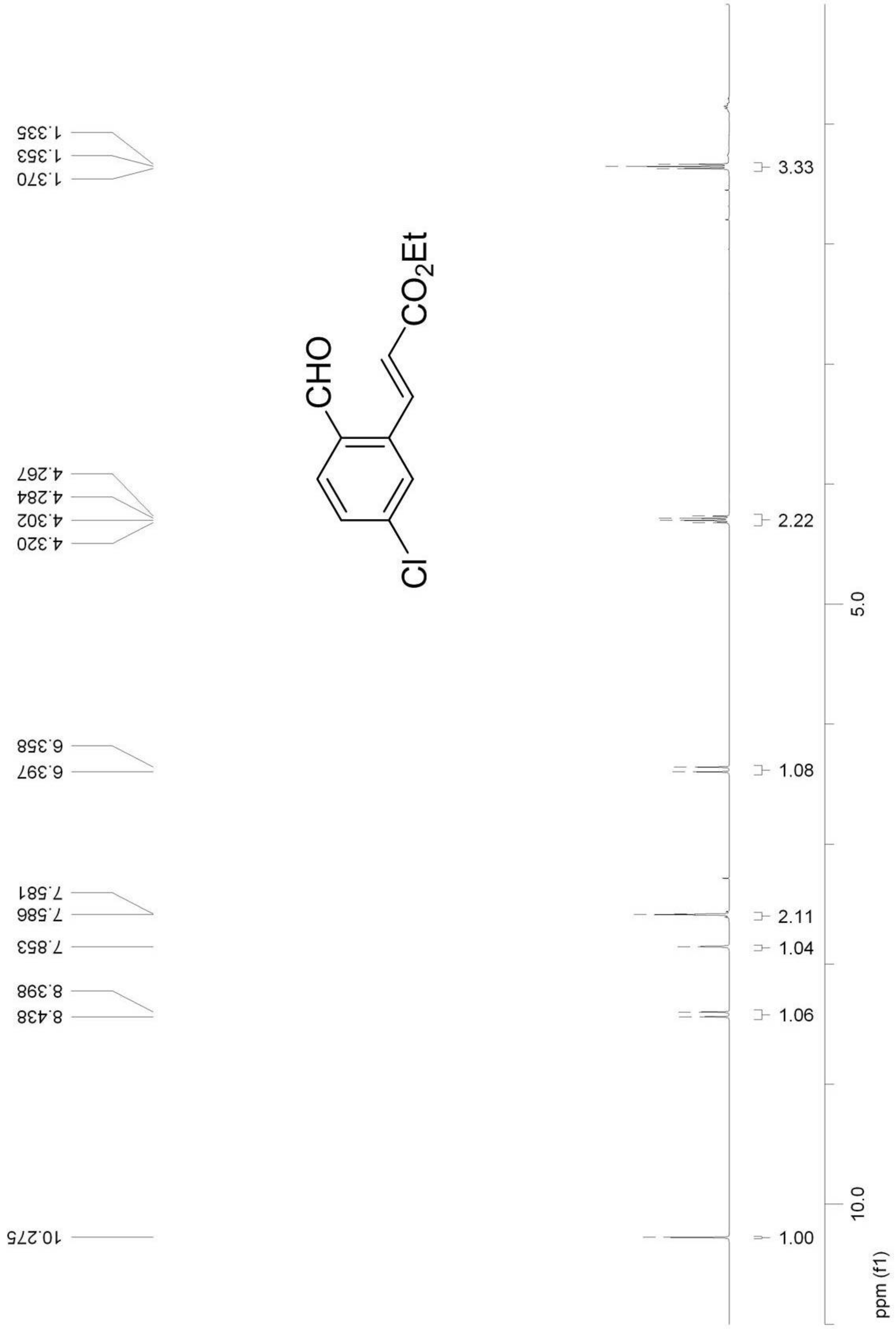

14.295
60.854
62.220
121.464
126.665
129.880
130.034
134.043
134.737
137.921
139.998
166.657
CH2OH
CO2Et
Cl
50
100
150
ppm (f1)


1.305
1.322
1.340
2.944
2.956
2.969
4.215
4.233
4.251
4.269
4.766
4.778
6.308
6.348
7.246
7.250
7.267
7.272
7.455
7.459
7.472
7.493
7.854
7.894
CH$_2$OH
CO$_2$Et
Cl
3.08
0.99
1.85
2.05
0.99
1.07
2.07
1.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

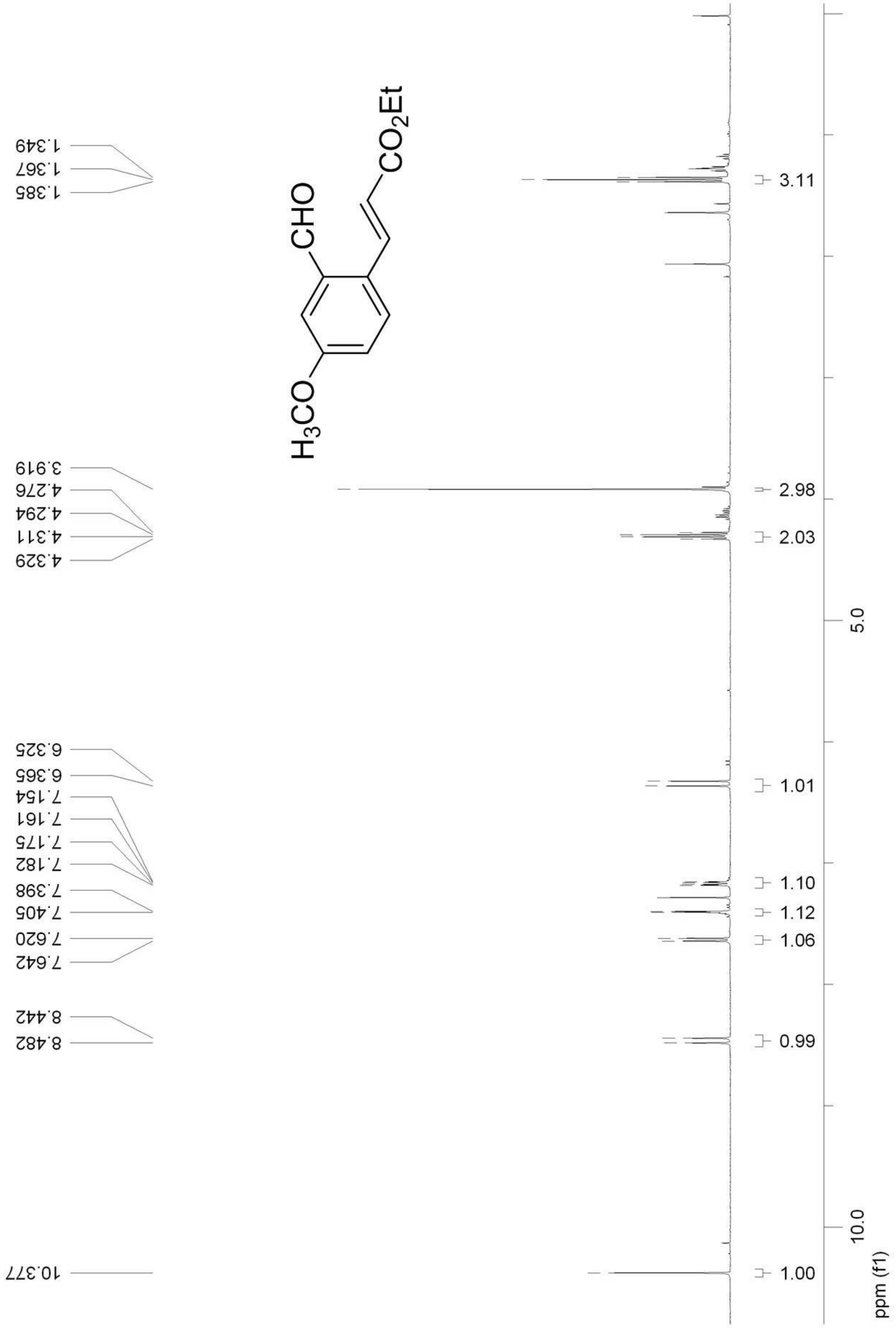

166.964
141.467
140.140
136.072
131.130
128.321
128.081
128.022
120.433
62.072
60.852
14.293
CH2OH
Cl
CO2Et
150
100
50
ppm (f1)

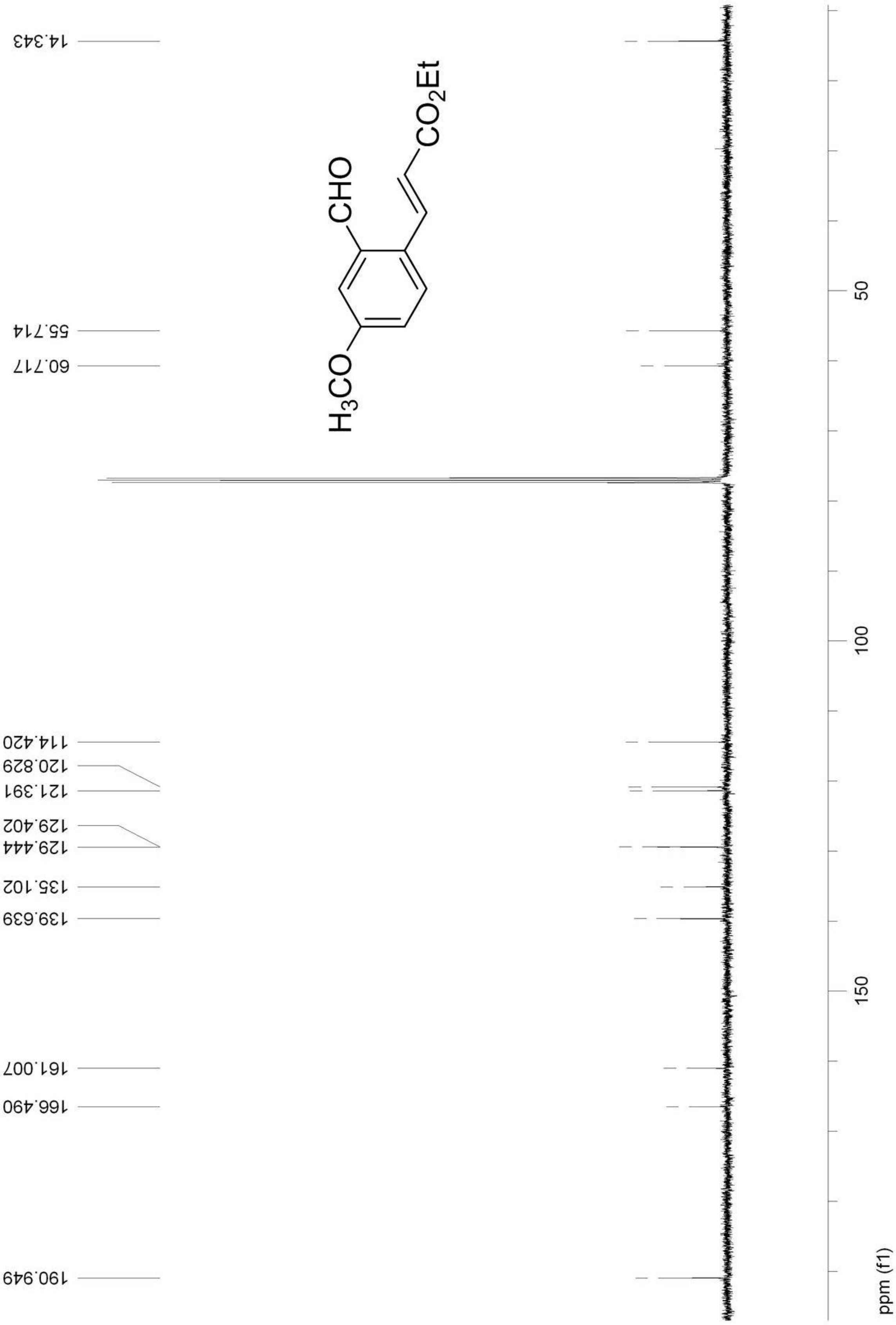

10.260
8.459
8.419
7.845
7.824
7.610
7.605
7.534
7.529
7.514
7.509
6.410
6.371
4.324
4.306
4.288
4.270
1.373
1.355
1.337
Cl
CHO
$CO_2Et$
1.00
0.98
1.08
1.01
0.91
0.99
2.01
3.14
10.0
5.0
ppm (f1)


14.280
60.965
124.437
128.013
129.942
132.103
133.327
138.296
139.369
140.470
165.781
190.330
Cl
CHO
CO2Et
50
100
150
200
ppm (f1)

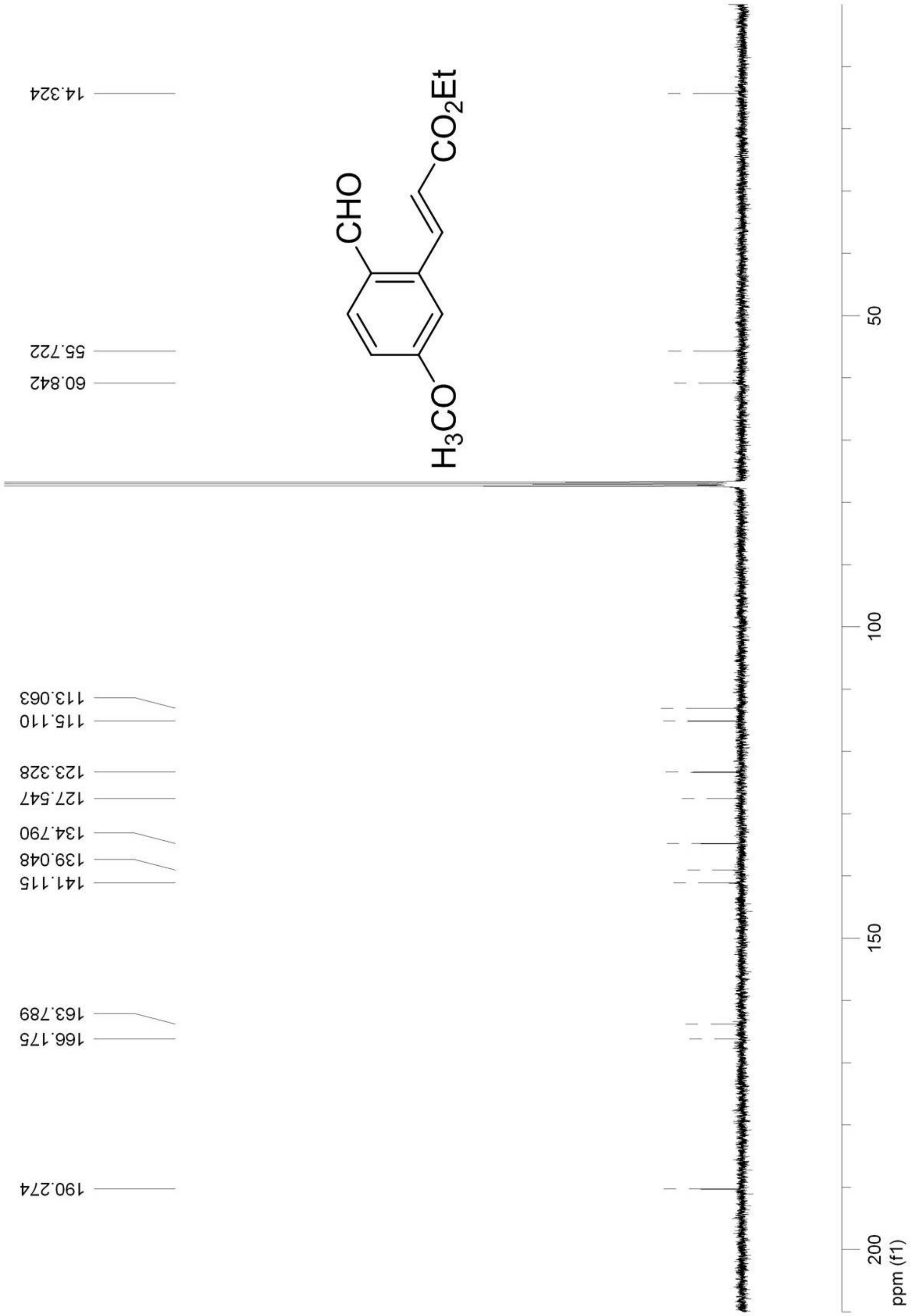

1.335
1.353
1.370
4.267
4.284
4.302
4.320
6.358
6.397
7.581
7.586
7.853
8.398
8.438
10.275
CHO
CO2Et
Cl
3.33
2.22
1.08
2.11
1.04
1.06
1.00
5.0
10.0
ppm (f1)

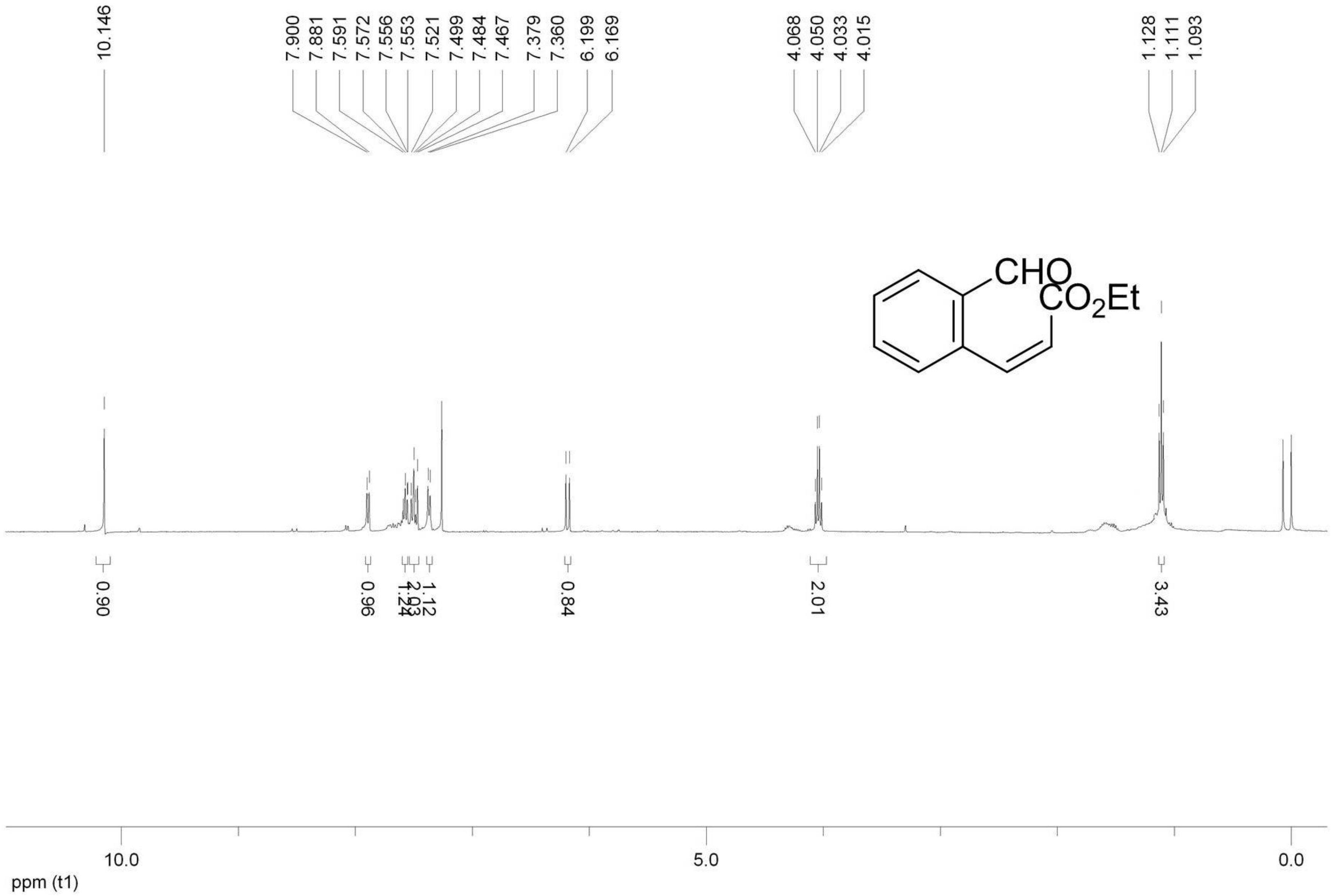

14.292
60.933
123.860
129.382
131.356
133.902
134.853
135.026
136.306
139.283
165.915
190.073
CHO
$CO_2Et$
Cl
50
100
150
200
ppm (f1)

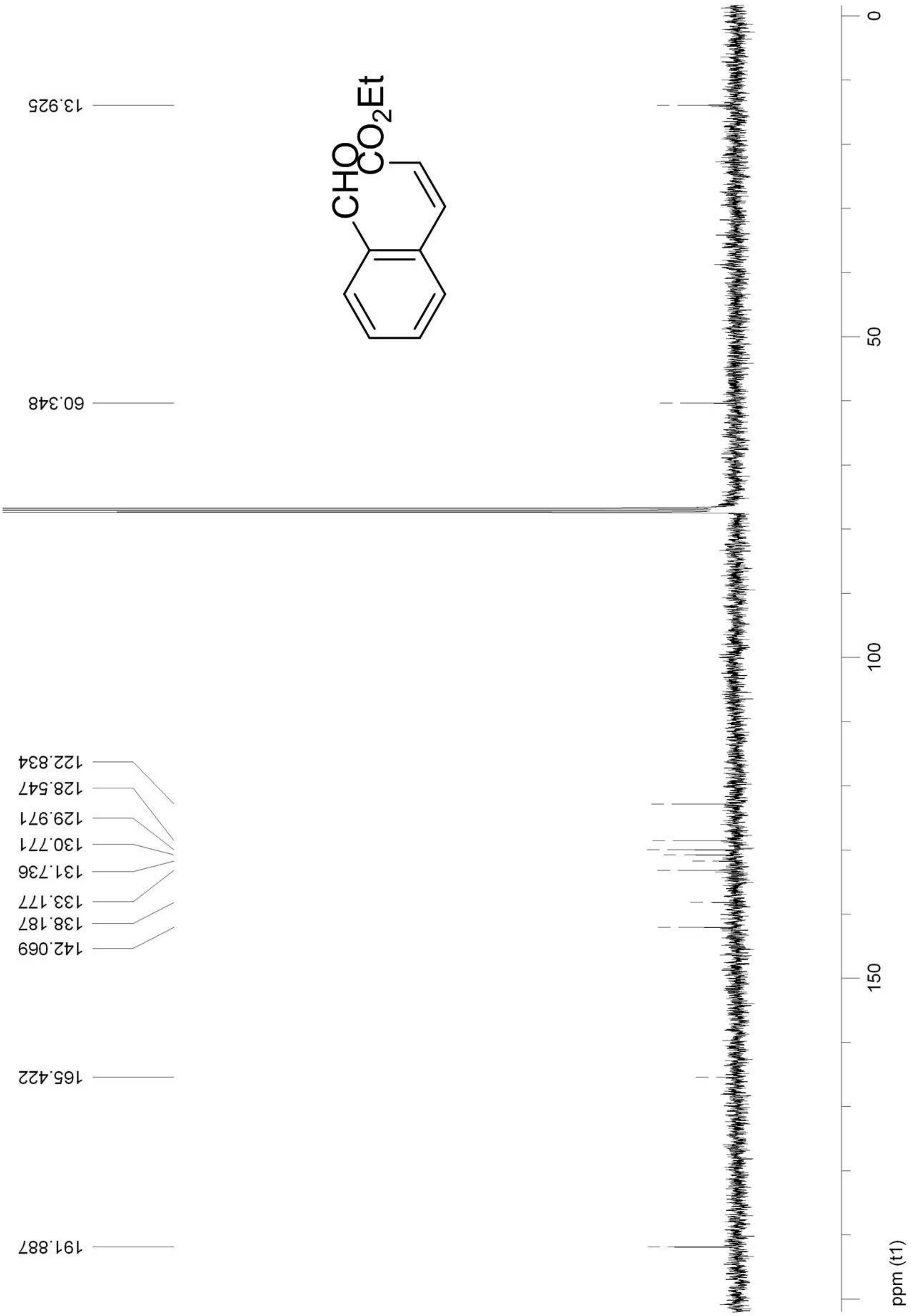

1.349
1.367
1.385
3.919
4.276
4.294
4.311
4.329
6.325
6.365
7.154
7.161
7.175
7.182
7.398
7.405
7.620
7.642
8.442
8.482
10.377
H3CO
CHO
CO2Et
3.11
2.98
2.03
1.01
1.10
1.12
1.06
0.99
1.00
5.0
10.0
ppm (f1)

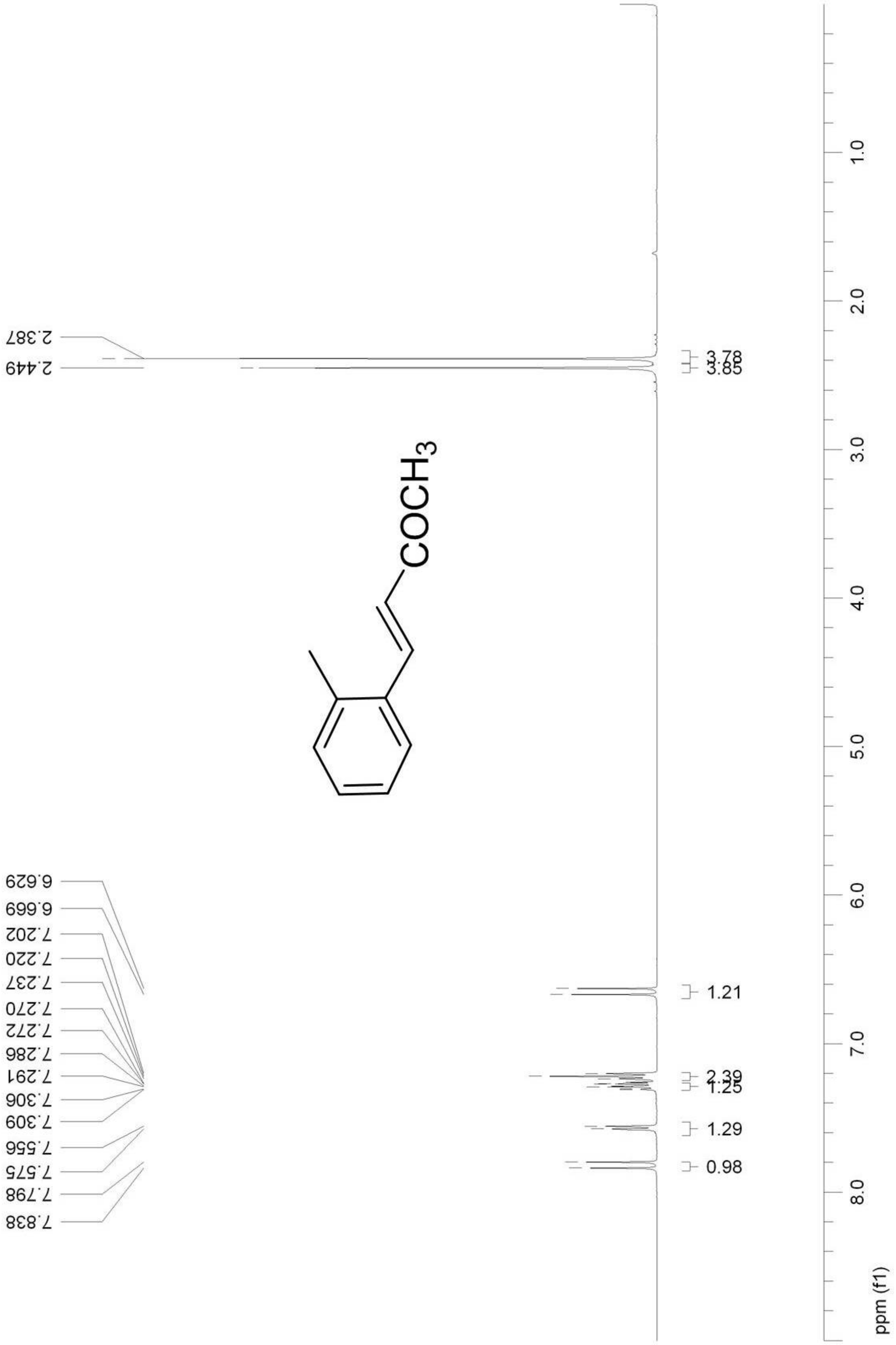

14.343
55.714
60.717
114.420
120.829
121.391
129.402
129.444
135.102
139.639
161.007
166.490
190.949
CHO
$CO_2Et$
$H_3CO$
50
100
150
ppm (f1)

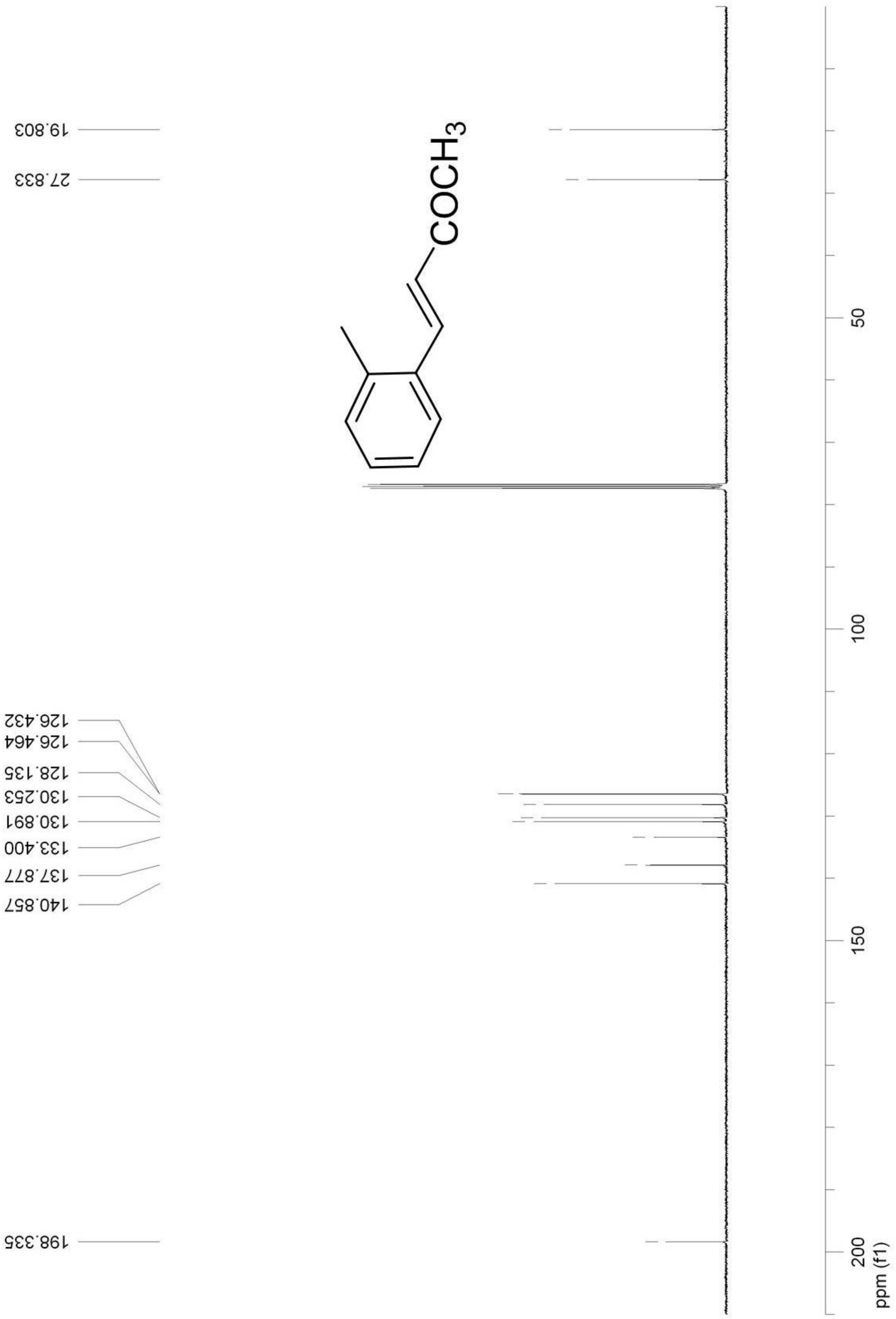

CHO
CO$_2$Et
H$_3$CO
1.339
1.357
1.375
3.916
4.269
4.287
4.305
4.323
6.341
6.381
7.020
7.027
7.042
7.048
7.072
7.078
7.830
7.852
8.501
8.541
10.163
3.13
2.88
2.15
1.03
2.07
1.03
1.01
0.99
5.0
10.0
ppm (f1)

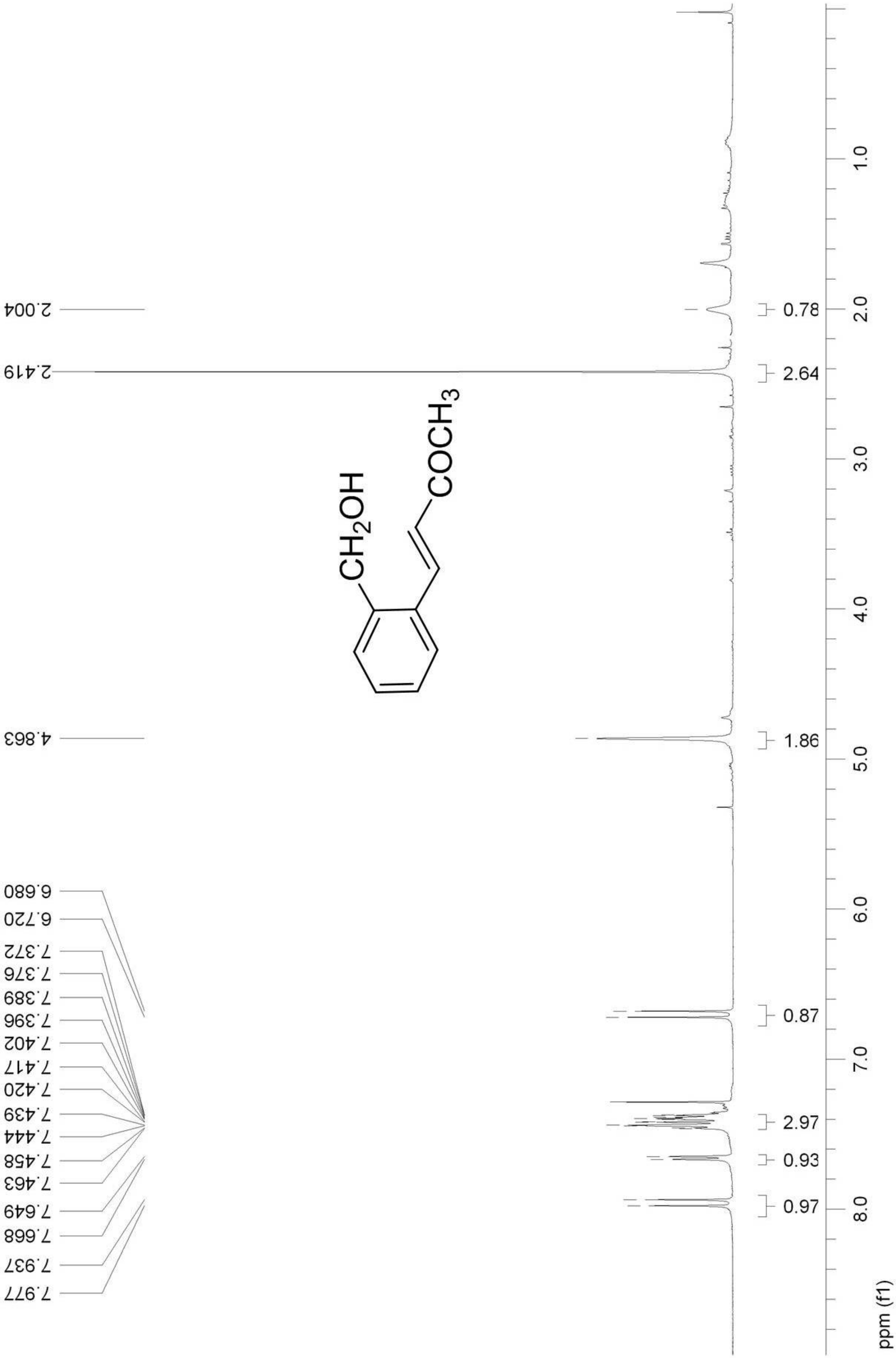

14.324
55.722
60.842
113.063
115.110
123.328
127.547
134.790
139.048
141.115
163.789
166.175
190.274
CHO
$CO_2Et$
$H_3CO$
50
100
150
200
ppm (f1)

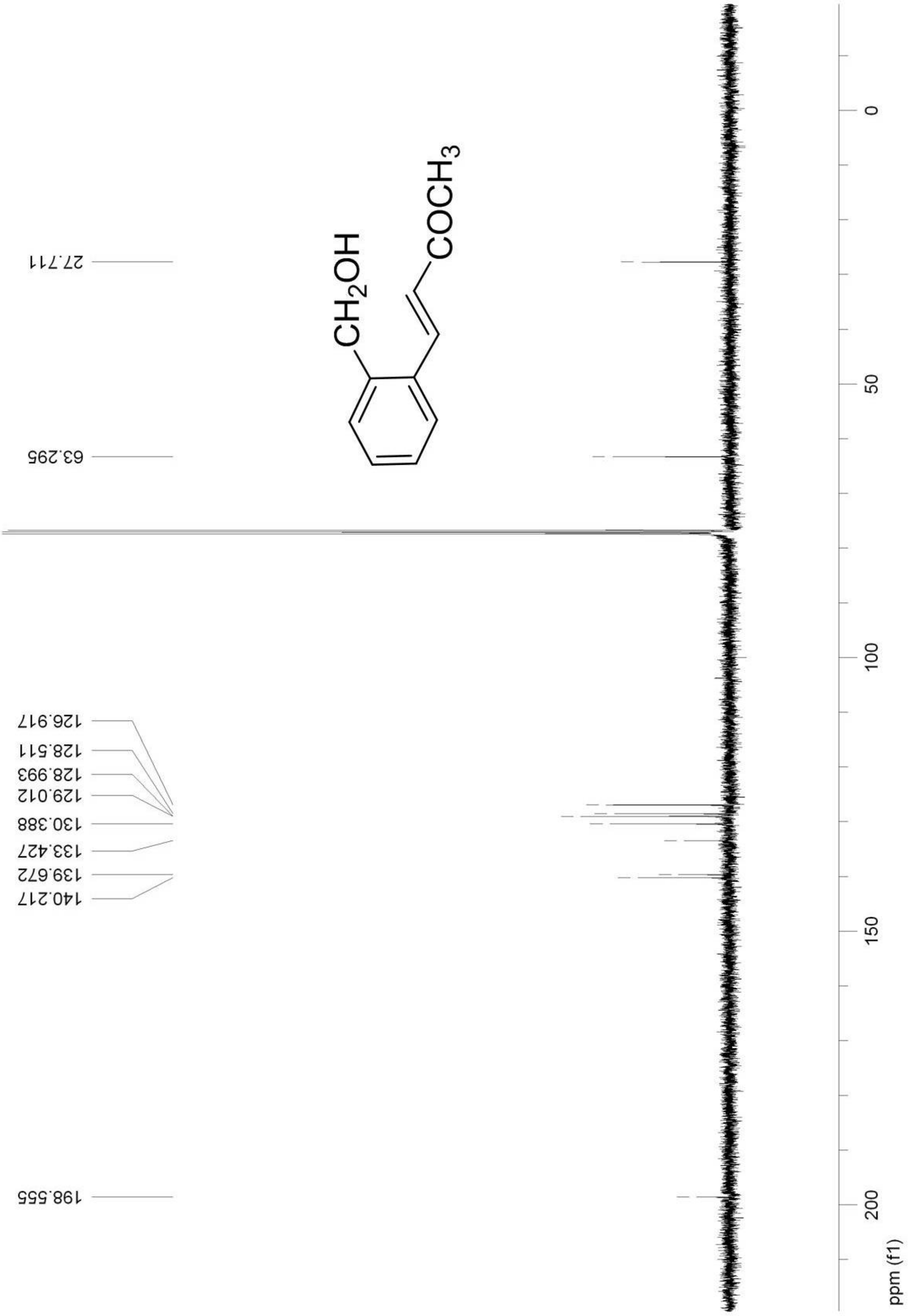

10.146
7.900
7.881
7.591
7.572
7.556
7.553
7.521
7.499
7.484
7.467
7.379
7.360
6.199
6.169
4.068
4.050
4.033
4.015
1.128
1.111
1.093
CHO
CO2Et
0.90
0.96
1.24
2.03
1.12
0.84
2.01
3.43
10.0
5.0
0.0
ppm (t1)

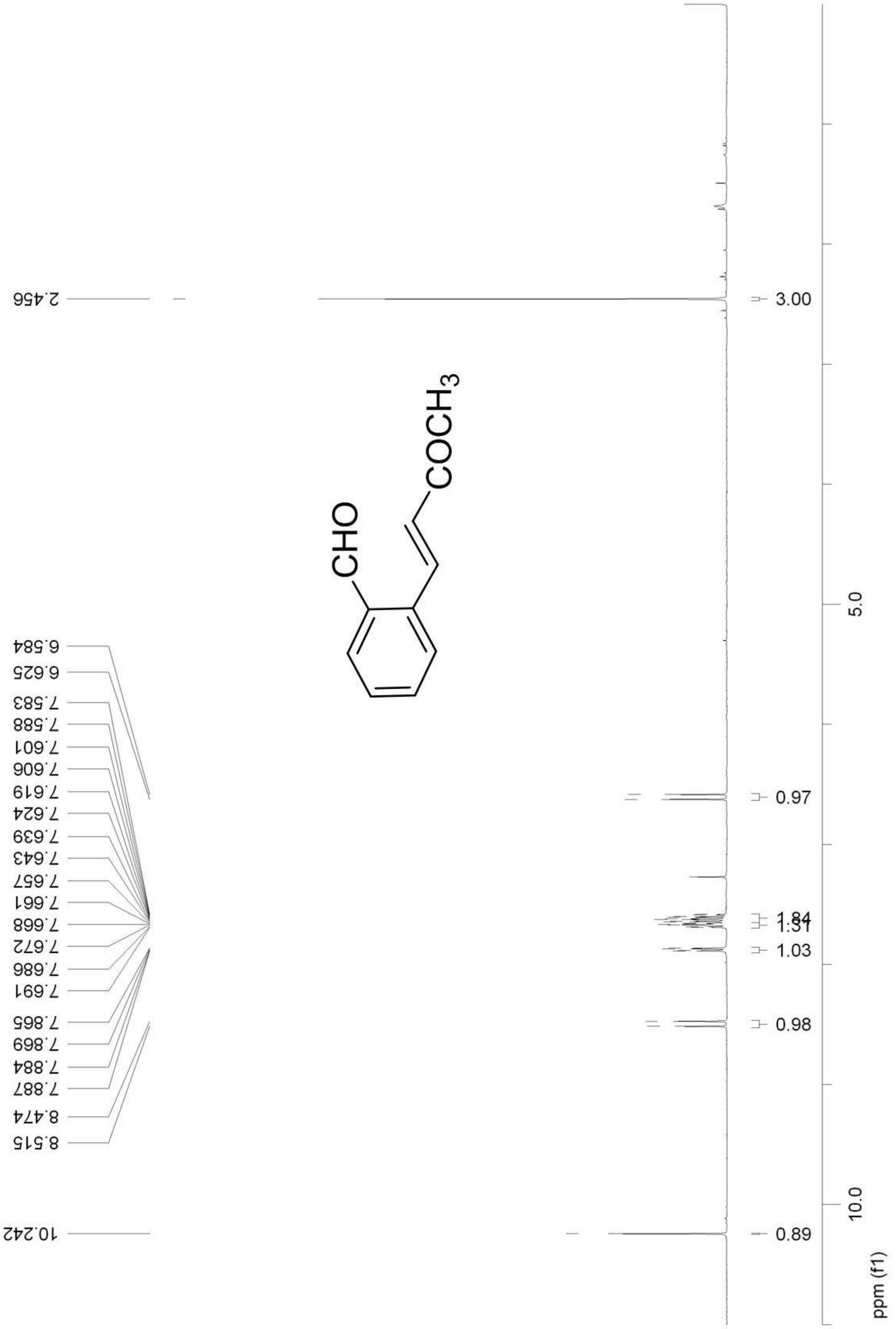

13.925
60.348
122.834
128.547
129.971
130.771
131.736
133.177
138.187
142.069
165.422
191.887
CHO
CO2Et
0
50
100
150
ppm (t1)

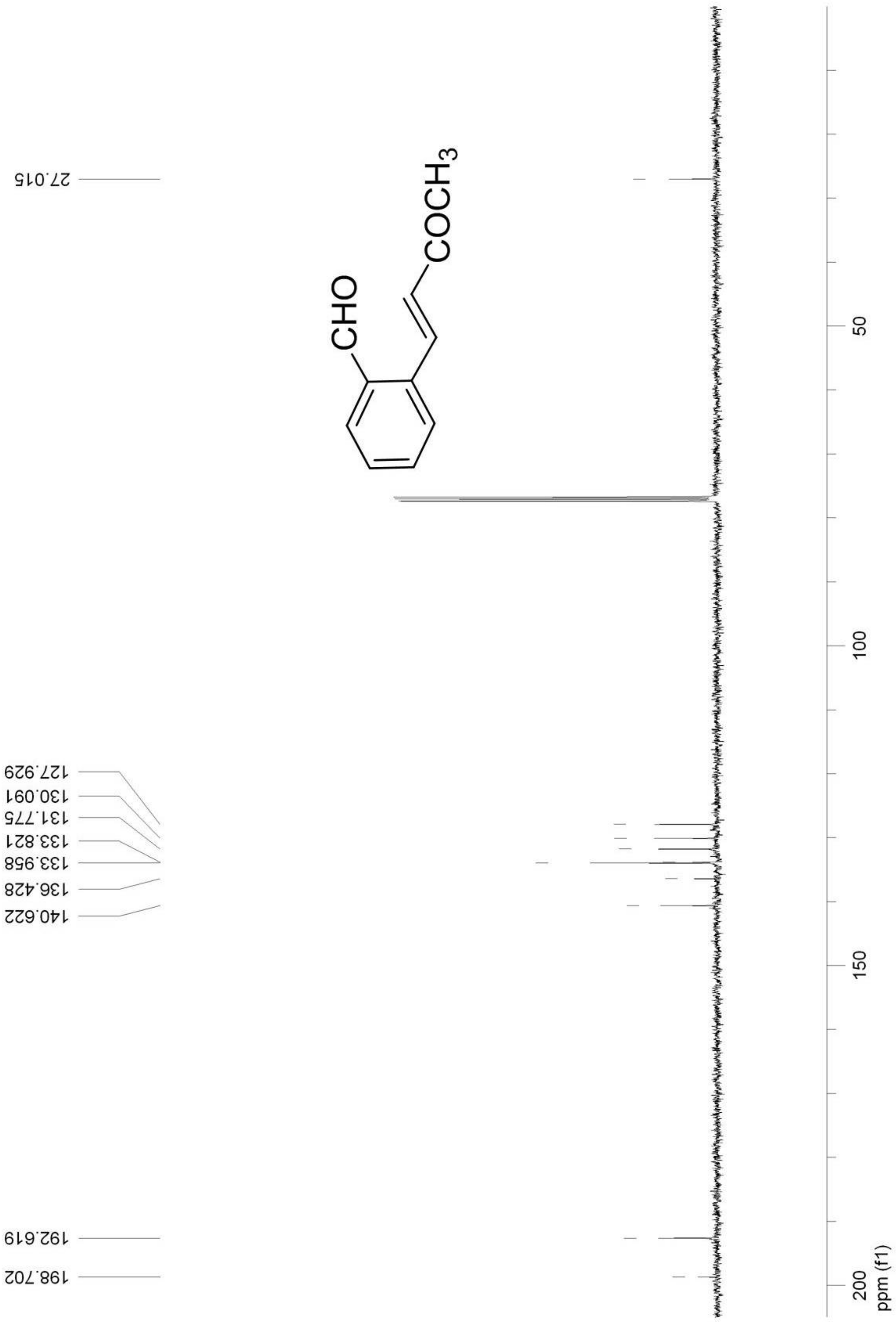

2.387
2.449
6.629
6.669
7.202
7.220
7.237
7.270
7.272
7.286
7.291
7.306
7.309
7.556
7.575
7.798
7.838
3.78
3.85
1.21
2.39
1.25
1.29
0.98
COCH3
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

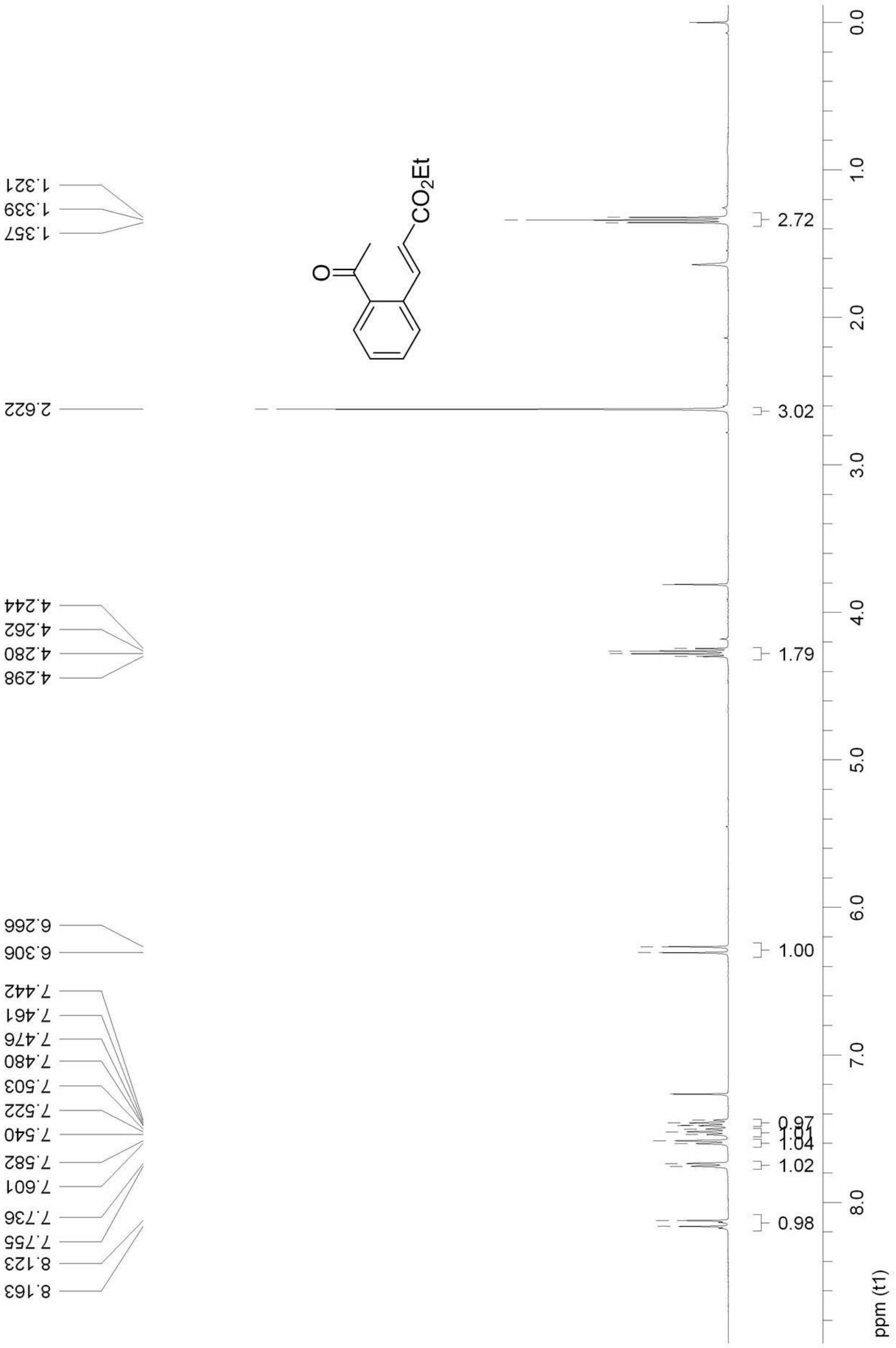

19.803
27.833
126.432
126.464
128.135
130.253
130.891
133.400
137.877
140.857
198.335
COCH3
50
100
150
200
ppm (f1)

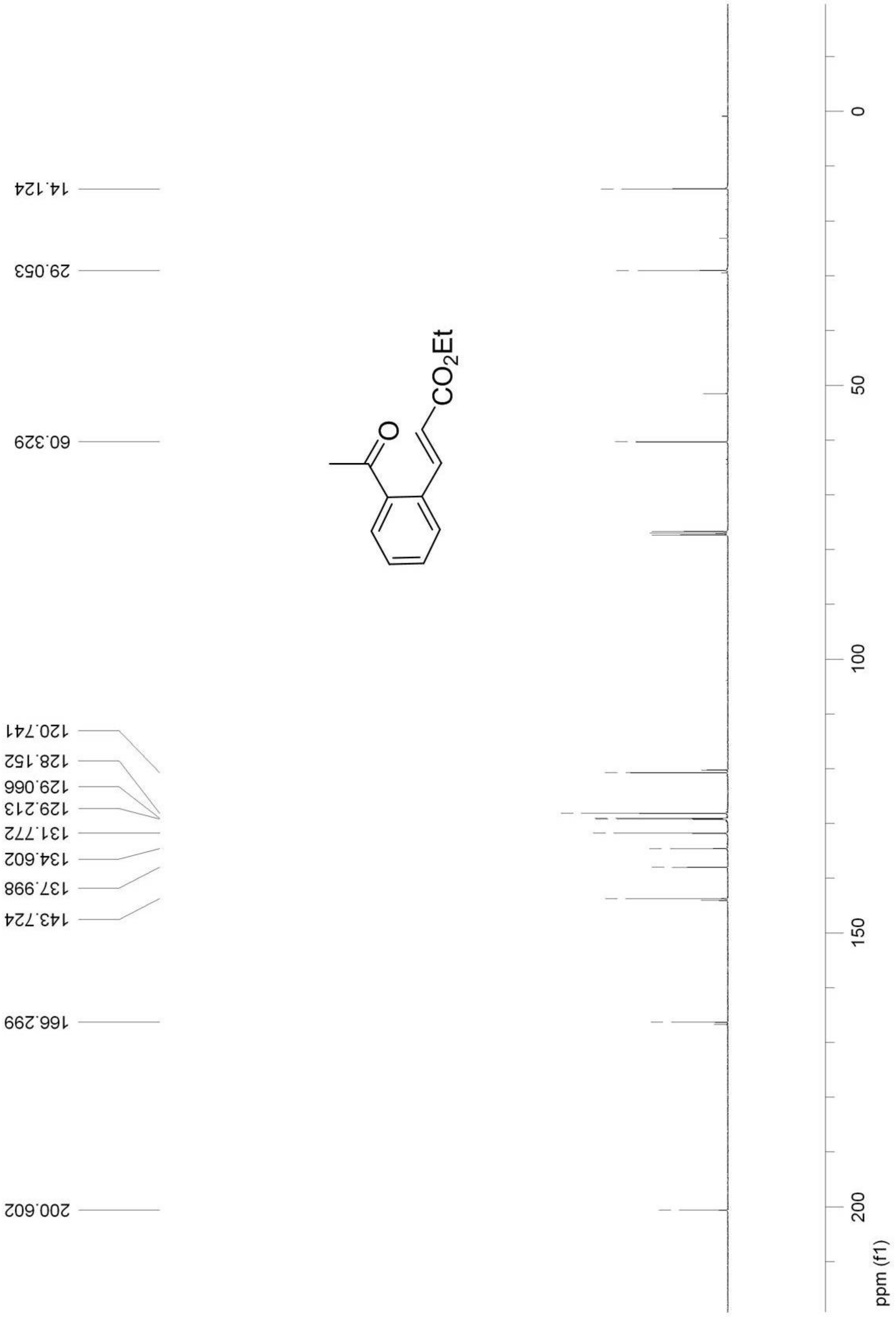

2.004
2.419
4.863
6.680
6.720
7.372
7.376
7.389
7.396
7.402
7.417
7.420
7.439
7.444
7.458
7.463
7.649
7.668
7.937
7.977
CH2OH
COCH3
0.78
2.64
1.86
0.87
2.97
0.93
0.97
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

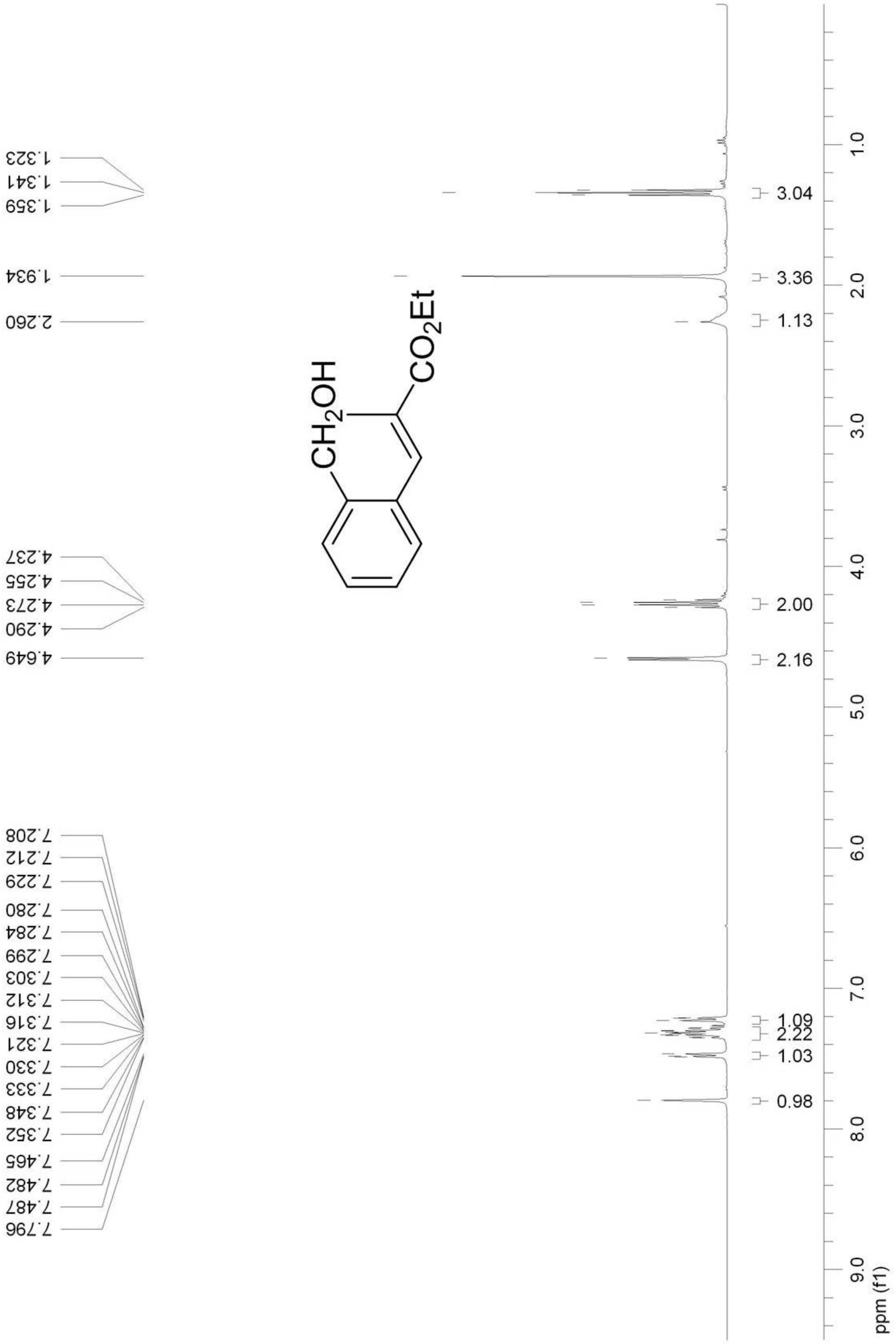

CH2OH
COCH3
27.711
63.295
126.917
128.511
128.993
129.012
130.388
133.427
139.672
140.217
198.555
0
50
100
150
200
ppm (f1)

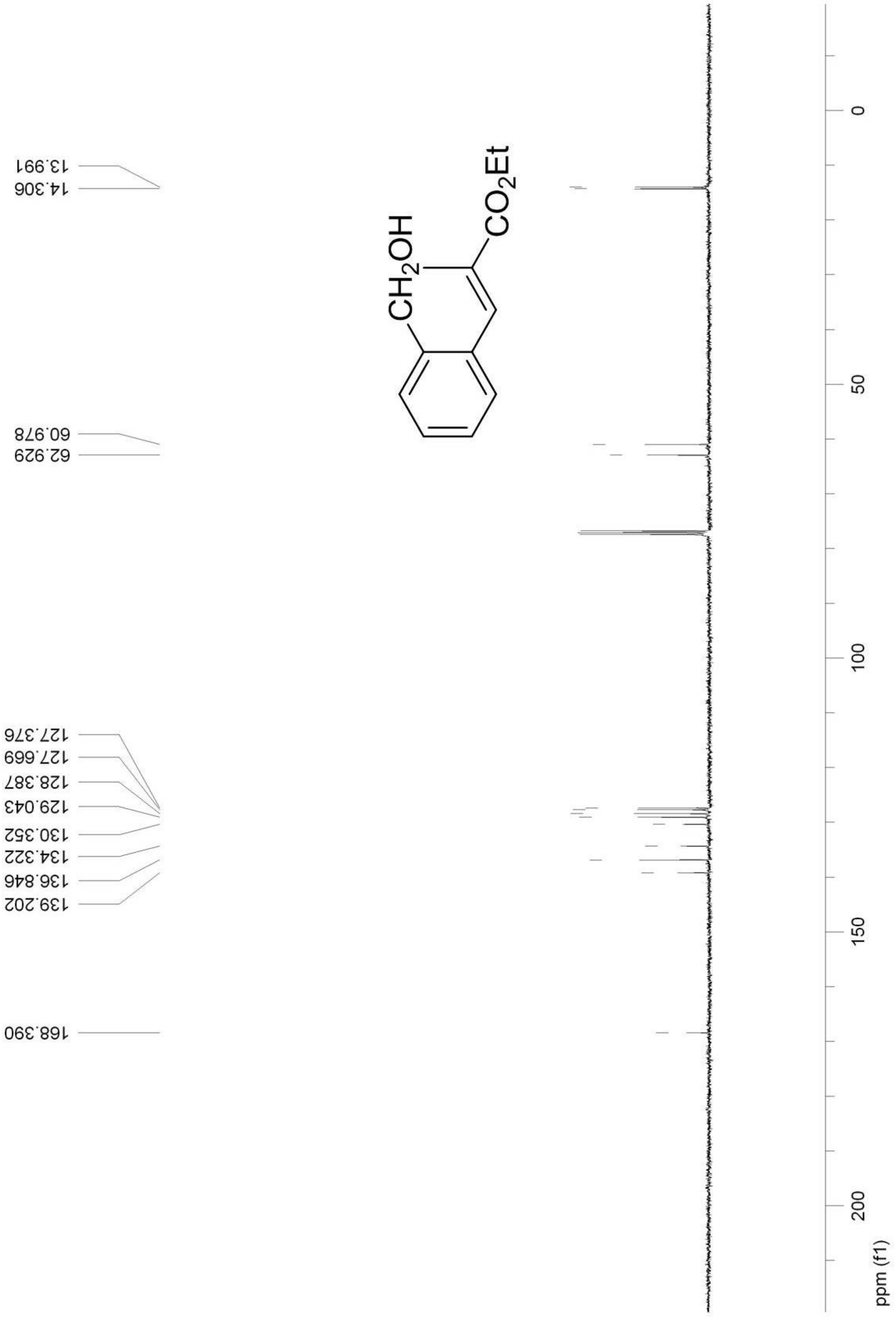

2.456
6.584
6.625
7.583
7.588
7.601
7.606
7.619
7.624
7.639
7.643
7.657
7.661
7.668
7.672
7.686
7.691
7.865
7.869
7.884
7.887
8.474
8.515
10.242
3.00
0.97
1.84
1.31
1.03
0.98
0.89
5.0
10.0
ppm (f1)
CHO
COCH$_3$


CHO
COCH3
27.015
127.929
130.091
131.775
133.821
133.958
136.428
140.622
192.619
198.702
50
100
150
200
ppm (f1)

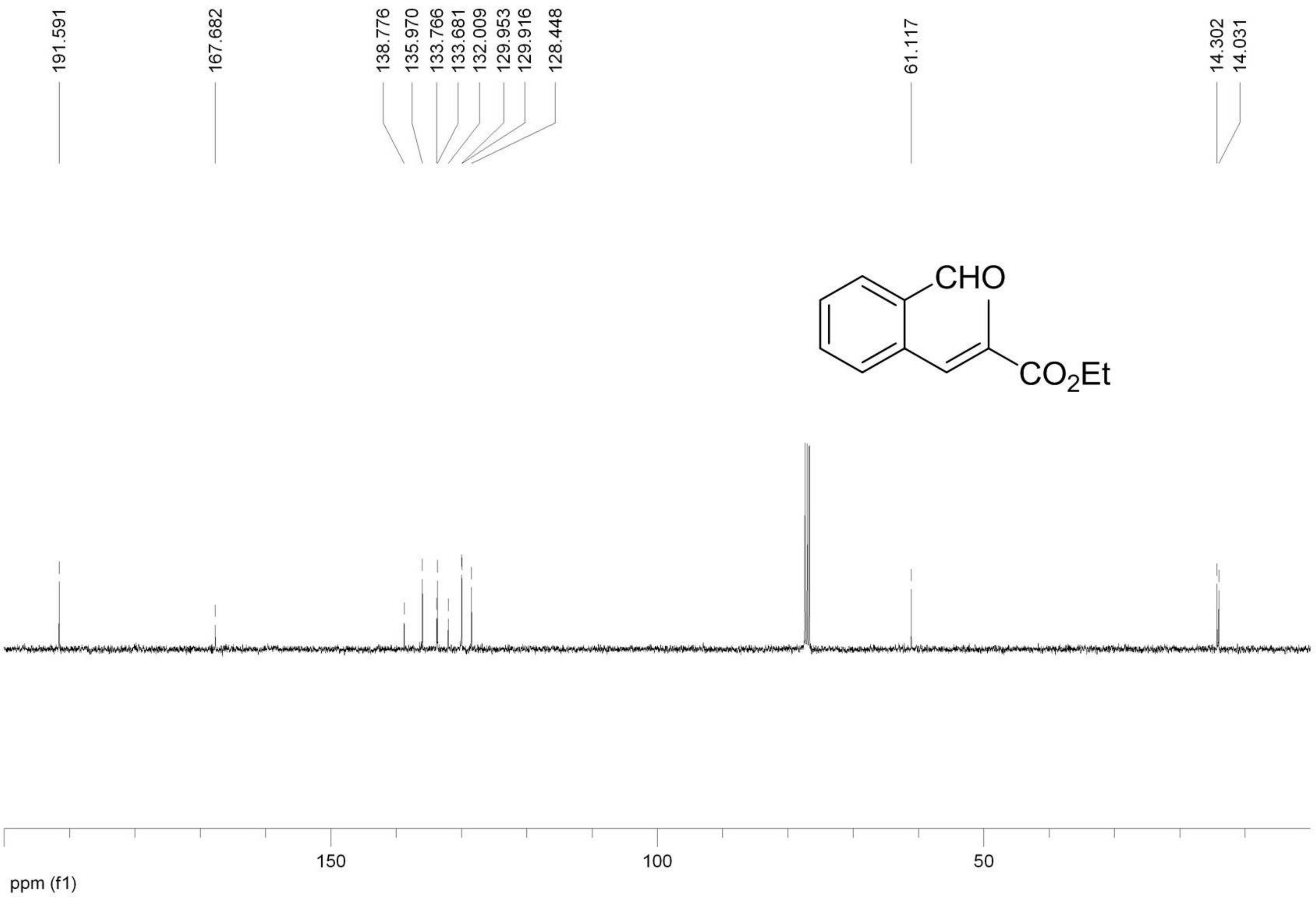

1.321
1.339
1.357
2.622
4.244
4.262
4.280
4.298
6.266
6.306
7.442
7.461
7.476
7.480
7.503
7.522
7.540
7.582
7.601
7.736
7.755
8.123
8.163
CO$_2$Et
O
2.72
3.02
1.79
1.00
0.97
1.01
1.04
1.02
0.98
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (t1)

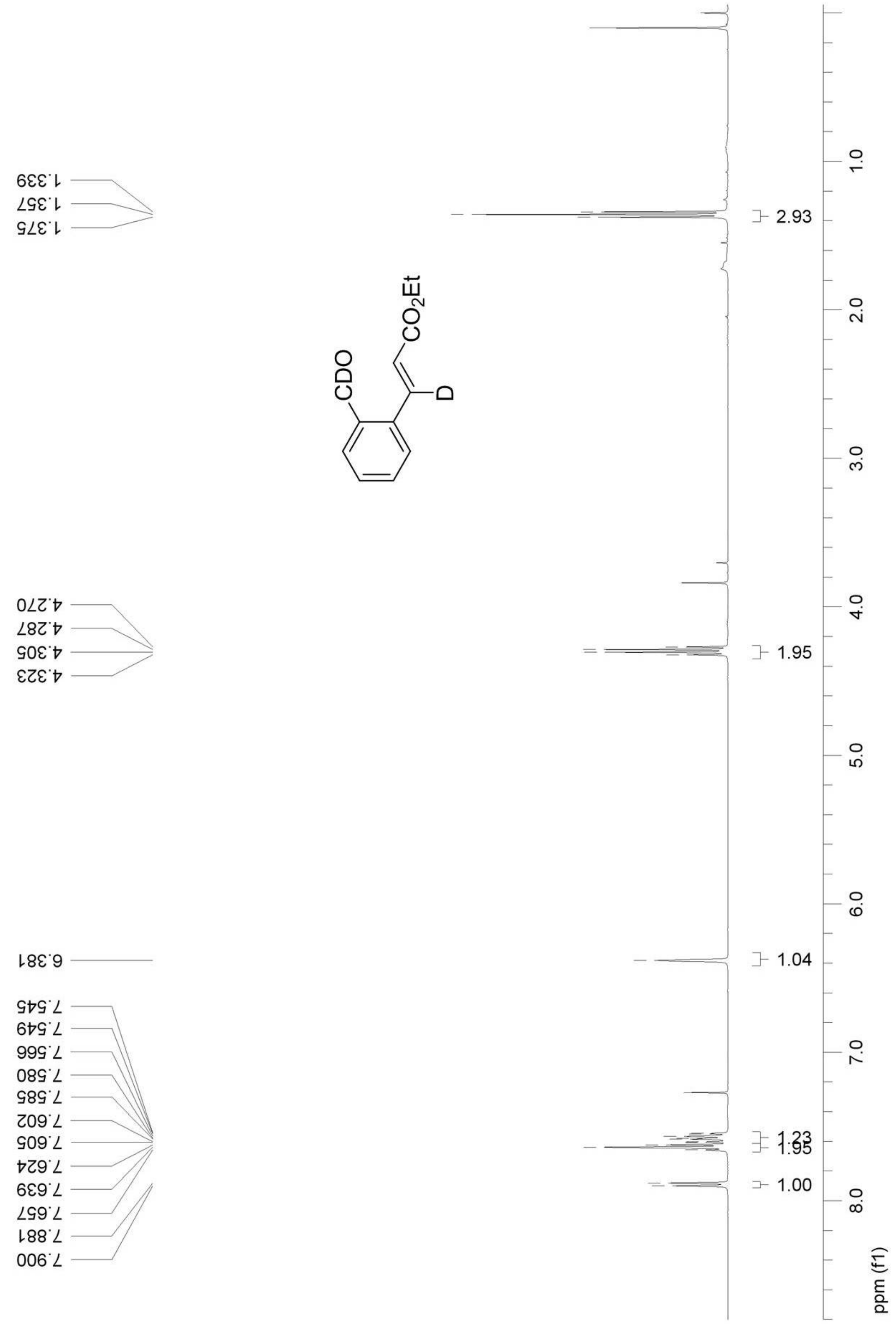

14.124
29.053
60.329
120.741
128.152
129.066
129.213
131.772
134.602
137.998
143.724
166.299
200.602
O
$CO_2Et$
0
50
100
150
200
ppm (f1)

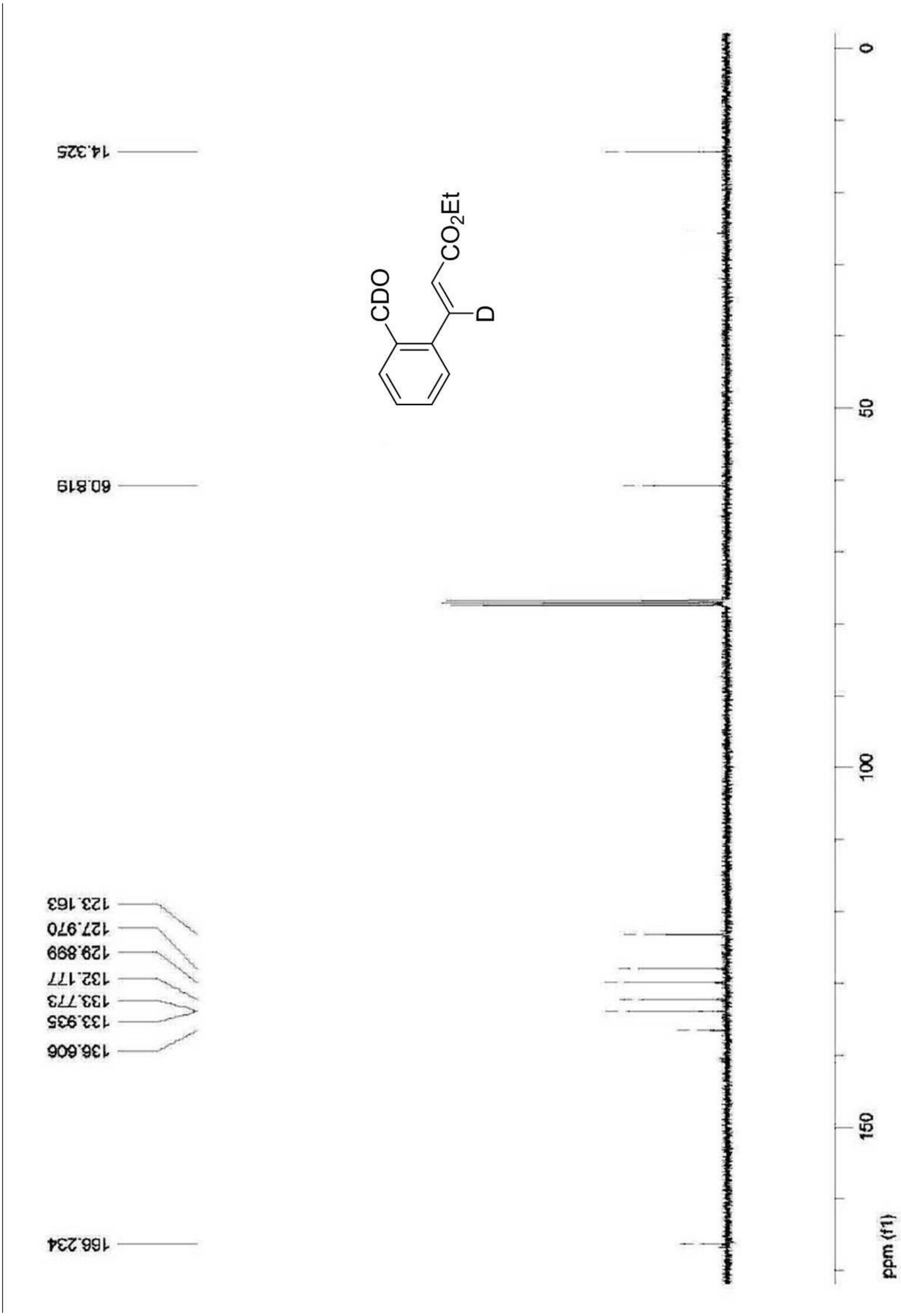

1.323
1.341
1.359
1.934
2.260
4.237
4.255
4.273
4.290
4.649
7.208
7.212
7.229
7.280
7.284
7.299
7.303
7.312
7.316
7.321
7.330
7.333
7.348
7.352
7.465
7.482
7.487
7.796
CH2OH
CO2Et
3.04
3.36
1.13
2.00
2.16
1.09
2.22
1.03
0.98
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)

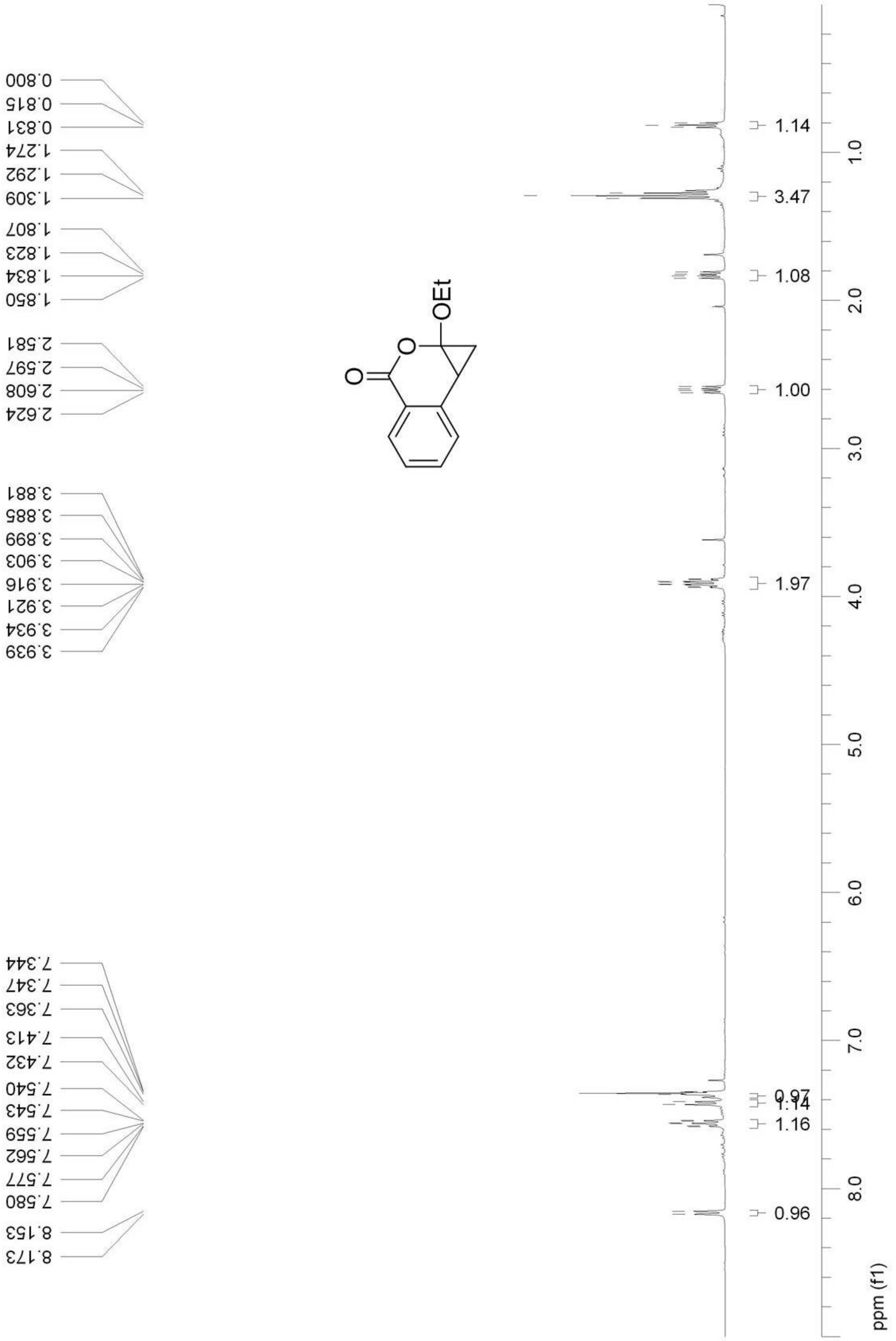

13.991
14.306
60.978
62.929
127.376
127.669
128.387
129.043
130.352
134.322
136.846
139.202
168.390
CH2OH
CO2Et
0
50
100
150
200
ppm (f1)

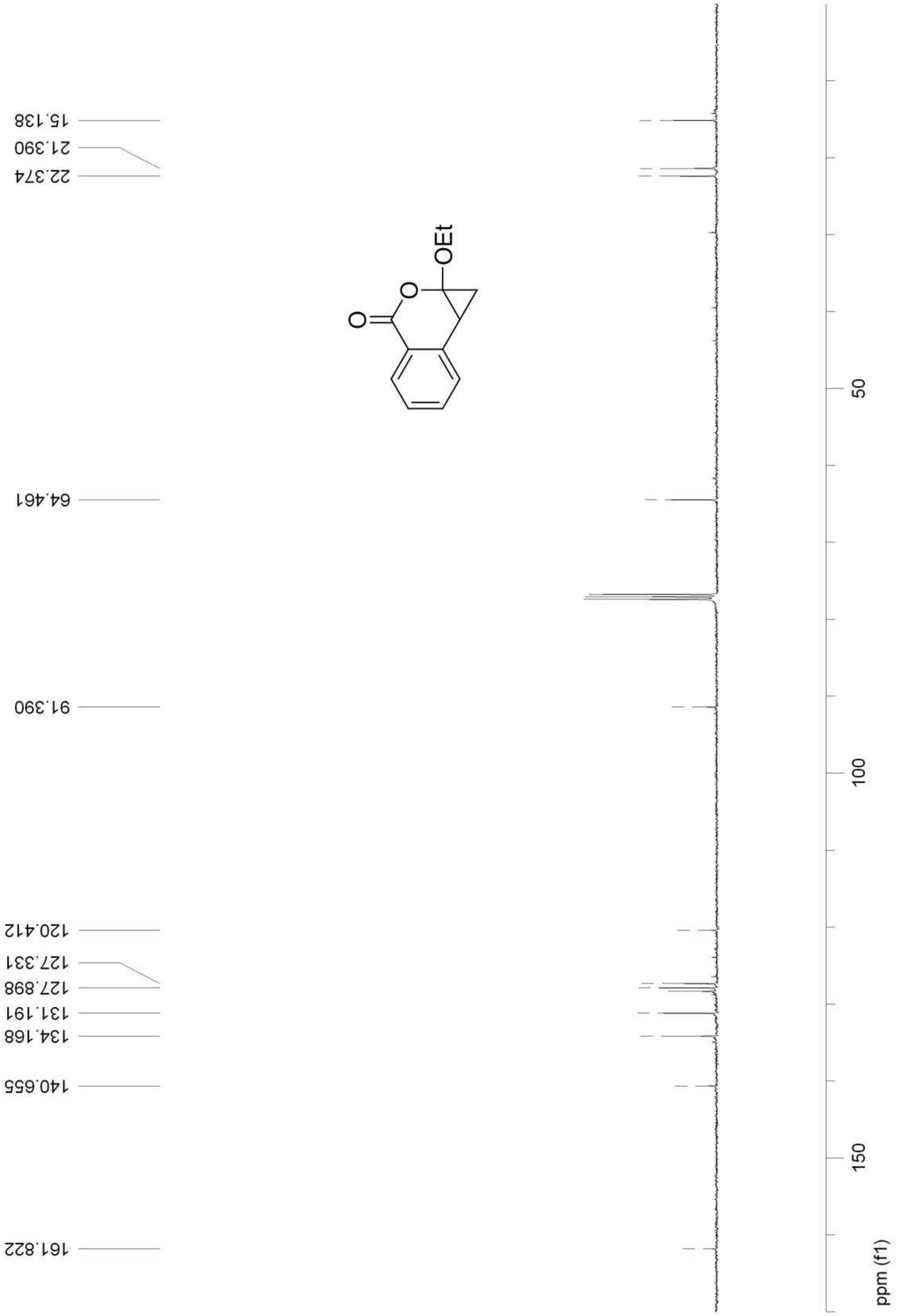

1.350
1.368
1.386
1.904
1.908
4.279
4.297
4.315
4.332
7.307
7.326
7.475
7.493
7.512
7.600
7.603
7.619
7.622
7.638
7.641
7.925
7.928
7.945
7.947
8.065
10.175
CHO
CO2Et
2.71
2.94
1.79
0.93
1.01
1.00
0.96
0.95
0.96
5.0
10.0
ppm (f1)

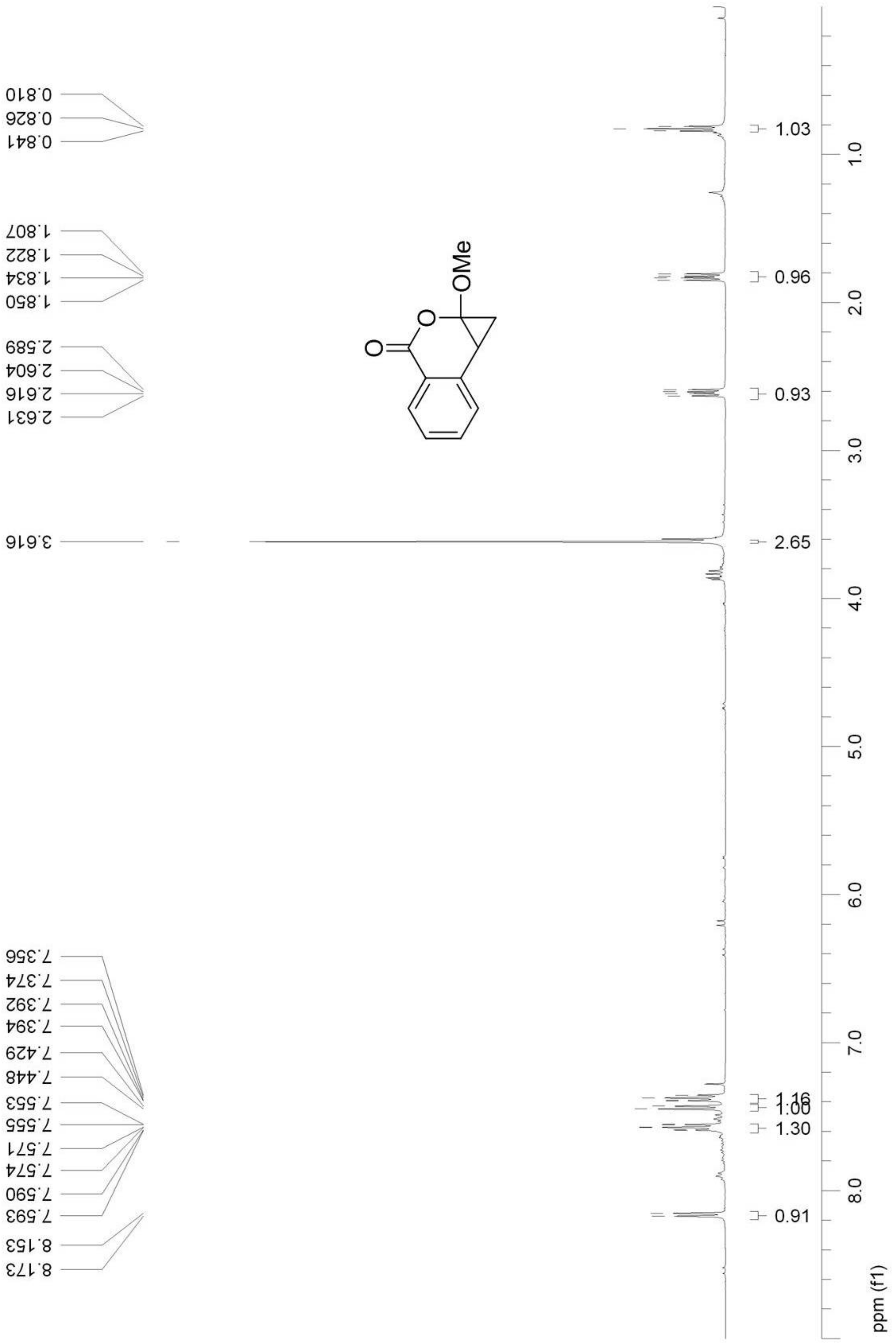

191.591
167.682
138.776
135.970
133.766
133.681
132.009
129.953
129.916
128.448
61.117
14.302
14.031
CHO
CO2Et
150
100
50
ppm (f1)

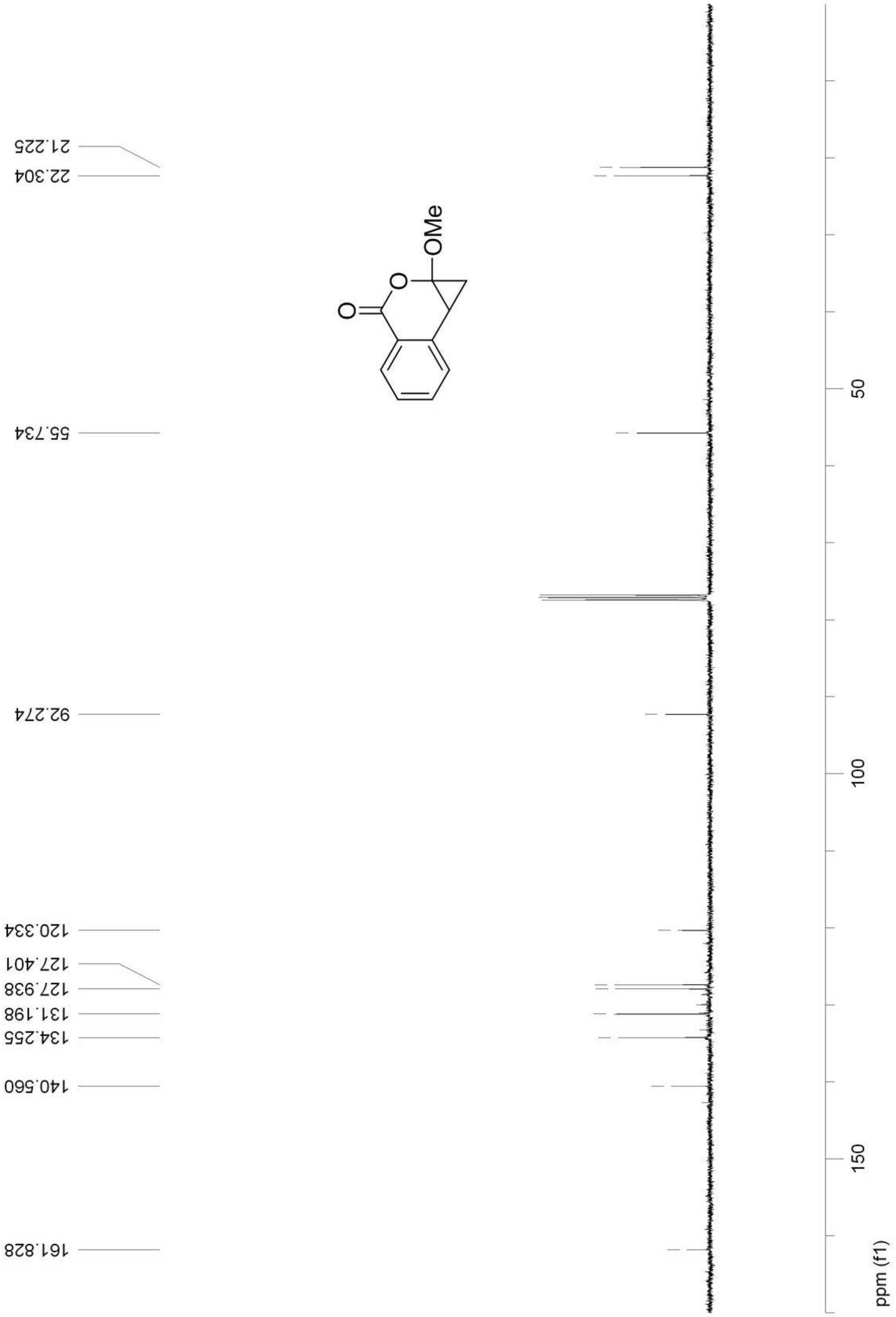

1.339
1.357
1.375
4.270
4.287
4.305
4.323
6.381
7.545
7.549
7.566
7.580
7.585
7.602
7.605
7.624
7.639
7.657
7.881
7.900
CDO
CO$_2$Et
D
2.93
1.95
1.04
1.23
1.95
1.00
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

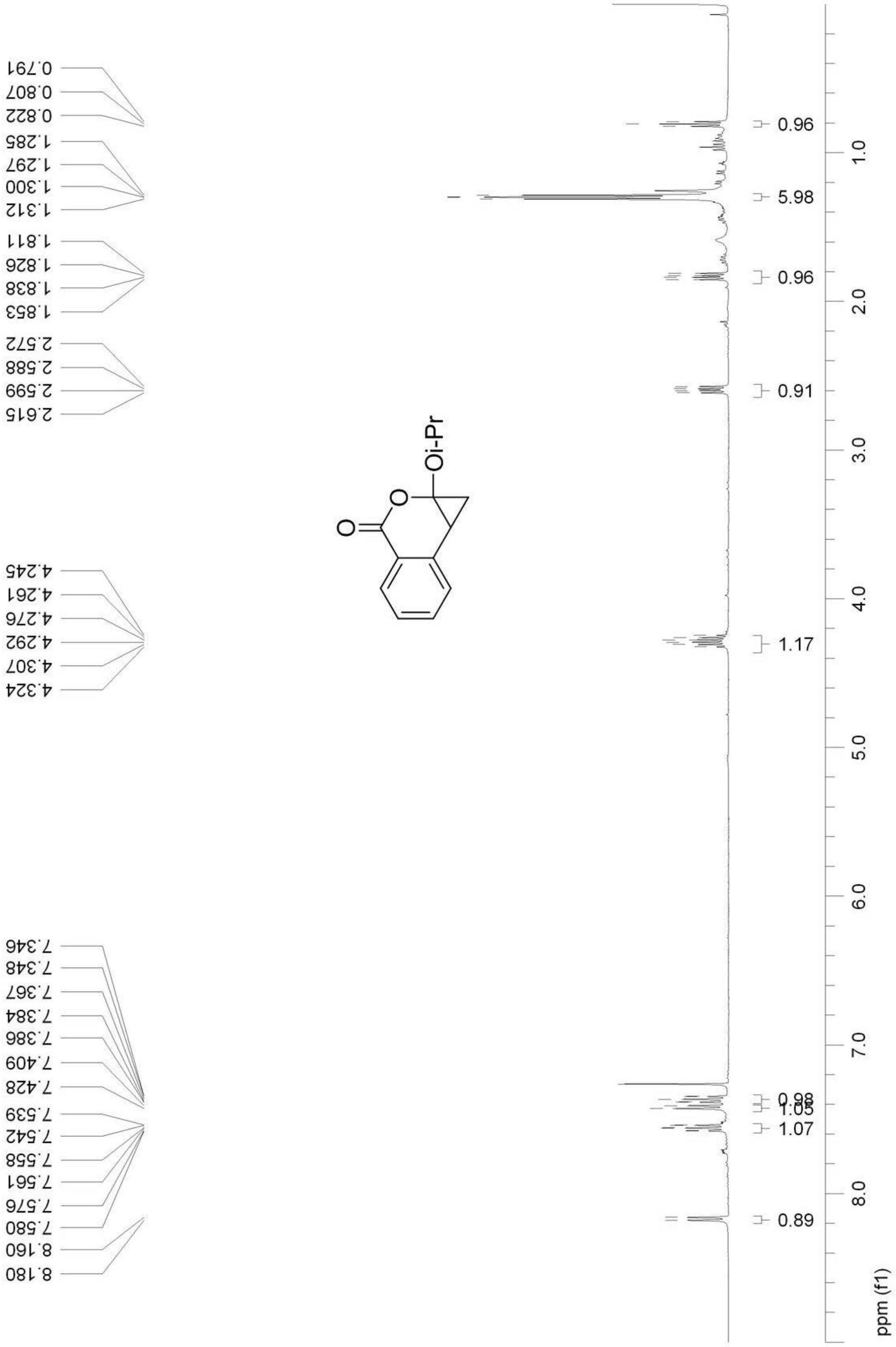

14.325
60.819
123.163
127.970
129.899
132.177
133.773
133.935
136.606
166.234
CDO
$CO_2Et$
D
0
50
100
150
ppm (f1)

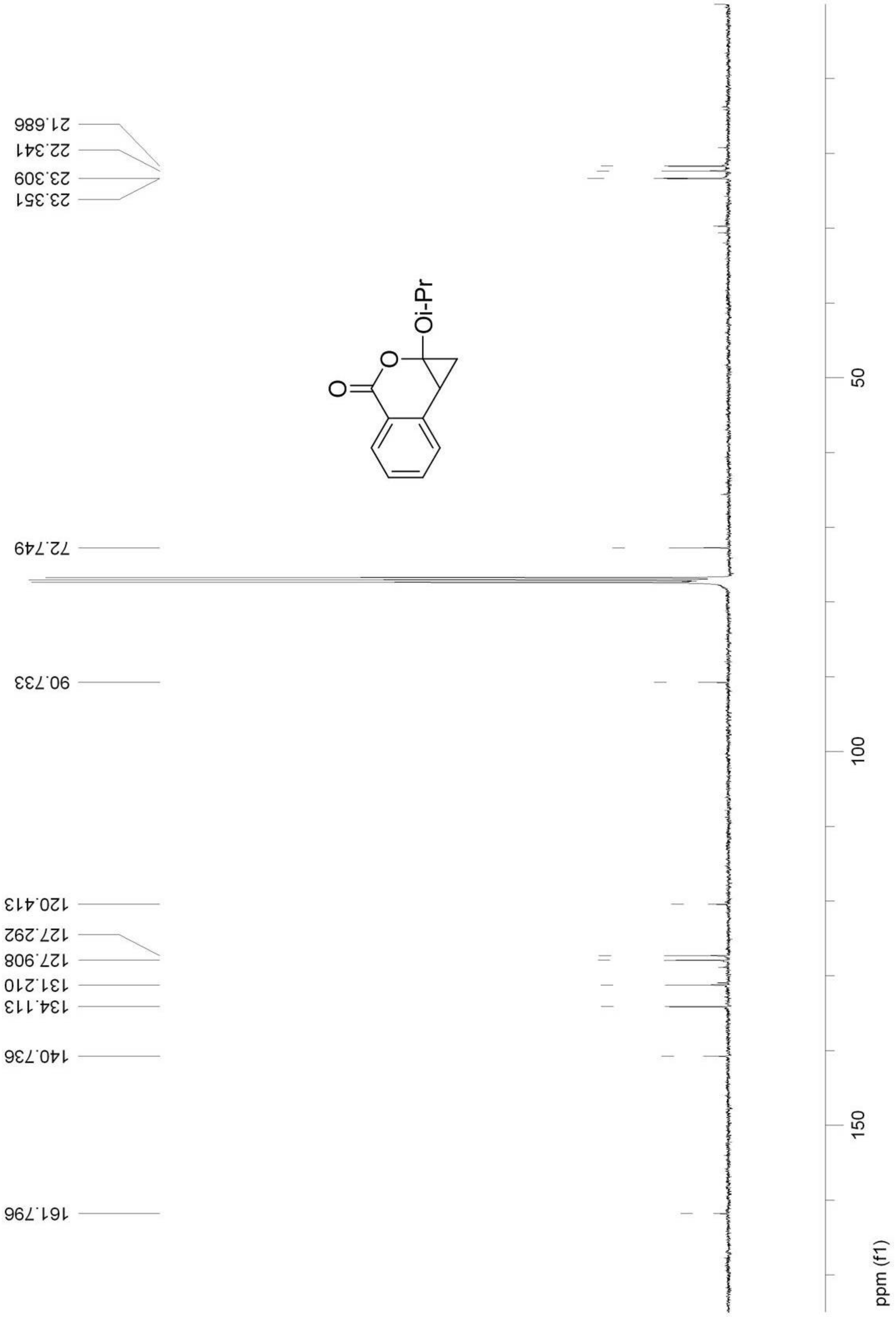

0.800
0.815
0.831
1.274
1.292
1.309
1.807
1.823
1.834
1.850
2.581
2.597
2.608
2.624
3.881
3.885
3.899
3.903
3.916
3.921
3.934
3.939
7.344
7.347
7.363
7.413
7.432
7.540
7.543
7.559
7.562
7.577
7.580
8.153
8.173
O
O
OEt
1.14
3.47
1.08
1.00
1.97
0.97
1.14
1.16
0.96
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

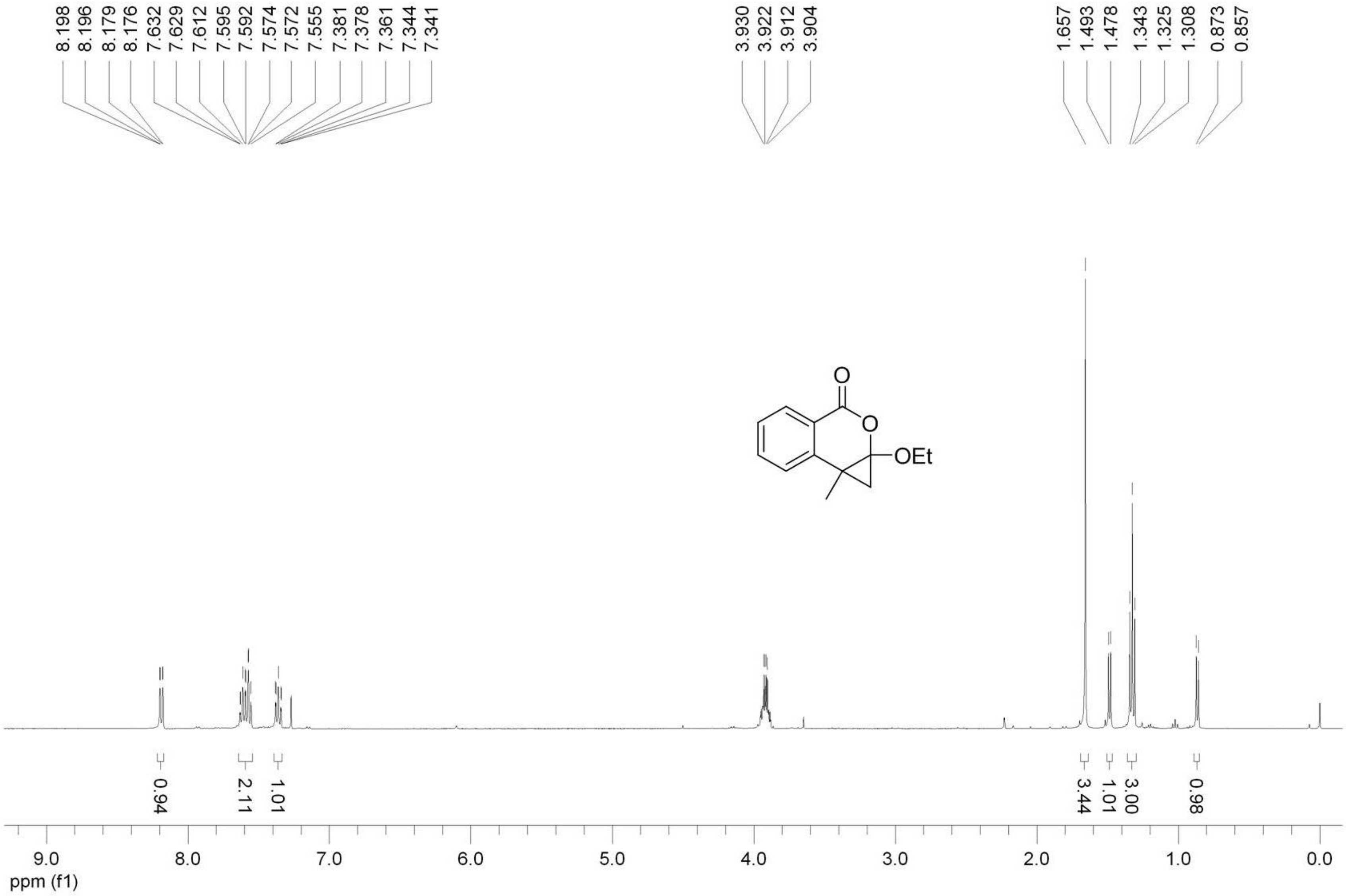

15.138
21.390
22.374
64.461
91.390
120.412
127.331
127.898
131.191
134.168
140.655
161.822
O
O
OEt
50
100
150
ppm (f1)

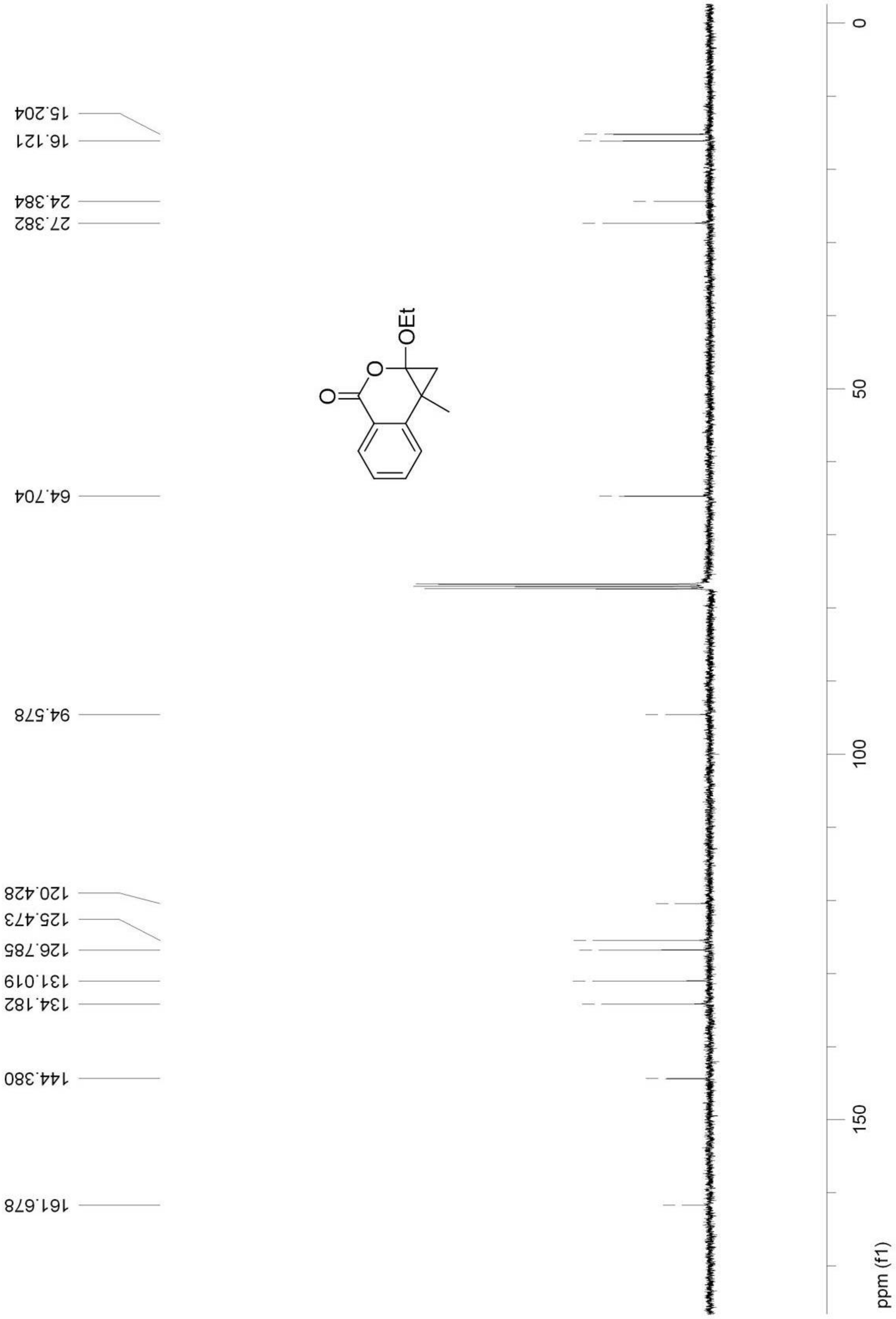

0.810
0.826
0.841
1.807
1.822
1.834
1.850
2.589
2.604
2.616
2.631
3.616
7.356
7.374
7.392
7.394
7.429
7.448
7.553
7.555
7.571
7.574
7.590
7.593
8.153
8.173
OMe
O
O
1.03
0.96
0.93
2.65
1.16
1.00
1.30
0.91
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

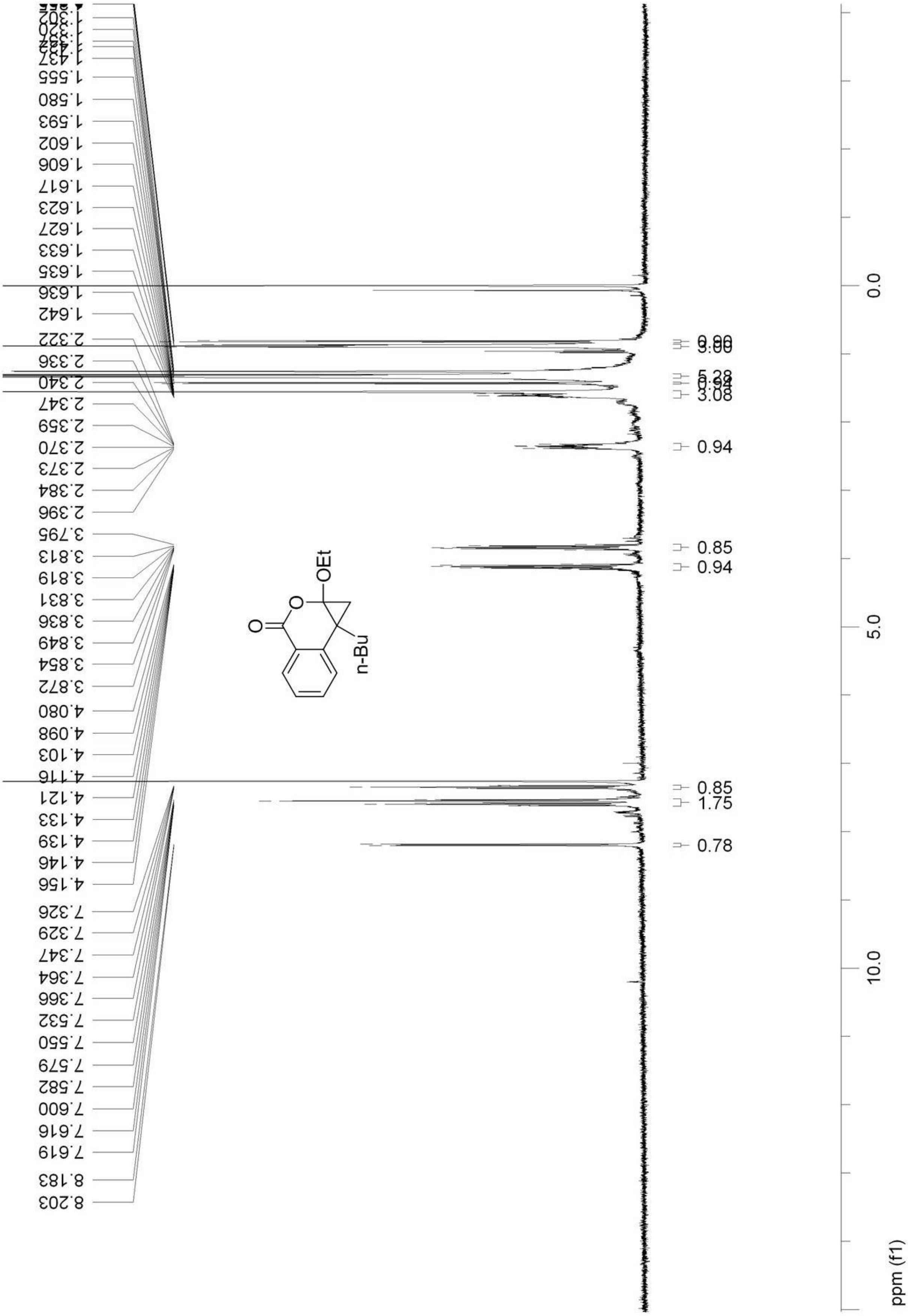

21.225
22.304
55.734
92.274
120.334
127.401
127.938
131.198
134.255
140.560
161.828
OMe
O
O
50
100
150
ppm (f1)


0.791
0.807
0.822
1.285
1.297
1.300
1.312
1.811
1.826
1.838
1.853
2.572
2.588
2.599
2.615
4.245
4.261
4.276
4.292
4.307
4.324
7.346
7.348
7.367
7.384
7.386
7.409
7.428
7.539
7.542
7.558
7.561
7.576
7.580
8.160
8.180
Oi-Pr
O
O
0.96
5.98
0.96
0.91
1.17
0.98
1.05
1.07
0.89
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)


21.686
22.341
23.309
23.351
72.749
90.733
120.413
127.292
127.908
131.210
134.113
140.736
161.796
O
O
Oi-Pr
50
100
150
ppm (f1)


8.198
8.196
8.179
8.176
7.632
7.629
7.612
7.595
7.592
7.574
7.572
7.555
7.381
7.378
7.361
7.344
7.341
3.930
3.922
3.912
3.904
1.657
1.493
1.478
1.343
1.325
1.308
0.873
0.857
O
O
OEt
0.94
2.11
1.01
3.44
1.01
3.00
0.98
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)


15.204
16.121
24.384
27.382
64.704
94.578
120.428
125.473
126.785
131.019
134.182
144.380
161.678
O
O
OEt
0
50
100
150
ppm (f1)


1.302
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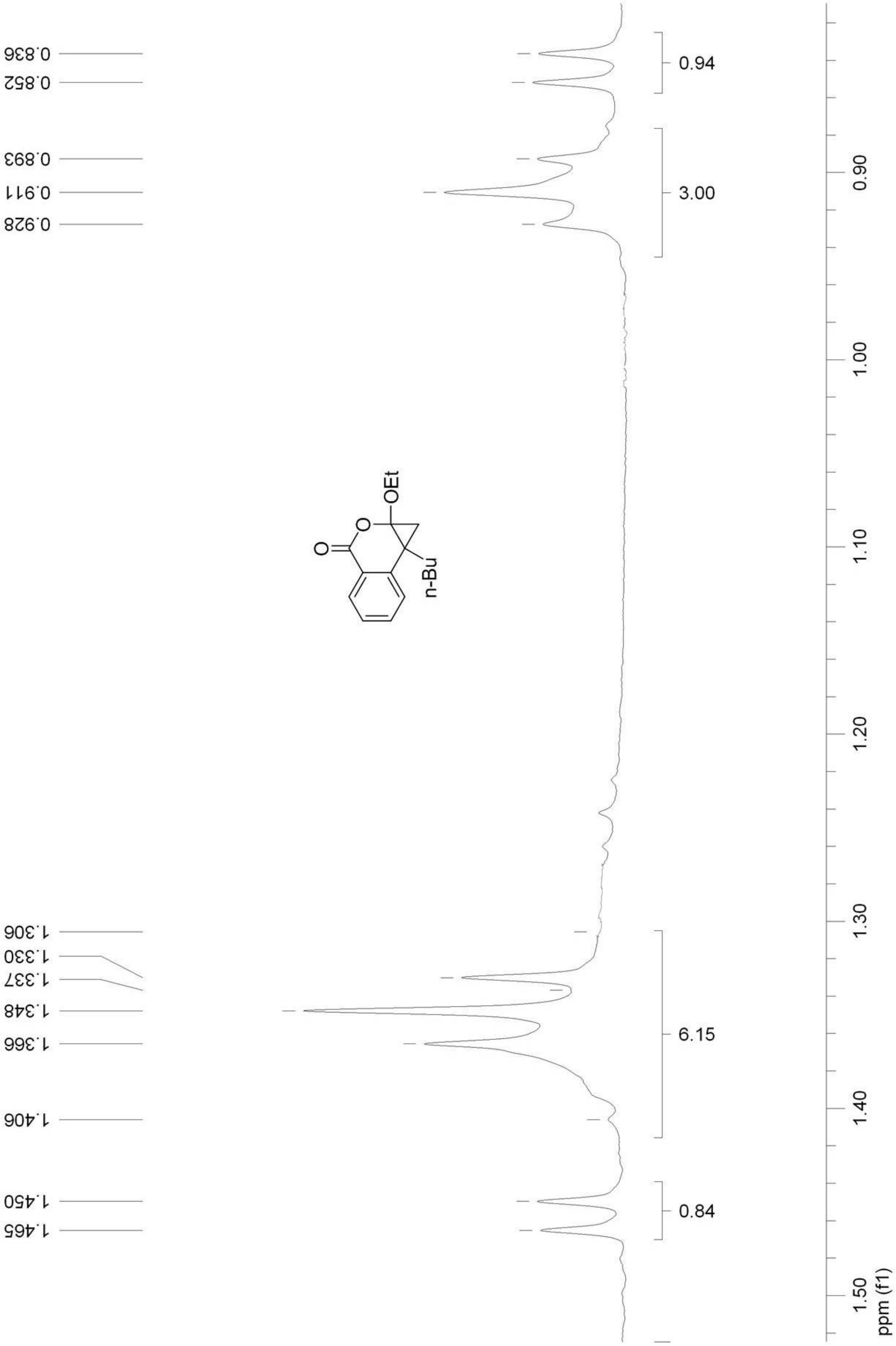
1.437
1.555
1.580
1.593
1.602
1.606
1.617
1.623
1.627
1.633
1.635
1.636
1.642
2.322
2.336
2.340
2.347
2.359
2.370
2.373
2.384
2.396
3.795
3.813
3.819
3.831
3.836
3.849
3.854
3.872
4.080
4.098
4.103
4.116
4.121
4.133
4.139
4.146
4.156
7.326
7.329
7.347
7.364
7.366
7.532
7.550
7.579
7.582
7.600
7.616
7.619
8.183
8.203
0.90
3.00
5.28
0.94
3.08
0.94
0.85
0.94
0.85
1.75
0.78
0.0
5.0
10.0
ppm (f1)
O
O
OEt
n-Bu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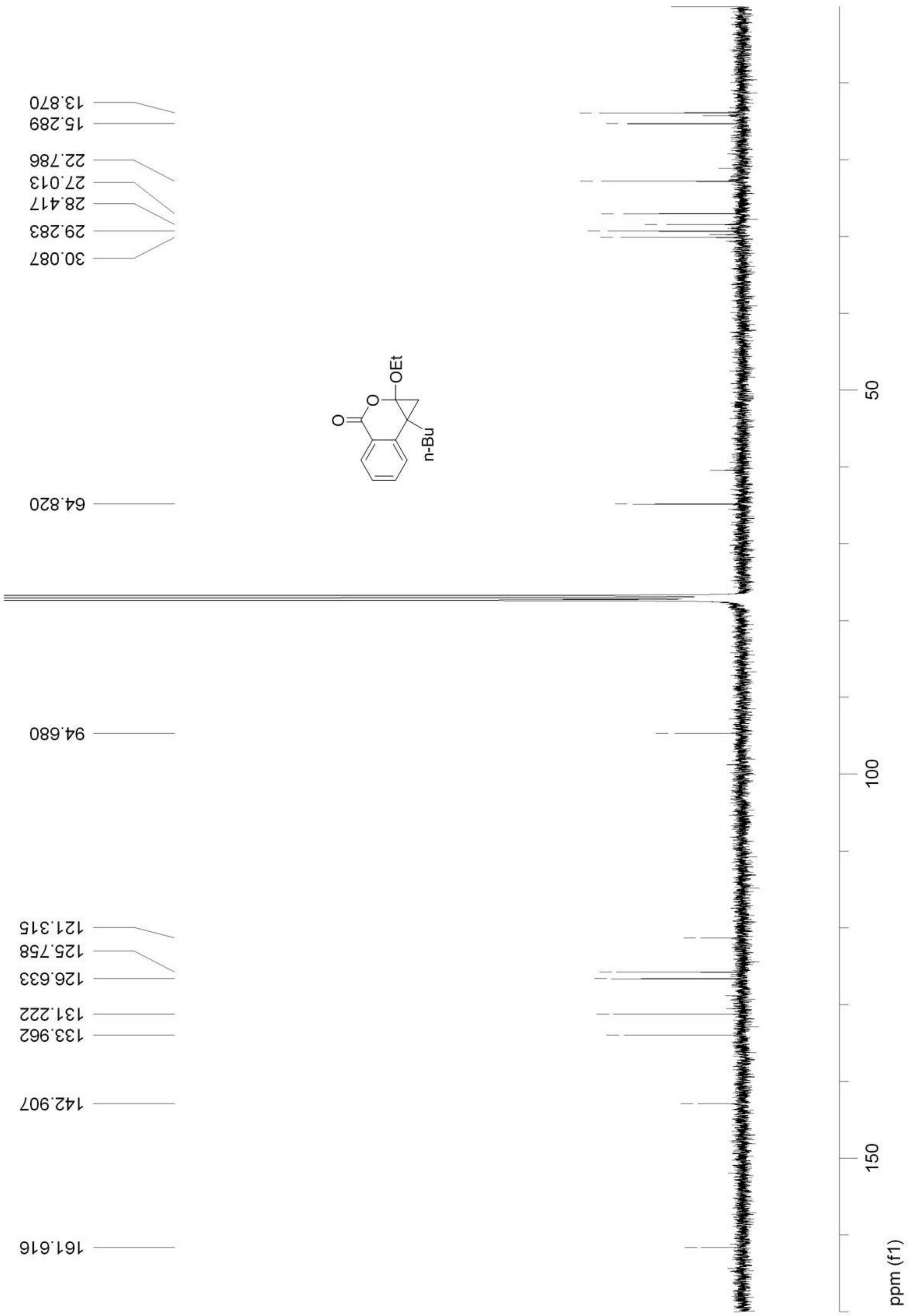
0.852
0.893
0.911
0.928
1.306
1.330
1.337
1.348
1.366
1.406
1.450
1.465
0.94
3.00
6.15
0.84
O
O
OEt
n-Bu
0.90
1.00
1.10
1.20
1.30
1.40
1.50
ppm (f1)


13.870
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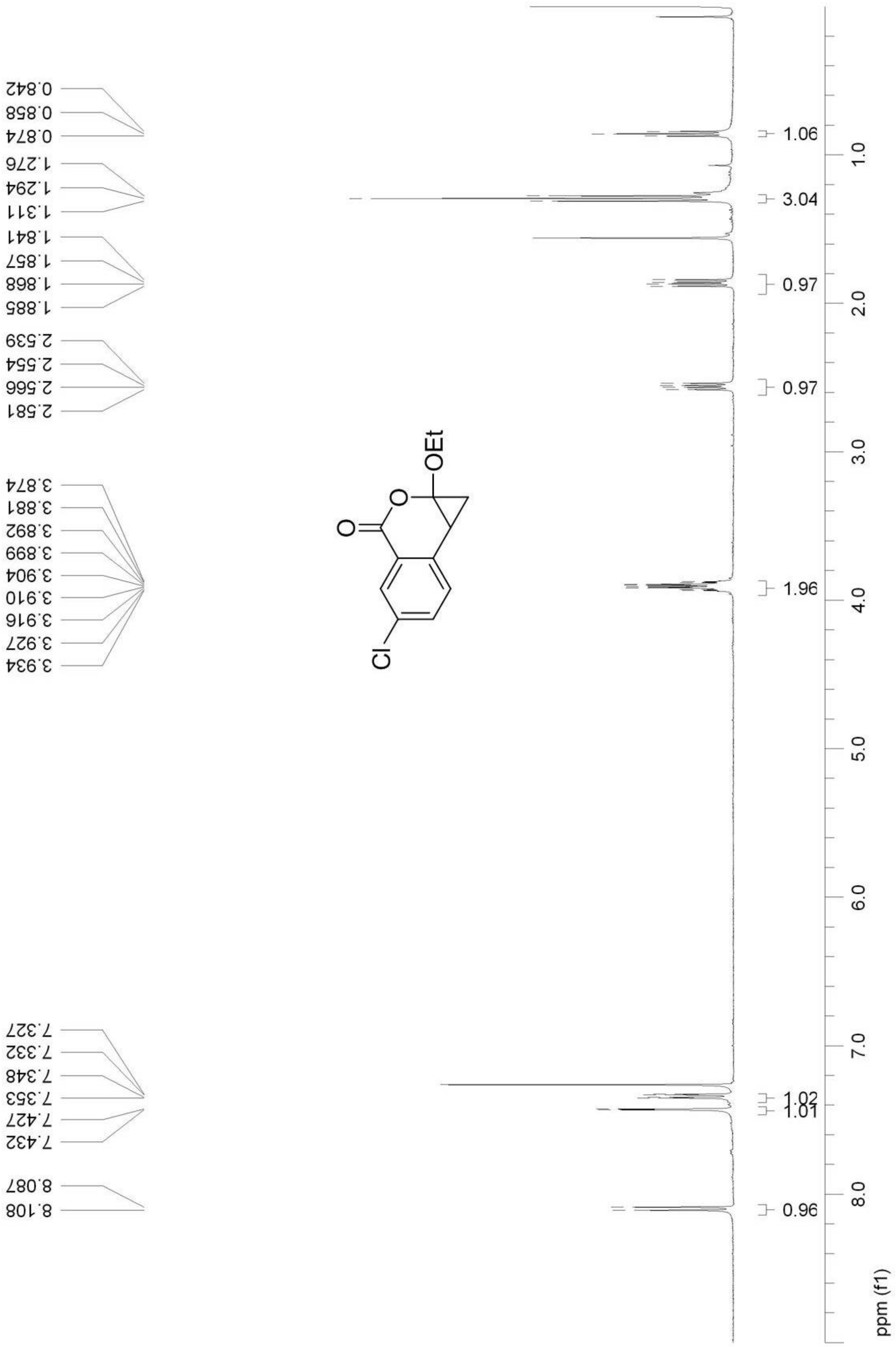
22.786
27.013
28.417
29.283
30.087
64.820
94.680
121.315
125.758
126.633
131.222
133.962
142.907
161.616
O
O
OEt
n-Bu
50
100
150
ppm (f1)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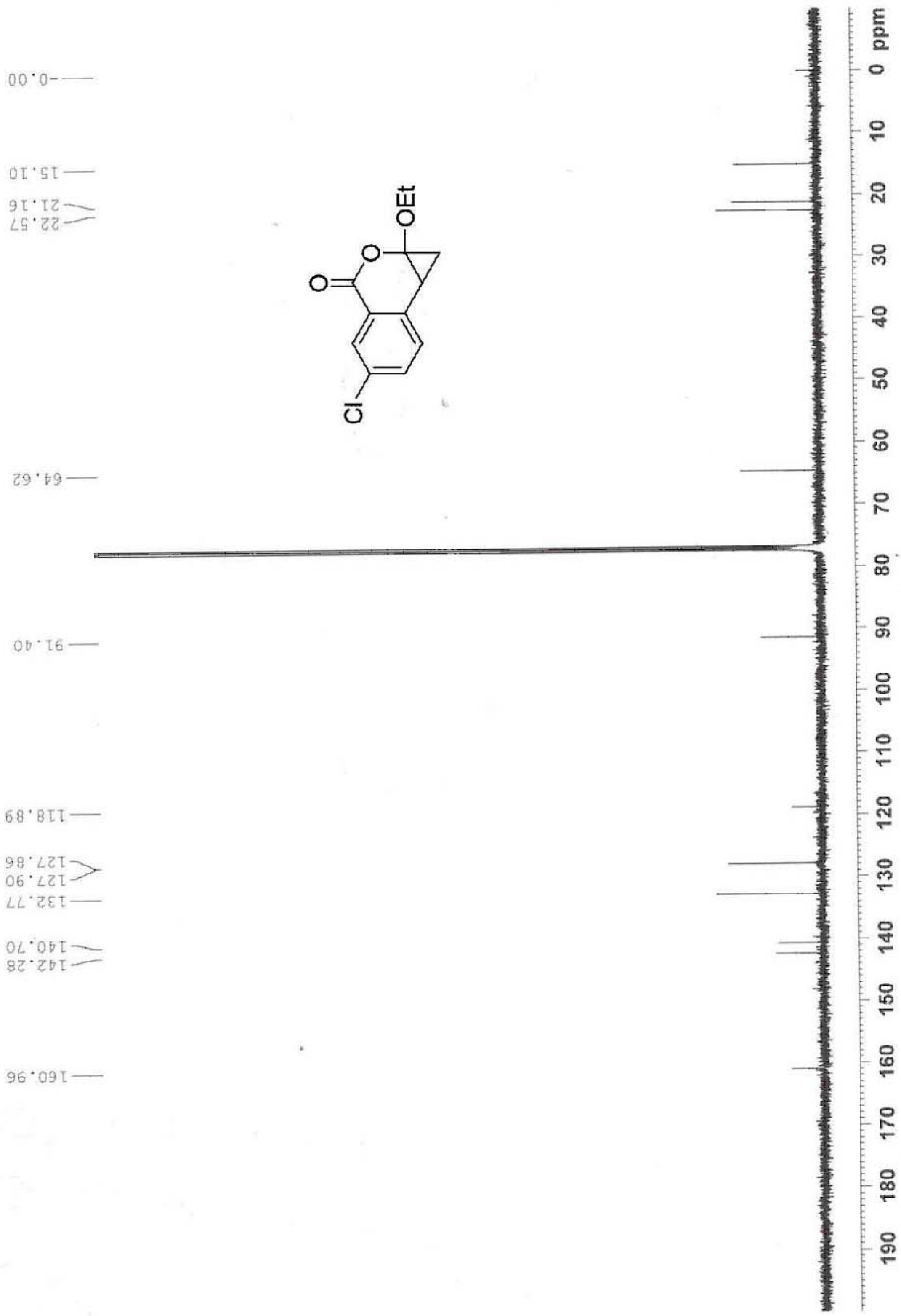
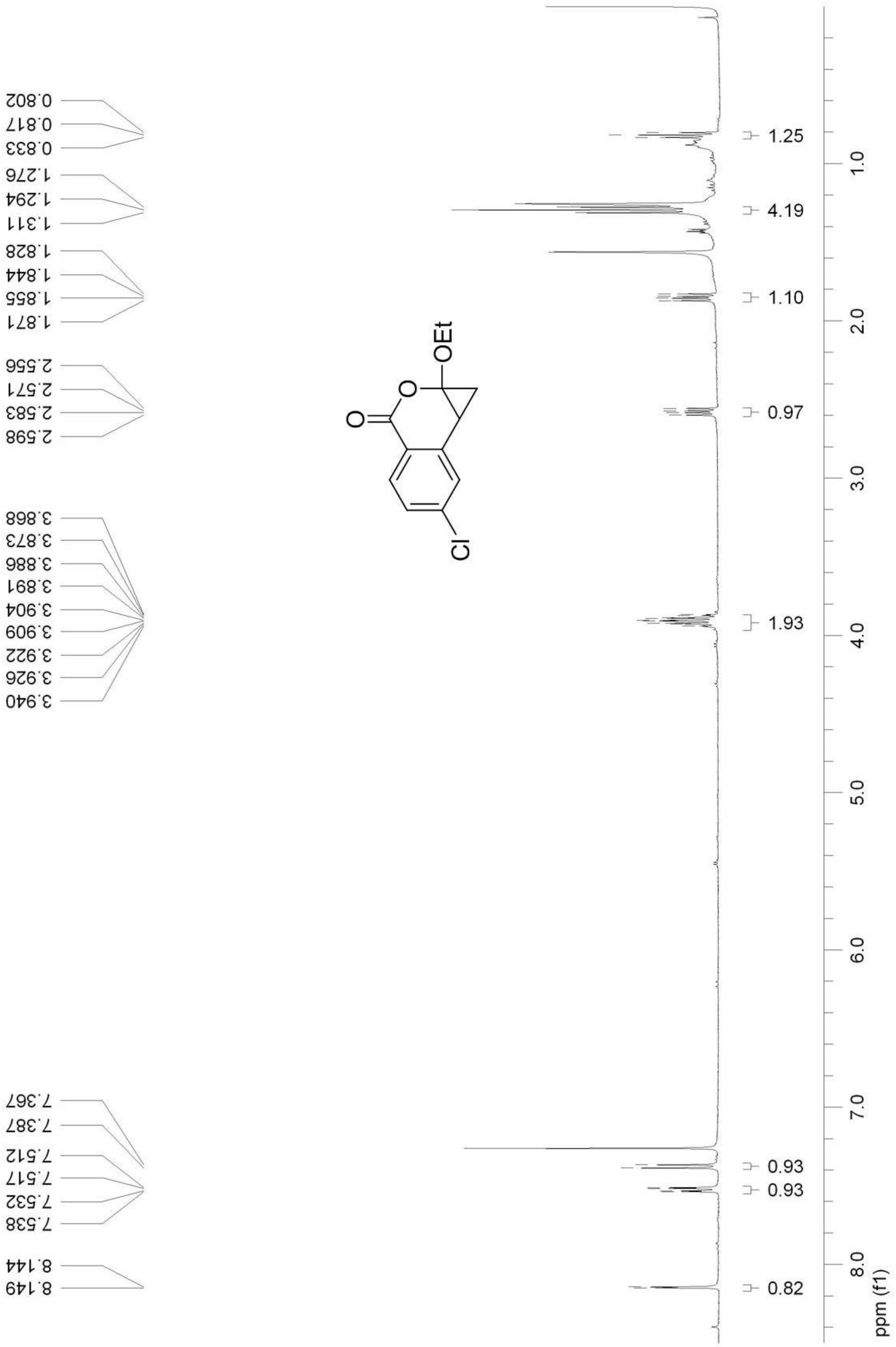
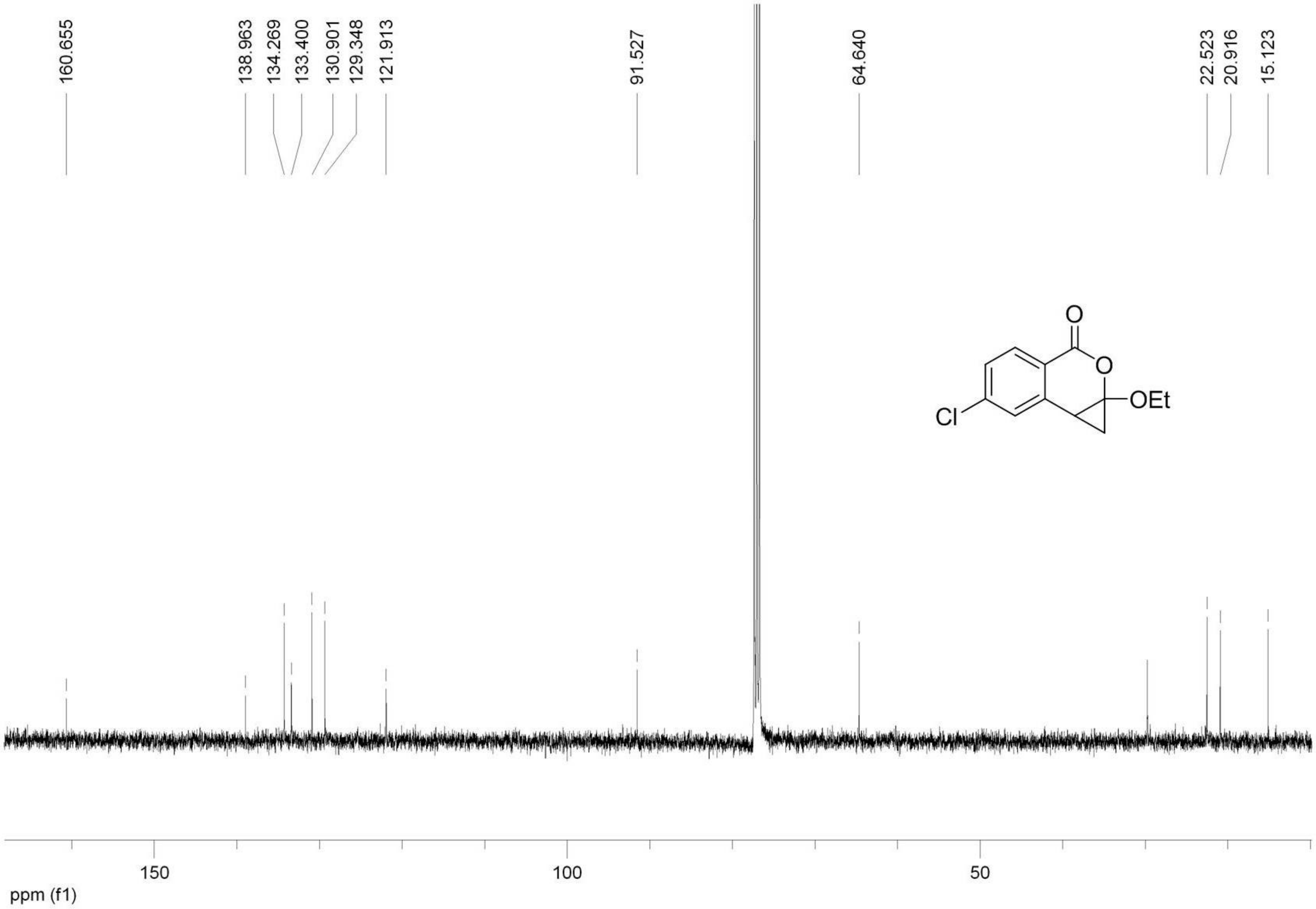
0.858
0.874
1.276
1.294
1.311
1.841
1.857
1.868
1.885
2.539
2.554
2.566
2.581
3.874
3.881
3.892
3.899
3.904
3.910
3.916
3.927
3.934
7.327
7.332
7.348
7.353
7.427
7.432
8.087
8.108
1.06
3.04
0.97
0.97
1.96
1.02
1.01
0.96
OEt
O
O
Cl
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)


-0.00
15.10
21.16
22.57
64.62
91.40
118.89
127.86
127.90
132.77
140.70
142.28
160.96
O
O
OEt
Cl
0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
ppm


0.802
0.817
0.833
1.276
1.294
1.311
1.828
1.844
1.855
1.871
2.556
2.571
2.583
2.598
3.868
3.873
3.886
3.891
3.904
3.909
3.922
3.926
3.940
7.367
7.387
7.512
7.517
7.532
7.538
8.144
8.149
O
O
OEt
Cl
1.25
4.19
1.10
0.97
1.93
0.93
0.93
0.82
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)


160.655
138.963
134.269
133.400
130.901
129.348
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91.527
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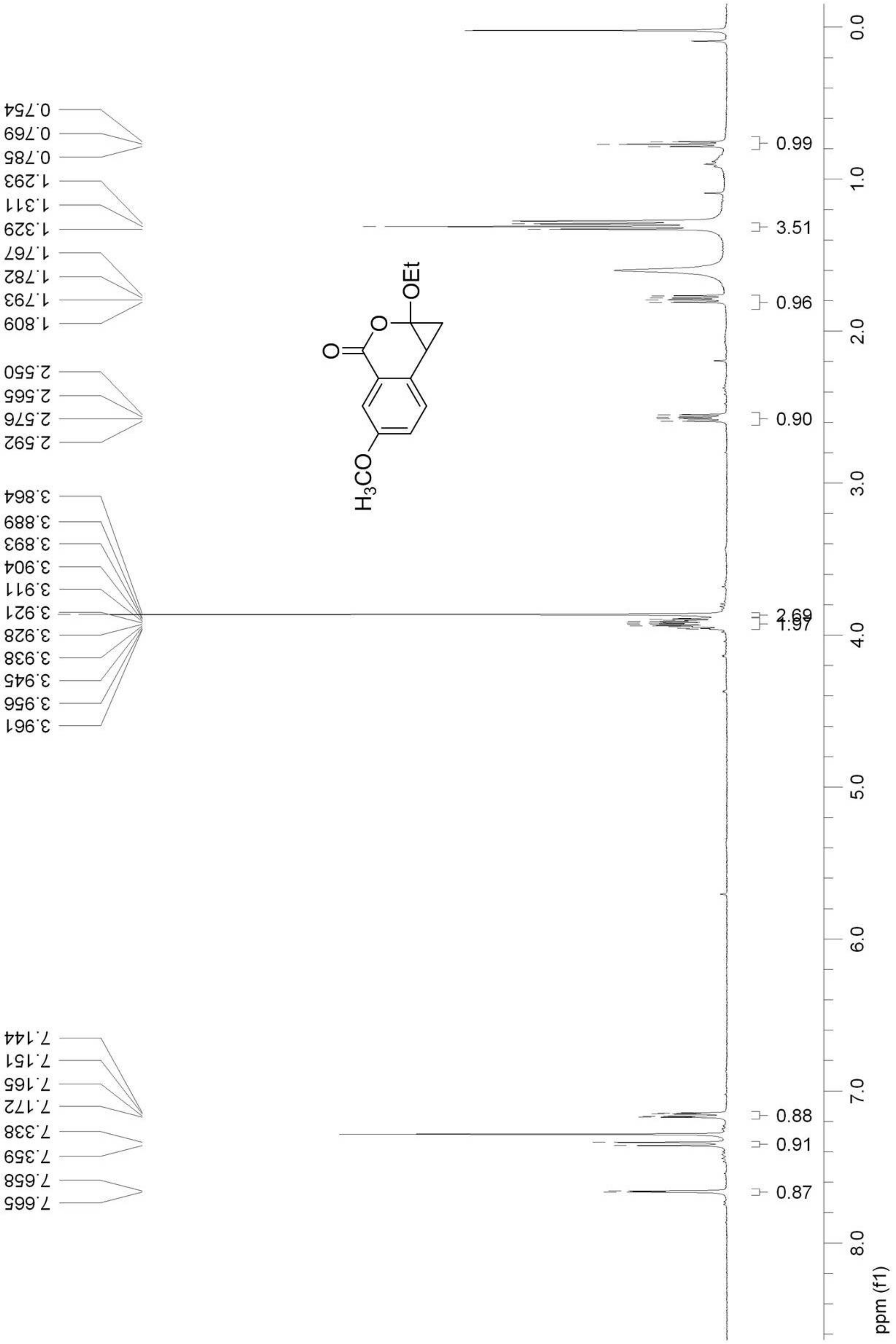
20.916
15.123
O
O
OEt
Cl
150
100
50
ppm (f1)


0.754
0.769
0.785
1.293
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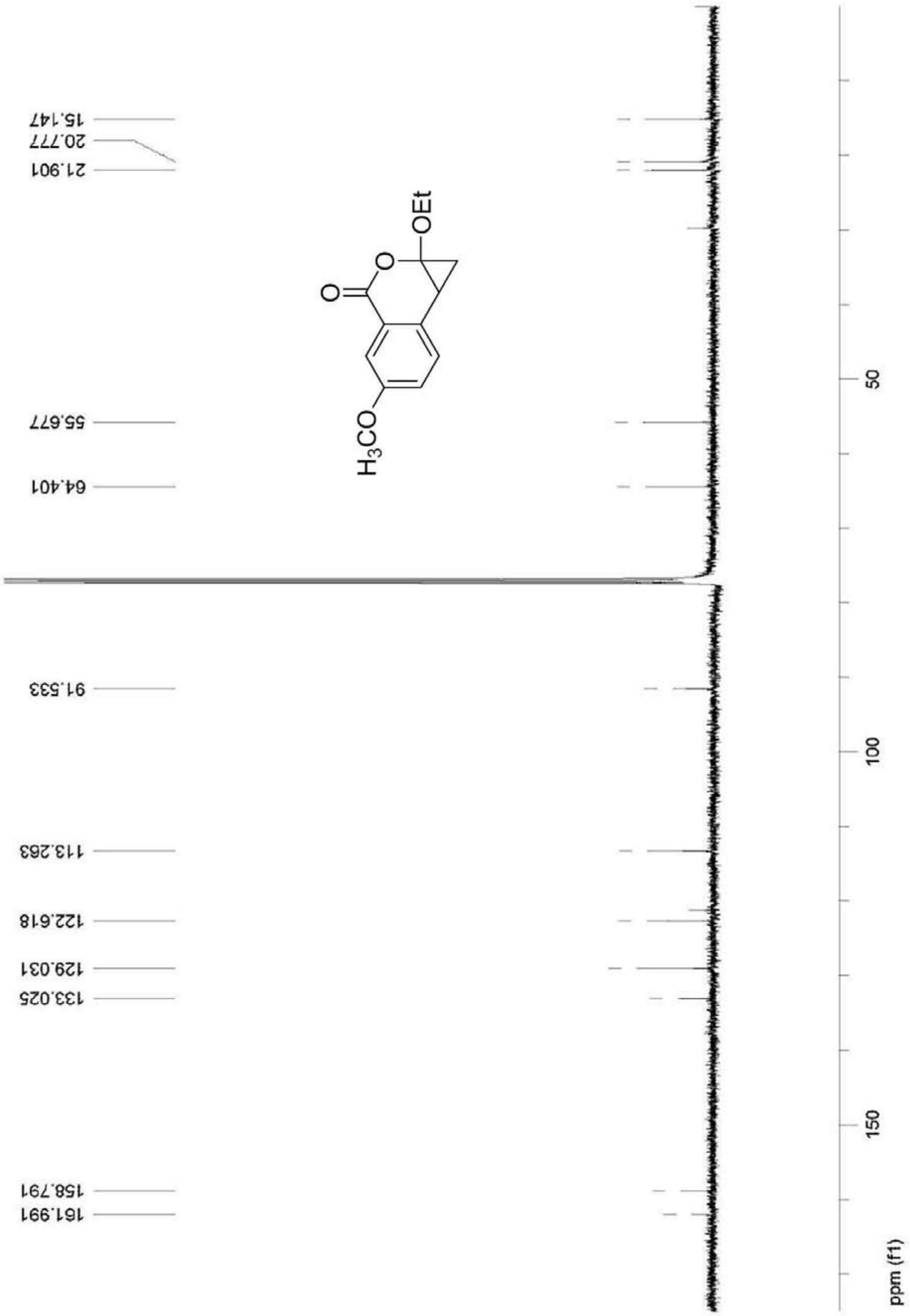
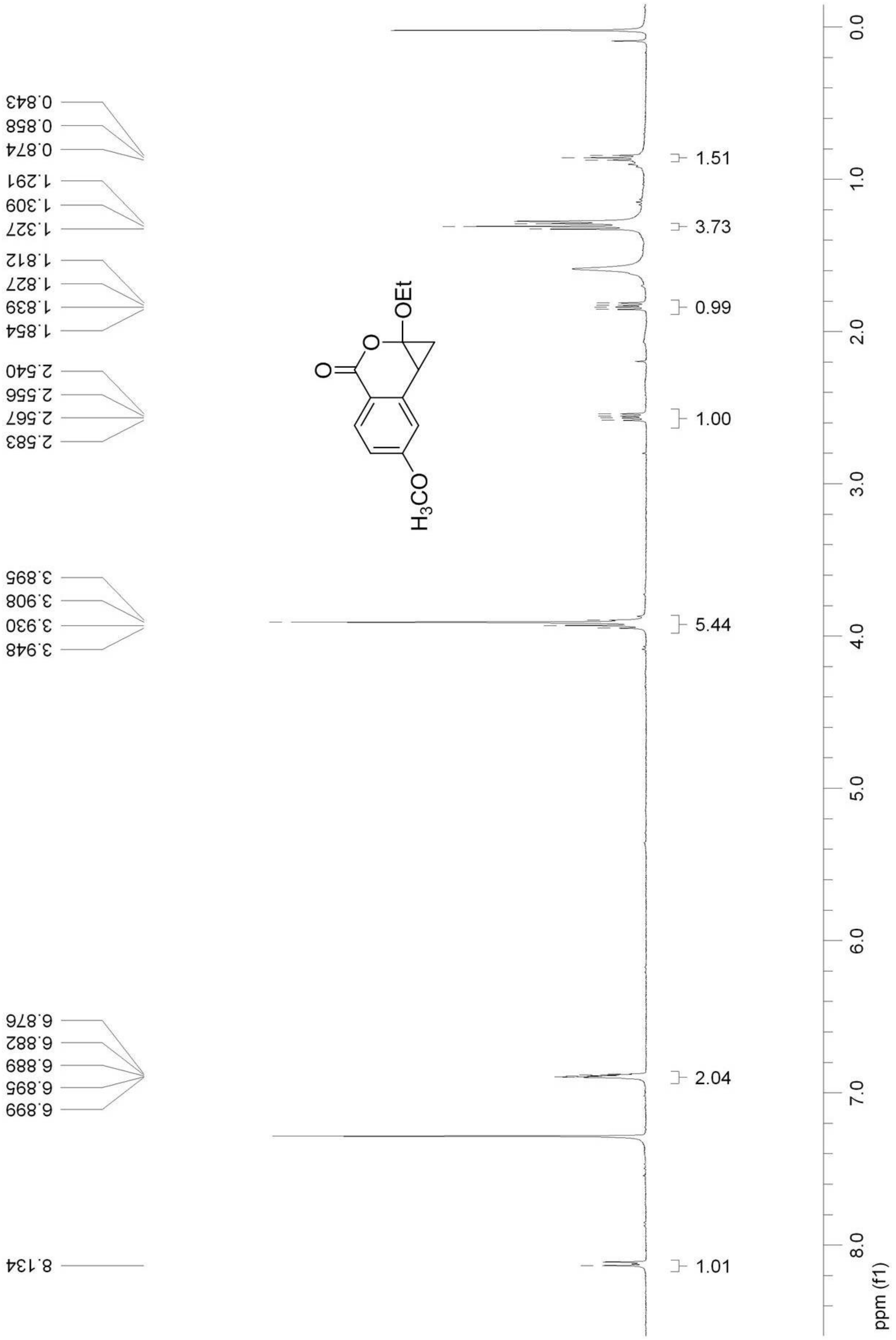
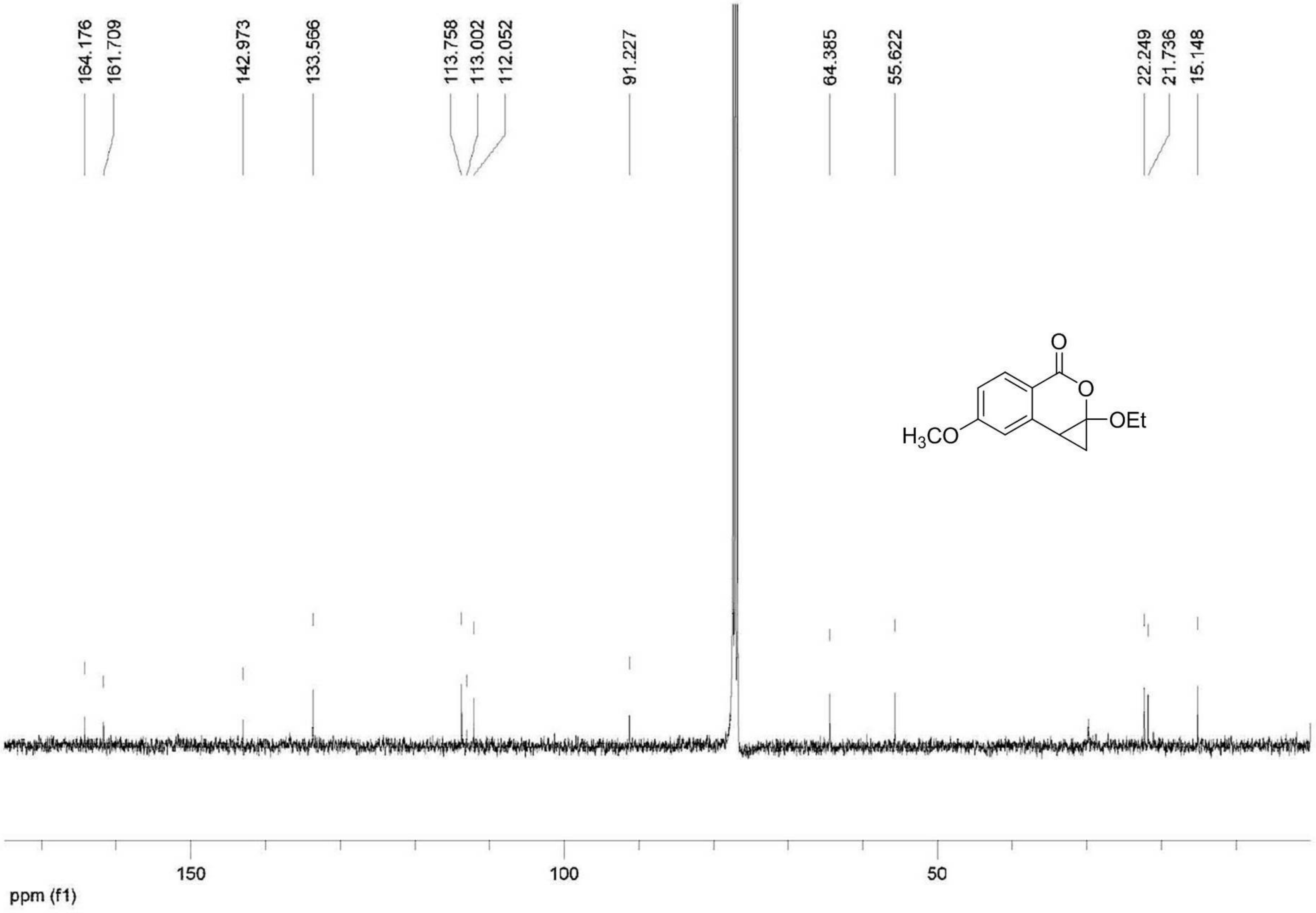
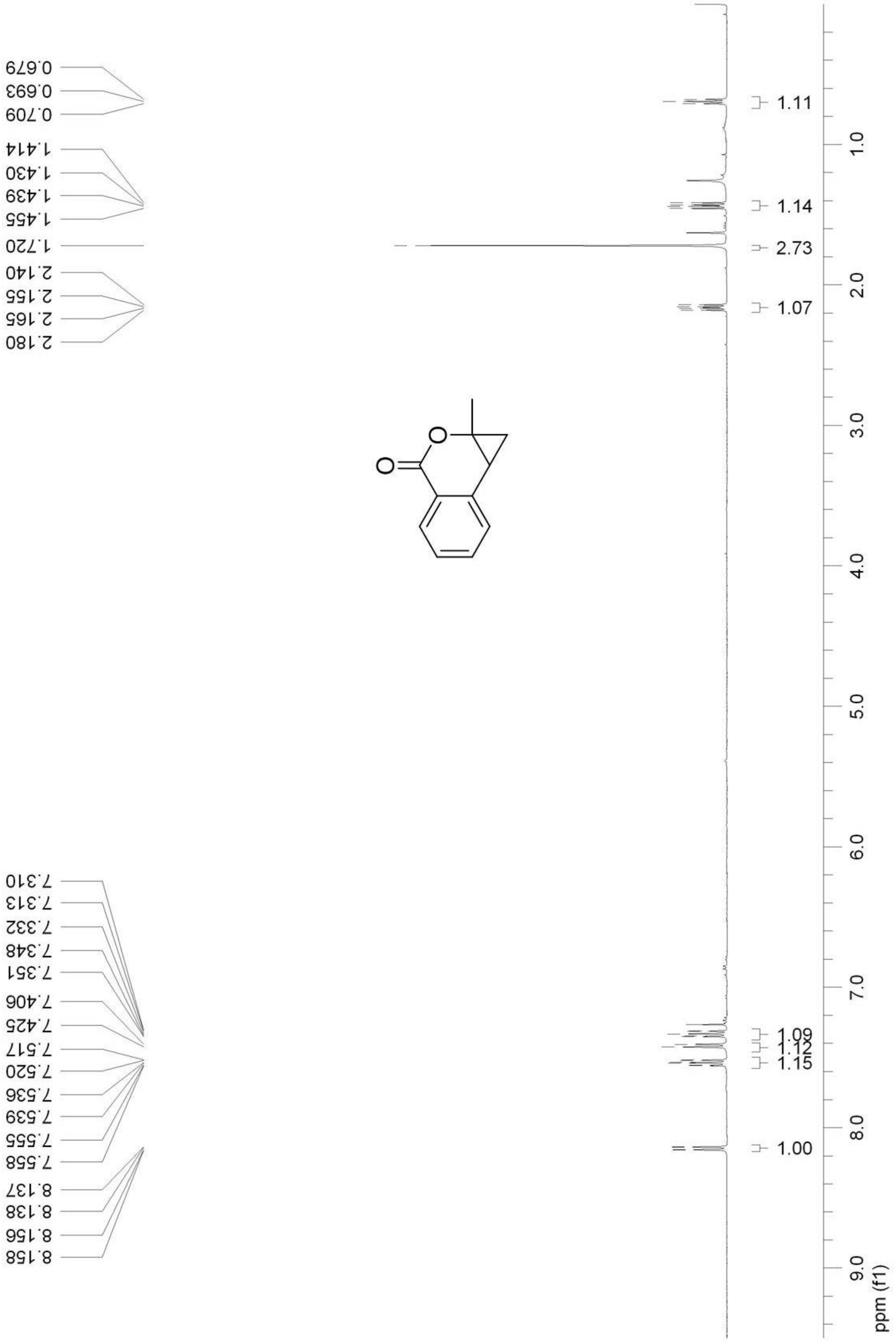
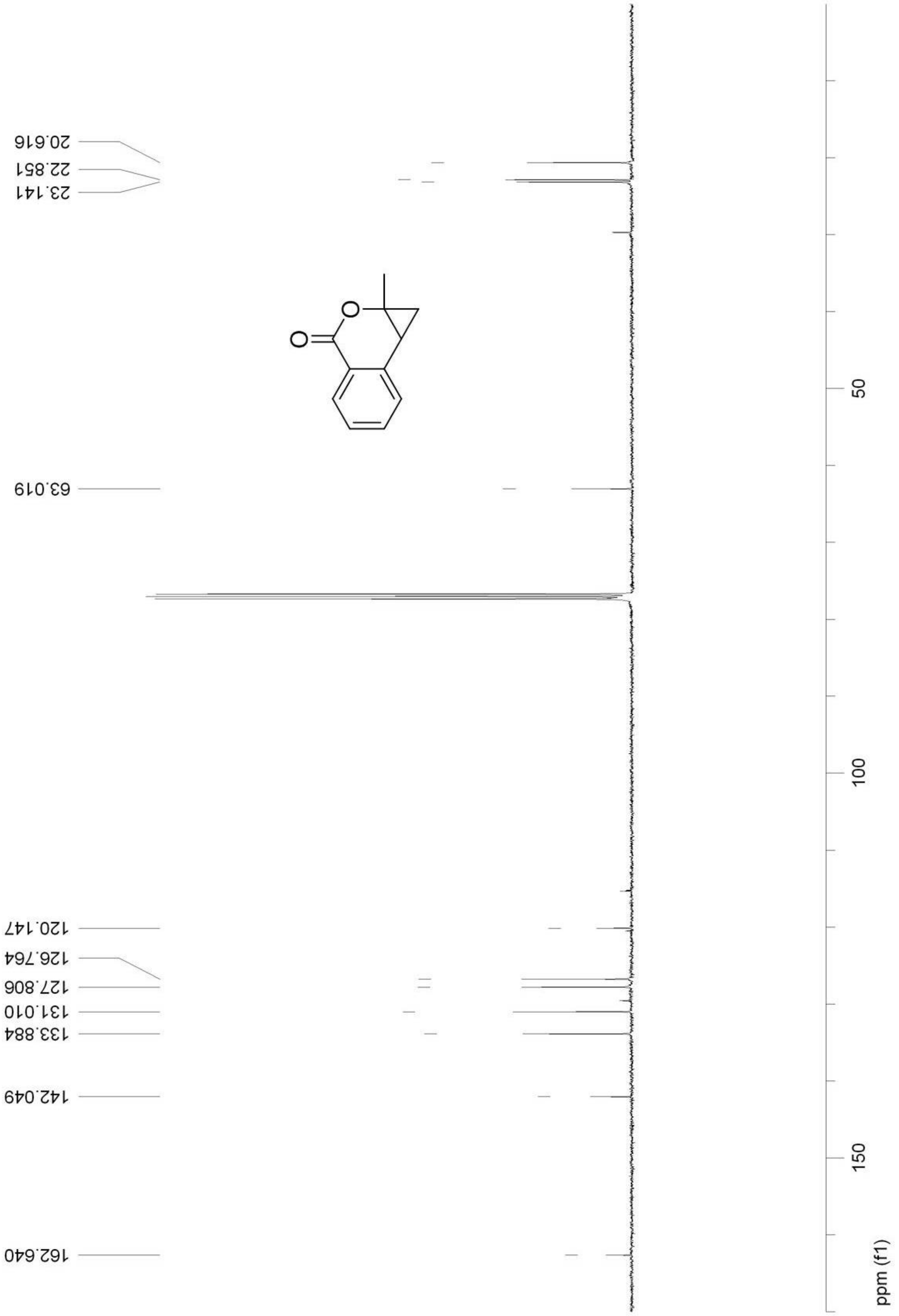
1.329
1.767
1.782
1.793
1.809
2.550
2.565
2.576
2.592
3.864
3.889
3.893
3.904
3.911
3.921
3.928
3.938
3.945
3.956
3.961
7.144
7.151
7.165
7.172
7.338
7.359
7.658
7.665
OEt
O
O
H3CO
0.99
3.51
0.96
0.90
2.69
1.97
0.88
0.91
0.87
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

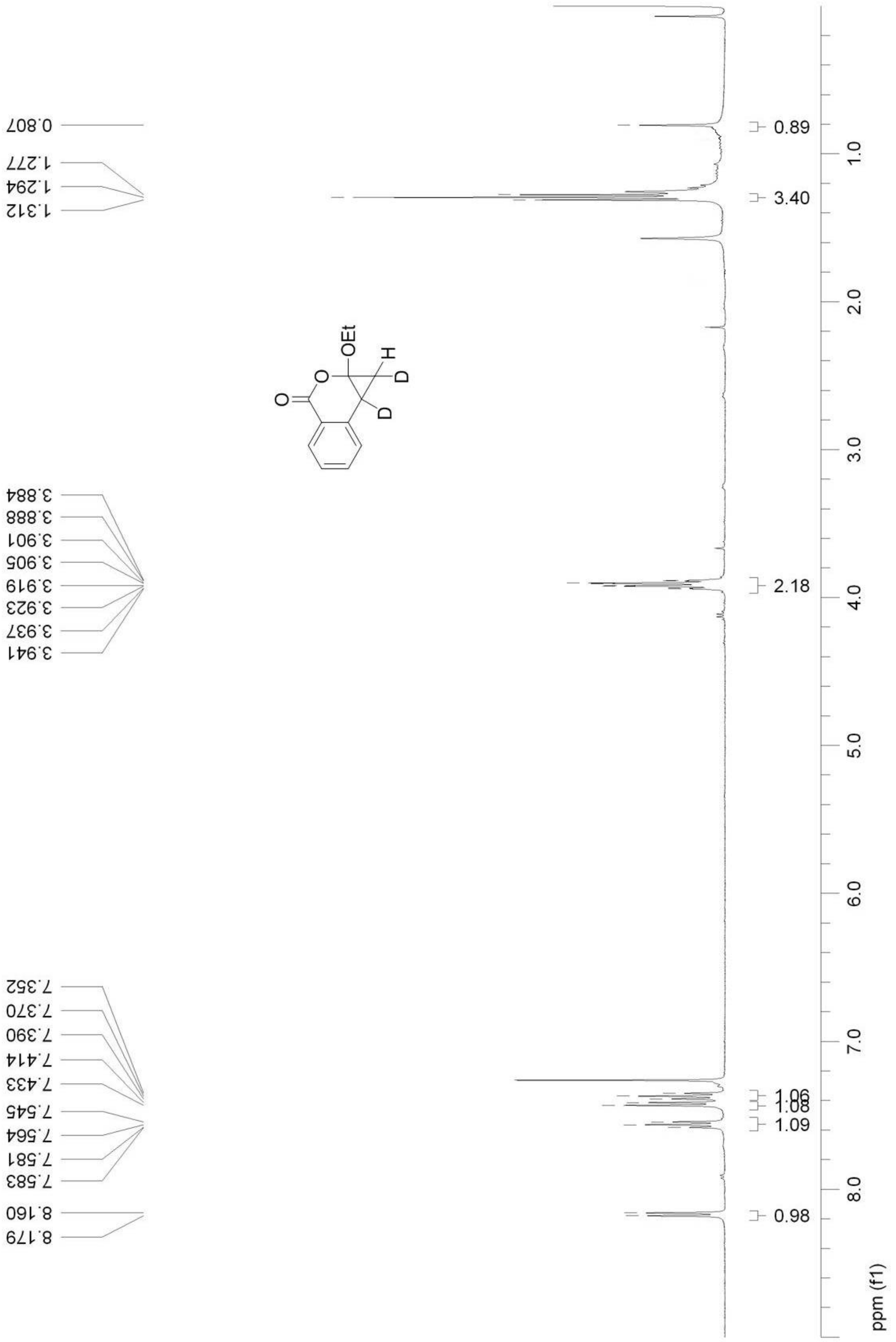

15.147
20.777
21.901
55.677
64.401
91.533
113.263
122.618
129.031
133.025
158.791
161.991
OEt
O
O
$H_3CO$
50
100
150
ppm (f1)

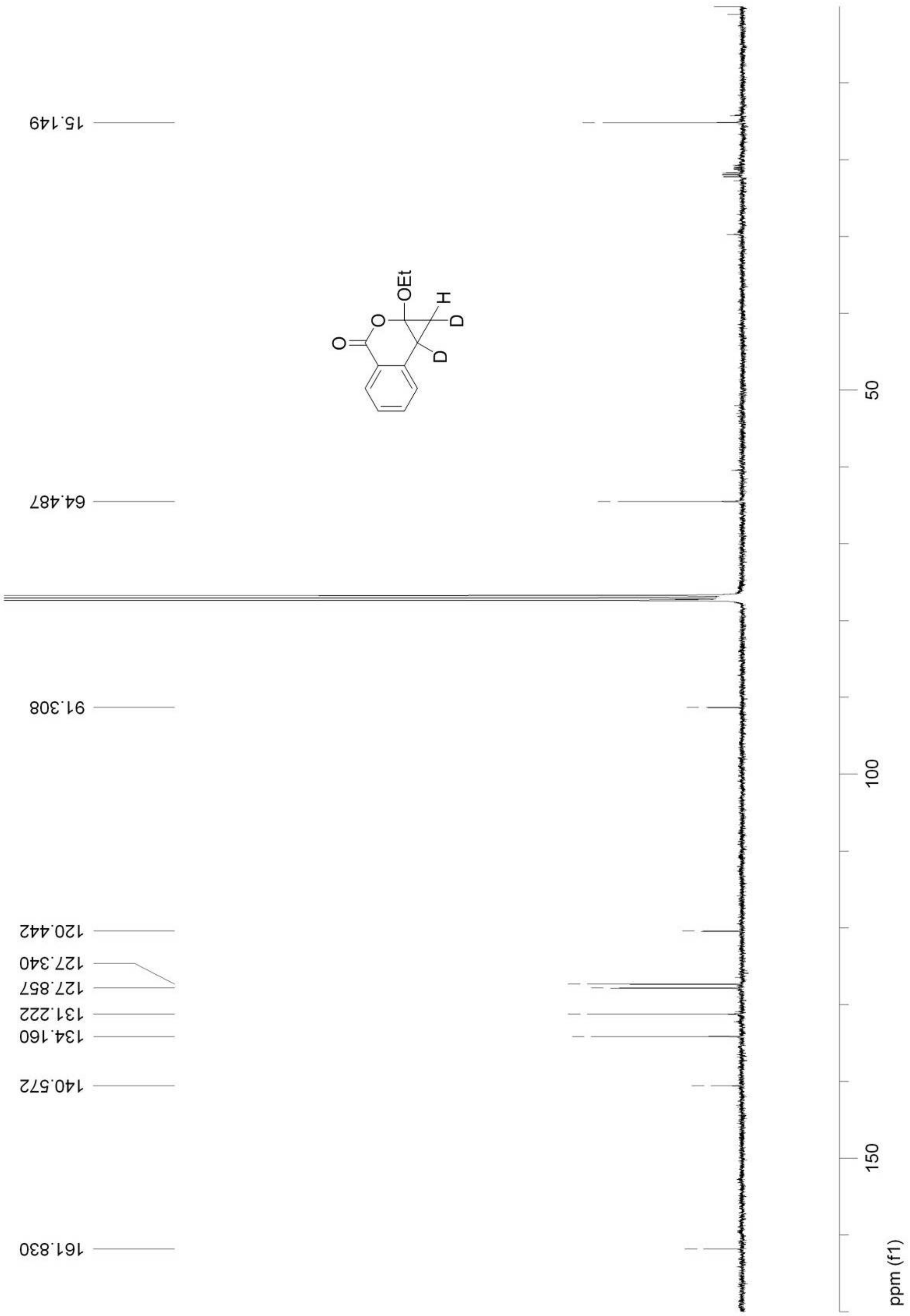

0.843
0.858
0.874
1.291
1.309
1.327
1.812
1.827
1.839
1.854
2.540
2.556
2.567
2.583
3.895
3.908
3.930
3.948
6.876
6.882
6.889
6.895
6.899
8.134
1.51
3.73
0.99
1.00
5.44
2.04
1.01
O
O
OEt
H3CO
0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)


164.176
161.709
142.973
133.566
113.758
113.002
112.052
91.227
64.385
55.622
22.249
21.736
15.148
$H_3CO$
OEt
O
O
150
100
50
ppm (f1)


0.679
0.693
0.709
1.414
1.430
1.439
1.455
1.720
2.140
2.155
2.165
2.180
7.310
7.313
7.332
7.348
7.351
7.406
7.425
7.517
7.520
7.536
7.539
7.555
7.558
8.137
8.138
8.156
8.158
1.11
1.14
2.73
1.07
1.09
1.12
1.15
1.00
O
O
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
ppm (f1)


20.616
22.851
23.141
63.019
120.147
126.764
127.806
131.010
133.884
142.049
162.640
O
O
50
100
150
ppm (f1)


0.807
1.277
1.294
1.312
3.884
3.888
3.901
3.905
3.919
3.923
3.937
3.941
7.352
7.370
7.390
7.414
7.433
7.545
7.564
7.581
7.583
8.160
8.179
O
O
OEt
H
D
D
0.89
3.40
2.18
1.06
1.08
1.09
0.98
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)


15.149
64.487
91.308
120.442
127.340
127.857
131.222
134.160
140.572
161.830
O
O
OEt
H
D
D
50
100
150
ppm (f1)