Supporting Informations

A Radical Exchange Process: Synthesis of BCP Derivatives of Functionalized Xanthates

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General information:

Xanthate reactions were performed in a seal tube. DCE used in these reactions was purchased from Acros (99.9% extra dry AcrosealTM). Otherwise, [1.1.1] Propellane was prepared according to the literature reports. DLP was purchased from VWR or Acros. Other commercial reagents were purchased from Acros, Fluorochem, TCI, Sigma-Aldrich, VWR or Alfa-Aesar and used as received. Thin Layer Chromatography were performed on aluminium plates bearing a 0.25 mm of Merck Silica Gel 60F254, visualized by fluorescence quenching at 254 nm and chemical revelation using acidic solution of paraanisaldehyde or basic solution of potassium permanganate. Flash chromatography was performed using silica gel 60 (40-63 µm). NMR analysis was performed at room temperature on Bruker 300 MHz Fourier Transform Spectrometer. Residual solvent peaks of $CDCl_3$ were used as internal references: 7.26 ppm for 1H spectra and 77.18 ppm for 13C spectra. Chemical shifts (δ) are reported in ppm and spin-spin coupling constants (J) are given in Hz. The following abbreviations were used in order to describe de peaks multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, quint = quintuplet, hex = hexuplet, hept = heptuplet, m = multiplet, br = broad. HRMS spectra

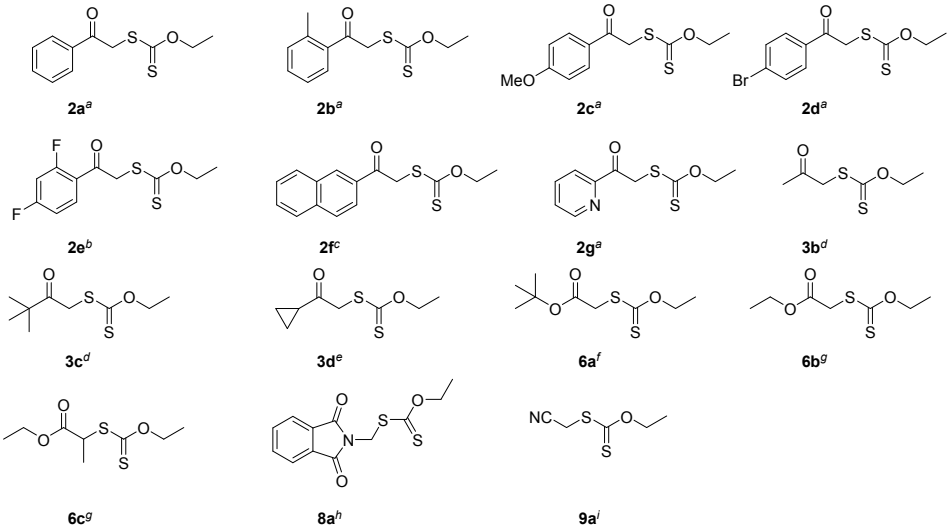
were recorded using Thermo Scientific QExactive. Infrared absorptions were recorded as a liquid deposition on a ZnSe crystal on a Shimadzu FTIR 8400 Spectrophotometer.

Preparation of the Solution of [1.1.1]Propellane in Diethyl Ether[5b(reference in manuscript)]**:**

In a dry round bottom flask 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (2 g, 3.41 mmol) was mixed with Et_2O (6.5 mL) and the flask was placed into an isopropanol/dry ice bath (T = −45 °C). Phenyllithium (7.6 mL, 6.82 mmol, 1.8M in dibutyl ether) was added dropwise via syringe. When the addition had been complete, the mixture was stirred for 5 min more at −45 °C and then the bath was replaced with an ice bath. After 2 h, a distillation started at 200 mbar while the reaction flask was still in the ice bath. The collector Schlenk tube was immersed into an acetone/dry ice bath (T = −78 °C). Pressure was gradually lowered to 120 mbar and then the reaction flask was removed from the ice bath. Then, pressure was gradually lowered to 45 mbar approx after 15 min the distillation was stopped and the system was filled with argon. Total volume of the solution collected is 4.5 mL. An aliquot (0.1 mL) of the solution was analyzed by NMR\ with CH_2Cl_2 as a standard. Average concentration of [1.1.1]propellane is 0.6–0.8 M. The solution was stored at −25 °C.

Xanthate Synthesis:

The following Xanthates are readily made by displacement of bromide or chloride group from commercially available α–halogenetaed ketones with O-Ethyl- xanthogante potassium salts.



General Procedure for the Synthesis of Xanthates (2a, 2b, 2c, 2d, 2e, 2f, 2g, 3b, 3c, 3d, 6a, 6b, 6c, 8a, 9a):

A solution of alpha halo ketone (1 equiv.) in acetone was added to a stirred suspension of KSCSOEt (1.2 equiv) in acetone (1M) at 0 °C to room temperature, and stirring was continued for 5-6 h. Acetone was removed under reduced pressure, water was added, and the mixture was extracted with DCM solution, was washed with brine, dried, and the solvent evaporated. The crude product was purified by recrystallization or flash chromatography on silica gel.

[a]A. Cordero-Vargas, I. Pérez-Martín, B. Quiclet-Sire and S. Z. Zard, *Org. Bio. Chem*, 2004, **2**, 3018.

[b]J. Boivin , P. Boutillier and S. Z. Zarda *Tetrahedron Lett*. 1999, **40**, 2529

[c]R. F. Guignard and S. Z. Zard *Chem. Commun*., 2011, **47**, 12185

[d]M. D. Brown, D. W. Gillon, G. D. Meakins," and G. H. Whitham. *Journal of the Chemical Society, Perkin Transactions 1: Organic and Bio-Organic Chemistry,* 1985, 1, 1623

[e]H. Hayashi, A. Kaga, B. Wang, F. Gagoszb and S. Chiba, *Chem Comm*, 2018, **54**, 7535

[f]S. R. Woulfe and M. J Miller. *J. Org.Chem*, 1986, **51**, 3133

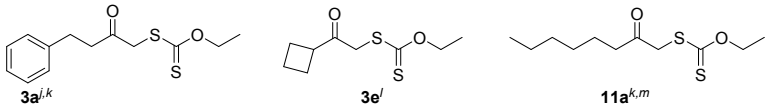
[g]S. Wang, X. Huang, Y. Wen, Z. Ge, X. Wang and R. Li *Tetrahedron*, 2015, **71**, 8117

[h]Z. Huang and J. Xu *Tetrahedron*, 2013, **69**, 1050

[i]S. Kakaei , N. Chen , J. Xu, *Tetrahedron*, 2013, **69**, 302

Xanthate Synthesis:

The Ethyl Xanthates (**3a, 3e, 11a**) were synthesized in two steps, commercially available ketones undergoes bromination in presence of acetic acid, then displacement of the bromine group with O-Ethyl- xanthogante potassium salts.



3a[j,k] **3e**[l] **11a**[k,m]

General Procedure for the Synthesis of Xanthates (3a, 3e, 11a):

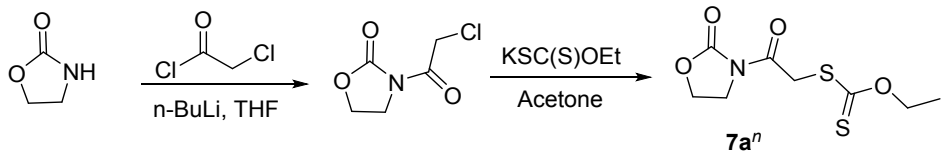
Acetophenone is dissolved in acetic acid and bromine is added dropwise to this solution. After complete decolouration from brown to pale yellow, the solution is diluted to diethyl ether and washed with three times with a saturated solution of $NaHCO_3$ aq., washed with brine solution, dried on a Na_2SO_4 and concentrated under vacuum. The crude is then dissolved in acetone and O-ethyl xanthogenoate potassium salts is added portion wise at 0 °C. At the end of the addition the temperature is brought into room temperature and the acetone was removed under vacuum. The crude is taken up in DCM and washed with water three times water and one time with NH_4Cl solution, dried over Na_2SO_4 and concentrated under vacuum. The resulting crude was then purified by a flash chromatography on silica gel or by recrystlaization, using the appropriate eluent.

[j]MIRAE FINE CHEMICAL CO LTD[KR]; J. H. Jeong, Y. L. Sim, W. L. Yang, S. K. Hwang, J. H. Park and S. H. Choe, *KR2017/25682*, 2017, A.

[k]H. Jullien, B. Quiclet-Sire, T. Te´tart and S. Z. Zard *Org. Lett.*2014, 16, 1302

[l]L. Debien and S. Z. Zard *J. Am. Chem. Soc*. 2013, **135**, 3808

[m]Y. Jiang, Y. Wang, J. Yang, J. hua, B. Wang, S. Qian and H. Tian *Journal of Polymer Science, Part A: Polymer Chemistry*, 2011, **49** 1830



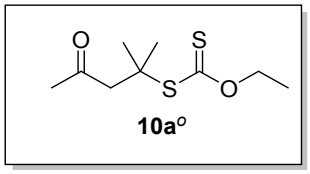
7a[n]

Procedure for the synthesis Synthesis of Xanthates 7a:

A stirred solution of oxazolidin-2-one in dry THF at -10 °C and under nitrogen, then dropwise 1.6 M solution of n-BuLi in hexane was added. Chloroacetyl chloride was then added dropwise. After 15 min of stirring, the reaction mixture was poured into a mixture of a saturated solution of NH_4Cl. The aqueous layer was extracted with EtOAc and the combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel. Under nitrogen, KSC(S)OEt were slowly added to a stirred solution containing 1 3-(2-chloroacetyl)oxazolidin-2-one in acetone. After a few minutes of stirring, the solvent was removed under reduced pressure. The residue was dissolved in EtOAc and washed with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed under reduced pressure to give a yellow solid. Recrystallisation from heptane–EtOAc afforded the compound as colourless.

[n]E. Bacqué, F. Pautratb and S. Z. Zard *Chem Comm*, 2002, **20**, 2312

Procedure for the synthesis Synthesis of Xanthates 10a:



10a[o]

Mesityl oxide was treated with excess amount of potassium O-ethylxanthate in a mixture of dichloromethane and acetic acid at 0 °C for 12 hours resulted in the clean formation of the michael addition product.

[o]G. Binot, B. Quiclet-Sire, T. Saleh, S. Z. Zard Synlett 2003, 3, 382

General Procedure for the Synthesis of BCP Xanthate moiety for aromatic substrates:

A Flame dried seal tube was loaded with the xanthate (1 equiv.) in DCE (the amount of DCE was calculated in order to obtain a final concentration of 2.0 M of xanthate after the addiction of the diethylether solution of propelane) and [1.1.1] Propellane (0.6~ 0.8 M in Et_2O, 2.0 equiv) was added to the solution. The DLP (0.1 equiv) for were added to the resulting solution. The mixture was put in to a preheated oil bath 80 ^oC for 8 to 10 h. After completion, the reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

General Procedure for the Synthesis of BCP Xanthate moiety for aliphatic substrates:

A Flame dried seal tube was loaded with the xanthate (1 equiv.) in DCE (the amount of DCE was calculated in order to obtain a final concentration of 2.0 M of xanthate after the addiction of the diethylether solution of propelane) and [1.1.1] Propellane (0.6~ 0.8 M in Et_2O, 2.0 equiv) was added to the solution. The DLP (0.2 equiv) for were added to the resulting solution. The mixture was put in to a preheated oil bath 80 ^oC for 8 to 10 h. After completion, the reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel to yield the desired compounds.

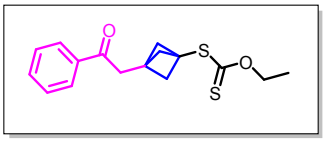
***O*-Ethyl S-(3-(2-oxo-2-phenylethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate(4a):**

$C_{16}H_{18}O_2S_2$, crystal dimensions 0.25 x 0.23 x 0.07 mm, M_r = 306.42, monoclinic, space group Pn, a = 5.43658(16), b = 5.70292(17), c = 25.1230(6) Å, α = 90 ^{o}, β = 93.371(2) ^{o}, γ = 90 ^{o}, V = 777.58(4) Å^3, Z = 2, ρ_{calcd} = 1.309 mg/m^3, μ = 0.341 mm^{-1}, F(000) = 324, reflection collected / unique = 2525 / 2482, refinement method = full-matrix least-squares on F^2, final R indices [I

> 2σ(*I*)]: $R_1 = 0.0253$, $wR_2 = 0.0680$, *R* indices (all data): $R_1 = 0.0262$, $wR_2 = 0.0688$, goodness of fit = 1.076. CCDC-1911714 for *O*-Ethyl S-(3-(2-oxo-2-phenylethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate**(4a)** contains the supplementary crystallographic data for this paper.

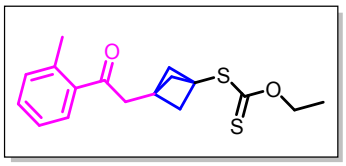
Spectral Data

O-ethyl S-(3-(2-oxo-2-phenylethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate(4a):



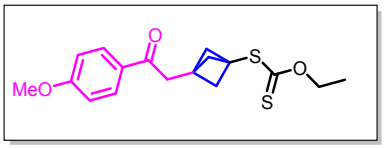
Procedure A: Yield: 47 mg (61%), mp: 47 °C as a white solid: A Flame dried seal tube was loaded with the O-ethyl S-(2-oxo-2-phenylethyl) carbonodithioate (**1**) (61.3 mg, 1 equiv.) in DCE 0.5 mL and [1.1.1] Propellane (**a**) (0.85 mL, 0.6 M in Et_2O, 2.0 equiv) was added to the solution. The DLP (10.2 mg, 0.1 equiv.) were added to the resulting solution. The mixture was put in to a preheated oil bath 80 °C for 10 h. After completion, the reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with the eluent system (9.9: 0.1 PE/EtOAc) to yield the desired compounds. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.89–7.92 (m, 2H), 7.55-7.61 (m, 1H), 7.44–7.50 (m, 2H), 4.65 (q, 1H, J = 7.1 Hz)), 3.24 (s, 2H), 2.20 (s, 6H), 1.45 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.4, 197.9, 137.0, 133.4, 128.7, 128.3, 69.5, 55.5, 41.0, 40.4, 40.0, 13.9; IR (KBr): 2995, 1681, 1448, 1357, 1286, 1215, 1132, 1188, 1047, 999, 889, 858, 773, 744, 713, cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{18}O_2S_2$ (MH^+) 307.08210.; found 307.08169.

O-ethyl S-(3-(2-oxo-2-(o-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4b):



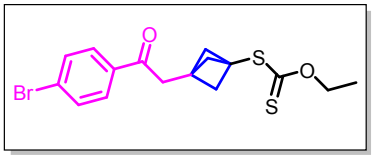
Following the standard **procedure A** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (35 mg, 44%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.57 (t, 1H, J = 7.6 Hz), 7.35-7.41 (m, 1H), 7.23-7.28 (m, 2H), 4.64 (q, 2H, J = 7.1 Hz), 3.16 (s, 2H), 2.50 (s, 3H), 2.15 (s, 6H), 1.45 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 201.9, 138.4, 137.9, 132.2, 131.7, 128.9, 125.8, 69.5, 55.5, 43.4, 41.0, 40.2, 21.4, 13.9; IR (KBr): 2977, 2916, 2878, 1683, 1454, 1213, 1187, 1130, 1111, 1045, 998, 889, 857, 769, 753 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{20}O_2S_2$ (MH^+) 321.09775; found 321.09781.

_O_-ethylS-(3-(2-(4-methoxyphenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4c):



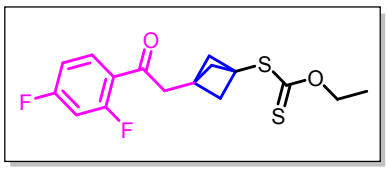
Following the standard **procedure A** flash chromatography: PE/EtOAc 9.8:0.2, Yield: (45 mg, 53%) as a yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.90 (d, 2H, J = 8.9 Hz), 6.95 (d, 2H, J = 8.9 Hz), 4.65 (q, 2H, J = 7.1 Hz), 3.87 (s, 3H,), 3.17 (s, 2H), 2.18 (s, 6H), 1.45 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.5, 196.5, 163.7, 130.7, 130.1, 113.9, 69.5, 55.6, 55.5, 40.9, 40.3, 40.2, 13.9; IR (KBr): 2997, 1672, 1508, 1258, 1223, 1112, 1048, 984, 852, 802 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{20}O_3S_2$ (MH^+) 337.09266; found 337.09263.

_S_-(3-(2-(4-bromophenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (4d):



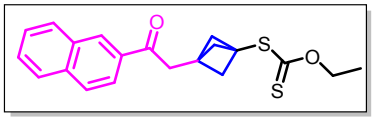
Following the standard **procedure A** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (60 mg, 62%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.78 (d, 2H, J = 8.6 Hz), 7.62 (d, 2H, J = 8.6 Hz), 4.65 (q, 2H, J = 7.1 Hz), 3.20 (s, 2H), 2.19 (s, 6H), 1.46 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.4, 196.8, 135.7, 132.1, 129.8, 128.7, 69.5, 55.5, 41.0, 40.4, 39.9, 14.0; IR (KBr): 2861, 2844, 1686, 1583, 1286, 1219, 1176, 1111, 1107, 1043, 982, 889, 805, 745 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{17}BrO_2S_2$ (MH^+) 386.99043; found 386.99013.

_S_-(3-(2-(2,4-difluorophenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl)O-ethyl carbonodithioate (4e):



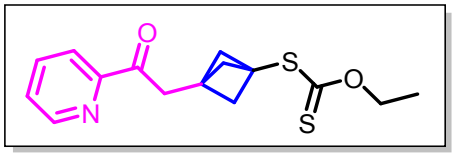
Following the standard **procedure A** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (56 mg, 65%) as a gummy solid: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.86-7.94 (m, 1H), 6.94-7.01 (m, 1H), 6.84-6.91 (m, 1H), 4.66 (q, 2H, J = 7.1 Hz), 3.22 (d, 2H, J = 3.1 Hz), 2.20 (s, 6H), 1.47 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 194.56, 194.50 167.7, 164.45, 164.29, 161.01, 132.92, 132.87, 132.78, 132.73, 130.09, 130.01, 128.3, 127.2, 122.4, 117.59, 117.22, 112.67, 112.43, 105.3, 104.94, 104.60, 69.5, 55.5, 45.0, 44.9, 41.2, 39.8, 13.9; IR (KBr): 2984, 2912, 2878, 1689, 1495, 1427, 1266, 1232, 1196, 1131, 1095, 1047, 1007, 970, 895, 850 cm^{-1}; HRMS (ESI): calcd. for $C_{16}H_{16}F_2O_2S_2$ (MH^+) 343.06325; found 343.06254.

***O*-ethyl S-(3-(2-(naphthalen-2-yl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4f):**



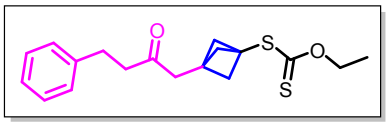
Following the standard **procedure A** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (45 mg, 51%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.40 (s, 1H), 7.87-8.00 (m, 4H), 7.54-7.64 (m, 2H), 4.65 (q, 2H, J = 7.1 Hz), 3.37 (s, 2H,), 2.23 (s, 6H,), 1.45 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 197.9, 135.8, 134.3, 132.6, 130.2, 129.7, 128.8, 128.7, 127.9, 127.0, 123.9, 69.5, 55.6, 41.0, 40.6, 40.2, 13.9; IR (KBr): 3060, 2980, 2912, 2874, 1678, 1469, 1359, 1216, 1185, 1129, 1110, 1044, 999, 890, 858, 811, 745 cm^{-1}; HRMS (ESI): calcd. for $C_{20}H_{20}O_2S_2$ (MH^+) 357.09775; found 357.09764.

***O*-ethyl S-(3-(2-oxo-2-(pyridin-2-yl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4g):**



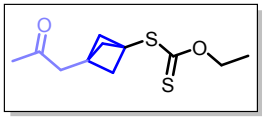
Following the standard **procedure A** flash chromatography: PE/EtOAc 9:1, Yield: (32 mg, 41%) as a gummy: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 8.65-8.68 (m, 1H), 8.01-8.04 (m, 1H), 7.81-7.87 (m, 1H), 7.45–7.50 (m, 1H), 4.66 (q, 2H, *J* =7.2 Hz), 3.50 (s, 2H), 2.19 (s, 6H), 1.46 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.7, 199.6, 153.3, 149.0, 137.2, 127.4, 122.0, 69.5, 55.6, 41.1, 40.0, 39.3, 13.9; IR (KBr): 2969, 2921, 2855, 1697, 1363, 1217, 1187, 1044, 993, 889, 857, 781 cm^{-1}; HRMS (ESI): calcd. for $C_{15}H_{17}NO_2S_2$ (MH^+) 308.07735; found 308.07736.

***O*-ethyl S-(3-(2-oxo-4-phenylbutyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (5a):**



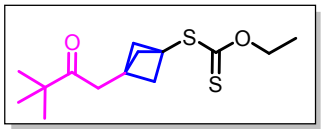
Procedure B: Yield: (32 mg, 38 %), as a yellow oil: A Flame dried seal tube was loaded with the O-ethyl S-(2-oxo-2-phenylethyl) carbonodithioate (**1**) (61.3 mg, 1 equiv.) in DCE 0.5 mL and [1.1.1] Propellane (**a**) (0.85 mL, 0.6 M in Et_2O, 2.0 equiv) was added to the solution. The DLP (20.3 mg, 0.2 equiv.) for were added to the resulting solution. The mixture was put in to a preheated oil bath 80 ^{o}C for 10 h. After completion, the reaction mixture was then cooled down to room temperature and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with the eluent systeam (9.9:0.1, PE/EtOAc) to yield the desired compounds. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.28-7.31 (m, 1H), 7.14–7.24 (m, 4H), 4.65 (q, 2H, *J* = 7.1 Hz), 2.86 (q, 3H, *J* = 7.6 Hz), 2.64-2.73 (m, 4H), 2.14 (d, 5H, *J* = 8.7 Hz), 1.47 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.4, 207.4, 141.0, 128.6, 128.4, 126.3, 69.5, 55.4, 45.2, 44.6, 40.9, 39.6, 29.6, 14.0; IR (KBr): 2993, 1682, 1354, 1283, 1182, 1139, 1045, 1001, 855, 887, 754, cm^{-1}; HRMS (ESI): calcd. for $C_{18}H_{22}O_2S_2$ (MH^+) 335.11340; found 335.11328.

_O_-ethyl S-(3-(2-oxopropyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (5b):



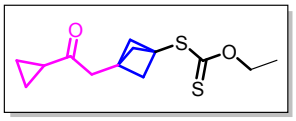
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (29 mg, 48%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): 4.66 (q, 2H, J = 7.1 Hz), 2.69 (s, 2H), 2.18 (s, 6H), 2.12 (s, 3H), 1.47 (t, 3H, J = 7.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 213.4, 206.3, 69.5, 55.3, 45.3, 40.9, 39.5, 30.8, 13.9; IR (KBr): 2978, 2914, 2874, 1712, 1361, 1220, 1188, 1111, 1043, 1131, 997, 889, 857 cm^{-1}; HRMS (ESI): calcd.for C11H16O2S2 (MH^+) 245.06645; found 245.06621.

_S_-(3-(3,3-dimethyl-2-oxobutyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5c):



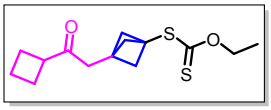
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield:(45 mg, 62%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.67 (q, 2H, J = 7.1 Hz), 2.74 (s, 2H), 2.17 (s, 6H), 1.46 (t, 3H, J = 7.1 Hz), 1.10 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.7, 213.5, 69.5, 55.4, 44.4, 41.0, 40.1, 37.6, 26.1, 14.0; IR (KBr) 2970, 2915, 2874, 1707, 1477, 1394, 1365, 1221, 1188, 1130, 1112, 1002, 890, 859, cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{22}O_2S_2$ (MH^+) 287.11340; found 287.11328.

_S_-(3-(2-cyclopropyl-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5d):



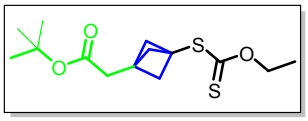
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield:(46 mg, 68%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.66 (q, 2H, J = 7.1 Hz), 2.80 (s, 2H), 2.19 (s, 6H), , 1.81-1.90 (m, 1H), 1.47 (t, 3H, J = 7.1 Hz), 0.99-1.04 (m, 2H), 0.85-0.91 (m, 2H),; ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.4, 208.3, 69.5, 55.4, 45.7, 40.9, 39.7, 21.0, 13.9, 11.1; IR (KBr) 2988, 2916, 2878, 1694, 1442, 1382, 1219, 1187, 1130, 1110, 1044, 1013, 889, 856 cm^{-1}; HRMS (ESI): calcd.for $C_{13}H_{18}O_2S_2$ (MH^+) 271.08210; found 271.08191.

_S_-(3-(2-cyclobutyl-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5e):



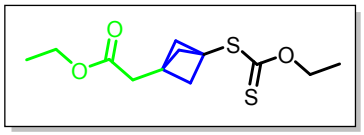
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield:(51 mg, 71%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.66 (q, 2H, J = 7.1 Hz), 3.13-3.25 (m, 1H), 2.60 (s, 2H), 2.08-2.22 (m, 10H), 1.90-202 (m, 1H,), 1.74-1.87 (m, 1H), 1.47 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 209.4, 69.5, 55.4, 45.9, 41.5, 40.9, 39.7, 24.2, 17.7, 13.9; IR (KBr) 2982, 1704, 1361, 1220, 1188, 1111, 1046, 999, 906, 890, 728 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{20}O_2S_2$ (MH^+) 285.09775; found 285.09766.

Tert-butyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)acetate (12a):



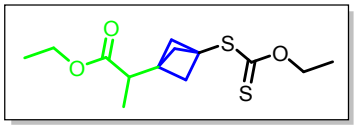
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (45 mg, 59%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.66 (q, 2H, J = 7.1 Hz), 2.48 (s, 2H), 2.17 (s, 6H), 1.47 (q, 12H. J = 6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 213.5, 170.1, 80.8, 69.5, 56.0, 55.2, 40.6, 39.9, 38.6, 28.3, 14.0; IR (KBr) 2977, 2931, 1730, 1457, 1367, 1300, 1219, 1141, 1109, 1044, 947, 850 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{22}O_3S_2$ (MH^+) 303.10831; found 303.10826.

Ethyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)acetate (12b):



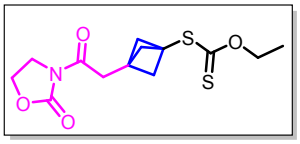
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (45 mg, 65%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.66 (q, 2H, J = 7.1 Hz), 4.17 (q, 2H, J = 7.1 Hz), 2.57 (s, 2H), 2.18 (s, 6H), 1.47 (t, 3H, J = 7.1 Hz), 1.23 (t, J = 7.1 Hz); ^{13}CNMR (75 MHz, $CDCl_3$): δ (ppm) 213.4, 170.8, 69.5, 60.6, 55.2, 40.6, 39.6, 37.1, 14.4, 13.9; IR (KBr): 2984, 2939, 1734, 1365, 1294, 1217, 1148, 1110, 1044, 863, 888 cm^{-1}; HRMS (ESI): calcd.for $C_{12}H_{18}O_3S_2$ (MH^+) 275.07701; found 275.07669.

Ethyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)propanoate (12c):



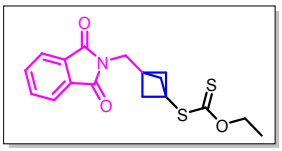
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.9:0.1, Yield: (52 mg, 72%) as a colourless oil : ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm) 4.65 (q, 2H, *J* = 7.1 Hz), 4.09-4.18 (m, 2H), 2.68 (q, 1H, *J* = 7.1 Hz), 2.09 (s, 6H), 1.45 (t, 3H, *J*= 7.1 Hz), 1.28 (t, 3H, *J* =7.1 Hz), 1.12 (d, 3H, *J* = 3.9 Hz) ^{13}C NMR (75 MHz, $CDCl_3$) δ (ppm) 213.4, 173.6, 69.5, 60.5, 53.4, 44.4, 40.7, 40.0, 14.5, 13.9, 13.6; IR (KBr) 2978, 2916, 2878, 1731, 1449, 1367, 1333, 1219, 1186, 1148, 1130, 1110, 964, 890, 857 cm^{-1}; HRMS (ESI): calcd. for $C_{13}H_{20}O_3S_2$ (MH^+) 289.09266; found 289.09250.

***O*-ethyl S-(3-(2-oxo-2-(2-oxooxazolidin-3-yl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (13a):**



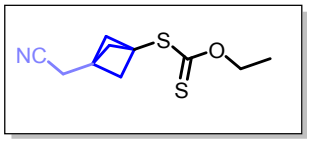
Following the standard **procedure B** flash chromatography: PE/EtOAc 8:2, Yield: (30 mg, 38%) as a gummy oil: H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.57–4.67 (m, 2H), 4.44 (q, 2H, *J* =7.8 Hz), 4.0 (q, 2H, *J* = 8.3 Hz), 3.24 (s, 2H), 2.21 (s, 6H), 1.47 (t, 3H, *J* = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 170.6, 153.5, 69.5, 62.1, 55.4, 42.5, 41.0, 39.5, 36.8, 14.0; IR (KBr): 2988, 2924, 1774, 1705, 1388, 1364, 1335, 1221, 1049, 1111, 1015, 957, 757 cm^{-1}; HRMS (ESI): calcd. for $C_{13}H_{17}NO_4S_2$ (MH^+) 316.06718; found 316.06716.

S-(3-((1,3-dioxoisoindolin-2-yl)methyl)bicyclo[1.1.1]pentan-1-yl) *O*-ethyl carbonodithioate (14a):



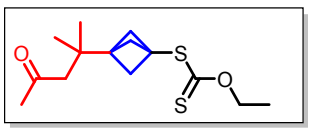
Following the standard **procedure B** flash chromatography: PE/EtOAc 8:2, Yield: (46 mg, 53%) as a gummy solid: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.84-7.88 (m, 2H), 7.72- 7.76 (m, 2H), 4.72 (q, 2H, J = 7.1 Hz), 3.85 (s, 2H), 2.12 (s, 6H), 1.47 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.2, 168.1, 134.5, 132.0, 123.5, 70.6, 54.2, 41.8, 41.3, 38.7, 13.8; IR (KBr): 2988, 2924, 2852, 1713, 1408, 1391, 1379, 1282, 1222, 1187, 1111, 1042, 1026, 1000, 913, 851, 790, 720 cm^{-1}; HRMS (ESI): calcd. for $C_{17}H_{17}NO_3S_2$ (MH^+) 348.07226; found 348.07233.

***S*-(3-cyanobicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (15a):**



Following the standard **procedure B** flash chromatography: PE/EtOAc 9.7:0.3, Yield: (18 mg, 34%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.68 (q, 2H, J = 7.1 Hz), 2.66 (s, 2H), 2.25 (s, 6H), 1.48 (t, 3H, J = 7.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 212.5, 116.7, 69.6, 54.6, 40.3, 38.2, 21.0, 13.9; IR (KBr): 2984, 2919, 2882, 2855, 2253, 1447, 1264, 1226, 1112, 1194, 1132, 1046, 999, 896, 732 cm^{-1}; HRMS (ESI): calcd. for $C_9H_{11}NOS_2$ (MH^+) 228.05113.; found 228.05106.

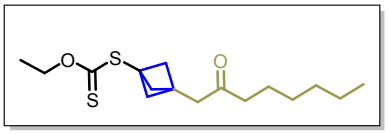
***O*-ethyl S-(3-(2-methyl-4-oxopentan-2-yl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (16a):**



Following the standard **procedure B** flash chromatography: PE/EtOAc 9.8:0.2, Yield: 29 mg, 41%) as a colourless oil: ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.67 (q, 2H, J = 7.1 Hz), 2.30 (s, 2H), 2.14 (s, 3 H), 1.99 (s, 6H), 1.47 (t, 3H, J = 7.1 Hz), 0.99 (s, 6H); ^{13}C NMR (75 MHz,

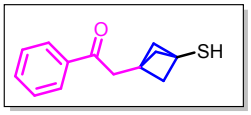
$CDCl_3$): δ (ppm) 213.7, 208.3, 69.4, 52.0, 51.8, 50.9, 39.3, 33.3, 32.5, 23.2, 13.9; IR (KBr): 2962, 2916, 2874, 1709, 1446, 1360, 1217, 1195, 1132, 1046, 1004, 979, 884, 857 cm^{-1}; HRMS (ESI): calcd. for $C_{14}H_{22}O_2S_2$ (MH^+) 287.11340; found 287.11339..

***O*-ethyl S-(3-(2-oxooctyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (17a):**



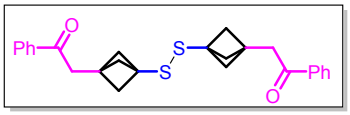
Following the standard **procedure B** flash chromatography: PE/EtOAc 9.8:0.2, Yield: (50 mg, 63%) as a colourless oil: ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 4.66 (q, 2H, *J* = 7.2 Hz), 2.65 (s, 2H), 2.38 (t, 2H, *J* = 7.3 Hz), 2.17 (s, 6H), 1.47 (t, 3H, *J* = 7.1 Hz), 1.26-1.28 (m, 8H), 0.90 (t, 3H, *J* = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 213.5, 208.7, 69.5, 55.4, 44.3, 43.7, 40.9, 39.7, 31.7, 29.0, 23.6, 22.6, 14.1, 13.9; IR (KBr): 2955, 2917, 2873, 1713, 1448, 1362, 1291, 1219, 1188, 1110, 1045, 1001, 890, 857 cm^{-1}; HRMS (ESI): calcd. for C16H26O2S2 (MH^+) 315.14770; found 315.14473.

2-(3-Mercaptobicyclo[1.1.1]pentan-1-yl)-1-phenylethan-1-one (18)[11(reference in manuscript)]**:**



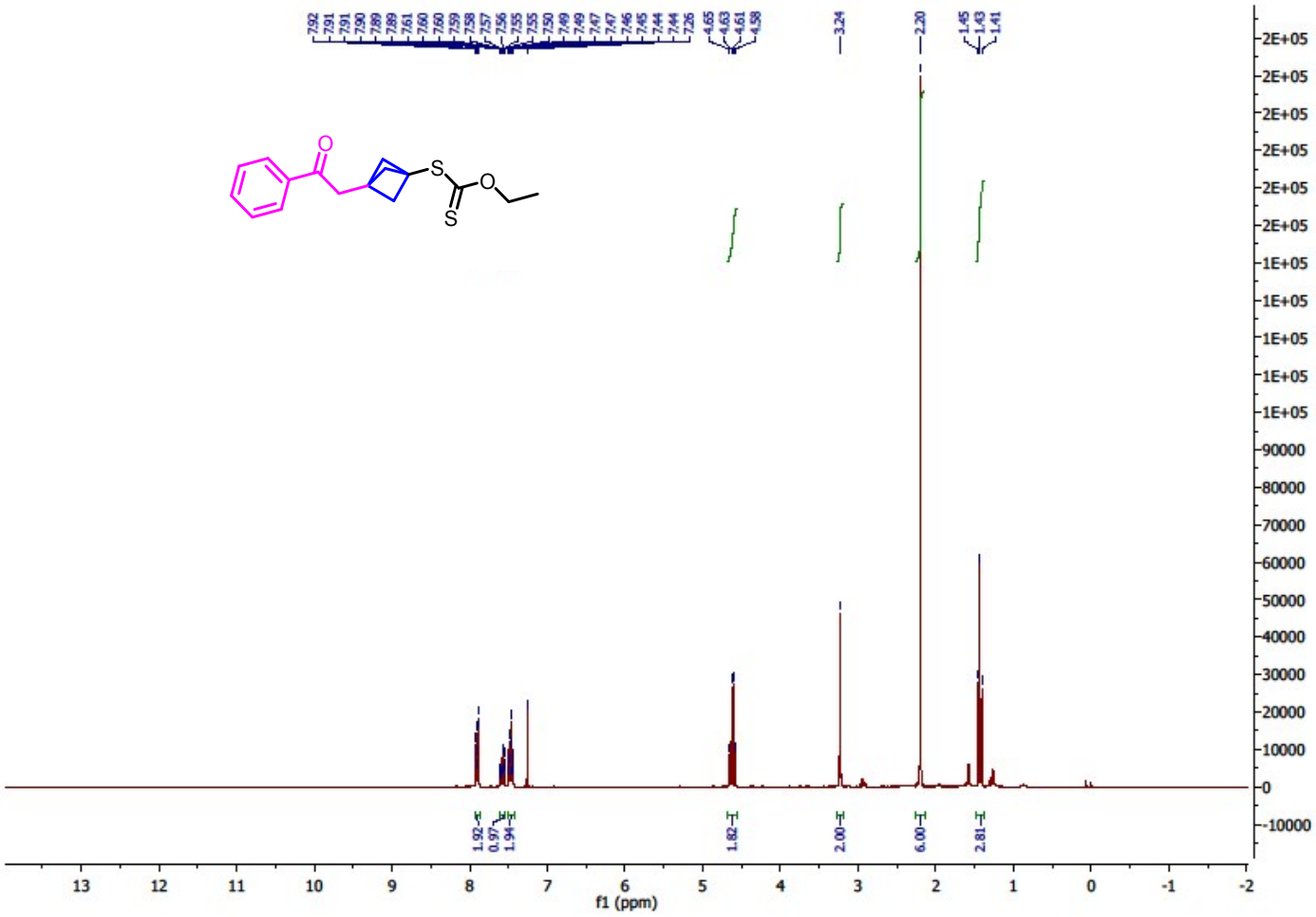
To a solution of xanthate **1a** (58.7 mg, 0.19 mmol) in EtOH (0.9 mL) was added ethylene diamine (50 uL, 0.74 mmol), leading to persistence of a yellow color. After 4 h the solvent was concentrated in vacuo, Et_2O (2 mL) was added to it and washed with 2M H_2SO_4 (2 mL), brine (2 mL), dried over Na_2SO_4, and concentrated in vacuo to obatied thiol **21** as a yellow oil (28 mg, 66% yield), which was further purified by flash chromatography : PE/EtOAc 9.8:0.2: ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.88–7.91 (m, 2H), 7.54-7.60 (m, 1H), 7.43–7.49 (m, 2H), 3.19 (s, 2H), 2.04 (s, 1H), 1.91 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 198.1, 137.1, 133.3, 128.8, 128.4, 54.7, 42.8, 40.5, 36.5; IR (KBr): 2983, 2909, 2873, 1682, 1448, 1187, 1007, 891, 771, 689 cm^{-1}; HRMS (ESI): calcd. for $C_{13}H_{14}OS$ (MH^+) 217.06816.; found 207.06823.

2,2'-(Disulfanediylbis(bicyclo[1.1.1]pentane-3,1-diyl))bis(1-phenylethan-1-one) (19):

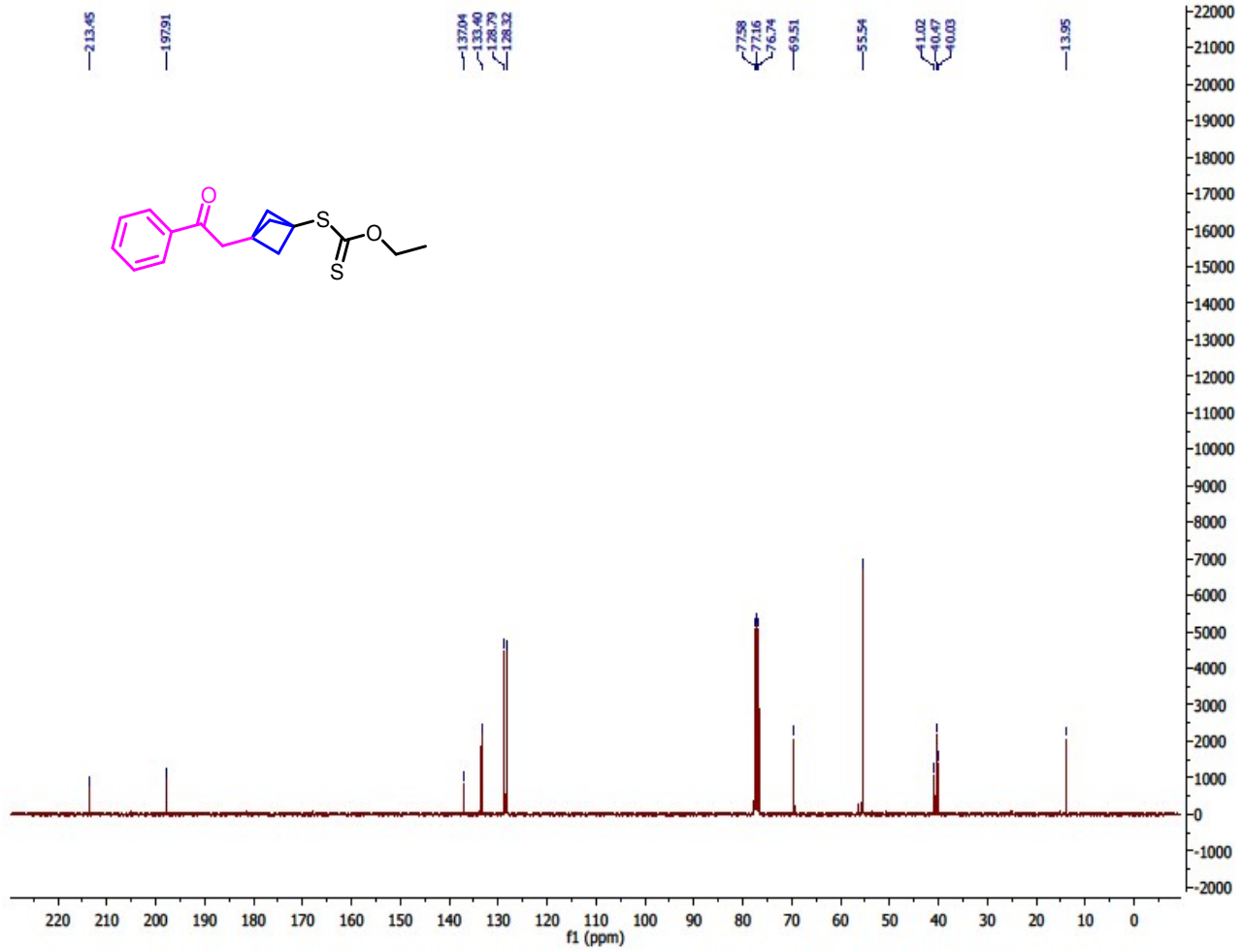


^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) 7.87–7.91 (m, 2H), 7.54-7.59 (m, 1H), 7.43–7.48 (m, 2H), 3.19 (s, 2H), 1.91 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ (ppm) 198.1, 137.1, 133.4, 128.8, 128.4, 54.7, 42.8, 40.6, 36.6; IR (KBr): 2970, 2909, 2874, 1679, 1447, 1213, 1185, 999, 713, 687 cm^{-1}; HRMS (ESI): calcd. for $C_{26}H_{26}O_2S_2$ (MH^+) 435.14470.; found 435.14469.

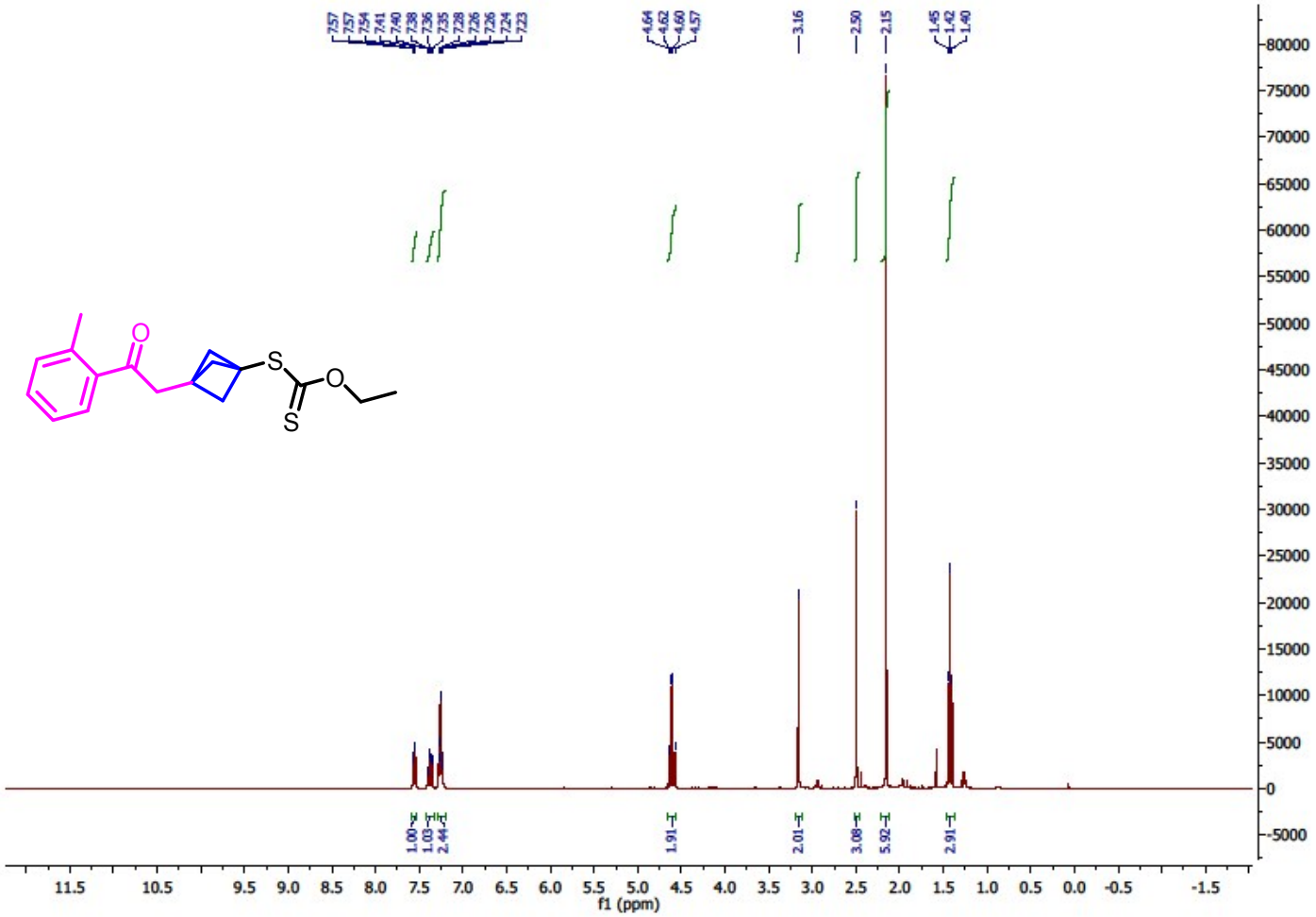
_O_-Ethyl S-(3-(2-oxo-2-phenylethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4a): ^{1}H NMR (300 MHz, $CDCl_3$)



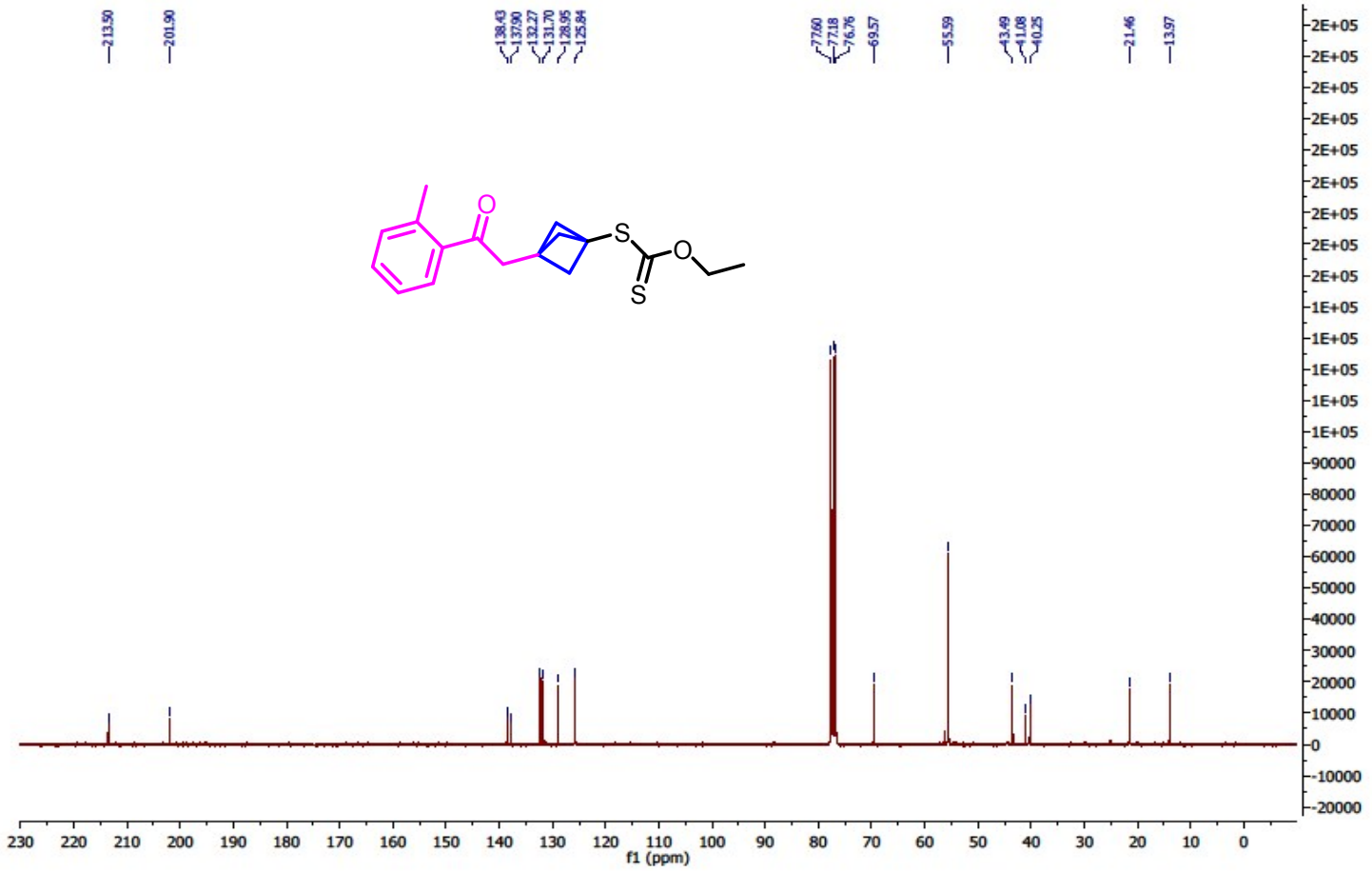
O-ethyl S-(3-(2-oxo-2-phenylethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4a): ^{13}C NMR (75 MHz, $CDCl_3$)



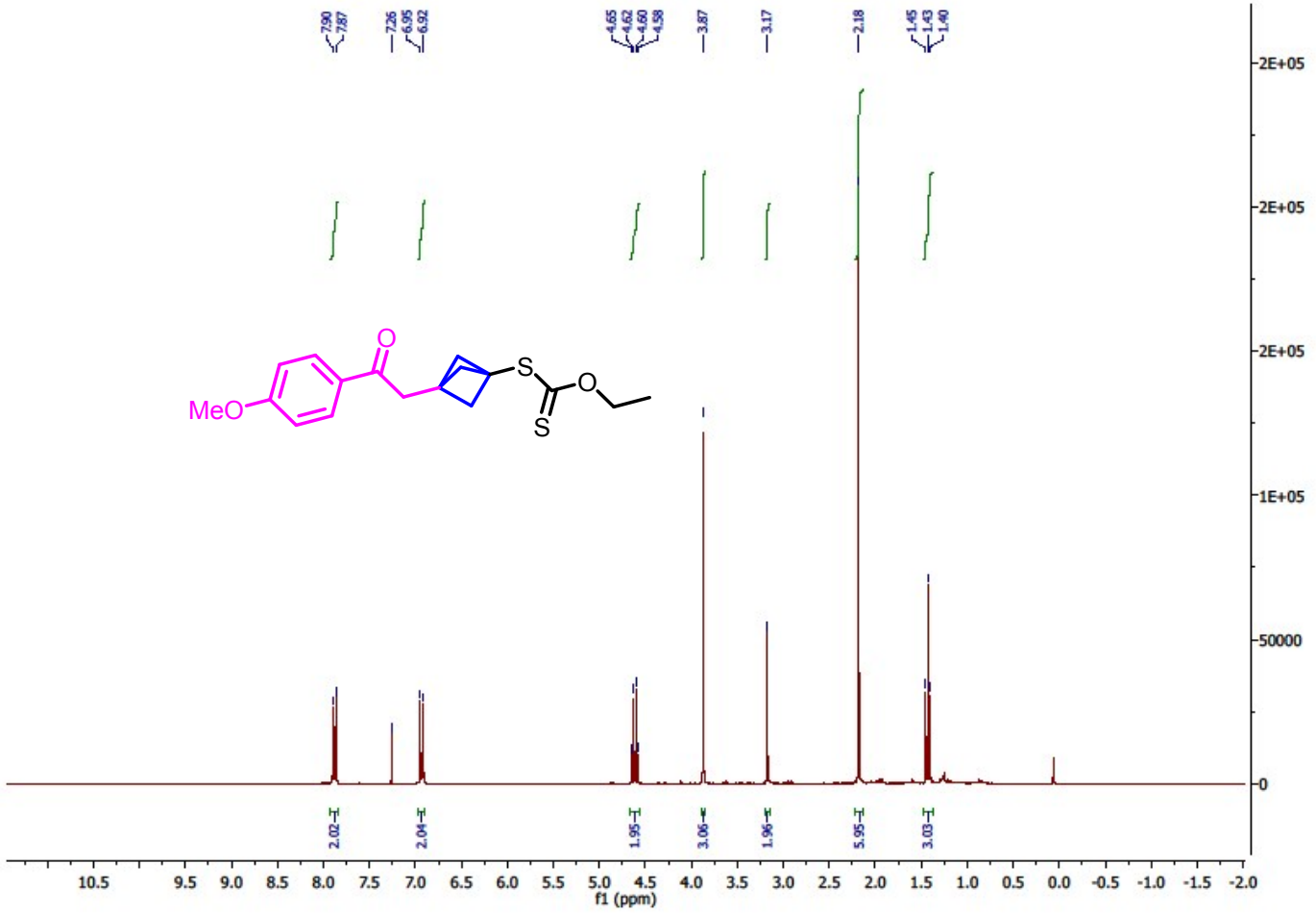
O-ethyl S-(3-(2-oxo-2-(o-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4b): ^{1}H NMR (300 MHz, $CDCl_3$)



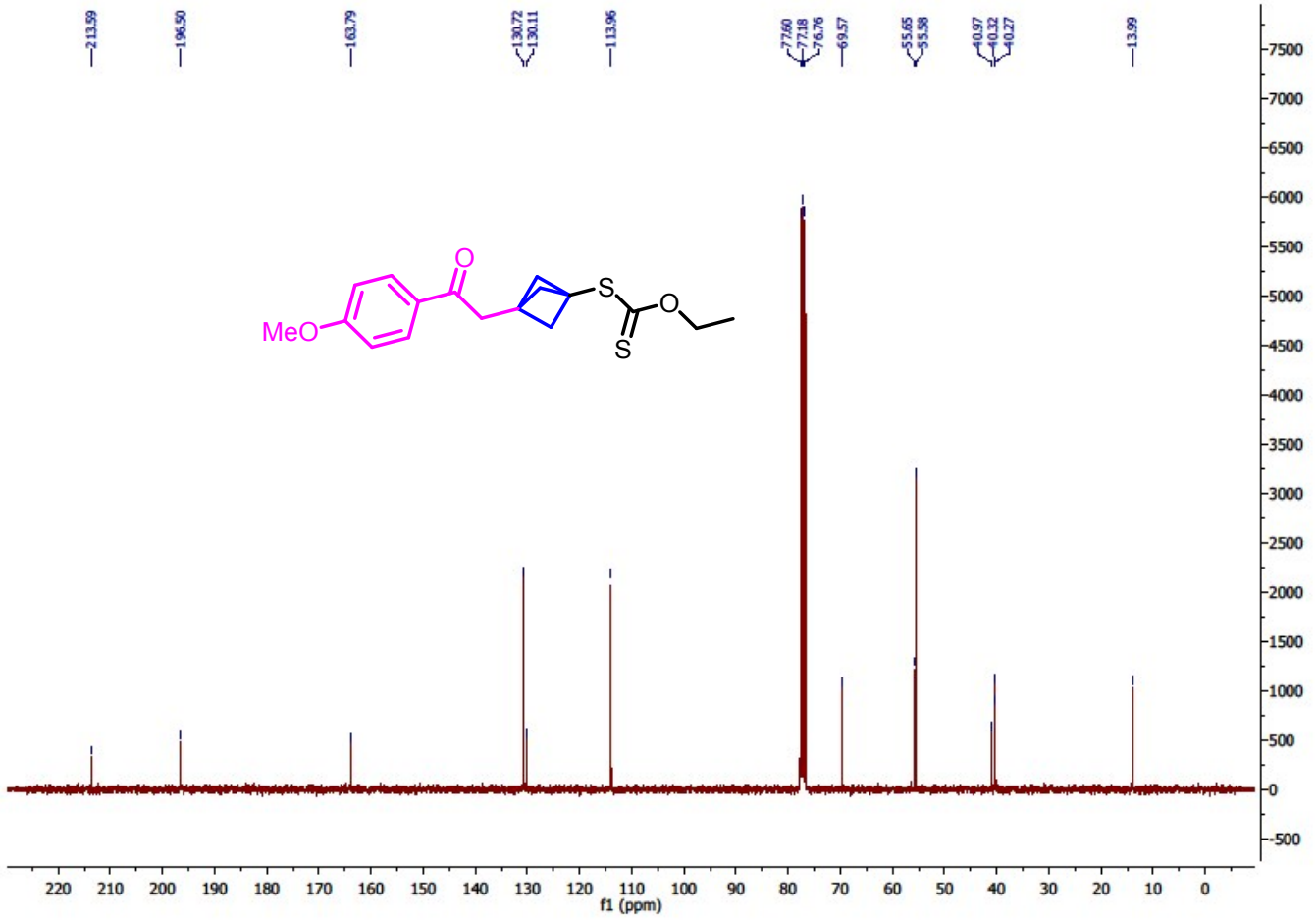
O-ethyl S-(3-(2-oxo-2-(o-tolyl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4b): ^{13}C NMR (75 MHz, $CDCl_3$)



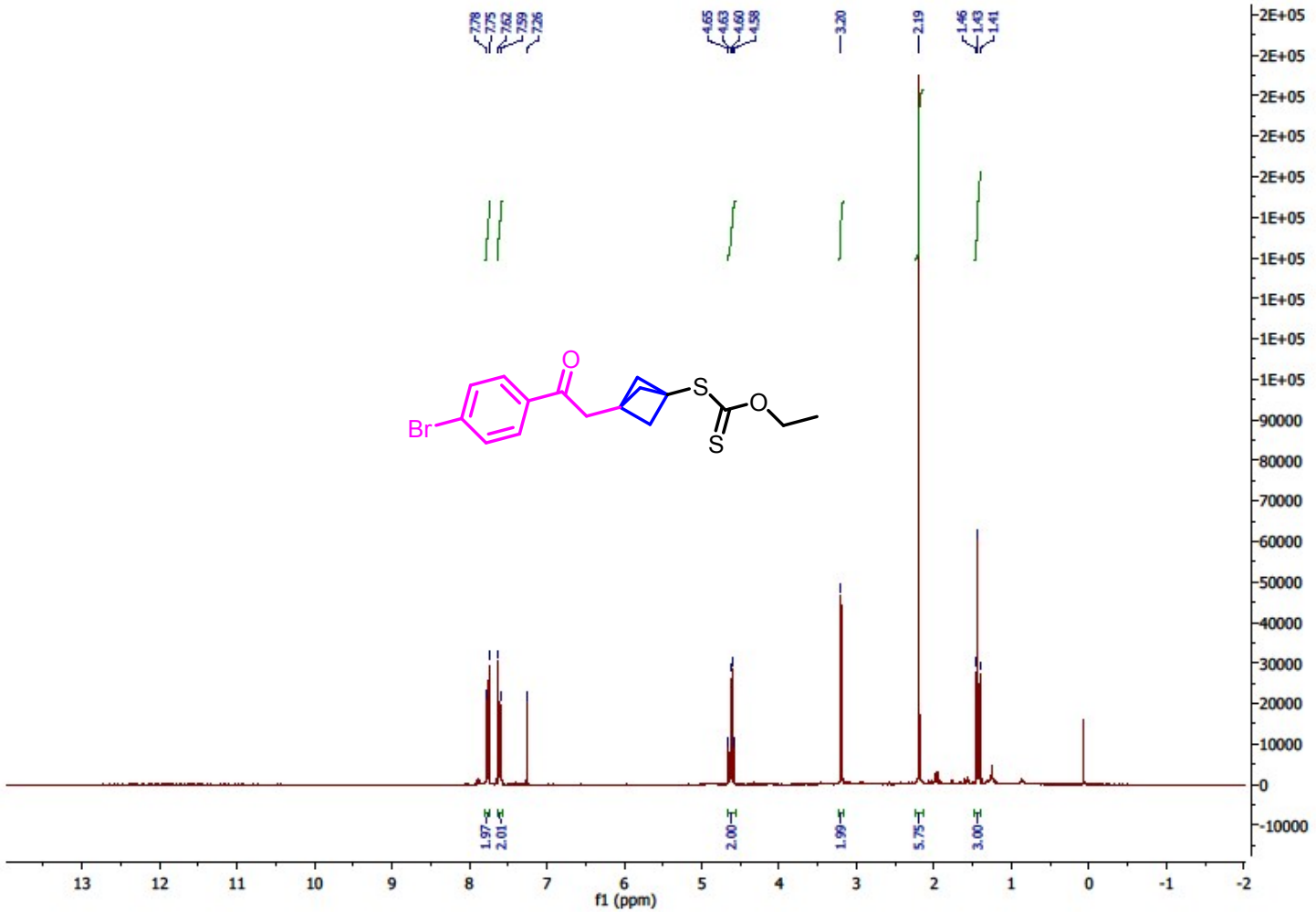
O-ethylS-(3-(2-(4-methoxyphenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4c): ^{1}H NMR (300 MHz, $CDCl_3$)



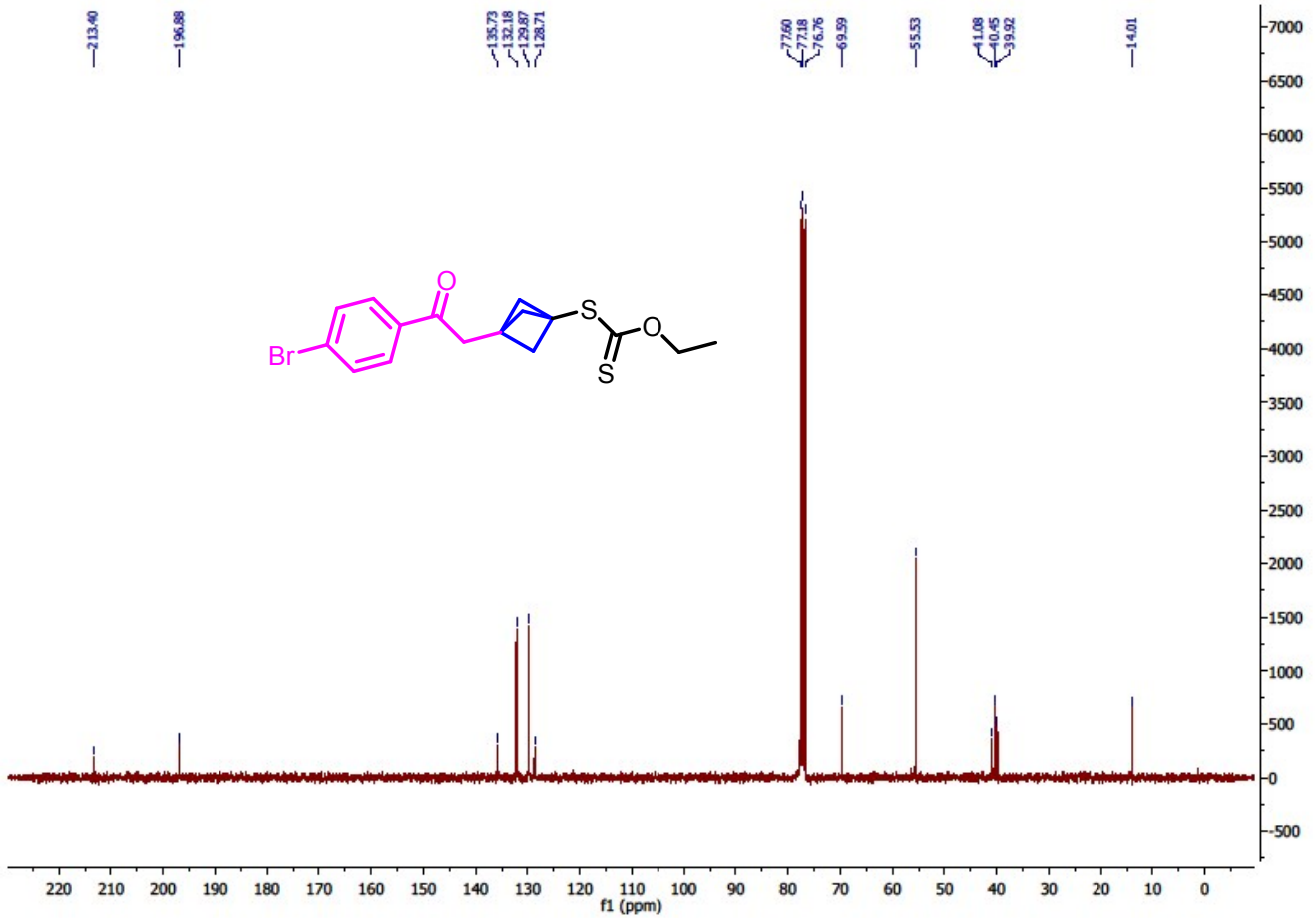
O-ethylS-(3-(2-(4-methoxyphenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4c): ^{13}C NMR (75 MHz, $CDCl_3$)



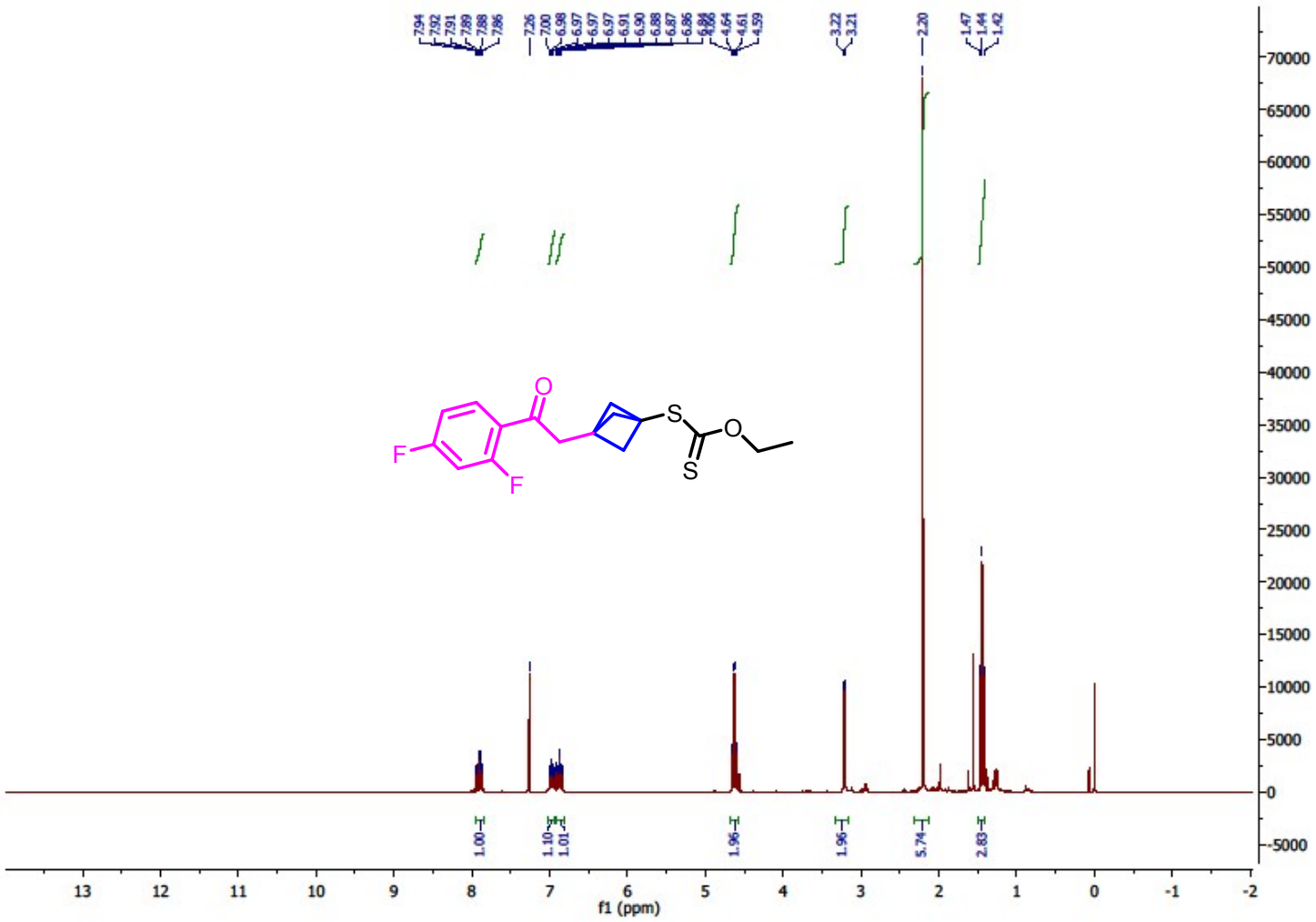
S-(3-(2-(4-bromophenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (4d): ^{1}H NMR (300 MHz, $CDCl_3$)



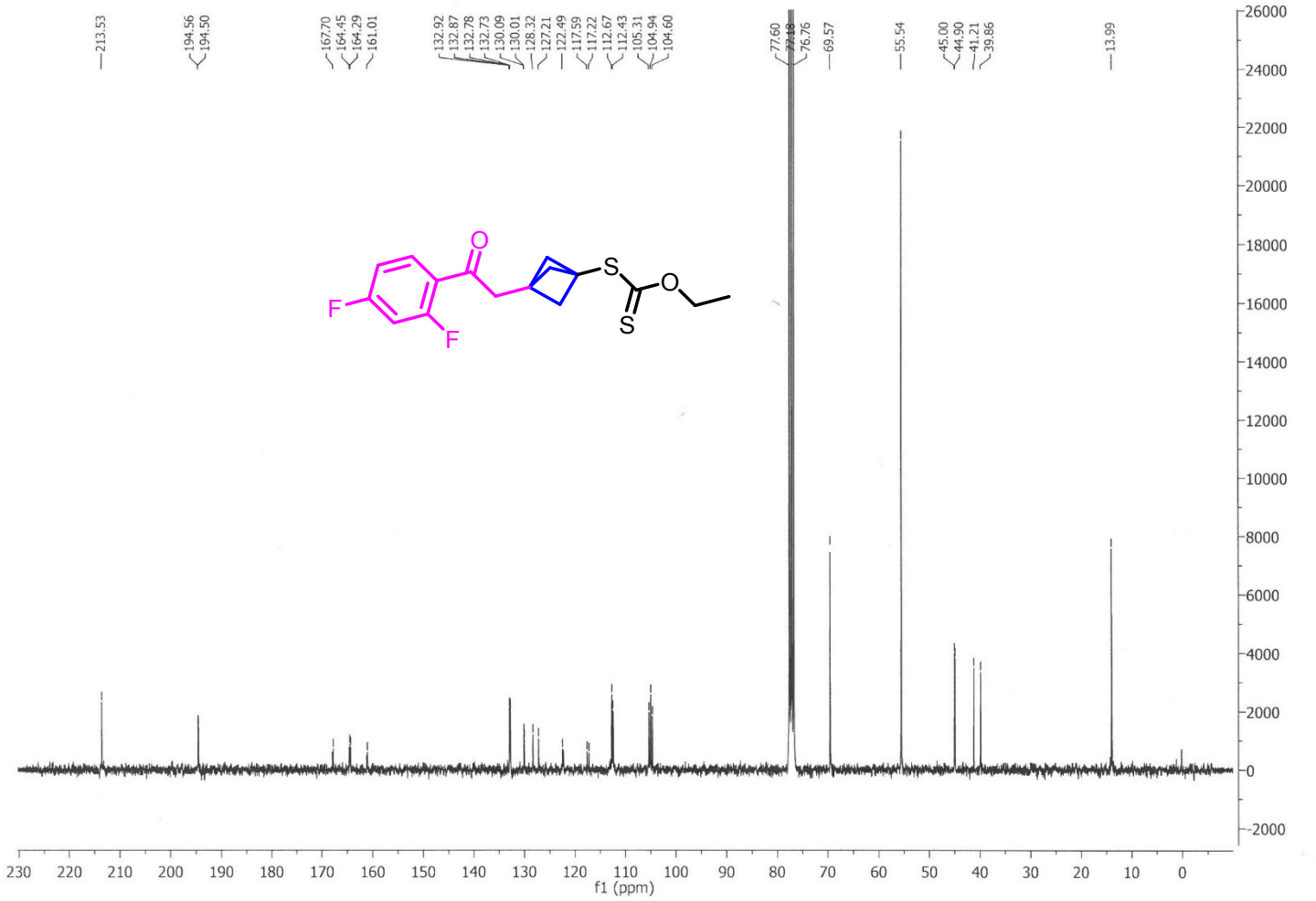
S-(3-(2-(4-bromophenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (4d): ^{13}C NMR (100 MHz, $CDCl_3$)



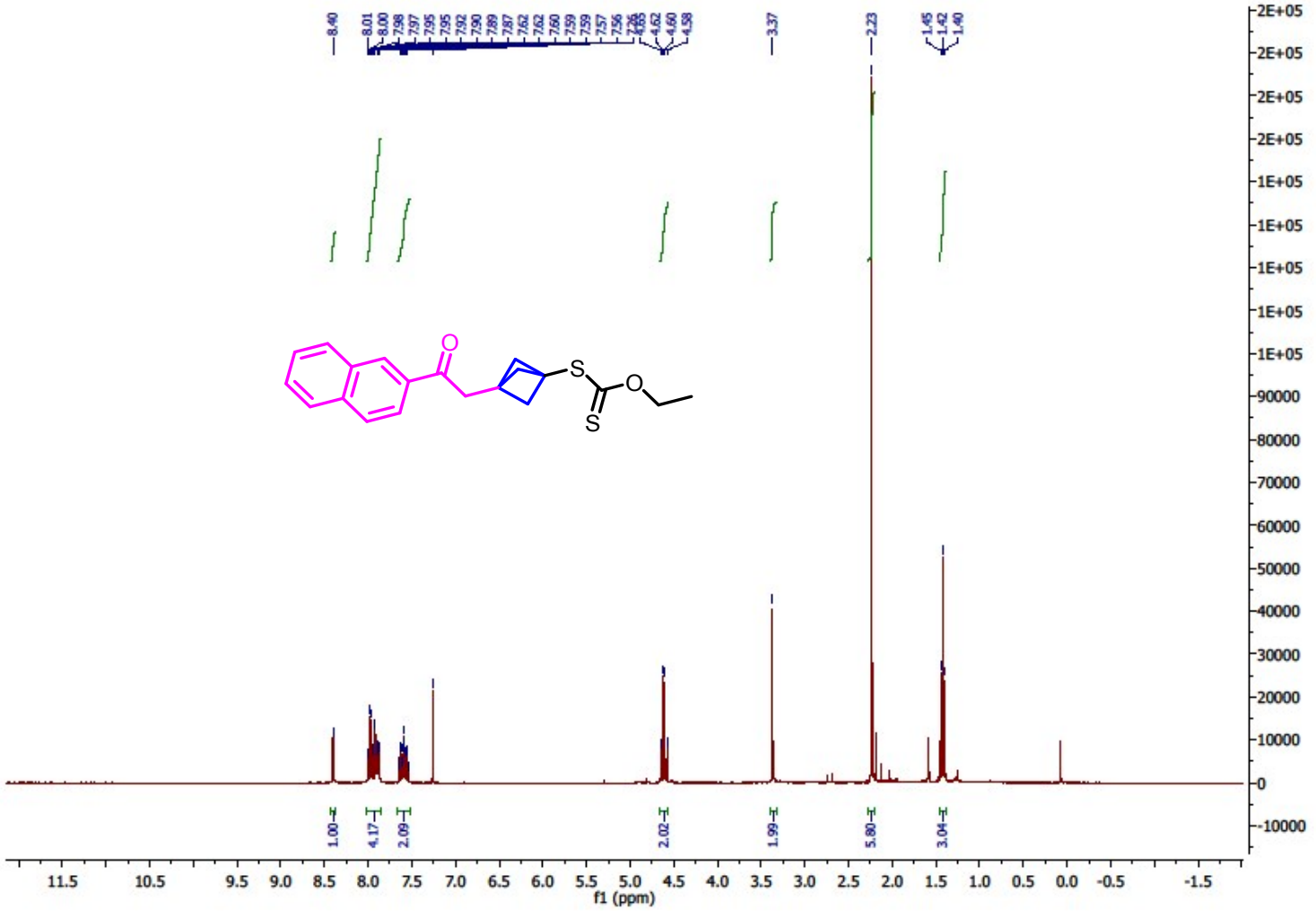
_S_-(3-(2-(2,4-difluorophenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl)O-ethyl carbonodithioate (4e): ^{1}H NMR (300 MHz, $CDCl_3$)



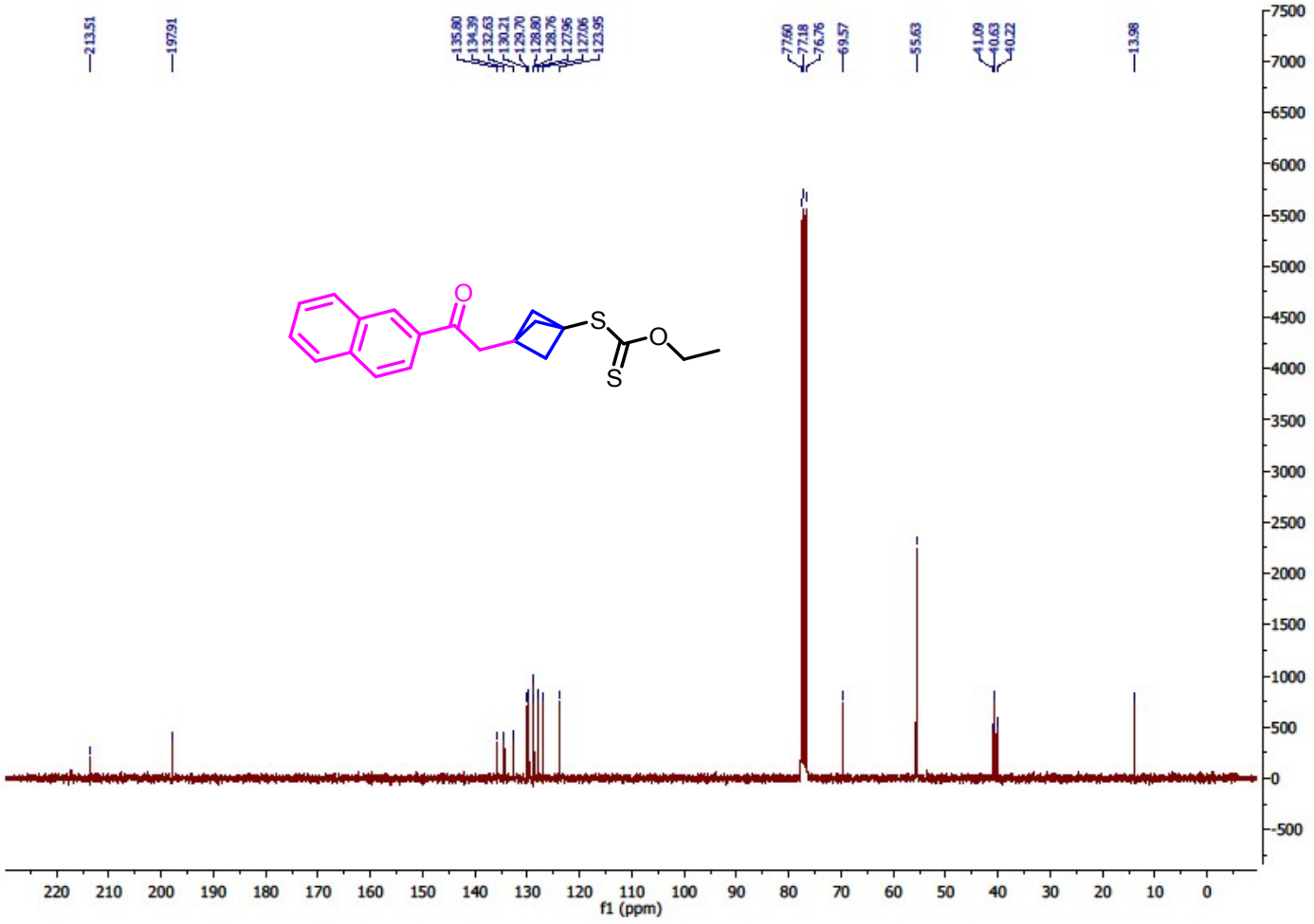
_S_-(3-(2-(2,4-difluorophenyl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl)O-ethyl carbonodithioate (4e): ^{13}C NMR (75 MHz, $CDCl_3$)



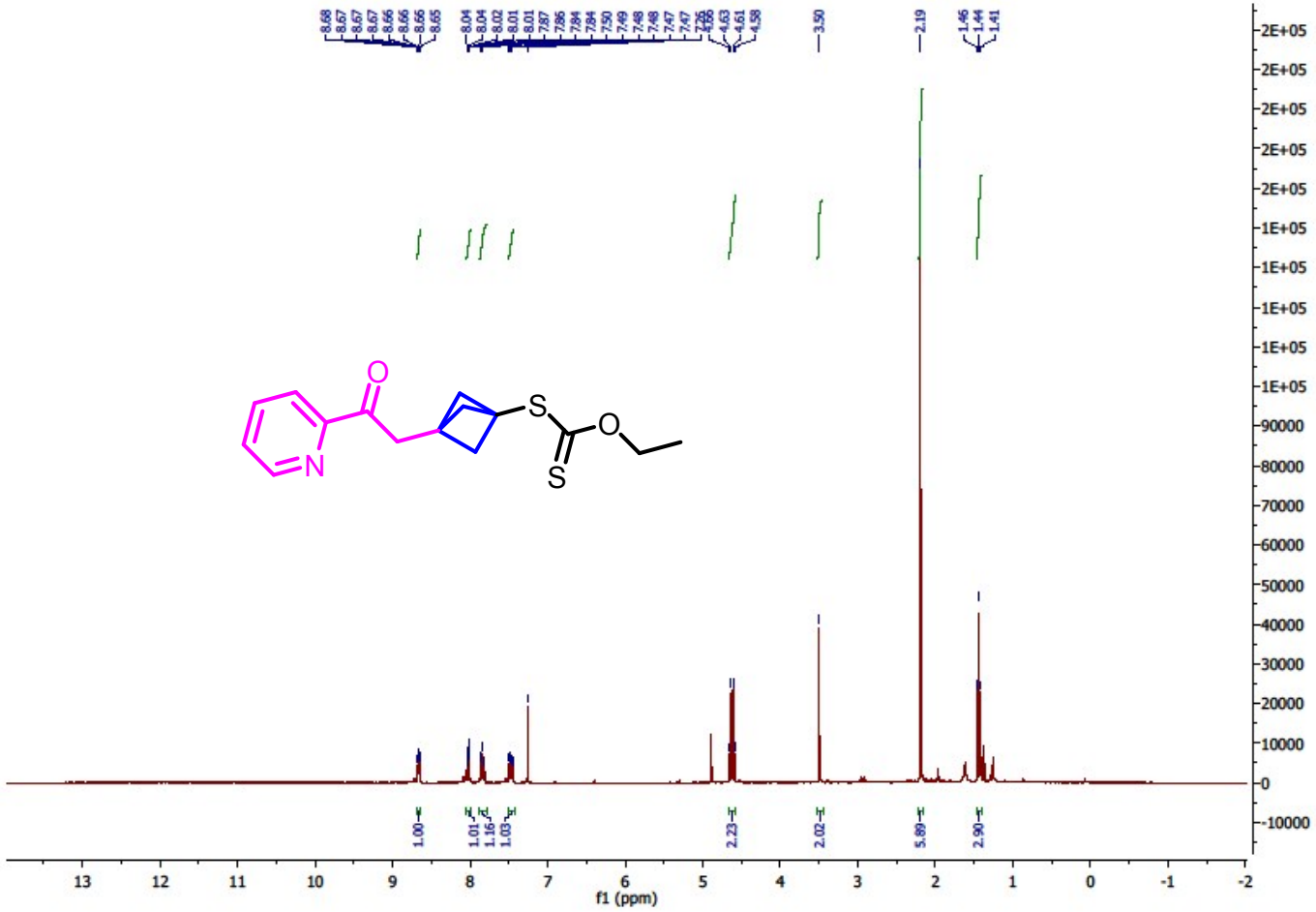
O-ethyl S-(3-(2-(naphthalen-2-yl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4f): ^{1}H NMR (300 MHz, $CDCl_3$)



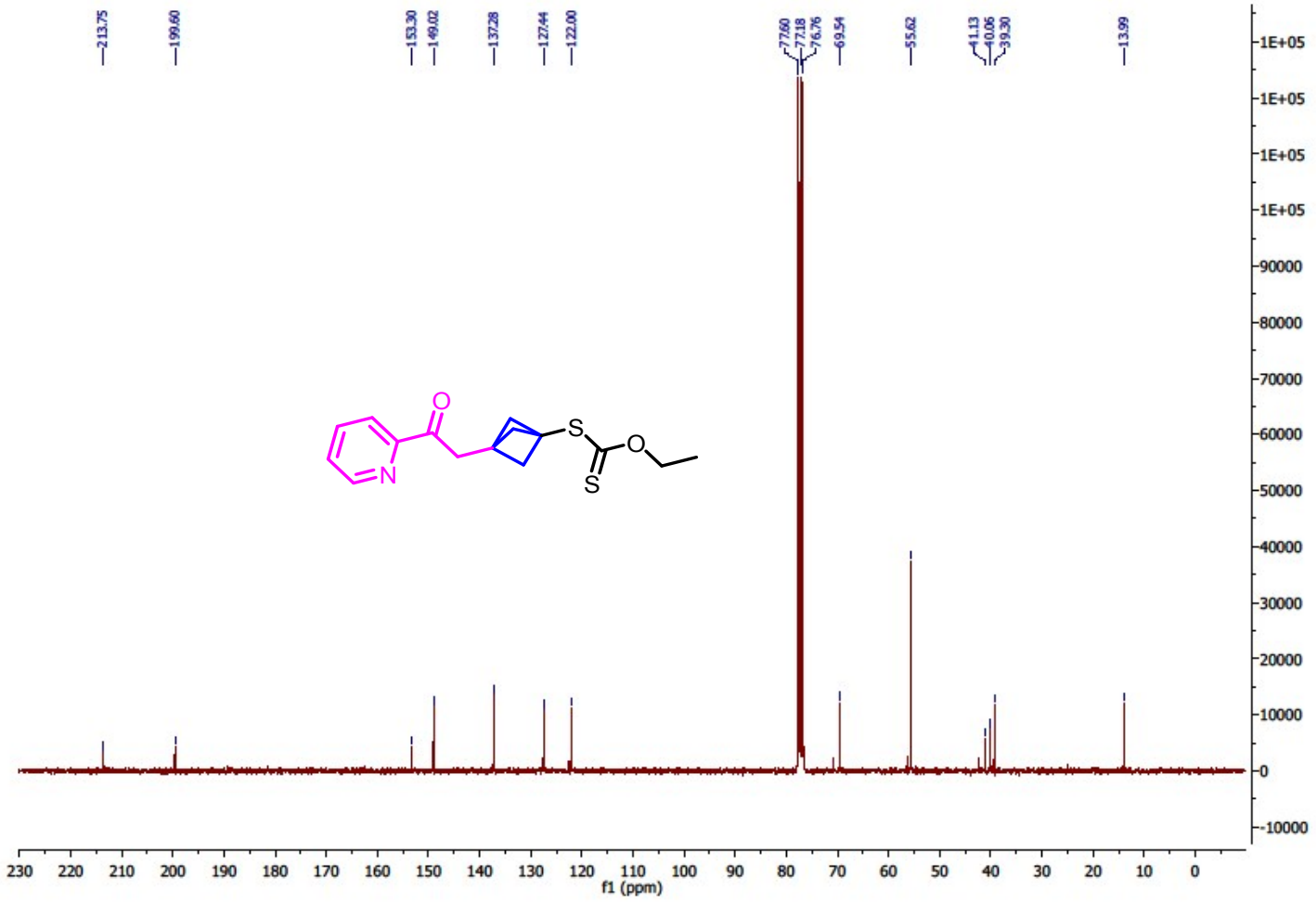
O-ethyl S-(3-(2-(naphthalen-2-yl)-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4f): ^{13}C NMR (75 MHz, $CDCl_3$)



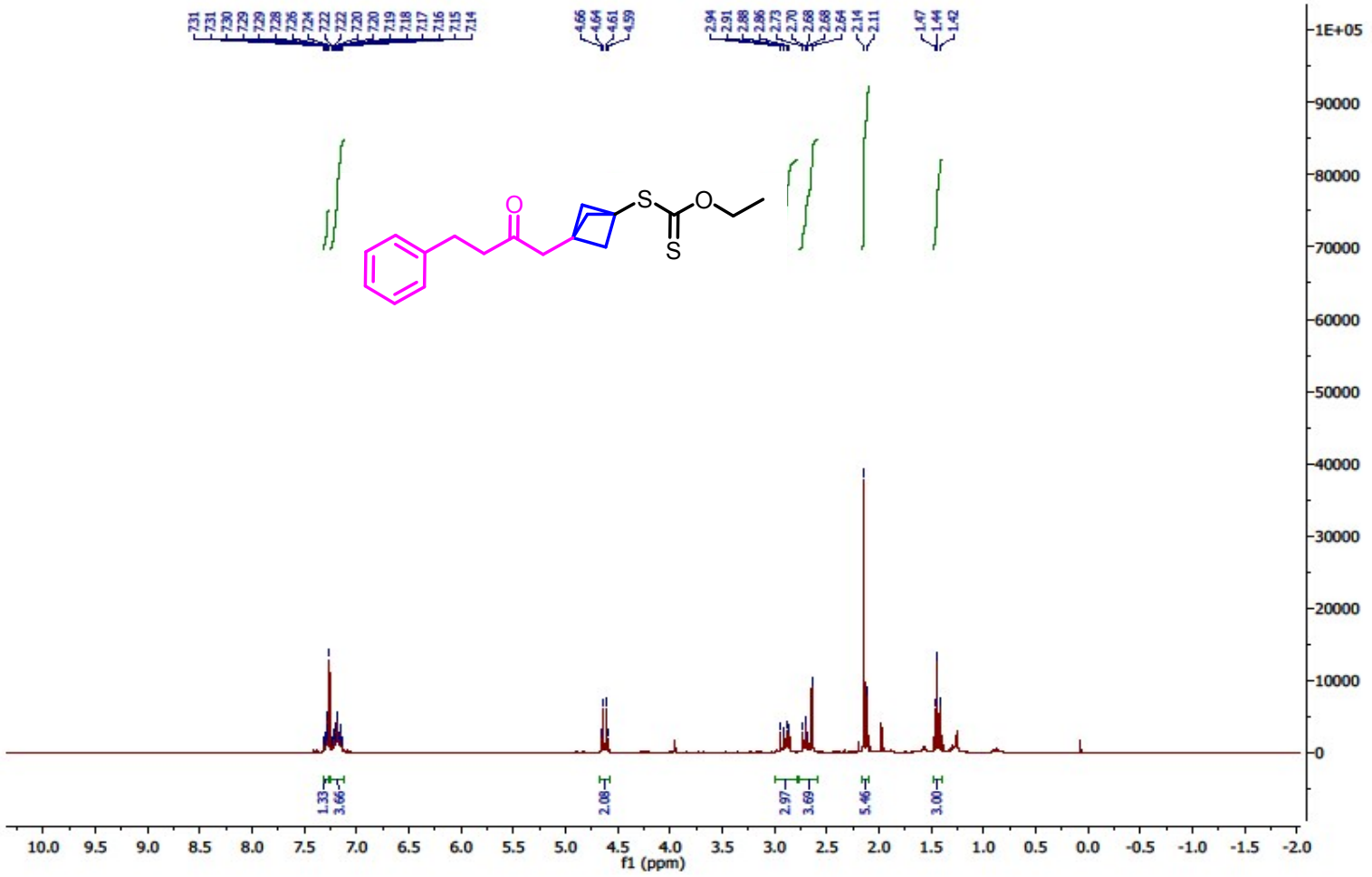
O-ethyl S-(3-(2-oxo-2-(pyridin-2-yl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (4g): ^{1}H NMR (300 MHz, $CDCl_3$)



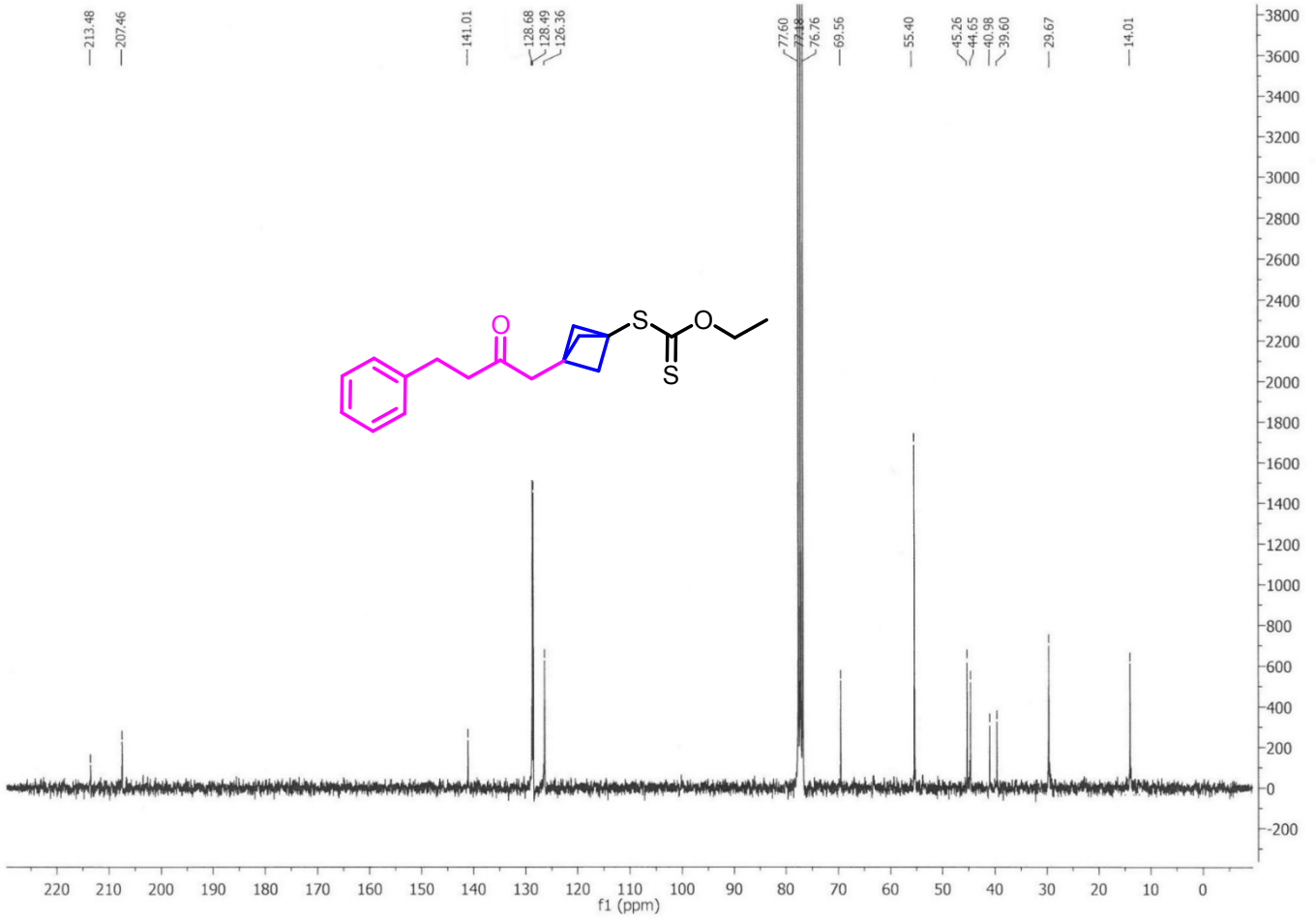
O-ethyl S-(3-(2-oxo-2-(pyridin-2-yl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioat (4g): ^{13}C NMR (75 MHz, $CDCl_3$)



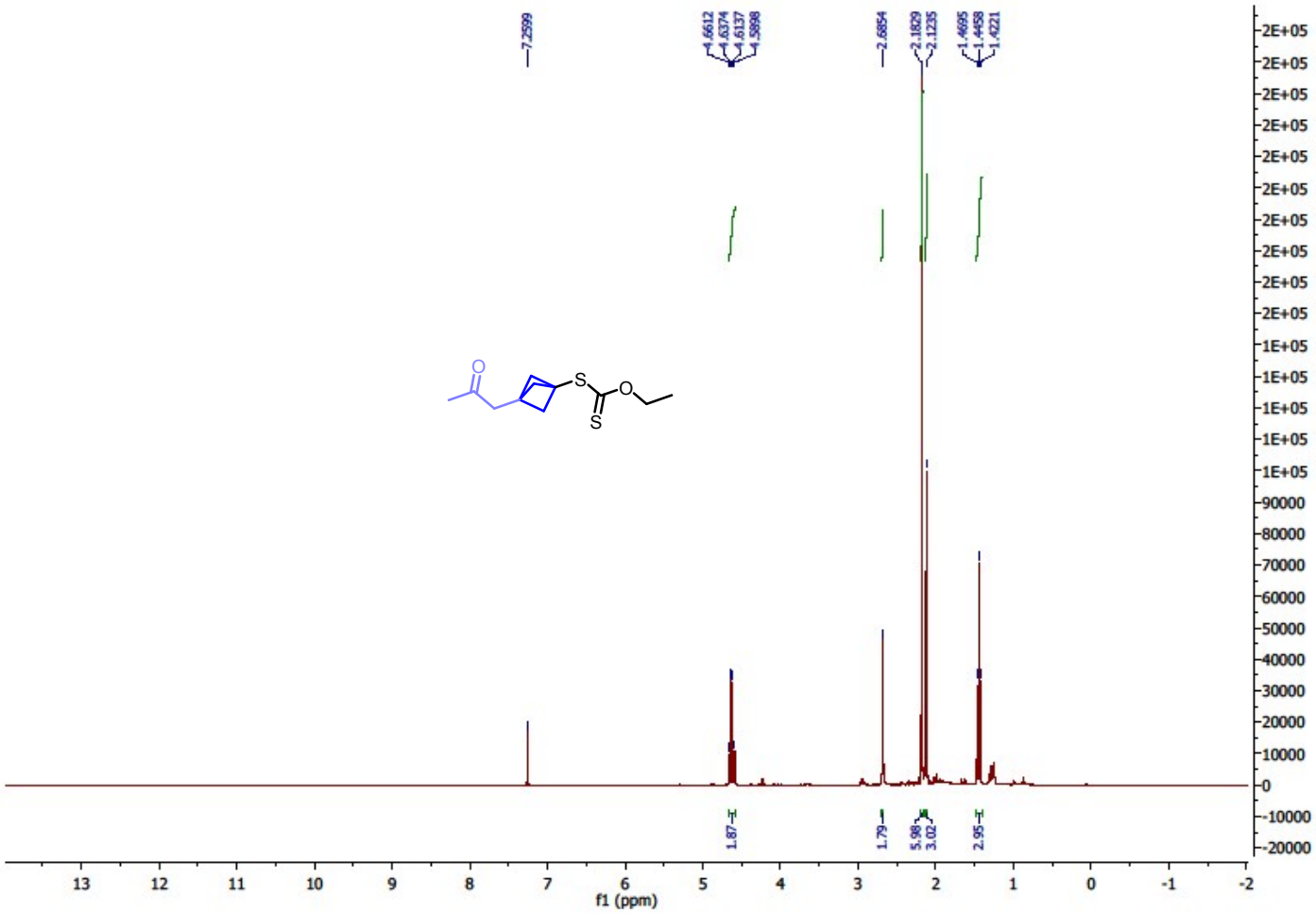
***O*-ethyl S-(3-(2-oxo-4-phenylbutyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (5a): (300 MHz, $CDCl_3$)**



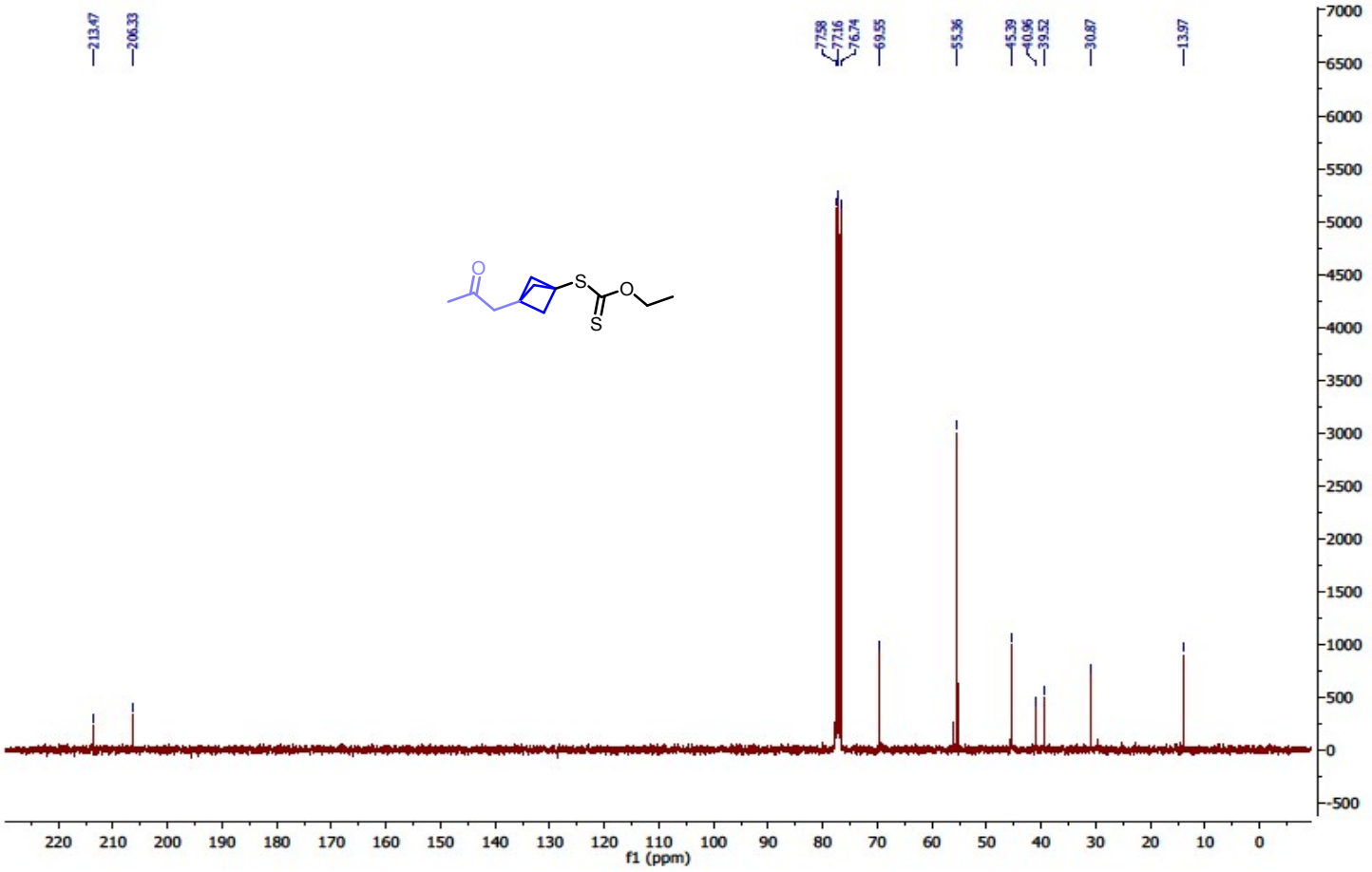
_O_-ethyl S-(3-(2-oxo-4-phenylbutyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (5a): ^{13}C NMR (75 MHz, $CDCl_3$)



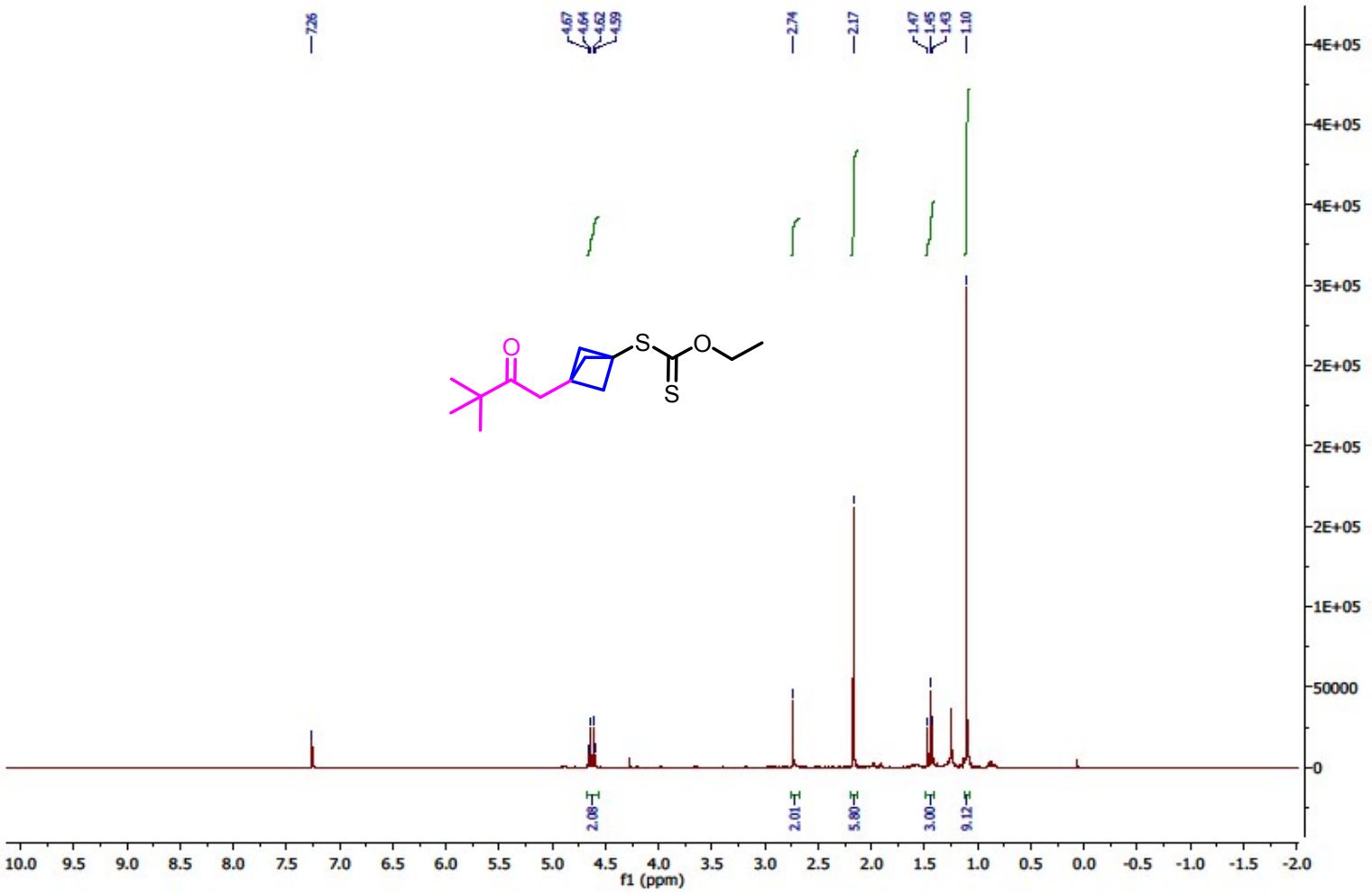
O-ethyl S-(3-(2-oxopropyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (5b): ^{1}H NMR (300 MHz, $CDCl_3$)



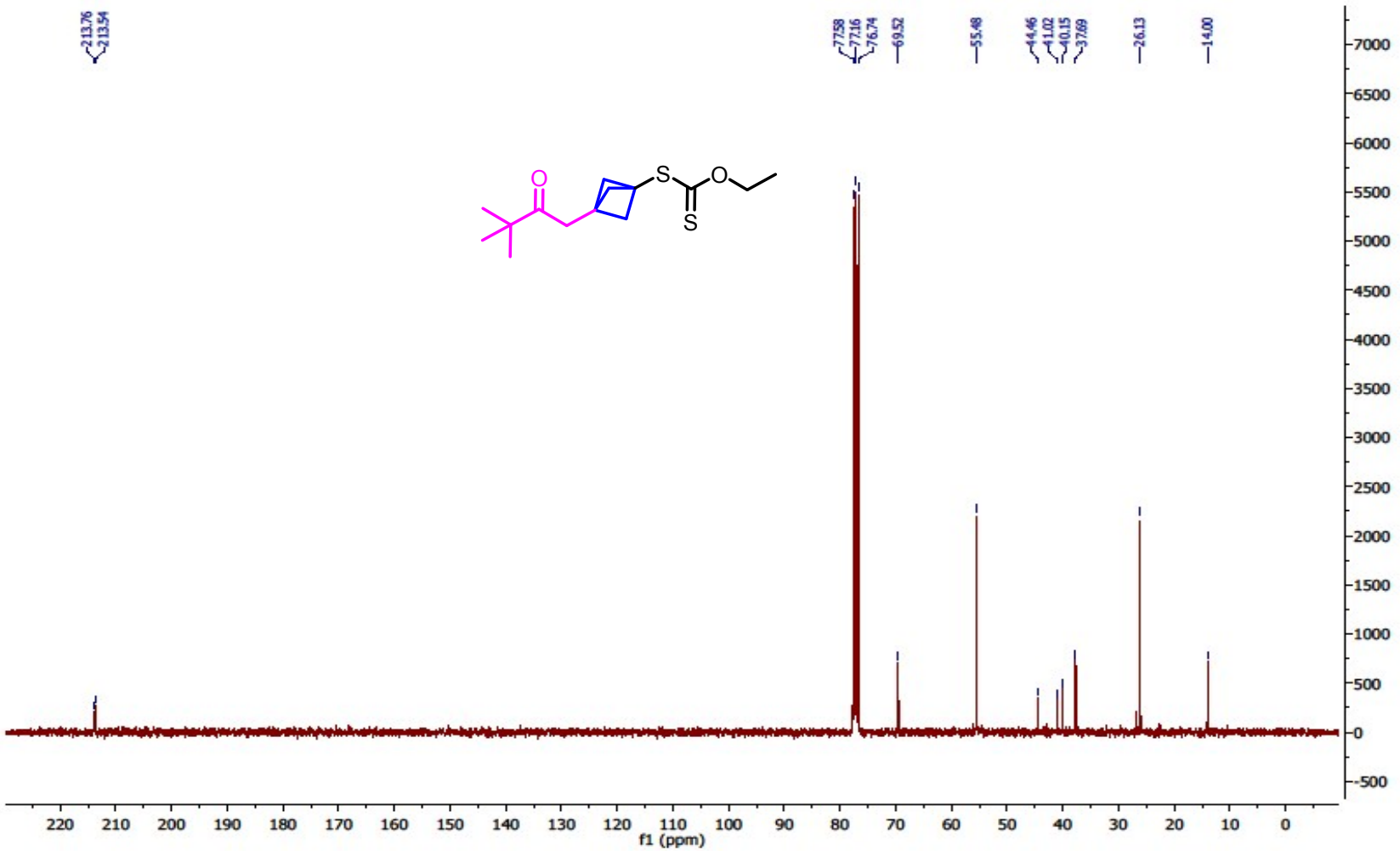
O-ethyl S-(3-(2-oxopropyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (5b): ^{13}C NMR (100 MHz, $CDCl_3$)



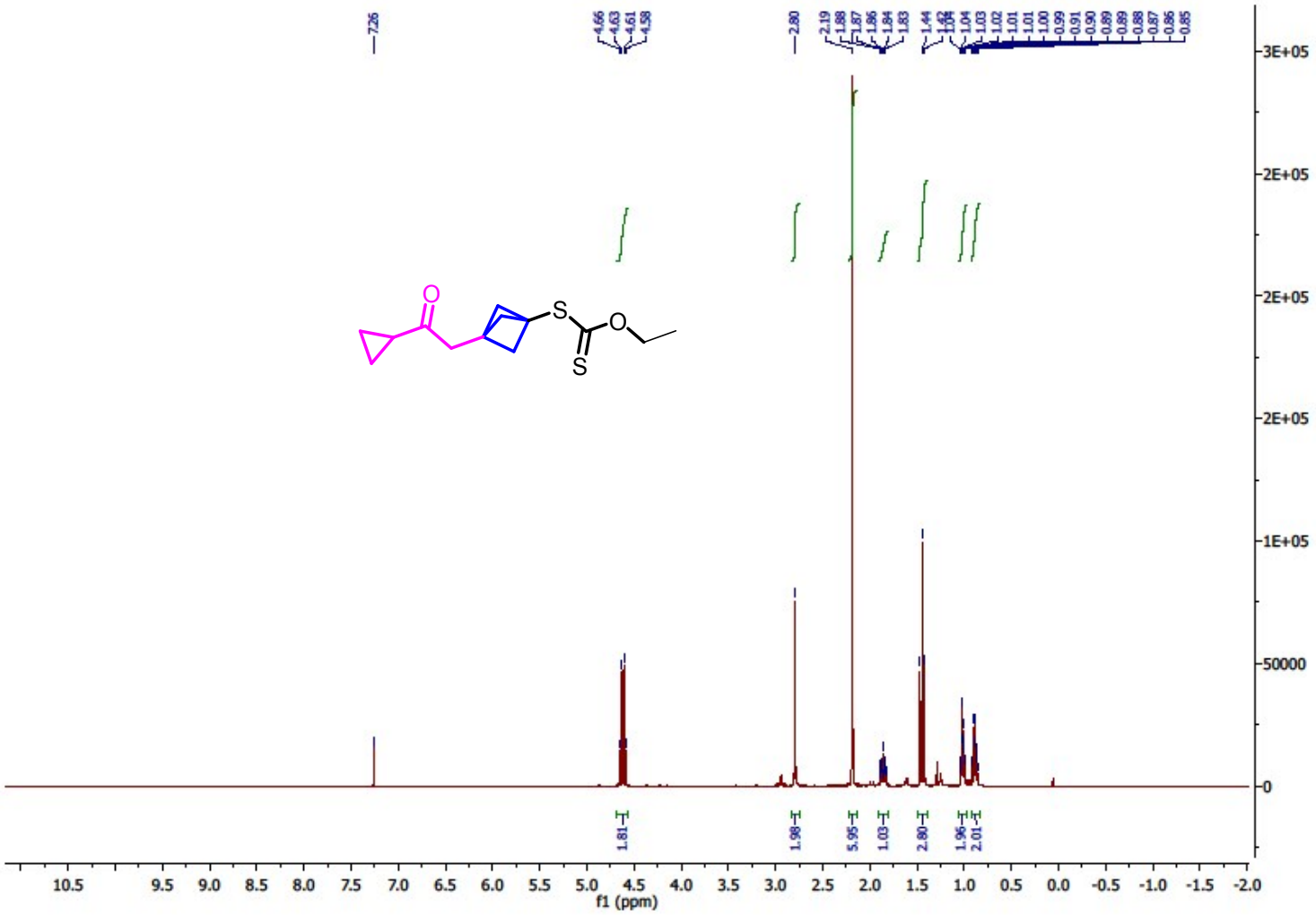
S-(3-(3,3-dimethyl-2-oxobutyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5c): ^{1}H NMR (300 MHz, $CDCl_3$)



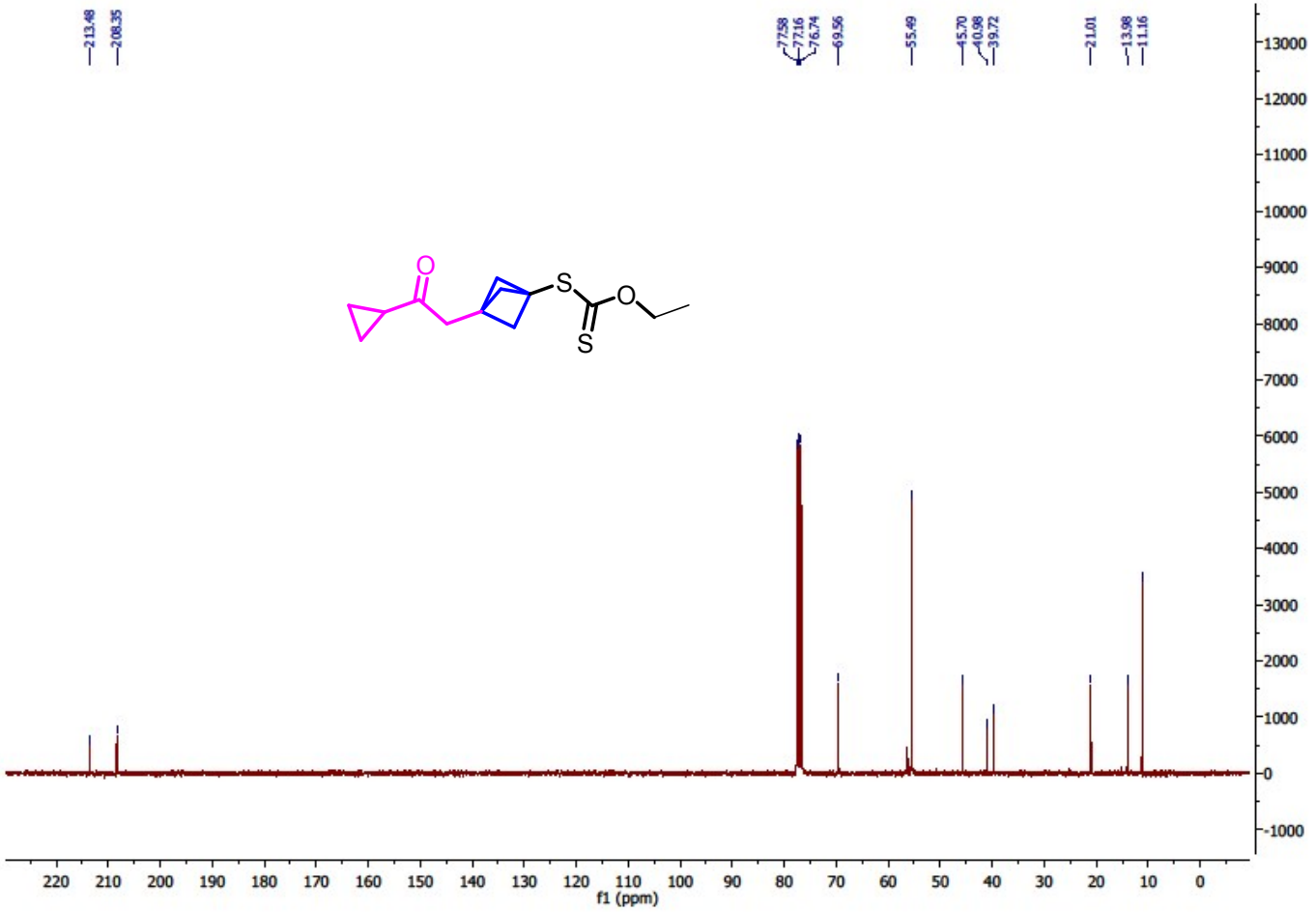
S-(3-(3,3-dimethyl-2-oxobutyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5c): ^{13}C NMR (75 MHz, $CDCl_3$)



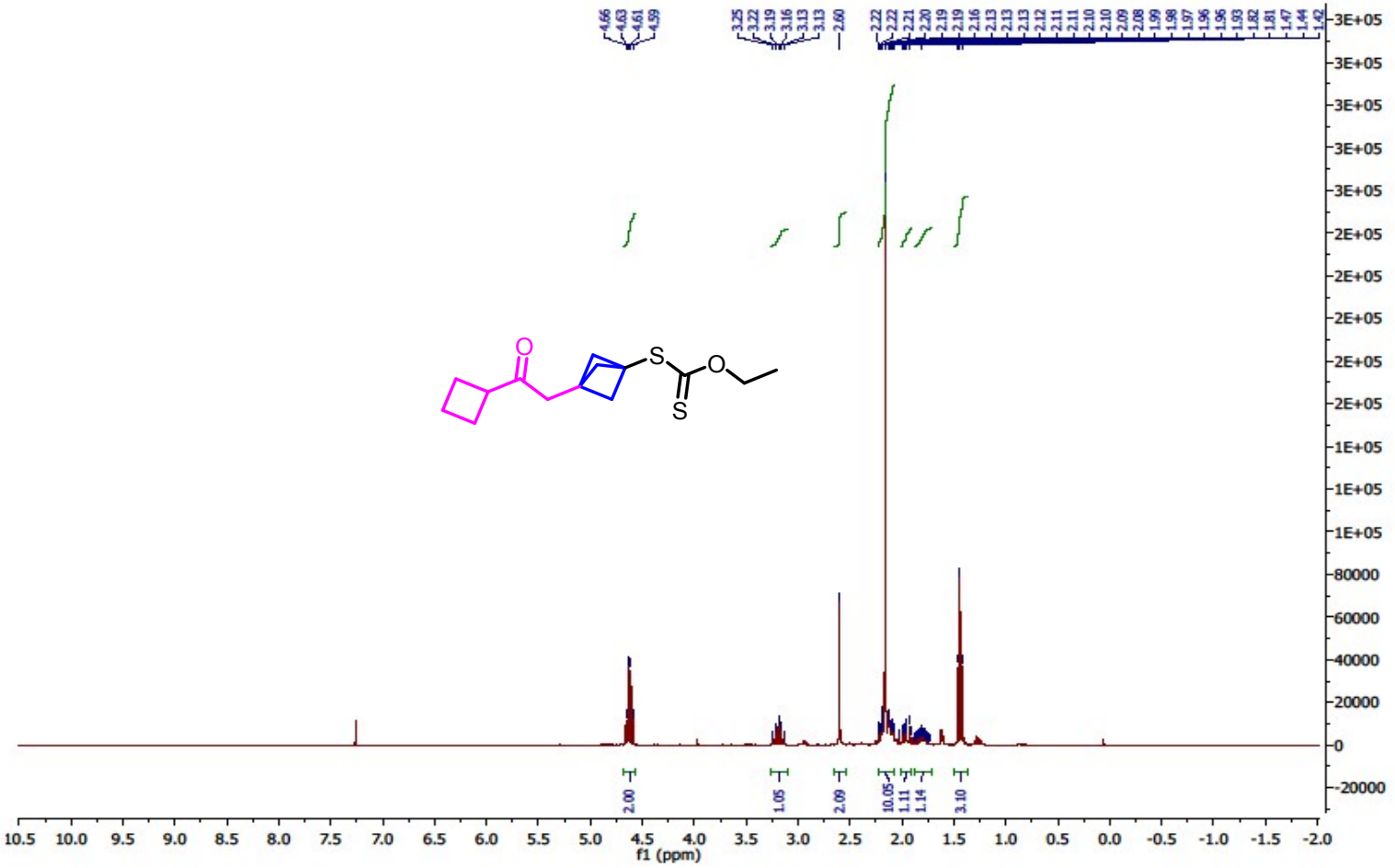
S-(3-(2-cyclopropyl-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5d): ^{1}H NMR (300 MHz, $CDCl_3$)



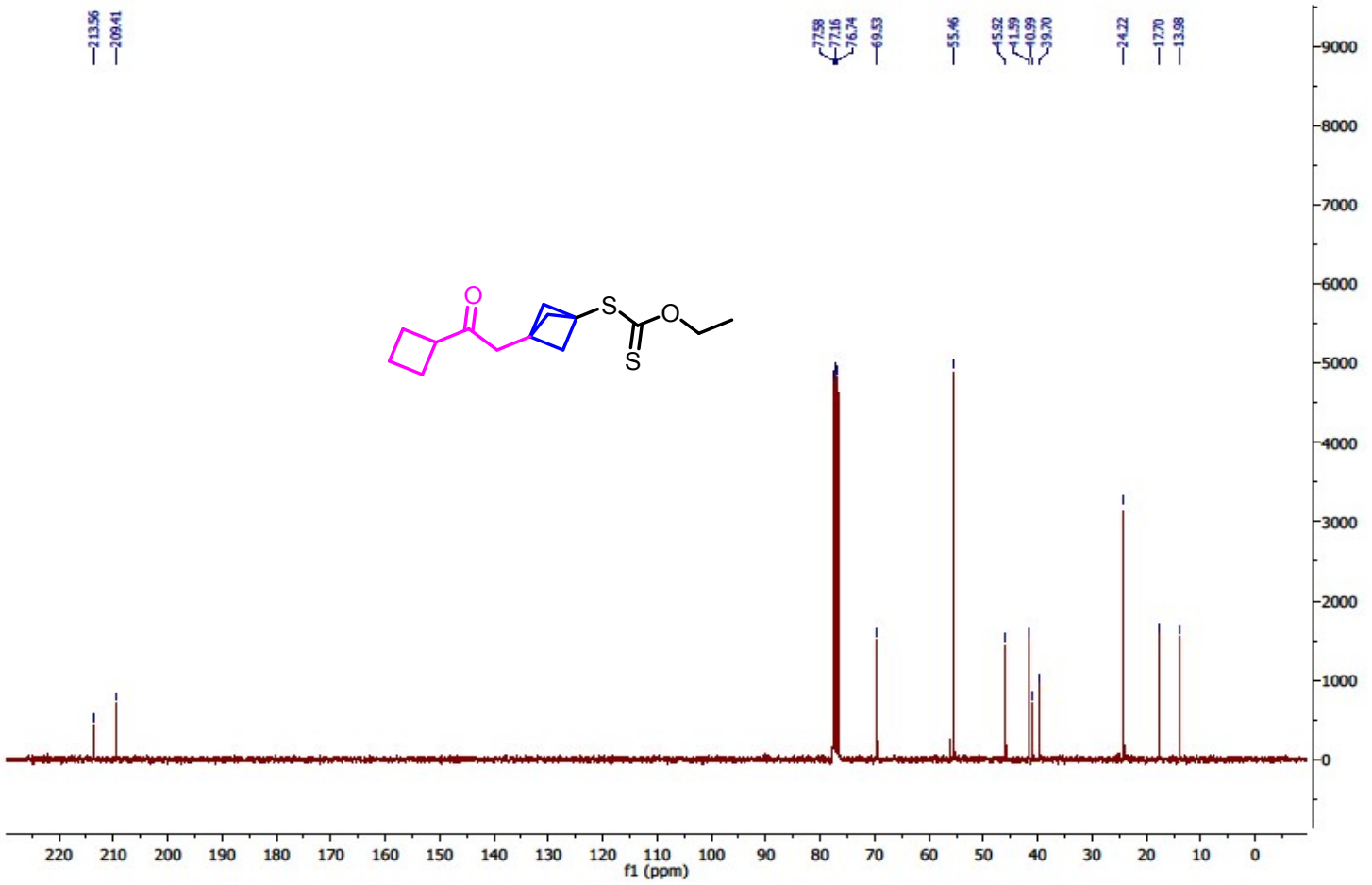
S-(3-(2-cyclopropyl-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5d): ^{13}C NMR (75 MHz, $CDCl_3$)



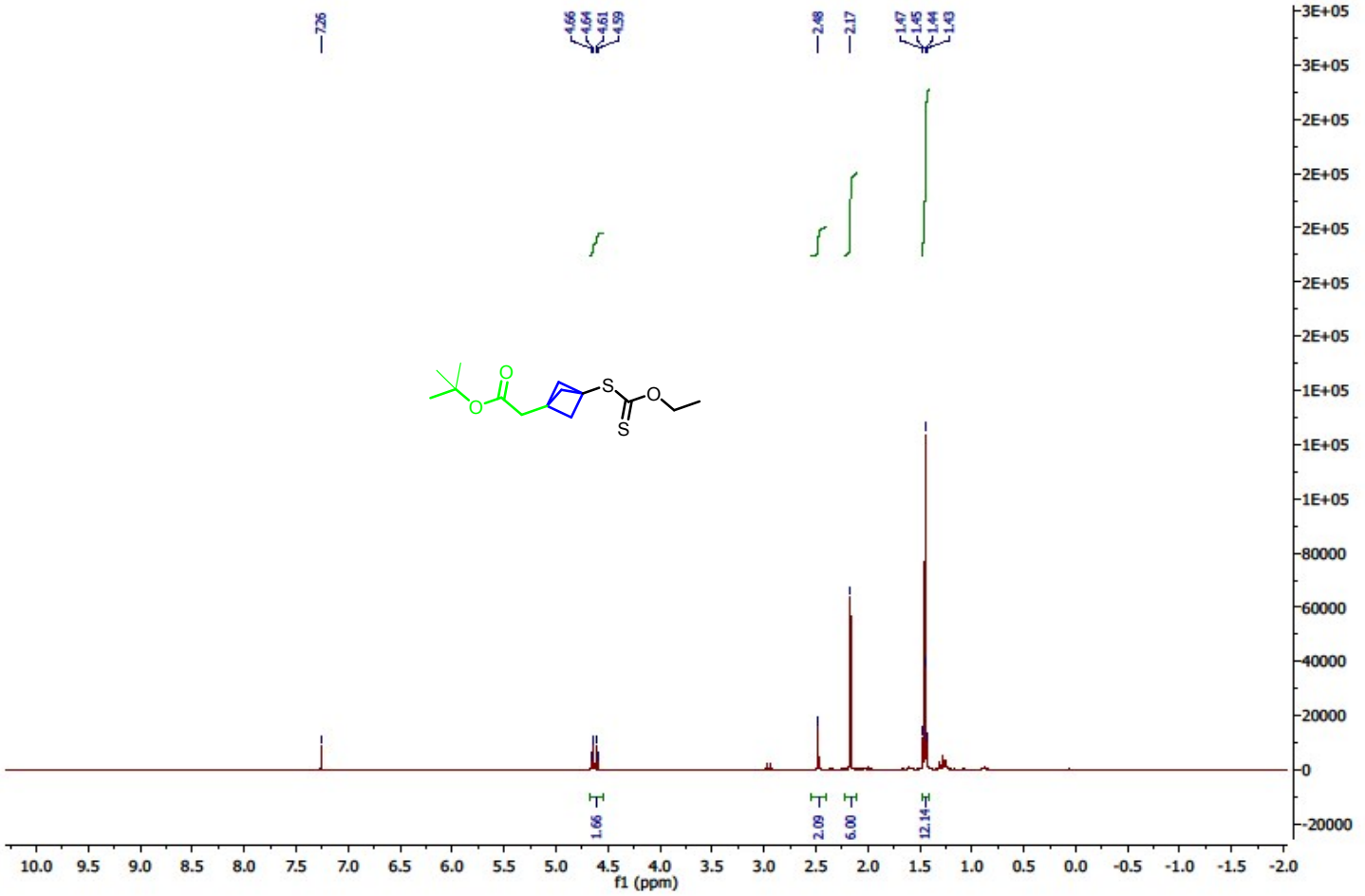
S-(3-(2-cyclobutyl-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5e): ^{1}H NMR (300 MHz, $CDCl_3$)



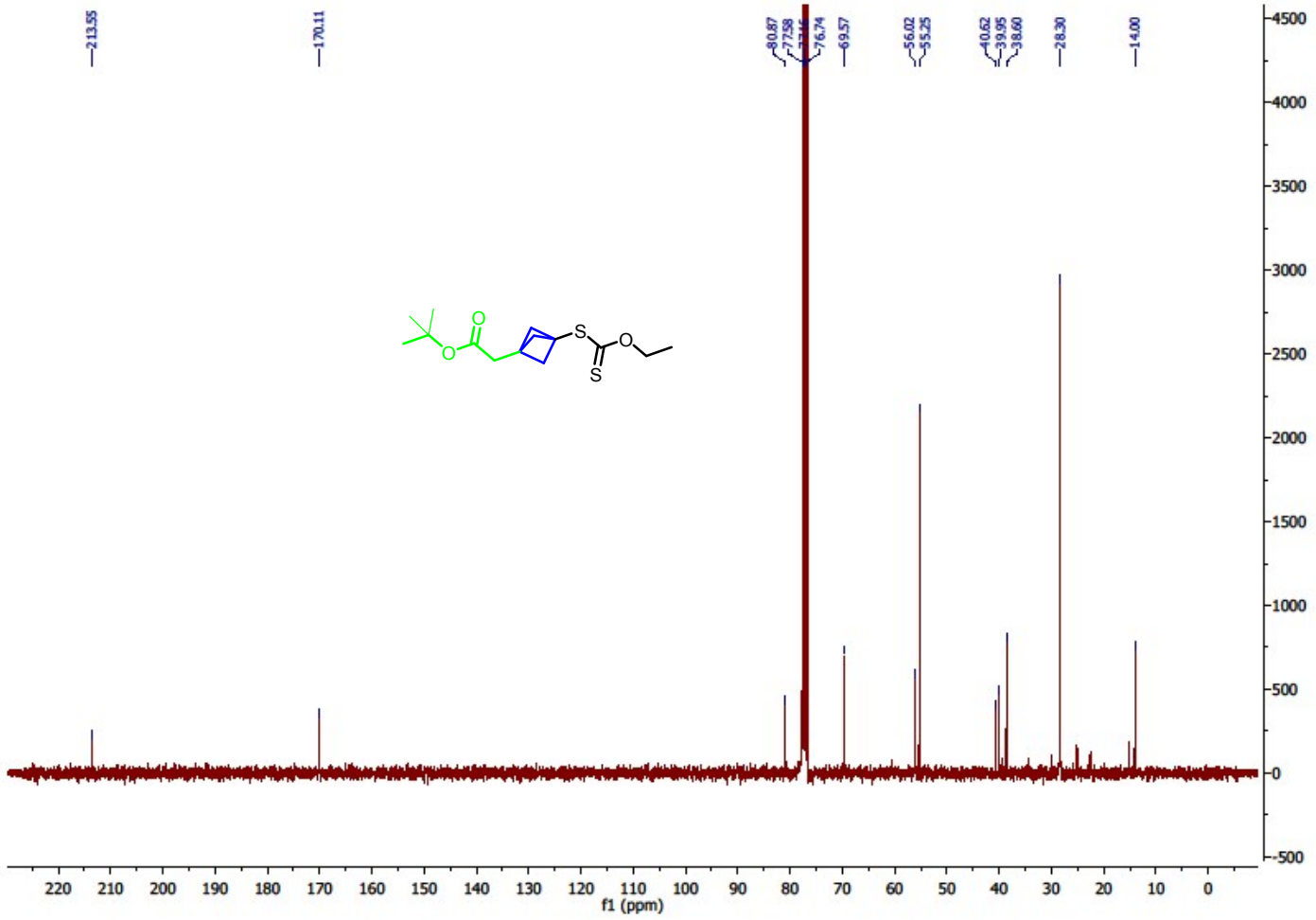
S-(3-(2-cyclobutyl-2-oxoethyl)bicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (5e): ^{13}C NMR (75 MHz, $CDCl_3$)



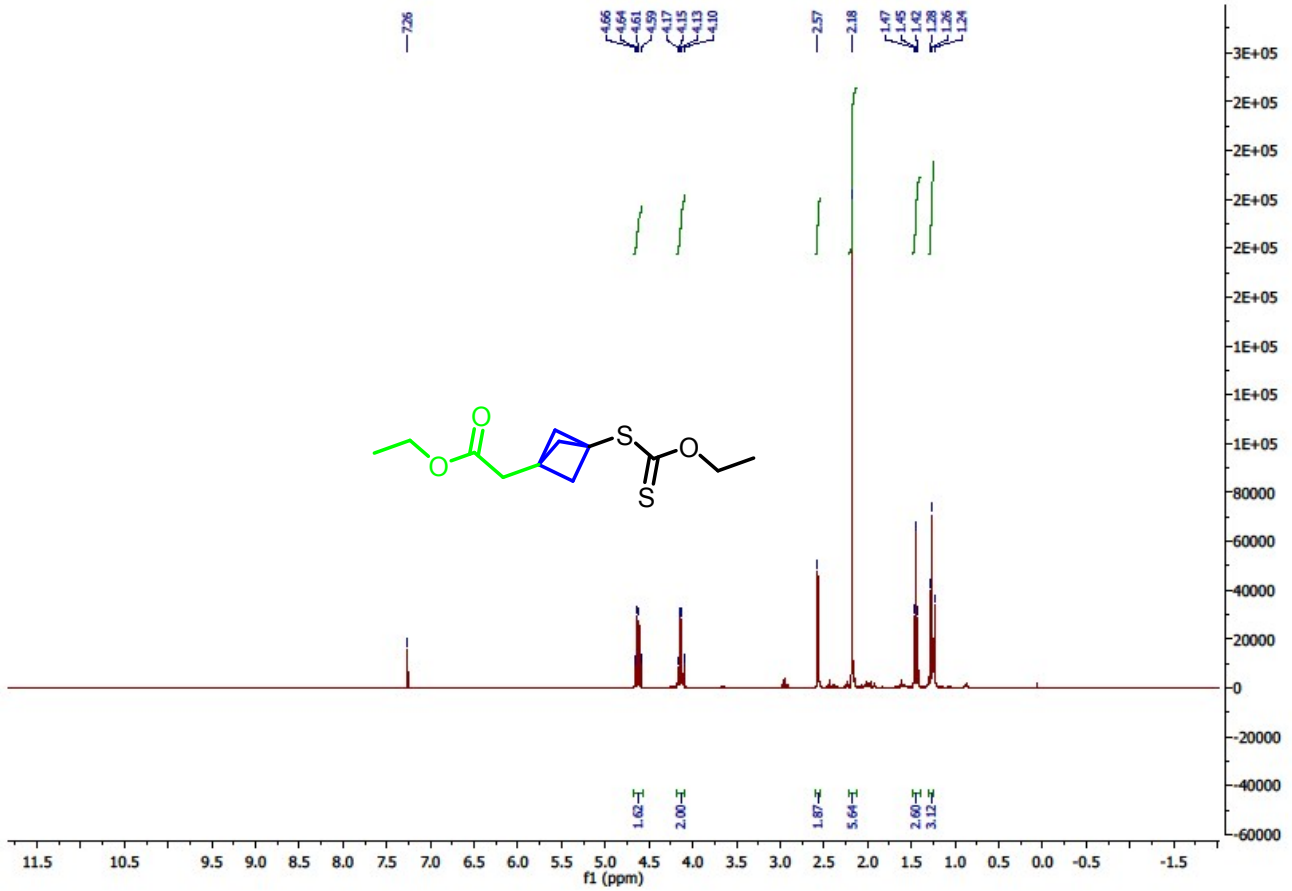
tert-butyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)acetate (12a): ^{1}H NMR (300 MHz, $CDCl_3$)



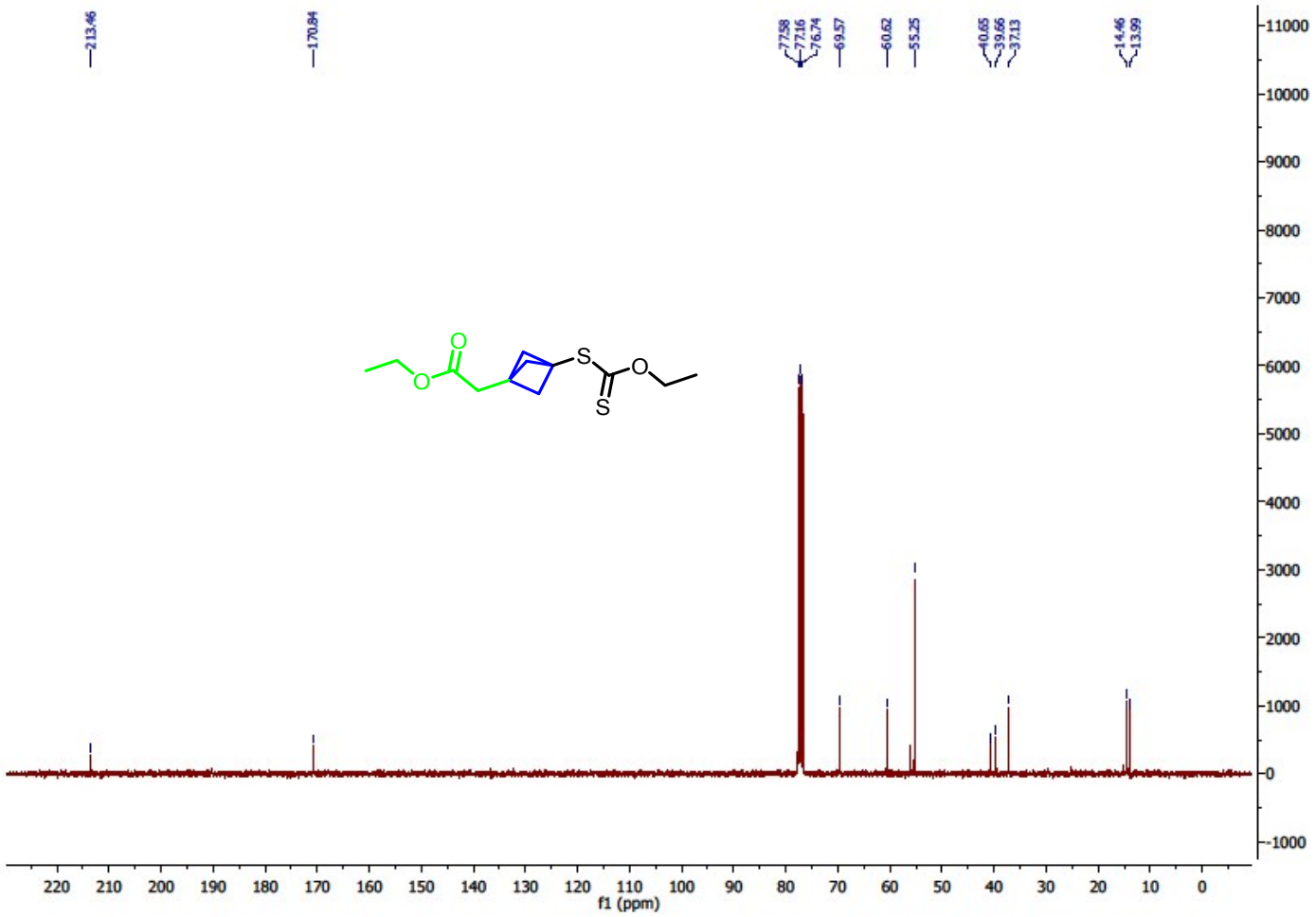
tert-butyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)acetate (12a): ^{13}C NMR (75 MHz, $CDCl_3$)



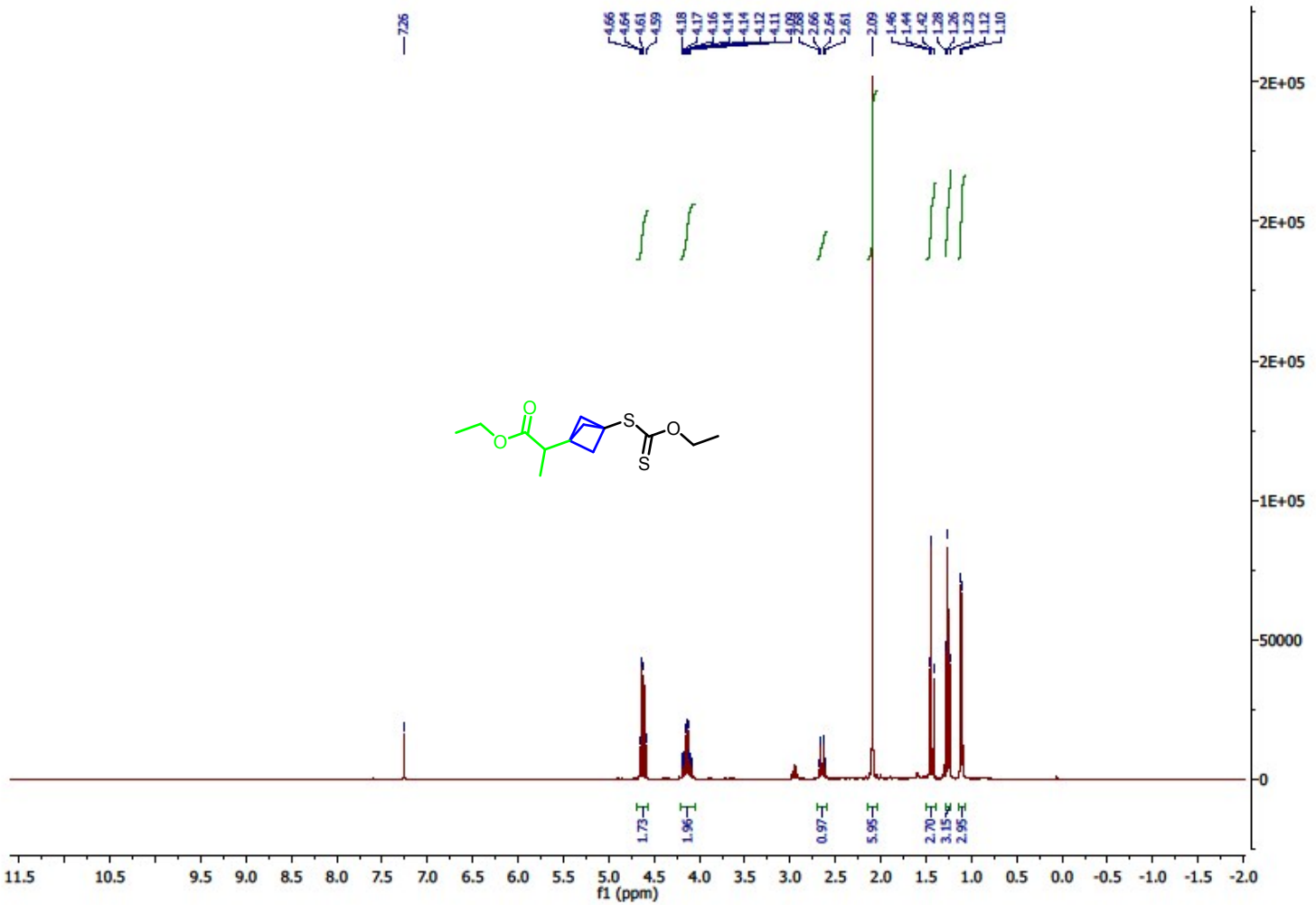
ethyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)acetate (12b): ^{1}H NMR (300 MHz, $CDCl_3$)



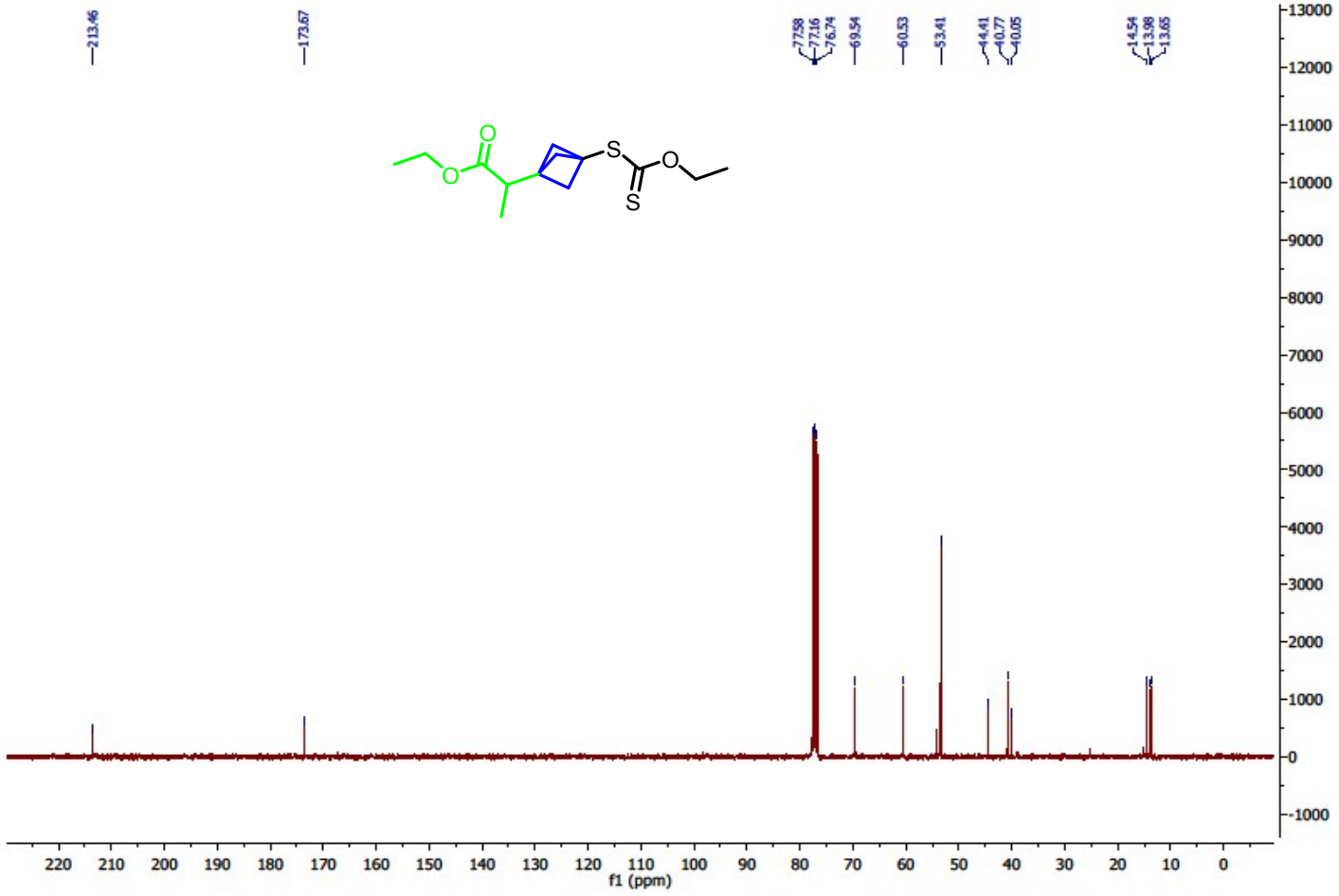
ethyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)acetate (12b): ^{13}C NMR (75 MHz, $CDCl_3$)



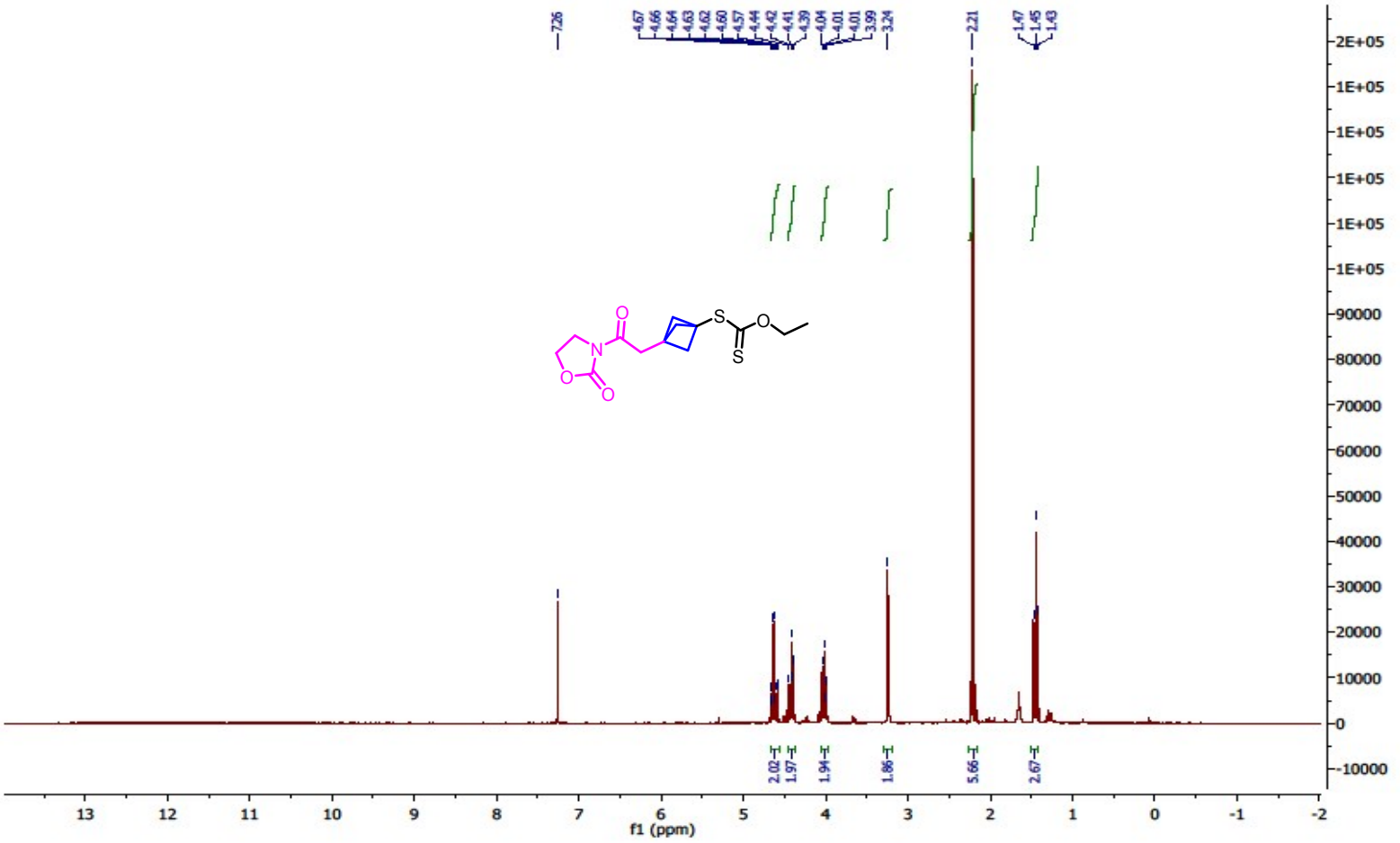
ethyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)propanoate (12c): ^{1}H NMR (300 MHz, $CDCl_3$)



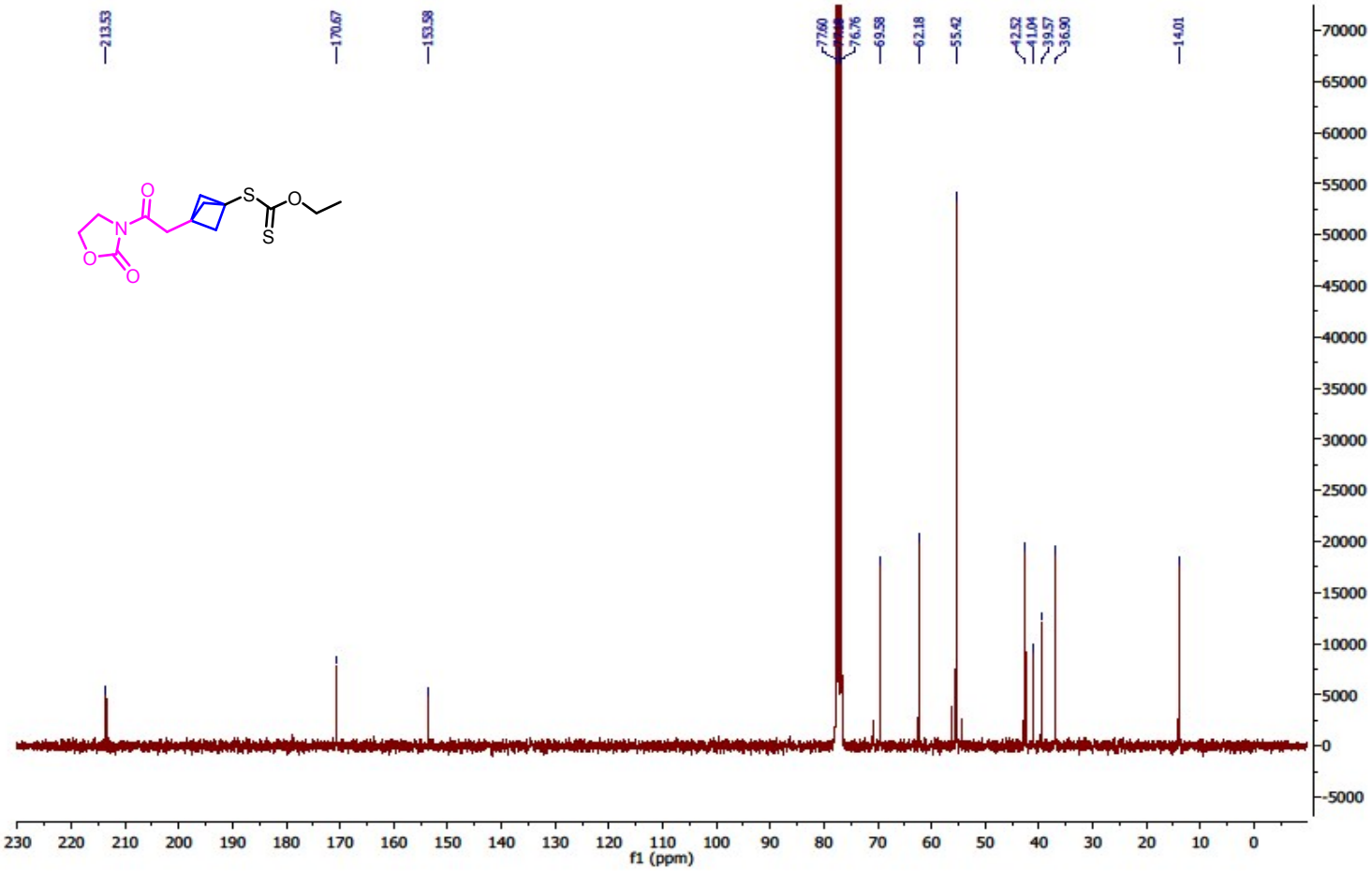
ethyl 2-(3-((ethoxycarbonothioyl)thio)bicyclo[1.1.1]pentan-1-yl)propanoate (12c): ^{13}C NMR (75 MHz, $CDCl_3$)



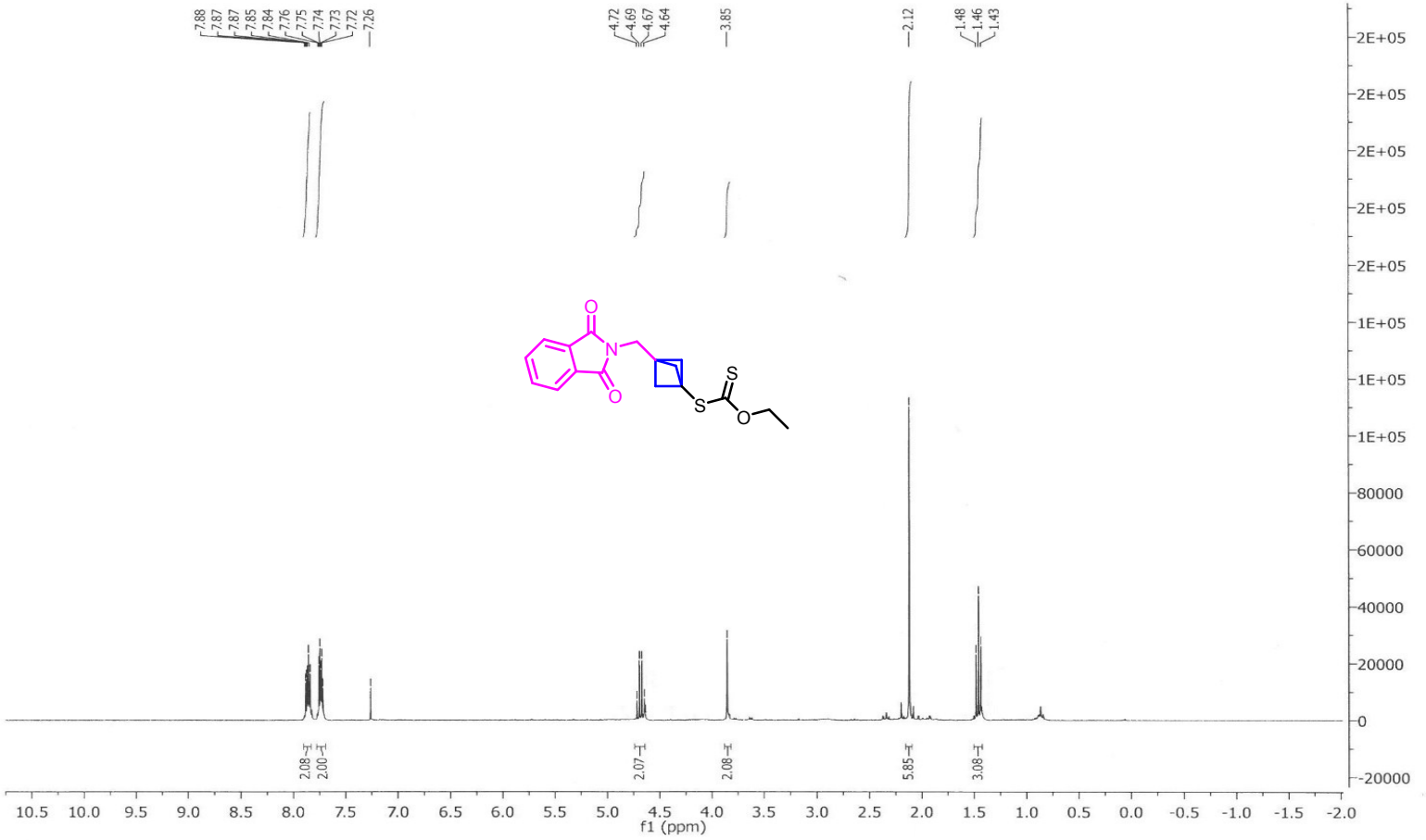
O-ethyl S-(3-(2-oxo-2-(2-oxooxazolidin-3-yl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (13a): ^{1}H NMR (300 MHz, $CDCl_3$)



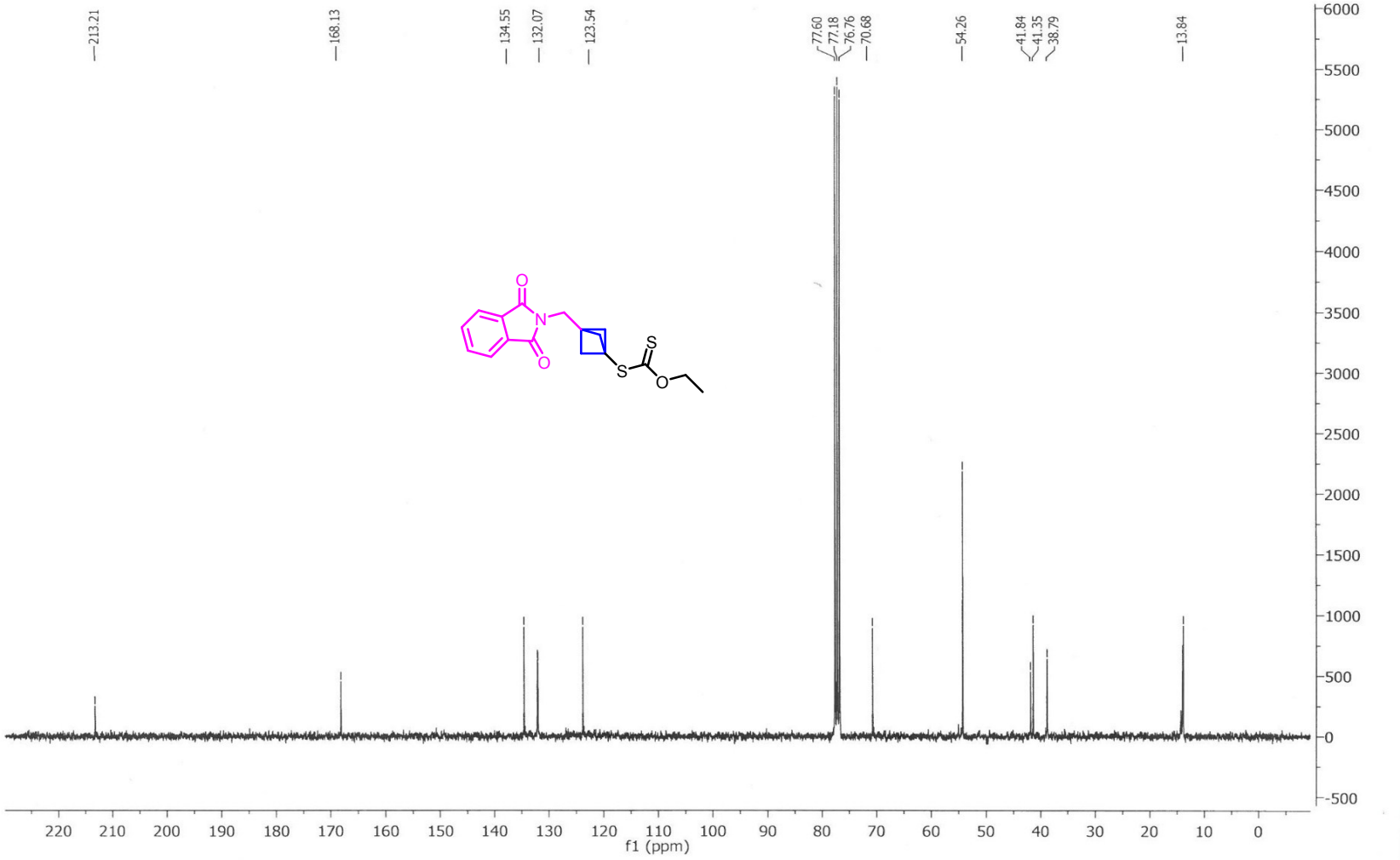
O-ethyl S-(3-(2-oxo-2-(2-oxooxazolidin-3-yl)ethyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (13a): ^{13}C NMR (75 MHz, $CDCl_3$)



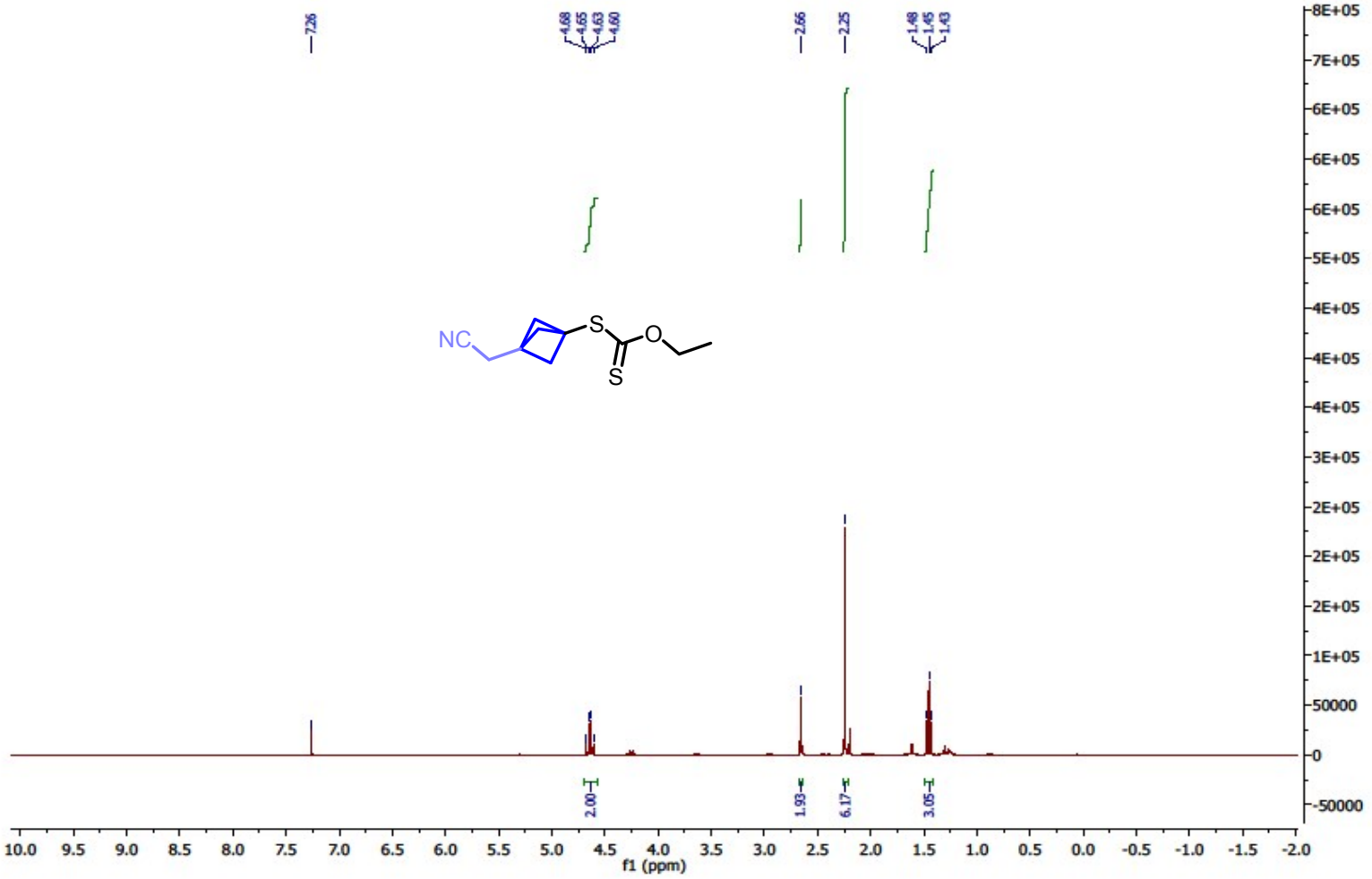
S-(3-((1,3-dioxoisoindolin-2-yl)methyl)bicyclo[1.1.1]pentan-1-yl) *O*-ethyl carbonodithioate (14a): ^{1}H NMR (300 MHz, $CDCl_3$)



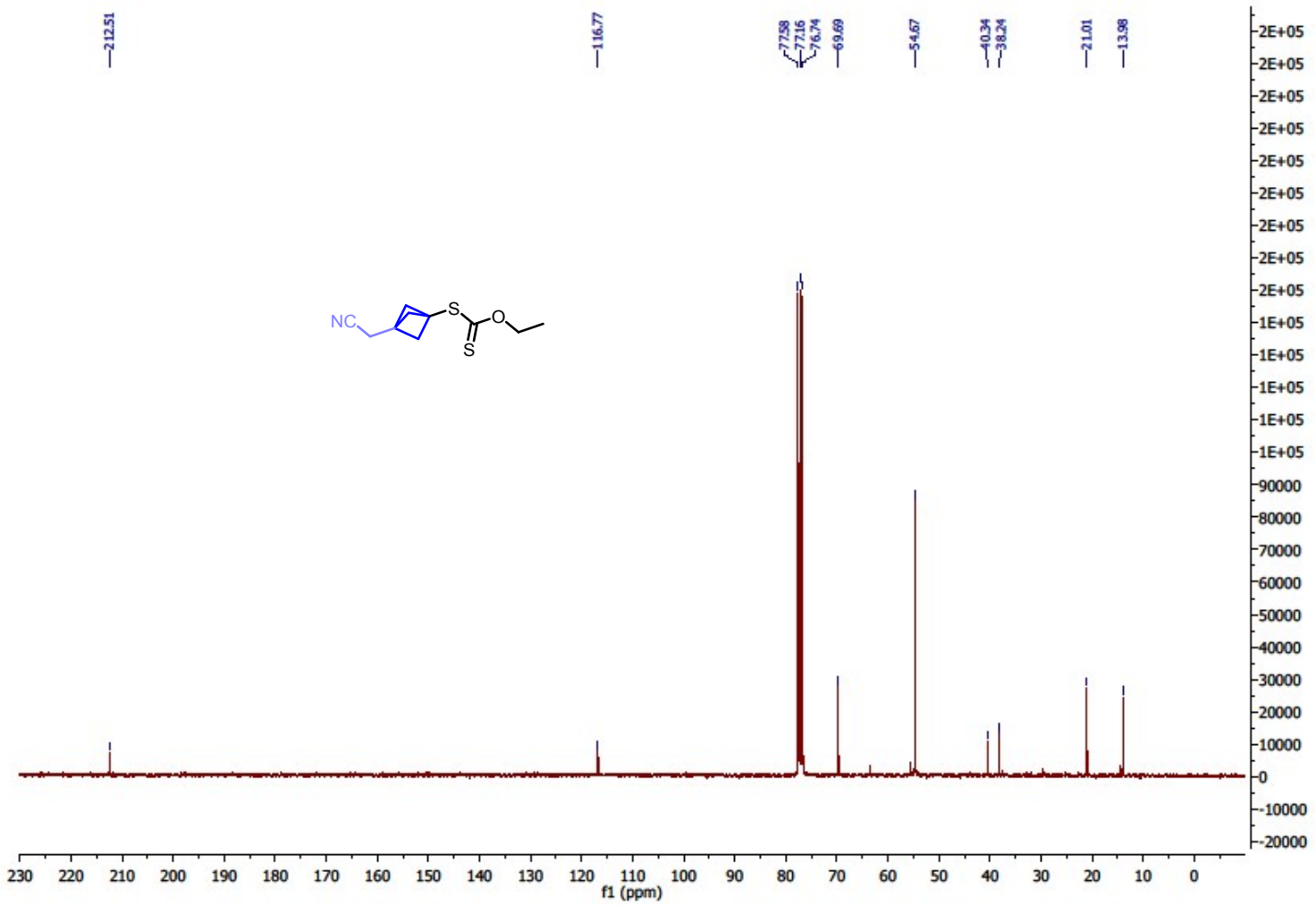
5-Methyl-2-(pyridine-2-yl)phenyl 4-(*tert*-butyl)benzoate (14a): ^{13}C NMR (150 MHz, $CDCl_3$)



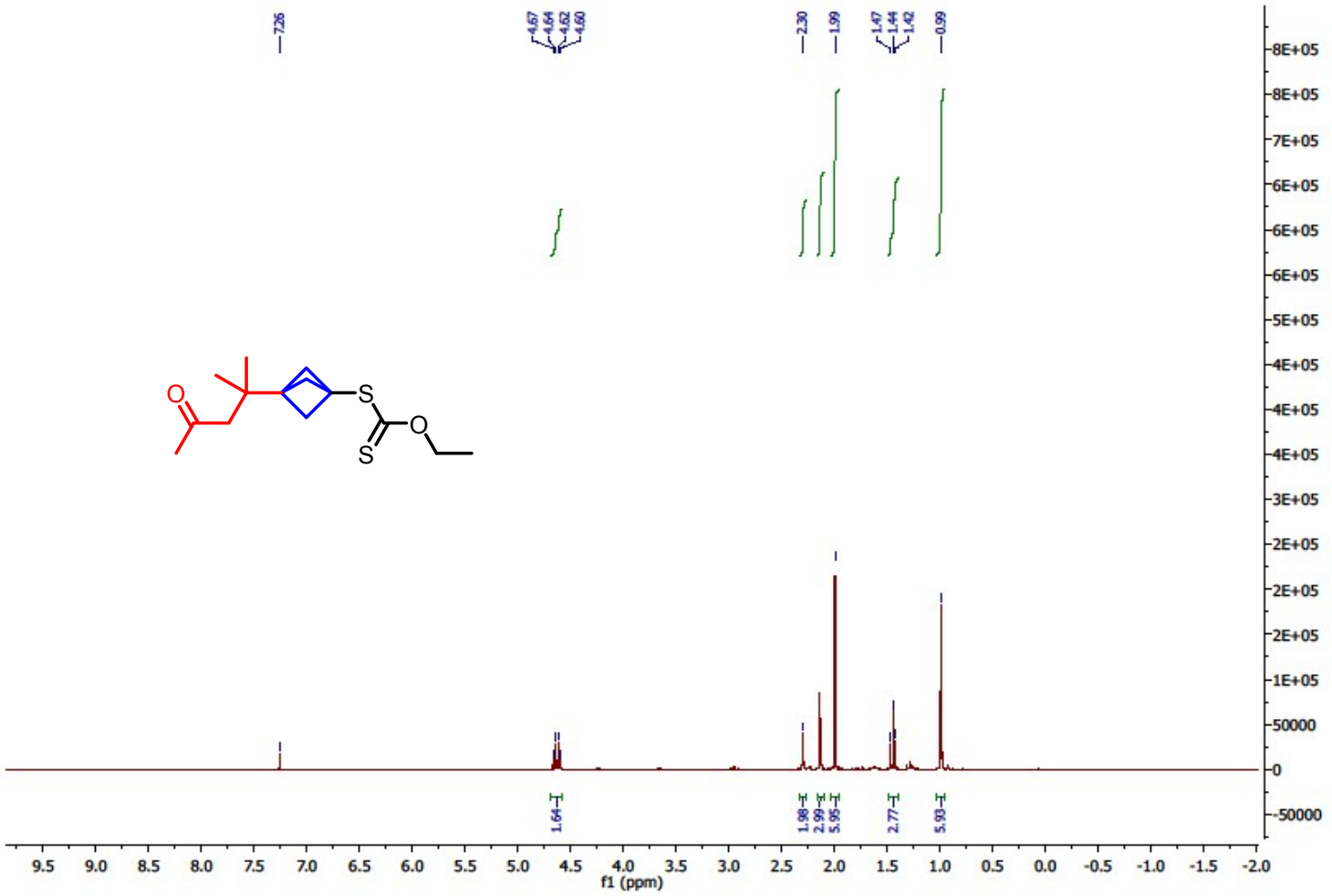
S-(3-cyanobicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (15a): ^{1}H NMR (300 MHz, $CDCl_3$)



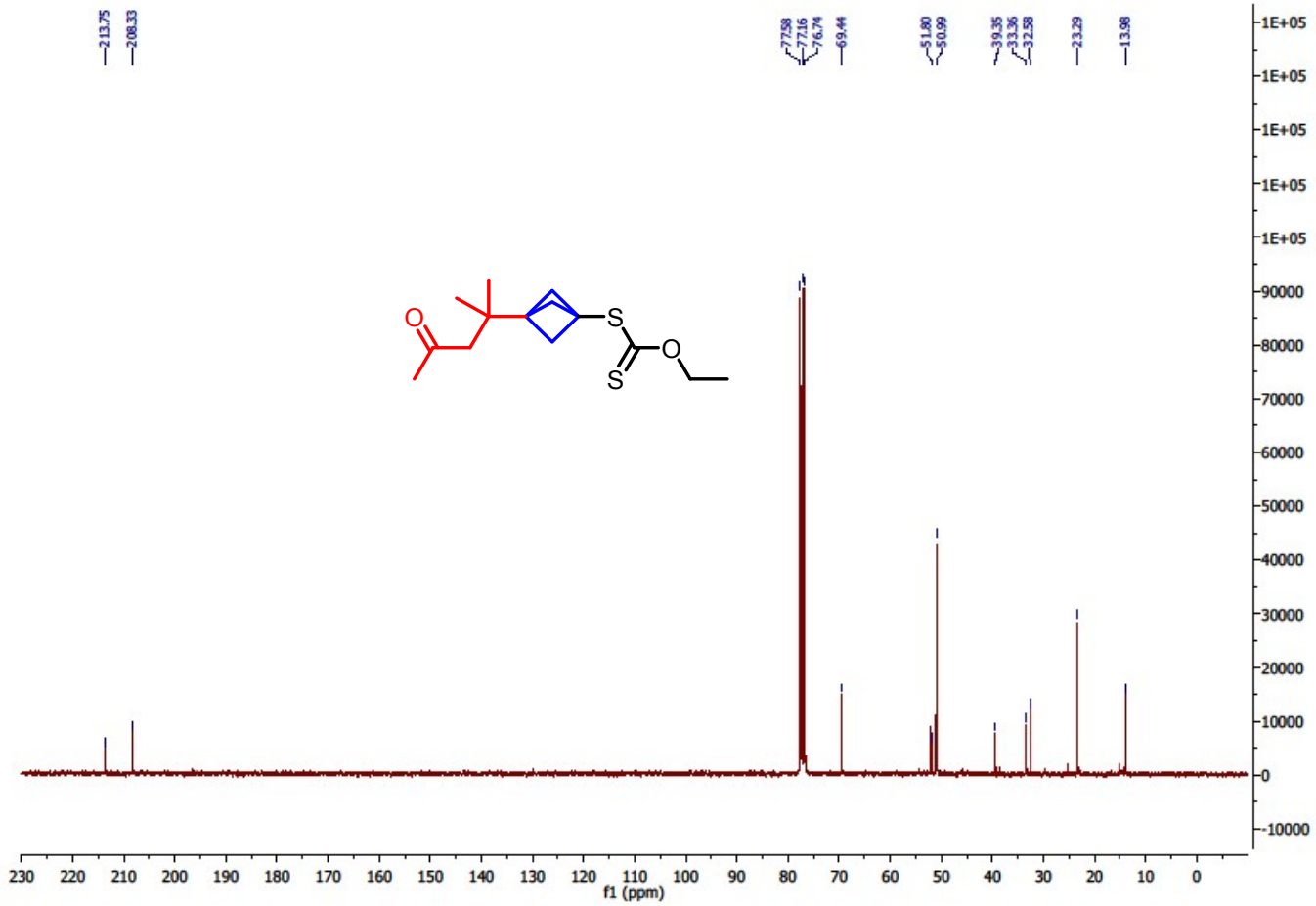
S-(3-cyanobicyclo[1.1.1]pentan-1-yl) O-ethyl carbonodithioate (15a): ^{13}C NMR (75 MHz, $CDCl_3$)



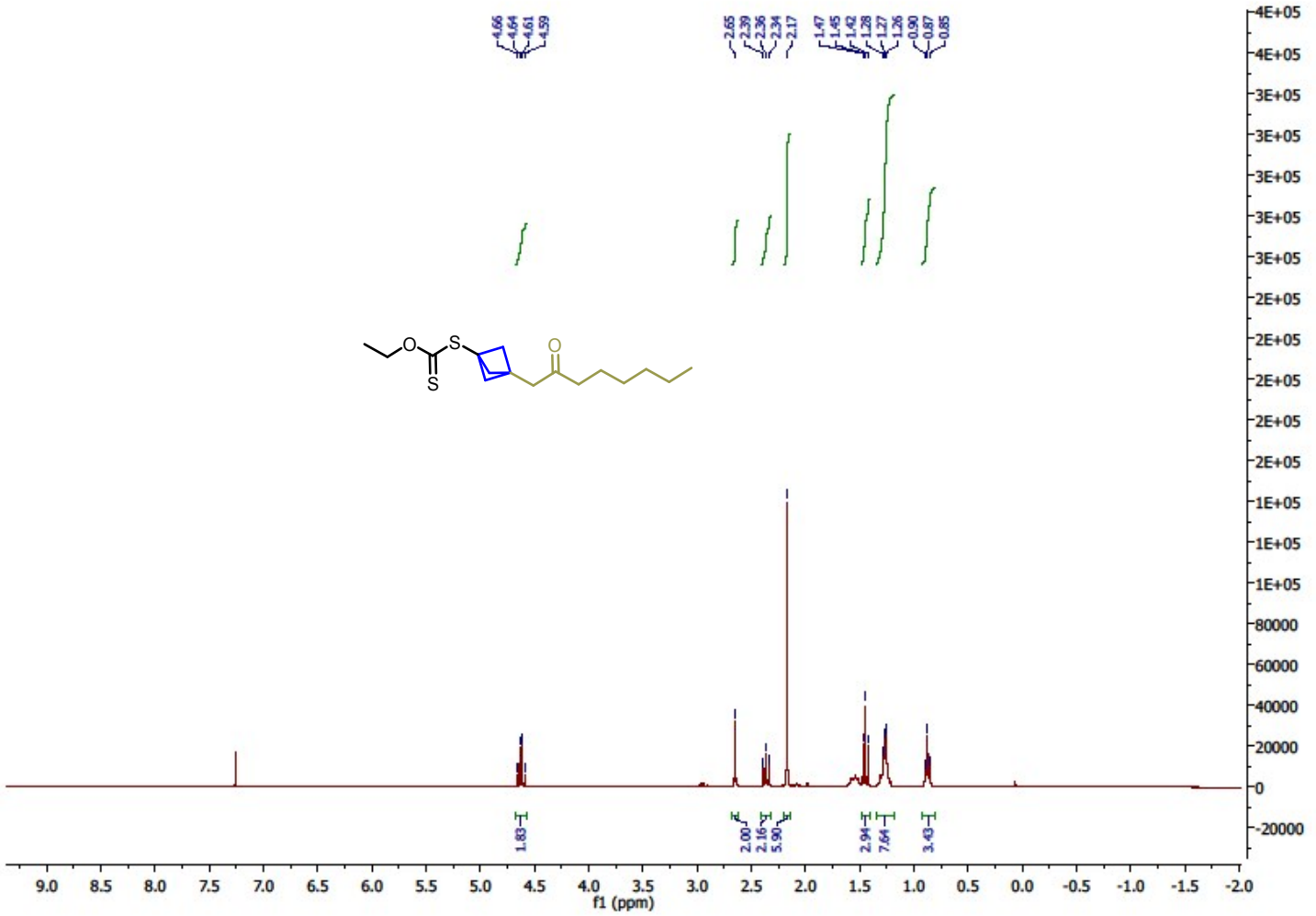
O-ethyl S-(3-(2-methyl-4-oxopentan-2-yl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (16a): ^{1}H NMR (300 MHz, $CDCl_3$)



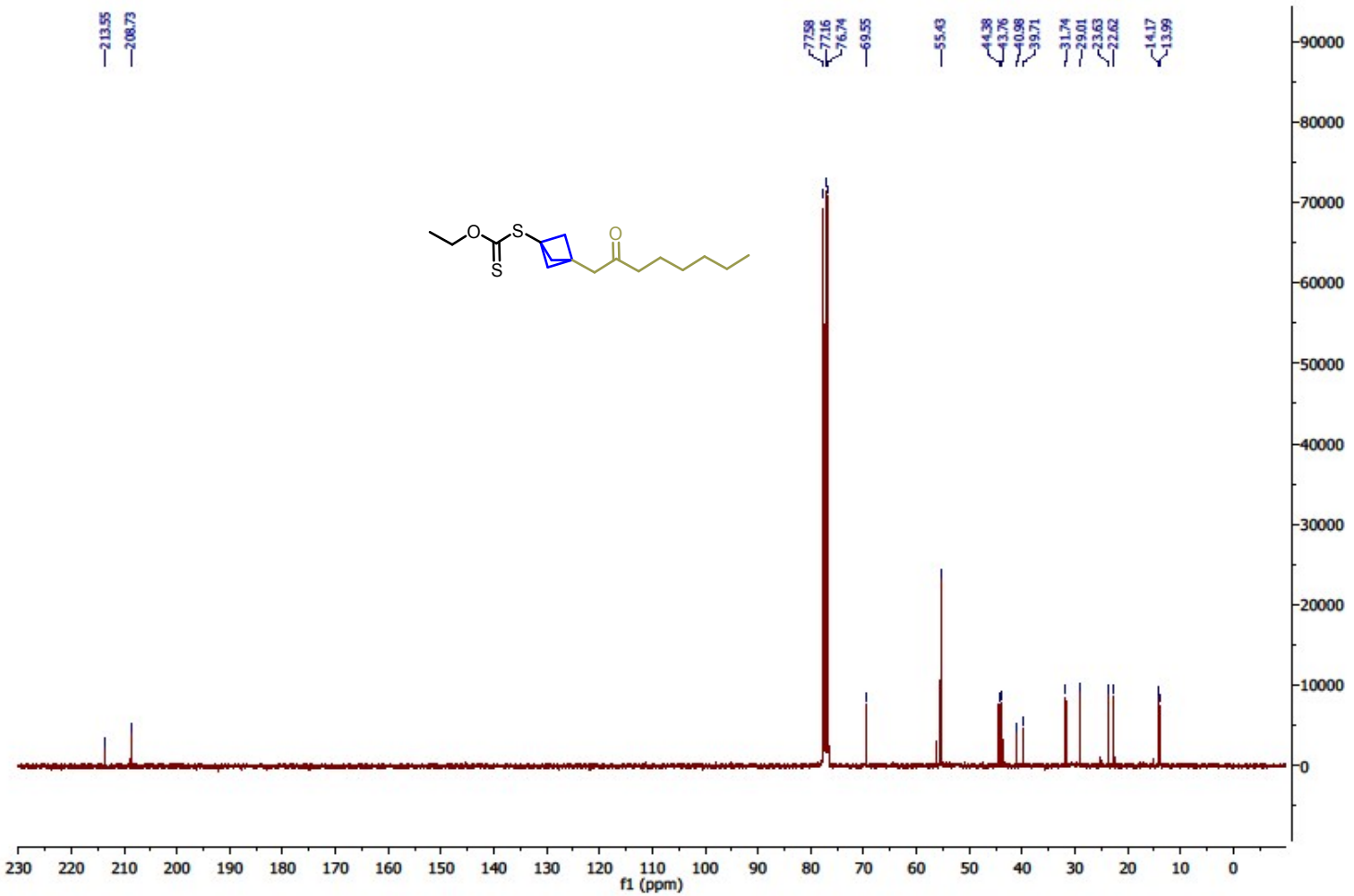
O-ethyl S-(3-(2-methyl-4-oxopentan-2-yl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (16a): ^{13}C NMR (75 MHz, $CDCl_3$)



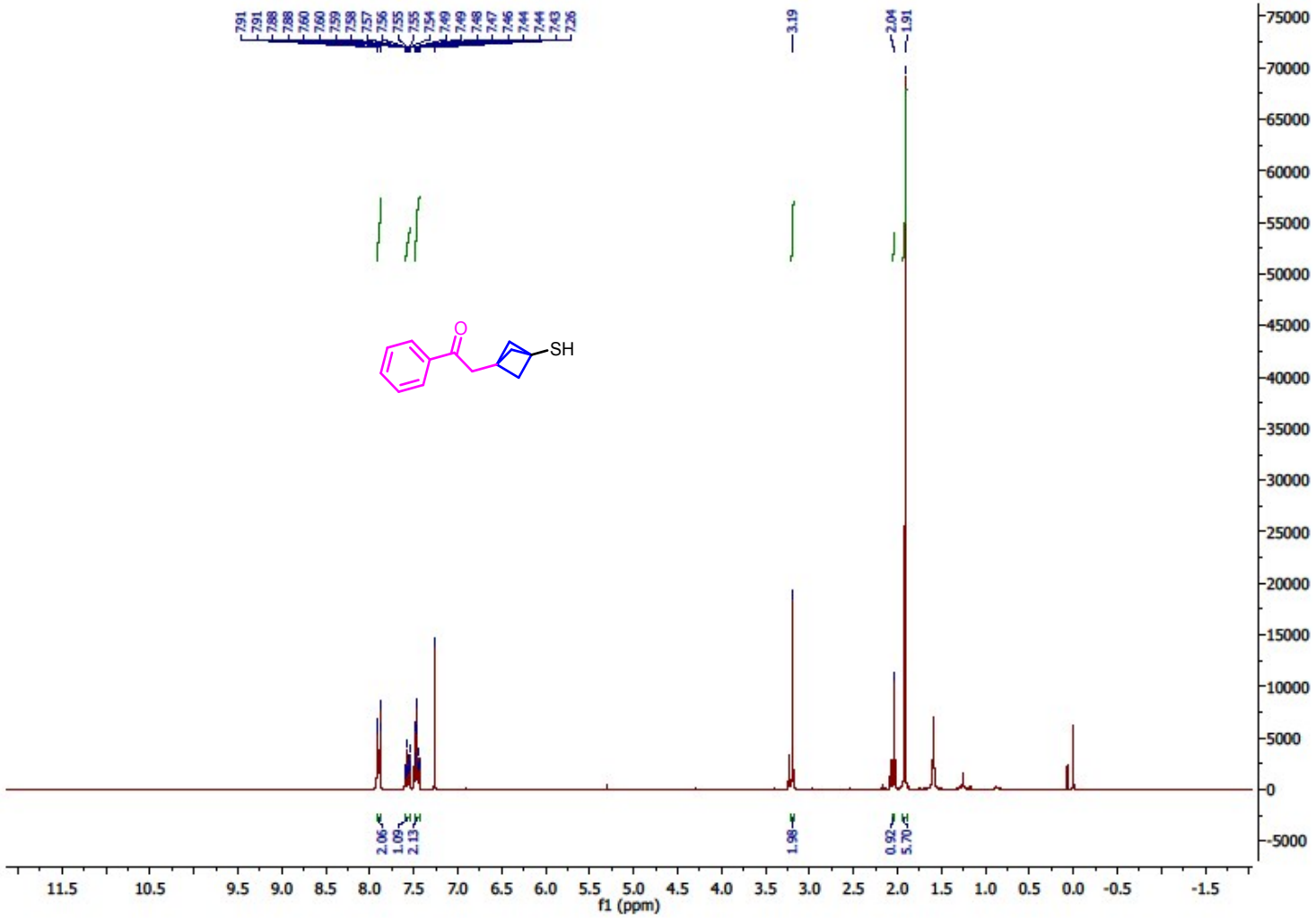
O-ethyl S-(3-(2-oxooctyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (17a): ^{1}H NMR (300 MHz, $CDCl_3$)



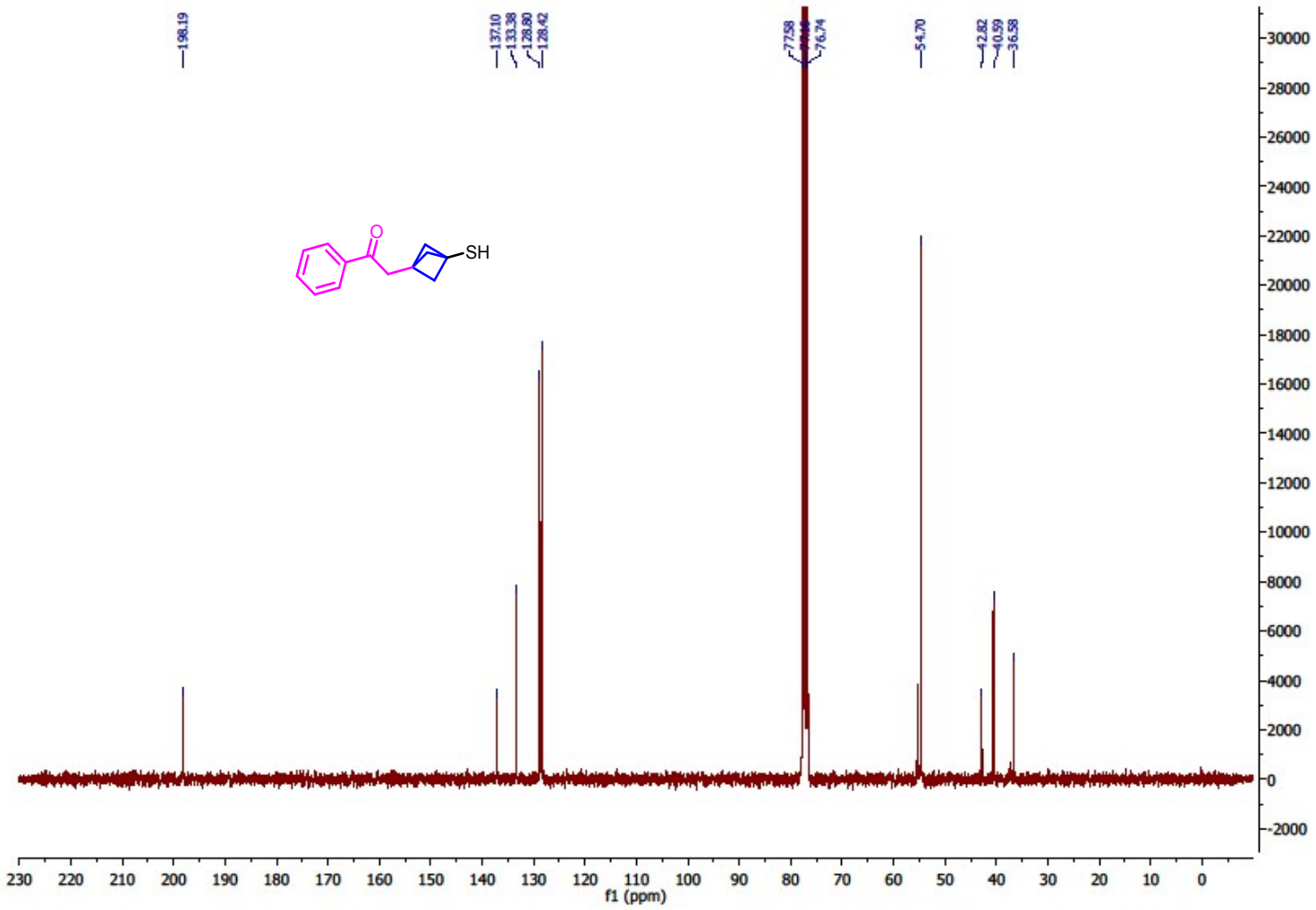
O-ethyl S-(3-(2-oxooctyl)bicyclo[1.1.1]pentan-1-yl) carbonodithioate (17a): ^{13}C NMR (75 MHz, $CDCl_3$)



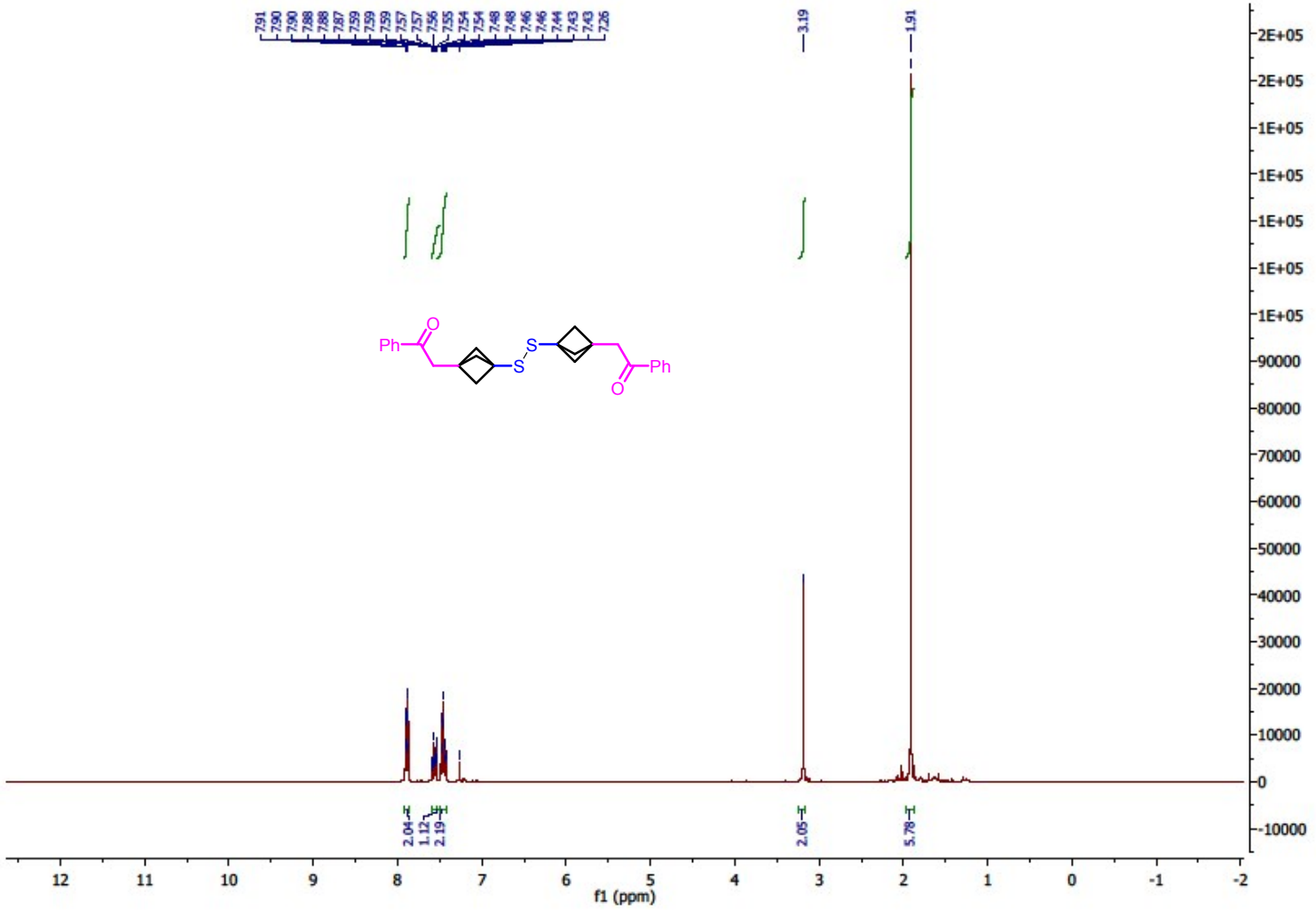
2-(3-Mercaptobicyclo[1.1.1]pentan-1-yl)-1-phenylethan-1-one (18): ^{1}H NMR (300 MHz, $CDCl_3$)



2-(3-Mercaptobicyclo[1.1.1]pentan-1-yl)-1-phenylethan-1-one (18): ^{13}C NMR (75 MHz, $CDCl_3$)



2,2'-(Disulfanediylbis(bicyclo[1.1.1]pentane-3,1-diyl))bis(1-phenylethan-1-one) (19): ^{1}H NMR (300 MHz, $CDCl_3$)



2,2'-(Disulfanediylbis(bicyclo[1.1.1]pentane-3,1-diyl))bis(1-phenylethan-1-one) (19): ^{13}C NMR (75 MHz, $CDCl_3$)