Electronic Supplementary Information

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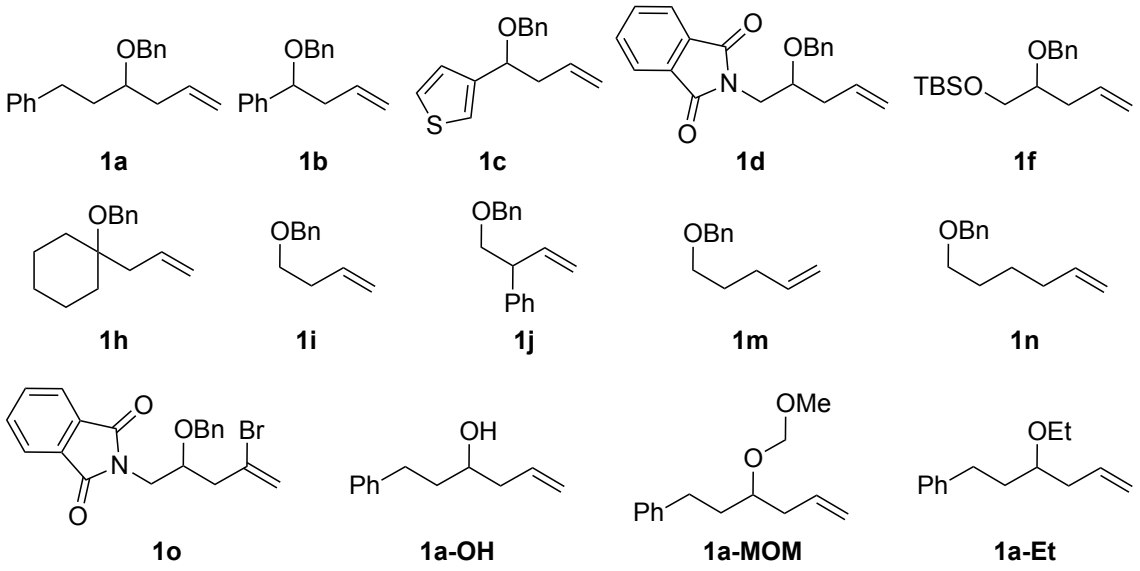
1. General

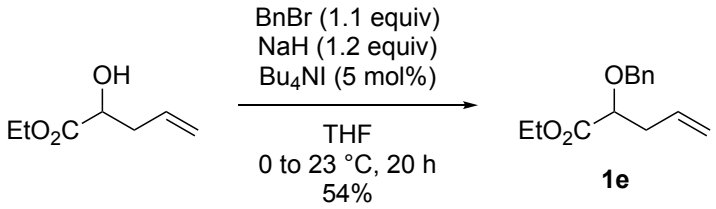
^{1}H (300, 400, or 500 MHz) spectra were recorded on a Bruker Avance 300, 400, 500, or JEOL ECA400SL spectrometer in $CDCl_3$ [using TMS (for ^{1}H, $\delta = 0.00$) as internal standard] or C_6D_6 [using C_6D_6 (for ^{1}H, $\delta = 7.16$) as internal standard]. ^{13}C NMR spectra (75 or 100 MHz) were recorded on a Bruker Avance 300, 400, or JEOL ECA400SL spectrometer in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, $\delta = 77.00$) as internal standard] or C_6D_6 [using C_6D_6 (for ^{13}C, $\delta = 128.02$) as internal standard]. ^{19}F NMR (377 MHz) spectra were recorded on a Bruker Avance 400 spectrometer. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, br = broad. High-resolution mass spectra were obtained with a Waters Q-Tof Premier mass spectrometer. Flash chromatography was performed using Merck silica gel 60 with distilled solvents. Tetrahydrofuran (THF) and dichloromethane (CH_2Cl_2) were taken from a solvent purification system (PS-400-5, innovative technology Inc.). 1,2-Dichloroethane ($ClCH_2CH_2Cl$) was distilled over CaH_2. Dilauroyl peroxide (97%, CAS:105-74-8) was purchased from Sigma-Aldrich and used as received. Other solvents and reagents, otherwise noted, were commercially available and used as received.

2. Synthesis of alkenes 1

Alkenes **1a-1d**,[1] **1f**,[2] **1h**,[3] **1i**,[4] **1j**,[1] **1m**,[5] **1n**,[6] **1o**,[1] **1a-OH**,[7] **1a-MOM**,[8] and **1a-Et**[9] were known compounds and prepared according to the reported procedures.



2.1. Synthesis of ethyl 2-(benzyloxy)pent-4-enoate (1e) (typical procedure A)



To a suspension of NaH (378 mg, 9.46 mmol) in THF (60 mL) was added ethyl 2-hydroxypent-4-enoate[10] (1.14 g, 7.88 mmol) at 0 °C under a N_2 atmosphere. After stirring at 0 °C for 30 min, benzyl bromide (1.00 mL, 8.67 mmol) and Bu_4NI (140 mg, 0.379 mmol) were added to the mixture successively at 0 °C. The reaction mixture was then stirred at 23 °C for 20 h and quenched with saturated aqueous NH_4Cl at 0 °C. The resulting organic materials were extracted twice with Et_2O. The combined extracts were washed with brine, dried over

[1] G. H. Lonca, D. Y. Ong, T. M. H. Tran, C. Tejo, S. Chiba and F. Gagosz, *Angew. Chem., Int. Ed.*, 2017, **56**, 11440.
[2] G. K. Friestad, J.-C. Marié and A. M. Deveau, *Org. Lett.*, 2004, **6**, 3249.
[3] K. Murugan, S. Srimurugan and C. Chen, *Tetrahedron*, 2011, **67**, 5621.
[4] P. A. Cleary and K. A. Woerpel, *Org. Lett.*, 2005, **7**, 5531.
[5] P. Srihari, B. Kumaraswamy, R. Somaiah and J. S. Yadav, *Synthesis*, 2010, 1039.
[6] P. Srihari, E. V. Bhasker, S. J. Harshavardhan and J. S. Yadav, *Synthesis*, 2006, 4041.
[7] M. R. Tatton, I. Simpson and T. J. Donohoe, *Org. Lett.*, 2014, **16**, 1920.
[8] K. Liu, R. E. Taylor and R. Kartika, *Org. Lett.*, 2006, **8**, 5393.
[9] K. M. McQuaid and D. Sames, *J. Am. Chem. Soc.*, 2009, **131**, 402.
[10] H. Zhu, J. G. Wickenden, N. E. Campbell, J. C. T. Leung, K. M. Johnson and G. M. Sammis, *Org. Lett.*, 2009, **11**, 2019.

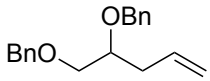
$MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc = 100:0 - 98:2) to give alkene **1e** (999 mg, 4.27 mmol) in 54% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.26 (5H, m), 5.83 (1H, ddt, *J* = 17.2, 10.6, 6.2 Hz), 5.12 (1H, d, *J* = 17.2 Hz), 5.09 (1H, d, *J* = 10.6 Hz), 4.72 (1H, d, *J* = 11.8 Hz), 4.45 (1H, d, *J* = 11.8 Hz), 4.27-4.18 (2H, m), 3.99 (1H, t, *J* = 6.2 Hz), 2.53 (2H, dd, *J* = 6.2, 6.2 Hz), 1.28 (3H, t, *J* = 7.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.1, 137.5, 133.1, 128.4, 128.0, 127.8, 117.9, 77.8, 72.3, 60.9, 37.4, 14.3.

ESIHRMS Found: m/z 235.1337; Calcd for $C_{14}H_{19}O_3$ $(M+H)^+$ 235.1334.

2.2. Synthesis of ((pent-4-ene-1,2-diylbis(oxy))bis(methylene))dibenzene (1g)



Prepared using 1-(benzyloxy)pent-4-en-2-ol[11] (2.04 g, 10.6 mmol) as the substrate following typical procedure A (page S3).

Purification: Hexane:EtOAc = 100:0-99:1

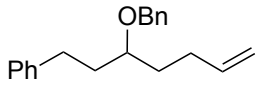
Yield: 1.75 g (6.19 mmol, 58% yield, 13 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.26 (10H, m), 5.85 (1H, ddt, *J* = 19.1, 10.4, 7.0 Hz), 5.10 (1H, d, *J* = 19.1 Hz), 5.06 (1H, d, *J* = 10.4 Hz), 4.68 (1H, d, *J* = 11.8 Hz), 4.62 (1H, d, *J* = 11.8 Hz), 4.55 (2H, s), 3.71-3.65 (1H, m), 3.59-3.54 (2H, m), 2.42-2.36 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.8, 138.4, 134.6, 128.34, 128.28, 127.7, 127.6, 127.54, 127.46, 117.1, 77.7, 73.3, 72.2, 71.8, 36.3.

ESIHRMS Found: m/z 283.1696; Calcd for $C_{19}H_{23}O_2$ $(M+H)^+$ 283.1698.

2.3. Synthesis of (3-(benzyloxy)hept-6-en-1-yl)benzene (1l)



Prepared using 1-phenylhept-6-en-3-ol[12] (982 mg, 5.16 mmol) as the substrate following typical procedure A (page S3).

[11] N. Nishizono, Y. Akama, M. Agata, M. Sugo, Y. Yamaguchi and K. Oda, *Tetrahedron*, 2011, **67**, 358.
[12] C. Palmer, N. A. Morra, A. C. Stevens, B. Bajtos, B. P. Machin and B. L. Pagenkopf, *Org. Lett.*, 2009, **11**, 5614.

Purification: Hexane:EtOAc = 90:10-80:20

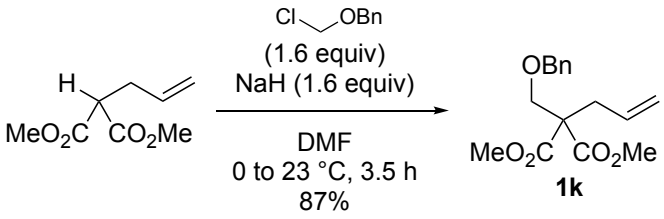
Yield: 597 mg (2.13 mmol, 41% yield, 13.5 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.32 (4H, m), 7.30-7.25 (3H, m), 7.19-7.16 (3H, m), 5.84 (1H, ddt, *J* = 17.1, 10.2, 6.6 Hz), 5.03 (1H, d, *J* = 17.1 Hz), 4.98 (1H, d, *J* = 10.2 Hz), 4.54 (2H, s), 3.48-3.42 (1H, m), 2.79-2.71 (1H, m), 2.69-2.61 (1H, m), 2.20-2.09 (2H, m), 1.94-1.79 (2H, m), 1.77-1.59 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 138.9, 138.6, 128.4, 128.3 (overlapped), 127.8, 127.5, 125.7, 114.6, 77.7, 70.8, 35.6, 33.0, 31.6, 29.6.

ESIHRMS Found: m/z 281.1905; Calcd for $C_{20}H_{25}O$ $(M+H)^+$ 281.1905.

2.4. Synthesis of Dimethyl 2-allyl-2-((benzyloxy)methyl)malonate (1k)



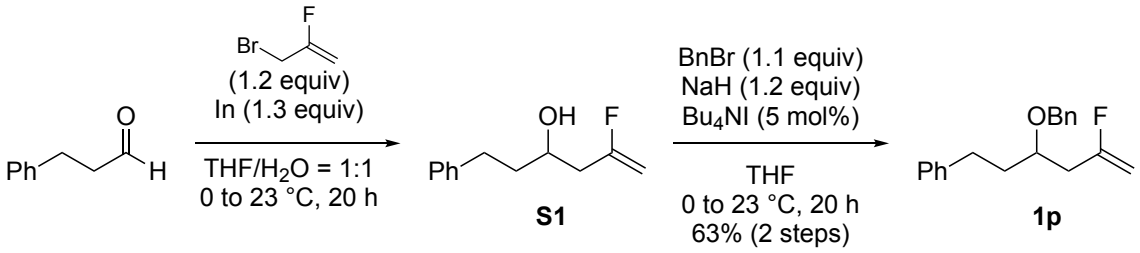
To a suspension of NaH (307 mg, 7.69 mmol) in DMF (20 mL) was added dimethyl allylmalonate (CAS: 40637-56-7) (827 mg, 4.80 mmol) slowly at 0 °C under a N_2 atmosphere. After stirring at 0 °C for 30 min, benzyl chloromethyl ether (1.10 mL, 7.91 mmol) was added to the reaction mixture. The mixture was stirred at 23 °C for 3.5 h and quenched with saturated aqueous NH_4Cl. The organic materials were extracted thrice with Et_2O and the combined extracts were washed with brine and dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc = 100:0 - 95:5) to give alkene **1k** (1.22 g, 4.17 mmol) in 87% yield as a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (5H, m), 5.61 (1H, ddt, *J* = 12.9, 10.0, 7.5 Hz), 5.09 (1H, d, *J* = 12.9 Hz), 5.06 (1H, d, *J* = 10.0 Hz), 4.51 (2H, s), 3.83 (2H, s), 3.70 (6H, s), 2.80 (2H, d, *J* = 7.5 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.9, 137.9, 132.3, 128.3, 127.6, 127.5, 119.3, 73.3, 69.3, 58.6, 52.4, 35.3.

ESIHRMS Found: m/z 293.1388; Calcd for $C_{16}H_{21}O_5$ $(M+H)^+$ 293.1389.

2.5. Synthesis of (3-(benzyloxy)-5-fluorohex-5-en-1-yl)benzene (1p)



To a solution of hydrocinnamaldehyde (CAS:104-53-0) (412 mg, 3.07 mmol) and 3-bromo-2-fluoroprop-1-ene (CAS: 35386-83-5) (507 mg, 3.65 mmol) in THF (10 mL) and H_2O (10 mL) was added indium powder (454 mg, 3.95 mmol) at 0 °C under a N_2 atmosphere. The reaction mixture was stirred at 23 °C for 20 h and quenched with saturated aqueous NH_4Cl. The mixture was filtered through a Celite pad with washing with EtOAc. The collected filtrate was extracted thrice with EtOAc and the combined organic extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude materials including alcohol **S1**, which was used to next step without further purification.

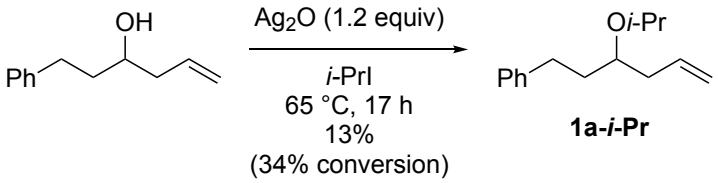
To a suspension of NaH (147 mg, 3.68 mmol) in THF (15 mL) was added a solution of crude alcohol **S1** in THF (5 mL) slowly at 0 °C under a N_2 atmosphere. After stirring at 0 °C for 30 min, benzyl bromide (0.40 mL, 3.38 mmol) and Bu_4NI (56.7 mg, 0.154 mmol) were added to the mixture successively at 0 °C. The reaction mixture was then stirred at 23 °C for 20 h and quenched with saturated aqueous NH_4Cl at 0 °C. The resulting organic materials were extracted twice with Et_2O. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc = 100:0-99:1) to give alkene **1p** (545 mg, 1.92 mmol) in 63% yield over 2 steps as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.32 (4H, m), 7.30-7.23 (3H, m), 7.19-7.14 (3H, m), 4.63-4.55 (1H, m + 1H, d, *J* = 12.1 Hz), 4.50 (1H, d, *J* = 12.1 Hz), 4.31 (1H, dd, *J* = 50.0, 2.7 Hz), 3.67 (1H, tt, *J* = 6.2, 6.1 Hz), 2.83-2.76 (1H, m), 2.68-2.50 (2H, m), 2.44-2.34 (1H, m), 1.94-1.87 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 163.8 (d, *J* = 255.1 Hz), 142.0, 138.4, 128.4 (3 carbons were overlapped), 127.9, 127.7, 125.8, 92.2 (d, *J* = 19.8 Hz), 75.3, 71.5, 37.2 (d, *J* = 26.5 Hz), 36.0, 31.5.

ESIHRMS Found: m/z 285.1659; Calcd for $C_{19}H_{22}OF$ $(M+H)^+$ 285.1655.

2.6. Synthesis of (3-isopropoxyhex-5-en-1-yl)benzene (1a-*i*-Pr)



To a solution of 1-phenylhex-5-en-3-ol[7] (1.52 g, 8.60 mmol) in 2-iodopropane (10 mL) was added Ag_2O (2.39 g, 10.3 mmol) at 23 °C under a N_2 atmosphere. The reaction mixture was heated to 65 °C and stirred for 17 h. The reaction mixture was cooled down to 23 °C and the mixture was filtered through a Celite pad with washing with Et_2O. The collected filtrate was concentrated *in vacuo* to afford the crude material. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc = 95:5-90:10) to give alkene **1a-*i*-Pr** (242 mg, 1.11 mmol) in 13% yield as a colorless oil, along with recovery of 1-phenylhex-5-en-3-ol (1.00 g, 5.67 mmol) in 66% yield.

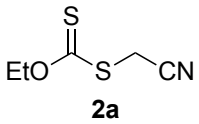
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.24 (2H, m), 7.20-7.15 (3H, m), 5.82 (1H, ddt, *J* = 17.3, 10.2, 7.1 Hz), 5.07 (1H, d, *J* = 17.3 Hz), 5.03 (1H, d, *J* = 10.2 Hz), 3.68-3.62 (1H, m), 3.39 (1H, qq, *J* = 6.0, 6.0 Hz), 2.81-2.73 (1H, m), 2.64-2.56 (1H, m), 2.29-2.26 (2H, m), 1.82-1.72 (2H, m), 1.16 (3H, d, *J* = 6.0 Hz), 1.15 (3H, d, *J* = 6.0 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 135.1, 128.34, 128.28, 125.6, 116.8, 76.0, 69.7, 39.4, 36.3, 31.9, 23.1, 22.6.

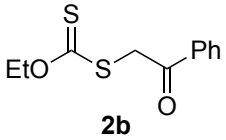
ESIHRMS Found: m/z 219.1750; Calcd for $C_{15}H_{23}O$ $(M+H)^+$ 219.1749.

3. Synthesis of xanthates 2

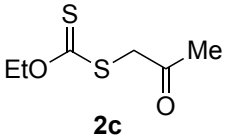
Xanthates **2a**-**2c**,[13] **2e**,[14] **2f**,[13] and **2h**[13] were known compounds and prepared according to the reported procedures.



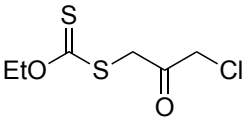
2a



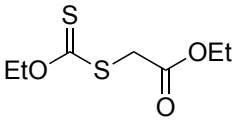
2b



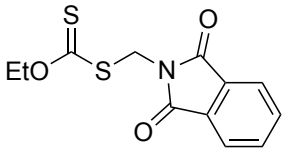
2c



2e

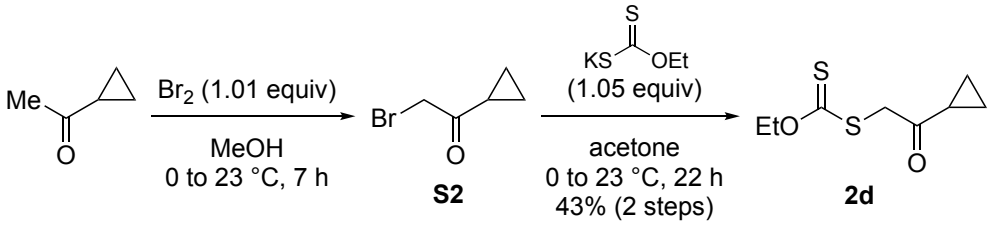


2f



2h

3.1. Synthesis of *S*-(cyanomethyl) *O*-ethyl carbonodithioate (2d)



To a solution of cyclopropyl methyl ketone (CAS: 765-43-5) (2.09 g, 24.9 mmol) in methanol (16 mL) was added bromine (1.30 mL, 25.4 mmol) dropwise at 0 °C under a N_2 atmosphere. The mixture was stirred at 23 °C for 7 h and quenched with cold water. The organic materials were extracted thrice with Et_2O and the combined organic extracts were washed with water, saturated aqueous $NaHCO_3$ and brine. The organic extracts were dried over $MgSO_4$, filtered and concentrated *in vacuo* to afford the crude materials including bromide **S2**, which was used to next step without further purification.

To a solution of crude bromide **S2** in acetone (100 mL) was added potassium ethyl xanthogenate (4.21 g, 26.3 mmol) portion-wise at 0 °C under a N_2 atmosphere. The reaction mixture was stirred at 23 °C for 22 h and quenched with water. The organic materials were extracted twice with EtOAc. The combined organic extracts were washed with water and brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: hexane : EtOAc =30:1) to yield xanthate **2d** (2.17 g, 10.6 mmol) in 43% yield over 2 steps as a yellow oil.

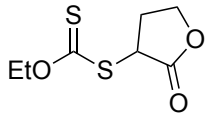
[13] S. Kakaei, N. Chen and J. X. Xu, *Tetrahedron*, 2013, **69**, 302.
[14] M. de Greef and S. Z. Zard, *Org. Lett.*, 2007, **9**, 1773.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.64 (2H, q, *J* = 7.1 Hz), 4.15 (2H, s), 2.18 (1H, tt, *J* = 7.7, 4.5 Hz), 1.42 (3H, t, *J* = 7.1 Hz), 1.14-1.10 (2H, m), 1.01-0.96 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 213.2, 203.2, 70.7, 46.1, 19.9, 13.7, 11.9.

ESIHRMS Found: m/z 205.0358; Calcd for $C_8H_{13}O_2S_2$ $(M+H)^+$ 205.0357.

3.2. Synthesis of *O*-ethyl *S*-(2-oxotetrahydrofuran-3-yl) carbonodithioate (2g)



Synthesis of **2g** was conducted by nucleophilic substitution of α-bromo-γ-butyrolactone (CAS: 5061-21-2) (2.53 g, 15.3 mmol) with potassium ethyl xanthogenate (2.95 g, 18.4 mmol) following a procedure similar to that used for **2d** (first step).

Purification: Hexane:EtOAc = 80:20

Yield: 2.96 g (14.4 mmol, 94% yield, 2 h) of a yellow oil.

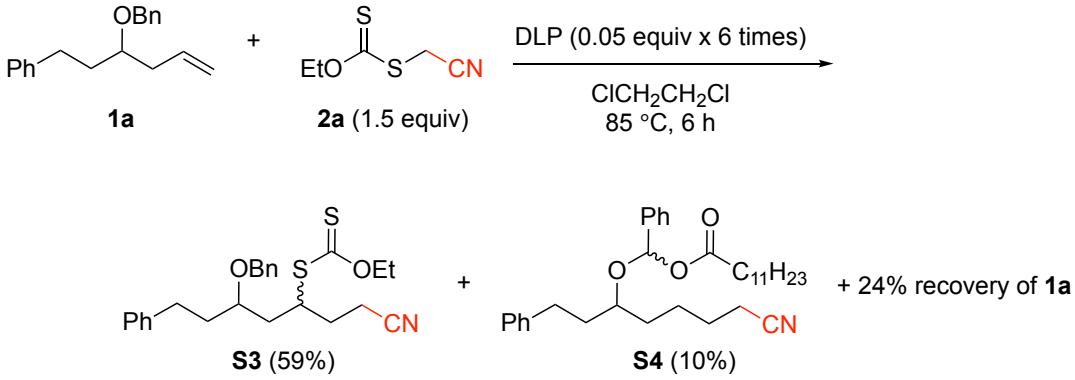
^{1}H NMR (400 MHz, $CDCl_3$): δ 4.68 (2H, q, *J* = 7.1 Hz), 4.53-4.44 (2H, m), 4.39-4.33 (1H, m), 2.94-2.86 (1H, m), 2.49-2.39 (1H, m), 1.44 (3H, t, *J* = 7.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 210.7, 173.2, 71.0, 66.5, 46.0, 29.8, 13.6.

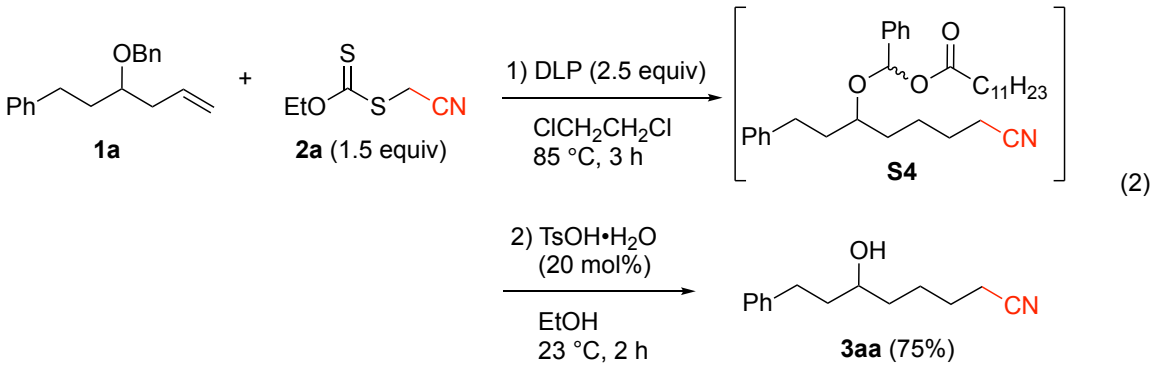
ESIHRMS Found: m/z 207.0155; Calcd for $C_7H_{11}O_3S_2$ $(M+H)^+$ 207.0150.

4. Optimization of the reaction conditions

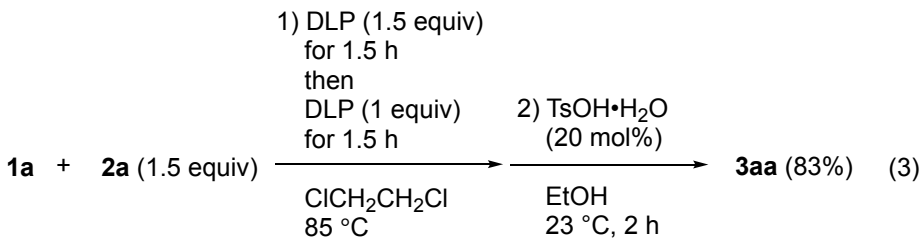
In the reaction of alkene **1a** and xanthate **2a** with DLP (total 0.3 equiv) in 1,2-dichloroethane at 85 °C, we observed the formation of xanthate adduct **S3** in 59% NMR yield along with ketal **S4** in 10% NMR yield [Eq.(1)] (see S45). The presence of ketal **S4** was confirmed by the ^{1}H NMR (see S48) and mass spectrometry (MS = 506 $[M+H]^{+}$) analyses of the crude mixture.



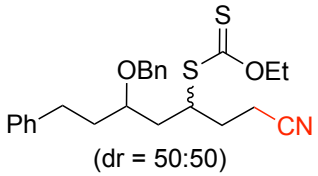
Additionally, we found that the use of 2.5 equiv of dilauroyl peroxide (DLP) ensured the full conversion of alkene **1a** to ketal **S4** [Eq.(2)]. Subsequent solvolysis of ketal **S4** was conducted using 20 mol% of TsOH with EtOH what afforded alcohol **3aa** in 75% yield.



Further optimization of the reaction conditions revealed that the portion-wise addition of DLP (1.5 equiv and 1 equiv) afforded alcohol **3aa** in higher yield (83%) [Eq.(3)].



***S*-(5-(benzyloxy)-1-cyano-7-phenylheptan-3-yl) *O*-ethyl carbonodithioate (S3)**



(dr = 50:50)

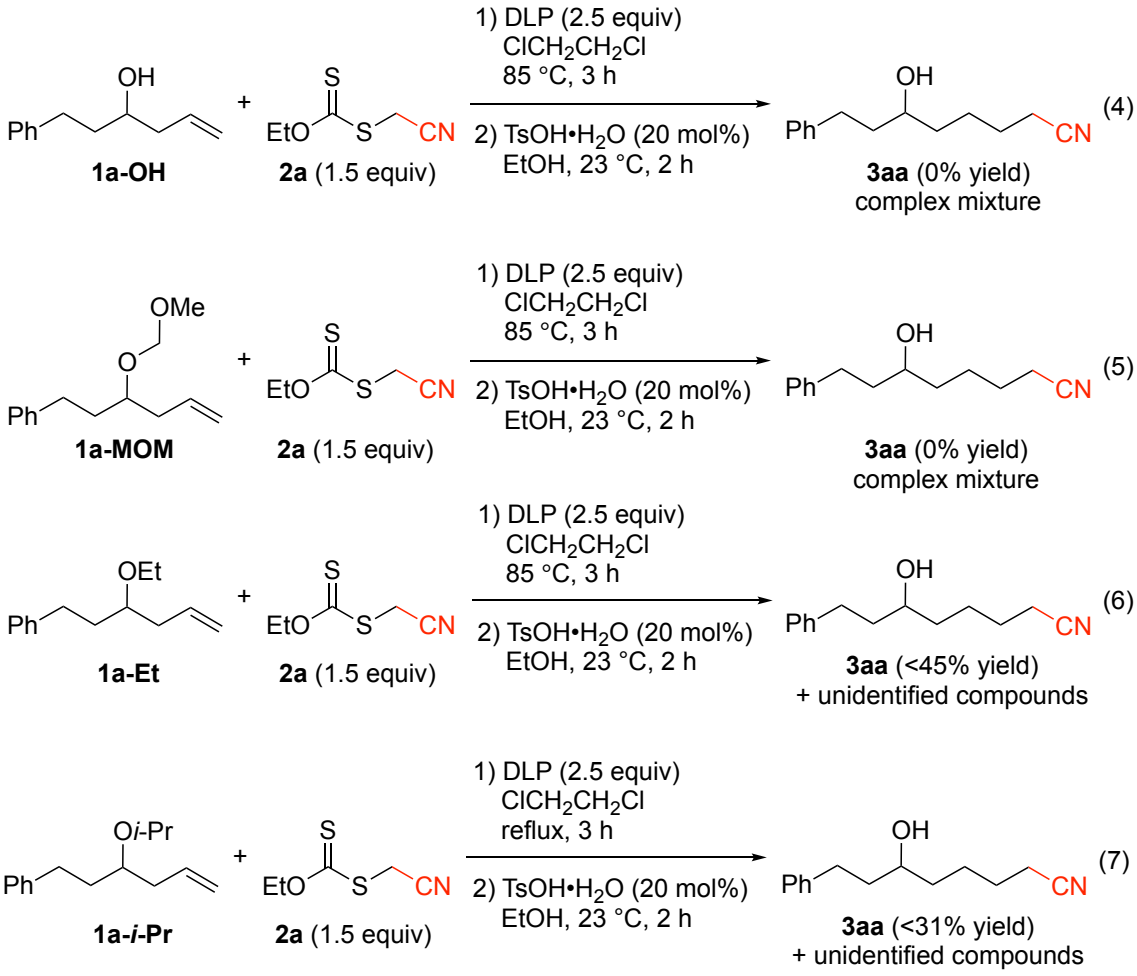
^{1}H NMR (400 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 7.38-7.27 (7H×0.50, m + 7H×0.50, m), 7.22-7.16 (3H×0.50, m + 3H×0.50, m), 4.67-4.60 (2H×0.50, m + 2H×0.50, m), 4.57-4.53 (1H×0.50, m + 1H×0.50, m), 4.45-4.40 (1H×0.50, m + 1H×0.50, m), 4.07-4.01 (1H×0.50, m), 3.96-3.89 (1H×0.50, m), 3.71-3.65 (1H×0.50, m), 3.60-3.54 (1H×0.50, m), 2.73-2.62 (2H×0.50, m + 2H×0.50, m), 2.48-2.31 (2H×0.50, m + 2H×0.50, m), 2.19-2.10 (1H×0.50, m), 2.08-1.99 (2H×0.50, m + 1H×0.50, m), 1.96-1.77 (4H×0.50, m + 4H×0.50, m), 1.42 (3H×0.50, t, J = 7.1 Hz), 1.41 (3H×0.50, t, J = 7.1 Hz).

^{13}C NMR (75 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 213.0, 212.7, 141.82, 141.80, 138.3, 128.54, 128.50, 128.43, 128.36, 128.1, 127.9, 127.8, 126.03, 126.00, 119.3, 119.1, 76.0, 75.4, 71.7, 70.8, 70.42, 70.36, 47.3, 47.0, 38.7, 38.2, 35.6, 35.3, 31.8, 31.3, 31.2, 30.4, 14.9, 14.8, 13.8.

ESIHRMS *for the mixture of diastereoisomers* Found: m/z 428.1714; Calcd for $C_{24}H_{30}NO_2S_2$ $(M+H)^+$ 428.1718.

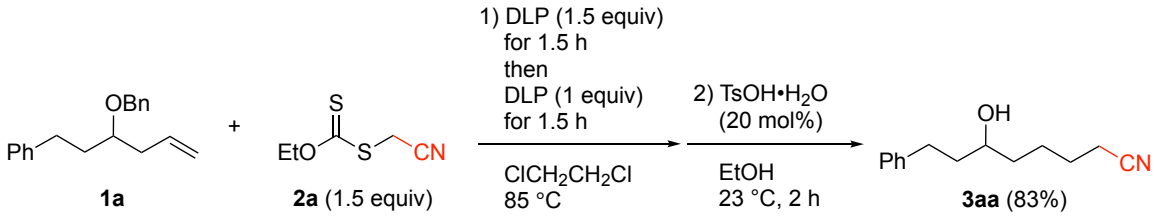
5. Investigation of the reactivity of alcohol and other ethers

The reaction of homoallylic alcohol **1a-OH** [Eq.(4)] with xanthate **2a** under the optimized reaction conditions did not provide the hydrocyanomethylation product **3aa**, thus showing the importance of the presence of an ethereal moiety for the precise hydrogen delivery. In addition, the reactions of *O*-methoxymethyl (MOM) ether **1a-MOM** [Eq.(5)], *O*-ethyl ether **1a-Et** [Eq.(6)], and *O*-isopropyl ether **1a-*i*-Pr** [Eq.(7)] with xanthate **2a** under the optimized reaction conditions resulted in a yield of **3aa** lower than that obtained with *O*-Bn ether **1a**.



6. *Anti*-Markovnikov hydrofunctionalization of alkenes with xanthates: substrate scope of alkenes 1 with cyanomethyl xanthate 2a (Scheme 3)

6.1. Synthesis of 6-hydroxy-8-phenyloctanenitrile (3aa) (typical procedure B)



To a 10 mL sealed tube containing alkene **1a** (133 mg, 0.501 mmol) and xanthate **2a** (121 mg, 0.752 mmol) were added 1,2-dichloroethane (1 mL) and dilauroyl peroxide (DLP) (300 mg, 0.752 mmol) at 23 °C under a N_2 atmosphere. The tube was sealed and the solution was then stirred at 85 °C for 1.5 h. Additional DLP (200 mg, 0.501 mmol) was added at 23 °C and the reaction mixture was stirred at 85 °C for 1.5 h. After confirmation of the full consumption of xanthate adduct **S3** (based on TLC analysis), the reaction mixture was cooled to 23 °C.

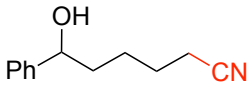
To the reaction mixture including ketal **S4** was added TsOH•H_2O (19.0 mg, 0.100 mmol) in EtOH (1 mL) at 23 °C. The reaction mixture was stirred at 23 °C for 2 h and then quenched with saturated aqueous $NaHCO_3$. The resulting organic materials were extracted thrice with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc:MeOH = 20:80:1) to give alcohol **3aa** (90.1 mg, 0.415 mmol) in 83% yield as a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (2H, m), 7.20-7.17 (3H, m), 3.63-3.61 (1H, m), 2.81-2.75 (1H, m), 2.71-2.63 (1H, m), 2.33 (2H, t, J = 6.9 Hz), 1.80-1.75 (2H, m), 1.73-1.61 (3H, m), 1.59-1.46 (4H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 128.4, 128.3, 125.9, 119.6, 70.8, 39.1, 36.5, 32.0, 25.3, 24.8, 17.1.

ESIHRMS Found: m/z 218.1544; Calcd for $C_{14}H_{20}NO$ $(M+H)^+$ 218.1545.

6.2. Synthesis of 6-hydroxy-6-phenylhexanenitrile (3ba)



Prepared using alkene **1b** (122 mg, 0.513 mmol) and xanthate **2a** (124 mg, 0.770 mmol) with DLP (307 mg, 0.770 mmol for 1 h and then, 205 mg, 0.513 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 90:10:1-75:25:1

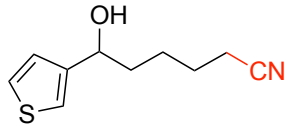
Yield: 63.1 mg (0.333 mmol, 65% yield, 2 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.26 (5H, m), 4.67 (1H, t, *J* = 6.5 Hz), 2.32 (2H, t, *J* = 7.1 Hz), 1.97 (1H, br), 1.87-1.77 (1H, m), 1.75-1.53 (4H, m), 1.50-1.41 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 128.4, 127.6, 125.7, 119.6, 74.0, 38.0, 25.2, 24.9, 17.0.

ESIHRMS Found: m/z 212.1049; Calcd for $C_{12}H_{15}NONa$ $(M+Na)^+$ 212.1051.

6.3. Synthesis of 6-hydroxy-6-(thiophen-3-yl)hexanenitrile (3ca)



Prepared using alkene **1c** (123 mg, 0.501 mmol) and xanthate **2a** (121 mg, 0.752 mmol) with DLP (300 mg, 0.752 mmol for 1 h and then, 199 mg, 0.501 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 80:20:1-65:35:1

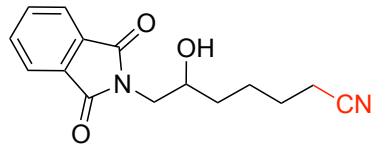
Yield: 53.4 mg (0.273 mmol, 55% yield, 2 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (1H, dd, *J* = 4.8, 3.1 Hz), 7.19 (1H, dd, *J* = 3.2, 3.1 Hz), 7.07 (1H, dd, *J* = 4.8, 3.2 Hz), 4.79 (1H, t, *J* = 6.5 Hz), 2.34 (2H, t, *J* = 7.3 Hz), 1.89-1.74 (3H, m), 1.71-1.63 (2H, m), 1.62-1.51 (1H, m), 1.50-1.42 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 145.9, 126.4, 125.4, 120.8, 119.6, 70.2, 37.4, 25.3, 24.9, 17.1.

ESIHRMS Found: m/z 196.0796; Calcd for $C_{10}H_{14}NOS$ $(M+H)^+$ 196.0796.

6.4. Synthesis of 7-(1,3-dioxoisoindolin-2-yl)-6-hydroxyheptanenitrile (3da)



Prepared using alkene **3d** (172 mg, 0.535 mmol) and xanthate **1a** (129 mg, 0.803 mmol) with DLP (320 mg, 0.803 mmol for 1 h and then, 213 mg, 0.535 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 70:30:1-50:50:1

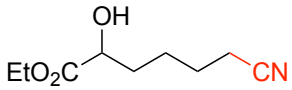
Yield: 97.8 mg (0.359 mmol, 67% yield, 2 h) of a pale yellow solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (2H, dd, *J* = 5.1, 3.2 Hz), 7.74 (2H, dd, *J* = 5.1, 3.2 Hz), 3.96-3.87 (1H, m), 3.80 (1H, dd, *J* = 14.3, 3.5 Hz), 3.76 (1H, dd, *J* = 14.3, 7.1 Hz), 2.54 (1H, br), 2.36 (2H, t, *J* = 6.7 Hz), 1.73-1.63 (3H, m), 1.61-1.47 (3H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 169.0, 134.2, 131.8, 123.5, 119.6, 70.2, 44.4, 34.0, 25.3, 24.7, 17.1.

ESIHRMS Found: m/z 273.1243; Calcd for $C_{15}H_{17}N_2O_3$ $(M+H)^+$ 273.1239.

6.5. Synthesis of ethyl 6-cyano-2-hydroxyhexanoate (3ea)



Prepared using alkene **3e** (120 mg, 0.512 mmol) and xanthate **1a** (124 mg, 0.768 mmol) with DLP (306 mg, 0.768 mmol for 1 h and then, 204 mg, 0.512 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 80:20:1-70:30:1

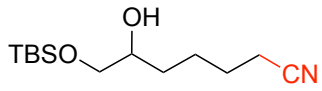
Yield: 68.4 mg (0.369 mmol, 72% yield, 2 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.27 (2H, q, *J* = 7.1 Hz), 4.20-4.16 (1H, m), 2.81 (1H, br), 2.38 (2H, t, *J* = 6.2 Hz), 1.90-1.81 (1H, m), 1.77-1.55 (5H, m), 1.33 (3H, t, *J* = 7.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 174.8, 119.4, 69.9, 61.7, 33.2, 25.0, 23.9, 16.9, 14.1.

ESIHRMS Found: m/z 186.1133; Calcd for $C_9H_{16}NO_3$ $(M+H)^+$ 186.1130.

6.6. Synthesis of 7-((*tert*-butyldimethylsilyl)oxy)-6-hydroxyheptanenitrile (3fa)



Prepared using alkene **3f** (151 mg, 0.494 mmol) and xanthate **1a** (120 mg, 0.741 mmol) with DLP (295 mg, 0.742 mmol for 1 h and then, 197 mg, 0.494 mmol for 1 h) following the typical procedure B (page S12). Solvolysis was conducted using AcOH (50 μL, 0.874 mmol) with H_2O (1 mL) instead of TsOH (20 mol%) in EtOH.

Purification: Hexane:EtOAc = 90:10-80:20

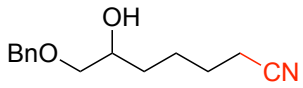
Yield: 73.0 mg (0.284 mmol, 57% yield, 2 h) of a yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.63-3.60 (2H, m), 3.42-3.37 (1H, m), 2.44 (1H, br), 2.36 (2H, t, *J* = 7.0 Hz), 1.75-1.66 (2H, m), 1.65-1.56 (1H, m), 1.55-1.49 (1H, m), 1.47-1.41 (2H, m), 0.91 (9H, s), 0.080 (6H, s).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7, 71.4, 67.1, 31.9, 25.9, 25.5, 24.8, 18.3, 17.1, -5.36, -5.42.

ESIHRMS Found: m/z 258.1886; Calcd for $C_{13}H_{28}NO_2Si$ $(M+H)^+$ 258.1889.

6.7. Synthesis of 7-(benzyloxy)-6-hydroxyheptanenitrile (3ga)



Prepared using alkene **1g** (144 mg, 0.510 mmol) and xanthate **2a** (123 mg, 0.765 mmol) with DLP (305 mg, 0.765 mmol for 1.5 h and then, 203 mg, 0.510 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 80:20:1-60:40:1

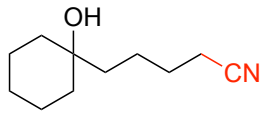
Yield: 67.4 mg (0.289 mmol, 57% yield, 2.5 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.28 (5H, m), 4.55 (2H, s), 3.85-3.77 (1H, m), 3.49 (1H, dd, *J* = 9.4, 3.2 Hz), 3.33 (1H, dd, *J* = 9.4, 7.8 Hz), 2.44 (1H, br), 2.34 (2H, t, *J* = 6.9 Hz), 1.72-1.57 (3H, m), 1.54-1.43 (3H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 137.8, 128.5, 127.8, 127.7, 119.6, 74.3, 73.3, 69.9, 32.1, 25.3, 24.7, 17.0.

ESIHRMS Found: m/z 234.1499; Calcd for $C_{14}H_{20}NO_2$ $(M+H)^+$ 234.1494.

6.8. Synthesis of 5-(1-hydroxycyclohexyl)pentanenitrile (3ha)



Prepared using alkene **1h** (110 mg, 0.477 mmol) and xanthate **2a** (116 mg, 0.716 mmol) with DLP (285 mg, 0.716 mmol for 2 h and then, 190 mg, 0.476 mmol for 1.5 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc = 90:10-70:30

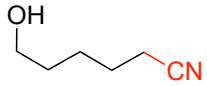
Yield: 62.1 mg (0.343 mmol, 72% yield, 3.5 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.36 (2H, t, *J* = 7.0 Hz), 1.71-1.62 (2H, m), 1.59-1.39 (14H, m), 1.32-1.26 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7, 71.2, 41.4, 37.4, 25.9, 25.7, 22.21, 22.16, 17.2.

ESIHRMS Found: m/z 182.1550; Calcd for $C_{11}H_{20}NO$ $(M+H)^+$ 182.1545.

6.9. Synthesis of 6-hydroxyhexanenitrile (3ia)[15]



Prepared using alkene **1i** (81.3 mg, 0.501 mmol) and xanthate **2a** (121 mg, 0.752 mmol) with DLP (300 mg, 0.752 mmol for 1 h and then, 200 mg, 0.501 mmol for 1 h) following typical procedure B (page S12). Analytical data match those reported in literature.

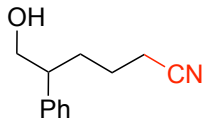
Purification: Hexane:EtOAc = 90:10-20:80

Yield: 34.4 mg (0.304 mmol, 61% yield, 2 h) of a white solid.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (2H, t, *J* = 6.1 Hz), 2.37 (2H, t, *J* = 7.0 Hz), 1.75-1.68 (2H, m), 1.65-1.51 (5H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.6, 62.3, 31.7, 25.2, 25.0, 17.1.

6.10. Synthesis of 6-hydroxy-5-phenylhexanenitrile (3ja)



Prepared using alkene **1j** (117 mg, 0.493 mmol) and xanthate **2a** (119 mg, 0.740 mmol) with DLP (295 mg, 0.740 mmol for 1 h and then, 197 mg, 0.493 mmol for 1 h) following typical procedure B (page S12).

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[15] S. Chiampanichayakul, M. Pohmakotr, V. Reutrakul, T. Jaipetch and C. Kuhakarn, *Synthesis,* 2008, 2045.

Purification: Hexane:EtOAc = 70:30-50:50

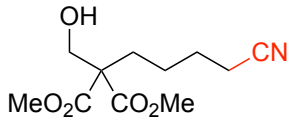
Yield: 63.3 mg (0.334 mmol, 68% yield, 2 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.33 (2H, m), 7.29-7.25 (1H, m), 7.22-7.19 (2H, m), 3.77-3.74 (2H, m), 2.83-2.76 (1H, m), 2.29 (2H, t, *J* = 7.1 Hz), 1.96-1.87 (1H, m), 1.79-1.69 (1H, m), 1.63-1.52 (2H, m), 1.34 (1H, br).

^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 128.9, 127.9, 127.1, 119.5, 67.3, 48.1, 30.9, 23.3, 17.2.

ESIHRMS Found: m/z 190.1229; Calcd for $C_{12}H_{16}NO$ $(M+H)^+$ 190.1232.

6.11. Synthesis of dimethyl 2-(4-cyanobutyl)-2-(hydroxymethyl)malonate (3ka)



Prepared using alkene **1k** (144 mg, 0.493 mmol) and xanthate **2a** (119 mg, 0.740 mmol) with DLP (295 mg, 0.740 mmol for 1 h and then, 197 mg, 0.493 mmol for 1 h) following typical procedure B (page S12). Solvolysis was conducted using TsOH (20 mol%) in MeOH.

Purification: Hexane:EtOAc = 60:40-20:80

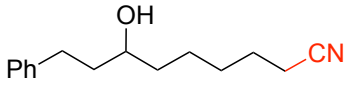
Yield: 75.9 mg (0.312 mmol, 63% yield, 2 h) of a colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.95 (2H, d, *J* = 7.0 Hz), 3.78 (6H, s), 2.55-2.52 (1H, m), 2.37 (2H, t, *J* = 7.1 Hz), 1.97-1.93 (2H, m), 1.68 (2H, tt, *J* = 7.5, 7.2 Hz), 1.51-1.45 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 119.3, 64.4, 59.4, 52.7, 30.6, 25.5, 23.6, 16.8.

ESIHRMS Found: m/z 244.1181; Calcd for $C_{11}H_{18}NO_5$ $(M+H)^+$ 244.1185.

6.12. Synthesis of 7-hydroxy-9-phenylnonanenitrile (3la)



Prepared using alkene **1l** (142 mg, 0.506 mmol) and xanthate **2a** (122 mg, 0.760 mmol) with DLP (303 mg, 0.760 mmol for 1.5 h and then, 202 mg, 0.506 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 80:20:1-60:40:1

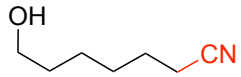
Yield: 64.4 mg (0.278 mmol, 55% yield, 2.5 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (2H, m), 7.21-7.17 (3H, m), 3.65-3.61 (1H, m), 2.83-2.76 (1H, m), 2.71-2.64 (1H, m), 2.33 (2H, t, *J* = 7.1 Hz), 1.83-1.75 (2H, m), 1.70-1.63 (2H, m), 1.49-1.36 (6H, m), 1.33-1.32 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 128.41, 128.36, 125.8, 119.7, 71.1, 39.1, 37.1, 32.0, 28.6, 25.3, 24.8, 17.0.

ESIHRMS Found: m/z 232.1703; Calcd for $C_{15}H_{22}NO$ $(M+H)^+$ 232.1701.

6.13. Synthesis of 7-hydroxyheptanenitrile (3ma)[16]



Prepared using alkene **1m** (91.6 mg, 0.520 mmol) and xanthate **2a** (126 mg, 0.780 mmol) with DLP (311 mg, 0.780 mmol for 1 h and then, 207 mg, 0.520 mmol for 1 h) following the typical procedure B (page S12). Analytical data match those reported in literature.

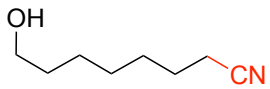
Purification: Hexane:EtOAc = 80:20-20:80

Yield: 38.1 mg (0.300 mmol, 58% yield, 2 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (2H, t, *J* = 6.5 Hz), 2.35 (2H, t, *J* = 7.1 Hz), 1.72-1.65 (2H, m), 1.63-1.56 (2H, m), 1.53-1.38 (5H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7, 62.6, 32.3, 28.4, 25.3, 25.0, 17.1.

6.14. Synthesis of 8-hydroxyoctanenitrile (3na)[17]



Prepared using alkene **1n** (95.1 mg, 0.500 mmol) and xanthate **2a** (121 mg, 0.750 mmol) and DLP (299 mg, 0.750 mmol for 1 h and then, 199 mg, 0.500 mmol for 1 h) following typical procedure B (page S12). Analytical data match those reported in literature.

Purification: Hexane:EtOAc = 70:30-50:50

Yield: 25.5 mg (0.181 mmol, 36% yield, 2 h) of a pale yellow oil.

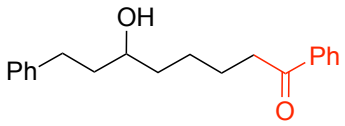
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (2H, t, *J* = 6.5 Hz), 2.35 (2H, t, *J* = 7.1 Hz), 1.72-1.64 (2H, m), 1.62-1.55 (2H, m), 1.52-1.44 (2H, m), 1.43-1.32 (5H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 119.8, 62.7, 32.5, 28.54, 28.49, 25.4, 25.2, 17.1.

[16] D. C. Johnson and T. S. Widlanski, *J. Org. Chem.*, 2003, **68**, 5300.
[17] Z. Li, Y. Xiao and Z.-Q. Liu, *Chem. Commun.*, 2015, **51**, 9969.

7. *Anti*-Markovnikov hydrofunctionalization of alkenes with xanthates: Substrate scope of xanthate 2 with alkenes 1a or 1i (Scheme 4)

7.1. Synthesis of 6-hydroxy-1,8-diphenyloctan-1-one (3ab)



Prepared using alkene **1a** (134 mg, 0.503 mmol) and xanthate **2b** (181 mg, 0.755 mmol) with DLP (301 mg, 0.755 mmol for 1 h and then, 201 mg, 0.503 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 80:20:1

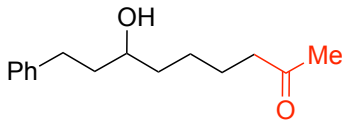
Yield: 109 mg (0.368 mmol, 73% yield, 2 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (2H, d, *J* = 7.7 Hz), 7.55 (1H, t, *J* = 7.4 Hz), 7.46 (2H, dd, *J* = 7.7, 7.4 Hz), 7.30-7.26 (2H, m), 7.21-7.16 (3H, m), 3.67-3.63 (1H, m), 2.98 (2H, t, *J* = 7.2 Hz), 2.84-2.77 (1H, m), 2.71-2.64 (1H, m), 1.84-1.69 (4H, m), 1.68-1.50 (4H, m), 1.48-1.41 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 200.3, 142.1, 136.9, 132.9, 128.5, 128.4, 128.3, 128.0, 125.7, 71.0, 39.1, 38.4, 37.3, 32.0, 25.3, 24.1.

ESIHRMS Found: m/z 297.1854; Calcd for $C_{20}H_{25}O_2$ $(M+H)^+$ 297.1855.

7.2. Synthesis of 7-hydroxy-9-phenylnonan-2-one (3ac)



Prepared using alkene **1a** (135 mg, 0.506 mmol) and xanthate **2c** (135 mg, 0.759 mmol) with DLP (303 mg, 0.759 mmol for 1 h and then, 202 mg, 0.506 mmol for 2 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 70:30:1

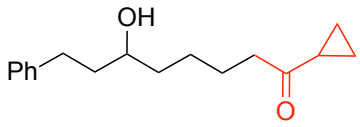
Yield: 103 mg (0.440 mmol, 87% yield, 3 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (2H, m), 7.21-7.18 (3H, m), 3.66-3.60 (1H, m), 2.83-2.75 (1H, m), 2.70-2.63 (1H, m), 2.43 (2H, t, *J* = 7.3 Hz), 2.13 (3H, s), 1.82-1.68 (2H, m), 1.68-1.53 (3H, m), 1.51-1.38 (3H, m), 1.34-1.26 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 209.2, 142.1, 128.4 (overlapped), 125.8, 71.0, 43.6, 39.1, 37.2, 32.0, 29.9, 25.1, 23.6.

ESIHRMS Found: m/z 235.1701; Calcd for $C_{15}H_{23}O_2$ $(M+H)^+$ 235.1698.

7.3. Synthesis of 1-cyclopropyl-6-hydroxy-8-phenyloctan-1-one (3ad)



Prepared using alkene **1a** (137 mg, 0.514 mmol) and xanthate **2d** (158 mg, 0.771 mmol) with DLP (307 mg, 0.771 mmol for 1 h and then, 205 mg, 0.514 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc = 90:10-60:40

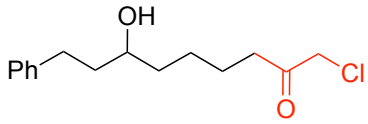
Yield: 75.7 mg (0.291 mmol, 57% yield, 2 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (2H, m), 7.21-7.16 (3H, m), 3.67-3.61 (1H, m), 2.83-2.76 (1H, m), 2.70-2.63 (1H, m), 2.56 (2H, t, J = 7.2 Hz), 1.94-1.88 (1H, m), 1.82-1.74 (3H, m), 1.63-1.56 (2H, m), 1.52-1.39 (3H, m), 1.36-1.30 (1H, m), 1.02-0.98 (2H, m), 0.86-0.82 (2H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 211.1, 142.1, 128.4 (overlapped), 125.8, 71.0, 43.3, 39.1, 37.2, 32.1, 25.2, 23.7, 20.4, 10.6.

ESIHRMS Found: m/z 261.1858.; Calcd for $C_{17}H_{25}NO_2$ $(M+H)^+$ 261.1855.

7.4. Synthesis of 1-chloro-7-hydroxy-9-phenylnonan-2-one (3ae)



Prepared using alkene **1a** (136 mg, 0.511 mmol) and xanthate **2e** (163 mg, 0.767 mmol) with DLP (306 mg, 0.767 mmol for 1 h and then, 204 mg, 0.511 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 90:10:1-80:20:1

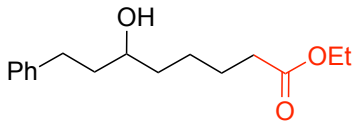
Yield: 101 mg (0.376 mmol, 74% yield, 2 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.26 (2H, m), 7.21-7.17 (3H, m), 4.06 (2H, s), 3.64-3.60 (1H, m), 2.83-2.75 (1H, m), 2.71-2.63 (1H, m), 2.60 (2H, t, J = 7.3 Hz), 1.80-1.72 (2H, m), 1.70-1.61 (3H, m), 1.53-1.41 (3H, m), 1.40-1.33 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 202.7, 142.0, 128.40, 128.37, 125.8, 71.0, 48.1, 39.5, 39.1, 37.1, 32.0, 25.0, 23.4.

ESIHRMS Found: m/z 269.1307; Calcd for $C_{15}H_{22}O_2Cl$ $(M+H)^+$ 269.1308.

7.5. Synthesis of ethyl 6-hydroxy-8-phenyloctanoate (3af)



Prepared using alkene **1a** (135 mg, 0.507 mmol) and xanthate **2f** (158 mg, 0.761 mmol) with DLP (303 mg, 0.761 mmol for 1.5 h and then, 202 mg, 0.507 mmol for 2 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 80:20:1

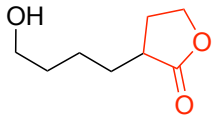
Yield: 104 mg (0.393 mmol, 77% yield, 3.5 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29-7.26 (2H, m), 7.20-7.16 (3H, m), 4.12 (2H, q, *J* = 7.1 Hz), 3.66-3.60 (1H, m), 2.83-2.75 (1H, m), 2.70-2.63 (1H, m), 2.30 (2H, t, *J* = 7.4 Hz), 1.82-1.68 (3H, m), 1.66-1.59 (2H, m), 1.53-1.43 (3H, m), 1.41-1.34 (1H, m), 1.25 (3H, t, *J* = 7.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 173.7, 142.1, 128.4 (overlapped), 125.8, 71.0, 60.2, 39.1, 37.1, 34.2, 32.0, 25.1, 24.8, 14.2.

ESIHRMS Found: m/z 265.1802; Calcd for $C_{16}H_{25}O_3$ $(M+H)^+$ 265.1804.

7.6. Synthesis of 3-(4-hydroxybutyl)dihydrofuran-2(3*H*)-one (3ig)[18]



Prepared using alkene **1i** (80.9 mg, 0.499 mmol) and xanthate **2g** (154 mg, 0.748 mmol) with DLP (298 mg, 0.748 mmol for 1 h and then, 199 mg, 0.499 mmol for 1 h) following typical procedure B (page S12). Analytical data match those reported in literature.

Purification: Hexane:EtOAc = 30:70:1-0:100

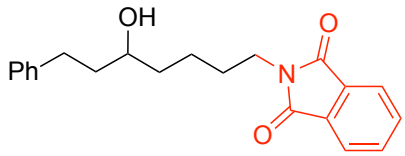
Yield: 45.5 mg (0.288 mmol, 58% yield, 2 h) of a pale yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 4.39-4.34 (1H, m), 4.24-4.18 (1H, m), 3.71-3.68 (2H, m), 2.58-2.52 (1H, m), 2.44-2.38 (1H, m), 2.02-1.91 (2H, m), 1.67-1.58 (2H, m), 1.55-1.47 (3H, m), 1.31 (1H, br).

^{13}C NMR (100 MHz, $CDCl_3$): δ 179.5, 66.5, 62.4, 39.2, 32.3, 30.0, 28.6, 23.5.

[18] H. Yorimitsu, H. Shinokubo and K. Oshima, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 225.

7.7. Synthesis of 2-(5-hydroxy-7-phenylheptyl)isoindoline-1,3-dione (3ah)



Prepared using alkene **1a** (133 mg, 0.500 mmol) and xanthate **2h** (211 mg, 0.750 mmol) with DLP (299 mg, 0.750 mmol for 3 h, 199 mg, 0.500 mmol for 1 h and then, another 199 mg, 0.500 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 90:10:1-70:30:1

Yield: 112 mg (0.331 mmol, 66% yield, 5 h) of a pale yellow oil.

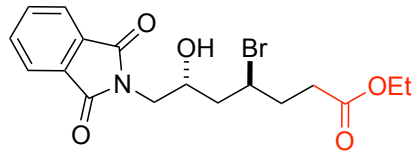
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (2H, dd, *J* = 5.4, 3.0 Hz), 7.70 (2H, dd, *J* = 5.4, 3.0 Hz), 7.28-7.24 (2H, m), 7.19-7.14 (3H, m), 3.69 (2H, t, *J* = 7.1 Hz), 3.64-3.60 (1H, m), 2.82-2.75 (1H, m), 2.70-2.62 (1H, m), 1.81-1.65 (5H, m), 1.57-1.45 (3H, m), 1.40-1.36 (1H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ 168.5, 142.1, 133.9, 132.1, 128.4 (overlapped), 125.8, 123.2, 71.0, 39.1, 37.7, 36.9, 32.0, 28.5, 22.8.

ESIHRMS Found: m/z 338.1758.; Calcd for $C_{21}H_{24}NO_3$ $(M+H)^+$ 338.1756.

8. Diastereoselective HAT onto haloalkenes (Scheme 5)

8.1. Synthesis of ethyl (4*S**,6*R**)-4-bromo-7-(1,3-dioxoisoindolin-2-yl)-6-hydroxyheptanoate (3of)



Prepared using alkene **1o** (407 mg, 1.02 mmol) and xanthate **2f** (319 mg, 1.53 mmol) with DLP (610 mg, 1.53 mmol for 2 h and then, 407 mg, 1.02 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc = 90:10-70:30

Yield: 290 mg (0.728 mmol, 71% yield, 3 h) of a white solid as an inseparable mixture of diastereoisomers (dr = 74:26, determined by ^{1}H NMR analysis).

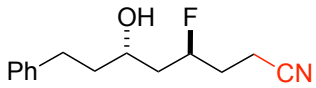
^{1}H NMR (500 MHz, C_6D_6): *for the mixture of diastereoisomers* δ 7.42-7.40 (2H×0.74, m + 2H×0.26, m), 6.87-6.86 (2H×0.74, m + 2H×0.26, m), 4.32-4.29 (1H×0.74, m), 4.24-4.19 (1H×0.74, m + 1H×0.26, m), 4.06-4.00 (1H×0.26, m), 3.92-3.87 (2H×0.74, m + 2H×0.26, m), 3.48-3.40 (2H×0.74, m + 2H×0.26, m), 2.58 (1H×0.26, br), 2.42-2.34 (2H×0.74, m + 1H×0.26, m), 2.33-2.25 (1H×0.74, m + 1H×0.26, m), 2.11-2.06 (1H×0.26, m), 1.98-1.85

(2H×0.74, m + 2H×0.26, m), 1.71-1.65 (1H×0.74, m + 1H×0.26, m), 1.53-1.48 (1H×0.74, m), 0.93 (3H×0.74, t, J = 7.2 Hz + 3H×0.26, m).

^{13}C NMR (100 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 172.9, 172.7, 168.82, 168.78, 134.1, 131.8, 123.4, 68.35, 68.28, 60.6, 60.5, 53.1, 52.0, 44.1, 43.9, 43.5, 34.5, 33.0, 32.2, 32.1, 14.1.

ESIHRMS *for the mixture of diastereoisomers* Found: m/z 398.0606; Calcd for $C_{17}H_{21}NO_5Br$ $(M+H)^+$ 398.0603.

8.2. Synthesis of (4*S**,6*S**)-4-fluoro-6-hydroxy-8-phenyloctanenitrile (3pa)



Prepared using alkene **1p** (116 mg, 0.407 mmol) and xanthate **2a** (98.3 mg, 0.610 mmol) with DLP (243 mg, 0.610 mmol for 1.5 h and then, 162 mg, 0.407 mmol for 1 h) following typical procedure B (page S12).

Purification: Hexane:EtOAc:MeOH = 90:10:1-70:30:1

Yield: 73.2 mg (0.311 mmol, 76% yield, 3 h) of a pale yellow oil as an inseparable mixture of diastereoisomers (dr = 78:22, determined by ^{19}F NMR analysis).

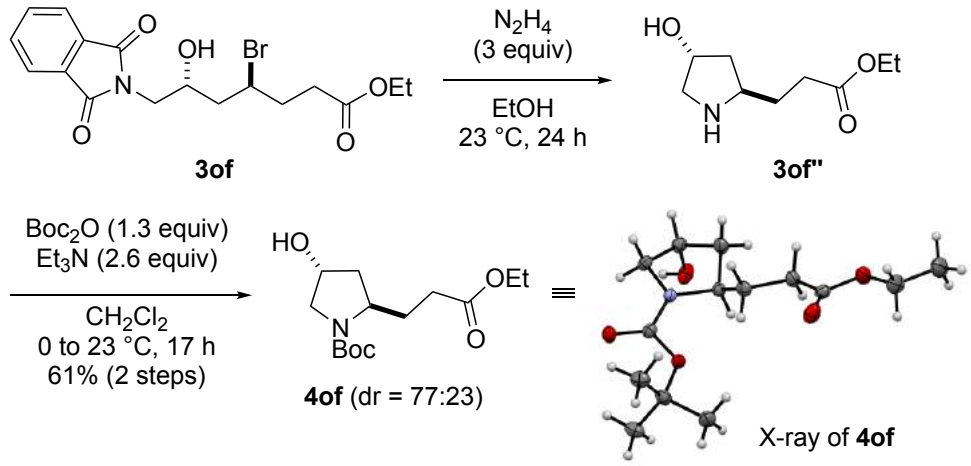
^{1}H NMR (400 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 7.31-7.26 (2H×0.78, m + 2H×0.22, m), 7.21-7.19 (3H×0.78, m + 3H×0.22, m), 4.97-4.74 (1H×0.78, m + 1H×0.22, m), 3.94-3.83 (1H×0.78, m + 1H×0.22, m), 2.83-2.76 (1H×0.78, m + 1H×0.22, m), 2.73-2.65 (1H×0.78, m + 1H×0.22, m), 2.57-2.44 (2H×0.78, m + 2H×0.22, m), 2.03-1.87 (2H×0.78, m + 2H×0.22, m), 1.85-1.75 (3H×0.78, m + 3H×0.22, m), 1.72-1.54 (2H×0.78, m + 2H×0.22, m).

^{13}C NMR (100 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 141.5, 128.4, 128.30, 128.27, 125.9, 119.0, 118.9, 91.3 (d, J = 167.1 Hz), 89.4 (d, J = 167.9 Hz), 68.6 (d, J = 4.2 Hz), 67.1 (d, J = 3.1 Hz), 42.2 (d, J = 20.0 Hz), 41.7 (d, J = 19.0 Hz), 39.5, 38.9, 31.8, 31.7, 31.3 (d, J = 21.1 Hz), 31.0 (d, J = 21.2 Hz) 13.3 (d, J = 5.0 Hz), 13.2 (d, J = 5.5 Hz).

^{19}F NMR (377 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ-183.9 – -184.3 (1F×0.22, m), -186.2 – -186.6 (1F×0.78, m).

ESIHRMS *for the mixture of diastereoisomers* Found: m/z 236.1456; Calcd for $C_{14}H_{19}NOF$ $(M+H)^+$ 236.1451.

8.3. Synthesis of *tert*-butyl (2*R,4*R**)-2-(3-ethoxy-3-oxopropyl)-4-hydroxypyrrolidine-1-carboxylate (4of)**



To a solution of **3of** (194 mg, 0.487 mmol) in EtOH (5.0 mL) was added hydrazine (80% in water, 64.4 μL, 1.46 mmol) at 23 °C under a N_2 atmosphere. The reaction mixture was stirred at 23 °C for 24 h and then cooled to 0 °C. The resulting precipitate was filtered and washed with cold Et_2O. The filtrate was concentrated *in vacuo*, diluted with Et_2O, and filtered again to afford crude materials including amine **3of''**, which was used in the next step without further purification.

The crude amine **3of''** was dissolved in CH_2Cl_2 (5.0 mL). To the resulting solution were added Et_3N (128 mg, 1.27 mmol) and Boc_2O (138 mg, 0.633 mmol) at 0 °C under a N_2 atmosphere. The mixture was gradually warmed up to 23 °C over 17 h and quenched with water. The resulting organic materials were extracted thrice with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc = 60:40-20:80) to give **4of** (85.3 mg, 0.297 mmol) in 61% yield as an inseparable mixture of diastereoisomers (dr = 77:23, determined by ^{1}H NMR analysis), as a pale yellow solid. Single colorless crystal was obtained through recrystallization from CH_2Cl_2/hexane, and the structure of which was secured by X-ray crystallographic analysis (CCDC 1843320).

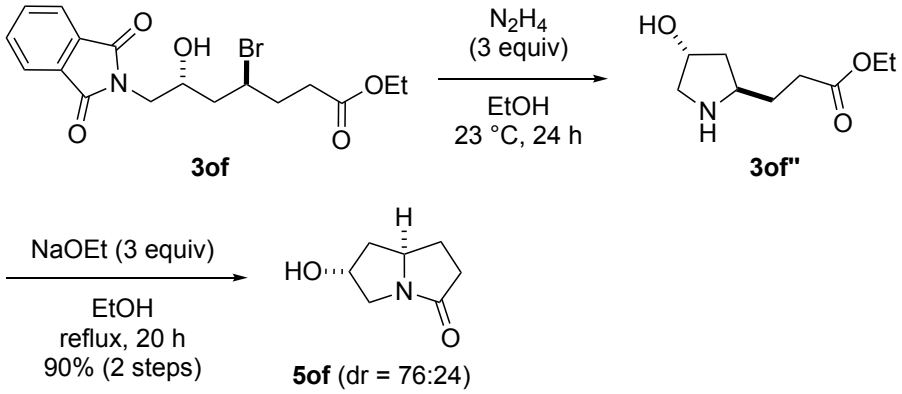
^{1}H NMR (400 MHz, $CDCl_3$ at 55 °C): *for the mixture of diastereoisomers* δ 4.39 (1H×0.77, m + 1H×0.23, m), 4.12 (2H×0.77, q, *J* = 7.6 Hz, + 2H×0.23, m), 3.99-3.95 (1H×0.77, m), 3.87-3.85 (1H×0.23, m), 3.69-3.67 (1H×0.23, m), 3.54-3.51 (1H×0.77, m), 3.37 (1H×0.77, dd, *J* = 11.9, 4.6 Hz), 3.26 (1H×0.23, dd, *J* = 12.4, 3.2 Hz), 2.36-1.96 (5H×0.77, m + 6H×0.23,

m), 1.82-1.73 (2H×0.77, m + 1H×0.23, m), 1.46 (9H×0.77, s + 9H×0.23, s), 1.23 (3H×0.77, t, J = 7.6 Hz + 3H×0.23, m).

^{13}C NMR (100 MHz, $CDCl_3$ at 55 °C): *for the mixture of diastereoisomers* δ 173.6, 173.2, 155.1, 154.7, 79.6, 79.5, 70.3, 69.7, 60.3, 56.4, 55.4, 54.9, 54.8, 40.0, 38.9, 31.3, 30.8, 30.3, 30.1, 28.5, 14.2.

ESIHRMS *for the mixture of diastereoisomers* Found: m/z 288.1806; Calcd for $C_{14}H_{26}NO_5$ $(M+H)^+$ 288.1811.

8.4. Synthesis of (6*R**,7a*R**)-6-hydroxyhexahydro-3*H*-pyrrolizin-3-one (5of)



To a solution of **3of** (290 mg, 0.728 mmol) in EtOH (7.0 mL) was added hydrazine (80% in water, 77.0 μL, 2.18 mmol) at 23 °C under a N_2 atmosphere. The reaction mixture was stirred at 23 °C for 24 h and then cooled to 0 °C. The resulting precipitate was filtered and washed with cold Et_2O. The filtrate was concentrated *in vacuo* to afford crude materials including amine **3of''**, which was used in the next step without further purification.

The crude amine **3of''** was dissolved in EtOH (7.0 mL). To the resulting solution was added NaOEt (148 mg, 2.18 mmol) under a N_2 atmosphere and the reaction was stirred under reflux conditions for 20 h. The reaction mixture was cooled to 23 °C and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: CH_2Cl_2:MeOH = 95:5) to give **5of** (93.0 mg, 0.659 mmol) in 90% yield as a mixture of diastereoisomers (dr = 76:24, determined by ^{1}H NMR analysis as the inseparable mixture), as a pale yellow solid.

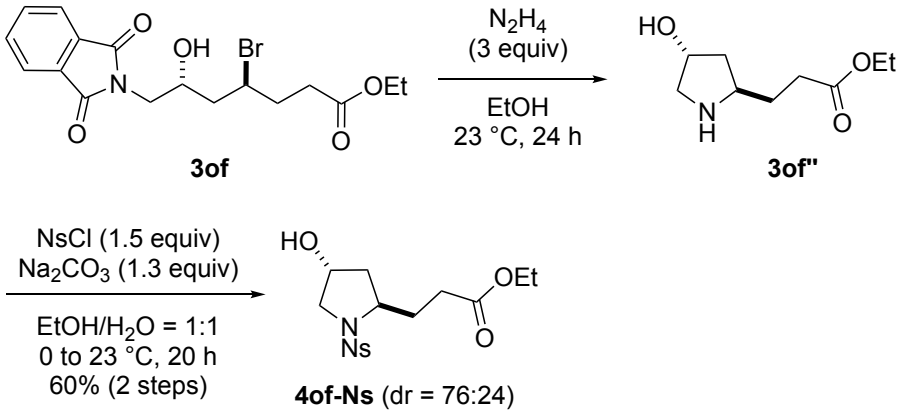
^{1}H NMR (400 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 4.72-4.69 (1H×0.76, m), 4.60-4.57 (1H×0.24, m), 4.28-4.21 (1H×0.76, m), 3.96-3.92 (1H×0.24, m), 3.85 (1H×0.76, dd, J = 12.9, 5.3 Hz), 3.66 (1H×0.24, dd, J = 12.4, 2.8 Hz), 3.15 (1H×0.24, dd, J = 12.4, 5.3 Hz), 3.02 (1H×0.76, d, J = 12.9 Hz), 2.80-2.63 (1H×0.76, m + 1H×0.24, m), 2.47-2.29 (2H×0.76,

m + 2H×0.24, m), 2.08 (1H×0.76, dd, *J* = 13.0, 5.3 Hz + 1H×0.24, m), 1.99-1.56 (2H×0.76, m + 2H×0.24, m), 1.52-1.45 (1H×0.76, m + 1H×0.24, m).

^{13}C NMR (100 MHz, $CDCl_3$): *for the mixture of diastereoisomers* δ 176.8, 175.0, 73.6, 72.9, 60.0, 59.9, 51.0, 50.9, 42.1, 40.5, 35.1, 34.2, 28.8, 27.0.

ESIHRMS *for the mixture of diastereoisomers* Found: m/z 142.0865; Calcd for $C_7H_{12}NO_2$ $(M+H)^+$ 142.0868.

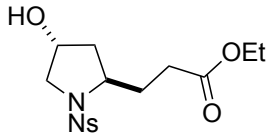
8.5. Synthesis of ethyl 3-(4-hydroxy-1-((2-nitrophenyl)sulfonyl)pyrrolidin-2-yl)propanoate (4of-Ns) for elucidation of the stereochemistry



To a solution of **3of** (296 mg, 0.743 mmol) in EtOH (7.0 mL) was added hydrazine (80% in water, 98.3 μL, 2.23 mmol) at 23 °C under a N_2 atmosphere. The reaction mixture was stirred at 23 °C for 24 h and then cooled to 0 °C. The resulting precipitate was filtered and washed with cold Et_2O. The filtrate was concentrated *in vacuo*, diluted with Et_2O, and filtered again to afford crude materials including amine **3of''**, which was used in the next step without further purification.

The crude amine **3of''** was dissolved in Et_2O (3.5 mL) and H_2O (3.5 mL). To the resulting solution were added Na_2CO_3 (102 mg, 0.967 mmol) and 2-nitrobenzenesulfonyl chloride (247 mg, 1.11 mmol) at 0 °C under a N_2 atmosphere. The mixture was gradually warmed up to 23 °C over 20 h and then quenched with water. The resulting organic materials were extracted thrice with CH_2Cl_2. The combined extracts were washed with brine, dried over $MgSO_4$, filtered and concentrated *in vacuo*. The resulting crude material was purified by flash column chromatography (silica gel: Hexane:EtOAc = 50:50-0:100) to give ***trans*-4of-Ns** (127 mg, 0.341 mmol) in 46 % yield as a colorless oil and ***cis*-4of-Ns** (40.1 mg, 0.108 mmol) in 14 % yield as a colorless oil.

Ethyl 3-((2*R,4*R**)-4-hydroxy-1-((2-nitrophenyl)sulfonyl)pyrrolidin-2-yl)propanoate (*trans*-4of-Ns)**

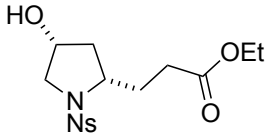


^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09-8.07 (1H, m), 7.70-7.66 (2H, m), 7.58-7.55 (1H, m), 4.40-4.36 (1H, m), 4.18-4.10 (3H, m), 3.77-3.71 (1H, m), 3.49 (1H, dd, *J* = 12.6, 3.3 Hz), 2.41-2.28 (2H, m), 2.23-2.16 (1H, m), 2.13-2.04 (1H, m), 1.92-1.84 (1H, m), 1.83-1.74 (2H, m), 1.25 (3H, t, *J* = 7.1 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 148.4, 133.5, 132.0, 131.4, 131.3, 123.8, 70.0, 60.6, 58.6, 57.0, 40.4, 30.5, 30.3, 14.2.

ESIHRMS Found: m/z 373.1069; Calcd for $C_{15}H_{21}N_2O_7S$ $(M+H)^+$ 373.1069.

Ethyl 3-((2*S,4*R**)-4-hydroxy-1-((2-nitrophenyl)sulfonyl)pyrrolidin-2-yl)propanoate (*cis*-4of-Ns)**

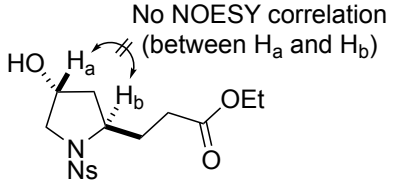


^{1}H NMR (400 MHz, C_6D_6): δ 7.79 (1H, dd, *J* = 8.4, 1.4 Hz), 6.70-6.66 (2H, m), 6.55-6.51 (1H, m), 4.05-4.02 (1H, m), 3.97-3.92 (2H, m), 3.65-3.63 (1H, m), 3.58-3.54 (1H, m), 3.17 (1H, dd, *J* = 11.4, 3.0 Hz), 2.24-2.18 (3H, m), 1.96-1.92 (1H, m), 1.52-1.45 (1H, m), 1.28-1.11 (1H, m), 0.97 (3H, t, *J* =7.1 Hz), 0.58 (1H, br).

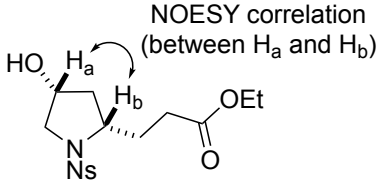
^{13}C NMR (100 MHz, C_6D_6): δ 173.0, 148.9, 133.1, 132.8, 131.2, 130.9, 123.7, 70.4, 60.4, 59.7, 56.5, 39.0, 30.9, 30.8, 14.3.

ESIHRMS Found: m/z 373.1073; Calcd for $C_{15}H_{21}N_2O_7S$ $(M+H)^+$ 373.1069.

NOESY correlation: NOESY correlations were observed between H_a and H_b only with ***cis*-4of-Ns** as shown below.



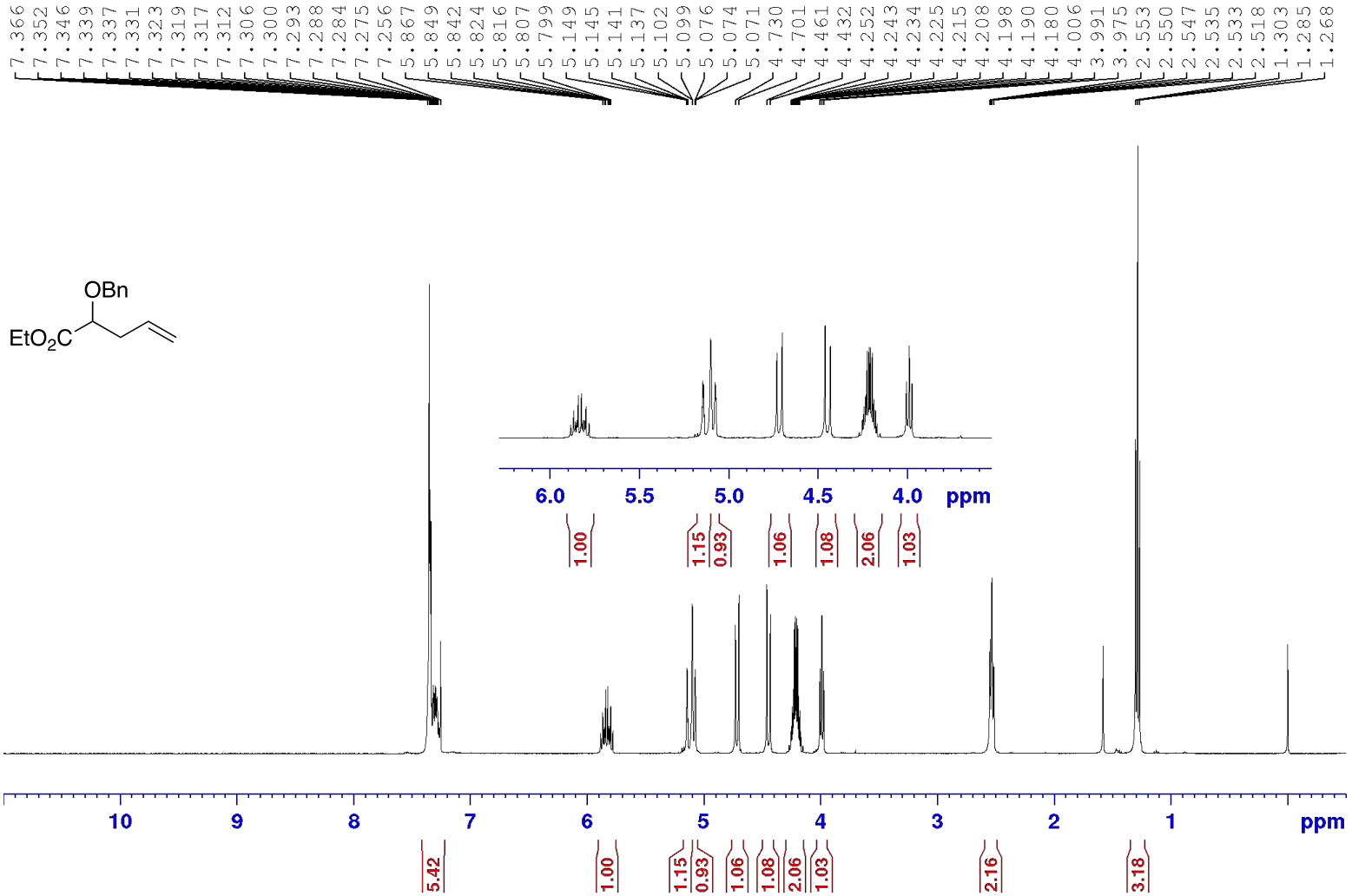
***trans*-4of-Ns**



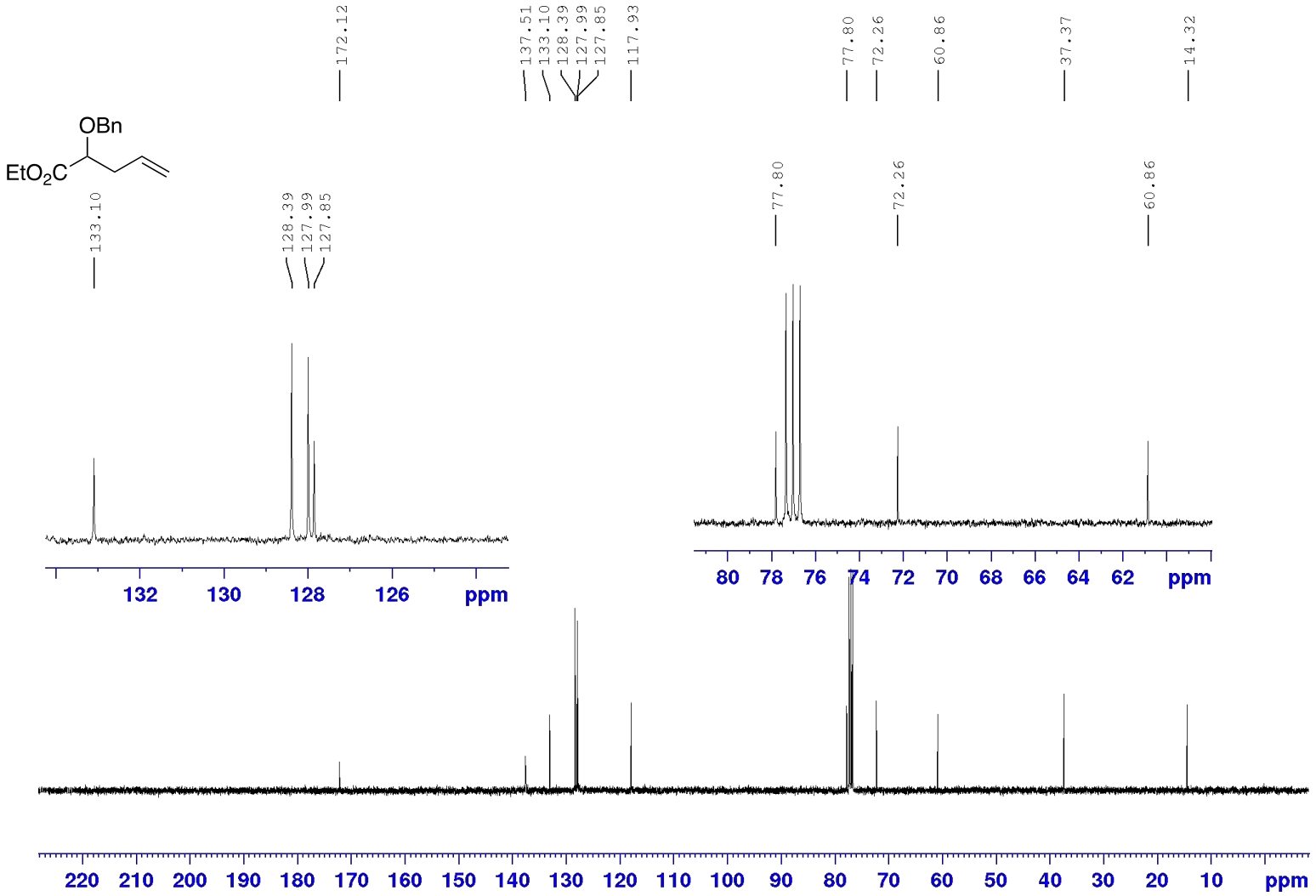
***cis*-4of-Ns**

9. ^{1}H and ^{13}C NMR spectra for new compounds

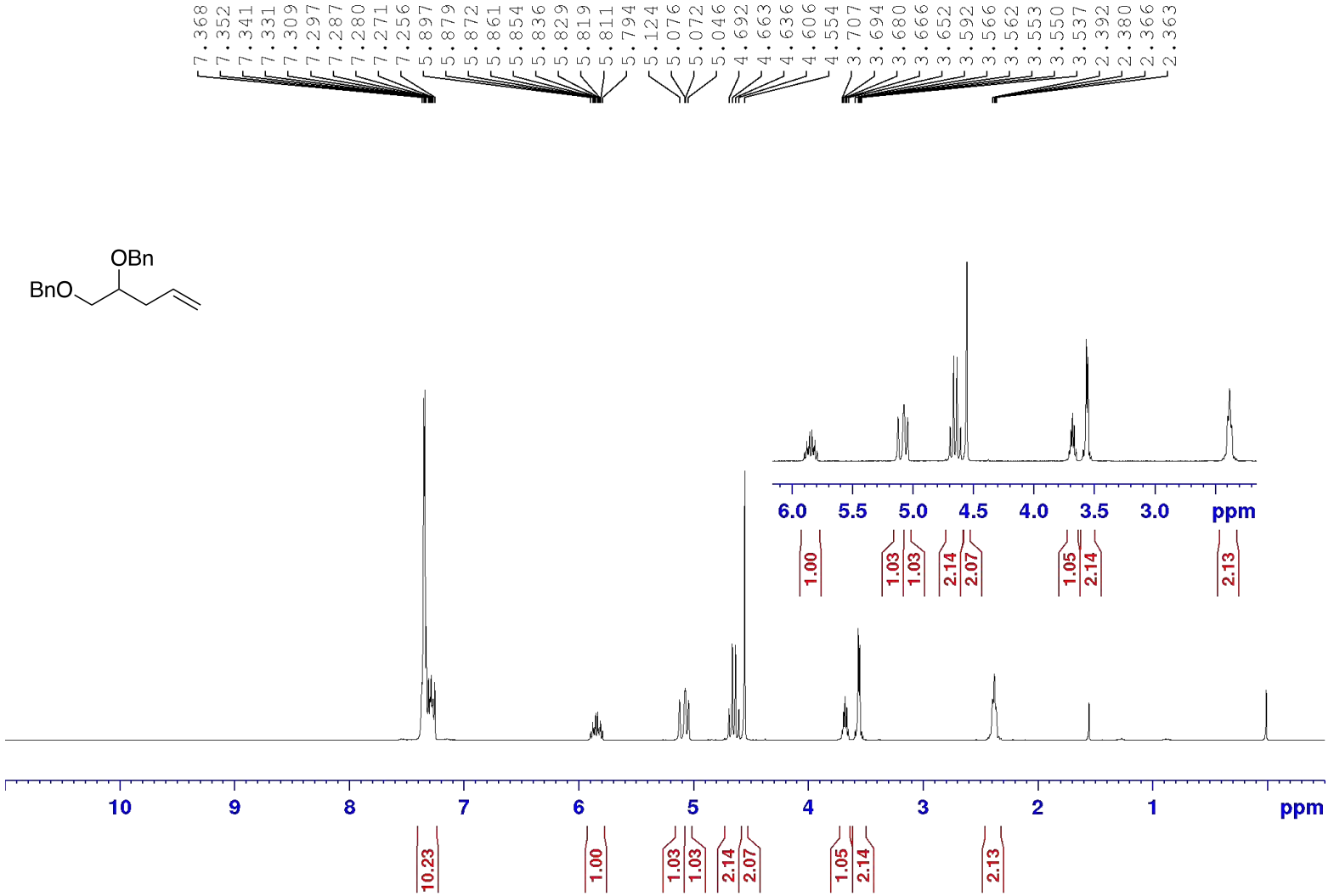
^{1}H NMR Spectrum of **1e** (400 MHz, $CDCl_3$)



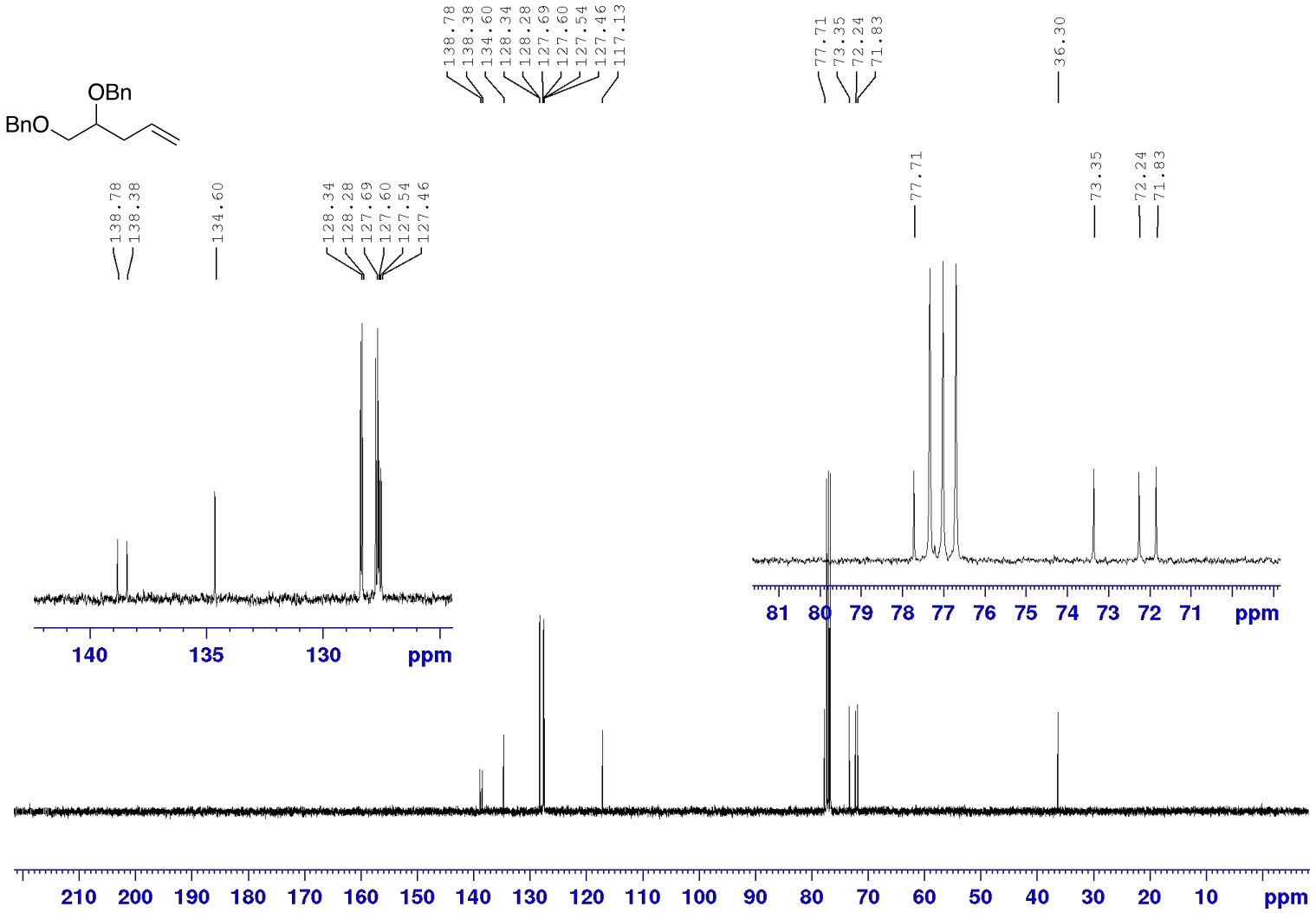
^{13}C NMR Spectrum of **1e** (100 MHz, $CDCl_3$)



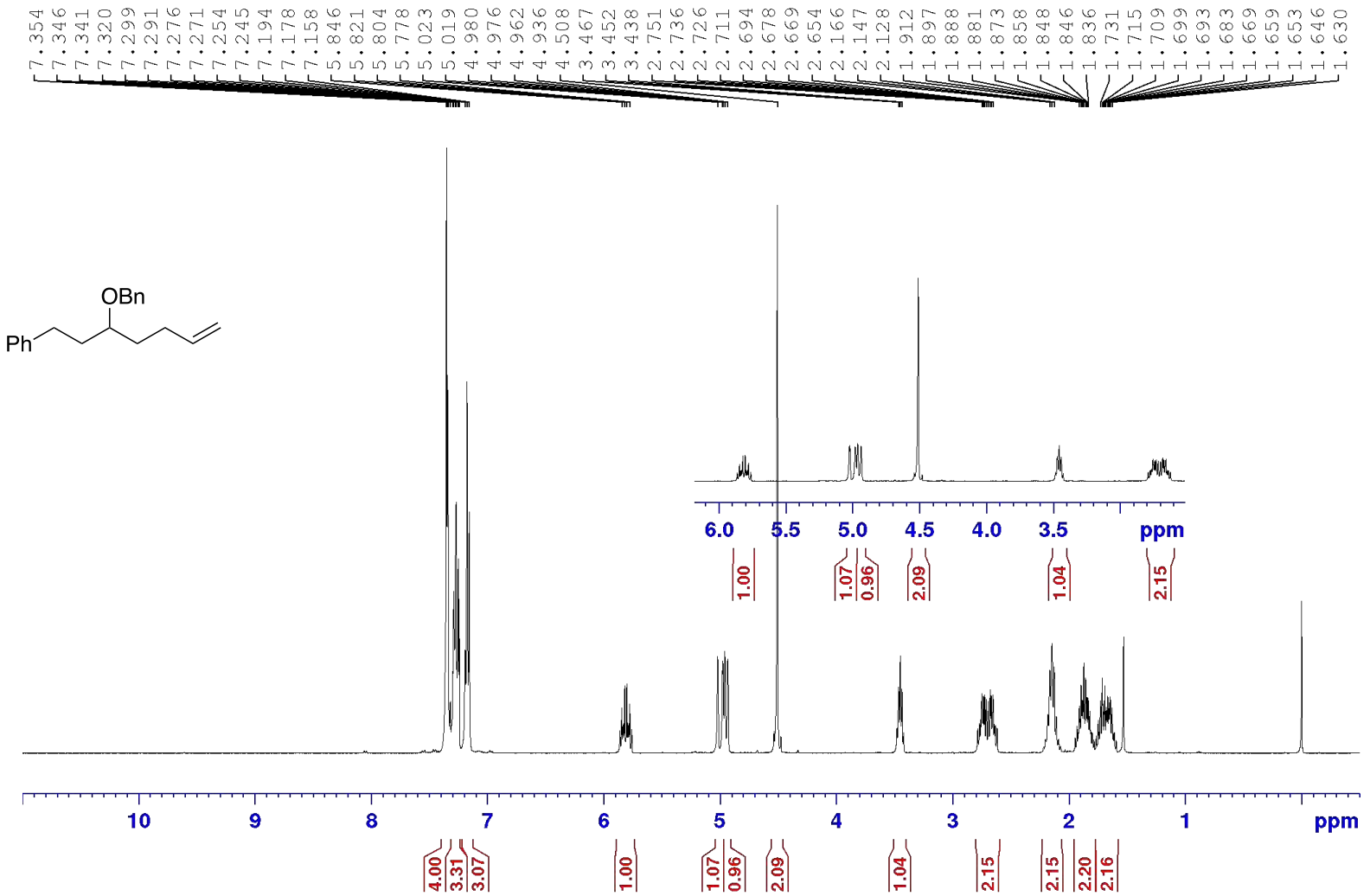
^{1}H NMR Spectrum of **1g** (400 MHz, $CDCl_3$)



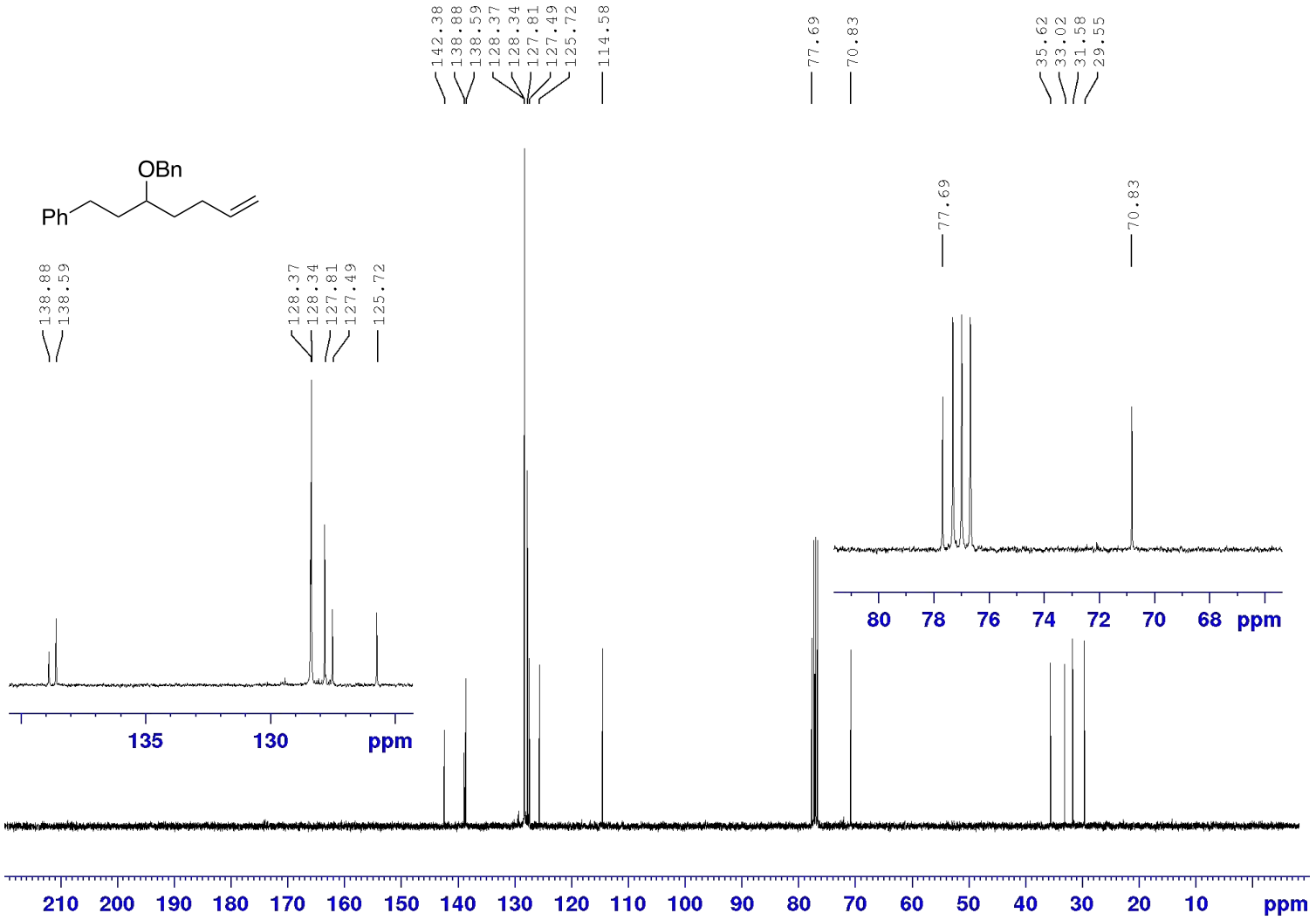
^{13}C NMR Spectrum of **1g** (100 MHz, $CDCl_3$)



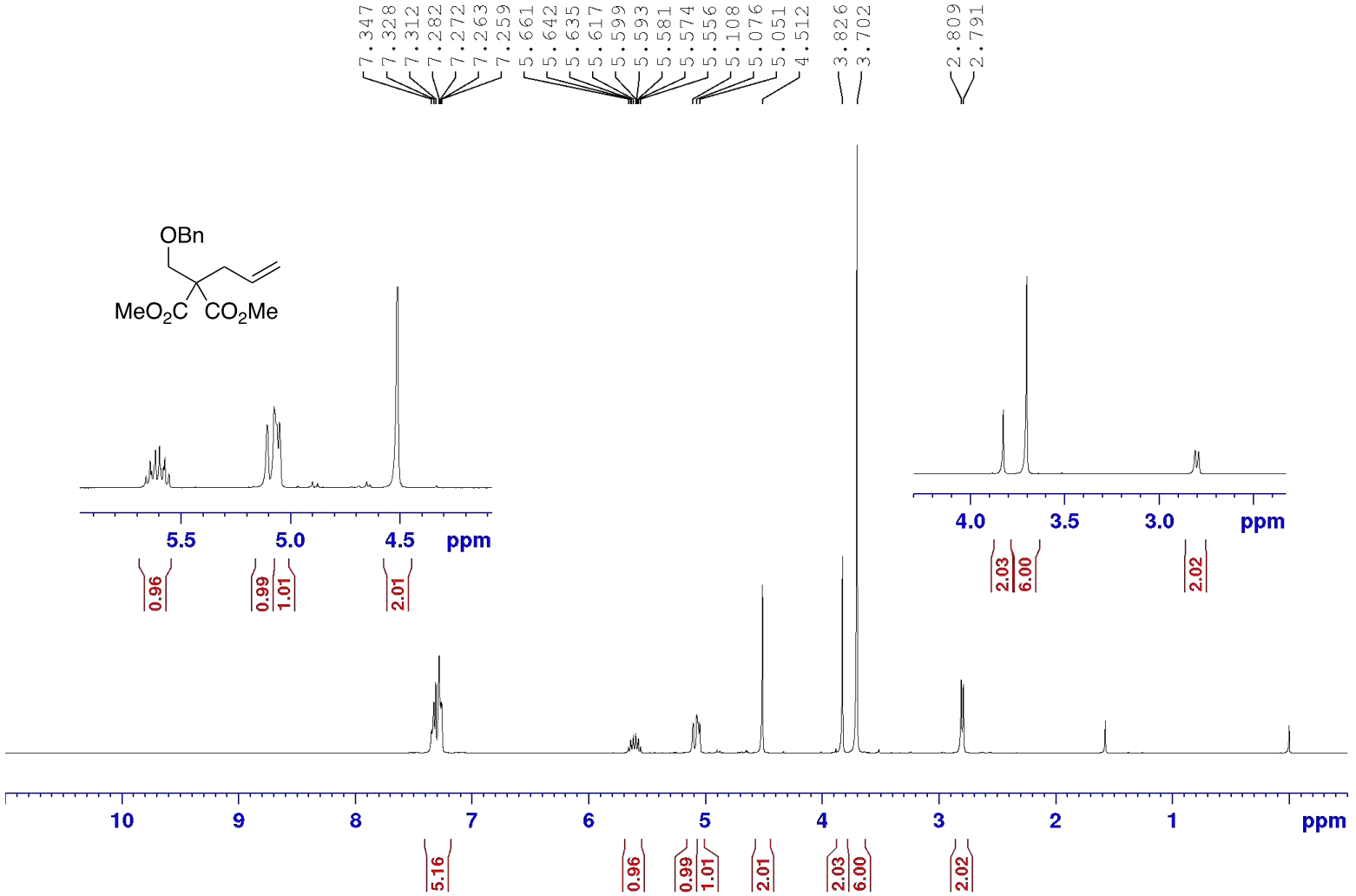
^{1}H NMR Spectrum of **1l** (400 MHz, $CDCl_3$)



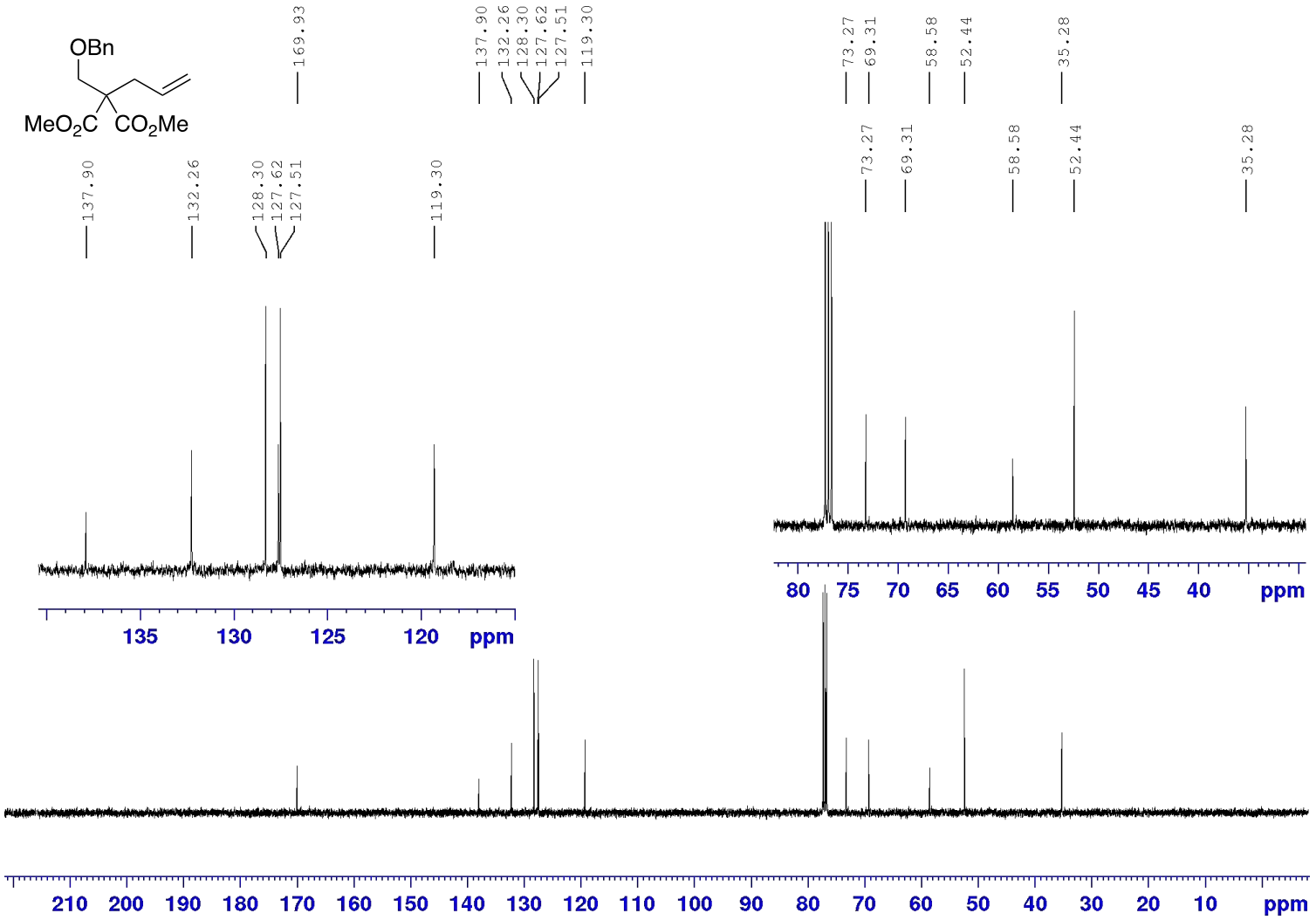
^{13}C NMR Spectrum of **11** (100 MHz, $CDCl_3$)



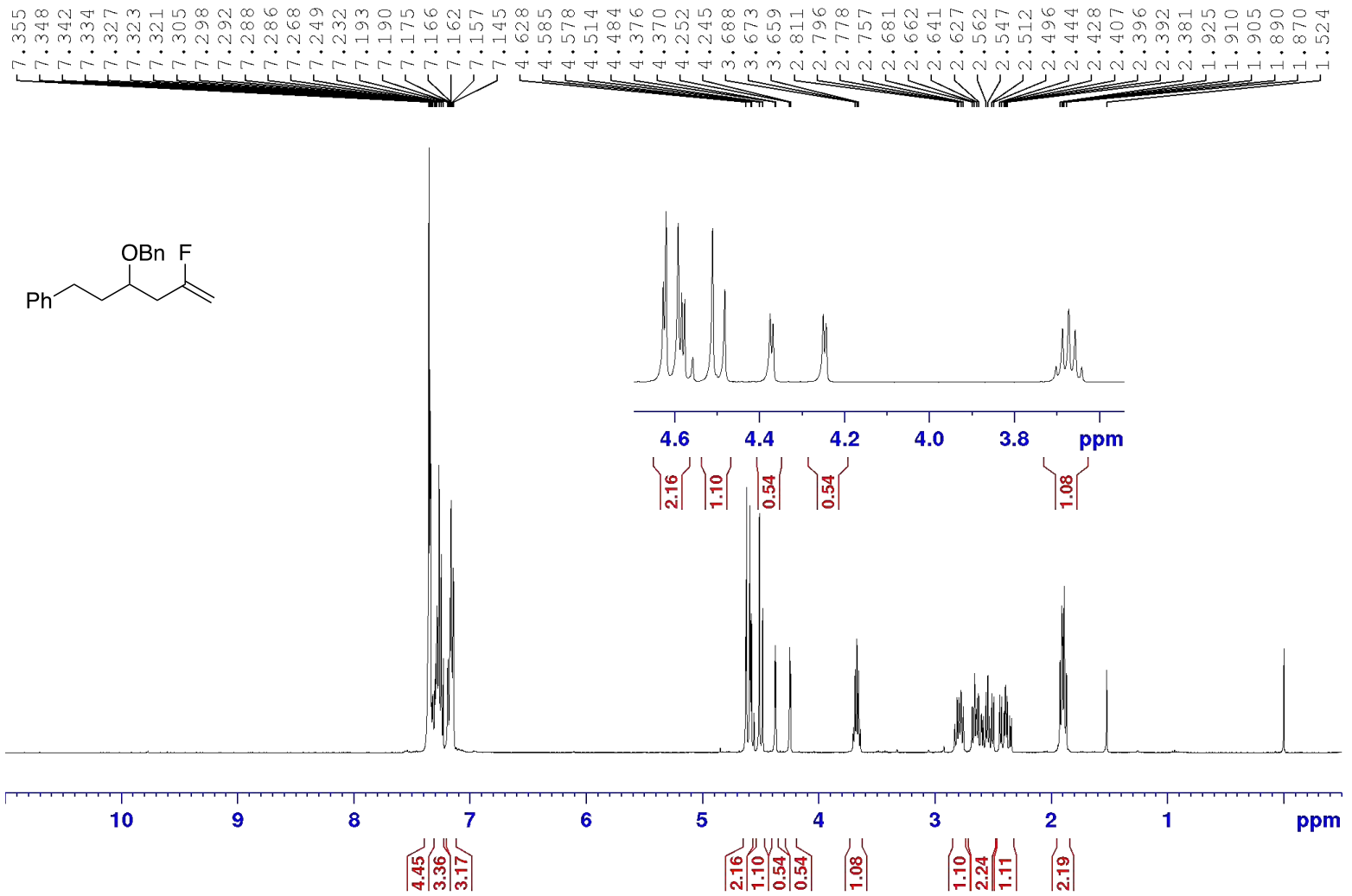
^{1}H NMR Spectrum of **1k** (400 MHz, $CDCl_3$)



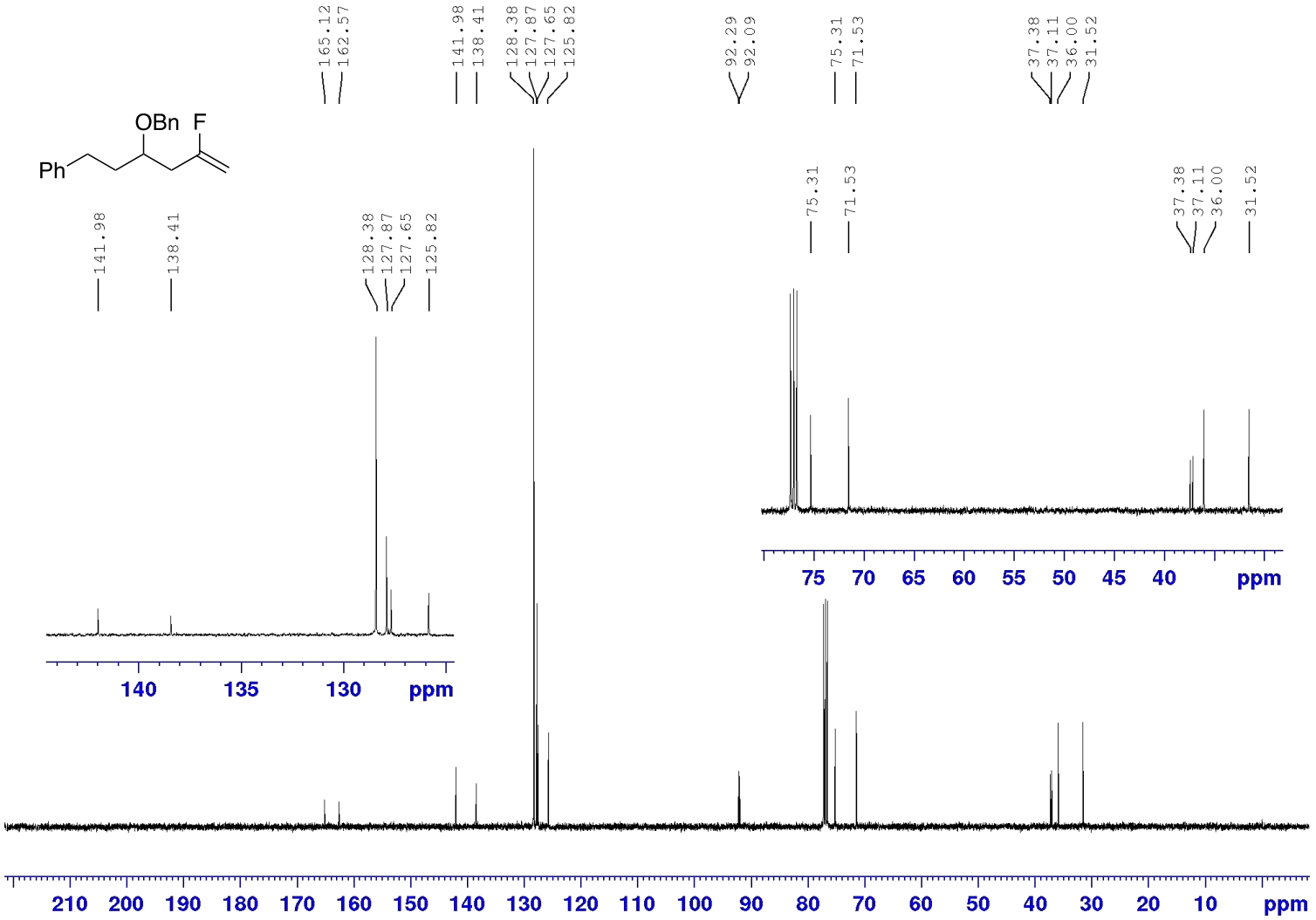
^{13}C NMR Spectrum of **1k** (100 MHz, $CDCl_3$)



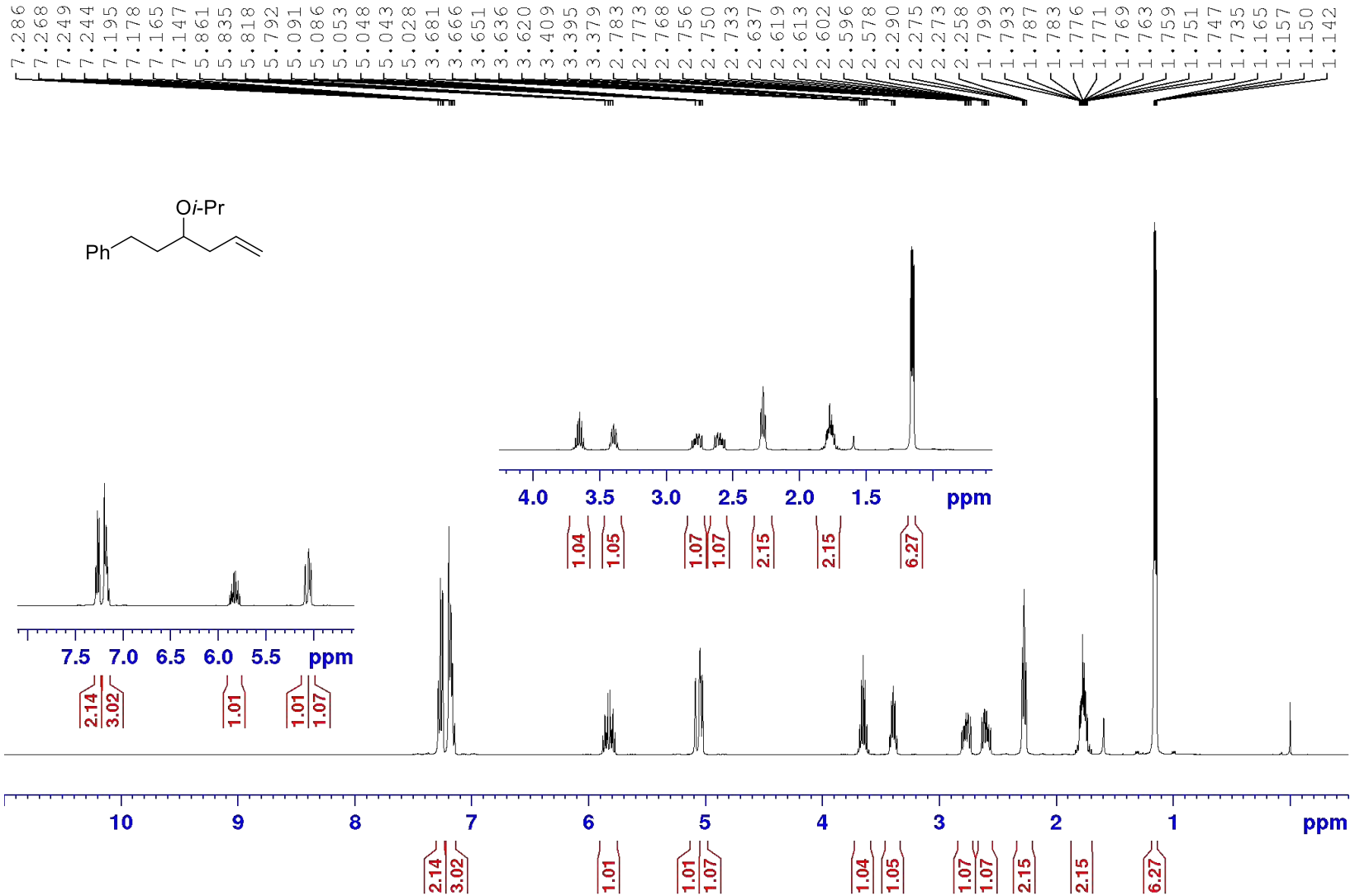
^{1}H NMR Spectrum of **1p** (400 MHz, $CDCl_3$)



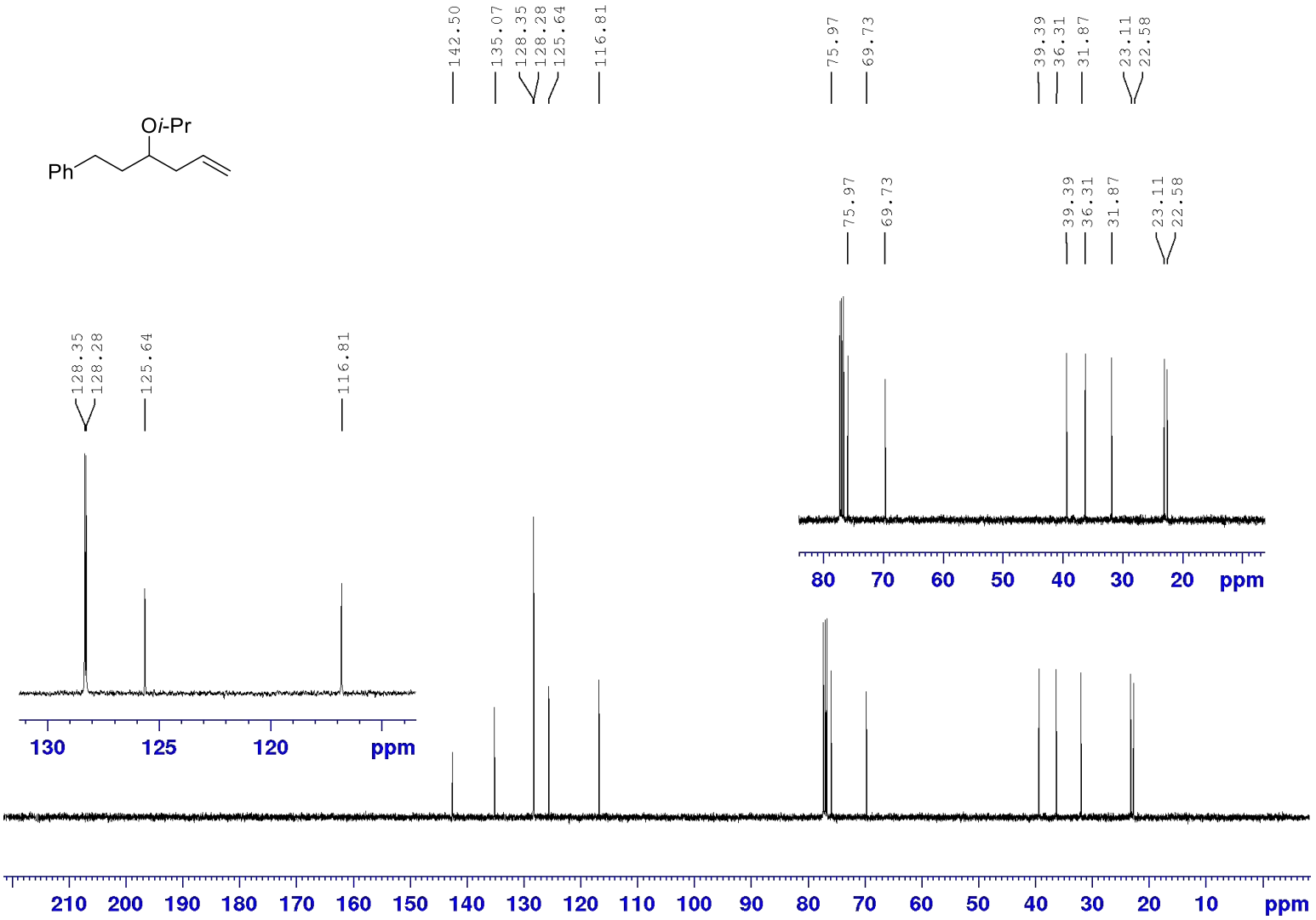
^{13}C NMR Spectrum of **1p** (100 MHz, $CDCl_3$)



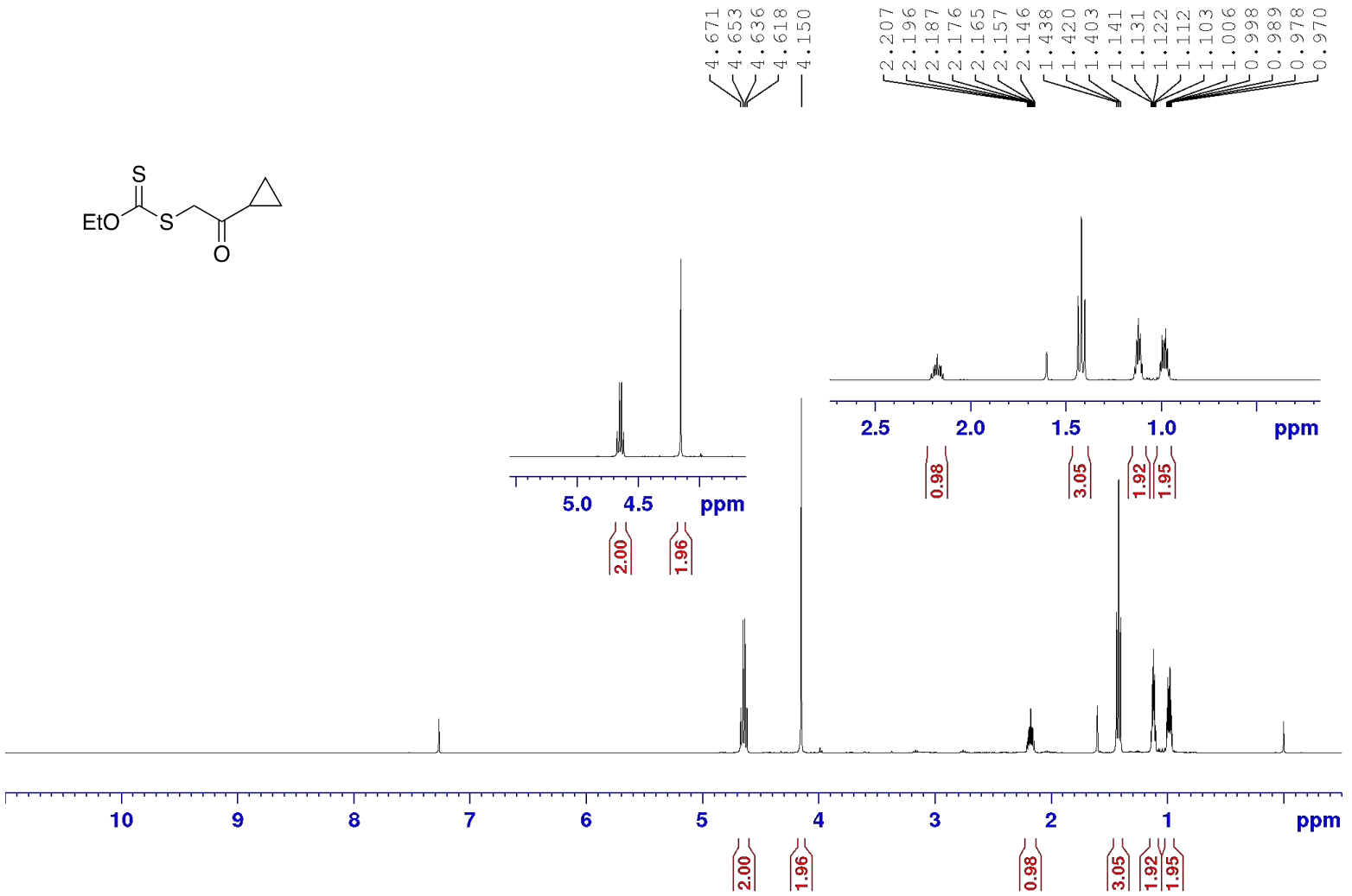
^{1}H NMR Spectrum of **1a-*i*-Pr** (400 MHz, $CDCl_3$)



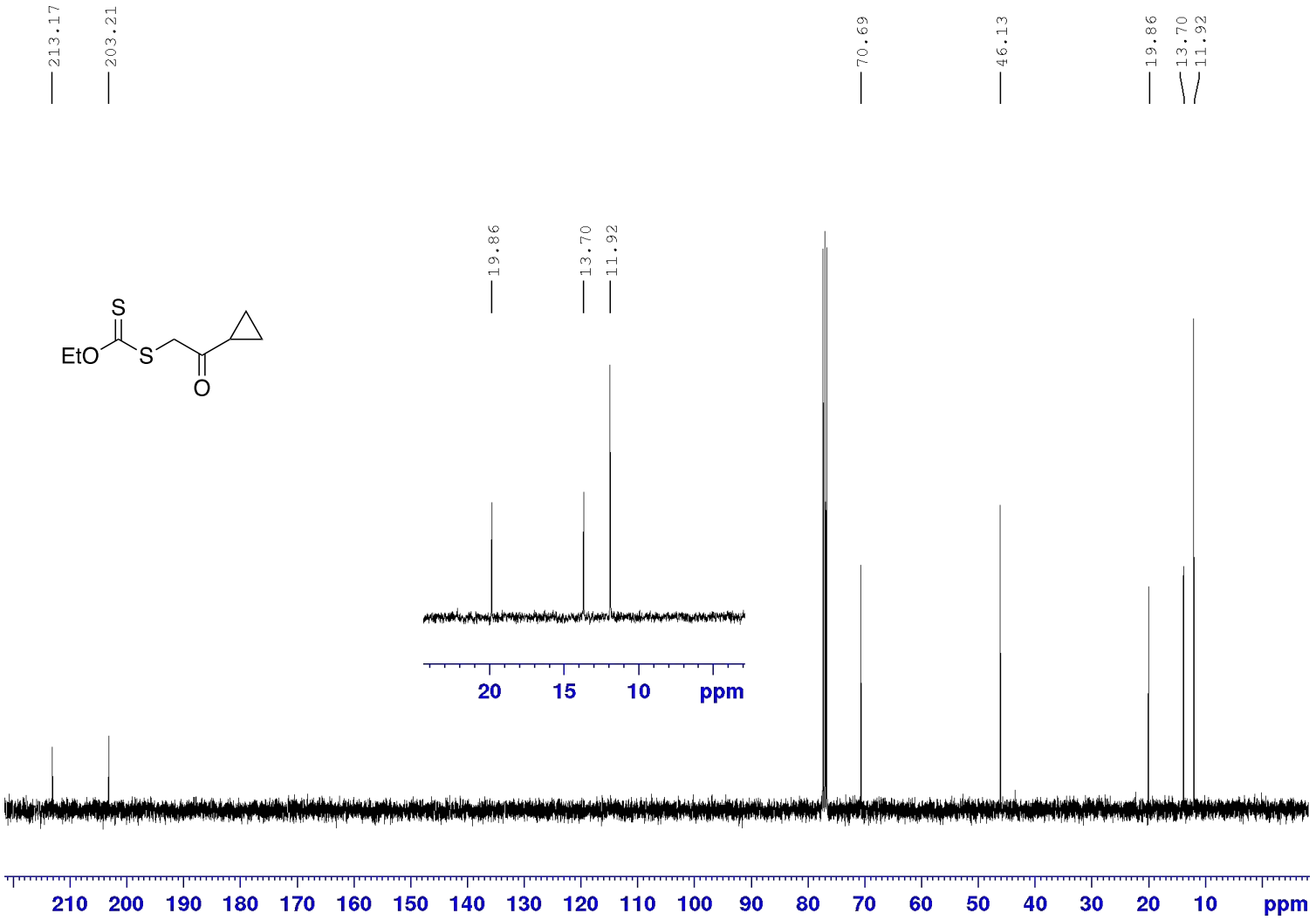
^{13}C NMR Spectrum of **1a-*i*-Pr** (100 MHz, $CDCl_3$)



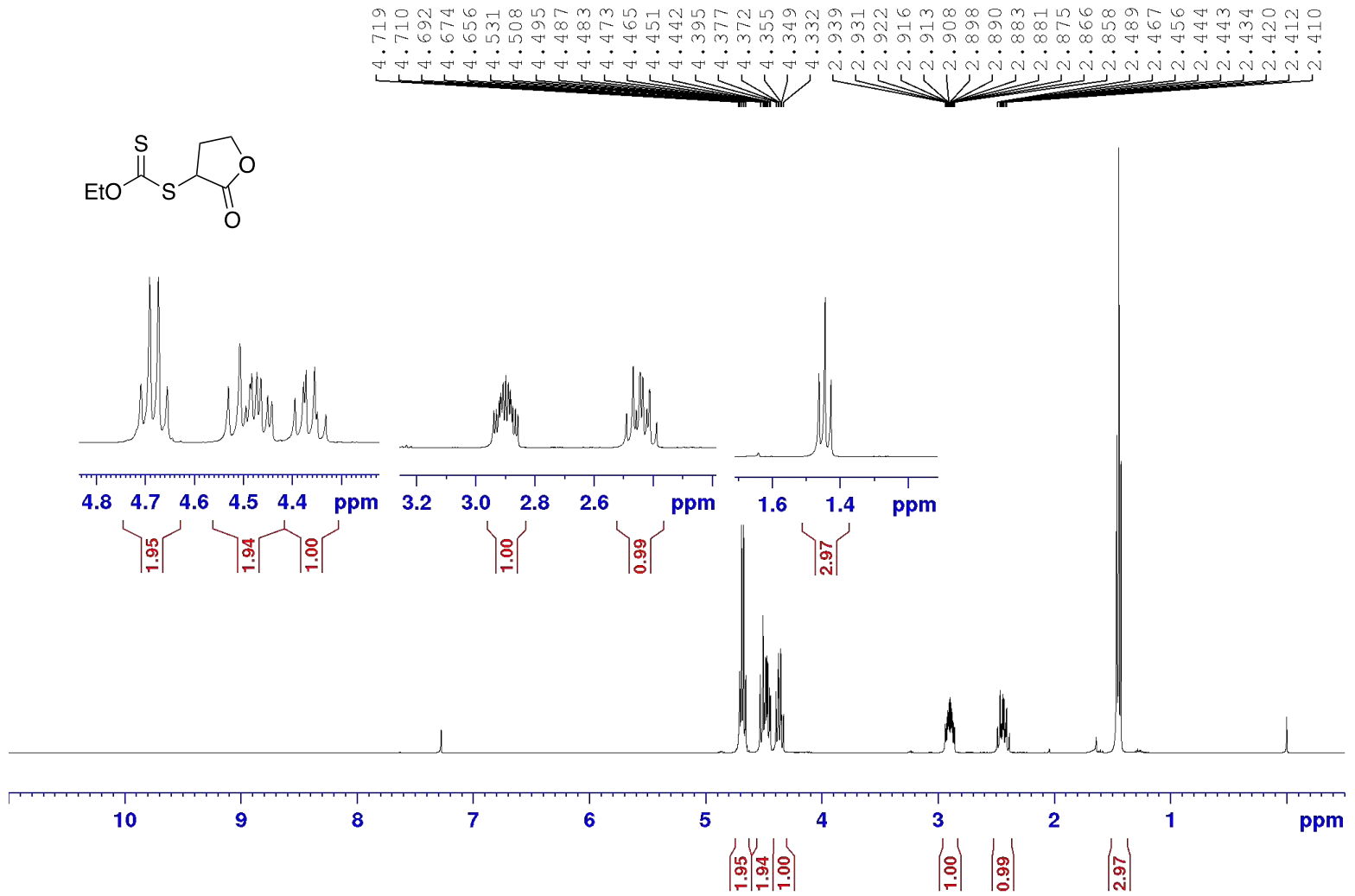
^{1}H NMR Spectrum of **2d** (400 MHz, $CDCl_3$)



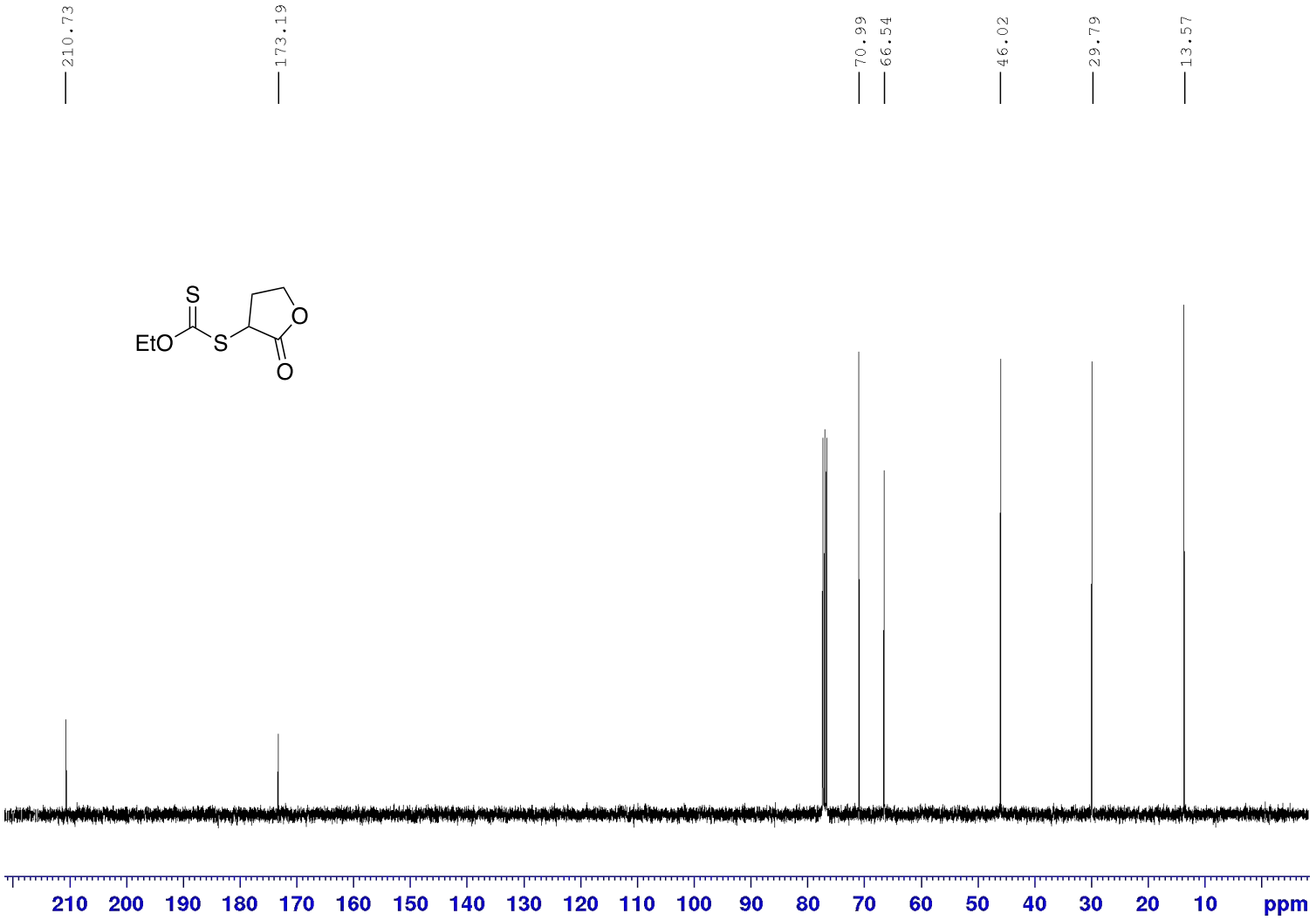
^{13}C NMR Spectrum of **2d** (100 MHz, $CDCl_3$)



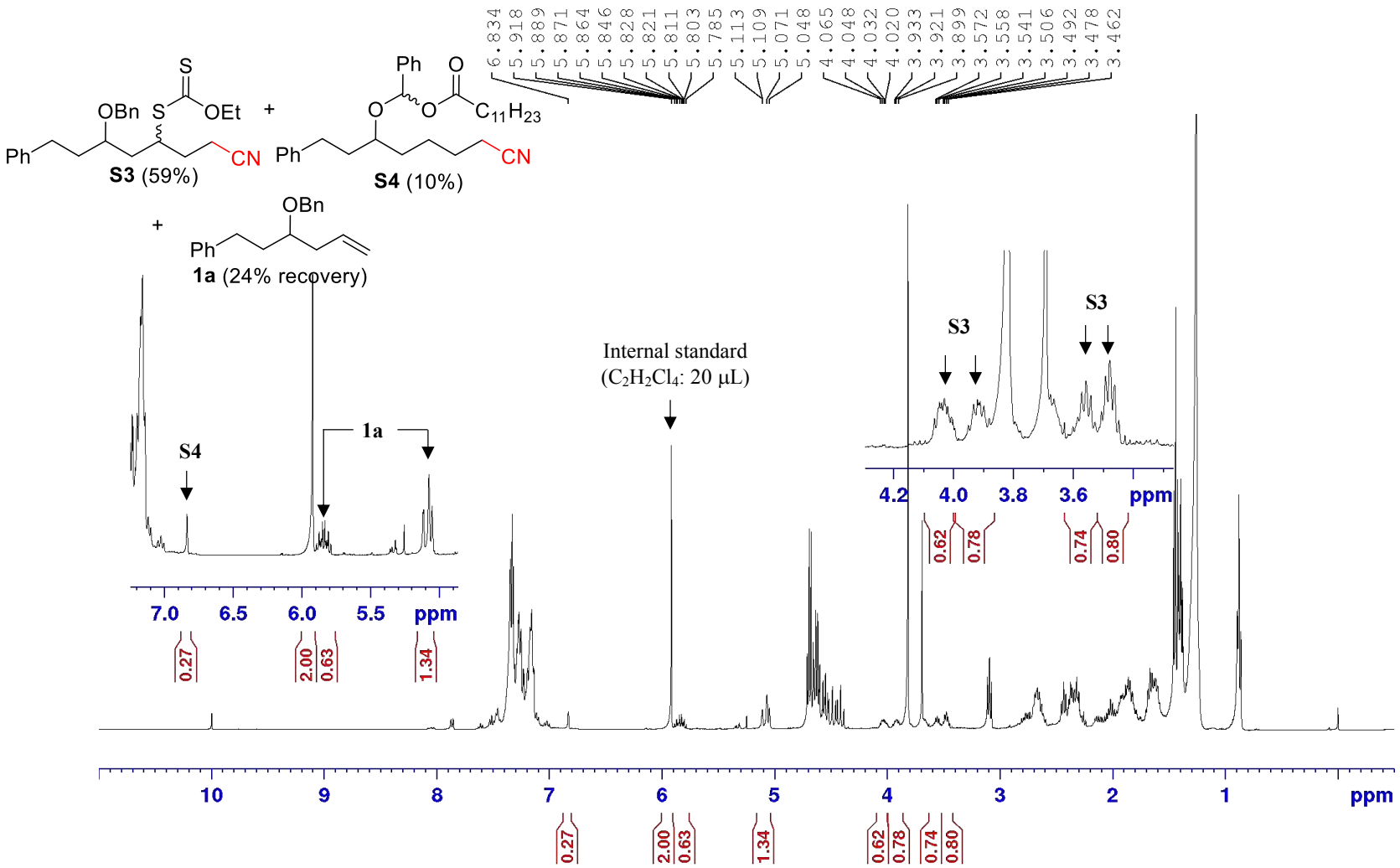
^{1}H NMR Spectrum of **2g** (400 MHz, $CDCl_3$)



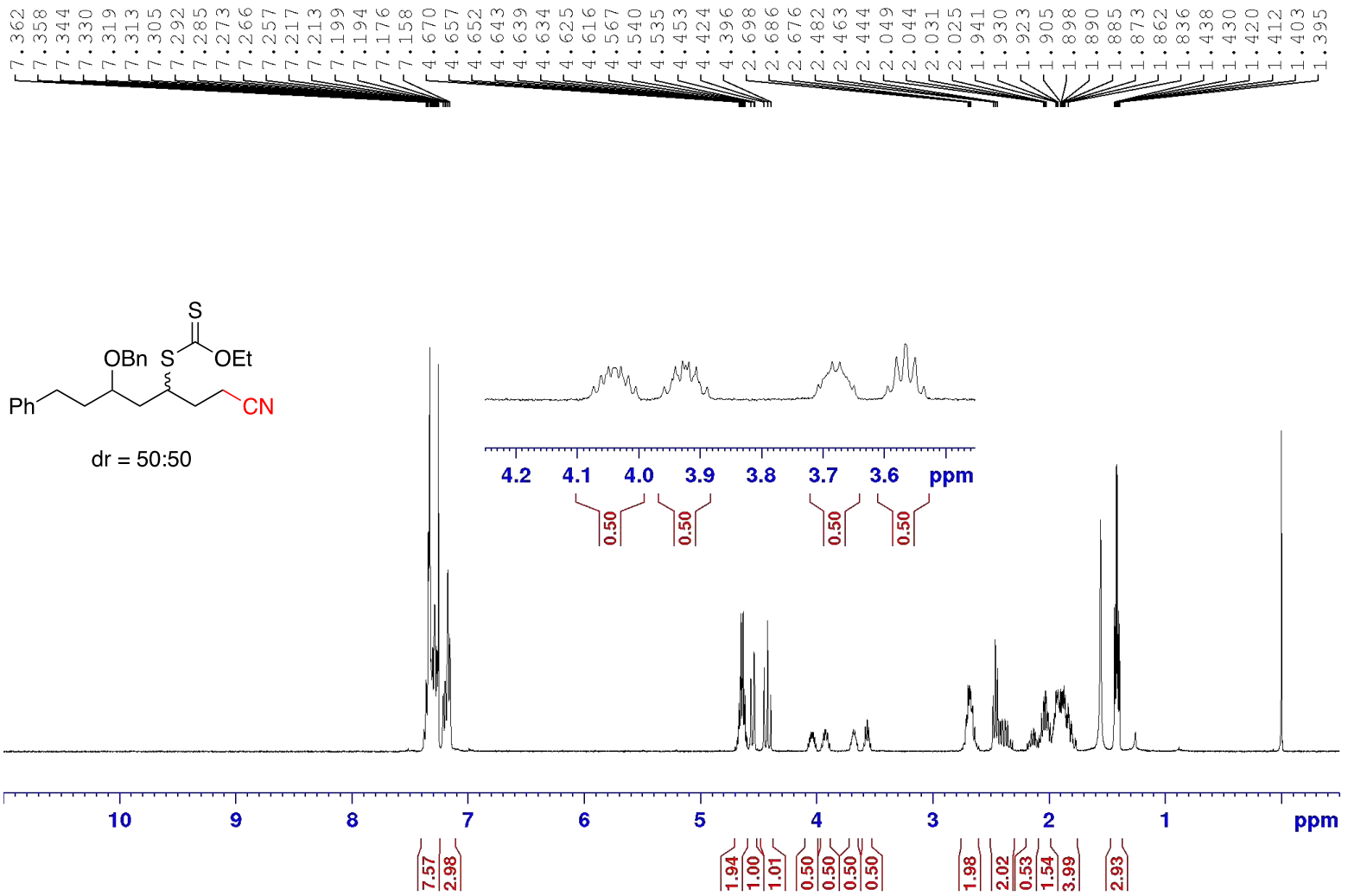
^{13}C NMR Spectrum of **2g** (100 MHz, $CDCl_3$)



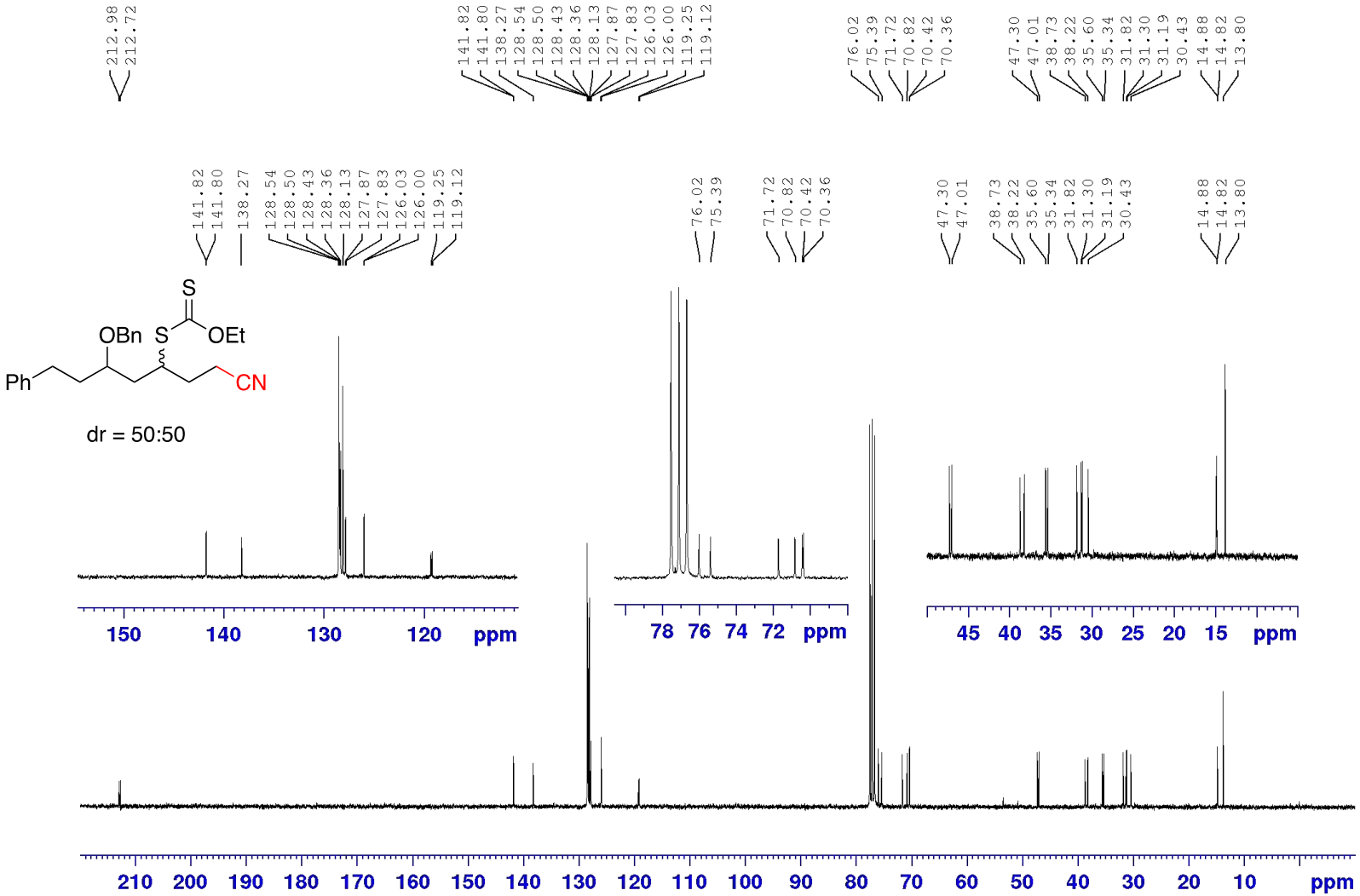
^{1}H NMR Spectrum of crude mixtures obtained from the reaction of **1a** and **2a** with DLP (0.3 equiv) (400 MHz, $CDCl_3$)



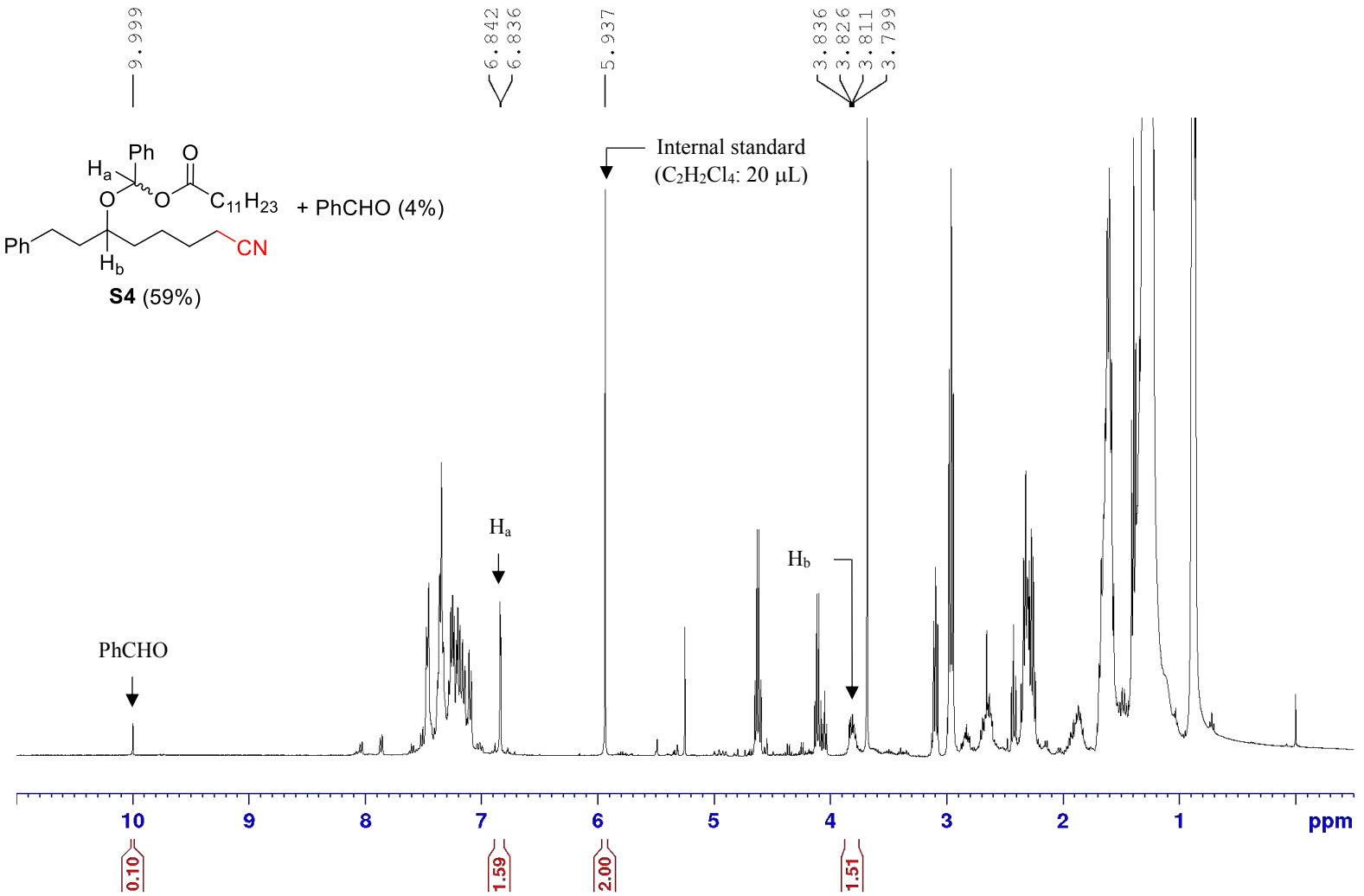
^{1}H NMR Spectrum of **S3** (400 MHz, $CDCl_3$)



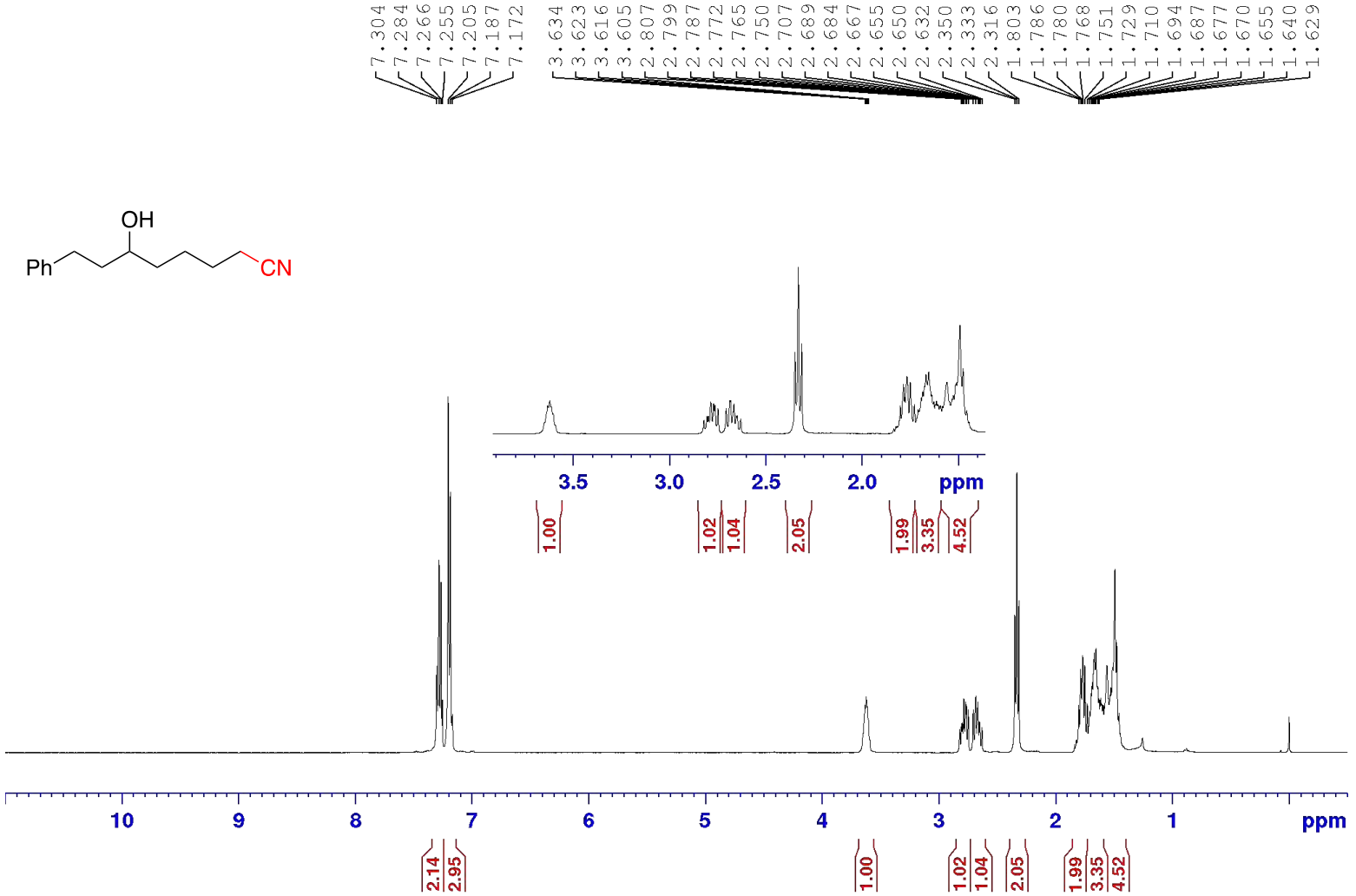
^{13}C NMR Spectrum of **S3** (75 MHz, $CDCl_3$)



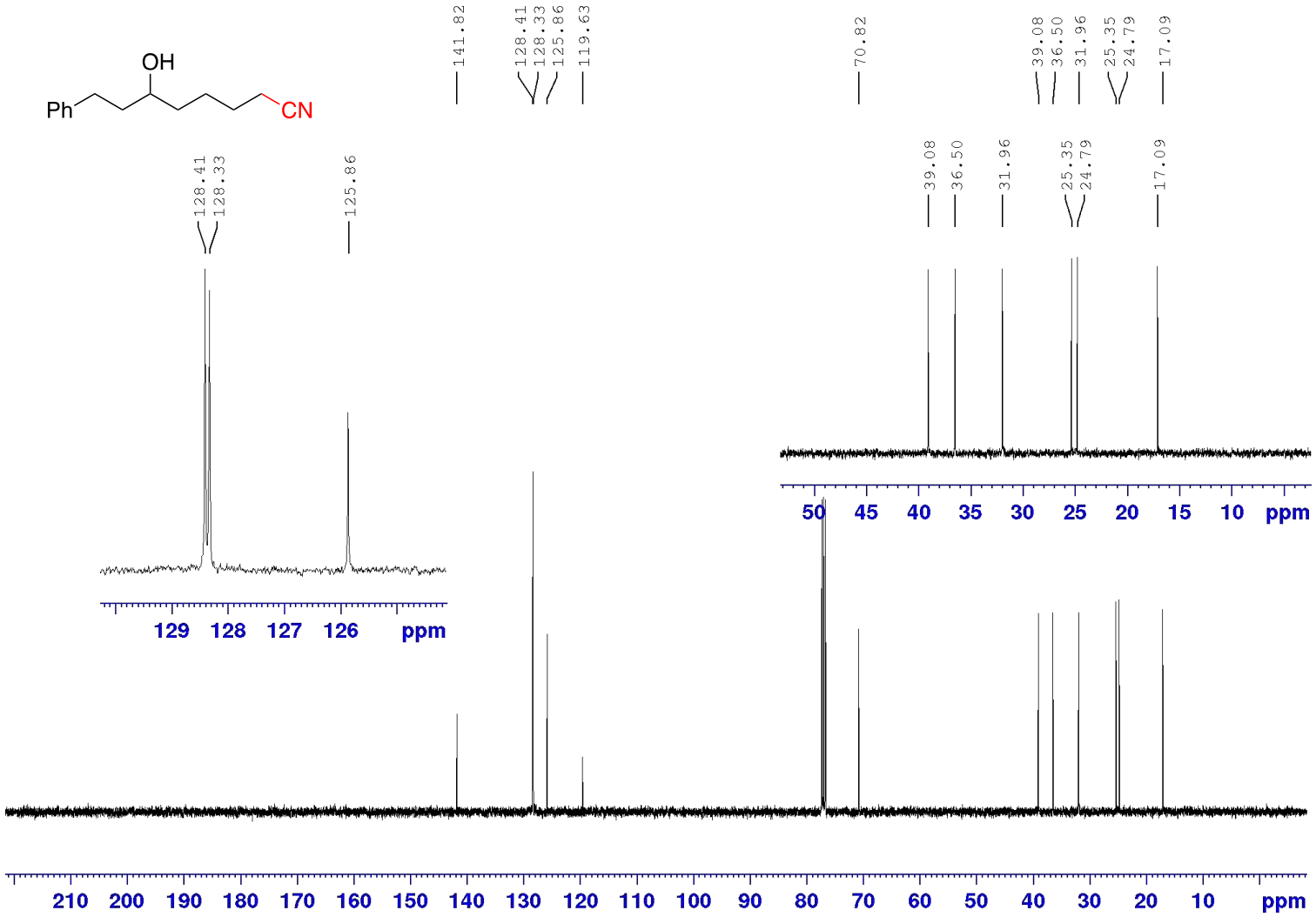
Evidence of the presence of ketal **S4**: crude NMR of the reaction of **1a** and **2a** with DLP (2.5 equiv) without acidic treatment (400 MHz, $CDCl_3$)



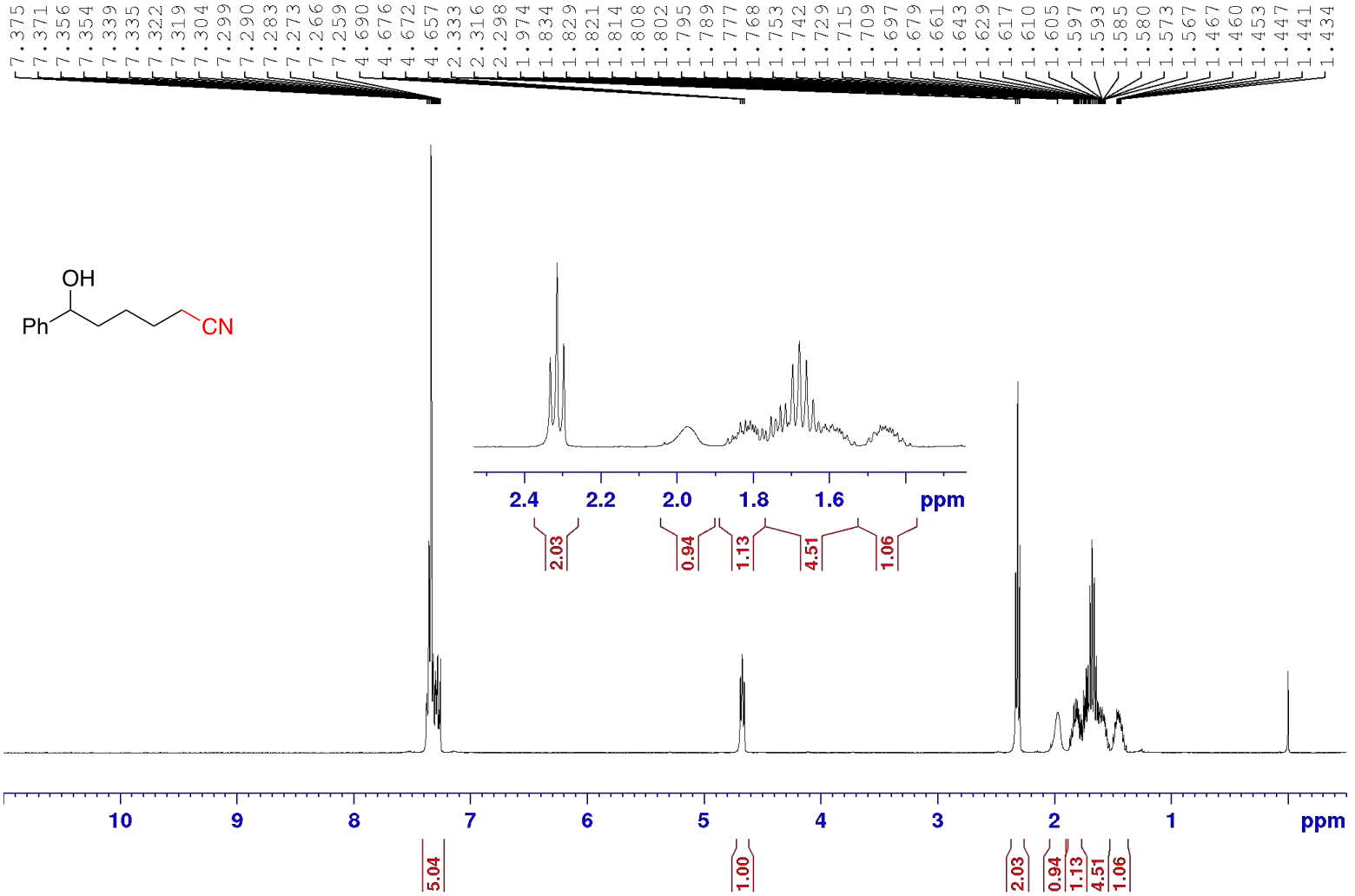
^{1}H NMR Spectrum of **3aa** (400 MHz, $CDCl_3$)



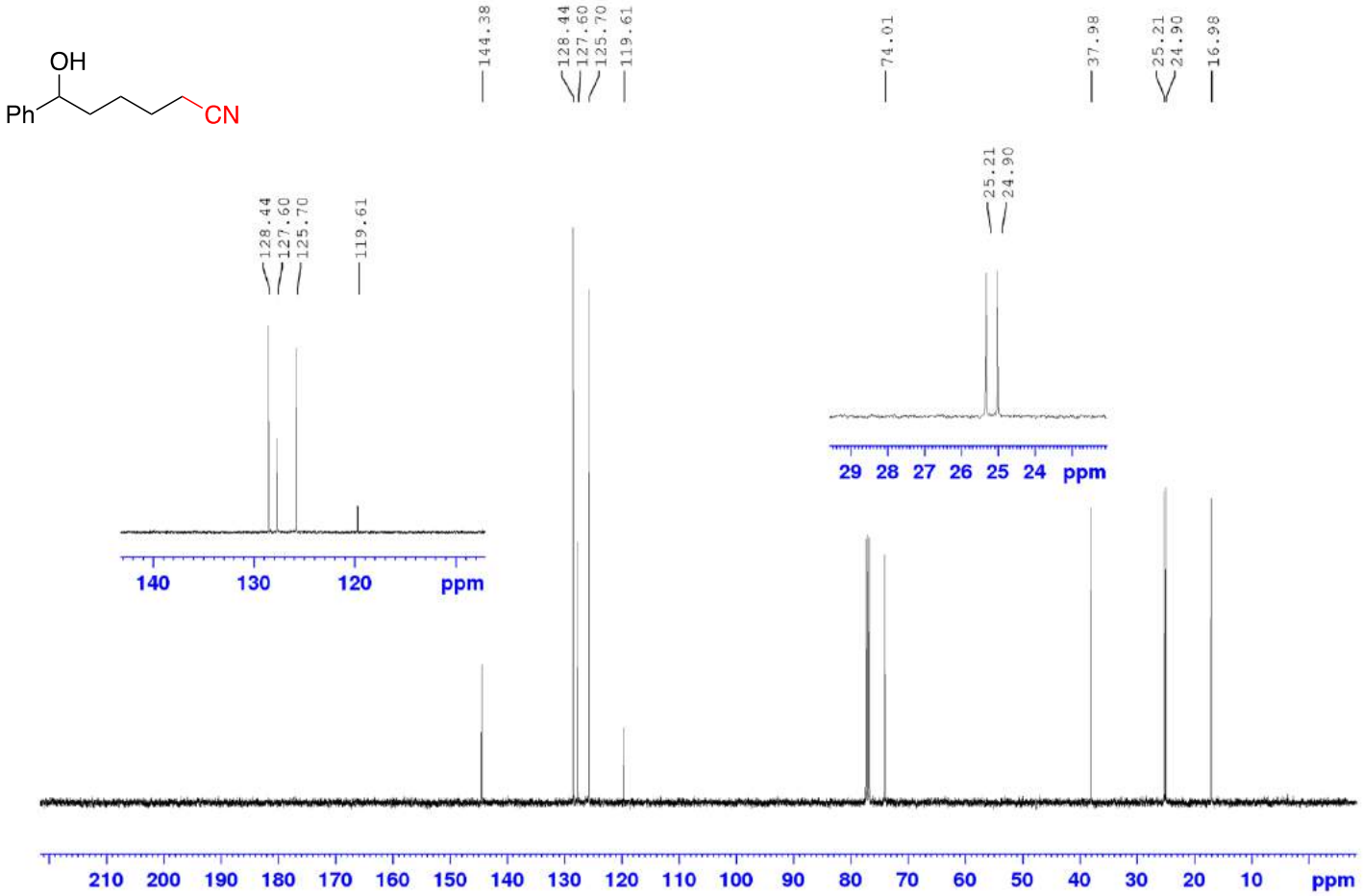
^{13}C NMR Spectrum of **3aa** (100 MHz, $CDCl_3$)



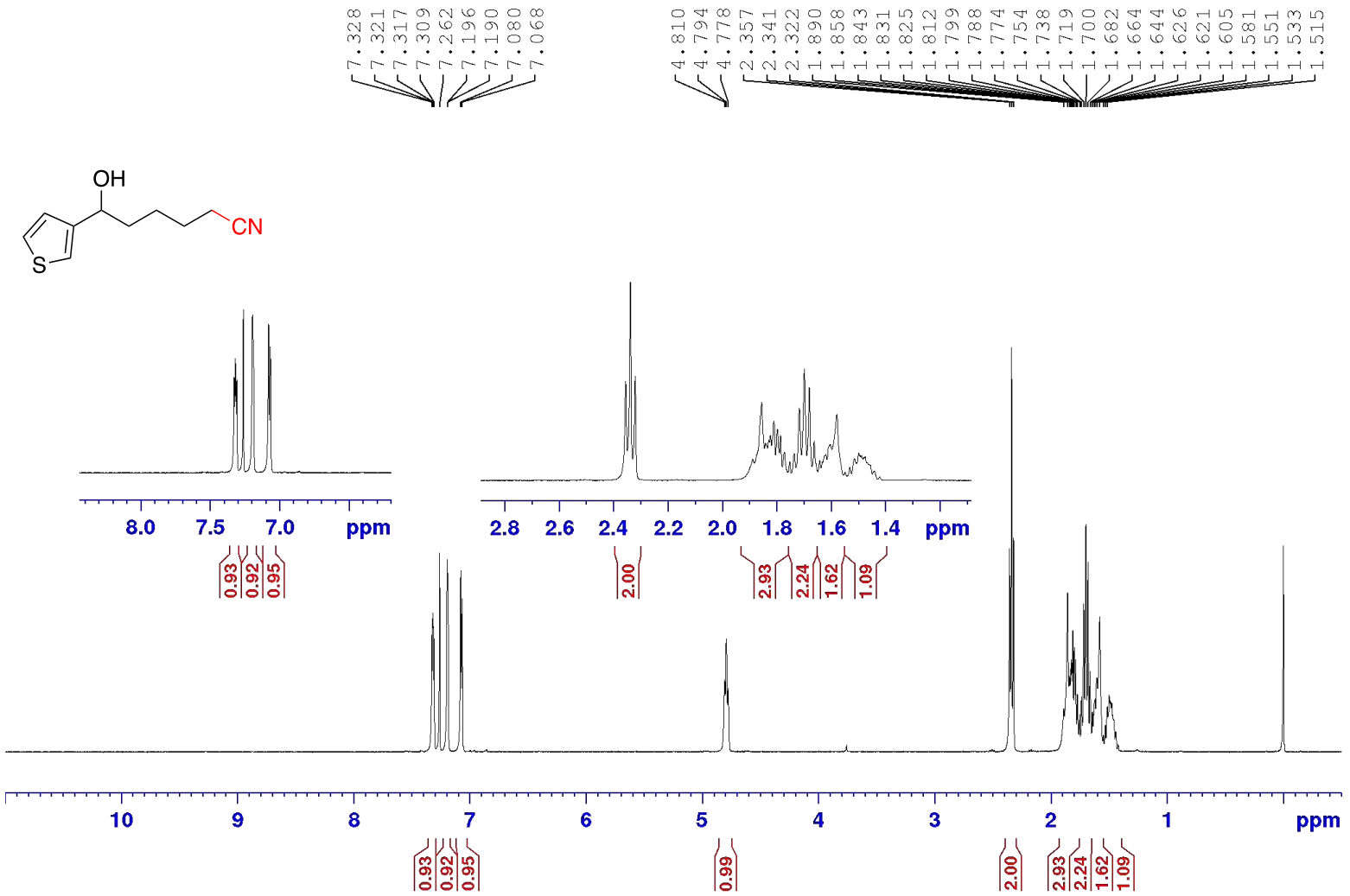
^{1}H NMR Spectrum of **3ba** (400 MHz, $CDCl_3$)



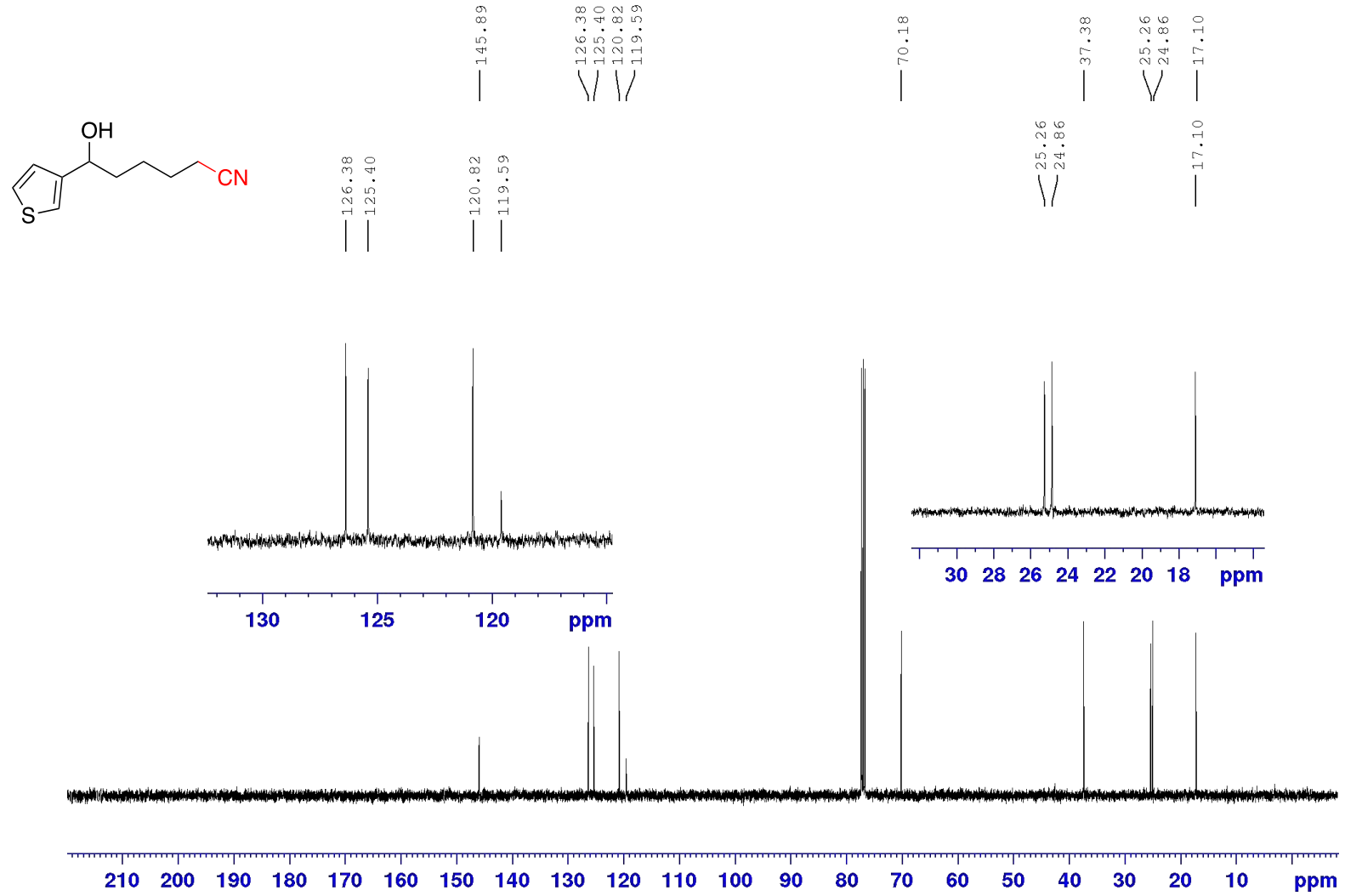
^{13}C NMR Spectrum of **3ba** (100 MHz, $CDCl_3$)



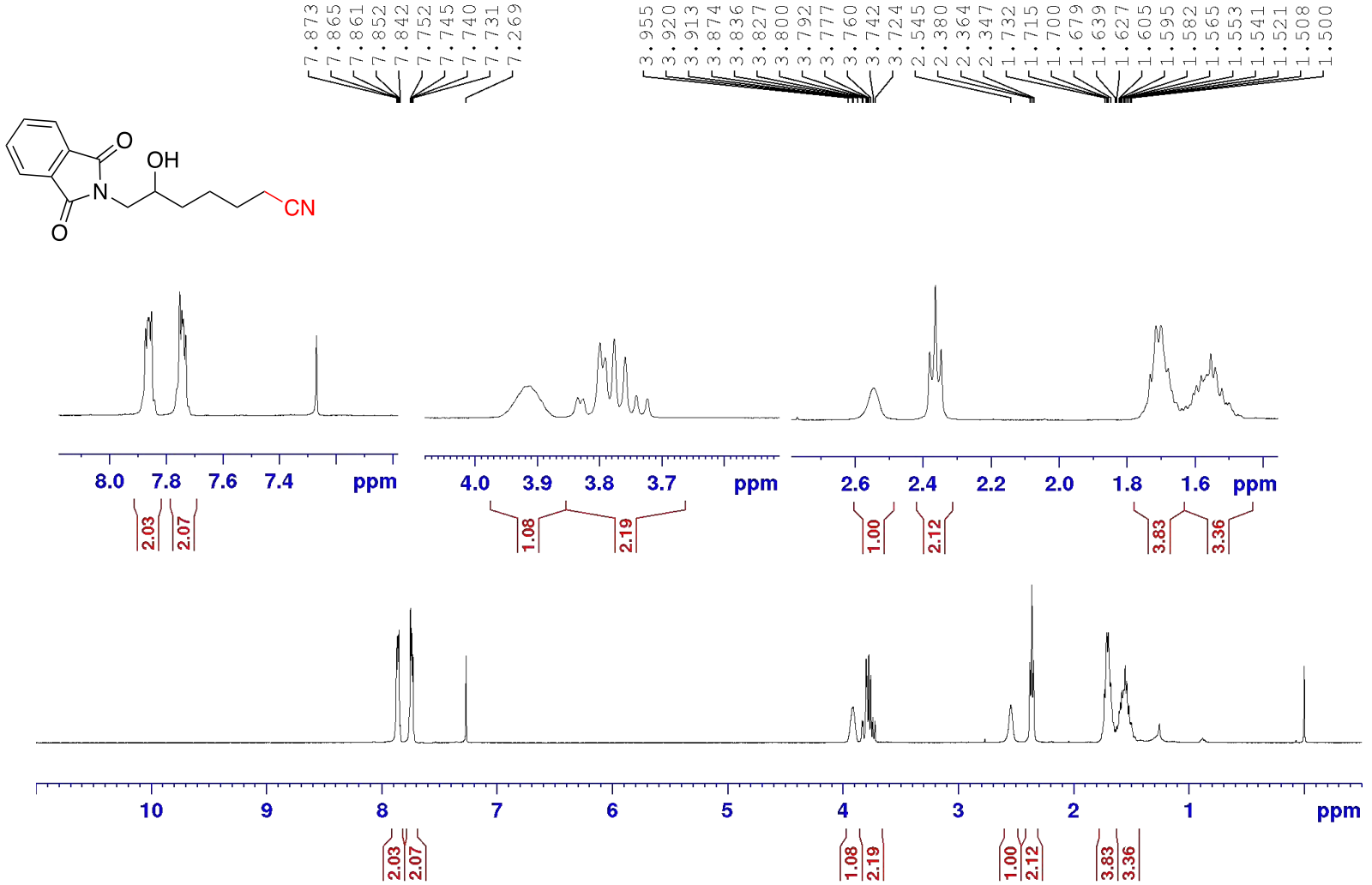
^{1}H NMR Spectrum of **3ca** (400 MHz, $CDCl_3$)



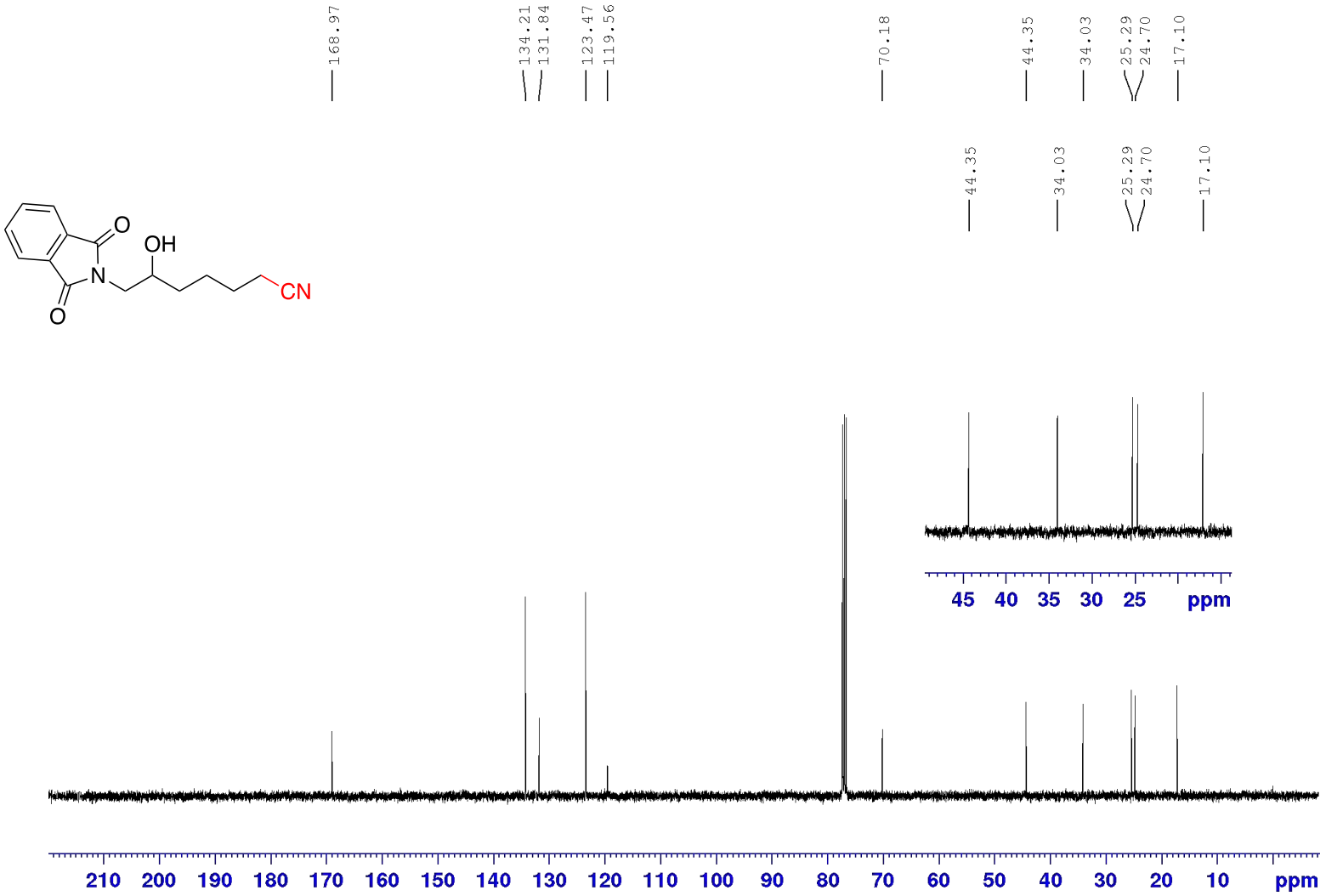
^{13}C NMR Spectrum of **3ca** (100 MHz, $CDCl_3$)



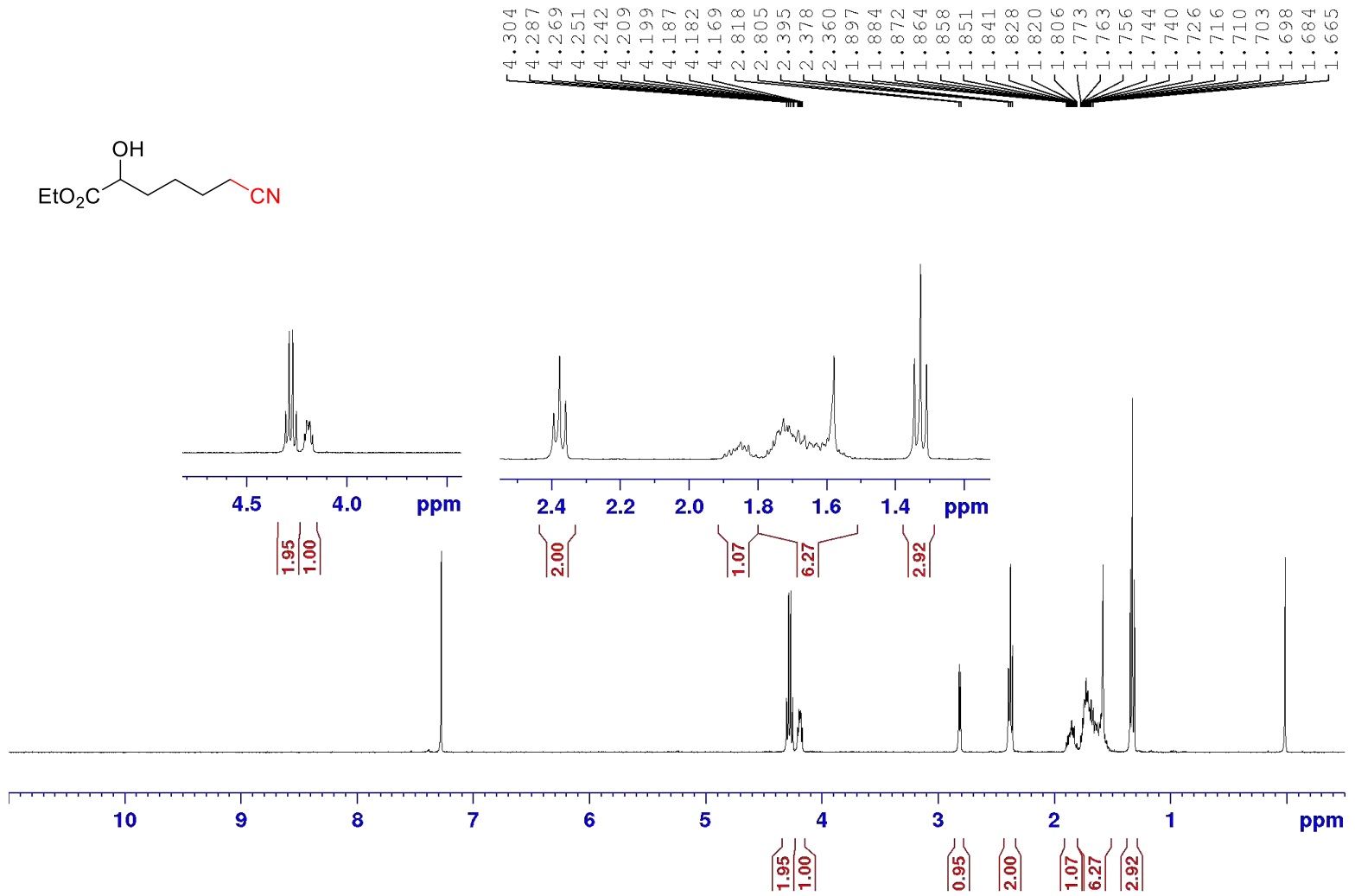
^{1}H NMR Spectrum of **3da** (400 MHz, $CDCl_3$)



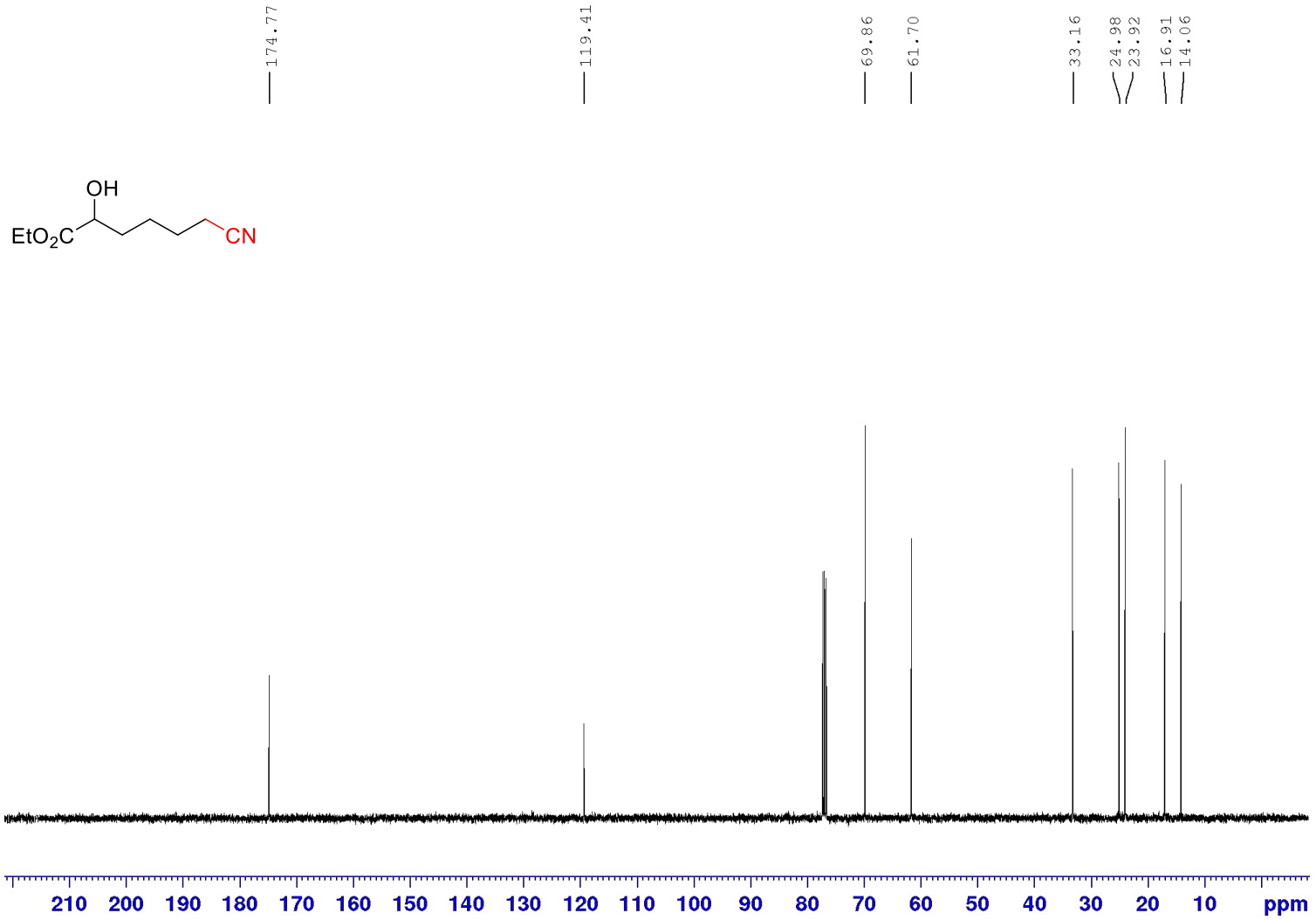
^{13}C NMR Spectrum of **3da** (100 MHz, $CDCl_3$)



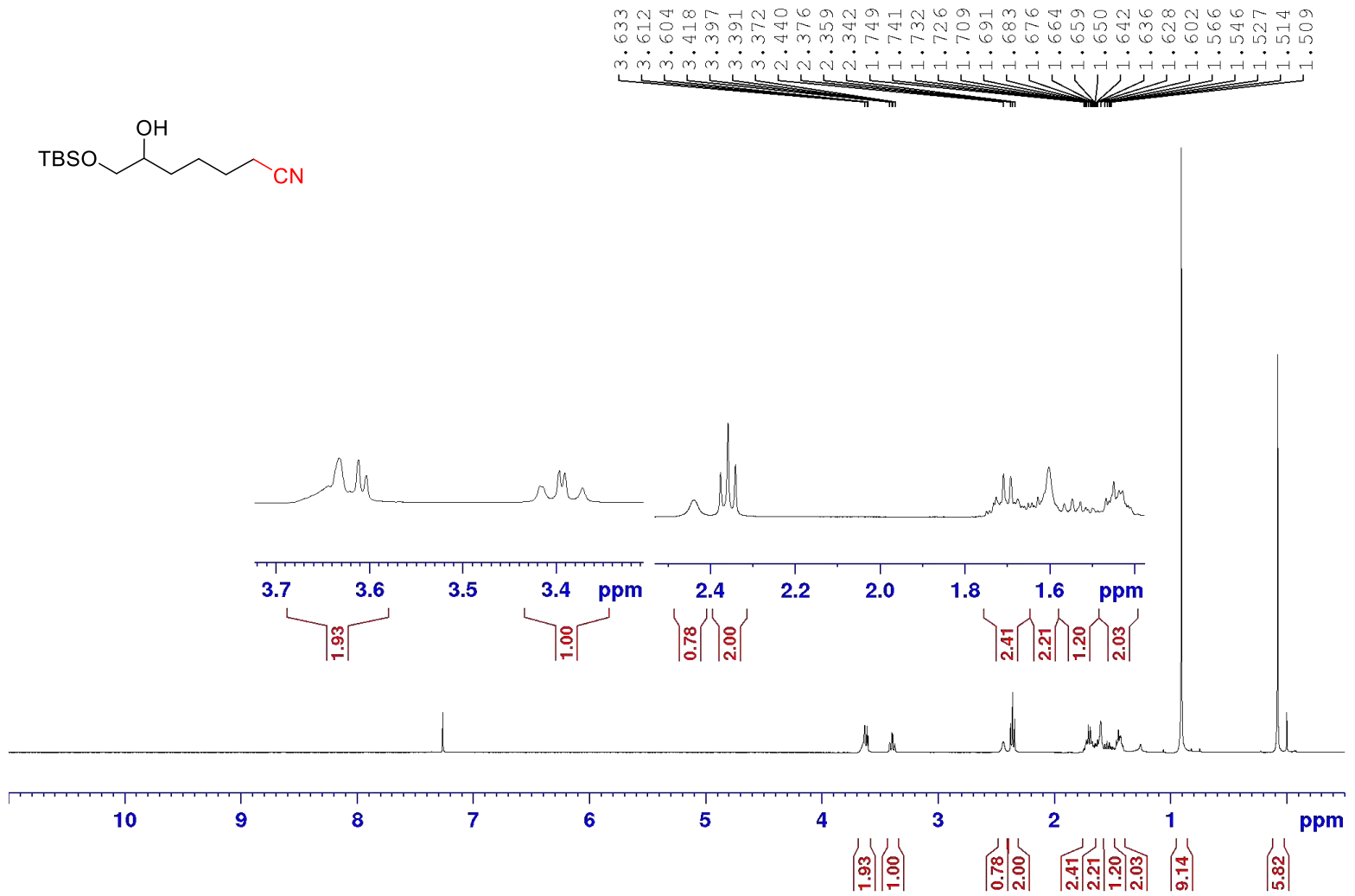
^{1}H NMR Spectrum of **3ea** (400 MHz, $CDCl_3$)



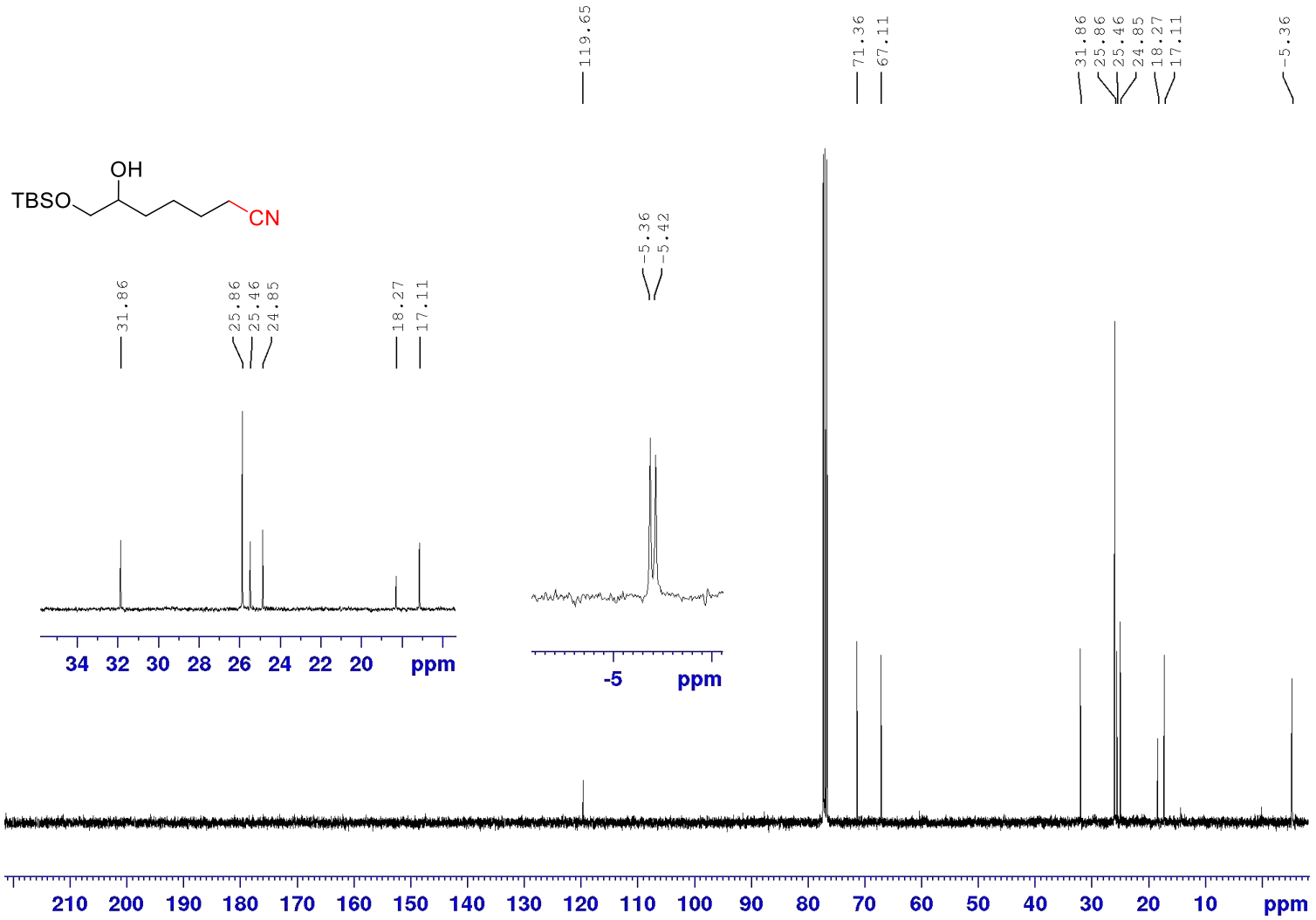
^{13}C NMR Spectrum of **3ea** (100 MHz, $CDCl_3$)



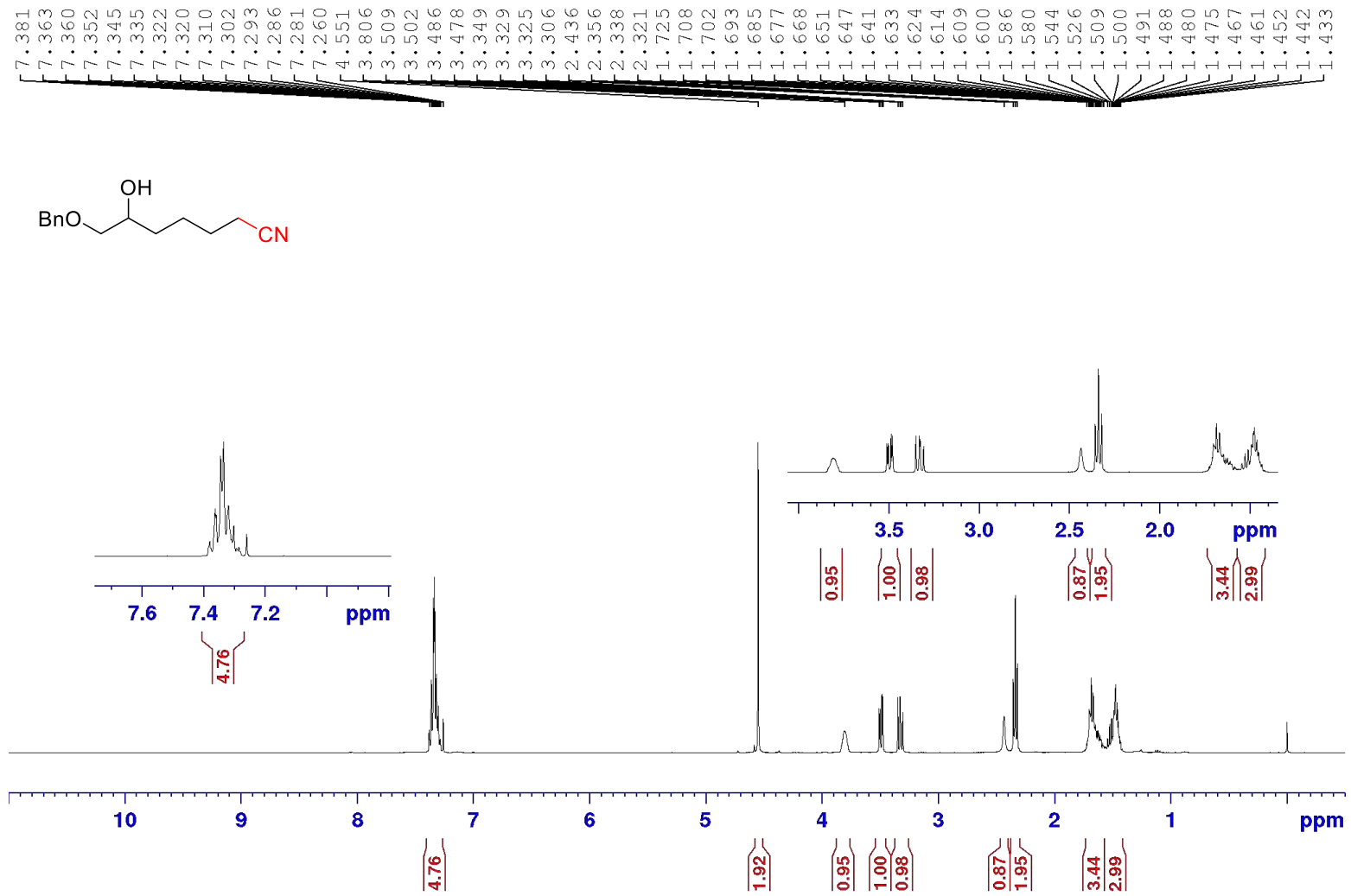
^{1}H NMR Spectrum of **3fa** (400 MHz, $CDCl_3$)



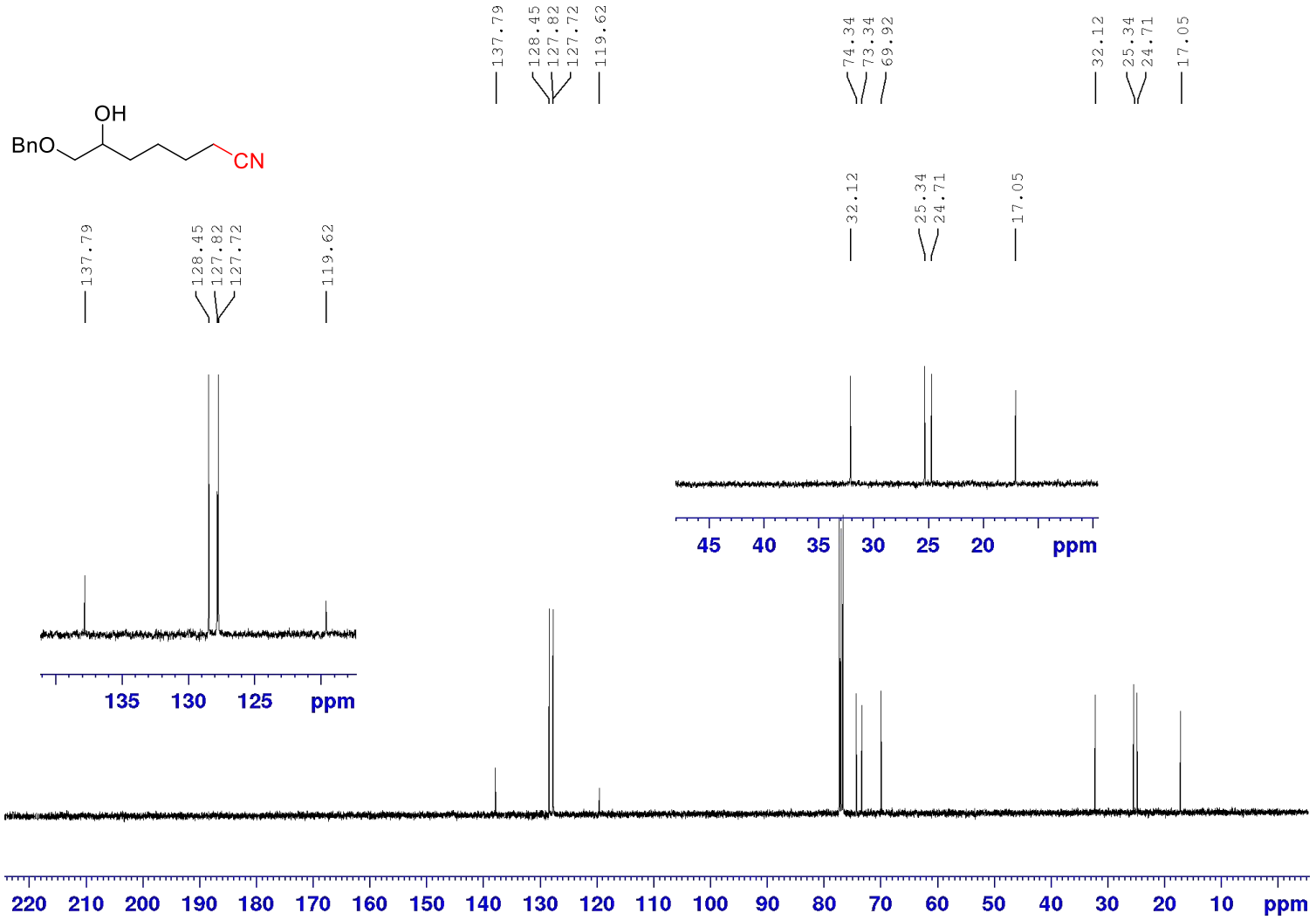
^{13}C NMR Spectrum of **3fa** (100 MHz, $CDCl_3$)



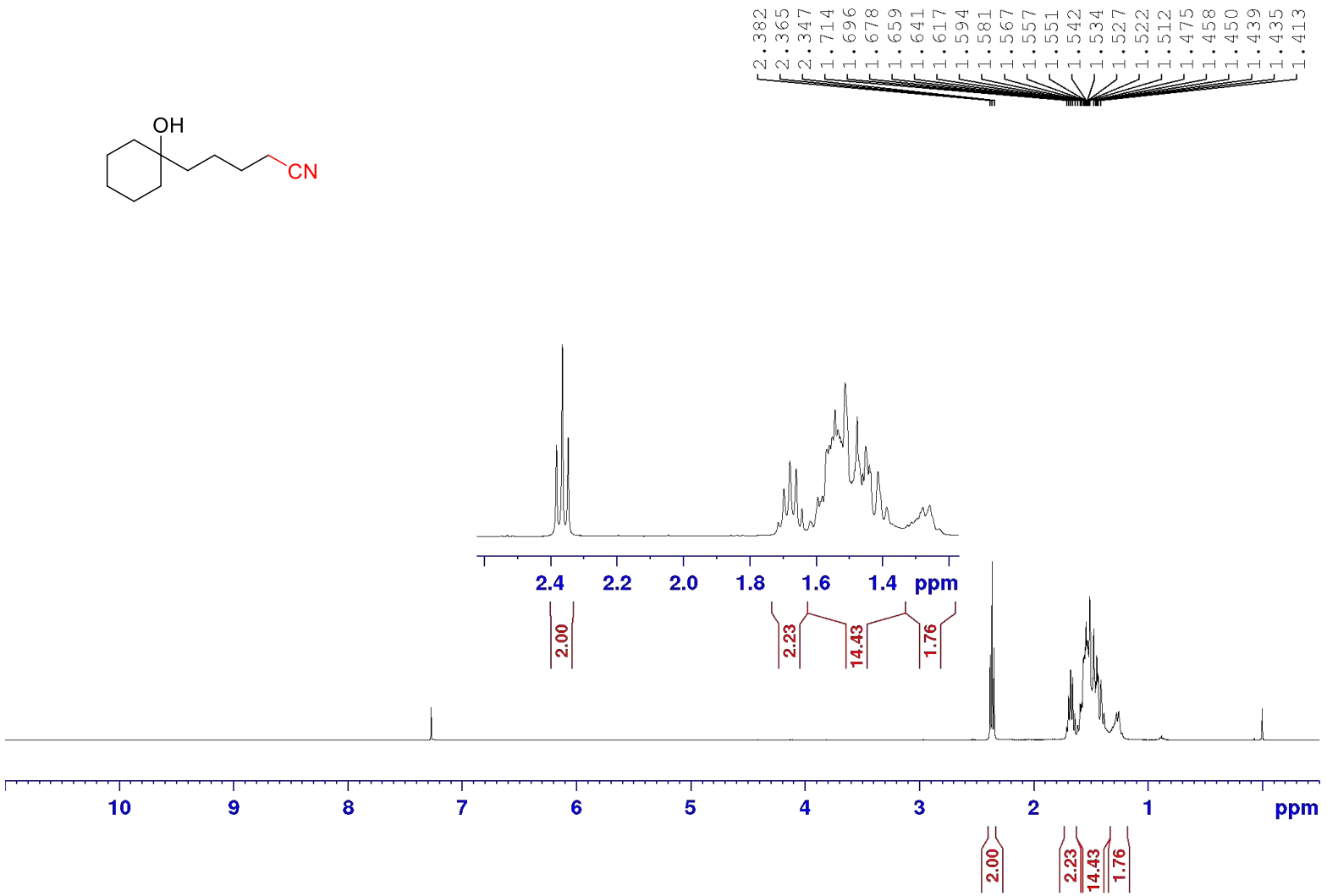
^{1}H NMR Spectrum of **3ga** (400 MHz, $CDCl_3$)



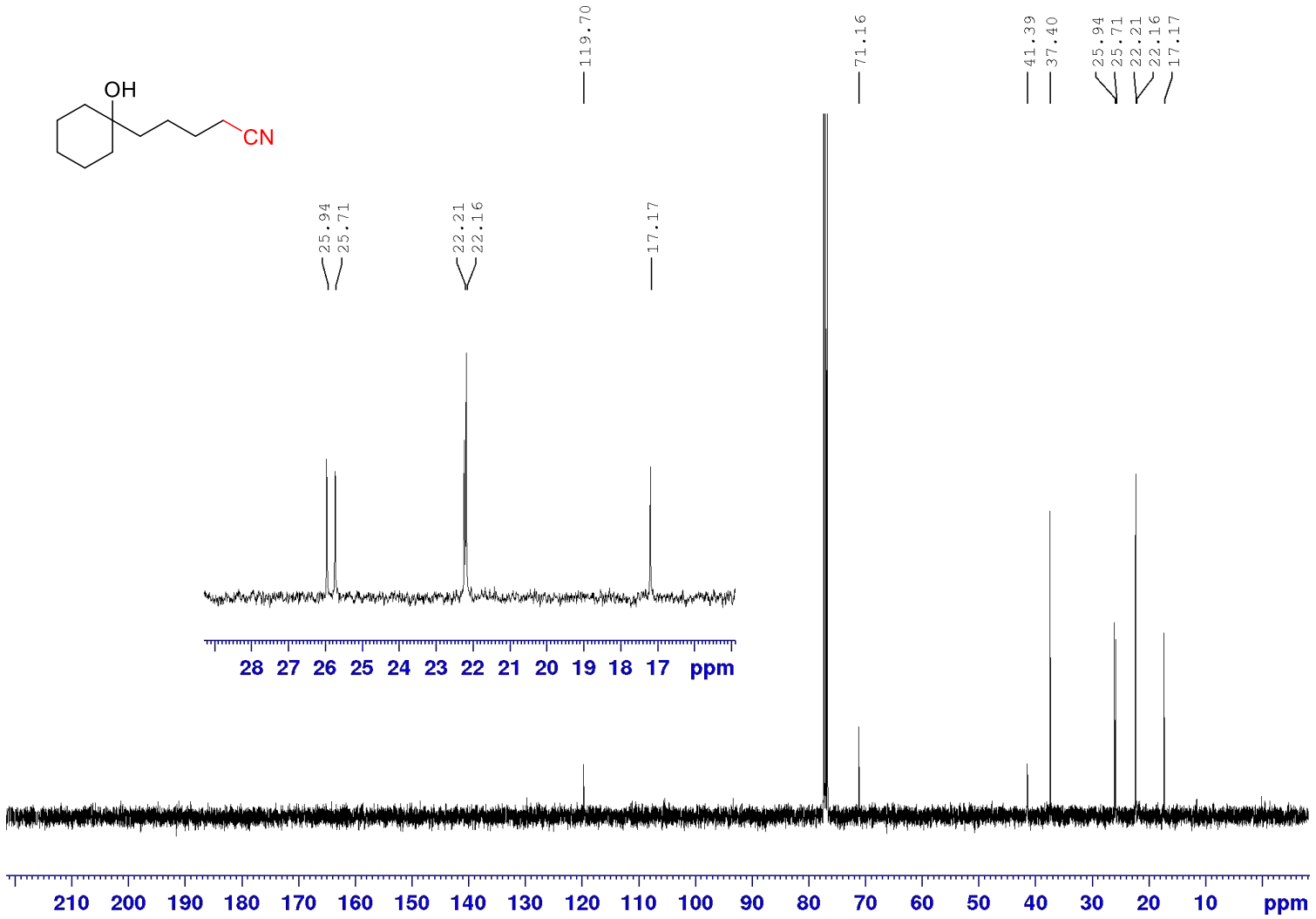
^{13}C NMR Spectrum of **3ga** (100 MHz, $CDCl_3$)



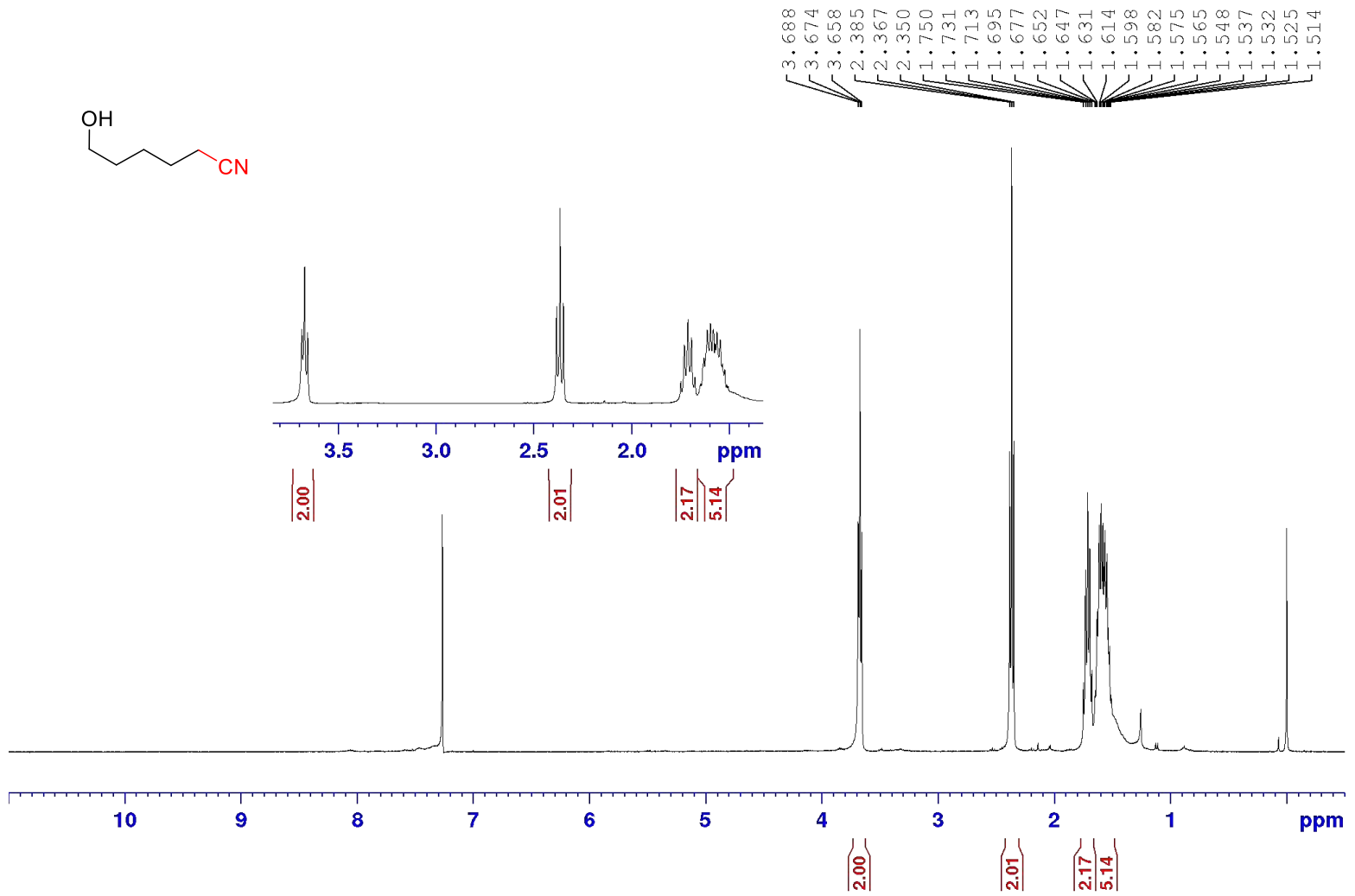
^{1}H NMR Spectrum of **3ha** (400 MHz, $CDCl_3$)



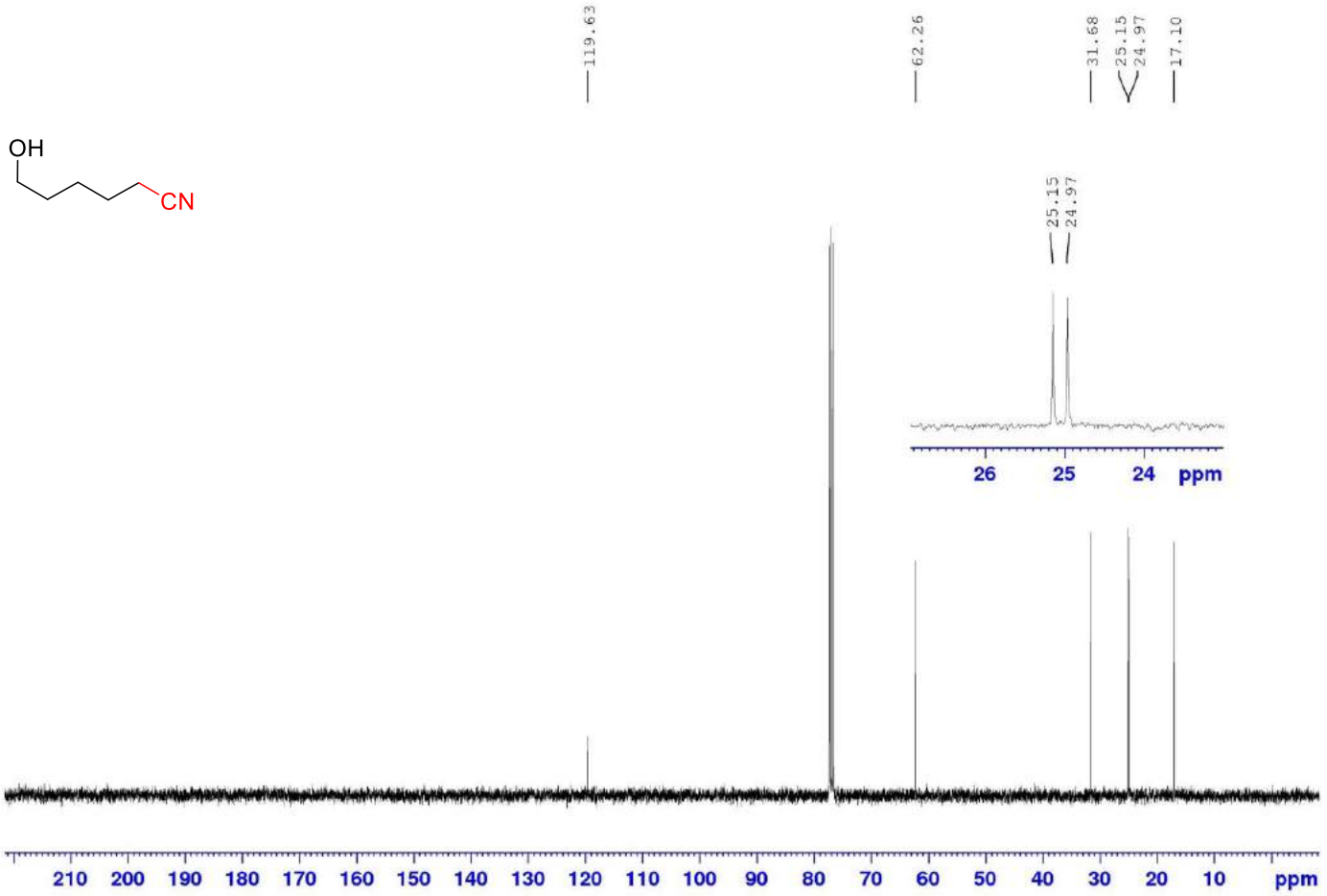
^{13}C NMR Spectrum of **3ha** (100 MHz, $CDCl_3$)



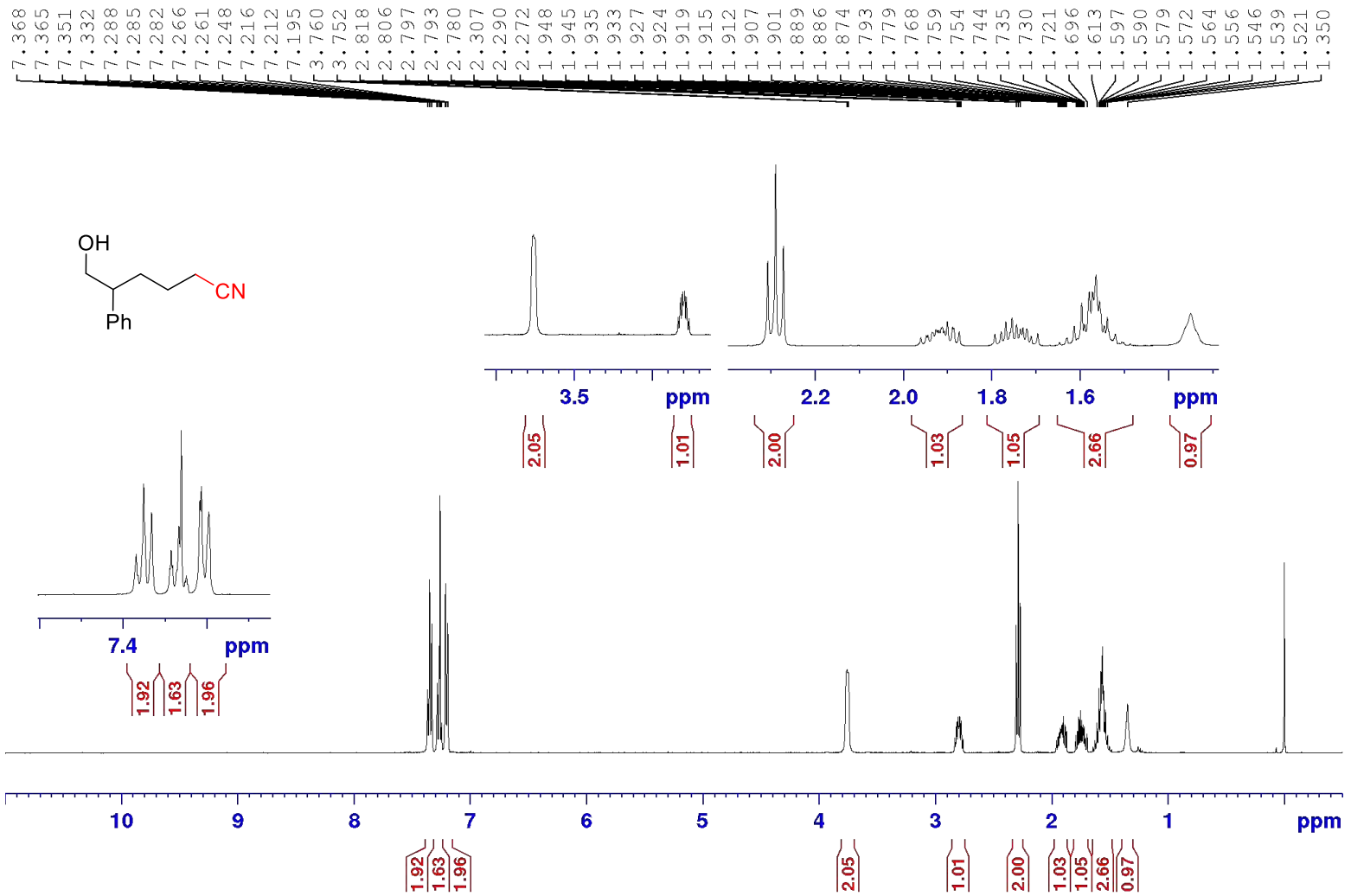
H NMR Spectrum of **3ia** (400 MHz, $CDCl_3$)



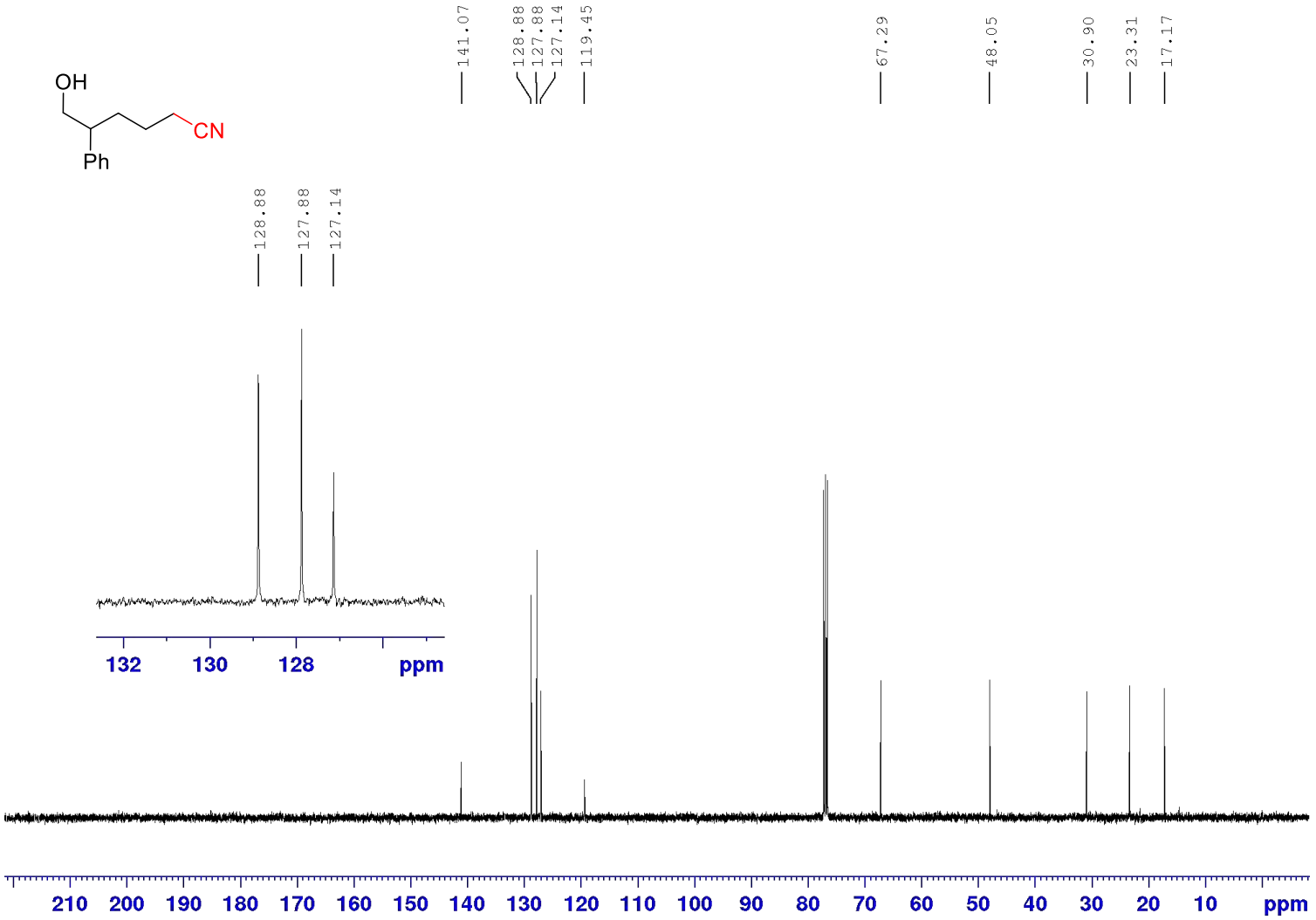
^{13}C NMR Spectrum of **3ia** (100 MHz, $CDCl_3$)



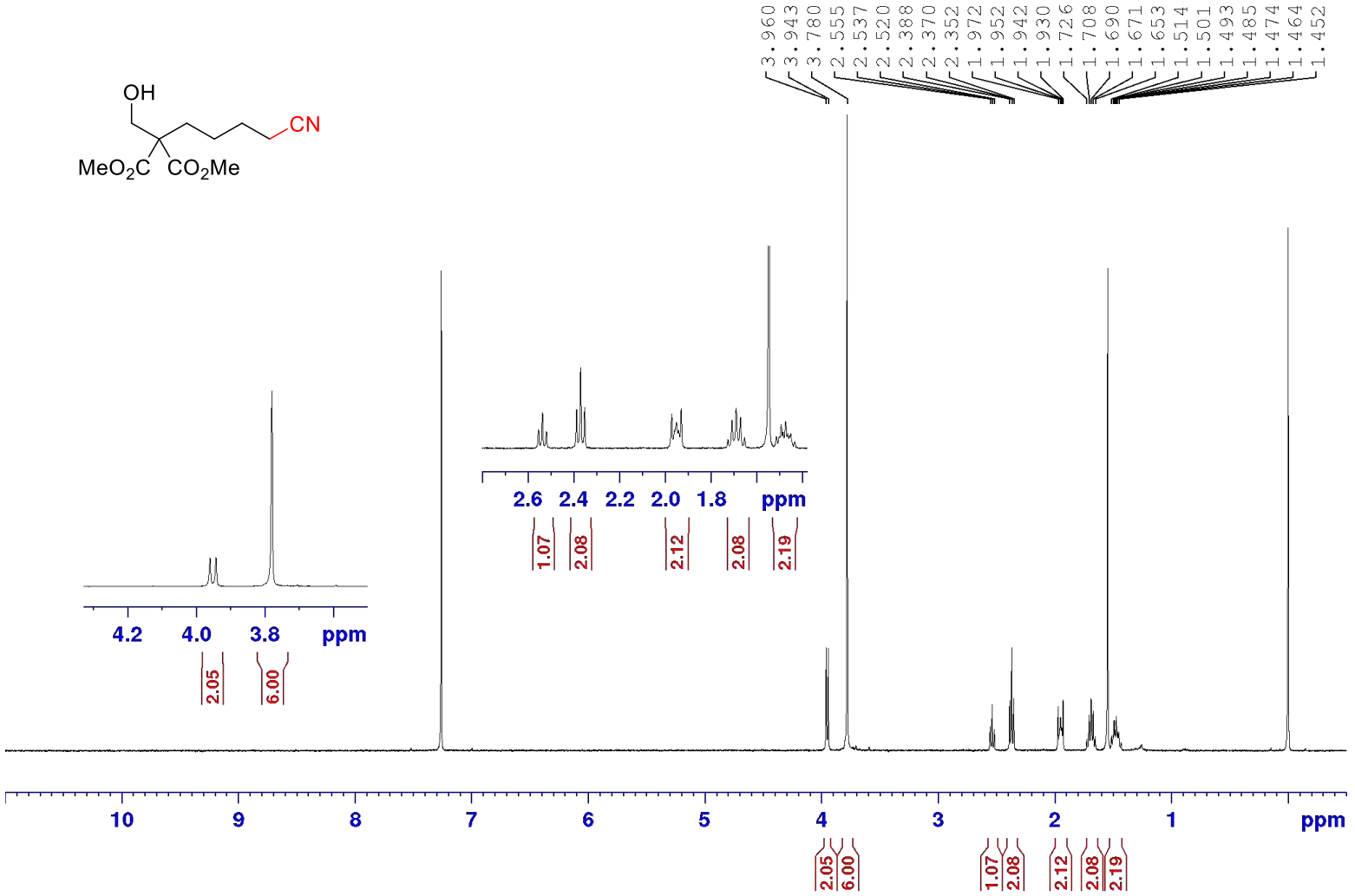
^{1}H NMR Spectrum of **3ja** (400 MHz, $CDCl_3$)



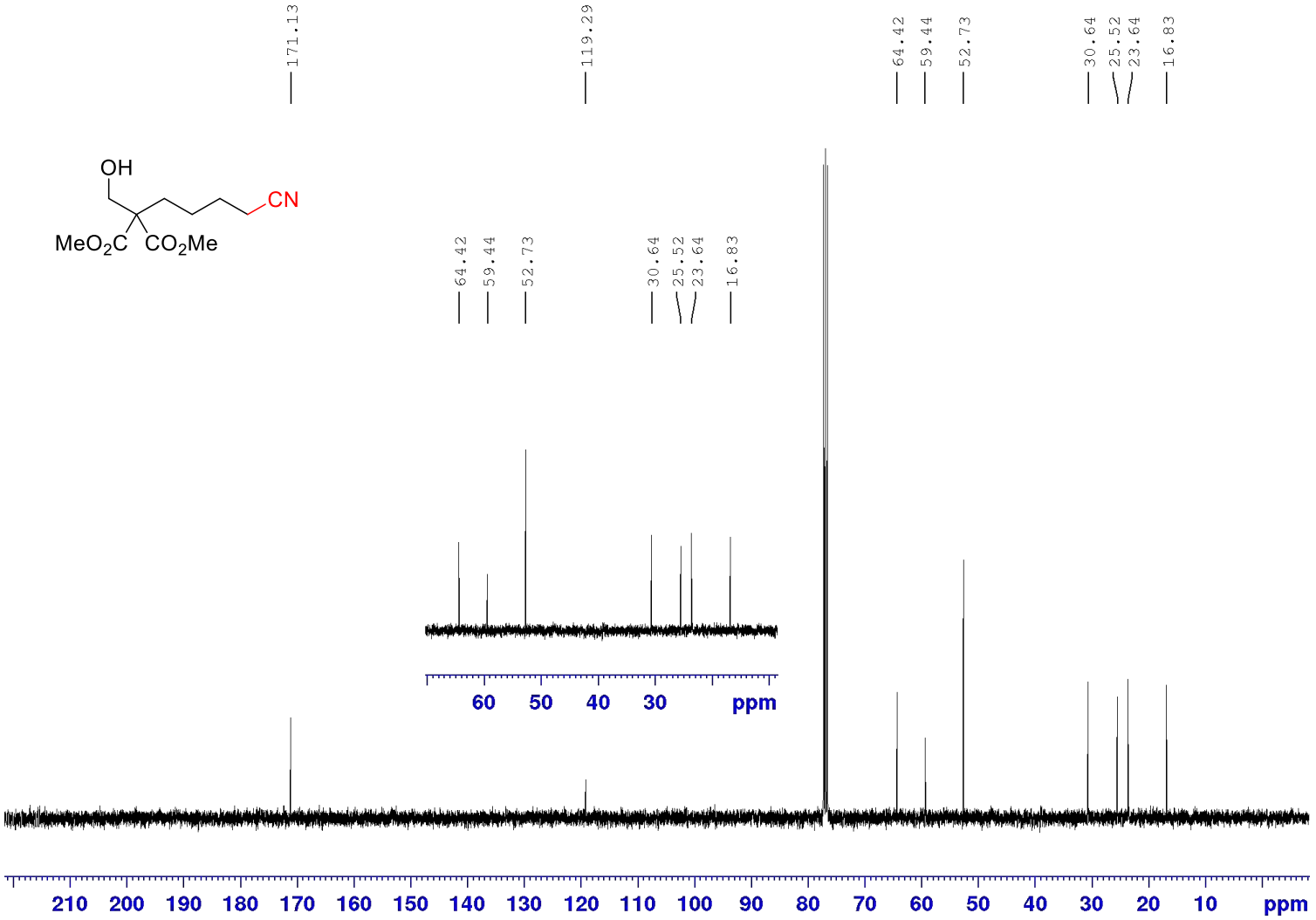
^{13}C NMR Spectrum of **3ja** (100 MHz, $CDCl_3$)



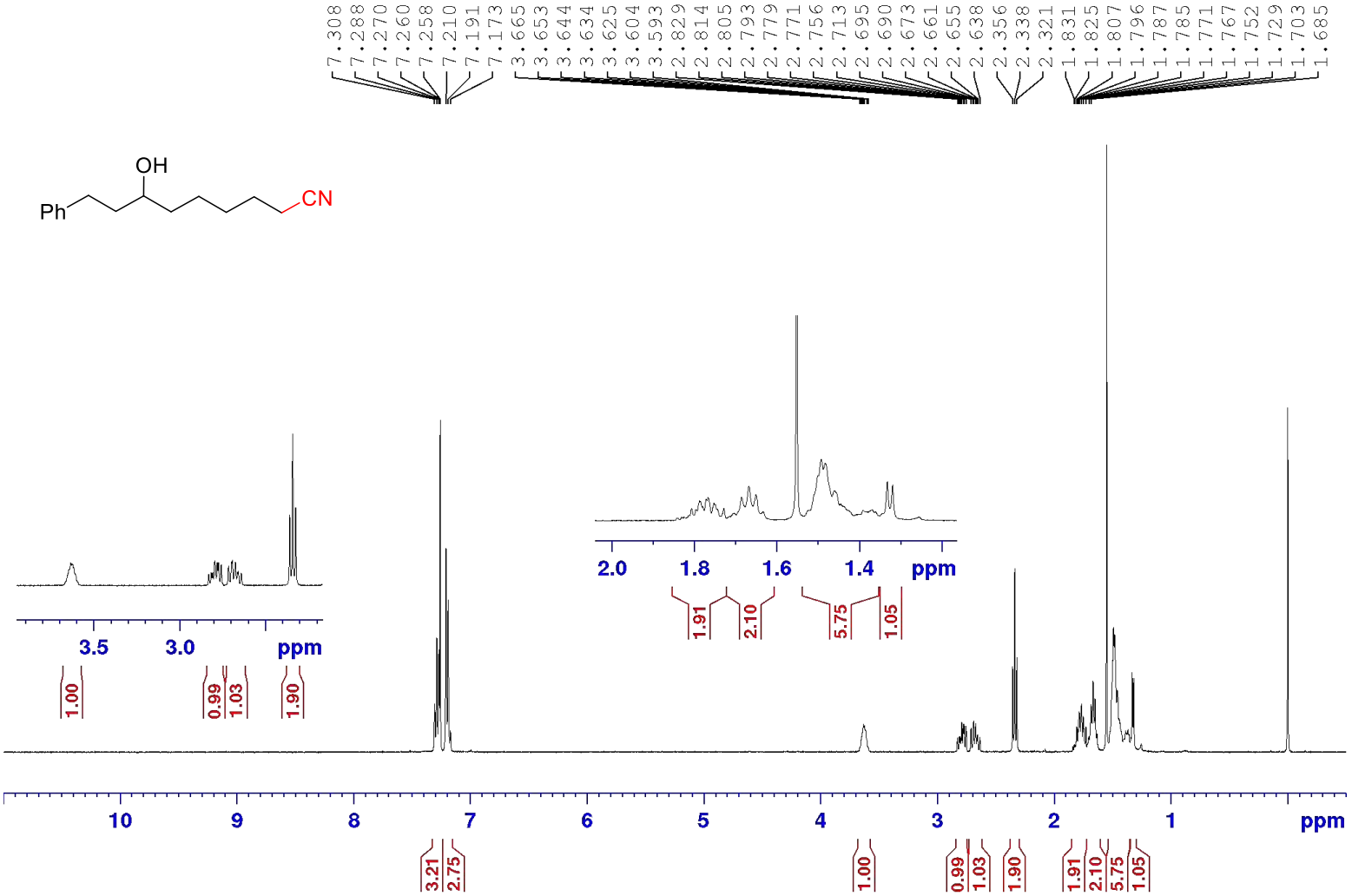
1H NMR Spectrum of **3ka** (400 MHz, $CDCl_3$)



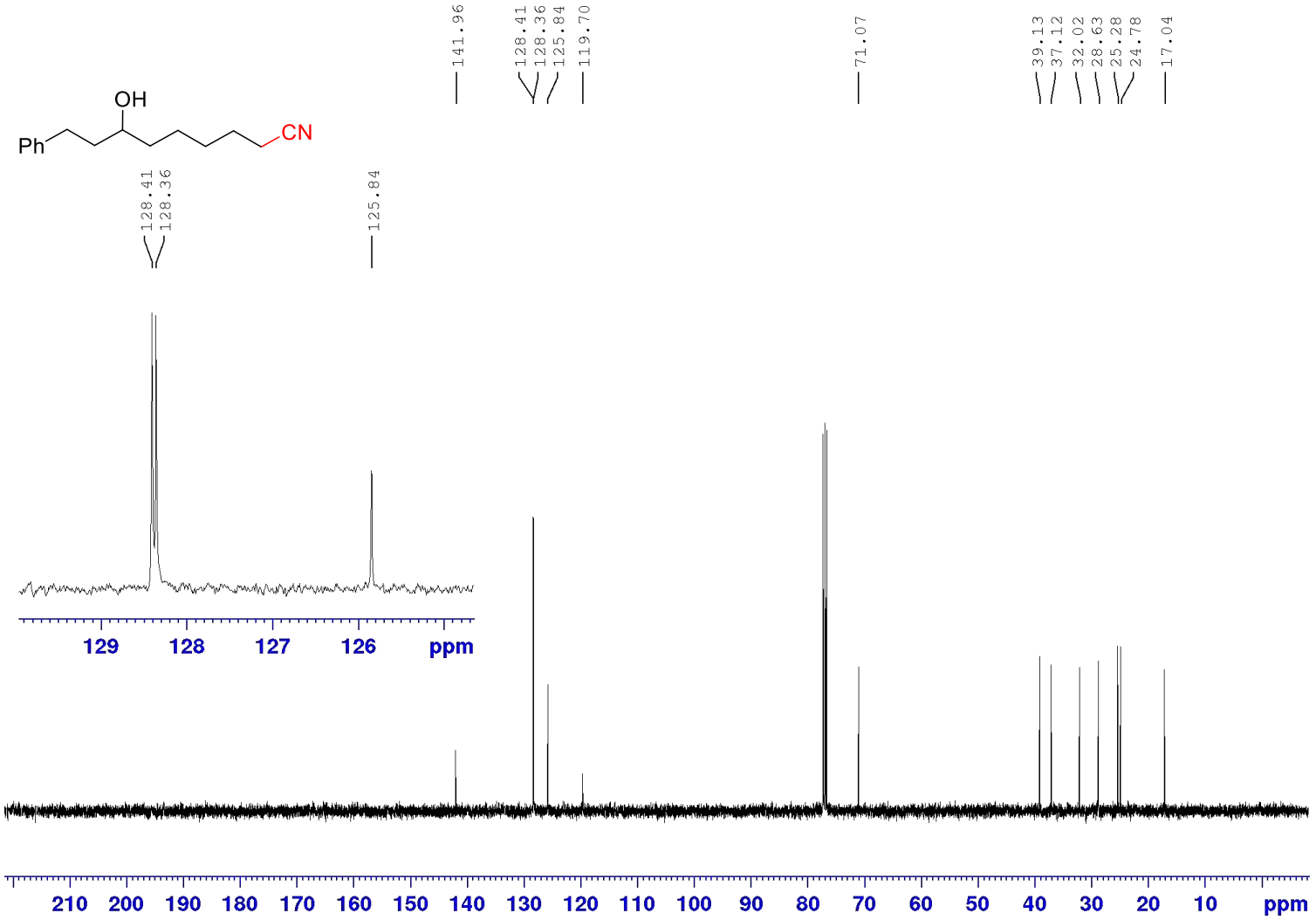
^{13}C NMR Spectrum of **3ka** (100 MHz, $CDCl_3$)



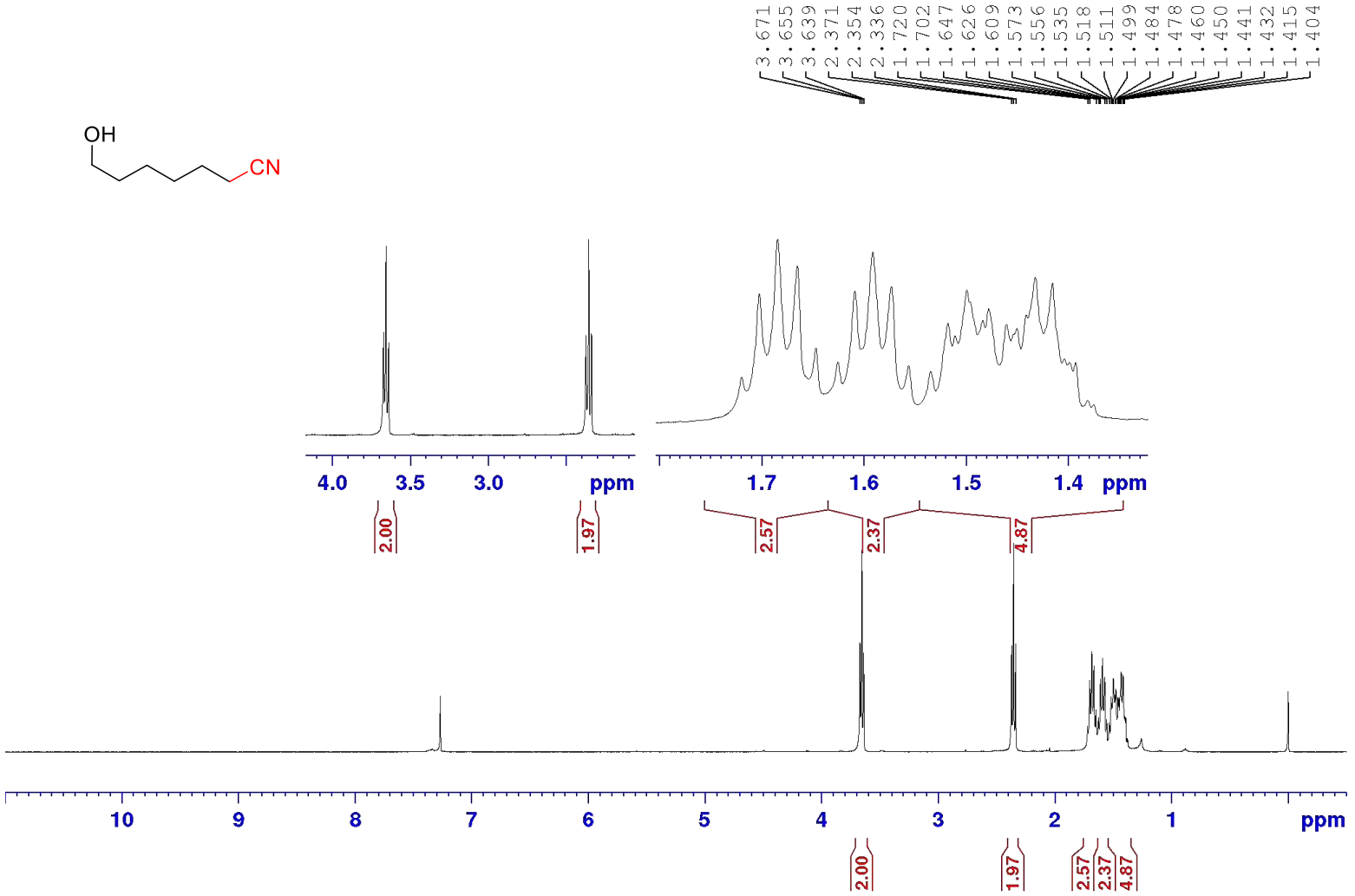
^{1}H NMR Spectrum of **3la** (400 MHz, $CDCl_3$)



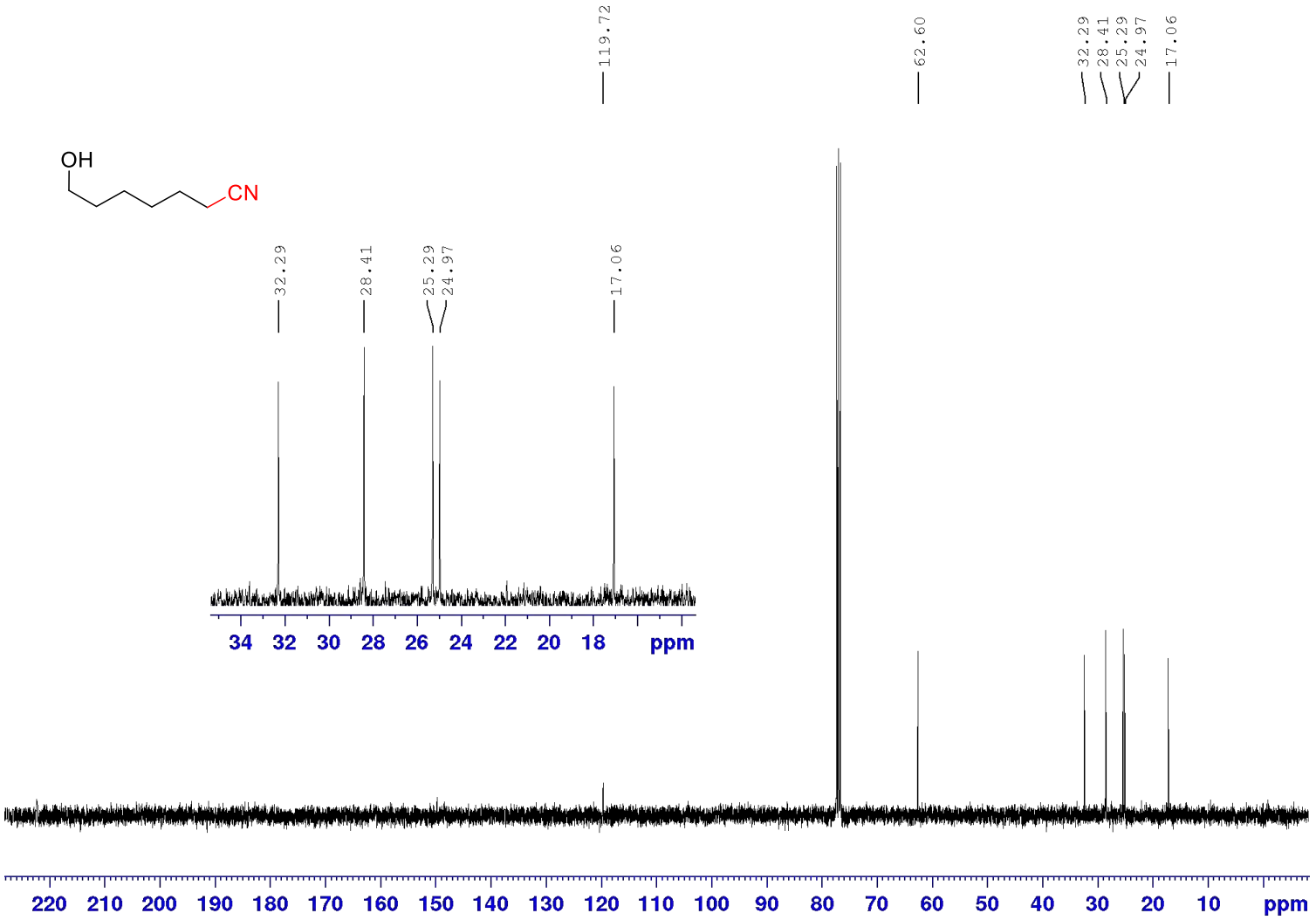
^{13}C NMR Spectrum of **3la** (100 MHz, $CDCl_3$)



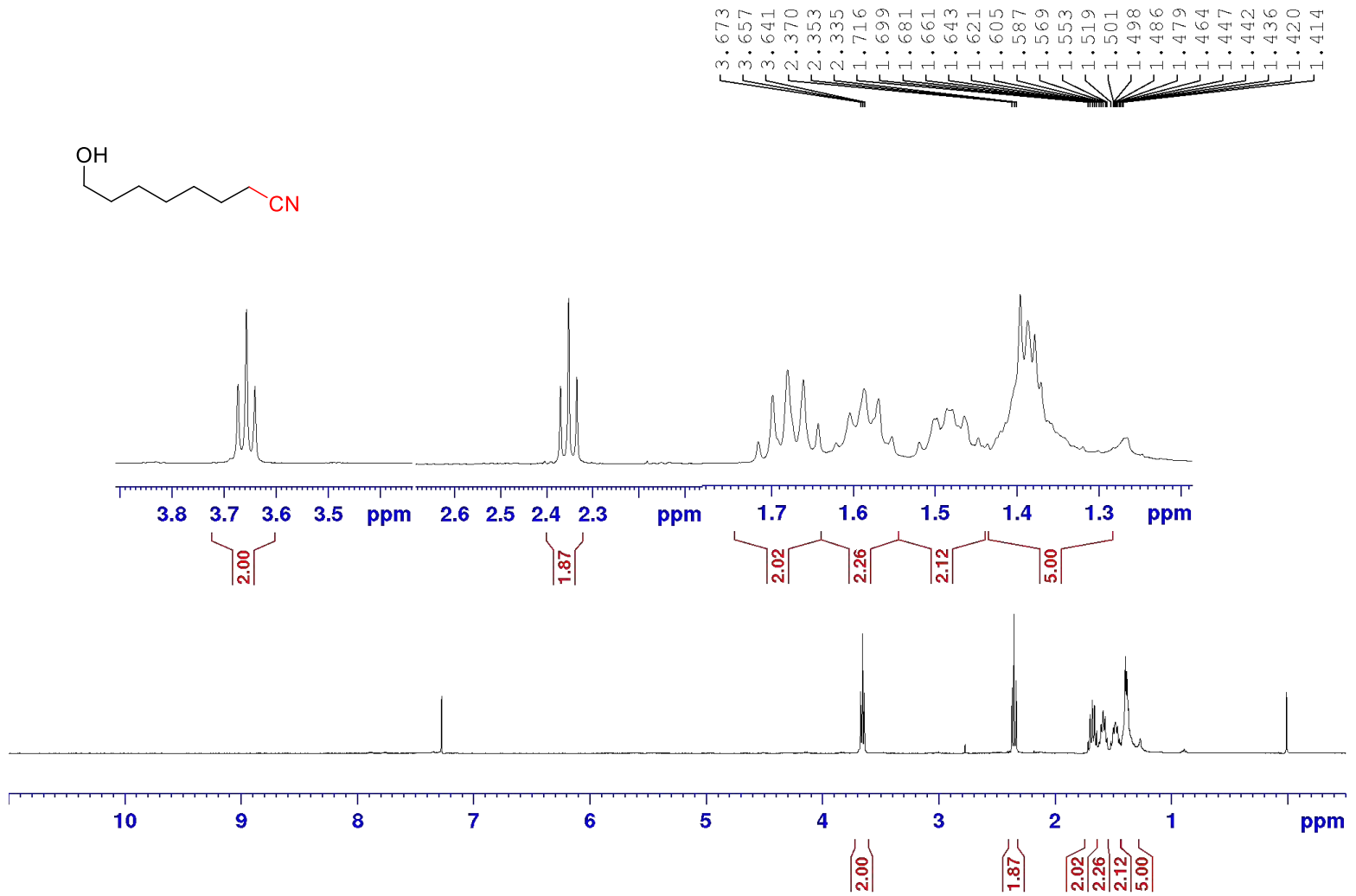
^{1}H NMR Spectrum of **3ma** (400 MHz, $CDCl_3$)



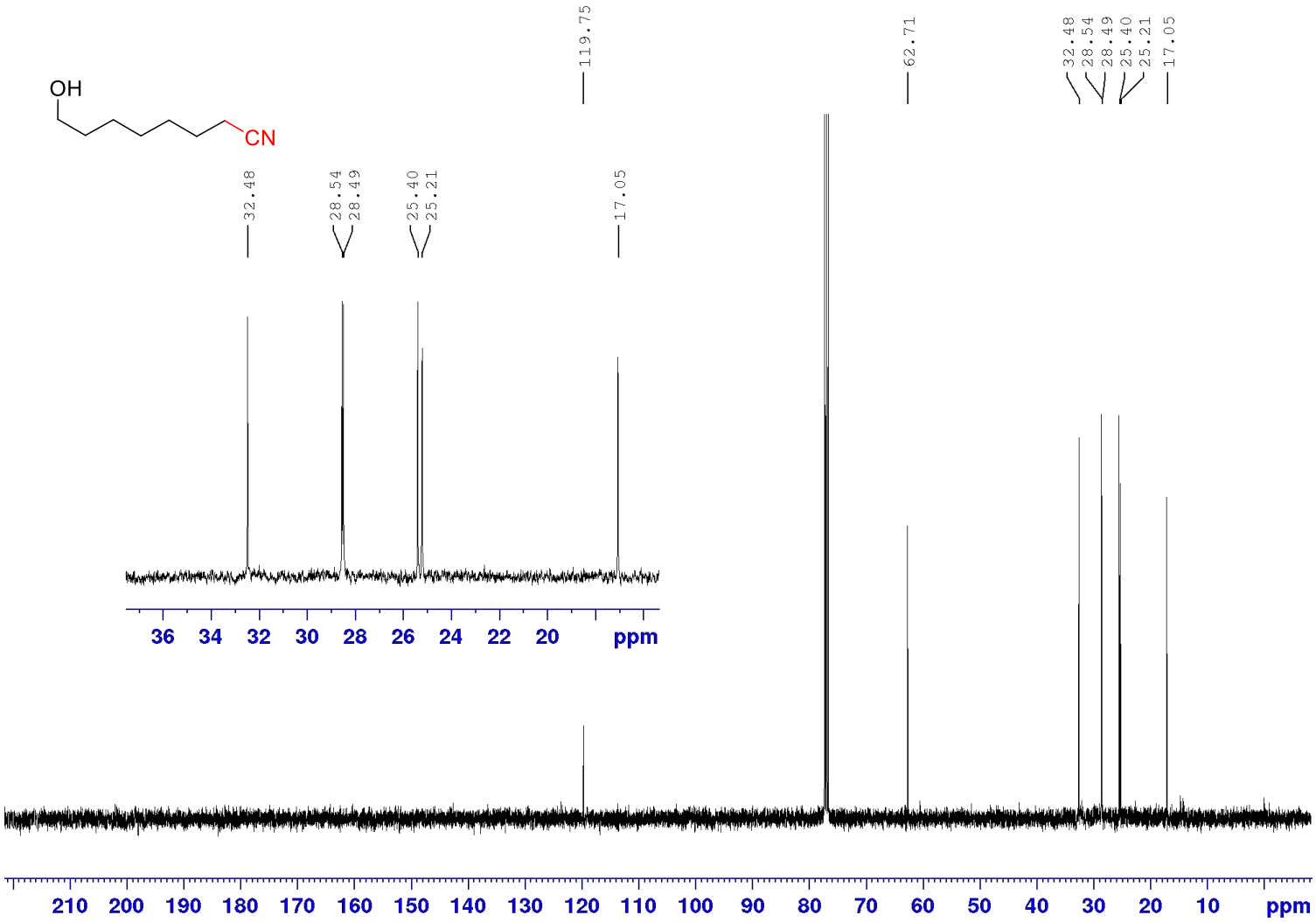
^{13}C NMR Spectrum of **3ma** (100 MHz, $CDCl_3$)



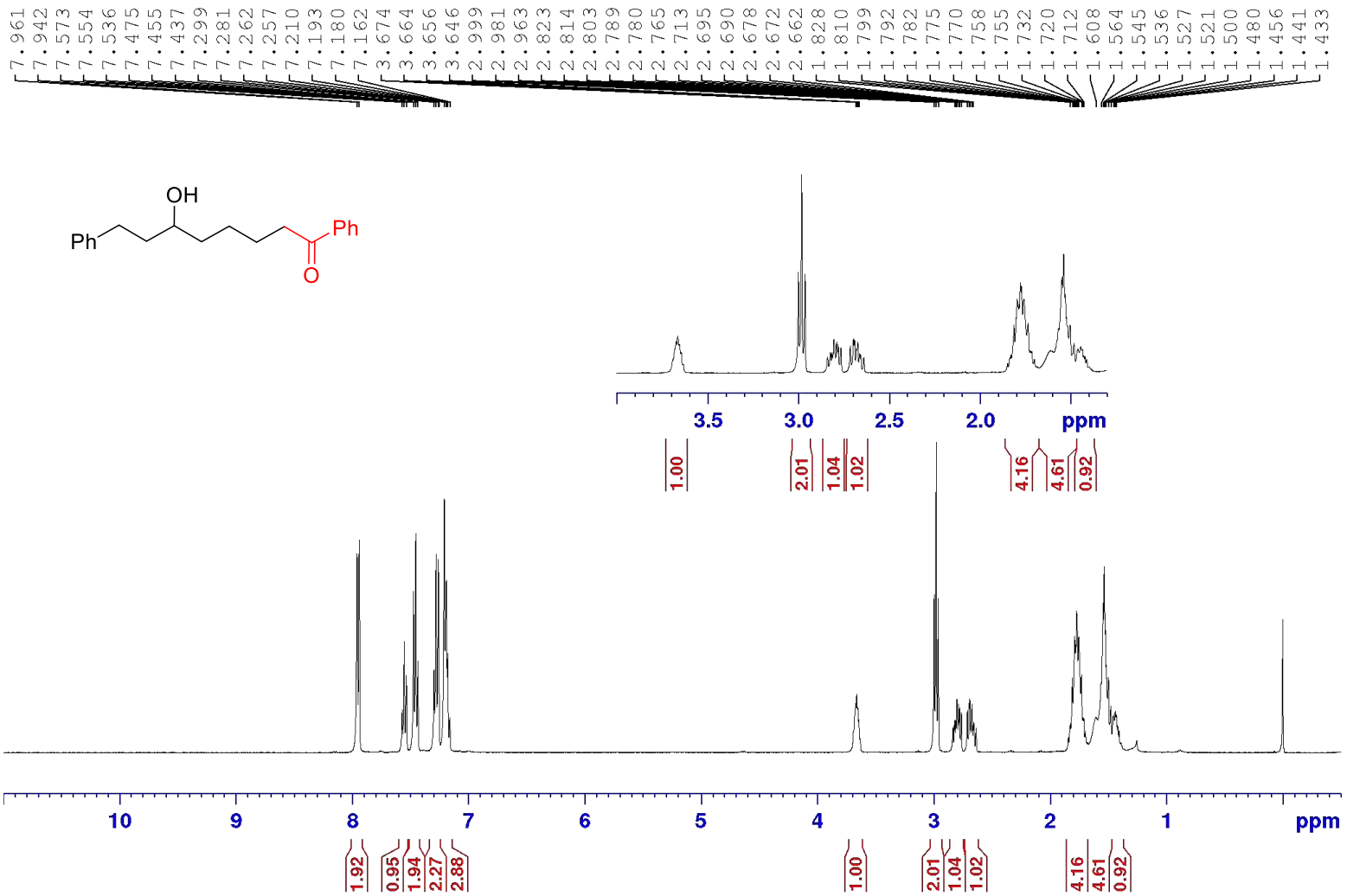
^{1}H NMR Spectrum of **3na** (400 MHz, $CDCl_3$)



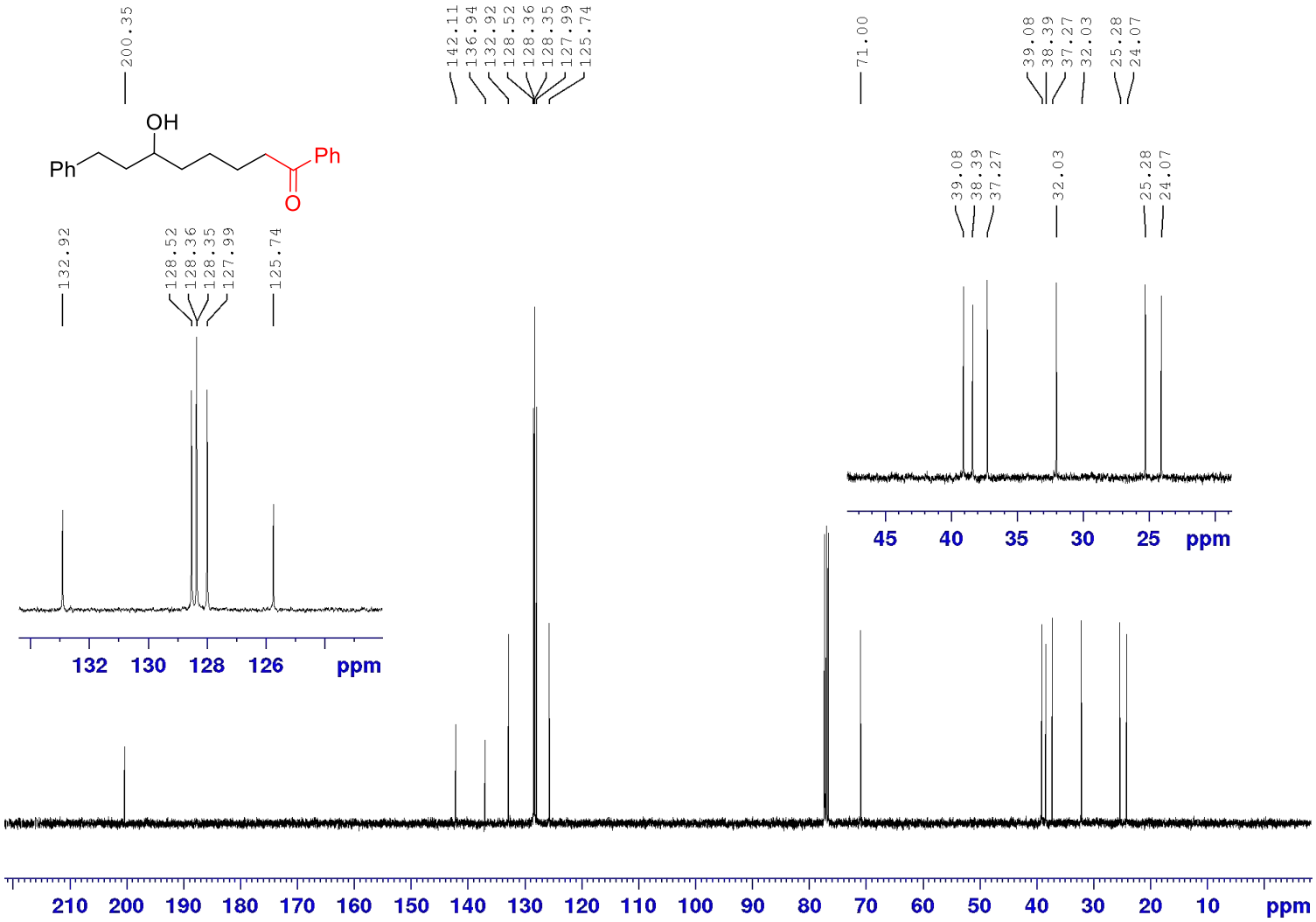
^{13}C NMR Spectrum of **3na** (100 MHz, $CDCl_3$)



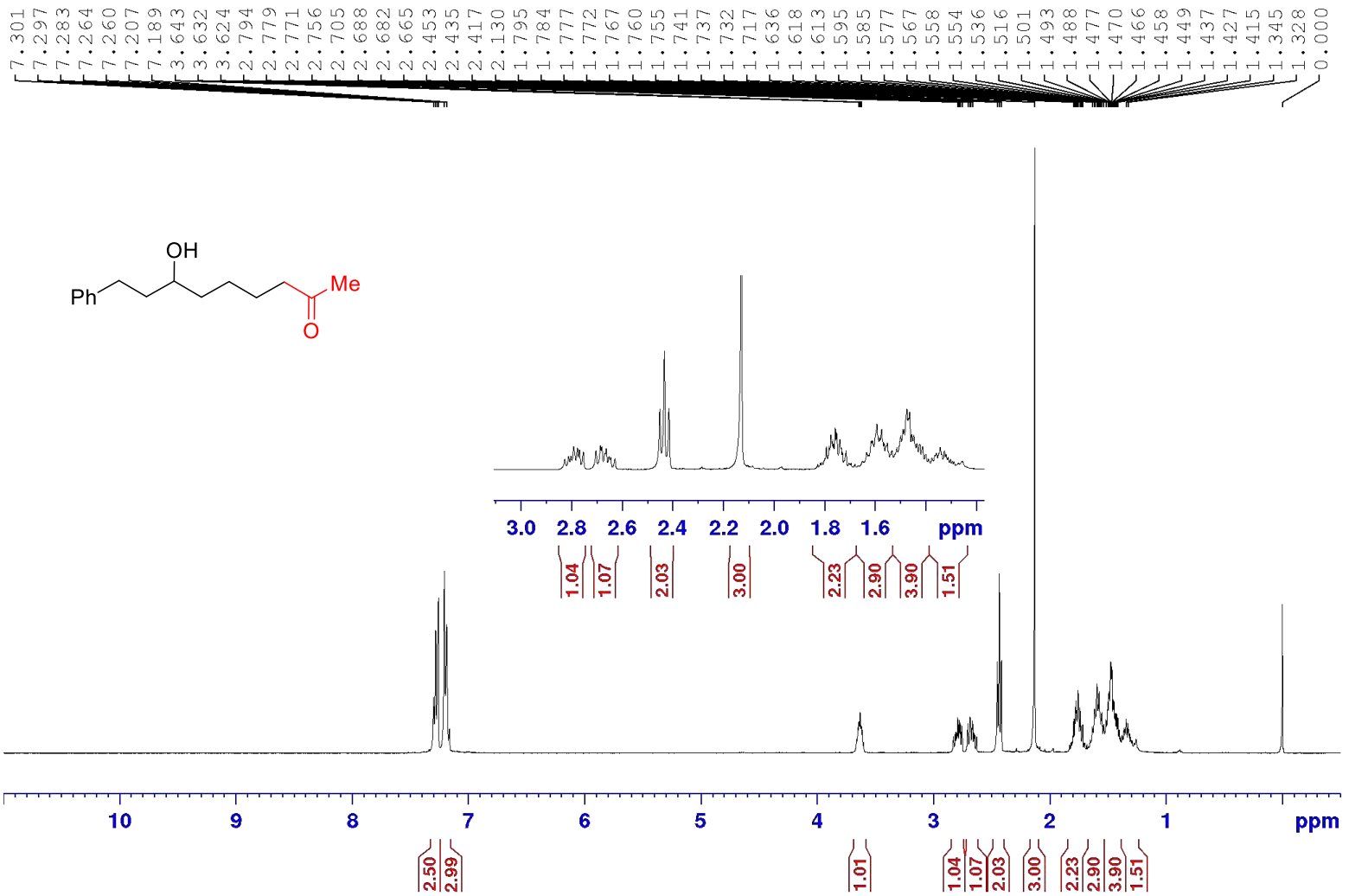
^{1}H NMR Spectrum of **3ab** (400 MHz, $CDCl_3$)



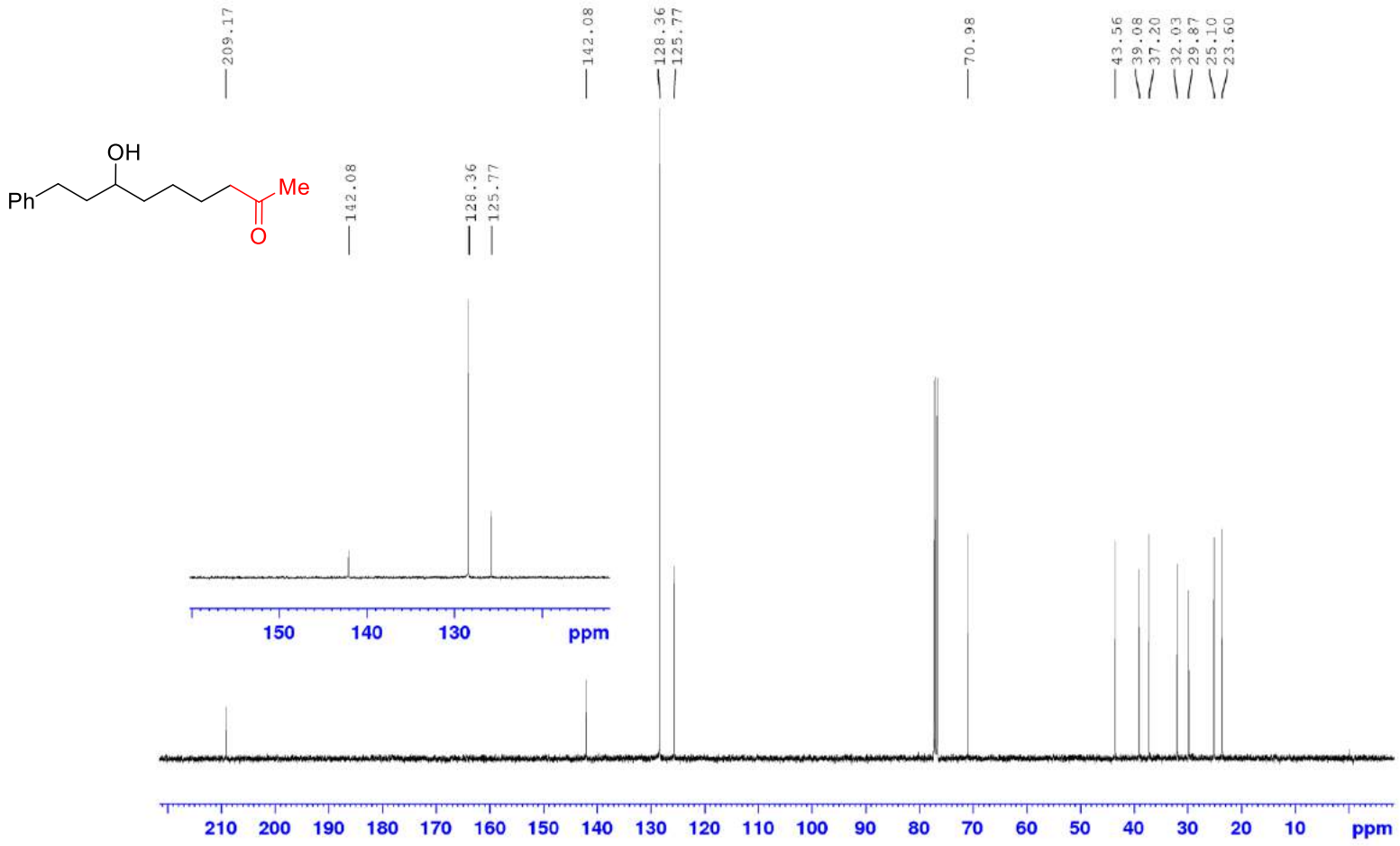
^{13}C NMR Spectrum of **3ab** (100 MHz, $CDCl_3$)



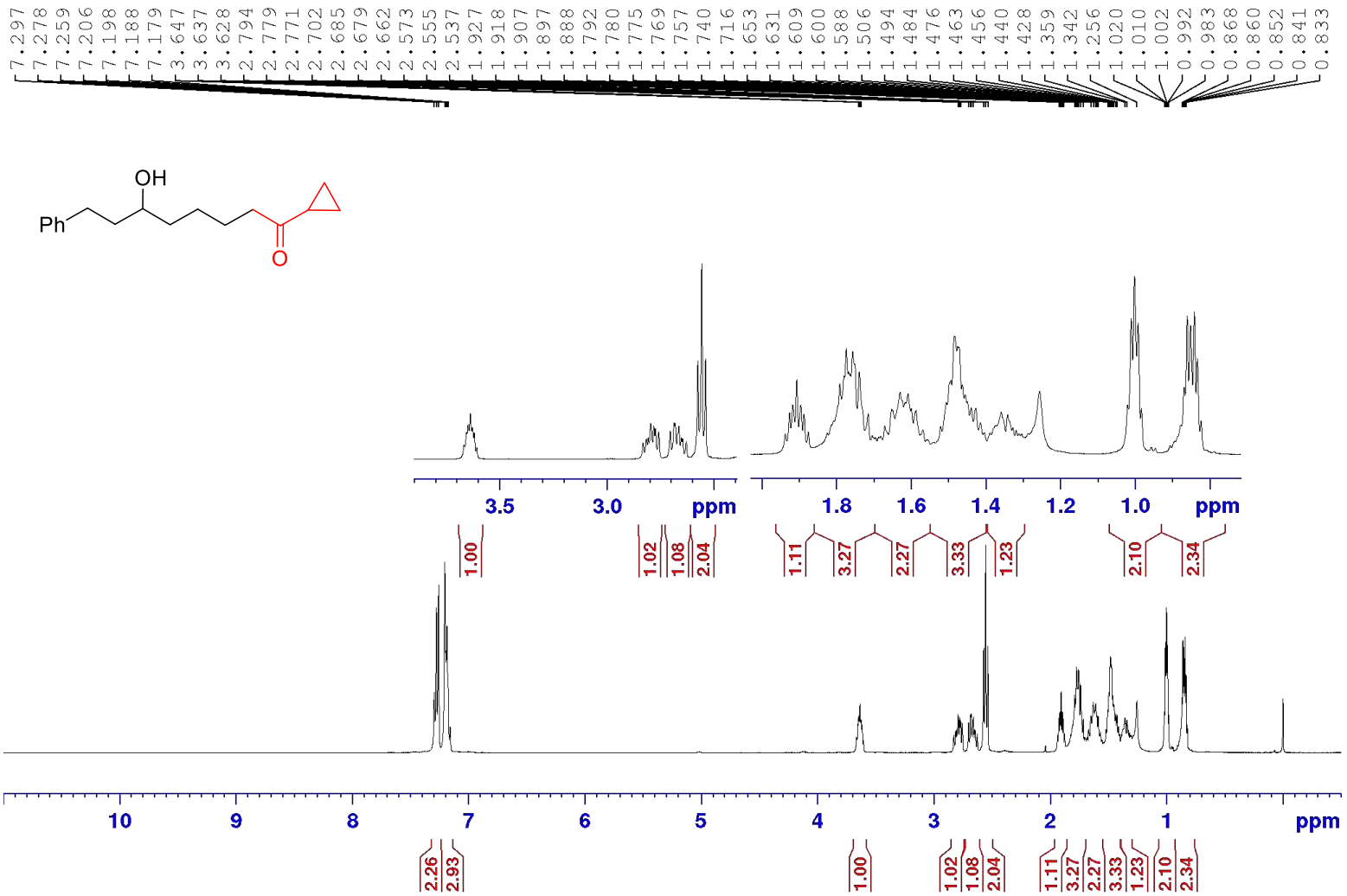
^{1}H NMR Spectrum of **3ac** (400 MHz, $CDCl_3$)



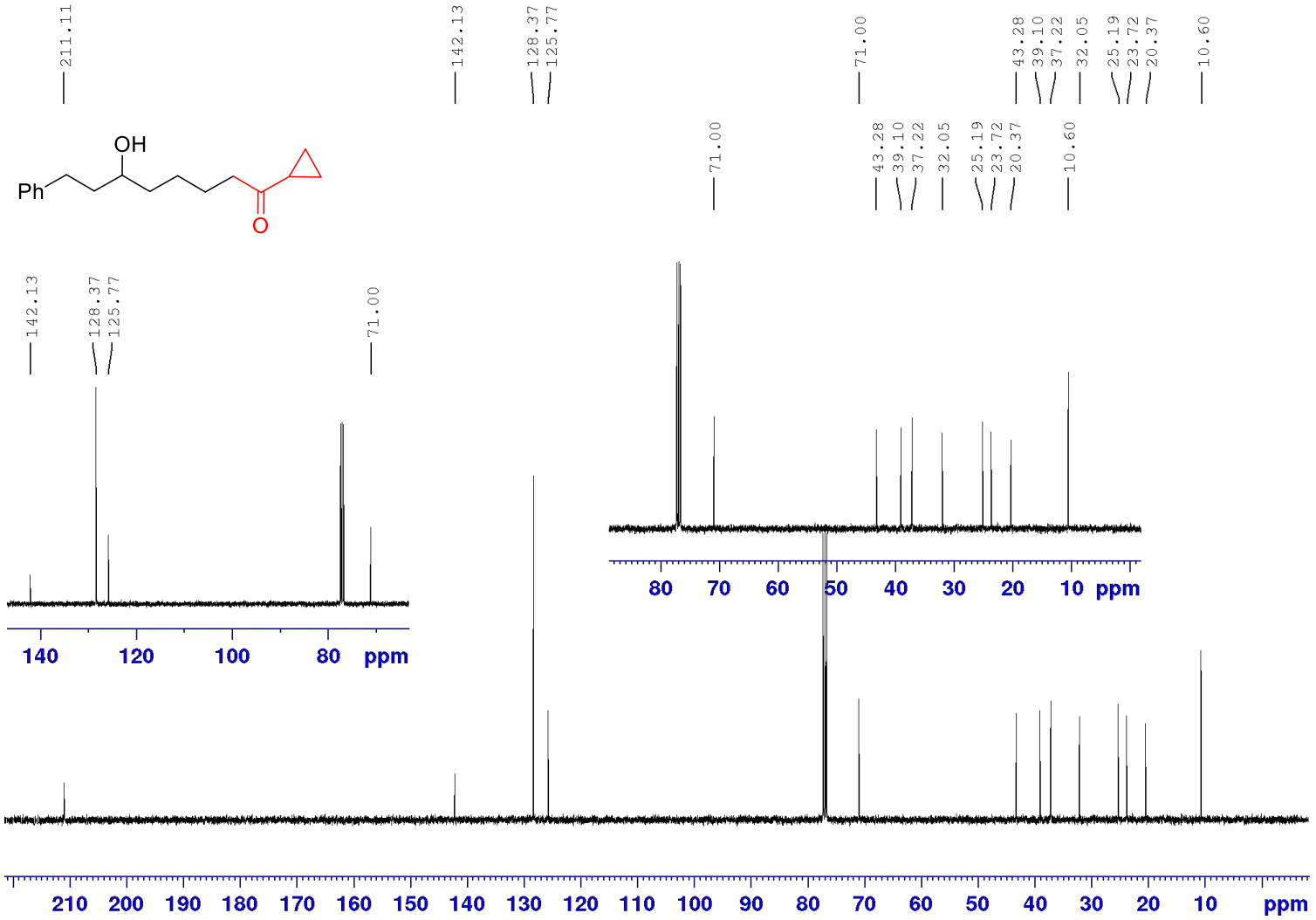
^{13}C NMR Spectrum of **3ac** (100 MHz, $CDCl_3$)



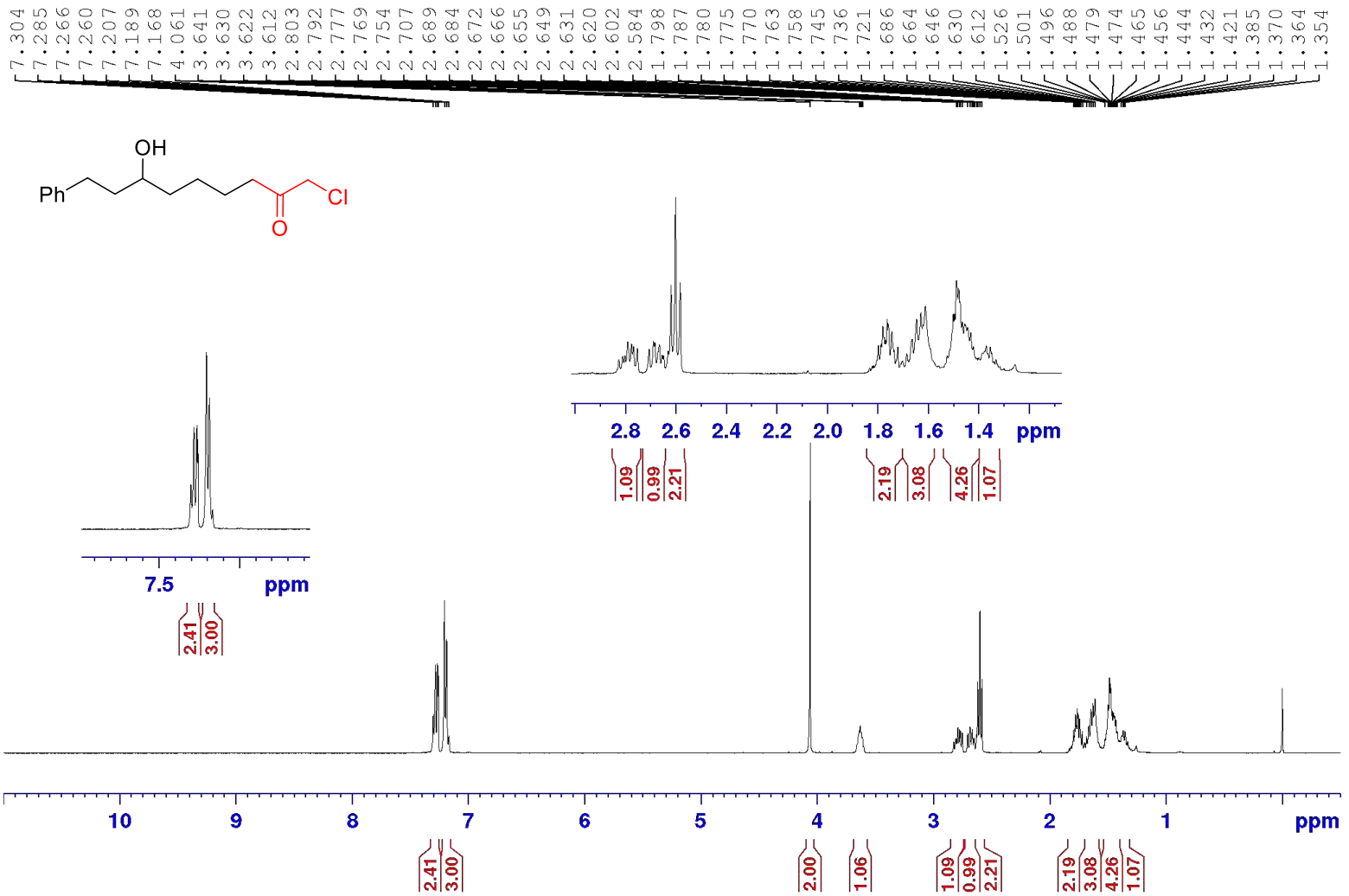
^{1}H NMR Spectrum of **3ad** (400 MHz, $CDCl_3$)



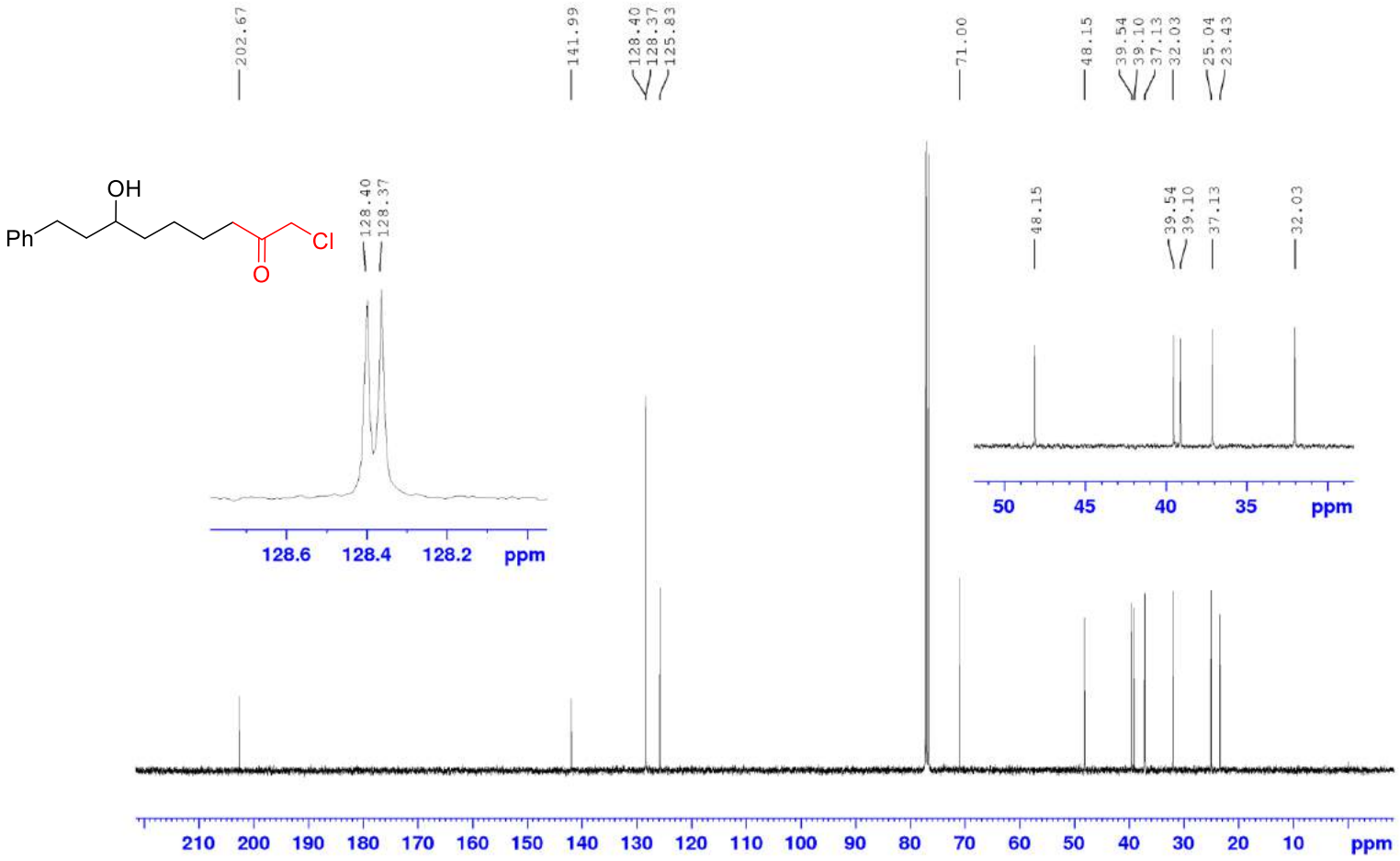
^{13}C NMR Spectrum of **3ad** (100 MHz, $CDCl_3$)



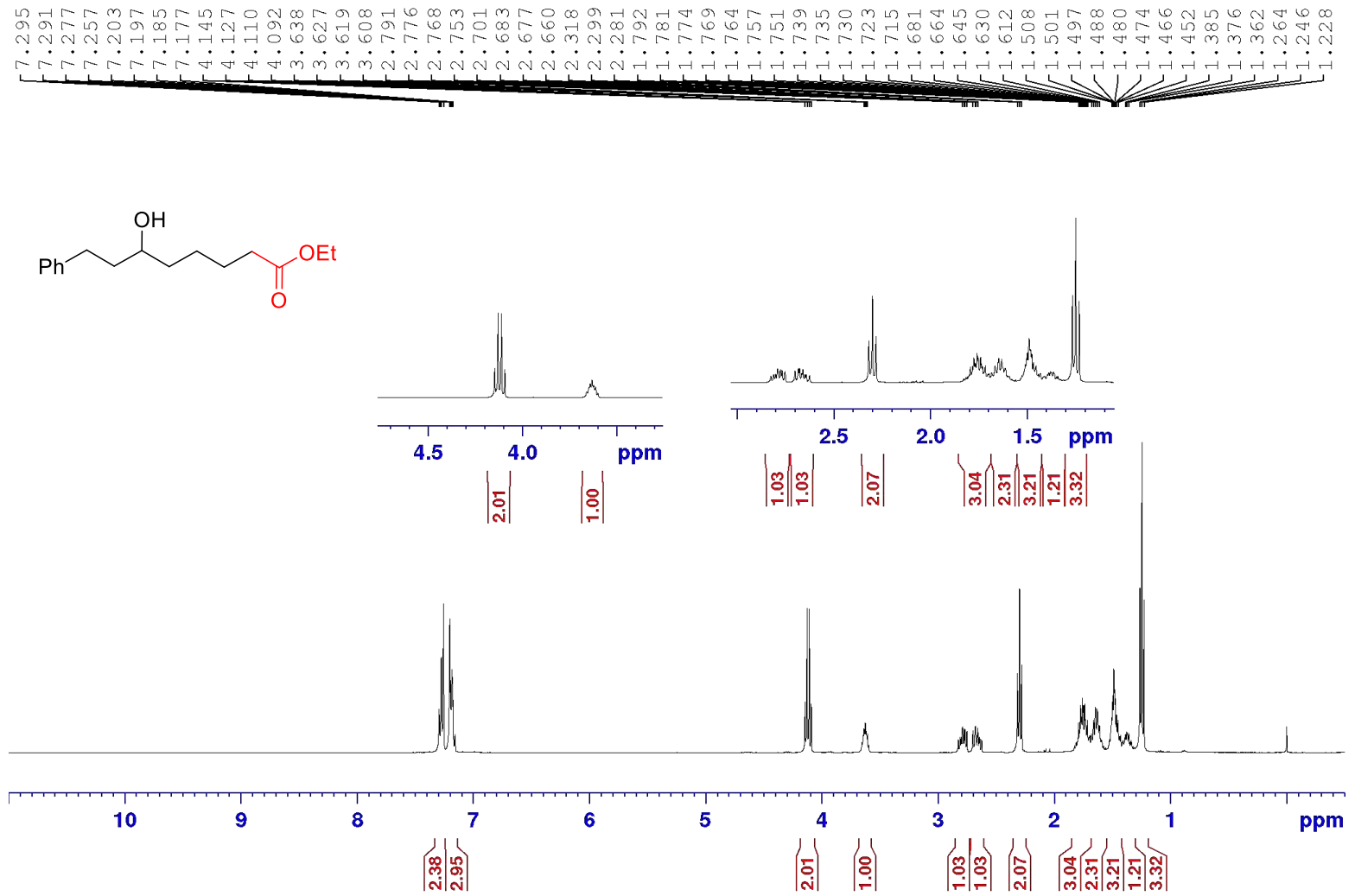
^{1}H NMR Spectrum of **3ae** (400 MHz, $CDCl_3$)



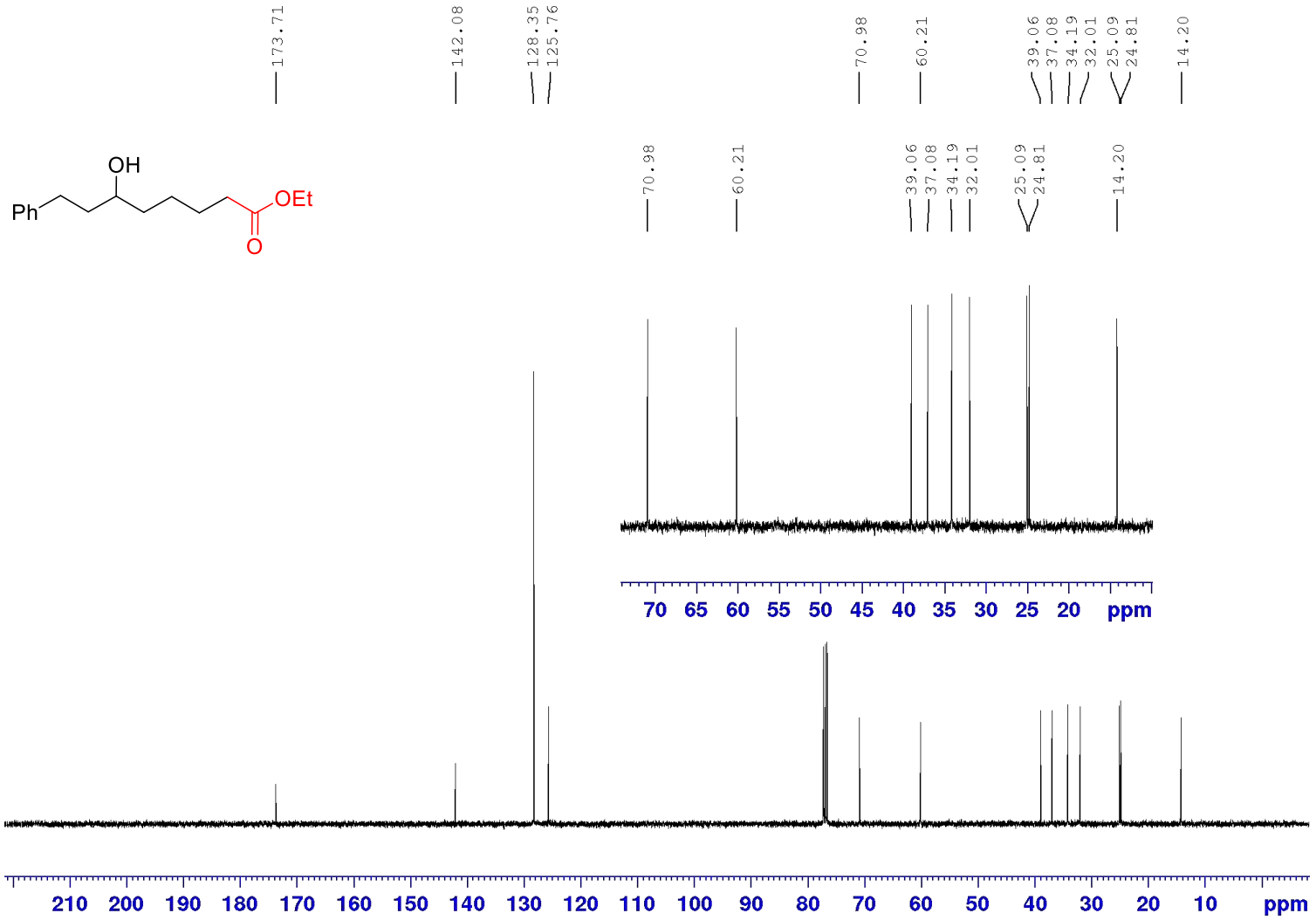
^{13}C NMR Spectrum of **3ae** (100 MHz, $CDCl_3$)



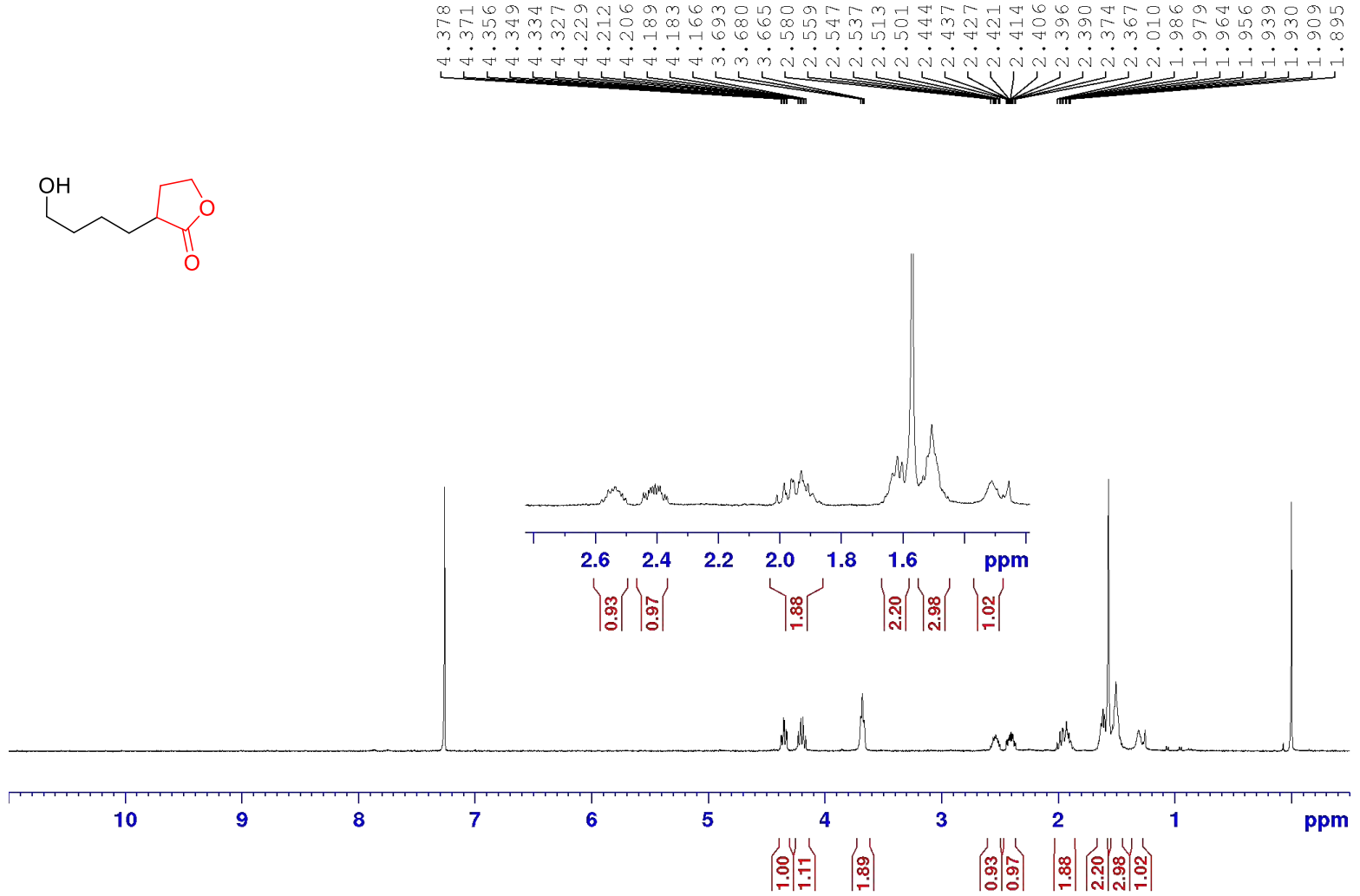
^{1}H NMR Spectrum of **3af** (400 MHz, $CDCl_3$)



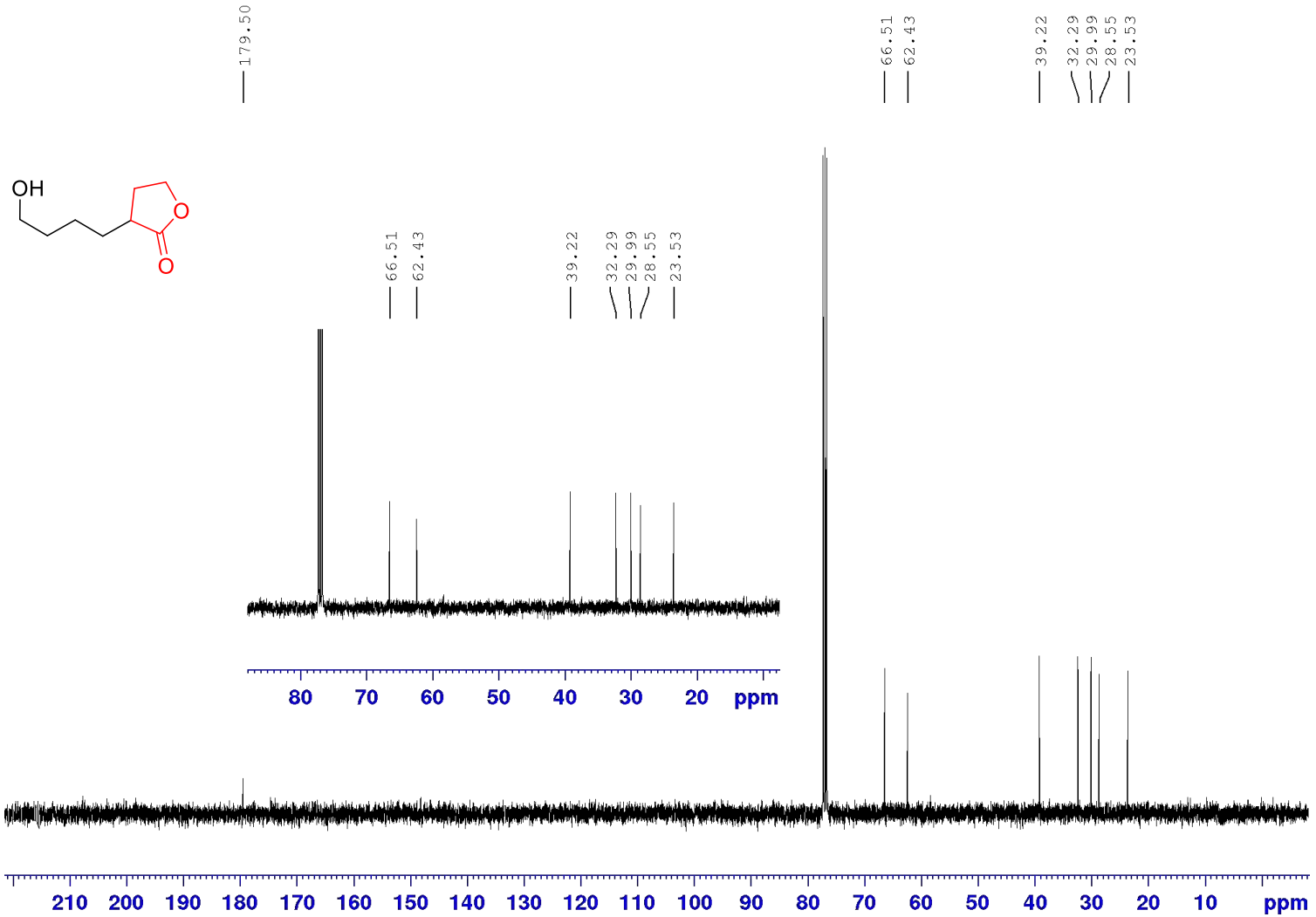
^{13}C NMR Spectrum of **3af** (100 MHz, $CDCl_3$)



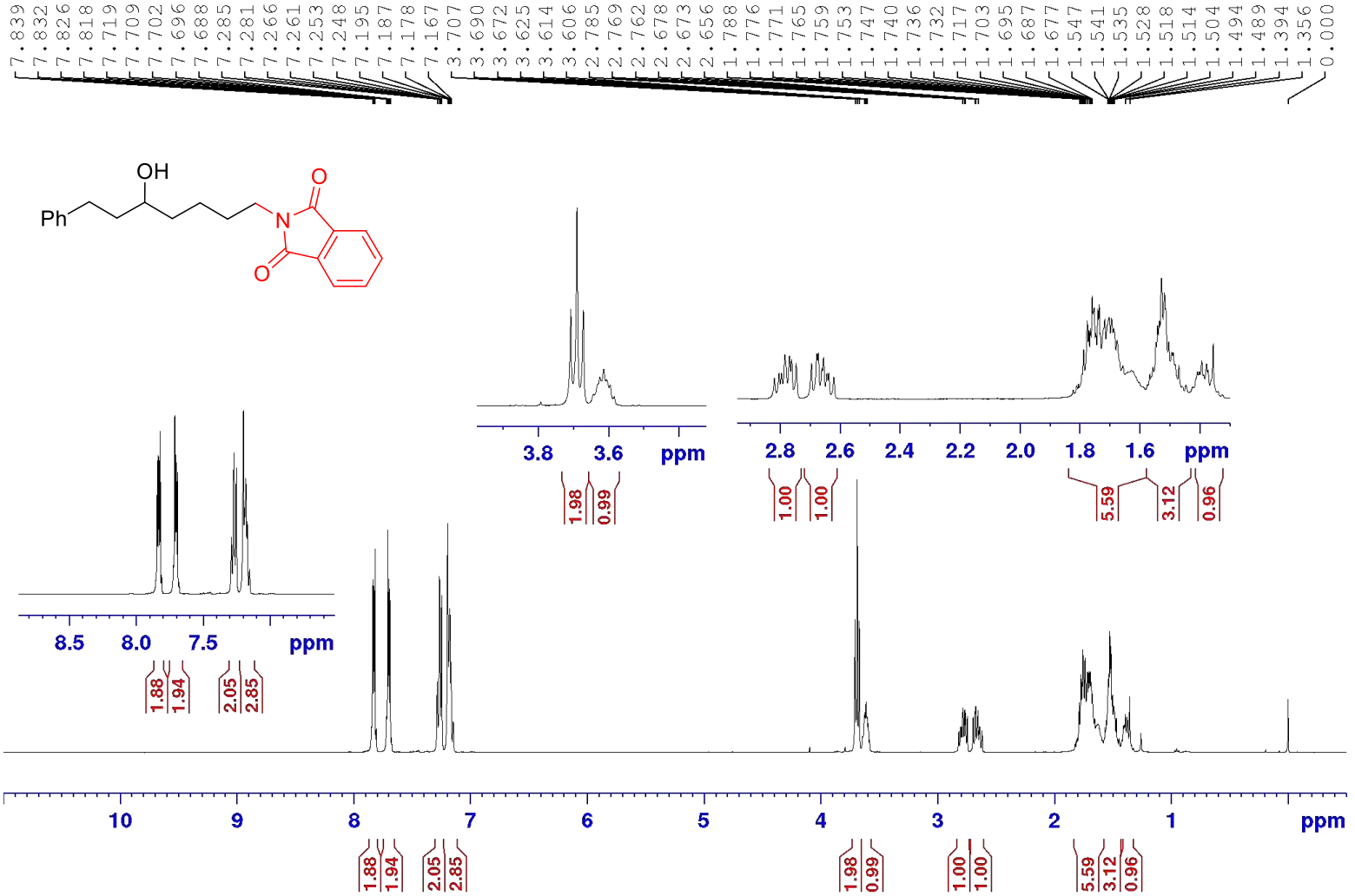
^{1}H NMR Spectrum of **3ig** (400 MHz, $CDCl_3$)



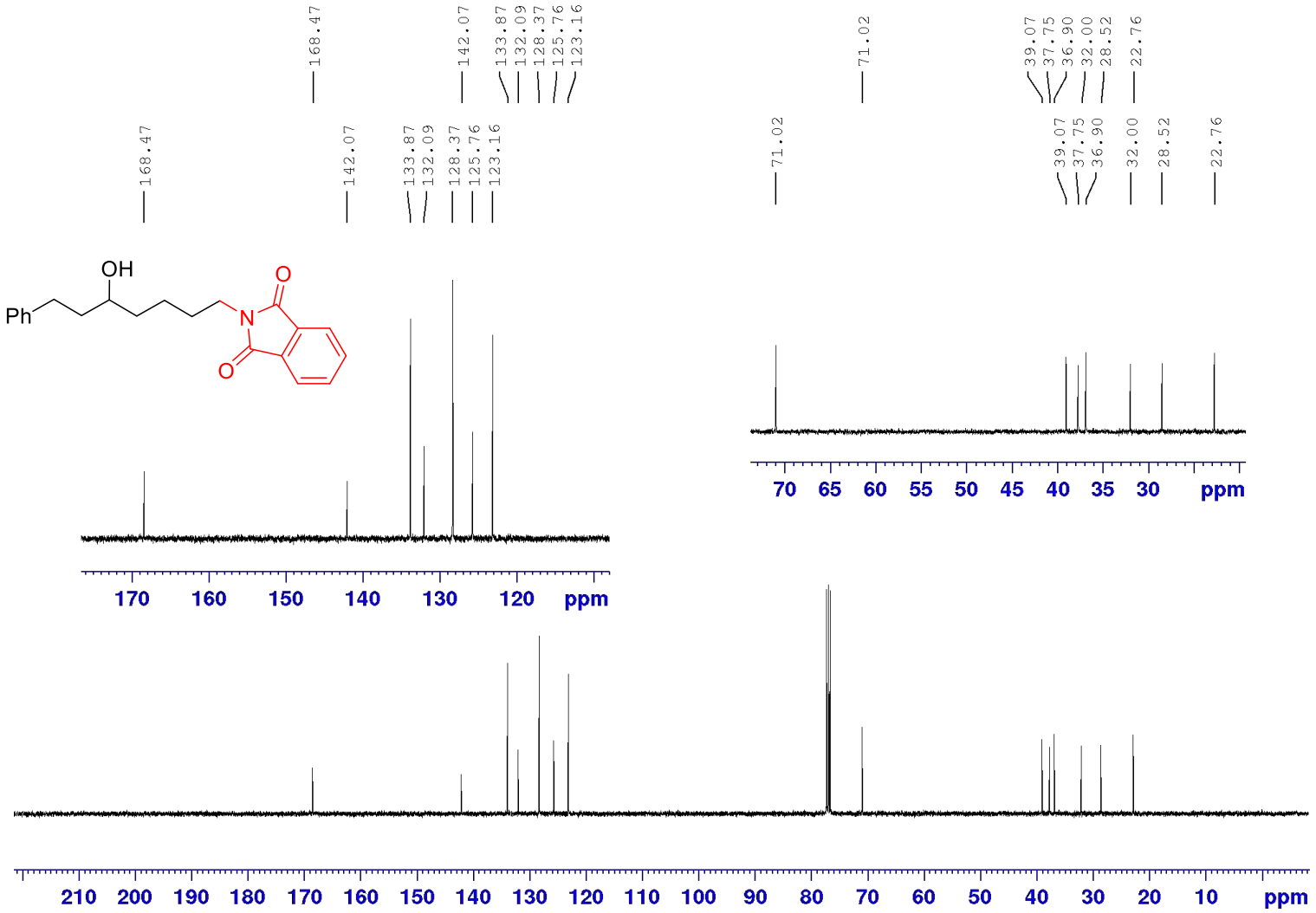
^{13}C NMR Spectrum of **3ig** (100 MHz, $CDCl_3$)



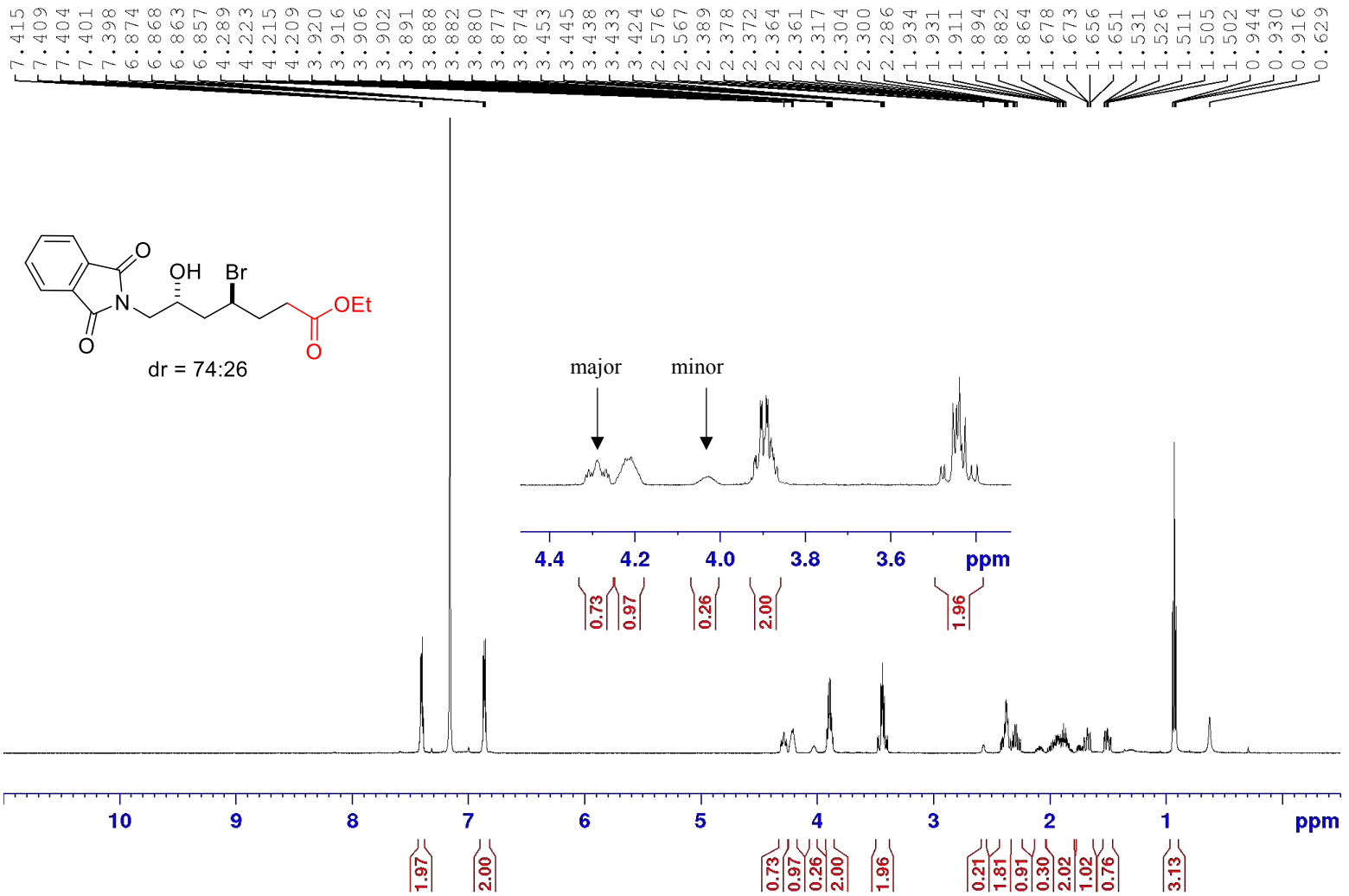
^{1}H NMR Spectrum of **3ah** (400 MHz, $CDCl_3$)



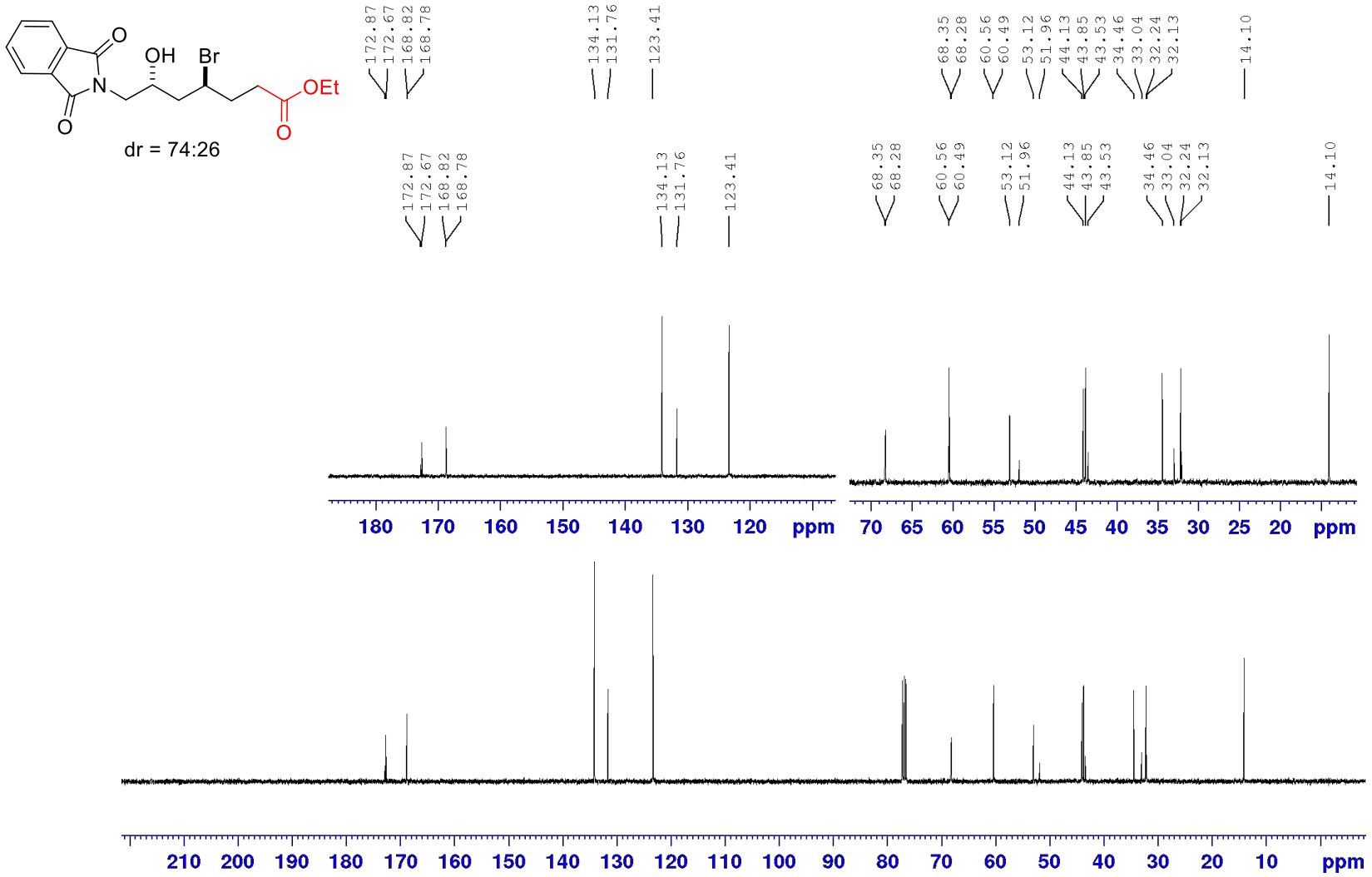
^{13}C NMR Spectrum of **3ah** (100 MHz, $CDCl_3$)



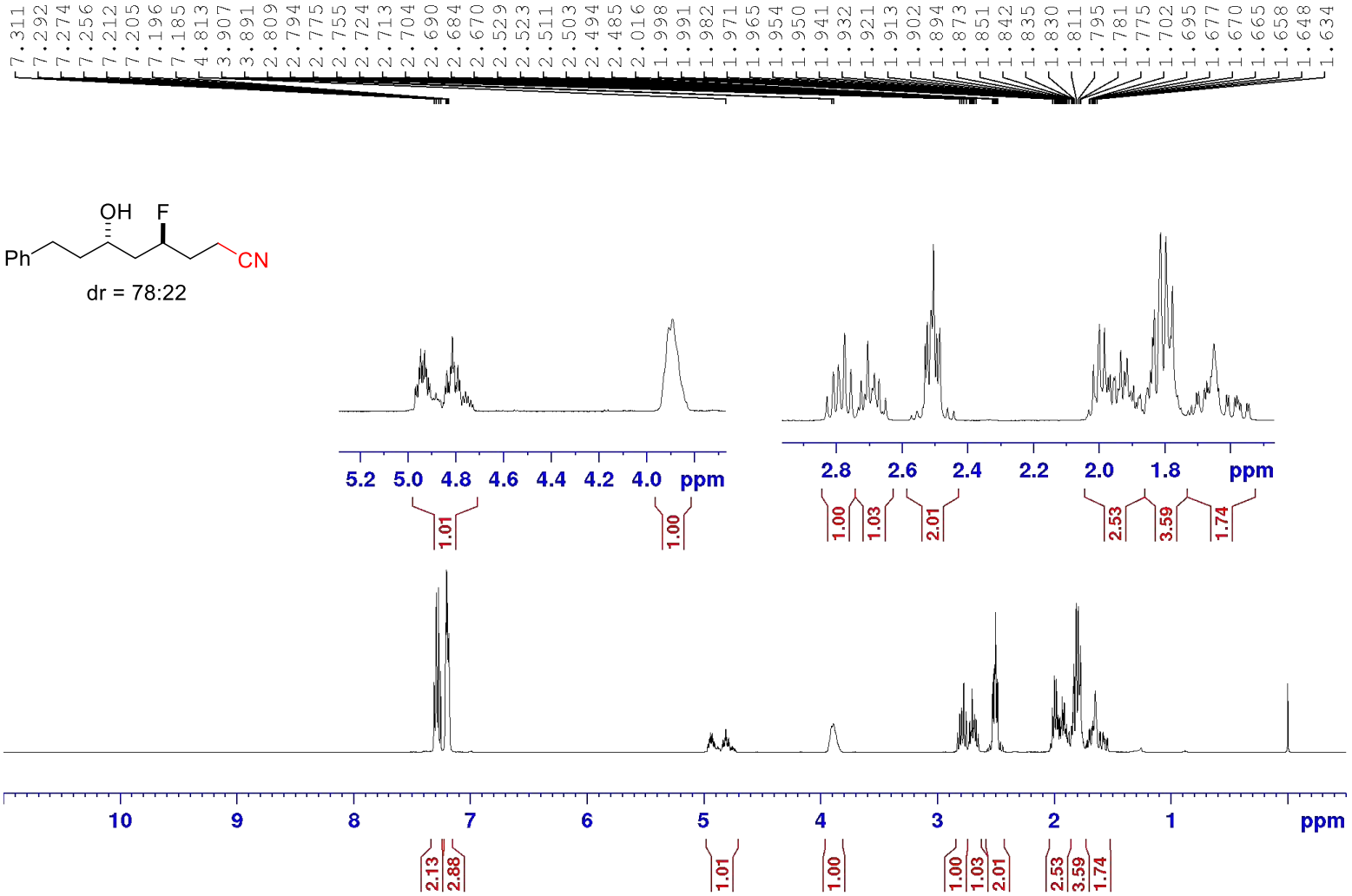
^{1}H NMR Spectrum of **3of** (500 MHz, C_6D_6)



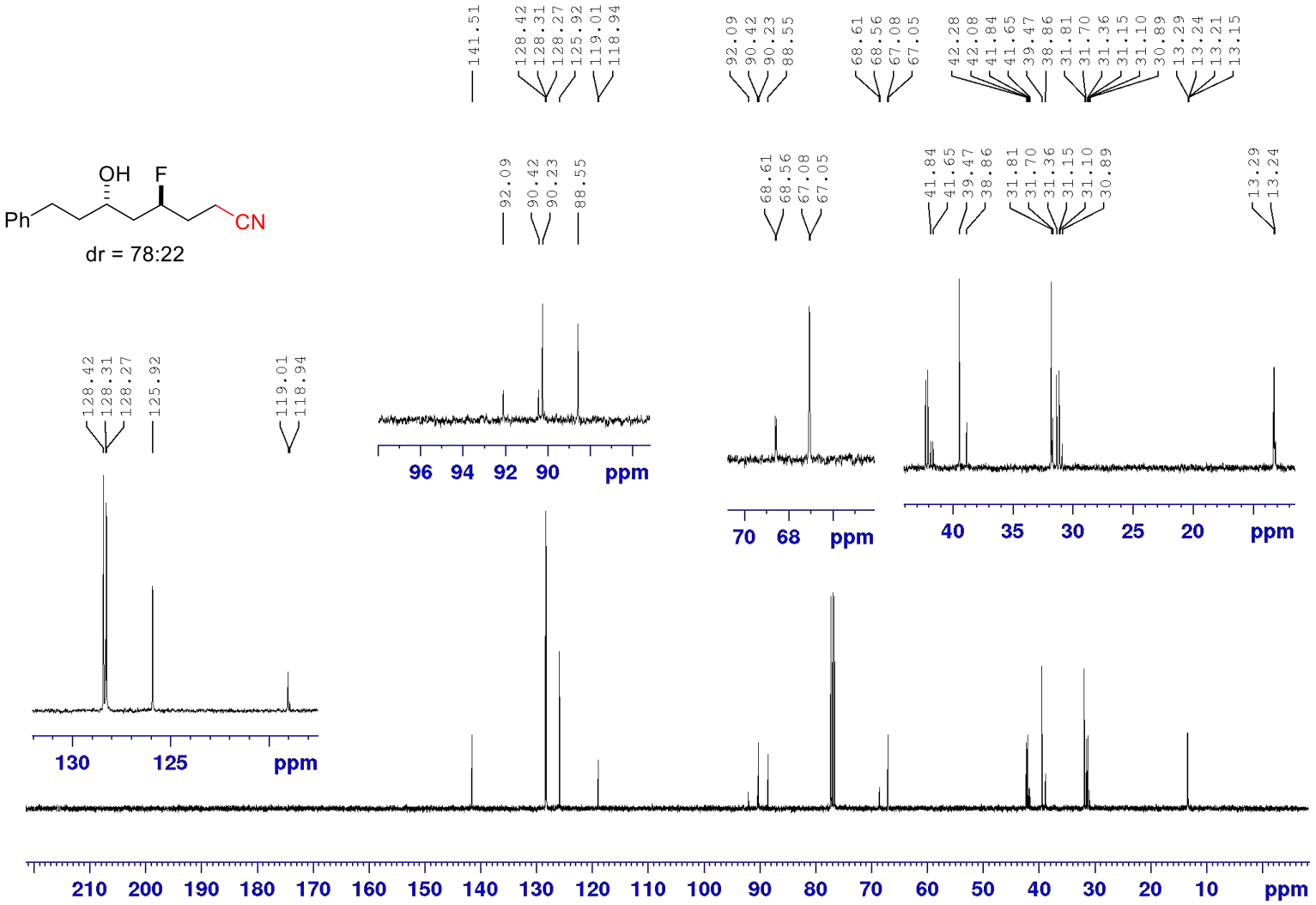
^{13}C NMR Spectrum of **3of** (100 MHz, $CDCl_3$)



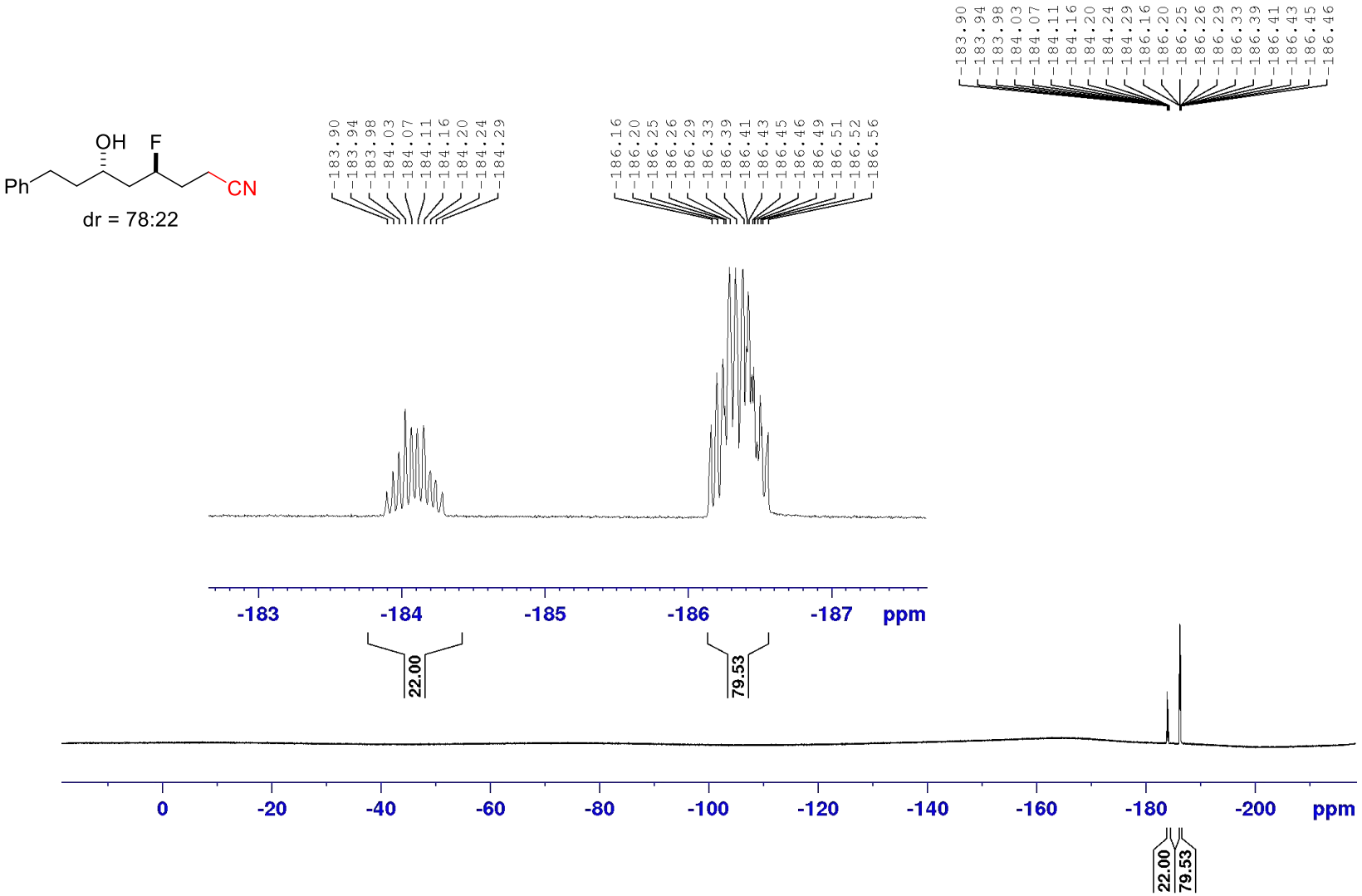
^{1}H NMR Spectrum of **3pa** (400 MHz, $CDCl_3$)



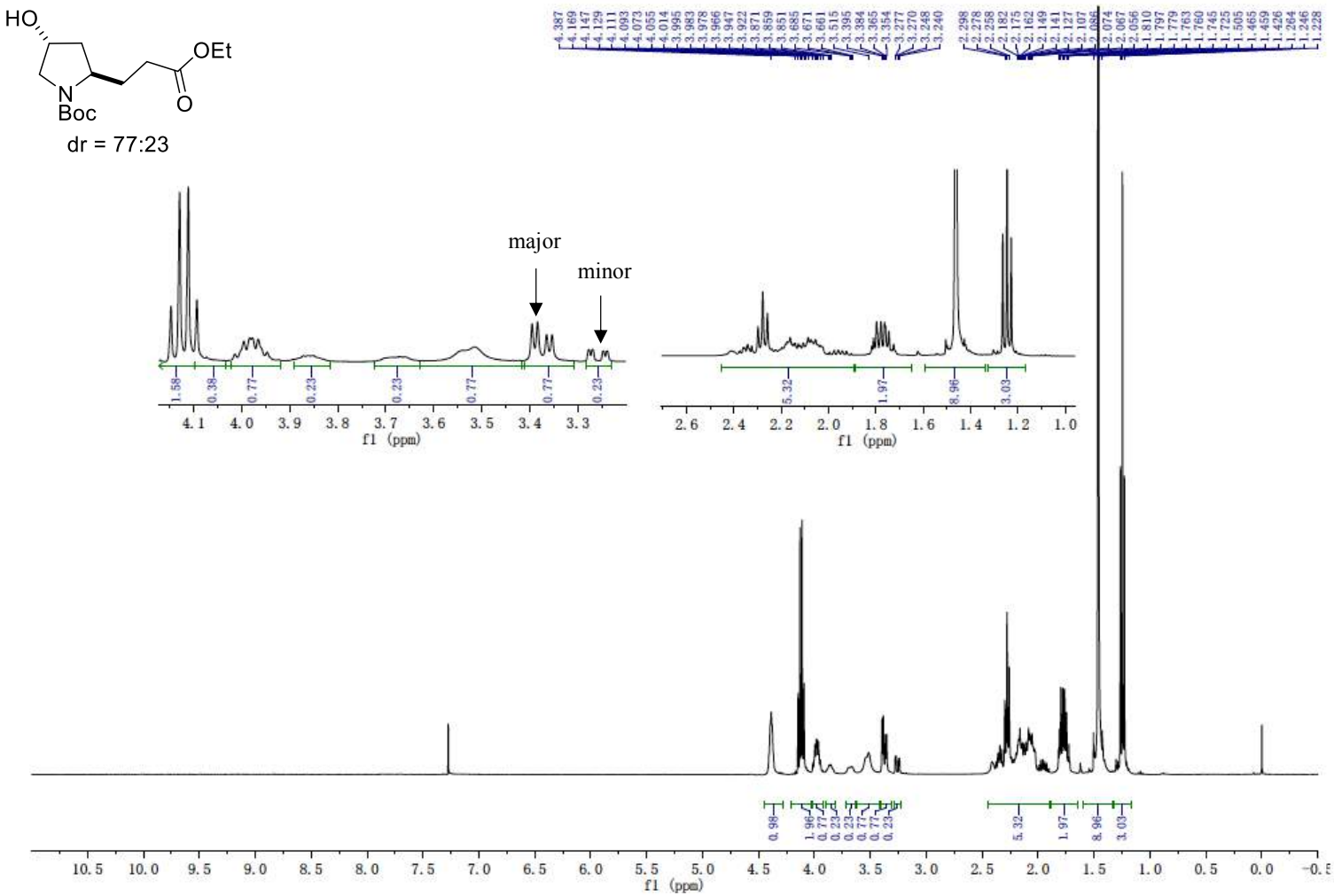
^{13}C NMR Spectrum of **3pa** (100 MHz, $CDCl_3$)



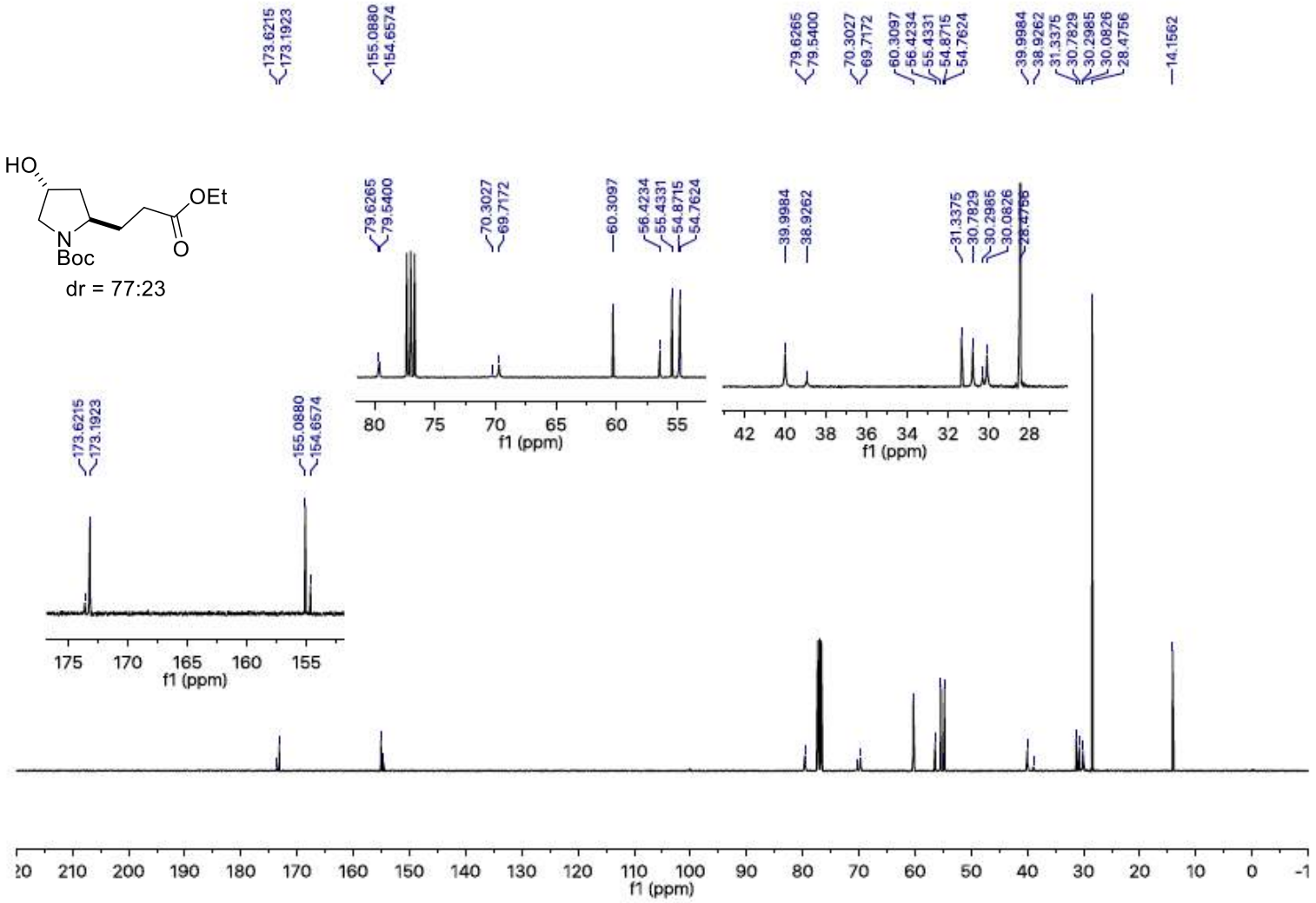
^{19}F NMR Spectrum of **3pa** (377 MHz, $CDCl_3$)



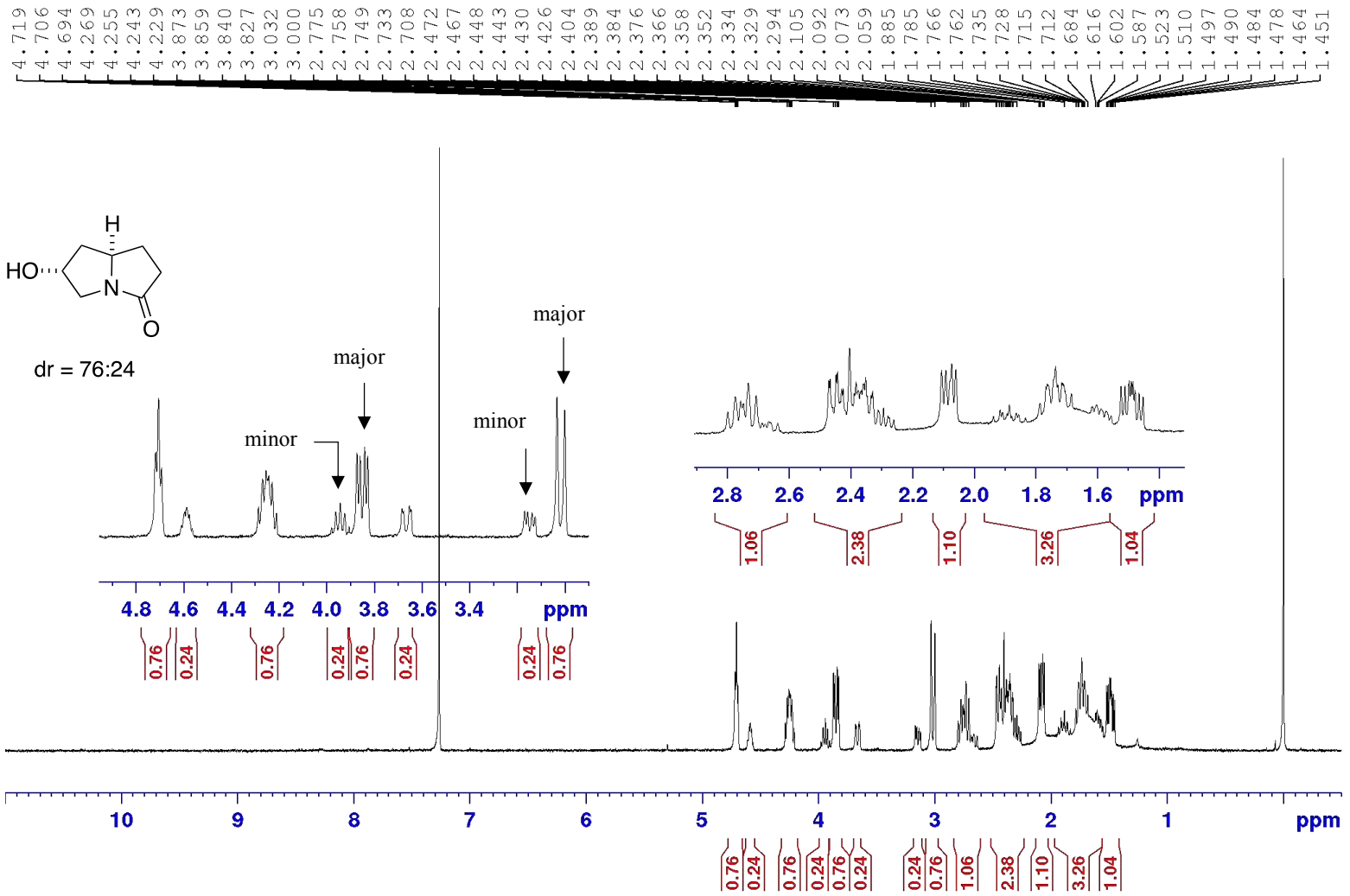
^{1}H NMR Spectrum of **4of** (400 MHz, $CDCl_3$ at 55 °C)



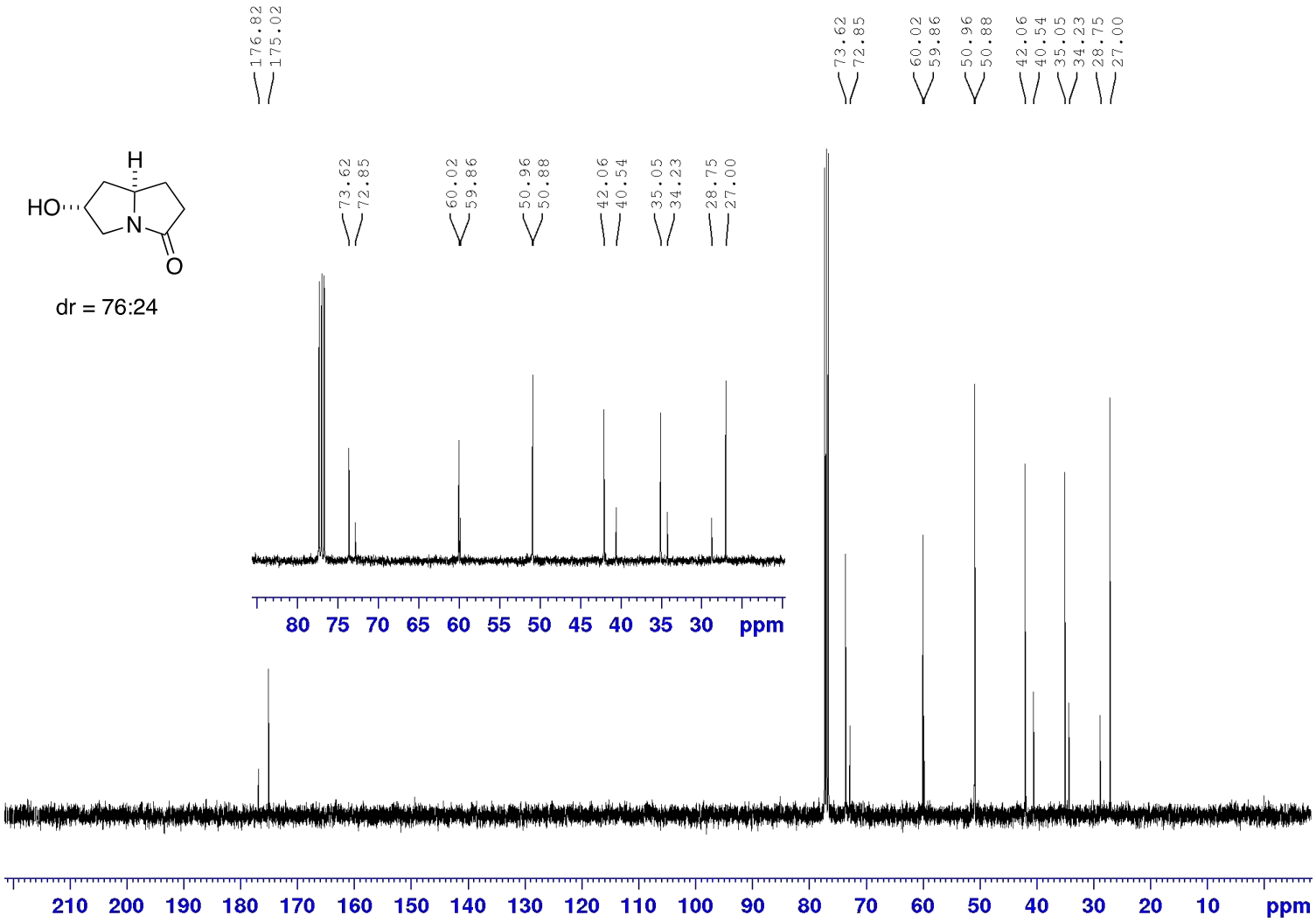
^{13}C NMR Spectrum of **4of** (100 MHz, $CDCl_3$ at 55 °C)



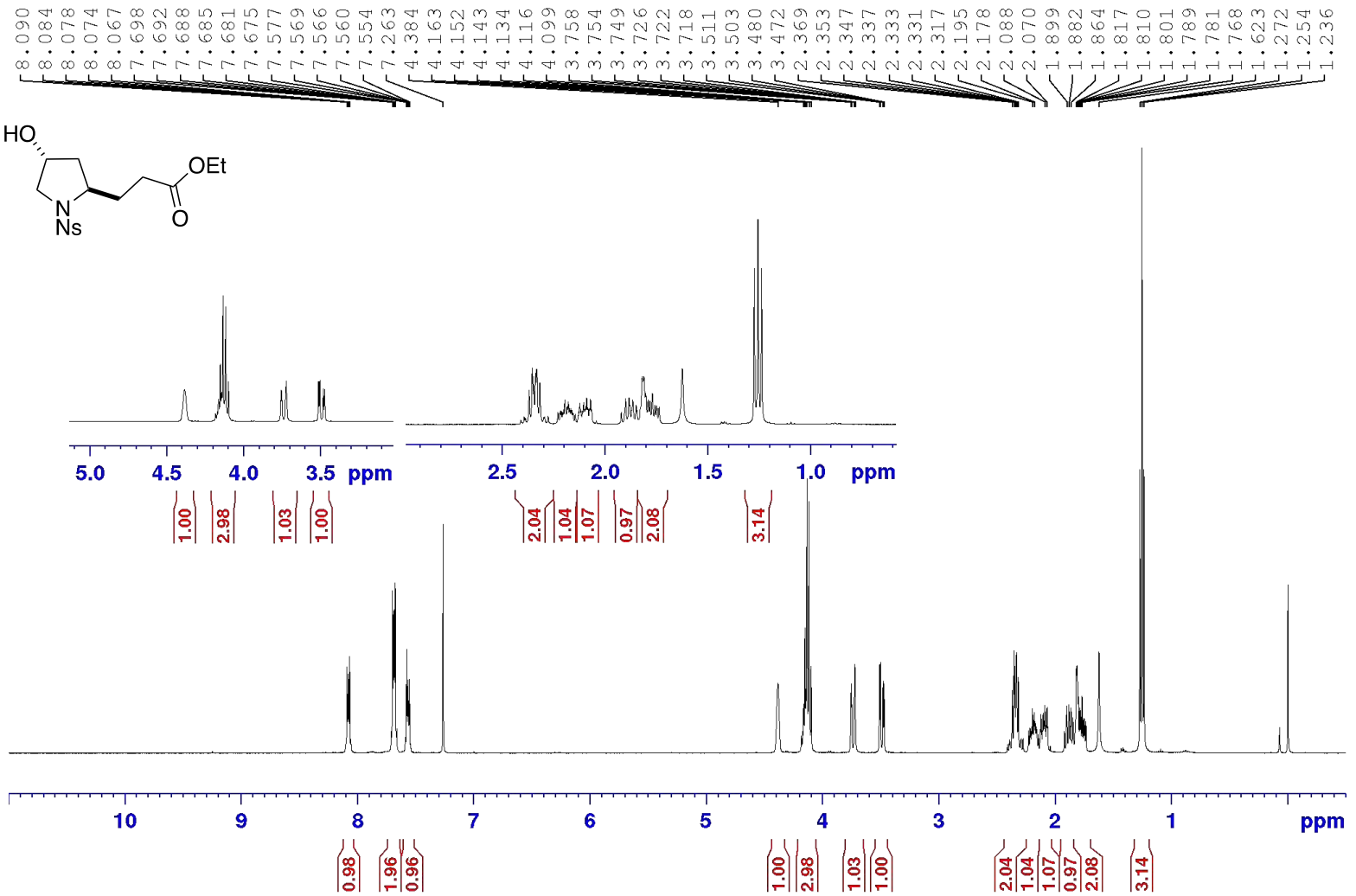
^{1}H NMR Spectrum of **5of** (400 MHz, $CDCl_3$)



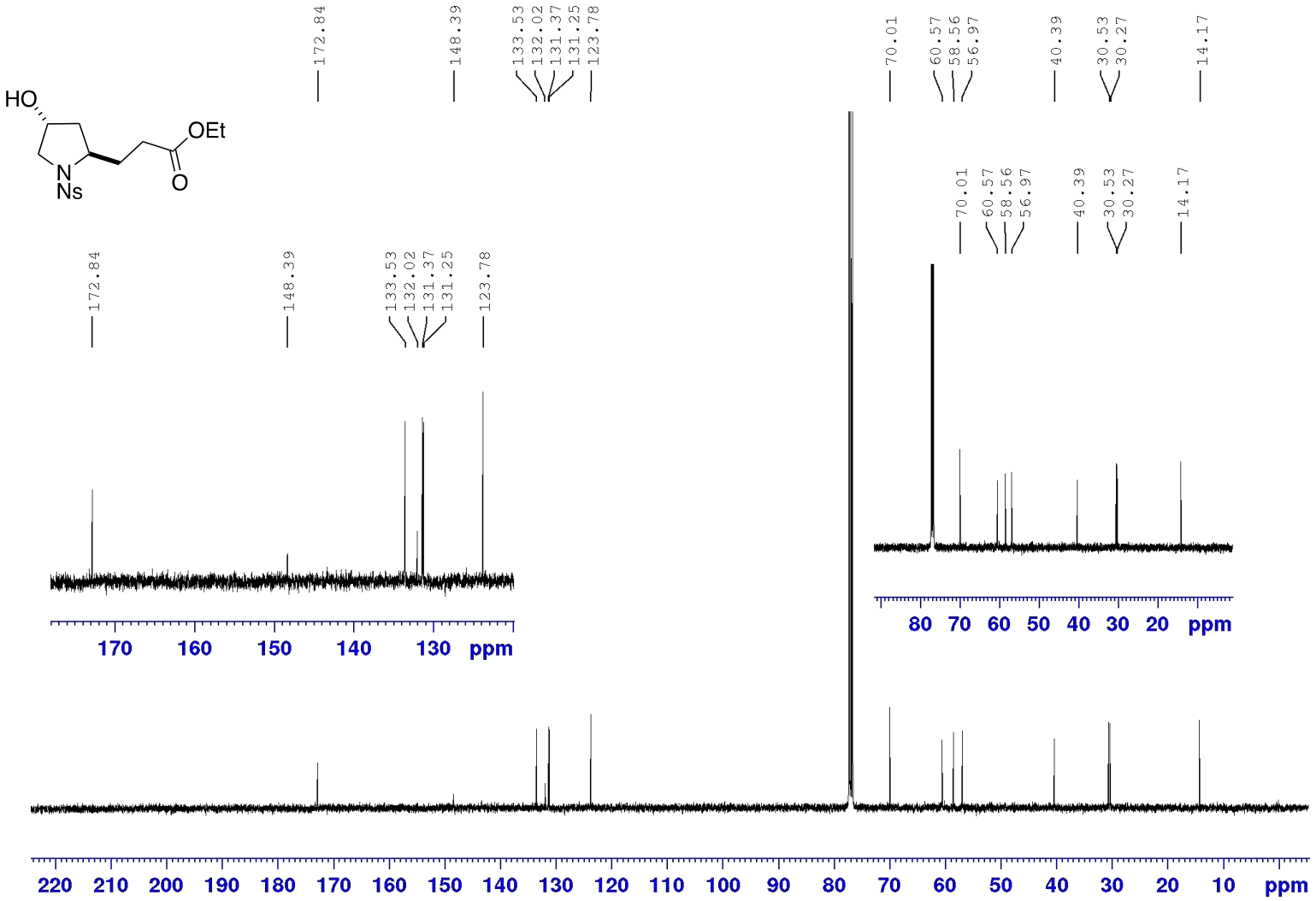
^{13}C NMR Spectrum of **5of** (100 MHz, $CDCl_3$)



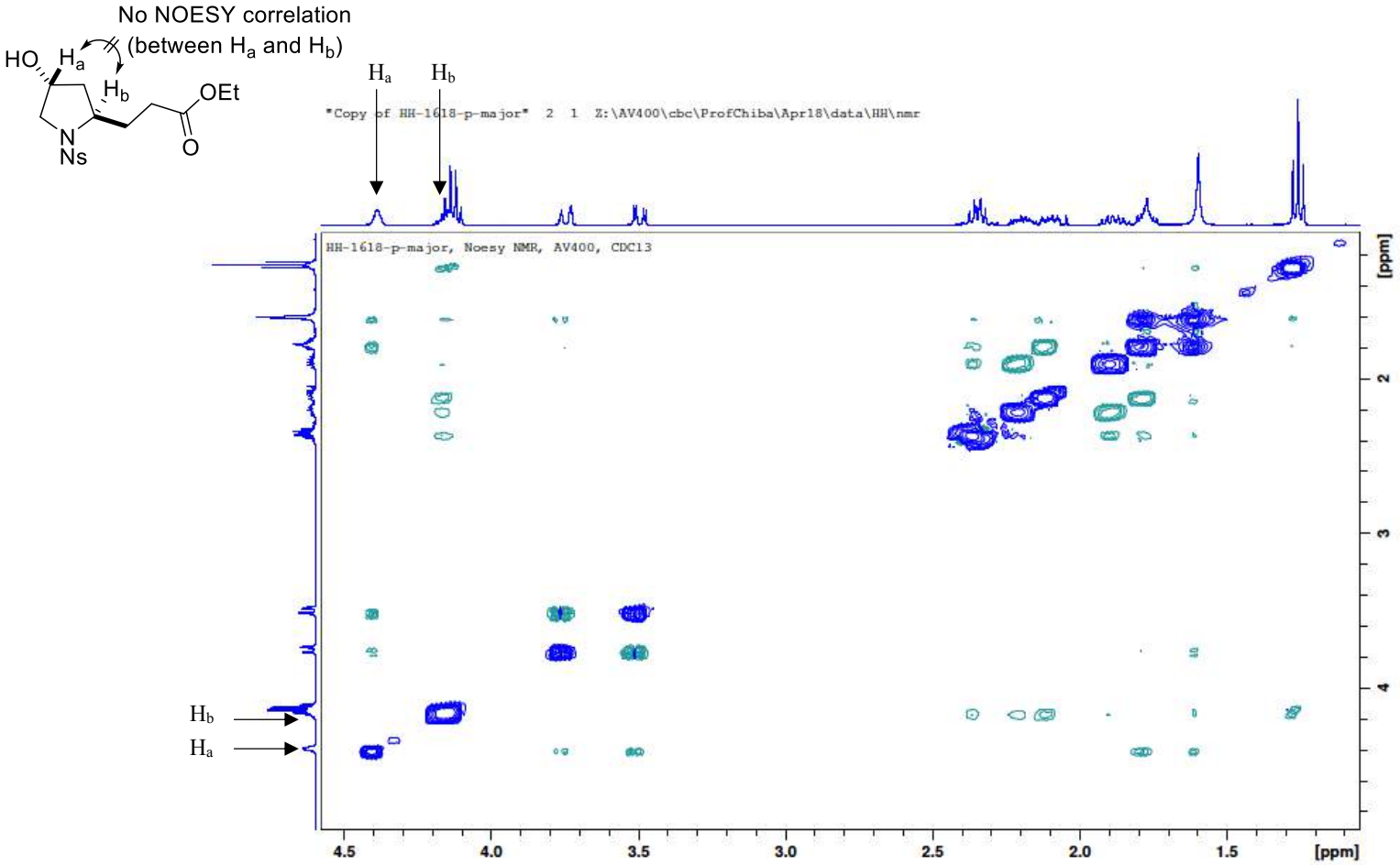
^{1}H NMR Spectrum of ***trans*-4of-Ns** (400 MHz, $CDCl_3$)



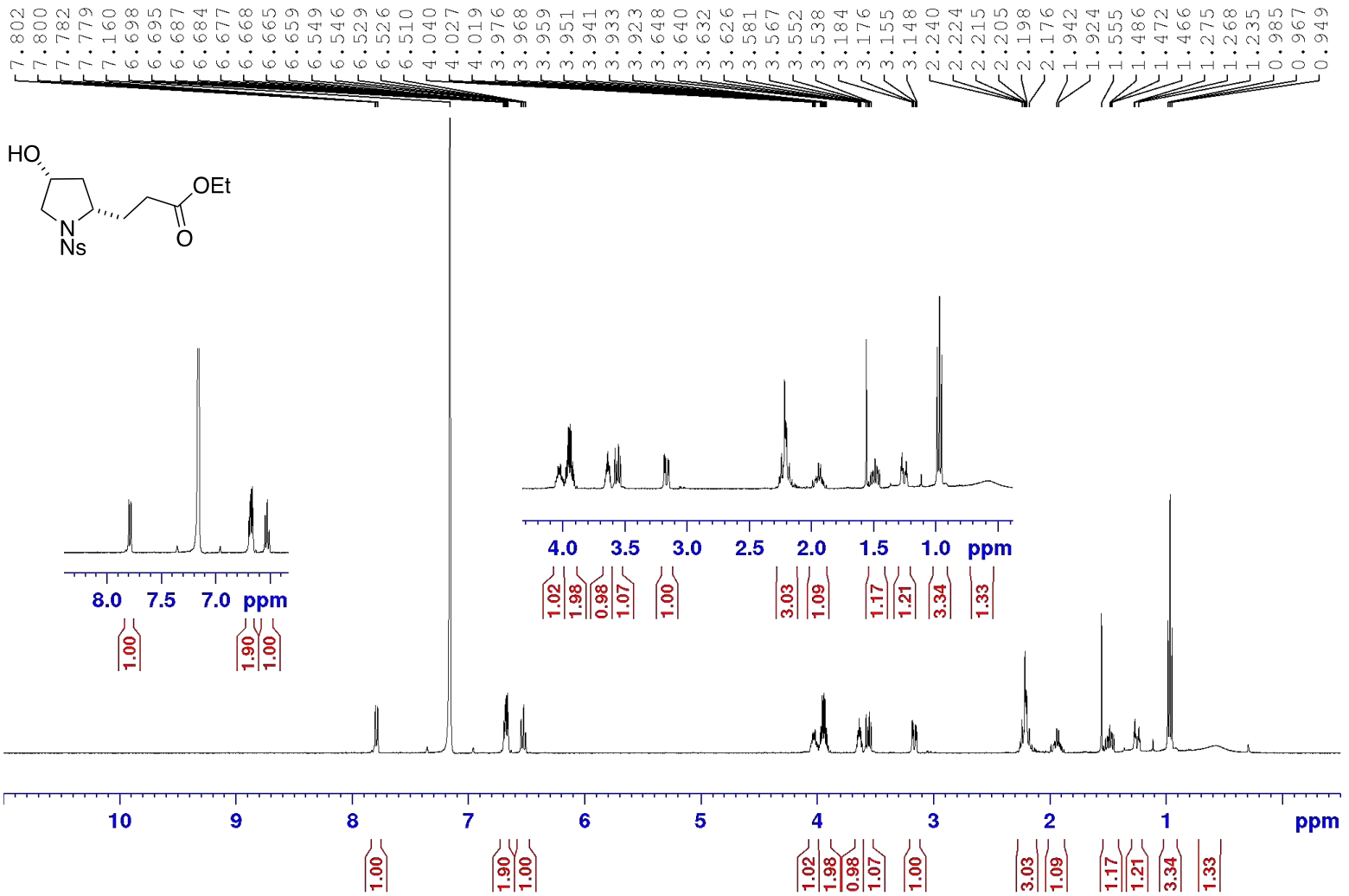
^{13}C NMR Spectrum of ***trans*-4of-Ns** (100 MHz, $CDCl_3$)



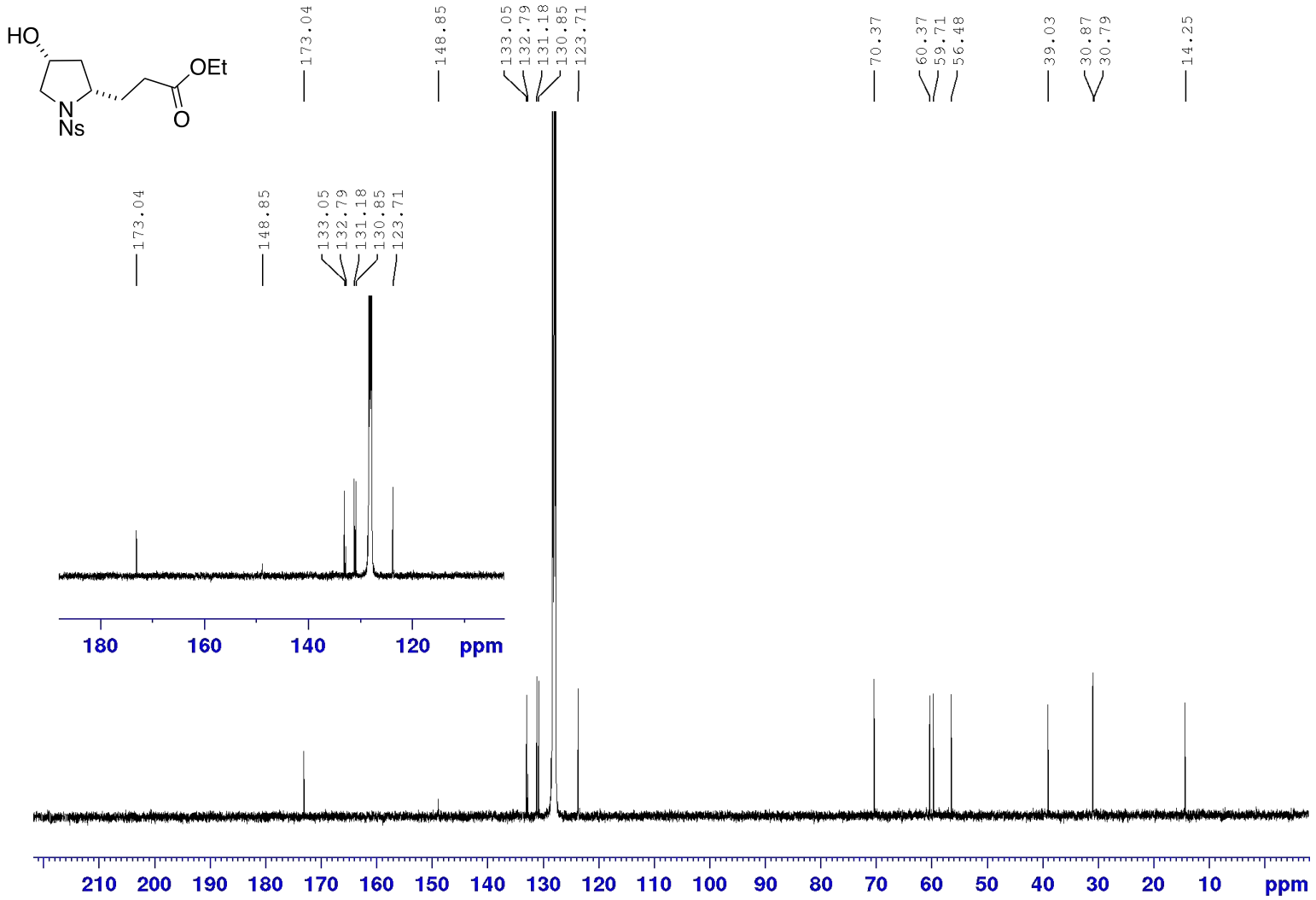
NOESY spectrum of ***trans*-4of-Ns** (400 MHz, $CDCl_3$)



^{1}H NMR Spectrum of ***cis*-4of-Ns** (400 MHz, C_6D_6)



^{13}C NMR Spectrum of ***cis*-4of-Ns** (100 MHz, C_6D_6)



NOESY spectrum of ***cis*-4of-Ns** (400 MHz, C_6D_6)