Supporting Information

S_N2-Type Nucleophilic Opening of β-Thiolactones (Thietan-2-ones) as a Source of Thioacids for Coupling Reactions

David Crich* and Kasinath Sana

Department of Chemistry, Wayne State University, 5101 Cass Avenue, Detroit, MI 48202 and

Centre de Recherche CNRS de Gif-sur-Yvette, Institut de Chimie des Substances Naturelles,

Avenue de la Terrasse, Gif-sur-Yvette, France

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General. Unless otherwise stated ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ solution. Optical rotations were recorded in $CHCl_3$ solutions, unless otherwise stated. All organic extracts were dried over sodium sulfate, and concentrated under aspirator vacuum. Chromatographic purifications were carried out over silica gel.

3-Methylthietan-2-one (1), thietan-2-one (9), and 3-benzylthietan-2-one (10) were prepared according to the literature protocols and had spectral data consistent with that given in the literature.[1]

Methyl 1-iodomethylcyclohexane carboxylate (12): Prepared according to the lit. procedure,[2] from methyl cyclohexane carboxylate in 65% yield. Light brown liquid; ^{1}H NMR (500 MHz) δ: 3.72 (s, 3H), 3.32 (s, 2H), 2.14-2.11 (m, 2H), 1.60-1.28 (m, 8H); ^{13}C NMR (125 MHz) δ: 174.7, 52.3, 47.7, 34.5, 25.8, 23.2, 15.9; ESI-HRMS Calcd for $C_9H_{15}O_2I$ $[M + Na]^+$: 305.0015. Found: 305.0031.

Methyl 1-acetylsulfanylmethylcyclohexane carboxylate (13): Prepared according to the lit. procedure,[2] from methyl 1-iodomethylcyclohexane carboxylate in 98% yield. Brown syrup; ^{1}H NMR (500 MHz) δ: 3.67 (s, 3H), 3.13 (s, 2H), 2.32 (s, 3H), 2.03-1.59 (m, 2H), 1.59-1.57 (m, 2H), 1.53-1.50 (m, 1H), 1.39-1.28 (m, 5H); ^{13}C NMR (125 MHz) δ: 195.2, 175.8, 52.1, 47.5, 37.4, 33.4, 30.8, 25.7, 23.0; ESI-HRMS Calcd for $C_{11}H_{18}O_3S$ $[M + Na]^+$: 253.0874. Found: 253.0888.

NMR investigation of 16 with a chiral shift reagent: A stock solution of DL-*tert*-butyl thietan-2-on-3-yl carbamate (9 mg, 0.044 mmol) in $CDCl_3$ (150 μL) was prepared. 50 μL of the stock solution was introduced into an NMR tube (5 mm i.d.) and diluted with $CDCl_3$ (700 μL), and the ^{1}H NMR spectrum of the sample was recorded at 500 MHz. A stock solution of tris[3-(heptafluoropropylhydroxymethylene)-(+)-camphorato], europium(III) [Eu(hfc)$_3$] (26 mg, 0.22 mmol) was prepared in $CDCl_3$ (75 μL). Then a 5 μL (~0.1 equiv) increments of the Eu(hfc)$_3$ solution were added to the NMR tube and the ^{1}H NMR spectrum recorded after each addition. The same procedure was repeated for the L-isomer of the carbamate.

3-(4-Chlorophenylthio)-*N*-phenethylpropanamide (20): Following general procedure A, using thietan-2-one and eluting with 32% ethyl acetate in hexane, **20** was obtained in 67% yield. White solid, crystallized from chloroform/hexane, mp: 78.8-79.5 ^{o}C. ^{1}H NMR (300 MHz) δ: 7.33-7.17 (m, 9H), 5.62 (s, 1H), 3.54-3.48 (q, J = 6.6 Hz, 2H), 3.18-3.13 (t, J = 7.2 Hz, 2H), 2.83-2.78 (t, J = 6.6, 2H), 2.41-2.37 (t, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz) δ: 170.9, 138.9, 134.2, 132.6, 131.1, 129.4, 129.0, 128.9, 126.8, 40.9, 36.2, 35.8, 29.8; ESI-HRMS Calcd for $C_{17}H_{18}NOSCl$ $[M + Na]^+$: 342.0695. Found: 342.0680.

Methyl 2-(3-oxo-3-(phenethylamino)propylthio)benzoate (21): Following general procedure A, using thietan-2-one and eluting with 40% ethyl acetate in hexane, **21** was obtained in 56% yield. Light yellow syrup; ^{1}H NMR (300 MHz) δ: 7.95-7.92 (dd, J = 1.8, 8.0 Hz, 1H), 7.47-7.40 (m, 1H), 7.36-7.29 (m, 4H), 7.26-7.14 (m, 3H), 5.79 (s, 1H), 3.88 (s, 3H), 3.54-3.47 (q, J = 6.6 Hz, 2H), 3.24-3.19 (t, J = 7.2 Hz, 2H), 2.82-2.78 (t, J = 6.6, 2H), 2.52-2.47 (t, J = 7.2 Hz, 2H); ^{13}C NMR (75 MHz) δ: 171.1, 167.2, 140.8, 139.0, 132.7, 131.5, 129.0, 128.9, 128.2, 126.8, 126.2, 124.5, 52.4, 41.0, 35.8, 35.5, 28.0; ESI-HRMS Calcd for $C_{19}H_{21}NO_3S$ $[M + Na]^+$: 366.1140. Found: 366.1145.

***N*-3-(4-Chlorophenylthio)propanoyl piperidine (22):** Following general procedure A, using thietan-2-one and eluting with 40% ethyl acetate in hexane, **22** was obtained in 59% yield. Colorless syrup; ^{1}H

NMR (500 MHz) δ: 7.30-7.25 (m, 4H), 3.56-3.54 (t, J = 5.5 Hz, 2H), 3.34-3.32 (t, J = 5.5 Hz, 2H), 3.24-3.21 (t, J = 7.5 Hz, 2H), 2.64-2.61 (t, J = 7.5 Hz, 2H), 1.67-1.62 (m, 2H), 1.56-1.53 (m, 4H); ^{13}C NMR (125 MHz) δ: 169.2, 134.9, 132.2, 130.6, 129.3, 46.7, 43.1, 33.1, 29.5, 26.7, 25.7, 24.7; ESI-HRMS Calcd for $C_{14}H_{18}NOSCl$ $[M + Na]^+$: 306.0695. Found: 306.0694.

Methyl *N*-(3-(phenylthio)-propanoyl)-L-phenylalaninate (23): Following general procedure A, using thietan-2-one and eluting with 30% ethyl acetate in hexane, **23** was obtained in 61% yield. Colorless syrup; $[\alpha]^{23}_D$ +59.2 (*c* 0.6); ^{1}H NMR (500 MHz) δ: 7.35-7.20 (m, 8H), 7.11-7.09 (d, J = 6.5 Hz, 2H), 6.00 (s, 1H), 4.93-4.89 (q, J = 6.0 Hz, 1H), 3.74 (s, 3H), 3.20-3.15 (m, 3H), 3.13-3.09 (dd, J = 5.5, 13.8 Hz, 1H), 2.54-2.46 (m, 2H); ^{13}C NMR (125 MHz) δ: 172.1, 170.6, 135.9, 135.4, 130.1, 129.5, 129.3, 128.8, 127.4, 126.7, 53.3, 52.6, 38.1, 36.2, 29.5; ESI-HRMS Calcd for $C_{19}H_{21}NO_3S$ $[M + Na]^+$: 366.1140. Found: 366.1133.

***N*-3-(4-Chlorophenylthio)-2-methylpropanoyl piperidine (25):** Following general procedure B, using 3-methylthietan-2-one and eluting with 25% ethyl acetate in hexane, **25** was obtained in 58% yield. White solid, crystallized from chloroform/hexane, mp: 49.3-50.0 ^{o}C. ^{1}H NMR (500 MHz) δ: 7.29-7.25 (m, 4H), 3.61-3.53 (m, 2H), 3.34-3.29 (m, 3H), 2.95-2.91 (m, 2H), 1.66-1.61 (m, 2H), 1.57-1.50 (m, 4H), 1.23-1.22 (d, J = 6.5 Hz, 3H); ^{13}C NMR (125 MHz) δ: 173.0, 135.3, 132.3, 130.9, 129.3, 46.9, 43.3, 38.2, 35.8, 27.0, 25.9, 24.8, 17.9; ESI-HRMS Calcd for $C_{15}H_{20}NOSCl$ $[M + Na]^+$: 320.0852. Found: 320.0839.

2-Benzyl-*N*-phenethyl-3-(phenylthio)propanamide (26): Following general procedure A, using 3-benzylthietan-2-one and eluting with 20% ethyl acetate in hexane, **26** was obtained in 64% yield. White solid, crystallized from chloroform/hexane, mp: 78.1-78.7 ^{o}C. ^{1}H NMR (500 MHz) δ: 7.30-7.16 (m, 11H), 7.14-7.12 (d, J = 7.5 Hz, 2H), 7.03-7.02 (d, J = 7.0 Hz, 2H), 5.23 (s, 1H), 3.46-3.34 (m, 2H), 3.25-3.21 (dd, J = 9.0, 13.3 Hz, 1H), 3.08-3.04 (dd, J = 5.0, 13.8 Hz, 1H), 2.99-2.95 (dd, J = 9.0, 13.3 Hz,

1H), 2.92-2.88 (dd, *J* = 6.5, 13.5 Hz, 1H), 2.72-2.67 (m, 1H), 2.60-2.55 (m, 1H), 2.41-2.36 (m, 1H); ^{13}C NMR (125 MHz) δ: 173.1, 139.2, 139.1, 136.0, 129.3, 129.2, 129.0, 128.8, 128.7, 126.8, 126.6, 126.4, 50.0, 40.7, 38.8, 35.8, 35.6; ESI-HRMS Calcd for $C_{24}H_{25}NOS$ $[M + Na]^+$: 398.1555. Found: 398.1549.

2-Benzyl-3-(4-chlorophenylthio)-*N*-phenethylpropanamide (27): Following general procedure A, using 3-benzylthietan-2-one and eluting with 20% ethyl acetate in hexane, **27** was obtained in 68% yield. White solid, crystallized from chloroform/hexane, mp: 119.8-120.4 ^{o}C. ^{1}H NMR (500 MHz) δ: 7.31-7.20 (m, 8H), 7.13-7.10 (t, *J* = 8.5 Hz, 4H), 7.03-7.02 (d, *J* = 7.0 Hz, 2H), 5.22 (s, 1H), 3.46-3.34 (m, 2H), 3.24-3.19 (dd, *J* = 9.0, 13.3 Hz, 1H), 3.03-3.00 (dd, *J* = 5.0, 13.8 Hz, 1H), 2.98-2.93 (dd, *J* = 9.0, 13.3 Hz, 1H), 2.89-2.85 (dd, *J* = 6.5, 13.5 Hz, 1H), 2.73-2.68 (m, 1H), 2.60-2.55 (m, 1H), 2.38-2.31 (m, 1H); ^{13}C NMR (125 MHz) δ: 173.0, 139.1, 139.0, 134.5, 132.3, 130.6, 129.4, 129.3, 129.2, 129.0, 128.8, 126.9, 126.7, 50.0, 40.7, 38.8, 35.8, 35.7; ESI-HRMS Calcd for $C_{24}H_{24}NOSCl$ $[M + Na]^+$: 432.1165. Found: 432.1167.

***N*-[2-Benzyl-3-(4-chlorophenylthio)]propanoyl piperidine (28):** Following general procedure B, using 3-benzylthietan-2-one and eluting with 20% ethyl acetate in hexane, **28** was obtained in 59% yield. White solid, crystallized from chloroform/hexane, mp: 89.0-90.0 ^{o}C. ^{1}H NMR (500 MHz) δ: 7.29-7.26 (m, 2H), 7.23-7.20 (m, 3H), 7.18-7.13 (m, 4H), 3.60-3.56 (m, 1H), 3.39-3.35 (m, 1H), 3.35-3.31 (dd, *J* = 8.5, 13.3 Hz, 1H), 3.17-3.12 (m, 1H), 3.07-2.99 (m, 2H), 2.97-2.92 (m, 2H), 2.89-2.85 (dd, *J* = 6.5, 13 Hz, 1H), 1.49-1.43 (m, 4H), 1.36-1.26 (m, 2H); ^{13}C NMR (125 MHz) δ: 171.6, 139.1, 135.0, 132.1, 130.4, 129.3, 129.2, 128.7, 126.8, 46.9, 43.3, 43.2, 39.5, 36.4, 26.3, 25.8, 24.6; ESI-HRMS Calcd for $C_{21}H_{24}NOSCl$ $[M + Na]^+$: 396.1165. Found: 396.1159.

***N*-[2-Benzyl-3-(pyridine-2-ylthio)]propanoyl piperidine (29):** Following general procedure B, using 3-benzylthietan-2-one and eluting with 25% ethyl acetate in hexane, **29** was obtained in 57% yield. White solid, crystallized from chloroform/hexane, mp: 73.0-74.0 ^{o}C. ^{1}H NMR (500 MHz) δ: 8.41-8.40

(m, 1H), 7.48-7.45 (m, 1H), 7.27-7.15 (m, 6H), 6.99-6.96 (m, 1H), 3.59-3.55 (m, 1H), 3.49-3.38 (m, 4H), 3.13-3.08 (m, 1H), 3.07-2.97 (m, 3H), 1.49-1.41 (m, 4H), 1.26-1.21 (m, 2H); ^{13}C NMR (125 MHz) δ: 172.3, 159.1, 149.6, 139.8, 136.1, 129.3, 128.5, 126.5, 122.5, 119.6, 46.9, 43.3, 43.2, 39.3, 33.3, 26.3, 25.9, 24.7; ESI-HRMS Calcd for $C_{20}H_{24}N_2OS$ $[M + Na]^+$: 363.1507. Found: 363.1497.

2,4-Dinitro-*N*-phenethylbenzenesulfonamide (31) was prepared according to the literature method and had spectroscopic data corresponding to the literature values.[3]

(*R*)-*O*-(*tert*-Butyl) *N*-3-(pyridin-2-ylthio)-1-(phenethylaminocarbonyl)propan-2-yl) carbamate (32): Following general procedure C, eluting with 30% ethyl acetate in hexane, **32** was obtained in 61% yield. White solid, crystallized from chloroform/hexane, mp: 97.0-97.5 ^{o}C. $[\alpha]^{22}_{D}$ -4.7 (*c* 0.9); ^{1}H NMR (500 MHz) δ: 8.31 (s, 1H), 7.54-7.50 (m, 1H), 7.29-7.19 (m, 6H), 7.06-7.03 (t, *J* = 6.0 Hz, 1H), 6.92 (s, 1H), 6.74 (s, 1H), 4.39 (b, 1H), 3.56-3.52 (m, 4H), 2.83-2.80 (t, *J* = 7.0 Hz, 2H), 1.40 (s, 9H); ^{13}C NMR (125 MHz) δ: 171.0, 158.8, 156.7, 149.2, 139.1, 136.7, 129.0, 128.8, 126.7, 123.1, 120.3, 80.0, 56.5, 40.9, 36.0, 33.2, 28.5; ESI-HRMS Calcd for $C_{21}H_{27}N_3O_3S$ $[M + Na]^+$: 424.1671. Found: 424.1673.

***N*-(4-Bromophenyl)-2,4-dinitrobenzenesulfonamide (33):** To a solution of 4-bromoaniline (500 mg, 2.9 mmol) and 2,4-dinitrophenylsulfonyl chloride (930 mg, 3.5 mmol) in methylene chloride (3 mL) was added pyridine (350 μL, 4.4 mmol) dropwise at 0 ^{o}C. The reaction mixture was stirred at 0 ^{o}C for 15 min. and 4 h at room temperature. Then the organic layer was washed with 1M HCl, water, brine, dried and concentrated. Chromatographic purification using 20% ethyl acetate in hexane as eluent afforded **33** (680 mg, 58%). Brown solid, crystallized from ethyl acetate/hexane, mp: 143.7-144.4 ^{o}C. ^{1}H NMR (500 MHz) δ: 8.69-8.68 (d, *J* = 2.0 Hz, 1H), 8.44-8.42 (dd, *J* = 2.0, 8.8 Hz, 1H), 8.07-8.06 (d, *J* = 8.8 Hz, 1H), 7.45-7.43 (d, *J* = 8.8 Hz, 2H), 7.29 (s, 1H), 7.12-7.10 (d, *J* = 9.0 Hz); ^{13}C NMR (125 MHz) δ:150.4, 148.7, 137.5, 133.8, 133.7, 133.2, 127.2, 125.3, 121.2, 121.0; ESI-HRMS Calcd for $C_{12}H_7N_3O_6SBr$ $[M - H]^-$: 399.9239. Found: 399.9243.

(*R*)-*O*-(*tert*-Butyl) *N*-3-(phenylthio)-1-(4-bromophenylaminocarbonyl)propan-2-yl) carbamate (34): Following general procedure C, eluting with 20% ethyl acetate in hexane, **34** was obtained in 57% yield. White solid, crystallized from chloroform/hexane, mp: 128.0-129.0 ^{o}C. $[\alpha]^{22}_{D}$ -3.5 (*c* 0.95); ^{1}H NMR (500 MHz) δ: 8.31 (s, 1H), 7.43-7.41 (m, 4H), 7.36-7.35 (d, *J* = 9.0 Hz, 2H), 7.32-7.29 (t, *J* = 7.5 Hz, 2H), 7.24-7.21 (t, *J* = 7.5 Hz, 1H), 5.34-5.33 (d, *J* = 7.5 Hz, 1H), 4.35-4.33 (d, *J* = 6.5 Hz, 1H), 3.43-3.33 (m, 2H), 1.46 (s, 9H); ^{13}C NMR (125 MHz) δ: 168.8, 156.0, 136.6, 134.4, 132.2, 130.6, 129.5, 127.4, 121.7, 117.4, 81.4, 54.9, 36.0, 28.5; ESI-HRMS Calcd for $C_{20}H_{23}N_2O_3SBr$ $[M + Na]^+$: 473.0510. Found: 473.0500.

Methyl *N*-[(2,4-dinitrophenyl)sulfonyl]–L-phenylalaninate (35) was prepared according to the literature method and had spectroscopic data corresponding to the literature values.[4]

1-[(2,4-Dinitrophenylsulfanyl)methyl]-*N*-phenethylcyclohexane carboxamide (39): To a stirred solution of 2-thiaspiro[3.5]nonan-1-one (**14**) (50 mg, 0.32 mmol) in DMF (2 mL) were added 4-chlorothiophenol (70 mg, 0.48 mmol) and Cs_2CO_3 (104 mg, 0.32 mmol) at room temperature. The reaction mixture was allowed to stir for 2 h before 2,4-dinitrofluorobenzene (90 mg, 0.48 mmol) was added, followed immediately by 2-phenethylamine (36 μL, 0.29 mmol). Upon addition of 2,4-dinitrofluorobenzene and 2-phenethylamine the reaction mixture became a dark red color. The reaction mixture was allowed to stir for 2 h, after which the DMF was removed under high vacuum and the crude mixture was dissolved in EtOAc and washed with water, brine and dried. Evaporation of solvent, followed by column chromatographic purification using 30% ethyl acetate in hexane elutant afforded **39** (102 mg, 80%). Yellow solid, crystallized from ethyl acetate/hexane, mp: 99.0-99.5 ^{o}C. ^{1}H NMR (500 MHz) δ: 9.03-9.02 (d, *J* = 2.0 Hz, 1H), 8.36-8.34 (dd, *J* = 2.5, 9.0 Hz, 1H), 7.65-7.63 (d, *J* = 9.0 Hz, 1H), 7.33-7.20 (m, 5H), 5.88 (s, 1H), 3.54-3.51 (q, 7.0 Hz, 2H), 3.23 (s, 2H), 2.84-2.81 (t, *J* = 7.0 Hz, 2H), 2.01-1.98 (m, 2H), 1.65-1.58 (m, 6H), 1.37-1.35 (m, 2H); ^{13}C NMR (125 MHz) δ: 174.0, 146.7,

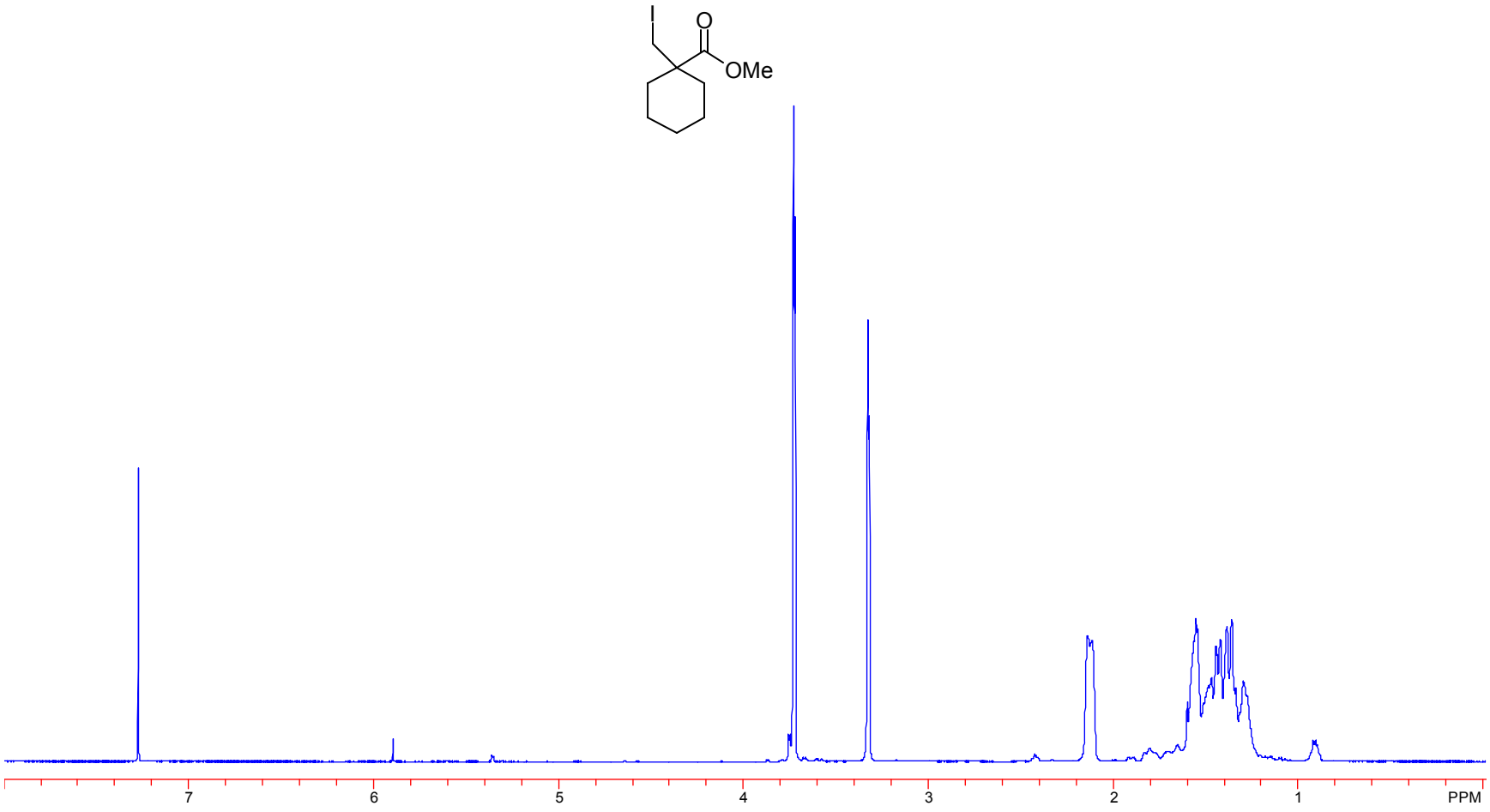
145.5, 144.1, 138.8, 129.0, 128.9, 127.9, 127.2, 126.9, 121.7, 46.7, 42.0, 41.1, 35.6, 34.0, 25.7, 22.7; ESI-HRMS Calcd for $C_{22}H_{25}N_3O_5S$ $[M + Na]^+$: 466.1413. Found: 466.1409.

2-Mercaptomethyl-3-phenylpropanoyl morpholine (40): To a stirred solution of 3-benzylthietan-2-one (45 mg, 0.25 mmol) in DMF (2 mL) was added morpholine (26 μL, 0.3 mmol) at room temperature. The reaction mixture was allowed to stir for 4 h, after which the DMF was removed under high vacuum and the crude mixture was dissolved in EtOAc and washed with water, brine and dried. Evaporation of solvent, followed by column chromatographic purification using 30% ethyl acetate in hexane elutant afforded **40** (45 mg, 67%). Colorless syrup; ^{1}H NMR (300 MHz) δ: 7.30-7.13 (m, 5H), 3.67-3.55 (m, 2H), 3.50-3.12 (m, 4H), 3.11-2.96 (m, 3H), 2.94-2.78 (m, 3H), 2.62-2.53 (m, 1H), 1.52-1.47 (t, J = 8.1 Hz, 1H); ^{13}C NMR (75 MHz) δ: 172.2, 138.9, 129.2, 128.8, 127.0, 67.0, 66.5, 47.7, 46.3, 42.4, 39.7, 27.4; ESI-HRMS Calcd for $C_{14}H_{19}NO_2S$ $[M + Na]^+$: 288.1034. Found: 288.1021.

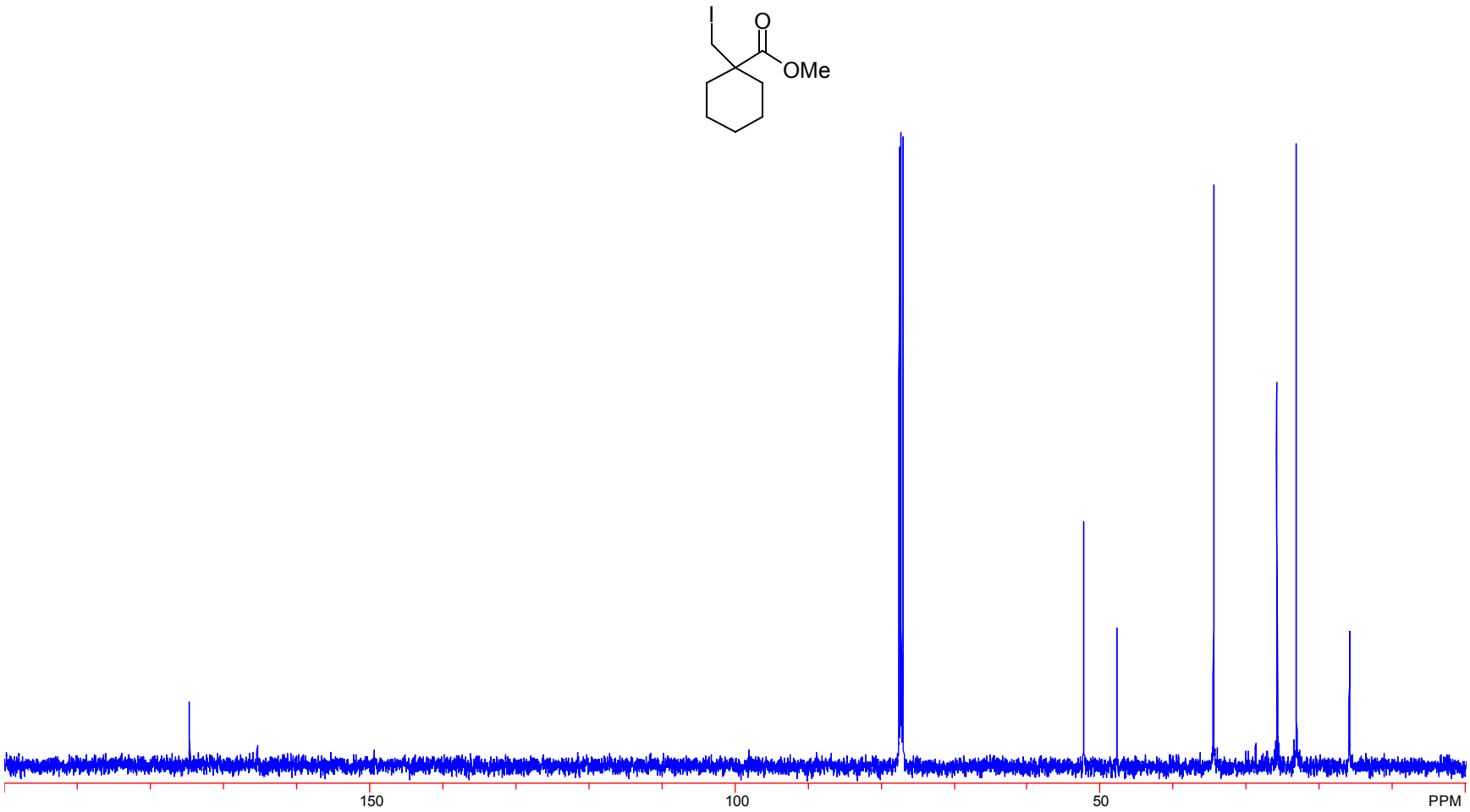
References:

1. Lee, H. B.; Park, H.-Y.; Lee, B.-S.; Kim, Y. G. *Magn. Reson. Chem.* **2000**, *38*, 468-471.
2. Hannah, D. R.; Dyke, H. J.; Sharpe, A.; Baxter, A. D.; PCT Int. Appl. 851145 (2001).
3. Nihei, K.-I.; Kato, M. J.; Yamane, T.; Palma, M. S.; Konno, K. *Synlett* **2001**, 1167-1169.
4. Crich, D.; Sana, K.; Guo, S. *Org. Lett.* **2007**, *9*, 4423-4426.

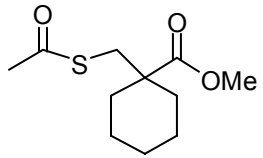
Methyl 1-iodomethylcyclohexane carboxylate (12)
(500 MHz, $CDCl_3$)

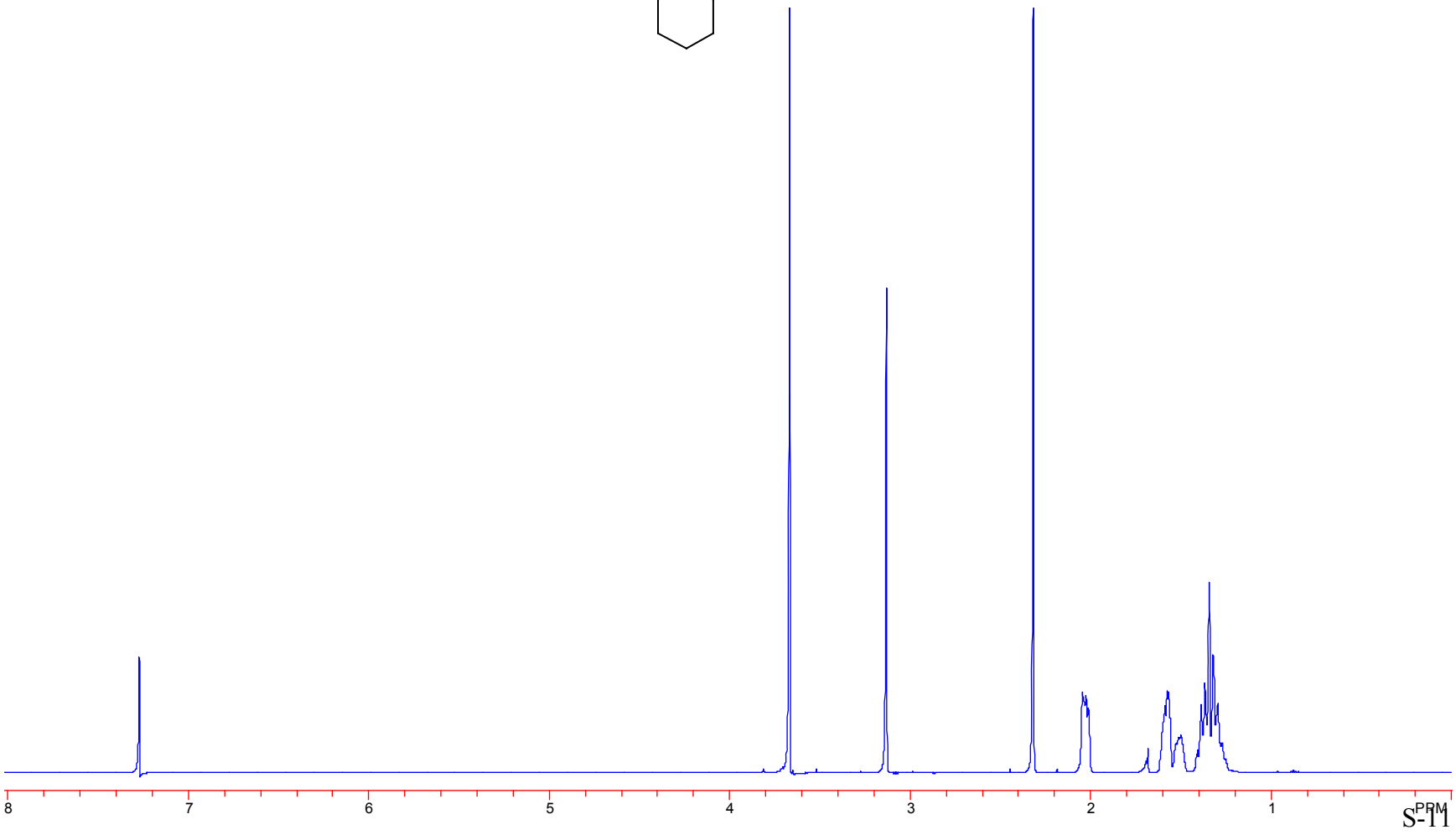


Methyl 1-iodomethylcyclohexane carboxylate (12)
(125 MHz, $CDCl_3$)

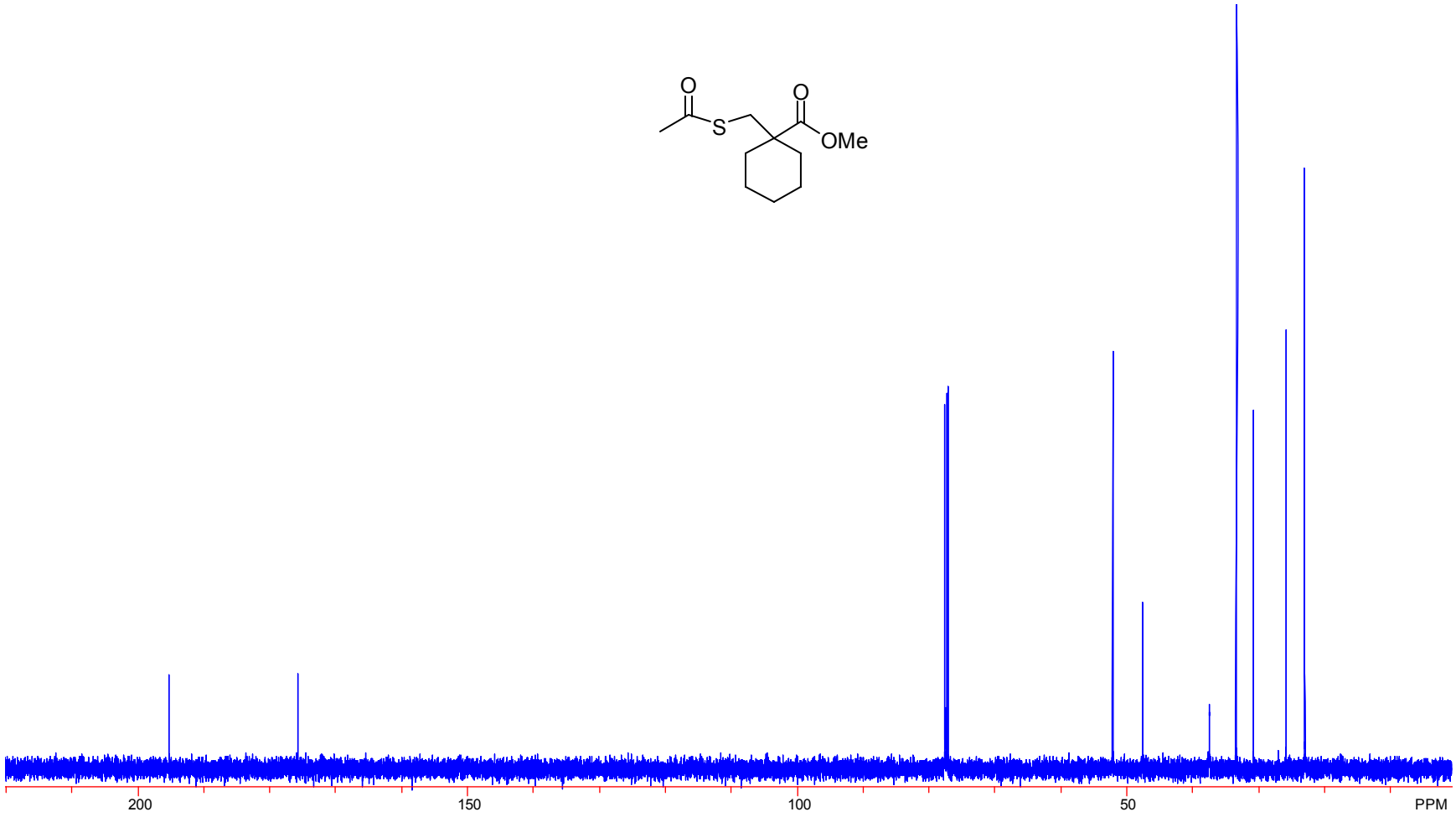


Methyl 1-acetylsulfanylmethylcyclohexane carboxylate (13)
(500 MHz, $CDCl_3$)

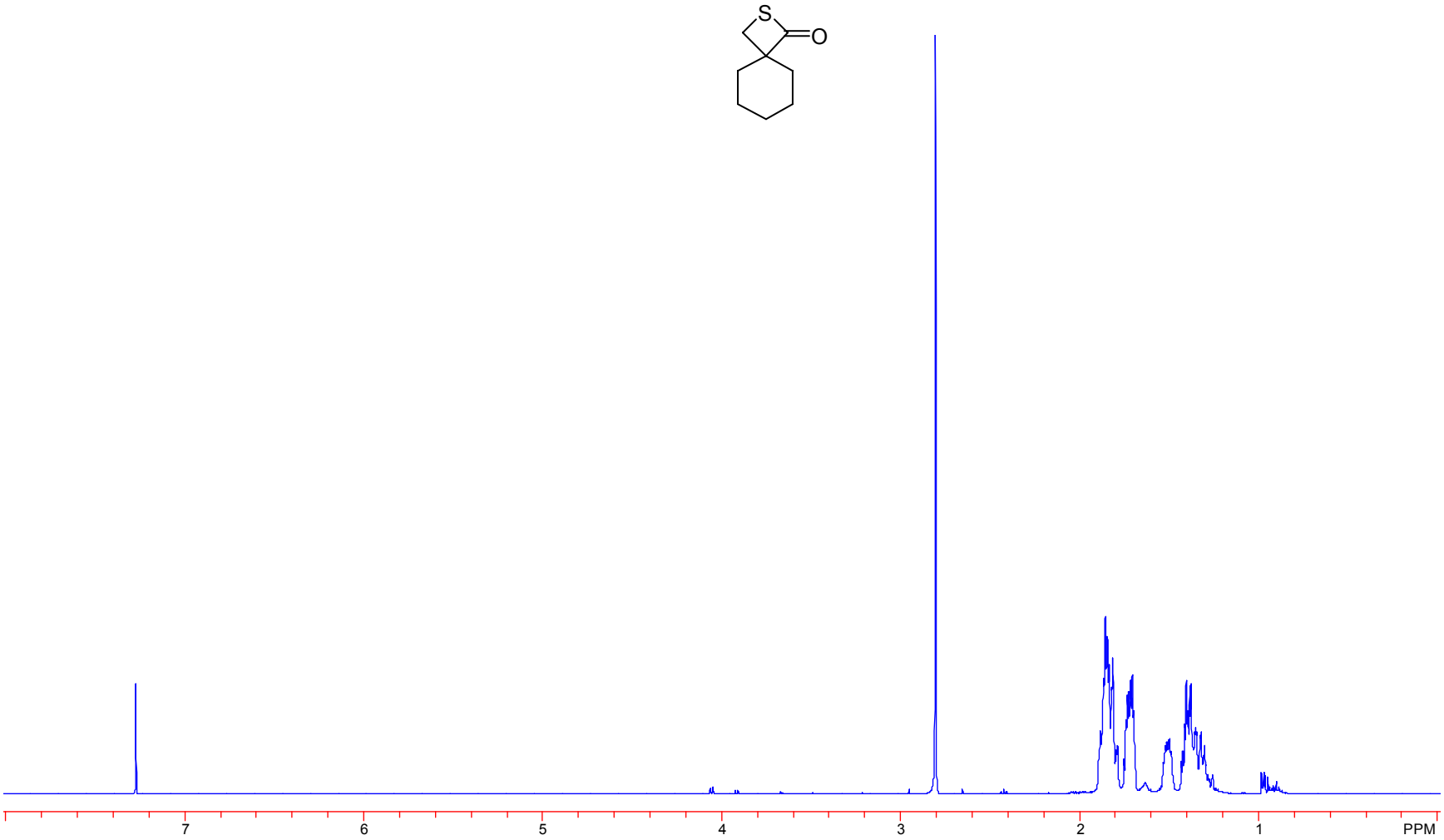




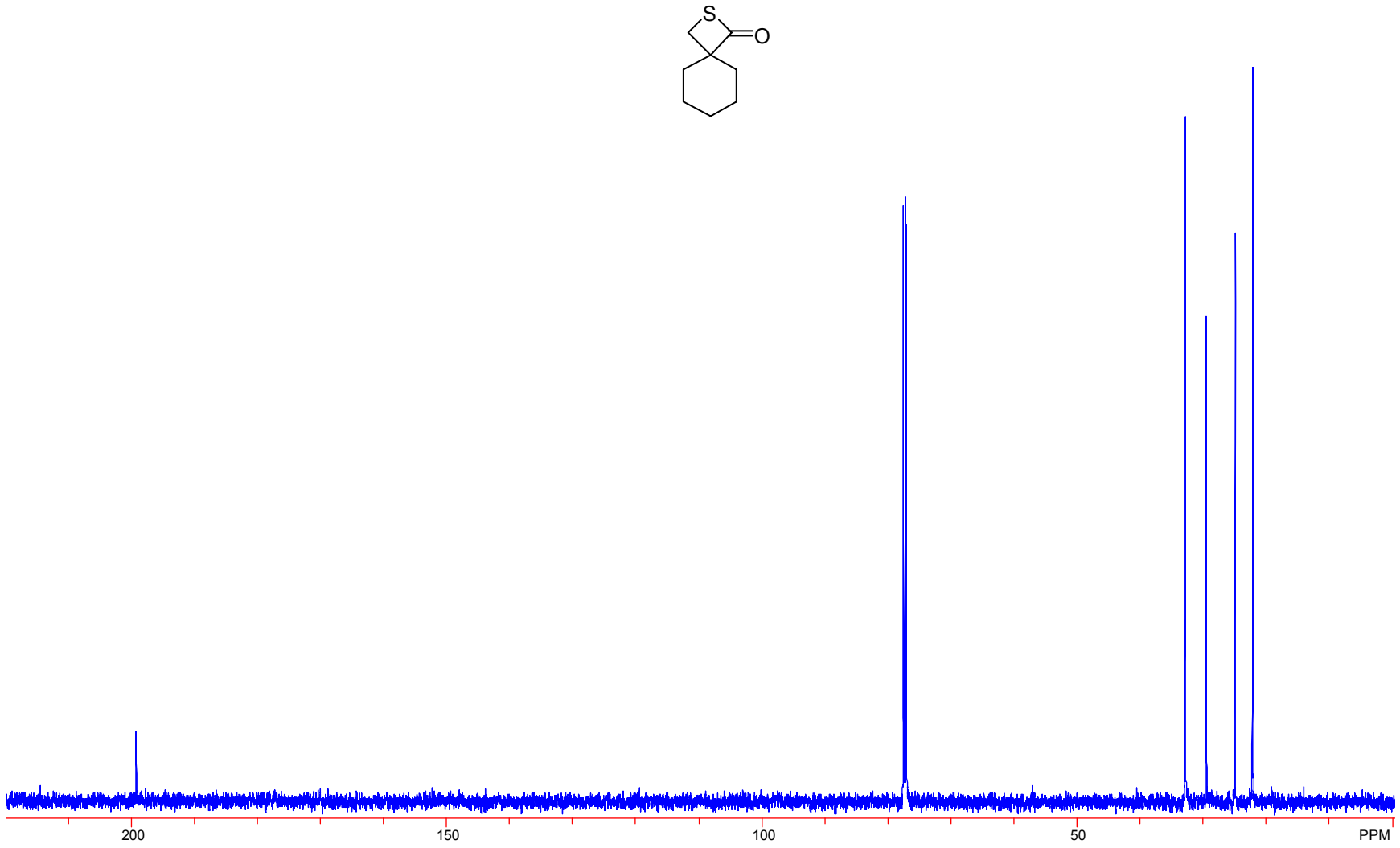
Methyl 1-acetylsulfanylmethylcyclohexane carboxylate (13)
(125 MHz, $CDCl_3$)



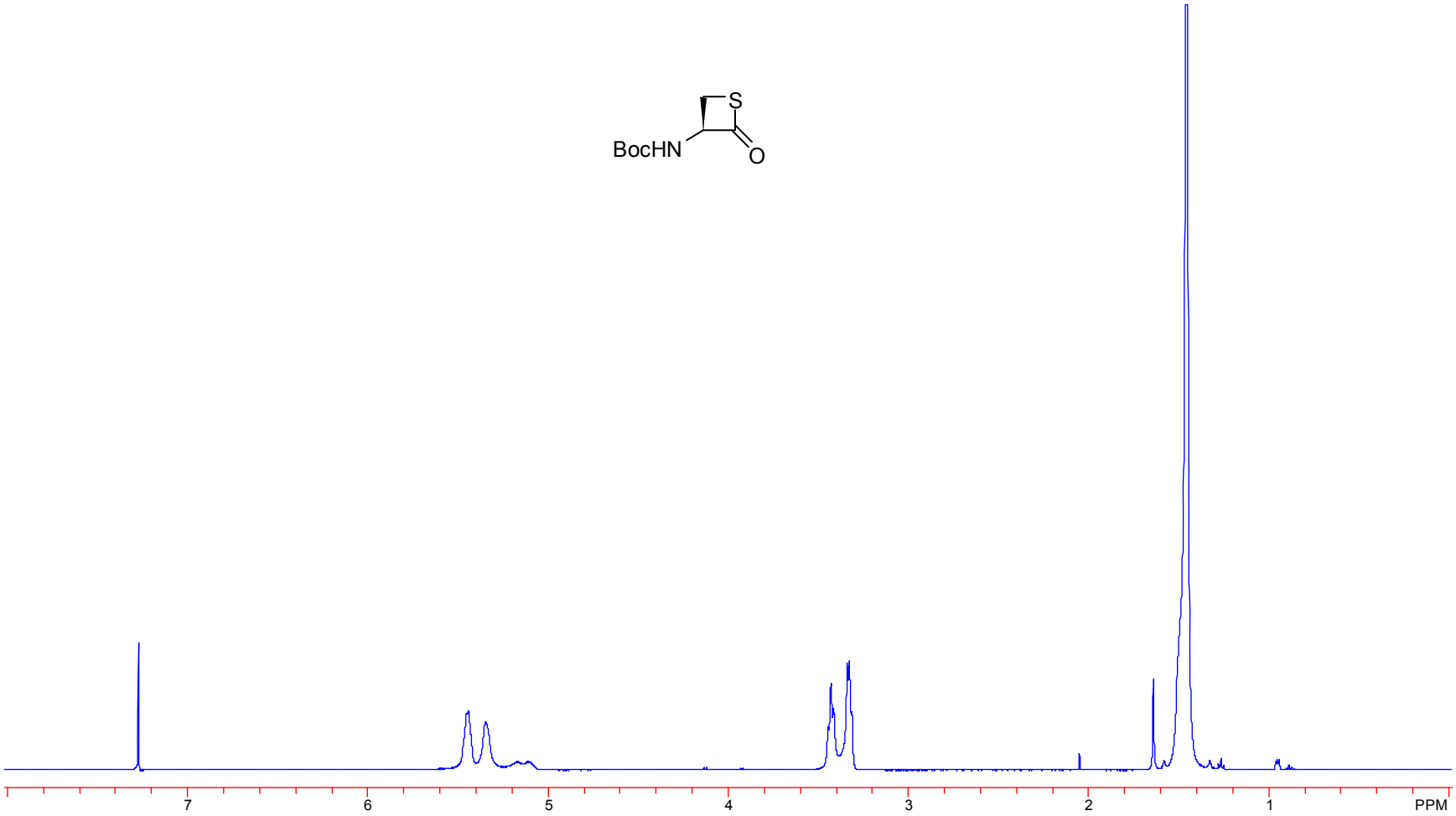
2-Thiaspiro[3.5]nonan-1-one (14)
(500 MHz, $CDCl_3$)



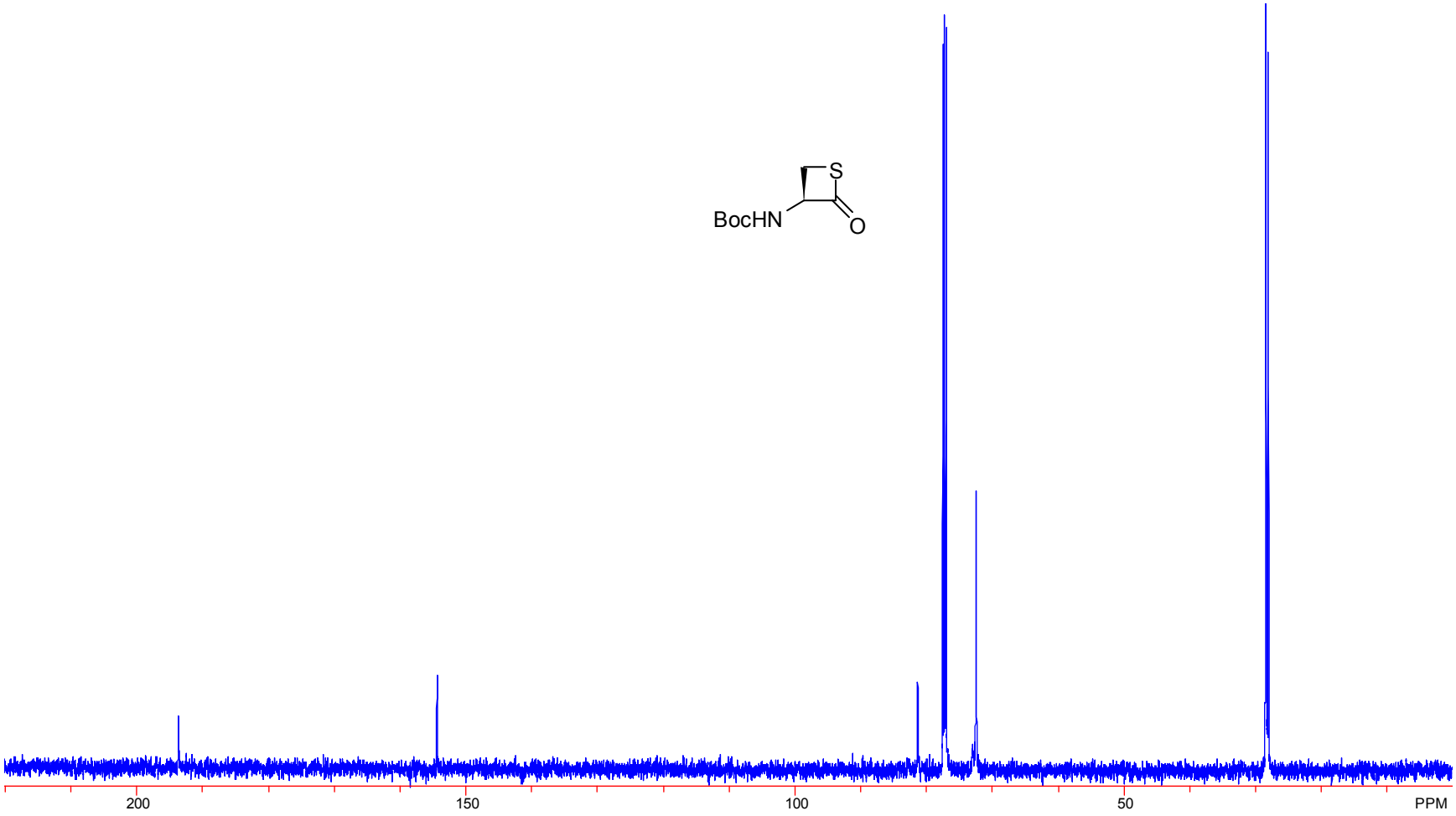
2-Thiaspiro[3.5]nonan-1-one (14)
(125 MHz, $CDCl_3$)



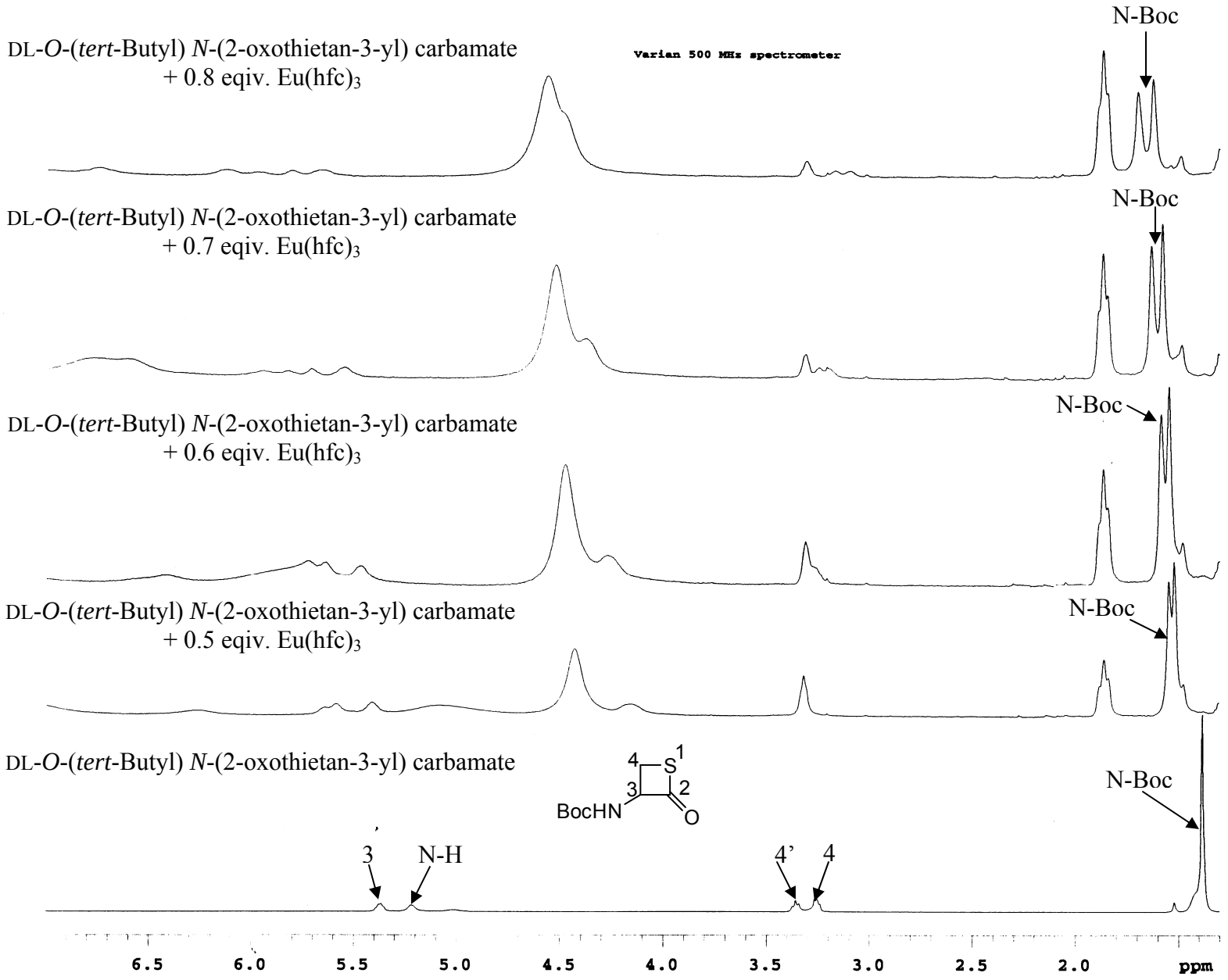
(*S*)-*O*-(*tert*-Butyl) *N*-(thietan-2-on-3-yl) carbamate (16)
(500 MHz, $CDCl_3$)



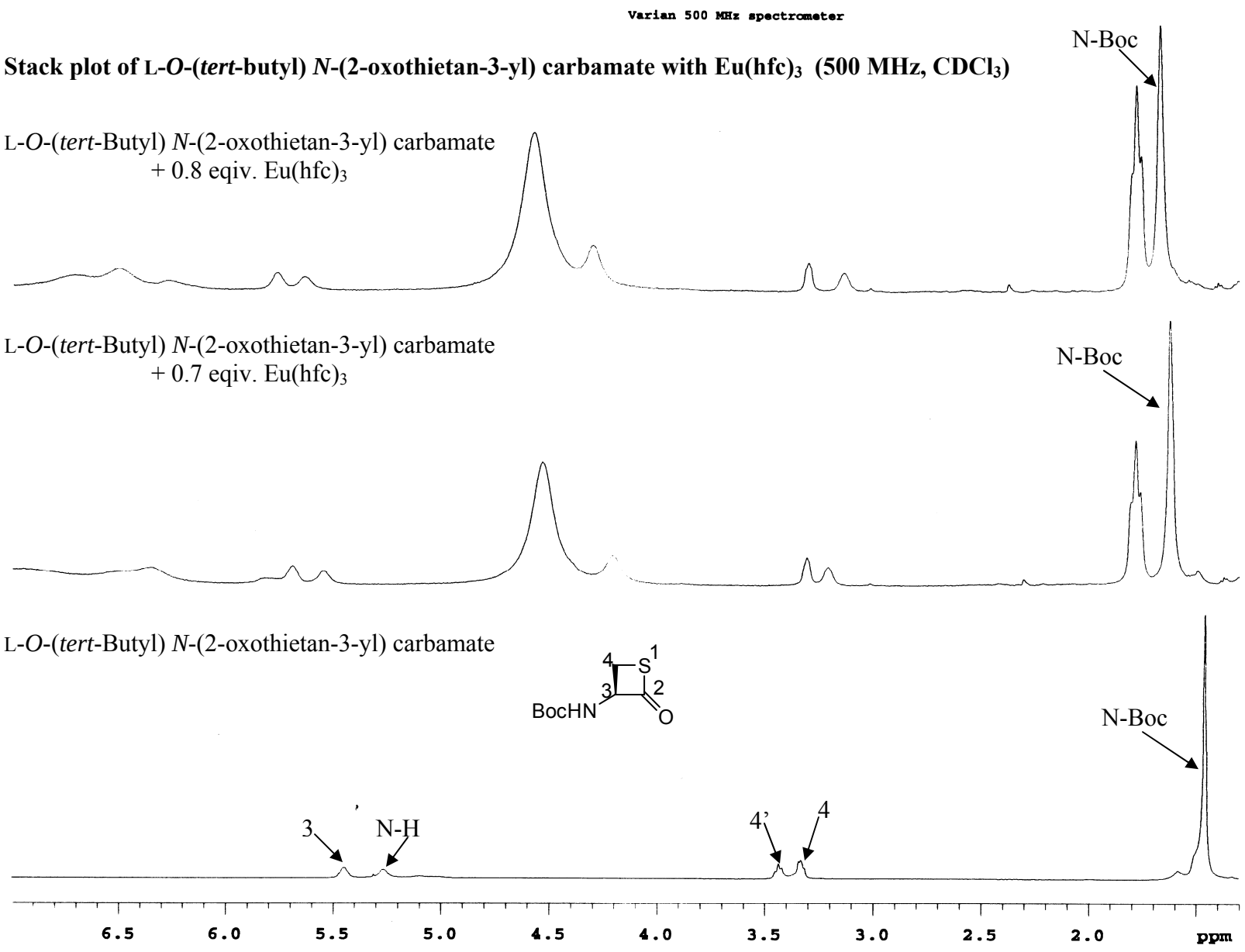
(*S*)-*O*-(*tert*-Butyl) *N*-(thietan-2-on-3-yl) carbamate (16)
(125 MHz, $CDCl_3$)



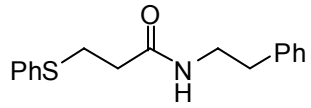
Stack plot of DL-*O*-(*tert*-butyl) *N*-(2-oxothietan-3-yl) carbamate with Eu(hfc)$_3$ (500 MHz, $CDCl_3$)

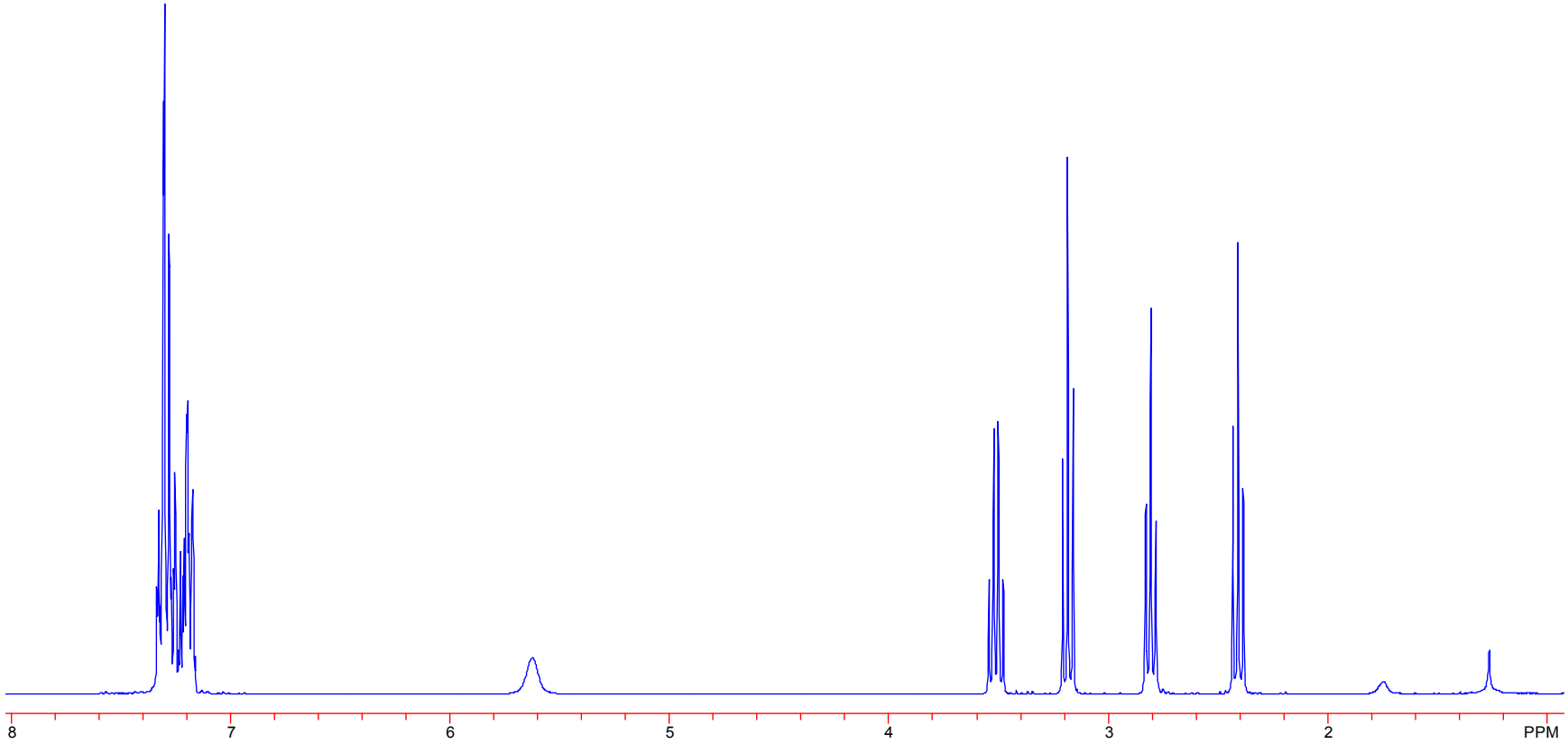


Stack plot of L-*O*-(*tert*-butyl) *N*-(2-oxothietan-3-yl) carbamate with Eu(hfc)$_3$ (500 MHz, $CDCl_3$)

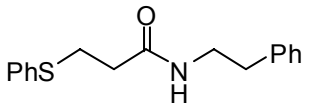


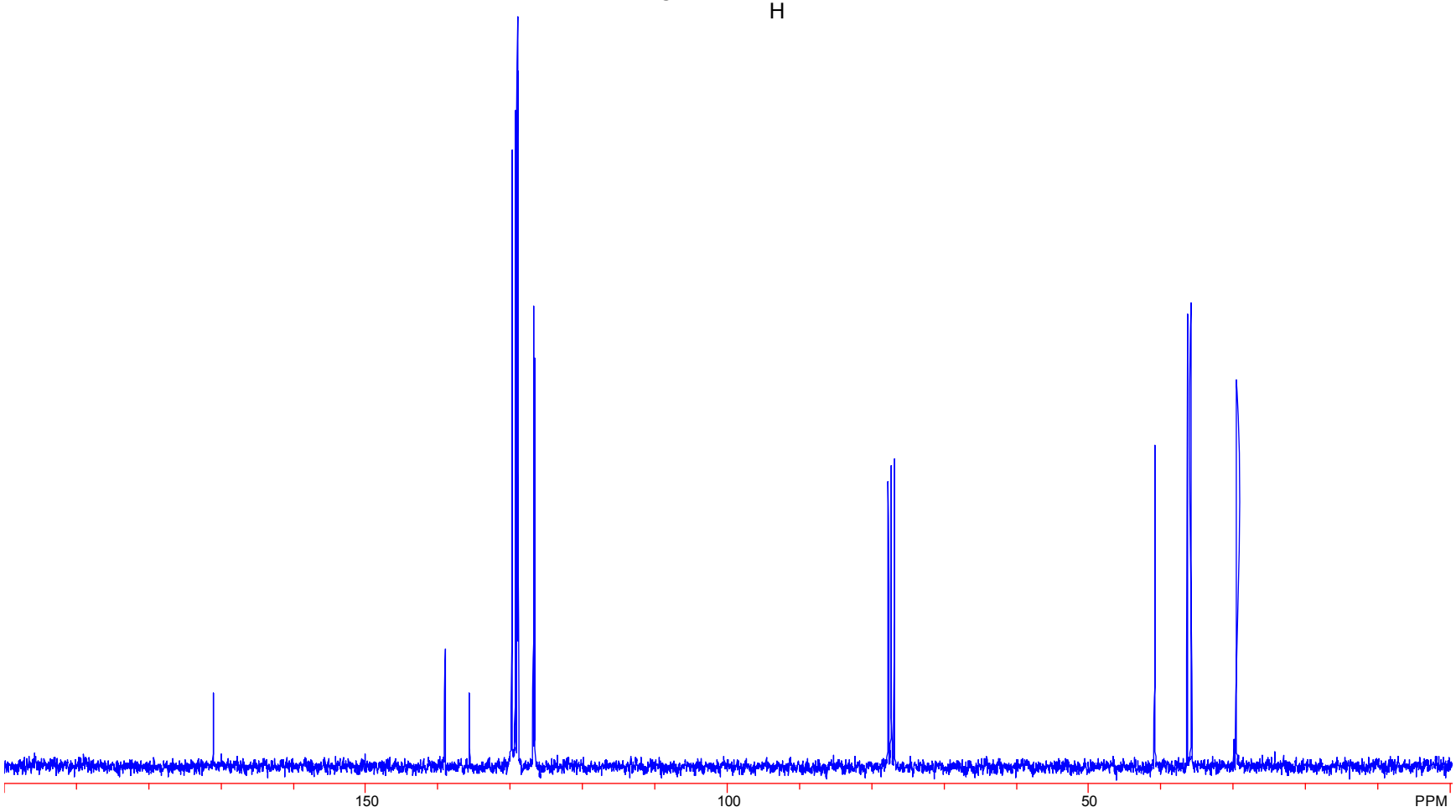
_N_-Phenethyl-3-(phenylthio)propanamide (19)
(300 MHz, $CDCl_3$)



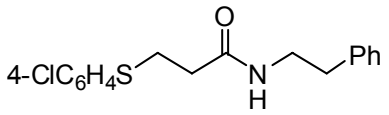


_N_-Phenethyl-3-(phenylthio)propanamide (19)
(75 MHz, $CDCl_3$)

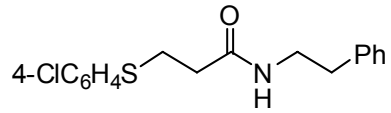


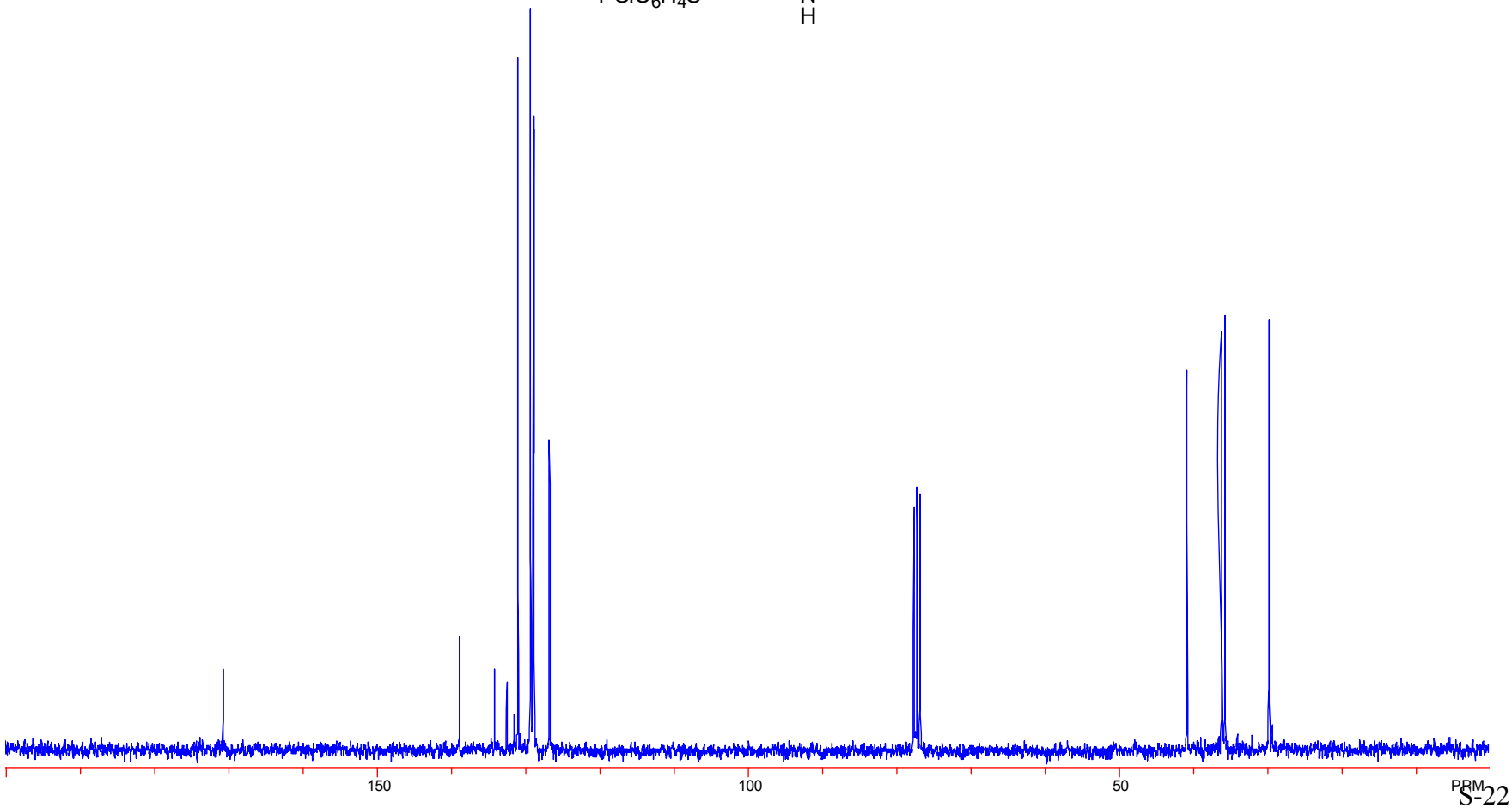


3-(4-Chlorophenylthio)-*N*-phenethylpropanamide (20)
(300 MHz, $CDCl_3$)

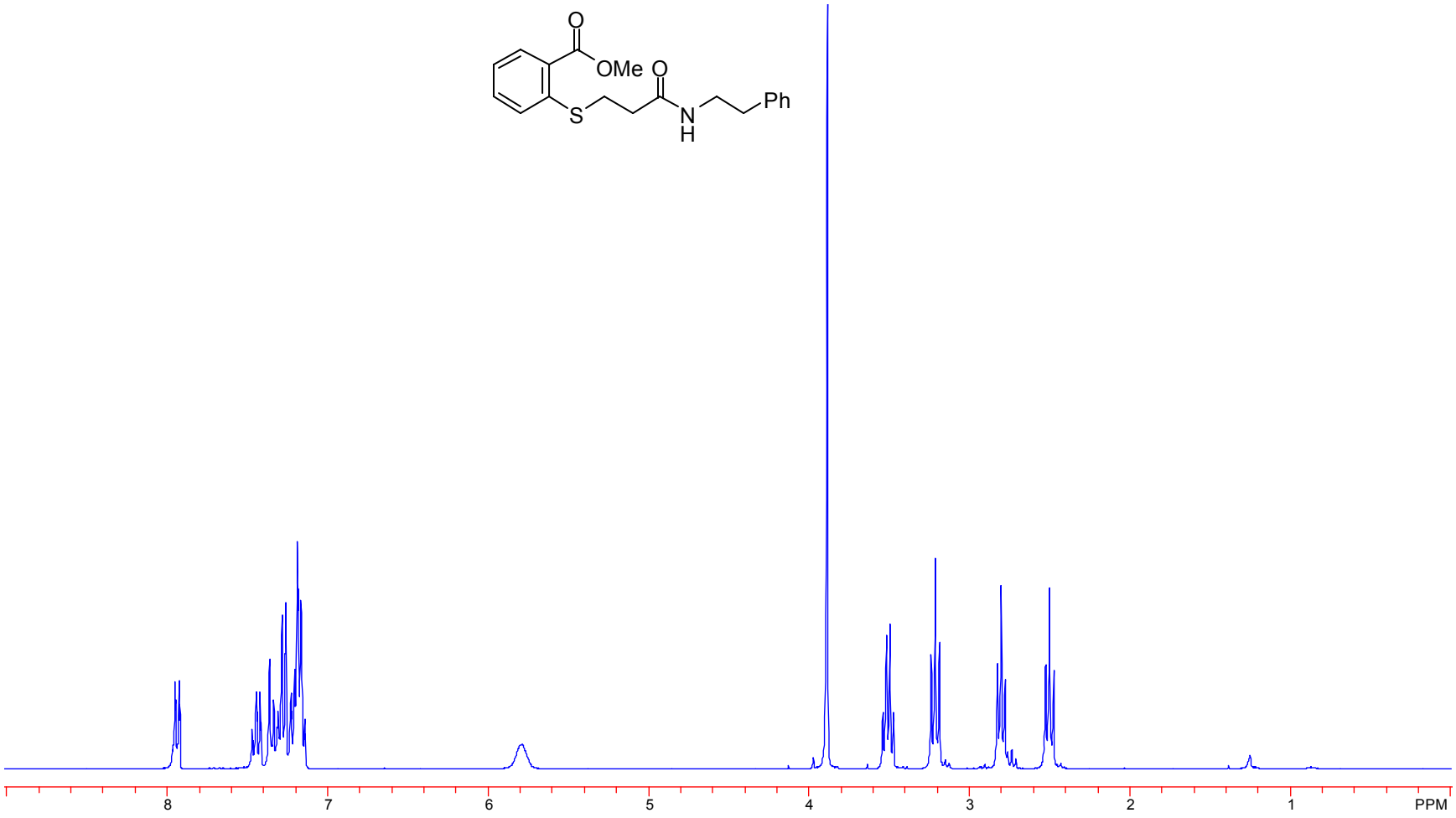


3-(4-Chlorophenylthio)-*N*-phenethylpropanamide (20)
(75 MHz, $CDCl_3$)

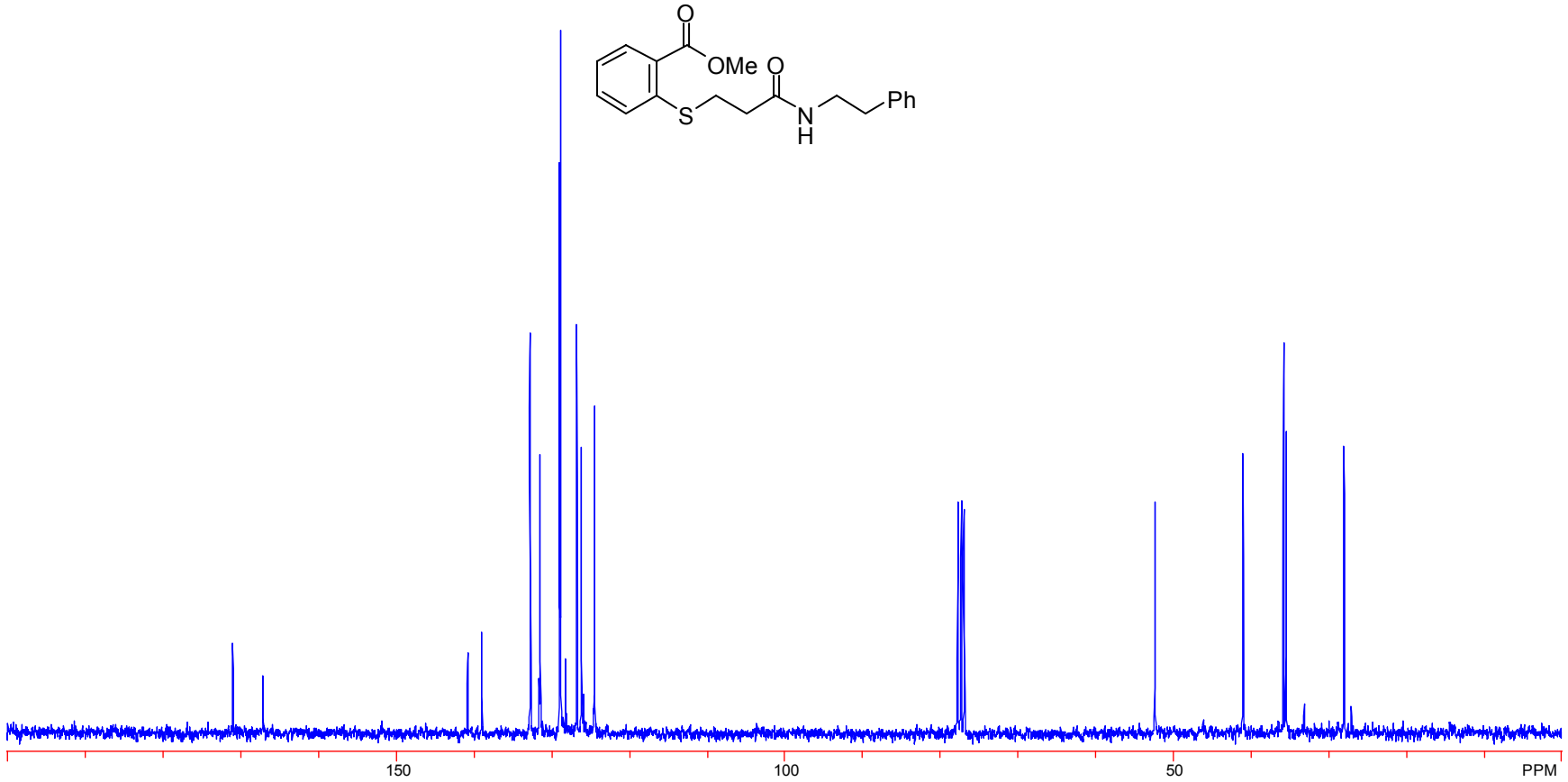




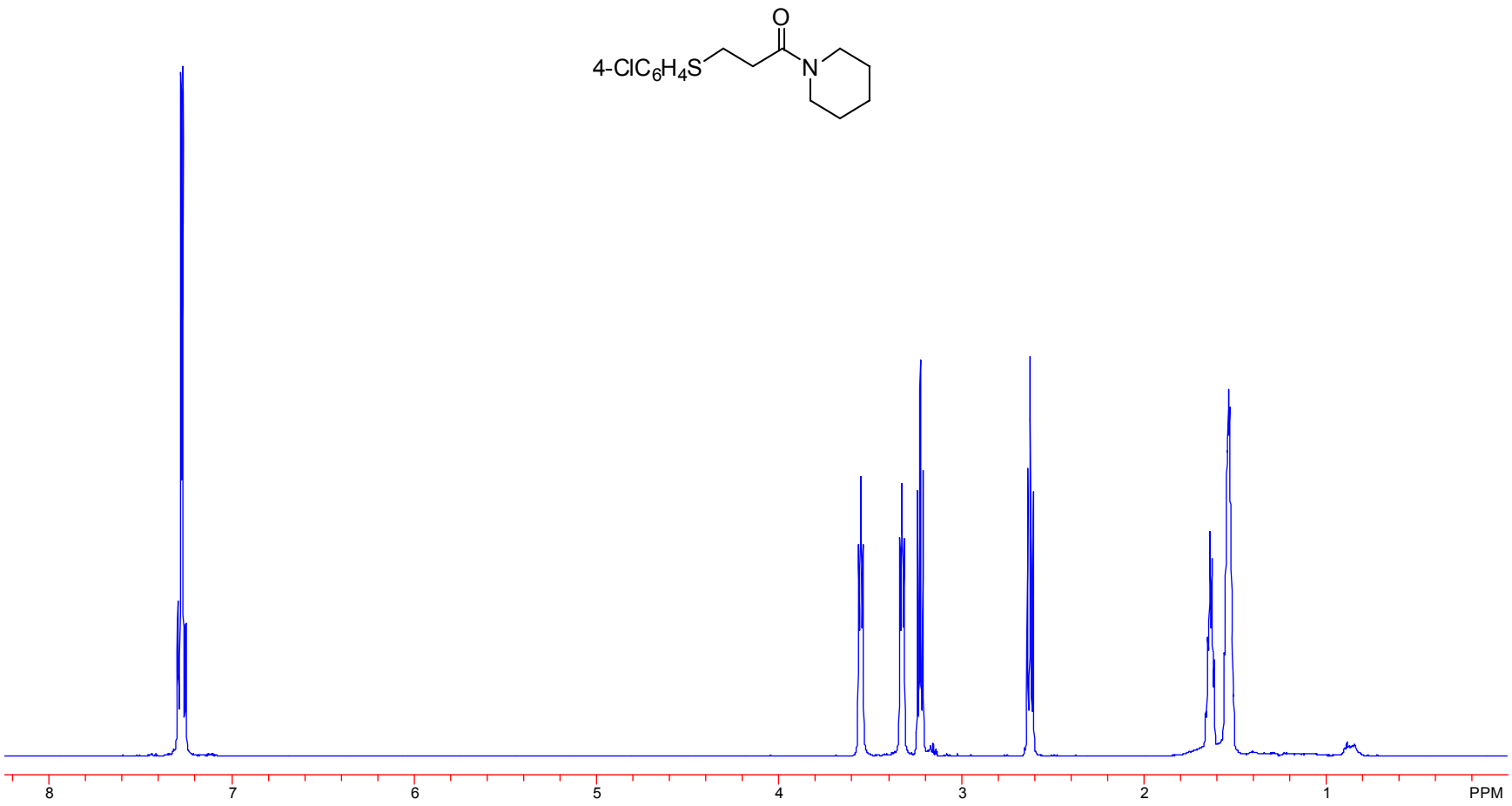
Methyl 2-(3-oxo-3-(phenethylamino)propylthio)benzoate (21)
(300 MHz, $CDCl_3$)



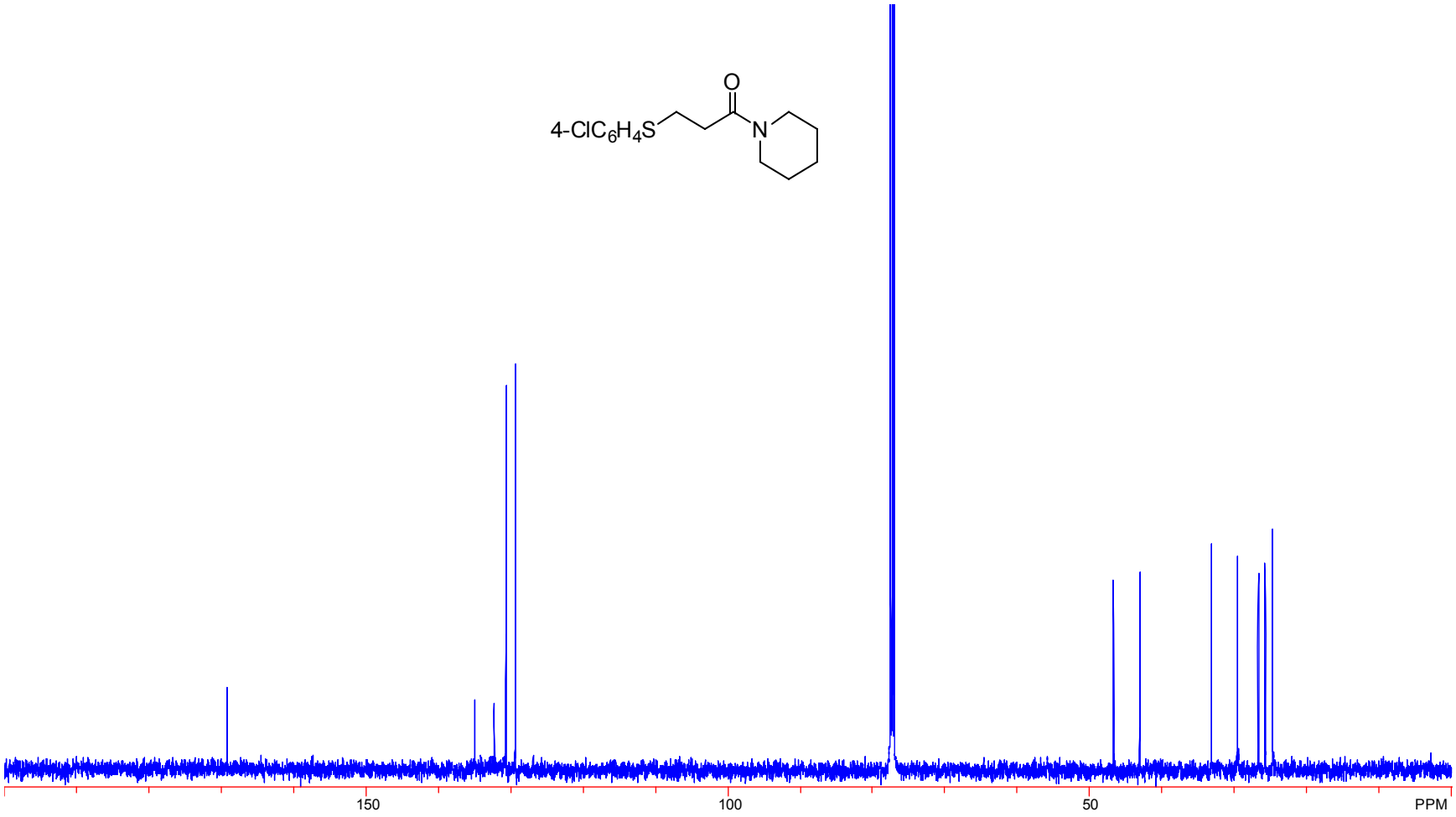
Methyl 2-(3-oxo-3-(phenethylamino)propylthio)benzoate (21)
(75 MHz, $CDCl_3$)



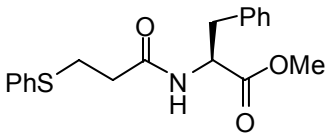
_N_-3-(4-Chlorophenylthio)propanoyl piperidine (22)
(500 MHz, $CDCl_3$)



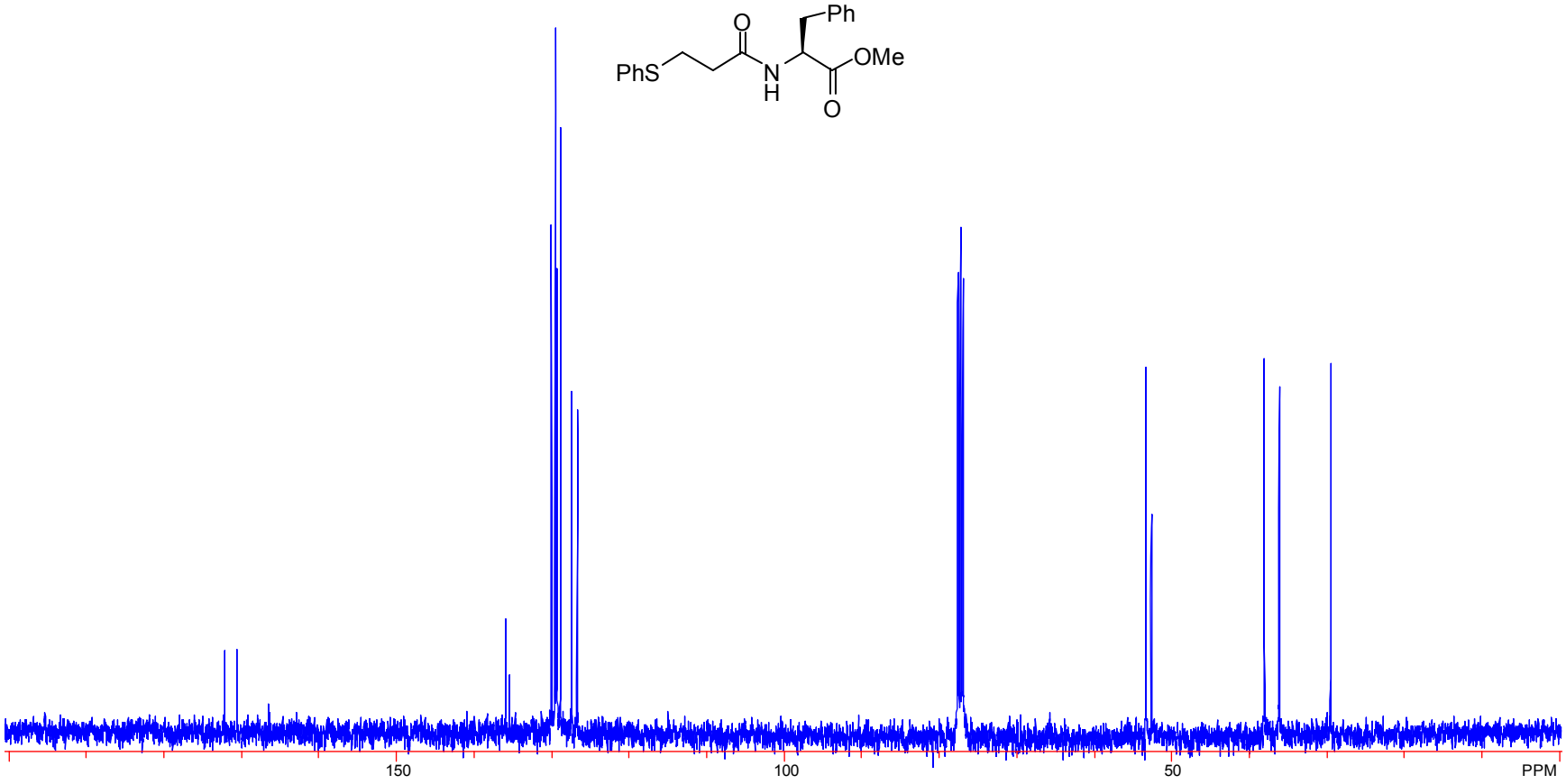
_N_-3-(4-Chlorophenylthio)propanoyl piperidine (22)
(125 MHz, $CDCl_3$)



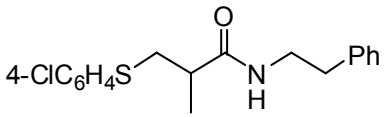
Methyl *N*-(3-(phenylthio)-propanoyl)-L-phenylalaninate (23)
(500 MHz, $CDCl_3$)



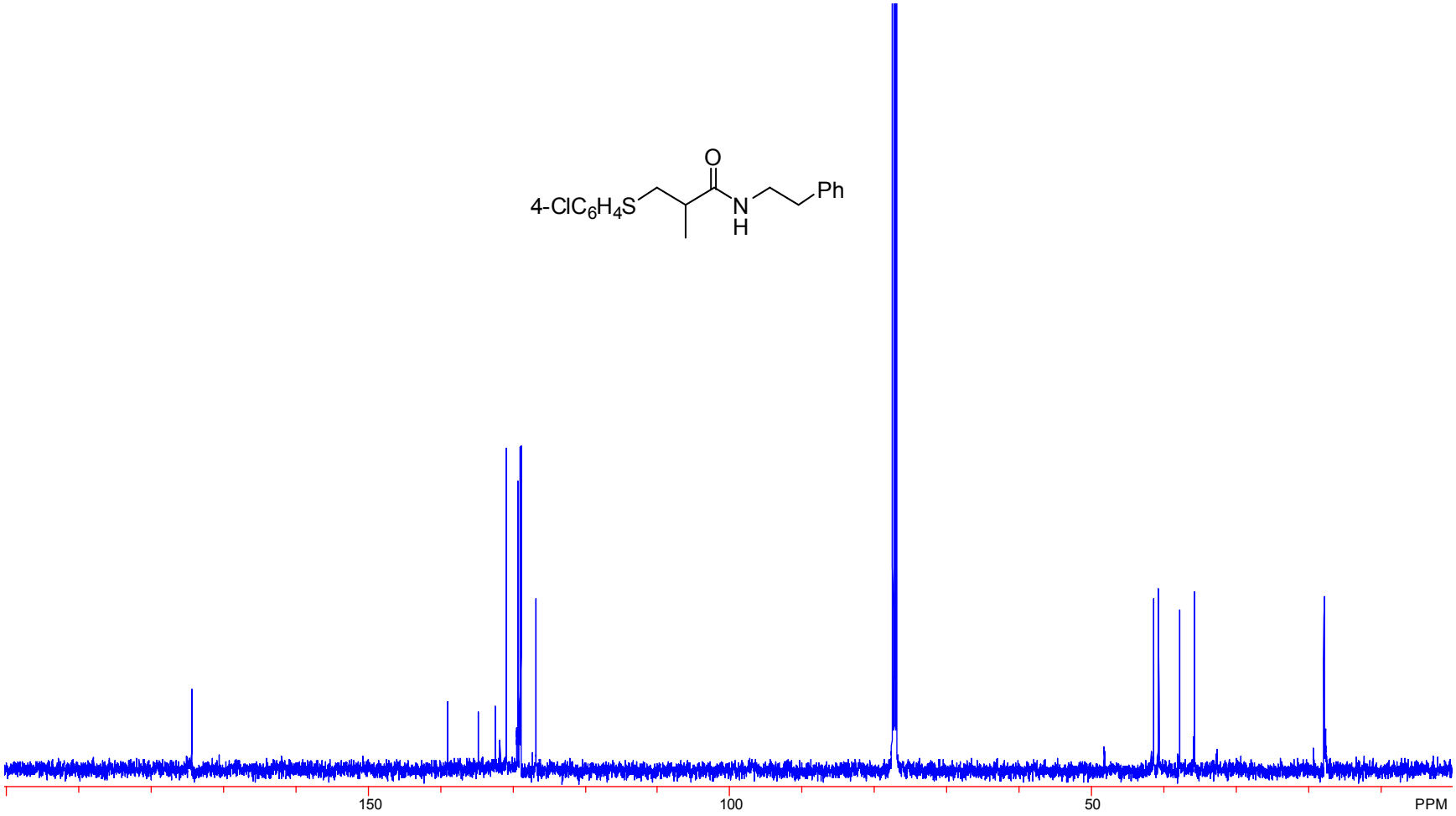
Methyl *N*-(3-(phenylthio)-propanoyl]-L-phenylalaninate (23)
(125 MHz, $CDCl_3$)



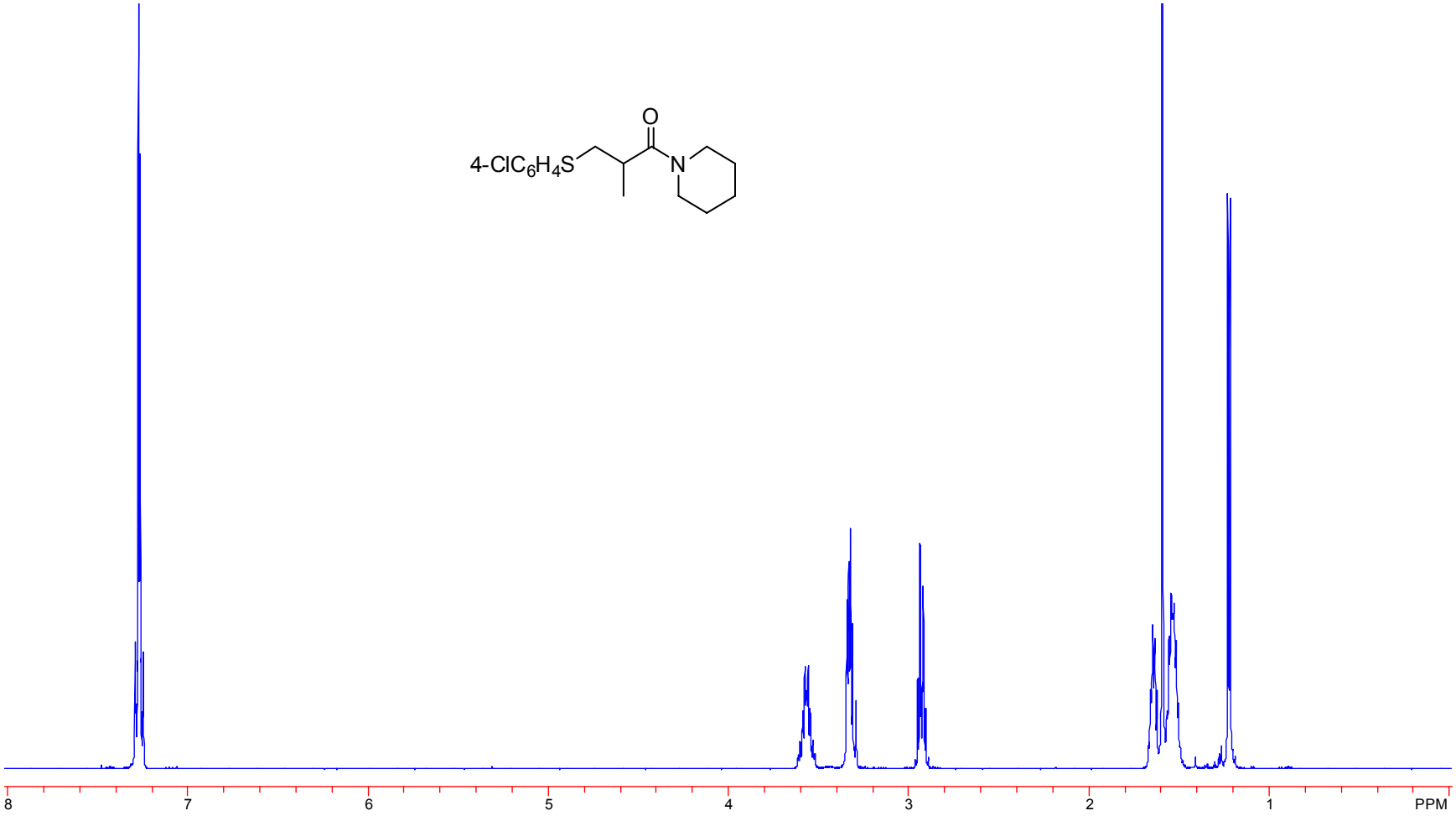
3-(4-Chlorophenylthio)-2-methyl-*N*-phenethylpropanamide (24)
(500 MHz, $CDCl_3$)



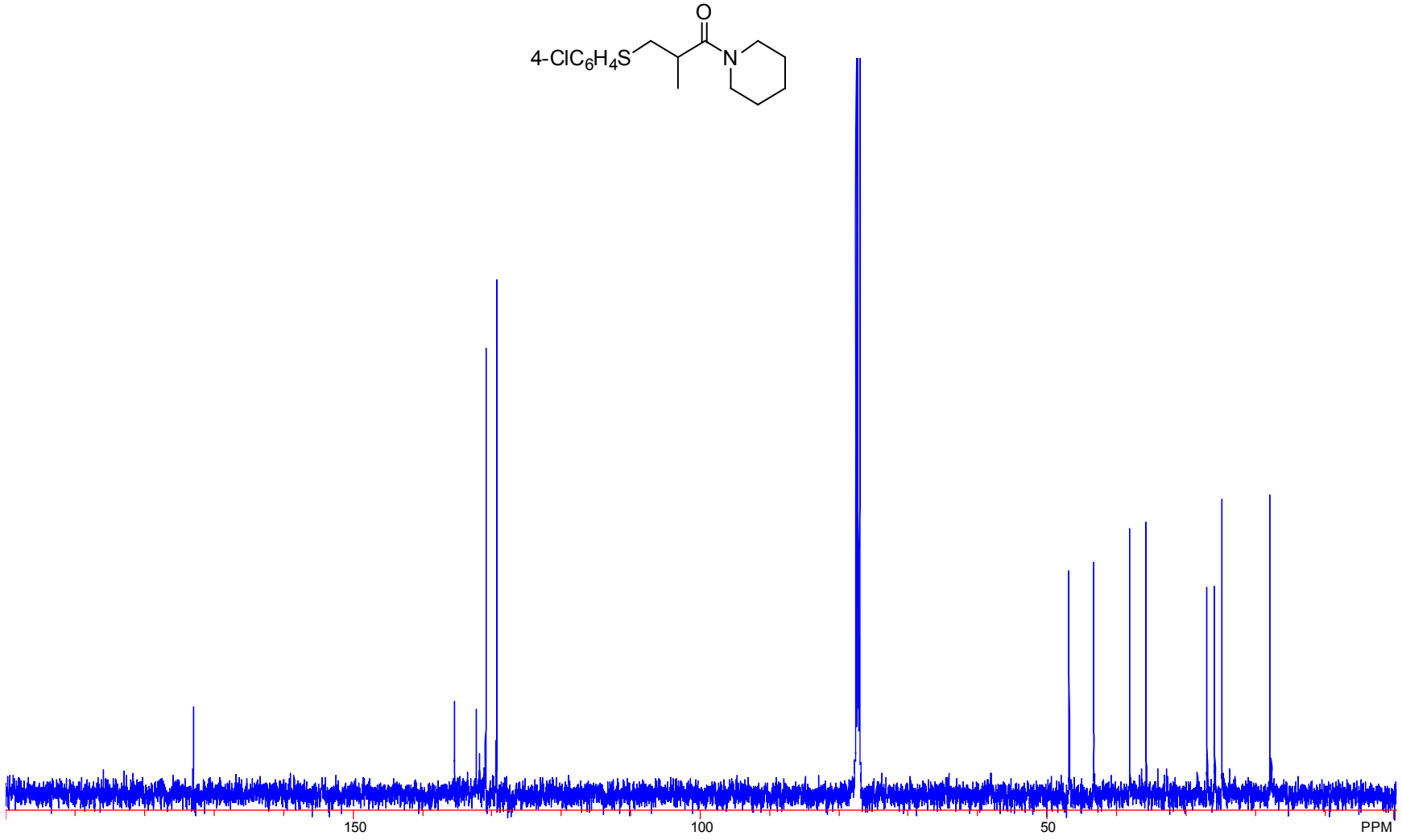
3-(4-Chlorophenylthio)-2-methyl-*N*-phenethylpropanamide (24)
(75 MHz, $CDCl_3$)



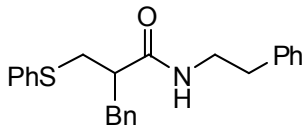
3-(4-Chlorophenylthio)-2-methyl-1-(piperidin-1-yl)propan-1-one (25)
(500 MHz, $CDCl_3$)



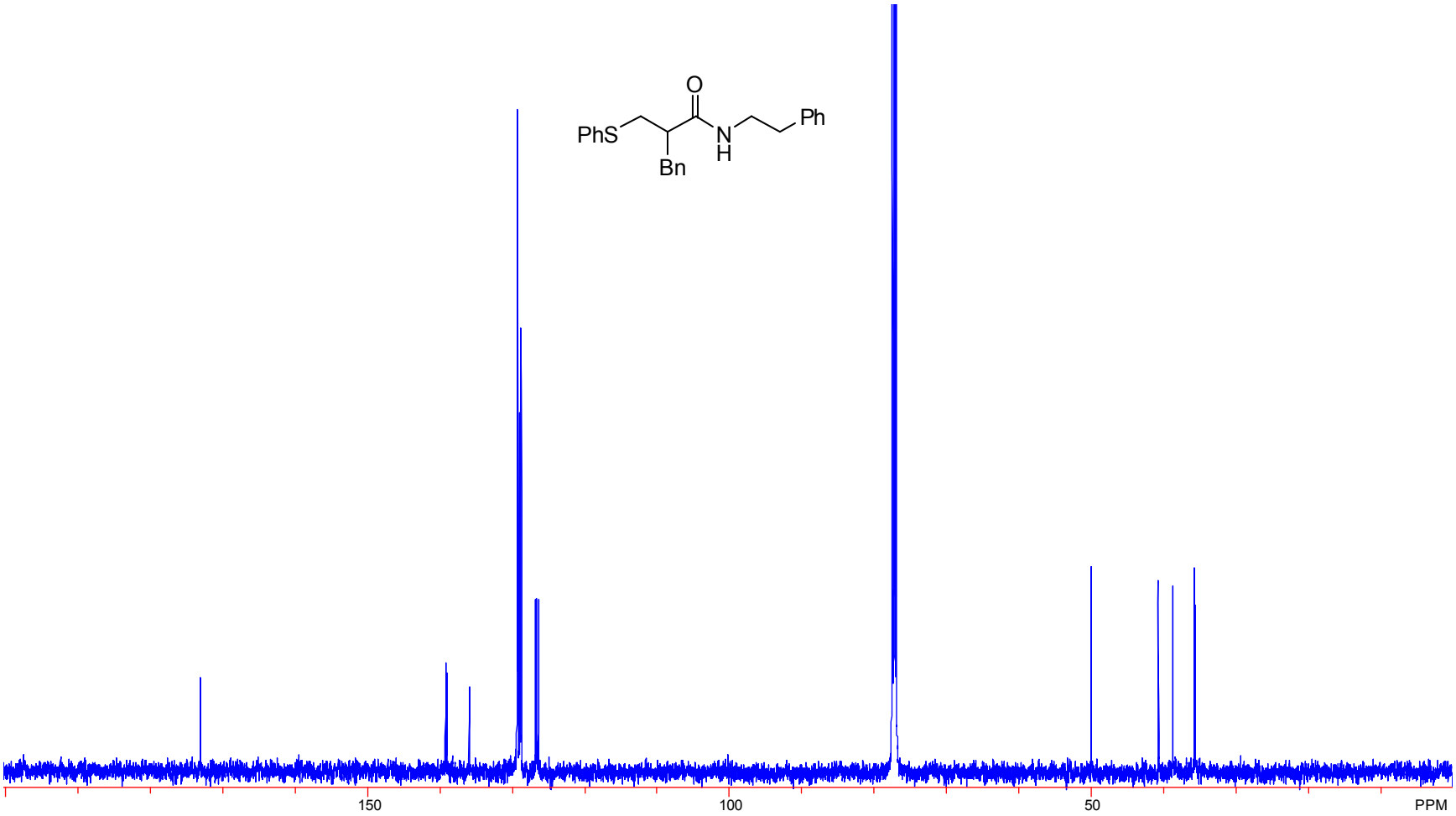
3-(4-Chlorophenylthio)-2-methyl-1-(piperidin-1-yl)propan-1-one (25)
(125 MHz, $CDCl_3$)



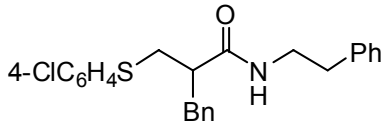
2-Benzyl-*N*-phenethyl-3-(phenylthio)propanamide (26)
(500 MHz, $CDCl_3$)



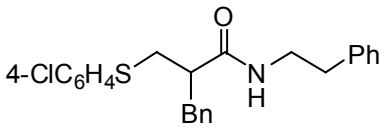
2-Benzyl-*N*-phenethyl-3-(phenylthio)propanamide (26)
(125 MHz, $CDCl_3$)



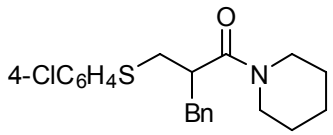
2-Benzyl-3-(4-chlorophenylthio)-*N*-phenethylpropanamide (27)
(500 MHz, $CDCl_3$)



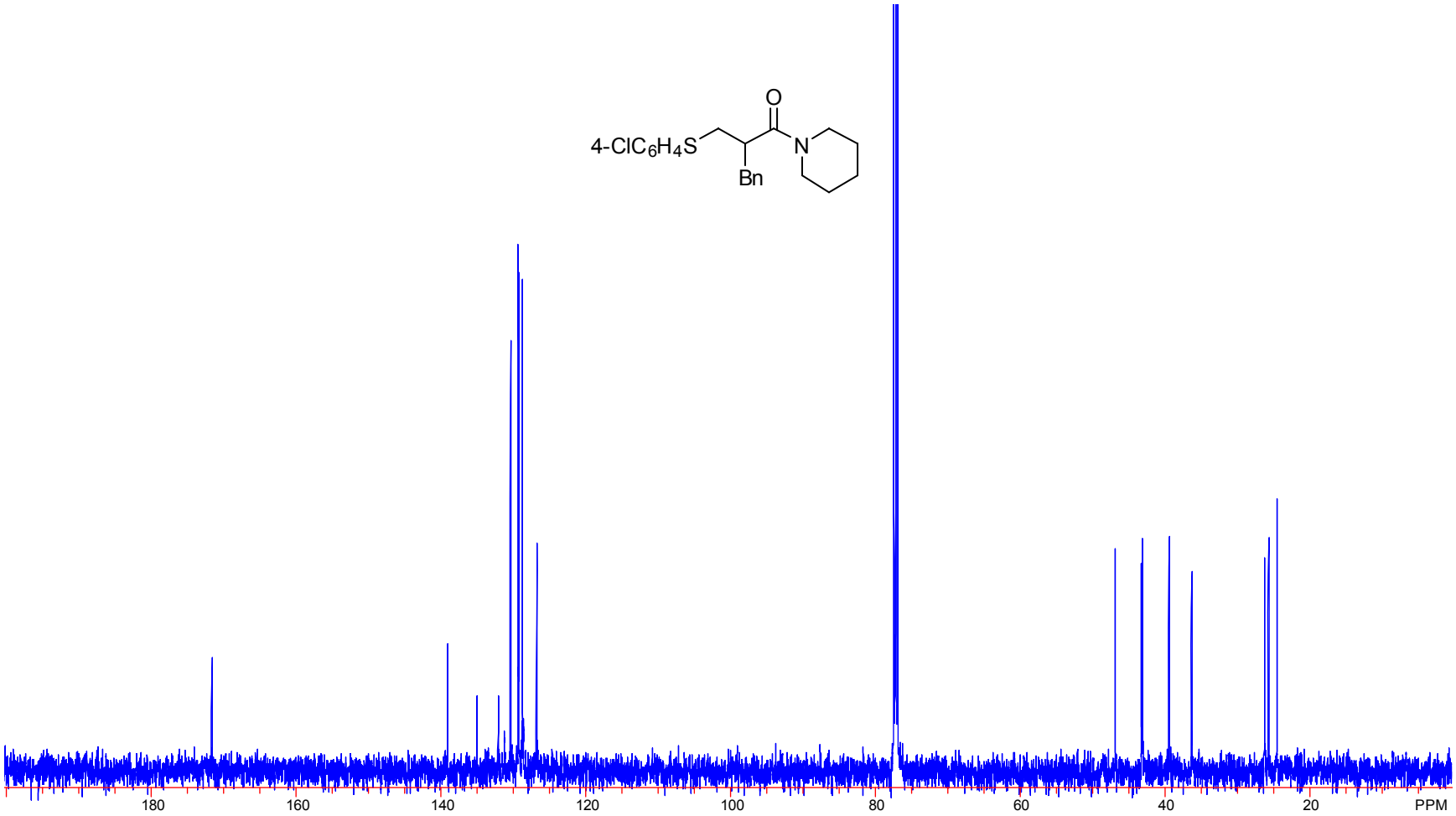
2-Benzyl-3-(4-chlorophenylthio)-*N*-phenethylpropanamide (27)
(125 MHz, $CDCl_3$)



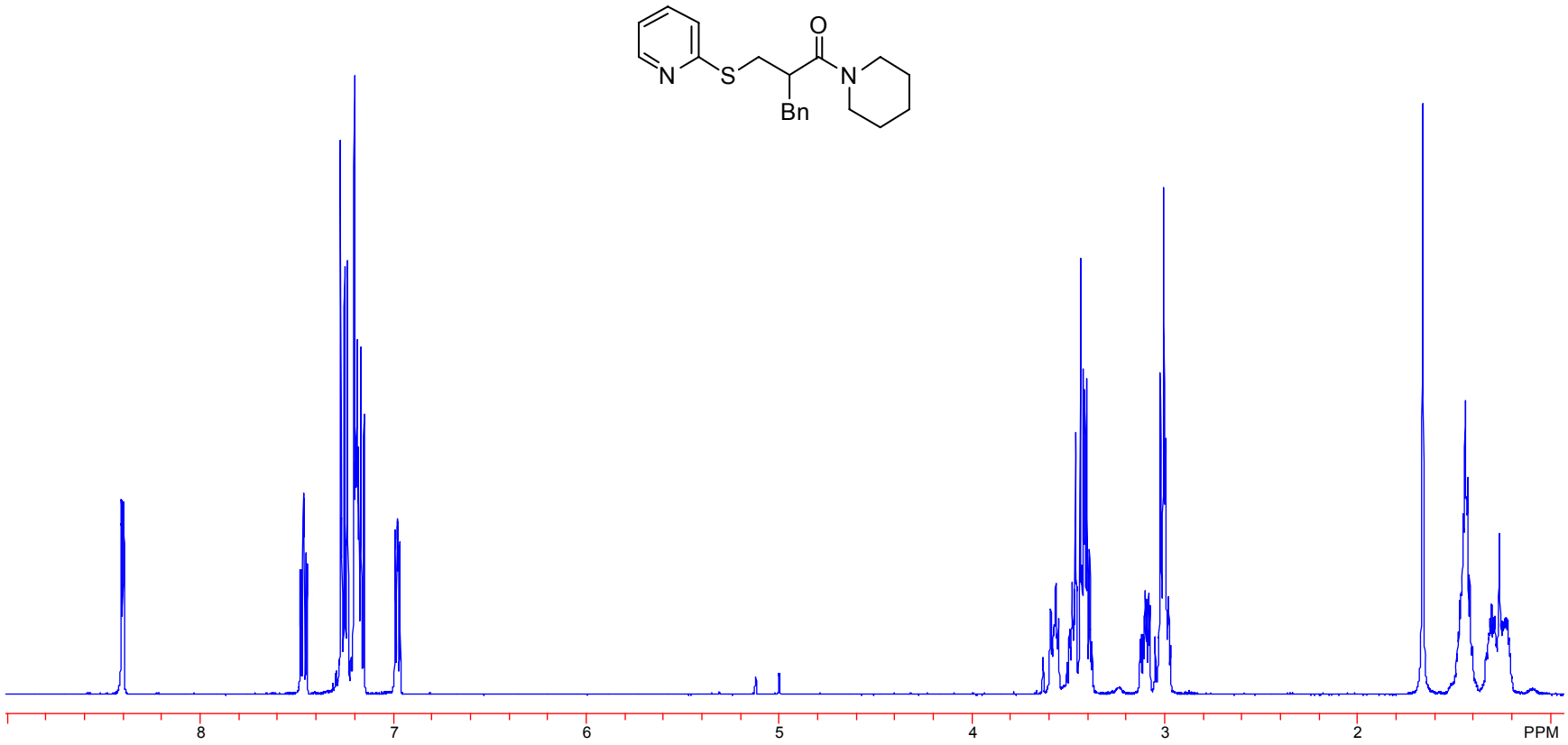
_N_-[2-Benzyl-3-(4-chlorophenylthio)]propanoyl piperidine (28)
(500 MHz, $CDCl_3$)



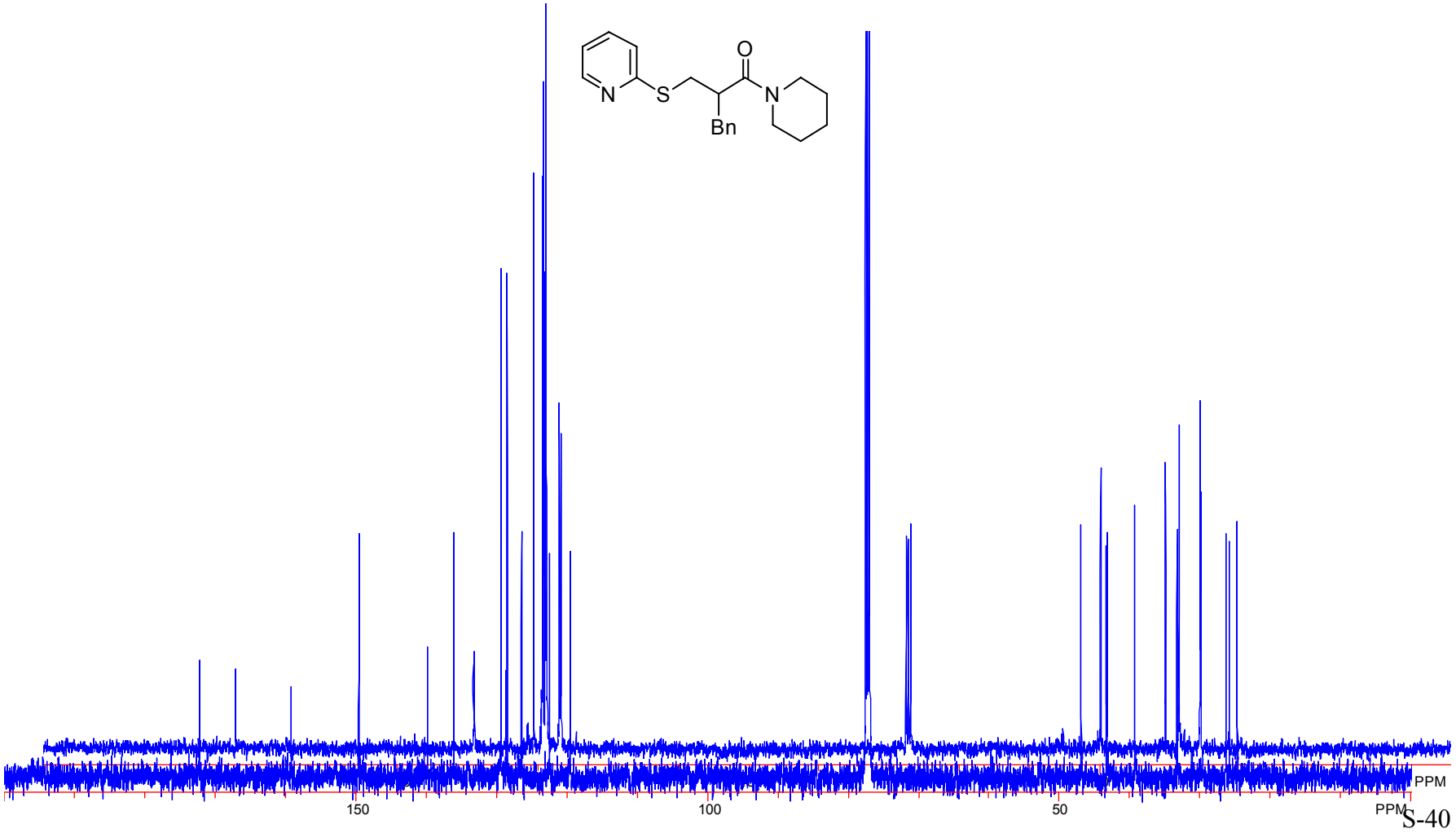
_N_-[2-Benzyl-3-(4-chlorophenylthio)]propanoyl piperidine (28)
(125 MHz, $CDCl_3$)



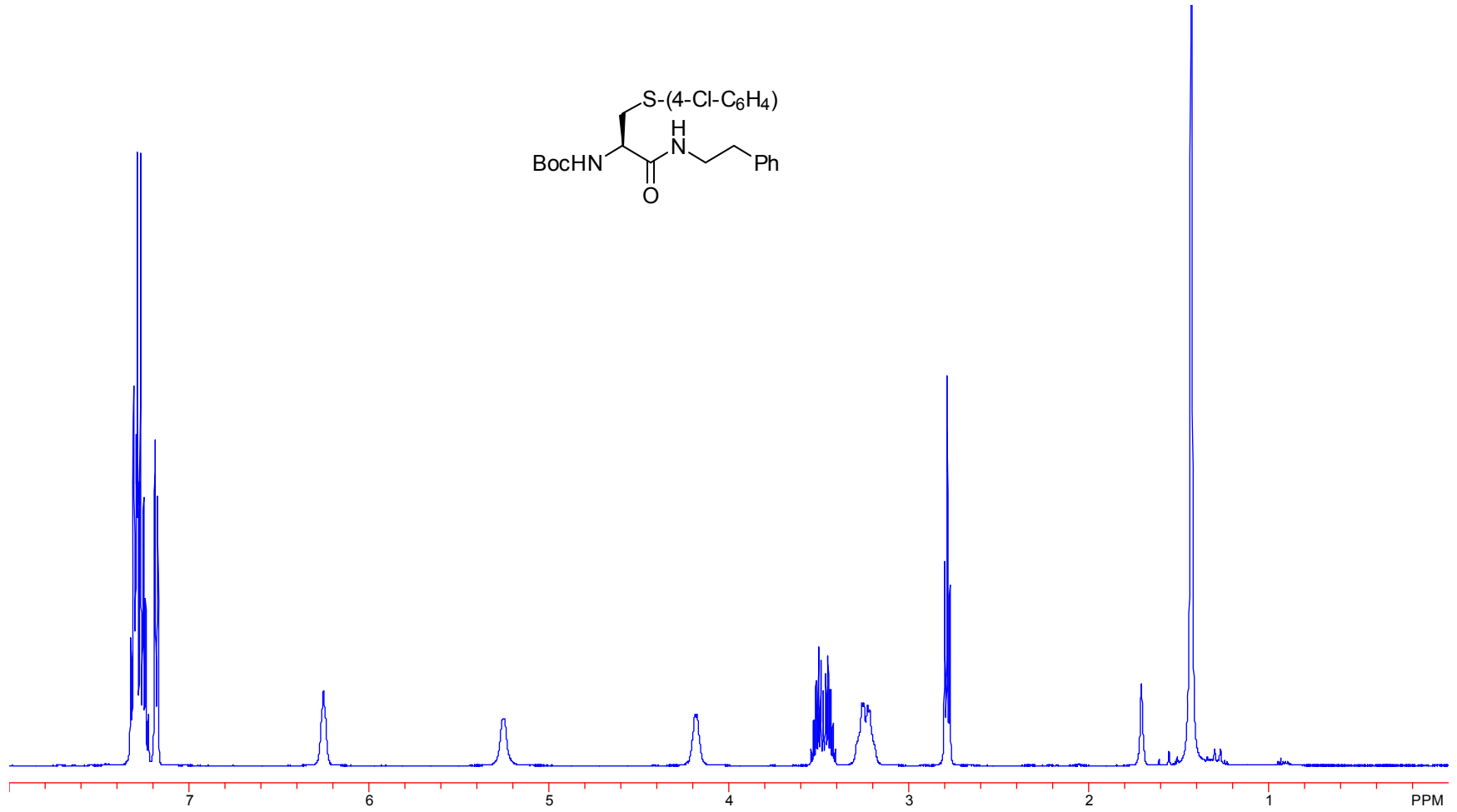
_N_-[2-Benzyl-3-(pyridine-2-ylthio)]propanoyl piperidine (29)
(500 MHz, $CDCl_3$)



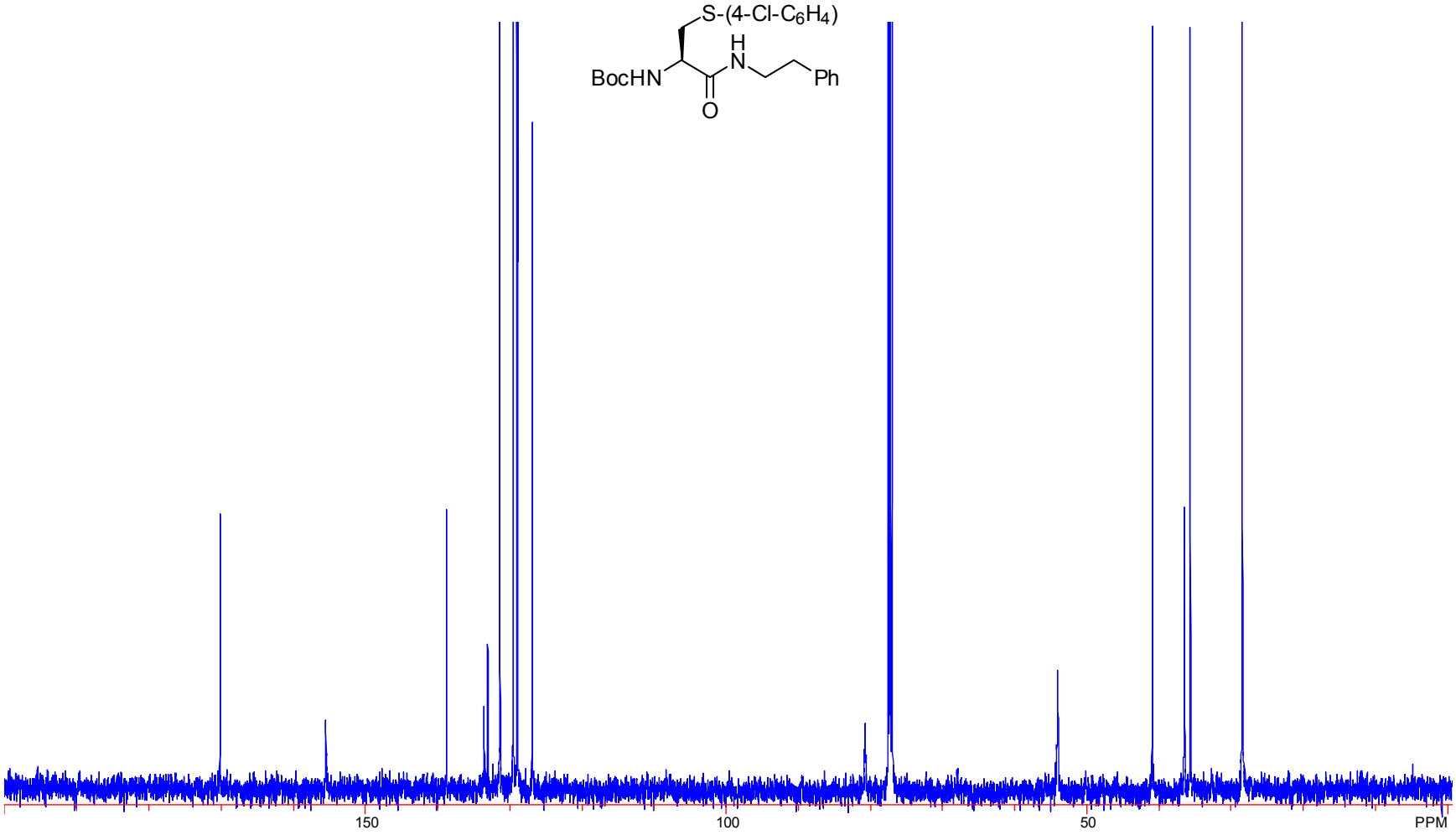
_N_-[2-Benzyl-3-(pyridine-2-ylthio)propanoyl piperidine (29)
(125 MHz, $CDCl_3$)



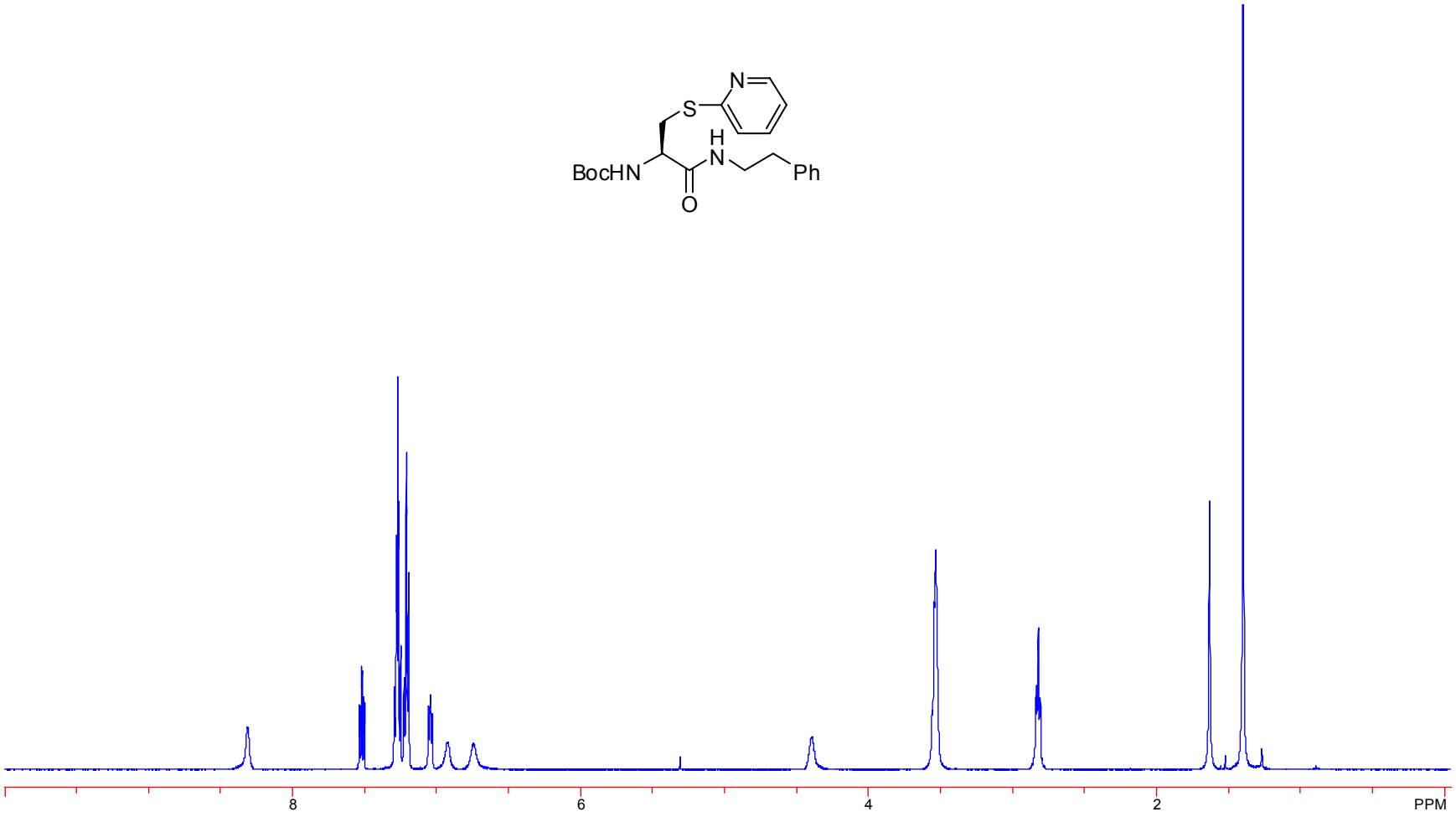
(*R*)-*O*-(*tert*-Butyl) *N*-(3-(4-chlorophenylthio)-1-(phenethylaminocarbonyl)propan-2-yl) carbamate (30)
(500 MHz, $CDCl_3$)



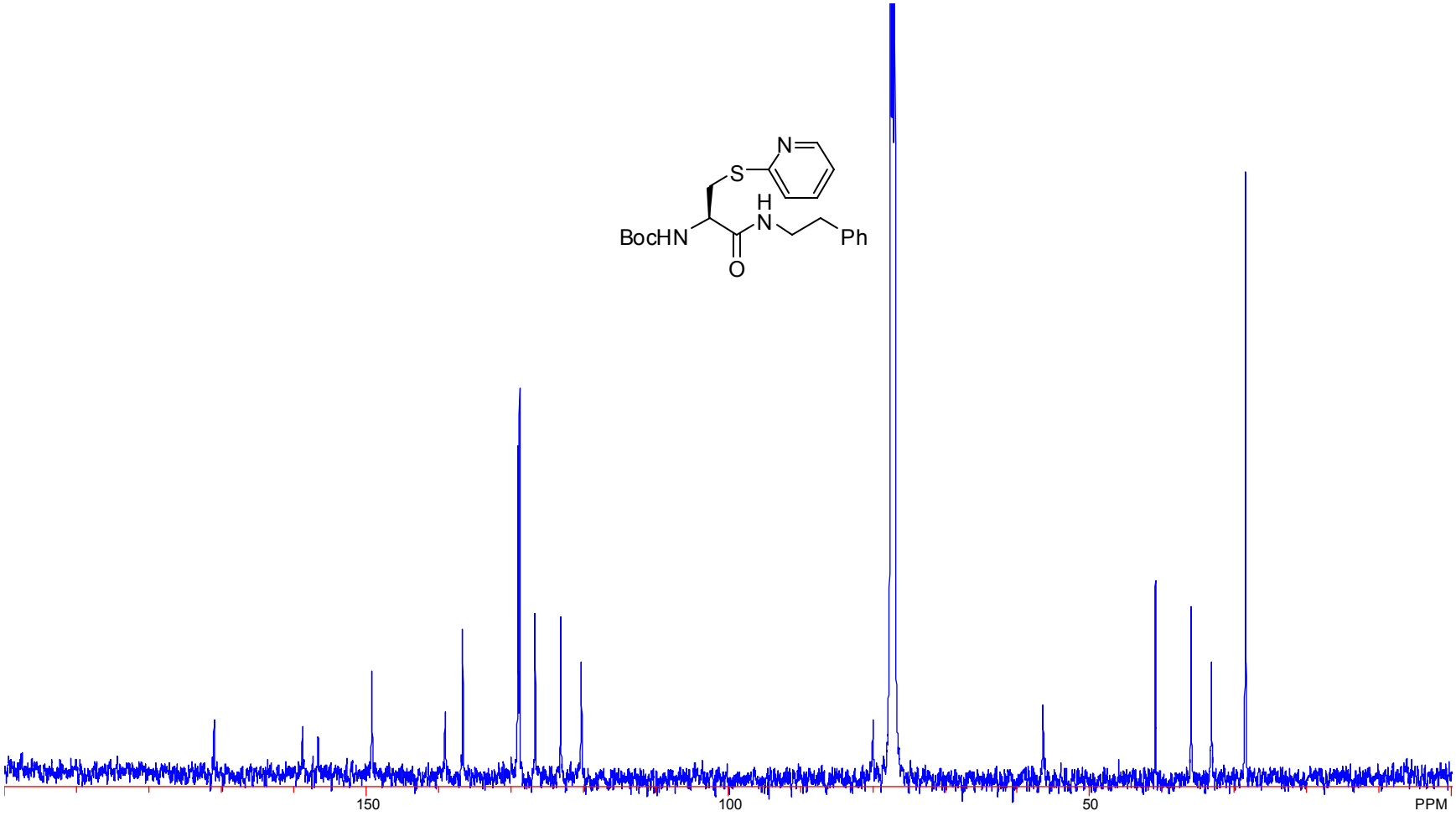
(*R*)-*O*-(*tert*-Butyl) *N*-(3-(4-chlorophenylthio)-1-(phenethylaminocarbonyl)propan-2-yl) carbamate (30)
(125 MHz, $CDCl_3$)



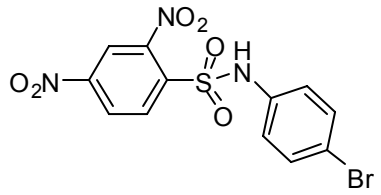
(*R*)-*O*-(*tert*-Butyl) *N*-3-(pyridin-2-ylthio)-1-(phenethylaminocarbonyl)propan-2-yl) carbamate (32)
(500 MHz, $CDCl_3$)

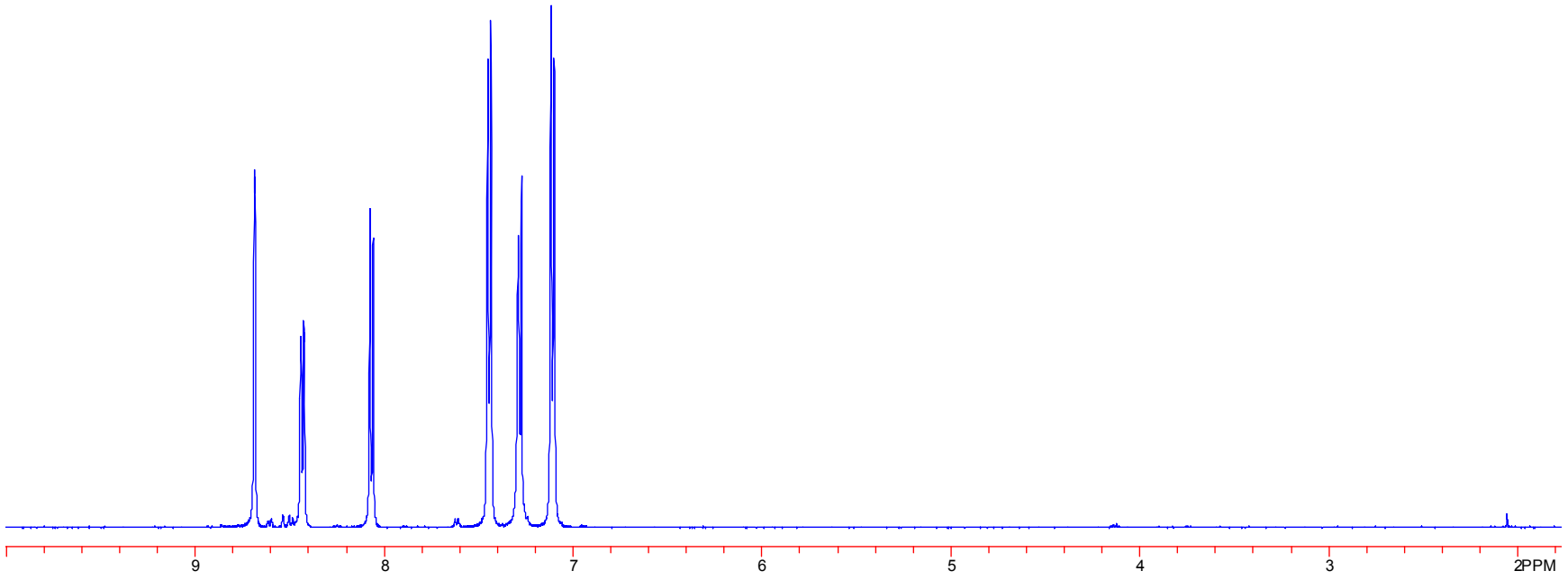


(*R*)-*O*-(*tert*-Butyl) *N*-3-(pyridin-2-ylthio)-1-(phenethylaminocarbonyl)propan-2-yl) carbamate (32)
(125 MHz, $CDCl_3$)

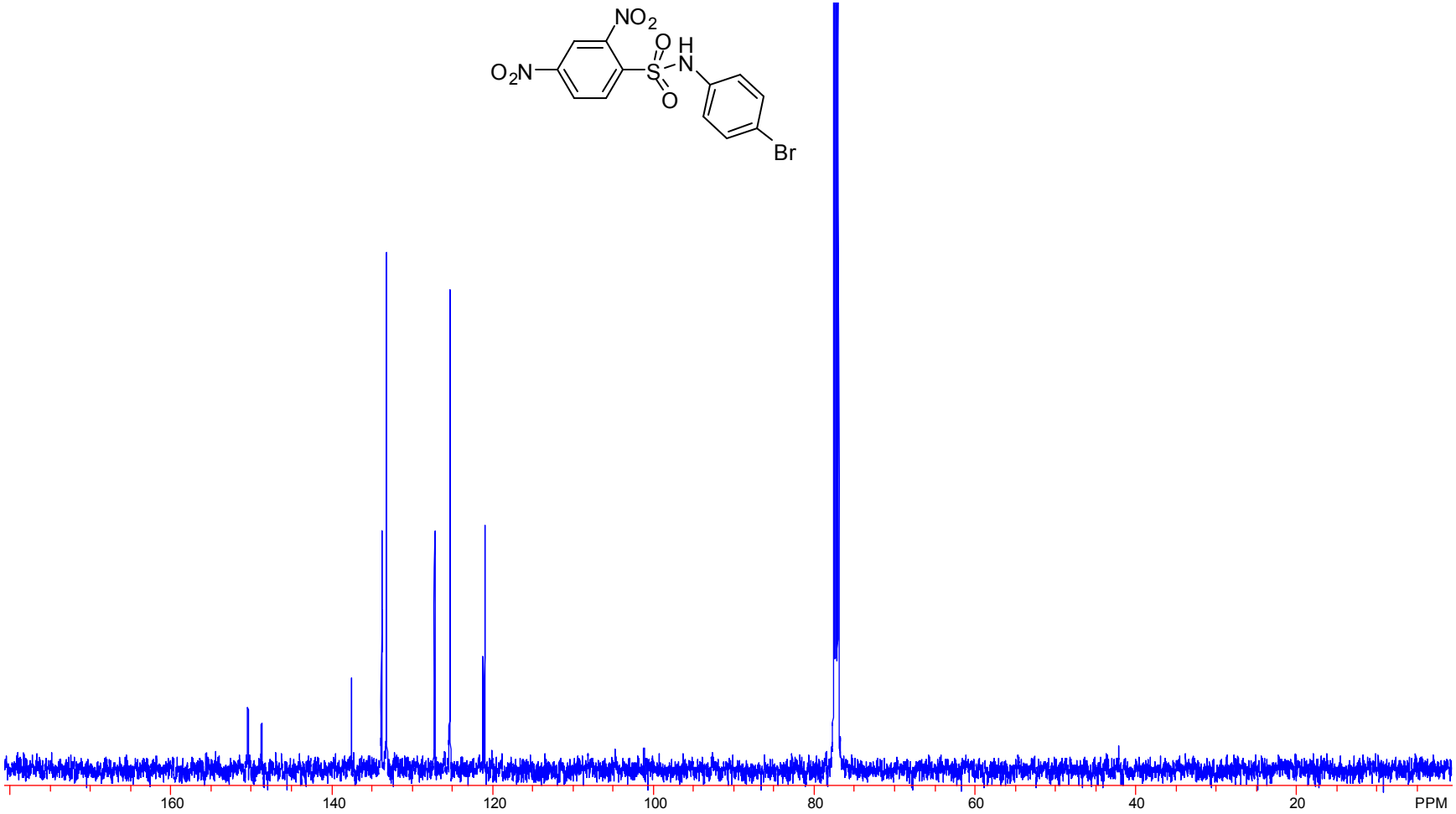


_N_-(4-Bromophenyl)-2,4-dinitrobenzenesulfonamide (33)
(500 MHz, $CDCl_3$)

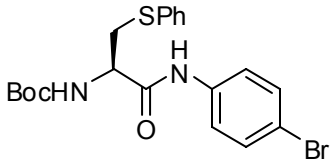




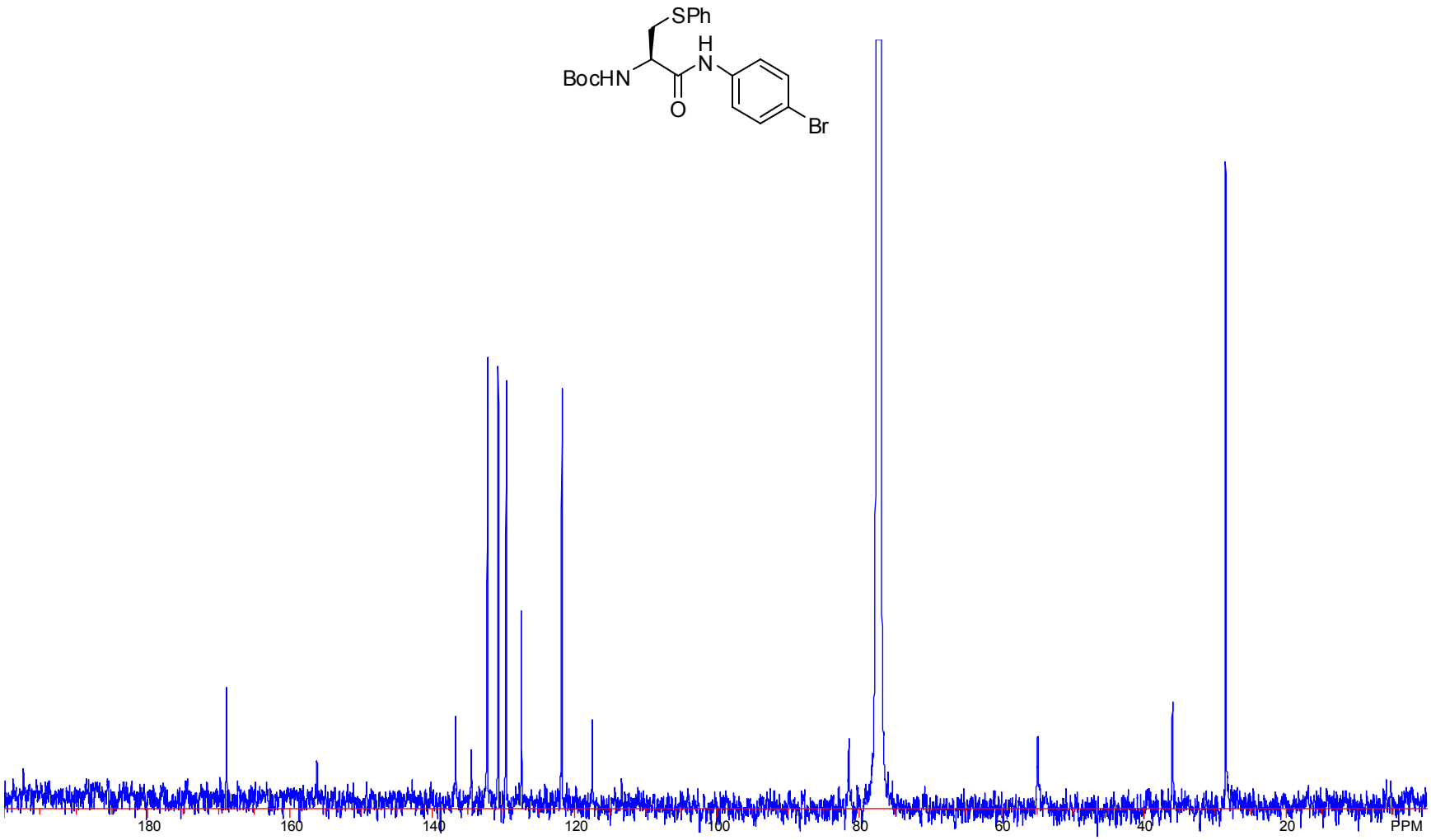
_N_-(4-Bromophenyl)-2,4-dinitrobenzenesulfonamide (33)
(125 MHz, $CDCl_3$)



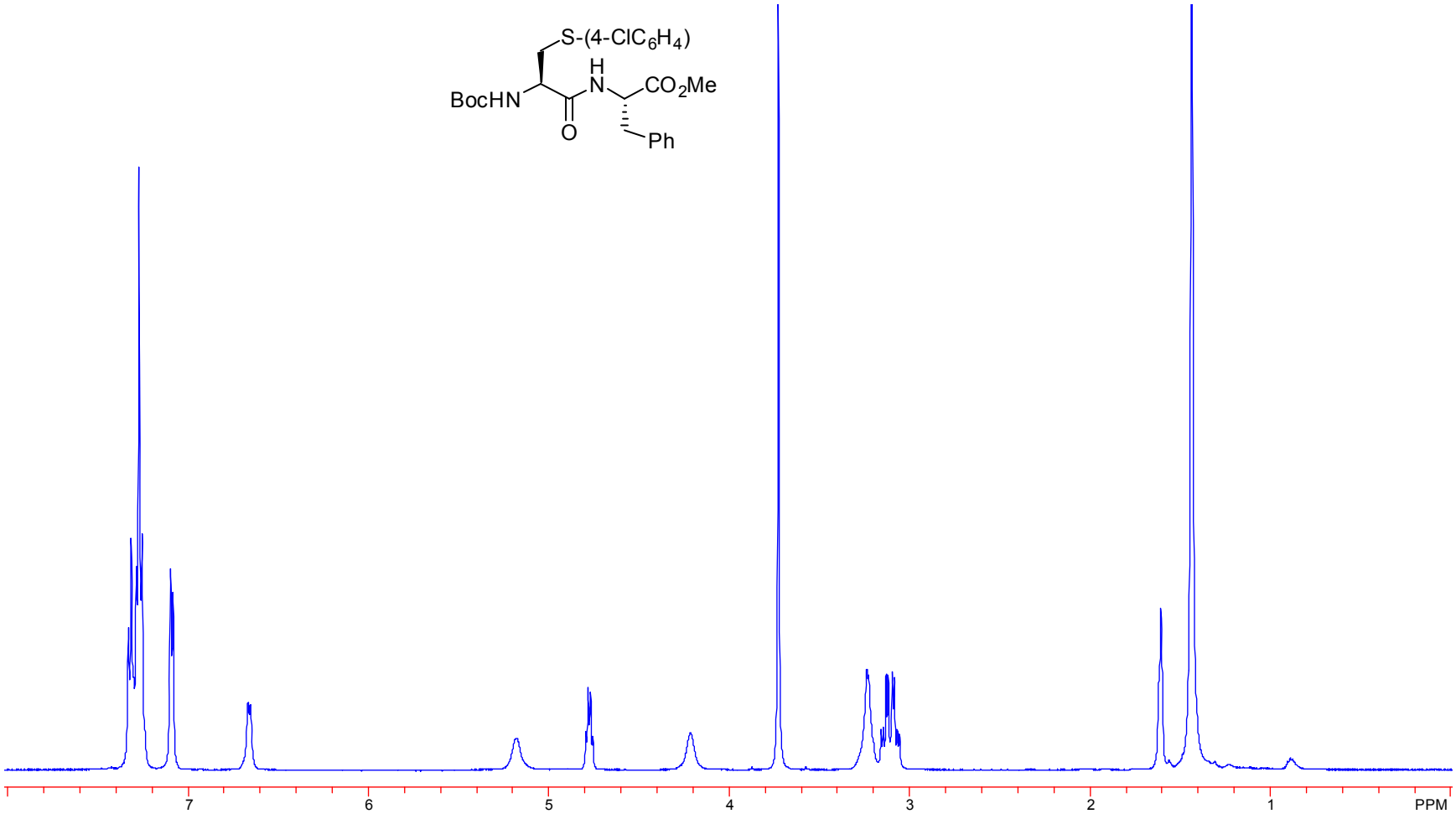
(*R*)-*O*-(*tert*-Butyl) *N*-3-(phenylthio)-1-(4-bromophenylaminocarbonyl)propan-2-yl) carbamate (34)
(500 MHz, $CDCl_3$)



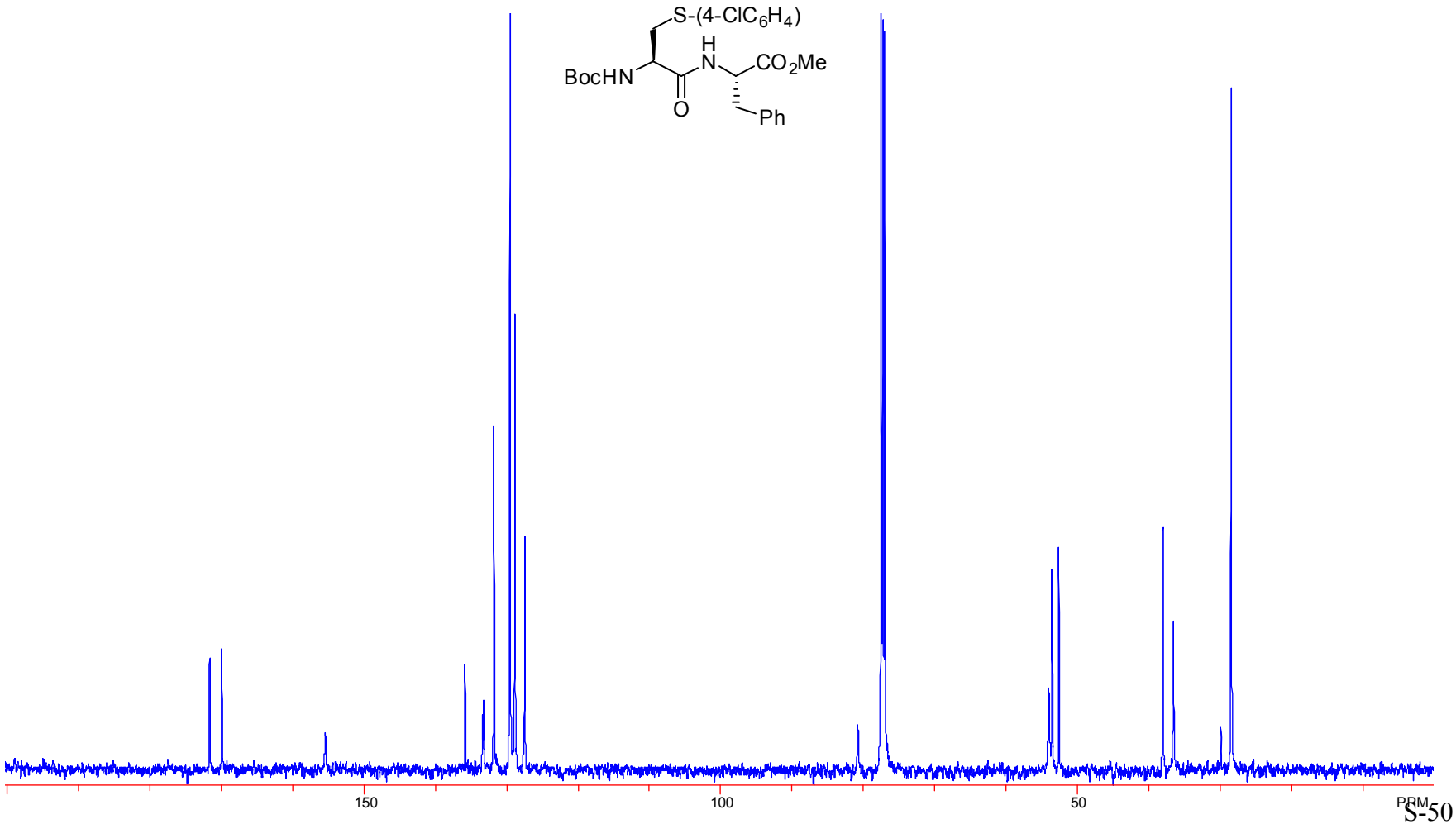
(*R*)-*O*-(*tert*-Butyl) *N*-3-(phenylthio)-1-(4-bromophenylaminocarbonyl)propan-2-yl) carbamate (34)
(125 MHz, $CDCl_3$)



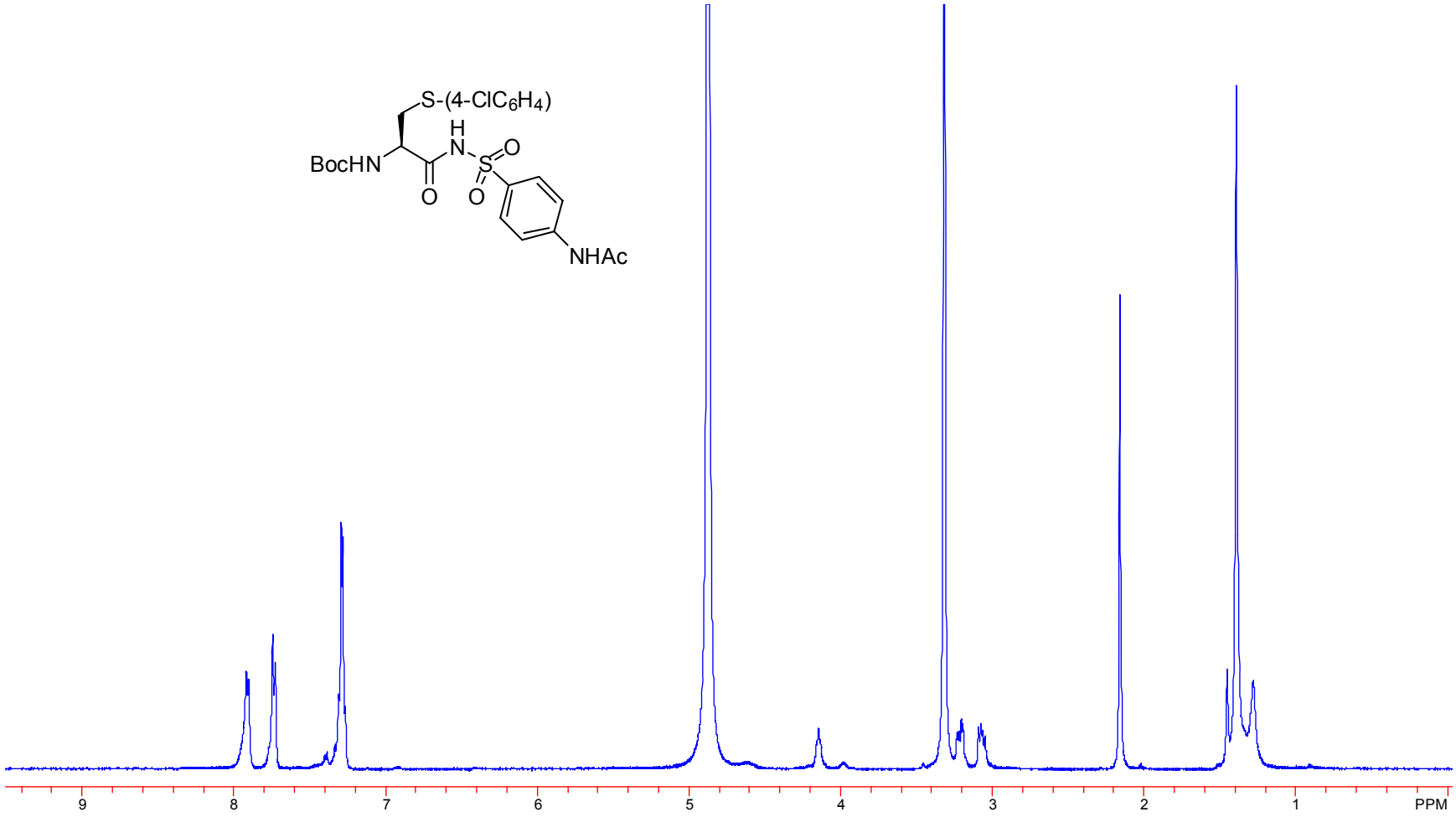
Methyl *N*-*tert*-Butoxycarbonyl-(4-chlorophenylsulfanyl)-L-alaninyl-L-phenylalaninate (36)
(500 MHz, $CDCl_3$)



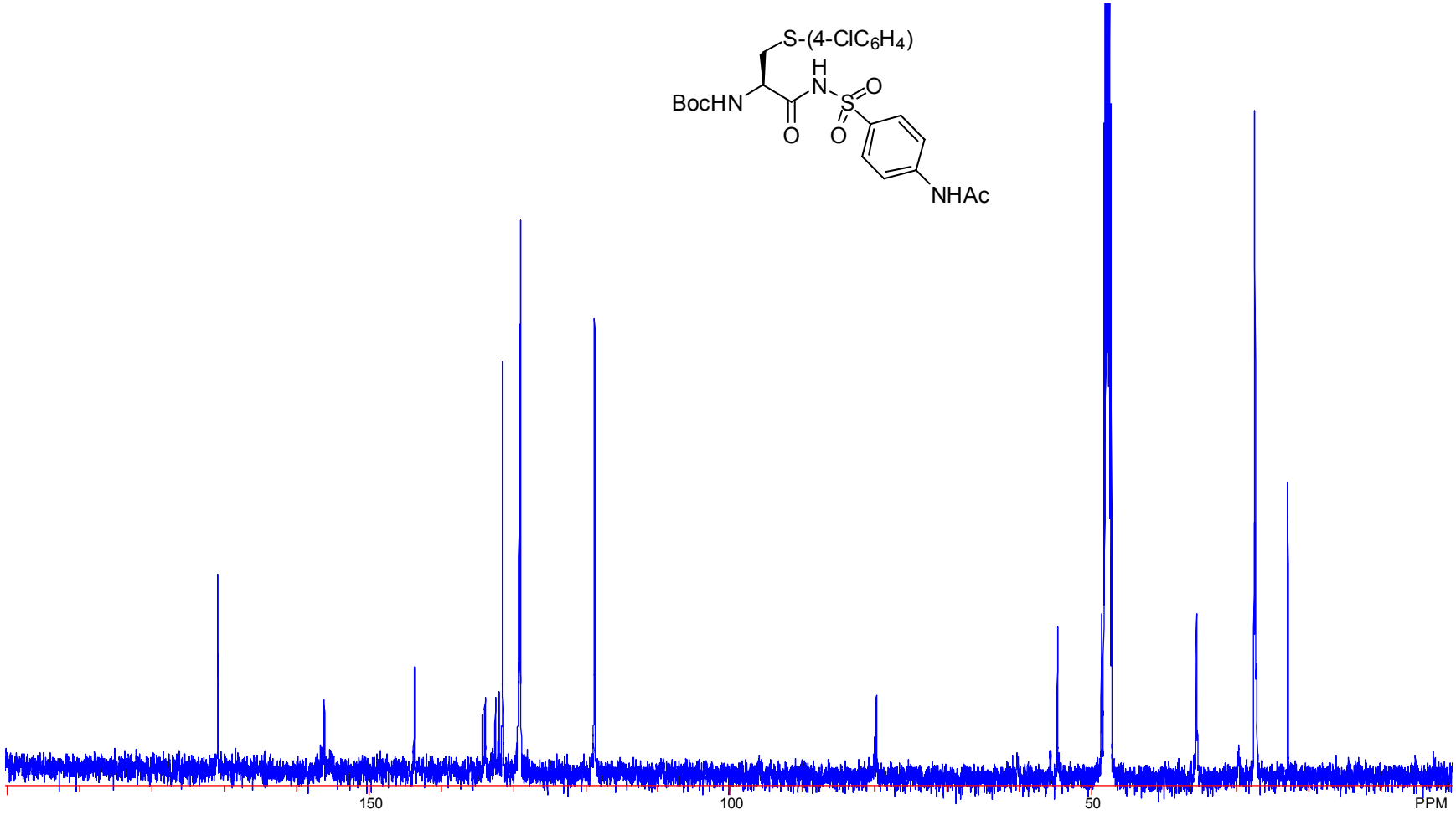
Methyl *N*-*tert*-butoxycarbonyl-(4-chlorophenylsulfanyl)-L-alaninyl-L-phenylalaninate (36)
(125 MHz, $CDCl_3$)



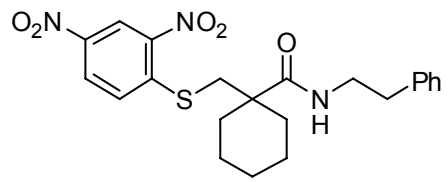
(*R*)-*O*-(*tert*-Butyl) *N*-3-(4-chlorophenylthio)-1-(4-acetamidophenylsulfonamido)propan-2-yl) carbamate (38)
(500 MHz, $CDCl_3$)

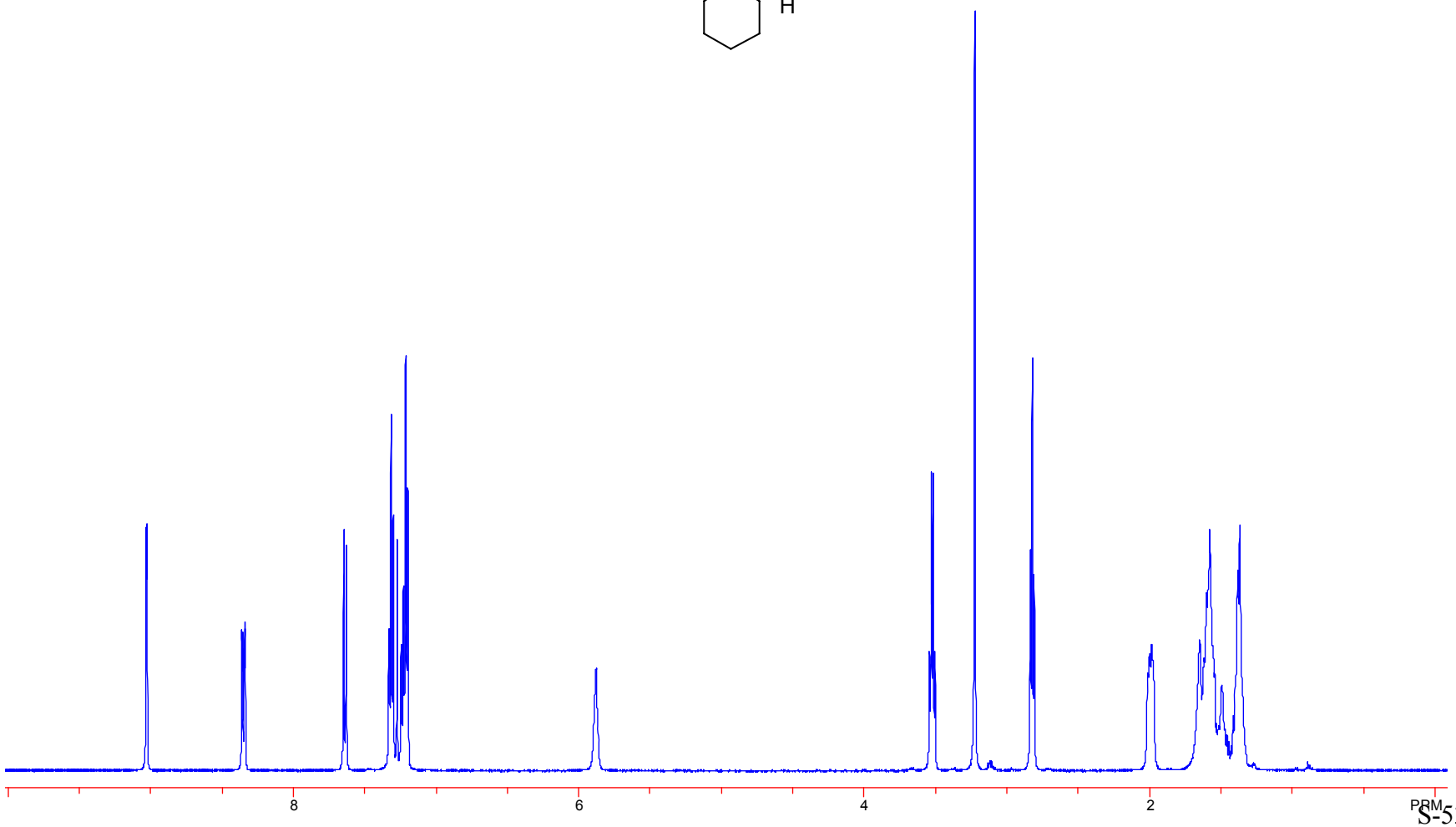


(*R*)-*O*-(*tert*-Butyl) *N*-3-(4-chlorophenylthio)-1-(4-acetamidophenylsulfonamido)propan-2-yl) carbamate (38)
(125 MHz, $CDCl_3$)

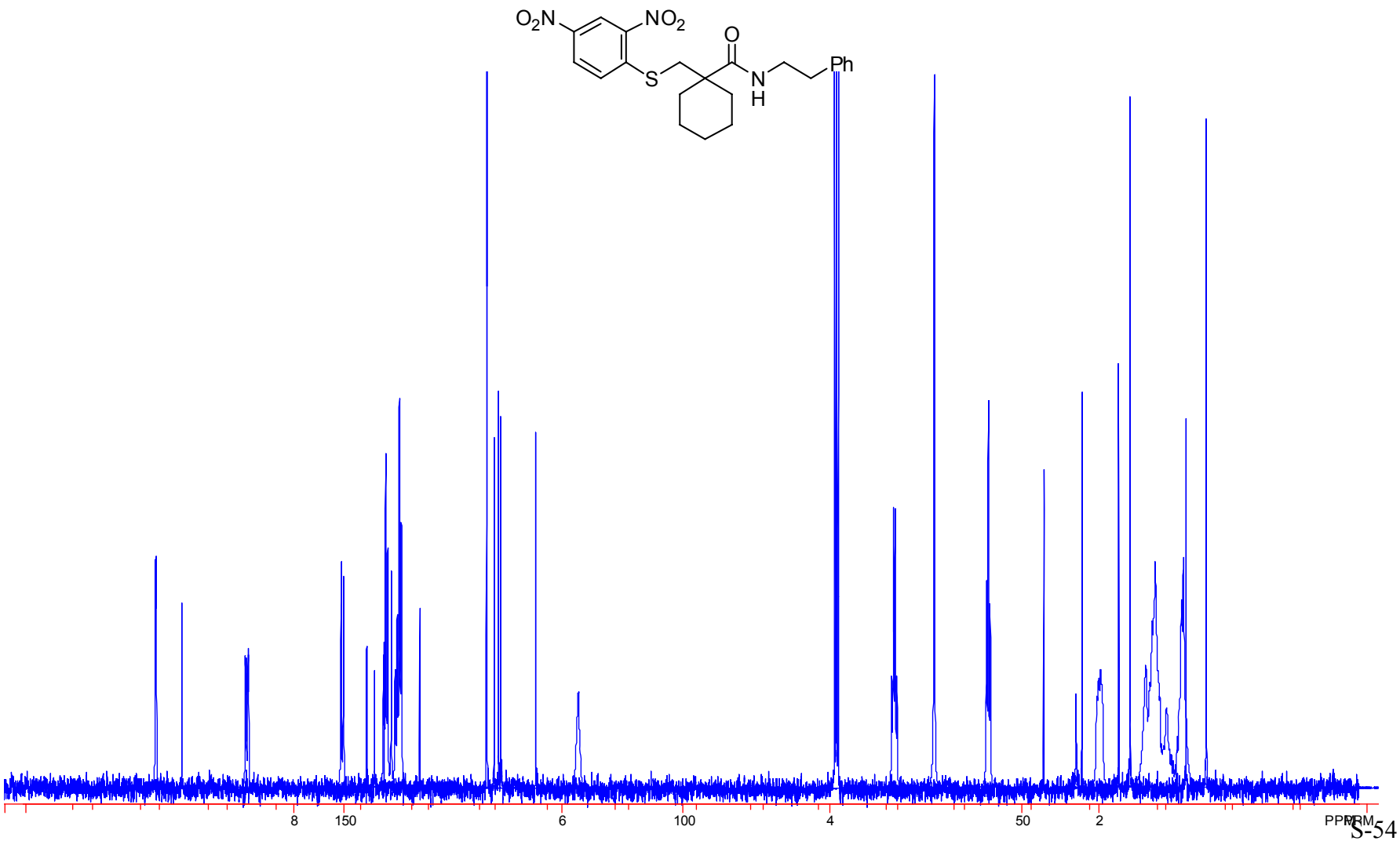


1-[(2,4-Dinitrophenylsulfanyl)methyl]-*N*-phenethylcyclohexane carboxamide (39)
(500 MHz, $CDCl_3$)

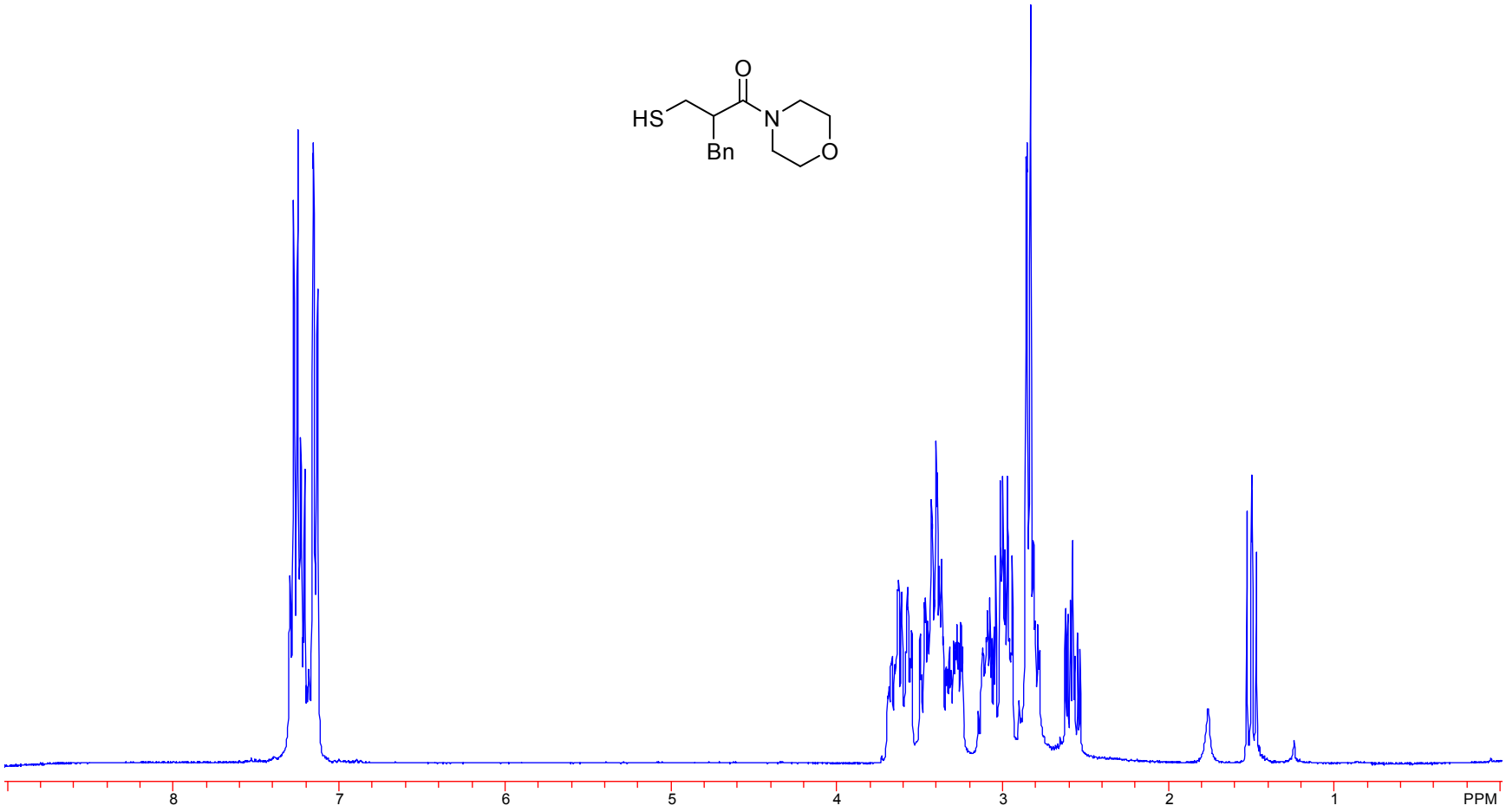




1-[(2,4-Dinitrophenylsulfanyl)methyl]-*N*-phenethylcyclohexane carboxamide (39)
(125 MHz, $CDCl_3$)



2-Mercaptomethyl-3-phenylpropanoyl morpholine (40)
(300 MHz, $CDCl_3$)



2-Mercaptomethyl-3-phenylpropanoyl morpholine (40)
(75 MHz, $CDCl_3$)