Photoredox-Catalyzed Intramolecular Cyclopropanation of Alkenes with α-Bromo-β-keto Esters

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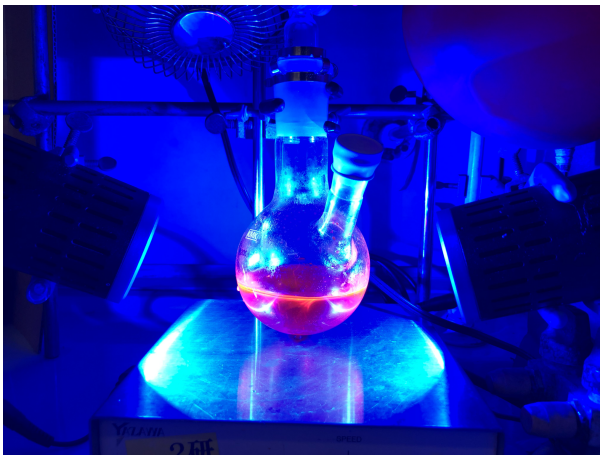
1. General Remarks

All moisture or air sensitive reactions were carried out under a positive atmosphere of argon in a dried glassware. Materials were obtained from commercial suppliers and used without further purification unless otherwise mentioned. DMF was distilled from CaH_2. Anhydrous THF, CH_3CN, and CH_2Cl_2 were purchased from commercial suppliers. Flash column chromatography was performed on Silica Gel 60N (spherical neutral, 40-50 μm) using the indicated solvent. Preparative TLC and analytical TLC were performed on Merck 60 F254 glass plates precoated with a 0.25 mm thickness of silica gel. Automated MPLC purification was conducted by a Biotage Isolera One ACITM Spektra using prepacked silica gel column (HP-Sphere^{TM}, 25 μm). NMR spectra were recorded on a JNM-AL400 spectrometer or a JEOL ECA600 spectrometer. Chemical shifts for ^{1}H NMR are reported in parts per million (ppm) downfield from tetramethylsilane as the internal standard and coupling constants are in Hertz (Hz). The following abbreviations are used for description of spin multiplicity: s = singlet, d = doublet, t = triplet, q = quartet, quin = quintet, m = multiplet, and br = broad. Chemical shifts for ^{13}C NMR are reported in ppm, relative to the central line of a triplet at 77.0 ppm for deuteriochloroform. IR spectra were measured on a FT-IR spectrometer. Mass spectra were recorded on a ESI-TOF mass spectrometer, a JMS-T100GC spectrometer, or a JMS-700 spectrometer.

Reaction Apparatus:

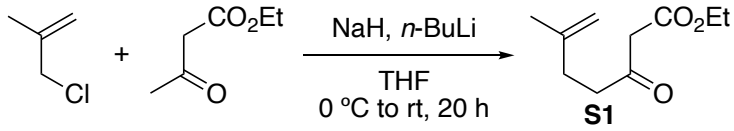
Photoredox-catalyzed reactions were carried out under irradiation of visible light using a commercially available blue LEDs (Kessil A160WE TUNA blue 40W) on the both sides of the reaction flask at a distance of 7-8 cm.



2. Preparation of β-Keto Esters

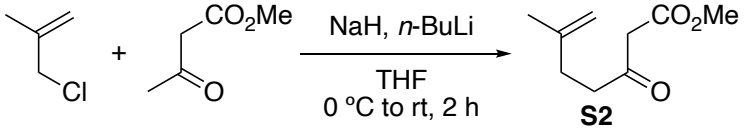
General Procedure A for Preparation of β-Keto Esters

Ethyl 6-methyl-3-oxohept-6-enoate (S1)



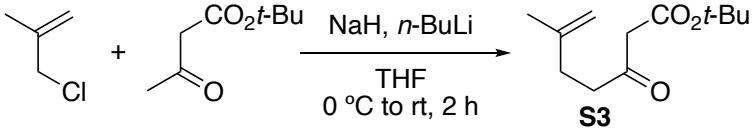
To a solution of NaH (6.18 g, 154 mmol, 60 wt% in mineral oil) in dry THF (350 mL) was added ethyl acetoacetate (19.5 mL, 154 mmol) dropwise over 10 minutes at 0 ºC. The resultant mixture was allowed to warm up to room temperature over 30 minutes. *n*-BuLi (55.0 mL, 154 mmol, 2.80 M in hexane) was then added to the solution dropwise over 10 minutes at 0 ºC. After stirring at room temperature for 30 minutes, 3-chloro-2-methylprop-1-ene (10.0 mL, 102.9 mmol) was added to the solution at 0 ºC. After stirring at room temperature for 20 hours, the reaction was quenched with saturated aqueous NH_4Cl solution. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford β-keto ester **S1** (15.6 g, 84.7 mmol, 82%) as a 12:1 mixture of keto form and enol form as a colorless oil. R_f = 0.40 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.75 (s, 1H), 4.67 (s, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.45 (s, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.12 (s, 1H), 4.99 (s, 1H). These spectra data were identical with those reported in the literature.[1)]

Methyl 6-methyl-3-oxohept-6-enoate (S2)



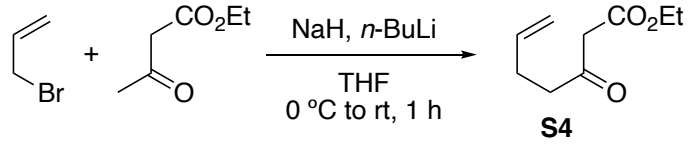
The titled compound **S2** was prepared according to the general procedure A using 3-chloro-2-methylprop-1-ene (1.10 mL, 11.3 mmol), methyl acetoacetate (2.57 mL, 22.6 mmol), NaH (949 mg, 23.7 mmol, 60 wt% in mineral oil), and *n*-BuLi (8.69 mL, 22.6 mmol, 2.6 M in hexane) in THF (50 mL). Purification of the crude product by silica gel column chromatography (hexane/EtOAc = 9:1) afforded β-keto ester **S2** (1.40 g, 8.21 mmol, 72%) as a colorless oil. R_f = 0.32 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.75 (s, 1H), 4.67 (s, 1H), 3.75 (s, 3H), 3.48 (s, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 167.6, 143.9, 110.4, 52.3, 49.0, 41.1. 31.0, 22.5; IR (neat, cm^{-1}): 2955, 2917, 1748, 1716, 1684, 1652, 1635, 1558, 1541, 1507, 1456, 1446, 1438, 1407, 1362, 1320, 1260, 1197, 1155, 891; HRMS (ESI) *m*/*z*: calcd. for $C_9H_{14}NaO_3$ ($[M+Na]^+$) 193.0835, found 193.0839.

tert-Butyl 6-methyl-3-oxohept-6-enoate (S3)



The titled compound **S3** was prepared according to the general procedure A using 3-chloro-2-methylprop-1-ene (1.10 mL, 11.3 mmol), *tert*-butyl acetoacetate (3.76 mL, 22.6 mmol), NaH (949 mg, 23.7 mmol, 60 wt% in mineral oil), and *n*-BuLi (8.69 mL, 22.6 mmol, 2.6 M in hexane) in THF (50 mL). Purification of the crude product by silica gel column chromatography (hexane/EtOAc = 9:1) afforded β-keto ester **S3** (1.72 g, 8.10 mmol, 73%) as a colorless oil. R_f = 0.53 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.74 (s, 1H), 4.67 (s, 1H), 3.36 (s, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.73 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 166.4, 144.1, 110.3, 81.9, 50.7, 41.0, 31.1, 28.0, 22.6; IR (neat, cm^{-1}): 3004, 2979, 2934, 1739, 1715, 1651, 1457, 1410, 1395, 1369, 1320, 1254, 1164, 1147, 890; HRMS (ESI) *m*/*z*: calcd. for $C_{12}H_{20}NaO_3$ ($[M+Na]^+$) 235.1305, found 235.1315.

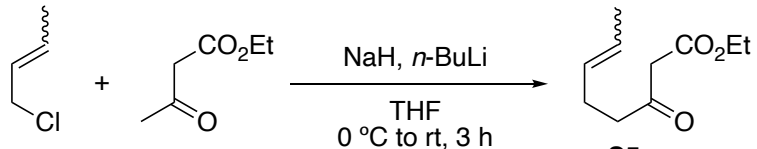
Ethyl 3-oxohept-6-enoate (S4)



S4

The titled compound **S4** was prepared according to the general procedure A using allyl bromide (1.28 mL, 14.8 mmol), ethyl acetoacetate (3.83 mL, 29.6 mmol), NaH (1.18 g, 29.6 mmol, 60 wt% in mineral oil), and *n*-BuLi (10.6 mL, 29.6 mmol, 2.80 M in hexane) in THF (50 mL). Purification of the crude product by automated column chromatography on silica gel (gradient: 4–17% EtOAc in hexanes) afforded β-keto ester **S4** (2.13 g, 12.5 mmol, 85%) as a 16:1 mixture of keto form and enol form as a colorless oil. R_f = 0.34 (hexanes/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.81 (ddt, *J* = 17.2, 10.4, 6.0 Hz, 1H), 5.05 (brd, *J* = 17.2, 1H), 5.00 (brd, *J* = 10.4 Hz, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.44 (s, 2H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.6 Hz, 2H), 1.28 (t, *J* = 7.2 Hz, 3H); enol form: δ 12.11 (s, 1H). These spectral data were identical with those reported in the literature.[2)]

Ethyl 3-oxooct-6-enoate (S5)

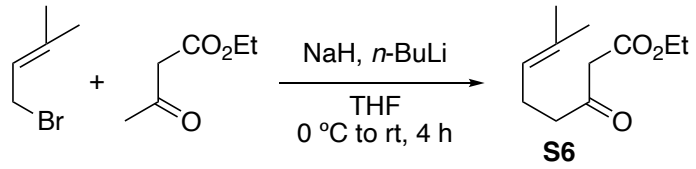


S5

The titled compound **S5** was prepared according to the general procedure A using 1-chloro-2-butene (1.51 mL, 15.4 mmol), ethyl acetoacetate (3.90 mL, 30.9 mmol), NaH (1.30 g, 30.9 mmol, 60 wt% in mineral oil), and *n*-BuLi (11.0 mL, 30.9 mmol, 2.80 M in hexane) in THF (75 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded β-keto ester **S5** (1.81 g, 9.82 mmol, 63%) as a ca 5:1 *E*/*Z* mixture and 9:1 keto form and enol form as a colorless oil. R_f = 0.47 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) *E* isomer of keto form: δ 5.53–5.30 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.43 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.31–2.25 (m, 2H), 1.66–1.62 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); characteristic peaks of *E* isomer of enol form: δ 12.11 (s, 1H), 4.99 (s, 1H), 2.36–2.31 (m, 2H); *Z* isomer of keto form: δ 5.53–5.30 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.44 (s, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.31–2.25 (m, 2H), 1.66–1.62 (m, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.2, 178.1, 172.7, 167.1, 129.2, 129.0, 128.1, 126.2, 126.1, 125.4, 89.2, 89.1, 61.29, 61.26, 61.24, 59.9, 49.34, 49.31, 42.7, 42.6, 35.1, 29.1, 26.4, 21.0, 17.8, 14.2, 14.0, 12.6; IR (neat, cm^{-1}): 2982, 2967, 2937, 2921, 2857, 1746, 1717, 1649, 1315, 1238, 1190, 1151, 1095, 1035, 968; HRMS

(ESI) *m*/*z*: calcd. for $C_{10}H_{16}NaO_3$ ([M+Na]$^+$) 207.0992, found 207.0988.

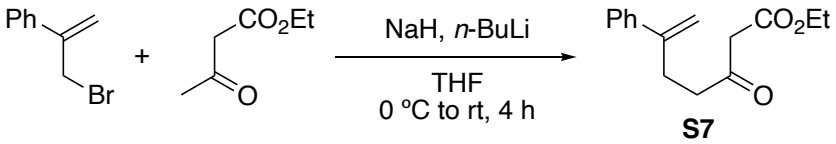
Ethyl 7-methyl-3-oxooct-6-enoate (S6)



S6

The titled compound **S6** was prepared according to the general procedure A using 1-bromo-3-methyl-2-butene (1.55 mL, 13.4 mmol), ethyl acetoacetate (3.44 mL, 26.8 mmol), NaH (1.07 g, 26.8 mmol, 60 wt% in mineral oil), and *n*-BuLi (9.60 mL, 26.8 mmol, 2.80 M in hexane) in THF (50 mL). Purification by automated column chromatography on silica gel (gradient: 4–14% EtOAc in hexanes) afforded β-keto ester **S6** (1.84 g, 9.28 mmol, 69%) as a 9:1 mixture of keto form and enol form as a colorless oil. R_f = 0.44 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.08–5.04 (m, 1H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.42 (s, 2H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.31–2.25 (m, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.28 (t, *J* = 7.2 Hz, 3H); enol form: δ 12.09 (s, 1H), 4.98 (s, 1H). These spectral data were identical with those reported in the literature.[3)]

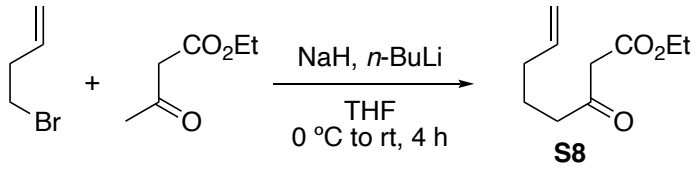
Ethyl 3-oxo-6-phenylhept-6-enoate (S7)



S7

The titled compound **S7** was prepared according to the general procedure A using (3-bromoprop-1-en-2-yl)benzene (2.03 g, 10.3 mmol), ethyl acetoacetate (2.60 mL, 20.6 mmol), NaH (864 mg, 21.6 mmol, 60 wt% in mineral oil), and *n*-BuLi (13.2 mL, 20.6 mmol, 1.56 M in hexane) in THF (50 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded β-keto ester **S7** (1.56 g, 6.33 mmol, 61%) as a 14:1 mixture of keto form and enol form as a colorless oil. R_f = 0.34 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 7.40–7.26 (m, 5H), 5.30 (s, 1H), 5.08 (s, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.38 (s, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.72–2.68 (m, 2H), 1.25 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.12 (s, 1H), 4.95 (s, 1H), 2.35 (t, *J* = 7.6 Hz, 2H). These spectral data were identical with those reported in the literature.[4)]

Ethyl 3-oxooct-7-enoate (S8)

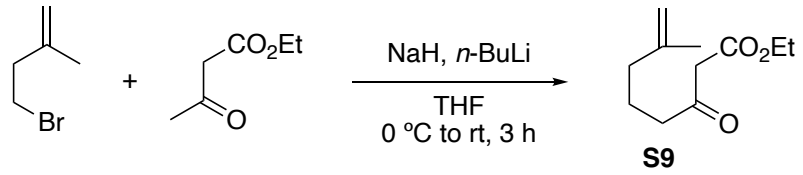


S8

The titled compound **S8** was prepared according to the general procedure A using 4-bromo-1-butene (1.50 mL, 14.8 mmol), ethyl acetoacetate (3.83 mL, 29.6 mmol), NaH (1.18 g, 29.6 mmol, 60 wt% in mineral oil), and *n*-BuLi (10.6 mL, 29.6 mmol, 2.80 M in hexane) in THF (50 mL). Purification by automated column chromatography on silica gel (gradient: 4–15% EtOAc in hexanes) to afford β-keto ester **S8** (1.83 g, 9.93 mmol, 69%) as a 14:1 mixture of keto form and enol form as a colorless oil. R_f = 0.37 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.82–5.71 (ddd, *J* = 17.2, 10.0, 7.2 Hz, 1H), 5.06–4.97 (m, 2H), 4.20 (q, *J* = 7.2 Hz, 2H), 3.43 (s, 2H), 2.55 (t, *J* = 7.6 Hz, 2H),

2.10–2.05 (m, 2H), 1.71 (tt, J = 7.6, 7.6 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); enol form: δ 12.11 (s, 1H), 2.21 (t, J = 7.6 Hz, 2H); These spectral data were identical with those reported in the literature.[5)]

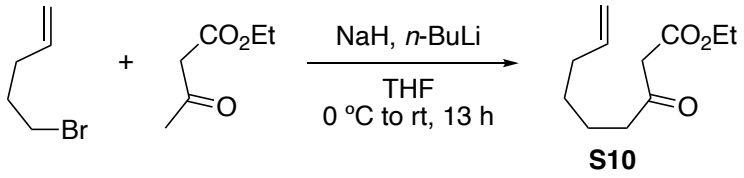
Ethyl 7-methyl-3-oxooct-7-enoate (S9)



S9

The titled compound **S9** was prepared according to the general procedure A using 4-bromo-2-methylbut-1-ene (1.53 g, 10.3 mmol), ethyl acetoacetate (2.60 mL, 20.6 mmol), NaH (864 mg, 21.6 mmol, 60 wt% in mineral oil), and *n*-BuLi (13.2 mL, 20.6 mmol, 1.56 M in hexane) in THF (50 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded β-keto ester **S9** (1.36 g, 6.86 mmol, 67%) as a 14:1 mixture of keto form and enol form as a colorless oil. R_f = 0.38 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.74 (s, 1H), 4.68 (s, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.43 (s, 2H), 2.54 (t, J = 7.6 Hz, 2H), 2.03 (t, J = 7.6 Hz, 2H), 1.75 (tt, J = 7.6, 7.6 Hz, 2H), 1.71 (s, 3H), 1.28 (t, J = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.11 (s, 1H), 4.99 (s, 1H), 2.19 (t, J = 7.6 Hz, 2H). These spectral data were identical with those reported in the literature.[6)]

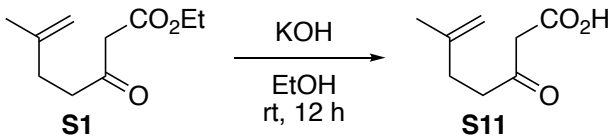
Ethyl 3-oxonon-8-enoate (S10)



S10

The titled compound **S10** was prepared according to the general procedure A using 5-bromo-1-pentene (1.00 g, 6.71 mmol), ethyl acetoacetate (1.71 mL, 13.4 mmol), NaH (564 mg, 14.1 mmol, 60 wt% in mineral oil), and *n*-BuLi (4.79 mL, 13.4 mmol, 2.80 M in hexane) in THF (25 mL). Purification by silica gel column chromatography (hexane/EtOAc = 25:1) afforded β-keto ester **S10** (877 mg, 4.42 mmol, 66%) as a colorless oil. R_f = 0.38 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.78 (ddt, J = 17.2, 10.4, 6.8 Hz, 1H), 5.00 (dq, J = 17.2, 1.6 Hz, 1H), 4.95 (brd, J = 10.4 Hz, 1H), 4.20 (q, J = 7.2 Hz, 2H), 3.43 (s, 2H), 2.55 (t, J = 7.2 Hz, 2H), 2.06 (q, J = 7.2 Hz, 2H), 1.62 (quin, J = 7.2 Hz, 2H), 1.40 (quin, J = 7.2 Hz, 2H), 1.28 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 167.2, 138.3, 114.7, 61.3, 49.3, 42.8, 33.4, 28.2, 22.8, 14.1; IR (neat, cm^{-1}): 2980, 2935, 2861, 1747, 1716, 1685, 1644, 1457, 1437, 1416, 1368, 1316, 1237, 1183, 1155, 1032, 912; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{18}NaO_3$ ([M+Na]$^+$) 221.1148, found 221.1141.

6-Methyl-3-oxohept-6-enoic acid (S11)



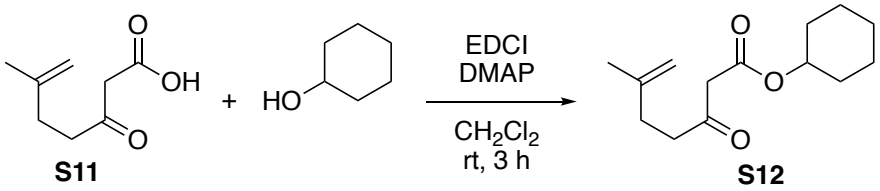
S1 **S11**

To a stirred solution of KOH (11.2 g, 200 mmol) in EtOH (190 mL) was added a solution of keto ester **S1** (7.29 g, 39.6 mmol) in EtOH (10 mL) at room temperature. After stirring at room temperature

for 12 hours, the reaction mixture was diluted with Et_2O. Then, aqueous 1 M HCl was added until pH of the solution turned to be 1. The separated organic layer was extracted with CH_2Cl_2 three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was washed with hexane twice to afford white crystalline solid. Hexanes in the solid was removed under reduced pressure to afford β-keto acid **S11** (3.66 g, 23.4 mmol, 59%) as a 7:1 mixture of keto form and enol form and as a pale yellow amorphas. R_f = 0.25 ($CHCl_3$/MeOH = 4:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.77 (s, 1H), 4.68 (s, 1H), 3.54 (s, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.74 (s, 3H); characteristic peaks of enol form: δ 11.82 (s, 1H), 5.06 (s, 1H), 4.72 (s, 1H), 2.58 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 203.4, 181.2, 176.5, 171.3, 143.8, 143.6, 110.9, 110.7, 88.4, 47.9, 41.3, 34.0, 33.6, 31.0, 22.5, 22.3; IR (neat, cm^{-1}): 3086, 2968, 2937, 2913, 1723, 1704, 1654, 1433, 1410, 1384, 1296, 1256, 1198, 1132, 1092, 893, 805, 742, 700, 630, 558; HRMS (ESI) *m/z*: calcd. for $C_8H_{12}NaO_3$ ([M+Na]$^+$) 179.0679, found 179.0670. β-Keto acid **S11** was subjected to the next reaction without further purification.

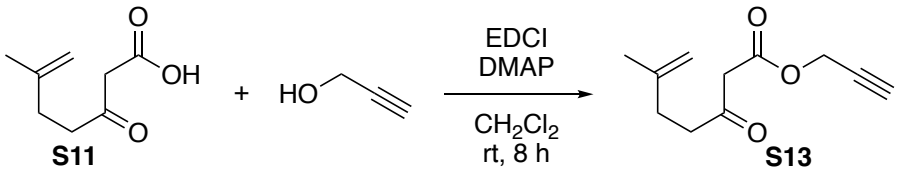
General Procedure B for Preparation of Malonates and β-Keto Esters

Cyclohexyl 6-methyl-3-oxohept-6-enoate (S12)



To a solution of cyclohexanol (120 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), and DMAP (24.4 mg, 0.20 mmol) in CH_2Cl_2 (8 mL) was added EDCI (479 mg, 2.50 mmol) at room temperature. The resultant solution was stirred at room temperature for three hours. The reaction was then quenched with saturated aqueous $NaHCO_3$ solution. The separated organic layer was washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by automated column chromatography on silica gel (gradient: 4–8% EtOAc in hexanes) to afford β-keto ester **S12** (210 mg, 0.883 mmol, 88%) as a 16:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.45 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) keto form: δ 4.84–4.80 (m, 1H), 4.74 (s, 1H), 4.67 (s, 1H), 3.43 (s, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.31 (t, *J* = 7.8 Hz, 2H), 1.88–1.85 (m, 2H), 1.74–1.68 (m, 5H), 1.56–1.52 (m, 1H), 1.47–1.41 (m, 2H), 1.40–1.33 (m, 2H), 1.29–1.23 (m, 1H); characteristic peaks of enol form: δ 12.20 (s, 1H), 4.98 (s, 1H), 4.71 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.4, 166.7, 144.0, 110.4, 73.9, 49.7, 41.1, 31.5, 31.1, 25.3, 23.7, 22.6; IR (neat, cm^{-1}): 2938, 2860, 1740, 1716, 1652, 1636, 1507, 1456, 1418, 1319, 1257, 1234, 1187, 1015, 891; HRMS (ESI) *m/z*: calcd. for $C_{14}H_{22}NaO_3$ ([M+Na]$^+$) 261.1461, found 261.1450.

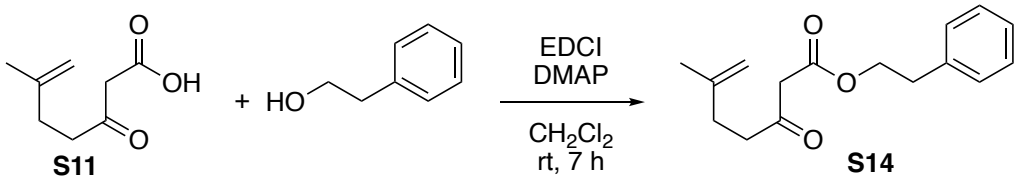
Prop-2-yn-1-yl 6-methyl-3-oxohept-6-enoate (S13)



The titled compound **S13** was prepared according to the general procedure B using 2-propyn-1-ol (224 mg, 4.00 mmol), β-keto acid **S11** (750 mg, 4.80 mmol), DMAP (97.7 mg, 0.800 mmol), and EDCI

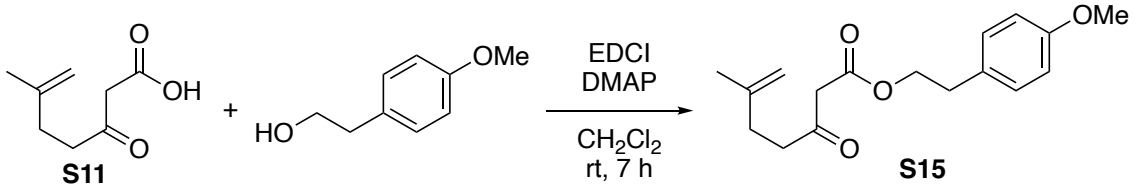
(1.92 g, 10.0 mmol) in CH_2Cl_2 (40 mL). Purification by automated column chromatography on silica gel (gradient: 4–19% EtOAc in hexanes) afforded β-keto ester **S13** (719 mg, 3.70 mmol, 93%) as a 9:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.36 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) keto form: δ 4.75 (brs, 1H), 4.74 (d, *J* = 3.0 Hz, 2H), 4.67 (brs, 1H), 3.52 (s, 2H), 2.71 (t, *J* = 7.8 Hz, 2H), 2.51 (t, *J* = 3.0 Hz, 1H), 2.31 (t, *J* = 7.8 Hz, 2H), 1.73 (s, 3H); characteristic peaks of enol form: δ 11.82 (s, 1H), 5.01 (s, 1H), 4.71 (s, 1H), 2.40–2.35 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.5, 179.4, 171.7, 166.3, 143.91, 143.87, 110.8, 110.5, 88.6, 77.7, 75.4, 74.9, 52.7, 51.4, 48.9, 41.24, 41.20, 34.0, 33.4, 31.0, 22.6, 22.4; IR (neat, cm^{-1}): 3289, 2971, 2938, 2920, 1751, 1718, 1651, 1439, 1411, 1372, 1315, 1273, 1249, 1183, 1149, 1000, 893; HRMS (EI) *m/z*: calcd. for $C_{11}H_{14}O_3$ ($[M]^+$) 194.0943, found 194.0943.

Phenethyl 6-methyl-3-oxohept-6-enoate (S14)



The titled compound **S14** was prepared according to the general procedure B using 2-phenylethanol (147 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 4–15% EtOAc in hexanes) afforded β-keto ester **S14** (169 mg, 0.65 mmol, 65%) as a colorless oil. R_f = 0.33 (hexanes/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31–7.29 (m, 2H), 7.24–7.20 (m, 3H), δ 4.74 (s, 1H), 4.65 (s, 1H), 4.36 (t, *J* = 7.2 Hz, 2H), 3.44 (s, 2H), 2.96 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.2 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.0, 167.1, 143.9, 137.4, 128.9, 128.6, 126.7, 110.4, 65.8, 49.2, 41.2, 35.0, 31.1, 22.6; IR (neat, cm^{-1}): 3030, 2966, 2936, 1746, 1716, 1652, 1497, 1455, 1437, 1411, 1377, 1317, 1237, 1184, 1151, 1130, 1087, 1000, 891, 749, 700; HRMS (ESI) *m/z*: calcd. for $C_{16}H_{20}NaO_3$ ($[M+Na]^+$) 283.1305, found 283.1299.

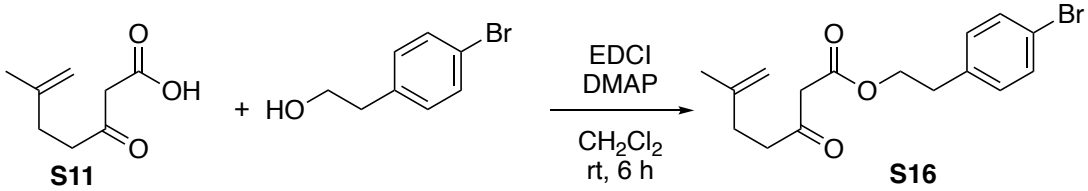
4-Methoxyphenethyl 6-methyl-3-oxohept-6-enoate (S15)



The titled compound **S15** was prepared according to the general procedure B using 4-methoxyphenethyl alcohol (184 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 4–18% EtOAc in hexanes) afforded β-keto ester **S15** (186.9 mg, 0.64 mmol, 64%) as a colorless oil. R_f = 0.27 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.74 (s, 1H), 4.65 (s, 1H), 4.32 (t, *J* = 6.8 Hz, 2H), 3.79 (s, 3H), 3.44 (s, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.64 (t, *J* = 7.2 Hz, 2H), 2.28 (t, *J* = 7.6 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.1, 167.1, 158.4, 143.9, 129.8, 129.4, 114.0, 110.4, 66.0, 55.2, 49.3, 41.1, 34.1, 31.1, 22.6; IR (neat, cm^{-1}): 2958, 2937, 2912, 2837, 1746, 1715, 1652,

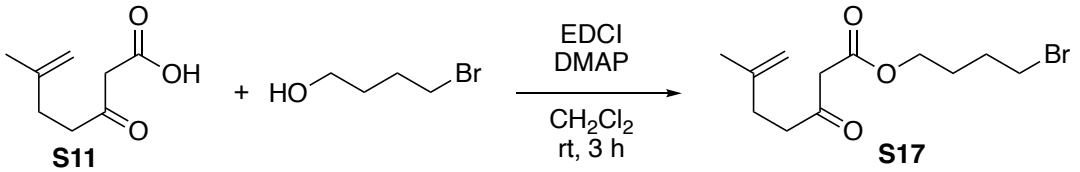
1614, 1515, 1457, 1444, 1411, 1376, 1362, 1318, 1302, 1248, 1178, 1152, 1114, 1035, 1008, 891, 828, 560, 501; HRMS (ESI) *m/z*: calcd. for $C_{17}H_{22}NaO_4$ ([M+Na]$^+$) 313.1410, found 313.1409.

4-Bromophenethyl 6-methyl-3-oxohept-6-enoate (S16)



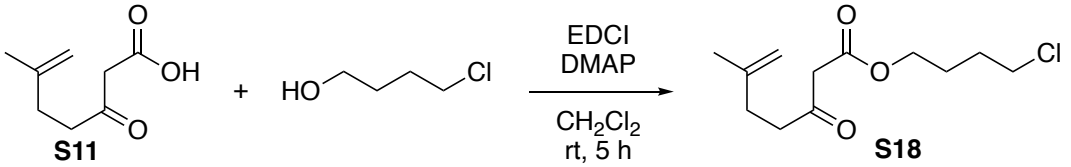
The titled compound **S16** was prepared according to the general procedure B using 2-(4-bromophenyl)ethyl alcohol (241 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.200 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 4–20% EtOAc in hexanes) afforded β-keto ester **S16** (312 mg, 0.919 mmol, 92%) as a 10:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.38 (hexane/EtOAc = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$) keto form: δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 4.74 (s, 1H), 4.65 (s, 1H), 4.33 (t, *J* = 6.6 Hz, 2H), 3.43 (s, 2H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.63 (t, *J* = 7.8 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.72 (s, 3H); characteristic peaks of enol form: δ 12.02 (s, 1H), 4.98 (s, 1H), 4.71 (s, 1H), 2.37–2.33 (m, 2H), 1.74 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.9, 178.6, 172.5, 167.0, 144.0, 143.8, 136.8, 136.4, 131.62, 131.57, 130.60, 130.57, 120.6, 120.5, 110.7, 110.4, 88.9, 65.3, 64.0, 49.1, 41.1, 34.5, 34.3, 34.0, 33.4, 31.0, 22.6, 22.4; IR (neat, cm^{-1}): 2966, 2935, 1746, 1716, 1651, 1636, 1626, 1489, 1406, 1376, 1244, 1184, 1150, 1129, 1072, 1010, 891, 815; HRMS (EI) *m/z*: calcd. for $C_{16}H_{19}BrO_3$ ([M]$^+$) 338.0518, found 338.0505.

4-Bromobutyl 6-methyl-3-oxohept-6-enoate (S17)



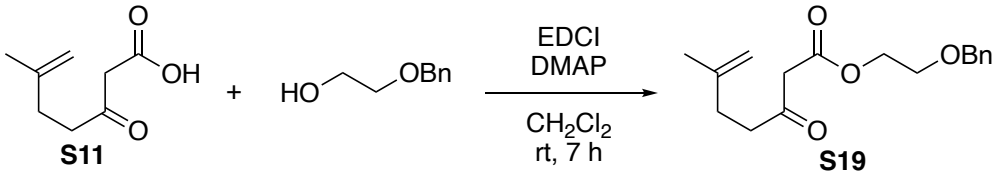
The titled compound **S17** was prepared according to the general procedure B using 4-bromo-1-butanol (153 mg, 1.00 mmol), β-keto acid **S11** (187 mg, 1.20 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 4–23% EtOAc in hexanes) afforded β-keto ester **S17** (266 mg, 0.91 mmol, 91%) as a 12:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.30 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.75 (s, 1H), 4.67 (s, 1H), 4.18 (t, *J* = 6.0 Hz, 2H), 3.47 (s, 2H), 3.43 (t, *J* = 6.0 Hz, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.98–1.91 (m, 2H), 1.86–1.79 (m, 2H), 1.74 (s, 3H); characteristic peaks of enol form: δ 12.05 (s, 1H), 5.00 (s, 1H), 4.71 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.0, 167.1, 143.9, 110.5, 64.3, 49.2, 41.3, 32.9, 31.1, 29.1, 27.2, 22.6; IR (neat, cm^{-1}): 2967, 2940, 1744, 1716, 1647, 1636, 1456, 1438, 1411, 1375, 1362, 1318, 1253, 1187, 1160, 1116, 1102, 1035, 889; HRMS (ESI) *m/z*: calcd. for $C_{12}H_{19}BrNaO_3$ ([M+Na]$^+$) 313.0410, found 313.0405.

4-Chlorobutyl 6-methyl-3-oxohept-6-enoate (S18)



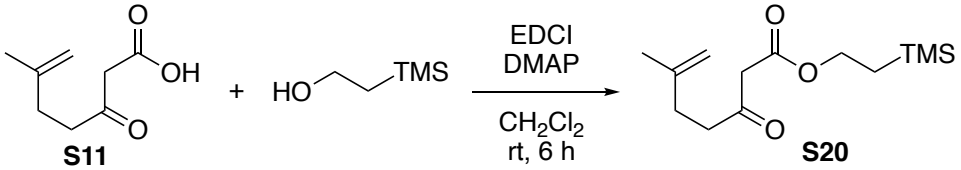
The titled compound **S18** was prepared according to the general procedure B using 4-chloro-1-butanol (130 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 4–32% EtOAc in hexanes) afforded β-keto ester **S18** (88.3 mg, 0.36 mmol, 36%) as a 16:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.28 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.75 (s, 1H), 4.67 (s, 1H), 4.19 (t, *J* = 6.0 Hz, 2H), 3.57 (t, *J* = 6.0 Hz, 2H), 3.47 (s, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 7.6 Hz, 2H), 1.88–1.78 (m, 4H), 1.74 (s, 3H); characteristic peaks of enol form: δ 12.06 (s, 1H), 5.00 (s, 1H), 4.72 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 202.1, 167.1, 143.9, 110.5, 64.5, 49.2, 44.4, 41.2, 31.1, 28.9, 25.9, 22.6; IR (neat, cm^{-1}): 2963, 2941, 1746, 1716, 1651, 1446, 1411, 1318, 1271, 1252, 1186, 1152, 891; HRMS (EI) *m*/*z*: calcd. for $C_{12}H_{19}ClO_3$ ($[M]^+$) 246.1023, found 246.1023.

2-Benzyloxyethyl 6-methyl-3-oxohept-6-enoate (S19)



The titled compound **S19** was prepared according to the general procedure B using 2-(benzyloxy)ethanol (184 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 8–32% EtOAc in hexanes) afforded β-keto ester **S19** (207 mg, 0.71 mmol, 71%) as a colorless oil. R_f = 0.50 (hexane/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): 7.38–7.27 (m, 5H), δ 4.74 (s, 1H), 4.66 (s, 1H), 4.56 (s, 2H), 4.33 (t, *J* = 4.8 Hz, 2H), 3.70–3.68 (m, 2H), 3.50 (s, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.30 (t, *J* = 7.6 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.9, 167.1, 143.9, 137.7, 128.4, 127.75, 127.69, 110.4, 73.1, 67.6, 64.3, 49.1, 41.1, 31.0, 22.5; IR (neat, cm^{-1}): 2966, 2934, 2903, 2864, 1747, 1716, 1652, 1455, 1411, 1376, 1362, 1315, 1254, 1187, 1150, 1107, 1038, 890, 740, 699; HRMS (ESI) *m*/*z*: calcd. for $C_{17}H_{22}NaO_4$ ($[M+Na]^+$) 313.1410, found 313.1401.

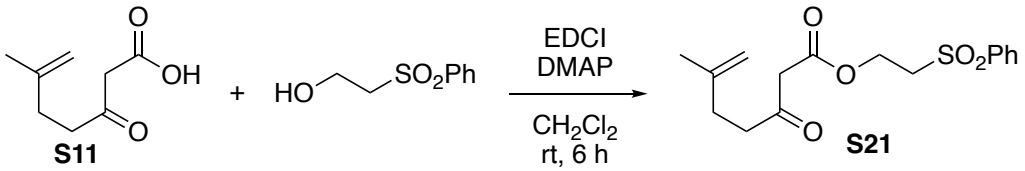
2-(Trimethylsilyl)ethyl 6-methyl-3-oxohept-6-enoate (S20)



The titled compound **S20** was prepared according to the general procedure B using 2-(trimethylsilyl)ethanol (142 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 4–12% EtOAc in hexanes) afforded β-keto ester **S20** (240 mg,

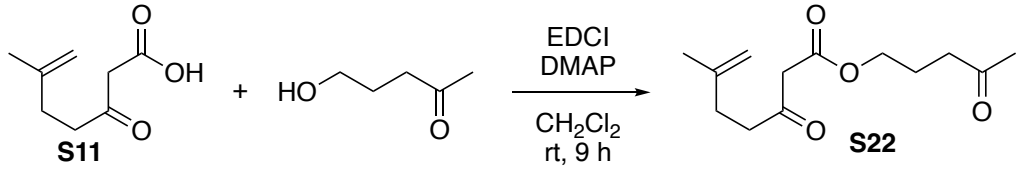
0.936 mmol, 93%) as a colorless oil. R_f = 0.58 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.75 (s, 1H), 4.67 (s, 1H), 4.25–4.21 (m, 2H), 3.44 (s, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.31 (t, *J* = 7.8 Hz, 2H), 1.73 (s, 3H), 1.04–0.99 (m, 2H), 0.04 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.2, 167.3, 144.0, 110.4, 63.8, 49.5, 41.2, 31.1, 22.6, 17.3, –1.5; IR (neat, cm^{-1}): 2954, 2900, 1743, 1717, 1652, 1457, 1418, 1316, 1251, 1235, 1178, 1152, 1043, 888, 860, 838; HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_{24}NaO_3Si$ ([M+Na]$^+$) 279.1387, found 279.1352.

2-(Phenylsulfonyl)ethyl 6-methyl-3-oxohept-6-enoate (S21)



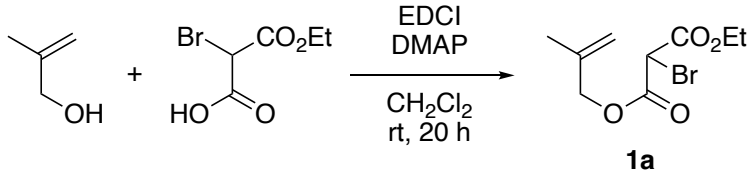
The titled compound **S21** was prepared according to the general procedure B using 2-(phenylsulfonyl)ethanol (223 mg, 1.20 mmol), β-keto acid **S11** (156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol), and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 12–61% EtOAc in hexanes) to afford β-keto ester **S21** (272 mg, 0.838 mmol, 84%) as a 14:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.43 (hexane/EtOAc = 1:1); ^{1}H NMR (600 MHz, $CDCl_3$) keto form: δ 7.93 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.68 (brt, *J* = 8.4 Hz 1H), 7.59 (brt, *J* = 8.4 Hz, 2H), 4.75 (s, 1H), 4.64 (s, 1H), 4.48 (t, *J* = 6.0 Hz, 2H), 3.47 (t, *J* = 6.0 Hz, 2H), 3.28 (s, 2H), 2.62 (t, *J* = 7.2 Hz, 2H), 2.27 (t, *J* = 7.2 Hz, 2H), 1.72 (s, 3H); characteristic peaks of enol form: δ 11.71 (s, 1H), 4.72 (s, 1H), 4.68 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 201.4, 179.3, 171.6, 166.5, 143.9, 143.8, 139.5, 139.3, 134.0, 133.9, 129.4, 129.3, 128.2, 110.8, 110.5, 88.3, 58.2, 57.2, 55.2, 54.8, 48.6, 41.2, 34.0, 33.4, 31.0, 22.6, 22.4; IR (neat, cm^{-1}): 2970, 2934, 1749, 1716, 1652, 1447, 1410, 1322, 1259, 1186, 1145, 1087, 1000, 893, 730, 689, 528; HRMS (ESI) *m*/*z*: calcd. for $C_{16}H_{20}NaO_5S$ ([M+Na]$^+$) 347.0924, found 347.0915.

4-Oxopentyl 6-methyl-3-oxohept-6-enoate (S22)



The titled compound **S22** was prepared according to the general procedure B using 5-hydroxy-2-pentanone (123 mg, 1.20 mmol), β-keto acid **S11 (**156 mg, 1.00 mmol), DMAP (24.4 mg, 0.20 mmol) and EDCI (479 mg, 2.50 mmol) in CH_2Cl_2 (8 mL). Purification by automated column chromatography on silica gel (gradient: 8–46% EtOAc in hexanes) to afford β-keto ester **S22** (181 mg, 0.75 mmol, 75%) as a 14:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.36 (hexane/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.75 (s, 1H), 4.71 (s, 1H), 4.16 (t, *J* = 6.4 Hz, 2H), 3.46 (s, 2H), 2.69 (t, *J* = 7.6 Hz, 2H), 2.54 (t, *J* = 7.6 Hz, 2H), 2.31 (t, *J* = 8.4 Hz, 2H), 2.16 (s, 3H), 1.93 (quin, *J* = 6.8 Hz, 2H), 1.74 (s, 3H); characteristic peaks of enol form: δ 12.06 (s, 1H), 4.99 (s, 1H), 4.71 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.6, 207.5, 202.1, 178.5, 172.6, 167.1, 144.0, 143.9, 110.7, 110.4, 88.9, 67.4, 64.4, 63.0, 49.1, 41.2, 39.8, 39.6, 34.0, 33.4, 31.0, 29.9, 22.8, 22.59, 22.57, 22.4; IR (neat, cm^{-1}): 2968, 2935, 2904, 1746, 1715, 1652, 1456, 1436, 1416, 1362, 1318, 1266, 1186, 1168; HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_{20}NaO_4$ ([M+Na]$^+$) 263.1254, found 263.1251.

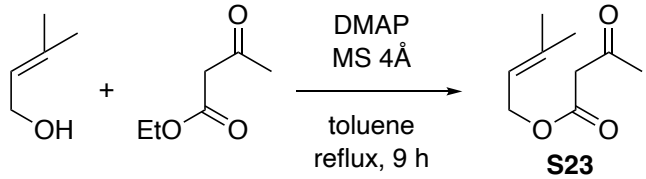
1-Ethyl 3-(2-methylallyl) 2-bromomalonate (1a)



1a

The titled compound **1a** was prepared according to the general procedure B using β-methallyl alcohol (380 mg, 5.26 mmol), 2-bromo-3-ethoxy-3-oxopropanoic acid (370 mg, 1.75 mmol)[7], DMAP (107 mg, 0.877 mmol), and EDCI (817 mg, 5.26 mmol) in CH_2Cl_2 (9 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded malonate **1a** (217 mg, 0.823 mmol, 47%) as a colorless oil. R_f = 0.42 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.03 (s, 1H), 4.98 (s, 1H), 4.87 (s, 1H), 4.64 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.77 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.3, 138.7, 114.2, 70.1, 63.3, 42.2, 19.3, 13.8; IR (neat, cm^{-1}): 2984, 2942, 2876, 1767, 1745, 1659, 1463, 1447, 1369, 1304, 1262, 1245, 1205, 1146, 1096, 1027, 1001, 964, 910, 864, 649; HRMS (ESI) *m*/*z*: calcd. for $C_9H_{13}BrNaO_4$ ([M+Na]$^+$) 286.9889, found 286.9895.

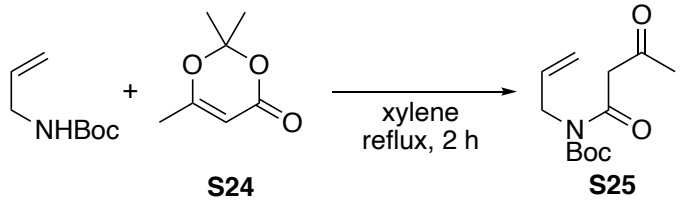
3-Methylbut-2-en-1-yl 3-oxobutanoate (S23)



S23

A mixture of ethyl acetoacetate (5.21 g, 40.0 mmol), 3-methyl-2-buten-1-ol (3.45 g, 40.0 mmol), and 4-(dimethylamino)pyridine (4.89 g, 40.0 mmol) in dry toluene (200 mL) and MS4Å (70 g) were placed in the vessel. The mixture was then heated at reflux over nine hours. After cooling to room temperature, the solution was washed with saturated aqueous NH_4Cl solution twice and dried over $MgSO_4$. Toluene was removed by evaporation, and the residue was purified by automated column chromatography on silica gel (gradient: 4–26% EtOAc in hexanes) to afford β-keto ester **S23** (5.63 g, 33.1 mmol, 83%) as a 11:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.38 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.37–5.33 (m, 1H), 4.64 (d, *J* = 7.2 Hz, 2H), 3.45 (s, 2H), 2.27 (s, 3H), 1.77 (s, 3H), 1.72 (s, 3H); enol form: δ 12.11 (s, 1H), 4.98 (s, 1H), 1.95 (s, 3H); These spectral data were identical with those reported in the literature.[8]

***tert*-Butyl allyl(3-oxobutanoyl)carbamate (S25)**

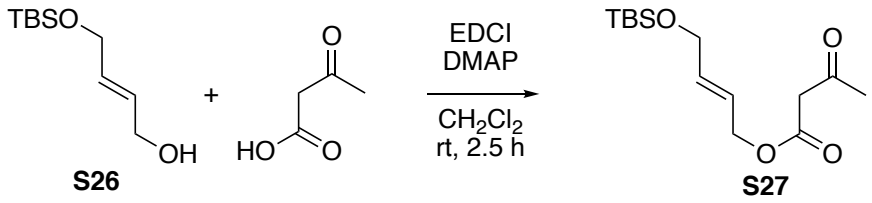


S24 **S25**

To a suspension of *tert*-butyl allylcarbamate (7.74 g, 45.0 mmol) in xylene (9.0 mL) was added 2,2,6-trimethyl-1,3-dioxin-4-one (**S24**) (8.32 g, 58.5 mmol) dropwise over five minutes at room temperature. After stirring vigorously for 2 hours at 150 ºC, the resulting mixture was cooled to room

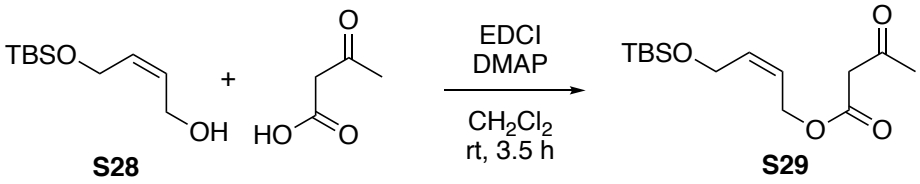
temperature and directly subjected column chromatography on silica gel (hexane/EtOAc = 5:1) to afford **S25** (6.87 g, 28.4 mmol, 63%) as a colorless oil. R_f = 0.25 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.81 (ddd, *J* = 17.6, 10.4, 5.6 Hz, 1H), 5.22–5.17 (m, 1H), 5.15–5.11 (m, 1H), 4.33–4.31 (m, 2H), 4.00 (s, 2H), 2.24 (s, 3H), 1.47 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.4, 168.9, 153.0, 132.9, 116.5, 83.4, 53.9, 46.1, 30.0, 27.9; IR (neat, cm^{-1}): 3006, 2981, 2935, 1732, 1698, 1626, 1457, 1434, 1395, 1368, 1320, 1296, 1241, 1195, 1147, 1118, 1088, 852; HRMS (ESI) *m*/*z*: calcd. for $C_{12}H_{19}NNaO_4$ ([M+Na]$^+$) 264.1206, found 264.1201.[9)]

(*E*)-4-(*tert*-Butyldimethylsilyloxy)but-2-en-1-yl 3-oxobutanoate (S27)



The titled compound **S27** was prepared according to the general procedure B using monoprotected *trans*-2-butenediol **S26** (500 mg, 2.47 mmol), acetoacetic acid (378 mg, 3.71 mmol), DMAP (60.4 mg, 0.494 mmol), and EDCI (1.18 g, 6.18 mmol) in CH_2Cl_2 (25 mL). Purification by automated column chromatography on silica gel (gradient: 4–22% EtOAc in hexanes) afforded **S27** (672 mg, 2.35 mmol, 95%) as a 8:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.35 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) keto form: δ 5.90–5.78 (m, 2H), 4.66–4.63 (m, 2H), 4.20–4.18 (m, 2H), 3.47 (s, 2H), 2.27 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); characteristic peaks of enol form: δ 12.0 (s, 1H), 5.00 (s, 1H), 1.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.4, 175.7, 172.3, 166.8, 134.9, 134.1, 123.5, 122.8, 89.6, 65.3, 63.9, 62.9, 62.7, 50.1, 30.1, 25.9, 25.8, 21.2, 18.4, –5.27, –5.29; IR (neat, cm^{-1}): 2955, 2930, 2887, 2857, 1746, 1721, 1362, 1316, 1255, 1141, 1106, 970, 837, 780; HRMS (ESI) *m*/*z*: calcd. for $C_{14}H_{26}NaO_4Si$ ([M+Na]$^+$) 309.1493, found 309.1496.

(*Z*)-4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl 3-oxobutanoate (S29)

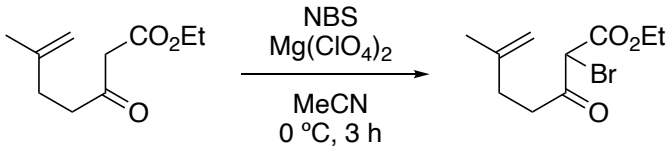


The titled compound **S29** was prepared according to the general procedure B using monoprotected *cis*-2-butenediol **S28** (810 mg, 4.00 mmol), acetoacetic acid (613 mg, 6.00 mmol), DMAP (97.8 mg, 0.800 mmol), and EDCI (1.91 g, 10.0 mmol) in CH_2Cl_2 (40 mL). Purification by silica gel column chromatography (hexane/EtOAc = 10:1) afforded β-keto ester **S29** (1.10 g, 3.84 mmol, 96%) as a 11:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.36 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) keto form: δ 5.78–5.72 (m, 1H), 5.60–5.55 (m, 1H), 4.73 (d, *J* = 4.4 H, 2H), 4.28 (d, *J* = 4.0 Hz, 2H), 3.46 (s, 2H), 2.27 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); characteristic peaks of enol form: δ 12.02 (s, 1H), 4.99 (s, 1H), 1.96 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.3, 175.7, 172.3, 166.9, 134.6, 134.2, 124.1, 123.5, 89.6, 61.3, 59.9, 59.6, 59.5, 50.0, 30.2, 25.9, 21.2, 18.3, –5.22, –5.24; IR (neat, cm^{-1}): 2955, 2930, 2886, 2857, 1745, 1720, 1463, 1408, 1361, 1312, 1255, 1151, 1091, 838, 778; HRMS (ESI) *m*/*z*: calcd. for $C_{14}H_{26}NaO_4Si$ ([M+Na]$^+$) 309.1493, found 309.1493.

3. Preparation of α-Bromo-β-keto Esters

General Procedure C for Bromination of β-Keto Esters

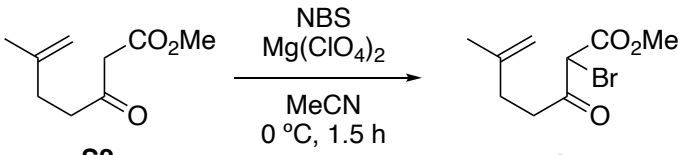
Ethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5a)



S1 **5a**

To a solution of β-keto ester **S1** (599 mg, 3.25 mmol) in MeCN (60 mL) was added magnesium perchlorate (239 mg, 1.07 mmol). The mixture was stirred for five minutes at room temperature. NBS (578 mg, 3.25 mmol) was then added to the stirred solution portionwise over three hours at 0 ºC. After stirring for additional 20 minutes, the resulting mixture was diluted with brine and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine twice, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 50:1) to afford α-bromo-β-keto ester **5a** (635 mg, 2.41 mmol, 74%) as a 10:1 mixture of keto form and enol form as a colorless oil. R_f = 0.42 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.81 (s, 1H), 4.77 (s, 1H), 4.69 (s, 1H), 4.29 (q, *J* = 7.2 Hz, 2H), 2.92 (td, *J* = 7.6, 2.0 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.75 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.82 (s, 1H), 2.71 (t, *J* = 7.2 Hz, 2H), 1.78 (s, 3H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.1, 165.1, 143.6, 110.7, 63.2, 48.8, 37.4, 31.4, 22.5, 13.9; IR (neat, cm^{-1}): 2981, 2939, 2909, 1758, 1730, 1651, 1445, 1369, 1302, 1269, 1146, 1022, 892; HRMS (ESI) *m*/*z*: calcd. for $C_{10}H_{15}BrNaO_3$ ([M+Na]$^+$) 285.0097, found 285.0091.

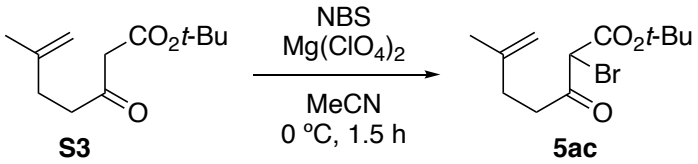
Methyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ab)



S2 **5ab**

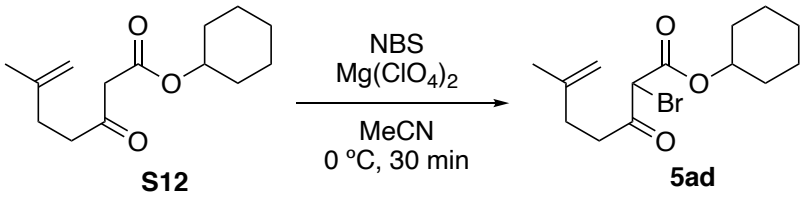
The titled compound **5ab** was prepared according to the general procedure C using **S2** (307 mg, 1.80 mmol), magnesium perchlorate (133 mg, 0.595 mmol), and NBS (321 mg, 1.80 mmol) in MeCN (15 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ab** (256 mg, 1.03 mmol, 57%) as a 33:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.49 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.82 (s, 1H), 4.77 (s, 1H), 4.69 (s, 1H), 3.84 (s, 3H), 2.94–2.90 (m, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.72 (s, 3H); characteristic peaks of enol form: δ 12.73 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 165.6, 143.5, 110.7, 53.8, 48.3, 37.4, 31.4, 22.5; IR (neat, cm^{-1}): 3078, 2956, 2912, 2854, 1733, 1651, 1603, 1437, 1303, 1279, 1233, 1158, 1076, 996, 892; HRMS (EI) *m*/*z*: calcd. for $C_9H_{13}BrO_3$ ([M]$^+$) 248.0048, found 248.0045.

***tert*-Butyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ac)**



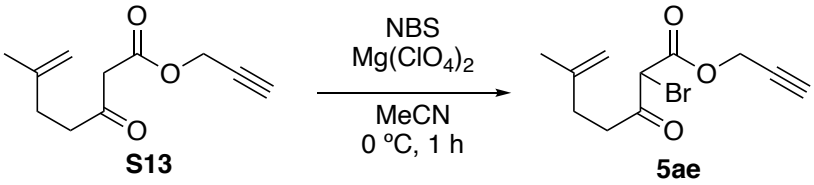
The titled compound **5ac** was prepared according to the general procedure C using **S3** (383 mg, 1.80 mmol), magnesium perchlorate (133 mg, 0.595 mmol), and NBS (321 mg, 1.80 mmol) in MeCN (15 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ac** (339 mg, 1.16 mmol, 65%) as a 20:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.62 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.76 (s, 1H), 4.72 (s, 1H), 4.70 (s, 1H), 3.00–2.82 (m, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.75 (s, 3H), 1.49 (s, 9H); characteristic peaks of enol form: δ 12.92 (s, 1H), 2.68 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.4, 164.0, 143.7, 110.6, 84.4, 50.3, 37.3, 31.5, 27.7, 22.5; IR (neat, cm^{-1}): 2980, 2936, 1726, 1457, 1371, 1306, 1258, 1150, 891, 846; HRMS (ESI) *m/z*: calcd. for $C_{12}H_{19}BrNaO_3$ ($[M+Na]^+$) 313.0410, found 313.0403.

Cyclohexyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ad)



The titled compound **5ad** was prepared according to the general procedure C using **S12** (119 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ad** (85.4 mg, 0.269 mmol, 54%) as a colorless oil. R_f = 0.57 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.91–4.86 (m, 1H), 4.79 (s, 1H), 4.76 (s, 1H), 4.69 (s, 1H), 2.96–2.86 (m, 2H), 2.34 (t, *J* = 7.8 Hz, 2H), 1.87–1.84 (m, 2H), 1.78–1.70 (m, 5H), 1.56–1.47 (m, 3H), 1.44–1.35 (m, 2H), 1.33–1.26 (m, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.2, 164.6, 143.7, 110.7, 75.9, 49.3, 37.4, 31.5, 31.1, 25.2, 23.4, 22.6; IR (neat, cm^{-1}): 2938, 2860, 1747, 1732, 1718, 1652, 1558, 1541, 1507, 1456, 1294, 1233, 1161, 1010, 892; HRMS (ESI) *m/z*: calcd. for $C_{14}H_{21}BrNaO_3$ ($[M+Na]^+$) 339.0566, found 339.0583.

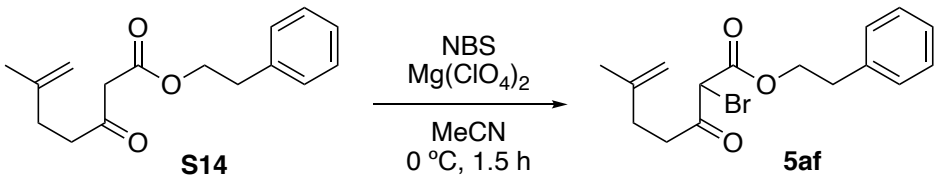
Prop-2-yn-1-yl 2-bromo-6-methyl-3-oxohept-6-enoate (5ae)



The titled compound **5ae** was prepared according to the general procedure C using **S13** (291 mg, 1.50 mmol), magnesium perchlorate (112 mg, 0.500 mmol), and NBS (267 mg, 1.50 mmol) in MeCN (60 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ae** (143 mg, 0.525 mmol, 35%) as a colorless oil. R_f = 0.36 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.85 (s, 1H), 4.81 (d, *J* = 2.8 Hz, 2H), 4.77 (s, 1H), 4.70 (s, 1H),

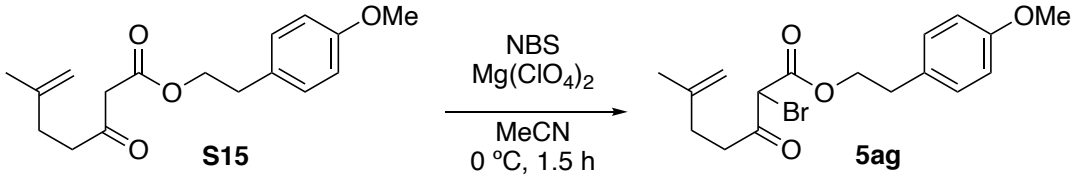
2.93 (t, J = 7.6 Hz, 2H), 2.55 (t, J = 2.8 Hz, 1H), 2.35 (t, J = 7.6 Hz, 2H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 164.4, 143.5, 110.8, 76.2, 76.1, 54.2, 48.1, 37.5, 31.3, 22.5; IR (neat, cm^{-1}): 3292, 3079, 2971, 2940, 2916, 2857, 2132, 1730, 1651, 1438, 1372, 1275, 1136, 991, 893, 681; HRMS (ESI) m/z: calcd. for $C_{11}H_{13}BrNaO_3$ ($[M+Na]^+$) 294.9940, found 294.9945.

Phenethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5af)



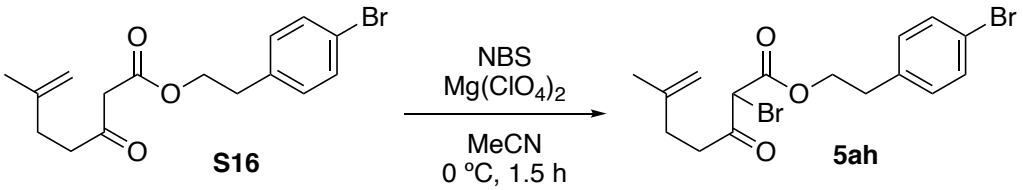
The titled compound **5af** was prepared according to the general procedure C using **S14** (130 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5af** (109 mg, 0.321 mmol, 64%) as a colorless oil. R_f = 0.44 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.20 (m, 5H), 4.78 (s, 1H), 4.75 (s, 1H), 4.66 (s, 1H), 4.44 (t, J = 7.2 Hz, 2H), 2.98 (t, J = 7.2 Hz, 2H), 2.90–2.74 (m, 2H), 2.28 (t, J = 7.2 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 165.1, 143.5, 136.9, 128.9, 128.6, 126.8, 110.7, 67.3, 48.7, 37.3, 34.7, 31.4, 22.5; IR (neat, cm^{-1}): 2967, 2939, 1758, 1733, 1652, 1497, 1456, 1376, 1296, 1276, 1199, 1157, 995, 750, 700; HRMS (ESI) m/z: calcd. for $C_{16}H_{19}BrNaO_3$ ($[M+Na]^+$) 361.0410, found 361.0409.

4-Methoxyphenethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ag)



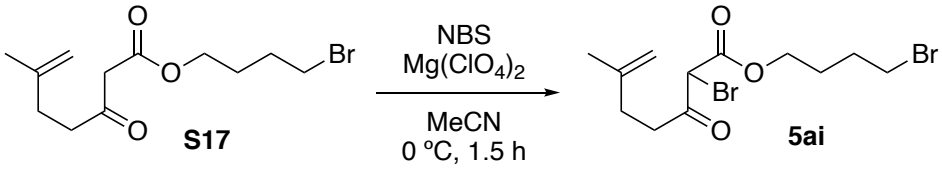
The titled compound **5ag** was prepared according to the general procedure C using **S15** (145 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ag** (111 mg, 0.300 mmol, 61%) as a colorless oil. R_f = 0.40 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (d, J = 8.8 Hz, 2H), 6.84 (d, J = 8.8 Hz, 2H), 4.78 (s, 1H), 4.75 (s, 1H), 4.66 (s, 1H), 4.39 (t, J = 7.2 Hz, 2H), 3.79 (s, 3H), 2.92 (t, J = 7.2 Hz, 2H), 2.89–2.74 (m, 2H), 2.29 (t, J = 7.2 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 165.1, 158.5, 143.6, 129.9, 128.9, 114.0, 110.6, 67.6, 55.2, 48.7, 37.3, 33.9, 31.4, 22.5; IR (neat, cm^{-1}): 2960, 2937, 2912, 1732, 1652, 1613, 1514, 1457, 1444, 1301, 1248, 1178, 1157, 1035, 825; HRMS (ESI) m/z: calcd. for $C_{17}H_{21}BrNaO_4$ ($[M+Na]^+$) 391.0515, found 391.0515.

4-Bromophenethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ah)



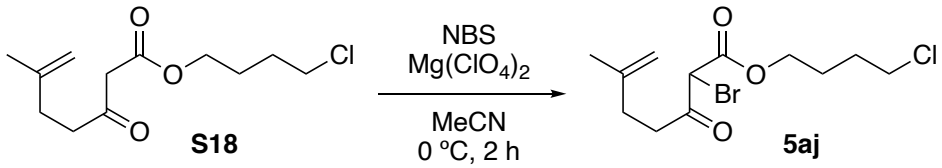
The titled compound **5ah** was prepared according to the general procedure C using **S16** (170 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ah** (118 mg, 0.282 mmol, 56%) as a colorless oil. R_f = 0.43 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 4.78 (s, 1H), 4.76 (s, 1H), 4.66 (s, 1H), 4.41 (td, *J* = 6.8, 1.6 Hz, 2H), 2.94 (t, *J* = 6.8 Hz, 2H), 2.90–2.77 (m, 2H), 2.29 (t, *J* = 7.6 Hz, 2H), 1.73 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.0, 165.0, 143.5, 136.0, 131.7, 130.6, 120.8, 110.7, 66.9, 48.5, 37.4, 34.2, 31.4, 22.6; IR (neat, cm^{-1}): 2966, 2936, 2922, 1733, 1718, 1489, 1457, 1437, 1397, 1279, 1145, 1072, 1011; HRMS (EI) *m*/*z*: calcd. for $C_{16}H_{18}Br_2O_3$ ([M]$^+$) 415.9623, found 415.9621.

4-Bromobutyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ai)



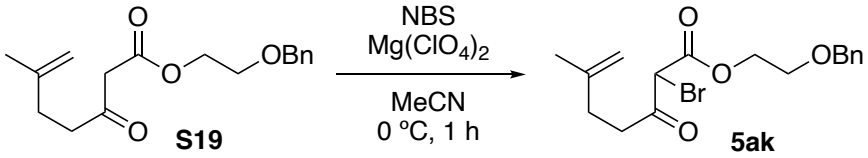
The titled compound **5ai** was prepared according to the general procedure C using **S17** (40.4 mg, 139 μmol), magnesium perchlorate (10.2 mg, 45.8 μmol), and NBS (24.7 mg, 139 μmol) in MeCN (6 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5ai** (31.7 mg, 85.7 μmol, 62%) as a colorless oil. R_f = 0.44 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.82 (s, 1H), 4.77 (s, 1H), 4.70 (s, 1H), 4.27 (t, *J* = 6.4 Hz, 2H), 3.44 (t, *J* = 6.4 Hz, 2H), 2.95–2.91 (m, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.99–1.92 (m, 2H), 1.90–1.82 (m, 2H), 1.75 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 165.2, 143.6, 110.7, 66.0, 48.4, 37.6, 32.8, 31.4, 28.9, 27.0, 22.6; IR (neat, cm^{-1}): 2964, 2937, 2920, 2852, 1732, 1651, 1443, 1376, 1295, 1281, 1254, 1157, 1029, 891; HRMS (EI) *m*/*z*: calcd. for $C_{12}H_{18}Br_2O_3$ ([M]$^+$) 367.9623, found 367.9627.

4-Bromobutyl 2-bromo-6-methyl-3-oxohept-6-enoate (5aj)



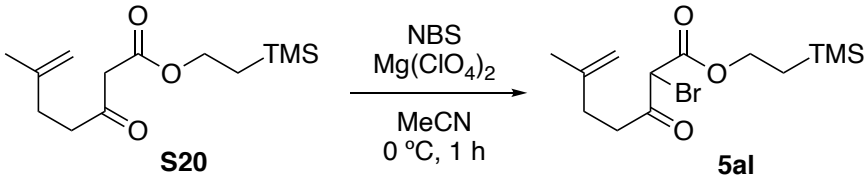
The titled compound **5aj** was prepared according to the general procedure C using **S18** (61.7 mg, 0.250 mmol), magnesium perchlorate (18.6 mg, 0.0833 mmol), and NBS (44.5 mg, 0.250 mmol) in MeCN (10 mL). Purification by automated column chromatography on silica gel (gradient: 4–14% EtOAc in hexanes) afforded α-bromo-β-keto ester **5aj** (61.0 mg, 0.187 mmol, 75%) as a 33:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.29 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.82 (s, 1H), 4.77 (s, 1H), 4.69 (s, 1H), 4.29–4.26 (m, 2H), 3.61–3.55 (m, 2H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 1.88–1.86 (m, 4H), 1.75 (s, 3H); characteristic peaks of enol form: δ 12.74 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.2, 165.2, 143.6, 110.7, 66.2, 48.5, 44.2, 37.6, 31.4, 28.8, 25.8, 22.6; IR (neat, cm^{-1}): 2964, 2943, 1758, 1732, 1651, 1445, 1376, 1298, 1281, 1232, 1158, 892; HRMS (EI) *m*/*z*: calcd. for $C_{12}H_{18}BrClO_3$ ([M]$^+$) 324.0128, found 324.0136.

2-(Benzyloxy)ethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5ak)



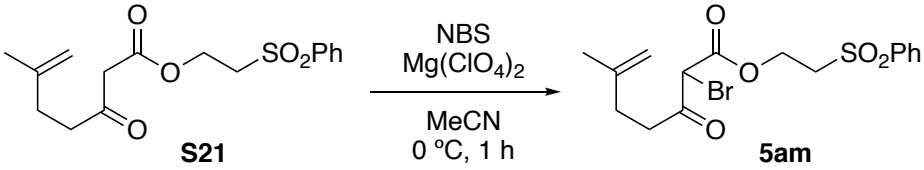
The titled compound **5ak** was prepared according to the general procedure C using **S19** (145.2 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.166 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 20:1) afforded β-keto ester **5ak** (148.7 mg, 0.403 mmol, 81%) as a colorless oil. R_f = 0.25 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38–7.28 (m, 5H), 4.85 (s, 1H), 4.75 (s, 1H), 4.68 (s, 1H), 4.55 (s, 2H), 4.42–4.39 (m, 2H), 3.71–3.69 (m, 2H), 2.94–2.90 (m, 2H), 2.32 (t, *J* = 7.6 Hz, 2H), 1.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 165.2, 143.6, 137.6, 128.5, 127.8, 127.7, 110.7, 73.2, 67.4, 66.0, 48.7, 37.4, 31.3, 22.5; IR (neat, cm^{-1}): 2967, 2937, 2904, 2864, 1733, 1454, 1361, 1296, 1206, 1159, 1125, 1107, 1026, 739, 698; HRMS (ESI) *m*/*z*: calcd. for $C_{17}H_{21}BrNaO_4$ ([M+Na]$^+$) 391.0515, found 391.0509.

2-(Trimethylsilyl)ethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5al)



The titled compound **5al** was prepared according to the general procedure C using **S20** (128 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by silica gel column chromatography (hexane/EtOAc = 100:1) afforded α-bromo-β-keto ester **5al** (101 mg, 0.302 mmol, 60%) as a colorless oil. R_f = 0.57 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.78 (s, 1H), 4.76 (s, 1H), 4.70 (s, 1H), 4.33–4.30 (m, 2H), 2.96–2.86 (m, 2H), 2.34 (t, *J* = 7.8 Hz, 2H), 1.75 (s, 3H), 1.06–1.03 (m, 2H), 0.06 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 198.2, 165.3, 143.6, 110.7, 65.8, 48.9, 37.4, 31.4, 22.6, 17.2, –1.6; IR (neat, cm^{-1}): 2955, 2900, 1732, 1652, 1456, 1297, 1252, 1177, 1157, 1042, 938, 889, 860, 838, 695; HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_{23}BrNaO_3Si$ ([M+Na]$^+$) 357.0492, found 357.0509.

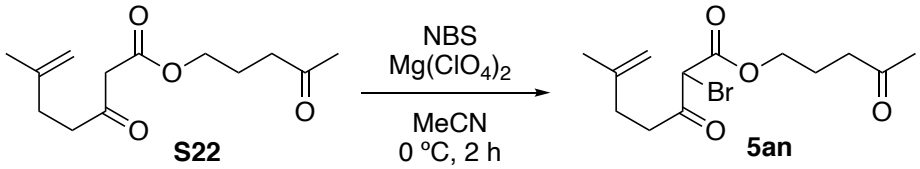
2-(Phenylsulfonyl)ethyl 2-bromo-6-methyl-3-oxohept-6-enoate (5am)



The titled compound **5am** was prepared according to the general procedure C using **S21** (162 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by automated column chromatography on silica gel (gradient: 12–61% EtOAc in hexanes) afforded α-bromo-β-keto ester **5am** (168 mg, 0.416 mmol, 83%) as a colorless oil. R_f = 0.54 (hexane/EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (brd, *J* = 8.4 Hz, 2H), 7.70 (ddt, *J* = 8.0, 8.0, 0.8 Hz, 1H), 7.62 (dd, *J* =7.6, 7.6 Hz, 2H), 4.77 (s, 1H), 4.68 (s, 1H), 4.60 (s, 1H), 4.56 (td, *J* = 6.4, 2.4 Hz, 2H), 3.49 (td, *J* =6.0, 2.0 Hz, 2H), 2.95–2.80 (m, 2H), 2.31 (t, *J* = 7.2 Hz, 2H),

1.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 164.6, 143.4, 139.0, 134.1, 129.5, 128.1, 110.7, 59.7, 54.5, 47.6, 37.5, 31.3, 22.5; IR (neat, cm^{-1}): 1760, 1748, 1733, 1717, 1652, 1541, 1507, 1447, 1322, 1296, 1145, 1087, 731, 690; HRMS (ESI) *m*/*z*: calcd. for $C_{16}H_{19}BrNaO_5S$ ($[M+Na]^+$) 425.0029, found 425.0029.

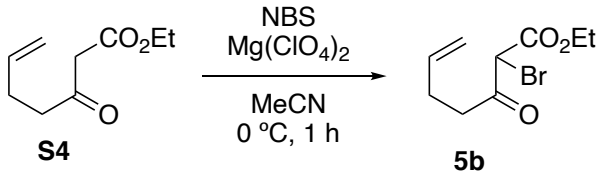
4-Oxopentyl 2-bromo-6-methyl-3-oxohept-6-enoate (5an)



S22 **5an**

The titled compound **5an** was prepared according to the general procedure C using **S22** (120 mg, 0.500 mmol), magnesium perchlorate (37.2 mg, 0.167 mmol), and NBS (89.0 mg, 0.500 mmol) in MeCN (20 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 4:1) afforded α-bromo-β-keto ester **5an** (107 mg, 0.335 mmol, 67%) as a colorless oil. R_f = 0.44 (hexane/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.81 (s, 1H), 4.77 (s, 1H), 4.70 (s, 1H), 4.25 (t, *J* = 7.2 Hz, 2H), 2.95–2.90 (m, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.34 (t, *J* = 7.6 Hz, 2H), 2.17 (s, 3H), 1.96 (quin, *J* = 7.2 Hz, 2H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.2, 198.2, 165.1, 143.5, 110.7, 66.1, 48.4, 39.3, 37.5, 31.3, 29.9, 22.5, 22.4; IR (neat, cm^{-1}): 2968, 2936, 2905, 1758, 1716, 1652, 1456, 1437, 1417, 1373, 1361, 1298, 1273, 1231, 1167, 893; HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_{19}BrNaO_4$ ($[M+Na]^+$) 341.0359, found 341.0364.

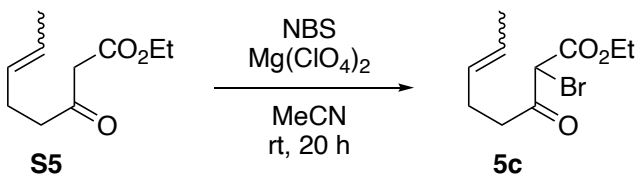
Ethyl 2-bromo-3-oxohept-6-enoate (5b)



S4 **5b**

The titled compound **5b** was prepared according to the general procedure C using **S4** (750 mg, 4.41 mmol), magnesium perchlorate (324 mg, 1.45 mmol), and NBS (784 mg, 4.41 mmol) in MeCN (50 mL). Purification by automated column chromatography on silica gel (gradient: 4–17% EtOAc in hexanes) afforded α-bromo-β-keto ester **5b** (530 mg, 2.13 mmol, 48%) as a colorless oil. R_f = 0.41 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.80 (ddt, *J* = 17.2, 10.4, 6.4 Hz, 1H), 5.07 (brd, *J* = 17.2 Hz, 1H), 5.02 (brd, *J* = 10.4 Hz, 1H), 4.79 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.87 (t, *J* = 7.2 Hz, 2H), 2.39 (q, *J* = 7.2 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.0, 165.2, 136.1, 116.0, 63.3, 48.8, 38.3, 27.8, 13.9; IR (neat, cm^{-1}): 2982, 2940, 1757, 1730, 1642, 1445, 1401, 1368, 1302, 1269, 1232, 1144, 1095, 1023, 918; HRMS (ESI) *m*/*z*: calcd. for $C_9H_{13}BrNaO_3$ ($[M+Na]^+$) 270.9940, found 270.9931.

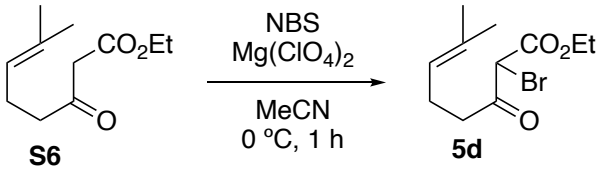
Ethyl 2-bromo-3-oxooct-6-enoate (5c)



S5 **5c**

The titled compound **5c** was prepared according to the general procedure C using **S5** (1.50 g, 8.14 mmol), magnesium perchlorate (600 mg, 2.69 mmol), and NBS (1.45 g, 8.14 mmol) in MeCN (100 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5c** (1.54 g, 5.85 mmol, 72%) as a *E*/*Z* mixture (ca. *E*/*Z*=5:1) and a 7:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.46 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form of *E* isomer: δ 5.54–5.30 (m, 2H), 4.78 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.81 (td, *J* = 7.6, 3.2 Hz, 2H), 2.39–2.28 (m, 2H), 1.66–1.62 (m, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form of *E* isomer: δ 12.81 (s, 1H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.37 (t, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); keto form of *Z* isomer: δ 5.54–5.30 (m, 2H), 4.79 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.81 (td, *J* = 7.6, 3.2 Hz, 2H), 2.39–2.28 (m, 2H), 1.66–1.62 (m, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) keto form: δ 198.2, 198.1, 176.6, 169.7, 165.1, 129.1, 128.6, 127.7, 126.6, 126.2, 125.7, 84.5, 63.12, 63.11, 63.08, 62.1, 48.92, 48.88, 48.86, 39.1, 38.9, 35.2, 28.7, 26.8, 21.4, 17.8, 14.1, 13.9, 12.7; IR (neat, cm^{-1}): 2982, 2938, 2919, 1758, 1728, 1445, 1368, 1302, 1267, 1173, 1143, 1024, 968; HRMS (ESI) *m*/*z*: calcd. for $C_{10}H_{15}BrNaO_3$ ($[M+Na]^+$) 285.0097, found 285.0099.

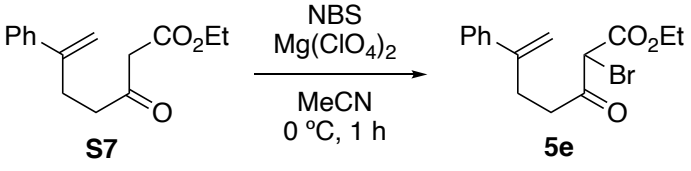
Ethyl 2-bromo-7-methyl-3-oxooct-6-enoate (5d)



S6 **5d**

The titled compound **5d** was prepared according to the general procedure C using **S6** (750 mg, 3.78 mmol), magnesium perchlorate (279 mg, 1.25 mmol), and NBS (673 mg, 3.78 mmol) in MeCN (50 mL). Purification by automated column chromatography on silica gel (gradient: 4–13% EtOAc in hexanes) afforded α-bromo-β-keto ester **5d** (611 mg, 2.20 mmol, 58%) as a 33:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.50 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.09–5.04 (m, 1H), 4.78 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.80–2.74 (m, 2H), 2.31 (q, *J* = 7.2 Hz, 2H), 1.68 (s, 3H), 1.62 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); enol form: δ 12.80 (s, 1H), 2.57 (t, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.3, 165.1, 133.4, 121.8, 63.1, 49.0, 39.2, 25.6, 22.6, 17.6, 13.9; IR (neat, cm^{-1}): 2979, 2930, 2913, 2860, 1758, 1731, 1446, 1399, 1369, 1343, 1302, 1268, 1200, 1151, 1113, 1070, 1023; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{17}BrNaO_3$ ($[M+Na]^+$) 299.0253, found 299.0242.

Ethyl 2-bromo-3-oxo-6-phenylhept-6-enoate (5e)

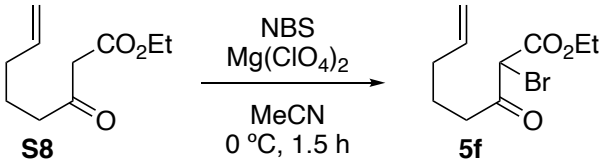


S7 **5e**

The titled compound **5e** was prepared according to the general procedure C using **S7** (500 mg, 2.23 mmol), magnesium perchlorate (150 mg, 0.672 mmol), and NBS (361 mg, 2.03 mmol) in MeCN (50 mL). Purification by automated column chromatography on silica gel (gradient: 4–16% EtOAc in hexanes) afforded α-bromo-β-keto ester **5e** (268 mg, 3.07 mmol, 41%) as a 25:1 mixture of keto form and enol form as a colorless oil. R_f = 0.42 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 7.41–7.27 (m, 5H), 5.33 (s, 1H), 5.11 (s, 1H), 4.76 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.94–2.83 (m, 4H), 1.28 (t, *J* = 7.2 Hz, 3H); enol form: δ 12.82 (s, 1H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.9, 165.1, 146.3, 140.2, 128.5, 127.7, 126.0, 113.2, 63.2, 48.8, 38.1, 29.4, 13.9;

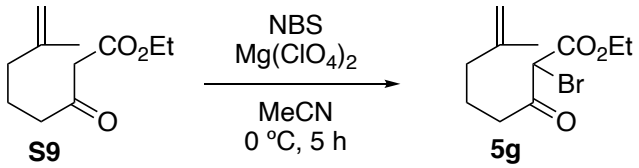
IR (neat, cm^{-1}): 2982, 2939, 1758, 1730, 1629, 1495, 1444, 1395, 1302, 1268, 1227, 1142, 1113, 1072, 1026, 901, 779, 705; HRMS (ESI) *m/z*: calcd. for $C_{15}H_{17}BrNaO_3$ ($[M+Na]^+$) 347.0253, found 347.0245.

2-Bromo-3-oxooct-7-enoate (5f)



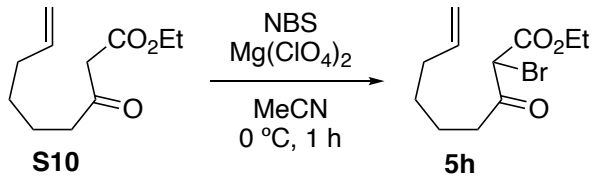
The titled compound **5f** was prepared according to the general procedure C using **S8** (750 mg, 4.07 mmol), magnesium perchlorate (300 mg, 1.34 mmol), and NBS (725 mg, 4.07 mmol) in MeCN (50 mL). Purification by automated column chromatography on silica gel (gradient: 4–13% EtOAc in hexanes) afforded α-bromo-β-keto ester **5f** (271 mg, 1.03 mmol, 25%) as a 16:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.46 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.76 (ddt, *J* = 17.2, 10.0, 6.8 Hz, 1H), 5.06–4.98 (m, 2H), 4.78 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.77 (td, *J* = 7.6, 1.6 Hz, 2H), 2.12–2.06 (m, 2H), 1.75 (quin, *J* = 7.6 Hz, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.81 (s, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.5, 165.1, 137.5, 115.5, 63.1, 48.9, 38.2, 32.6, 22.8, 13.9; IR (neat, cm^{-1}): 2980, 2939, 2908, 1758, 1731, 1640, 1445, 1368, 1302, 1268, 1250, 1173, 1143, 1022, 915; HRMS (EI) *m/z*: calcd. for $C_{10}H_{16}BrO_3$ ($[M+H]^+$) 263.0283, found 263.0287.

Ethyl 2-bromo-7-methyl-3-oxooct-7-enoate (5g)



The titled compound **5g** was prepared according to the general procedure C using **S9** (100 mg, 0.406 mmol), magnesium perchlorate (37.0 mg, 0.166 mmol), and NBS (99.0 mg, 0.555 mmol) in MeCN (10 mL). Purification by silica gel column chromatography (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester **5g** (84.5 mg, 0.300 mmol, 60%) as a 33:1 mixture of keto form and enol form as a colorless oil. R_f = 0.44 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 4.78 (s, 1H), 4.75 (s, 1H), 4.69 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.75 (m, 2H), 2.04 (t, *J* = 7.2 Hz, 2H), 1.79 (tt, *J* = 7.2, 7.2 Hz, 2H), 1.71 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.81 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.7, 165.2, 144.7, 110.9, 63.2, 49.0, 38.4, 36.7, 22.2, 21.6, 13.9; IR (neat, cm^{-1}): 3075, 2980, 2939, 2917, 1760, 1733, 1647, 1447, 1368, 1301, 1268, 1202, 1151, 1023, 890; HRMS (ESI) *m/z*: calcd. for $C_{11}H_{17}BrNaO_3$ ($[M+Na]^+$) 299.0253, found 299.0243.

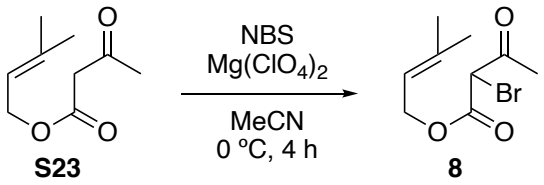
Ethyl 2-bromo-3-oxonon-8-enoate (5h)



The titled compound **5h** was prepared according to the general procedure C using **S10** (200 mg, 1.01 mmol), magnesium perchlorate (74.3 mg, 0.333 mmol), and NBS (179 mg, 1.01 mmol) in MeCN

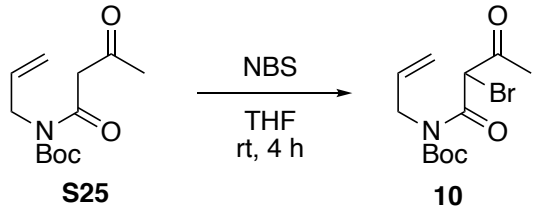
(15 mL). Purification by automated column chromatography on silica gel (gradient: 4–15% EtOAc in hexanes) afforded α-bromo-β-keto ester **5h** (212 mg, 0.775 mmol, 76%) as a 20:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.58 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.90 (ddt, *J* = 16.8, 10.0, 6.8 Hz, 1H), 5.10 (dq, *J* = 16.8, 2.0 Hz, 1H), 4.98 (brd, *J* = 10.0 Hz, 1H), 4.78 (s, 1H), 4.28 (q, *J* = 7.2 Hz, 2H), 2.80–2.74 (m, 2H), 2.10–2.04 (m, 2H), 1.66 (quin, *J* = 7.2 Hz, 2H), 1.45–1.38 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H); characteristic peaks of enol form: δ 12.81 (s, 1H), 2.57 (t, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 198.6, 165.2, 138.2, 114.8, 63.1, 48.9, 38.9, 33.3, 28.0, 23.2, 13.9; IR (neat, cm^{-1}): 3078, 2979, 2937, 2863, 1759, 1733, 1367, 1301, 1269, 1144, 1022, 912; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{17}BrNaO_3$ ($[M+Na]^+$) 299.0253, found 299.0247.

3-Methylbut-2-en-1-yl 2-bromo-3-oxobutanoate (8)



The titled compound **8** was prepared according to the general procedure C using **S23** (1.50 g, 8.81 mmol), magnesium perchlorate (644 mg, 2.91 mmol), and NBS (1.57 g, 8.81 mmol) in MeCN (75 mL). Purification by automated column chromatography on silica gel (gradient: 4–15% EtOAc in hexanes) afforded α-bromo-β-keto ester **8** (1.32 g, 5.30 mmol, 60%) as a 8:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.46 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.42–5.33 (m, 1H), 4.75 (s, 1H), 4.71 (d, *J* = 7.2 Hz, 2H), 2.43 (s, 3H), 1.78 (s, 3H), 1.73 (s, 3H); characteristic peaks of enol form: δ 12.72 (s, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.2, 174.0, 169.5, 165.1, 141.0, 139.9, 117.9, 117.2, 84.8, 63.9, 62.9, 49.2, 26.3, 25.8, 25.7, 22.0, 18.09, 18.06; IR (neat, cm^{-1}): 2975, 2937, 2917, 1727, 1674, 1446, 1381, 1360, 1280, 1247, 1225, 1144, 947; HRMS (EI) *m*/*z*: calcd. for $C_9H_{13}BrO_3$ ($[M]^+$) 248.0048, found 248.0044.

***tert*-Butyl allyl(2-bromo-3-oxobutanoyl)carbamate (10)**

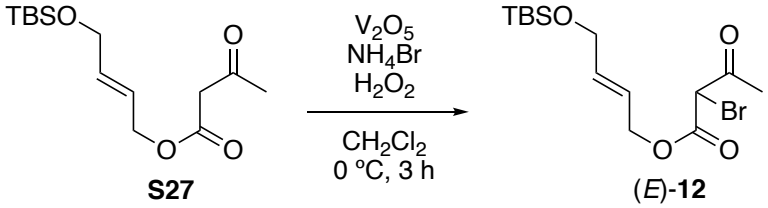


To a solution of keto amide **S25** (60.3 mg, 250 μmol) in THF (10 mL) was added NBS (44.5 mg, 250 μmol) portionwise over an hour at room temperature. After stirring for four hours at room temperature, the resulting mixture was diluted with brine and EtOAc. The organic layer was separated, and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with brine twice, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 6:1) to afford α-bromo-β-keto amide (**10**) (33.9 mg, 106 μmol, 42%) as a colorless oil. R_f = 0.40 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.01 (s, 1H), 5.80 (ddd, *J* = 17.6, 10.0, 6.0 Hz, 1H), 5.20 (ddd, *J* = 17.6, 2.8, 1.6 Hz, 1H), 5.16 (ddd, *J* = 10.8, 2.4, 1.6 Hz, 1H), 4.37 (ddt, *J* = 15.6, 6.0, 1.2 Hz, 1H), 4.32 (ddt, *J* = 15.6, 6.0, 1.2 Hz, 1H), 2.46 (s, 3H), 1.48 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 165.2, 153.3, 132.2,

117.1, 84.5, 55.9, 47.2, 27.8, 27.2; IR (neat, cm^{-1}): 3006, 2981, 2935, 1478, 1457, 1435, 1395, 1369, 1308, 1236, 1149, 1102, 1032, 991, 977, 849, 735, 554, 505; HRMS (ESI) *m*/*z*: calcd. for $C_{12}H_{18}BrNNaO_4$ ($[M+Na]^+$) 342.0311, found 342.0307.

General Procedure D for Bromination of β-Keto Esters

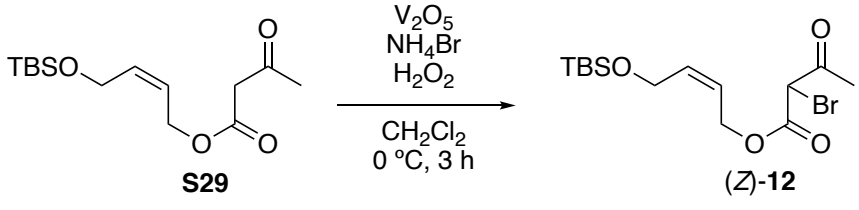
(*E*)-4-(*tert*-butyldimethylsilyloxy)but-2-en-1-yl 2-bromo-3-oxobutanoate ((*E*)-12)



S27 (*E*)-**12**

To a stirred solution of V_2O_5 (182 mg, 1.00 mmol) in water (2.6 mL) was added 34% hydrogen peroxide (3.40 mL, 38.0 mmol) at 0 ºC. The color of the solution changed from light orange to deep red after 30 minutes, then NH_4Br (294 mg, 3.00 mmol) was added. After stirring for additional 10 minutes at 0 °C, a solution of **S27** (573 mg, 2.00 mmol) in CH_2Cl_2 (2.6 mL) was added and the reaction mixture was then stirred for additional three hours at the same temperature. After TLC indicated completion of the reaction, the reaction mixture was extracted with dichloromethane twice and the combined organic layers were washed with saturated aqueous $Na_2S_2O_5$ solution to reduce unreacted molecular bromine. The separated organic layer was washed with water and brine, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 20:1) to afford α-bromo-β-keto ester (*E*)-**12** (173 mg, 0.447 mmol, 24%) as a colorless oil. R_f = 0.36 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.91 (dtt, *J* = 15.6, 4.2, 1.2 Hz, 1H), 5.81 (dtt, *J* = 15.6, 6.6, 1.8 Hz, 1H), 4.77 (s, 1H), 4.72 (dq, *J* = 6.6, 1.2 Hz, 2H), 4.21–4.19 (m, 2H), 2.44 (s, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 196.2, 164.9, 135.8, 121.9, 66.9, 62.6, 49.0, 26.4, 25.9, 18.4, –5.3; IR (neat, cm^{-1}): 2955, 2930, 2886, 2857, 1730, 1361, 1288, 1255, 1222, 1138, 1108, 969, 837, 778; HRMS (ESI) *m*/*z*: calcd. for $C_{14}H_{25}BrNaO_4Si$ ($[M+Na]^+$) 387.0598, found 387.0599.

(*Z*)-4-(*tert*-Butyldimethylsilyloxy)but-2-en-1-yl 2-bromo-3-oxobutanoate ((*Z*)-12)



S29 (*Z*)-**12**

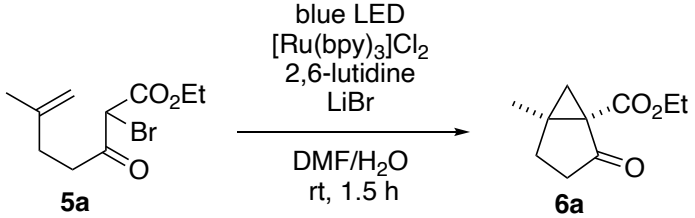
The titled compound (*Z*)-**12** was prepared according to the general procedure D using **S29** (286 mg, 1.00 mmol), V_2O_5 (90.9 mg, 0.500 mmol), 34% hydrogen peroxide (1.70 mL, 19.0 mmol), and NH_4Br (147 mg, 1.50 mmol) in CH_2Cl_2 (1.3 mL). Purification by column chromatography on silica gel (hexane/EtOAc = 50:1) afforded α-bromo-β-keto ester (*Z*)-**12** (62.7 mg, 172 mmol, 17%) as a 12:1 mixture of keto form and enol form and as a colorless oil. R_f = 0.49 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$) keto form: δ 5.82–5.77 (m, 1H), 5.60–5.54 (m, 1H), 4.82 (d, *J* = 6.8 Hz, 2H), 4.76 (s, 1H), 4.29 (d, *J* = 6.4 Hz, 2H), 2.44 (s, 3H), 0.90 (s, 9H), 0.08 (s, 6H); characteristic peaks of enol form: δ 12.64 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 196.1, 174.5, 164.9, 135.3, 134.7, 123.2, 122.6, 62.9, 62.0, 60.0, 59.6, 48.9, 26.4, 25.88, 25.86, 25.7, 22.1, 18.3, –5.26, –5.29; IR (neat,

cm^{-1}): 2955, 2930, 2886, 2857, 1728, 1463, 1361, 1255, 1223, 1142, 1092, 1007, 958, 838, 778; HRMS (ESI) *m*/*z*: calcd. for $C_{14}H_{25}BrNaO_4Si$ ([M+Na]$^+$) 387.0598, found 387.0587.

4. Photoredox-catalyzed Cyclopropanation

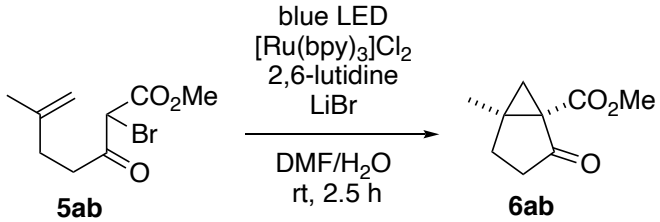
General Procedure E for Intramolecular Photoredox-catalyzed Cyclopropanation

Ethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6a)



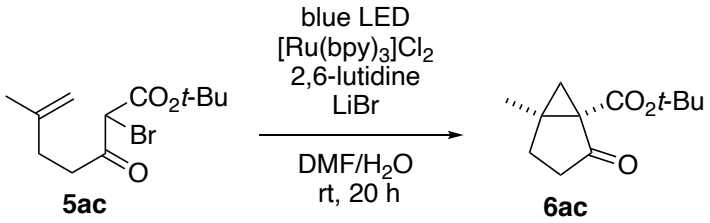
To a solution of α-bromo-β-keto ester **5a** (33.8 mg, 128 μmol) in a mixture of DMF (1.5 mL) and H_2O (4.5 mL) were added $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%) and $LiBr \cdot H_2O$ (11.9 mg, 114 μmol). The solution was degassed by microwave irradiation under reduced pressure. After addition of 2,6-lutidine (26.4 μL, 228 μmol), the resulting mixture was stirred and irradiated by blue LED lamps for 1.5 hour at room temperature. The reaction mixture was diluted with Et_2O and brine, and then extracted with Et_2O five times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 5:1) to afford bicyclic cyclopropane **6a** (18.4 mg, 101 μmol, 79%) as a colorless oil. R_f = 0.19 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.26–4.19 (m, 2H), 2.29–2.18 (m, 2H), 2.13–2.10 (m, 1H), 2.03–1.97 (m, 1H), 1.95 (d, *J* = 3.2 Hz, 1H), 1.43 (d, *J* = 3.2 Hz, 1H), 1.40 (s, 3H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.9, 167.4, 61.2, 44.4, 40.6, 34.2, 28.5, 25.9, 18.1, 14.3; IR (neat, cm^{-1}): 2981, 2958, 2937, 1732, 1446, 1390, 1374, 1342, 1301, 1259, 1249, 1218, 1194, 1158, 1060, 1137, 756; HRMS (ESI) *m*/*z*: calcd. for $C_{10}H_{14}NaO_3$ ([M+Na]$^+$) 205.0835, found 205.0835.

Methyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ab)



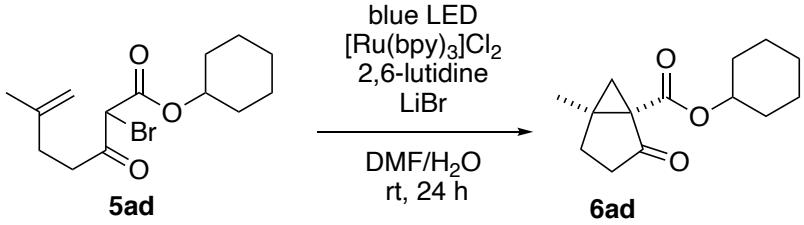
The titled compound **6ab** was obtained according to the general procedure E using **5ab** (30.1 mg, 121 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 2:1) afforded bicyclic cyclopropane **6ab** (18.1 mg, 108 μmol, 89%) as a colorless oil. R_f = 0.18 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 3H), 2.32–2.10 (m, 3H), 2.04–1.96 (m, 2H), 1.47 (d, *J* = 4.8 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.8, 168.0, 52.4, 44.3, 41.0, 34.2, 28.5, 26.3, 18.1; IR (neat, cm^{-1}): 2953, 2932, 2874, 1731, 1438, 1362, 1348, 1302, 1251, 1201, 1159, 1061, 1038; HRMS (ESI) *m*/*z*: calcd. for $C_9H_{12}NaO_3$ ([M+Na]$^+$) 191.0679, found 191.0675.

***tert*-Butyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ac)**



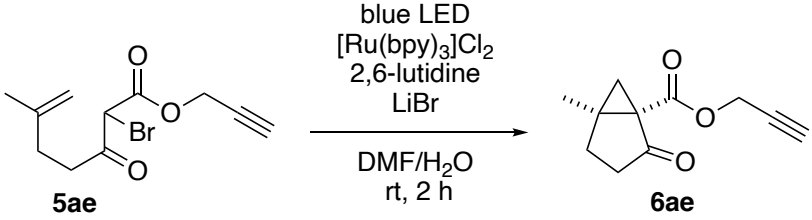
The titled compound **6ac** was obtained according to the general procedure E using **5ac** (28.9 mg, 99.2 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6ac** (14.3 mg, 68.0 μmol, 69%) as a colorless oil. R_f = 0.32 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.28–1.94 (m, 4H), 1.85 (d, *J* = 4.8 Hz, 1H), 1.48 (s, 9H), 1.40 (s, 3H), 1.35 (d, *J* = 5.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.1, 166.5, 81.6, 45.1, 39.9, 34.2, 28.5, 28.2, 25.5, 18.2; IR (neat, cm^{-1}): 2978, 2933, 1736, 1716, 1457, 1390, 1367, 1350, 1300, 1254, 1156, 1060, 1032; HRMS (ESI) *m*/*z*: calcd. for $C_{12}H_{18}NaO_3$ ($[M+Na]^+$) 233.1148, found 233.1140.

Cyclohexyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ad)



The titled compound **6ad** was obtained according to the general procedure E using **5ad** (38.6 mg, 122 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6ad** (15.2 mg, 64.3 μmol, 53%) as a colorless oil. R_f = 0.28 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.88–4.84 (m, 1H), 2.28–2.16 (m, 2H), 2.10 (ddd, *J* = 13.2, 8.4, 2.4 Hz, 1H), 2.02–1.97 (m, 1H), 1.92–1.91 (d, *J* = 5.4 Hz, 1H), 1.89–1.82 (m, 2H), 1.78–1.68 (m, 2H), 1.55–1.49 (m, 2H), 1.48–1.42 (m, 1H), 1.41–1.24 (m, 7H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.9, 166.8, 73.5, 44.6, 40.2, 34.2, 31.7, 31.5, 28.5, 25.6, 25.4, 23.62, 23.60, 18.2; IR (neat, cm^{-1}): 2937, 2861, 1734, 1716, 1541, 1507, 1456, 1379, 1361, 1341, 1250, 1195, 1037; HRMS (ESI) *m*/*z*: calcd. for $C_{14}H_{20}NaO_3$ ($[M+Na]^+$) 259.1305, found 259.1302.

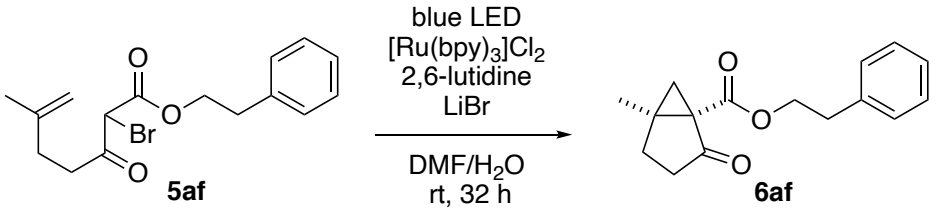
Prop-2-yn-1-yl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ae)



The titled compound **6ae** was obtained according to the general procedure E using **5ae** (30.1 mg, 110 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 3:1) afforded bicyclic cyclopropane **6ae** (16.6 mg, 86.4 μmol, 78%)

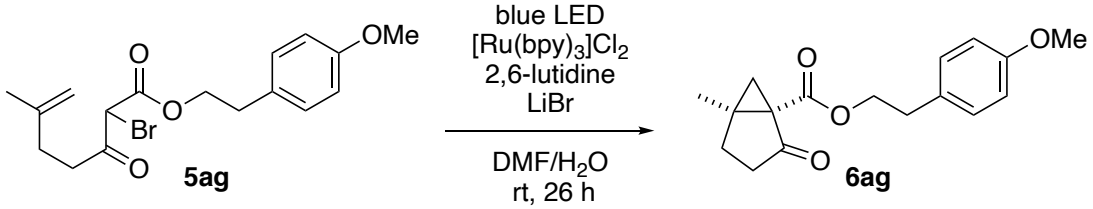
as a colorless oil. R_f = 0.13 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.80 (dd, *J* = 15.6, 2.4 Hz, 1H), 4.73 (dd, *J* = 15.6, 2.4 Hz, 1H), 2.46 (t, *J* = 2.4 Hz, 1H), 2.31–2.19 (m, 2H), 2.13 (ddd, *J* = 13.2, 8.4, 3.6 Hz, 1H), 2.05–2.00 (m, 2H), 1.50 (d, *J* = 5.4 Hz, 1H), 1.43 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.1, 166.8, 77.5, 75.0, 52.5, 44.1, 41.5, 34.1, 28.5, 26.3, 18.1; IR (neat, cm^{-1}): 3269, 2938, 2874, 1731, 1445, 1381, 1340, 1303, 1246, 1186, 1156, 1061, 1038, 1003; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{12}NaO_3$ ($[M+Na]^+$) 215.0679, found 215.0672.

Phenethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6af)



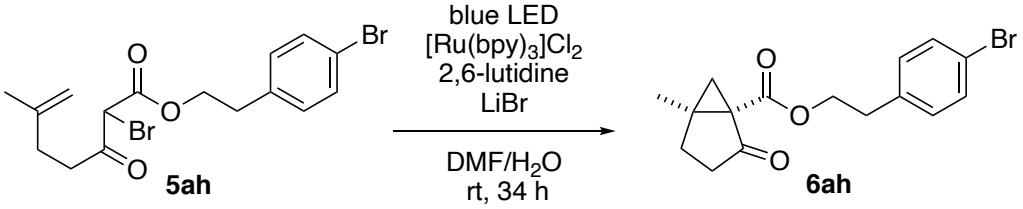
The titled compound **6af** was obtained according to the general procedure E using **5af** (40.0 mg, 118 μmol), $[Ru(bpy)_3]Cl_2·6H_2O$ (1.8 mg, 2.0 mol%), $LiBr·H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6af** (19.4 mg, 75.1 μmol, 59%) as a colorless oil. R_f = 0.11 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31–7.28 (m, 2H), 7.24–7.21 (m, 3H), 4.42–4.34 (m, 2H), 2.98 (t, *J* = 7.2 Hz, 2H), 2.28–2.17 (m, 2H), 2.09 (ddd, *J* = 12.6, 8.4, 2.4 Hz, 1H), 1.99–1.93 (m, 1H), 1.90 (d, *J* = 4.8 Hz, 1H), 1.43 (d, *J* = 4.8 Hz, 1H), 1.28 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.7, 167.4, 137.6, 129.0, 128.4, 126.5, 65.6, 44.3, 40.8, 35.1, 34.2, 28.5, 26.0, 18.0; IR (neat, cm^{-1}): 2953, 2928, 2871, 1732, 1455, 1388, 1342, 1301, 1248, 1188, 1159, 1060, 1034, 749, 701; HRMS (ESI) *m*/*z*: calcd. for $C_{16}H_{18}NaO_3$ ($[M+Na]^+$) 281.1148, found 281.1143.

4-Methoxyphenethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ag)



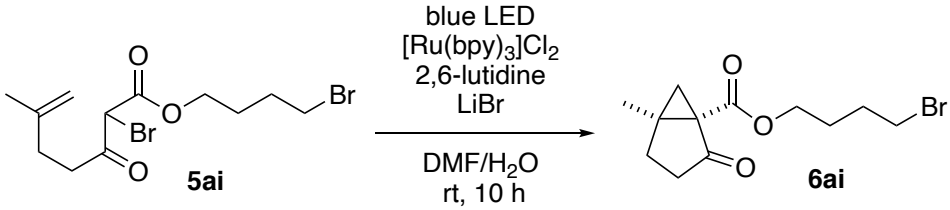
The titled compound **6ag** was obtained according to the general procedure E using **5ag** (43.7 mg, 118 μmol), $[Ru(bpy)_3]Cl_2·6H_2O$ (1.8 mg, 2.0 mol%), $LiBr·H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 3:1) afforded bicyclic cyclopropane **6ag** (21.9 mg, 76.0 μmol, 64%) as a colorless oil. R_f = 0.31 (hexane/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.15 (d, *J* = 8.8 Hz, 2H), 6.84 (d, *J* = 8.8 Hz, 2H), 4.34 (t, *J* = 7.2 Hz, 2H), 3.79 (s, 3H), 2.91 (t, *J* = 7.2 Hz, 2H), 2.31–2.16 (m, 2H), 2.10 (ddd, *J* = 12.4, 4.8, 2.4 Hz, 1H), 2.01–1.95 (m, 1H), 1.91 (d, *J* = 4.8 Hz, 1H), 1.43 (d, *J* = 5.6 Hz, 1H), 1.30 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.7, 167.4, 158.3, 129.9, 129.6, 113.9, 65.9, 55.2, 44.3, 40.8, 34.22, 34.16, 28.5, 26.1, 18.1; IR (neat, cm^{-1}): 2917, 1733, 1717, 1541, 1514, 1457, 1388, 1340, 1301, 1247, 1181, 1160, 1034; HRMS (ESI) *m*/*z*: calcd. for $C_{17}H_{20}NaO_4$ ($[M+Na]^+$) 311.1254, found 311.1250.

4-Bromophenethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ah)



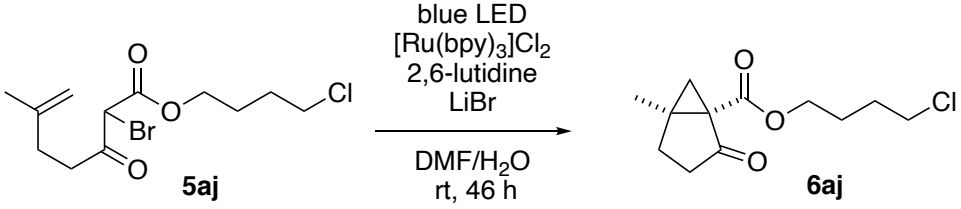
The titled compound **6ah** was obtained according to the general procedure E using **5ah** (43.5 mg, 104 μmol), $[Ru(bpy)_3]Cl_2·6H_2O$ (1.8 mg, 2.0 mol%), $LiBr·H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 2:1) afforded bicyclic cyclopropane **6ah** (19.4 mg, 57.5 μmol, 55%) as a colorless oil. R_f = 0.23 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.42 (d, *J* = 8.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 4.35 (t, *J* = 7.2 Hz, 2H), 2.93 (t, *J* = 7.2 Hz, 2H), 2.31–2.18 (m, 2H), 2.16–2.04 (m, 1H), 2.01–1.90 (m, 2H), 1.44 (t, *J* = 5.2 Hz, 1H), 1.29 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 167.4, 136.7, 131.5, 130.8, 120.5, 65.2, 44.3, 40.9, 34.5, 34.2, 28.5, 26.1, 18.0; IR (neat, cm^{-1}): 2953, 2933, 2871, 1732, 1489, 1446, 1387, 1342, 1301, 1247, 1188, 1159, 1061, 1034, 1011, 815; HRMS (ESI) *m*/*z*: calcd. for $C_{16}H_{17}BrNaO_3$ ($[M+Na]^+$) 359.0253, found 359.0277.

4-Bromobutyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ai)



The titled compound **6ai** was obtained according to the general procedure E using **5ai** (22.5 mg, 60.8 μmol), $[Ru(bpy)_3]Cl_2·6H_2O$ (1.8 mg, 2.0 mol%), $LiBr·H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 3:1) afforded bicyclic cyclopropane **6ai** (12.8 mg, 44.3 μmol, 73%) as a colorless oil. R_f = 0.14 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26–4.17 (m, 2H), 3.46 (t, *J* = 6.4 Hz, 2H), 2.31–2.19 (m, 2H), 2.17–2.10 (m, 1H), 2.05–1.94 (m, 4H), 1.87–1.80 (m, 2H), 1.45 (d, *J* = 5.2 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 167.5, 64.2, 44.4, 40.8, 34.2, 33.2, 29.2, 28.5, 27.3, 26.1, 18.2; IR (neat, cm^{-1}): 2957, 2937, 2872, 1732, 1446, 1389, 1342, 1301, 1249, 1190, 1159, 1061, 1036; HRMS (EI) *m*/*z*: calcd. for $C_{12}H_{17}BrO_3$ ($[M]^+$) 288.0361, found 288.0364.

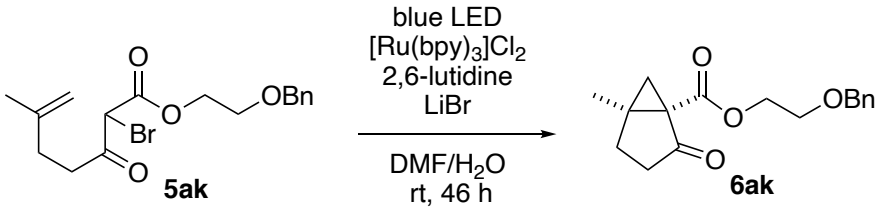
4-Chlorobutyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6aj)



The titled compound **6aj** was obtained according to the general procedure E using **5aj** (38.9 mg, 120 μmol), $[Ru(bpy)_3]Cl_2·6H_2O$ (1.8 mg, 2.0 mol%), $LiBr·H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) afforded bicyclic cyclopropane **6aj** (24.9 mg, 102 μmol,

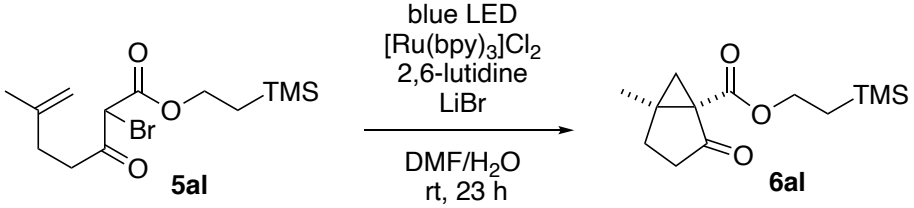
74%) as a colorless oil. R_f = 0.17 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26–4.17 (m, 2H), 3.59 (t, *J* = 6.0 Hz, 2H), 2.31–2.19 (m, 2H), 2.17–2.10 (m, 1H), 2.05–1.80 (m, 6H), 1.45 (d, *J* = 4.8 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 167.5, 64.3, 44.5, 44.4, 40.7, 34.2, 29.0, 28.5, 26.03, 26.02, 18.2; IR (neat, cm^{-1}): 2958, 2873, 1732, 1446, 1417, 1389, 1343, 1302, 1248, 1191, 1160, 1060, 1036; HRMS (ESI) *m*/*z*: calcd. for $C_{12}H_{17}ClNaO_3$ ($[M+Na]^+$) 267.0758, found 267.0757.

2-(Benzyloxy)ethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6ak)



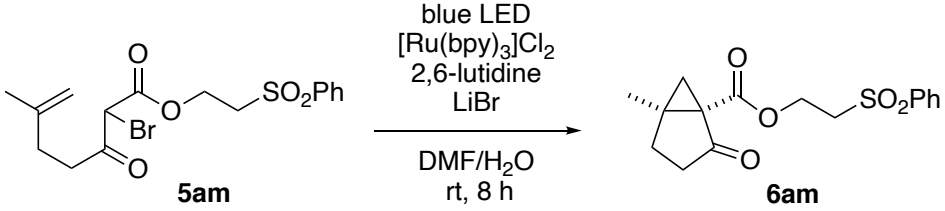
The titled compound **6ak** was obtained according to the general procedure E using **5ak** (43.3 mg, 117 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 2:1) afforded bicyclic cyclopropane **6ak** (17.9 mg, 62.1 μmol, 54%) as a colorless oil. R_f = 0.11 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35c7.27 (m, 5H), 4.57 (s, 2H), 4.39–4.33 (m, 2H), 3.74–3.65 (m, 2H), 2.29–2.18 (m, 2H), 2.11 (ddd, *J* = 12.6, 9.6, 2.4 Hz, 1H), 2.02–1.96 (m, 2H), 1.45 (d, *J* = 5.4 Hz, 1H), 1.39 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.6, 167.4, 138.0, 128.4, 127.7, 73.1, 67.9, 64.2, 44.3, 40.9, 34.2, 28.5, 26.1, 18.2; IR (neat, cm^{-1}): 2951, 2930, 2871, 1750, 1733, 1453, 1384, 1365, 1340, 1301, 1249, 1190, 1162, 1107, 1059, 1038, 741, 699; HRMS (ESI) *m*/*z*: calcd. for $C_{17}H_{20}NaO_4$ ($[M+Na]^+$) 311.1254, found 311.1258.

2-(Trimethylsilyl)ethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6al)



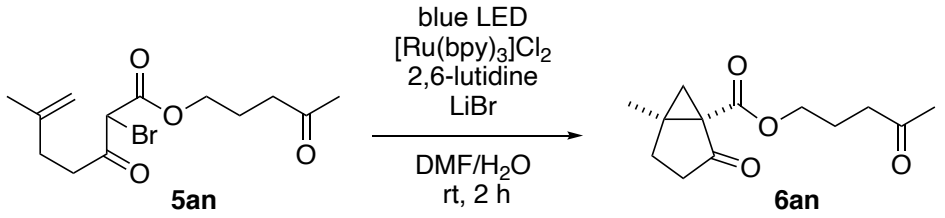
The titled compound **6al** was obtained according to the general procedure E using **5al** (35.8 mg, 107 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 20:1) afforded bicyclic cyclopropane **6al** (9.7 mg, 38.1 μmol, 36%) as a colorless oil. R_f = 0.31 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.31–4.21 (m, 2H), 2.28–2.17 (m, 2H), 2.11 (ddd, *J* = 13.2, 8.4, 2.4 Hz, 1H), 2.02–1.96 (m, 1H), 1.94 (d, *J* = 4.8 Hz, 1H), 1.42 (d, *J* = 4.8 Hz, 1H), 1.40 (s, 3H), 1.06–1.03 (m, 2H), 0.04 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.9, 167.6, 63.6, 44.5, 40.6, 34.2, 28.5, 25.9, 18.2, 17.6, –1.5; IR (neat, cm^{-1}): 2953, 2899, 2875, 1737, 1717, 1456, 1417, 1386, 1341, 1301, 1250, 1189, 1159, 1060, 1036, 935, 861, 838, 758; HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_{22}NaO_3Si$ ($[M+Na]^+$) 277.1230, found 277.1222.

2-(Phenylsulfonyl)ethyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6am)



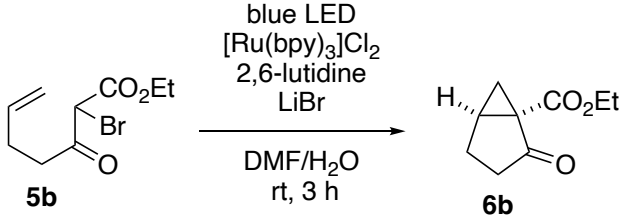
The titled compound **6am** was obtained according to the general procedure E using **5am** (46.7 mg, 116 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 1:1) afforded bicyclic cyclopropane **6am** (29.3 mg, 90.9 μmol, 79%) as a colorless oil. R_f = 0.28 (hexane/EtOAc = 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 7.6 Hz, 2H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 4.59–4.52 (m, 1H), 4.46–4.39 (m, 1H), 3.50 (t, *J* = 6.0 Hz, 2H), 2.20–2.06 (m, 3H), 1.99–1.89 (m, 1H), 1.85 (d, *J* = 4.8 Hz, 1H), 1.41 (d, *J* = 4.8 Hz, 1H), 1.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 206.9, 167.0, 139.3, 133.9, 129.4, 128.2, 58.2, 55.0, 43.9, 41.4, 34.1, 28.4, 26.3, 18.1; IR (neat, cm^{-1}): 3021, 2954, 2931, 2874, 1748, 1731, 1447, 1389, 1345, 1321, 1308, 1248, 1186, 1144, 1085, 1062, 1037, 762, 731, 690, 528; HRMS (ESI) *m*/*z*: calcd. for $C_{16}H_{18}NaO_5S$ ($[M+Na]^+$) 345.0767, found 345.0772.

4-Oxopentyl 5-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6an)



The titled compound **6an** was obtained according to the general procedure E using **5an** (40.0 mg, 125 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 3:1) afforded bicyclic cyclopropane **6an** (24.1 mg, 101 μmol, 81%) as a colorless oil. R_f = 0.18 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.26–4.12 (m, 2H), 2.68–2.54 (m, 2H), 2.31–2.10 (m, 6H), 2.05–1.90 (m, 4H), 1.45 (d, *J* = 4.8 Hz, 1H), 1.40 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.8, 207.7, 167.4, 64.2, 44.4, 40.7, 39.6, 34.1, 30.0, 28.4, 26.0, 22.7, 18.1; IR (neat, cm^{-1}): 2956, 2933, 1732, 1716, 1447, 1417, 1389, 1361, 1343, 1302, 1249, 1191, 1162, 1061, 1037; HRMS (ESI) *m*/*z*: calcd. for $C_{13}H_{18}NaO_4$ ($[M+Na]^+$) 261.1097, found 261.1102.

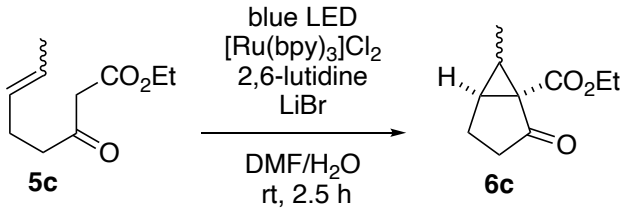
Ethyl 2-oxobicyclo[3.1.0]hexane-1-carboxylate (6b)



The titled compound **6b** was obtained according to the general procedure E using **5b** (30.6 mg, 123 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6b** (13.9 mg, 82.6 μmol, 69%)

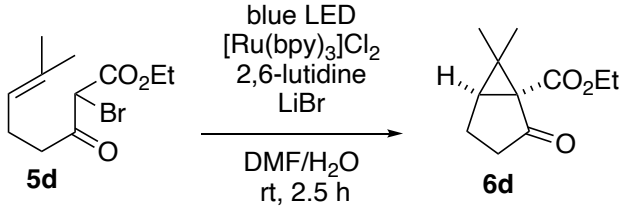
as a colorless oil. R_f = 0.10 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.24–4.18 (m, 2H), 2.63–2.57 (m, 1H), 2.29–2.15 (m, 3H), 2.07–1.98 (m, 2H), 1.38 (t, *J* = 5.2 Hz, 1H), 1.29 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 207.0, 168.3, 61.3, 37.7, 33.7, 32.9, 22.0, 20.9, 14.2; IR (neat, cm^{-1}): 2981, 2947, 1755, 1717, 1447, 1417, 1396, 1379, 1319, 1305, 1265, 1189, 1095, 1037; HRMS (EI) *m*/*z*: calcd. for $C_9H_{12}O_3$ ($[M]^+$) 168.0786, found 168.0787.

Ethyl 6-methyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6c)



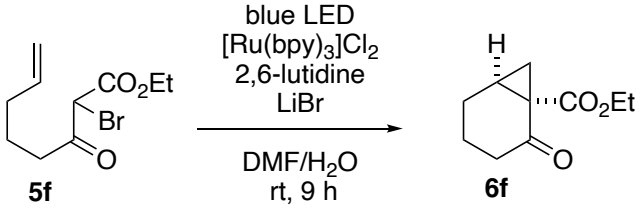
The titled compound **6c** was obtained according to the general procedure E using **5c** (31.9 mg, 121 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6c** (18.0 mg, 98.8 μmol, 82%) as 2.2:1 mixture of two diastereomers as a colorless oil. R_f = 0.14 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$) the major isomer: δ 4.29–4.21 (m, 2H), 2.39 (t, *J* = 4.8 Hz, 1H), 2.24–2.20 (m, 2H), 2.18–2.13 (m, 1H), 2.02–1.98 (m, 1H), 1.75–1.70 (m, 1H), 1.31 (t, *J* = 7.2 Hz, 3H), 1.25 (d, *J* = 6.0 Hz, 3H); ^{1}H NMR (600 MHz, $CDCl_3$) the minor isomer: δ 4.21–4.16 (m, 2H), 2.62 (dd, *J* = 8.4, 6.6 Hz, 1H), 2.52 (ddd, *J* = 19.8, 12.0, 3.6 Hz, 1H), 2.33–2.26 (m, 1H), 2.24–2.20 (m, 1H), 2.13–2.09 (m, 1H), 1.88 (ddd, *J* = 13.2, 9.0, 3.6 Hz, 1H), 1.28 (t, *J* = 7.2 Hz, 3H), 1.17 (d, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$) a mixture of two diastreomers: δ 207.7, 207.2, 169.0, 166.6, 61.20, 61.15, 44.4, 42.9, 39.4, 38.0, 35.4, 33.7, 29.5, 28.9, 21.0, 17.1, 14.3, 14.1, 12.7, 8.8; IR (neat, cm^{-1}): 2979, 2939, 1750, 1732, 1457, 1415, 1387, 1371, 1342, 1309, 1284, 1260, 1190, 1037; HRMS (ESI) *m*/*z*: calcd. for $C_{10}H_{14}NaO_3$ ($[M+Na]^+$) 205.0835, found 205.0835.

Ethyl 6,6-dimethyl-2-oxobicyclo[3.1.0]hexane-1-carboxylate (6d)



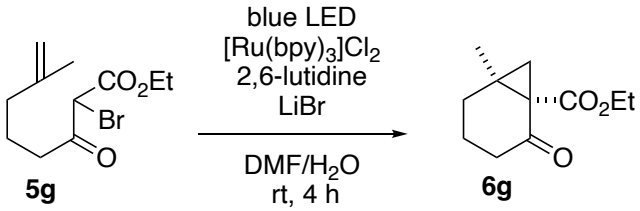
The titled compound **6d** was obtained according to the general procedure E using **5d** (30.3 mg, 109 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6d** (13.3 mg, 67.7 μmol, 62%) as a colorless oil. R_f = 0.18 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27–4.21 (m, 2H), 2.53–2.42 (m, 2H), 2.31–2.14 (m, 2H), 1.88–1.82 (m, 1H), 1.30 (t, *J* = 7.2 Hz, 3H), 1.24 (s, 3H), 1.20 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 167.1, 61.3, 49.4, 39.4, 39.3, 33.6, 23.0, 17.6, 17.0, 14.4; IR (neat, cm^{-1}): 2957, 2928, 2875, 1720, 1459, 1385, 1308, 1281, 1249, 1214, 1183, 1106, 1037; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{16}NaO_3$ ($[M+Na]^+$) 219.0992, found 219.0994.

Ethyl 2-oxobicyclo[4.1.0]heptane-1-carboxylate (6f)



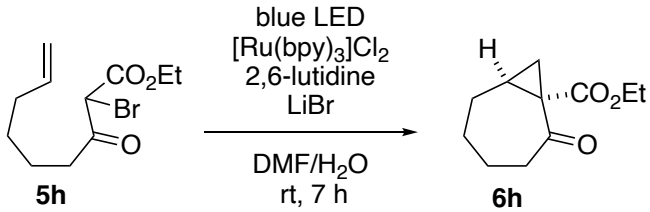
The titled compound **6f** was obtained according to the general procedure E using **5f** (27.9 mg, 106 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6f** (14.6 mg, 80.1 μmol, 76%) as a colorless oil. R_f = 0.16 (hexane/EtOAc = 5:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.20–4.15 (m, 2H), 2.35 (dt, *J* = 17.4, 4.2 Hz, 1H), 2.16 (ddd, *J* = 17.4, 12.6, 6.0 Hz, 1H), 2.08–1.96 (m, 3H), 1.83 (dd, *J* = 8.4, 6.0 Hz, 1H), 1.81–1.75 (m, 1H), 1.58–1.50 (m, 1H), 1.31 (dd, *J* = 7.2, 5.4 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 202.7, 170.2, 61.4, 38.5, 35.4, 25.6, 21.4, 17.7, 16.2, 14.1; IR (neat, cm^{-1}): 2941, 1717, 1707, 1383, 1271, 1212, 1188, 1093, 1082, 1068; HRMS (ESI) *m*/*z*: calcd. for $C_{10}H_{14}NaO_3$ ($[M+Na]^+$) 205.0835, found 205.0829.

Ethyl 6-methyl-2-oxobicyclo[4.1.0]heptane-1-carboxylate (6g)



The titled compound **6g** was obtained according to the general procedure E using **5g** (29.3 mg, 106 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **6g** (15.4 mg, 78.5 μmol, 74%) as a colorless oil. R_f = 0.50 (hexane/EtOAc = 2:1); ^{1}H NMR (600 MHz, $CDCl_3$): δ 4.25–4.18 (m, 2H), 2.37 (ddd, *J* = 18.0, 4.8, 3.0 Hz, 1H), 2.18–2.10 (m, 1H), 1.99 (dt, *J* = 14.4, 4.2 Hz, 1H), 1.86 (td, *J* = 13.2, 4.8, Hz, 1H), 1.80–1.75 (m, 1H), 1.58–1.50 (m, 3H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.22 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 203.8, 168.9, 61.3, 44.6, 36.9, 29.1, 28.6, 20.8, 20.2, 17.7, 14.2; IR (neat, cm^{-1}): 2979, 2954, 2936, 1731, 1696, 1445, 1387, 1371, 1339, 1308, 1241, 1214, 1109, 1077; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{16}NaO_3$ ($[M+Na]^+$) 219.0992, found 219.0990.

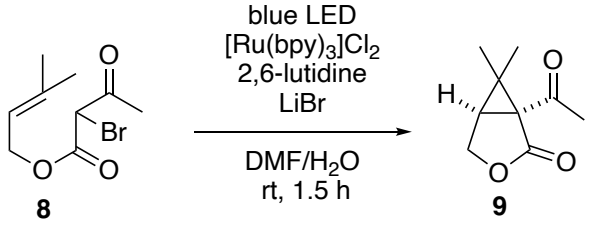
Ethyl 2-oxobicyclo[5.1.0]octane-1-carboxylate (6h)



The titled compound **6h** was obtained according to the general procedure E using **5h** (28.8 mg, 104 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 μmol), and 2,6-lutidine (26.4 μL, 228 μmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column

chromatography (hexane/EtOAc = 20:1) afforded bicyclic cyclopropane **6h** (15.1 mg, 76.9 µmol, 74%) as a colorless oil. R_f = 0.47 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.28–4.11 (m, 2H), 2.88 (ddd, *J* = 12.8, 10.8, 4.4 Hz, 1H), 2.57–2.51 (m, 1H), 2,45–2.38 (m, 1H), 1,98–1,90 (m, 1H), 1.81–1.65 (m, 2H), 1.54–1.51 (m, 1H), 1.50–1.31 (m, 2H), 1.27 (t, *J* = 7.2 Hz, 3H), 1.24 (d, *J* = 6.4 Hz, 1H), 0.62–0.52 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.3, 171.4, 61.3, 43.9, 39.7, 30.4, 26.2, 25.7, 25.1, 22.1, 14.1; IR (neat, cm^{-1}): 2932, 2859, 1732, 1711, 1507, 1456, 1330, 1304, 1277, 1248, 1192, 1156, 1109; HRMS (ESI) *m*/*z*: calcd. for $C_{11}H_{16}NaO_3$ ([M+Na]$^+$) 219.0992, found 219.0993.

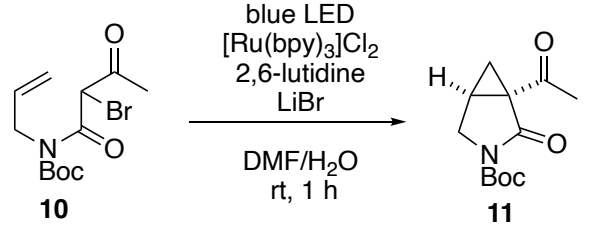
1-Acetyl-6,6-dimethyl-3-oxabicyclo[3.1.0]hexan-2-one (9)



8 **9**

The titled compound **9** was obtained according to the general procedure E using **8** (33.9 mg, 136 µmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 µmol), and 2,6-lutidine (26.4 µL, 228 µmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded bicyclic cyclopropane **9** (15.7 mg, 93.3 µmol, 69%) as a colorless oil. R_f = 0.13 (hexane/EtOAc = 5:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.33 (dd, *J* = 10.0, 4.8 Hz, 1H), 4.12 (dd, *J* = 10.0, 1.2 Hz, 1H), 2.69 (brd, *J* = 5.6 Hz, 1H), 2.56 (s, 3H), 1.33 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 200.0, 171.8, 64.7, 35.4, 34.8, 29.9, 20.0, 16.2; IR (neat, cm^{-1}): 2959, 2918, 2849, 1765, 1698, 1360, 1302, 1277, 1219, 1186, 1105, 1075, 1049, 1012; HRMS (ESI) *m*/*z*: calcd. for $C_9H_{12}NaO_3$ ([M+Na]$^+$) 191.0679, found 191.0679.

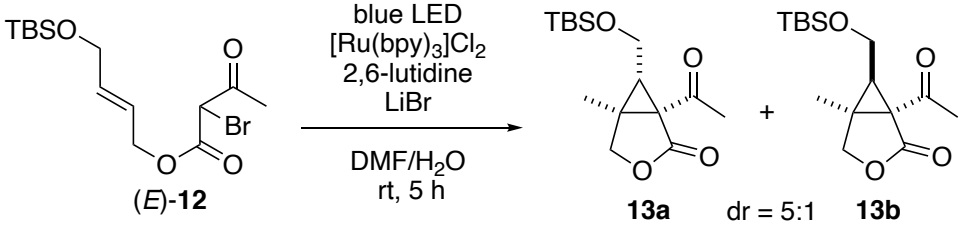
***tert*-Butyl 1-acetyl-2-oxo-3-azabicyclo[3.1.0]hexane-3-carboxylate (11)**



10 **11**

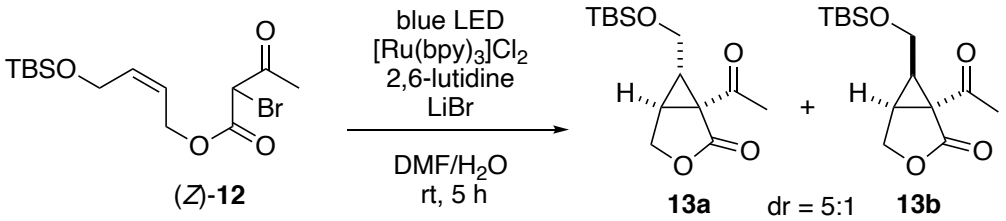
The titled compound **11** was obtained according to the general procedure E using **10** (36.5 mg, 60.9 µmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (1.8 mg, 2.0 mol%), $LiBr \cdot H_2O$ (11.9 mg, 114 µmol), and 2,6-lutidine (26.4 µL, 228 µmol) in DMF (1.5 mL) and H_2O (4.5 mL). Purification by silica gel column chromatography (hexane/EtOAc = 2:1) afforded bicyclic cyclopropane **11** (7.7 mg, 32 µmol, 48%) as a colorless oil. R_f = 0.33 (hexane/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.79 (dd, *J* = 11.2, 5.6 Hz, 1H), 3.69 (d, *J* = 11.6 Hz, 1H), 2.59 (s, 3H), 2.45 (ddd, *J* = 8.0, 5.6, 5.6 Hz, 1H), 1.98 (dd, *J* = 8.0, 4.4 Hz, 1H), 1.53 (s, 9H), 1.30 (dd, *J* = 5.6, 4.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 201.8, 170.0, 150.2, 83.4, 46.1, 40.0, 29.6, 28.0, 24.3, 24.1; IR (neat, cm^{-1}): 2979, 1782, 1748, 1716, 1698, 1477, 1458, 1369, 1308, 1291, 1259, 1212, 1155, 1024, 974, 851, 587, 569; HRMS (ESI) *m*/*z*: calcd. for $C_{12}H_{17}NNaO_4$ ([M+Na]$^+$) 262.1050, found 262.1045.

1-Acetyl-6-(*tert*-butyldimethylsilyloxymethyl)-3-oxabicyclo[3.1.0]hexan-2-one



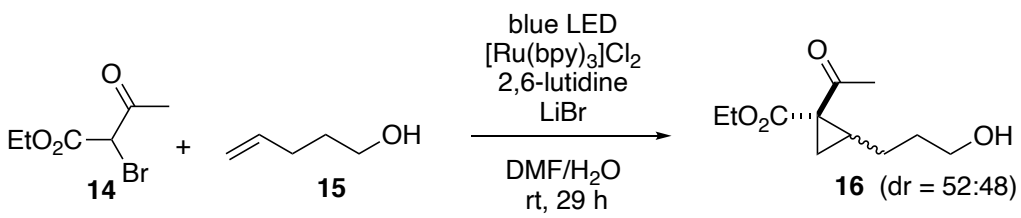
The titled compounds **13a** and **13b** were obtained according to the general procedure E using (*E*)-**12** (78.0 mg, 216 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3.0 mg, 2.0 mol%), $LiBr \cdot H_2O$ (20.9 mg, 200 μmol), 2,6-lutidine (46.3 μL, 400 μmol) in DMF (3.0 mL) and H_2O (9.0 mL). Purification by silica gel column chromatography (hexanes/EtOAc = 5:1) afforded a 5:1 mixture of diastereomeric bicyclic cyclopropanes **13a** and **13b** (24.5 mg, 86.1 μmol, 40%) as a colorless oil. R_f = 0.22 (hexanes/EtOAc = 5:1). ^{1}H NMR (600 MHz, $CDCl_3$) **13a**: δ 4.26 (dd, *J* = 9.0, 4.8 Hz, 1H), 4.19 (d, *J* = 9.0 Hz, 1H), 3.94 (dd, *J* = 11.4, 4.8 Hz, 1H), 3.40 (dd, *J* = 11.4, 9.6 Hz, 1H), 2.76 (dd, *J* = 4.8, 4.8 Hz, 1H), 2.64 (s, 3H), 2.03 (dt, *J* = 9.6, 4.8 Hz, 1H), 0.87 (s, 9H), 0.03 (s, 3H), 0.01 (s, 3H); ^{1}H NMR (600 MHz, $CDCl_3$) **13b**: δ 4.39 (dd, *J* = 10.2, 5.4 Hz, 1H), 4.27–4.23 (m, 1H), 3.81 (dd, *J* = 12.0, 7.2 Hz, 1H), 3.68 (dd, *J* = 12.0, 7.8 Hz, 1H), 2.93 (ddd, *J* = 8.4, 5.4, 1.2 Hz, 1H), 2.58 (s, 3H), 2.50 (q, *J* = 7.8 Hz, 1H), 0.89 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H);^{13}C NMR (100 MHz, $CDCl_3$) a mixture of **13a** and **13b**: δ 200.7, 199.2, 172.3, 171.2, 66.9, 64.4, 58.8, 57.4, 42.0, 41.1, 39.0, 36.6, 33.6, 29.8, 29.2, 28.0, 25.8, 18.21, 18.19, –5.40, –5.46, –5.50, –5.6; IR (neat, cm^{-1}): 2952, 2929, 2887, 2857, 1760, 1699, 1464, 1393, 1362, 1252, 1099, 1041, 999, 838, 778, 501; HRMS (ESI) *m/z*: calcd. for $C_{14}H_{24}NaO_4Si$ ($[M+Na]^+$) 307.1336, found 307.1345.

1-Acetyl-6-(*tert*-butyldimethylsilyloxymethyl)-3-oxabicyclo[3.1.0]hexan-2-one



The titled compounds **13a** and **13b** were obtained according to the general procedure E using (*Z*)-**12** (79.0 mg, 216 μmol), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (3.0 mg, 2.0 mol%), $LiBr \cdot H_2O$ (20.9 mg, 200 μmol), and 2,6-lutidine (46.3 μL, 400 μmol) in DMF (3.0 mL) and H_2O (9.0 mL). Purification by silica gel column chromatography (hexane/EtOAc = 5:1) afforded a 5:1 mixture of diastereomeric bicyclic cyclopropanes **13a** and **13b** (21.1 mg, 74.2 μmol, 34%) as a colorless oil. R_f = 0.22 (hexane/EtOAc = 5:1). The spectral data of **13a** and **13b** were in complete agreement with those of **13a** and **13b** obtained from (*E*)-**12**.

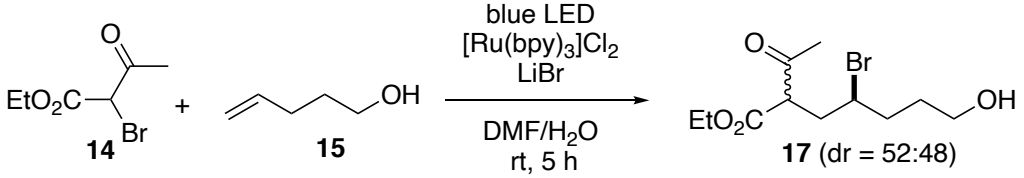
Ethyl-1-acetyl-2-(3-hydroxypropyl)cyclopropane-1-carboxylate (16)



To a solution of 4-penten-1-ol (**15**) (46.0 mg, 0.530 mmol) and α-bromo-β-keto ester **14** (209 mg, 1.00 mmol) in DMF (0.1 mL) and H_2O (0.4 mL) were added $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (7.5 mg, 2.0 mol%)

and $LiBr \cdot H_2O$ (105 mg, 1.00 mmol). The mixture was degassed by microwave irradiation under reduced pressure. After addition of 2,6-lutidine (174 μL, 1.50 mmol), the resulting mixture was stirred at room temperature under irradiation of visible light using 40 W blue LED lamps for 29 hours. The reaction mixture was diluted with EtOAc and brine, and then extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford **16** (91.0 mg, 425 μmol, 80%) as a mixture of two diastereomers (52:48) as a pale yellow oil. R_f = 0.23 (hexanes/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) the major isomer: δ 4.32–4.13 (m, 2H), 3.65 (t, *J* = 10.0 Hz, 2H), 2.41 (s, 3H), 2.05–1.92 (m, 1H), 1.70–1.60 (m, 2H), 1.58–1.49 (m, 2H), 1.48–1.13 (m, 6H); ^{1}H NMR (400 MHz, $CDCl_3$) the minor isomer: δ 4.32–4.13 (m, 2H), 3.65 (t, *J* = 10.0 Hz, 2H), 2.37 (s, 3H), 2.05–1.92 (m, 1H), 1.70–1.60 (m, 2H), 1.58–1.49 (m, 2H), 1.48–1.13 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) a mixture of two diastereomers: δ 203.0, 202.1, 171.2, 169.7, 62.03, 62.02, 61.4, 61.3, 41.7, 40.7, 32.2, 31.9, 31.2, 31.0, 30.8, 29.3, 24.5, 23.7, 23.6, 20.9, 14.1, 14.0; IR (neat, cm^{-1}): 3433, 2982, 2937, 2870, 1719, 1698, 1447, 1393, 1360, 1313, 1272, 1242, 1191, 1122, 1057, 1022; HRMS (ESI) *m/z*: calcd. for $C_{11}H_{18}NaO_4$ ($[M+Na]^+$) 237.1097, found 237.1102.

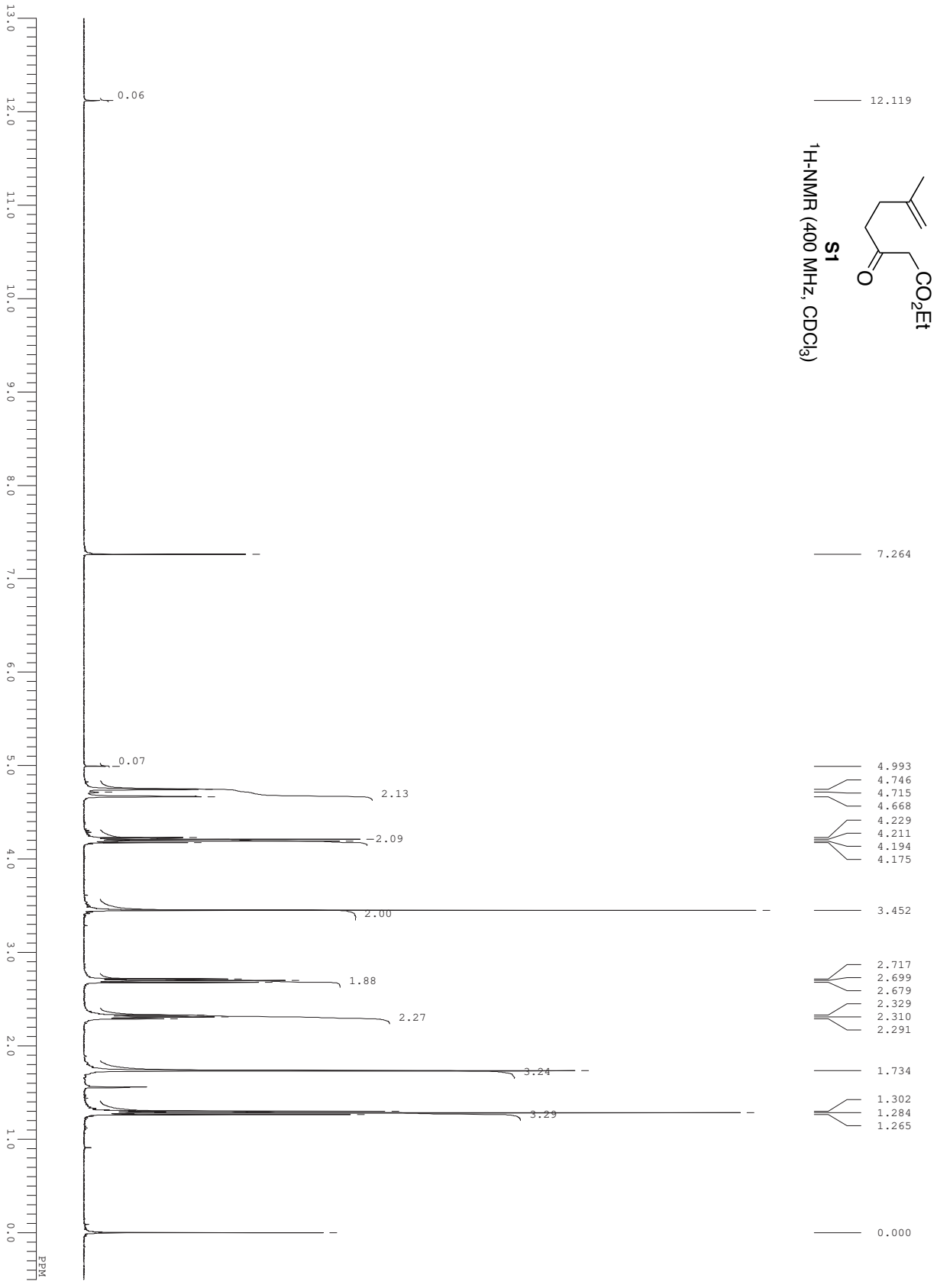
Ethyl-2-acetyl-4-bromo-7-hydroxyheptanoate (17)



To a solution of 4-penten-1-ol (**15**) (43.1 mg, 0.500 mmol) and α-bromo-β-keto ester **14** (209 mg, 1.00 mmol) in DMF (0.1 mL) and H_2O (0.4 mL) was added $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (7.5 mg, 2.0 mol%) and $LiBr \cdot H_2O$ (105 mg, 1.00 mmol). The mixture was degassed by microwave irradiation under reduced pressure. The resulting mixture was stirred at room temperature under irradiation of visible light using 40W blue LED lamps for five hours. The reaction mixture was diluted with EtOAc and brine, and then extracted with EtOAc three times. The combined organic extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/EtOAc = 2:1) to afford **17** (119.3 mg, 404 μmol, 81%) as a mixture of diastereomers (dr = 52:48) and a yellow pale oil. R_f = 0.16 (hexanes/EtOAc = 2:1); ^{1}H NMR (400 MHz, $CDCl_3$) the major isomer: δ 4.27–4.17 (m, 2H), 4.06–3.90 (m, 2H), 3.70–3.67 (m, 2H), 2.58–2.40 (m, 1H), 2.30 (s, 3H), 2.21–2.12 (m, 1H), 2.03–1.80 (m, 3H), 1.77–1.65 (m, 1H), 1.32–1.27 (m, 3H); ^{1}H NMR (400 MHz, $CDCl_3$) the minor isomer: δ 4.27–4.17 (m, 2H), 4.06–3.90 (m, 2H), 3.70–3,67 (m, 2H), 2.58–2.40 (m, 1H), 2.33 (s, 3H), 2.21–2.12 (m, 1H), 2.03–1.80 (m, 3H), 1.77–1.65 (m, 1H), 1.32–1.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) a mixture of keto and enol form for two diastereomers: δ 202.5, 202.1, 168.9, 168.9, 61.9, 61.71, 61.68, 61.66, 58.2, 57.4, 55.2, 55.1, 36.9, 36.7, 35.9, 35.8, 30.4, 29.2, 14.0, 13.9; IR (neat, cm^{-1}): 3432, 2979, 2938, 2874, 1739, 1716, 1647, 1445, 1367, 1247, 1150, 1060, 1023; HRMS (ESI) *m/z*: calcd. for $C_{11}H_{19}BrNaO_4$ ($[M+Na]^+$) 317.0359, found 317.0361.

5. References

1) A. Padwa, Y. S. Kulkarni and Z. Zhang, *J. Org. Chem*., 1990, **55**, 4144–4153.
2) S. Pan, S. Y. Jang, D. Wang, S. S. Liew, Z. Li, J. S. Lee and S. Q. Yao, *Angew. Chem. Int. Ed.*, 2017, **56**, 11816–11821.
3) D. S. Rawat and R. A. Gibbs, *Org. Lett.*, 2002, **4**, 3027–3030.
4) S. W. Baldwin, J. D. Wilson and J. Aubé, *J. Org. Chem.*, 1985, **50**, 4432–4439.
5) J. A. Turner and W. S. Jacks**,** *J. Org. Chem*. 1989, **54**, 4229–4231.
6) K. Ishihara, A. Mori and H. Yamamoto, *Tetrahedron*, 1990, **46**, 1595–4612.
7) T. Xavier, S. Condon, C. Pichon, E. L. Gall, and M. Presset*. Org. Lett.* 2019, **21**, 6135–6139.
8) J. C. Gilbert and T. A. Kelly, *J. Org. Chem*., 1988, **53**, 449–450.
9) R. J. Clemens and J. A. Hyatt, *J. Org. Chem.* 1985, **50***,* 2431–2435.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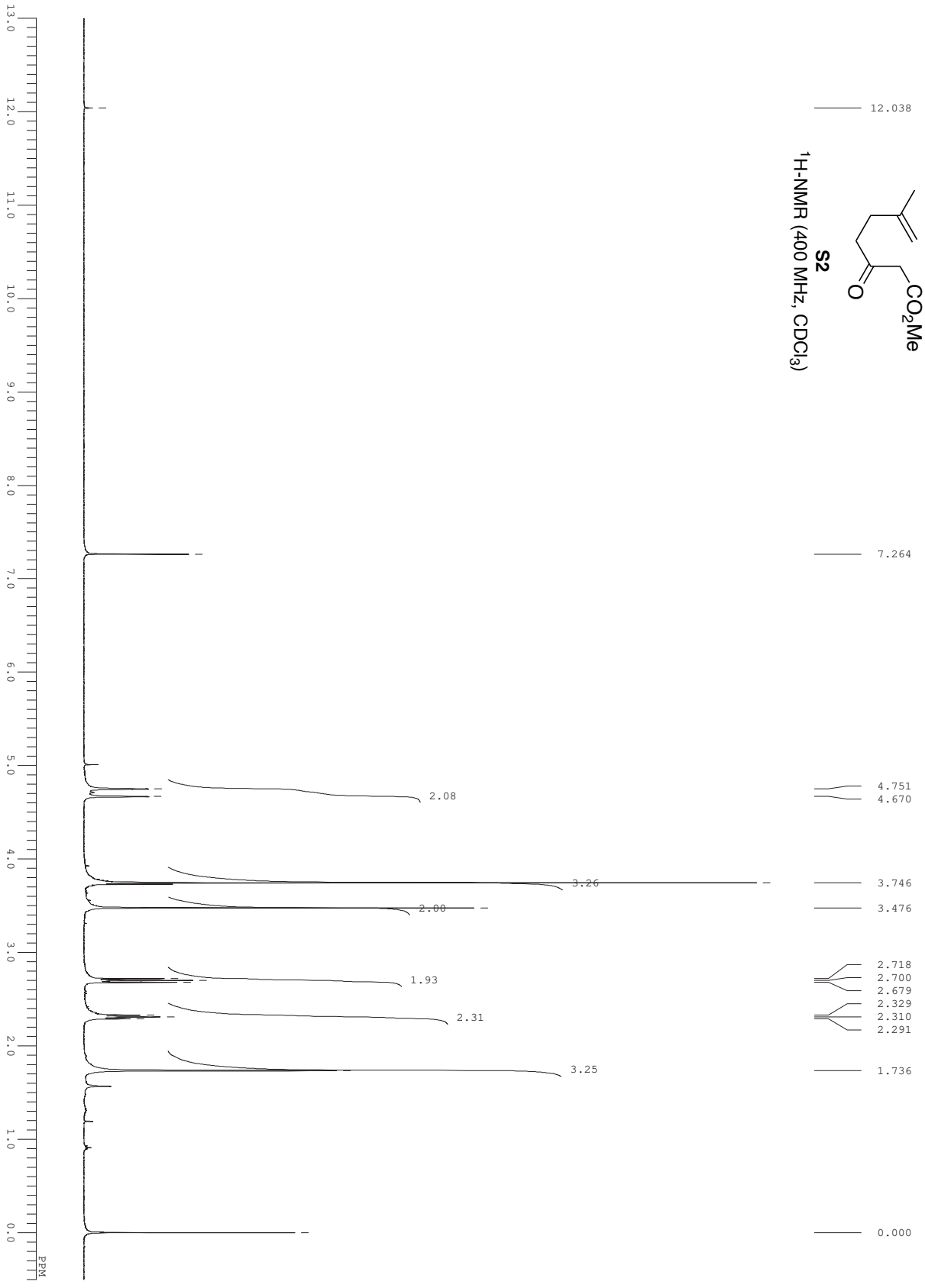
7.264
4.993
4.746
4.715
4.668
4.229
4.211
4.194
4.175
3.452
2.717
2.699
2.679
2.329
2.310
2.291
1.734
1.302
1.284
1.265
0.000
0.06
0.07
2.13
2.09
2.00
1.88
2.27
3.24
3.29
PPM


S2
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CO$_2$Me
O
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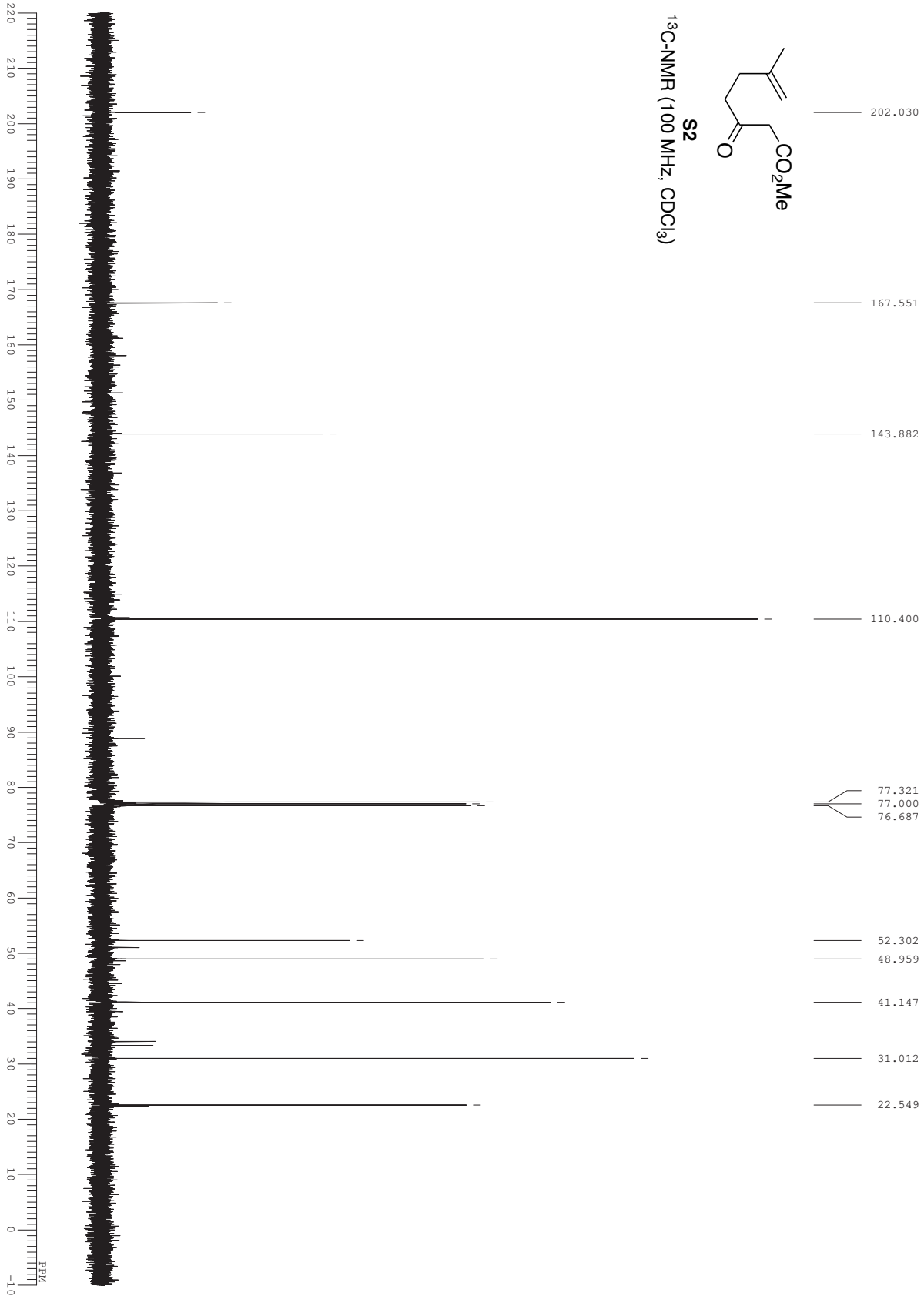
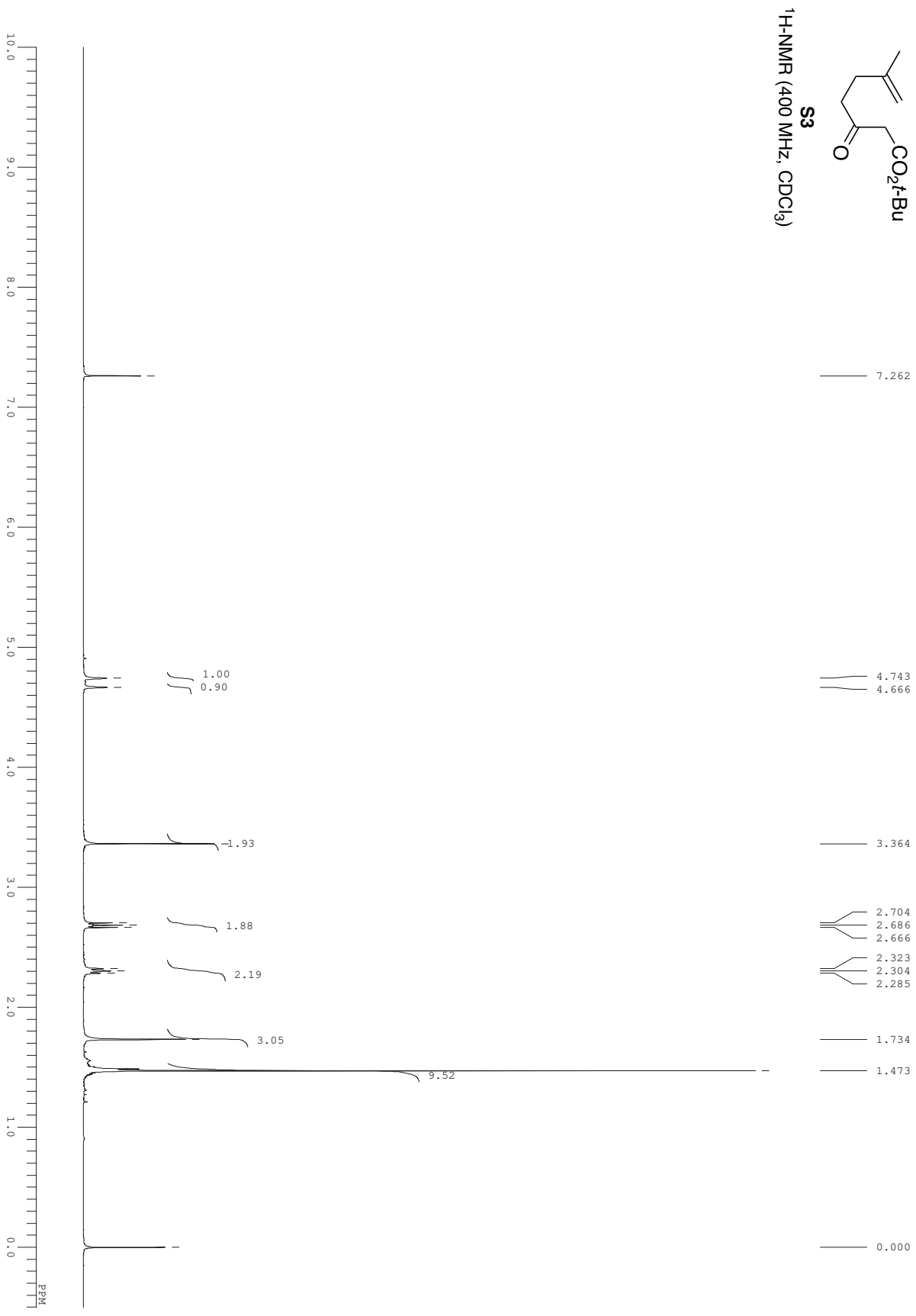
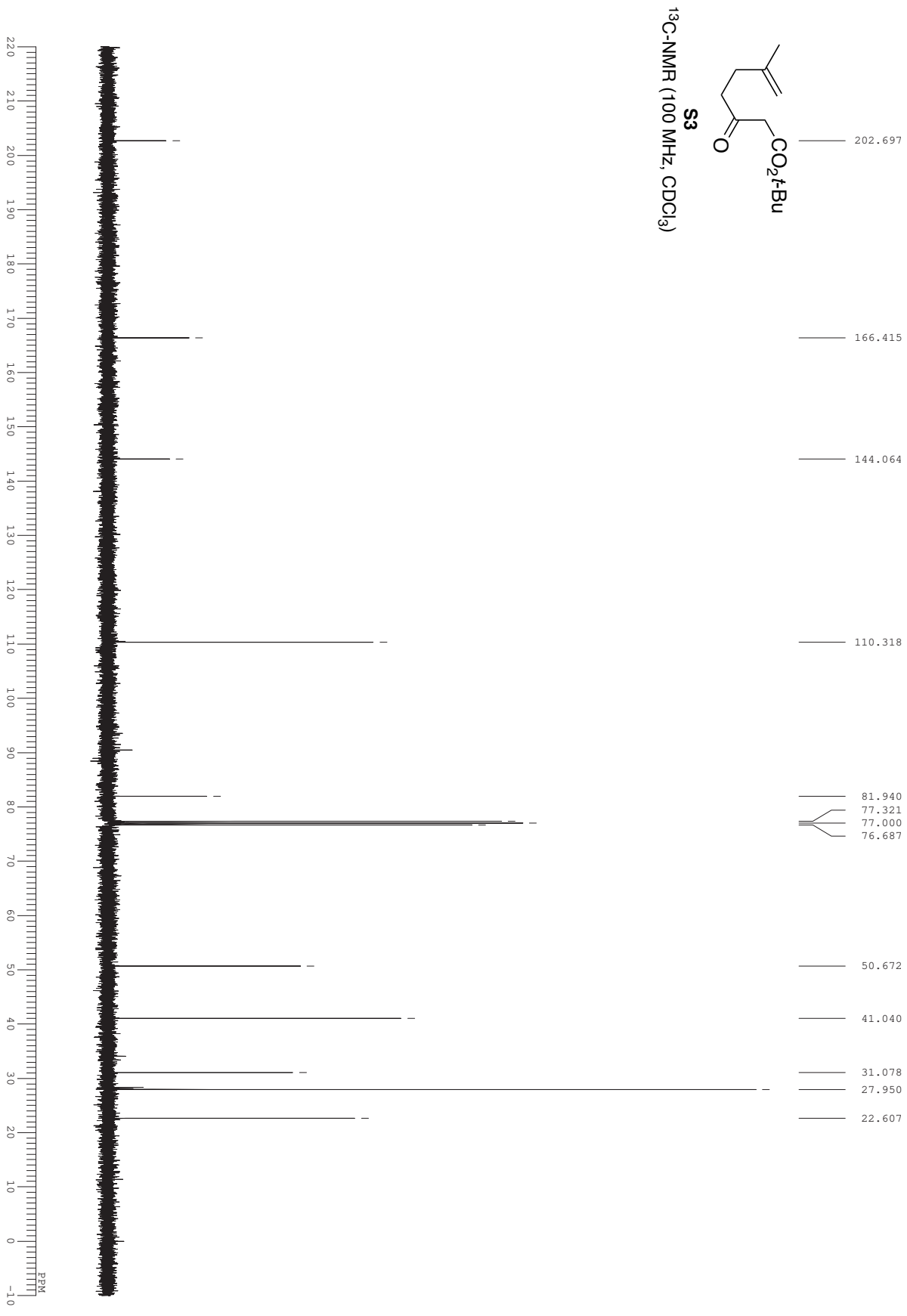
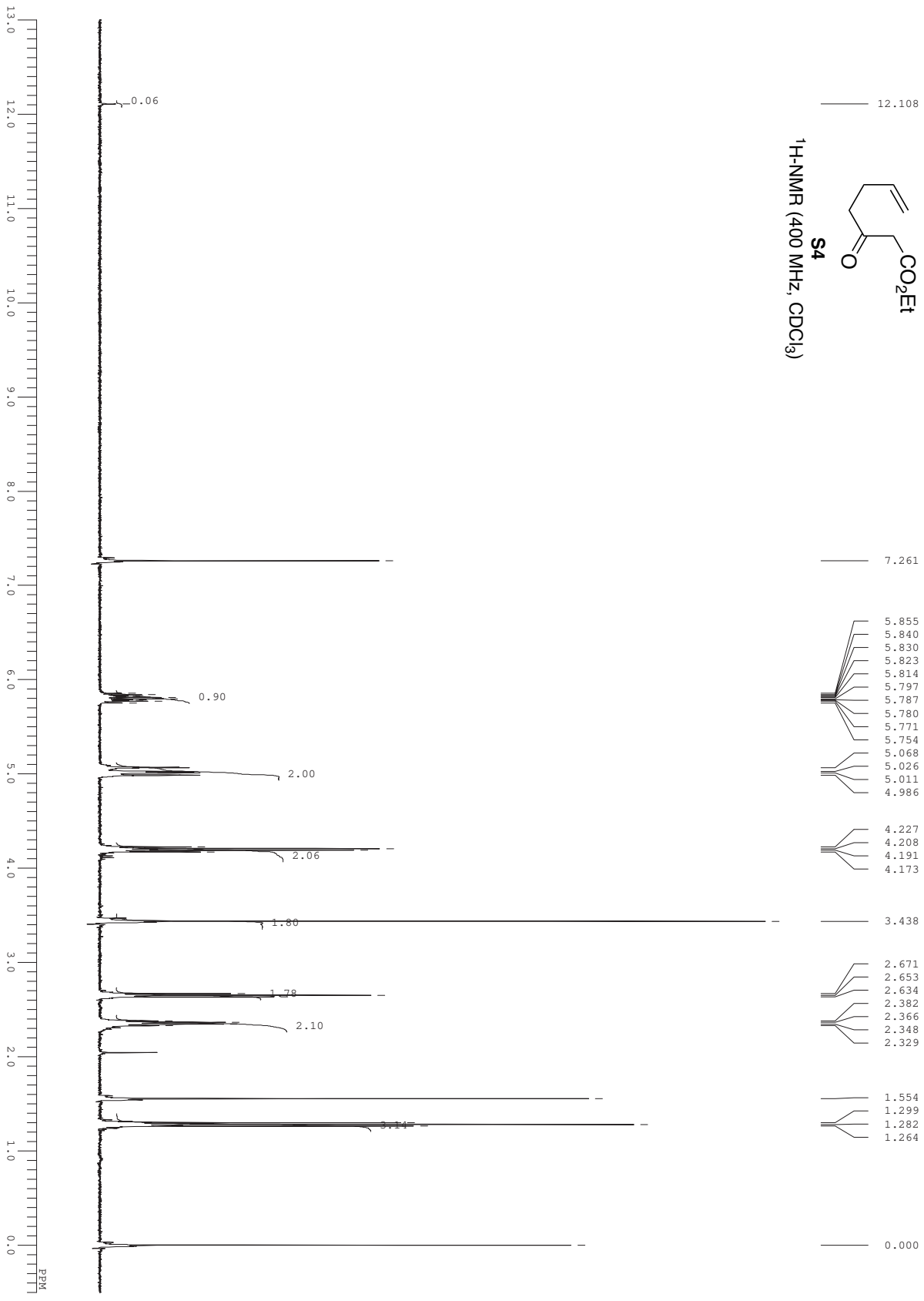
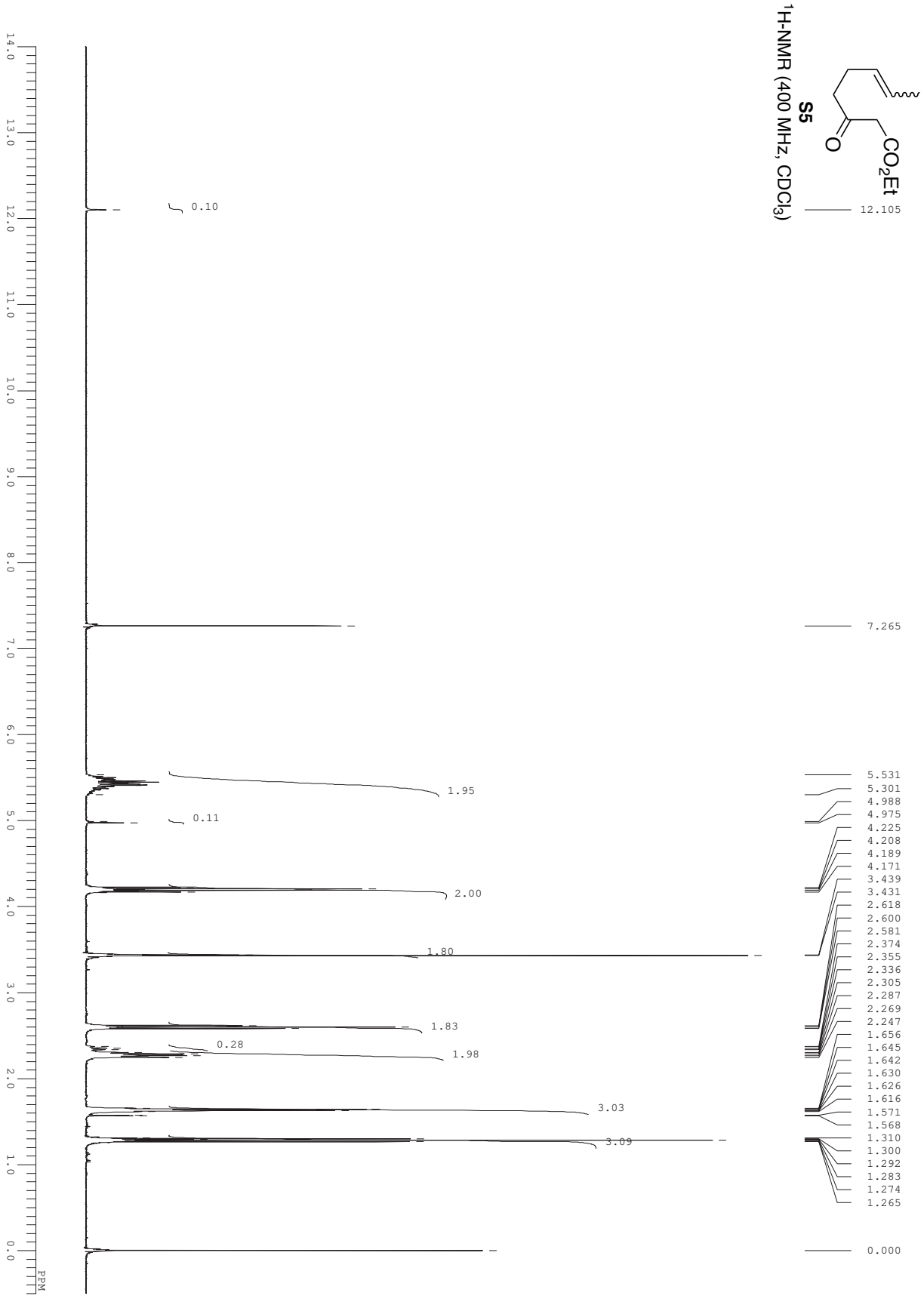
7.264
4.751
4.670
3.746
3.476
2.718
2.700
2.679
2.329
2.310
2.291
1.736
0.000
2.08
3.26
2.00
1.93
2.31
3.25
PPM

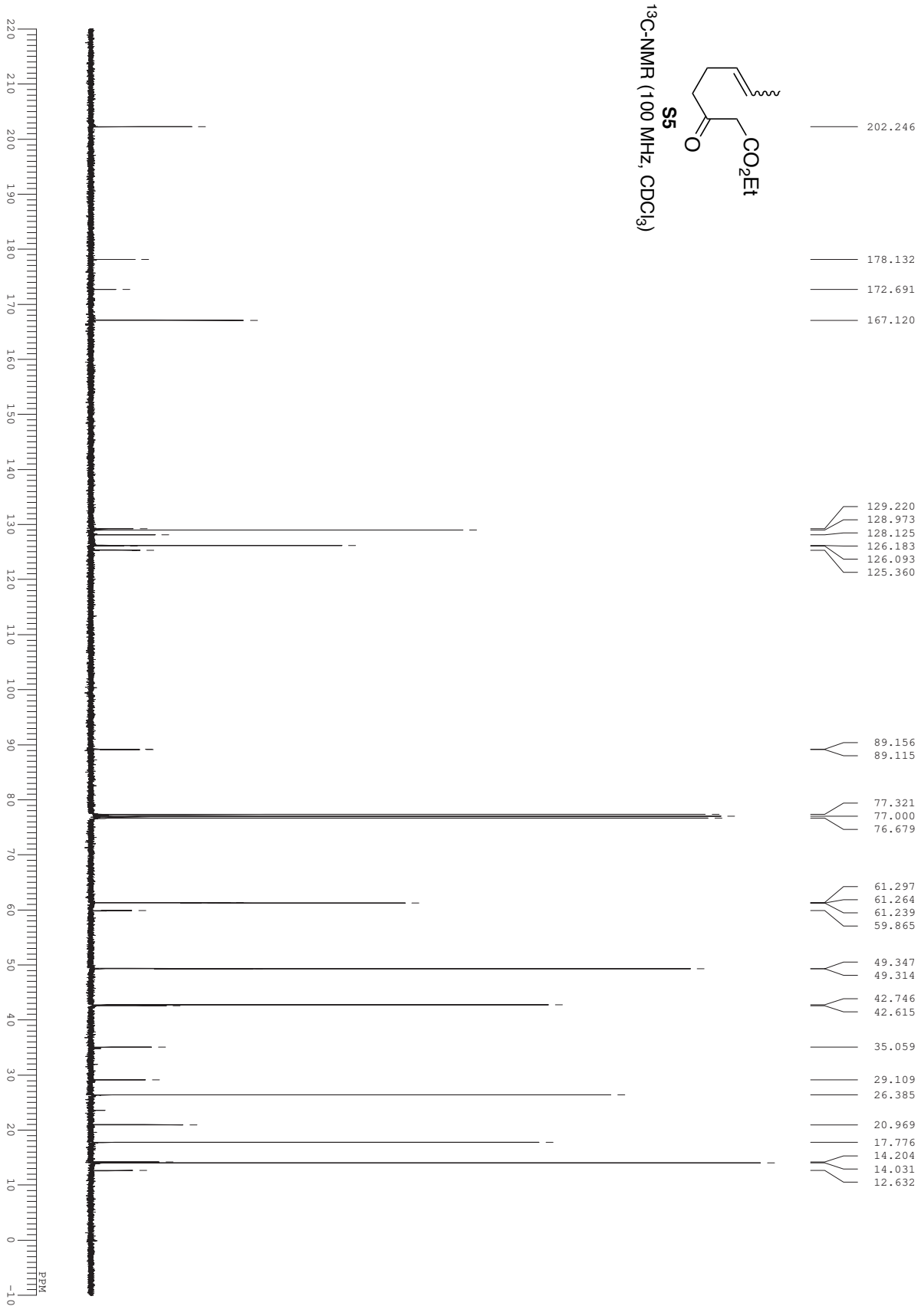

S2
^{13}C-NMR (100 MHz, CDCl$_3$)
CO$_2$Me
O
202.030
167.551
143.882
110.400
77.321
77.000
76.687
52.302
48.959
41.147
31.012
22.549
PPM

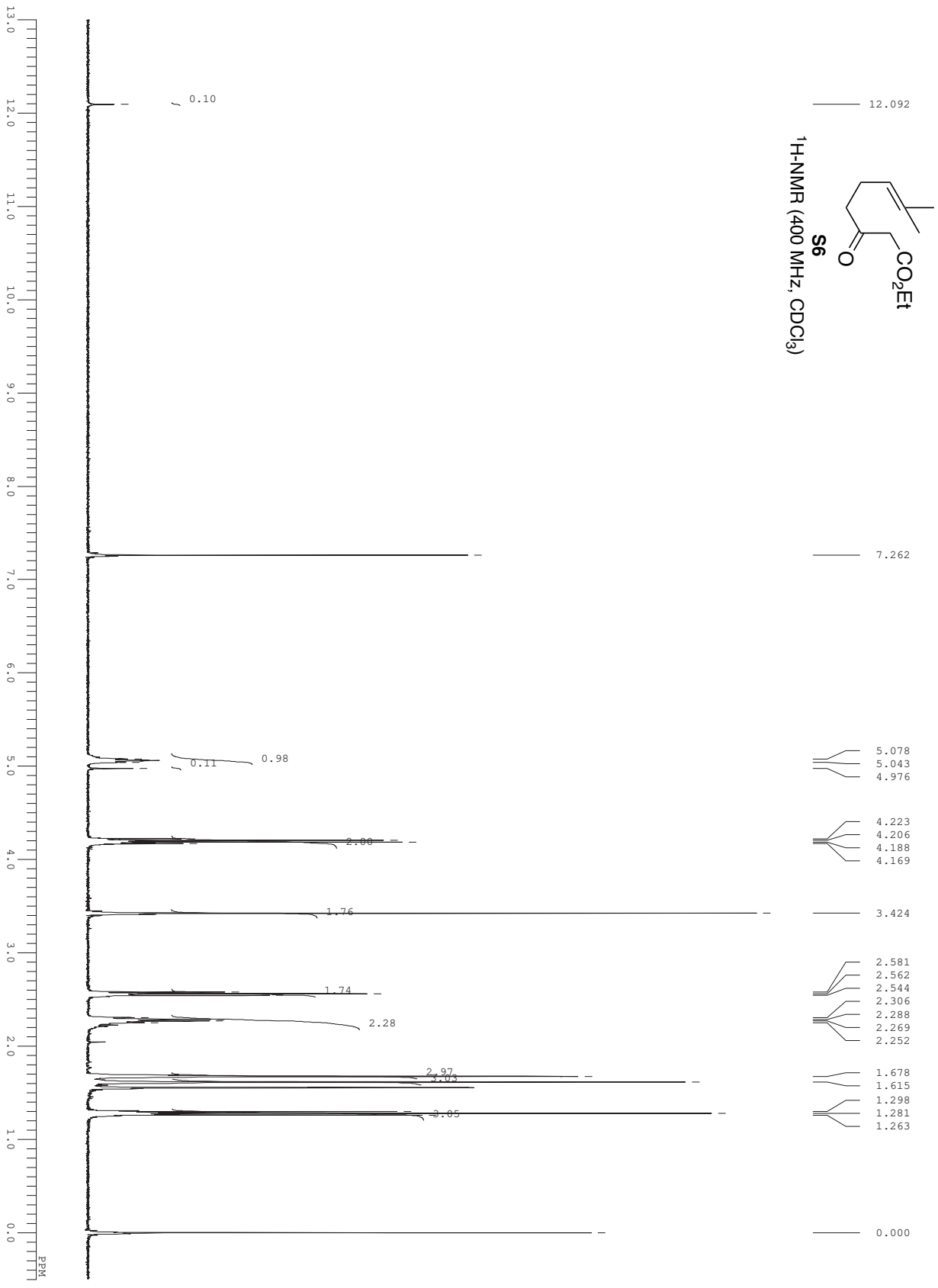

S3
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2t-Bu
O
7.262
4.743
4.666
3.364
2.704
2.686
2.666
2.323
2.304
2.285
1.734
1.473
0.000
1.00
0.90
1.93
1.88
2.19
3.05
9.52
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

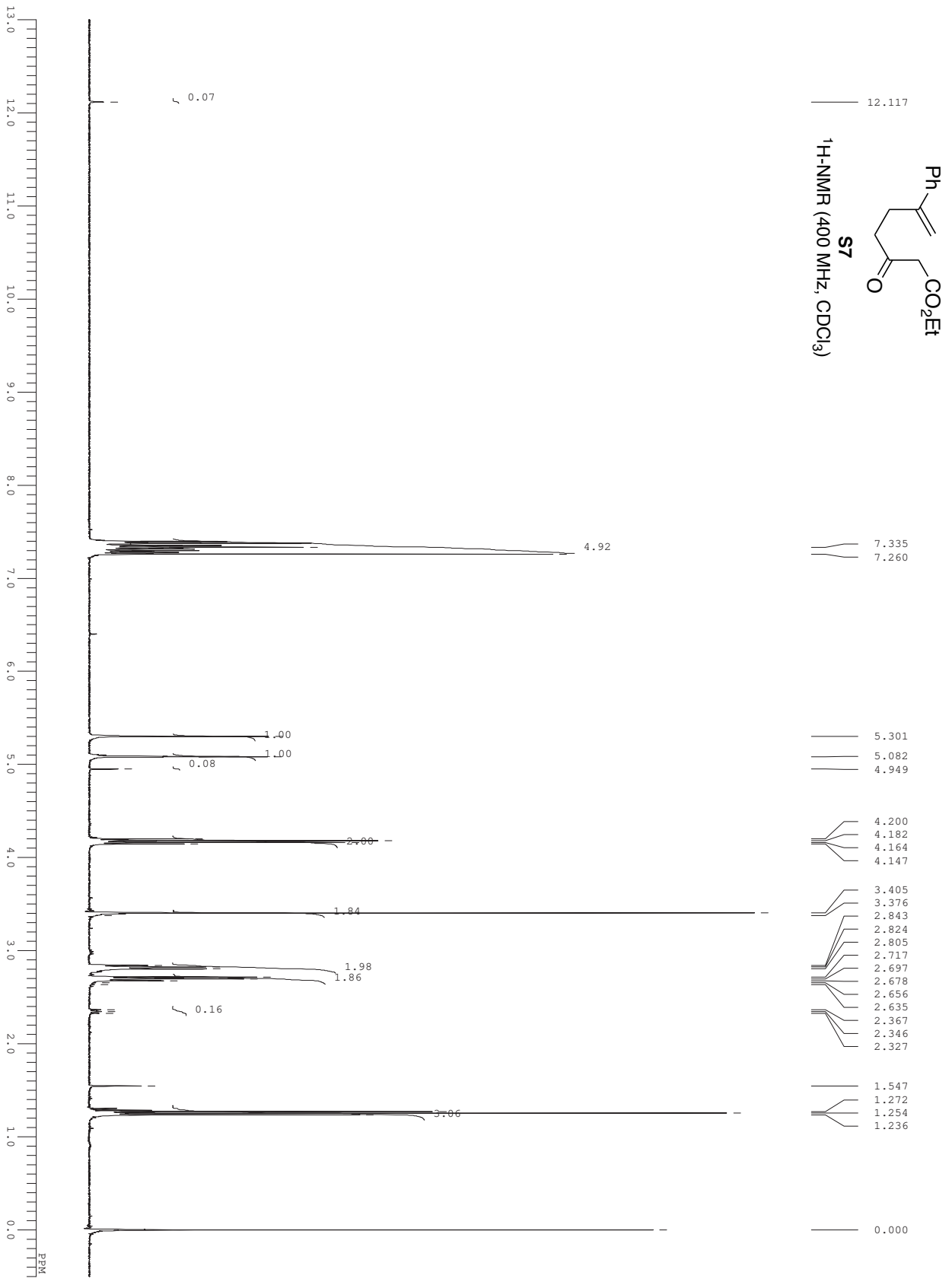

S3
^{13}C-NMR (100 MHz, CDCl$_3$)
O
CO_2t-Bu
202.697
166.415
144.064
110.318
81.940
77.321
77.000
76.687
50.672
41.040
31.078
27.950
22.607
PPM

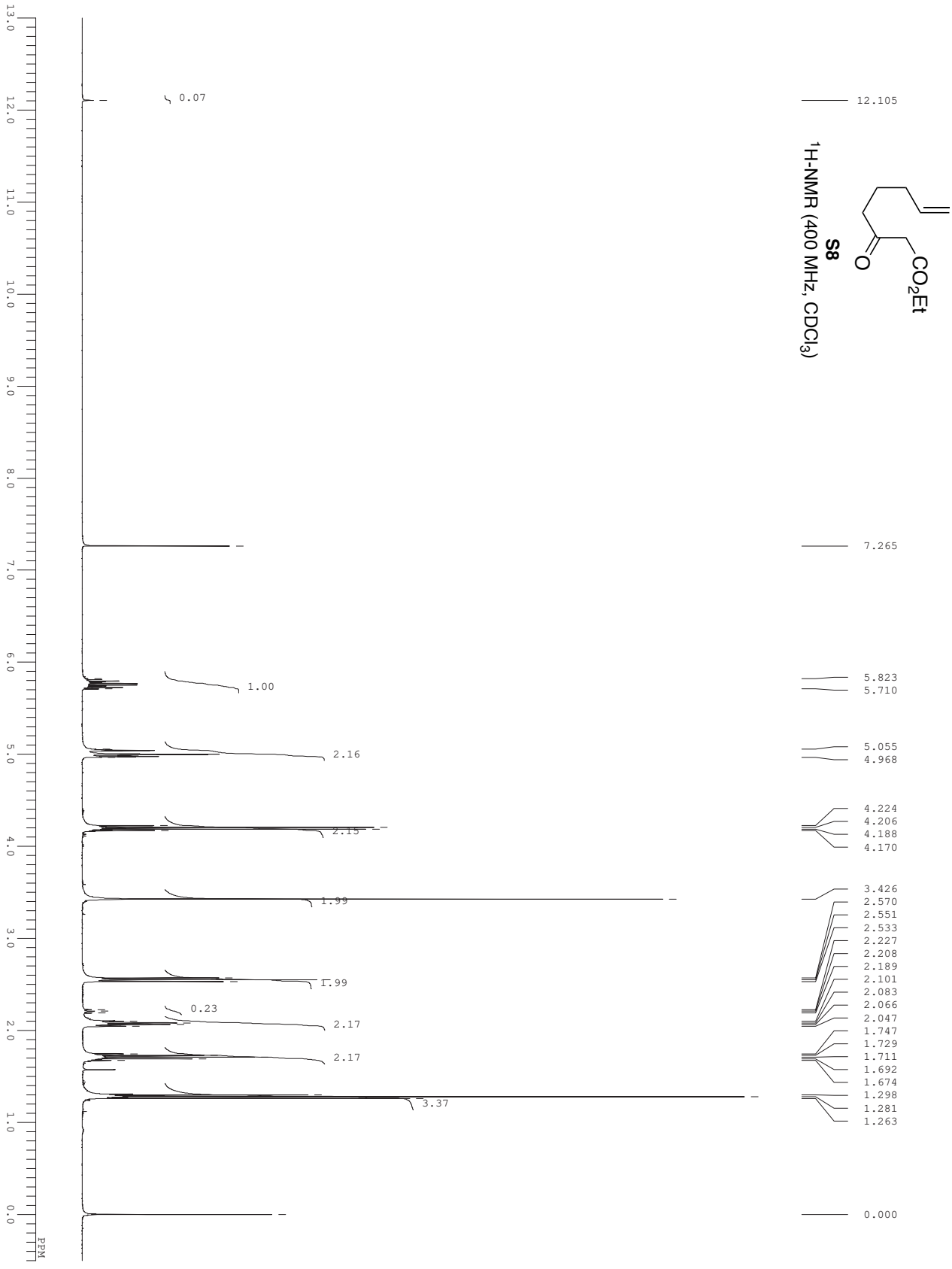

S4
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
O
12.108
7.261
5.855
5.840
5.830
5.823
5.814
5.797
5.787
5.780
5.771
5.754
5.068
5.026
5.011
4.986
4.227
4.208
4.191
4.173
3.438
2.671
2.653
2.634
2.382
2.366
2.348
2.329
1.554
1.299
1.282
1.264
0.000
0.06
0.90
2.00
2.06
1.80
1.78
2.10
3.14
PPM

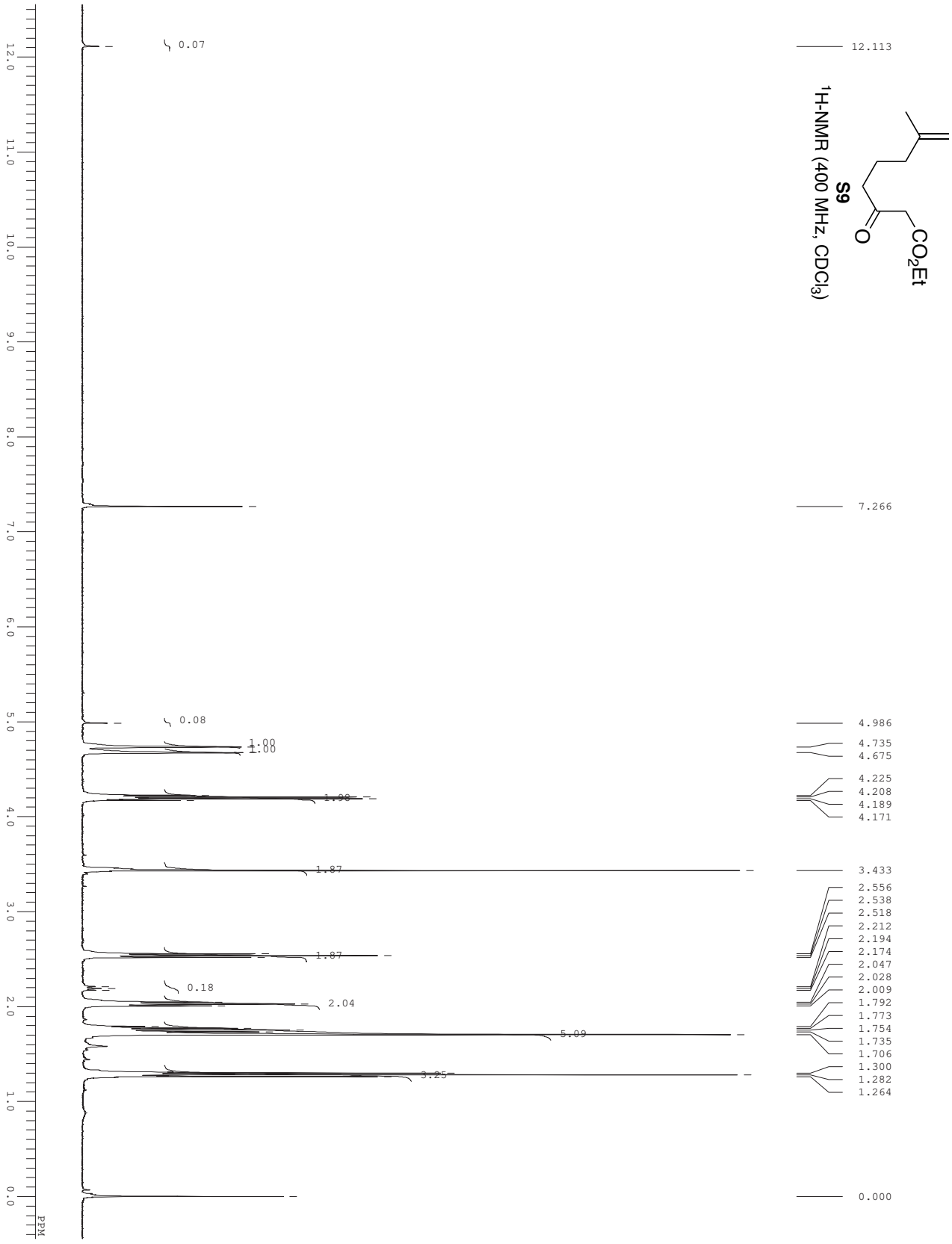

S5
^{1}H-NMR (400 MHz, CDCl$_3$)
CO$_2$Et
O
0.10
1.95
0.11
2.00
1.80
1.83
0.28
1.98
3.03
3.09
12.105
7.265
5.531
5.301
4.988
4.975
4.225
4.208
4.189
4.171
3.439
3.431
2.618
2.600
2.581
2.374
2.355
2.336
2.305
2.287
2.269
2.247
1.656
1.645
1.642
1.630
1.626
1.616
1.571
1.568
1.310
1.300
1.292
1.283
1.274
1.265
0.000
PPM

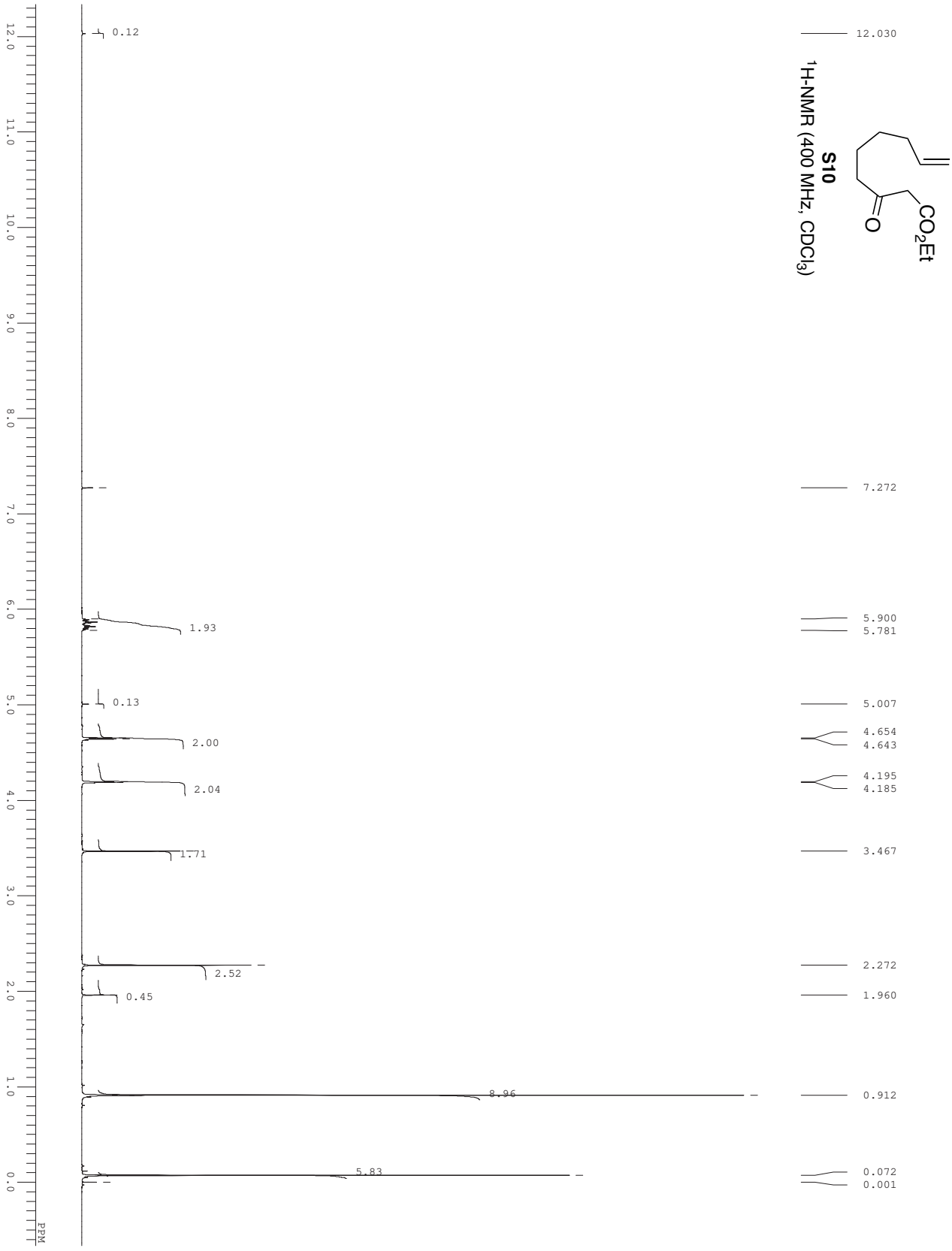

S5
^{13}C-NMR (100 MHz, $CDCl_3$)
O
CO_2Et
202.246
178.132
172.691
167.120
129.220
128.973
128.125
126.183
126.093
125.360
89.156
89.115
77.321
77.000
76.679
61.297
61.264
61.239
59.865
49.347
49.314
42.746
42.615
35.059
29.109
26.385
20.969
17.776
14.204
14.031
12.632
PPM

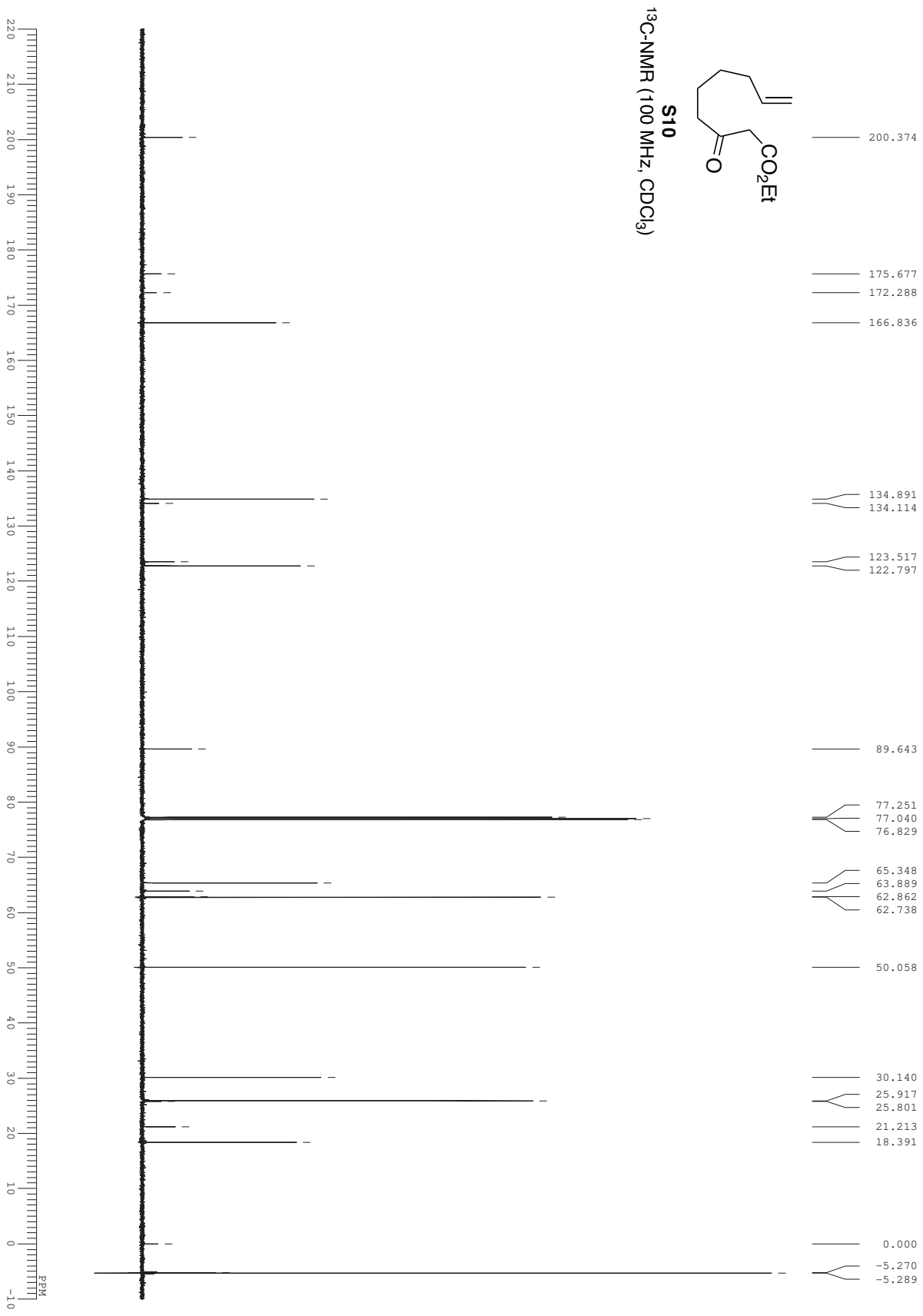

S6
^{1}H-NMR (400 MHz, CDCl$_3$)
CO$_2$Et
O
12.092
7.262
5.078
5.043
4.976
4.223
4.206
4.188
4.169
3.424
2.581
2.562
2.544
2.306
2.288
2.269
2.252
1.678
1.615
1.298
1.281
1.263
0.000
0.10
0.11
0.98
2.00
1.76
1.74
2.28
2.97
3.03
3.05
PPM

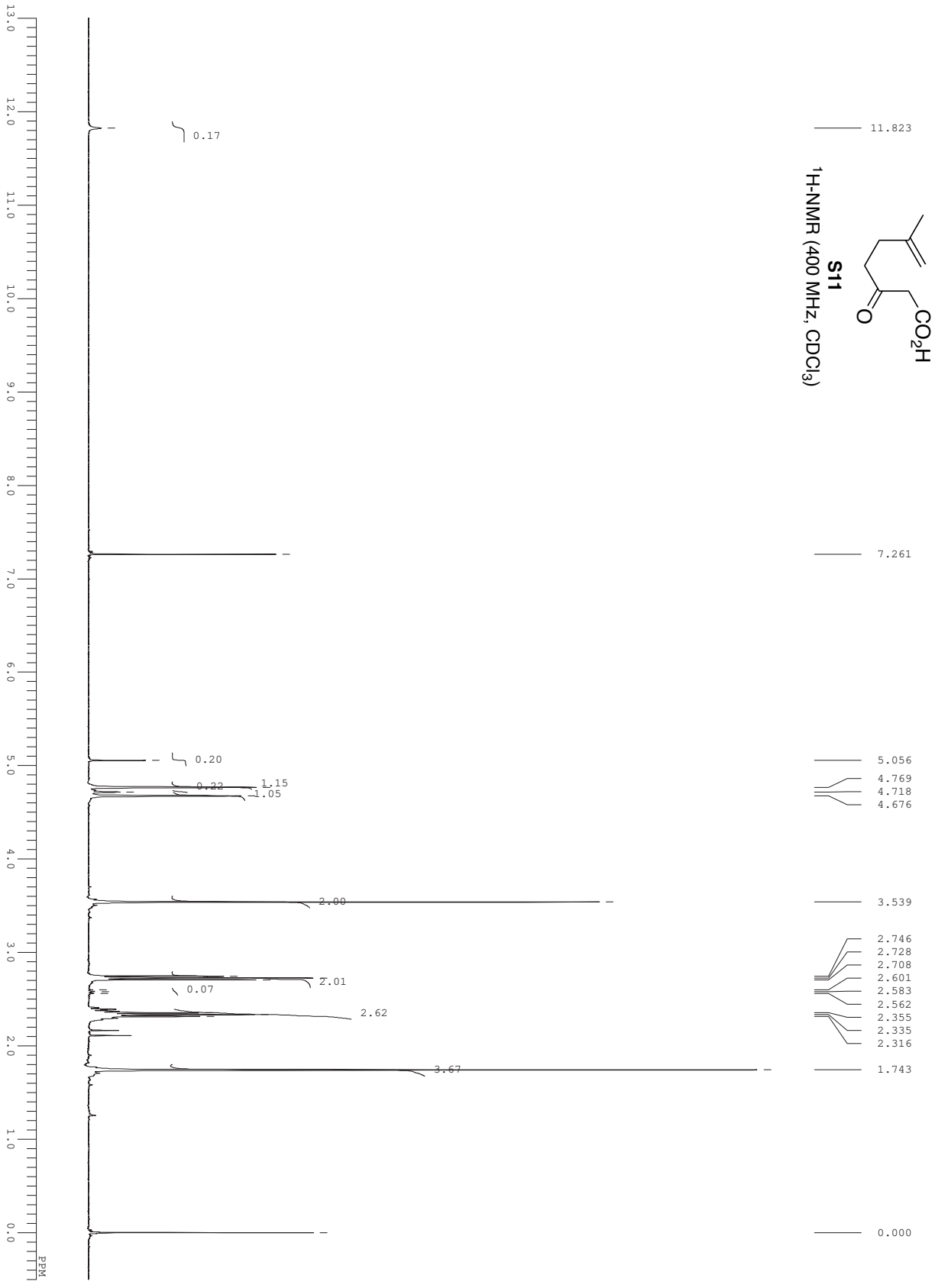

S7
^{1}H-NMR (400 MHz, CDCl$_3$)
Ph
CO$_2$Et
O
12.117
7.335
7.260
5.301
5.082
4.949
4.200
4.182
4.164
4.147
3.405
3.376
2.843
2.824
2.805
2.717
2.697
2.678
2.656
2.635
2.367
2.346
2.327
1.547
1.272
1.254
1.236
0.000
0.07
4.92
1.00
1.00
0.08
2.00
1.84
1.98
1.86
0.16
3.06
PPM

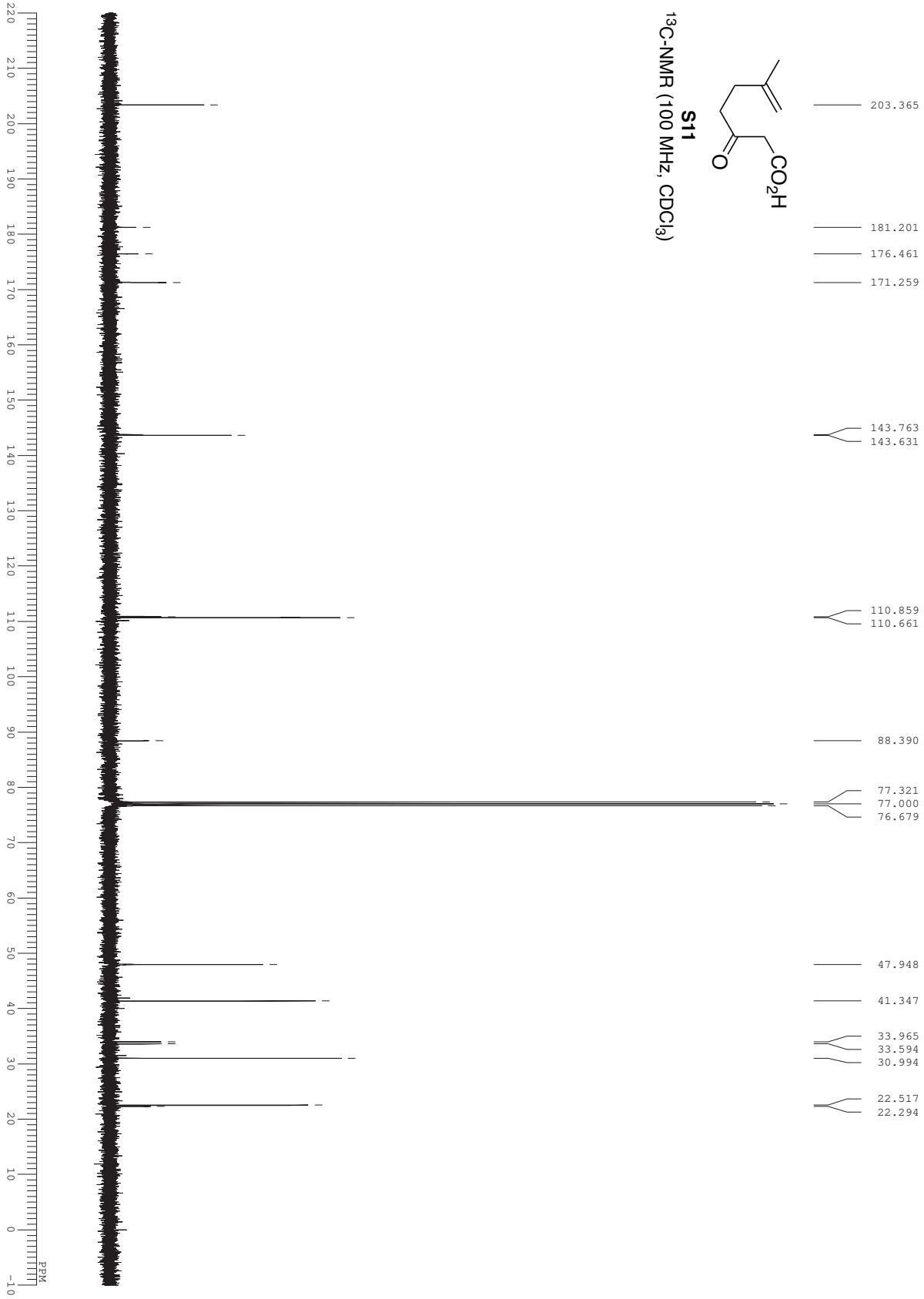

S8
^{1}H-NMR (400 MHz, CDCl$_3$)
CO$_2$Et
O
12.105
7.265
5.823
5.710
5.055
4.968
4.224
4.206
4.188
4.170
3.426
2.570
2.551
2.533
2.227
2.208
2.189
2.101
2.083
2.066
2.047
1.747
1.729
1.711
1.692
1.674
1.298
1.281
1.263
0.000
0.07
1.00
2.16
2.15
1.99
1.99
0.23
2.17
2.17
3.37
PPM

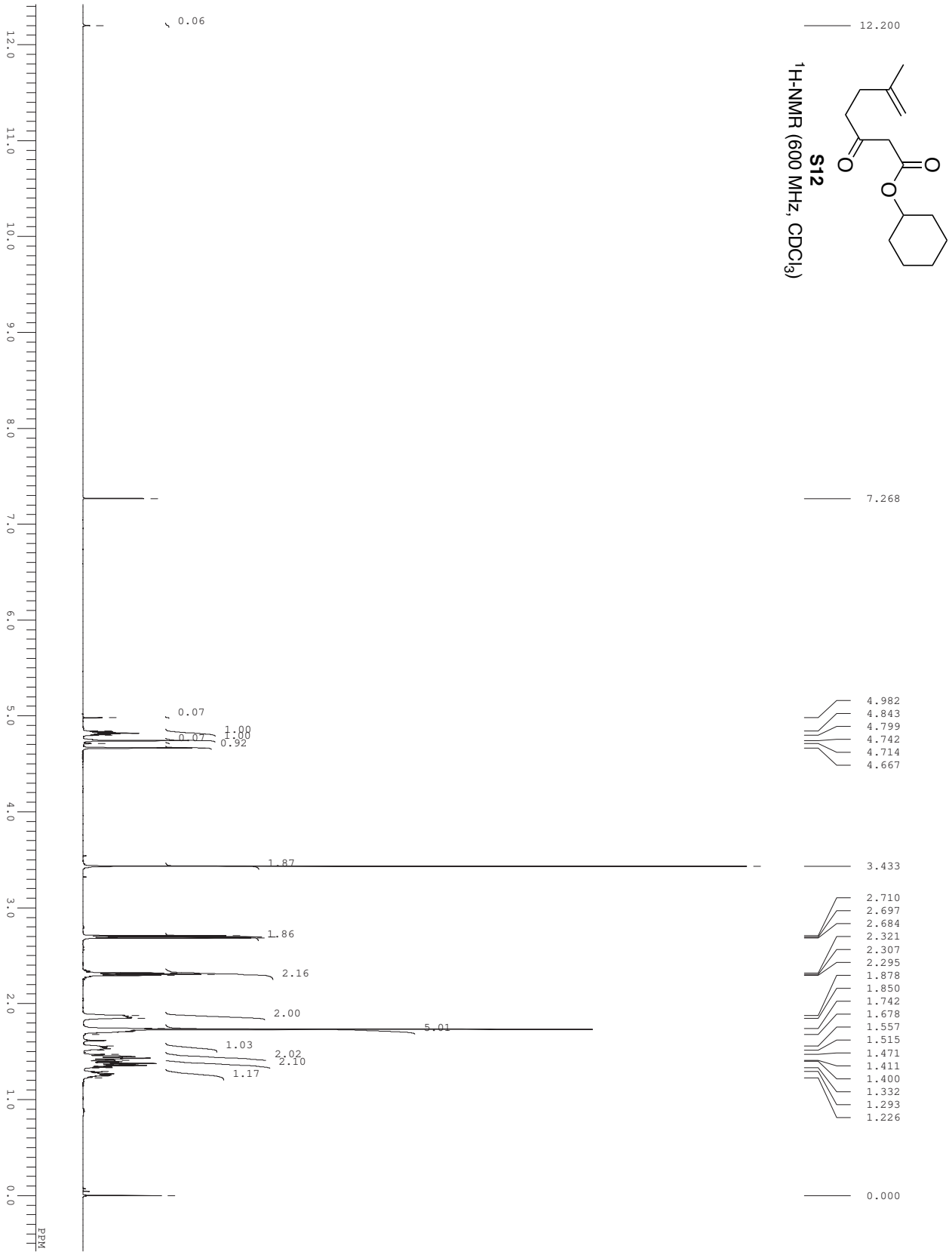

S9
^{1}H-NMR (400 MHz, CDCl$_3$)
CO_2Et
O
12.113
7.266
4.986
4.735
4.675
4.225
4.208
4.189
4.171
3.433
2.556
2.538
2.518
2.212
2.194
2.174
2.047
2.028
2.009
1.792
1.773
1.754
1.735
1.706
1.300
1.282
1.264
0.000
0.07
0.08
1.00
1.00
1.98
1.87
1.87
0.18
2.04
5.09
3.25
PPM

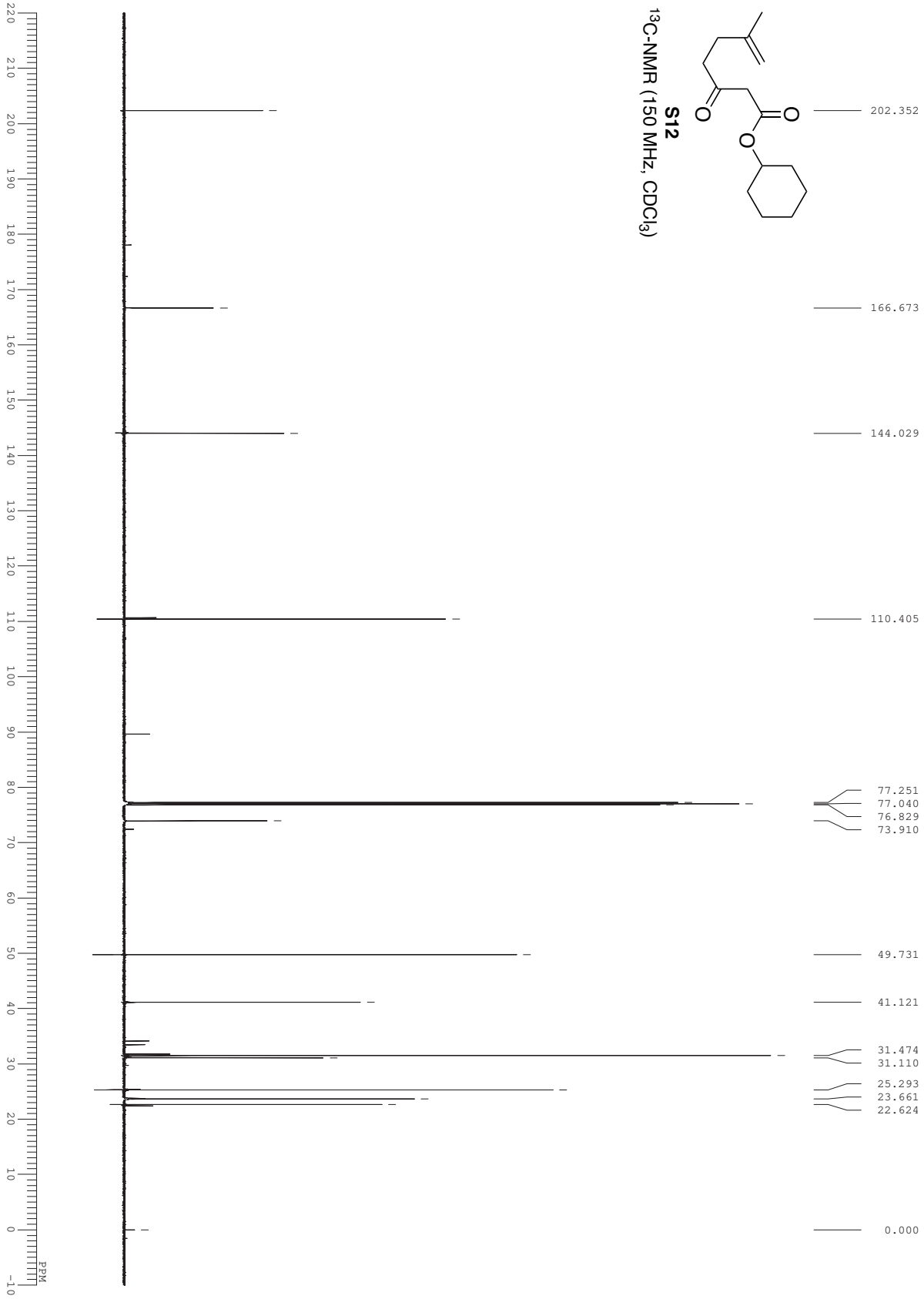

S10
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
O
12.030
7.272
5.900
5.781
5.007
4.654
4.643
4.195
4.185
3.467
2.272
1.960
0.912
0.072
0.001
0.12
1.93
0.13
2.00
2.04
1.71
2.52
0.45
8.96
5.83
ppm

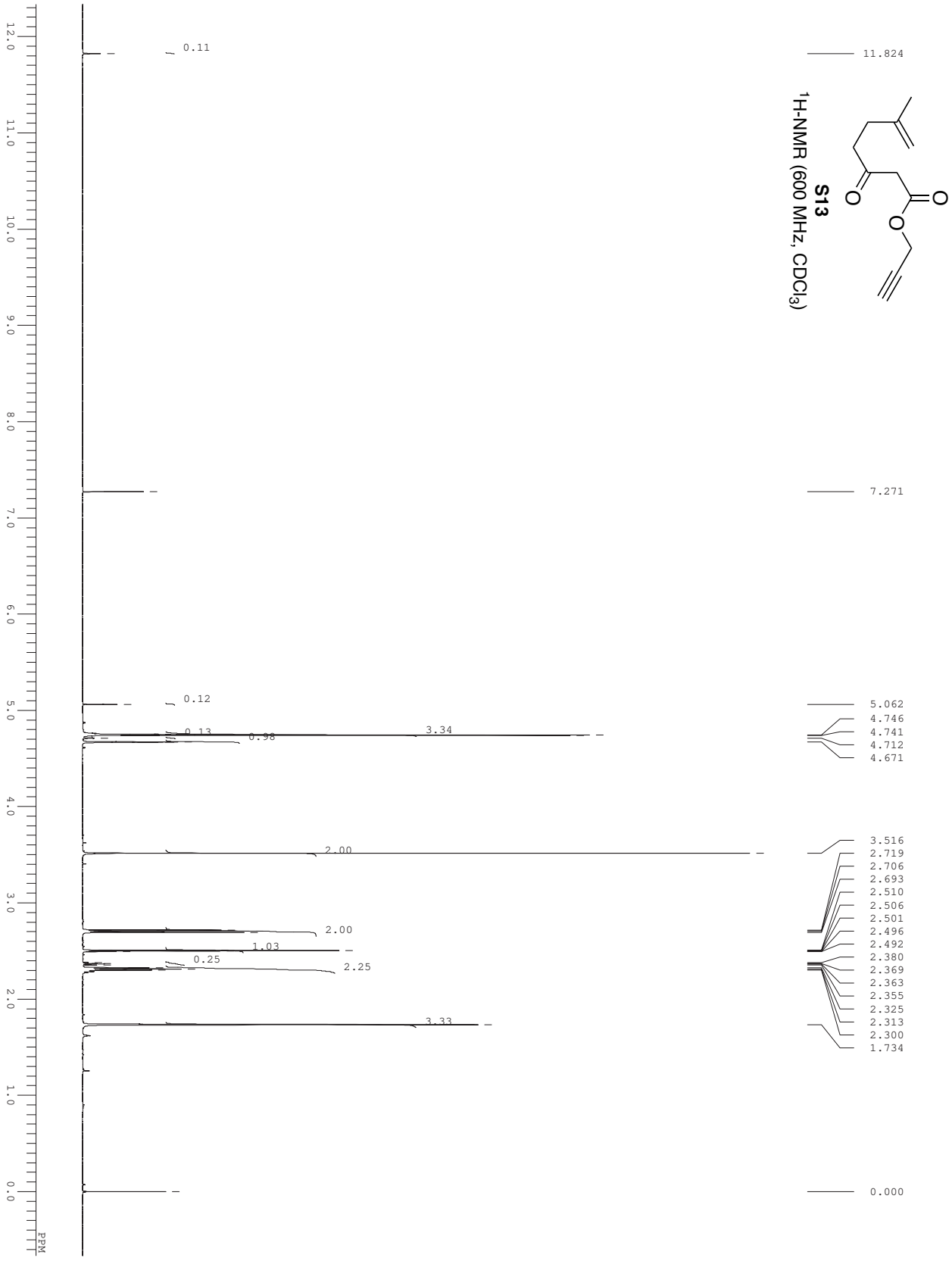

S10
^{13}C-NMR (100 MHz, CDCl$_3$)
O
CO$_2$Et
200.374
175.677
172.288
166.836
134.891
134.114
123.517
122.797
89.643
77.251
77.040
76.829
65.348
63.889
62.862
62.738
50.058
30.140
25.917
25.801
21.213
18.391
0.000
-5.270
-5.289
PPM

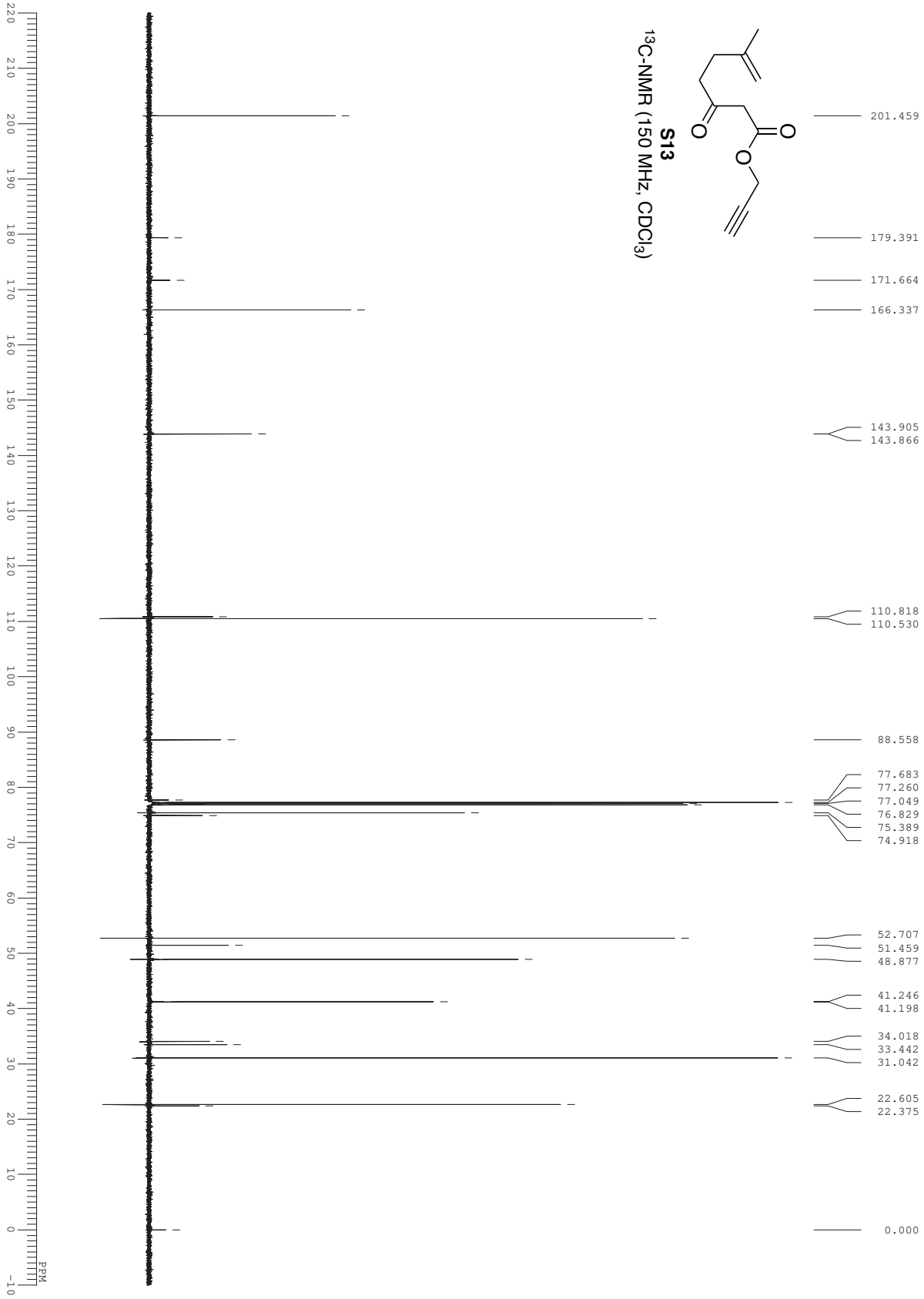

S11
^{1}H-NMR (400 MHz, CDCl$_3$)
CO$_2$H
O
11.823
7.261
5.056
4.769
4.718
4.676
3.539
2.746
2.728
2.708
2.601
2.583
2.562
2.355
2.335
2.316
1.743
0.000
0.17
0.20
0.22
1.15
1.05
2.00
2.01
0.07
2.62
3.67
PPM

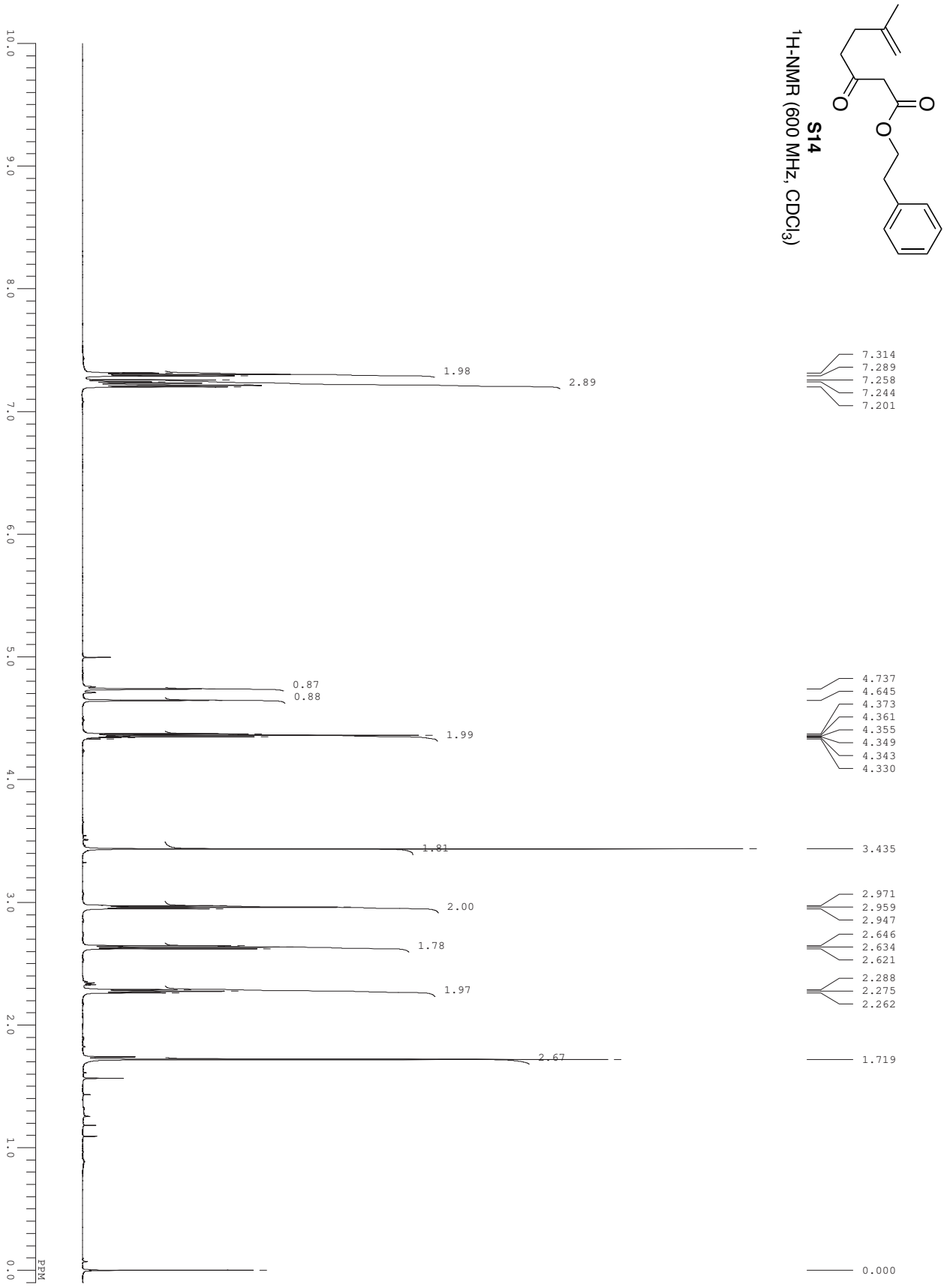

S11
^{13}C-NMR (100 MHz, CDCl$_3$)
O
CO$_2$H
203.365
181.201
176.461
171.259
143.763
143.631
110.859
110.661
88.390
77.321
77.000
76.679
47.948
41.347
33.965
33.594
30.994
22.517
22.294
PPM

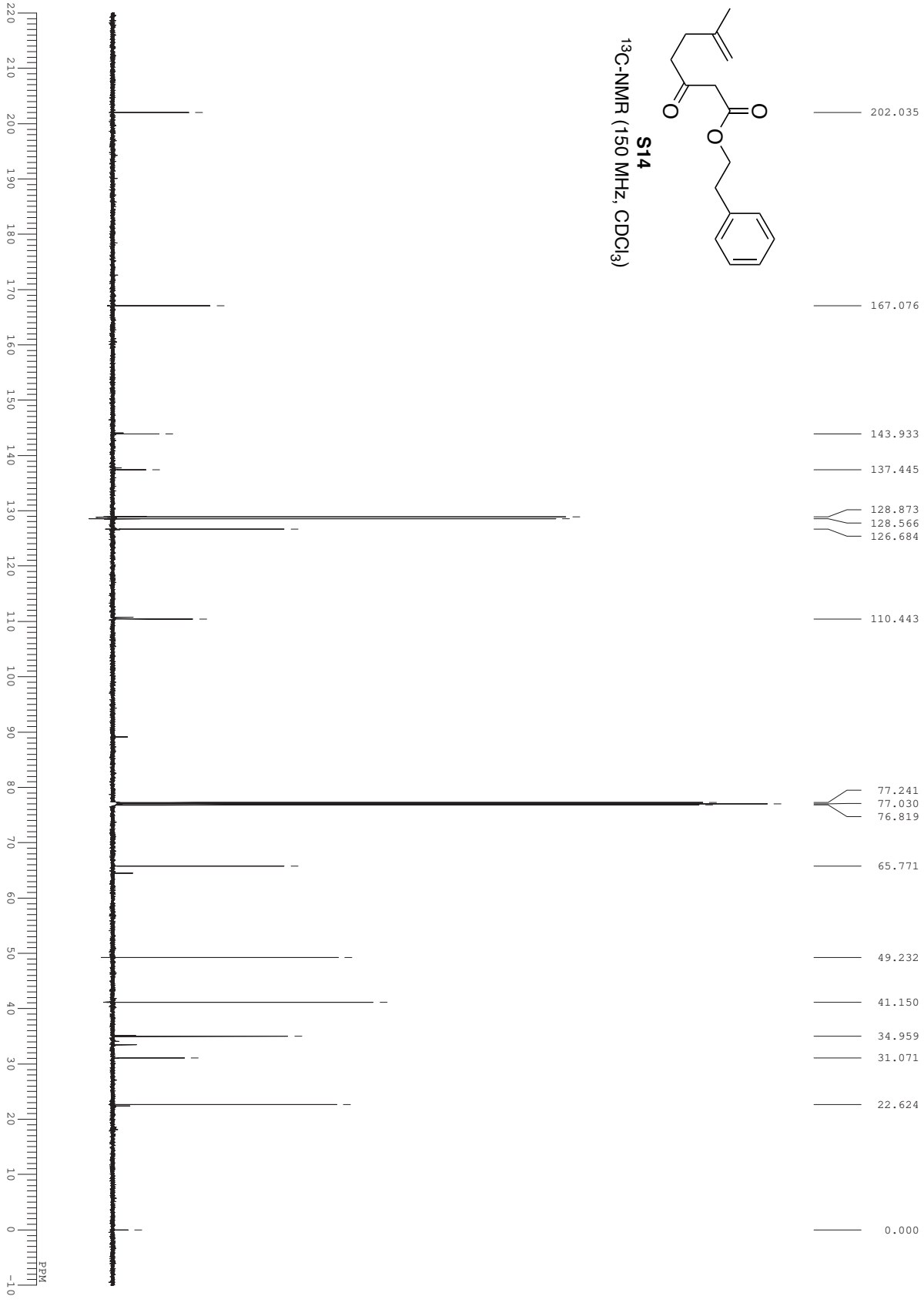

S12
^{1}H-NMR (600 MHz, $CDCl_3$)
12.200
7.268
4.982
4.843
4.799
4.742
4.714
4.667
3.433
2.710
2.697
2.684
2.321
2.307
2.295
1.878
1.850
1.742
1.678
1.557
1.515
1.471
1.411
1.400
1.332
1.293
1.226
0.000
0.06
0.07
1.00
1.00
0.92
1.87
1.86
2.16
2.00
5.01
1.03
2.02
2.10
1.17
PPM

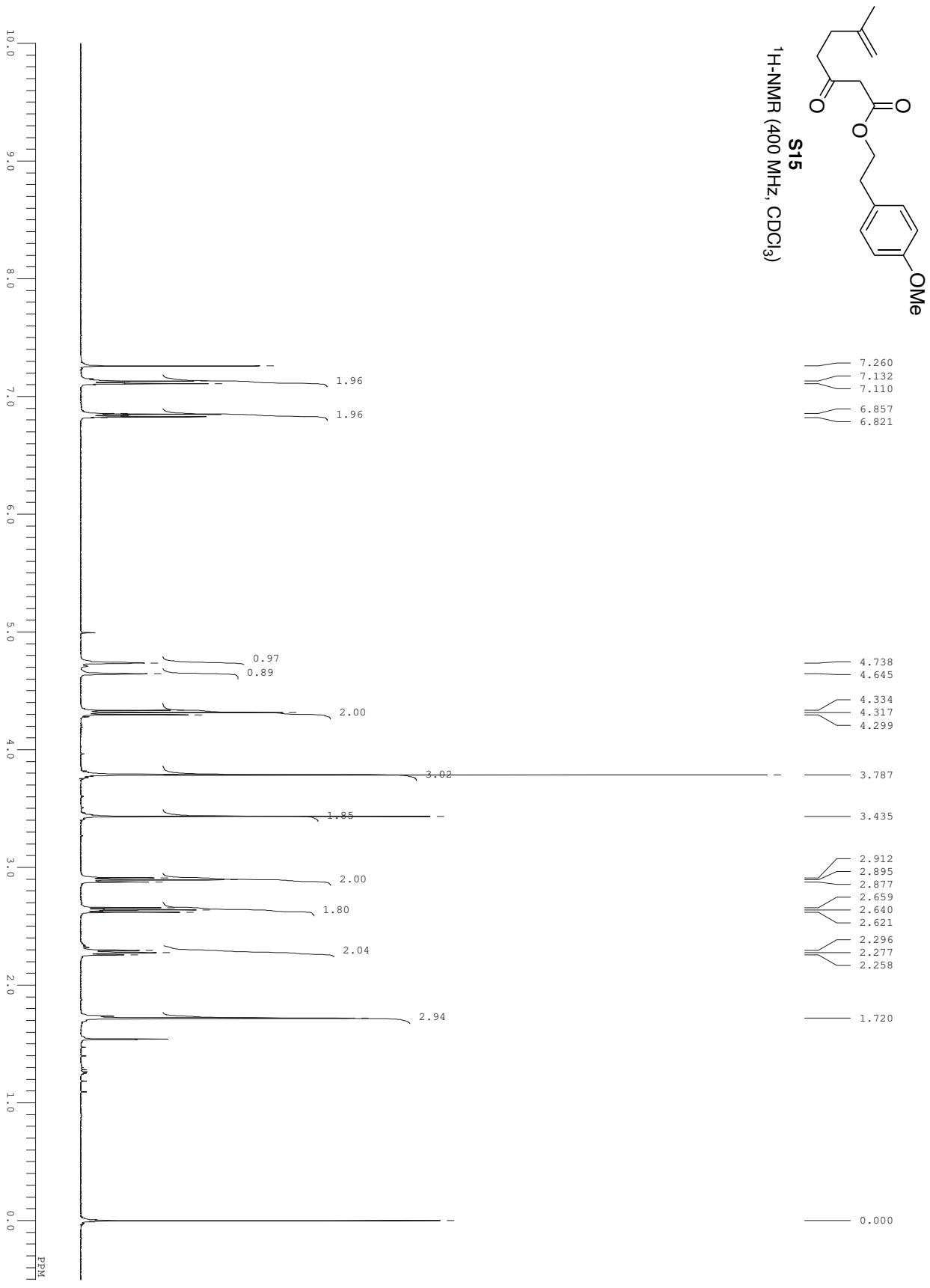

S12
^{13}C-NMR (150 MHz, CDCl$_3$)
O
O
O
202.352
166.673
144.029
110.405
77.251
77.040
76.829
73.910
49.731
41.121
31.474
31.110
25.293
23.661
22.624
0.000
PPM

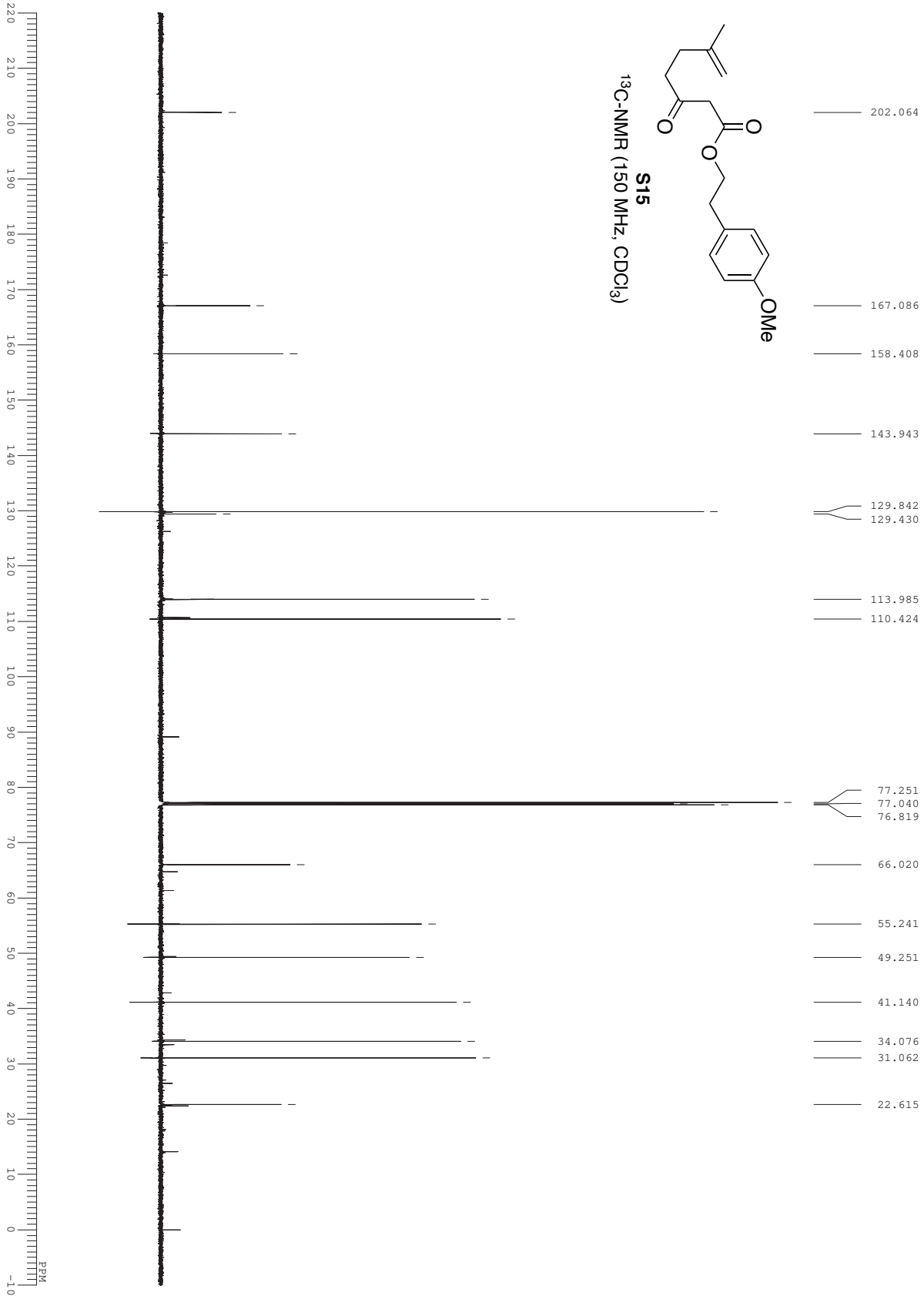

S13
^{1}H-NMR (600 MHz, $CDCl_3$)
11.824
7.271
5.062
4.746
4.741
4.712
4.671
3.516
2.719
2.706
2.693
2.510
2.506
2.501
2.496
2.492
2.380
2.369
2.363
2.355
2.325
2.313
2.300
1.734
0.000
0.11
0.12
0.13
0.98
3.34
2.00
2.00
1.03
0.25
2.25
3.33
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

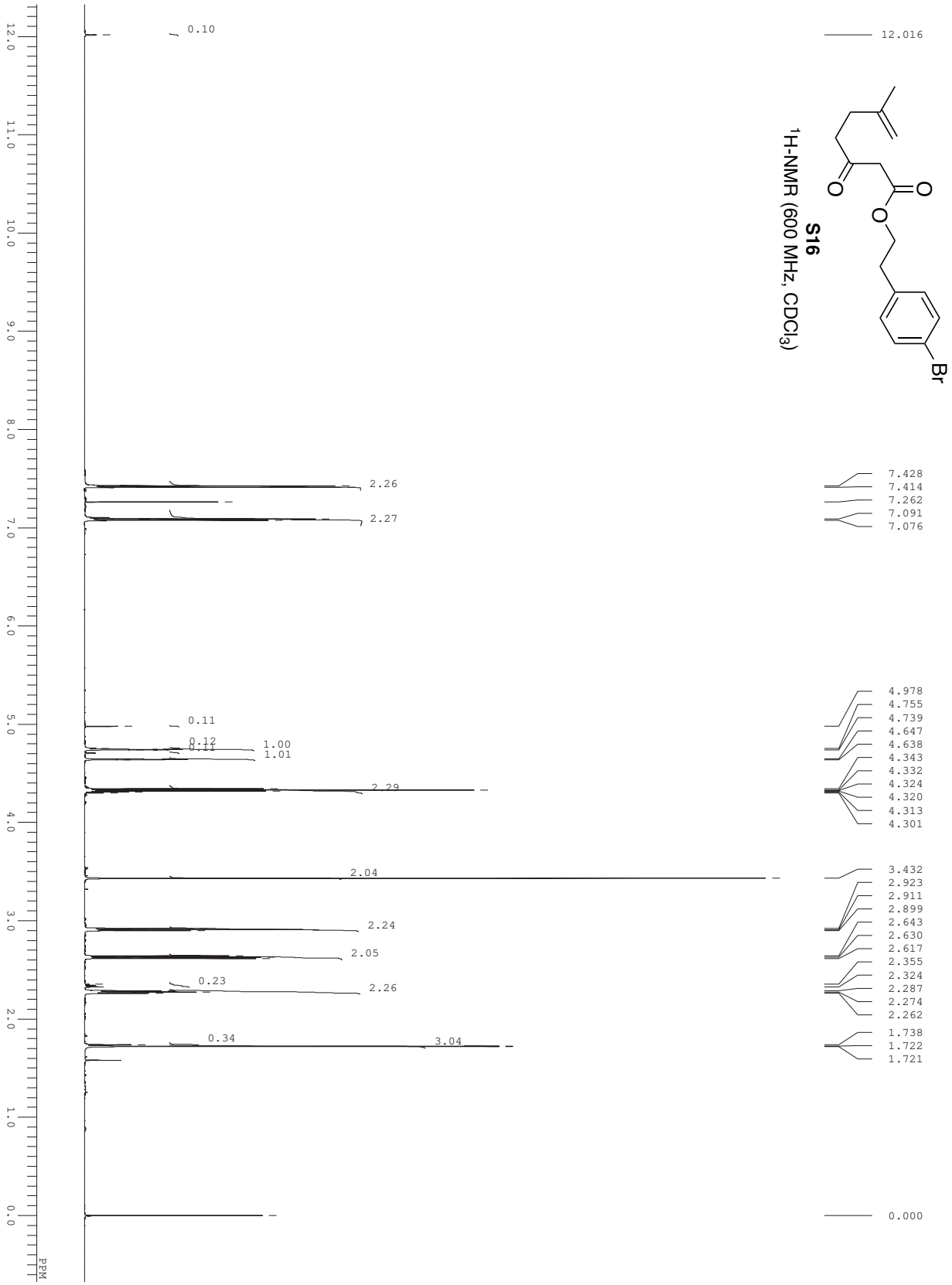

S13
^{13}C-NMR (150 MHz, $CDCl_3$)
O
O
O
O
201.459
179.391
171.664
166.337
143.905
143.866
110.818
110.530
88.558
77.683
77.260
77.049
76.829
75.389
74.918
52.707
51.459
48.877
41.246
41.198
34.018
33.442
31.042
22.605
22.375
0.000
PPM

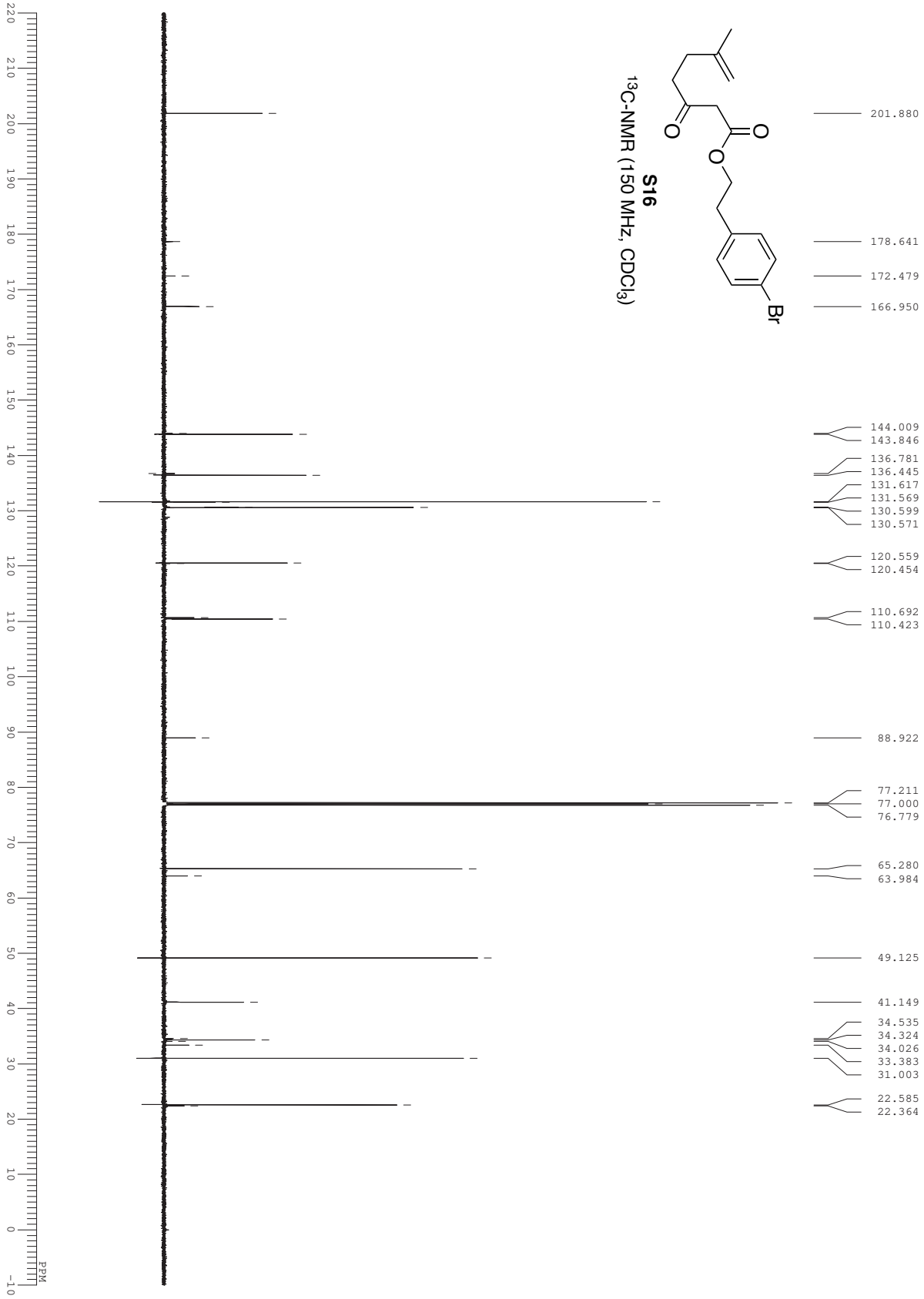

S14
1H-NMR (600 MHz, CDCl3)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
1.98
2.89
0.87
0.88
1.99
1.81
2.00
1.78
1.97
2.67
7.314
7.289
7.258
7.244
7.201
4.737
4.645
4.373
4.361
4.355
4.349
4.343
4.330
3.435
2.971
2.959
2.947
2.646
2.634
2.621
2.288
2.275
2.262
1.719
0.000

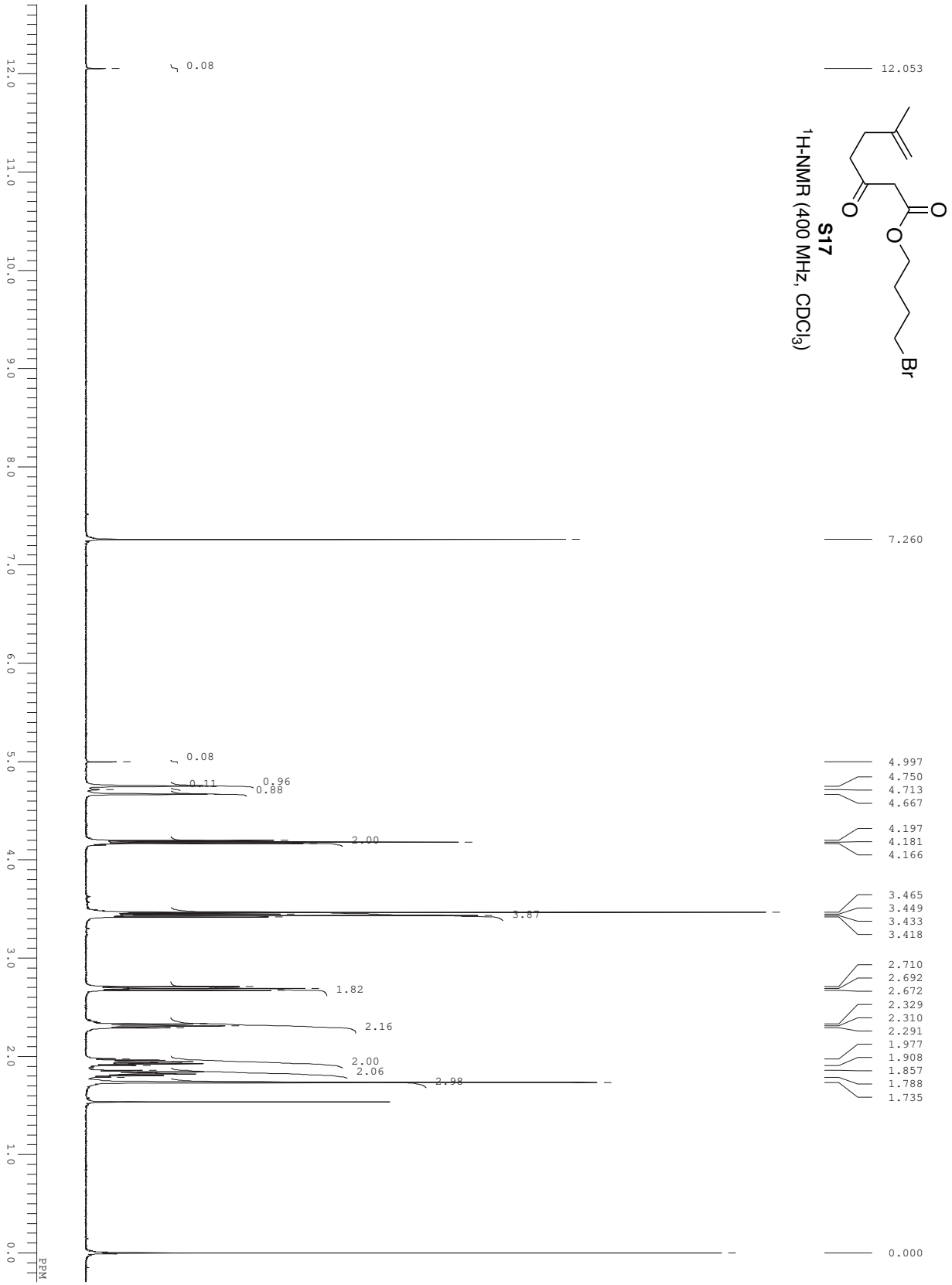

S14
^{13}C-NMR (150 MHz, CDCl$_3$)
O
O
O
202.035
167.076
143.933
137.445
128.873
128.566
126.684
110.443
77.241
77.030
76.819
65.771
49.232
41.150
34.959
31.071
22.624
0.000
PPM

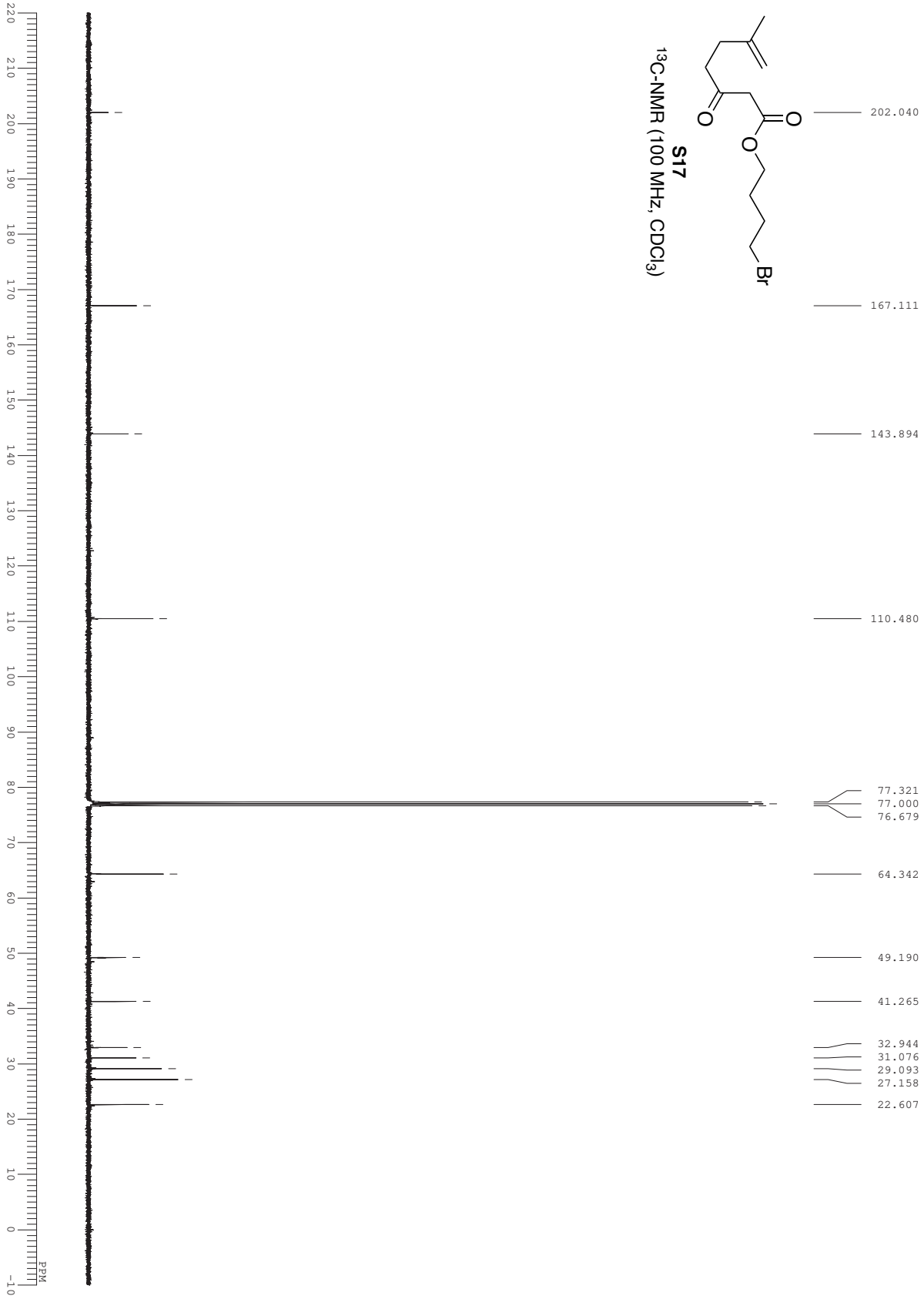

S15
1H-NMR (400 MHz, CDCl3)
OMe
7.260
7.132
7.110
6.857
6.821
4.738
4.645
4.334
4.317
4.299
3.787
3.435
2.912
2.895
2.877
2.659
2.640
2.621
2.296
2.277
2.258
1.720
0.000
1.96
1.96
0.97
0.89
2.00
3.02
1.85
2.00
1.80
2.04
2.94
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

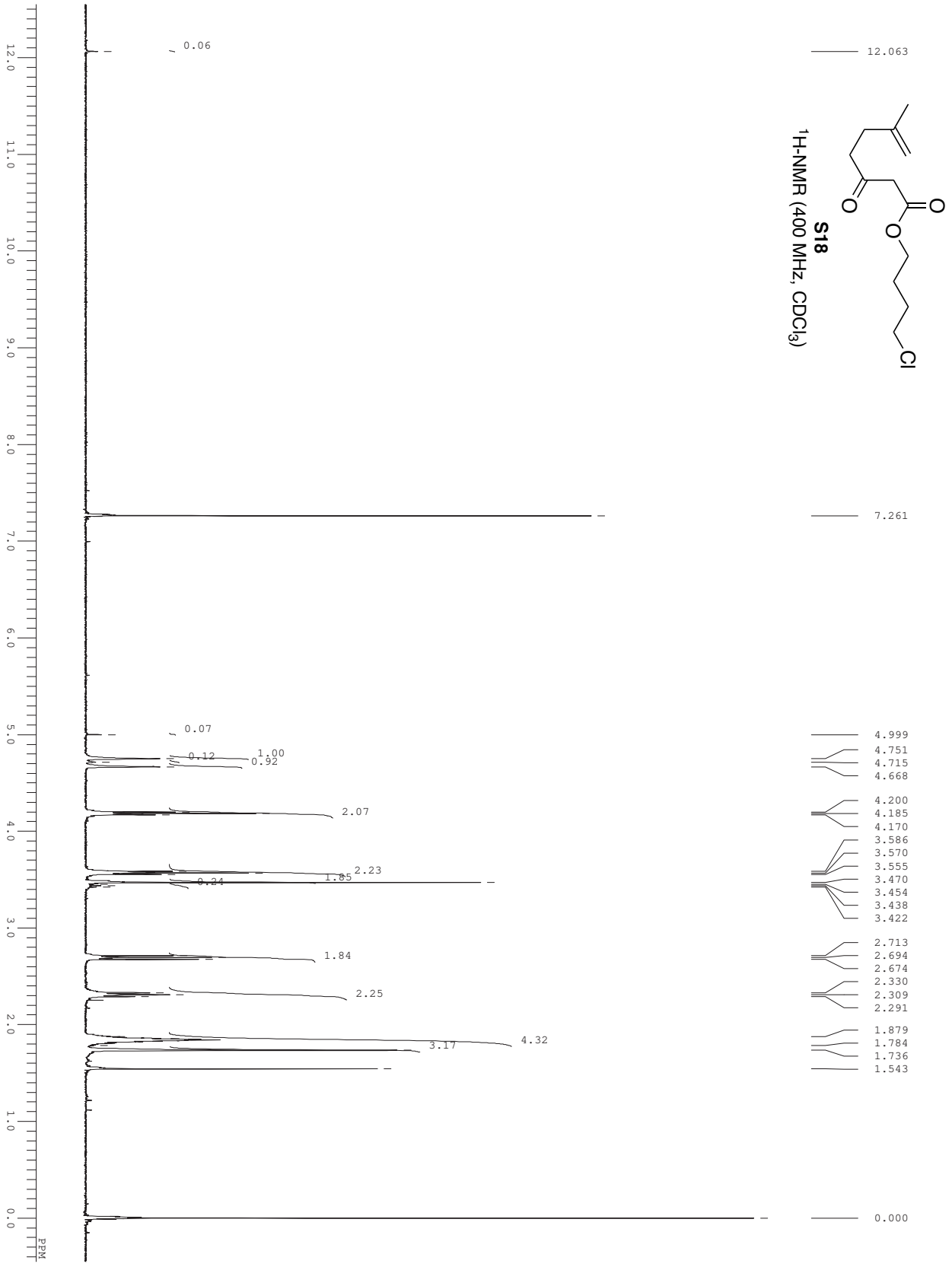

S15
^{13}C-NMR (150 MHz, CDCl$_3$)
OMe
202.064
167.086
158.408
143.943
129.842
129.430
113.985
110.424
77.251
77.040
76.819
66.020
55.241
49.251
41.140
34.076
31.062
22.615
PPM

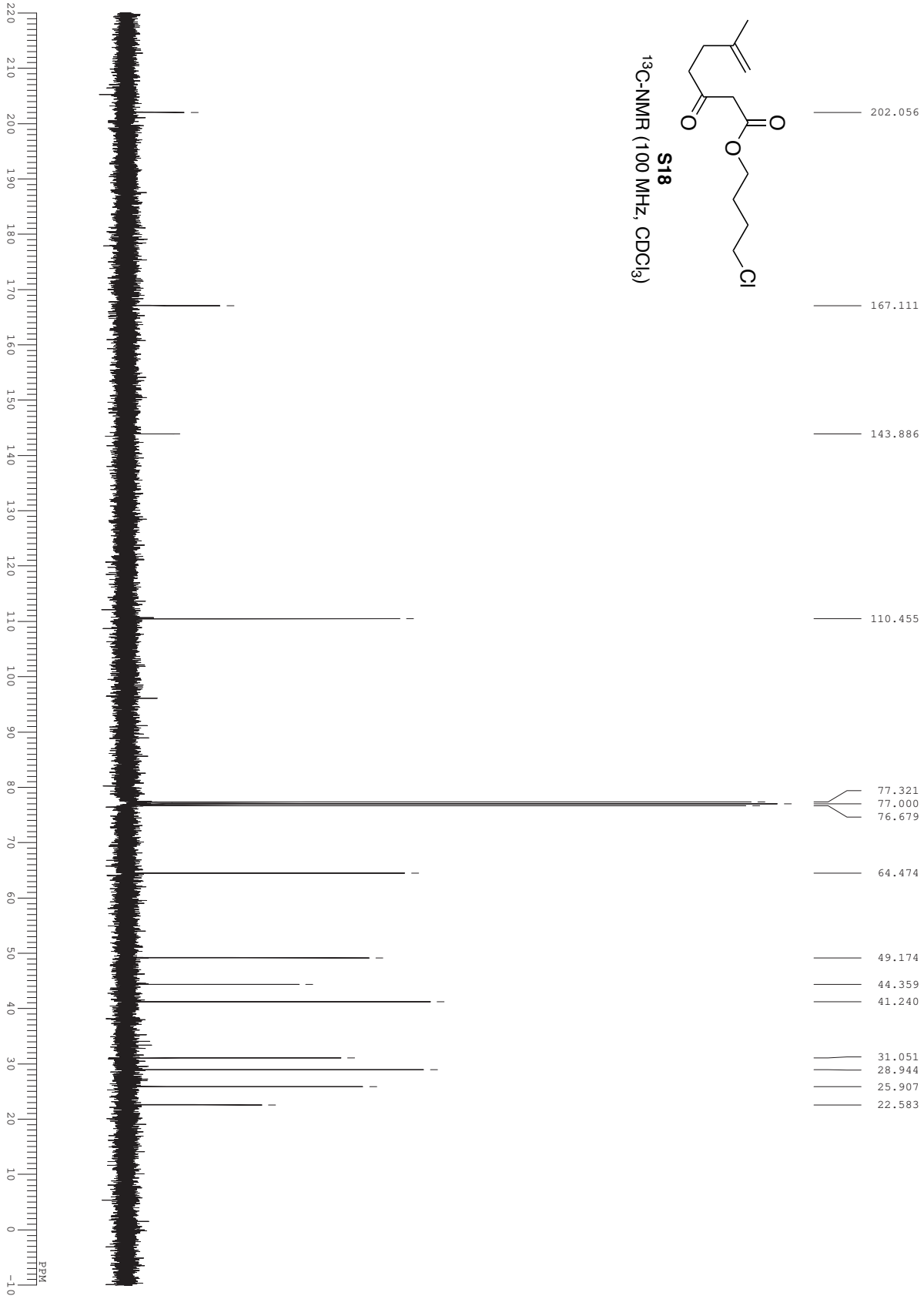

S16
^{1}H-NMR (600 MHz, CDCl$_3$)
Br
12.016
7.428
7.414
7.262
7.091
7.076
4.978
4.755
4.739
4.647
4.638
4.343
4.332
4.324
4.320
4.313
4.301
3.432
2.923
2.911
2.899
2.643
2.630
2.617
2.355
2.324
2.287
2.274
2.262
1.738
1.722
1.721
0.000
0.10
2.26
2.27
0.11
0.12
0.11
1.00
1.01
2.29
2.04
2.24
2.05
0.23
2.26
0.34
3.04
PPM

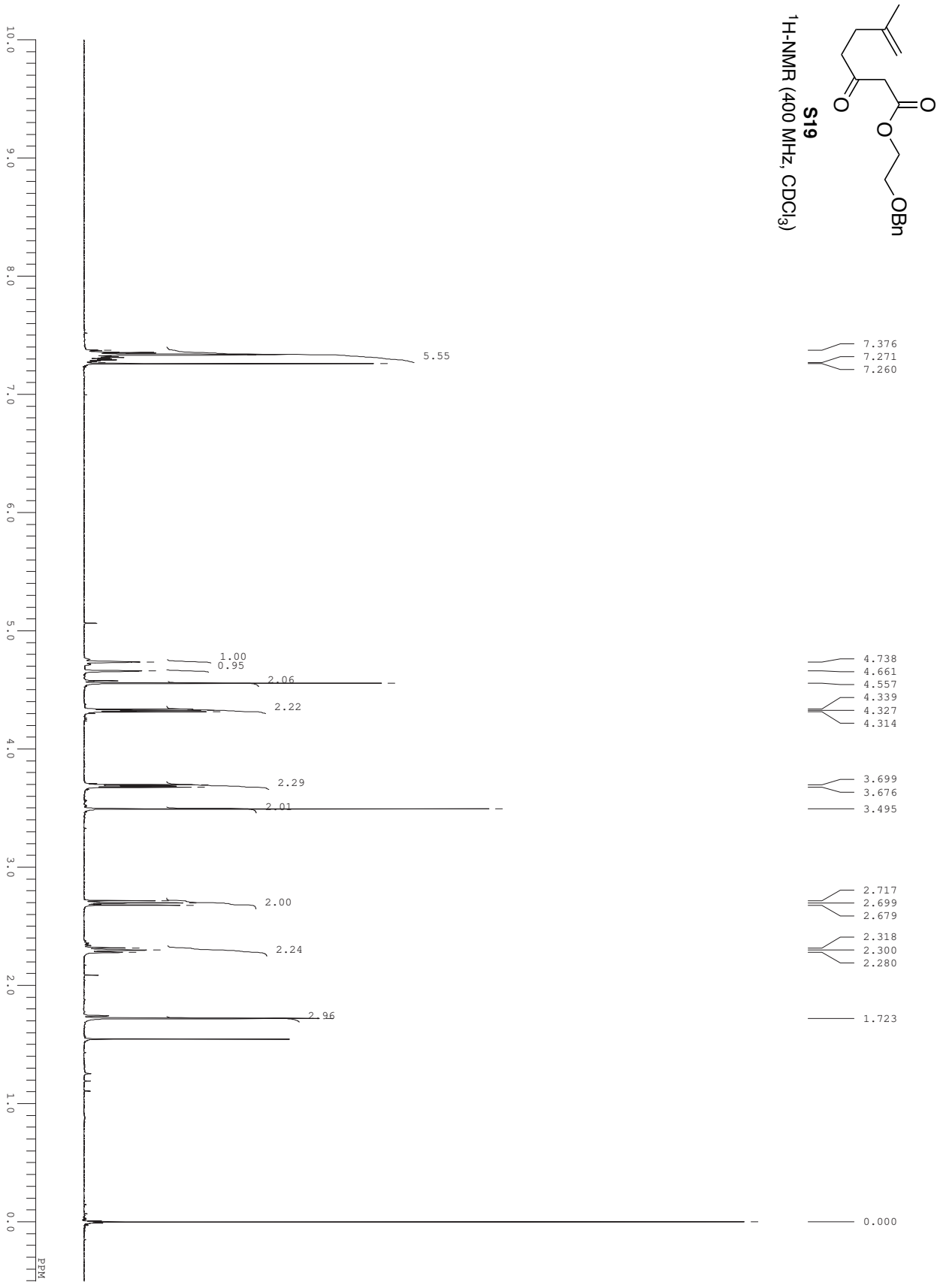

S16
^{13}C-NMR (150 MHz, CDCl$_3$)
O
O
O
Br
201.880
178.641
172.479
166.950
144.009
143.846
136.781
136.445
131.617
131.569
130.599
130.571
120.559
120.454
110.692
110.423
88.922
77.211
77.000
76.779
65.280
63.984
49.125
41.149
34.535
34.324
34.026
33.383
31.003
22.585
22.364
PPM

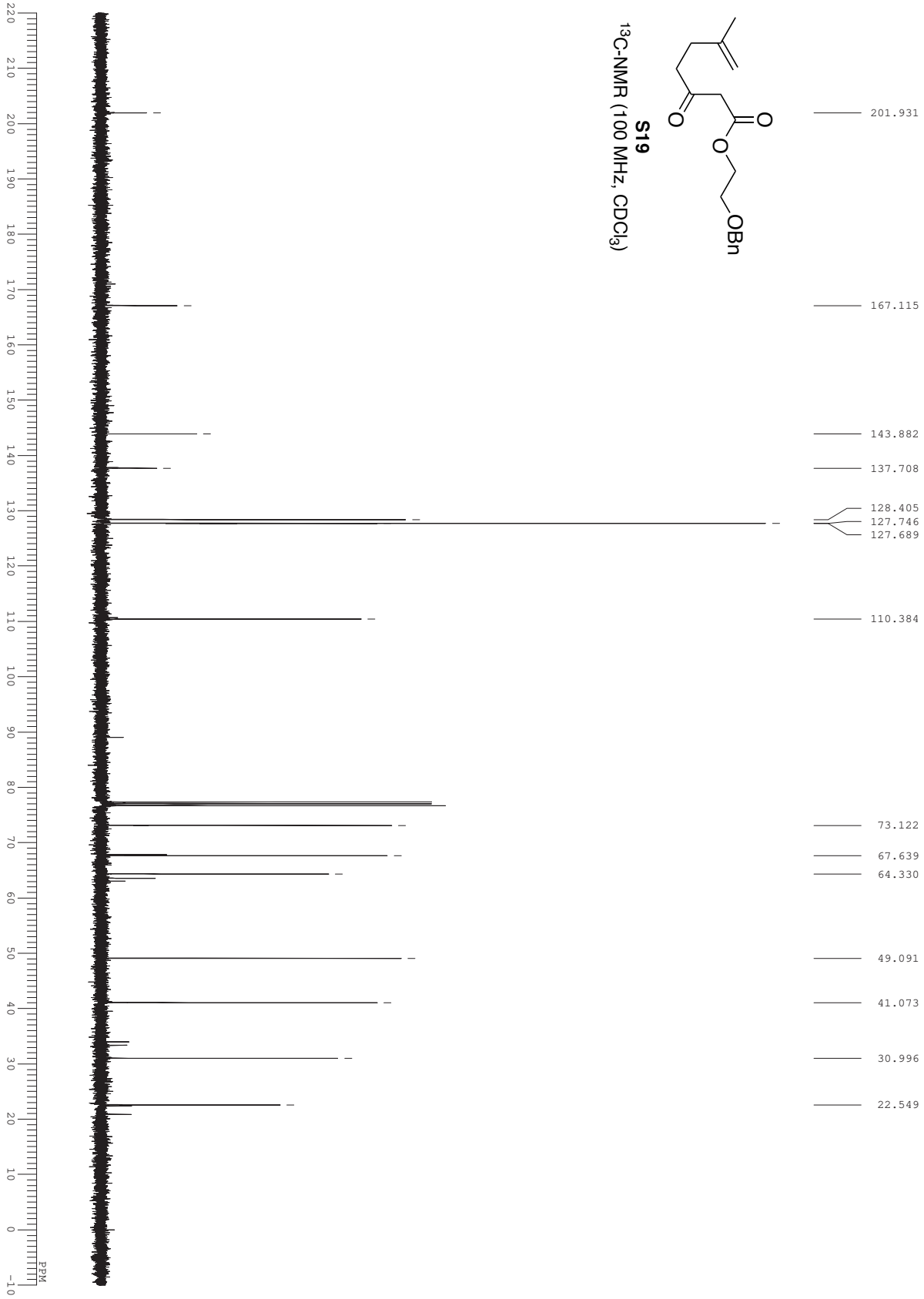

S17
^{1}H-NMR (400 MHz, $CDCl_3$)
O
O
O
Br
12.053
7.260
4.997
4.750
4.713
4.667
4.197
4.181
4.166
3.465
3.449
3.433
3.418
2.710
2.692
2.672
2.329
2.310
2.291
1.977
1.908
1.857
1.788
1.735
0.000
0.08
0.08
0.11
0.96
0.88
2.00
3.87
1.82
2.16
2.00
2.06
2.98
PPM

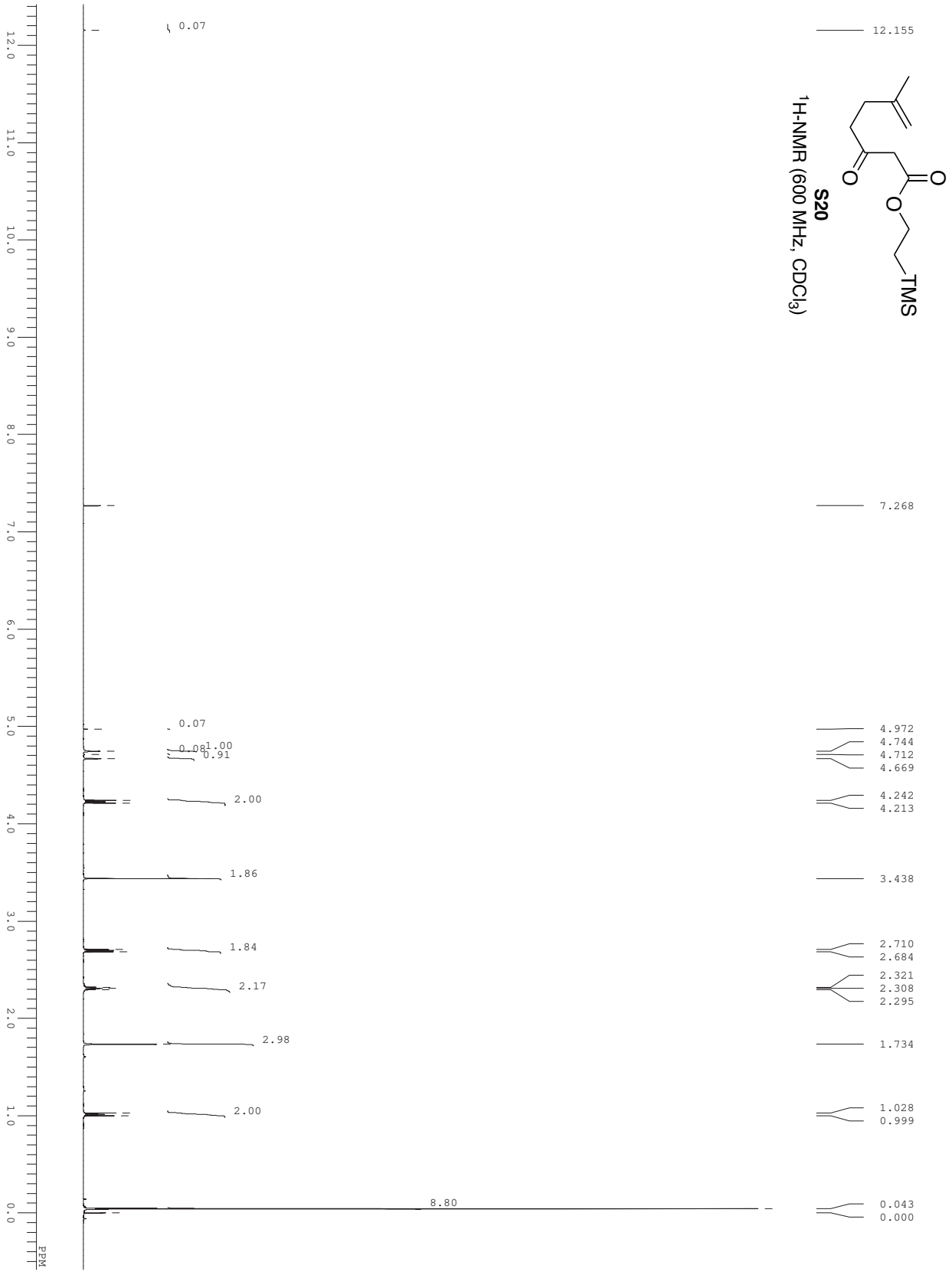

S17
^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
O
Br
202.040
167.111
143.894
110.480
77.321
77.000
76.679
64.342
49.190
41.265
32.944
31.076
29.093
27.158
22.607
PPM

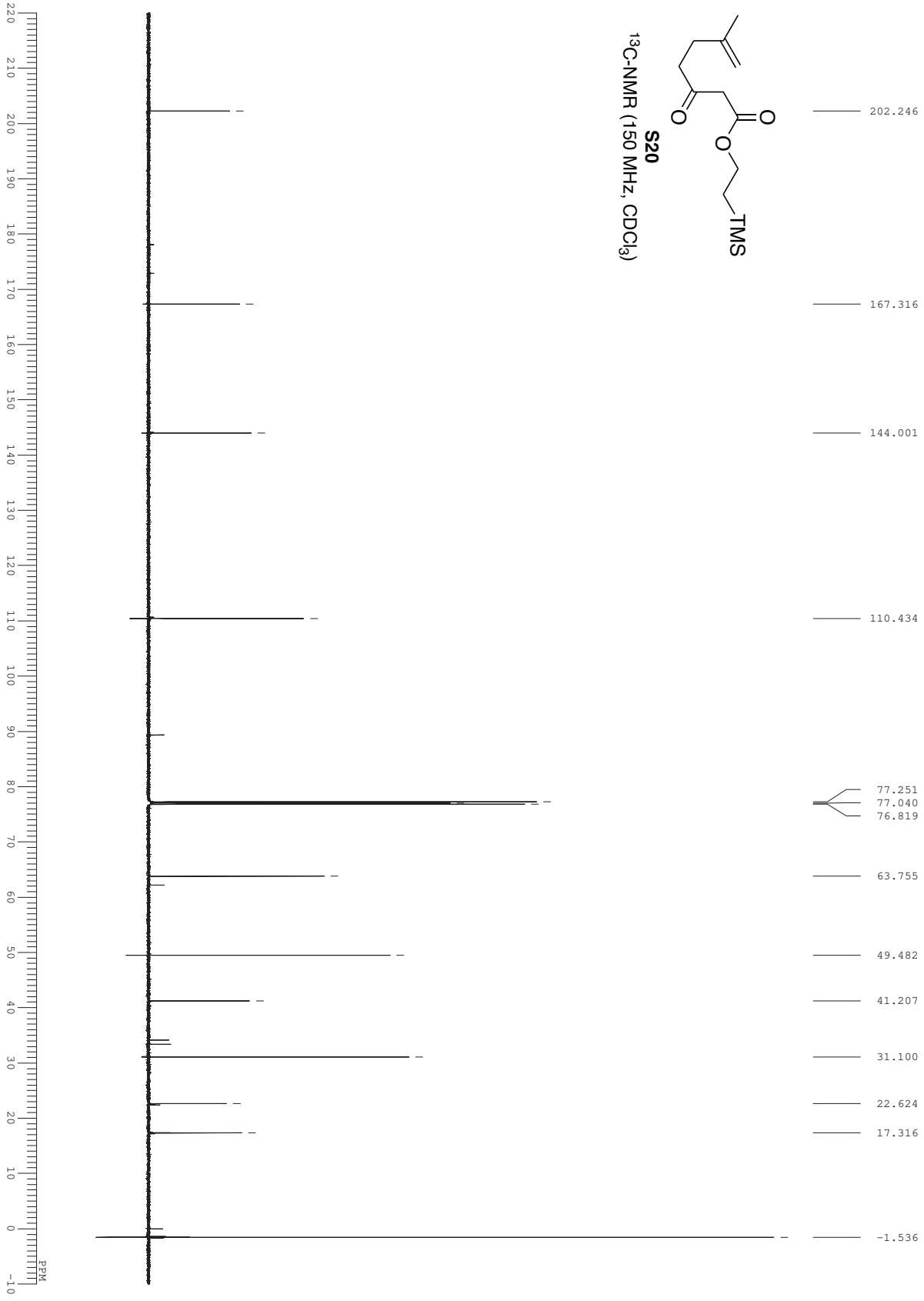

S18
^{1}H-NMR (400 MHz, $CDCl_3$)
Cl
12.063
7.261
0.000
4.999
4.751
4.715
4.668
4.200
4.185
4.170
3.586
3.570
3.555
3.470
3.454
3.438
3.422
2.713
2.694
2.674
2.330
2.309
2.291
1.879
1.784
1.736
1.543
0.06
0.07
0.12
1.00
0.92
2.07
2.23
1.85
0.24
1.84
2.25
3.17
4.32
ppm

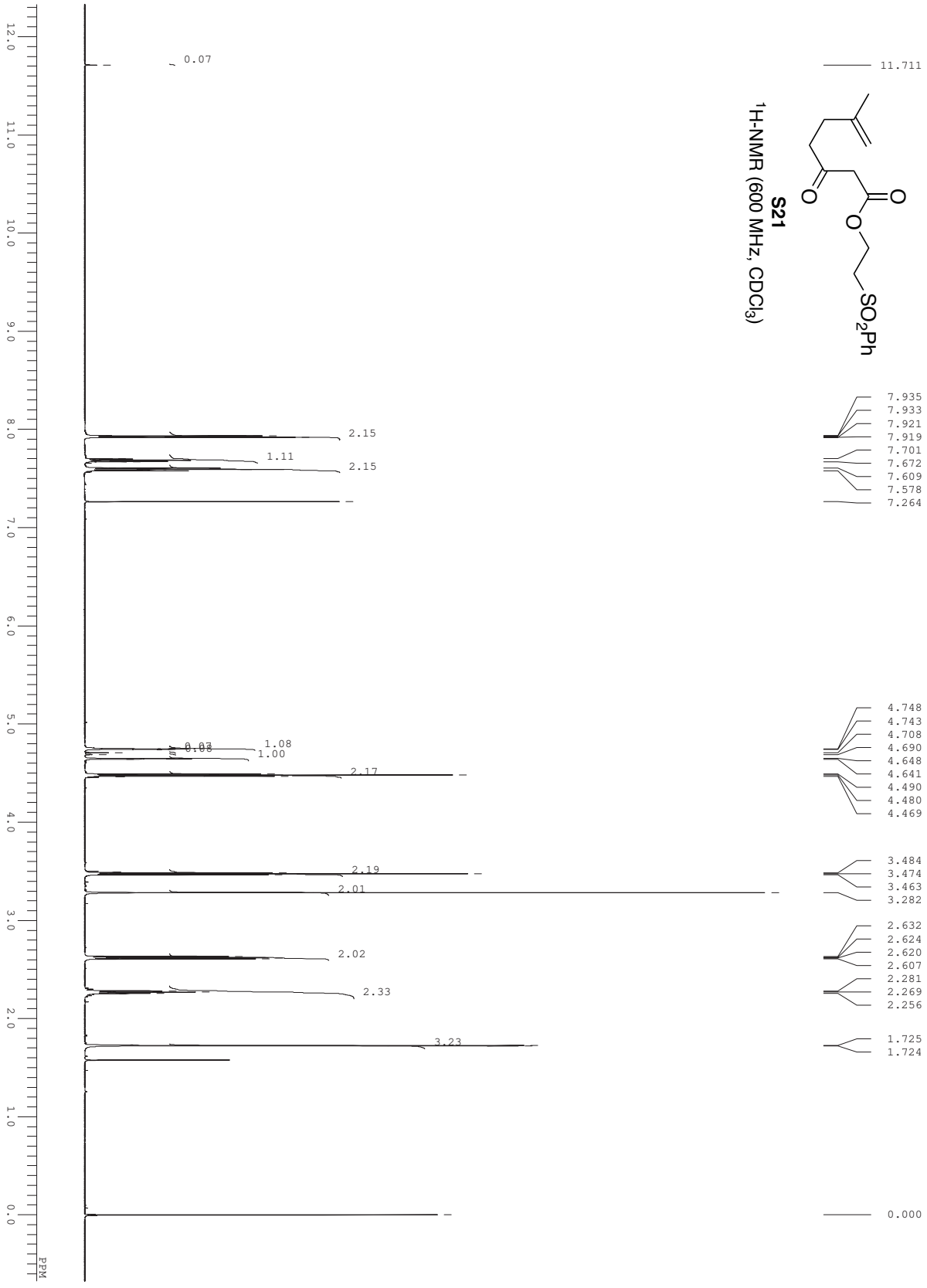

S18
^{13}C-NMR (100 MHz, $CDCl_3$)
O
O
O
Cl
202.056
167.111
143.886
110.455
77.321
77.000
76.679
64.474
49.174
44.359
41.240
31.051
28.944
25.907
22.583
PPM

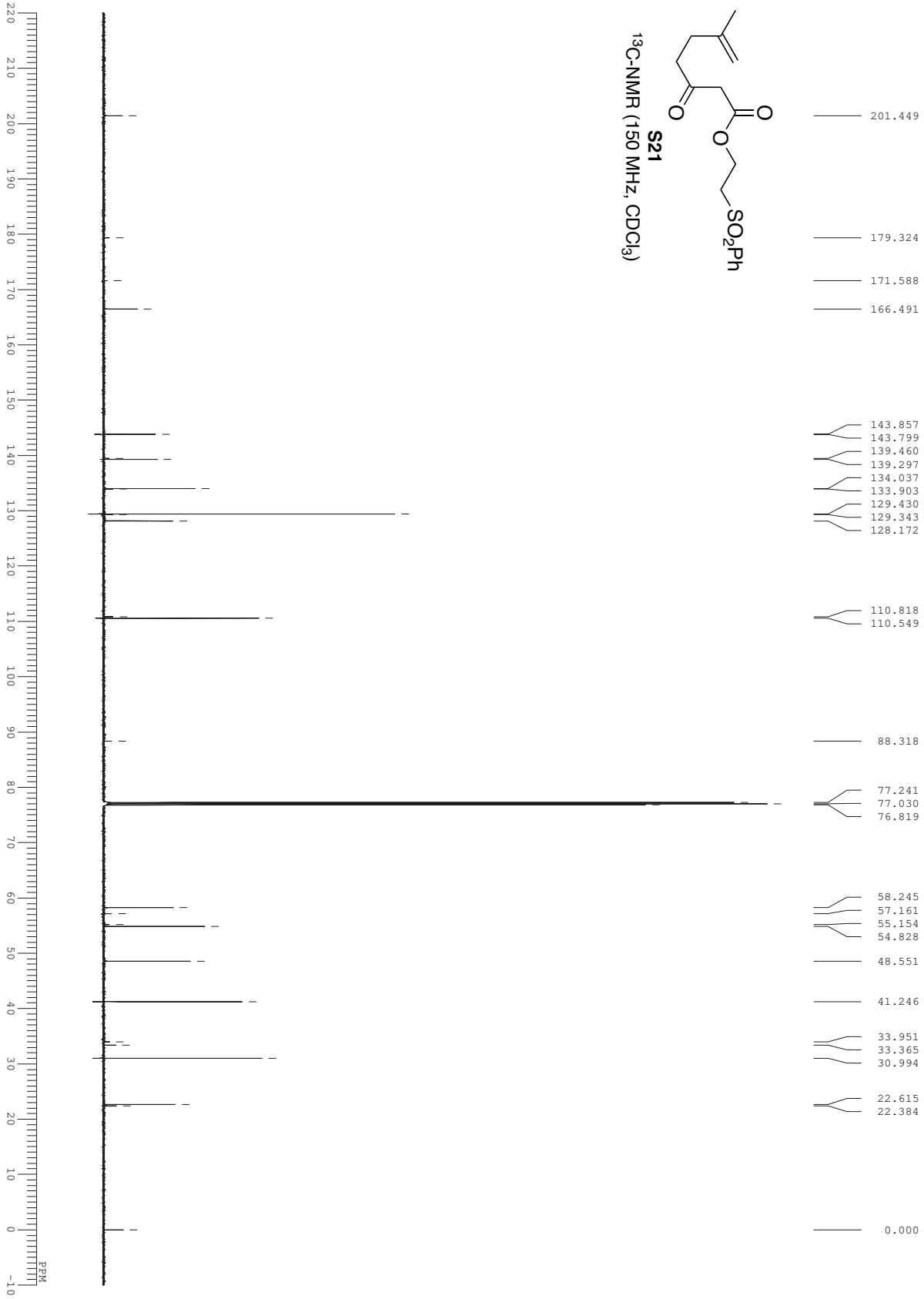

S19
1H-NMR (400 MHz, CDCl3)
OBn
7.376
7.271
7.260
4.738
4.661
4.557
4.339
4.327
4.314
3.699
3.676
3.495
2.717
2.699
2.679
2.318
2.300
2.280
1.723
0.000
5.55
1.00
0.95
2.06
2.22
2.29
2.01
2.00
2.24
2.96
PPM

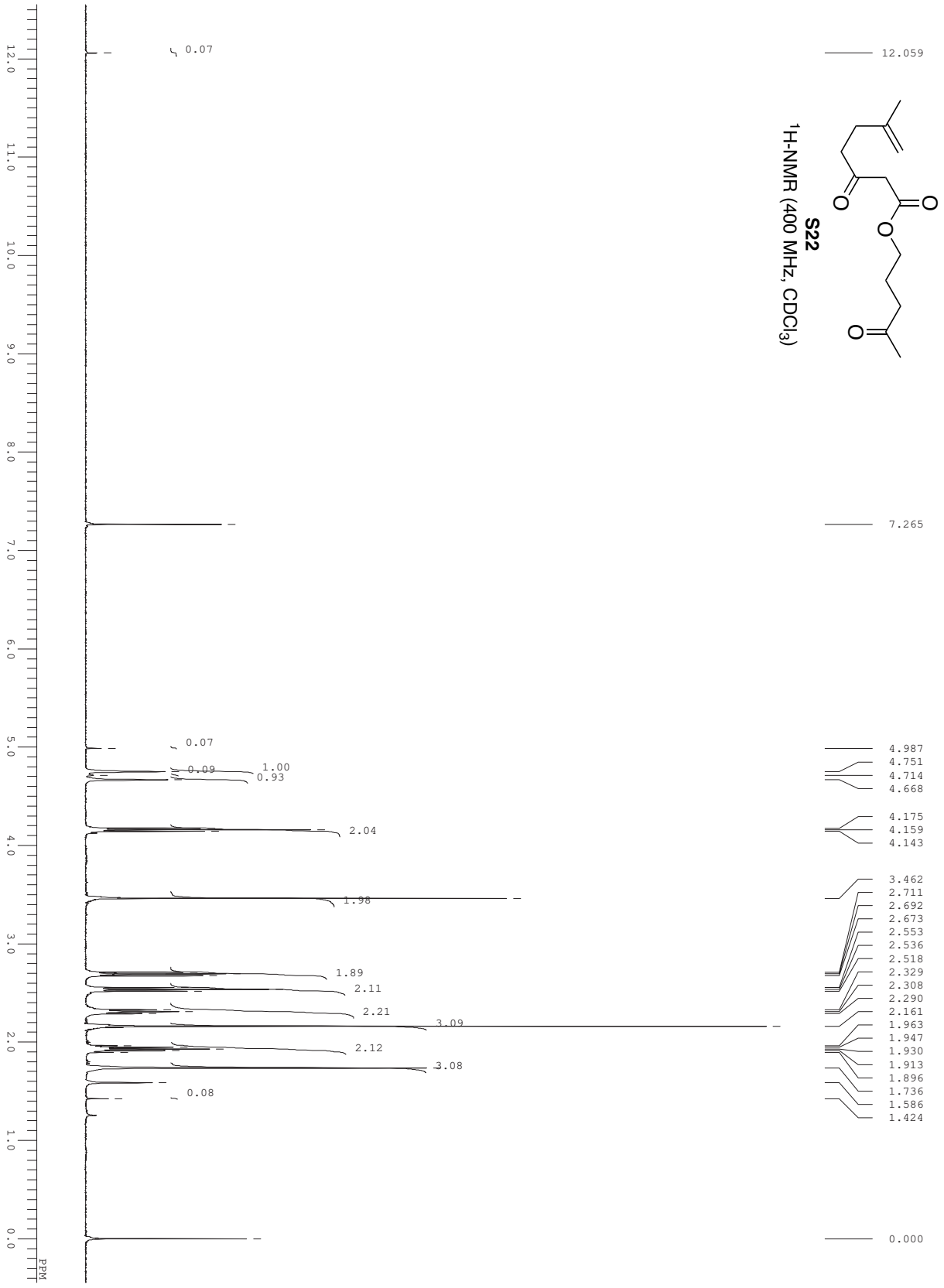

S19
^{13}C-NMR (100 MHz, $CDCl_3$)
OBn
201.931
167.115
143.882
137.708
128.405
127.746
127.689
110.384
73.122
67.639
64.330
49.091
41.073
30.996
22.549
PPM

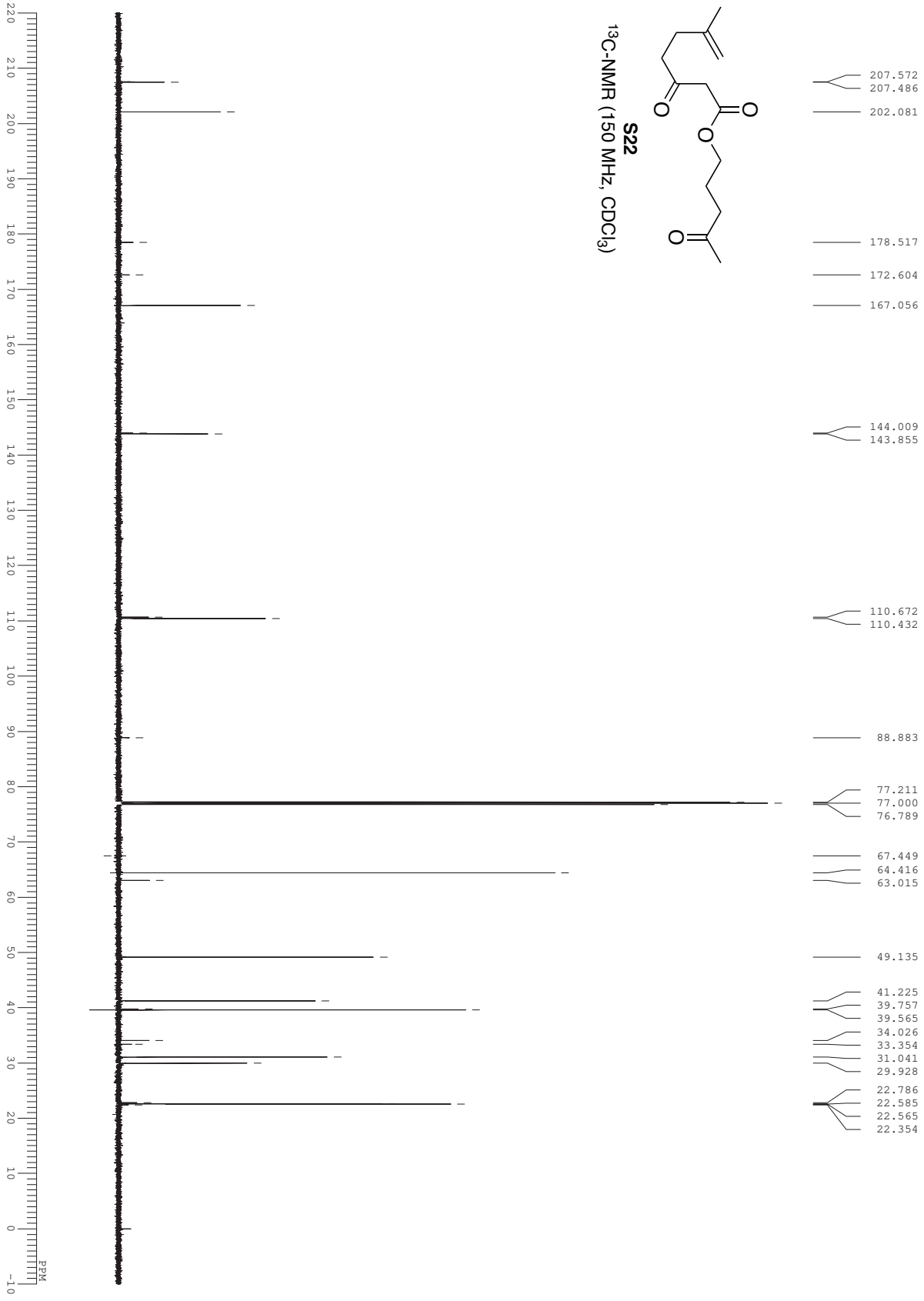

S20
1H-NMR (600 MHz, CDCl3)
TMS
12.155
7.268
4.972
4.744
4.712
4.669
4.242
4.213
3.438
2.710
2.684
2.321
2.308
2.295
1.734
1.028
0.999
0.043
0.000
0.07
1.00
0.91
2.00
1.86
1.84
2.17
2.98
2.00
8.80
PPM

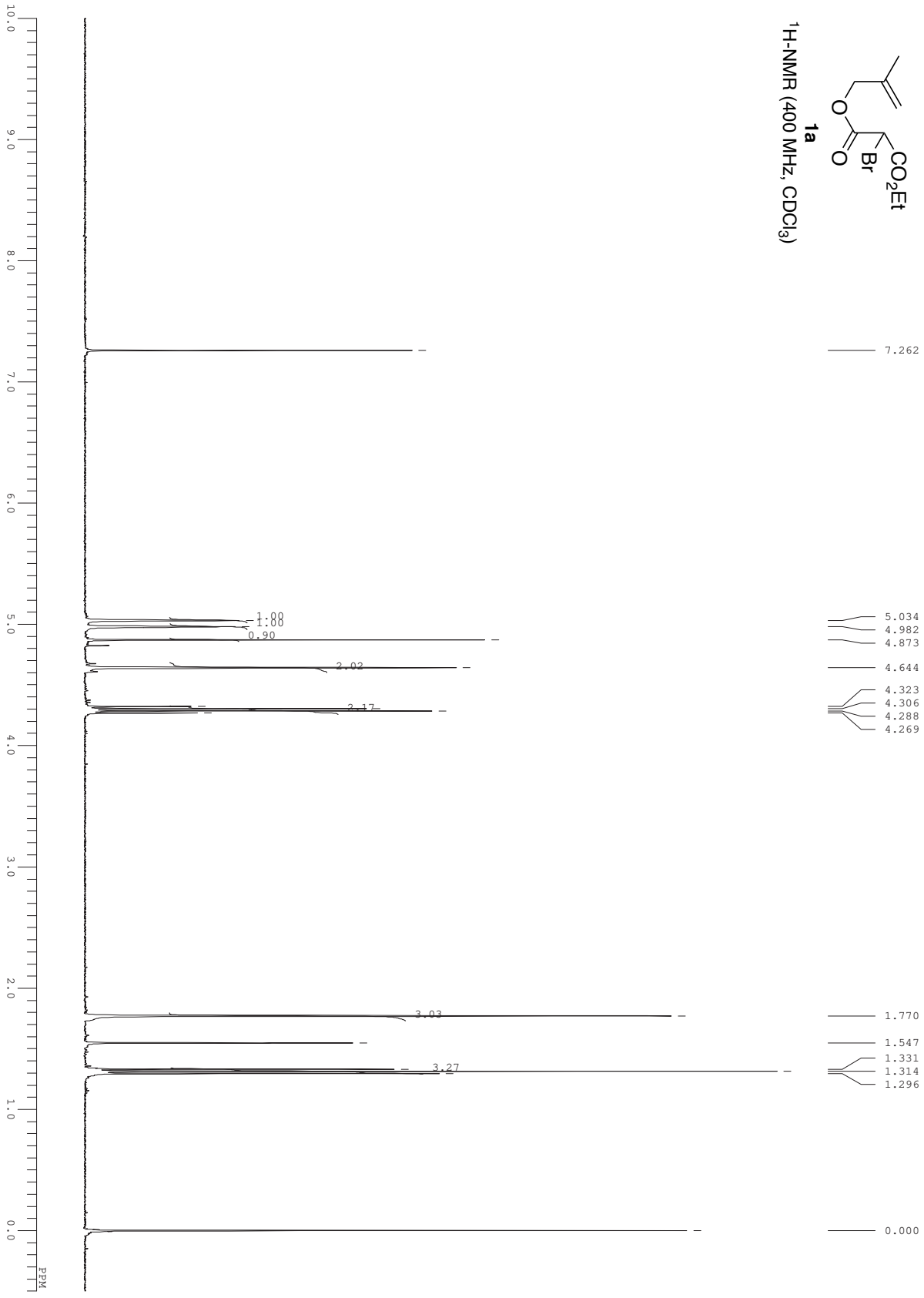

S20
^{13}C-NMR (150 MHz, $CDCl_3$)
O
O
O
TMS
202.246
167.316
144.001
110.434
77.251
77.040
76.819
63.755
49.482
41.207
31.100
22.624
17.316
-1.536
PPM

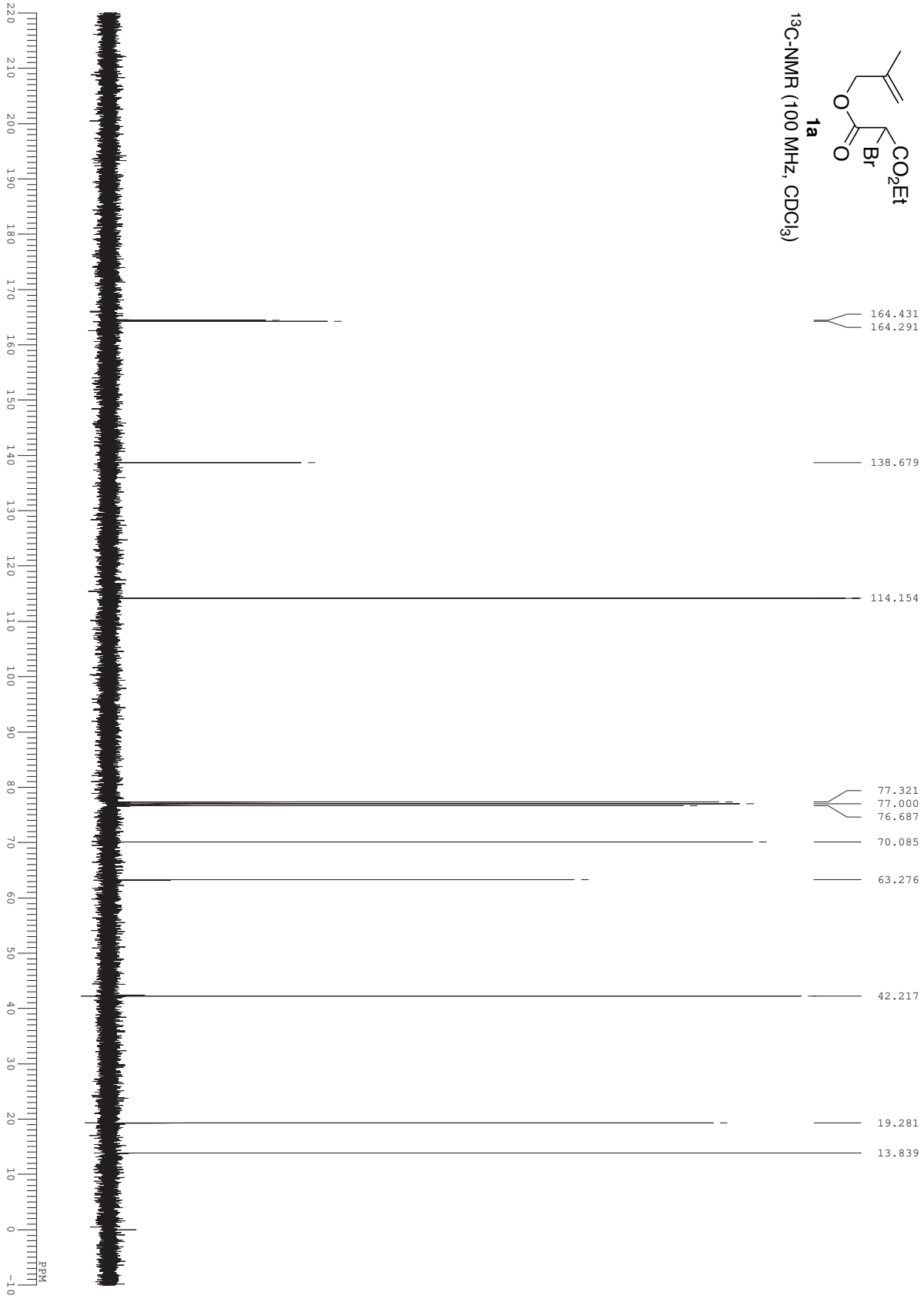

S21
^{1}H-NMR (600 MHz, CDCl$_3$)
SO$_2$Ph
11.711
7.935
7.933
7.921
7.919
7.701
7.672
7.609
7.578
7.264
4.748
4.743
4.708
4.690
4.648
4.641
4.490
4.480
4.469
3.484
3.474
3.463
3.282
2.632
2.624
2.620
2.607
2.281
2.269
2.256
1.725
1.724
0.000
0.07
2.15
1.11
2.15
1.08
1.00
2.17
2.19
2.01
2.02
2.33
3.23
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

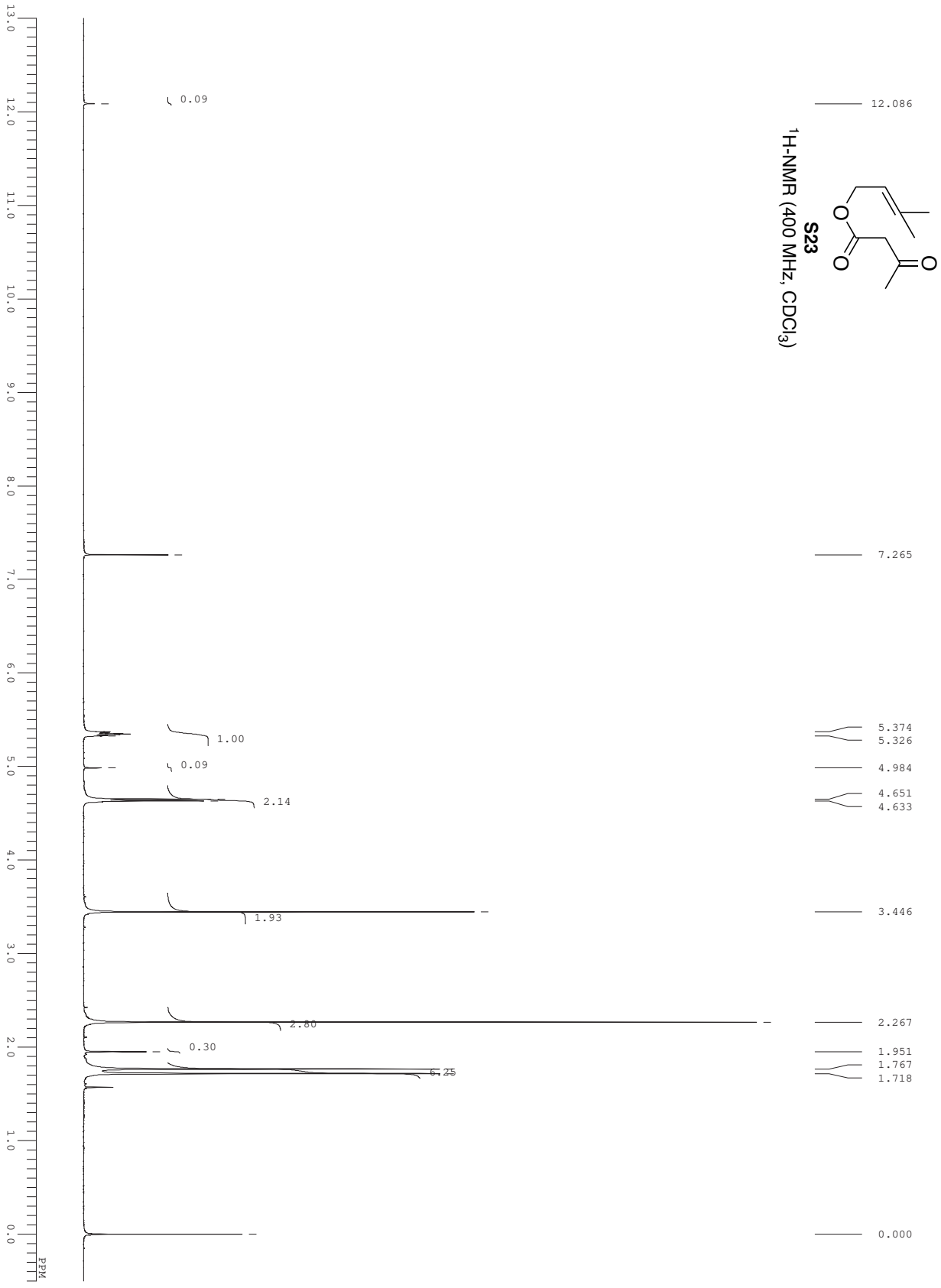

S21
13C-NMR (150 MHz, CDCl3)
O
O
O
SO2Ph
201.449
179.324
171.588
166.491
143.857
143.799
139.460
139.297
134.037
133.903
129.430
129.343
128.172
110.818
110.549
88.318
77.241
77.030
76.819
58.245
57.161
55.154
54.828
48.551
41.246
33.951
33.365
30.994
22.615
22.384
0.000
PPM

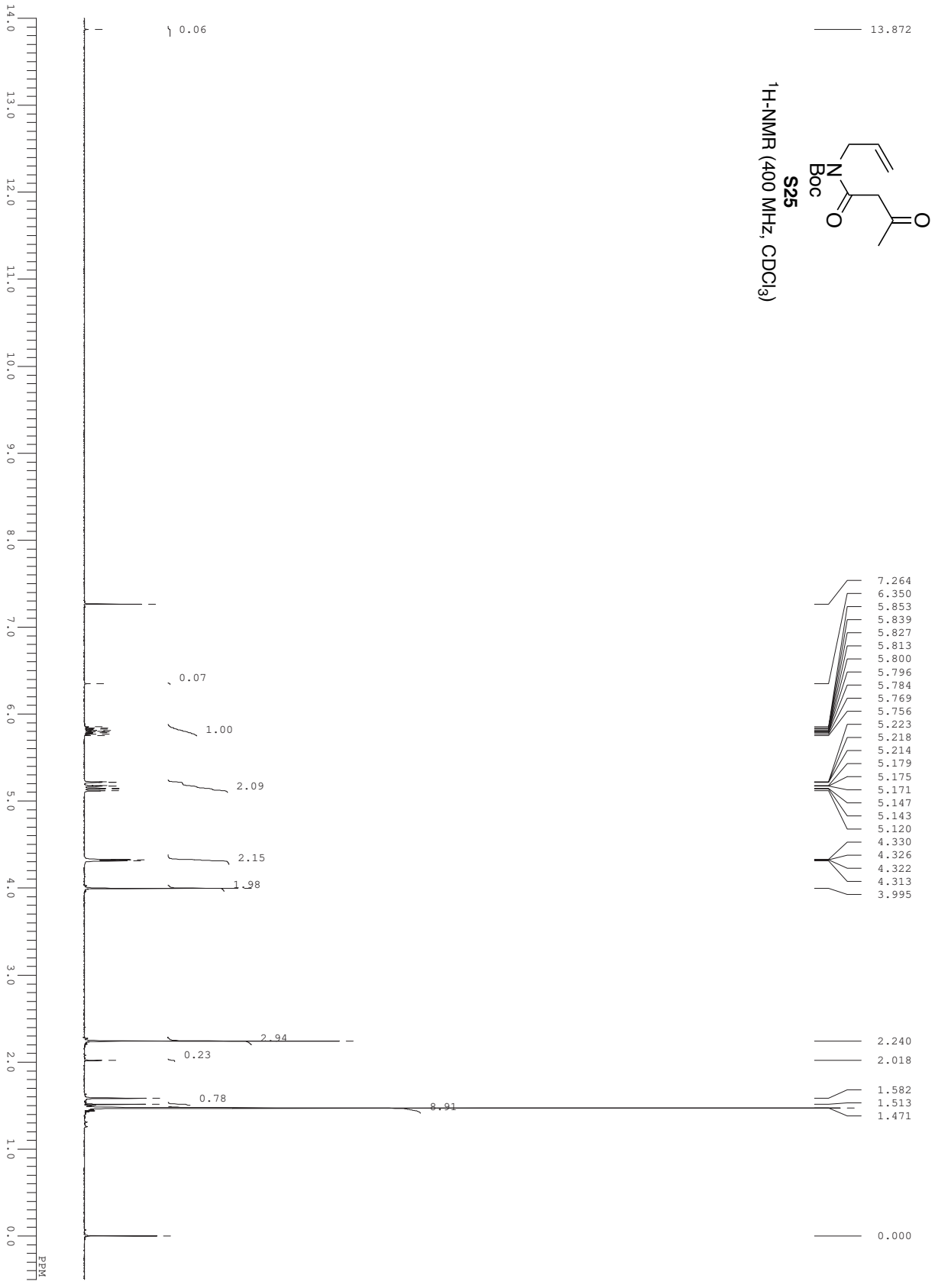

S22
1H-NMR (400 MHz, CDCl3)
12.059
7.265
4.987
4.751
4.714
4.668
4.175
4.159
4.143
3.462
2.711
2.692
2.673
2.553
2.536
2.518
2.329
2.308
2.290
2.161
1.963
1.947
1.930
1.913
1.896
1.736
1.586
1.424
0.000
0.07
0.09
1.00
0.93
2.04
1.98
1.89
2.11
2.21
3.09
2.12
3.08
0.08
PPM

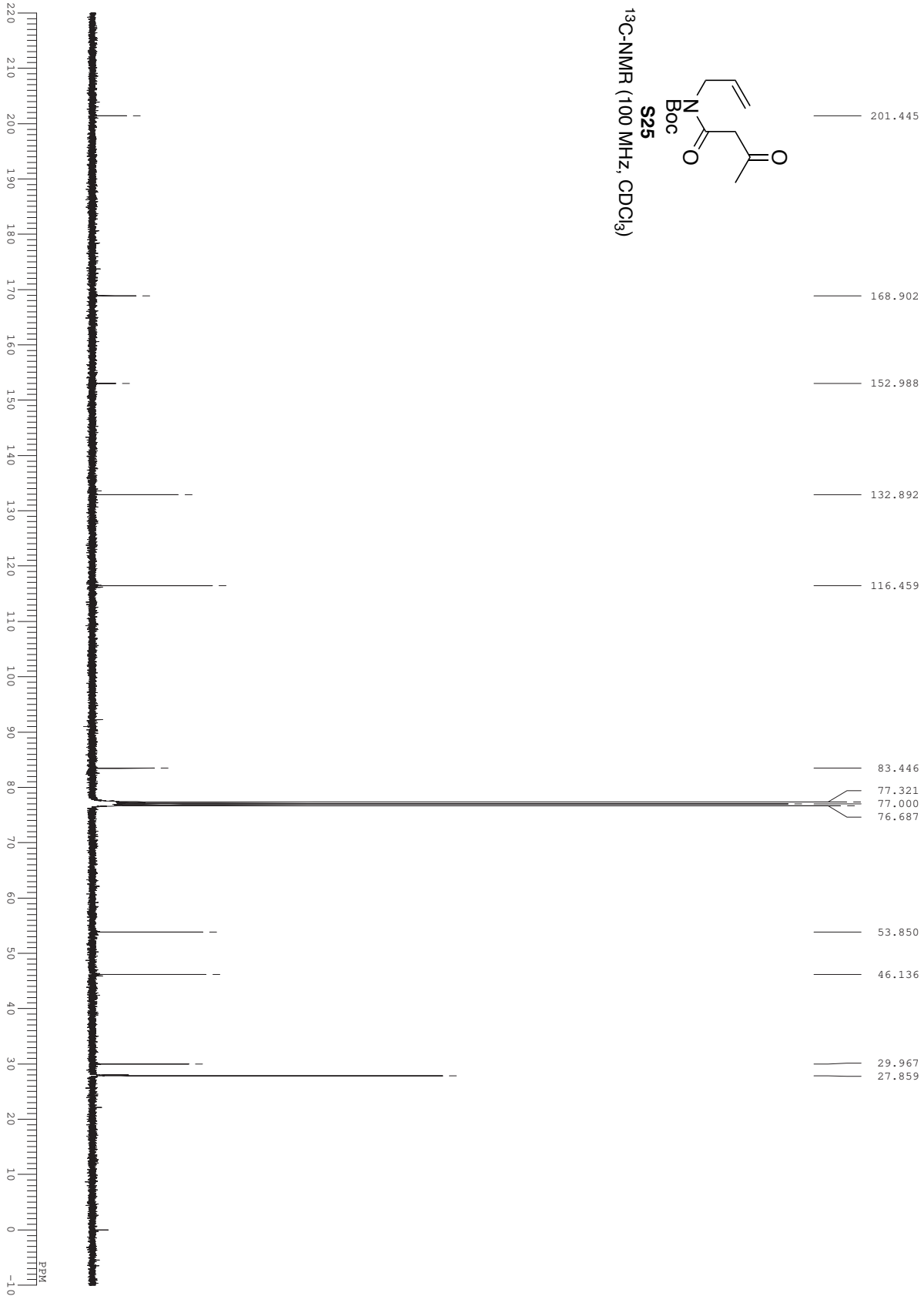

S22
13C-NMR (150 MHz, CDCl3)
O
O
O
O
207.572
207.486
202.081
178.517
172.604
167.056
144.009
143.855
110.672
110.432
88.883
77.211
77.000
76.789
67.449
64.416
63.015
49.135
41.225
39.757
39.565
34.026
33.354
31.041
29.928
22.786
22.585
22.565
22.354
PPM

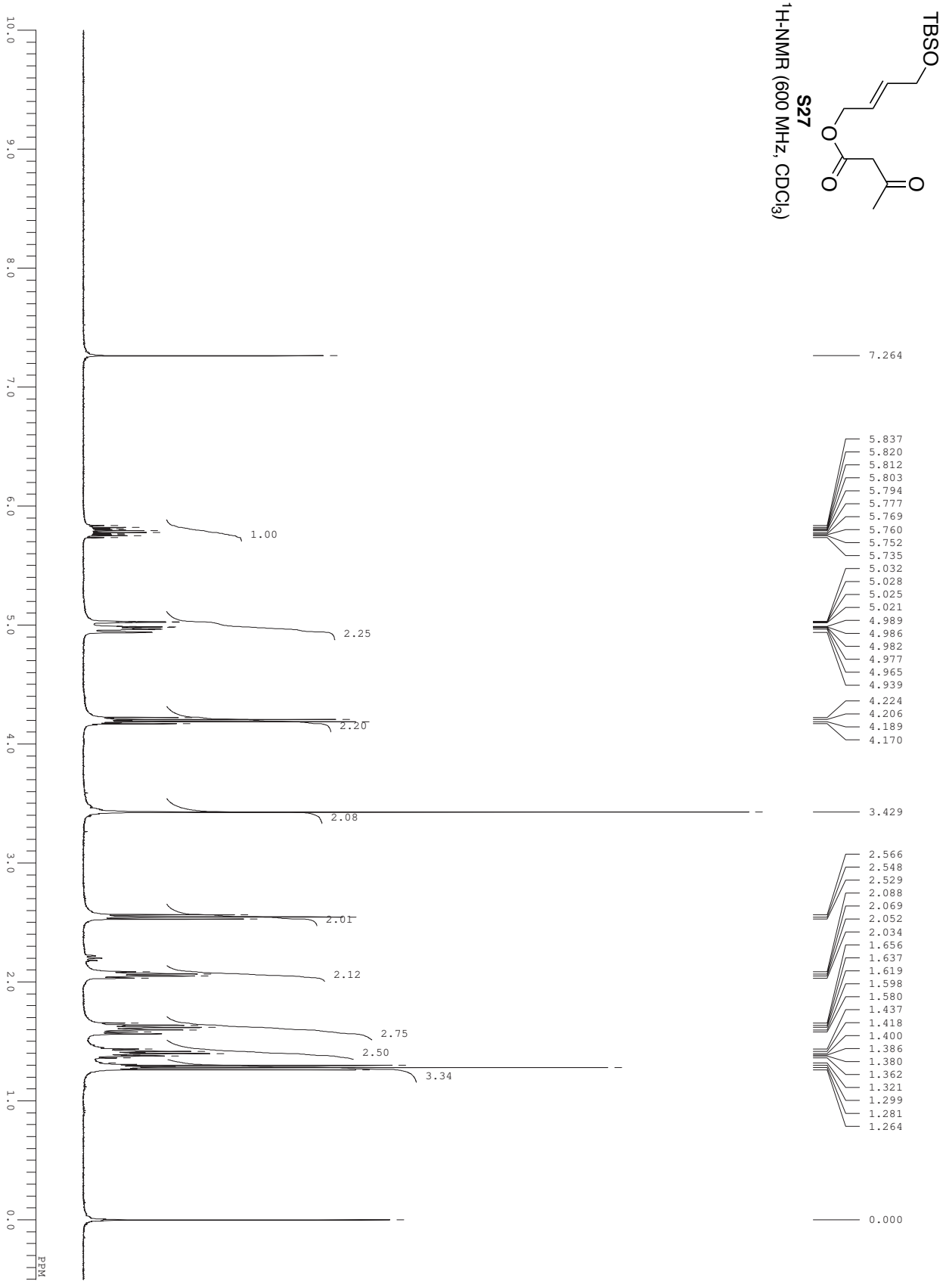

1a
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
O
7.262
5.034
4.982
4.873
4.644
4.323
4.306
4.288
4.269
1.770
1.547
1.331
1.314
1.296
0.000
1.00
1.08
0.90
2.02
2.17
3.03
3.27
PPM

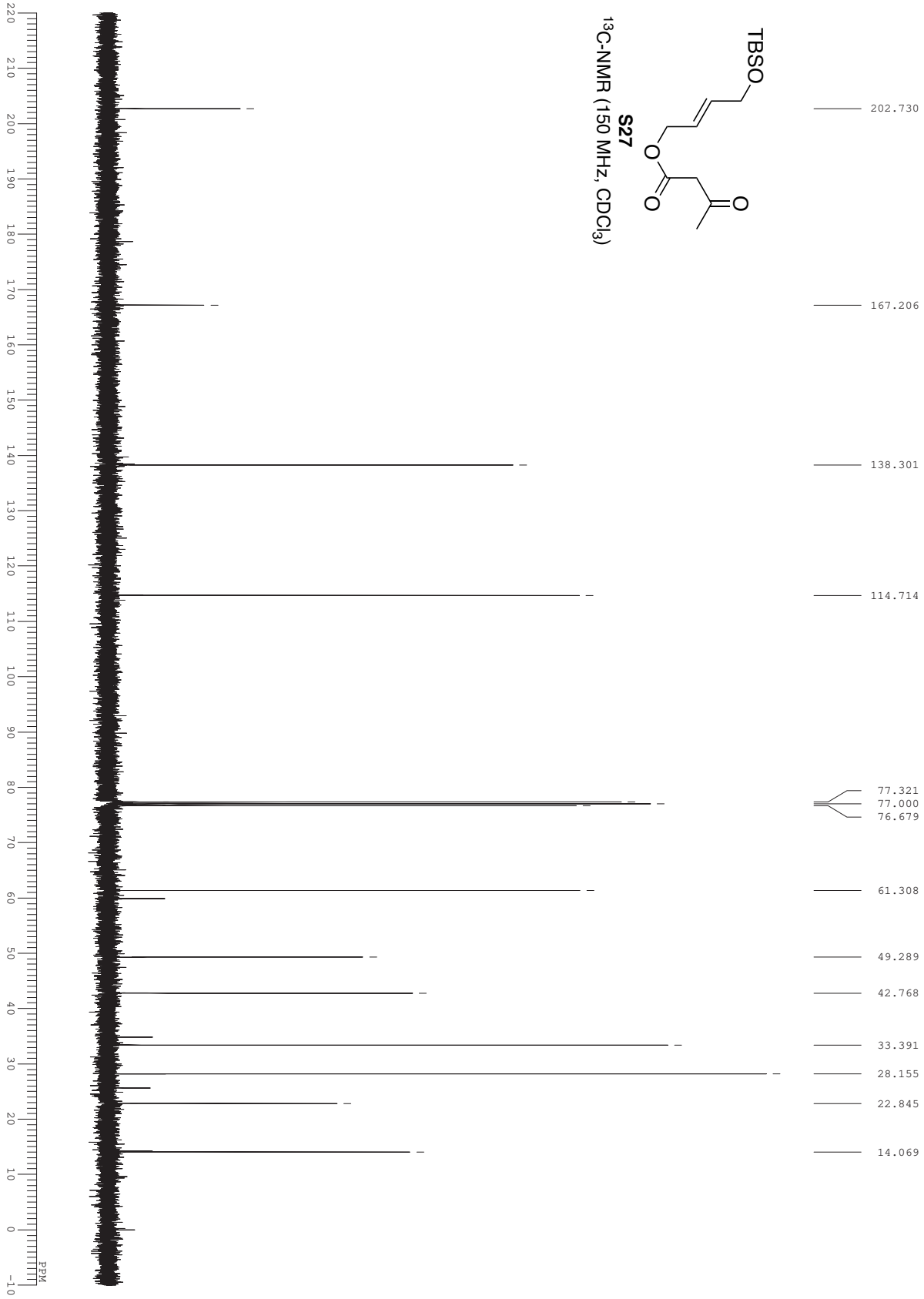

1a
13C-NMR (100 MHz, CDCl3)
CO2Et
Br
O
O
164.431
164.291
138.679
114.154
77.321
77.000
76.687
70.085
63.276
42.217
19.281
13.839
PPM

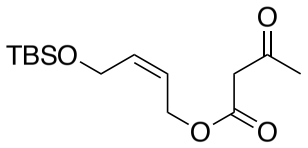

S23
^{1}H-NMR (400 MHz, CDCl$_3$)
12.086
7.265
5.374
5.326
4.984
4.651
4.633
3.446
2.267
1.951
1.767
1.718
0.000
0.09
1.00
0.09
2.14
1.93
2.80
0.30
6.25
PPM


S25
1H-NMR (400 MHz, CDCl3)
N
Boc
O
O
13.872
7.264
6.350
5.853
5.839
5.827
5.813
5.800
5.796
5.784
5.769
5.756
5.223
5.218
5.214
5.179
5.175
5.171
5.147
5.143
5.120
4.330
4.326
4.322
4.313
3.995
2.240
2.018
1.582
1.513
1.471
0.000
0.06
0.07
1.00
2.09
2.15
1.98
2.94
0.23
0.78
8.91
PPM


S25
13C-NMR (100 MHz, CDCl3)
N
Boc
O
O
201.445
168.902
152.988
132.892
116.459
83.446
77.321
77.000
76.687
53.850
46.136
29.967
27.859
PPM

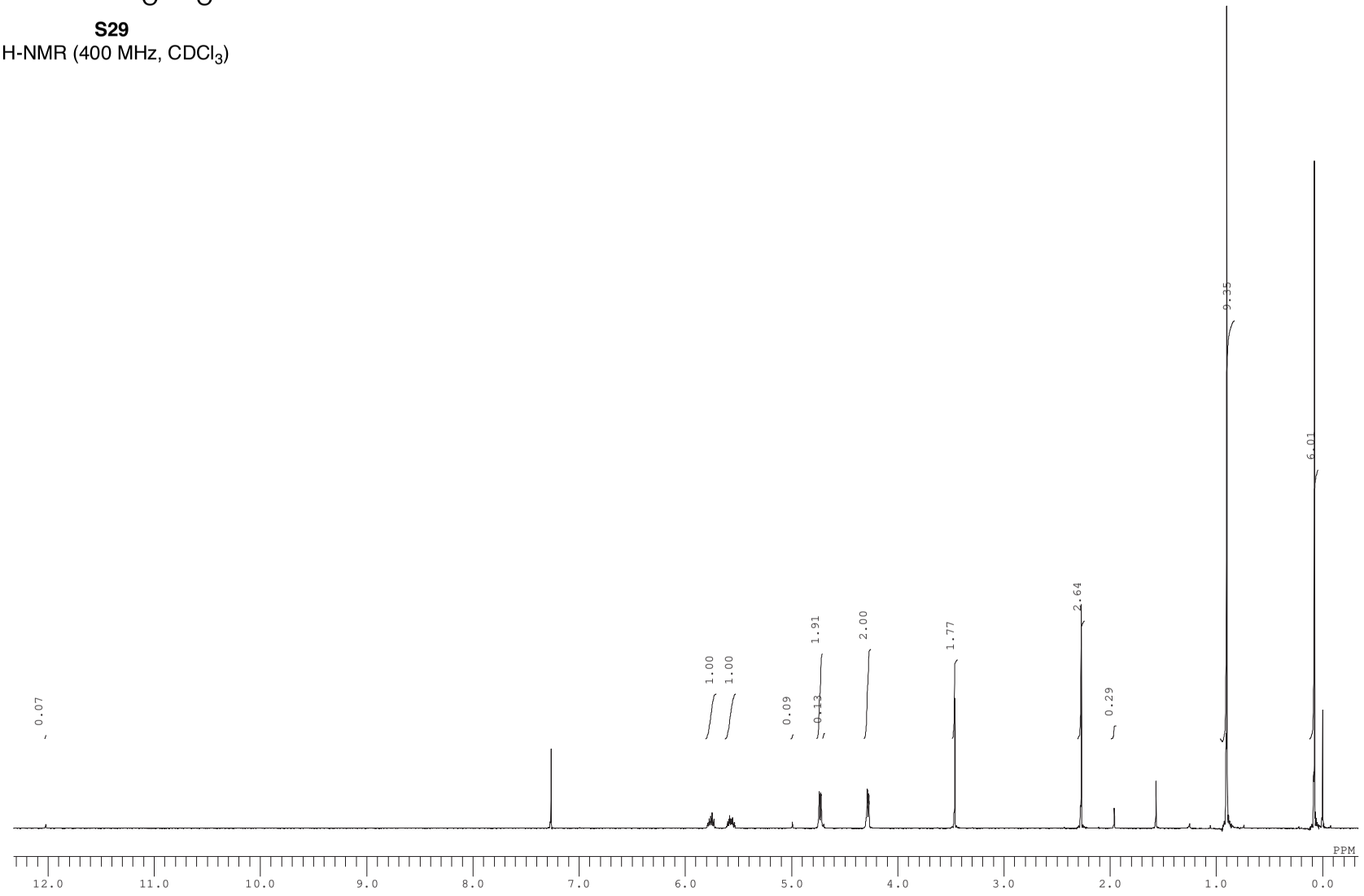

TBSO
O
O
O
O
S27
1H-NMR (600 MHz, CDCl3)
7.264
5.837
5.820
5.812
5.803
5.794
5.777
5.769
5.760
5.752
5.735
5.032
5.028
5.025
5.021
4.989
4.986
4.982
4.977
4.965
4.939
4.224
4.206
4.189
4.170
3.429
2.566
2.548
2.529
2.088
2.069
2.052
2.034
1.656
1.637
1.619
1.598
1.580
1.437
1.418
1.400
1.386
1.380
1.362
1.321
1.299
1.281
1.264
0.000
1.00
2.25
2.20
2.08
2.01
2.12
2.75
2.50
3.34
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

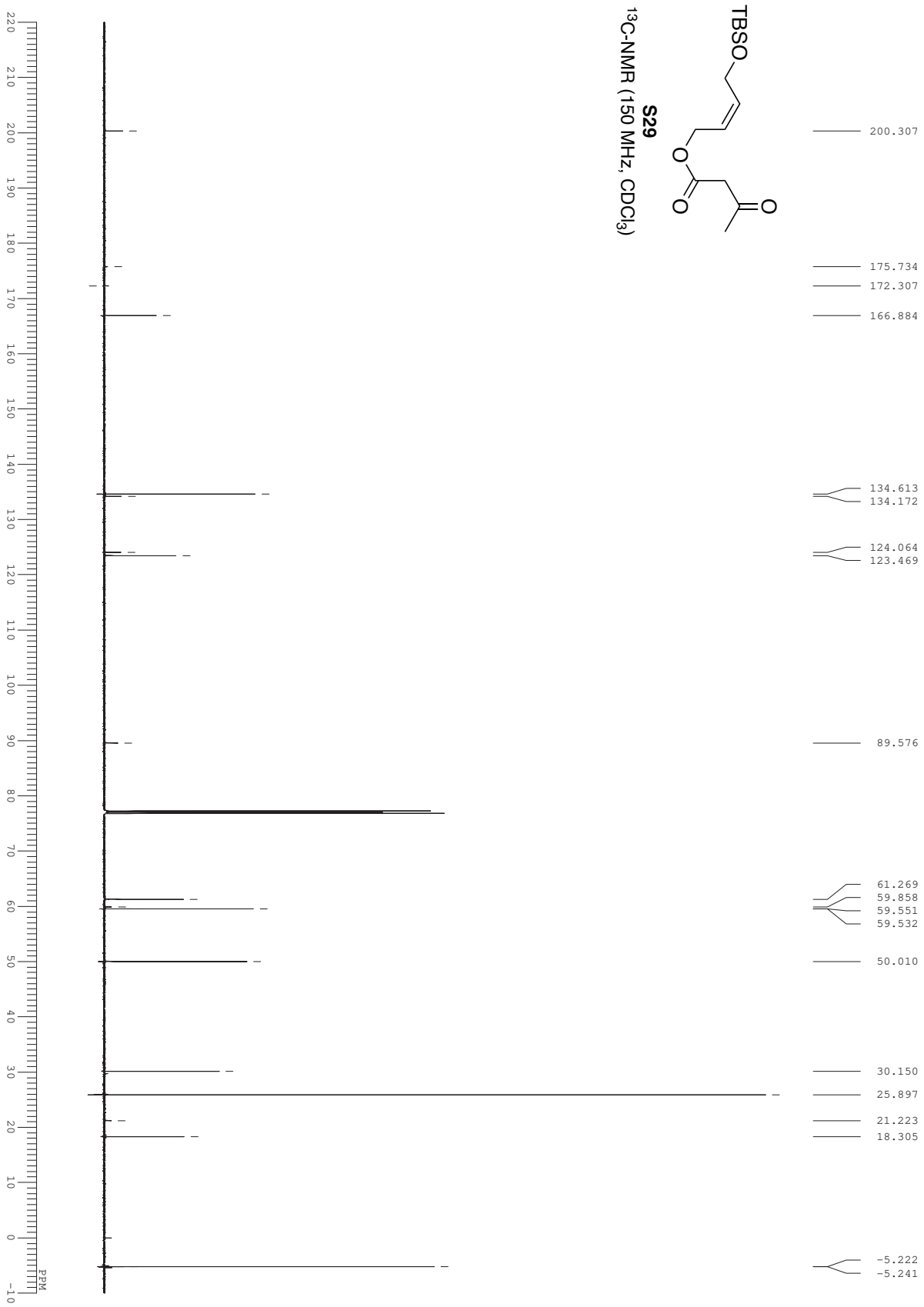

S27
^{13}C-NMR (150 MHz, CDCl$_3$)
TBSO
O
O
O
202.730
167.206
138.301
114.714
77.321
77.000
76.679
61.308
49.289
42.768
33.391
28.155
22.845
14.069
PPM

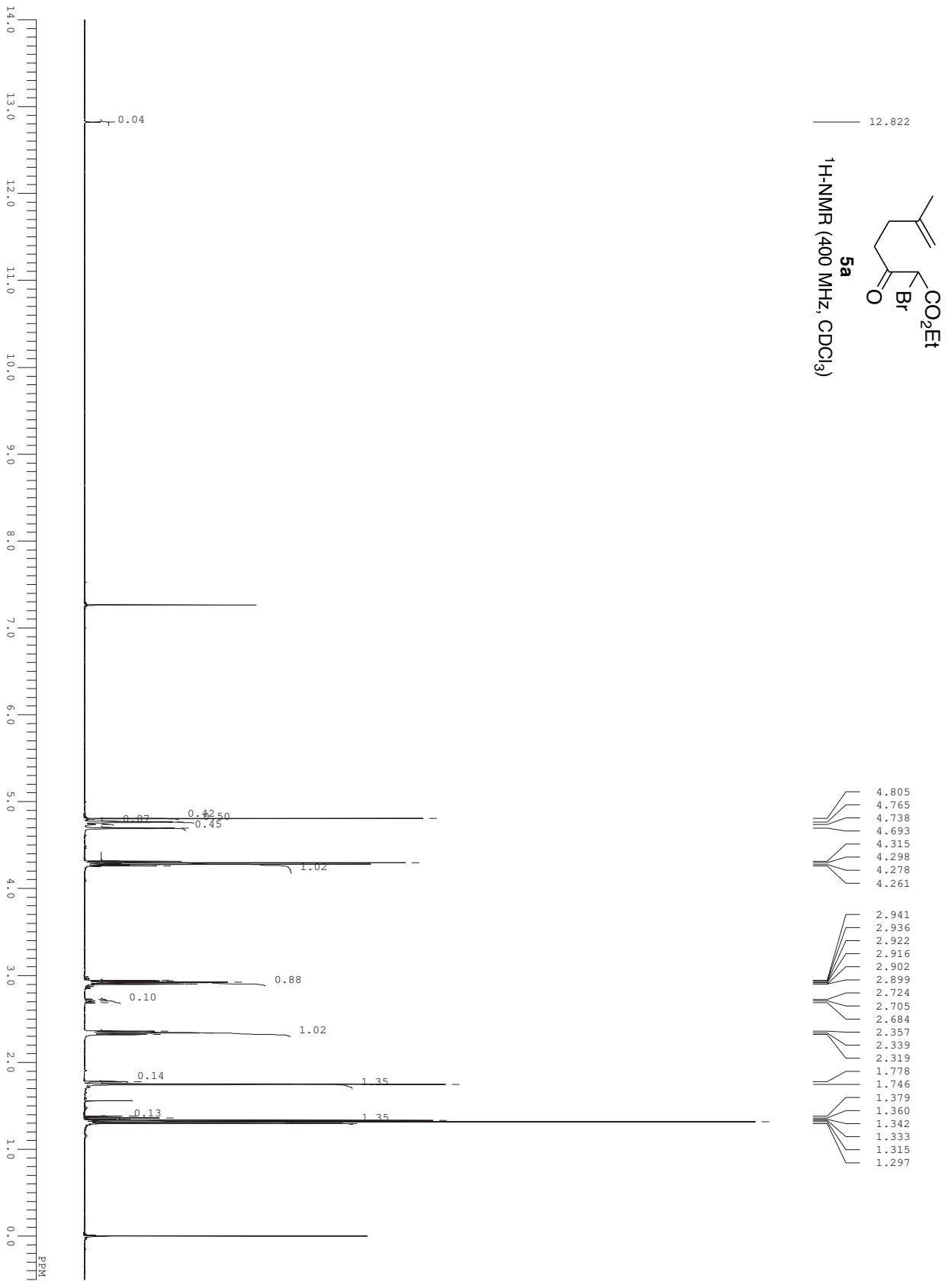


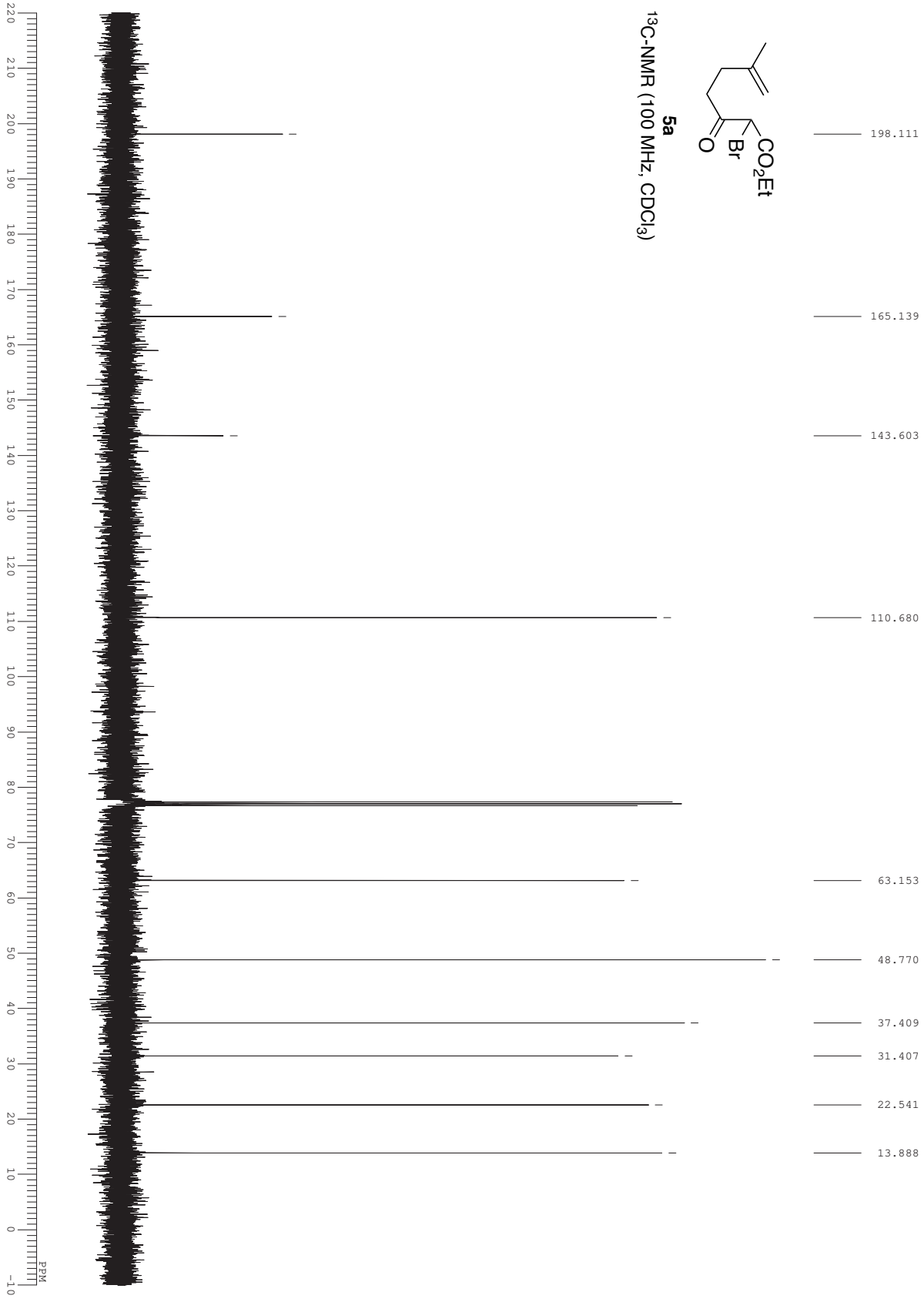
S29

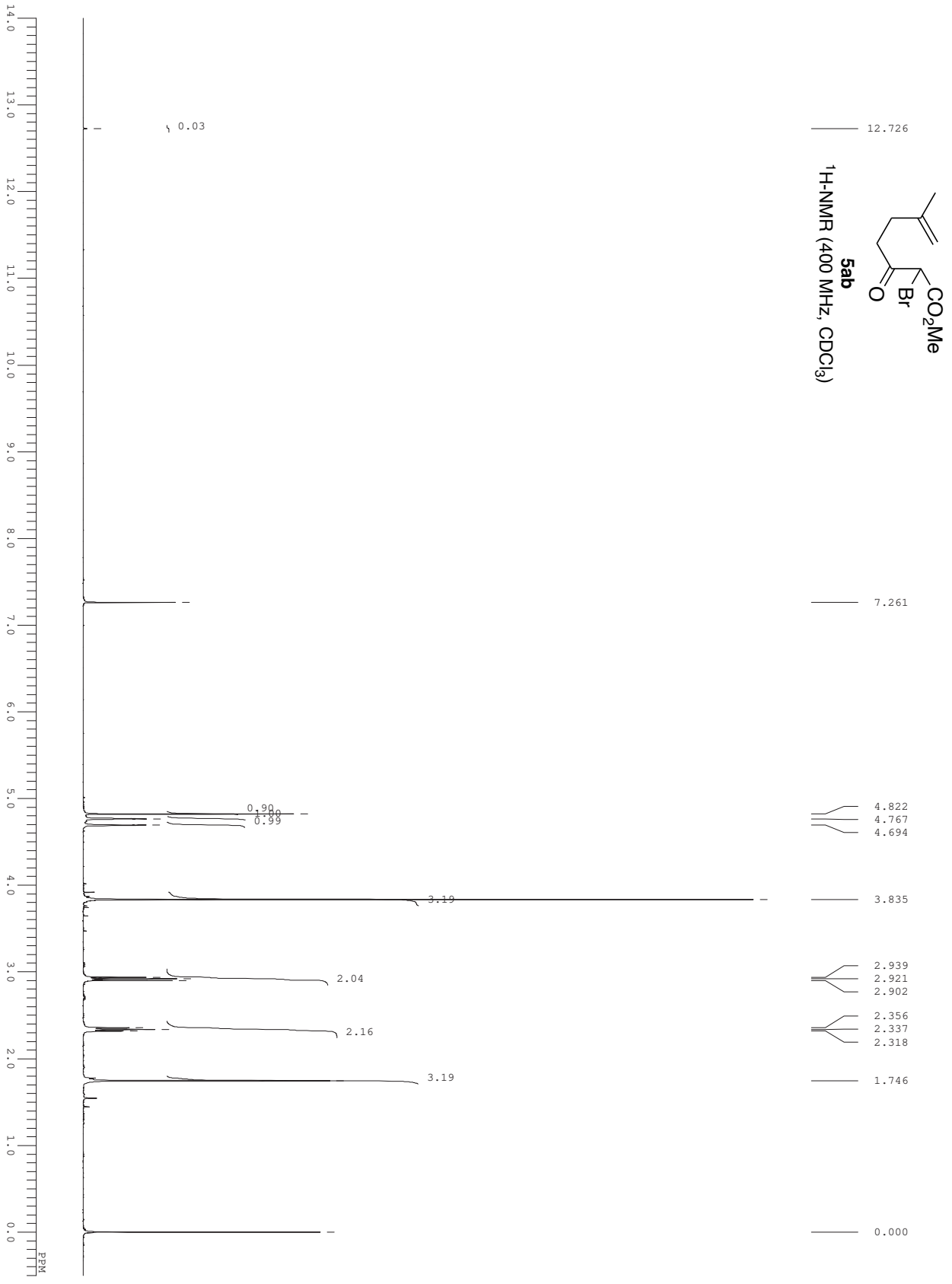
^{1}H-NMR (400 MHz, $CDCl_3$)

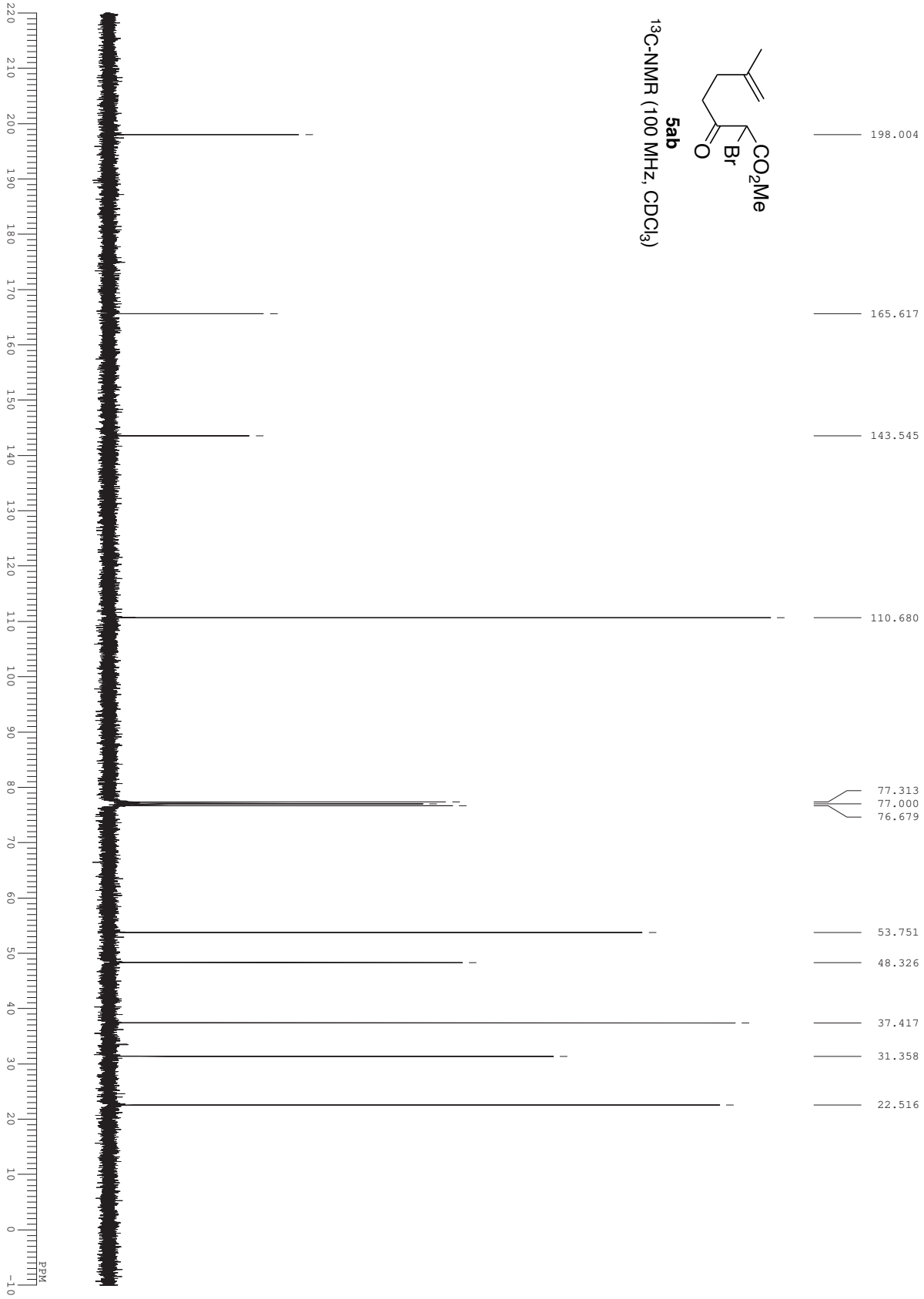


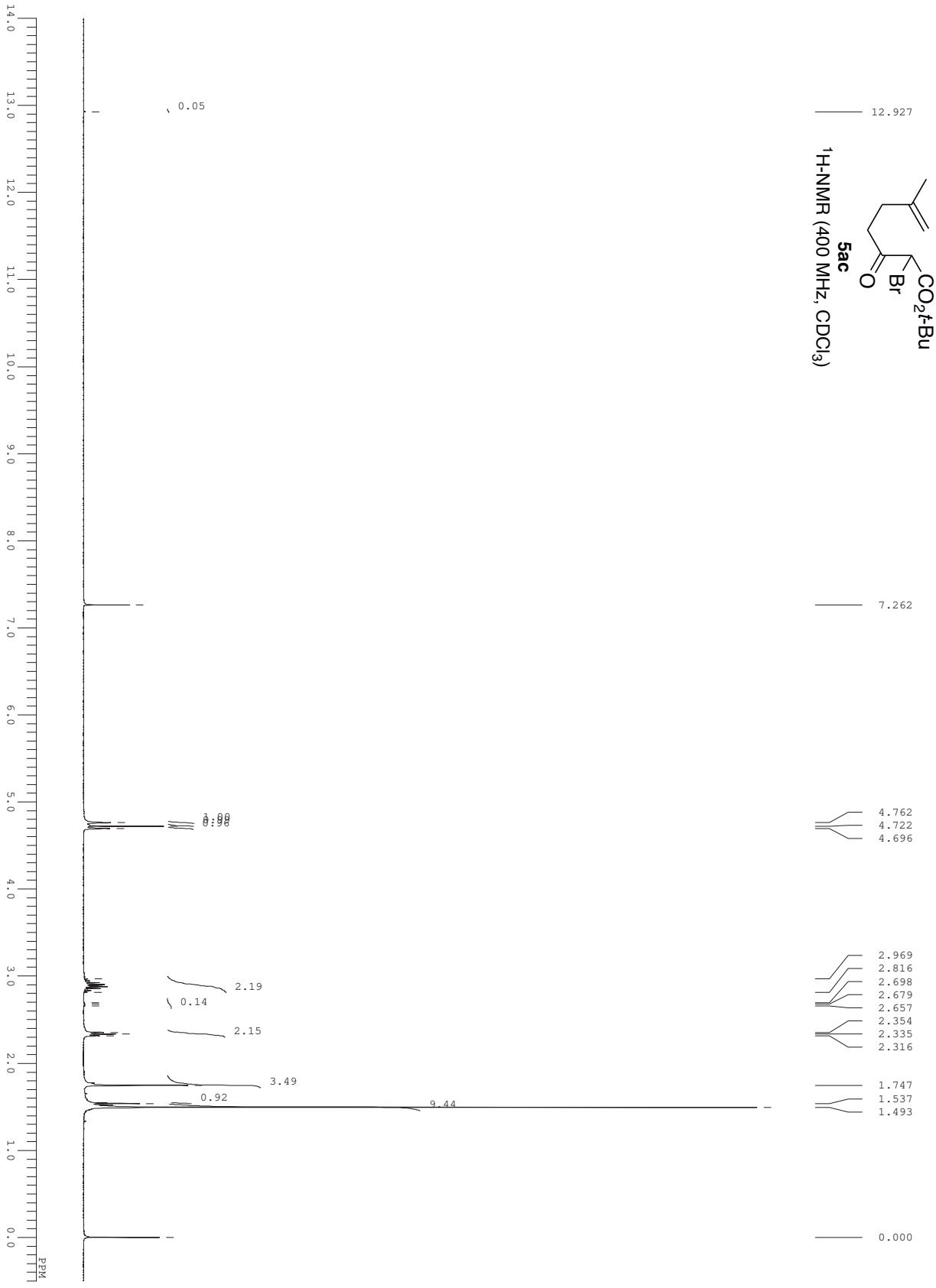

S29
13C-NMR (150 MHz, CDCl3)
TBSO
O
O
O
200.307
175.734
172.307
166.884
134.613
134.172
124.064
123.469
89.576
61.269
59.858
59.551
59.532
50.010
30.150
25.897
21.223
18.305
-5.222
-5.241
PPM

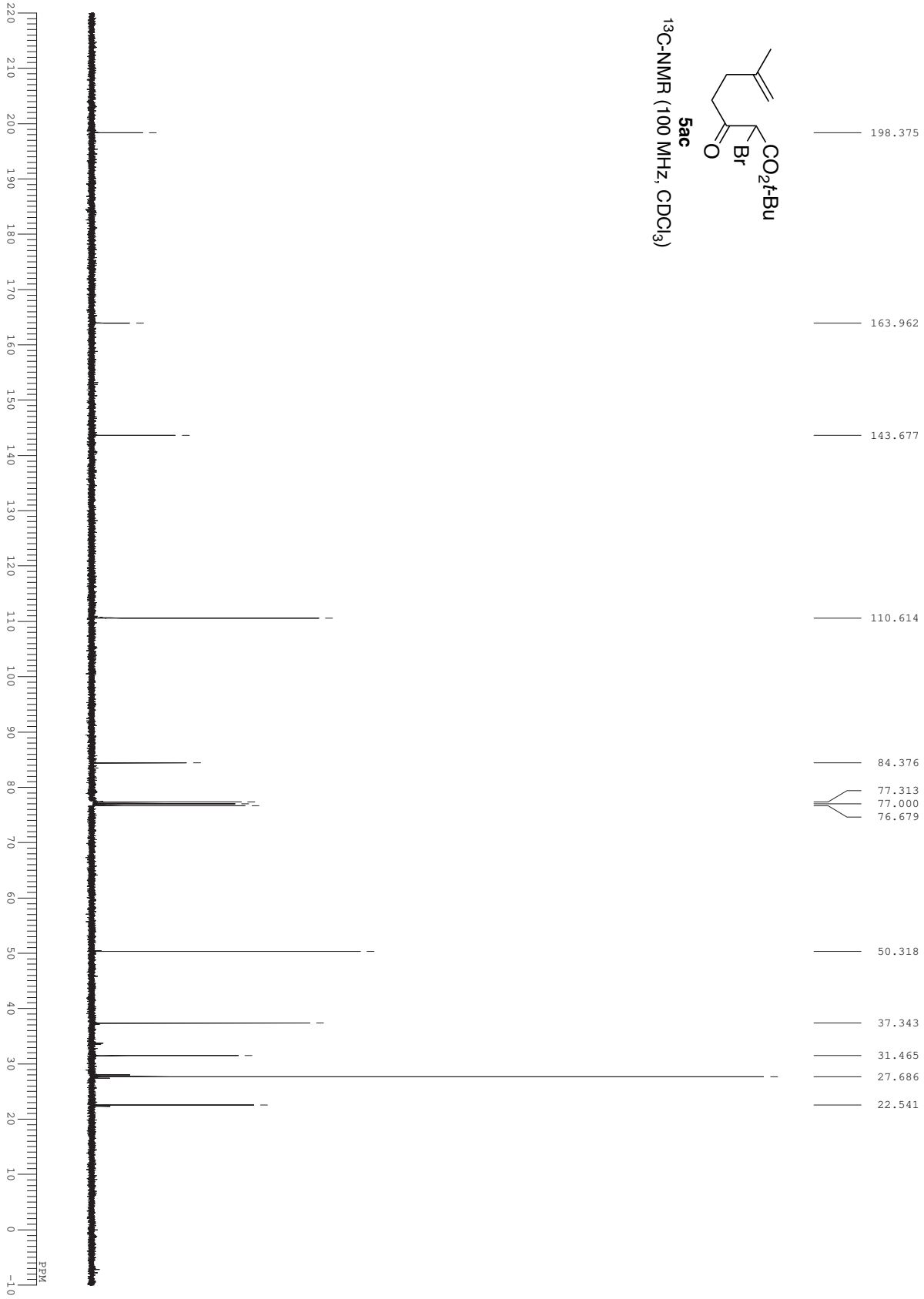

5a
^{1}H-NMR (400 MHz, CDCl$_3$)
CO$_2$Et
Br
O
12.822
4.805
4.765
4.738
4.693
4.315
4.298
4.278
4.261
2.941
2.936
2.922
2.916
2.902
2.899
2.724
2.705
2.684
2.357
2.339
2.319
1.778
1.746
1.379
1.360
1.342
1.333
1.315
1.297
0.04
0.07
0.42
0.45
1.02
0.88
0.10
1.02
0.14
1.35
0.13
1.35
PPM

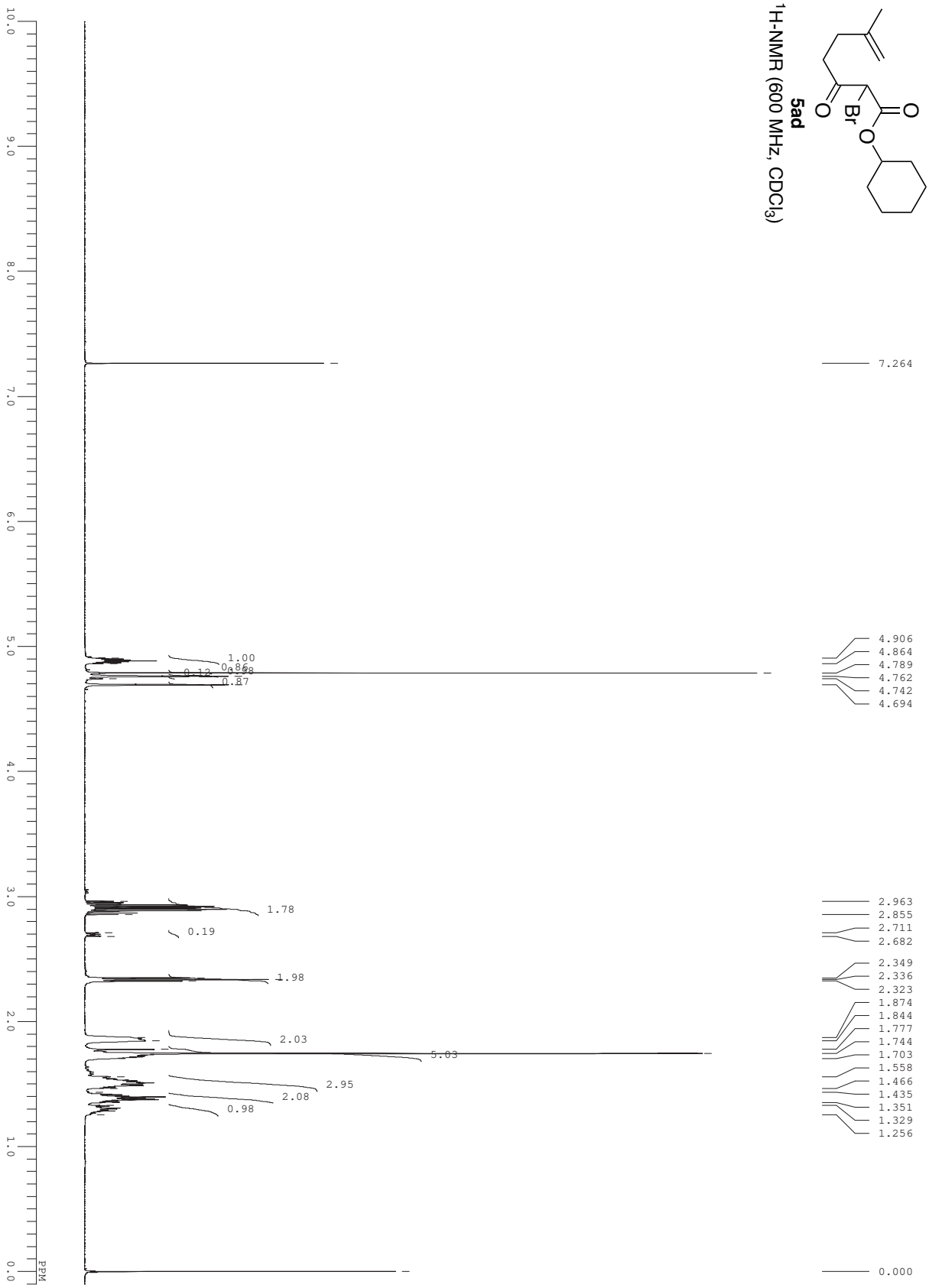

5a
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Et
Br
O
198.111
165.139
143.603
110.680
63.153
48.770
37.409
31.407
22.541
13.888
PPM

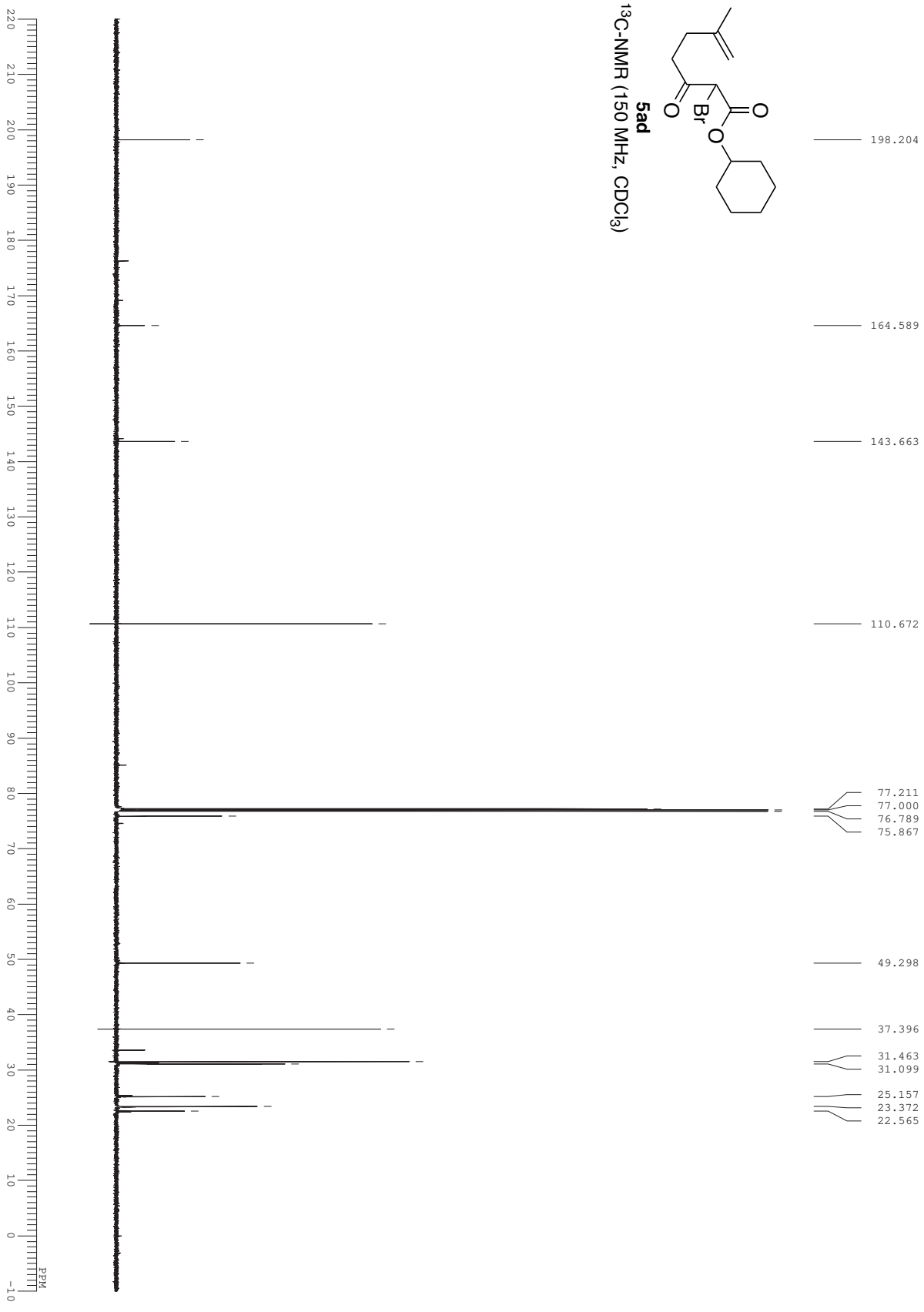

5ab
^{1}H-NMR (400 MHz, CDCl$_3$)
CO$_2$Me
Br
O
12.726
7.261
4.822
4.767
4.694
3.835
2.939
2.921
2.902
2.356
2.337
2.318
1.746
0.000
0.03
0.90
1.00
0.99
3.19
2.04
2.16
3.19
PPM

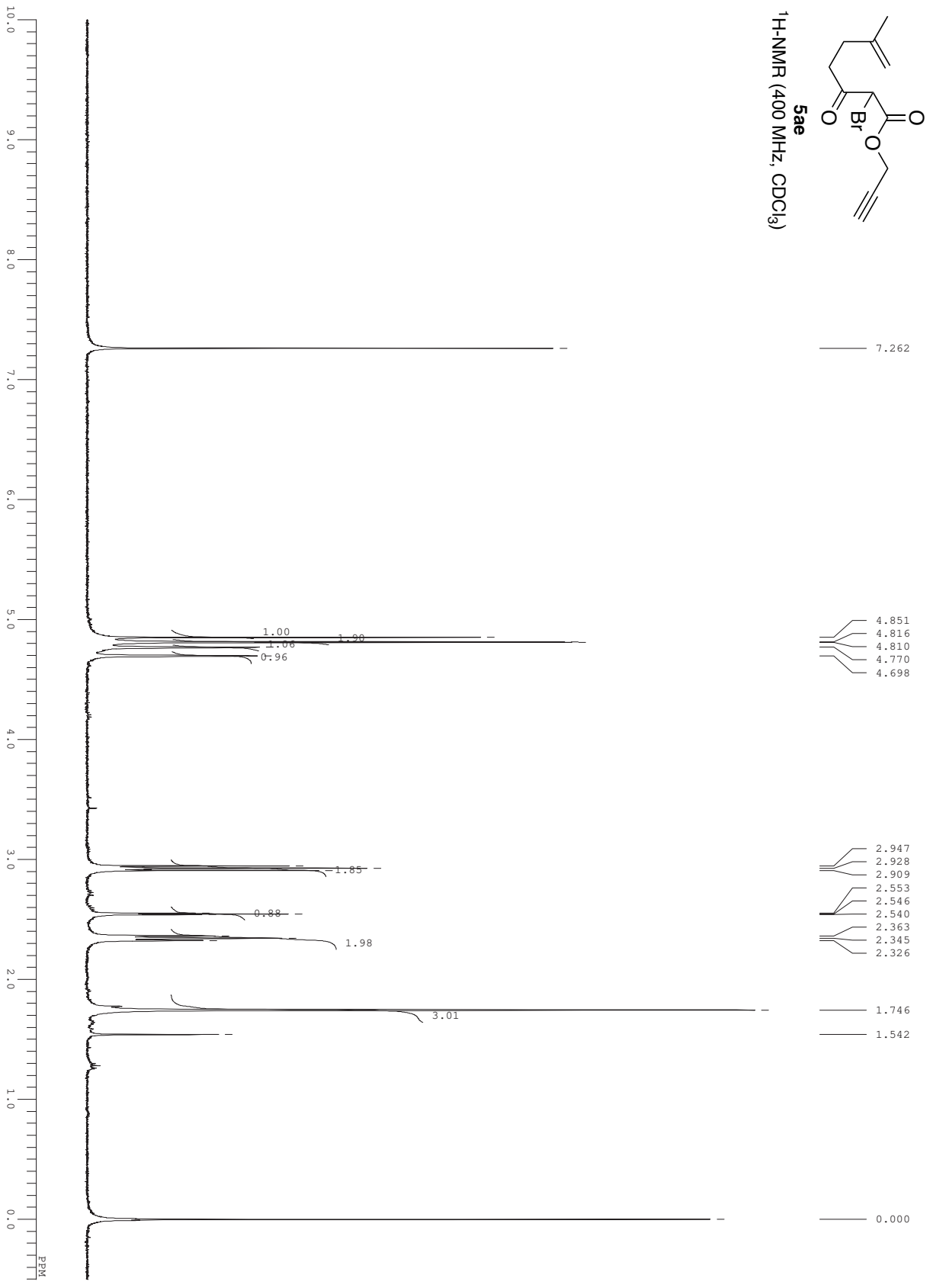

5ab
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Me
Br
O
198.004
165.617
143.545
110.680
77.313
77.000
76.679
53.751
48.326
37.417
31.358
22.516
PPM

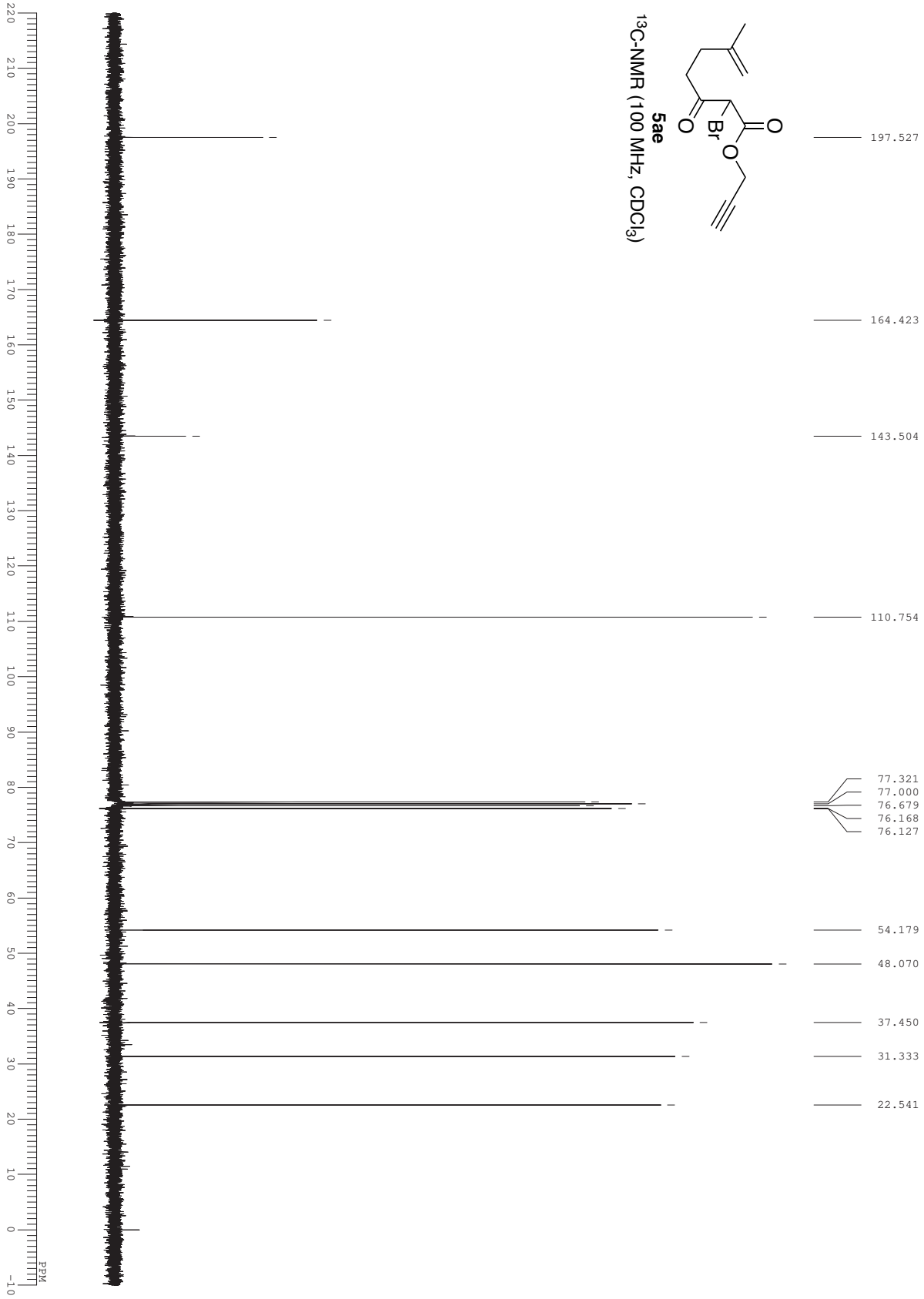

5ac
^{1}H-NMR (400 MHz, CDCl$_3$)
CO_2t-Bu
Br
O
12.927
7.262
4.762
4.722
4.696
2.969
2.816
2.698
2.679
2.657
2.354
2.335
2.316
1.747
1.537
1.493
0.000
0.05
1.00
0.98
2.19
0.14
2.15
3.49
0.92
9.44
PPM

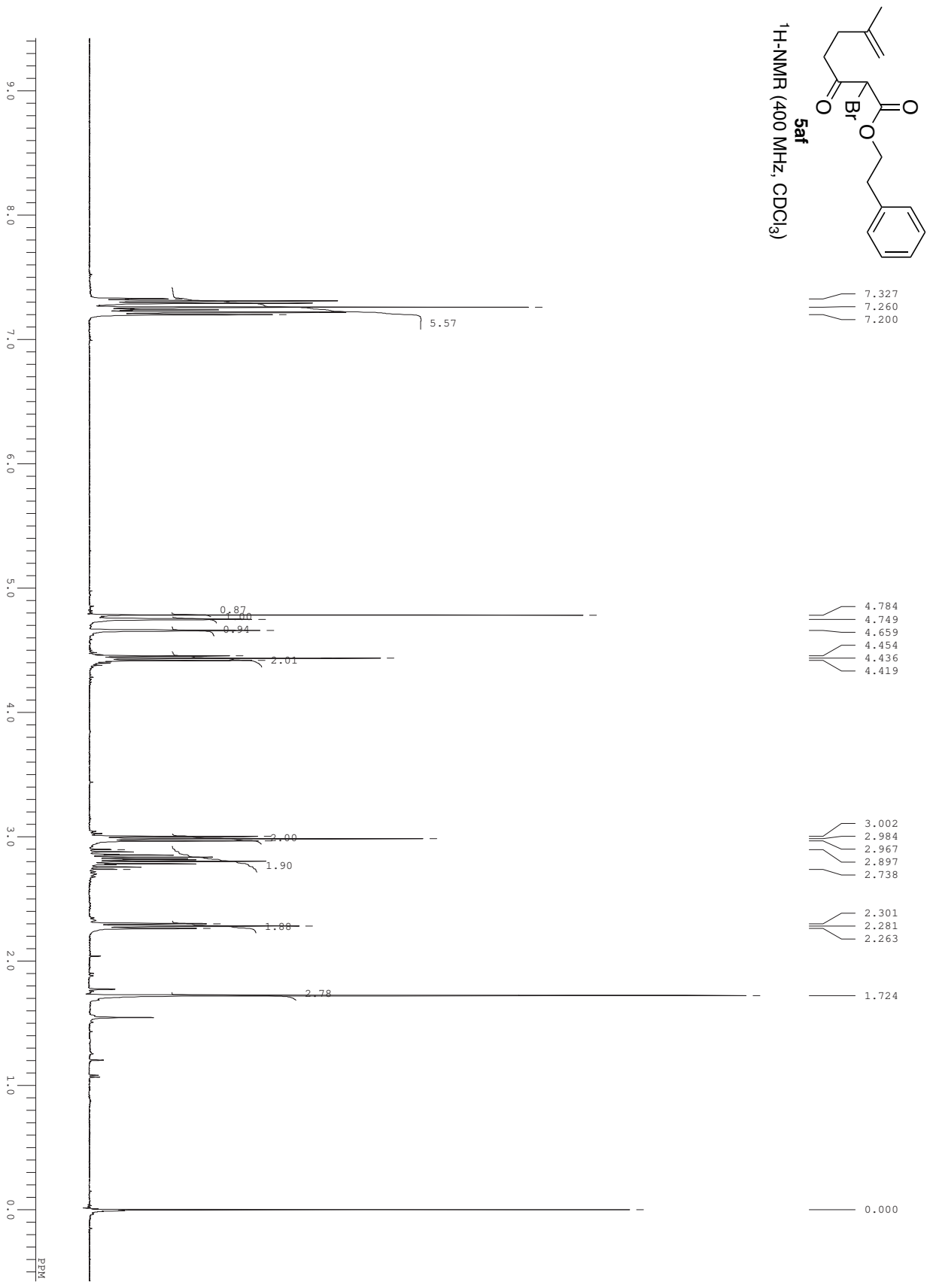

5ac
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2t-Bu
Br
O
198.375
163.962
143.677
110.614
84.376
77.313
77.000
76.679
50.318
37.343
31.465
27.686
22.541
PPM

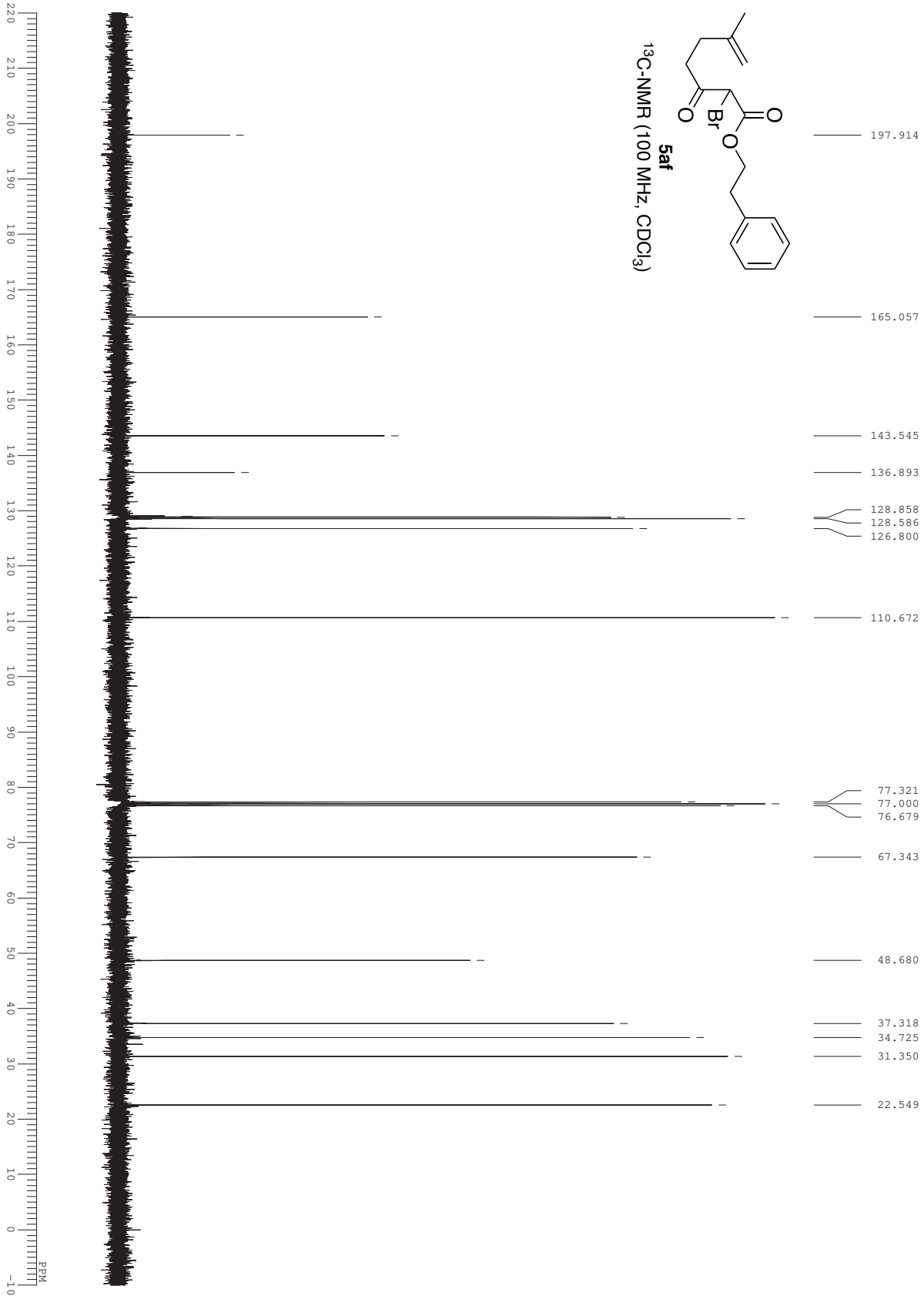

5ad
1H-NMR (600 MHz, CDCl3)
Br
O
O
O
7.264
4.906
4.864
4.789
4.762
4.742
4.694
2.963
2.855
2.711
2.682
2.349
2.336
2.323
1.874
1.844
1.777
1.744
1.703
1.558
1.466
1.435
1.351
1.329
1.256
0.000
1.00
0.86
0.87
1.78
0.19
1.98
2.03
5.03
2.95
2.08
0.98
ppm

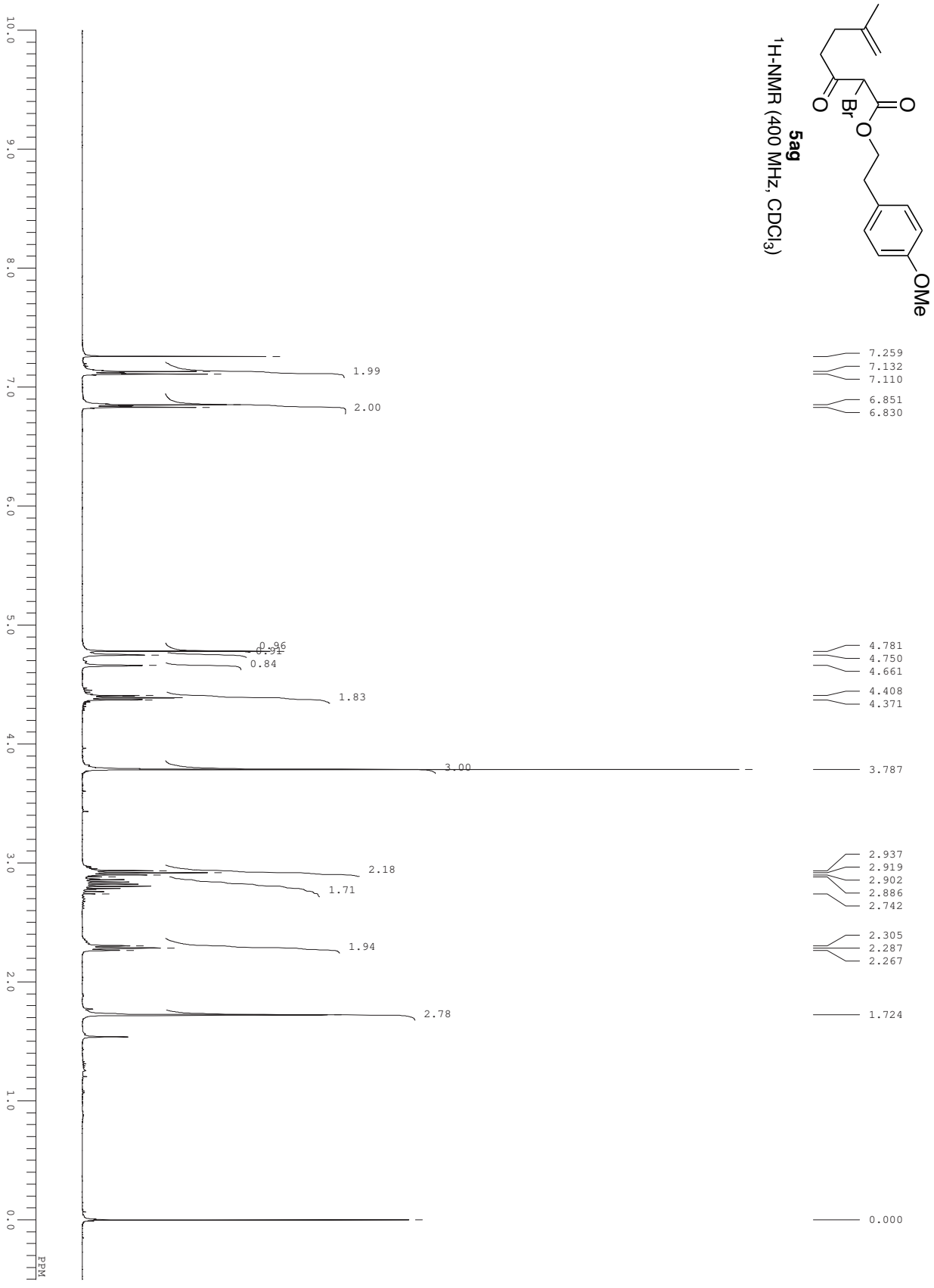

5ad
^{13}C-NMR (150 MHz, $CDCl_3$)
Br
O
O
O
198.204
164.589
143.663
110.672
77.211
77.000
76.789
75.867
49.298
37.396
31.463
31.099
25.157
23.372
22.565
PPM

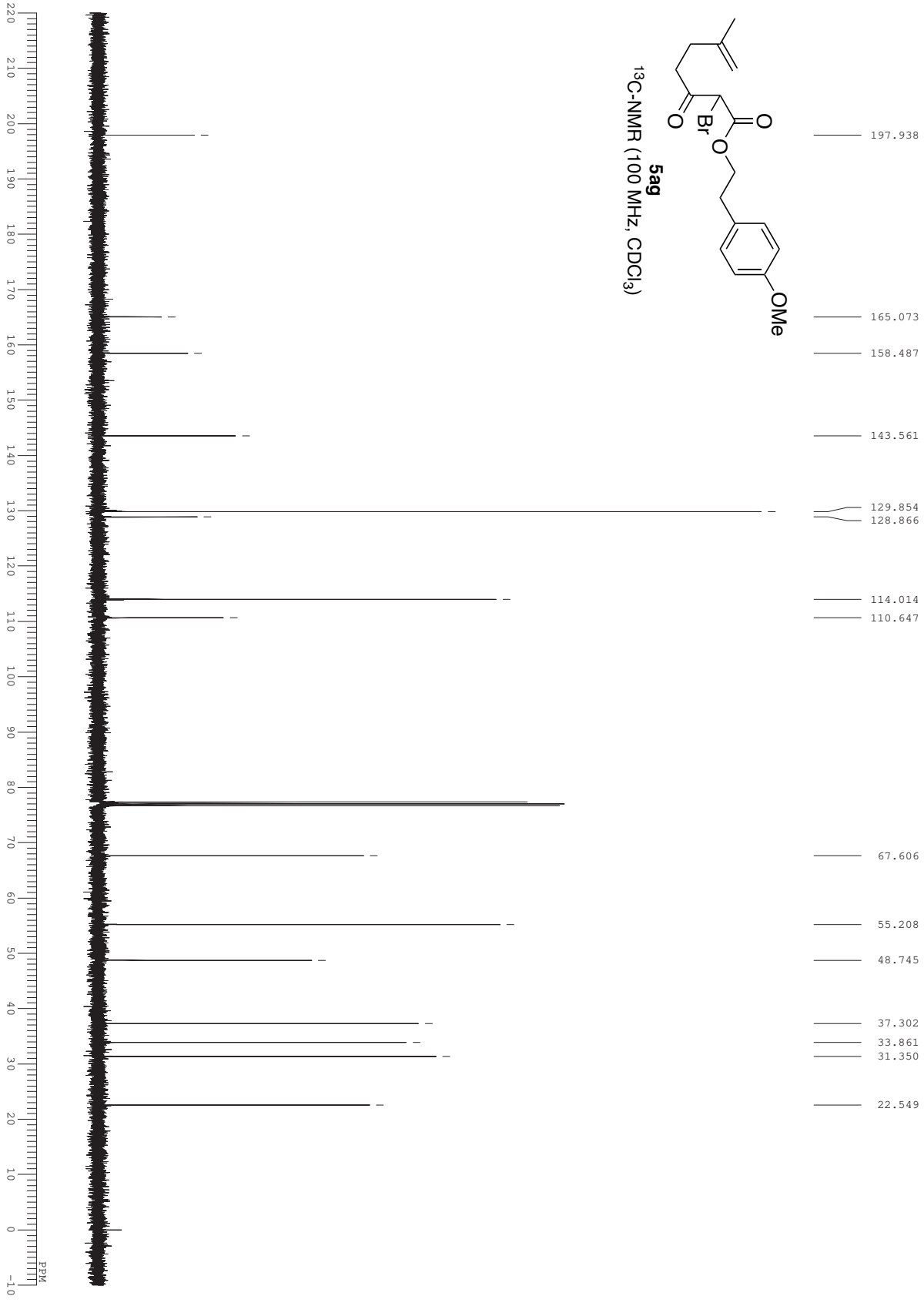

5ae
1H-NMR (400 MHz, CDCl3)
Br
O
O
O
O
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
1.00
1.80
1.06
0.96
1.85
0.88
1.98
3.01
7.262
4.851
4.816
4.810
4.770
4.698
2.947
2.928
2.909
2.553
2.546
2.540
2.363
2.345
2.326
1.746
1.542
0.000

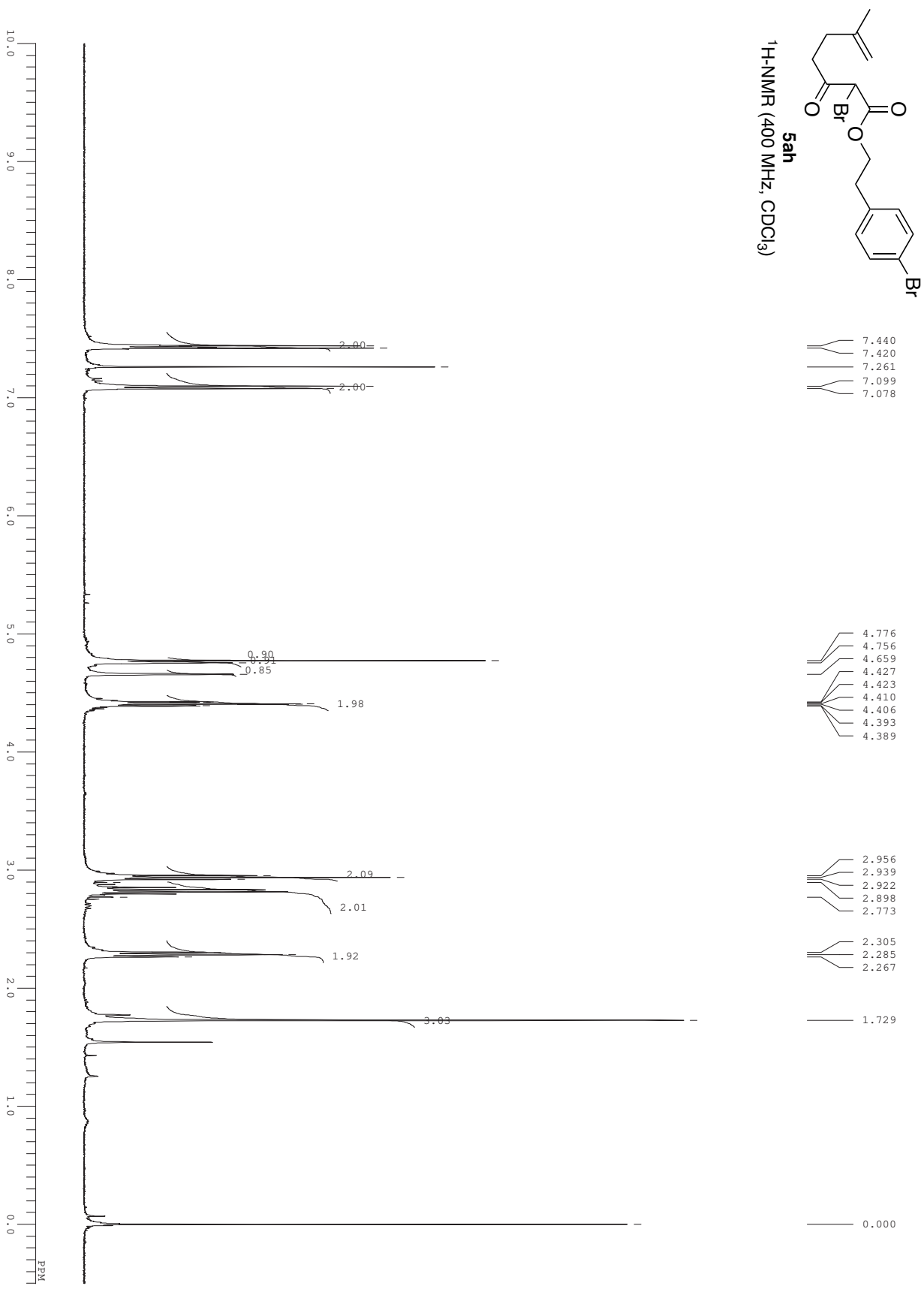

5ae
^{13}C-NMR (100 MHz, CDCl$_3$)
Br
O
O
O
O
197.527
164.423
143.504
110.754
77.321
77.000
76.679
76.168
76.127
54.179
48.070
37.450
31.333
22.541
PPM

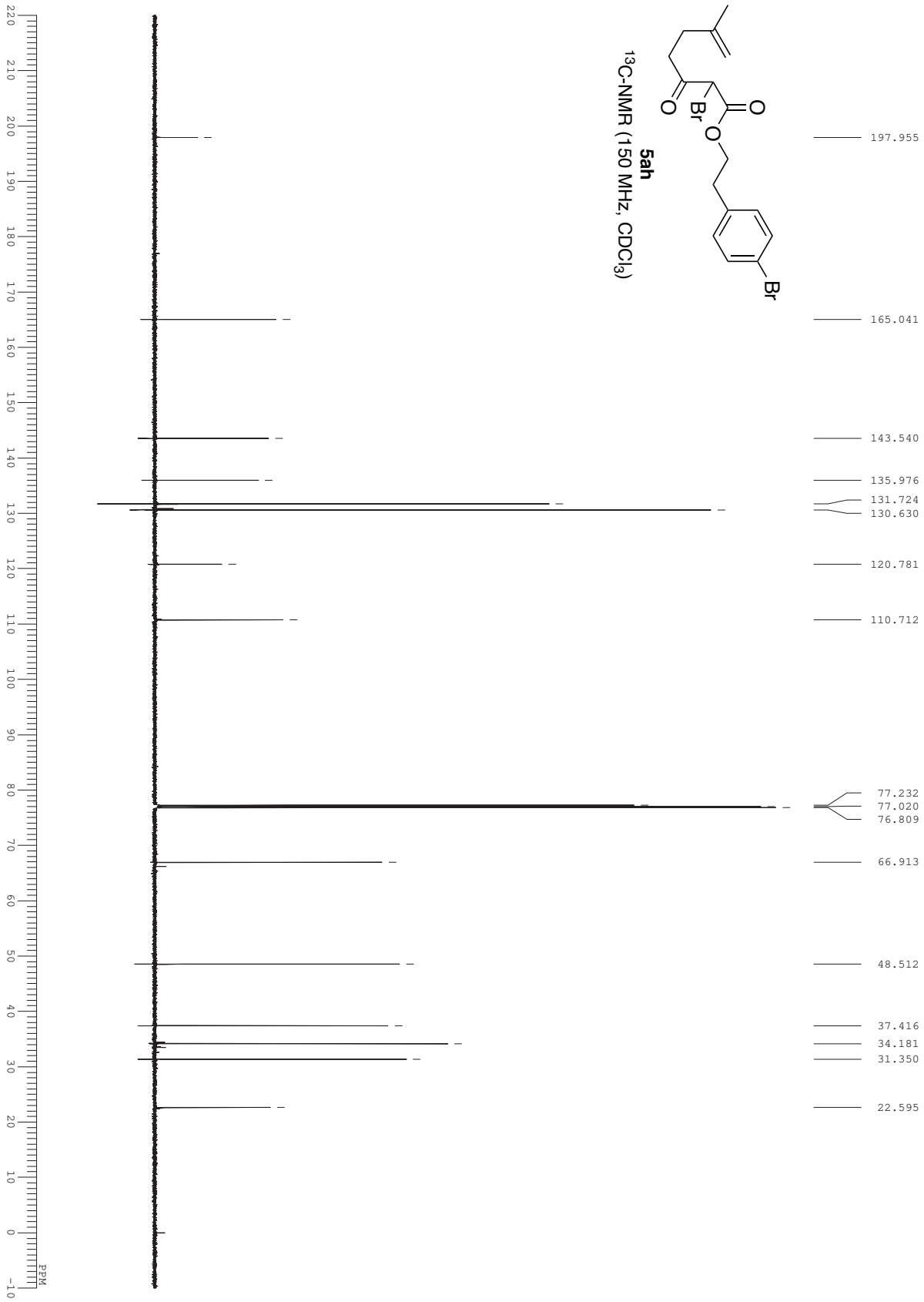

5af
1H-NMR (400 MHz, CDCl3)
Br
O
O
O
7.327
7.260
7.200
4.784
4.749
4.659
4.454
4.436
4.419
3.002
2.984
2.967
2.897
2.738
2.301
2.281
2.263
1.724
0.000
5.57
0.87
1.00
0.94
2.01
2.00
1.90
1.88
2.78
PPM

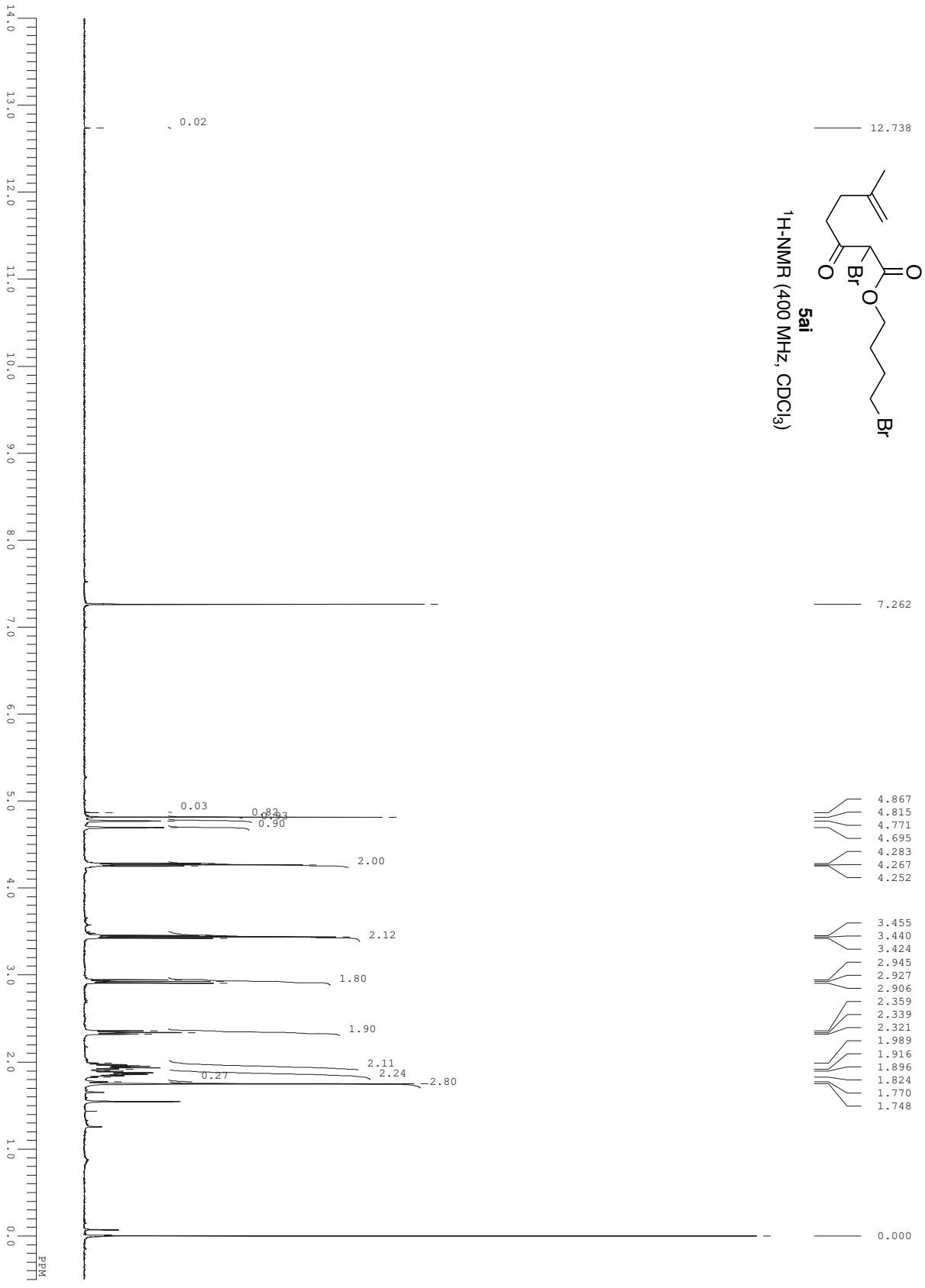

5af
^{13}C-NMR (100 MHz, CDCl$_3$)
Br
O
O
O
197.914
165.057
143.545
136.893
128.858
128.586
126.800
110.672
77.321
77.000
76.679
67.343
48.680
37.318
34.725
31.350
22.549
PPM

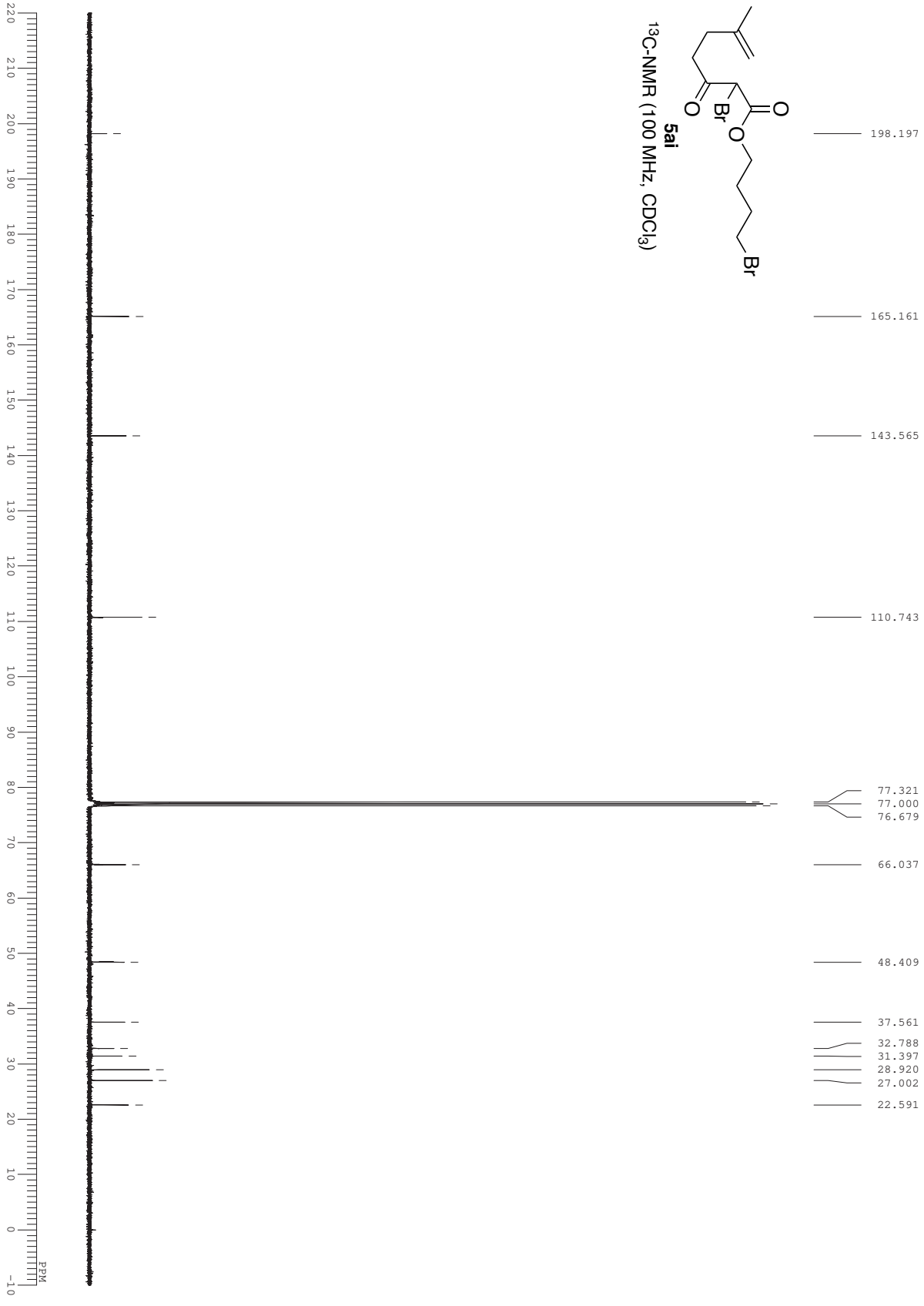

5ag
^{1}H-NMR (400 MHz, CDCl$_3$)
Br
O
O
O
OMe
7.259
7.132
7.110
6.851
6.830
4.781
4.750
4.661
4.408
4.371
3.787
2.937
2.919
2.902
2.886
2.742
2.305
2.287
2.267
1.724
0.000
1.99
2.00
0.96
0.91
0.84
1.83
3.00
2.18
1.71
1.94
2.78
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

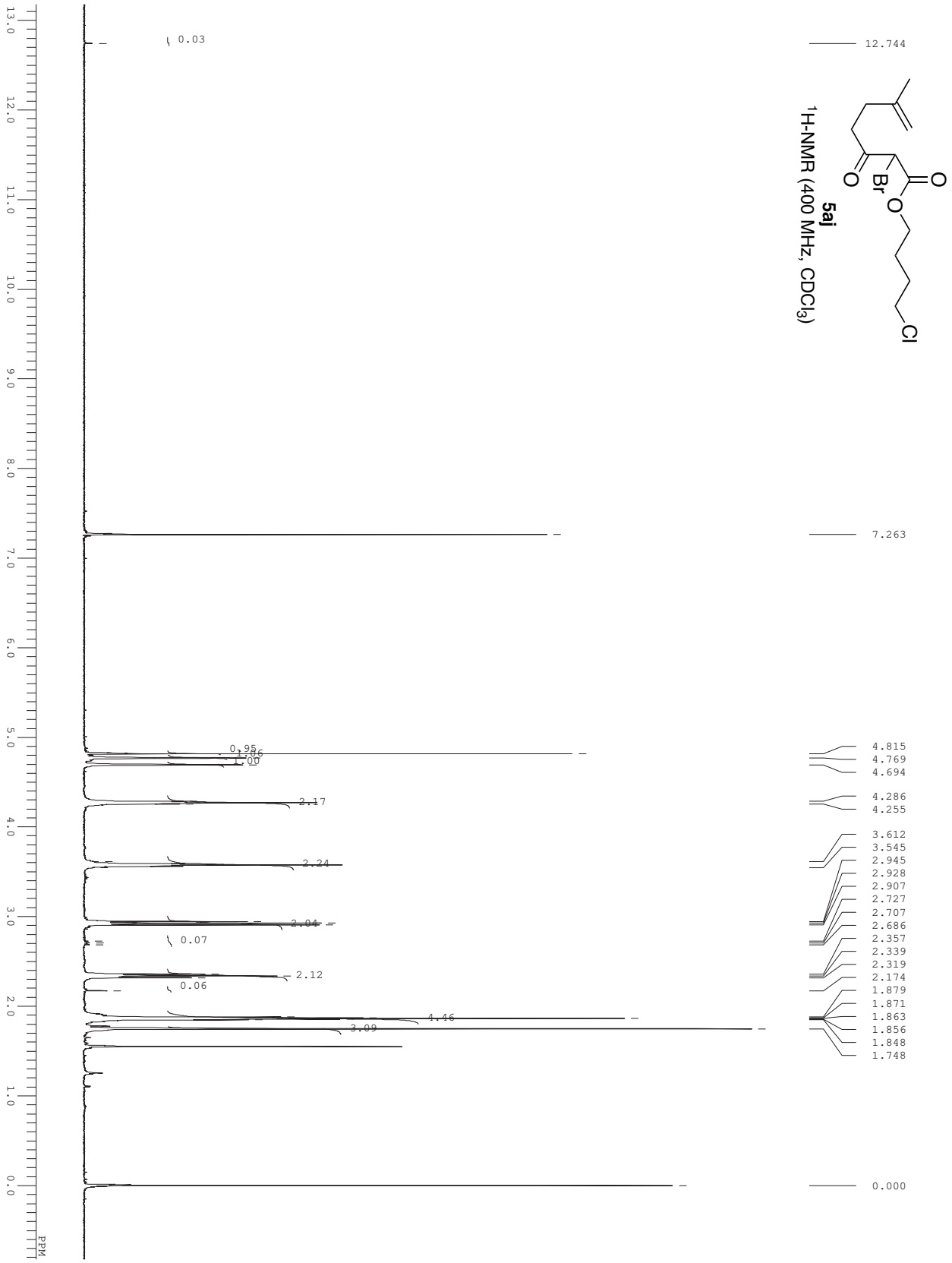

5ag
^{13}C-NMR (100 MHz, $CDCl_3$)
Br
O
O
O
OMe
197.938
165.073
158.487
143.561
129.854
128.866
114.014
110.647
67.606
55.208
48.745
37.302
33.861
31.350
22.549
PPM

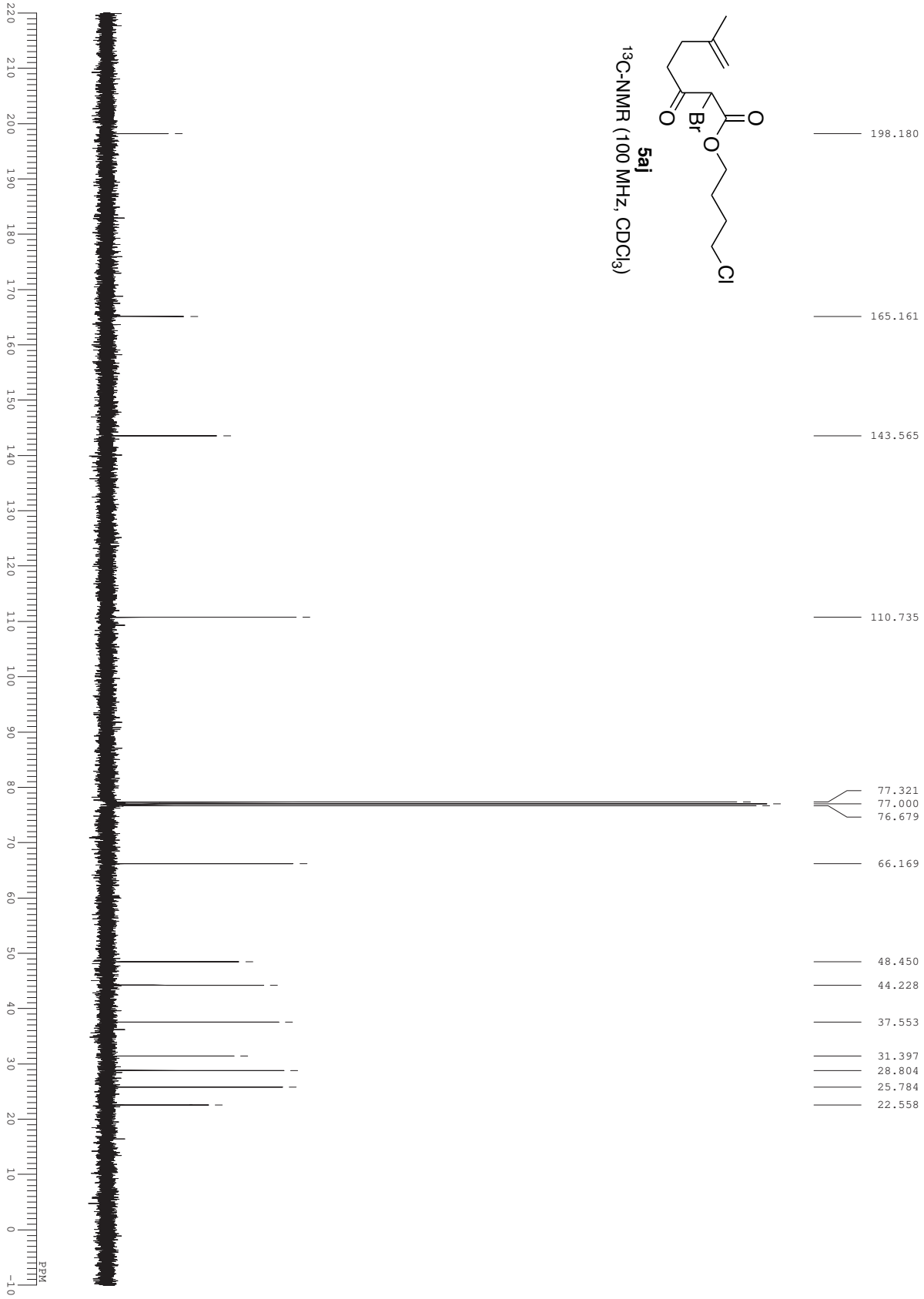

5ah
^{1}H-NMR (400 MHz, CDCl$_3$)
Br
O
O
O
Br
7.440
7.420
7.261
7.099
7.078
4.776
4.756
4.659
4.427
4.423
4.410
4.406
4.393
4.389
2.956
2.939
2.922
2.898
2.773
2.305
2.285
2.267
1.729
0.000
2.00
2.00
0.90
0.91
0.85
1.98
2.09
2.01
1.92
3.03
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

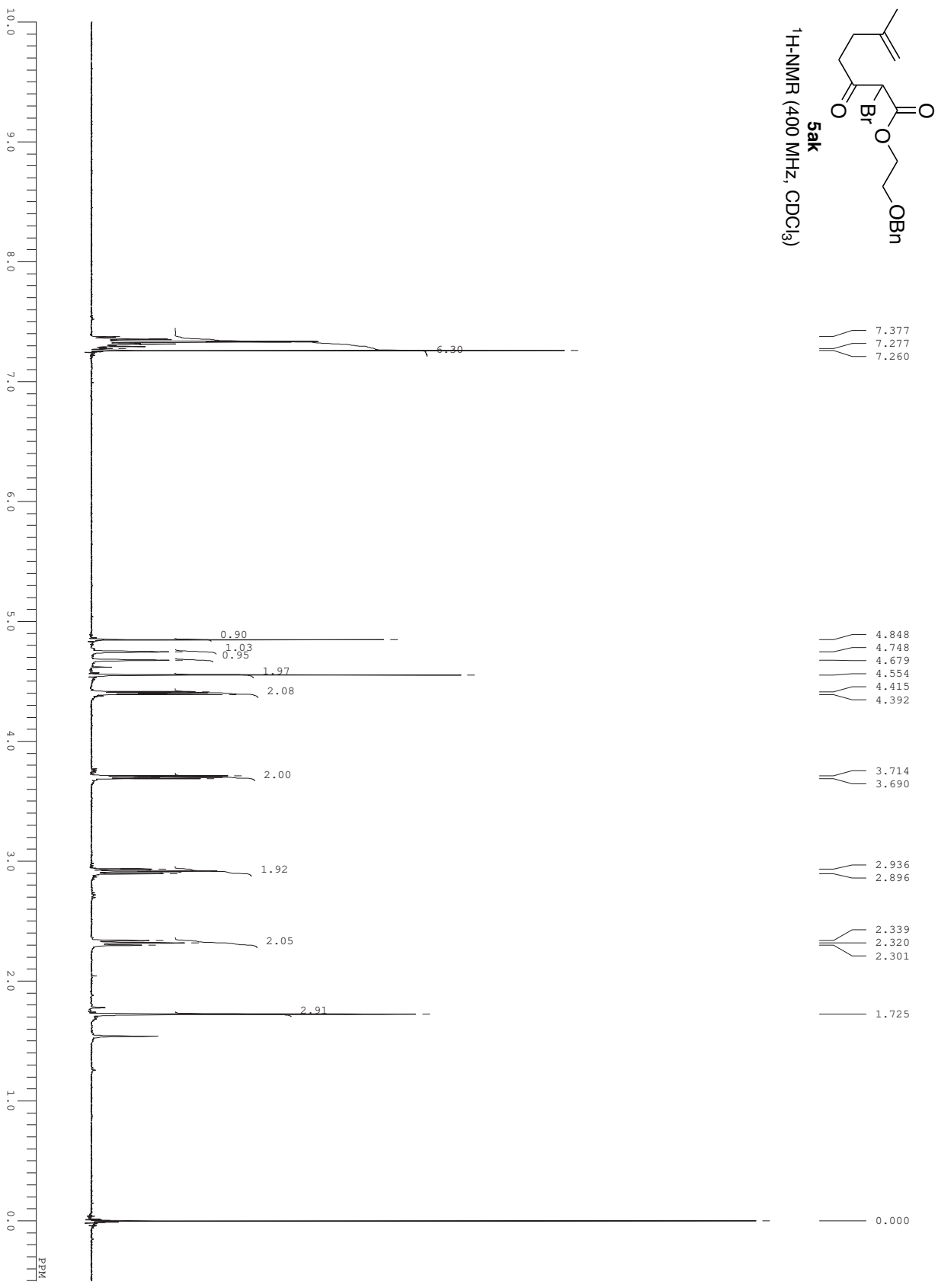

5ah
^{13}C-NMR (150 MHz, CDCl$_3$)
Br
O
O
O
Br
197.955
165.041
143.540
135.976
131.724
130.630
120.781
110.712
77.232
77.020
76.809
66.913
48.512
37.416
34.181
31.350
22.595
PPM

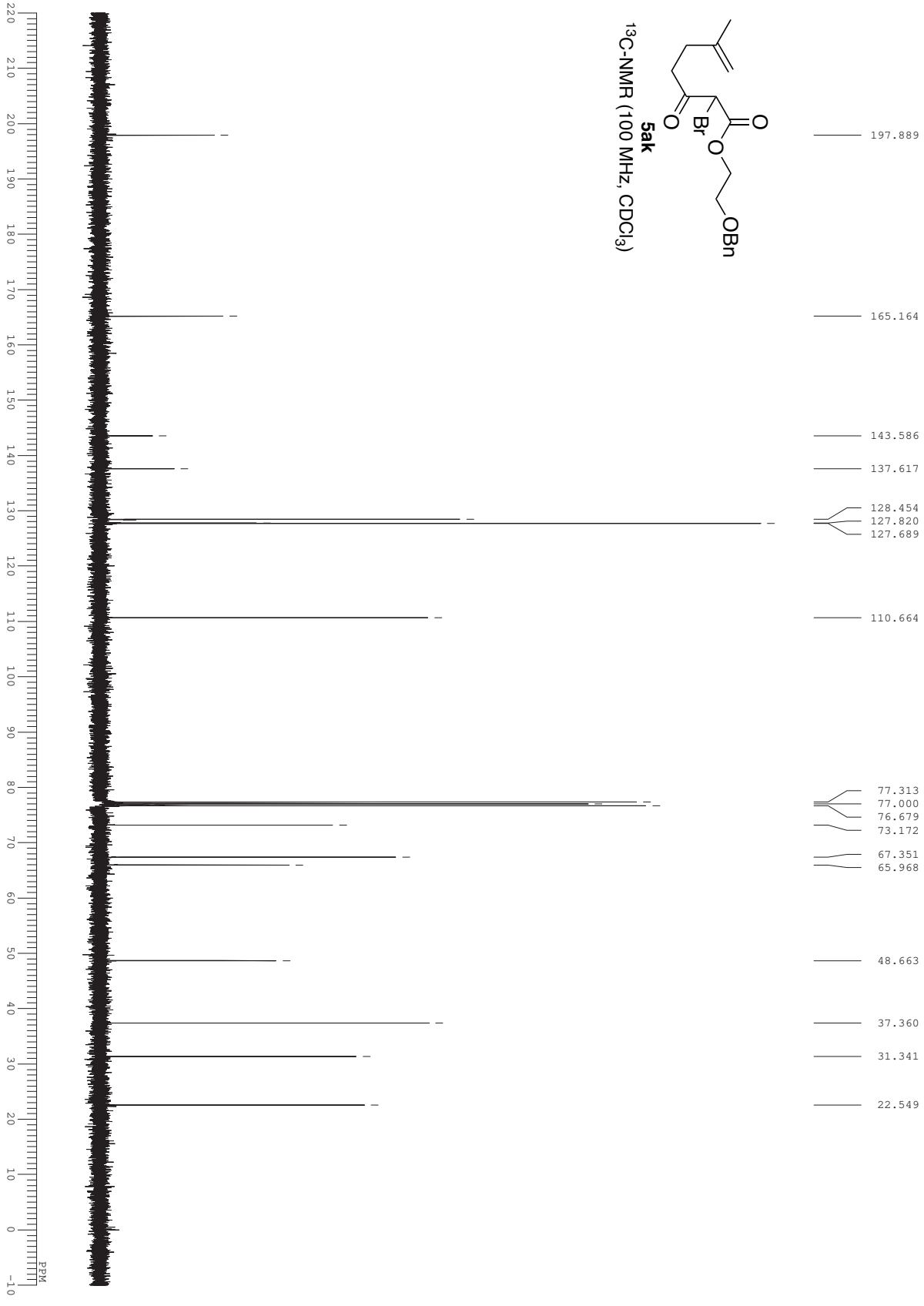

5ai
1H-NMR (400 MHz, CDCl3)
Br
O
O
O
Br
12.738
7.262
0.000
4.867
4.815
4.771
4.695
4.283
4.267
4.252
3.455
3.440
3.424
2.945
2.927
2.906
2.359
2.339
2.321
1.989
1.916
1.896
1.824
1.770
1.748
0.02
0.03
0.82
0.90
2.00
2.12
1.80
1.90
2.11
2.24
0.27
2.80
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

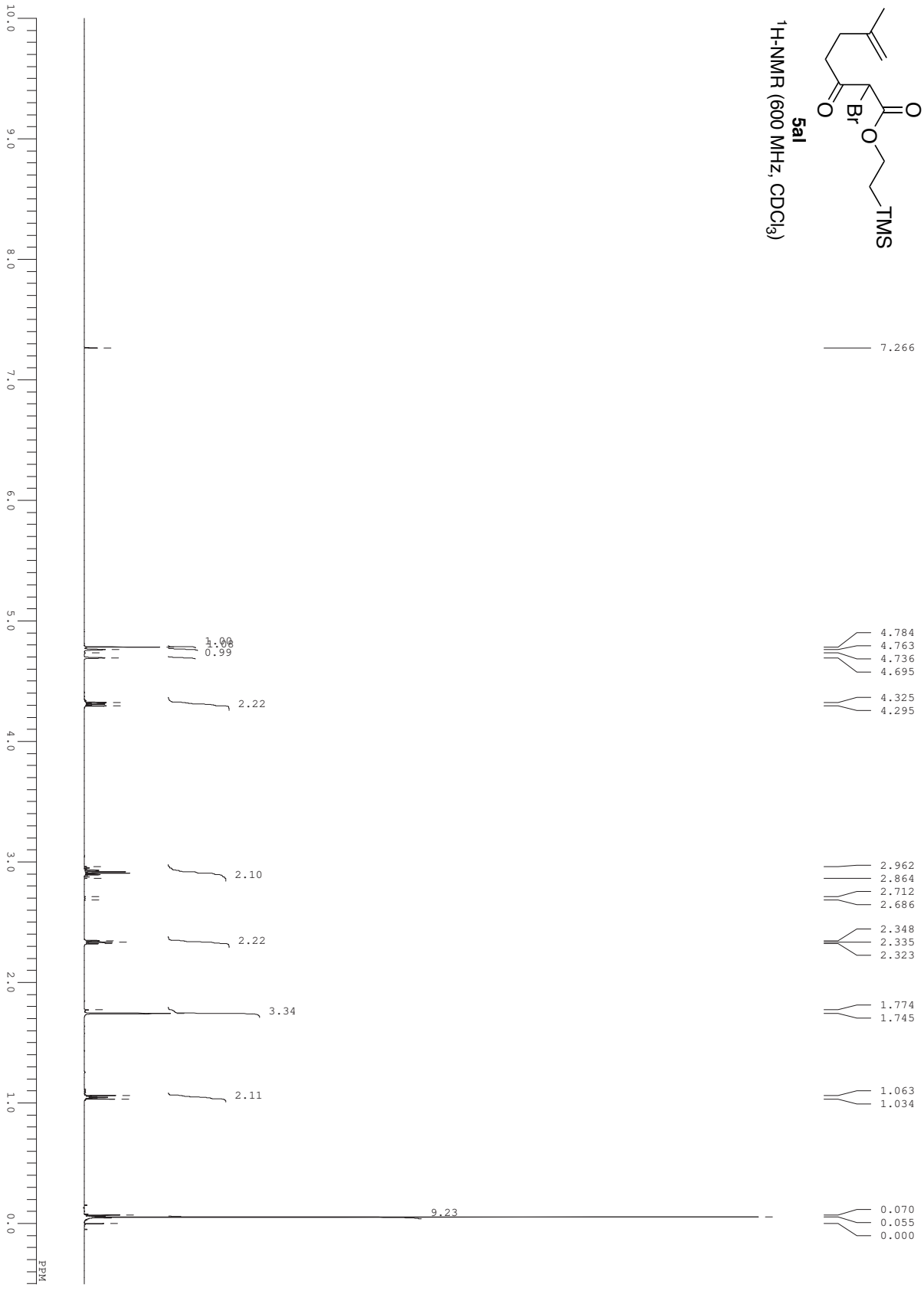

5ai
^{13}C-NMR (100 MHz, $CDCl_3$)
Br
O
O
O
Br
198.197
165.161
143.565
110.743
77.321
77.000
76.679
66.037
48.409
37.561
32.788
31.397
28.920
27.002
22.591
PPM

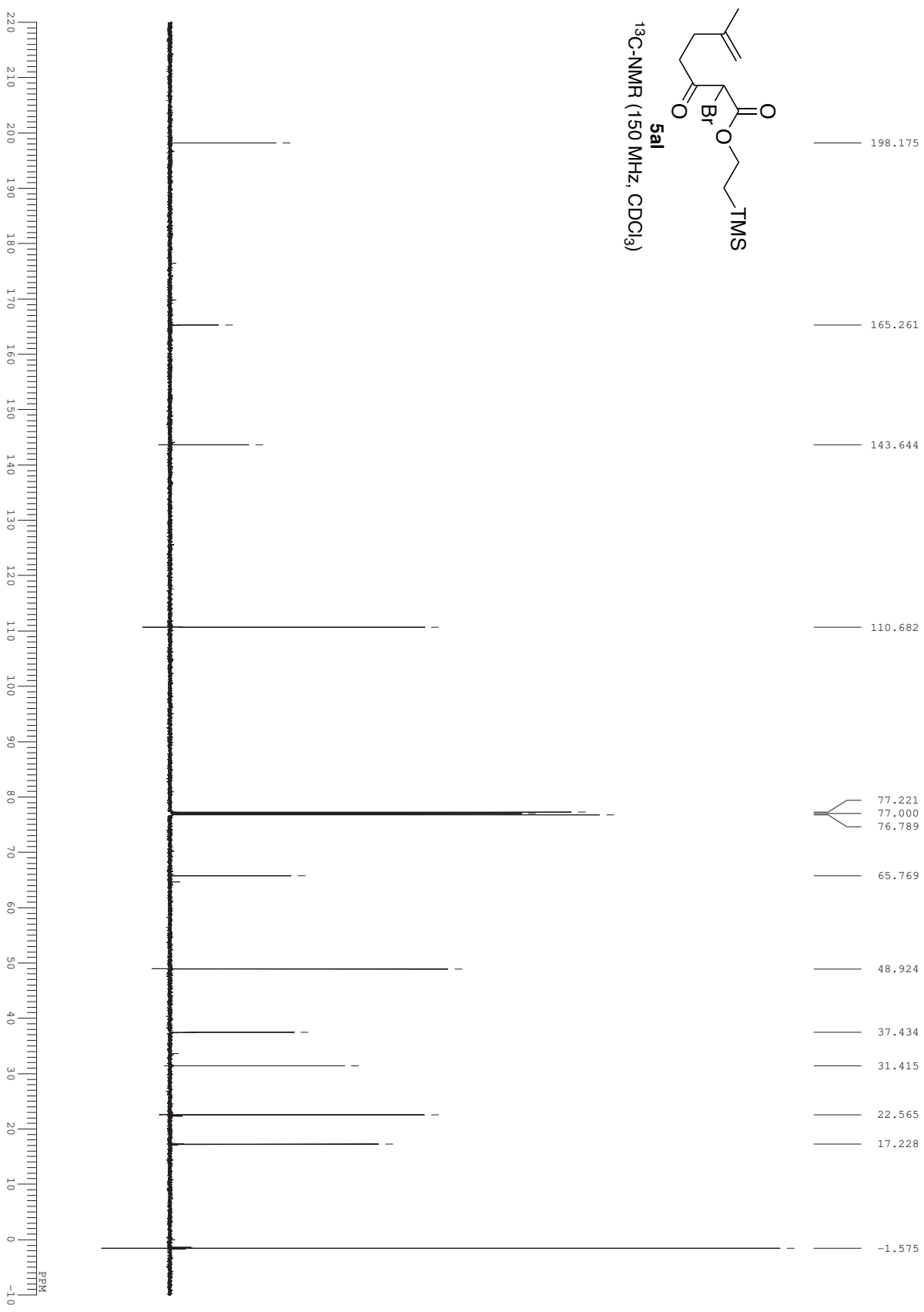

5aj
1H-NMR (400 MHz, CDCl3)
Br
O
O
O
O
Cl
12.744
7.263
0.000
4.815
4.769
4.694
4.286
4.255
3.612
3.545
2.945
2.928
2.907
2.727
2.707
2.686
2.357
2.339
2.319
2.174
1.879
1.871
1.863
1.856
1.848
1.748
0.03
0.95
1.86
1.00
2.17
2.24
2.04
0.07
2.12
0.06
4.46
3.09
PPM

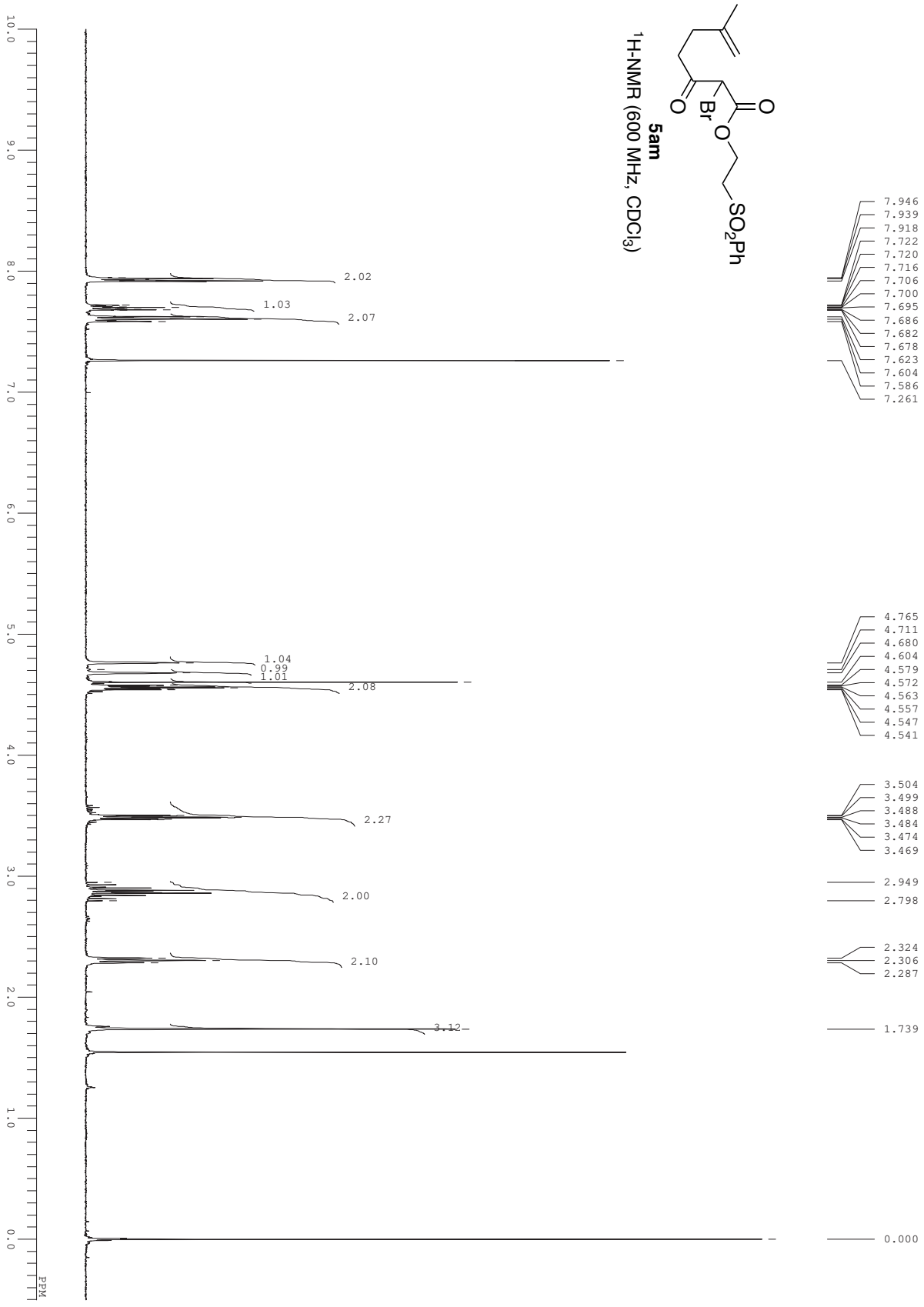

5aj
^{13}C-NMR (100 MHz, CDCl$_3$)
O
Br
O
O
O
Cl
198.180
165.161
143.565
110.735
77.321
77.000
76.679
66.169
48.450
44.228
37.553
31.397
28.804
25.784
22.558
PPM

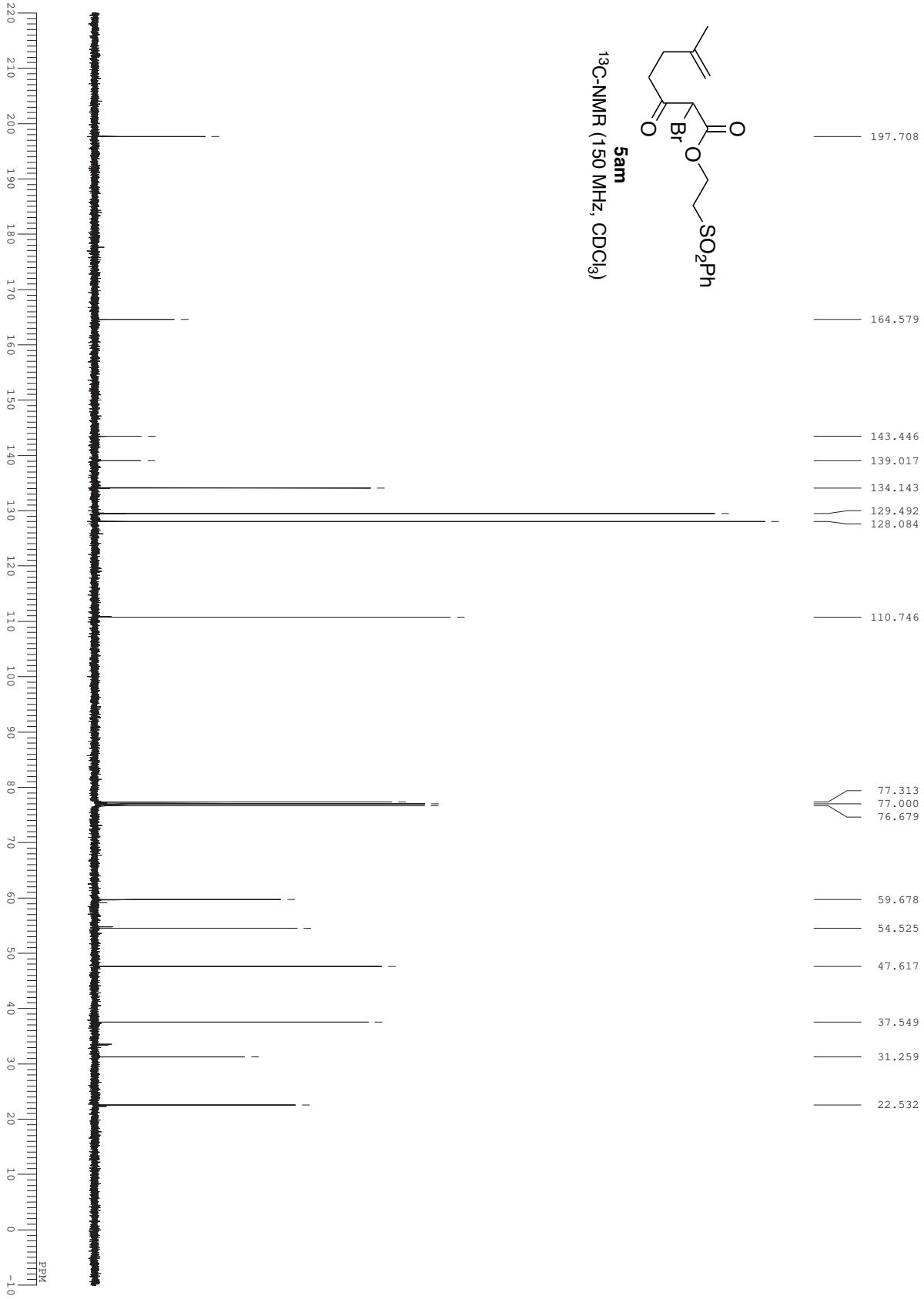

5ak
1H-NMR (400 MHz, CDCl3)
Br
O
OBn
7.377
7.277
7.260
4.848
4.748
4.679
4.554
4.415
4.392
3.714
3.690
2.936
2.896
2.339
2.320
2.301
1.725
0.000
6.30
0.90
1.03
0.95
1.97
2.08
2.00
1.92
2.05
2.91
PPM

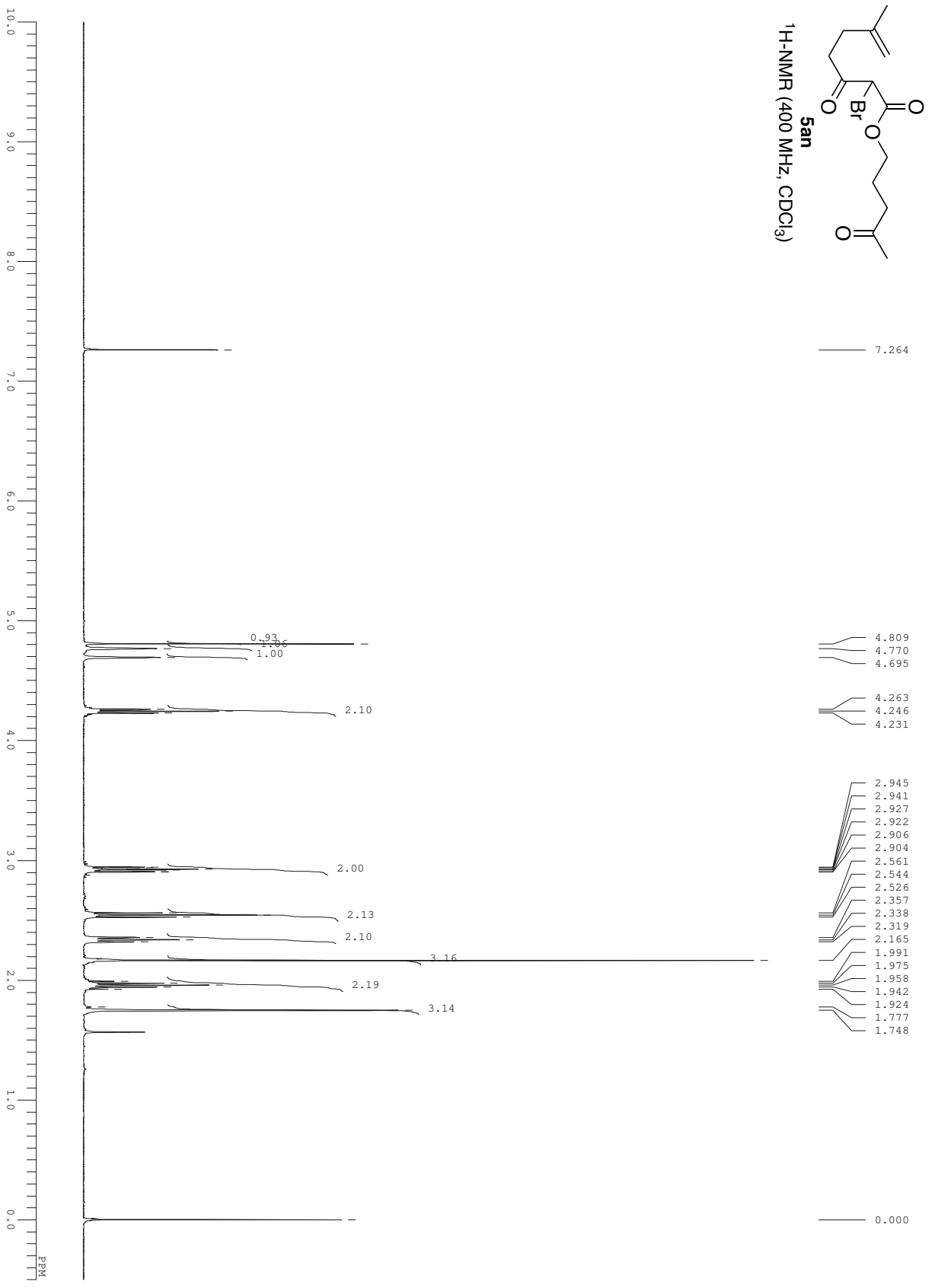

5ak
^{13}C-NMR (100 MHz, $CDCl_3$)
197.889
165.164
143.586
137.617
128.454
127.820
127.689
110.664
77.313
77.000
76.679
73.172
67.351
65.968
48.663
37.360
31.341
22.549
PPM

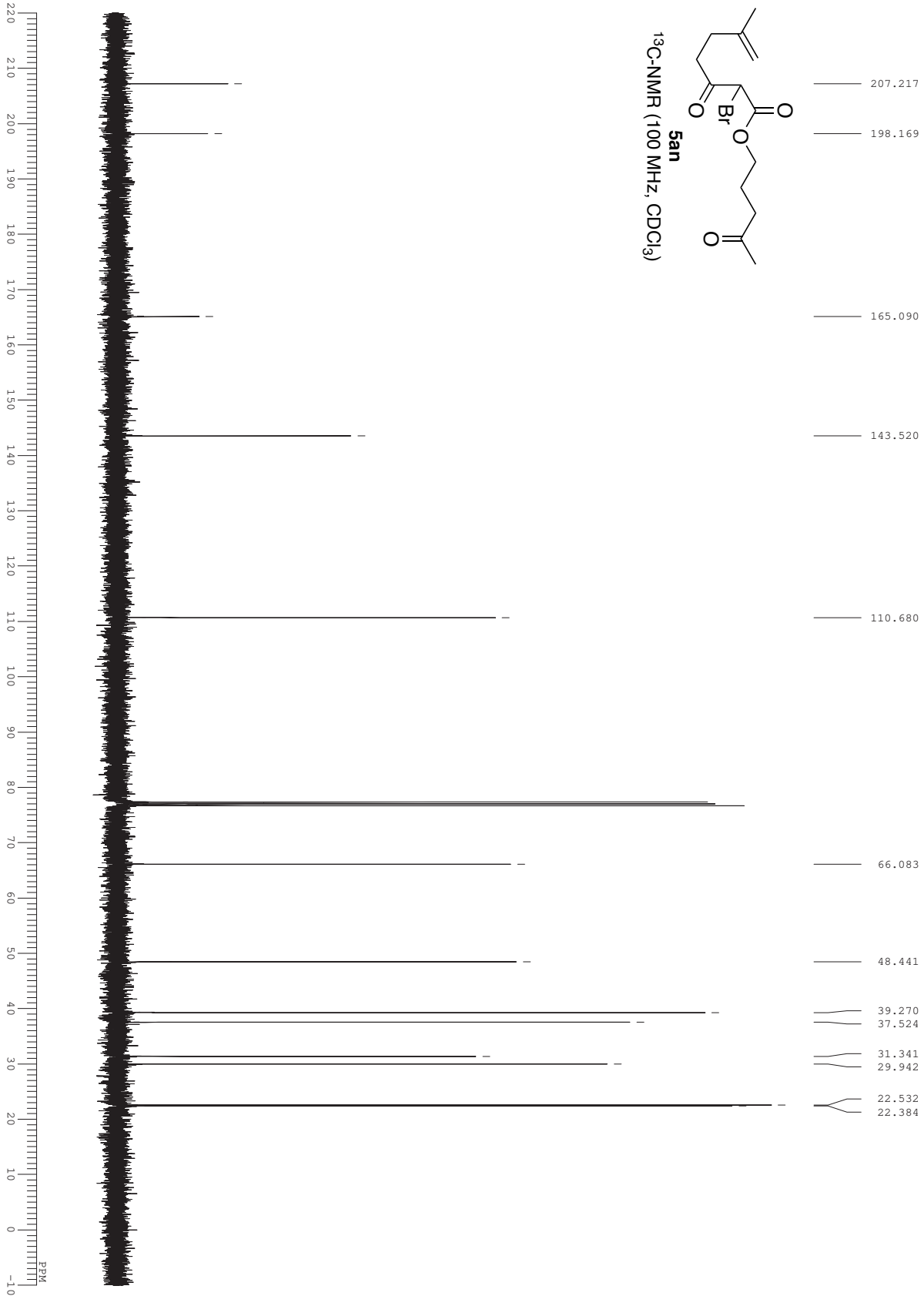

5al
^{1}H-NMR (600 MHz, $CDCl_3$)
Br
O
TMS
7.266
4.784
4.763
4.736
4.695
4.325
4.295
2.962
2.864
2.712
2.686
2.348
2.335
2.323
1.774
1.745
1.063
1.034
0.070
0.055
0.000
1.00
1.08
0.99
2.22
2.10
2.22
3.34
2.11
9.23
PPM

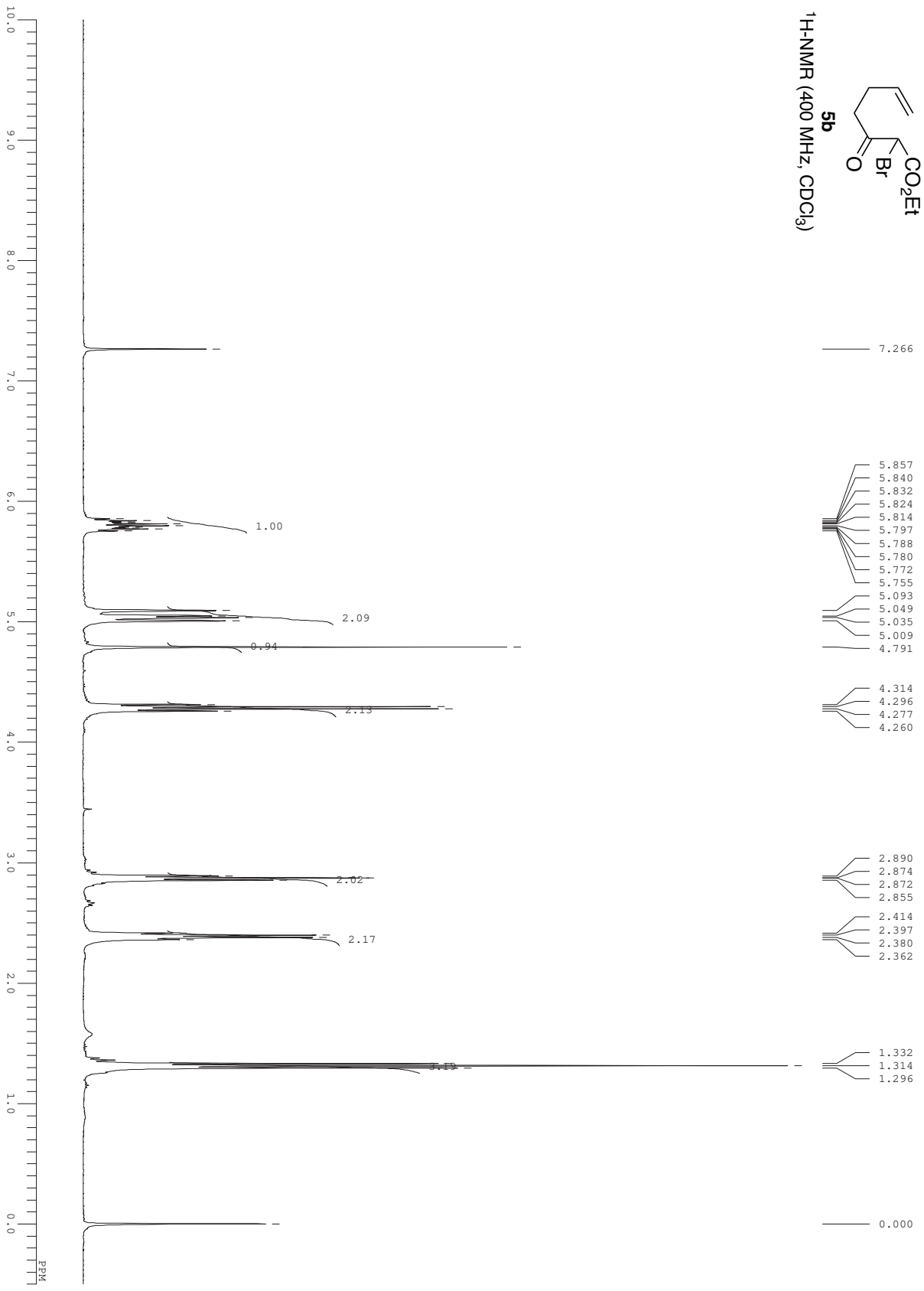

5al
13C-NMR (150 MHz, CDCl3)
Br
O
O
O
TMS
198.175
165.261
143.644
110.682
77.221
77.000
76.789
65.769
48.924
37.434
31.415
22.565
17.228
-1.575
PPM

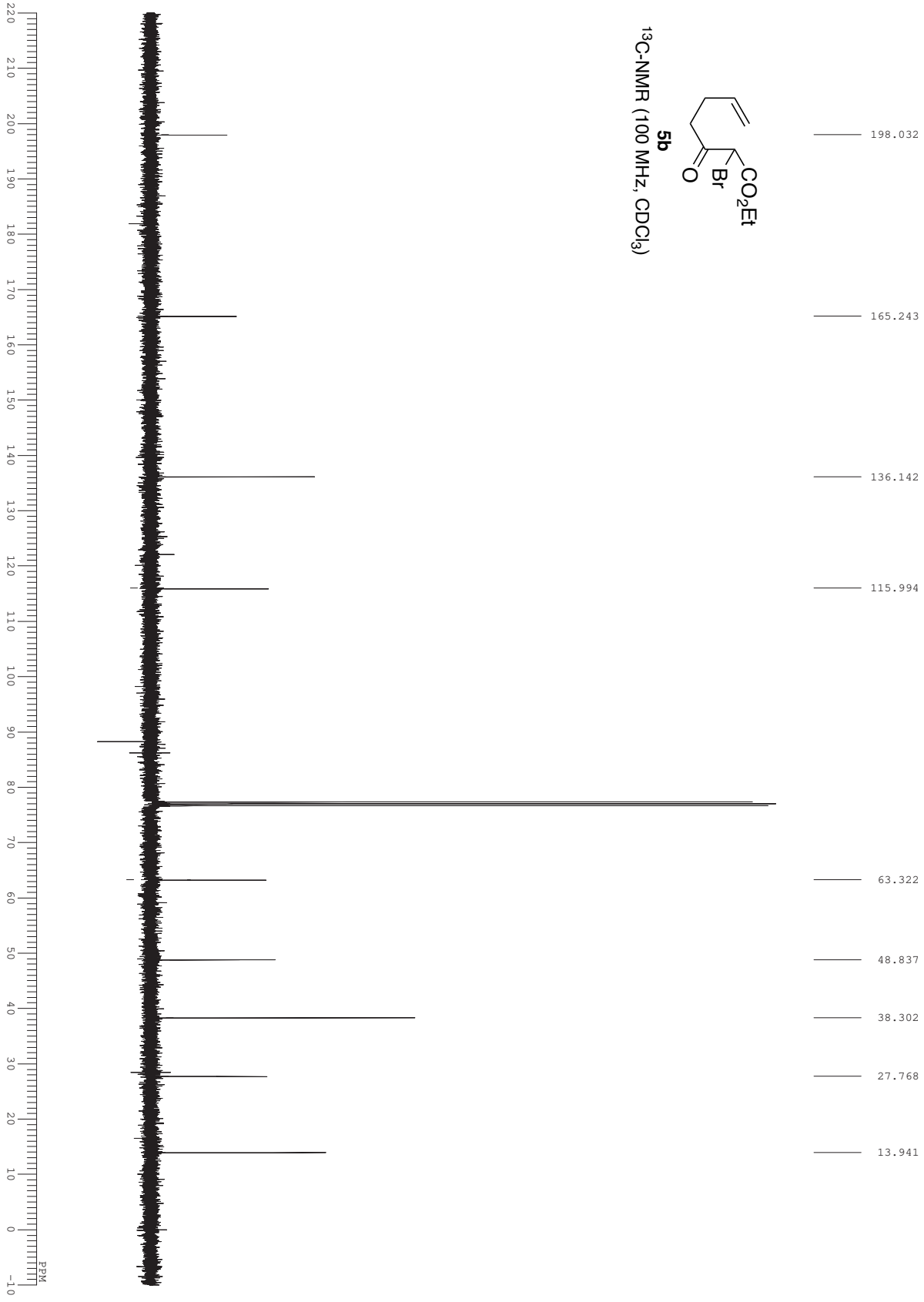

5am
^{1}H-NMR (600 MHz, $CDCl_3$)
Br
O
O
O
O
SO_2Ph
7.946
7.939
7.918
7.722
7.720
7.716
7.706
7.700
7.695
7.686
7.682
7.678
7.623
7.604
7.586
7.261
4.765
4.711
4.680
4.604
4.579
4.572
4.563
4.557
4.547
4.541
3.504
3.499
3.488
3.484
3.474
3.469
2.949
2.798
2.324
2.306
2.287
1.739
0.000
2.02
1.03
2.07
1.04
0.99
1.01
2.08
2.27
2.00
2.10
3.12
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

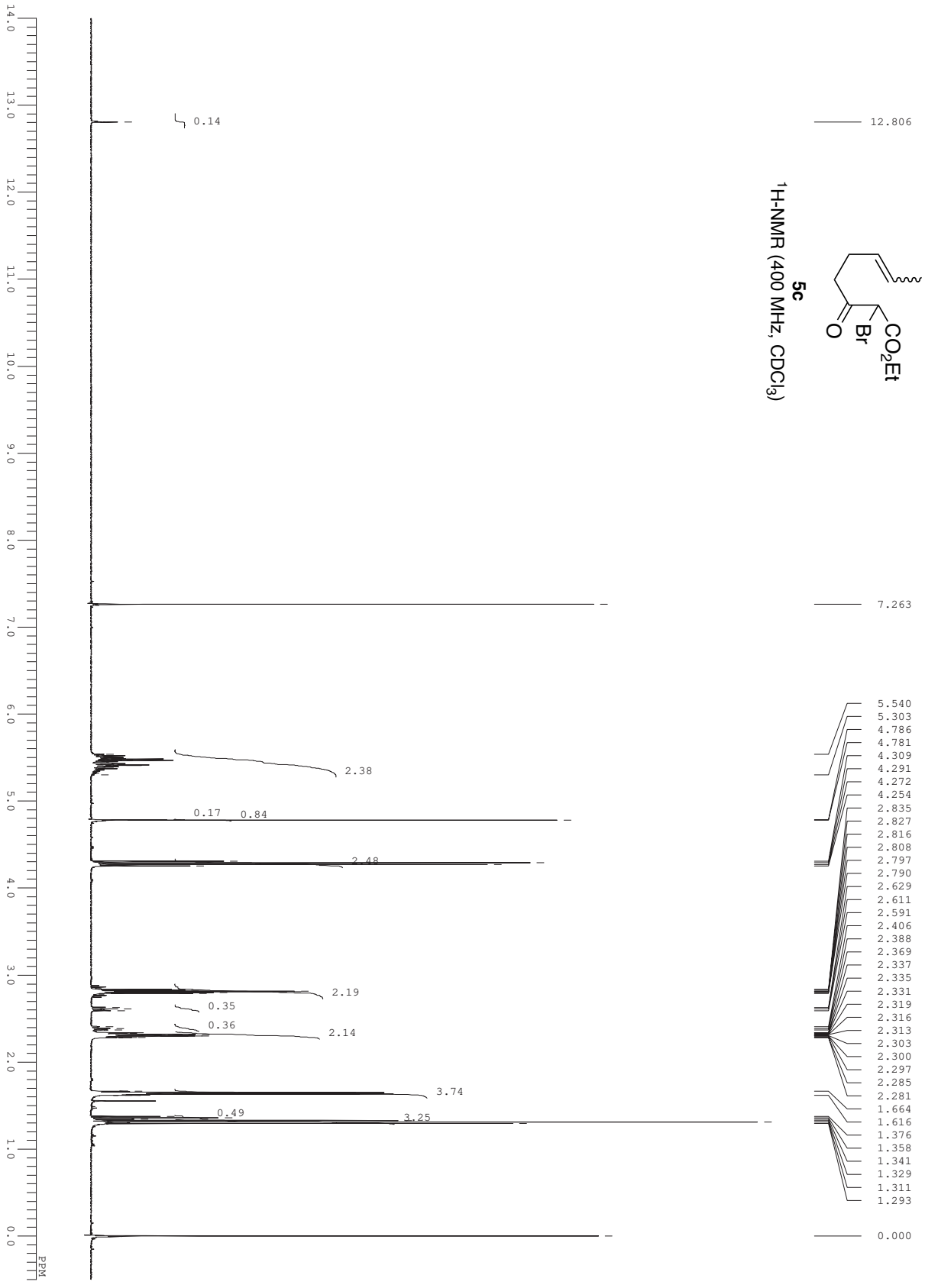

5am
13C-NMR (150 MHz, CDCl3)
O
O
Br
O
O
SO2Ph
197.708
164.579
143.446
139.017
134.143
129.492
128.084
110.746
77.313
77.000
76.679
59.678
54.525
47.617
37.549
31.259
22.532
PPM

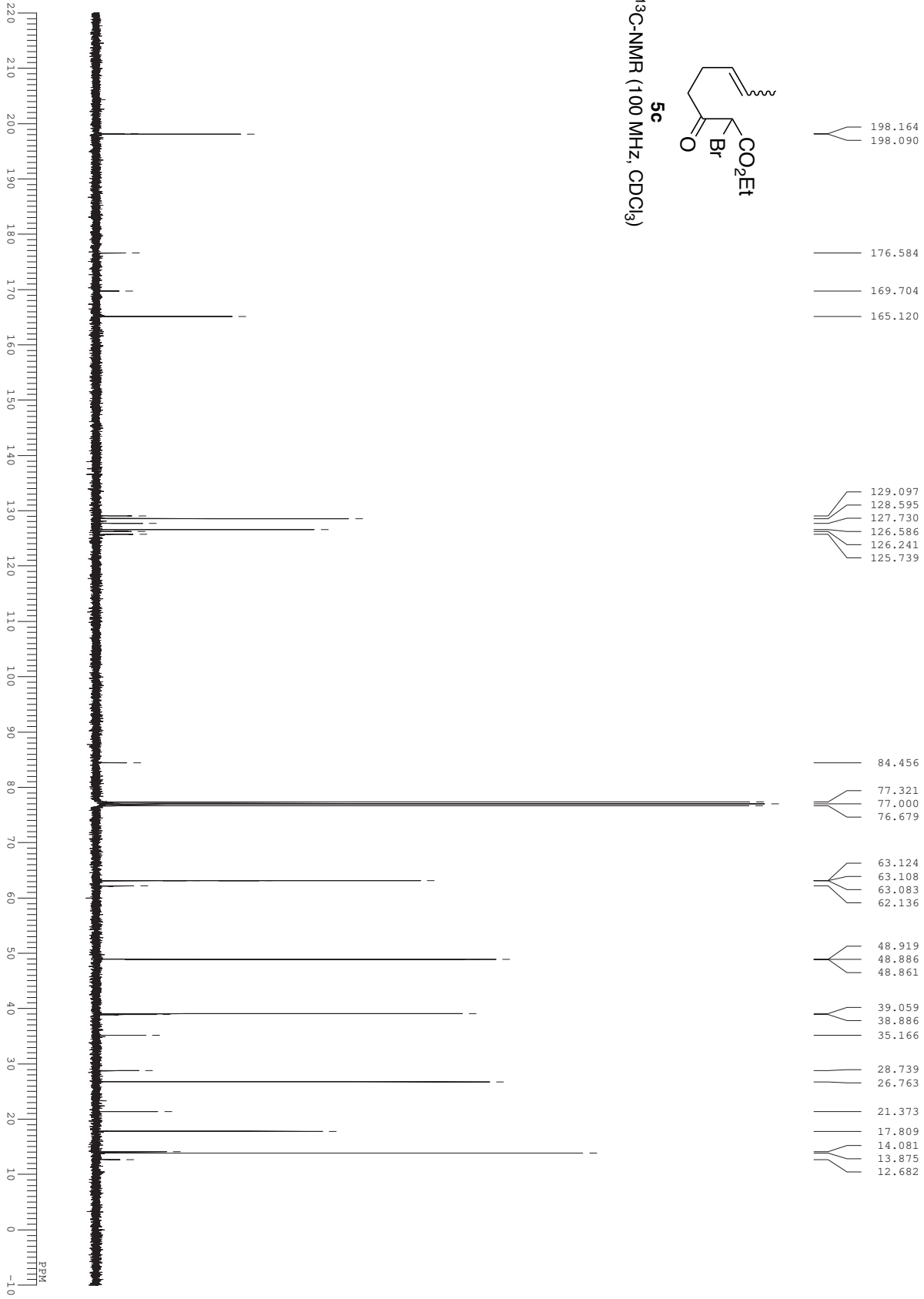

5an
^{1}H-NMR (400 MHz, $CDCl_3$)
Br
O
7.264
4.809
4.770
4.695
4.263
4.246
4.231
2.945
2.941
2.927
2.922
2.906
2.904
2.561
2.544
2.526
2.357
2.338
2.319
2.165
1.991
1.975
1.958
1.942
1.924
1.777
1.748
0.000
0.93
1.06
1.00
2.10
2.00
2.13
2.10
3.16
2.19
3.14
PPM

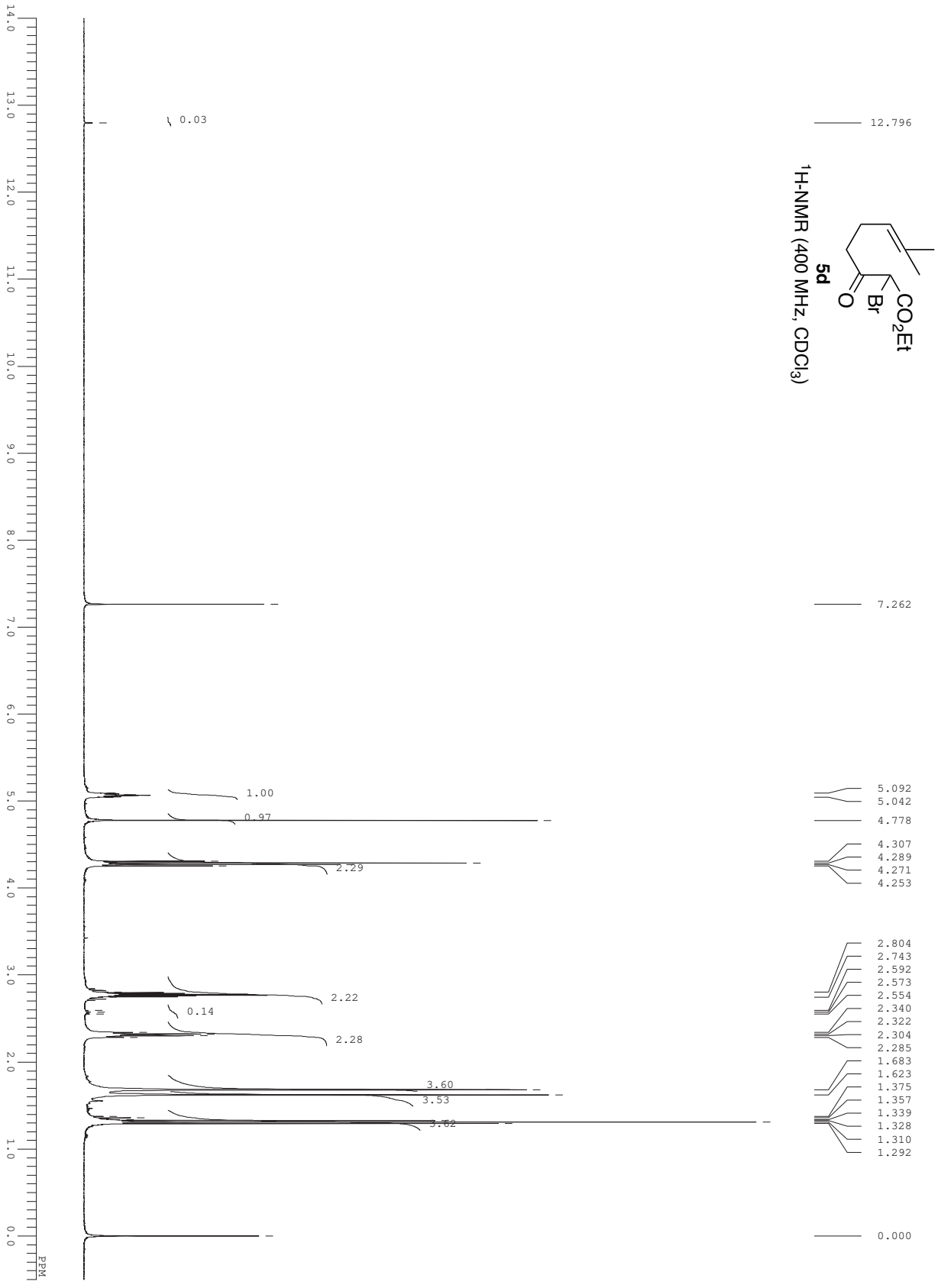

5an
^{13}C-NMR (100 MHz, $CDCl_3$)
Br
O
O
O
O
O
207.217
198.169
165.090
143.520
110.680
66.083
48.441
39.270
37.524
31.341
29.942
22.532
22.384
PPM

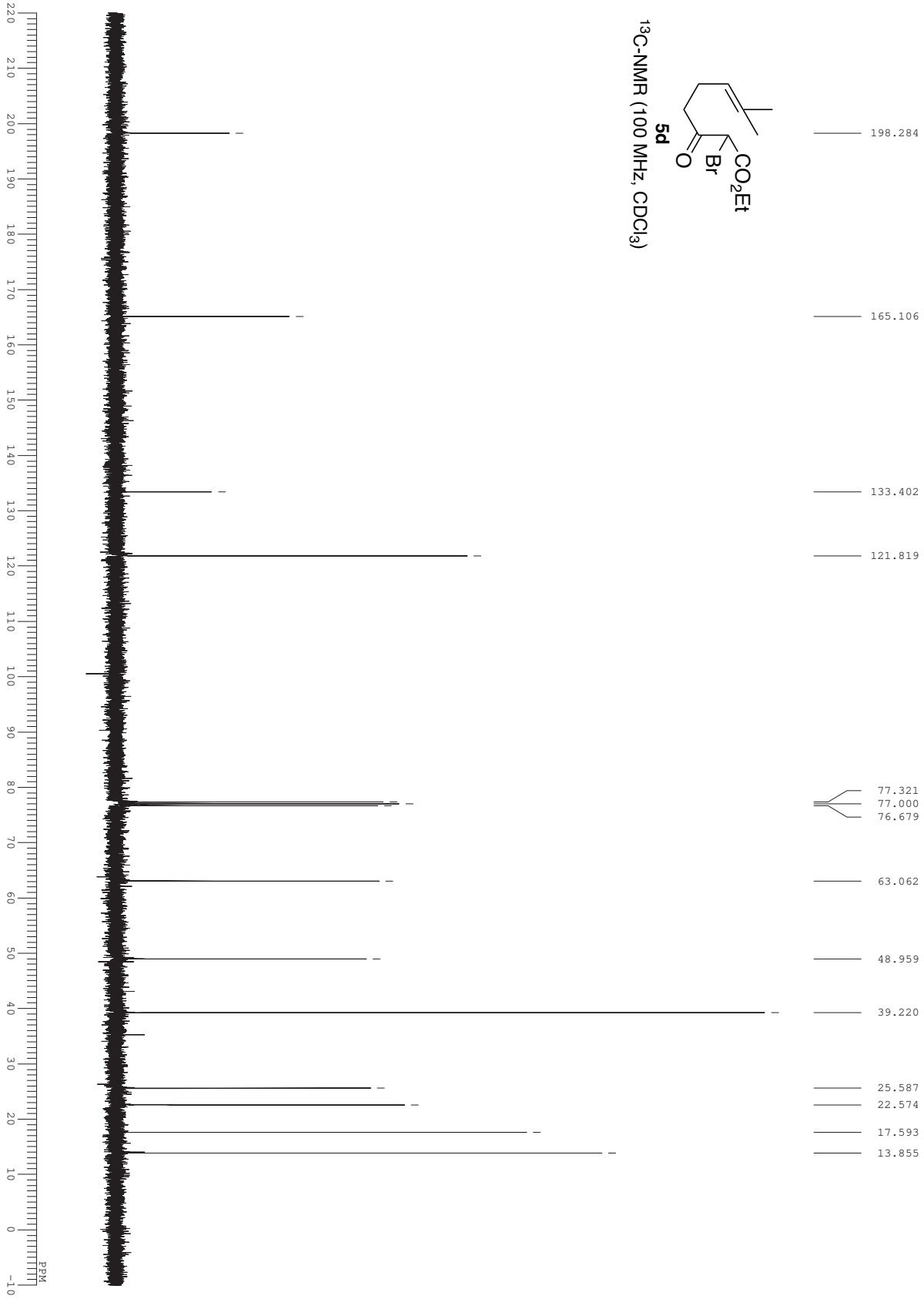

5b
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
7.266
5.857
5.840
5.832
5.824
5.814
5.797
5.788
5.780
5.772
5.755
5.093
5.049
5.035
5.009
4.791
4.314
4.296
4.277
4.260
2.890
2.874
2.872
2.855
2.414
2.397
2.380
2.362
1.332
1.314
1.296
0.000
1.00
2.09
0.94
2.13
2.02
2.17
3.19
PPM

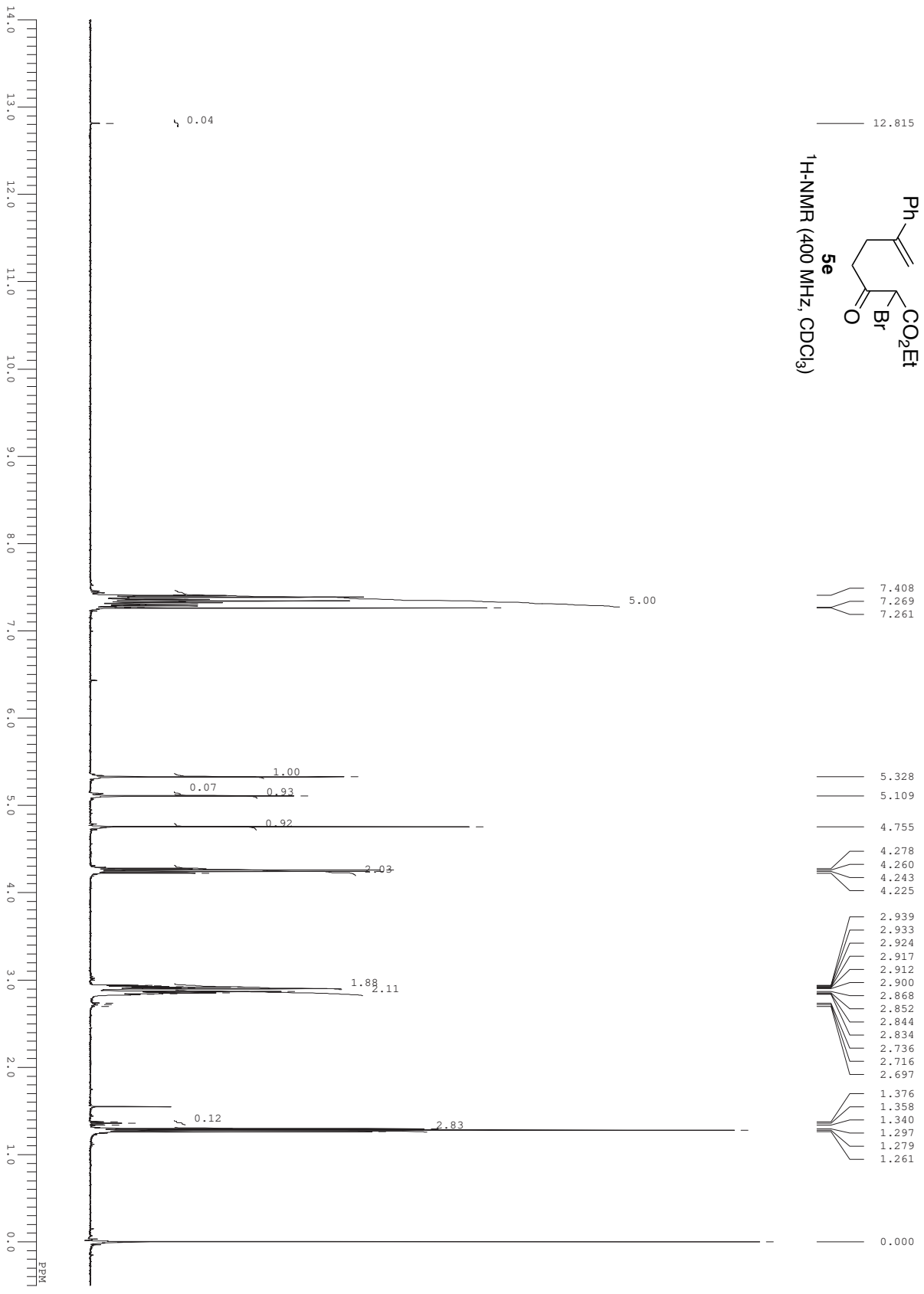

5b
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Et
Br
O
198.032
165.243
136.142
115.994
63.322
48.837
38.302
27.768
13.941
PPM

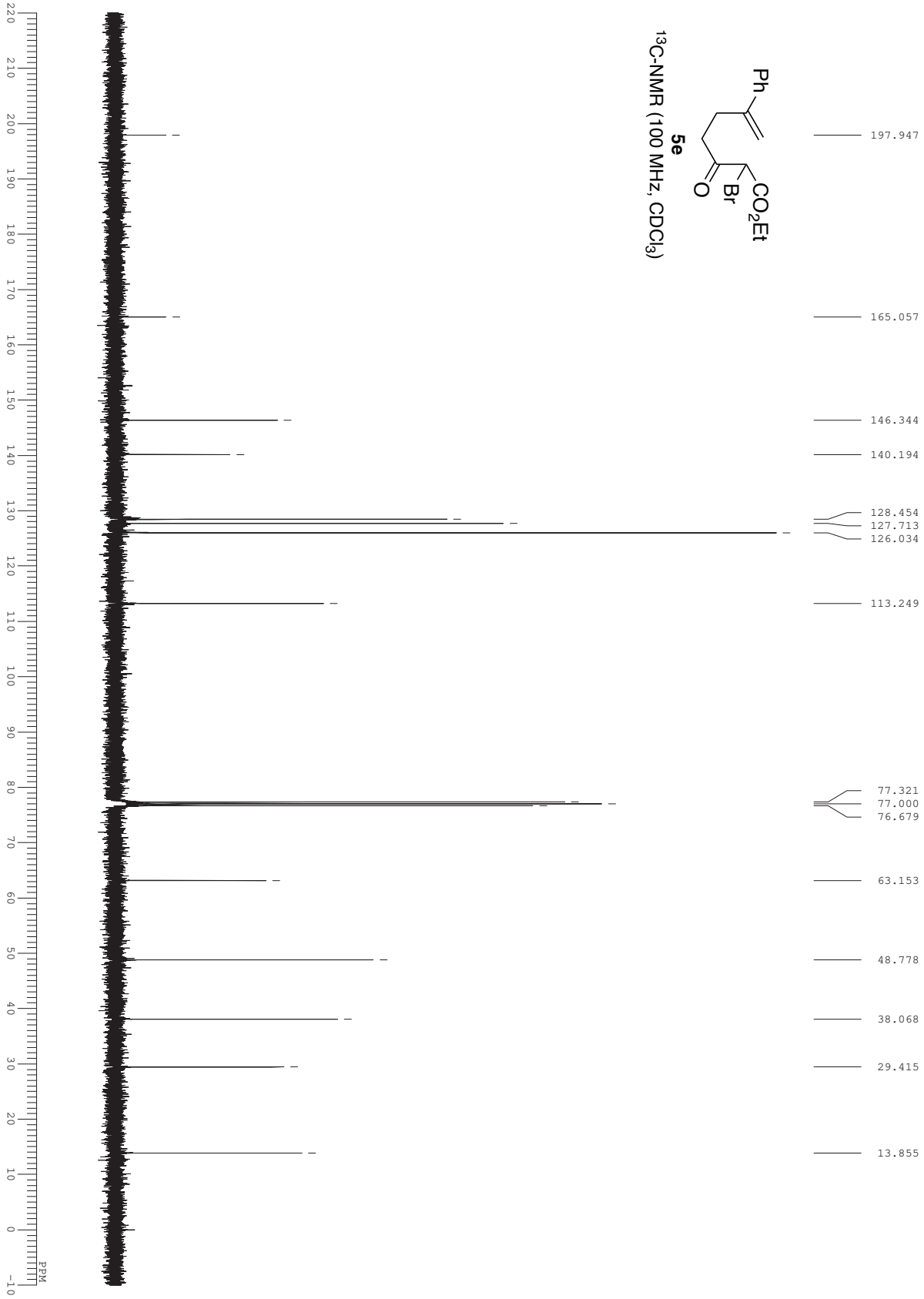

5c
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
12.806
7.263
0.14
2.38
0.17
0.84
2.48
2.19
0.35
0.36
2.14
3.74
0.49
3.25
0.000
5.540
5.303
4.786
4.781
4.309
4.291
4.272
4.254
2.835
2.827
2.816
2.808
2.797
2.790
2.629
2.611
2.591
2.406
2.388
2.369
2.337
2.335
2.331
2.319
2.316
2.313
2.303
2.300
2.297
2.285
2.281
1.664
1.616
1.376
1.358
1.341
1.329
1.311
1.293
PPM

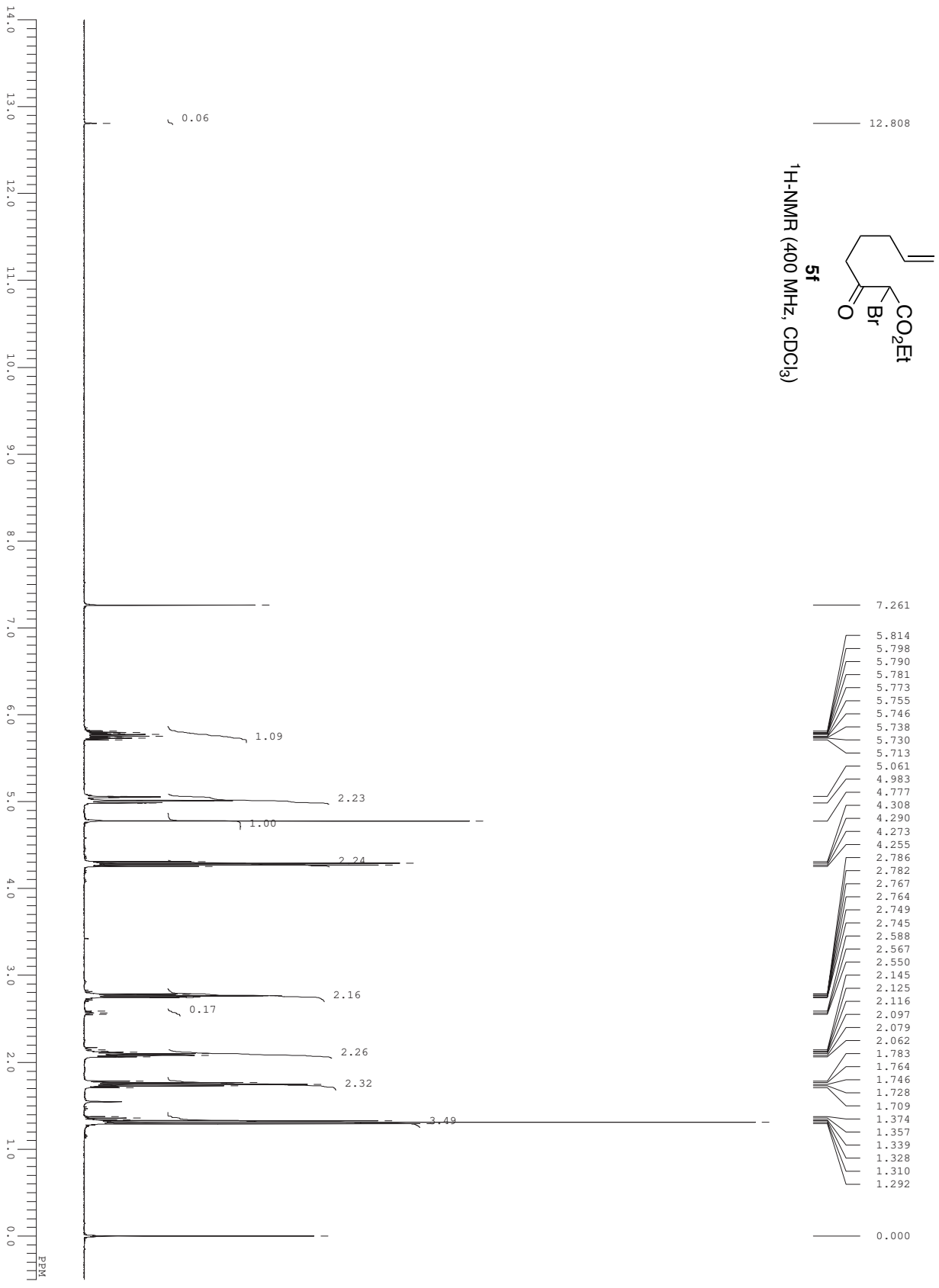

5c
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Et
Br
O
198.164
198.090
176.584
169.704
165.120
129.097
128.595
127.730
126.586
126.241
125.739
84.456
77.321
77.000
76.679
63.124
63.108
63.083
62.136
48.919
48.886
48.861
39.059
38.886
35.166
28.739
26.763
21.373
17.809
14.081
13.875
12.682
PPM

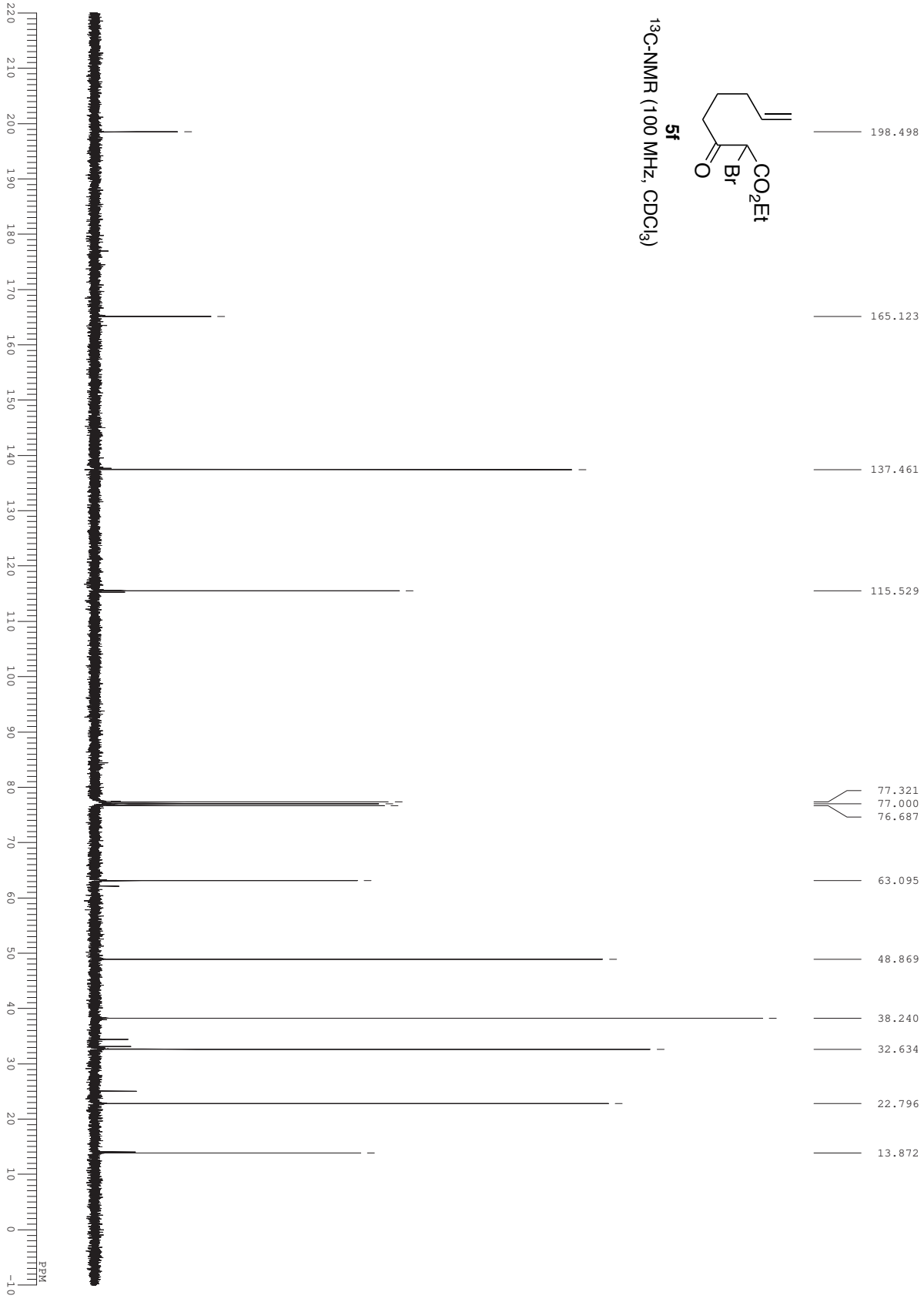

5d
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
12.796
7.262
5.092
5.042
4.778
4.307
4.289
4.271
4.253
2.804
2.743
2.592
2.573
2.554
2.340
2.322
2.304
2.285
1.683
1.623
1.375
1.357
1.339
1.328
1.310
1.292
0.000
0.03
1.00
0.97
2.29
2.22
0.14
2.28
3.60
3.53
3.62
PPM

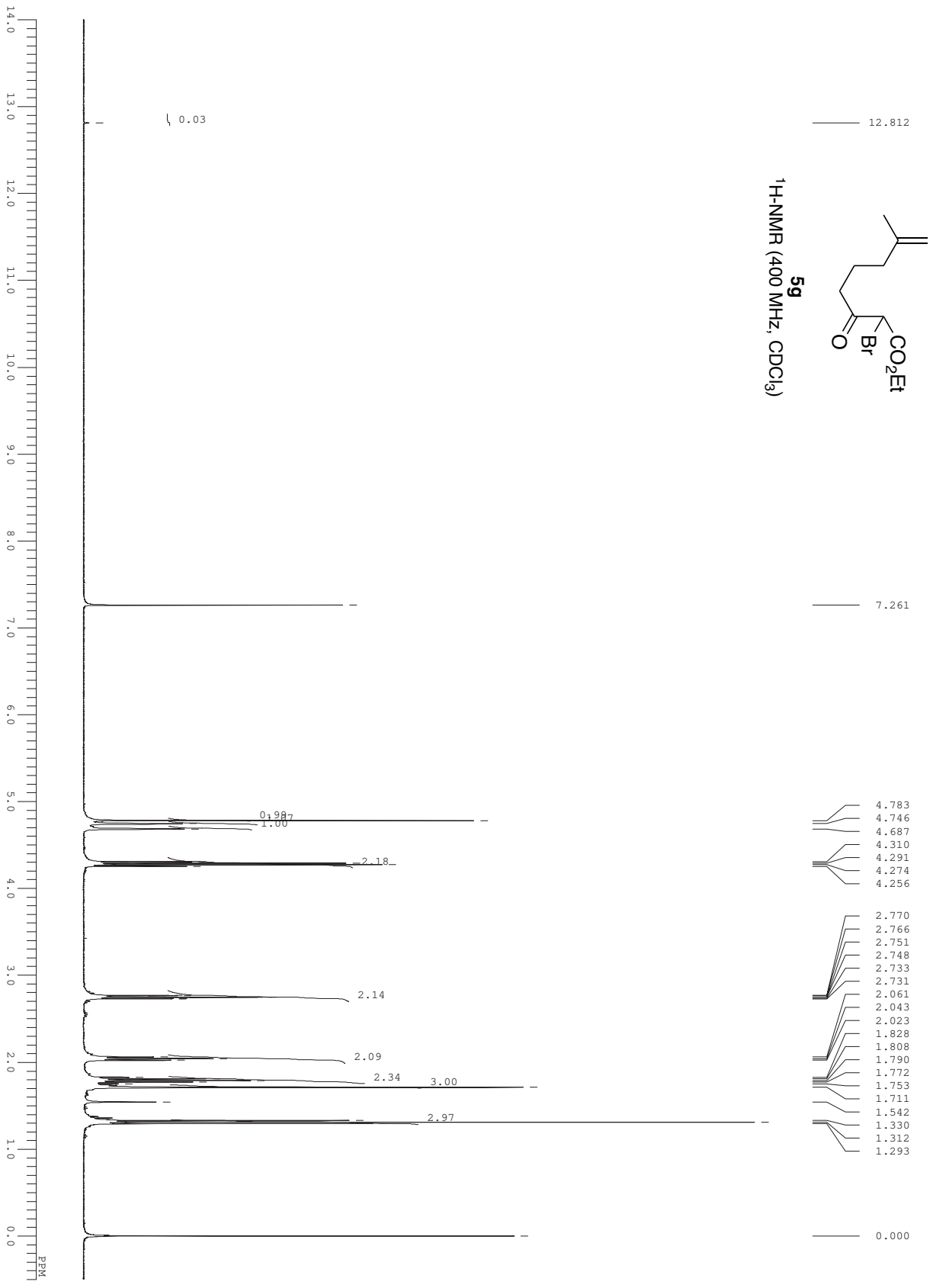

5d
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Et
Br
O
198.284
165.106
133.402
121.819
77.321
77.000
76.679
63.062
48.959
39.220
25.587
22.574
17.593
13.855
PPM

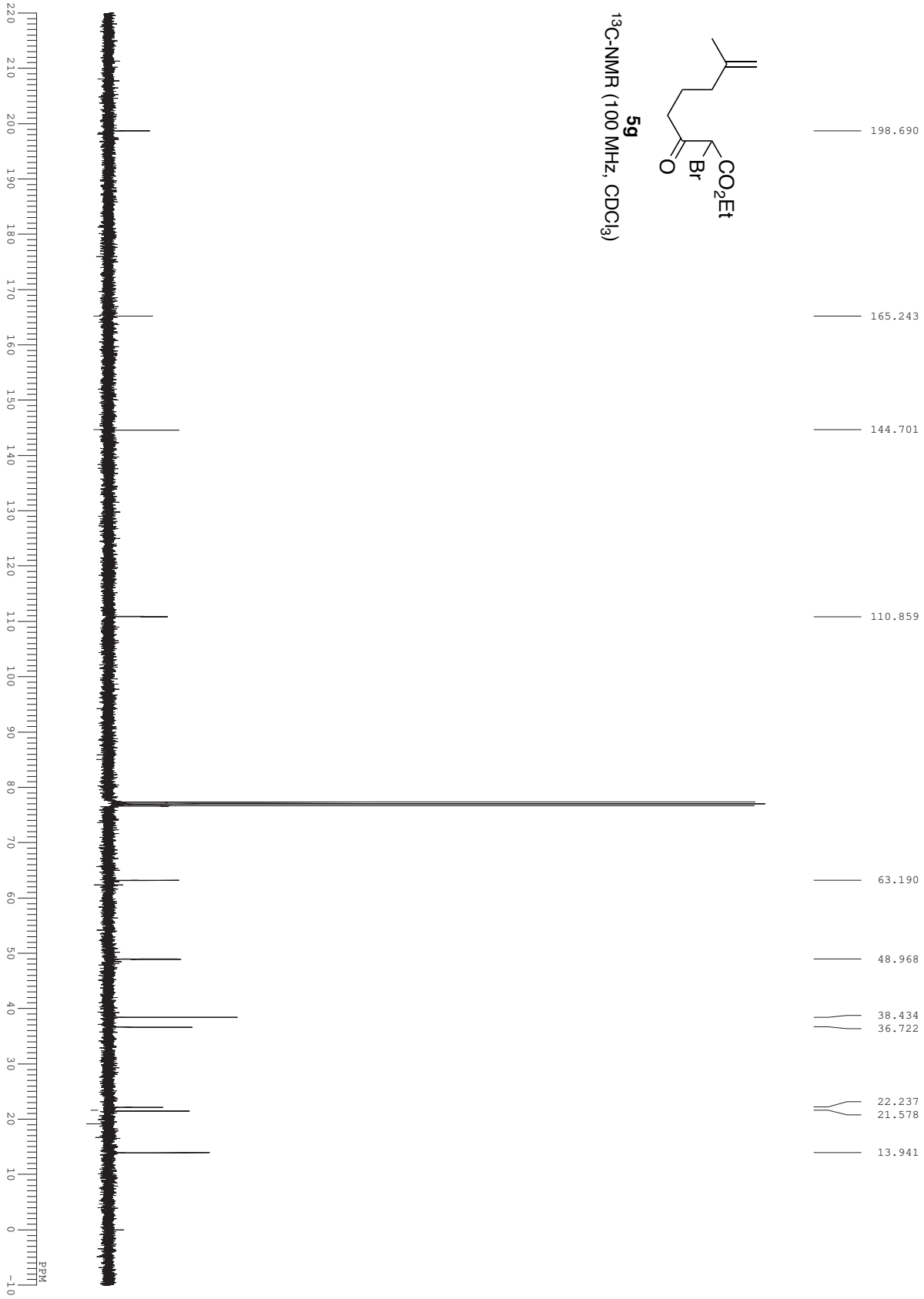

Ph
CO2Et
Br
O
5e
1H-NMR (400 MHz, CDCl3)
12.815
7.408
7.269
7.261
5.328
5.109
4.755
4.278
4.260
4.243
4.225
2.939
2.933
2.924
2.917
2.912
2.900
2.868
2.852
2.844
2.834
2.736
2.716
2.697
1.376
1.358
1.340
1.297
1.279
1.261
0.000
0.04
5.00
1.00
0.07
0.93
0.92
2.03
1.88
2.11
0.12
2.83
PPM

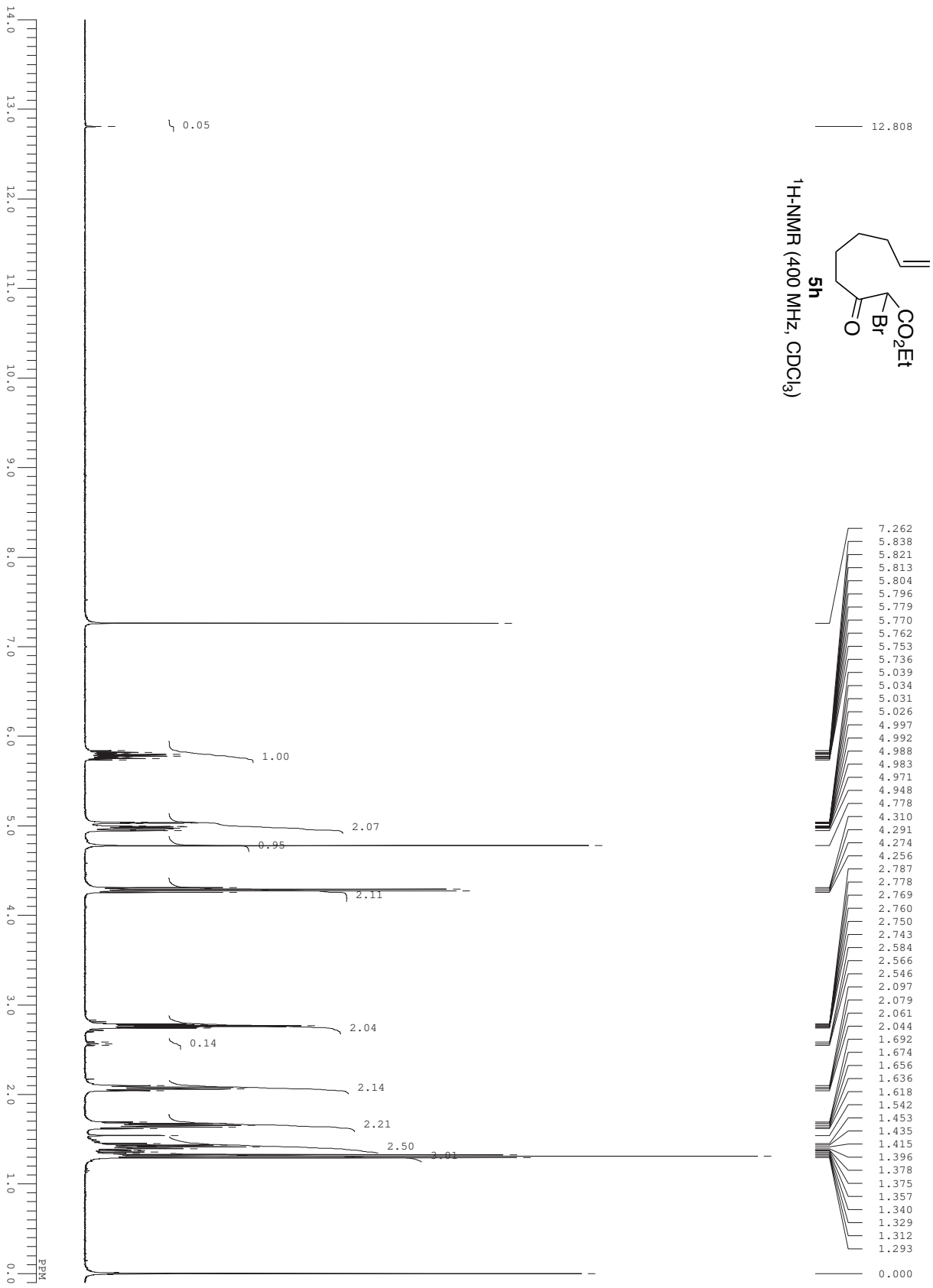

5e
^{13}C-NMR (100 MHz, $CDCl_3$)
Ph
CO_2Et
Br
O
197.947
165.057
146.344
140.194
128.454
127.713
126.034
113.249
77.321
77.000
76.679
63.153
48.778
38.068
29.415
13.855
PPM

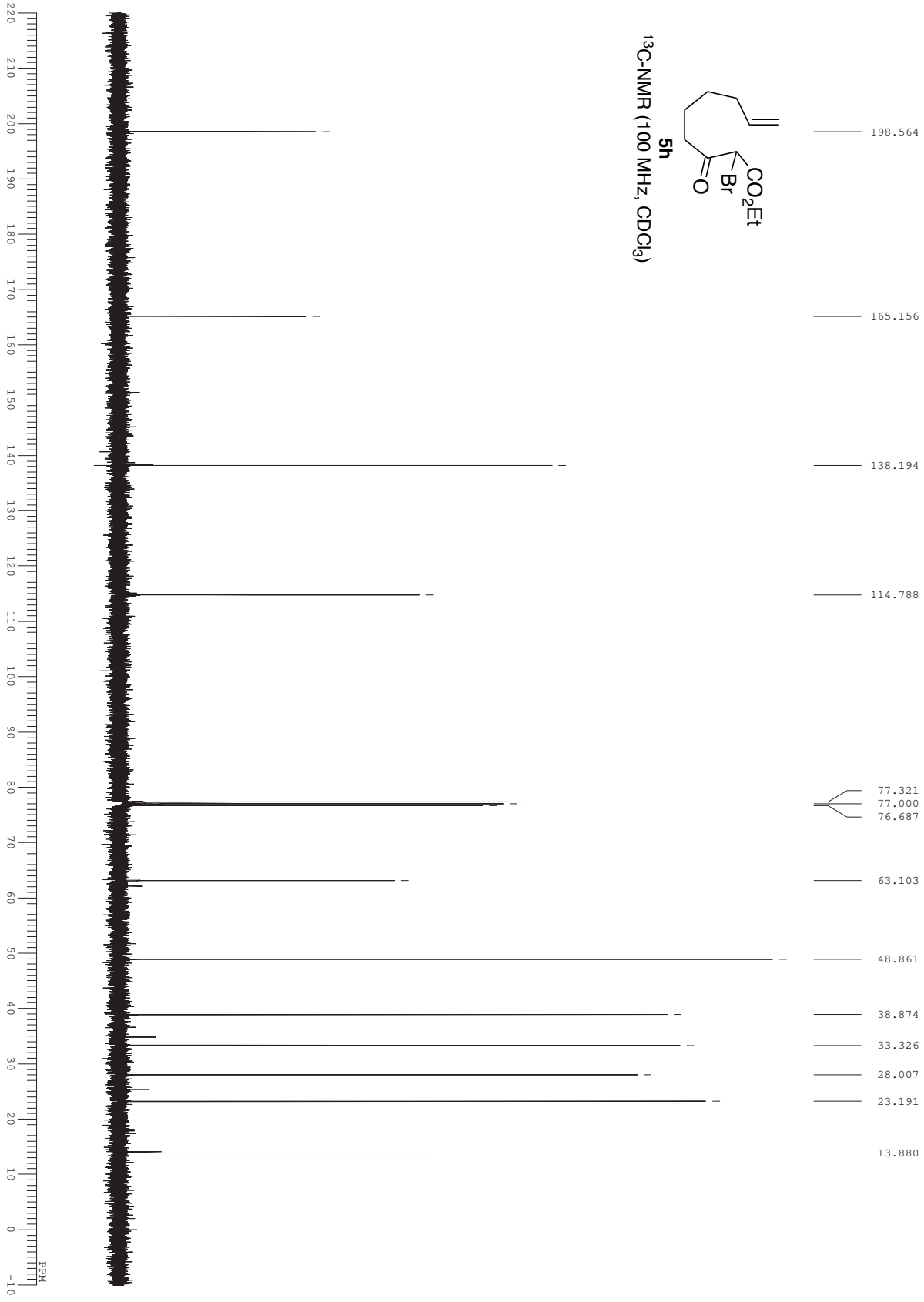

5f
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
12.808
7.261
5.814
5.798
5.790
5.781
5.773
5.755
5.746
5.738
5.730
5.713
5.061
4.983
4.777
4.308
4.290
4.273
4.255
2.786
2.782
2.767
2.764
2.749
2.745
2.588
2.567
2.550
2.145
2.125
2.116
2.097
2.079
2.062
1.783
1.764
1.746
1.728
1.709
1.374
1.357
1.339
1.328
1.310
1.292
0.000
0.06
1.09
2.23
1.00
2.24
2.16
0.17
2.26
2.32
3.49
14.0
13.0
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

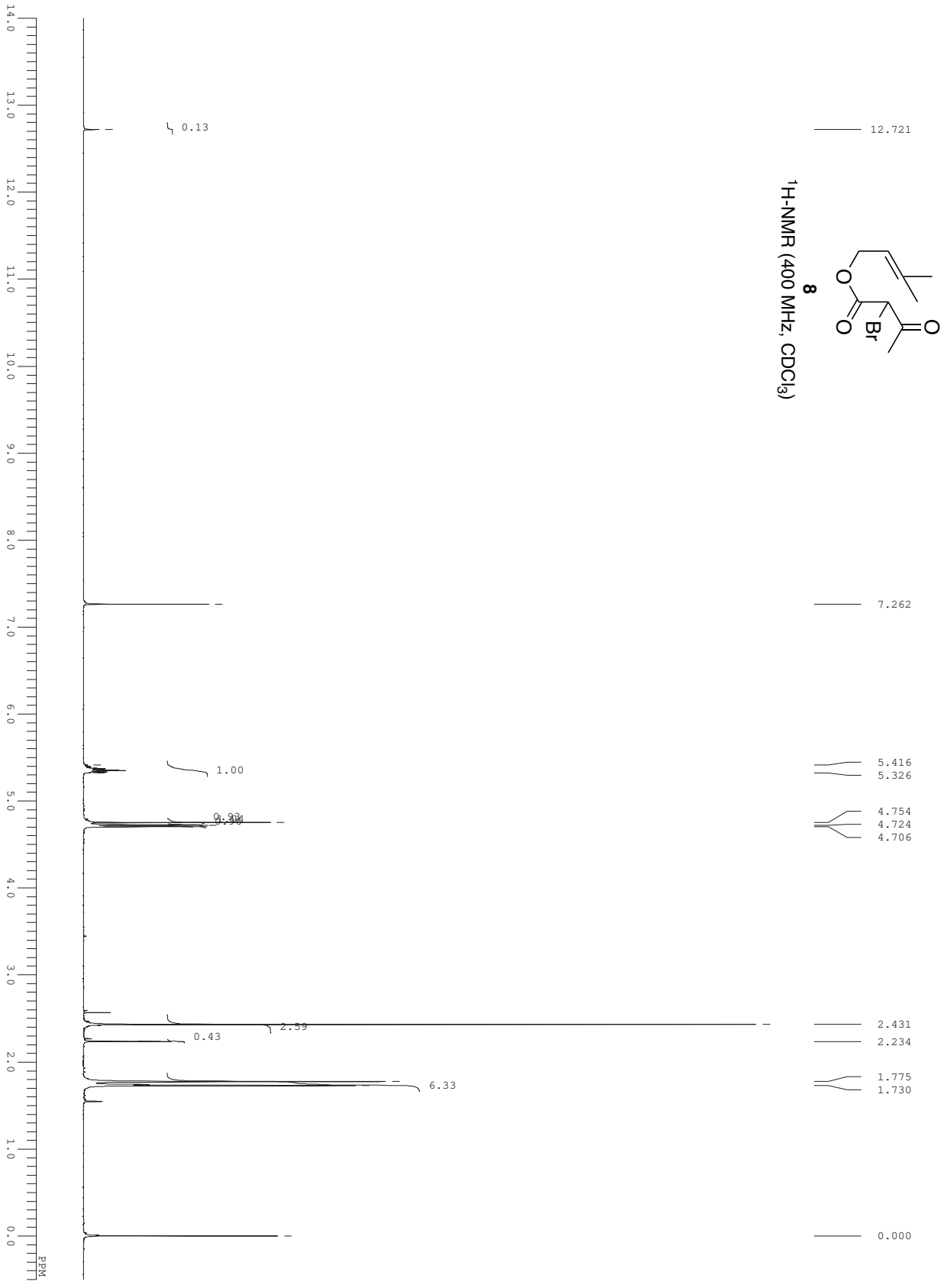

5f
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Et
Br
O
198.498
165.123
137.461
115.529
77.321
77.000
76.687
63.095
48.869
38.240
32.634
22.796
13.872
PPM

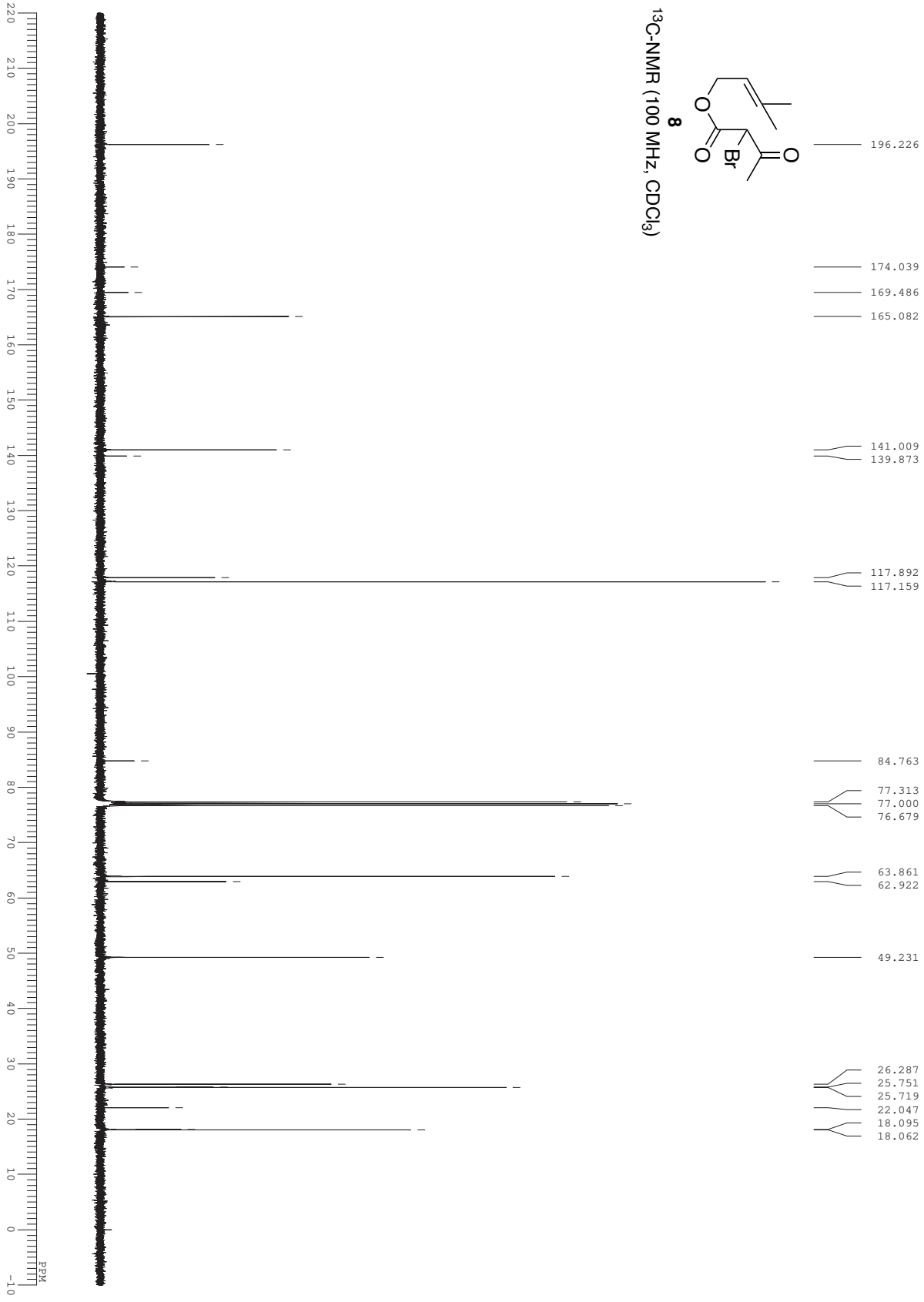

5g
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
12.812
7.261
4.783
4.746
4.687
4.310
4.291
4.274
4.256
2.770
2.766
2.751
2.748
2.733
2.731
2.061
2.043
2.023
1.828
1.808
1.790
1.772
1.753
1.711
1.542
1.330
1.312
1.293
0.000
0.03
0.98
1.00
2.18
2.14
2.09
2.34
3.00
2.97
PPM

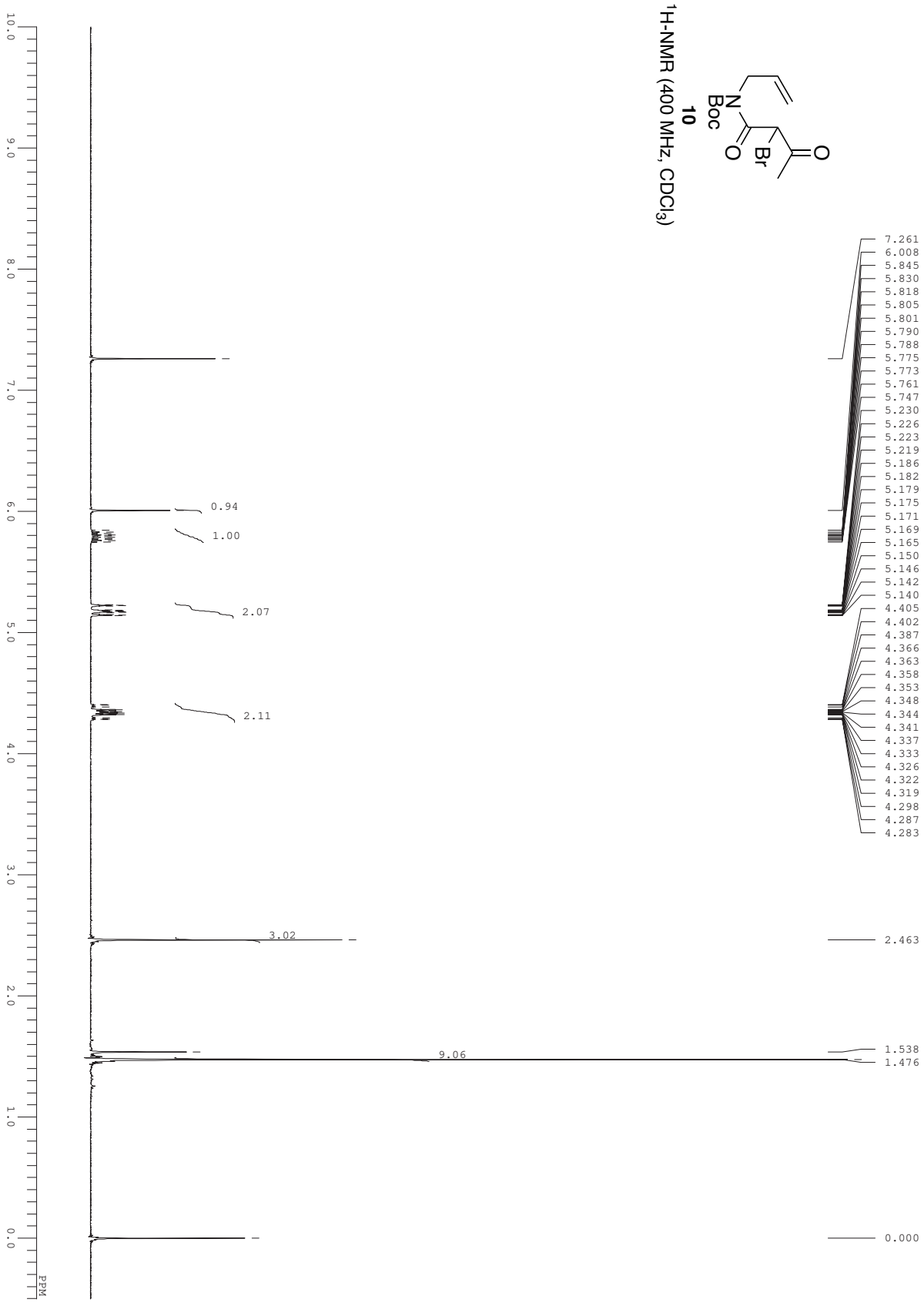

5g
^{13}C-NMR (100 MHz, $CDCl_3$)
CO_2Et
Br
O
198.690
165.243
144.701
110.859
63.190
48.968
38.434
36.722
22.237
21.578
13.941
PPM

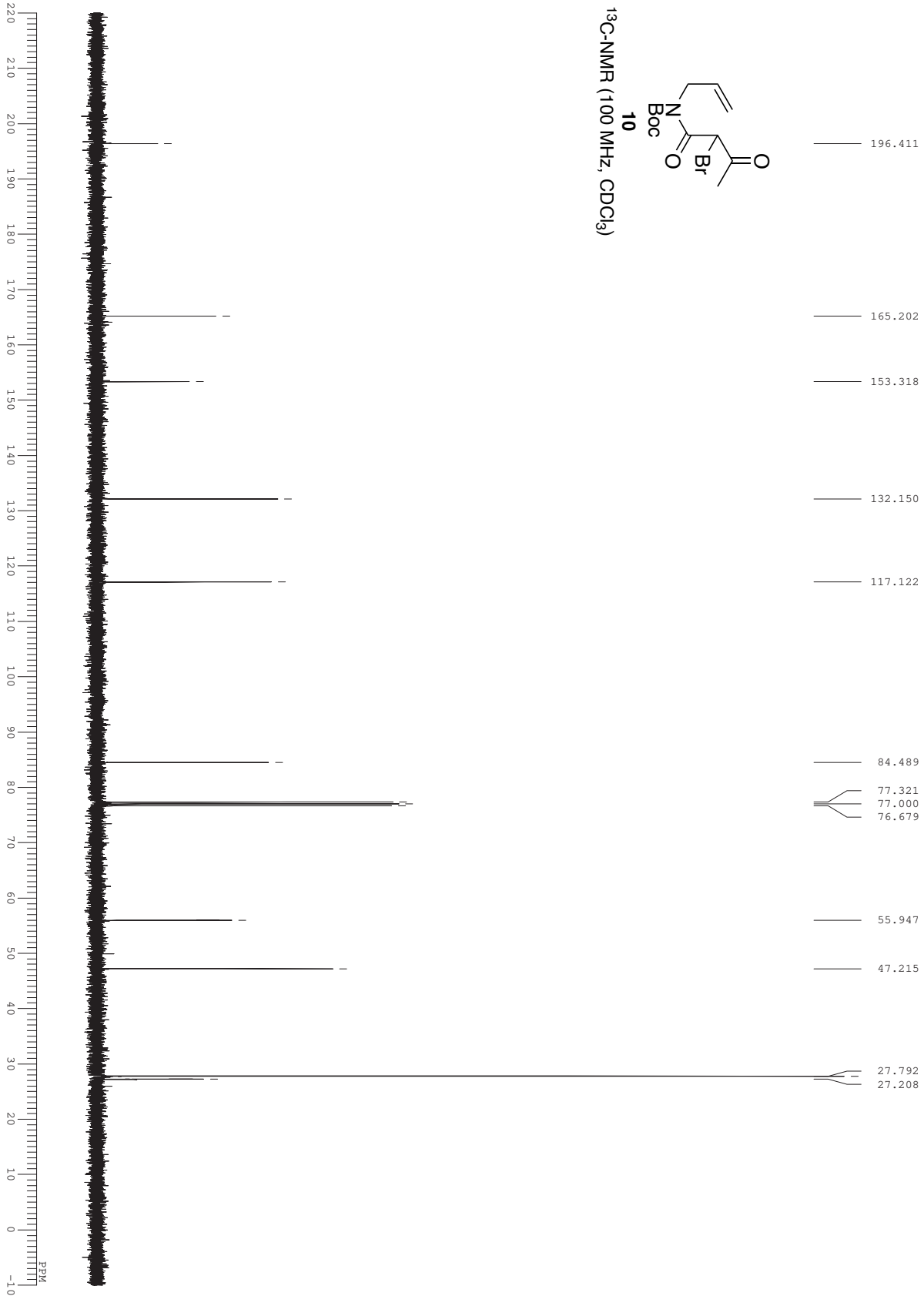

5h
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
Br
O
12.808
7.262
5.838
5.821
5.813
5.804
5.796
5.779
5.770
5.762
5.753
5.736
5.039
5.034
5.031
5.026
4.997
4.992
4.988
4.983
4.971
4.948
4.778
4.310
4.291
4.274
4.256
2.787
2.778
2.769
2.760
2.750
2.743
2.584
2.566
2.546
2.097
2.079
2.061
2.044
1.692
1.674
1.656
1.636
1.618
1.542
1.453
1.435
1.415
1.396
1.378
1.375
1.357
1.340
1.329
1.312
1.293
0.000
0.05
1.00
2.07
0.95
2.11
2.04
0.14
2.14
2.21
2.50
3.01
PPM

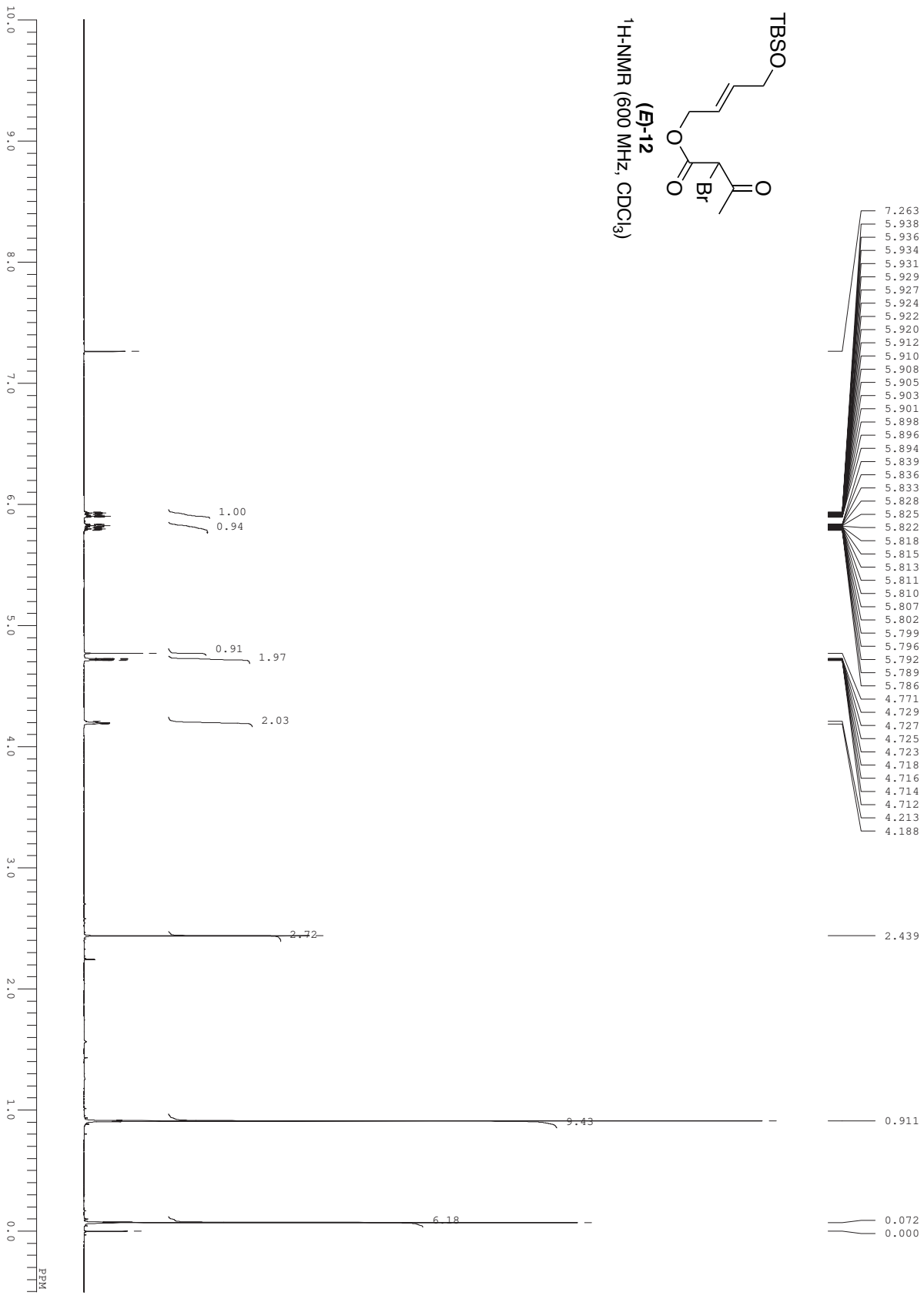

5h
^{13}C-NMR (100 MHz, CDCl$_3$)
CO$_2$Et
Br
O
198.564
165.156
138.194
114.788
77.321
77.000
76.687
63.103
48.861
38.874
33.326
28.007
23.191
13.880
PPM

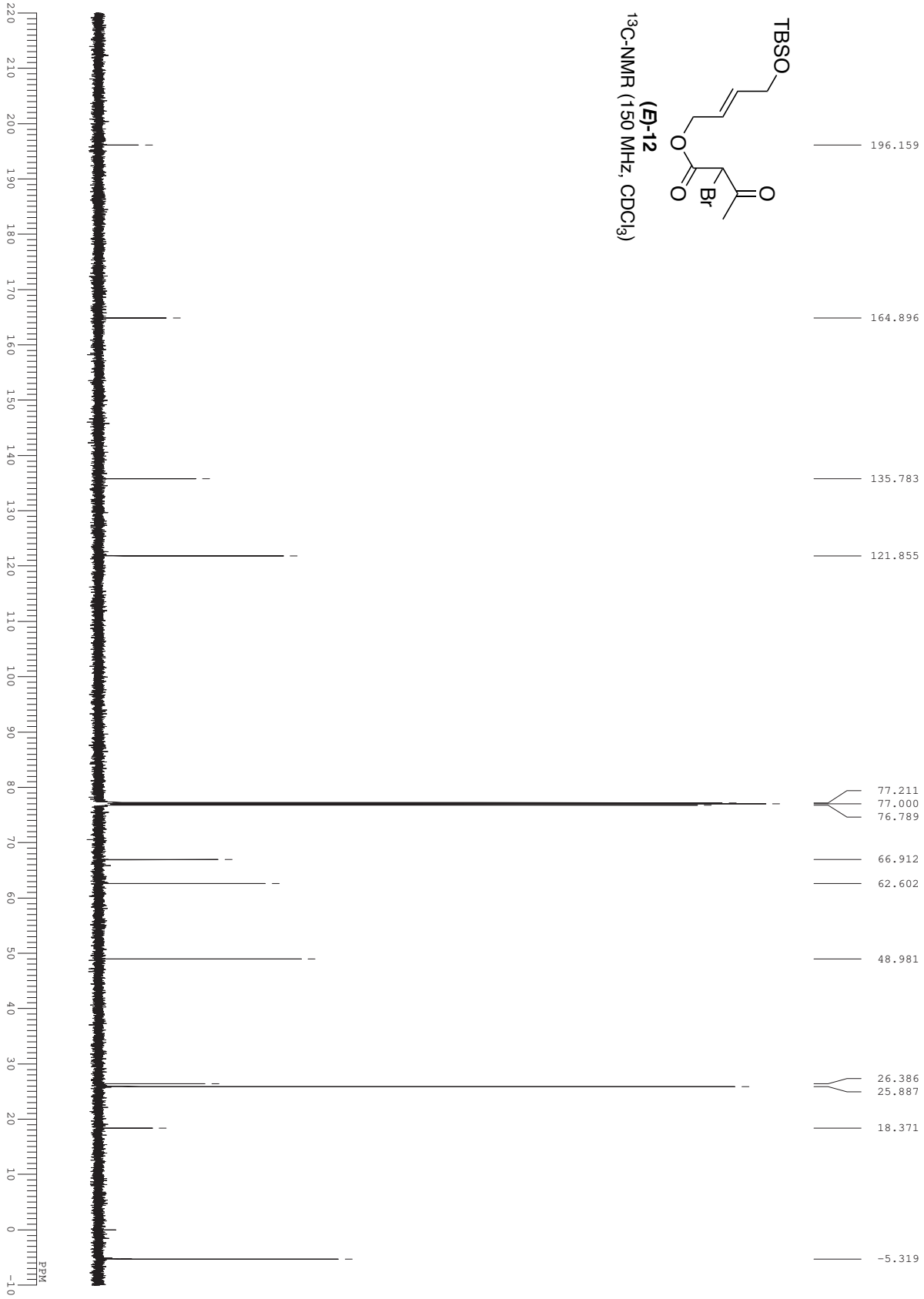

8
^{1}H-NMR (400 MHz, CDCl$_3$)
Br
O
O
O
12.721
7.262
5.416
5.326
4.754
4.724
4.706
2.431
2.234
1.775
1.730
0.000
0.13
1.00
2.59
0.43
6.33
PPM

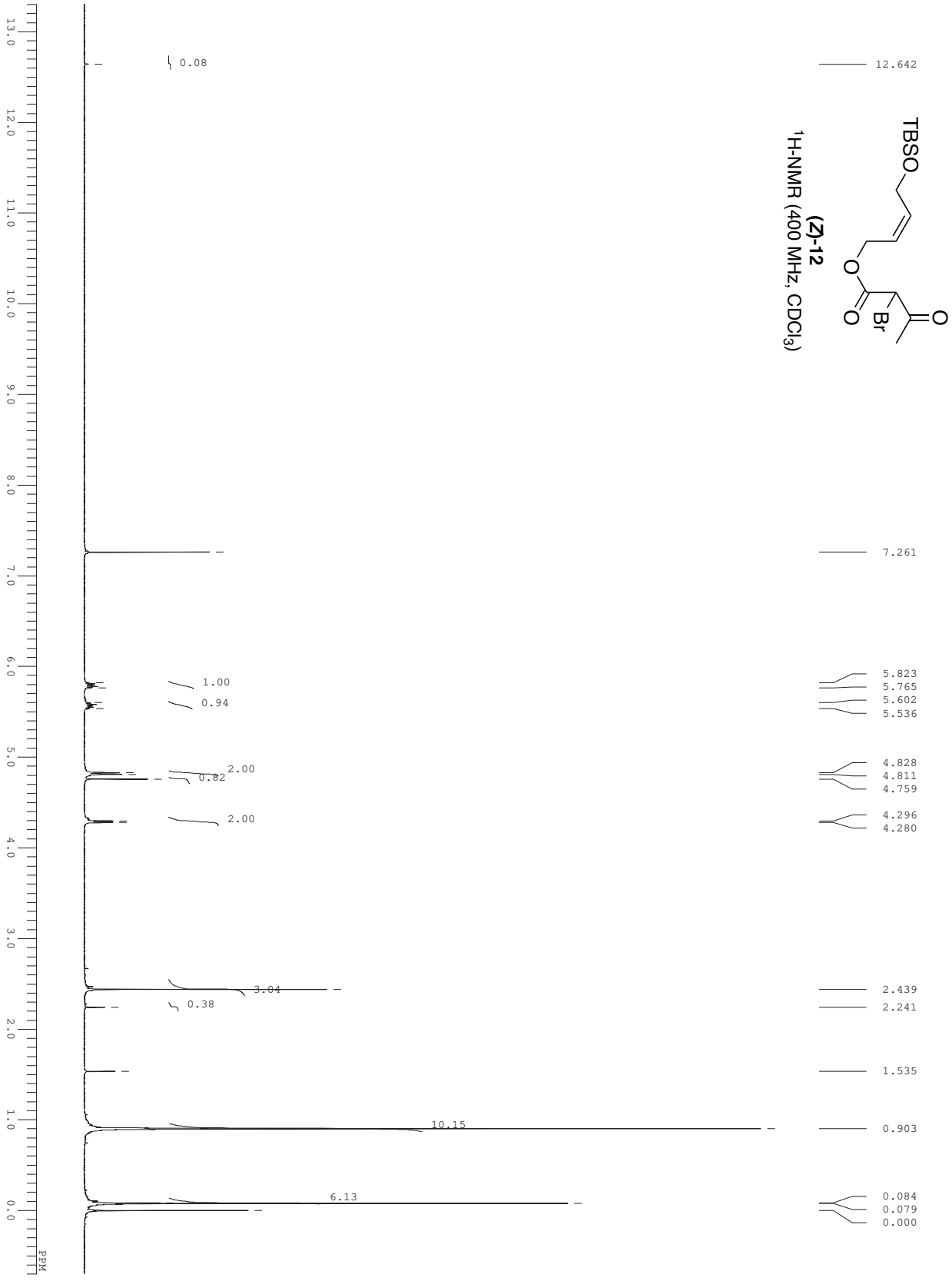

8
^{13}C-NMR (100 MHz, CDCl$_3$)
O
O
Br
O
196.226
174.039
169.486
165.082
141.009
139.873
117.892
117.159
84.763
77.313
77.000
76.679
63.861
62.922
49.231
26.287
25.751
25.719
22.047
18.095
18.062
PPM

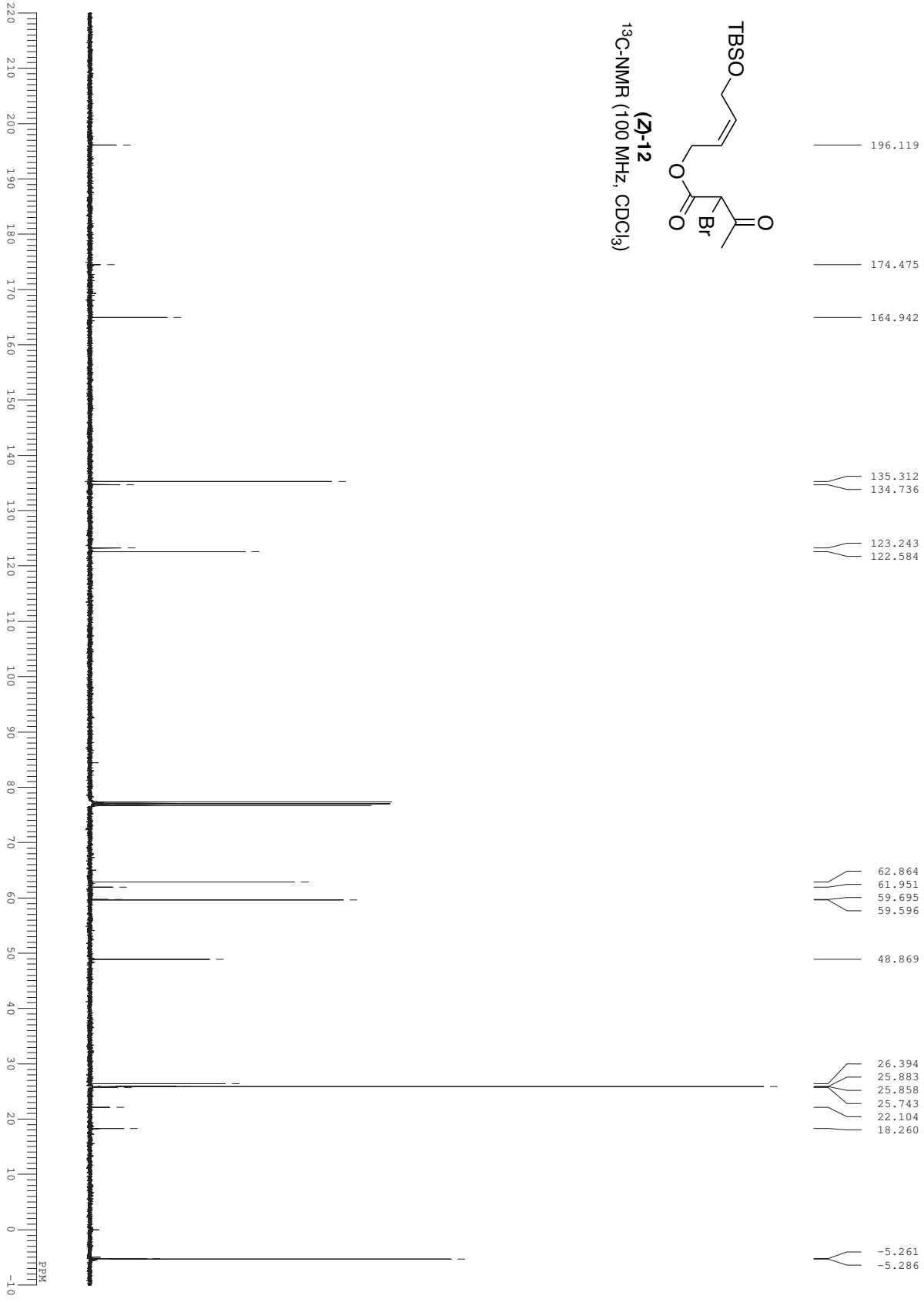

10
1H-NMR (400 MHz, CDCl3)
N
Boc
O
Br
O
7.261
6.008
5.845
5.830
5.818
5.805
5.801
5.790
5.788
5.775
5.773
5.761
5.747
5.230
5.226
5.223
5.219
5.186
5.182
5.179
5.175
5.171
5.169
5.165
5.150
5.146
5.142
5.140
4.405
4.402
4.387
4.366
4.363
4.358
4.353
4.348
4.344
4.341
4.337
4.333
4.326
4.322
4.319
4.298
4.287
4.283
2.463
1.538
1.476
0.000
0.94
1.00
2.07
2.11
3.02
9.06
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

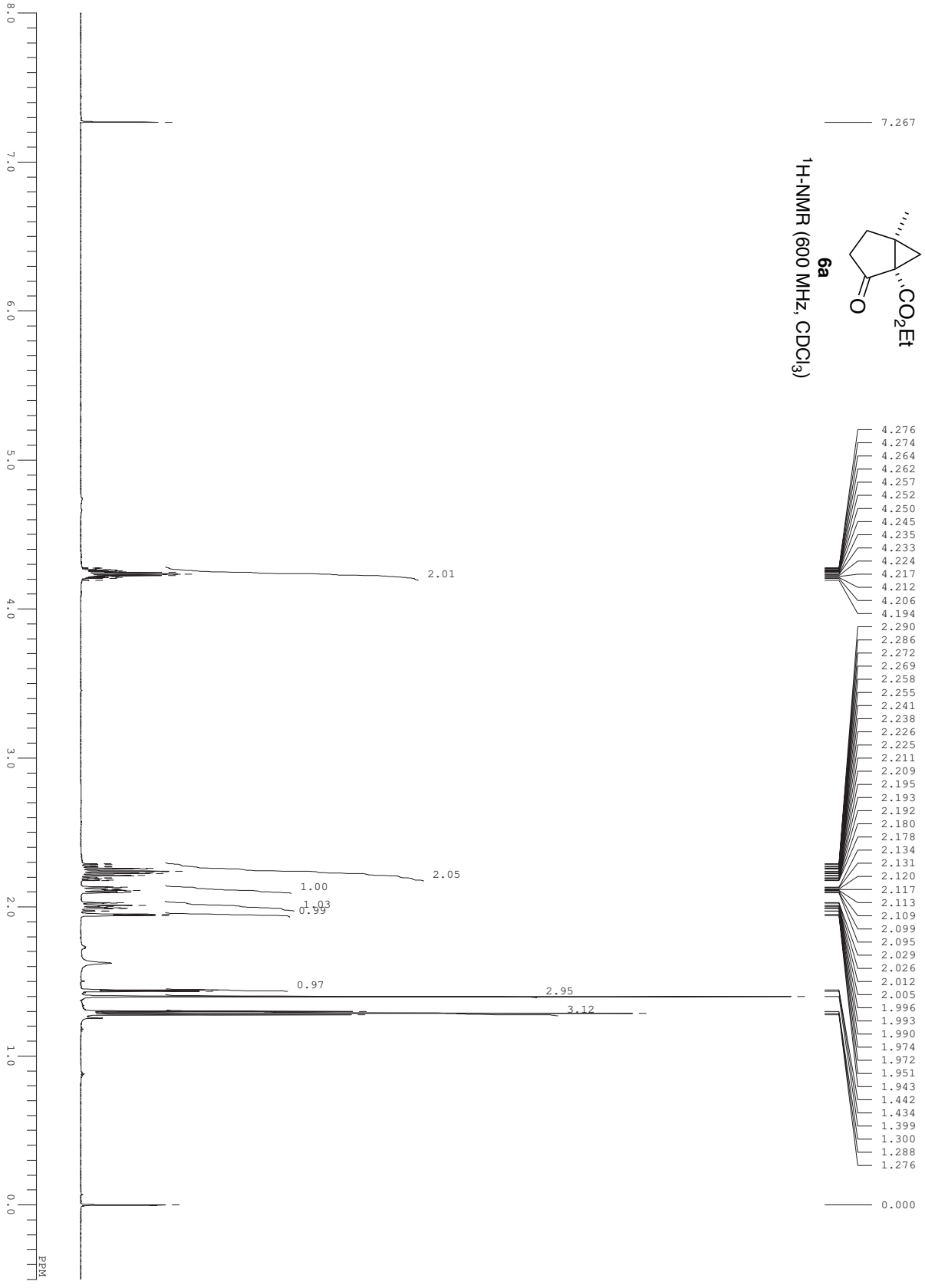

13C-NMR (100 MHz, CDCl3)
10
N
Boc
O
Br
O
196.411
165.202
153.318
132.150
117.122
84.489
77.321
77.000
76.679
55.947
47.215
27.792
27.208
PPM

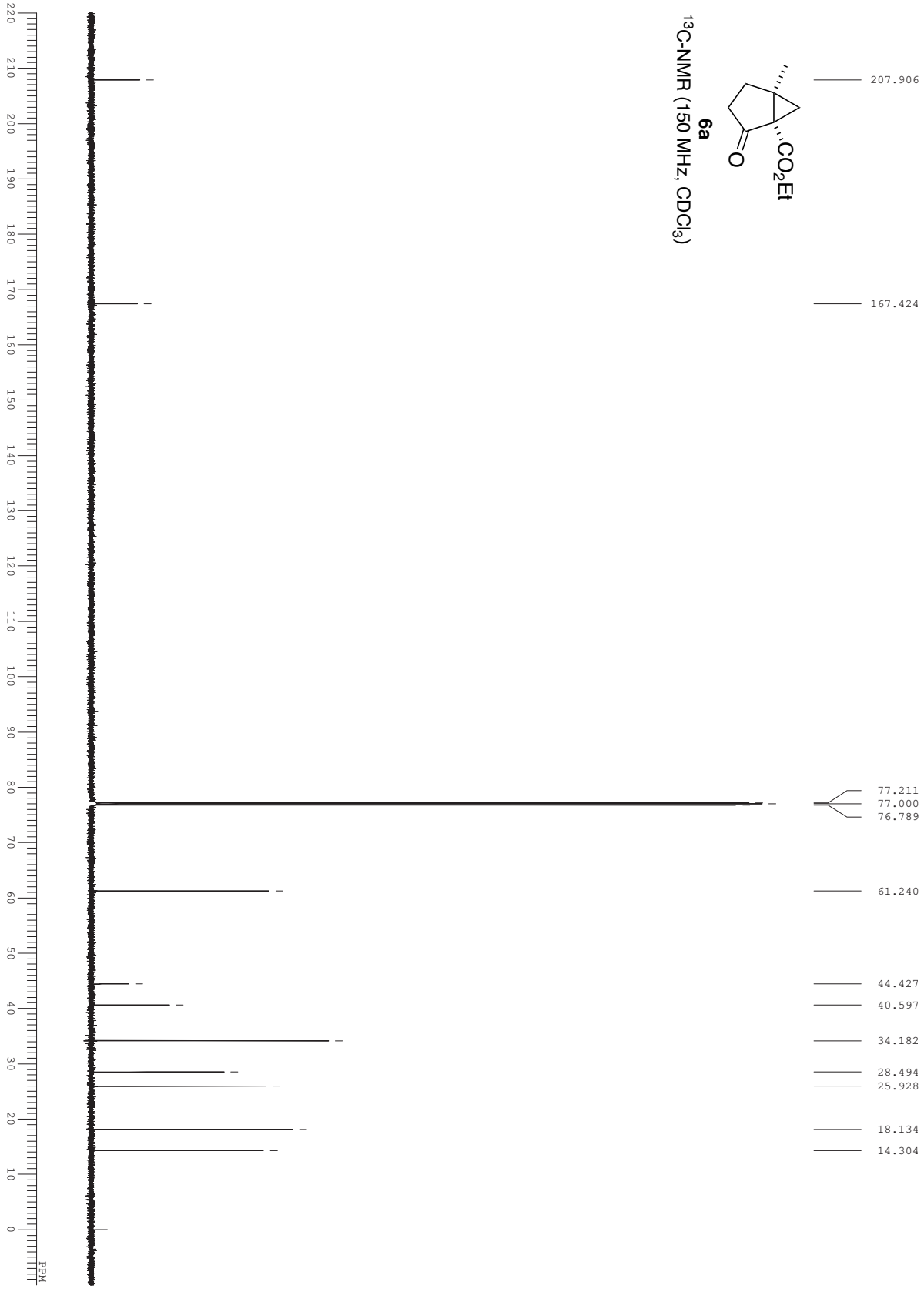

(E)-12
1H-NMR (600 MHz, CDCl3)
TBSO
O
O
Br
O
7.263
5.938
5.936
5.934
5.931
5.929
5.927
5.924
5.922
5.920
5.912
5.910
5.908
5.905
5.903
5.901
5.898
5.896
5.894
5.839
5.836
5.833
5.828
5.825
5.822
5.818
5.815
5.813
5.811
5.810
5.807
5.802
5.799
5.796
5.792
5.789
5.786
4.771
4.729
4.727
4.725
4.723
4.718
4.716
4.714
4.712
4.213
4.188
2.439
0.911
0.072
0.000
1.00
0.94
0.91
1.97
2.03
2.72
9.43
6.18
PPM

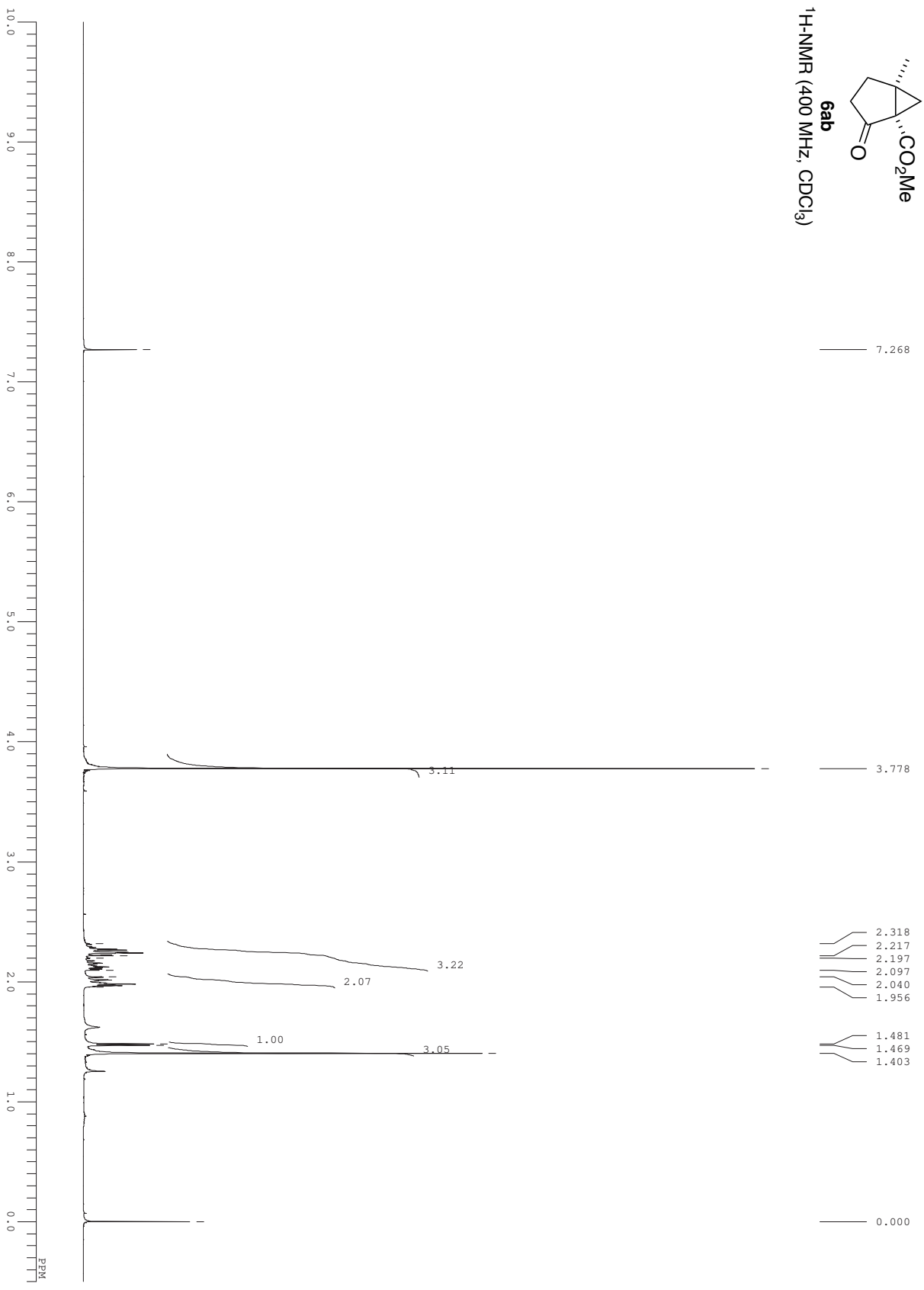

(E)-12
13C-NMR (150 MHz, CDCl3)
TBSO
O
O
Br
O
196.159
164.896
135.783
121.855
77.211
77.000
76.789
66.912
62.602
48.981
26.386
25.887
18.371
-5.319
PPM

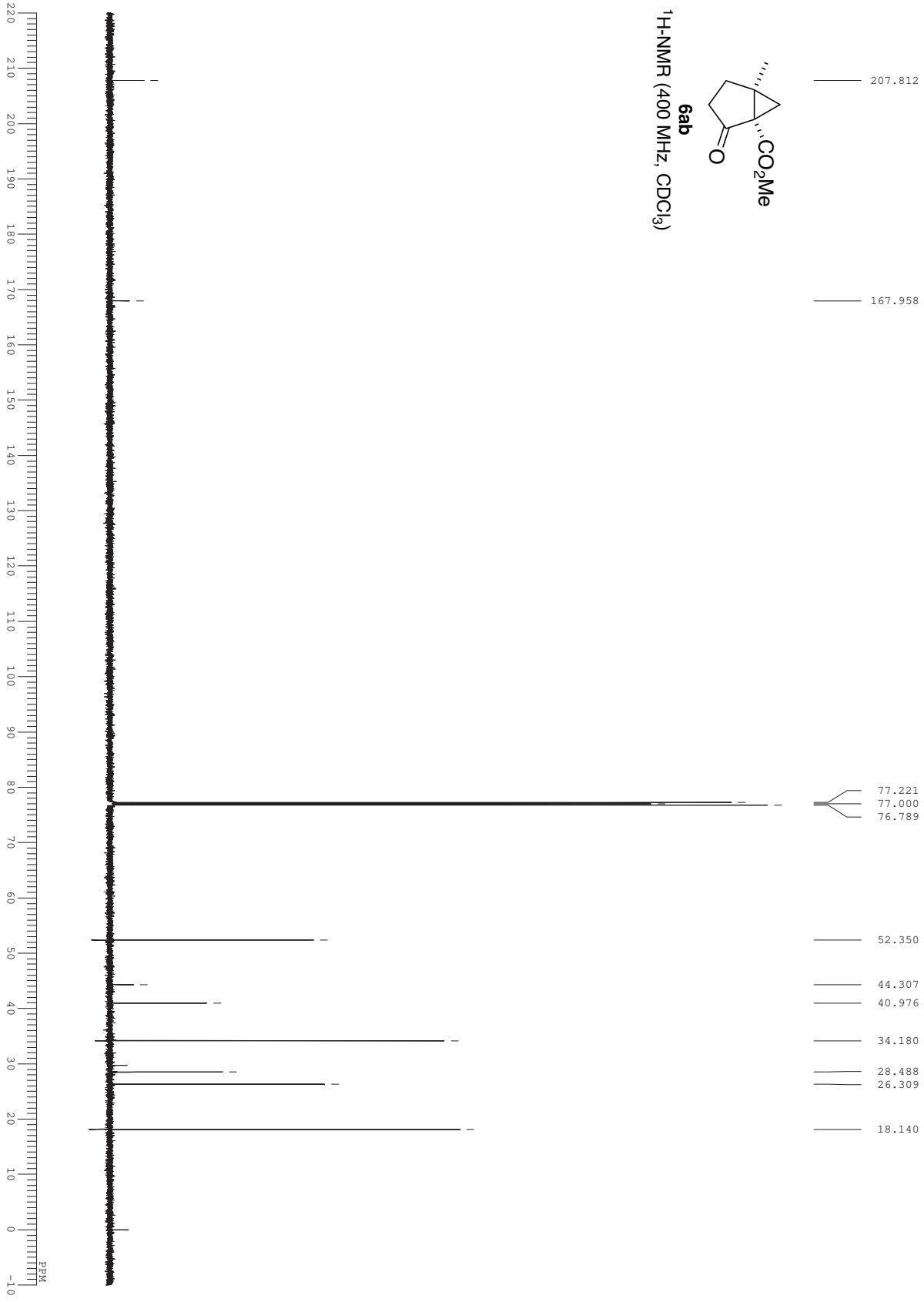

(Z)-12
^{1}H-NMR (400 MHz, CDCl$_3$)
TBSO
O
O
O
Br
12.642
7.261
5.823
5.765
5.602
5.536
4.828
4.811
4.759
4.296
4.280
2.439
2.241
1.535
0.903
0.084
0.079
0.000
0.08
1.00
0.94
2.00
0.82
2.00
3.04
0.38
10.15
6.13
PPM

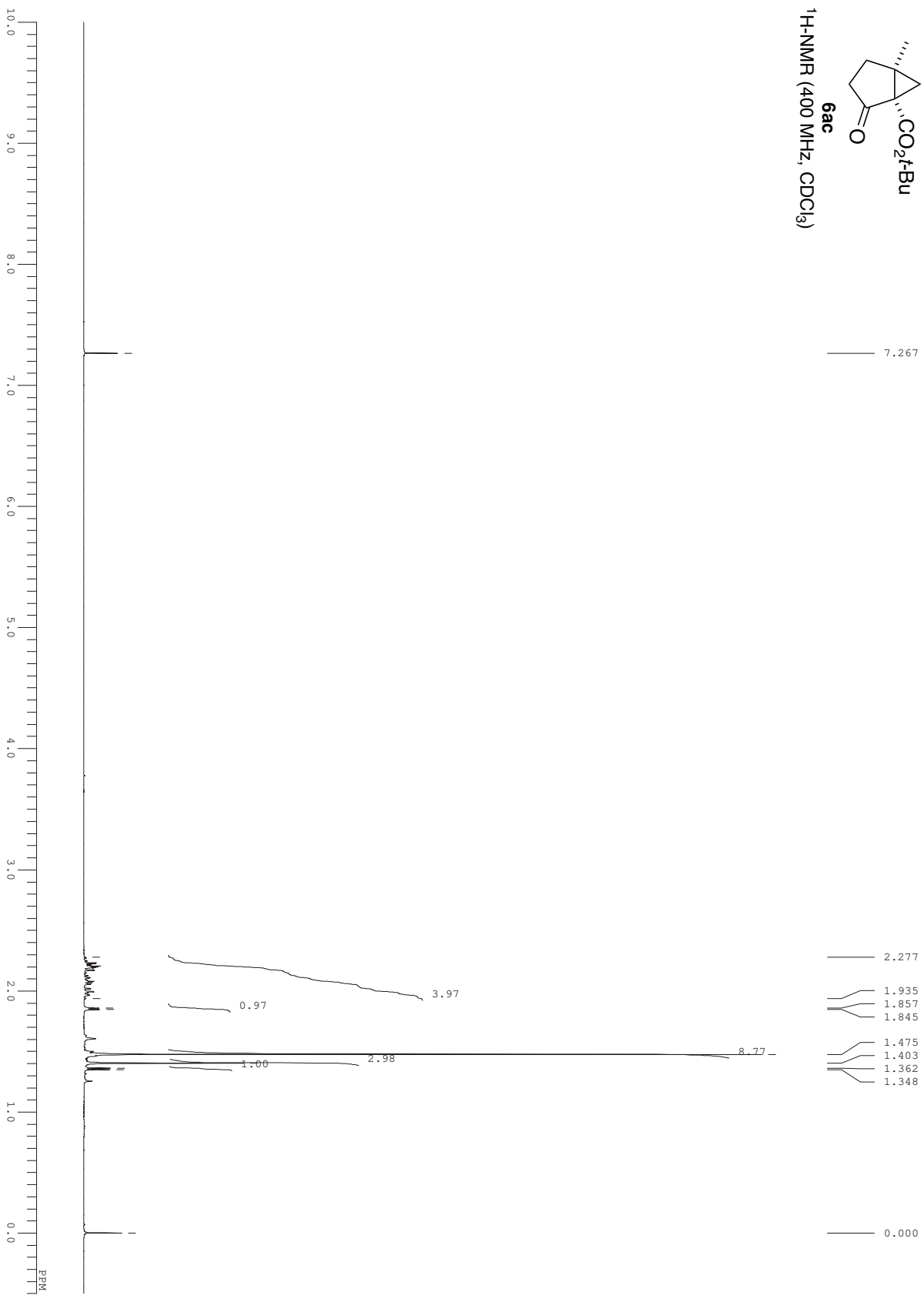

(Z)-12
^{13}C-NMR (100 MHz, $CDCl_3$)
TBSO
O
O
Br
O
196.119
174.475
164.942
135.312
134.736
123.243
122.584
62.864
61.951
59.695
59.596
48.869
26.394
25.883
25.858
25.743
22.104
18.260
-5.261
-5.286
PPM

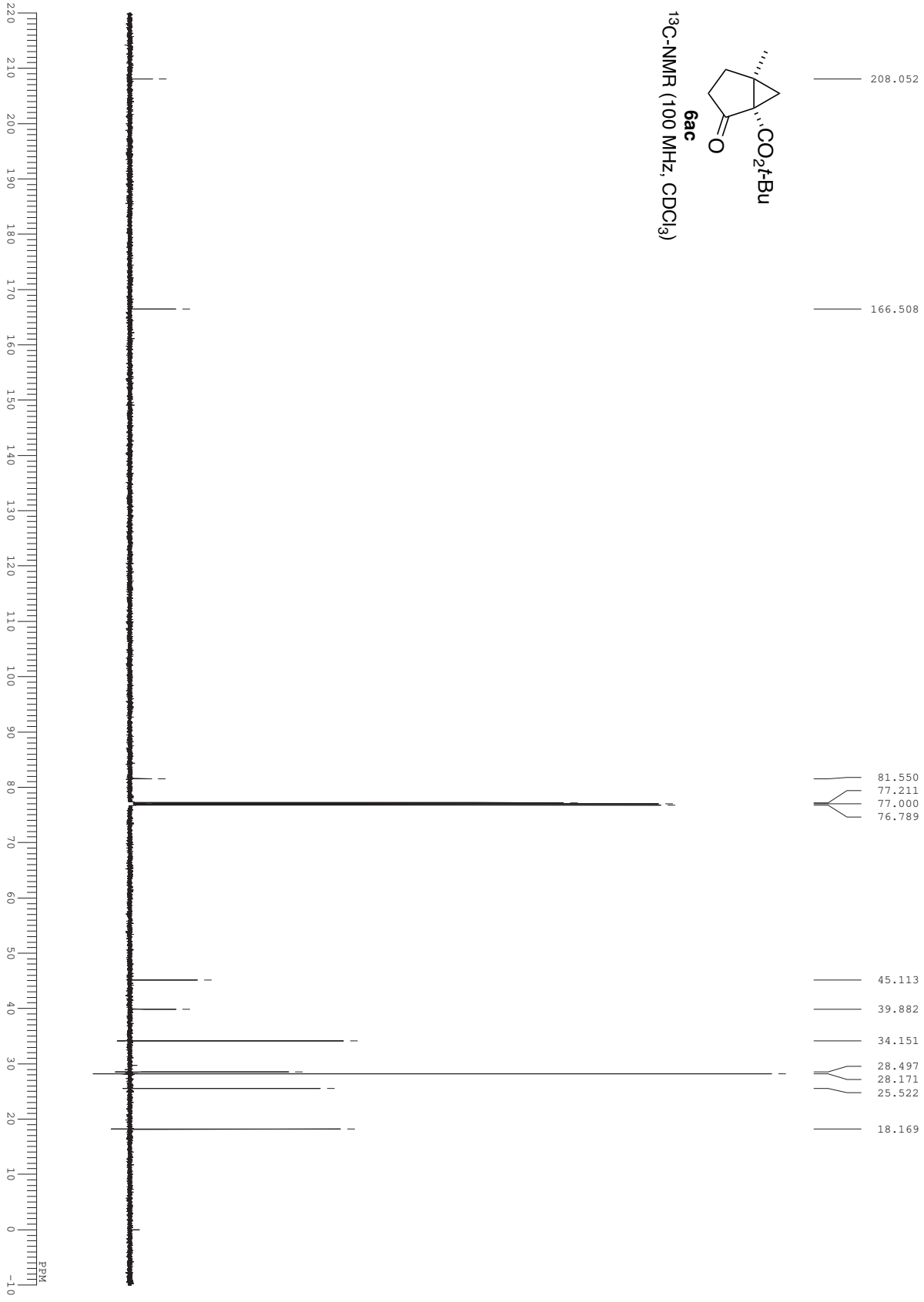

6a
^{1}H-NMR (600 MHz, $CDCl_3$)
CO_2Et
O
7.267
4.276
4.274
4.264
4.262
4.257
4.252
4.250
4.245
4.235
4.233
4.224
4.217
4.212
4.206
4.194
2.290
2.286
2.272
2.269
2.258
2.255
2.241
2.238
2.226
2.225
2.211
2.209
2.195
2.193
2.192
2.180
2.178
2.134
2.131
2.120
2.117
2.113
2.109
2.099
2.095
2.029
2.026
2.012
2.005
1.996
1.993
1.990
1.974
1.972
1.951
1.943
1.442
1.434
1.399
1.300
1.288
1.276
0.000
2.01
2.05
1.00
1.03
0.99
0.97
2.95
3.12
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

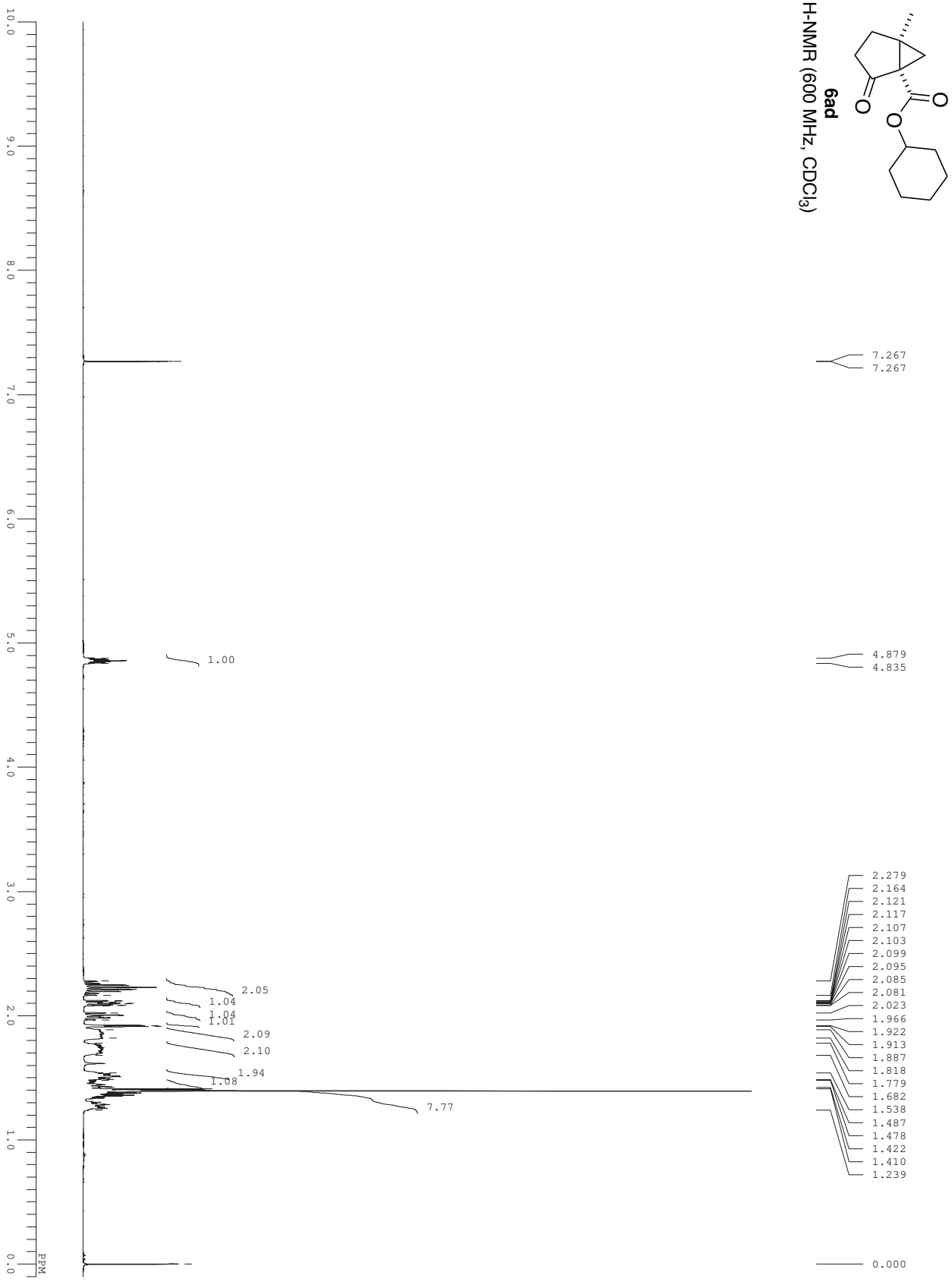

6a
13C-NMR (150 MHz, CDCl3)
CO2Et
O
207.906
167.424
77.211
77.000
76.789
61.240
44.427
40.597
34.182
28.494
25.928
18.134
14.304
PPM

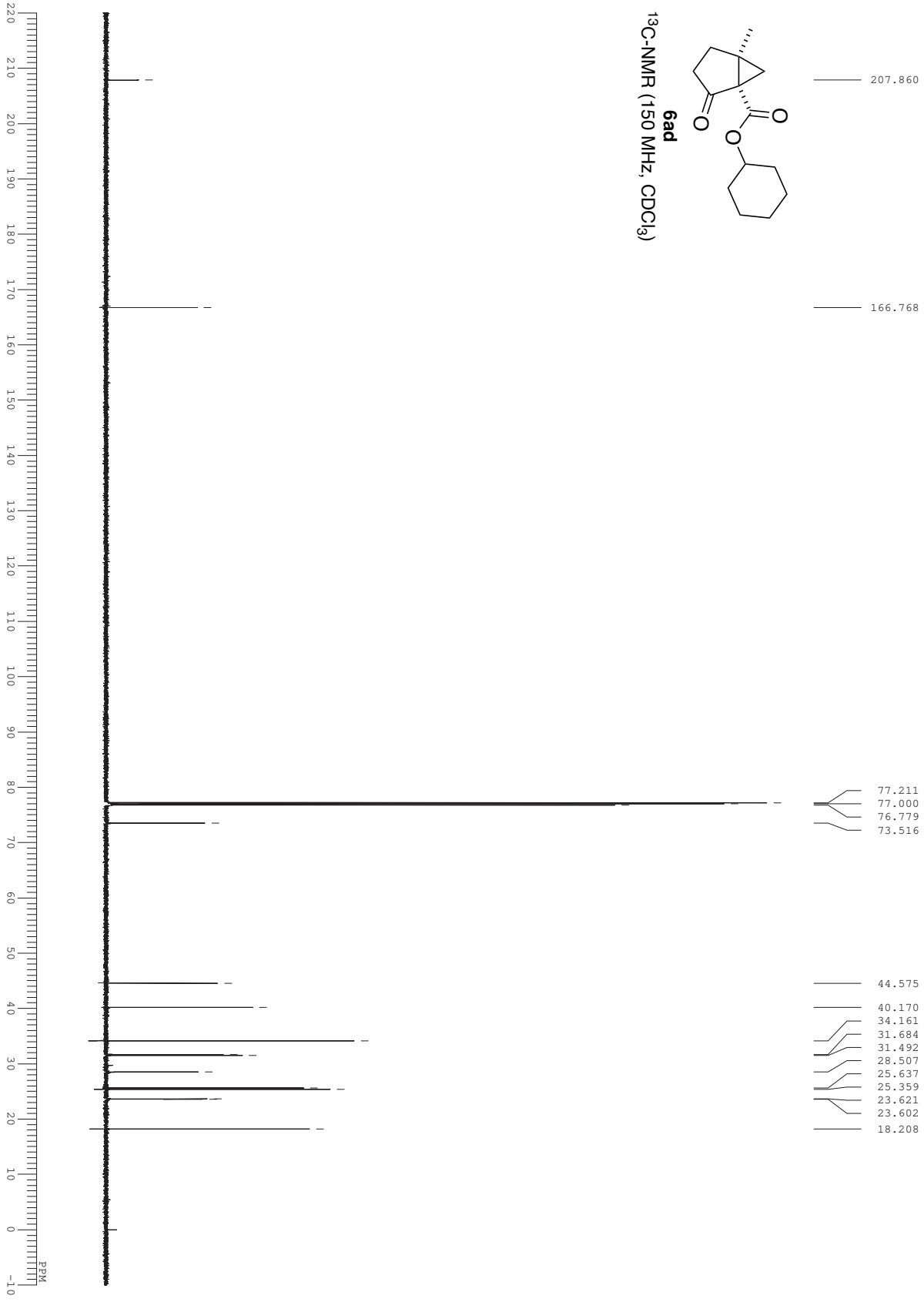

CO2Me
O
6ab
1H-NMR (400 MHz, CDCl3)
7.268
3.778
2.318
2.217
2.197
2.097
2.040
1.956
1.481
1.469
1.403
0.000
3.11
3.22
2.07
1.00
3.05
PPM

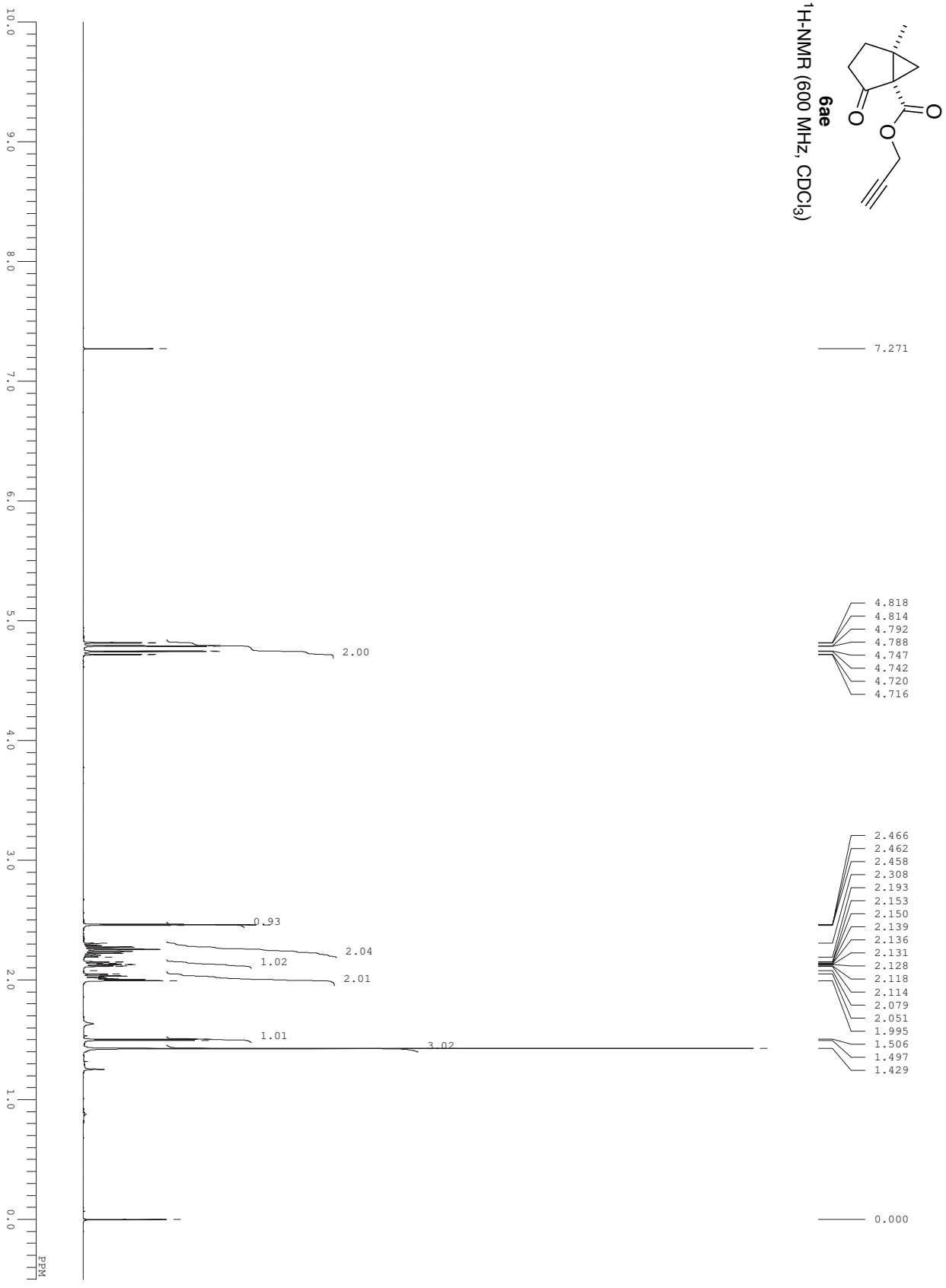

6ab
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Me
O
207.812
167.958
77.221
77.000
76.789
52.350
44.307
40.976
34.180
28.488
26.309
18.140
PPM

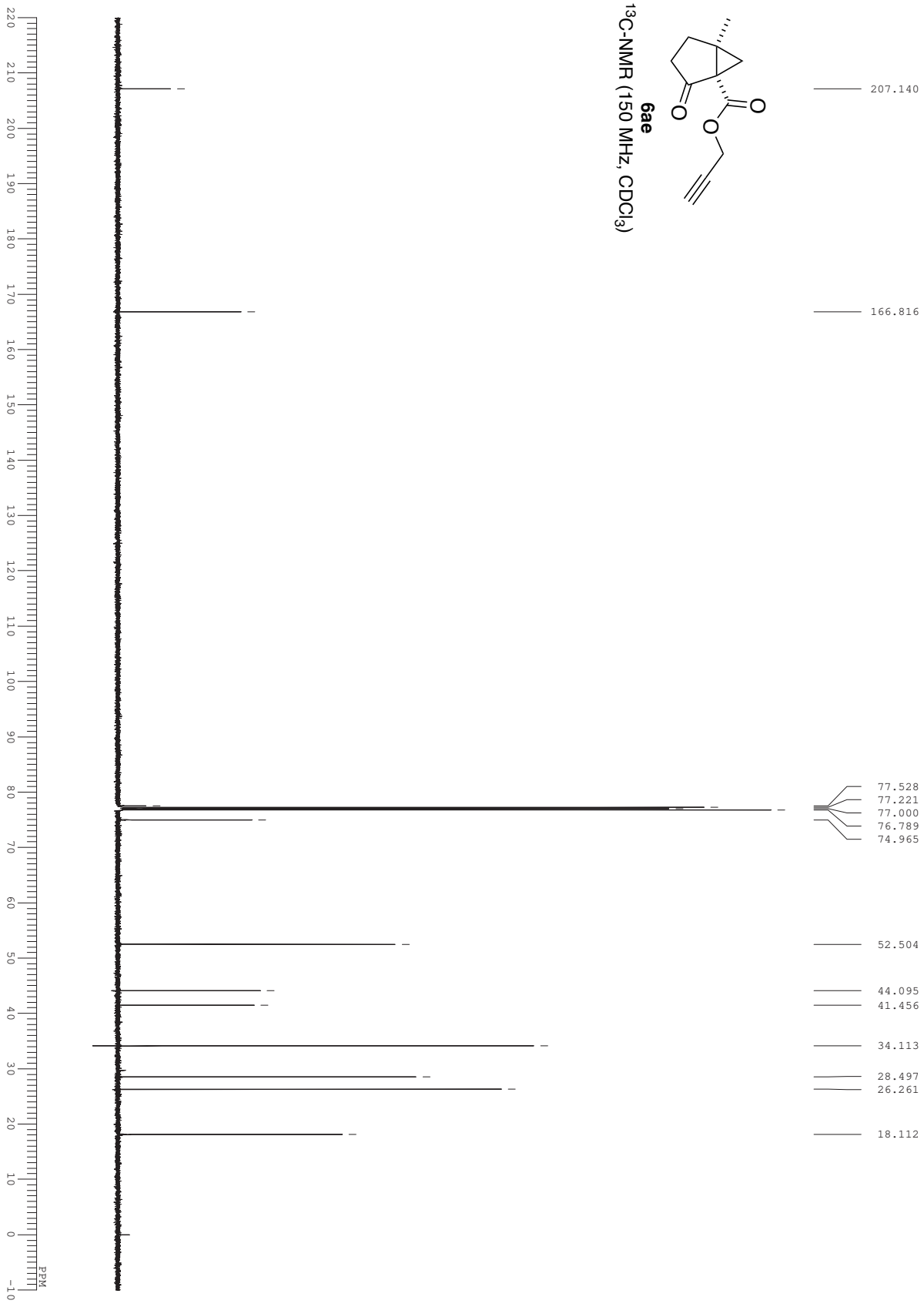

6ac
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2t-Bu
O
7.267
2.277
1.935
1.857
1.845
1.475
1.403
1.362
1.348
0.000
3.97
0.97
8.77
2.98
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

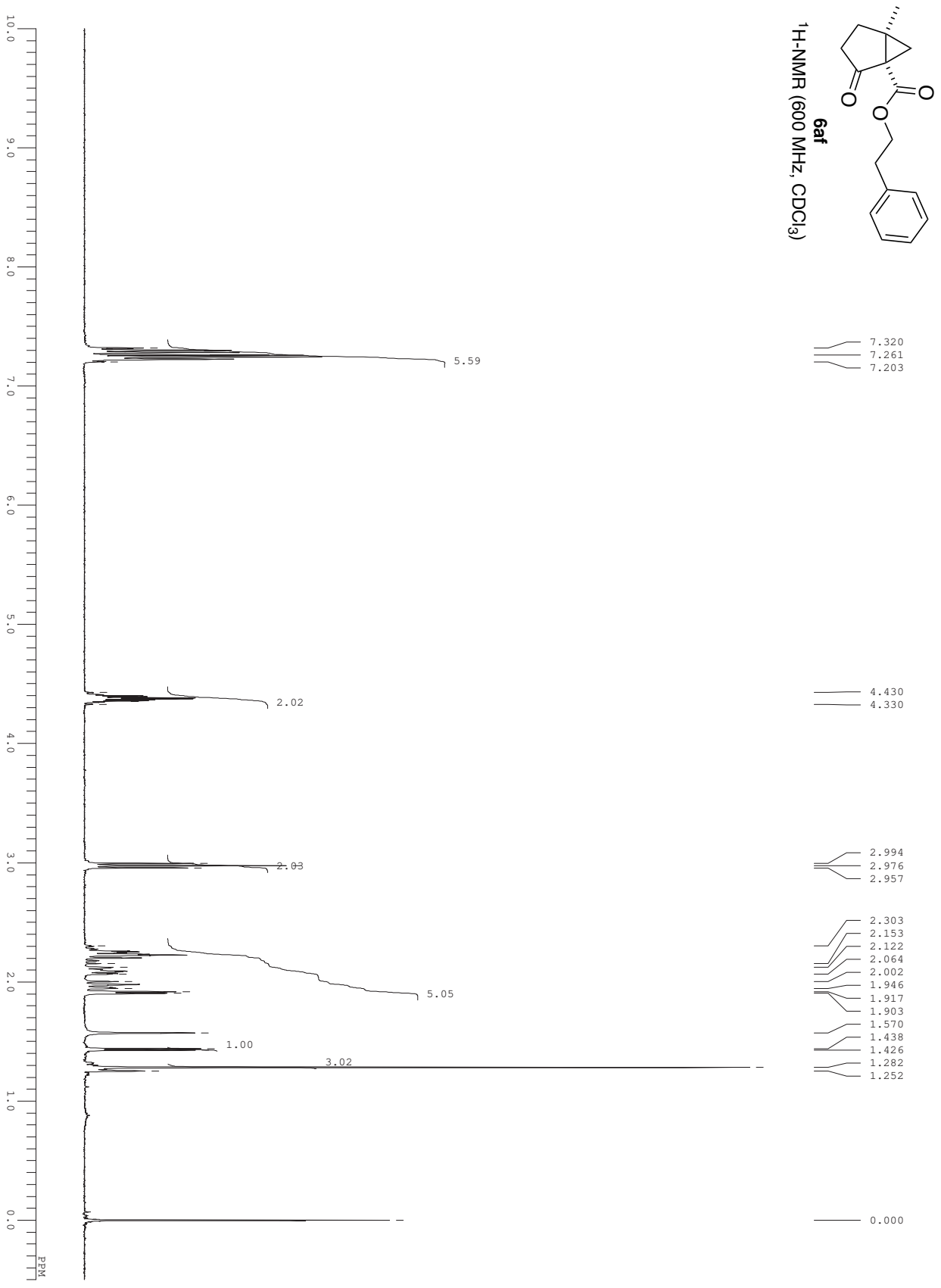

6ac
^{13}C-NMR (100 MHz, CDCl$_3$)
CO_2t-Bu
O
208.052
166.508
81.550
77.211
77.000
76.789
45.113
39.882
34.151
28.497
28.171
25.522
18.169
PPM

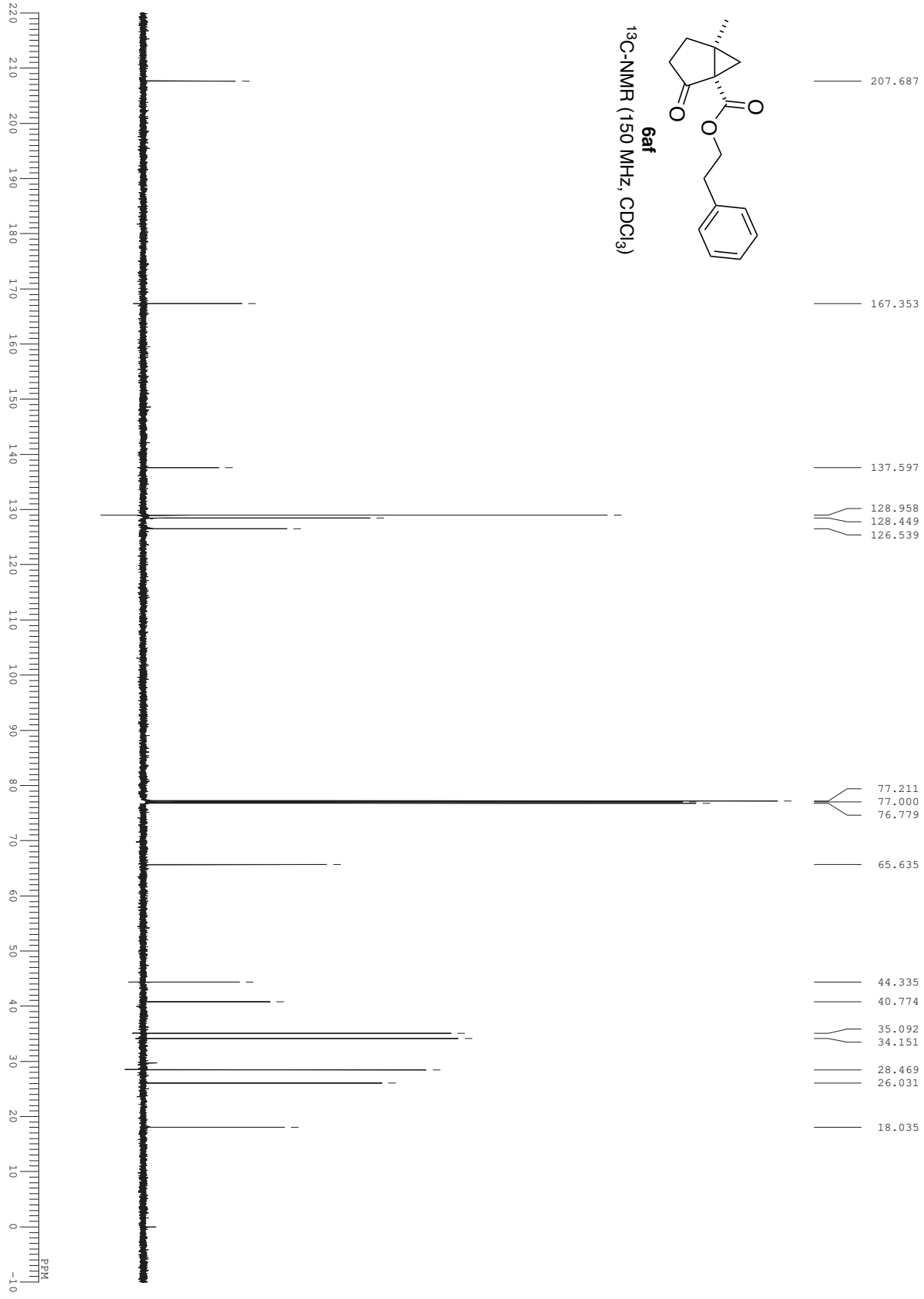

6ad
1H-NMR (600 MHz, CDCl3)
7.267
7.267
4.879
4.835
2.279
2.164
2.121
2.117
2.107
2.103
2.099
2.095
2.085
2.081
2.023
1.966
1.922
1.913
1.887
1.818
1.779
1.682
1.538
1.487
1.478
1.422
1.410
1.239
0.000
1.00
2.05
1.04
1.04
1.01
2.09
2.10
1.94
1.08
7.77
PPM

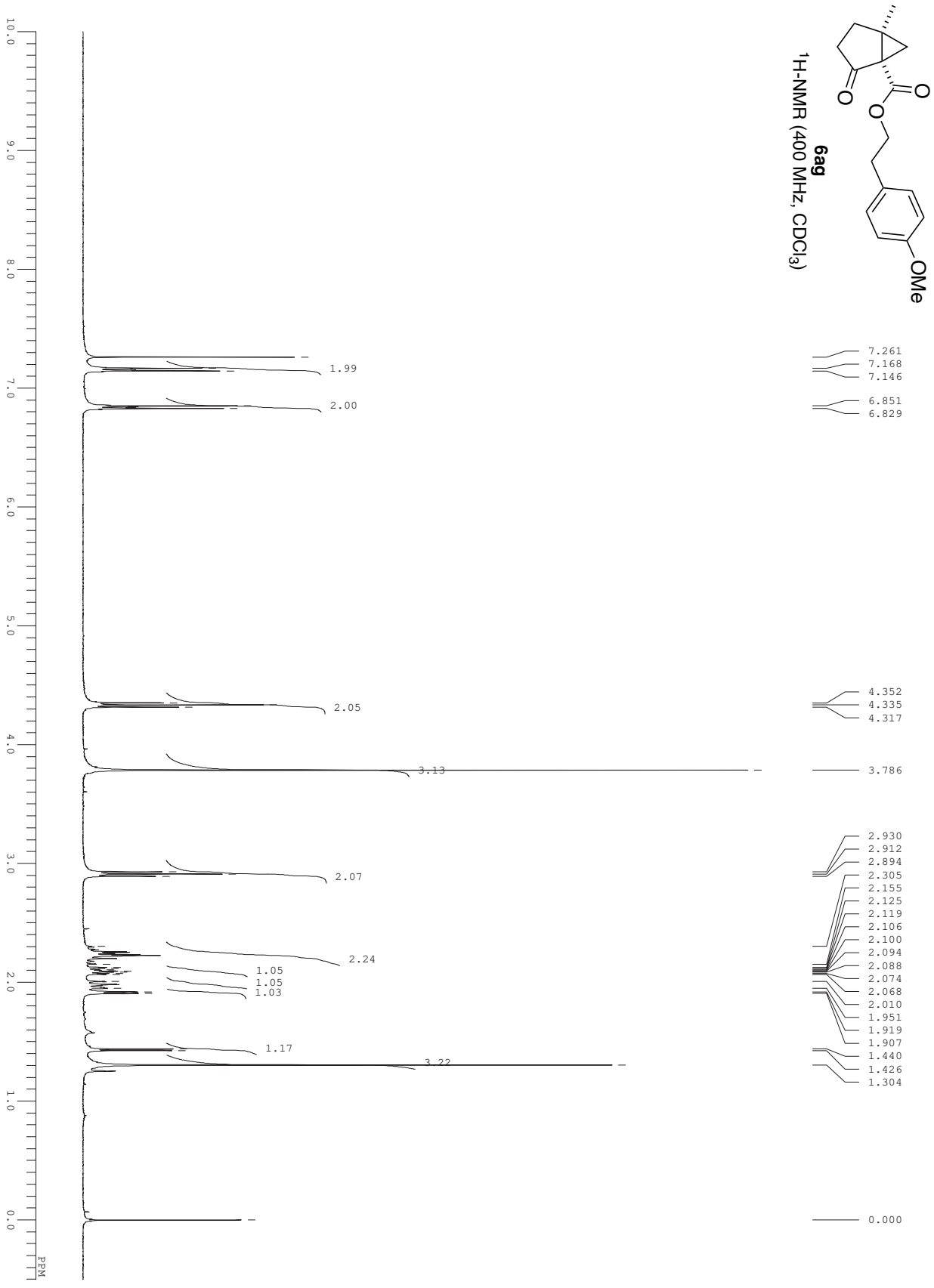

6ad
13C-NMR (150 MHz, CDCl3)
207.860
166.768
77.211
77.000
76.779
73.516
44.575
40.170
34.161
31.684
31.492
28.507
25.637
25.359
23.621
23.602
18.208
PPM

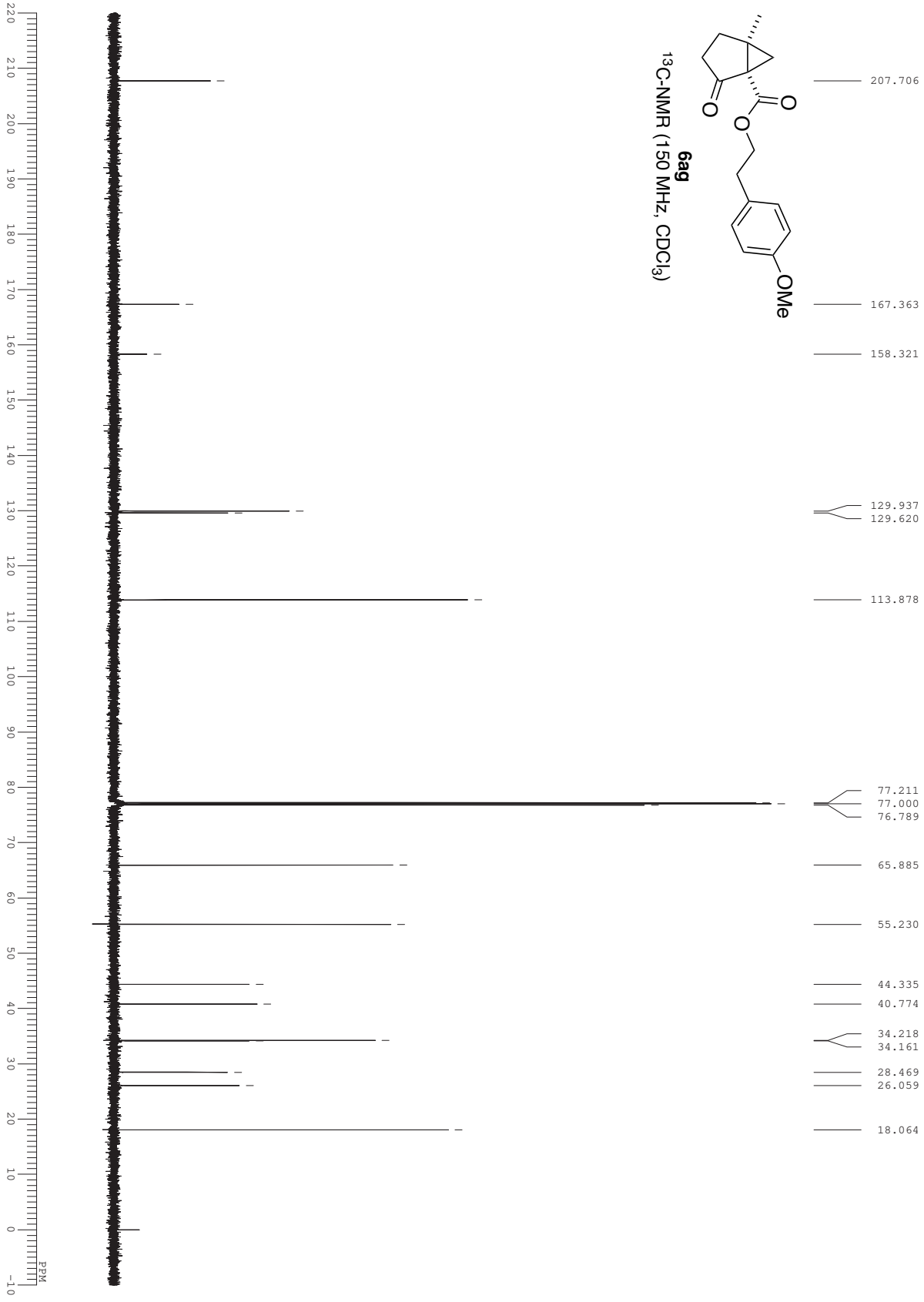

6ae
1H-NMR (600 MHz, CDCl3)
7.271
4.818
4.814
4.792
4.788
4.747
4.742
4.720
4.716
2.466
2.462
2.458
2.308
2.193
2.153
2.150
2.139
2.136
2.131
2.128
2.118
2.114
2.079
2.051
1.995
1.506
1.497
1.429
0.000
2.00
0.93
2.04
1.02
2.01
1.01
3.02
PPM

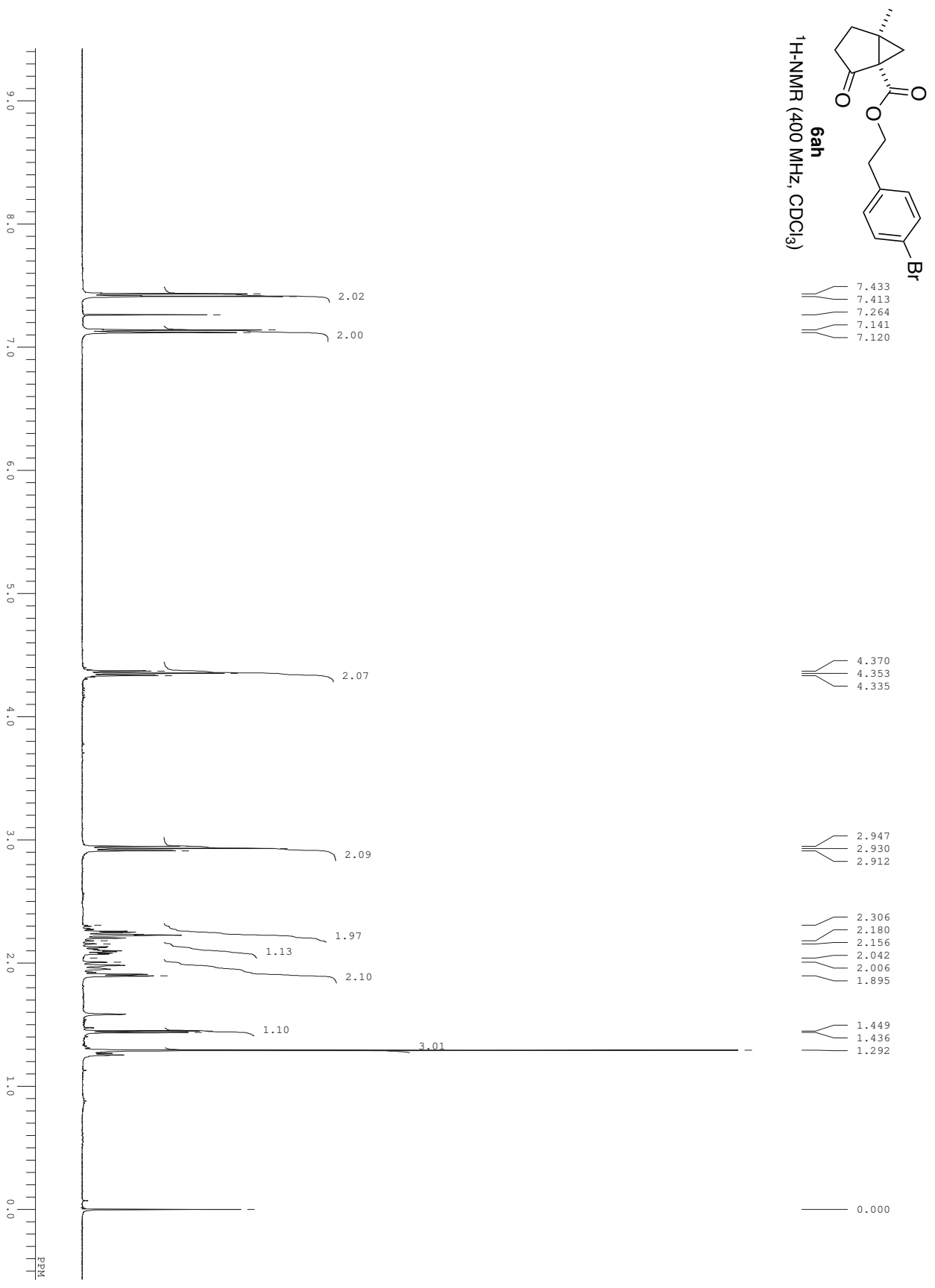

6ae
13C-NMR (150 MHz, CDCl3)
207.140
166.816
77.528
77.221
77.000
76.789
74.965
52.504
44.095
41.456
34.113
28.497
26.261
18.112
PPM

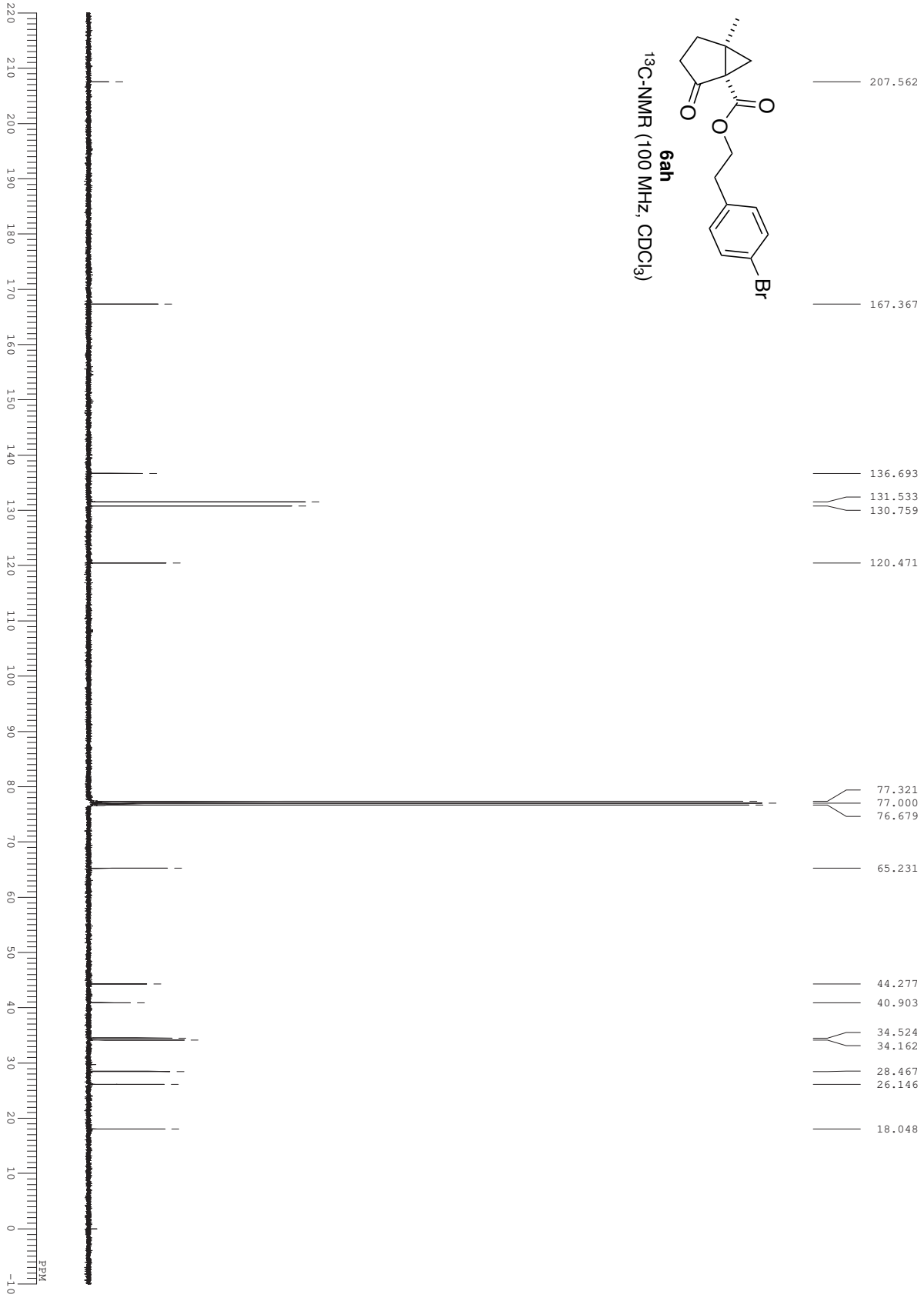

6af
1H-NMR (600 MHz, CDCl3)
7.320
7.261
7.203
4.430
4.330
2.994
2.976
2.957
2.303
2.153
2.122
2.064
2.002
1.946
1.917
1.903
1.570
1.438
1.426
1.282
1.252
0.000
5.59
2.02
2.03
5.05
1.00
3.02
PPM

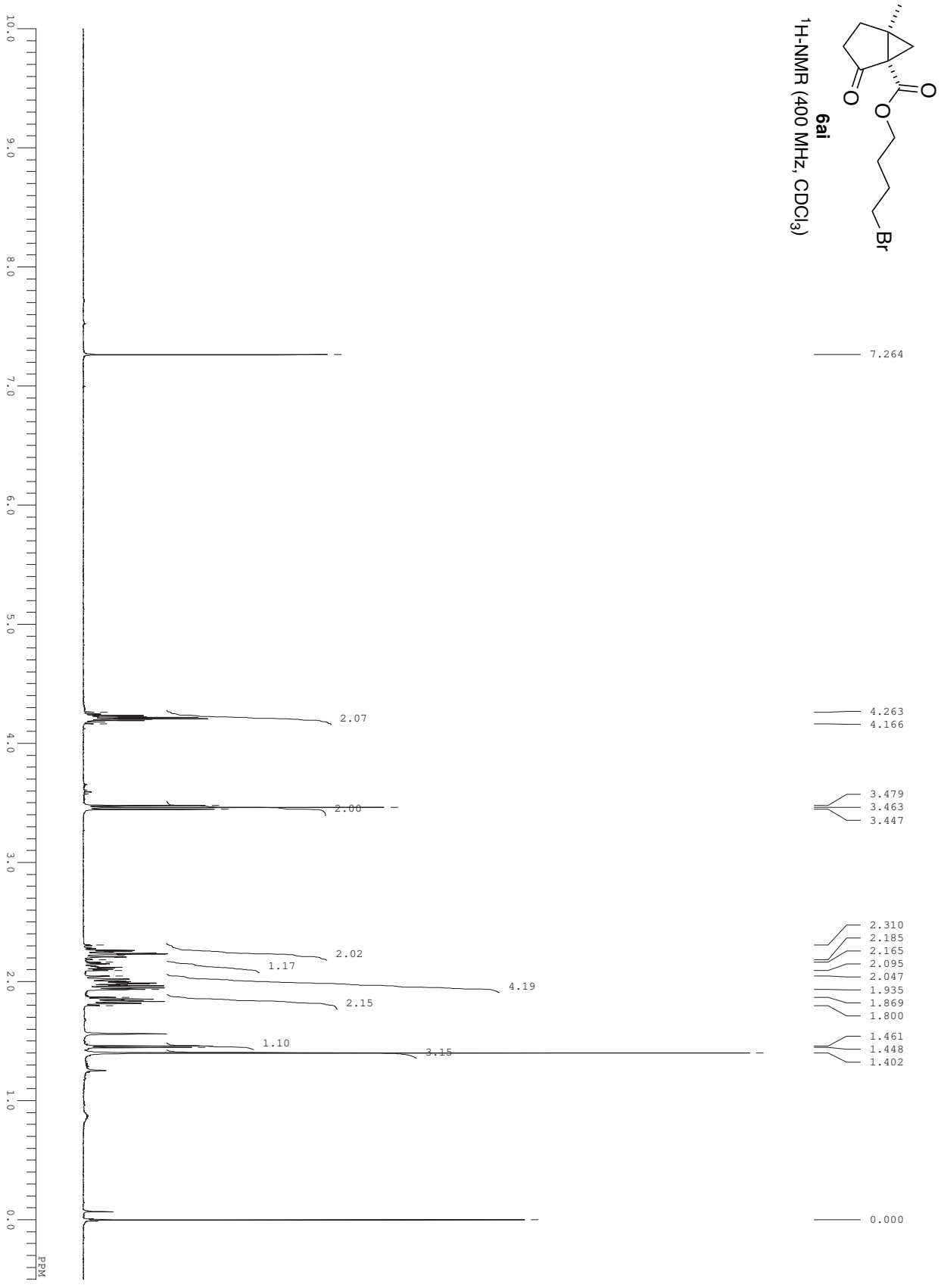

6af
^{13}C-NMR (150 MHz, CDCl$_3$)
O
O
O
207.687
167.353
137.597
128.958
128.449
126.539
77.211
77.000
76.779
65.635
44.335
40.774
35.092
34.151
28.469
26.031
18.035
PPM

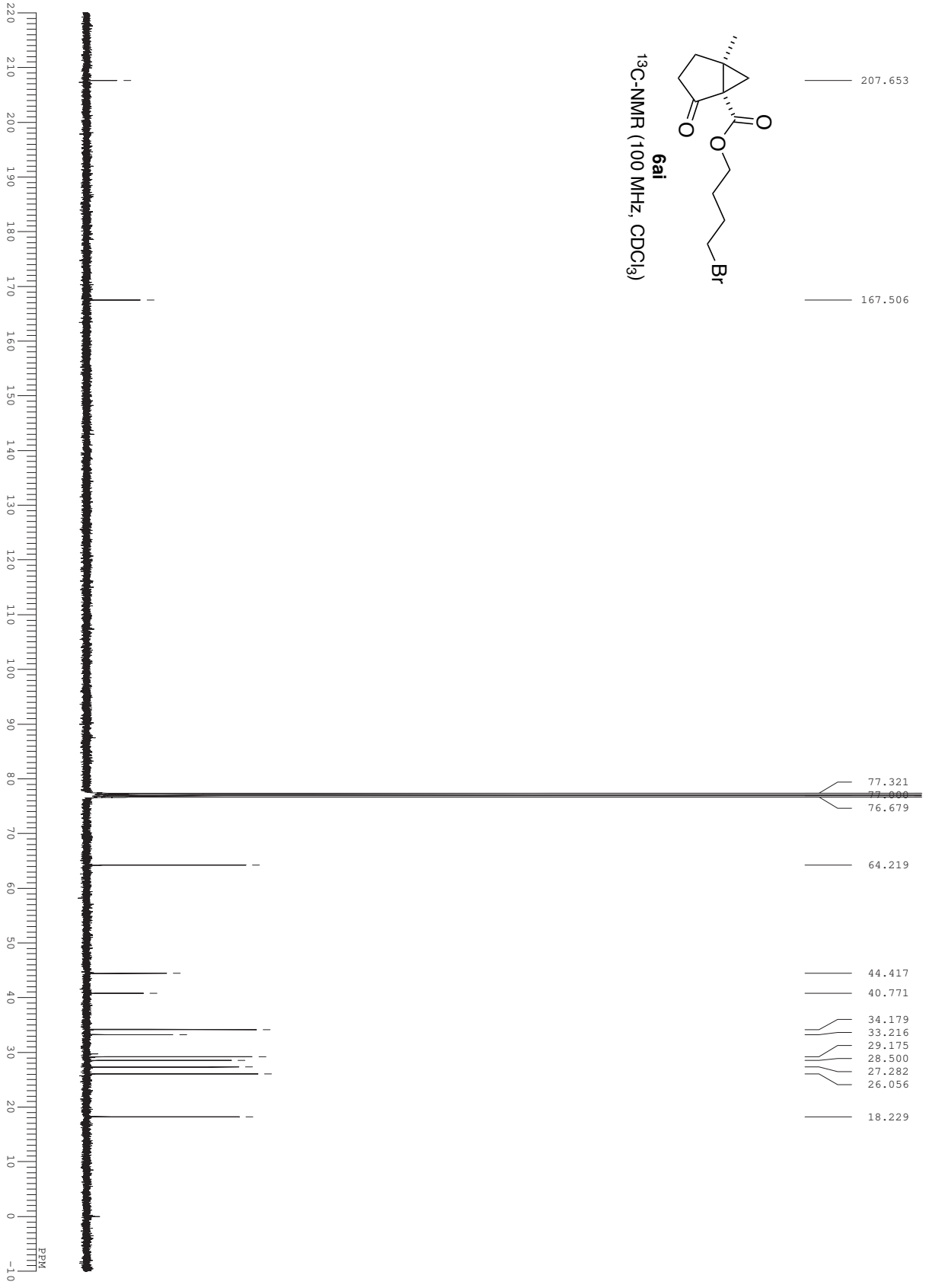

6ag
^{1}H-NMR (400 MHz, $CDCl_3$)
OMe
7.261
7.168
7.146
6.851
6.829
4.352
4.335
4.317
3.786
2.930
2.912
2.894
2.305
2.155
2.125
2.119
2.106
2.100
2.094
2.088
2.074
2.068
2.010
1.951
1.919
1.907
1.440
1.426
1.304
0.000
1.99
2.00
2.05
3.13
2.07
2.24
1.05
1.05
1.03
1.17
3.22
PPM

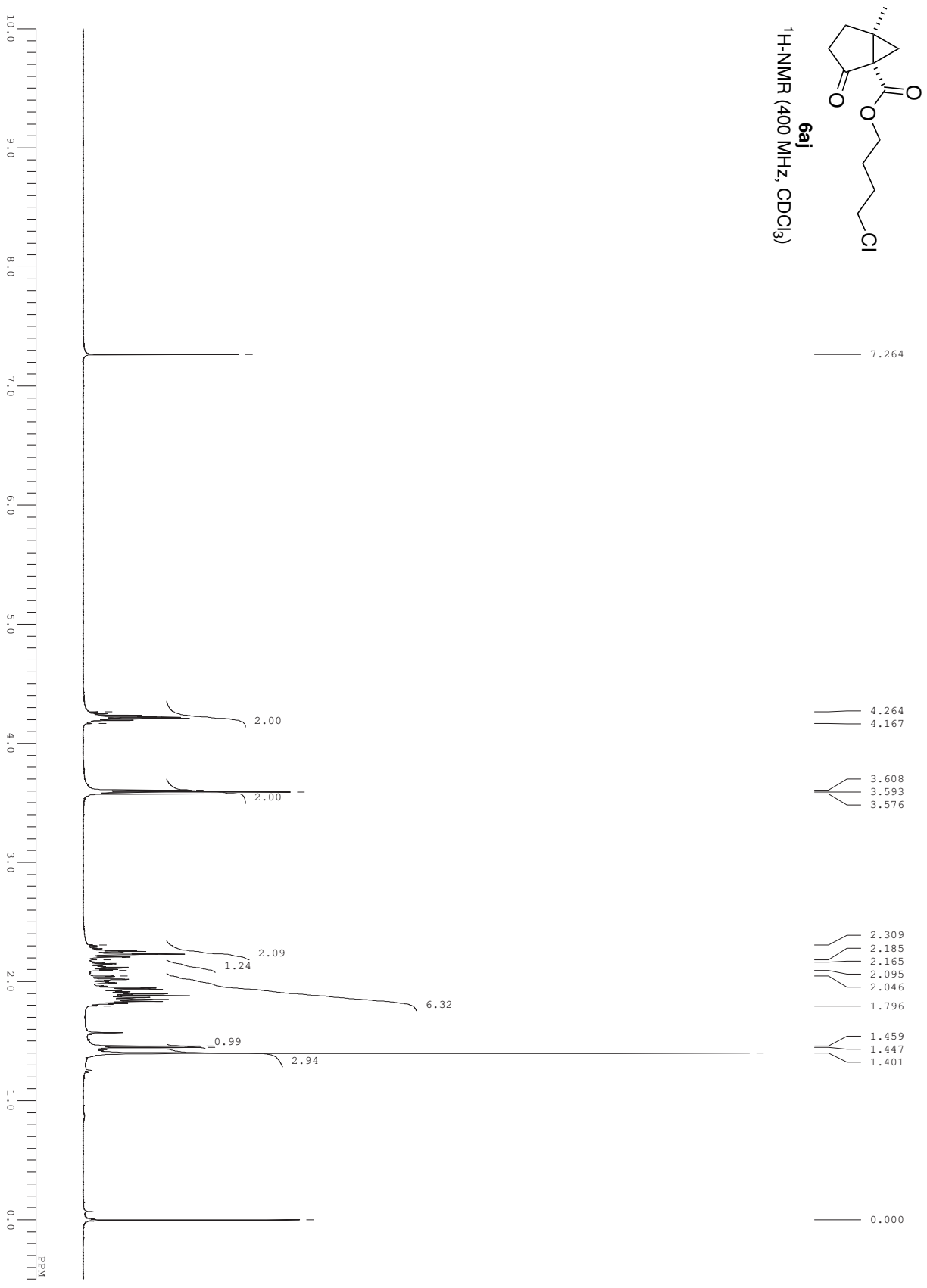

6ag
13C-NMR (150 MHz, CDCl3)
OMe
207.706
167.363
158.321
129.937
129.620
113.878
77.211
77.000
76.789
65.885
55.230
44.335
40.774
34.218
34.161
28.469
26.059
18.064
PPM

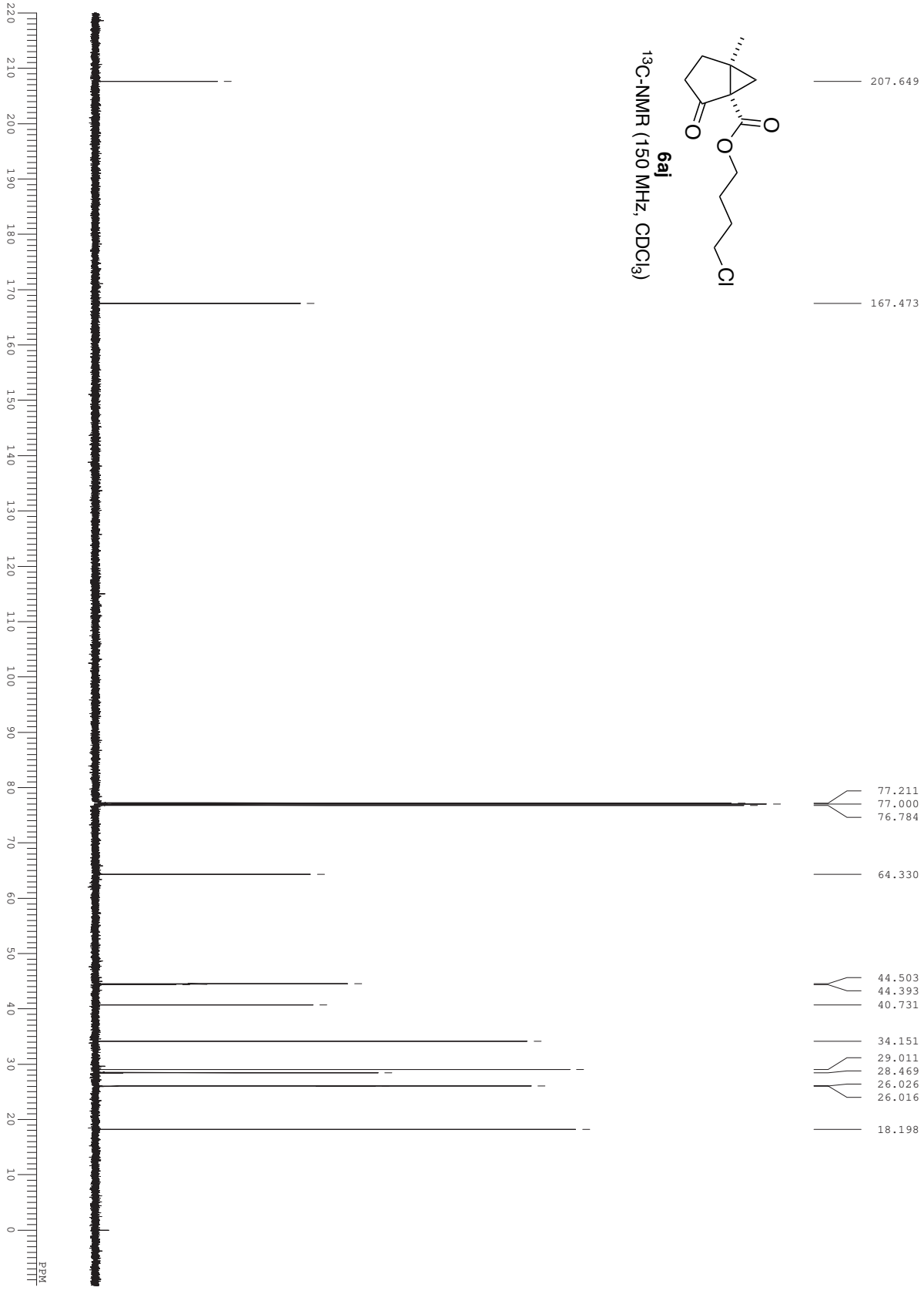

6ah
1H-NMR (400 MHz, CDCl3)
O
O
O
Br
7.433
7.413
7.264
7.141
7.120
4.370
4.353
4.335
2.947
2.930
2.912
2.306
2.180
2.156
2.042
2.006
1.895
1.449
1.436
1.292
0.000
2.02
2.00
2.07
2.09
1.97
1.13
2.10
1.10
3.01
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

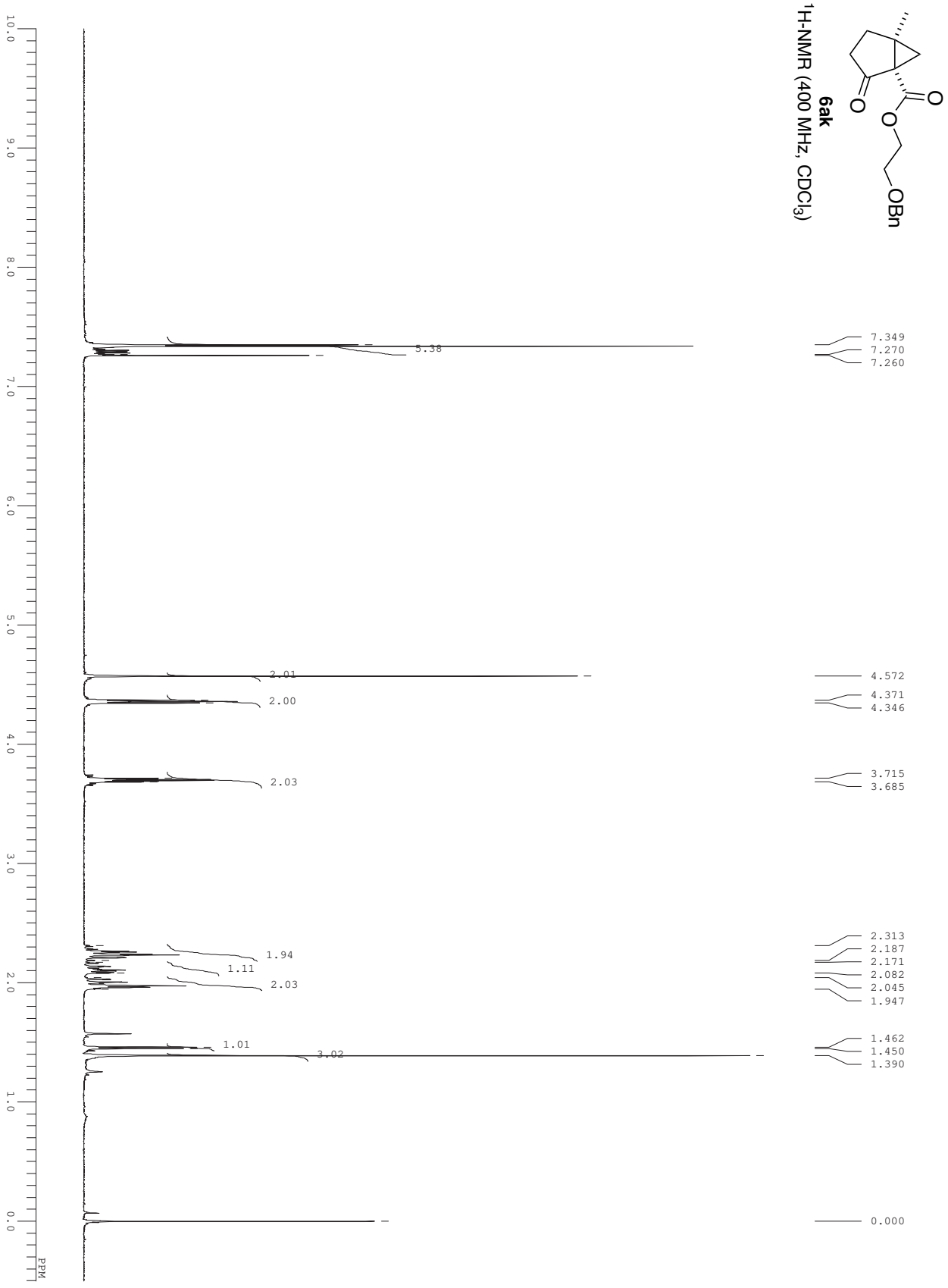

6ah
13C-NMR (100 MHz, CDCl3)
O
O
O
Br
207.562
167.367
136.693
131.533
130.759
120.471
77.321
77.000
76.679
65.231
44.277
40.903
34.524
34.162
28.467
26.146
18.048
PPM

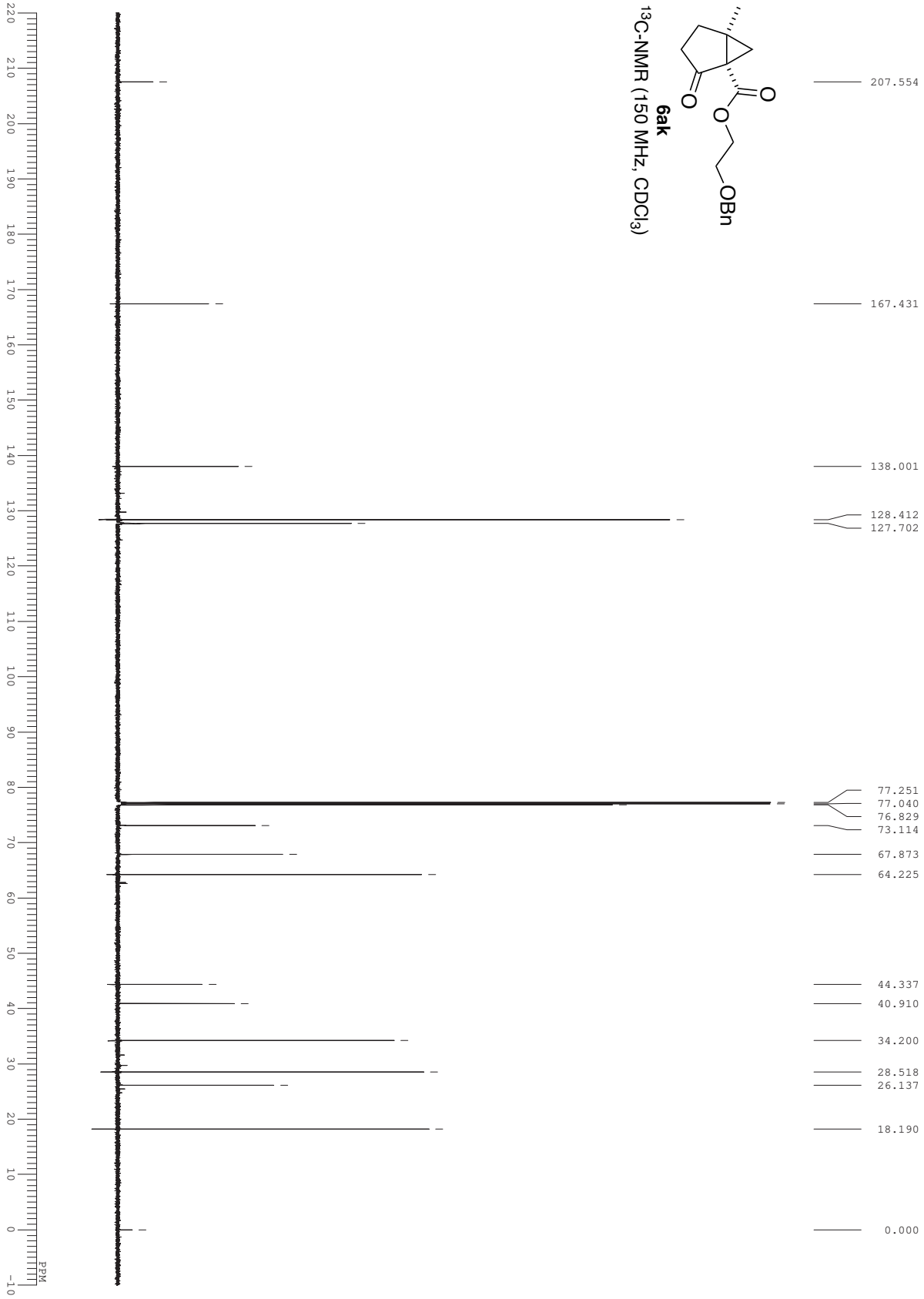

6ai
^{1}H-NMR (400 MHz, $CDCl_3$)
O
O
O
Br
7.264
4.263
4.166
3.479
3.463
3.447
2.310
2.185
2.165
2.095
2.047
1.935
1.869
1.800
1.461
1.448
1.402
0.000
2.07
2.00
2.02
1.17
4.19
2.15
1.10
3.15
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

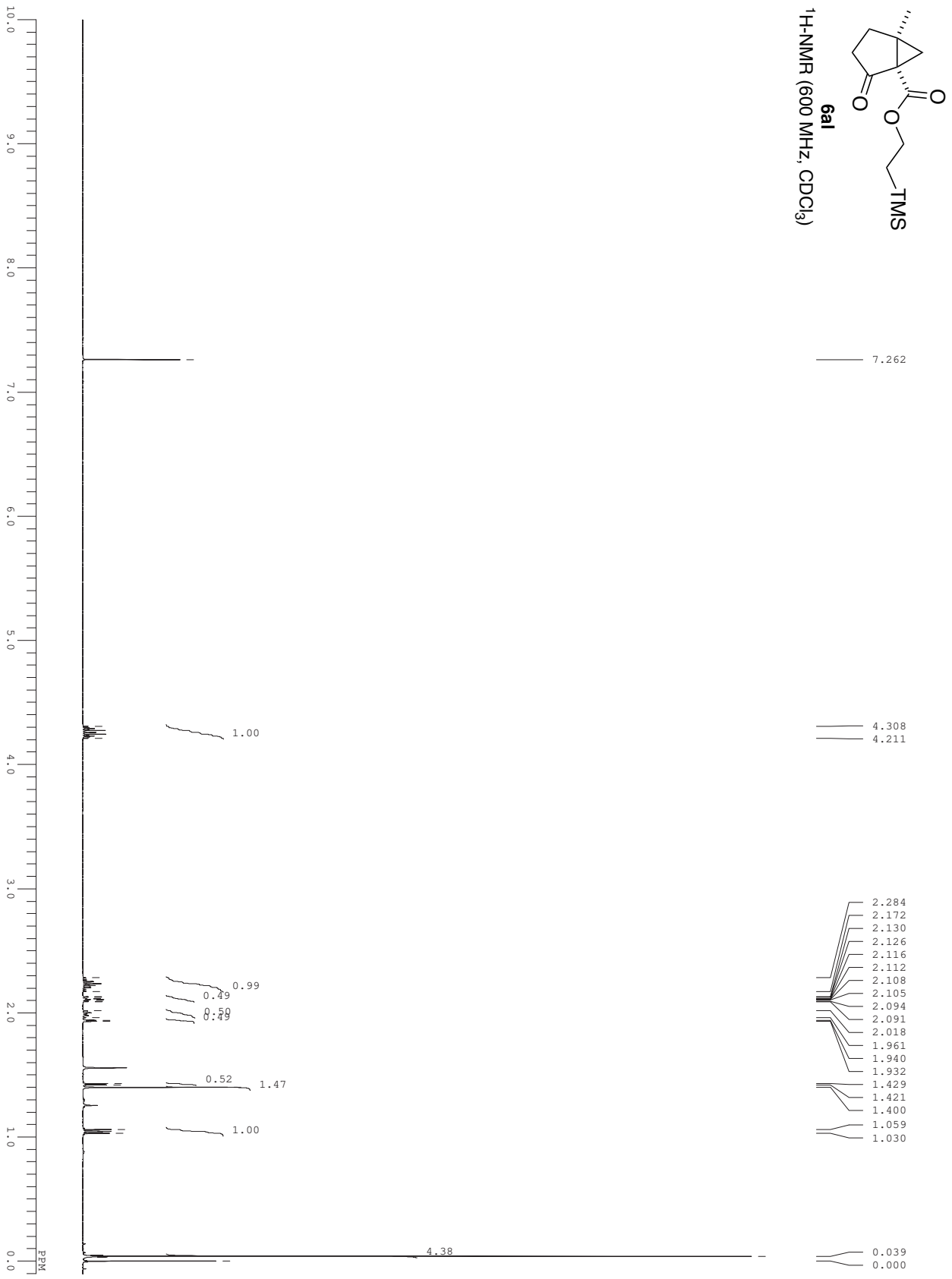

6ai
13C-NMR (100 MHz, CDCl3)
O
O
O
Br
207.653
167.506
77.321
77.000
76.679
64.219
44.417
40.771
34.179
33.216
29.175
28.500
27.282
26.056
18.229
PPM

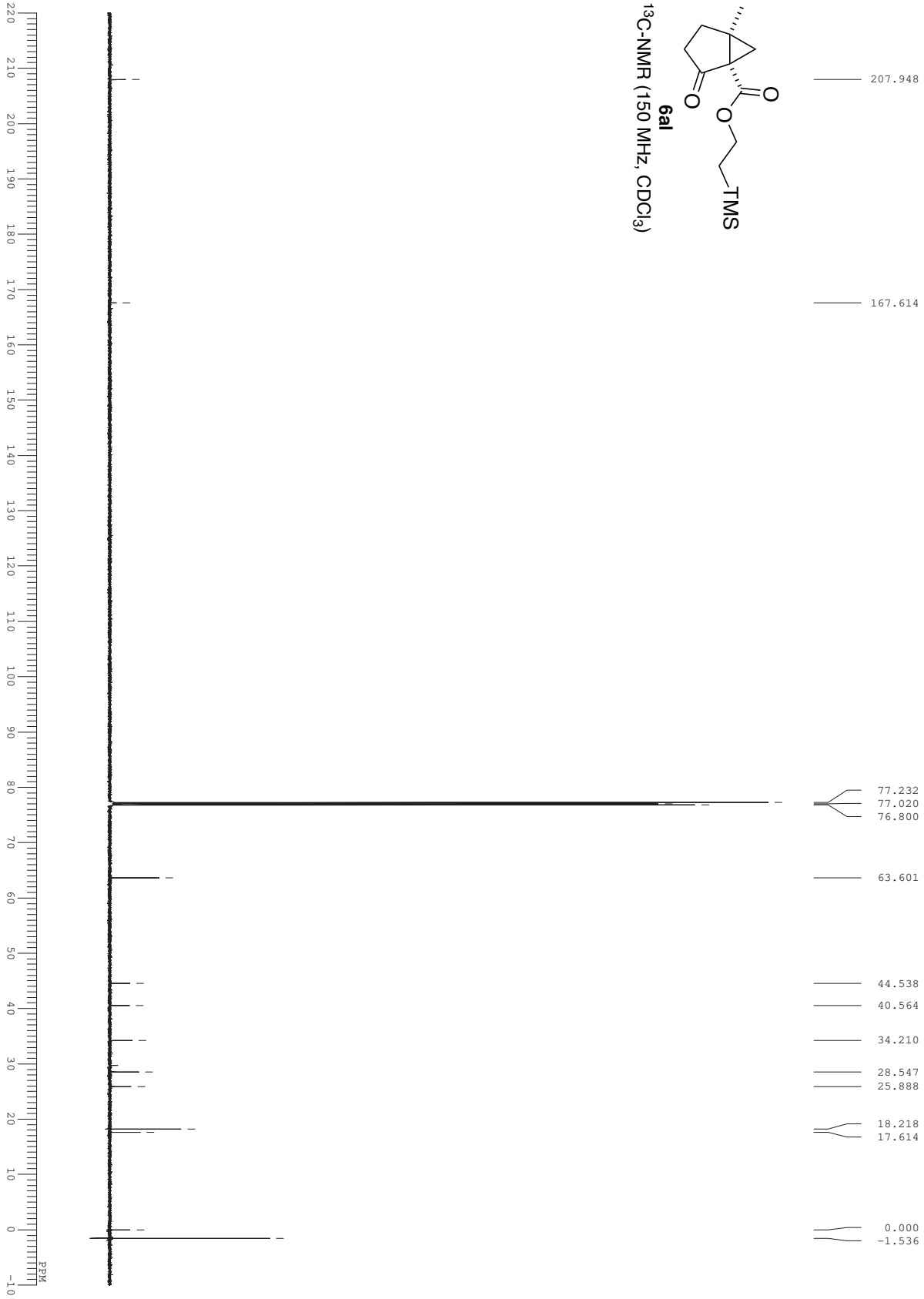

6aj
1H-NMR (400 MHz, CDCl3)
Cl
7.264
4.264
4.167
3.608
3.593
3.576
2.309
2.185
2.165
2.095
2.046
1.796
1.459
1.447
1.401
0.000
2.00
2.00
2.09
1.24
6.32
0.99
2.94
PPM

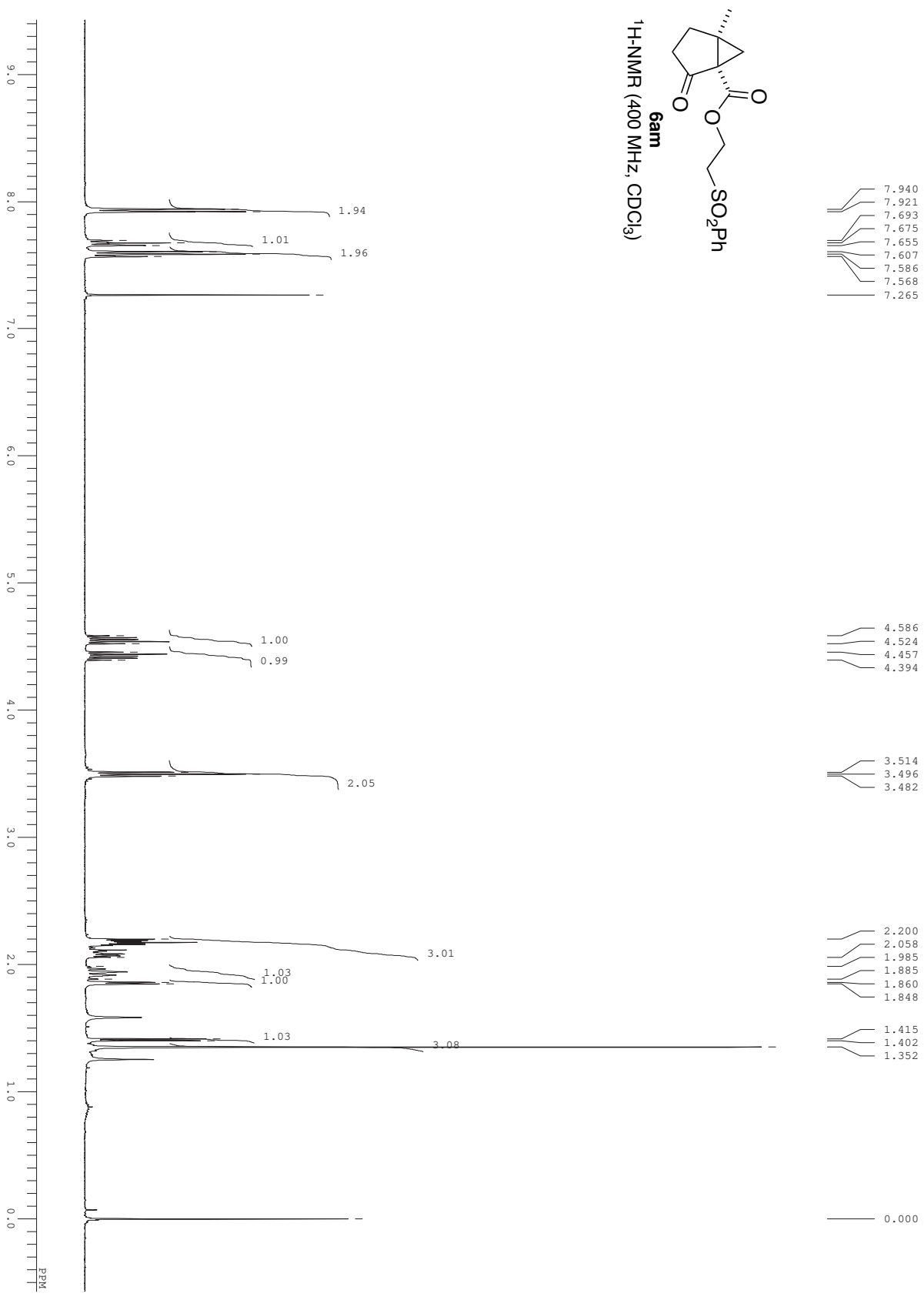

6aj
^{13}C-NMR (150 MHz, CDCl$_3$)
O
O
O
Cl
207.649
167.473
77.211
77.000
76.784
64.330
44.503
44.393
40.731
34.151
29.011
28.469
26.026
26.016
18.198
PPM

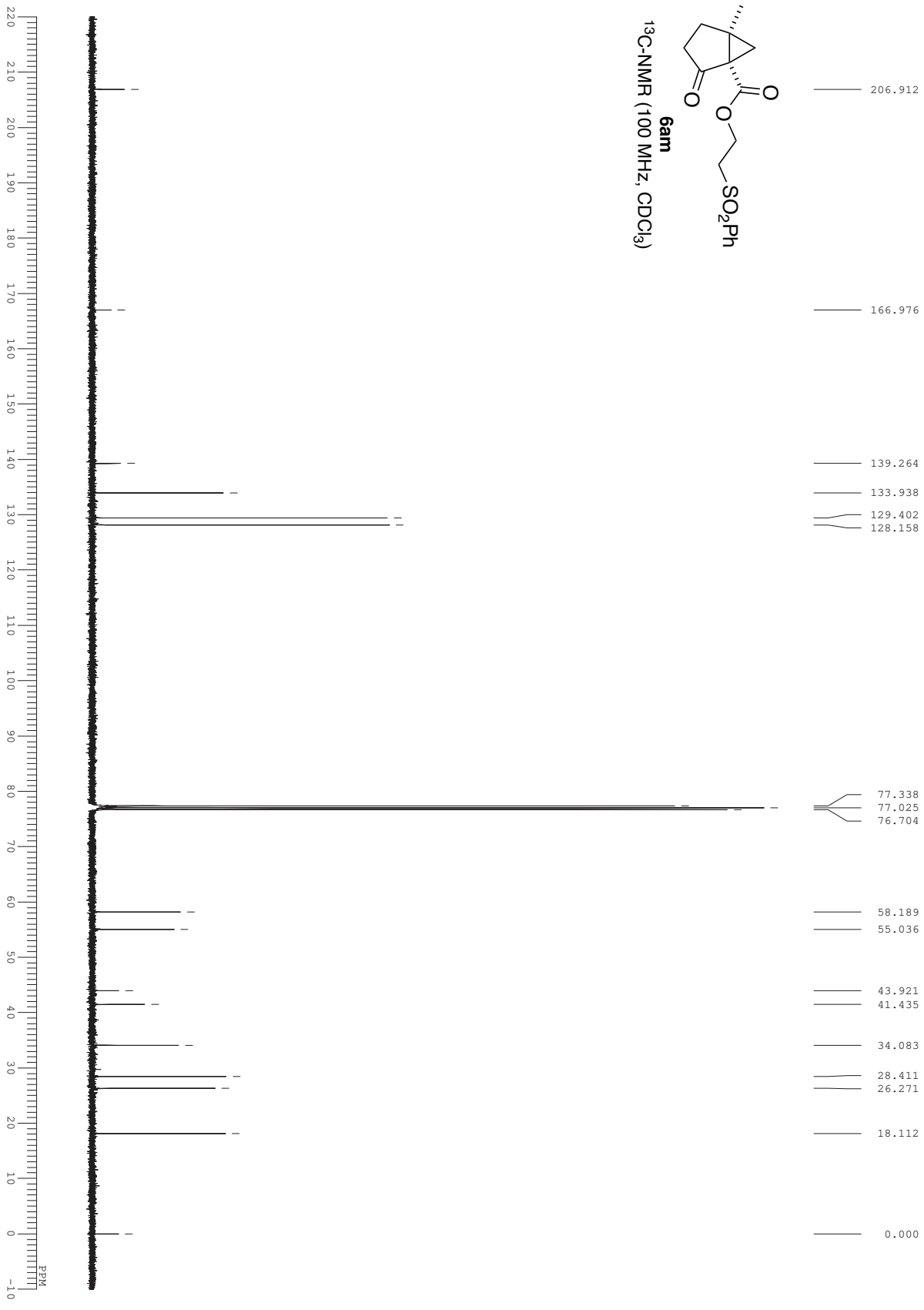

6ak
^{1}H-NMR (400 MHz, $CDCl_3$)
OBn
7.349
7.270
7.260
4.572
4.371
4.346
3.715
3.685
2.313
2.187
2.171
2.082
2.045
1.947
1.462
1.450
1.390
0.000
5.38
2.01
2.00
2.03
1.94
1.11
2.03
1.01
3.02
PPM

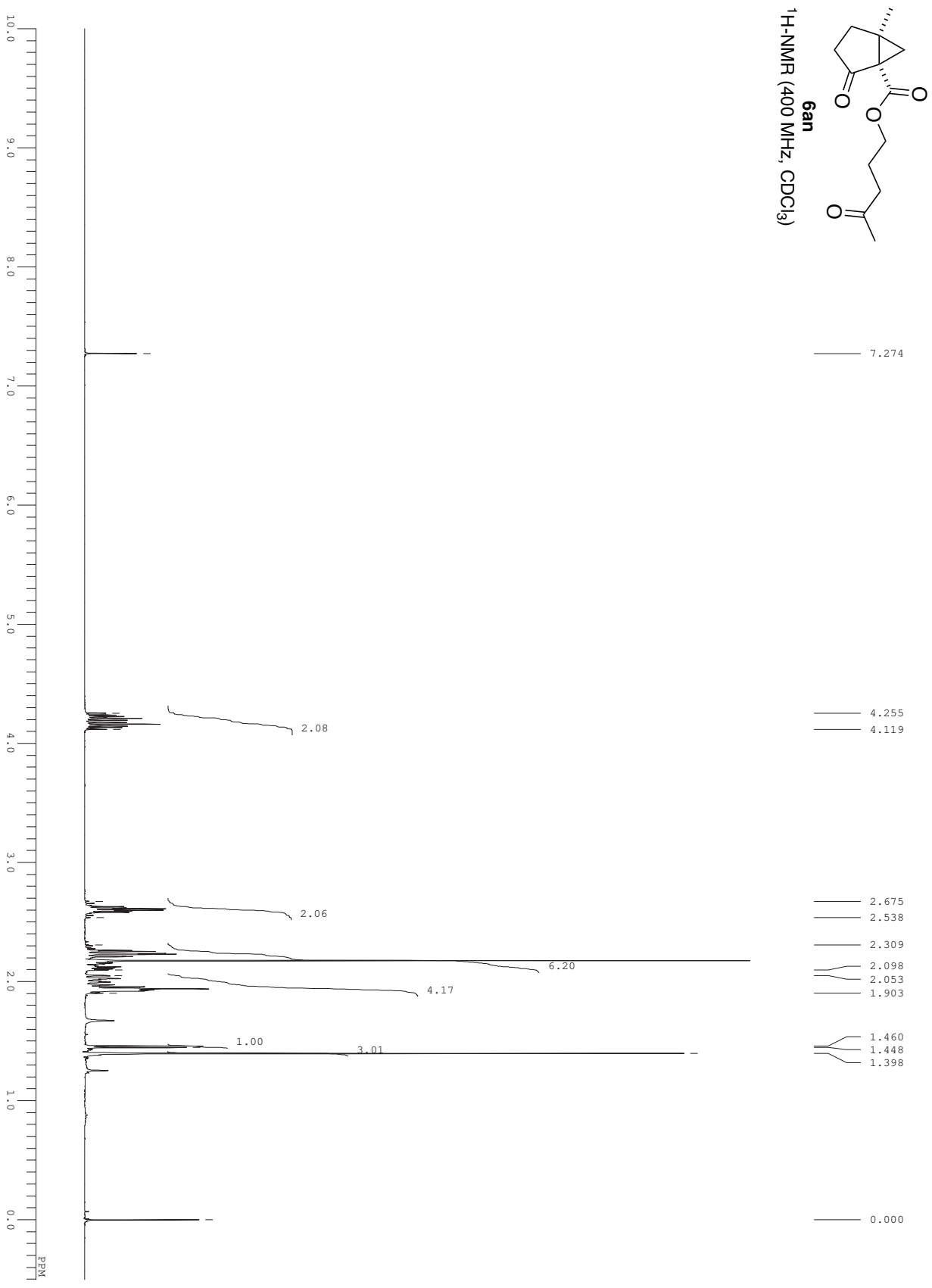

6ak
13C-NMR (150 MHz, CDCl3)
O
O
O
O
OBn
207.554
167.431
138.001
128.412
127.702
77.251
77.040
76.829
73.114
67.873
64.225
44.337
40.910
34.200
28.518
26.137
18.190
0.000
PPM

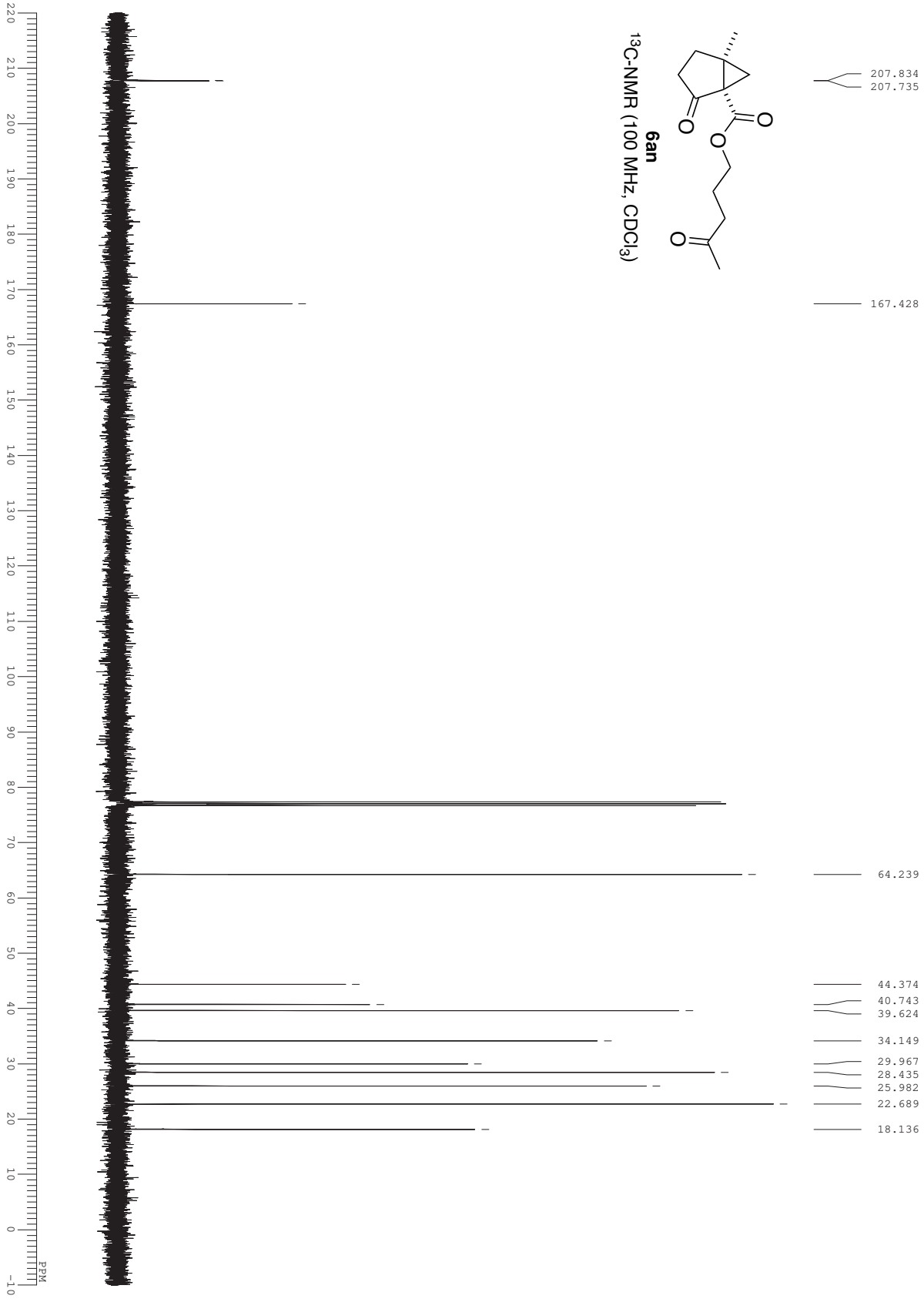

6al
^{1}H-NMR (600 MHz, CDCl$_3$)
TMS
7.262
4.308
4.211
2.284
2.172
2.130
2.126
2.116
2.112
2.108
2.105
2.094
2.091
2.018
1.961
1.940
1.932
1.429
1.421
1.400
1.059
1.030
0.039
0.000
1.00
0.99
0.49
0.50
0.49
0.52
1.47
1.00
4.38
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

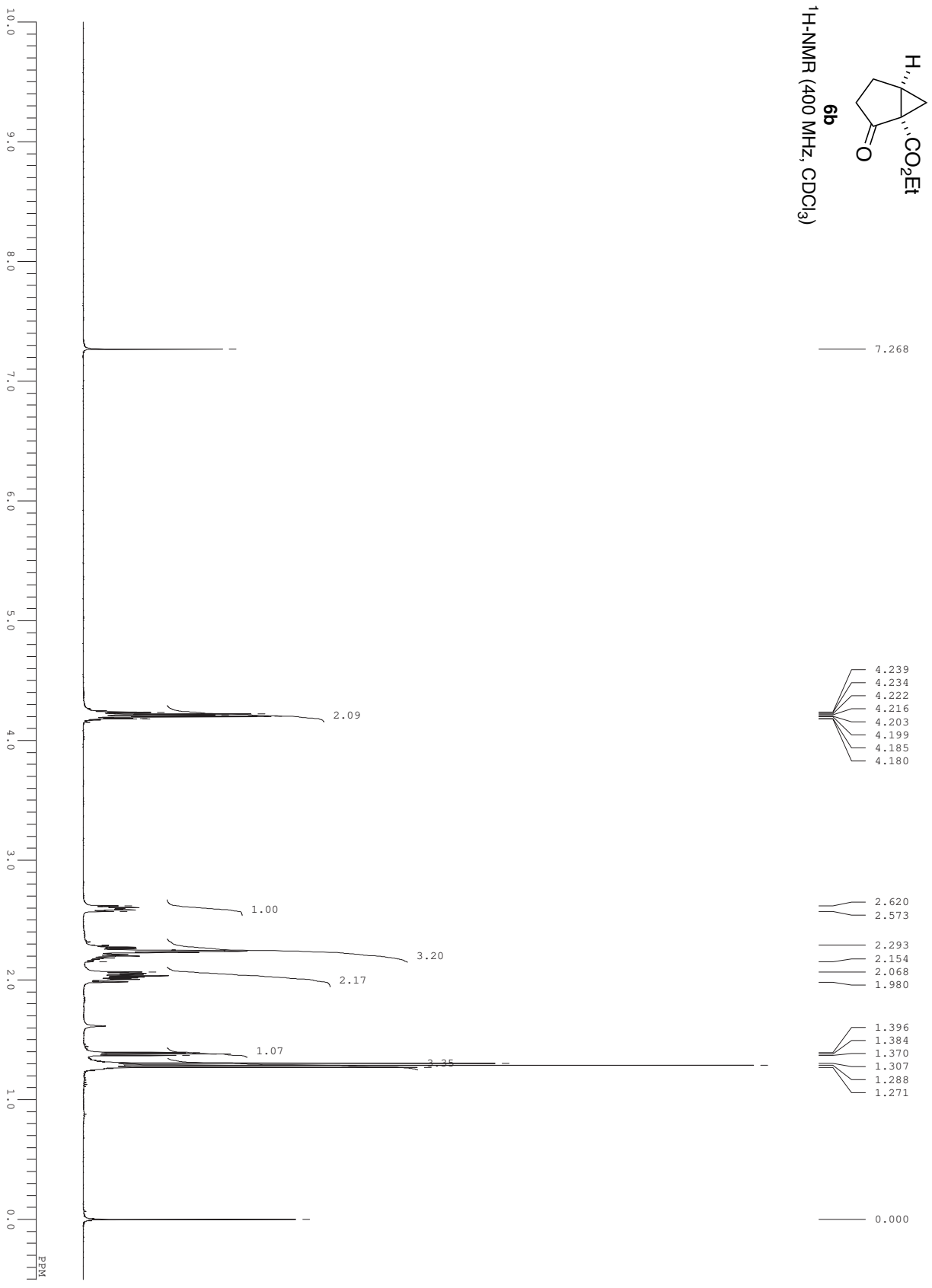

6al
^{13}C-NMR (150 MHz, CDCl$_3$)
TMS
O
O
O
207.948
167.614
77.232
77.020
76.800
63.601
44.538
40.564
34.210
28.547
25.888
18.218
17.614
0.000
-1.536
PPM

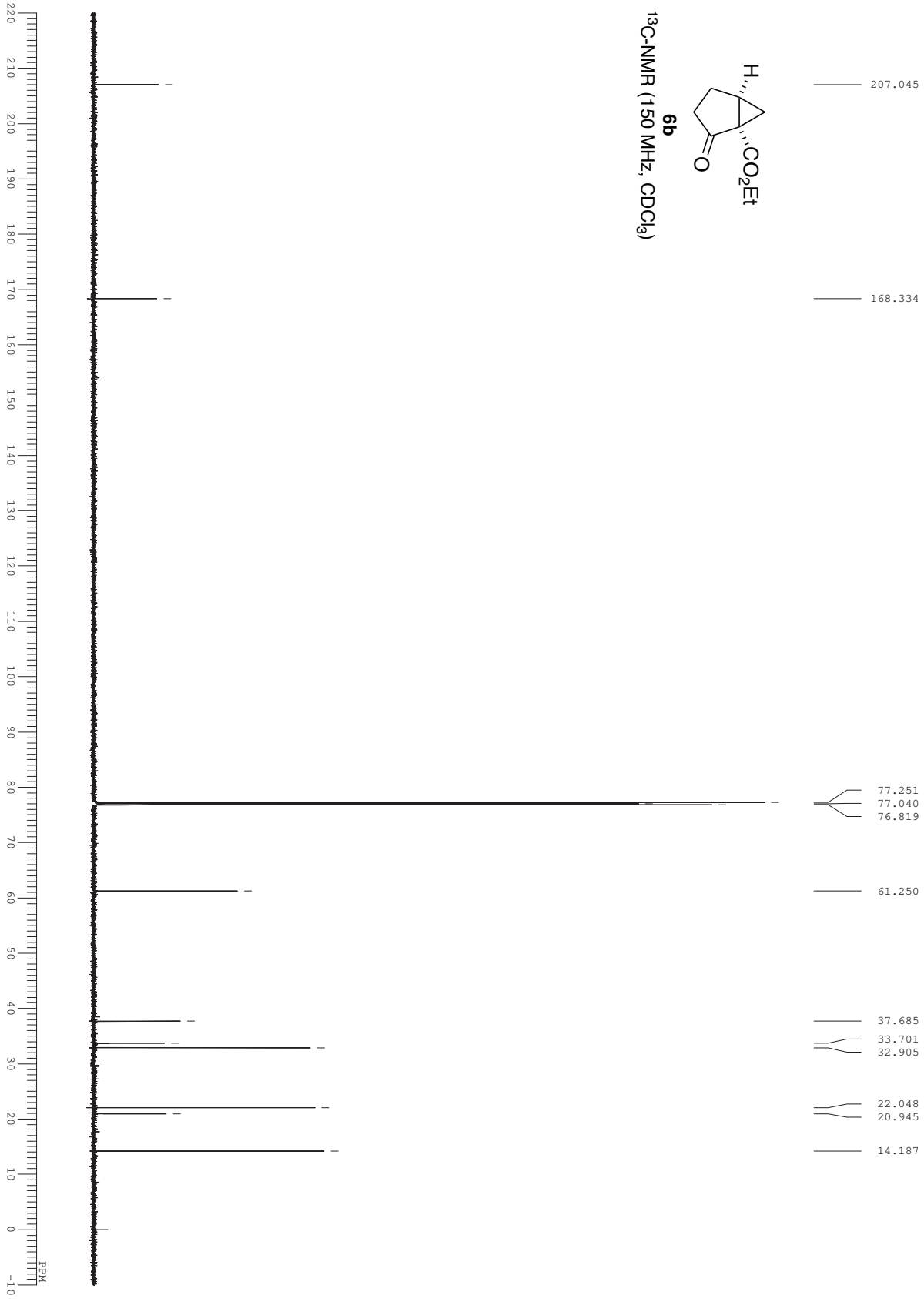

6am
^{1}H-NMR (400 MHz, $CDCl_3$)
SO_2Ph
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM
1.94
1.01
1.96
1.00
0.99
2.05
3.01
1.03
1.00
1.03
3.08
7.940
7.921
7.693
7.675
7.655
7.607
7.586
7.568
7.265
4.586
4.524
4.457
4.394
3.514
3.496
3.482
2.200
2.058
1.985
1.885
1.860
1.848
1.415
1.402
1.352
0.000

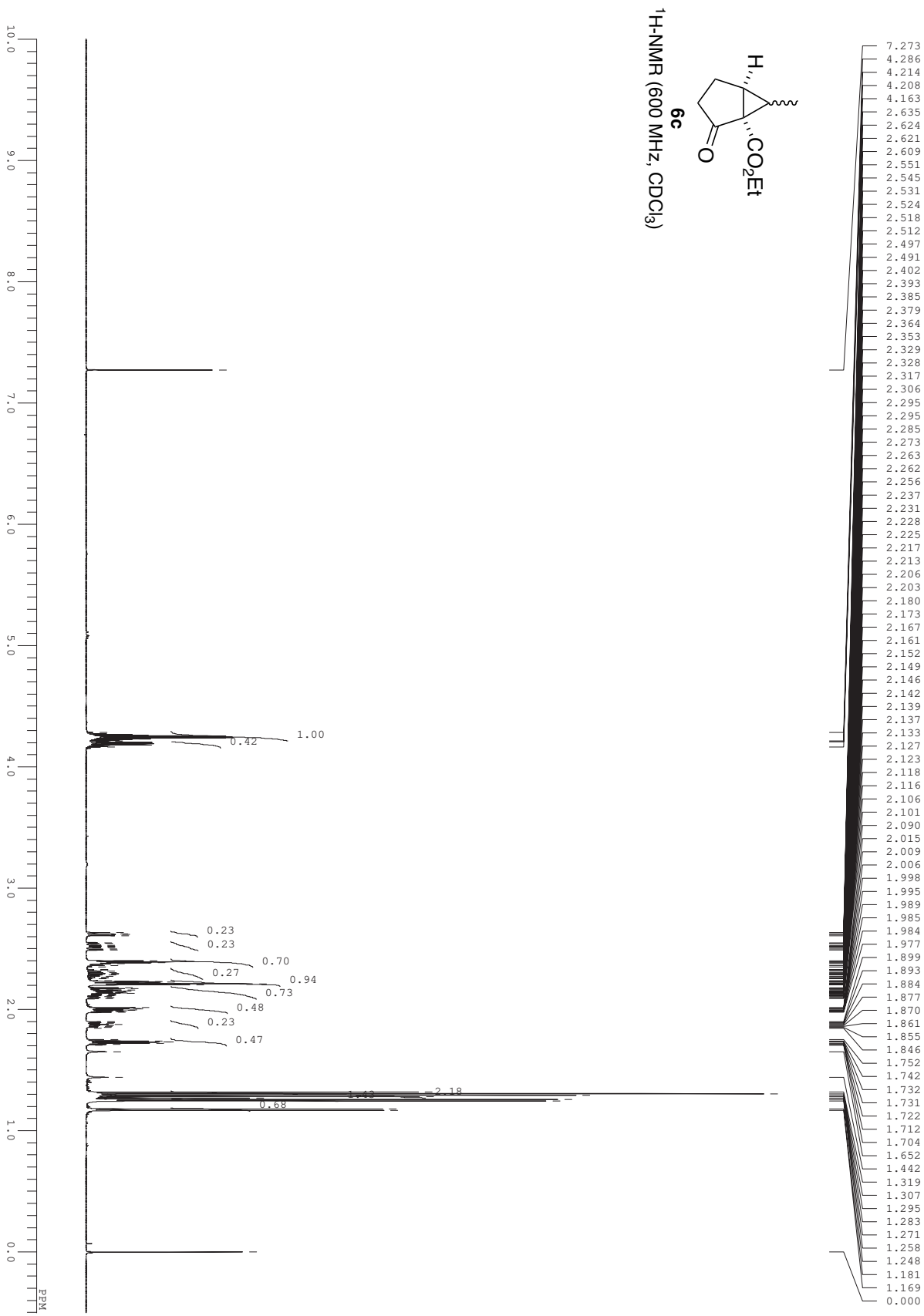

6am
^{13}C-NMR (100 MHz, CDCl$_3$)
206.912
166.976
139.264
133.938
129.402
128.158
77.338
77.025
76.704
58.189
55.036
43.921
41.435
34.083
28.411
26.271
18.112
0.000
PPM

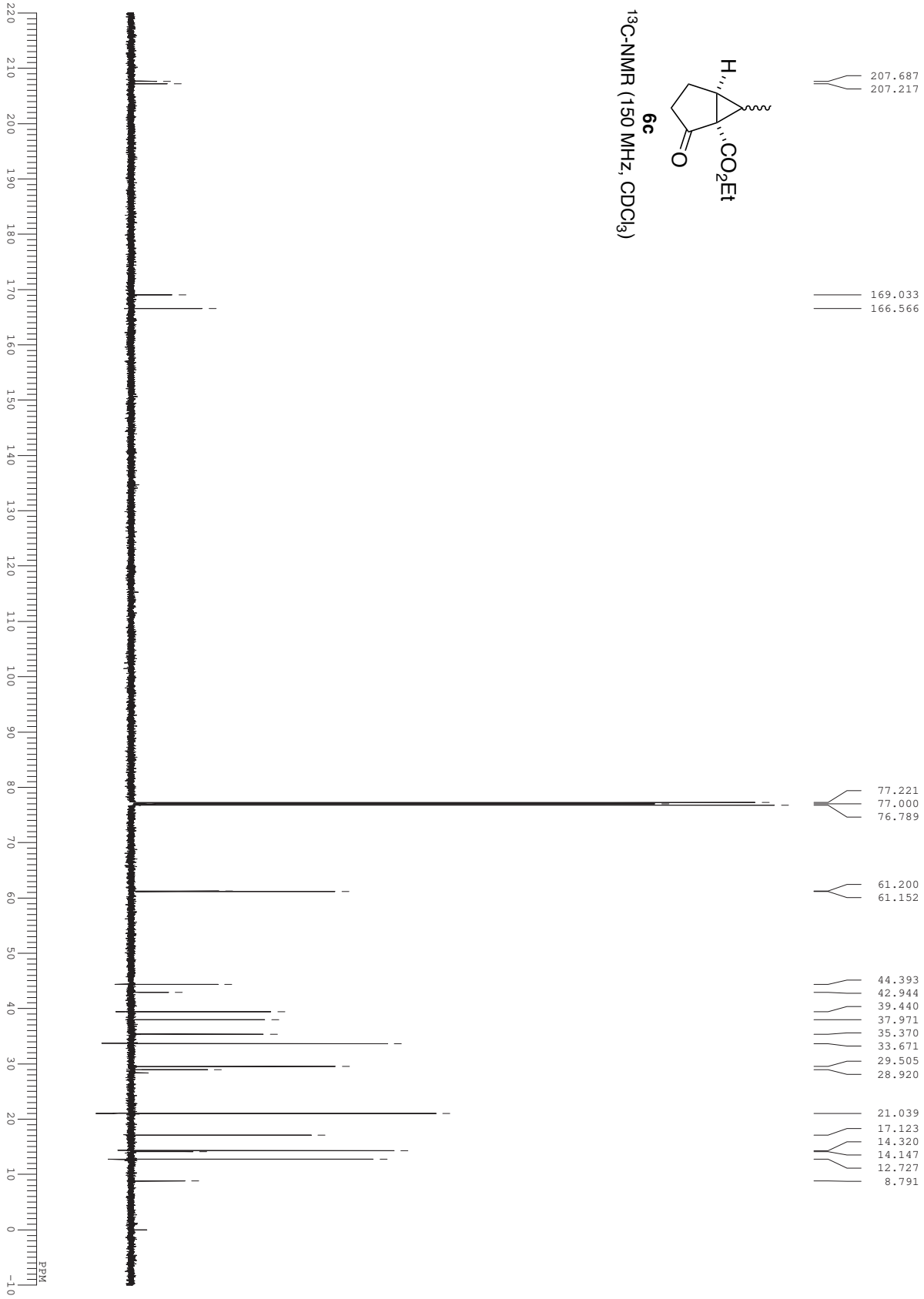

6an
^{1}H-NMR (400 MHz, $CDCl_3$)
7.274
4.255
4.119
2.675
2.538
2.309
2.098
2.053
1.903
1.460
1.448
1.398
0.000
2.08
2.06
6.20
4.17
1.00
3.01
PPM

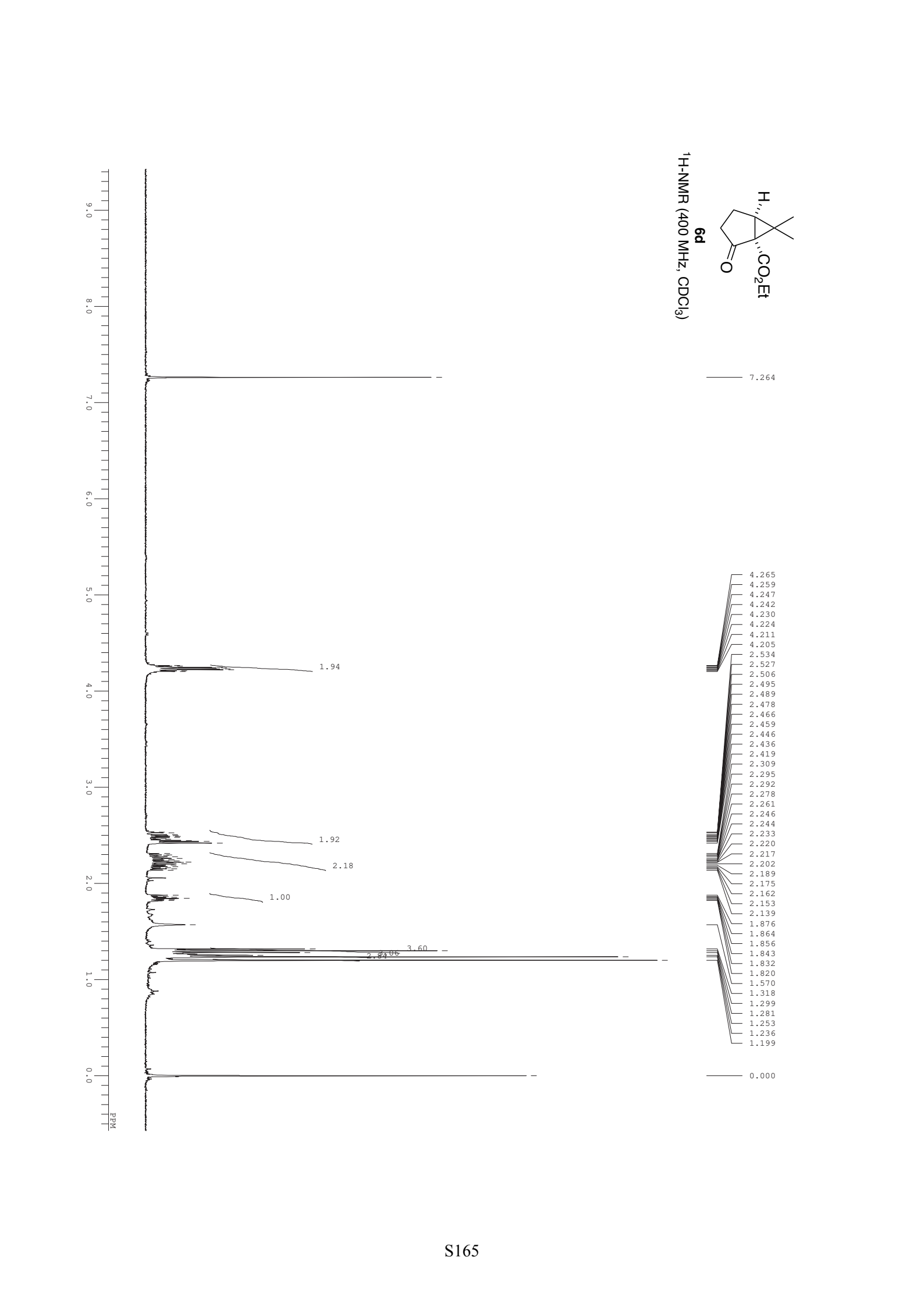

6an
13C-NMR (100 MHz, CDCl3)
207.834
207.735
167.428
64.239
44.374
40.743
39.624
34.149
29.967
28.435
25.982
22.689
18.136
PPM

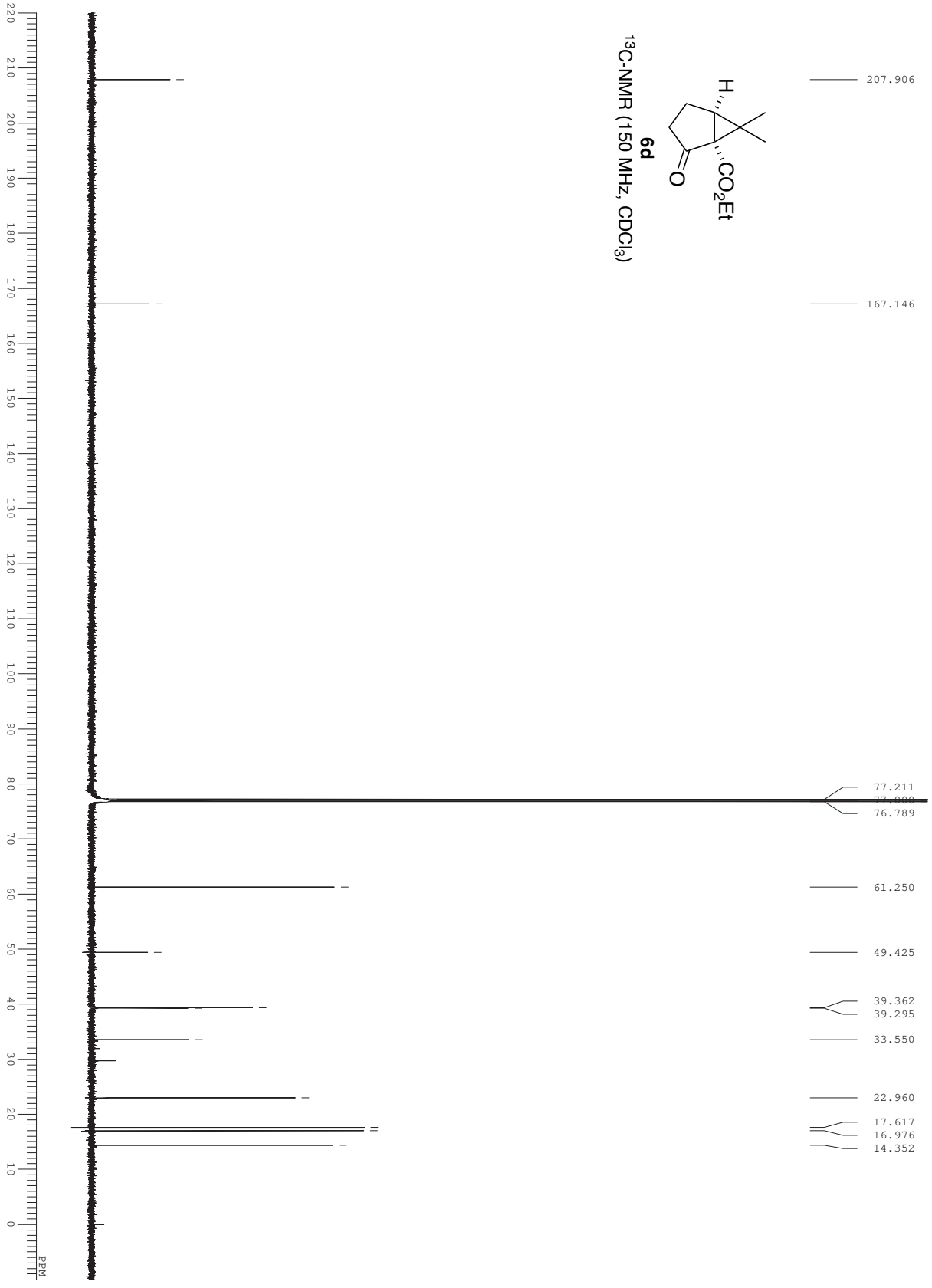

6b
^{1}H-NMR (400 MHz, $CDCl_3$)
CO_2Et
O
7.268
4.239
4.234
4.222
4.216
4.203
4.199
4.185
4.180
2.620
2.573
2.293
2.154
2.068
1.980
1.396
1.384
1.370
1.307
1.288
1.271
0.000
2.09
1.00
3.20
2.17
1.07
3.35
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

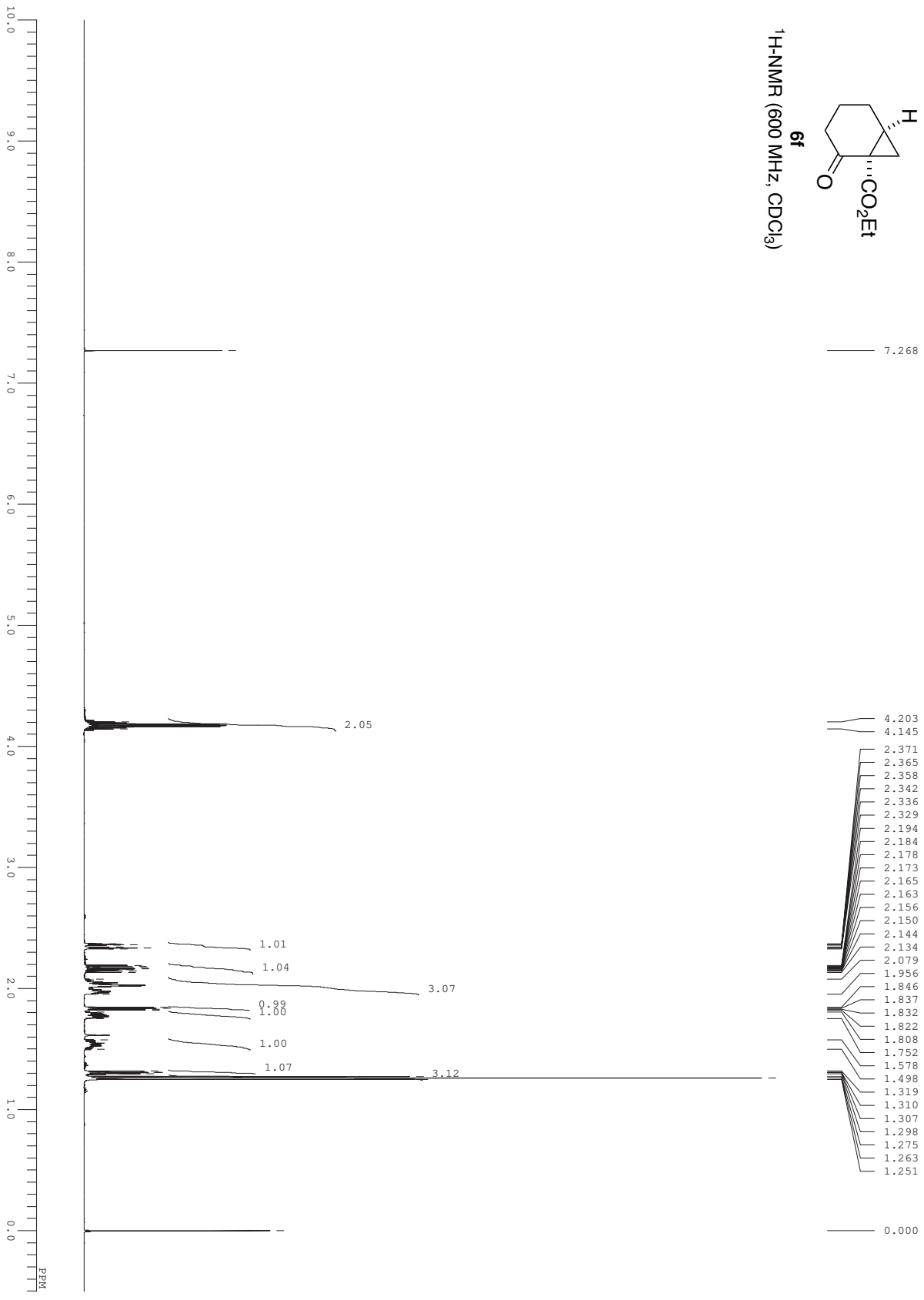

6b
^{13}C-NMR (150 MHz, $CDCl_3$)
CO_2Et
O
207.045
168.334
77.251
77.040
76.819
61.250
37.685
33.701
32.905
22.048
20.945
14.187
PPM

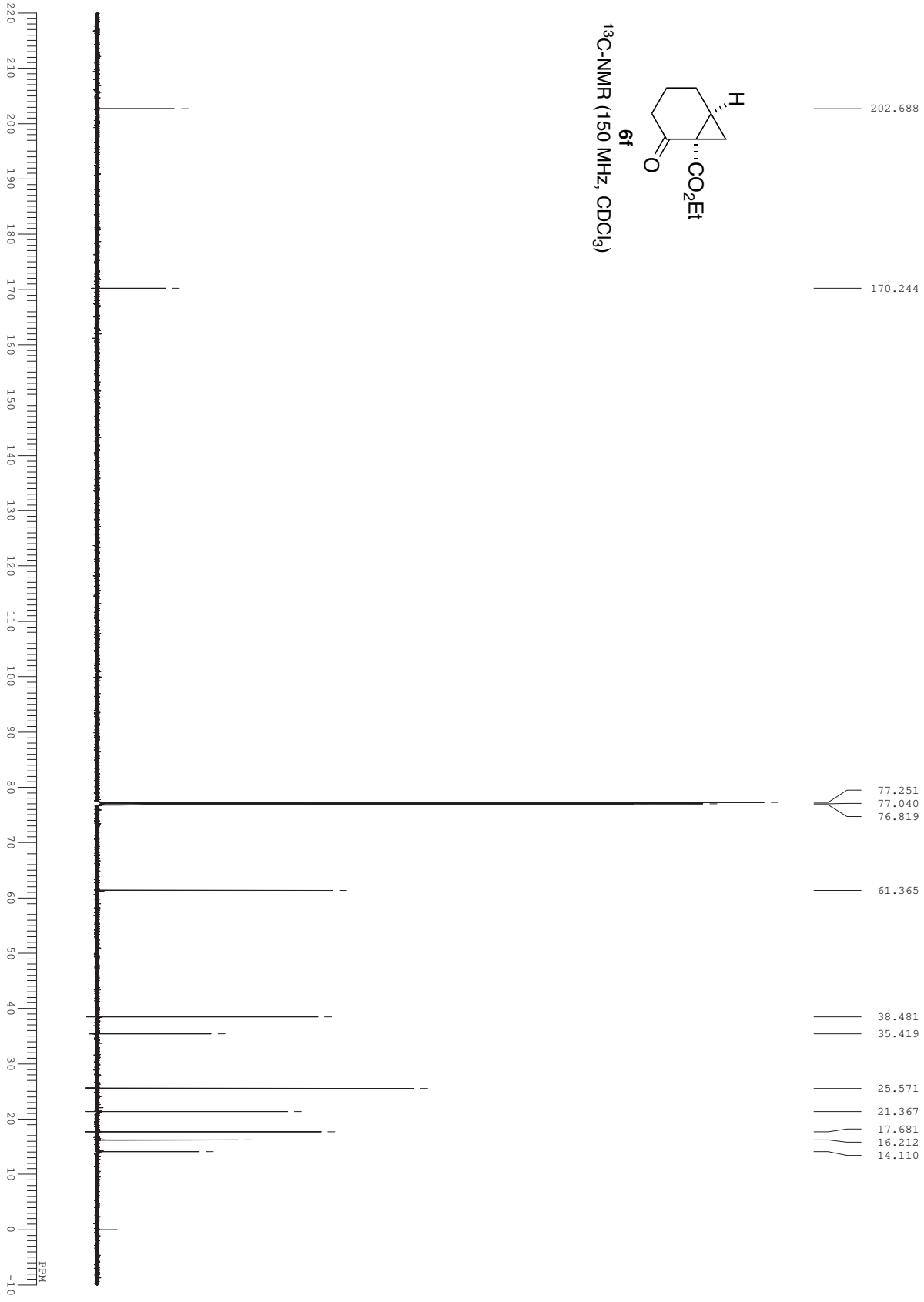

6c
^{1}H-NMR (600 MHz, $CDCl_3$)
H
CO_2Et
O
1.00
0.42
0.23
0.23
0.70
0.27
0.94
0.73
0.48
0.23
0.47
2.18
0.68
PPM

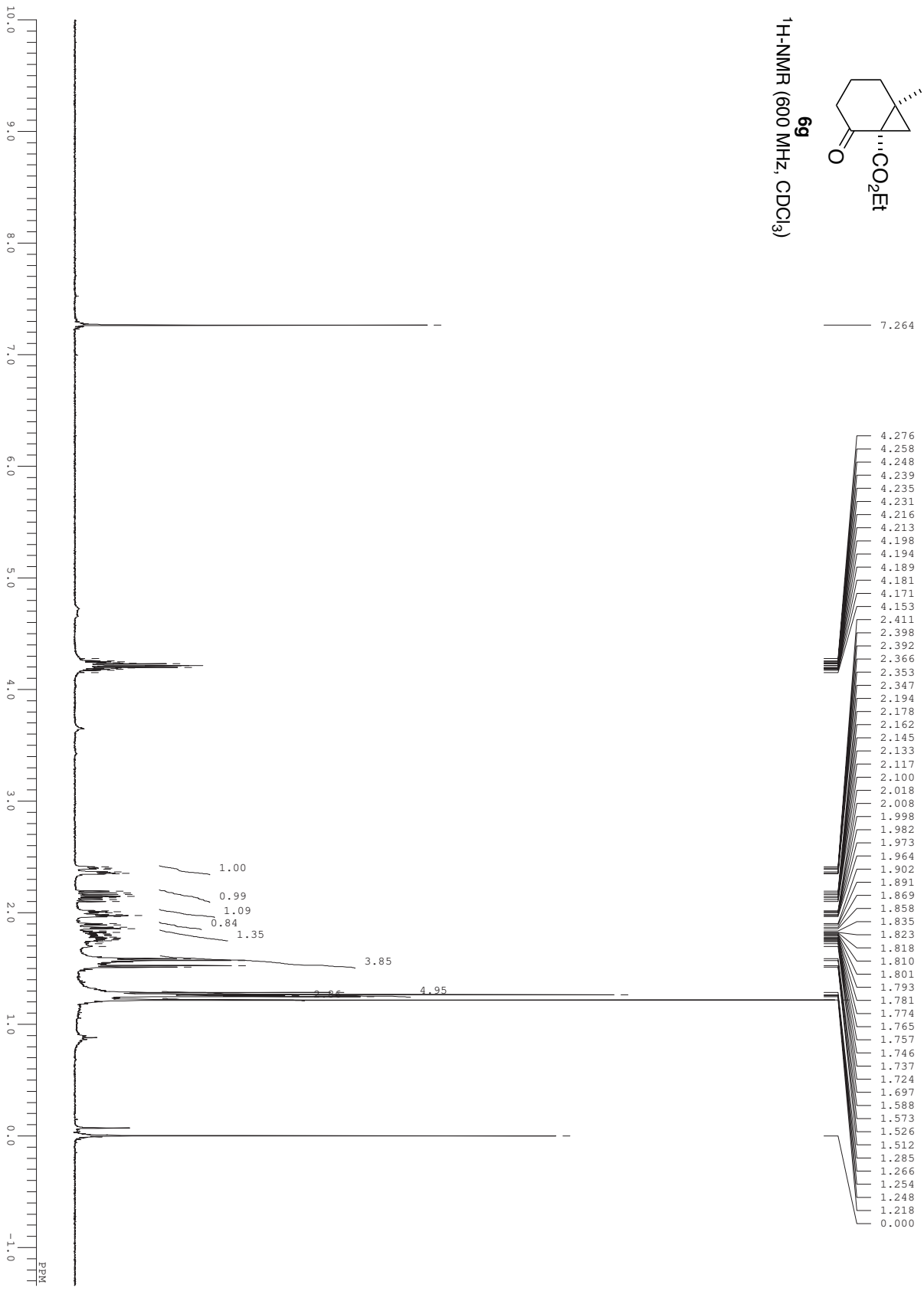

13C-NMR (150 MHz, CDCl3)
6c
H
CO2Et
O
207.687
207.217
169.033
166.566
77.221
77.000
76.789
61.200
61.152
44.393
42.944
39.440
37.971
35.370
33.671
29.505
28.920
21.039
17.123
14.320
14.147
12.727
8.791
PPM

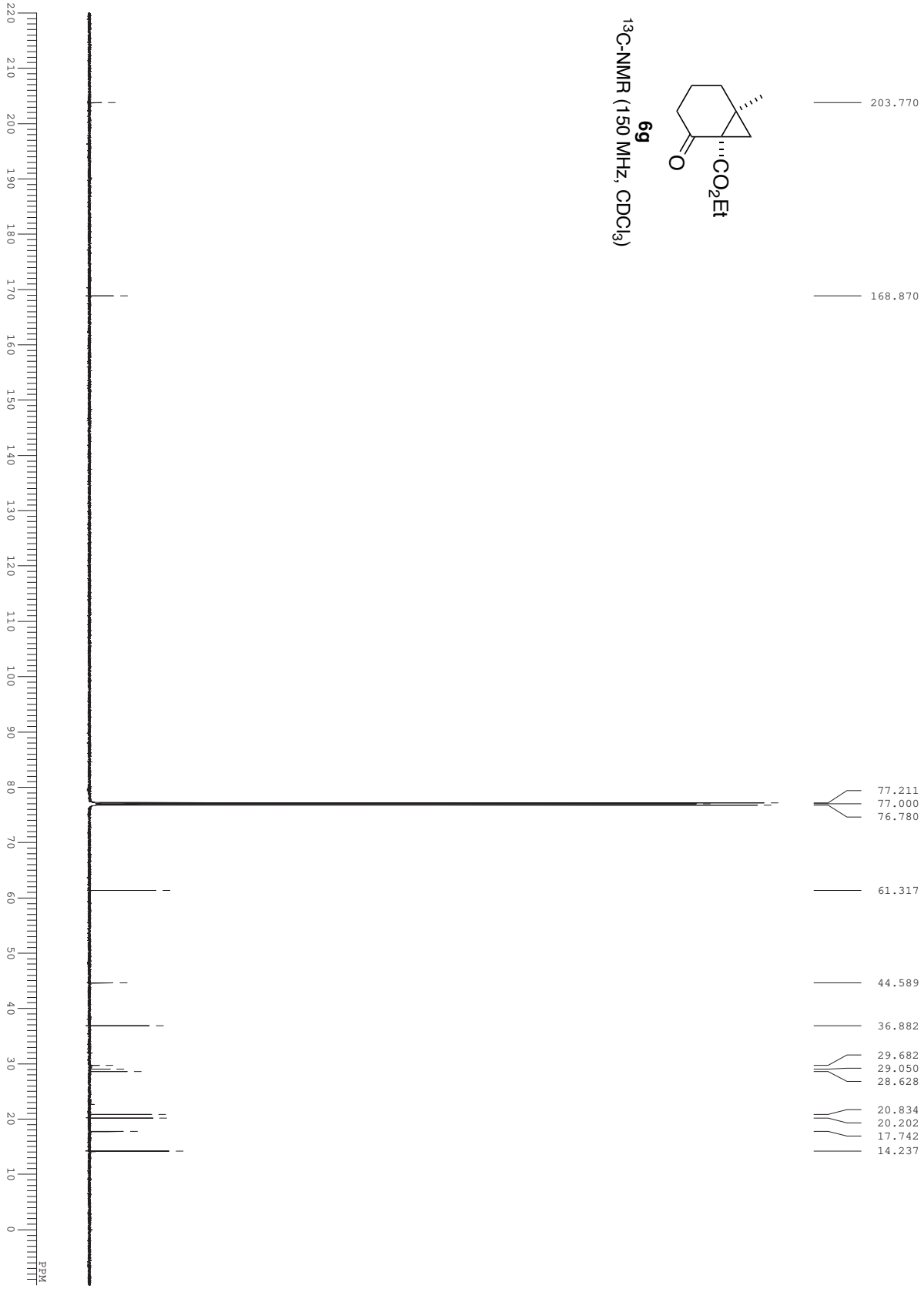

6d
1H-NMR (400 MHz, CDCl3)
H
CO2Et
O
7.264
4.265
4.259
4.247
4.242
4.230
4.224
4.211
4.205
2.534
2.527
2.506
2.495
2.489
2.478
2.466
2.459
2.446
2.436
2.419
2.309
2.295
2.292
2.278
2.261
2.246
2.244
2.233
2.220
2.217
2.202
2.189
2.175
2.162
2.153
2.139
1.876
1.864
1.856
1.843
1.832
1.820
1.570
1.318
1.299
1.281
1.253
1.236
1.199
0.000
1.94
1.92
2.18
1.00
3.60
2.84
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

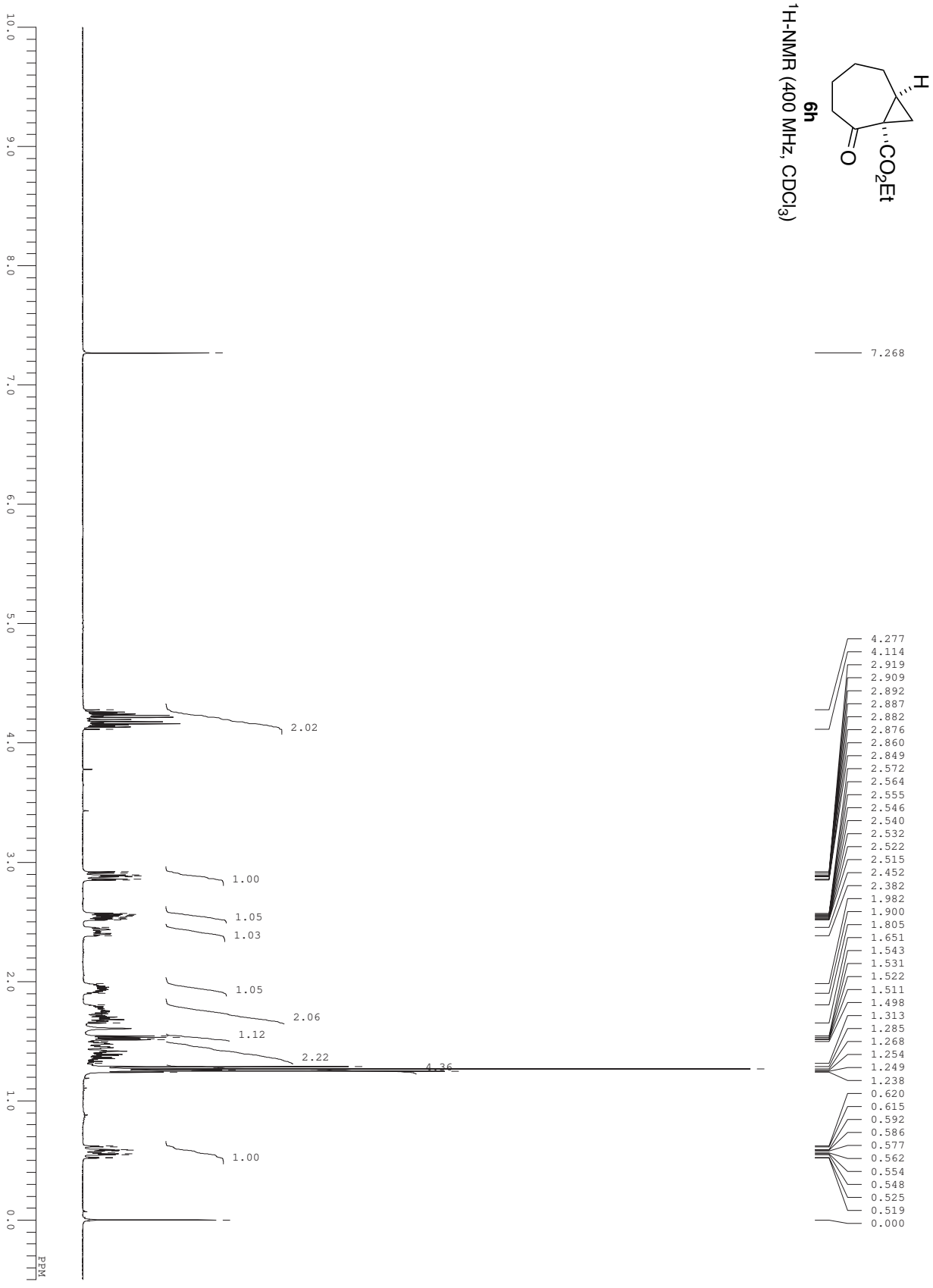

6d
^{13}C-NMR (150 MHz, $CDCl_3$)
H
CO_2Et
O
207.906
167.146
77.211
77.000
76.789
61.250
49.425
39.362
39.295
33.550
22.960
17.617
16.976
14.352
PPM

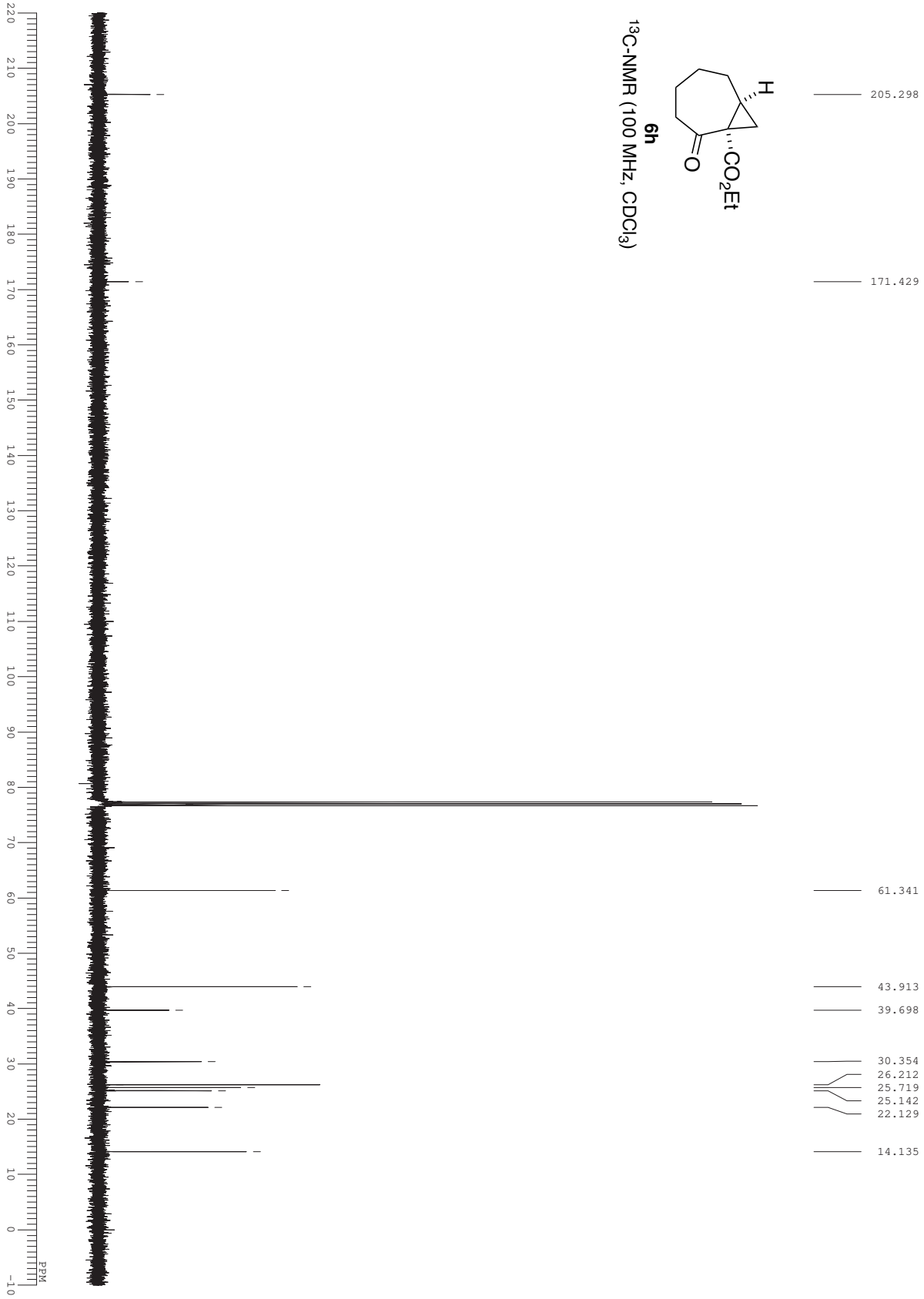

6f
^{1}H-NMR (600 MHz, CDCl$_3$)
H
CO$_2$Et
O
7.268
4.203
4.145
2.371
2.365
2.358
2.342
2.336
2.329
2.194
2.184
2.178
2.173
2.165
2.163
2.156
2.150
2.144
2.134
2.079
1.956
1.846
1.837
1.832
1.822
1.808
1.752
1.578
1.498
1.319
1.310
1.307
1.298
1.275
1.263
1.251
0.000
2.05
1.01
1.04
3.07
0.99
1.00
1.00
1.07
3.12
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

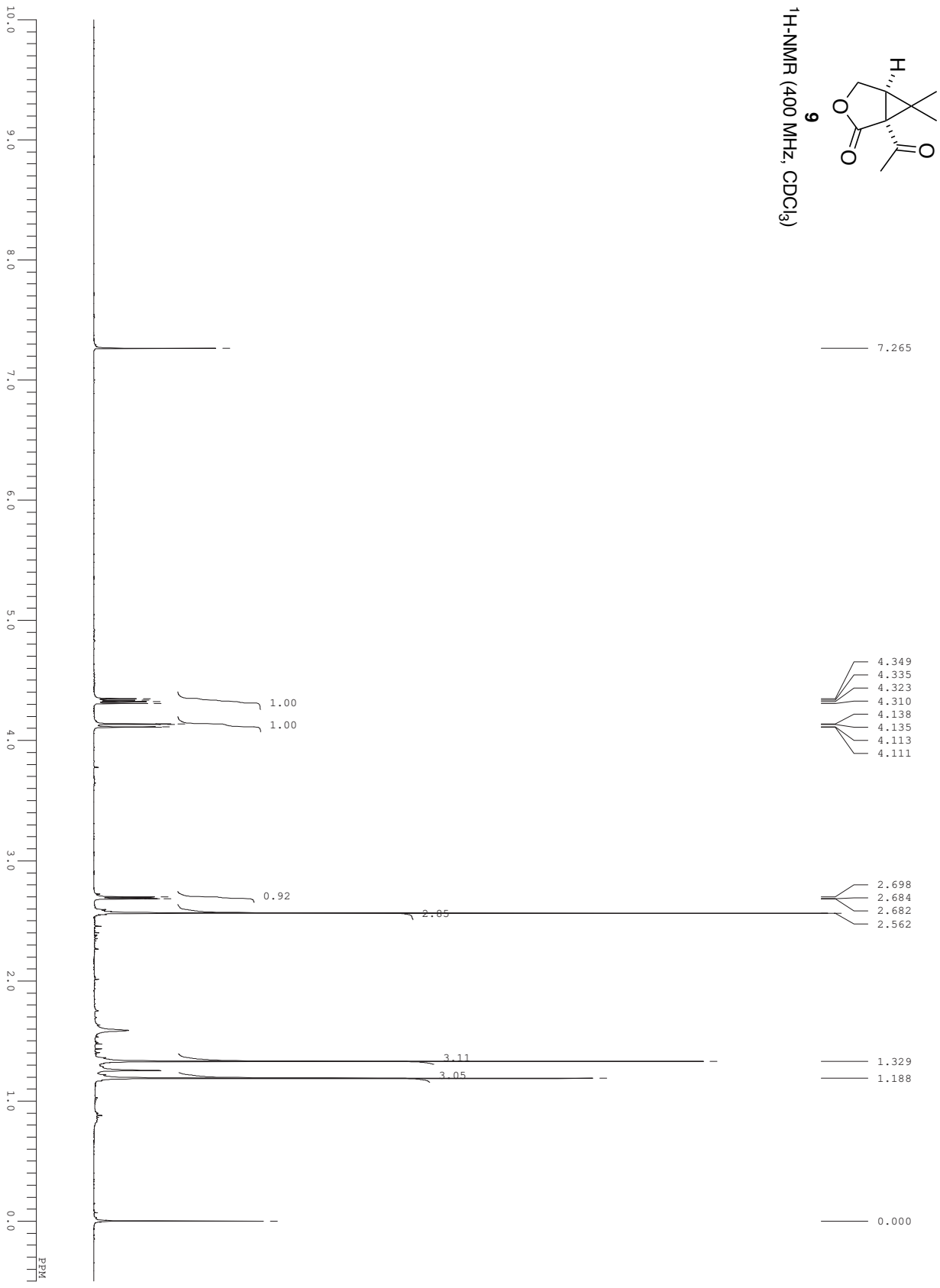

13C-NMR (150 MHz, CDCl3)
6f
H
CO2Et
O
202.688
170.244
77.251
77.040
76.819
61.365
38.481
35.419
25.571
21.367
17.681
16.212
14.110
PPM

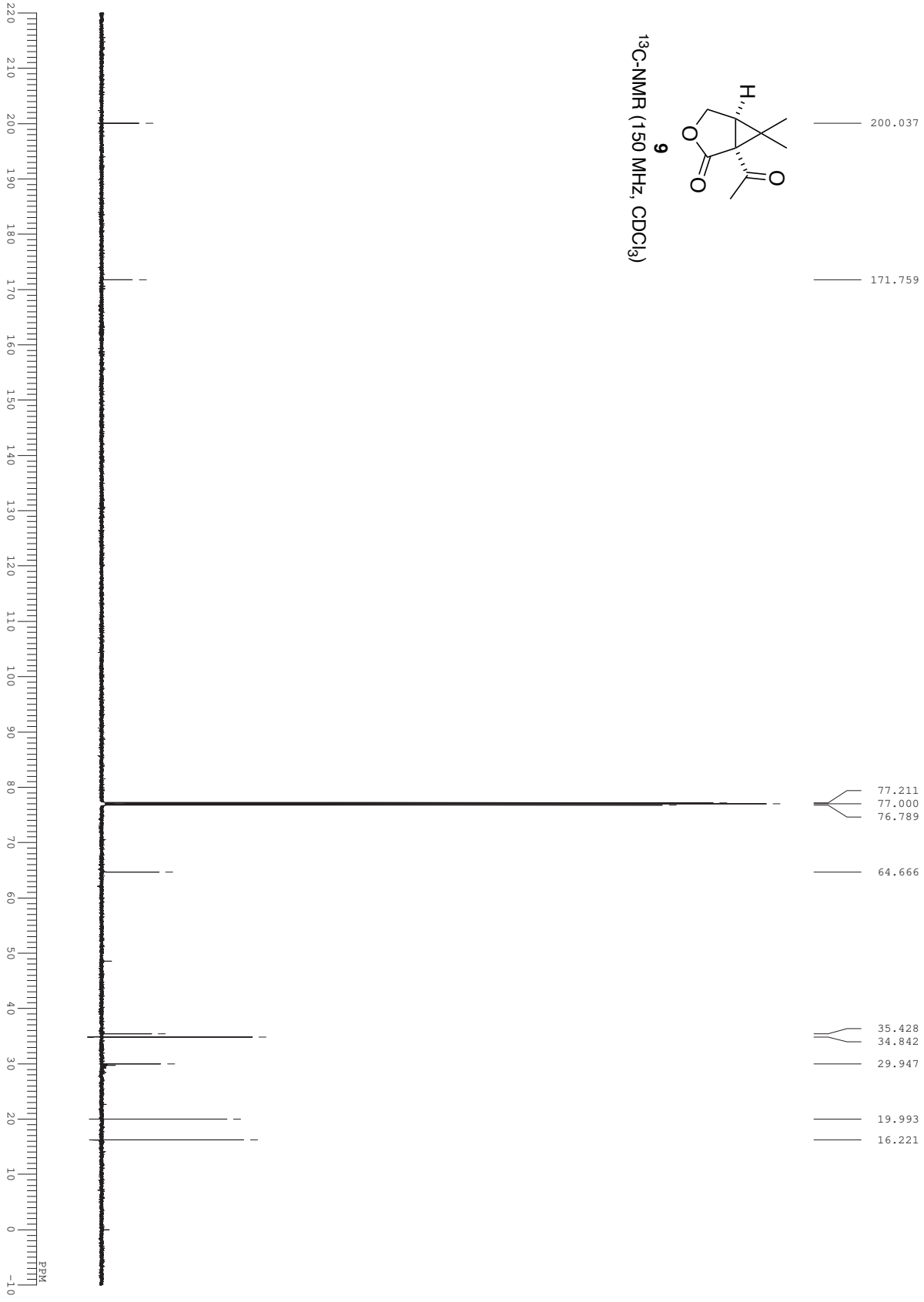

6g
^{1}H-NMR (600 MHz, CDCl$_3$)
O
CO$_2$Et
7.264
4.276
4.258
4.248
4.239
4.235
4.231
4.216
4.213
4.198
4.194
4.189
4.181
4.171
4.153
2.411
2.398
2.392
2.366
2.353
2.347
2.194
2.178
2.162
2.145
2.133
2.117
2.100
2.018
2.008
1.998
1.982
1.973
1.964
1.902
1.891
1.869
1.858
1.835
1.823
1.818
1.810
1.801
1.793
1.781
1.774
1.765
1.757
1.746
1.737
1.724
1.697
1.588
1.573
1.526
1.512
1.285
1.266
1.254
1.248
1.218
0.000
1.00
0.99
1.09
0.84
1.35
3.85
4.95
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
PPM

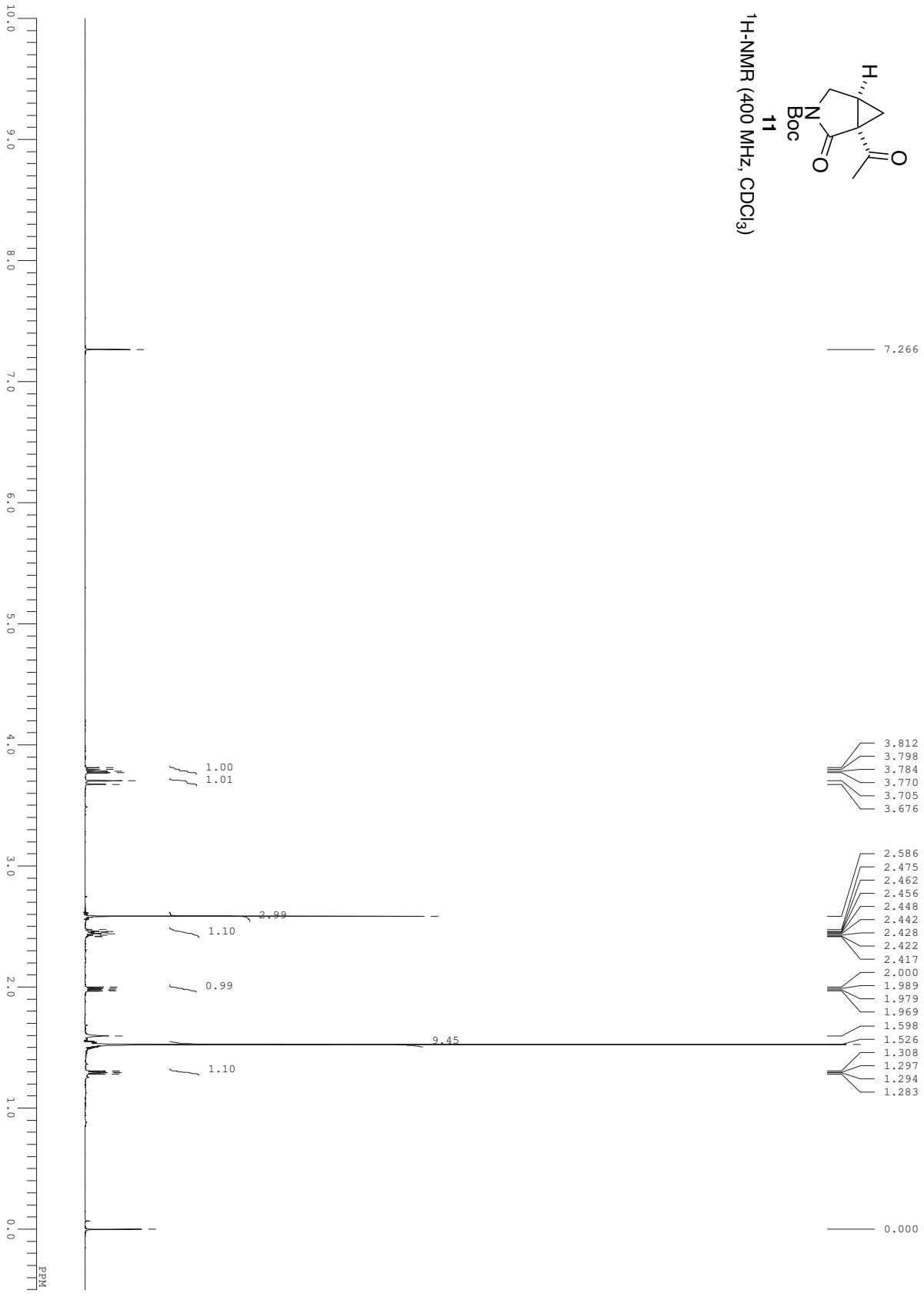

6g
^{13}C-NMR (150 MHz, CDCl$_3$)
CO$_2$Et
O
203.770
168.870
77.211
77.000
76.780
61.317
44.589
36.882
29.682
29.050
28.628
20.834
20.202
17.742
14.237
PPM

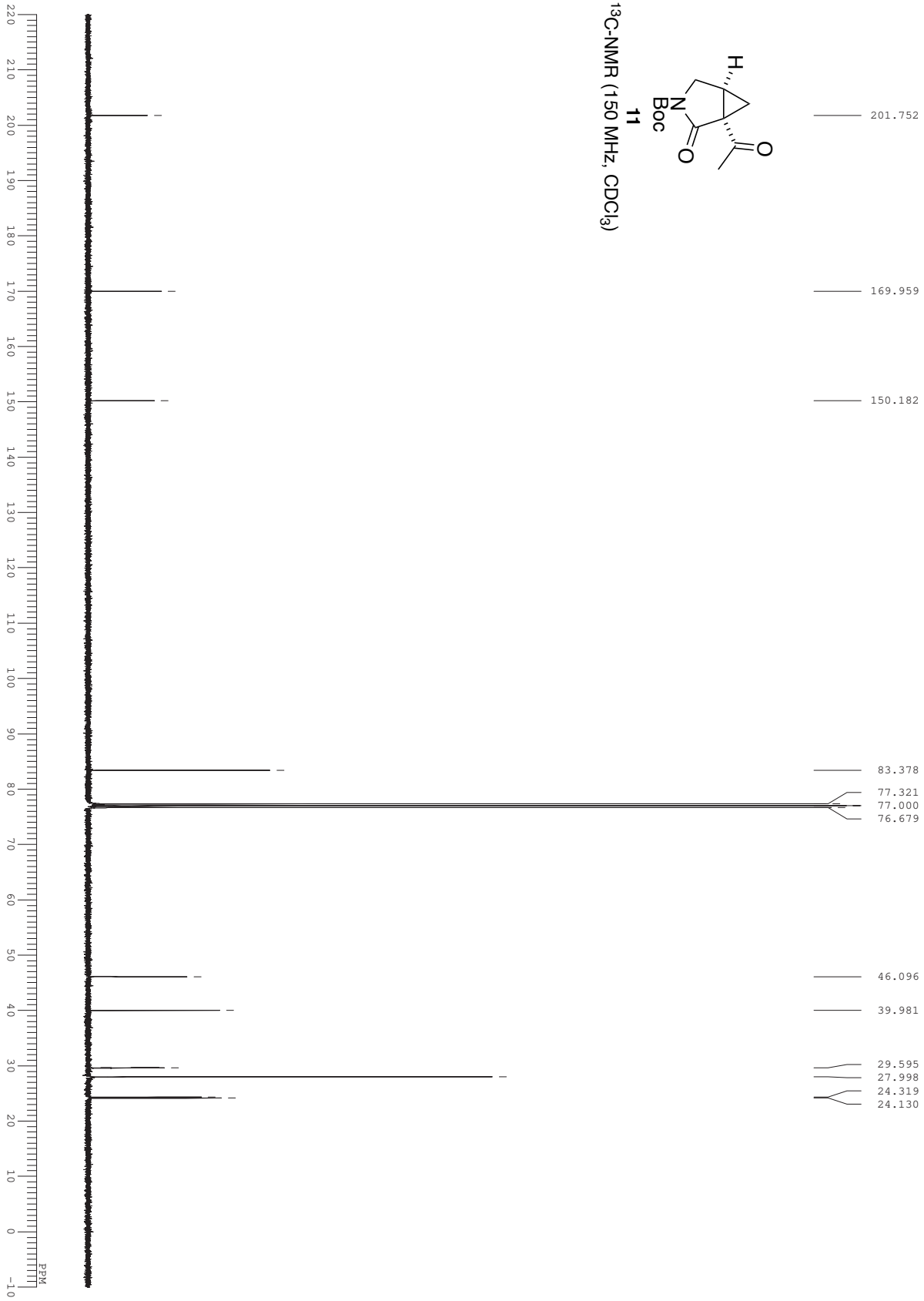

6h
^{1}H-NMR (400 MHz, CDCl$_3$)
H
CO$_2$Et
O
7.268
4.277
4.114
2.919
2.909
2.892
2.887
2.882
2.876
2.860
2.849
2.572
2.564
2.555
2.546
2.540
2.532
2.522
2.515
2.452
2.382
1.982
1.900
1.805
1.651
1.543
1.531
1.522
1.511
1.498
1.313
1.285
1.268
1.254
1.249
1.238
0.620
0.615
0.592
0.586
0.577
0.562
0.554
0.548
0.525
0.519
0.000
2.02
1.00
1.05
1.03
1.05
2.06
1.12
2.22
4.36
1.00
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

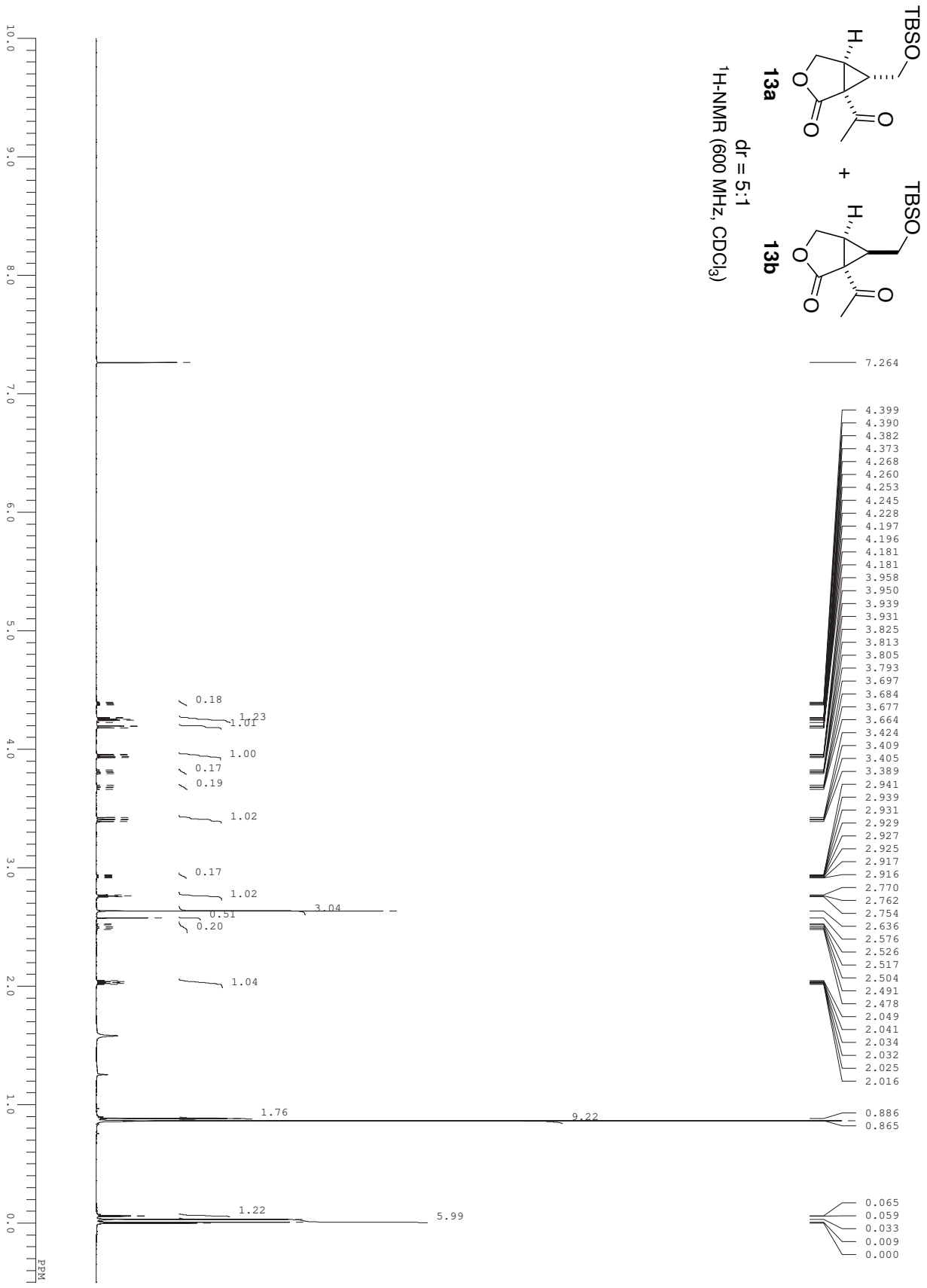

6h
^{13}C-NMR (100 MHz, $CDCl_3$)
H
CO_2Et
O
205.298
171.429
61.341
43.913
39.698
30.354
26.212
25.719
25.142
22.129
14.135
PPM

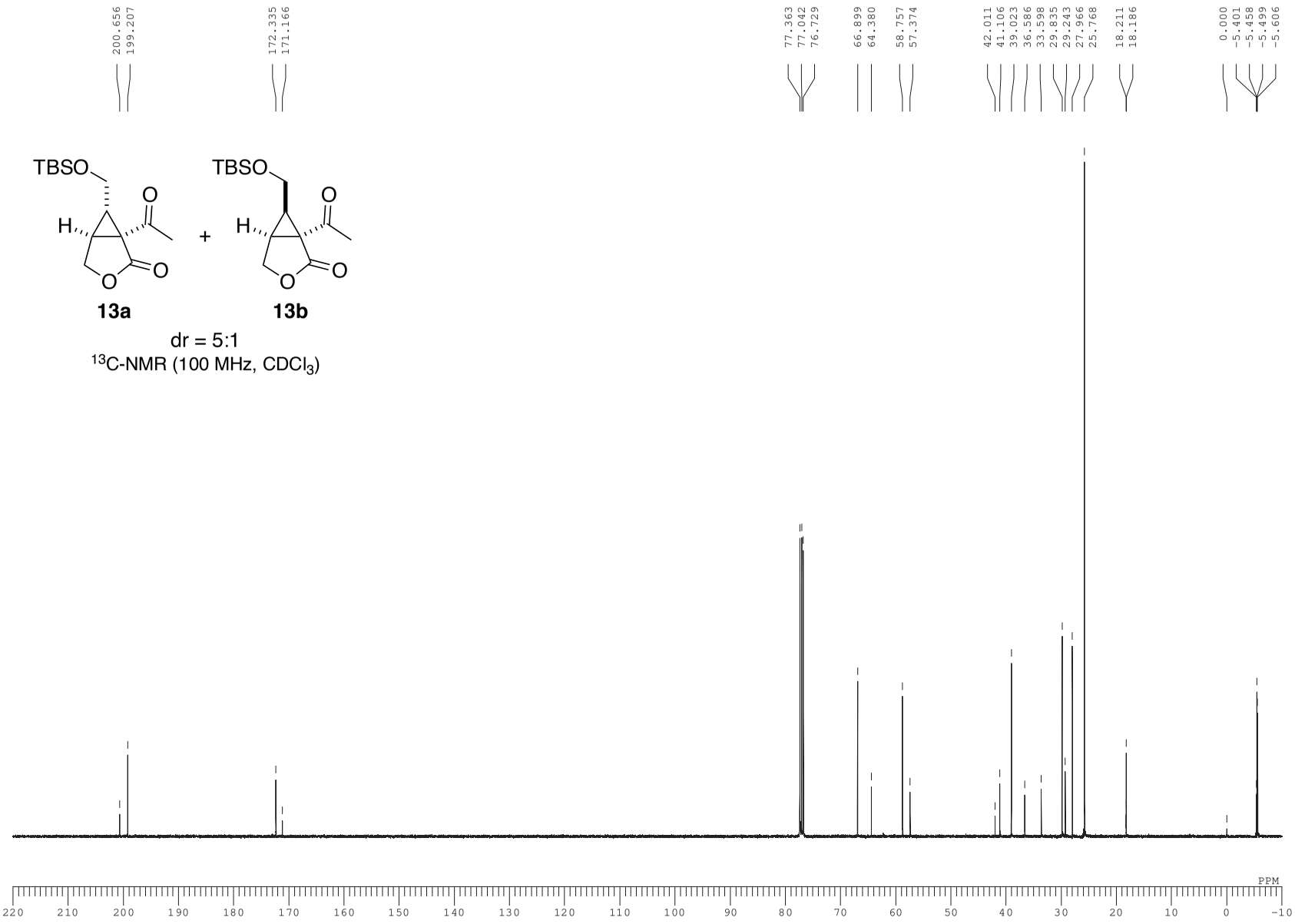

9
1H-NMR (400 MHz, CDCl3)
7.265
4.349
4.335
4.323
4.310
4.138
4.135
4.113
4.111
2.698
2.684
2.682
2.562
1.329
1.188
0.000
1.00
1.00
0.92
2.05
3.11
3.05
PPM

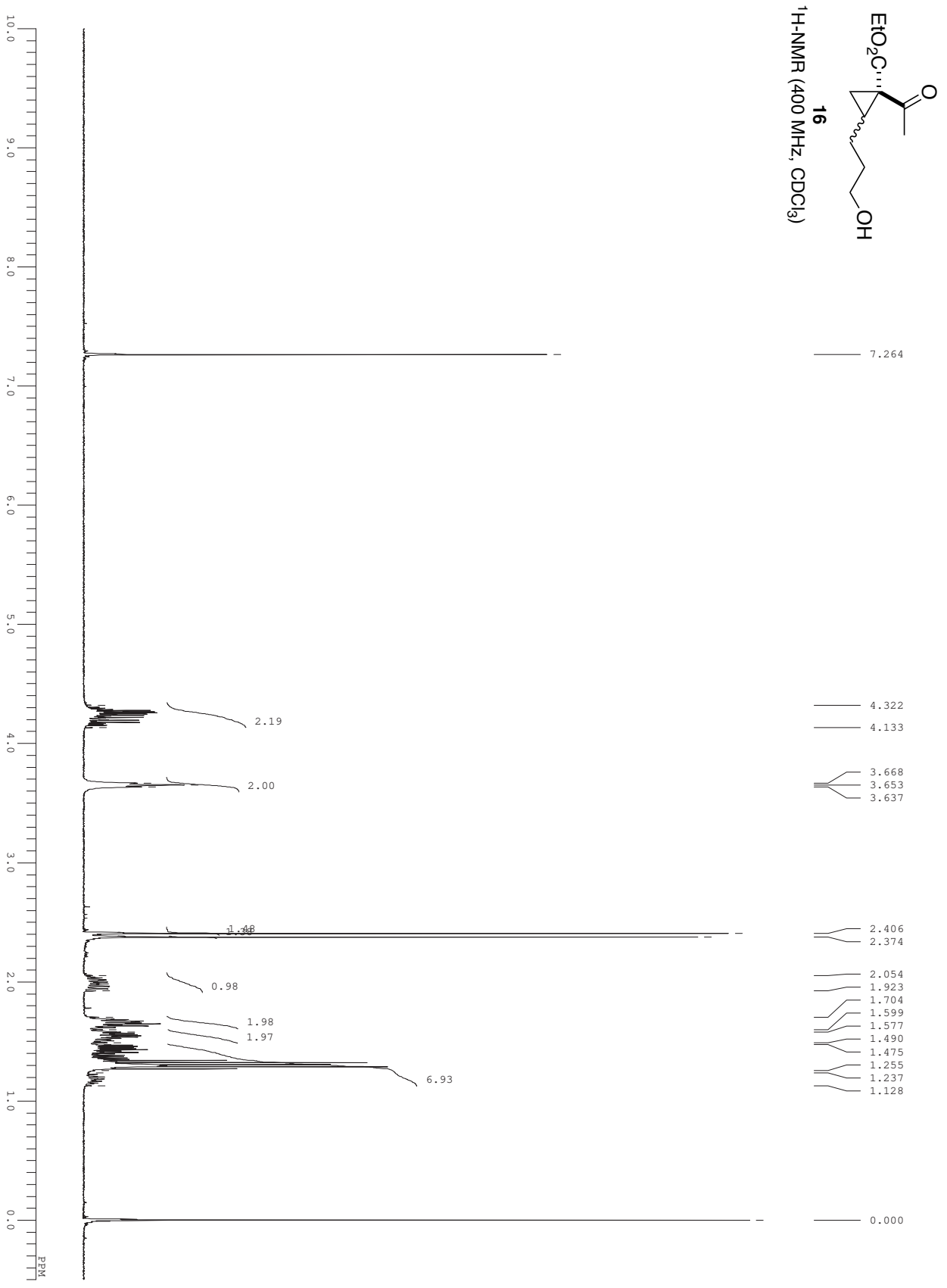

9
^{13}C-NMR (150 MHz, $CDCl_3$)
200.037
171.759
77.211
77.000
76.789
64.666
35.428
34.842
29.947
19.993
16.221
PPM

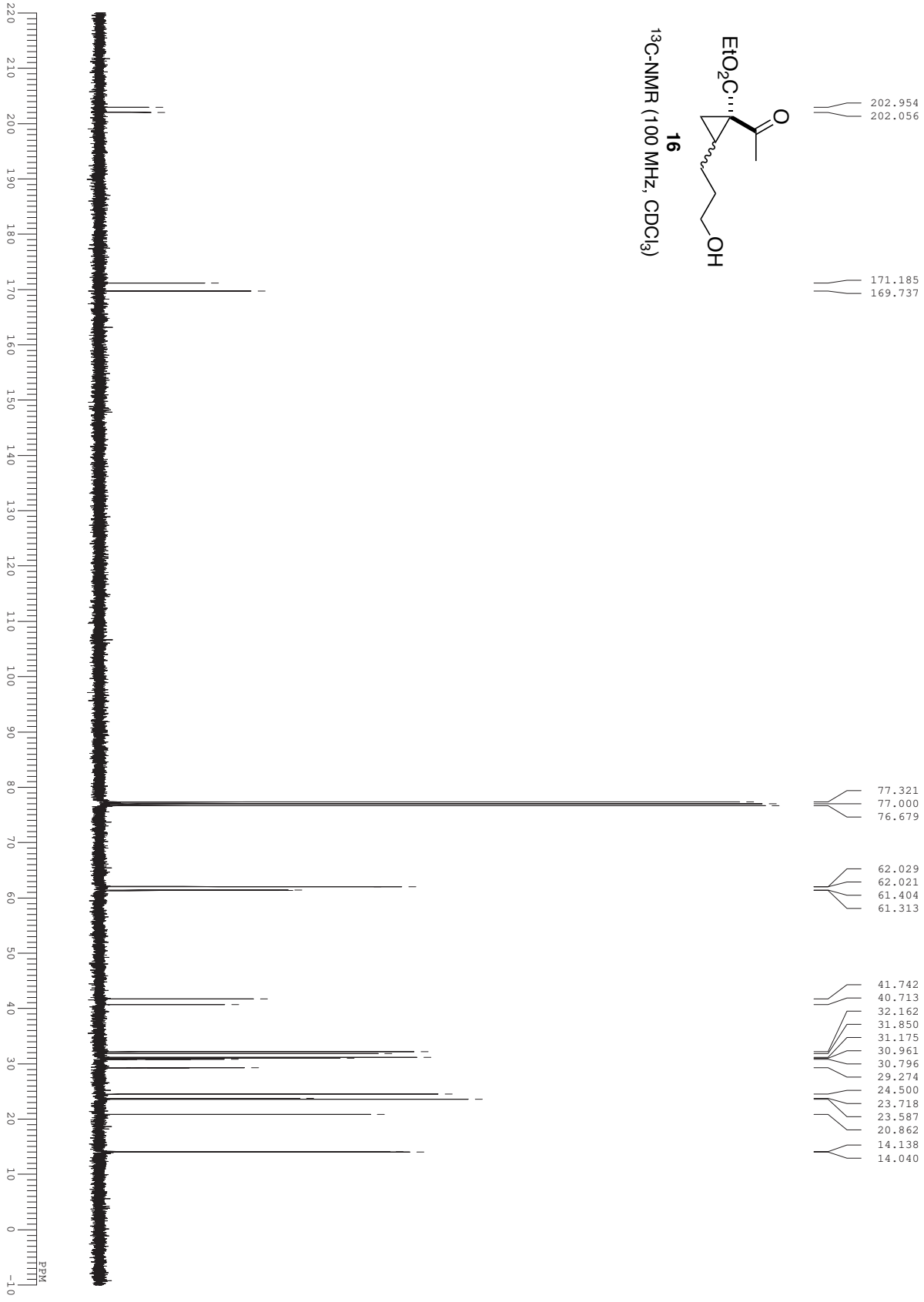

11
1H-NMR (400 MHz, CDCl3)
Boc
N
O
O
H
7.266
3.812
3.798
3.784
3.770
3.705
3.676
2.586
2.475
2.462
2.456
2.448
2.442
2.428
2.422
2.417
2.000
1.989
1.979
1.969
1.598
1.526
1.308
1.297
1.294
1.283
0.000
1.00
1.01
2.99
1.10
0.99
9.45
1.10
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM

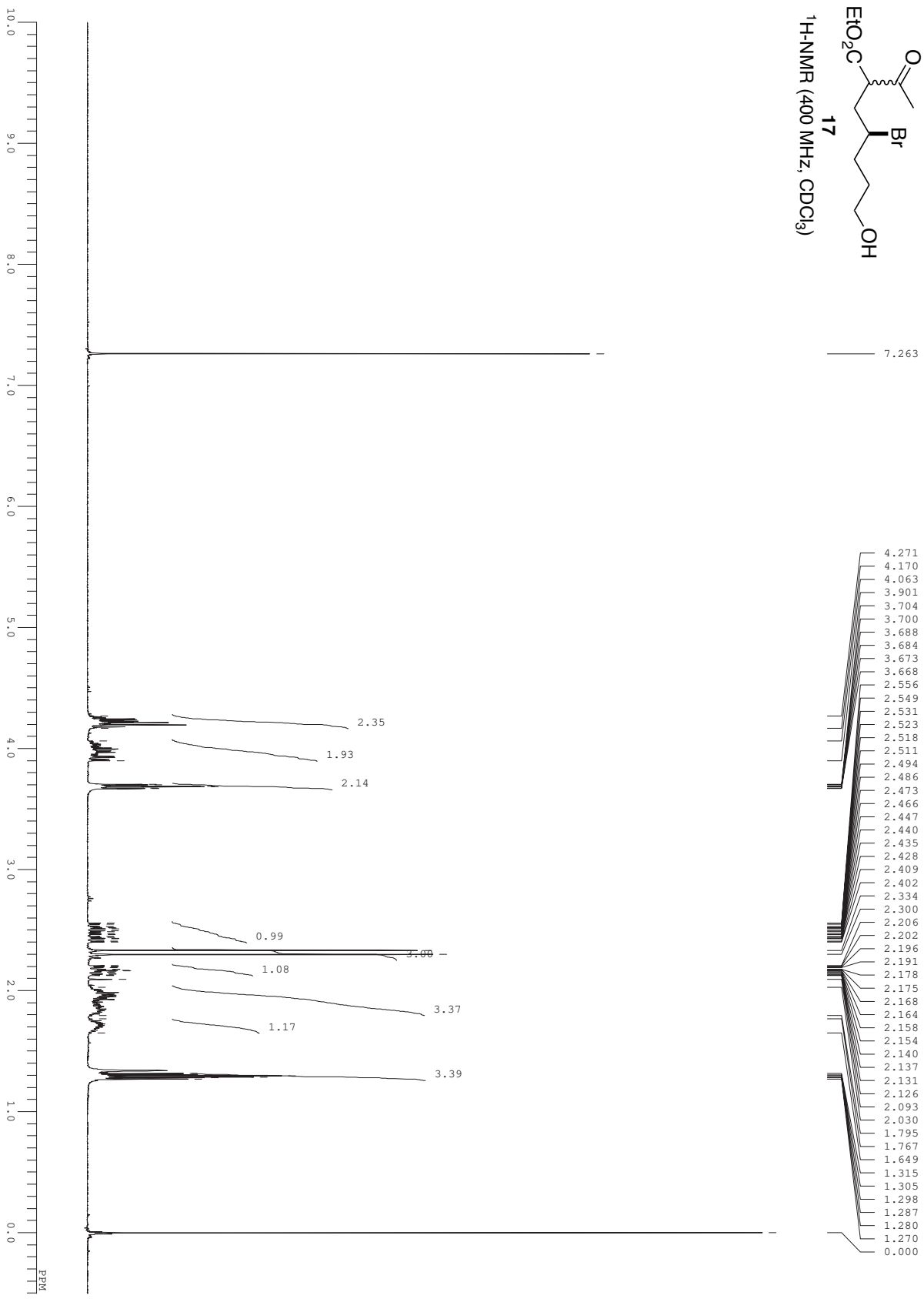

11
13C-NMR (150 MHz, CDCl3)
N
Boc
O
O
H
201.752
169.959
150.182
83.378
77.321
77.000
76.679
46.096
39.981
29.595
27.998
24.319
24.130
PPM

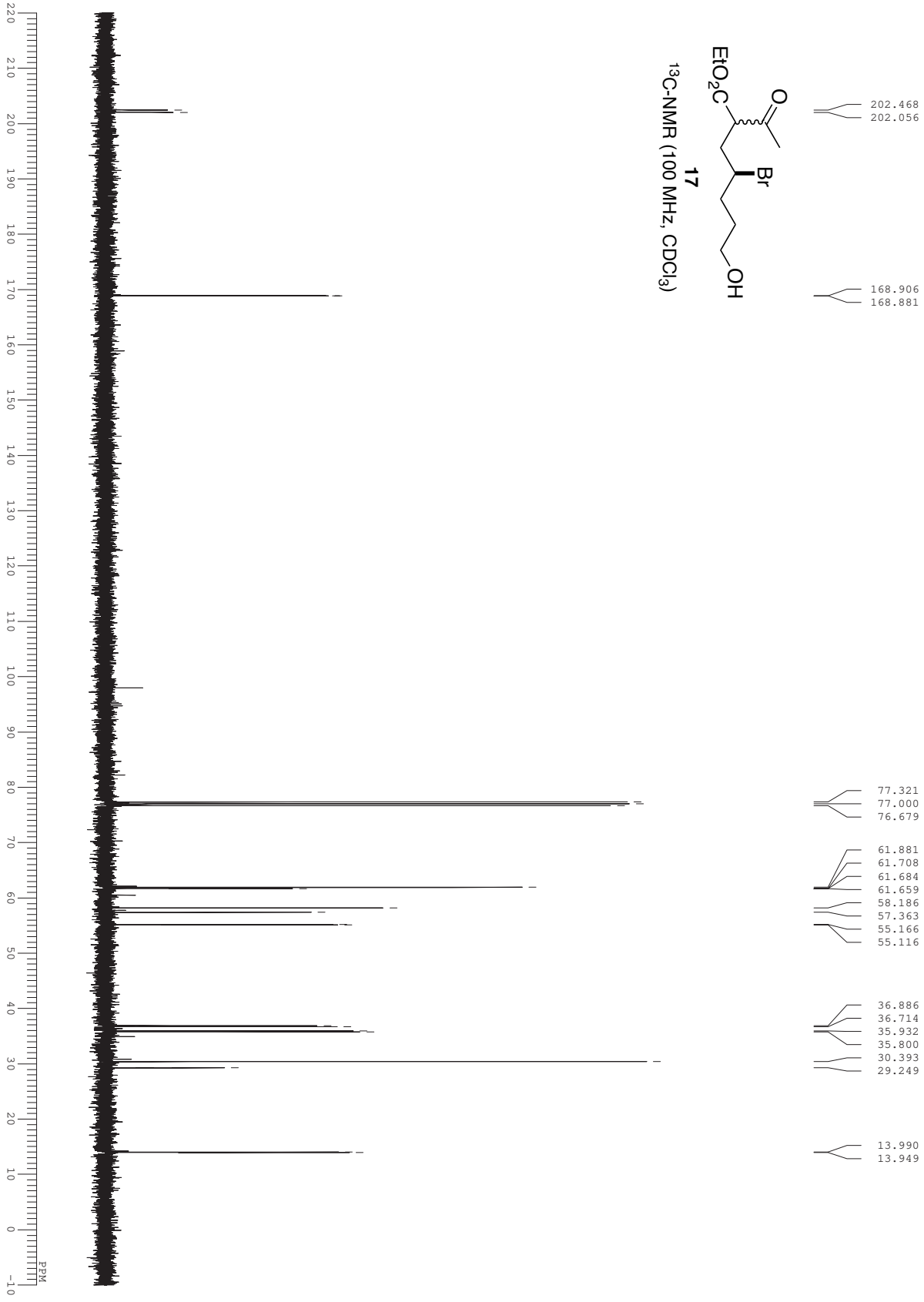

TBSO
H
O
O
O
13a
+
TBSO
H
O
O
O
13b
dr = 5:1
1H-NMR (600 MHz, CDCl3)
7.264
4.399
4.390
4.382
4.373
4.268
4.260
4.253
4.245
4.228
4.197
4.196
4.181
4.181
3.958
3.950
3.939
3.931
3.825
3.813
3.805
3.793
3.697
3.684
3.677
3.664
3.424
3.409
3.405
3.389
2.941
2.939
2.931
2.929
2.927
2.925
2.917
2.916
2.770
2.762
2.754
2.636
2.576
2.526
2.517
2.504
2.491
2.478
2.049
2.041
2.034
2.032
2.025
2.016
0.886
0.865
0.065
0.059
0.033
0.009
0.000
0.18
1.23
1.01
1.00
0.17
0.19
1.02
0.17
1.02
3.04
0.51
0.20
1.04
1.76
9.22
1.22
5.99
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


200.656
199.207
172.335
171.166
77.363
77.042
76.729
66.899
64.380
58.757
57.374
42.011
41.106
39.023
36.586
33.598
29.835
29.243
27.966
25.768
18.211
18.186
0.000
-5.401
-5.458
-5.499
-5.606
TBSO
O
H
O
O
+
TBSO
O
H
O
O
13a
13b
dr = 5:1
13C-NMR (100 MHz, CDCl3)
PPM
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10


EtO2C
O
OH
16
1H-NMR (400 MHz, CDCl3)
7.264
4.322
4.133
3.668
3.653
3.637
2.406
2.374
2.054
1.923
1.704
1.599
1.577
1.490
1.475
1.255
1.237
1.128
0.000
2.19
2.00
0.98
1.98
1.97
6.93
PPM


16
13C-NMR (100 MHz, CDCl3)
EtO2C
O
OH
202.954
202.056
171.185
169.737
77.321
77.000
76.679
62.029
62.021
61.404
61.313
41.742
40.713
32.162
31.850
31.175
30.961
30.796
29.274
24.500
23.718
23.587
20.862
14.138
14.040
PPM


EtO2C
O
Br
OH
17
1H-NMR (400 MHz, CDCl3)
7.263
4.271
4.170
4.063
3.901
3.704
3.700
3.688
3.684
3.673
3.668
2.556
2.549
2.531
2.523
2.518
2.511
2.494
2.486
2.473
2.466
2.447
2.440
2.435
2.428
2.409
2.402
2.334
2.300
2.206
2.202
2.196
2.191
2.178
2.175
2.168
2.164
2.158
2.154
2.140
2.137
2.131
2.126
2.093
2.030
1.795
1.767
1.649
1.315
1.305
1.298
1.287
1.280
1.270
0.000
2.35
1.93
2.14
0.99
3.00
1.08
3.37
1.17
3.39
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
PPM


17
^{13}C-NMR (100 MHz, $CDCl_3$)
EtO_2C
O
Br
OH
202.468
202.056
168.906
168.881
77.321
77.000
76.679
61.881
61.708
61.684
61.659
58.186
57.363
55.166
55.116
36.886
36.714
35.932
35.800
30.393
29.249
13.990
13.949
PPM