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Supporting Information

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Lanthanide Complexes of Monovacant Dawson Polyoxotungstate [α_1-$P_2W_{17}O_{61}]^{10-}$, as Selective and Recoverable Catalysts for Lewis-Acid Promoted Organic Transformations

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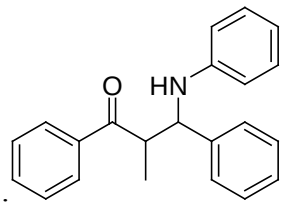
General remarks: Reagents and chemicals were purchased from commercial sources and used as received. Reactions were carried out under argon, with magnetic stirring. CH_3CN was dried and distilled from CaH_2. Thin-layer chromatography (TLC) was performed on Merck 60F254 silica gel. Merck Geduran SI 60 Å silica gel (40-63 μm) was used for column chromatography. The melting points reported were measured with a Reichert hot-stage apparatus and are uncorrected. IR spectra were recorded from a Bruker Tensor 27 ATR diamond PIKE spectrometer. ^{1}H NMR [^{13}C NMR] spectra were recorded at room temperature with a 400 MHz [100 MHz] Bruker AVANCE 400 spectrometer. Chemical shifts are given in ppm, referenced to the residual proton resonances of the solvents (δ = 7.26 or 77.2, respectively, for $CDCl_3$; δ = 2.50 or 39.5, respectively, for $(CD_3)_2SO$; δ = 2.05 or 29.84 and 206.26, respectively, for $(CD_3)_2CO$). Coupling constants (*J*) are given in Hertz (Hz). Elemental analysis and High Resolution Mass Spectra were performed by the ICSN (CNRS, Gif).

General procedure 1 (GP1): *Mannich type reaction* :

To a solution of the catalyst $TBA_5H_2[\alpha_1\text{-}LnP_2W_{17}O_{61}]$ (20 mol%, 0.1 mmol) in CH_3CN (3 mL) was added imine (0.5 mmol, 1 equiv.) and trimethyl-(1-phenyl-propenyloxy)-silane (0.5 mmol, 103 mg). After completion (unless otherwise noted), 6 mL of a solution of acetone/ethanol (1/1) was added followed by 60 mL of diethyl ether. The white precipitate formed was centrifugated and separated from the reaction products. The organic layer was concentrated under reduced pressure. The residue was purified by flash column chromatography (pentane/ethylacetate: 95/5) to afford the desired β-amino ketones as an inseparable mixture of the 2 diastereomers.

General procedure 2 (GP2): *Imino Diels-Alder reaction*:

To a solution of the catalyst $TBA_5H_2[\alpha_1\text{-}YbP_2W_{17}O_{61}]$ (10 mol%, 0.05 mmol, 280 mg) in CH_3CN (3 mL) was added the imine (0.5 mmol, 1 equiv.) and diene or enol ether (0.75 mmol, 1.5 equiv.). After completion, 6 mL of a solution of acetone/ethanol (1/1) was added followed by 60 mL of diethyl ether. The white precipitate formed was centrifugated and separated from the reaction products. The organic layer was concentrated under reduced pressure. The residue was purified by flash column chromatography to afford desired cyclic adducts.

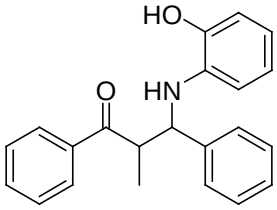


$C_{22}H_{21}NO$

M = 315.41 g.mol^{-1}

2-Methyl-1,3-diphenyl-3-phenylamino-propan-1-one ***(1a)***:

Following GP1 (reaction time: 2 days), product **1a** was isolated (pentane/ethyl acetate: 80/20) as an inseparable mixture of the 2 diastereomers (ratio 50/50, pale yellow solid, 0.48 mmol, 151 mg, 96 %). Spectral data coresponded to those described in the literature.[1] See ^{1}H and ^{13}C NMR spectra. HRMS calcd. for $C_{22}H_{21}NONa$ ($[M + Na]^+$) 338.1521, found 338.1500. Elemental analysis (%) for $C_{22}H_{21}NO$ (315.41); calcd: C 83.78, H 6.71, N 4.44; found: C 83.62, H 6.68, N 4.34.



$C_{22}H_{21}NO_2$

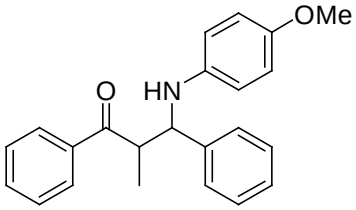
M = 331.41 g.mol^{-1}

3-(2-Hydroxy-phenylamino)-2-methyl-1,3-diphenyl-propan-1-one ***(1b)***:

Following GP1 (reaction time: 3 days), product **1b** was isolated (pentane/ethyl acetate 80/20) as an inseparable mixture of the 2 diastereomers (ratio 50/50, brown gum, 0.42 mmol, 138 mg, 84 %). See ^{1}H and ^{13}C NMR spectra. HRMS calcd. for $C_{22}H_{21}NO_2Na$ ($[M + Na]^+$) 354.1470, found 354.1463.

IR (ATR): ν = 3375, 3058, 3026, 2931, 1670 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.15 (d, J = 7.0 Hz, 3 H, CH_3, one *dia.*), 1.31 (d, J = 7.1 Hz, 3 H, CH_3, one *dia.*), 3.96-4.10 (m, 2 H, *CH*CH_3, 2 *dias.*), 4.64 (d, J = 8.1 Hz, 1 H, CHN, one *dia.*), 4.82 (d, J = 5.8 Hz, 1 H, CHN, one *dia.*), 6.31 (d, J = 7.8 Hz, 1 H, arom., one *dia.*), 6.38 (d, J = 7.8 Hz, 1 H, arom., one *dia.*), 6.46-6.52 (m, 1 H, arom., one *dia.*), 6.57-6.62 (m, 3 H, arom., 2 *dias.*), 6.71-6.77 (m, 2 H,

arom., 2 *dias.*), 7.15-7.30 (m, 8 H, arom., 2 *dias.*), 7.38-7.45 (m, 6 H, arom., 2 *dias.*), 7.50-7.56 (m, 2 H, arom., 2 *dias.*), 7.88 (d, J = 7.3 Hz, 2 H, arom., one *dia.*), 7.92 (d, J = 8.5 Hz, 2 H, arom., one *dia.*); ^{13}C NMR (100 MHz, $CDCl_3$): δ= 12.3 (CH_3, one *dia.*), 16.6 (CH_3, one *dia.*), 46.9 (*CH*CH_3, one *dia.*), 47.6 (*CH*CH_3, one *dia.*), 59.6 (CHN, one *dia.*), 62.5 (CHN, one *dia.*), 113.2 (CH arom.), 114.4 (CH arom.), 114.8 (CH arom.), 117.6 (CH arom.), 120.5 (CH arom.), 121.1 (CH arom.), 127.0 (CH arom.), 127.1 (CH arom.), 127.2 (CH arom.), 127.5 (CH arom.), 128.3 (CH arom.), 128.5 (CH arom.), 128.58 (CH arom.), 128.61 (CH arom.), 128.7 (CH arom.), 128.9 (CH arom.), 133.3 (CH arom.), 133.4 (CH arom.), 134.9 (C arom.), 136.1 (C arom.), 136.4 (C arom.), 136.9 (C arom.), 141.4 (C arom.), 141.9 (C arom.), 144.0 (C arom.), 146.5 (C arom.), 203.5 (CO, one *dia.*), 204.8 (CO, one *dia.*).

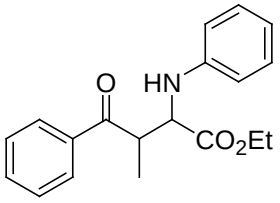


$C_{23}H_{23}NO_2$

M = 345.43 g.mol^{-1}

3-(4-Methoxy-phenylamino)-2-methyl-1,3-diphenyl-propan-1-one ***(1c)***:

Following GP1 (reaction time: 6 days), product **1c** was isolated (pentane/ethyl acetate 90/10) as an inseparable mixture of the 2 diastereomers (ratio 50/50, pale yellow solid, 0.4 mmol, 139 mg, 81 %). Spectral data coresponded to those described in the literature.[2] See ^{1}H and ^{13}C NMR spectra. HRMS calcd. for $C_{22}H_{21}NONa$ ([M + Na]$^+$) 368.1626, found 368.1612. Elemental analysis (%) for $C_{23}H_{23}NO_2$ (345.43); calcd: C 79.97, H 6.71, N 4.05; found: C 79.61, H 6.71, N 3.86.



$C_{19}H_{21}NO_3$

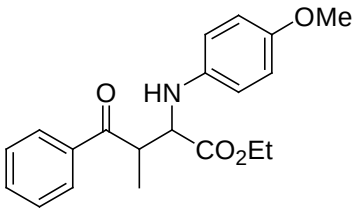
M = 311.37 g.mol^{-1}

3-Methyl-4-oxo-4-phenyl-2-phenylamino-butyric acid ethyl ester ***(1d)***:

Following GP1 (reaction time: 45 min.), product **1d** was isolated (pentane/ethyl acetate 80/20) as an inseparable mixture of the 2 diastereomers (ratio 70/30, white solid, 0.35 mmol, 109 mg, 70 %). See ^{1}H and ^{13}C NMR spectra. Elemental analysis (%) for $C_{19}H_{21}NO_3$ (311.37); calcd: C 73.29, H 6.80, N 4.50; found: C 73.07, H 6.77, N 4.63.

IR (ATR): ν= 3379, 3025, 2978, 1728, 1678, 1600 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 1.13-1.19 (m, 6 H, CH_2*CH*$_3$, 2 *dias.*), 1.32 (d, J = 7.0 Hz, 3 H, CH*CH*$_3$, *minor dia.*), 1.37

(d, J = 7.1 Hz, 3 H, CH*CH*$_3$, *major dia.*), 4.03-4.13 (m, 6 H, *CH*CH$_3$, and OCH$_2$, 2 *dias.*), 4.46 (d, J = 6.6 Hz, 1 H, CHN, *minor dia.*), 4.49 (d, J = 6.8 Hz, 1 H, CHN, *major dia.*), 6.46-6.77 (m, 6 H, arom., 2 *dias.*), 7.14-7.20 (m, 4 H, arom., 2 *dias.*), 7.46-7.51 (m, 4 H, arom., 2 *dias.*), 7.56-7.61 (m, 2 H, arom., 2 *dias.*), 7.95-7.98 (m, 4 H, arom., 2 *dias.*); ^{13}C NMR (100 MHz, CDCl$_3$): δ= 14.0 (CH*CH*$_3$, *major dia.*), 14.1 (CH$_2$*CH*$_3$, 2 *dias.*), 14.8 (CH*CH*$_3$, *minor dia.*), 43.5 (*CH*CH$_3$, *minor dia.*), 43.9 (*CH*CH$_3$, *major dia.*), 59.1 (CHN, *major dia.*), 59.6 (CHN, *minor dia.*), 61.5 (*CH*$_2$CH$_3$, 2 *dia.*), 113.9 (CH arom., *major dia.*), 114.1 (CH arom., *minor dia.*), 118.6 (CH arom., 2 *dias.*), 128.4 (CH arom., 2 *dias.*), 128.8 (CH arom., 2 *dias.*), 129.3 (CH arom., 2 *dias.*), 133.3 (CH arom., *major dia.*), 133.4 (CH arom., *minor dia.*), 136.1 (C arom., *major dia.*), 136.6 (C arom., *minor dia.*), 146.8 (C arom., *major dia.*), 147.2 (C arom., *minor dia.*), 172.7 (CO$_2$, *major dia.*), 172.9 (CO$_2$, *minor dia.*), 201.5 (CO, *major dia.*), 202.1 (CO, *minor dia.*).



$C_{20}H_{23}NO_4$

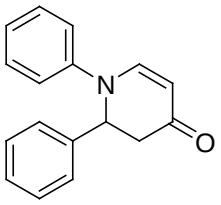
M = 341.40 g.mol^{-1}

2-(4-Methoxy-phenylamino)-3-methyl-4-oxo-4-phenyl-butyric acid ethyl ester **(1e)**:

Following GP1 (reaction time: 30 min.), product **1e** was isolated (pentane/ethyl acetate 80/20) as an inseparable mixture of the 2 diastereomers (ratio 70/30, brown solid, 0.39 mmol, 131 mg, 77%). See ^{1}H and ^{13}C NMR spectra. Elemental analysis (%) for $C_{20}H_{23}NO_4$ (341.40); calcd: C 70.36, H 6.79, N 4.10; found: C 70.62, H 6.81, N 3.92.

IR (ATR): ν= 3349, 2986, 2928, 1721, 1672 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ= 1.14 (t, J = 7.3 Hz, 3 H, CH$_2$*CH*$_3$, *major dia.*), 1.15 (t, J = 7.3 Hz, 3 H, CH$_2$*CH*$_3$, *minor dia.*), 1.29 (d, J = 7.1 Hz, 3 H, CH*CH*$_3$, *minor dia.*), 1.34 (d, J = 7.1 Hz, 3 H, CH*CH*$_3$, *major dia.*), 3.70 (s, 3 H, OMe, *major dia.*), 3.71 (s, 3 H, OMe, *minor dia.*), 3.99-4.12 (m, 6 H, O*CH*$_2$CH$_3$ and *CH*CH$_3$, 2 *dias.*), 4.37 (d, J = 6.8 Hz, 1 H, CHN, *minor dia.*), 4.38 (d, J = 6.6 Hz, 1 H, CHN, *major dia.*), 6.56-6.59 (m, 2 H, arom., *major dia.*), 6.66-6.68 (m, 2 H, arom., *minor dia.*), 6.70-6.76 (m, 4 H, arom., 2 *dias.*), 7.45-7.48 (m, 4 H, arom., 2 *dias.*), 7.55-7.59 (m, 2 H, arom., 2 *dias.*), 7.94-7.97 (m, 4 H, arom., 2 *dias.*); ^{13}C NMR (100 MHz, CDCl$_3$): δ= 13.7 (CH$_3$, *major dia.*), 14.10 (CH$_3$, *major dia.*), 14.13 (CH$_3$, *minor dia.*), 14.7 (CH$_3$, *minor dia.*), 43.3 (*CH*CH$_3$, *minor dia.*), 43.8 (*CH*CH$_3$, *major dia.*), 55.6 (OMe, 2 *dias.*), 60.4 (CHN, *major dia.*), 61.1 (CHN, *minor dia.*), 61.2 (OCH$_2$, *minor dia.*), 61.3 (OCH$_2$, *major*

dia.), 114.7 (CH arom., 2 *dias.*), 115.6 (CH arom., one *dia.*), 116.0 (CH arom., one *dia.*), 128.3 (CH arom., 2 *dias.*), 128.8 (CH arom., 2 *dias.*), 133.2 (CH arom., *major dia.*), 133.3 (CH arom., *minor dia.*), 136.1 (C arom., *major dia.*), 136.6 (C arom., *minor dia.*), 140.9 (C arom., *major dia.*), 141.1 (C arom., *minor dia.*), 152.9 (*C*OMe, *major dia.*), 153.0 (*C*OMe, *minor dia.*), 172.9 (CO_2, *major dia.*), 173.2 (CO_2, *minor dia.*), 201.5 (CO, *major dia.*), 201.9 (CO, *minor dia.*).

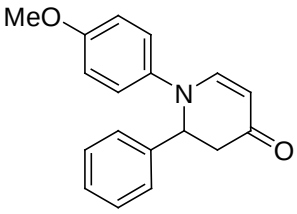


$C_{17}H_{15}NO$

$M = 249{,}31 g.mol^{-1}$

1,2-Diphenyl-2,3-dihydro-1H-pyridin-4-one **(2a)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 90.6 mg), after 4 hours, pyridinone **2a** was isolated (pentane/ethyl acetate 7:3; 0.45 mmol, 111.5 mg; 89 %) as a pale yellow oil. Spectral data coresponded to those described in the literature.[3] See ^{1}H and ^{13}C NMR spectra.

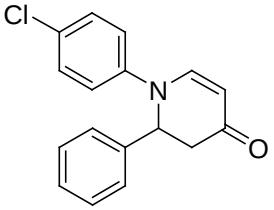


$C_{18}H_{17}NO_2$

$M = 279.33 g.mol^{-1}$

1-(4-Methoxy-phenyl)-2-phenyl-2,3-dihydro-1H-pyridin-4-one **(2b)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 105.5 mg), after 6 hours, pyridinone **2b** was isolated (pentane/ethyl acetate: 5/5; 0.49 mmol, 137 mg; 98 %) as orange cristals, mp = 111°C. Spectral data coresponded to those described in the literature.[3] See ^{1}H and ^{13}C NMR spectra.



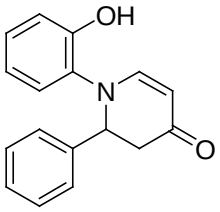
$C_{17}H_{14}ClNO$

$M = 283.75 g.mol^{-1}$

1-(4-Chloro-phenyl)-2-phenyl-2,3-dihydro-1H-pyridin-4-one **(2c)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 107.9 mg), after 22 hours, pyridinone **2c** was isolated (pentane/ethyl acetate: 5/5; 0.38 mmol, 108 mg, 76 %) as a

white solid, mp 149°C (*Litt.* mp 150°C).[3] Spectral data coresponded to those described in the literature.[3] See ^{1}H and ^{13}C NMR spectra.

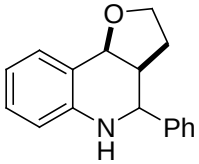


$C_{17}H_{15}NO_2$

M = 265.11 g.mol^{-1}

1-(2-Hydroxy-phenyl)-2-phenyl-2,3-dihydro-1H-pyridin-4-one **(2d)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 98.6 mg), after 2 days, pyridinone **2d** was isolated (pentane/ethyl acetate: 6/4 to 4/6; 0.29 mmol, 76 mg, 57 %) as an orange gum. See ^{1}H and ^{13}C NMR spectra. IR (ATR): $\nu = 3062, 2873, 1450$ cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 2.89$ (B of ABX, J = 16.7, 6.6 Hz, 1 H, C*H*H), 3.29 (A of ABX, J = 16.7, 7.3 Hz, 1 H, CH*H*), 5.23 (d, J = 7.4 Hz, 1 H, CO*CH*=CH), 5.33 (dd, J = 7.3, 6.6 Hz, 1 H, C*H*Ph), 6.67 (dd, J = 7.3, 1.2 Hz, 1 H, arom.), 6.86-7.01 (m, 3 H, arom.), 7.17-7.27 (m, 5 H, arom.), 7.44 (d, J = 7.4 Hz, 1 H, COCH=*CH*), 9.92 (bs, 1 H, OH); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 42.7$ (CH_2), 62.3 (*CH*Ph), 98.5 (CO*CH*=CH), 117.2 (CH arom.), 119.7 (CH arom.), 126.4 (CH arom.), 127.1 (CH arom.), 128.1 (CH arom.), 128.5 (CH arom.), 128.7 (CH arom.), 131.5 (C arom.), 138.5 (C arom.), 151.9 (C arom.), 156.0 (COCH=*CH*), 192.2 (CO).

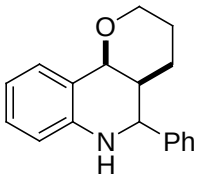


$C_{17}H_{17}NO$

M = 251.32 g.mol^{-1}

4-Phenyl-2,3,3a,4,5,9b-hexahydro-furo[3,2-c]quinoline **(3a)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 90.6 mg), after 4 hours, tetrahydroquinoline **3a** was isolated (pentane/ethyl acetate: 95/5; 0.34 mmol, 84 mg, 67 %). The diastereoisomers (*trans/cis* ratio: 60/40) were separated on silica column chromatography. The *trans* isomer is a colourless oil and the *cis* isomer is a white solid, mp 114-115°C (*Litt.* mp 117-118°C).[4] Spectral data coresponded to those described in the literature.[4] See ^{1}H and ^{13}C NMR spectra. Elemental analysis (%) for $C_{17}H_{17}NO$ (251.32); calcd: C 81.24, H 6.82, N 5.57; found: C 80.96, H 6.99, N 5.32.

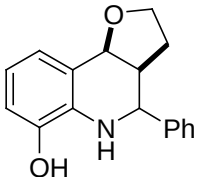


$C_{18}H_{19}NO$

M = 265.35 g.mol^{-1}

5-Phenyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline **(3b)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 90.6 mg), after 6 hours, tetrahydroquinoline **3b** was isolated (pentane/ethyl acetate: 95/5; 0.4 mmol, 105 mg; 79. The diastereoisomers (*trans/cis* ratio: 80/20) were separated on silica column chromatography. The *trans* isomer is a colourless oil and the *cis* isomer is a white solid, mp 131-133°C (*Litt.* mp 130-132°C).[4] Spectral data coresponded to those described in the literature.[4] See ^{1}H and ^{13}C NMR spectra. Elemental analysis (%) for $C_{18}H_{19}NO$ (265.35); calcd: C 81.47, H 7.22, N 5.28; found: C 81.35, H 7.22, N 5.28.

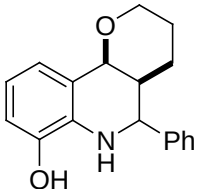


$C_{17}H_{17}NO_2$

M = 267.32 g.mol^{-1}

4-Phenyl-2,3,3a,4,5,9b-hexahydro-furo[3,2-c]quinolin-6-ol **(3c)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 98.6 mg), after 24 hours, tetrahydroquinoline **3c** was isolated (pentane/ethyl acetate: 9/1; 0.32 mmol, 84 mg; 63 %). The diastereoisomers (*trans/cis* ratio: 90/10) were separated on silica column chromatography. The *trans* isomer is a yellow-brown oil and the *cis* isomer is a whitish solid, mp 192-193°C (*Litt.* mp 188-189°C).[4] Spectral data coresponded to those described in the literature.[4] See ^{1}H and ^{13}C NMR spectra. Elemental analysis (%) for $C_{17}H_{17}NO_2$ (267.32); calcd: C 76.38, H 6.41, N 5.24; found: C 75.85, H 6.53, N 4.92.



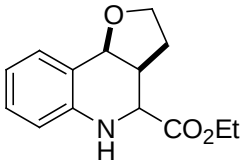
$C_{18}H_{19}NO_2$

M = 281,35 g.mol^{-1}

5-Phenyl-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinolin-7-ol **(3d)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 98.6 mg), after 24 hours, tetrahydroquinoline **3b** was isolated (pentane/ethyl acetate: 85/15; 0.2 mmol, 55 mg; 39 %). The 2 diastereoisomers (*trans/cis* ratio: 80/20) were separated on silica column chromatography. The *trans* isomer is a beige solid, mp 188-189°C (*Litt.* mp 190-191°C); the

cis isomer is a white solid, mp 219-220°C (*Litt.* mp 218-219°C).[4] Spectral data coresponded to those described in the literature.[4] See ^{1}H and ^{13}C NMR spectra. HRMS calcd. for $C_{18}H_{20}NO_2$ ($[M + H]^+$) 282.1494, found 282.1455. Elemental analysis (%) for $C_{18}H_{19}NO_2$ (281.35); calcd: C 76.84, H 6.81, N 4.98; found: C 76.56, H 6.72, N 4.92.



$C_{14}H_{17}NO_3$

M = 247.12 g.mol^{-1}

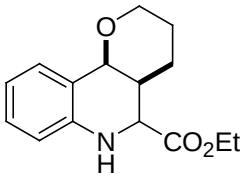
2,3,3a,4,5,9b-Hexahydro-furo[3,2-c]quinoline-4-carboxylic acid ethyl ester **(3e)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 88.6 mg), after 6 hours, tetrahydroquinoline **3e** was isolated (pentane/ethyl acetate: 8/2; 0.2 mmol, 49 mg; 39 %).The diastereoisomers (*trans/cis* ratio: 50/50) were separated on silica column chromatography. The *trans* isomer is a yellow oil and the *cis* isomer is a white solid, mp 59-60°C (*Litt.* mp 61-62°C)[5]; IR (ATR): ν = 3380, 2976, 2873, 1730, 1608, 1487, 1210 cm^{-1}. Spectral data coresponded to the partial description of the literature.[5] See ^{1}H and ^{13}C NMR spectra. Elemental analysis (%) for $C_{14}H_{17}NO_3$ (247.12); calcd: C 68.00, H 6.93, N 5.66; found: C 68.01, H 6.72, N 5.76.

Cis isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 1.27 (t, J = 7.1 Hz 3 H, CH_2CH_3), 1.80-1.89 (m, 1 H, C*H*HCH$_2$O), 1.90-1.99 (m, 1 H, CH*H*CH$_2$O), 2.84-3.03 (m, 1 H, *CH*CHN), 3.60 (B of ABX, J = 15.2, 7.6, 4.6 Hz, 1 H, *CH*HOCH), 3.70 (A of ABX, J = 15.2, 7.6, 7.6 Hz, 1 H, CH*H*OCH), 4.15-4.30 (m, 3 H, OCH_2CH$_3$ + CHN), 4.97 (bs, 1 H, NH), 5.10 (d, J = 8.1 Hz, 1 H, CHO), 6.66 (td, J = 7.6, 1 Hz, 1 H, arom.), 6.73 (dd, J = 8.1, 1 Hz, 1 H, arom.), 6.97-7.02 (m, 1 H, arom.), 7.16 (dd, J = 7.6, 0.8 Hz, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = 14.6 (CH_2CH_3), 26.0 (CH_2CH_2O), 41.3 (*CH*CHN), 56.0 (CHN), 61.7 (OCH_2), 66.7 (OCH_2), 76.2 (CHO), 115.6 (CH arom.), 119.0 (CH arom.), 123.0 (C arom.), 129.0 (CH arom.), 130.7 (CH arom.), 145.5 (C arom.), 172.0 (CO).

Trans isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 1.24 (t, J = 7.3 Hz, 3 H, CH_2CH_3), 2.07-2.13 (m, 1 H, C*H*HCH$_2$O), 2.18-2.27 (m, 1 H, CH*H*CH$_2$O), 2.54-2.61 (m, 1 H, *CH*CHN), 3.61 (dd, J = 8.6, 1.2 Hz, 1 H, CHN), 3.73 (B of ABX, J = 16.6, 8.3, 7.1 Hz, 1 H, *CH*HOCH), 3.83 (A of ABX, J = 16.6, 8.3, 5.1 Hz, 1 H, C*H*HOCH), 4.12-4.25 (m, 2 H, OCH_2CH$_3$), 4.57 (d, J = 6.0 Hz, 1 H, CHO), 6.63-6.67 (m, 1 Hz, 1 H, arom.), 6.73-6.75 (m, 1 H, arom.), 7.03-7.05 (m, 1 H, arom.), 7.19-7.21 (m, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$):

δ= 14.6 (CH_2CH_3), 29.9 (CH_2CH_2O), 40.0 (CHCHN), 56.5 (CHN), 61.6 (OCH_2), 65.8 (OCH_2), 75.4 (CHO), 115.6 (CH arom.), 118.4 (CH arom.), 121.2 (C arom.), 129.3 (CH arom.), 131.4 (CH arom.), 145.1 (C arom.), 173.0 (CO).



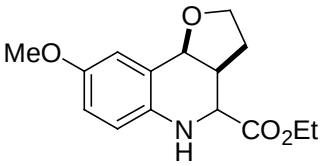
$C_{15}H_{19}NO_3$

M = 261.32 g.mol^{-1}

3,4,4a,5,6,10b-Hexahydro-2H-pyrano[3,2-c]quinoline-5-carboxylic acid ethyl ester **(3f)**:
Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 88.6 mg), after 6 hours, tetrahydroquinoline **3f** was isolated (pentane/ethyl acetate: 8/2; 0.2 mmol, 52 mg, 40 %). The diastereoisomers (*trans/cis* ratio: 50/50) were separated on silica column chromatography. The *trans* isomer is a beige solid, mp 89-91°C; the *cis* isomer is a beige solid, mp 109-111°C. IR (ATR): ν = 3377, 3057, 2984, 2933, 1719, 1665, 1600 cm^{-1}. See ^{1}H and ^{13}C NMR spectra.

Cis isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ= 1.28 (t, J = 7.1 Hz, 3 H, CH_3CH$_2$), 1.39-1.50 (m, 3 H, CH$_2$CH_2CH + CHHCH$_2$O), 1.58-170 (m, 1 H, CHHCH$_2$O), 2.41-2.58 (m, 1 H, CHCHN), 3.20-3.34 (m, 1 H, CH$_2$CHHO), 3.47-3.52 (m, 1 H, CH$_2$CHHO), 4.17-4.30 (m, 3 H, CHN + OCH_2CH$_3$), 4.99 (s, 1 H, NH), 5.12 (d, 1 H, J = 5.6 Hz, 1 H, CHO), 6.60-6.74 (m, 2 H, arom.), 6.97-7.03 (m, 1 H, arom), 7.23 (d, J = 7.8 Hz, 1 H, arom); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ= 14.5 (CH_3CH$_2$), 20.1 (CH$_2$), 26.0 (CH$_2$), 35.1 (CHCHN), 57.5 (CHN), 60.5 (OCH_2), 61.7 (OCH_2), 71.9 (CHO), 115.1 (CH arom.), 118.1 (CH arom.), 119.5 (C arom.), 127.7 (CH arom.), 128.8 (CH arom.), 144.9 (C arom.), 171.9 (CO).

Trans isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ = 1.24 (t, J = 7.1 Hz, 3 H, CH_3CH$_2$), 1.50-1.60 (m, 1 H, CHHCH$_2$O), 1.64-1.85 (m, 3 H, CHHCH$_2$O + CH$_2CH_2$), 2.19-2.26 (m, 1 H, CHCHN), 3.56-3.62 (m, 1 H, CH$_2$CHHO), 3.65-3.70 (m, 1 H, CH$_2$CHHO), 4.05-4.08 (m, 1 H, CHN), 4.11-4.24 (m, 2 H, OCH_2CH$_3$), 4.53 (d, J = 4.0 Hz, 1 H, CHO), 5.41 (bs, 1 H, NH), 6.57-6.64 (m, 2 H, arom.), 6.97-7.03 (m, 1 H, arom.), 7.13 (d, J = 7.6 Hz, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ= 14.5 (CH_3CH$_2$), 24.5 (CH_2CH), 25.2 (CH_2CH$_2$O), 35.3 (CHCHN), 56.6 (CHN), 61.3 (OCH_2), 64.9 (OCH_2), 72.2 (CHO), 114.9 (CH arom.), 117.5 (CH arom.), 120.2 (C arom.), 129.2 (CH arom.), 129.6 (CH arom.), 144.9 (C arom.), 173.6 (CO).



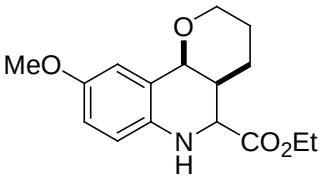
$C_{15}H_{19}NO_4$

M = 277.32 g.mol^{-1}

8-Methoxy-2,3,3a,4,5,9b-hexahydro-furo[3,2-c]quinoline-4-carboxylic acid ethyl ester **(3g)**: Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 103.5 mg), after 30 minutes, tetrahydroquinoline **3g** was isolated (pentane/ethyl acetate: 8/2; 0.34 mmol, 93 mg, 67 %). The diastereoisomers (*trans/cis* ratio: 50/50) were separated on silica column chromatography. The *trans* isomer is a pale yellow oil and the *cis* isomer is a white solid, mp 94-95°C (*Litt.*mp 96-97°C).[5] IR (ATR): ν = 3363, 2954, 2926, 1730 cm^{-1}. Spectral data coresponded to the partial description of the literature.[5] See ^{1}H and ^{13}C NMR spectra. HRMS calcd. for $C_{15}H_{19}NO_4Na$ ([M + Na]$^+$) 300.1212, found 300.1178. Elemental analysis (%) for $C_{15}H_{19}NO_4$ (277.32); calcd: C 64.97, H 6.91, N 5.05; found: C 65.01, H 6.85, N 4.93.

Cis isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ= 1.27 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 1.79-1.87 (m, 1 H, OCH_2CHH), 1.91-2.00 (m, 1 H, OCH_2CHH), 2.82-2.92 (m, 1 H, CHCHN), 3.61 (B of ABX, J = 16.6, 8.6, 4.5 Hz, 1 H, CH_2CHHO), 3.67-3.73 (m, 1 H, CH_2CHHO), 3.69 (s, 3 H, OMe), 4.14 (d, J = 3.8 Hz, 1 H, CHN), 4.16-4.28 (m, 2 H, OCH_2CH_3), 4.68 (bs, 1 H, NH), 5.08 (d, J = 8.1 Hz, 1 H, CHO), 6.63-6.73 (m, 2 H, arom.), 6.76 (d, J = 2.7 Hz, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ= 14.5 (CH_3CH_2), 25.9 (CH_2CH), 41.4 (CHCHN), 55.7 (OMe), 56.5 (CHN), 61.5 (OCH_2), 66.7 (OCH_2), 76.4 (CHO), 114.7 (CH arom.), 115.9 (CH arom.), 116.8 (CH arom.), 124.0 (C arom.), 139.3 (C arom.), 153.6 (C arom.), 171.9 (CO).

Trans isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ= 1.24 (t, J = 7.1 Hz, 3 H, CH_3CH_2), 2.00-2.10 (m, 1 H, OCH_2CHH), 2.16-2.25 (m, 1 H, OCH_2CHH), 2.56-2.64 (m, 1 H, CHCHN), 3.54-3.58 (m, 1 H, CHN), 3.67-3.75 (m, 1 H, CH_2CHHO), 3.70 (s, 3 H, OMe), 3.78-3.86 (m, 1 H, CH_2CHHO), 4.13-4.22 (m, 2 H, OCH_2CH_3), 4.57 (d, J = 6.3 Hz, 1 H, CHO), 5.07 (bs, 1 H, NH), 6.66-6.78 (m, 2 H, arom.), 6.81 (d, J = 2.3 Hz, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = 14.5 (CH_3CH_2), 30.1 (CH_2CH), 40.2 (CHCHN), 55.7 (OMe), 57.1 (CHN), 61.5 (OCH_2), 65.9 (OCH_2), 75.5 (CHO), 115.2 (CH arom.), 116.3 (CH arom.), 116.8 (CH arom.), 122.4 (C arom.), 139.0 (C arom.), 153.2 (C arom.), 173.0 (CO).



$C_{16}H_{21}NO_4$

M = 291.34 g.mol^{-1}

9-Methoxy-3,4,4a,5,6,10b-hexahydro-2H-pyrano[3,2-c]quinoline-5-carboxylic acid ethyl ester **(3h)**:

Following GP2 with 0.5 mmol of starting imine (0.5 mmol, 1 equiv., 103.5 mg), after 30 minutes, tetrahydroquinoline **3h** was isolated (pentane/ethyl acetate: 8/2; 0.31 mmol, 90 mg; 62 %). The diastereoisomers (*trans/cis* ratio: 50/50) were separated on silica column chromatography. The *trans* isomer is a pale yellow oil and the *cis* isomer is a white solid, mp 113-115°C. IR (ATR): $\nu = 3304$, 2922, 2854, 1743 cm^{-1}. Elemental analysis (%) for $C_{16}H_{21}NO_4$ (291.34); calcd: C 65.96, H 7.27, N 4.81; found: C 65.91, H 7.27, N 4.52.

Cis isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ= 1.27 (t, J = 7.2 Hz, 3 H, CH_3CH_2), 1.38-1.50 (m, 3 H, CH_2CH_2 + $CHHCH_2O$), 1.58-1.70 (m, 1 H, $CHHCH_2O$), 2.39-2.47 (m, 1 H, CHCHN), 3.26-3.34 (m, 1 H, CH_2CHHO), 3.49-3.55 (m, 1 H, CH_2CHHO), 3.69 (s, 3 H, OMe), 4.16 (d, J = 2.5 Hz, 1 H, CHN), 4.18-4.31 (m, 2 H, OCH_2CH_3), 4.66 (bs, 1 H, NH), 5.09 (d, J = 5.5 Hz, 1 H, CHO), 6.65-6.70 (m, 2 H, arom.), 6.84-6.87 (m, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ= 14.5 (CH_3CH_2), 20.1 (CH_2CH_2), 26.0 (CH_2CH_2), 35.2 (CHCHN), 55.8 (OMe), 57.9 (CHN), 60.7 (OCH_2), 61.6 (OCH_2), 72.1 (CHO), 112.2 (CH arom.), 115.6 (CH arom.), 116.6 (CH arom.), 120.9 (C arom.), 138.8 (C arom.), 153.5 (C arom.), 171.9 (CO).

Trans isomer: ^{1}H NMR (400 MHz, $(CD_3)_2CO$): δ= 1.23 (t, J = 7.2 Hz, 3 H, CH_3CH_2), 1.54-1.85 (m, 2 H, CH_2CH_2), 2.23-2.29 (m, 1 H, CHCHN), 3.59-3.63 (m, 2 H, CH_2CH_2O), 3.68 (s, 3 H, OMe), 3.99 (d, J = 6.3 Hz, 1 H, CHN), 4.11-4.20 (m, 2 H, OCH_2CH_3), 4.53 (d, J = 4.3 Hz, 1 H, CHO), 5.07 (bs, 1 H, NH), 6.59 (d, J = 8.8 Hz, 1 H, arom.), 6.65-6.69 (m, 1 H, arom.), 6.77 (d, J = 2.8 Hz, 1 H, arom.); ^{13}C NMR (100 MHz, $(CD_3)_2CO$): δ = 14.6 (CH_3CH_2), 24.8 (CH_2CH_2), 25.2 (CH_2CH_2), 35.4 (CHCHN), 55.8 (OMe), 57.1 (CHN), 61.3 (OCH_2), 64.6 (OCH_2), 72.06 (CHO), 113.8 (CH arom.), 116.2 (CH arom.), 116.3 (CH arom.), 121.2 (C arom.), 138.9 (C arom.), 152.8 (C arom.), 173.8 (CO).

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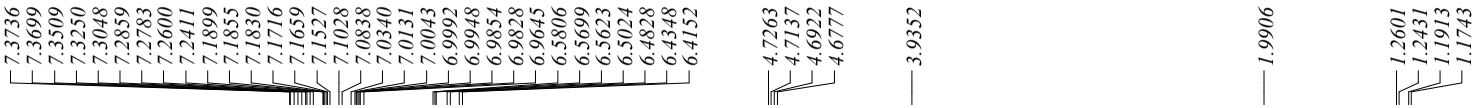
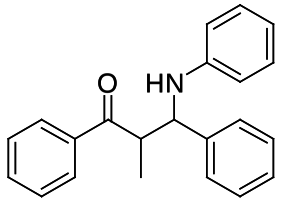
[3] S. Kobayashi, H. Ishitani, S. Nagayama, *Synthesis* **1995**, 1195–1202.

[4] Y. Ma, C. Qian, M. Xie, J. Sun, *J. Org. Chem.* **1999**, *64*, 6462–6467.

[5] E. Borrione, M. Prato, G. Scorrano, M. Stivanello, *J. Het. Chem.* **1988**, *25*, 1831–1835.





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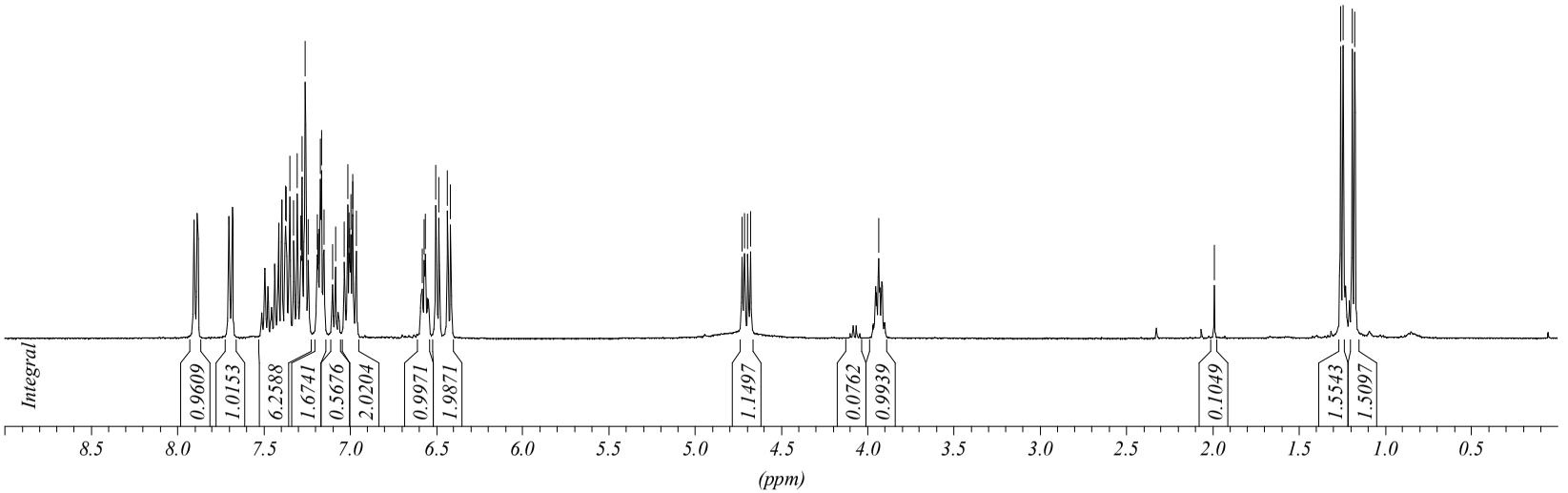

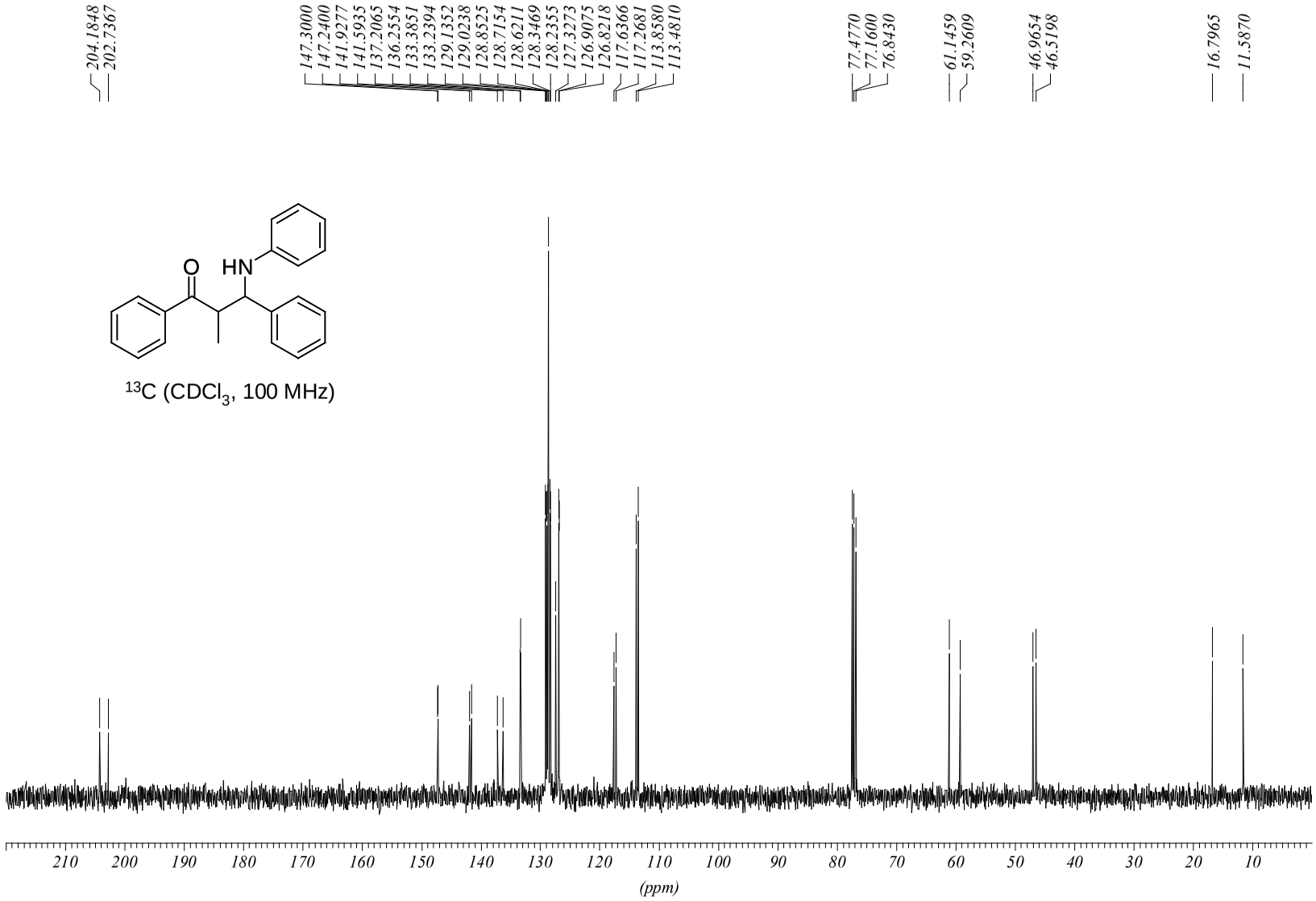
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129.0238
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200
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20
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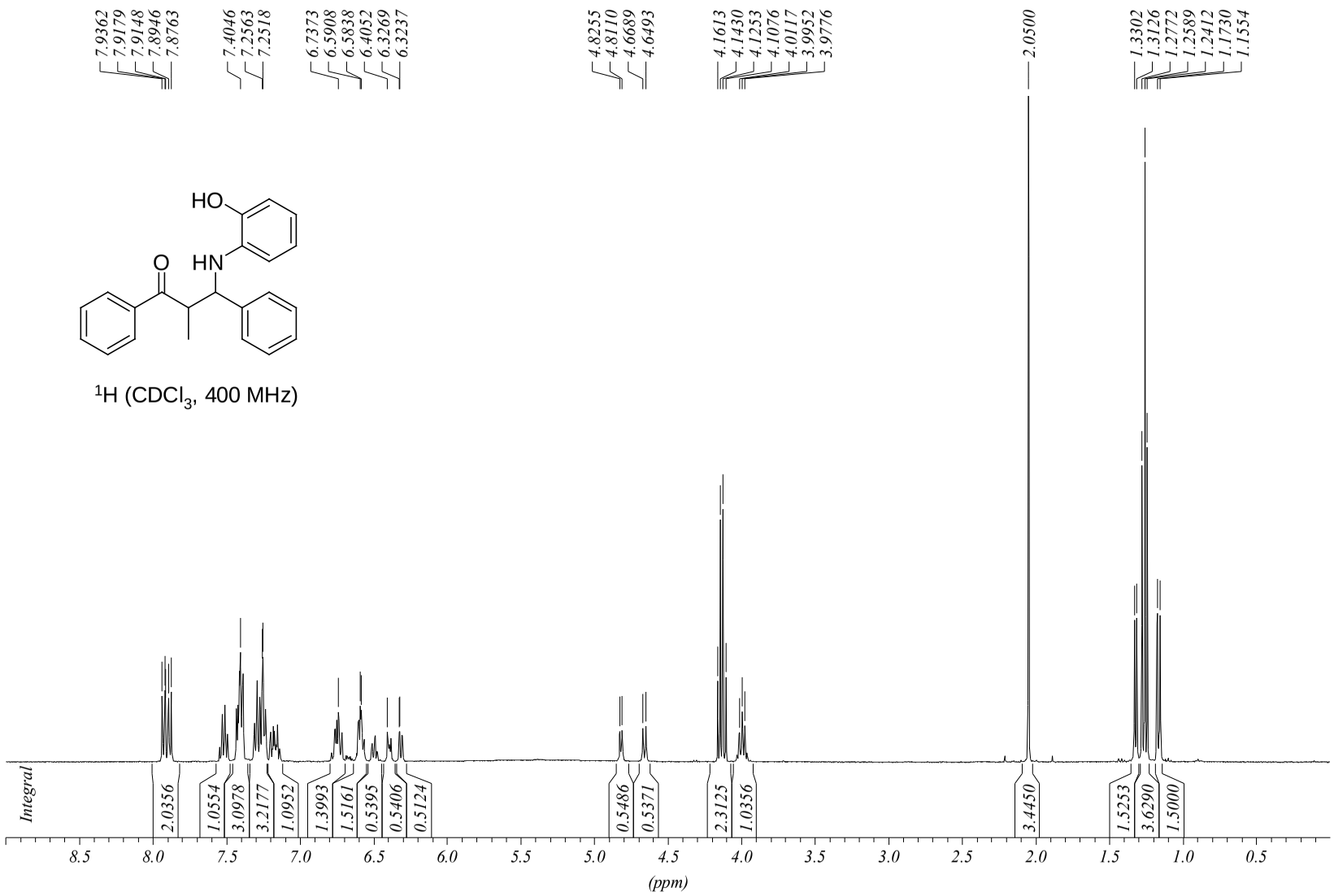
(ppm)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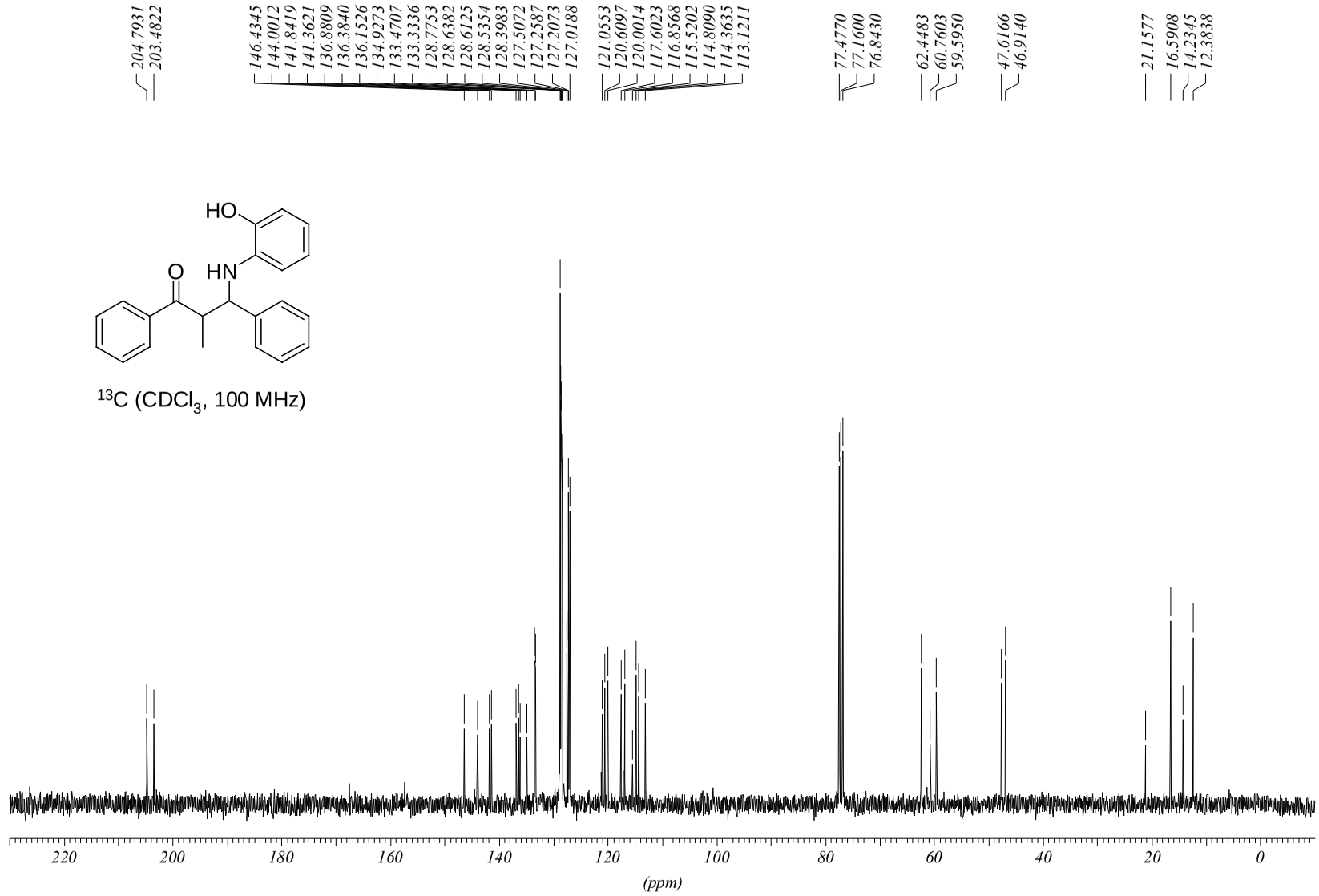
(ppm)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113.1211
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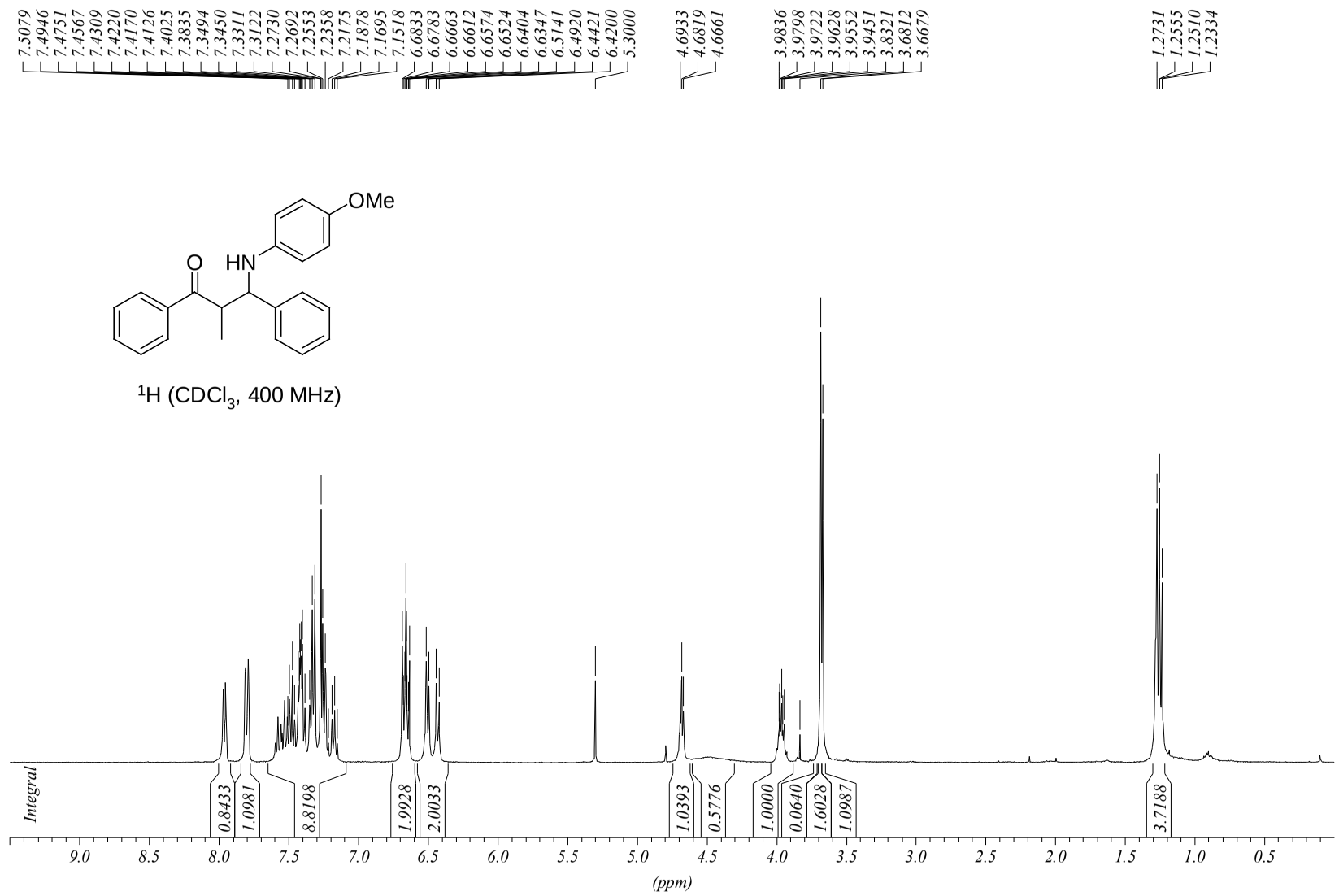
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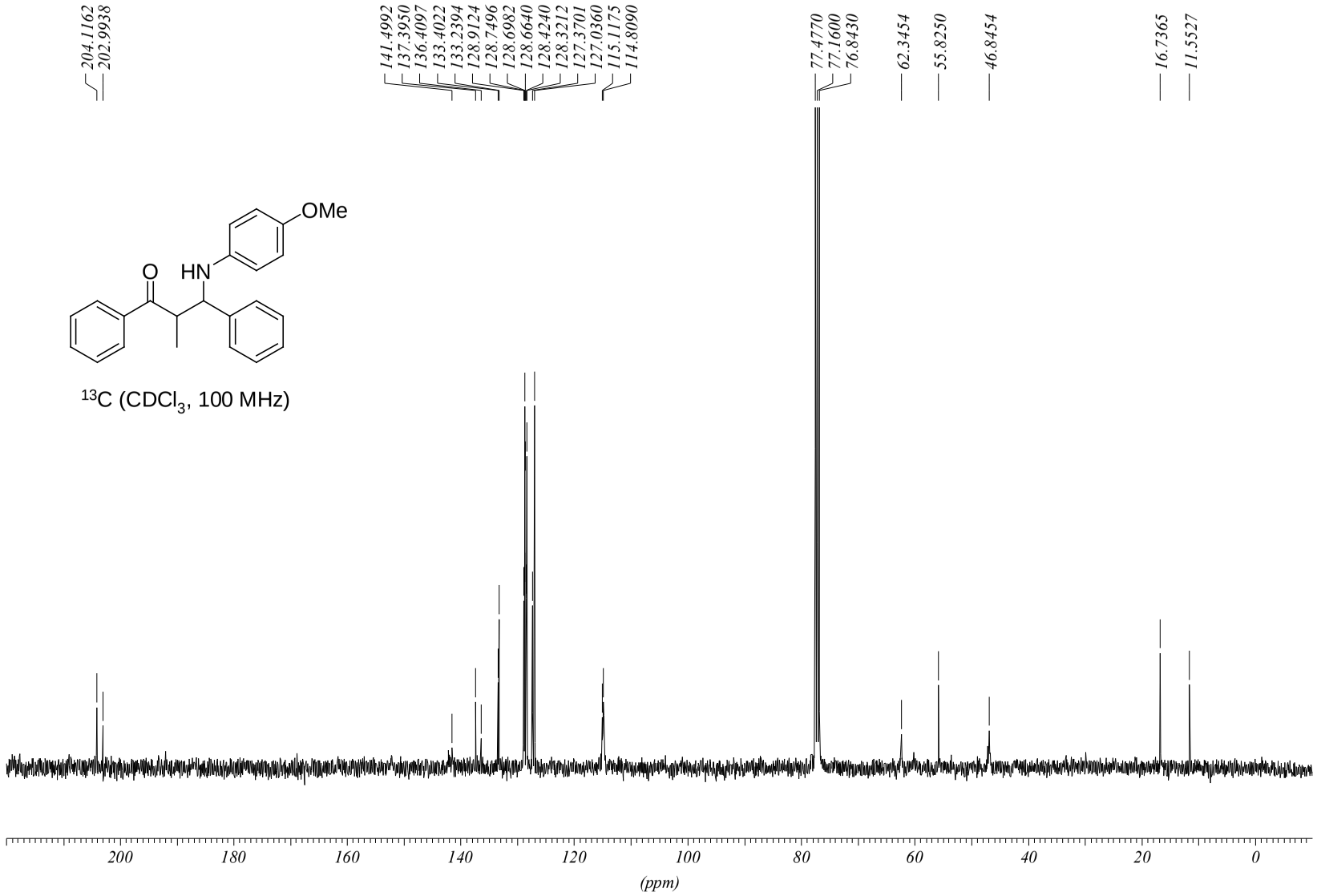
(ppm)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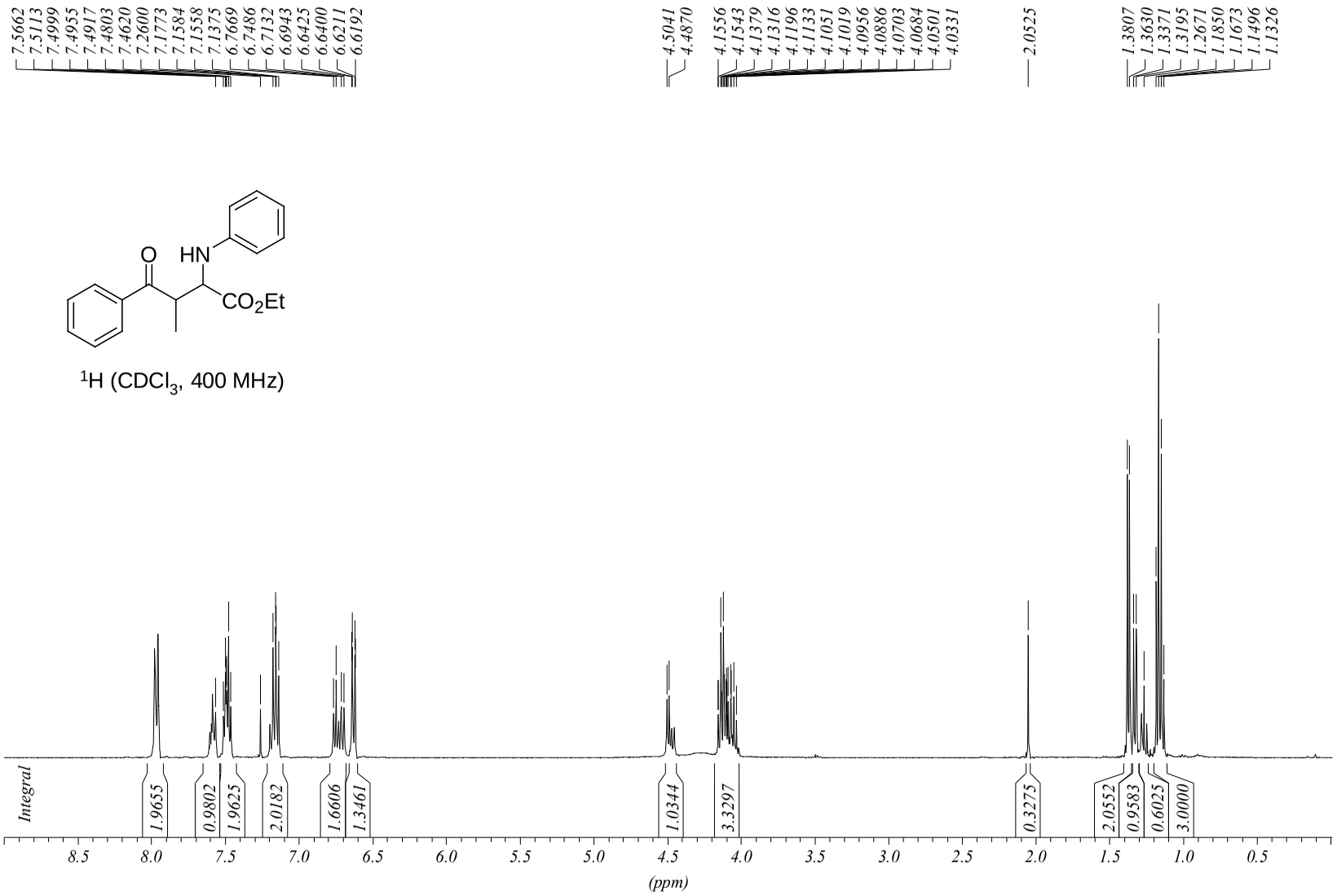
(ppm)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4.1051
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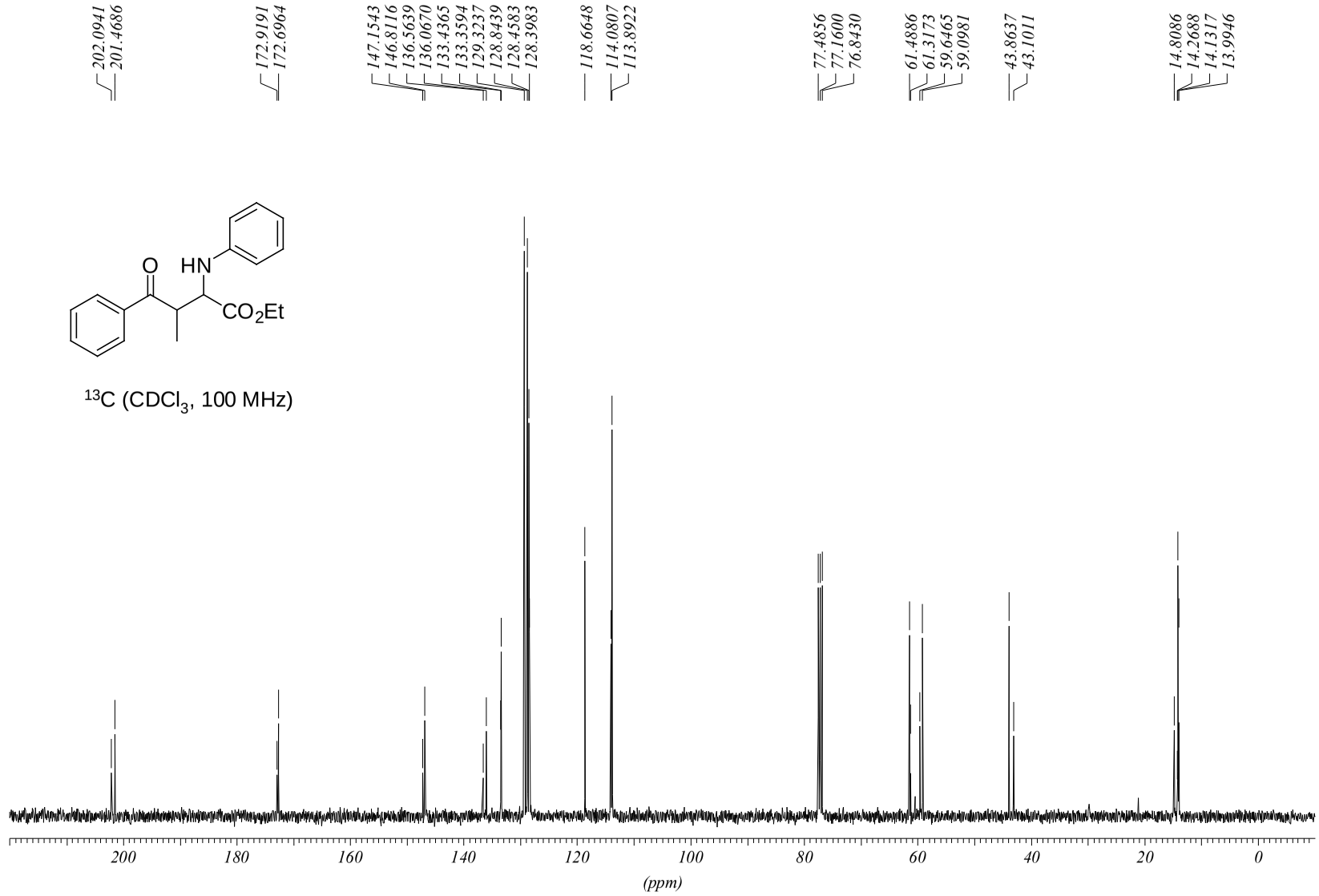
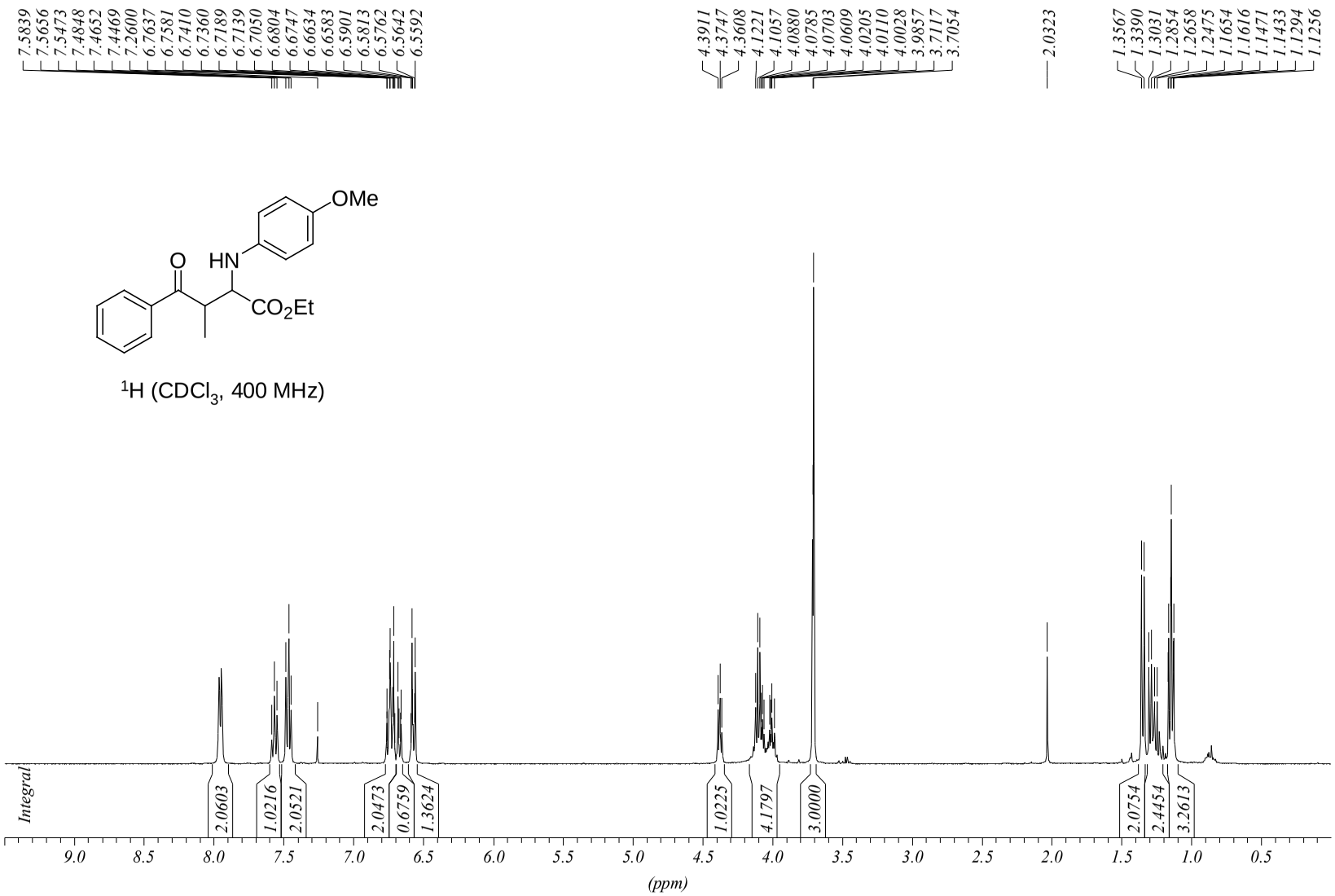
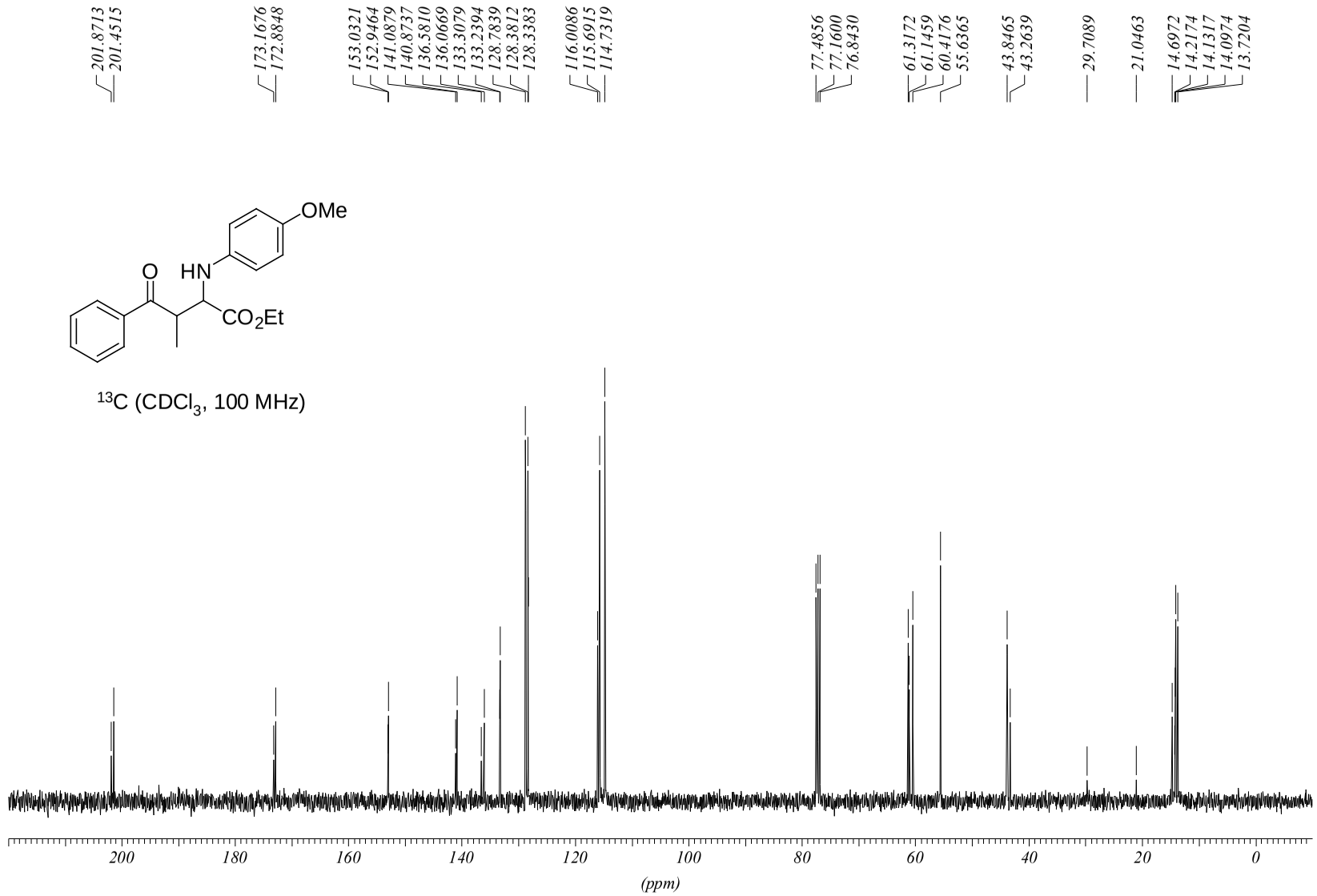
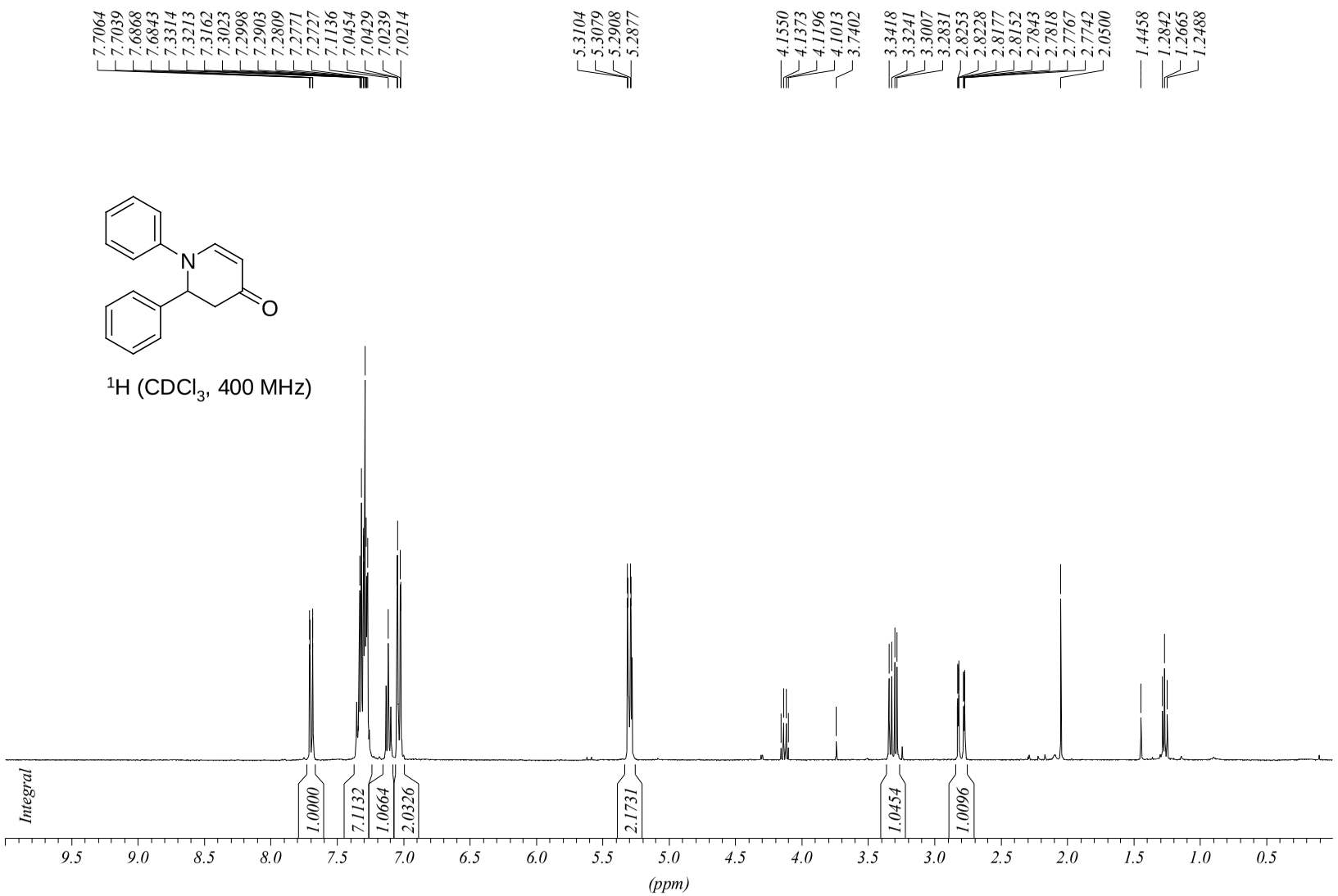
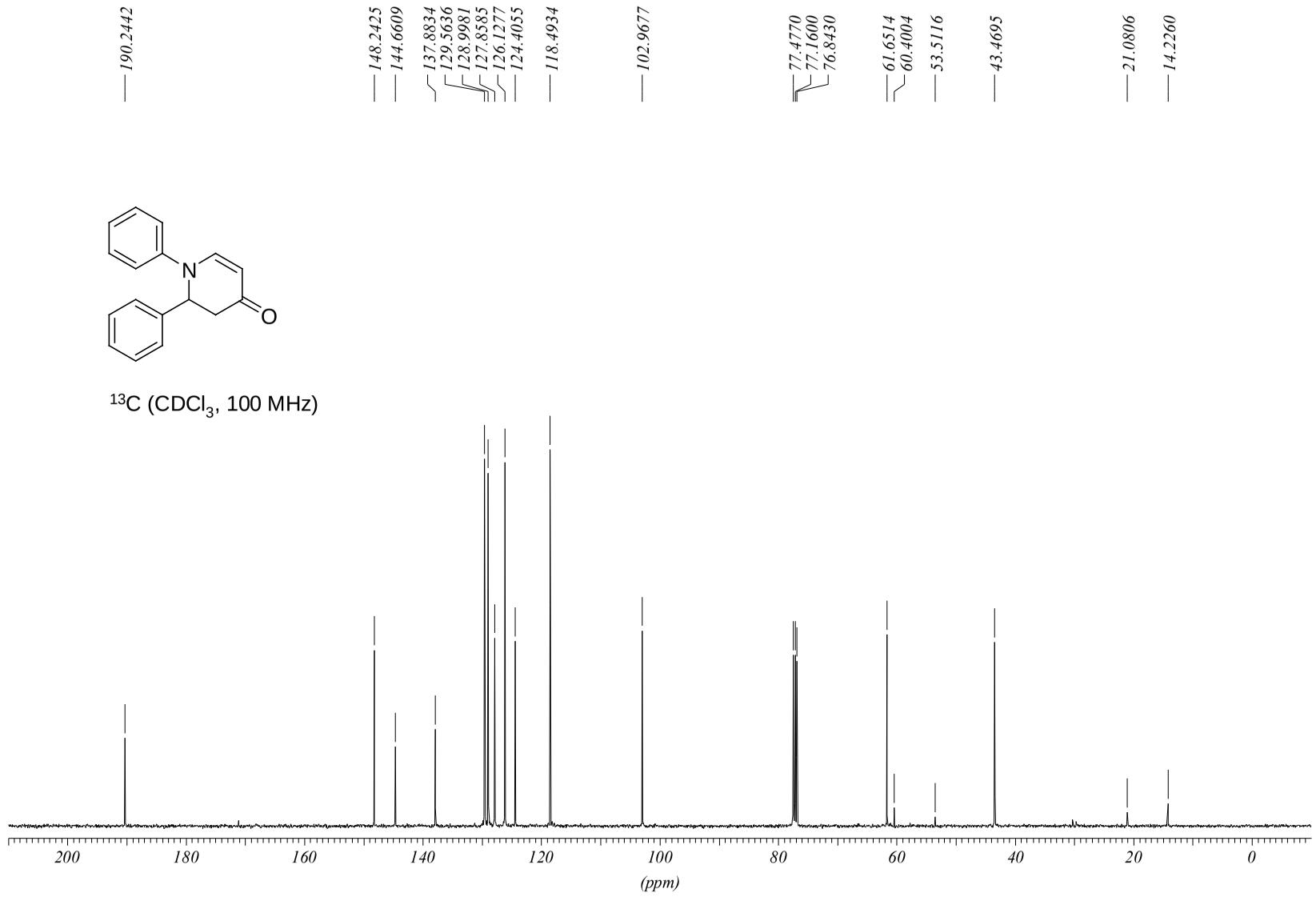
4.0956
4.0886
4.0703
4.0684
4.0501
4.0331
2.0525
1.3807
1.3630
1.3371
1.3195
1.2671
1.1850
1.1673
1.1496
1.1326
O
HN
CO2Et
1H (CDCl3, 400 MHz)
Integral
1.9655
0.9802
1.9625
2.0182
1.6606
1.3461
1.0344
3.3297
0.3275
2.0552
0.9583
0.6025
3.0000
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

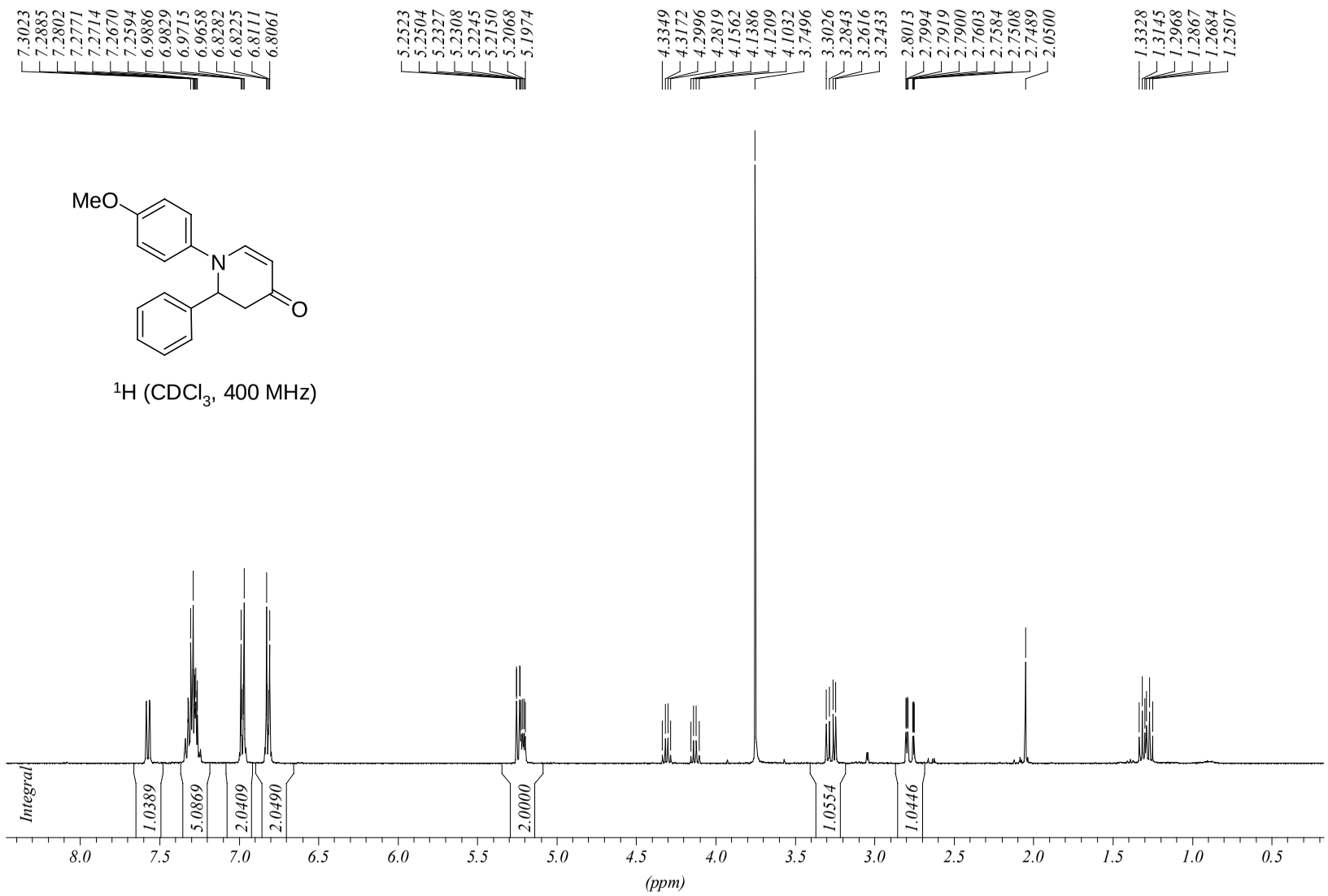

202.0941
201.4686
172.9191
172.6964
147.1543
146.8116
136.5639
136.0670
133.4365
133.3594
129.3237
128.8439
128.4583
128.3983
118.6648
114.0807
113.8922
77.4856
77.1600
76.8430
61.4886
61.3173
59.6465
59.0981
43.8637
43.1011
14.8086
14.2688
14.1317
13.9946
O
HN
CO2Et
13C (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

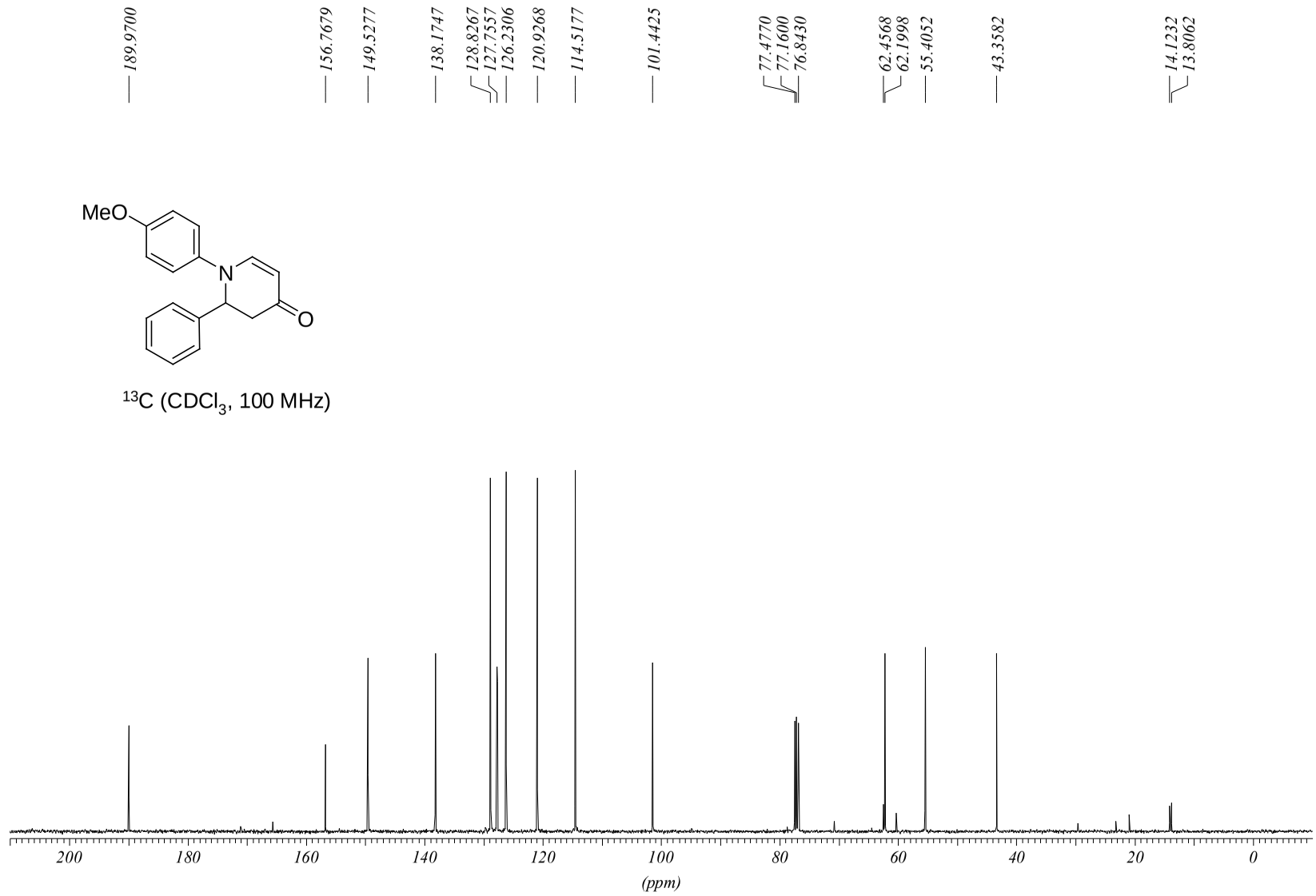

7.5839
7.5656
7.5473
7.4848
7.4652
7.4469
7.2600
6.7637
6.7581
6.7410
6.7360
6.7189
6.7139
6.7050
6.6804
6.6747
6.6634
6.6583
6.5901
6.5813
6.5762
6.5642
6.5592
4.3911
4.3747
4.3608
4.1221
4.1057
4.0880
4.0785
4.0703
4.0609
4.0205
4.0110
4.0028
3.9857
3.7117
3.7054
2.0323
1.3567
1.3390
1.3031
1.2854
1.2658
1.2475
1.1654
1.1616
1.1471
1.1433
1.1294
1.1256
OMe
O
HN
CO2Et
1H (CDCl3, 400 MHz)
Integral
2.0603
1.0216
2.0521
2.0473
0.6759
1.3624
1.0225
4.1797
3.0000
2.0754
2.4454
3.2613
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


201.8713
201.4515
173.1676
172.8848
153.0321
152.9464
141.0879
140.8737
136.5810
136.0669
133.3079
133.2394
128.7839
128.3812
128.3383
116.0086
115.6915
114.7319
77.4856
77.1600
76.8430
61.3172
61.1459
60.4176
55.6365
43.8465
43.2639
29.7089
21.0463
14.6972
14.2174
14.1317
14.0974
13.7204
OMe
O
HN
CO2Et
13C (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

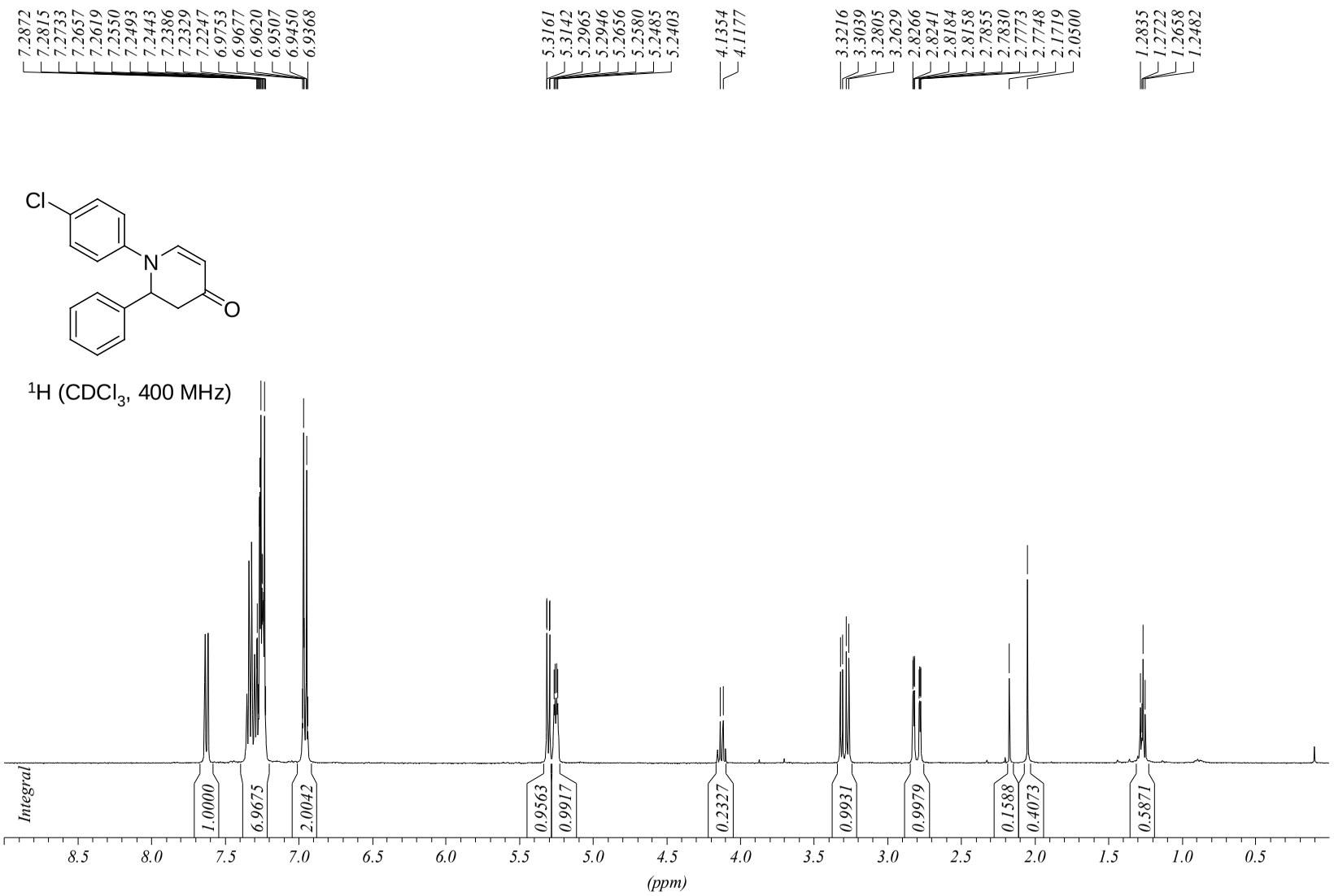

7.7064
7.7039
7.6868
7.6843
7.3314
7.3213
7.3162
7.3023
7.2998
7.2903
7.2809
7.2771
7.2727
7.1136
7.0454
7.0429
7.0239
7.0214
5.3104
5.3079
5.2908
5.2877
4.1550
4.1373
4.1196
4.1013
3.7402
3.3418
3.3241
3.3007
3.2831
2.8253
2.8228
2.8177
2.8152
2.7843
2.7818
2.7767
2.7742
2.0500
1.4458
1.2842
1.2665
1.2488
N
O
1H (CDCl3, 400 MHz)
Integral
1.0000
7.1132
1.0664
2.0326
2.1731
1.0454
1.0096
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

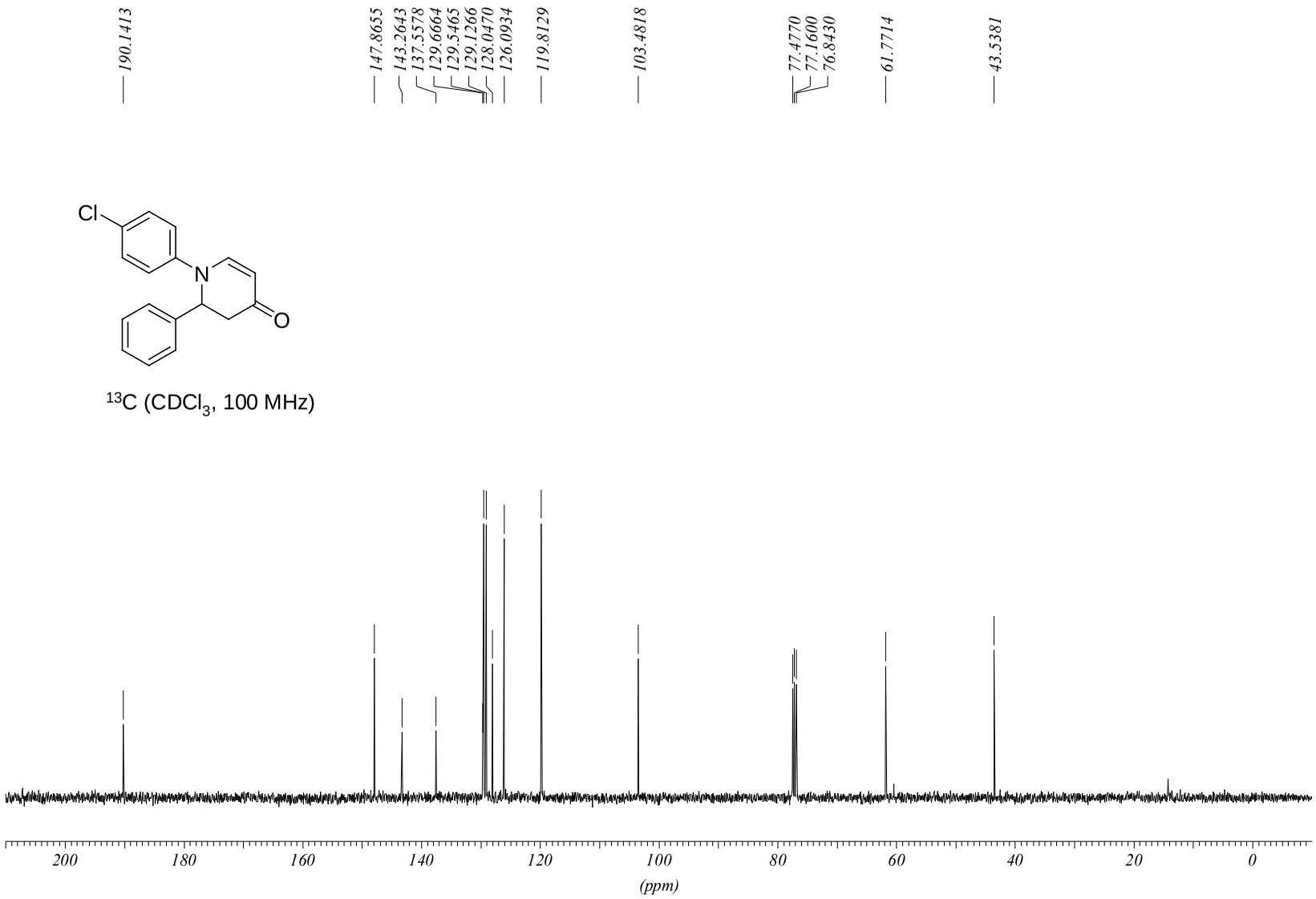

190.2442
148.2425
144.6609
137.8834
129.5636
128.9981
127.8585
126.1277
124.4055
118.4934
102.9677
77.4770
77.1600
76.8430
61.6514
60.4004
53.5116
43.4695
21.0806
14.2260
N
O
13C (CDCl3, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
(ppm)


7.3023
7.2885
7.2802
7.2771
7.2714
7.2670
7.2594
6.9886
6.9829
6.9715
6.9658
6.8282
6.8225
6.8111
6.8061
5.2523
5.2504
5.2327
5.2308
5.2245
5.2150
5.2068
5.1974
4.3349
4.3172
4.2996
4.2819
4.1562
4.1386
4.1209
4.1032
3.7496
3.3026
3.2843
3.2616
3.2433
2.8013
2.7994
2.7919
2.7900
2.7603
2.7584
2.7508
2.7489
2.0500
1.3328
1.3145
1.2968
1.2867
1.2684
1.2507
MeO
N
O
1H (CDCl3, 400 MHz)
Integral
1.0389
5.0869
2.0409
2.0490
2.0000
1.0554
1.0446
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

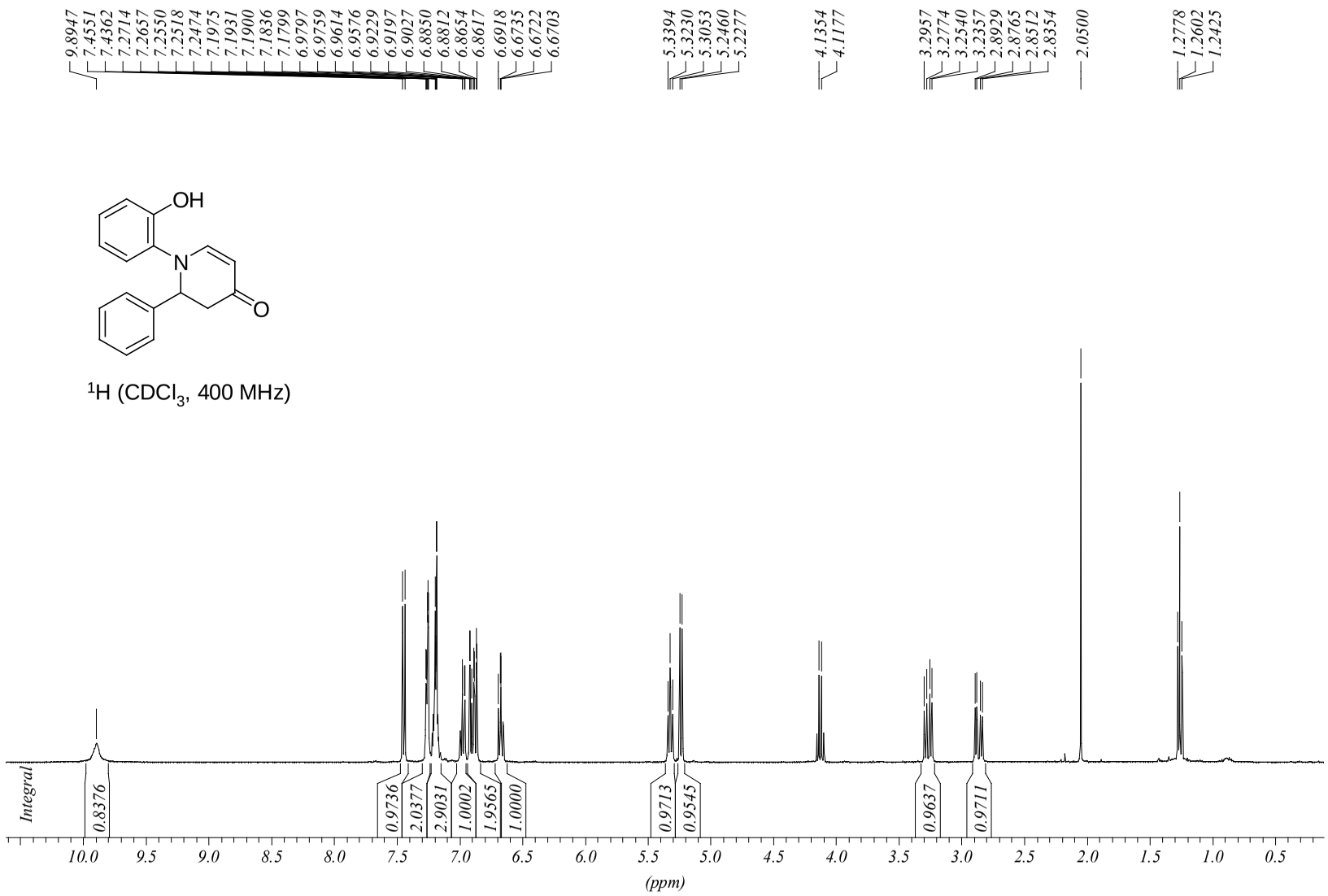


^{13}C ($CDCl_3$, 100 MHz)

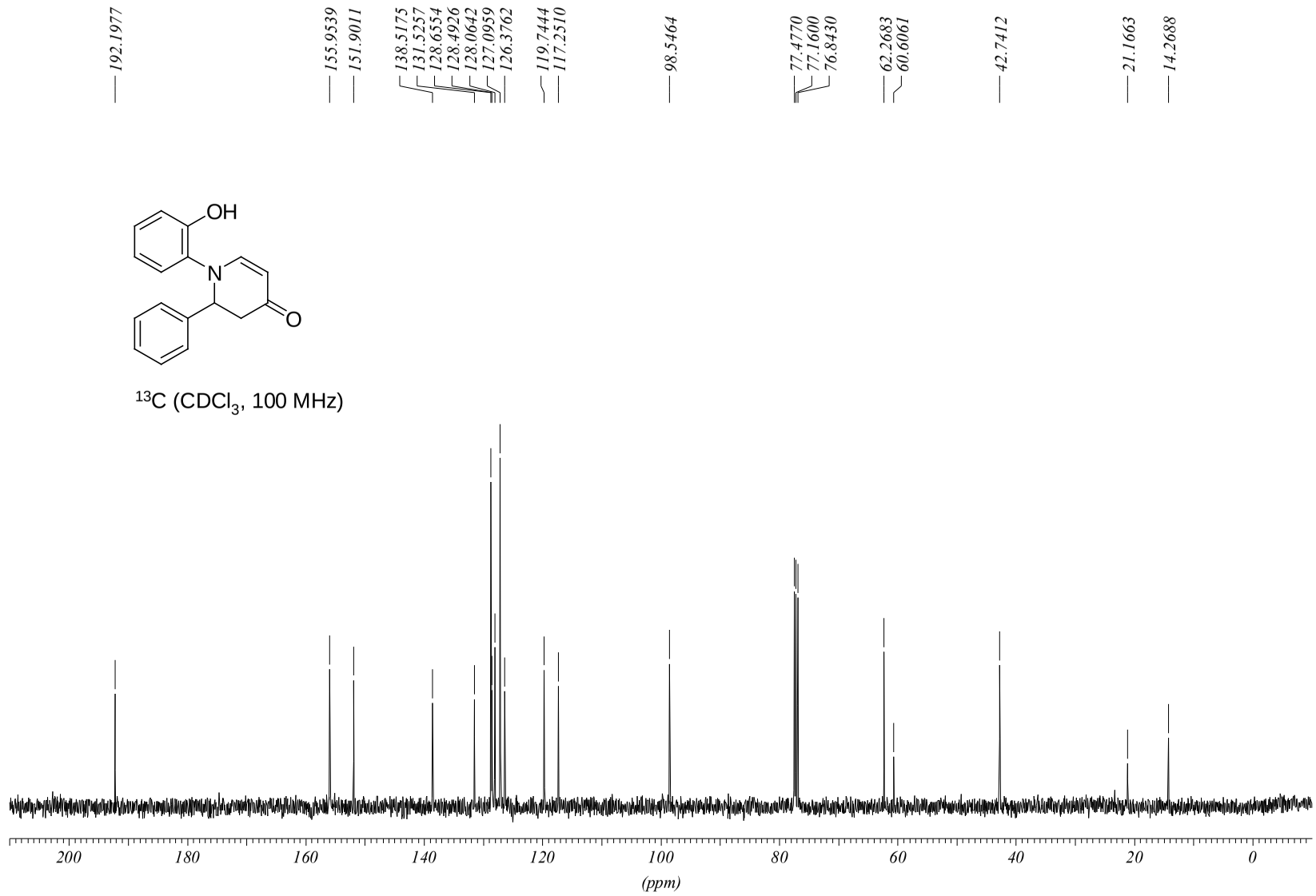

7.2872
7.2815
7.2733
7.2657
7.2619
7.2550
7.2493
7.2443
7.2386
7.2329
7.2247
6.9753
6.9677
6.9620
6.9507
6.9450
6.9368
5.3161
5.3142
5.2965
5.2946
5.2656
5.2580
5.2485
5.2403
4.1354
4.1177
3.3216
3.3039
3.2805
3.2629
2.8266
2.8241
2.8184
2.8158
2.7855
2.7830
2.7773
2.7748
2.1719
2.0500
1.2835
1.2722
1.2658
1.2482
Cl
N
O
1H (CDCl3, 400 MHz)
Integral
1.0000
6.9675
2.0042
0.9563
0.9917
0.2327
0.9931
0.9979
0.1588
0.4073
0.5871
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

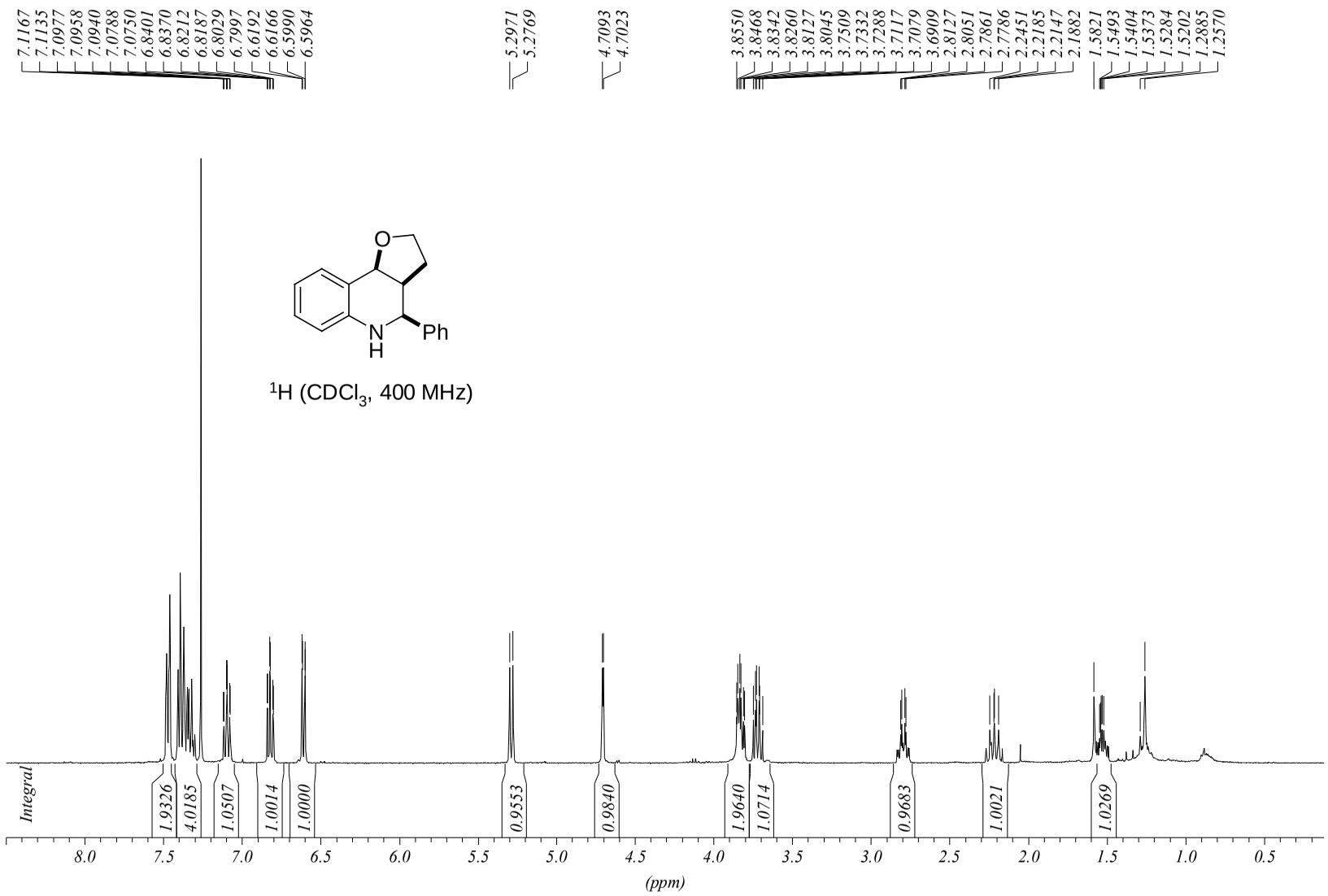


^{13}C ($CDCl_3$, 100 MHz)

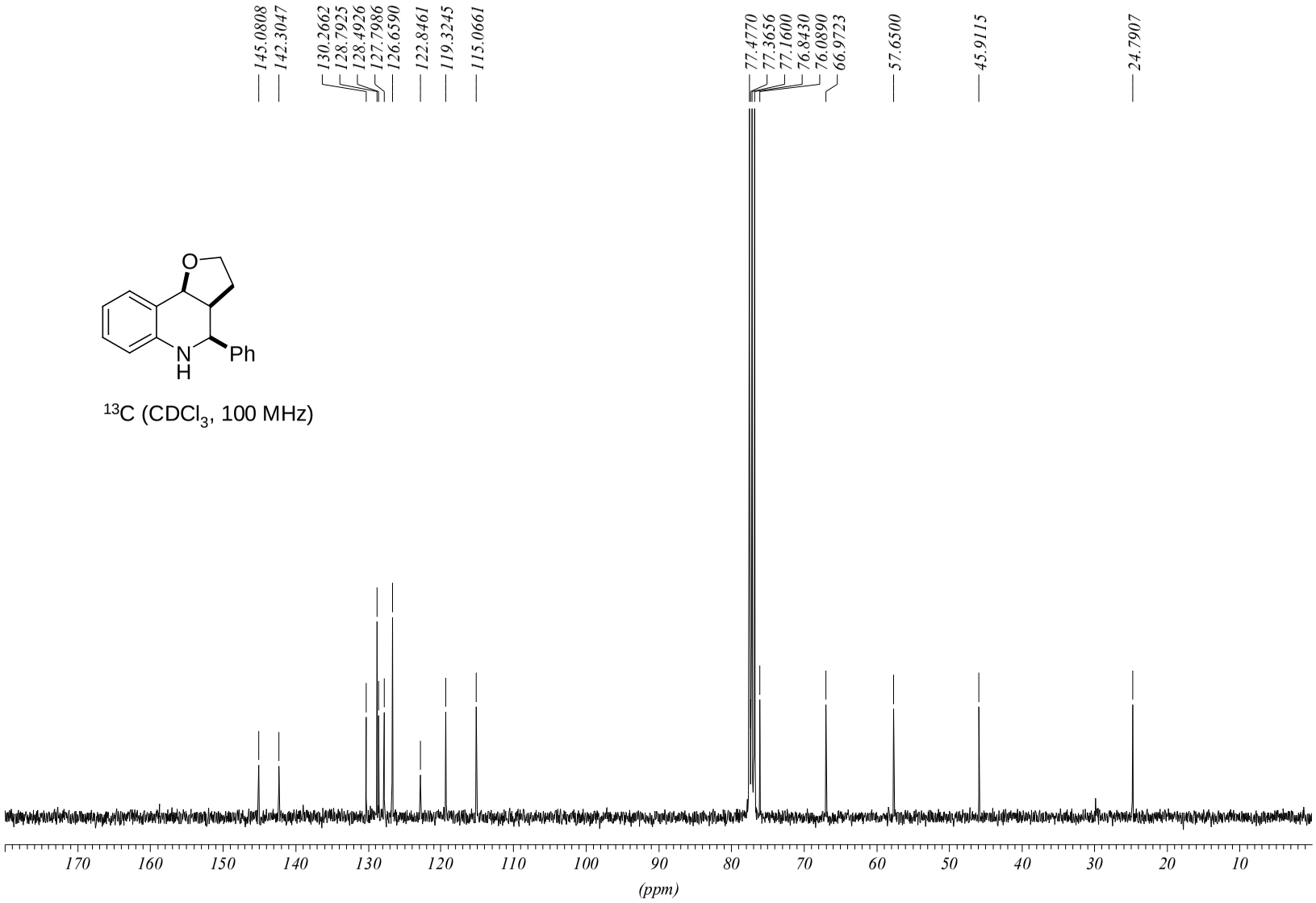


^{1}H ($CDCl_3$, 400 MHz)

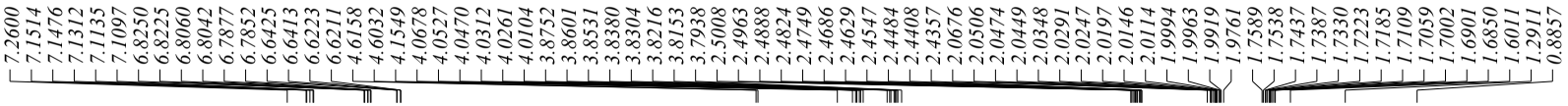

192.1977
155.9539
151.9011
138.5175
131.5257
128.6554
128.4926
128.0642
127.0959
126.3762
119.7444
117.2510
98.5464
77.4770
77.1600
76.8430
62.2683
60.6061
42.7412
21.1663
14.2688
OH
N
O
^{13}C (CDCl$_3$, 100 MHz)
200
180
160
140
120
100
80
60
40
20
0
(ppm)

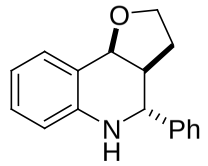


^{1}H ($CDCl_3$, 400 MHz)

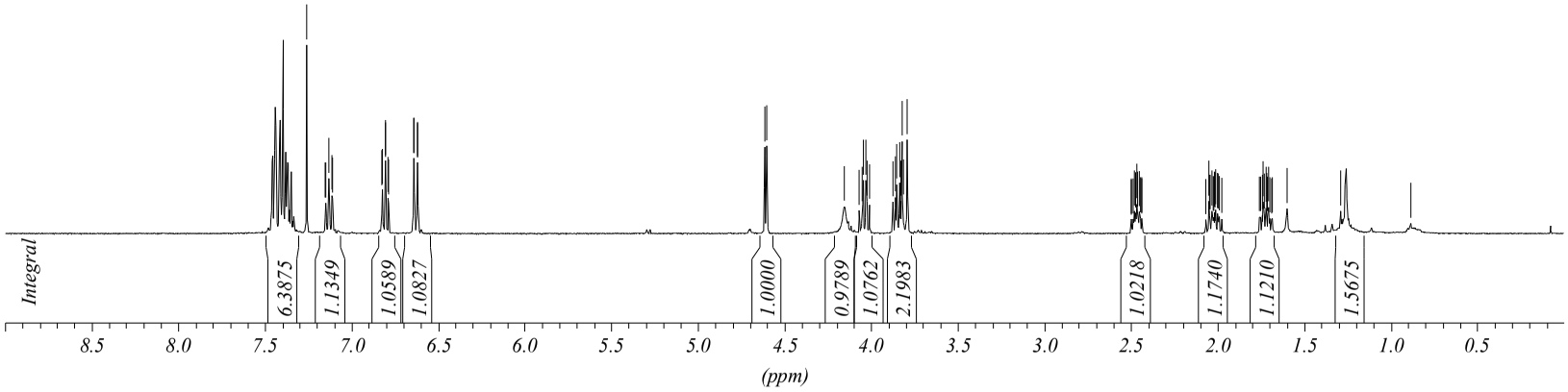


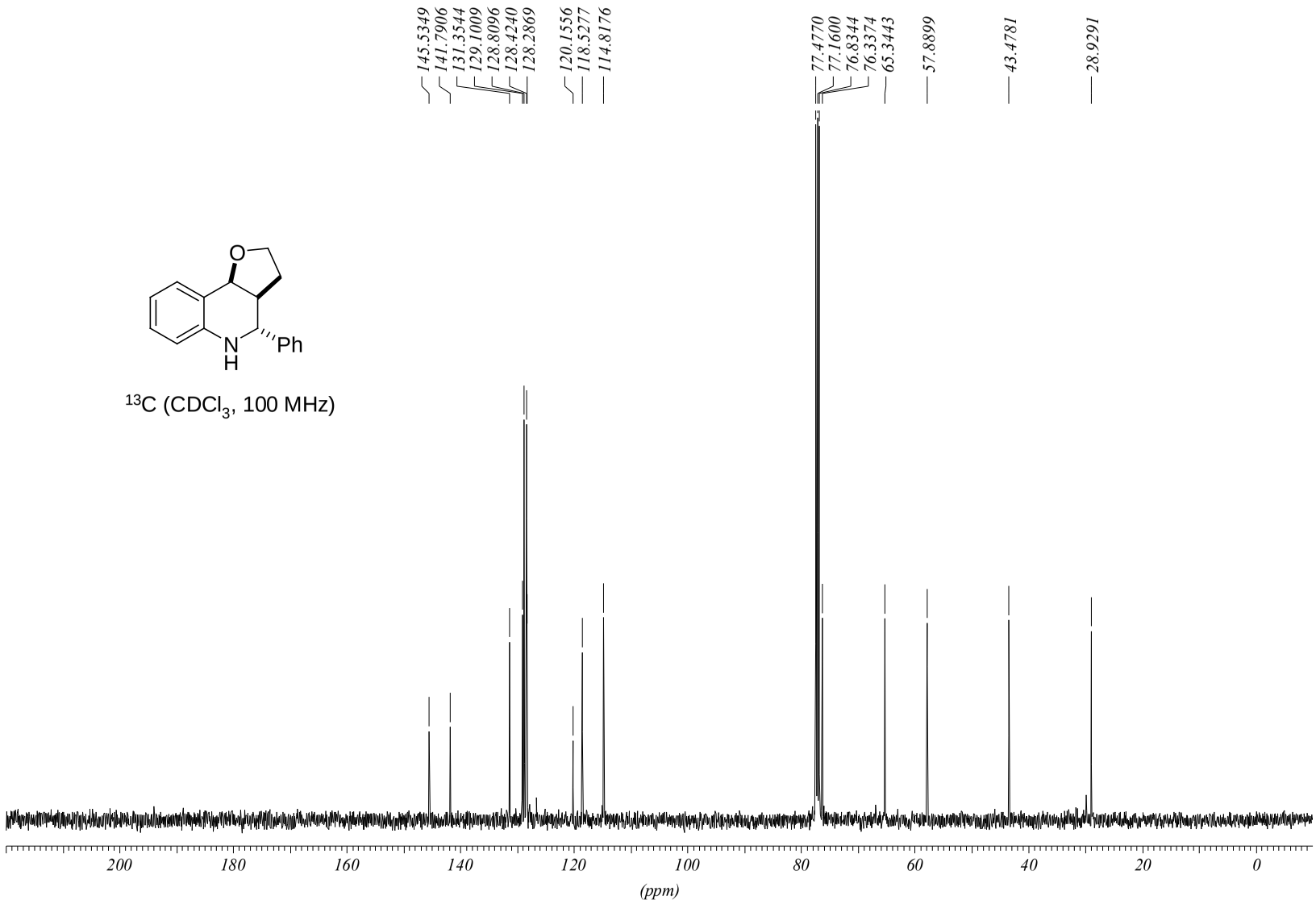
^{13}C ($CDCl_3$, 100 MHz)



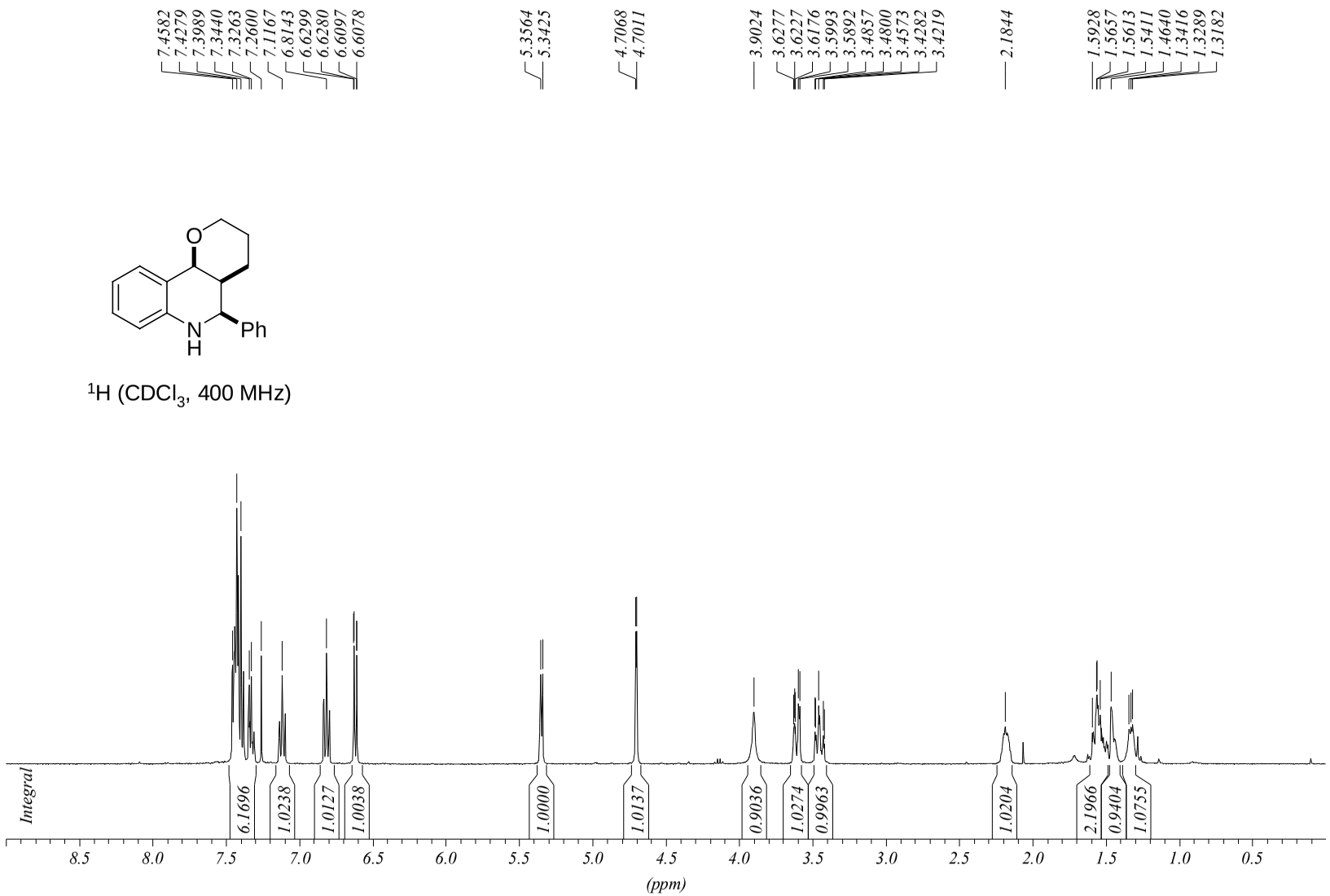


^{1}H ($CDCl_3$, 400 MHz)

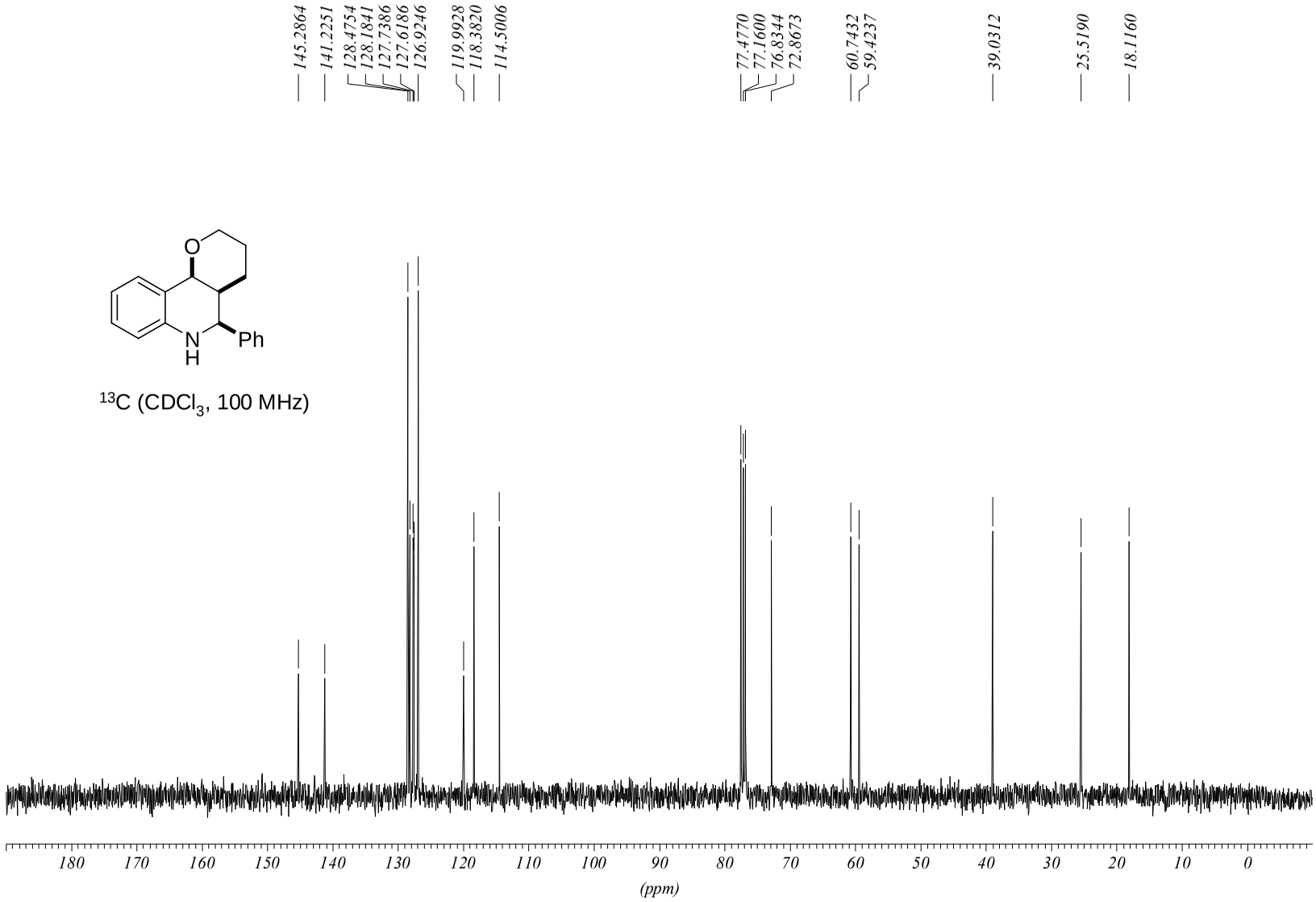


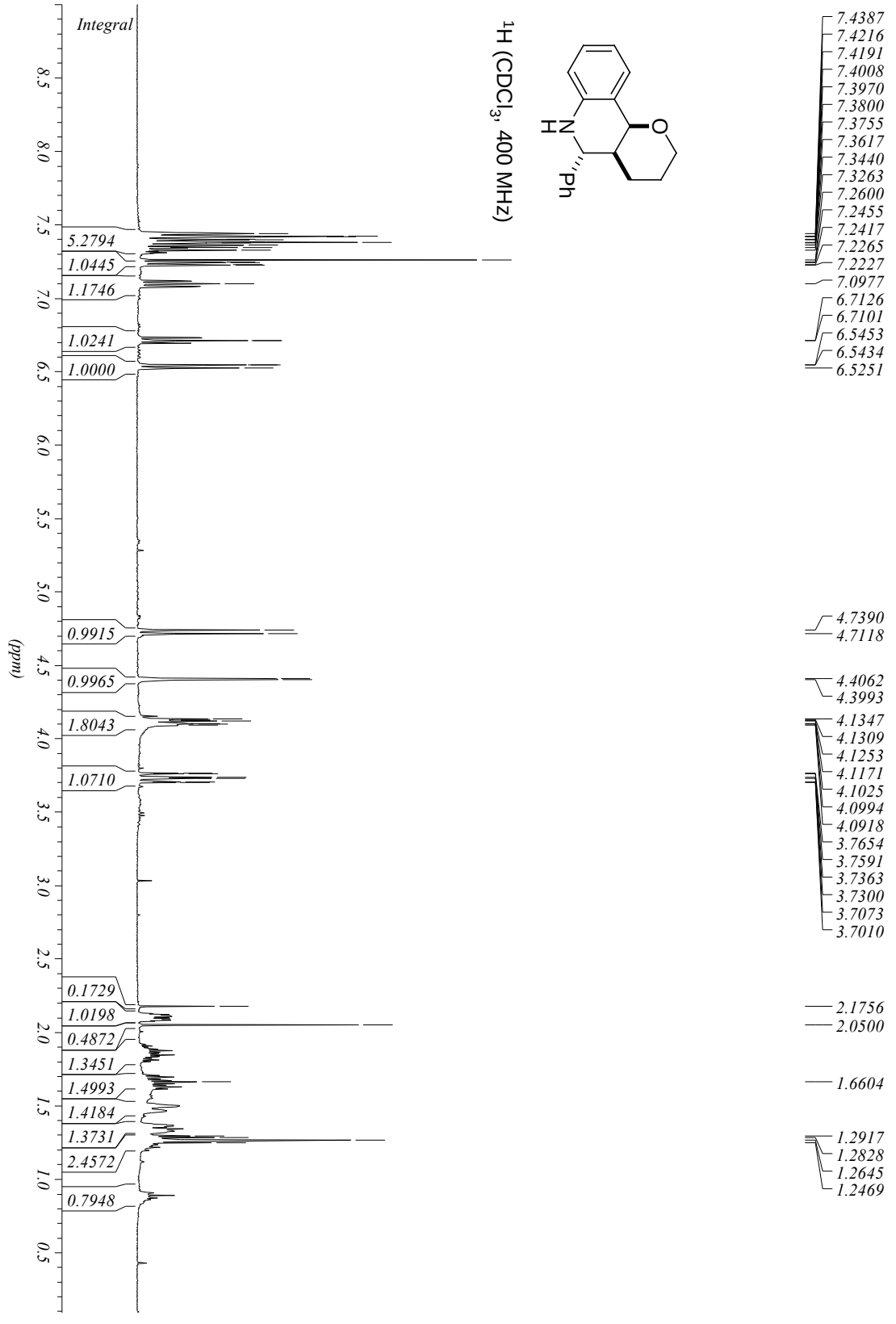


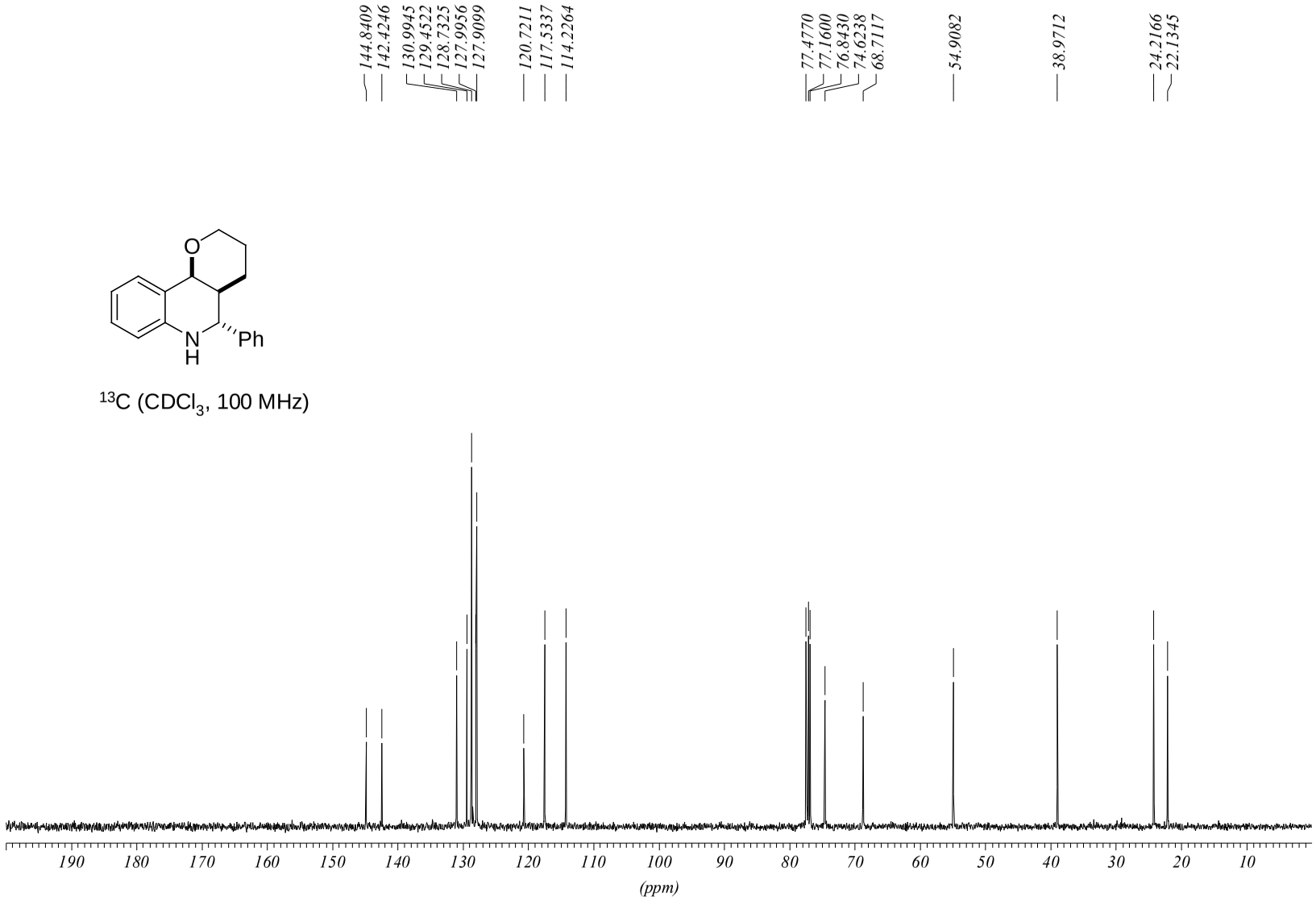
^{13}C ($CDCl_3$, 100 MHz)

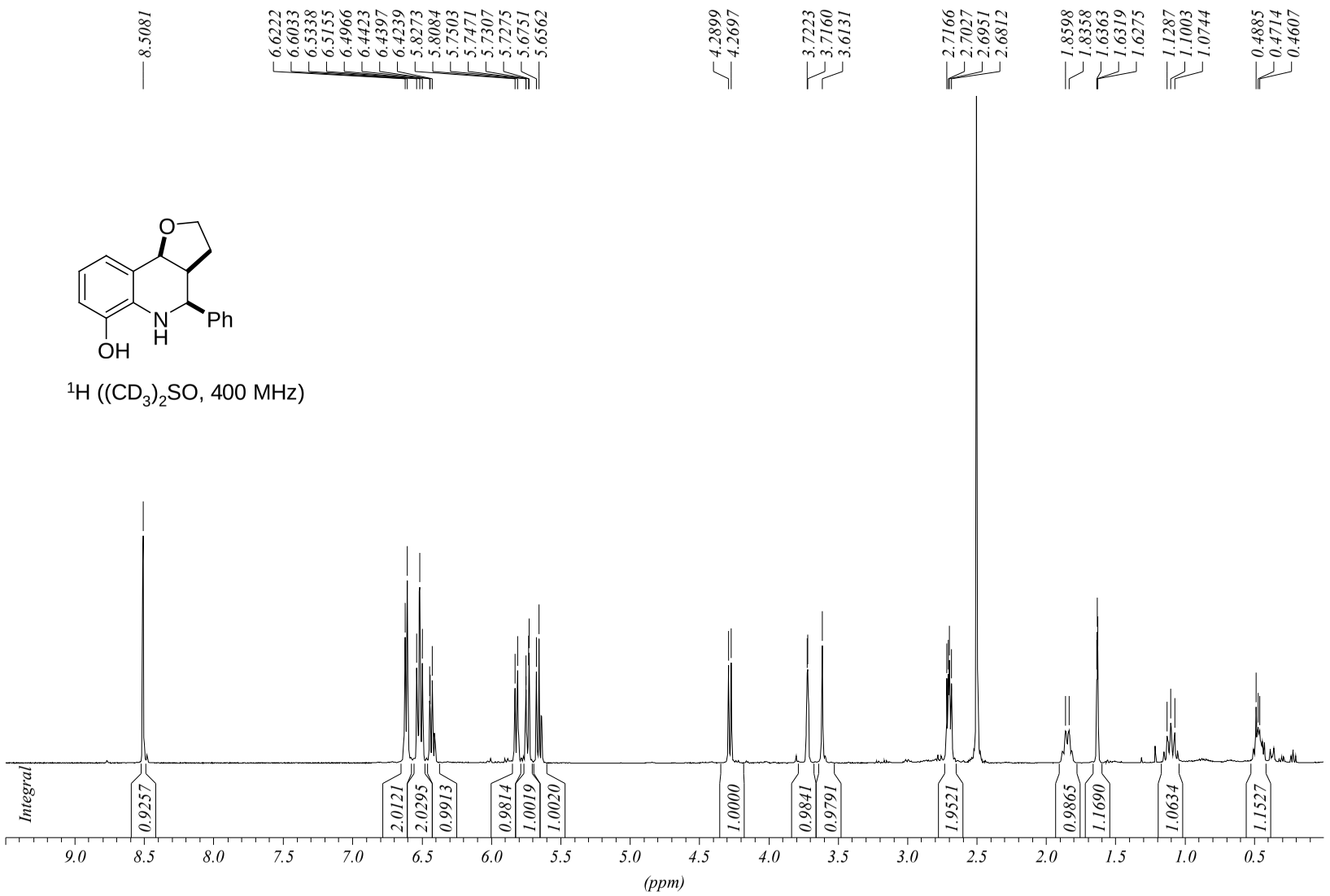


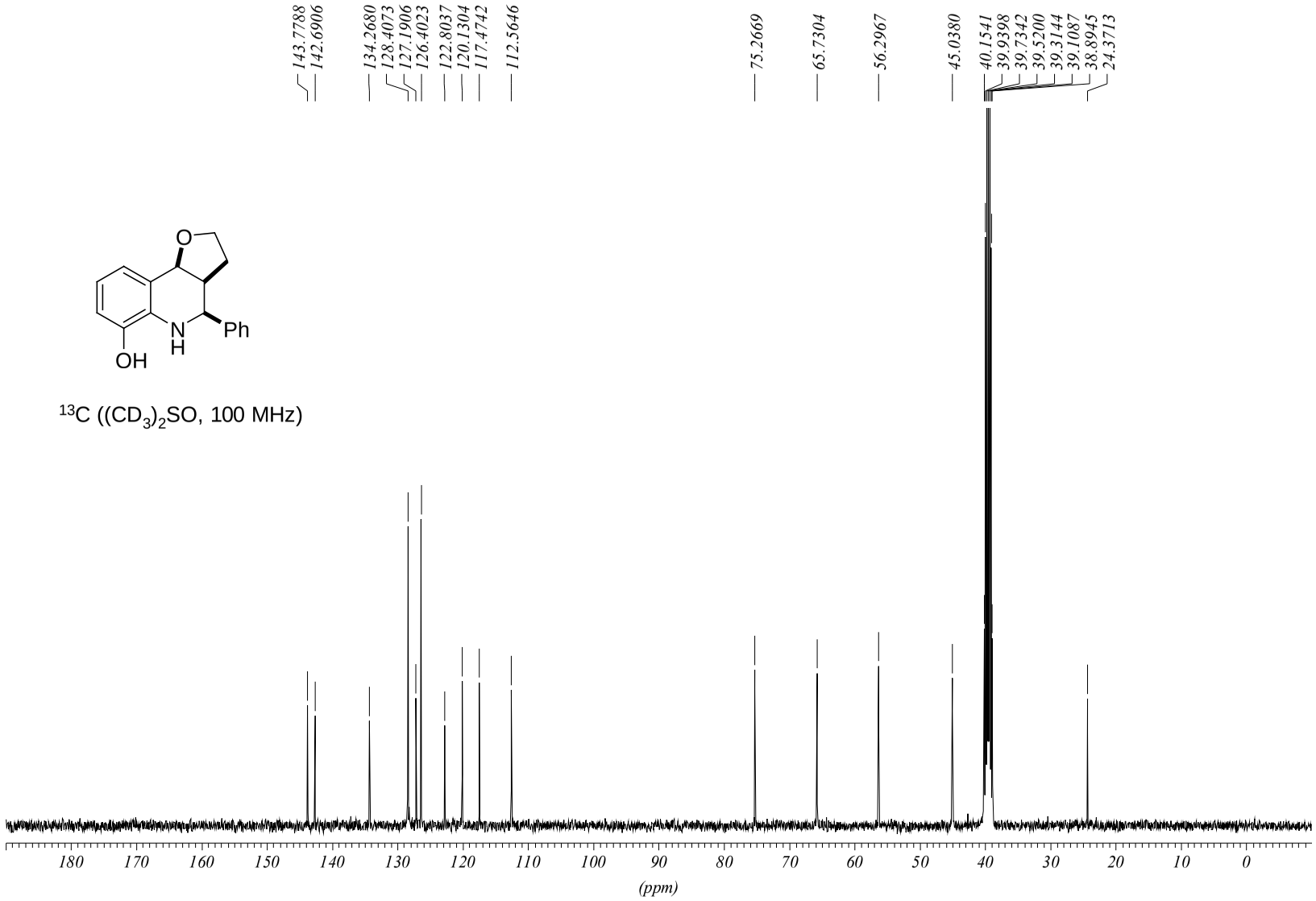
^{1}H ($CDCl_3$, 400 MHz)


145.2864
141.2251
128.4754
128.1841
127.7386
127.6186
126.9246
119.9928
118.3820
114.5006
77.4770
77.1600
76.8344
72.8673
60.7432
59.4237
39.0312
25.5190
18.1160
O
N
H
Ph
13C (CDCl3, 100 MHz)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

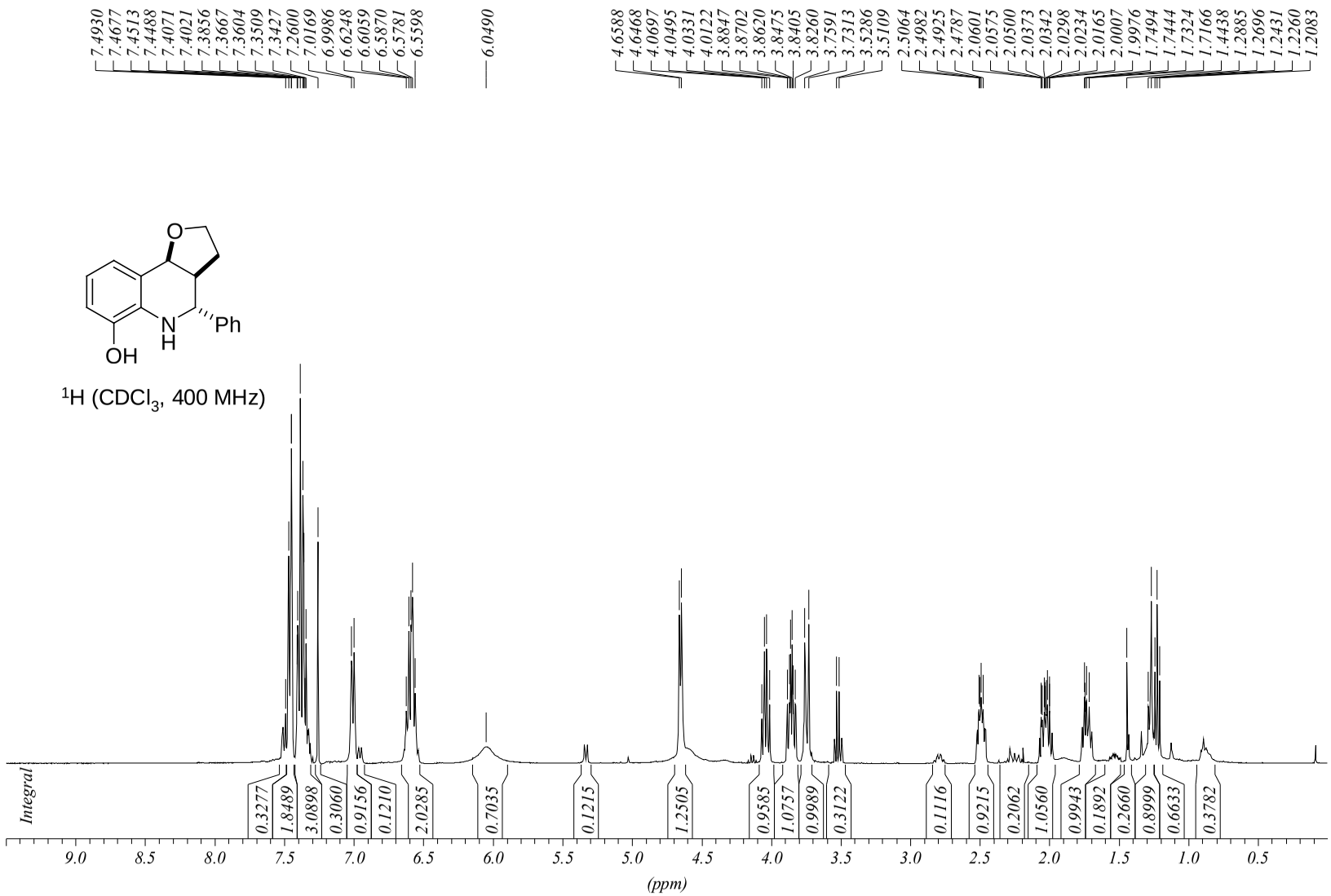

^{1}H (CDCl$_3$, 400 MHz)
Integral
(ppm)
5.2794
1.0445
1.1746
1.0241
1.0000
0.9915
0.9965
1.8043
1.0710
0.1729
1.0198
0.4872
1.3451
1.4993
1.4184
1.3731
2.4572
0.7948
7.4387
7.4216
7.4191
7.4008
7.3970
7.3800
7.3755
7.3617
7.3440
7.3263
7.2600
7.2455
7.2417
7.2265
7.2227
7.0977
6.7126
6.7101
6.5453
6.5434
6.5251
4.7390
4.7118
4.4062
4.3993
4.1347
4.1309
4.1253
4.1171
4.1025
4.0994
4.0918
3.7654
3.7591
3.7363
3.7300
3.7073
3.7010
2.1756
2.0500
1.6604
1.2917
1.2828
1.2645
1.2469
N
H
O
Ph

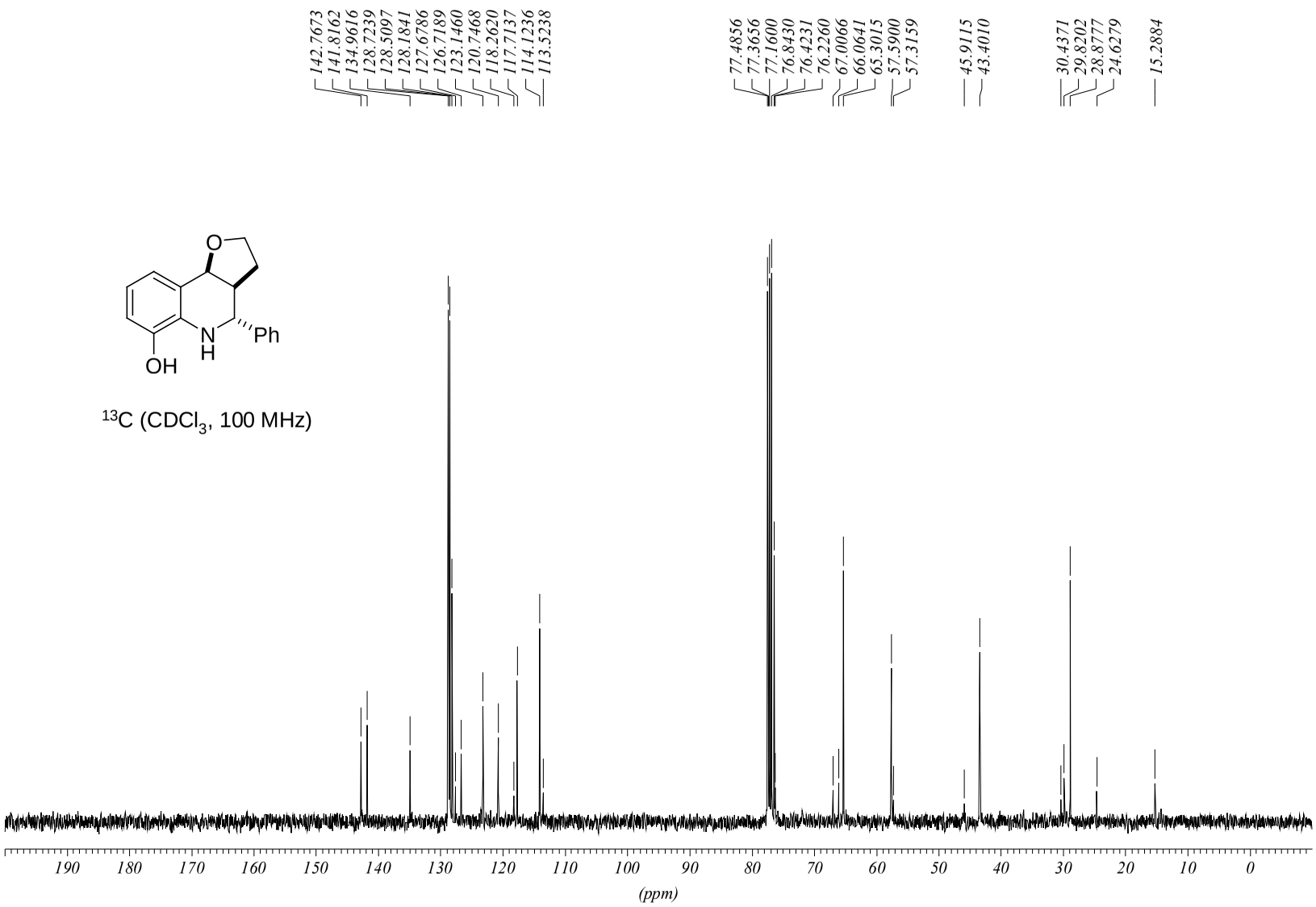

144.8409
142.4246
130.9945
129.4522
128.7325
127.9956
127.9099
120.7211
117.5337
114.2264
77.4770
77.1600
76.8430
74.6238
68.7117
54.9082
38.9712
24.2166
22.1345
O
N
H
Ph
13C (CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
(ppm)

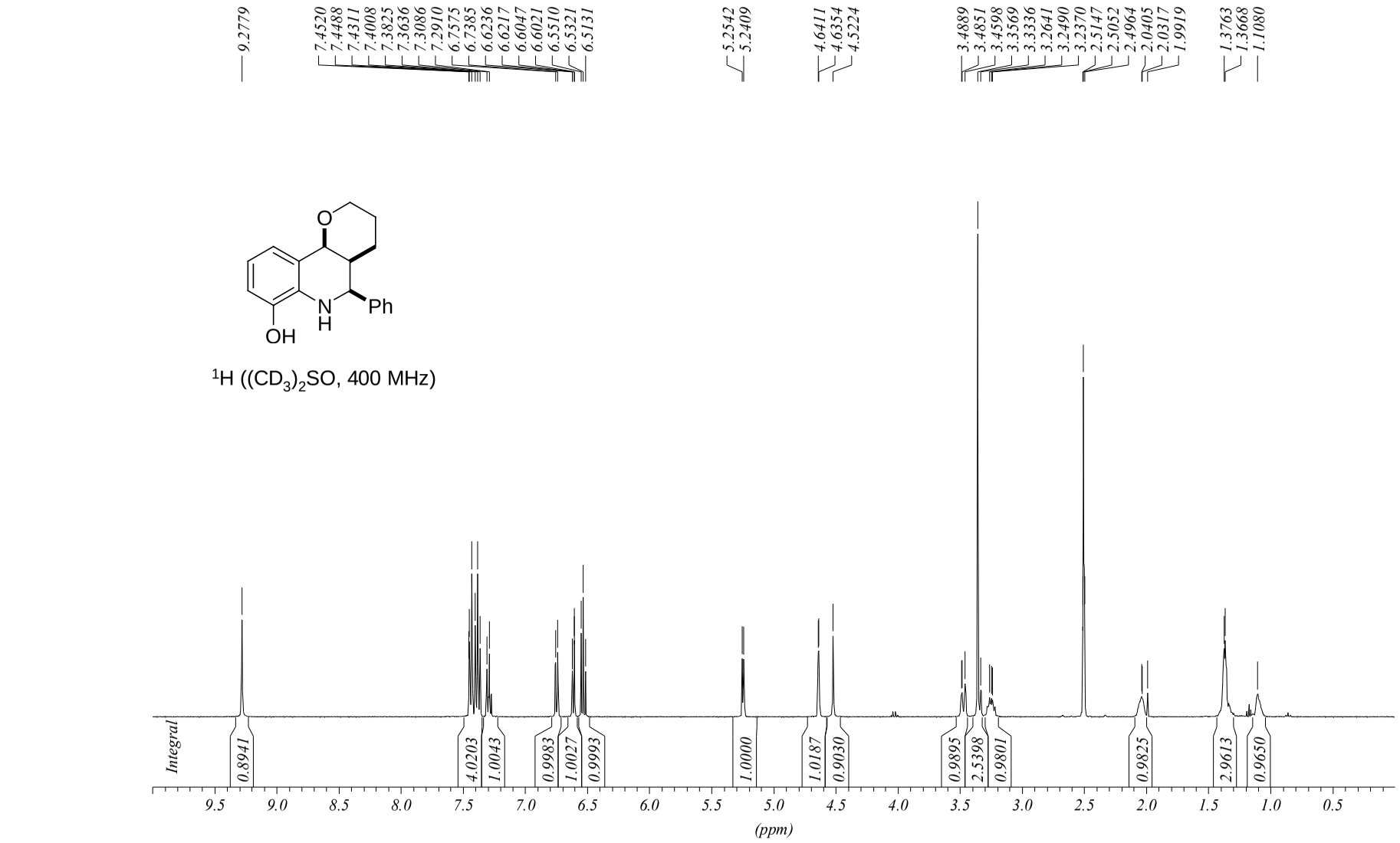

8.5081
6.6222
6.6033
6.5338
6.5155
6.4966
6.4423
6.4397
6.4239
5.8273
5.8084
5.7503
5.7471
5.7307
5.7275
5.6751
5.6562
4.2899
4.2697
3.7223
3.7160
3.6131
2.7166
2.7027
2.6951
2.6812
1.8598
1.8358
1.6363
1.6319
1.6275
1.1287
1.1003
1.0744
0.4885
0.4714
0.4607
O
N
H
Ph
OH
1H ((CD3)2SO, 400 MHz)
Integral
0.9257
2.0121
2.0295
0.9913
0.9814
1.0019
1.0020
1.0000
0.9841
0.9791
1.9521
0.9865
1.1690
1.0634
1.1527
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

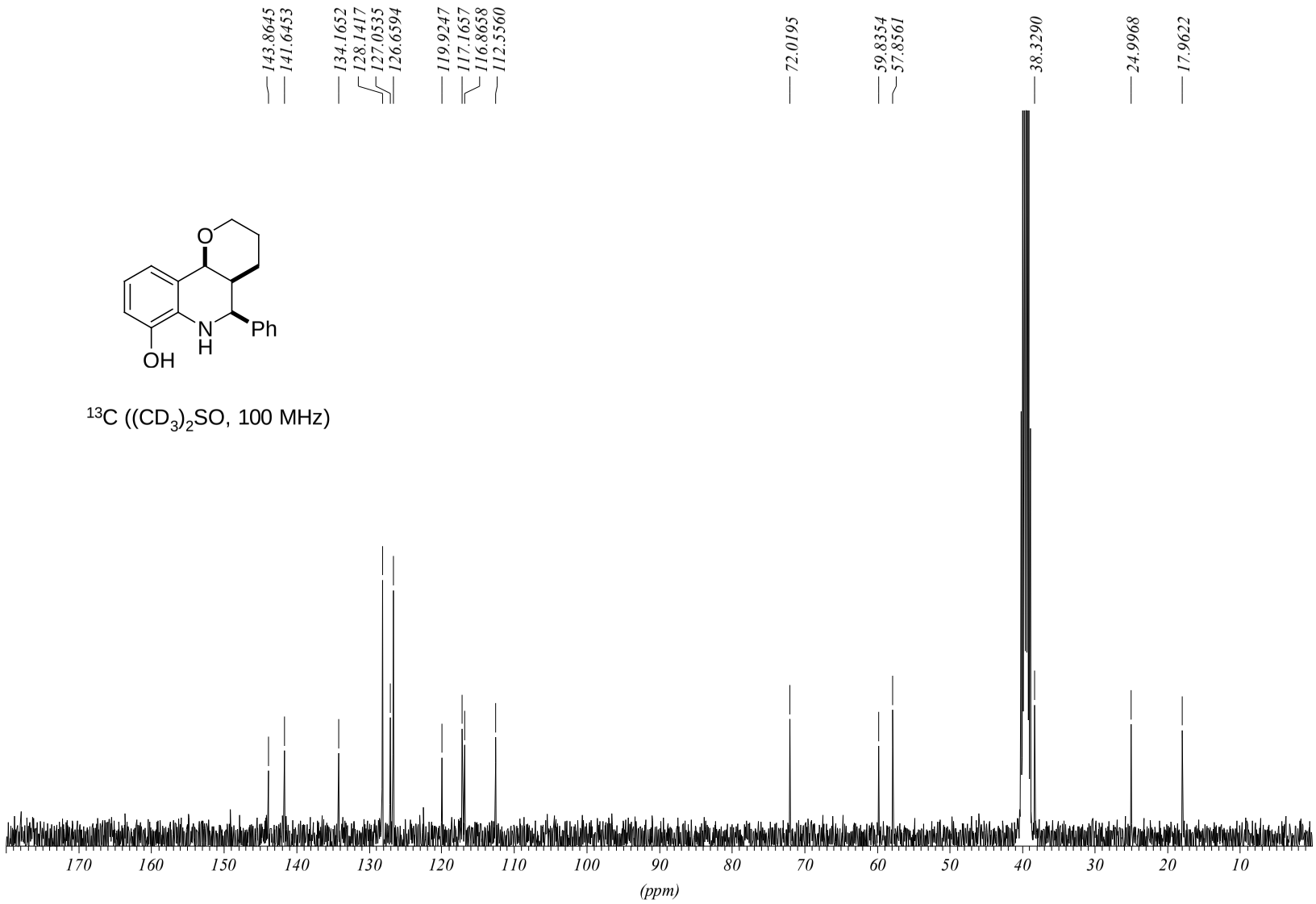


^{13}C ($(CD_3)_2SO$, 100 MHz)

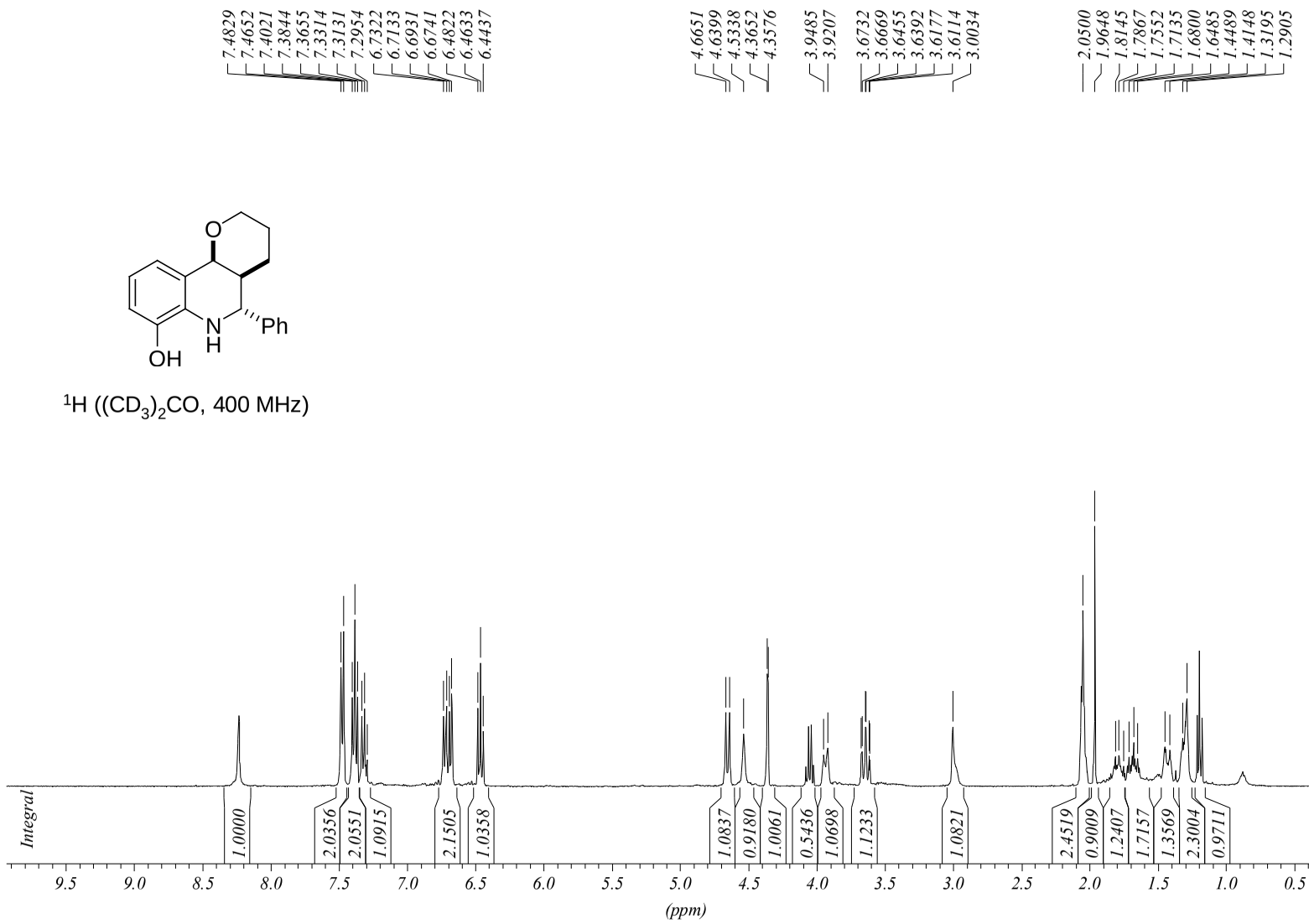

7.4930
7.4677
7.4513
7.4488
7.4071
7.4021
7.3856
7.3667
7.3604
7.3509
7.3427
7.2600
7.0169
6.9986
6.6248
6.6059
6.5870
6.5781
6.5598
6.0490
4.6588
4.6468
4.0697
4.0495
4.0331
4.0122
3.8847
3.8702
3.8620
3.8475
3.8405
3.8260
3.7591
3.7313
3.5286
3.5109
2.5064
2.4982
2.4925
2.4787
2.0601
2.0575
2.0500
2.0373
2.0342
2.0298
2.0234
2.0165
2.0007
1.9976
1.7494
1.7444
1.7324
1.7166
1.4438
1.2885
1.2696
1.2431
1.2260
1.2083
O
N
H
Ph
OH
1H (CDCl3, 400 MHz)
Integral
0.3277
1.8489
3.0898
0.3060
0.9156
0.1210
2.0285
0.7035
0.1215
1.2505
0.9585
1.0757
0.9989
0.3122
0.1116
0.9215
0.2062
1.0560
0.9943
0.1892
0.2660
0.8999
0.6633
0.3782
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


142.7673
141.8162
134.9616
128.7239
128.5097
128.1841
127.6786
126.7189
123.1460
120.7468
118.2620
117.7137
114.1236
113.5238
77.4856
77.3656
77.1600
76.8430
76.4231
76.2260
67.0066
66.0641
65.3015
57.5900
57.3159
45.9115
43.4010
30.4371
29.8202
28.8777
24.6279
15.2884
O
N
H
Ph
OH
13C (CDCl3, 100 MHz)
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

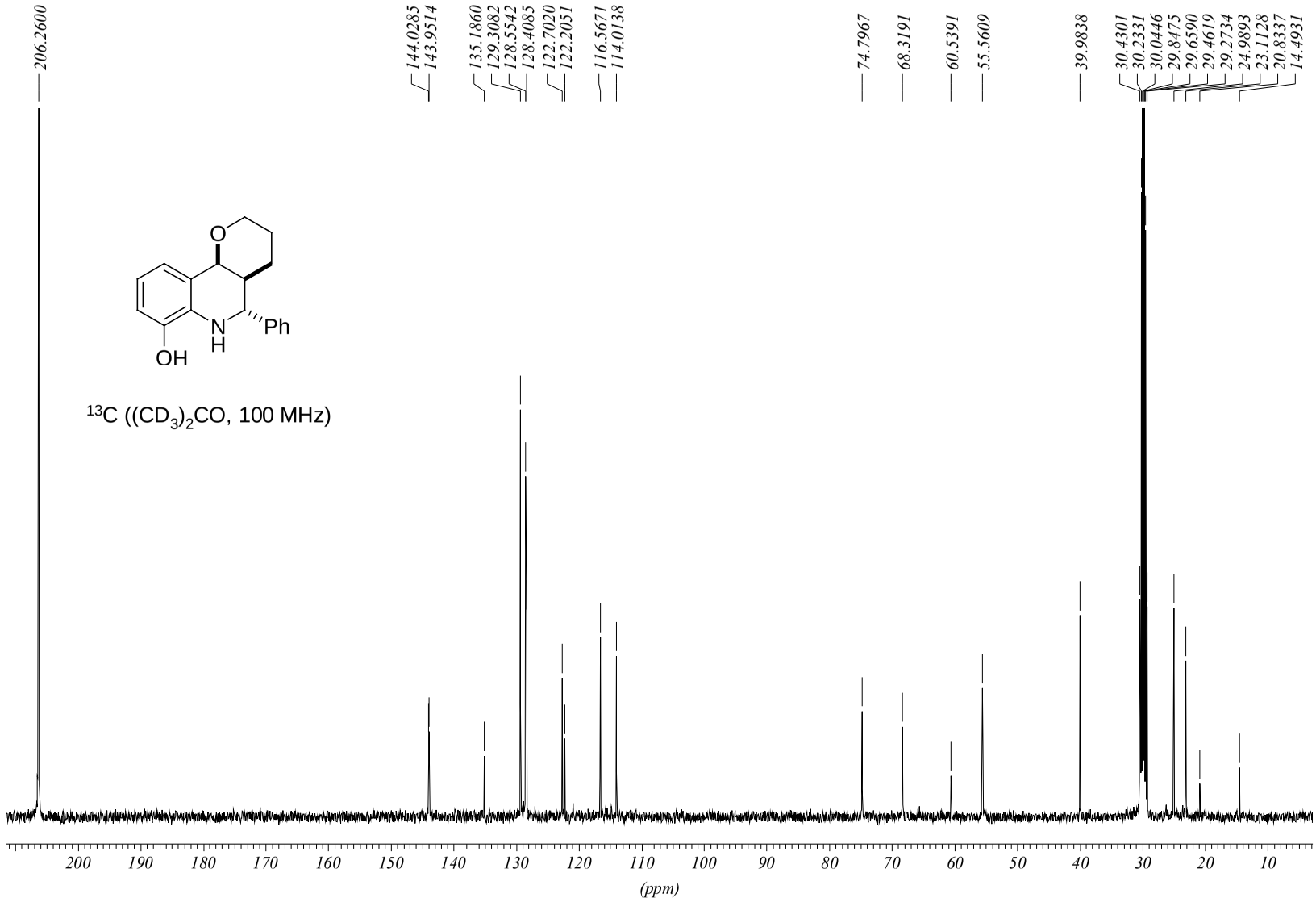

9.2779
7.4520
7.4488
7.4311
7.4008
7.3825
7.3636
7.3086
7.2910
6.7575
6.7385
6.6236
6.6217
6.6047
6.6021
6.5510
6.5321
6.5131
5.2542
5.2409
4.6411
4.6354
4.5224
3.4889
3.4851
3.4598
3.3569
3.3336
3.2641
3.2490
3.2370
2.5147
2.5052
2.4964
2.0405
2.0317
1.9919
1.3763
1.3668
1.1080
O
N
H
Ph
OH
1H ((CD3)2SO, 400 MHz)
Integral
0.8941
4.0203
1.0043
0.9983
1.0027
0.9993
1.0000
1.0187
0.9030
0.9895
2.5398
0.9801
0.9825
2.9613
0.9650
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

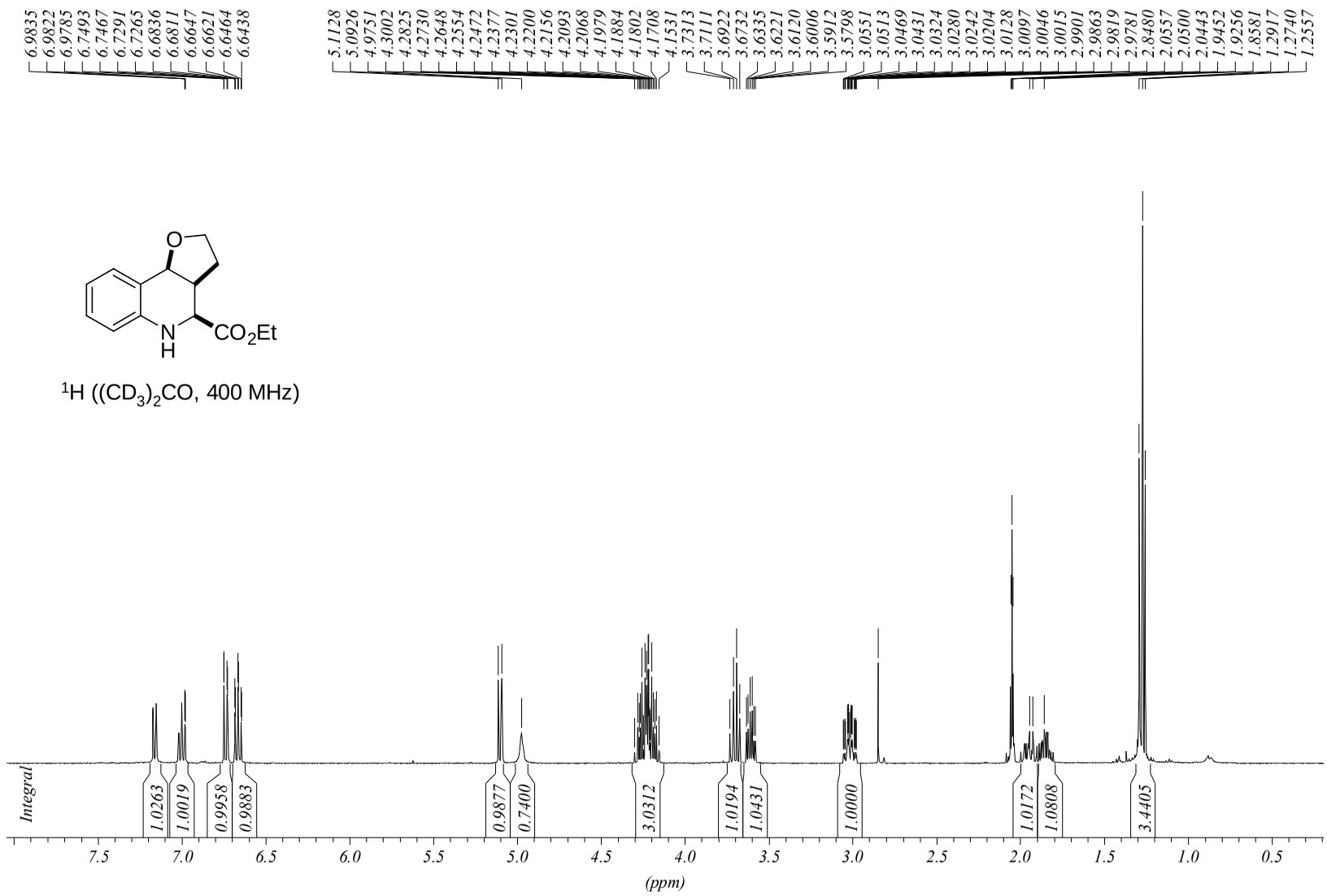


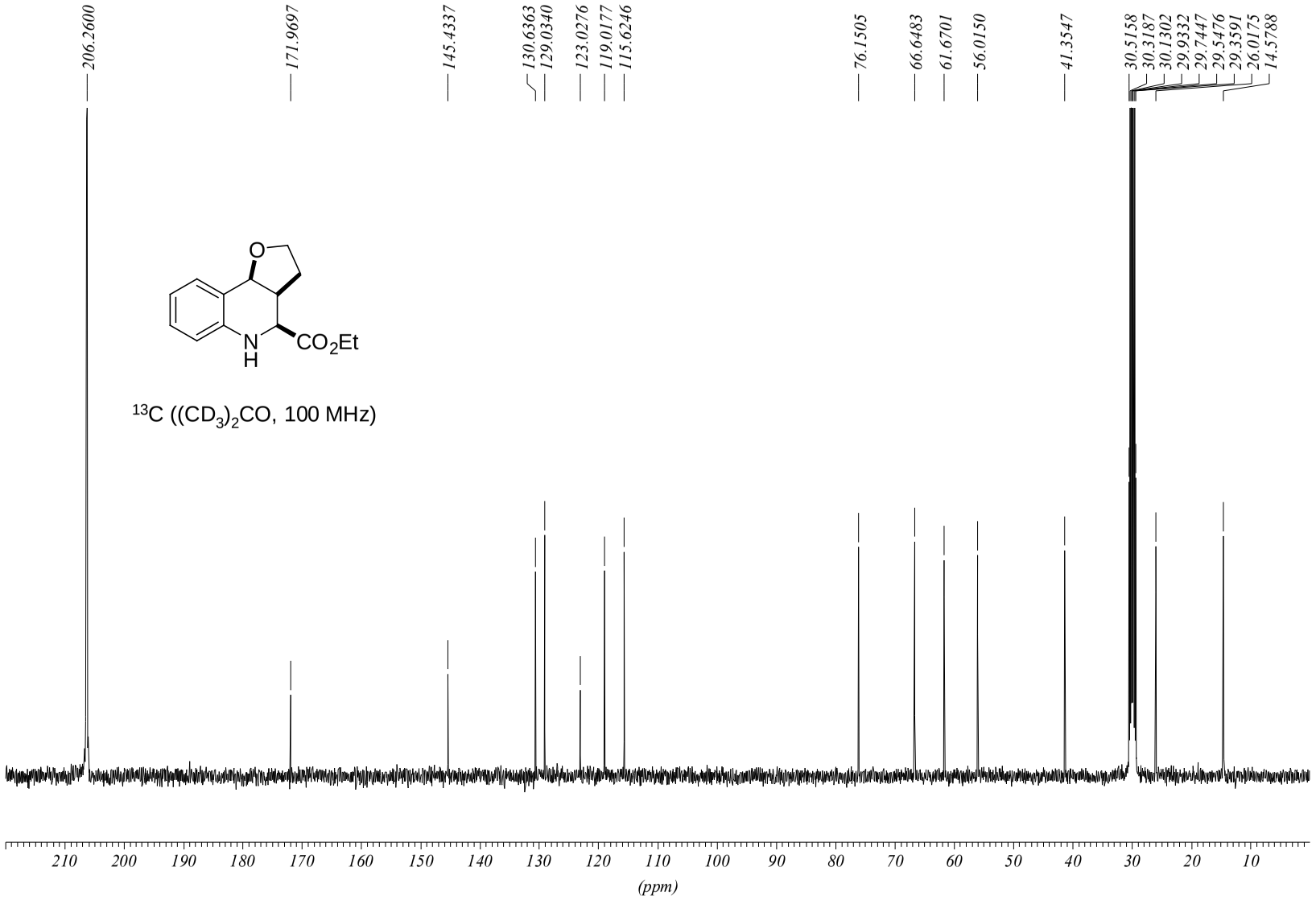
^{13}C ($(CD_3)_2SO$, 100 MHz)

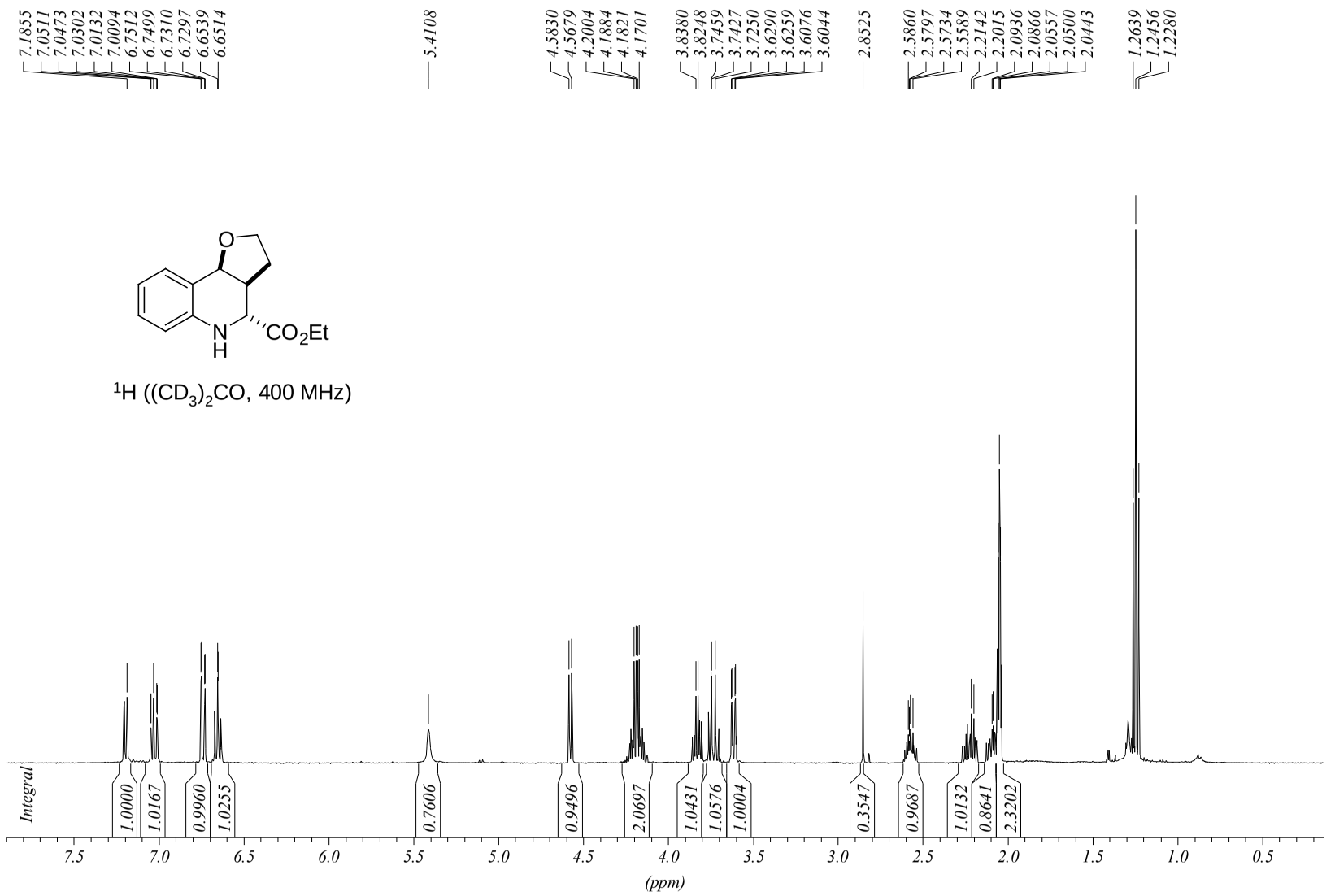


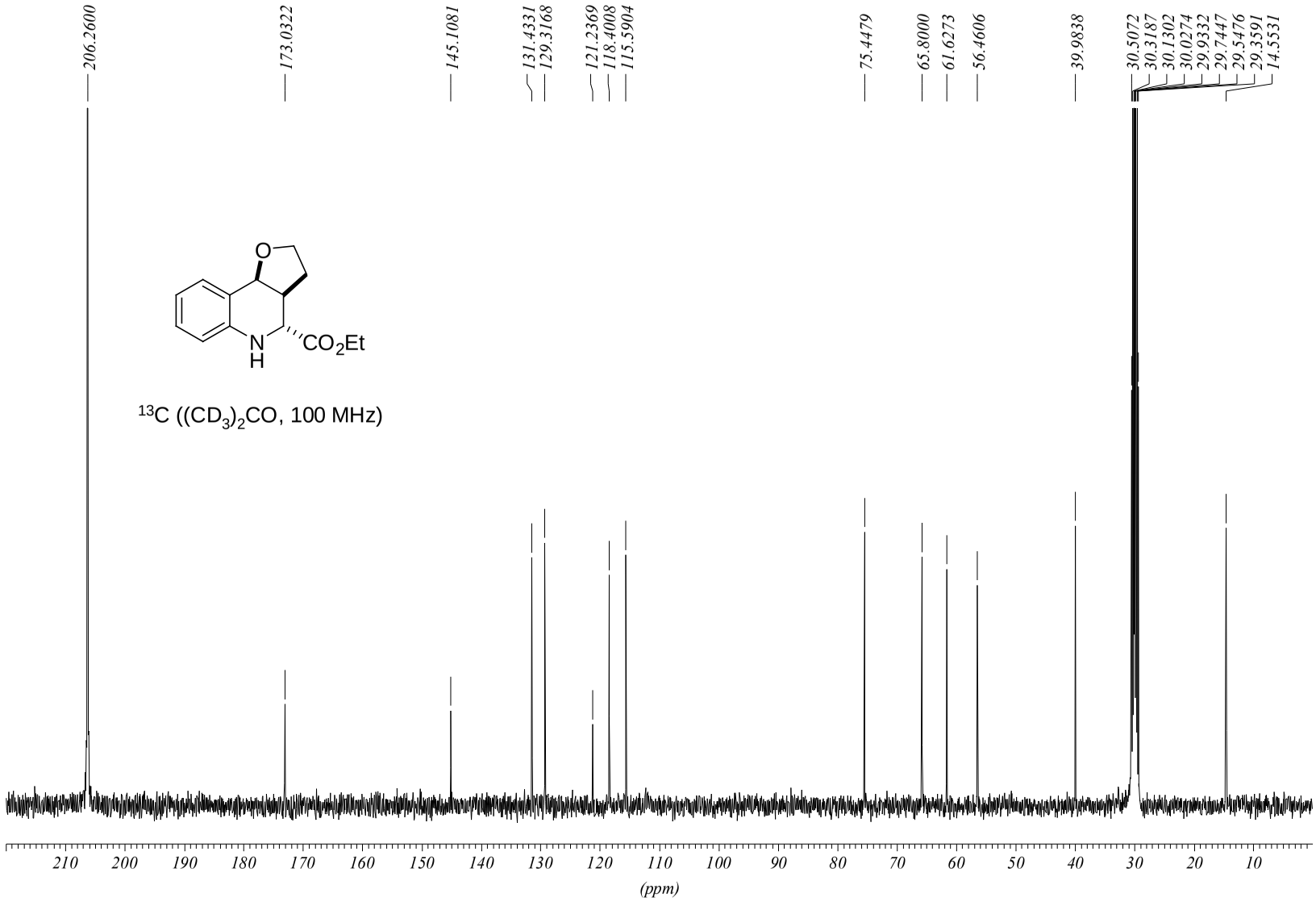
^{1}H ((CD$_3$)$_2$CO, 400 MHz)

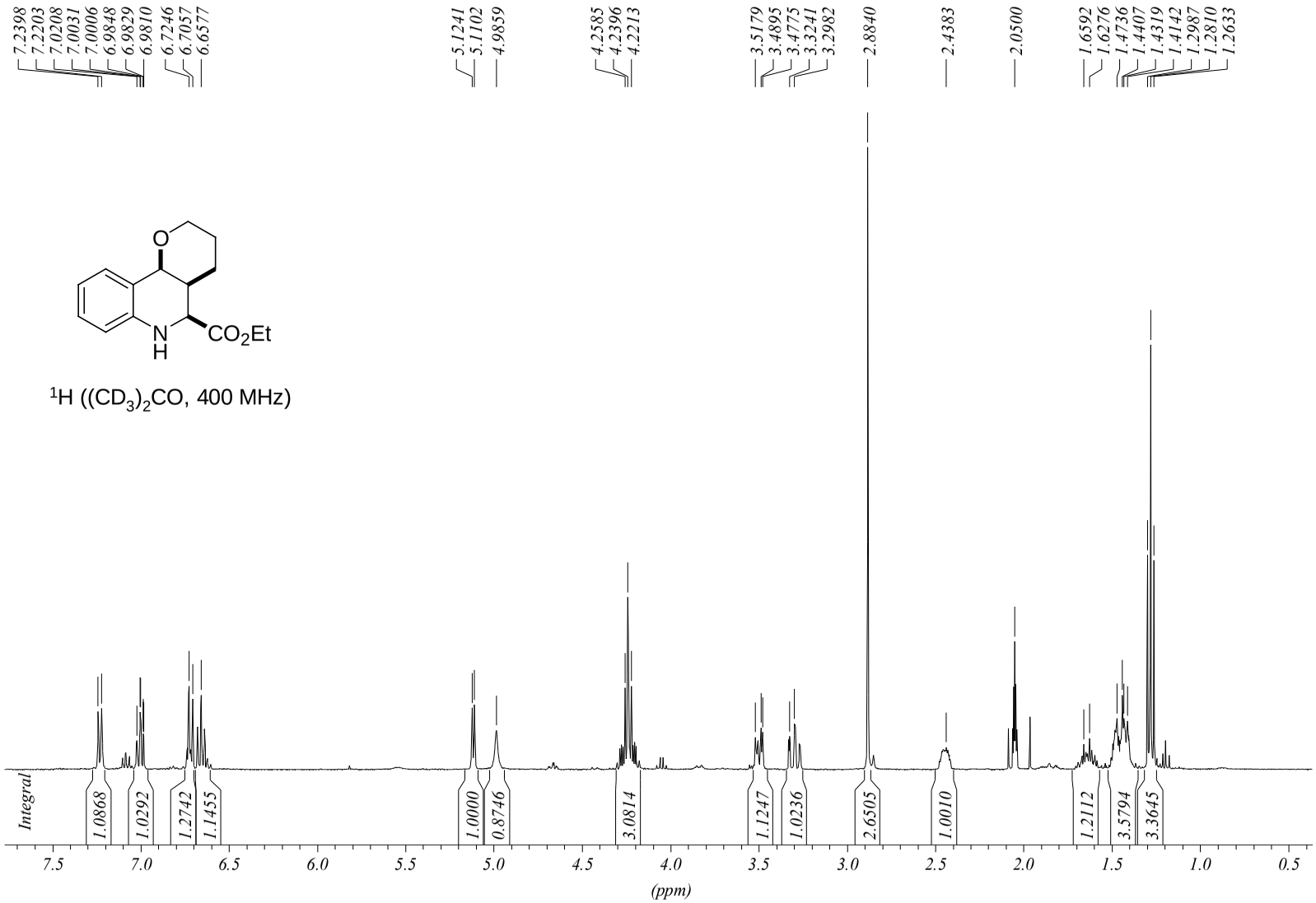

206.2600
144.0285
143.9514
135.1860
129.3082
128.5542
128.4085
122.7020
122.2051
116.5671
114.0138
74.7967
68.3191
60.5391
55.5609
39.9838
30.4301
30.2331
30.0446
29.8475
29.6590
29.4619
29.2734
24.9893
23.1128
20.8337
14.4931
O
N
H
Ph
OH
13C ((CD3)2CO, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

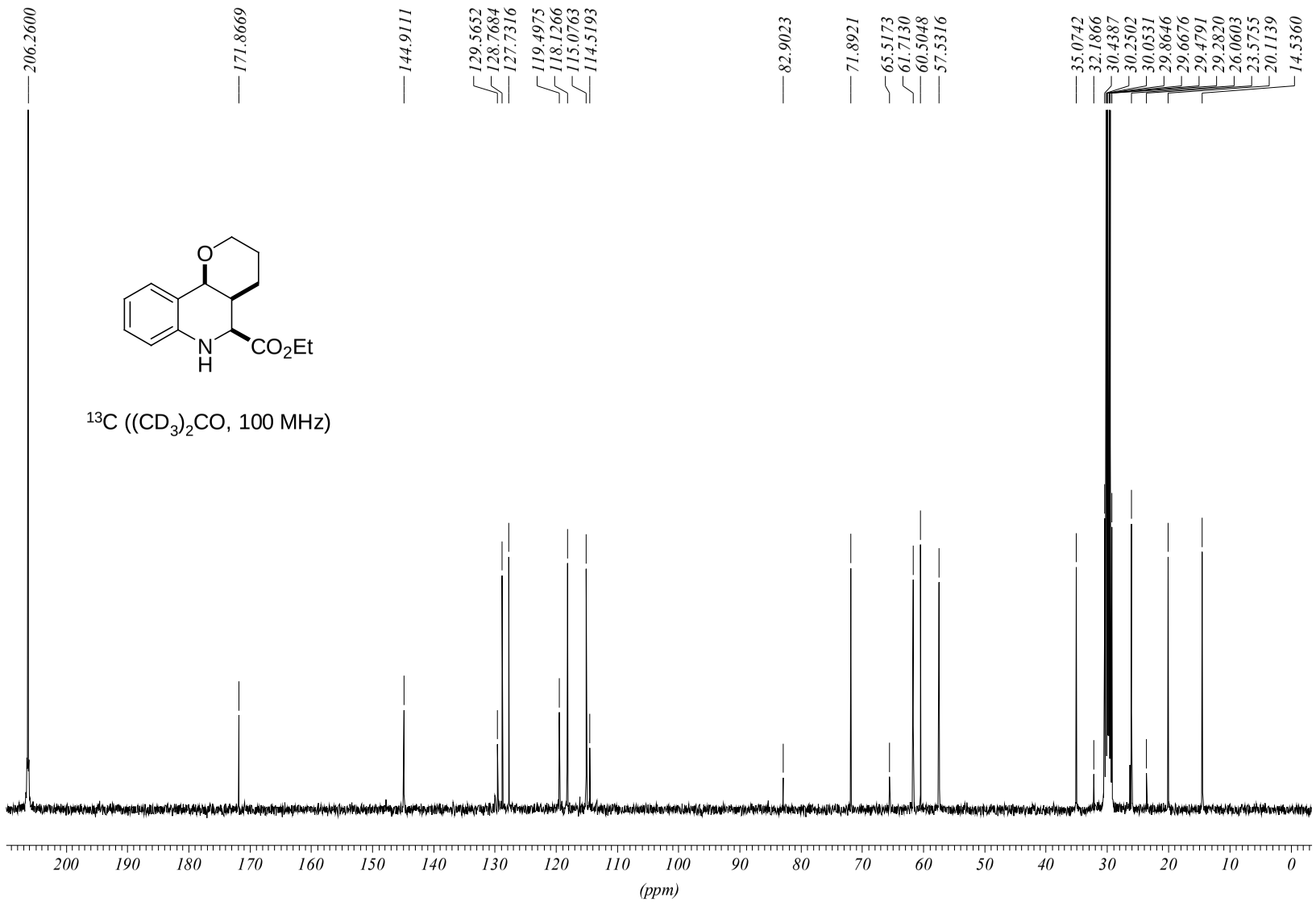

6.9835
6.9822
6.9785
6.7493
6.7467
6.7291
6.7265
6.6836
6.6811
6.6647
6.6621
6.6464
6.6438
5.1128
5.0926
4.9751
4.3002
4.2825
4.2730
4.2648
4.2554
4.2472
4.2377
4.2301
4.2200
4.2156
4.2093
4.2068
4.1979
4.1884
4.1802
4.1708
4.1531
3.7313
3.7111
3.6922
3.6732
3.6335
3.6221
3.6120
3.6006
3.5912
3.5798
3.0551
3.0513
3.0469
3.0431
3.0324
3.0280
3.0242
3.0204
3.0128
3.0097
3.0046
3.0015
2.9901
2.9863
2.9819
2.9781
2.8480
2.0557
2.0500
2.0443
1.9452
1.9256
1.8581
1.2917
1.2740
1.2557
O
N
H
CO2Et
1H ((CD3)2CO, 400 MHz)
Integral
1.0263
1.0019
0.9958
0.9883
0.9877
0.7400
3.0312
1.0194
1.0431
1.0000
1.0172
1.0808
3.4405
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

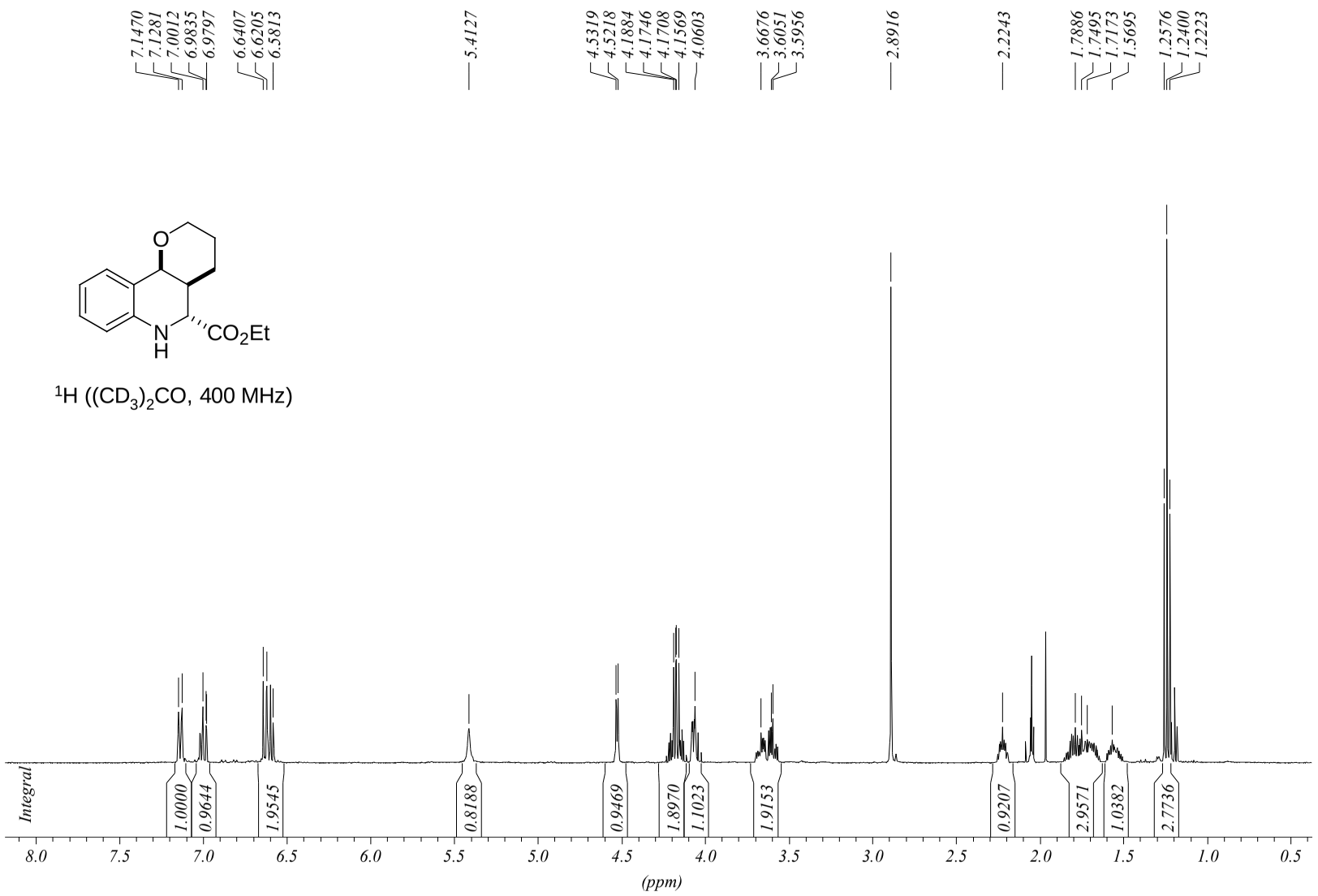

206.2600
171.9697
145.4337
130.6363
129.0340
123.0276
119.0177
115.6246
76.1505
66.6483
61.6701
56.0150
41.3547
30.5158
30.3187
30.1302
29.9332
29.7447
29.5476
29.3591
26.0175
14.5788
O
N
H
CO2Et
13C ((CD3)2CO, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

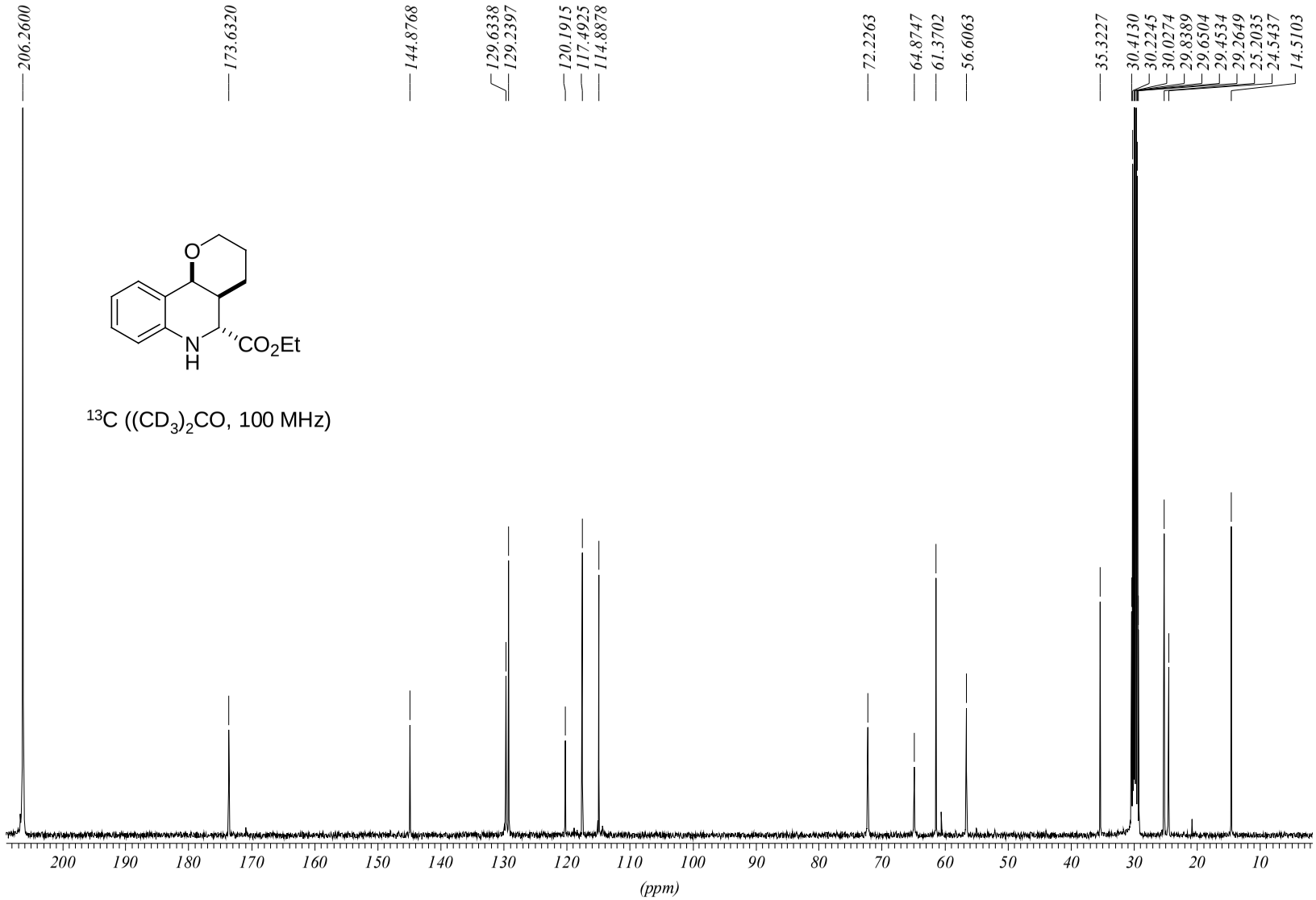

7.1855
7.0511
7.0473
7.0302
7.0132
7.0094
6.7512
6.7499
6.7310
6.7297
6.6539
6.6514
5.4108
4.5830
4.5679
4.2004
4.1884
4.1821
4.1701
3.8380
3.8248
3.7459
3.7427
3.7250
3.6290
3.6259
3.6076
3.6044
2.8525
2.5860
2.5797
2.5734
2.5589
2.2142
2.2015
2.0936
2.0866
2.0557
2.0500
2.0443
1.2639
1.2456
1.2280
O
N
H
CO2Et
1H ((CD3)2CO, 400 MHz)
Integral
1.0000
1.0167
0.9960
1.0255
0.7606
0.9496
2.0697
1.0431
1.0576
1.0004
0.3547
0.9687
1.0132
0.8641
2.3202
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

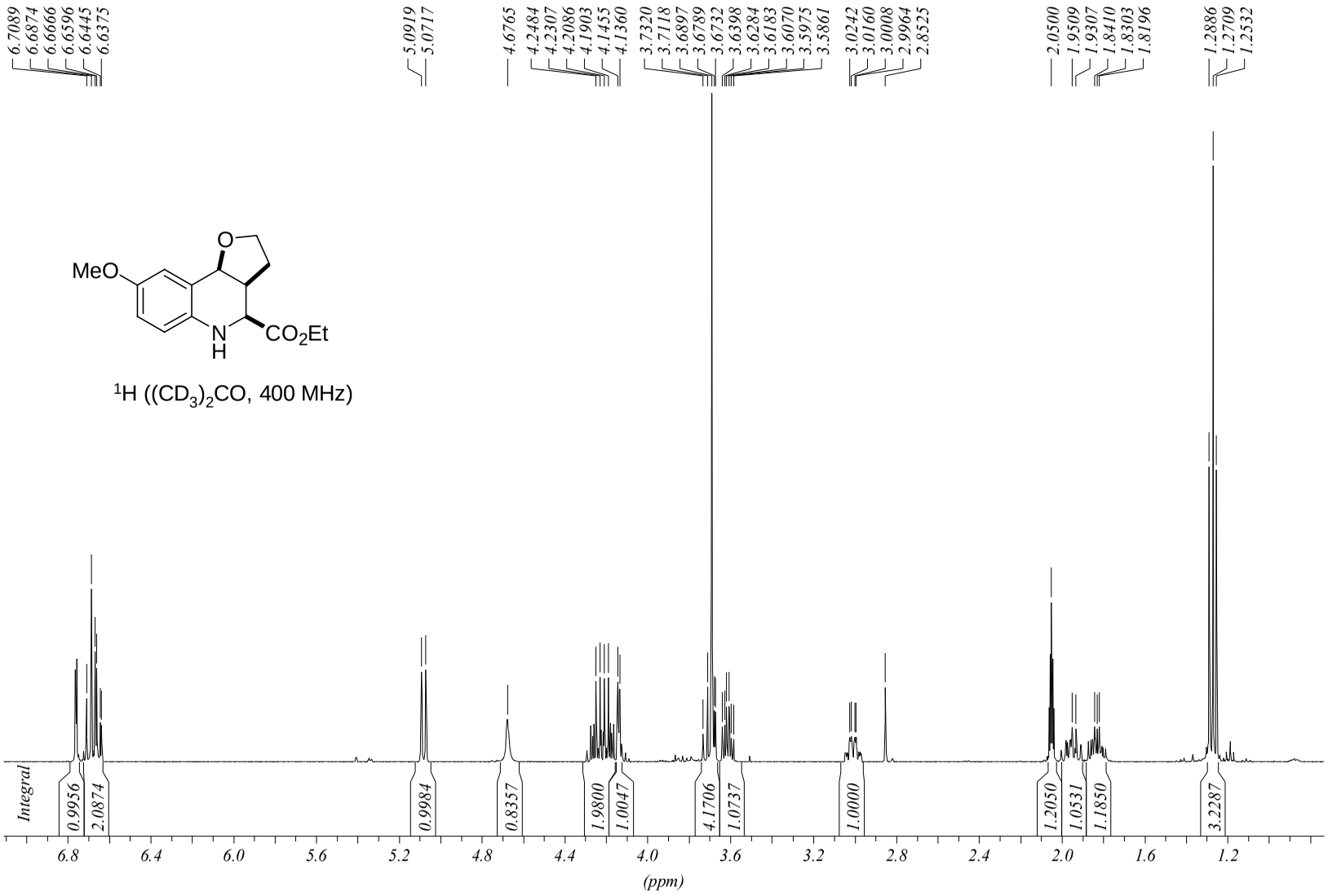

206.2600
173.0322
145.1081
131.4331
129.3168
121.2369
118.4008
115.5904
75.4479
65.8000
61.6273
56.4606
39.9838
30.5072
30.3187
30.1302
30.0274
29.9332
29.7447
29.5476
29.3591
14.5531
O
N
H
CO2Et
13C ((CD3)2CO, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)

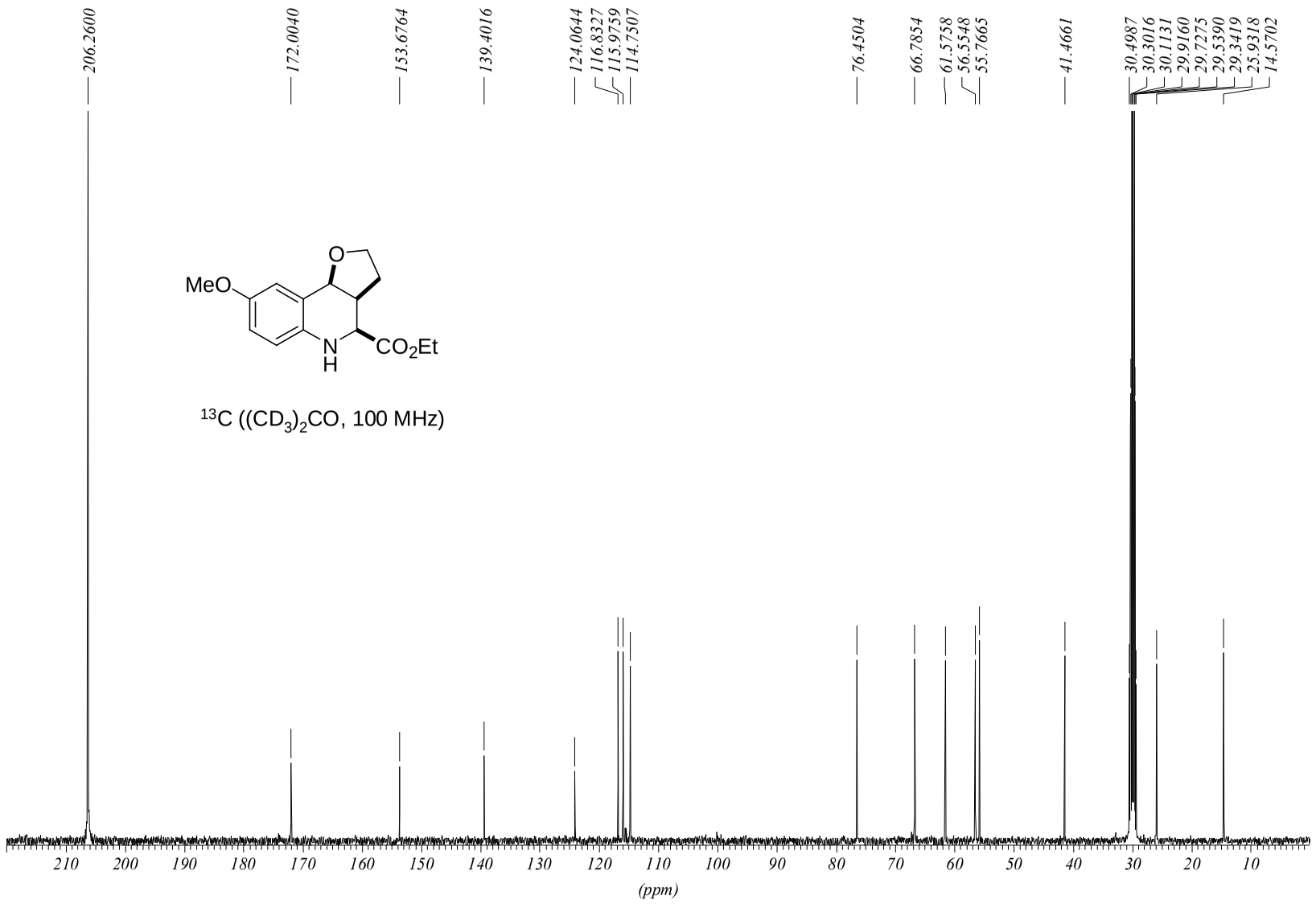

7.2398
7.2203
7.0208
7.0031
7.0006
6.9848
6.9829
6.9810
6.7246
6.7057
6.6577
5.1241
5.1102
4.9859
4.2585
4.2396
4.2213
3.5179
3.4895
3.4775
3.3241
3.2982
2.8840
2.4383
2.0500
1.6592
1.6276
1.4736
1.4407
1.4319
1.4142
1.2987
1.2810
1.2633
O
N
H
CO2Et
1H ((CD3)2CO, 400 MHz)
Integral
1.0868
1.0292
1.2742
1.1455
1.0000
0.8746
3.0814
1.1247
1.0236
2.6505
1.0010
1.2112
3.5794
3.3645
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)

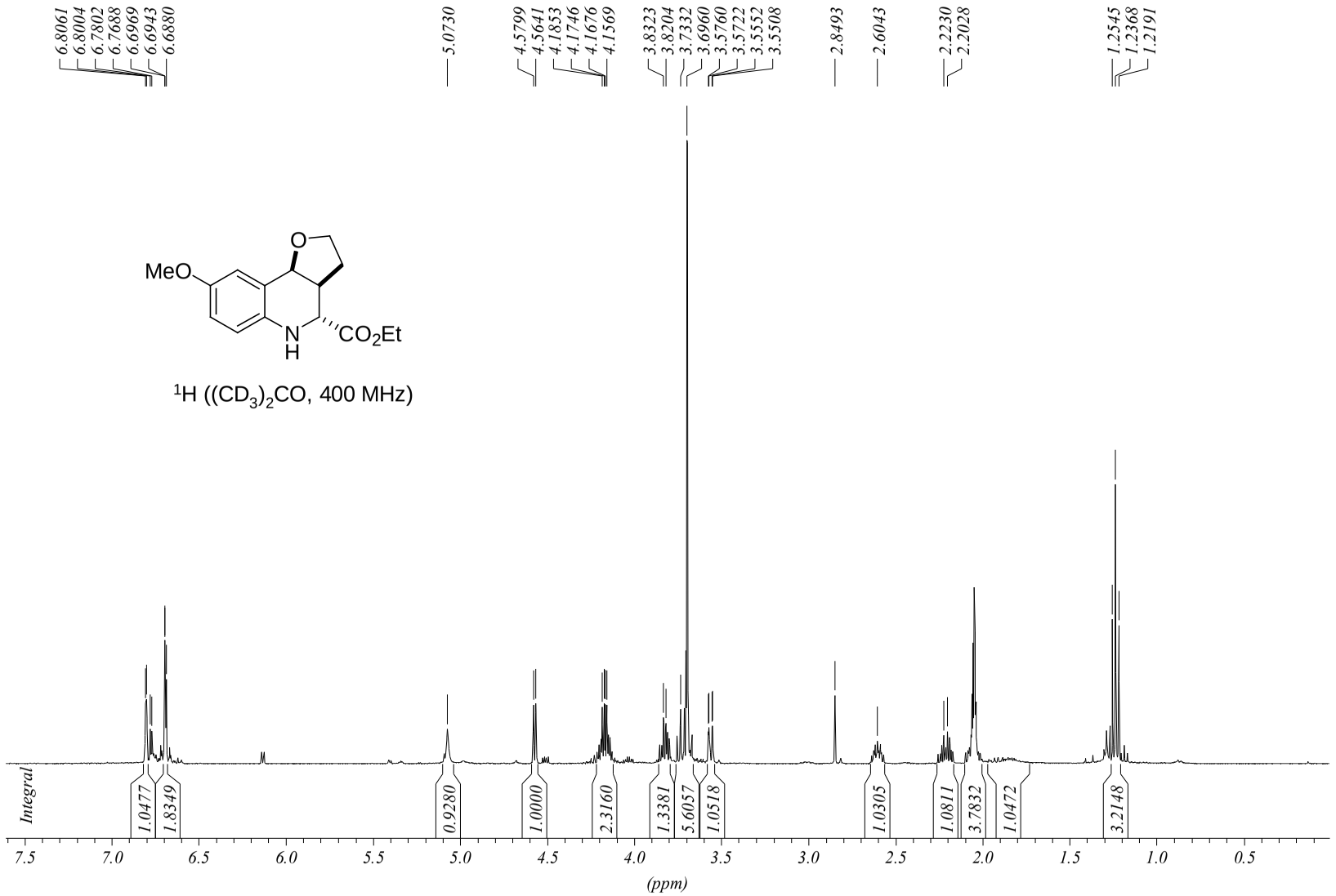

206.2600
171.8669
144.9111
129.5652
128.7684
127.7316
119.4975
118.1266
115.0763
114.5193
82.9023
71.8921
65.5173
61.7130
60.5048
57.5316
35.0742
32.1866
30.4387
30.2502
30.0531
29.8646
29.6676
29.4791
29.2820
26.0603
23.5755
20.1139
14.5360
O
N
H
CO2Et
13C ((CD3)2CO, 100 MHz)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
(ppm)

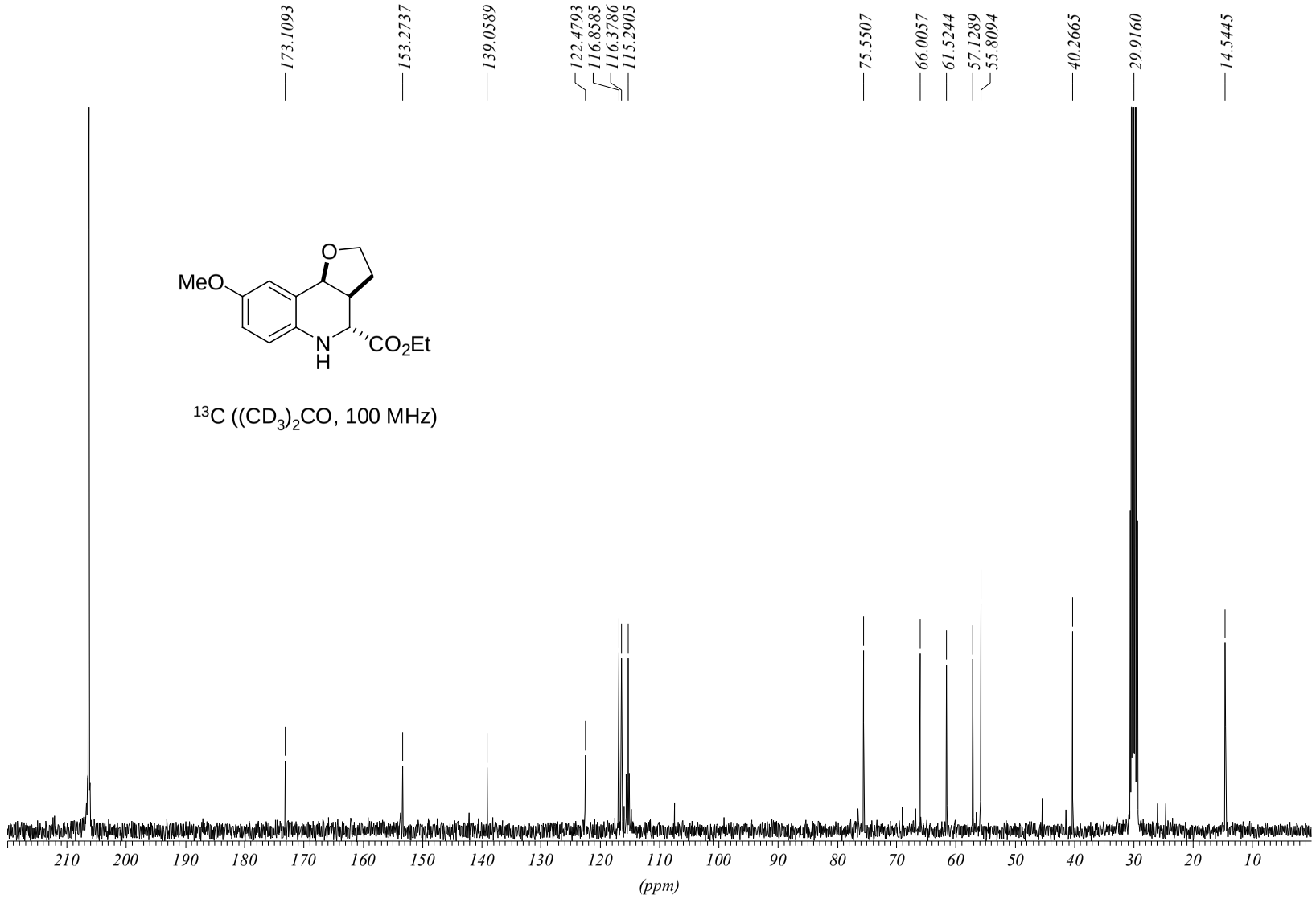

7.1470
7.1281
7.0012
6.9835
6.9797
6.6407
6.6205
6.5813
5.4127
4.5319
4.5218
4.1884
4.1746
4.1708
4.1569
4.0603
3.6676
3.6051
3.5956
2.8916
2.2243
1.7886
1.7495
1.7173
1.5695
1.2576
1.2400
1.2223
O
N
H
CO2Et
1H ((CD3)2CO, 400 MHz)
Integral
1.0000
0.9644
1.9545
0.8188
0.9469
1.8970
1.1023
1.9153
0.9207
2.9571
1.0382
2.7736
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


206.2600
173.6320
144.8768
129.6338
129.2397
120.1915
117.4925
114.8878
72.2263
64.8747
61.3702
56.6063
35.3227
30.4130
30.2245
30.0274
29.8389
29.6504
29.4534
29.2649
25.2035
24.5437
14.5103
O
N
H
CO2Et
13C ((CD3)2CO, 100 MHz)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


6.7089
6.6874
6.6666
6.6596
6.6445
6.6375
5.0919
5.0717
4.6765
4.2484
4.2307
4.2086
4.1903
4.1455
4.1360
3.7320
3.7118
3.6897
3.6789
3.6732
3.6398
3.6284
3.6183
3.6070
3.5975
3.5861
3.0242
3.0160
3.0008
2.9964
2.8525
2.0500
1.9509
1.9307
1.8410
1.8303
1.8196
1.2886
1.2709
1.2532
MeO
O
N
H
CO2Et
1H ((CD3)2CO, 400 MHz)
Integral
0.9956
2.0874
0.9984
0.8357
1.9800
1.0047
4.1706
1.0737
1.0000
1.2050
1.0531
1.1850
3.2287
6.8
6.4
6.0
5.6
5.2
4.8
4.4
4.0
3.6
3.2
2.8
2.4
2.0
1.6
1.2
(ppm)


206.2600
172.0040
153.6764
139.4016
124.0644
116.8327
115.9759
114.7507
76.4504
66.7854
61.5758
56.5548
55.7665
41.4661
30.4987
30.3016
30.1131
29.9160
29.7275
29.5390
29.3419
25.9318
14.5702
MeO
O
N
H
CO2Et
13C ((CD3)2CO, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)


6.8061
6.8004
6.7802
6.7688
6.6969
6.6943
6.6880
5.0730
4.5799
4.5641
4.1853
4.1746
4.1676
4.1569
3.8323
3.8204
3.7332
3.6960
3.5760
3.5722
3.5552
3.5508
2.8493
2.6043
2.2230
2.2028
1.2545
1.2368
1.2191
MeO
O
N
H
CO2Et
1H ((CD3)2CO, 400 MHz)
Integral
1.0477
1.8349
0.9280
1.0000
2.3160
1.3381
5.6057
1.0518
1.0305
1.0811
3.7832
1.0472
3.2148
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
(ppm)


173.1093
153.2737
139.0589
122.4793
116.8585
116.3786
115.2905
75.5507
66.0057
61.5244
57.1289
55.8094
40.2665
29.9160
14.5445
MeO
O
N
H
CO2Et
13C ((CD3)2CO, 100 MHz)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
(ppm)