Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Access to 5-bromopentanal and 6-bromohexanal derivatives via bromination / hydrolysis of C,O-bis-zirconocenes generated from unsaturated Weinreb amides.

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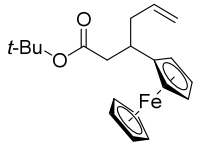
Electronic Supplementary Information

Experimental procedures and characterization of compounds.

All reactions involving organometallics were conducted under an atmosphere of argon. ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$, unless specified, on a Bruker AC-500. Samples were analyzed by Q-TOF HRMS system. The analysis was performed on a Waters SYNAPT G2-Si High Resolution Mass Spectrometry equipped with electrospray ionization (ESI) source (Waters Corp., Manchester, UK). Mass detection was conducted in positive ion mode, with the source temperature at 120◦C, capillary voltage and cone voltage were set at 3 KV and 40 V. The desolvation gas was optimized to 900 L/h, the cone gas flow of 50 L/h and the scan range was from 50 to 2000 m/z. Samples were analyzed in infusion mode and the mass was corrected during acquisition using external reference (Lock-Spray) consisting of a 1 ng/µL solution of leucine encephalin at a flow rate of 5 µL/min, in order to make sure the accuracy and reproducibility during the MS analysis. All data collected were acquired using MassLynxTM (V4.1) software in centroid mode.

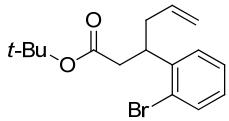
Experimental procedures and characterization of compounds

***Tert*-Butyl 3-(ferrocenyl)hex-5-enoate S1**



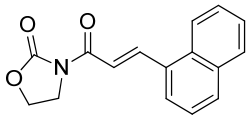
To a solution of **(*E*)-*Tert*-butyl 3-(ferrocenyl)acrylate** (0.95 g, 2.97 mmol) in DMF (7 mL) was added TMAF (0.36 g, 3.86 mmol) and allyltrimethylsilane (0.89 mL, 5.94 mmol) at 0°C. The mixture was stirred for 2 h at 0°C, then a saturated aqueous solution of water (5 mL) was added. The aqueous layer was extracted with AcOEt (3 x 8 mL), the organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **S1** as a red oil (835 mg, 2.36 mmol, 80%). ^{1}H NMR (500 MHz, DMSO) δ 5.73 (ddt, *J* = 16.2, 11.3, 7.2 Hz, 1 H), 5.07-4.92 (m, 2 H), 4.14 (s, 5 H), 4.13-4.06 (m, 2 H), 4.09-4.02 (m, 2 H), 2.87 (tt, *J* = 7.8, 5.4 Hz, 1 H), 2.47 (d, *J* = 5.6 Hz, 1 H), 2.39 (dd, *J* = 15.1, 8.0 Hz, 1 H), 2.36-2.33 (m, 1 H), 2.21 (dt, *J* = 14.1, 7.5 Hz, 1 H), 1.40 (s, 9 H); ^{13}C NMR (126 MHz, DMSO) δ 171.5, 136.3, 116.7, 92.5, 79.6, 68.2, 66.8, 66.8, 66.7, 66.4, 40.4, 39.0, 34.6, 27.7; HRMS-ESI *m/z* $[M]^+$ calcd for $C_{20}H_{26}O_2Fe$: 354.1282; found: 354.1281.

***Tert*-Butyl 3-(2-bromophenyl)hex-5-enoate S2**



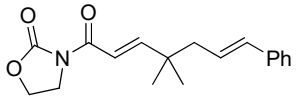
Prepared according to the above procedure from ***Tert*-butyl (*E*)-3-(2-bromophenyl)acrylate** (2.80 g, 10 mmol) as a red oil (430 mg, 1.32 mmol, 13%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.23 (dd, *J* = 7.6, 2.1 Hz, 1 H), 7.19 (td, *J* = 7.3, 1.2 Hz, 1 H), 7.06 (td, *J* = 7.9, 2.0 Hz, 1 H), 5.80 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1 H), 5.10 (dq, *J* = 17.1, 1.6 Hz, 1 H), 5.05 (ddt, *J* = 10.1, 2.0, 1.1 Hz, 1 H), 2.97 (dd, *J* = 13.7, 9.3 Hz, 1 H), 2.90 (dd, *J* = 13.7, 5.8 Hz, 1 H), 2.80 (ddt, *J* = 9.1, 8.1, 5.8 Hz, 1 H), 2.40 (dddt, *J* = 14.1, 8.4, 7.1, 1.2 Hz, 1 H), 2.27 (dddt, *J* = 13.9, 6.9, 5.6, 1.3 Hz, 1 H), 1.33 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.0, 139.0, 135.3, 132.9, 131.5, 128.1, 127.2, 124.8, 117.1, 80.5, 45.9, 38.2, 36.8, 28.1; MS-CI *m/z* : 325 $[M+H]^+$ (38%).

(*E*)-3-[3-(Naphthalen-1-yl)acryloyl]oxazolidin-2-one S3



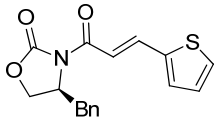
To a solution of **oxazolidin-2-one** (0.78 g, 9 mmol) in THF (40 mL) was added a solution of n-BuLi (2.4 M in hexane, 3.75 mL, 9 mmol) at -78°C. After 15 min of stirring, **(*E*)-3-(naphthalen-1-yl)acryloyl chloride** (2.04 g, 9.42 mmol) was added. The reaction mixture was stirred 30 min at -78°C, then 2 h at rt. A saturated aqueous solution of NH_4Cl (10 mL) was added. The aqueous layer was extracted with AcOEt (3 x 20 mL), the organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with DCM to give **S3** (1.37 g, 5.12 mmol, 57%) as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 15.5 Hz, 1 H), 8.27 (d, *J* = 8.4 Hz, 1 H), 8.03 (d, *J* = 15.5 Hz, 1 H), 7.94 (d, *J* = 7.7 Hz, 2 H), 7.92-7.89 (m, 1 H), 7.65-7.42 (m, 3 H), 4.51 (dd, *J* = 8.5, 7.6 Hz, 2 H), 4.21 (dd, *J* = 8.6, 7.5 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.5, 153.7, 143.1, 131.1, 128.9, 127.1, 126.3, 125.8, 125.6, 123.4, 119.1, 62.2, 43.0; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{16}H_{14}NO_3$: 268.0974 found: 268.0970.

3-[(2*E*,6*E*)-4,4-dimethyl-7-phenylhepta-2,6-dienoyl]oxazolidin-2-one S4



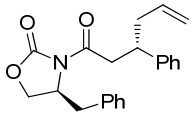
Prepared according to the above procedure from **oxazolidin-2-one** (0.50 g, 9.00 mmol) and isolated as a colorless oil (1.33 g, 4.87 mmol, 85%) Rf 0.8, CH_2Cl_2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-7.15 (m, 7 H), 6.40 (d, *J* = 15.7 Hz, 1 H), 6.14 (dt, *J* = 15.5, 7.5 Hz, 1 H), 4.40 (dd, *J* = 8.5, 7.5 Hz, 2 H), 4.06 (dd, *J* = 8.6, 7.5 Hz, 2 H), 2.31 (dd, *J* = 7.6, 1.4 Hz, 2 H), 1.15 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.7, 159.8, 153.6, 137.5, 133.1, 128.5, 127.2, 126.2, 126.1, 117.0, 62.1, 45.6, 42.8, 38.0, 26.4; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{18}H_{22}NO_3$: 300.1600 found: 300.1601.

(*R,E*)-4-Benzyl-3-[3-(thiophen-2-yl)acryloyl]oxazolidin-2-one S5



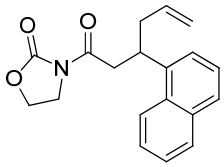
To a solution of **(*R*)-4-benzyloxazolidin-2-one** (1.39 g, 7.85 mmol) in THF (40 mL) was added a solution of n-BuLi (2.4 M in hexane, 3.27 mL, 7.85 mmol) at -78°C. After 15 min of stirring, (*E*)-3-(thiophen-2-yl)acryloyl chloride (1.62 g, 9.42 mmol) was added. The reaction mixture was stirred 30 min at -78°C 2h at rt then, a saturated aqueous solution of NH_4Cl (10 mL) was added. The aqueous layer was extracted with AcOEt (3 x 20 mL), the organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with $CH_2Cl_2$to give **S5** (2.02 g, 6.45 mmol, 82%) as a colorless oil; $[\alpha]_D$ +72° (*c* 1.02, CH_2Cl_2);^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 15.4 Hz, 1 H), 7.72 (d, *J* = 15.4 Hz, 1 H), 7.44 (d, *J* = 5.0 Hz, 1 H), 7.39-7.32 (m, 3 H), 7.32-7.23 (m, 3 H), 7.08 (dd, *J* = 5.0, 3.6 Hz, 1 H), 4.79 (ddt, *J* = 9.4, 7.6, 3.2 Hz, 1 H), 4.24 (dd, *J* = 9.0, 7.7 Hz, 1 H), 4.20 (dd, *J* = 9.0, 2.9 Hz, 1 H), 3.37 (dd, *J* = 13.4, 3.3 Hz, 1 H), 2.84 (dd, *J* = 13.4, 9.5 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 165.1, 153.6, 140.1, 138.8, 135.4, 131.9, 129.6, 129.5, 129.1, 128.3, 127.4, 115.7, 66.2, 55.5, 38.0. HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{17}H_{16}NO_3S$: 314.0851; found: 314.0853.

(*S*)-4-Benzyl-3-[(*S*)-3-phenylhex-5-enoyl)]oxazolidin-2-one S6[1] **Procedure A**[2]



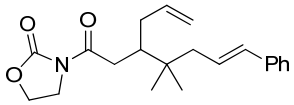
To a suspension of $CuBr.SMe_2$ (1.59 g, 7.75 mmol) in THF (50 mL) was added a solution of allylmagnesium bromide (1 M in Et_2O, 15.5 mL, 15.5 mmol) at -50°C. The mixture was stirred for 30 min, then cooled down to -78°C. A solution of **(*S*)-4-Benzyl-3-cinnamoyloxazolidin-2-one** [3] (1.70 g, 5.54 mmol) in THF (20 mL) was added at -78°C. The resulting mixture was stirred for 3 h at -78°C, then a saturated aqueous solution of NH_4Cl (10 mL) was added. The aqueous layer was extracted with AcOEt (3 x 20 mL), the organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **S4a** (1.58 g, 5.35 mmol, 96%) as a colorless oil. $[\alpha]_D$ + 65° (c 1, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.11 (m, 10 H), 5.71 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1 H), 5.05 (dq, *J* = 17.1, 1.7 Hz, 1 H), 5.00 (dd, *J* = 10.2, 1.8 Hz, 1 H), 4.49 (ddt, *J* = 10.3, 7.7, 3.0 Hz, 1 H), 4.07 (dd, *J* = 9.0, 2.5 Hz, 1 H), 3.99 (t, *J* = 8.4 Hz, 1 H), 3.53-3.30 (m, 2 H), 3.24 (dd, *J* = 15.0, 4.0 Hz, 1 H), 3.19 (dd, *J* = 10.0, 3.4 Hz, 1 H), 2.65 (dd, *J* = 13.4, 9.9 Hz, 1 H), 2.52-2.42 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.0, 153.6, 143.7, 136.2, 135.4, 129.5, 129.0, 128.5, 127.8, 127.4, 126.7, 117.1, 66.2, 55.3, 41.56, 41.20, 41.09, 37.9.

3-[3-(Naphthalen-1-yl)hex-5-enoyl]oxazolidin-2-one S7



Prepared according to **procedure A** from **S3** (1.37 g, 5.12 mmol) and isolated as a colorless oil (0.65 g, 1.53 mmol, 51%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.5 Hz, 1 H), 7.85 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.72 (dd, *J* = 6.9, 2.5 Hz, 1 H), 7.54 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1 H), 7.50-7.38 (m, 3 H), 5.73 (dddd, *J* = 16.7, 10.2, 7.7, 6.3 Hz, 1 H), 5.06 (dd, *J* = 17.1, 1.7 Hz, 1 H), 4.97 (ddt, *J* = 10.2, 2.1, 1.1 Hz, 1 H), 4.37-4.20 (m, 3 H), 3.89-3.76 (m, 2 H), 3.50 (dd, *J* = 17.0, 7.6 Hz, 1 H), 3.44 (dd, *J* = 16.9, 6.7 Hz, 1 H), 2.62 (dt, J = 13.3, 6.5 Hz, 1 H), 2.54 (dt, *J* = 14.3, 7.5 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.5, 153.9, 140.2, 136.4, 134.3, 132.0, 129.3, 127.3, 126.3, 125.8, 123.5, 117.3, 62.3, 42.8, 40.9 , 40.7., 39.9 (br s); HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{19}H_{20}NO_3$: 310.1438 found: 310.1442.

(*E*)-3-(3-Allyl-4,4-dimethyl-7-phenylhept-6-enoyl)oxazolidin-2-one S8



Prepared according to **procedure A** from **S4** (1.33 g, 4.67 mmol) and isolated as a colorless oil (0.62 g, 1.82 mmol, 39%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.33 (m, 2 H), 7.30 (dd, *J* = 8.5, 6.9 Hz, 2 H), 7.23-7.13 (m, 1 H), 6.38 (d, *J* = 15.7 Hz, 1 H), 6.26 (dt, *J* = 15.5, 7.4 Hz, 1 H), 5.79-5.66 (m, 1H), 5.05-4.97 (m, 2 H), 4.93 (dt, *J* = 10.0, 1.9 Hz, 1 H), 4.36 (d, *J* = 8.1, 4.1 Hz, 1 H), 4.34 (dd, *J* = 8.2, 4.0 Hz, 1 H), 3.95 (t, *J* = 8.1 Hz, 2 H), 3.06 (dd, *J* = 17.4, 4.5 Hz, 1 H), 2.86 (dd, *J* = 17.4, 7.2 Hz, 1 H),2.44 (dddd, *J* = 14.0, 5.0, 3.0, 1.7 Hz, 1 H), 2.25 (dddd, *J* = 10.4, 7.5, 4.5, 3.2 Hz, 1 H) 2.19 (dd, *J* = 7.4, 1.2 Hz, 2 H), 1.88 (dt, *J* = 14.0, 9.8 Hz, 1 H), 0.94 (s, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.8, 153.7, 138.5, 137.8, 132.5, 128.6, 127.2, 127.0, 126.1, 115.9, 61.9, 44.14, 42.9, 41.6, 37.0, 35.4, 35.2, 24.9, 24.9; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{21}H_{28}NO_3$: 342.2069 found: 342.2072.

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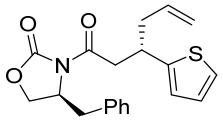
[1] A. B. Smith III, L.-D. Cantin, A. Pasternak, L. Guise-Zawacki, W. Yao, A. K. Charnley, J. Barbosa, P. A. Sprengeler, R. Hirschmann, S. Munshi, D. B. Olsen, W. A. Schleif and L. C. Kuo, *J. Med. Chem.,* 2003, **46**, 1831.

[2] D.-G. Liu, Y. Gao, X. Wang, J. A. Kelley, and T. R. Burke, Jr, *J. Org. Chem*, 2002, **67**, 1448.

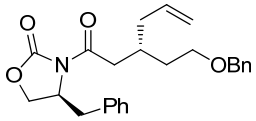
[3] M. Neisius and B. Plietker, *J. Org. Chem.,* 2008, **73**, 3218.

(S)-4-Benzyl-3-[(S)-3-(thiophen-2-yl)hex-5-enoyl]oxazolidin-2-one S9



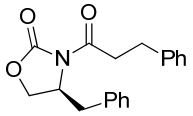
Prepared according to **procedure A** from **S5** (1.14 g, 3.51 mmol) and isolated as a colorless oil (0.99 g, 2.8 mmol, 80%).$[\alpha]_D$ 72° (*c* 1.02 , CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.26 (m, 3 H), 7.21-7.16 (m, 2 H), 7.14 (dd, *J* = 5.1, 1.2 Hz, 1 H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1 H), 6.89 (d, *J* = 3.1 Hz, 1 H), 5.77 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1 H), 5.09 (dq, *J* = 17.3, 1.8 Hz, 1 H), 5.08-5.02 (m, 1 H), 4.58 (ddt, *J* = 10.3, 6.9, 3.3 Hz, 1 H), 4.15-4.06 (m, 2 H), 3.76-3.68 (m, 1 H), 3.38 (dd, *J* = 16.9, 8.8 Hz, 1 H), 3.28 (dd, *J* = 16.9, 5.2 Hz, 1 H), 2.69 (dd, *J* = 13.4, 9.9 Hz, 1 H), 2.58-2.43 (m, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 153.5, 147.5, 135.7, 135.4, 129.5, 129.1, 127.4, 126.7, 124.2, 123.3, 117.6, 66.3, 55.3, 42.2, 41.8, 37.9, 36.6; HRMS-ESI *m/z* $[M+H]_+$ calcd for $C_{20}H_{22}NO_3S$: 356.1320; found: 356.1318.

(S)-4-Benzyl-3-{(*R*)-3-[2-(benzyloxy)ethyl]hex-5-enoyl}oxazolidin-2-one S10



Prepared according to **procedure A** from **(*S*,*E*)-4-benzyl-3-[5-(benzyloxy)pent-2-enoyl]oxazolidin-2-one**[4] (0.51 g, 1.41 mmol) and isolated as a colorless oil (0.30 g, 0.73 mmol, 50%). **1**H NMR (500 MHz, $CDCl_3$) δ 7.36-7.11 (m, 10 H), 5.80 (ddt, *J* = 17.3, 10.4, 7.2 Hz, 1 H), 5.14-5.00 (m, 2 H), 4.61-4.53 (m, 1 H), 4.50 (d, *J* = 11.9 Hz, 1 H), 4.46 (d, *J* = 12.0 Hz, 1 H), 4.06 (dd, *J* = 9.0, 2.6 Hz, 1 H), 3.95 (dd, *J* = 9.0, 7.9 Hz, 1 H), 3.56 (t, *J* = 6.4 Hz, 2 H), 3.28 (dd, *J* = 13.4, 3.3 Hz, 1 H), 2.96 (d, *J* = 6.6 Hz, 2 H), 2.67 (dd, *J* = 13.4, 9.8 Hz, 1 H), 2.38-2.31 (m, 1 H), 2.22 (dt, *J* = 13.0, 6.5 Hz, 1 H), 2.13 (dt, *J* = 14.1, 7.2 Hz, 1 H), 1.78-1.65 (m, 2 H); ^{13}CNMR (126 MHz, $CDCl_3$) ^{13}C δ 172.7, 153.5, 138.7, 136.4, 135.5, 129.5, 129.0, 128.4, 127.5, 127.4, 117.1, 72.9, 68.5, 66.1, 55.3, 39.6, 38.8, 38.0, 33.7, 31.5; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{25}H_{30}NO_4$: 408.2175; found: 408.2178.

(S)-4-Benzyl-3-(3-phenylpropanoyl)oxazolidin-2-one S11[5]

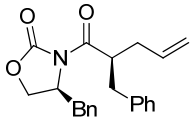


To a solution of **(S)-4-benzyloxazolidin-2-one** (0.75 g, 4.24 mmol) in THF (15 mL) was slowly added a solution of n-BuLi (2.5 M in THF, 1.7 mL, 4.24 mmol) at 0°C. The mixture was cooled down to -70°C then, a solution of 4-phenylbutanoyl chloride (0.77 g, 4.24 mmol) in THF (5 mL) was added dropwise. The stirring was continued for 1h at -70°C then warmed to rt prior to the addition of a saturated aqueous solution of NH_4Cl (20 mL). The organic solution was washed with brine (20 mL), dried over $NaSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of PE/EA (80:20) to give **S11** (2.65 g, 8.97 mmol, 78%, 0.99 g, 3.2 mmol, 75%) as a colorless oil. Rf 0.35 (PE/EA, 80:20); $[\alpha]_D$ + 98 (c 1.07, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.13 (m, 10 H), 4.69 (ddt, *J* = 9.5, 6.9, 3.4 Hz, 1 H), 4.24-4.15 (m, 2 H), 3.39-3.22 (m, 3 H), 3.11-2.99 (m, 2H), 2.78 (dd, *J* = 13.4, 9.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 153.6, 140.6, 135.3, 129.6, 129.1, 128.7, 128.6, 127.5, 126.4, 66.3, 55.3, 38.0, 37.3, 30.4.

[4] G. Pattenden, N. J. Ashweek, C. A. G. Baker-Glenn, J. Kempson, G. M. Walker and J. G. K. Yee, *Org. Biomol. Chem*., 2008, **6**, 1478.

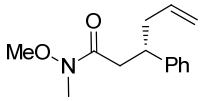
[5] M. K. Edmonds, F. H. M. Graichen, J. Gardiner and A. D. Abel, *Org. Lett*., 2008, **10**, 885.

(*S*)-4-Benzyl-3-[(*S*)-2-benzylpent-4-enoyl]oxazolidin-2-one S12[6]



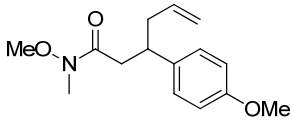
To a solution of **S11** (0.97 g, 3.14 mmol) in THF (20 mL) was slowly added a solution of NaHMDS (1 M in THF, 4.1 mL, 4.1 mmol) at -70°C. After 1 h of stirring at -70°C, allyl bromide (0.88 mL, 10 mmol) was added dropwise. The reaction mixture was stirred at- 50°C for 3 h, prior to the addition of a saturated solution of NH_4Cl (20 mL). The layers were separated and the aqueous phase was extracted with AcOEt (2 x 20 mL). The organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of PE/Et_2O to give **S12** (0.77 g, 2.2 mmol, 70%) as a colorless oil. Rf 0.50 (PE/EA, 80:20); $[\alpha]_D$ + 113 (c 1, $CHCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.16 (m, 10 H), 5.86 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1 H), 5.13 (dq, *J* = 17.1, 1.6 Hz, 1 H), 5.08 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1 H), 4.50-4.41 (m, 1 H), 4.38-4.29 (m, 1 H), 4.01 (dd, *J* = 9.0, 2.3 Hz, 1 H), 3.23 (dd, *J* = 13.4, 3.4 Hz, 1 H), 2.96 (dd, *J* = 13.4, 8.9 Hz, 1 H), 2.85 (dd, *J* = 13.4, 6.5 Hz, 1 H), 2.65 (dd, *J* = 13.4, 9.9 Hz, 1 H), 2.56 (dt, *J* = 14.4, 7.8 Hz, 1 H), 2.36 (dt, *J* = 12.7, 5.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.4, 153.1, 139.0, 135.5, 135.1, 129.5, 129.2, 129.0, 128.4, 127.4, 126.5, 117.5, 65.9, 55.6, 44.0, 38.4, 38.1, 36.4.

(*S*)-*N*-Methoxy-*N*-methyl-3-phenylhex-5-enamide 1aa[7] **Procedure B**



To a solution of MeNHOMe·HCl (503 mg, 5.16 mmol) in CH_2Cl_2 (20 mL) was added a solution of $AlMe_3$ (2 M in heptane, 2.6 mL, 5.2 mmol) at 0°C. The mixture was stirred 30 min at 0°C then 30 min at rt and cooled down to 0°C. A solution of **(*S*)-4-benzyl-3-[(S)-3-phenylhex-5-enoyl)oxazolidin-2-one** (600 mg, 1.72 mmol) in CH_2Cl_2 (15 mL) was added at 0°C, then the resulting mixture was stirred 20 min at 0°C and 1 h at rt. A solution of Rochelle salt (10%, 20 mL) was added. After 30 min of stirring, the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **1ba** as a colorless oil (284 mg, 1.22 mmol, 71%). $[\alpha]_D$ = 0 (c 1.8, $CDCl_3$). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 2 H), 7.28-7.16 (m, 3 H), 5.70 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1 H), 5.05-4.99 (m, 1 H), 4.97 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1 H), 3.57 (s, 3 H), 3.35 (quint, *J* = 7.3 Hz, 1 H), 3.12 (s, 3 H), 2.76 (d, *J* = 7.3 Hz, 2 H), 2.52-2.38 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.5, 136.5, 128.5, 127.7, 126.4, 116.6, 61.3, 41.2, 40.5, 38.1, 32.2, 1C (C=O) is missing; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{14}H_{20}NO_2$: 234.1494; found: 234.1495.

***N*-Methoxy-3-(4-methoxyphenyl)-*N*-methylhex-5-enamide 1ab**[7]

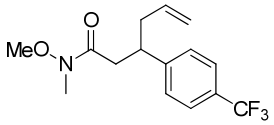


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23-7.12 (m, 2 H), 6.90-6.77 (m, 2 H), 5.69 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.04-4.92 (m, 2 H), 3.79 (s, 3 H), 3.57 (s, 3 H), 3.30 (quint, *J* = 7.3 Hz, 1 H), 3.11 (s, 3 H), 2.72 (br d, *J* = 7.3 Hz, 2 H), 2.42 (qt, *J* = 8.8, 6.7 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.0, 136.6, 128.5, 116.5, 113.7, 61.2, 55.2, 40.6, 40.4, 38.3, 32.1; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{15}H_{22}NO_3$: 264.1594; found: 264.1587.

[6] M. Tredwell, J. A. R. Luft, M. Schuler, K. Tenza, K. N. Houk and V.Gouverneur, *Angew. Chem. Int. Ed*., 2008, **47**, 357.

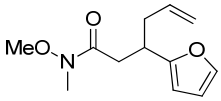
[7] A. Coelho, M.-S. Souvenir Zafindrajaona, A. Vallée, J.-B. Behr and J.-L. Vasse, *Chem. Eur. J.*, 2022**, 28**, e202103789

***N*-Methoxy-*N*-methyl-3-[4-(trifluoromethyl)phenyl]hex-5-enamide 1ac**[7]



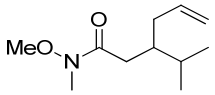
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (d, *J* = 8.0 Hz, 2 H), 7.36 (d, *J* = 8.0 Hz, 2 H), 5.66 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1 H), 5.05-4.96 (m, 2 H), 3.61 (s, 3 H), 3.42 (quint, *J* = 7.3 Hz, 1 H), 3.12 (s, 3 H), 2.78 (d, *J* = 7.3 Hz, 2 H), 2.50-2.39 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 148.6, 135.8, 128.7 (q, *J* = 32.2 Hz), 128.1, 125.4 (q, *J* = 3.7 Hz), 124.40 (q, *J* = 272 Hz), 117.2, 61.3, 41.0, 40.5, 37.1, 32.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.36; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{15}H_{19}F_3NO_2$: 302.1368; found: 302.1368.

3-(Furan-2-yl)-*N*-methoxy-*N*-methylhex-5-enamide 1ad[7]



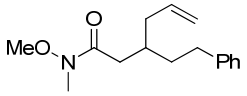
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 1.8, 0.9 Hz, 1 H), 6.26 (dd, *J* = 3.2, 1.9 Hz, 1 H), 6.04 (d, *J* = 3.2 Hz, 1 H), 5.71 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1 H), 5.07-4.99 (m, 1 H), 5.02-4.96 (m, 1 H), 3.62 (s, 3 H), 3.50-3.43 (m, 1 H), 3.15 (s, 3 H), 2.80 (dd, *J* = 15.8, 7.3 Hz, 1 H), 2.66 (dd, *J* = 15.9, 6.7 Hz, 1 H), 2.54-2.36 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 141.1, 136.0, 116.9, 110.1, 105.3, 61.3, 38.1, 35.5, 34.7, 29.2; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{12}H_{18}NO_3$: 224.1287; found: 224.1285.

3-Isopropyl-*N*-methoxy-*N*-methylhex-5-enamide 1ae[7]



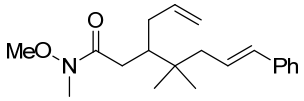
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.76 (ddt, *J* = 16.8, 10.2, 6.8 Hz, 1 H), 5.03-4.97 (m, 2 H), 3.67 (s, 3 H), 3.16 (s, 3 H), 2.40-2.25 (m, 2 H), 2.16-2.06 (m, 1 H), 2.05-1.93 (m, 2 H), 1.81-1.70 (m, 1 H), 0.88 (d, *J* = 5.2 Hz, 3 H), 0.87 (d, *J* = 5.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 137.8, 116.0, 68.1, 39.7, 35.7, 32.7, 29.7, 19.3, 18.9; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{11}H_{22}NO_2$: 200.1651; found: 200.1651.

***N*-Methoxy-*N*-methyl-3-phenethylhex-5-enamide 1af**[7]



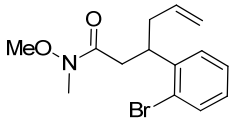
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.25 (m, 2 H), 7.23-7.16 (m, 3 H), 5.82 (ddt, *J* = 17.1, 10.3, 6.9 Hz, 1 H), 5.13-5.03 (m, 2 H), 3.68 (s, 3 H), 3.20 (s, 3 H), 2.76-2.58 (m, 2 H), 2.44 (qd, *J* = 15.3, 5.5 Hz, 2 H), 2.30-2.09 (m, 3H), 1.68 (td, *J* = 8.2, 5.9 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.7, 136.6, 128.4, 128.4, 125.8, 1168, 61.3, 38.3, 36.1, 35.9, 34.0, 33.3, 32.3.

(*E*)-3-Allyl-*N*-methoxy-*N*,4,4-trimethyl-7-phenylhept-6-enamide 1ag



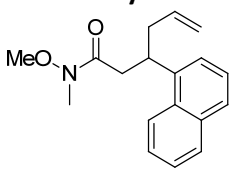
Prepared according to **procedure B** from **S8** (476 mg, 1.39 mmol) and isolated as a colorless oil (340 mg, 1.13 mmol, 81%). ^{1}H NMR (500 MHz, C $CDCl_3$) δ 7.37-7.33 (m, 2 H), 7.31-7.27 (m, 2 H), 7.23-7.15 (m, 1 H), 6.38 (d, *J* = 15.7 Hz, 1 H), 6.28 (dt, *J* = 15.6, 7.3 Hz, 1 H), 5.78 (dddd, *J* = 17.1, 10.0, 8.8, 5.2 Hz, 1 H), 5.01 (dq, *J* = 17.2, 1.7 Hz, 1 H), 4.96 (dt, *J* = 10.0, 1.9 Hz, 1 H), 3.66 (s, 3 H), 3.14 (s, 3 H), 2.53 (dd, *J* = 16.1, 4.7 Hz, 1 H,), 2.42 (dtd, *J* = 14.0, 3.5, 1.7 Hz, 1 H), 2.30 (dd, *J* = 16.1, 6.9 Hz, 1 H), 2.23-2.20 (m, 1 H), 2.18 (dd, *J* = 7.4, 1.1 Hz, 2 H), 1.87 (dt, *J* = 14.0, 9.3 Hz, 1 H), 0.93 (s, 3 H), 0.93 (s, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.7, 138.4, 137.7, 132.5, 128.6, 127.2, 127.1, 126.1, 116.1, 62.6, 44.1, 43.0, 42.7, 37.3, 37.1, 35.5, 25.1, 24.8; HRMS-ESI *m/z* $[M+H]_+$ calcd for $C_{20}H_{30}NO_2$: 316.2277; found: 316.2279.

3-(2-Bromophenyl)-*N*-methoxy-*N*-methylhex-5-enamide 1ah



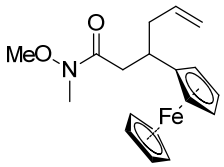
Prepared according to **procedure B** from **S2** (145 mg, 0.45 mmol) and isolated as a colorless oil (112 mg, 0.36 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.29-7.19 (m, 2 H), 7.04 (ddd, *J* = 7.8, 6.9, 2.1 Hz, 1 H), 5.69 (ddt, *J* = 17.2, 10.1, 7.0 Hz, 1 H), 5.03-4.95 (m, 1H), 4.99-4.92 (m, 1 H), 3.88 (p, *J* = 7.2 Hz, 1 H), 3.64 (s, 3 H), 3.12 (s, 3 H), 2.76 (d, *J* = 7.3 Hz, 2 H), 2.45 (t, *J* = 7.0 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 143.1, 135.8, 133.1, 127.8, 127.4, 125.0, 116.9, 61.3, 39.4, 39.3, 36.8, 32.2; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{14}H_{19}NO_2Br$: 312.0599; found: 312.0605.

***N*-Methoxy-*N*-methyl-3-(naphthalen-1-yl)hex-5-enamide 1ai**



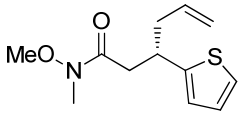
Prepared according to **procedure B** from **S7** (0.65 g, 2.00 mmol) and isolated as a colorless oil (420 mg, 1.48 mmol, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.5 Hz, 1 H), 7.85 (dd, *J* = 8.1, 1.4 Hz, 1 H), 7.72 (d, *J* = 8.0 Hz, 1 H), 7.53 (ddd, *J* = 8.5, 6.8, 1.5 Hz, 1 H), 7.50-7.45 (m, 1 H), 7.44 (d, *J* = 7.8 Hz, 1 H), 7.40 (dd, *J* = 7.2, 1.4 Hz, 1 H), 5.71 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1 H), 5.04 (dd, *J* = 17.1, 1.8 Hz, 1 H), 4.94 (ddt, *J* = 10.2, 2.2, 1.1 Hz, 1 H), 4.31 (p, *J* = 7.0 Hz, 1 H), 3.60 (s, 3 H), 3.12 (s, 3 H), 2.97-2.81 (m, 2 H), 2.66-2.58 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.6, 136.4, 134.1, 131.8, 128.9, 126.9, 126.1, 125.5, 125.4, 123.5, 116.7, 61.3, 39.9, 37.9, 34.8 (br s), 32.3 (br s). HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{18}H_{22}NO_2$: 284.1651 found: 284.1653.

3-Ferrocenyl-*N*-methoxy-*N*-methylhex-5-enamide 1aj



To a solution of **S1** (430 mg, 1.21 mmol) in THF (20 mL) and $CH_3NH(OCH_3)$.HCl (0.455 g, 4.86 mmol) was slowly added a solution of *i*-PrMgCl (2 M in hexanes, 4.86 mL, 9.72 mmol) at 0°C. The stirring was continued for 2 h at rt, then a saturated aqueous solution of NH_4Cl (5 mL) and water (5 mL) were added. The layers were separated and the aqueous phase was extracted with CH_2Cl_2 (2 x 10 mL).The organic phases were combined, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of PE/EA to give **1aj** as a red oil (380 mg, 1.11 mmol, 92%). ^{1}H NMR (500 MHz, DMSO) δ 5.74 (ddt, *J* = 18.7, 9.3, 7.1 Hz, 1 H), 5.02-4.95 (m, 2 H), 4.13 (s, 5 H), 4.13-4.06 (m, 2 H), 4.09-4.03 (m, 2 H), 3.61 (s, 3 H), 3.09 (s, 3 H), 2.99 (p, *J* = 7.2 Hz, 1 H), 2.70-2.55 (m, 2 H), 2.41-2.33 (m, 1 H), 2.22 (dt, *J* = 14.2, 7.5 Hz, 1 H); ^{13}C NMR (126 MHz, DMSO) δ 136.7, 116.4, 93.1, 68.2, 66.8, 66.7, 66.5, 61.0, 36.4, 33.7; HRMS-ESI *m/z* $[M]^+$ calcd for $C_{18}H_{23}NO_2Fe$: 341.1078; found: 341.1081.

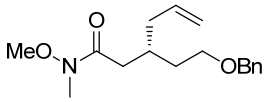
***(S)*-*N*-Methoxy-*N*-methyl-3-(thiophen-2-yl)hex-5-enamide 1ak**



Prepared according to **procedure B** from **S9** (406 mg, 1.54 mmol) and isolated as a colorless oil (269 mg, 1.13 mmol, 73%). $[\alpha]_D$ = 5.4° (c 1.28, CH_2Cl_2).^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (dd, *J* = 5.1, 1.2 Hz, 1 H), 6.92 (dd, *J* = 5.1, 3.4 Hz, 1 H), 6.87 (dd, *J* = 3.3, 1.1 Hz, 1 H), 5.75 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1 H), 5.06 (dq, *J* = 17.1, 1.7 Hz, 1 H), 5.02 (ddd, *J* = 10.2, 2.2, 1.1 Hz, 1 H), 3.70 (quint, *J* = 7.1 Hz, 1 H), 3.60 (s,

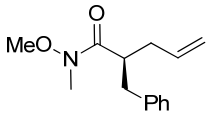
3 H), 3.15 (s, 3 H), 2.77 (q, *J* = 8.9, 8.3 Hz, 2 H), 2.49 (tt, *J* = 7.0, 1.4 Hz, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 148.3, 135.9, 126.6, 124.0, 123.0, 117.1, 61.3, 41.4, 38.9, 36.5, 32.2; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{12}H_{18}NO_2S$: 240.1053; found: 240.1047.

(*R*)-3-[2-(Benzyloxy)ethyl)-*N*-methoxy-*N*-methylhex-5-enamide 1al



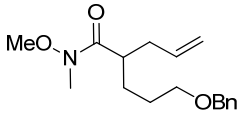
Prepared according to **procedure B** from **S10** (2.51 g, 6.00 mmol) and isolated as a colorless oil (1.13 g, 3.9 mmol, 65%). $[\alpha]_D$ = 5.4° (c 1.28, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.25 (m, 5 H), 5.85-5.74 (m, 1 H), 5.08-5.01 (m, 2H), 4.52 (AB system, d, *J* = 11.9 Hz, 1 H), 4.50 (AB system, d, *J* = 11.9 Hz, 1 H), 3.64 (s, 3H), 3.58-3.52 (m, 2 H), 3.17 (s, 3 H), 2.49-2.36 (m, 2 H), 2.29-2.08 (m, 3 H), 1.75-1.65 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.7, 136.6, 128.4, 127.8, 127.6, 116.8, 73.0, 68.7, 61.3, 38.7, 36.2, 33.8, 32.0, 31.7; HRMS-ESI *m/z* $[M+Na]^+$ calcd for $C_{17}H_{25}NO_3Na$: 314.1732; found: 314.1732.

(*S*)-2-Benzyl-*N*-methoxy-*N*-methylpent-4-enamide 1ba[7]



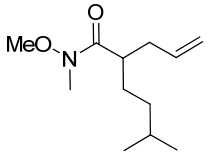
Prepared from **S12** (0.45 g, 2.37 mmol) and isolated as a colorless oil (0.355 g, 1.52 mmol, 64%). $[\alpha]_D$ + 40 (c 1, CH_2Cl_2). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.14 (m, 5 H), 5.76 (ddt, *J* = 17.1, 10.1, 7.0 Hz, 1 H), 5.07 (dq, *J* = 17.1, 1.7 Hz, 1 H), 5.01 (dd, *J* = 10.3, 2.0 Hz, 1 H), 3.32 (s, 3 H), 3.20 (br s, 1 H), 3.08 (s, 3 H), 2.97 (dd, *J* = 13.3, 9.0 Hz, 1 H), 2.71 (dd, *J* = 13.3, 5.8 Hz, 1 H), 2.44 (dt, *J* = 14.8, 7.7 Hz, 1 H), 2.24 (dt, *J* = 13.5, 6.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 140.1, 135.8, 129.2, 128.4, 126.3, 116.8, 61.2, 43.2, 38.3, 36.7, 32.0; HMRS ESI m/z $[M+H]^+$ calcd for $C_{14}H_{20}NO_2$: 234.1494; found: 234.1496.

2-[3-(Benzyloxy)propyl]-*N*-methoxy-*N*-methylpent-4-enamide 1bb[8]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.52-7.20 (m, 5 H), 5.75 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1 H), 5.05 (dq, *J* = 17.1, 1.6 Hz, 1 H), 4.99 (dq, *J* = 10.1, 1.0 Hz, 1 H), 4.49 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 3.63 (s, 3 H), 3.45 (tdd, *J* = 9.2, 6.2, 3.0 Hz, 2 H), 3.17 (s, 3 H), 2.93 (br s, 1 H), 2.38 (dt, *J* = 15.0, 7.6 Hz, 1 H), 2.19 (dt, *J* = 13.6, 6.6 Hz, 1 H), 1.71-1.54 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.1, 138.6, 136.1, 128.4, 127.7, 127.6, 116.6, 73.0, 70.3, 61.5, 40.6, 37.0, 32.2, 28.8, 27.8. HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{17}H_{25}NO_3$: 292.1913; found: 292.1915.

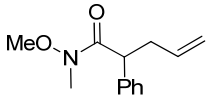
2-Allyl-*N*-methoxy-*N*,5-dimethylhexanamide 1bc



Prepared according to **procedure B** from **methyl 2-allyl-5-methylhexanoate** (0.55 g, 3 mmol) and isolated as a colorless oil (579 mg, 2.72 mmol, 92%).^{1}H NMR (500 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.0, 9.9, 7.1 Hz, 1 H), 5.04 (dq, *J* = 17.0, 1.5 Hz, 1 H), 4.97 (ddt, *J* = 10.2, 2.0, 1.1 Hz, 1 H), 3.66 (s, 3 H), 3.17 (s, 3 H), 2.86 (s, 1 H), 2.36 (dt, *J* = 15.0, 7.6 Hz, 1 H), 2.17 (dt, *J* = 13.7, 6.6 Hz, 1 H), 1.68-1.57 (m, 1H), 1.52-1.38 (m, 2 H), 1.18-1.00 (m, 2 H), 0.85 (d, *J* = 6.7 Hz, 6 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 177.4, 136.4, 116.4, 61.5, 41.0, 36.9, 36.7, 30.1, 28.3, 22.7, 22.6; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{12}H_{24}NO_2$: 214.1807; found: 214.1806.

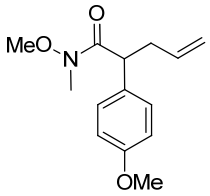
[8] A. Coelho, C. Machado-Rodrigues, J.-B. Behr and J.-L. Vasse, *Org. Lett.,* 2021, **23**, 772.

***N*-Methoxy-*N*-methyl-2-phenylpent-4-enamide 1bd**[9]



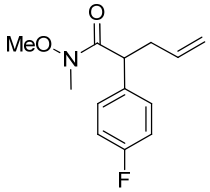
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37-7.18 (m, 5 H), 5.74 (ddt, *J* = 17.1, 10.1, 6.9 Hz, 1 H), 5.05 (dq, *J* = 17.1, 1.7 Hz, 1 H), 5.01-4.94 (m, 1 H), 4.14-3.97 (m, 1 H), 3.46 (s, 3 H), 3.15 (s, 3 H), 2.84 (ddd, *J* = 14.1, 8.4, 7.0 Hz, 1 H), 2.46 (dtt, *J* = 14.0, 6.9, 1.4 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.7, 136.2, 128.6, 128.2, 127.0, 116.6, 61.3, 47.7, 38.3, 32.3.

***N*-Methoxy-2-(4-methoxyphenyl)-*N*-methylpent-4-enamide 1be**[7]



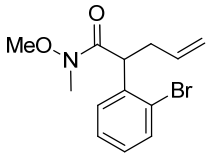
^{1}H NMR (500 MHz $CDCl_3$) δ 7.26-7.20 (m, 2 H), 6.87-6.80 (m, 2 H), 5.73 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1 H), 5.04 (dq, *J* = 17.1, 1.6 Hz, 1 H), 4.97 (ddt, *J* = 10.1, 2.0, 1.1 Hz, 1 H), 4.03 (br s, 1 H), 3.77 (s, 3 H), 3.48 (s, 3 H), 3.14 (s, 3 H), 2.79 (dt, *J* = 14.3, 7.6 Hz, 1 H), 2.43 (dt, *J* = 14.0, 6.9 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.6, 136.3, 131.8, 129.2, 116.5, 114.0, 61.4, 55.3, 46.7, 38.3, 32.3; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{14}H_{20}NO_3$: 250.1443; found: 250.1444.

2-(4-Fluorophenyl)-*N*-methoxy-*N*-methylpent-4-enamide 1bf[7]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 2 H), 6.98 (t, *J* = 8.7 Hz, 2 H), 5.71 (ddt, *J* = 17.0, 10.0, 6.9 Hz, 1 H), 5.04 (dq, *J* = 17.2, 1.6 Hz, 1 H), 4.98 (dq, *J* = 10.2, 2.0 Hz, 1 H), 4.06 (br s, 1 H), 3.50 (s, 3 H), 3.15 (s, 3 H), 2.80 (dt, *J* = 14.9, 7.6 Hz, 1 H), 2.43 (dt, *J* = 14.1, 7.0 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.9, 161.0, 135.9, 129.8, 129.7, 116.9, 115.5, 115.4, 61.4, 46.8, 38.3, 32.3 (br s); ^{19}F NMR (471 MHz, $CDCl_3$) δ -115.85; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{13}H_{17}FNO_2$: 238.1243; found: 238.1244.

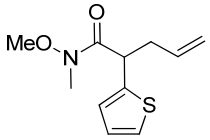
2-(2-Bromophenyl)-*N*-methoxy-*N*-methylpent-4-enamide 1bg[7]



^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 8.0, 1.3 Hz, 1 H), 7.40 (dd, *J* = 7.8, 1.7 Hz, 1 H), 7.29-7.23 (m, 1 H), 7.09 (ddd, *J* = 8.1, 7.3, 1.8 Hz, 1 H), 5.82 (ddt, *J* = 17.1, 10.2, 6.9 Hz, 1 H), 5.06 (dq, *J* = 17.1, 1.6 Hz, 1 H), 4.99 (ddt, *J* = 10.1, 1.9, 1.1 Hz, 1 H), 4.60 (br s, 1 H), 3.46 (s, 3 H), 3.16 (s, 3 H), 2.75 (dt, *J* = 14.8, 7.7 Hz, 1 H), 2.39 (dddt, *J* = 14.6, 7.4, 6.2, 1.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.4, 135.8, 132.9, 128.7, 128.4, 128.0, 116.8, 61.4, 46.7, 37.7, 32.5, 29.8; HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{13}H_{17}BrNO_2$: 298.0443; found: 298.0448.

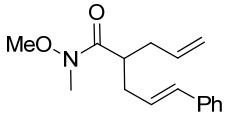
[9] Z. Escobar, M. Johansson, A. Bjartell, R. Hellsten and O. Sterner, *Int. J. Org. Chem*., 2014, **4**, 225.

_N_-Methoxy-_N_-methyl-2-(thiophen-2-yl)pent-4-enamide 1bh[7]



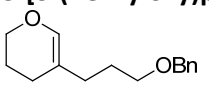
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (dd, *J* = 5.0, 1.3 Hz, 1 H), 7.00-6.94 (m, 1 H), 6.93 (dd, *J* = 5.0, 3.5 Hz, 1 H), 5.75 (ddt, *J* = 17.0, 10.1, 6.9 Hz, 1 H), 5.09 (dq, *J* = 17.1, 1.6 Hz, 1 H), 5.02 (ddt, *J* = 10.3, 2.0, 1.0 Hz, 1 H), 4.45 (br s, 1 H), 3.63 (s, 3 H), 3.19 (s, 3 H), 2.83 (dddt, *J* = 15.3, 8.3, 6.9, 1.2 Hz, 1 H), 2.55 (dtt, *J* = 13.9, 6.9, 1.3 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 135.5, 126.6, 125.2, 124.5, 117.2, 61.6, 42.3, 39.3, 32.4 (br s); HRMS-ESI *m/z* $[M+H]^+$ calcd for $C_{11}H_{16}NO_2S$: 226.0902; found: 226.0902.

(_E_)-2-Allyl-_N_-methoxy-_N_-methyl-5-phenylpent-4-enamide 1bi[7]



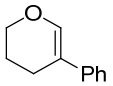
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38-7.18 (m, 5 H), 6.45 (d, *J* = 15.8 Hz, 1 H), 6.19 (dt, *J* = 15.8, 7.3 Hz, 1 H), 5.81 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1 H), 5.11 (dq, *J* = 17.1, 1.6 Hz, 1 H), 5.05 (ddt, *J* = 10.1, 2.0, 1.0 Hz, 1 H), 3.68 (s, 3H), 3.20 (s, 3 H), 3.10 (br s, 1 H), 2.56 (dt, *J* = 14.3, 7.3 Hz, 1 H), 2.47 (dt, *J* = 15.1, 7.6 Hz, 1 H), 2.40 (dt, *J* = 13.7, 7.3 Hz, 1 H), 2.29 (dt, *J* = 13.7, 6.6 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 176.2, 137.6, 135.9, 132.0, 128.6, 127.7, 127.1, 126.1, 116.8, 61.7, 41.1, 36.4, 35.6, 32.3 (br s); HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{16}H_{22}NO_2$: 260.1651; found: 260.1654.

5-[3-(Benzyloxy)propyl]-3,4-dihydro-2H-pyran 4b



To a solution of **2bb** (53 mg, 0.18 mmol) in THF (2 mL) was added *t*-BuOK (20 mg, 0.18 mmol) at 0°C. The resulting mixture was stirred 30 min at rt, then water (10 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of PE/Et_2O (80/20) to give **4b** as a colorless oil (34 mg, 0.14 mmol, 80%). **^{1}**H NMR (500 MHz, $CDCl_3$) δ 7.42-7.25 (m, 5 H), 6.22 (t, *J* = 1.5 Hz, 1 H), 4.50 (s, 2 H), 3.87 (t, *J* = 5.1 Hz, 2 H), 3.46 (t, *J* = 6.5 Hz, 2 H), 1.98-1.90 (m, 4 H), 1.89-1.80 (m, 2 H), 1.74-1.63 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.2, 138.7, 128.5, 127.7, 127.6, 112.0, 73.0, 69.9, 65.3, 29.8, 28.1, 23.1, 22.7; HRMS ESI *m/z* $[M+H]_+$ calcd for $C_{15}H_{21}O_2$: 233.1542; found: 233.1542.

5-Phenyl-3,4-dihydro-2H-pyran 4d[10]

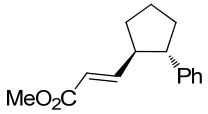


To a solution of **1bd** (75 mg, 0.34 mmol) in CH_2Cl_2 (3.5 mL) was added $Cp_2Zr(H)Cl$ (176 mg, 0.68 mmol) in one portion at room temperature. The resulting mixture was stirred until complete dissolution (ca 30 min). Then NBS (61 mg, 0.34 mmol) was added dropwise at rt, then the stirring was continued for 30 min at rt. Water (5 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. To a solution of crude **2bd** in THF (3.5mL) was added *t*-BuOK at 0°C. The resulting mixture was stirred 30 min at rt, then, water (10 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column

[10] J. J. Verendel, J.-Q. Li, X. Quan, B. Peters, T. Zhou, O. R. Gautun, T. Govender and P. G. Andersson, *Chem. Eur. J.*, 2012, **18**, 6509.

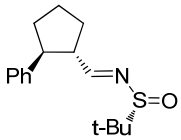
chromatography on silica gel eluting with a mixture of PE/Et_2O 80/20 to give **4d** as a colorless oil (47 mg, 0.29 mmol, 86%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (d, *J* = 4.3 Hz, 4 H), 7.09 (dt, *J* = 8.7, 4.2 Hz, 1 H), 6.85 (s, 1 H), 3.95 (t, *J* = 5.2 Hz, 2 H), 2.34 (td, *J* = 6.4, 1.6 Hz, 2 H), 1.96-1.91 (m, 2 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.2, 139.7, 128.5, 125.9, 124.2, 113.0, 65.7, 22.5, 22.4.

Methyl (*E*)-3-[(1*R*,2*S*)-2-phenylcyclopentyl]acrylate 6a



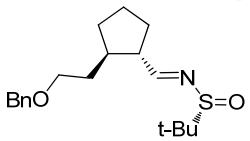
To a solution of **5a** (210 mg, 1.21 mmol) in CH_2Cl_2 (5 mL) was added **methyl 2-(triphenylphosphoranylidene)acetate** (808 mg, 2.42 mmol at room temperature. The resulting mixture was stirred 24 h at 80°C and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 (Rf 0.8) to give **6a** as a colorless oil (271 mg, 1.17 mmol, 97%), E/Z 93:7, $[\alpha]_D$ +123° (*c* 1.26 , CH_2Cl_2). NMR (500 MHz, $CDCl_3$) ^{1}H δ 7.39-7.24 (m, 2 H), 7.23-7.07 (m, 3 H), 6.90 (dd, *J* = 15.7, 8.1 Hz, 1 H), 5.65 (dd, *J* = 15.7, 1.1 Hz, 1 H), 3.67 (s, 3 H), 2.82 (td, *J* = 9.7, 7.9 Hz, 1 H), 2.74-2.65 (m, 1 H), 2.20-2.13 (m, 1 H), 2.10-2.01 (m, 1 H), 1.89-1.73 (m, 3 H), 1.73-1.57 (m, 1 H); NMR (126 MHz, $CDCl_3$) ^{13}C δ 167.1, 151.8, 143.5, 128.4, 127.3, 126.3, 120.2, 52.2, 51.3, 50.7, 35.2, 32.5, 24.3; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{15}H_{19}O_2$: 231.1385; found: 231.1380.

(*R*)-2-Methyl-*N*-{(E)-[(1S,2S)-2-phenylcyclopentyl]methylene}propane-2-sulfinamide 7a



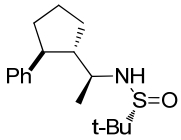
To a solution of **5a** (114 mg, 0.66 mmol) in CH_2Cl_2 (3 mL) was added (*R*)-2-methylpropane-2-sulfinamide (80 mg, 0.66 mmol) and $CuSO_4$ (209 mg, 1.32 mmol). The resulting mixture was stirred 72h at 80°C. Brine (5 mL) was added, and the layers were separated and the aqueous phase was extracted with AE (2 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **7a** as a colorless oil (184 mg, 0.66 mmol, 100%), $[\alpha]_D$ - 31 (*c* 1.42 , CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.2 Hz, 1 H), 7.31-7.08 (m, 5 H), 3.21-3.02 (m, 2 H), 2.30-2.22 (m, 1 H), 2.16-2.07 (m, 1 H), 1.98-1.77 (m, 4 H), 0.96 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.3, 142.9, 128.6, 127.6, 126.5, 56.5, 53.9, 50.7, 35.7, 30.3, 24.7, 22.2; HRMS ESI *m/z* $[M+Na]^+$ calcd for $C_{16}H_{24}NOS$: 278.1579; found: 278.1581.

(*R,E*)-*N*-({(1*S*,2*R*)-2-[2-(Benzyloxy)ethyl]cyclopentyl}methylene)-2-methylpropane-2-sulfinamide 7l



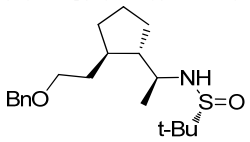
Prepared according to the above procedure from **5l** (24 mg, 0.10 mmol) and isolated as a colorless oil (35 mg, 0.10 mmol, 100%). $[\alpha]_D$ -143 (*c 0.61* CH_2Cl_2) ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 6.2 Hz, 1 H), 7.40-7.26 (m, 5 H), 4.51 (d, *J* = 12.0 Hz, 1 H), 4.47 (d, *J* = 12.0 Hz, 1 H), 3.56-3.44 (m, 2 H), 2.63 (qd, *J* = 8.2, 6.2 Hz, 1 H), 2.12 (pd, *J* = 8.6, 5.1 Hz, 1 H), 2.02-1.83 (m, 3 H), 1.81-1.65 (m, 3 H), 1.59 (ddt, *J* = 13.2, 9.0, 6.4 Hz, 1 H), 1.34 (dq, *J* = 12.6, 8.4 Hz, 1 H), 1.22 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.4, 138.6, 128.5, 127.7, 127.6, 73.0, 69.3, 56.6, 52.2, 41.2, 34.8, 32.7, 30.1, 24.7, 22.5; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{19}H_{30}NO_2S$:336.1997; found: 326.2003.

(*R*)-2-Methyl-*N*-{(S)-1-[(1*S*,2*S*)-2-phenylcyclopentyl]ethyl}propane-2-sulfinamide 8a



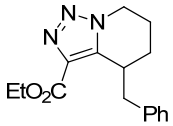
To a solution of **7a** (135 mg, 0.49 mmol) in CH_2Cl_2 (3 mL) was added MeMgBr (*c* 3 M in Et_2O, 0.33 mL, 1 mmol) at -50°C. The resulting mixture was stirred 4 h at -50°C, then overnight at rt. Water (5 mL) was added. The layers were separated and the aqueous phase was extracted with AcOEt (2 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **8a** as a colorless oil (137 mg, 0.47 mmol, 96%), $[\alpha]_D$ + 34 (*c* 0.98 , CH_2Cl_2); NMR (500 MHz, $CDCl_3$) δ 7.33-7.27 (m, 2 H), 7.26-7.10 (m, 3 H), 3.41-3.29 (m, 1 H), 3.04-2.74 (m, 2 H), 2.11-1.99 (m, 2 H), 1.94-1.87 (m, 1 H), 1.86-1.78 (m, 1 H), 1.74-1.61 (m, 2 H), 1.54-1.45 (m, 1 H), 1.23 (d, *J* = 6.7 Hz, 3 H), 1.15 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 145.4, 128.6, 127.7, 126.2, 56.0, 54.7, 54.5, 48.1, 36.2, 27.4, 24.7, 22.8, 22.7; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{17}H_{28}NOS$: 294.1892; found: 294.1889.

(S)-*N*-[(*S*)-1-{(1*S*,2*R*)-2-[2-(Benzyloxy)ethyl]cyclopentyl}ethyl]-2-methylpropane-2-sulfinamide 8l



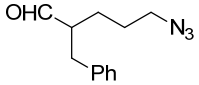
Prepared according to the above procedure from **7l** (31 mg, 0.092 mmol), and isolated as a corlorless oil (32 mg, 0.091 mmol, 98%). $[\alpha]_D$: +9 (*c 0.61* CH_2Cl_2); NMR ^{1}H (500 MHz, $CDCl_3$) δ 7.39-7.26 (m, 5 H), 4.50 (d, *J* = 12.0 Hz, 1 H), 4.46 (d, *J* = 11.9 Hz, 1 H), 3.56-3.33 (m, 3 H), 2.83 (d, *J* = 9.1 Hz, 1 H), 1.89-1.66 (m, 5 H), 1.58-1.44 (m, 4 H), 1.30 (d, *J* = 6.6 Hz, 3 H), 1.23-1.19 (m, 1 H), 1.18 (s, 9 H); NMR ^{13}C (126 MHz, $CDCl_3$) δ 138.7, 128.4, 127.7, 127.6, 72.9, 69.6, 56.1, 55.1, 52.6, 38.5, 35.3, 32.7, 27.2, 24.5, 23.2, 22.9; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{20}H_{34}NO_2S$: 352.2310; found: 352.2310.

Ethyl 4-benzyl-4,5,6,7-tetrahydro-[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 9



To a solution of **3ba** (130 mg, 0.42 mmol) in acetone (1.5 mL) was added NaN_3 (137 mg, 2.1 mmol) at room temperature. The resulting mixture was stirred 72h at 55°C and concentrated under reduced pressure. Water (4 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 4 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of cyclohexane/AE (80:20) Rf 0.1, to give **9** as a white solid (107 mg, 0.38 mmol, 90%). Mp 113°C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.11 (m, 5 H), 4.58 (ddd, *J* = 13.4, 5.7, 2.9 Hz, 1 H), 4.47 (q, *J* = 7.1 Hz, 2 H), 4.19 (ddd, *J* = 13.4, 11.1, 5.1 Hz, 1 H), 3.71 (ddt, *J* = 11.6, 6.2, 3.1 Hz, 1 H), 3.35 (dd, *J* = 13.5, 3.5 Hz, 1 H), 2.57 (dd, *J* = 13.5, 11.1 Hz, 1 H), 2.20-2.14 (m, 1 H), 2.00 (ddt, *J* = 13.8, 5.4, 3.0 Hz, 1 H), 1.85 (ddt, *J* = 14.3, 5.5, 2.8 Hz, 1 H), 1.66 (ddt, *J* = 17.8, 14.2, 3.1 Hz, 1 H), 1.45 (t, *J* = 7.1 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.6, 142.6, 139.0, 135.4, 129.3, 128.7, 126.8, 61.1, 46.7, 38.9, 33.1, 22.1, 18.2, 14.6; HRMS ESI *m/z* $[M+H]_+$ calcd for $C_{16}H_{20}N_3O_2$: 286.1556; found: 286.1558.

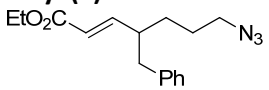
5-azido-2-benzylpentanal 10



To a solution of **2ba** (87 mg, 0.34 mmol) in DMF (1.5 mL) was added NaN_3 (27 mg, 0.41 mmol) in one portion at rt. The resulting mixture was stirred overnight at rt. Water (2 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 10 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **10** as a

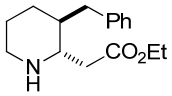
colorless oil (74 mg, 0.34 mmol, 100%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.69 (d, *J* = 2.2 Hz, 1 H), 7.34-7.27 (m, 2 H), 7.25-7.19 (m, 1 H), 7.18-7.15 (m, 2 H), 3.26 (t, *J* = 6.5 Hz, 2 H), 3.02 (dd, *J* = 14.0, 7.1 Hz, 1 H), 2.74 (dd, *J* = 14.0, 7.2 Hz, 1 H), 2.69-2.60 (m, 1 H), 1.77-1.48 (m, 4 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 203.9, 138.4, 129.0, 128.8, 126.7, 53.0, 51.3, 35.2, 26.5, 25.6; HRMS ESI *m/z* $[M-N_2]_+$ calcd for $C_{12}H_{16}NO$: 190.1233; found: 190.1233.

Ethyl (*E*)-7-azido-4-benzylhept-2-enoate 11



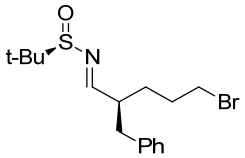
To a solution of **10** (70 mg, 0.32 mmol) in CH_2Cl_2 (2 mL) was added **ethyl 2-(triphenylphosphoranylidene)acetate** (129 mg, 0.39 mmol) at room temperature. The resulting mixture was stirred 1 h at rt and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of CH_2Cl_2 (Rf 0.9) to give **11** a colorless oil (70 mg, 0.24, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.23 (m, 2 H), 7.22-7.18 (m, 1 H), 7.14-7.08 (m, 2 H), 6.78 (dd, *J* = 15.7, 9.1 Hz, 1 H), 5.70 (dd, *J* = 15.6, 0.9 Hz, 1 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.30-3.09 (m, 2 H), 2.71 (d, *J* = 7.1 Hz, 2 H), 2.52-2.42 (m, 1 H), 1.68-1.34 (m, 4 H), 1.27 (t, *J* = 7.1 Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.4, 151.4, 139.1, 129.2, 128.5, 126.4, 122.1, 60.4, 51.4, 44.1, 41.1, 30.7, 26.8, 14.3; HRMS ESI *m/z* $[M+H]_+$ calcd for $C_{16}H_{22}N_3O_2Br$: 288.1712; found: 288.1713.

Ethyl 3-benzylpiperidine-2-carboxylate 12



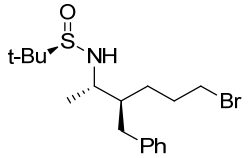
To a solution of **11** (60 mg, 0.21 mmol) in THF (2.5 mL) was added Ph_3P (66 mg, 0.25 mmol) at room temperature. The resulting mixture was stirred overnight at rt and concentrated under reduced pressure. Water (4 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 4 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with a mixture of PE :AE to give **12** as a colorless oil (36 mg, 0.13 mmol, 64%) dr 70:30. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40-6.99 (m, 5 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.08-2.97 (m, 1 H), 2.91 (dd, *J* = 13.4, 4.1 Hz, 1 H), 2.86-2.70 (m, 2 H), 2.68-2.57 (m, 2 H), 2.53 (br s, 1 H), 2.20 (dd, *J* = 13.4, 10.0 Hz, 1 H), 1.76-1.53 (m, 2 H), 1.47-1.31 (m, 1 H), 1.28 (t, *J* = 7.1 Hz, 3 H), 1.01 (qd, *J* = 12.6, 3.7 Hz, 1 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.9, 140.1, 129.3, 128.4, 126.1, 60.7, 58.3, 46.4, 42.3, 39.2, 38.6, 30.2, 26.1, 14.3; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{16}H_{24}NO_2$: 262.1807; found: 262.1810.

(*R*)-*N*-[(*S*,*E*)-2-Benzyl-5-bromopentylidene]-2-methylpropane-2-sulfinamide 13



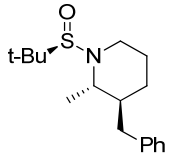
To a solution of (-)-**2ba-Br** (149 mg, 0.59 mmol) in CH_2Cl_2 (4 mL) was added $CuSO_4$ (188 mg, 1.17 mmol) and (*R*)-2-methylpropane-2-sulfinamide at room temperature. The resulting mixture was refluxed for 24 h. The reaction mixture was cooled down to rt, then water (5 mL) was added. The layers were separated and the aqueous phase was extracted with AcOEt (2 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **13** as a yellow oil (185 mg, 0.52 mmol, 88%), $[\alpha]_D$ -185 (*c* 1.44 , CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 5.6 Hz, 1 H), 7.42-7.08 (m, 5 H), 3.38 (t, *J* = 6.6 Hz, 2 H), 2.94-2.80 (m, 3 H), 2.01-1.80 (m, 2 H), 1.78-1.66 (m, 2 H), 1.03 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.5, 138.6, 129.1, 128.7, 126.6, 56.7, 46.7, 38.7, 33.3, 30.5, 30.2, 22.3; HRMS ESI *m/z* $[M+Na]^+$ calcd for $C_{16}H_{24}NONaSBr$: 380.0660; found: 380.0667.

(*R*)-*N*-[(2*S*,3*S*)-3-Benzyl-6-bromohexan-2-yl]-2-methylpropane-2-sulfinamide 14



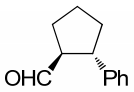
To a solution of **13** (180 mg, 0.50 mmol) in CH_2Cl_2 (3 mL) was added MeMgBr (3 M in Et_2O, 0.34 mL, 1 mmol) at -50°C. The resulting mixture was stirred 4 h at -50°C, then overnight at rt. Water (5 mL) was added. The layers were separated and the aqueous phase was extracted with AcOEt (2 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **14** as a yellow oil (176 mg, 0.47 mmol, 94%), dr >98:2 $[\alpha]_D$ -15° (*c* 1.3 , CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-6.67 (m, 5 H), 3.51-3.46 (m, 1 H), 3.40-3.27 (m, 2 H), 2.84 (d, *J* = 7.5 Hz, 1 H), 2.74 (dd, *J* = 13.7, 6.9 Hz, 1 H), 2.46 (dd, *J* = 13.7, 7.3 Hz, 1 H), 1.88-1.79 (m, 3 H), 1.50 (ddt, *J* = 13.0, 9.1, 6.1 Hz, 1 H), 1.41-1.32 (m, 1 H), 1.27 (d, *J* = 6.7 Hz, 3 H), 1.21 (s, 9 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 140.8, 129.2, 128.6, 126.2, 55.9, 53.8, 45.7, 36.2, 33.8, 30.8, 28.7, 22.9, 19.6; HRMS ESI *m/z* $[M+H]_+$ calcd for $C_{17}H_{29}NOSBr$: 374.1553; found: 374.1156.

(2*S*,3*S*)-3-Benzyl-1-[(*R*)-*tert*-butylsulfinyl]-2-methylpiperidine 15

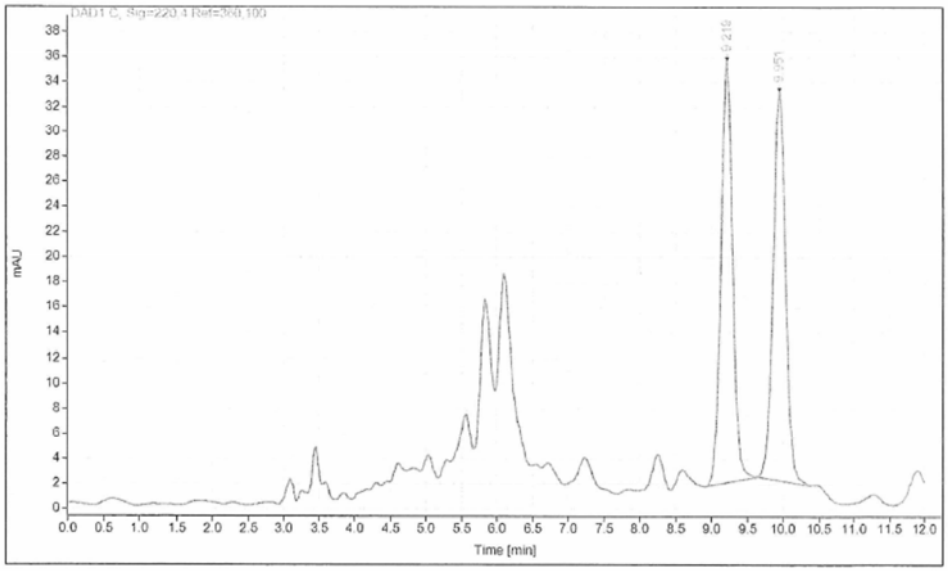


To a solution of **14** (170 mg, 0.46 mmol) in THF (2 mL) was added NaH (13 mg, 0.55 mmol) at 0°C. The resulting mixture was stirred 2 h at rt then, water (5 mL) was added. The layers were separated and the aqueous phase was extracted with Et_2O (2 x 5 mL). The organic phases were combined, dried over Na_2SO_4, filtered and concentrated under reduced pressure to give **15** as a yellow oil (128 mg, 0.44 mmol, 96%), dr >95:5 $[\alpha]_D$ +19 (*c* 1.2 , CH_2Cl_2); NMR (500 MHz, $CDCl_3$) ^{1}H δ 7.43-6.84 (m, 5 H), 3.31 (qd, *J* = 6.8, 2.6 Hz, 1 H), 3.08 (dt, *J* = 13.1, 3.4 Hz, 1 H), 3.01 (ddd, *J* = 13.3, 11.1, 3.2 Hz, 1 H), 2.87 (dd, *J* = 13.7, 6.5 Hz, 1 H), 2.78 (dd, *J* = 13.7, 8.5 Hz, 1 H), 1.85-1.65 (m, 4 H), 1.45-1.39 (m, 1 H), 1.36 (d, *J* = 6.8 Hz, 3 H), 1.25 (s, 9 H); NMR (126 MHz, $CDCl_3$) ^{13}C δ 141.0, 129.1, 128.4, 126.0, 58.7, 58.4, 41.7, 39.0, 38.8, 23.8, 23.2, 21.3, 16.9; HRMS ESI *m/z* $[M+H]^+$ calcd for $C_{17}H_{18}NOS$: 294.1892; found: 294.1890.

HPLC of **(1*S*,2*S*)-2-phenylcyclopentane-1-carbaldehyde 5a**



Instrument:	LC1260	Location:	Vial 1
Injection date:	11/12/2021 10:59:46 AM	Injection:	1 of 1
Acq. method:	COELHO_IC_HEX-IPA_90-10.M	Injection volume:	2.000
Analysis method:	COELHO_IC_HEX-IPA_90-10.M	Acq. operator:	SYSTEM
Last changed:	11/12/2021 11:30:16 AM (modified after loading)		



Signal: DAD1 C, Sig=220,4 Ref=360,100

RT [min]	Area %	Plates	Symm.	Resolution
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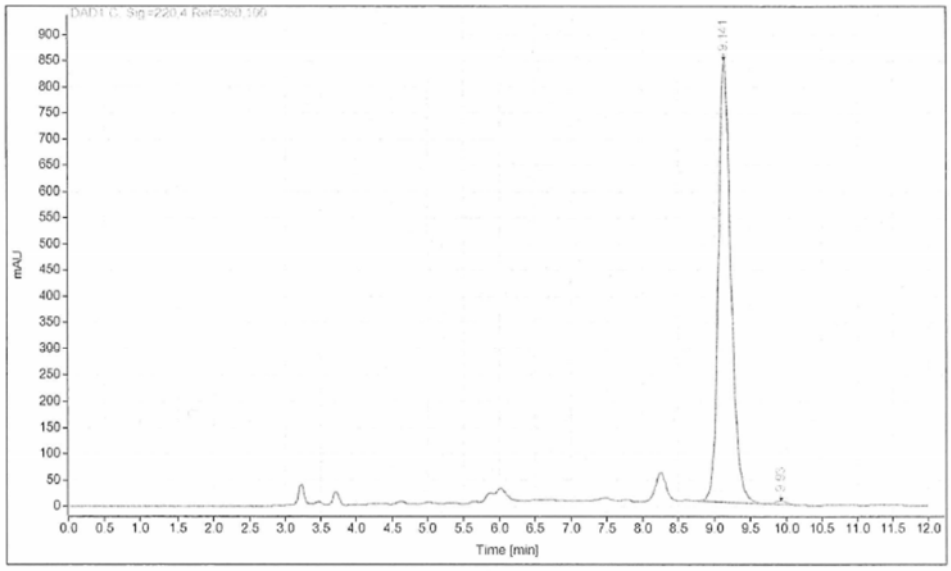
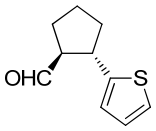
9.95	49.60	16109	0.97	2.41



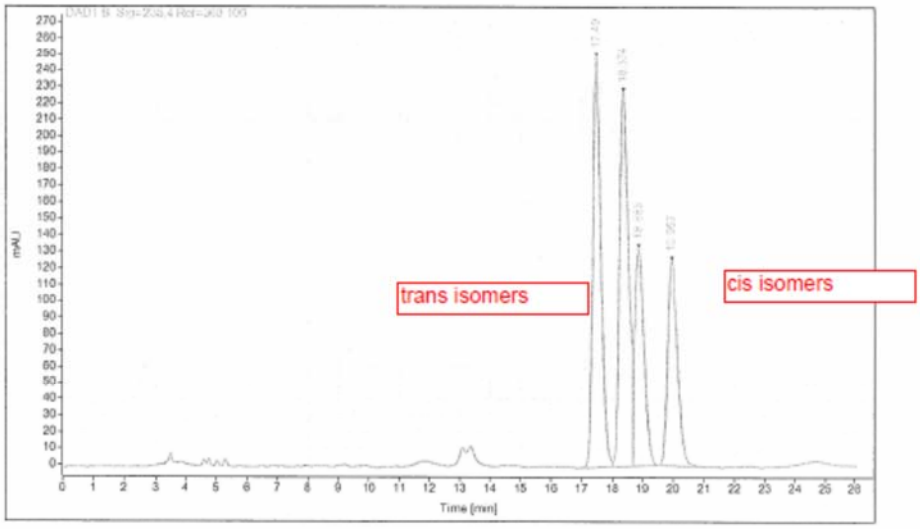
Signal: DAD1 C, Sig=220,4 Ref=360,100

RT [min]	Area %	Plates	Symm.	Resolution
9.14	99.25	13426	0.75	
9.93	0.7499	15983	0.97	2.51

(1*S*,2*S*)-2-(Thiophen-2-yl)cyclopentane-1-carbaldehyde 5k



Data file:	D:\UMR7312\DATA\COELHO\AC763_291121-4 2021-11-29 15-51-00.D		
Sample name:	AC763_291121-4		
Description:	AC763 dans hexane, colonne IC, hexane/DCM 85:15, 1 mL/min, 42 bar, 220, 235 nm, 22°C, 5 µL		
Sample amount:	1.000	Sample type:	Sample
Instrument:		Location:	Vial 2
Injection date:	11/29/2021 3:52:33 PM	Injection:	1 of 1
Acq. method:		Injection volume:	
Analysis method:	COELHO_IC_HEX-DCM_50-50.M	Acq. operator:	SYSTEM
Last changed:	11/29/2021 3:48:50 PM (modified after loading)		



Signal: DAD1 B, Sig=235,4 Ref=360,100

RT [min]	Area %	Plates	Symm.	Resolution
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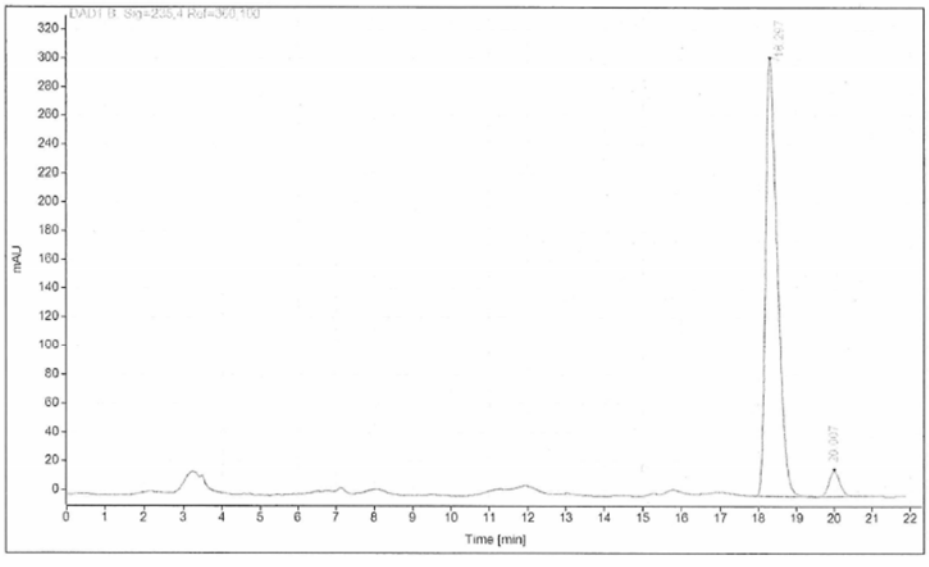
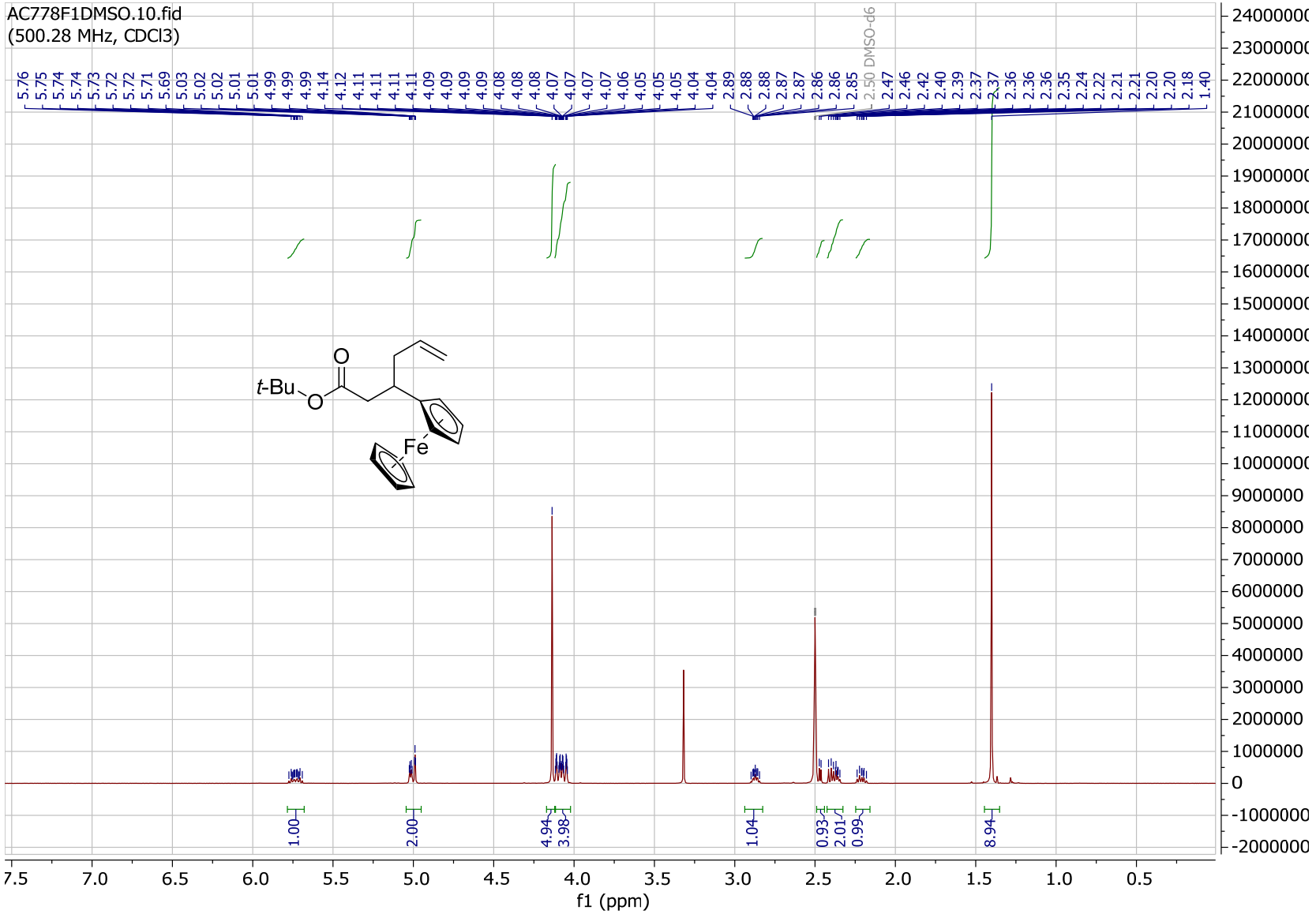
18.37	30.49	17879	0.65	1.70
18.88	19.31	13153	0.72	0.85
19.96	18.75	18892	0.66	1.74

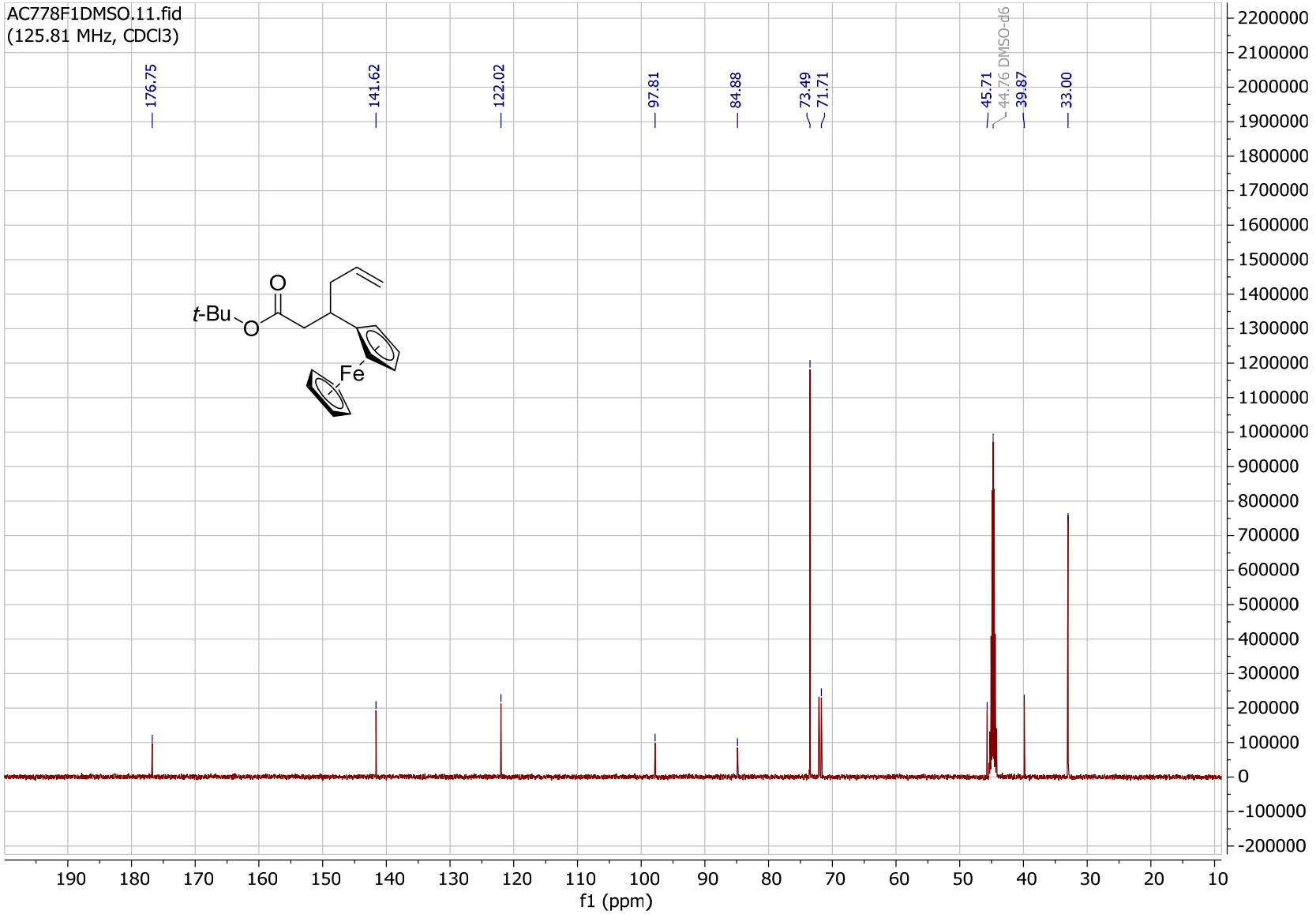


Signal: DAD1 B, Sig=235,4 Ref=360,100

RT [min]	Area %	Plates	Symm.	Resolution
18.30	94.80	17086	0.52	
20.01	5.202	22102	0.90	3.12

Tert-Butyl 3-(ferrocenyl)hex-5-enoate S1

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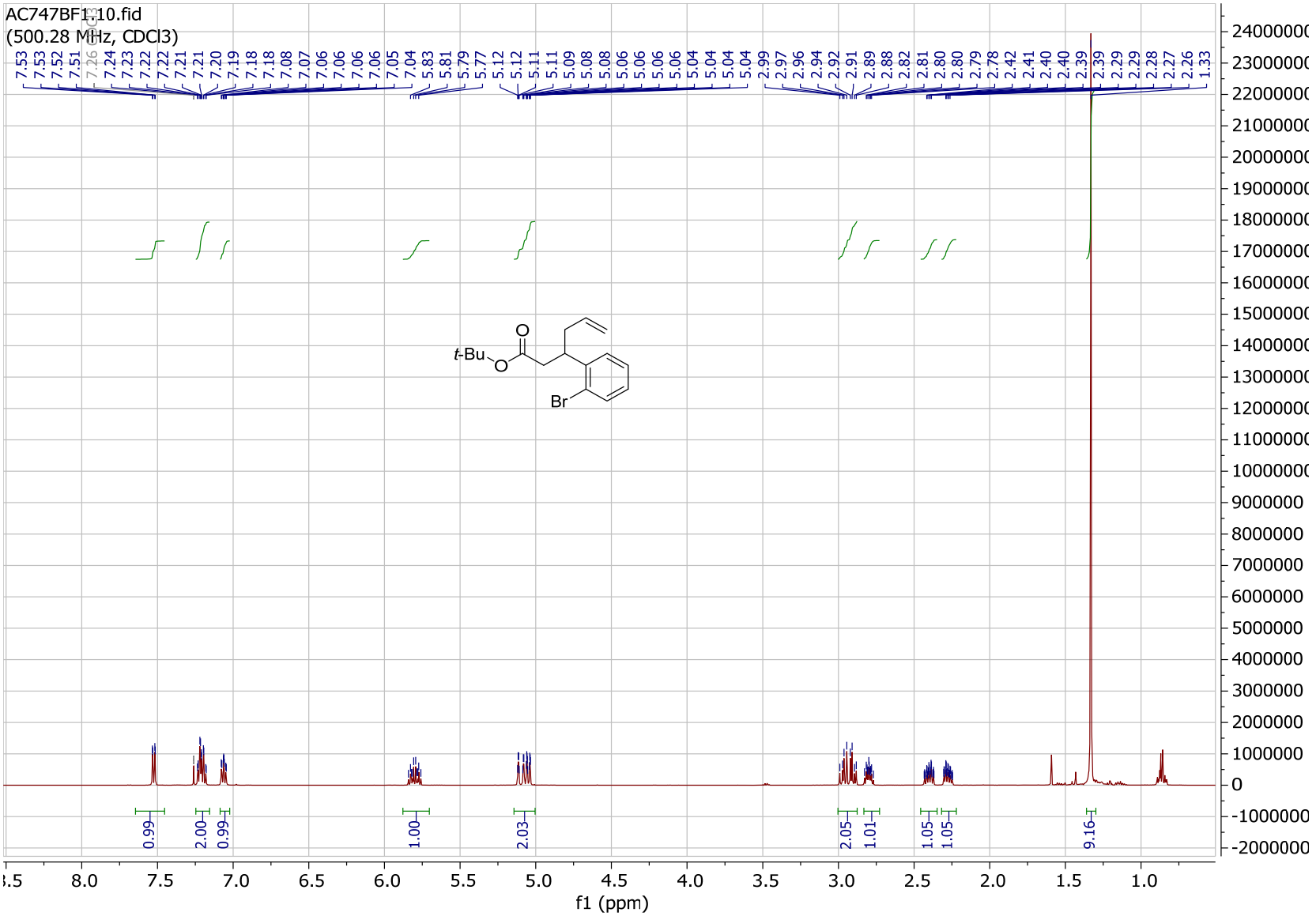
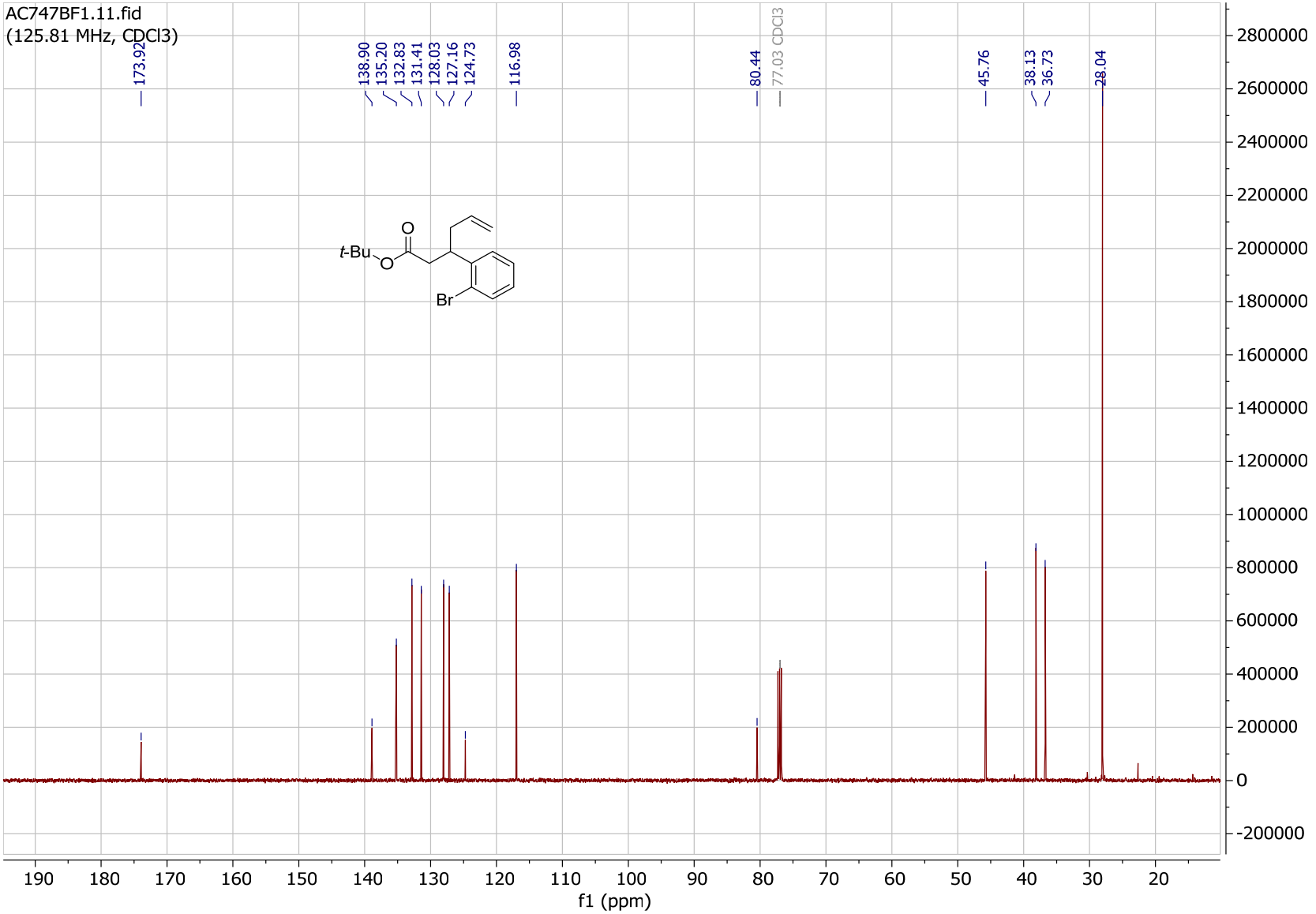
84.88
73.49
71.71
45.71
44.76 DMSO-d6
39.87
33.00
t-Bu
O
O
Fe
f1 (ppm)

Tert-Butyl 3-(2-bromophenyl)hex-5-enoate S2

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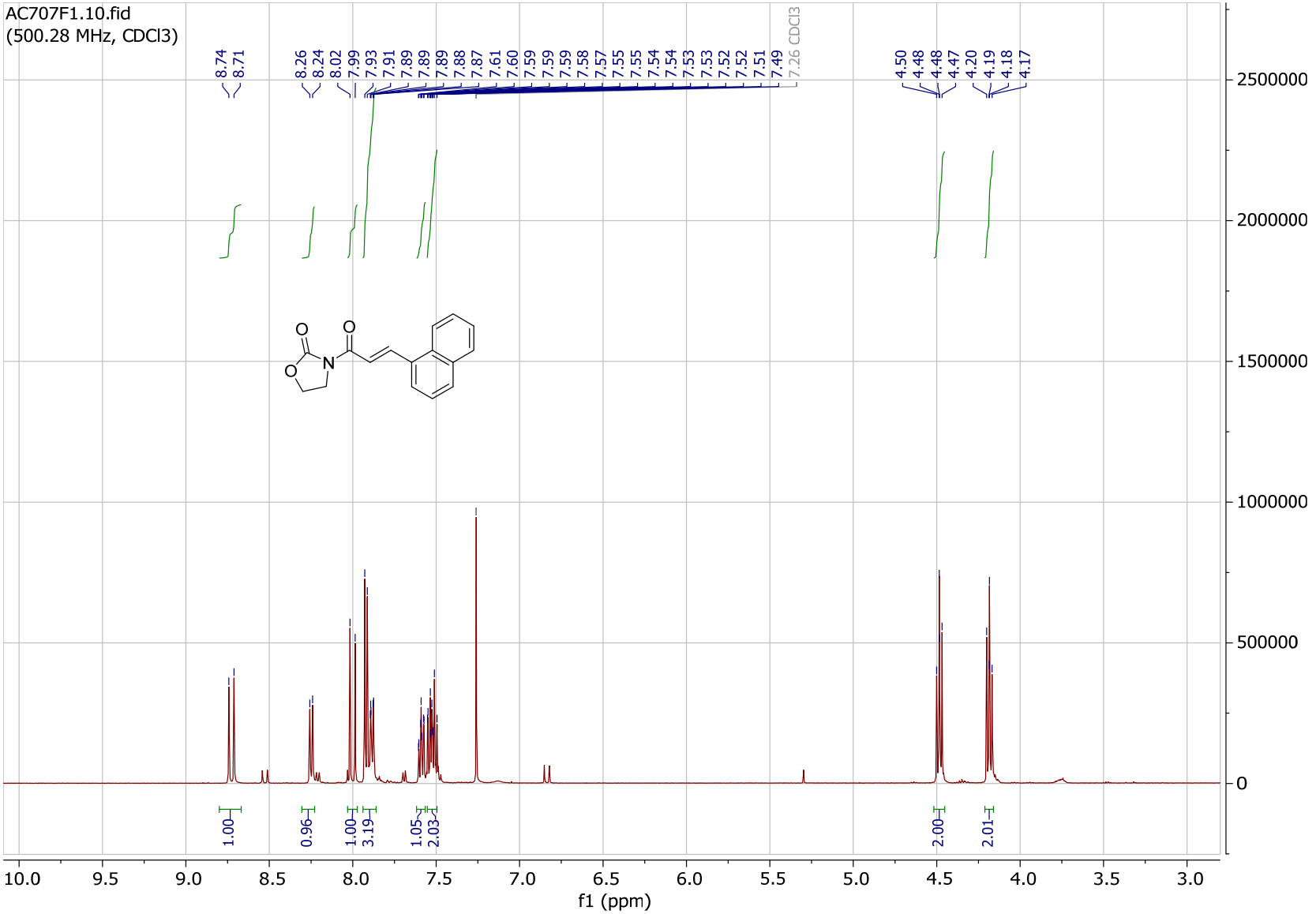
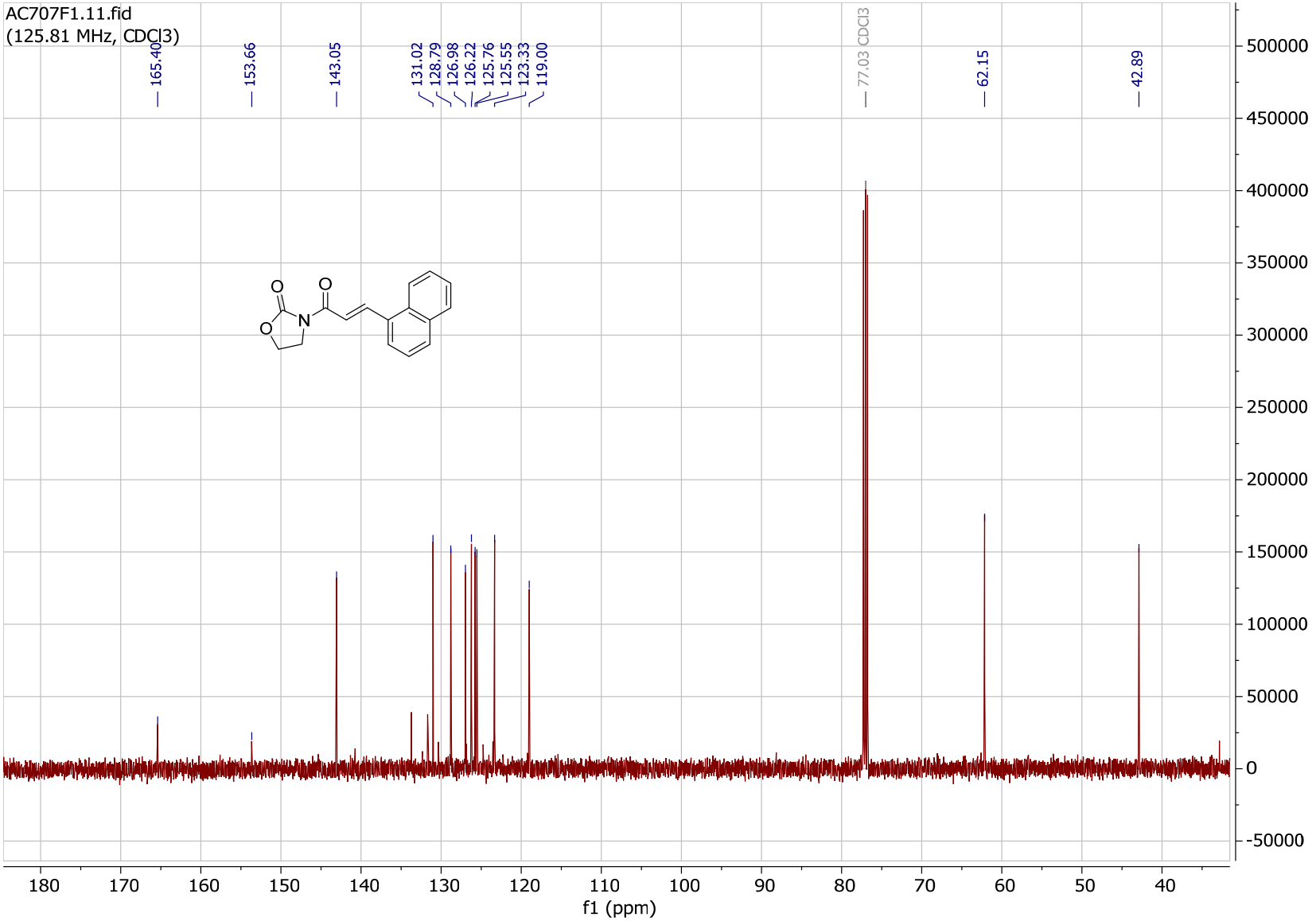
132.83
131.41
128.03
127.16
124.73
116.98
80.44
77.03 CDCl3
45.76
38.13
36.73
28.04
t-Bu
O
O
Br
2800000
2600000
2400000
2200000
2000000
1800000
1600000
1400000
1200000
1000000
800000
600000
400000
200000
0
-200000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

(*E*)-3-[3-(Naphthalen-1-yl)acryloyl]oxazolidin-2-one S3

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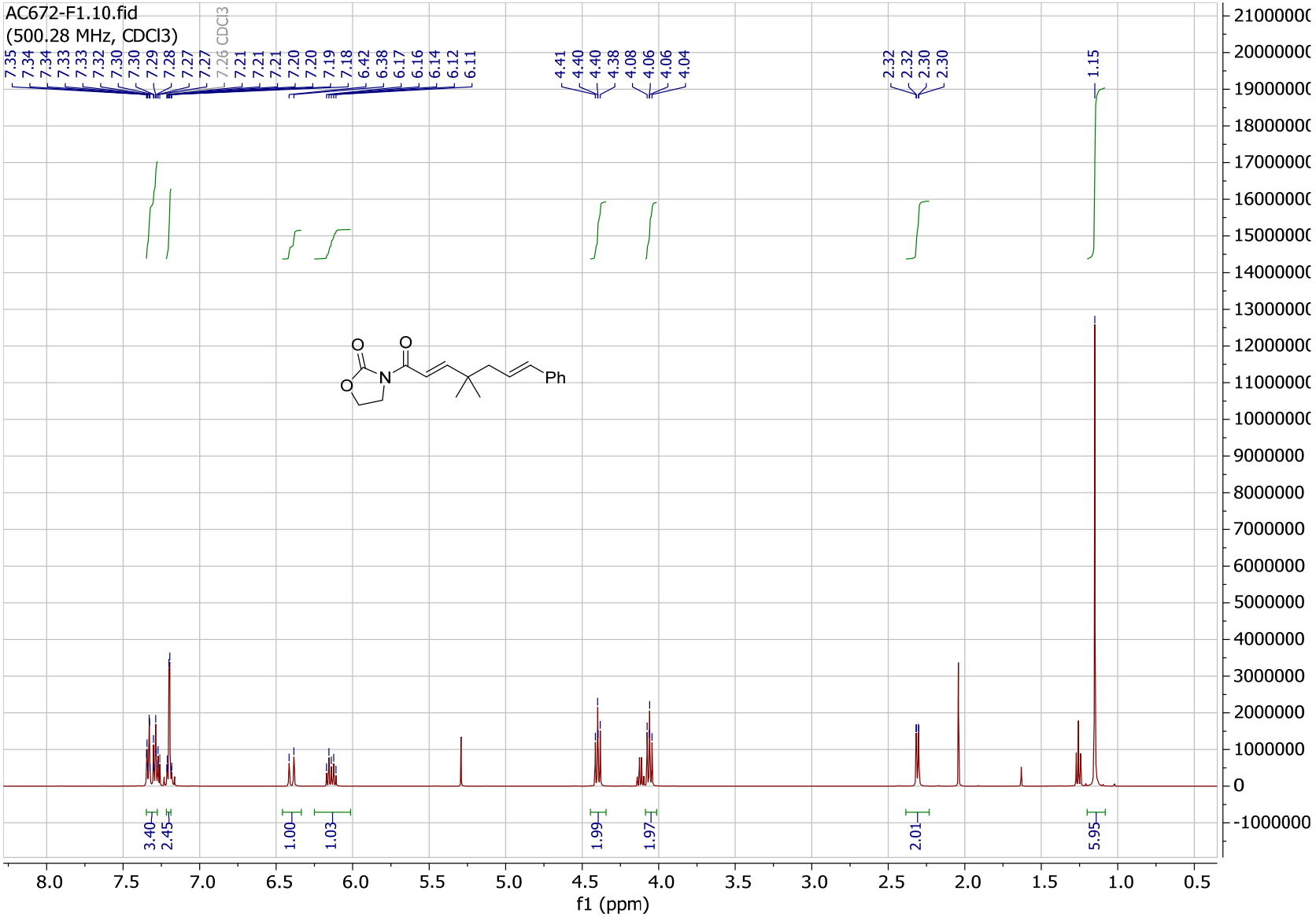
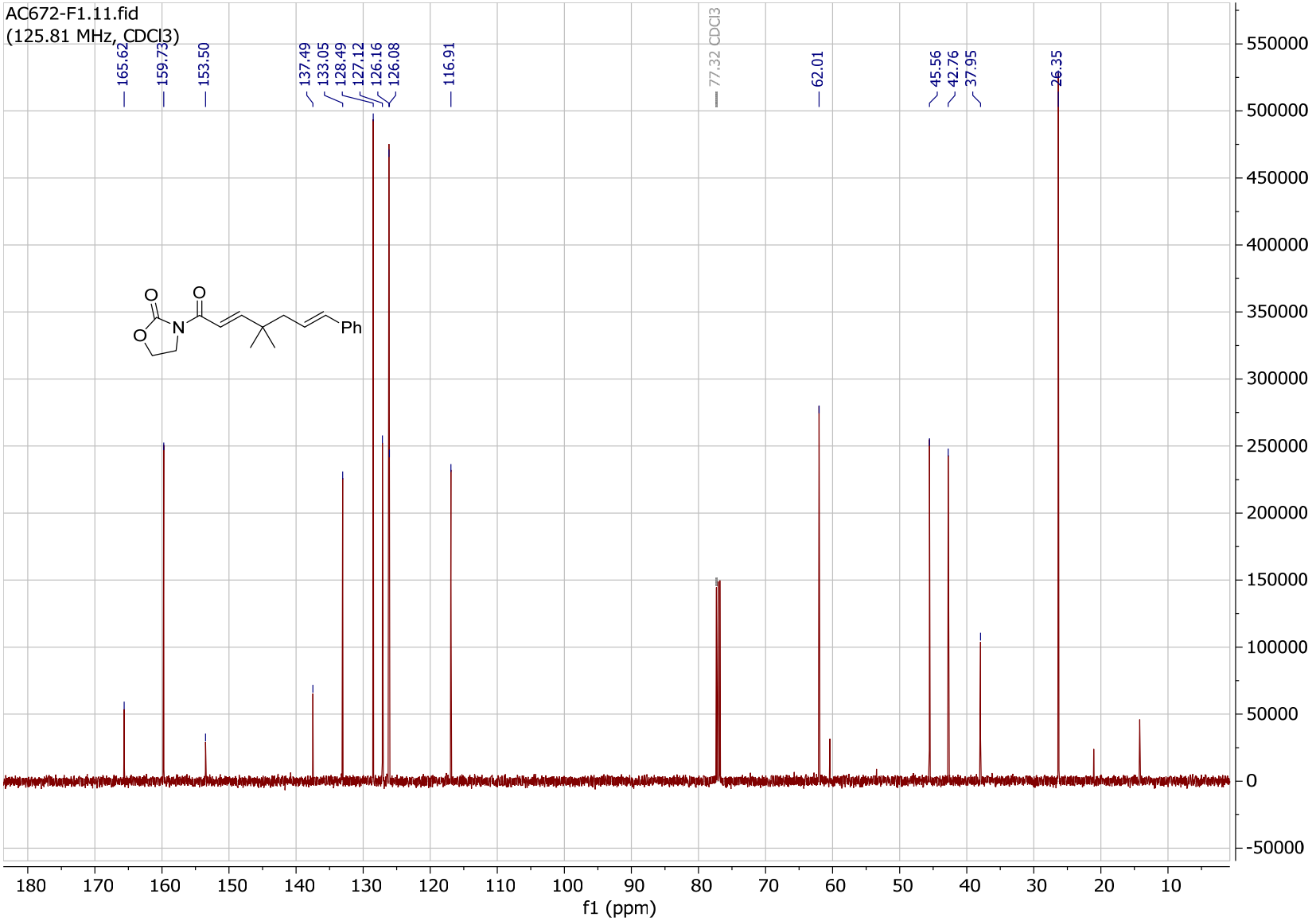
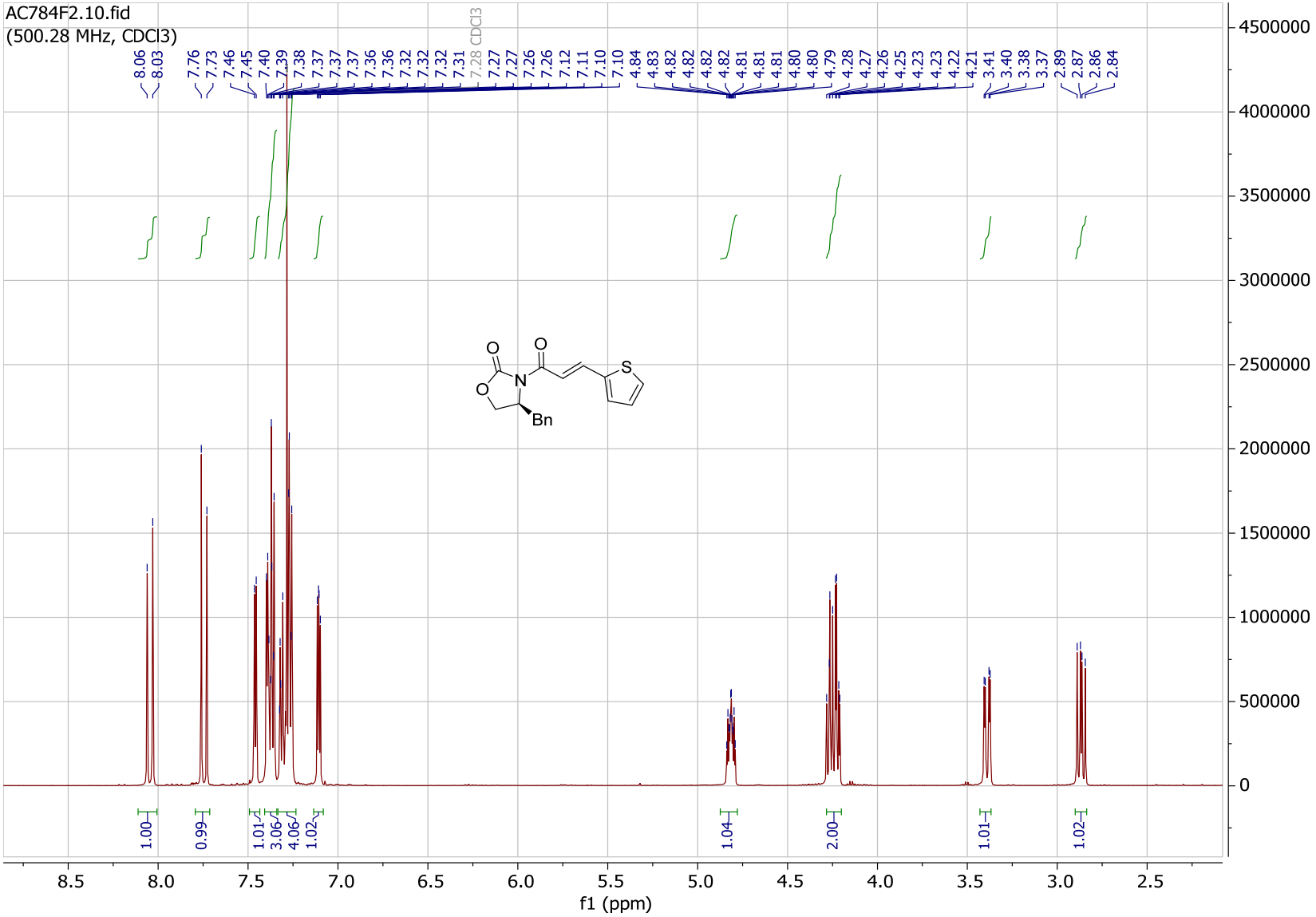
143.05
131.02
128.79
126.98
126.22
125.76
125.55
123.33
119.00
77.03 CDCl3
62.15
42.89
O
O
O
N
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
f1 (ppm)

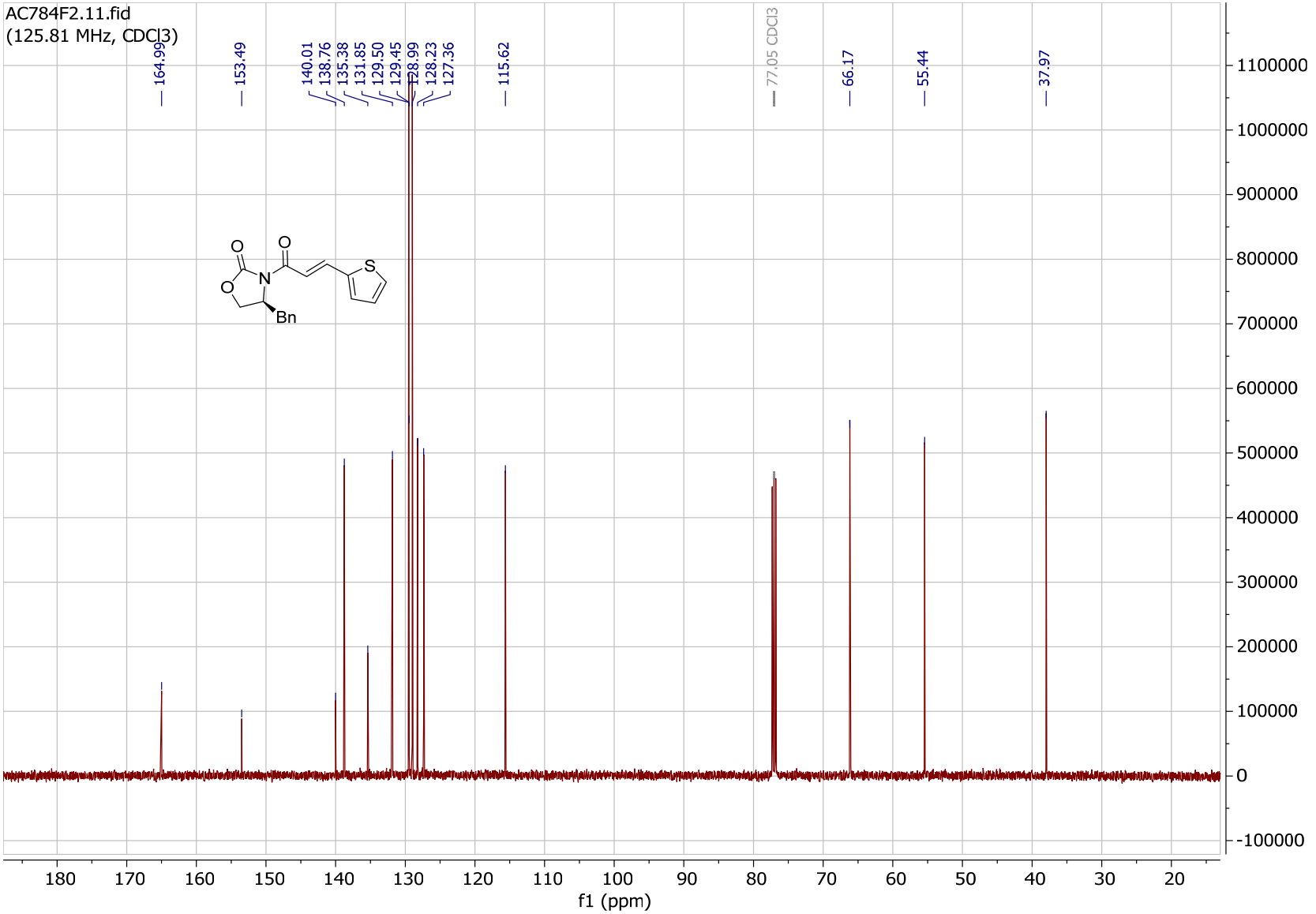
3-[(2*E*,6*E*)-4,4-Dimethyl-7-phenylhepta-2,6-dienoyl]oxazolidin-2-one S4



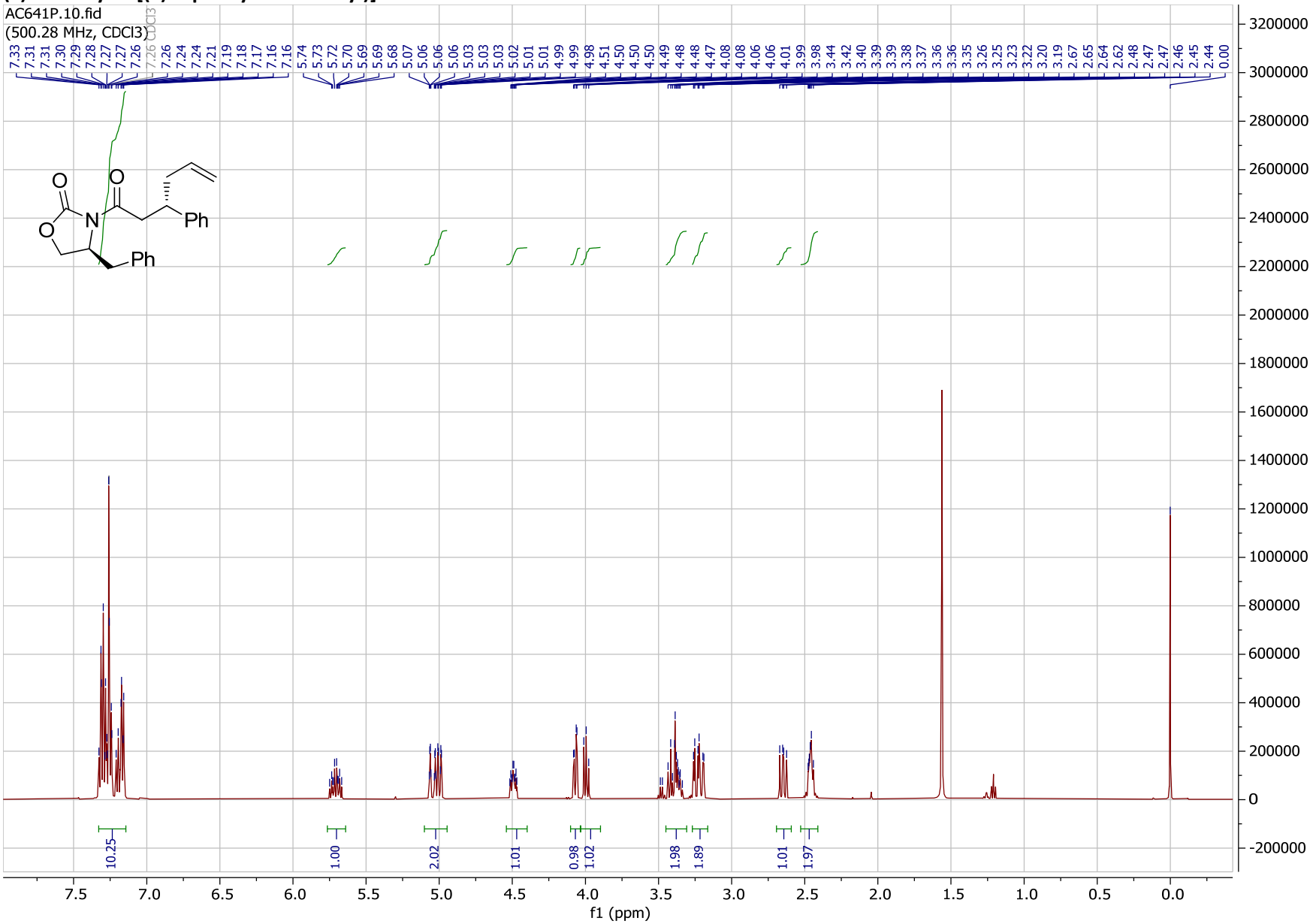

AC672-F1.11.fid
(125.81 MHz, CDCl3)
165.62
159.73
153.50
137.49
133.05
128.49
127.12
126.16
126.08
116.91
77.32 CDCl3
62.01
45.56
42.76
37.95
26.35
O
O
O
N
Ph
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

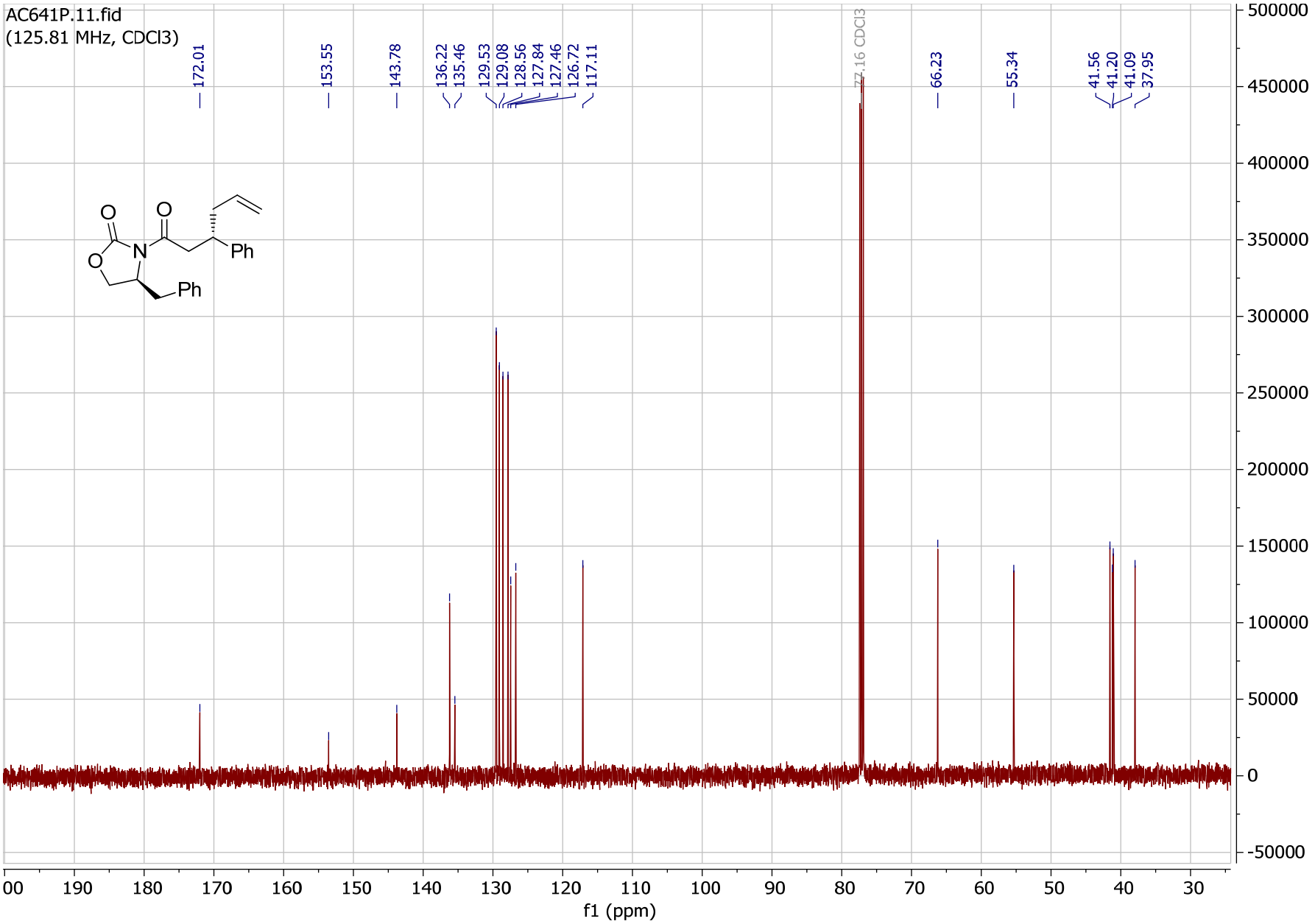
(*R*,*E*)-4-Benzyl-3-[3-(thiophen-2-yl)acryloyl]oxazolidin-2-one S5



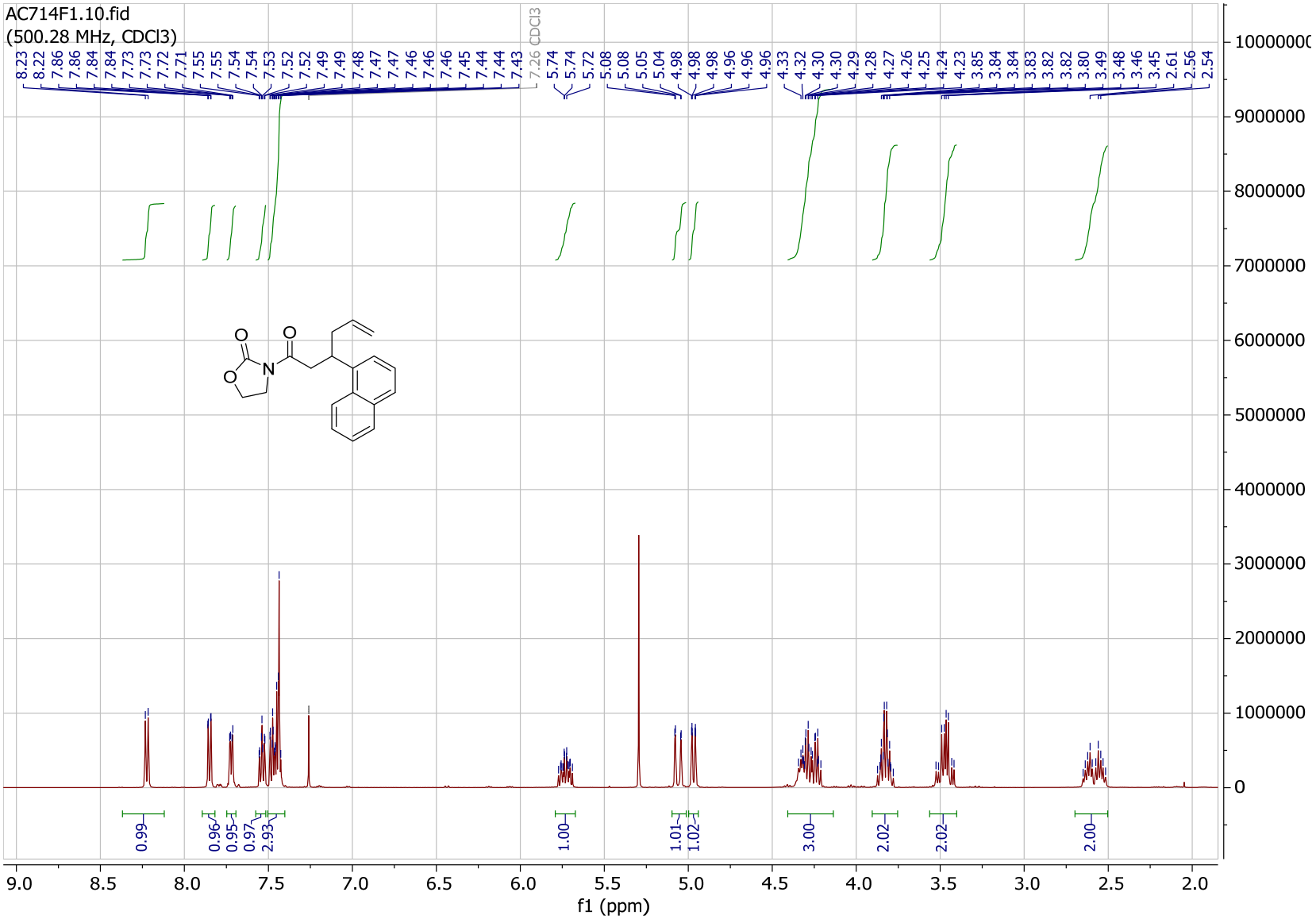

AC784F2.11.fid
(125.81 MHz, CDCl3)
164.99
153.49
140.01
138.76
135.38
131.85
129.50
129.45
128.99
128.23
127.36
115.62
77.05 CDCl3
66.17
55.44
37.97
O
O
N
O
S
Bn
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

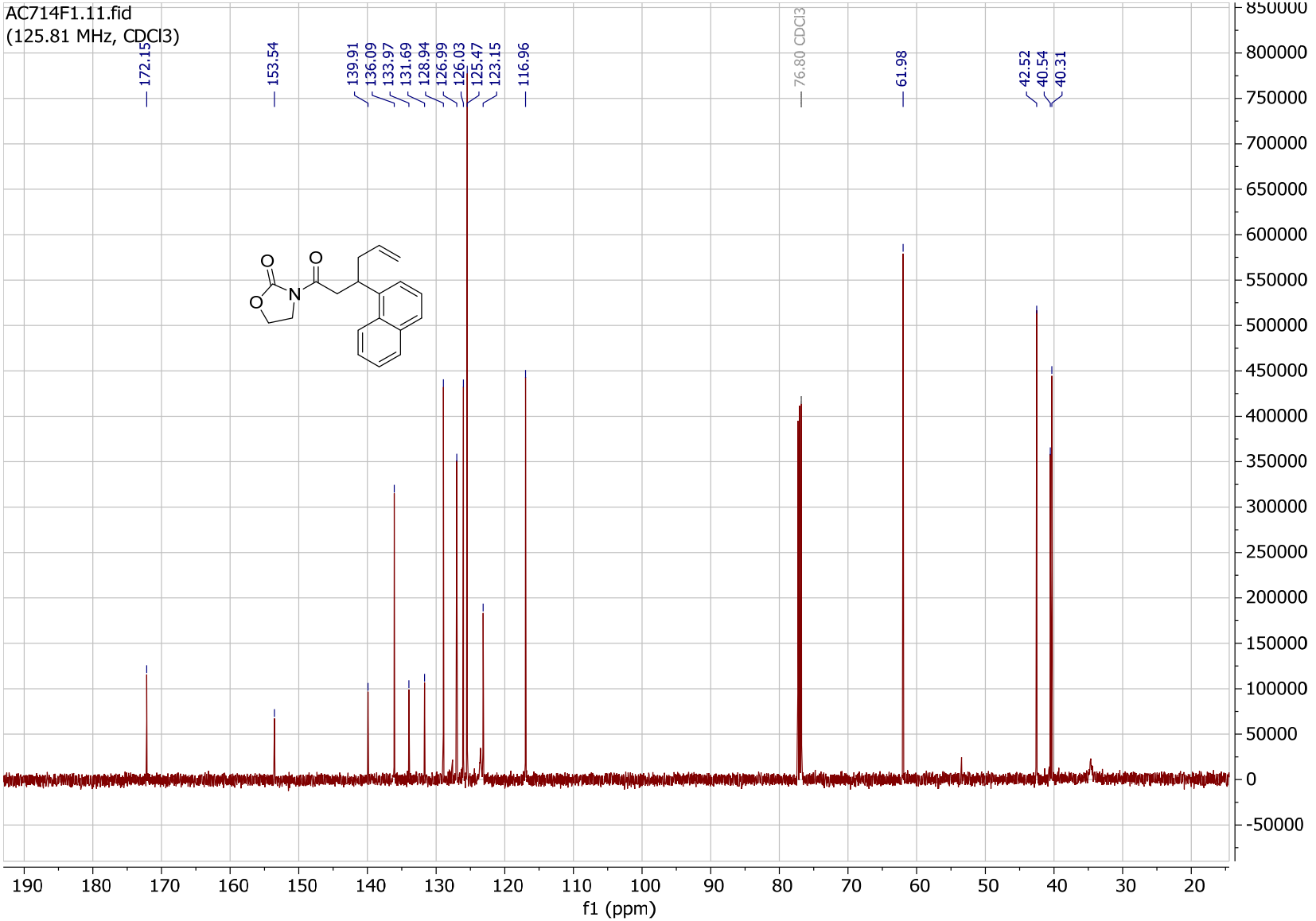
(S)-4-Benzyl-3-[(S)-3-phenylhex-5-enoyl)]oxazolidin-2-one S6



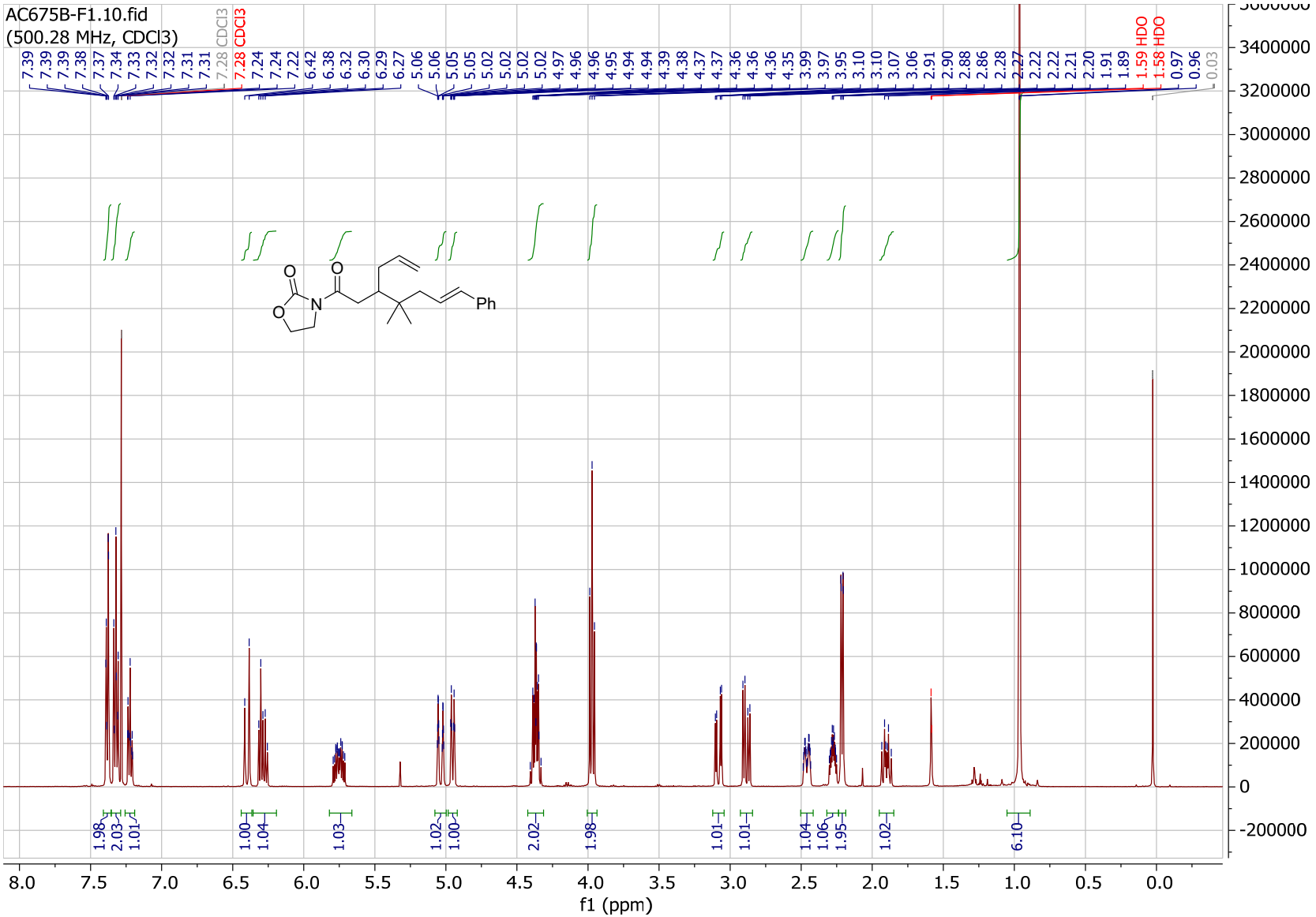

AC641P.11.fid
(125.81 MHz, CDCl3)
172.01
153.55
143.78
136.22
135.46
129.53
129.08
128.56
127.84
127.46
126.72
117.11
77.16 CDCl3
66.23
55.34
41.56
41.20
41.09
37.95
O
O
N
O
Ph
Ph
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

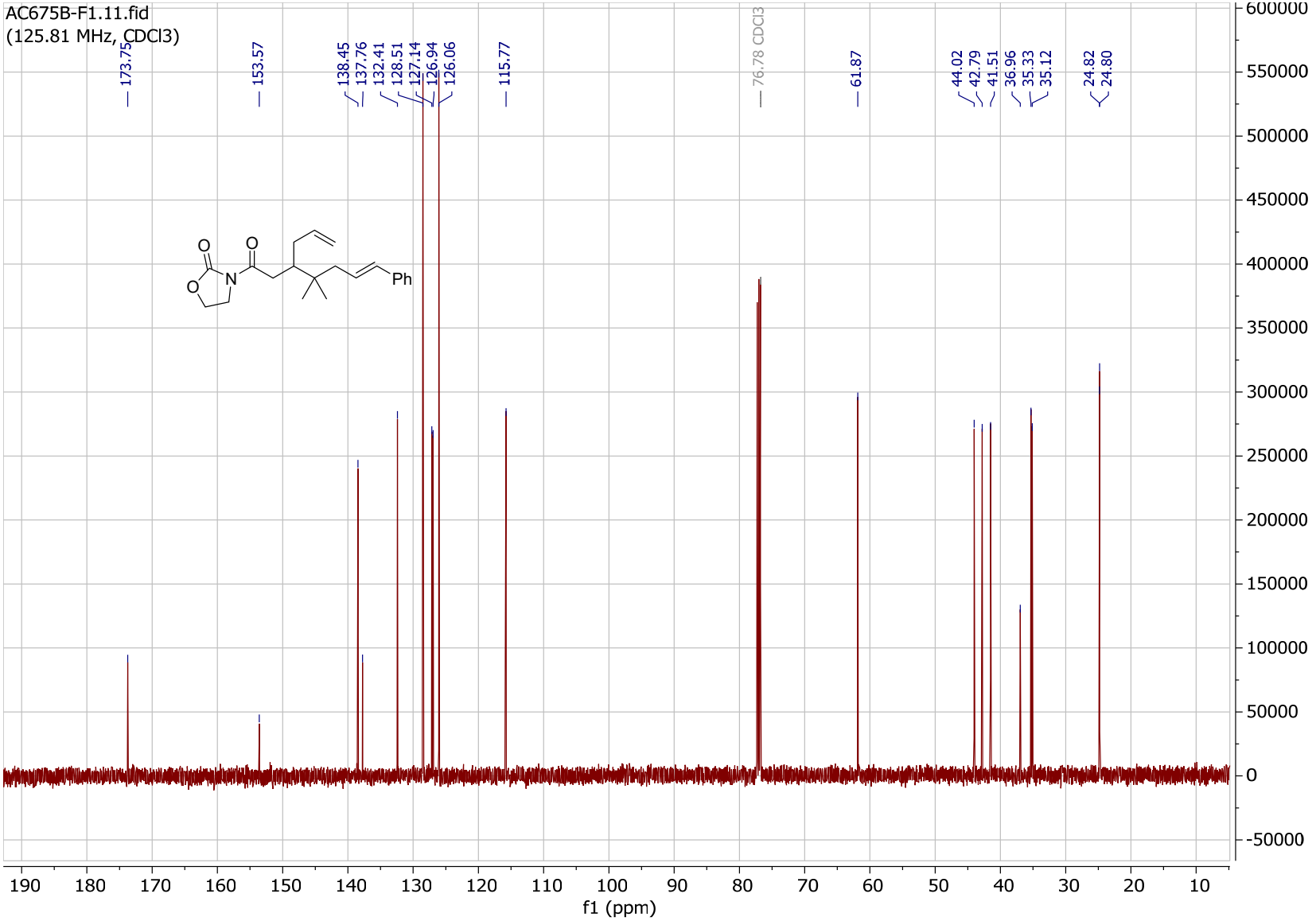
3-[3-(Naphthalen-1-yl)hex-5-enoyl]oxazolidin-2-one S7



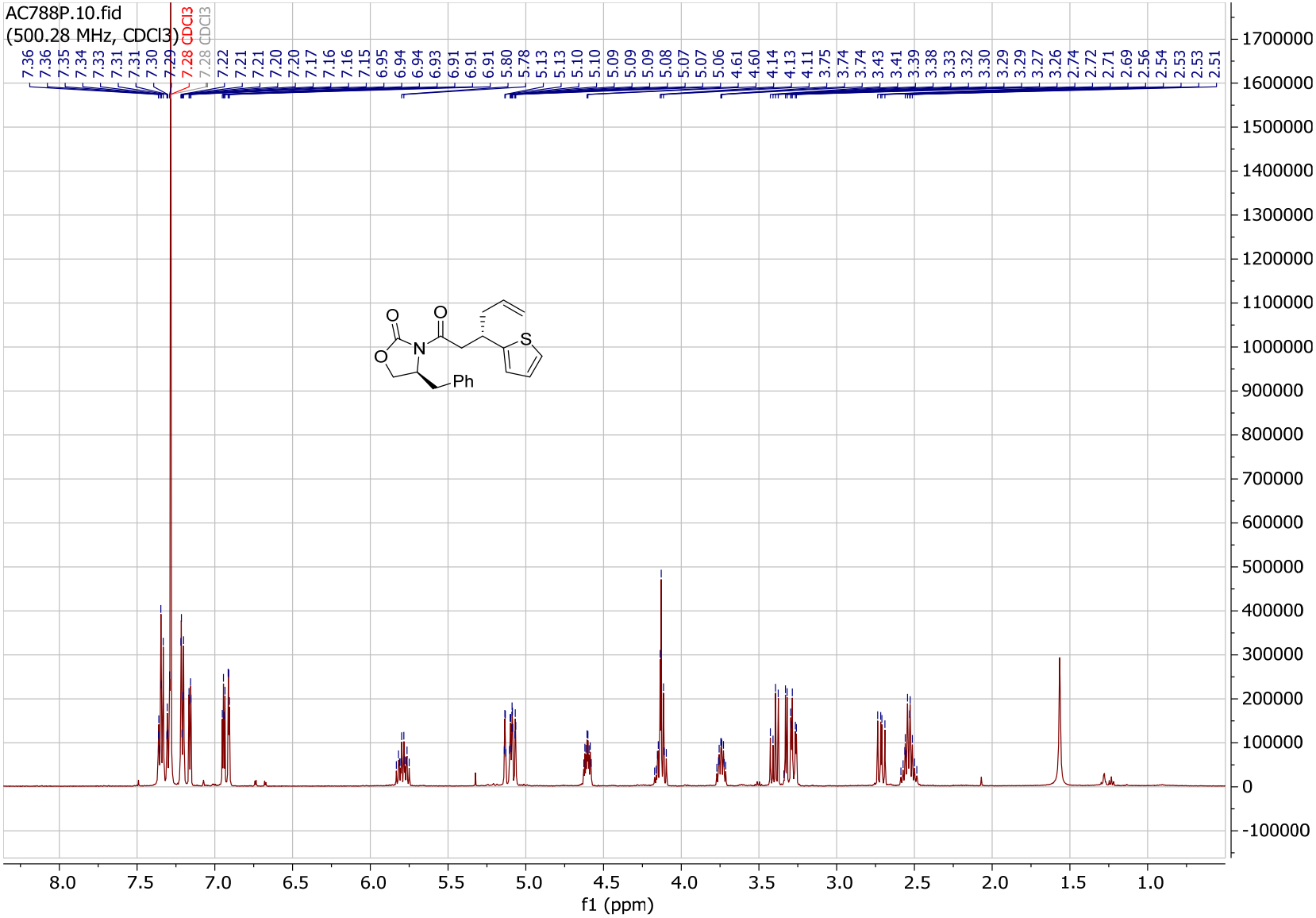

AC714F1.11.fid
(125.81 MHz, CDCl3)
172.15
153.54
139.91
136.09
133.97
131.69
128.94
126.99
126.03
125.47
123.15
116.96
76.80 CDCl3
61.98
42.52
40.54
40.31
O
O
O
N
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

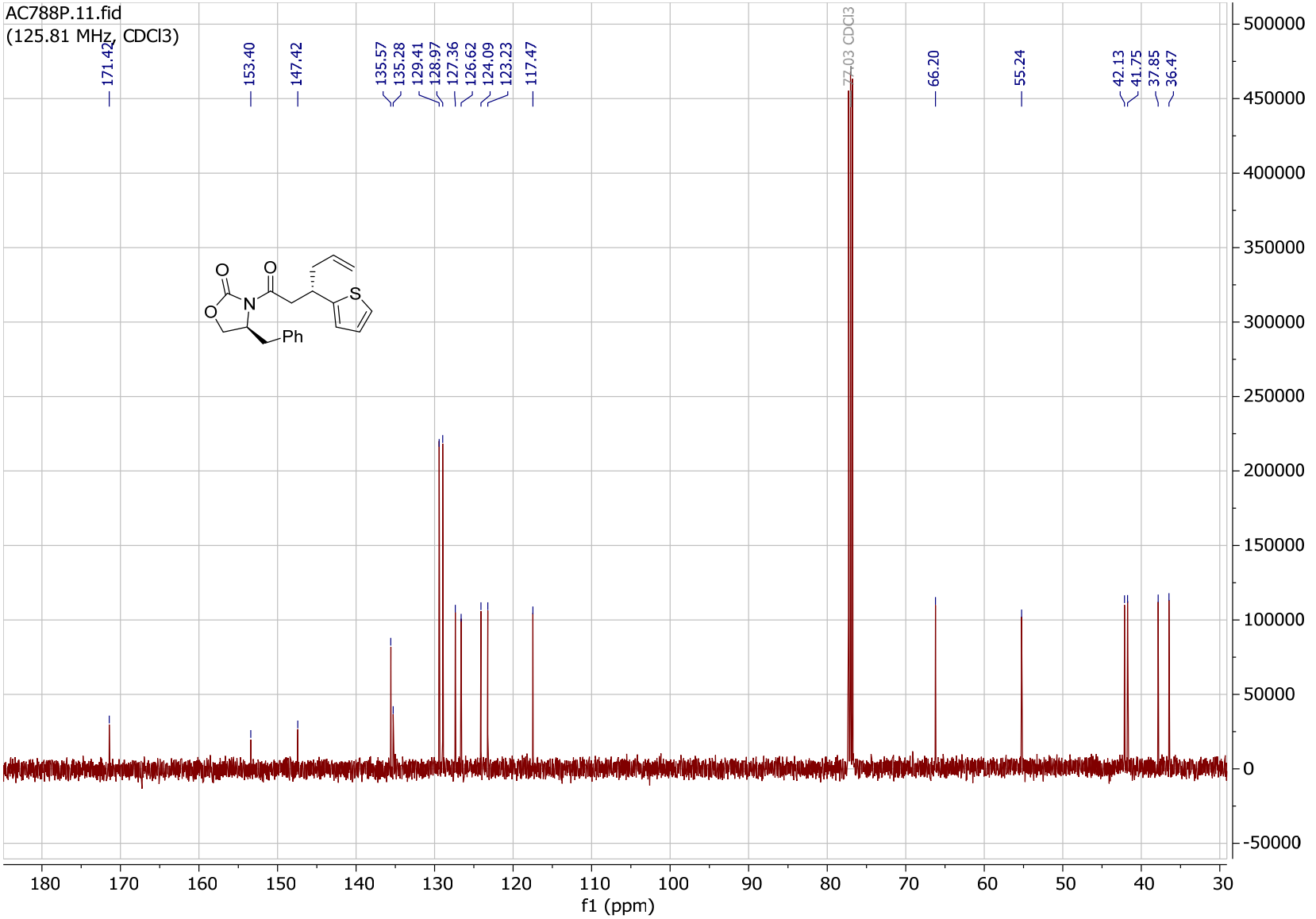
(*E*)-3-(3-Allyl-4,4-dimethyl-7-phenylhept-6-enoyl)oxazolidin-2-one S8



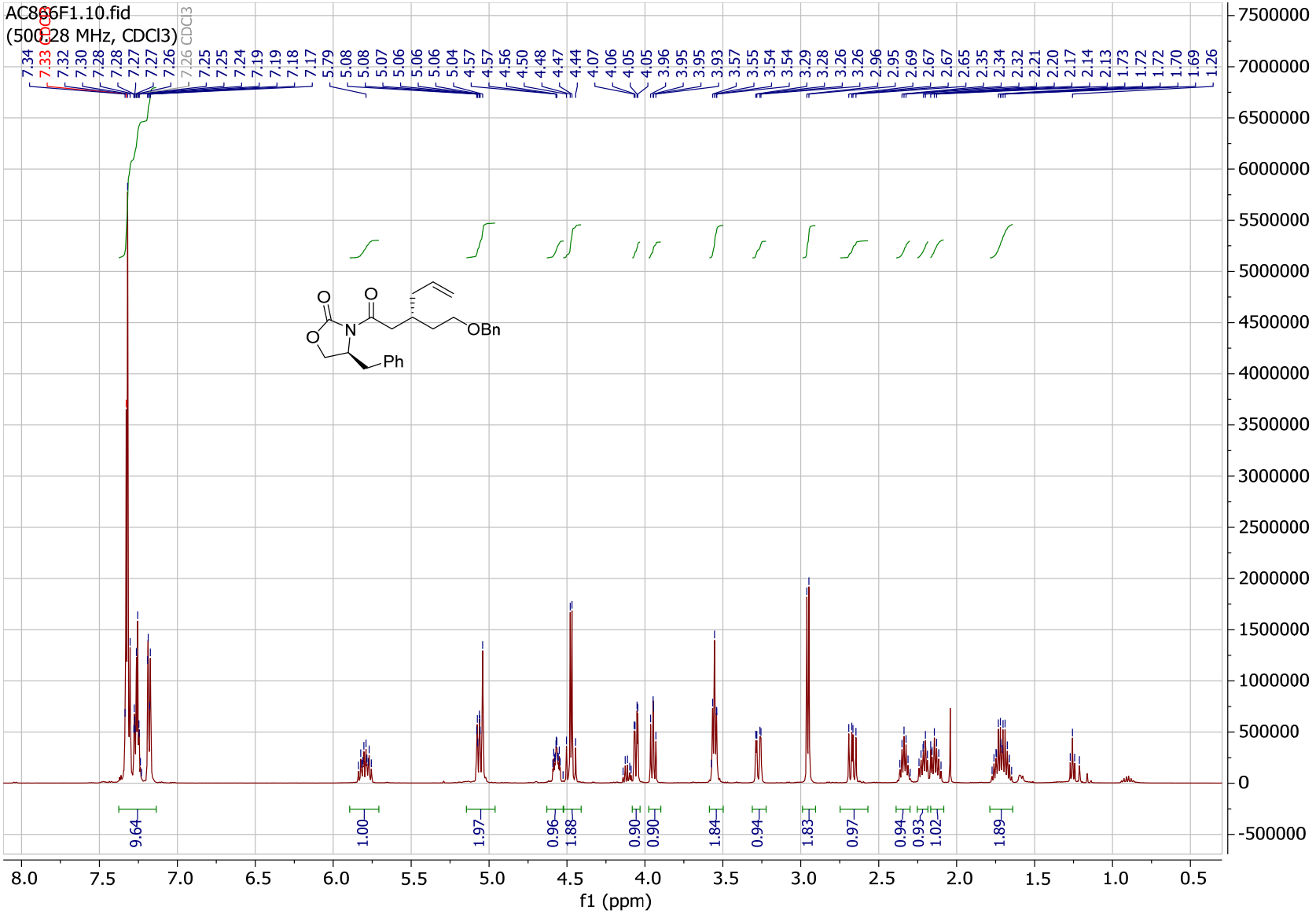

AC675B-F1.11.fid
(125.81 MHz, CDCl3)
173.75
153.57
138.45
137.76
132.41
128.51
127.14
126.94
126.06
115.77
76.78 CDCl3
61.87
44.02
42.79
41.51
36.96
35.33
35.12
24.82
24.80
O
O
O
N
Ph
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

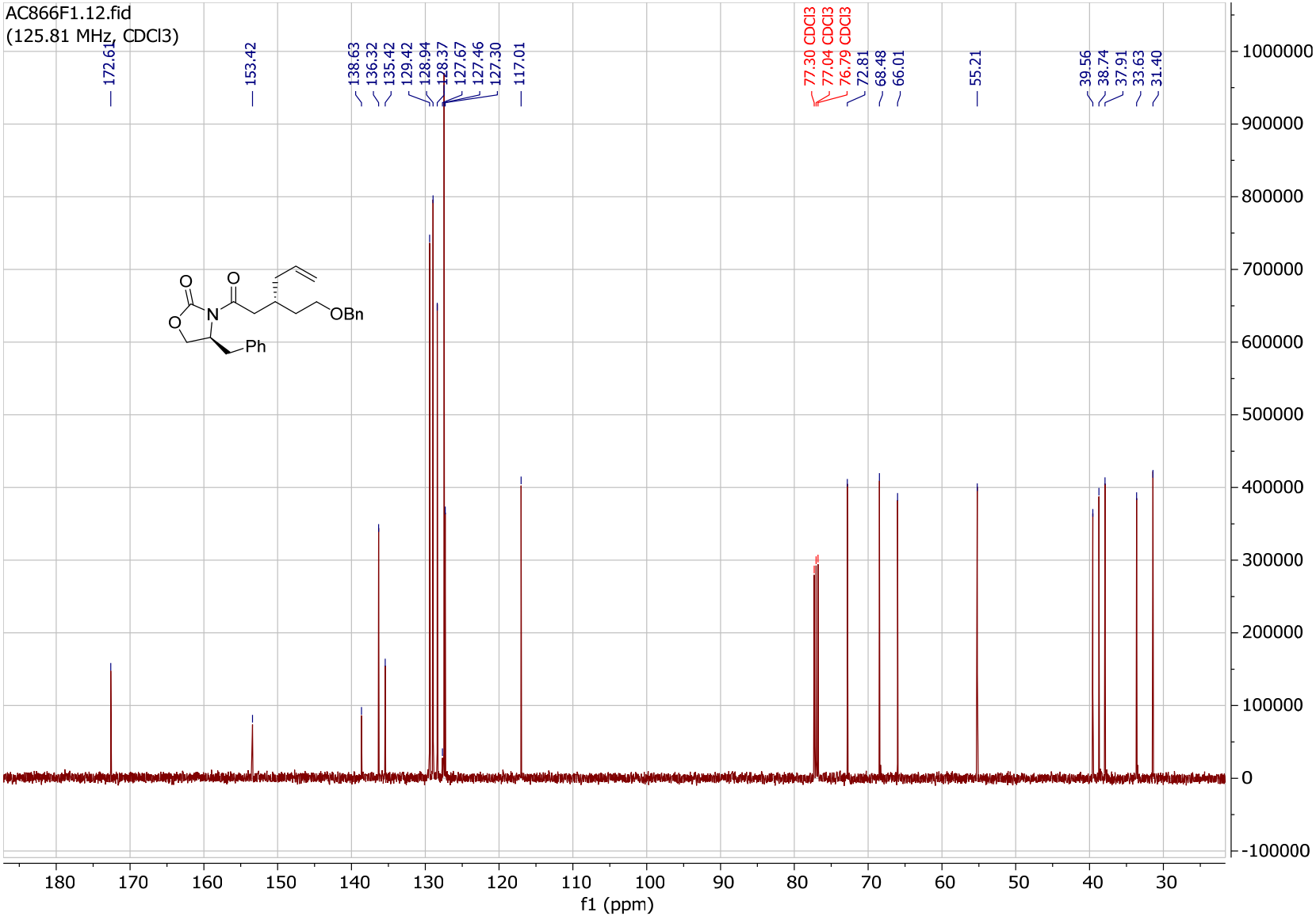
(S)-4-Benzyl-3-[(S)-3-(thiophen-2-yl)hex-5-enoyl]oxazolidin-2-oneS9



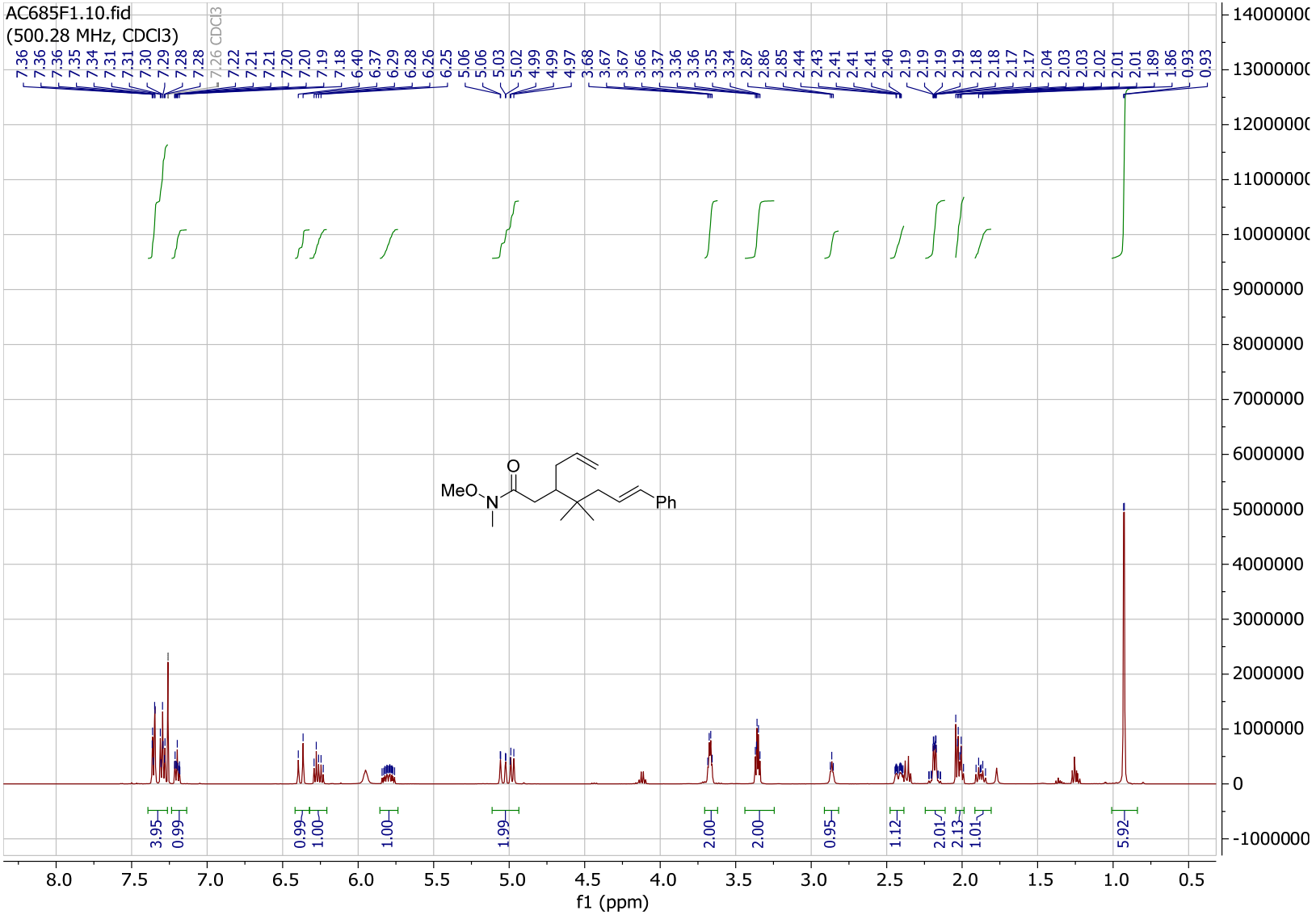

AC788P.11.fid
(125.81 MHz, CDCl3)
171.42
153.40
147.42
135.57
135.28
129.41
128.97
127.36
126.62
124.09
123.23
117.47
77.03 CDCl3
66.20
55.24
42.13
41.75
37.85
36.47
O
O
N
O
S
Ph
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

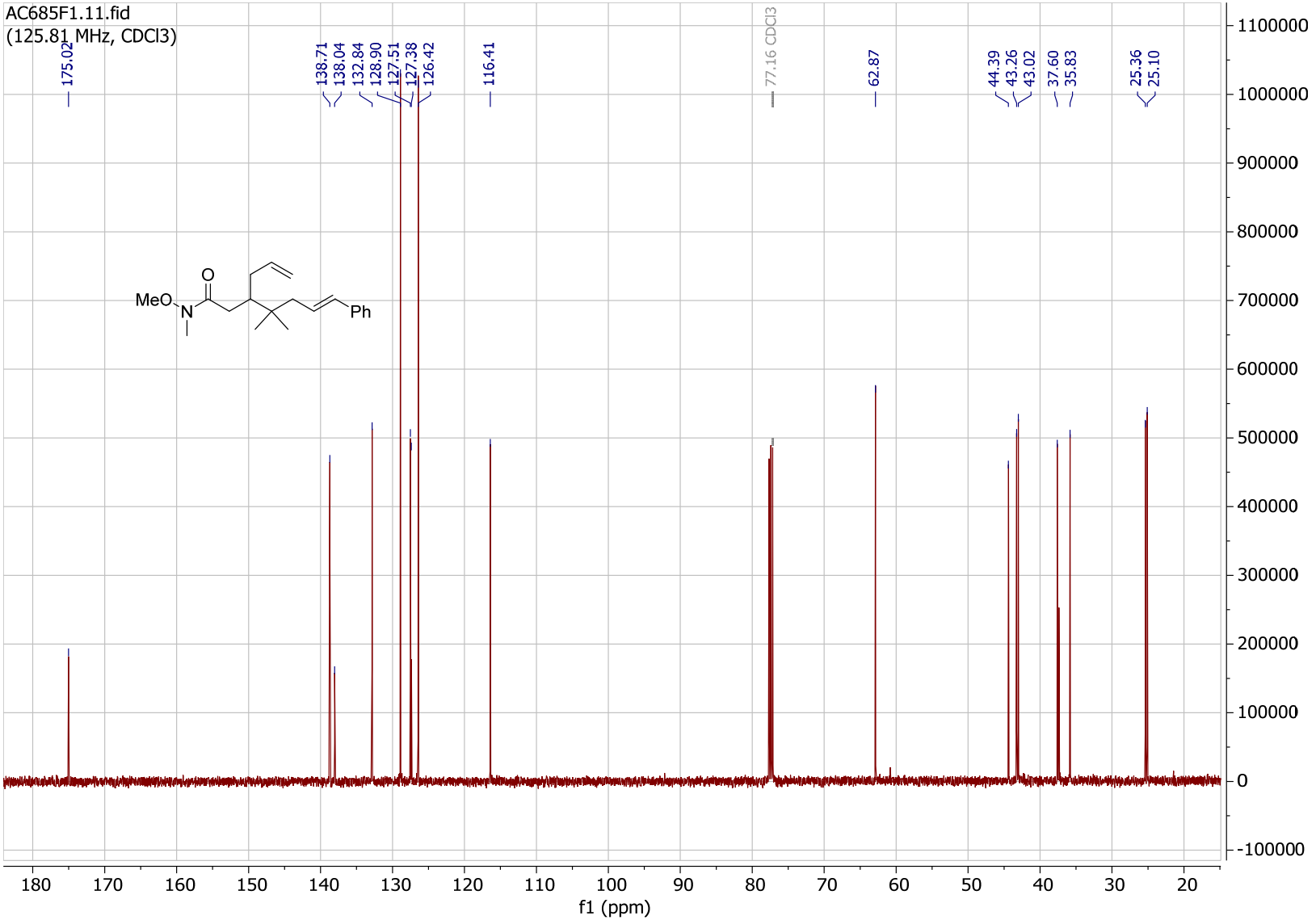
(S)-4-Benzyl-3-{(*R*)-3-[2-(benzyloxy)ethyl]hex-5-enoyl}oxazolidin-2-one S10



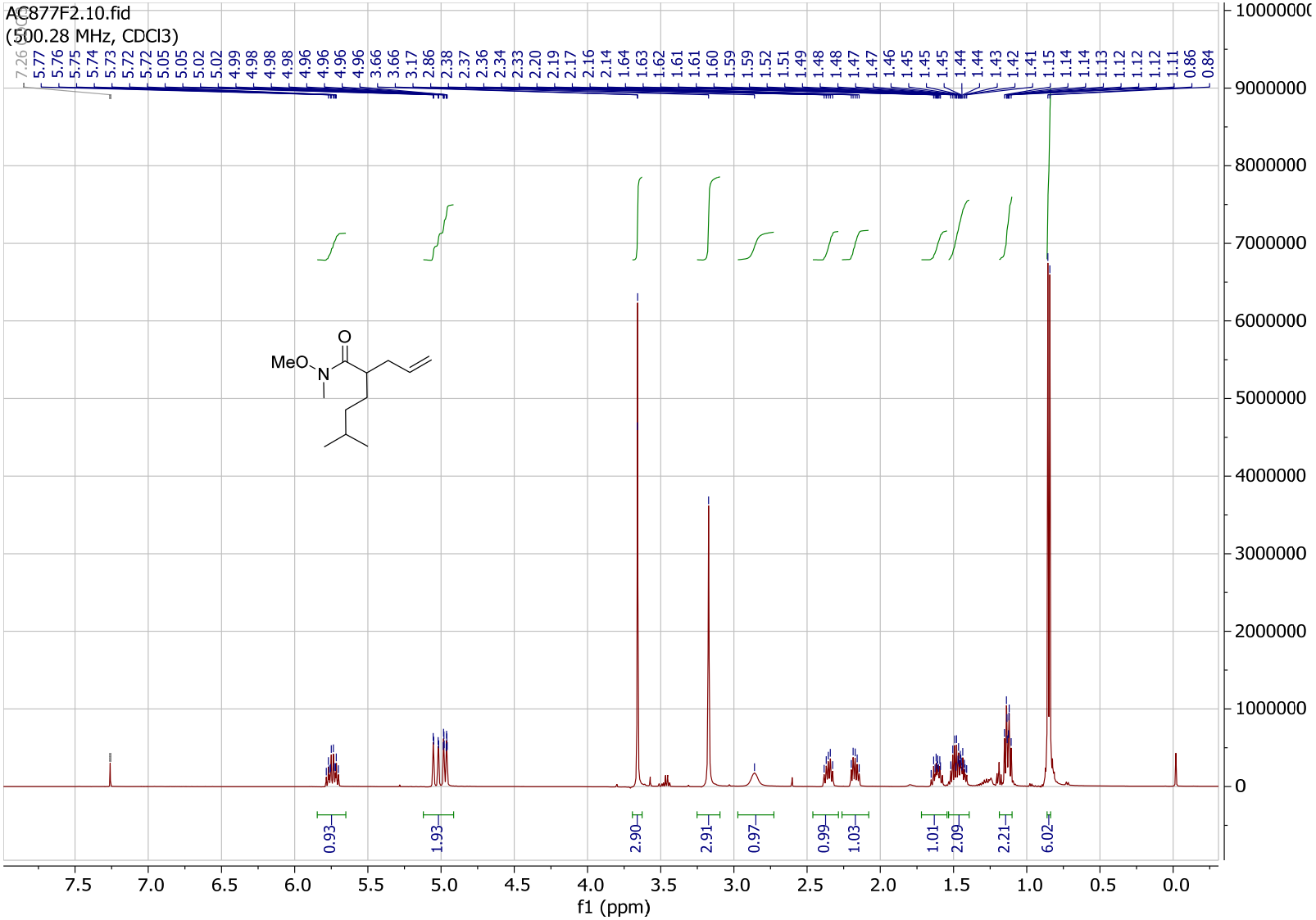

AC866F1.12.fid
(125.81 MHz, CDCl3)
172.61
153.42
138.63
136.32
135.42
129.42
128.94
128.37
127.67
127.46
127.30
117.01
77.30 CDCl3
77.04 CDCl3
76.79 CDCl3
72.81
68.48
66.01
55.21
39.56
38.74
37.91
33.63
31.40
O
O
N
O
OBn
Ph
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

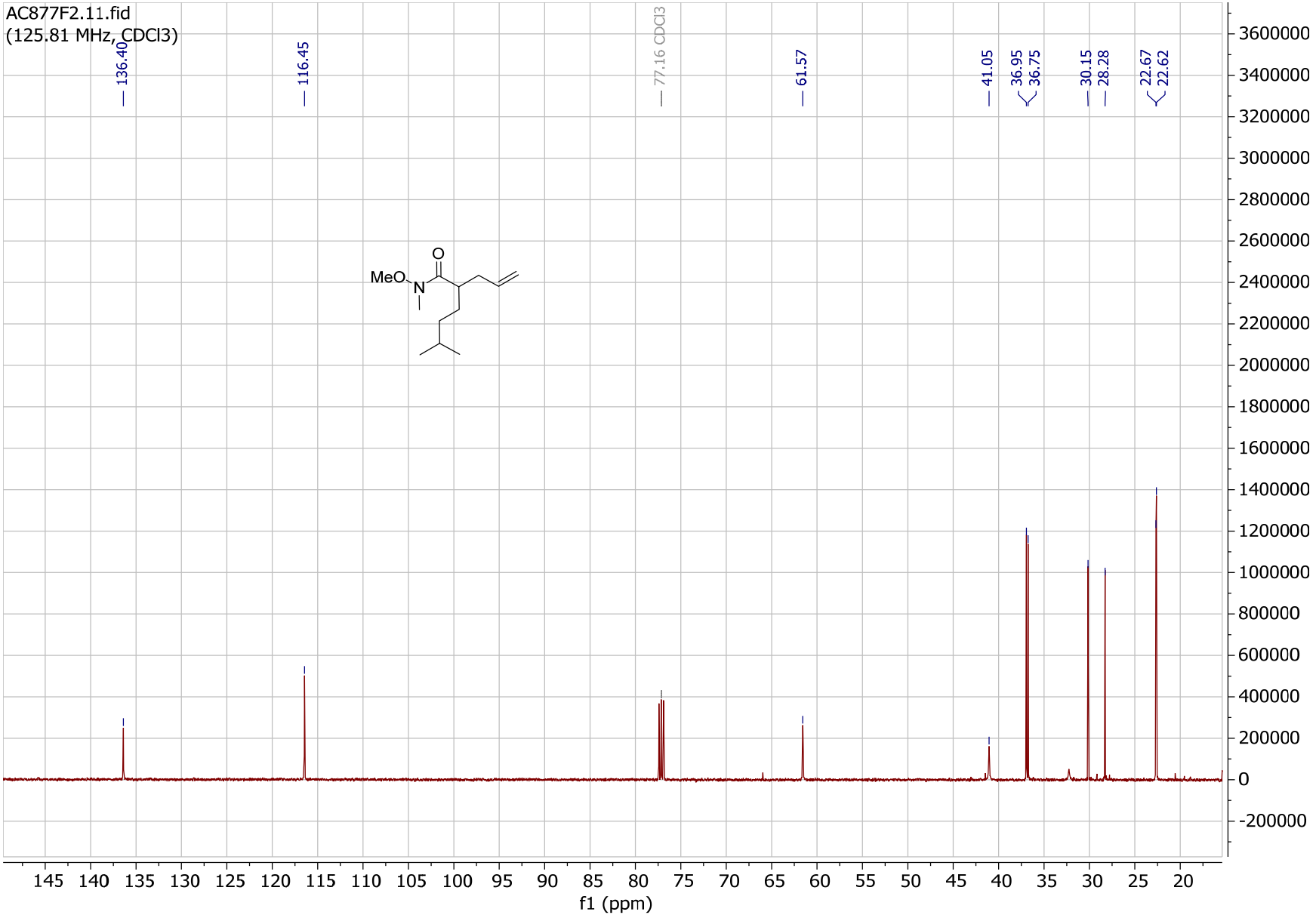
(*E*)-3-Allyl-*N*-methoxy-*N*,4,4-trimethyl-7-phenylhept-6-enamide 1ag



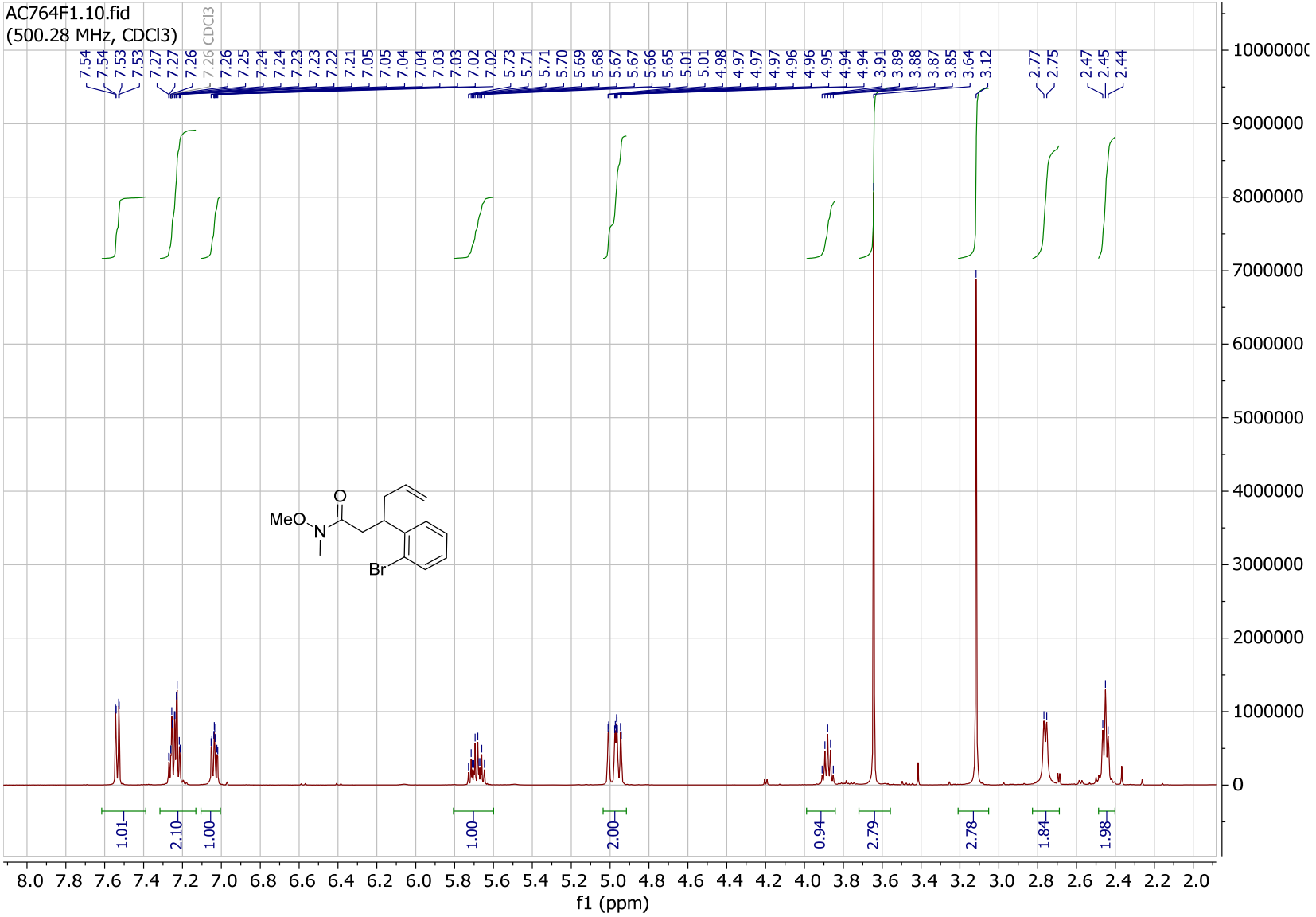

AC685F1.11.fid
(125.81 MHz, CDCl3)
175.02
138.71
138.04
132.84
128.90
127.51
127.38
126.42
116.41
77.16 CDCl3
62.87
44.39
43.26
43.02
37.60
35.83
25.36
25.10
MeO
N
O
Ph
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

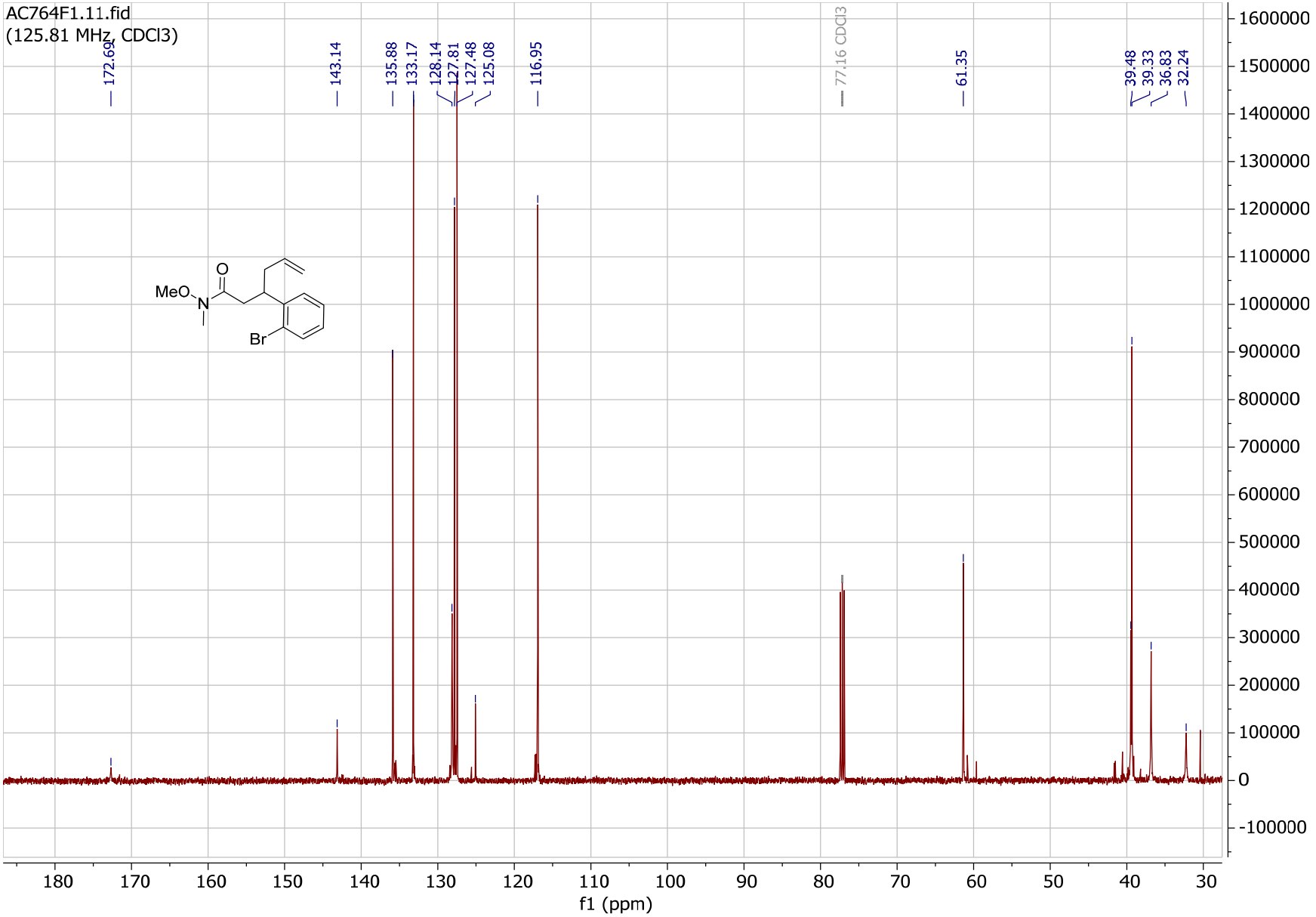
2-Allyl-*N*-methoxy-*N*,5-dimethylhexanamide 1bc



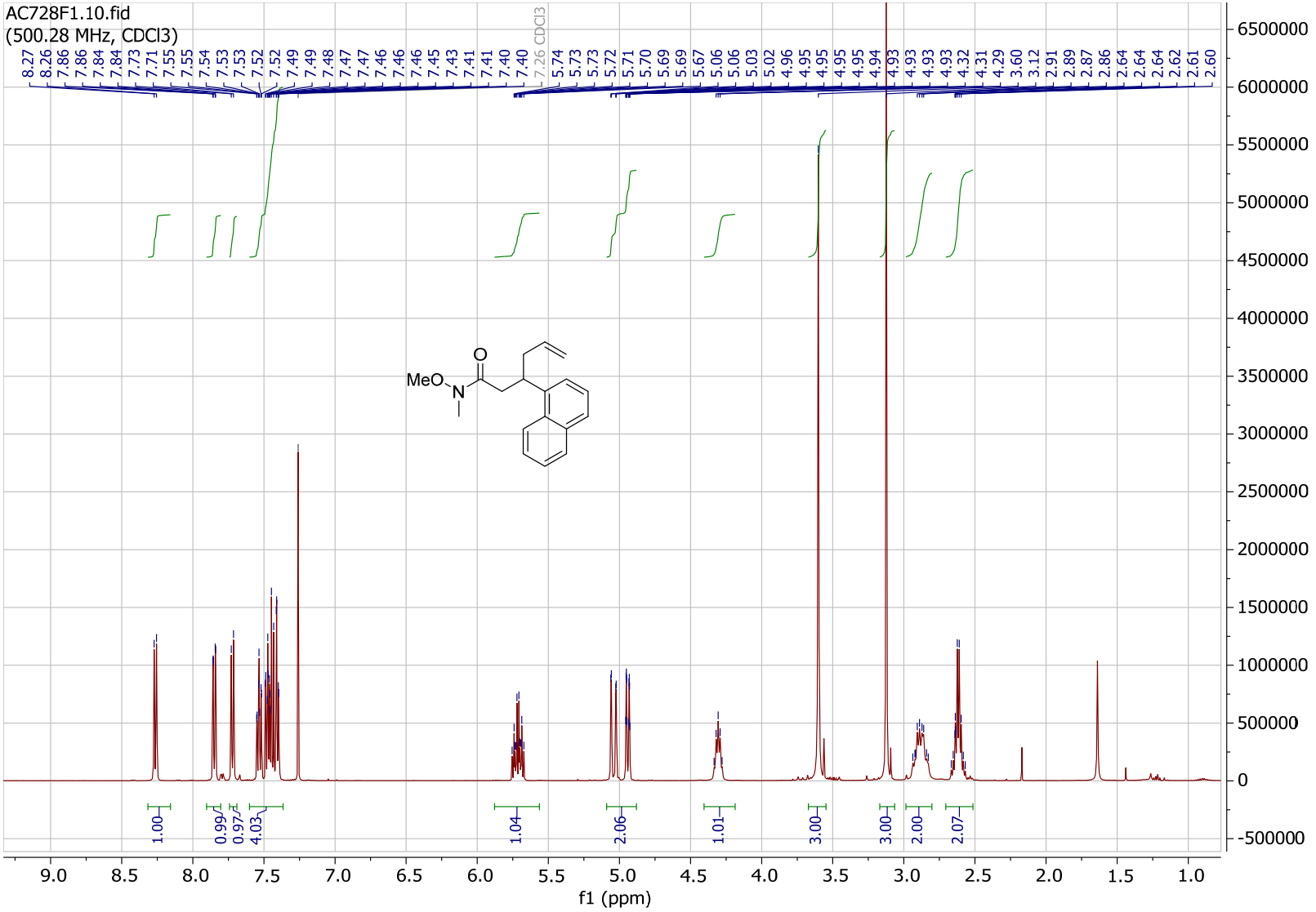

AC877F2.11.fid
(125.81 MHz, CDCl3)
136.40
116.45
77.16 CDCl3
61.57
41.05
36.95
36.75
30.15
28.28
22.67
22.62
MeO
N
O
f1 (ppm)

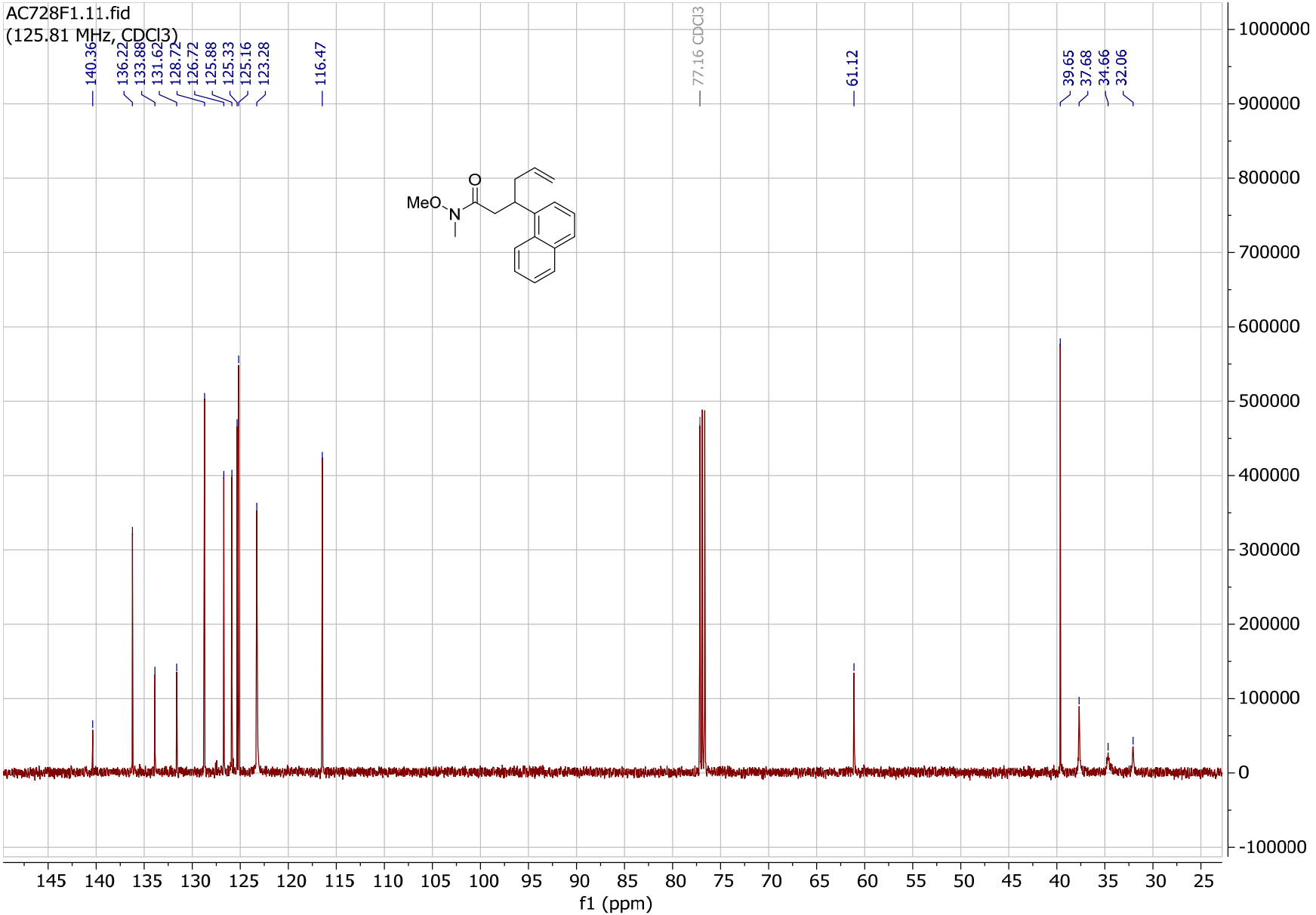
3-(2-Bromophenyl)-*N*-methoxy-*N*-methylhex-5-enamide 1ah



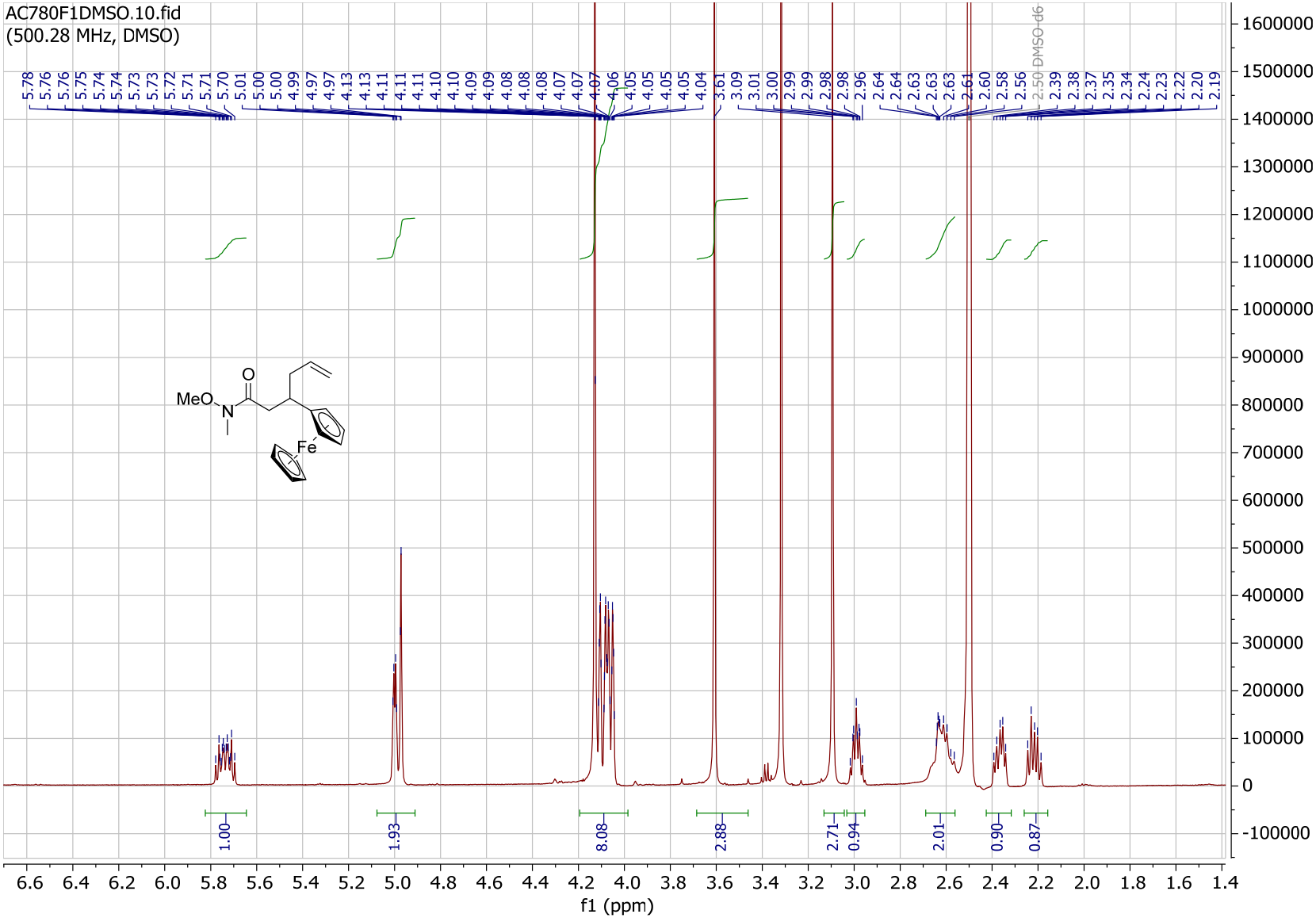

AC764F1.11.fid
(125.81 MHz, CDCl3)
172.69
143.14
135.88
133.17
128.14
127.81
127.48
125.08
116.95
77.16 CDCl3
61.35
39.48
39.33
36.83
32.24
MeO
N
O
Br
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

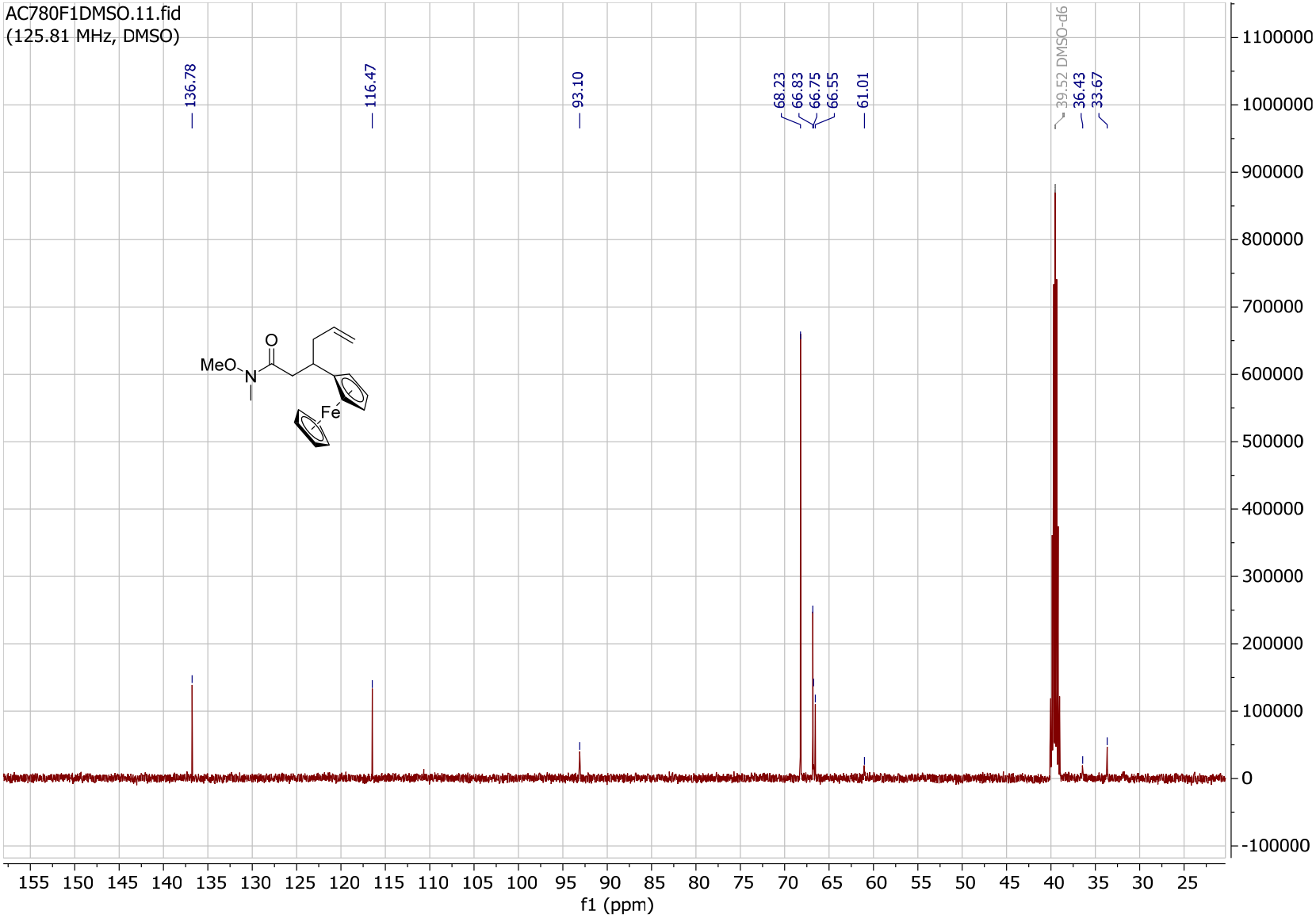
_N_-Methoxy-_N_-methyl-3-(naphthalen-1-yl)hex-5-enamide 1ai



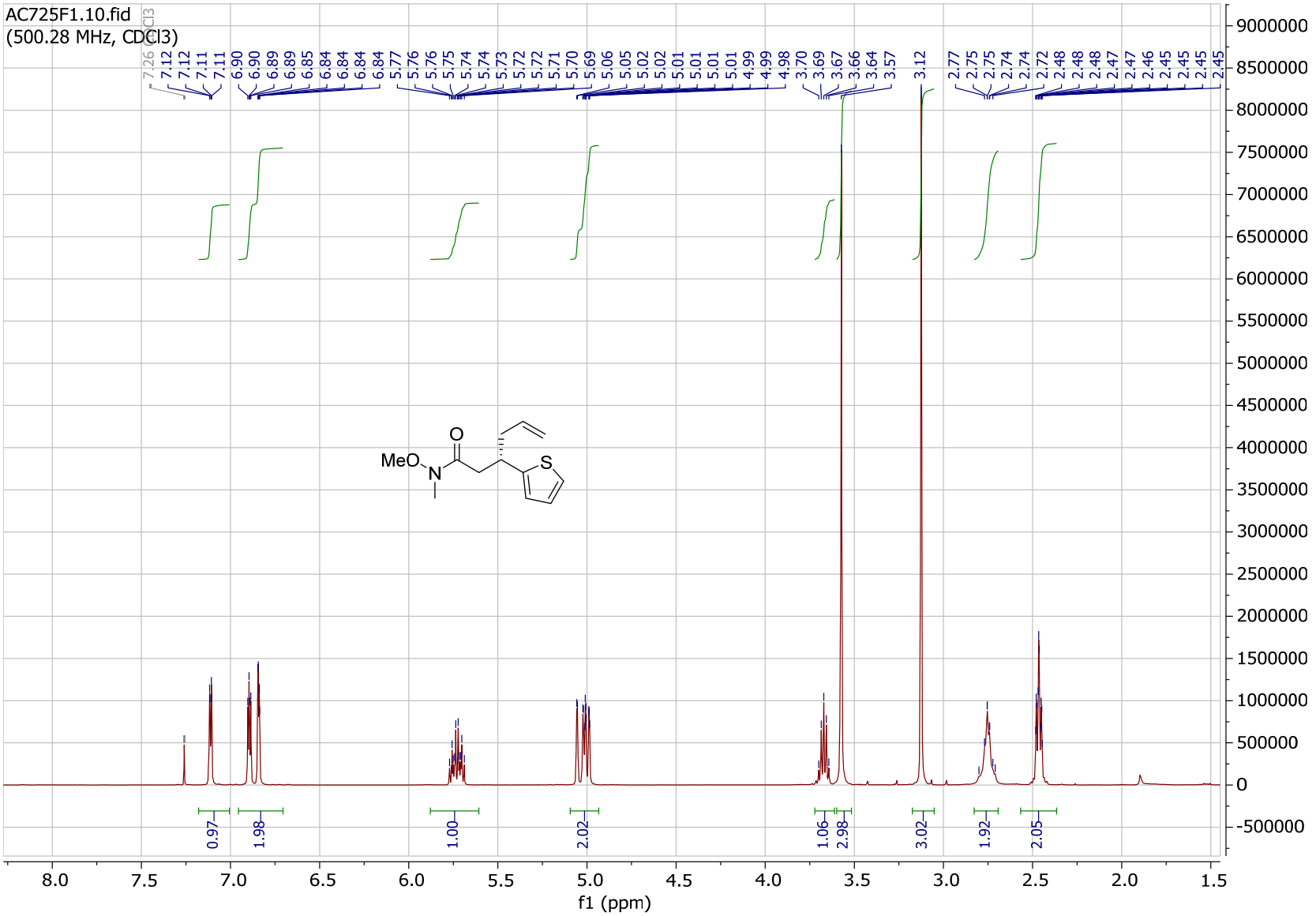

AC728F1.11.fid
(125.81 MHz, CDCl3)
140.36
136.22
133.88
131.62
128.72
126.72
125.88
125.33
125.16
123.28
116.47
77.16 CDCl3
61.12
39.65
37.68
34.66
32.06
MeO
N
O
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

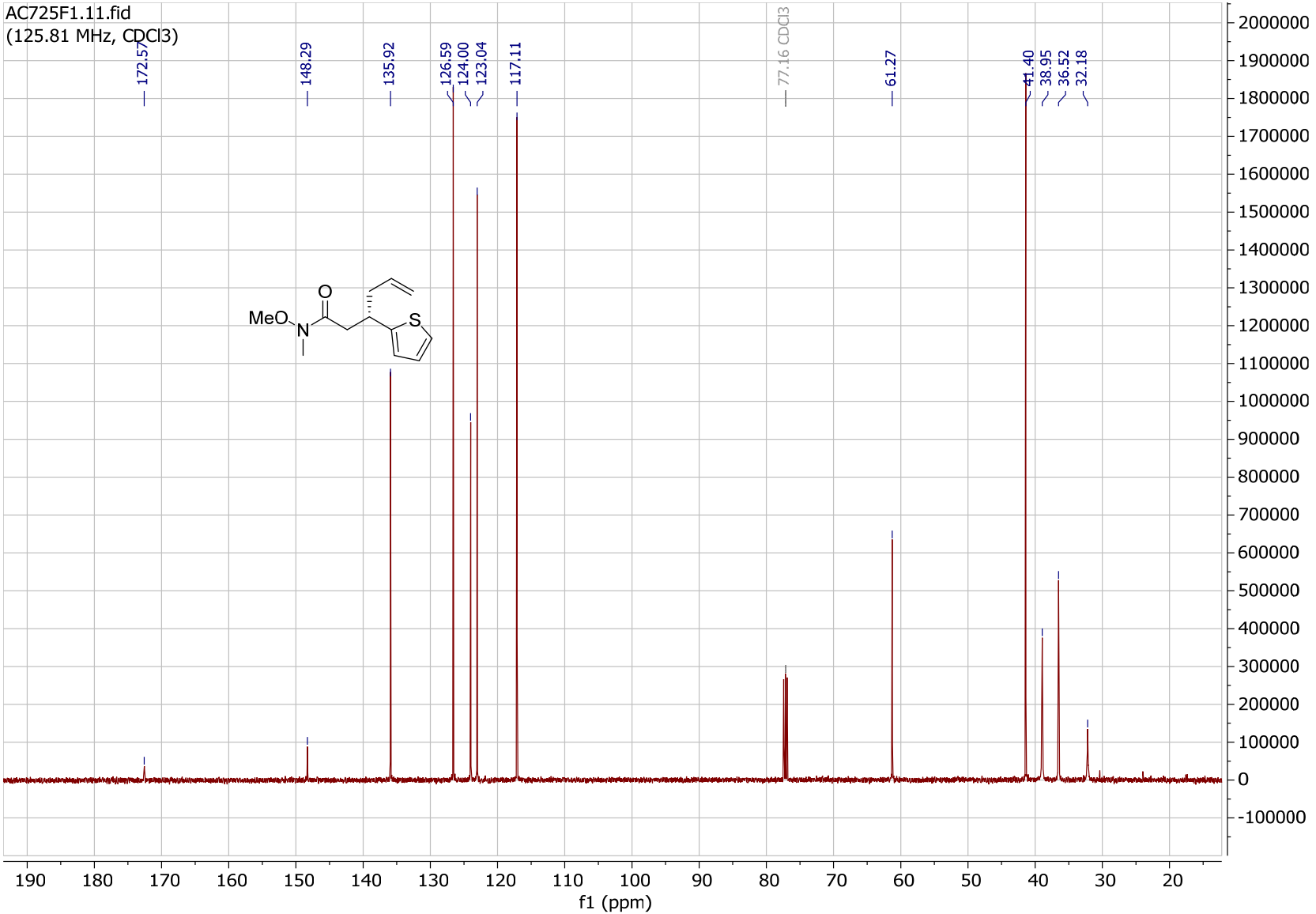
3-Ferrocenyl-*N*-methoxy-*N*-methylhex-5-enamide 1aj



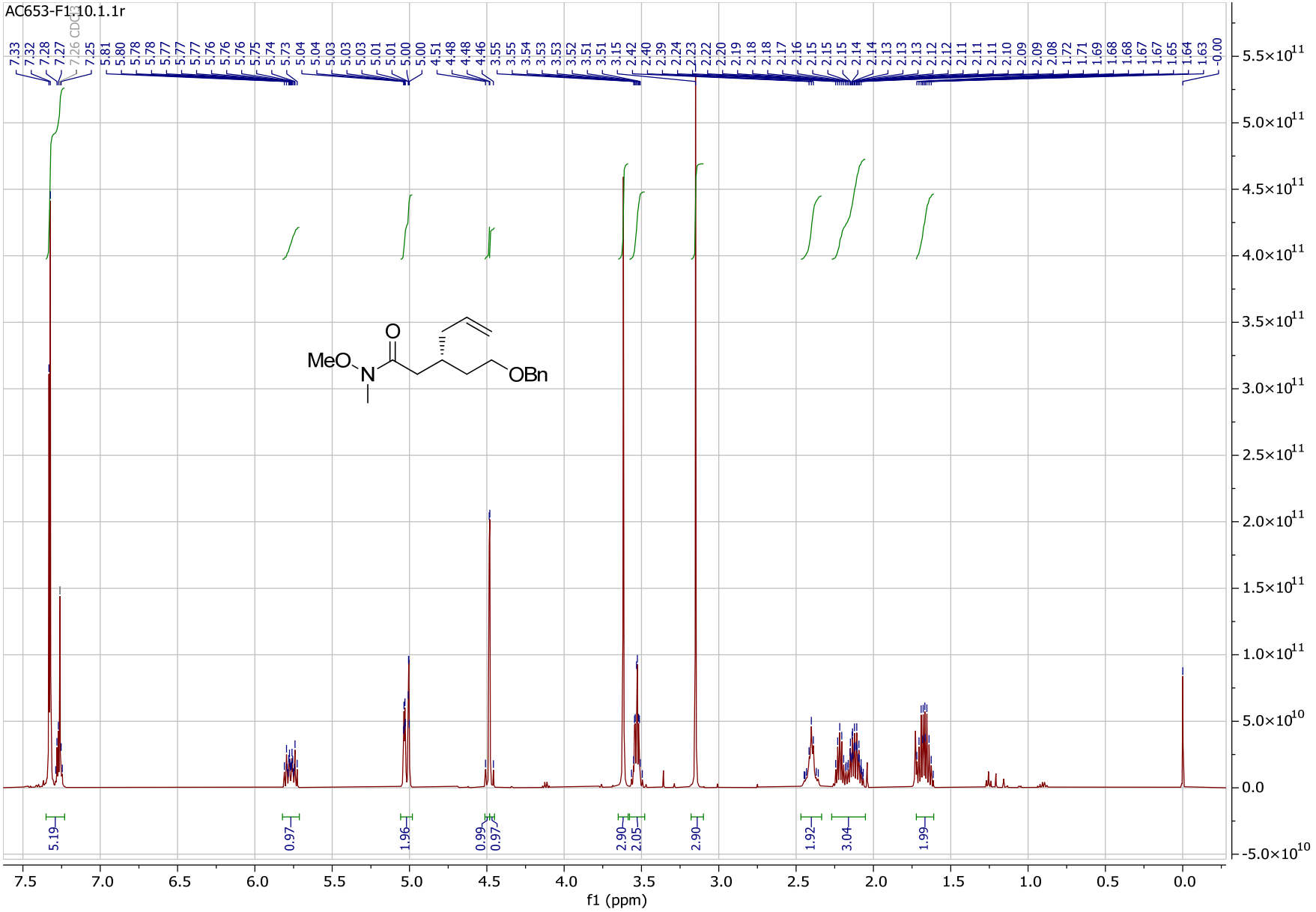

AC780F1DMSO.11.fid
(125.81 MHz, DMSO)
136.78
116.47
93.10
68.23
66.83
66.75
66.55
61.01
39.52 DMSO-d6
36.43
33.67
MeO
N
O
Fe
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

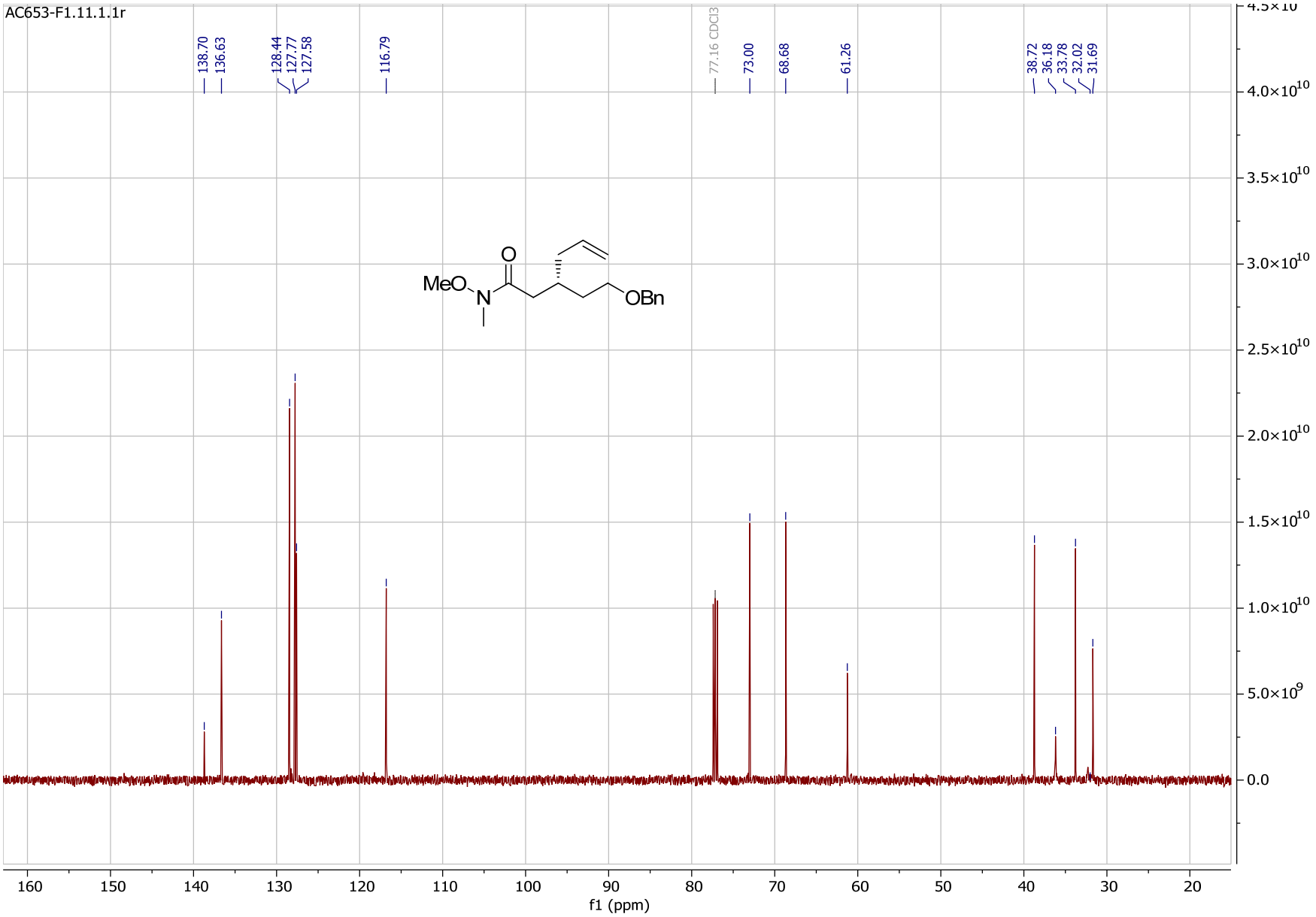
***(S)*-*N*-Methoxy-*N*-methyl-3-(thiophen-2-yl)hex-5-enamide 1ak**



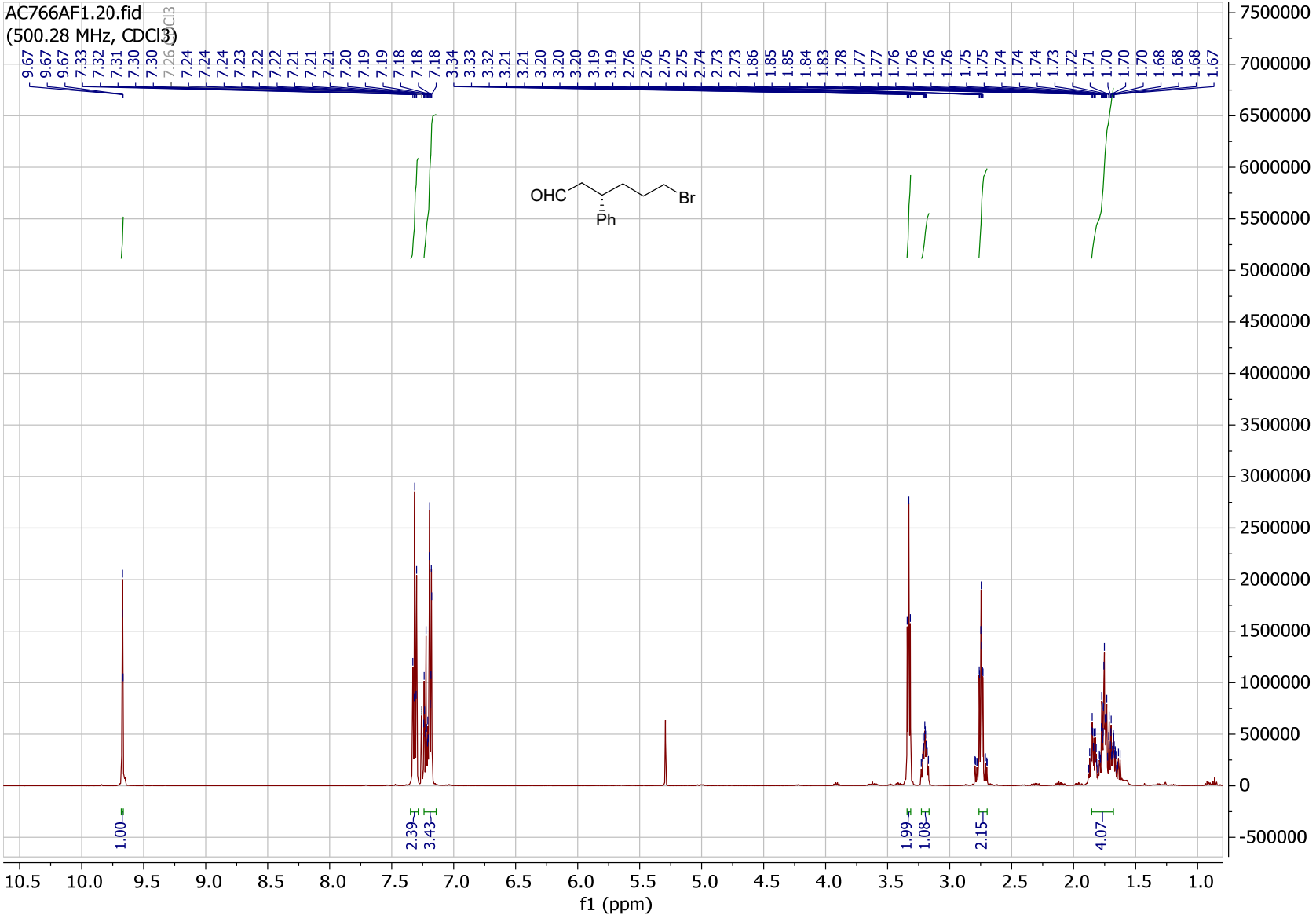

AC725F1.11.fid
(125.81 MHz, CDCl3)
172.57
148.29
135.92
126.59
124.00
123.04
117.11
77.16 CDCl3
61.27
41.40
38.95
36.52
32.18
MeO
N
O
S
2000000
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

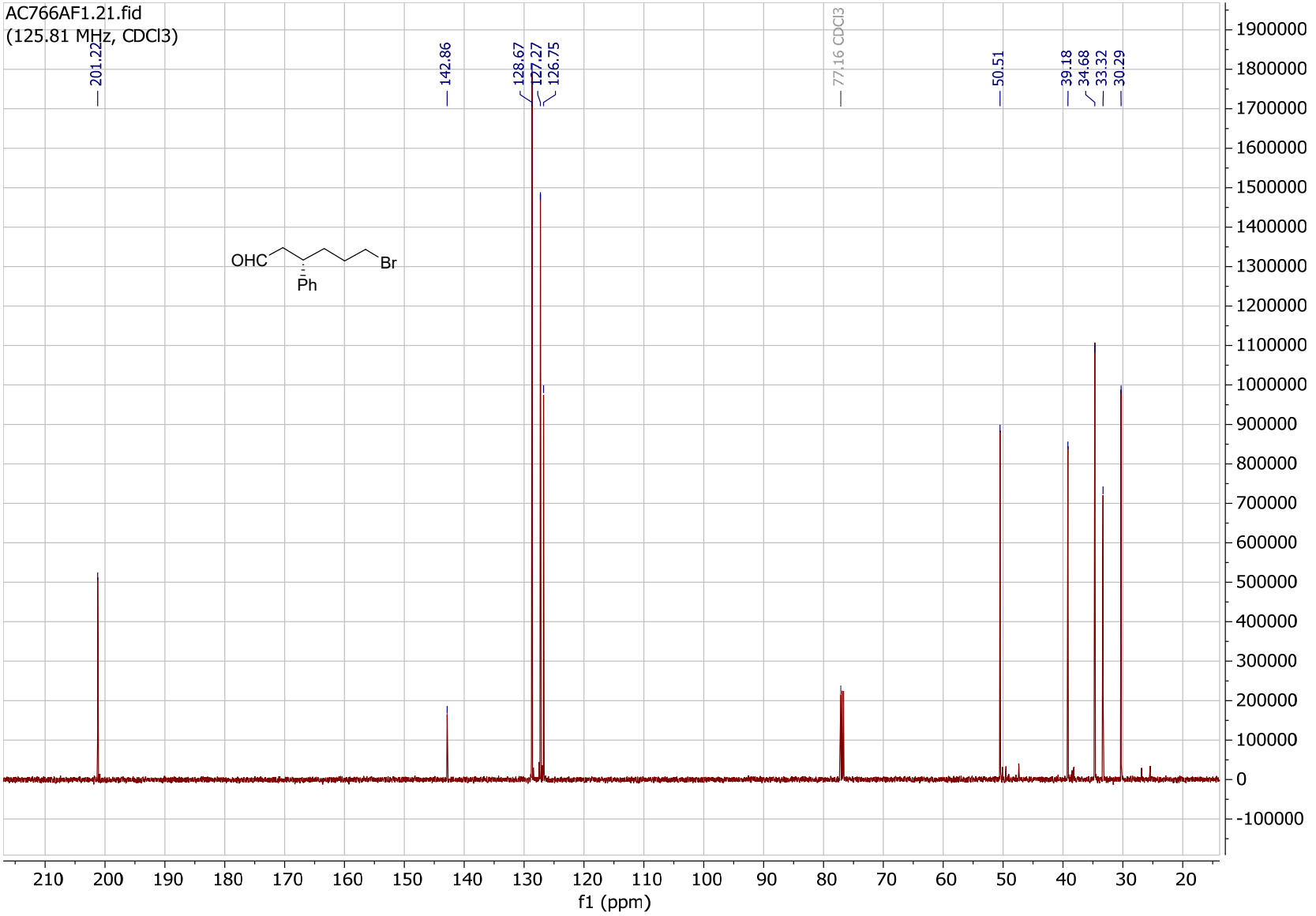
(*R*)-3-[2-(Benzyloxy)ethyl)-*N*-methoxy-*N*-methylhex-5-enamide 1al



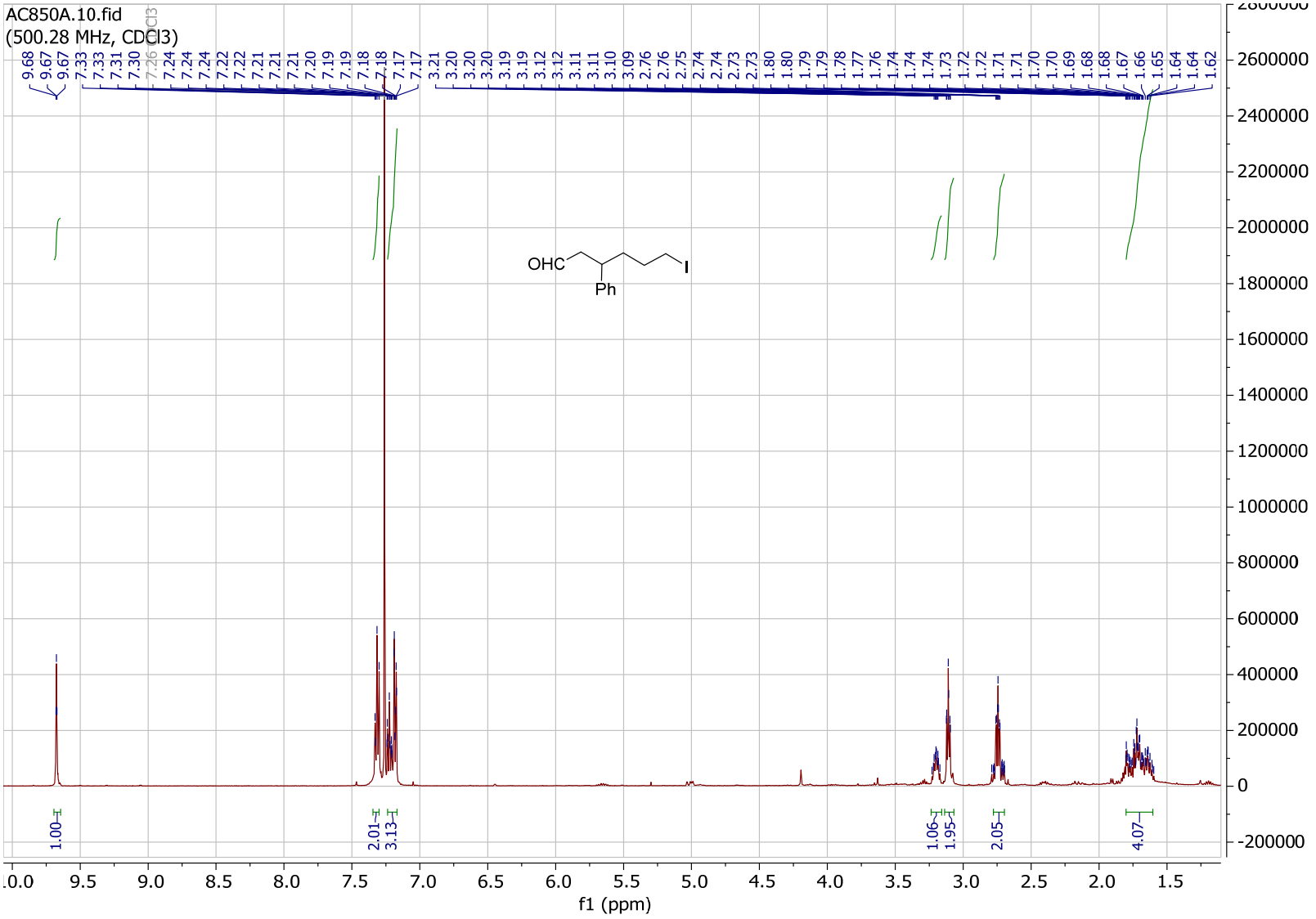

AC653-F1.11.1.1r
138.70
136.63
128.44
127.77
127.58
116.79
77.16 CDCl3
73.00
68.68
61.26
38.72
36.18
33.78
32.02
31.69
MeO
N
O
OBn
4.5×10
4.0×10^10
3.5×10^10
3.0×10^10
2.5×10^10
2.0×10^10
1.5×10^10
1.0×10^10
5.0×10^9
0.0
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

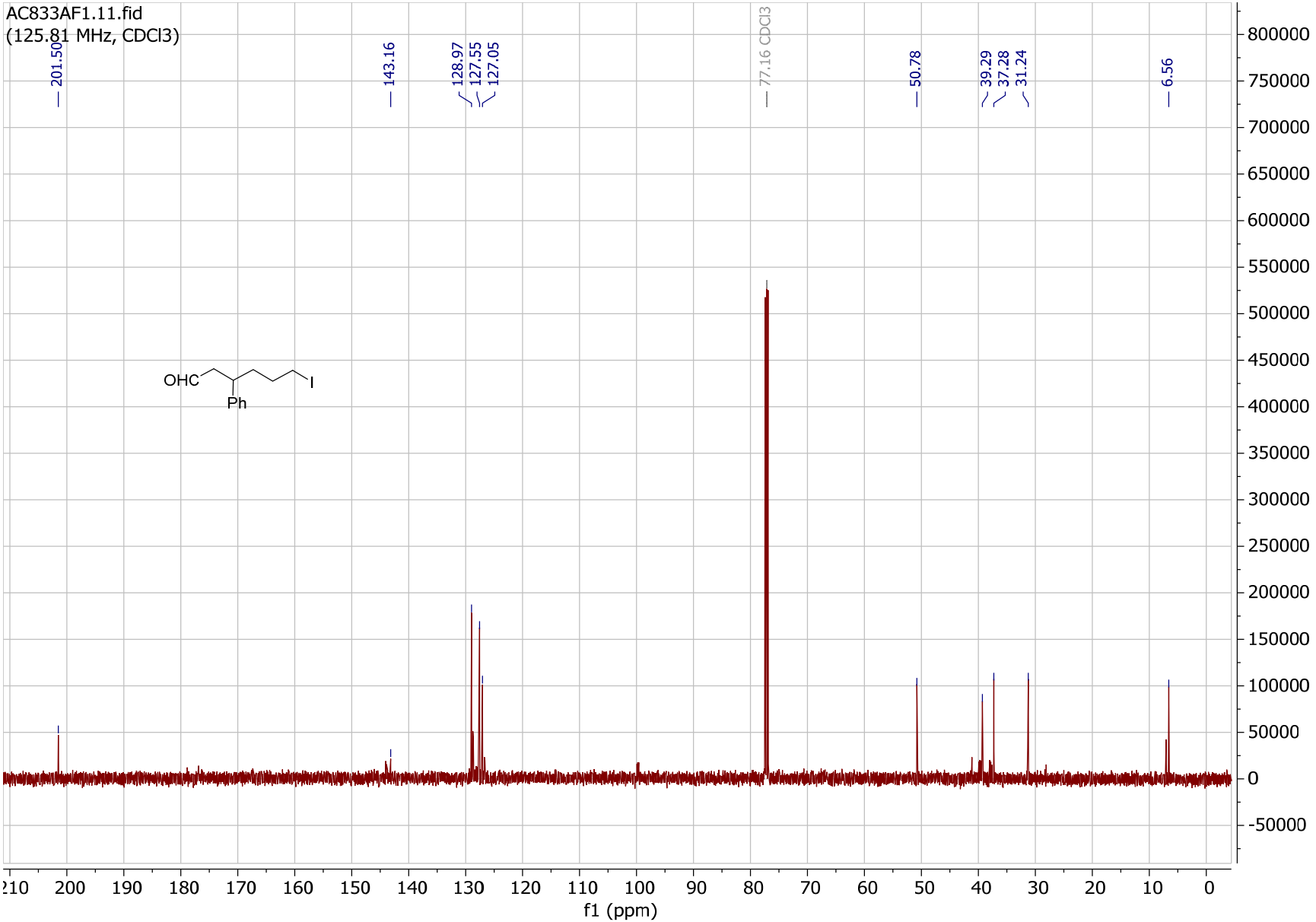
(*S*)-6-Bromo-3-phenylhexanal 2aa-Br



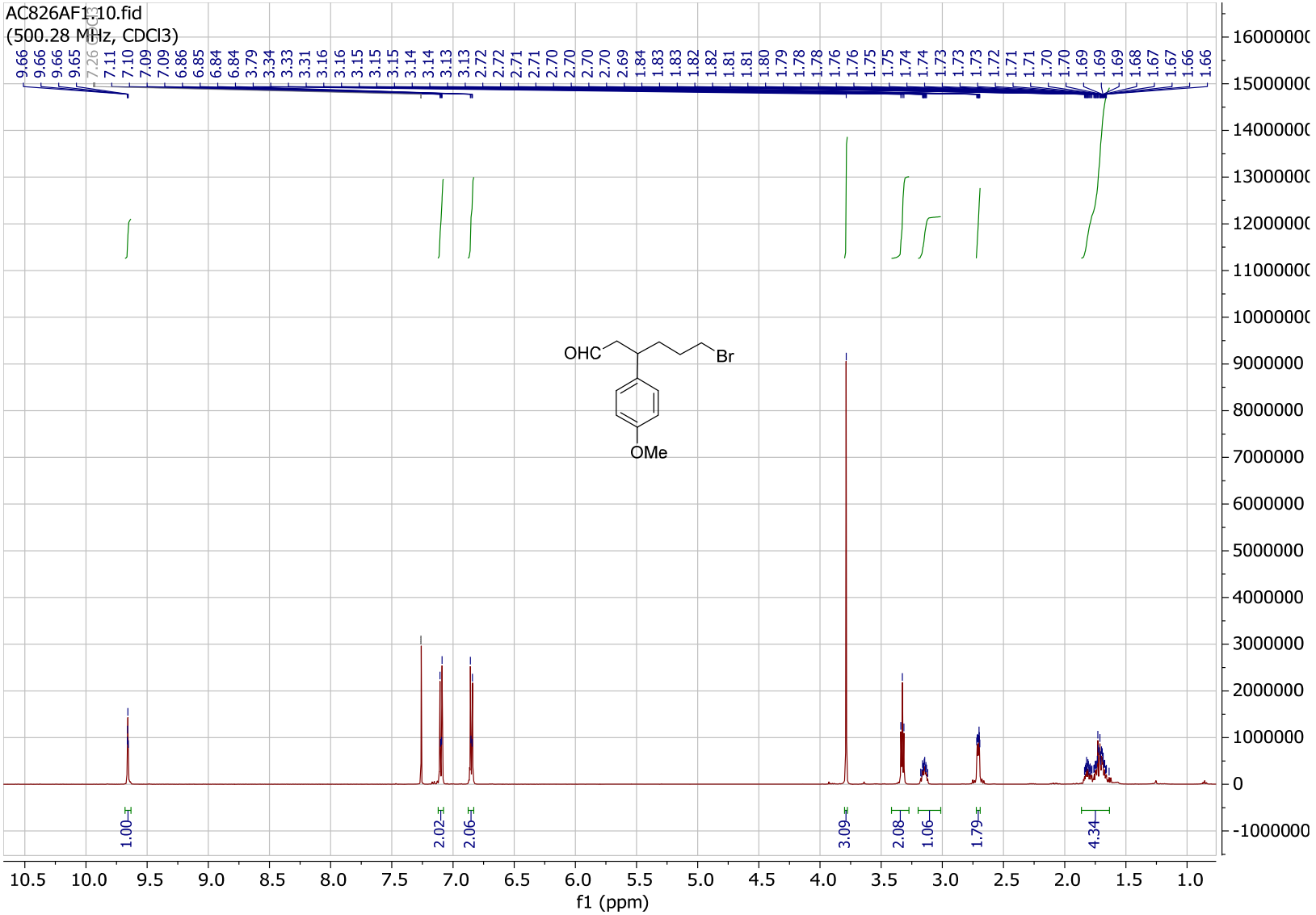

AC766AF1.21.fid
(125.81 MHz, CDCl3)
201.22
142.86
128.67
127.27
126.75
77.16 CDCl3
50.51
39.18
34.68
33.32
30.29
OHC
Br
Ph
1900000
1800000
1700000
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

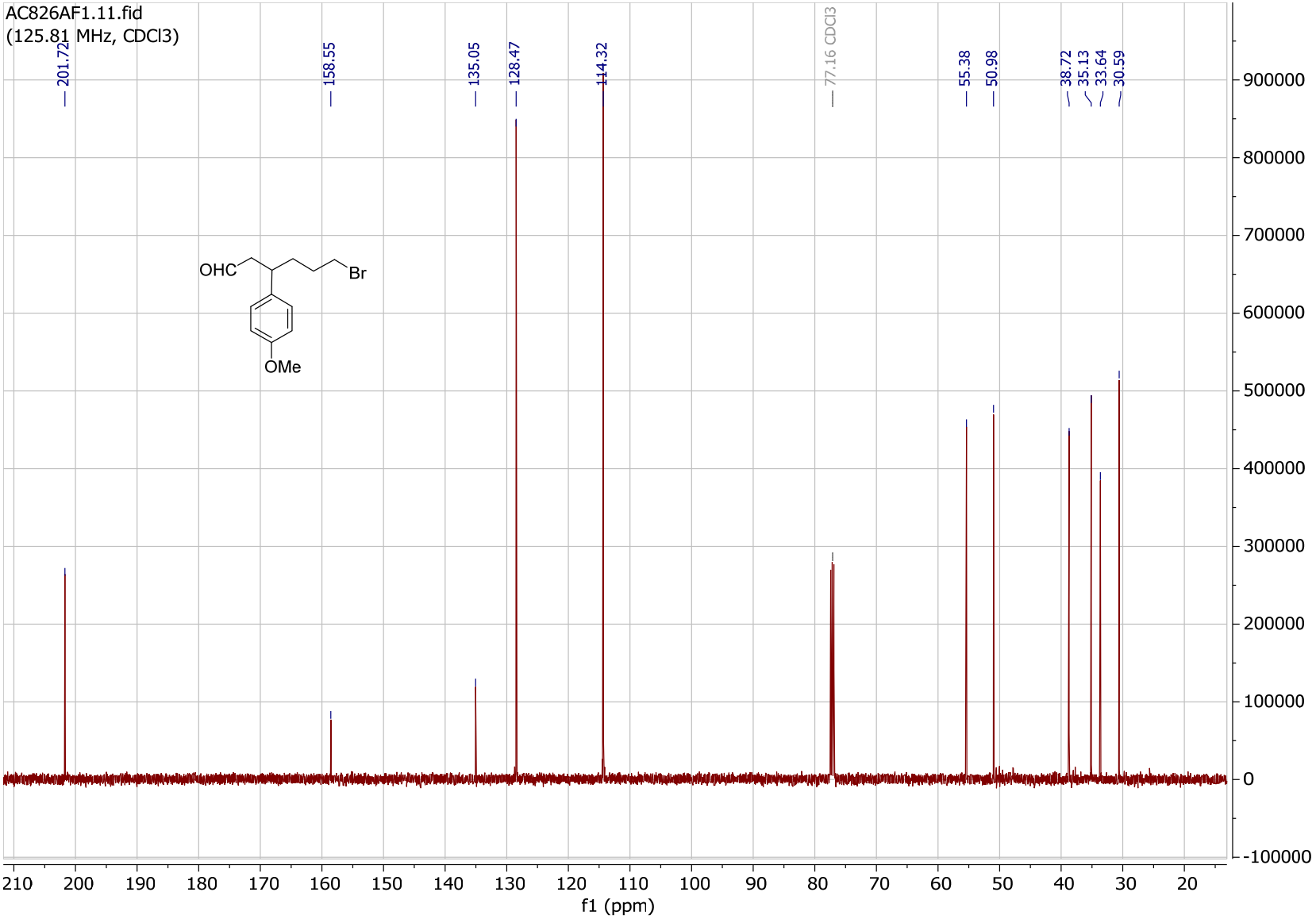
6-Iodo-3-phenylhexanal 2aa-I



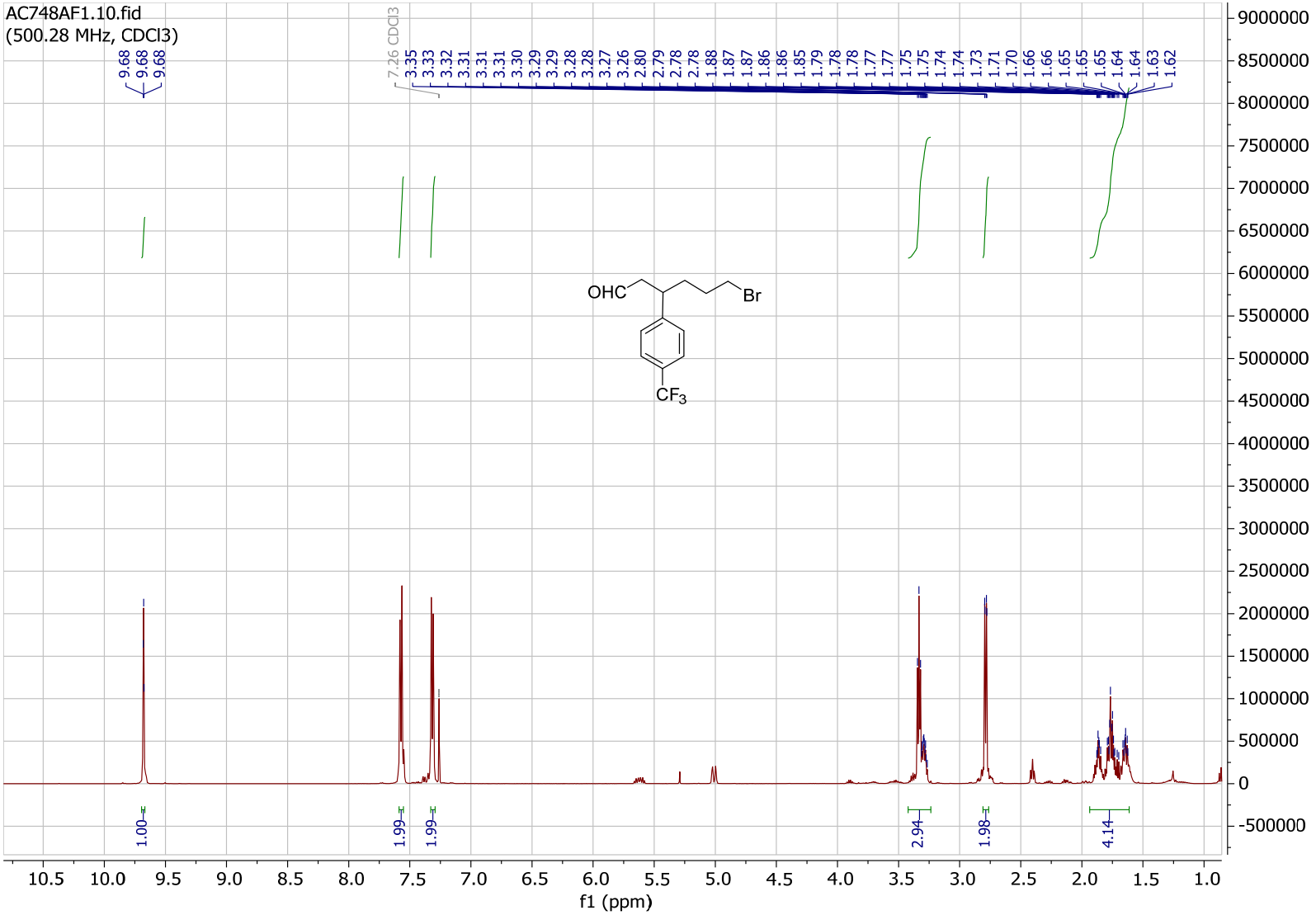

AC833AF1.11.fid
(125.81 MHz, CDCl3)
201.50
143.16
128.97
127.55
127.05
77.16 CDCl3
50.78
39.29
37.28
31.24
6.56
OHC
Ph
I
f1 (ppm)

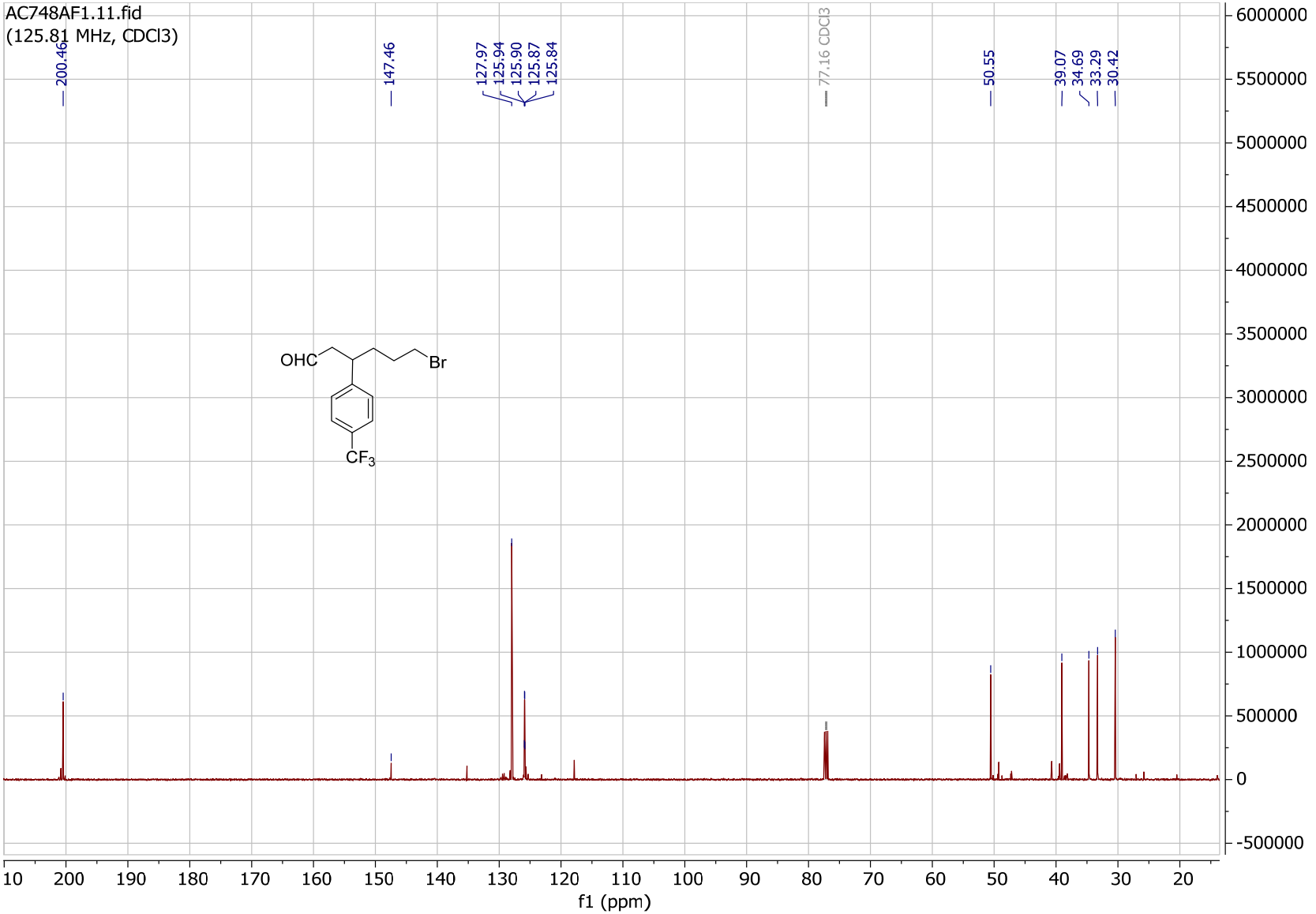
6-Bromo-3-(4-methoxyphenyl)hexanal 2ab

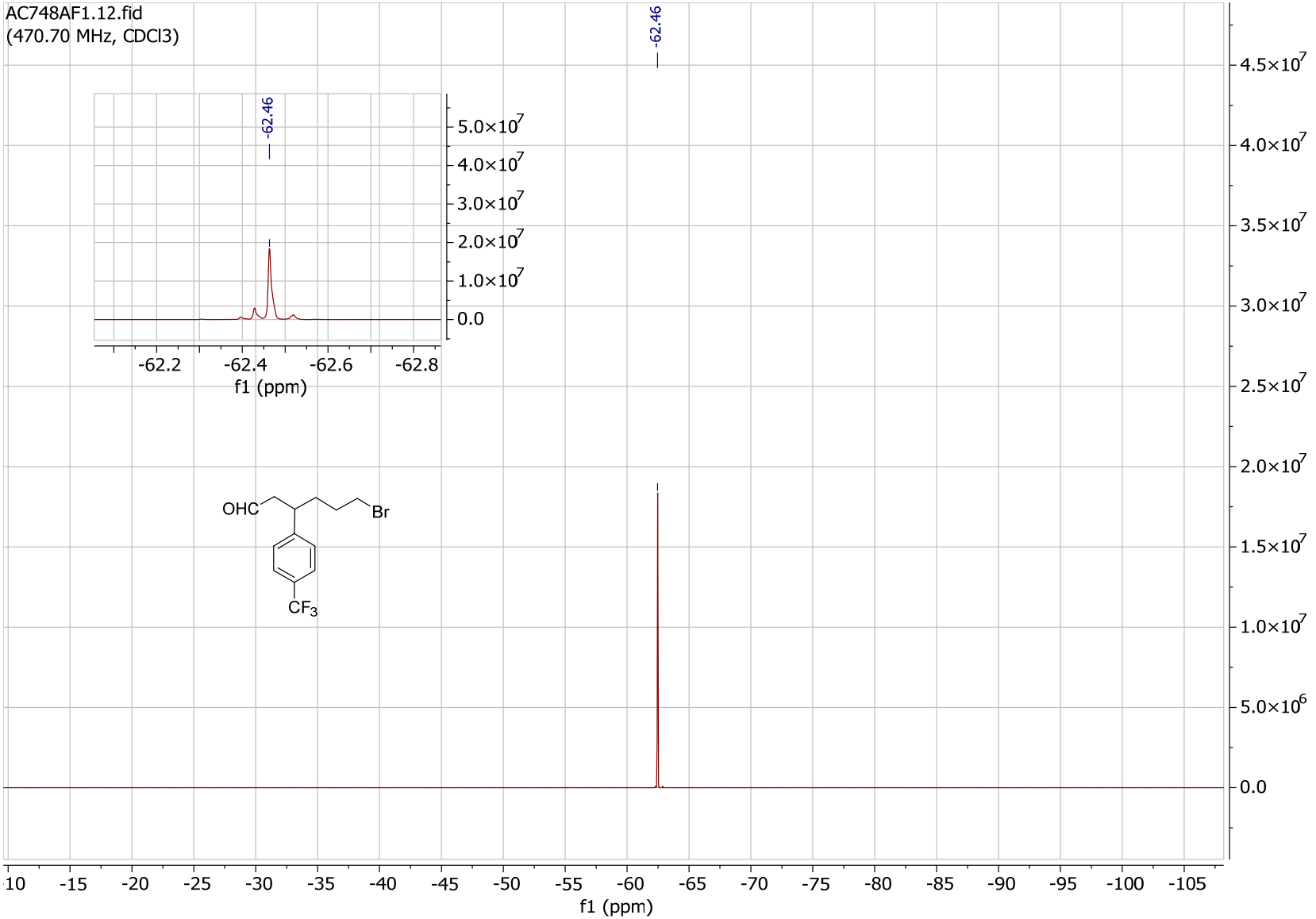



AC826AF1.11.fid
(125.81 MHz, CDCl3)
201.72
158.55
135.05
128.47
114.32
77.16 CDCl3
55.38
50.98
38.72
35.13
33.64
30.59
OHC
Br
OMe
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

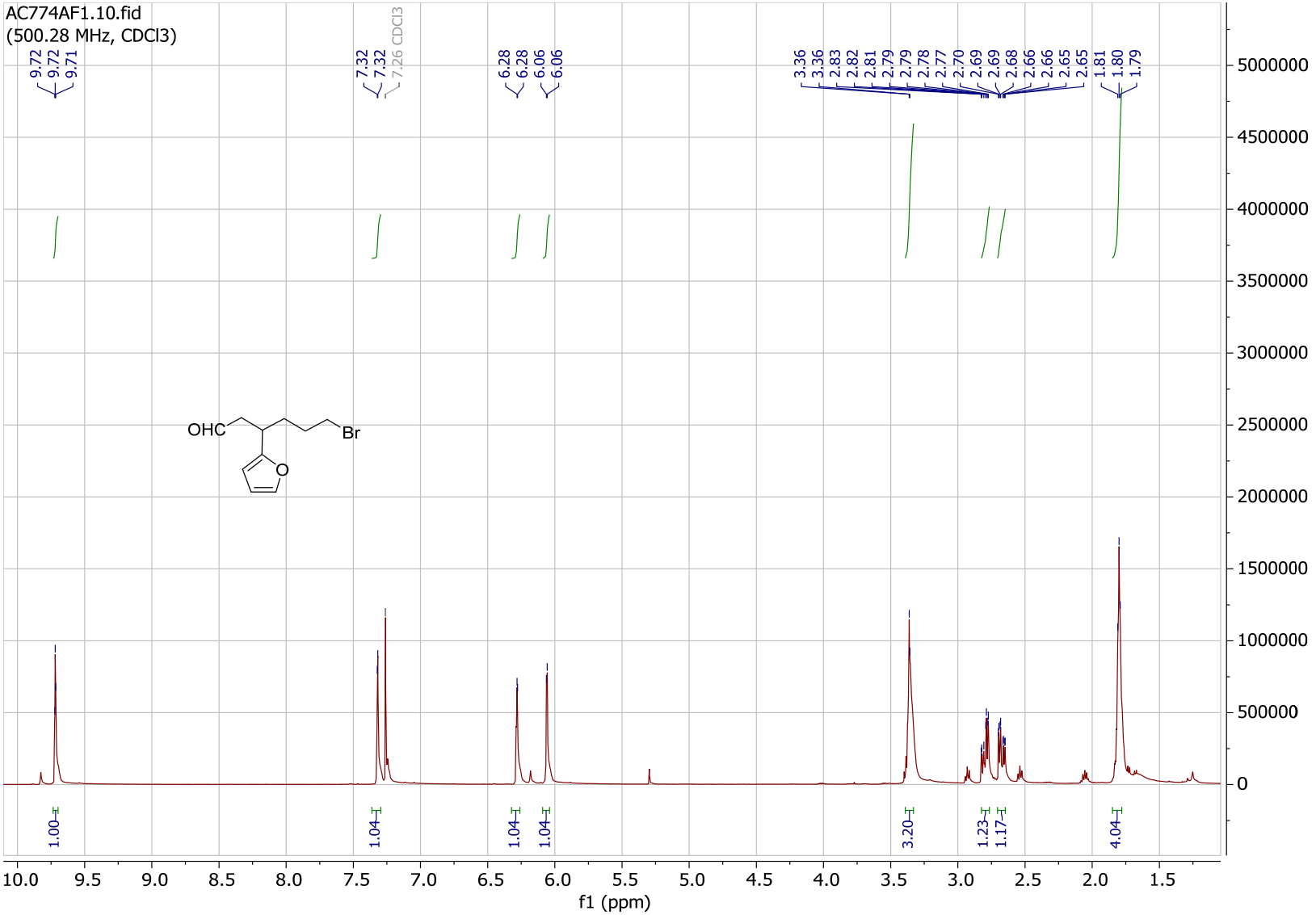
6-Bromo-3-(4-(trifluoromethyl)phenyl)hexanal 2ac

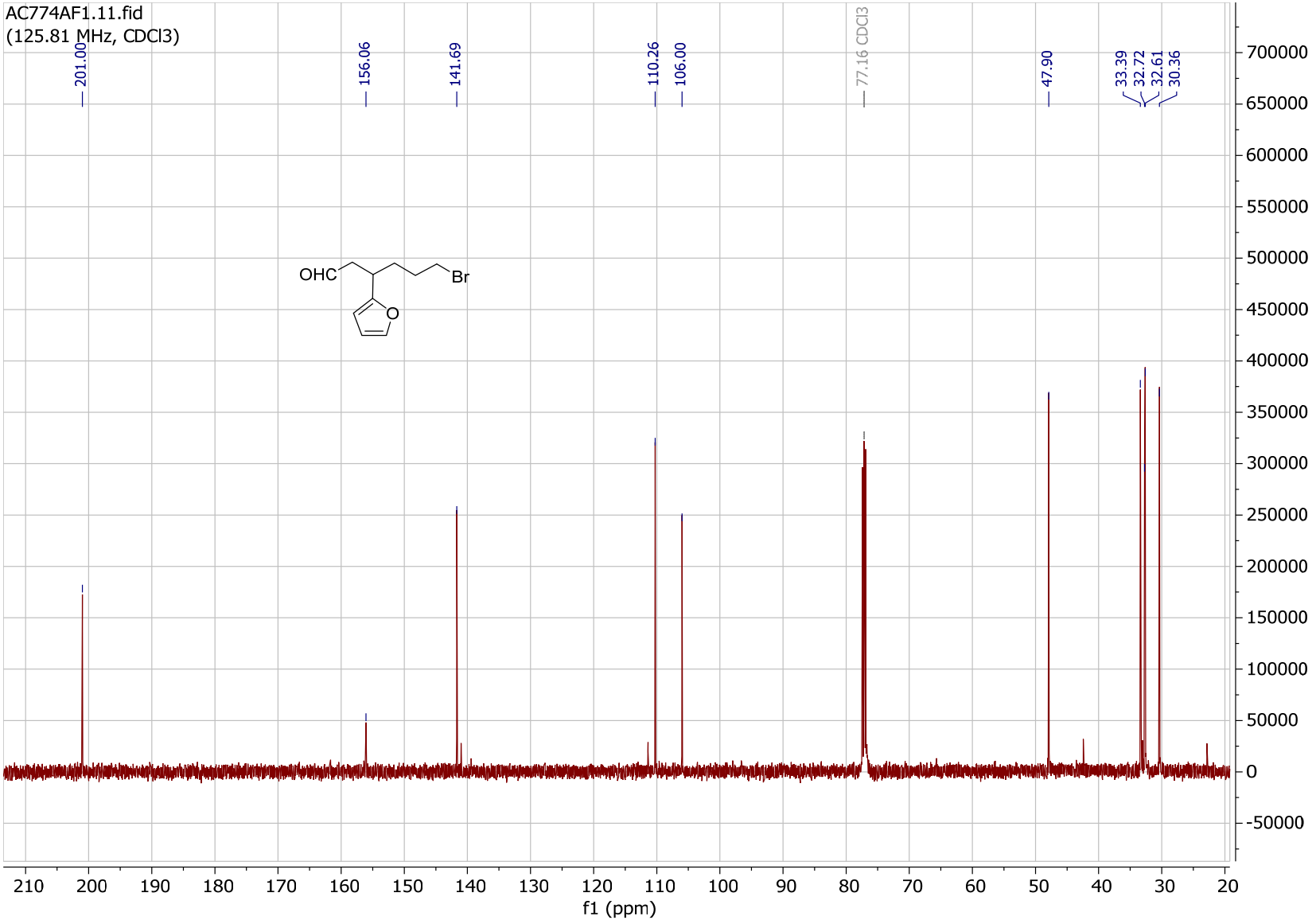



AC748AF1.11.fid
(125.81 MHz, CDCl3)
200.46
147.46
127.97
125.94
125.90
125.87
125.84
77.16 CDCl3
50.55
39.07
34.69
33.29
30.42
OHC
Br
CF3
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
10
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

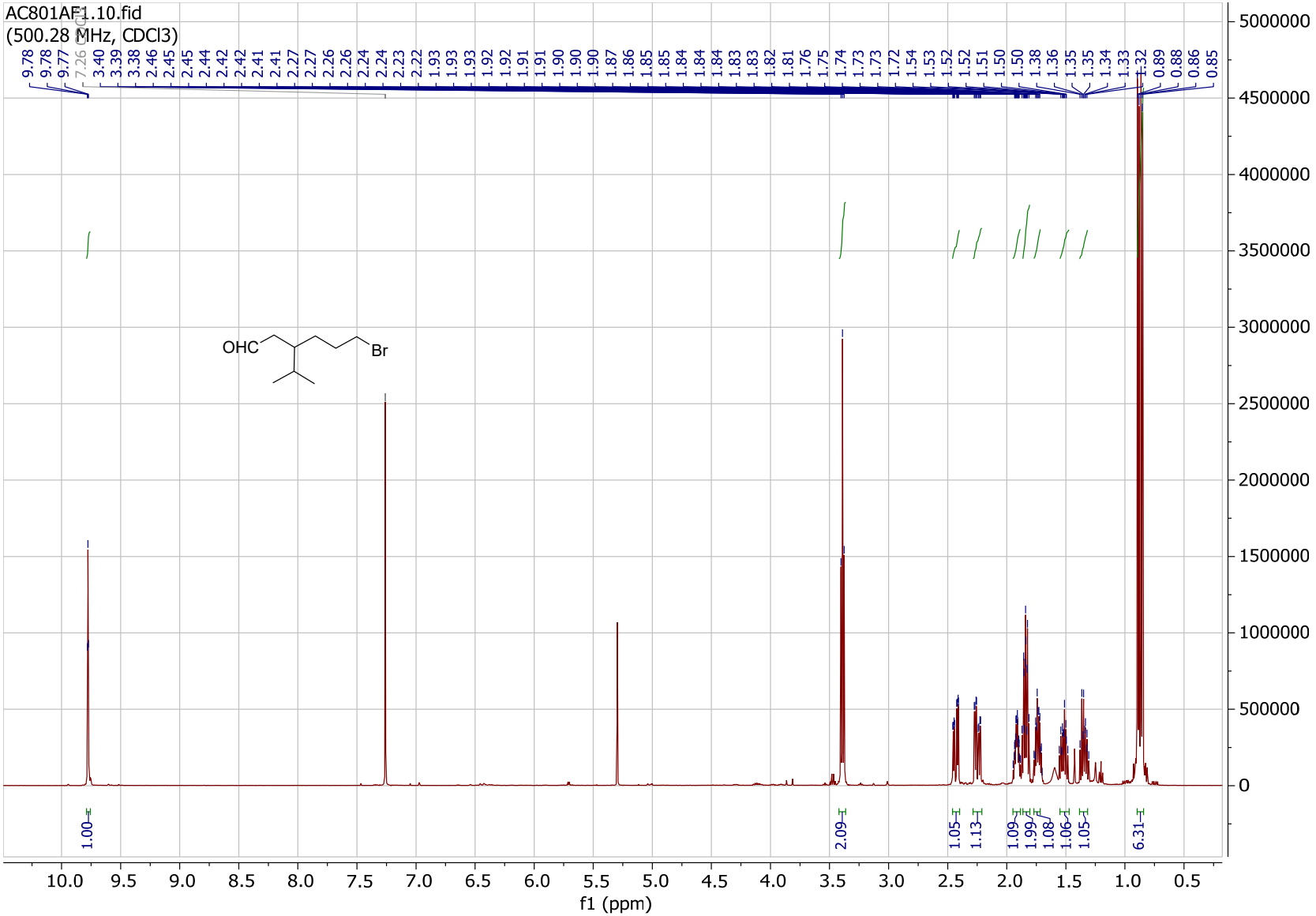

AC748AF1.12.fid
(470.70 MHz, CDCl3)
-62.46
4.5×10^7
4.0×10^7
3.5×10^7
3.0×10^7
2.5×10^7
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105
f1 (ppm)
-62.46
5.0×10^7
4.0×10^7
3.0×10^7
2.0×10^7
1.0×10^7
0.0
-62.2 -62.4 -62.6 -62.8
f1 (ppm)
OHC
Br
CF3

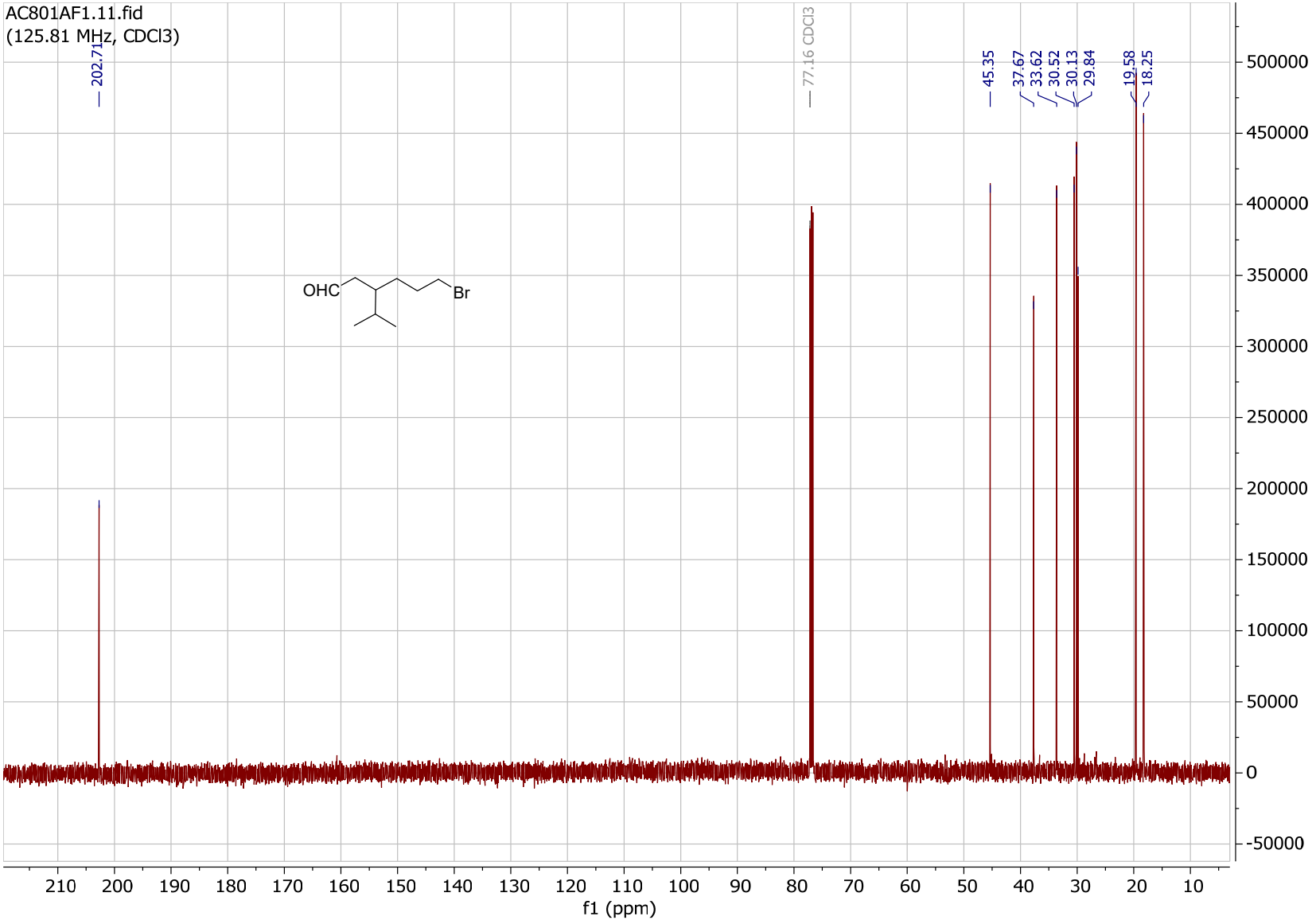
6-Bromo-3-(furan-2-yl)hexanal 2ad



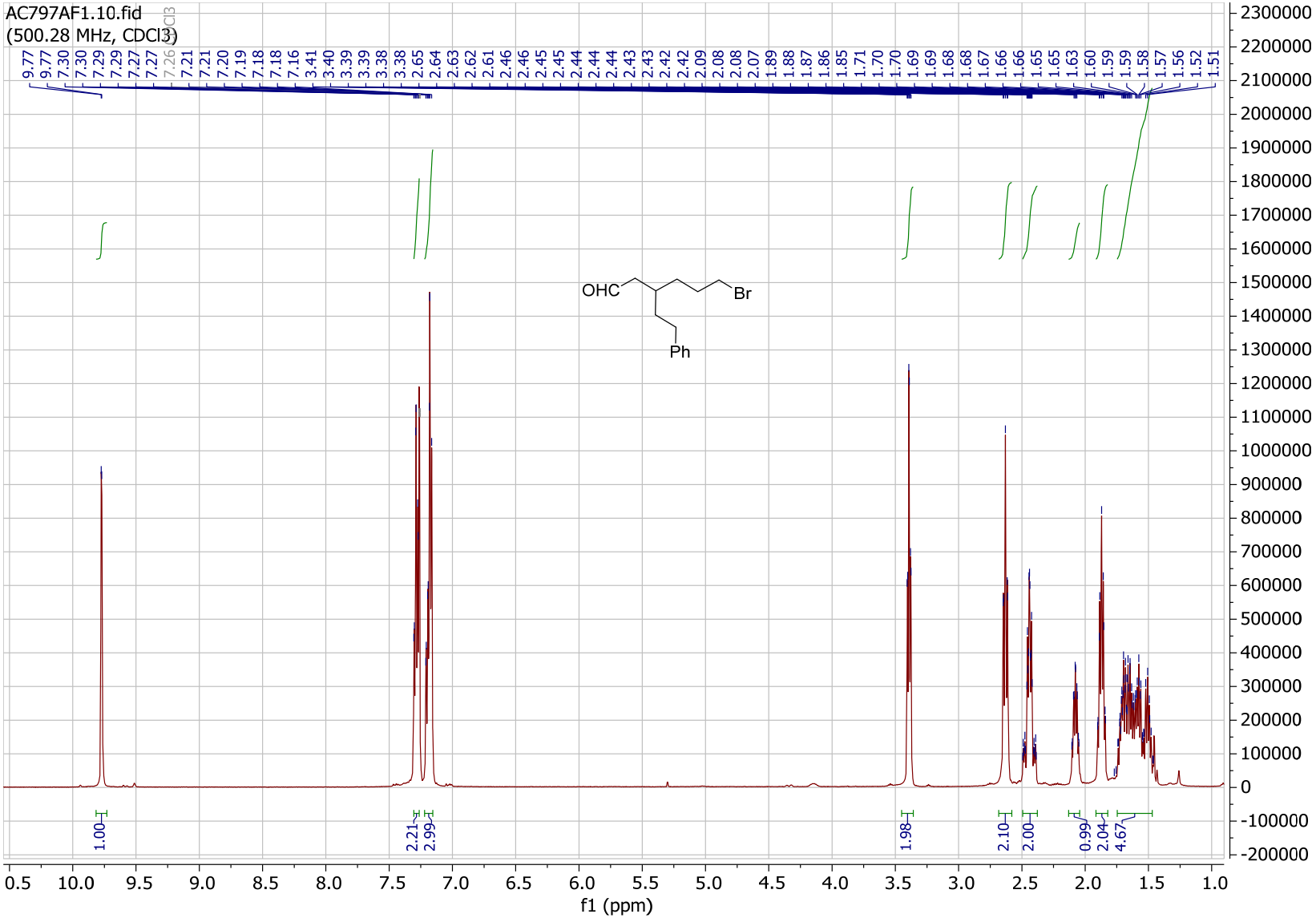

AC774AF1.11.fid
(125.81 MHz, CDCl3)
201.00
156.06
141.69
110.26
106.00
77.16 CDCl3
47.90
33.39
32.72
32.61
30.36
OHC
Br
O
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

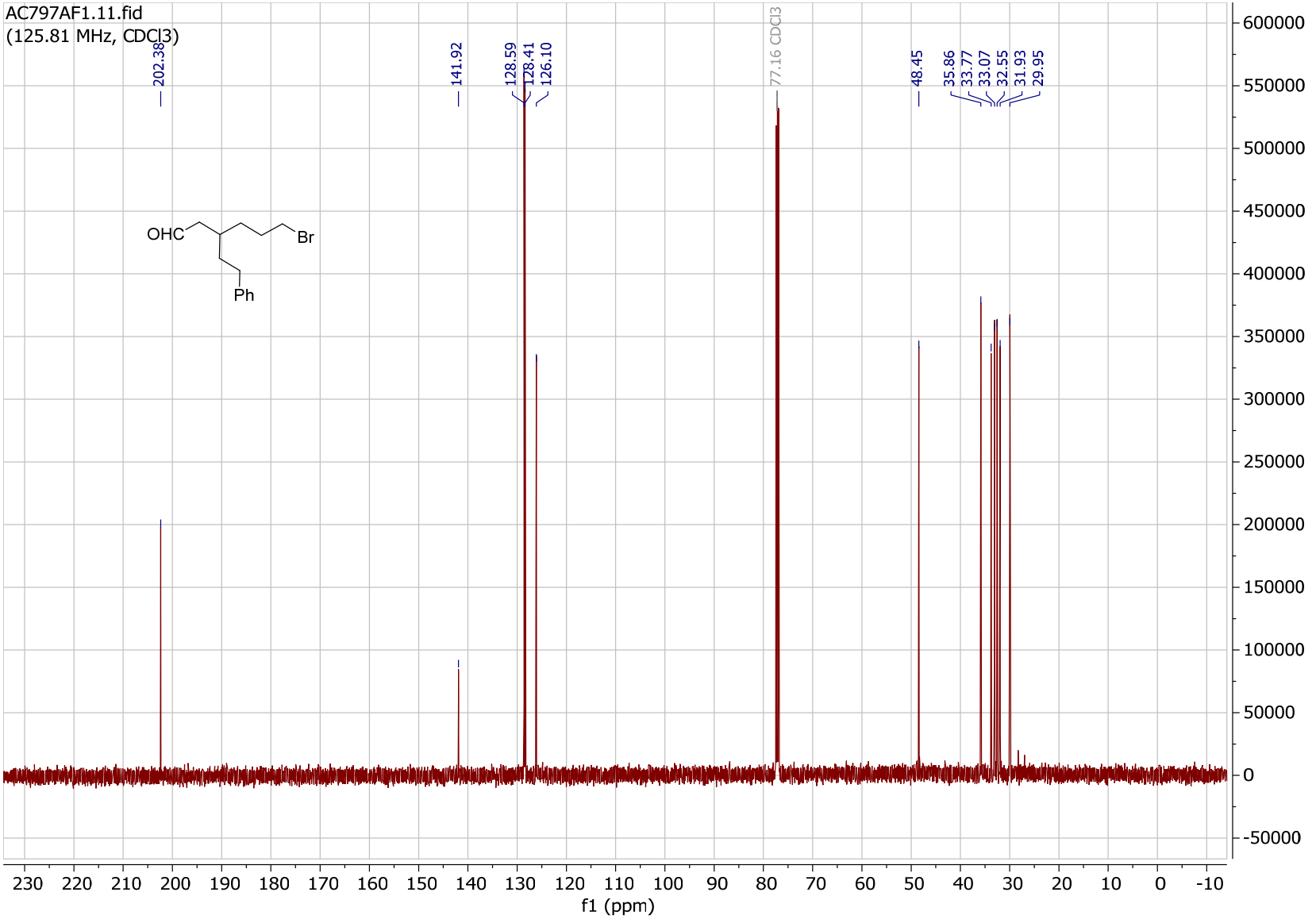
6-Bromo-3-isopropylhexanal 2ae



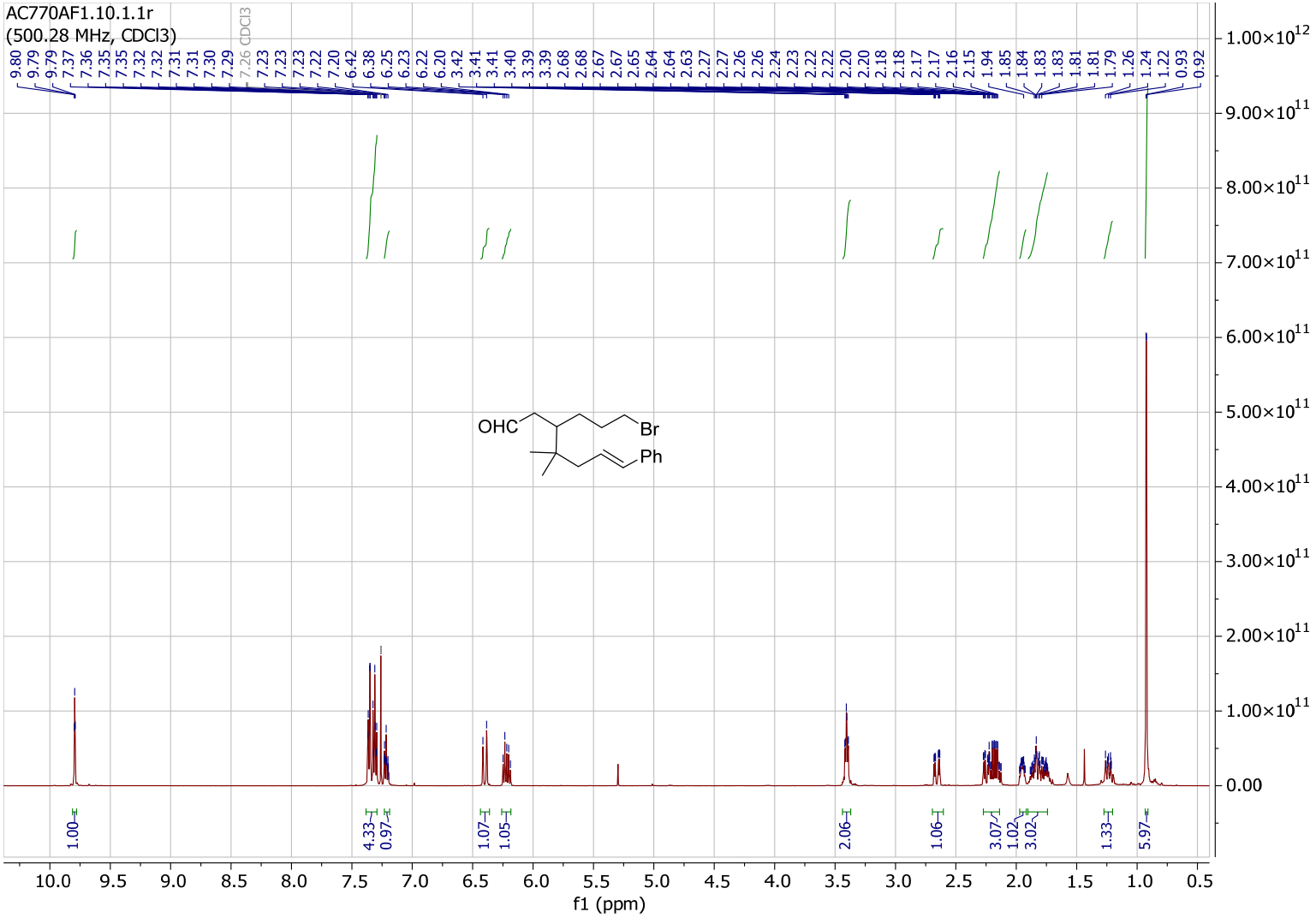

AC801AF1.11.fid
(125.81 MHz, CDCl3)
202.71
77.16 CDCl3
45.35
37.67
33.62
30.52
30.13
29.84
19.58
18.25
OHC
Br
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

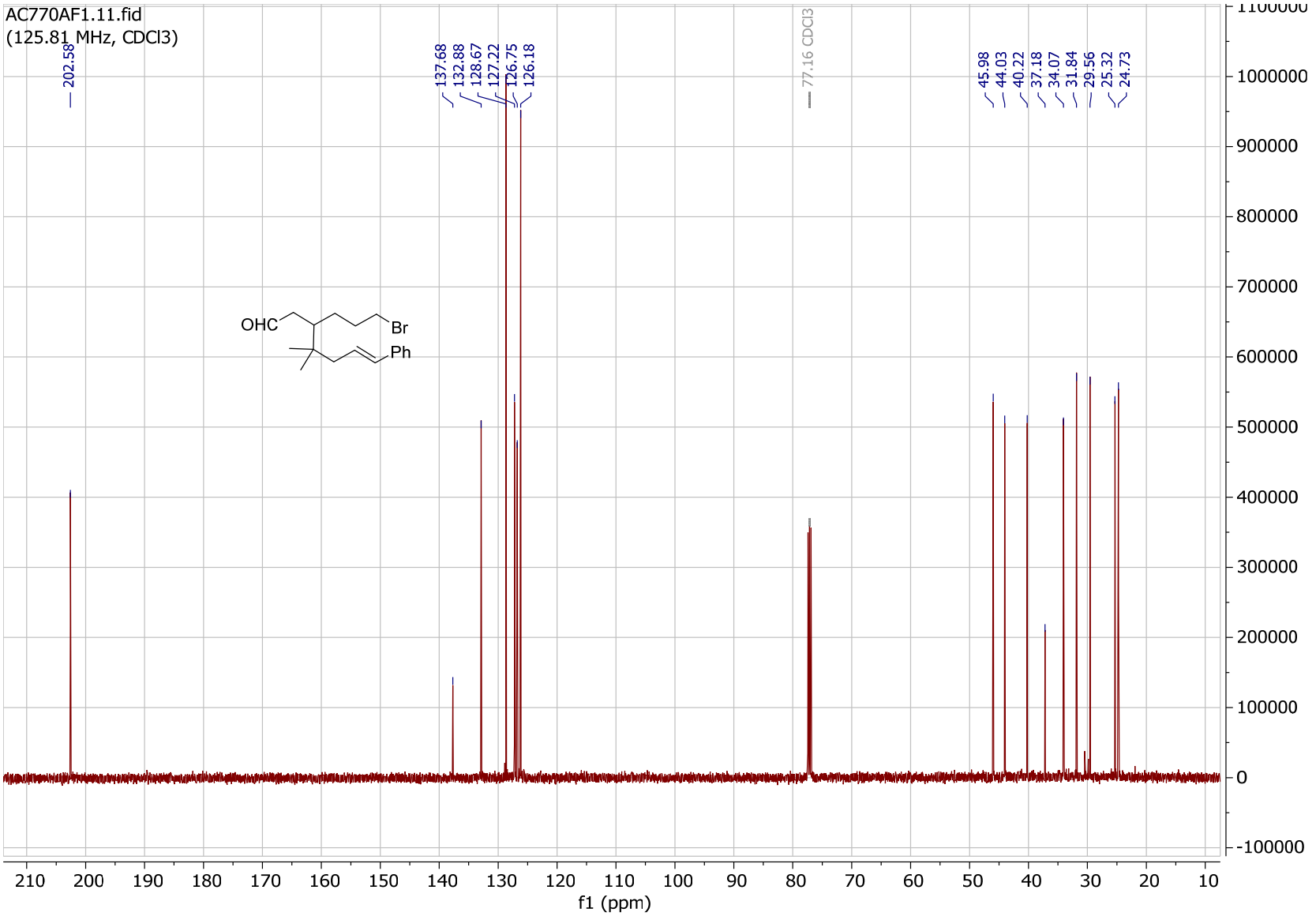
6-Bromo-3-phenethylhexanal 2af



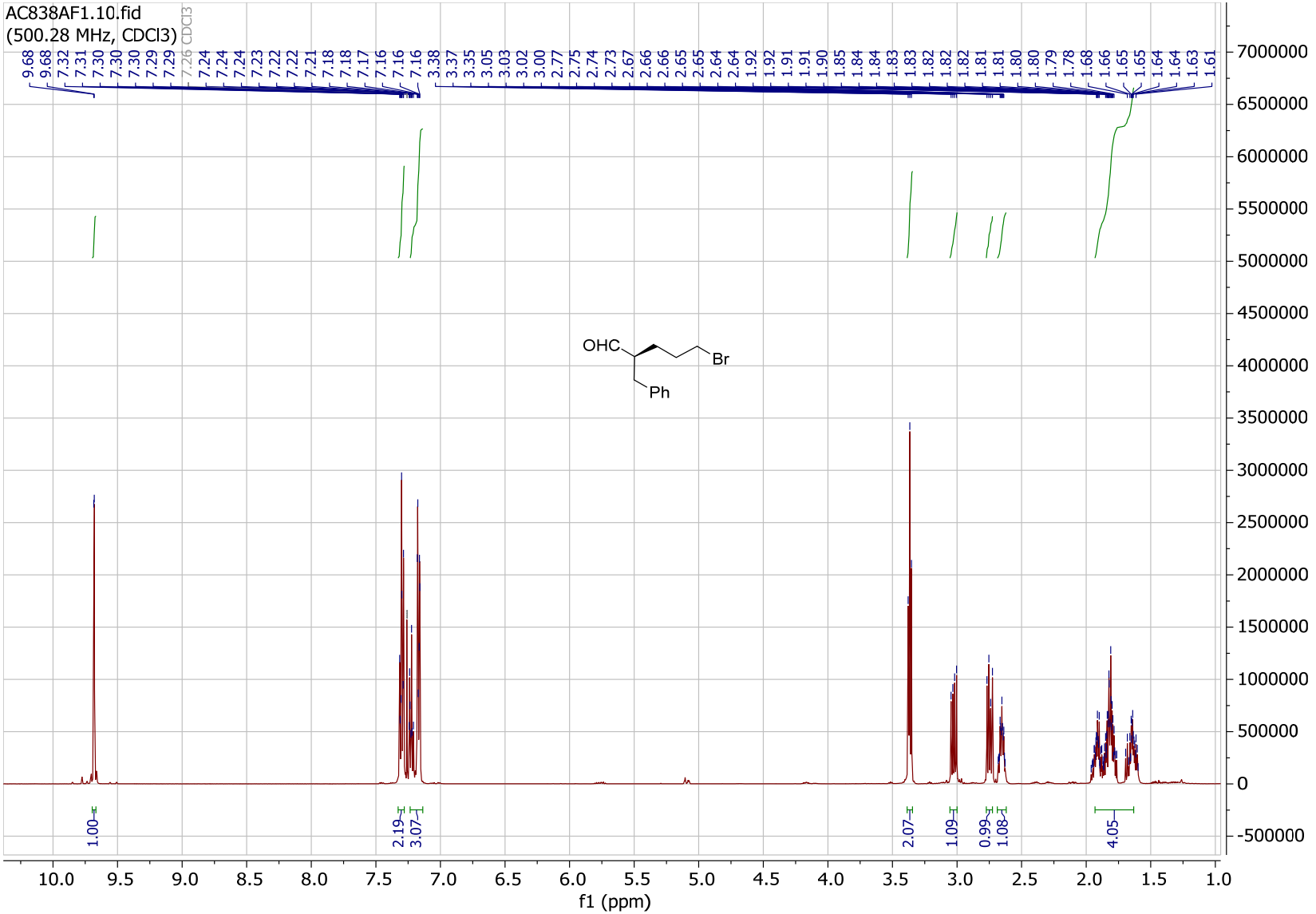

AC797AF1.11.fid
(125.81 MHz, CDCl3)
202.38
141.92
128.59
128.41
126.10
77.16 CDCl3
48.45
35.86
33.77
33.07
32.55
31.93
29.95
OHC
Br
Ph
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

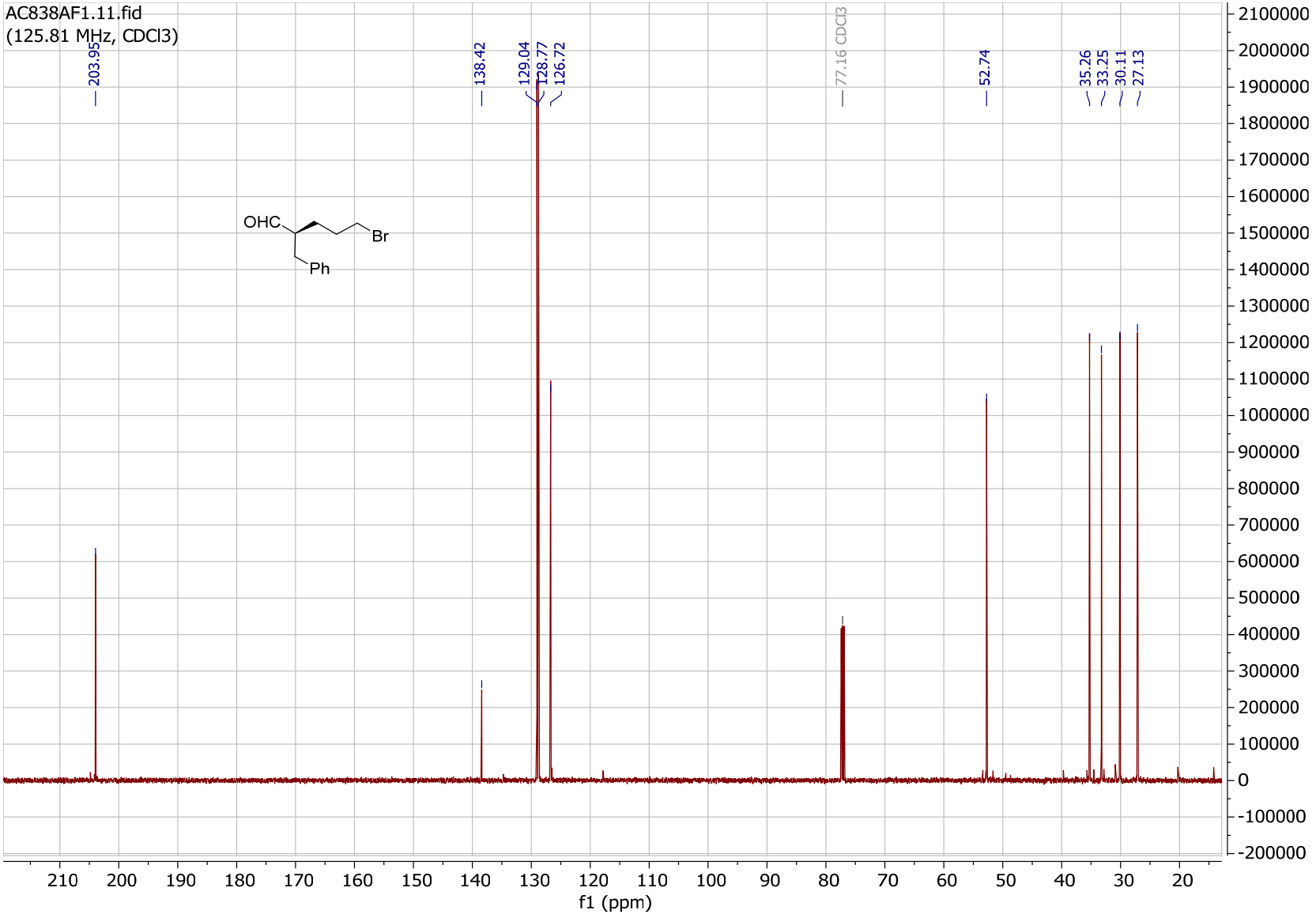
(*E*)-3-(3-Bromopropyl)-4,4-dimethyl-7-phenylhept-6-enal 2ag



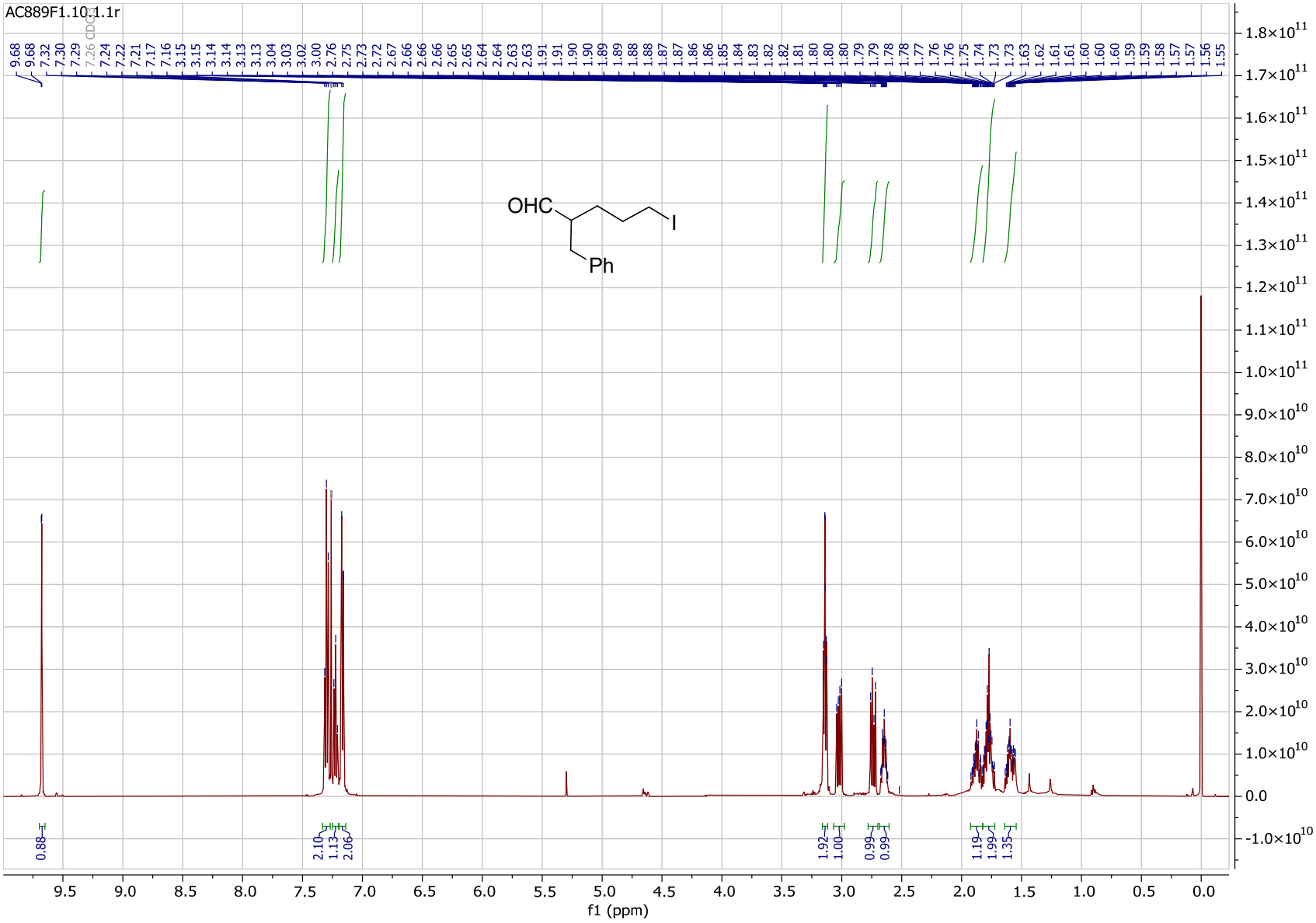

AC770AF1.11.fid
(125.81 MHz, CDCl3)
202.58
137.68
132.88
128.67
127.22
126.75
126.18
77.16 CDCl3
45.98
44.03
40.22
37.18
34.07
31.84
29.56
25.32
24.73
OHC
Br
Ph
f1 (ppm)

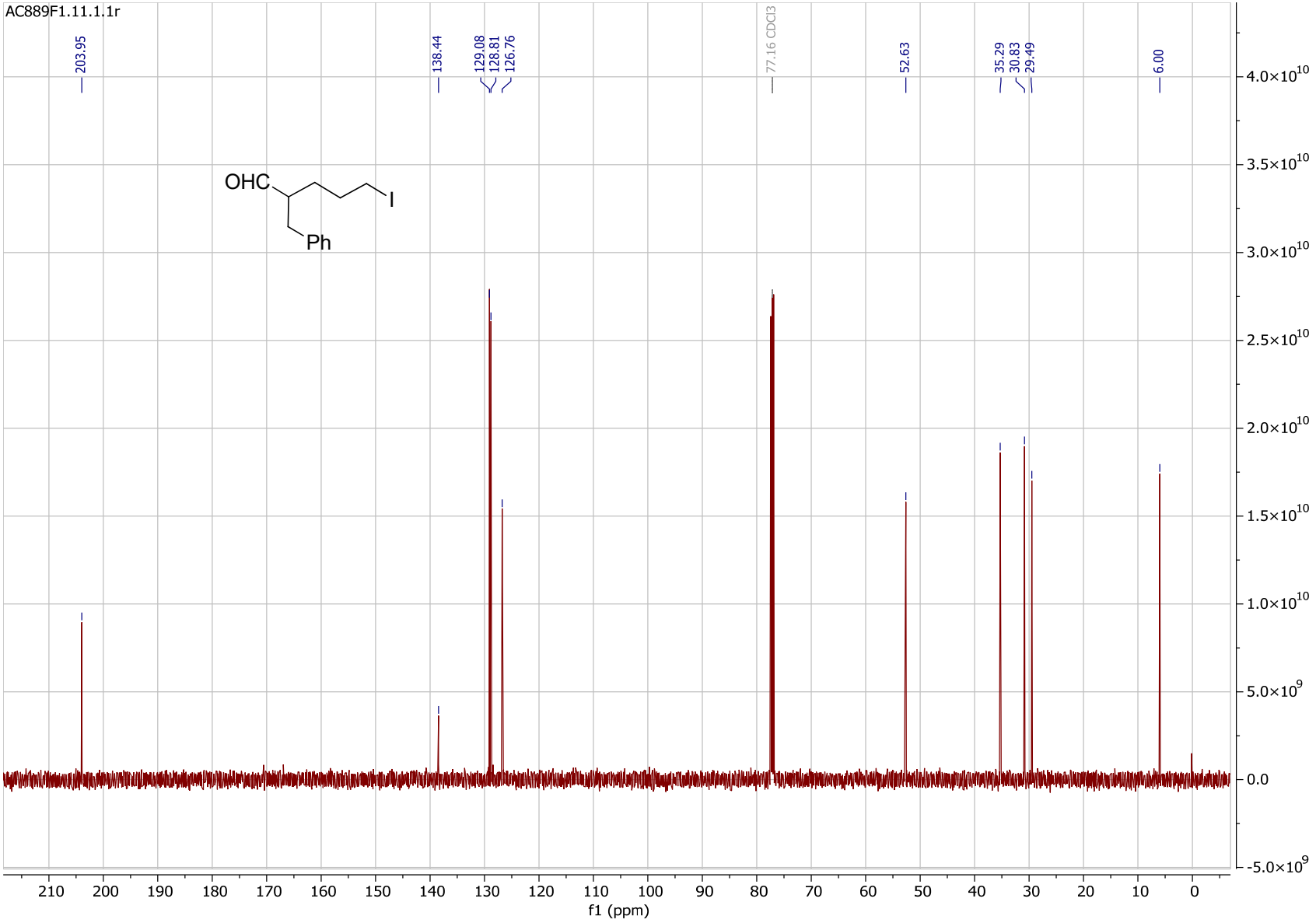
(S)-2-Benzyl-5-bromopentanal 2ba-Br



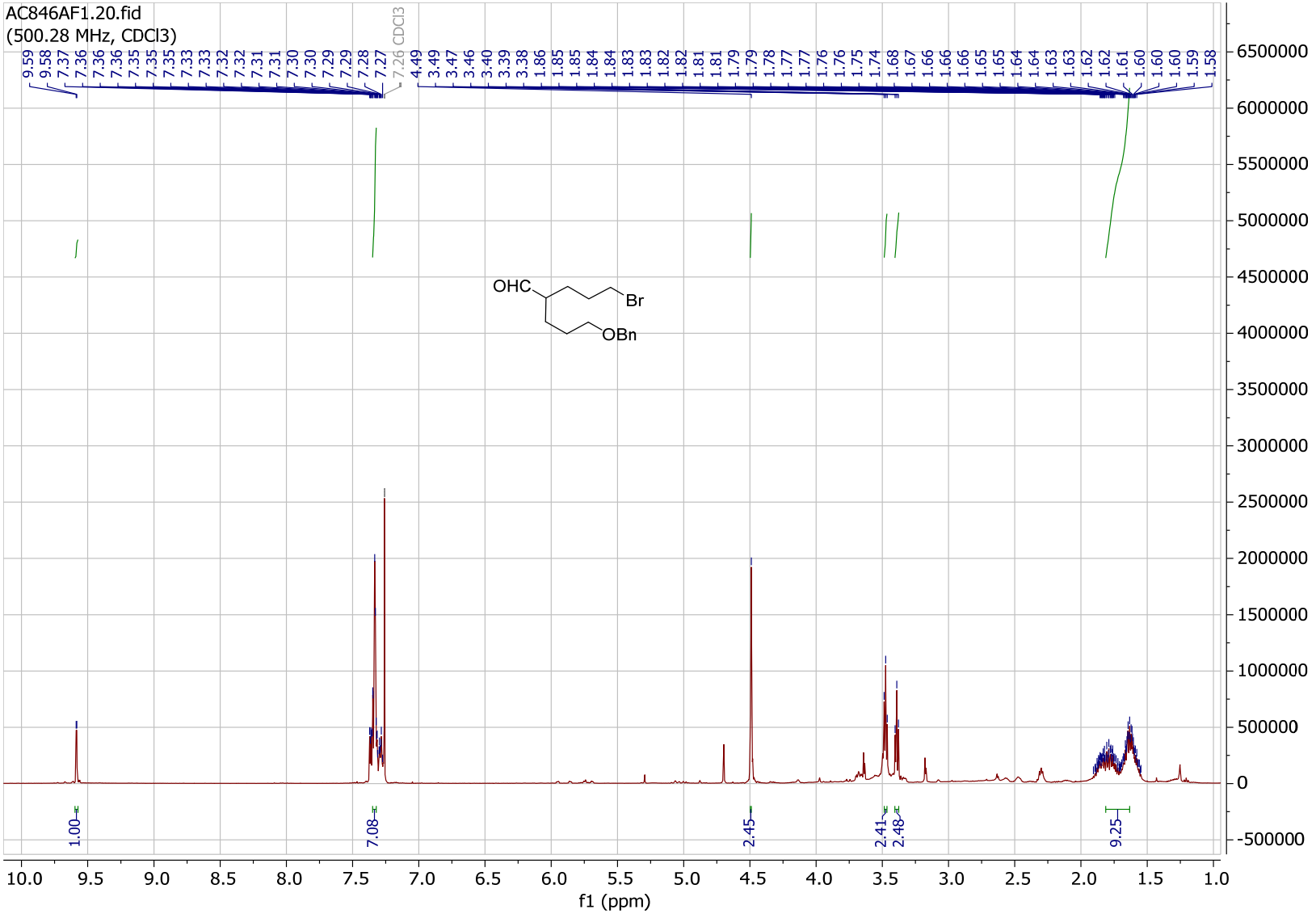

AC838AF1.11.fid
(125.81 MHz, CDCl3)
203.95
138.42
129.04
128.77
126.72
77.16 CDCl3
52.74
35.26
33.25
30.11
27.13
OHC
Br
Ph
f1 (ppm)

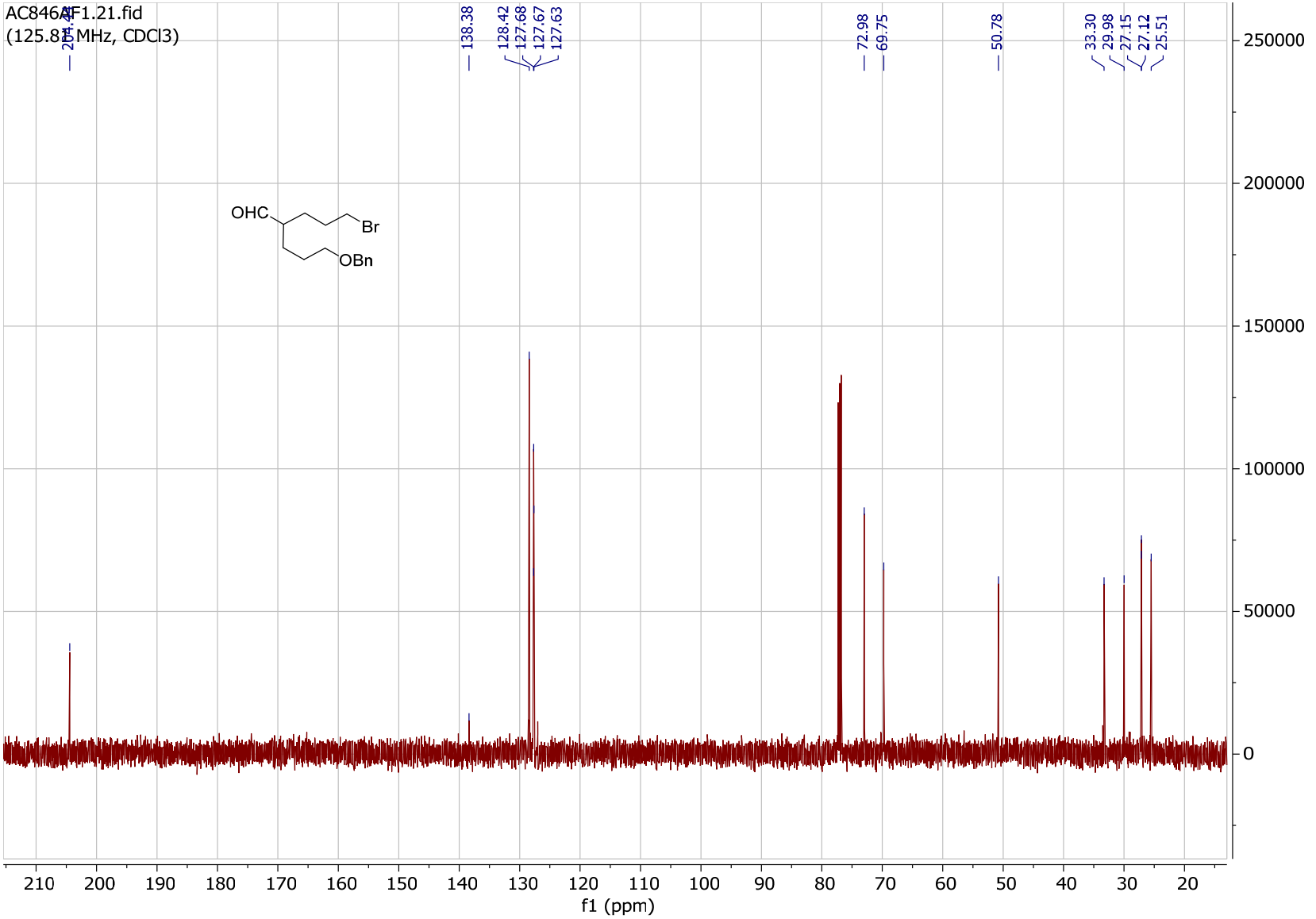
2-Benzyl-5-iodopentanal 2ba-I



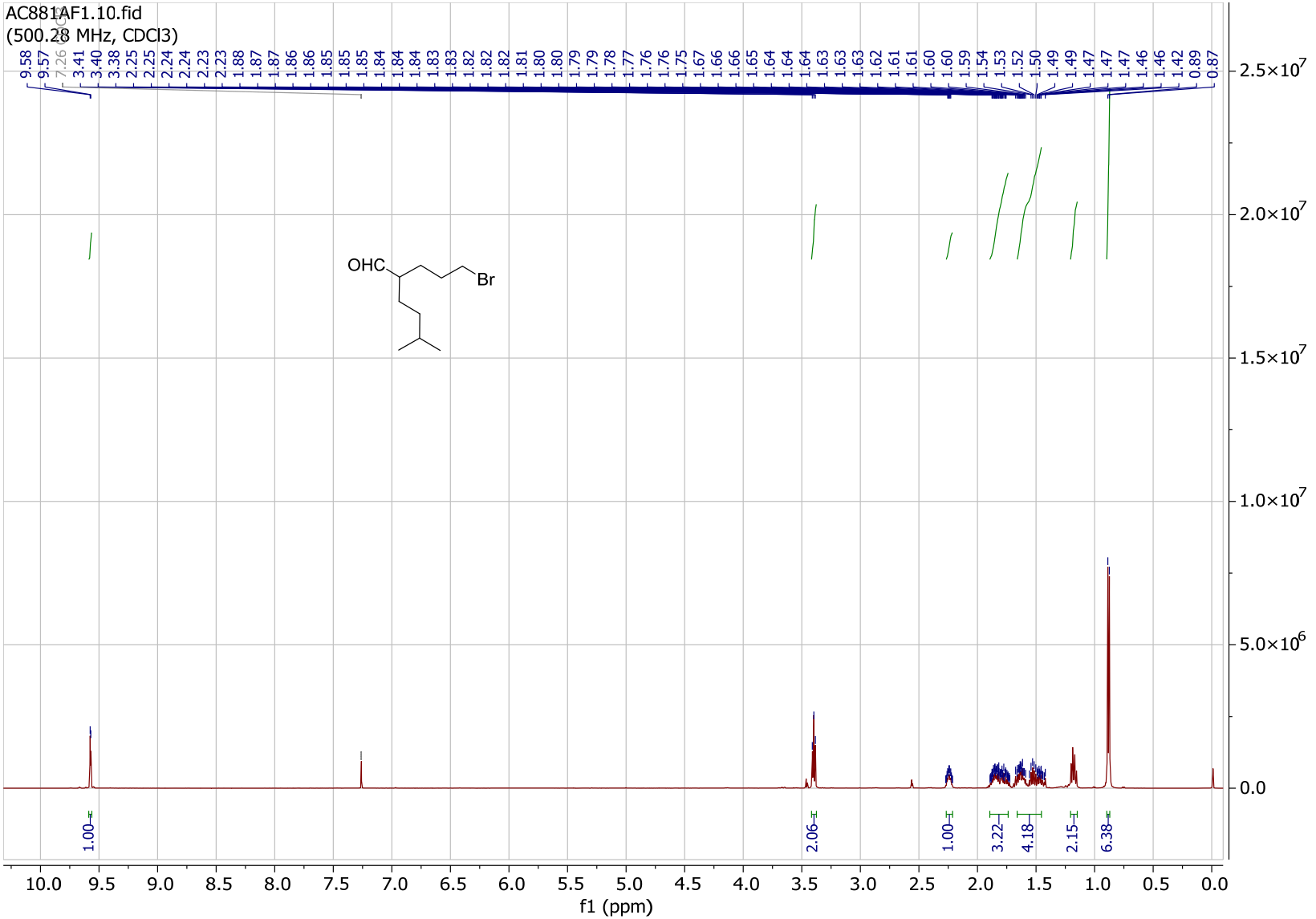

AC889F1.11.1.1r
203.95
138.44
129.08
128.81
126.76
77.16 CDCl3
52.63
35.29
30.83
29.49
6.00
OHC
I
Ph
4.0×10^10
3.5×10^10
3.0×10^10
2.5×10^10
2.0×10^10
1.5×10^10
1.0×10^10
5.0×10^9
0.0
-5.0×10^9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

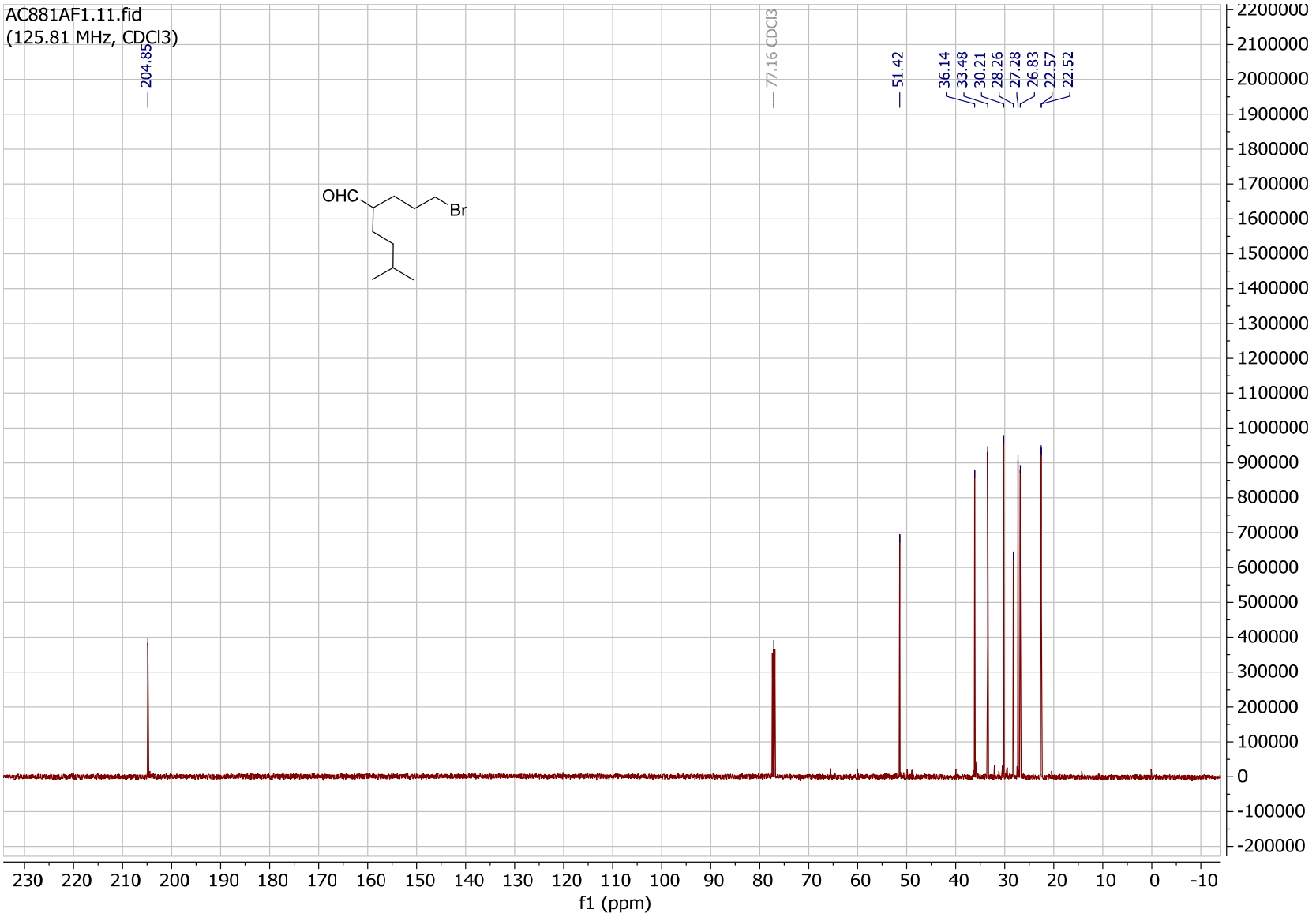
5-(Benzyloxy)-2-(3-bromopropyl)pentanal 2bb



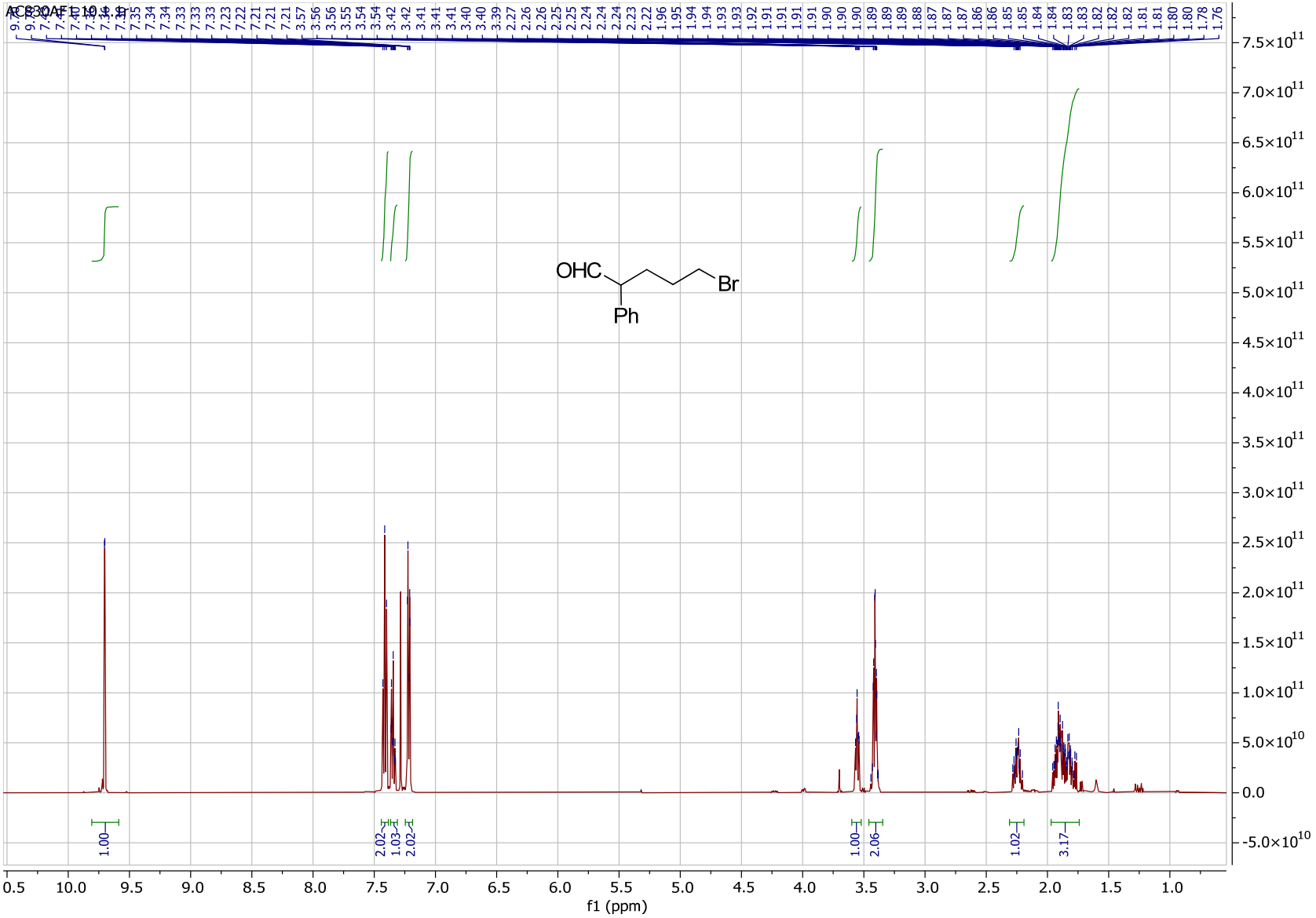

AC846AF1.21.fid
(125.81 MHz, CDCl3)
204.44
138.38
128.42
127.68
127.67
127.63
72.98
69.75
50.78
33.30
29.98
27.15
27.12
25.51
OHC
Br
OBn
250000
200000
150000
100000
50000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

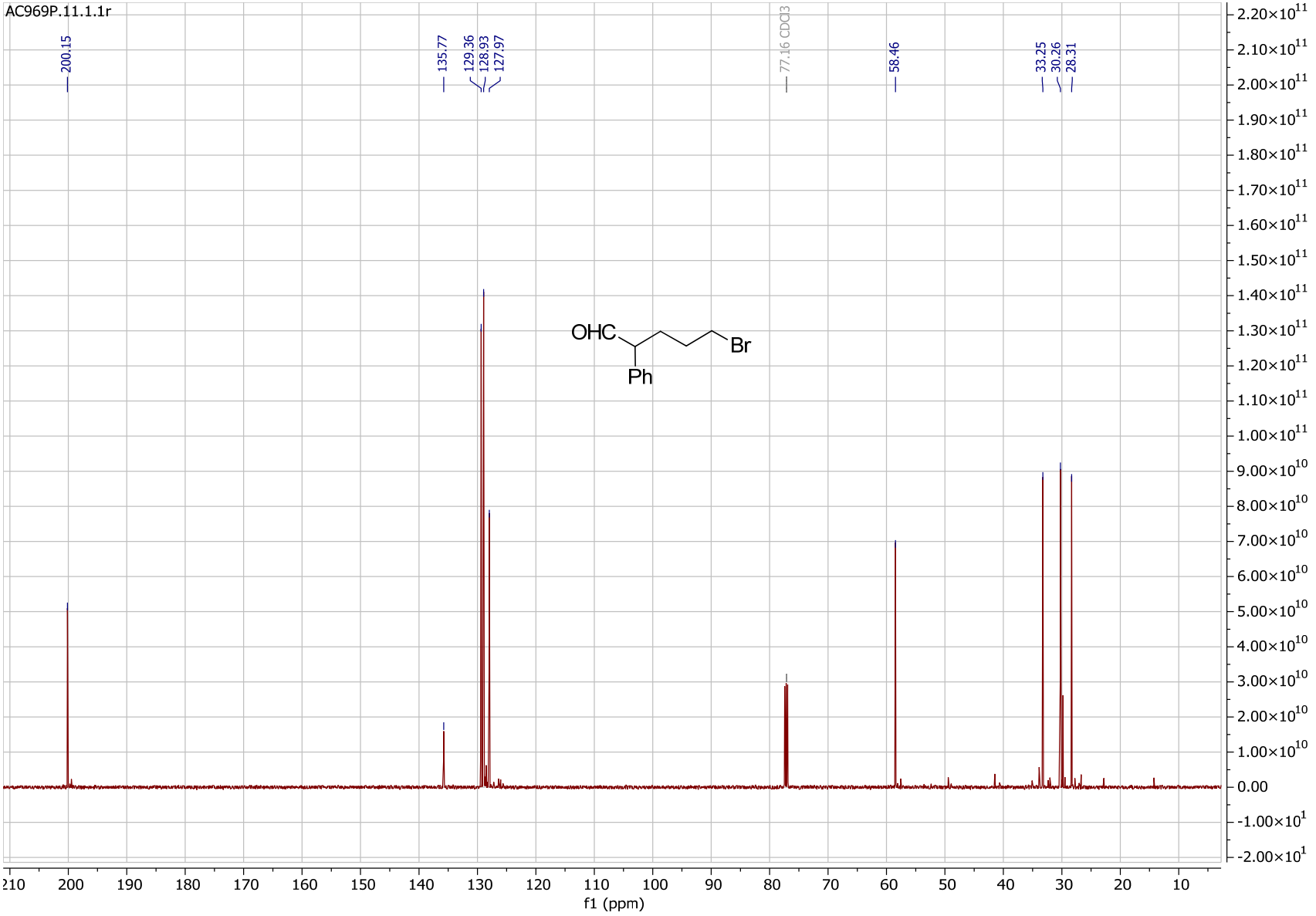
2-(3-Bromopropyl)-5-methylhexanal 2bc



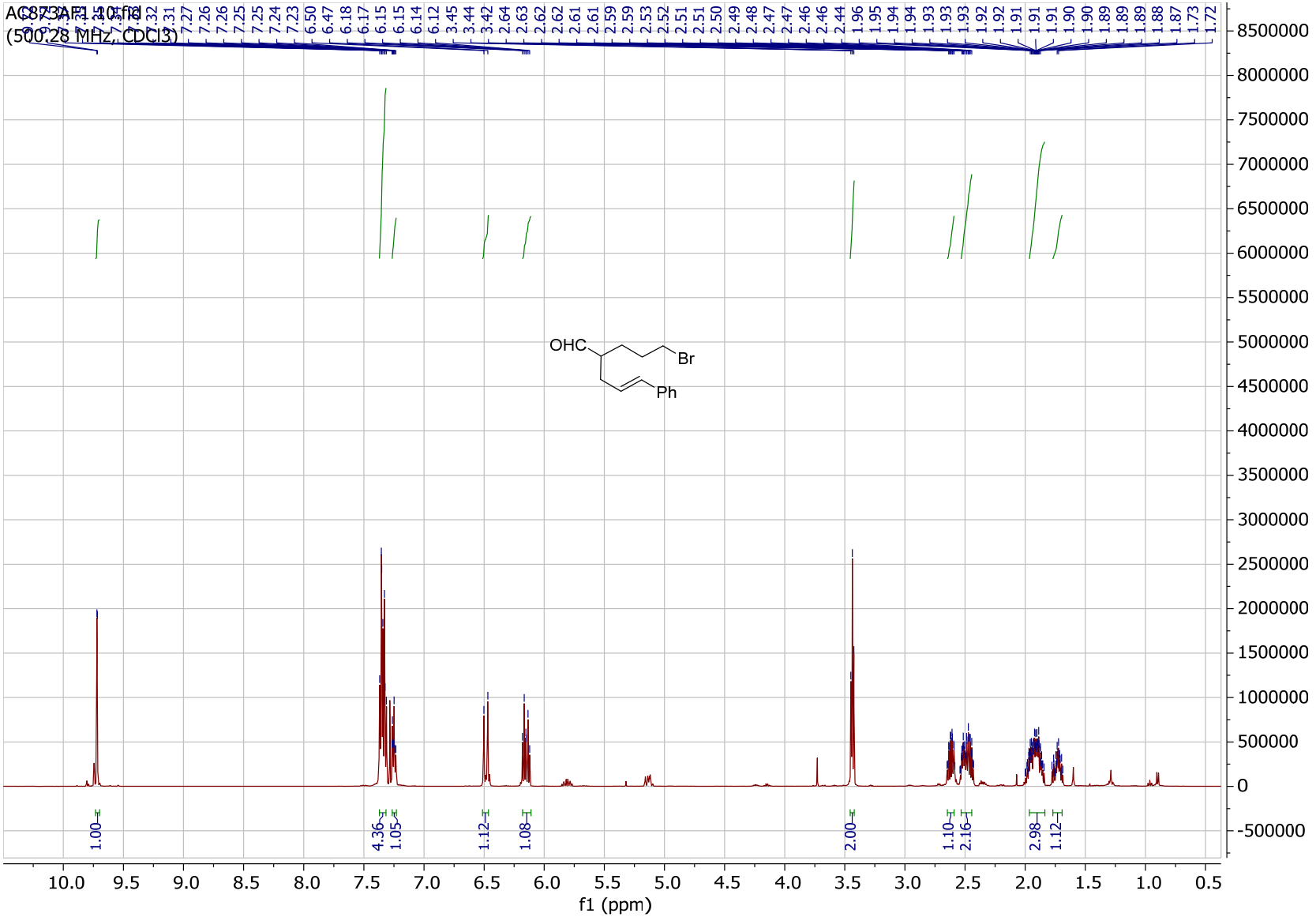

AC881AF1.11.fid
(125.81 MHz, CDCl3)
204.85
77.16 CDCl3
51.42
36.14
33.48
30.21
28.26
27.28
26.83
22.57
22.52
OHC
Br
f1 (ppm)

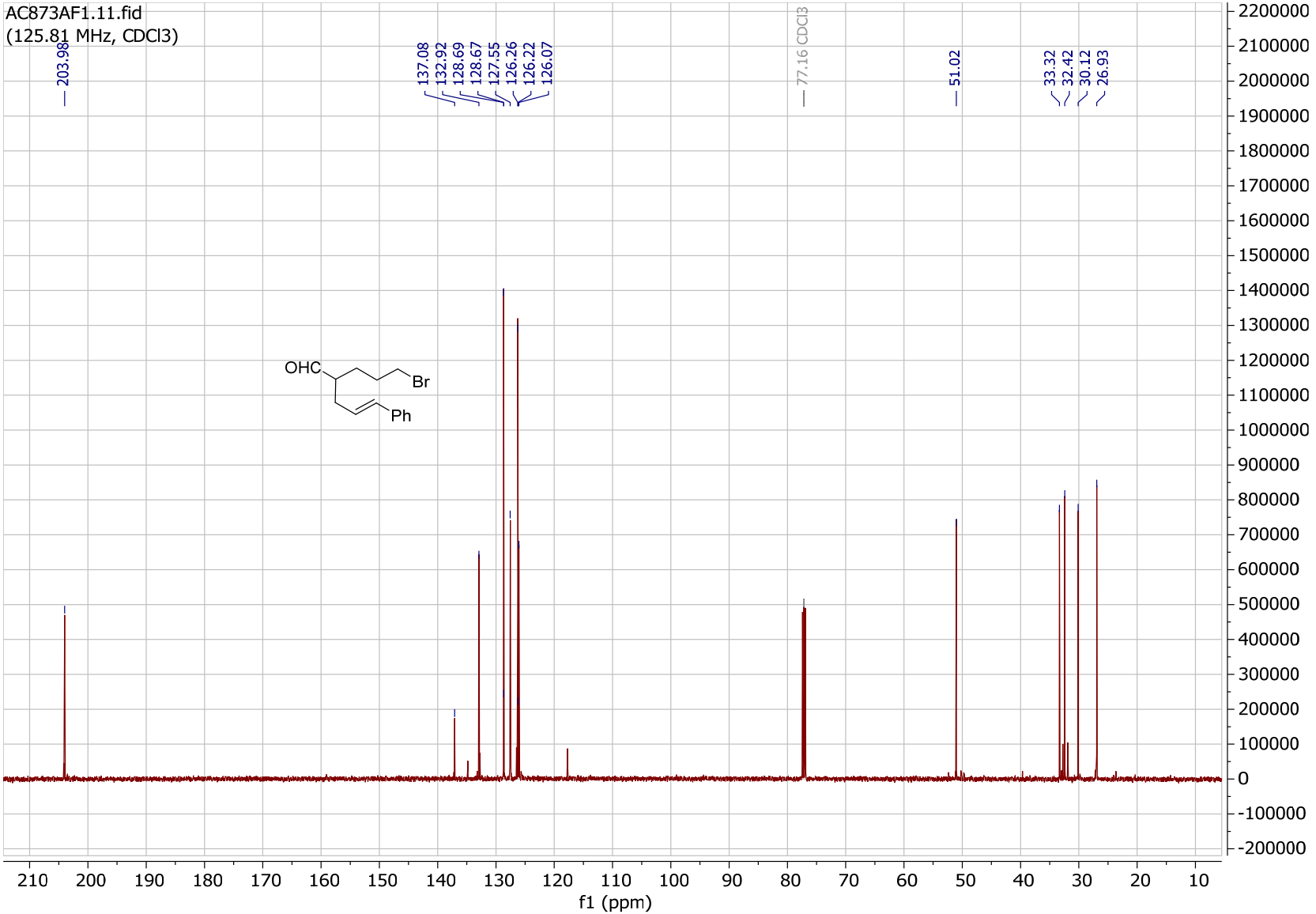
5-Bromo-2-phenylpentanal 2bd



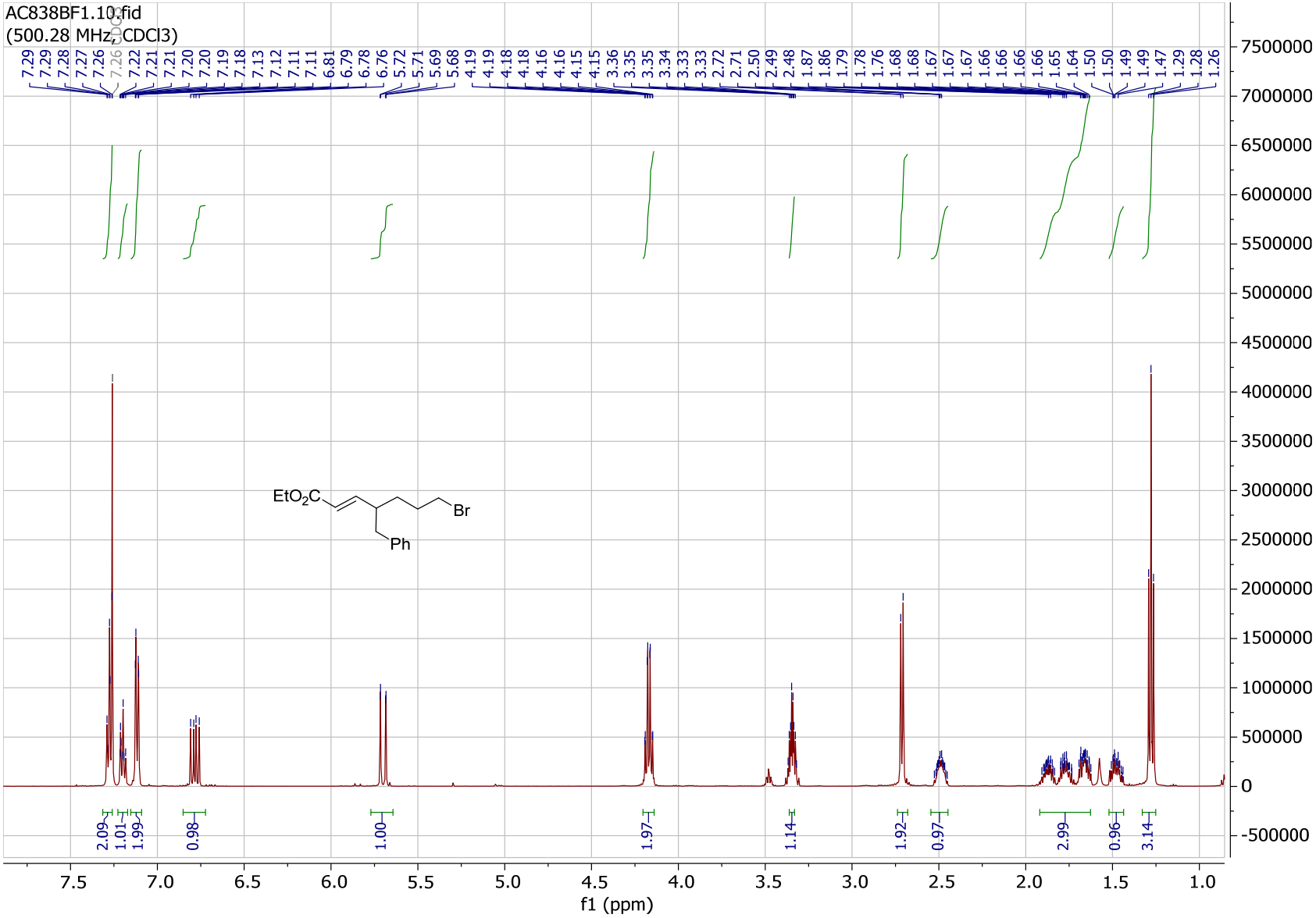

AC969P.11.1.1r
200.15
135.77
129.36
128.93
127.97
77.16 CDCl3
58.46
33.25
30.26
28.31
OHC
Br
Ph
f1 (ppm)

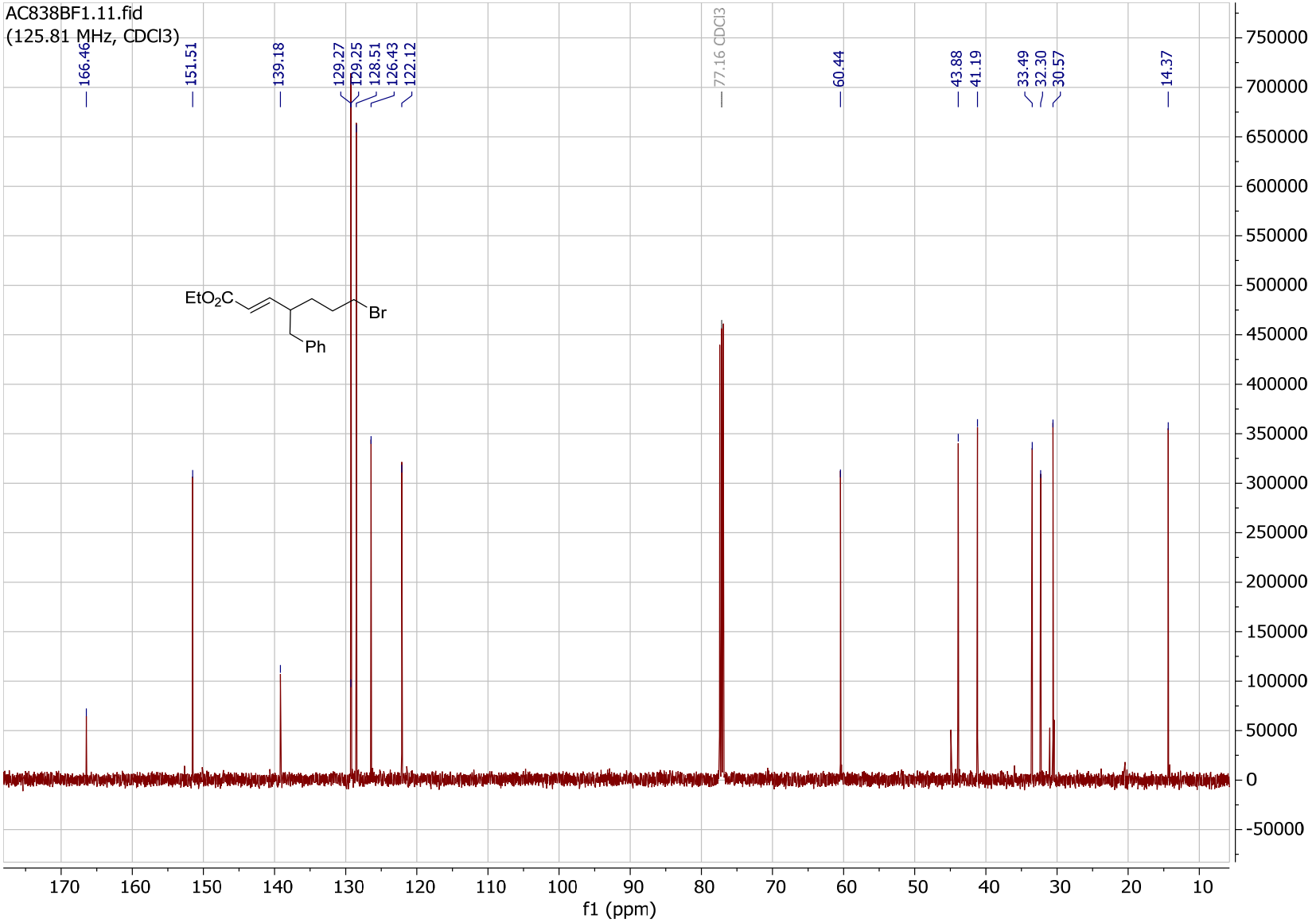
(*E*)-2-(3-Bromopropyl)-5-phenylpent-4-enal 2bi



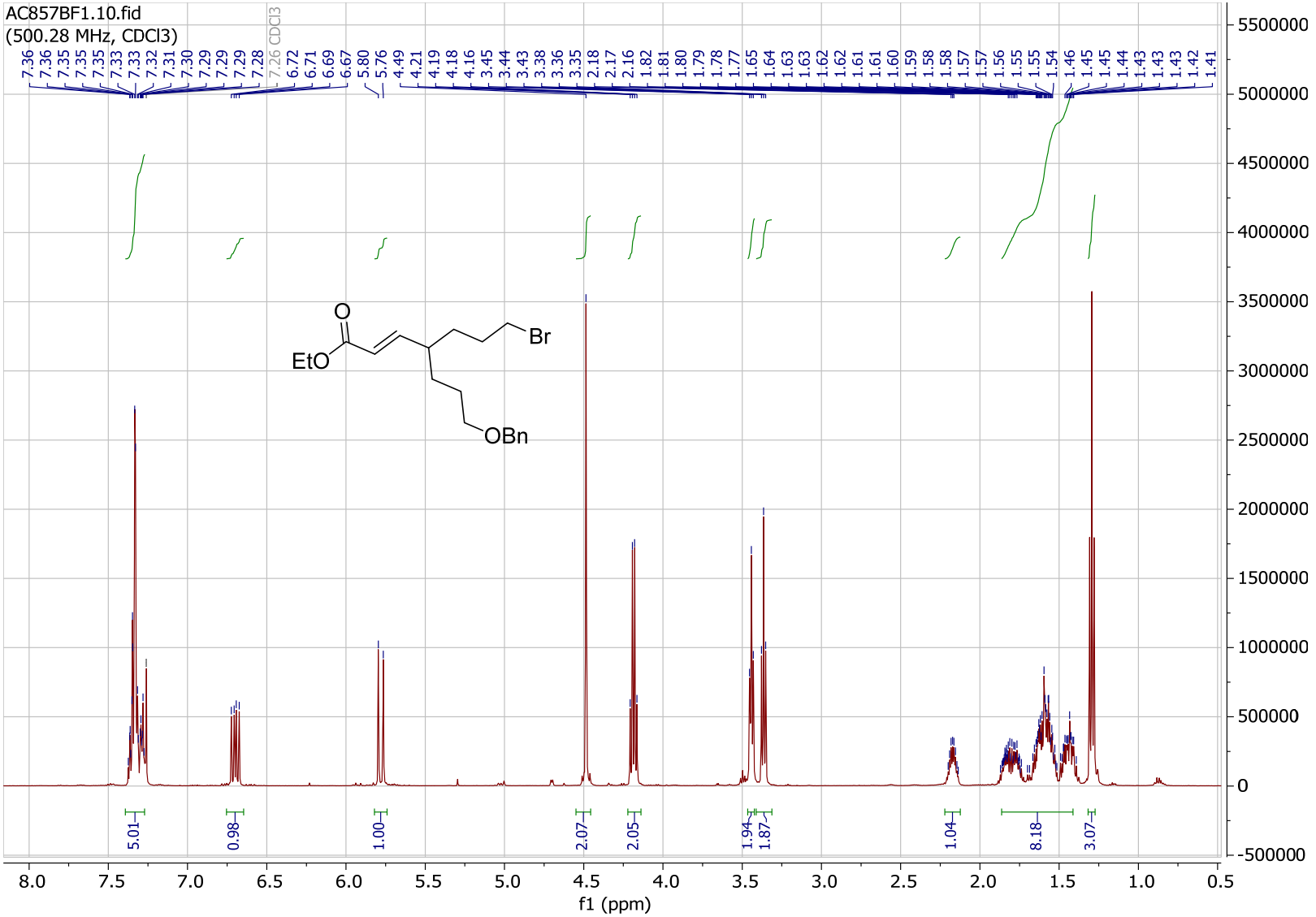

AC873AF1.11.fid
(125.81 MHz, CDCl3)
203.98
137.08
132.92
128.69
128.67
127.55
126.26
126.22
126.07
77.16 CDCl3
51.02
33.32
32.42
30.12
26.93
OHC
Br
Ph
f1 (ppm)

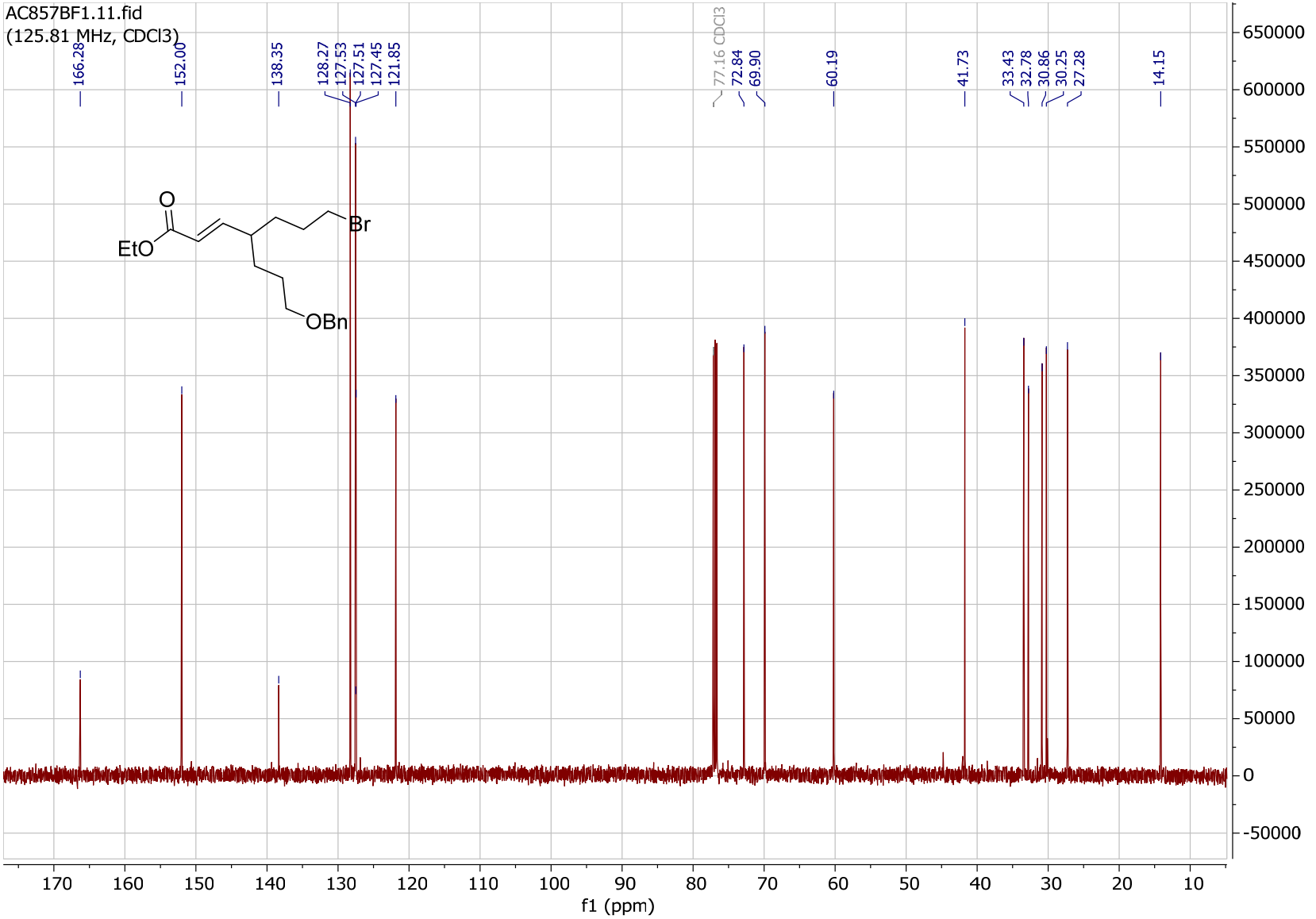
Ethyl (*E*)-4-benzyl-7-bromohept-2-enoate 3ba



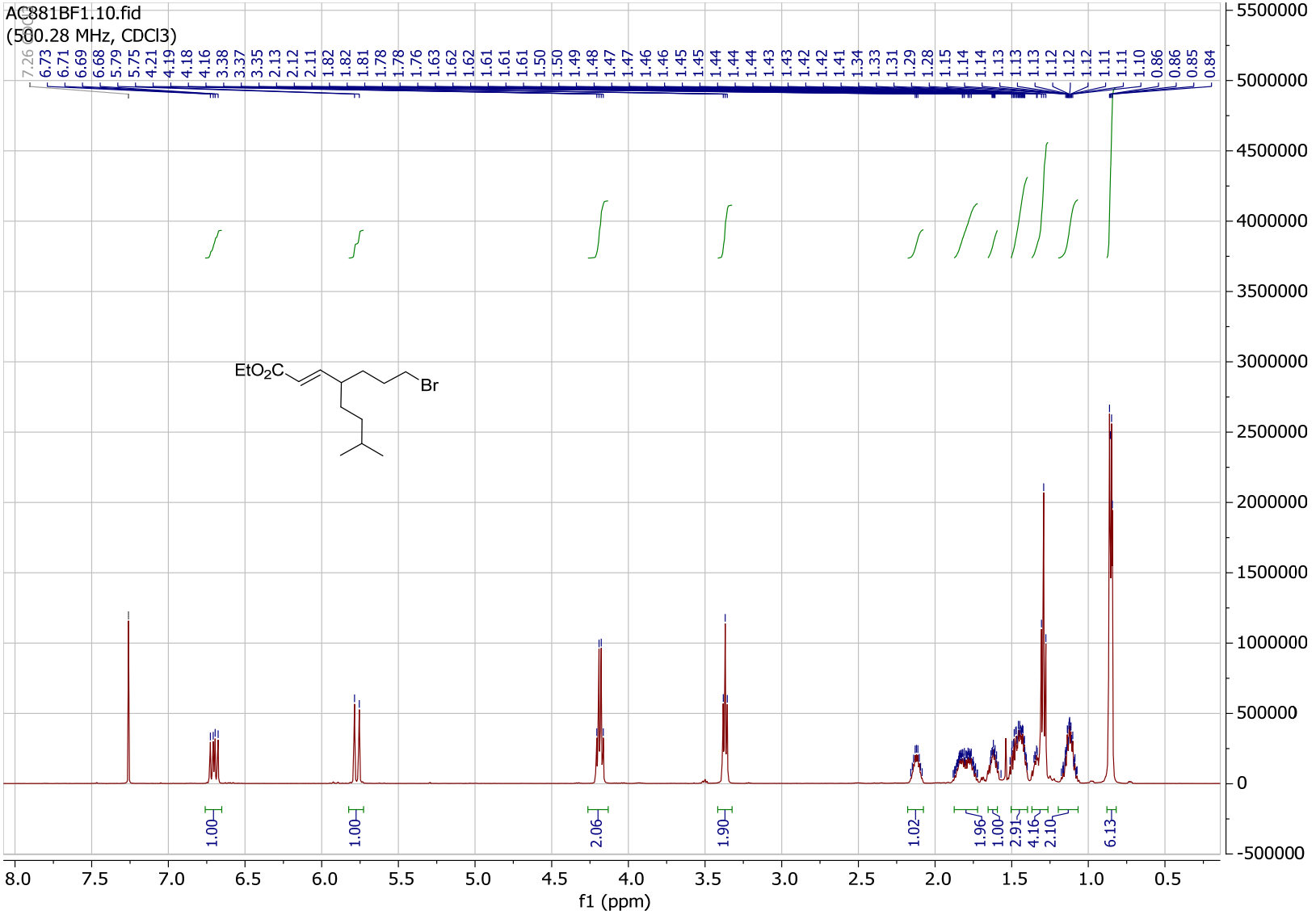

AC838BF1.11.fid
(125.81 MHz, CDCl3)
166.46
151.51
139.18
129.27
129.25
128.51
126.43
122.12
77.16 CDCl3
60.44
43.88
41.19
33.49
32.30
30.57
14.37
EtO2C
Br
Ph
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

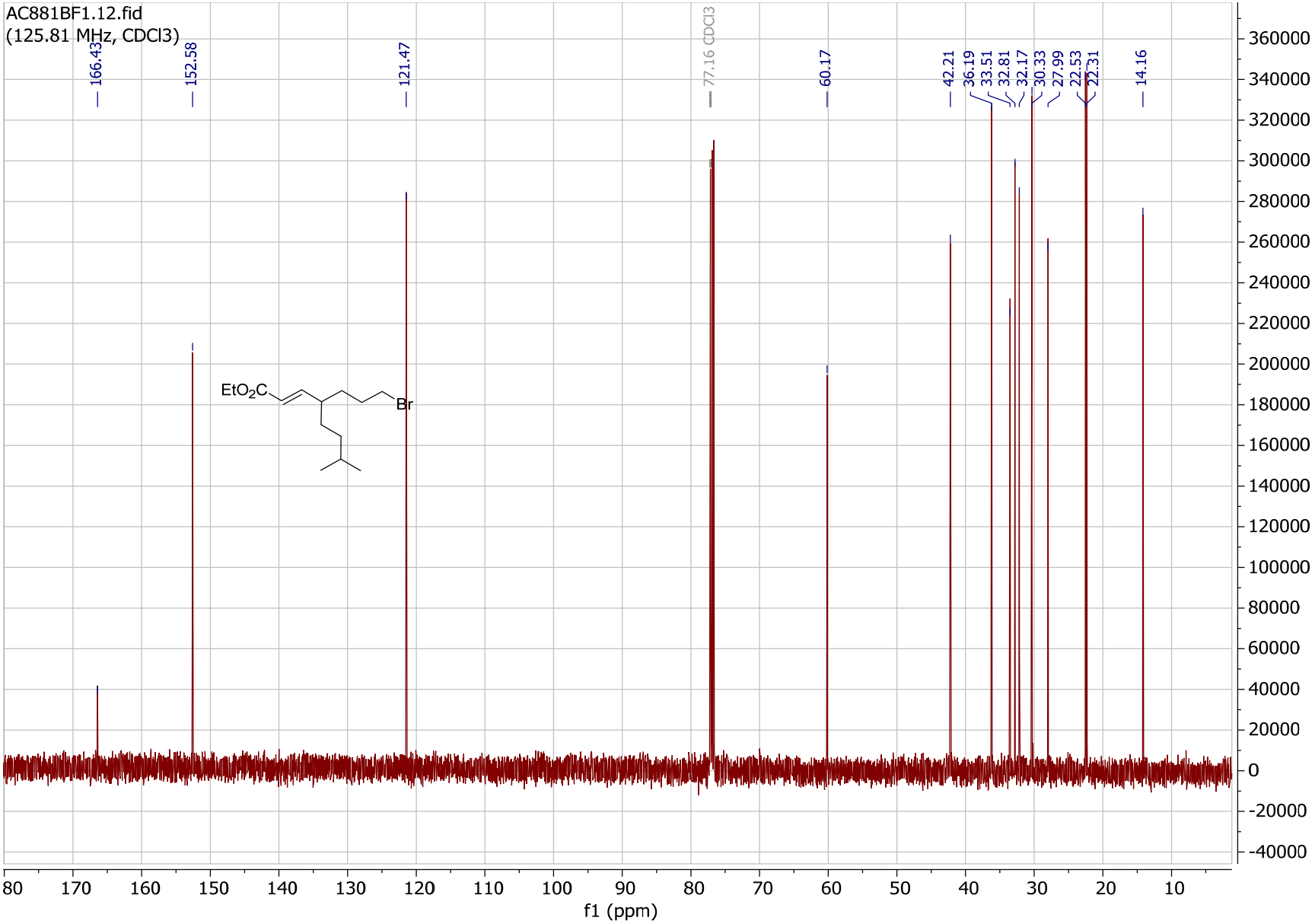
Ethyl (*E*)-7-(benzyloxy)-4-(3-bromopropyl)hept-2-enoate 3bb



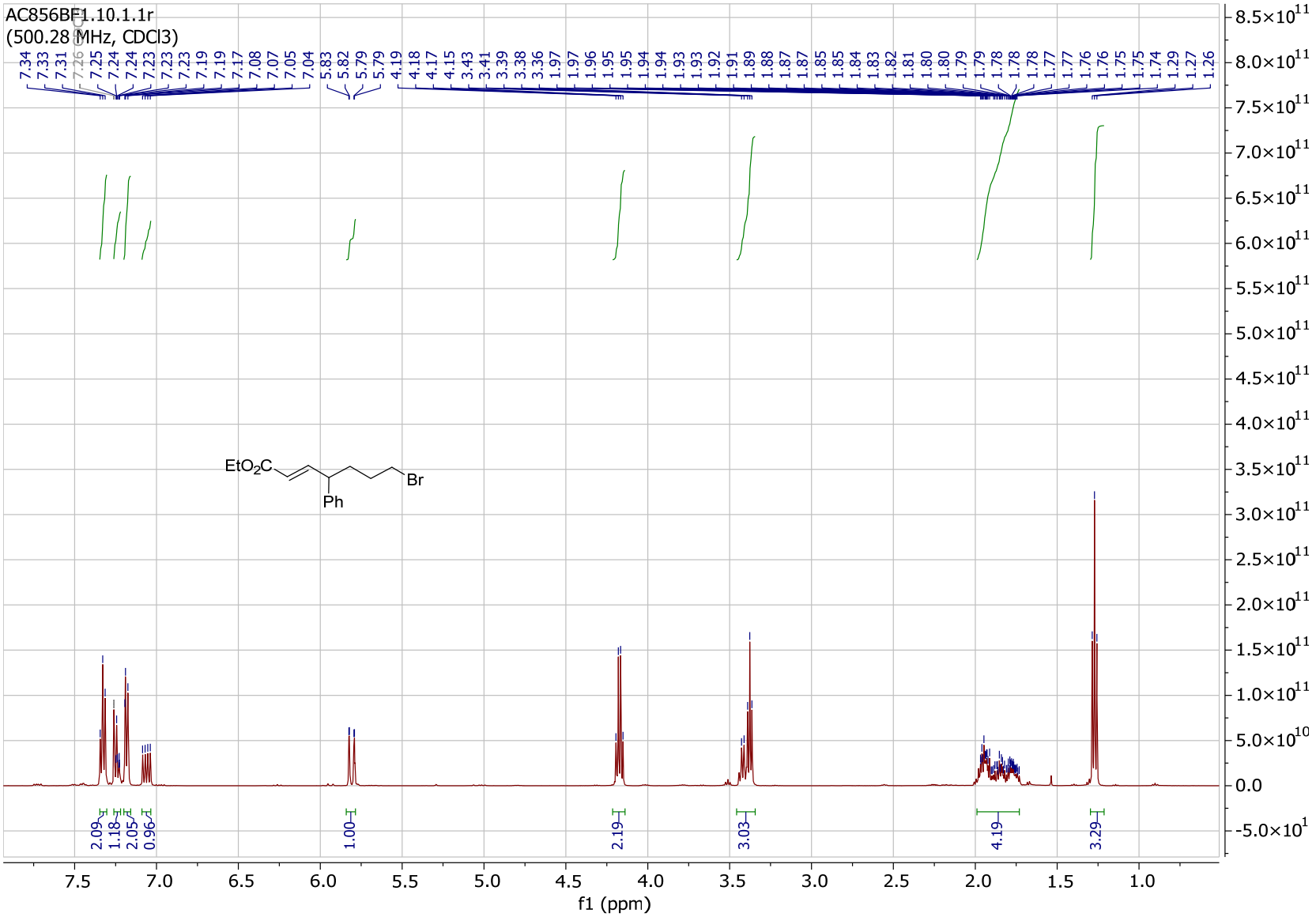

AC857BF1.11.fid
(125.81 MHz, CDCl3)
166.28
152.00
138.35
128.27
127.53
127.51
127.45
121.85
77.16 CDCl3
72.84
69.90
60.19
41.73
33.43
32.78
30.86
30.25
27.28
14.15
O
EtO
Br
OBn
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

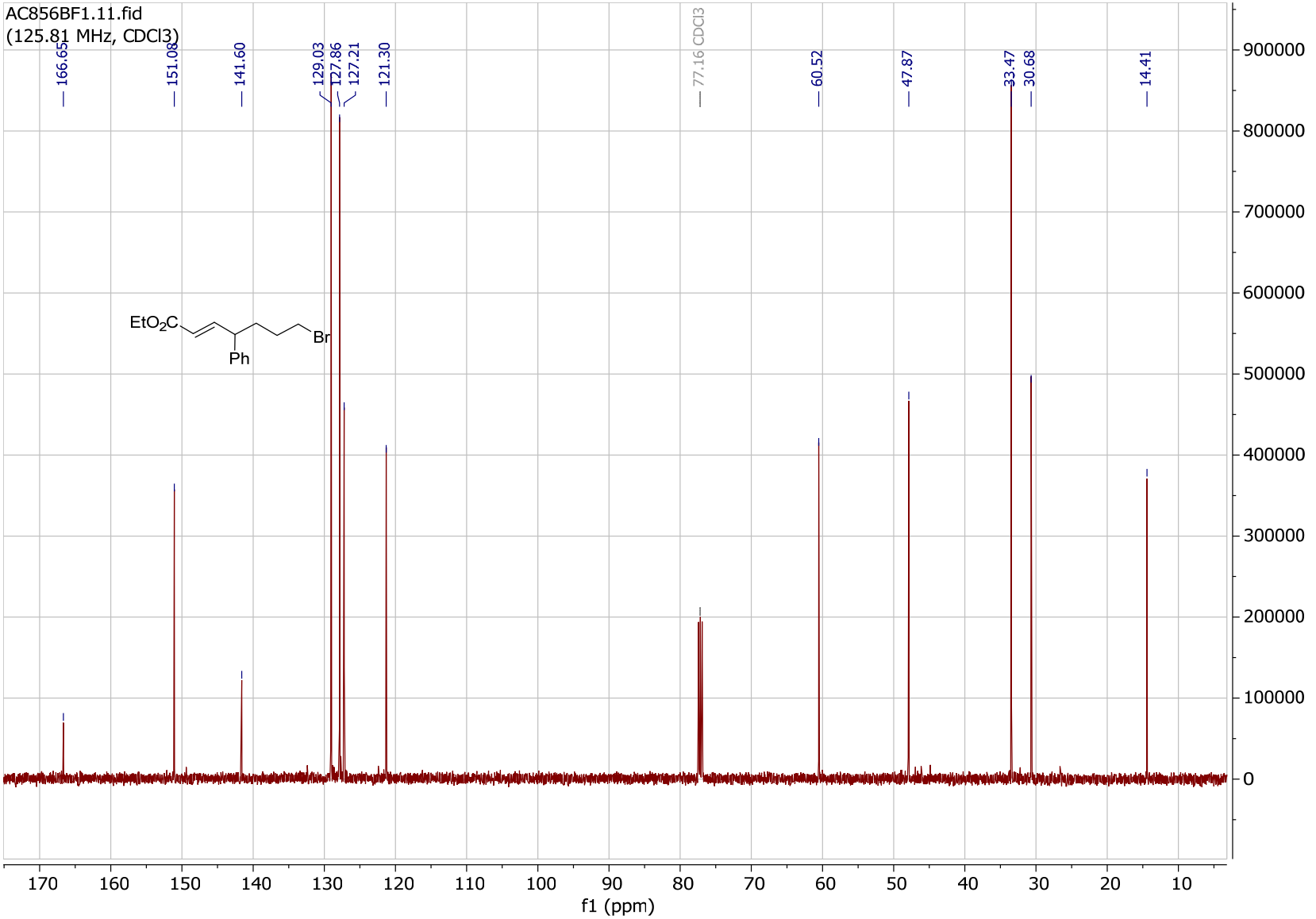
Ethyl (*E*)-4-(3-bromopropyl)-7-methyloct-2-enoate 3bc



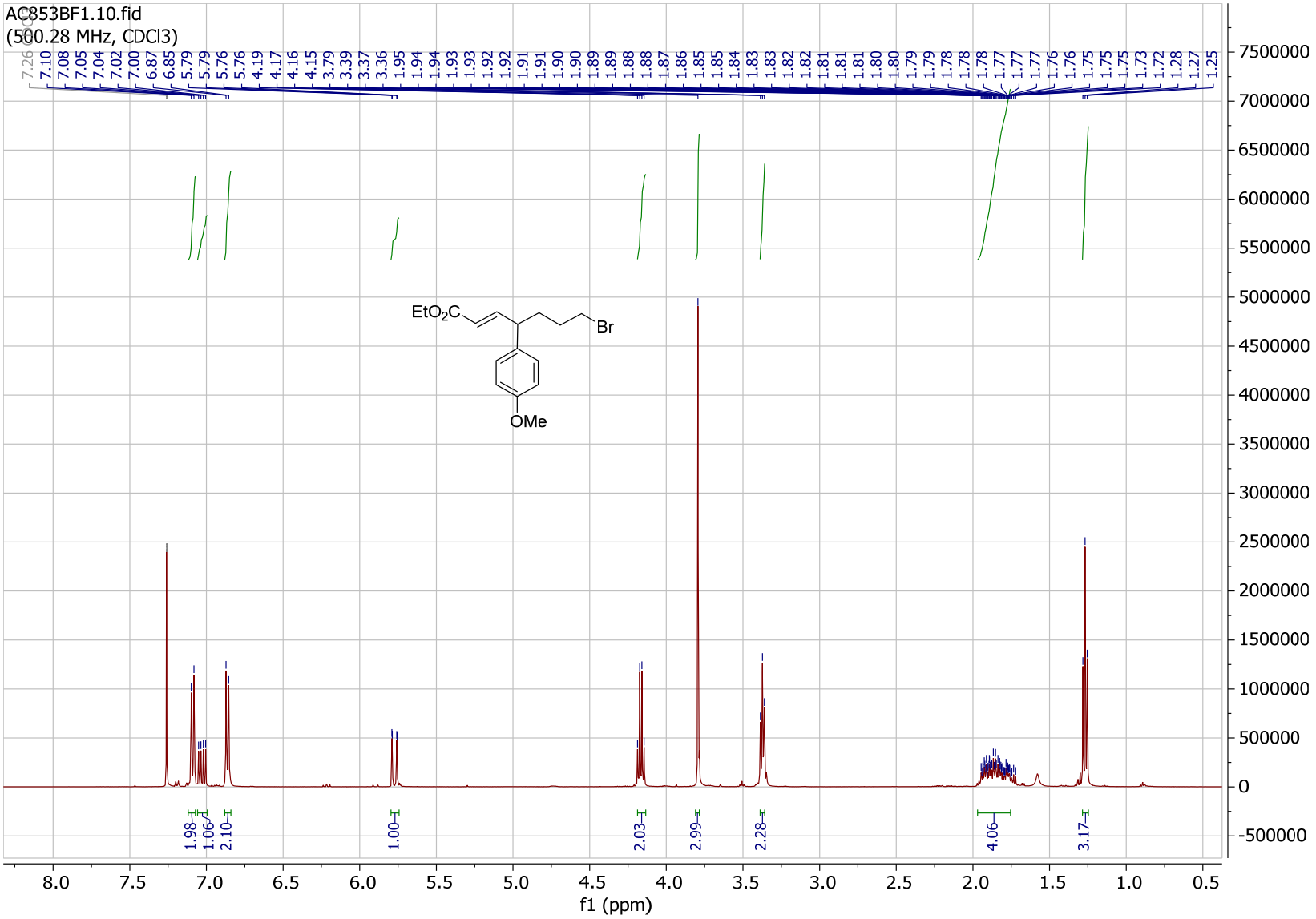

AC881BF1.12.fid
(125.81 MHz, CDCl3)
166.43
152.58
121.47
77.16 CDCl3
60.17
42.21
36.19
33.51
32.81
32.17
30.33
27.99
22.53
22.31
14.16
EtO2C
Br
f1 (ppm)

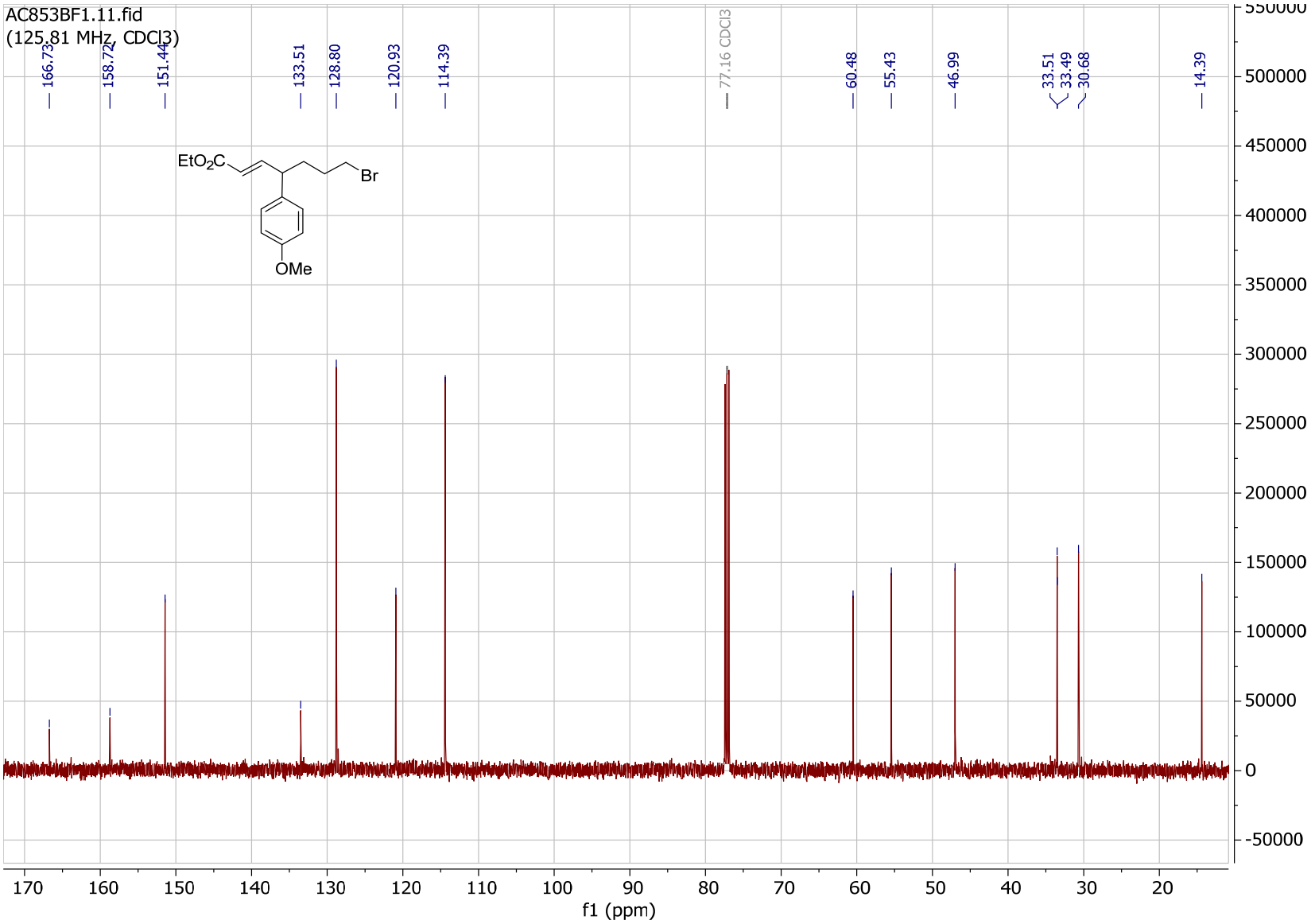
Ethyl (*E*)-7-bromo-4-phenylhept-2-enoate 3bd



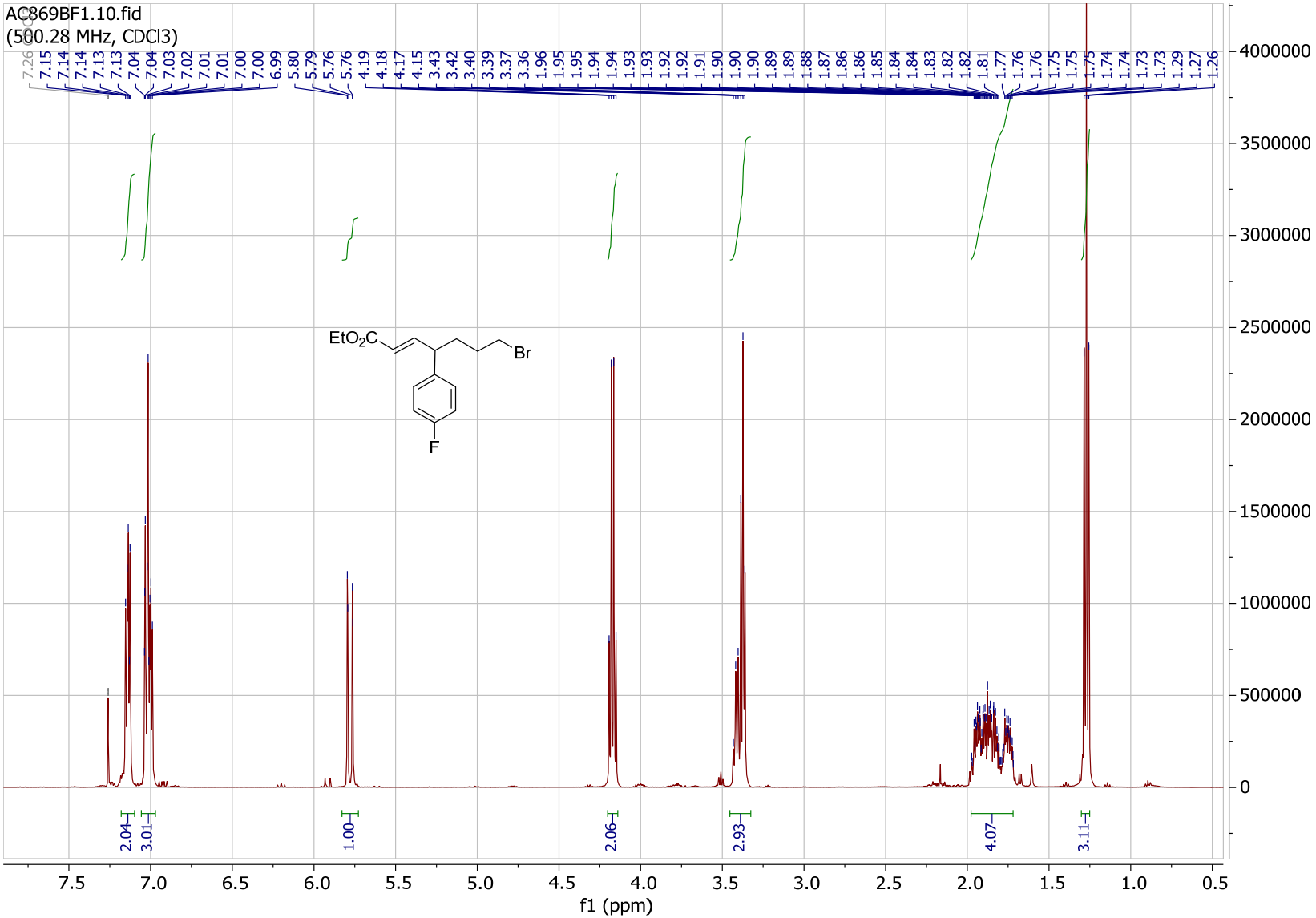

AC856BF1.11.fid
(125.81 MHz, CDCl3)
166.65
151.08
141.60
129.03
127.86
127.21
121.30
77.16 CDCl3
60.52
47.87
33.47
30.68
14.41
EtO2C
Br
Ph
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

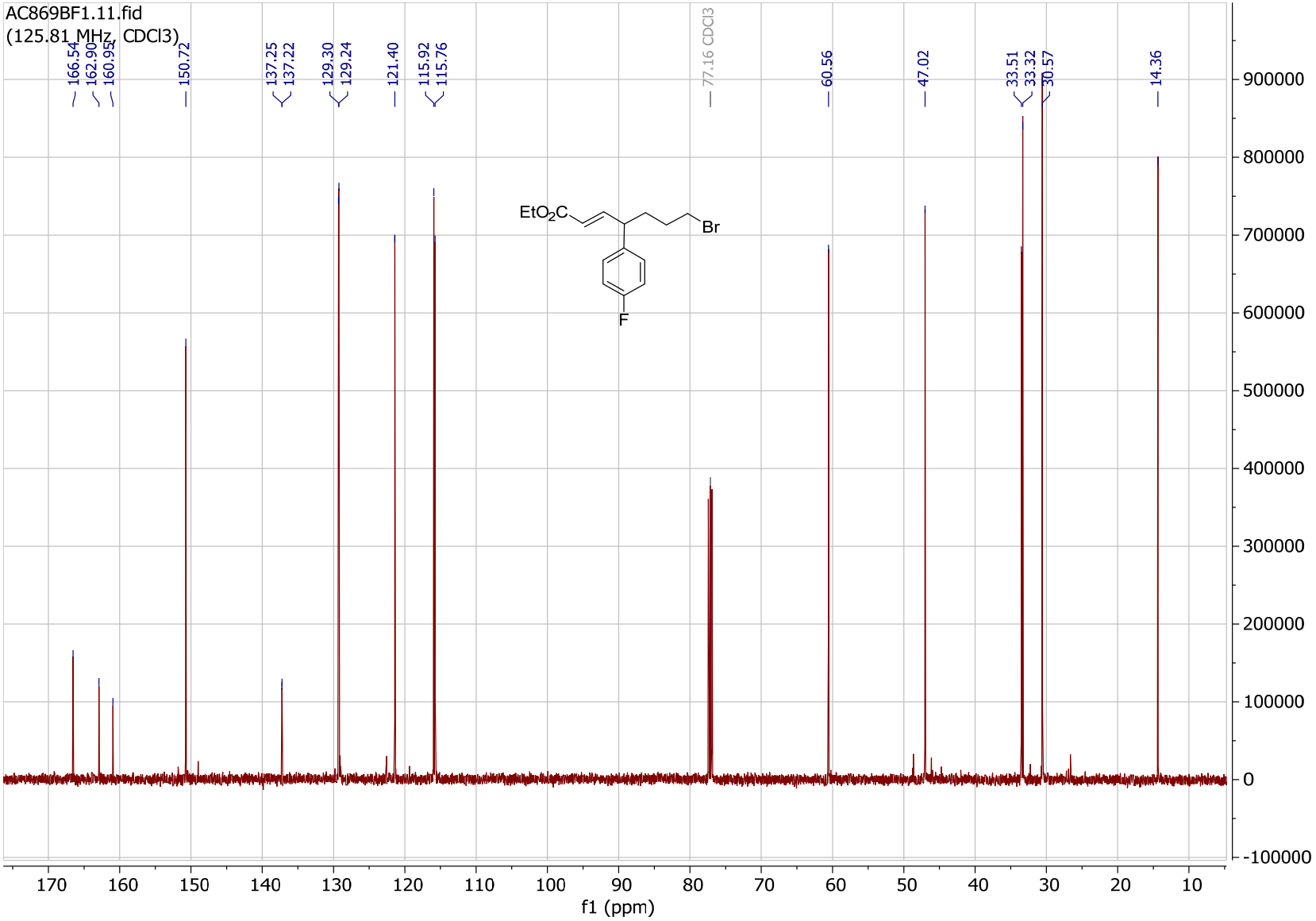
Ethyl (*E*)-7-bromo-4-(4-methoxyphenyl)hept-2-enoate 3be

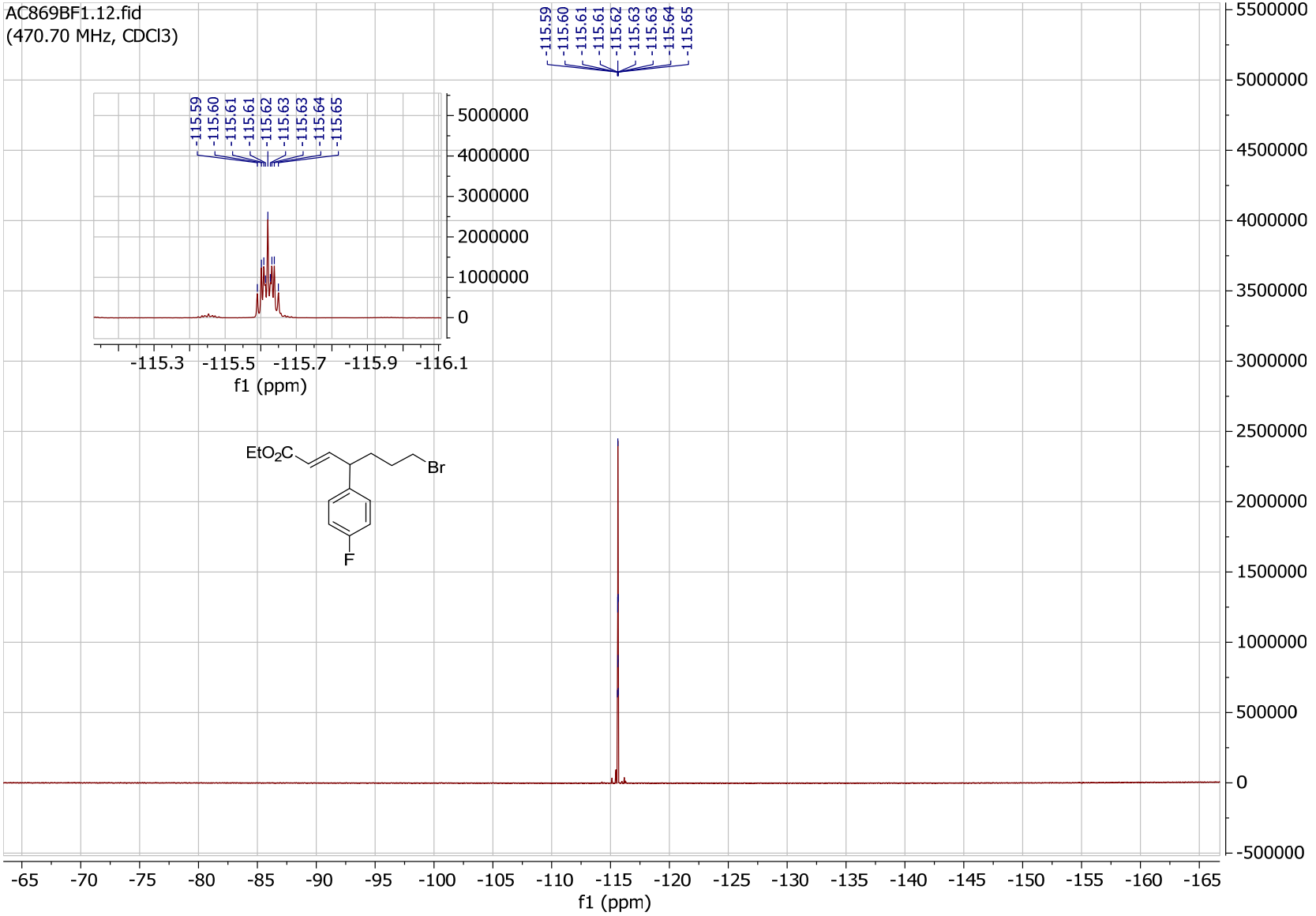



AC853BF1.11.fid
(125.81 MHz, CDCl3)
166.73
158.72
151.44
133.51
128.80
120.93
114.39
77.16 CDCl3
60.48
55.43
46.99
33.51
33.49
30.68
14.39
EtO2C
Br
OMe
f1 (ppm)

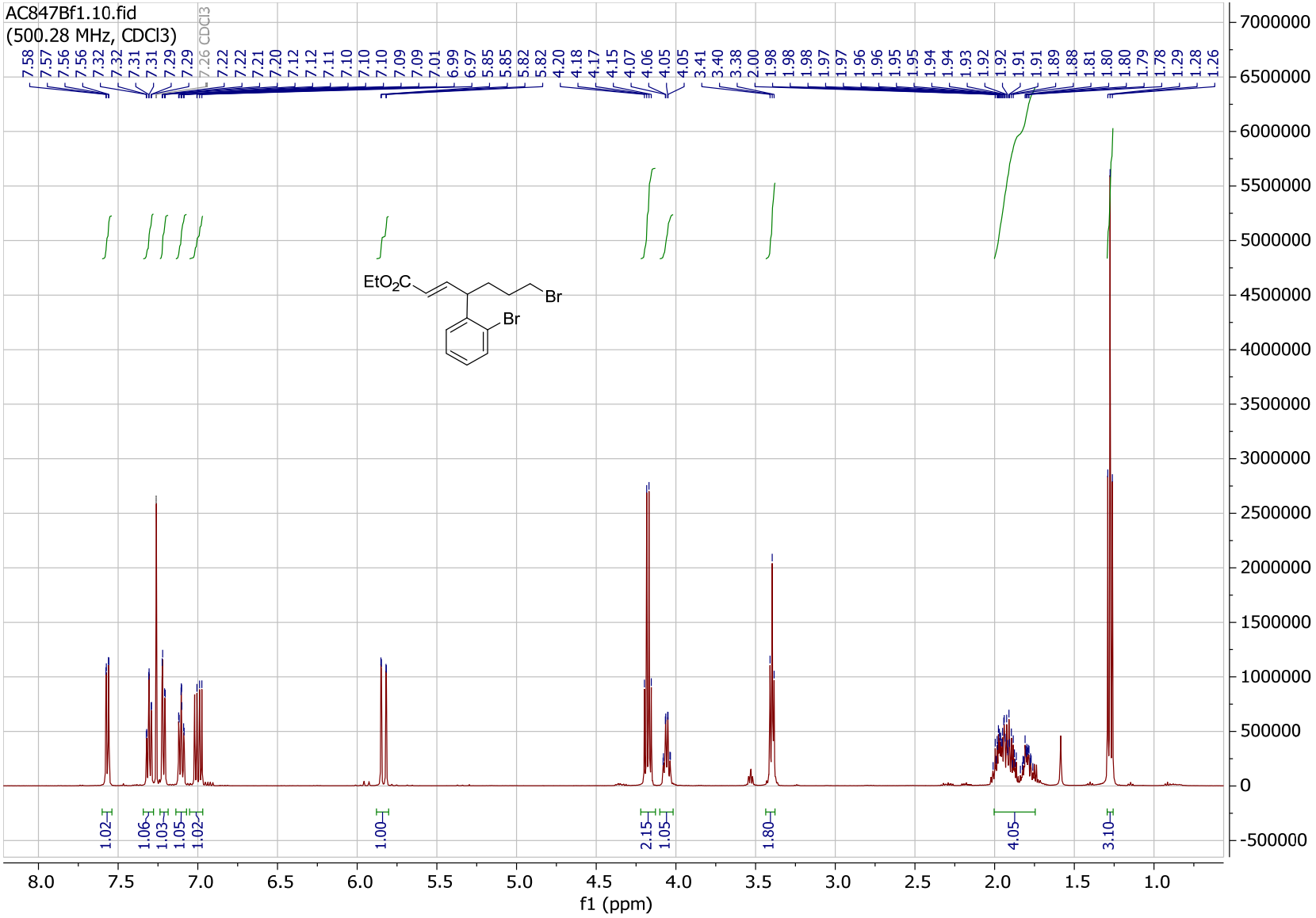
Ethyl (E)-7-bromo-4-(4-fluorophenyl)hept-2-enoate 3bf

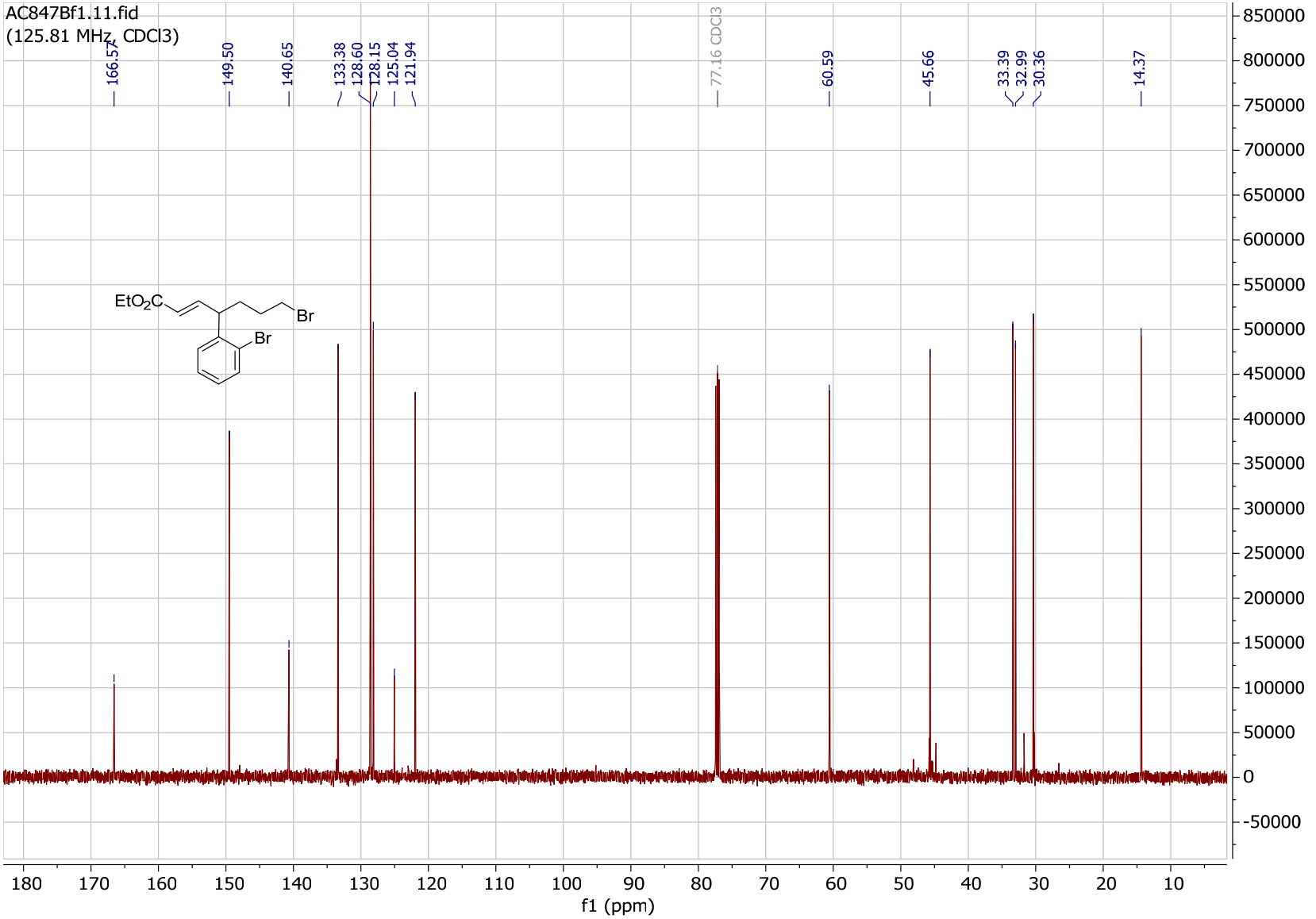



AC869BF1.11.fid
(125.81 MHz, CDCl3)
166.54
162.90
160.95
150.72
137.25
137.22
129.30
129.24
121.40
115.92
115.76
77.16 CDCl3
60.56
47.02
33.51
33.32
30.57
14.36
EtO2C
Br
F
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

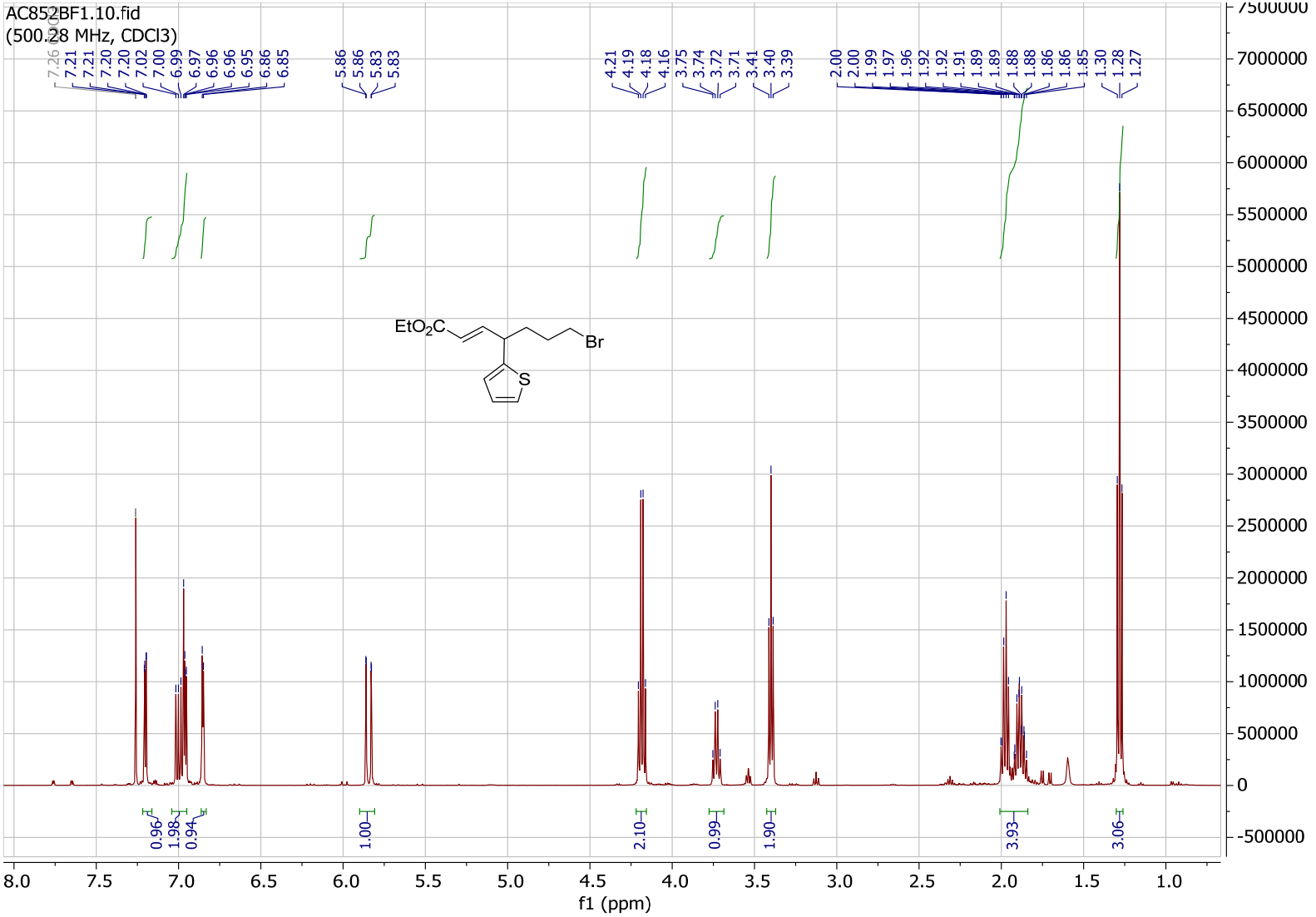

AC869BF1.12.fid
(470.70 MHz, CDCl3)
-115.59
-115.60
-115.61
-115.61
-115.62
-115.63
-115.63
-115.64
-115.65
5000000
4000000
3000000
2000000
1000000
0
-115.3
-115.5
-115.7
-115.9
-116.1
f1 (ppm)
EtO2C
Br
F
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
-65
-70
-75
-80
-85
-90
-95
-100
-105
-110
-115
-120
-125
-130
-135
-140
-145
-150
-155
-160
-165
f1 (ppm)

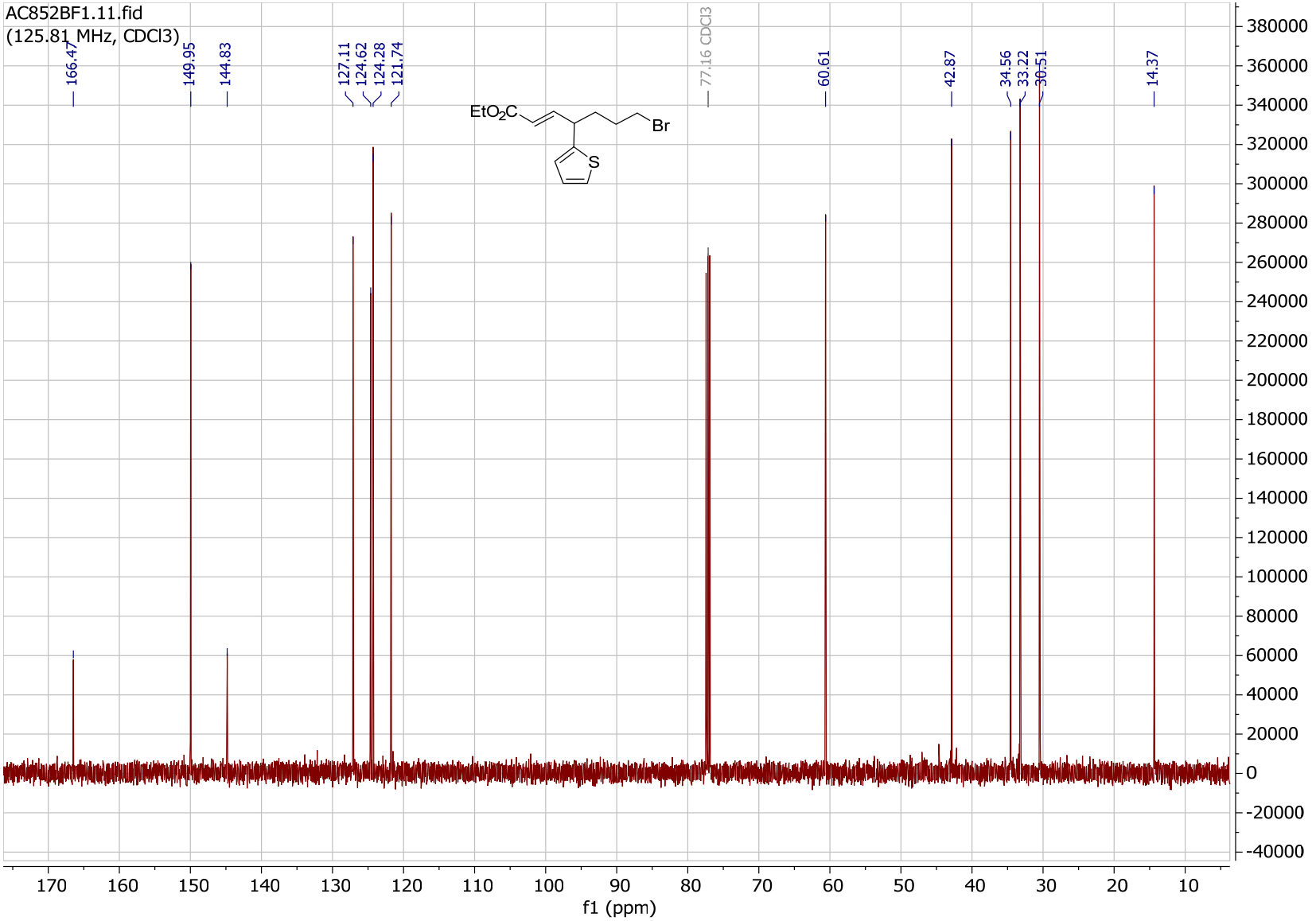
Ethyl (E)-7-bromo-4-(2-bromophenyl)hept-2-enoate 3bg



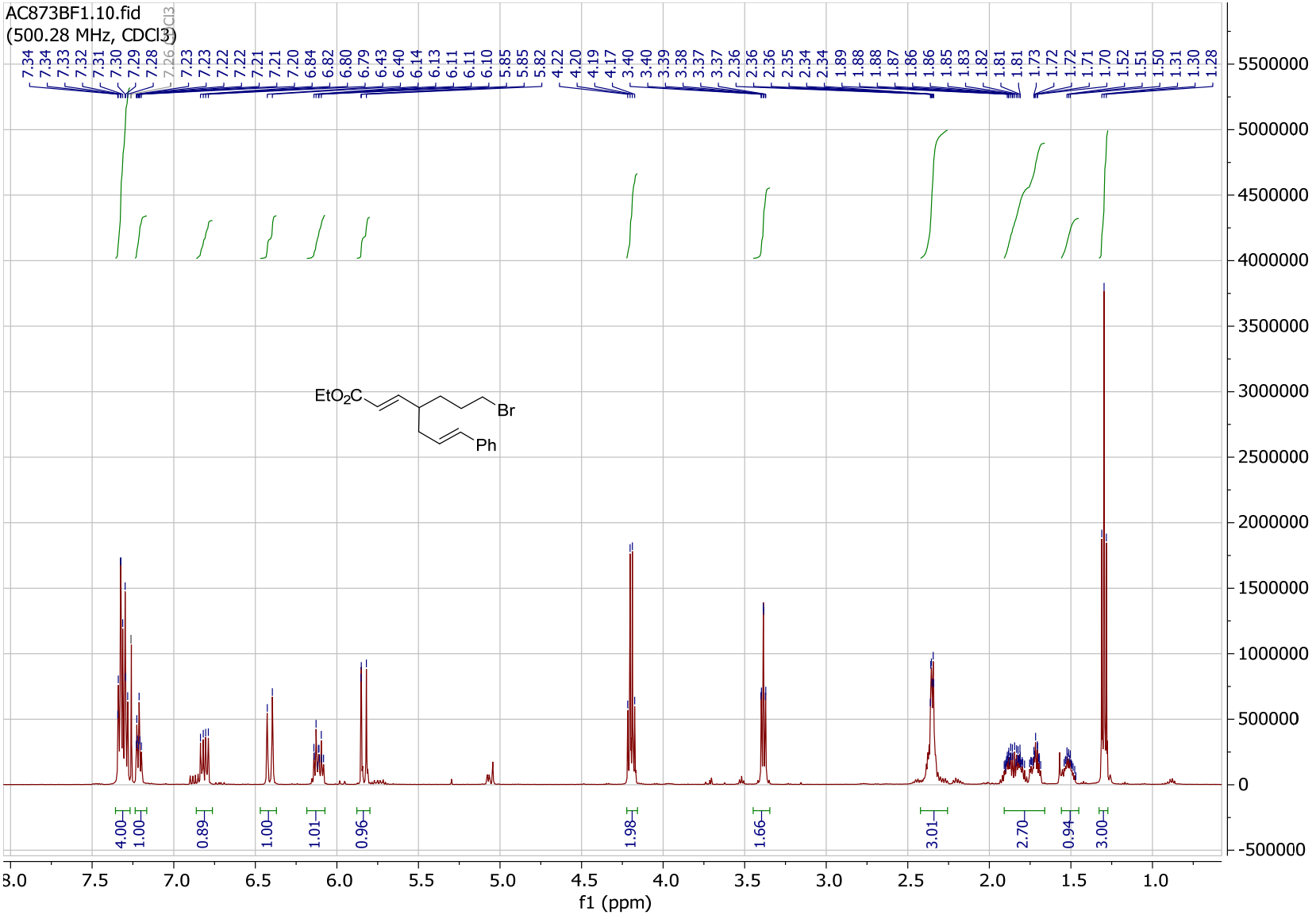

AC847Bf1.11.fid
(125.81 MHz, CDCl3)
166.57
149.50
140.65
133.38
128.60
128.15
125.04
121.94
77.16 CDCl3
60.59
45.66
33.39
32.99
30.36
14.37
EtO2C
Br
Br
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

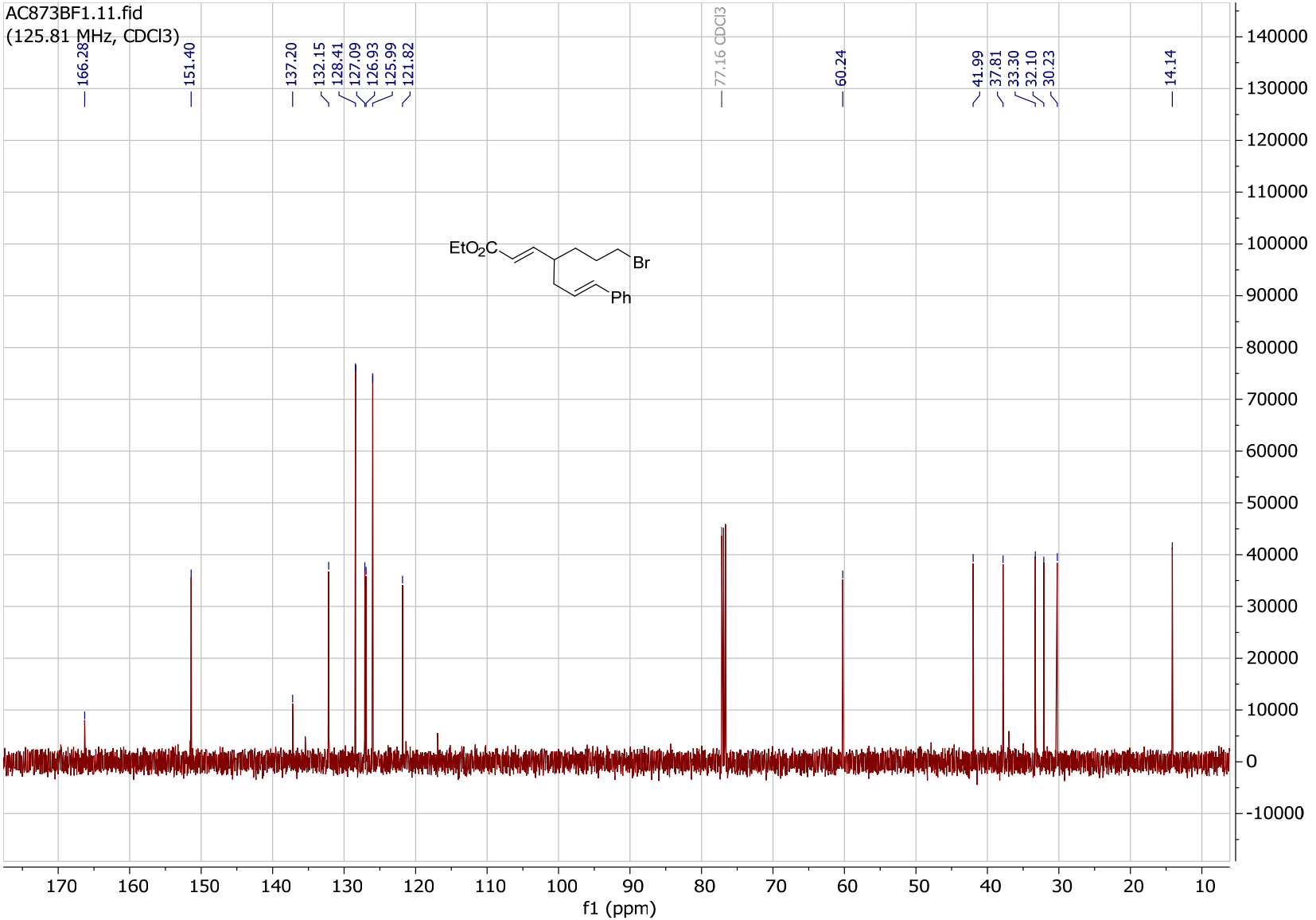
Ethyl (*E*)-7-bromo-4-(thiophen-2-yl)hept-2-enoate 3bh



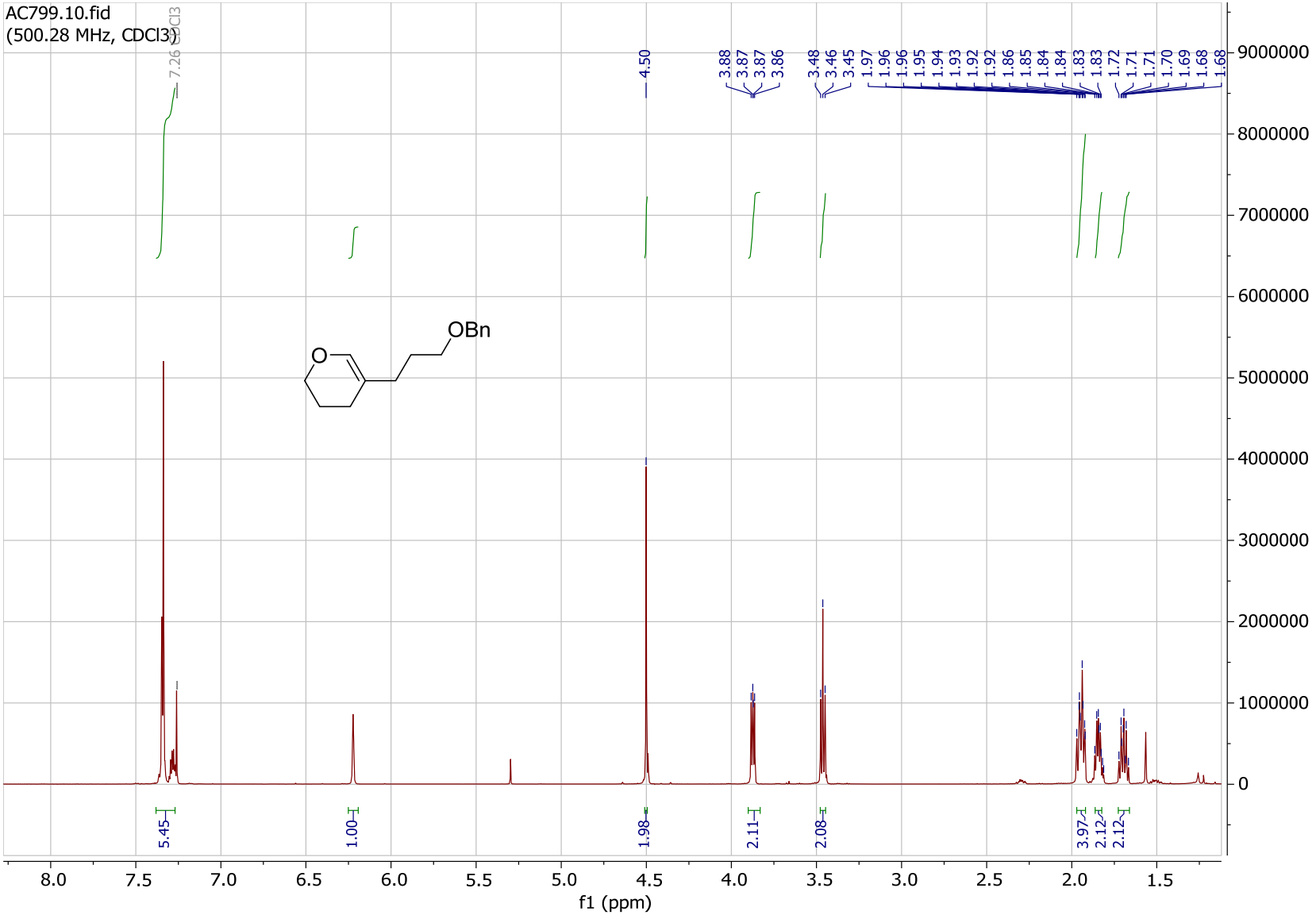

AC852BF1.11.fid
(125.81 MHz, CDCl3)
166.47
149.95
144.83
127.11
124.62
124.28
121.74
77.16 CDCl3
60.61
42.87
34.56
33.22
30.51
14.37
EtO2C
Br
S
380000
360000
340000
320000
300000
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
-40000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

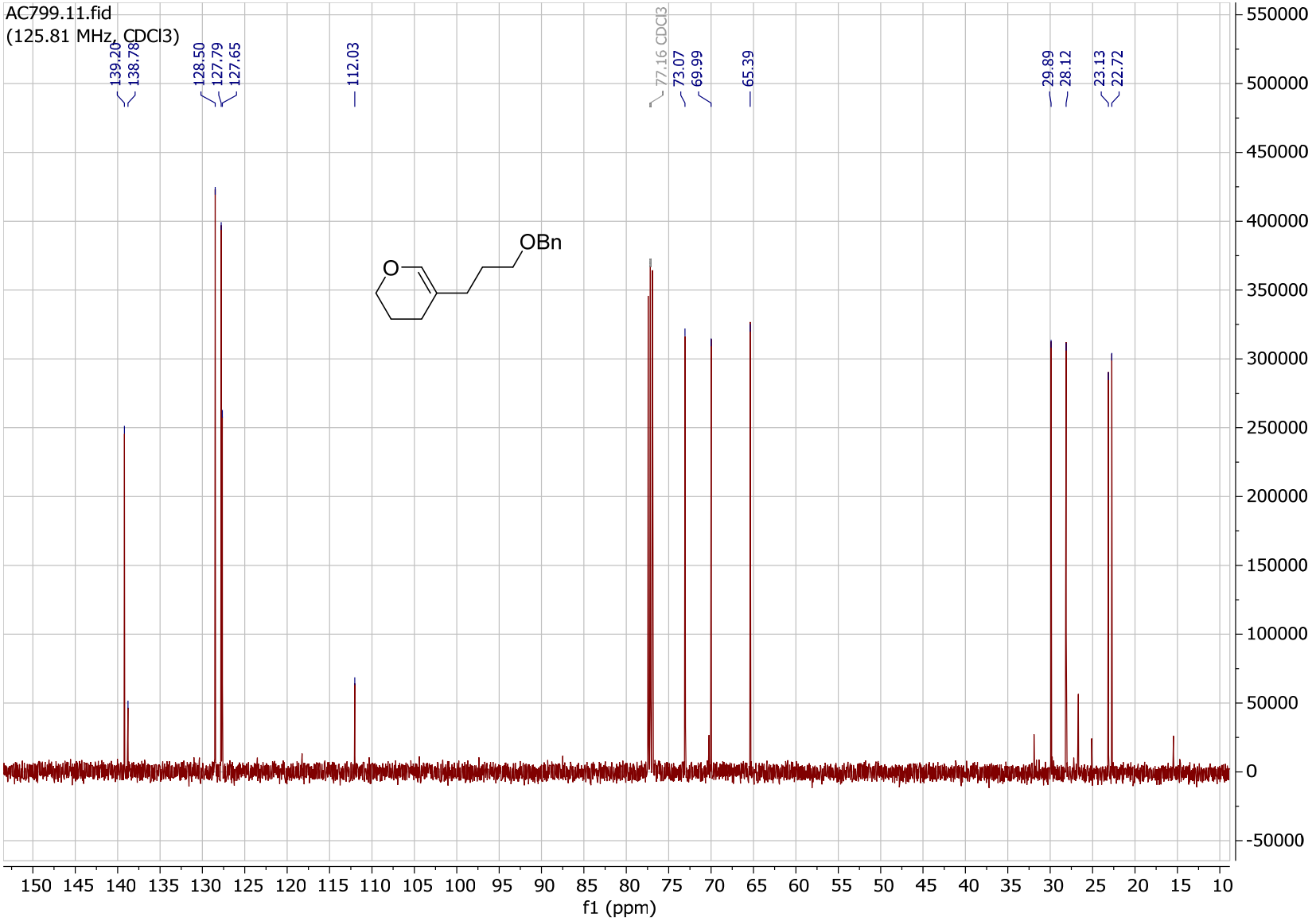
Ethyl (2*E*,6*E*)-4-(3-bromopropyl)-7-phenylhepta-2,6-dienoate 3bi



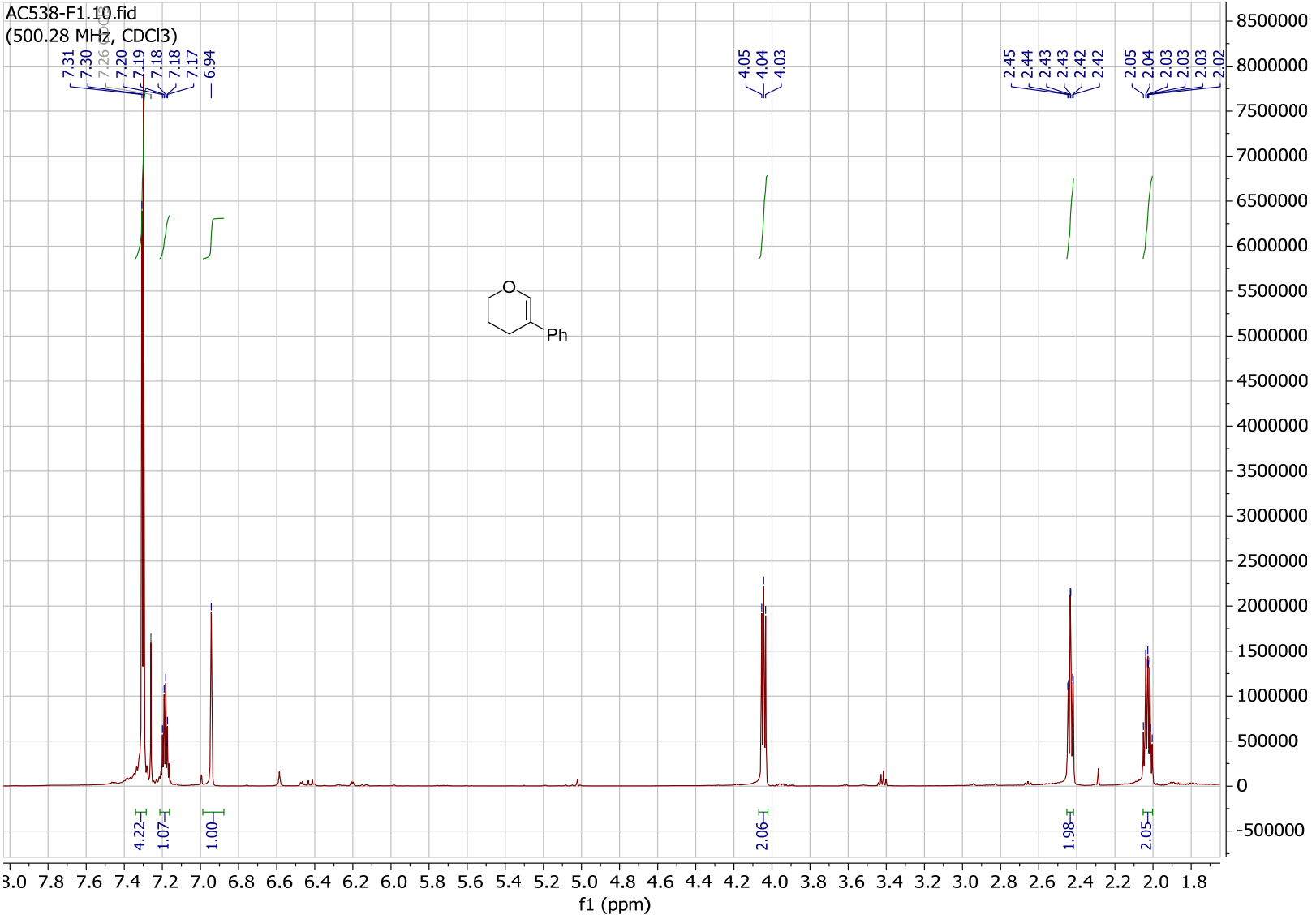

AC873BF1.11.fid
(125.81 MHz, CDCl3)
166.28
151.40
137.20
132.15
128.41
127.09
126.93
125.99
121.82
77.16 CDCl3
60.24
41.99
37.81
33.30
32.10
30.23
14.14
EtO2C
Br
Ph
f1 (ppm)

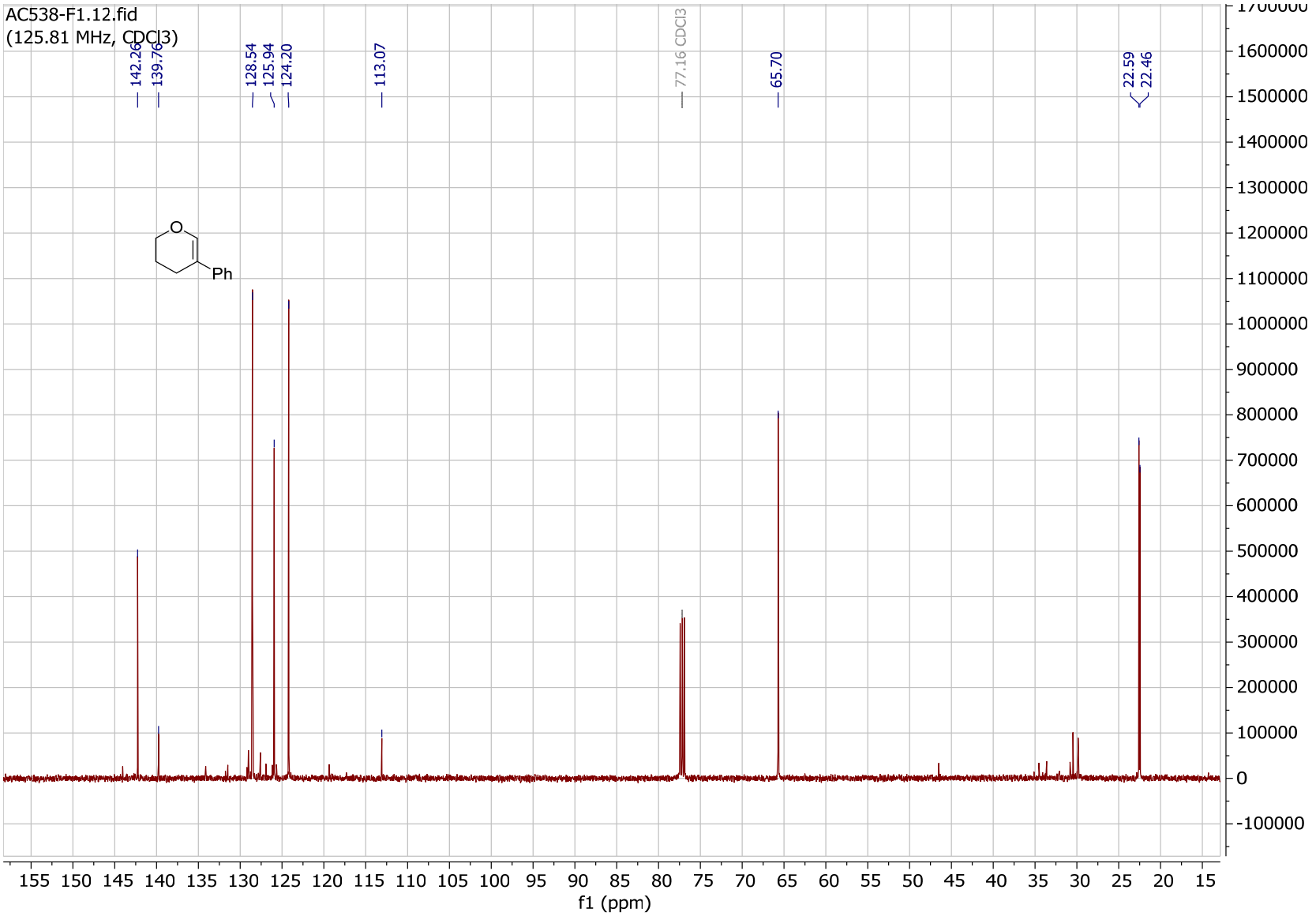
5-(3-(benzyloxy)propyl)-3,4-dihydro-2H-pyran 4b



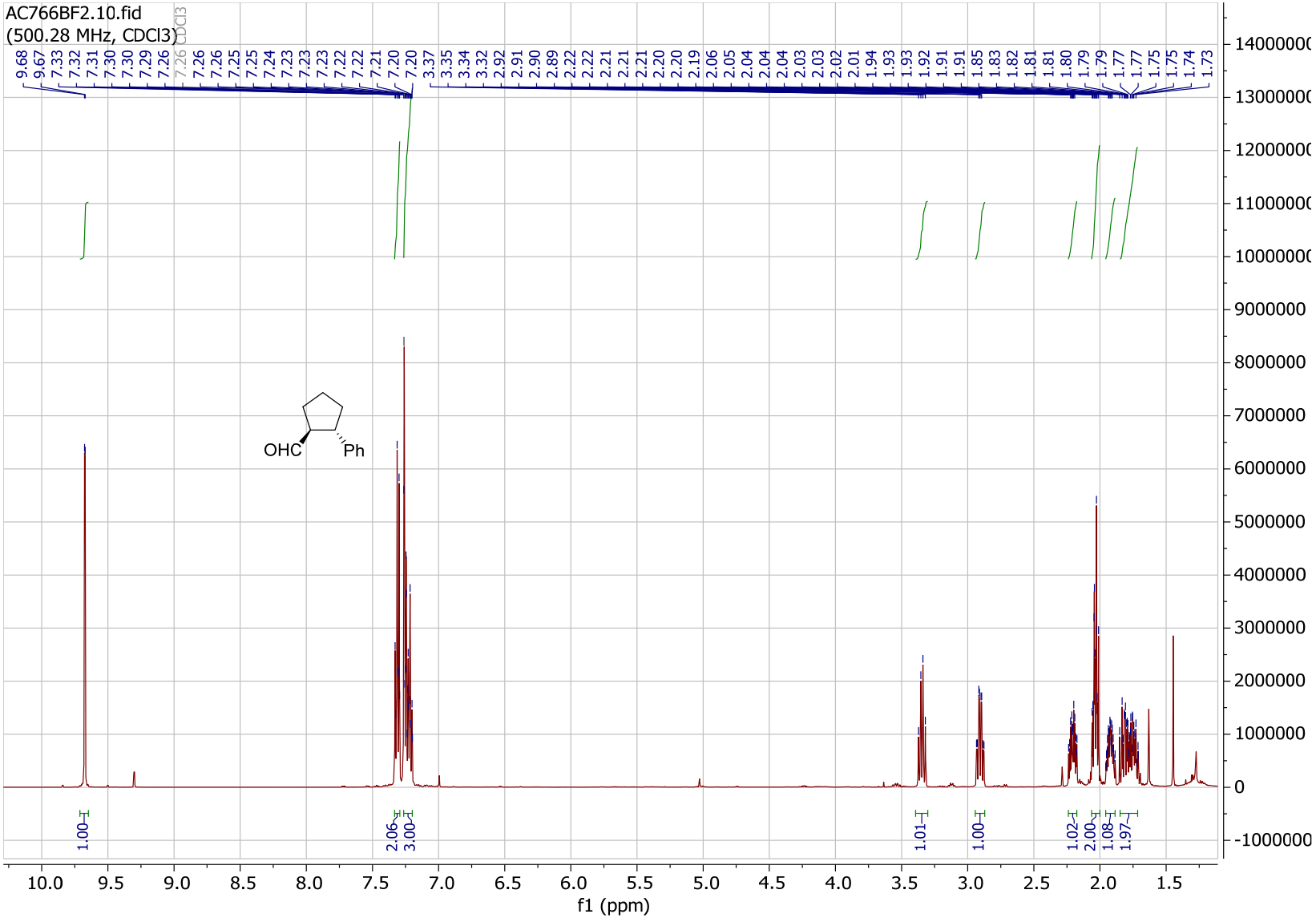

AC799.11.fid
(125.81 MHz, CDCl3)
139.20
138.78
128.50
127.79
127.65
112.03
77.16 CDCl3
73.07
69.99
65.39
29.89
28.12
23.13
22.72
OBn
O
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)

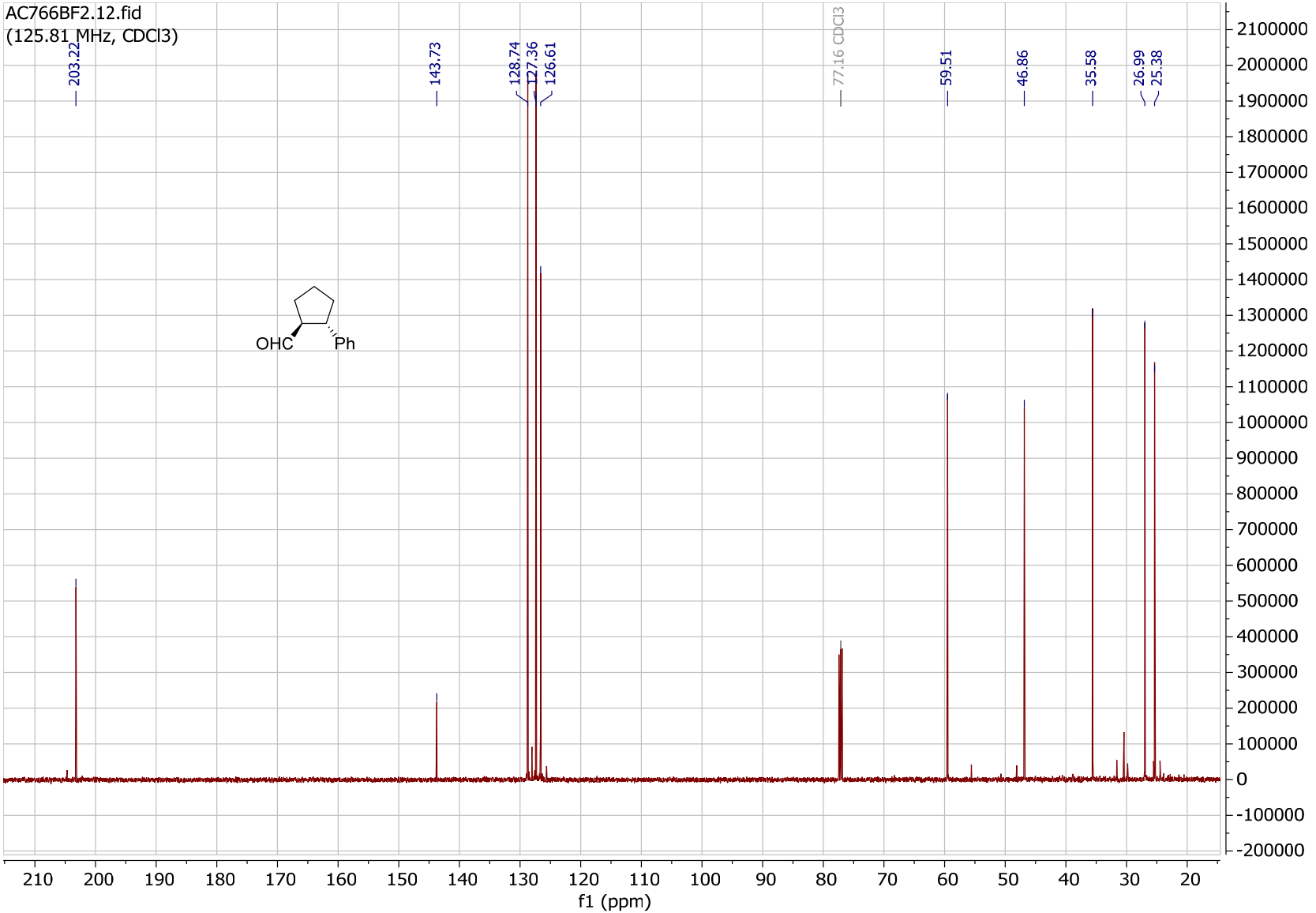
5-phenyl-3,4-dihydro-2H-pyran 4d



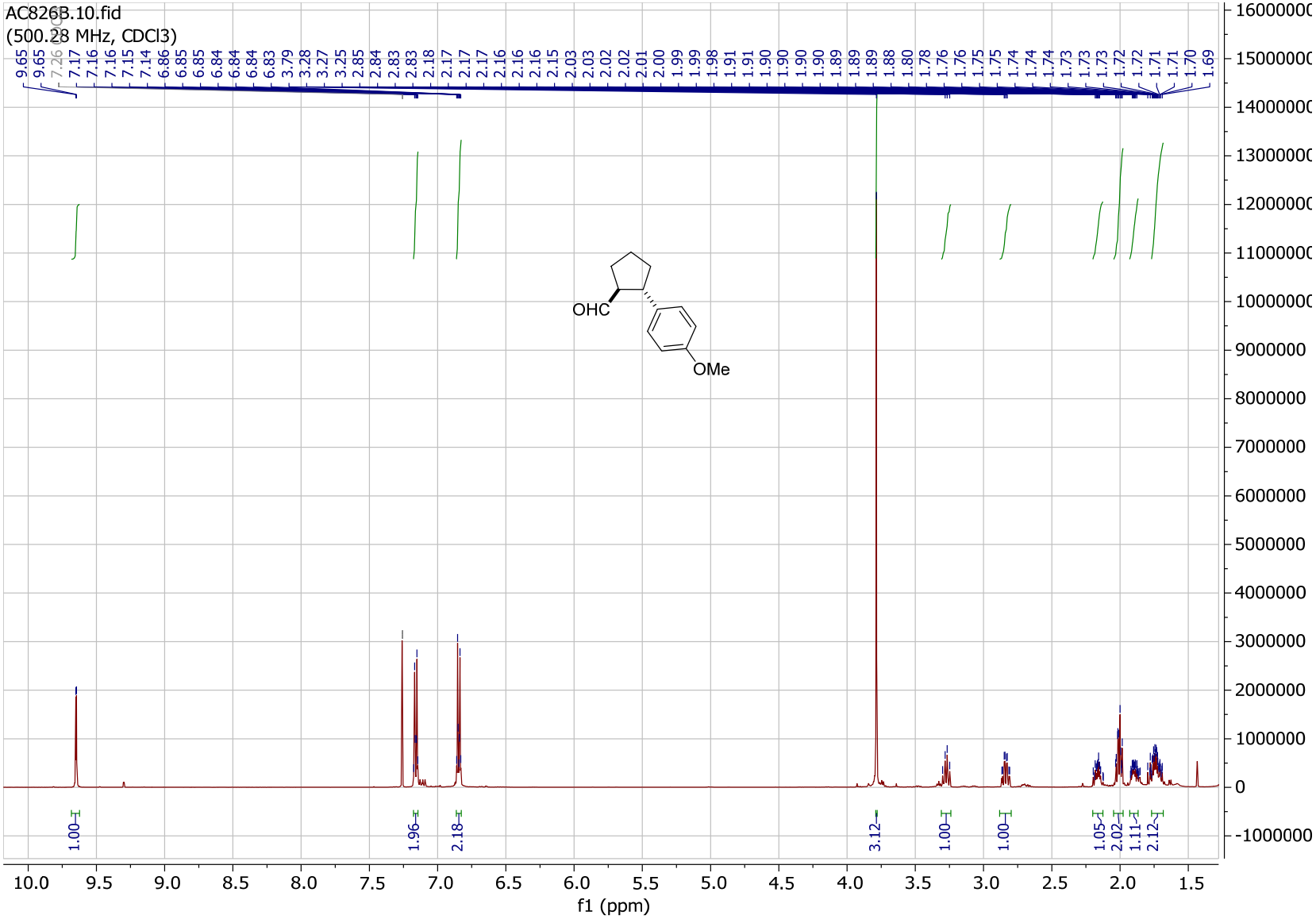

AC538-F1.12.fid
(125.81 MHz, CDCl3)
142.26
139.76
128.54
125.94
124.20
113.07
77.16 CDCl3
65.70
22.59
22.46
O
Ph
f1 (ppm)

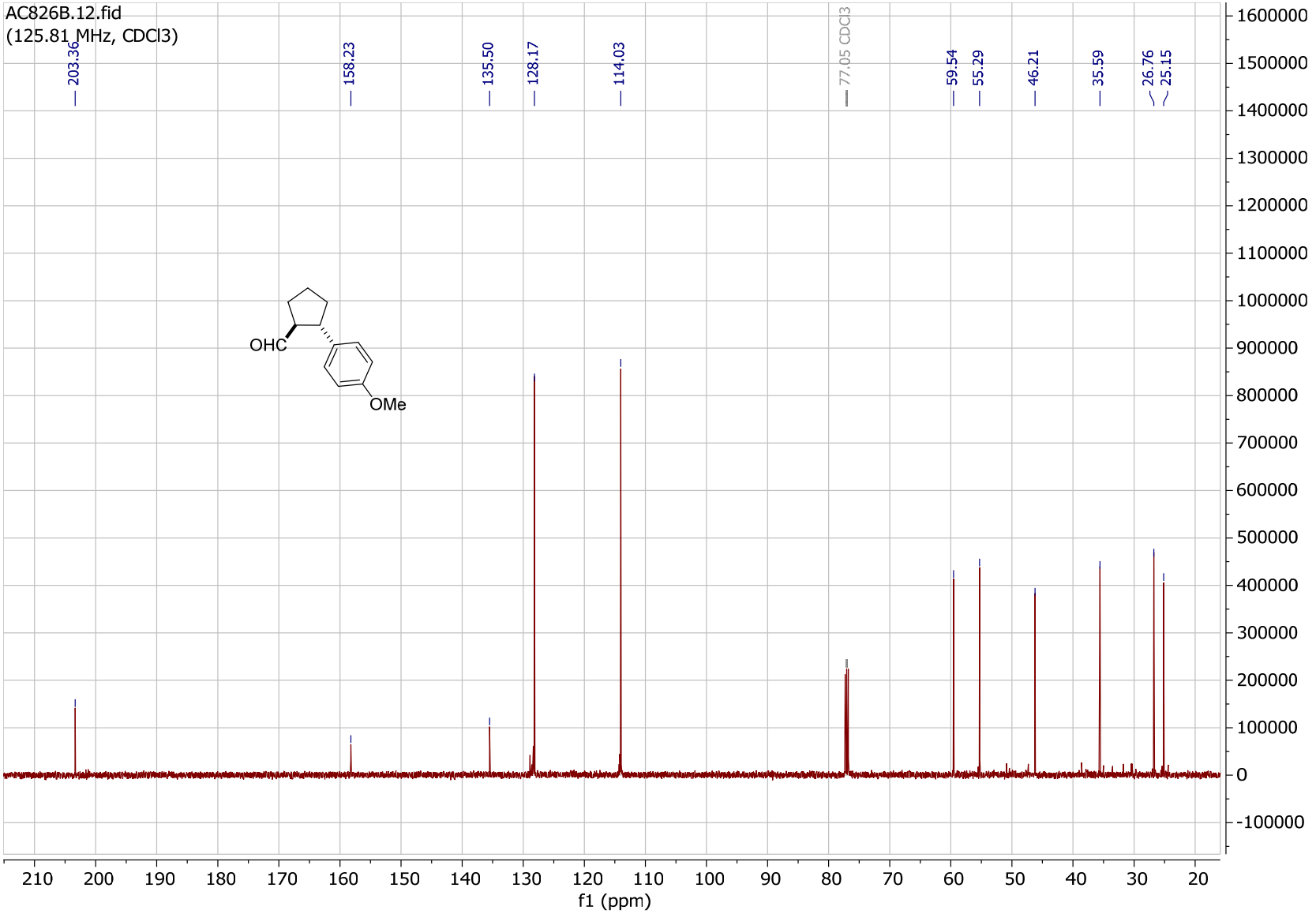
(1*S*,2*S*)-2-Phenylcyclopentane-1-carbaldehyde 5a



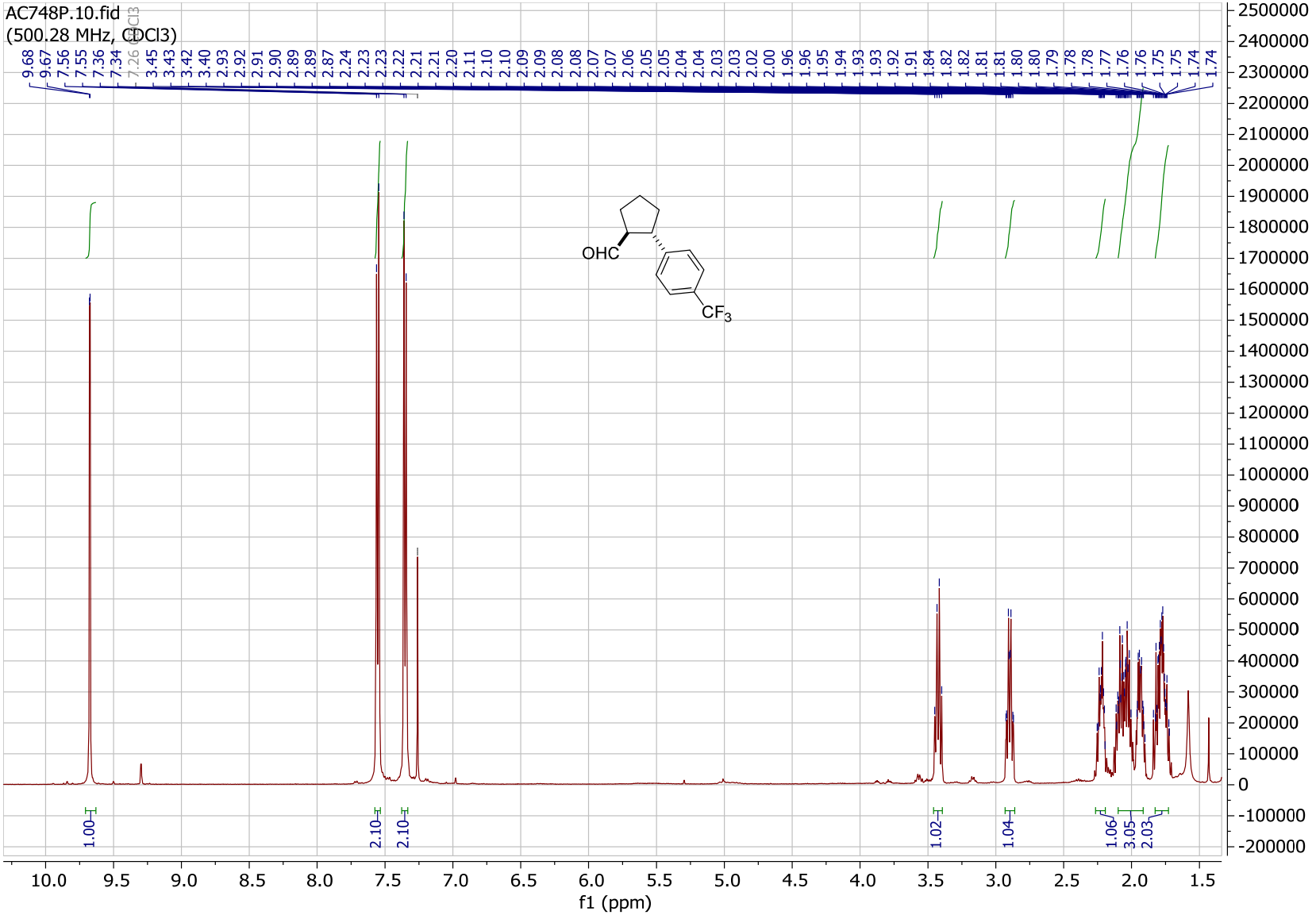

AC766BF2.12.fid
(125.81 MHz, CDCl3)
203.22
143.73
128.74
127.36
126.61
77.16 CDCl3
59.51
46.86
35.58
26.99
25.38
OHC
Ph
f1 (ppm)

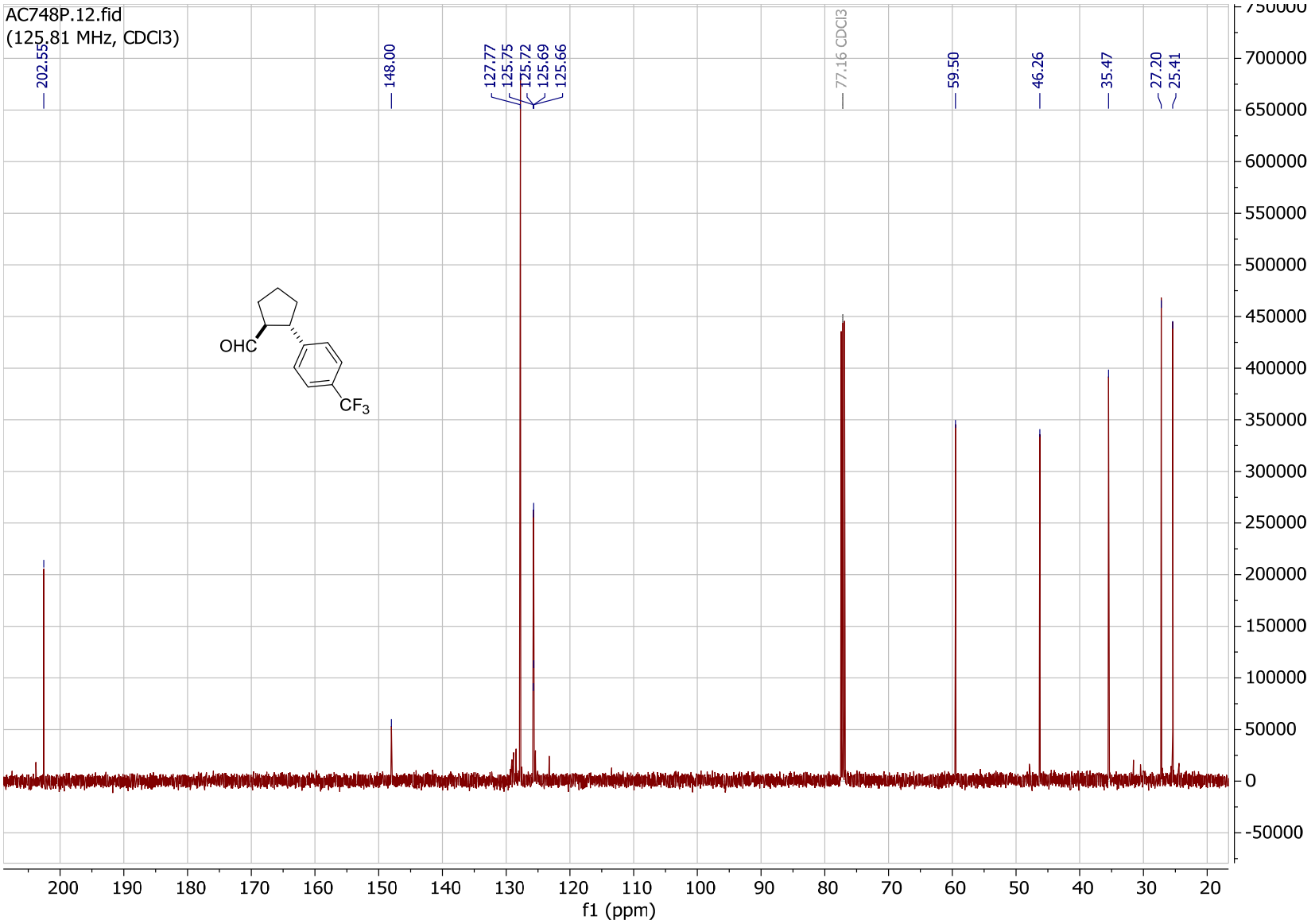
(1*SR*,2*SR*)-2-(4-Methoxyphenyl)cyclopentane-1-carbaldehyde 5b

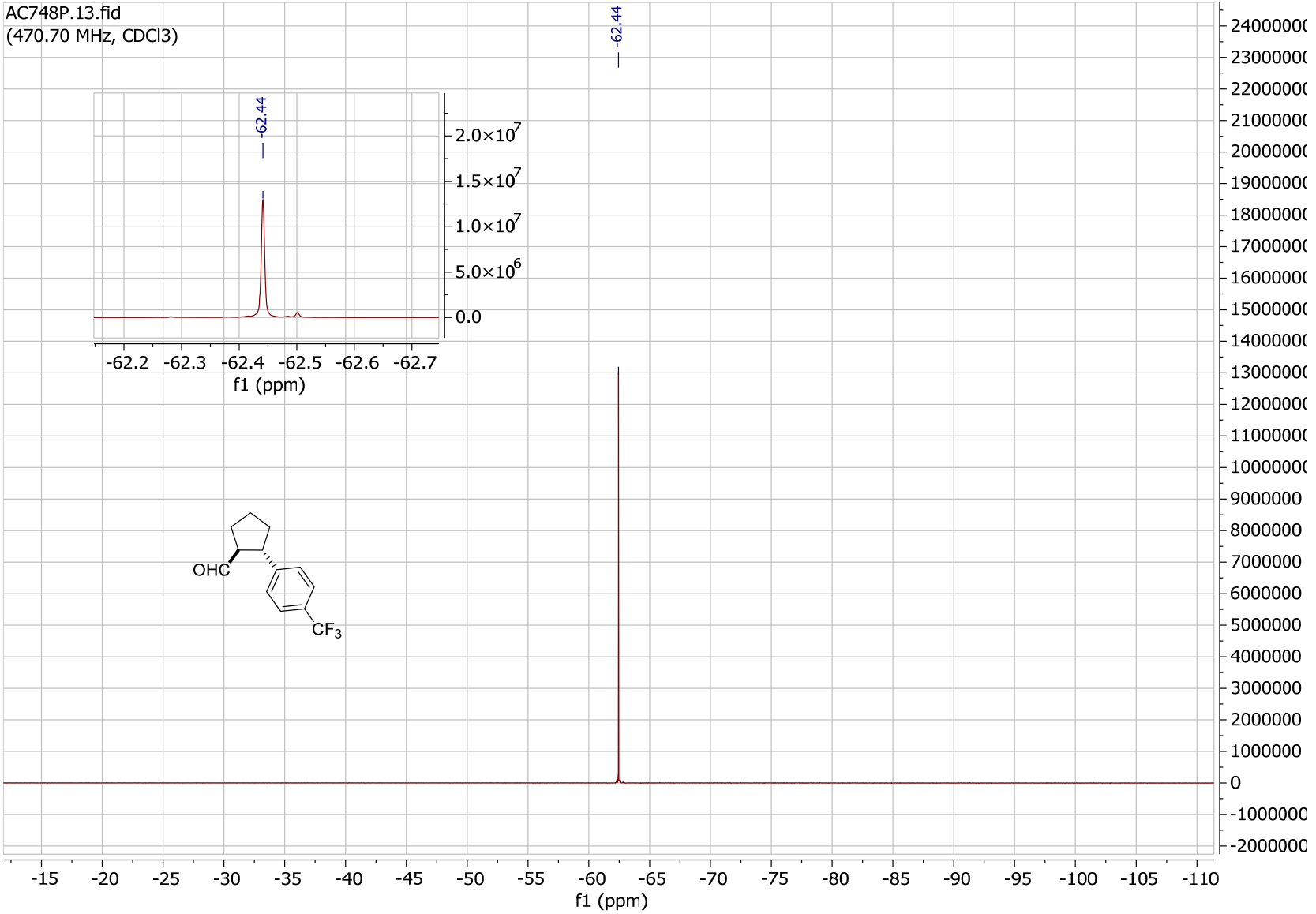



AC826B.12.fid
(125.81 MHz, CDCl3)
203.36
158.23
135.50
128.17
114.03
77.05 CDCl3
59.54
55.29
46.21
35.59
26.76
25.15
OHC
OMe
1600000
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

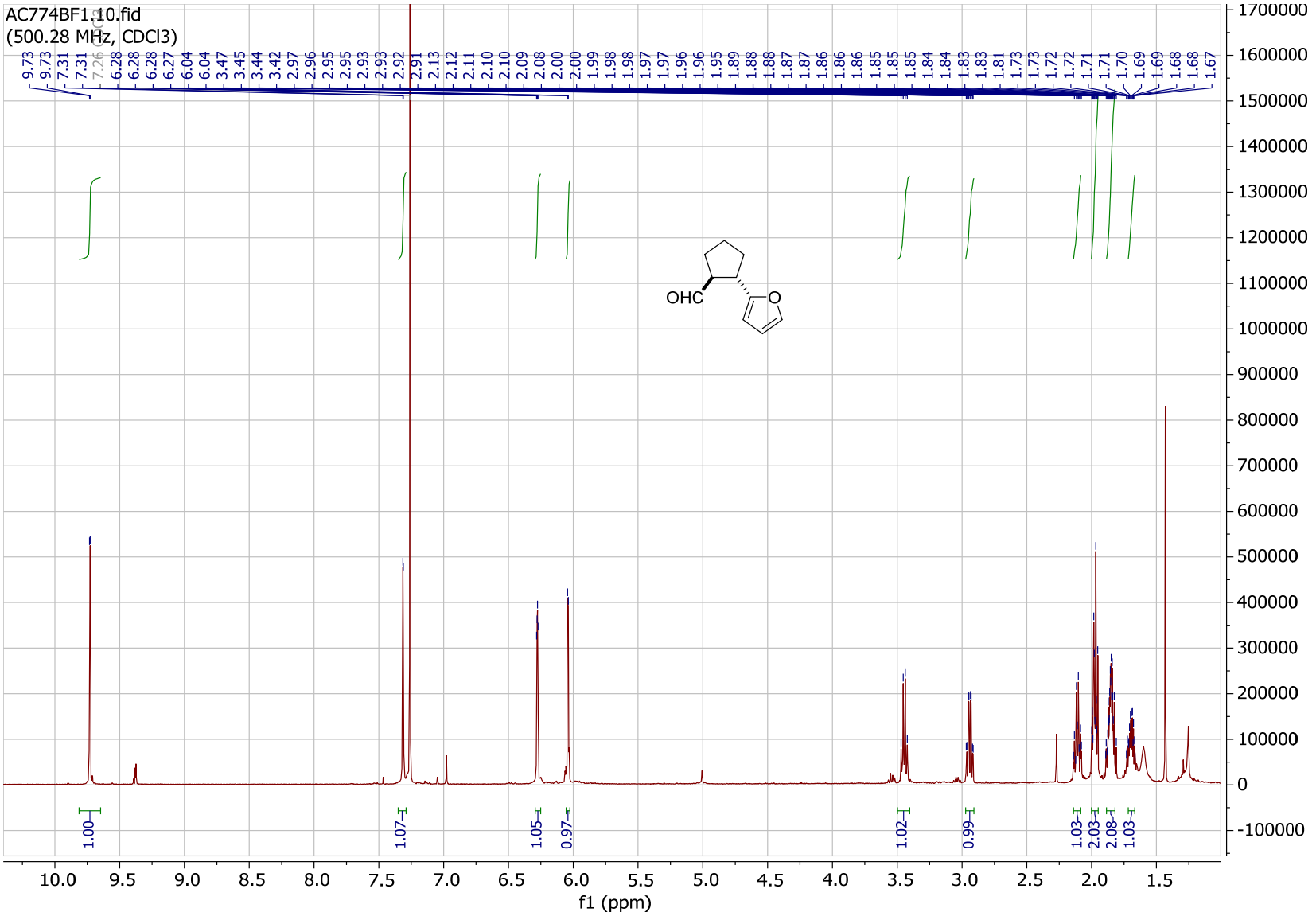
(1*SR*,2*SR*)-2-[4-(Trifluoromethyl)phenyl]cyclopentane-1-carbaldehyde 5c

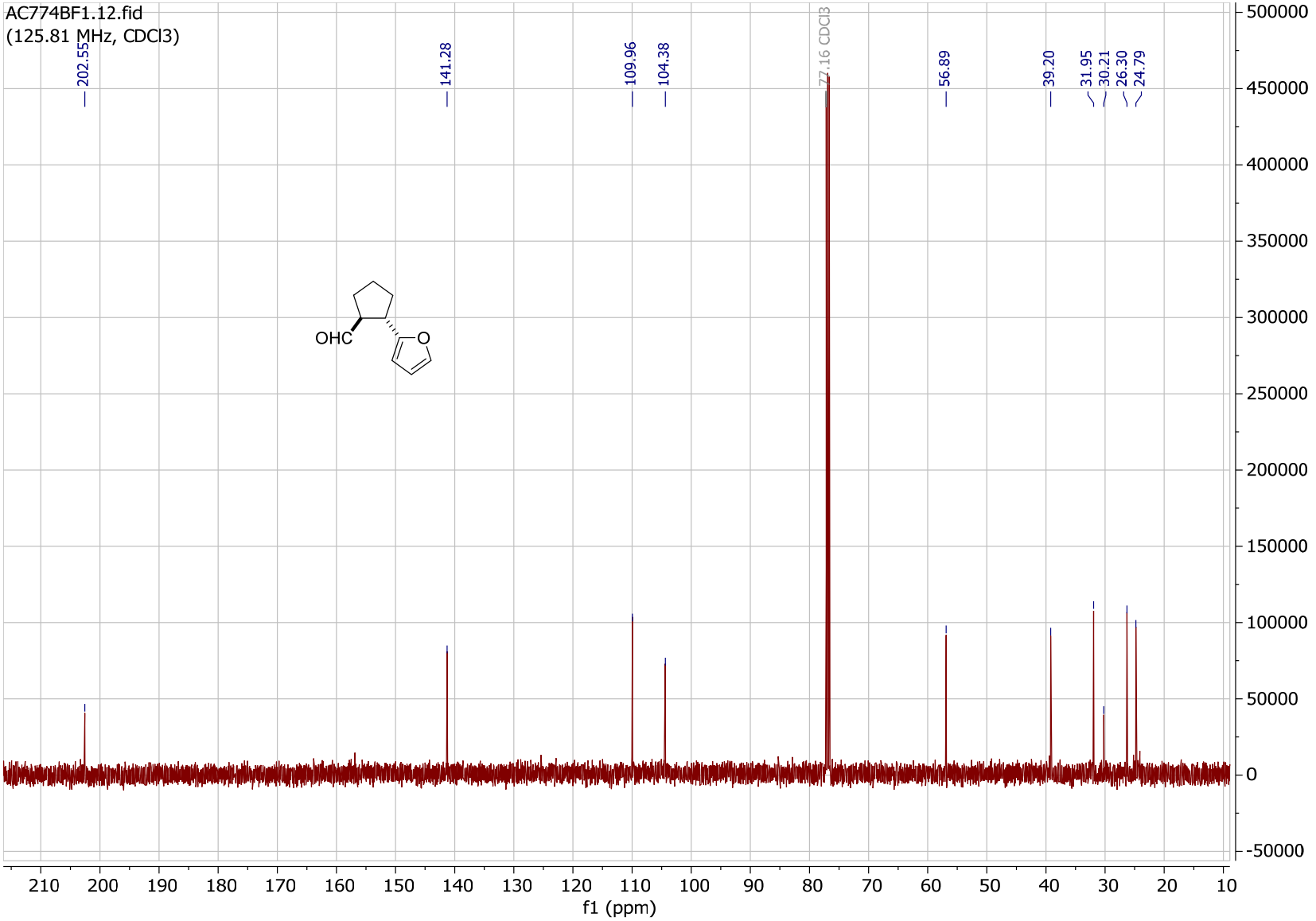



AC748P.12.fid
(125.81 MHz, CDCl3)
202.55
148.00
127.77
125.75
125.72
125.69
125.66
77.16 CDCl3
59.50
46.26
35.47
27.20
25.41
OHC
CF3
f1 (ppm)

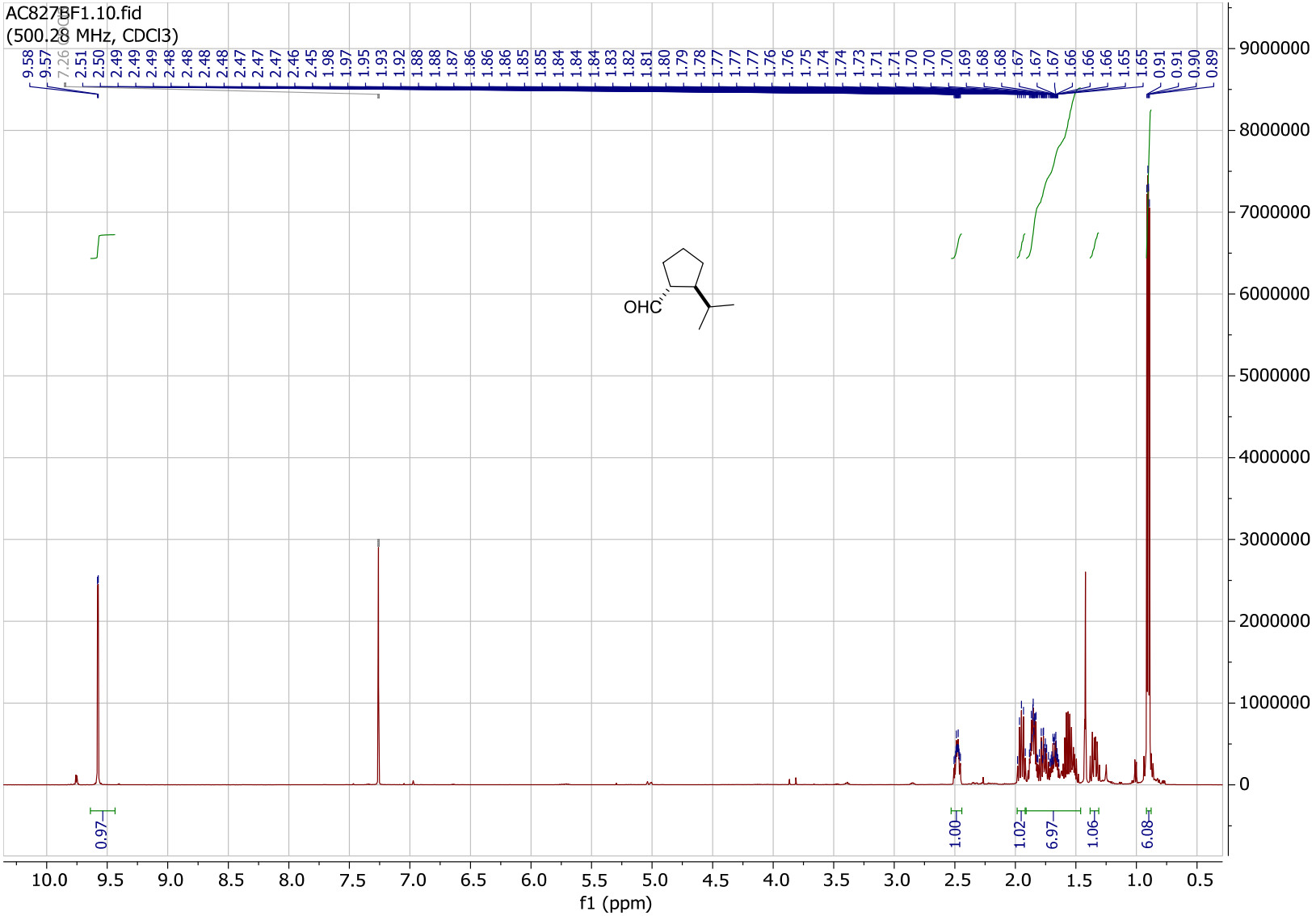

AC748P.13.fid
(470.70 MHz, CDCl3)
-62.44
-62.44
2.0×10^7
1.5×10^7
1.0×10^7
5.0×10^6
0.0
-62.2 -62.3 -62.4 -62.5 -62.6 -62.7
f1 (ppm)
OHC
CF3
-15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110
f1 (ppm)

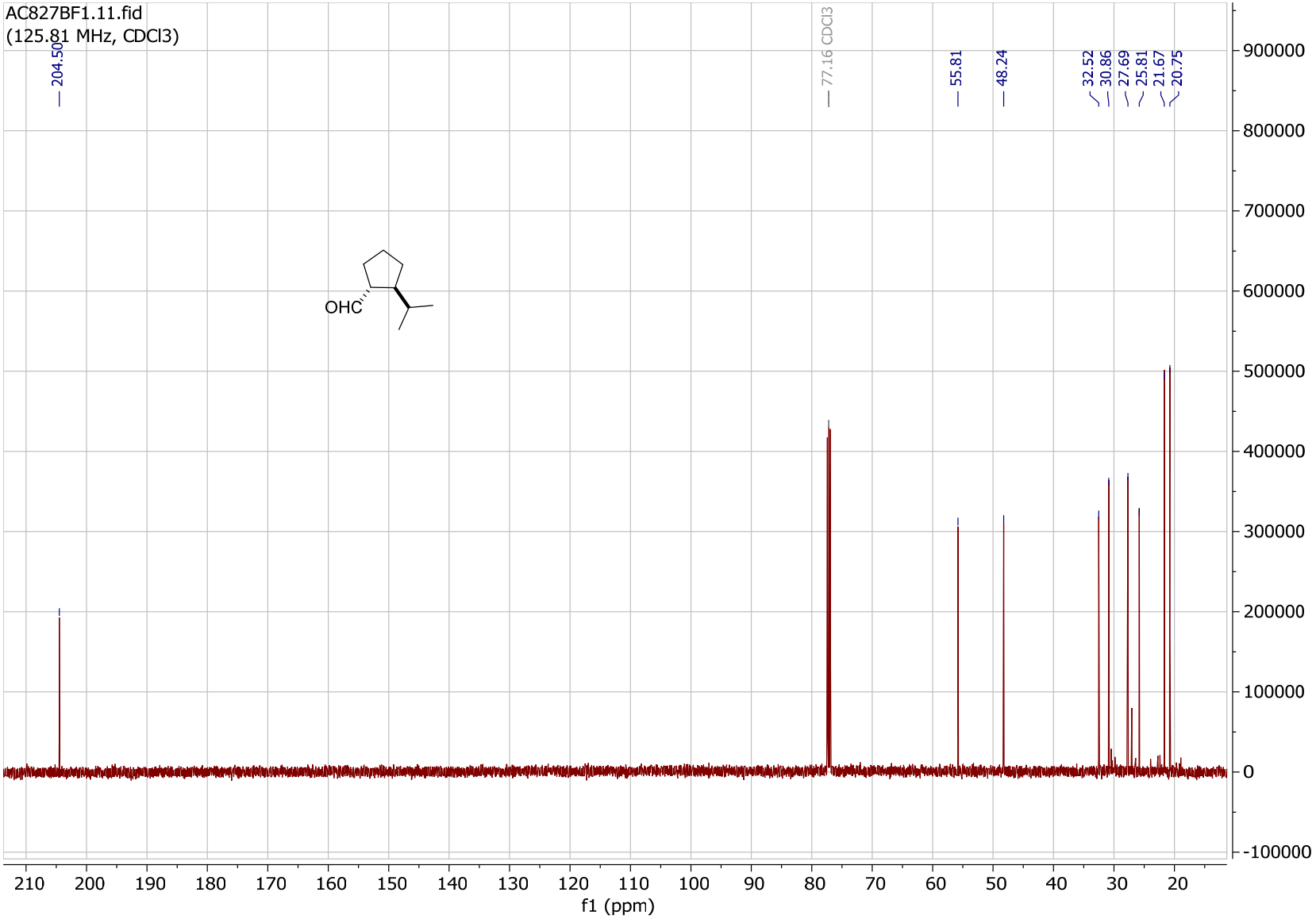
2-(Furan-2-yl)cyclopentane-1-carbaldehyde 5d



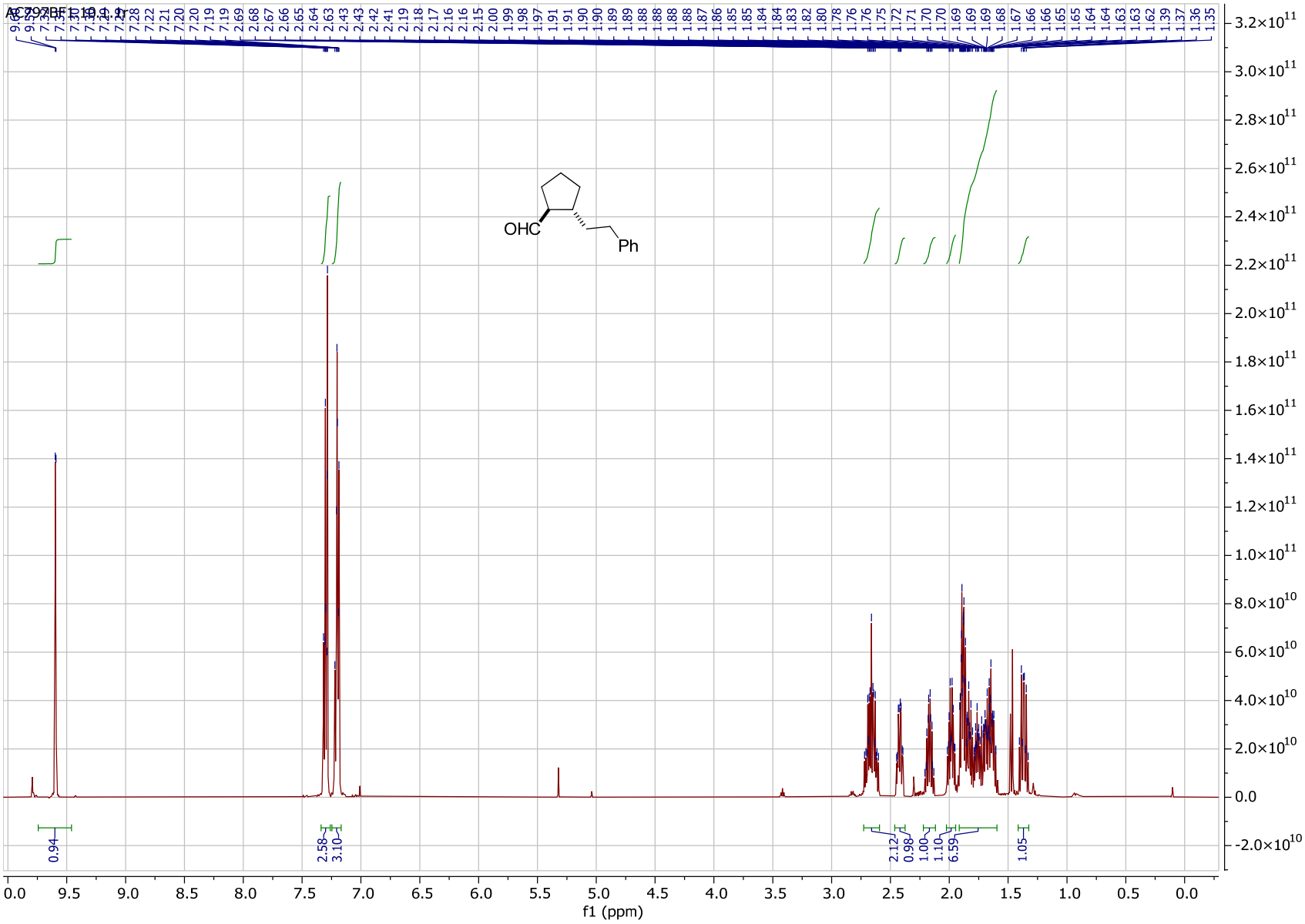

AC774BF1.12.fid
(125.81 MHz, CDCl3)
202.55
141.28
109.96
104.38
77.16 CDCl3
56.89
39.20
31.95
30.21
26.30
24.79
OHC
O
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

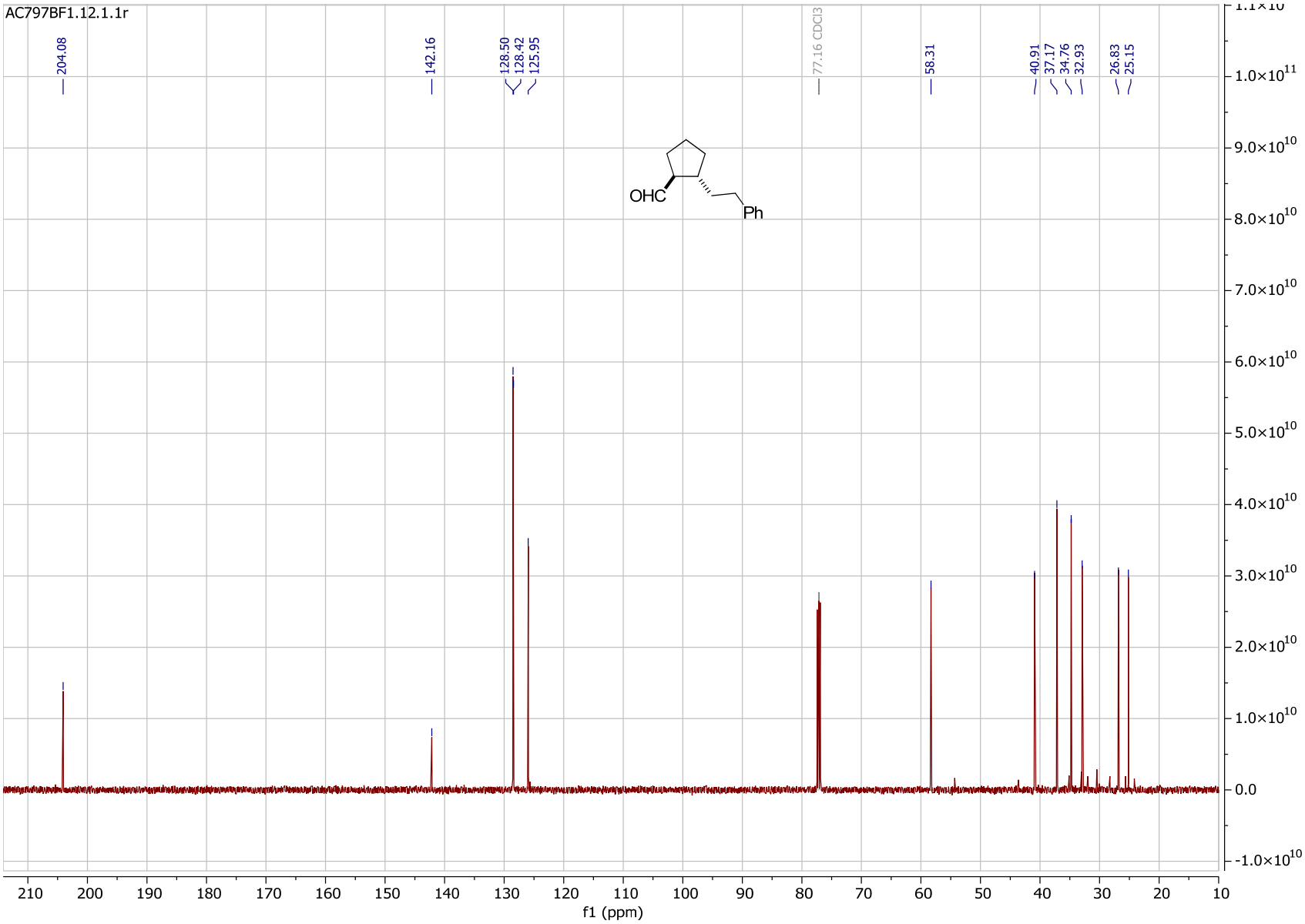
2-isopropylcyclopentane-1-carbaldehyde 5e



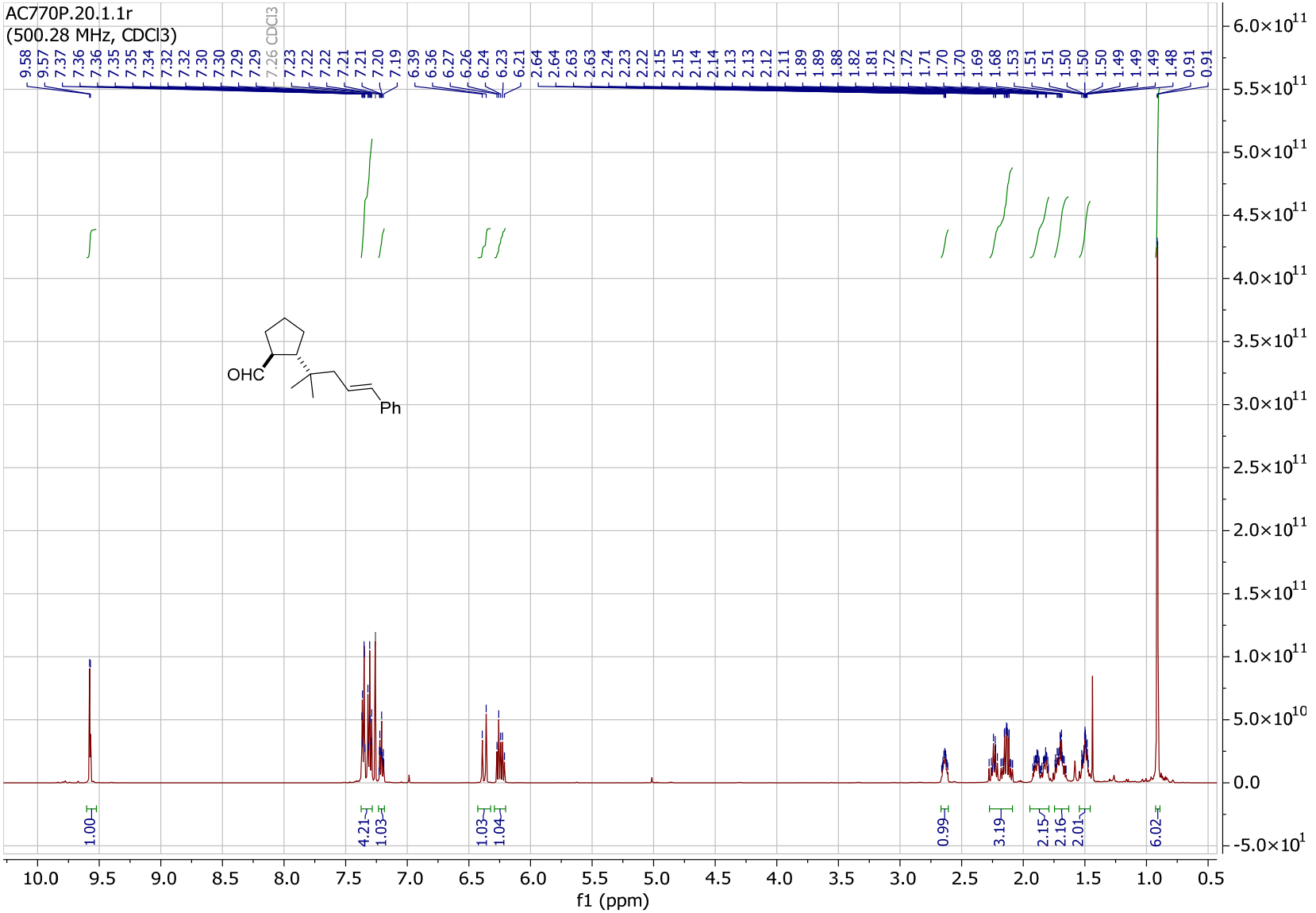

AC827BF1.11.fid
(125.81 MHz, CDCl3)
204.50
77.16 CDCl3
55.81
48.24
32.52
30.86
27.69
25.81
21.67
20.75
OHC
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

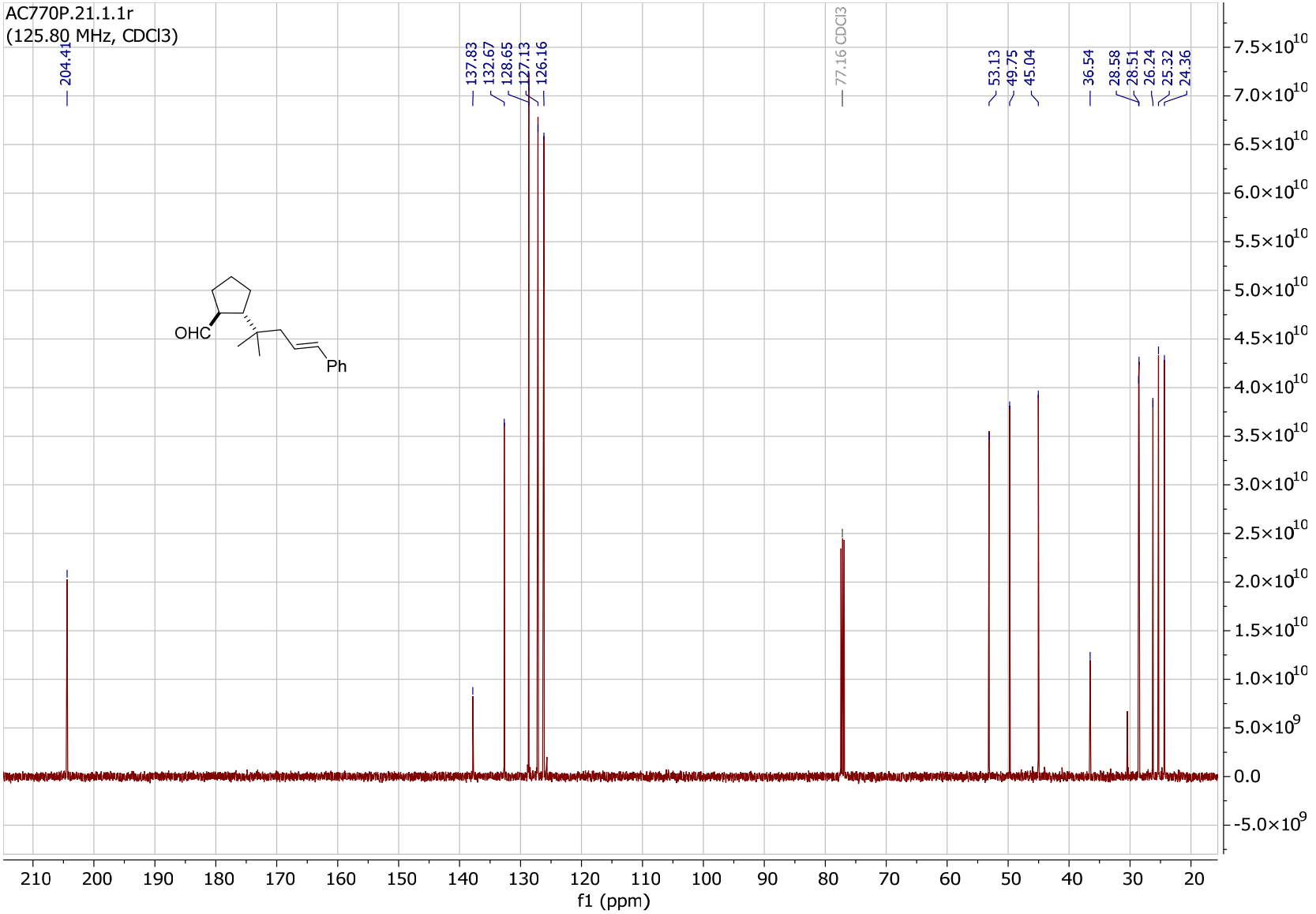
(1*SR*,2*RS*)-2-Phenethylcyclopentanecarbaldehyde 5f



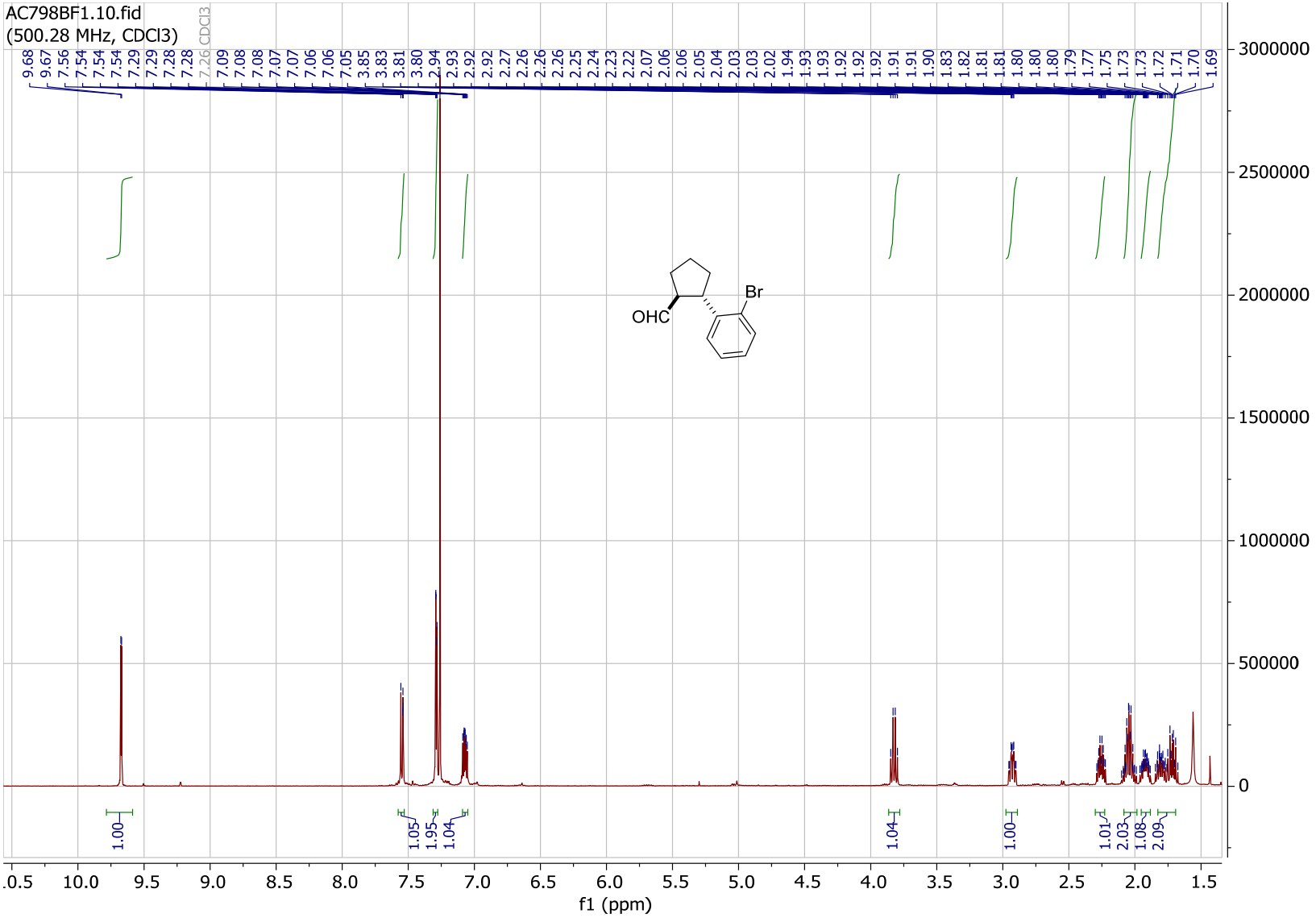

AC797BF1.12.1.1r
204.08
142.16
128.50
128.42
125.95
77.16 CDCl3
58.31
40.91
37.17
34.76
32.93
26.83
25.15
OHC
Ph
1.0×10^11
9.0×10^10
8.0×10^10
7.0×10^10
6.0×10^10
5.0×10^10
4.0×10^10
3.0×10^10
2.0×10^10
1.0×10^10
0.0
-1.0×10^10
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

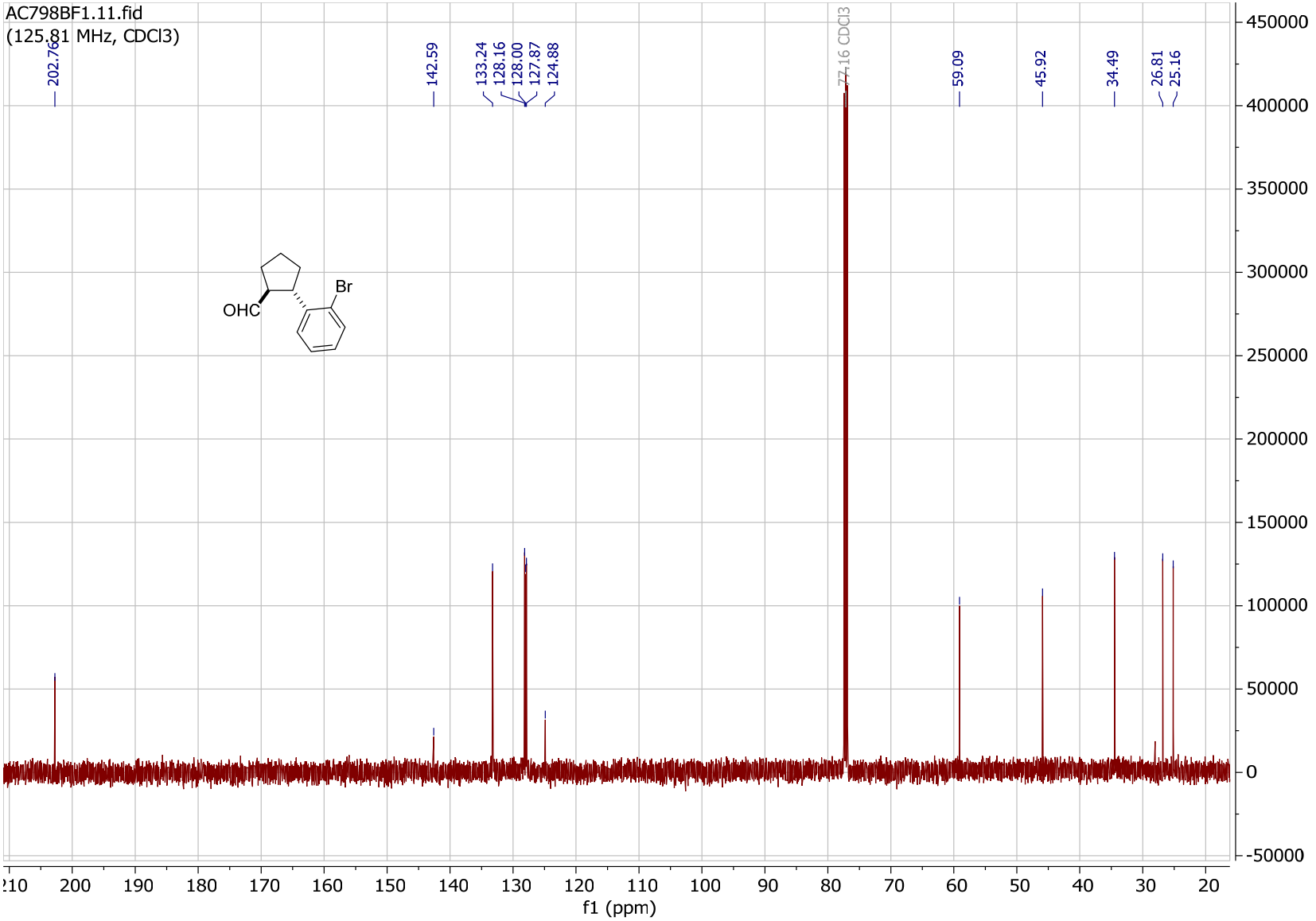
(1*SR*,2*SR*)-2-[(*E*)-2-Methyl-5-phenylpent-4-en-2-yl]cyclopentane-1-carbaldehyde 5g



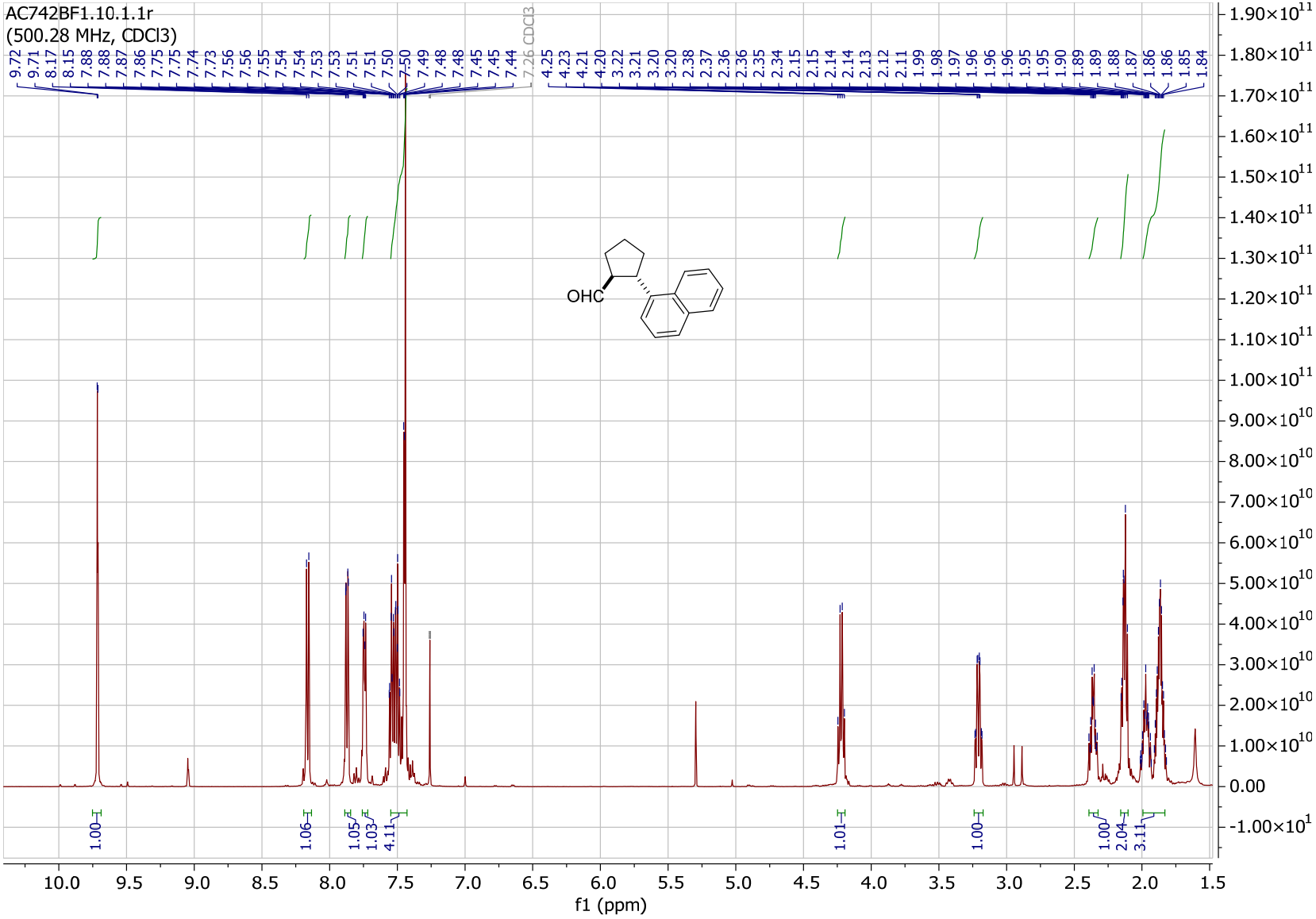

AC770P.21.1.1r
(125.80 MHz, CDCl3)
204.41
137.83
132.67
128.65
127.13
126.16
77.16 CDCl3
53.13
49.75
45.04
36.54
28.58
28.51
26.24
25.32
24.36
OHC
Ph
f1 (ppm)

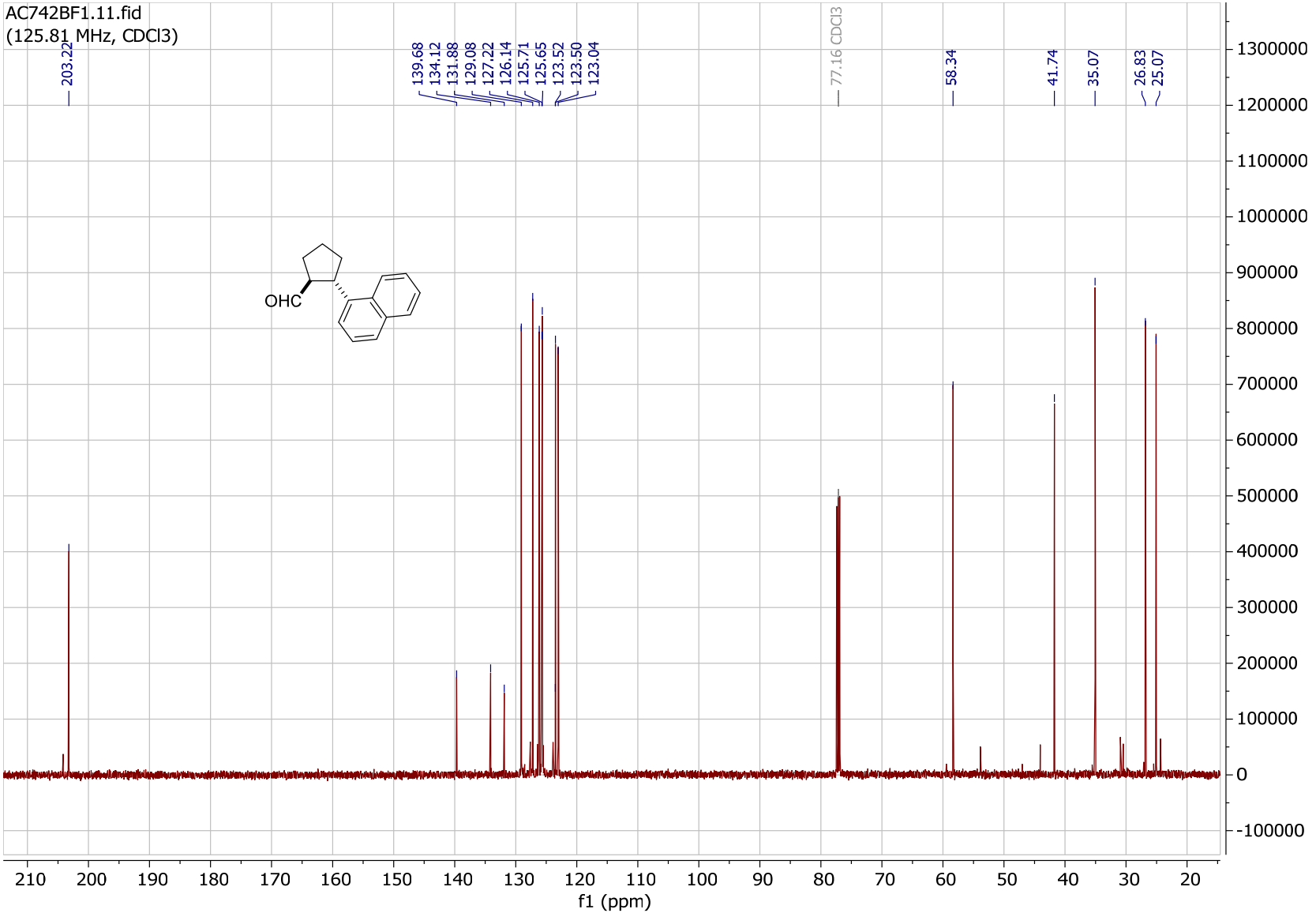
2-(2-Bromophenyl)cyclopentane-1-carbaldehyde 5h



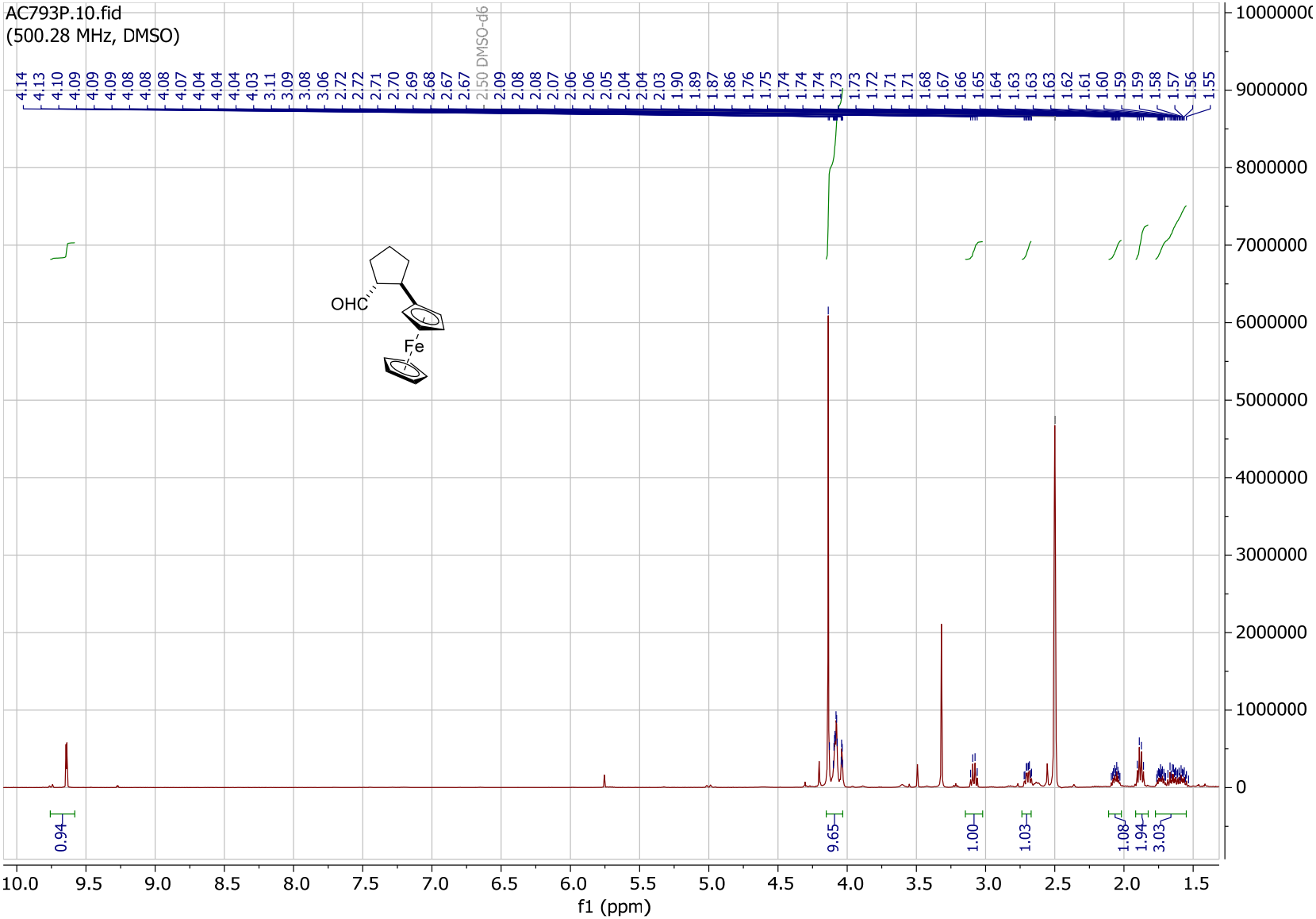

AC798BF1.11.fid
(125.81 MHz, CDCl3)
202.76
142.59
133.24
128.16
128.00
127.87
124.88
77.16 CDCl3
59.09
45.92
34.49
26.81
25.16
OHC
Br
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

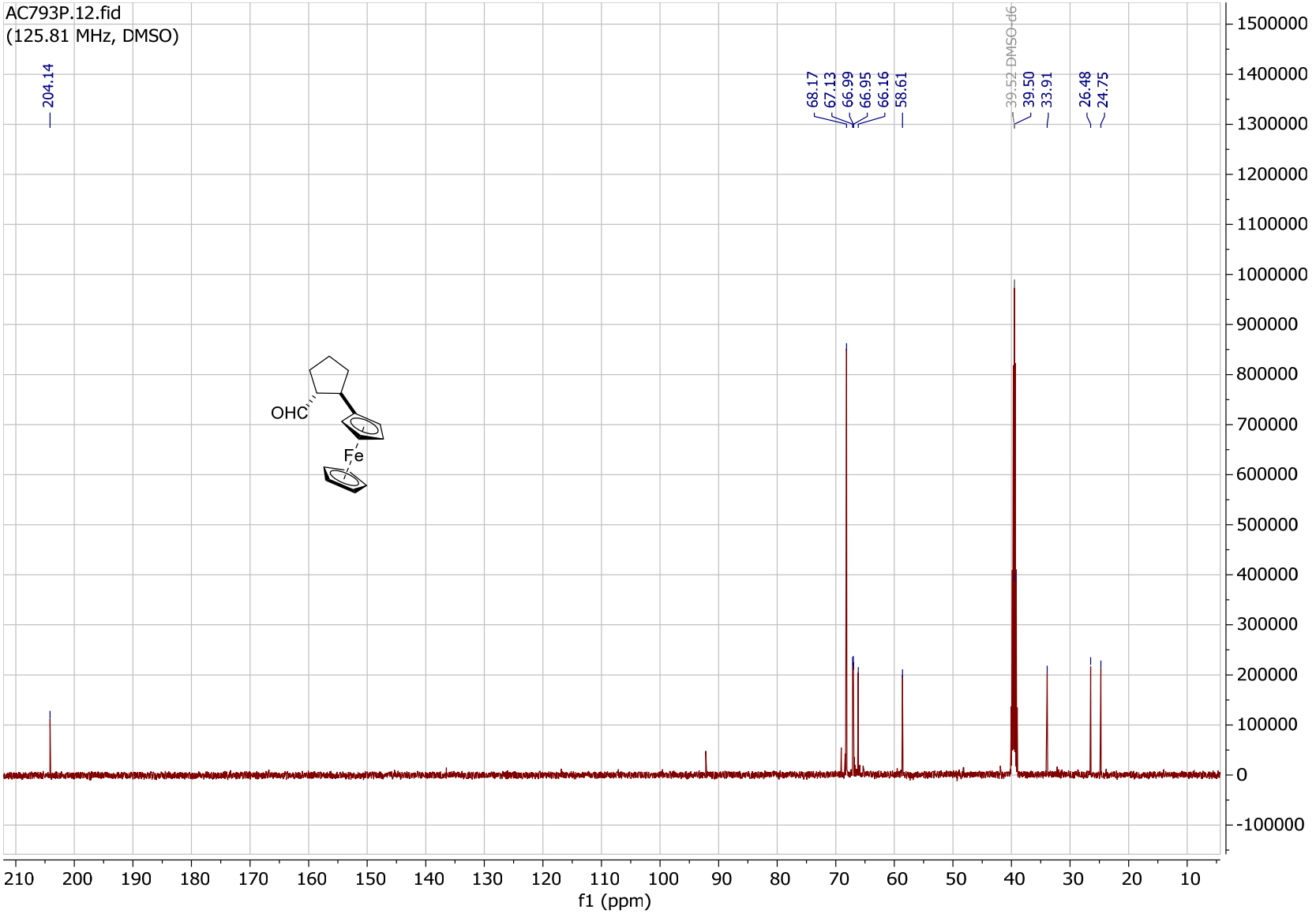
(1*SR*,2*SR*)-2-(Naphthalen-1-yl)cyclopentane-1-carbaldehyde 5i



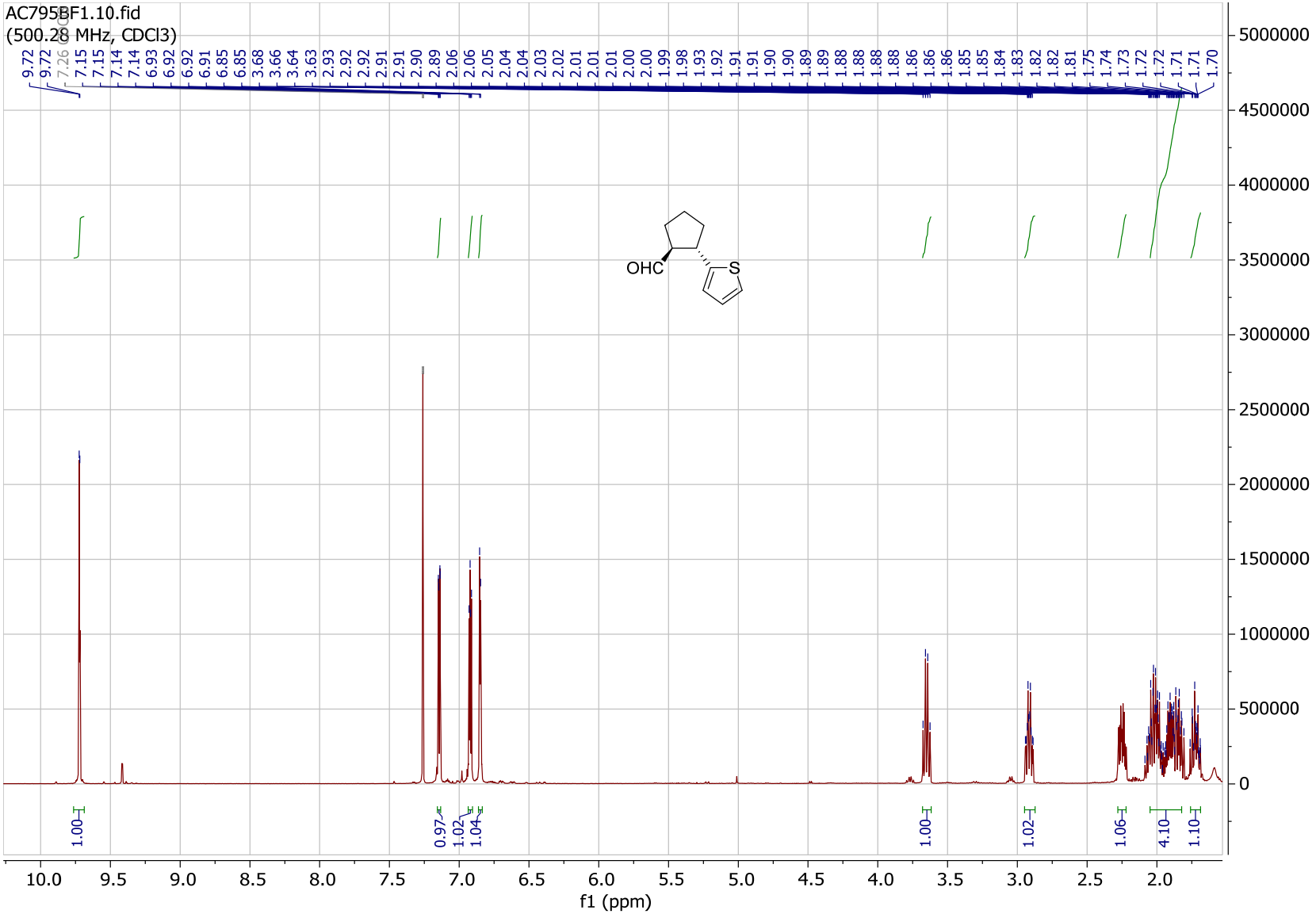

AC742BF1.11.fid
(125.81 MHz, CDCl3)
203.22
139.68
134.12
131.88
129.08
127.22
126.14
125.71
125.65
123.52
123.50
123.04
77.16 CDCl3
58.34
41.74
35.07
26.83
25.07
OHC
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

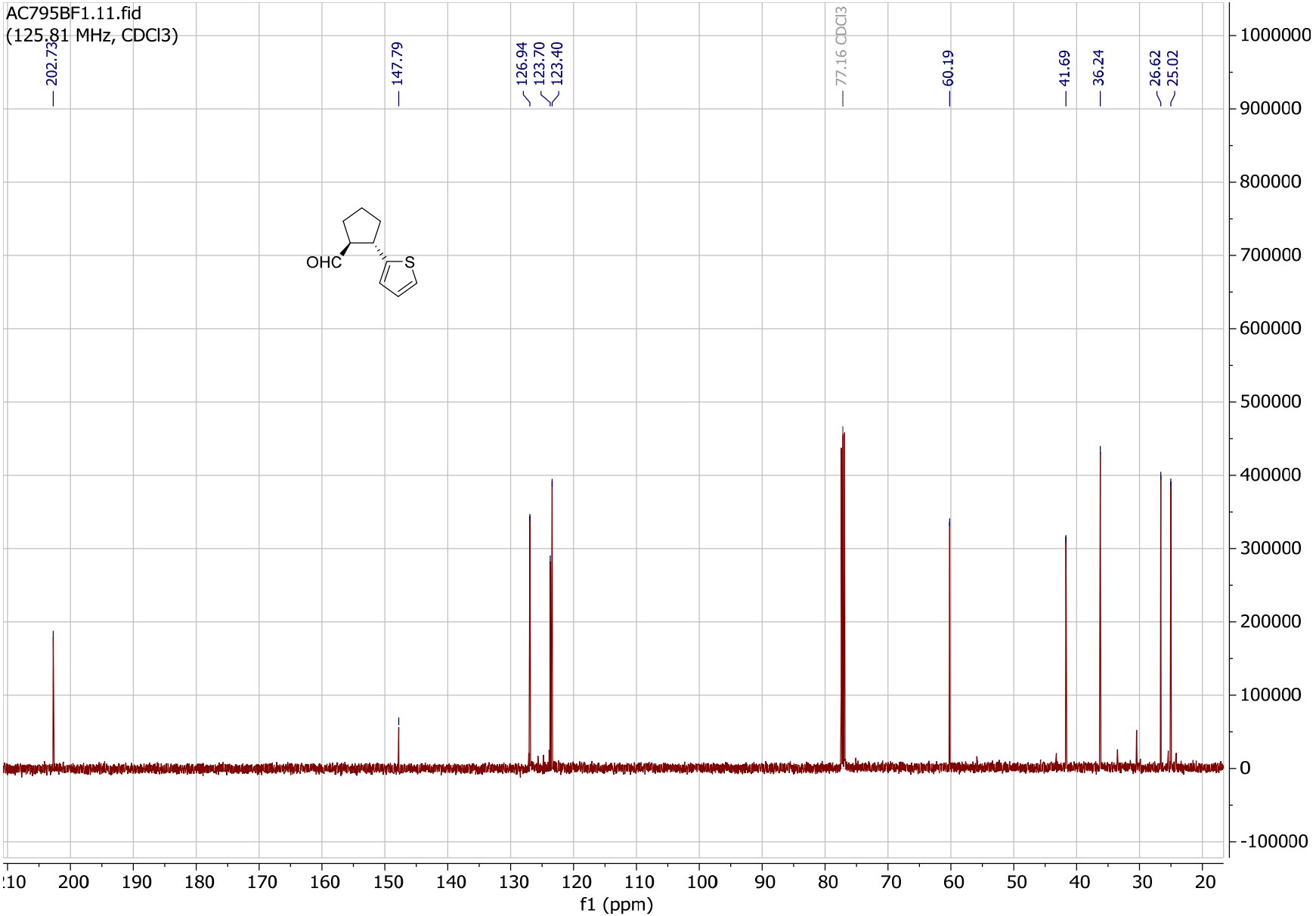
2-Ferrocenylcyclopentane-1-carbaldehyde 5j



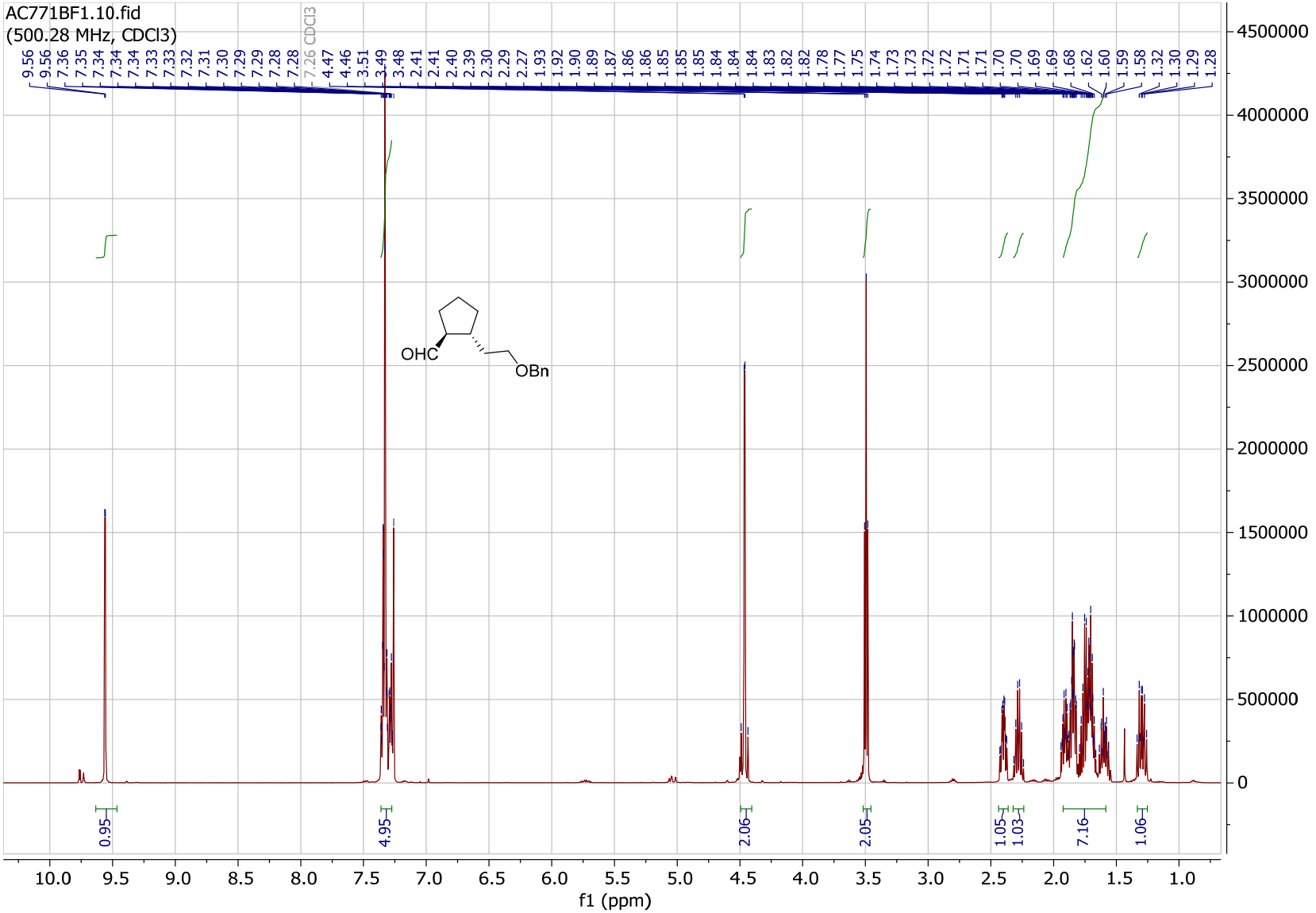

AC793P.12.fid
(125.81 MHz, DMSO)
204.14
68.17
67.13
66.99
66.95
66.16
58.61
39.52 DMSO-d6
39.50
33.91
26.48
24.75
OHC
Fe
1500000
1400000
1300000
1200000
1100000
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

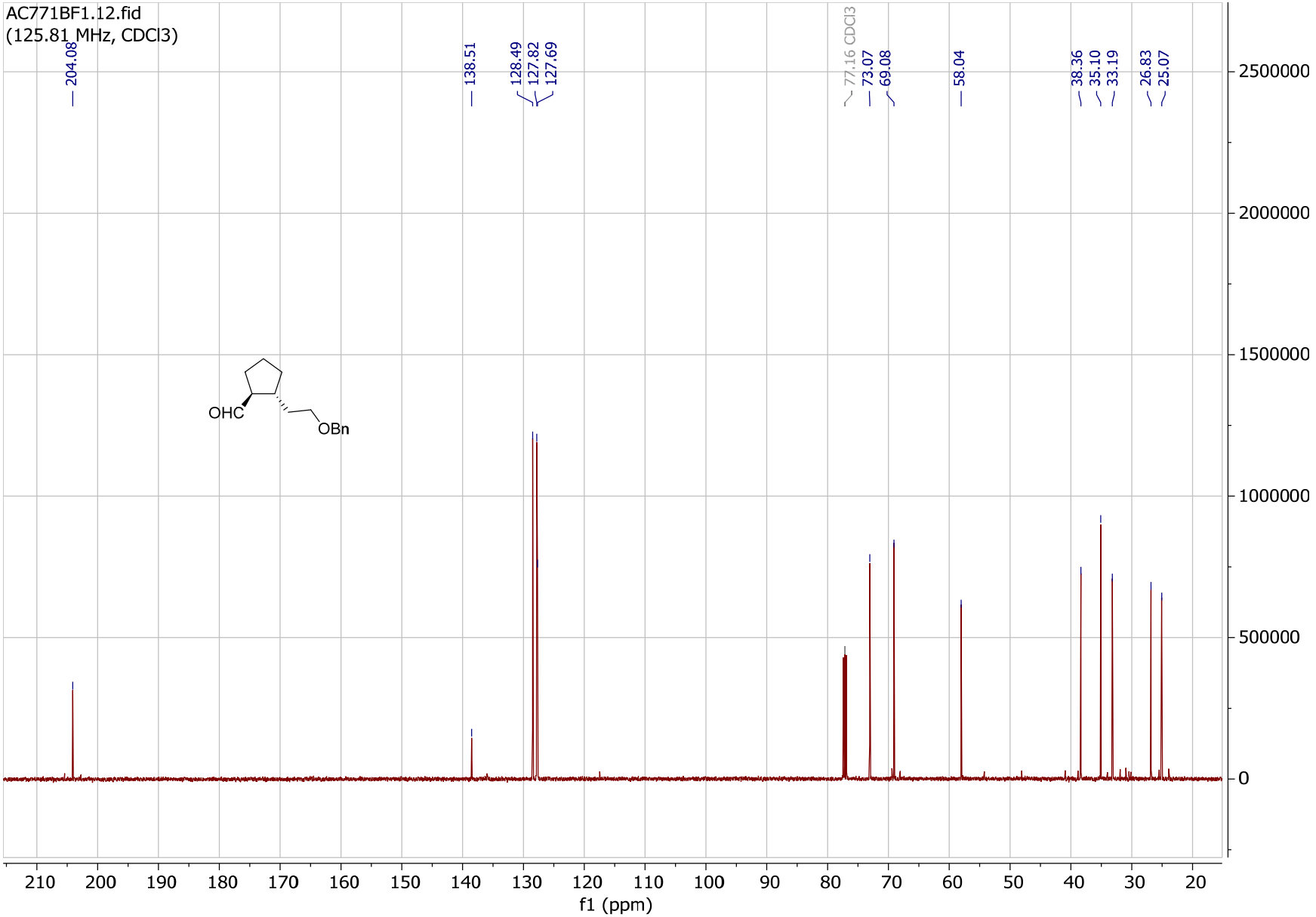
(1*S*,2*S*)-2-(Thiophen-2-yl)cyclopentane-1-carbaldehyde 5k



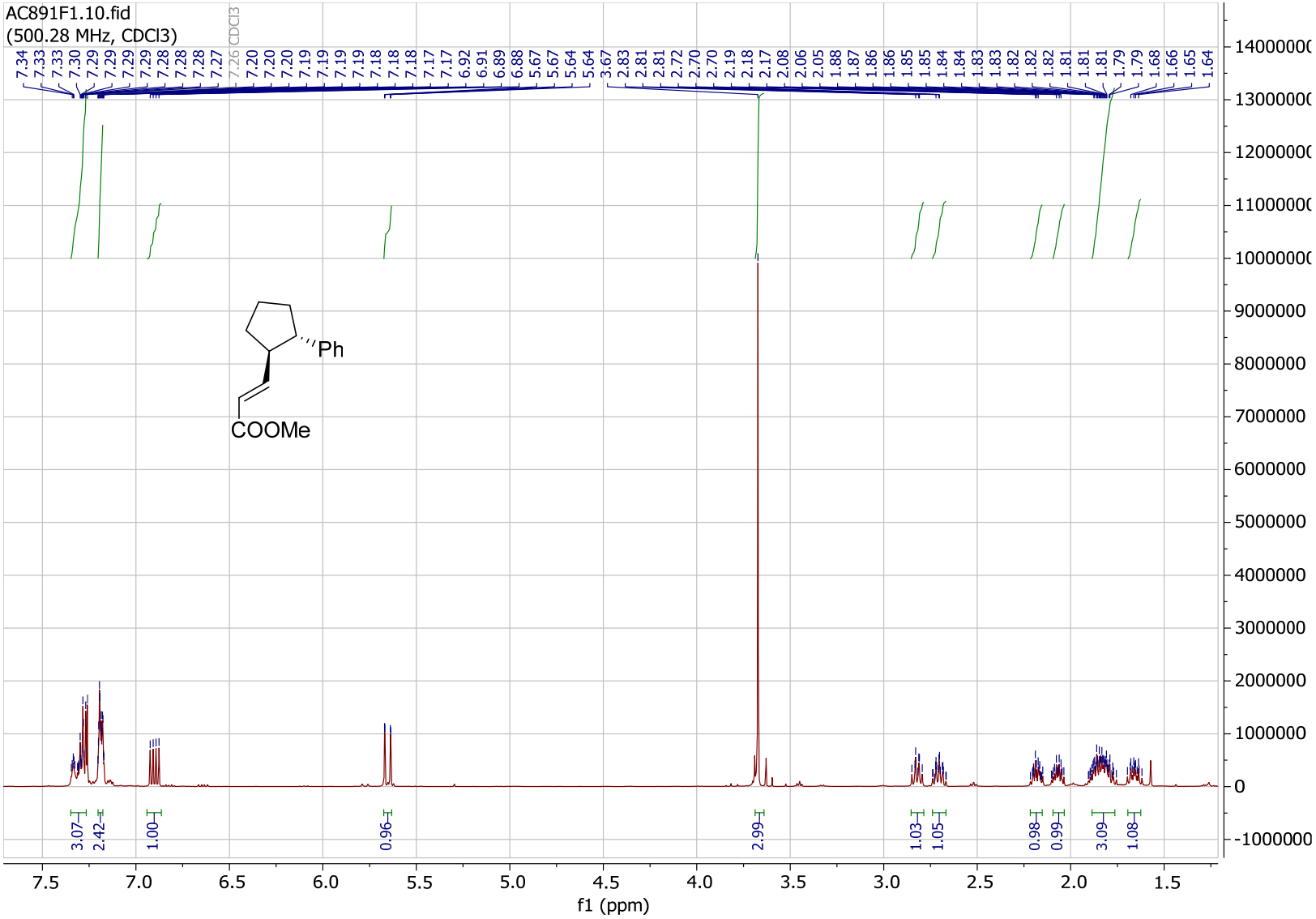

AC795BF1.11.fid
(125.81 MHz, CDCl3)
202.73
147.79
126.94
123.70
123.40
77.16 CDCl3
60.19
41.69
36.24
26.62
25.02
OHC
S
1000000
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
-100000
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

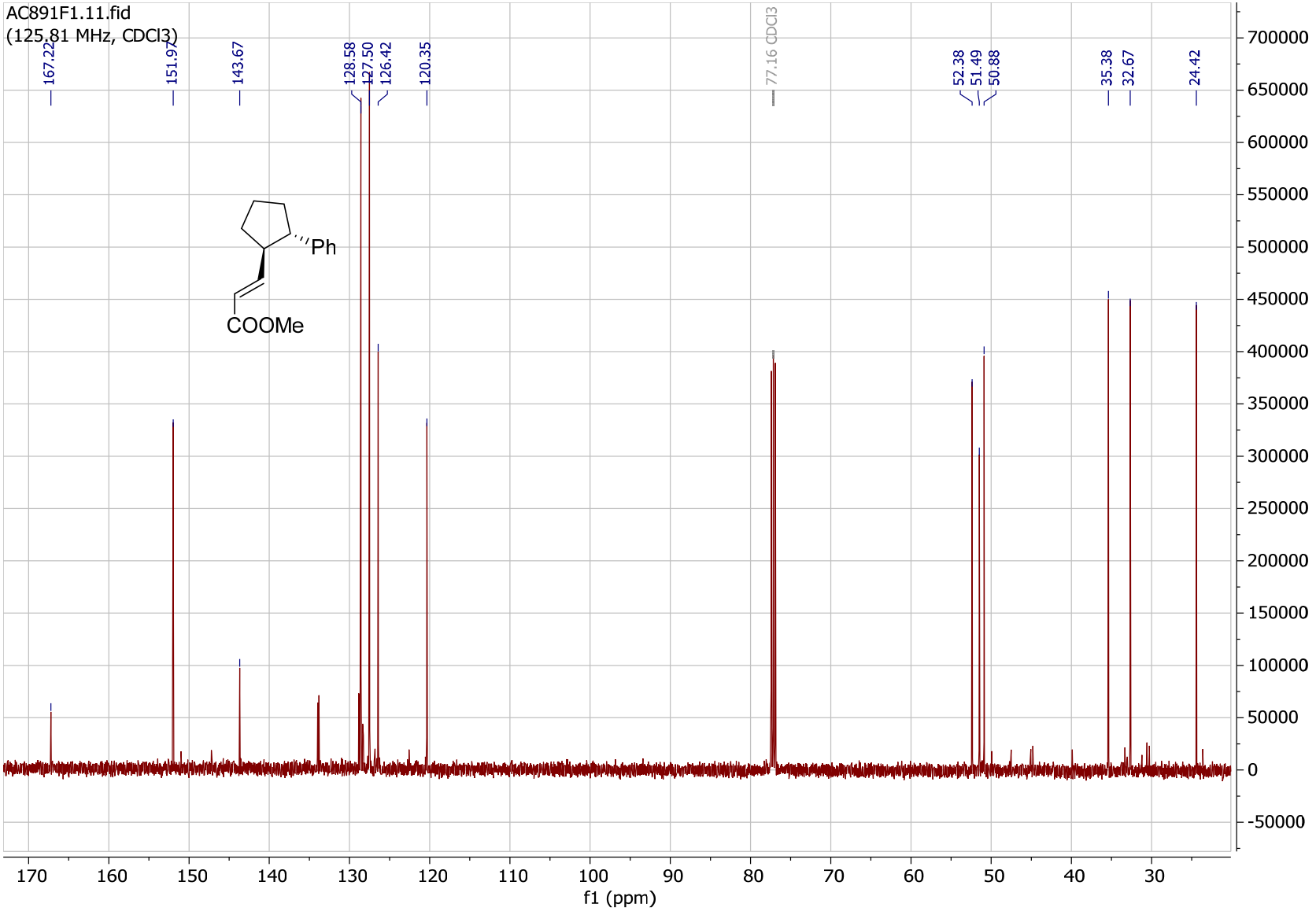
(1*SR*,2*SR*)-2-[2-(Benzyloxy)ethyl]cyclopentane-1-carbaldehyde 5l



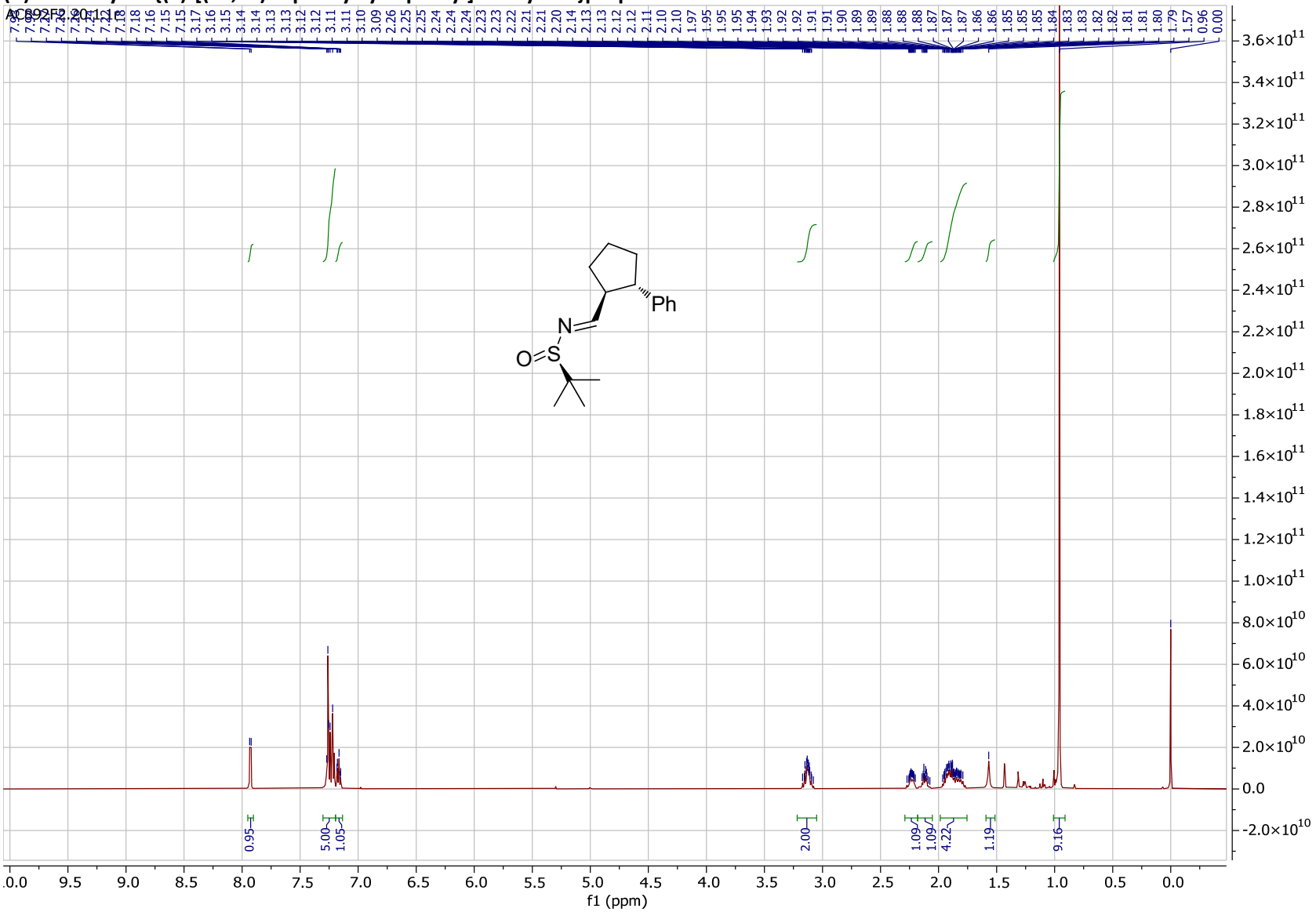

AC771BF1.12.fid
(125.81 MHz, CDCl3)
204.08
138.51
128.49
127.82
127.69
77.16 CDCl3
73.07
69.08
58.04
38.36
35.10
33.19
26.83
25.07
OHC
OBn
2500000
2000000
1500000
1000000
500000
0
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

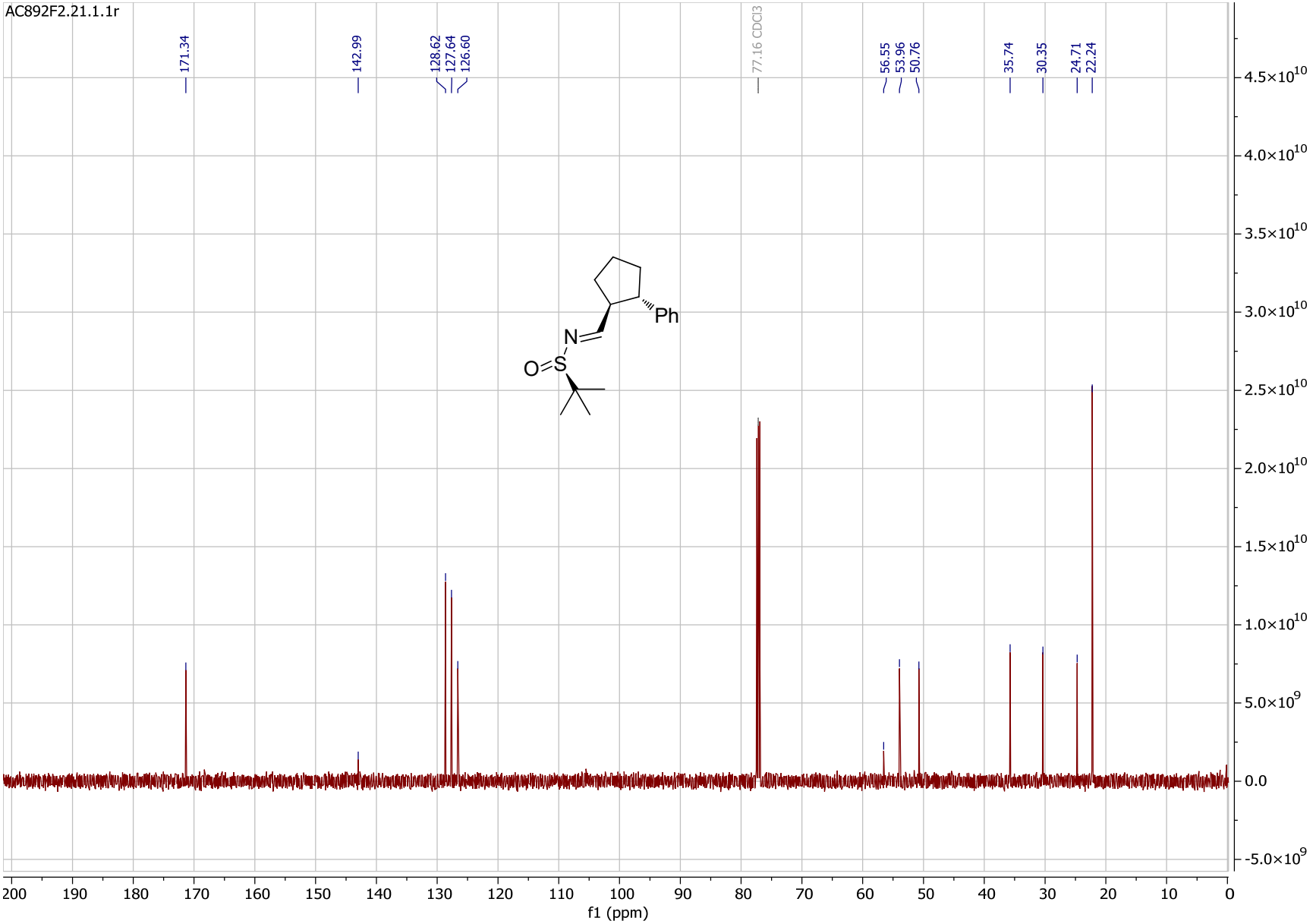
Methyl (*E*)-3-[(1R,2S)-2-phenylcyclopentyl)acrylate 6a



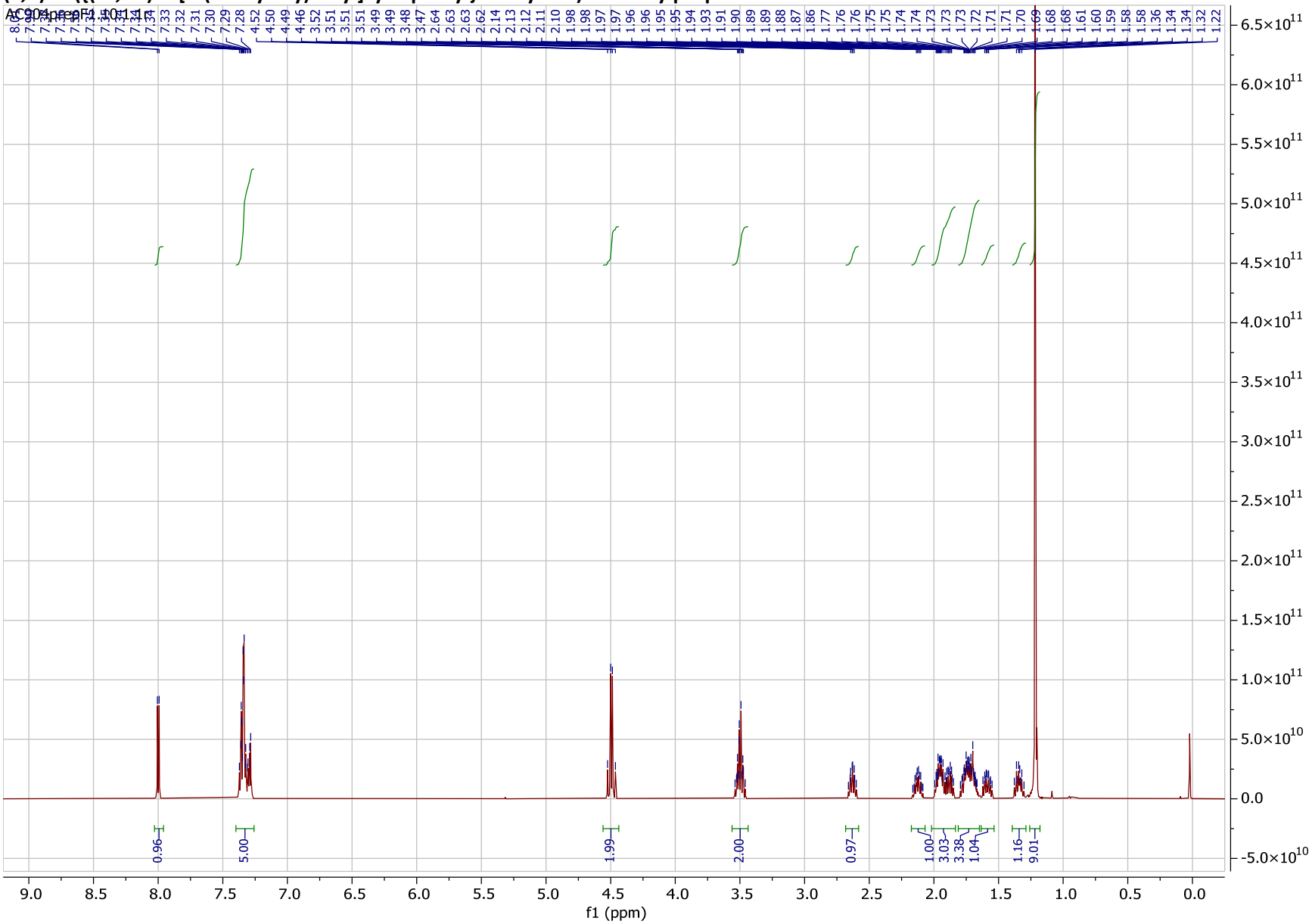

AC891F1.11.fid
(125.81 MHz, CDCl3)
167.22
151.97
143.67
128.58
127.50
126.42
120.35
77.16 CDCl3
52.38
51.49
50.88
35.38
32.67
24.42
Ph
COOMe
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
f1 (ppm)

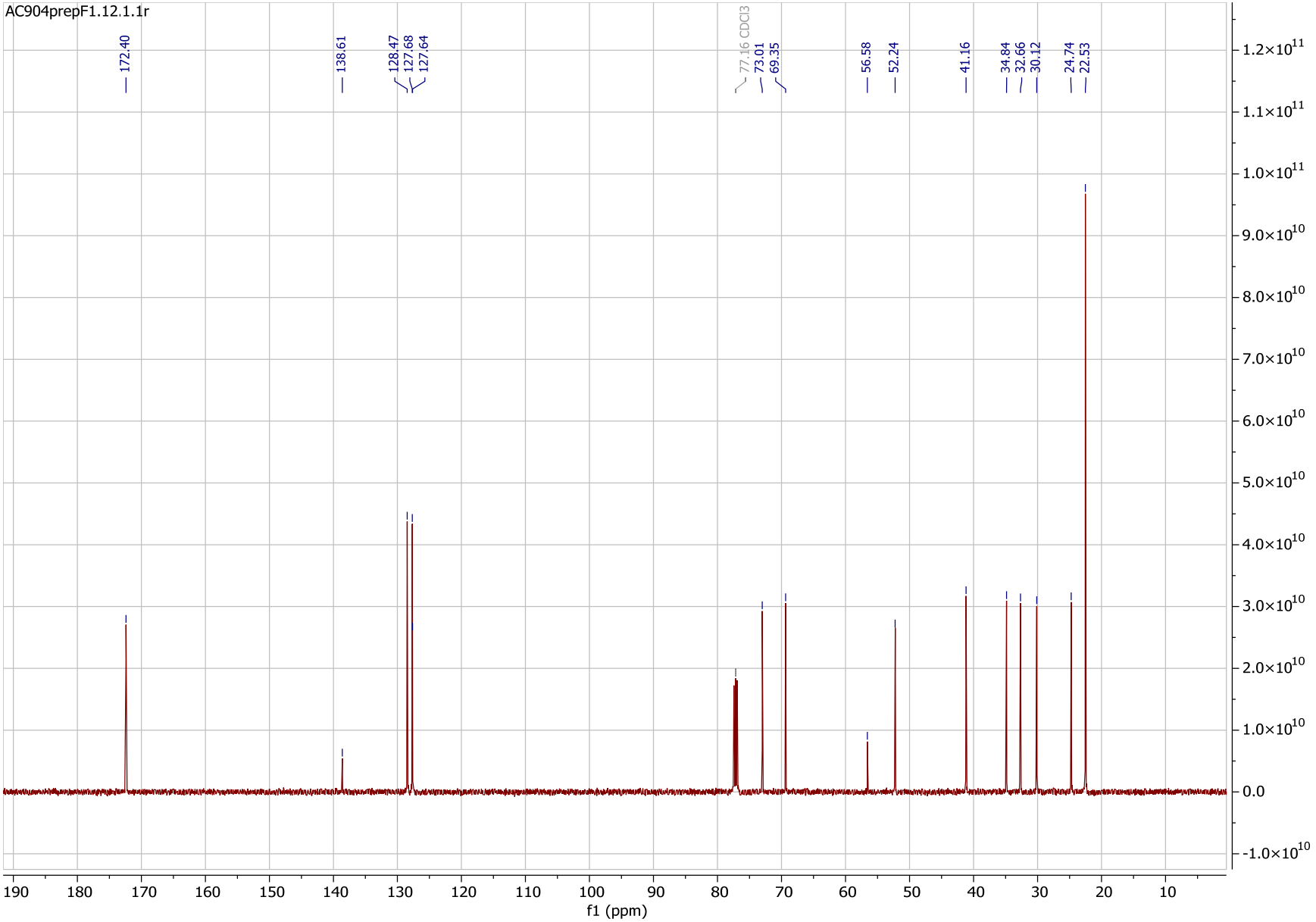
(*R*)-2-Methyl-*N*-{(E)-[(1*S*,2*S*)-2-phenylcyclopentyl]methylene}propane-2-sulfinamide 7a



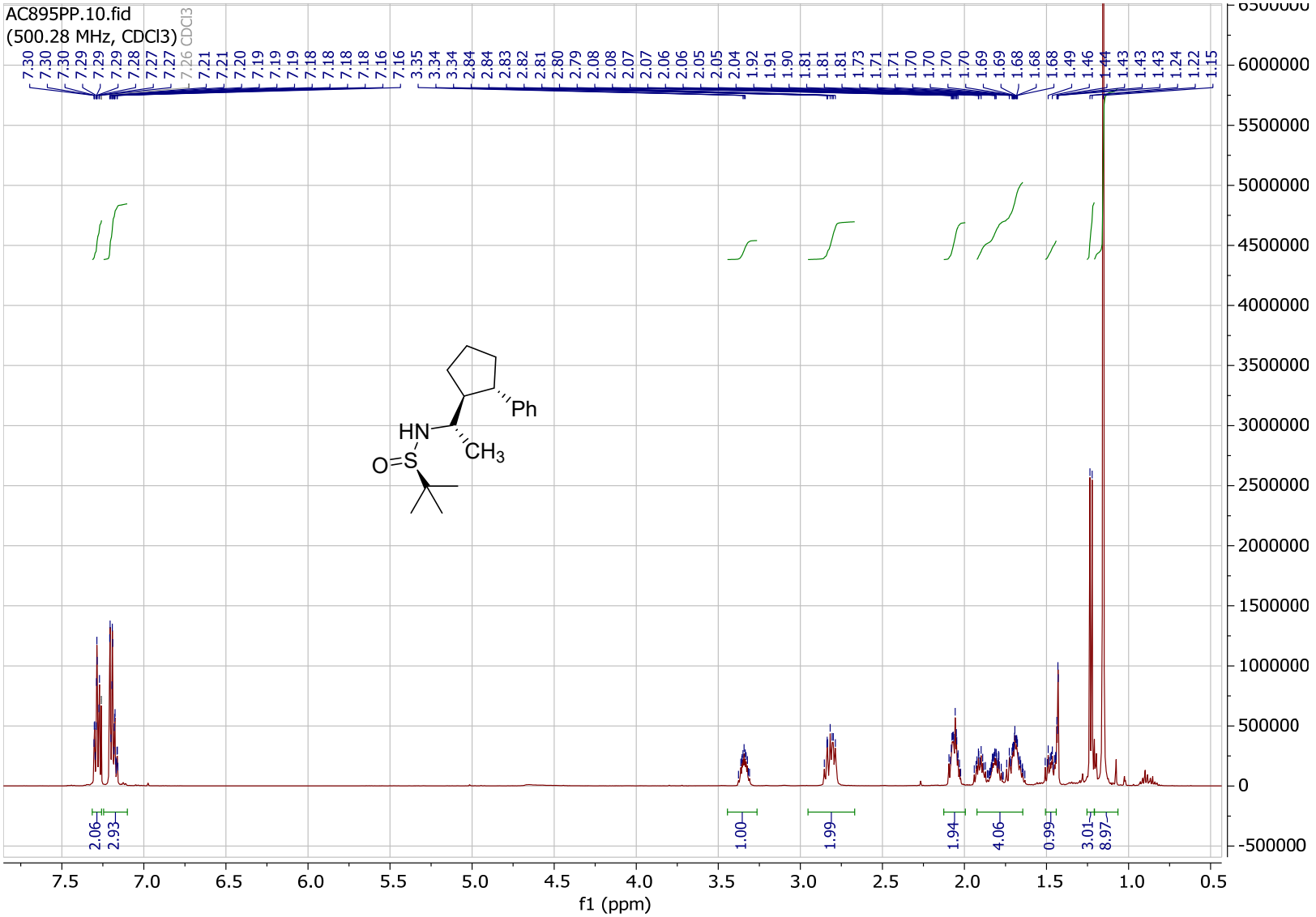

AC892F2.21.1.1r
171.34
142.99
128.62
127.64
126.60
77.16 CDCl3
56.55
53.96
50.76
35.74
30.35
24.71
22.24
Ph
N
O
S
4.5×10^10
4.0×10^10
3.5×10^10
3.0×10^10
2.5×10^10
2.0×10^10
1.5×10^10
1.0×10^10
5.0×10^9
0.0
-5.0×10^9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

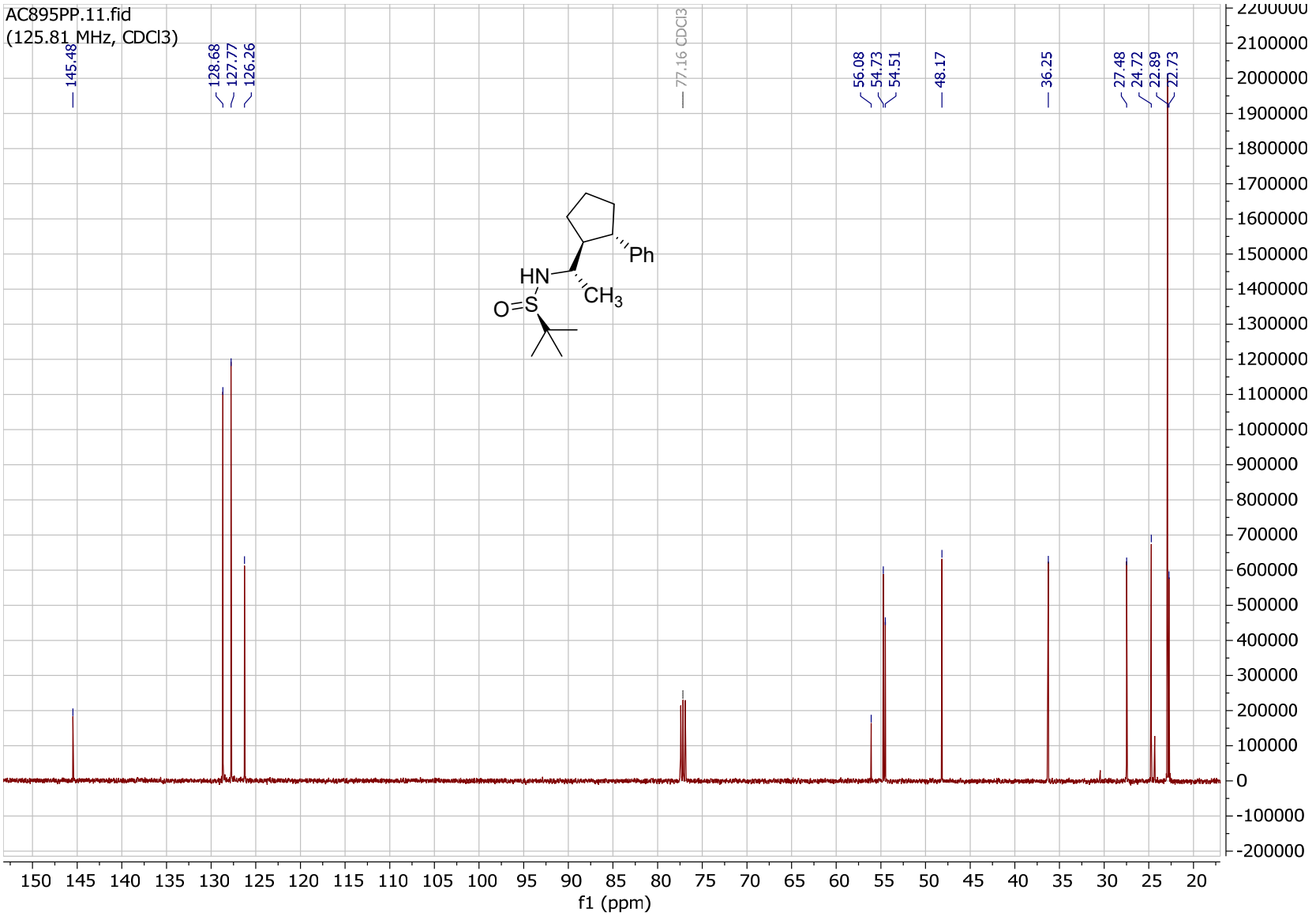
(*R*,*E*)-*N*-({(*1S*,*2R*)-2-[2-(Benzyloxy)ethyl]cyclopentyl}methylene)-2-methylpropane-2-sulfinamide 7l



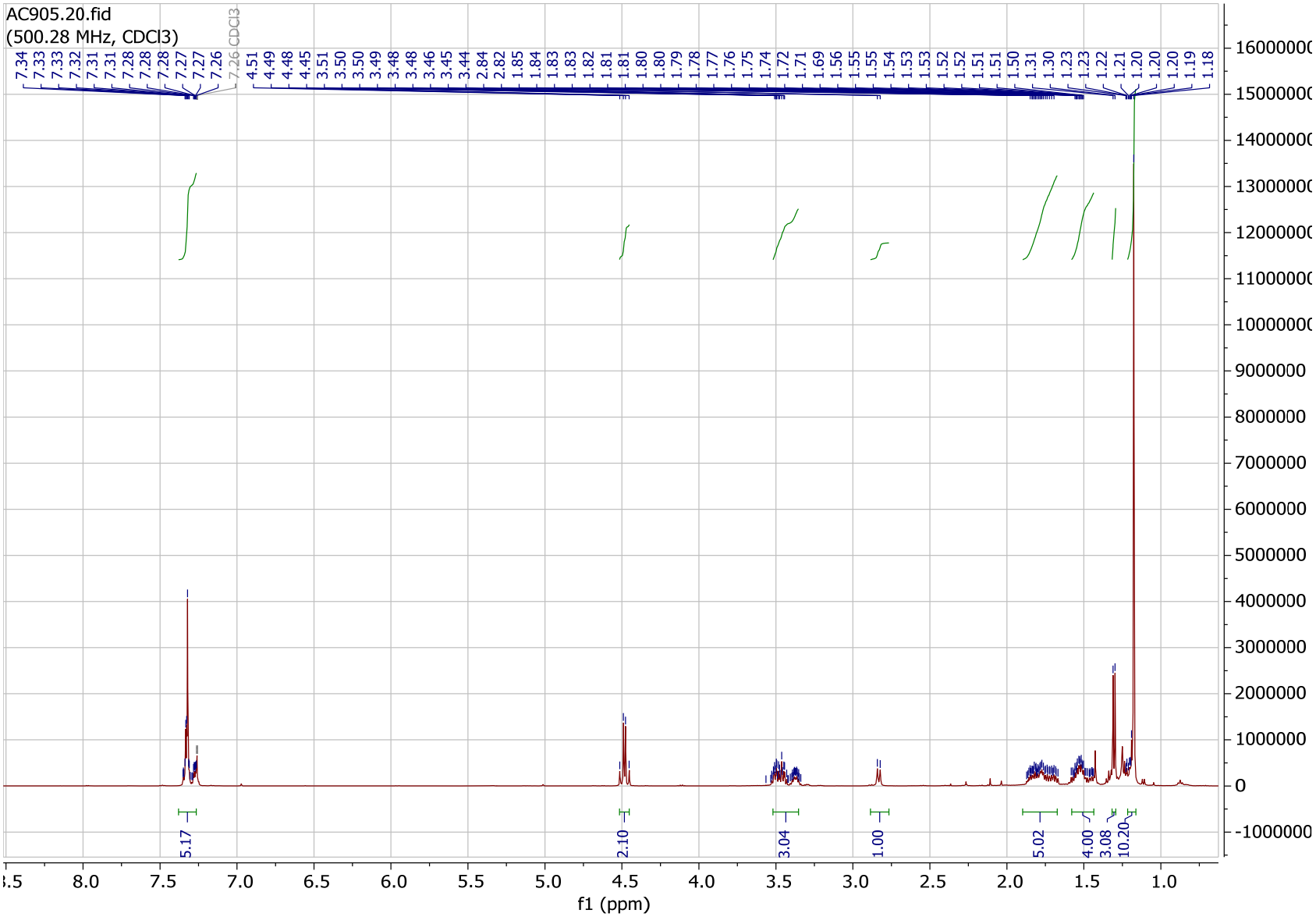

AC904prepF1.12.1.1r
172.40
138.61
128.47
127.68
127.64
77.16 CDCl3
73.01
69.35
56.58
52.24
41.16
34.84
32.66
30.12
24.74
22.53
1.2×10^11
1.1×10^11
1.0×10^11
9.0×10^10
8.0×10^10
7.0×10^10
6.0×10^10
5.0×10^10
4.0×10^10
3.0×10^10
2.0×10^10
1.0×10^10
0.0
-1.0×10^10
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

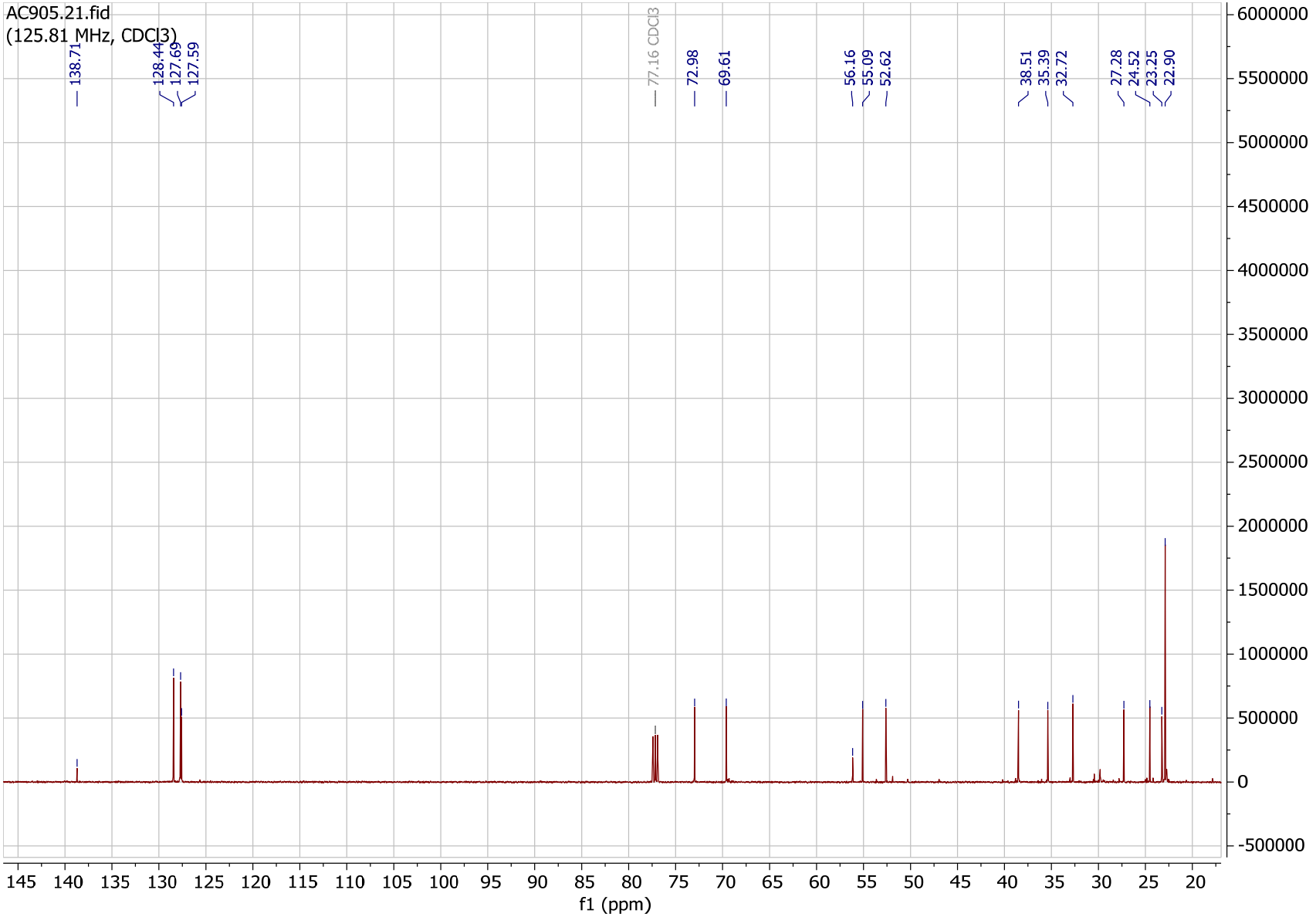
(*R*)-2-Methyl-*N*-{(S)-1-[(1*S*,2*S*)-2-phenylcyclopentyl]ethyl}propane-2-sulfinamide 8a



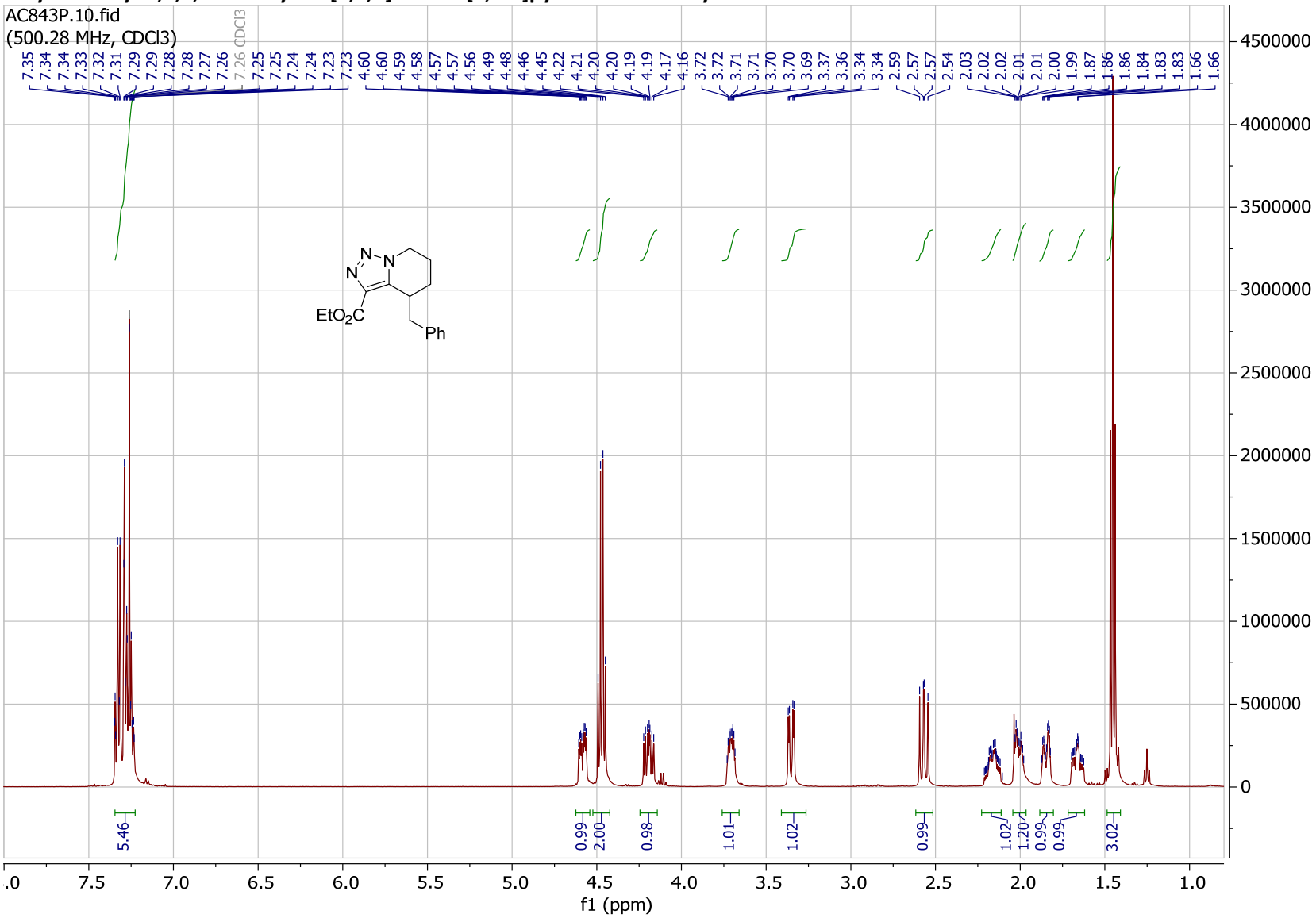

AC895PP.11.fid
(125.81 MHz, CDCl3)
145.48
128.68
127.77
126.26
77.16 CDCl3
56.08
54.73
54.51
48.17
36.25
27.48
24.72
22.89
22.73
Ph
HN
CH3
O=S
f1 (ppm)

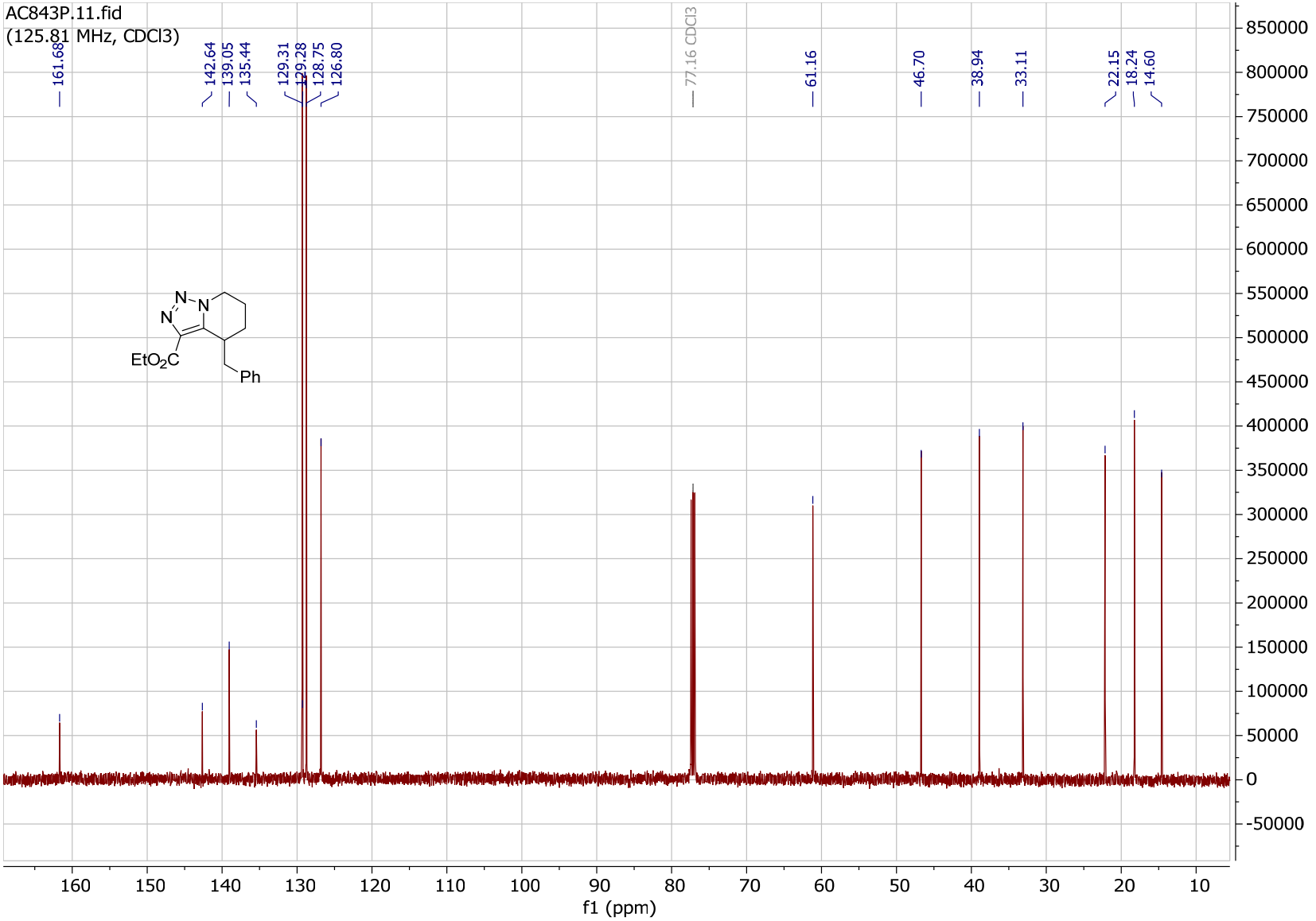
(S)-*N*-((*S*)-1-{(1*S*,2*R*)-2-[2-(Benzyloxy)ethyl]cyclopentyl}ethyl)-2-methylpropane-2-sulfinamide 8l



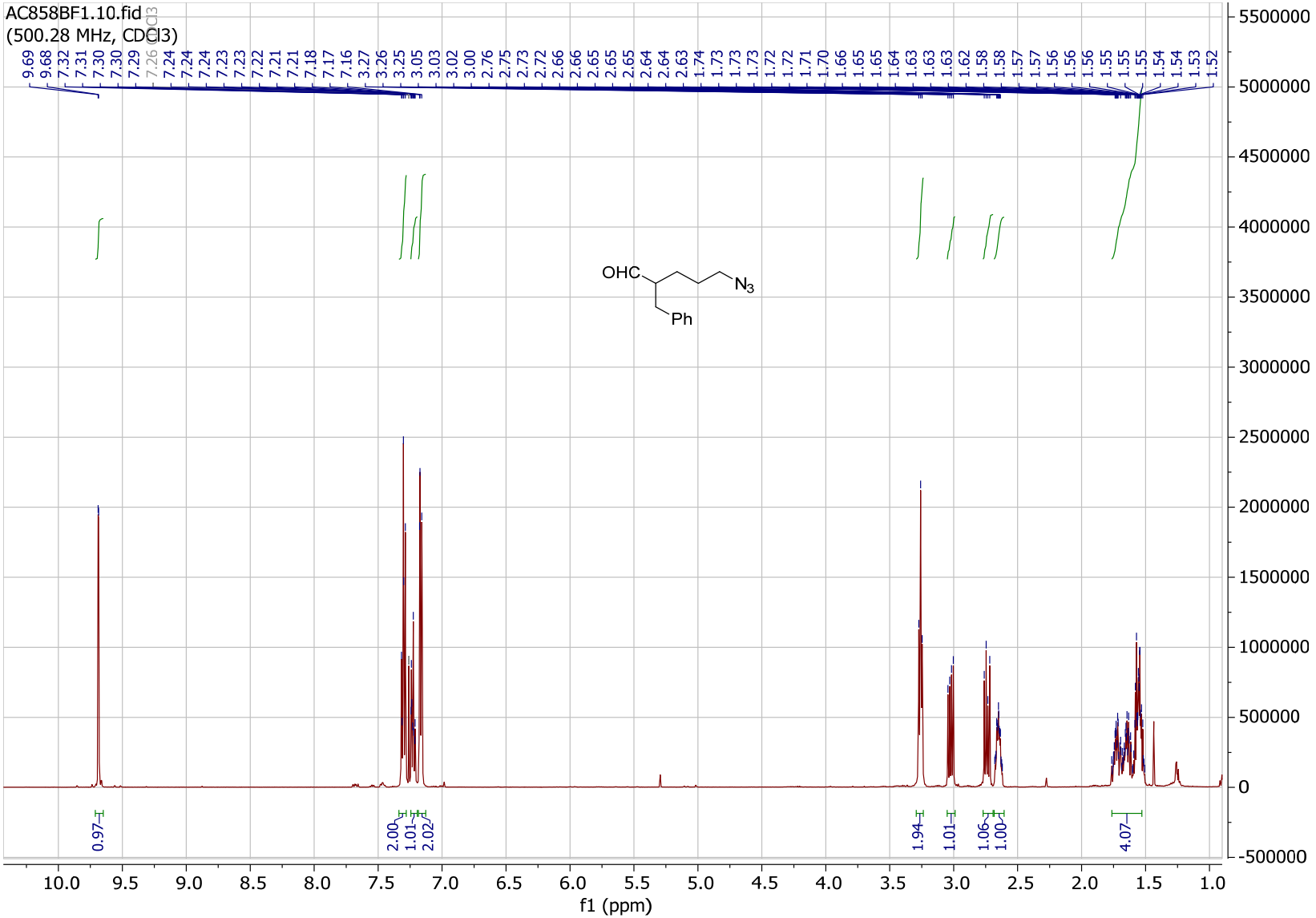

AC905.21.fid
(125.81 MHz, CDCl3)
138.71
128.44
127.69
127.59
77.16 CDCl3
72.98
69.61
56.16
55.09
52.62
38.51
35.39
32.72
27.28
24.52
23.25
22.90
6000000
5500000
5000000
4500000
4000000
3500000
3000000
2500000
2000000
1500000
1000000
500000
0
-500000
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20
f1 (ppm)

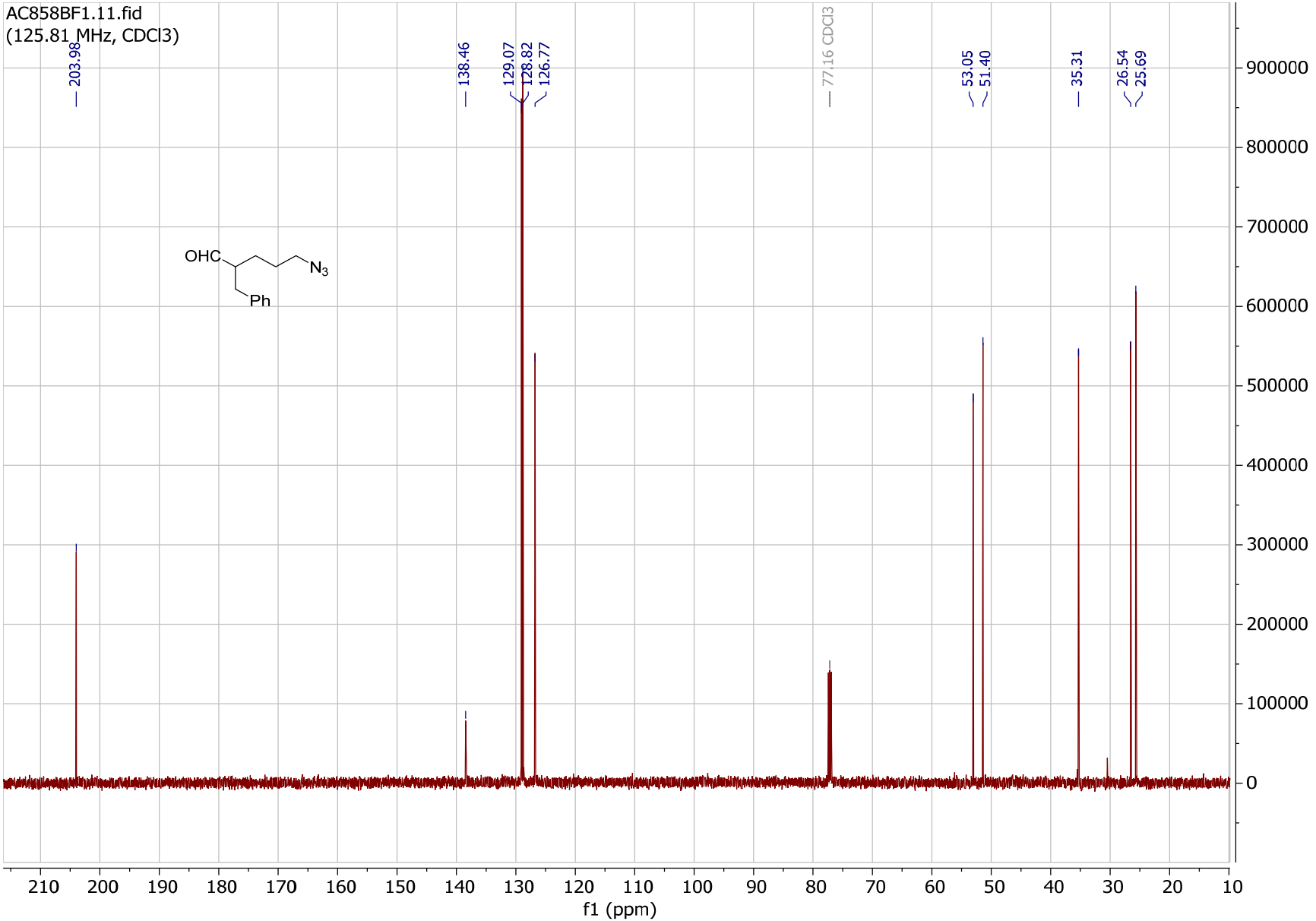
Ethyl 4-benzyl-4,5,6,7-tetrahydro-[1,2,3]triazolo[1,5-a]pyridine-3-carboxylate 9



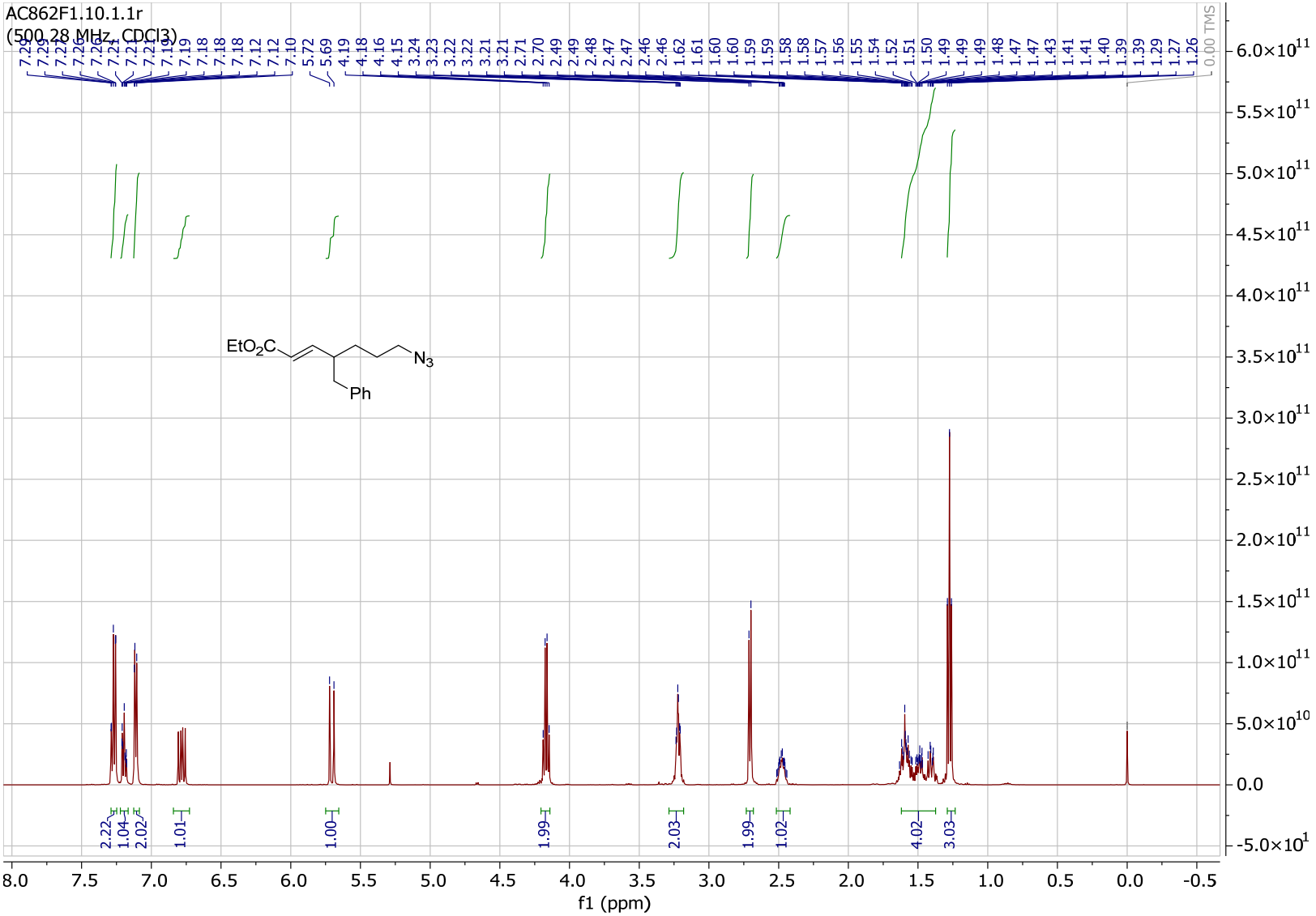

AC843P.11.fid
(125.81 MHz, CDCl3)
161.68
142.64
139.05
135.44
129.31
129.28
128.75
126.80
77.16 CDCl3
61.16
46.70
38.94
33.11
22.15
18.24
14.60
N
N
N
EtO2C
Ph
850000
800000
750000
700000
650000
600000
550000
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

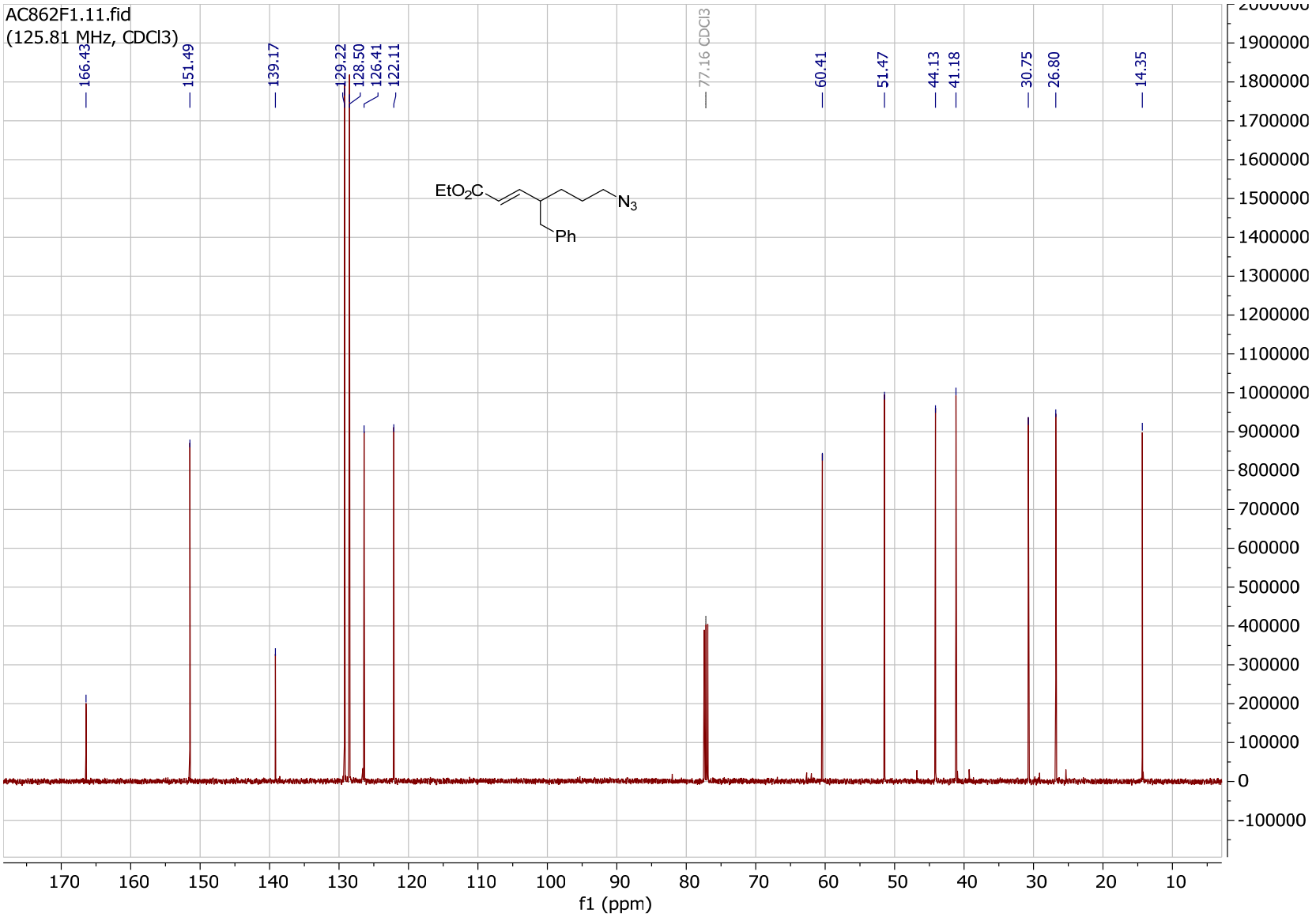
5-Azido-2-benzylpentanal 10



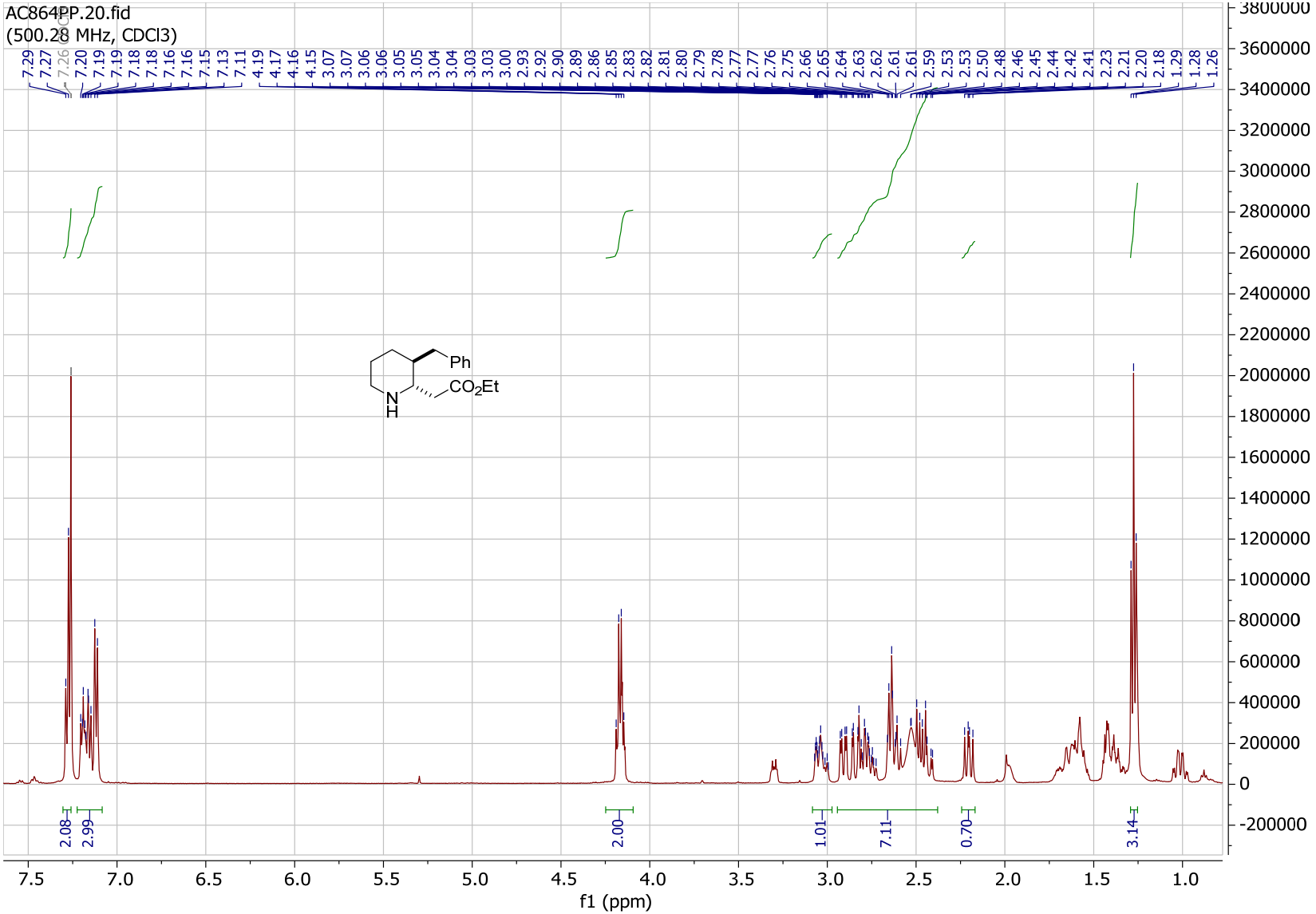

AC858BF1.11.fid
(125.81 MHz, CDCl3)
203.98
138.46
129.07
128.82
126.77
77.16 CDCl3
53.05
51.40
35.31
26.54
25.69
OHC
N3
Ph
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

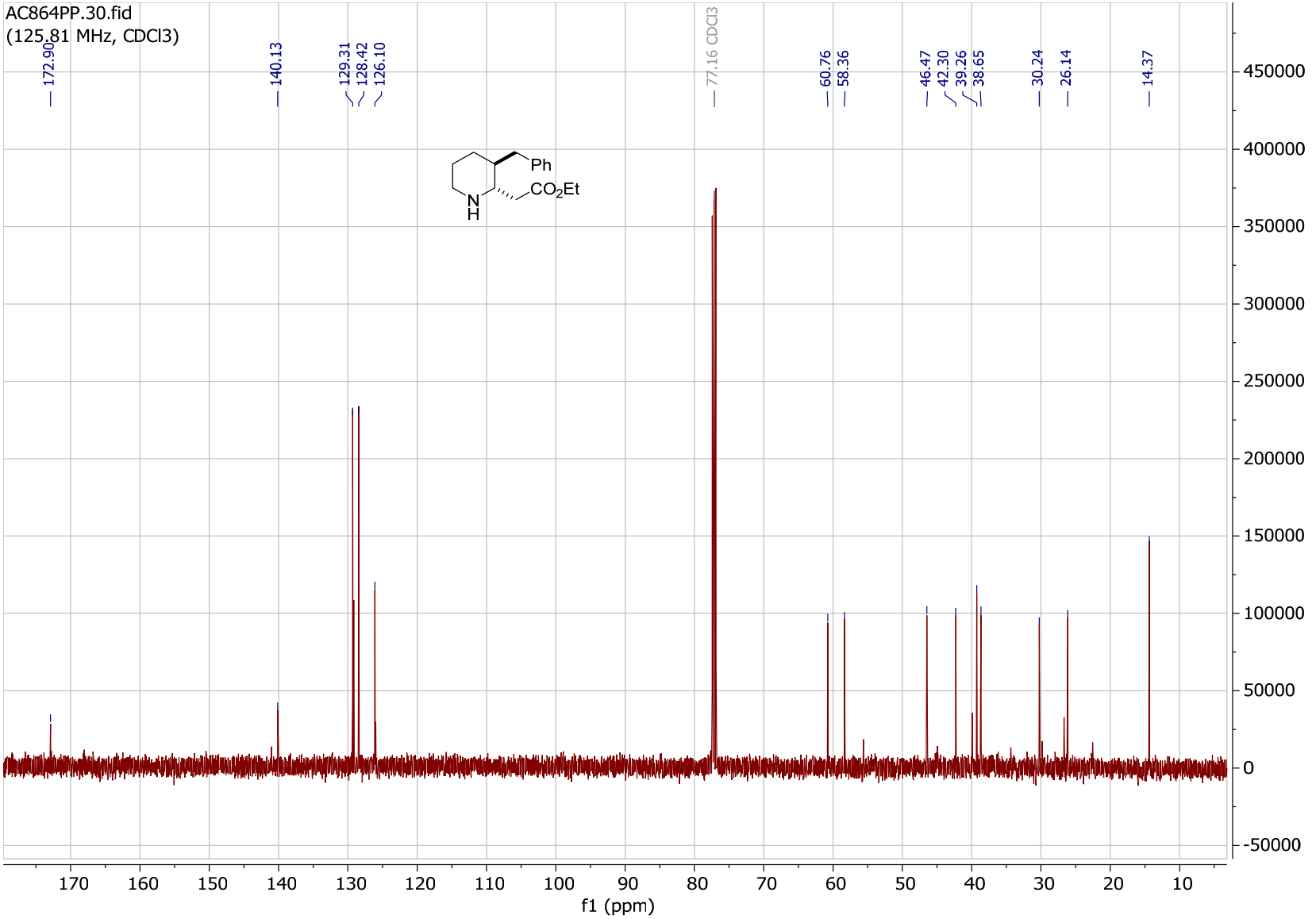
Ethyl (*E*)-7-azido-4-benzylhept-2-enoate 11



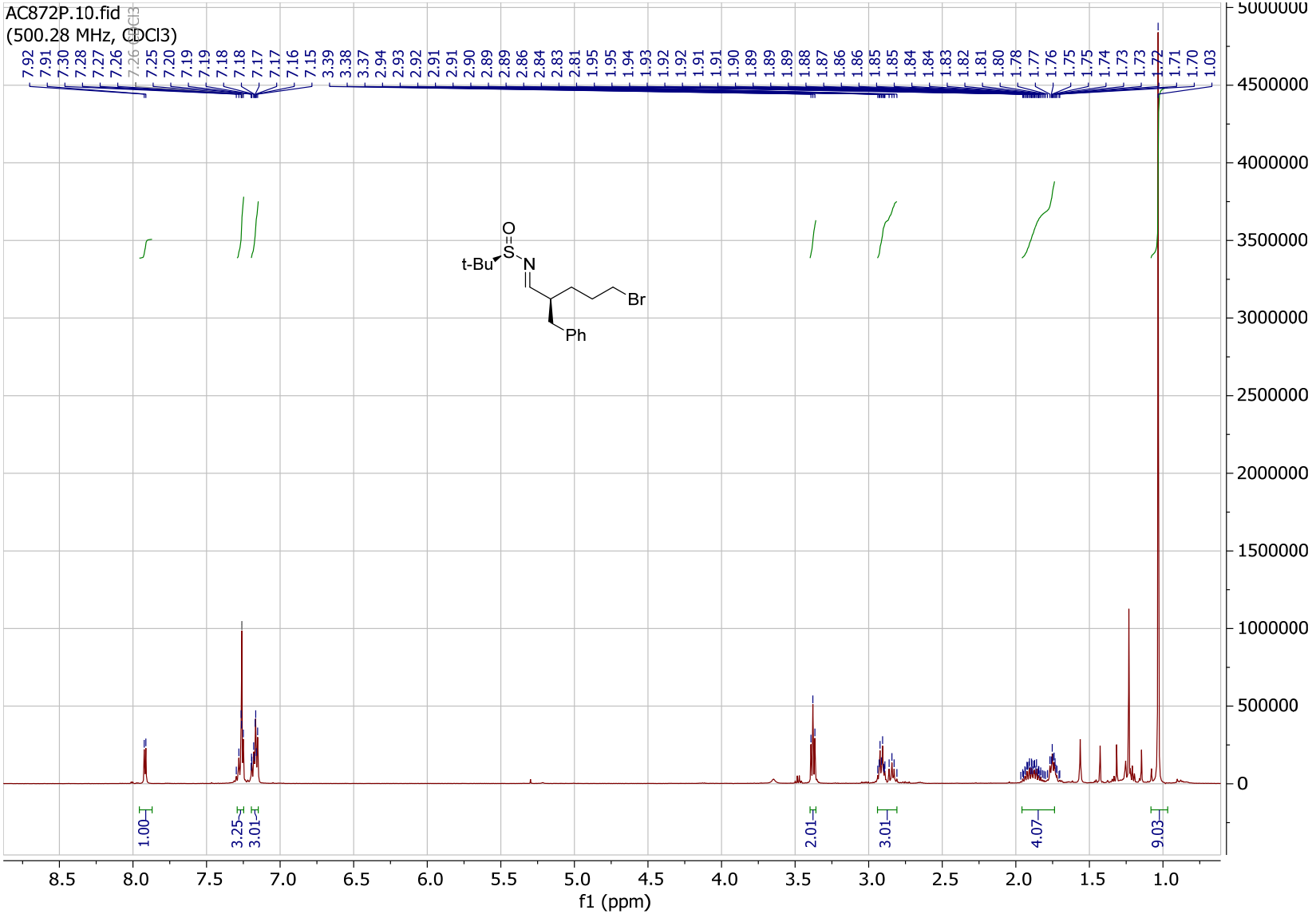

AC862F1.11.fid
(125.81 MHz, CDCl3)
166.43
151.49
139.17
129.22
128.50
126.41
122.11
77.16 CDCl3
60.41
51.47
44.13
41.18
30.75
26.80
14.35
EtO2C
N3
Ph
f1 (ppm)

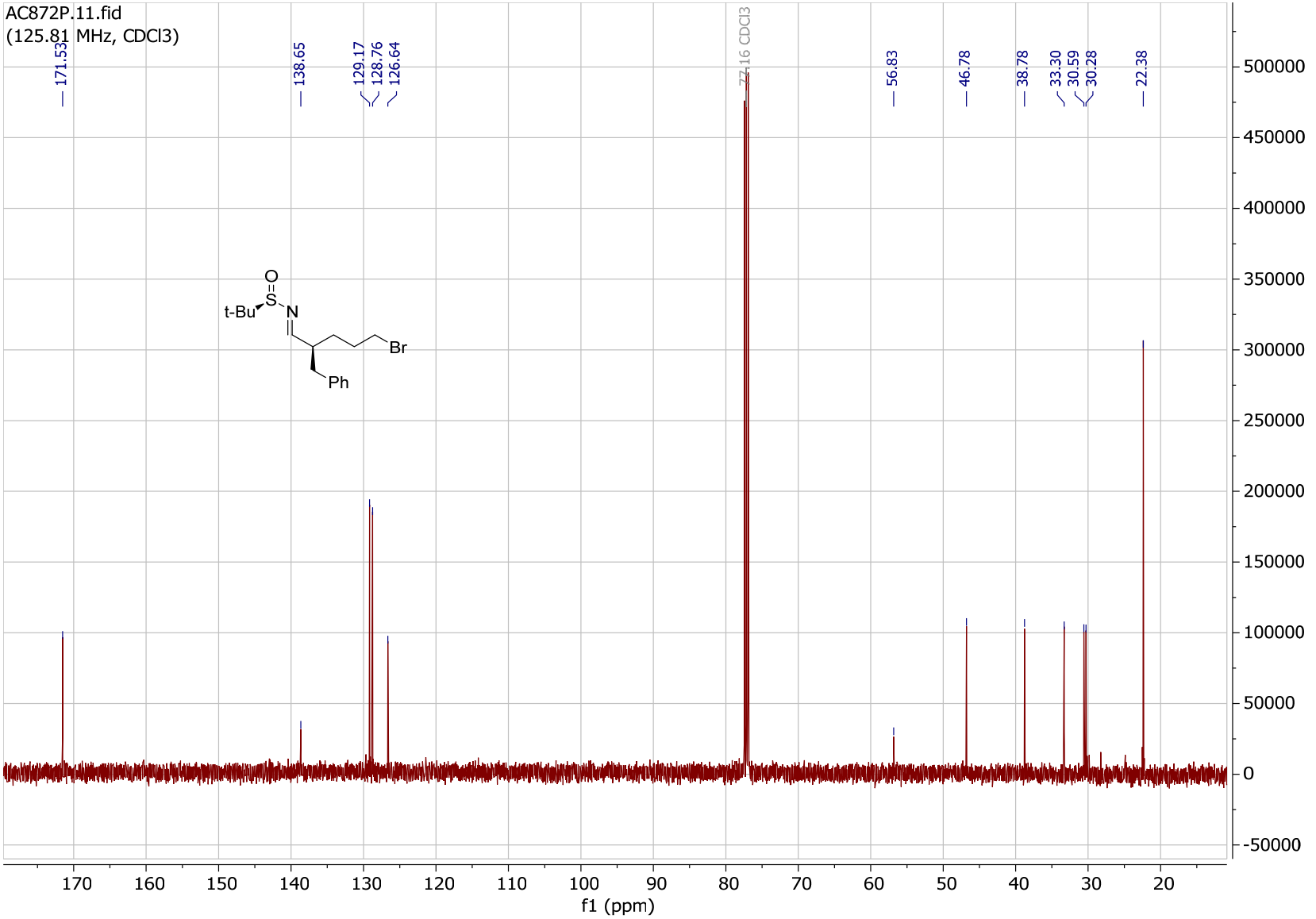
Ethyl 3-benzylpiperidine-2-carboxylate 12



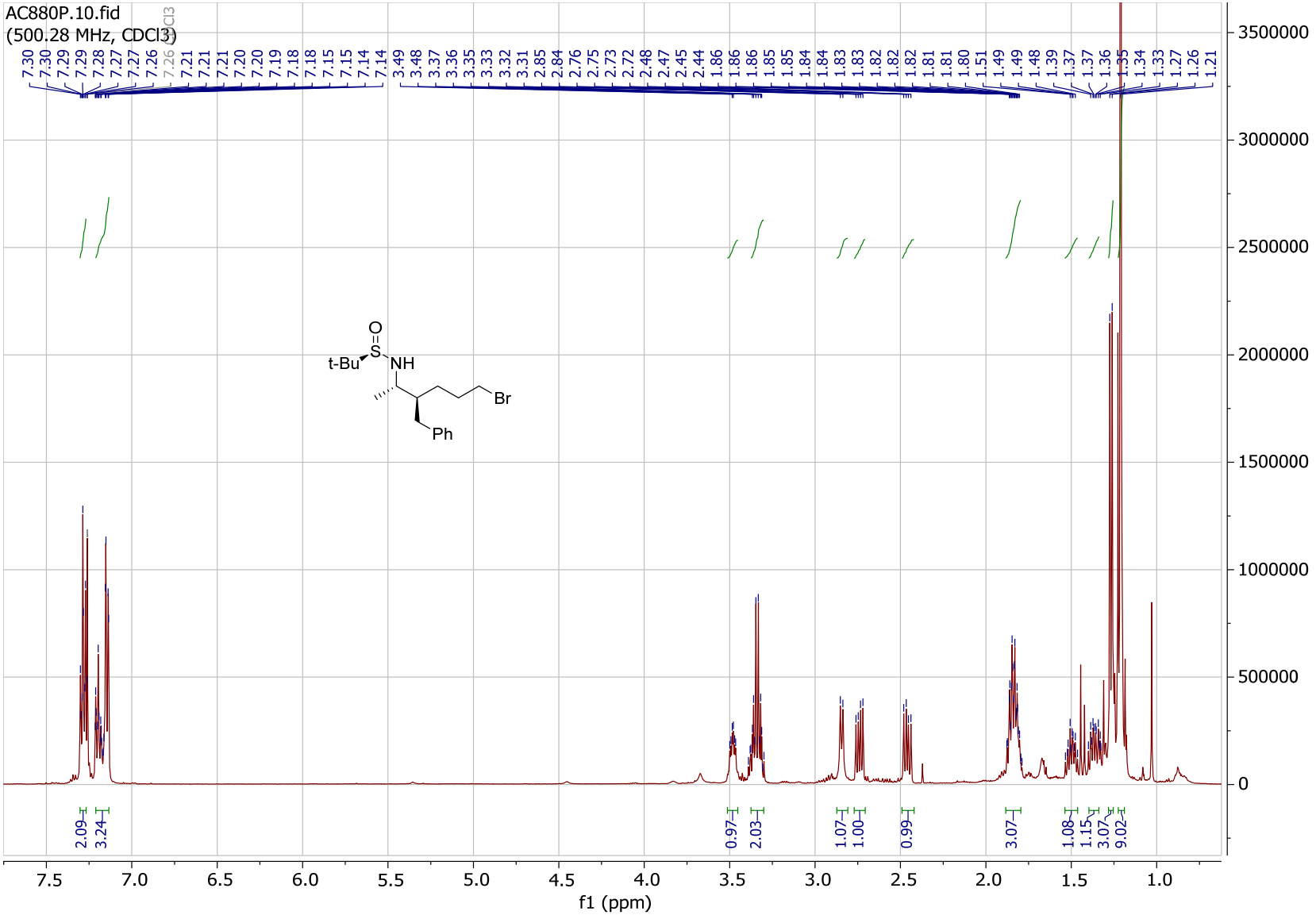

AC864PP.30.fid
(125.81 MHz, CDCl3)
172.90
140.13
129.31
128.42
126.10
77.16 CDCl3
60.76
58.36
46.47
42.30
39.26
38.65
30.24
26.14
14.37
Ph
CO2Et
N
H
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

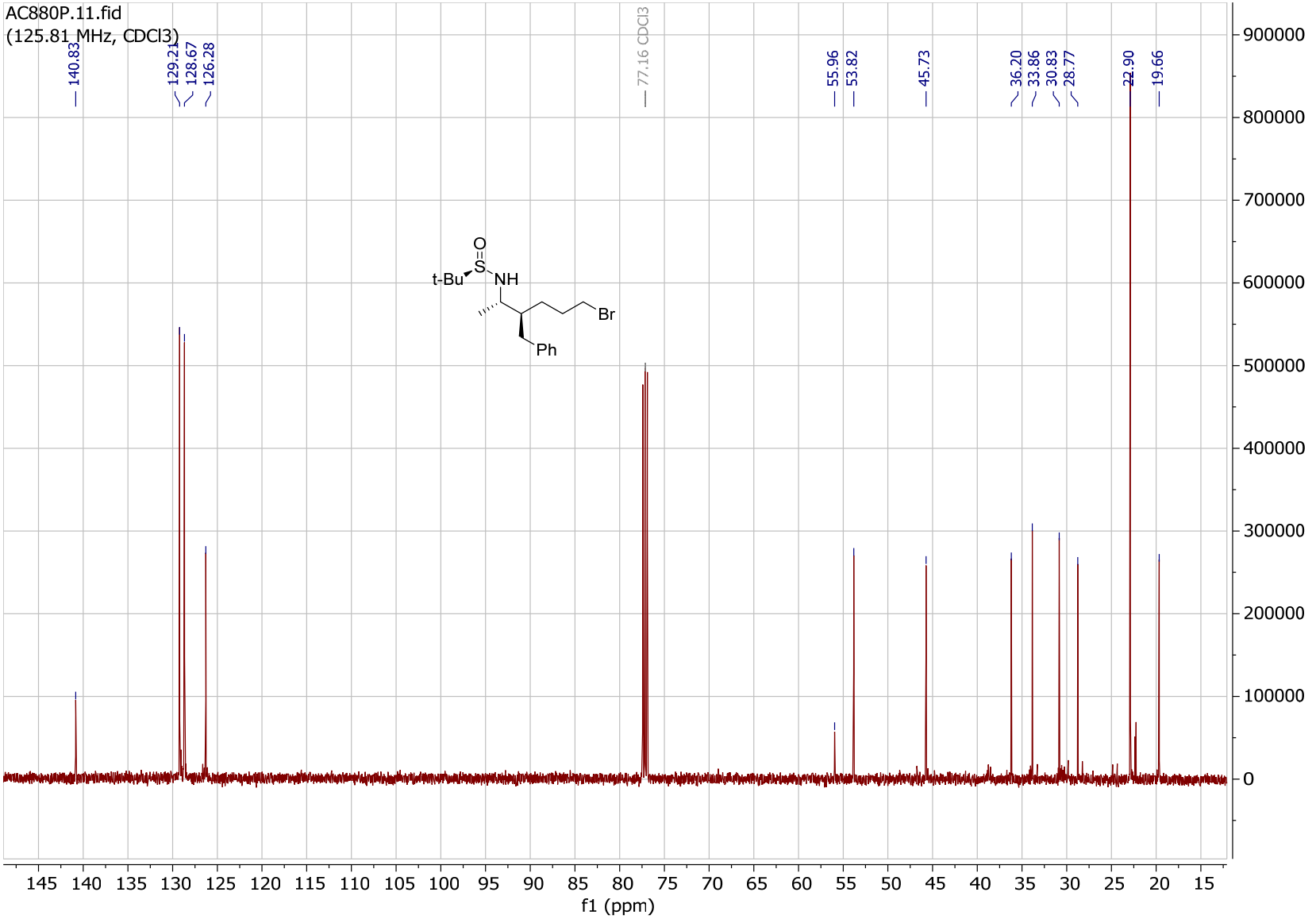
(*R*)-*N*-[(*S*,E)-2-Benzyl-5-bromopentylidene]-2-methylpropane-2-sulfinamide 13



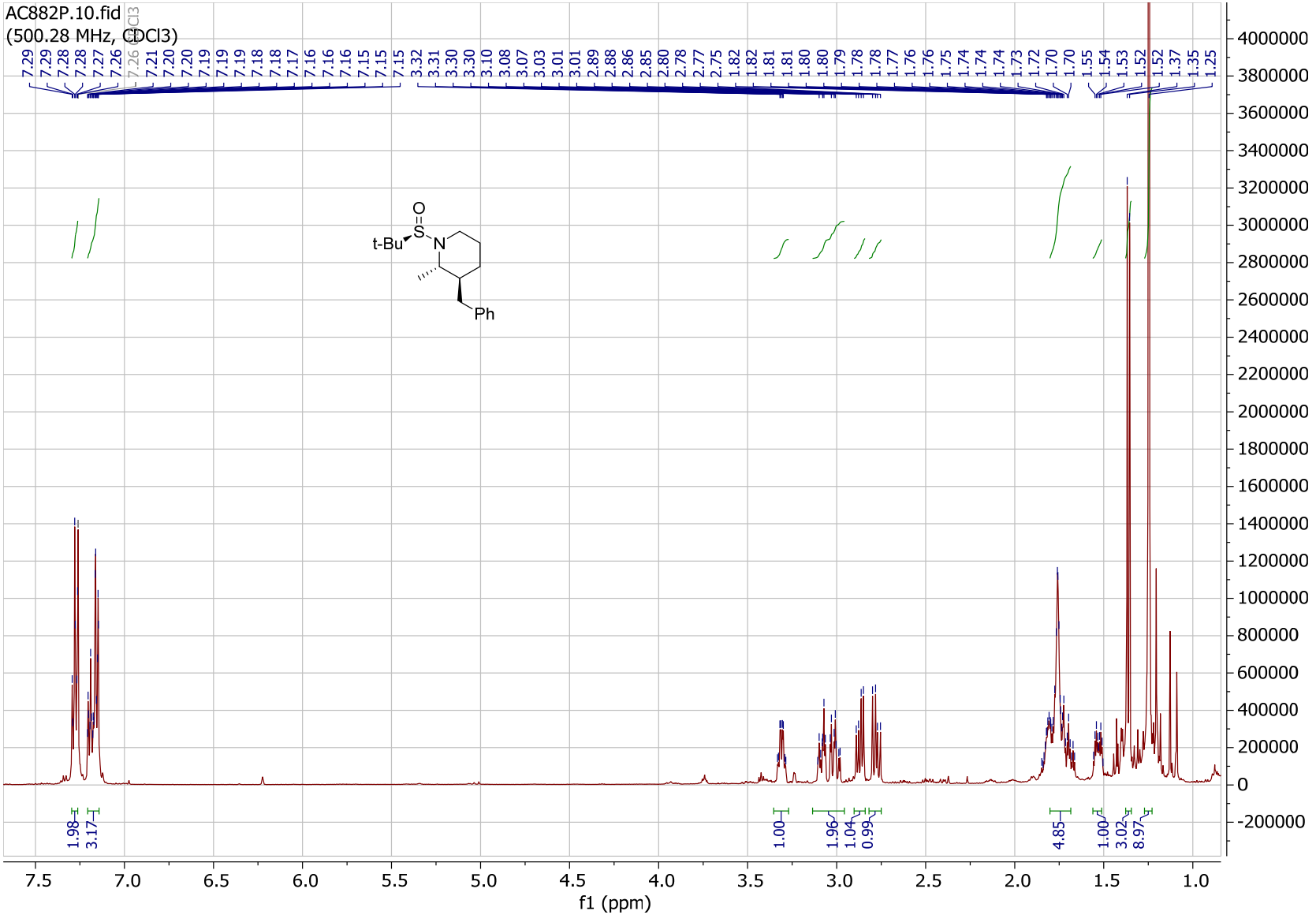

AC872P.11.fid
(125.81 MHz, CDCl3)
171.53
138.65
129.17
128.76
126.64
77.16 CDCl3
56.83
46.78
38.78
33.30
30.59
30.28
22.38
t-Bu
O
S
N
Br
Ph
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
-50000
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)

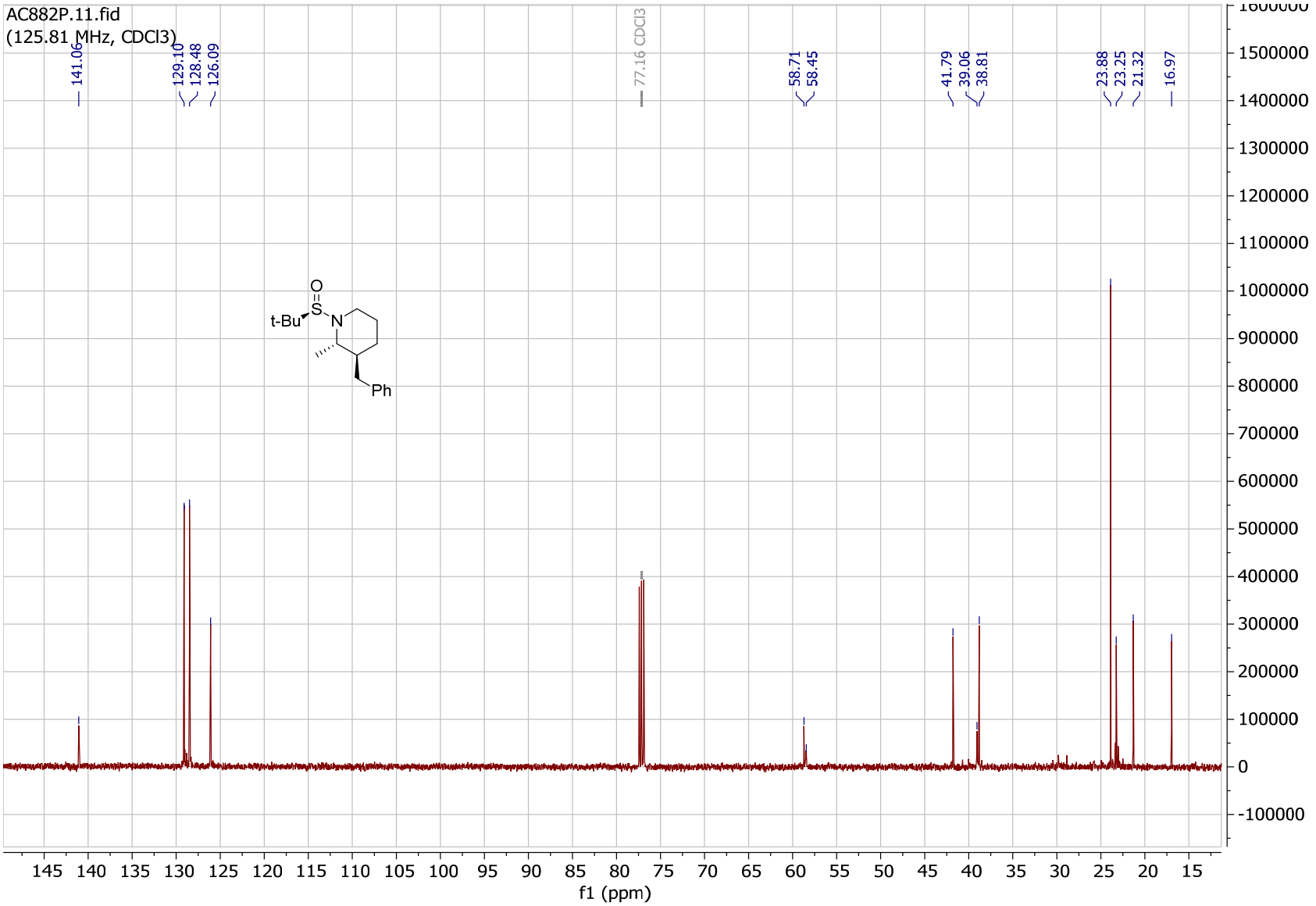
(*R*)-*N*-[(2S,3S)-3-Benzyl-6-bromohexan-2-yl]-2-methylpropane-2-sulfinamide 14




AC880P.11.fid
(125.81 MHz, CDCl3)
140.83
129.21
128.67
126.28
77.16 CDCl3
55.96
53.82
45.73
36.20
33.86
30.83
28.77
22.90
19.66
O
S
NH
t-Bu
Br
Ph
900000
800000
700000
600000
500000
400000
300000
200000
100000
0
145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15
f1 (ppm)

(2*S*,3*S*)-3-Benzyl-1-[(*R*)-*tert*-butylsulfinyl]-2-methylpiperidine 15




AC882P.11.fid
(125.81 MHz, CDCl3)
141.06
129.10
128.48
126.09
77.16 CDCl3
58.71
58.45
41.79
39.06
38.81
23.88
23.25
21.32
16.97
t-Bu
O
S
N
Ph
f1 (ppm)