Supporting Information

Pericylic Reaction of a Zwiterionic Salt of an Enedione-diazoester. A Novel Strategy for the Synthesis of Highly Functionalized Resorcinols

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General. Reactions were performed in oven-dried (140°C) or flame-dried glassware. Dichloromethane (DCM) was passed through a solvent column prior to use and was not distilled. Thin layer chromatography (TLC) was carried out using EM Science silica gel 60 F_{254} plates. The developed chromatogram was analyzed by UV lamp (254 nm) or ethanolate phosphomolybdic acid (PMA). Liquid chromatography was performed using a forced flow (flash chromatography) of the indicated system on silica gel (230-400 mesh). Metal triflate salts were purchased from Aldrich and used as received. *trans*-4-Methoxy-3-buten-2-one (90%) was purchased from Acros or Aldrich and used as received. All TBSO-substituted vinyldiazoesters were prepared by the method described by Davies.[1]

NMR spectra were measured on Bruker AV-400 (^{1}H at 400 MHz, ^{13}C at 100 MHz). High Resolution Mass Spectra (HRMS) were recorded by JEOL Accu TOF-CS (ESI, positive mode). Infrared (IR) spectra were measured on a JESCO FT/IR-4100 instrument.

General Procedure for Mukaiyama-Michael Addition and In-situ Elimination. To an oven-dried 4 dr vial under nitrogen was added zinc triflate (4 mg, 0.01 mmol), followed by *trans*-4-methoxy-3-buten-2-one (**2**) (103 mg, 0.930mmol) and 4 mL of dry DCM. The mixture was stirred at 0°C. Methyl 3-*tert*-butyldimethylsilanyloxy-2-diazobut-3-enoate (**1**) (307 mg, 1.20 mmol) was added via syringe all at once. The yellow solution was stirred vigorously and slowly warmed to room temperature. After 16 hours the crude reaction mixture was concentrated under reduced pressure. At this point substrate **2** was fully

consumed and intermediate methyl 3,7-dioxo-2-diazo-(*E*)-oct-5-enoate(**4**) was produced, as indicated by a ^{1}H NMR spectrum of the reaction mixture. The E-geometry was also established by NMR: a 16 Hz coupling constant of the vinyl protons indicates *trans* geometry of the double bond. (Figure 1)

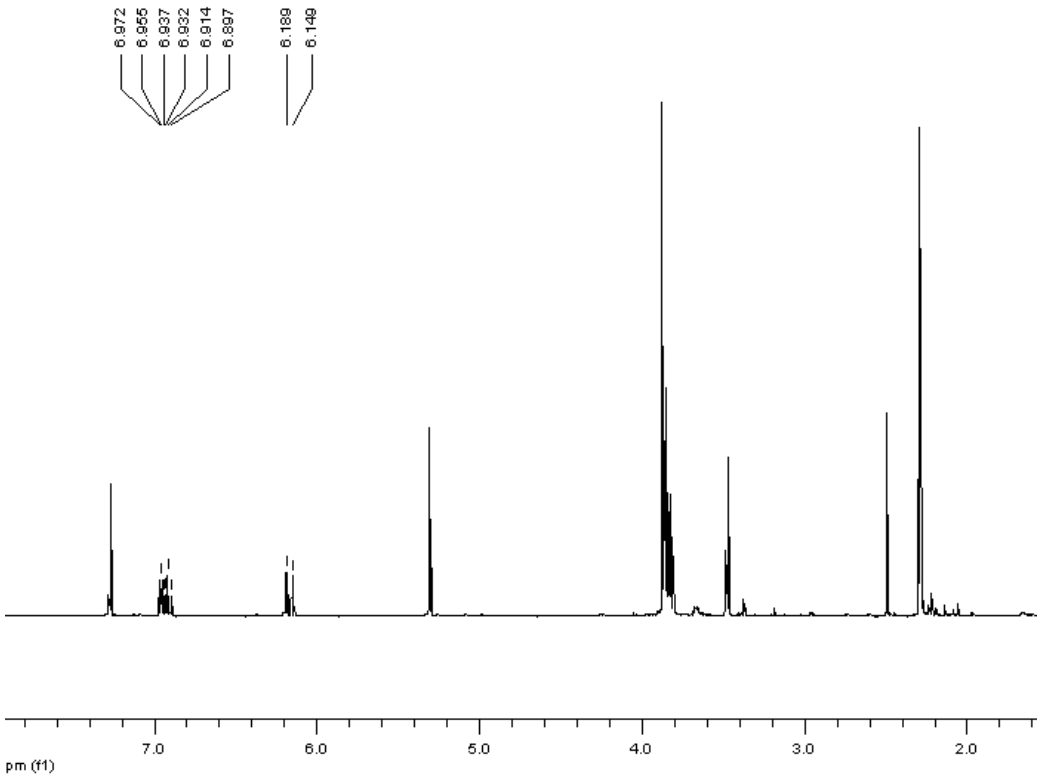
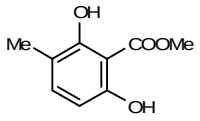


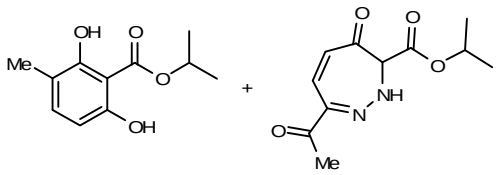
Figure 1



5

Synthesis of methyl 2,6-dihydroxy-3-methylbenzoate(4). To a 4 dr vial was added methyl-3,7-dioxo-2-diazo-(*E*)-oct-5-enoate(**3**) from the Mukaiyama-Michael addition and in-situ elimination step without purification, followed by 2 mL of DCM and1.0 mL 0.10 mol/L NaOH aqueous solution (0.10 mmol). The reaction mixture was stirred vigorously at room temperature. After stirring for two hours, a deep red aqueous phase and a yellow

organic phase was formed. The organic phase was removed by pipette and was flashed through a short silica plug to remove water. The resulting solution was concentrated under reduced pressure to give the crude product as yellow oil. The crude product was purified by silica gel chromatography, eluting with 1:10 EtOAc/hexane to give 141 mg of a pale yellow liquid as product **5** (0.77 mmol, 83% yield). **5:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.06 (br, 1H), 9.30 (br, 1H), 7.19 (d, *J* = 8.0 Hz, 1H), 6.41 (d, *J* = 8.0 Hz, 1H), 4.07 (s, 1H), 2.14 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 158.6, 158.5, 137.4, 116.6, 107.2, 99.5, 52.7, 15.2; IR (neat): 3430, 3129 (br), 2960, 2922, 1674, 1634, 1599 cm^{-1}; HRMS (ESI) for $C_9H_{11}O_4$ $[M+H]^+$ calcd 183.0658; found 183.0666.



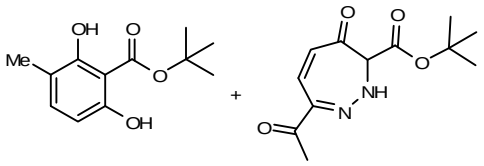
12a 13a

Synthesis of isopropyl 2,6-dihydroxy-3-methylbenzoate(12a) and (1E,5Z)-*iso*-propyl 7-acetyl-3,4-dihydro-4-oxo-2H-1,2-diazepine-3-carboxylate(13a). To an oven-dried 4 dr vial under nitrogen was added zinc triflate (4 mg, 0.01 mmol), followed by *trans*-4-methoxy-3-buten-2-one (**2**) (103 mg, 0.930mmol) and 4 mL of dry DCM. The mixture was stirred at 0^{o}C. Isopropyl 3-*tert*-butyldimethylsilanyloxy-2-diazobut-3-enoate (341 mg, 1.20 mmol), which was prepared according to procedure previously reported by Davies[1], was added via syringe all at once. The yellow solution was stirred vigorously and slowly warmed to room temperature. After 16 hours the crude reaction mixture was concentrated under reduced pressure. At this point substrate **2** was fully consumed and intermediate isopropyl 3,7-dioxo-2-diazo-(*E*)-oct-5-enoate(**11a**) was produced, as indicated by a ^{1}H NMR spectrum of the reaction mixture. **11a** from the Mukaiyama-Michael addition and in-situ elimination step was used without purification and same procedure as synthesis of **5** was employed. The crude product was purified by silica gel chromatography, eluting with 1:10 EtOAc/hexane to give a pale yellow liquid as product **12a** (59% yield). Then the eluent was

switched to 1:4 EtOAc/hexane to elute product **13a** (14% yield) as a reddish yellow oil.

12a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.19 (br, 1H), 9.57 (br, 1H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.40 (d, *J* = 8.0 Hz, 1H), 5.46 (sept, *J* = 4.0 Hz, 1H), 2.14 (s, 3H), 1.48 (d, *J* = 4.0 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 158.7, 158.6, 137.5, 116.4, 107.1, 99.8, 71.3, 22.0, 15.2; IR (neat): 3436, 3139 (br), 2983, 2929, 1666, 1632, 1599 cm^{-1}; HRMS (ESI) for $C_{11}H_{15}O_4$ $[M+H]^+$ calcd 211.0971; found.211.0980.

13a: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14(br, 1H), 7.60 (d, *J* = 12.0 Hz, 1H), 6.74(d, *J* = 12.0 Hz, 1H), 5.27 (sept, *J* = 4.0 Hz, 1H), 4.12 (d, *J* = 4.0 Hz, 1H), 2.45 (s, 3H), 1.38 (d, *J* = 4.0 Hz, 3H), 1.32 (d, *J* = 4.0 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 176.2, 165.0, 140.2, 133.4, 130.0, 71.5, 68.3, 25.0, 21.7, 21.7; IR (neat): 3288(br), 2982, 2939, 1737, 1669 cm^{-1}; HRMS (ESI) for $C_{11}H_{15}N_2O_4$ $[M+H]^+$ calcd 239.1032; found 239.1029.



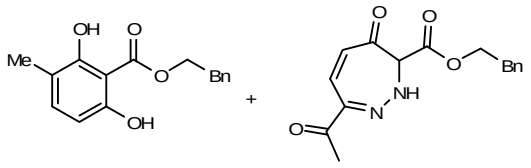
12b 13b

Synthesis of *tert*-butyl 2,6-dihydroxy-3-methylbenzoate(12b) and *tert*-butyl (1*E*,5*Z*)-7-acetyl-3,4-dihydro-4-oxo-2H-1,2-diazepine-3-carboxylate(13b). To an oven-dried 4 dr vial under nitrogen was added zinc triflate (4 mg, 0.01 mmol), followed by *trans*-4-methoxy-3-buten-2-one (**2**) (103 mg, 0.930mmol) and 4 mL of dry DCM. The mixture was stirred at 0^{o}C. *tert*-butyl 3-*tert*-butyldimethylsilanyloxy-2-diazobut-3-enoate (358 mg, 1.20 mmol), which was prepared according to procedure previously reported by Davies[1],was added via syringe all at once. The yellow solution was stirred vigorously and slowly warmed to room temperature. After 16 hours the crude reaction mixture was concentrated under reduced pressure. At this point substrate **2** was fully consumed and intermediate *tert*-butyl 3,7-dioxo-2-diazo-(*E*)-oct-5-enoate(**11b**) was produced, as indicated by a ^{1}H NMR spectrum of the reaction mixture. To a 4 dr vial was added **11b** from the Mukaiyama-Michael addition and in-situ elimination step without purification and 2.0 mL DCM, followed by 1 mL 0.20 mol/L NaOH aqueous solution (0.20 mmol). The reaction

mixture was allowed to react at room temperature and was stirred vigorously. After stirring for 2.0 hours, a deep red aqueous phase and a yellow organic phase was formed. The organic phase was removed by pipette and filtered through a short silica plug to remove small amount of water. The resulted solution was concentrated under reduced pressure to give the crude product as yellow oil. The crude product was purified by silica gel chromatography, eluting with 1:15 EtOAc/hexane to give 94 mg of a pale yellow liquid as product **12b** (0.47 mmol, 52% yield). Then the eluent was switched to 1:4 EtOAc/hexane to elute product **13b** (0.18 mmol, 20% yield) as a yellow oil.

12b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.27 (br, 1H), 9.71 (br, 1H), 7.15 (d, J = 8.0 Hz, 1H), 6.38 (d, J = 8.0 Hz, 1H), 2.13 (s, 1H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 158.7, 158.6, 137.1, 116.3, 107.1, 100.6, 86.5, 28.4, 15.2; IR (neat): 3395, 3114 (br), 2927, 1665, 1633, 1600 cm^{-1}; HRMS (ESI) for $C_{12}H_{17}O_4$ $[M+H]^+$ calcd 225.1128; found 225.1138.

13b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (br, 1H), 7.59 (d, J = 12.0 Hz, 1H), 6.72 (d, J = 12.0 Hz, 1H), 4.02 (d, J = 4.0 Hz,1H), 2.45 (s, 3H), 1.56 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.5, 176.4, 164.5, 140.2, 133.4, 130.0, 85.1, 68.4, 28.0, 25.0; IR (neat): 3295, 2980, 2927, 2137, 1739, 1715, 1682, 1662 cm^{-1}; HRMS (ESI) for $C_{12}H_{17}N_2O_4$$[M+H]^+$ calcd 253.1188; found 253.1190.



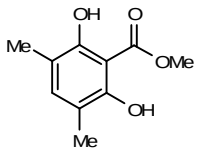
12c 13c

Synthesis of benzyl 2,6-dihydroxy-3-methylbenzoate (12c) and benzyl (1*E*,5*Z*)-7-acetyl-3,4-dihydro-4-oxo-2H-1,2-diazepine-3-carboxylate (13c). To an oven-dried 4 dr vial under nitrogen was added zinc triflate (4 mg, 0.01 mmol), followed by *trans*-4-methoxy-3-buten-2-one (**2**) (103 mg, 0.930mmol) and 4 mL of dry DCM. The mixture was stirred at 0^{o}C.Benzyl-3-*tert*-butyldimethylsilanyloxy-2-diazobut-3-enoate (398 mg, 1.20 mmol), which was prepared according to procedure previously reported by Davies[1],was added via syringe all at once. The yellow solution was stirred vigorously and

slowly warmed to room temperature. After 16 hours the crude reaction mixture was concentrated under reduced pressure. At this point substrate **2** was fully consumed and intermediate benzyl 3,7-dioxo-2-diazo-(*E*)-oct-5-enoate(**11c**) was produced, as indicated by a ^{1}H NMR spectrum of the reaction mixture. To a 4 dr vial was added **11c** from the Mukaiyama-Michael addition and in-situ elimination step without purification, followed by 4.0 mL DCE and 1.0 mL 0.20 mol/L NaOH aqueous solution (0.20 mmol). The reaction mixture was heated to reflux and was stirred at the maximum speed of the stirrer. After stirring for 2.0 hours, the stirrer was turned down and the reaction was left alone for a few minutes. At this point, a deep red aqueous phase and a yellow organic phase was formed. The organic phase was then removed by pipet and run through a short silica plug to remove small amount of water. The resulted solution was concentrated under reduced pressure. The crude reaction mixture was purified by silica gel chromatography, eluting with 1:10 EtOAc/hexane to give 113 mg of a yellow liquid as product **12c** (0.44 mmol, 49% yield). Then the eluent was switched to 1:4 EtOAc/hexane to elute product **13c** (0.22 mmol, 24% yield) as a yellow oil.

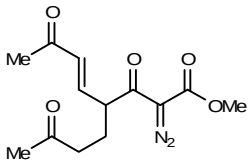
12c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.04 (br, 1H), 9.42 (br, 1H), 7.46~7.38 (comp, 5H), 7.18 (d, *J* = 8.0 Hz, 1H), 6.39 (d, *J* = 8.0 Hz, 1H), 5.49 (s, 2H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 158.7, 158.6, 137.8, 133.9, 129.3, 129.1, 128.8, 116.6, 107.3, 99.6, 68.1, 15.2; IR (neat): 3424, 3124(br), 2921, 2850, 1667, 1631, 1588 cm^{-1}; HRMS (FAB) for $C_{15}H_{15}O_4$ $[M+H]^+$ calcd 259.0971; found 259.0978.

13c: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (br, 1H), 7.57 (d, *J* = 12.0 Hz, 1H), 7.35-7.40 (comp, 5H), 6.71 (d, *J* = 12.0 Hz, 1H), 5.35 (d, *J* = 4.0 Hz, 2H), 4.22 (s,1H), 2.42 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.4, 176.2, 165.5, 140.3, 134.3, 133.3, 130.1, 128.9, 128.7, 128.6, 69.0, 25.0; IR (neat): 3302(br), 3065, 3035, 2956, 2926, 2140, 1744, 1715, 1669 cm^{-1}; HRMS (ESI) for $C_{15}H_{15}N_2O_4[M+H]^+$ calcd 287.1032; found.287.1041



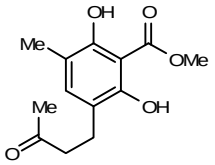
17

Synthesis of methyl 2,6-dihydroxy-3,5-dimethylbenzoate (17). To an oven-dried 4 dr vial under nitrogen was added zinc triflate (4 mg, 0.0 mmol), followed by *trans*-4-methoxy-3-buten-2-one (**2**) (100 mg, 0.900 mmol) and 4 mL of dry DCM. The mixture was stirred at 0°C. Methyl 3-*tert*-butyldimethylsilanyloxy-2-diazopent-3-enoate (**15**) (405 mg, 1.50 mmol), which was prepared according to procedure previously reported by Davies[1], was added via syringe all at once. The yellow solution was stirred vigorously and slowly warmed to room temperature. After 16 hours the crude reaction mixture was concentrated under reduced pressure. At this point substrate **2** was fully consumed and intermediate methyl 3,7-dioxo-2-diazo-4-methyl-(*E*)-oct-5-enoate (**16**) was produced, as indicated by a ^{1}H NMR spectrum of the reaction mixture. To a 25 mL round bottom flask was added **16** from the Mukaiyama-Michael addition and in-situ elimination step without purification, followed by 4mL DCE and 0.50 mL 0.20 mol/L NaOH aqueous solution (0.10 mmol). The reaction mixture was heated to reflux and was stirred vigorously. After stirring for 2 hours, a deep red aqueous phase and a yellow organic phase was formed. The organic phase was removed by pipette and filtered through a short silica plug to remove small amount of water. The resulted solution was concentrated under reduced pressure. The crude reaction mixture was purified by silica gel chromatography, eluting with 1:15 EtOAc/hexane to give 76 mg of a yellow liquid as product **17**(0.39 mmol, 43% yield). The product turned into a light yellow wax upon refrigerator storage. **17:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.70 (br, 2H), 7.08 (s, 1H), 4.07 (s, 3H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.4, 156.2, 139.3, 115.5, 99.1, 52.7, 15.1; IR (neat): 3429, 3132, 2955, 2925, 2857, 1666, 1626, 1607 cm^{-1};HRMS (FAB) for $C_{10}H_{13}O_4$ $[M+H]^+$. calcd 197.0814; found 197.0822.



18

Synthesis of methyl 3,7-dioxo-4-(3-oxo-butyl)-2-diazo-(*E*)-oct-5-enoate (18). To a 4 dr vial was added methyl-3,7-dioxo-2-diazo-(*E*)-oct-5-enoate (**4**) from the Mukaiyama-Michael addition and in-situ elimination step without purification, 4.0 mmol methyl vinyl ketone and 2.0 mL DCM. The solution was cooled down to 0^{o}C with ice bath and was stirred at the maximum speed of the stirrer. 1.0 mL 0.10 mol/L NaOH aqueous solution (0.10 mmol) was then added to the reaction. After stirring for 2.0 hours, At this point, A lot yellow precipitate was accumulated in the aqueous phase and a reddish yellow organic phase was formed. The organic phase was then removed by pipette and run through a short silica plug to remove small amount of water. The resulting solution was concentrated under reduced pressure. The crude reaction mixture was purified by silica gel chromatography, eluting with 1:2 EtOAc/hexane, using short column and fast air flow to minimize decomposition of the product. After chromatograph, 173 mg (65%) product was isolated **18:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.69 (dd, J_1= 8.0 Hz, J_2= 16.0 Hz, 1H), 6.07 (d, J = 16.0 Hz, 1H), 4.31 (q, J = 8.0 Hz, 1H), 3.78 (s, 3H); 2.41-2.35 (comp, 2H), 2.19 (s, 3H), 2.05 (s, 3H), 2.08-2.03 (comp, 1H), 1.89-1.82 (comp, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.2, 198.0, 191.0, 161.0, 143.6, 133.2, 52.3, 49.3, 40.5, 29.9, 26.9, 25.1; IR (neat): 2956, 2921, 2852, 2340, 2359, 2141, 1712, 1675, 1651cm^{-1}; HRMS (ESI) for $C_{13}H_{17}N_2O_5$ $[M+H]^+$ calcd 281.1137; found: 281.1121



19

Synthesis of methyl 2,6-dihydroxy-3-methyl-5-(3-oxobutyl)-benzoate (19). To a 4 dr vial was added 151mg methyl-3,7-dioxo-4-(3-oxo-butyl)-2-diazo-(*E*)-oct-5-enoate (**18**) (0.5 mmol) and 1mL DCM. 6 mg of triethylamine (0.05mmol) was then added to the

solution. In a short period of time, a lot of bubbles were formed from the solution and the color of the reaction turned from bright yellow to brownish yellow. The reaction mixture was stirred at room temperature for 30 minutes. The resulting yellow solution was concentrated under reduced pressure. The crude reaction mixture was purified by silica gel chromatography, eluting with 1:2 EtOAc/hexane to yield 65 mg (45%) yellow oil as product. **13a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (br, 2H), 7.09 (s, 1H), 4.07 (s, 3H), 2.79 (t, J = 8.0 Hz, 2H), 2.71 (t, J = 8.0 Hz, 2H), 2.13 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 208.7, 170.4, 156.8, 156.1, 138.8, 118.4, 115.9, 99.2, 52.7, 43.4, 29.9, 24.1, 15.1; IR (neat): 3437, 3141, 2959, 2921, 2849, 1713, 1669, 1625cm^{-1}; HRMS (ESI) for $C_{13}H_{17}O_5$ $[M+H]^+$ calcd 253.1076; found 253.1072.

(1) Davies, H. M. L.; Ahmed, G.; Churchill, M. R. *J. Am. Chem. Soc.* **1996**, *118*, 10774-10780.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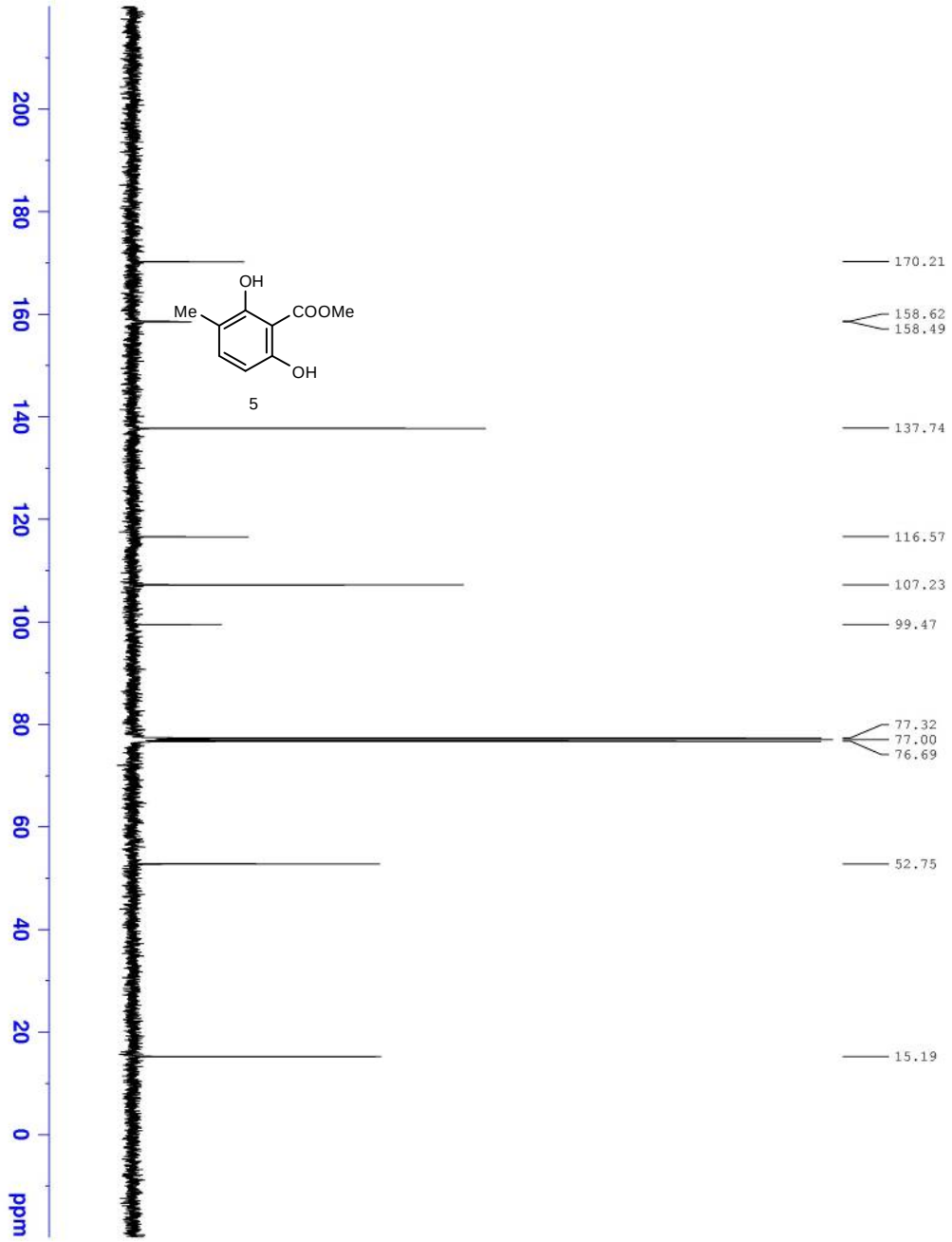
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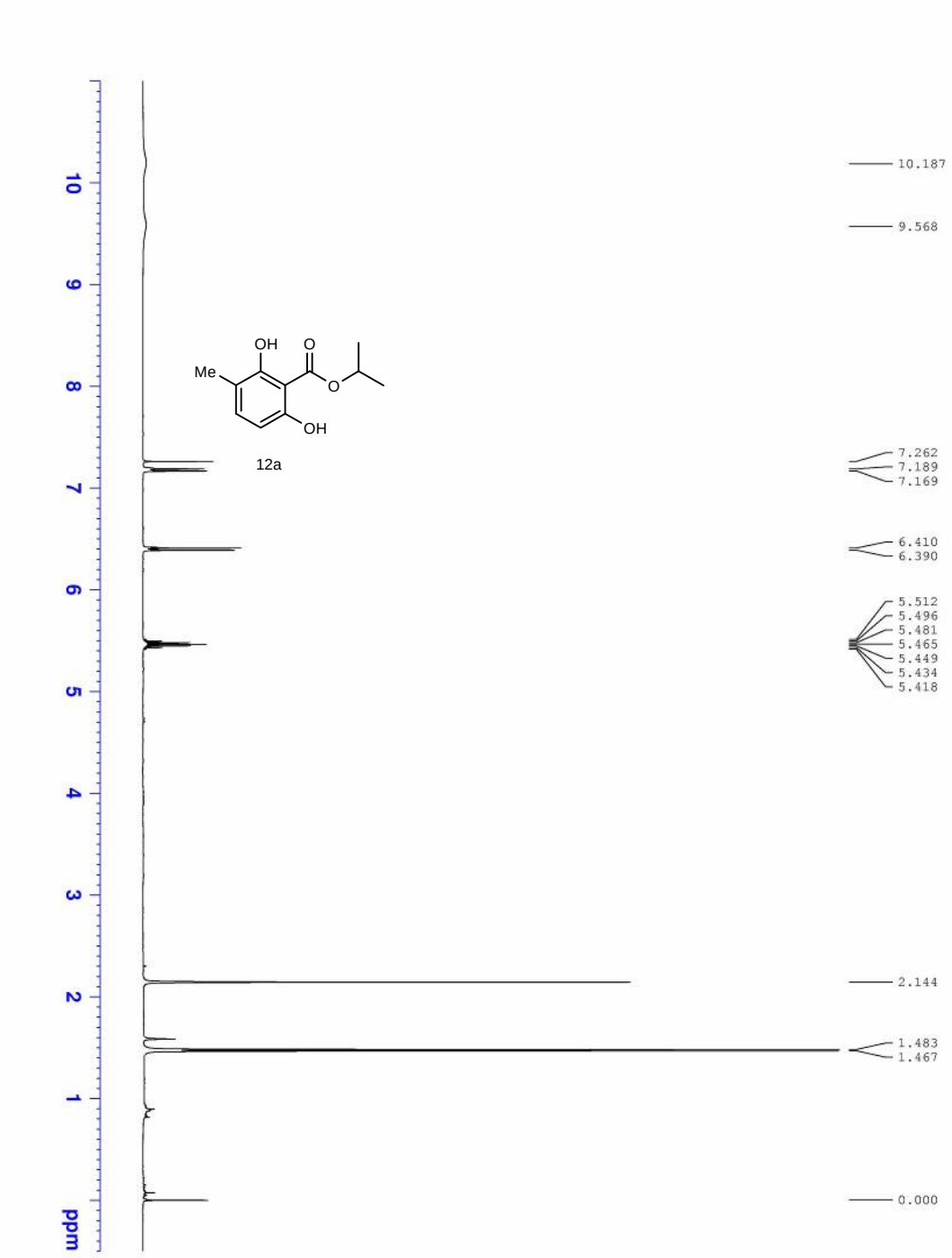
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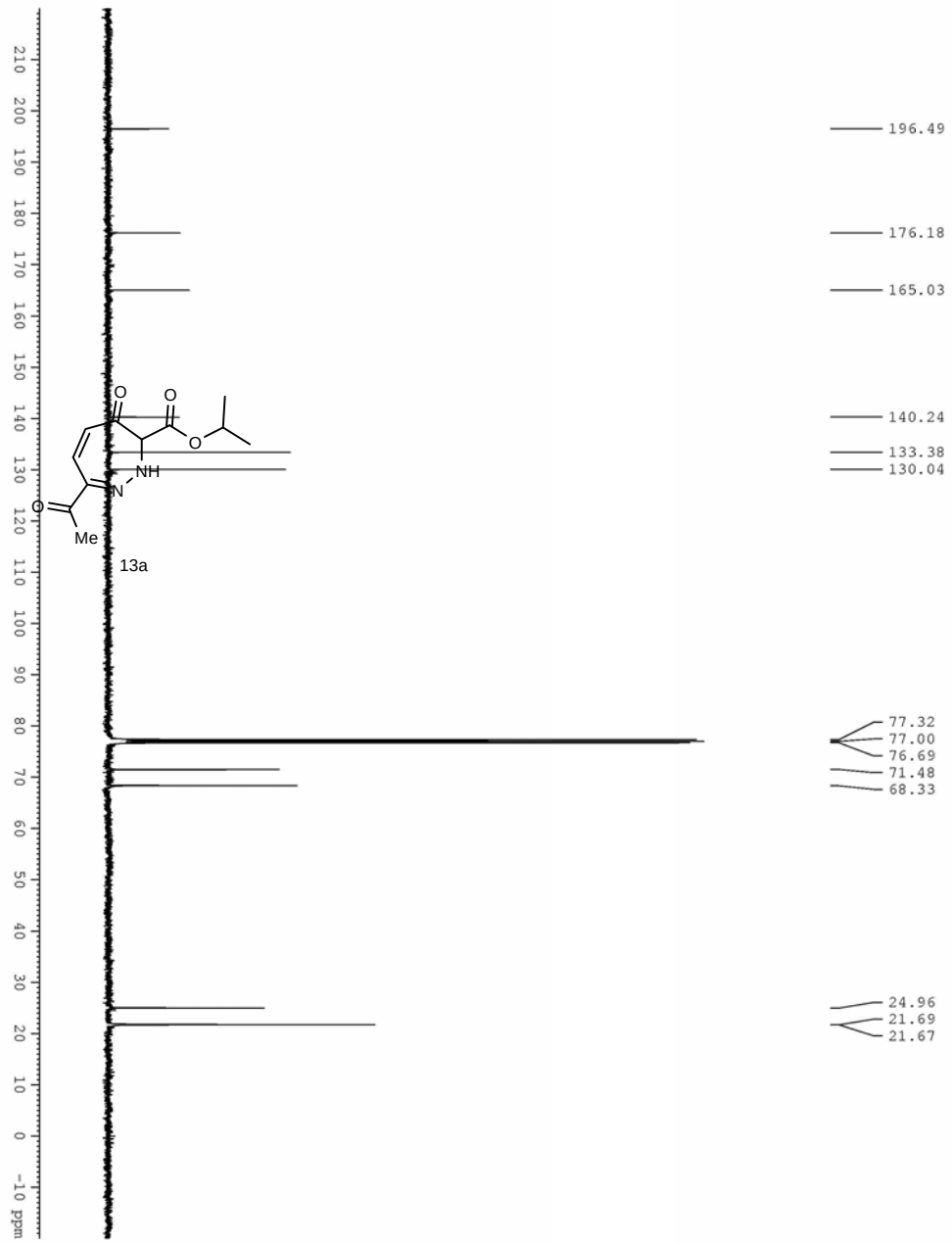
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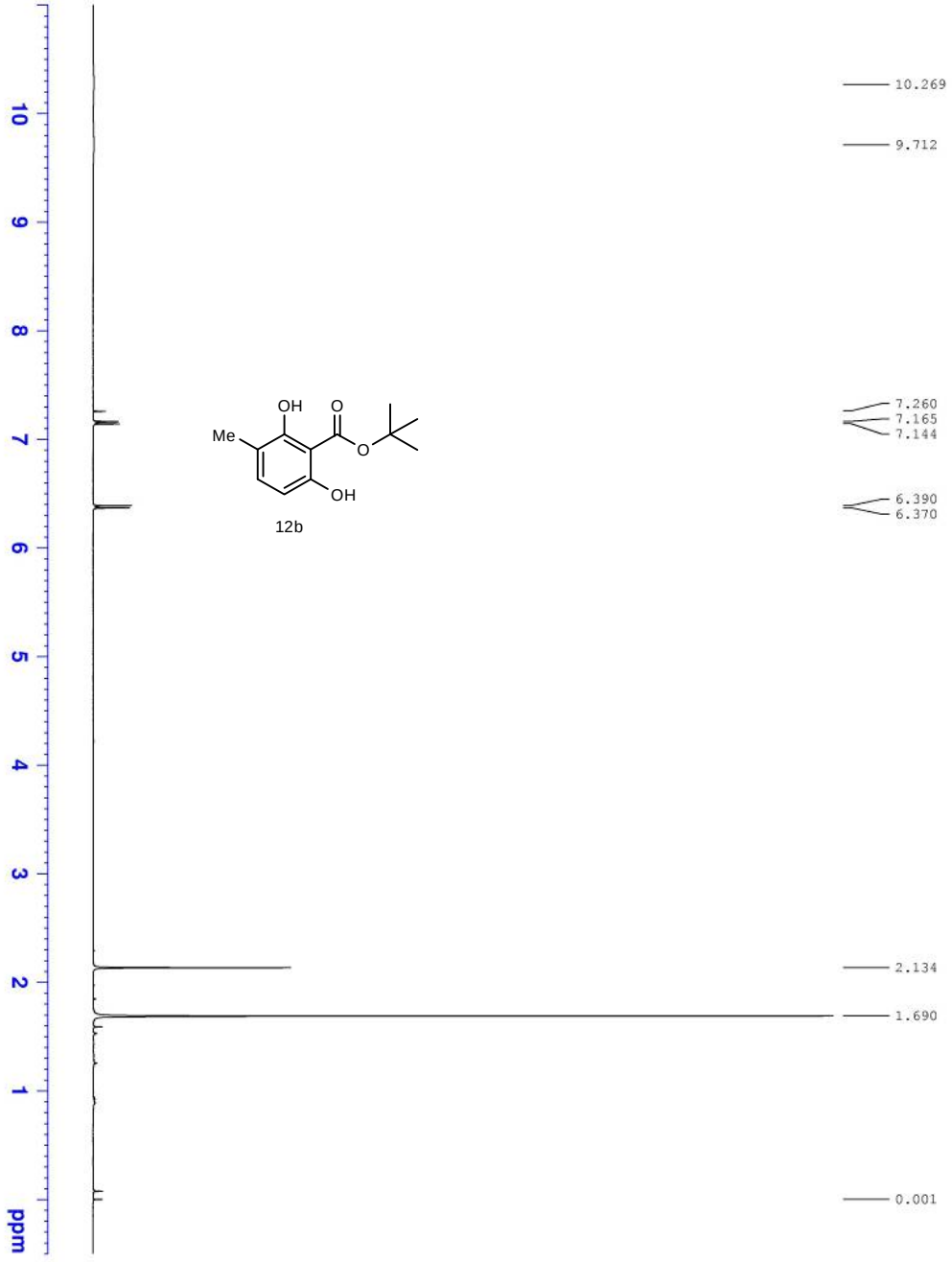
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12b


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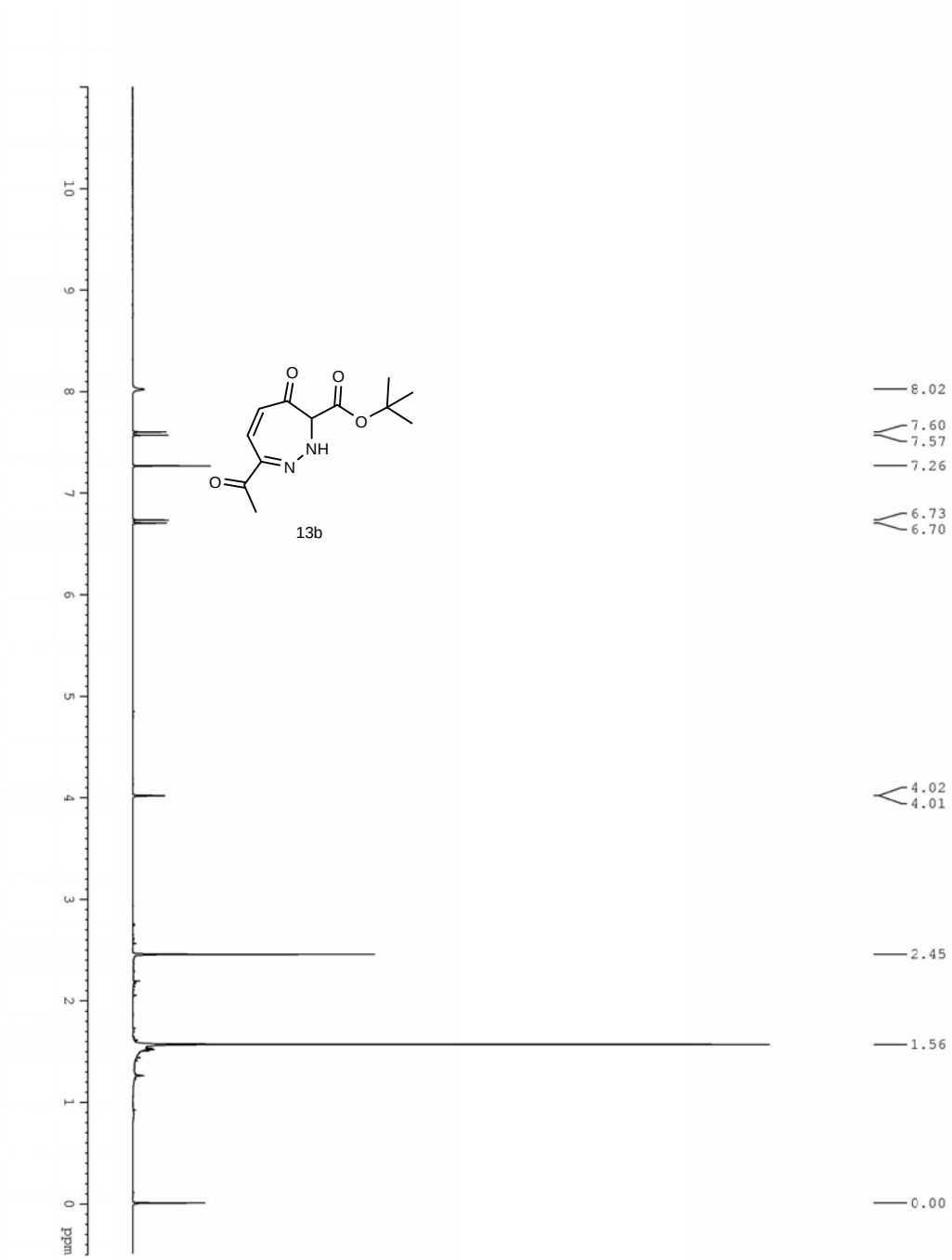
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N
O
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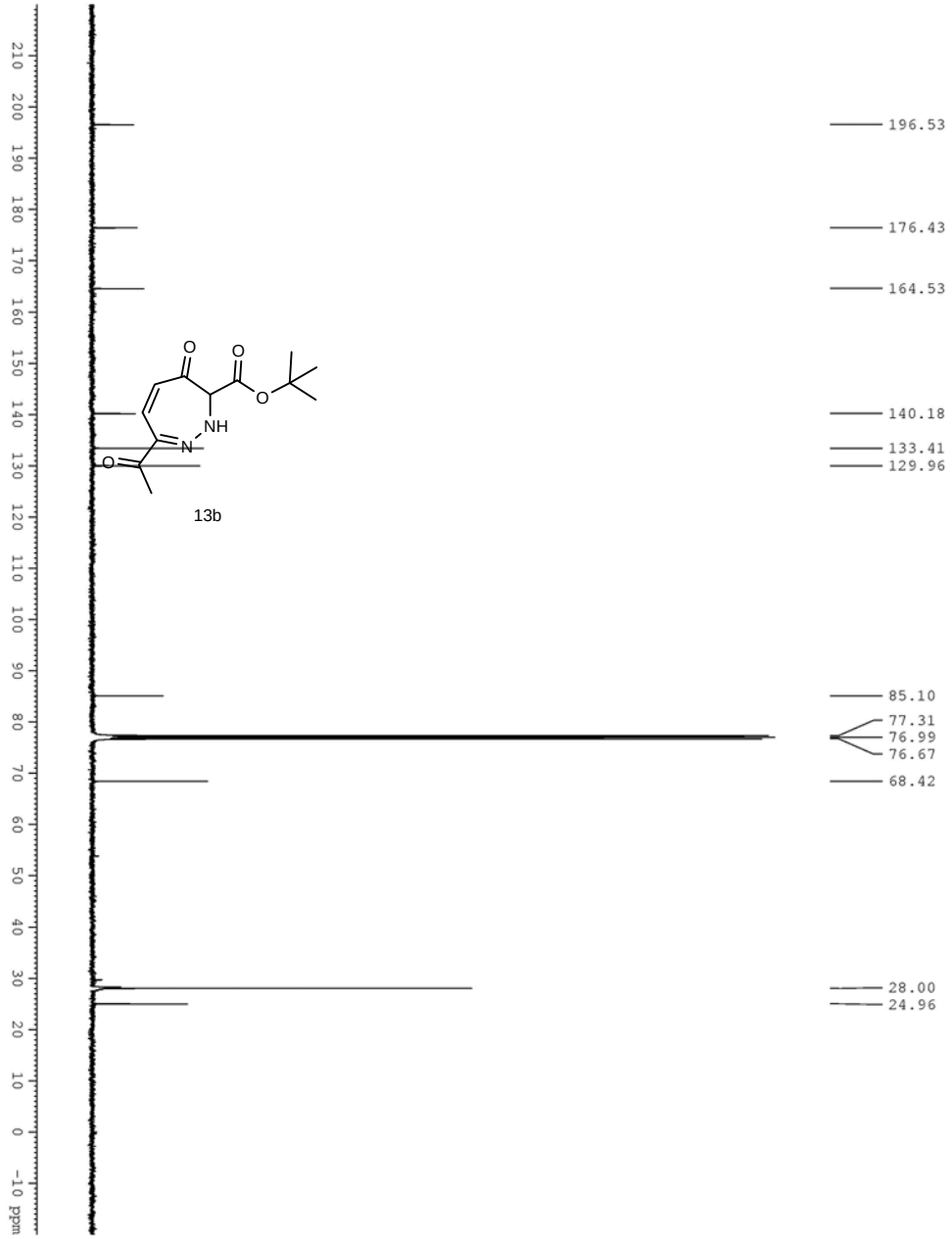
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77.31
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O
O
O
NH
N
O
13b
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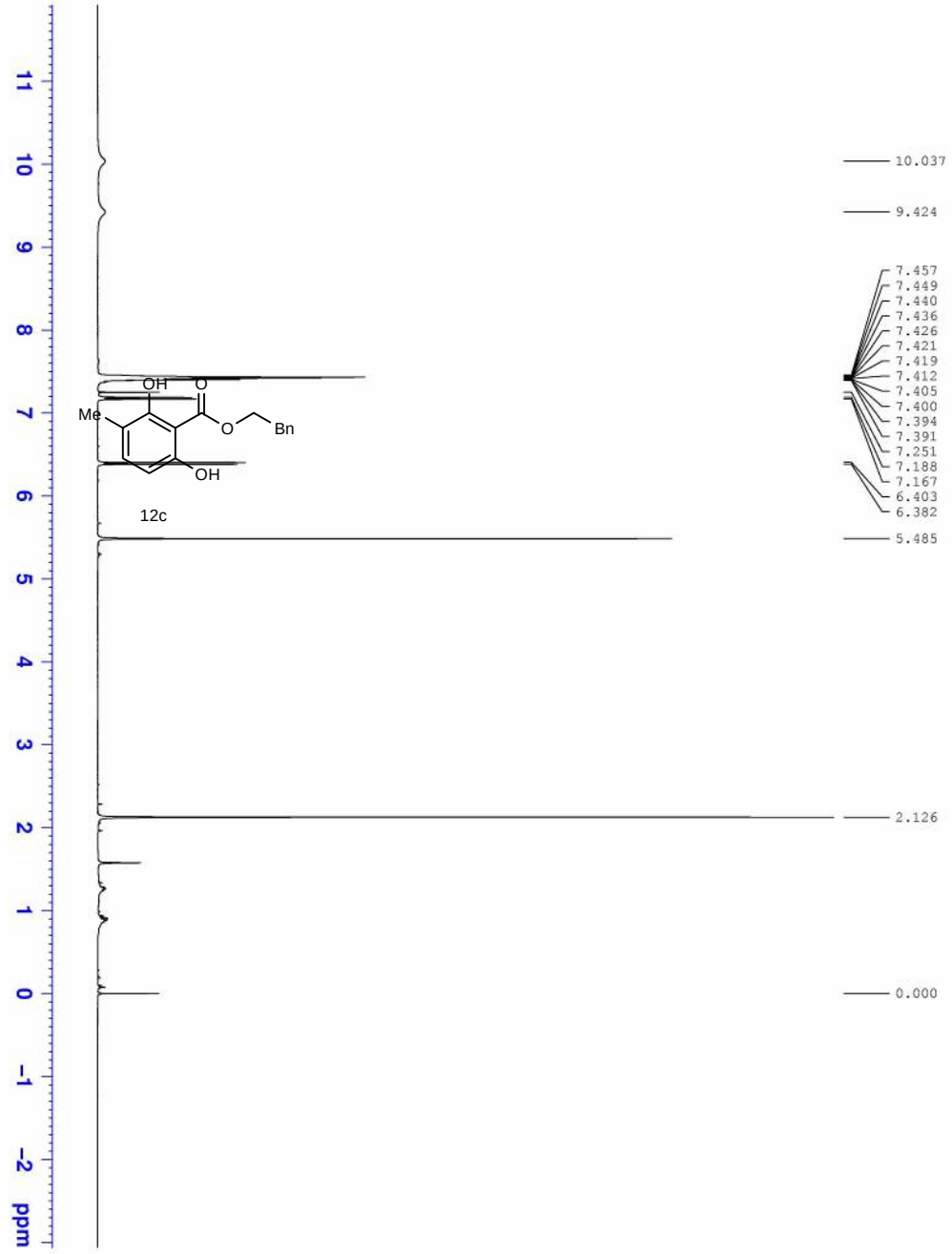
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−1
−2
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O
Bn
OH
12c
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7.440
7.436
7.426
7.421
7.419
7.412
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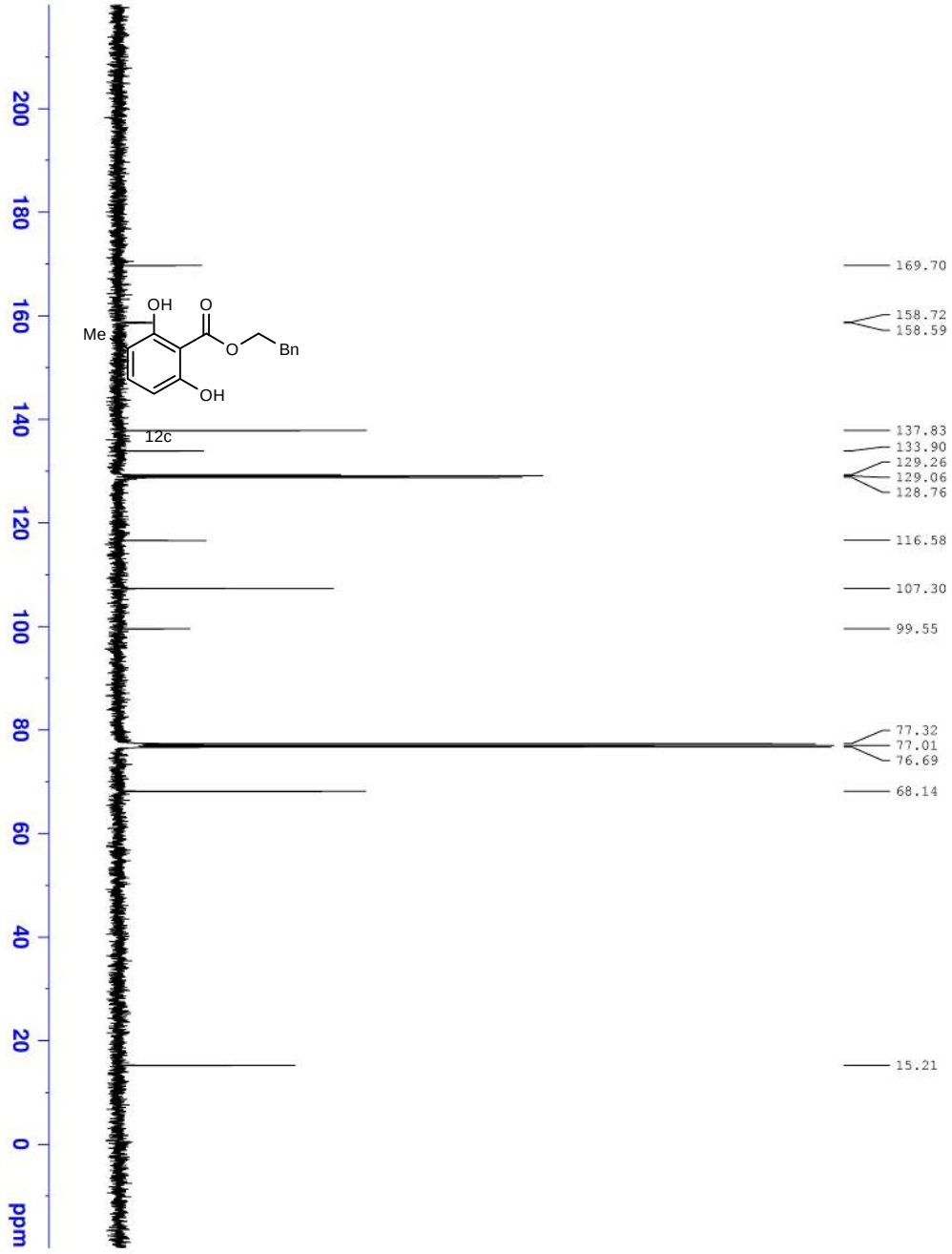
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128.76
116.58
107.30
99.55
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68.14
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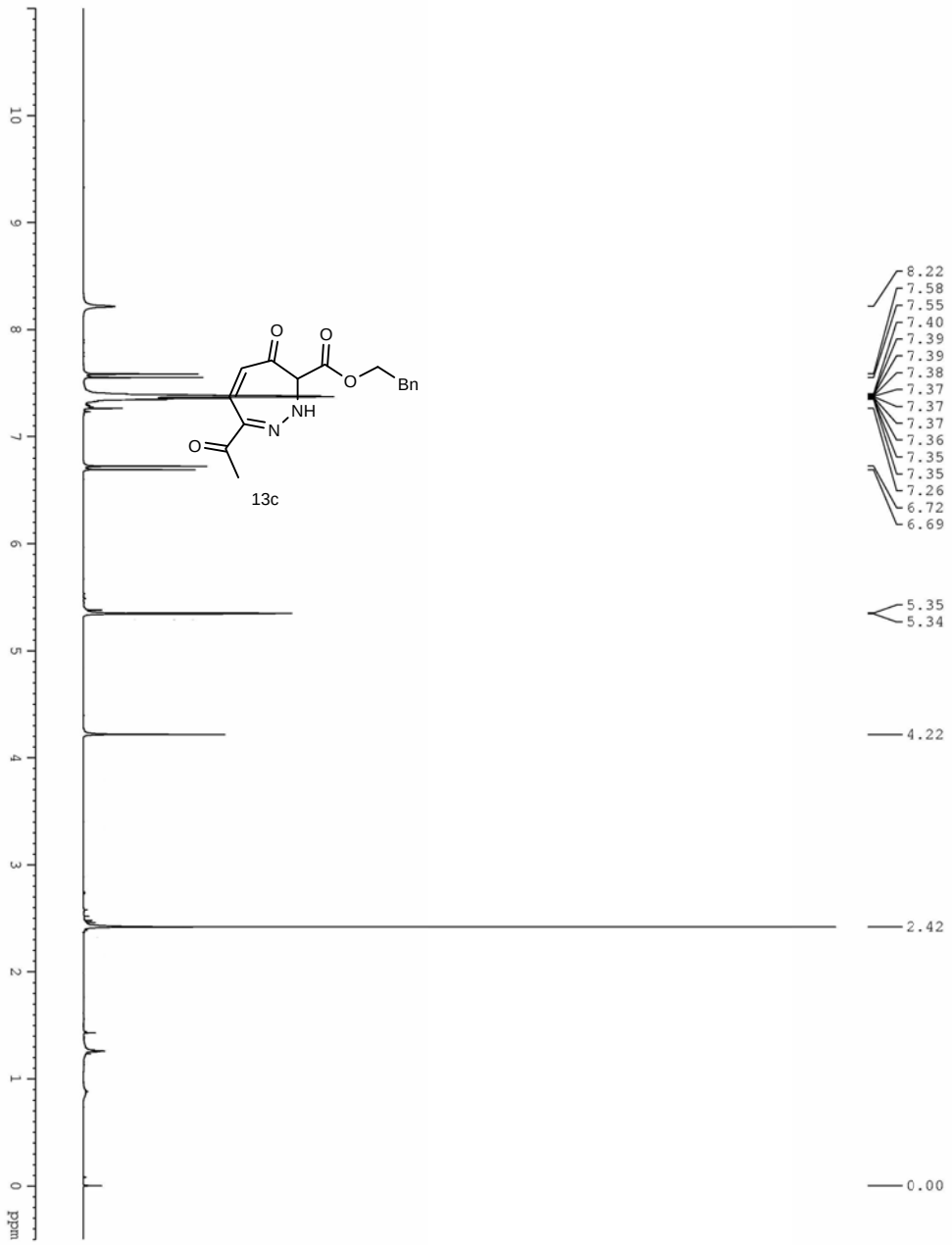
0
ppm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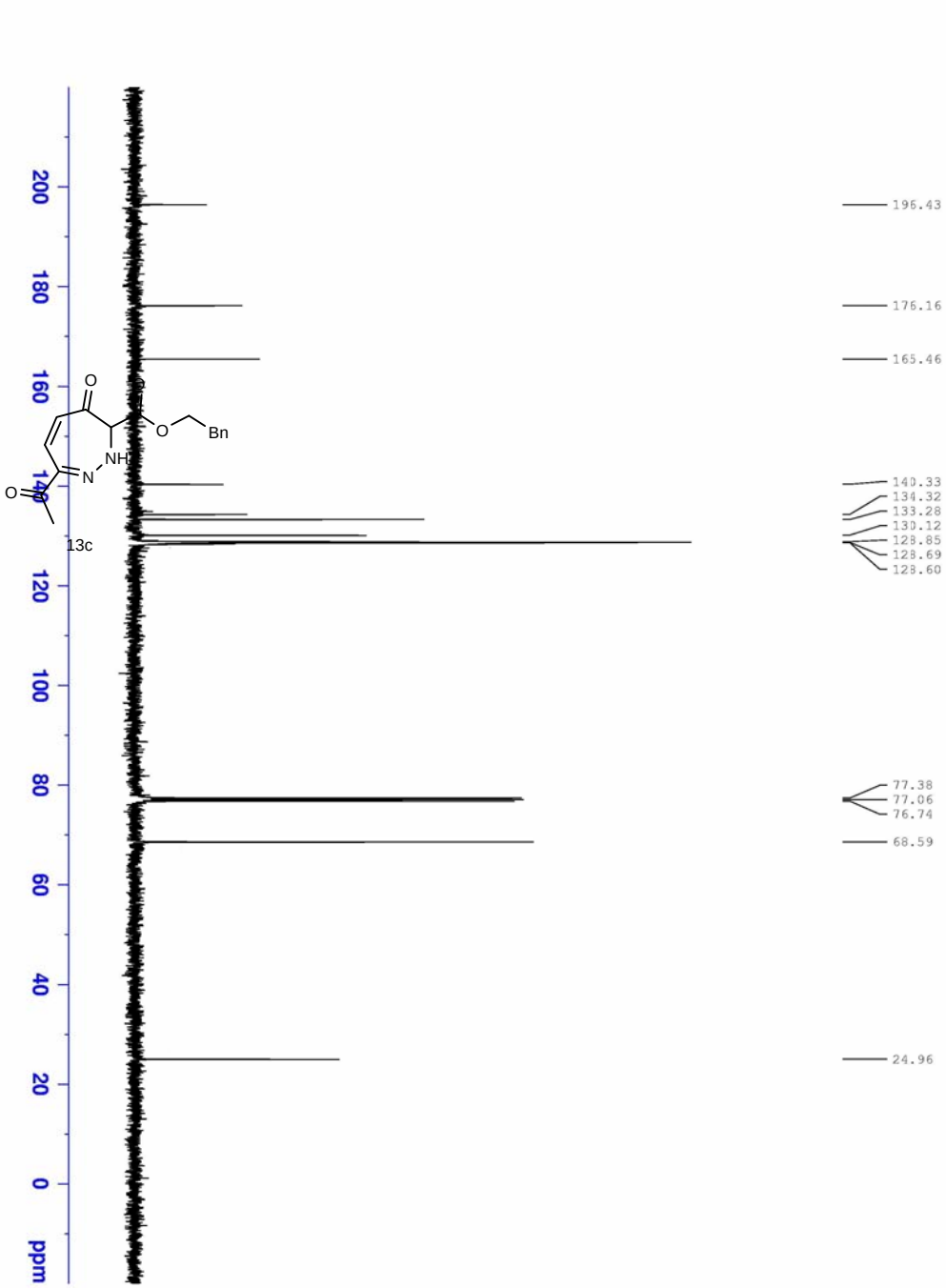
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Bn
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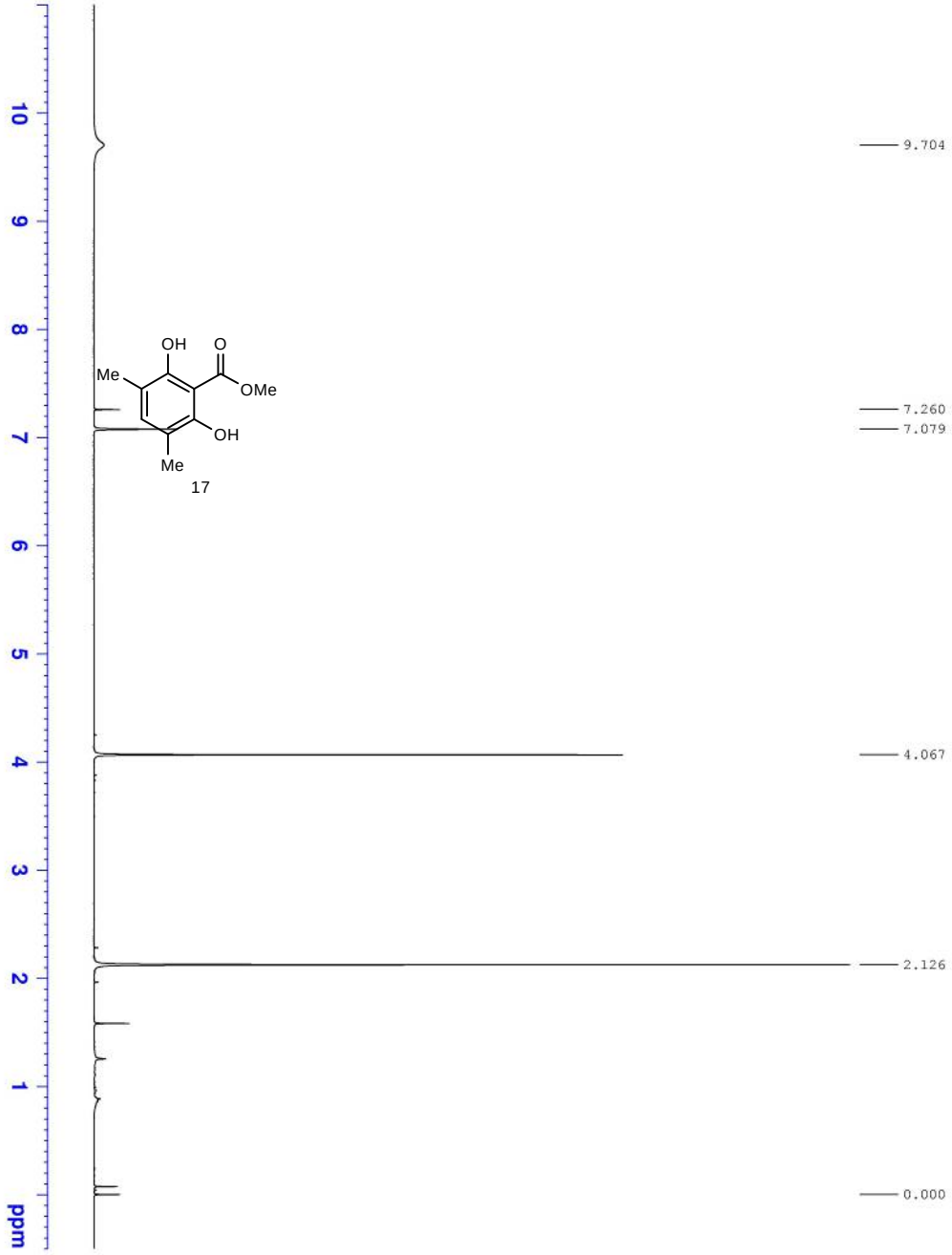
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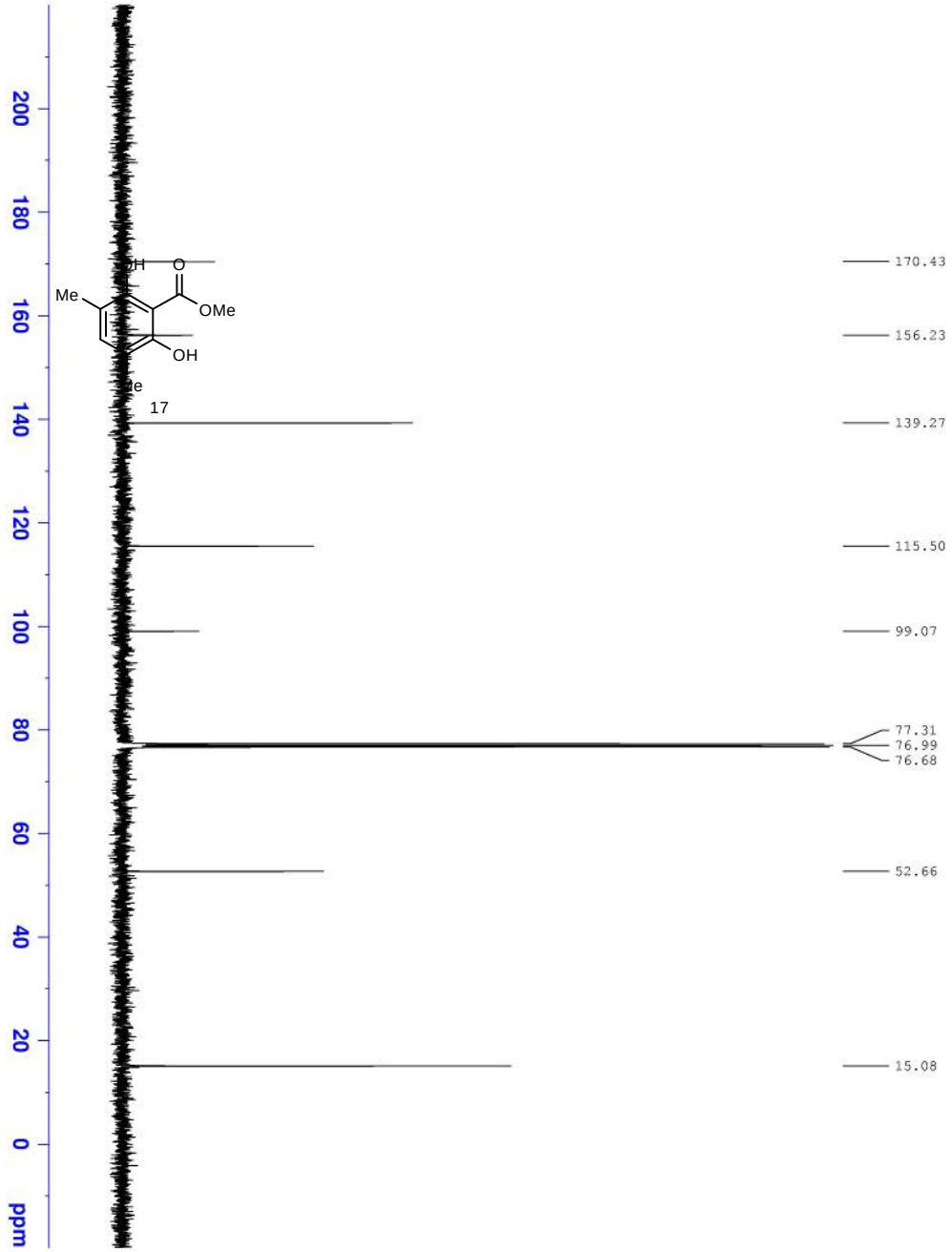
4
3
2
1
ppm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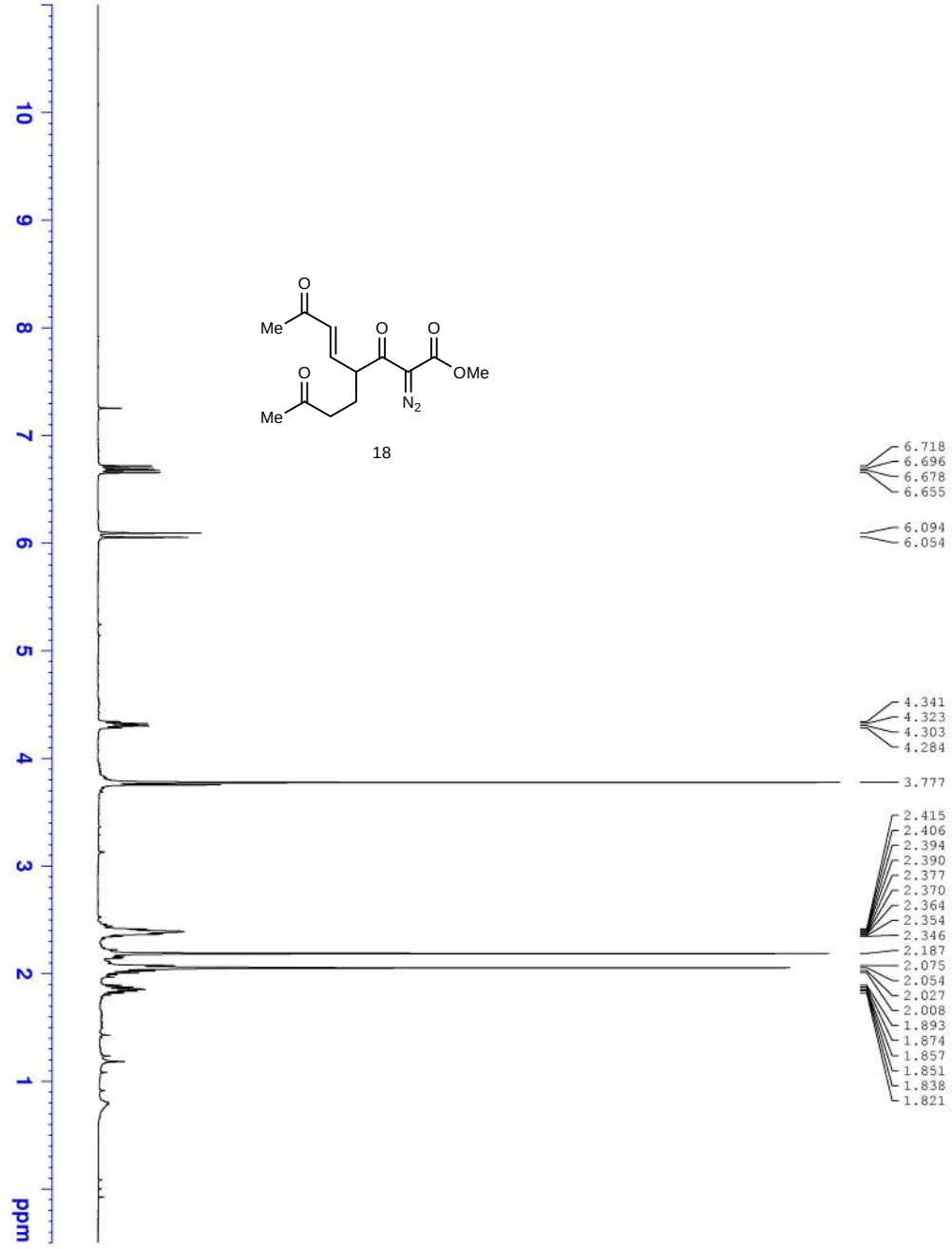
52.66
15.08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4.323
4.303
4.284
3.777
2.415
2.406
2.394
2.390
2.377
2.370
2.364
2.354
2.346
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2.054
2.027
2.008
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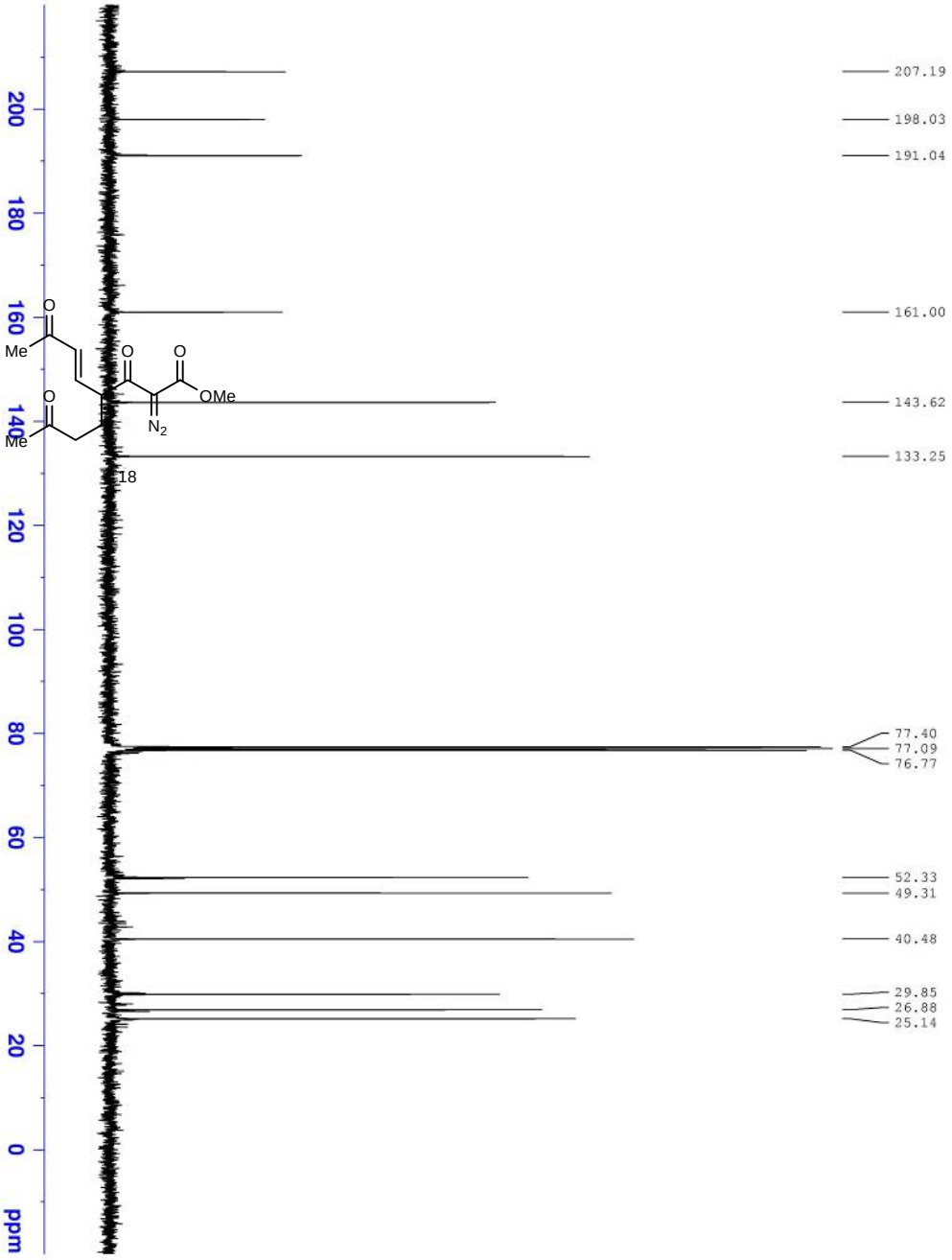
1.821
ppm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26.88
25.14
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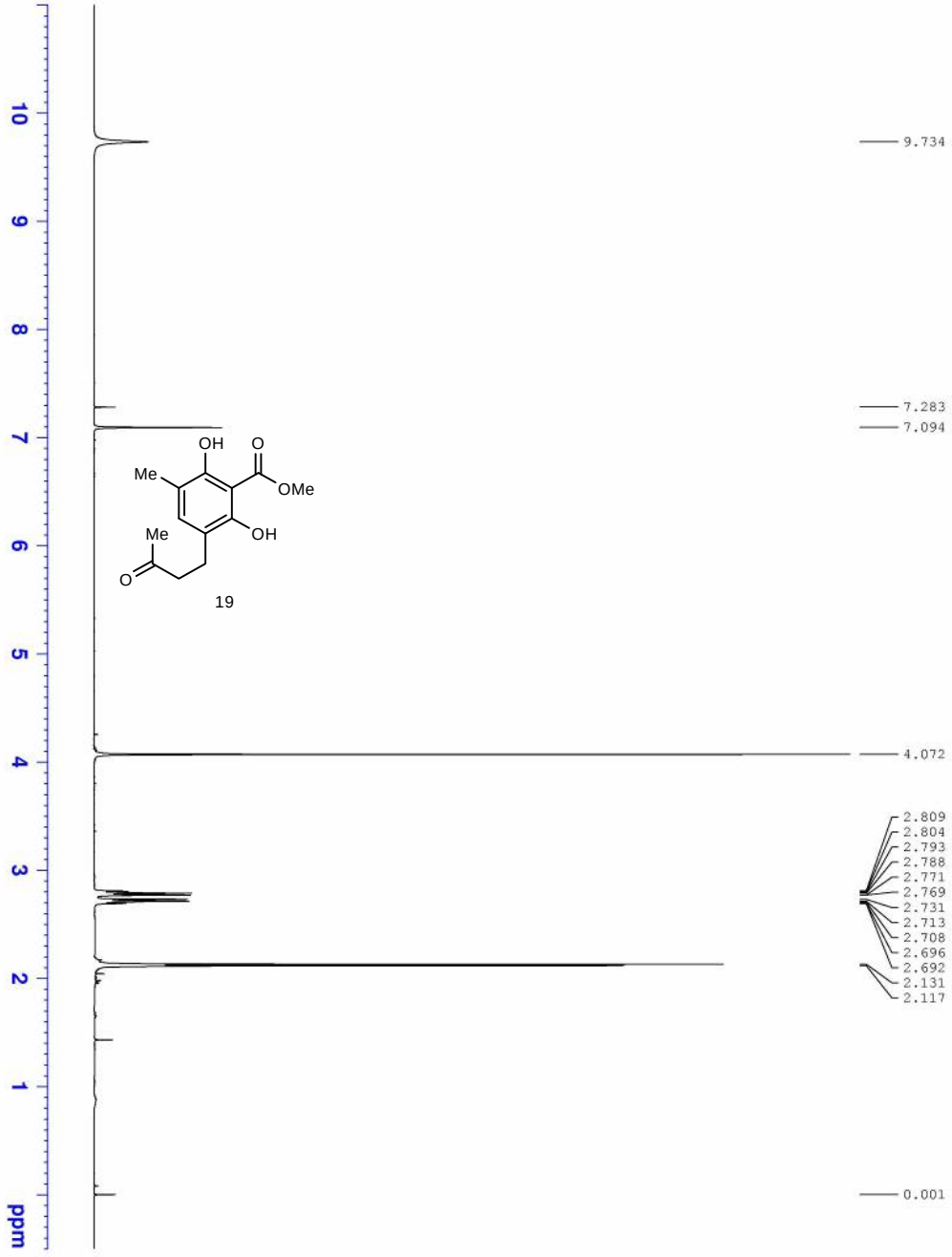
O
O
OMe
N2
O
Me
18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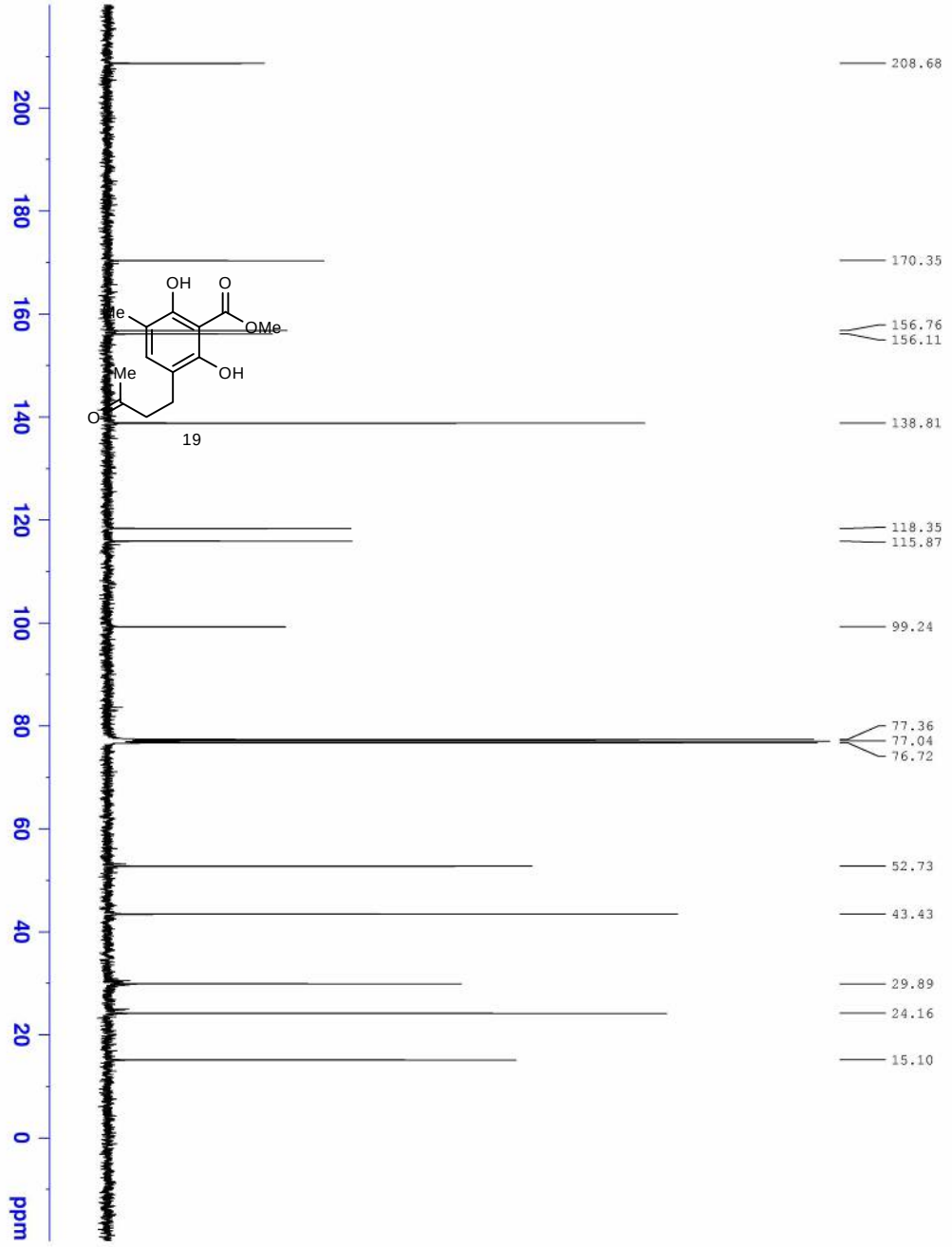
O

19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15.10
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OMe
Me
OH
O
19
200
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140
120
100
80
60
40
20
0
ppm

Crystal Structure Information for *tert*-butyl (1*E*,5*Z*)- 7-acetyl-3,4-dihydro-4-oxo -2H -1,2-diazepine-3-carboxylate(13b)

A yellow plates of C12H16N2O4, approximate dimensions 0.035□0.25□0.50 mm3, was used for the X-ray crystallographic analysis. The X-ray intensity data were measured at 150(2) K on a three-circle diffractometer system equipped with Bruker Smart Apex II CCD area detector using a graphite monochromator and a MoK□ fine-focus sealed tube (□= 0.71073 Å) . The detector was placed at a distance of 6.000 cm from the crystal.

A total of 1223 frames were collected with a scan width of -0.5° an exposure time of 60 sec/frame using Apex2 (Bruker, 2005). The total data collection time was 22.4 hours. The frames were integrated with Apex2 software package using a narrow-frame integration algorithm. The integration of the data using a Triclinic unit cell yielded a total of 4914 reflections to a maximum □ angle of 24.99°, of which 2202 were independent (completeness = 99.7%, Rint = 1.80%, Rsig = 2.26%) and 1867 were greater than 2□(I). The final cell dimensions of a = 5.9230(13) Å, b = 10.189(2) Å, c = 11.365(3) Å, □ = 106.520(3)°, □ = 104.950(3)°, □ = 94.331(3)°, V = 627.1(2) Å3, are based upon the refinement of the XYZ-centroids of 2779 reflections with 2.4 < □ < 28.5° using Apex2 software. Analysis of the data showed 0 % decay during data collection. Data were corrected for absorption effects with the Semi-empirical from equivalents method using SADABS (Sheldrick, 1996). The minimum and maximum transmission coefficients were 0.868 and 0.996. The structure was solved and refined using the SHELXS-97 (Sheldrick, 1990) and SHELXL-97 (Sheldrick, 1997) software in the space group P-1 with Z = 2 for the formula unit C12H16N2O4. The final anisotropic full-matrix least-squares refinement on F2 with 186 variables converged at R1 = 3.20 % for the observed data and wR2 = 6.52 % for all data. The goodness-of-fit was 1.000. The largest peak on the final difference map was 0.193□e/Å3 and the largest hole was -0.172□e/Å3. On the basis of the final model, the calculated density was 1.336 g/cm3 and F(000), 268 e.

Table 1. Crystal data and structure refinement for **13b**.

X-ray lab book No.	1935

Crystal ID		Doyle/Yu Liu 05/13/2010 $C_{12}H_{16}O_4$ 150K
Empirical formula		$C_{12}H_{16}N_2O_4$
Formula weight		252.27
Temperature		150(2) K
Wavelength		0.71073 Å
Crystal size		0.50×0.25×0.035 mm^3
Crystal habit		yellow plates
Crystal system		Triclinic
Space group		P-1
Unit cell dimensions		a = 5.9230(13) Å α = 106.520(3)°
		b = 10.189(2) Å β = 104.950(3)°
		c = 11.365(3) Å γ = 94.331(3)°
Volume		627.1(2) $Å^3$
Z		2
Density, ρ_{calc}		1.336 g/cm^3
Absorption coefficient, μ		0.101 mm^{-1}
F(000)		268 e
Diffractometer		Bruker Smart Apex II CCD area detector
Radiation source		fine-focus sealed tube, MoKα
Detector distance		6.000 cm
Data collection method		ω and φ scans
Total frames		1223
Frame size		512 pixels
Frame width		-0.5°
Exposure per frame		60 sec
Total measurement time		22.4 hours
θ range for data collection		1.95 to 24.99°
Index ranges		$-7 \le h \le 7$, $-12 \le k \le 12$, $-13 \le l \le 13$
Reflections collected		4914
Independent reflections		2202
Observed reflection, I>2σ(I)		1867
Coverage of independent reflections		99.7 %
Variation in check reflections		0 %
Absorption correction		Semi-empirical from equivalents
		SADABS (Sheldrick, 1996)
Max. and min. transmission		0.996 and 0.868
Structure solution technique		direct
Structure solution program		SHELXS-97 (Sheldrick, 1990)
Refinement technique		Full-matrix least-squares on F^2
Refinement program		SHELXL-97 (Sheldrick, 1997)
Function minimized		$\Sigma w(F_o^2 - F_c^2)^2$
Data / restraints / parameters		2202 / 0 / 186
Goodness-of-fit on F^2		1.000
Δ/σ_{max}		0.001
Final R indices:	R_1, I>2σ(I)	0.0320
	wR_2, all data	0.0652
	R_{int}	0.0180
	R_{sig}	0.0226
Weighting scheme		$w = 1/[\sigma^2(F_o^2)+ (0.01P)^2 + 0.334P]$,
		$P = [\max(F_o^2,0) + 2F_c^2]/3$
Largest diff. peak and hole		0.193 and -0.172 e/$Å^3$

$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table 2. Atomic coordinates and equivalent* isotropic atomic displacement parameters (Å^2) for **13b**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
O1	-0.19105(18)	0.30470(11)	0.39987(9)	0.0351(3)
C1	0.1414(3)	0.21241(16)	0.49244(15)	0.0358(4)
C2	-0.0422(2)	0.30634(15)	0.49793(13)	0.0262(3)
C3	-0.0385(2)	0.40195(14)	0.62460(13)	0.0220(3)
N1	0.1289(2)	0.39033(12)	0.72184(11)	0.0240(3)
N2	0.1674(2)	0.47589(12)	0.83800(11)	0.0258(3)
C4	-0.2388(2)	0.47410(15)	0.62899(14)	0.0253(3)
C5	-0.2976(2)	0.55503(15)	0.72911(14)	0.0275(3)
C6	-0.1406(2)	0.61939(14)	0.85876(13)	0.0229(3)
O2	-0.20794(17)	0.67289(10)	0.95126(10)	0.0295(2)
C7	0.1245(2)	0.61844(14)	0.87017(13)	0.0216(3)
C8	0.2779(2)	0.69456(14)	1.00714(13)	0.0215(3)
O3	0.27433(16)	0.82904(9)	1.03539(9)	0.0242(2)
O4	0.38182(16)	0.63402(10)	1.07649(9)	0.0262(2)
C9	0.3927(2)	0.92393(14)	1.16872(13)	0.0239(3)
C10	0.3227(3)	1.06184(15)	1.16104(15)	0.0327(4)
C11	0.2974(3)	0.87617(16)	1.26407(14)	0.0301(3)
C12	0.6587(2)	0.92861(16)	1.19724(15)	0.0319(4)

* U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3. Anisotropic atomic displacement parameters* (Å^2) for **13b**.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	0.0316(6)	0.0433(7)	0.0224(5)	0.0069(5)	-0.0014(5)	0.0045(5)
C1	0.0321(9)	0.0362(9)	0.0286(8)	-0.0016(7)	0.0035(7)	0.0082(7)
C2	0.0225(7)	0.0264(8)	0.0248(8)	0.0068(6)	0.0021(6)	-0.0025(6)
C3	0.0186(7)	0.0215(7)	0.0231(7)	0.0077(6)	0.0015(6)	0.0004(5)
N1	0.0223(6)	0.0236(6)	0.0215(6)	0.0042(5)	0.0015(5)	0.0043(5)
N2	0.0257(6)	0.0251(6)	0.0206(6)	0.0046(5)	-0.0020(5)	0.0092(5)
C4	0.0196(7)	0.0276(8)	0.0239(8)	0.0084(6)	-0.0015(6)	0.0017(6)

C5	0.0172(7)	0.0306(8)	0.0322(8)	0.0100(7)	0.0026(6)	0.0056(6)
C6	0.0231(7)	0.0195(7)	0.0277(8)	0.0101(6)	0.0066(6)	0.0058(6)
O2	0.0292(6)	0.0289(6)	0.0313(6)	0.0076(5)	0.0120(5)	0.0072(4)
C7	0.0214(7)	0.0216(7)	0.0206(7)	0.0071(6)	0.0035(6)	0.0045(5)
C8	0.0177(7)	0.0229(7)	0.0239(7)	0.0069(6)	0.0060(5)	0.0047(5)
O3	0.0242(5)	0.0212(5)	0.0222(5)	0.0048(4)	0.0007(4)	0.0038(4)
O4	0.0254(5)	0.0257(5)	0.0245(5)	0.0075(4)	0.0012(4)	0.0082(4)
C9	0.0213(7)	0.0235(7)	0.0207(7)	0.0017(6)	0.0017(6)	0.0020(6)
C10	0.0355(9)	0.0246(8)	0.0315(8)	0.0045(6)	0.0035(7)	0.0045(6)
C11	0.0277(8)	0.0329(8)	0.0284(8)	0.0068(7)	0.0086(6)	0.0069(6)
C12	0.0215(8)	0.0346(9)	0.0327(8)	0.0040(7)	0.0045(6)	0.0001(6)

* The anisotropic atomic displacement factor exponent takes the form:$-2\pi^2 [h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12}]$

Table 4. Hydrogen atom coordinates and isotropic atomic displacement parameters (Å^2) for **13b**.

Atom	*x/a*	*y/b*	*z/c*	U_{iso}
H1A	0.1232	0.1600	0.4028	0.068(4)
H1B	0.1209	0.1478	0.5398	0.068(4)
H1C	0.2997	0.2682	0.5311	0.068(4)
H2	0.269(3)	0.4562(17)	0.8972(16)	0.042(5)
H4	-0.354(3)	0.4448(15)	0.5453(14)	0.026(4)
H5	-0.451(3)	0.5828(15)	0.7157(14)	0.032(4)
H7	0.167(3)	0.6596(15)	0.8117(14)	0.026
H10A	0.3812	1.0879	1.0963	0.039(3)
H10B	0.3919	1.1330	1.2447	0.039(3)
H10C	0.1498	1.0539	1.1371	0.039(3)
H11A	0.1239	0.8607	1.2350	0.040(3)
H11B	0.3536	0.9475	1.3484	0.040(3)
H11C	0.3530	0.7896	1.2704	0.040(3)
H12A	0.6981	0.8376	1.1999	0.042(3)
H12B	0.7385	0.9986	1.2804	0.042(3)
H12C	0.7112	0.9526	1.1299	0.042(3)

Table 5. Bond lengths (Å), valence and torsion angles (°) for UM#1935.

O1-C2	1.2246(17)	C1-C2	1.504(2)	C2-C3	1.485(2)
C3-N1	1.3209(17)	C3-C4	1.4464(19)	N1-N2	1.3095(16)
N2-C7	1.4523(18)	N2-H2	0.860(17)	C4-C5	1.346(2)
C4-H4	0.967(15)	C5-C6	1.455(2)	C5-H5	0.961(16)
C6-O2	1.2186(17)	C6-C7	1.5428(19)	C7-C8	1.5256(19)
C7-H7	0.954(15)	C8-O4	1.2100(16)	C8-O3	1.3186(16)
O3-C9	1.4962(16)	C9-C10	1.514(2)	C9-C11	1.518(2)
C9-C12	1.5188(19)				
O1-C2-C3	120.62(13)	O1-C2-C1	120.72(13)	C3-C2-C1	118.66(12)
N1-C3-C4	128.04(13)	N1-C3-C2	113.85(12)	C4-C3-C2	116.95(12)
N2-N1-C3	120.83(12)	N1-N2-C7	125.77(12)	N1-N2-H2	115.2(11)
C7-N2-H2	115.4(11)	C5-C4-C3	130.85(13)	C5-C4-H4	118.5(9)
C3-C4-H4	109.9(9)	C4-C5-C6	126.12(13)	C4-C5-H5	119.6(9)
C6-C5-H5	114.0(9)	O2-C6-C5	124.02(13)	O2-C6-C7	121.78(12)

C5-C6-C7	114.19(12)	N2-C7-C8	107.68(11)	N2-C7-C6	109.01(11)
C8-C7-C6	111.02(11)	N2-C7-H7	108.7(9)	C8-C7-H7	110.4(9)
C6-C7-H7	109.9(9)	O4-C8-O3	127.31(12)	O4-C8-C7	122.12(12)
O3-C8-C7	110.56(11)	C8-O3-C9	120.36(10)	O3-C9-C10	102.44(11)
O3-C9-C11	110.07(11)	C10-C9-C11	111.48(12)	O3-C9-C12	109.00(11)
C10-C9-C12	111.37(12)	C11-C9-C12	112.03(12)		

O1-C2-C3-N1	178.78(13)	C1-C2-C3-N1	-1.65(19)	O1-C2-C3-C4	10.1(2)
C1-C2-C3-C4	-170.31(13)	C4-C3-N1-N2	-18.8(2)	C2-C3-N1-N2	174.05(12)
C3-N1-N2-C7	-28.9(2)	N1-C3-C4-C5	5.8(3)	C2-C3-C4-C5	172.56(15)
C3-C4-C5-C6	16.9(3)	C4-C5-C6-O2	-167.54(15)	C4-C5-C6-C7	14.1(2)
N1-N2-C7-C8	-158.05(13)	N1-N2-C7-C6	81.42(17)	O2-C6-C7-N2	116.90(14)
C5-C6-C7-N2	-64.67(15)	O2-C6-C7-C8	176.87(12)	C5-C6-C7-C8	-1.56(18)
N2-C7-C8-O4	-10.38(18)	C6-C7-C8-O4	170.55(11)	C6-C7-C8-O3	108.87(14)
N2-C7-C8-O3	-70.19(14)	O4-C8-O3-C9	174.03(11)	C7-C8-O3-C9	-5.0(2)
C8-O3-C9-C10	-174.06(12)	C8-O3-C9-C11	-55.38(15)	C8-O3-C9-C12	67.86(15)