SUPPORTING INFORMATION

Catalytic Asymmetric Synthesis Using Feedstocks. An Enantioselective Route to 2-Arylpropionic Acids and 2-Arylethyl Amines via Hydrovinylation of Vinylarenes

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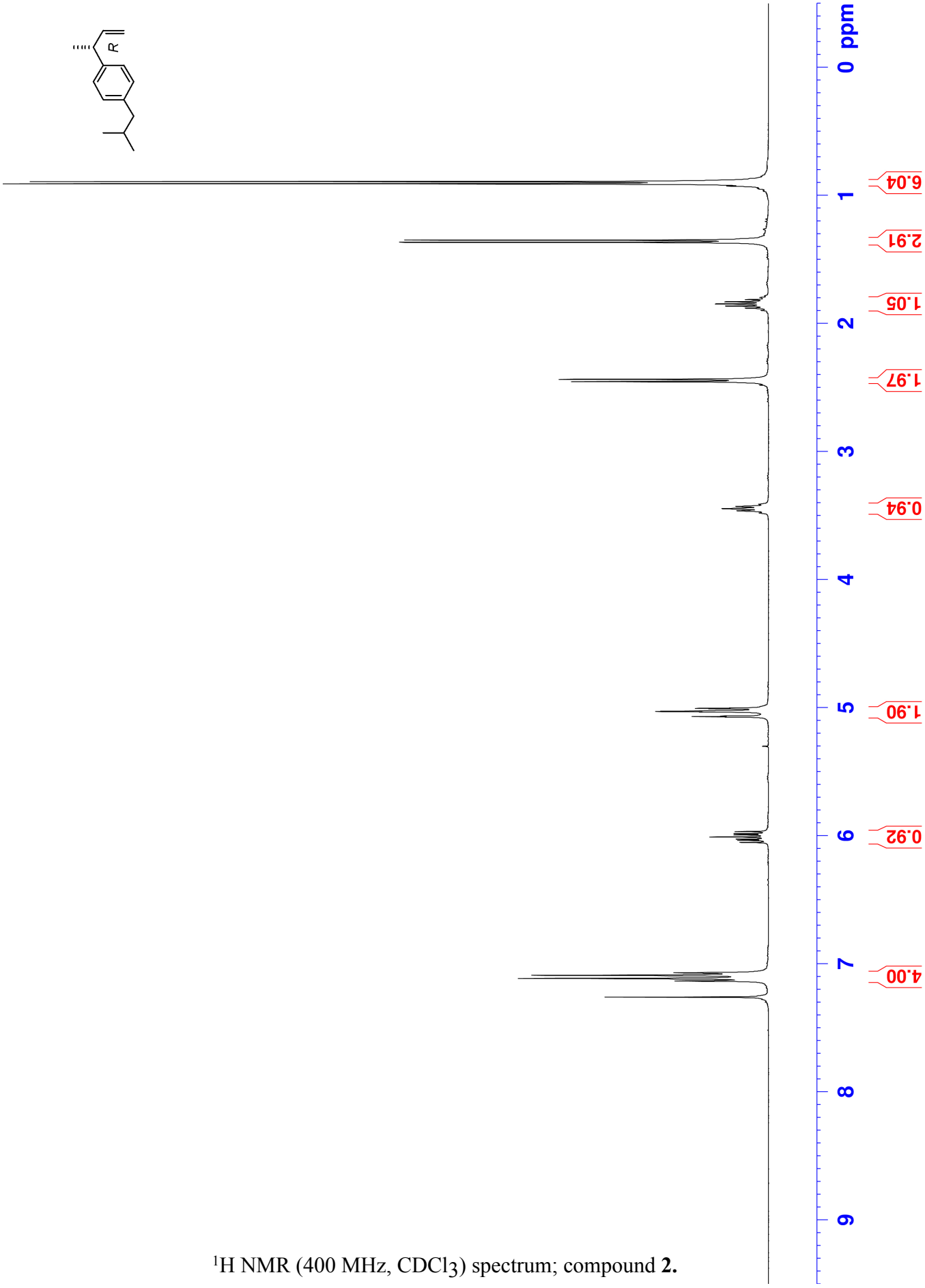
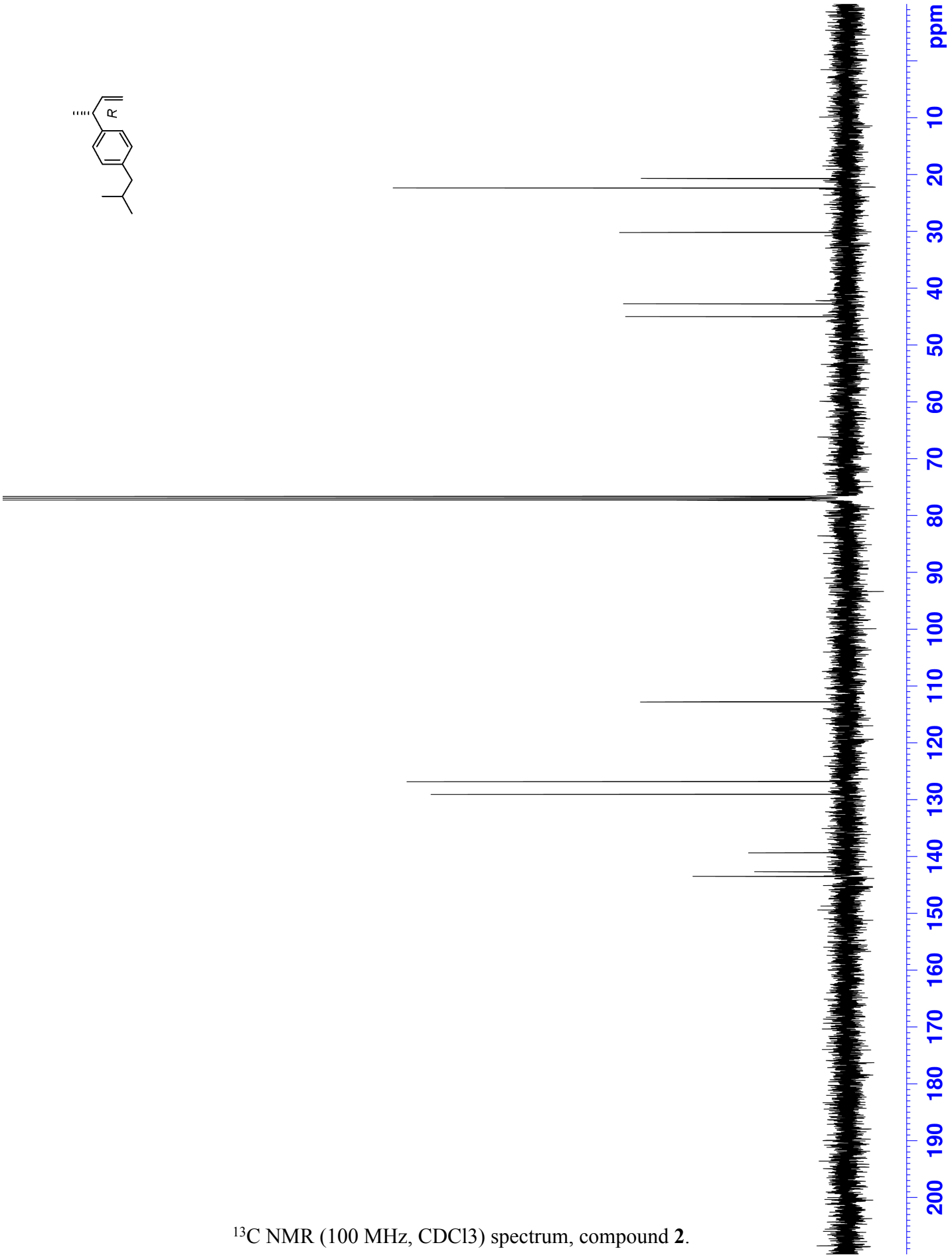
General methods. Reactions requiring air–sensitive manipulations were conducted under an inert atmosphere of nitrogen using Schlenk techniques or in a Vacuum Atmospheres glovebox. Methylene chloride was distilled from calcium hydride under a dry atmosphere and stored over molecular sieves. Tetrahydrofuran was distilled under nitrogen from sodium/benzophenone ketyl. Olefins were made from Wittig reactions of the corresponding aldehydes with triphenylphosphonium bromide in the presence of *n*-BuLi in THF at reflux or via a palladacycle-mediated Heck reaction[1] of the corresponding aryl bromide with ethylene. $Na^+[[3,5\text{-}(CF_3)_2C_6H_3]_4B]^-$ (NaBARF) and ligand[2,3] were prepared according to the literature. Ethylene (99.5%) was purchased from Matheson Inc., and passed through Drierite® before use. Analytical TLC was performed on precoated (0.25 mm) silica gel 60 F254 plates (olefins stained with $KMnO_4$; acids stained with bromocresol green). Flash column chromatography was carried out on silica gel 40. All chiral stationary phase gas chromatographic separations of the 2-arylpropionic acids were achieved via conversion of the acid to the (*L*)-menthyl ester. Enantiomeric excesses of chiral compounds **2**, **3**, **5**, **6**, and **7** were determined by chiral stationary phase gas chromatographic analyses, which were performed with Cyclodex B (25 m x 0.25 mm, 0.12 mm film thickness) capillary GC column. Enantiomeric excesses of chiral compounds **9**, **11**, **13** and **14** were determined by gas chromatographic analyses via the corresponding (*L*)-(-)-menthyl esters, which were performed on a chromatograph equipped with Chirasil-(*S*)-Val on WCOT fused silica (50 m x 0.25 mm, 0.12 mm film thickness) capillary GC column. Enantiomeric excess of compound **4** was determined by HPLC using a Daicel Chiralcel OJ-H column using hexane/isopropanol as solvents where base-line separation was obtained. Optical rotations were recorded the sodium D line in chloroform.

1. Herrmann, W. A.; Böhm, V. P. W.; Reisinger, C-P. *J. Organomet. Chem.* **1999**, *576*, 23.
2. Smith, C. R.; Zhang, A.; Mans, D.; RajanBabu, T. V. *Org. Synth.* **2008**, *85*, 248.
3. (a) Kobayashi, H.; Sonoda, A.; Iwamoto, H.; Yoshimura, M. *Chem. Lett.* **1981**, *10*, 579. (b) Brookhart, M.; Grant, B.; Volpe, A. F., Jr. *Organometallics*, **1992**, *11*, 3920-3922.

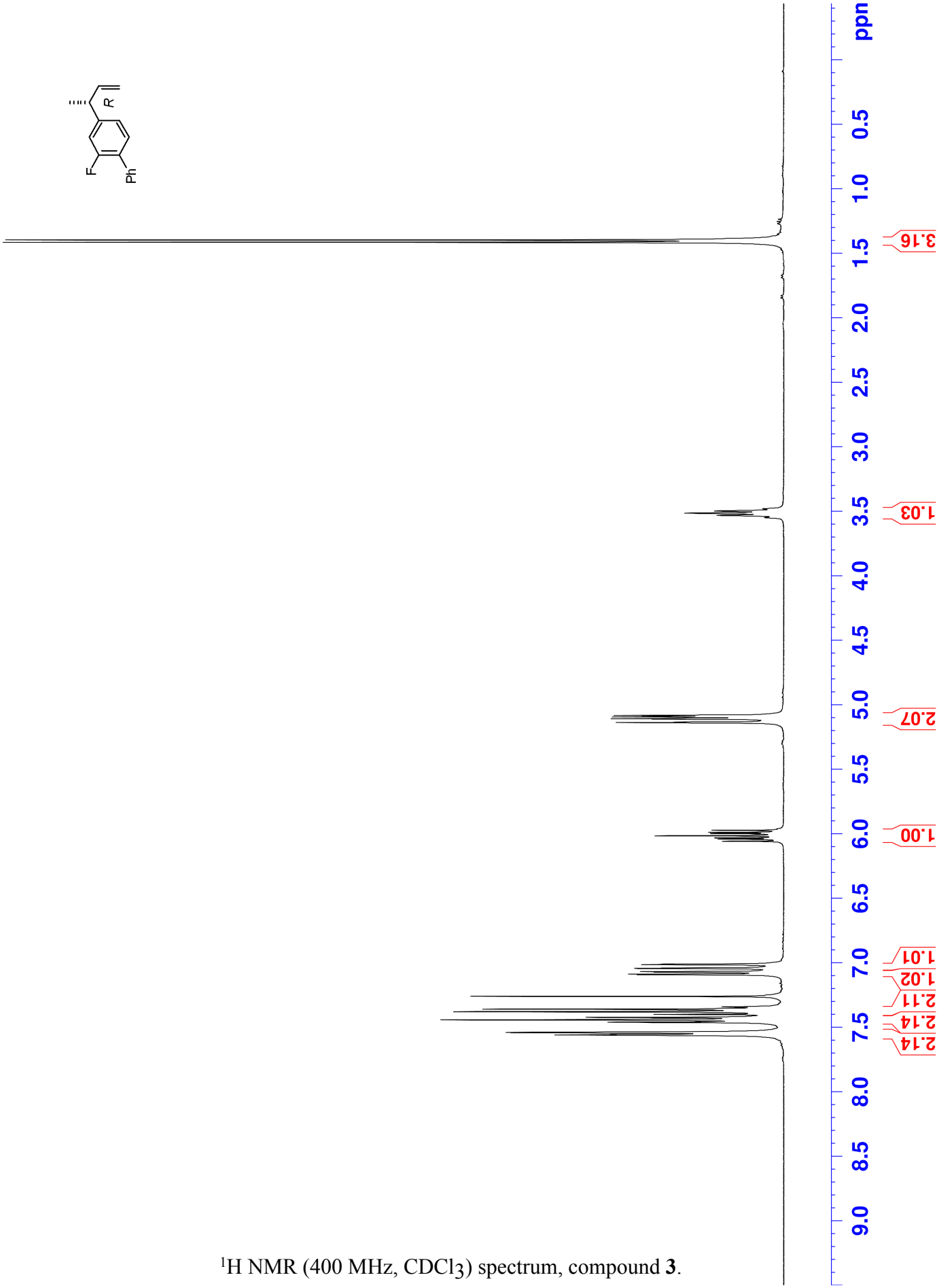
^{1}H and ^{13}C NMR Spectra and Chromatograms of Key Compounds



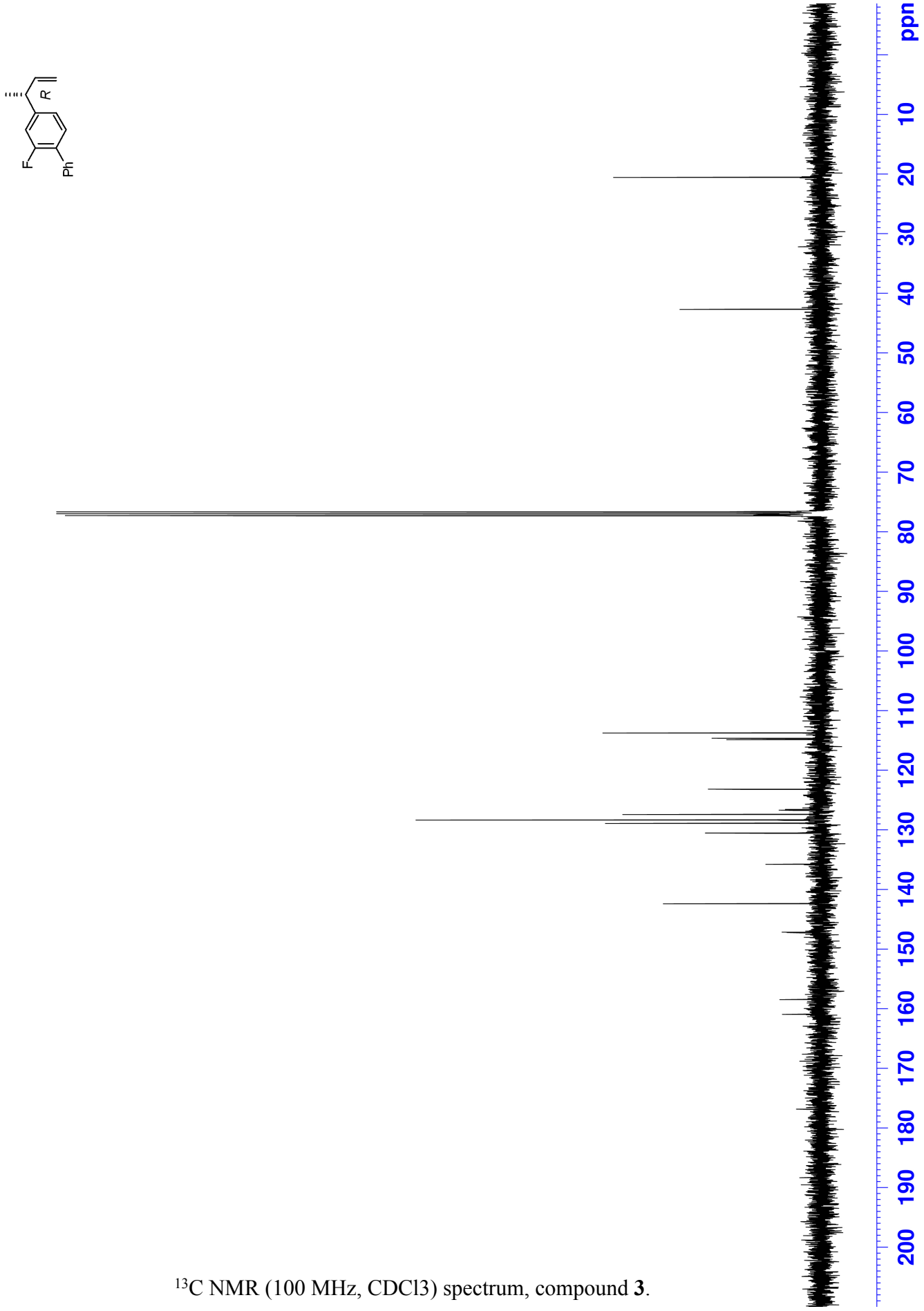
^{1}H NMR (400 MHz, $CDCl_3$) spectrum; compound **2.**



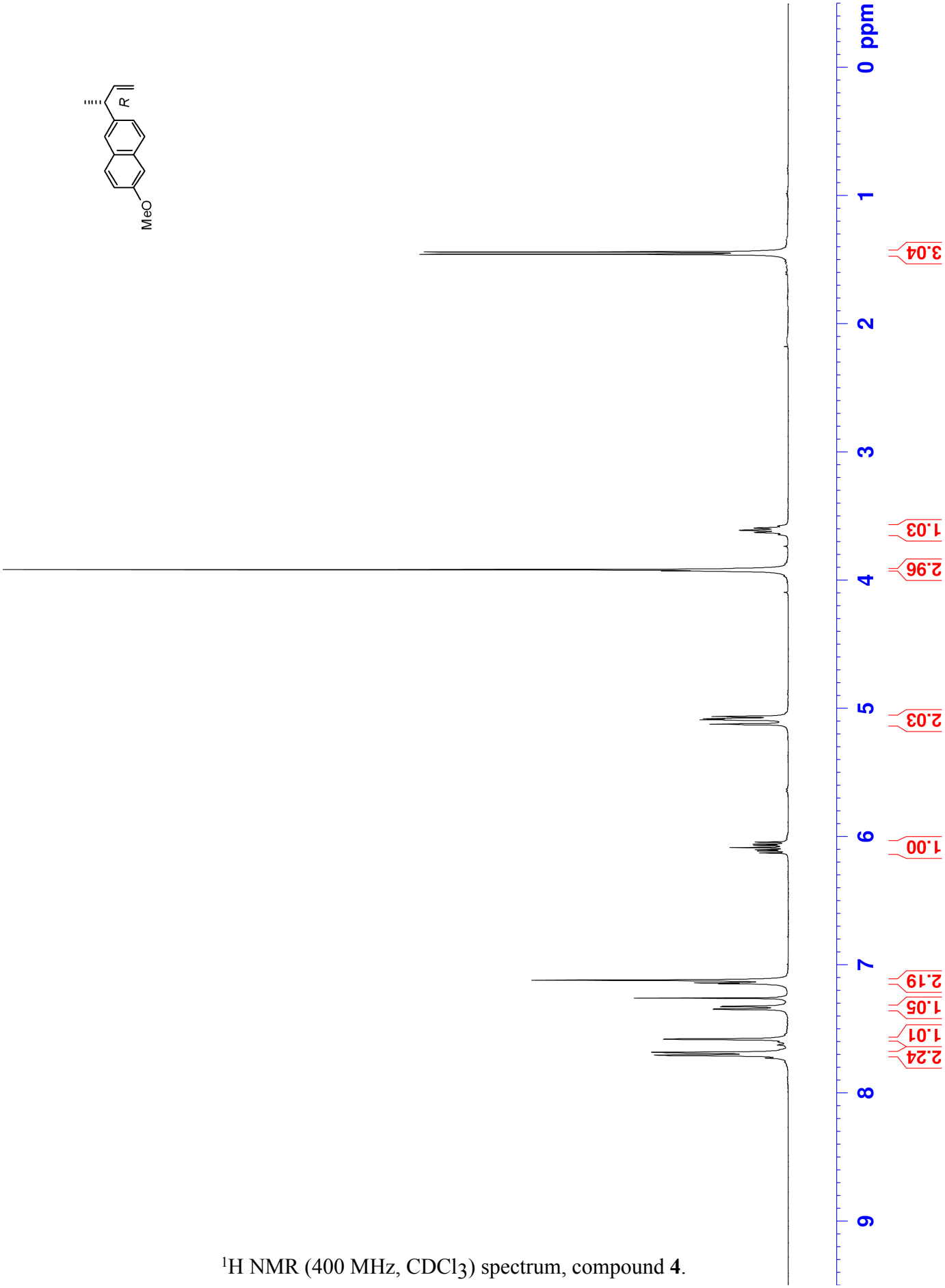
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **2**.



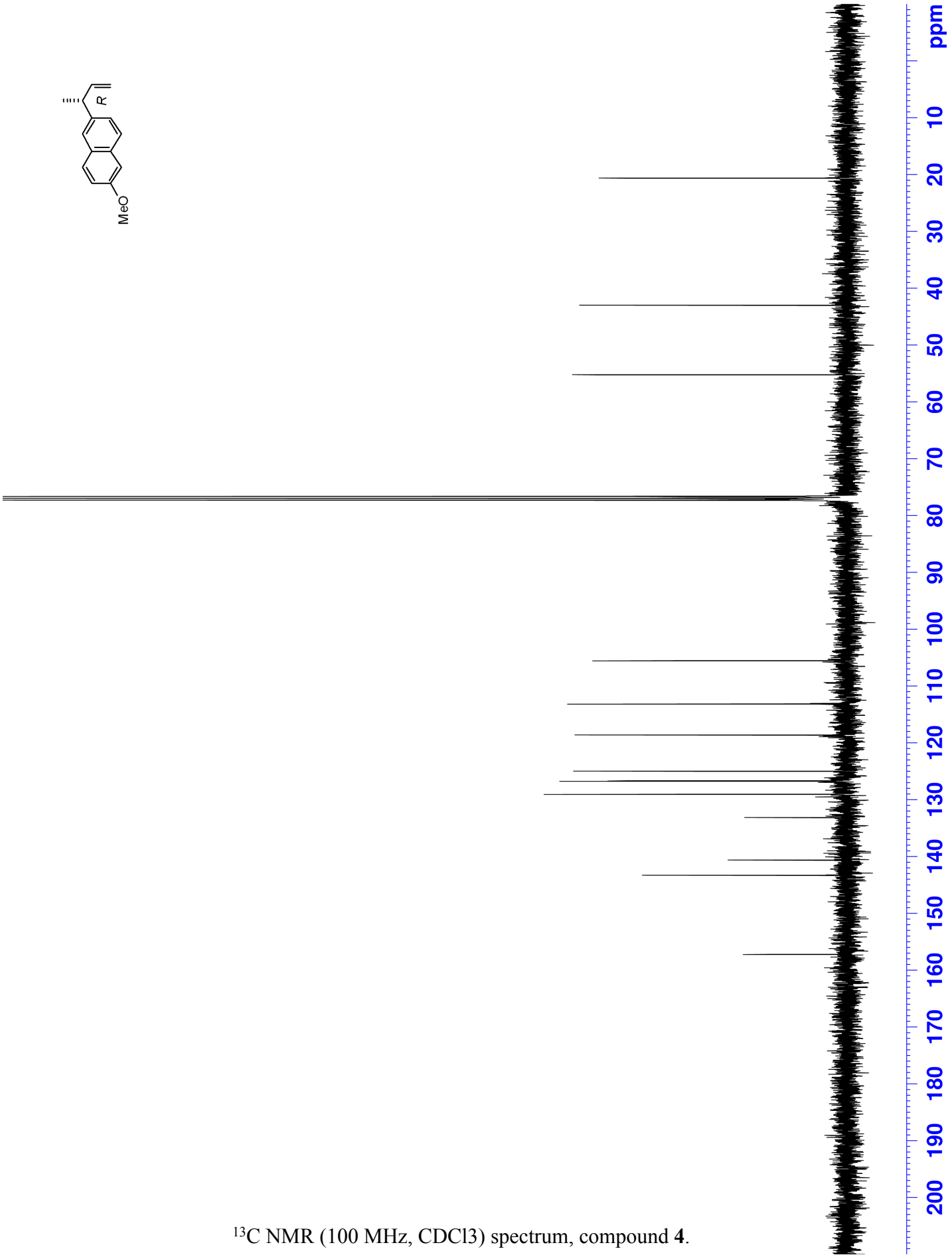
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **3**.



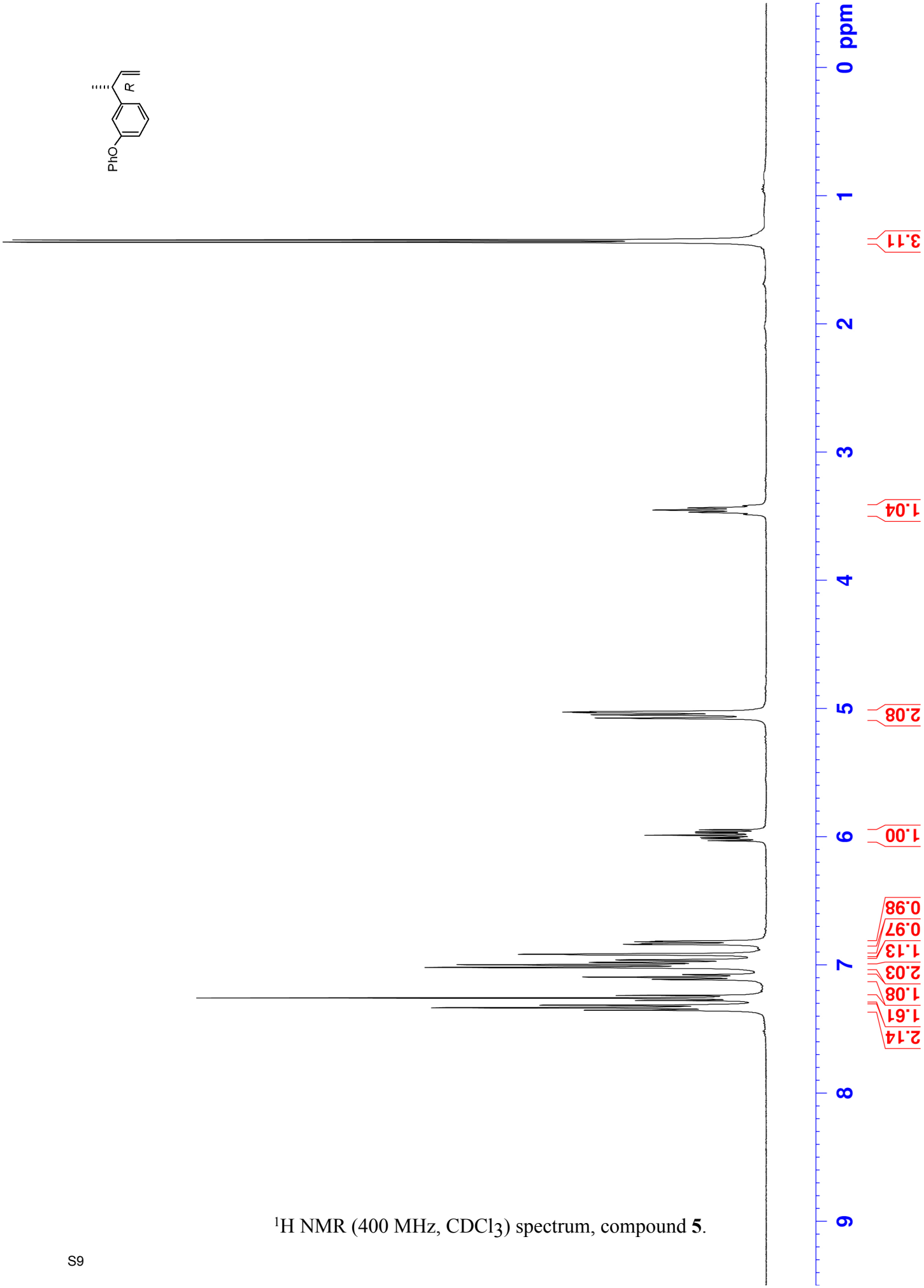
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **3**.



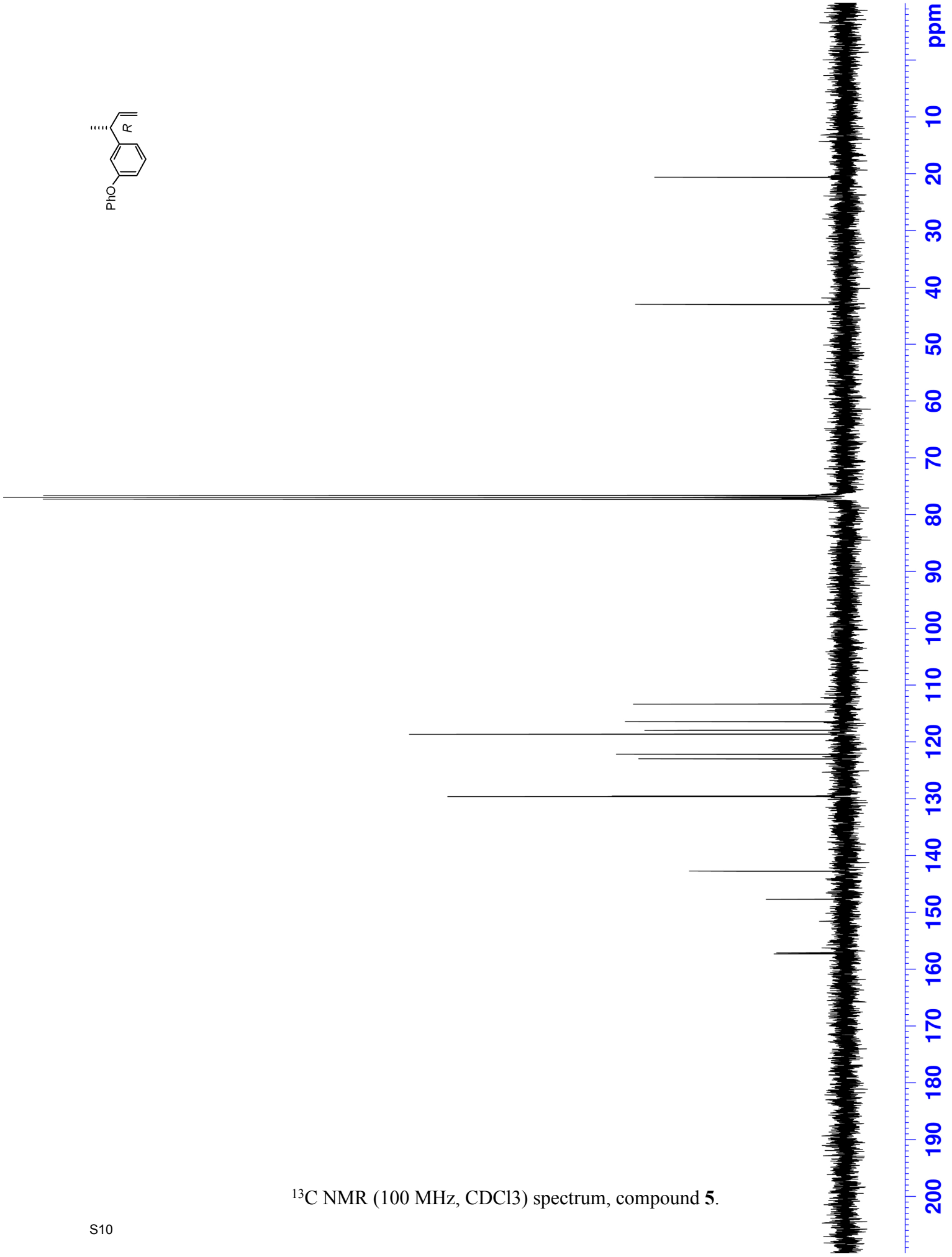
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **4**.



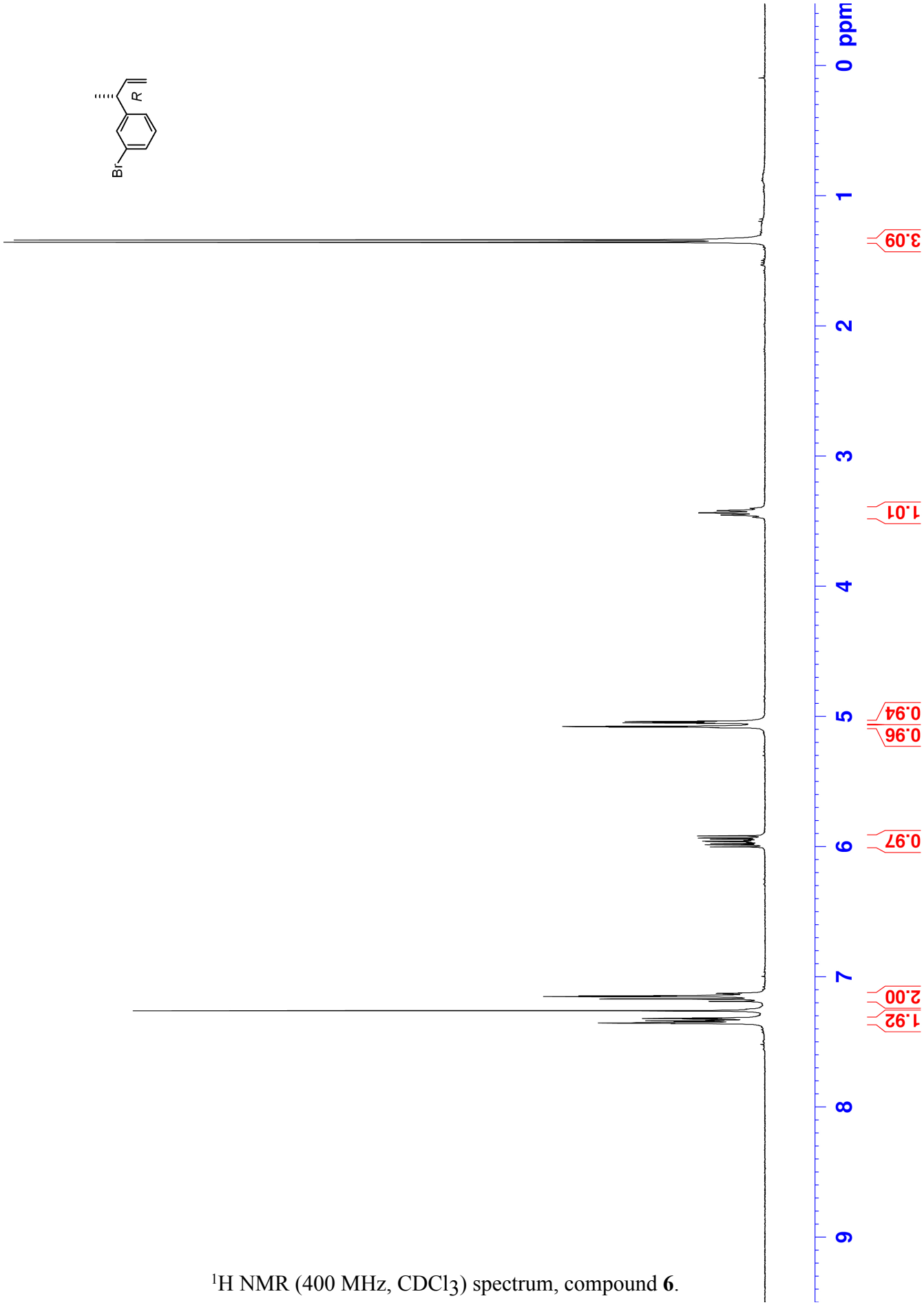
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **4**.



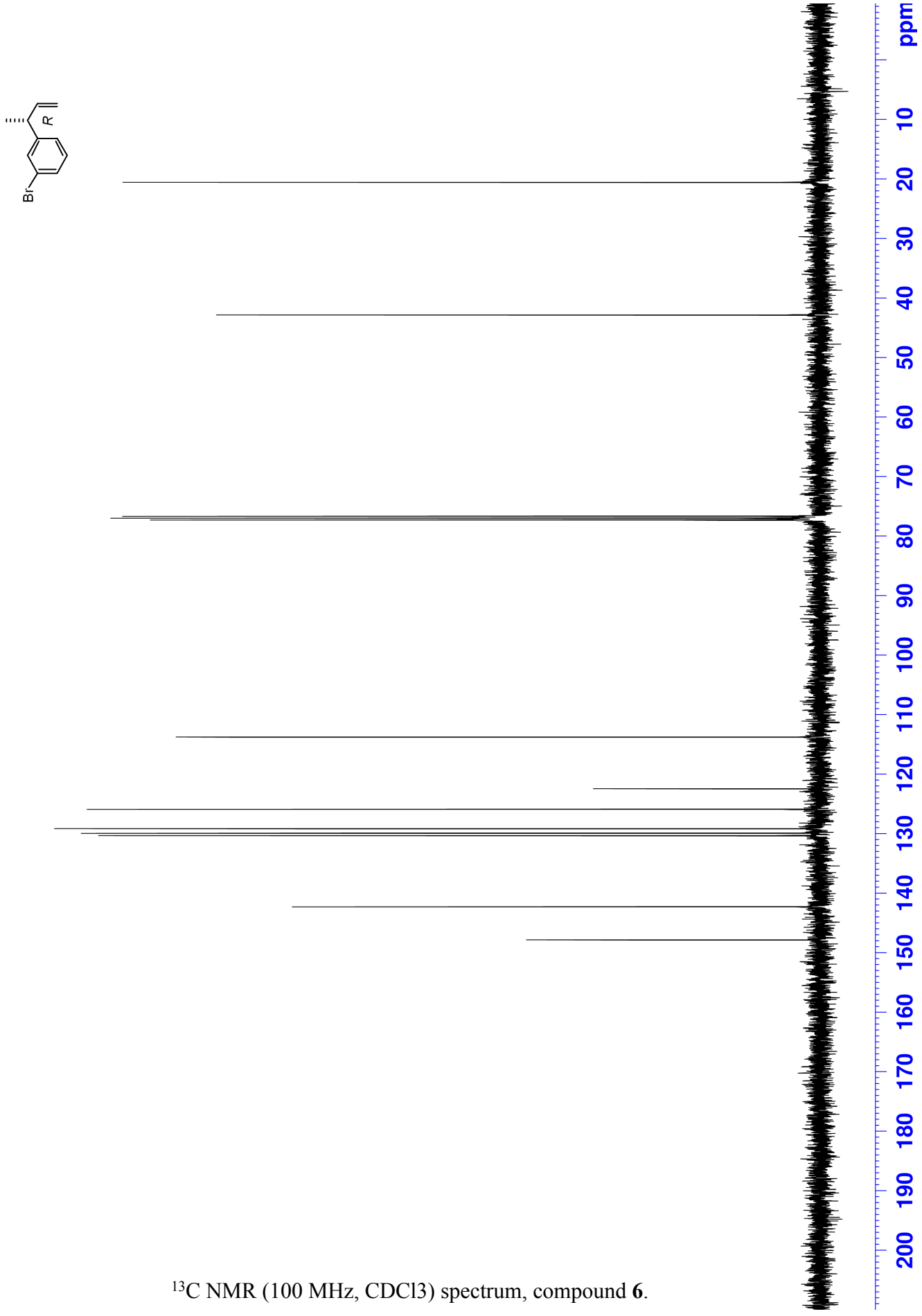
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **5**.



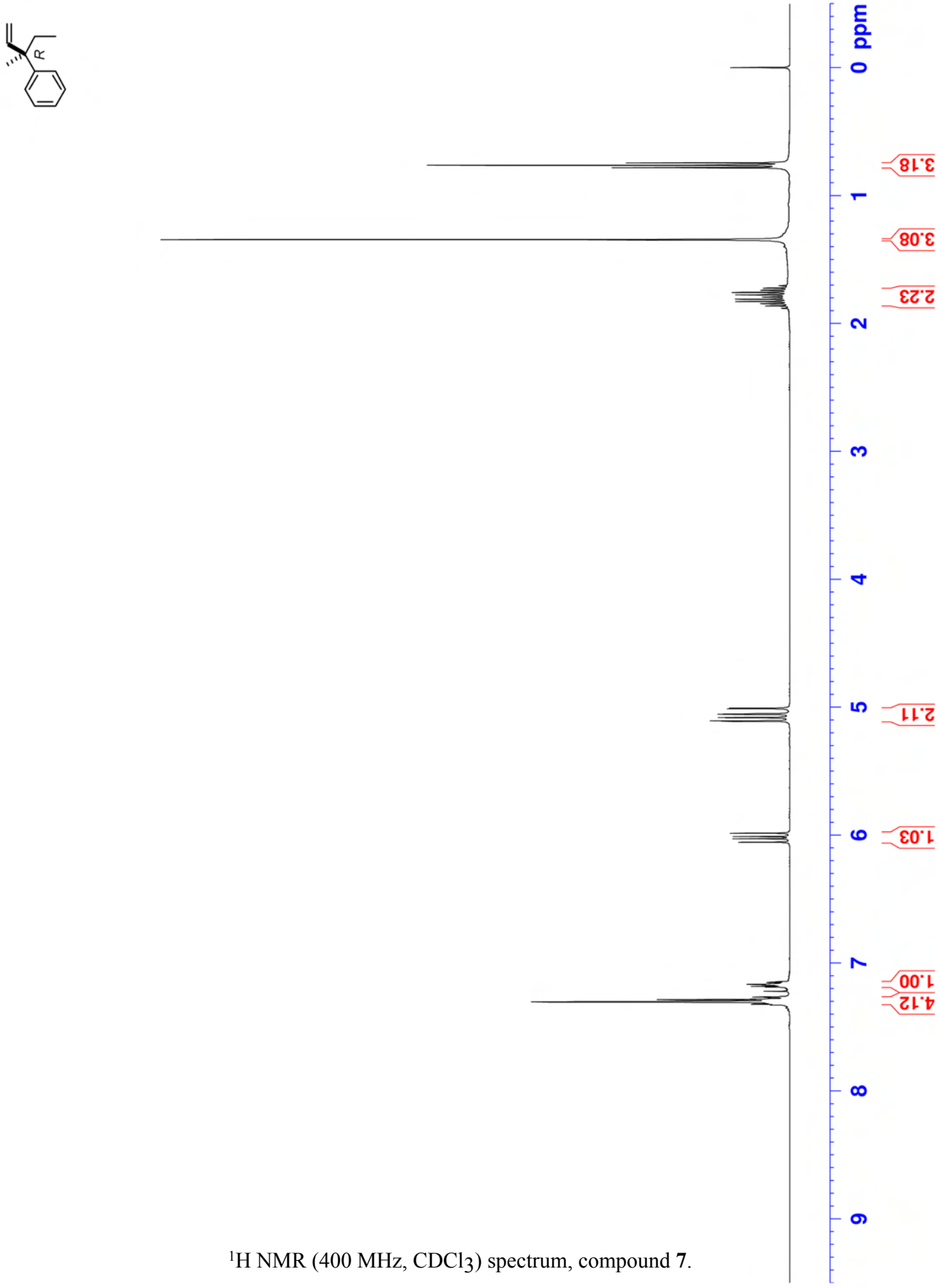
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **5**.



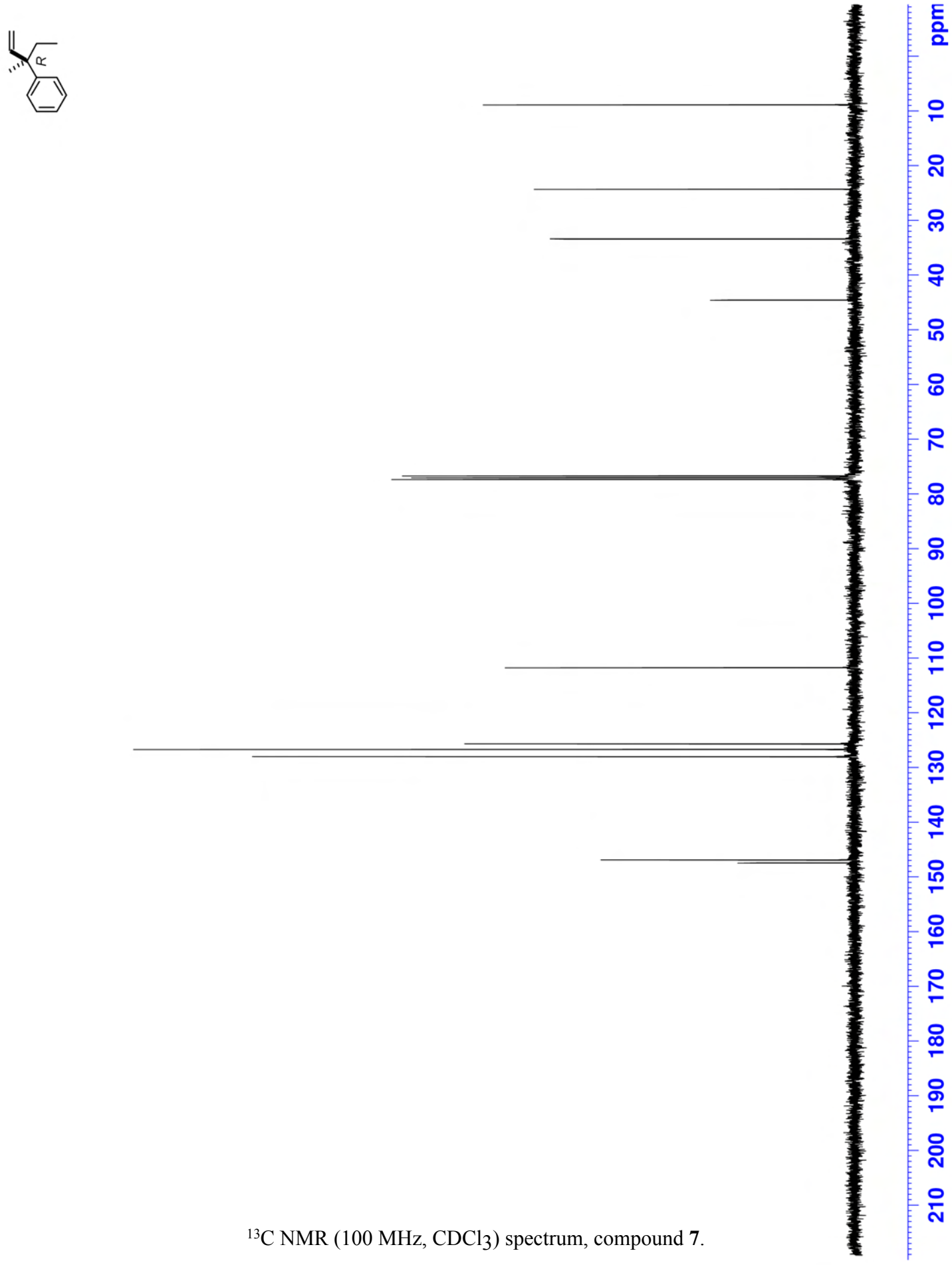
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **6**.



^{13}C NMR (100 MHz, CDCl3) spectrum, compound **6**.



^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **7**.

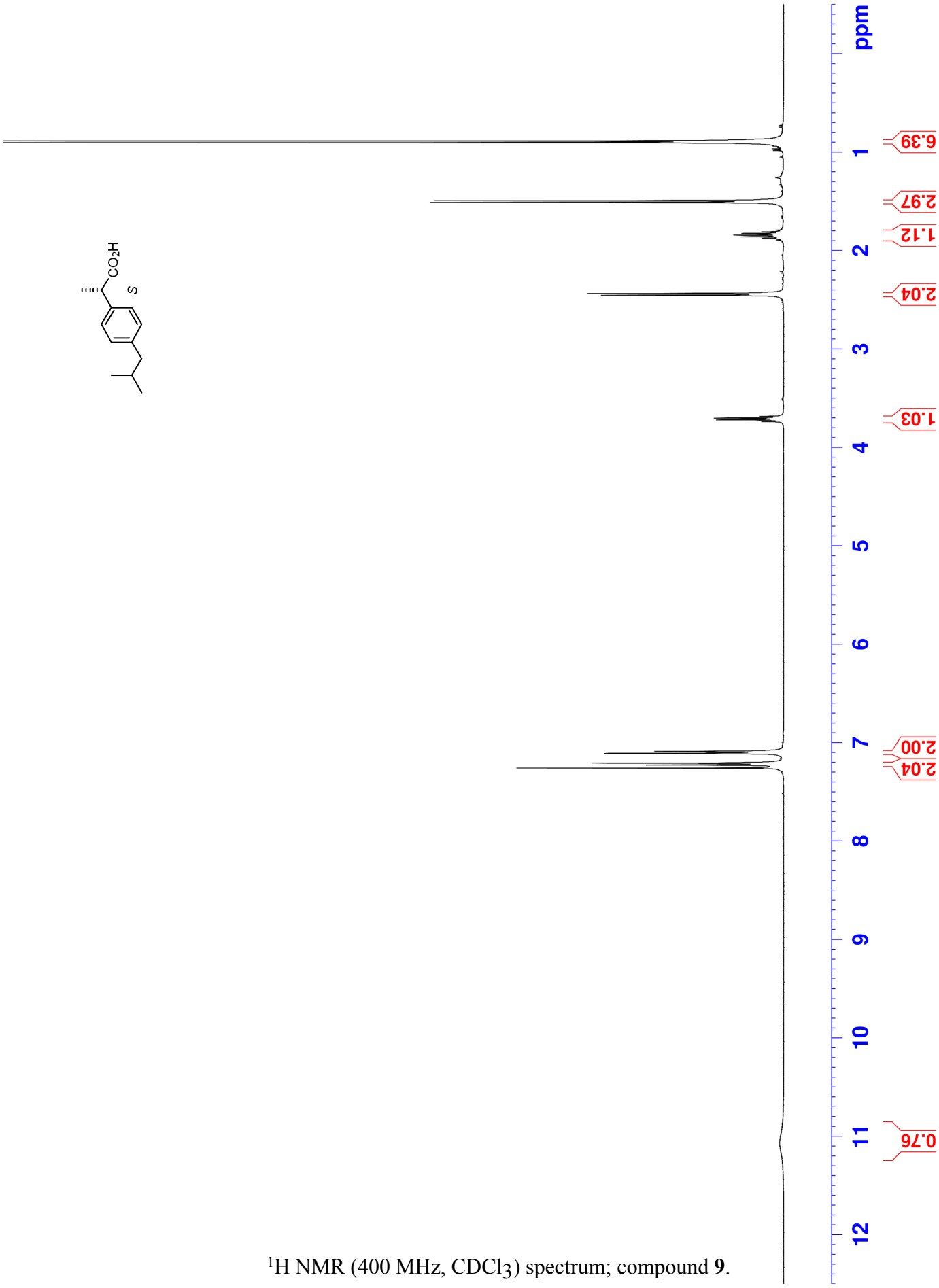


^{13}C NMR (100 MHz, $CDCl_3$) spectrum, compound **7**.

R_cR_c & S_cS_c (rac)

Chiral GC (racemic mixture): 40 min at 70°C, 5°C/min, 10 min at 90°C, compound **7**.

Chiral GC: 40 min at 70°C, 5°C/min, 10 min at 90°C, compound **7**.

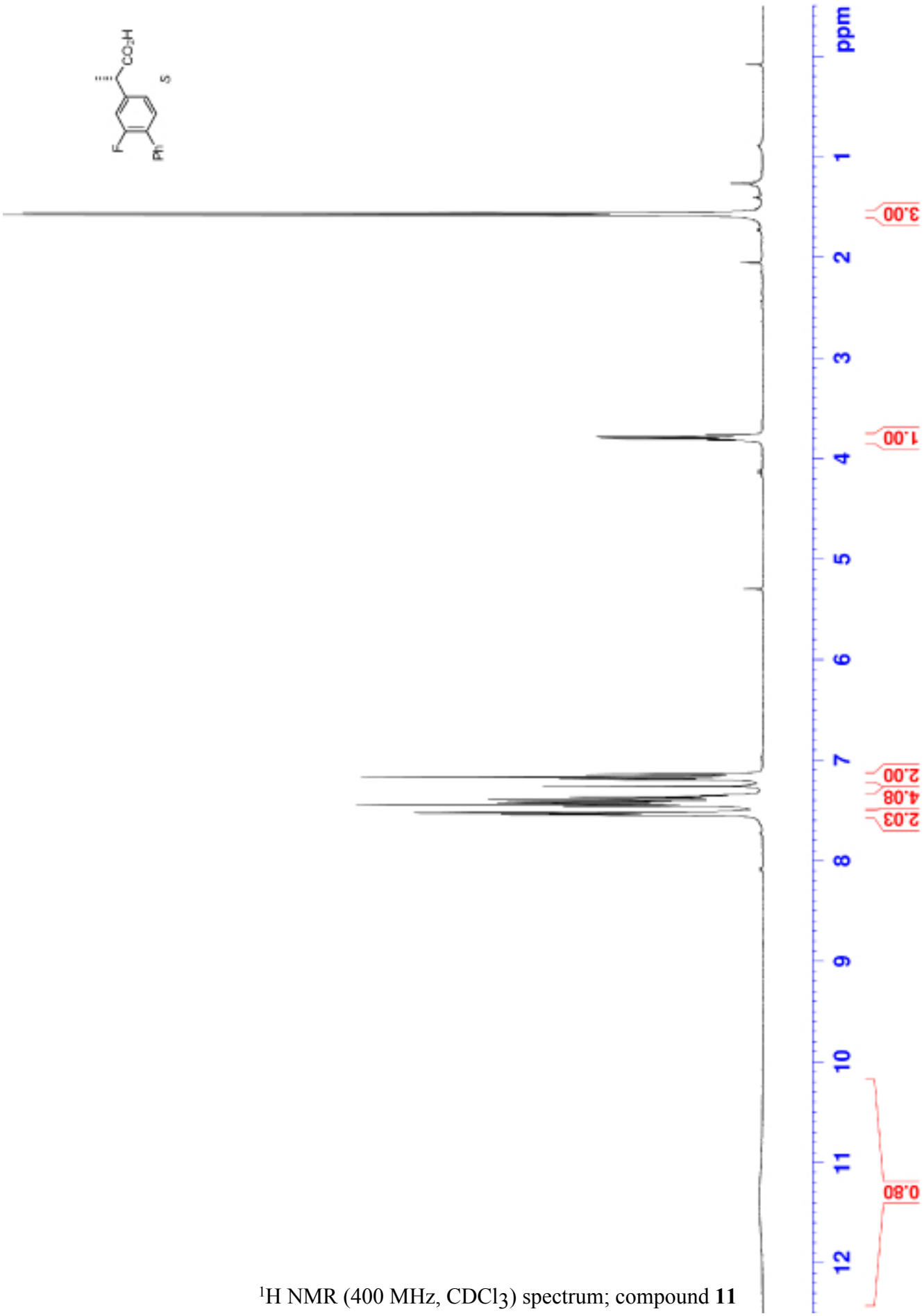


^{1}H NMR (400 MHz, $CDCl_3$) spectrum; compound **9**.

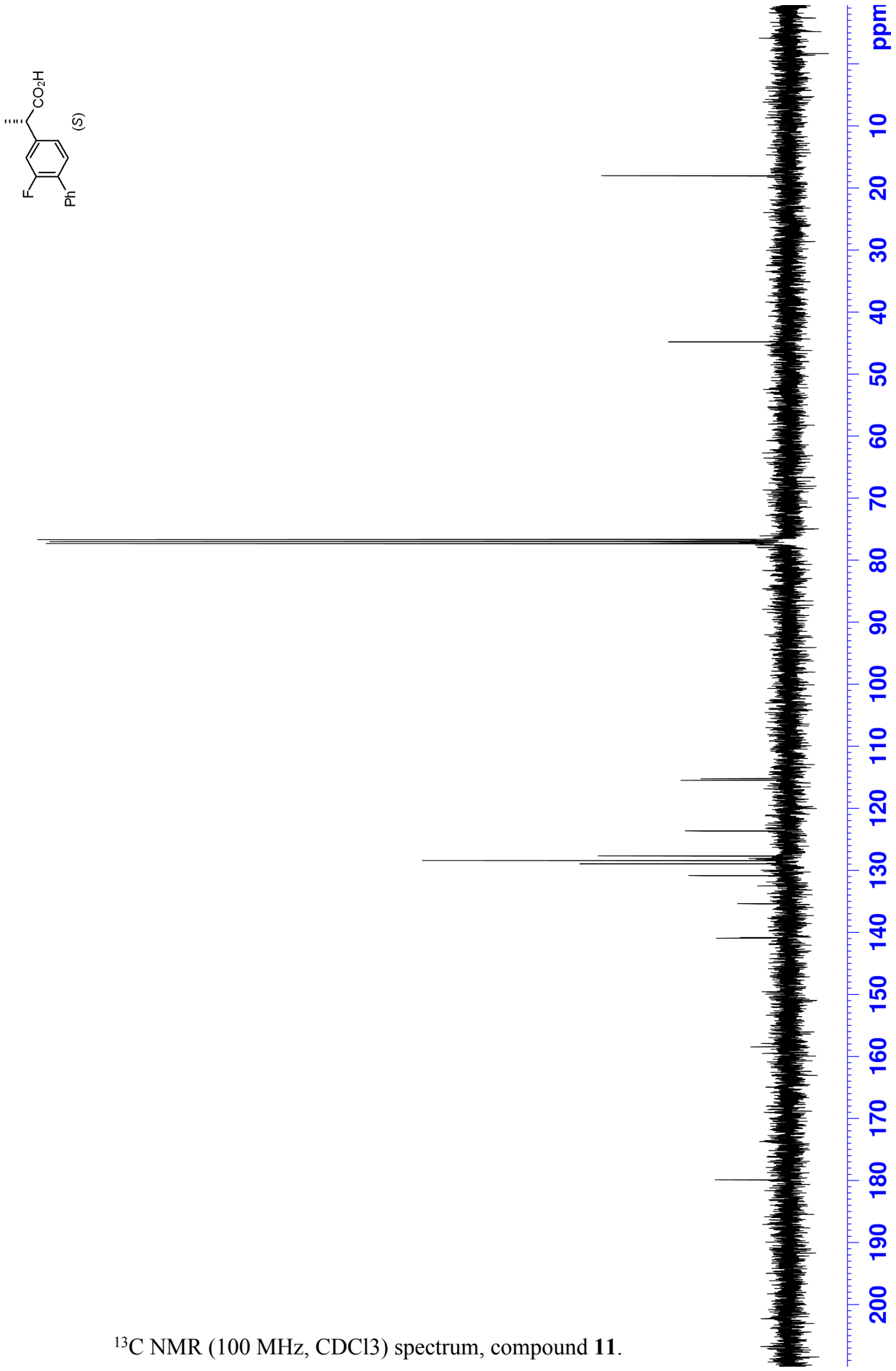
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **9**.

Chiral GC (Cyclodex-β): 60 min at 160°C;
L-menthyl ester of compound **9 (**enriched).

Chiral GC (Cyclodex-β): 60 min at 160°C;
L-menthyl ester of compound **9** (from **2**).



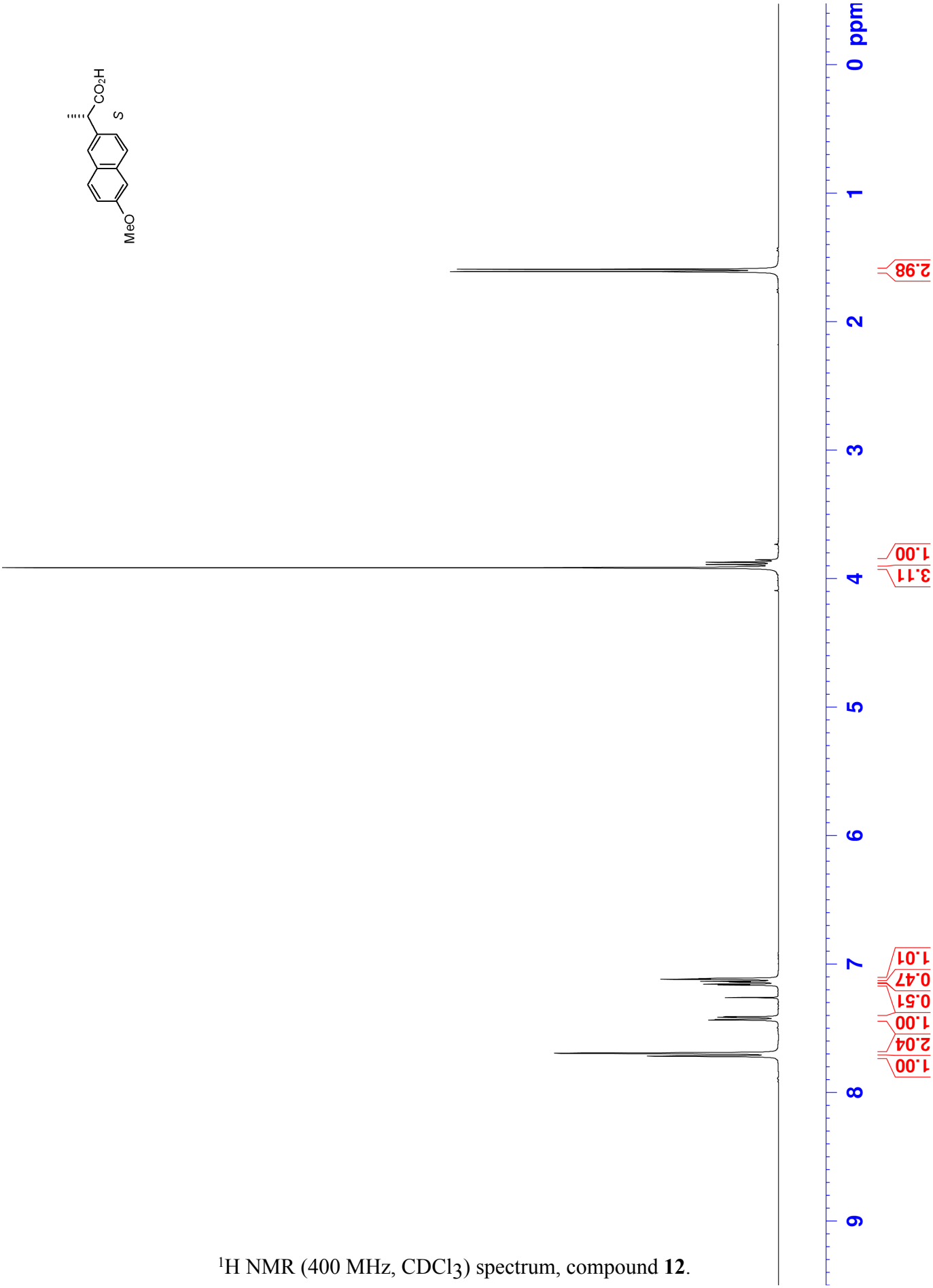
^{1}H NMR (400 MHz, $CDCl_3$) spectrum; compound **11**



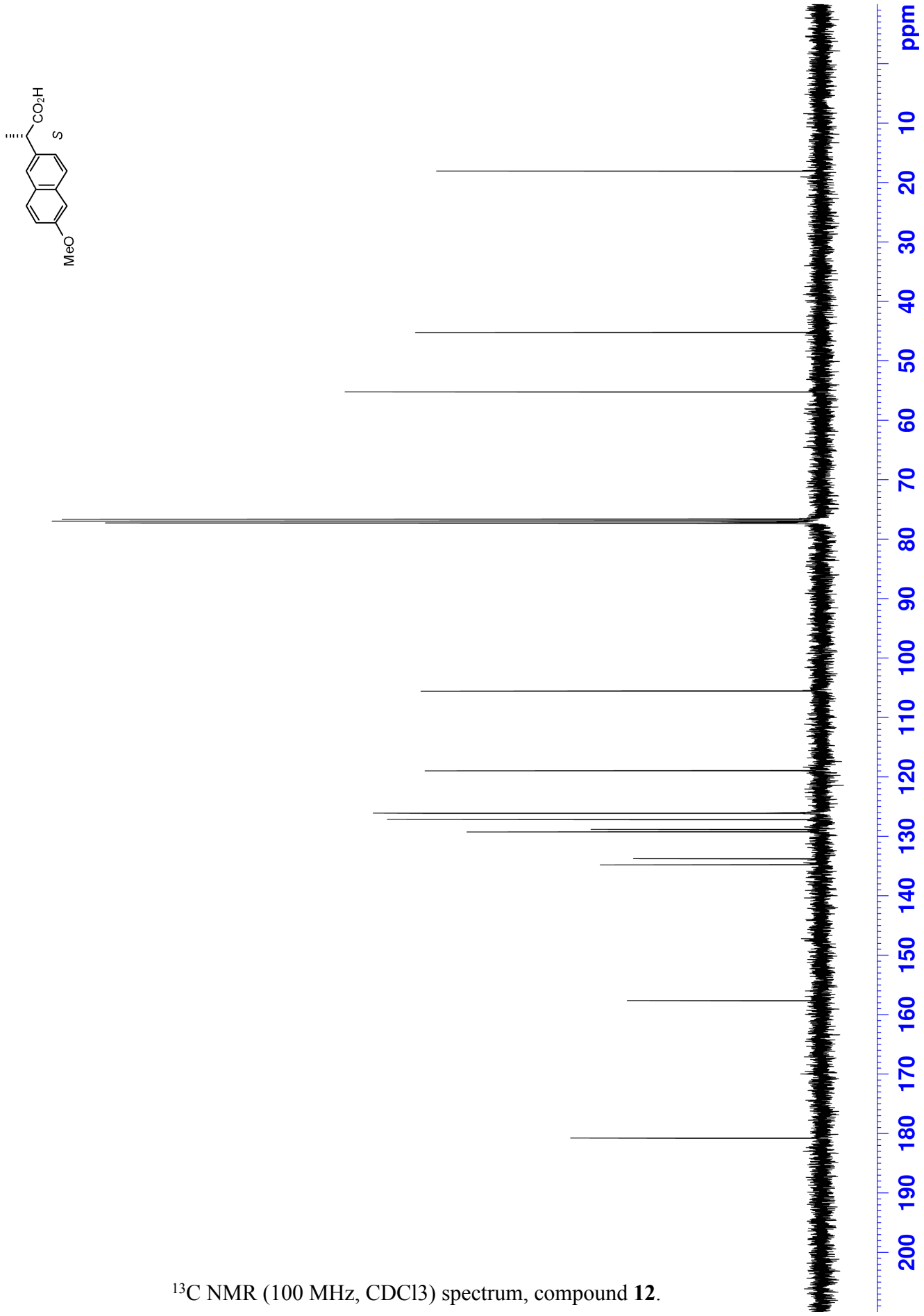
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **11**.

Chiral GC (Chirasil-*S*-Val): 120 min at 200°C;
L-menthyl ester of compound **11** (enriched).

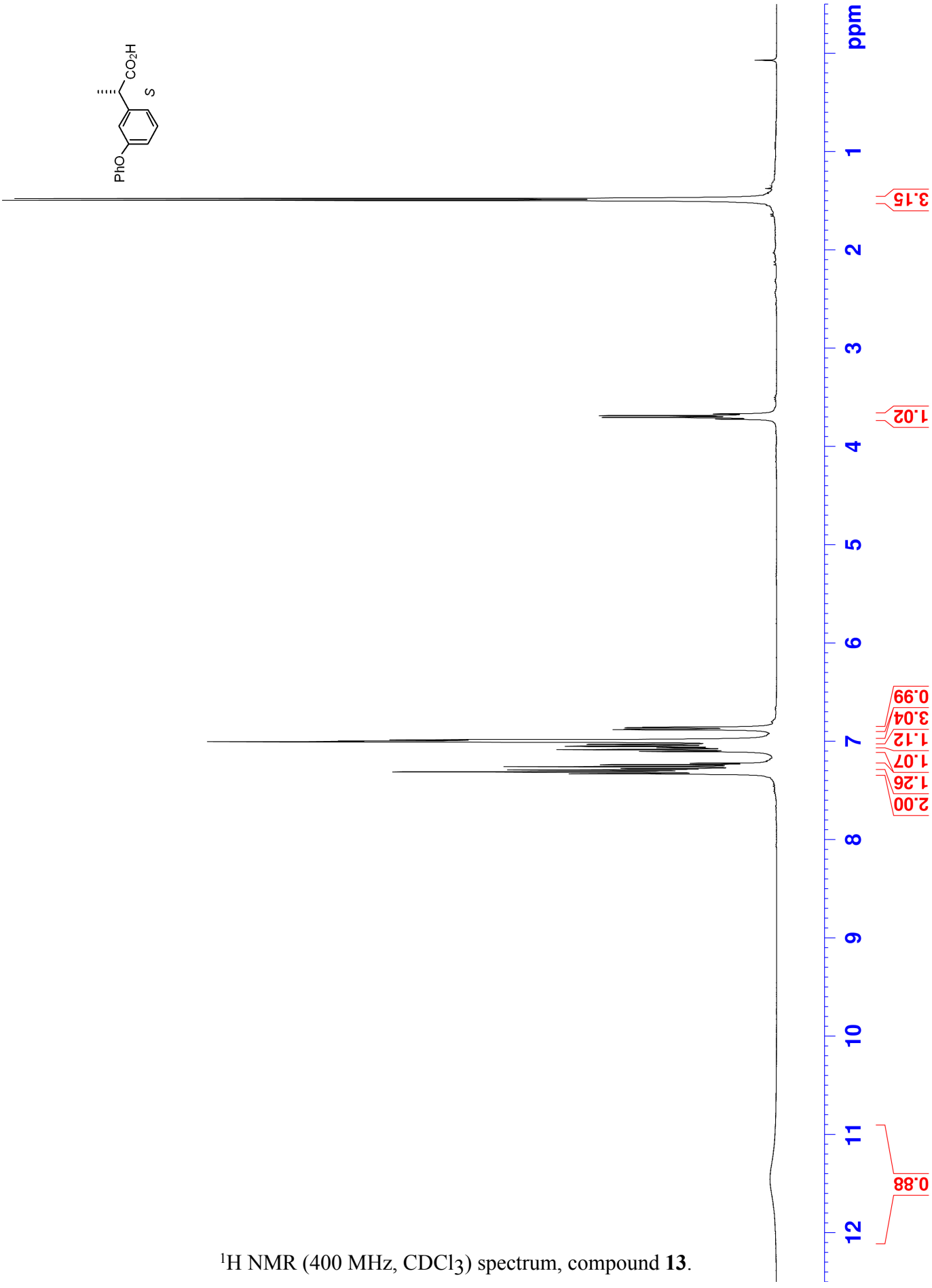
Chiral GC (Chirasil-*S*-Val): 120 min at 200°C;
L-menthyl ester of compound **11** from **3**.



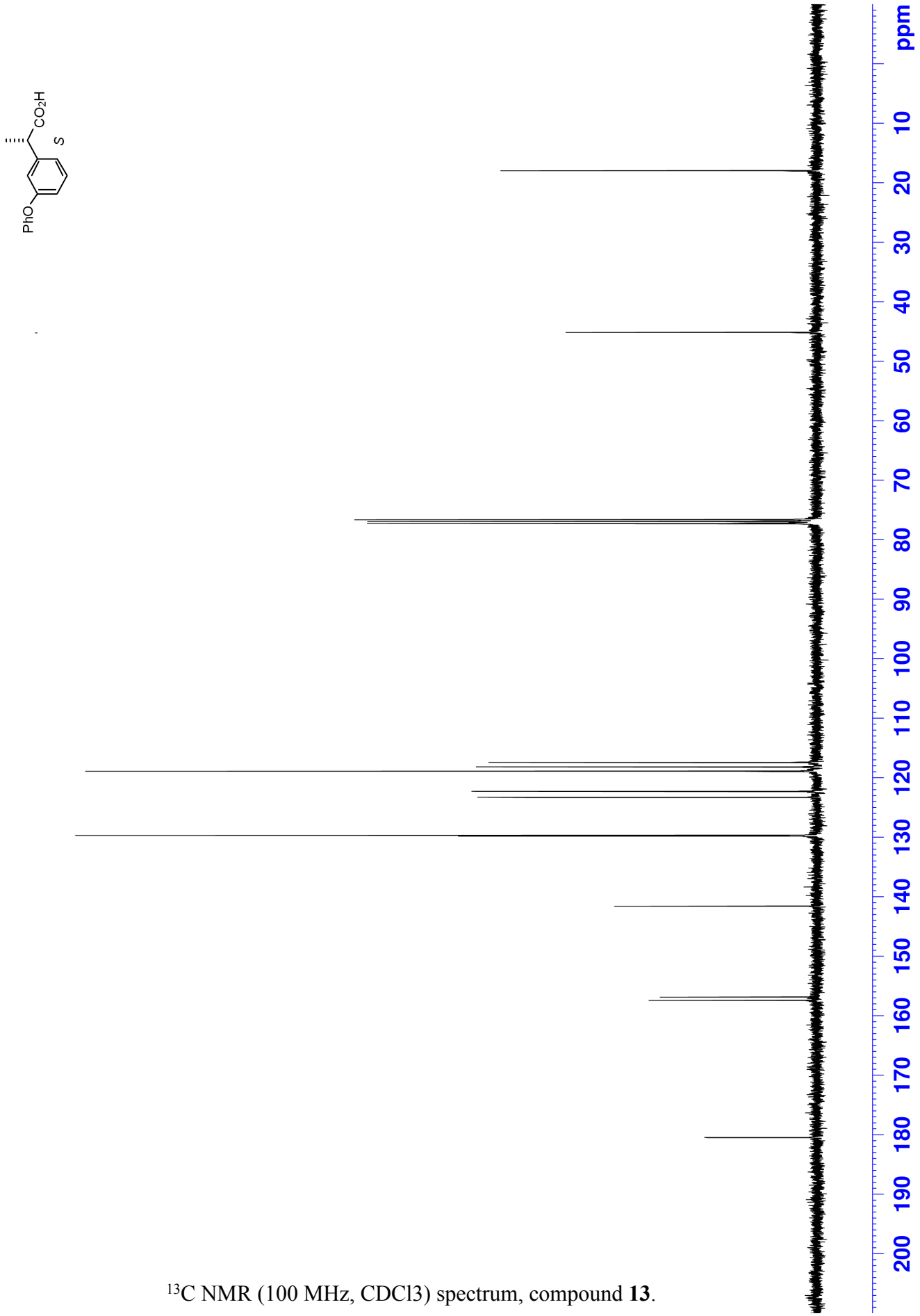
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **12**.



^{13}C NMR (100 MHz, CDCl3) spectrum, compound **12**.



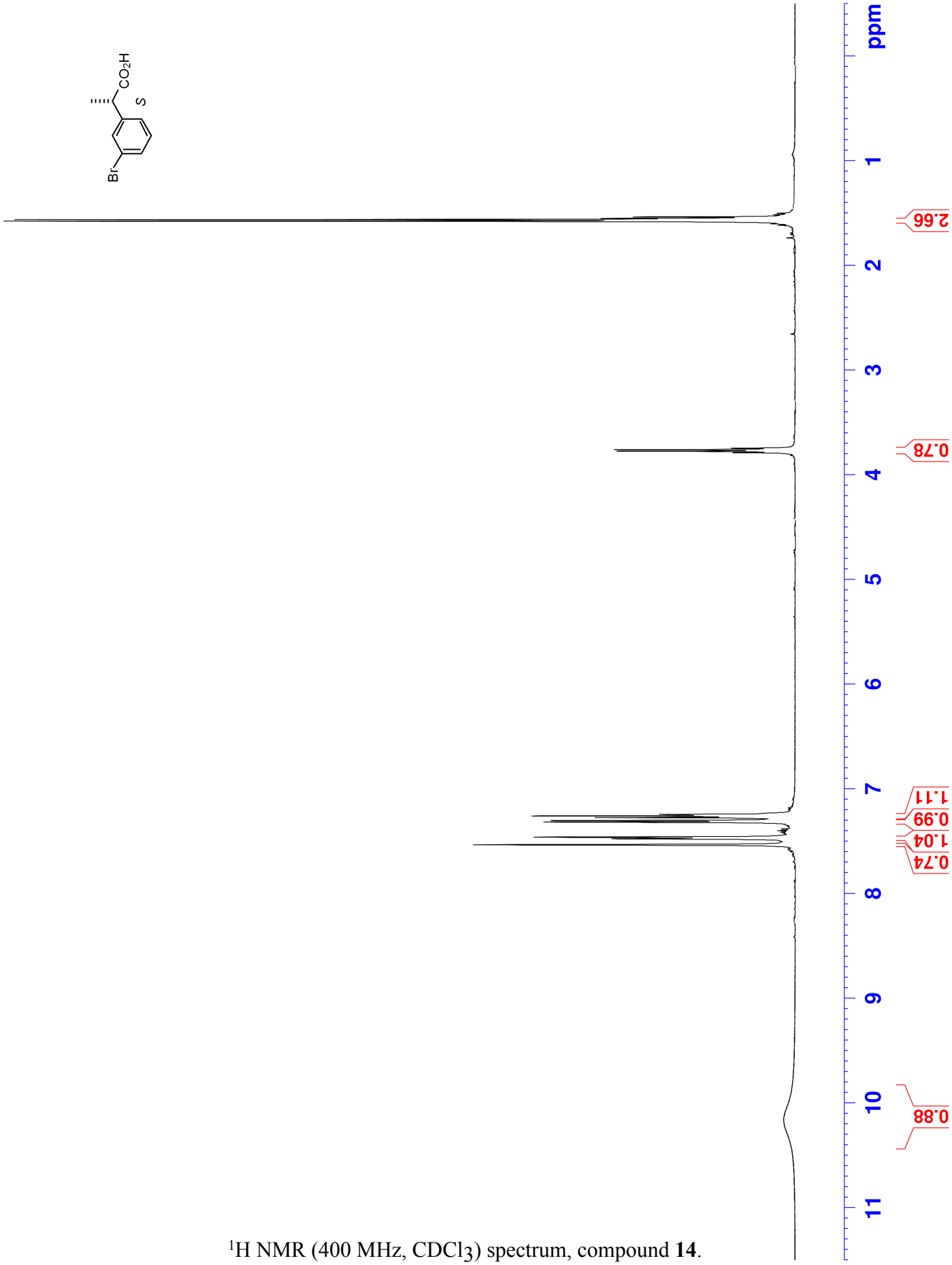
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **13**.



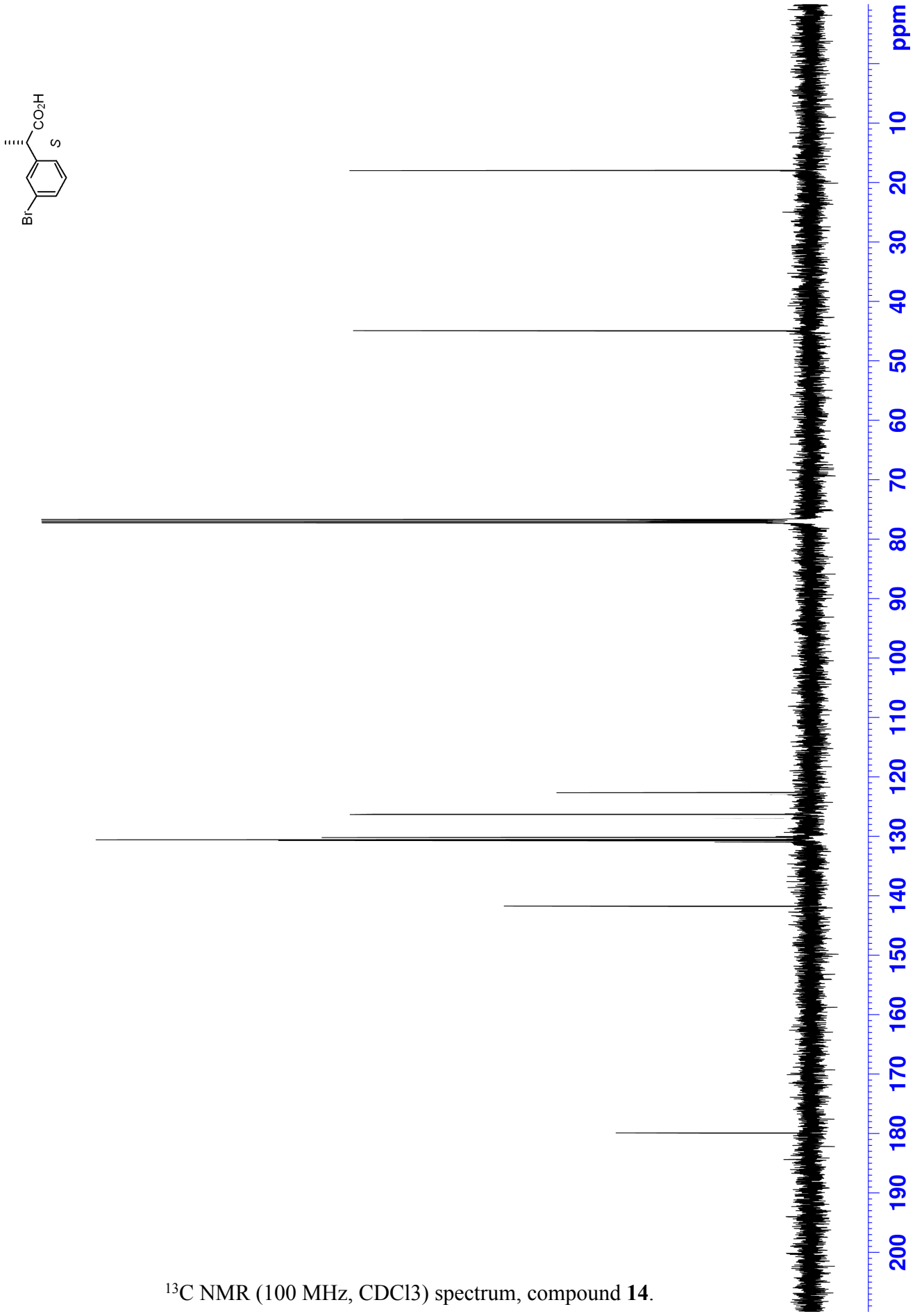
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **13**.

Chiral GC (Chirasil-*S*-Val): 120 min at 195°C;
L-menthyl ester of compound **13** (enriched).

Chiral GC (Chirasil-*S*-Val): 120 min at 195°C;
L-menthyl ester of compound **13** (from **5**).



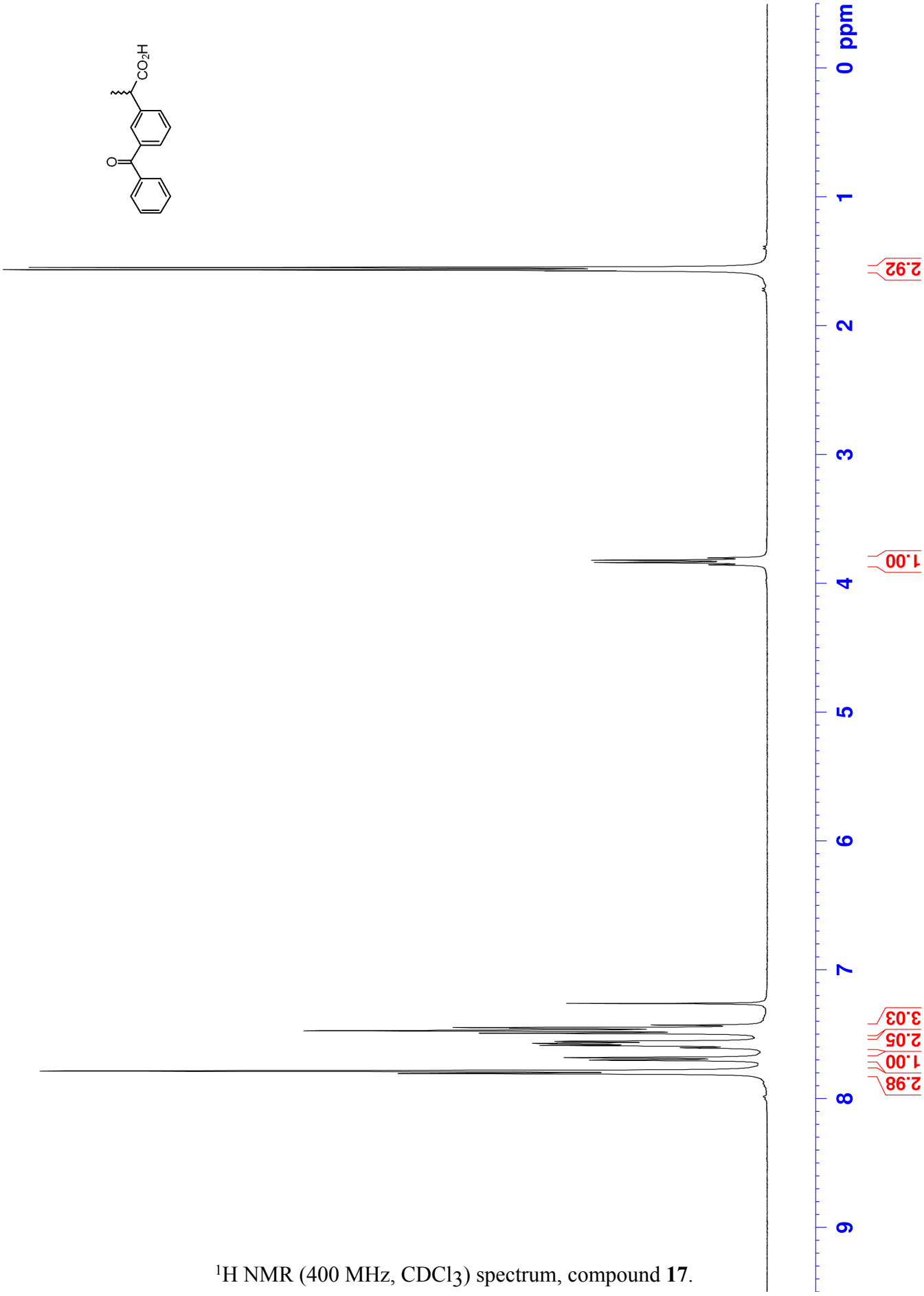
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **14**.



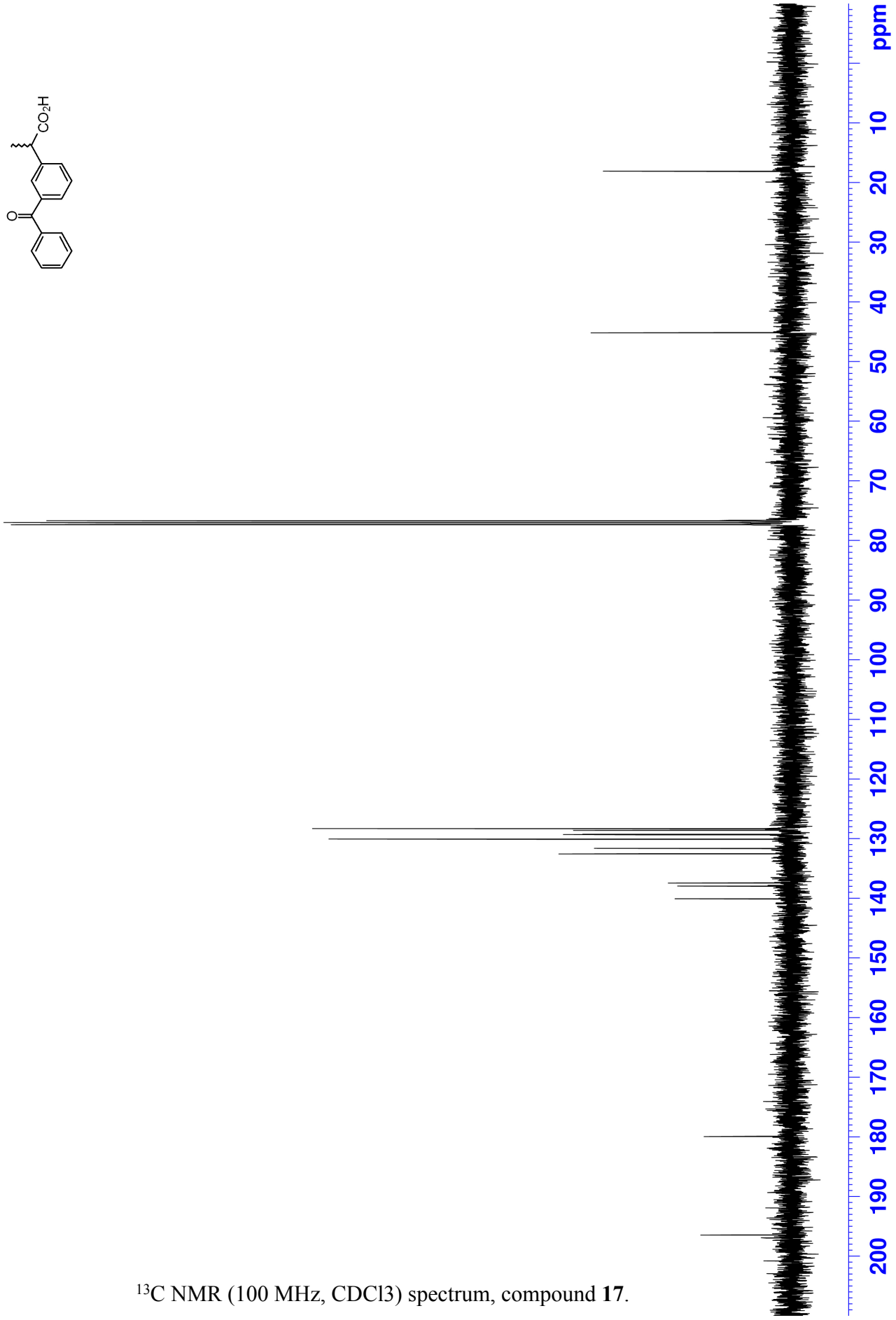
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **14**.

Chiral GC (Chirasil-*S*-Val): 45 min at 190°C;
(racemic mixture) (L)-menthyl esters of **14**
(enriched).

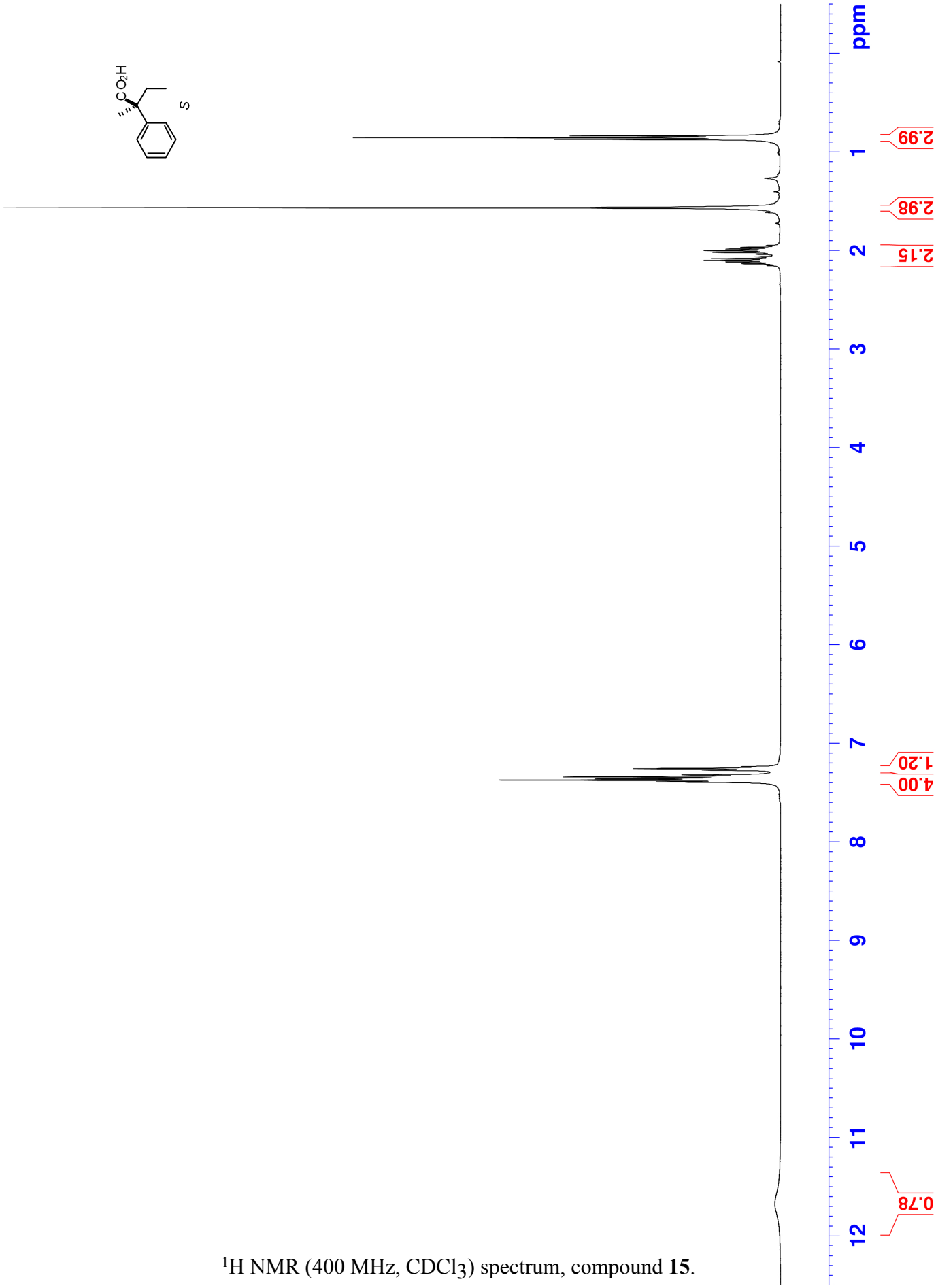
Chiral GC (Chirasil-*S*-Val): 45 min at 190°C;
(L)-mnthyl ester of **14** from **6**.



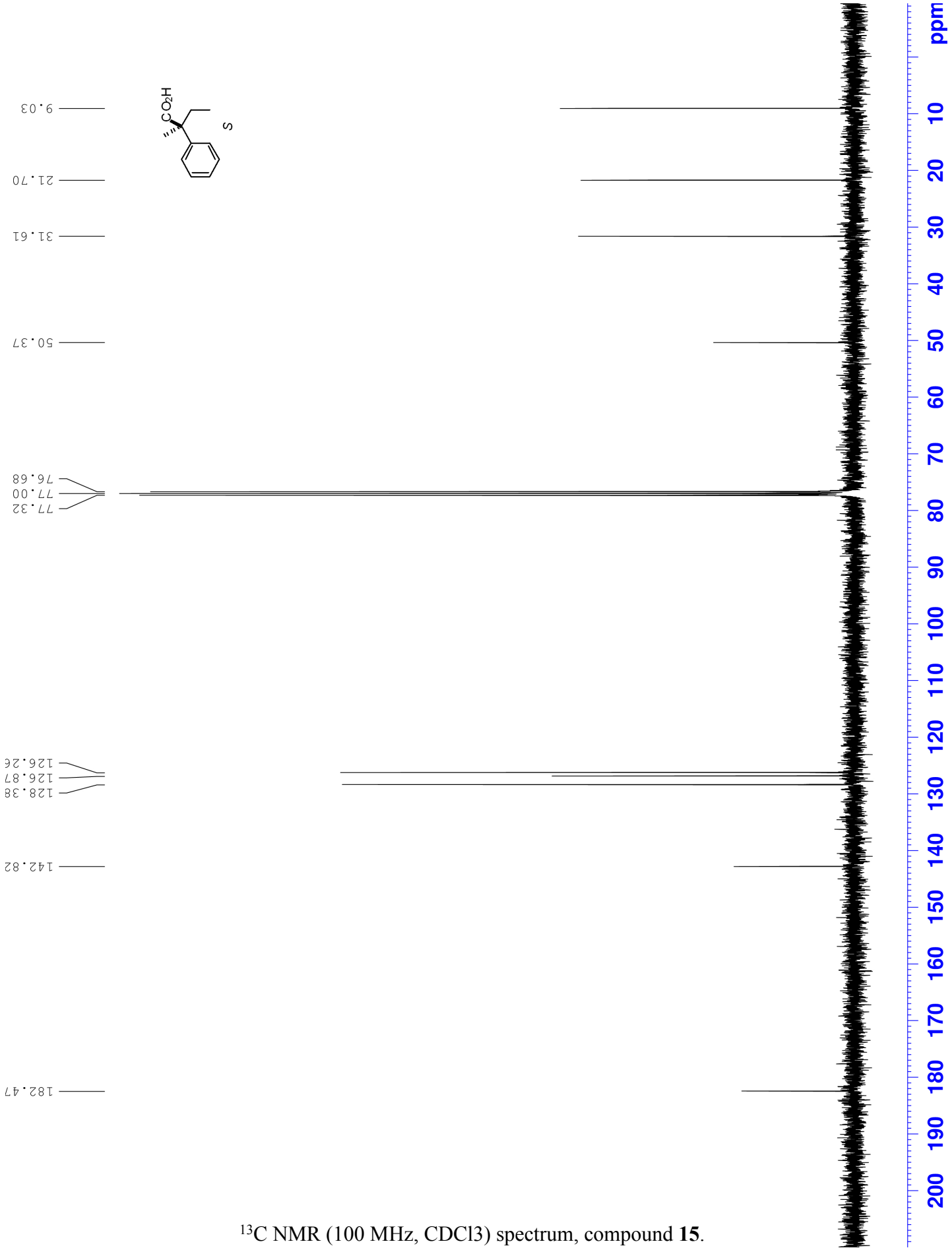
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **17**.



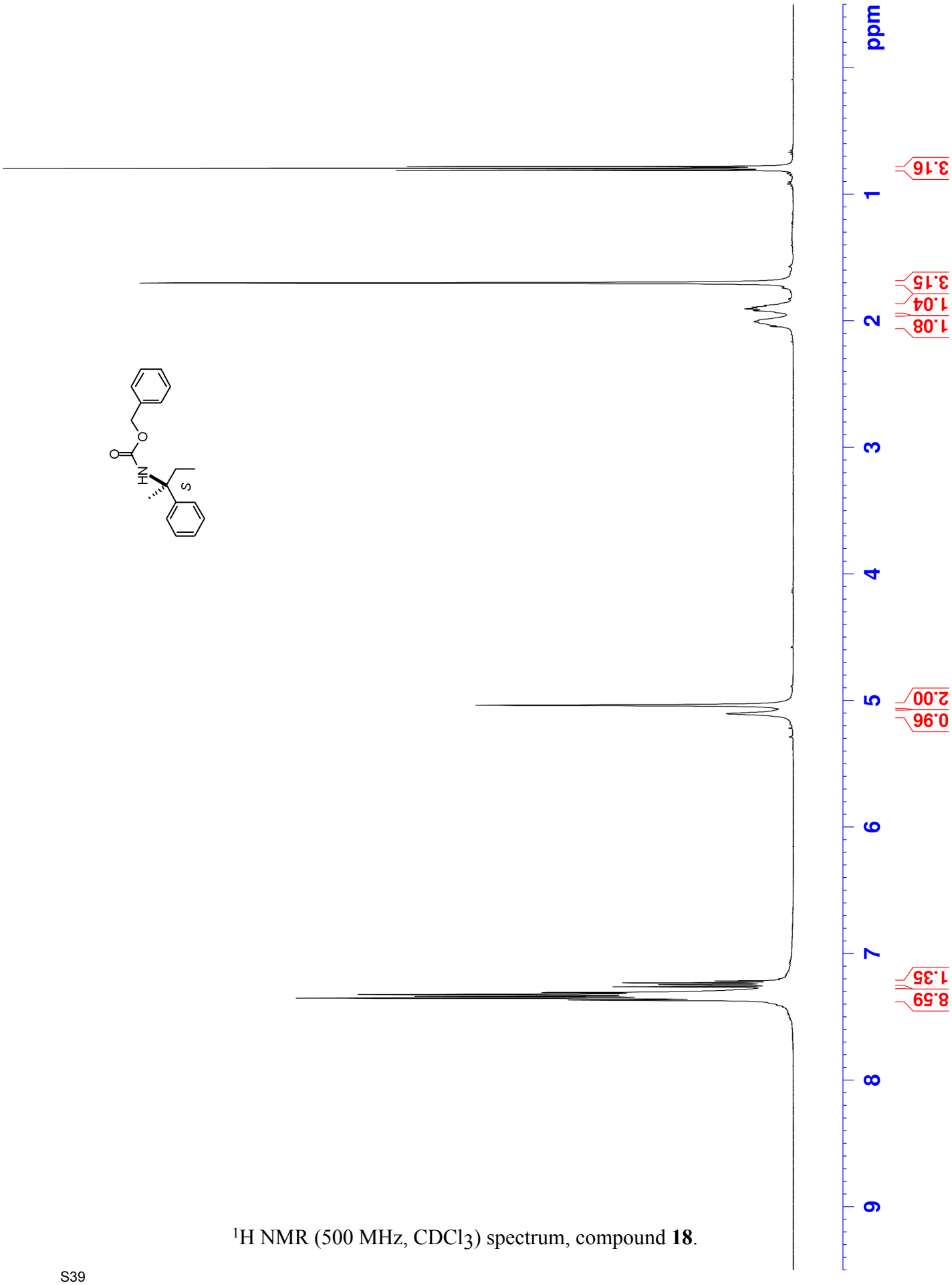
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **17**.



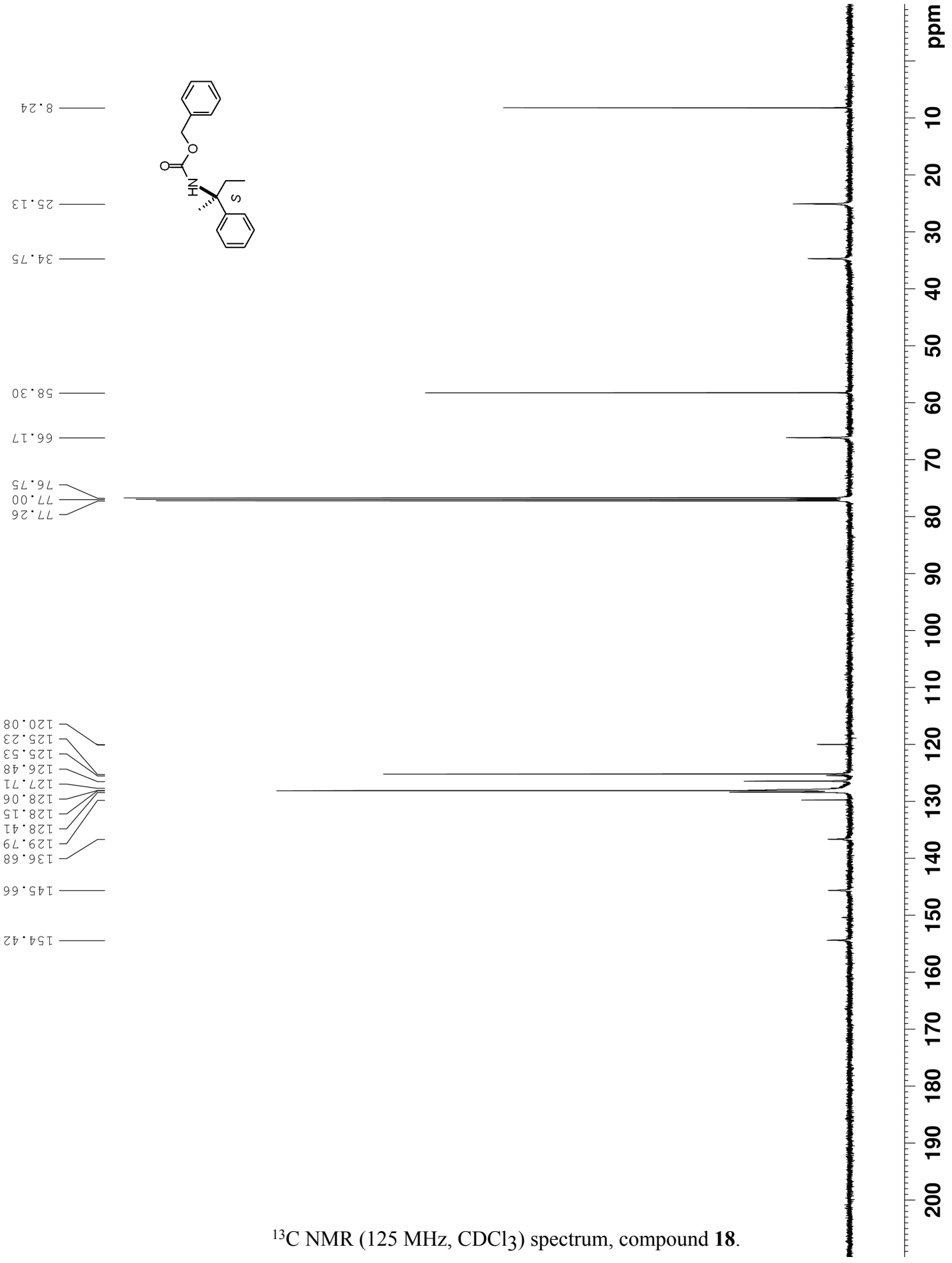
^{1}H NMR (400 MHz, $CDCl_3$) spectrum, compound **15**.



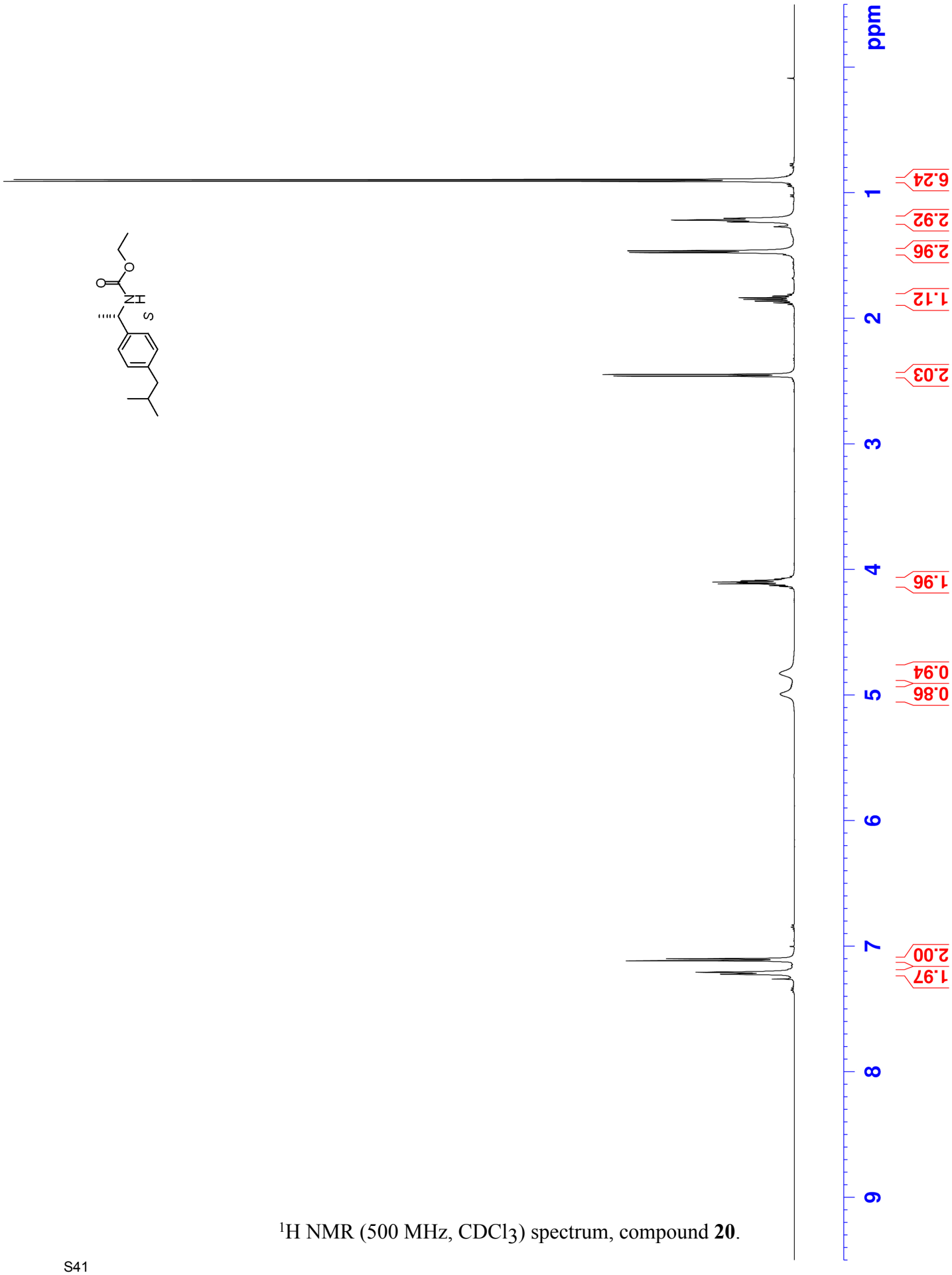
^{13}C NMR (100 MHz, CDCl3) spectrum, compound **15**.



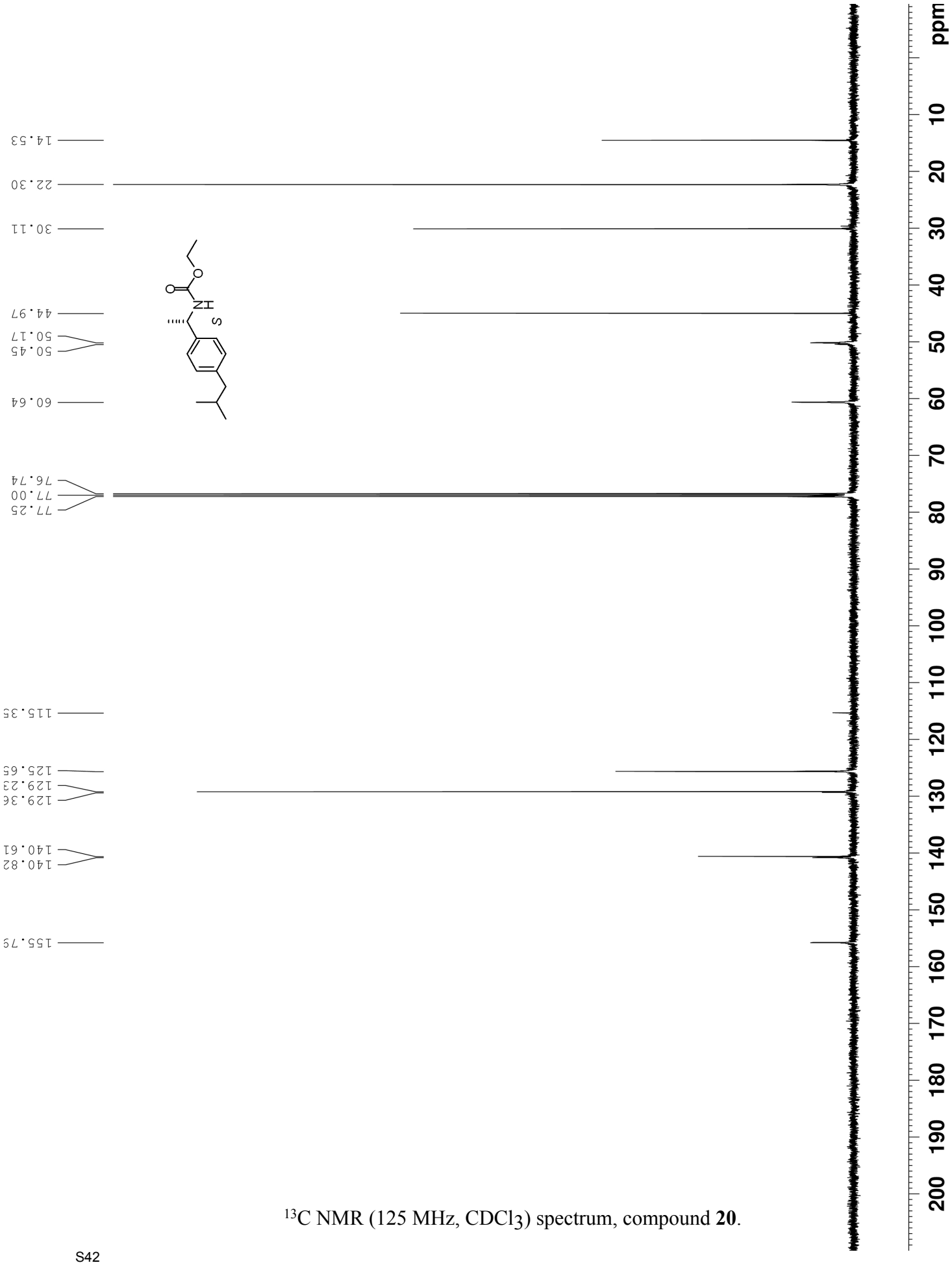
^{1}H NMR (500 MHz, $CDCl_3$) spectrum, compound **18**.



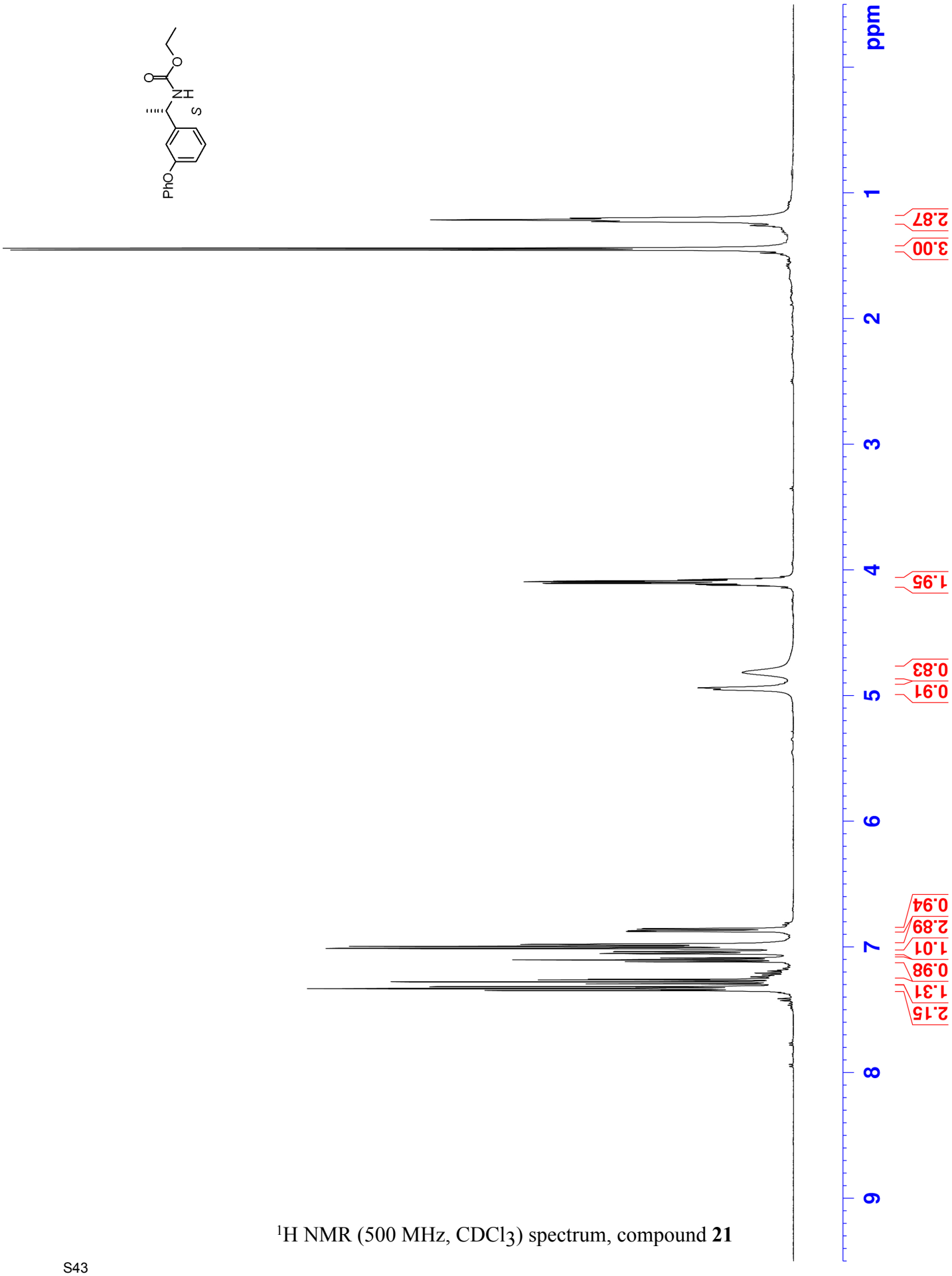
^{13}C NMR (125 MHz, $CDCl_3$) spectrum, compound **18**.



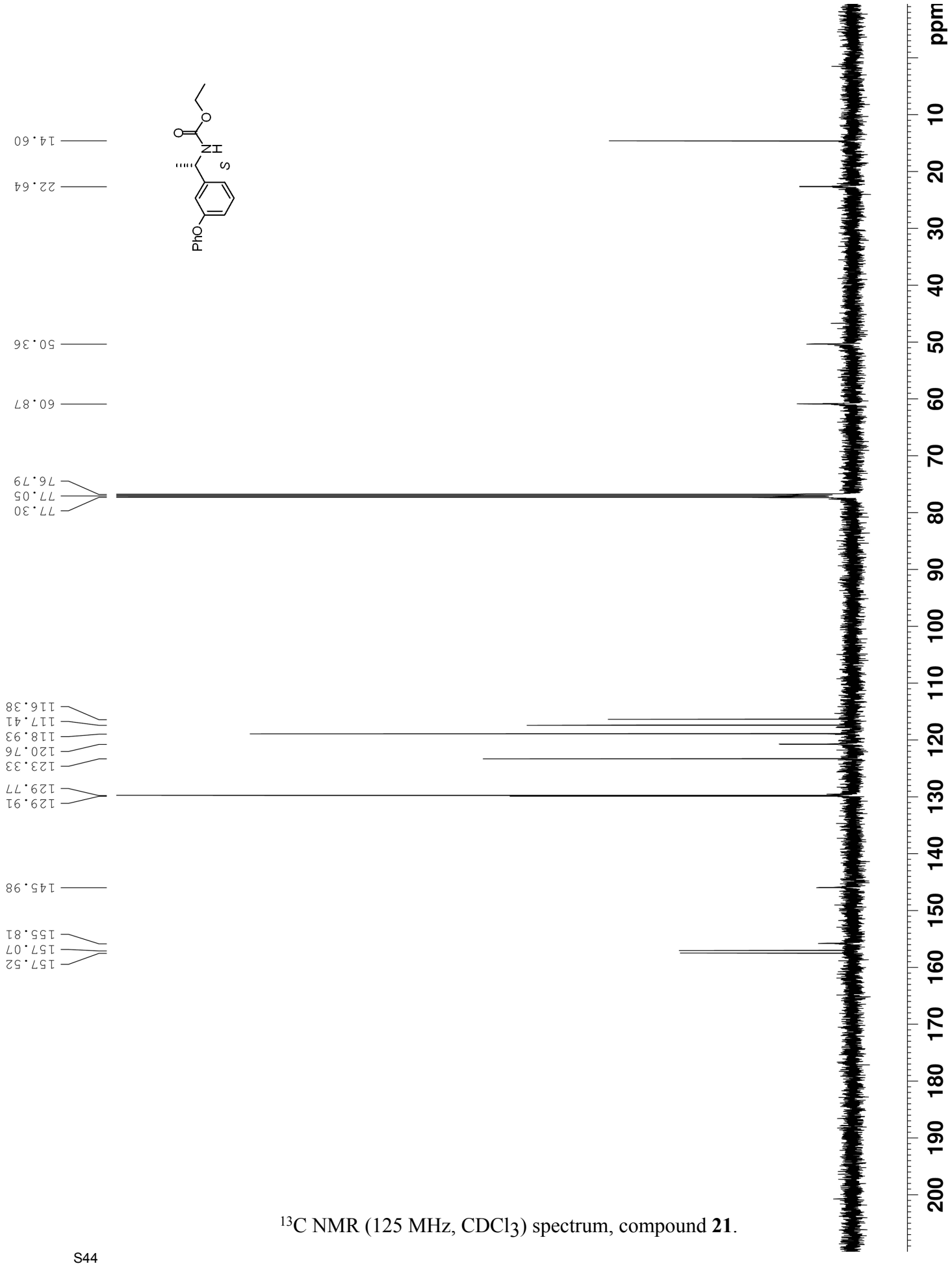
^{1}H NMR (500 MHz, $CDCl_3$) spectrum, compound **20**.



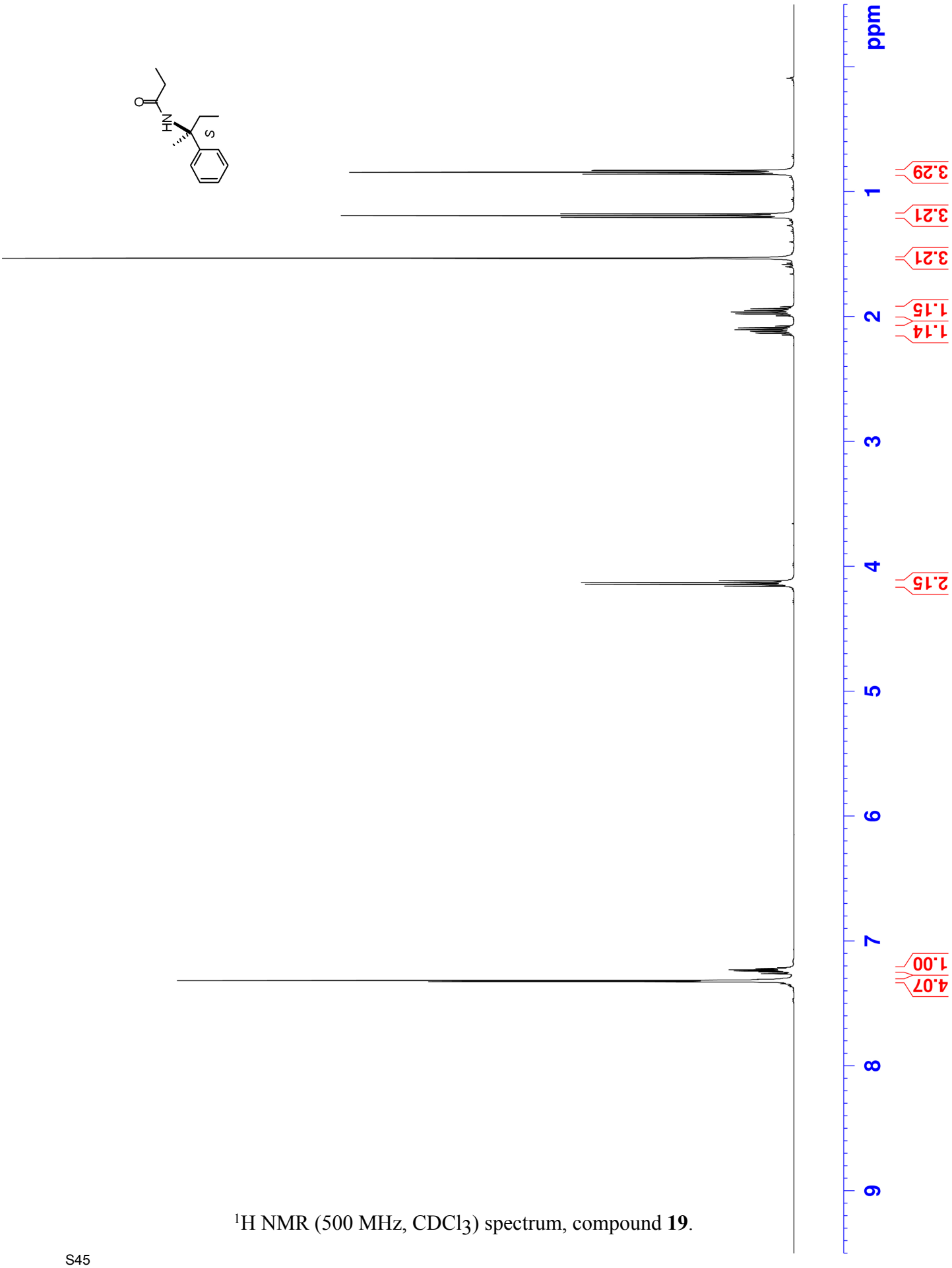
^{13}C NMR (125 MHz, $CDCl_3$) spectrum, compound **20**.



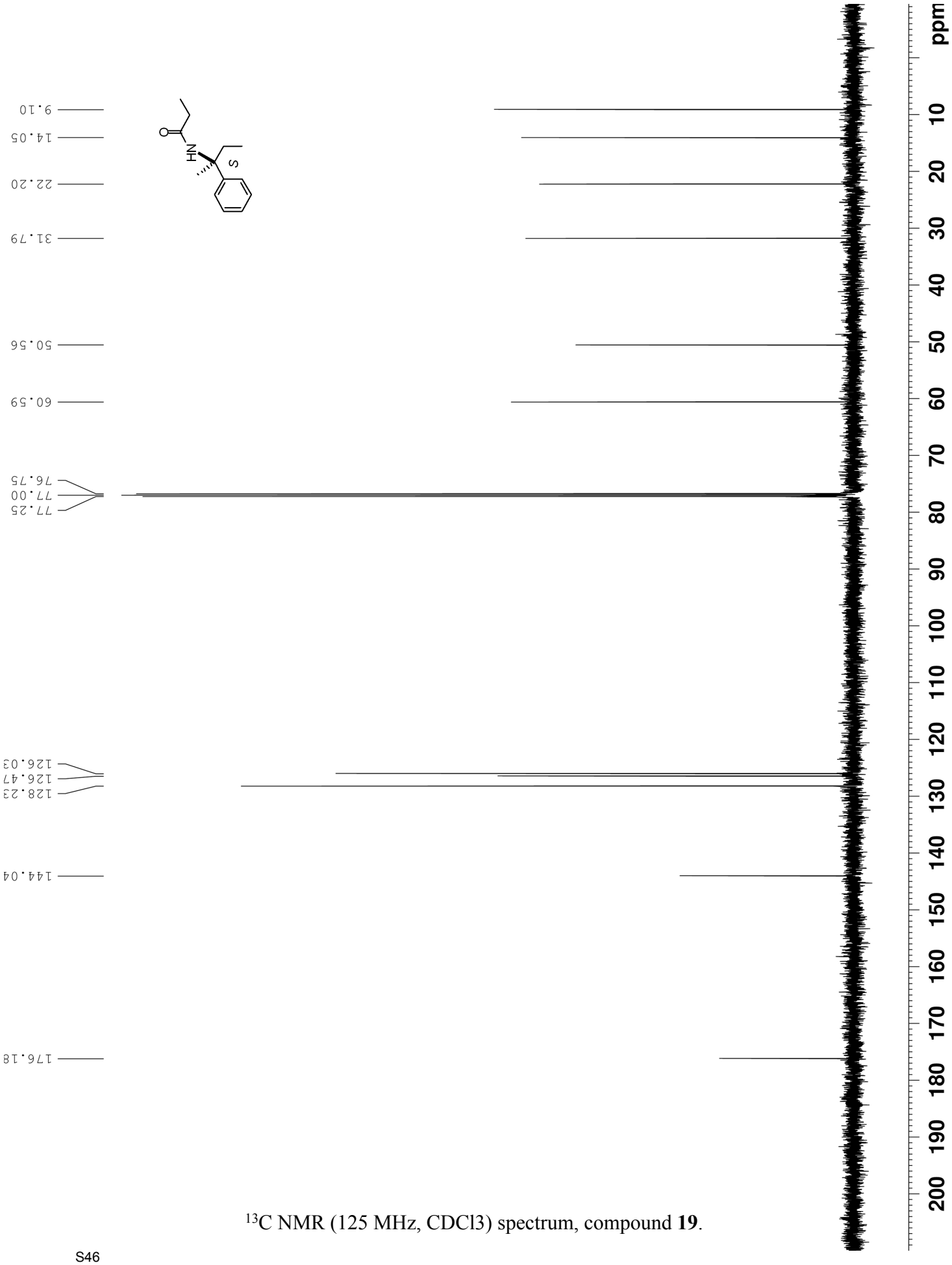
^{1}H NMR (500 MHz, $CDCl_3$) spectrum, compound **21**



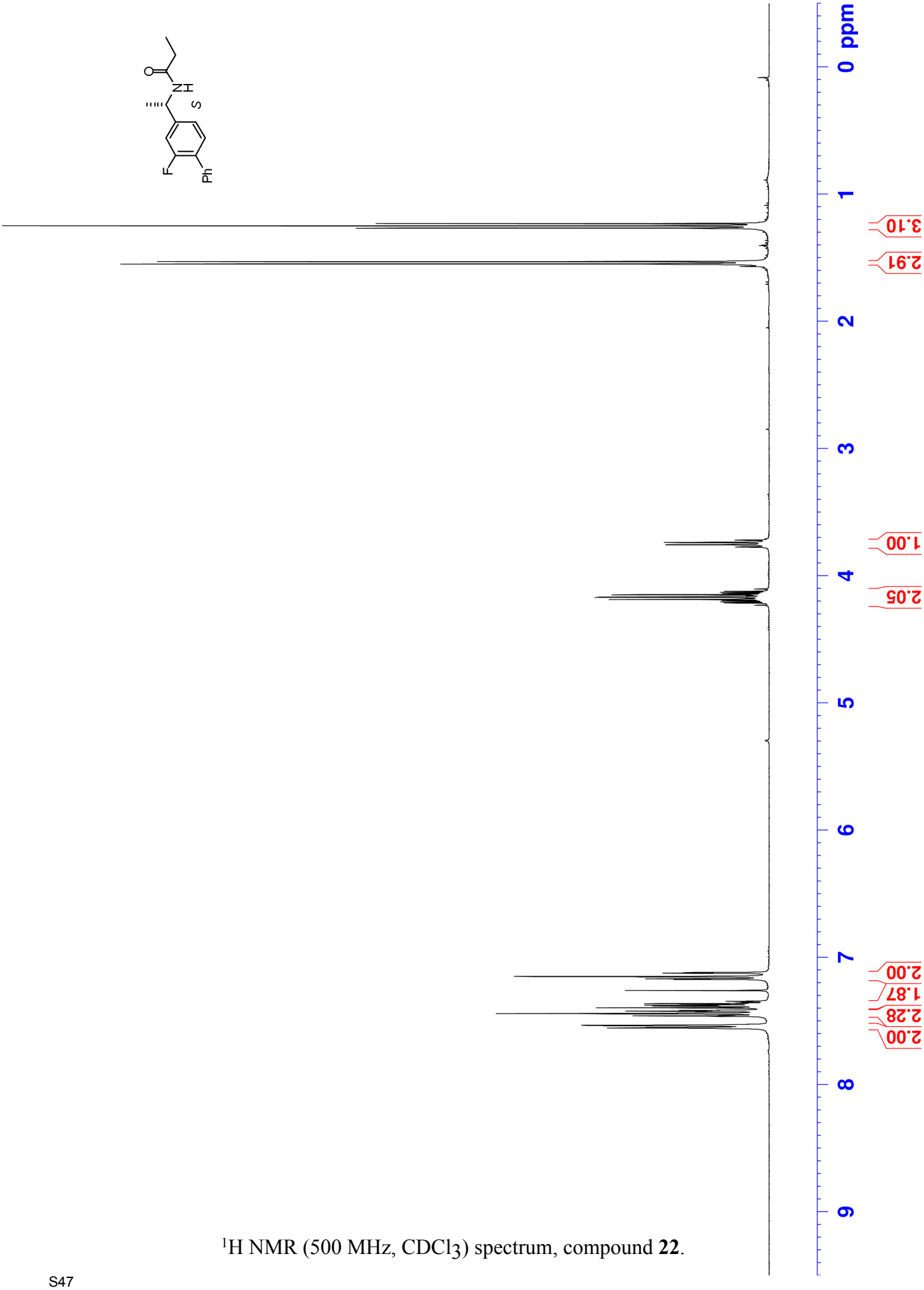
^{13}C NMR (125 MHz, $CDCl_3$) spectrum, compound **21**.



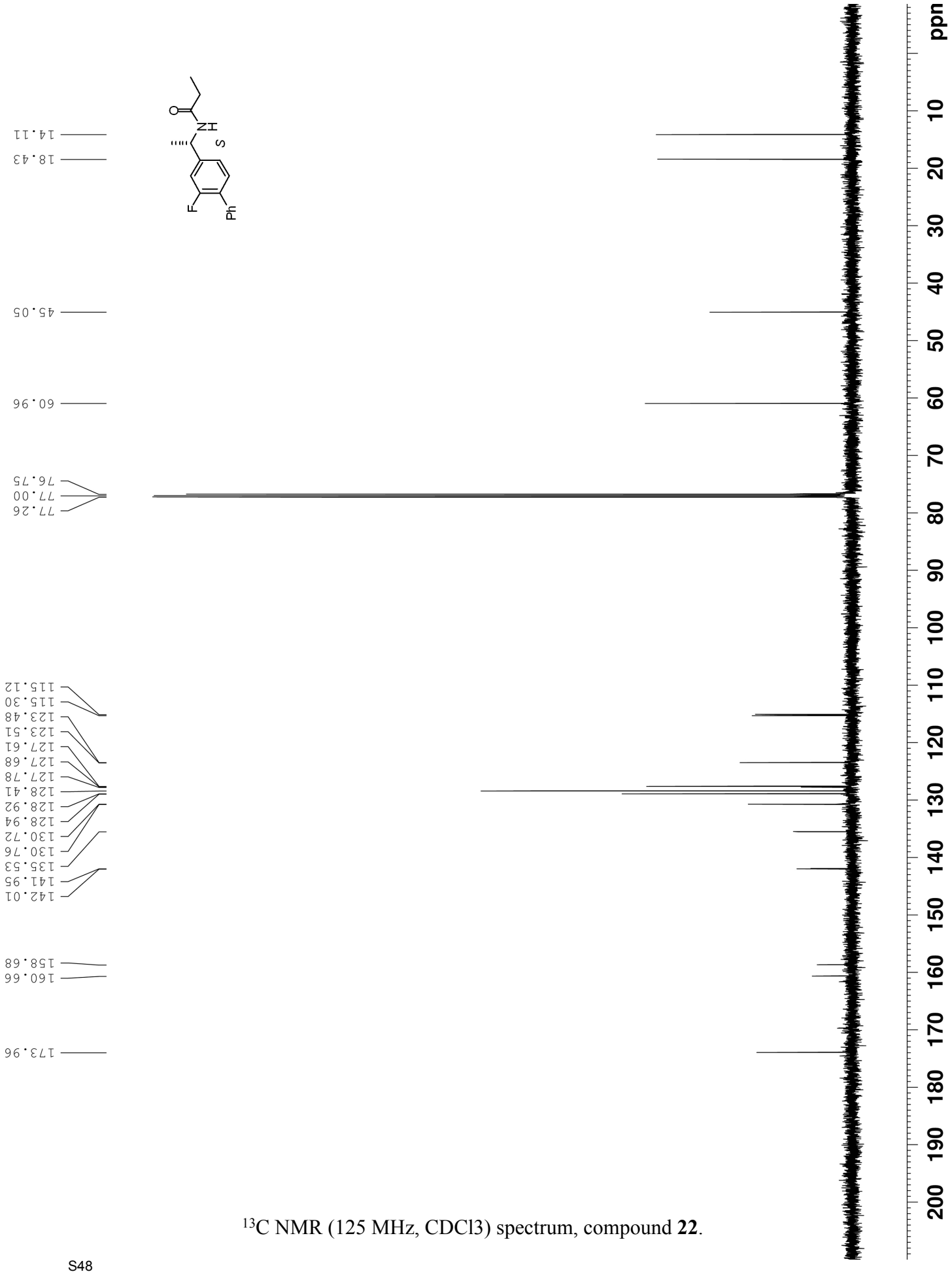
^{1}H NMR (500 MHz, $CDCl_3$) spectrum, compound **19**.



^{13}C NMR (125 MHz, CDCl3) spectrum, compound **19**.



^{1}H NMR (500 MHz, $CDCl_3$) spectrum, compound **22**.



^{13}C NMR (125 MHz, CDCl3) spectrum, compound **22**.

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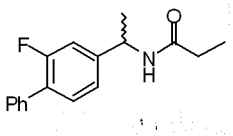

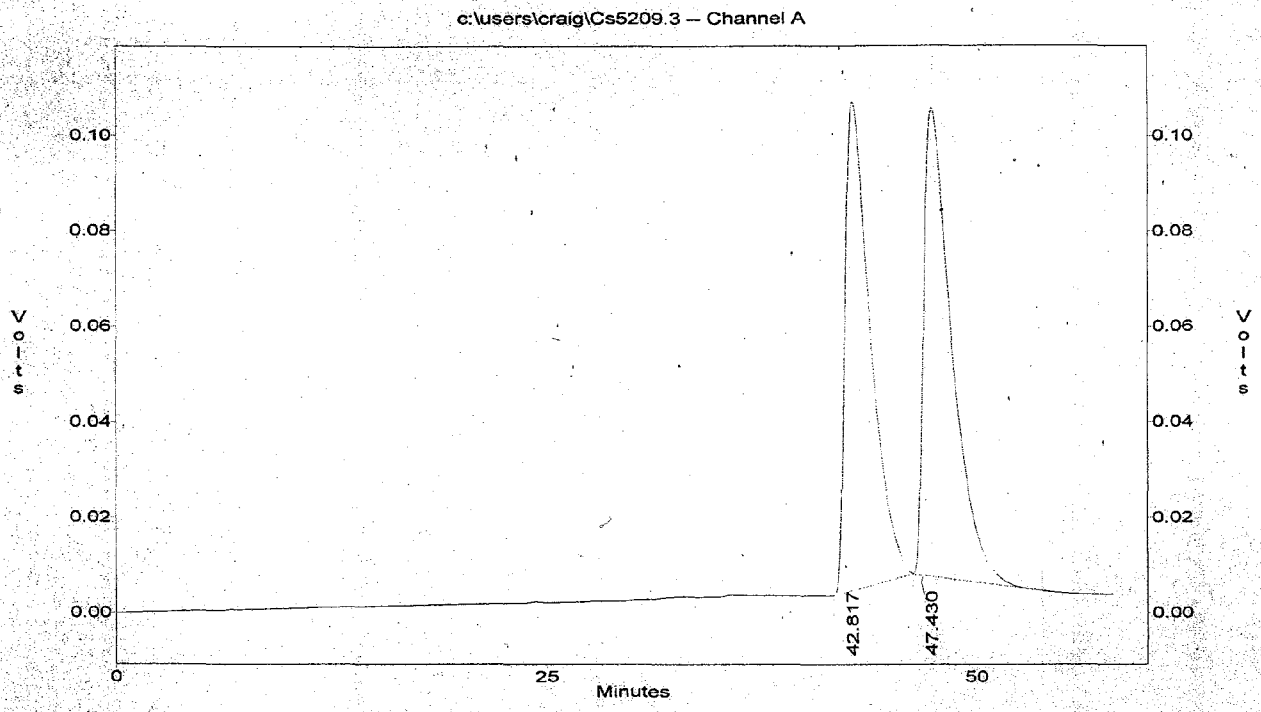

Channel A Results

Peak	Time	Area	Area %
1	42.82	10484576	48.830
2	47.43	10986850	51.170

Totals :

21471426	100.000	

Chiral HPLC (racemic mixture): hexanes
60 min at 0.50 mL/min, compound **22**.

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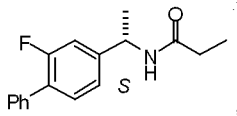

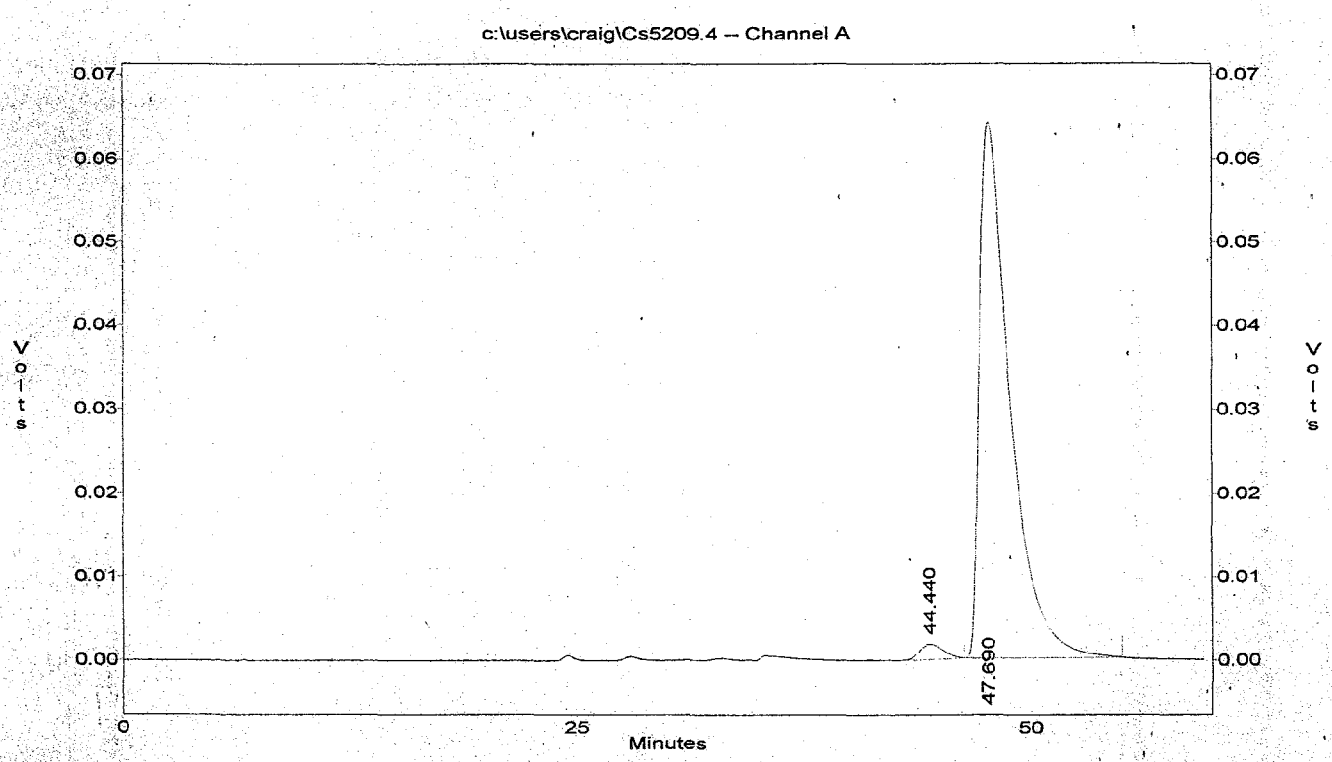

Channel A Results

Peak	Time	Area	Area %
1	44.44	162945	2.149
2	47.69	7418323	97.851

Totals :

	7581268	100.000

Chiral HPLC: hexanes; 60 min at 0.50 mL/min,
compound **22** from **7**.