Supporting Information

Synthesis of Dithioacetals via Gold-Catalyzed Hydrothiolation of Vinyl Sulfides

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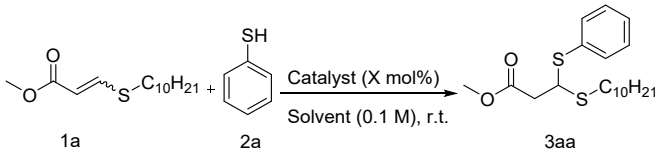
1. General Information

All reactions were conducted under a nitrogen atmosphere with oven-dried glassware and standard Schlenk or vacuum line techniques. Oil baths were used as a heat source for a reaction. All solutions were handled under nitrogen and transferred via syringe. Anhydrous solvents were purchased and stored over activated 4 Å molecular sieves. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Sigma-Aldrich, Acros, Alfa Aesar or TCI. Progress of reactions was monitored by thin-layer chromatography using Merck 60 F254 precoated silica gel plate and visualized by shortwave ultraviolet light as well as by treatment with basic solution of potassium permanganate. Flash chromatography was performed with Silica Flash P60 silica gel (230 – 400 mesh). ^{1}H and ^{13}C NMR spectra were obtained using an Agilent 400-MR DD2 Fourier-transform NMR spectrometer at 400 and 100 MHz, respectively. Chemical shifts were reported in units of parts per million (ppm) downfield from tetramethylsilane (TMS), and all coupling constants were reported in hertz. The residual solvent signals were taken as the reference ($CDCl_3$, 7.26 ppm for ^{1}H NMR spectra and $CDCl_3$, 77.0 ppm for ^{13}C NMR spectra). The signals observed are described as: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplets). High resolution mass analysis was performed with JOEL AccuTOF 4G+ DART-HRMS and JMS-700. Systematic nomenclature for the compounds follows the numbering system as defined by IUPAC with assistance from CS Chemdraw® software.

2. Optimization of reaction conditions

An oven-dried reaction tube equipped with a magnetic stirrer bar, was charged with catalyst (x mol%) and degassed with N_2 then added the solvent (2 mL) and followed by the addition of benzenethiol **2a** (1.5 equiv., 0.3 mmol) and methyl 3-(decylthio)acrylate **1a** (0.2 mmol). The reaction mixture was stirred at room temperature according to optimization table. After the reaction completion, the reaction was filtered and solvent had been removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford desired product methyl 3-(decylthio)-3-(phenylthio)propanoate **3aa.**



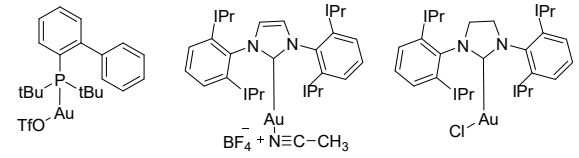
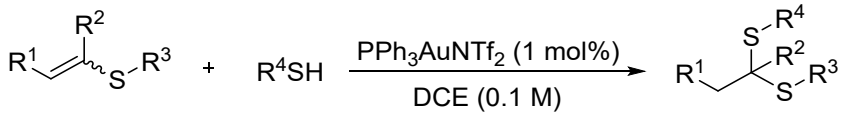


Table S1. Optimization of the reaction conditions

Entry[a]	Cat (X mol%)	Solvent	% Yield of 3aa[b]
1	AgOTf (5 mol%)	DCE	-
2	$AgNTf_2$ (5 mol%)	DCE	-
3	JohnPhosAuOTf (5 mol%)[c]	DCE	79
4	$IPrAu(MeCN)BF_4$ (5 mol%)[d]	DCE	-
5	SIPrAuCl (5 mol%)[e]	DCE	-
6	$NaAuCl_4$ (5 mol%)	DCE	-
7	$AuCl_3$ (5 mol%)	DCE	-
8	PPh_3AuCl (5 mol%)	DCE	-
9	PPh_3AuNTf_2 (5 mol%)	DCE	82
10	PPh_3AuNTf_2 (10 mol%)	DCE	69
11	PPh_3AuNTf_2 (2 mol%)	DCE	88
12	PPh_3AuNTf_2 (1 mol%)	DCE	93
13	PPh_3AuNTf_2 (1 mol%)	DCM	85
14	PPh_3AuNTf_2 (1 mol%)	Toluene	-
15	PPh_3AuNTf_2 (1 mol%)	THF	-
16	-	DCE	-

*[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), solvent (2 mL), All the reactions were carried out closed reaction tubes at room temperature; [b] Yields are for isolated products; [c] in situ generated from 5 mol% JohnPhosAuCl and 5 mol% AgOTf; [d] IPrAu(MeCN)BF_4: 1,3-Bis(2,6-di-i-propylphenyl)imidazol-2-ylidene(acetonitrile)gold(I) tetrafluoroborate; [e] SIPrAuCl: Chloro{1,3-bis[2,6-di-i-propylphenyl]-4,5-dihydroimidazol-2-ylidene}gold(I); DCE: 1,2-Dichloroethane; DCM: Dichloromethane; THF: Tetrahydrofuran*

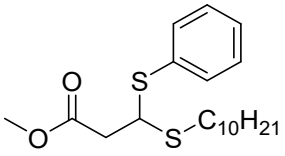
3. General procedure and characterization of Dithioacetals



1 2 3

General procedure (A) : An oven-dried reaction tube equipped with a magnetic stirrer bar, was charged with PPh_3AuNTf_2 (1 mol%) and degassed with N_2 then added DCE (0.1 M, 2 mL) and followed by the addition of thiol (1.5 equiv., 0.3 mmol) and vinyl sulfide (0.2 mmol). The reaction mixture was stirred until alkene was consumed. After the reaction completion, the reaction mixture was filtered and solvent had been removed under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford dithioacetal derivatives.

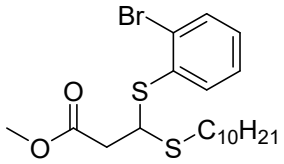
Methyl 3-(decylthio)-3-(phenylthio)propanoate (3aa)



Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and benzenethiol **2a** at r.t., 2 h, 93% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$ δ 7.50 (d, J = 6.9 Hz, 2H), 7.38 – 7.30 (m, 3H), 4.50 (t, J = 7.5 Hz, 1H), 3.69 (s, 3H), 2.88 – 2.66 (m, 4H), 1.67 – 1.56 (m, 2H), 1.42 – 1.23 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 133.7, 133.0, 128.9, 128.2, 51.9, 50.3, 41. 4, 31.9, 31.7, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{20}H_{32}NaO_2S_2^+$ ($[M+Na]^+$)

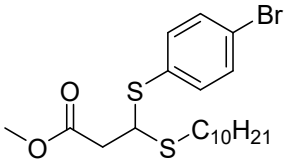
391.1736, found 391.1737.

Methyl 3-((2-bromophenyl)thio)-3-(decylthio)propanoate (3ab)



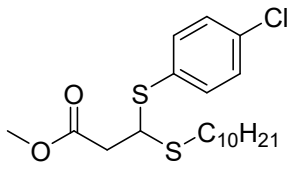
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 2-bromobenzenethiol **2b** at r.t., 2 h, 93% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.60 (d, J = 7.9 Hz, 1H), 7.54 (d, J = 7.7 Hz, 1H), 7.34 – 7.25 (m, 1H), 7.14 (t, J = 7.6 Hz, 1H), 4.68 (dd, J = 9.0, 5.6 Hz, 1H), 3.67 (s, 3H), 2.90 (dd, J = 16.0, 5.6 Hz, 1H), 2.86 – 2.77 (m, 2H), 2.77 – 2.67 (m, 1H), 1.61 (dd, J = 13.4, 5.8 Hz, 2H), 1.42 – 1.23 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 135.3, 133.6, 133.4, 129.0, 127.9, 127.2, 52.0, 49.1, 41.3, 31.9, 31.7, 29.5, 29.5, 29.3, 29.2, 29.1, 28.8, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{20}H_{31}BrNaO_2S_2^+$ ([M+Na]$^+$) 469.0841, found 469.0845.

Methyl 3-((4-bromophenyl)thio)-3-(decylthio)propanoate (3ac)



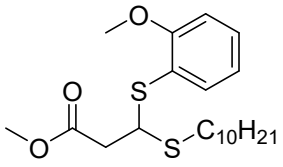
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 4-bromobenzenethiol **2c** at r.t., 2 h, 95% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 4.47 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.85 – 2.71 (m, 3H), 2.72 – 2.63 (m, 1H), 1.66 – 1.53 (m, 2H), 1.40 – 1.26 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 135.2, 132.0, 131.9, 122.7, 52.0, 50.4, 41.2, 31.8, 31.6, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for $C_{20}H_{31}BrNaO_2S_2^+$ ([M+Na]$^+$) 469.0841, found 469.0834

Methyl 3-((4-chlorophenyl)thio)-3-(decylthio)propanoate (3ad)



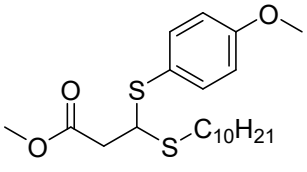
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 4-chlorobenzenethiol **2d** at r.t., 2 h, 94% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.43 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.4 Hz, 2H), 4.46 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.82 – 2.72 (m, 3H), 2.71 – 2.63 (m, 1H), 1.59 (p, J = 7.5, 7.1 Hz, 2H), 1.40 – 1.25 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 135.1, 134.6, 131.2, 129.1, 52.0, 50.6, 41.2, 31.8, 31.6, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for $C_{20}H_{31}ClNaO_2S_2^+$ ([M+Na]$^+$) 425.1346, found 425.1344

Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate (3ae)



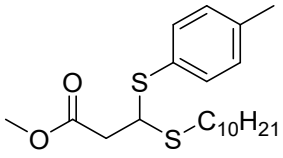
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 2-methoxybenzenethiol **2e** at r.t., 2 h, 79% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.42 (m, 1H), 7.32 – 7.25 (m, 1H), 6.94 – 6.87 (m, 2H), 4.67 (dd, J = 9.1, 5.6 Hz, 1H), 3.89 (s, 3H), 3.64 (s, 3H), 2.88 – 2.80 (m, 2H), 2.76 – 2.66 (m, 2H), 1.66 – 1.57 (m, 2H), 1.41 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 159.1, 134.9, 129.8, 121.5, 120.9, 110.9, 55.7, 51.8, 47.9, 41.5, 31.9, 31.5, 29.5, 29.5, 29.3, 29.2, 29.2, 28.9, 22.6, 14.1; HRMS (ESI) m/z calcd. for $C_{21}H_{34}NaO_3S_2^+$ ([M+Na]$^+$) 421.1842, found 421.1842

Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate (3af)



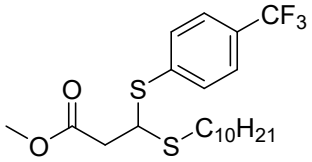
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 4-methoxybenzenethiol **2f** at r.t., 2 h, 81% yield; Colorless oil, **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 8.8 Hz, 2H), 6.87 (d, J = 8.8 Hz, 2H), 4.35 (t, J = 7.5 Hz, 1H), 3.81 (s, 3H), 3.69 (s, 3H), 2.84 – 2.74 (m, 2H), 2.71 – 2.64 (m, 2H), 1.60 (ddt, J = 14.9, 9.4, 3.6 Hz, 2H), 1.44 – 1.22 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 160.2, 136.9, 122.7, 114.4, 55.3, 51.9, 51.1, 41.2, 31.9, 31.6, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.6, 14.1; HRMS (ESI) m/z calcd. for $C_{21}H_{34}NaO_3S_2^+$ ([M+Na]$^+$) 421.1842, found 421.1842

Methyl 3-(decylthio)-3-(*p*-tolylthio)propanoate (3ag)



Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 4-methylbenzenethiol **2g** at r.t., 2 h, 68% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (d, J = 7.5 Hz, 2H), 7.15 (d, J = 7.7 Hz, 2H), 4.43 (t, J = 7.3 Hz, 1H), 3.69 (s, 3H), 2.85 – 2.76 (m, 2H), 2.74 – 2.64 (m, 2H), 2.35 (s, 3H), 1.66 – 1.58 (m, 2H), 1.38 – 1.26 (m, 14H), 0.88 (t, J = 6.5 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 138.6, 134.4, 129.7, 129.0, 51.9, 50.6, 41.3, 31.9, 31.6, 29.5, 29.5, 29.3, 29.2, 29.1, 28.9, 22.7, 21.2, 14.1; HRMS (ESI) m/z calcd. for $C_{21}H_{34}NaO_2S_2^+$ ([M+Na]$^+$) 405.1892, found 405.1892

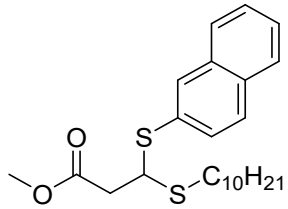
Methyl 3-(decylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3ah)



Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and 4-(trifluoromethyl)benzenethiol **2h** at r.t., 2 h, 88% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (s, 4H), 4.62 (dd, J = 7.9, 6.8 Hz, 1H), 3.70 (s, 3H), 2.91 – 2.77 (m, 2H), 2.81 – 2.72 (m, 1H), 2.73 – 2.63 (m, 1H), 1.60 (dt, J = 14.8, 6.8 Hz, 2H), 1.44 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 138.7, 131.9, 129.54 (q, J = 32.7

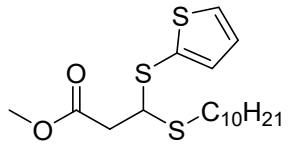
Hz), 125.71 (q, J = 3.7 Hz), 123.91 (q, J = 272.2 Hz), 52.0, 49.6, 41.3, 31.9, 31.7, 29.5, 29.5, 29.3, 29.1, 29.0, 28.8, 22.6, 14.1; HRMS (ESI) m/z calcd. for $C_{21}H_{31}F_3NaO_2S_2^+$ ($[M+Na]^+$) 459.1610, found 459.1608

Methyl 3-(decylthio)-3-(naphthalen-2-ylthio)propanoate (3ai)



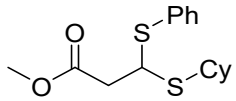
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and naphthalene-2-thiol **2i** at r.t., 2 h, 76% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.86 – 7.75 (m, 3H), 7.59 – 7.53 (m, 1H), 7.49 (dt, J = 9.4, 4.8 Hz, 2H), 4.61 (dd, J = 8.2, 6.6 Hz, 1H), 3.67 (s, 3H), 3.03 – 2.59 (m, 4H), 1.61 (p, J = 8.1 Hz, 2H), 1.43 – 1.22 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 133.5, 132.7, 130.6, 130.4, 128.5, 127.7, 127.7, 126.6, 126.6, 52.0, 50.3, 41.5, 31.9, 31.8, 29.5, 29.5, 29.3, 29.2, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{24}H_{34}NaO_2S_2^+$ ($[M+Na]^+$) 441.1892, found 441.1893

Methyl 3-(decylthio)-3-(thiophen-2-ylthio)propanoate (3aj)



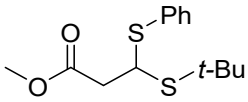
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and thiophene-2-thiol **2j** at 50 °C, overnight, 43% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (d, J = 5.3 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.08 – 7.00 (m, 1H), 4.32 (t, J = 7.1 Hz, 1H), 3.71 (s, 3H), 2.83 (td, J = 13.9, 12.2, 7.0 Hz, 2H), 2.69 (dd, J = 14.9, 7.7 Hz, 2H), 1.63 (dt, J = 13.8, 6.8 Hz, 2H), 1.46 – 1.23 (m, 14H), 0.88 (t, J = 6.0 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 136.7, 131.3, 129.9, 127.6, 52.3, 52.0, 40.9, 31.9, 31.9, 29.5, 29.5, 29.3, 29.2, 29.0, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{18}H_{30}NaO_2S_3^+$ ($[M+Na]^+$) 397.1300, found 397.1302

Methyl 3-(cyclohexylthio)-3-(phenylthio)propanoate (3ba)



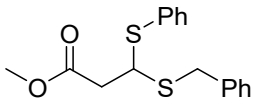
Prepared according to General procedure (A) using methyl 3-(cyclohexylthio)acrylate **1b** and benzenethiol **2a** at r.t., 4 h, 95% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 (d, J = 6.8 Hz, 2H), 7.33 (d, J = 6.3 Hz, 3H), 4.57 (t, J = 7.3 Hz, 1H), 3.68 (s, 3H), 3.00 (td, J = 10.1, 4.6 Hz, 1H), 2.83 (dd, J = 15.8, 6.3 Hz, 1H), 2.70 (dd, J = 15.8, 8.4 Hz, 1H), 2.11 – 1.90 (m, 2H), 1.80 – 1.69 (m, 2H), 1.67 – 1.49 (m, 1H), 1.42 – 1.32 (m, 3H), 1.30 – 1.22 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 133.6, 133.2, 129.0, 128.2, 51.9, 48.6, 44.2, 41.6, 33.6, 33.1, 26.0, 25.8, 25.7; HRMS (ESI) m/z calcd. for $C_{16}H_{22}NaO_2S_2^+$ ($[M+Na]^+$) 333.0953, found 333.0957

Methyl 3-(tert-butylthio)-3-(phenylthio)propanoate (3ca)



Prepared according to General procedure (A) using methyl 3-(tert-butylthio)acrylate **1c** and benzenethiol **2a** at r.t., 3 h, 87% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$7.50 (d, J = 7.5 Hz, 2H), 7.38 – 7.27 (m, 3H), 4.54 (dd, J = 9.1, 5.5 Hz, 1H), 3.67 (s, 3H), 2.85 (dd, J = 16.2, 5.2 Hz, 1H), 2.71 (dd, J = 15.4, 9.2 Hz, 1H), 1.40 (s, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 134.3, 133.0, 129.0, 128.0, 51.8, 46.6, 45.0, 42.8, 31.1; HRMS (ESI) m/z calcd. for $C_{14}H_{20}NaO_2S_2^+$ ($[M+Na]^+$) 307.0797, found 307.0794

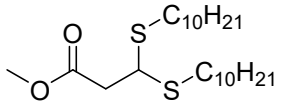
Methyl 3-(benzylthio)-3-(phenylthio)propanoate (3da)



Prepared according to General procedure (A) using methyl 3-(benzylthio)acrylate **1d** and benzenethiol **2a** at 50 °C, 2 h, 70% yield, Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 (dd, J = 6.3, 2.8 Hz, 3H), 7.31 (dd, J = 6.0, 2.9 Hz, 11H), 7.29 – 7.23 (m, 3H), 4.34 (t, J = 7.4 Hz, 1H), 4.05 – 3.84 (m, 2H), 3.62 (s, 4H), 2.78 (dd, J = 15.8, 7.0 Hz, 1H), 2.69 (dd, J = 15.9, 7.9 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 137.2, 133.7, 132.6, 129.1, 129.0, 128.6,

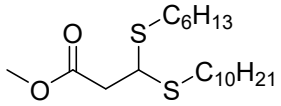
128.3, 127.3, 51.9, 49.4, 41.1, 36.0; HRMS (ESI) m/z calcd. for $C_{17}H_{18}NaO_2S_2^+$ ([M+Na]$^+$) 341.0640, found 341.0636

Methyl 3,3-bis(decylthio)propanoate (3ak)



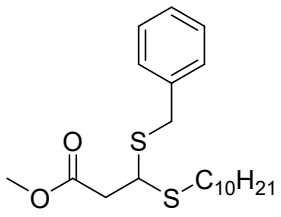
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate 1a and decane-1-thiol **2k** at r.t., 2 h, 84% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.21 (t, J = 7.6 Hz, 1H), 3.72 (s, 3H), 2.81 (d, J = 7.6 Hz, 2H), 2.72 – 2.63 (m, 2H), 2.62 – 2.54 (m, 2H), 1.58 (q, J = 9.1, 8.0 Hz, 4H), 1.41 – 1.24 (m, 28H), 0.88 (t, J = 6.7 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 51.9, 47.1, 41.7, 31.9, 30.4, 29.5, 29.5, 29.3, 29.2, 29.2, 29.0, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{24}H_{48}NaO_2S_2^+$ ([M+Na]$^+$) 455.2988, found 455.2981

Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3al)



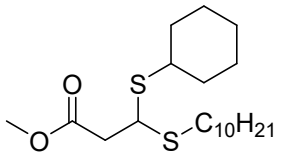
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and hexane-1-thiol **2l** at r.t., 6 h, 71% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.21 (t, J = 7.6 Hz, 1H), 3.72 (s, 3H), 2.81 (d, J = 7.6 Hz, 2H), 2.68 (dt, J = 14.2, 7.4 Hz, 2H), 2.62 – 2.54 (m, 2H), 1.59 (p, J = 7.2 Hz, 4H), 1.43 – 1.26 (m, 20H), 0.92 – 0.86 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 51.9, 47.1, 41.7, 31.9, 31.4, 30.4, 29.5, 29.5, 29.3, 29.2, 29.2, 28.9, 28.6, 22.6, 22.5, 14.1, 14.0; HRMS (ESI) m/z calcd. for $C_{20}H_{40}NaO_2S_2^+$ ([M+Na]$^+$) 399.2362, found 399.2400

Methyl 3-(benzylthio)-3-(decylthio)propanoate (3am)



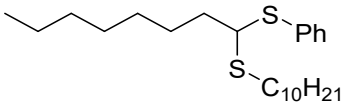
Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and phenylmethanethiol **2m** at r.t., 4 h, 63% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 4H), 7.28 – 7.19 (m, 1H), 4.09 (t, J = 7.6 Hz, 1H), 3.93 – 3.76 (m, 2H), 3.68 (s, 3H), 2.77 (d, J = 7.6 Hz, 2H), 2.62 (dt, J = 12.5, 7.4 Hz, 1H), 2.53 (dt, J = 12.4, 7.5 Hz, 1H), 1.53 (p, J = 7.3 Hz, 2H), 1.39 – 1.24 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.4, 137.7, 129.0, 128.5, 127.1, 51.9, 46.6, 41.5, 35.1, 31.9, 30.3, 29.6, 29.5, 29.3, 29.2, 29.2, 29.0, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{21}H_{34}NaO_2S_2^+$ ($[M+Na]^+$) 405.1892, found 405.1897

Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate (3an)



Prepared according to General procedure (A) using methyl 3-(decylthio)acrylate **1a** and cyclohexanethiol **2n** at r.t., 3 h, 42% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.27 (t, J = 7.5 Hz, 1H), 3.72 (s, 3H), 2.88 (tt, J = 10.0, 3.9 Hz, 1H), 2.81 (d, J = 7.6 Hz, 2H), 2.71 – 2.56 (m, 2H), 1.97 (ddd, J = 20.2, 9.9, 4.7 Hz, 2H), 1.75 (dt, J = 9.5, 4.5 Hz, 2H), 1.59 (p, J = 7.6, 7.1 Hz, 3H), 1.44 – 1.20 (m, 19H), 0.88 (t, J = 6.6 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.7, 51.9, 45.6, 43.4, 42.2, 33.8, 33.5, 31.9, 30.2, 29.5, 29.5, 29.3, 29.3, 29.2, 28.9, 26.1, 25.8, 25.7, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{20}H_{38}NaO_2S_2^+$ ($[M+Na]^+$) 397.2205, found 397.2202

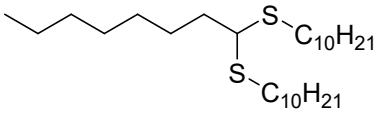
Decyl(1-(phenylthio)octyl)sulfane (3ea)



Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane **1e** and benzenethiol **2a** at reflux, 10 h, 38% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.42 (m, 2H), 7.35 – 7.23 (m, 3H), 4.08 (t, J = 6.7 Hz, 1H), 2.76 (dt, J = 12.5, 7.3 Hz, 1H), 2.65 (dt, J = 12.5, 7.5 Hz, 1H), 1.90 – 1.69 (m, 2H), 1.63 – 1.52 (m, 4H), 1.41 – 1.24 (m, 22H), 0.92 – 0.83 (m, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 134.6, 132.9, 128.8, 127.5, 55.4, 36.0,

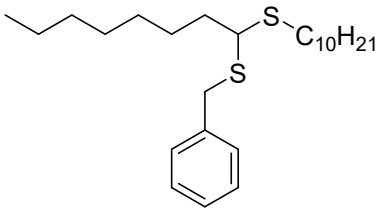
31.9, 31.7, 31.3, 29.6, 29.5, 29.3, 29.2, 29.1, 29.1, 29.0, 27.1, 22.7, 22.6, 14.1, 14.1.; HRMS (ESI) m/z calcd. for $C_{24}H_{42}NaS_2^+$ ($[M+Na]^+$) 417.2620, found 417.2623

Octane-1,1-diylbis(decylsulfane) (3ek)



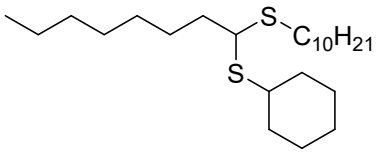
Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane **1e** and decane-1-thiol **2k** at reflux, 20 h, 74% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.73 (t, J = 7.0 Hz, 1H), 2.65 (dt, J = 14.5, 7.4 Hz, 2H), 2.54 (dt, J = 12.4, 7.4 Hz, 2H), 1.77 (q, J = 7.3 Hz, 2H), 1.55 (dp, J = 15.3, 7.6, 7.2 Hz, 6H), 1.43 – 1.22 (m, 36H), 0.88 (t, J = 6.8 Hz, 9H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 52.0, 36.1, 31.9, 31.8, 30.0, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 29.1, 27.5, 22.7, 22.6, 14.1, 14.1; HRMS (ESI) m/z calcd. for $C_{28}H_{58}NaS_2^+$ ($[M+Na]^+$) 481.3872, found 481.3873

Benzyl(1-(decylthio)octyl)sulfane (3em)



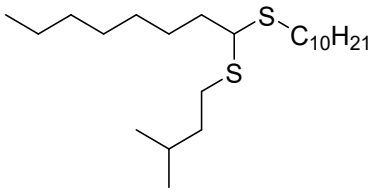
Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane **1e** and phenylmethanethiol **2m** at reflux, 1 h, 36% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 5H), 3.91 – 3.73 (m, 2H), 3.58 (t, J = 7.0 Hz, 1H), 2.65 – 2.47 (m, 2H), 1.75 (q, J = 7.4 Hz, 2H), 1.54 (dd, J = 14.3, 6.8 Hz, 2H), 1.45 (td, J = 6.9, 3.9 Hz, 2H), 1.36 (dd, J = 8.4, 5.2 Hz, 2H), 1.31 – 1.23 (m, 20H), 0.88 (td, J = 6.8, 4.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.3, 129.0, 128.4, 126.9, 51.2, 35.8, 34.8, 31.9, 31.8, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 29.1, 29.0, 27.3, 22.7, 22.6, 14.1, 14.1; HRMS (ESI) m/z calcd. for $C_{25}H_{44}NaS_2^+$ ($[M+Na]^+$) 431.2777, found 431.2771

Cyclohexyl(1-(decylthio)octyl)sulfane (3en)



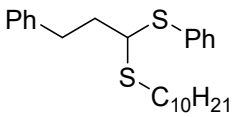
Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane **1e** and cyclohexanethiol **2n** at reflux, 20 h, 35% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.81 (t, J = 6.9 Hz, 1H), 2.88 (tt, J = 9.9, 3.9 Hz, 1H), 2.64 (dt, J = 12.4, 7.4 Hz, 1H), 2.56 (dt, J = 12.4, 7.4 Hz, 1H), 1.96 (ddd, J = 21.6, 10.0, 4.7 Hz, 2H), 1.83 – 1.73 (m, 3H), 1.63 – 1.48 (m, 5H), 1.44 – 1.22 (m, 28H), 0.88 (t, J = 6.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 50.4, 42.9, 36.6, 34.1, 33.7, 31.9, 31.8, 29.8, 29.6, 29.5, 29.5, 29.3, 29.3, 29.2, 29.1, 29.0, 27.4, 26.1, 25.9, 25.8, 22.7, 22.6, 14.1, 14.1; HRMS (ESI) m/z calcd. for $C_{24}H_{48}NaS_2^+$ ($[M+Na]^+$) 423.3090, found 423.3092

Decyl(1-(isopentylthio)octyl)sulfane (3eo)



Prepared according to General procedure (A) using decyl(oct-1-en-1-yl)sulfane **1e** and 3-methylbutane-1-thiol **2o** at 50 °C, 1 h, 51% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 3.74 (t, J = 7.0 Hz, 1H), 2.72 – 2.59 (m, 2H), 2.56 (dq, J = 12.4, 7.4 Hz, 2H), 1.78 (q, J = 7.9, 7.2 Hz, 2H), 1.69 (dt, J = 13.3, 6.7 Hz, 1H), 1.60 – 1.51 (m, 3H), 1.50 – 1.44 (m, 3H), 1.42 – 1.24 (m, 22H), 0.91 (d, J = 6.6 Hz, 6H), 0.90 – 0.86 (m, 6H). **^{13}C NMR** (100 MHz, CDCl3) δ 52.0, 38.4, 36.1, 36.1, 31.9, 31.8, 30.0, 29.5, 29.5, 29.4, 29.3, 29.2, 29.1, 29.0, 28.0, 27.5, 27.5, 22.7, 22.6, 22.3, 22.2, 14.1, 14.1; HRMS (EI) m/z calcd. for $C_{23}H_{48}S_2^+$ ($[M]^+$) 388.3197, found 388.3200

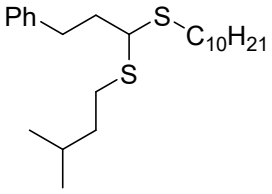
Decyl(3-phenyl-1-(phenylthio)propyl)sulfane (3fa)



Prepared according to General procedure (A) using decyl(3-phenylprop-1-en-1-yl)sulfane **1f** and benzenethiol **2a** at 50 °C, 2 h, 79% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ

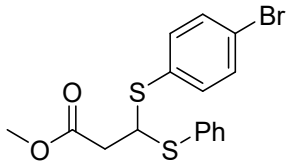
7.39 (dd, J = 7.5, 1.8 Hz, 2H), 7.31 – 7.24 (m, 5H), 7.19 (d, J = 7.2 Hz, 1H), 7.14 (d, J = 7.1 Hz, 2H), 4.03 (dd, J = 7.6, 5.9 Hz, 1H), 2.97 – 2.79 (m, 2H), 2.75 (dt, J = 12.7, 7.3 Hz, 1H), 2.65 (dt, J = 12.4, 7.6 Hz, 1H), 2.22 – 1.99 (m, 2H), 1.63 – 1.49 (m, 2H), 1.42 – 1.24 (m, 14H), 0.88 (t, J = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.9, 134.2, 132.7, 128.8, 128.5, 128.3, 127.5, 126.0, 54.0, 37.3, 33.0, 31.9, 31.3, 29.5, 29.5, 29.3, 29.3, 29.2, 28.9, 22.7, 14.1; HRMS (ESI) m/z calcd. for $C_{25}H_{36}NaS_2^+$ ($[M+Na]^+$) 423.2151, found 423.2153

Decyl(1-(isopentylthio)-3-phenylpropyl)sulfane (3fo)



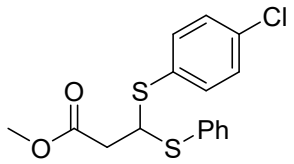
Prepared according to General procedure (A) using decyl(3-phenylprop-1-en-1-yl)sulfane **1f** and 3-methylbutane-1-thiol **2o** at 50 °C, 1 h, 80% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32 – 7.14 (m, 5H), 3.69 (t, J = 7.0 Hz, 1H), 2.85 (t, J = 7.6 Hz, 2H), 2.65 (dtd, J = 14.5, 7.6, 2.5 Hz, 2H), 2.55 (dq, J = 12.5, 7.5 Hz, 2H), 2.09 (q, J = 7.4 Hz, 2H), 1.67 (dt, J = 13.3, 6.7 Hz, 1H), 1.54 (q, J = 8.4 Hz, 2H), 1.44 (q, J = 7.4 Hz, 2H), 1.39 – 1.24 (m, 14H), 0.91 – 0.86 (m, 9H); **^{13}C NMR** (100 MHz, CDCl3) δ 141.2, 128.5, 128.4, 126.0, 51.0, 38.4, 37.7, 33.5, 31.9, 30.1, 29.6, 29.5, 29.4, 29.3, 29.3, 29.1, 28.1, 27.6, 22.7, 22.4, 22.3, 14.1; HRMS (EI) m/z calcd. for $C_{24}H_{42}S_2^+$ ($[M]^+$) 394.2728, found 394.2730

Methyl 3-((4-bromophenyl)thio)-3-(phenylthio)propanoate (3gc)



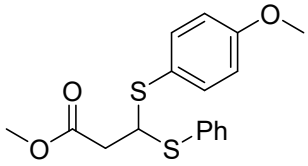
Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and 4-bromobenzenethiol **2c** at 50 °C, 4 h, 81% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 (dd, J = 12.7, 6.8 Hz, 4H), 7.38 – 7.31 (m, 5H), 4.77 (t, J = 7.3 Hz, 1H), 3.70 (s, 3H), 2.80 (dd, J = 7.0, 4.5 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 135.0, 133.5, 132.7, 132.2, 132.1, 129.1, 128.4, 122.8, 53.6, 52.1, 40.9; HRMS (ESI) m/z calcd. for $C_{16}H_{15}BrNaO_2S_2^+$ ($[M+Na]^+$) 404.9589, found 404.9587

Methyl 3-((4-chlorophenyl)thio)-3-(phenylthio)propanoate (3gd)



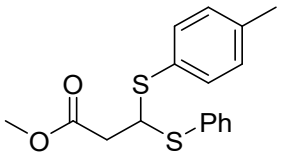
Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and 4-chlorobenzenethiol **2d** at 50 °C, 3 h, 82% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 6.4, 2.9 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.33 – 7.26 (m, 5H), 4.77 (t, J = 7.4 Hz, 1H), 3.69 (s, 3H), 2.80 (dd, J = 7.4, 4.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 134.9, 134.6, 133.5, 132.8, 131.3, 129.2, 129.1, 128.4, 53.7, 52.1, 40.9; HRMS (ESI) m/z calcd. for $C_{16}H_{15}ClNaO_2S_2^+$ ($[M+Na]^+$) 361.0094, found 361.0097

Methyl 3-((4-methoxyphenyl)thio)-3-(phenylthio)propanoate (3gf)



Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and 4-methoxybenzenethiol **2f** at 50 °C, 5 h, 47% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.47 (dd, J = 12.4, 7.8 Hz, 4H), 7.37 – 7.27 (m, 3H), 6.87 (d, J = 8.0 Hz, 2H), 4.67 (t, J = 7.4 Hz, 1H), 3.82 (s, 3H), 3.70 (s, 3H), 2.77 (d, J = 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 160.3, 136.8, 133.4, 133.0, 129.0, 128.0, 122.7, 114.5, 55.3, 54.2, 52.0, 40.9; HRMS (ESI) m/z calcd. for $C_{17}H_{18}NaO_3S_2^+$ ($[M+Na]^+$) 357.0590, found 357.0587

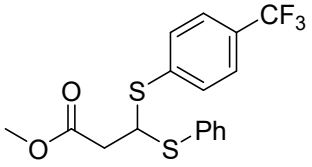
Methyl 3-(phenylthio)-3-(p-tolylthio)propanoate (3gg)



Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and 4-methylbenzenethiol **2g** at 50 °C, 5 h, 95% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.49 (d, J = 5.5 Hz, 1H), 7.39 (d, J = 7.7 Hz, 3H), 7.32 (d, J = 5.6 Hz, 2H), 7.14 (d, J = 7.5 Hz, 3H), 4.71 (dt, J = 24.7, 7.3 Hz, 1H), 3.69 (s, 3H), 2.78 (dd, J = 10.7, 7.7 Hz, 2H), 2.35 (s, 3H);

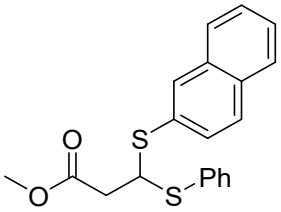
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.5, 138.5, 134.2, 134.0, 133.4, 133.3, 129.8, 129.0, 128.1, 53.7, 51.9, 41.0, 21.2; HRMS (ESI) m/z calcd. for $C_{17}H_{18}NaO_2S_2^+$ ([M+Na]$^+$) 341.0640, found 341.0639

Methyl 3-(phenylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate (3gh)



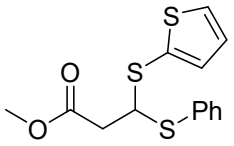
Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and 4-(trifluoromethyl)benzenethiol **2h** at 50 ^{o}C, 5 h, 77% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (s, 4H), 7.50 – 7.46 (m, 2H), 7.34 – 7.31 (m, 3H), 4.90 (t, J = 7.4 Hz, 1H), 3.71 (s, 3H), 2.85 (t, J = 7.4 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.2, 138.6, 133.8, 132.2, 131.7, 129.56 (q, J = 32.6 Hz), 129.1, 128.7, 125.77 (q, J = 3.7 Hz), 123.88 (q, J = 272.2 Hz), 52.8, 52.1, 40.8; HRMS (ESI) m/z calcd. for $C_{17}H_{15}F_3NaO_2S_2^+$ ([M+Na]$^+$) 395.0358, found 395.0358

Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate (3gi)



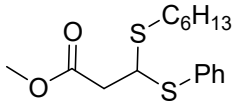
Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and naphthalene-2-thiol **2i** at 50 ^{o}C, 5 h, 95% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 1H), 7.78 (dq, J = 14.5, 6.9, 5.4 Hz, 4H), 7.58 – 7.47 (m, 6H), 7.32 (d, J = 4.7 Hz, 1H), 4.96 (dt, J = 43.3, 7.4 Hz, 1H), 3.69 (s, 3H), 2.88 (dd, J = 18.0, 7.3 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 133.6, 133.4, 132.8, 132.6, 130.3, 130.2, 129.0, 128.6, 128.3, 127.7, 126.6, 126.6, 53.4, 52.0, 41.1; HRMS (ESI) m/z calcd. for $C_{20}H_{18}NaO_2S_2^+$ ([M+Na]$^+$) 377.0640, found 377.0638

Methyl 3-(phenylthio)-3-(thiophen-2-ylthio)propanoate (3gj)



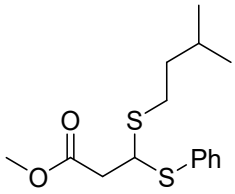
Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and thiophene-2-thiol **2j** at reflux, 8 h, 36% yield; Colorless oil; There were inseparable mixture, the yield was obtained by NMR yield; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.43 (m, 3H), 7.38 – 7.30 (m, 3H), 7.20 (d, J = 3.4 Hz, 1H), 7.04 (t, J = 4.6 Hz, 1H), 4.63 (t, J = 7.1 Hz, 1H), 3.71 (s, 3H), 2.82 (q, J = 8.7, 8.1 Hz, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.3, 136.8, 133.4, 133.3, 131.5, 129.1, 129.0, 128.3, 127.7, 55.3, 52.1, 40.6; HRMS (ESI) m/z calcd. for $C_{14}H_{14}NaO_2S_3^+$ ($[M+Na]^+$) 333.0048, found 333.0047

Methyl 3-(hexylthio)-3-(phenylthio)propanoate (3gl)



Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and hexane-1-thiol **2l** at 50 °C, 6 h, 39% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 – 7.46 (m, 2H), 7.39 – 7.28 (m, 3H), 4.50 (dd, J = 8.1, 6.8 Hz, 1H), 3.69 (s, 3H), 2.89 – 2.76 (m, 2H), 2.80 – 2.65 (m, 2H), 1.61 (dd, J = 10.6, 3.4 Hz, 2H), 1.42 – 1.26 (m, 6H), 0.89 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.6, 133.7, 133.0, 128.9, 128.2, 52.0, 50.3, 41.4, 31.7, 31.3, 29.1, 28.5, 22.5, 14.0; HRMS (ESI) m/z calcd. for $C_{16}H_{24}NaO_2S_2^+$ ($[M+Na]^+$) 335.1110, found 335.1114

Methyl 3-(isopentylthio)-3-(phenylthio)propanoate (3go)

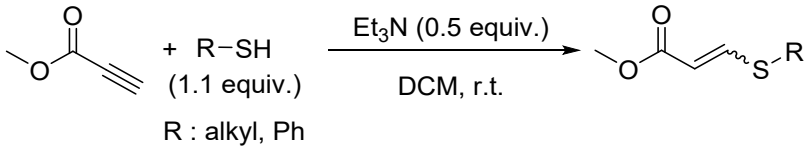


Prepared according to General procedure (A) using methyl 3-(phenylthio)acrylate **1g** and 3-methylbutane-1-thiol **2o** at 50 °C, 6 h, 52% yield; Colorless oil; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 – 7.48 (m, 2H), 7.36 – 7.30 (m, 3H), 4.51 (dd, J = 8.2, 6.7 Hz, 1H), 3.69 (s, 3H), 2.88 – 2.66 (m, 4H), 1.66 (dt, J = 13.3, 6.7 Hz, 1H), 1.49 (q, J = 7.5 Hz, 2H), 0.91 (dd, J = 6.6, 3.5

Hz, 6H) **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.5, 133.7, 133.0, 129.0, 128.2, 52.0, 50.3, 41.4, 38.0, 29.7, 27.4, 22.3, 22.2; HRMS (ESI) m/z calcd. for $C_{15}H_{22}NaO_2S_2^+$ ([M+Na]$^+$) 321.0953, found 321.0958

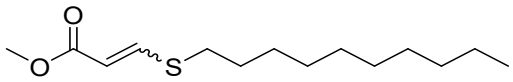
4. Synthesis of vinyl sulfides

4.1. General procedure of 1a, 1b, 1c, 1d, 1g



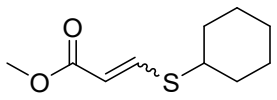
General procedure (B) : In a dry, clean round bottom flask, add corresponding thiol (1.1 equiv.) to the solution of methyl propiolate (1 equiv.) in DCM, followed by the addition of triethylamine (0.5 equiv.). Stir the reaction contents at room temperature until the reaction completion. After the reaction completion, most of the solvent had been removed under reduced pressure; the residue was used for the purification via column chromatography. The synthesized mixture of E and Z vinyl sulfides.

Methyl 3-(decylthio)acrylate (1a)



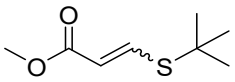
Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and decane-1-thiol (1.1 equiv.), E:Z = 10:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 15.1 Hz, 1H), 7.10 (d, *J* = 10.1 Hz, 0.1H), 5.85 (d, *J* = 10.3 Hz, 1H), 5.75 (d, *J* = 15.1 Hz, 0.1H), 3.74 (s, 0.3H), 3.73 (s, 3H), 2.79 (t, *J* = 7.4 Hz, 2H), 1.74 – 1.59 (m, 3H), 1.51 – 1.22 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H); The compound was identified by spectral comparison with literature data.[1]

Methyl 3-(cyclohexylthio)acrylate (1b)



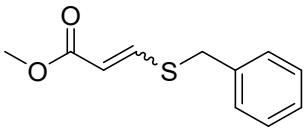
Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and cyclohexanethiol (1.1 equiv.), E:Z = 10:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 15.3 Hz, 1H), 7.17 (d, *J* = 10.2 Hz, 0.1H), 5.80 (d, *J* = 15.3 Hz, 1.1H), 3.72 (s, 0.3H), 3.70 (s, 3H), 3.05 (ddd, *J* = 14.2, 8.7, 4.0 Hz, 1.1H), 2.07 – 1.96 (m, 2H), 1.83 – 1.72 (m, 2H), 1.67 – 1.58 (m, 1H), 1.51 – 1.20 (m, 5H); The compound was identified by spectral comparison with literature data.[2]

Methyl 3-(tert-butylthio)acrylate (1c)



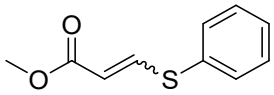
Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and 2-methylpropane-2-thiol (1.1 equiv.), E:Z = 3:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 15.5 Hz, 1H), 7.29 (d, *J* = 11.0 Hz, 0.3H), 5.93 (d, *J* = 15.5 Hz, 1H), 5.89 (d, *J* = 10.5 Hz, 0.3H), 3.74 (s, 1H), 3.73 (s, 3H), 1.43 (s, 9H), 1.41 (s, 3H). The compound was identified by spectral comparison with literature data.[3]

Methyl 3-(benzylthio)acrylate (1d)



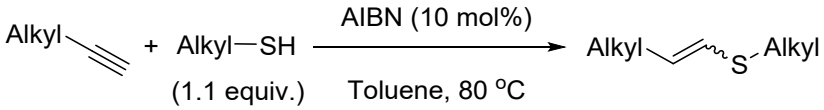
Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and phenylmethanethiol (1.1 equiv.), E:Z = 5:1; White solid; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 15.2 Hz, 1H), 7.36 – 7.27 (m, 6H), 7.06 (d, *J* = 10.2 Hz, 0.2H), 5.81 (d, *J* = 15.2 Hz, 1.2H), 4.02 (s, 2H), 3.96 (s, 0.4H), 3.72 (s, 0.6H), 3.71 (s, 3H); The compound was identified by spectral comparison with literature data.[4]

Methyl 3-(phenylthio)acrylate (1g)



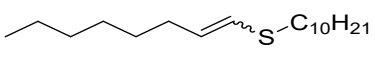
Prepared according to General procedure (B) using methyl propiolate (1 equiv.) and benzenethiol (1.1 equiv.), E:Z = 3:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 15.1 Hz, 1H), 7.51 – 7.45 (m, 3H), 7.43 – 7.34 (m, 3.6H), 7.29 (d, *J* = 10.1 Hz, 0.3H), 5.93 (d, *J* = 10.1 Hz, 0.3H), 5.66 (d, *J* = 15.1 Hz, 1H), 3.79 (s, 1H), 3.70 (s, 3H); The compound was identified by spectral comparison with literature data.[5]

4.2. General procedure and characterization of 1e and 1f



General procedure (C) : In a dry, clean reaction tube, AIBN (10 mol%) was taken and degassed with N_2 three times, then added the solution of alkyne in toluene followed by the addition of corresponding thiol (1.1 equiv.). The reaction contents are heated to 80 °C until the reaction completion. After the reaction completion, the reaction was diluted with DCM and washed with water followed by brine solution. The organic layer was dried over anhydrous Na_2SO_4. The solvent had been removed under reduced pressure. The crude product was purified via column chromatography.

Decyl(oct-1-en-1-yl)sulfane (1e)



Prepared according to General procedure (C) using oct-1-yne (1 equiv.) and decane-1-thiol (1.1 equiv.), 85% yield, E:Z = 3:1; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.91 (d, J = 5.6 Hz, 0.3H), 5.89 (d, J = 9.4 Hz, 1H), 5.66 – 5.51 (m, 1.3H), 2.63 (q, J = 7.3 Hz, 2.6H), 2.09 (dq, J = 14.4, 6.9 Hz, 2.6H), 1.65 – 1.58 (m, 2.6H), 1.42 – 1.23 (m, 29H), 0.88 (t, J = 6.3 Hz, 8H);**^{13}C NMR** (100 MHz, $CDCl_3$)

δ 130.8, 129.5, 124.9, 122.6, 33.9, 33.2, 32.7, 31.9, 31.7, 31.7, 30.3, 29.5, 29.5, 29.5, 29.3, 29.2, 29.1, 29.1, 29.0, 28.9, 28.8, 28.7, 28.6, 28.5, 28.4, 22.7, 22.6, 22.6, 14.1, 14.1; **HRMS (DART)** m/z calcd. for $C_{18}H_{37}S^+$ ($[M+H]^+$) 285.2610, found 285.2610

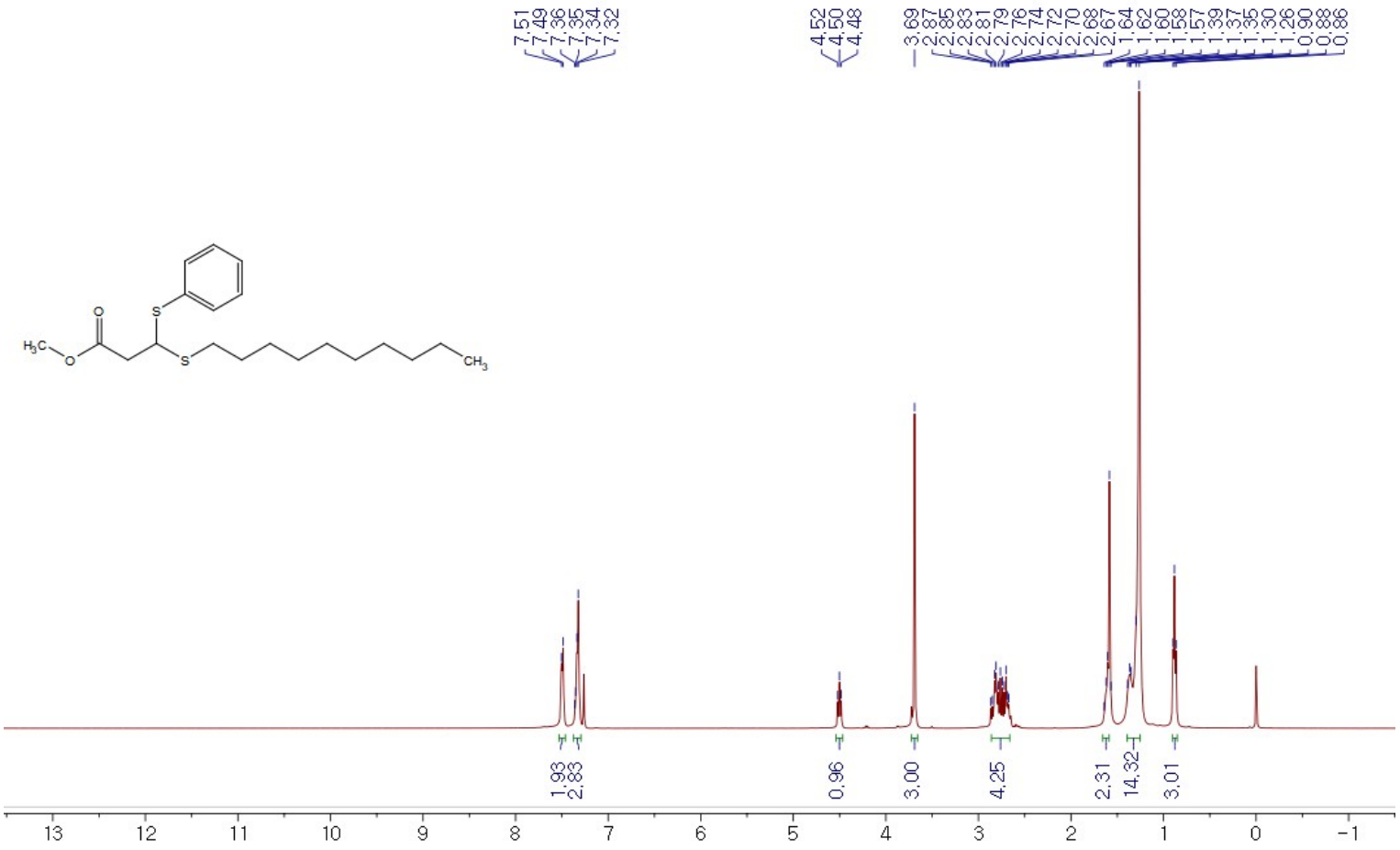
Decyl(3-phenylprop-1-en-1-yl)sulfane (1f)

Prepared according to General procedure (C) using prop-2-yn-1-ylbenzene (1 equiv.) and decane-1-thiol (1.1 equiv.), 73% yield, E:Z = 1:2.2; Colorless oil; The NMR spectrum was obtained as a mixture of E/Z isomers; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 – 7.14 (m, 7.26H), 6.05 (d, J = 9.3 Hz, 1H), 6.01 (d, J = 15.1 Hz, 0.45H), 5.73 (q, J = 7.3 Hz, 1.45H), 3.48 (d, J = 7.1 Hz, 2H), 3.42 (d, J = 6.9 Hz, 0.9H), 2.70 (t, J = 7.3 Hz, 2H), 2.65 (t, J = 7.4 Hz, 0.9H), 1.64 (dq, J = 13.6, 6.8 Hz, 2.9H), 1.47 – 1.21 (m, 20.6H), 0.88 (t, J = 6.4 Hz, 4.36H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 140.4, 140.0, 128.5, 128.4, 128.4, 127.7, 127.7, 126.3, 126.1, 126.0, 125.4, 124.8, 39.8, 39.4, 35.4, 34.0, 32.5, 31.9, 31.9, 30.3, 29.5, 29.5, 29.5, 29.5, 29.4, 29.3, 29.2, 29.2, 28.8, 28.6, 22.7, 22.4, 14.2, 14.1; **HRMS (DART)** m/z calcd. for $C_{19}H_{31}S^+$ ($[M+H]^+$) 291.2141, found 291.2147

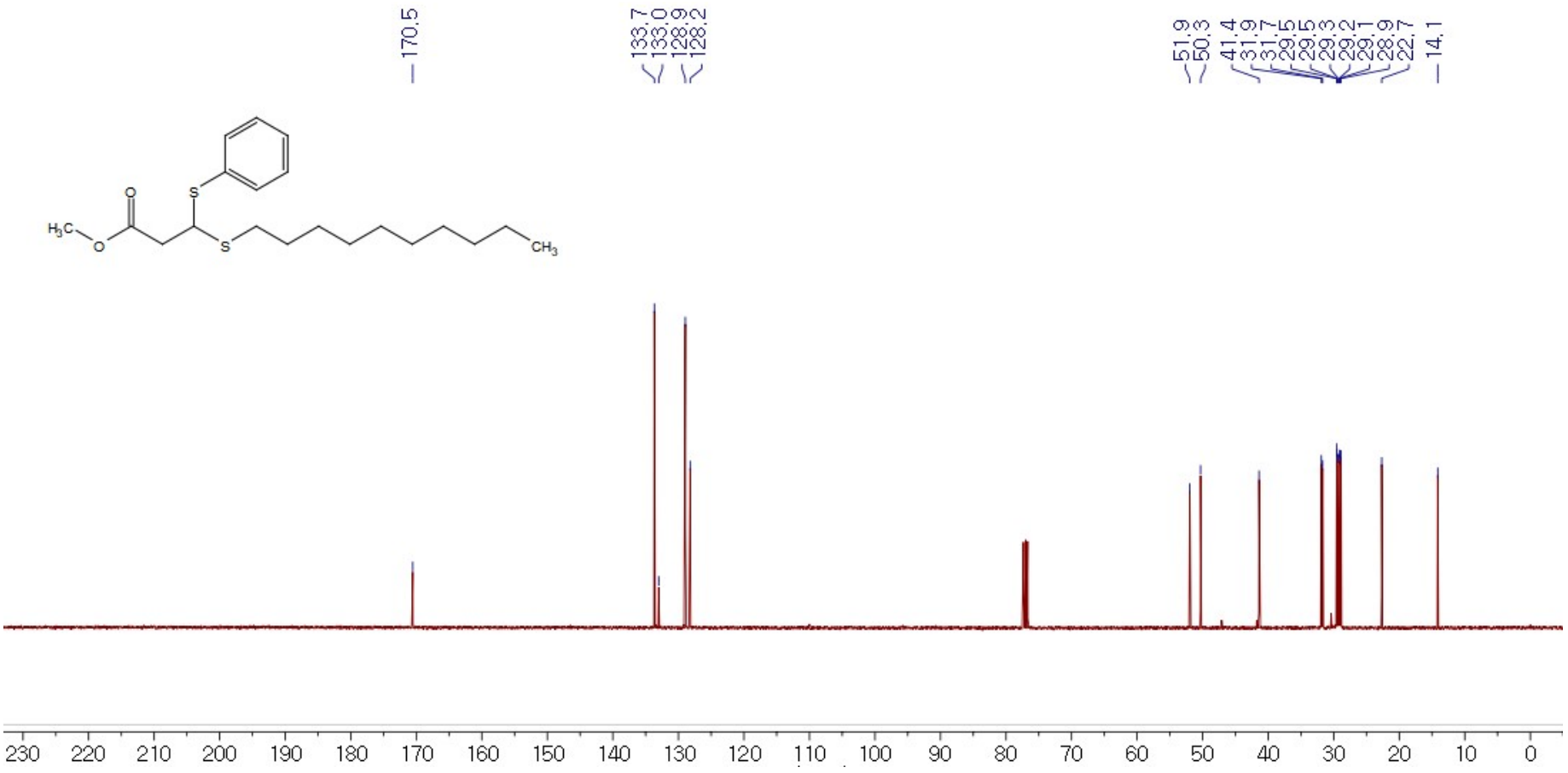
5. References

1. T. Craig, D. James, P. Gary, K. Francis, P. Nicole, EP1007509, 2004, B1
2. S. P. Singh, J. S. O'Donnell and A. L. Schwan, *Org. Biomol. Chem.*, 2010, **8**, 1712-1717.
3. Y. Li, C. Mück-Lichtenfeld and A. Studer, *Angew. Chem. Int. Ed.*, 2016, **55**, 14435-14438.
4. J. S. O'Donnell, S. P. Singh, T. A. Metcalf and A. L. Schwan, *Eur. J. Org. Chem.*, 2009, **2009**, 547-553.
5. D. C. Ladie Kimberly, D. C. Ladie Kimberly, J. Xingyue, P. Zhixiang, W. Binghe, WO2019/32879, 2019, A1

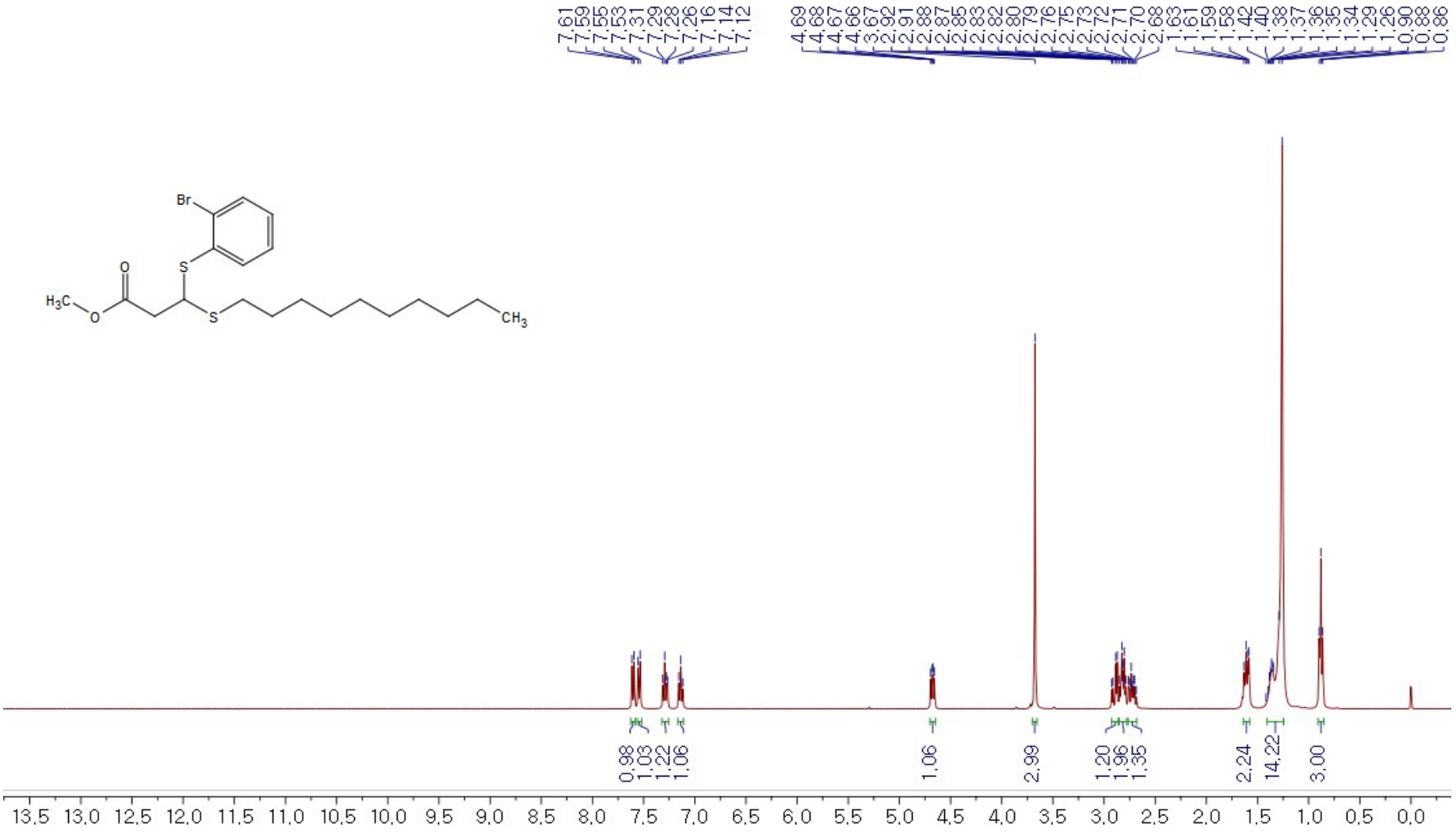
6. NMR spectra



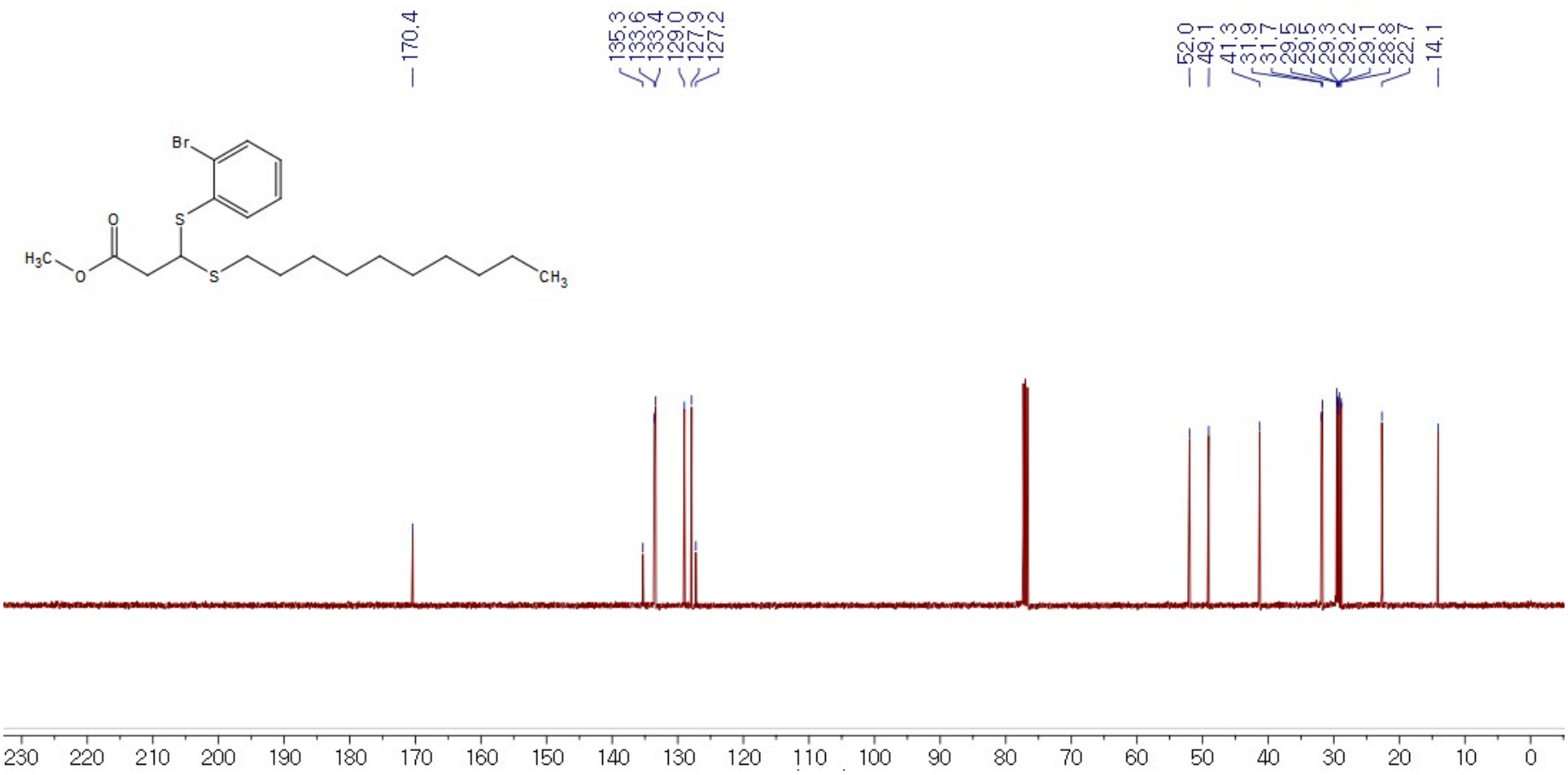
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(phenylthio)propanoate **(3aa)**



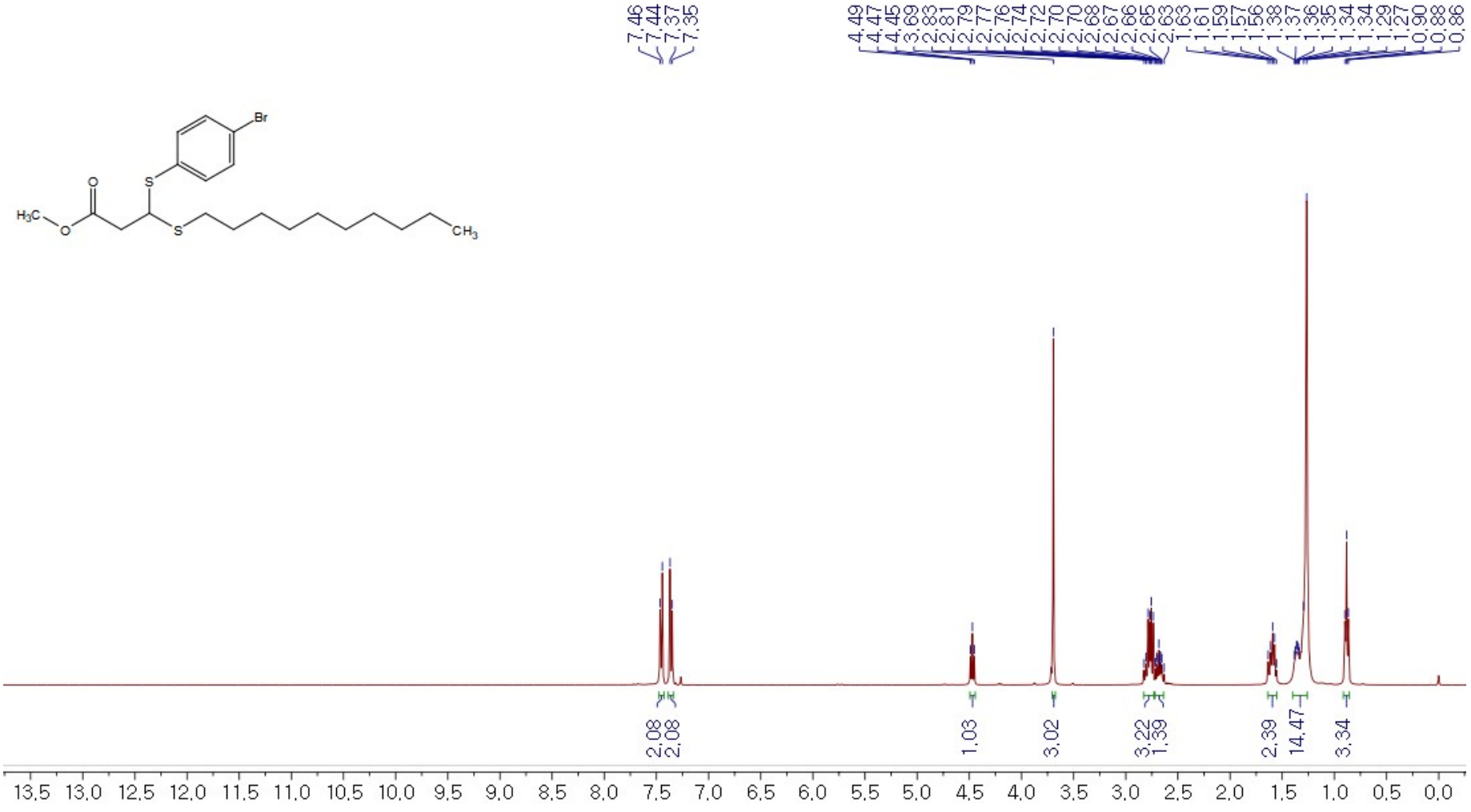
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(phenylthio)propanoate **(3aa)**



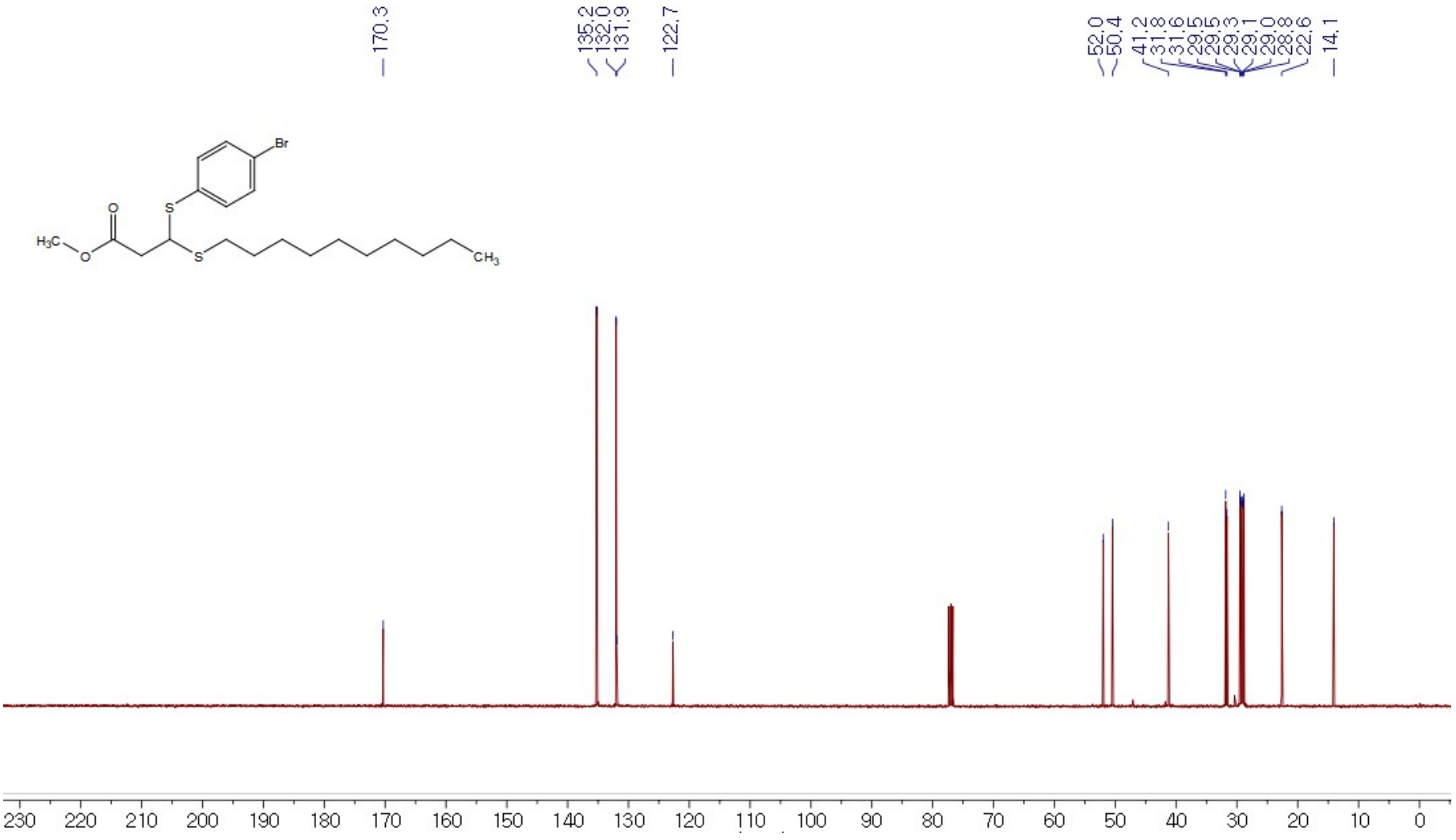
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-((2-bromophenyl)thio)-3-(decylthio)propanoate **(3ab)**



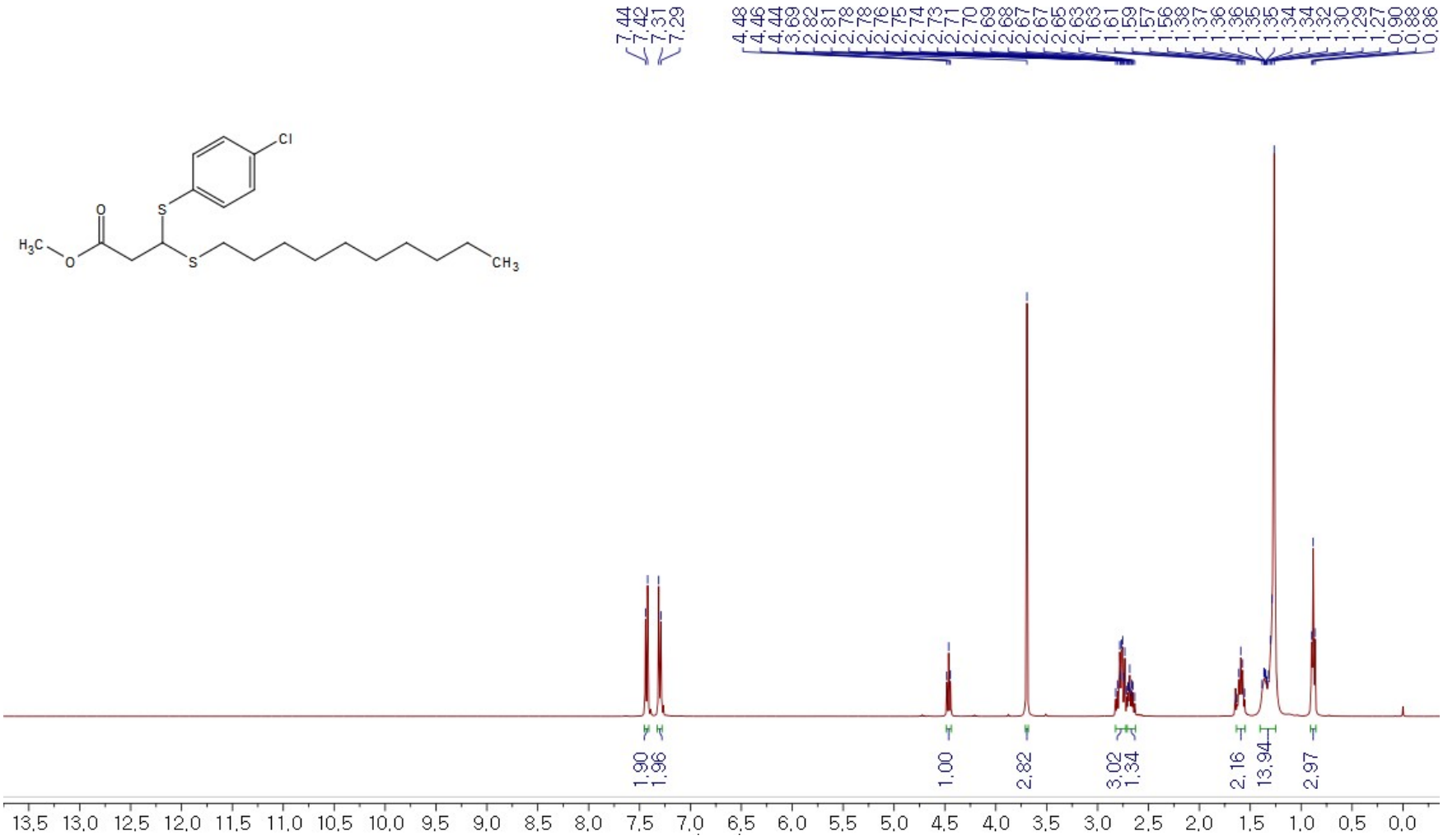
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-((2-bromophenyl)thio)-3-(decylthio)propanoate **(3ab)**



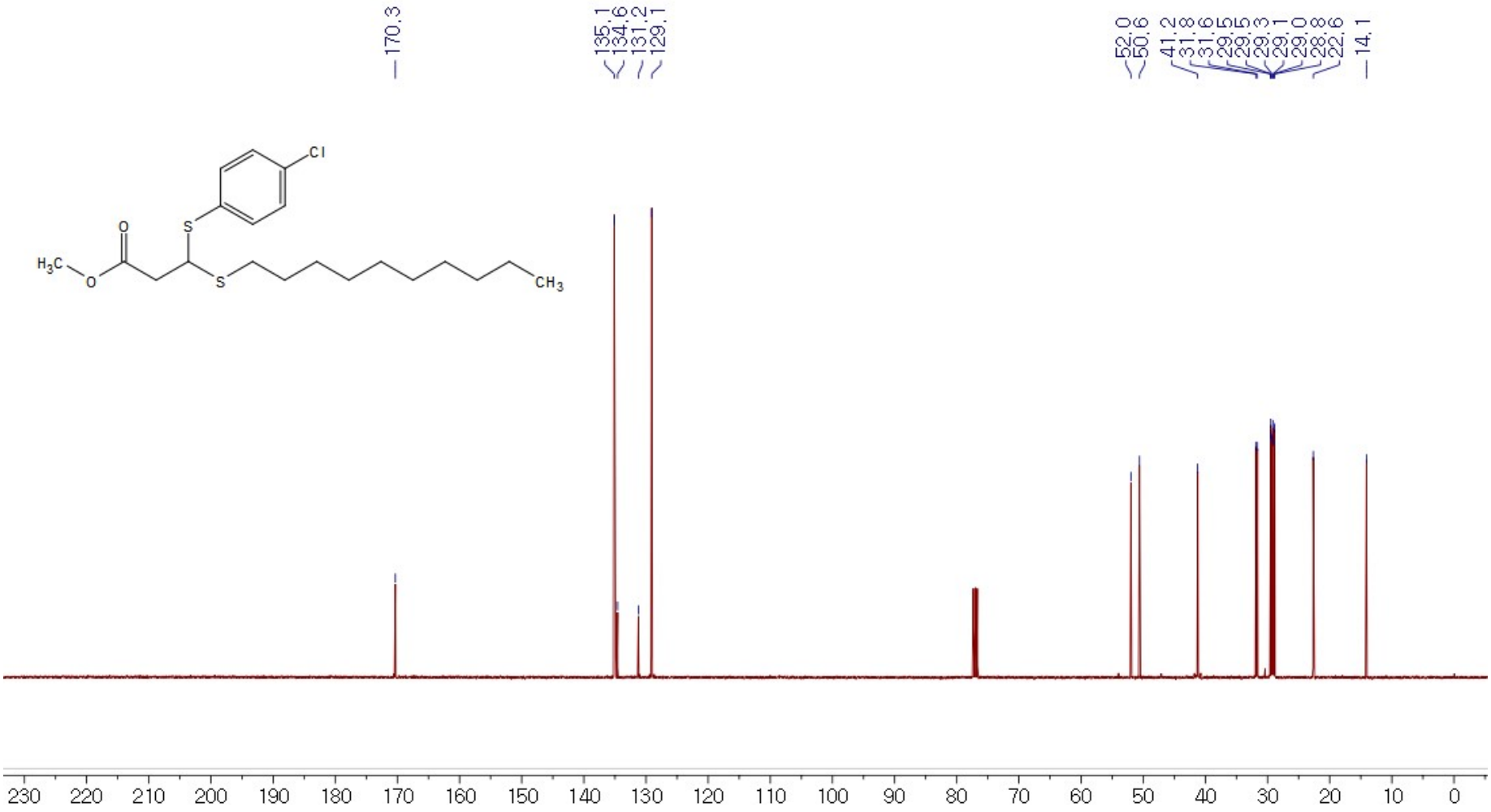
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(decylthio)propanoate **(3ac)**



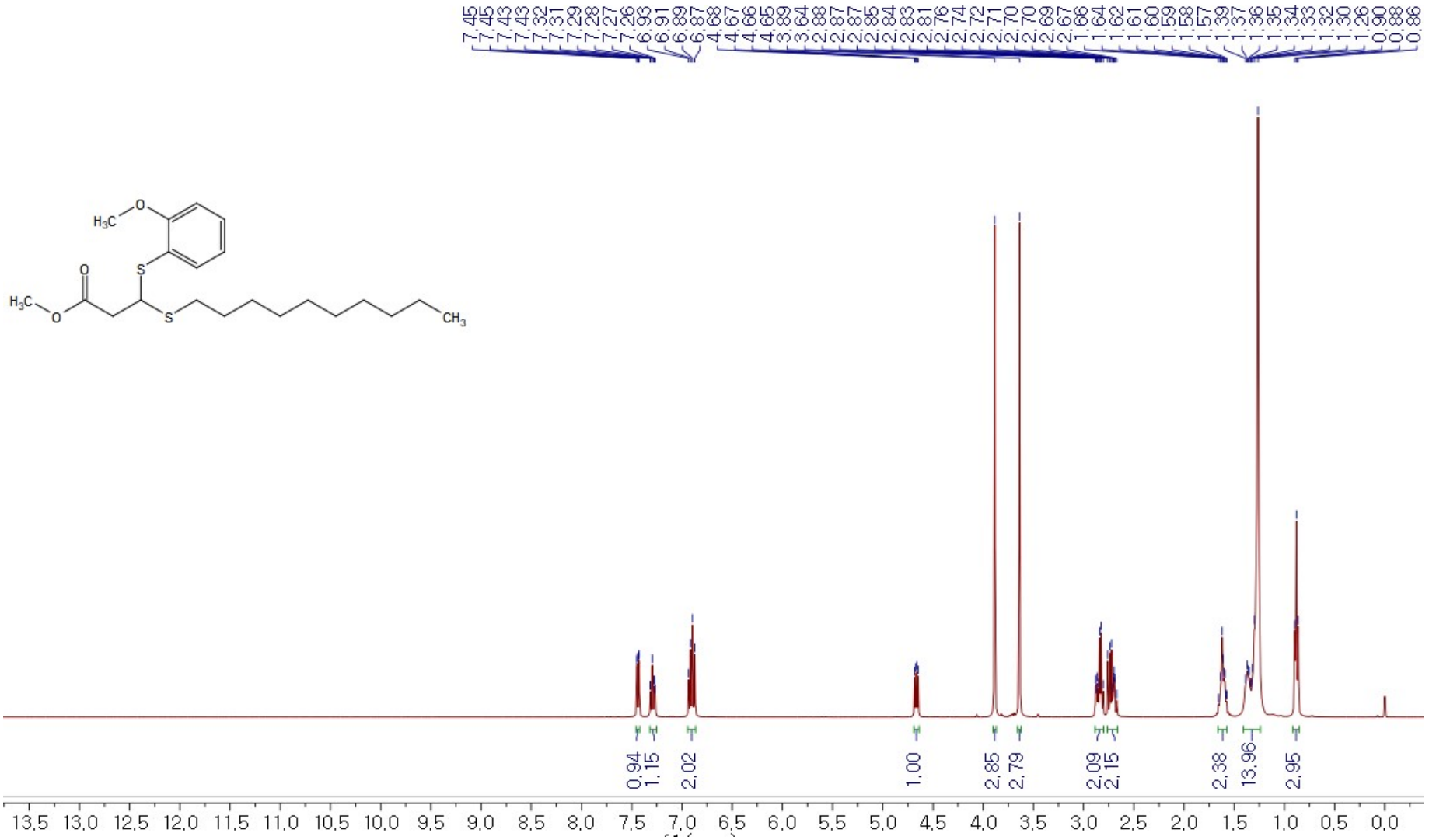
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(decylthio)propanoate **(3ac)**



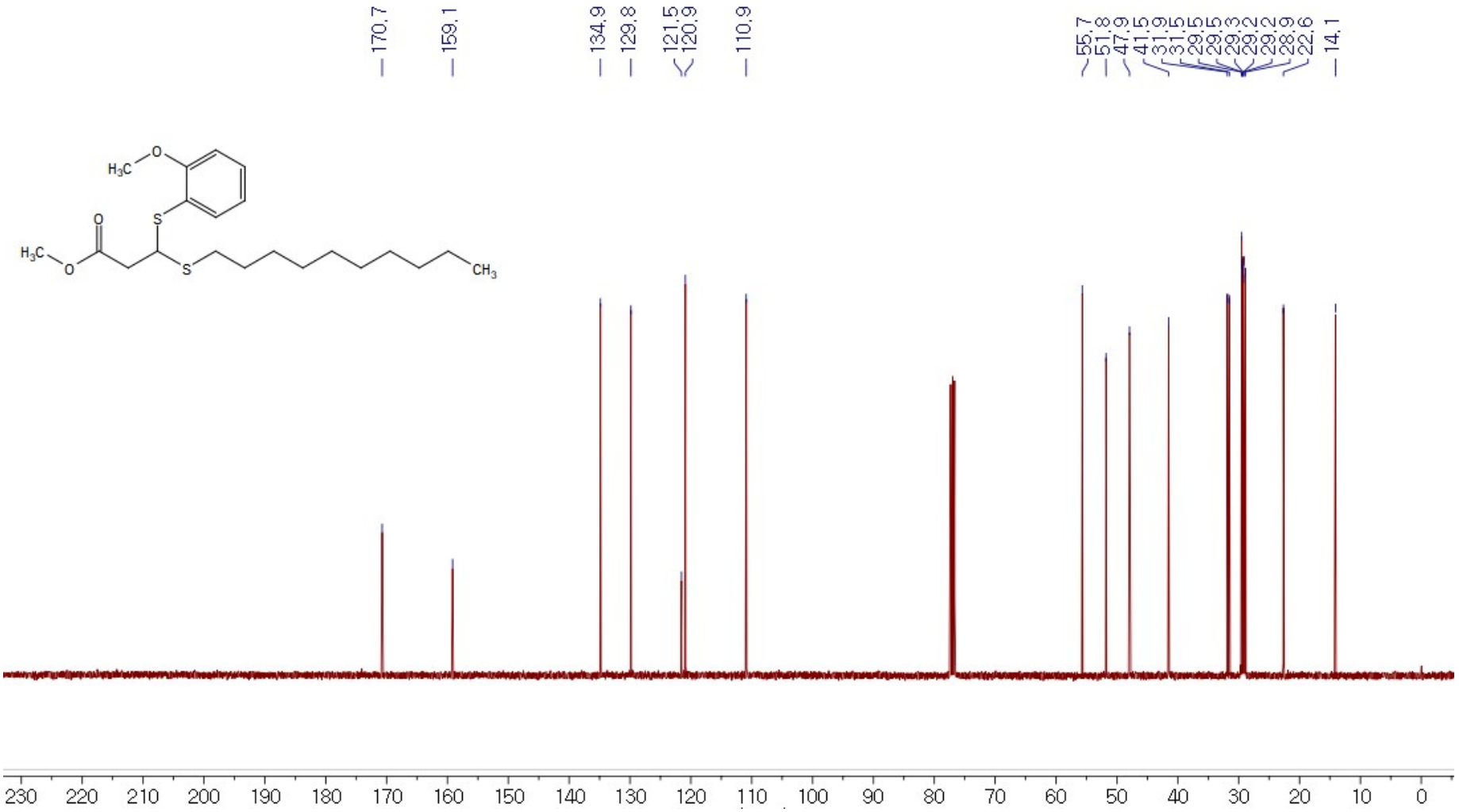
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(decylthio)propanoate **(3ad)**



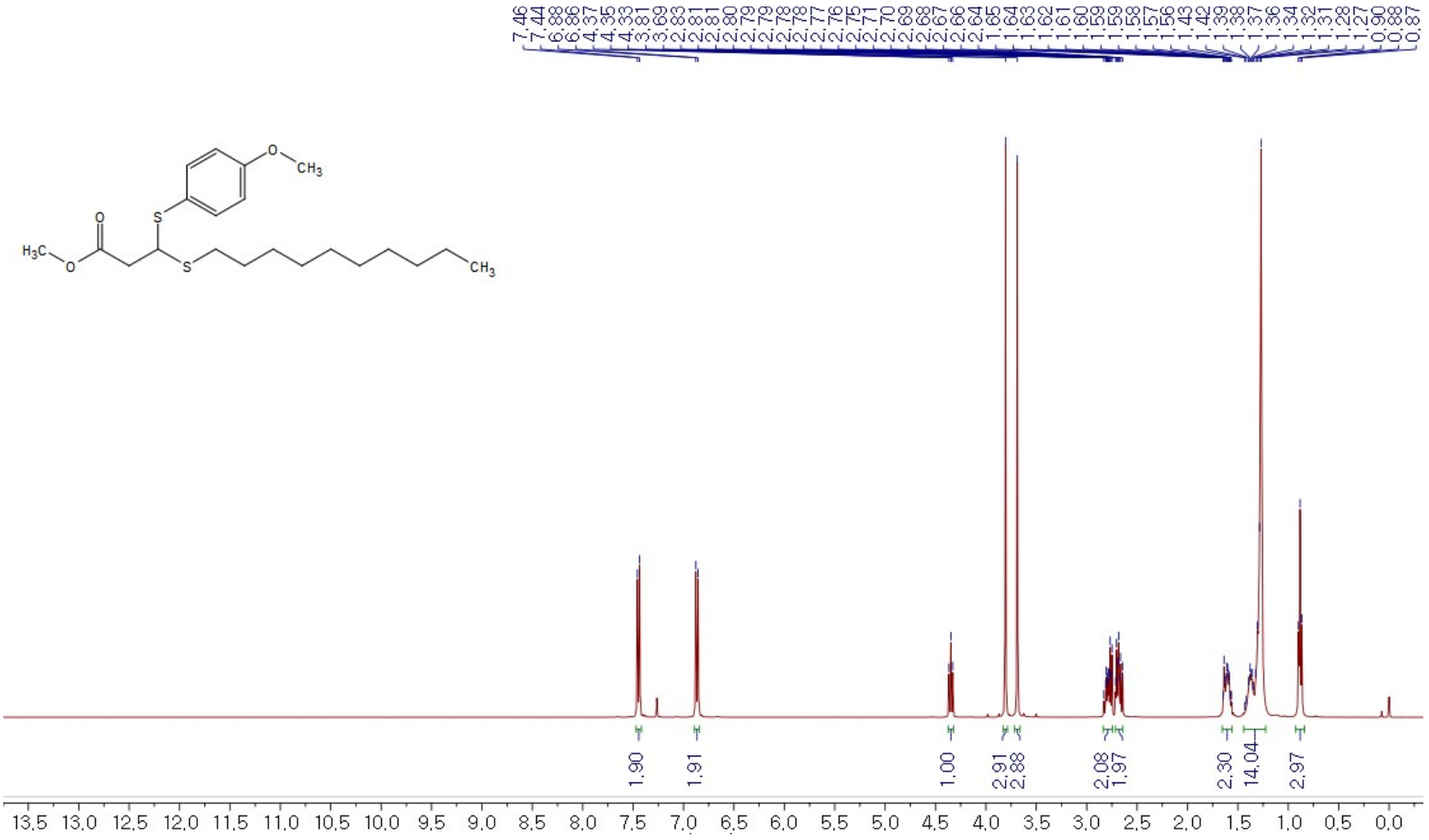
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(decylthio)propanoate **(3ad)**



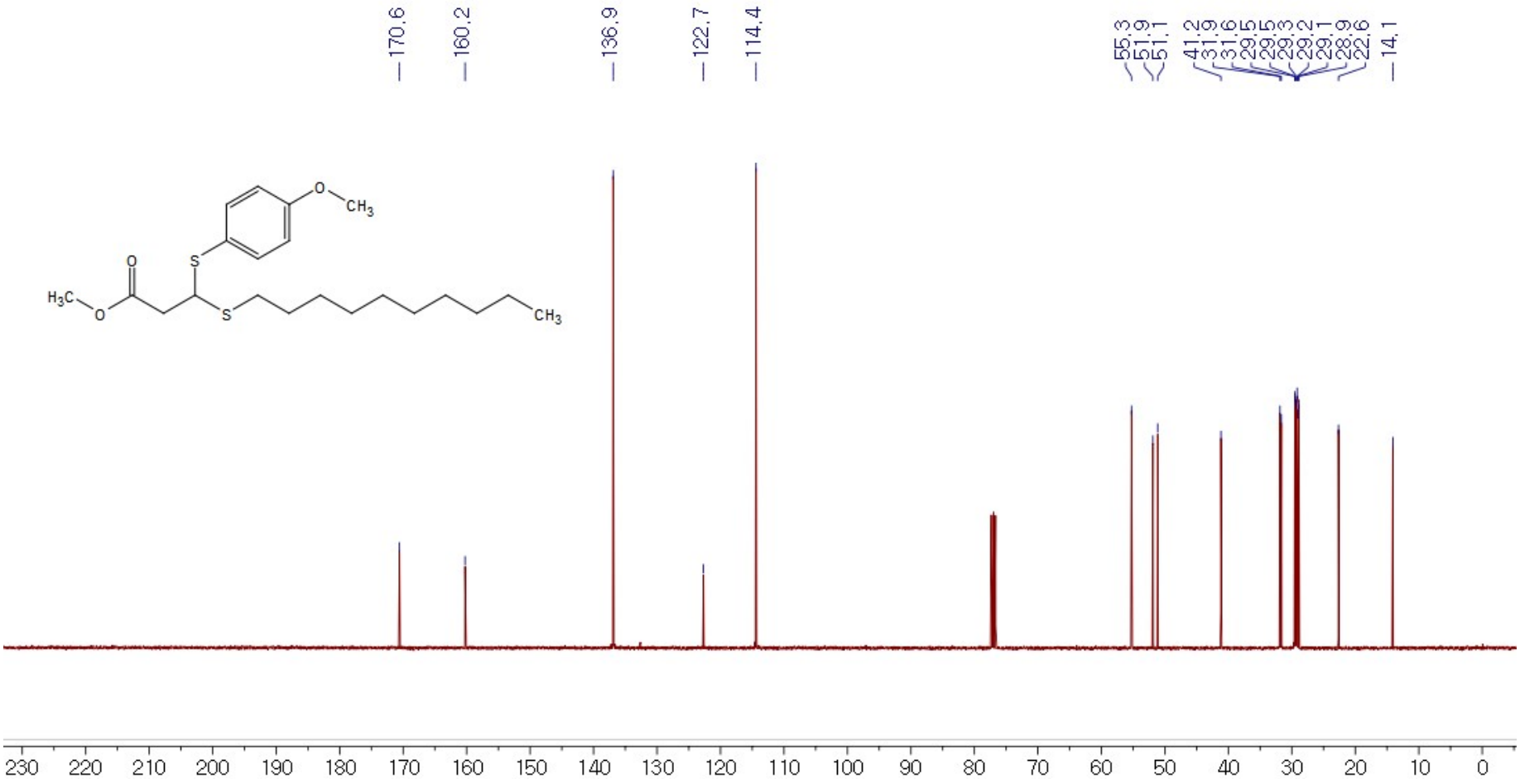
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate **(3ae)**



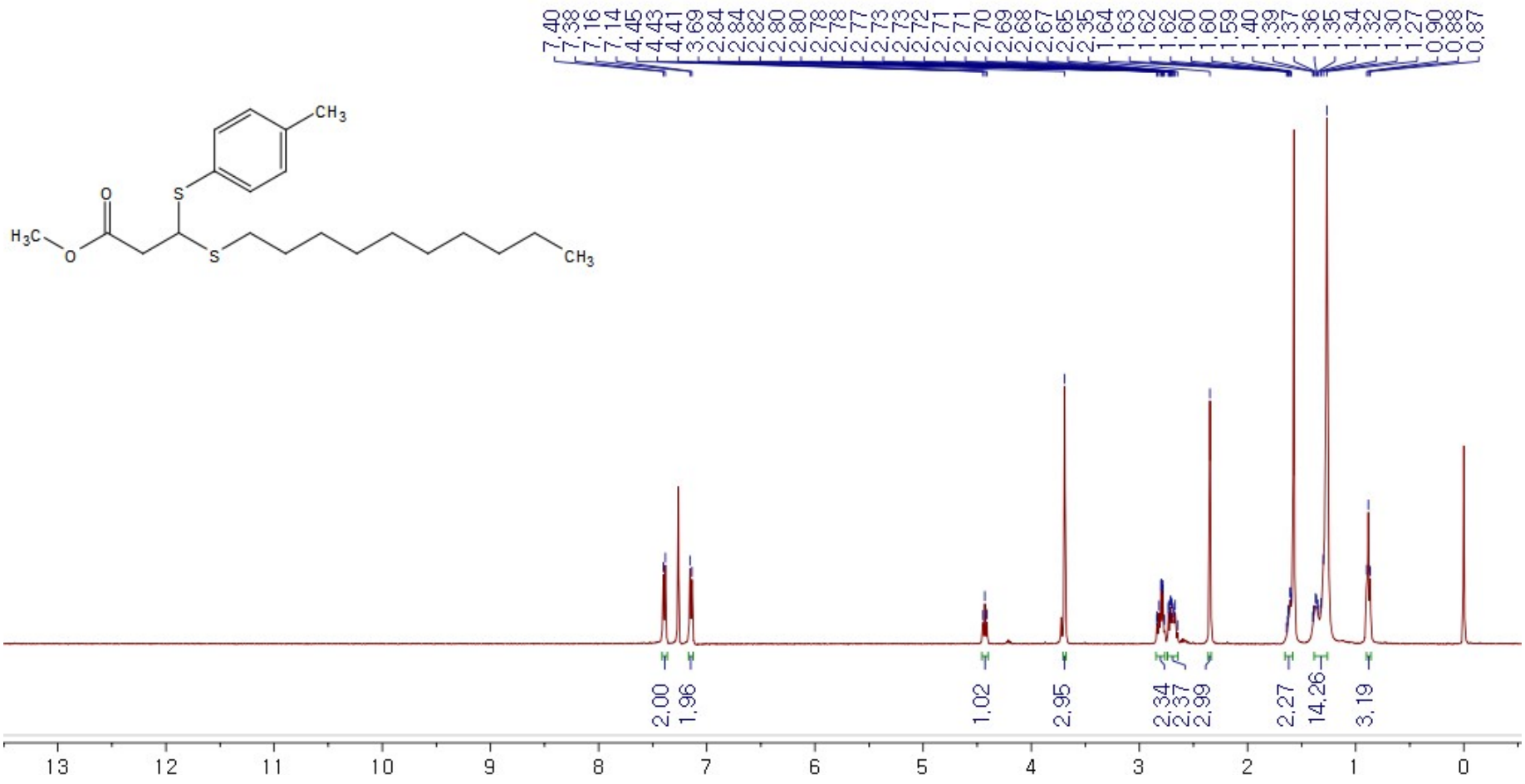
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-((2-methoxyphenyl)thio)propanoate **(3ae)**



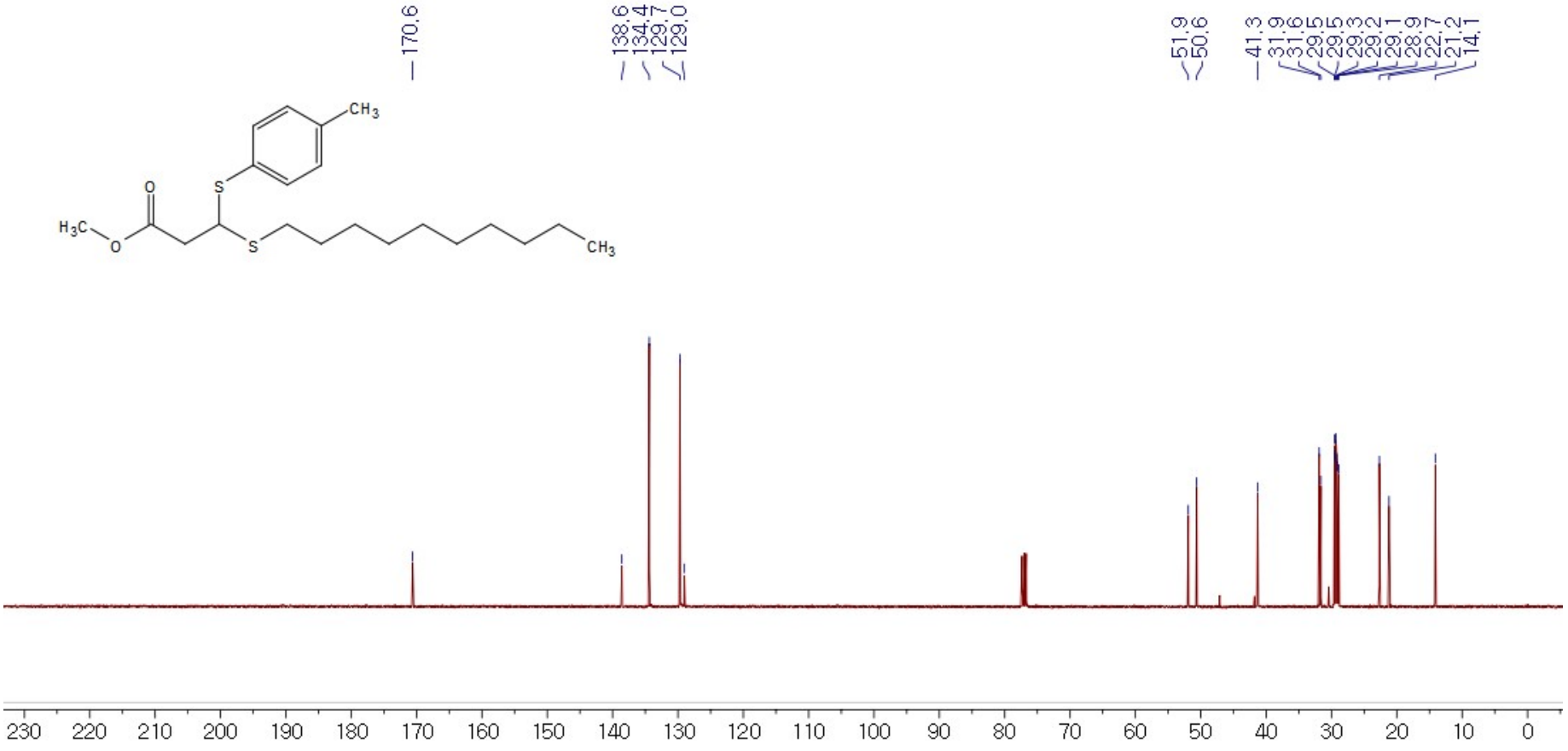
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate **(3af)**



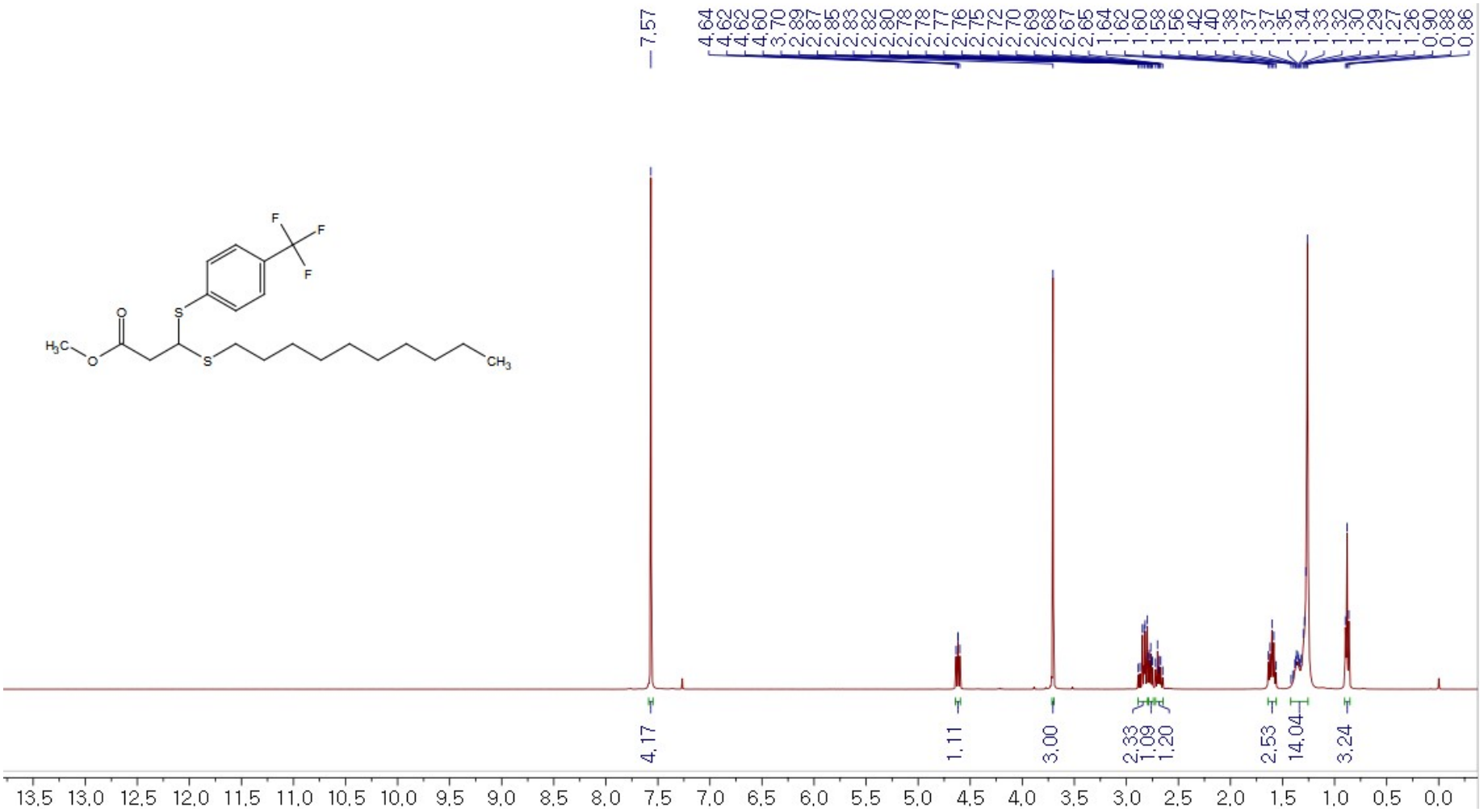
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-((4-methoxyphenyl)thio)propanoate **(3af)**



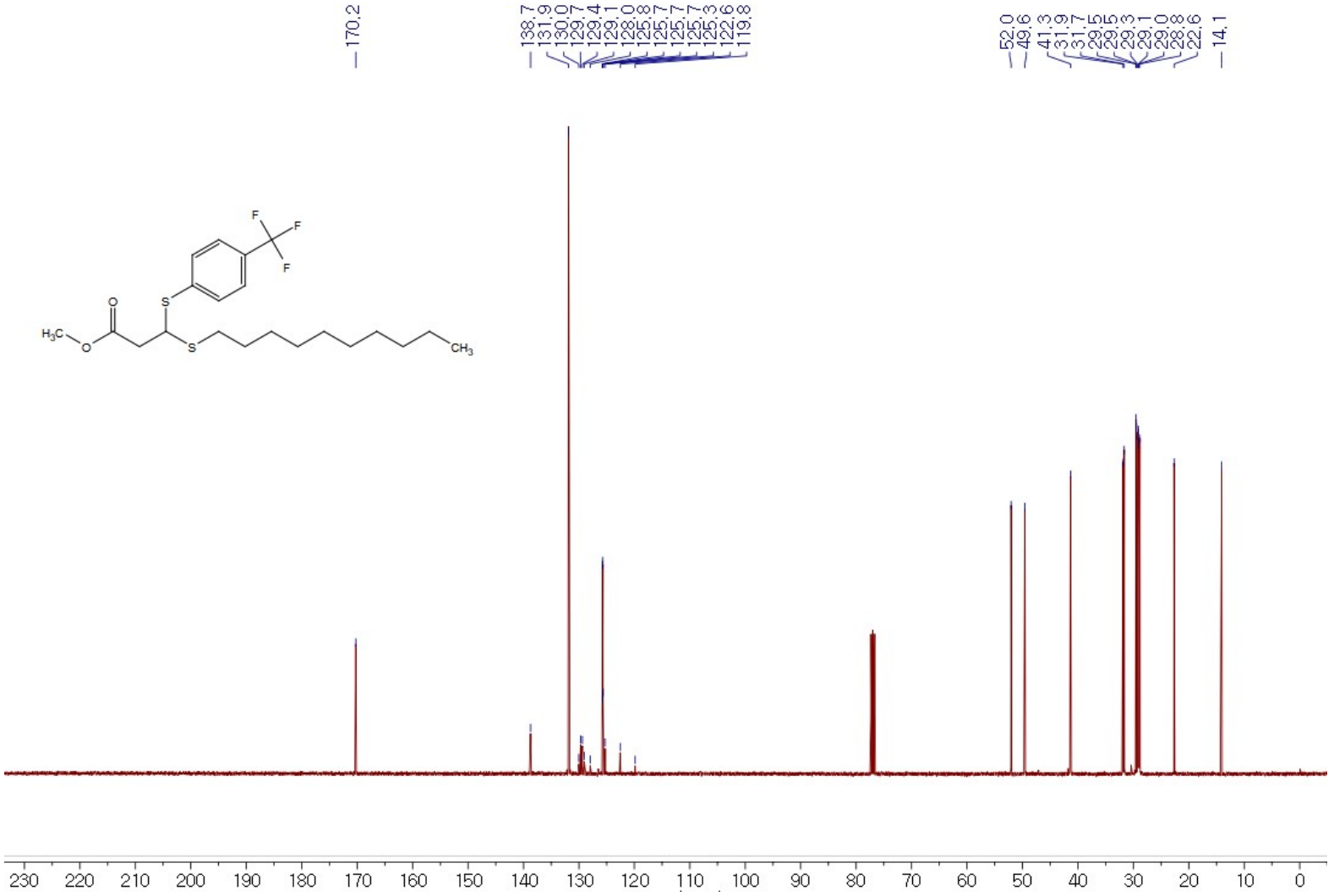
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(*p*-tolylthio)propanoate **(3ag)**



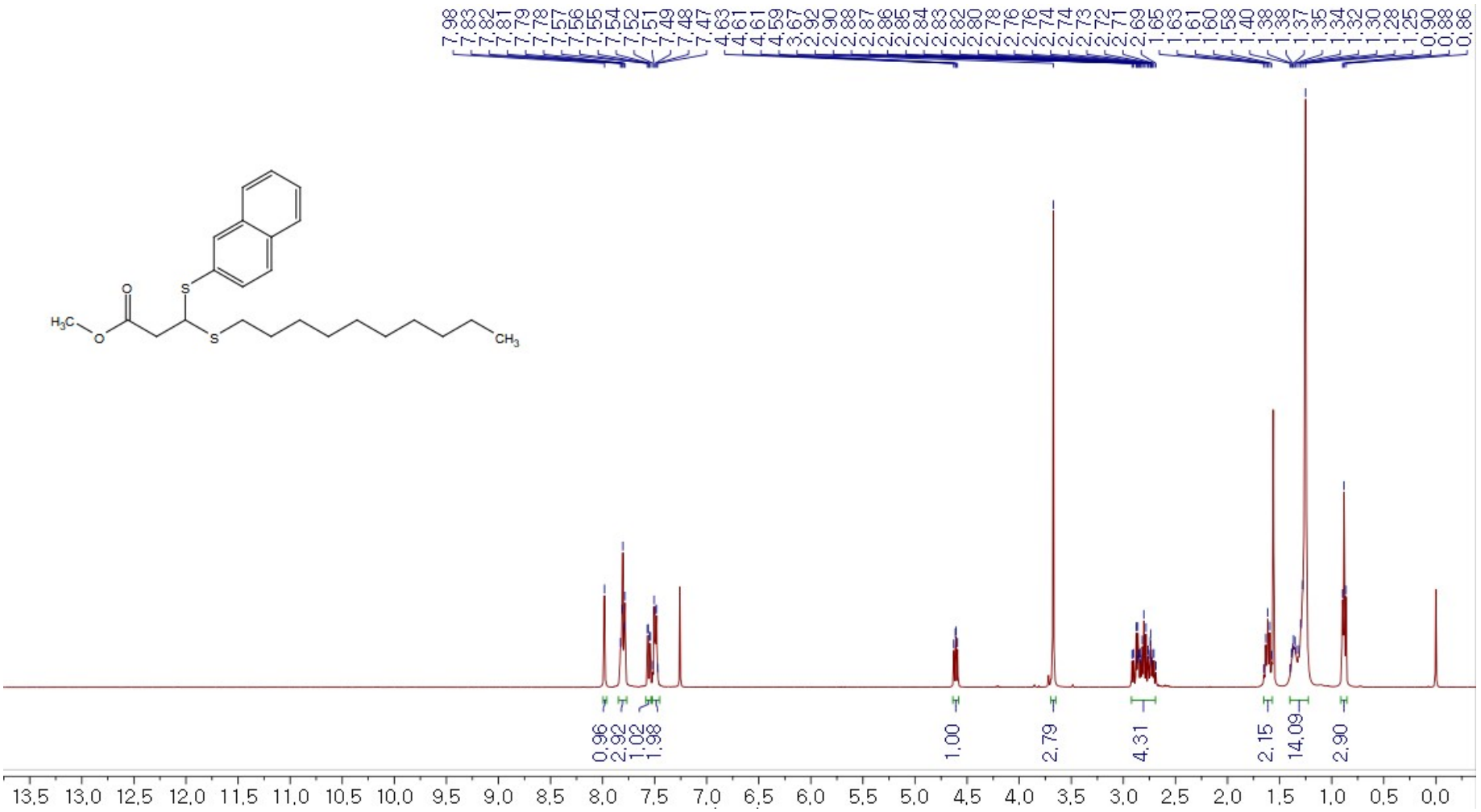
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(*p*-tolylthio)propanoate **(3ag)**



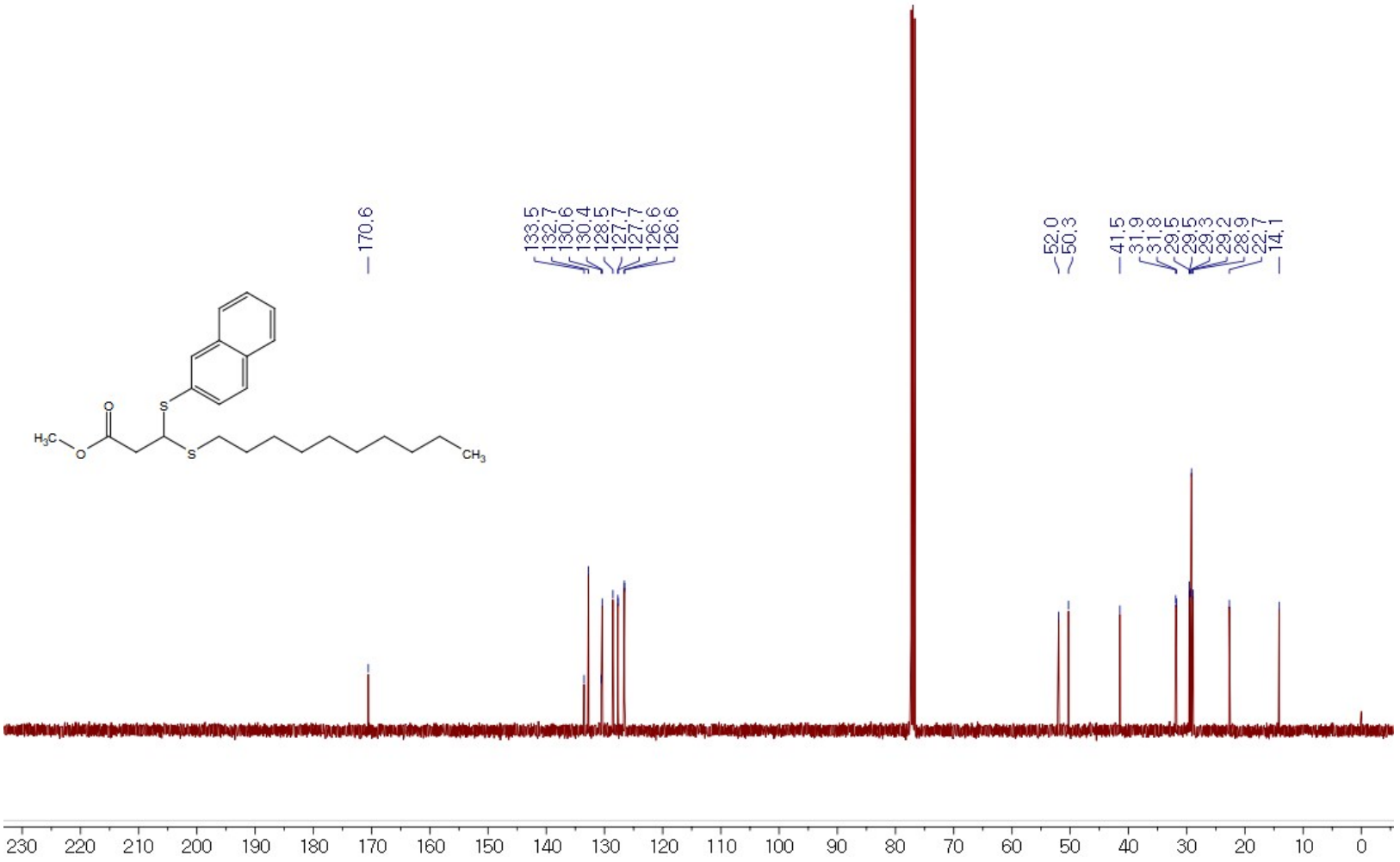
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate **(3ah)**



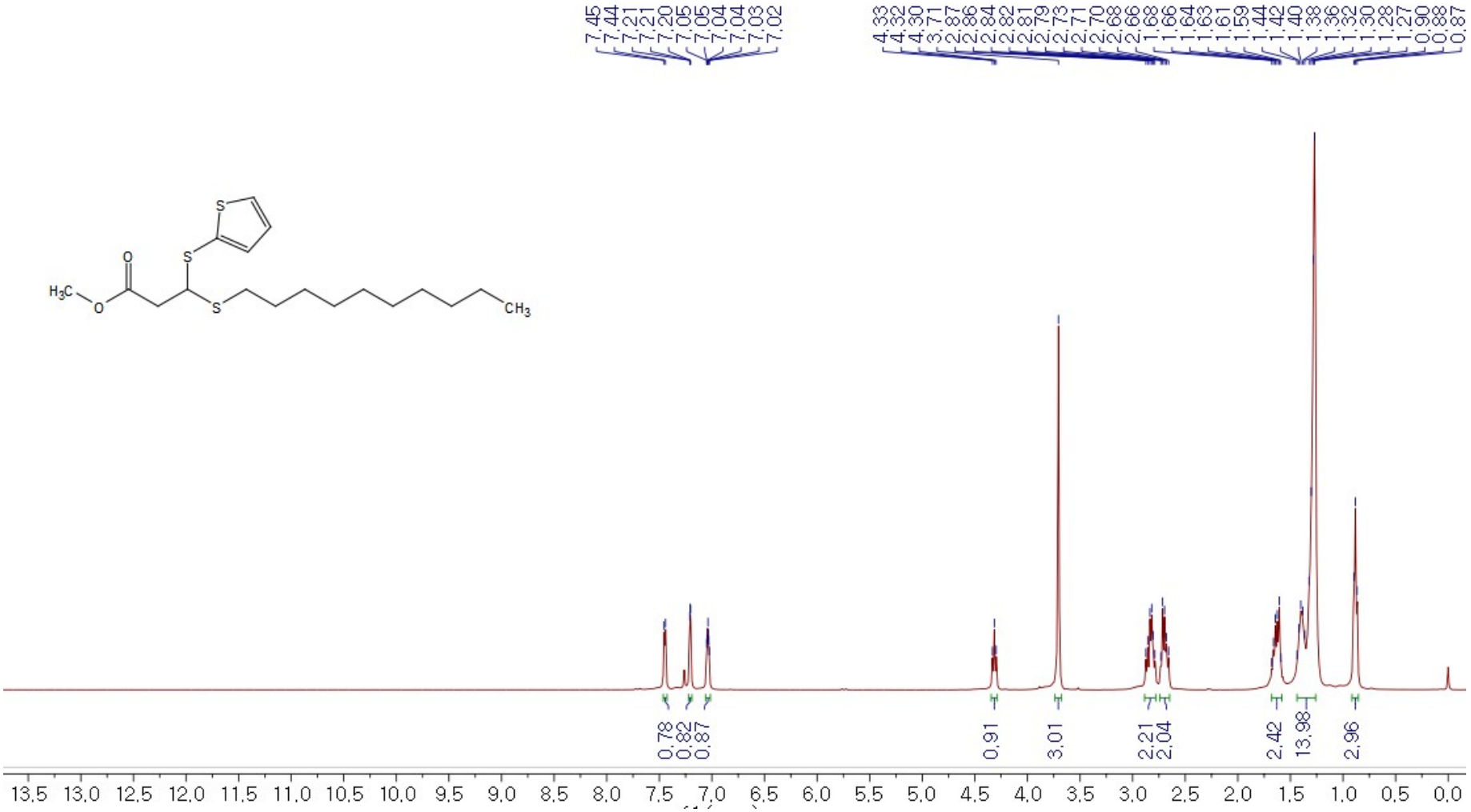
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate **(3ah)**



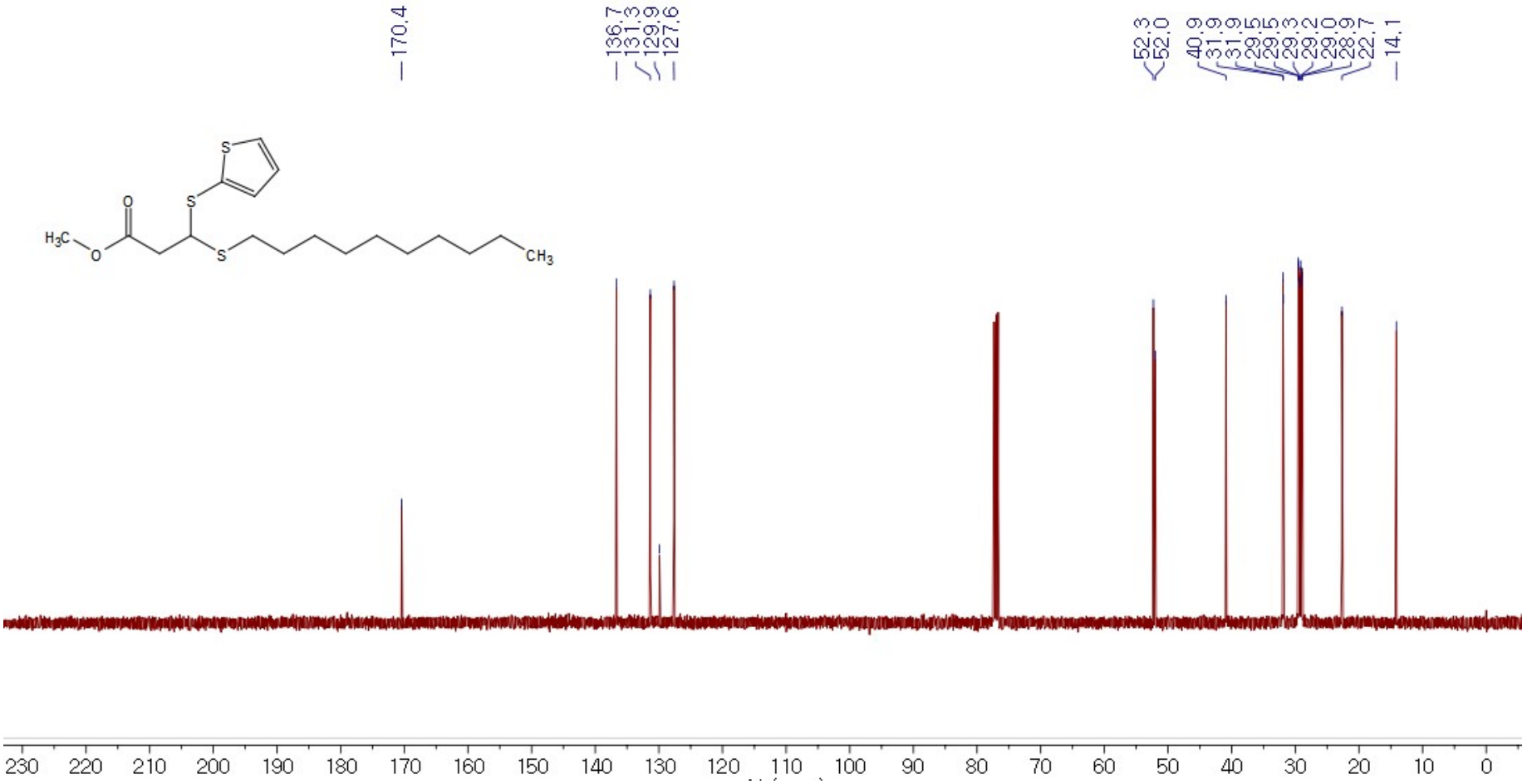
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(naphthalen-2-ylthio)propanoate **(3ai)**



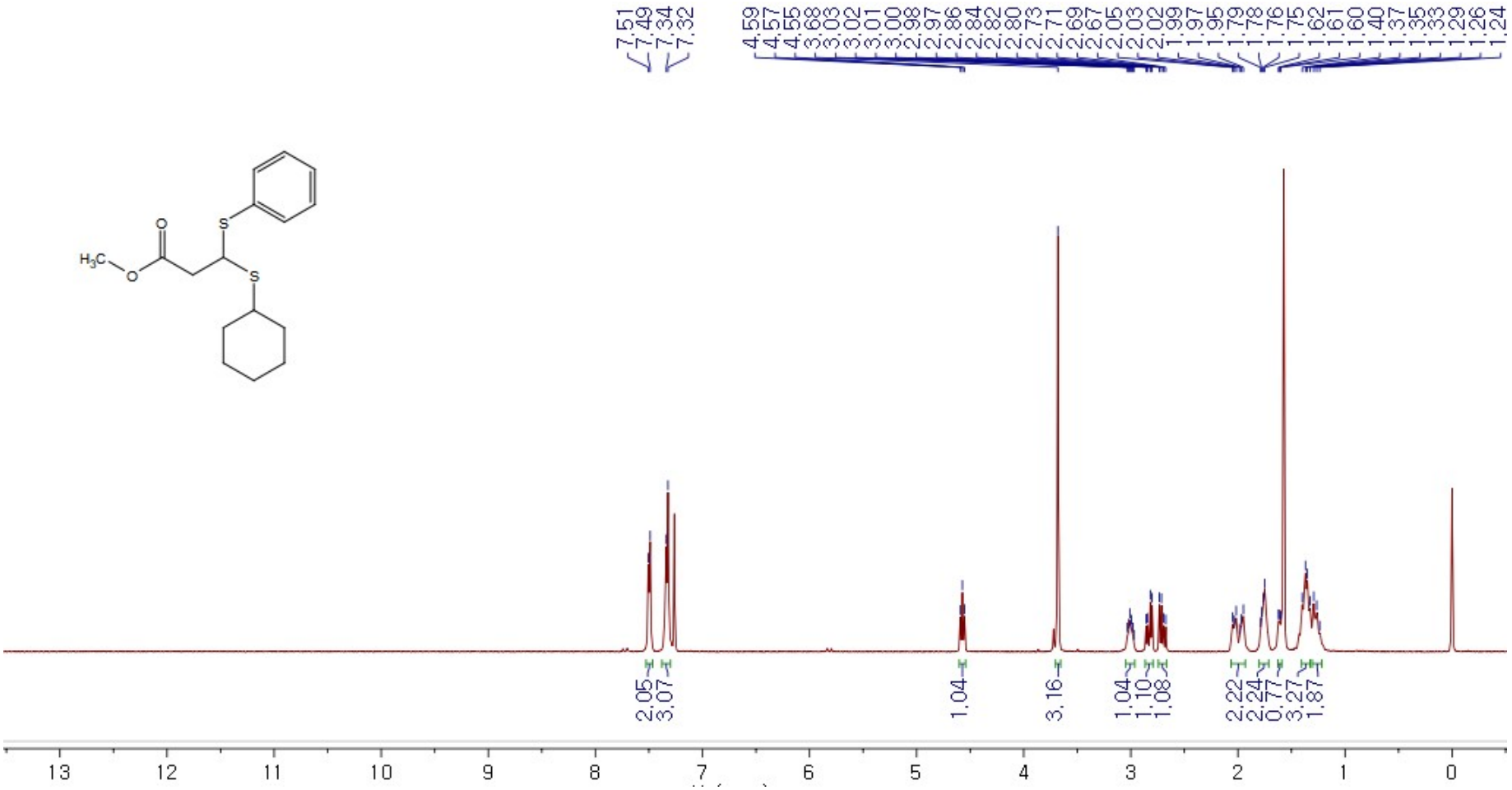
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(naphthalen-2-ylthio)propanoate **(3ai)**



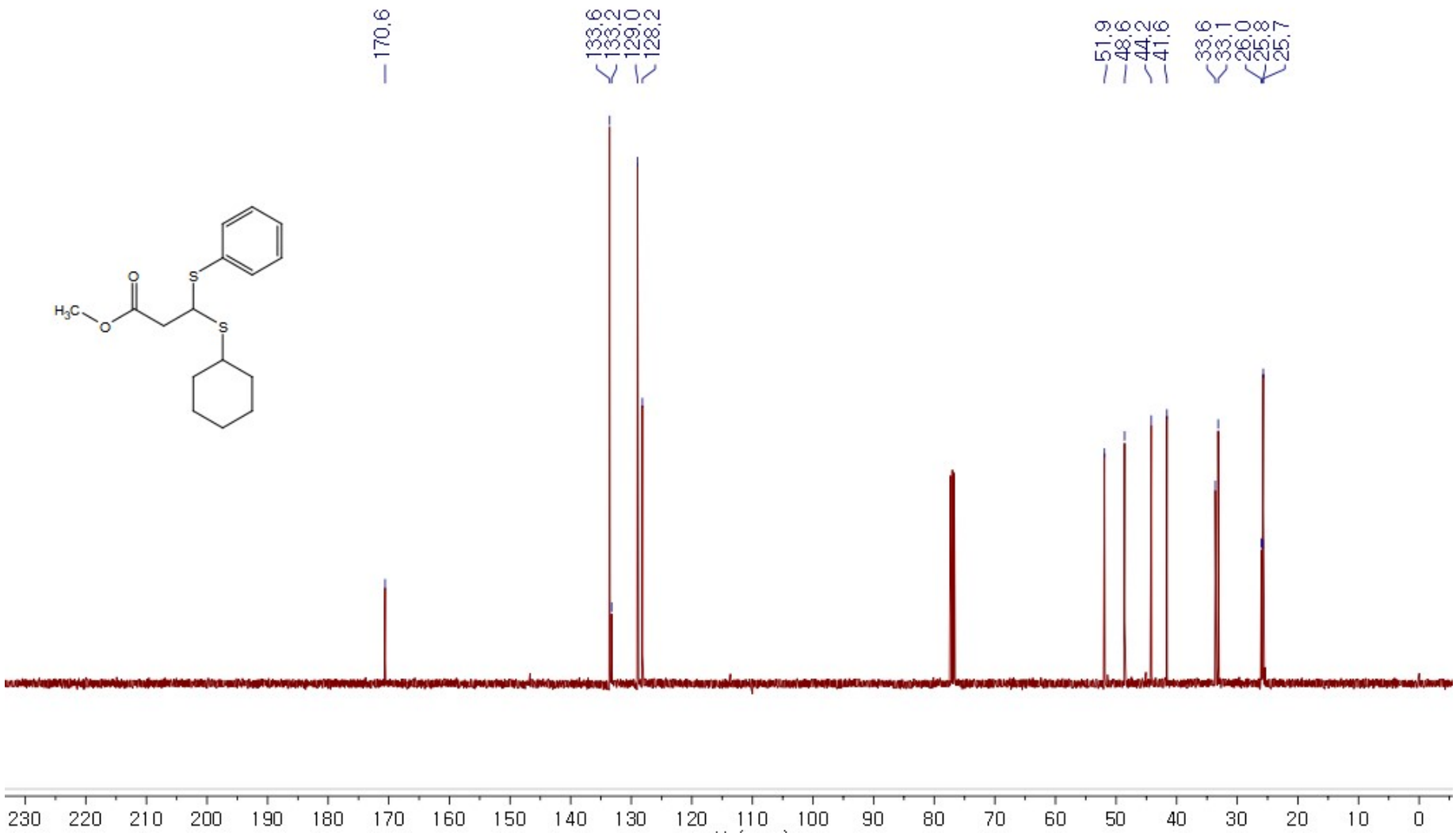
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(thiophen-2-ylthio)propanoate **(3aj)**



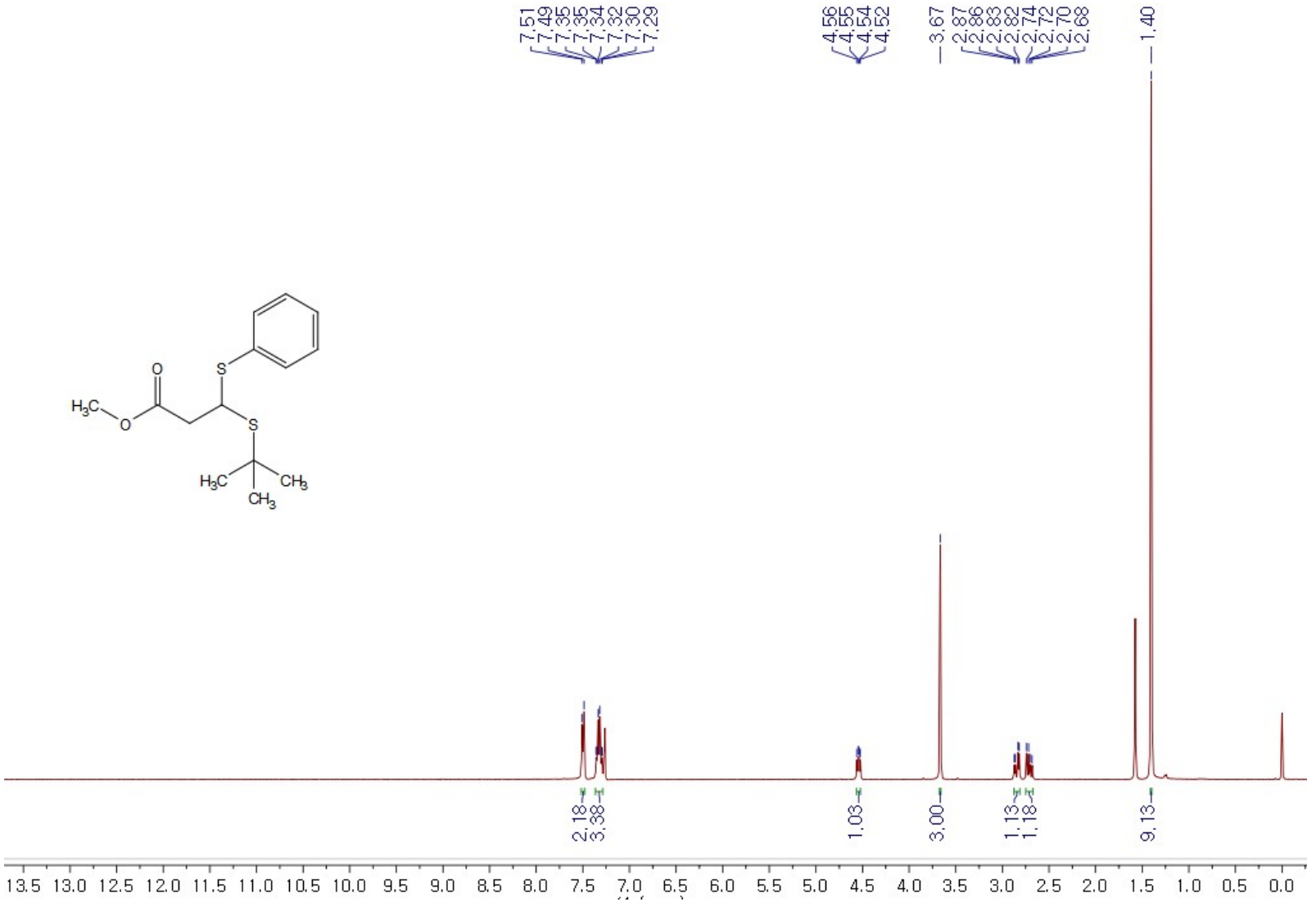
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)-3-(thiophen-2-ylthio)propanoate **(3aj)**



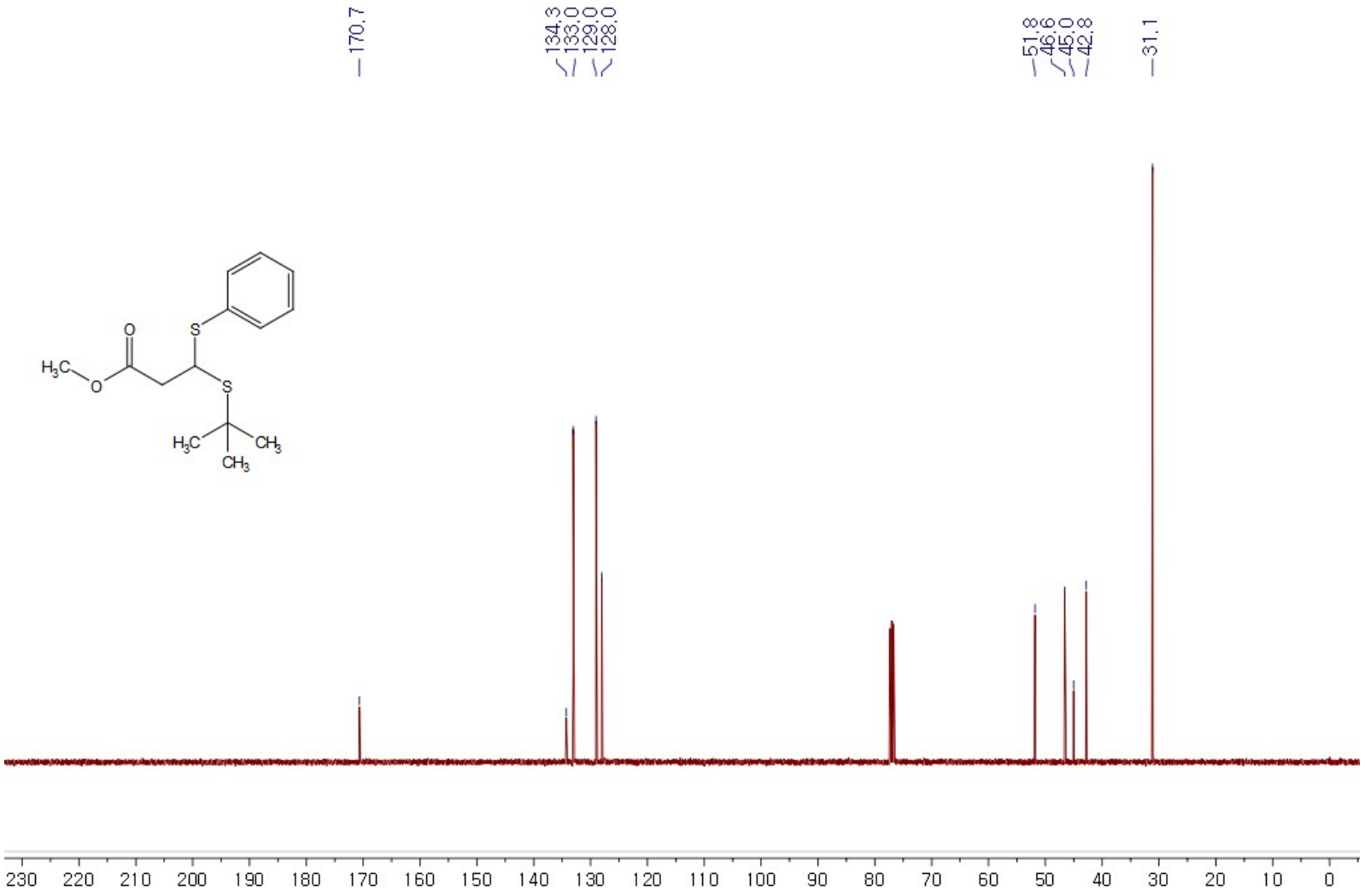
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)-3-(phenylthio)propanoate **(3ba)**



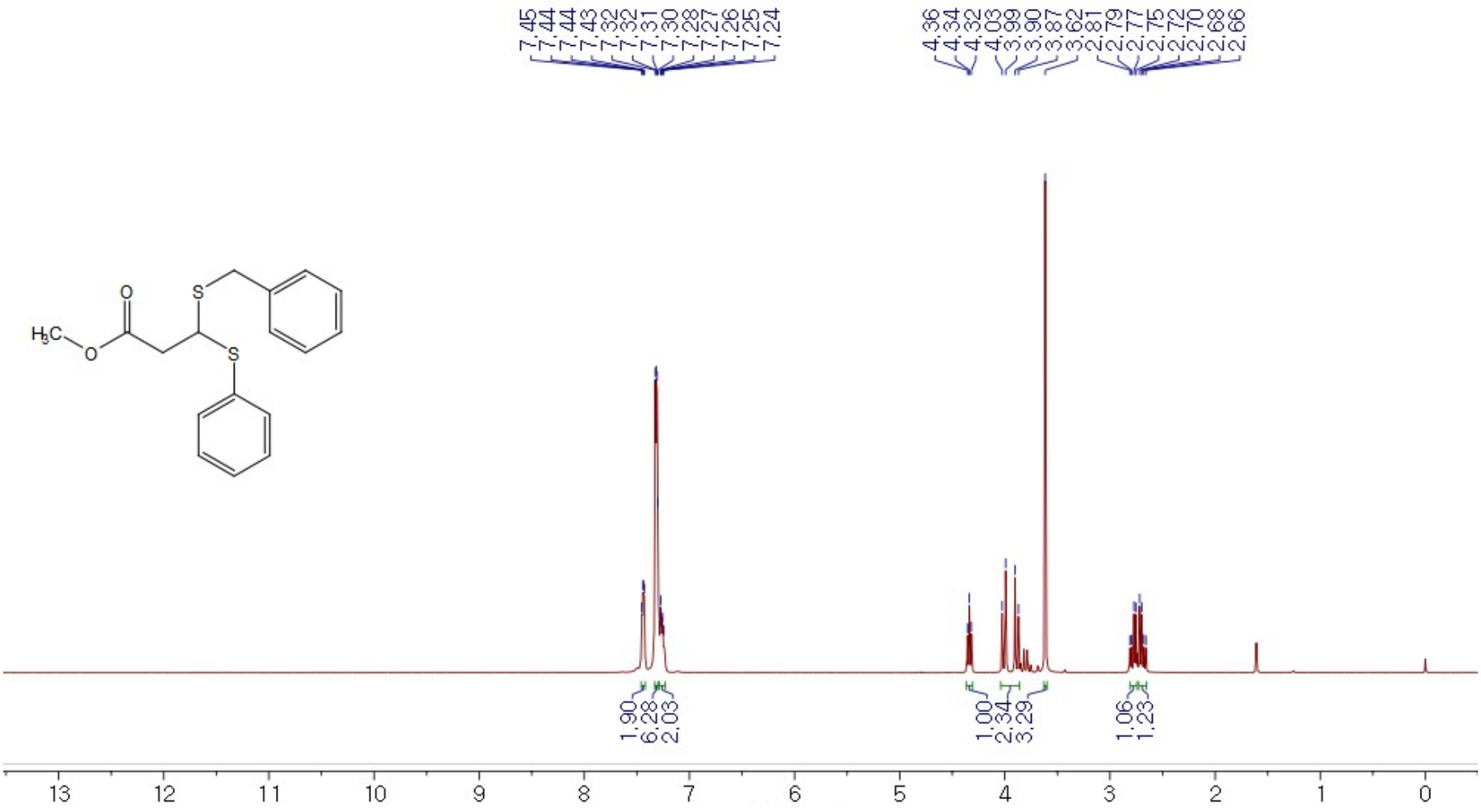
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)-3-(phenylthio)propanoate **(3ba)**



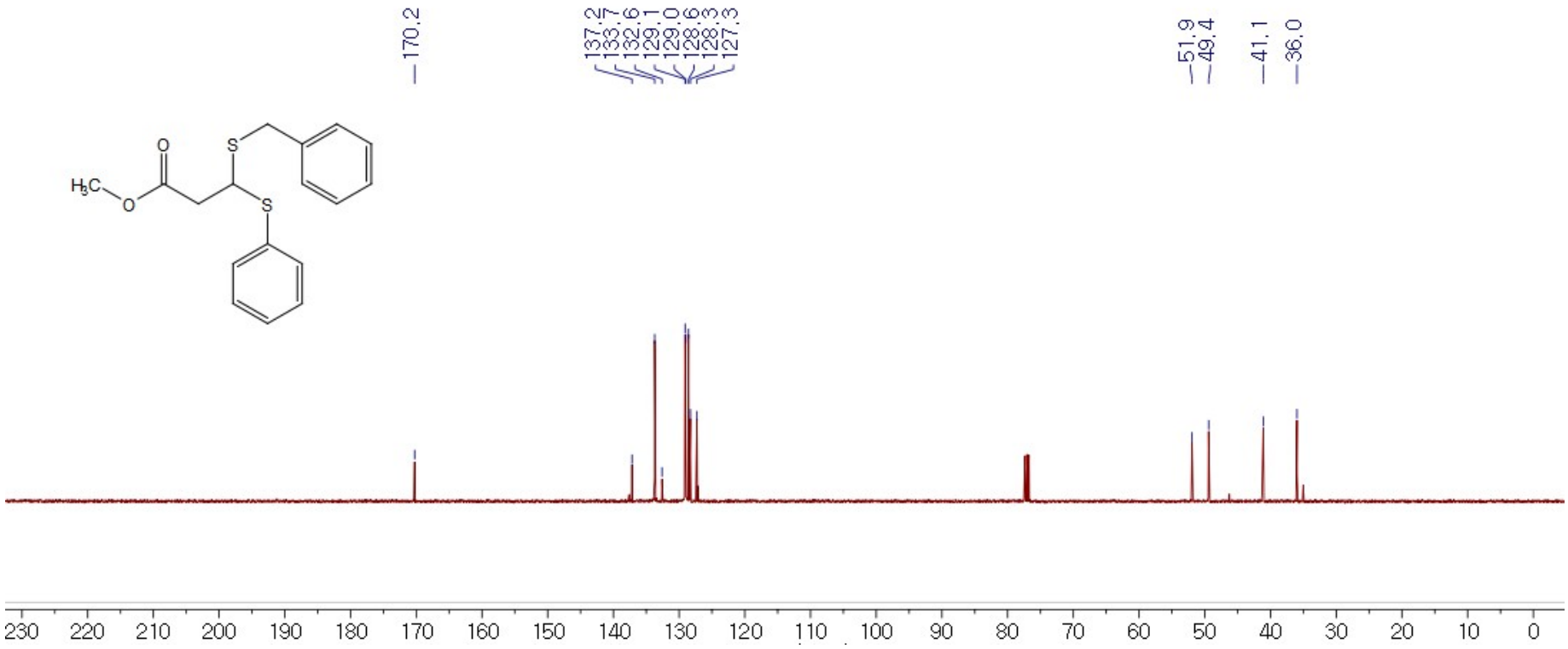
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(tert-butylthio)-3-(phenylthio)propanoate **(3ca)**



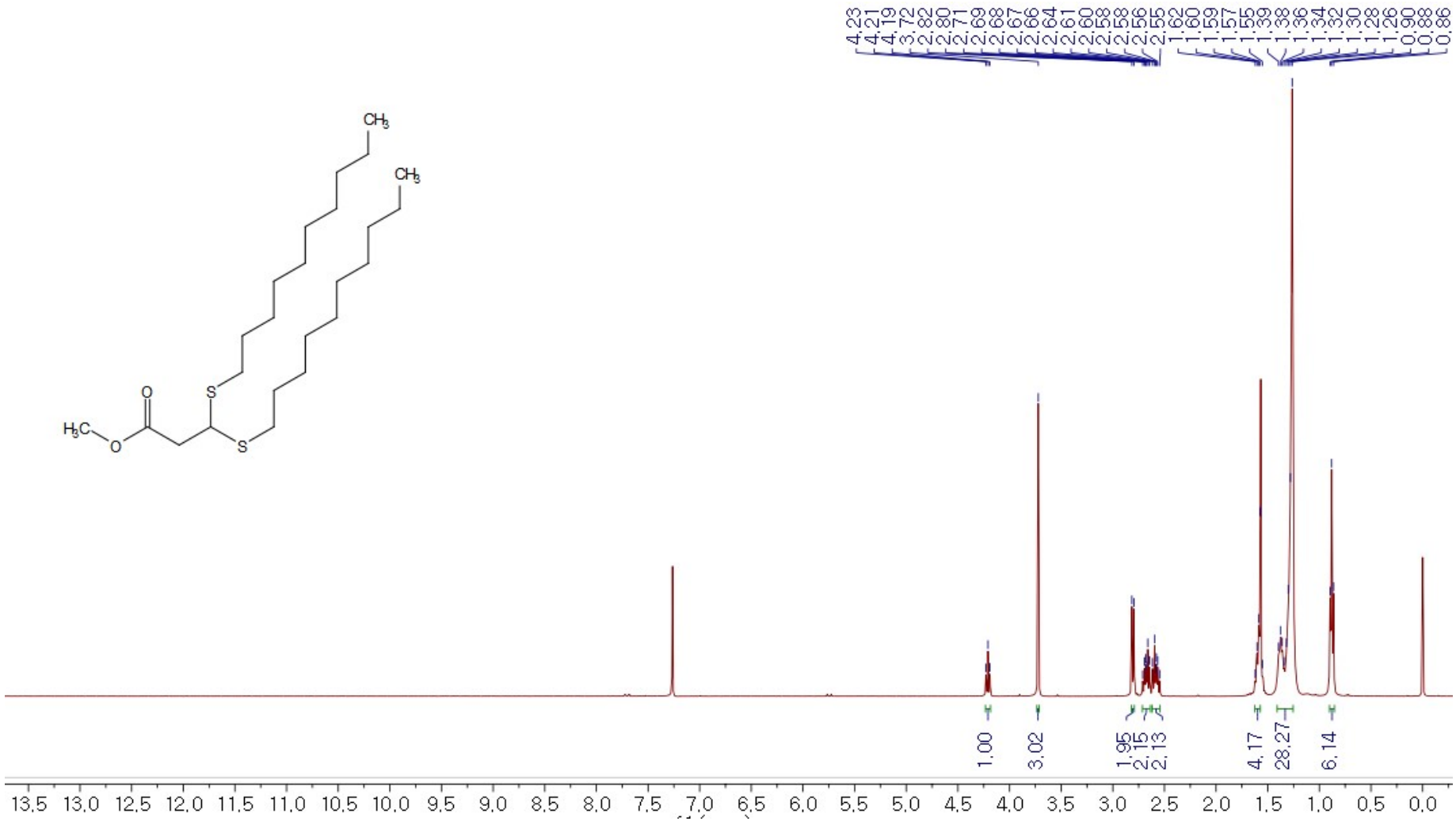
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(tert-butylthio)-3-(phenylthio)propanoate **(3ca)**



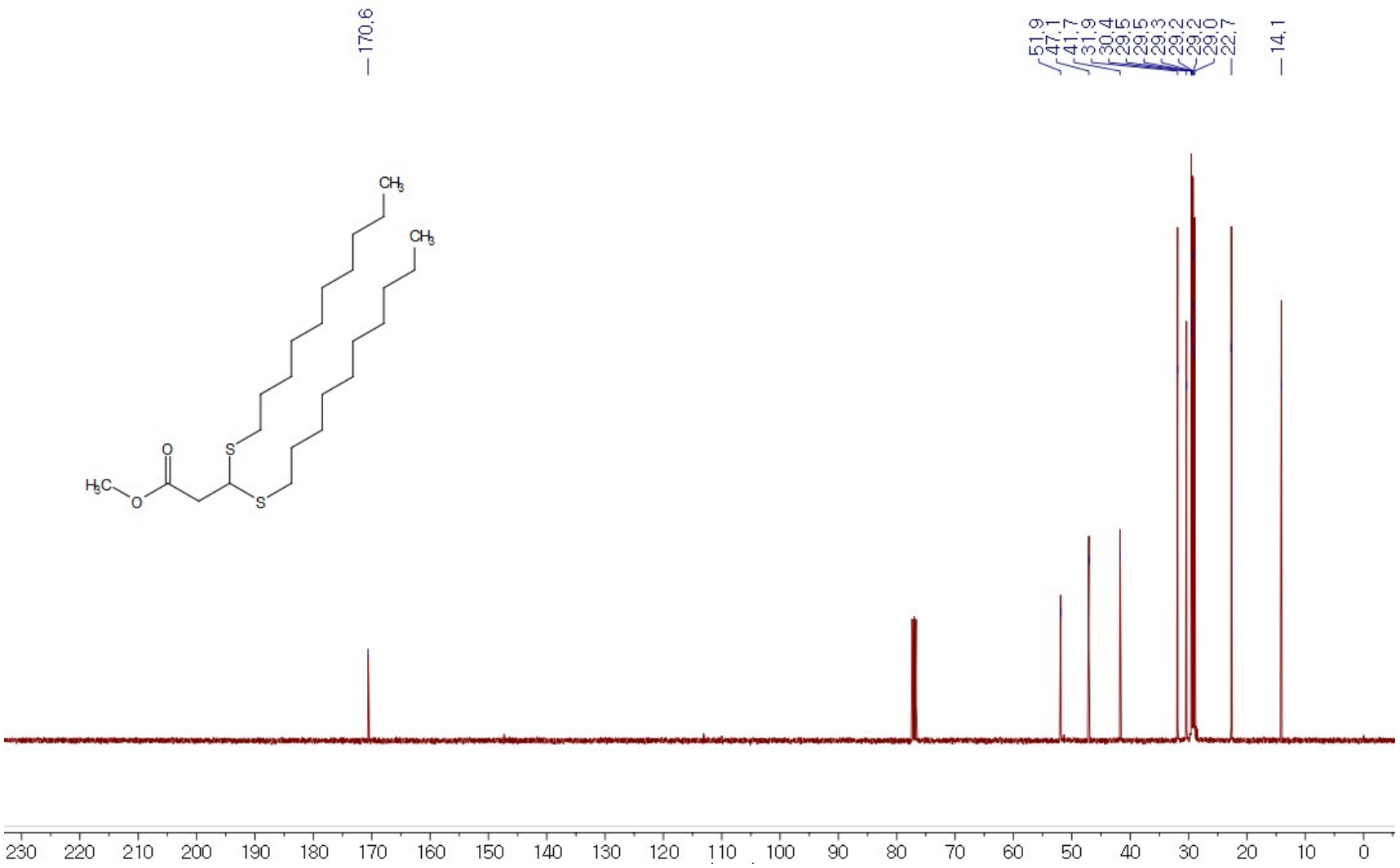
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(benzylthio)-3-(phenylthio)propanoate **(3da)**



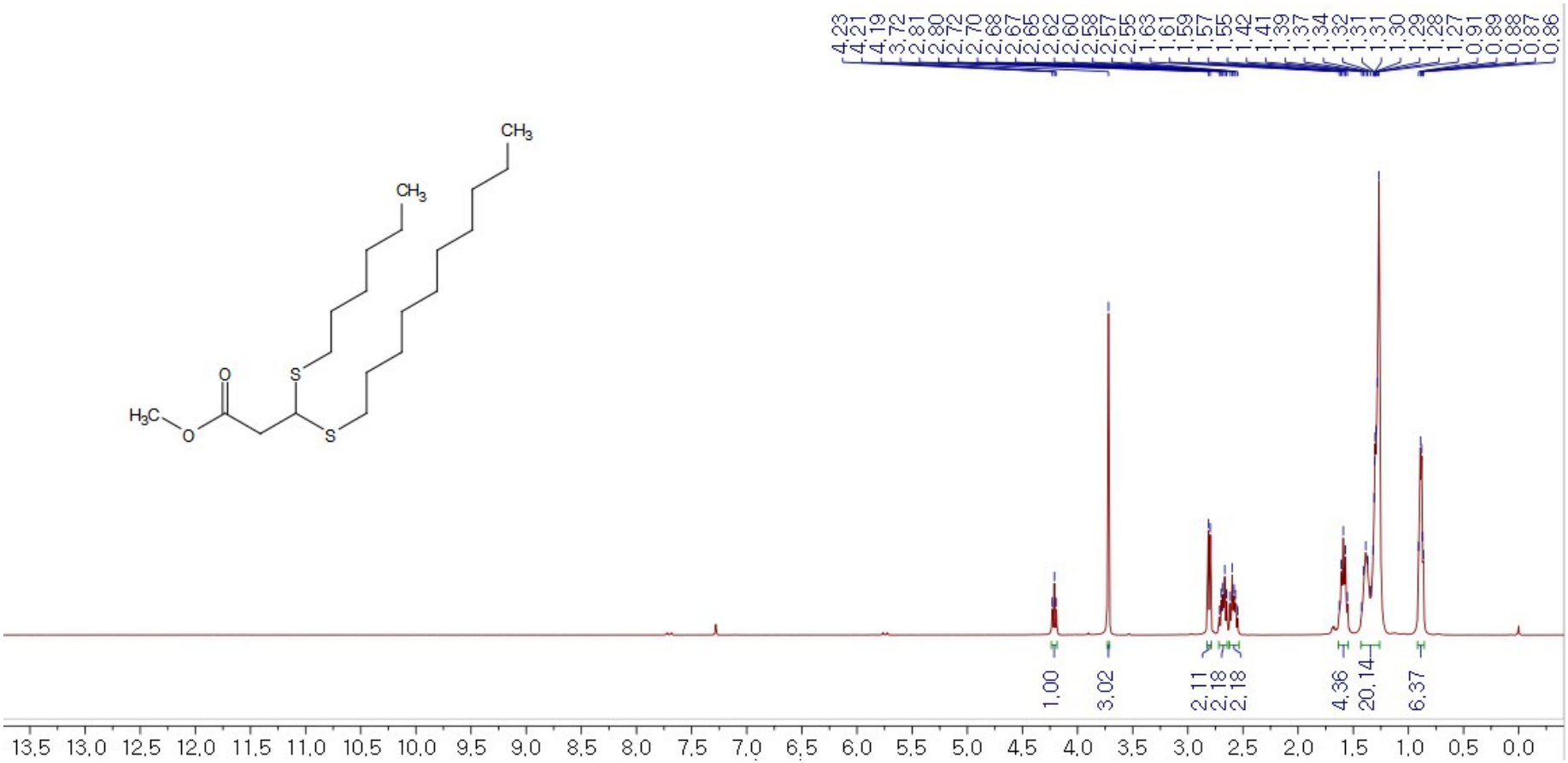
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(benzylthio)-3-(phenylthio)propanoate **(3da)**



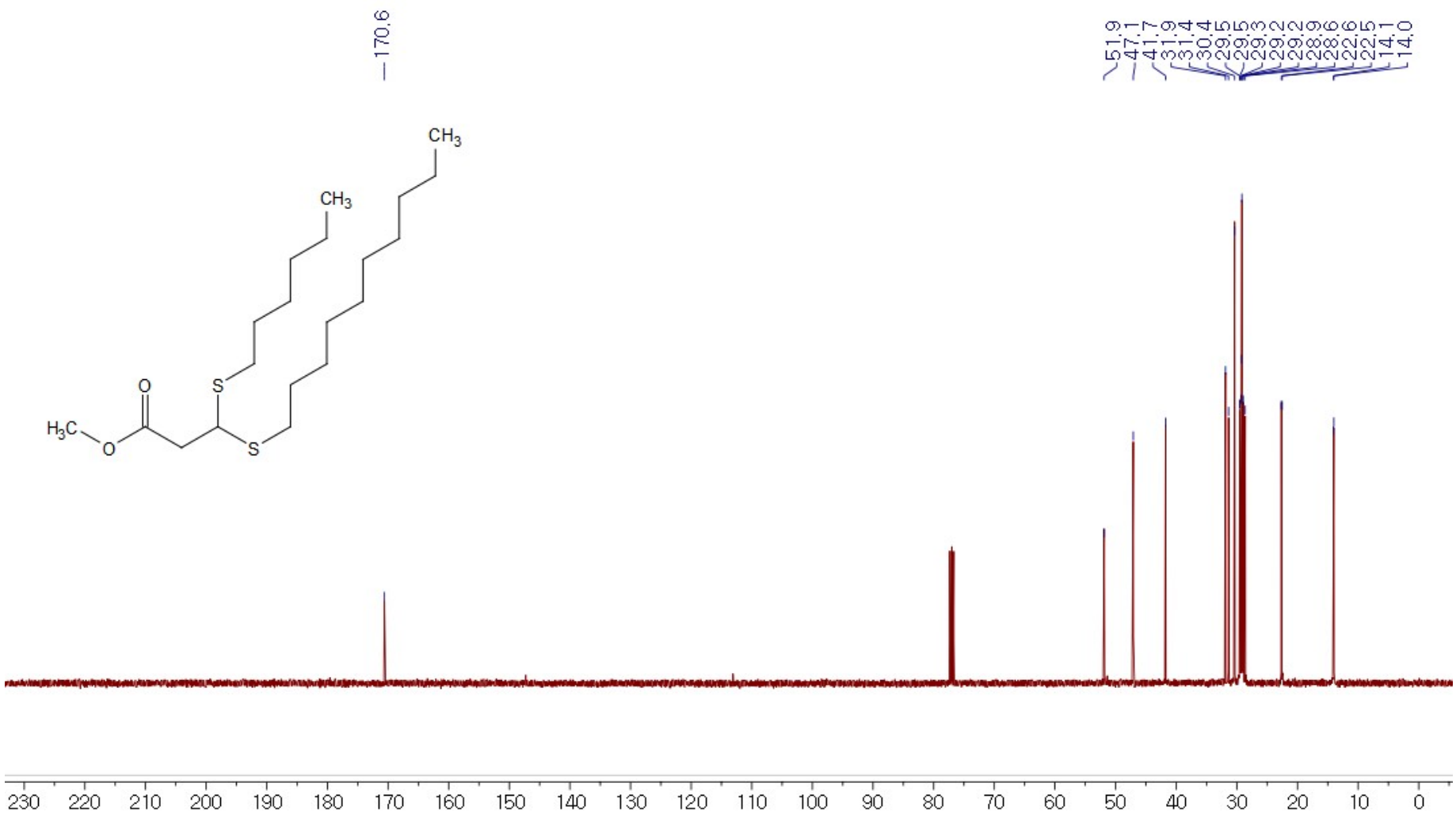
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3,3-bis(decylthio)propanoate **(3ak)**



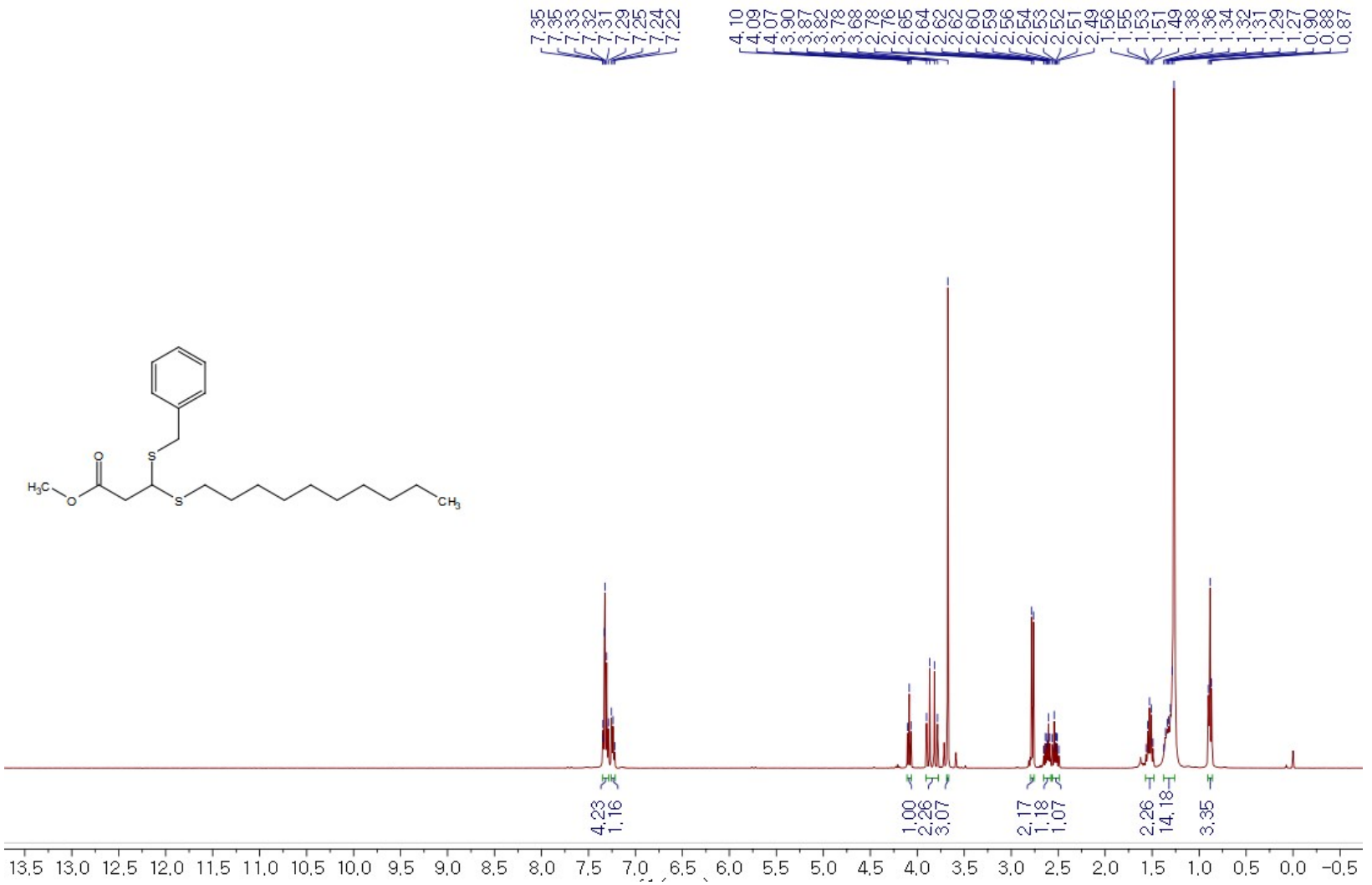
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3,3-bis(decylthio)propanoate **(3ak)**



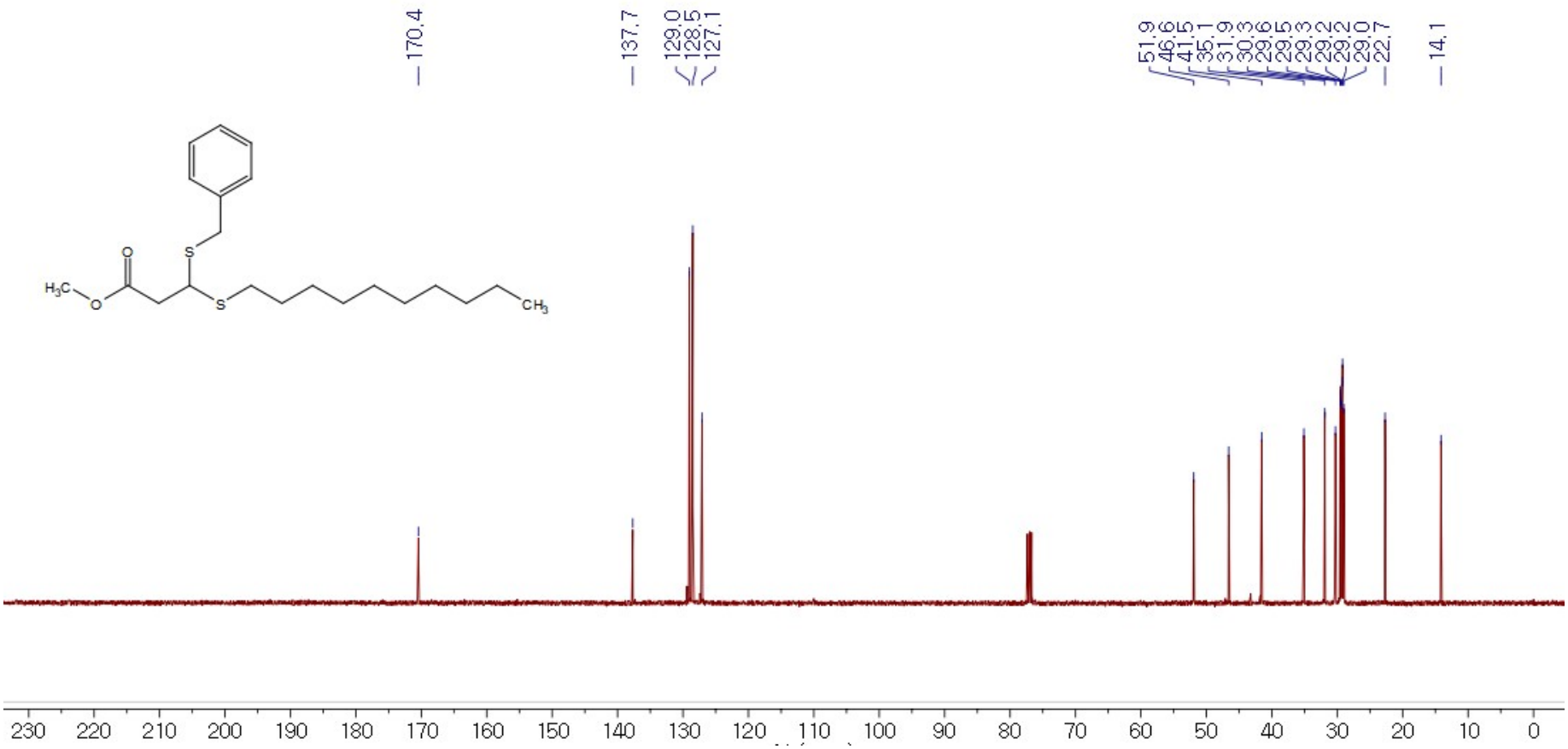
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate **(3al)**



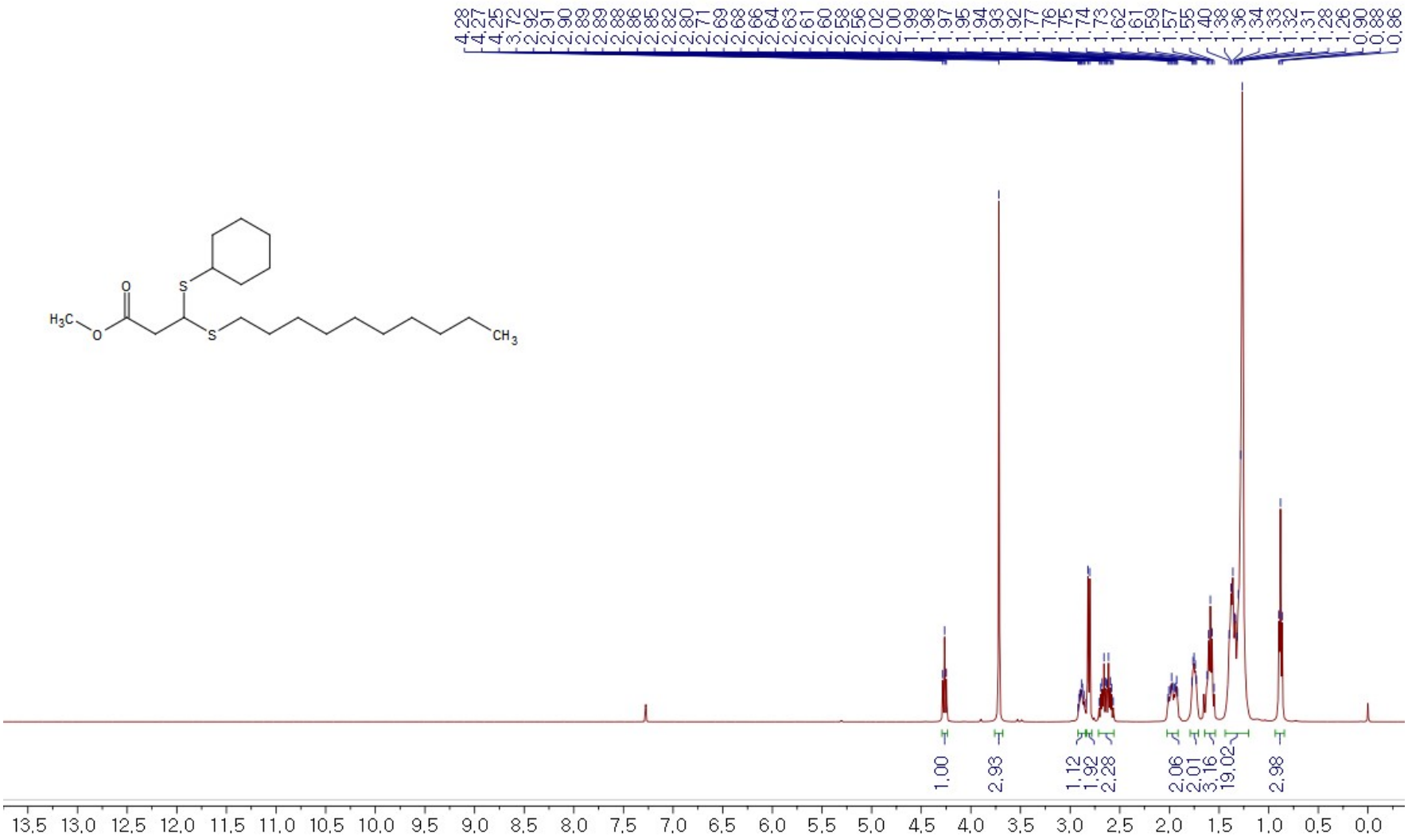
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate **(3al)**



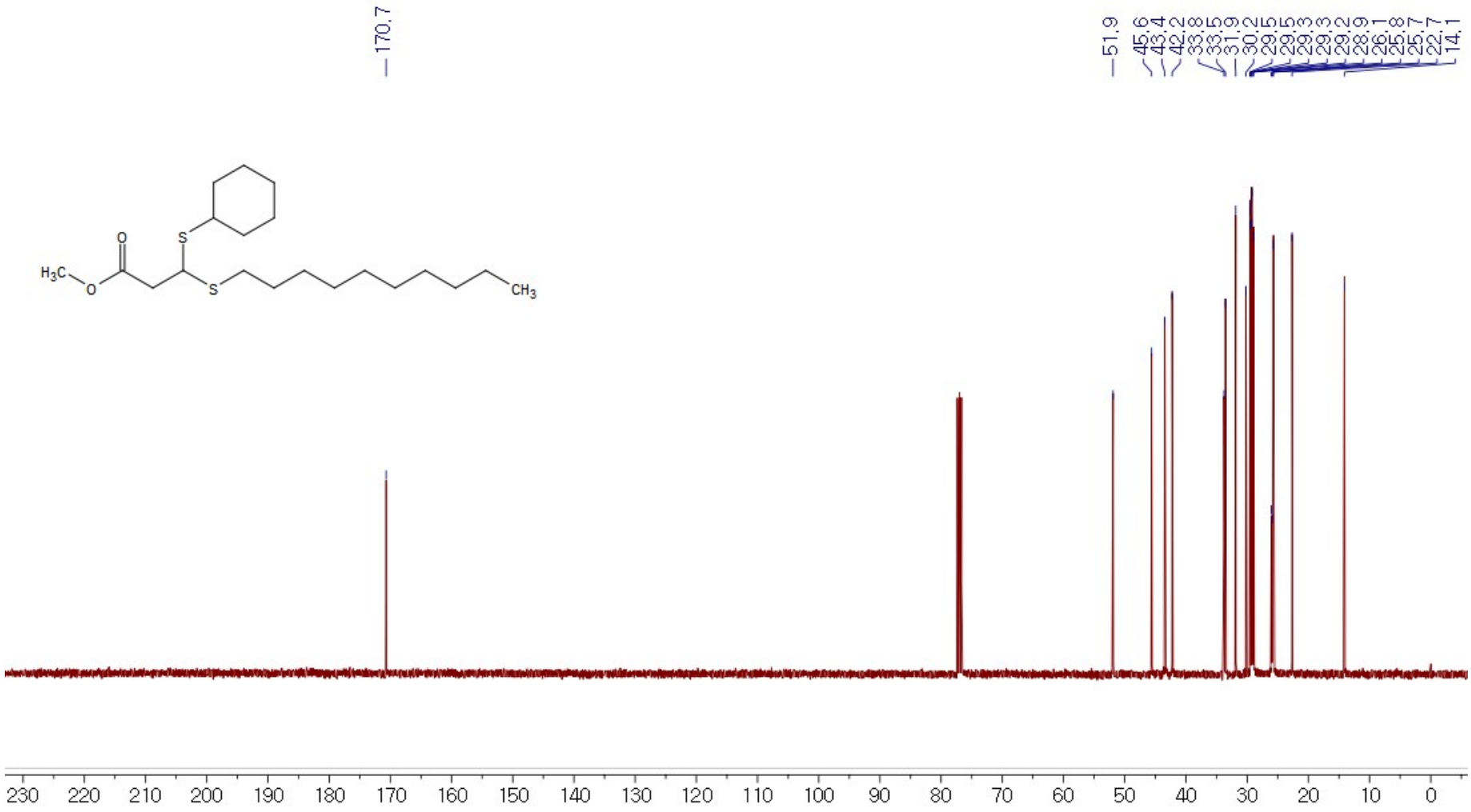
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(benzylthio)-3-(decylthio)propanoate **(3am)**



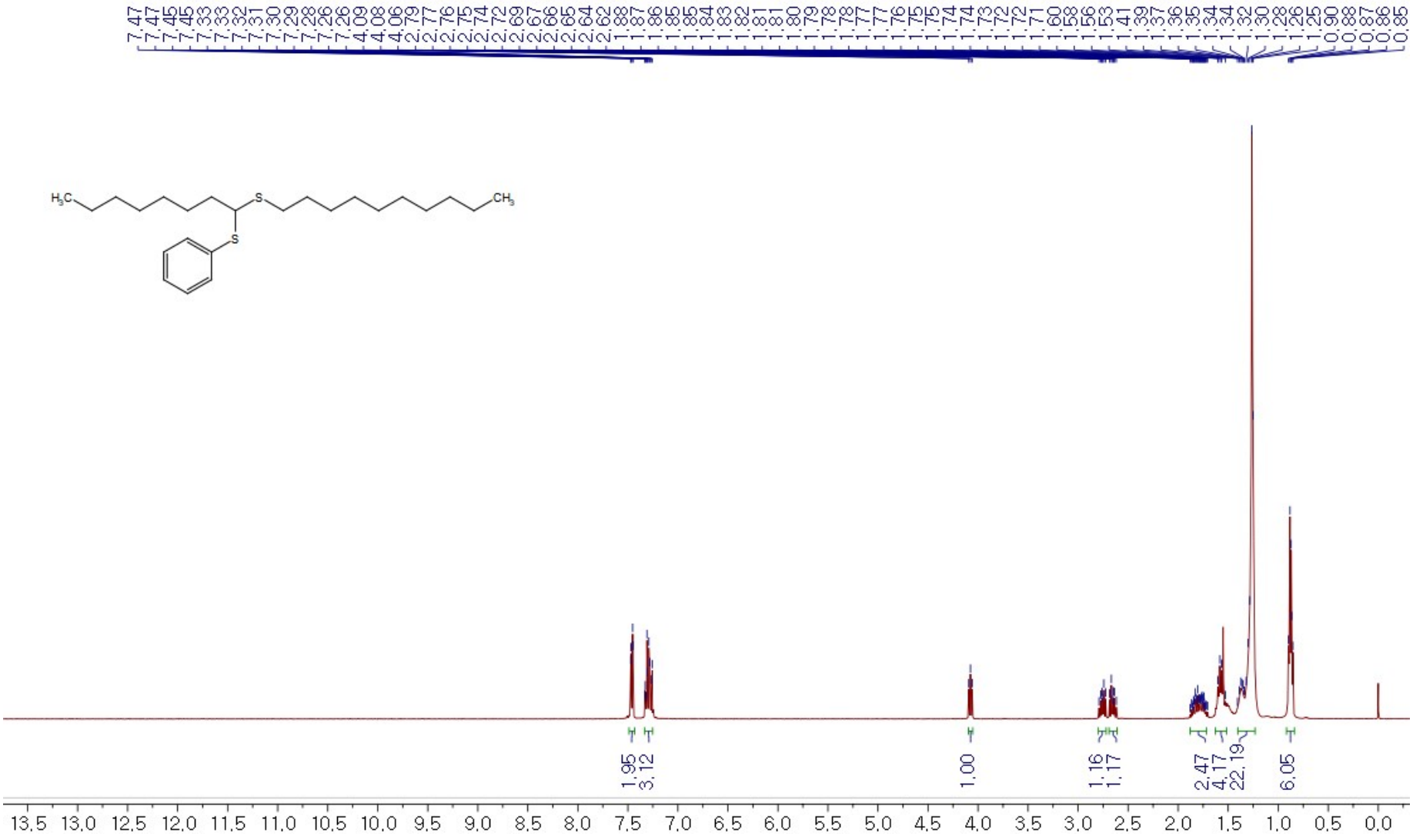
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(benzylthio)-3-(decylthio)propanoate **(3am)**



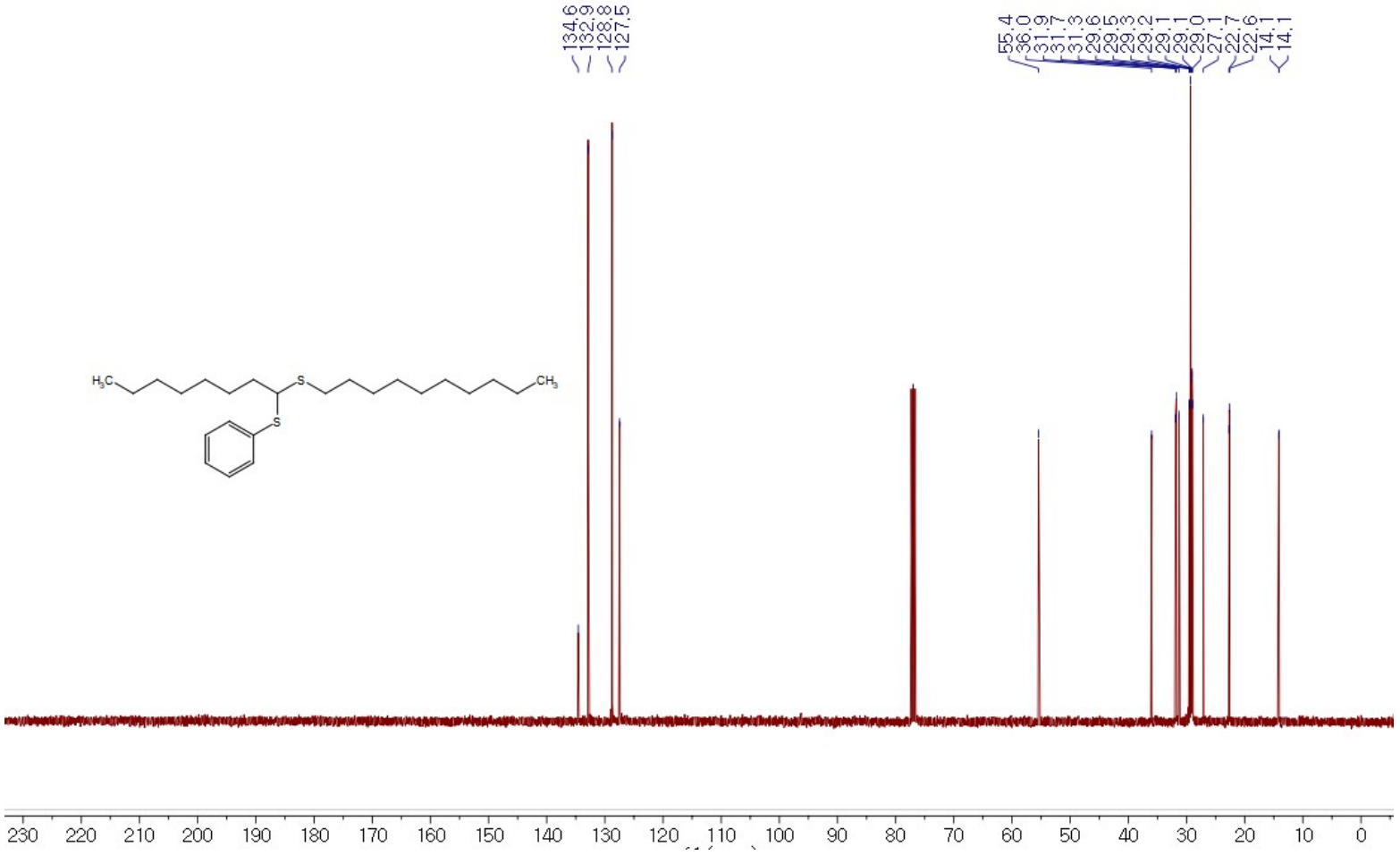
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate **(3an)**



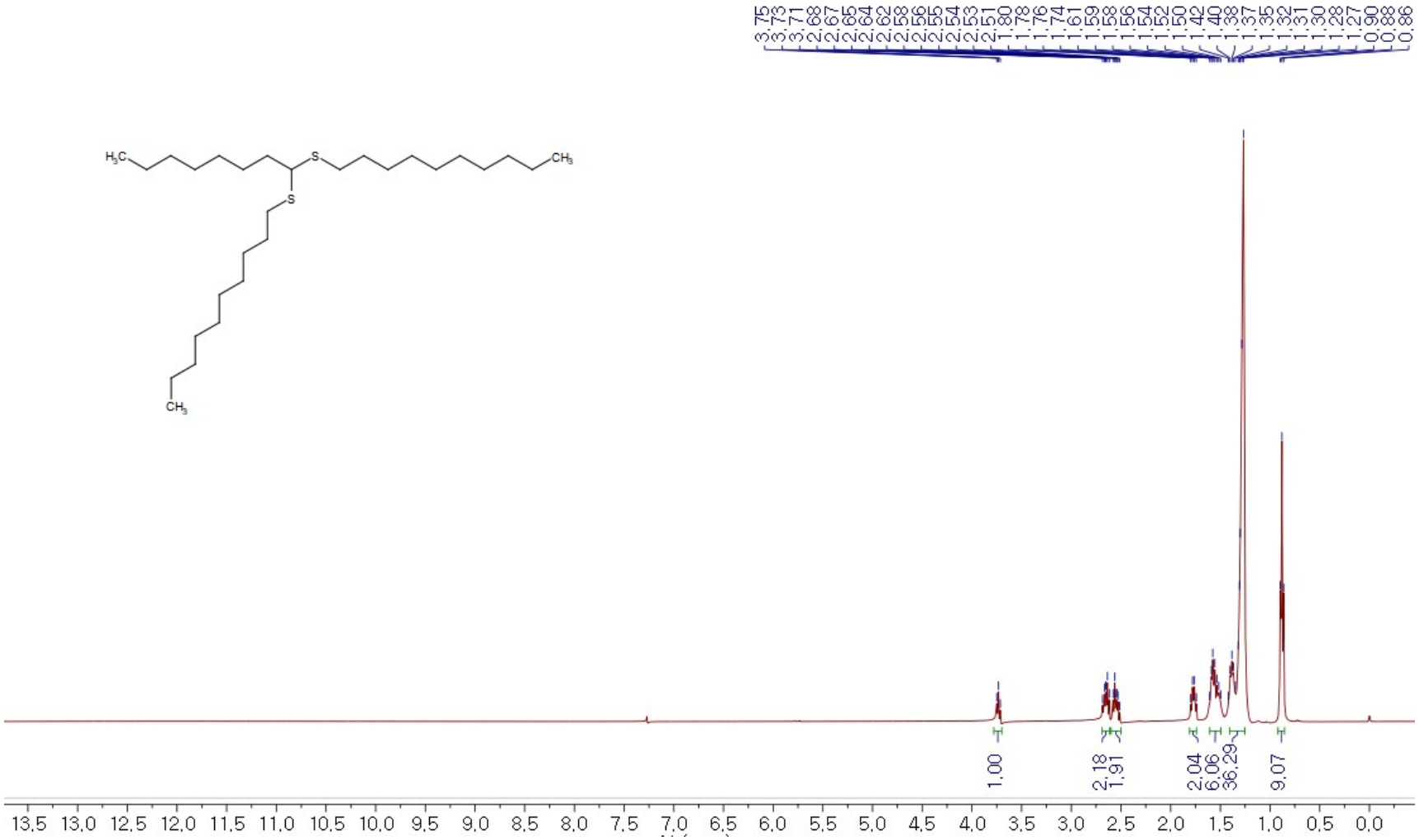
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)-3-(decylthio)propanoate **(3an)**



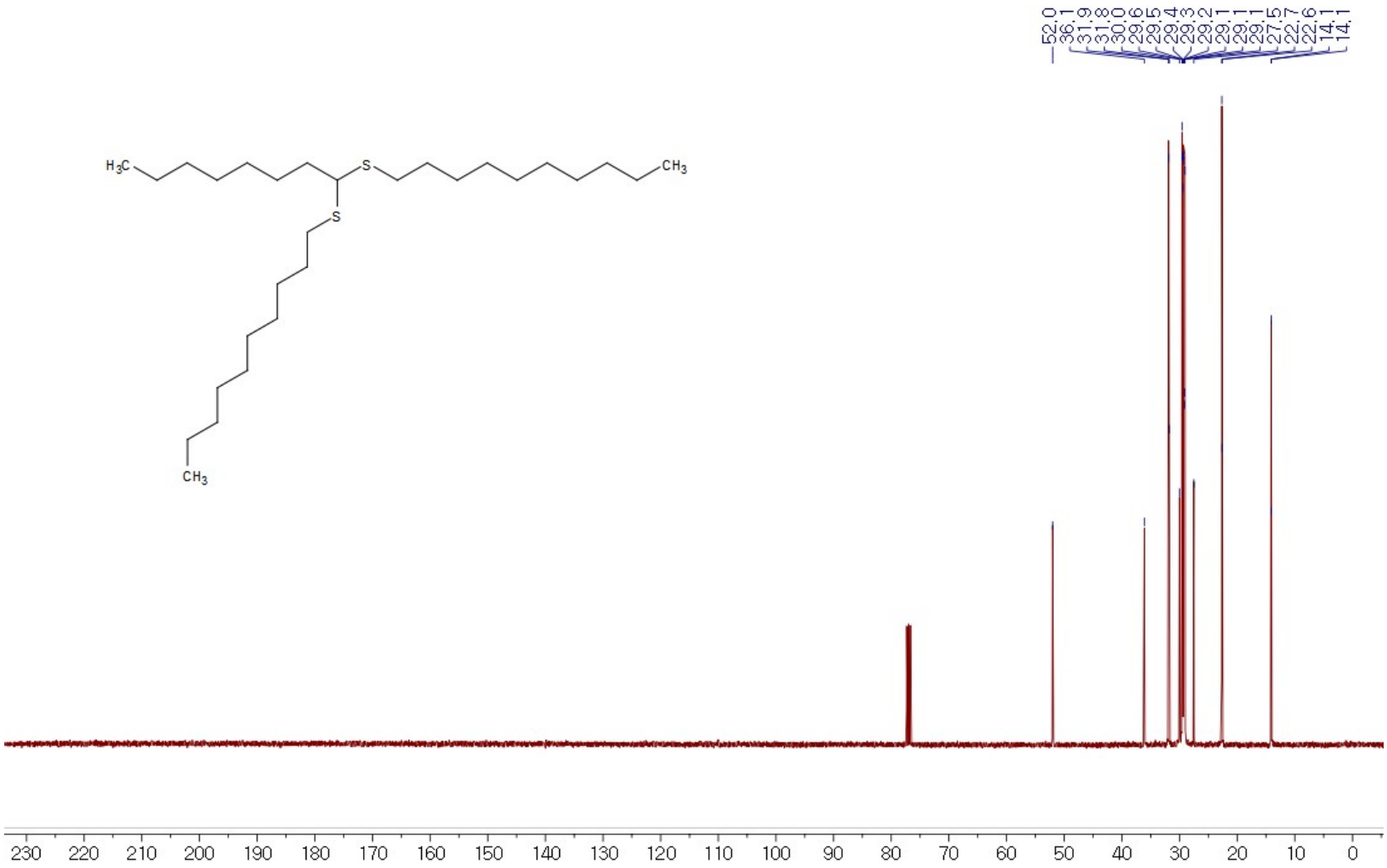
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Decyl(1-(phenylthio)octyl)sulfane **(3ea)**



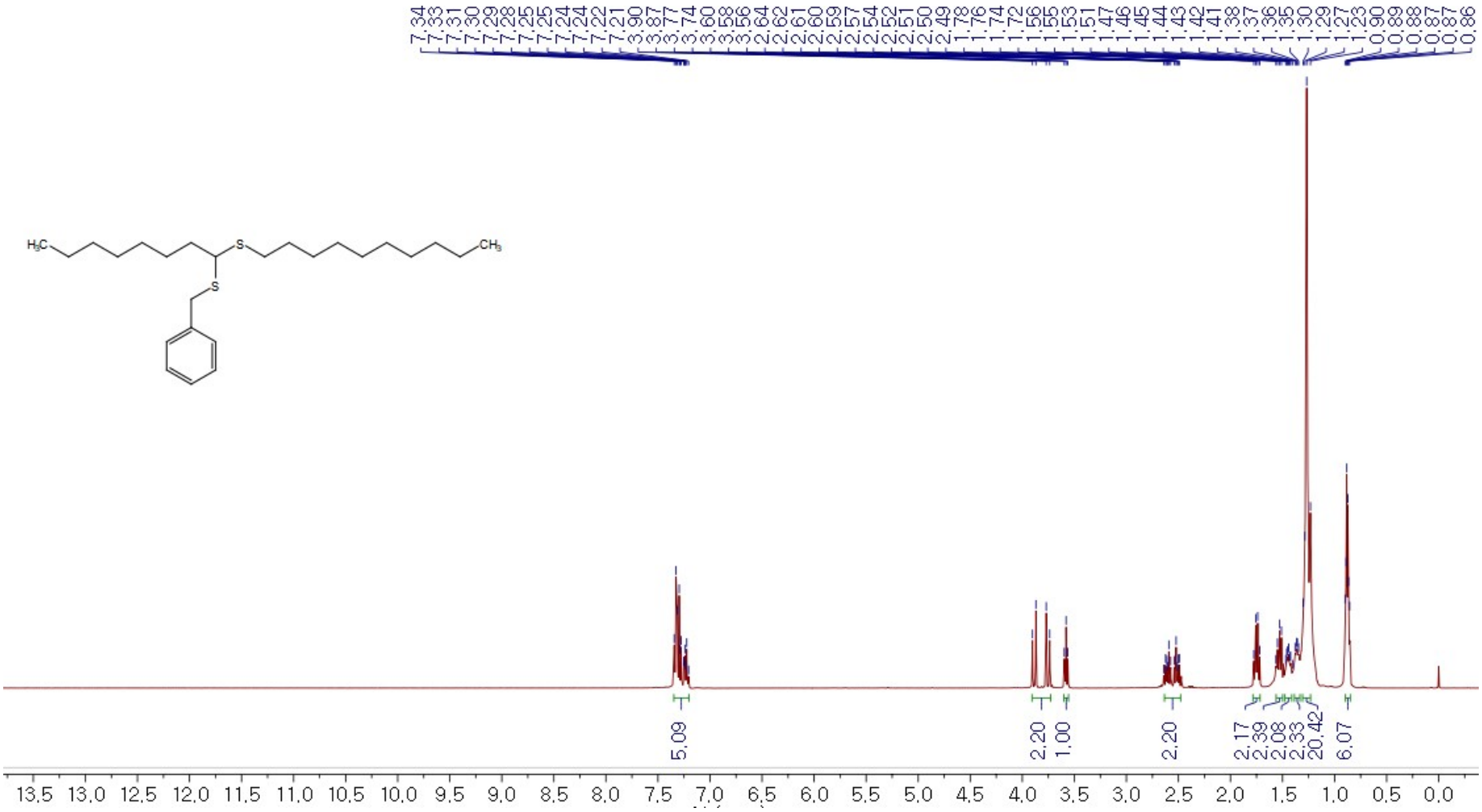
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Decyl(1-(phenylthio)octyl)sulfane **(3ea)**



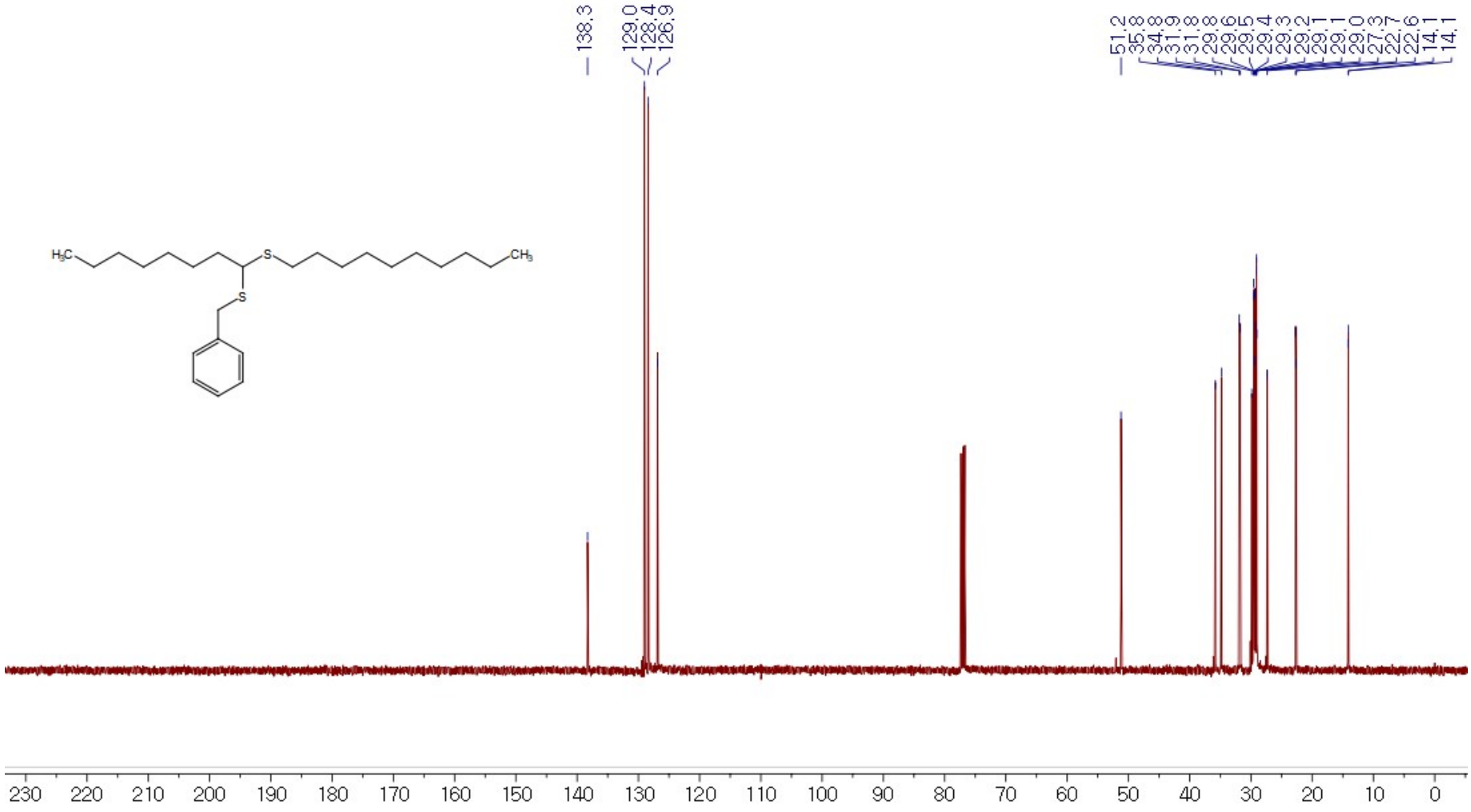
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Octane-1,1-diylbis(decylsulfane) **(3ek)**



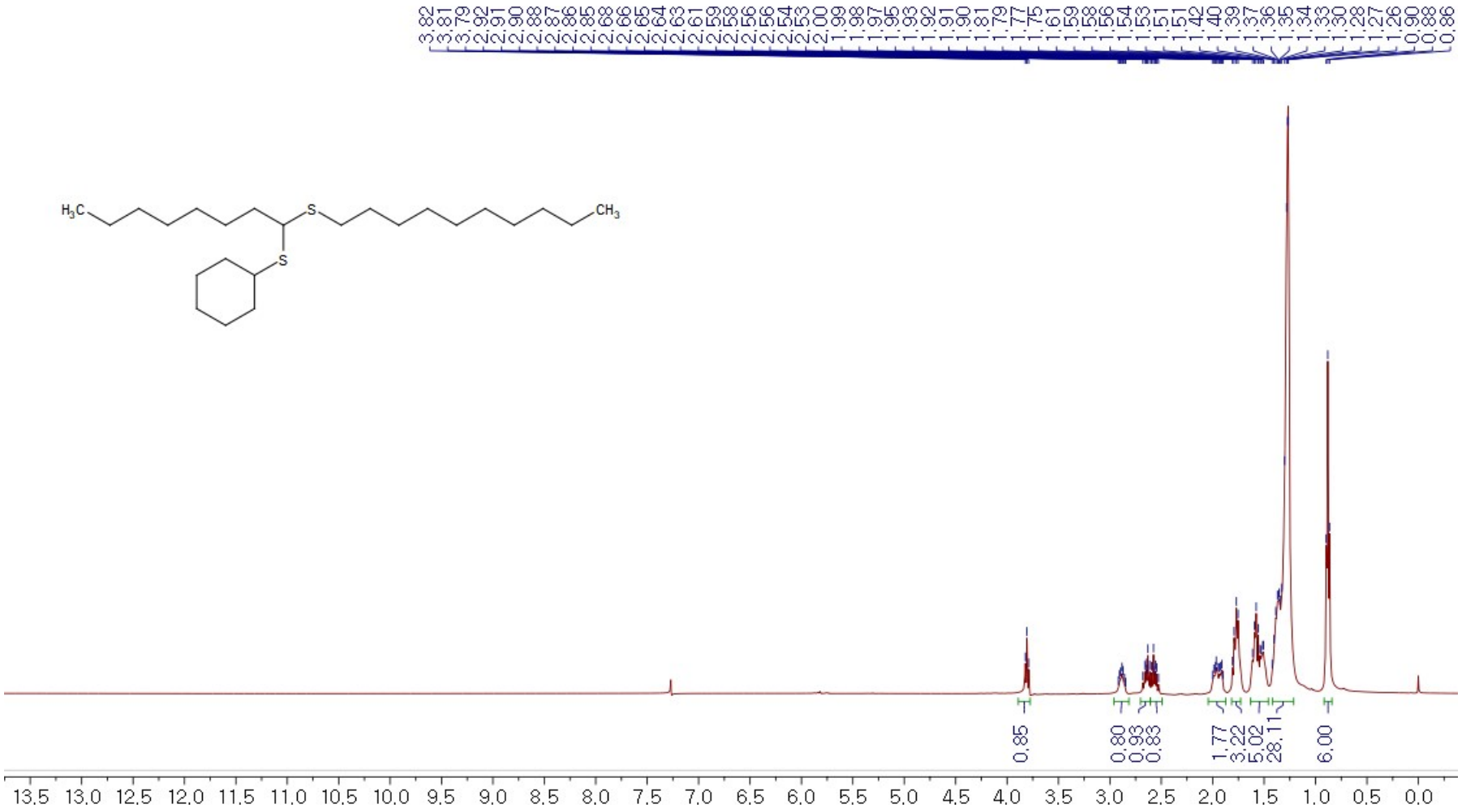
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Octane-1,1-diylbis(decylsulfane) **(3ek)**



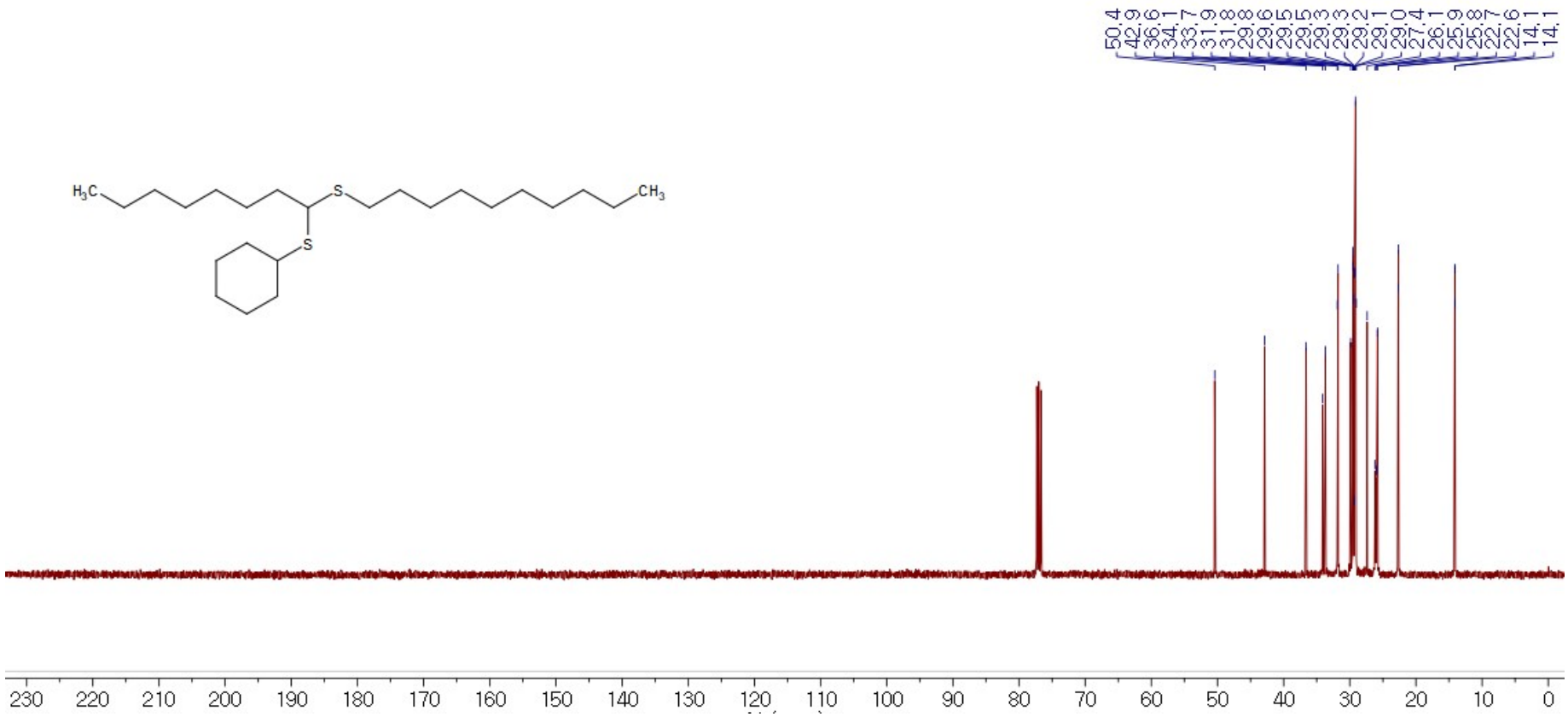
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Benzyl(1-(decylthio)octyl)sulfane **(3em)**



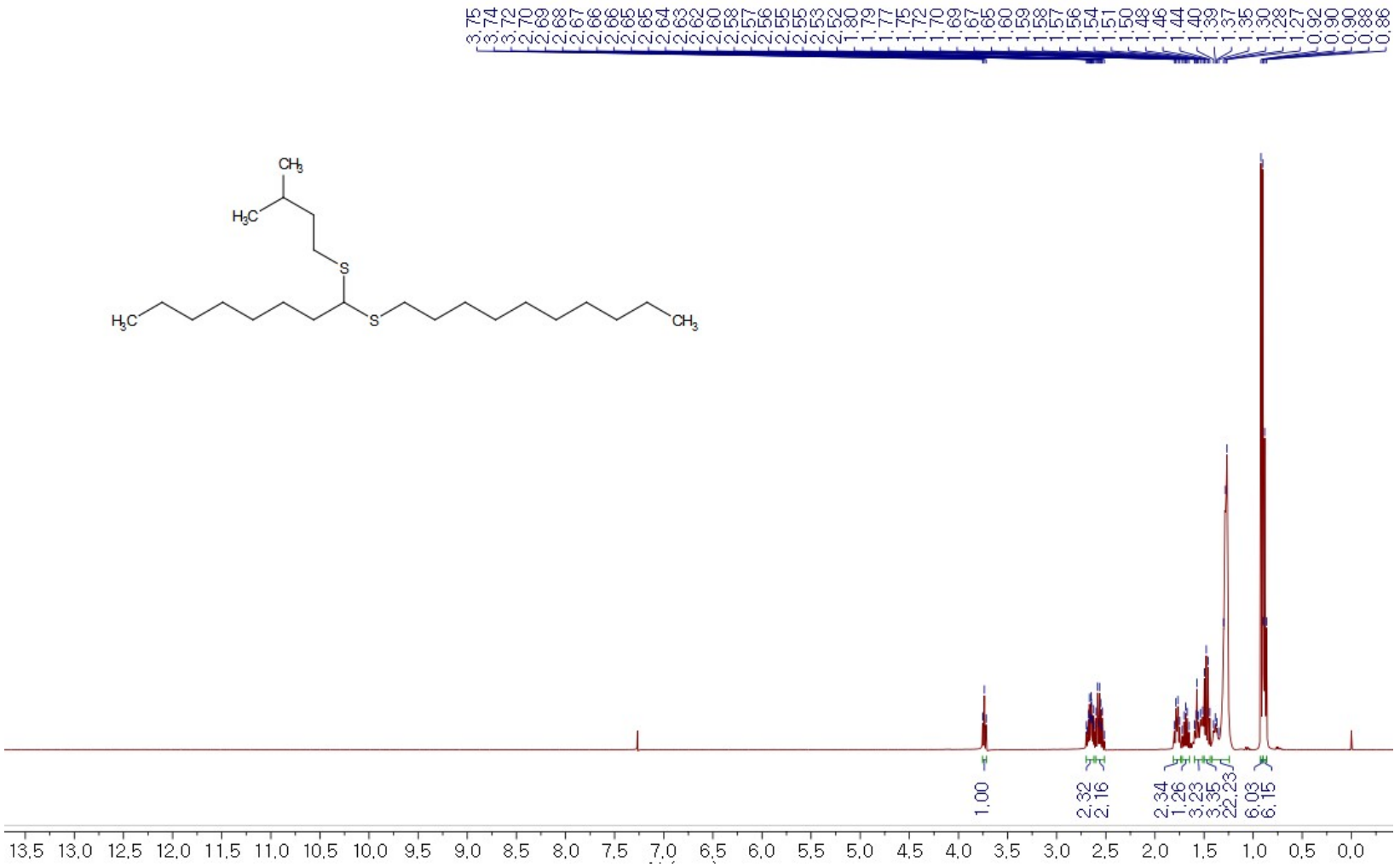
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Benzyl(1-(decylthio)octyl)sulfane **(3em)**



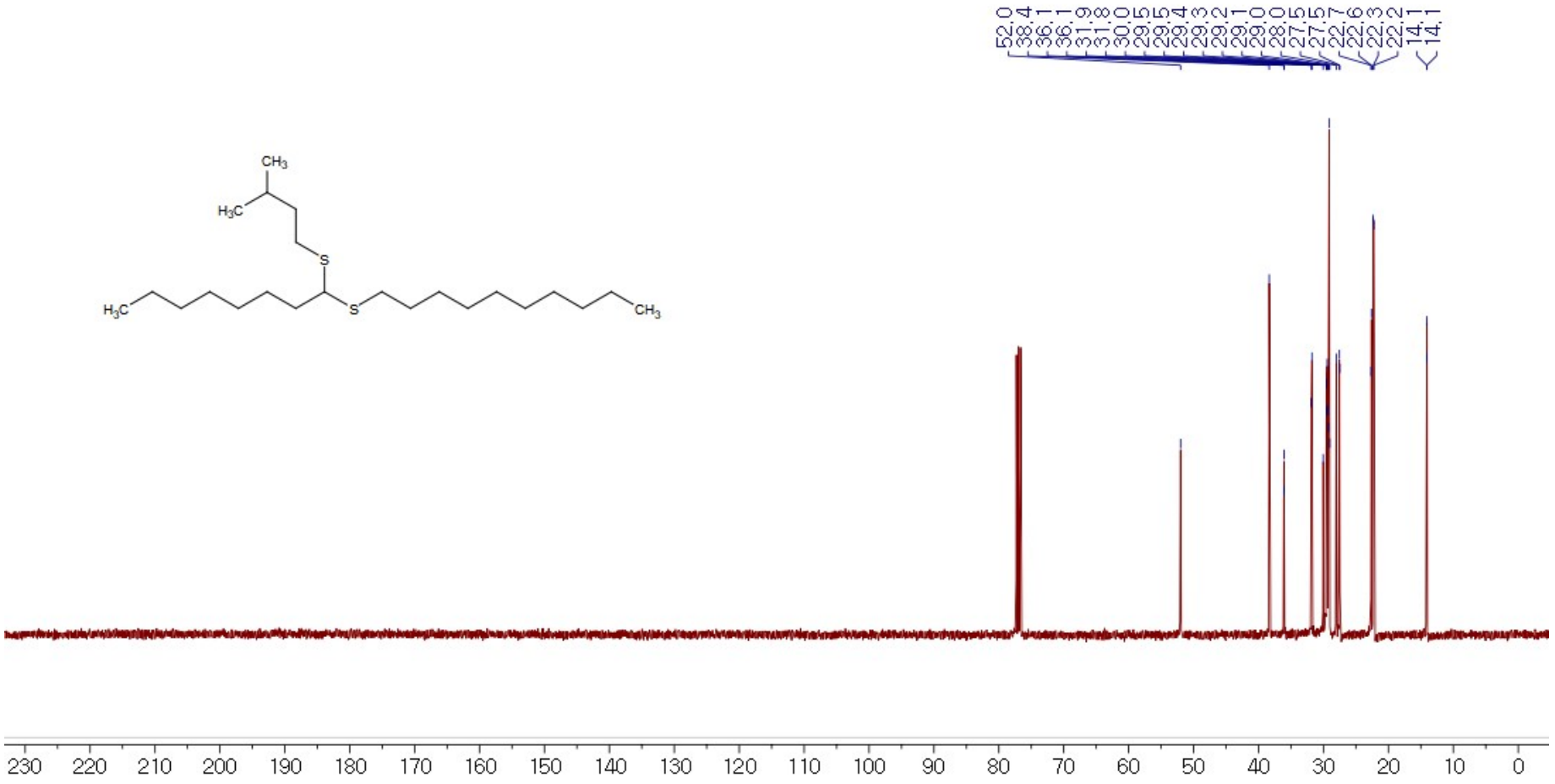
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Cyclohexyl(1-(decylthio)octyl)sulfane **(3en)**



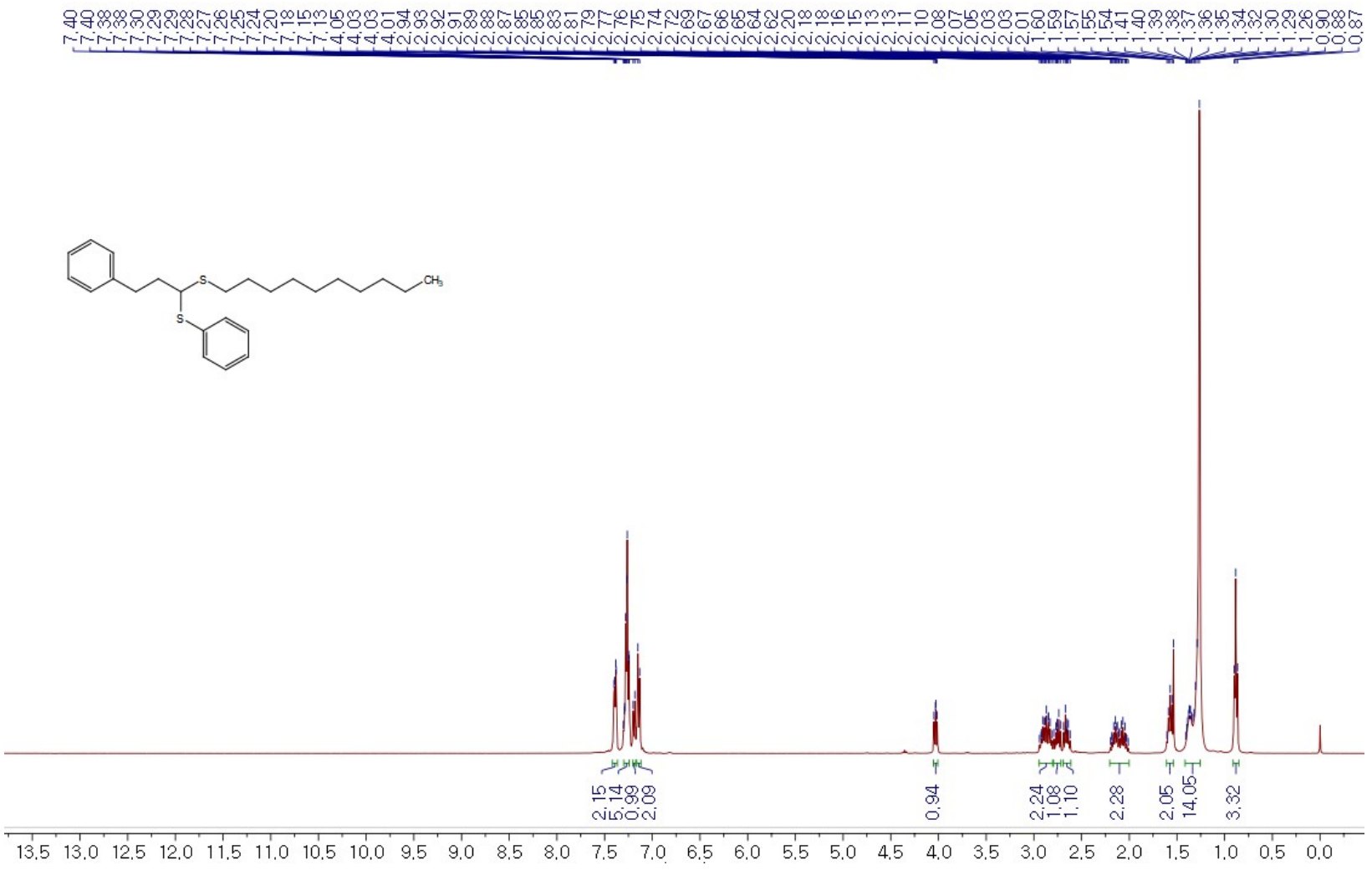
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Cyclohexyl(1-(decylthio)octyl)sulfane **(3en)**



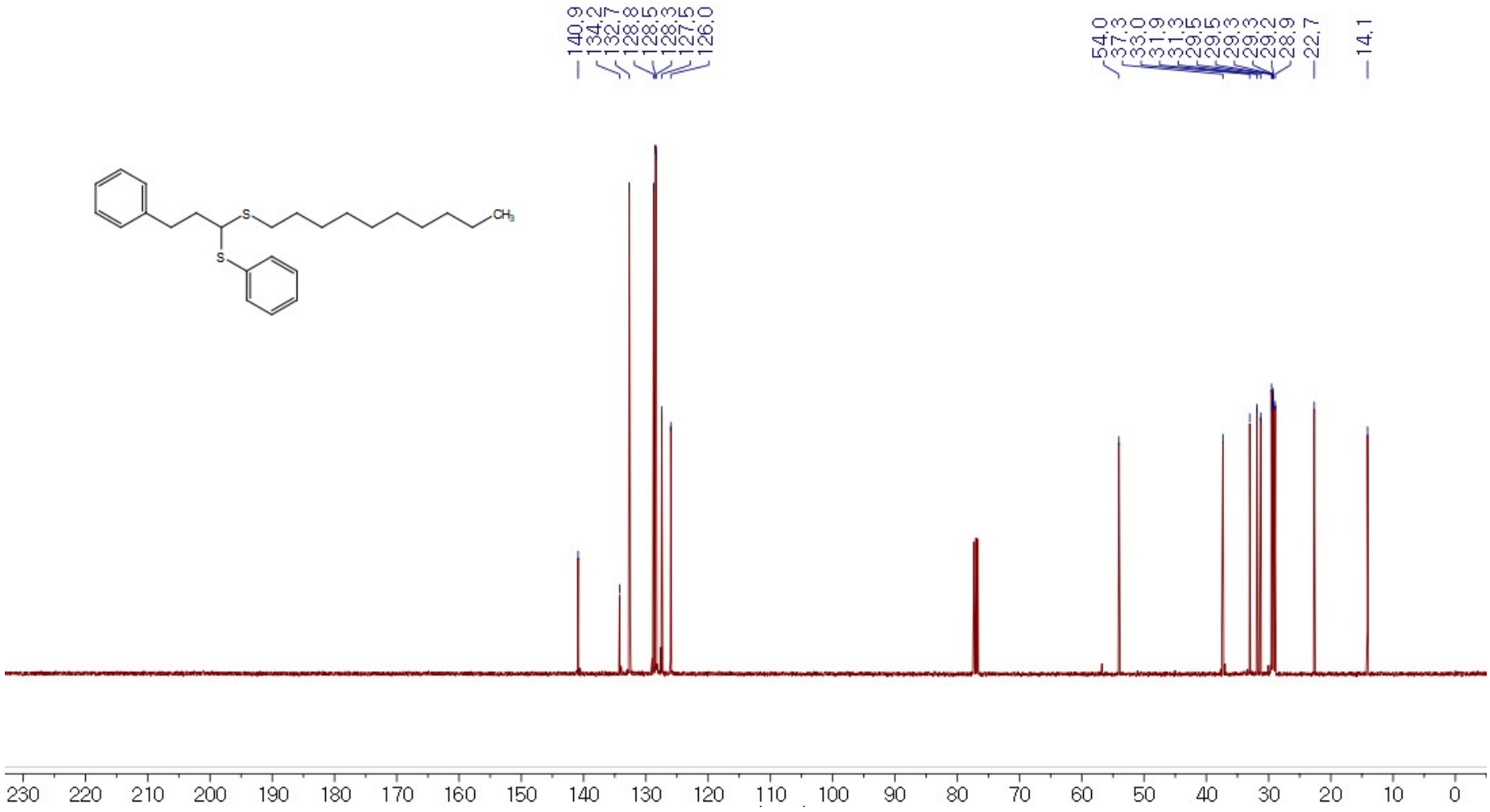
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Decyl(1-(isopentylthio)octyl)sulfane **(3eo)**



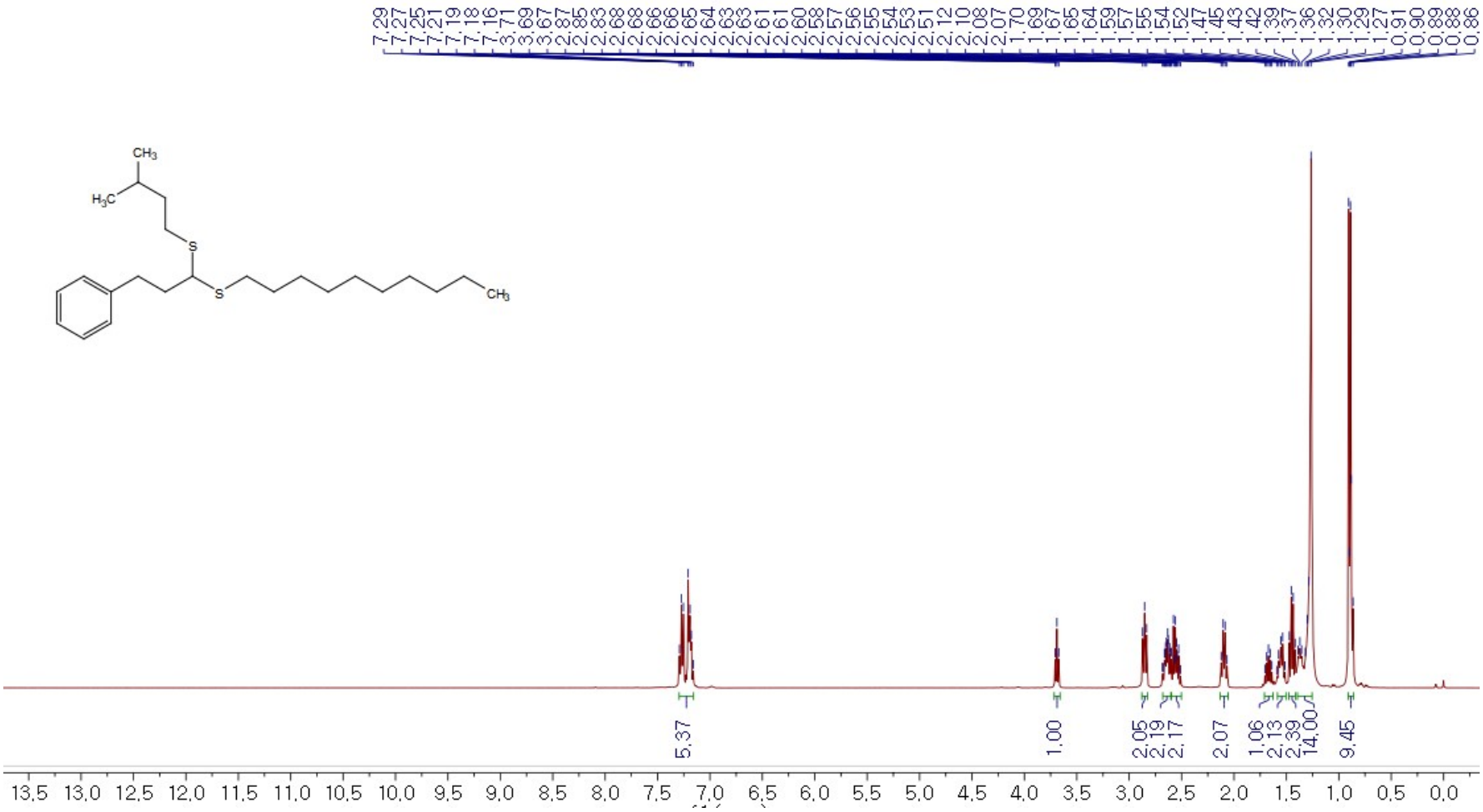
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Decyl(1-(isopentylthio)octyl)sulfane **(3eo)**



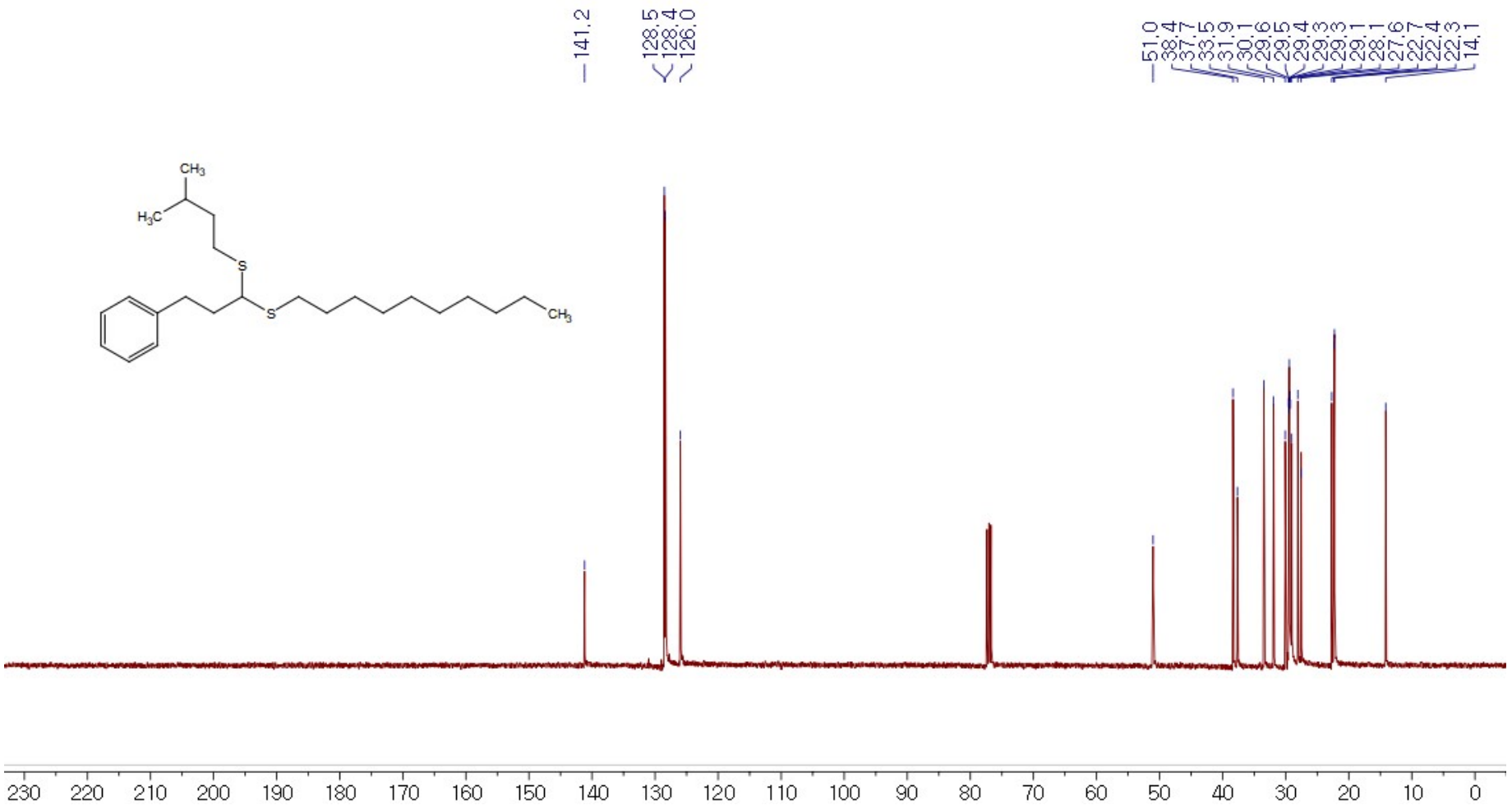
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Decyl(3-phenyl-1-(phenylthio)propyl)sulfane **(3fa)**



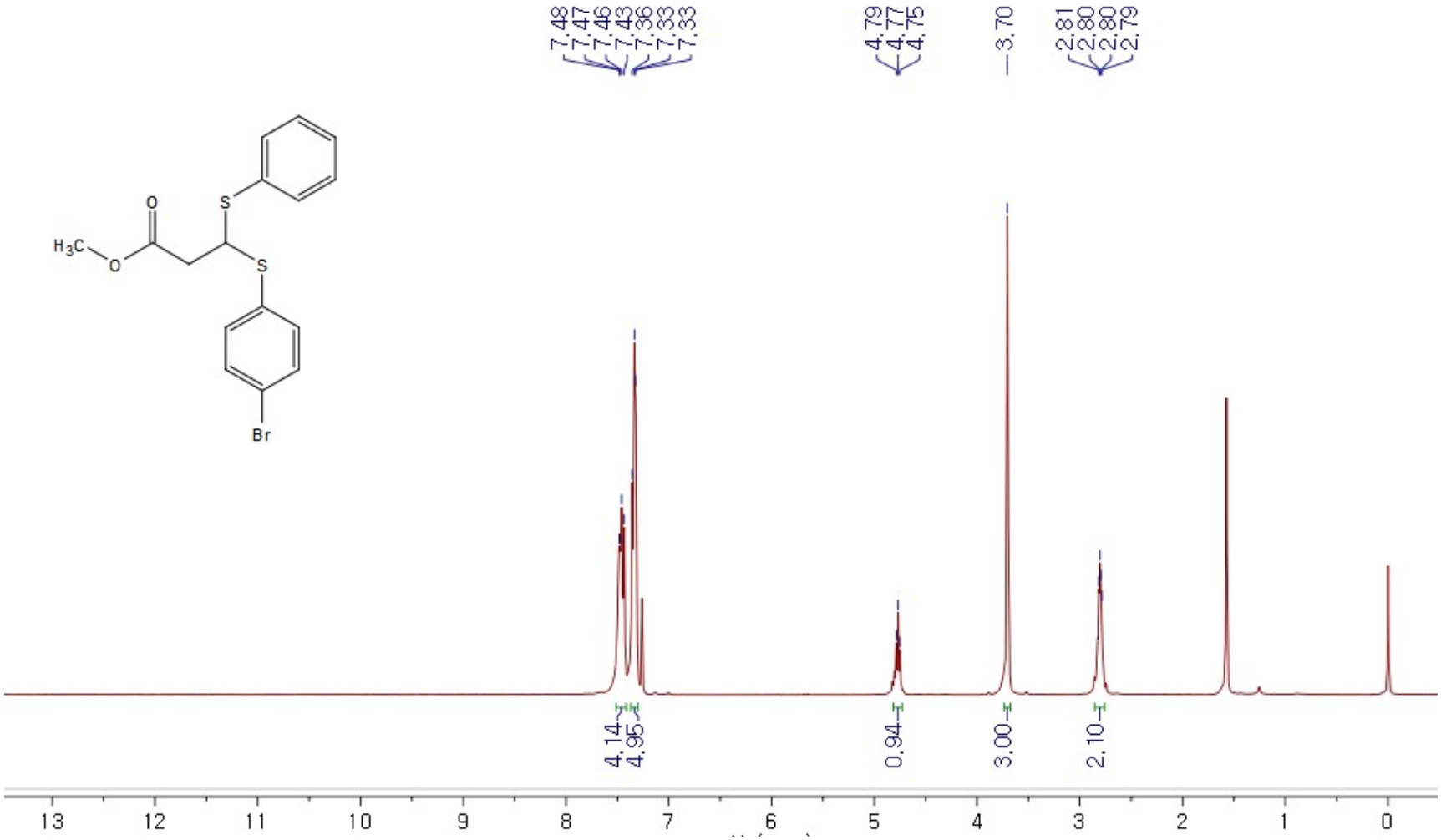
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Decyl(3-phenyl-1-(phenylthio)propyl)sulfane **(3fa)**



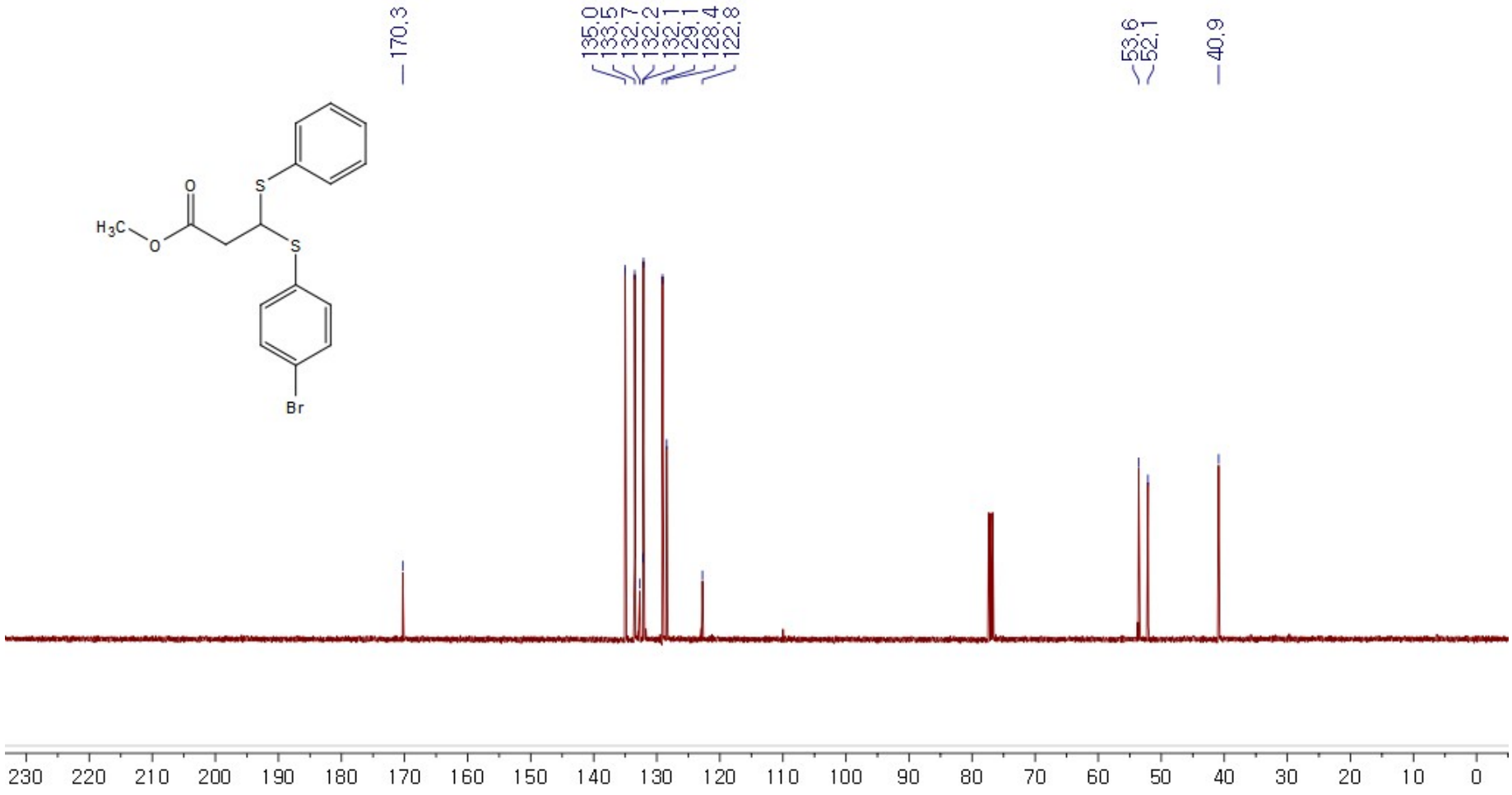
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Decyl(1-(isopentylthio)-3-phenylpropyl)sulfane **(3fo)**



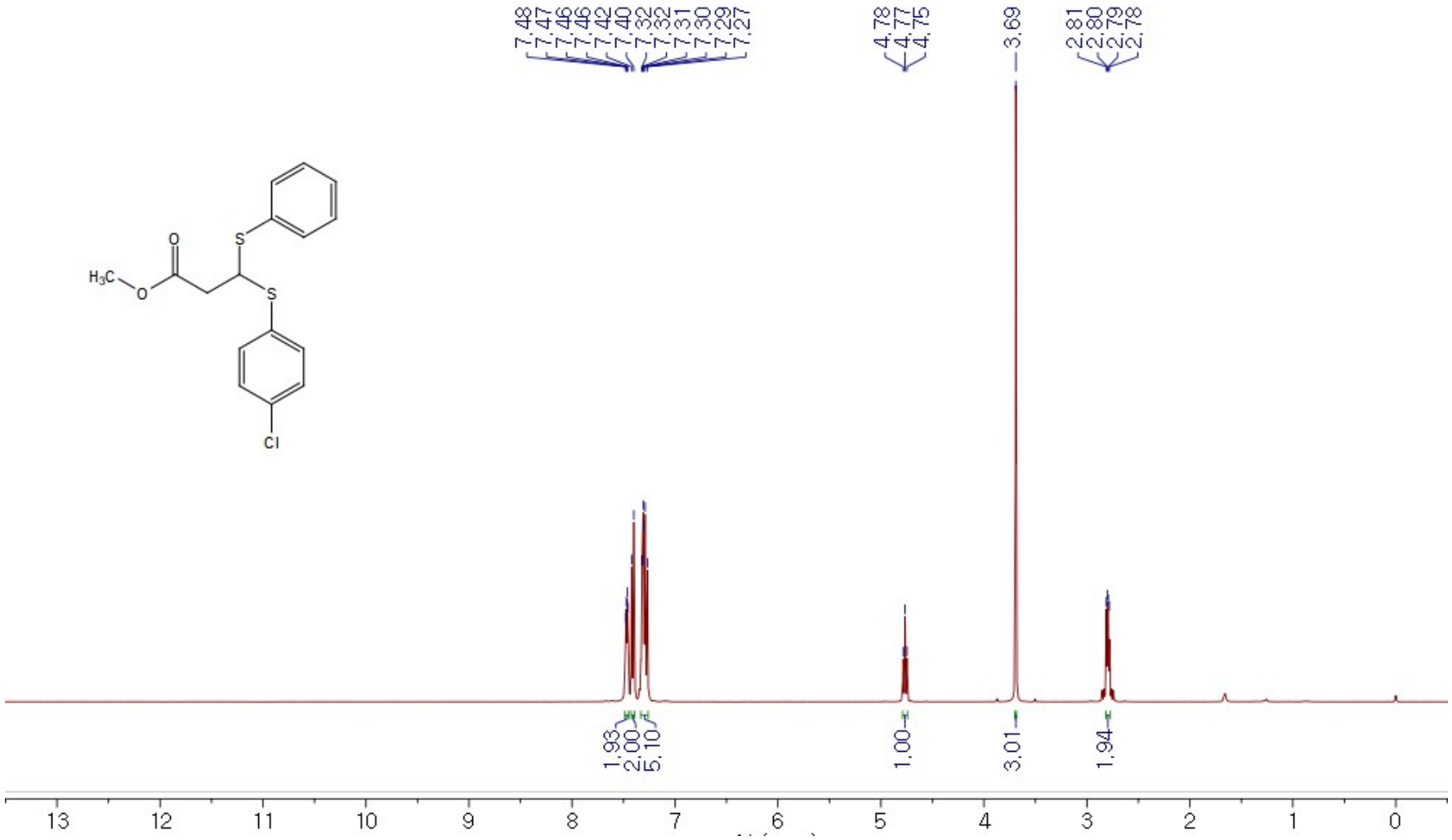
^{13}C NMR (100 MHz, $CDCl_3$) spectra of decyl(1-(isopentylthio)-3-phenylpropyl)sulfane **(3fo)**



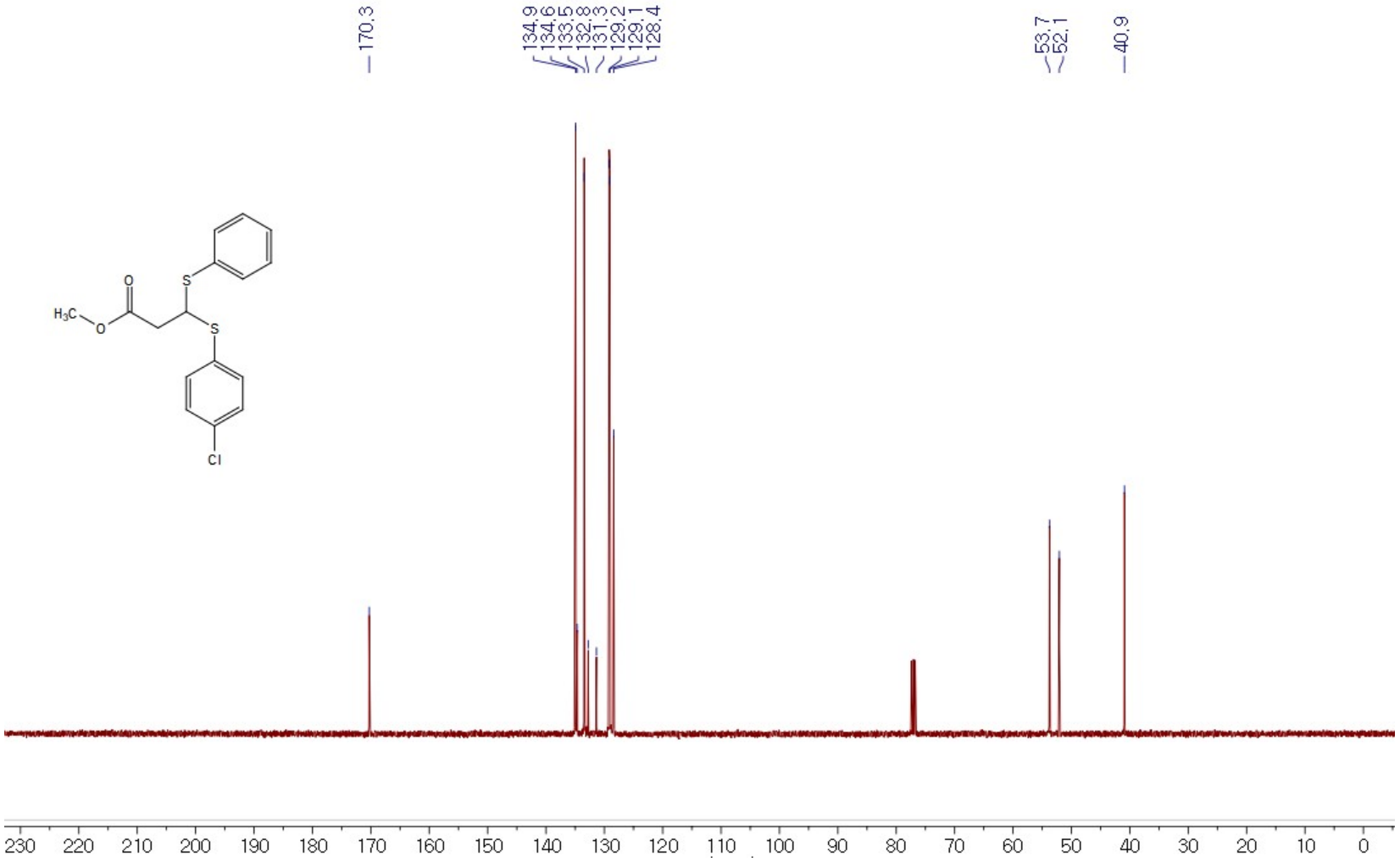
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(phenylthio)propanoate **(3gc)**



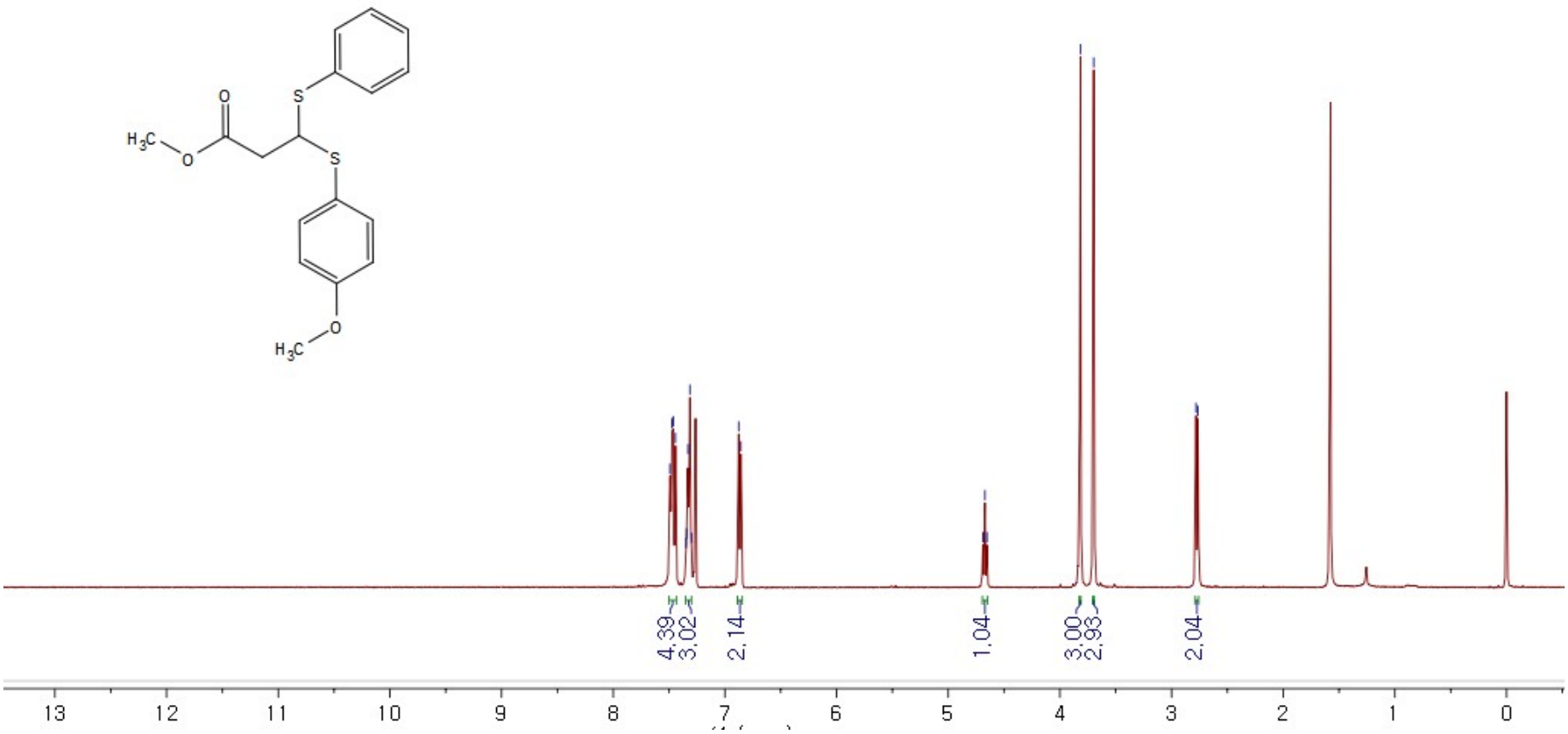
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-((4-bromophenyl)thio)-3-(phenylthio)propanoate **(3gc)**



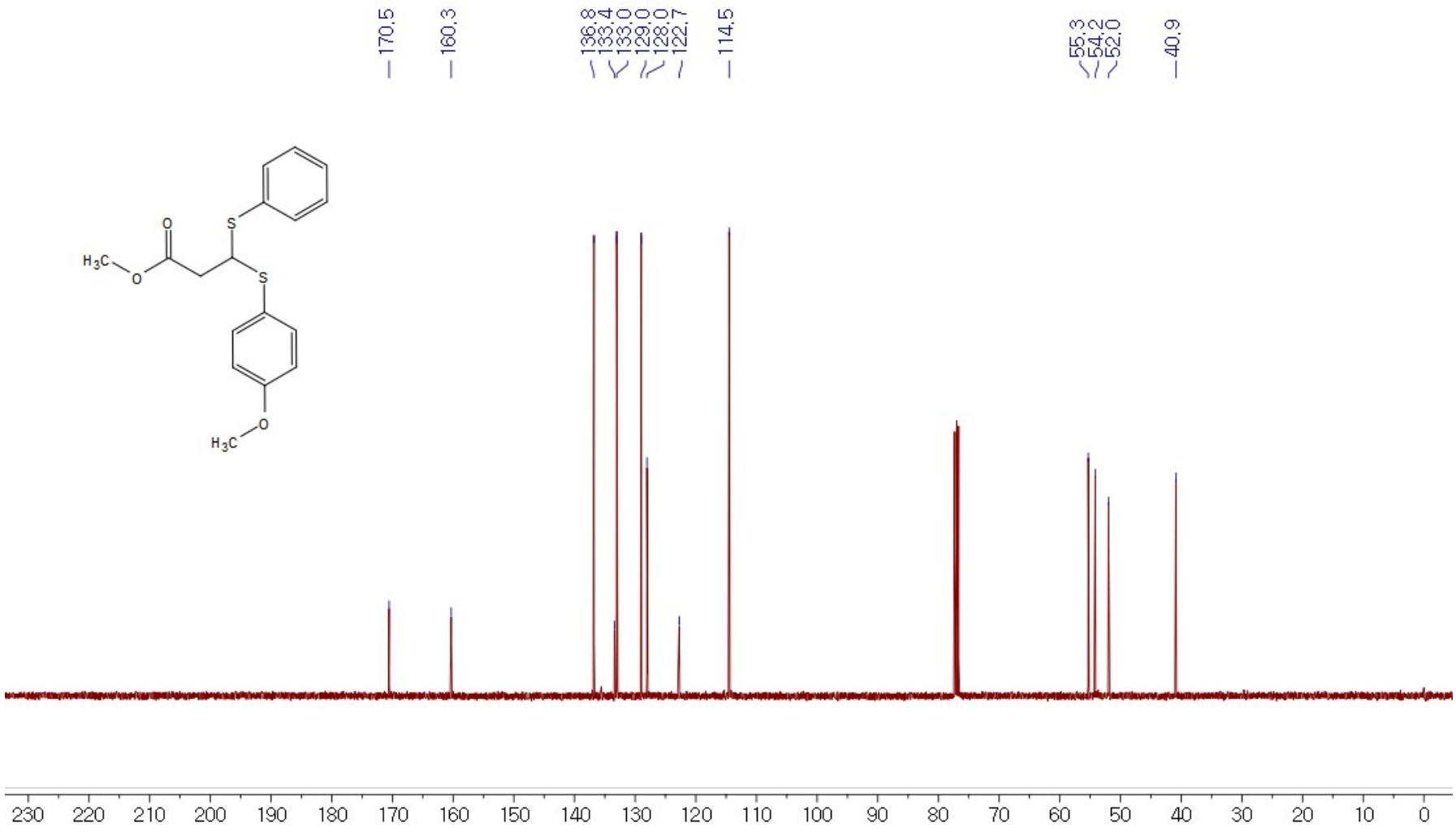
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(phenylthio)propanoate **(3gd)**



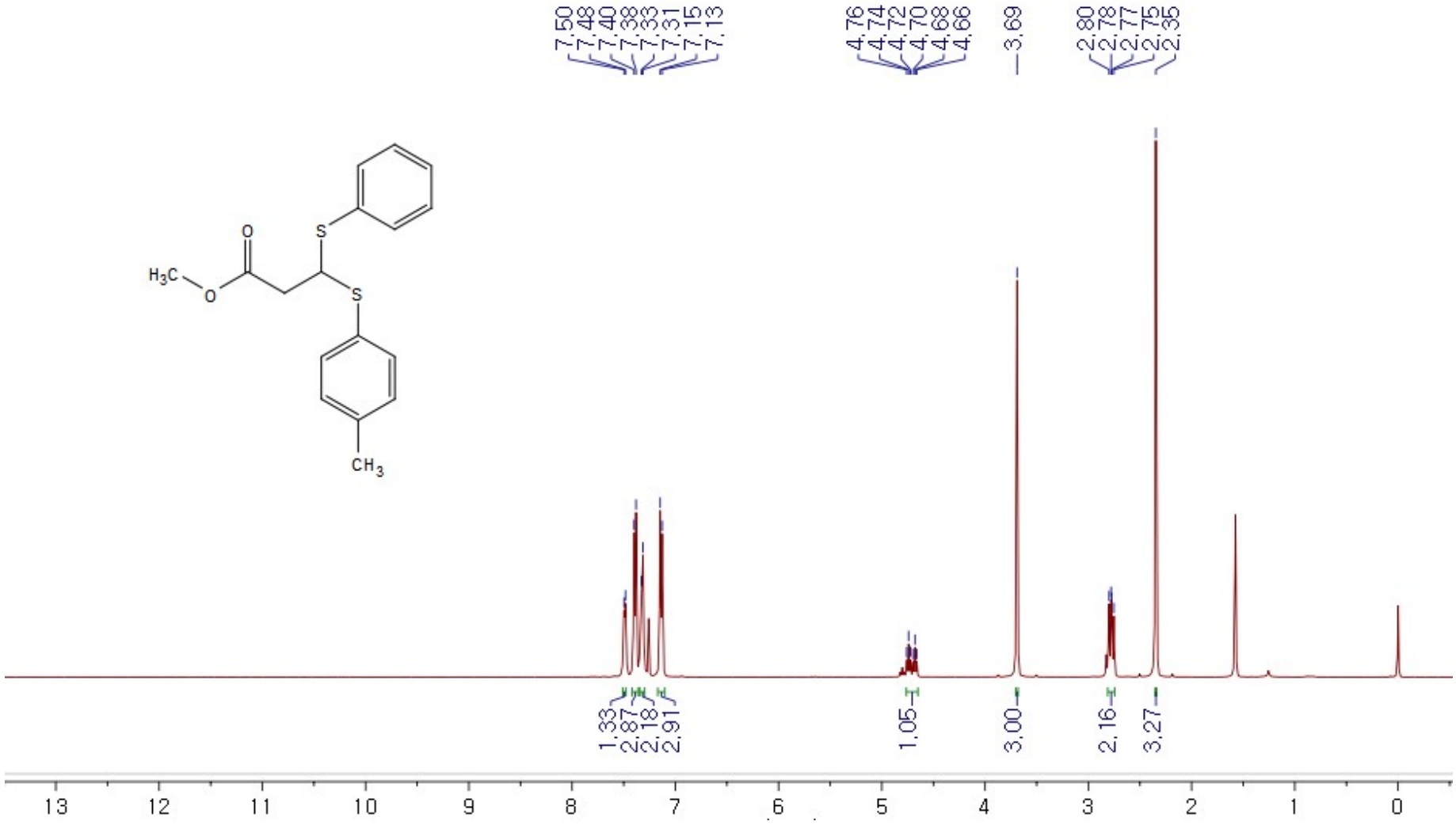
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-((4-chlorophenyl)thio)-3-(phenylthio)propanoate **(3gd)**



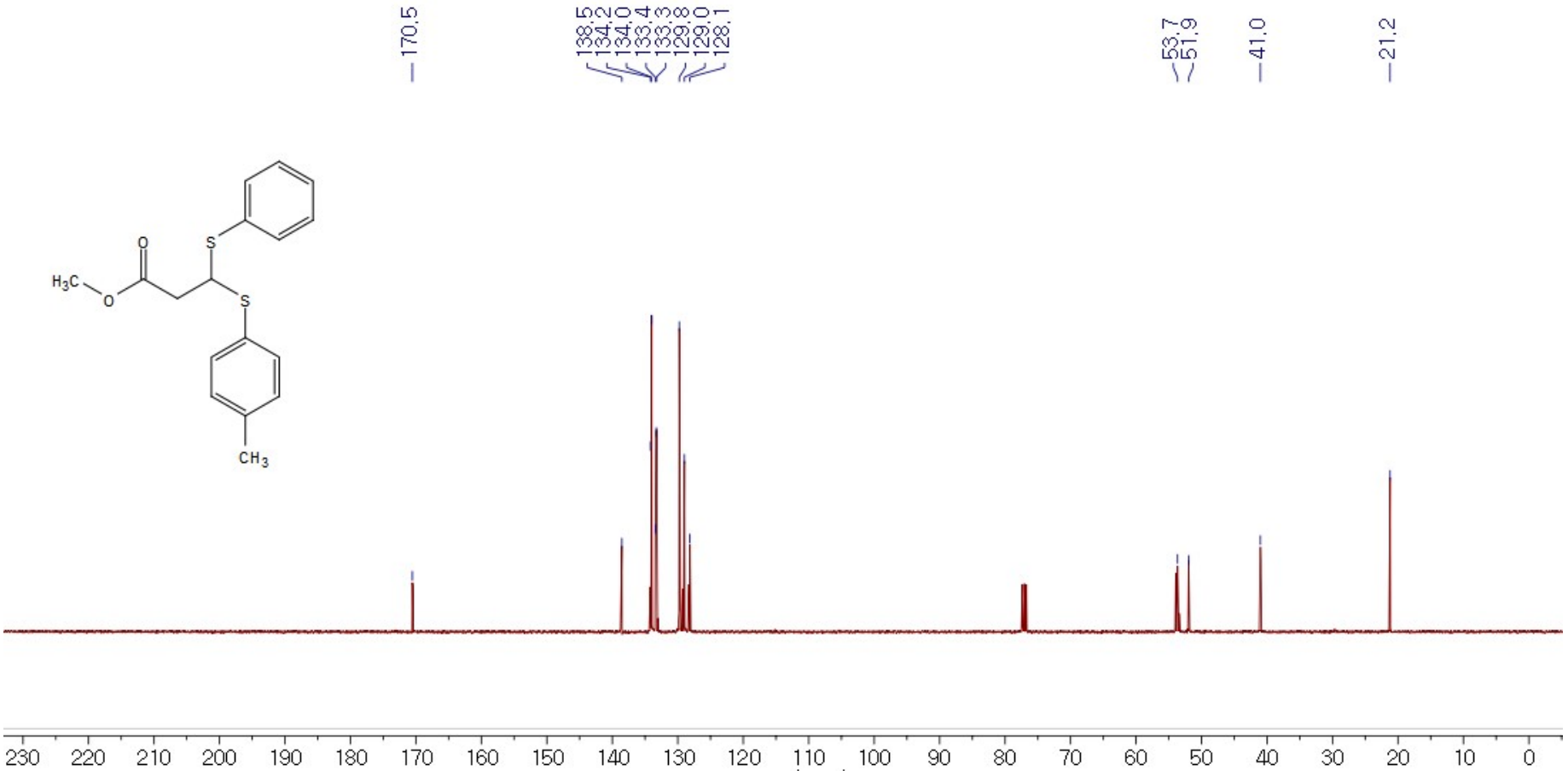
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-((4-methoxyphenyl)thio)-3-(phenylthio)propanoate **(3gf)**



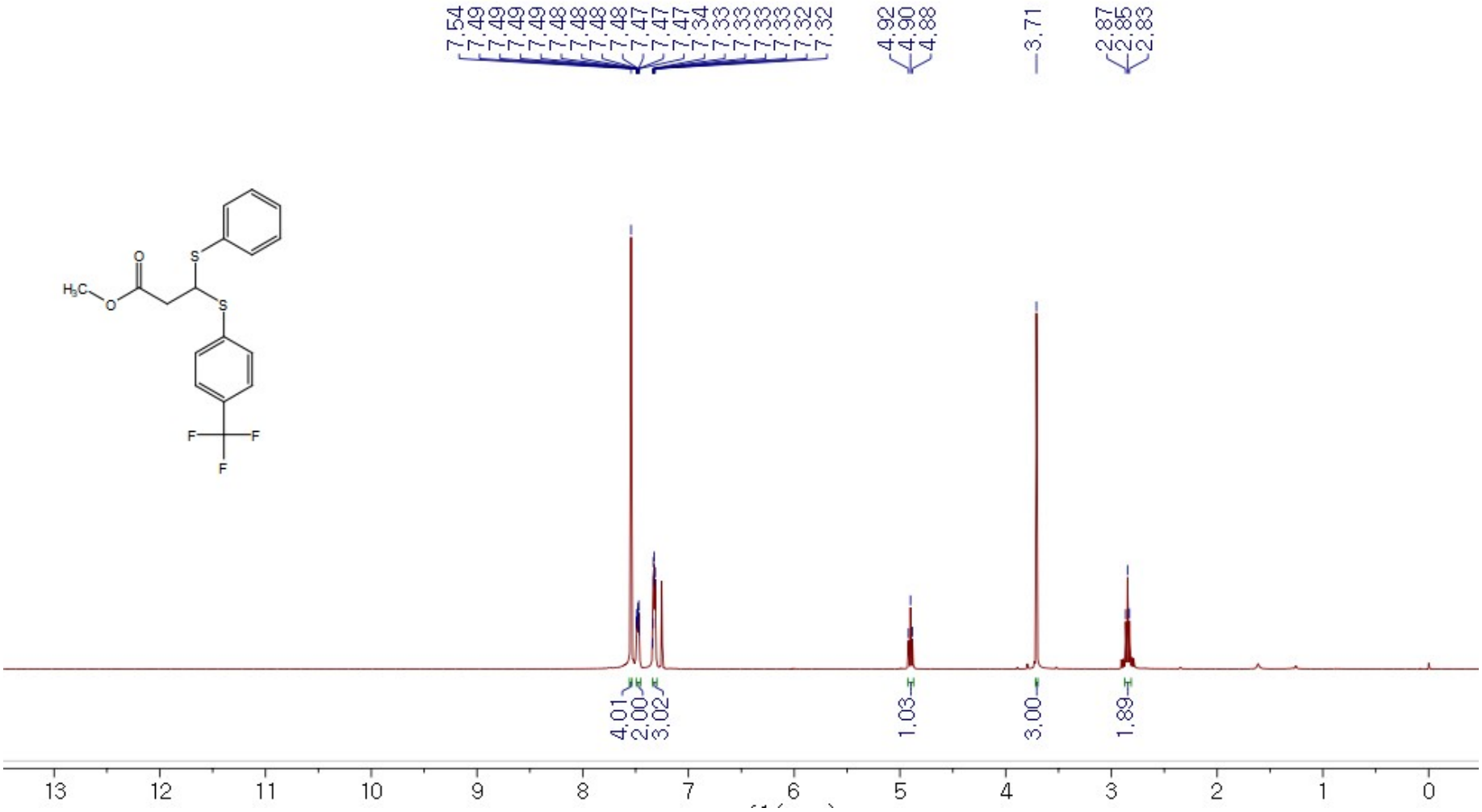
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-((4-methoxyphenyl)thio)-3-(phenylthio)propanoate **(3gf)**



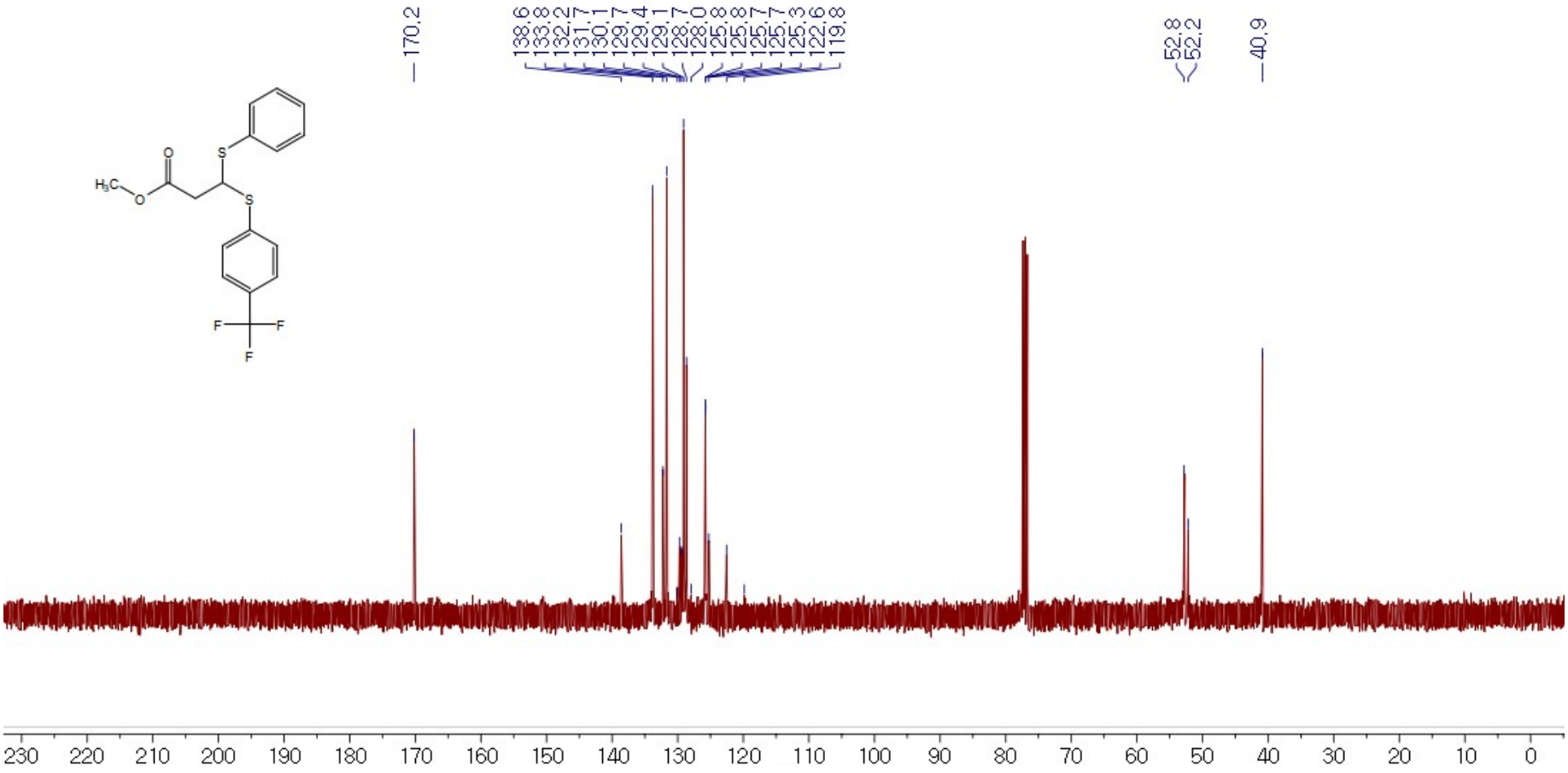
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)-3-(p-tolylthio)propanoate **(3gg)**



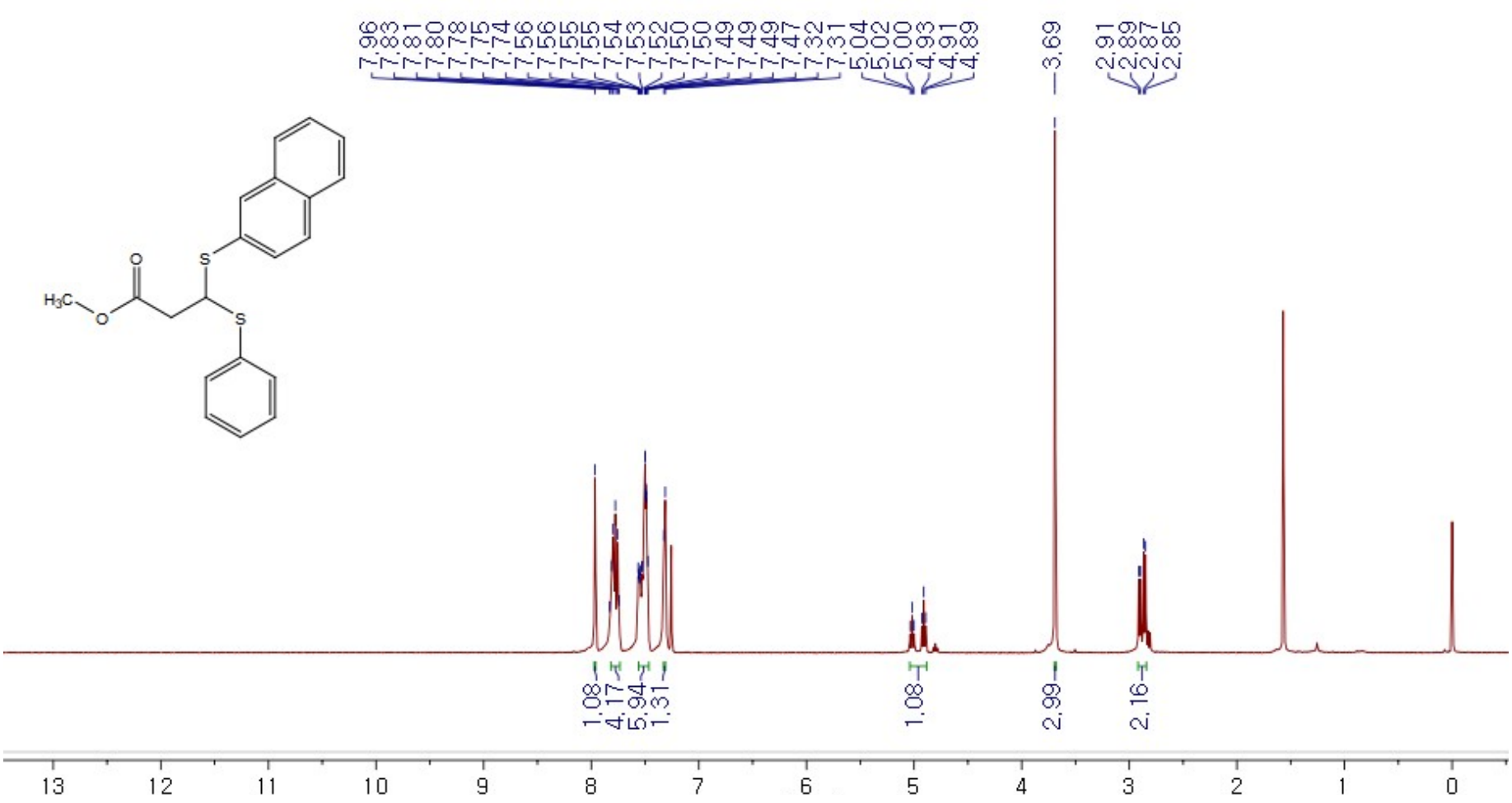
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)-3-(p-tolylthio)propanoate **(3gg)**



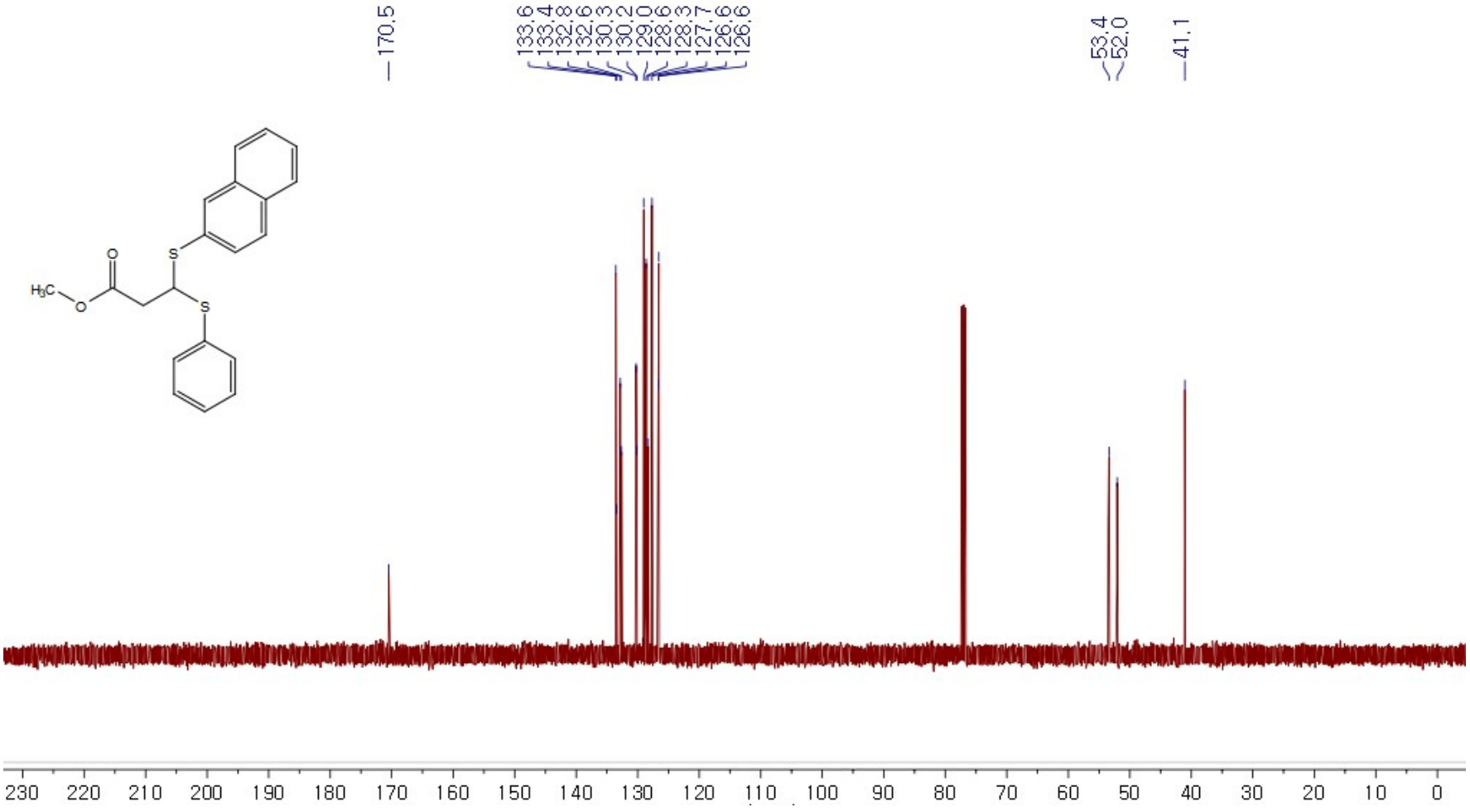
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate **(3gh)**



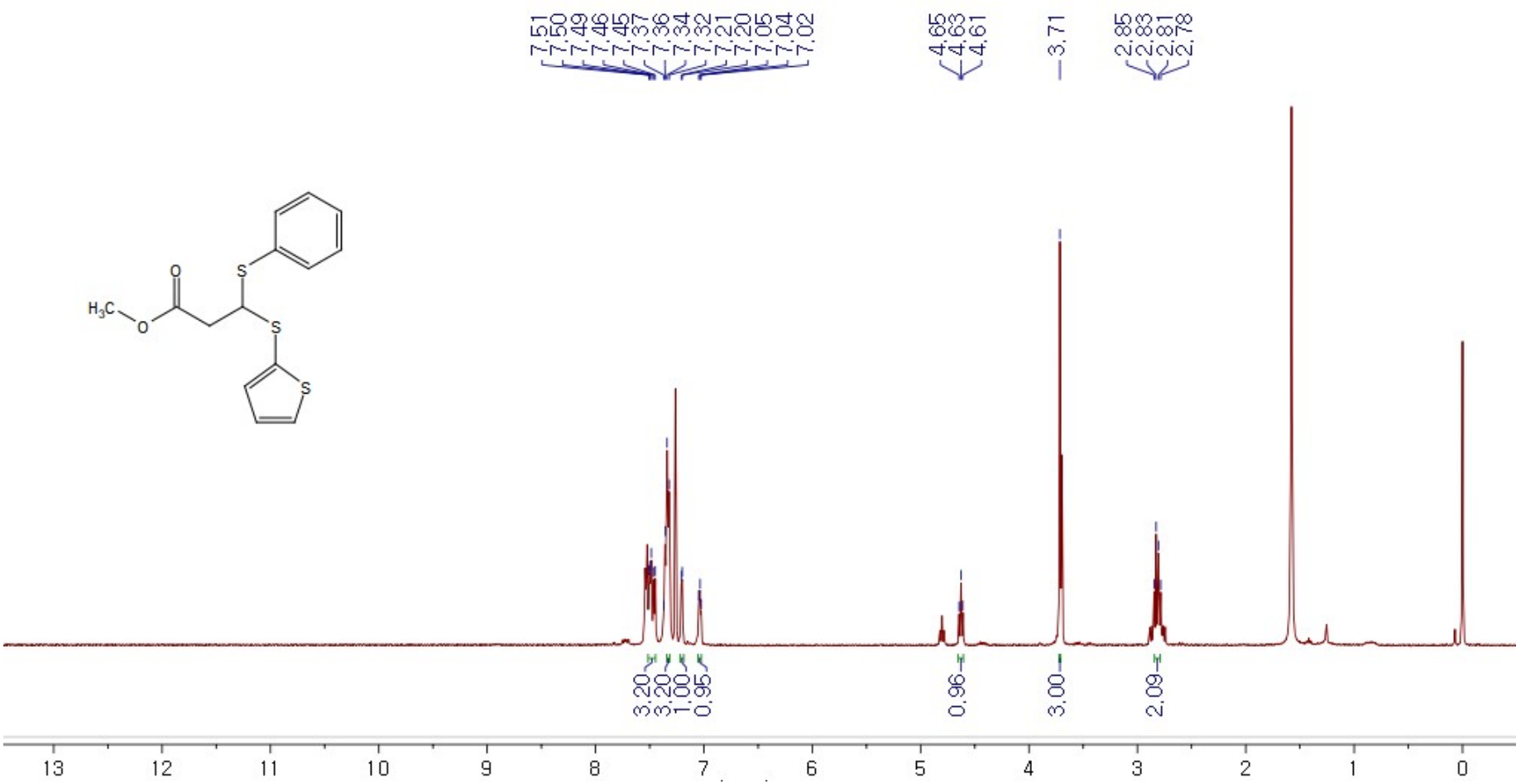
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)-3-((4-(trifluoromethyl)phenyl)thio)propanoate **(3gh)**



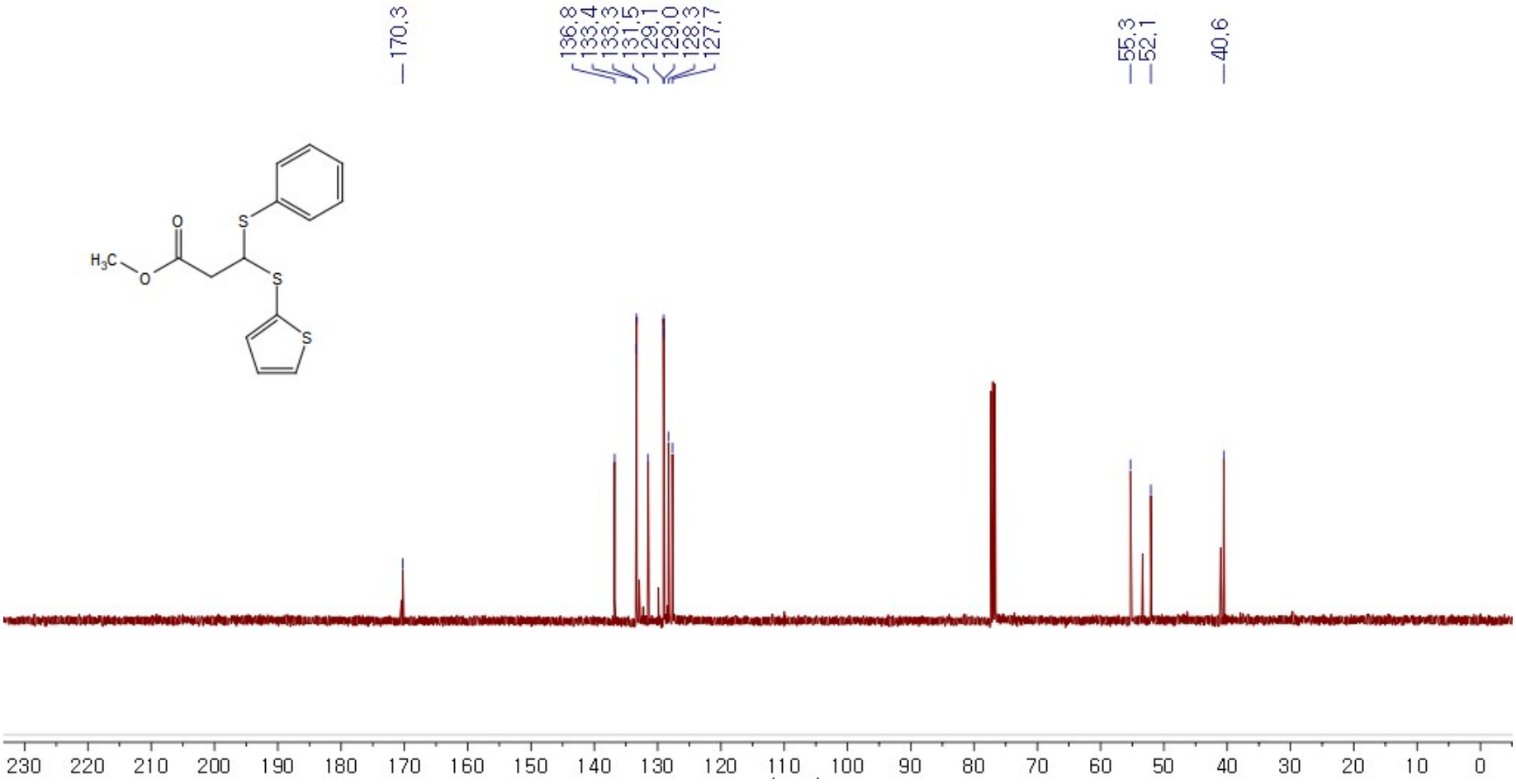
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate **(3gi)**



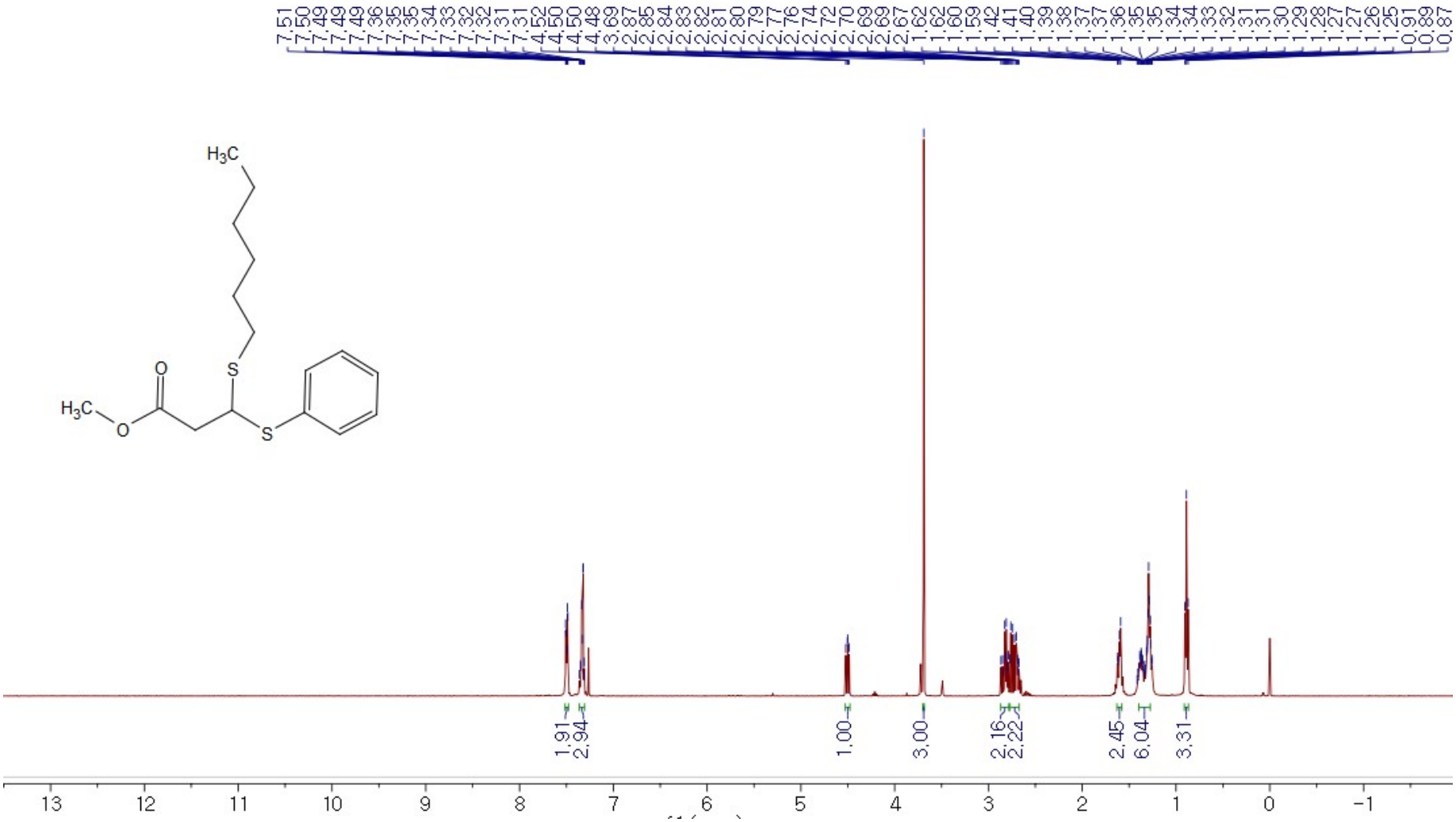
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(naphthalen-2-ylthio)-3-(phenylthio)propanoate **(3gi)**



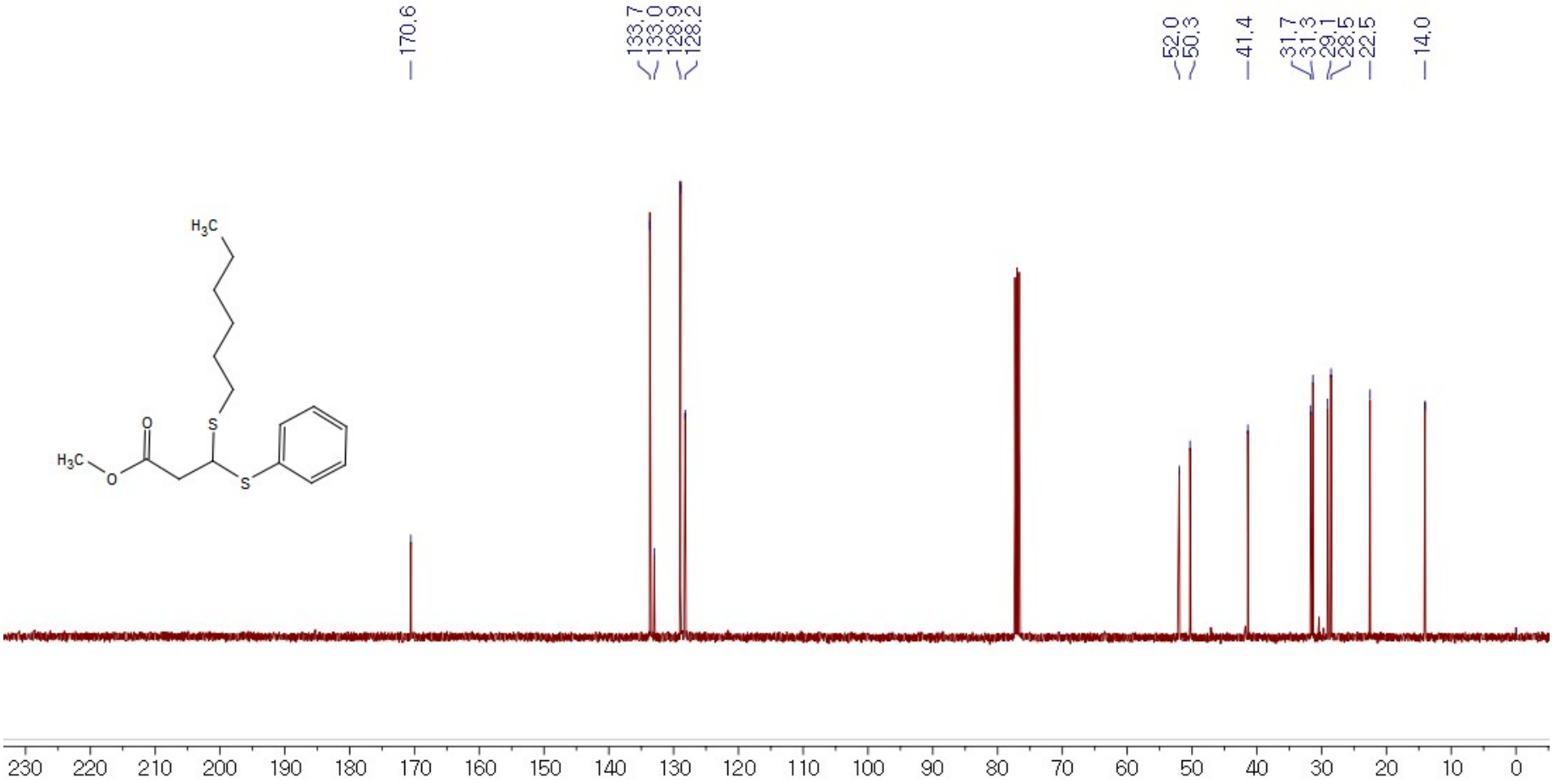
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)-3-(thiophen-2-ylthio)propanoate **(3gj)**



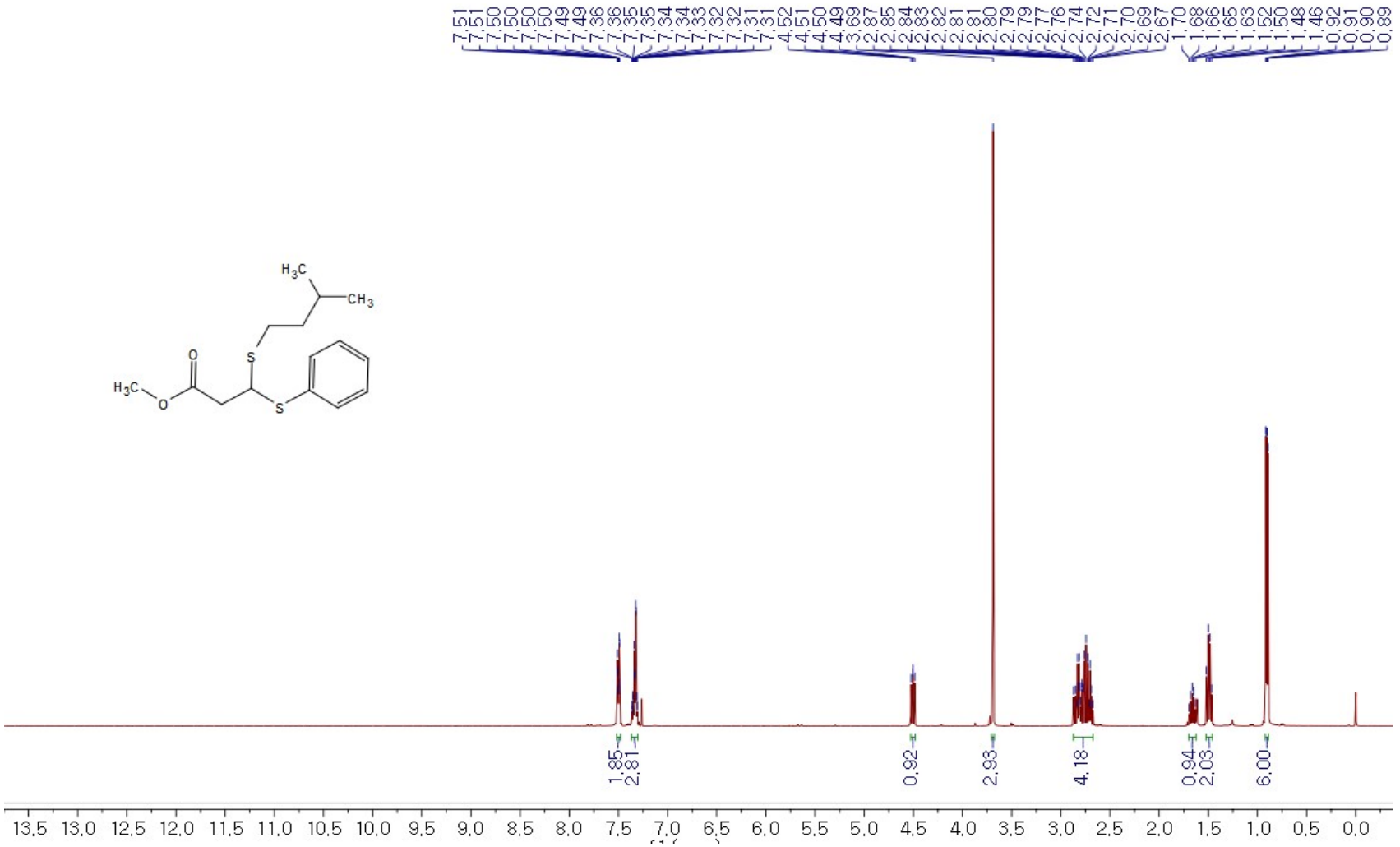
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)-3-(thiophen-2-ylthio)propanoate **(3gj)**



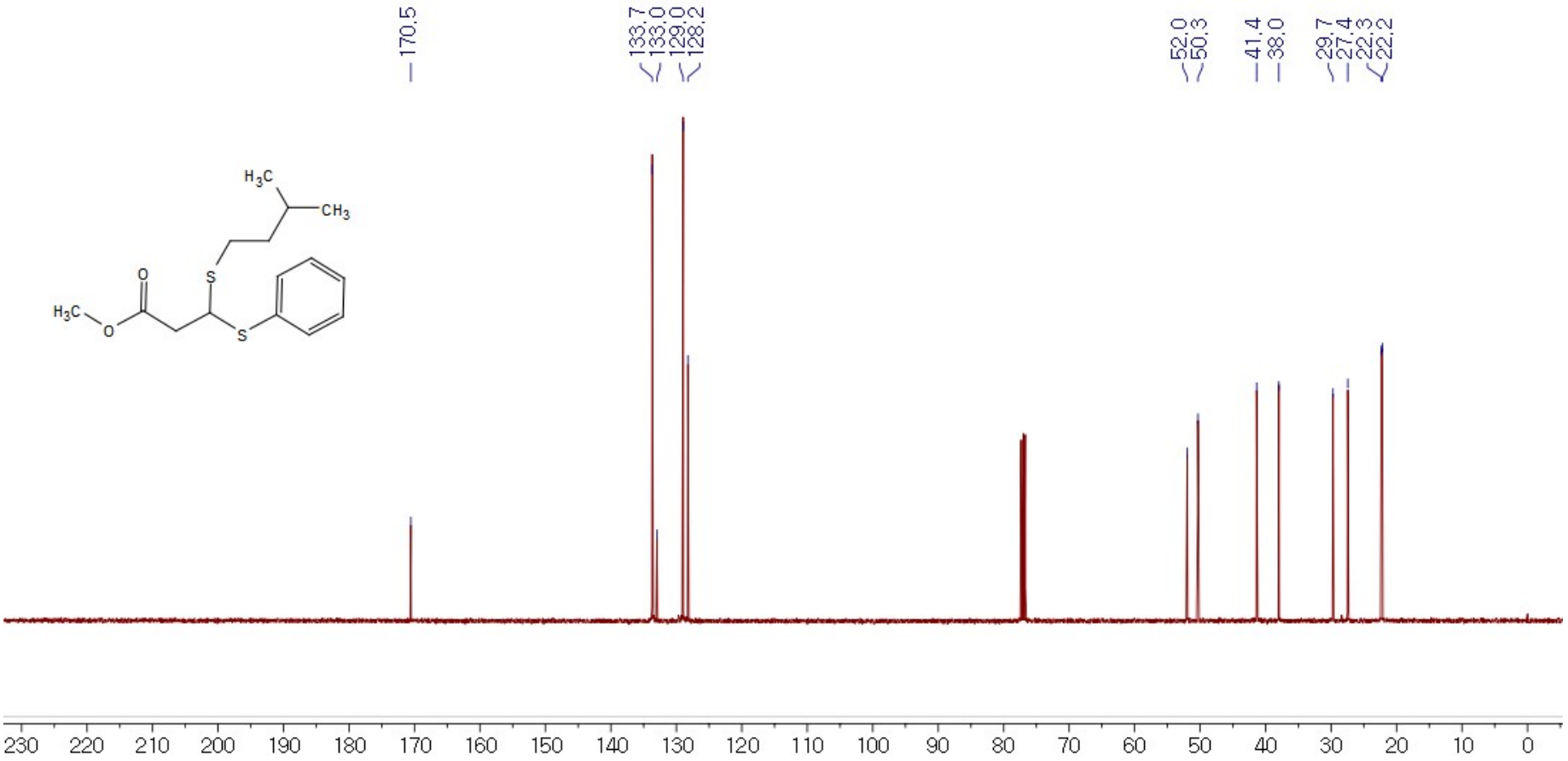
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(hexylthio)-3-(phenylthio)propanoate **(3gl)**



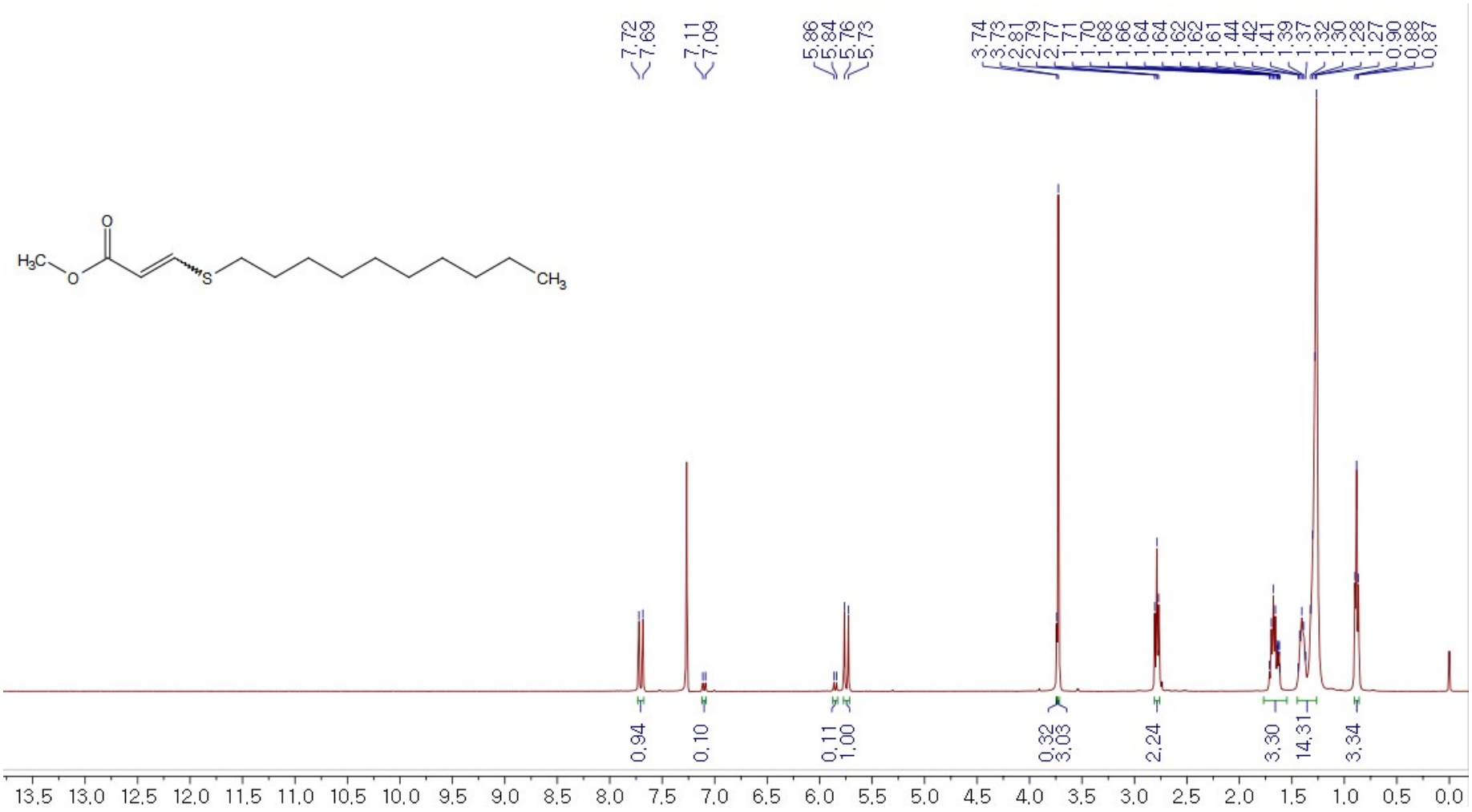
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(hexylthio)-3-(phenylthio)propanoate **(3gl)**



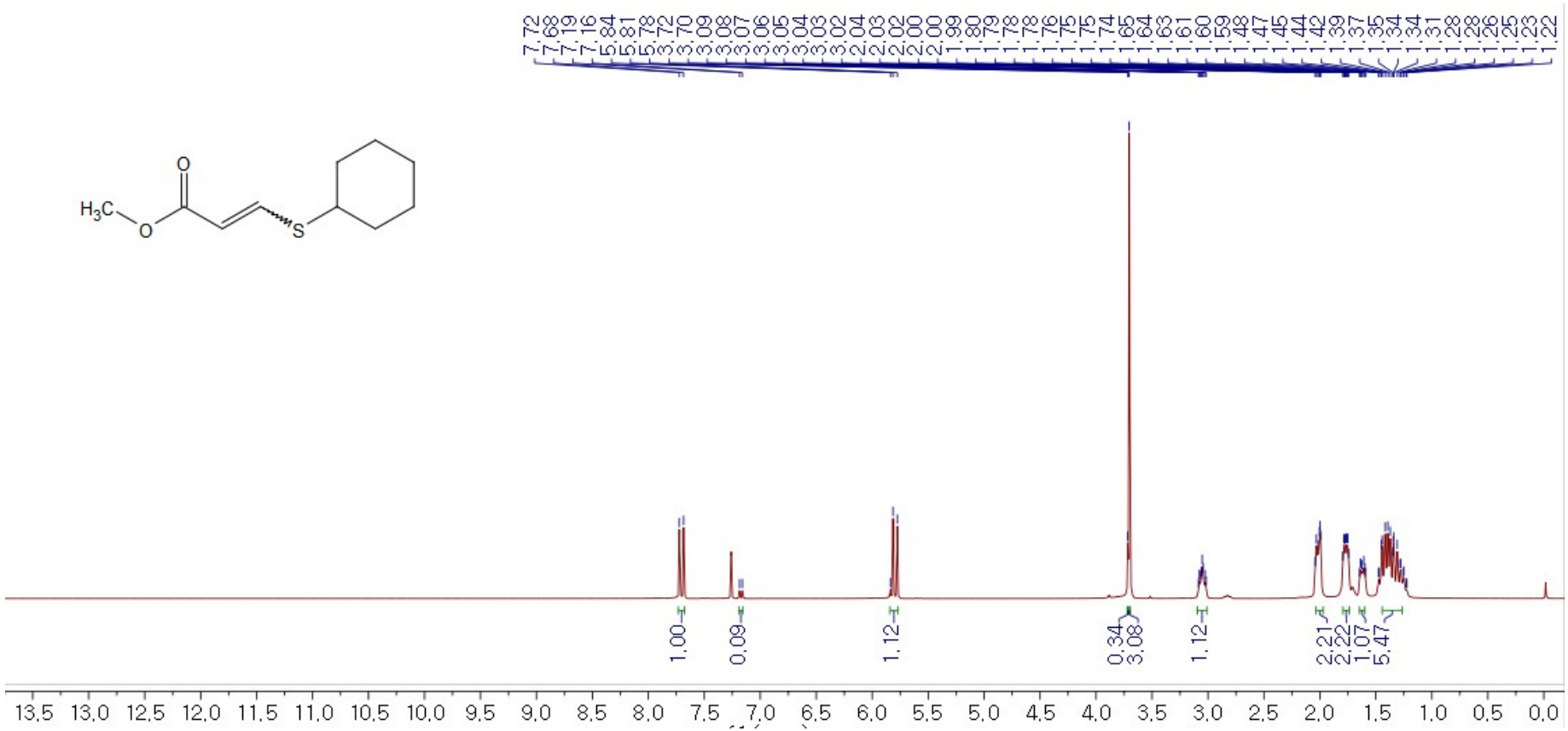
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(isopentylthio)-3-(phenylthio)propanoate **(3go)**



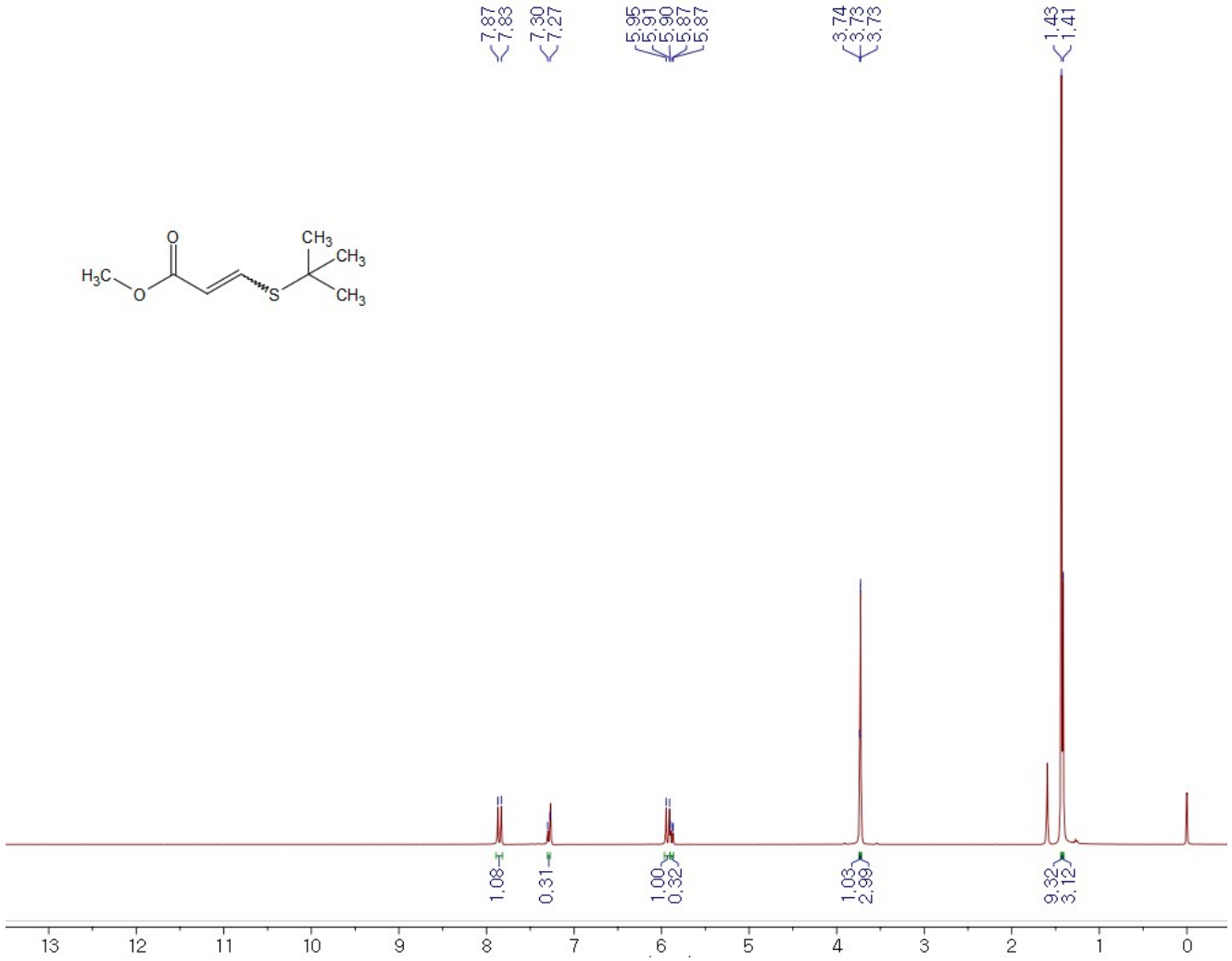
^{13}C NMR (100 MHz, $CDCl_3$) spectra of Methyl 3-(isopentylthio)-3-(phenylthio)propanoate **(3go)**



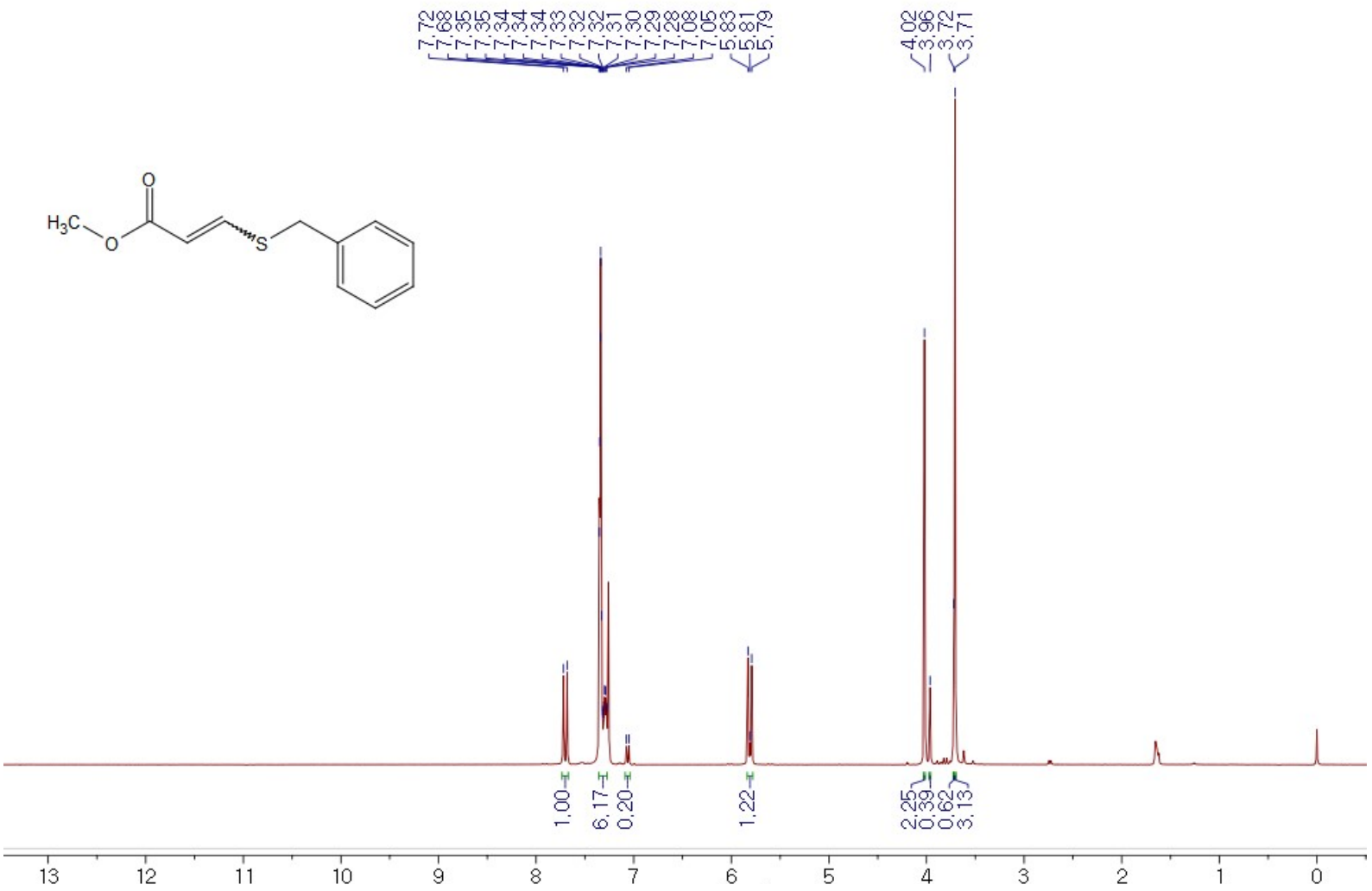
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(decylthio)acrylate **(1a)**



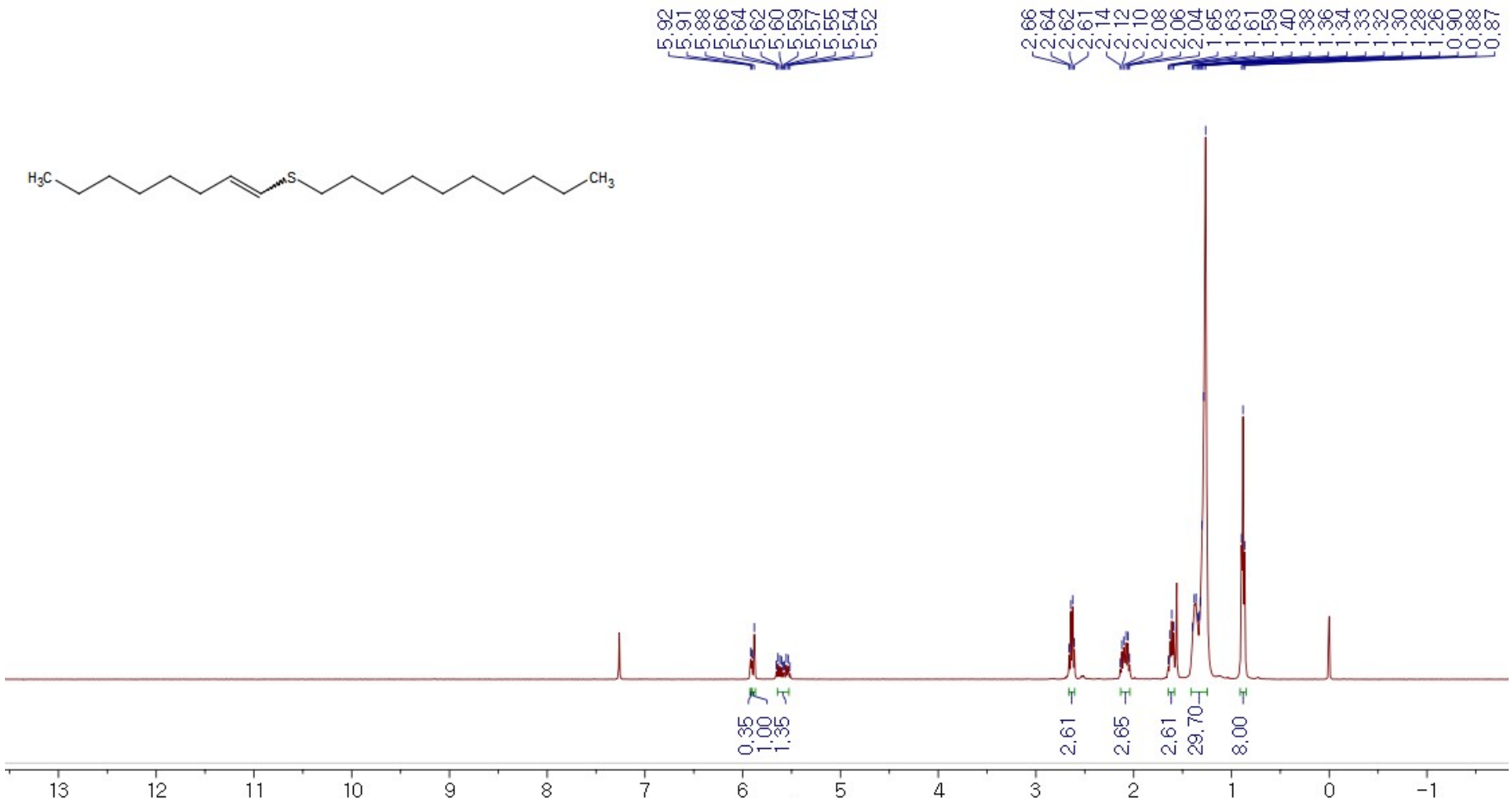
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(cyclohexylthio)acrylate **(1b)**



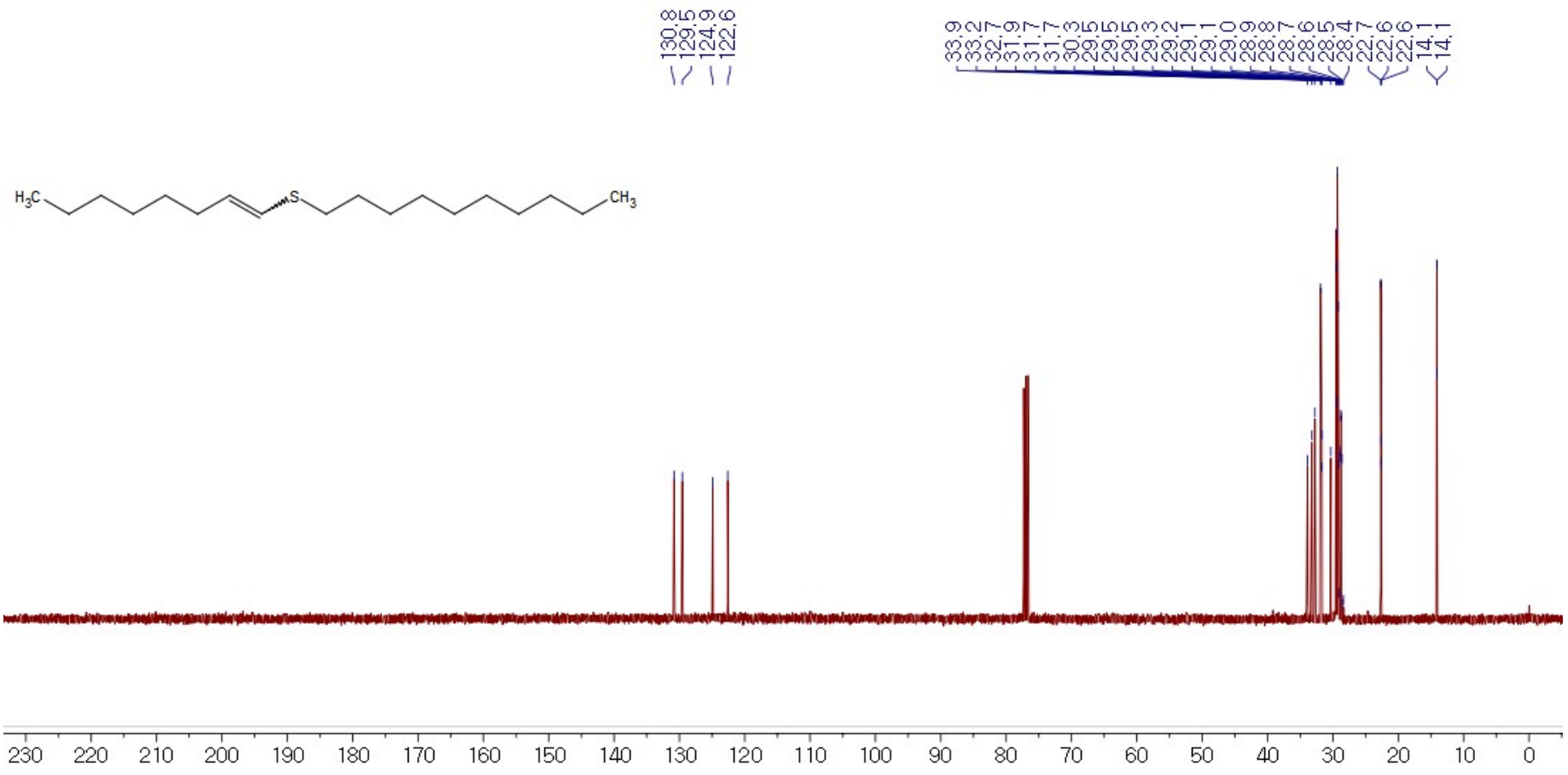
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(tert-butylthio)acrylate **(1c)**



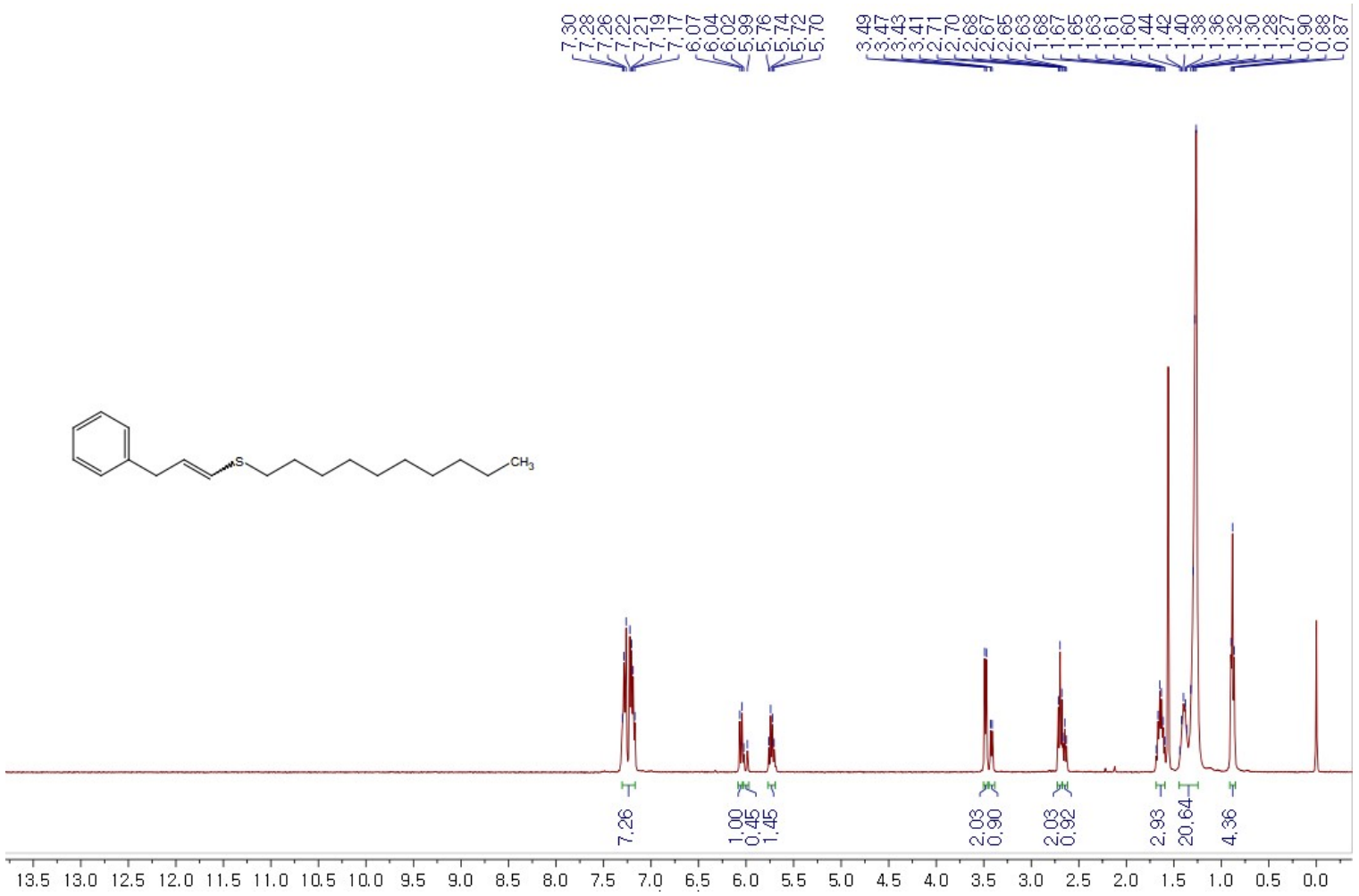
^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(benzylthio)acrylate **(1d)**



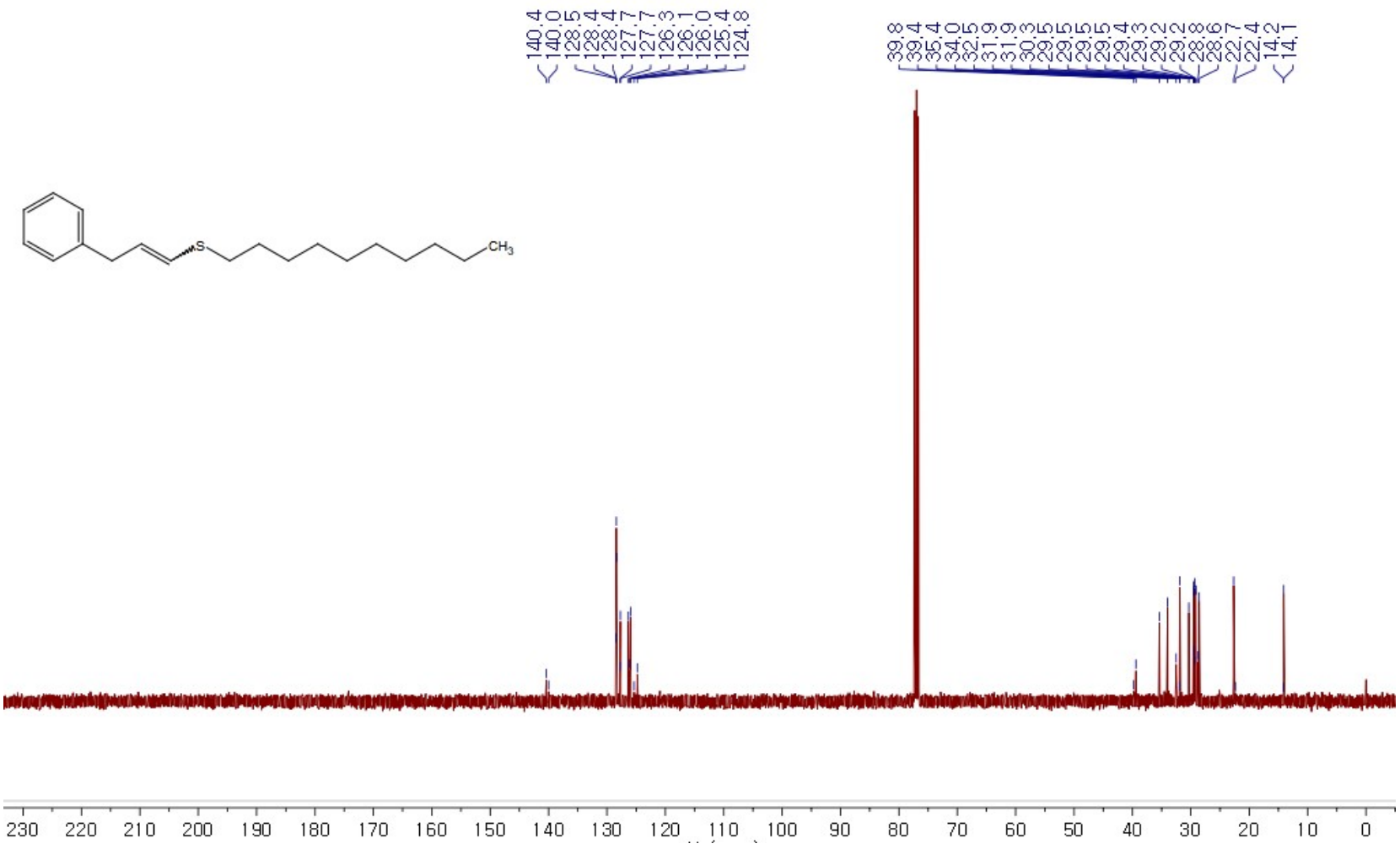
^{1}H NMR (400 MHz, $CDCl_3$) spectra of decyl(oct-1-en-1-yl)sulfane **(1e)**



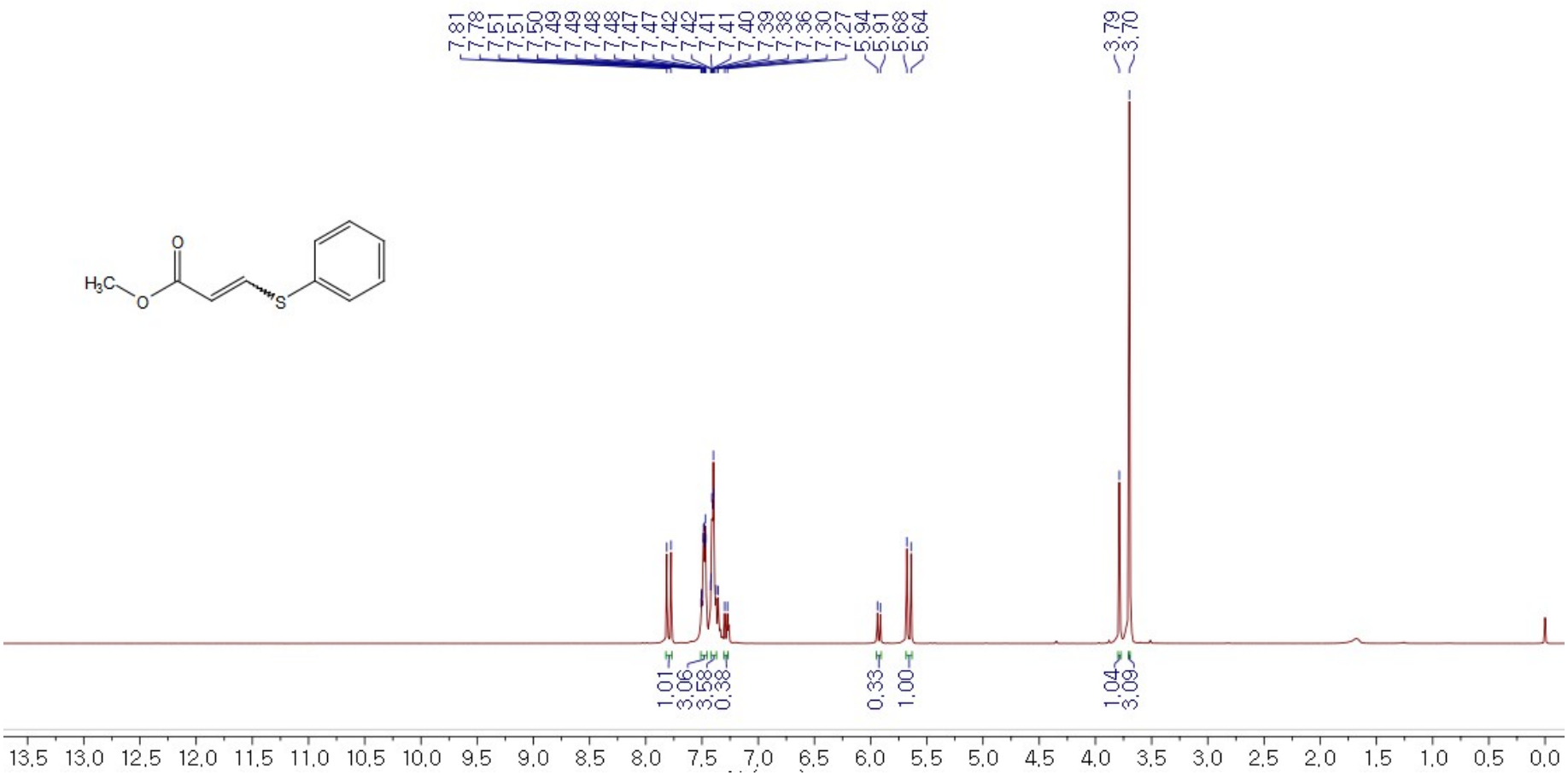
^{13}C NMR (100 MHz, $CDCl_3$) spectra of decyl(oct-1-en-1-yl)sulfane **(1e)**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of decyl(3-phenylprop-1-en-1-yl)sulfane **(1f)**



^{13}C NMR (100 MHz, $CDCl_3$) spectra of decyl(3-phenylprop-1-en-1-yl)sulfane **(1f)**



^{1}H NMR (400 MHz, $CDCl_3$) spectra of Methyl 3-(phenylthio)acrylate **(1g)**