Copper-Free Arylation of 3,3-Disubstituted Allylic Halides with Triazene-Softened Aryl Grignard Reagents

*Lijun Xu, Zhubo Liu, Weipeng Dong, Jinyu Song, Maozhong Miao, Jianfeng Xu and Hongjun Ren**

Department of Chemistry, Zhejiang Sci-Tech University

Hangzhou 310018 (P. R. China)

renhj@zstu.edu.cn

Supporting Information

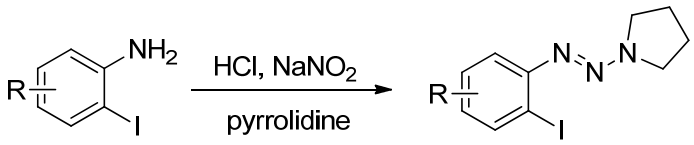
A. General Information

Air- or moisture-sensitive reactions were carried out under nitrogen. THF was dried with sodium and freshly distilled. The other materials were purchased from Aladdin and other commercial suppliers and used without additional purification unless otherwise stated. NMR spectra were recorded on a Bruke Avance operating at for ^{1}H NMR at 400 MHz, and ^{13}C NMR at 100 MHz using TMS as internal standard. Chemical shifts were given relative to $CDCl_3$ (7.26 ppm for ^{1}H NMR, 77.0 ppm for ^{13}C NMR). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument or Waters TOFMS GCT Premier or a low-resolution MS instrument using

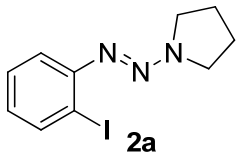
EI or ESI ionization. Infrared spectra were recorded on a Bruke ATR-FTIR spectrometer. Melting points were measured with WRS-1A digital point apparatus.

B. Synthesis of Starting Materials[1,2,3]

B.1. General Procedure of compound 2a-2l, 2n and 2o

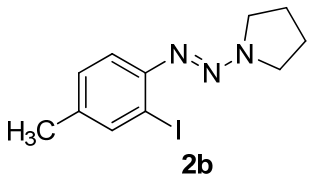


Substituted 2-iodoaniline (1.0 equiv) was dissolved in CH_3CN at room temperature, and then concentrated hydrochloric acid (2.5 equiv) was added. The solution was stirred and cooled to 0 °C. After 15 min, a solution of $NaNO_2$ (1.2 equiv) was added dropwise. The resulting solution of the diazonium salt was stirred for 30 min and then added pyrrolidine (1.2 equiv) and K_2CO_3 (1.7 equiv). After completion, monitored by thin layer chromatography (TLC), the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.



2a

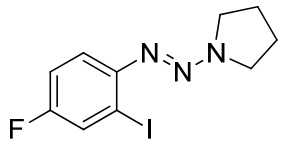
Yield: 95%; brown solid; R*f* = 0.61 (10:1 Petroleum ether/EtOAc); m.p. = 50-51 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.83 (d, *J* = 8.0 Hz, 1 H), 7.36 (d, *J* = 7.6 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 6.81 (t, *J* = 7.6 Hz, 1 H), 3.91 (br, 2 H), 3.72 (br, 2 H), 2.00 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.4, 138.9, 128.6, 126.4, 117.4, 96.3, 50.9, 47.0, 23.9, 23.5; IR(ATR-FTIR): 2870, 1402, 1313, 1014, 755 cm^{-1}.



2b

Yield: 94%; brown solid; R*f* = 0.63 (10:1 Petroleum ether/EtOAc); m.p. = 56-57 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.06 (d, *J* =

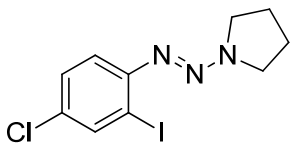
8.0 Hz, 1 H), 3.99-3.62 (m, 4 H), 2.27 (s, 3 H), 2.00 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.2, 139.2, 136.3, 129.5, 116.9, 96.2, 50.9, 46.9, 23.7, 23.5, 20.3; IR(ATR-FTIR): 2728, 1413, 1313, 1032, 781 cm^{-1}.



2c

Yield: 90%; brown oil; R*f* = 0.56 (10:1 Petroleum ether/EtOAc);

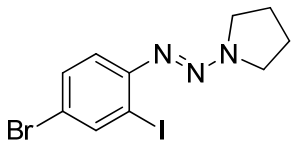
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (dd, *J* = 8.2 Hz, 2.6 Hz, 1 H), 7.33 (dd, *J* = 8.8 Hz, 5.6 Hz, 1 H), 7.02 (dt, *J* = 8.4 Hz, 2.4 Hz, 1 H), 3.91 (br, 2 H), 3.71 (br, 2 H), 2.02 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7 (d, $^{1}J_{C\text{-}F}$ = 246.2 Hz), 147.0 (d, $^{4}J_{C\text{-}F}$ = 3.0 Hz), 125.2 (d, $^{2}J_{C\text{-}F}$ = 23.9 Hz), 117.4 (d, $^{3}J_{C\text{-}F}$ = 8.0 Hz), 115.6 (d, $^{2}J_{C\text{-}F}$ = 21.8 Hz), 95.3 (d, $^{3}J_{C\text{-}F}$ = 8.2 Hz), 50.9, 47.0, 23.9, 23.4; IR(ATR-FTIR): 2871, 1416, 1025, 785 cm^{-1}.



2d

Yield: 97%; yellow solid; R*f* = 0.65 (10:1 Petroleum ether/EtOAc); m.p. = 49-50 ℃;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 1.6 Hz, 1 H), 7.29 (d, *J* = 8.8 Hz, 1 H), 7.22 (dd, *J* = 8.8 Hz, 1.6 Hz, 1 H), 3.96-3.85 (m, 2 H), 3.74-3.64 (m, 2 H), 2.08-1.95 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.1, 137.9, 130.3, 128.6, 117.5, 96.1, 51.0, 47.1, 23.9, 23.4; IR(ATR-FTIR): 2872, 1411, 1312, 1252, 1028, 821, 748 cm^{-1}.

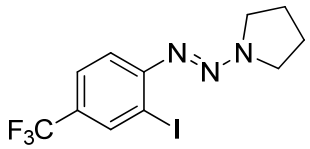


2e

Yield: 97%; brown solid; R*f* = 0.63 (10:1 Petroleum ether/EtOAc); m.p. = 48-49 ℃;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 2.0 Hz, 1 H), 7.37 (dd, *J* = 8.8 Hz, 1.6 Hz,

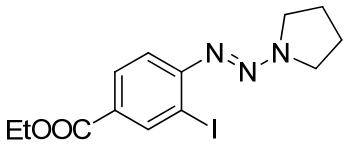
1 H), 7.24 (d, *J* = 8.8 Hz, 1 H), 3.93 (br, 2 H), 3.71 (br, 2 H), 2.04 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 140.7, 131.6, 118.15, 118.12, 96.6, 51.1, 47.2, 24.0, 23.4; IR(ATR-FTIR): 2872, 1457, 1312, 1163, 821, 745 cm^{-1}.



2f

Yield: 88%; brown oil; R*f* = 0.52 (10:1 Petroleum ether/EtOAc);

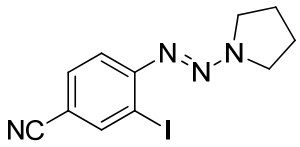
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1 H), 7.51 (d, *J* = 8.4 Hz, 1 H), 7.43 (d, *J* = 8.8 Hz, 1 H), 4.03-3.91 (m, 2 H), 3.81-3.71 (m, 2 H), 2.14-1.99 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.1, 136.1 (q, $^{3}J_{C\text{-}F}$ = 3.9 Hz), 127.6 (q, $^{2}J_{C\text{-}F}$ = 32.5 Hz), 125.7 (q, $^{3}J_{C\text{-}F}$ = 3.6 Hz), 95.5, 51.3, 47.5, 24.0, 23.4; IR(ATR-FTIR): 2871, 1469, 1180, 1026, 860, 785 cm^{-1}.



2g

Yield: 97%; yellow solid; R*f* = 0.46 (10:1 Petroleum ether/EtOAc); m.p. = 116-117 ℃;

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.50 (d, *J* = 0.8 Hz, 1 H), 7.92 (d, *J* = 8.4 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 4.00-3.91 (m, 2 H), 3.79-3.71 (m, 2 H), 2.10-1.99 (m, 4 H), 1.37 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.3, 153.8, 140.5, 130.0, 127.8, 116.4, 95.5, 60.9, 51.2, 47.5, 23.9, 23.3, 14.3; IR(ATR-FTIR): 2875, 1691, 1239, 1114, 768 cm^{-1}.

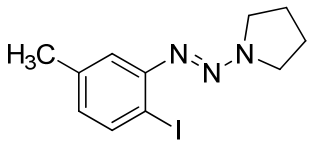


2h

Yield: 80%; yellow solid; R*f* = 0.34 (10:1 Petroleum ether/EtOAc); m.p. =

159-160 ℃;

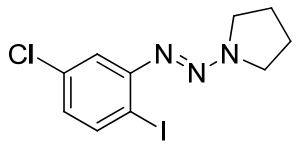
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (s, 1 H), 7.51 (d, *J* = 8.8 Hz, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 4.02-3.95 (m, 2 H), 3.80-3.74 (m, 2 H), 2.14-2.04 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 153.9, 142.6, 132.3, 118.0, 117.0, 108.8, 95.6, 51.5, 47.8, 23.9, 23.3; IR(ATR-FTIR): 2856, 2217, 1473, 1330, 1132, 770 cm^{-1}.



2i

Yield: 90%; brown solid; R*f* = 0.63 (10:1 Petroleum ether/EtOAc); m.p. = 50-51 ℃;

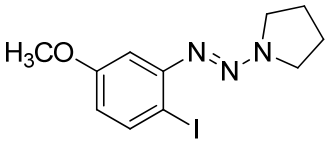
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.71 (d, *J* = 8.0 Hz, 1 H), 7.21 (s, 1 H), 6.69 (d, *J* = 8.0 Hz, 1 H), 3.93 (br, 2 H), 3.74 (br, 2 H), 2.31 (s, 3 H), 2.02 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.0, 138.5, 138.4, 127.5, 118.0, 92.3, 50.8, 46.9, 23.9, 23.3, 21.0; IR(ATR-FTIR): 2869, 1474, 1334, 1033, 781 cm^{-1}; MS (ES$^+$): m/z (%): 316 ([M+H]$^+$, 22), 245 (13), 217 (100), 108 (7); HRMS (ES$^+$-TOF) calcd for $C_{11}H_{14}IN_3$ ([M+H]$^+$): 316.0310, found: 316.0318.



2j

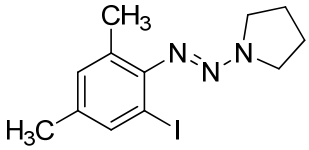
Yield: 92%; yellow solid; R*f* = 0.65 (10:1 Petroleum ether/EtOAc); m.p. = 48-49 ℃;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.4 Hz, 1 H), 7.38 (d, *J* = 1.6 Hz, 1 H), 6.82 (dd, *J* = 8.4 Hz, 2.0 Hz, 1 H), 3.99-3.91 (m, 2 H), 3.77-3.70 (m, 2 H), 2.11-2.00 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.3, 139.6, 134.8, 126.2, 117.4, 93.4, 51.2, 47.3, 24.0, 23.4; IR(ATR-FTIR): 2870, 1409, 1310, 1096, 820 cm^{-1}; MS (ES$^+$): m/z (%): 337 ([M+H]$^+$, Cl^{37}, 9), 336 ([M+H]$^+$, Cl^{35}, 3), 265 (26), 237 (100), 128 (5); HRMS (ES$^+$-TOF) calcd for $C_{10}H_{11}ClIN_3$ ([M+H]$^+$): 335.9764, found: 335.9767.



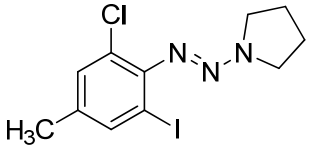
2k

Yield: 85%; brown solid; R*f* = 0.68 (10:1 Petroleum ether/EtOAc); m.p. = 66-67 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.68 (d, *J* = 8.4 Hz, 1 H), 6.99 (d, *J* = 2.8 Hz, 1 H), 6.49 (dd, *J* = 8.8 Hz, 2.8 Hz, 1 H), 3.93 (br, 2 H), 3.77 (s, 3 H), 3.73 (br, 2 H), 2.02 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.4, 151.0, 138.9, 113.6, 102.2, 85.4, 55.3, 50.9, 47.1, 23.9, 23.4; IR(ATR-FTIR): 2870, 1573, 1467, 1307, 1151, 853, 735 cm^{-1}.



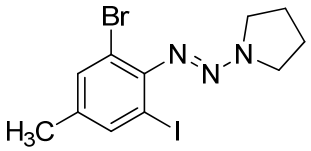
2l

Yield: 93%; brown oil; R*f* = 0.64 (10:1 Petroleum ether/EtOAc); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53 (s, 1 H), 6.95 (s, 1 H), 3.81 (br, 4 H), 2.25 (s, 3 H), 2.20 (s, 3 H), 2.10-1.99 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 136.9, 135.7, 131.9, 130.3, 93.6, 23.8, 20.1, 19.1 (three carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2869, 1419, 1318, 1109, 797 cm^{-1}.



2n

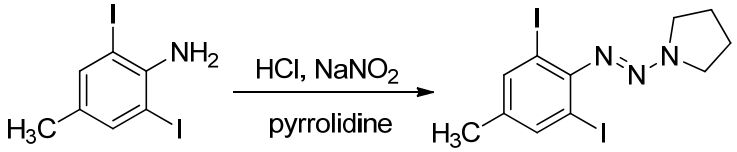
Yield: 95%; brown solid; R*f* = 0.66 (10:1 Petroleum ether/EtOAc); m.p. = 40-41 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1 H), 7.18 (s, 1 H), 3.93 (br, 2 H), 3.72 (br, 2 H), 2.24 (s, 3 H), 2.11-1.98 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 137.9, 136.7, 130.8, 125.6, 93.7, 50.9, 46.5, 23.8, 23.5, 19.9; IR(ATR-FTIR): 2872, 1416, 1260, 1161, 852, 745 cm^{-1}.



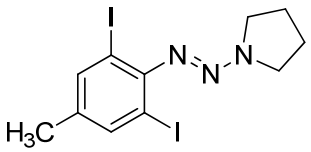
2o

Yield: 96%; brown solid; R*f* = 0.65 (10:1 Petroleum ether/EtOAc); m.p. = 73-74 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (s, 1 H), 7.38 (s, 1 H), 3.95 (br, 2 H), 3.72 (br, 2 H), 2.25 (s, 3 H), 2.11-1.99 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.3, 138.7, 137.2, 133.9, 115.3, 92.9, 51.0, 46.6, 23.9, 23.5, 19.9; IR(ATR-FTIR): 2871, 1413, 1314, 1134, 722 cm^{-1}.

B2.2 Procedure of Compound 2p



To a solution of 2,6-diiodo-4-methylaniline (1.0 equiv) in CH_3CN was added concentrated hydrochloric acid (2.5 equiv) to form a thick slurry. The slurry was cooled to -10°C and $NaNO_2$ (1.2 equiv) in H_2O was added dropwise over 15 min keeping the temperature below -3°C. The mixture was then allowed to stirred at -10°C for 30 min. The slurry was then slowly transferred to a quench solution at -10°C of K_2CO_3 (1.7 equiv), pyrrolidine (1.2 equiv) and H_2O:CH_3CN (2:1) keeping the temperature below 0°C. After completion, monitored by thin layer chromatography (TLC), the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.

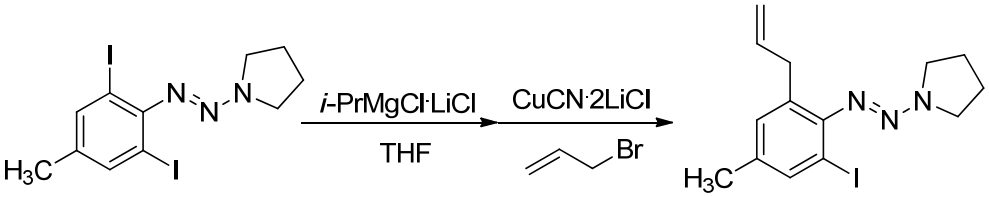


2p

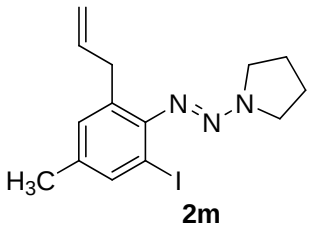
Yield: 89%; brown solid; R*f* = 0.35 (20:1 Petroleum ether/EtOAc); m.p. = 116-117 ℃; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65 (s, 2 H), 3.96 (br, 2 H), 3.72 (br, 2 H), 2.23 (s, 3 H), 2.06 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.2, 139.9, 137.7, 90.8, 51.0,

46.8, 23.9, 23.6, 19.6; IR(ATR-FTIR): 2871, 1408, 1309, 1106, 858, 704 cm^{-1}.

B2.3 Procedure of Compound 2m



A dry and N_2-flushed 50 mL Schlenk tube, equipped with a magnetic stirrer and a septum was charged with (*E*)-1-((2,6-diiodo-4-methylphenyl)diazenyl)pyrrolidine (1.0 equiv) in dry THF (4 mL). *i*-PrMgCl (1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C. After 3 h, a complete conversion to the corresponding Grignard reagent was observed as indicated by thin layer chromatography (TLC). CuCN·2LiCl (1.0 M in THF, 0.1 equiv) and 3-bromoprop-1-ene (1.5 equiv) were added. The reaction mixture was slowly warmed to room temperature for 12 h before quenched by NH_4Cl. The resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na_2SO_4, concentrated in vacuo and purified by silica gel chromatography.

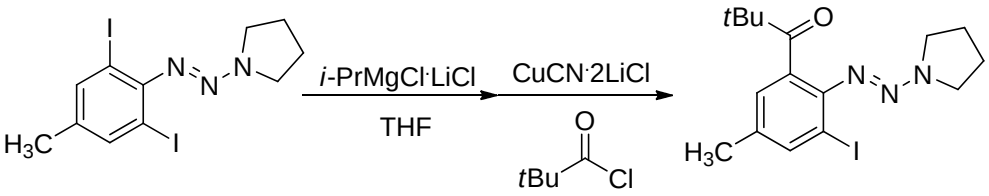


2m

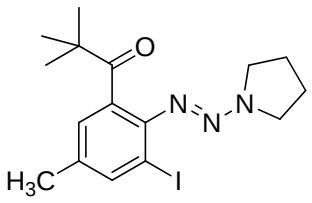
Yield: 85%; brown oil; R*f* = 0.63 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1 H), 6.98 (s, 1 H), 5.59-5.82 (m, 1 H), 5.07-4.98 (m, 2 H), 4.01-3.60 (m, 4 H), 3.32 (d, *J* = 6.8 Hz, 2 H), 2.26 (s, 3 H), 2.05 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.8, 137.4, 137.2, 136.0, 132.5, 130.9, 115.4, 93.4, 50.9, 46.3, 36.6, 23.8, 20.2 (one carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2869, 1420, 1319, 1031, 819 cm^{-1}.

B 2. Procedure of Compound 2q



A dry and N_2-flushed 50 mL Schlenk tube, equipped with a magnetic stirrer and a septum was charged with (*E*)-1-((2,6-diiodo-4-methylphenyl)diazenyl)pyrrolidine (1.0 equiv) in dry THF (4 mL). *i*-PrMgCl (1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C. After 3 h, a complete conversion to the corresponding Grignard reagent was observed as indicated by thin layer chromatography (TLC). $CuCN{\cdot}2LiCl$ (1.0 M in THF, 0.1 equiv) and pivaloyl chloride (1.5 equiv) were added. The reaction mixture was slowly warmed to room temperature for 12 h before quenched by NH_4Cl. The resulting mixture was extracted with ethyl acetate. The organic fractions were dried over Na_2SO_4, concentrated in vacuo and purified by silica gel chromatography.



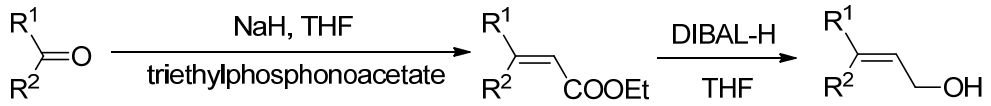
2q

Yield: 85%; yellow solid; R*f* = 0.40 (10:1 Petroleum ether/EtOAc); m.p. = 101-102 ℃;

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (s, 1 H), 6.79 (s, 1 H), 3.89-3.82 (m, 2 H), 3.72-3.64 (m, 2 H), 2.27 (s, 3 H), 2.07-1.95 (m, 4 H), 1.12 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 214.2, 144.2, 139.9, 135.7, 131.6, 127.3, 96.5, 50.8, 47.6, 44.6, 27.4, 24.1, 23.4, 20.3; IR(ATR-FTIR): 2870, 1686, 1411, 1313, 1131, 760 cm^{-1}; MS (ES^+): m/z (%): 400 ($[M+H]^+$, 40), 245 (53), 231 (100), 159 (36), 131 (17), 104 (16); HRMS (ES^+-TOF) calcd for $C_{16}H_{22}IN_3O$ ($[M+H]^+$): 400.0886, found: 400.0890.

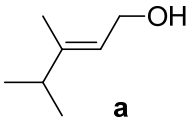
B3. General Procedure of compound 3, 4

B3.1 General Procedure for the synthesis of allylic alcohols[2]



To a stirred solution of triethylphosphonoacetate (1.7 equiv) in THF was added NaH (1.2 equiv) at 0°C. After stirring for 2 h at 0°C, the appropriate ketone (1.0 equiv) was added dropwise, and the reaction was stirred overnight at room temperature. Monitored by thin layer chromatography (TLC), the reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.

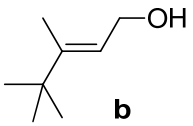
The ester (1.0 equiv) was dissolved in THF and cooled down to -78°C. Dibal-H (1.5 M in hexanes, 1.5 equiv) was added dropwise. The reaction mixture was stirred at -78°C for 3h, monitored by thin layer chromatography (TLC). The solution was quenched with a saturated solution of NH_4Cl at 0°C and stirred at room temperature for 20 min producing a white precipitate. The precipitate was filtered through a pad of Celite®. The reaction mixture was extracted with ethyl acetate. The organic layer was dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography.



a

Yield: 95%; colorless oil; R*f* = 0.21 (10:1 Petroleum ether/EtOAc);

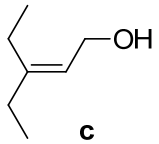
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.32 (t, *J* = 6.2 Hz, 1 H), 4.07 (d, *J* = 6.8 Hz, 2 H), 2.91-2.65 (m, 1 H), 2.24-2.12 (m, 1 H), 1.56 (s, 3 H), 0.94 (d, *J* = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 121.1, 58.9, 36.4, 21.0, 13.4; IR(ATR-FTIR): 3316, 2960, 1463, 1165, 996 cm^{-1}.



b

Yield: 96%; colorless oil; R*f* = 0.22 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (t, *J* = 6.4 Hz, 1 H), 4.13 (d, *J* = 6.8 Hz, 2 H), 2.45-2.20 (m, 1 H), 1.61 (s, 3 H), 1.01 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.5, 120.4, 59.7, 36.0, 28.7, 12.7; IR(ATR-FTIR): 3341, 2923, 1462, 1005, 750 cm^{-1}.

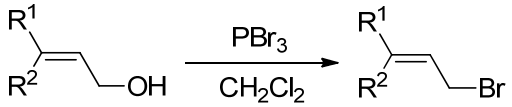


c

Yield: 95%; colorless oil; R*f* = 0.21 (10:1 Petroleum ether/EtOAc);

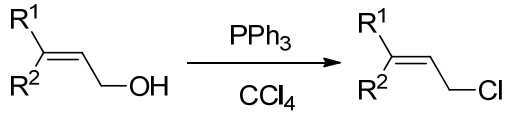
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.31-5.23 (m, 1 H), 4.08 (d, *J* = 6.8 Hz, 2 H), 2.77-2.50 (m, 1 H), 2.06-1.93 (m, 4 H), 1.02-0.85 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 121.5, 58.6, 28.9, 23.4, 13.4, 12.2; IR(ATR-FTIR): 3320, 2964, 1464, 1001, 729 cm^{-1}.

B3.2 General Procedure of compound 3[3]

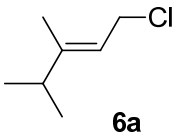


A solution of allylic alcohol (1.0 equiv) in dry CH_2Cl_2 was cooled to 0 °C, and PBr_3 (0.4 equiv) was added. The solution was allowed to stirried at 0 °C for 1 h, and H_2O was added to quench the reaction. The organic layer was separated, dried, and concentrated in vacuo. The product was used immediately in the subsequent step without further purification.

B3.3 General Procedure of compound 6[4]



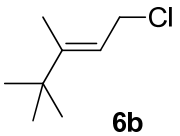
Triphenylphosphine (1.5 equiv) was slowly added to a solution of allylic alcohol (1.0 equiv) in carbon tetrachloride and the resulting mixture was refluxed for 8 h. Then, the mixture was cooled and pentane was added. The suspension was filtered off and washed with pentane. The solvent was removed under vacuum.



6a

Yield: 80%; yellow oil; R*f* = 0.85 (Petroleum ether);

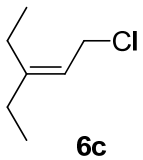
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.45 (t, *J* = 7.8 Hz, 1 H), 4.10 (d, *J* = 8.0 Hz, 2 H), 2.32-2.23 (m, 1 H), 1.69 (s, 3 H), 1.02 (d, *J* = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 118.1, 41.2, 36.6, 29.7, 21.0, 13.5; IR(ATR-FTIR): 2923, 1467, 1065, 850 cm^{-1}.



6b

Yield: 80%; colorless oil; R*f* = 0.86 (Petroleum ether);

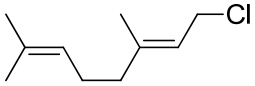
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.51 (t, *J* = 8.0 Hz, 1 H), 4.12 (d, *J* = 8.0 Hz, 2 H), 1.73 (s, 3 H), 1.06 (d, *J* = 7.2 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.5, 117.3, 41.7, 36.4, 28.7, 12.6; IR(ATR-FTIR): 2854, 1461, 1252, 1055, 857 cm^{-1}.



6c

Yield: 78%; yellow oil; R*f* = 0.84 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.39 (t, *J* = 8.2 Hz, 1 H), 4.12 (d, *J* = 8.0 Hz, 2 H), 2.17-2.04 (m, 4 H), 1.02 (t, *J* = 7.6 Hz, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.1, 118.4, 40.9, 29.1, 23.3, 13.4, 12.2; IR(ATR-FTIR): 2965, 1465, 1055, 856 cm^{-1}.



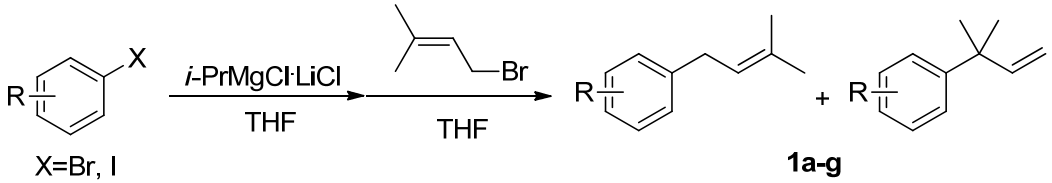
6e

Yield: 85%; yellow oil; R*f* = 0.85 (Petroleum ether);

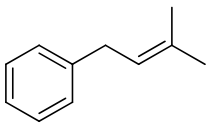
^{1}H NMR (400 MHz, $CDCl_3$): δ 5.44 (t, *J* = 8.0 Hz, 1 H), 5.08 (t, *J* = 6.6 Hz, 1 H), 4.08 (d, *J* = 8.0 Hz, 2 H), 2.15-2.02 (m, 4 H), 1.72 (s, 3 H), 1.68 (s, 3 H), 1.60 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 142.5, 131.7, 123.5, 120.3, 40.9, 39.3, 26.1, 25.5, 17.5, 15.9; IR(ATR-FTIR): 2854, 1472, 1075, 840 cm^{-1}.

C. General Procedure of Compound 1



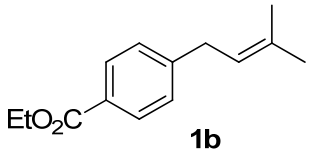
A dry and nitrogen-flushed 25 ml Schlenk tube equipped with a magnetic stirrer and a septum was charged with a solution of aryl halide (1 mmol, 1.0 equiv) in dry THF (4 ml). *i*-PrMgCl·LiCl (1.3 mL, 1.3 mmol, 1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C. After the reaction mixture was continuously stirred at –30 °C for 3 h, a complete Br/Mg exchange was observed as indicated by thin layer chromatography (TLC). Allyl bromide (3 mmol, 3.0 equiv) was added at –40 °C and then the resulting mixture was stirred for 24 h before the addition of saturated aqueous NH_4Cl solution (10ml). The resulting mixture was extracted with ethyl acetate (3 × 30 mL). The organic fractions were dried over Na_2SO_4, concentrated in vacuo and purified by silica gel chromatography.



1a

Yield: 90%; colourless oil; R*f* = 0.71 (Petroleum ether);

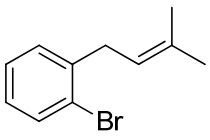
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.29 (m, 2 H), 7.25-7.19 (m, 3 H), 5.39 (t, *J* = 7.4 Hz, 1 H), 3.40 (d, *J* = 7.2 Hz, 2 H), 1.80 (s, 3 H), 1.78 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 132.5, 128.33, 128.30, 125.7, 123.2, 34.4, 25.7, 17.8; IR(ATR-FTIR): 1712, 1458, 807 cm^{-1}; MS (EI): m/z (%): 146 (M^+, 7), 105 (74), 91 (75), 77 (94), 72 (53), 59 (66), 43 (100), 39 (36); HRMS (EI-TOF) calcd for $C_{11}H_{14}$ (M^+): 146.1096, found: 146.1093.



1b

Yield: 85%; yellow oil; R*f* = 0.23 (Petroleum ether);

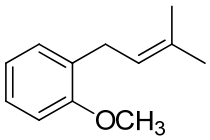
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, *J* = 8.4 Hz, 2 H), 7.22 (d, *J* = 8.0 Hz, 2 H), 5.30 (t, *J* = 7.2 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.37 (d, *J* = 8.0 Hz, 2 H), 1.75 (s, 3 H), 1.71 (s, 3 H), 1.37 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.5, 147.1, 133.3, 129.6, 128.2, 128.0, 122.0, 60.6, 34.3, 25.6, 17.7, 14.2; IR(ATR-FTIR): 2362, 1714, 1274, 1103, 761, 701 cm^{-1}; MS (EI): m/z (%): 218 (M^+, 24), 173 (35), 145 (100), 131 (68), 115 (32), 91 (52), 43 (79), 29 (97); HRMS (EI-TOF) calcd for $C_{11}H_{14}$ (M^+): 218.1307, found: 218.1307.



1c

Yield: 80%; colourless oil; R*f* = 0.81 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, *J* = 7.6 Hz, 1 H), 7.23-7.18 (m, 2 H), 7.08-6.99 (m, 1 H), 5.28 (t, *J* = 7.2 Hz, 1 H), 3.43 (d, *J* = 7.2 Hz, 2 H), 1.75 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 133.5, 132.6, 130.0, 127.40, 127.36, 124.5, 121.4, 34.7, 25.7, 18.0; IR(ATR-FTIR): 1465, 1024, 748 cm^{-1}; MS (EI): m/z (%): 226 (M^+, Br^{81}, 1), 224 (M^+, Br^{81}, 1), 144 (34), 129 (33), 102 (23), 51 (29), 43 (100), 27 (17); HRMS (EI-TOF) calcd for $C_{11}H_{13}Br$ (M^+): 224.0201, found: 224.0207.

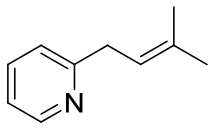


1d

Yield: 92%; colourless oil; R*f* = 0.68 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.10 (m, 2 H), 6.91-6.85 (m, 1 H), 6.85-6.79 (m,

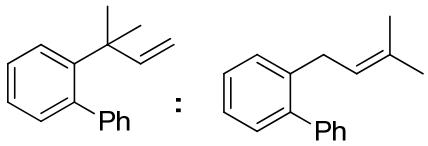
1 H), 5.38-5.26 (m, 1 H), 3.81 (s, 3 H), 3.35-3.29 (m, 2 H), 1.74 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.3, 132.3, 130.1, 129.3, 126.8, 122.6, 120.4, 110.2, 55.2, 28.4, 25.8, 17.7; IR(ATR-FTIR): 1598, 1242, 752 cm^{-1}; MS (EI): m/z (%): 176 (M^+, 16), 137 (33), 121 (59), 91 (87), 77 (54), 43 (100), 39 (49), 27 (20); HRMS (EI-TOF) calcd for $C_{12}H_{16}O$ (M^+): 176.1201, found: 176.1199.



1e

Yield: 95%; yellow oil; R*f* = 0.39 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, *J* = 4.4 Hz, 1 H), 7.52 (t, *J* = 7.4 Hz, 2 H), 7.08 (d, *J* = 8.0 Hz, 1 H), 7.05-6.99 (m, 1 H), 5.38 (t, *J* = 7.2 Hz, 1 H, SN2), 3.49 (d, *J* = 7.2 Hz, 2 H, SN2), 1.71 (s, 3 H, SN2), 1.64 (s, 3 H, SN2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.4, 149.1, 136.2, 133.5, 122.3, 121.2, 120.8, 37.0, 25.6, 17.8; IR(ATR-FTIR): 1589, 1378, 748 cm^{-1}; MS (EI): m/z (%): 147 (M^+, 46), 146 (100), 144 (36), 131 (87), 41 (43); HRMS (EI-TOF) calcd for $C_{10}H_{13}N$ (M^+): 147.1048, found: 147.1046.



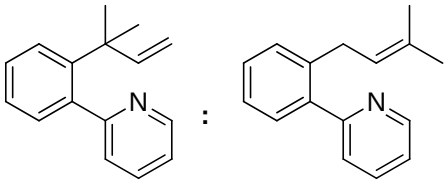
4 : 96

1f

Yield: 95%; colourless oil; R*f* = 0.47 (Petroleum ether);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.42 (m, 2 H), 7.41-7.33 (m, 5 H), 7.31-7.27 (m, 2 H), 5.26 (br, 1 H), 3.35 (d, *J* = 6.8 Hz, 2 H), 1.74 (s, 3 H), 1.57 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.01 (dd, *J* = 17.4 Hz, 10.2 Hz, 1 H), 4.84-4.75 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.8, 141.7, 139.2, 131.9, 129.9, 129.3, 129.2, 128.7, 128.0, 127.4, 127.1, 126.7, 125.7, 123.7, 32.0, 25.7, 17.7; IR(ATR-FTIR): 1476, 1139, 746, 701 cm^{-1}; MS (EI): m/z (%): 222 (M^+, 11), 179 (100), 165 (71), 154 (42), 43 (34); HRMS (EI-TOF) calcd for

$C_{17}H_{18}$ (M^+): 222.1409, found: 222.1405.

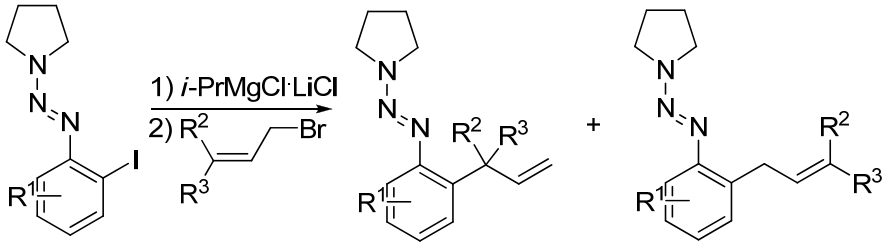


76 : 24
1g

Yield: 89%; brown oil; R*f* = 0.29 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (d, *J* = 4.0 Hz, 1 H), 7.59 (dt, *J* = 7.6 Hz, 1.6 Hz, 1 H), 7.52 (d, *J* = 8.0 Hz, 1 H), 7.38-7.31 (m, 2 H), 7.26-7.19 (m, 3 H), 7.11 (dd, *J* = 7.6 Hz, 0.8 Hz, 1 H), 5.84 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.68-4.50 (m, 2 H), 1.32 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.17 (t, *J* = 7.0 Hz, 1 H), 3.42 (d, *J* = 6.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 162.6, 149.1, 147.9, 147.7, 146.1, 141.1, 139.5, 136.0, 135.2, 131.9, 131.1, 129.7, 129.6, 128.7, 128.3, 128.0, 127.4, 126.8, 125.8, 125.5, 125.1, 124.2, 123.5, 121.7, 121.5, 108.8, 42.4, 31.8, 29.4, 25.6, 24.0, 17.7; IR(ATR-FTIR): 1585, 1466, 750 cm^{-1}; MS (EI): m/z (%): 223 (M^+, 43), 208 (80), 194 (51), 180 (100), 167 (79), 51 (24), 27 (28); HRMS (EI-TOF) calcd for $C_{16}H_{17}N$ (M^+): 223.1361, found: 223.1363.

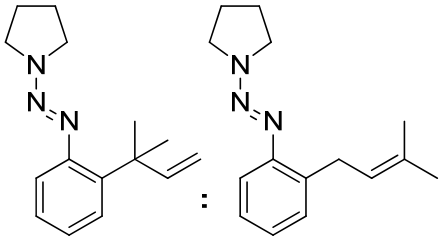
D. General Procedure of Compound 4



4a-u

A dry and nitrogen-flushed 25 ml Schlenk tube equipped with a magnetic stirrer and a septum was charged with a solution of (*E*)-1-((2-iodoophenyl)diazenyl)pyrrolidine (1 mmol, 1.0 equiv) in dry THF (4 ml). *i*-PrMgCl·LiCl (1.3 mL, 1.3 mmol, 1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C. After the reaction mixture was continuously stirred at –30 °C for 3 h, a complete Br/Mg exchange was observed as indicated by thin layer chromatography (TLC). Allyl bromide (3 mmol, 3.0 equiv)

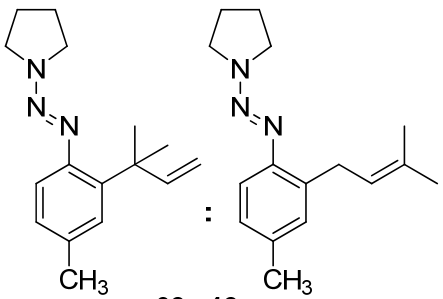
was added at –40 °C and then the resulting mixture was stirred for 24 h before the addition of saturated aqueous NH_4Cl solution (10ml). The resulting mixture was extracted with ethyl acetate (3 × 30 mL). The organic fractions were dried over Na_2SO_4, concentrated in vacuo and purified by silica gel chromatography.



91 : 9
4a

Yield: 90%; brown oil; R*f* = 0.66 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.31 (m, 2 H), 7.18 (t, *J* = 7.4 Hz, 1 H), 7.09 (t, *J* = 7.4 Hz, 1 H), 6.31 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.98-4.90 (m, 2 H), 3.80 (br, 4 H), 2.05-1.99 (m, 4 H), 1.57 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.37 (t, *J* = 7.4 Hz, 1 H), 3.58 (d, *J* = 7.6 Hz, 2 H), 1.74 (s, 3 H), 1.73 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 149.2, 141.6, 126.8, 126.5, 124.9, 117.8, 109.2, 41.3, 28.2, 23.9 (three carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 1412, 1215, 755 cm^{-1}; MS (EI): m/z (%): 243 (M^+, 4), 161 (30), 130 (65), 117 (85), 105 (46), 91 (100), 77 (28), 41 (81); HRMS (EI-TOF) calcd for $C_{15}H_{21}N_3$ (M^+): 243.1735, found: 243.1740.

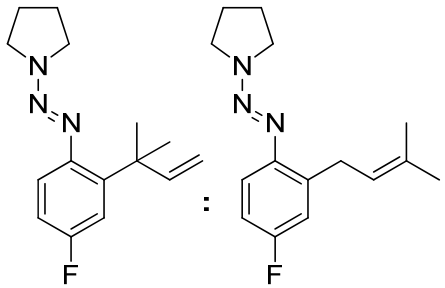


90 : 10
4b

Yield: 80%; brown oil; R*f* = 0.64 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (d, *J* = 8.0 Hz, 1 H), 7.15 (s, 1 H), 6.98 (d, *J* =

8.0 Hz, 1 H), 6.31 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.98-4.89 (m, 2 H), 3.77 (br, 4 H), 2.32 (s, 3 H), 2.03-1.99 (m, 4 H), 1.55 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.36 (t, *J* = 7.2 Hz, 1 H), 3.54 (d, *J* = 9.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 149.2, 138.8, 136.3, 126.4, 125.7, 118.5, 109.0, 41.0, 28.3, 23.9, 20.8 (three carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2968, 1413, 755 cm^{-1}; MS (EI): m/z (%): 257 (M^+, 5), 214 (12), 175 (36), 159 (34), 144 (86), 129 (100), 117 (49), 105 (98), 41 (98), 28 (35); HRMS (EI-TOF) calcd for $C_{16}H_{23}N_3$ (M^+): 257.1892, found: 257.1891.

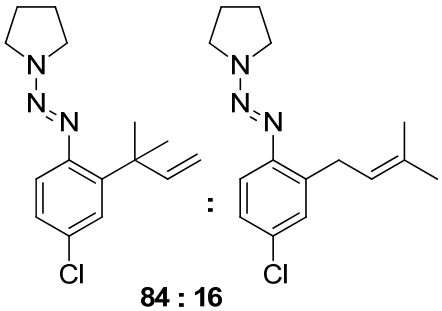


59 : 41

4c

Yield: 79%; brown oil; R*f* = 0.59 (10:1 Petroleum ether/EtOAc);

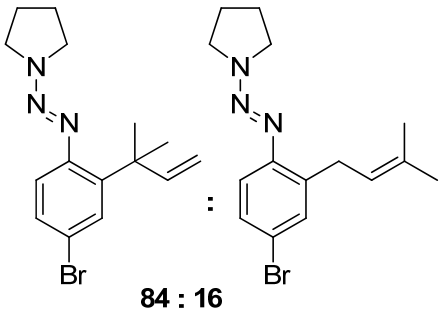
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.29 (m, 1 H), 7.07 (dd, *J* = 11.4 Hz, 1.8 Hz, 1 H), 6.92-6.81 (m, 1 H), 6.28 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 5.00-4.92 (m, 2 H), 3.56 (br, 4 H), 2.06-1.98 (m, 4 H), 1.55 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.35 (t, *J* = 7.2 Hz, 1 H), 3.54 (d, *J* = 7.2 Hz, 2 H), 1.75(s, 3 H), 1.73 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.7, 159.3, 148.4, 145.64, 145.60, 143.8, 143.7, 118.9, 118.8, 113.6, 113.4, 113.1, 112.87, 109.8, 41.3, 29.4, 28.0, 25.7, 23.8, 17.8; IR(ATR-FTIR): 2970, 1480, 816 cm^{-1}; MS (EI): m/z (%): 261 (M^+, 5), 162 (30), 148 (51), 135 (84), 123 (42), 109 (100), 83 (37), 28 (31); HRMS (EI-TOF) calcd for $C_{15}H_{20}FN_3$ (M^+): 261.1641, found: 261.1642.



84 : 16
4d

Yield: 85%; brown oil; R*f* = 0.62 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32-7.26 (m, 2 H), 7.14-7.12 (m, 1 H), 6.26 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.98-4.93 (m, 2 H), 3.80 (br, 2 H), 3.71 (br, 2 H), 2.02 (br, 4 H), 1.55 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.30 (t, *J* = 7.4 Hz, 1 H), 3.53 (d, *J* = 7.6 Hz, 2 H), 1.75 (s, 3 H), 1.73 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 147.8, 143.3, 130.0, 126.8, 126.6, 118.9, 110.0, 41.4, 29.4, 28.0, 23.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2969, 1420, 820 cm^{-1}; MS (EI): m/z (%): 279 (M^+, Cl^{37}, 2), 277 (M^+, Cl^{35}, 6), 195 (26), 144 (60), 129 (100), 115 (14), 83 (35), 41 (96); HRMS (EI-TOF) calcd for $C_{15}H_{20}ClN_3$ (M^+): 277.1346, found: 277.1345.

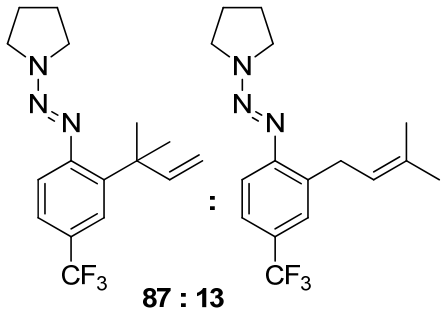


84 : 16
4e

Yield: 86%; brown oil; R*f* = 0.71 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (s, 1 H), 7.24-7.20 (m, 2 H), 6.22 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.96-4.88 (m, 2 H), 4.00-3.56 (m, 4 H), 2.03-1.95 (m, 4 H), 1.51 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.30 (t, *J* = 7.2 Hz, 1 H), 3.51 (d, *J* = 7.2 Hz, 2 H), 1.71 (s, 3 H), 1.70 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.4, 148.3, 143.7, 129.63, 129.58, 119.3, 118.2, 109.8, 50.6, 47.0, 41.3, 27.4, 28.0, 23.8; IR(ATR-FTIR): 2969, 1417, 819 cm^{-1}; MS (EI): m/z

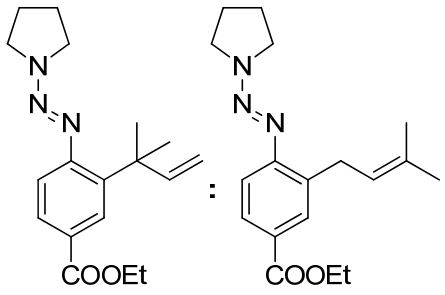
(%): 323 (M^+, Br^{81}, 4), 321 (M^+, Br^{79}, 4), 144 (42), 129 (100), 115 (16), 83 (18), 70 (16), 41 (47); HRMS (EI-TOF) calcd for $C_{15}H_{20}BrN_3$ (M^+): 321.0841, found: 321.0835.



87 : 13
4f

Yield: 84%; brown oil; R*f* = 0.57 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (s, 1 H), 7.46-7.40 (m, 2 H), 6.27 (dd, *J* = 17.8 Hz, 10.2 Hz, 1 H), 5.00-4.92 (m, 2 H), 3.95 (br, 2 H), 3.68 (br, 2 H), 2.09-2.02 (m, 4 H), 1.58 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.35 (t, *J* = 7.2 Hz, 1 H), 3.59 (d, *J* = 7.6 Hz, 2 H), 1.74 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.0, 148.4, 142.0, 126.0, 123.78, 123.73, 117.8, 110.0, 50.9, 47.2, 41.4, 28.0, 24.0, 23.6; IR(ATR-FTIR): 2875, 1316, 1079, 833 cm^{-1}; MS (EI): m/z (%): 311 (M^+, 11), 212 (24), 199 (51), 185 (50), 165 (42), 159 (44), 129 (43), 70 (49), 41 (100), 28 (46); HRMS (EI-TOF) calcd for $C_{15}H_{20}F_3N_3$ (M^+): 311.1609, found: 311.1613.

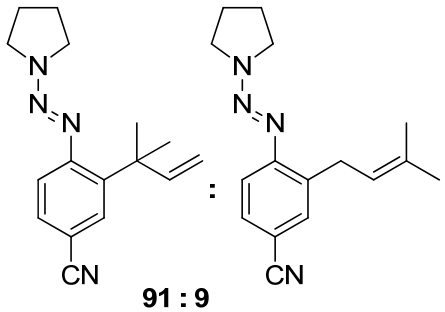


86 : 14
4g

Yield: 81%; brown oil; R*f* = 0.69 (5:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 6.28 (dd, *J* = 17.4 Hz, 11.0 Hz, 1 H), 4.98-4.89 (m, 2 H), 4.36 (q, *J* = 7.2

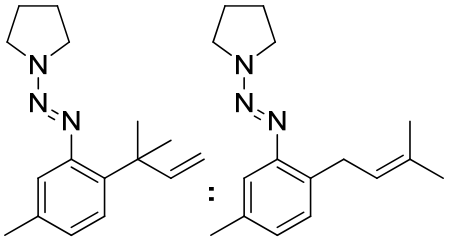
Hz, 2 H), 3.95 (br, 2 H), 3.68 (br, 2 H), 2.04 (br, 4 H), 1.57 (s, 6 H), 1.39 (t, *J* = 7.2 Hz, 3 H). The following signal is discernible for the minor isomer (α-selective product): 5.36 (t, J = 7.2 Hz, 1H), 3.58 (d, J = 7.2 Hz, 2 H), 1.74 (s, 3 H), 1.72 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 152.9, 148.7, 141.4, 128.3, 128.2, 126.1, 117.4, 109.6, 60.5, 50.7, 47.0, 41.2, 28.1, 24.0, 23.6, 14.3; IR(ATR-FTIR): 1708, 1245, 1107, 775 cm^{-1}; MS (EI): m/z (%): 315 (M^+, 8), 233 (29), 145 (70), 129 (84), 117 (45), 91 (38), 41 (66), 29 (100); HRMS (EI-TOF) calcd for $C_{18}H_{25}N_3O_2$ (M^+): 315.1947, found: 315.1950.



91 : 9
4h

Yield: 84%; brown oil; R*f* = 0.68 (5:1 Petroleum ether/EtOAc);

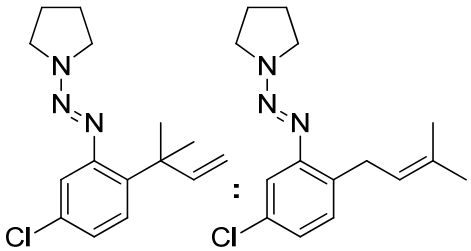
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1 H), 7.46-7.42 (m, 2 H), 6.21 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.98-4.90 (m, 2 H), 3.95 (br, 2 H), 3.67 (br, 2 H), 2.05 (br, 4 H), 1.54 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.30 (t, *J* = 7.4 Hz, 1 H), 3.53 (d, *J* = 7.6 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 147.9, 142.4, 131.0, 130.6, 120.0, 118.0, 110.2, 107.1, 51.0, 47.4, 41.3, 27.8, 23.9, 23.4; IR(ATR-FTIR): 2970, 2219, 1477, 907, 831, 736 cm^{-1}; MS (EI): m/z (%): 268 (M^+, 13), 225 (16), 169 (38), 156 (81), 142 (82), 128 (51), 116 (75), 70 (52), 41 (100), 28 (42); HRMS (EI-TOF) calcd for C16H20N4 (M^+): 268.1688, found: 268.1689.



90 : 10
4i

Yield: 86%; brown oil; R*f* = 0.70 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.21 (m, 1 H), 7.13 (s, 1 H), 6.95-6.87 (m, 1 H), 6.36-6.22 (m, 1 H), 4.99-4.86 (m, 2 H), 3.79 (br, 4 H), 2.30 (s, 3 H), 2.01 (br, 4 H), 1.58-1.52 (m, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.41-5.30 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 149.2, 138.8, 136.3, 126.4, 125.7, 118.5, 109.0, 41.0, 28.3, 23.9, 20.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2967, 1418, 811 cm^{-1}; MS (EI): m/z (%): 257 (M^+, 5), 214 (12), 175 (36), 159 (34), 144 (86), 129 (100), 117 (49), 105 (98), 41 (98), 28 (35); HRMS (EI-TOF) calcd for $C_{16}H_{23}N_3$ (M^+): 257.1892, found: 257.1891.

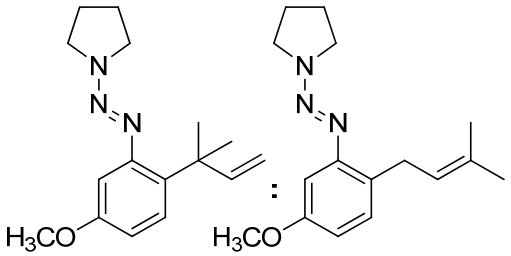


80 : 20
4j

Yield: 88%; brown oil; R*f* = 0.76 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, *J* = 2.4 Hz, 1 H), 7.25 (d, *J* = 8.4 Hz, 1 H), 7.01 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 6.24 (dd, *J* = 17.0 Hz, 11.0 Hz, 1 H), 4.95-4.88 (m, 2 H), 4.00-3.53 (m, 4 H), 2.04-1.99 (m, 4 H), 1.53 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.31 (t, *J* = 7.2 Hz, 1 H), 3.51 (d, *J* = 7.2 Hz, 2 H), 1.71 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 150.2, 148.8, 140.1, 132.4, 130.4, 124.3, 117.6, 109.5, 41.1, 29.1, 28.1, 25.7, 23.8, 17.9; IR(ATR-FTIR): 2969, 1414, 863, 810 cm^{-1}; MS (EI): m/z (%): 279 (M^+, Cl^{37}, 4), 277

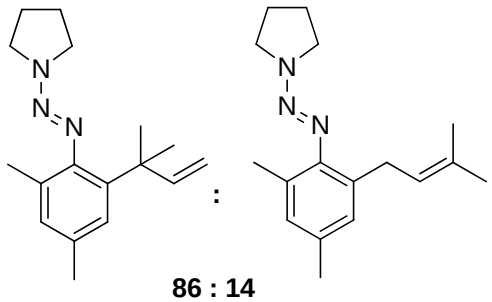
(M^+, Cl^{35}, 12), 195 (26), 165 (36), 144 (63), 129 (100), 115 (41), 84 (25), 70 (45), 41 (90); HRMS (EI-TOF) calcd for $C_{15}H_{20}ClN_3$ (M^+): 277.1346, found: 277.1347.



93 : 7
4k

Yield: 72%; brown oil; R*f* = 0.59 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.4 Hz, 1 H), 6.94 (d, *J* = 2.8 Hz, 1 H), 6.64 (dd, *J* = 8.4 Hz, 1.4 Hz, 1 H), 6.27 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.95-4.86 (m, 2 H), 3.87-3.70 (m, 7 H), 2.04-1.99 (m, 4 H), 1.53 (s, 6 H); The following signal is discernible for the minor isomer (α-selective product): 5.33 (t, *J* = 7.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.4, 150.2, 149.6, 134.4, 127.4, 110.6, 108.9, 102.7, 55.2, 40.8, 28.4, 23.9, 23.8 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2962, 1601, 1037, 808 cm^{-1}; MS (EI): m/z (%): 273 (M^+, 7), 191 (32), 174 (34), 160 (83), 145 (63), 121 (59), 91 (59), 77 (30), 41 (100), 28 (38); HRMS (EI-TOF) calcd for $C_{16}H_{23}N_3O$ (M^+): 273.1841, found: 273.1840.

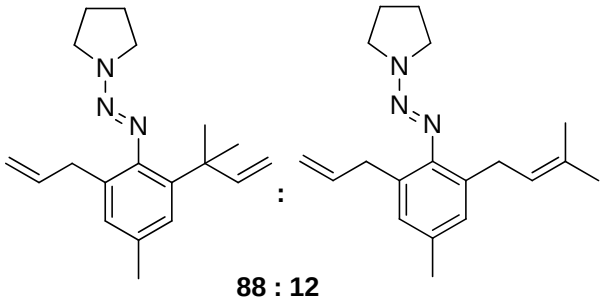


86 : 14
4l

Yield: 86%; brown oil; R*f* = 0.68 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.02 (s, 1 H), 6.90 (s, 1 H), 6.08 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.91-4.81 (m, 2 H), 3.76 (br, 4 H), 2.29 (s, 3 H), 2.07 (s, 3 H), 2.05-1.99 (m, 4 H), 1.43 (s, 6 H). The following signal is discernible for the minor isomer

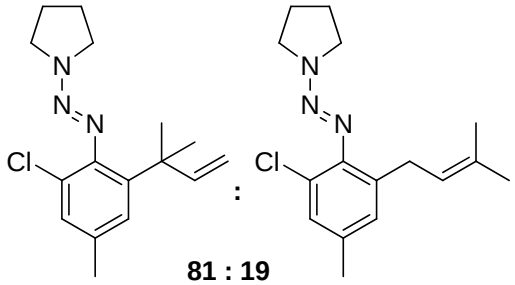
(α-selective product): δ 6.84 (s, 1 H), 5.25 (t, *J* = 7.2 Hz, 1 H), 3.25 (d, *J* = 7.2 Hz, 2 H), 2.27 (s, 3 H), 2.16 (s, 3 H), 1.71 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.6, 147.7, 140.6, 133.4, 130.0, 129.6, 125.0, 108.5, 41.1, 28.4, 24.0, 21.1, 19.2 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2869, 1433, 1324, 1132, 855, 762 cm^{-1}; MS (ES$^+$): m/z (%): 272 ([M+H]$^+$, 2), 173 (100), 168 (19), 143 (87), 128 (56), 119 (22); HRMS (ES$^+$-TOF) calcd for $C_{17}H_{25}N_3$ ([M+H]$^+$): 272.2126, found: 272.2125.



88 : 12
4m

Yield: 80%; brown oil; R*f* = 0.64 (10:1 Petroleum ether/EtOAc);

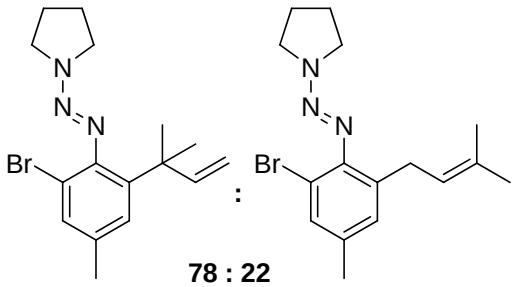
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.08 (s, 1 H), 6.94 (s, 1 H), 6.10 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 5.99-5.87 (m, 1 H), 5.09-4.99 (m, 2 H), 4.94-4.82 (m, 2 H), 3.77 (br, 4 H), 3.21 (d, *J* = 6.8 Hz, 2 H), 2.33 (s, 3 H), 2.06-1.98 (m, 4 H), 1.45 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.27 (t, *J* = 7.0 Hz, 1 H), 3.33 (d, *J* = 6.8 Hz, 2 H), 3.28 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.5, 147.4, 140.8, 138.2, 133.5, 131.8, 128.7, 125.4, 114.9, 108.4, 41.1, 36.6, 28.4, 23.9, 21.2; IR(ATR-FTIR): 2870, 1433, 1324, 857 cm^{-1}; MS (ES$^+$): m/z (%): 298 ([M+H]$^+$, 3), 227 (25), 199 (94), 171 (30), 157 (100), 143 (67), 115 (13); HRMS (ES$^+$-TOF) calcd for $C_{19}H_{27}N_3$ ([M+H]$^+$): 298.2283, found: 298.2274.



81 : 19
4n

Yield: 83%; brown oil; R*f* = 0.77 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12 (s, 1 H), 7.08 (s, 1 H), 6.04 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.92-4.83 (m, 2 H), 3.97-3.64 (m, 4 H), 2.30 (s, 3 H), 2.08-1.97 (m, 4 H), 1.43 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.22 (t, *J* = 7.2 Hz, 1 H), 3.26 (d, *J* = 7.6 Hz, 2 H), 3.28 (d, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 1.72 (s, 3 H), 1.66 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 145.7, 142.6, 134.5, 128.6, 126.6, 125.9, 109.0, 41.4, 28.1, 20.63, 20.6 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2871, 1424, 1321, 852, 758 cm^{-1}; MS (ES^+): m/z (%): 294 ($[M+H]^+$, Cl^{37}, 2), 292 ($[M+H]^+$, Cl^{35}, 6), 199 (26), 173 (50), 144 (60), 129 (100), 115 (14); HRMS (ES^+-TOF) calcd for $C_{15}H_{20}ClN_3$ ($[M+H]^+$): 292.1580, found: 292.1582.

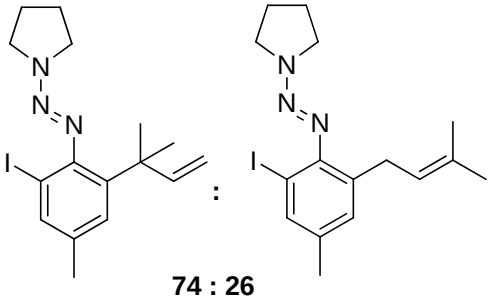


78 : 22
4o

Yield: 86%; brown oil; R*f* = 0.66 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (s, 1 H), 7.12 (s, 1 H), 6.03 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.92-4.84 (m, 2 H), 4.02-3.59 (m, 4 H), 2.30 (s, 3 H), 2.03 (br, 4 H), 1.42 (s, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.22 (t, *J* = 7.2 Hz, 1 H), 3.26 (d, *J* = 7.6 Hz, 2 H), 3.26 (d, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 1.72 (s, 3 H), 1.68 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.6, 146.8, 142.6, 135.0, 131.7, 126.7, 116.9, 109.0, 41.5, 28.2, 20.5 (four carbon signal of pyrrolidine

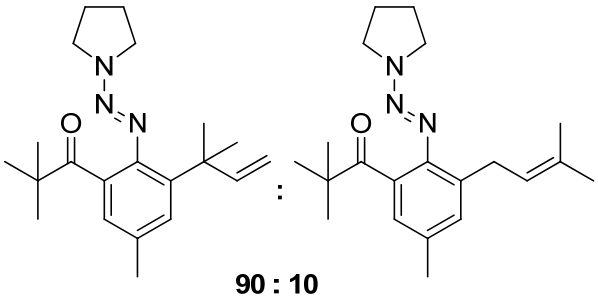
ring cannot be resolved); IR(ATR-FTIR): 2871, 1426, 1322, 853, 736 cm^{-1}; MS (ES^+): m/z (%): 338 ($[M+H]^+$, Br^{81}, 4), 336 ($[M+H]^+$, Br^{79}, 4), 171 (60), 144 (42), 129 (100), 115 (16); HRMS (ES^+-TOF) calcd for $C_{16}H_{22}BrN_3[M+H]^+$: 336.1075, found: 336.1070.



74 : 26
4p

Yield: 80%; brown oil; R*f* = 0.28 (50:1 Petroleum ether/EtOAc);

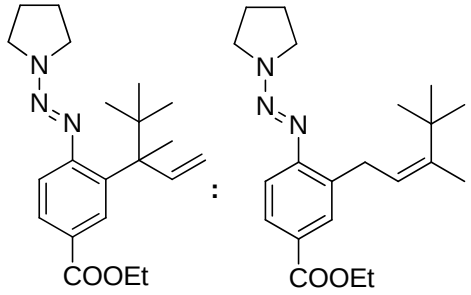
^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (s, 1 H), 7.14 (s, 1 H), 6.03 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.91-4.82 (m, 2 H), 3.81 (br, 4 H), 2.28 (s, 3 H), 2.05 (br, 4 H), 1.40 (s, 6 H); The following signal is discernible for the minor isomer (α-selective product): 7.53 (s, 1 H), 6.95 (s, 1 H), 5.21 (t, *J* = 7.2 Hz, 1 H), 3.25 (d, *J* = 7.2 Hz, 2 H), 2.26 (s, 3 H), 1.71 (s, 3 H), 1.65 (s, 3 H); ^{13}C NMR (the mixture of α- and β-selective products, 100 MHz, $CDCl_3$): δ 149.2, 148.8, 148.0, 141.8, 138.1, 137.1, 136.1, 135.7, 134.3, 131.8, 130.6, 127.9, 123.1, 109.0, 93.2, 93.0, 41.6, 30.8, 28.3, 25.7, 24.0, 23.9, 20.5, 20.3, 17.8; IR(ATR-FTIR): 2967, 1422, 902, 854 cm^{-1}; MS (EI): m/z (%): 383 (M^+, 4), 158 (25), 143 (100), 128 (35), 83 (26), 41 (35), 28 (20); HRMS (EI-TOF) calcd for $C_{16}H_{22}IN_3$ (M^+): 383.0858, found: 383.0860.



90 : 10
4q

Yield: 89%; brown oil; R*f* = 0.41 (20:1 Petroleum ether/EtOAc);

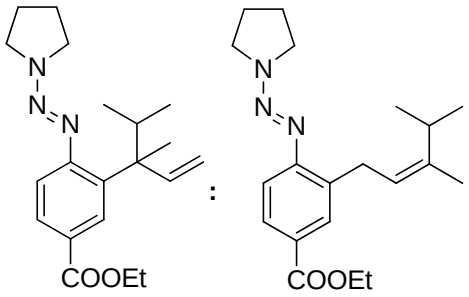
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 1 H), 6.69 (s, 1 H), 6.23 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.93-4.83 (m, 2 H), 3.91-3.56 (m, 4 H), 2.31 (s, 3 H), 1.97 (br, 4 H), 1.52 (s, 6 H), 1.08 (s, 9 H). The following signal is discernible for the minor isomer (α-selective product): 6.99 (s, 1 H), 6.66 (s, 1 H), 5.31 (t, *J* = 8.0 Hz, 1 H), 3.51 (d, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 1.71 (s, 6 H), 1.14 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.6, 149.2, 143.6, 142.2, 133.7, 132.5, 127.9, 125.7, 109.2, 44.3, 41.4, 28.4, 27.5, 21.1 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2968, 1682, 1416, 847, 738 cm^{-1}; MS (EI): m/z (%): 341 (M^+, 15), 284 (22), 244 (32), 187 (66), 143 (23), 98 (30), 84 (56), 69 (69), 57 (100), 41 (87), 29 (36); HRMS (EI-TOF) calcd for $C_{21}H_{31}N_3O$ (M^+): 341.2467, found: 341.2466.



50 : 50
4r

Yield: 83%; brown oil; R*f* = 0.70 (5:1 Petroleum ether/EtOAc);

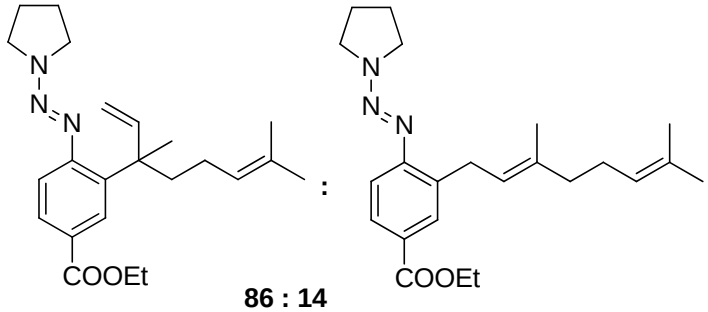
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (s, 1 H), 7.84-7.77 (m, 1 H), 7.30 (d, *J* = 6.4 Hz, 1 H), 7.04-7.10 (m, 1 H), 5.01-4.88 (m, 2 H), 4.39-4.31 (m, 2 H), 4.01-3.63 (m, 4 H), 2.03 (br, 4 H), 1.66 (s, 3 H), 1.42-1.35 (m, 3 H), 0.92 (s, 9 H). The following signal is discernible for the minor isomer (α-selective product): 7.87 (s, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 5.43 (t, *J* = 6.4 Hz, 1 H), 3.58 (d, *J* = 6.8 Hz, 2 H), 1.72 (s, 3 H), 1.06 (s, 9 H); ^{13}C NMR (β-selective product, 100 MHz, $CDCl_3$): δ 167.1, 153.8, 147.8, 140.0, 133.0, 127.7, 125.4, 118.4, 111.4, 60.5, 50.2, 38.1, 26.9, 23.4, 14.4 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2968, 1709, 1107, 722 cm^{-1}; MS (EI): m/z (%): 357 (M^+, 3), 342 (3), 300 (55), 231 (31), 216 (36), 143 (30), 129 (38), 84 (25), 70 (26), 41 (76), 29 (100); HRMS (EI-TOF) calcd for $C_{21}H_{31}N_3O_2$ (M^+): 357.2416, found: 357.2416.



74 : 26
4s

Yield: 85%; brown oil; R*f* = 0.44 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, *J* = 1.6 Hz, 1 H), 7.82 (dd, *J* = 8.6 Hz, 1.4 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 6.64 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.13-4.95 (m, 2 H), 4.35 (q, *J* = 7.2 Hz, 2 H), 4.05-3.64 (m, 4 H), 3.09-3.00 (m, 1 H), 2.09-2.01 (m, 4 H), 1.48 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 0.81 (d, *J* = 6.8 Hz, 3 H), 0.66 (d, *J* = 6.8 Hz, 3 H). The following signal is discernible for the minor isomer (α-selective product): 7.88 (s, 1 H), 5.38 (t, *J* = 7.2 Hz, 1 H), 3.58 (d, *J* = 6.8 Hz, 2 H), 2.33-2.24 (m, 1 H), 1.68 (s, 3 H), 1.01 (d, *J* = 6.4 Hz, 6 H); ^{13}C NMR (the mixture of α- and β-selective products, 100 MHz, $CDCl_3$): δ 167.1, 152.6, 145.5, 141.4, 129.5, 128.0, 126.1, 117.5, 112.3, 60.5, 48.4, 32.9, 21.4, 18.9, 18.3, 17.8, 14.4; IR(ATR-FTIR): 2965, 1704, 1108, 773 cm^{-1}; MS (EI): m/z (%): 343 (M^+, 15), 300 (31), 274 (37), 261 (41), 216 (47), 163 (39), 131 (60), 85 (69), 70 (43), 41 (91), 29 (100); HRMS (EI-TOF) calcd for $C_{20}H_{29}N_3O_2$ (M^+): 343.2260, found: 343.2263.

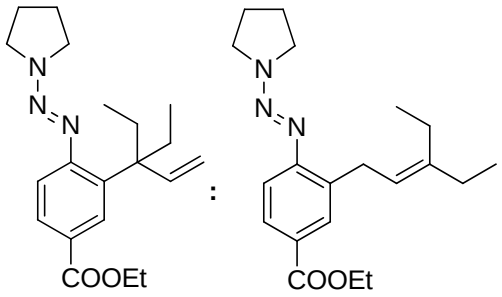


86 : 14
4t

Yield: 80%; brown oil; R*f* = 0.74 (5:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1 H), 7.84 (d, *J* = 8.8 Hz, 1 H), 7.39 (d, *J* = 8.4 Hz, 1 H), 6.34 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 5.04 (t, *J* = 6.8 Hz, 1 H), 5.00-4.91 (m, 2 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.94 (br, 2 H), 3.67 (br, 2 H), 2.26 (dt, *J* = 12.4 Hz,

5.2 Hz, 1 H), 2.04 (br, 4 H), 1.89 (dt, *J* = 12.3 Hz, 4.3 Hz, 1 H), 1.81-1.68 (m, 2 H), 1.62 (s, 3 H), 1.56 (s, 3 H), 1.47 (s, 3 H), 1.39 (t, *J* = 7.0 Hz, 3 H). The following signal is discernible for the minor isomer (α-selective product): 5.37 (t, *J* = 7.0 Hz, 1 H), 3.59 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.1, 152.9, 147.8, 139.9, 130.8, 129.4, 128.3, 126.1, 125.1, 117.3, 110.3, 60.6, 44.7, 39.7, 25.6, 25.3, 23.7, 17.5, 14.4 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2972, 1709, 1107, 774 cm^{-1}; MS (EI): m/z (%): 383 (M^+, 8), 299 (32), 216 (30), 143 (22), 129 (34), 84 (35), 69 (61), 41 (100), 29 (73); HRMS (EI-TOF) calcd for $C_{23}H_{33}N_3O_2$ (M^+): 383.2573, found: 383.2569.

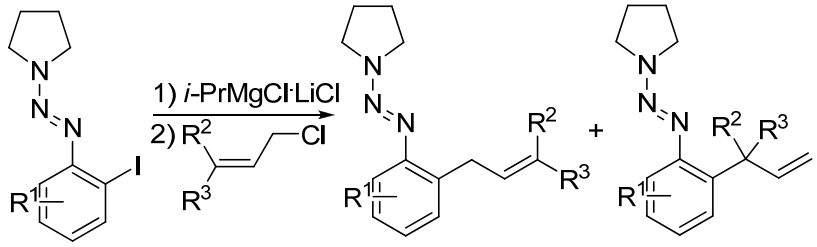


60 : 40
4u

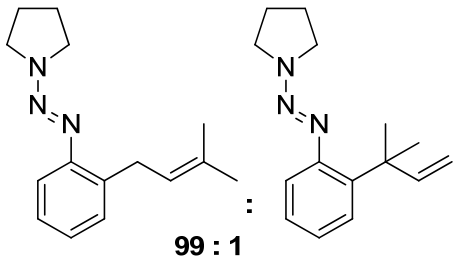
Yield: 80%; brown oil; R*f* = 0.45 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (d, *J* = 1.6 Hz, 1 H), 7.84 (d, *J* = 8.4 Hz, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 6.11 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.12-4.90 (m, 2 H), 4.39-4.33 (m, 2 H), 4.02-3.65 (m, 4 H), 2.10-2.01 (m, 4 H), 1.41-1.36 (m, 3 H), 1.00 (dt, *J* = 7.5 Hz, 2.1 Hz, 4 H), 0.69 (t, *J* = 7.4 Hz, 6 H). The following signal is discernible for the minor isomer (α-selective product): 5.32 (t, *J* = 7.4 Hz, 1 H), 3.61 (d, *J* = 7.2 Hz, 2 H); ^{13}C NMR (the mixture of α- and β-selective products, 100 MHz, $CDCl_3$): δ 167.2, 153.1, 145.8, 139.0, 130.7, 128.1, 126.0, 117.3, 111.1, 60.5, 48.6, 28.7, 14.4, 8.9 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2967, 1709, 1108, 772 cm^{-1}; MS (EI): m/z (%): 343 (M^+, 9), 314 (18), 261 (23), 143 (27), 117 (27), 55 (30), 41 (55), 29 (100); HRMS (EI-TOF) calcd for $C_{20}H_{29}N_3O_2$ (M^+): 343.2260, found: 343.2263.

E. General Procedure of Compound 5



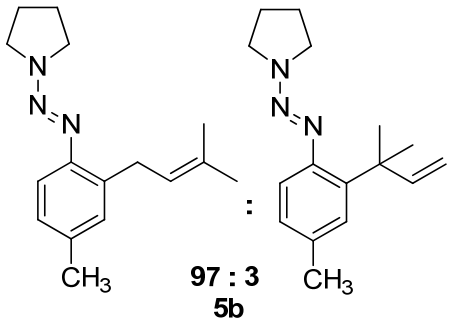
A dry and nitrogen-flushed 25 ml Schlenk tube equipped with a magnetic stirrer and a septum was charged with a solution of (*E*)-1-((2-iodoophenyl)diazenyl)pyrrolidine (1 mmol, 1.0 equiv) in dry THF (4 ml). *i*-PrMgCl·LiCl (1.3 mL, 1.3 mmol, 1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C. After the reaction mixture was continuously stirred at –30 °C for 3 h, a complete Br/Mg exchange was observed as indicated by thin layer chromatography (TLC). Allyl chloride (3 mmol, 3.0 equiv) was added at –30 °C and then the resulting mixture was stirred for 24 h before the addition of saturated aqueous NH_4Cl solution (10ml). The resulting mixture was extracted with ethyl acetate (3 × 30 mL). The organic fractions were dried over Na_2SO_4, concentrated in vacuo and purified by silica gel chromatography.



Yield: 94%; brown oil; R*f* = 0.66 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 1 H), 7.21 (d, *J* = 7.6 Hz, 1 H), 7.17 (t, *J* = 7.4 Hz, 1 H), 7.10 (t, *J* = 7.4 Hz, 1 H), 5.40 (t, *J* = 7.2 Hz, 1 H), 3.83 (br, 4 H), 3.61 (d, *J* = 7.2 Hz, 2 H), 2.07-2.00 (m, 4 H), 1.77 (s, 3 H), 1.75 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.34 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.01-4.92 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.5, 135.8, 131.4, 129.3, 126.3, 125.2, 123.8, 116.5, 29.6, 25.8, 23.8 (X2, carbon signal of

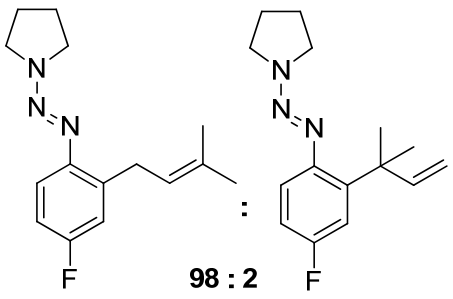
pyrrolidine ring), 17.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2970, 1413, 758 cm^{-1}; MS (EI): m/z (%): 243 (M^+, 6), 174 (23), 144 (40), 130 (75), 117 (100), 105 (48), 91 (94), 70 (30), 41 (69), 28 (31); HRMS (EI-TOF) calcd for $C_{15}H_{21}N_3$ (M^+): 243.1735, found: 243.1734.



5b

Yield: 82%; brown oil; R*f* = 0.64 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25 (d, *J* = 8.4 Hz, 1 H), 6.97 (s, 1 H), 6.94 (d, *J* = 8.4 Hz, 1 H), 5.35 (t, *J* = 7.4 Hz, 1 H), 3.77 (br, 4 H), 3.53 (d, *J* = 7.2 Hz, 2 H), 2.03-1.96 (m, 4 H), 1.73 (s, 3 H), 1.72 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.31 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.97-4.88 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.3, 135.6, 134.7, 131.2, 129.9, 127.0, 124.0, 116.3, 29.6, 25.8, 23.8 (X2, carbon signal of pyrrolidine ring), 21.0, 17.9 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2969, 1319, 818 cm^{-1}; MS (EI): m/z (%): 257 (M^+, 10), 187 (21), 159 (63), 144 (100), 131 (94), 105 (87), 83 (44), 41 (82), 28 (40); HRMS (EI-TOF) calcd for $C_{16}H_{23}N_3$ (M^+): 257.1892, found: 257.1894.

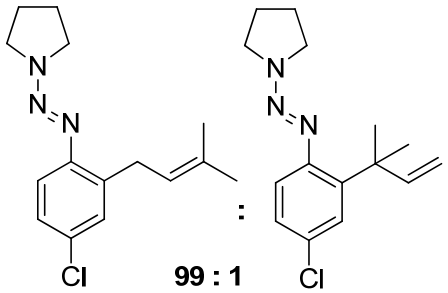


5c

Yield: 83%; brown oil; R*f* = 0.59 (10:1 Petroleum ether/EtOAc);

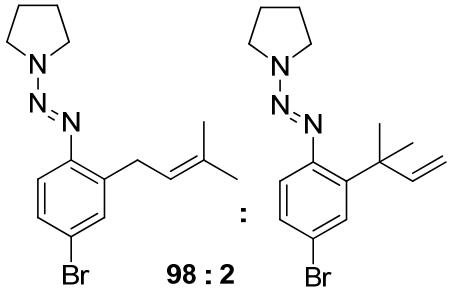
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.30 (m, 1 H), 6.89 (d, *J* = 9.2 Hz, 1 H),

6.87-6.80 (m, 1 H), 5.35 (t, *J* = 7.2 Hz, 1 H), 3.78 (br, 4 H), 3.56 (d, *J* = 7.6 Hz, 2 H), 2.06-1.99 (m, 4 H), 1.76 (s, 3 H), 1.73 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.28 (dd, *J* = 17.8 Hz, 11.0 Hz, 1 H), 5.00-4.93 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.8 (d, $^1J_{C\text{-}F}$ = 241.3 Hz), 144.9 (d, $^4J_{C\text{-}F}$ = 2.5 Hz), 137.7 (d, $^3J_{C\text{-}F}$ = 7.6 Hz), 132.4, 122.8, 117.6 (d, $^3J_{C\text{-}F}$ = 8.3 Hz), 115.4 (d, $^2J_{C\text{-}F}$ = 21.9 Hz), 112.8 (d, $^2J_{C\text{-}F}$ = 22.6 Hz), 29.4, 25.7, 23.8 (X2, carbon signal of pyrrolidine ring), 17.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2971, 1482, 815 cm^{-1}; MS (EI): m/z (%): 261 (M^+, 7), 249 (17), 221 (21), 162 (30), 148 (56), 135 (100), 123 (42), 109 (88), 83 (47), 41 (84), 28 (39); HRMS (EI-TOF) calcd for $C_{15}H_{20}FN_3$ (M^+): 261.1641, found: 261.1643.



Yield: 85%; brown oil; R*f* = 0.62 (10:1 Petroleum ether/EtOAc);

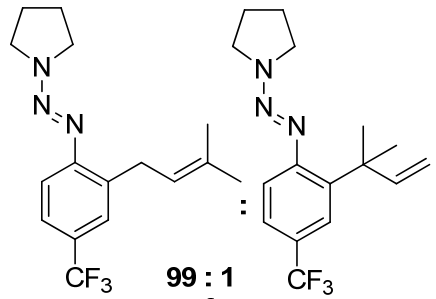
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (d, *J* = 8.8 Hz, 1 H), 7.15 (s, 1 H), 7.09 (dd, *J* = 8.6 Hz, 1.8 Hz, 1 H), 5.34 (t, *J* = 7.4 Hz, 1 H), 3.85 (br, 4 H), 3.55 (d, *J* = 7.6 Hz, 2 H), 2.06-1.99 (m, 4 H), 1.75 (s, 3 H), 1.73 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.27 (dd, *J* = 17.2 Hz, 10.8 Hz, 1 H), 4.99-4.93 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 137.5, 132.3, 130.2, 129.0, 126.2, 122.9, 117.6, 29.4, 25.7, 23.7 (X2, carbon signal of pyrrolidine ring), 17.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2972, 1106, 817 cm^{-1}; MS (EI): m/z (%): 279 (M^+, Cl^{37}, 5), 277 (M^+, Cl^{35}, 11), 207 (21), 178 (25), 144 (91), 129 (100), 112 (40), 83 (58), 41 (84), 28 (41); HRMS (EI-TOF) calcd for $C_{15}H_{20}ClN_3$ (M^+): 277.1346, found: 277.1350.



5e

Yield: 81%; brown oil; R*f* = 0.71 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 (s, 1 H), 7.25-7.21 (m, 2 H), 5.32 (t, *J* = 7.4 Hz, 1 H), 3.79 (br, 4 H), 3.52 (d, *J* = 7.2 Hz, 2 H), 2.05-1.98 (m, 4 H), 1.73 (s, 3 H), 1.72 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.25 (dd, *J* = 18.0 Hz, 10.4 Hz, 1 H), 4.97-4.90 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.5, 137.9, 132.3, 131.9, 129.2, 122.9, 118.3, 118.0, 29.3, 25.8, 23.7 (X2, carbon signal of pyrrolidine ring), 17.9 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2970, 1314, 816 cm^{-1}; MS (EI): m/z (%): 323 (M^+, Br^{81}, 25), 321 (M^+, Br^{79}, 21), 253 (13), 144 (49), 129 (100), 112 (49), 83 (40), 70 (26), 41 (43); HRMS (EI-TOF) calcd for $C_{15}H_{20}BrN_3$ (M^+): 321.0841, found: 321.0843.

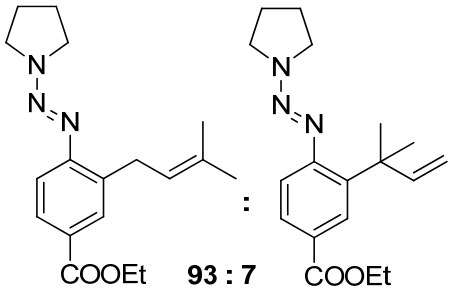


5f

Yield: 77%; brown oil; R*f* = 0.57 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 1 H), 7.42 (s, 1 H), 7.38 (d, *J* = 8.4 Hz, 1 H), 5.35 (t, *J* = 7.2 Hz, 1 H), 3.96 (br, 2 H), 3.70 (br, 2 H), 3.60 (d, *J* = 7.6 Hz, 2 H), 2.05 (br, 4 H), 1.75 (s, 6 H). The following signal is discernible for the minor isomer (γ-selective product): 6.28 (dd, *J* = 17.4 Hz, 10.2 Hz, 1 H), 5.01-4.93 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.2, 136.1, 132.5, 126.7 (q, $^{2}J_{C\text{-}F}$ = 30.1 Hz), 126.2 (q, $^{3}J_{C\text{-}F}$ = 3.7 Hz), 123.3 (q, $^{3}J_{C\text{-}F}$ = 4.3 Hz), 122.8, 116.5, 51.0, 46.6, 29.6, 25.7, 23.8, 17.9 (the carbon signal of CF_3 cannot be resolved); IR(ATR-FTIR): 2974, 1404,

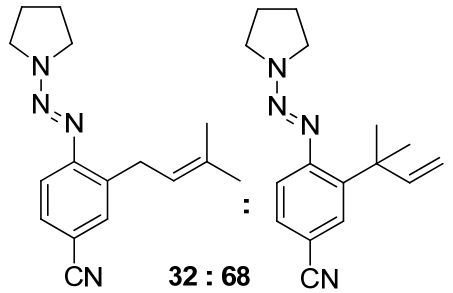
1107, 832 cm^{-1}; MS (EI): m/z (%): 311 (M^+, 11), 242 (23), 212 (40), 185 (79), 165 (48), 159 (47), 129 (47), 70 (61), 41 (100), 28 (46); HRMS (EI-TOF) calcd for $C_{15}H_{20}F_3N_3$ (M^+): 311.1609, found: 311.1608.



5g

Yield: 76%; brown oil; R*f* = 0.69 (5:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 1 H), 5.36 (t, *J* = 7.0 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.95 (br, 2 H), 3.70 (br, 2 H), 3.58 (d, *J* = 7.6 Hz, 2 H), 2.04 (br, 4 H), 1.74 (s, 3 H), 1.72 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.28 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.97-4.90 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 152.2, 135.7, 131.9, 131.1, 127.9, 126.5, 123.3, 116.1, 60.5, 52.0, 46.8, 29.7, 25.8, 23.8 (X2, two carbon signal of pyrrolidine ring), 17.9, 14.4; IR(ATR-FTIR): 2974, 1708, 1106, 771 cm^{-1}; MS (EI): m/z (%): 315 (M^+, 16), 270 (13), 145 (47), 129 (52), 117 (32), 91 (23), 41 (43), 29 (100); HRMS (EI-TOF) calcd for $C_{18}H_{25}N_3O_2$ (M^+): 315.1947, found: 315.1946.

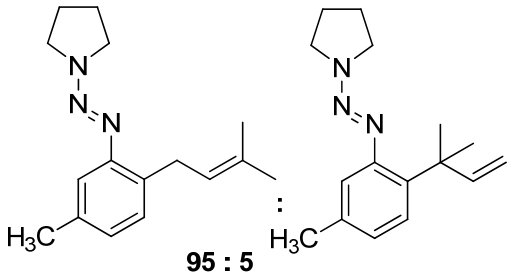


5h

Yield: 86%; brown oil; R*f* = 0.68 (5:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62 (s, 1 H), 7.35-7.50 (m, 2 H), 5.34 (t, *J* = 7.2 Hz, 1 H), 3.95 (br, 2 H), 3.67 (br, 2 H), 3.54 (d, *J* = 7.6 Hz, 2 H), 2.05 (br, 4 H), 1.75 (s, 3

H), 1.71 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.22 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.98-4.89 (m, 2 H), 1.54 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 151.9, 136.6, 133.2, 133.1, 130.2, 122.1, 120.0, 116.7, 107.3, 29.1, 25.7, 17.8 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2969, 2220, 1389, 831 cm^{-1}; MS (EI): m/z (%): 268 (M^+, 11), 225 (16), 169 (39), 156 (74), 142 (79), 128 (49), 116 (80), 70 (52), 41 (100), 28 (41); HRMS (EI-TOF) calcd for C16H20N4 (M^+): 268.1688, found: 268.1690.

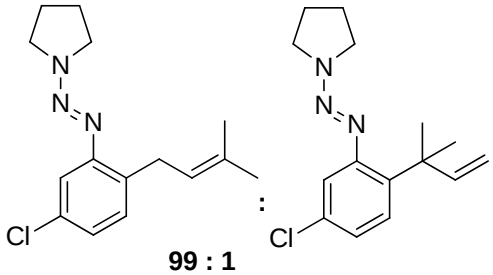


95 : 5

5i

Yield: 88%; brown oil; R*f* = 0.70 (10:1 Petroleum ether/EtOAc);

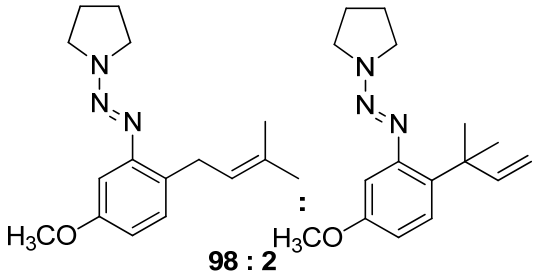
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18 (s, 1 H), 7.08 (d, *J* = 7.6 Hz, 1 H), 6.91 (d, *J* = 7.6 Hz, 1 H), 5.36 (t, *J* = 7.2 Hz, 1 H), 3.80 (br, 4 H), 3.54 (d, *J* = 7.6 Hz, 2 H), 2.32 (s, 3 H), 2.05-2.00 (m, 4 H), 1.74 (s, 3 H), 1.73 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.30 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.97-4.89 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.3, 135.8, 132.9, 131.1, 129.2, 126.1, 124.1, 117.0, 29.3, 25.8, 23.8 (X2, two carbon signal of pyrrolidine ring), 21.1, 17.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2969, 1418, 1102, 808 cm^{-1}; MS (EI): m/z (%): 257 (M^+, 10), 245 (22), 217 (36), 187 (24), 159 (57), 144 (100), 131 (88), 117 (51), 105 (91), 83 (46), 41 (83), 28 (38); HRMS (EI-TOF) calcd for $C_{16}H_{23}N_3$ (M^+): 257.1892, found: 257.1897.



99 : 1
5j

Yield: 85%; brown oil; R*f* = 0.76 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39 (d, *J* = 2.0 Hz, 1 H), 7.10 (d, *J* = 8.0 Hz, 1 H), 7.02 (dd, *J* = 8.0 Hz, 1.6 Hz, 1 H), 5.33 (t, *J* = 7.6 Hz, 1 H), 4.07-3.61 (m, 4 H), 3.52 (d, *J* = 7.2 Hz, 2 H), 2.08-1.99 (m, 4 H), 1.73 (s, 6 H). The following signal is discernible for the minor isomer (γ-selective product): 6.26 (dd, *J* = 17.4 Hz, 11.0 Hz, 1 H), 4.97-4.91 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.4, 134.2, 131.9, 131.8, 130.3, 124.7, 123.3, 116.4, 51.0, 46.3, 29.1, 25.7, 23.7 (X2), 17.8; IR(ATR-FTIR): 2971, 1416, 865, 807 cm^{-1}; MS (EI): m/z (%): 279 (M^+, Cl^{37}, 3), 277 (M^+, Cl^{35}, 8), 208 (25), 178 (38), 144 (85), 129 (100), 112 (39), 83 (43), 70 (41), 41 (96), 28 (45); HRMS (EI-TOF) calcd for $C_{15}H_{20}ClN_3$ (M^+): 277.1346, found: 277.1342.

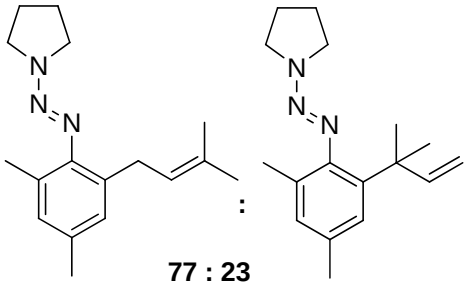


98 : 2
5k

Yield: 83%; brown oil; R*f* = 0.59 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, *J* = 8.0 Hz, 1 H), 6.98 (d, *J* = 2.8 Hz, 1 H), 6.68 (dd, *J* = 8.4 Hz, 1.2 Hz, 1 H), 5.35 (dt, *J* = 7.4 Hz, 1.2 Hz, 1 H), 3.87-3.72 (m, 7 H), 3.51 (d, *J* = 7.2 Hz, 2 H), 2.05-1.99 (m, 4 H), 1.74 (s, 3 H), 1.72 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.29 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 4.96-4.88 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.3, 149.1, 131.0, 130.0, 128.4, 124.3, 111.7, 101.1, 55.3, 28.9, 25.7, 23.8 (X2, two carbon signal of pyrrolidine ring), 17.8 (two carbon signal of pyrrolidine ring cannot be

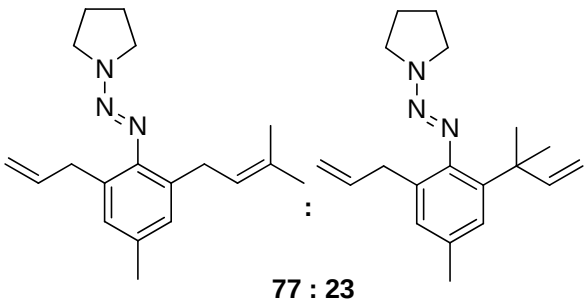
resolved); IR(ATR-FTIR): 2968, 1603, 1103, 854, 806 cm^{-1}; MS (EI): m/z (%): 273 (M^+, 6), 203 (20), 174 (62), 160 (84), 145 (55), 121 (64), 91 (53), 83 (39), 41 (100), 28 (39); HRMS (EI-TOF) calcd for $C_{16}H_{23}N_3O$ (M^+): 273.1841, found: 273.1842.



77 : 23
5l

Yield: 84%; brown oil; R*f* = 0.68 (10:1 Petroleum ether/EtOAc);

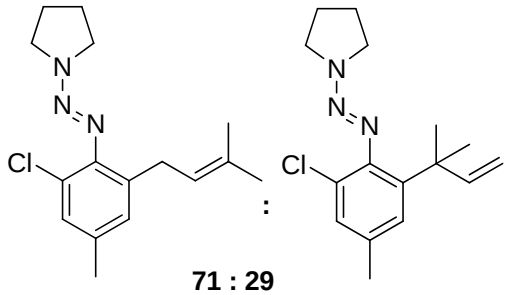
^1H NMR (400 MHz, $CDCl_3$): δ 6.85 (s, 1 H), 6.85 (s, 1 H), 5.27 (t, *J* = 7.2 Hz, 1 H), 3.77 (br, 4 H), 3.27 (d, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 2.18 (s, 3 H), 2.06-1.99 (m, 4 H), 1.73 (s, 3 H, SN2), 1.69 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 7.04 (s, 1 H), 6.91 (s, 1 H), 6.10 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.93-4.82 (m, 2 H), 2.31 (s, 3 H), 2.09 (s, 3 H), 1.45 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.4, 133.9, 133.7, 130.9, 129.7, 129.2, 127.7, 124.0, 30.3, 25.7, 23.8 (two carbon signal of pyrrolidine ring), 20.9, 18.5, 17.8 (two carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2968, 1430, 1323, 1212, 854 cm^{-1}; MS (ES^+): m/z (%): 257 ($[M+H]^+$, 10), 272 (3), 173 (100), 168 (23), 143 (100), 128 (67), 119 (25); HRMS (ES^+-TOF) calcd for $C_{17}H_{25}N_3$ ($[M+H]^+$): 272.2126, found: 272.2124.



77 : 23
5m

Yield: 85%; brown oil; R*f* = 0.64 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 6.888 (s, 1 H), 6.882 (s, 1 H), 6.01-5.88 (m, 1 H), 5.27 (t, *J* = 7.2 Hz, 1 H), 5.09-4.99 (m, 2 H), 3.78 (br, 4 H), 3.33 (d, *J* = 6.8 Hz, 2 H), 3.28 (d, *J* = 7.2 Hz, 2 H), 2.30 (s, 3 H), 2.08-1.98 (m, 4 H), 1.74 (s, 3 H), 1.70 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 7.07 (s, 1 H), 6.94 (s, 1 H), 6.10 (dd, *J* = 17.6 Hz, 10.4 Hz, 1 H), 4.93-4.83 (m, 2 H), 3.21 (d, *J* = 6.8 Hz, 2 H), 2.33 (s, 3 H), 1.46 (s, 6 H); ^{13}C NMR (the mixture of α- and β-selective products, 100 MHz, $CDCl_3$): δ 149.5, 147.4, 146.0, 140.8, 138.2, 138.0, 134.1, 133.6, 133.5, 131.9, 131.8, 131.1, 128.7, 128.2, 128.1, 125.4, 123.8, 114.9, 114.8, 108.4, 41.1, 36.6, 36.3, 30.2, 28.4, 25.8, 23.9, 23.8, 21.2, 20.9, 17.7; IR(ATR-FTIR): 2970, 1431, 1324, 1212, 856 cm^{-1}; MS (ES$^+$): m/z (%): 298 ([M+H]$^+$, 3), 227 (25), 199 (89), 171 (35), 157 (100), 143 (61), 115 (14); HRMS (ES$^+$-TOF) calcd for $C_{19}H_{27}N_3$ ([M+H]$^+$): 298.2283, found: 298.2283.

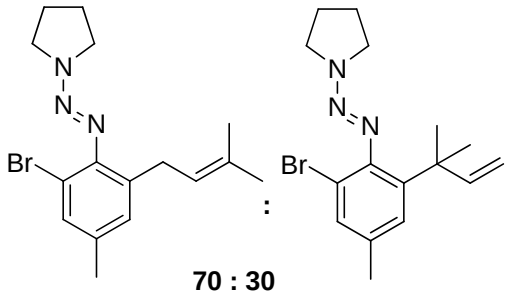


71 : 29
5n

Yield: 87%; brown oil; R*f* = 0.77 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (s, 1 H), 6.89 (s, 1 H), 5.22 (t, *J* = 7.0 Hz, 1 H), 3.95-3.63 (m, 4 H), 3.26 (d, *J* = 7.2 Hz, 2 H), 2.28 (s, 3 H), 2.03 (br, 4 H), 1.72 (s, 3 H), 1.66 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 7.21 (s, 1 H), 7.12 (s, 1 H), 6.04 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.93-4.84 (m, 2 H), 2.30 (s, 3 H), 1.43 (s, 6 H); ^{13}C NMR (the mixture of α- and β-selective products, 100 MHz, $CDCl_3$): δ 148.6, 145.7, 144.5, 142.6, 135.7, 135.0, 134.5, 131.7, 130.1, 128.6, 127.9, 126.5, 125.9, 122.9, 118.2, 109.0, 41.4, 30.3, 28.1, 25.7, 23.7, 20.9, 20.64, 20.57, 17.7; IR(ATR-FTIR): 2921, 1423, 1321, 851, 732 cm^{-1}; MS (ES$^+$): m/z (%): 294 ([M+H]$^+$, Cl^{37}, 3), 292 ([M+H]$^+$, Cl^{35}, 9), 208 (25), 178 (38), 144 (85), 129 (100), 112 (39), 83 (43), 70 (41), 41 (96), 28 (45); HRMS (ES$^+$-TOF) calcd for

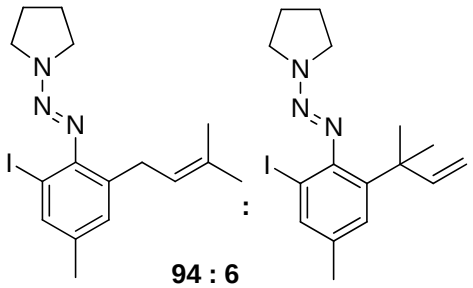
$C_{16}H_{22}ClN_3$ ([M+H]$^+$): 292.1580, found: 292.1581.



70 : 30
5o

Yield: 84%; brown oil; R*f* = 0.66 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24 (s, 1 H), 6.91 (s, 1 H), 5.20 (t, *J* = 7.2 Hz, 1 H), 3.96-3.61 (m, 4 H), 3.24 (d, *J* = 7.2 Hz, 2 H), 2.26 (s, 3 H), 2.02 (br, 4 H), 1.70 (s, 3 H), 1.64 (s, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 7.30 (s, 1 H), 7.10 (s, 1 H), 6.01 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.90-4.82 (m, 2 H), 2.81 (s, 3 H), 1.40 (s, 6 H); ^{13}C NMR (the mixture of α- and β-selective products, 100 MHz, $CDCl_3$): δ 148.6, 145.7, 142.6, 135.5, 135.0, 133.1, 131.74, 131.68, 130.9, 129.4, 128.5, 126.7, 122.9, 118.1, 116.8, 109.0, 41.5, 30.5, 28.2, 25.7, 23.8, 20.8, 20.5, 17.7; IR(ATR-FTIR): 2967, 1425, 1323, 852, 735 cm^{-1}; MS (ES$^+$): m/z (%): 323 ([M+H]$^{++}$, Br^{81}, 25), 321 ([M+H]$^{++}$, Br^{79}, 21), 253 (13), 144 (49), 129 (100), 112 (49), 105 (11); HRMS (ES$^+$-TOF) calcd for $C_{16}H_{22}BrN_3$ ([M+H]$^+$): 336.1075, found: 336.1079.

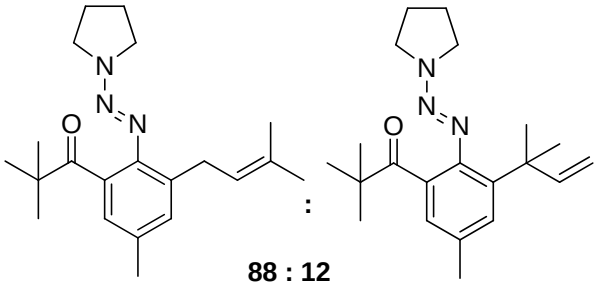


94 : 6
5p

Yield: 83%; brown oil; R*f* = 0.28 (50:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (s, 1 H), 6.95 (s, 1 H), 5.21 (dt, *J* = 8.9 Hz, 1.3 Hz, 1 H), 3.81 (br, 4 H), 3.25 (d, *J* = 7.2 Hz, 2 H), 2.26 (s, 3 H), 2.05 (br, 4 H), 1.71 (s, 3 H), 1.65 (s, 3 H). The following signal is discernible for the minor isomer

(γ-selective product): 7.58 (s, 1 H), 7.14 (s, 1 H), 6.03 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.91-4.83 (m, 2 H), 1.40 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.0, 137.1, 136.1, 134.3, 131.8, 130.7, 123.1, 93.2, 30.8, 25.7, 23.9 (X4), 20.3, 17.8; IR(ATR-FTIR): 2969, 1421, 852 cm^{-1}; MS (EI): m/z (%): 383 (M^+, 3), 158 (33), 143 (100), 128 (34), 83 (30), 41 (34), 28 (19); HRMS (EI-TOF) calcd for $C_{16}H_{22}IN_3$ (M^+): 383.0858, found: 383.0860.

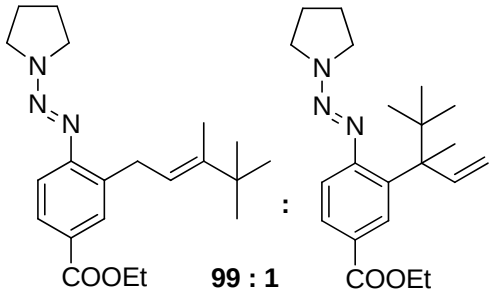


88 : 12

5q

Yield: 88%; brown oil; R*f* = 0.41 (20:1 Petroleum ether/EtOAc);

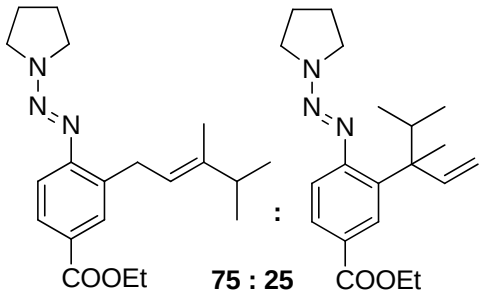
^{1}H NMR (400 MHz, $CDCl_3$): δ 6.99 (s, 1 H), 6.66 (s, 1 H), 5.31 (t, *J* = 7.2 Hz, 1 H), 3.72 (br, 4 H), 3.51 (d, *J* = 7.2 Hz, 2 H), 2.29 (s, 3 H), 1.98 (br, 4 H), 1.71 (s, 6 H), 1.14 (s, 9 H). The following signal is discernible for the minor isomer (γ-selective product): 7.18 (s, 1 H), 6.70 (s, 1 H), 6.23 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.93-4.85 (m, 2 H), 2.32 (s, 3 H), 1.53 (s, 6 H), 1.08 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 215.8, 142.8, 136.2, 134.3, 134.1, 132.0, 131.5, 124.8, 123.6, 44.6, 30.2, 27.2, 25.7, 20.9, 17.8 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2970, 1683, 1416, 736 cm^{-1}; MS (EI): m/z (%): 341 (M^+, 8), 273 (23), 231 (21), 203 (32), 187 (52), 159 (35), 98 (30), 119 (99), 105 (100), 91 (62), 69 (94), 57 (85), 41 (95), 29 (44); HRMS (EI-TOF) calcd for $C_{21}H_{31}N_3O$ (M^+): 341.2467, found: 341.2466.



5r

Yield: 83%; brown oil; R*f* = 0.70 (5:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1 H), 7.83 (dd, *J* = 8.6 Hz, 1.8 Hz, 1 H), 7.41 (d, *J* = 8.0 Hz, 1 H), 5.43 (t, *J* = 7.2 Hz, 1 H), 4.34 (q, *J* = 7.2 Hz, 2 H), 3.93 (br, 2 H), 3.69 (br, 2 H), 3.58 (d, *J* = 7.2 Hz, 2 H), 2.02 (br, 4 H), 1.72 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 1.06 (s, 9 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 152.3, 143.8, 135.7, 130.8, 127.8, 126.4, 119.7, 116.0, 60.5, 50.9, 46.4, 36.1, 29.7, 29.1, 24.0, 23.7, 14.3, 12.9; IR(ATR-FTIR): 2962, 1709, 1107, 772 cm^{-1}; MS (EI): m/z (%): 357 (M^+, 10), 300 (23), 288 (49), 175 (37), 163 (33), 131 (46), 83 (37), 70 (37), 57 (100), 41 (79), 29 (97); HRMS (EI-TOF) calcd for $C_{21}H_{31}N_3O_2$ (M^+): 357.2416, found: 357.2419.

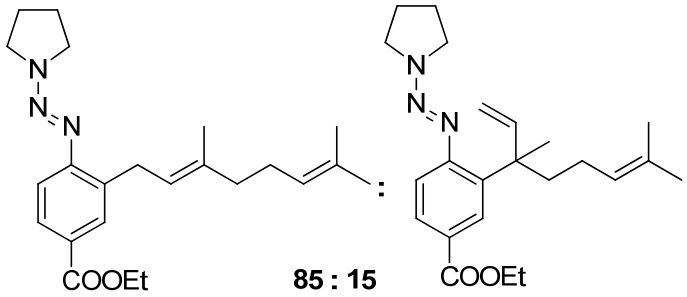


5s

Yield: 84%; brown oil; R*f* = 0.44 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1 H), 7.81 (d, *J* = 8.8 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 5.38 (t, *J* = 7.0 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 4.04-3.64 (m, 4 H), 3.57 (d, *J* = 7.2 Hz, 2 H), 2.34-2.23 (m, 1 H), 2.07-2.01 (m, 4 H), 1.68 (s, 3 H), 1.38 (t, *J* = 7.0 Hz, 3 H), 1.01 (d, *J* = 6.8 Hz, 6 H). The following signal is discernible for the minor isomer (γ-selective product): 6.64 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.11-4.95 (m, 2 H), 3.09-3.00 (m, 1 H), 0.81 (d, *J* = 7.2 Hz, 3 H), 0.66 (d, *J* = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 152.3, 141.6, 135.6, 130.8, 127.9, 126.4, 120.6, 116.0, 60.5, 36.8, 29.2, 21.4, 14.3, 13.4 (four carbon signal of pyrrolidine ring cannot

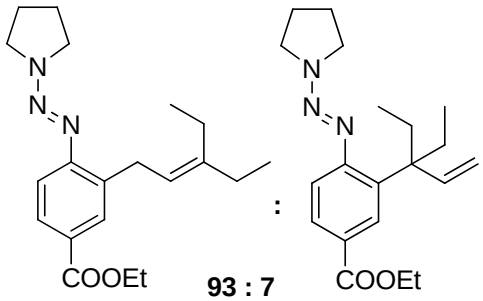
be resolved); IR(ATR-FTIR): 2961, 1709, 1106, 773 cm^{-1}; MS (EI): m/z (%): 343 (M^+, 9), 294 (21), 274 (36), 259 (22), 157 (31), 131 (60), 91 (31), 85 (33), 70 (37), 43 (73), 29 (100); HRMS (EI-TOF) calcd for $C_{20}H_{29}N_3O_2$ (M^+): 343.2260, found: 343.2256.



5t

Yield: 73%; brown oil; R*f* = 0.74 (5:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 5.37 (t, *J* = 6.6 Hz, 1 H), 5.10 (t, *J* = 6.8 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 4.05-3.64 (m, 4 H), 3.58 (d, *J* = 7.2 Hz, 2 H), 2.11-1.99 (m, 8 H), 1.74 (s, 3 H), 1.66 (s, 3 H), 1.58 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 8.02 (s, 1 H), 6.35 (dd, *J* = 17.4 Hz, 11.0 Hz, 1 H), 5.00-4.92 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 152.2, 135.7, 135.5, 131.2, 131.0, 127.9, 126.5, 124.3, 123.2, 116.1, 60.5, 39.7, 29.6, 26.7, 25.6, 23.7, 17.6, 16.2, 14.3 (four carbon signal of pyrrolidine ring cannot be resolved); IR(ATR-FTIR): 2973, 1709, 1107, 772 cm^{-1}; MS (EI): m/z (%): 383 (M^+, 4), 314 (17), 216 (19), 180 (20), 143 (25), 129 (27), 85 (26), 69 (88), 41 (100), 29 (70); HRMS (EI-TOF) calcd for $C_{23}H_{33}N_3O_2$ (M^+): 383.2573, found: 383.2583.

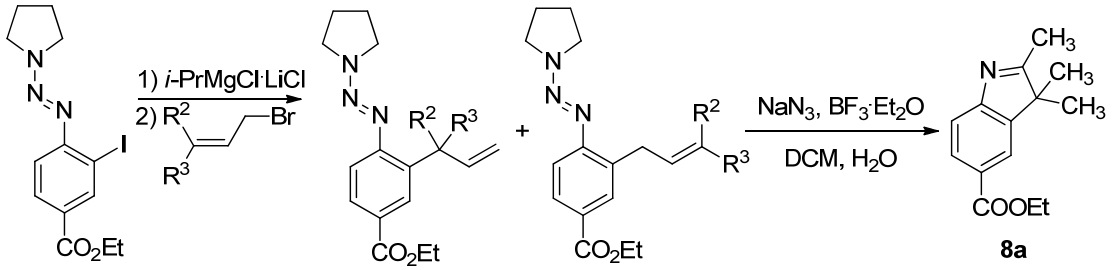


5u

Yield: 85%; brown oil; R*f* = 0.45 (10:1 Petroleum ether/EtOAc);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 (s, 1 H), 7.82 (d, *J* = 8.8 Hz, 1 H), 7.41 (d, *J* = 8.4 Hz, 1 H), 5.32 (t, *J* = 7.2 Hz, 1 H), 4.34 (q, *J* = 7.1 Hz, 2 H), 4.03-3.64 (m, 4 H), 3.61 (d, *J* = 7.2 Hz, 2 H), 2.18 (q, *J* = 7.6 Hz, 2 H), 2.08-2.00 (m, 6 H), 1.38 (t, *J* = 7.2 Hz, 3 H), 1.01 (dt, *J* = 7.6 Hz, 1.3 Hz, 6 H). The following signal is discernible for the minor isomer (γ-selective product): 8.01 (s, 1 H), 6.11 (dd, *J* = 17.6 Hz, 10.8 Hz, 1 H), 5.11-4.91 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.9, 152.2, 143.3, 135.8, 131.0, 127.8, 126.5, 121.2, 116.0, 60.4, 50.1, 46.2, 29.1, 28.9, 23.7 (X2), 23.5, 23.2, 14.3, 13.1, 12.9; IR(ATR-FTIR): 2965, 1709, 1107, 772 cm^{-1}; MS (EI): m/z (%): 343 (M^+, 6), 314 (14), 274 (40), 230 (23), 163 (30), 143 (42), 131 (55), 117 (47), 55 (38), 41 (69), 29 (100); HRMS (EI-TOF) calcd for $C_{20}H_{29}N_3O_2$ (M^+): 343.2260, found: 343.2264.

F. Synthesis of 4g and 5g in multigram scales and their synthetic application



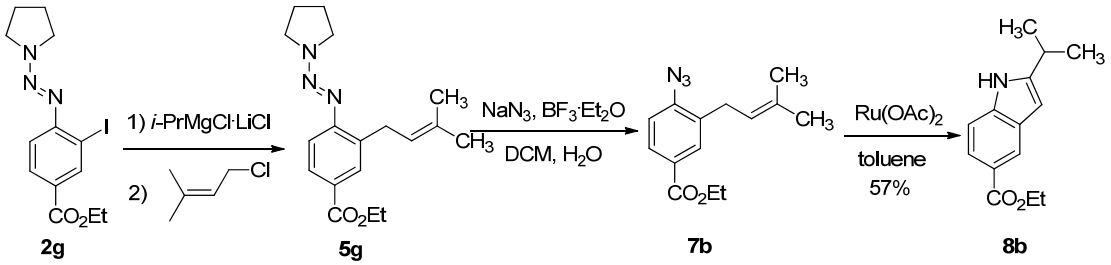
Typical procedure (synthesis of **4g**): A dry and nitrogen-flushed 250 ml Schlenk tube equipped with a magnetic stirrer and a septum was charged with a solution of (*E*)-ethyl 3-iodo-4-(pyrrolidin-1-yldiazenyl)benzoate (15 mmol, 1.0 equiv) in dry THF (40 ml). *i*-PrMgCl·LiCl (15 mL, 19.5 mmol, 1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C and the mixture was stirred at this temperature for 3h. 1-bromo-3-methylbut-2-ene (45 mmol, 3.0 equiv) was added at –40 °C and then the resulting mixture was stirred for 24 h before the addition of saturated aqueous NH_4Cl solution (50 ml). The resulting mixture was extracted with ethyl acetate (3 × 100 mL). The organic fractions were dried (Na_2SO_4), concentrated in vacuo and purified by silica gel chromatography using Petroleum ether/EtOAc (10:1) as an eluent, affording

4g (4.523 g, 90%) as a brown oil. R*f* = 0.69 (5:1 Petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1 H), 7.85 (d, *J* = 8.4 Hz, 1 H), 7.40 (d, *J* = 8.4 Hz, 1 H), 6.28 (dd, *J* = 17.4 Hz, 11.0 Hz, 1 H), 5.36 (t, *J* = 7.2 Hz, 1 H), 4.94 (d, *J* = 7.2 Hz, 1 H), 4.91 (s, 1H), 4.36 (q, *J* = 7.2 Hz, 2 H), 3.80-4.05 (br, 2 H), 3.60-3.80 (br, 2 H), 1.98-2.04 (br, 4 H), 1.57 (s, 6 H), 1.39 (t, *J* = 7.2 Hz, 3 H). The following signal is discernible for the minor isomer (α-selective product): 5.36 (t, *J* = 7.2 Hz, 1H), 3.58 (d, *J* = 7.2 Hz, 2 H), 1.74 (s, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.0, 152.9, 148.7, 141.4, 128.31, 128.27, 126.1, 117.4, 109.6, 60.5, 41.2, 28.1, 14.3; IR(ATR-FTIR): 1708, 1245, 1107, 775 cm-1; MS (EI): m/z (%): 315 (M^+, 8), 233 (29), 145 (70), 129 (84), 117 (45), 91 (38), 41 (66), 29 (100); HRMS (EI-TOF) calcd for $C_{18}H_{25}N_3O_2$ (M^+): 315.1947, found: 315.1950.

Typical procedure (synthesis of **8a**): To a mixture of **4g** (3.154 g, 10 mmol, 1.0 equiv) and NaN_3 (3.25 g, 50 mmol, 5.0 equiv) in CH_2Cl_2/H_2O (15/5 mL) was added $BF_3{\cdot}Et_2O$ (3.55 g, 25 mmol, 2.5 equiv) dropwise at 0 °C and the reaction mixture was stirred for 1 h. Then the aqueous phase was extracted with diethyl ether (3 × 30 mL). The organic fractions were washed with brine (20 mL), dried (Na_2SO_4) and concentrated in vacuo to give the crude product. Then the pure product **8a** (1.641 g, 71%) can obtained though recrystallization by using petroleum ether as yellow solid. m.p= 84.9-85.7℃; R*f* = 0.55 (10:1 Petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (dd, *J* = 8.0 Hz, 0.8 Hz, 1 H), 7.96 (s, 1 H), 7.55 (d, *J* = 8.4 Hz, 1 H), 4.38 (q, *J* = 7.1 Hz, 2 H), 2.31 (s, 3 H), 1.40 (t, *J* = 7.2 Hz, 3 H), 1.33 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 191.6, 166.8, 157.6, 145.7, 130.0, 127.2, 122.6, 119.5, 60.9, 53.8, 22.9, 15.7, 14.4; IR(ATR-FTIR): 1714, 1280, 1024, 750 cm-1; MS (ES^+): m/z (%): 232 ($[M+H]^+$, 100), 217 (38), 188 (70), 159 (45), 144 (31); HRMS (ES^+-TOF) calcd for $C_{14}H_{17}NO_2$ ($[M+H]^+$): 232.1337, found: 232.1337.



Typical procedure (synthesis of **5g**): A dry and nitrogen-flushed 250 ml Schlenk tube equipped with a magnetic stirrer and a septum was charged with a solution of (*E*)-ethyl 3-iodo-4-(pyrrolidin-1-yldiazenyl)benzoate (15 mmol, 1.0 equiv) in dry THF (40 ml). *i*-PrMgCl·LiCl (15 mL, 19.5 mmol, 1.0 M in THF, 1.3 equiv) was then added dropwise at –30 °C and the mixture was stirred at this temperature for 3h. 1-chloro-3-methylbut-2-ene (45 mmol, 3.0 equiv) was added at –30 °C and then the resulting mixture was stirred for 24 h before the addition of saturated aqueous NH_4Cl solution (50 ml). The resulting mixture was extracted with ethyl acetate (3 × 100 mL). The organic fractions were dried (Na_2SO_4), concentrated in vacuo and purified by silica gel chromatography using Petroleum ether/EtOAc (10:1) as an eluent, affording **5g** (3.785 g, 80%) as a brown oil. R*f* = 0.69 (5:1 Petroleum ether/EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (s, 1 H), 7.81 (d, *J* = 8.4 Hz, 1 H), 7.41 (d, *J* = 8.8 Hz, 1 H), 5.36 (t, *J* = 7.0 Hz, 1 H), 4.35 (q, *J* = 7.1 Hz, 2 H), 3.95 (br, 2 H), 3.70 (br, 2 H), 3.58 (d, *J* = 7.6 Hz, 2 H), 2.04 (br, 4 H), 1.74 (s, 3 H), 1.72 (s, 3 H), 1.38 (t, *J* = 7.2 Hz, 3 H). The following signal is discernible for the minor isomer (γ-selective product): 6.28 (dd, *J* = 17.4 Hz, 10.6 Hz, 1 H), 4.97-4.90 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 152.7, 151.9, 147.9, 142.4, 136.6, 133.2, 133.1, 131.0, 130.6, 130.2, 122.1, 120.1, 120.0, 118.1, 116.7, 110.2, 107.3, 107.2, 51.0, 47.4, 41.3, 29.2, 27.8, 25.7, 24.0, 23.9, 23.5, 17.8; IR(ATR-FTIR): 2974, 1708, 1106, 771 cm^{-1}; MS (EI): m/z (%): 315 (M^+, 16), 270 (13), 145 (47), 129 (52), 117 (32), 91 (23), 41 (43), 29 (100); HRMS (EI-TOF) calcd for $C_{18}H_{25}N_3O_2$ (M^+): 315.1947, found: 315.1946.

Typical procedure (synthesis of **7b**): To a solution of **5g** (3.465 g, 11 mmol, 1.0 equiv) and NaN_3 (3.575 g, 55 mmol, 5.0 equiv) in CH_2Cl_2/H_2O (15/5 mL) was added $BF_3{\cdot}Et_2O$ (3.905 g, 27.5 mmol, 2.5 equiv) at 0 °C. The reaction mixture was stirred 1 h. Then the aqueous phase was extracted with diethyl ether (3 × 30 mL). The organic

fractions were washed with brine (20 mL) and dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography gave **7b** (2.59 g, 10 mmol, 91%) as brown oil; R*f* = 0.52 (10:1 Petroleum ether/EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (dd, *J* = 8.2 Hz, 1.8 Hz, 1 H), 7.84 (d, *J* = 1.2 Hz, 1 H), 7.15 (d, *J* = 8.0 Hz, 1 H), 5.23 (dt, *J* = 6.5 Hz, 1.2 Hz, 1 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 3.29 (d, *J* = 7.6 Hz, 2 H), 1.74 (s, 3 H), 1.72 (s, 3 H), 1.39 (t, *J* = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.1, 142.5, 133.6, 133.1, 131.4, 128.7, 126.8, 121.3, 117.8, 60.9, 29.6, 25.7, 17.9, 14.3; IR(ATR-FTIR): 2121, 1716, 1111, 1024, 766 cm^{-1}; MS (ES^+): m/z (%): 260 ($[M+H]^+$, 100), 245 (20), 221 (22), 193 (14), 145 (19), 119 (10); HRMS (ES^+-TOF) calcd for $C_{14}H_{17}N_3O_2$ ($[M+H]^+$): 260.1399, found: 260.1404.

Typical procedure (synthesis of **8b**): In a 50 mL Schlenck tube, substituted (ethyl 4-azido-3-(3-methylbut-2-en-1-yl)benzoate (2.59 g, 10 mmol, 1.0 equiv) and $Ru(OAc)_2$ (140 mg, 0.5 mmol, 0.05 equiv) were dissolved in toluene (25 mL). The reaction mixture was heated to 100 °C in an oil bath and stirred for 12 h. On cooling the mixture to room temperature, water (30 mL) was added. The resulting mixture was extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and purified by silica gel chromatography gave **8b** (1.271 g, 5.5 mmol, 55%) as yellow solid; m.p = 99.0-99.6℃; R*f* = 0.21 (5:1 Petroleum ether/EtOAc)

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.43-8.26 (m, 2 H), 7.86 (d, *J* = 8.4 Hz, 1 H), 7.30 (d, *J* = 8.4 Hz, 1 H), 6.32 (s, 1 H), 4.40 (q, *J* = 7.2 Hz, 2 H), 3.13-3.00 (m, 1 H), 1.42 (t, *J* = 7.0 Hz, 3 H), 1.37 (s, 3 H), 1.36 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 168.0, 147.4, 138.5, 128.1, 122.7, 122.5, 121.7, 109.9, 98.5, 60.5, 27.6, 22.2, 14.4; IR(ATR-FTIR): 3331, 1683, 1257, 1091, 768, 701 cm^{-1}; MS (ES^+): m/z (%): 232 ($[M+H]^+$, 100), 204 (46), 186 (33), 159 (19), 146 (10), 118 (17); HRMS (ES^+-TOF) calcd for $C_{14}H_{17}NO_2$ ($[M+H]^+$): 232.1337, found: 232.1339.

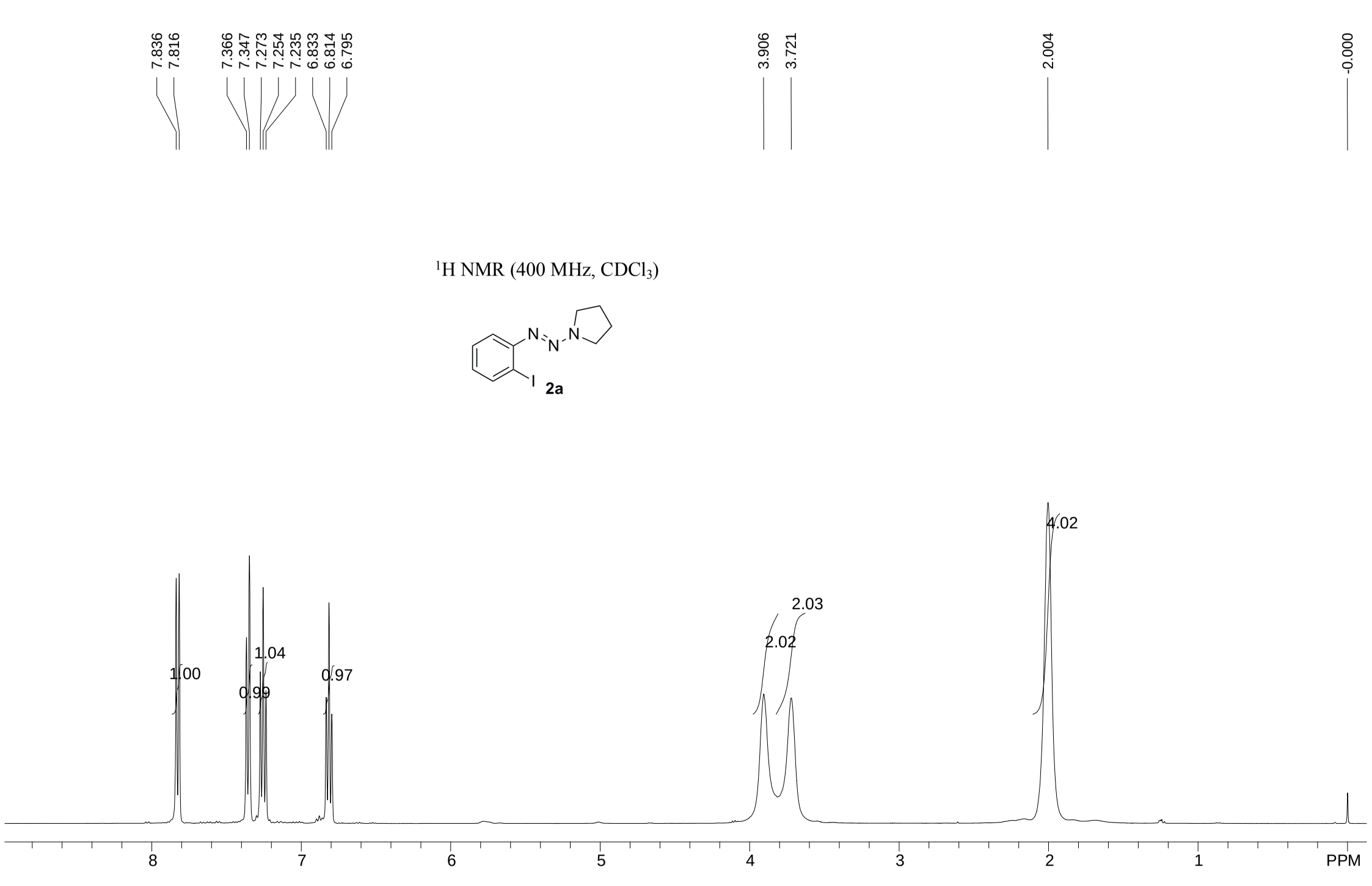
G. Reference

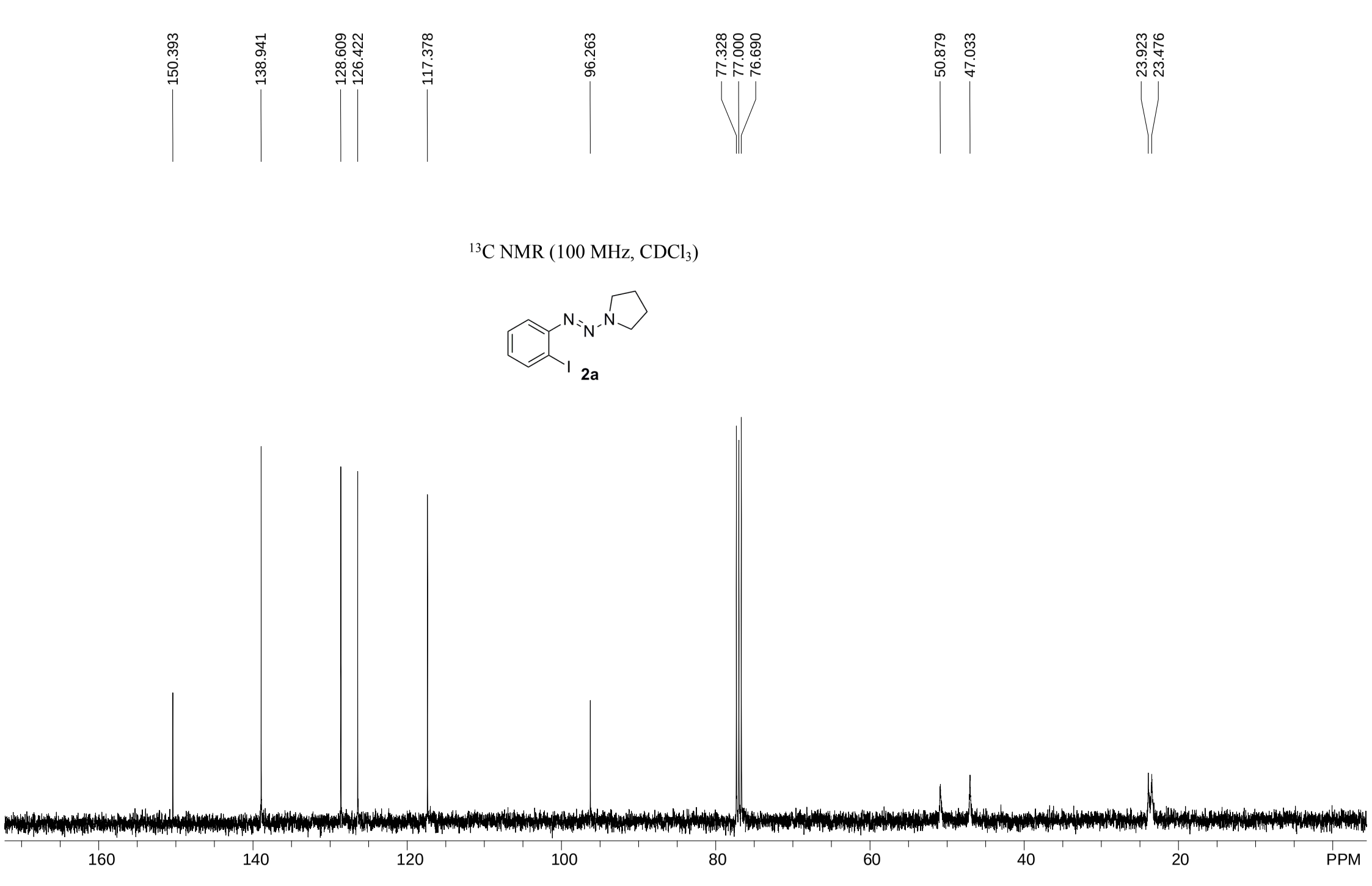
[1] a) Zhao, G.; Wang, B.; Yang, W.; Ren, H.; *Chem. Eur. J.*; **2012**, 6236-6247; b) Guthrie, D. B.; Curran, D. P.; *Org. Lett.* **2009**, 11, 249-251.

[2] Ren, K.; Hu, B.; Zhao, M.; Tu, Y.; Xie, X.; Zhang, Z.; *J. Org. Chem.* **2014**, 79, 2170-2177.

[3] Chow, S. Y.; Williams, H. J.; Huang, Q.; Nanda, S.; Scott, A.; *J. Org. Chem.* **2005**, 70, 9997-10003.

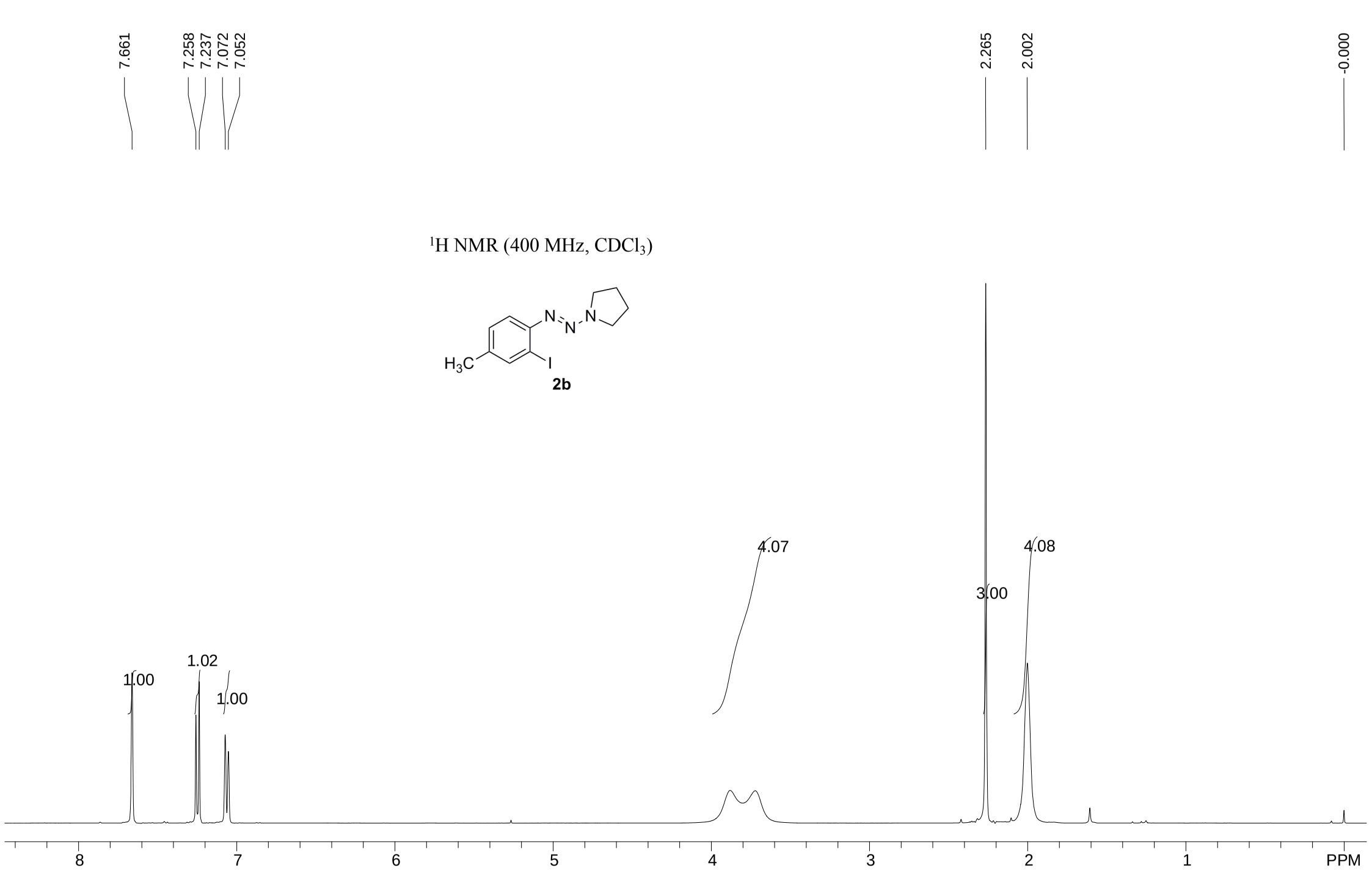
[4] Ren, H.; Dunet, G.; Mayer, P.; Knochel, P.; *J. Am. Chem. Soc.* **2007**, *129*, 5376-5377.


7.836
7.816
7.366
7.347
7.273
7.254
7.235
6.833
6.814
6.795
3.906
3.721
2.004
-0.000
1H NMR (400 MHz, CDCl3)
N
N
N
I
2a
1.00
0.99
1.04
0.97
2.02
2.03
4.02
8
7
6
5
4
3
2
1
PPM

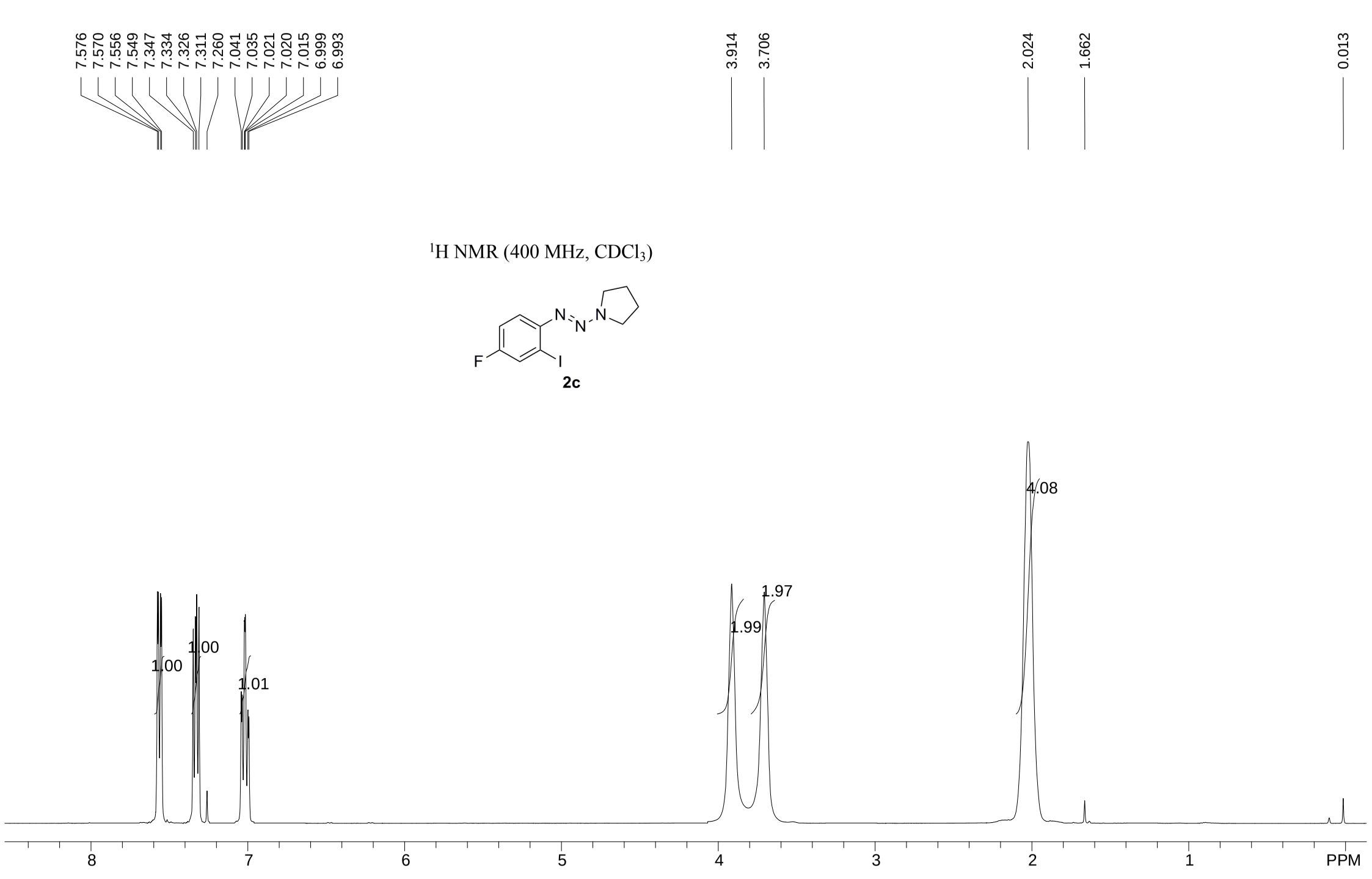


^{13}C NMR (100 MHz, $CDCl_3$)

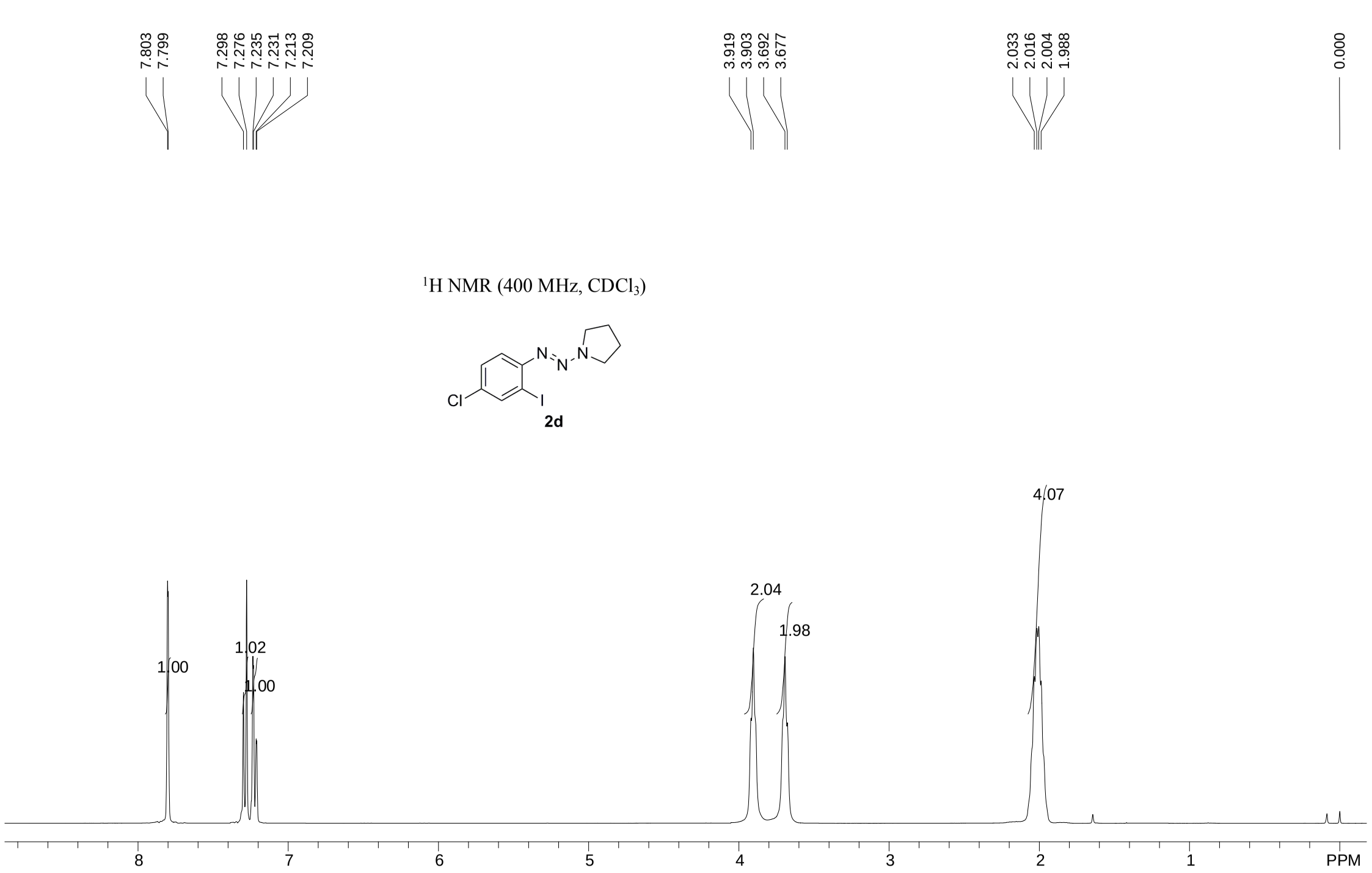
2a


7.661
7.258
7.237
7.072
7.052
2.265
2.002
-0.000
^{1}H NMR (400 MHz, $CDCl_3$)
H_3C
N
N
I
2b
1.00
1.02
1.00
4.07
3.00
4.08
8
7
6
5
4
3
2
1
PPM

160
140
120
100
80
60
40
20
PPM
148.157
139.175
136.307
129.471
116.911
96.186
77.312
77.000
76.680
50.874
46.895
23.735
23.541
20.309
^{13}C NMR (100 MHz, $CDCl_3$)
H_3C
I
N
N
N
2b


7.576
7.570
7.556
7.549
7.347
7.334
7.326
7.311
7.260
7.041
7.035
7.021
7.020
7.015
6.999
6.993
3.914
3.706
2.024
1.662
0.013
1H NMR (400 MHz, CDCl3)
N
N
N
F
I
2c
4.08
1.97
1.99
1.00
1.00
1.01
8
7
6
5
4
3
2
1
PPM

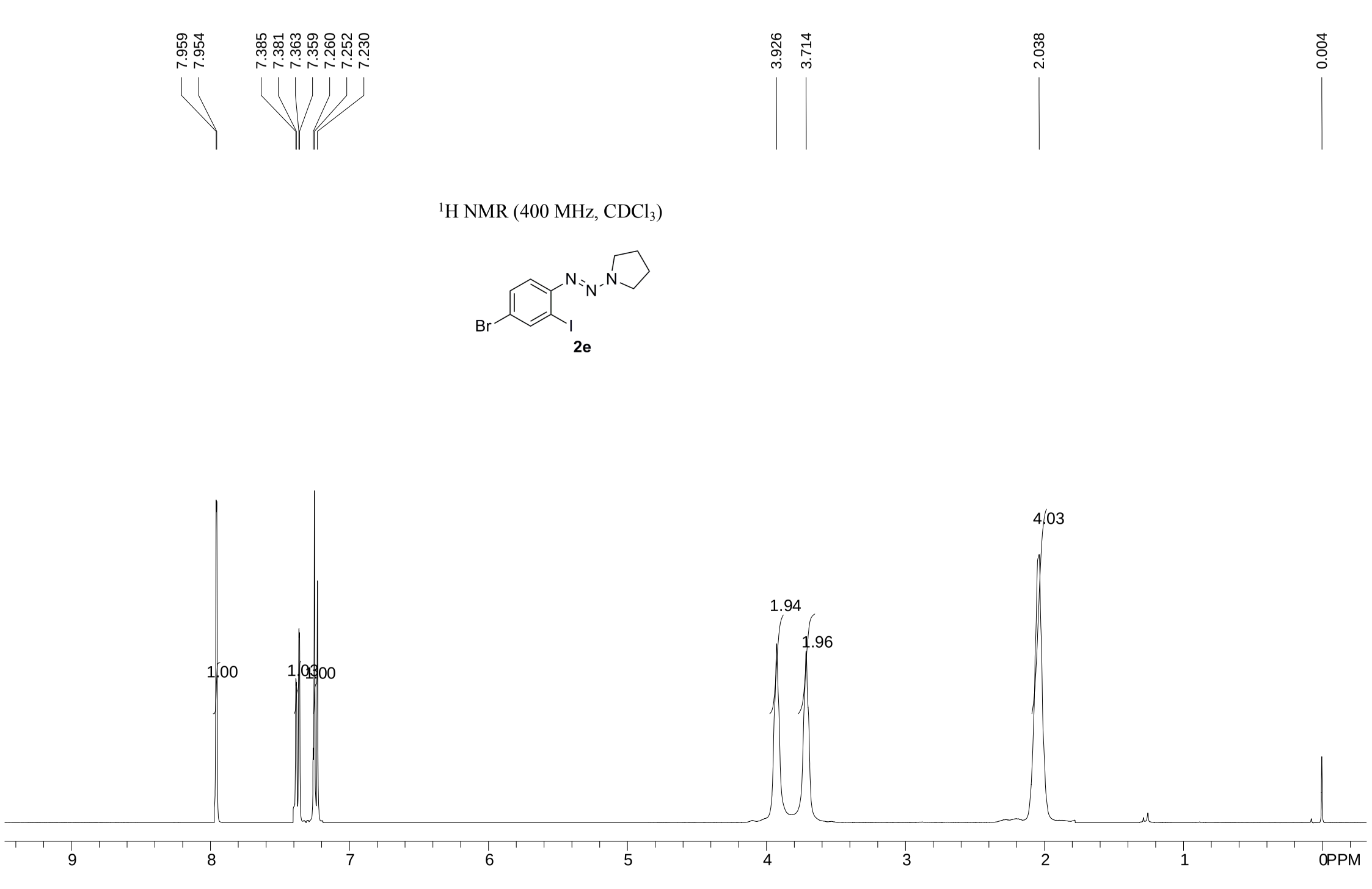
^{13}C NMR (100 MHz, $CDCl_3$)
2c
160.933
158.469
146.989
146.959
125.308
125.069
117.435
117.355
115.688
115.470
95.317
95.235
77.313
77.000
76.682
50.870
47.020
23.917
23.399
180
160
140
120
100
80
60
40
20
PPM

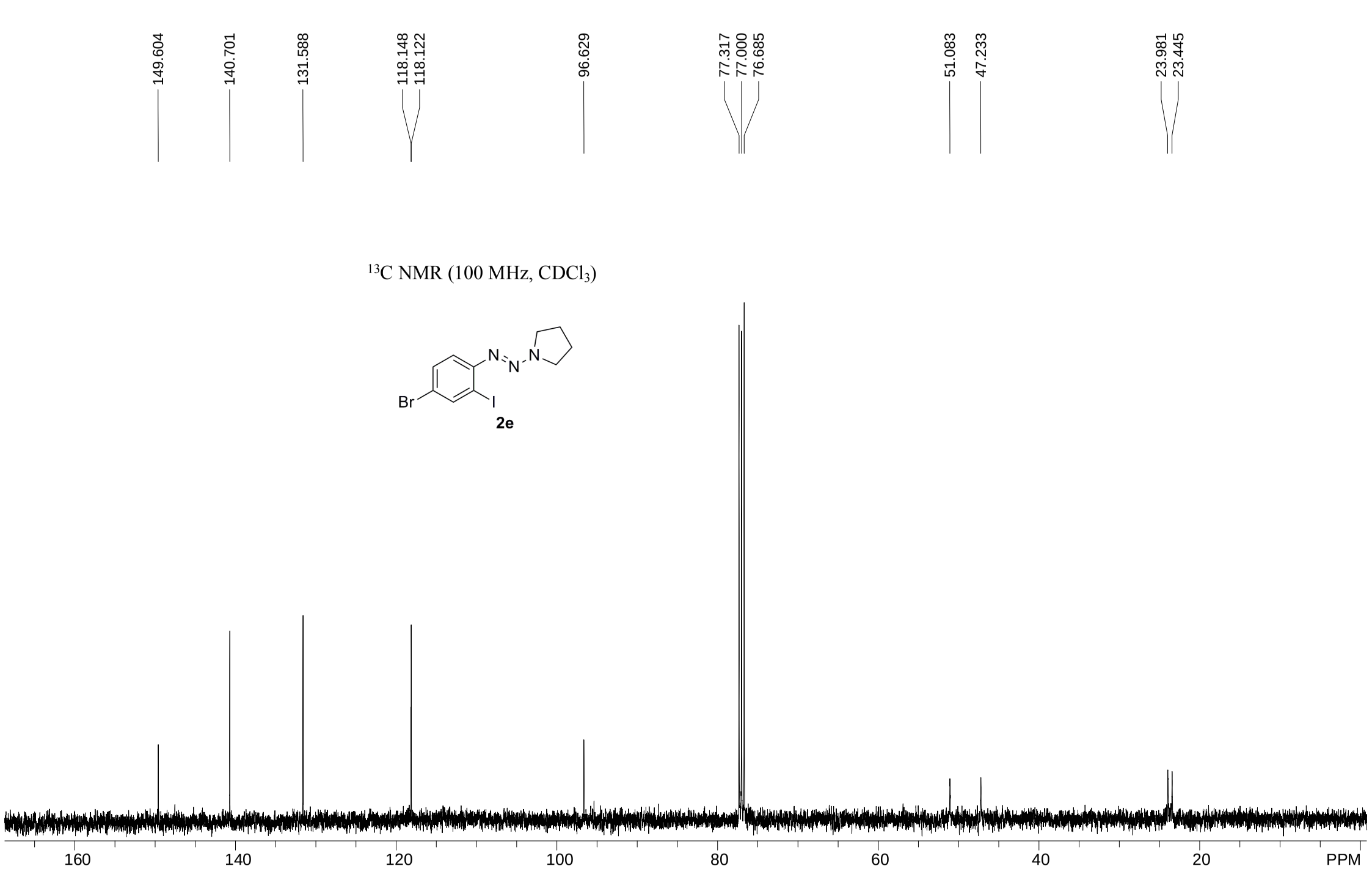


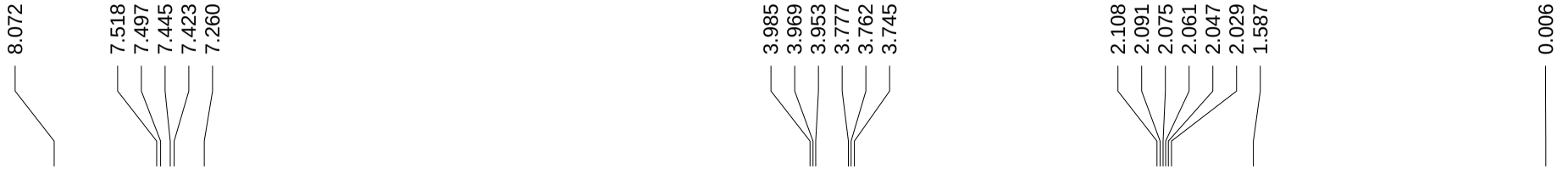
^{1}H NMR (400 MHz, $CDCl_3$)

2d

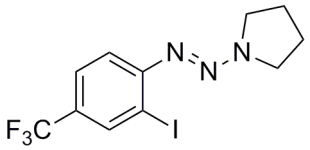
^{13}C NMR (100 MHz, CDCl$_3$)
149.064
137.901
130.252
128.633
117.525
96.056
77.315
77.000
76.672
50.966
47.130
23.904
23.362
160
140
120
100
80
60
40
20
PPM
Cl
I
N
N
N
2d


7.959
7.954
7.385
7.381
7.363
7.359
7.260
7.252
7.230
3.926
3.714
2.038
0.004
1H NMR (400 MHz, CDCl3)
N
N
N
Br
I
2e
1.00
1.03
1.00
1.94
1.96
4.03
9
8
7
6
5
4
3
2
1
0PPM

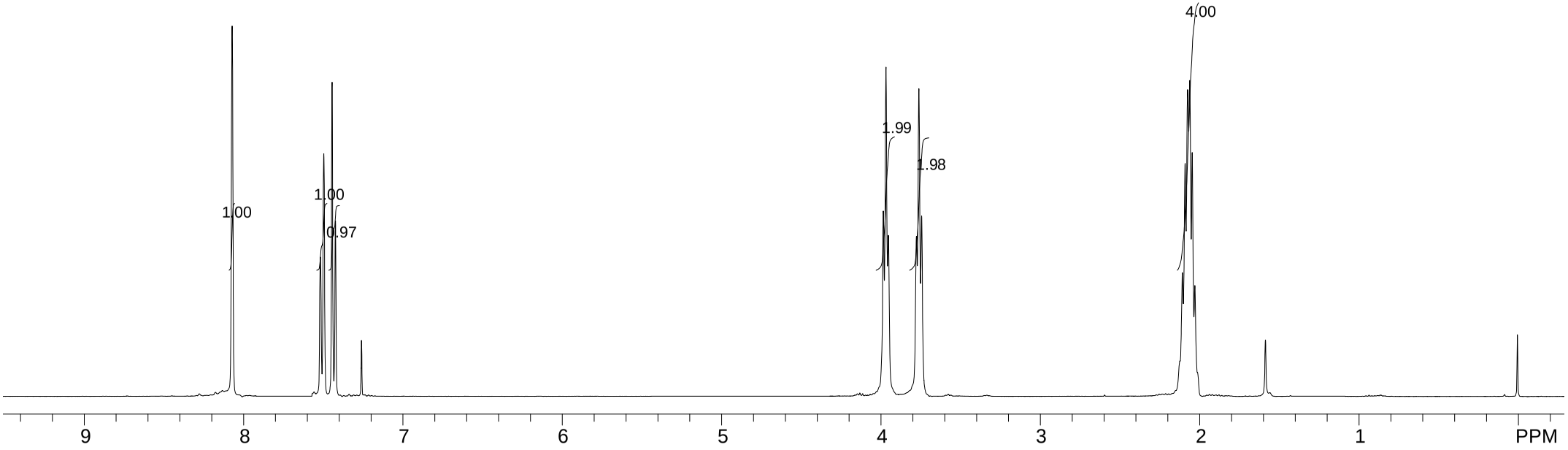

149.604
140.701
131.588
118.148
118.122
96.629
77.317
77.000
76.685
51.083
47.233
23.981
23.445
13C NMR (100 MHz, CDCl3)
N
N
N
Br
I
2e
160
140
120
100
80
60
40
20
PPM

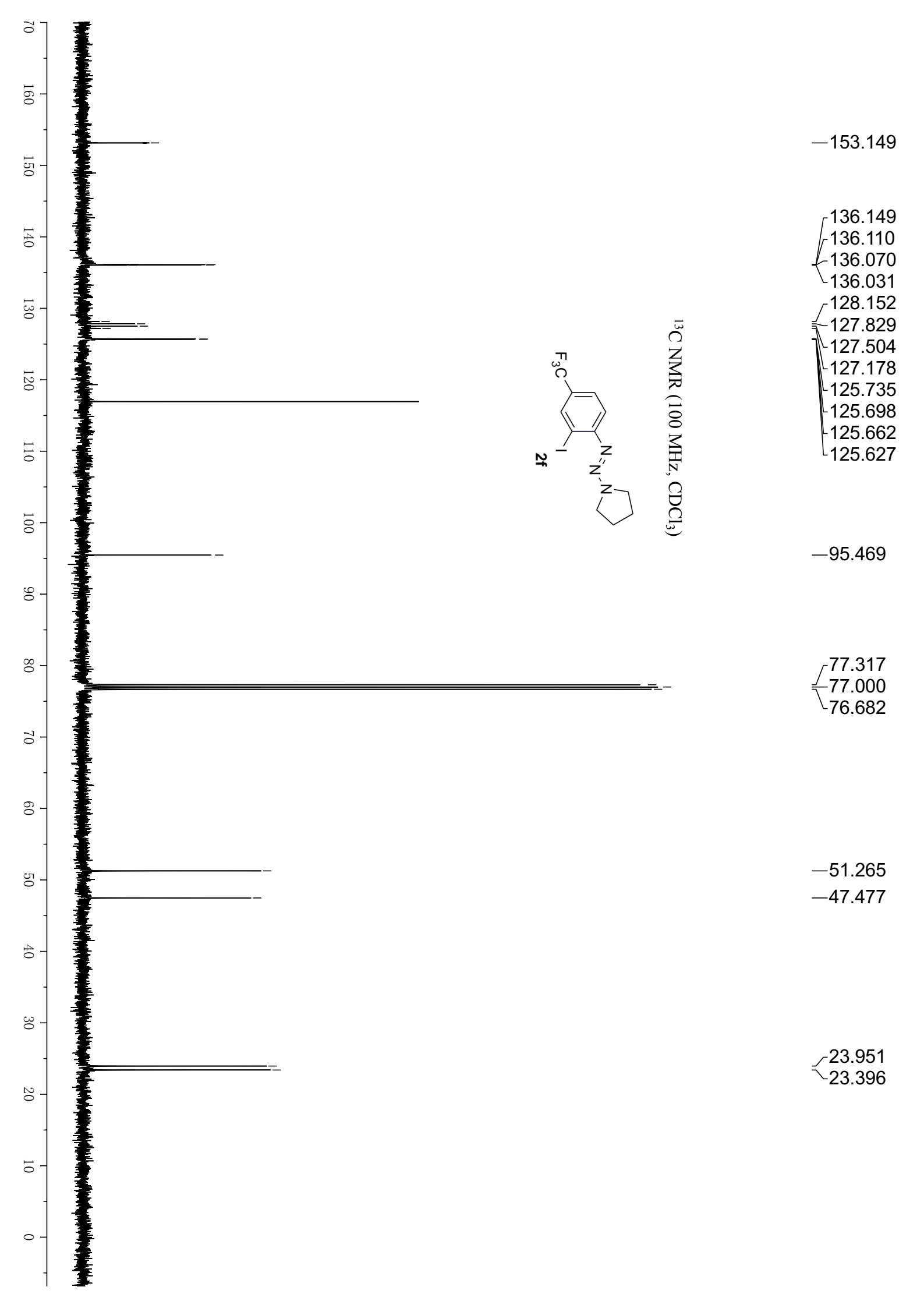


^{1}H NMR (400 MHz, $CDCl_3$)

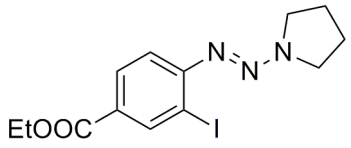


2f

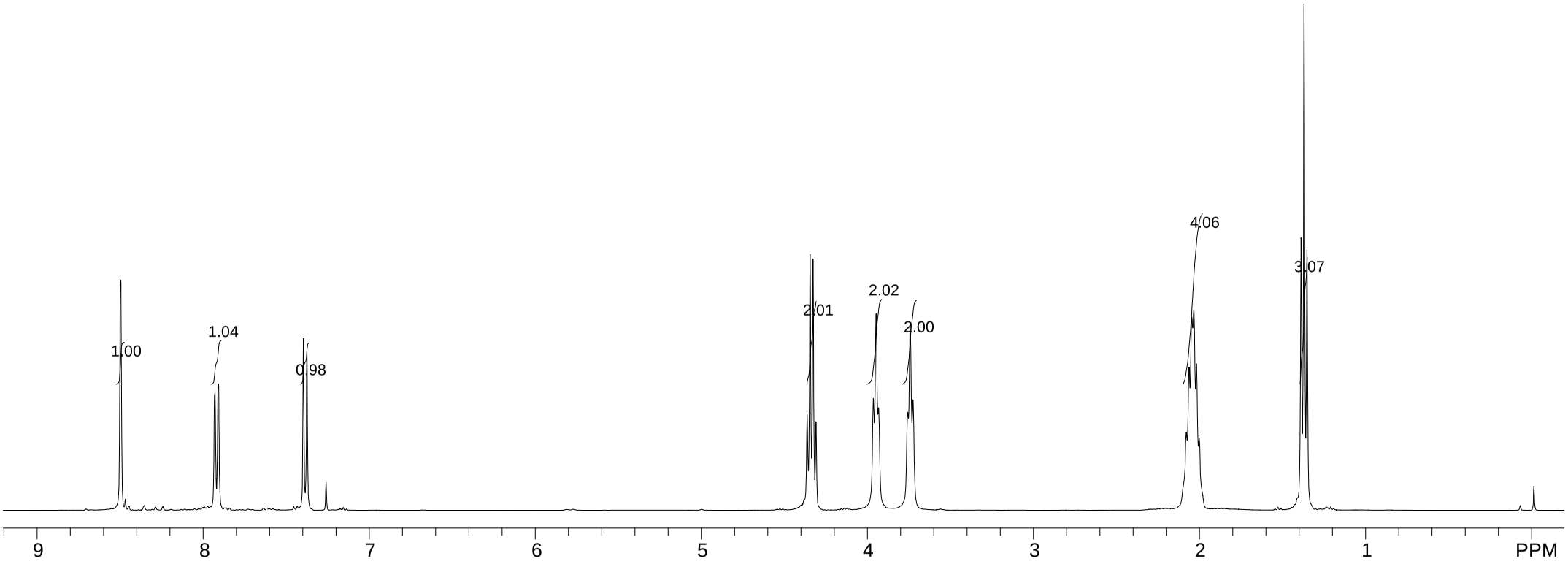



153.149
136.149
136.110
136.070
136.031
128.152
127.829
127.504
127.178
125.735
125.698
125.662
125.627
95.469
77.317
77.000
76.682
51.265
47.477
23.951
23.396
^{13}C NMR (100 MHz, CDCl$_3$)
2f

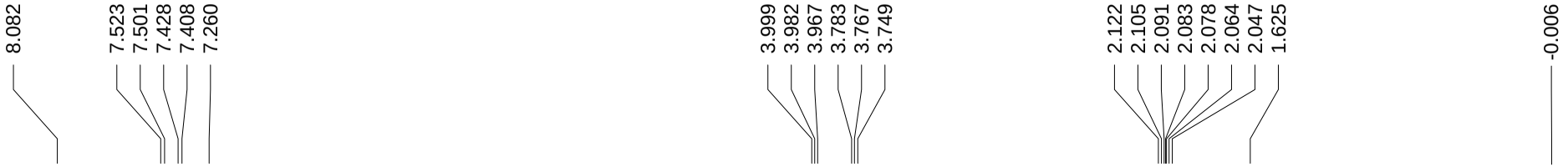
^{1}H NMR (400 MHz, $CDCl_3$)



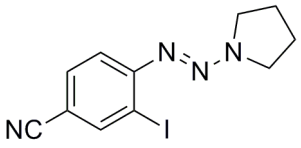
2g



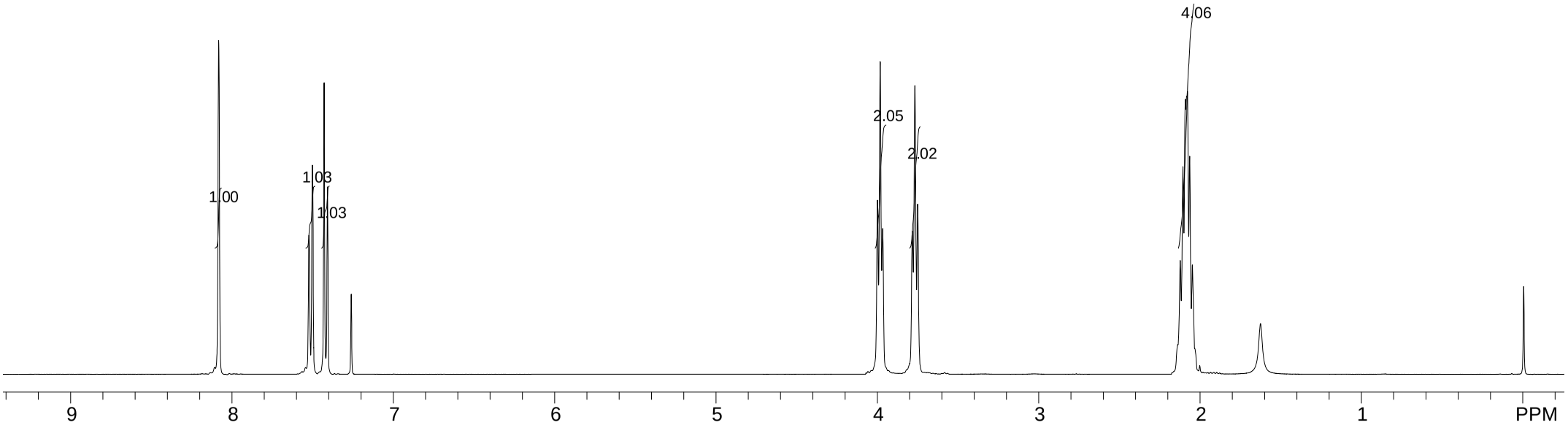
^{13}C NMR (100 MHz, CDCl$_3$)
EtOOC
I
2g
165.291
153.778
140.517
130.025
127.752
116.433
95.470
77.317
77.000
76.685
60.886
51.229
47.451
23.893
23.333
14.273
160
140
120
100
80
60
40
20
PPM



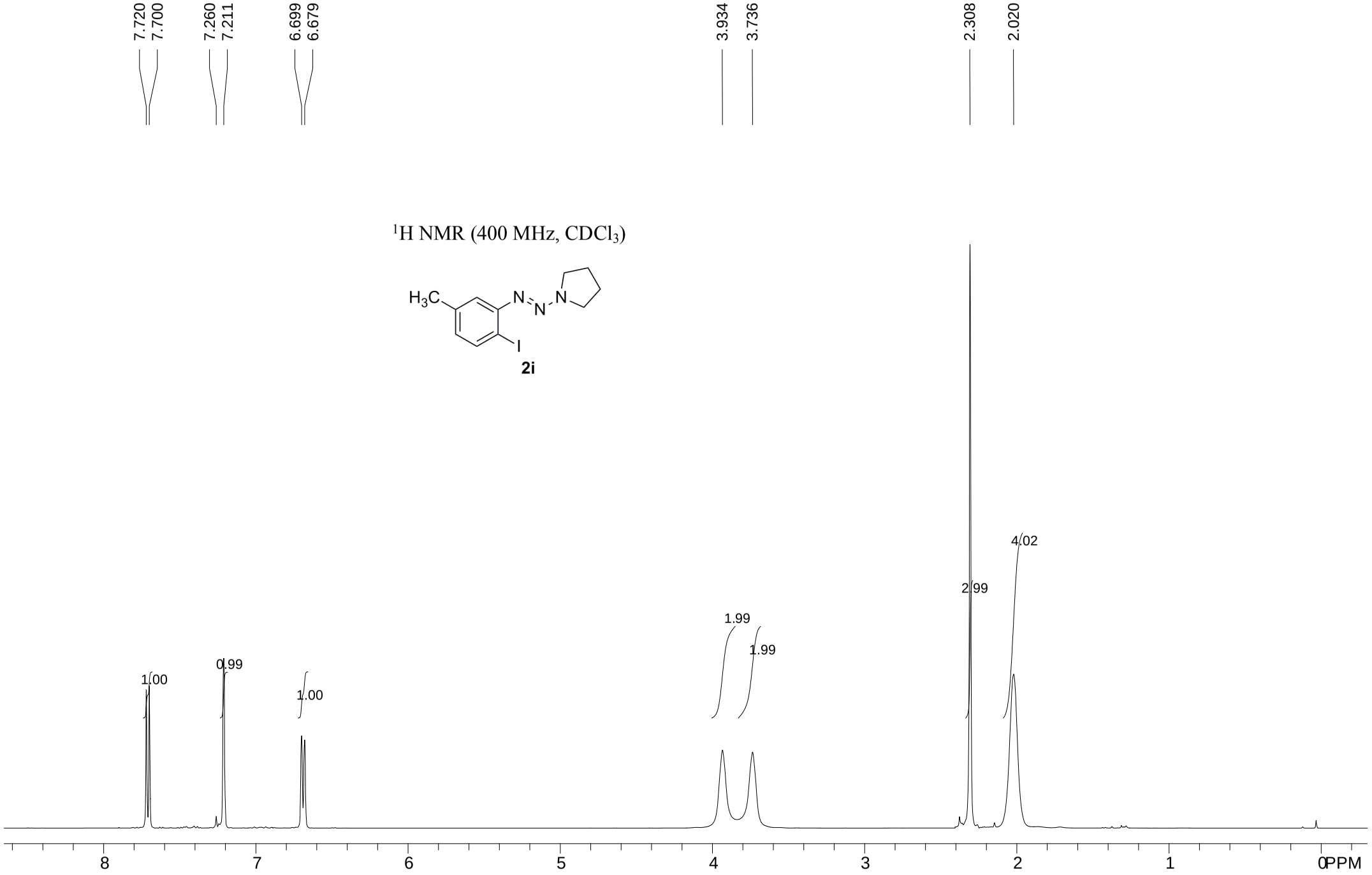
^{1}H NMR (400 MHz, $CDCl_3$)



2h



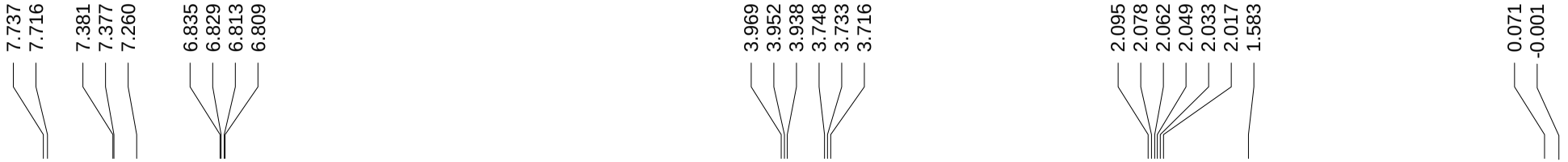
^{13}C NMR (100 MHz, CDCl$_3$)
NC
I
N
N
N
2h
153.926
142.633
132.327
118.034
116.990
108.820
95.561
77.318
77.000
76.685
51.489
47.764
23.916
23.340
160
140
120
100
80
60
40
20
PPM


7.720
7.700
7.260
7.211
6.699
6.679
3.934
3.736
2.308
2.020
1H NMR (400 MHz, CDCl3)
H3C
N
N
N
I
2i
1.00
0.99
1.00
1.99
1.99
2.99
4.02
8
7
6
5
4
3
2
1
0
PPM

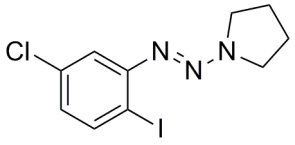
^{13}C NMR (100 MHz, $CDCl_3$)

2i

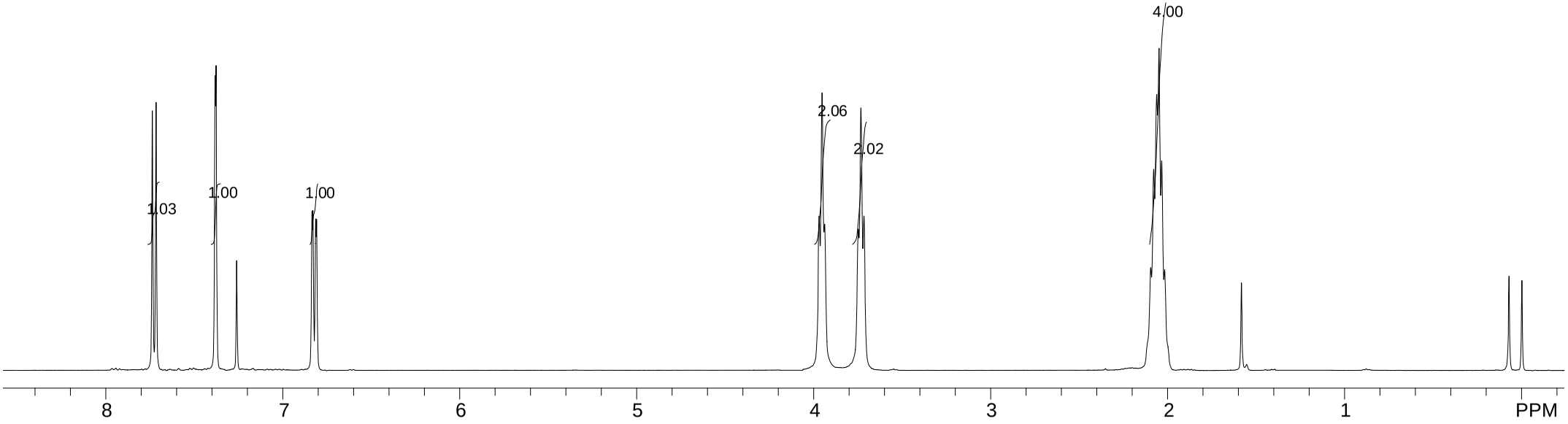
150.007
138.553
138.446
127.544
117.983
92.325
77.323
77.000
76.685
50.768
46.923
23.870
23.346
20.984



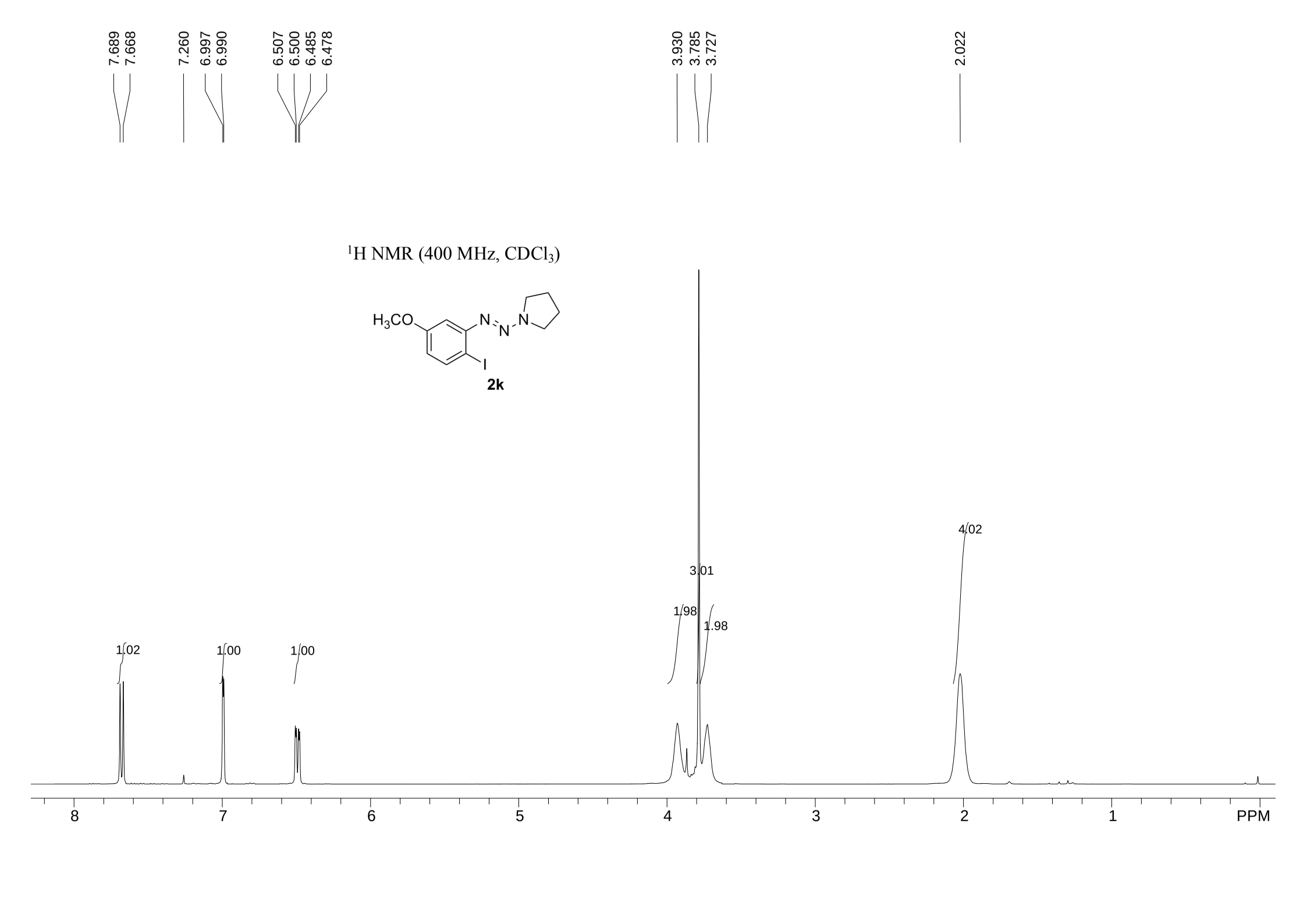
^{1}H NMR (400 MHz, $CDCl_3$)



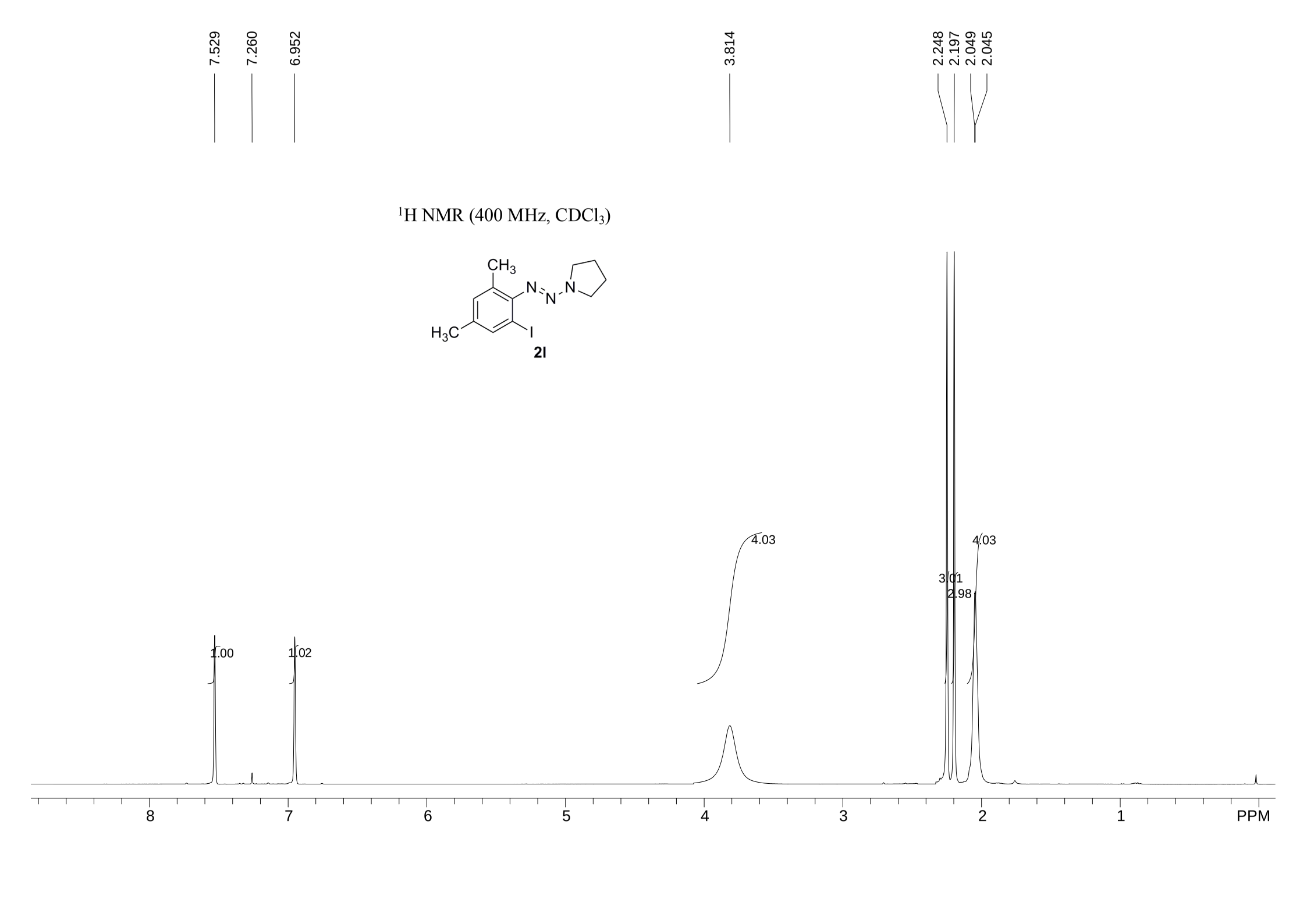
2j

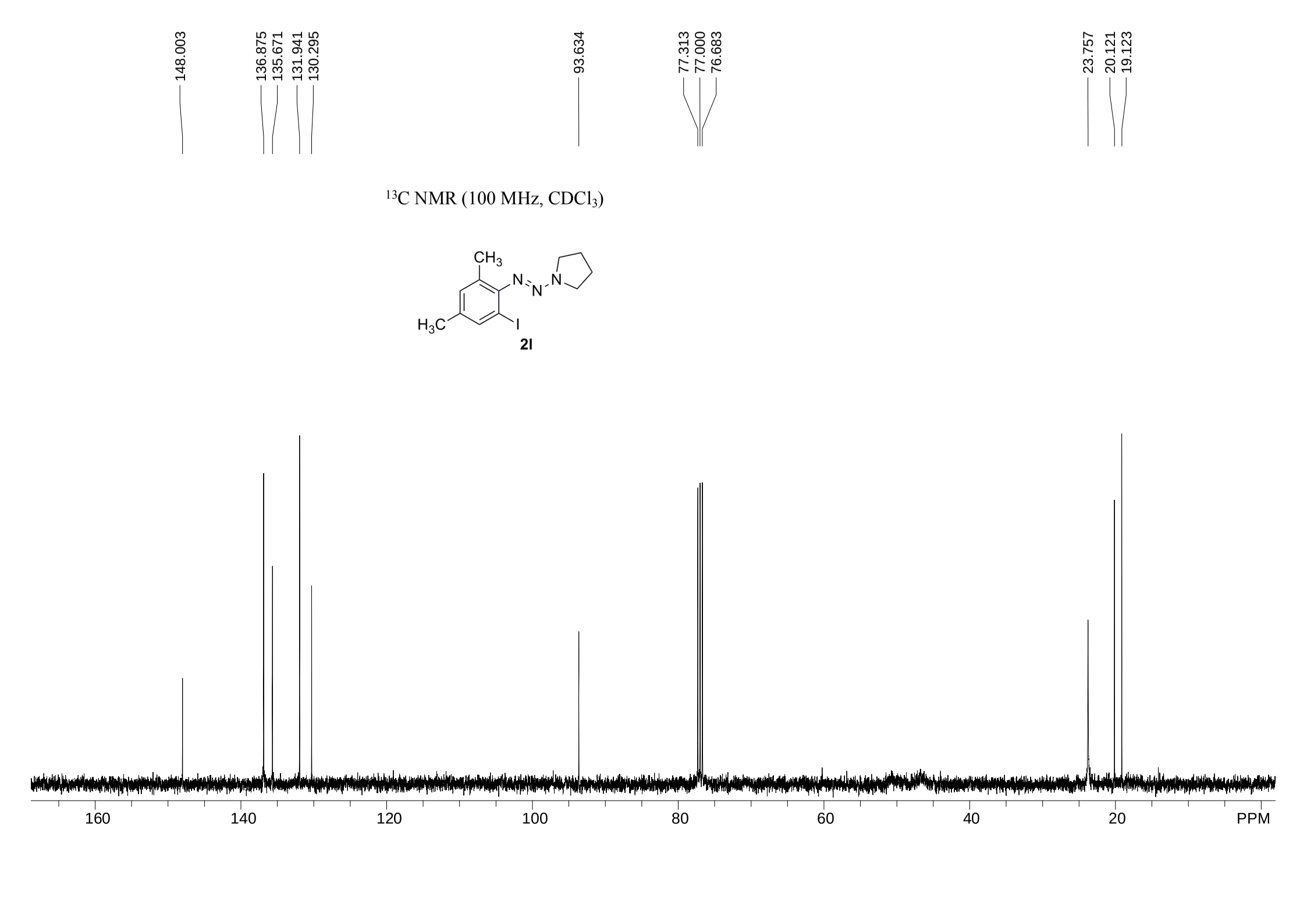


^{13}C NMR (100 MHz, CDCl$_3$)
2j
Cl
I
N
N
N
160
140
120
100
80
60
40
20
PPM
151.339
139.605
134.836
126.191
117.409
93.351
77.315
77.000
76.672
51.155
47.297
23.969
23.430


7.689
7.668
7.260
6.997
6.990
6.507
6.500
6.485
6.478
3.930
3.785
3.727
2.022
^{1}H NMR (400 MHz, $CDCl_3$)
H_3CO
N
N
N
I
2k
1.02
1.00
1.00
1.98
3.01
1.98
4.02
8
7
6
5
4
3
2
1
PPM

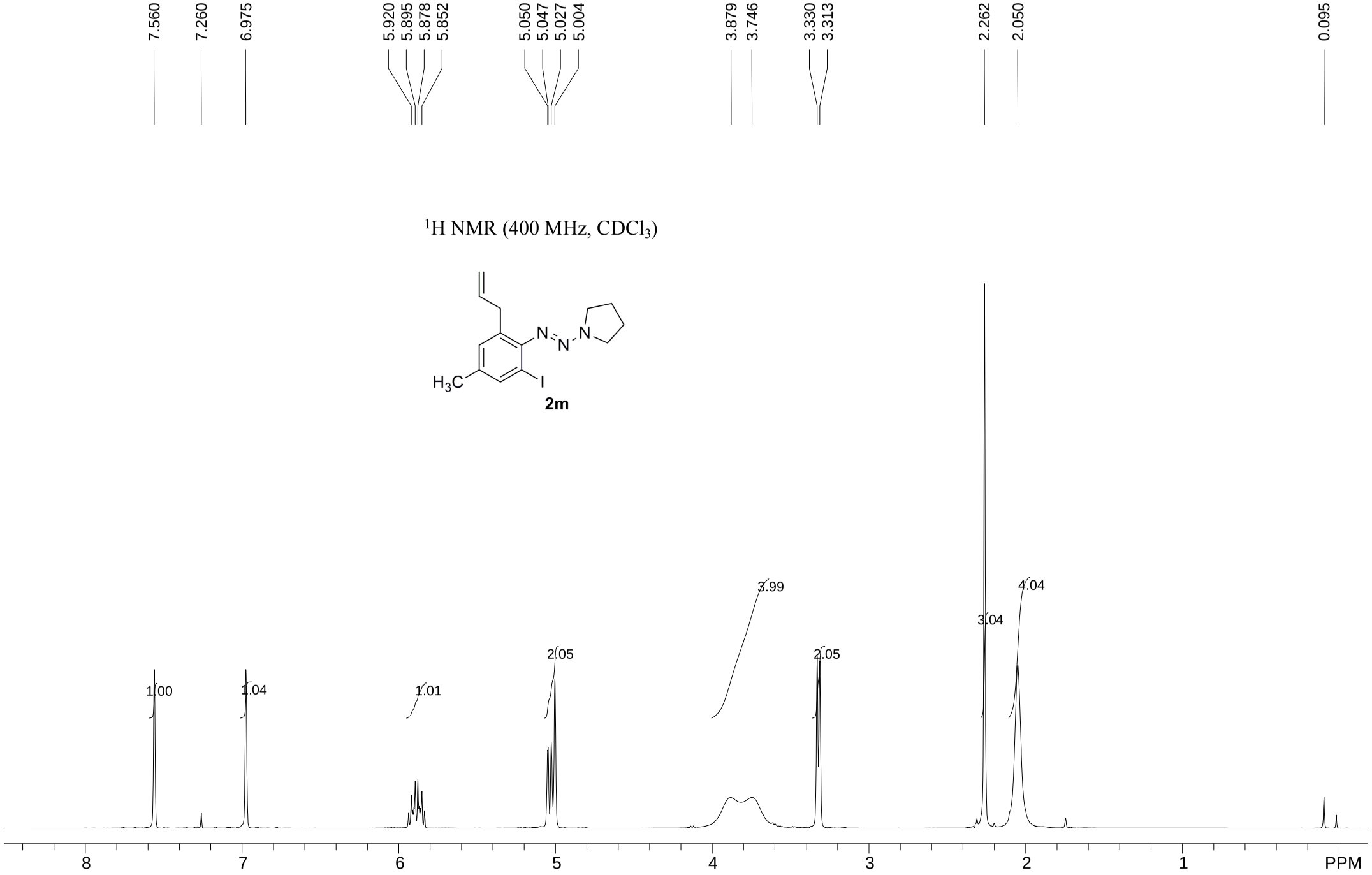
^{13}C NMR (100 MHz, $CDCl_3$)
H_3CO
I
2k
160.405
151.035
138.876
113.632
102.230
85.358
77.310
77.000
76.679
55.276
50.901
47.071
23.877
23.384
160
140
120
100
80
60
40
20
PPM


7.529
7.260
6.952
3.814
2.248
2.197
2.049
2.045
^{1}H NMR (400 MHz, $CDCl_3$)
CH_3
N
N
N
H_3C
I
2l
4.03
4.03
3.01
2.98
1.00
1.02
8
7
6
5
4
3
2
1
PPM



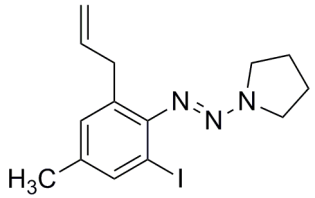
^{13}C NMR (100 MHz, $CDCl_3$)

2l

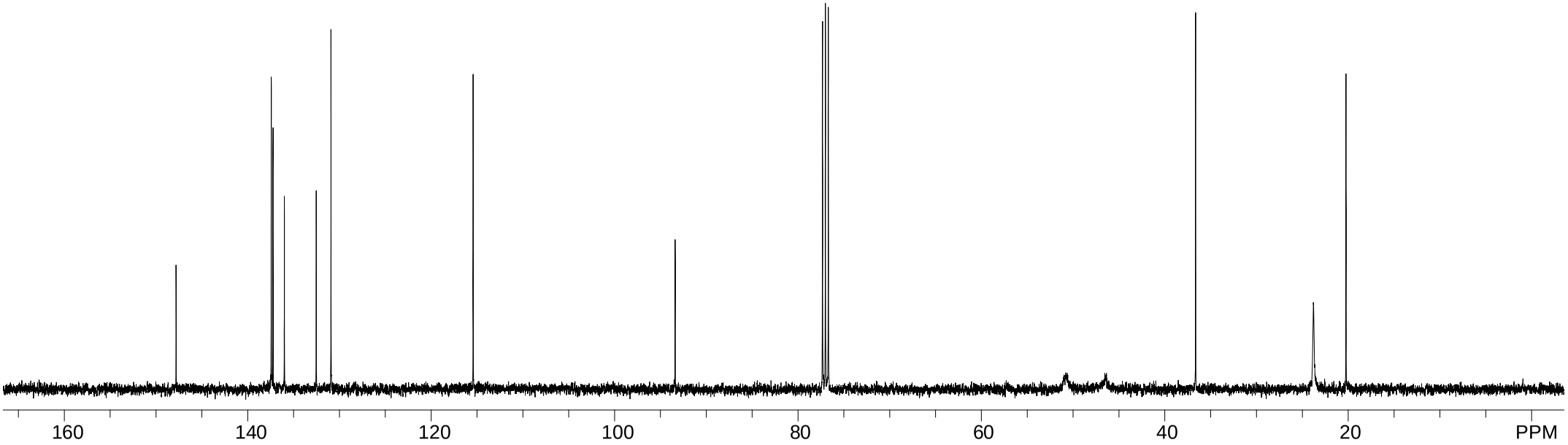

7.560
7.260
6.975
5.920
5.895
5.878
5.852
5.050
5.047
5.027
5.004
3.879
3.746
3.330
3.313
2.262
2.050
0.095
^{1}H NMR (400 MHz, $CDCl_3$)
H_3C
I
N
N
N
2m
1.00
1.04
1.01
2.05
3.99
2.05
3.04
4.04
8
7
6
5
4
3
2
1
PPM

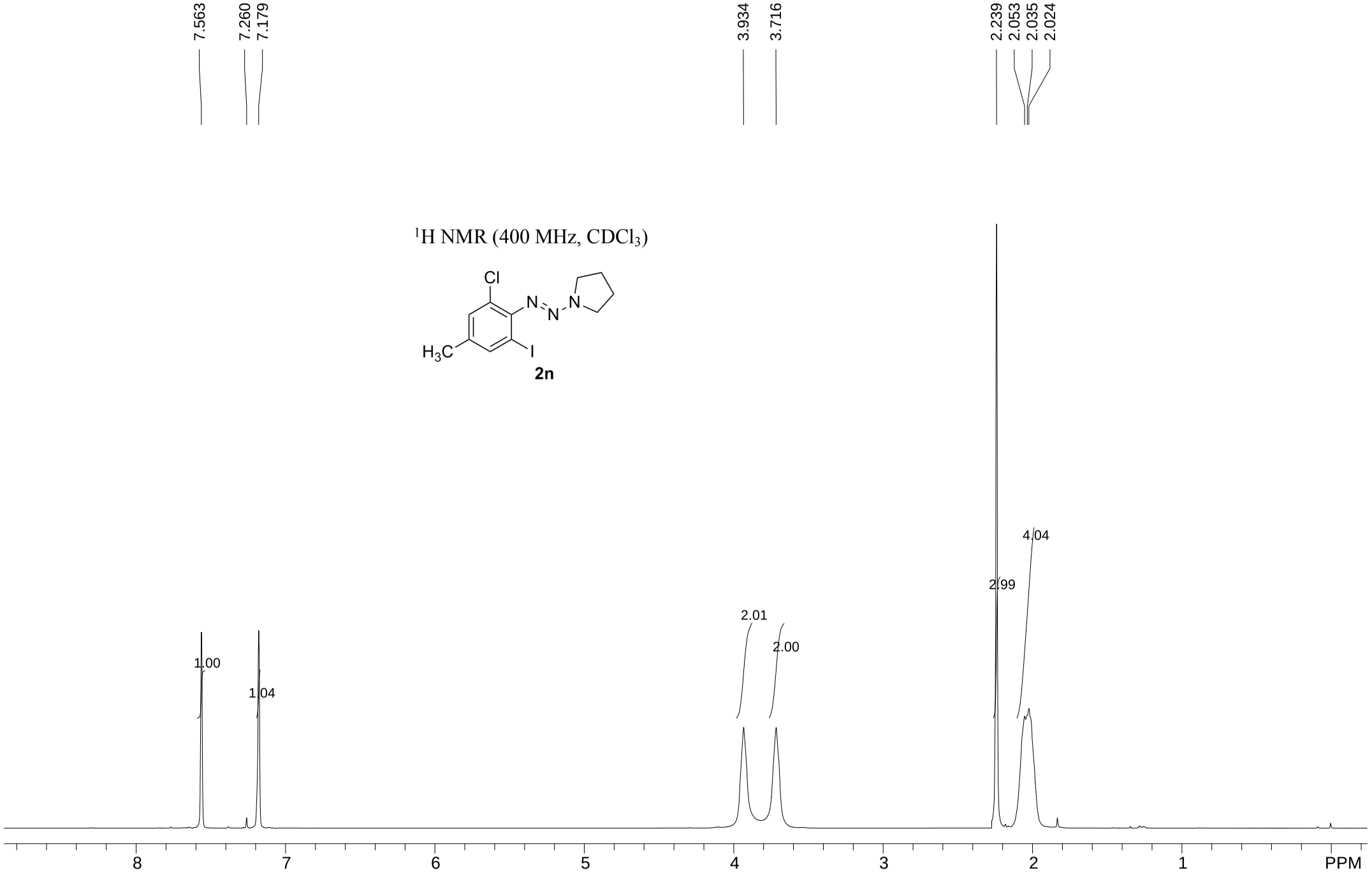
147.807
137.428
137.232
136.000
132.523
130.920
115.421
93.391
77.312
77.000
76.681
50.895
46.285
36.625
23.775
20.224

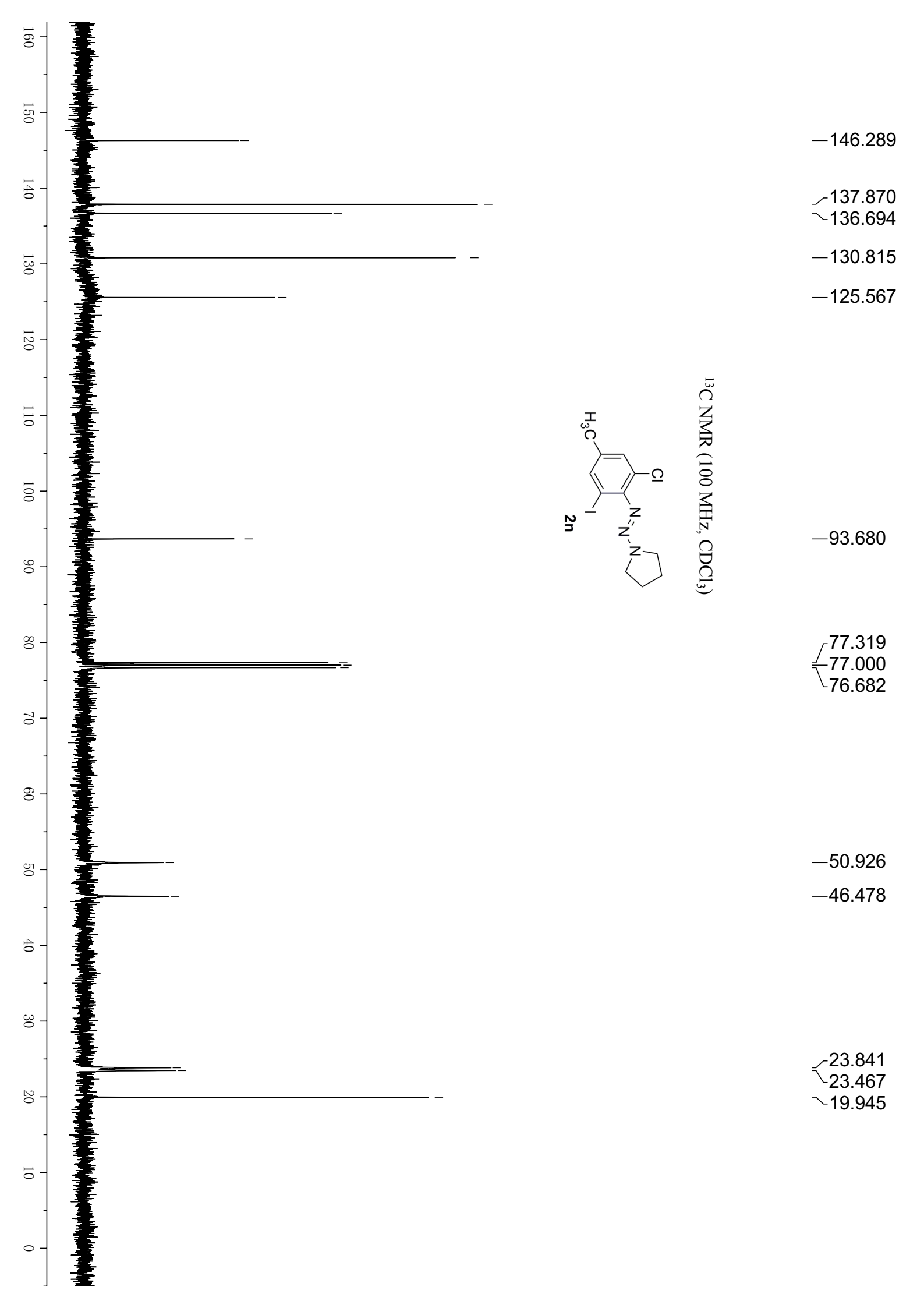
^{13}C NMR (100 MHz, $CDCl_3$)

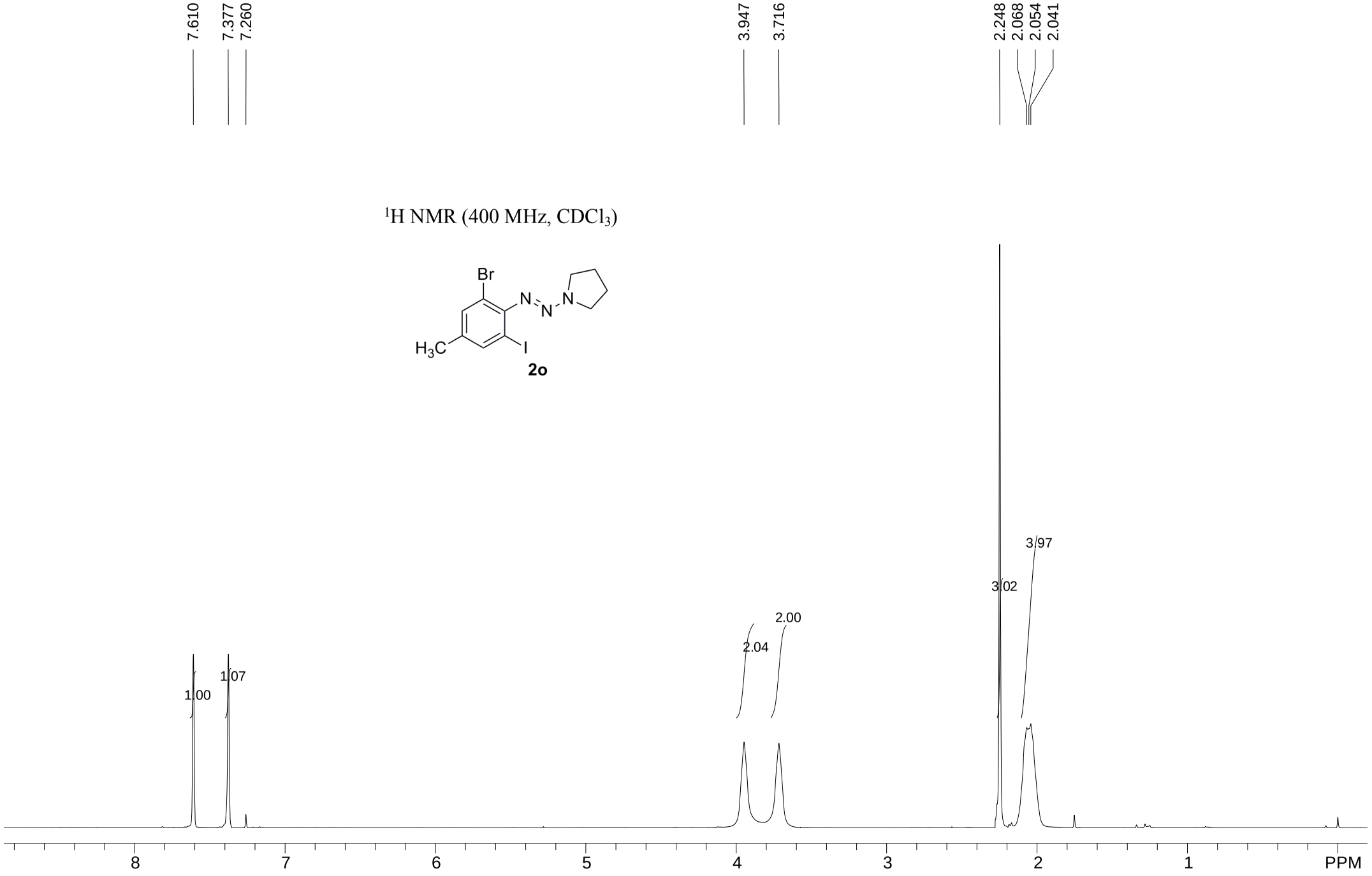


2m




7.563
7.260
7.179
3.934
3.716
2.239
2.053
2.035
2.024
1H NMR (400 MHz, CDCl3)
Cl
N
N
N
H3C
I
2n
1.00
1.04
2.01
2.00
2.99
4.04
8
7
6
5
4
3
2
1
PPM

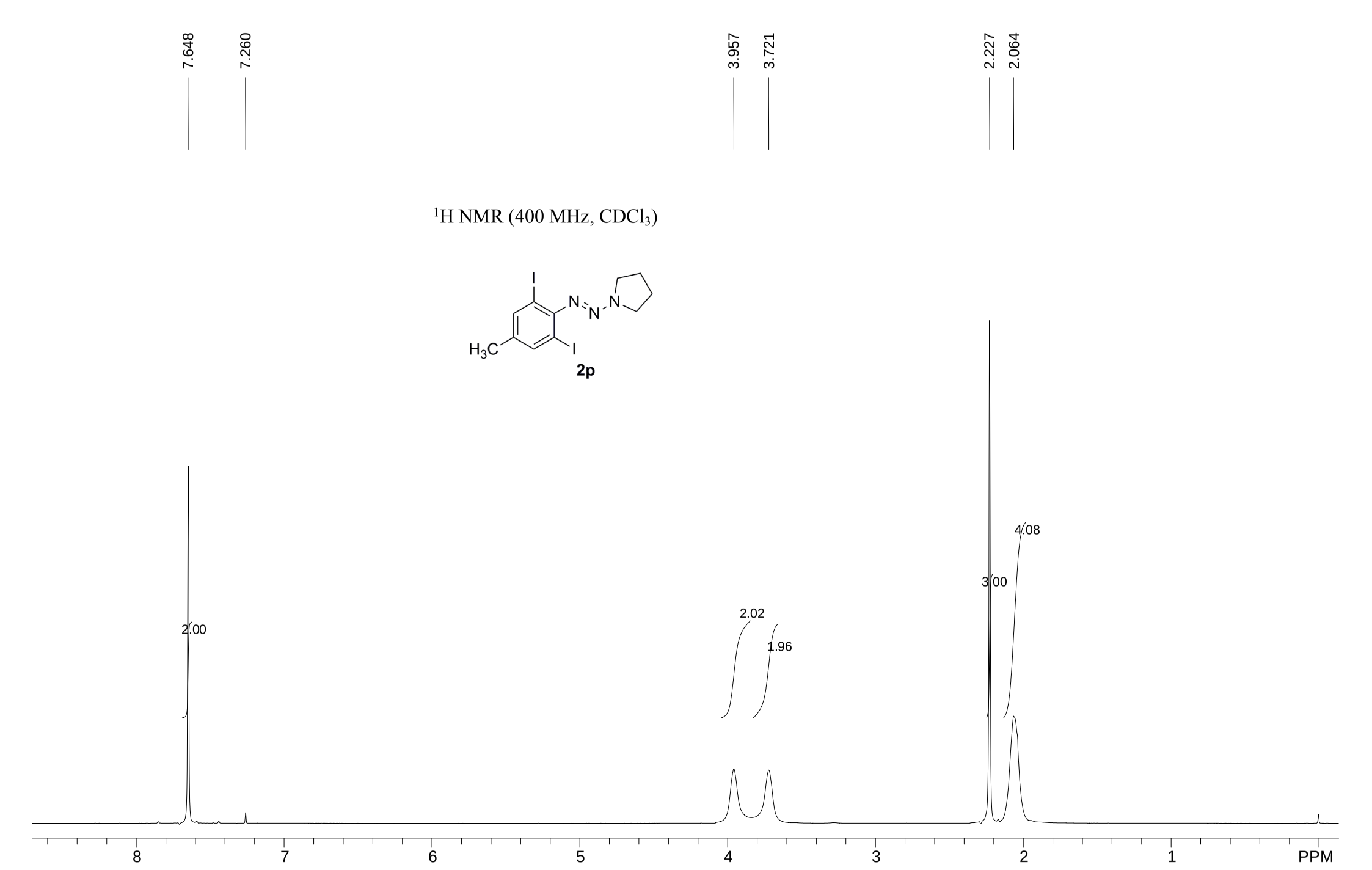

160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
146.289
137.870
136.694
130.815
125.567
93.680
77.319
77.000
76.682
50.926
46.478
23.841
23.467
19.945
^{13}C NMR (100 MHz, CDCl$_3$)
H$_3$C
Cl
I
N
N
N
2n



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

2o

^{13}C NMR (100 MHz, CDCl$_3$)
2o
Br
I
H$_3$C
N
N
N
147.322
138.732
137.242
133.852
115.303
92.931
77.325
77.000
76.687
50.986
46.600
23.900
23.541
19.863
160
140
120
100
80
60
40
20
PPM

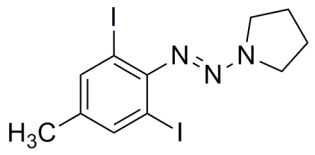


^{1}H NMR (400 MHz, $CDCl_3$)

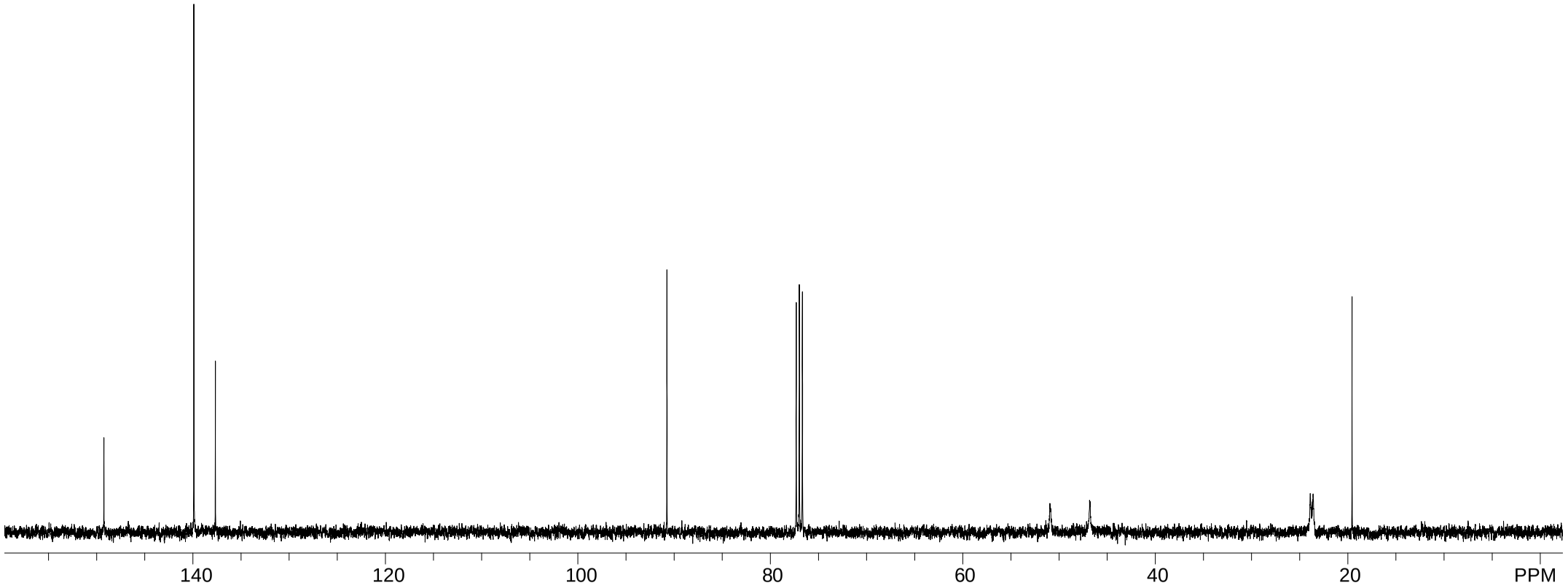
2p

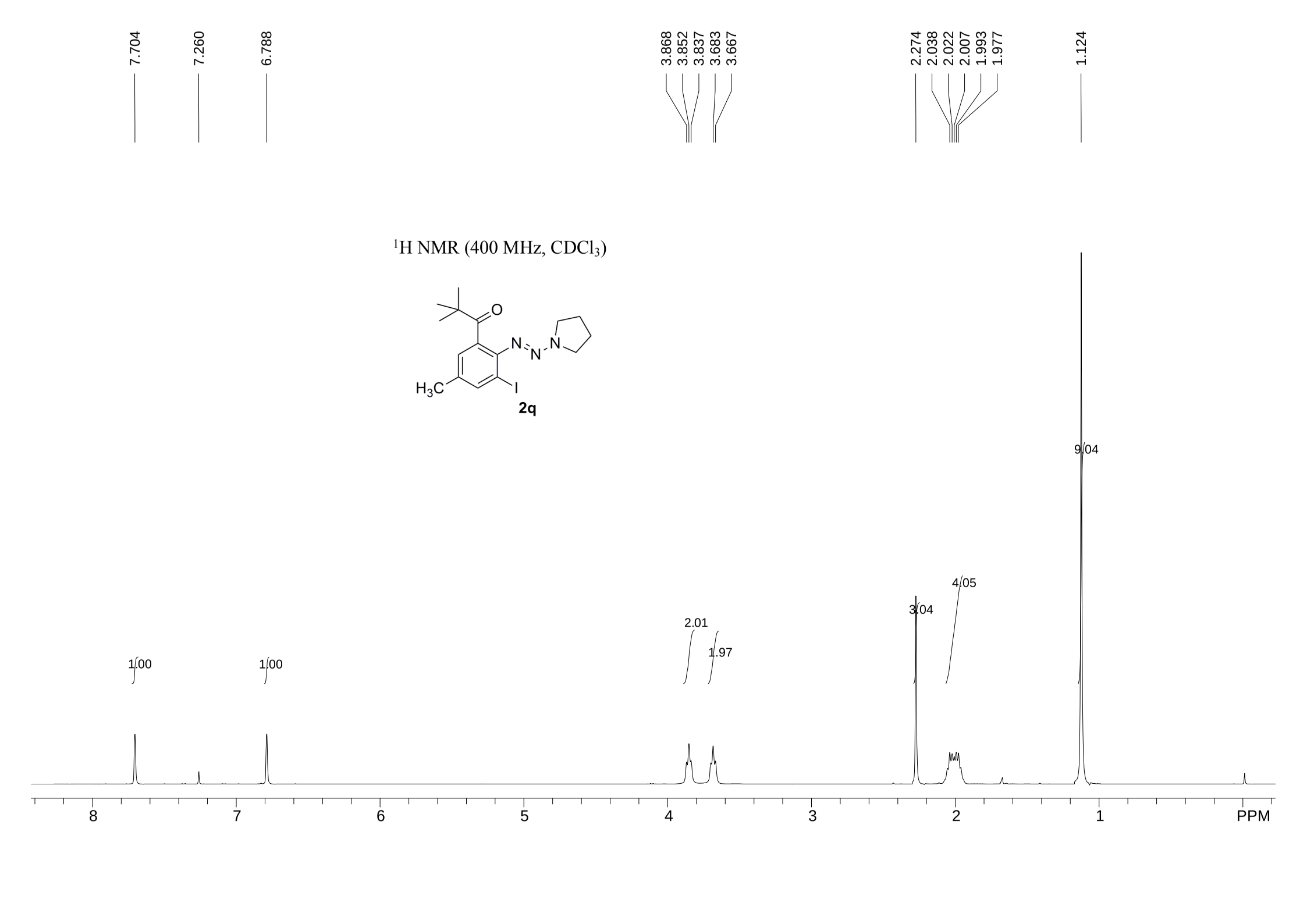
149.242
139.894
137.665
90.753
77.315
77.000
76.676
50.967
46.837
23.900
23.605
19.559

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



2p




7.704
7.260
6.788
3.868
3.852
3.837
3.683
3.667
2.274
2.038
2.022
2.007
1.993
1.977
1.124
^{1}H NMR (400 MHz, $CDCl_3$)
O
N
N
N
H_3C
I
2q
9.04
4.05
3.04
2.01
1.97
1.00
1.00
8
7
6
5
4
3
2
1
PPM

^{13}C NMR (100 MHz, CDCl$_3$)
214.239
144.203
139.932
135.729
131.625
127.345
96.535
77.318
77.000
76.684
50.831
47.583
44.620
27.426
24.078
23.353
20.294
200
150
100
50
0
PPM
H$_3$C
I
O
N
N
N
2q

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

7.260

5.339
5.323
5.308

4.075
4.058

2.770
2.753
2.736

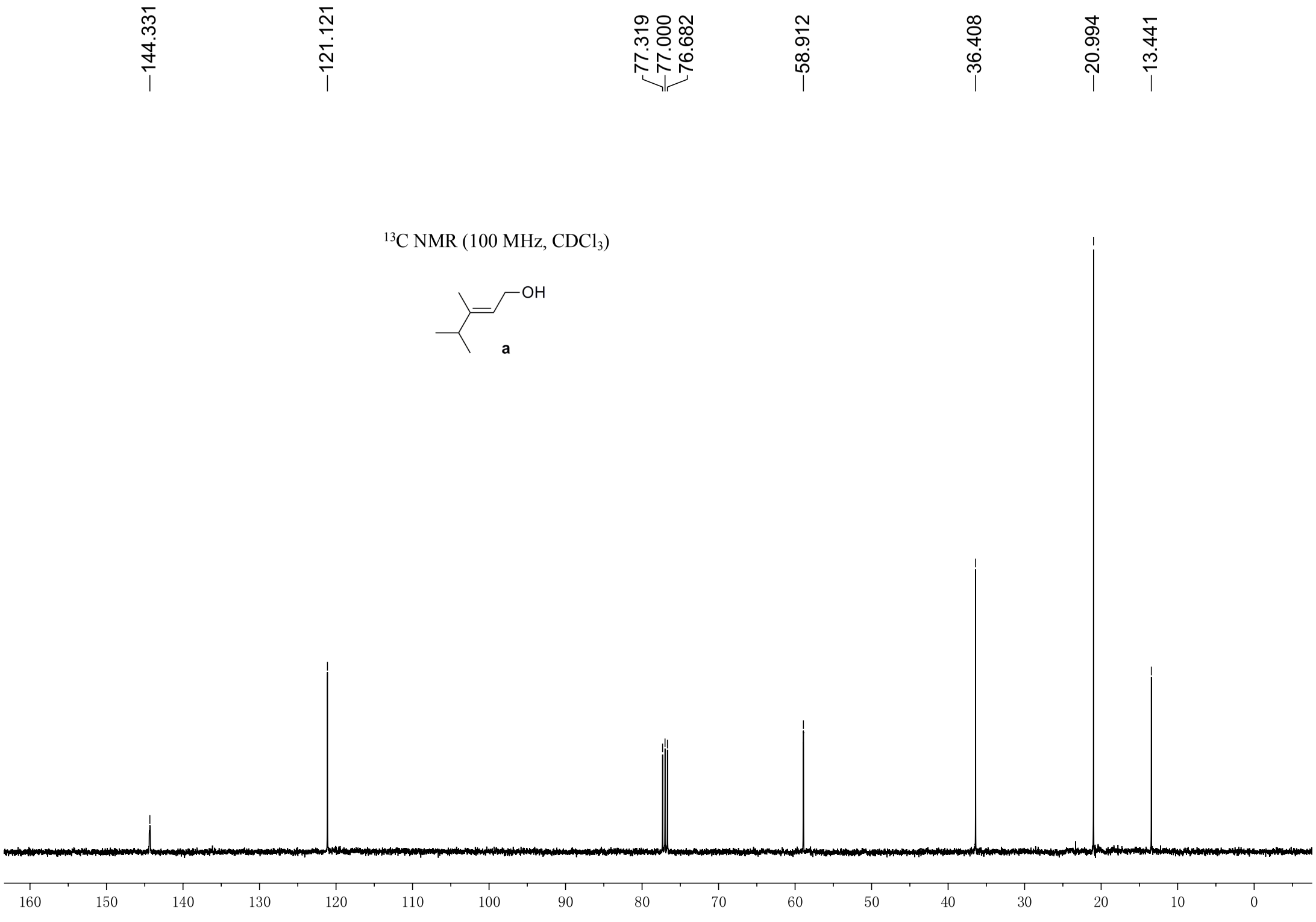
2.214
2.197
2.180
2.163
2.146

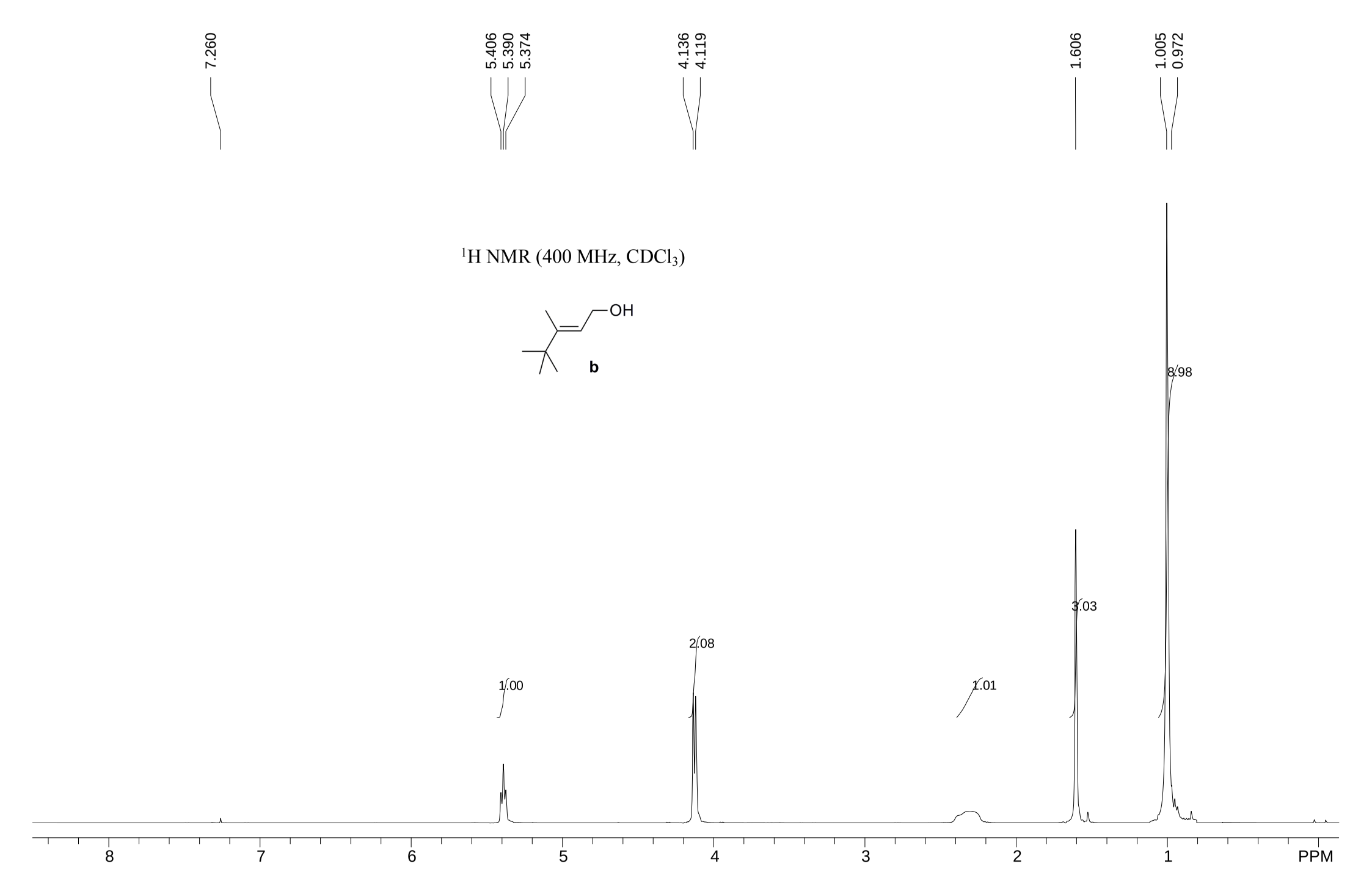
1.556

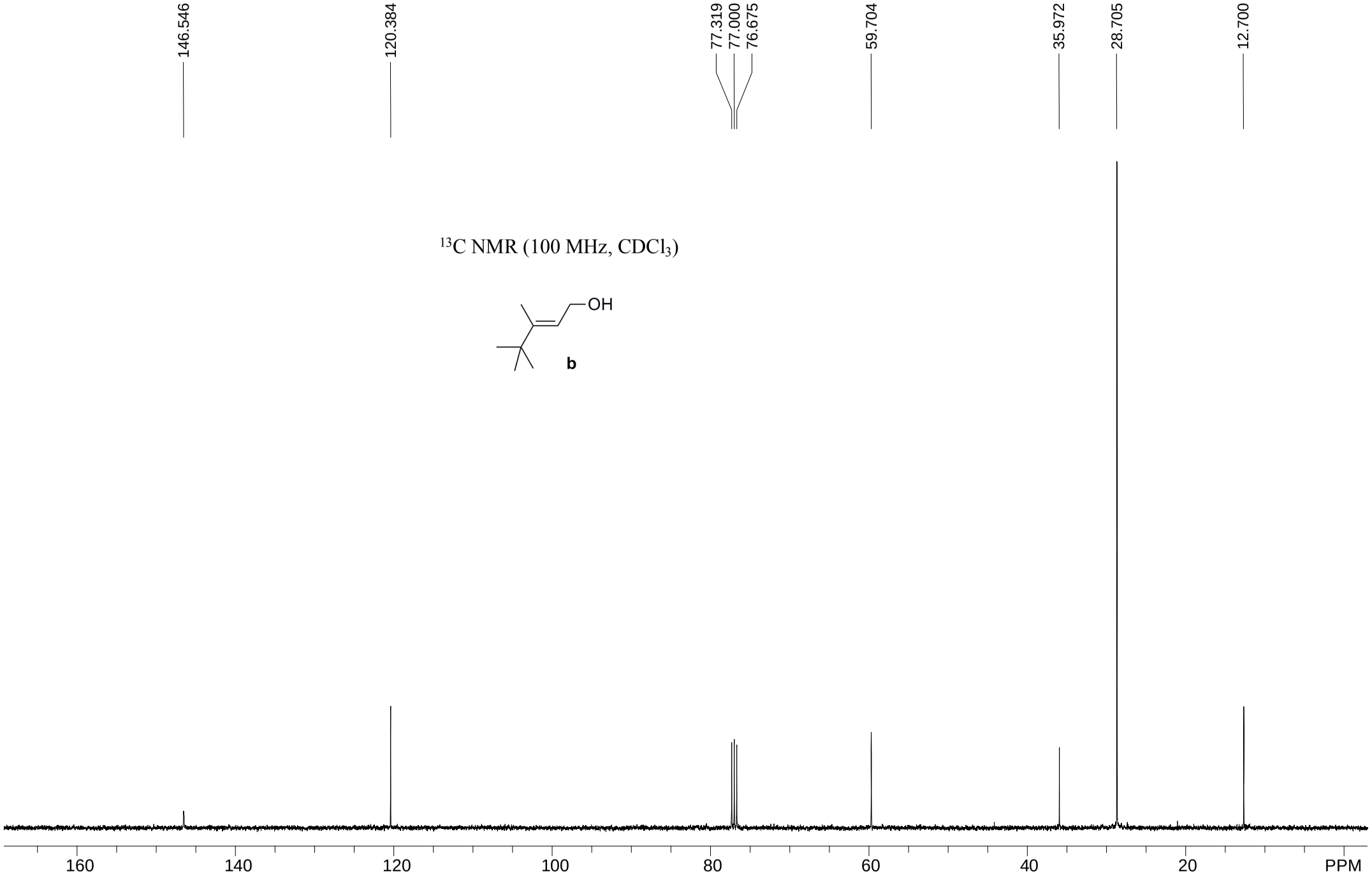
0.950
0.932

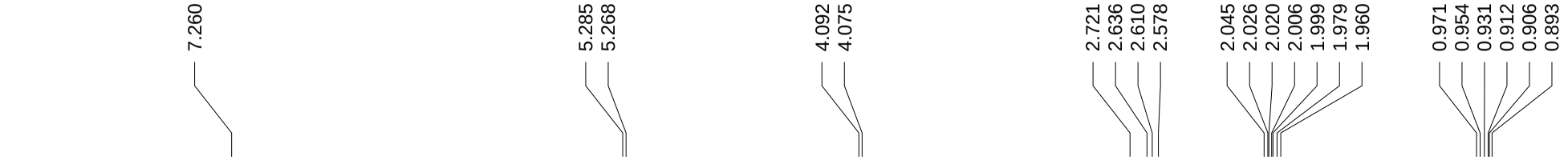
1.00
2.00
1.00
1.04
3.08
6.03

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 0.0

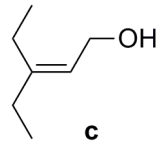

144.331
121.121
77.319
77.000
76.682
58.912
36.408
20.994
13.441
^{13}C NMR (100 MHz, $CDCl_3$)
OH
a
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.260
5.406
5.390
5.374
4.136
4.119
1.606
1.005
0.972
^{1}H NMR (400 MHz, $CDCl_3$)
OH
b
8.98
3.03
2.08
1.00
1.01
8
7
6
5
4
3
2
1
PPM

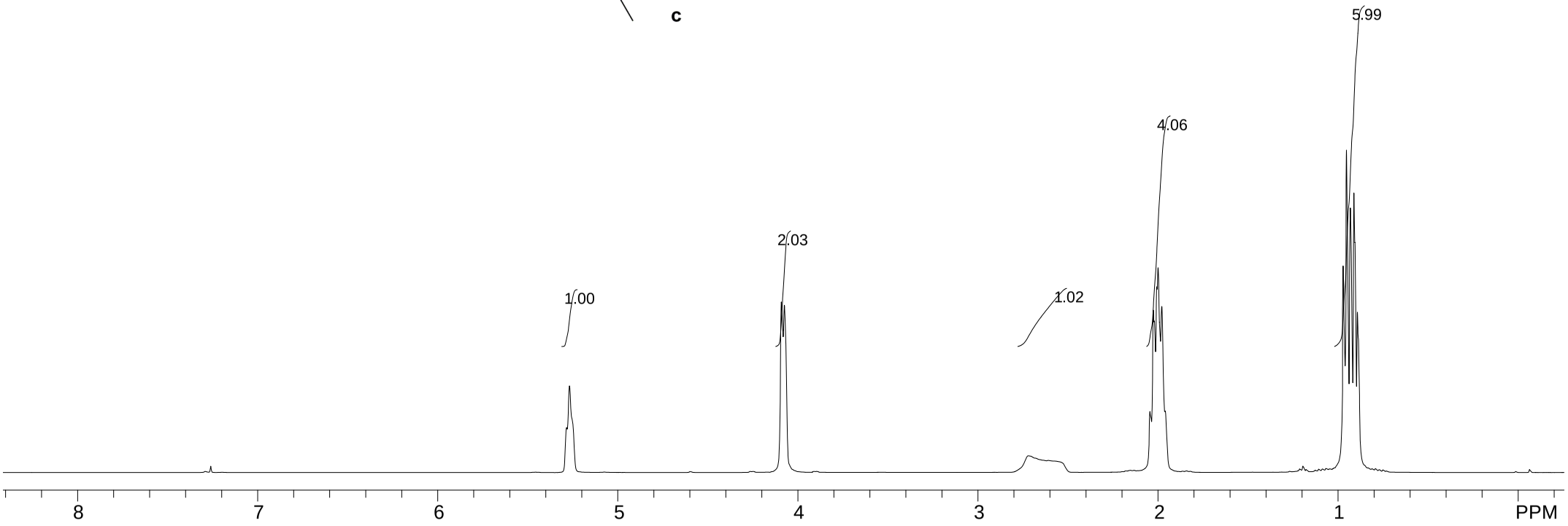

146.546
120.384
77.319
77.000
76.675
59.704
35.972
28.705
12.700
^{13}C NMR (100 MHz, $CDCl_3$)
OH
b
160
140
120
100
80
60
40
20
PPM

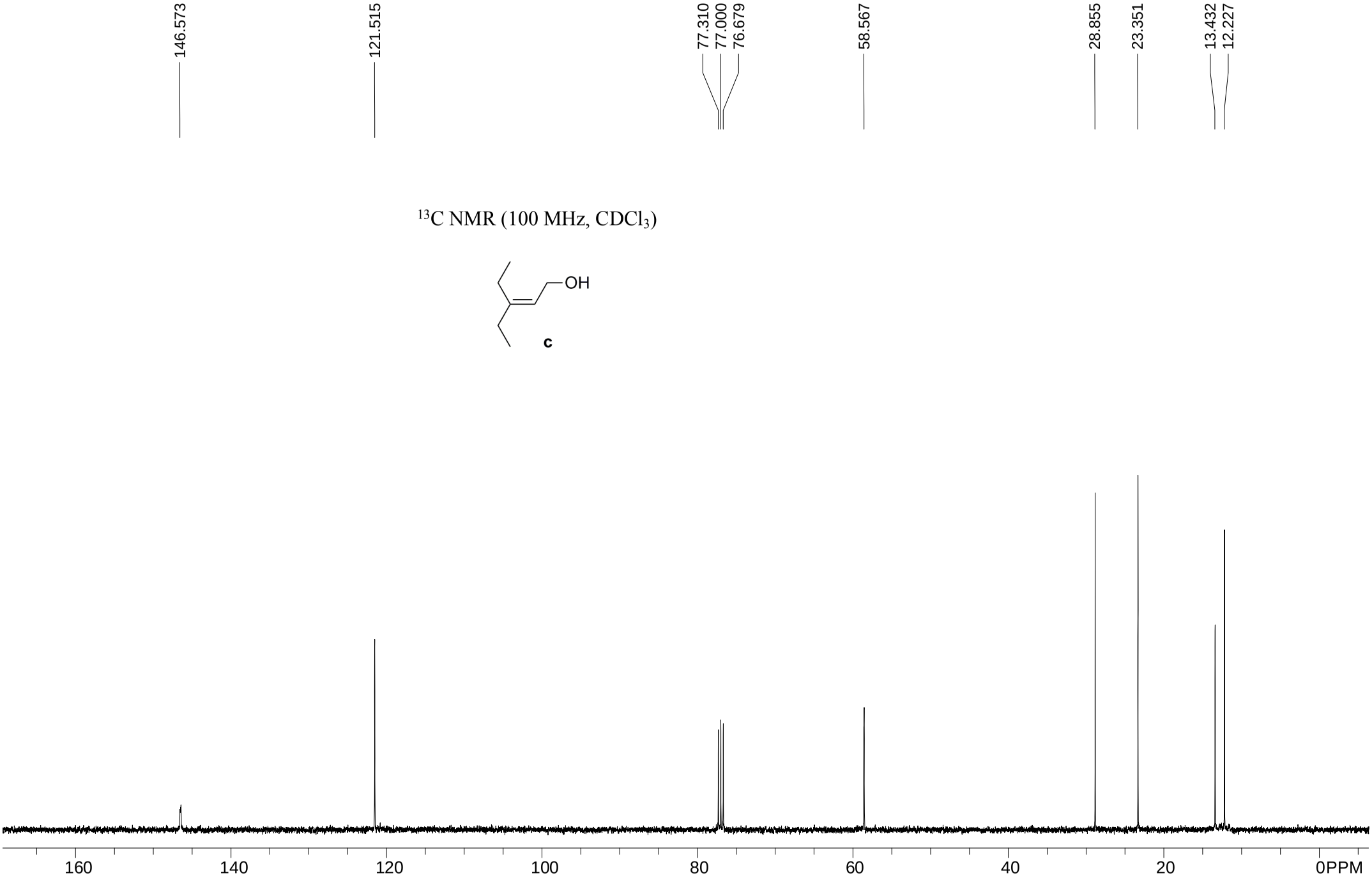


^{1}H NMR (400 MHz, $CDCl_3$)



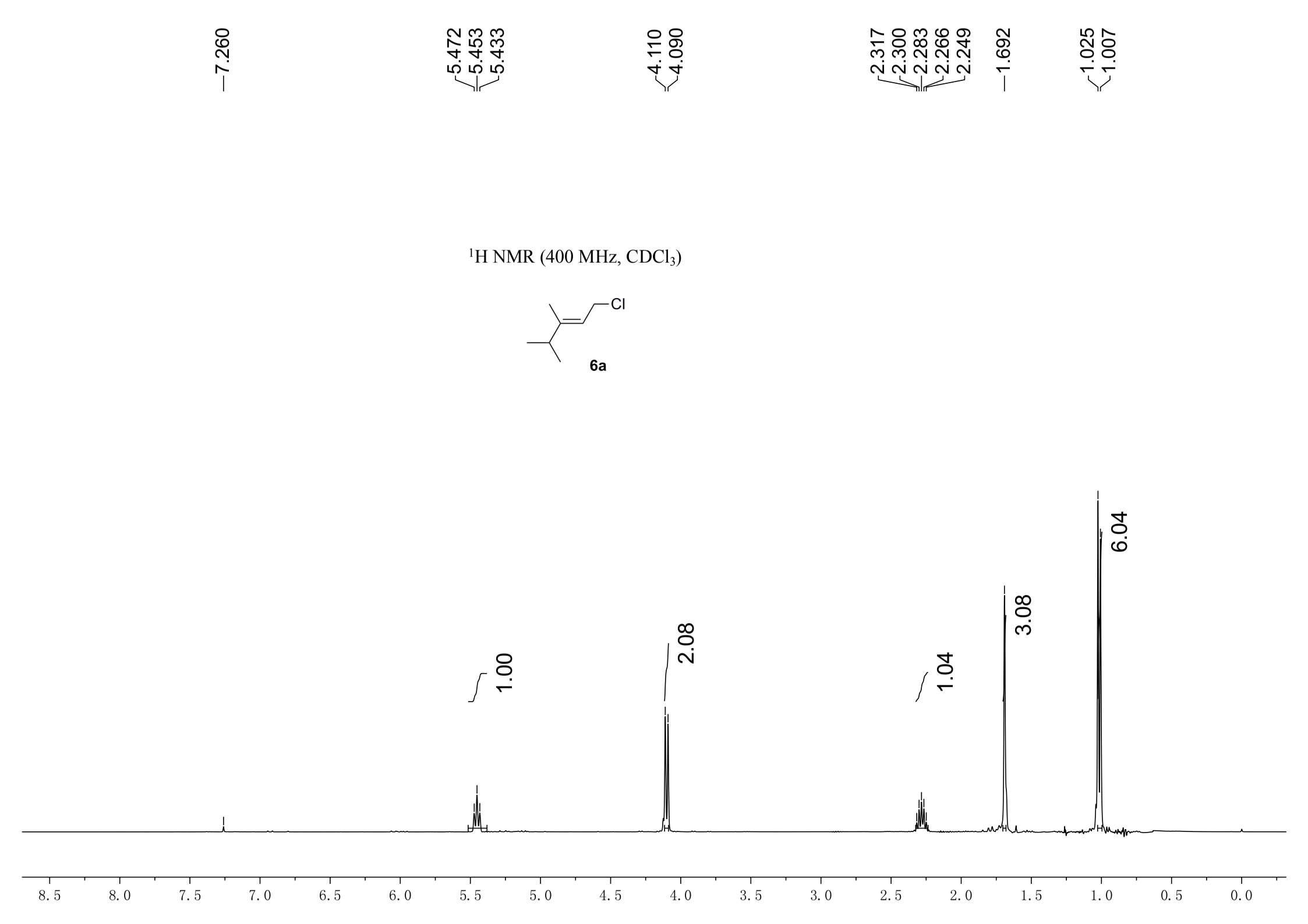
c





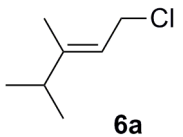
^{13}C NMR (100 MHz, $CDCl_3$)

c

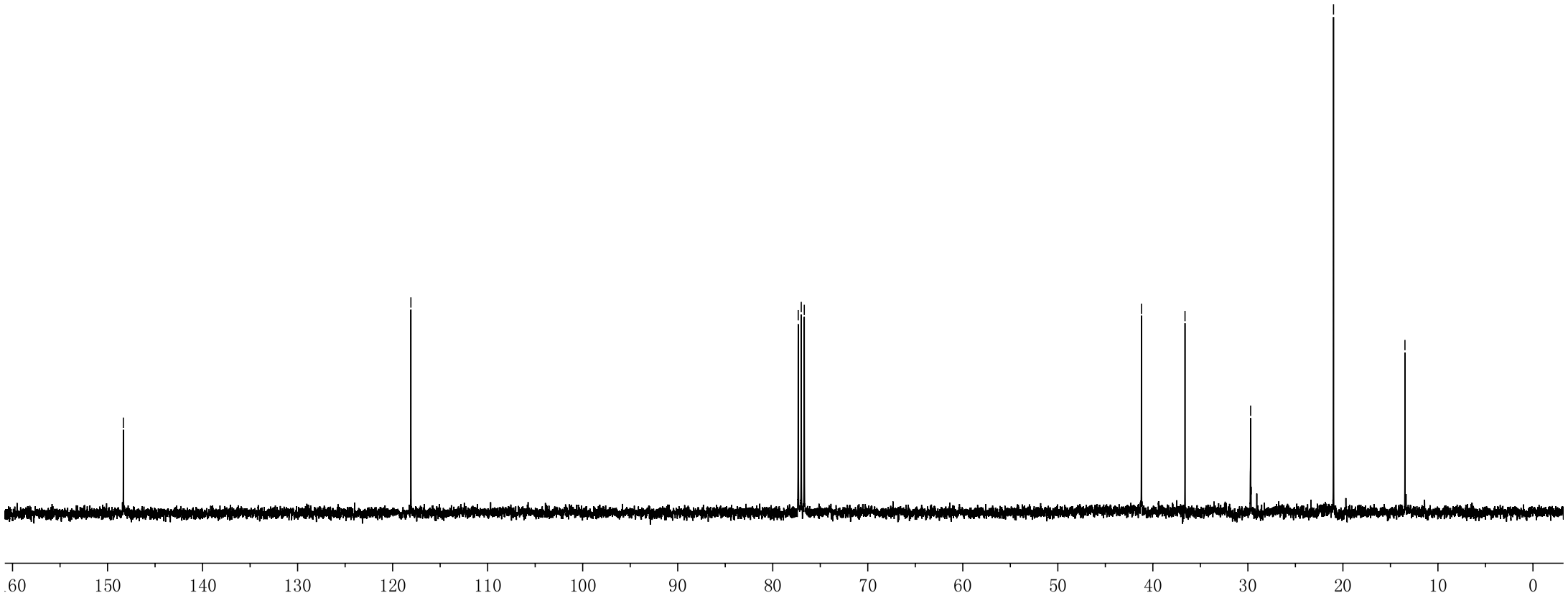

7.260
5.472
5.453
5.433
4.110
4.090
2.317
2.300
2.283
2.266
2.249
1.692
1.025
1.007
1H NMR (400 MHz, CDCl3)
Cl
6a
1.00
2.08
1.04
3.08
6.04
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

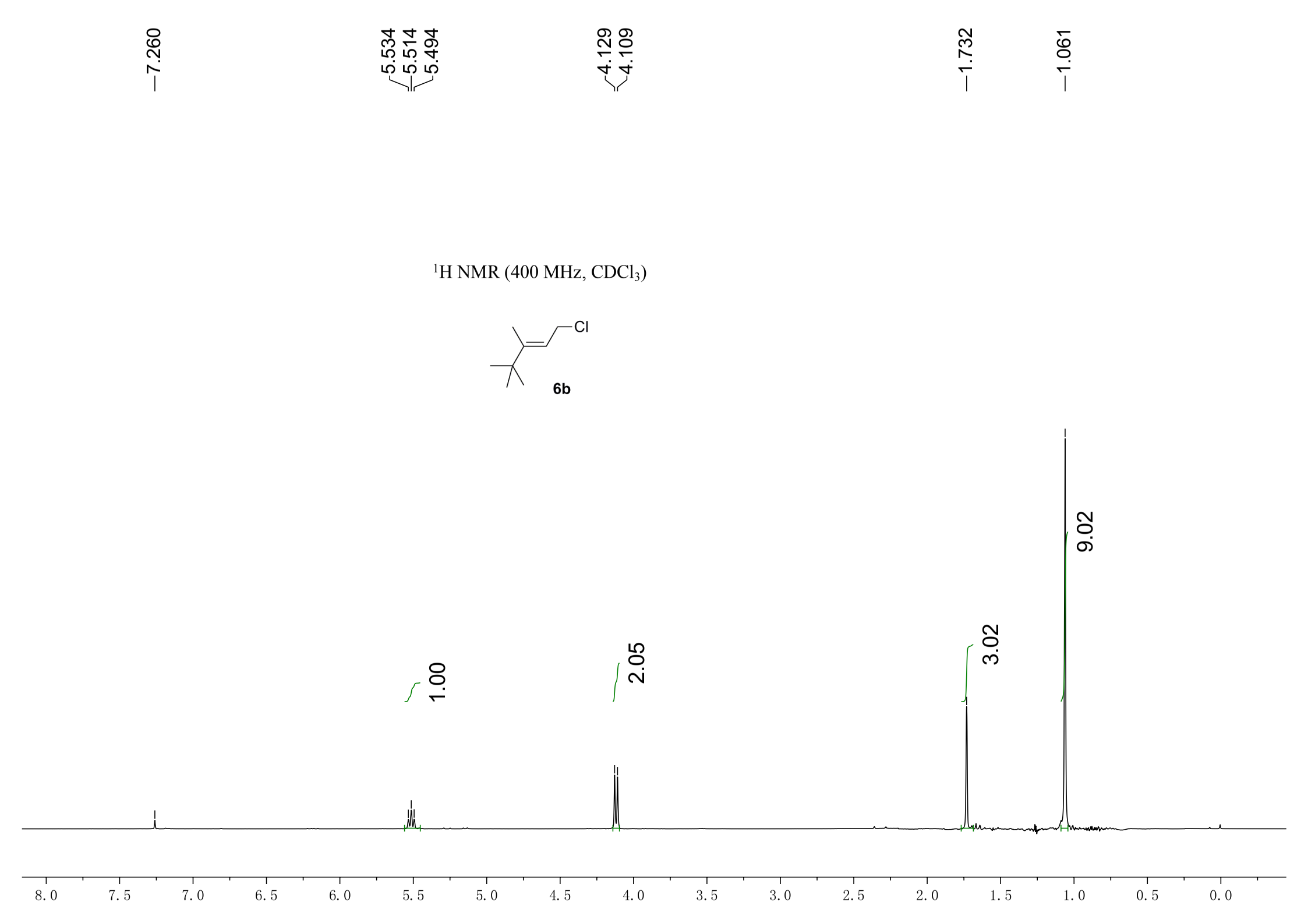
148.340
118.078
77.318
77.000
76.682
41.203
36.616
29.711
20.988
13.471

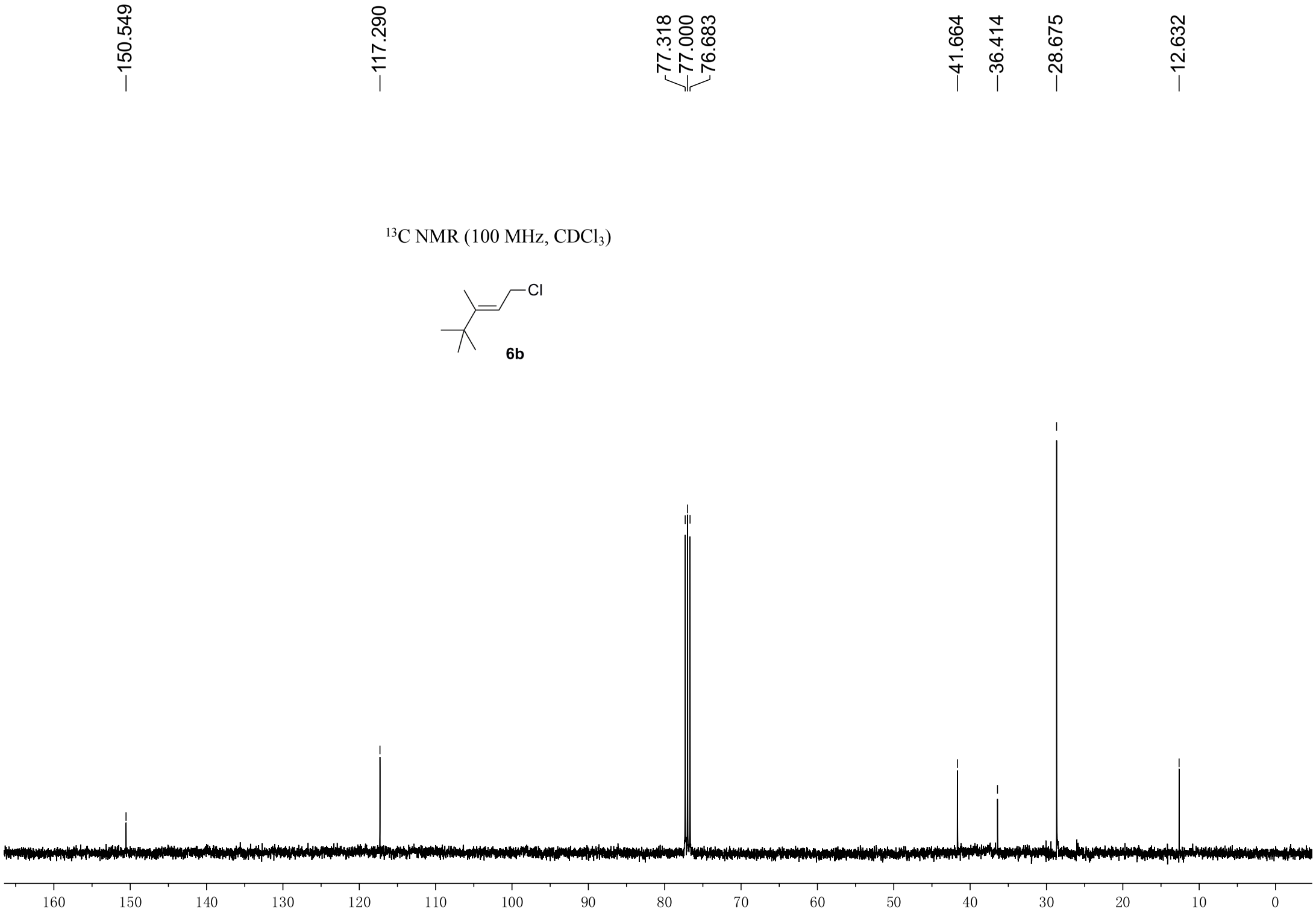
^{13}C NMR (100 MHz, $CDCl_3$)



6a

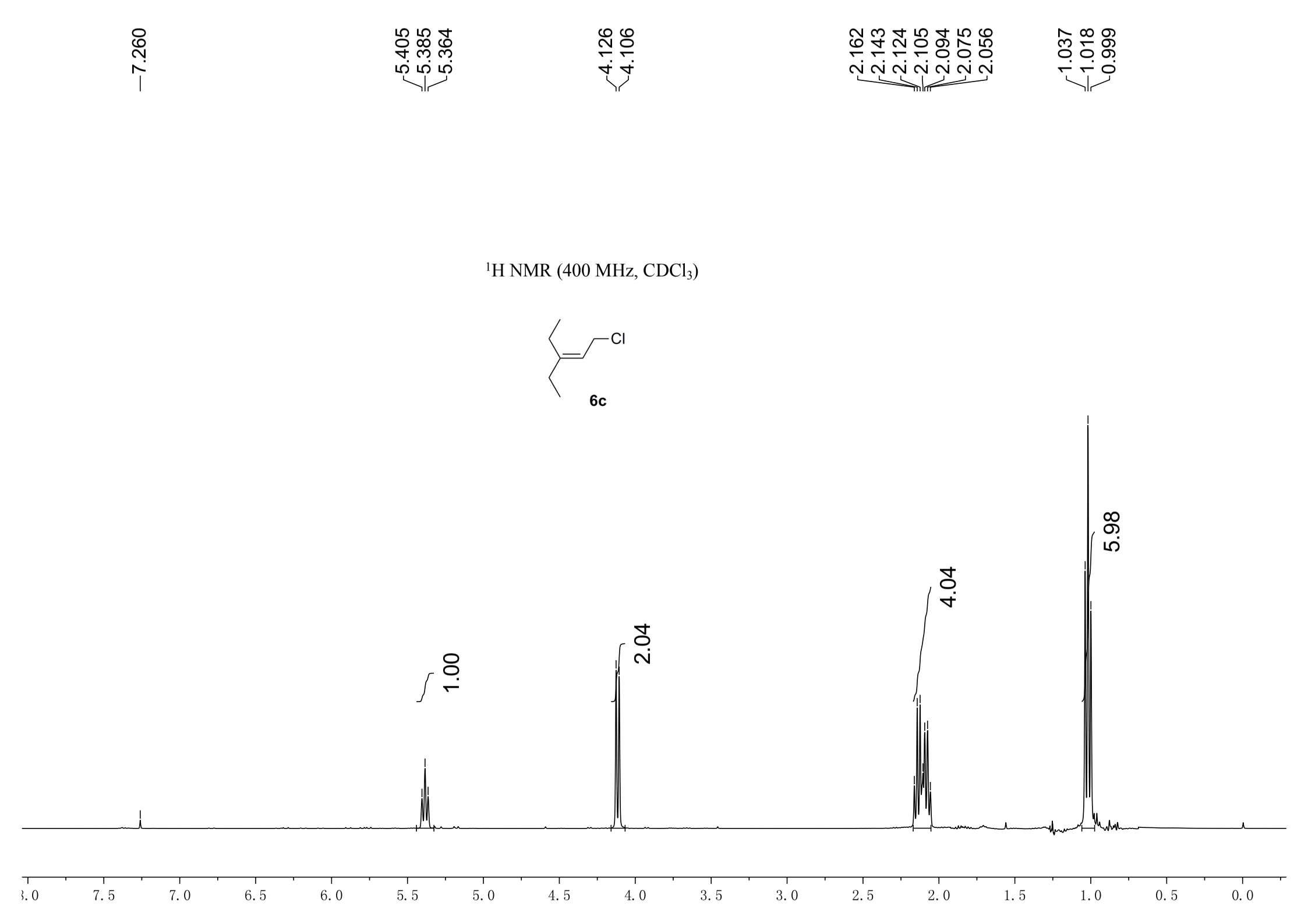



7.260
5.534
5.514
5.494
4.129
4.109
1.732
1.061
1H NMR (400 MHz, CDCl3)
Cl
6b
1.00
2.05
3.02
9.02
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

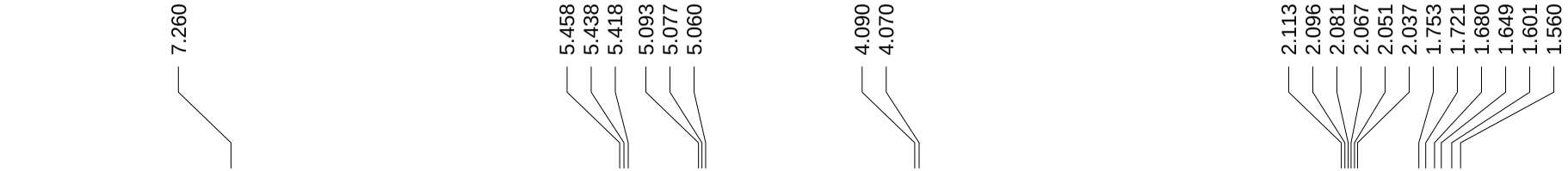


^{13}C NMR (100 MHz, $CDCl_3$)

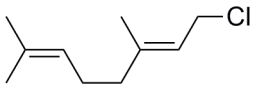
6b


7.260
5.405
5.385
5.364
4.126
4.106
2.162
2.143
2.124
2.105
2.094
2.075
2.056
1.037
1.018
0.999
1H NMR (400 MHz, CDCl3)
Cl
6c
1.00
2.04
4.04
5.98
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
0.0

150.148
118.411
77.317
77.000
76.682
40.887
29.053
23.343
13.354
12.203
^{13}C NMR (100 MHz, CDCl$_3$)
Cl
6c
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



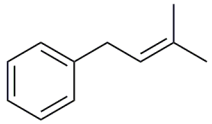
^{1}H NMR (400 MHz, $CDCl_3$)



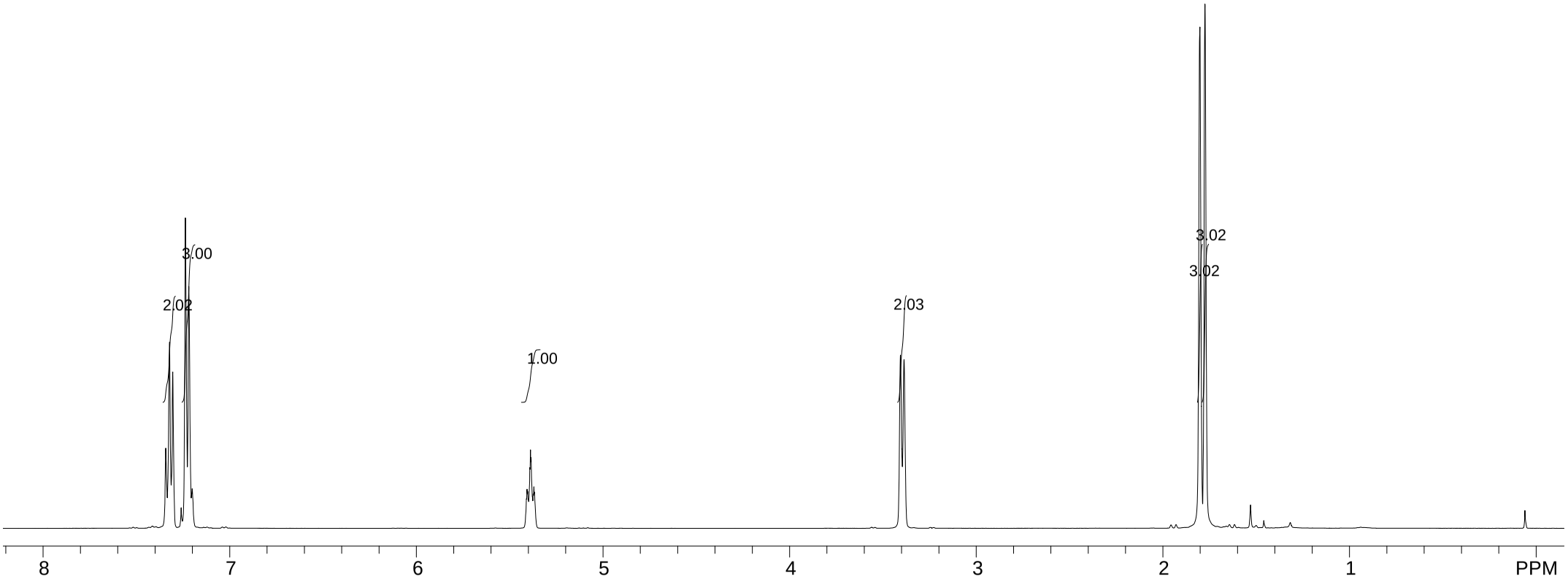
6e

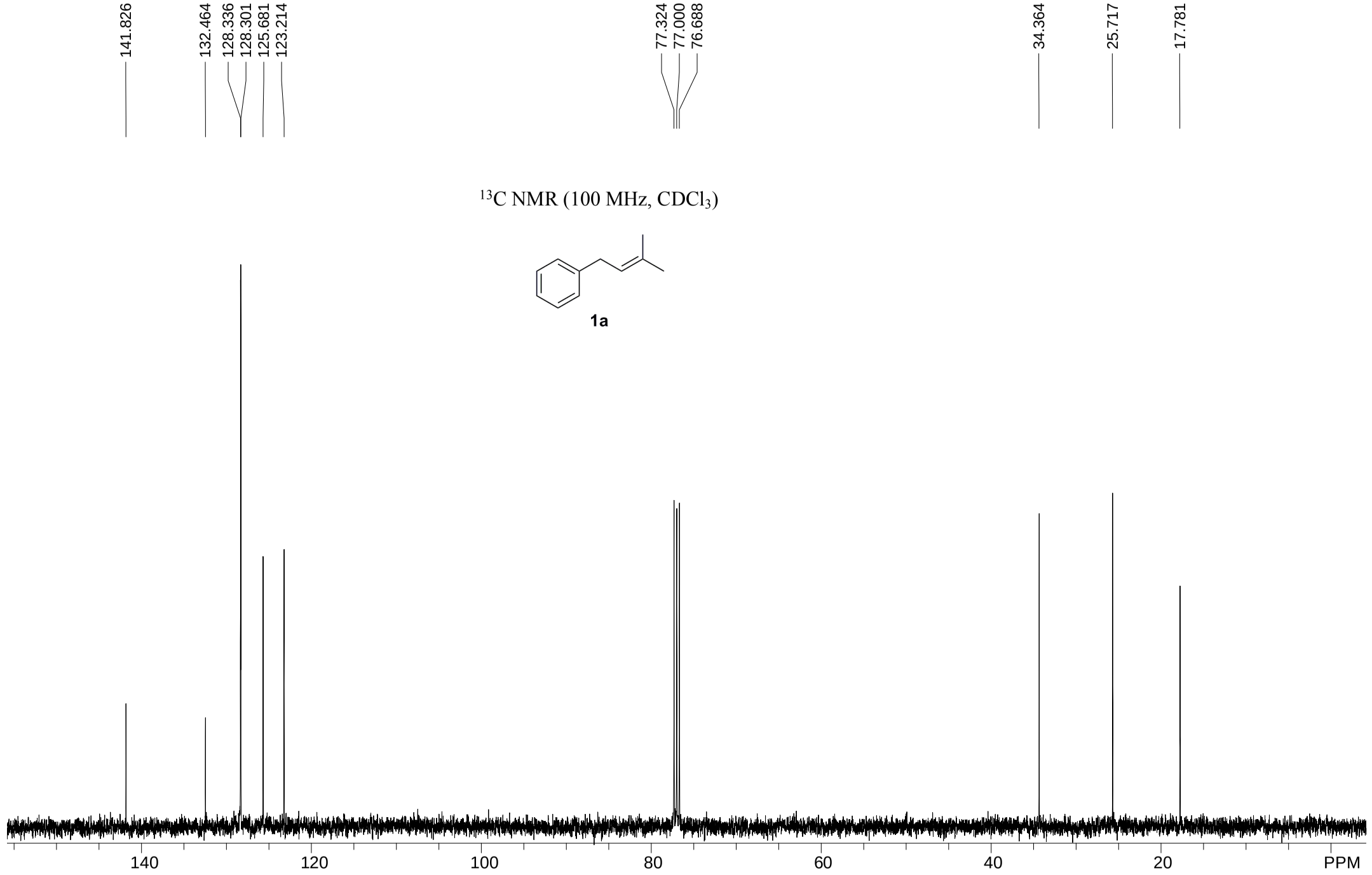
^{13}C NMR (100 MHz, $CDCl_3$)
6e
Cl
142.460
131.730
123.503
120.276
77.325
77.000
76.682
40.875
39.344
26.114
25.517
17.524
15.910
140
120
100
80
60
40
20
PPM

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



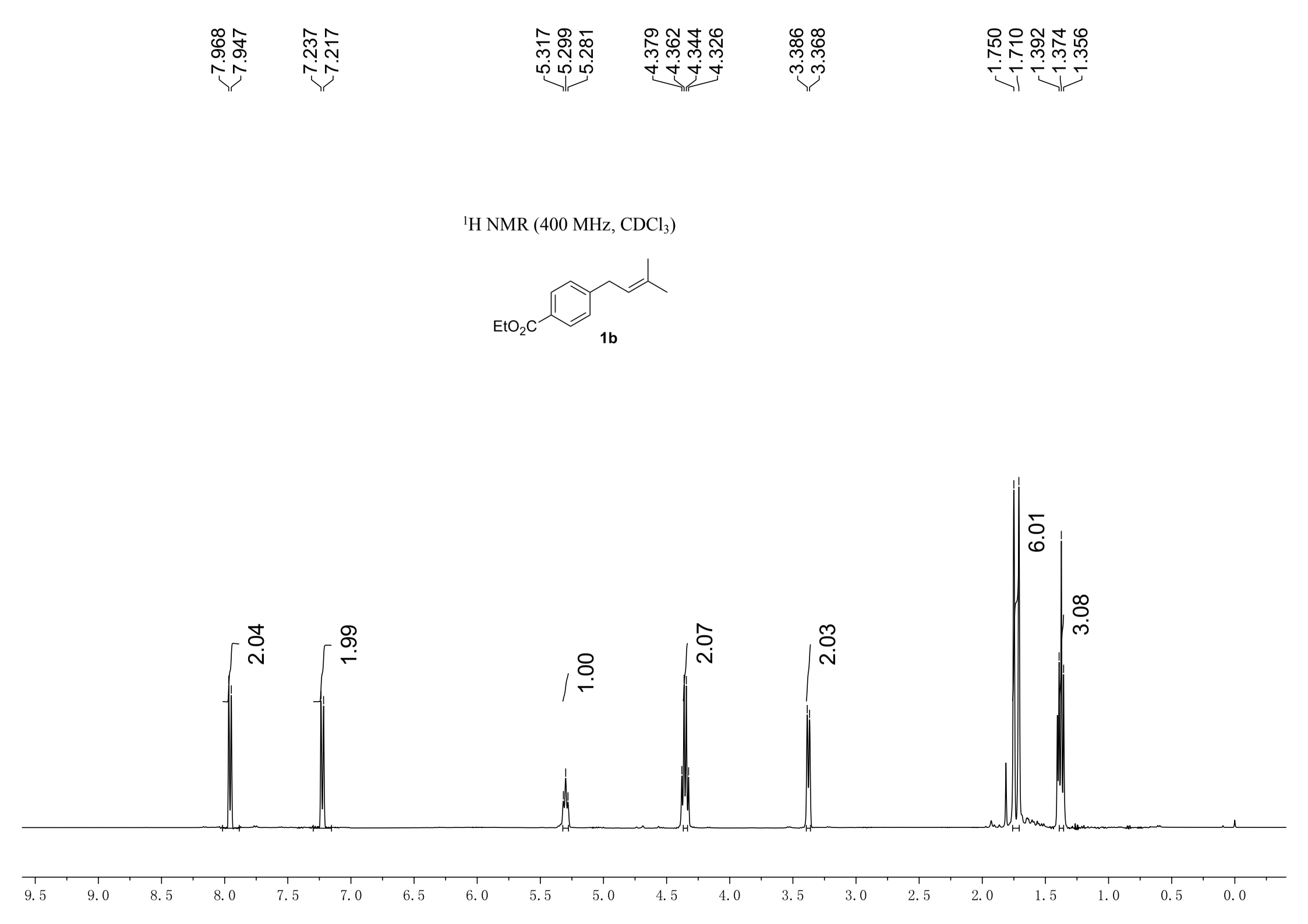
1a





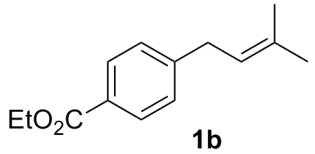
^{13}C NMR (100 MHz, $CDCl_3$)

1a

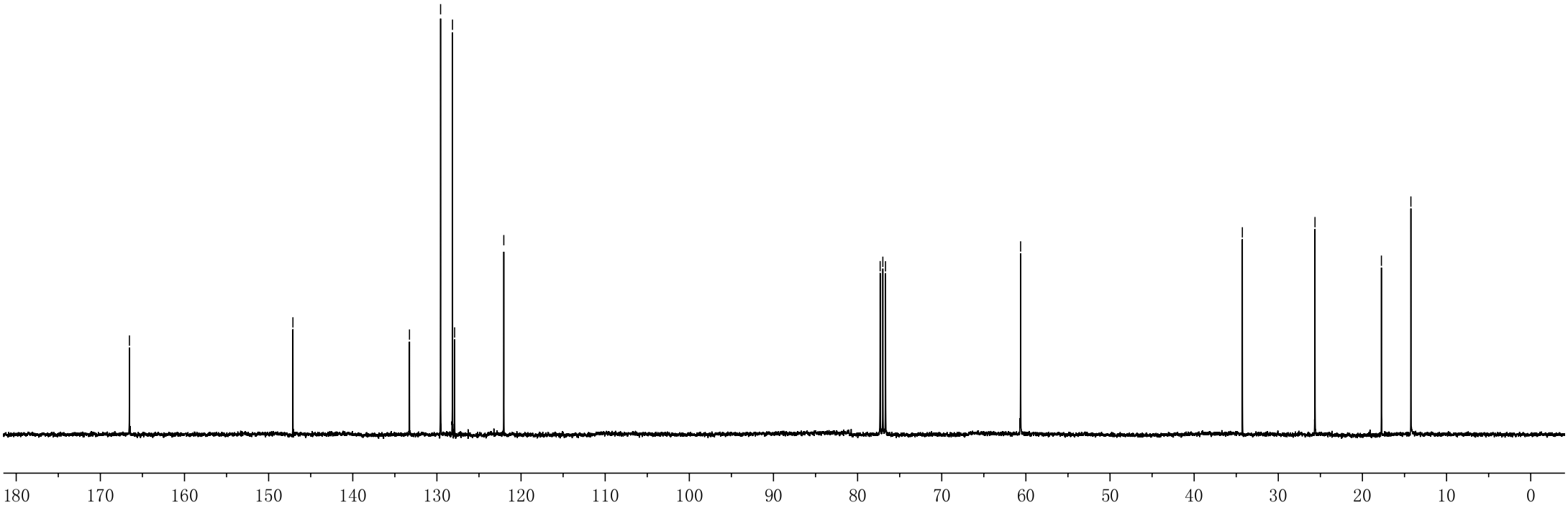

7.968
7.947
7.237
7.217
5.317
5.299
5.281
4.379
4.362
4.344
4.326
3.386
3.368
1.750
1.710
1.392
1.374
1.356
^{1}H NMR (400 MHz, $CDCl_3$)
EtO_2C
1b
2.04
1.99
1.00
2.07
2.03
6.01
3.08
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

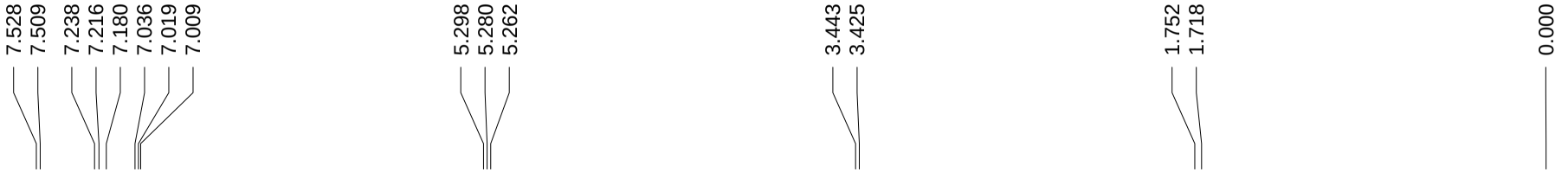
166.544
147.113
133.260
129.563
128.145
127.894
122.048
77.318
77.000
76.682
60.626
34.272
25.638
17.745
14.240

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

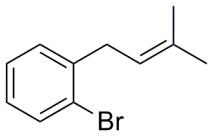


1b

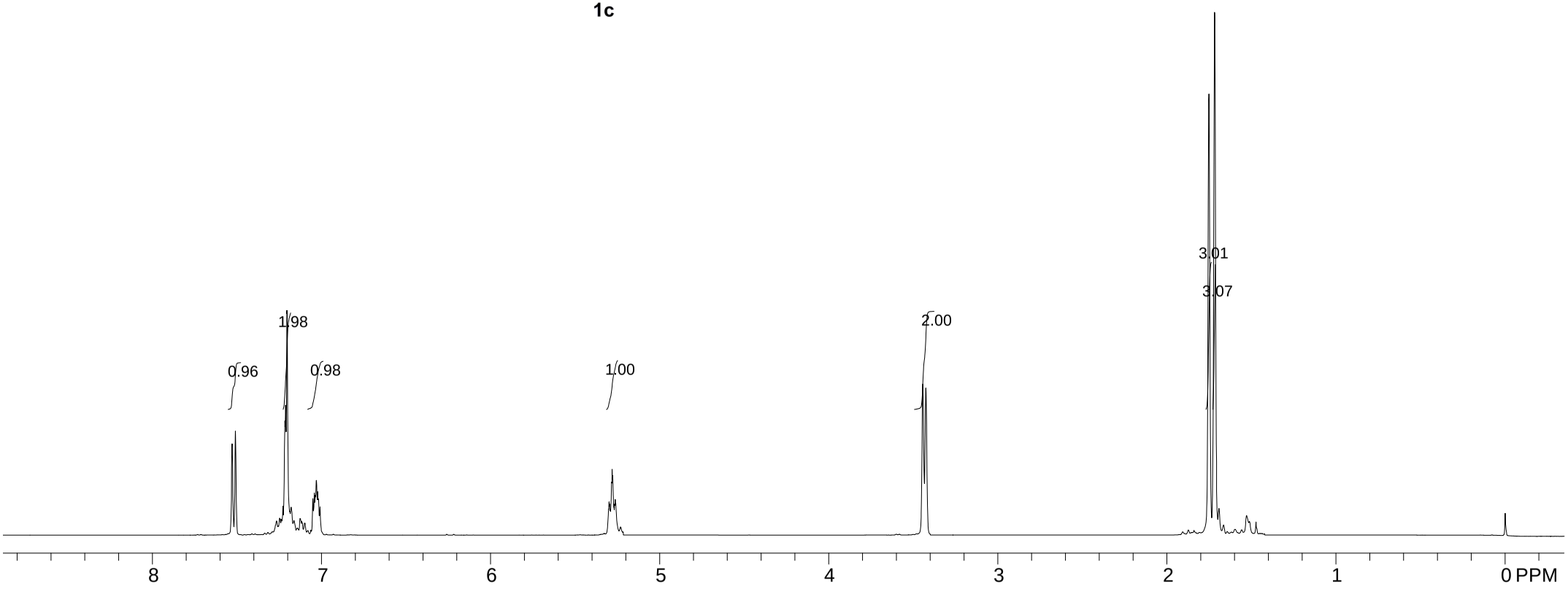


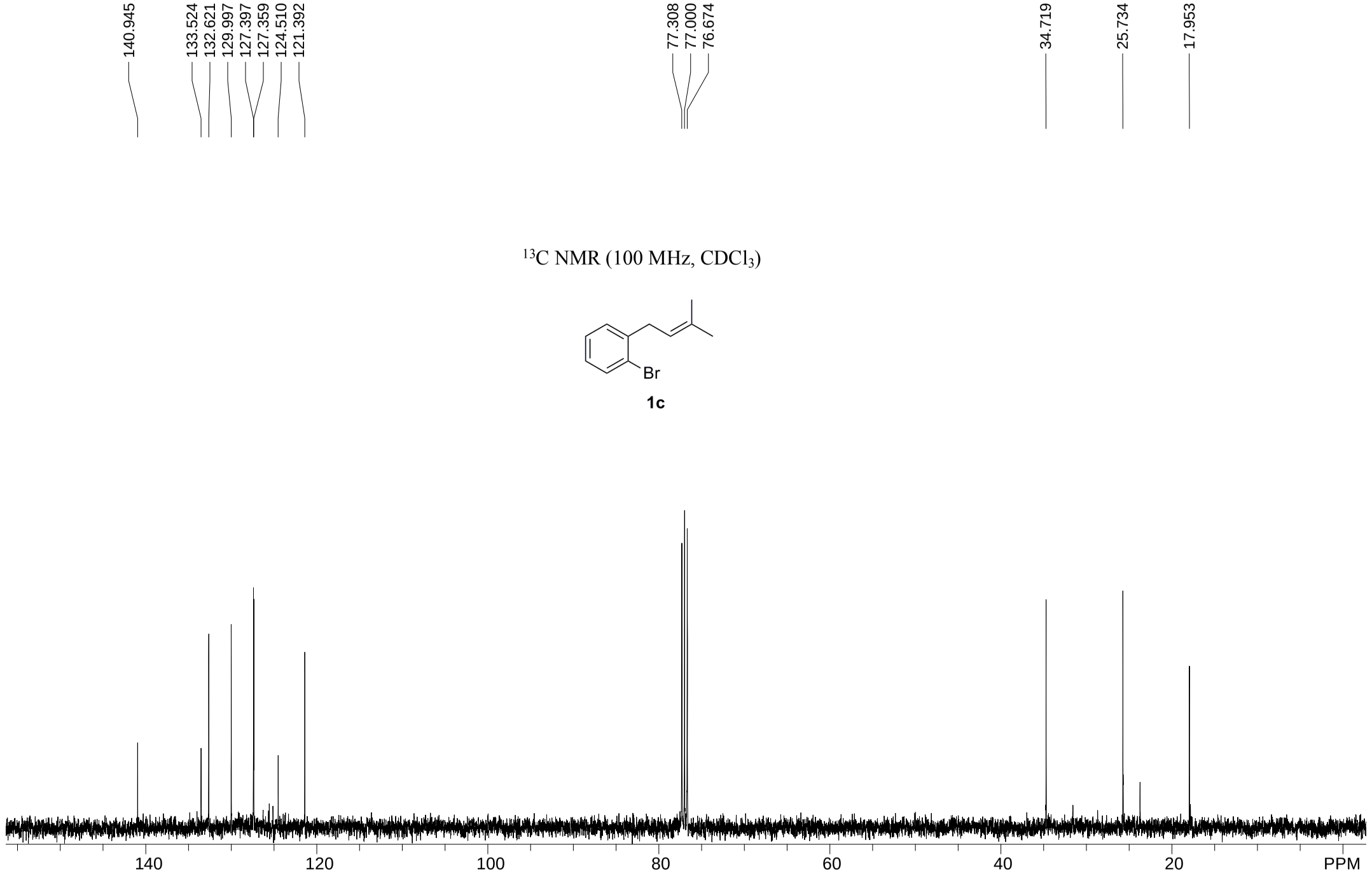


^{1}H NMR (400 MHz, $CDCl_3$)



1c

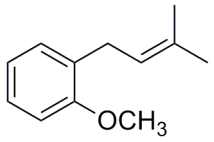




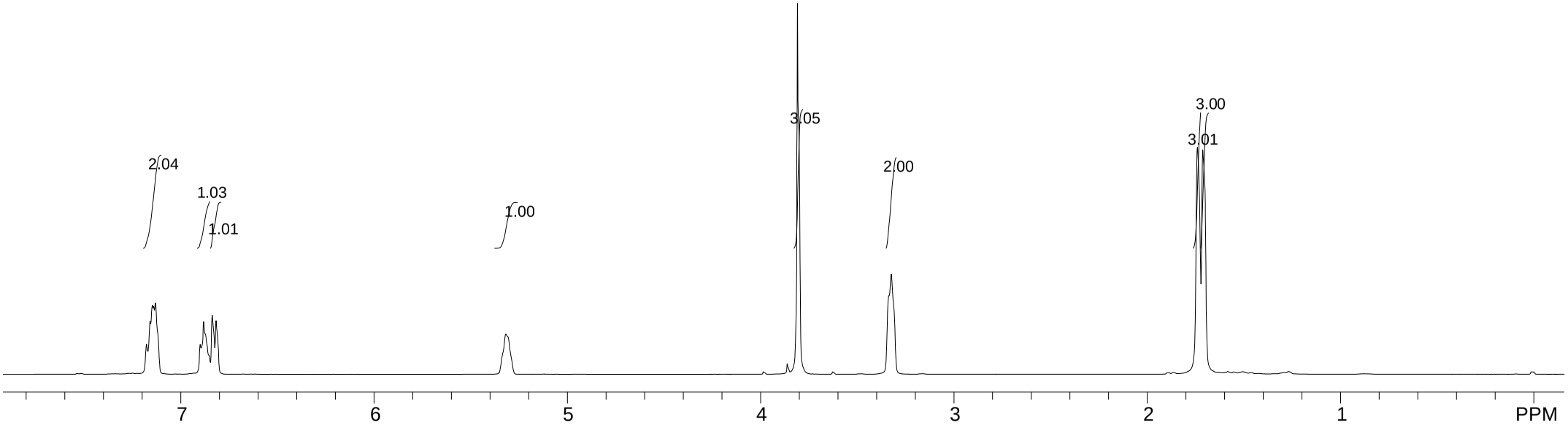
^{13}C NMR (100 MHz, $CDCl_3$)

1c

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

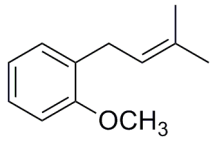


1d

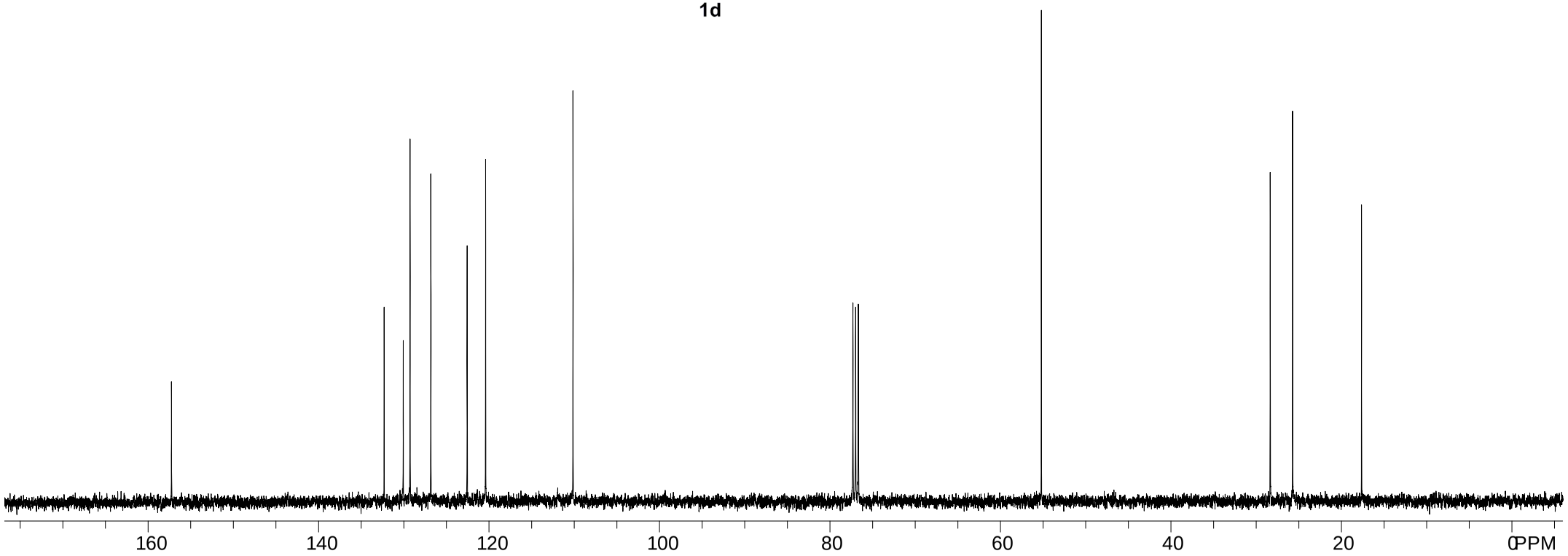


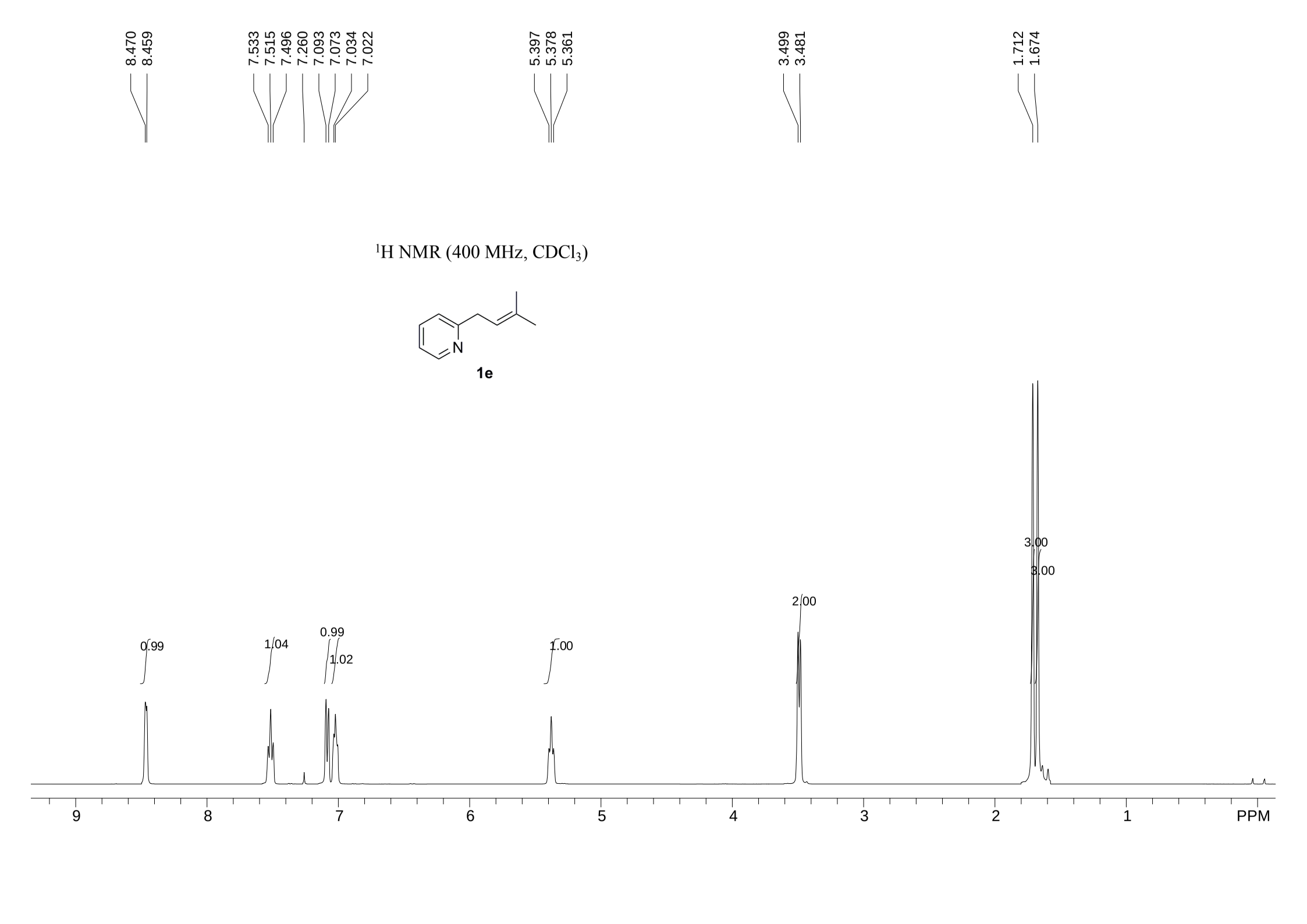
157.250
132.298
130.059
129.263
126.819
122.563
120.399
110.151
77.321
77.000
76.685
55.220
28.382
25.751
17.673

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

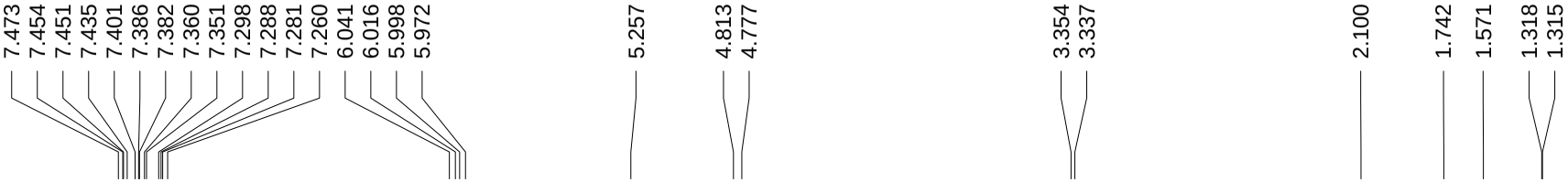


1d

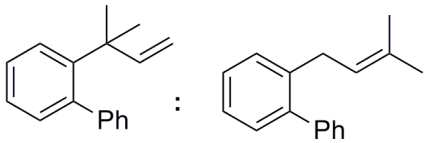



8.470
8.459
7.533
7.515
7.496
7.260
7.093
7.073
7.034
7.022
5.397
5.378
5.361
3.499
3.481
1.712
1.674
^{1}H NMR (400 MHz, $CDCl_3$)
N
1e
0.99
1.04
0.99
1.02
1.00
2.00
3.00
3.00
9
8
7
6
5
4
3
2
1
PPM

^{13}C NMR (100 MHz, CDCl$_3$)
N
1e
161.383
149.065
136.208
133.506
122.277
121.175
120.760
77.316
77.000
76.675
37.006
25.594
17.774
160
140
120
100
80
60
40
20
PPM

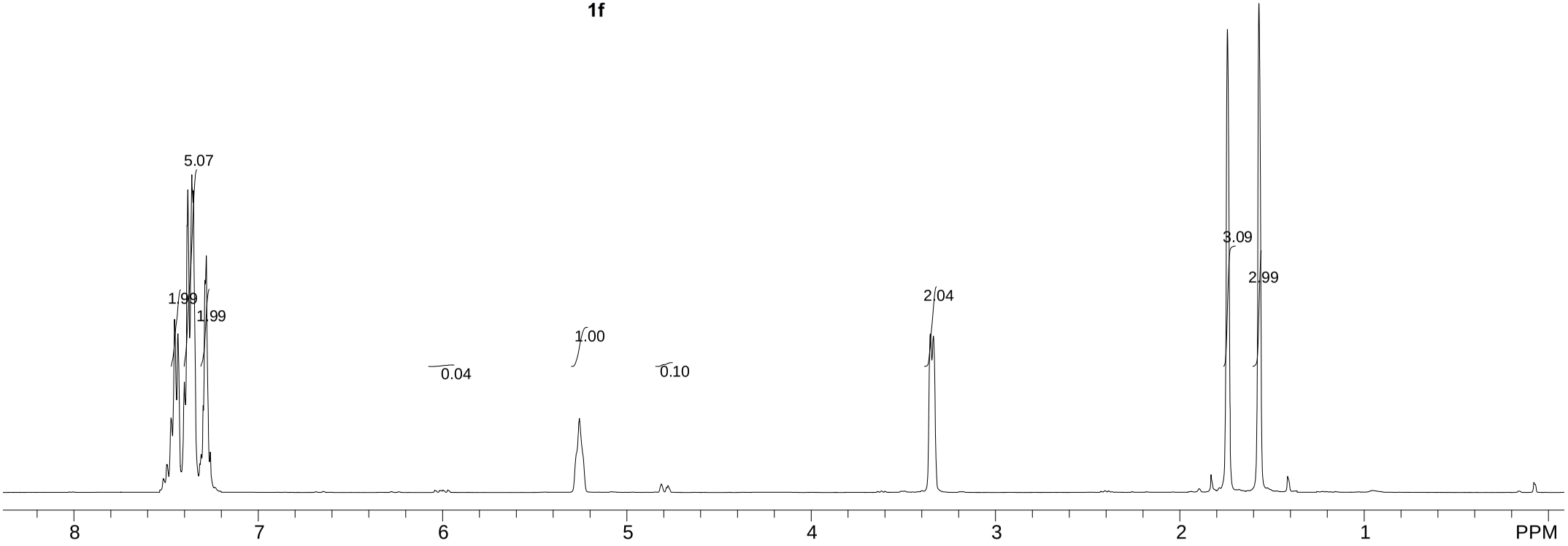


^{1}H NMR (400 MHz, $CDCl_3$)

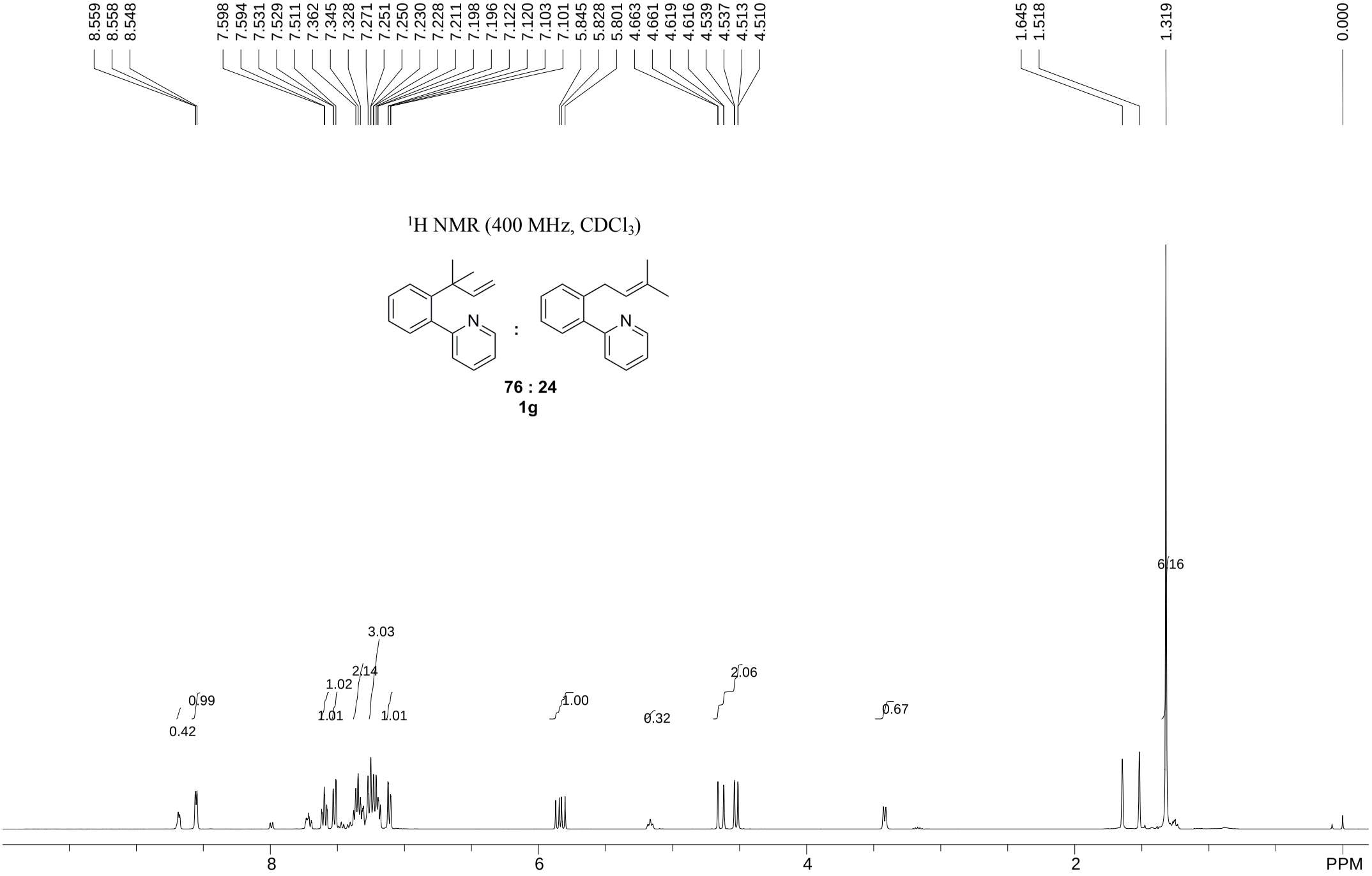


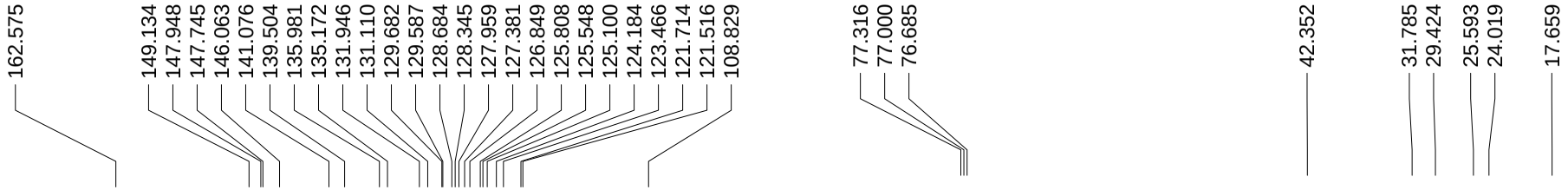
4 : 96

1f

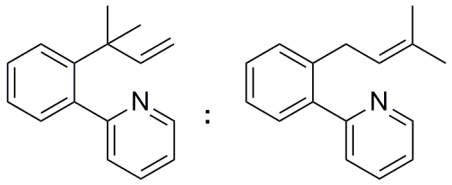


^{13}C NMR (100 MHz, $CDCl_3$)
Ph
Ph
4 : 96
1f
141.818
141.744
139.194
129.925
131.867
129.312
129.235
128.702
127.965
127.405
127.123
126.676
125.657
123.664
77.310
77.000
76.677
31.994
25.670
17.667
140
120
100
80
60
40
20
PPM


8.559
8.558
8.548
7.598
7.594
7.531
7.529
7.511
7.362
7.345
7.328
7.271
7.251
7.250
7.230
7.228
7.211
7.198
7.196
7.122
7.120
7.103
7.101
5.845
5.828
5.801
4.663
4.661
4.619
4.616
4.539
4.537
4.513
4.510
1.645
1.518
1.319
0.000
^{1}H NMR (400 MHz, $CDCl_3$)
N
:
N
76 : 24
1g
6.16
3.03
2.14
2.06
1.02
1.00
0.99
1.01
1.01
0.67
0.42
0.32
8
6
4
2
PPM

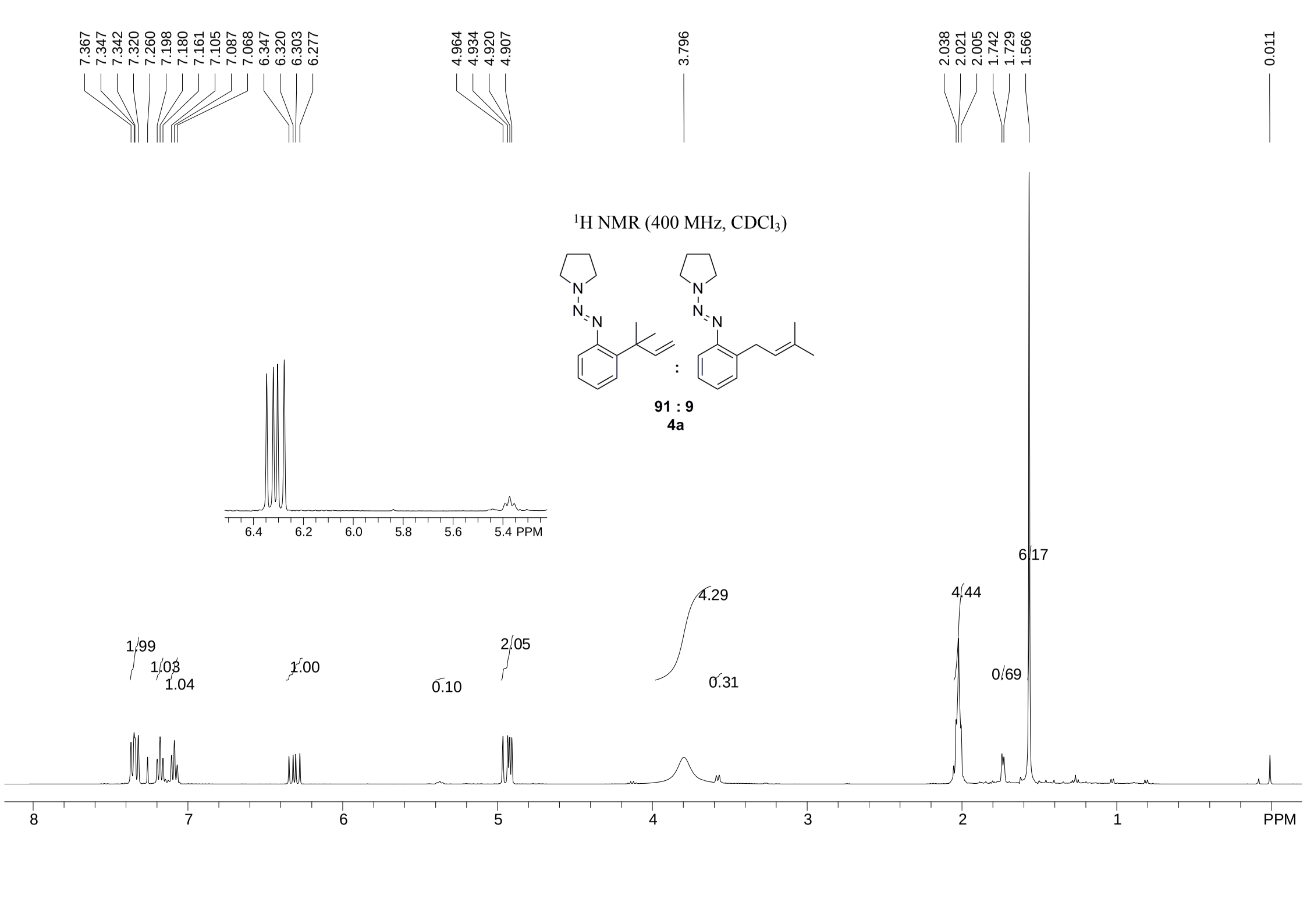


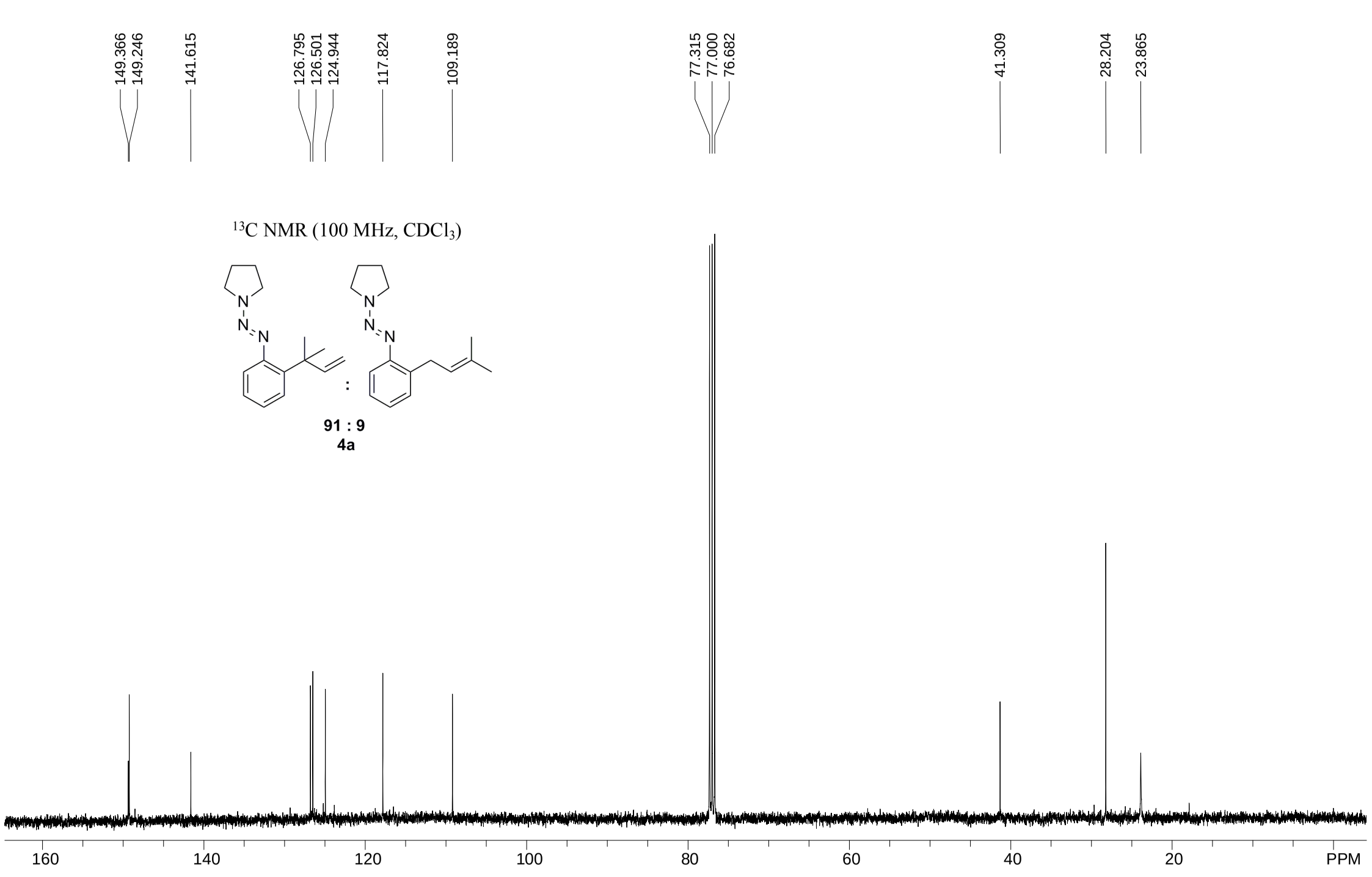
^{13}C NMR (100 MHz, $CDCl_3$)

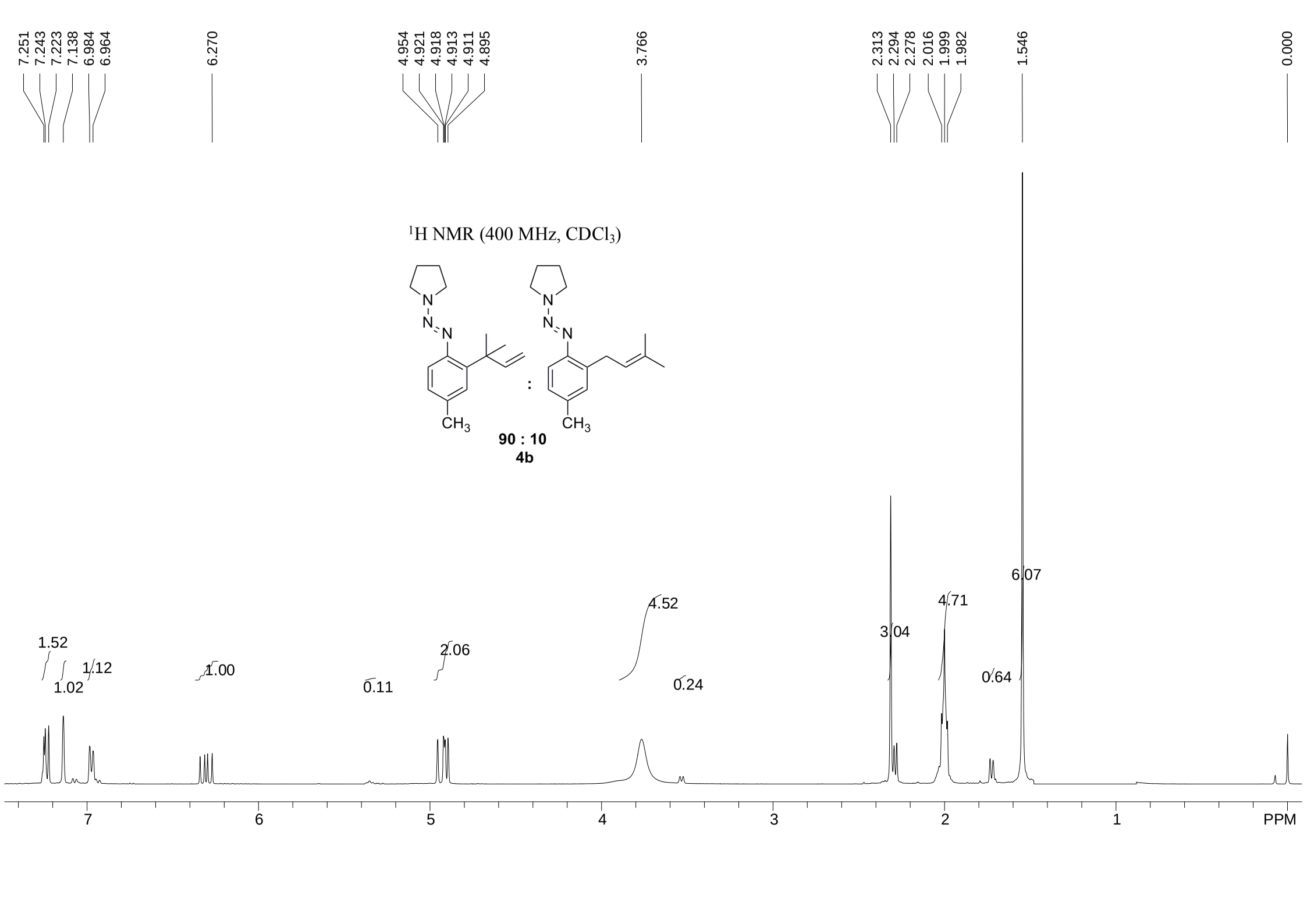


76 : 24

1g

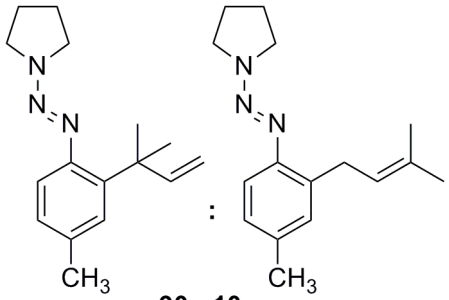

7.367
7.347
7.342
7.320
7.260
7.198
7.180
7.161
7.105
7.087
7.068
6.347
6.320
6.303
6.277
4.964
4.934
4.920
4.907
3.796
2.038
2.021
2.005
1.742
1.729
1.566
0.011
^{1}H NMR (400 MHz, $CDCl_3$)
91 : 9
4a
6.4
6.2
6.0
5.8
5.6
5.4 PPM
1.99
1.03
1.04
1.00
0.10
2.05
4.29
0.31
4.44
0.69
6.17
8
7
6
5
4
3
2
1
PPM


149.366
149.246
141.615
126.795
126.501
124.944
117.824
109.189
77.315
77.000
76.682
41.309
28.204
23.865
^{13}C NMR (100 MHz, $CDCl_3$)
91 : 9
4a
160
140
120
100
80
60
40
20
PPM

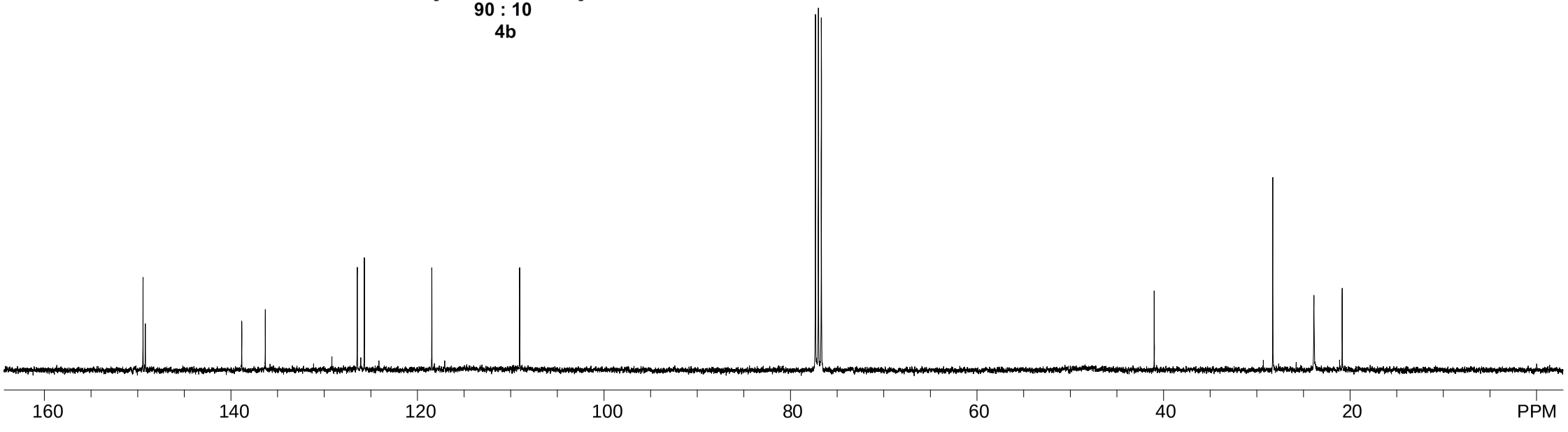

7.251
7.243
7.223
7.138
6.984
6.964
6.270
4.954
4.921
4.918
4.913
4.911
4.895
3.766
2.313
2.294
2.278
2.016
1.999
1.982
1.546
0.000
^{1}H NMR (400 MHz, $CDCl_3$)
90 : 10
4b
1.52
1.02
1.12
1.00
0.11
2.06
4.52
0.24
3.04
4.71
0.64
6.07
7
6
5
4
3
2
1
PPM

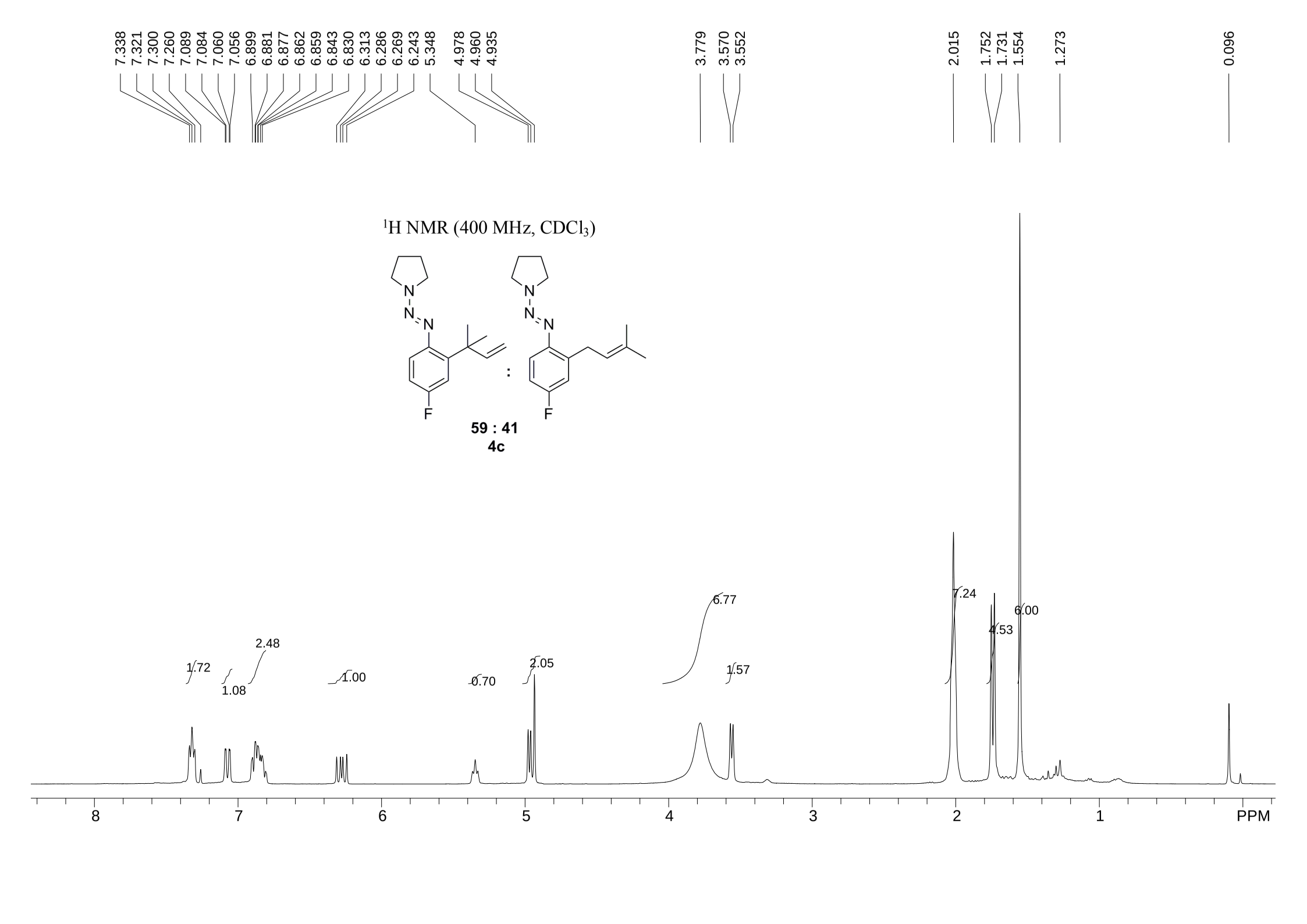
149.417
149.177
138.837
136.309
126.444
125.688
118.453
109.038
77.320
77.000
76.684
40.989
28.272
23.865
20.830

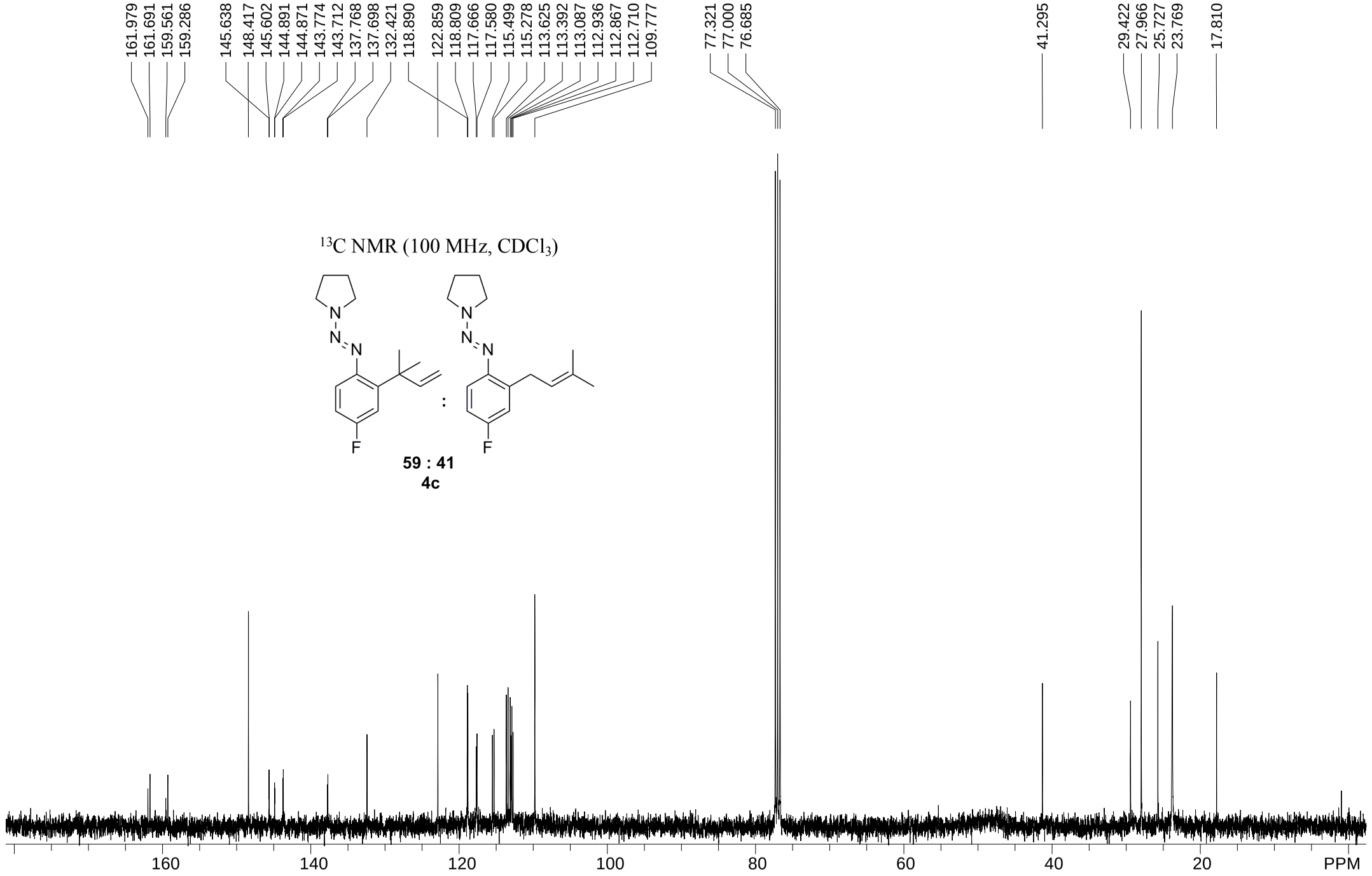
^{13}C NMR (100 MHz, $CDCl_3$)

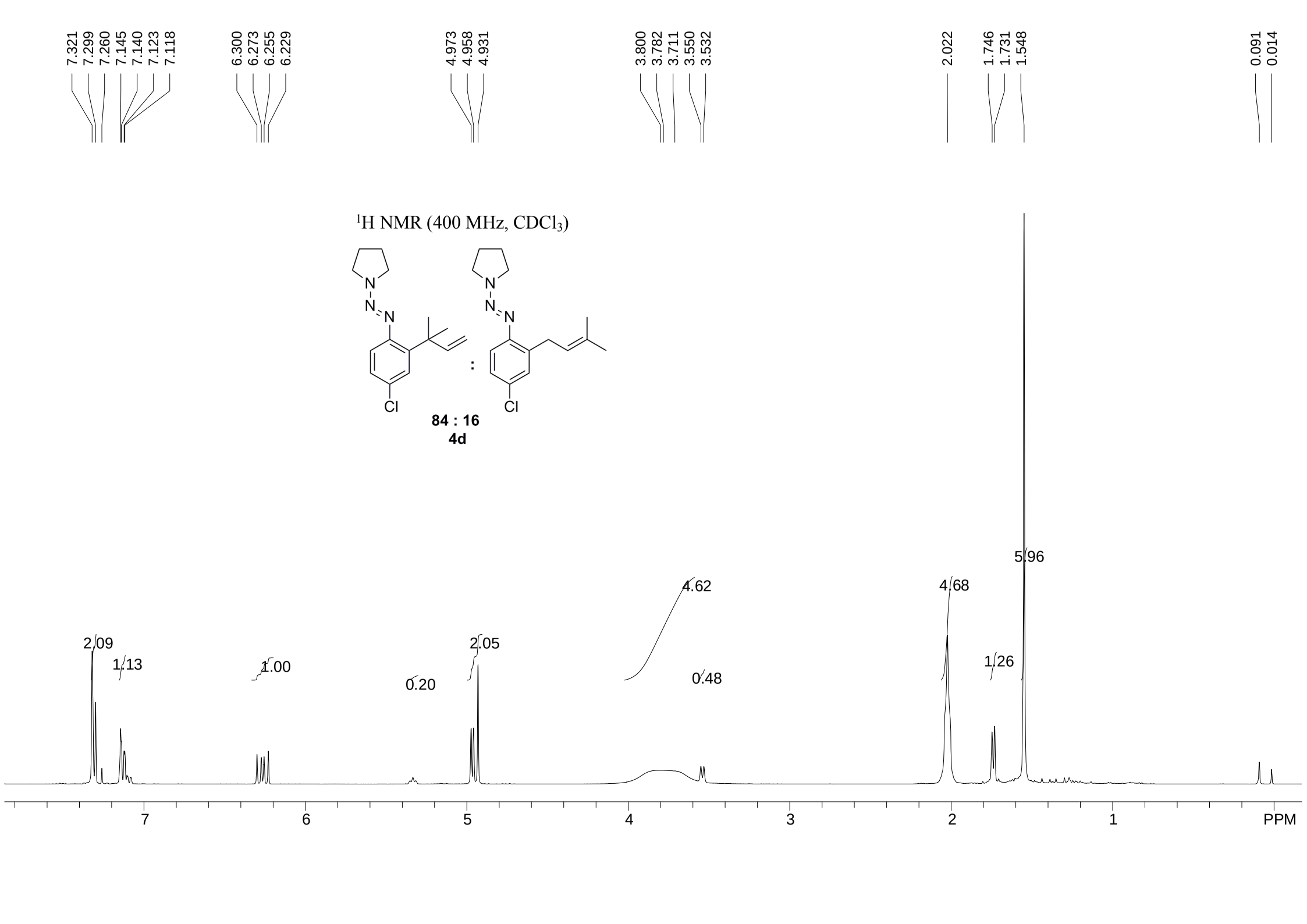


90 : 10
4b

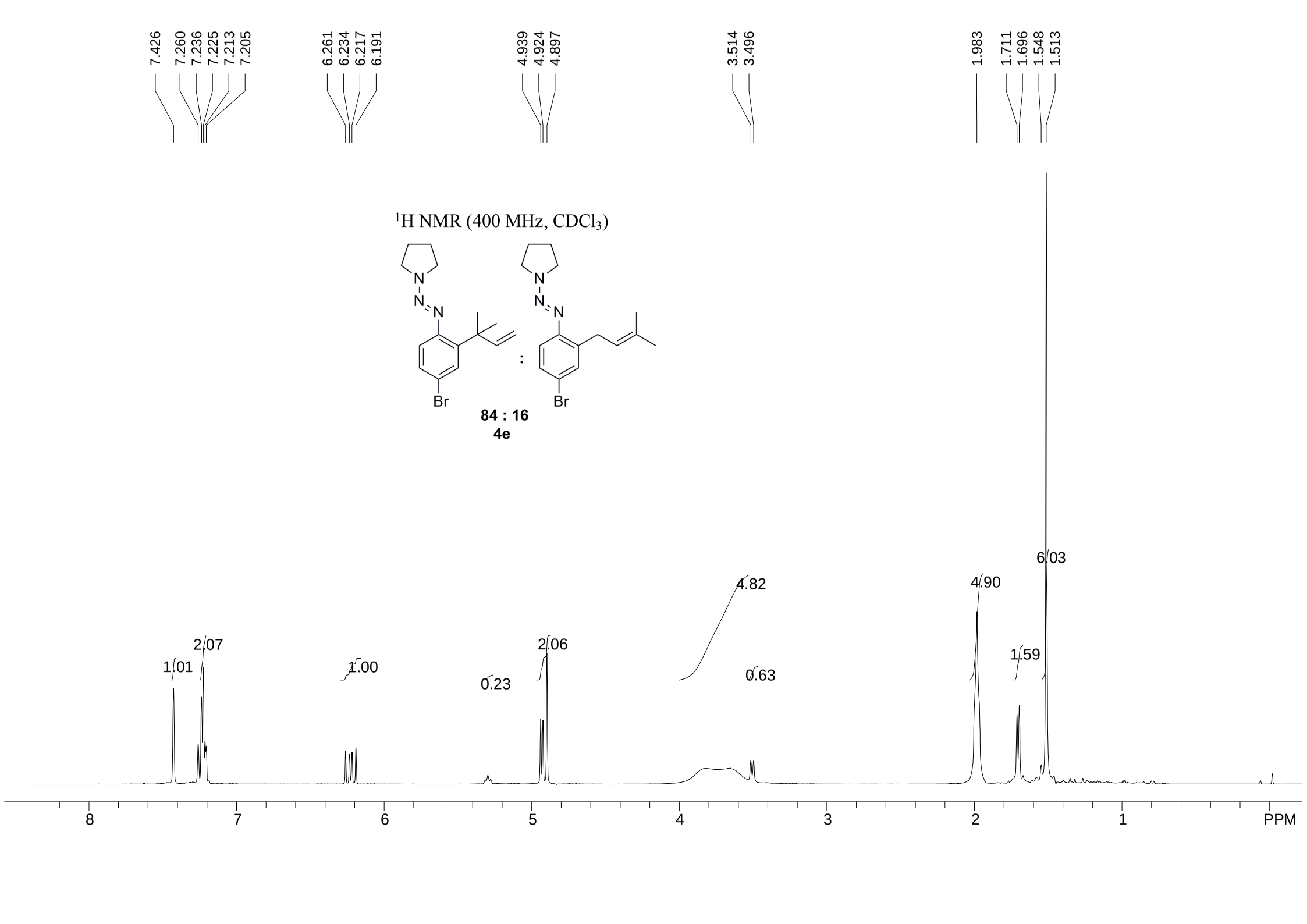



7.338
7.321
7.300
7.260
7.089
7.084
7.060
7.056
6.899
6.881
6.877
6.862
6.859
6.843
6.830
6.313
6.286
6.269
6.243
5.348
4.978
4.960
4.935
3.779
3.570
3.552
2.015
1.752
1.731
1.554
1.273
0.096
^{1}H NMR (400 MHz, $CDCl_3$)
59 : 41
4c
1.72
1.08
2.48
1.00
0.70
2.05
6.77
1.57
7.24
4.53
6.00
8
7
6
5
4
3
2
1
PPM


161.979
161.691
159.561
159.286
145.638
148.417
145.602
144.891
144.871
143.774
143.712
137.768
137.698
132.421
118.890
122.859
118.809
117.666
117.580
115.499
115.278
113.625
113.392
113.087
112.936
112.867
112.710
109.777
77.321
77.000
76.685
41.295
29.422
27.966
25.727
23.769
17.810
^{13}C NMR (100 MHz, $CDCl_3$)
59 : 41
4c
160
140
120
100
80
60
40
20
PPM

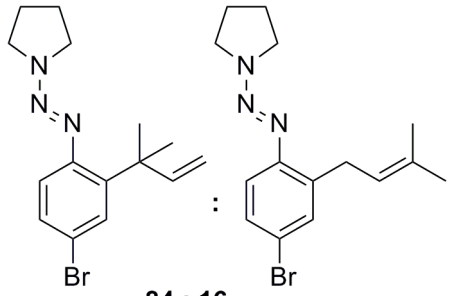

7.321
7.299
7.260
7.145
7.140
7.123
7.118
6.300
6.273
6.255
6.229
4.973
4.958
4.931
3.800
3.782
3.711
3.550
3.532
2.022
1.746
1.731
1.548
0.091
0.014
^{1}H NMR (400 MHz, $CDCl_3$)
Cl
:
Cl
84 : 16
4d
2.09
1.13
1.00
0.20
2.05
4.62
0.48
4.68
1.26
5.96
7
6
5
4
3
2
1
PPM

160
140
120
100
80
60
40
20
0
PPM
148.391
147.825
143.316
130.035
126.766
126.591
118.887
109.817
77.308
77.000
76.675
41.353
29.365
27.990
23.800
^{13}C NMR (100 MHz, CDCl$_3$)
Cl
N
N
N
:
84 : 16
4d


7.426
7.260
7.236
7.225
7.213
7.205
6.261
6.234
6.217
6.191
4.939
4.924
4.897
3.514
3.496
1.983
1.711
1.696
1.548
1.513
1H NMR (400 MHz, CDCl3)
N
N
N
Br
:
84 : 16
4e
1.01
2.07
1.00
0.23
2.06
4.82
0.63
4.90
1.59
6.03
8
7
6
5
4
3
2
1
PPM

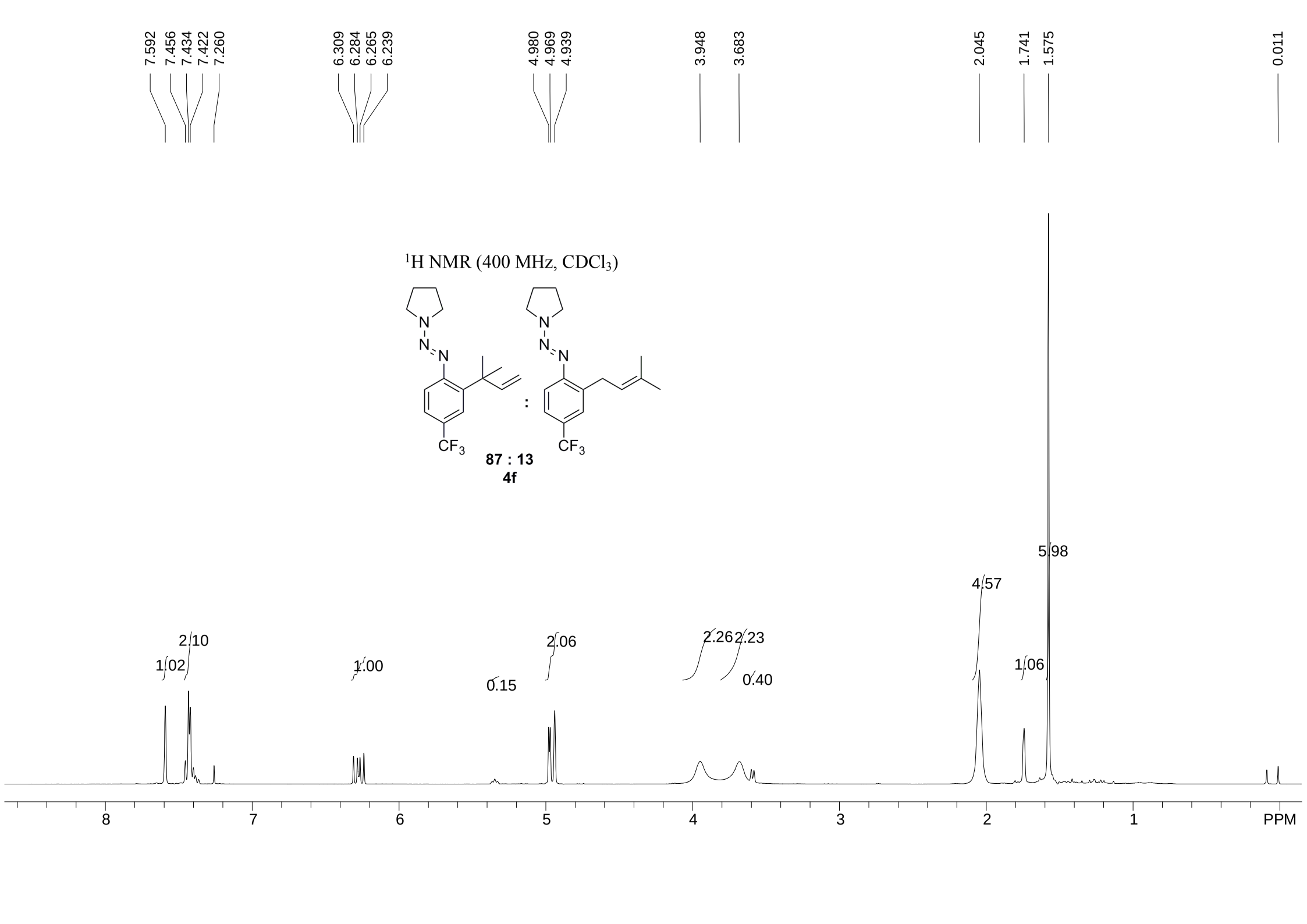
148.364
148.260
147.503
143.698
137.887
132.293
131.885
129.629
129.577
129.169
122.856
119.290
118.239
118.003
109.831
77.326
77.000
76.692
50.623
47.000
41.346
29.337
27.991
25.780
23.757
17.866

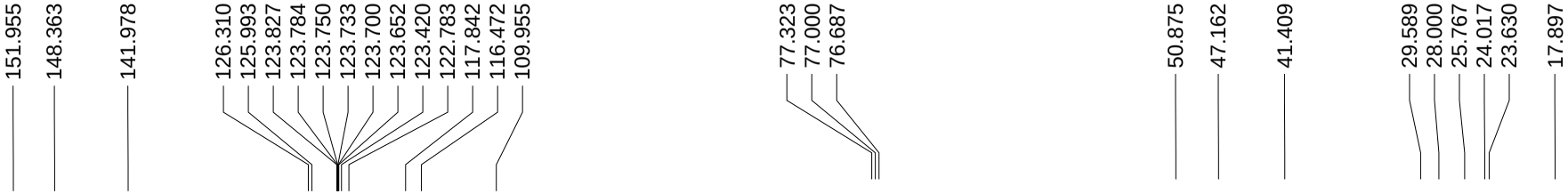
^{13}C NMR (100 MHz, $CDCl_3$)



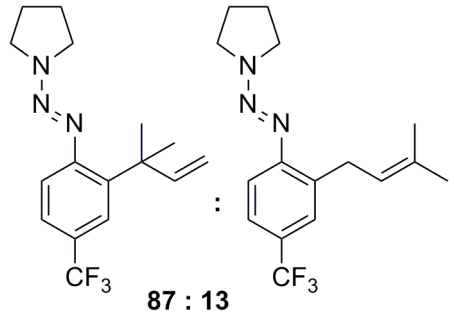
84 : 16

4e

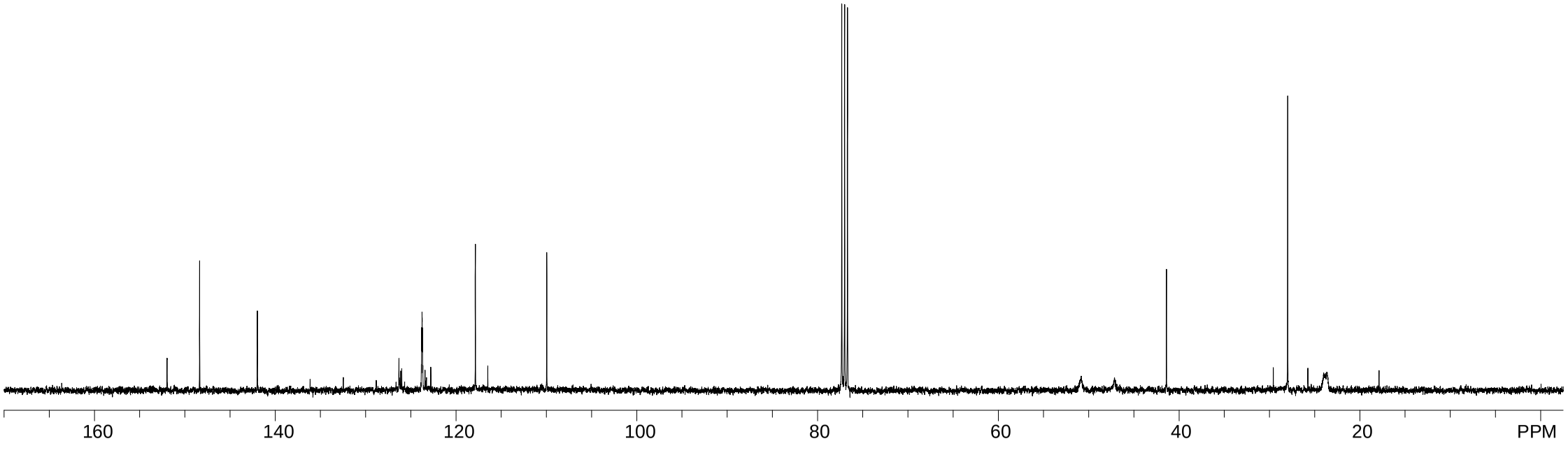

7.592
7.456
7.434
7.422
7.260
6.309
6.284
6.265
6.239
4.980
4.969
4.939
3.948
3.683
2.045
1.741
1.575
0.011
1H NMR (400 MHz, CDCl3)
N
N
N
CF3
:
87 : 13
4f
1.02
2.10
1.00
0.15
2.06
2.26
2.23
0.40
4.57
1.06
5.98
8
7
6
5
4
3
2
1
PPM

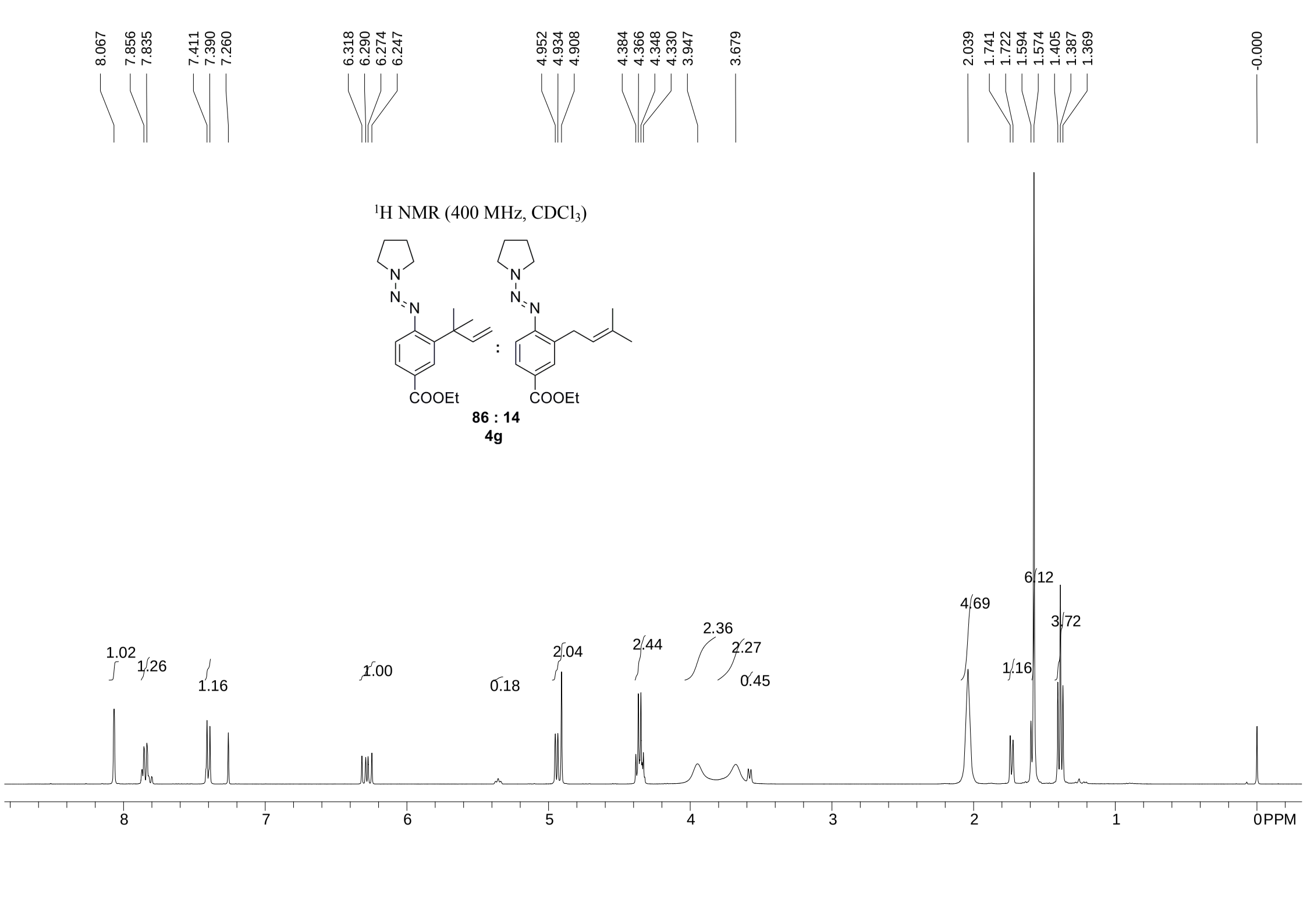


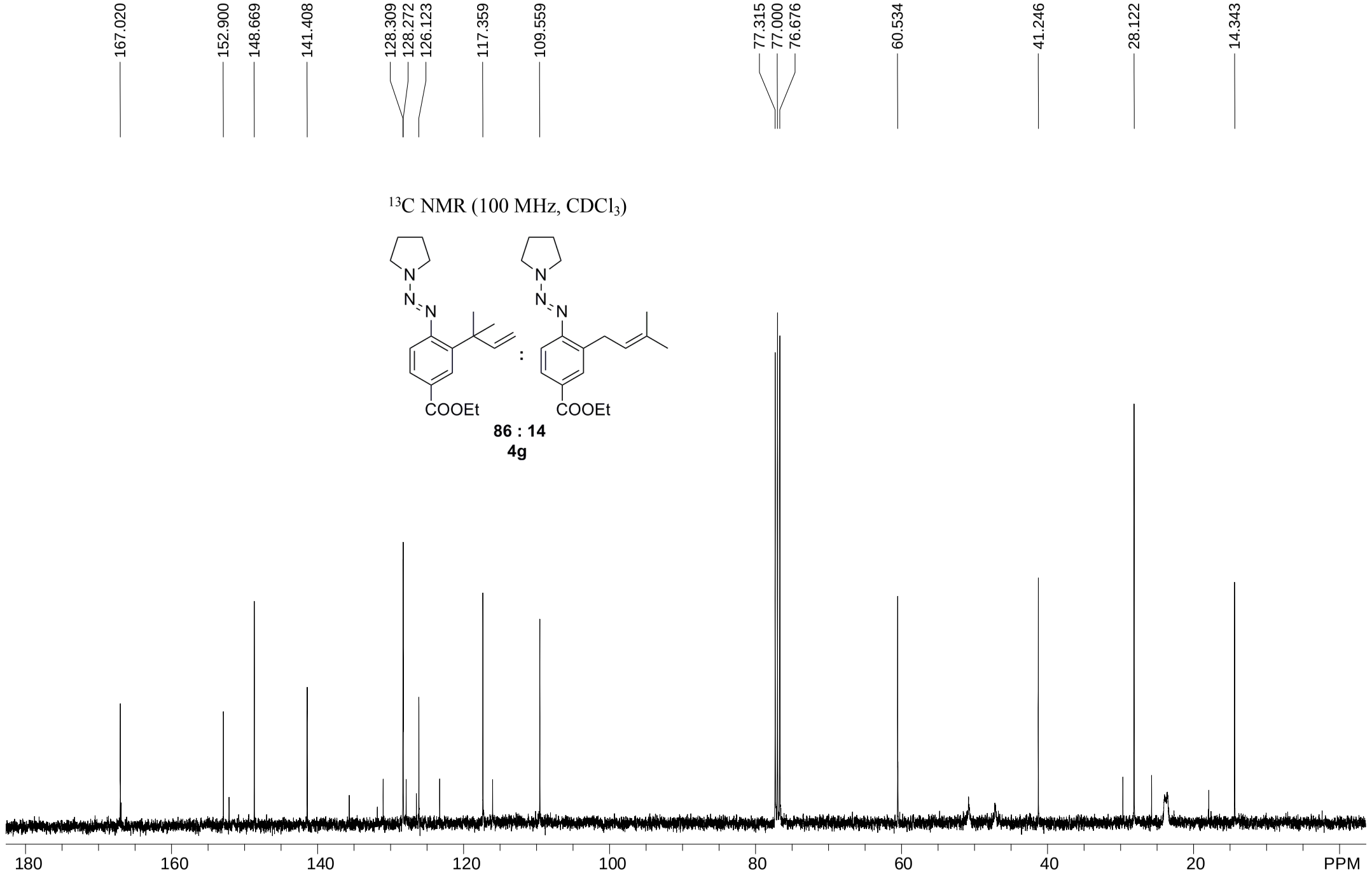
^{13}C NMR (100 MHz, $CDCl_3$)

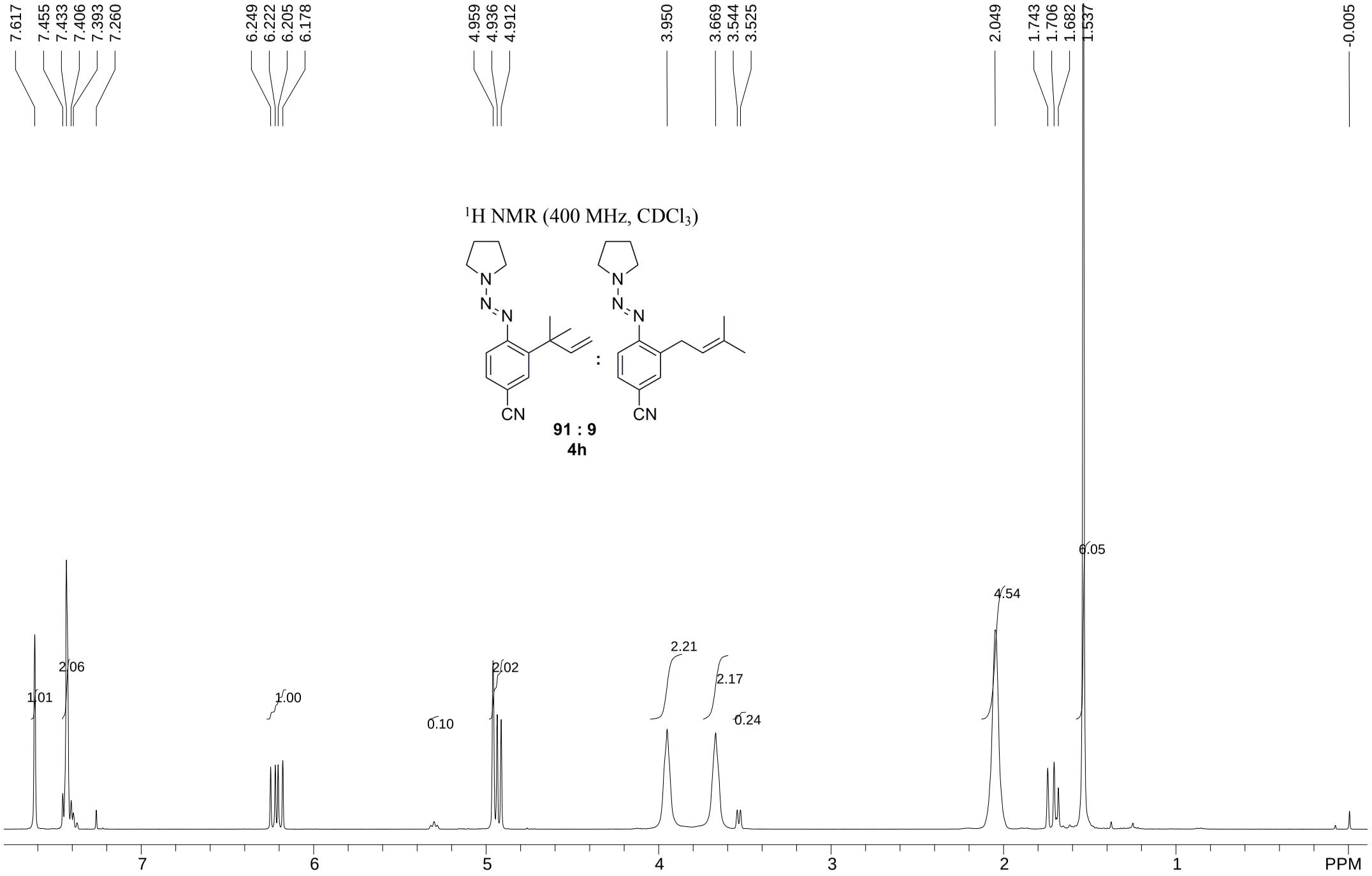


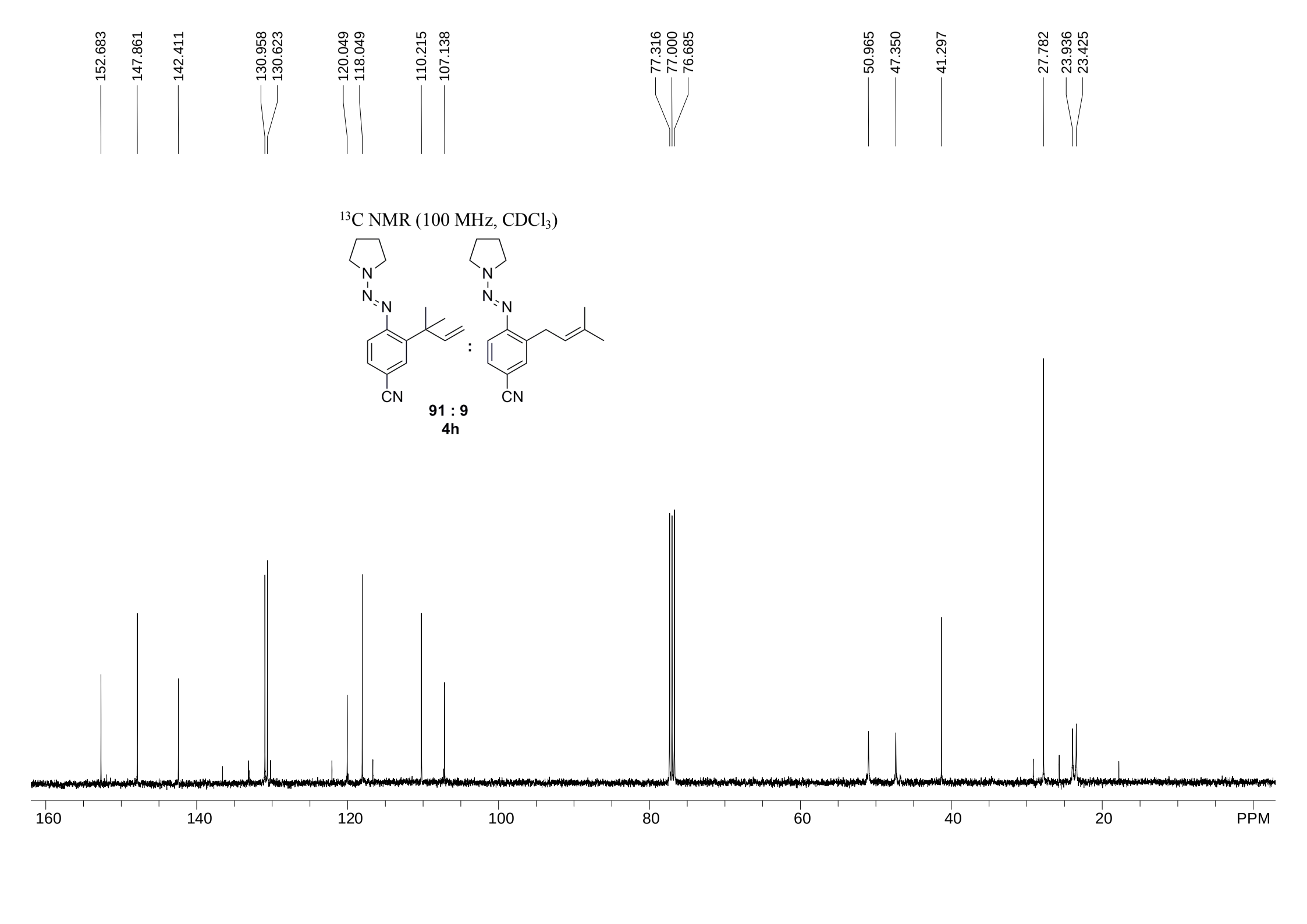
87 : 13
4f

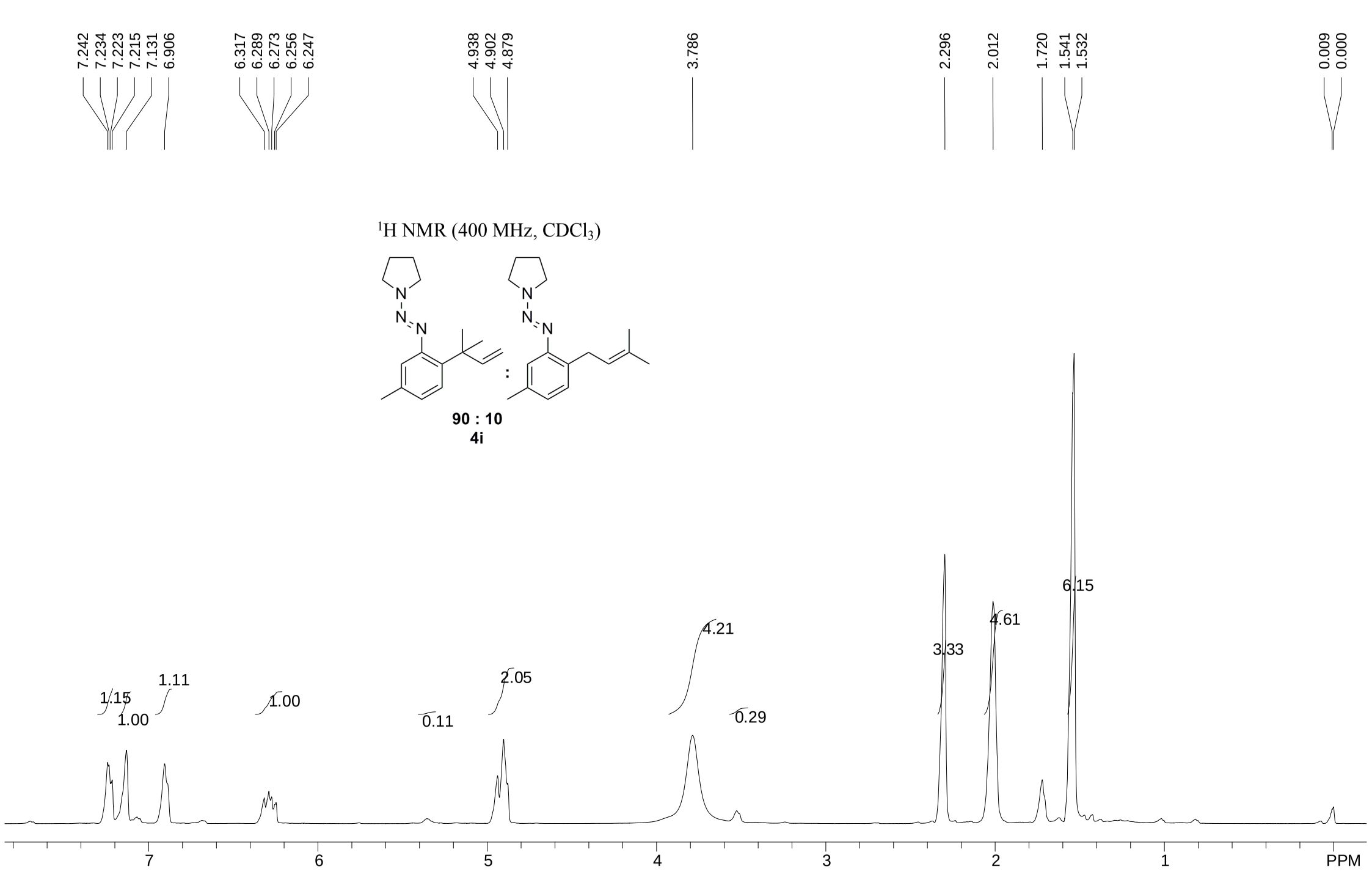



8.067
7.856
7.835
7.411
7.390
7.260
6.318
6.290
6.274
6.247
4.952
4.934
4.908
4.384
4.366
4.348
4.330
3.947
3.679
2.039
1.741
1.722
1.594
1.574
1.405
1.387
1.369
-0.000
^{1}H NMR (400 MHz, $CDCl_3$)
COOEt
COOEt
86 : 14
4g
1.02
1.26
1.16
1.00
0.18
2.04
2.44
2.36
2.27
0.45
4.69
1.16
6.12
3.72
8
7
6
5
4
3
2
1
0PPM


167.020
152.900
148.669
141.408
128.309
128.272
126.123
117.359
109.559
77.315
77.000
76.676
60.534
41.246
28.122
14.343
^{13}C NMR (100 MHz, $CDCl_3$)
COOEt
COOEt
86 : 14
4g
180
160
140
120
100
80
60
40
20
PPM

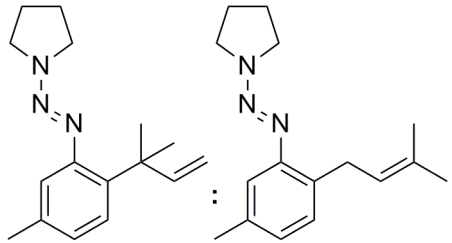

7.617
7.455
7.433
7.406
7.393
7.260
6.249
6.222
6.205
6.178
4.959
4.936
4.912
3.950
3.669
3.544
3.525
2.049
1.743
1.706
1.682
1.537
-0.005
1H NMR (400 MHz, CDCl3)
N
N
N
CN
:
91 : 9
4h
1.01
2.06
1.00
0.10
2.02
2.21
2.17
0.24
4.54
6.05
7
6
5
4
3
2
1
PPM


152.683
147.861
142.411
130.958
130.623
120.049
118.049
110.215
107.138
77.316
77.000
76.685
50.965
47.350
41.297
27.782
23.936
23.425
^{13}C NMR (100 MHz, $CDCl_3$)
N
N
N
CN
:
91 : 9
4h
160
140
120
100
80
60
40
20
PPM

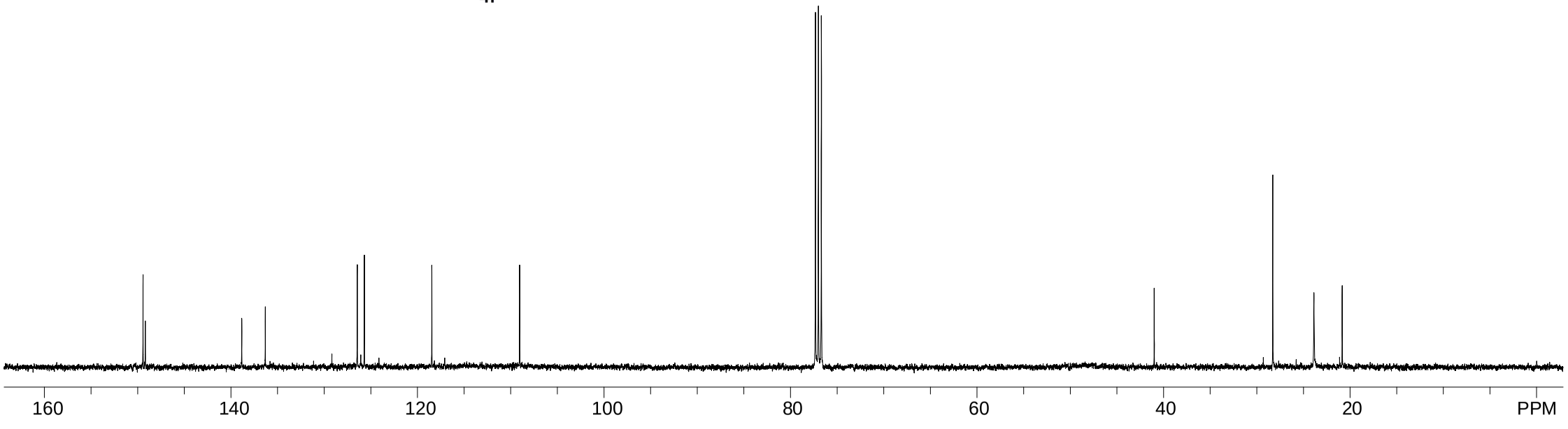

7.242
7.234
7.223
7.215
7.131
6.906
6.317
6.289
6.273
6.256
6.247
4.938
4.902
4.879
3.786
2.296
2.012
1.720
1.541
1.532
0.009
0.000
^{1}H NMR (400 MHz, $CDCl_3$)
90 : 10
4i
1.15
1.00
1.11
1.00
0.11
2.05
4.21
0.29
3.33
4.61
6.15
7
6
5
4
3
2
1
PPM

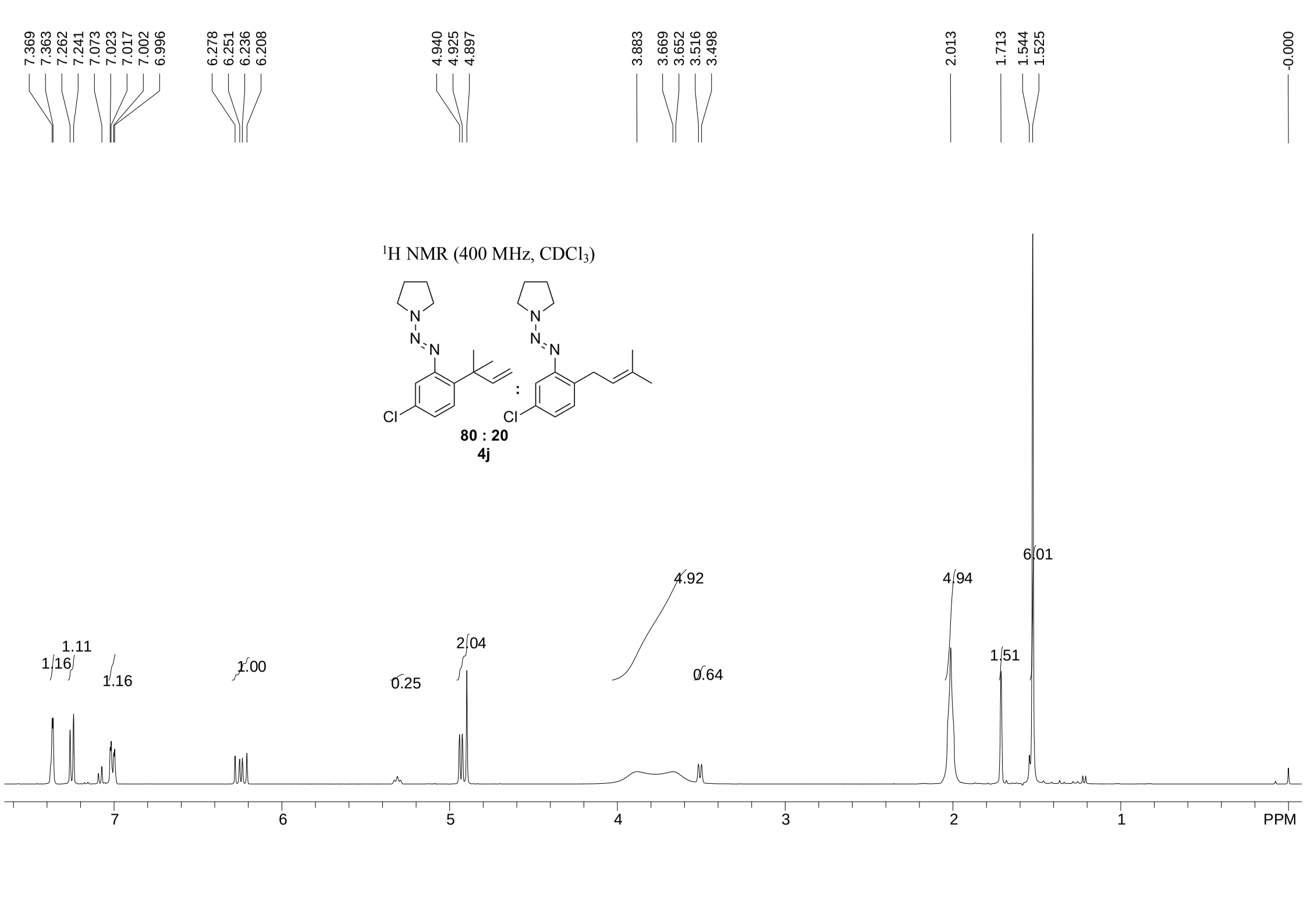
149.417
149.177
138.837
136.309
126.444
125.688
118.453
109.038
77.320
77.000
76.684
40.989
28.272
23.865
20.830

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

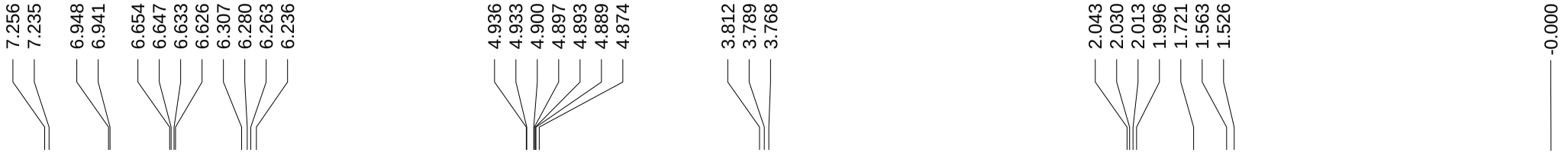


90 : 10
4i

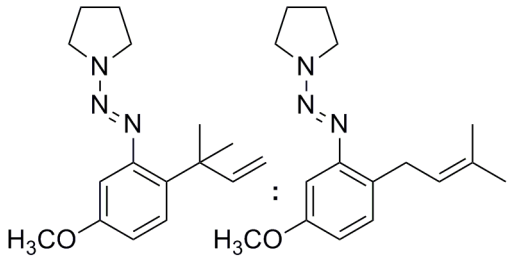



7.369
7.363
7.262
7.241
7.073
7.023
7.017
7.002
6.996
6.278
6.251
6.236
6.208
4.940
4.925
4.897
3.883
3.669
3.652
3.516
3.498
2.013
1.713
1.544
1.525
-0.000
^{1}H NMR (400 MHz, $CDCl_3$)
80 : 20
4j
1.16
1.11
1.16
1.00
0.25
2.04
4.92
0.64
4.94
1.51
6.01
7
6
5
4
3
2
1
PPM

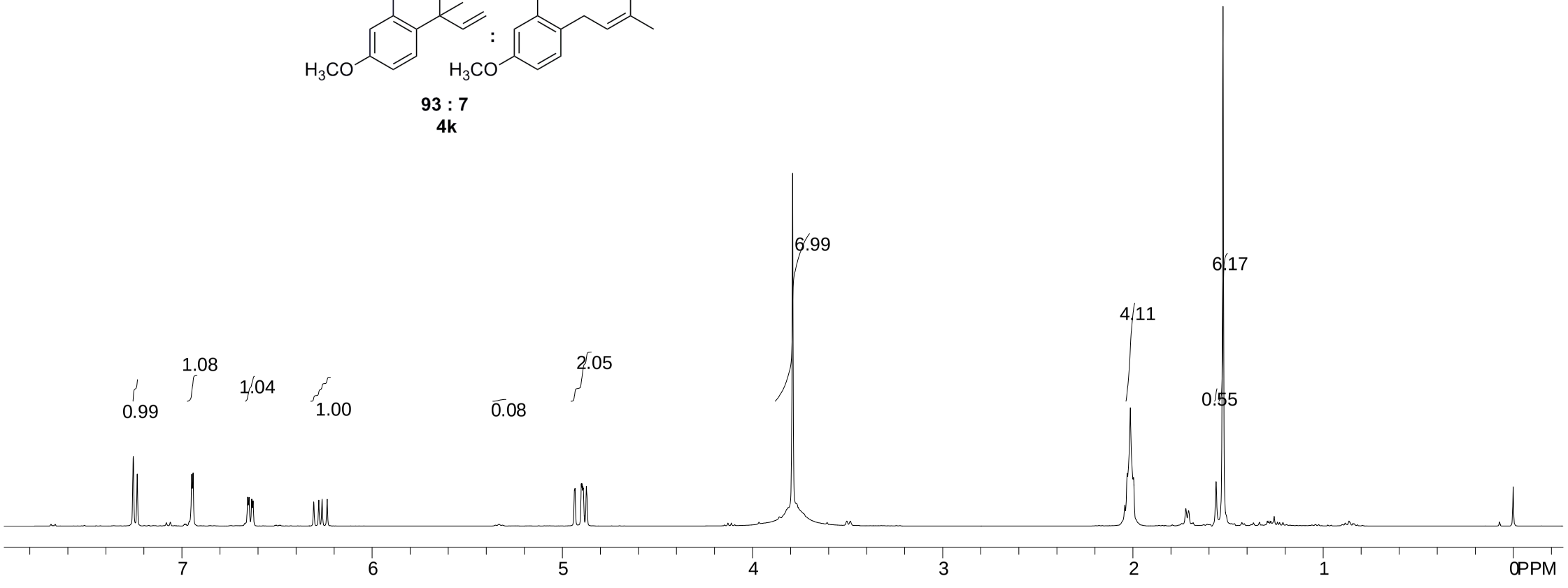
^{13}C NMR (100 MHz, CDCl$_3$)
80 : 20
4j
150.243
149.392
148.751
140.149
134.246
132.392
131.891
131.859
130.362
127.827
124.722
124.307
123.294
117.612
116.445
109.527
77.317
77.000
76.682
41.070
29.136
28.114
25.746
23.790
17.850
140
120
100
80
60
40
20
PPM



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

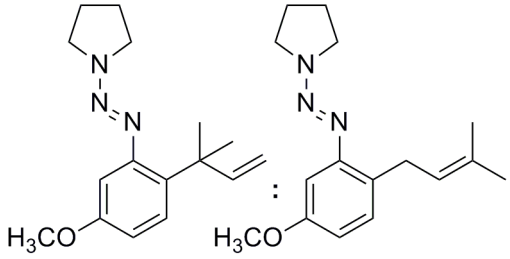


93 : 7
4k



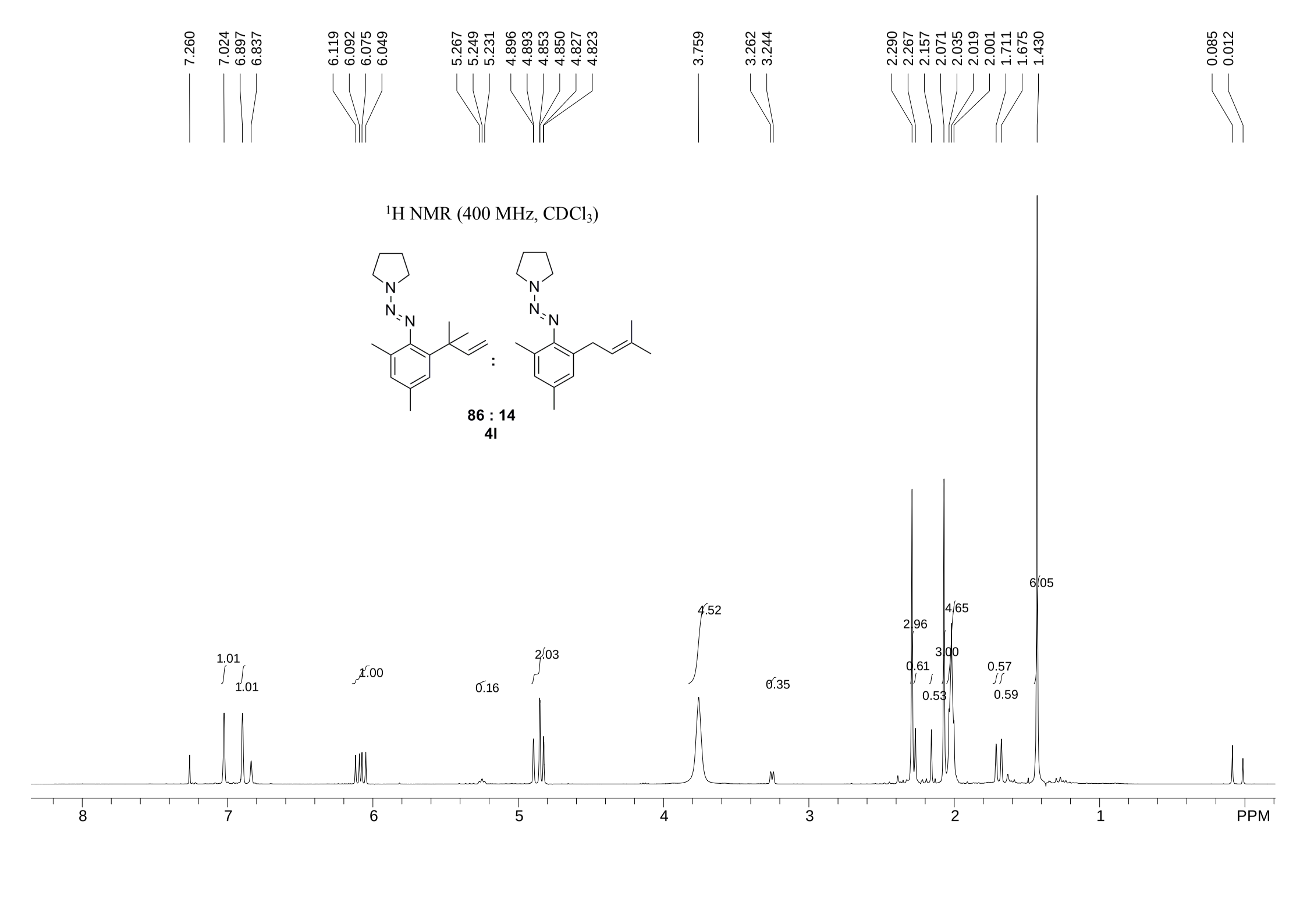
158.439
150.206
149.553
134.434
127.400
110.636
108.913
102.690
77.320
77.000
76.684
55.240
40.766
28.404
23.864
23.812

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



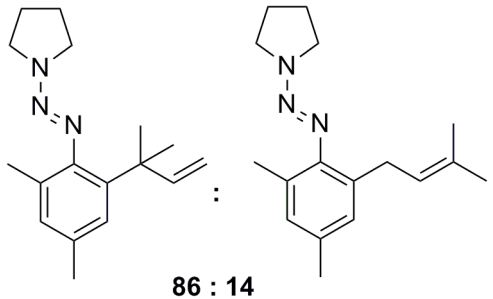
93 : 7
4k

160
140
120
100
80
60
40
20
PPM

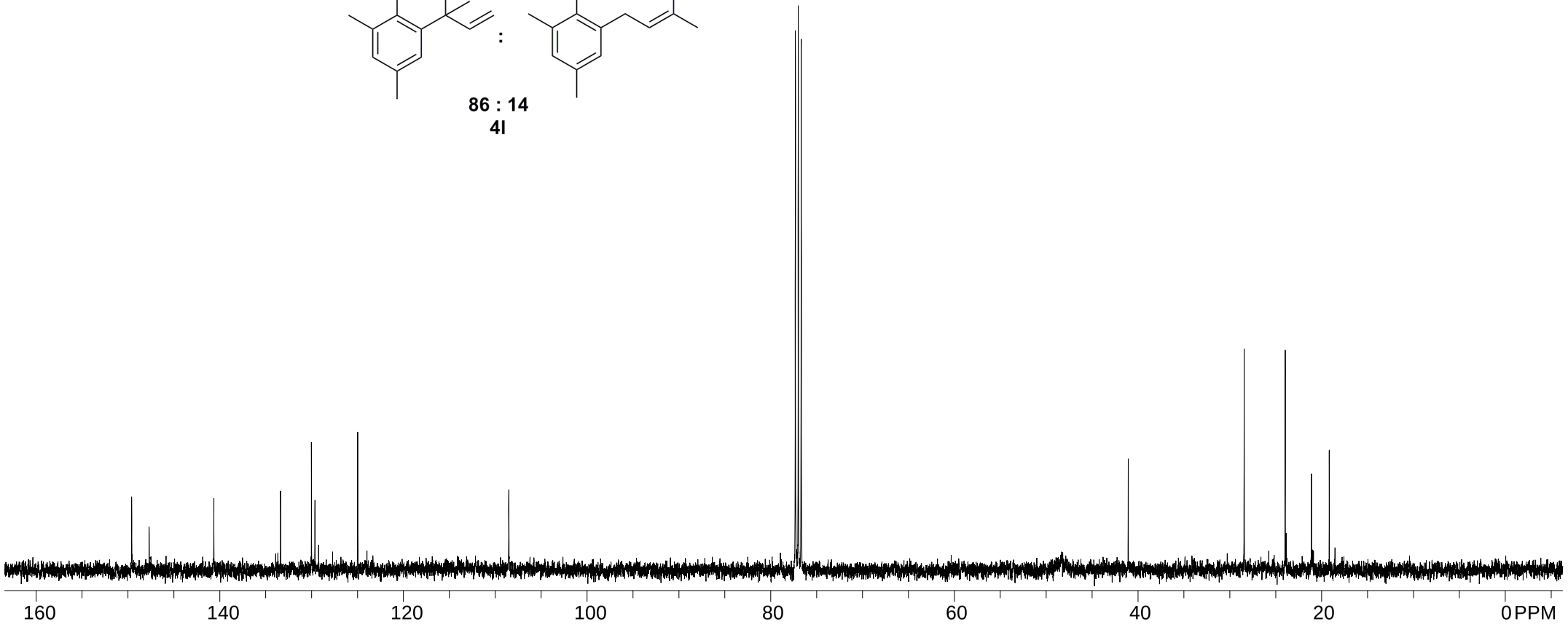

7.260
7.024
6.897
6.837
6.119
6.092
6.075
6.049
5.267
5.249
5.231
4.896
4.893
4.853
4.850
4.827
4.823
3.759
3.262
3.244
2.290
2.267
2.157
2.071
2.035
2.019
2.001
1.711
1.675
1.430
0.085
0.012
1H NMR (400 MHz, CDCl3)
86 : 14
4l
1.01
1.01
1.00
0.16
2.03
4.52
0.35
2.96
0.61
0.53
3.00
4.65
0.57
0.59
6.05
8
7
6
5
4
3
2
1
PPM

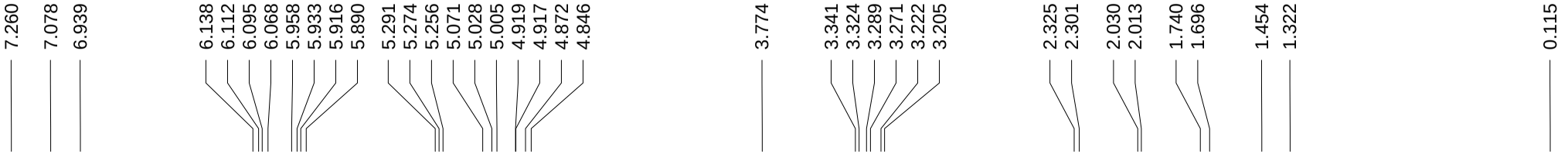
149.596
147.693
140.646
133.373
130.019
129.632
124.984
108.511
77.316
77.000
76.674
41.072
28.443
23.966
21.114
19.167

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

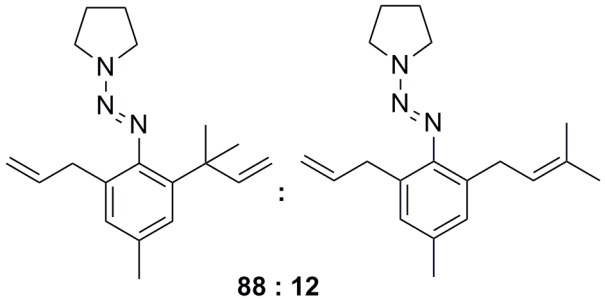


86 : 14
4l





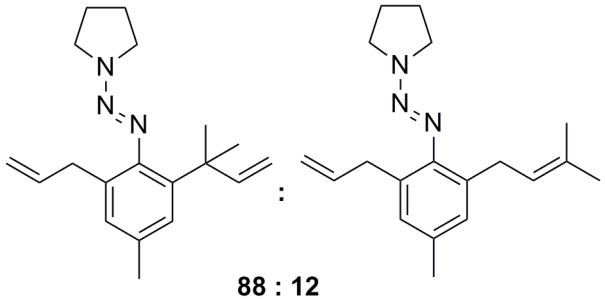
^{1}H NMR (400 MHz, $CDCl_3$)



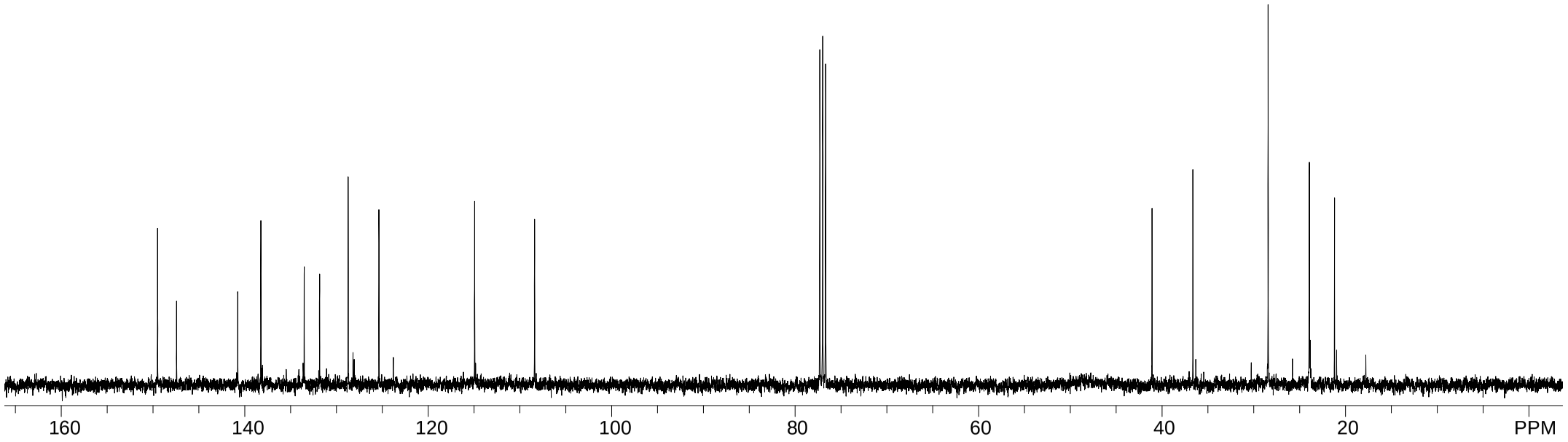
88 : 12
4m

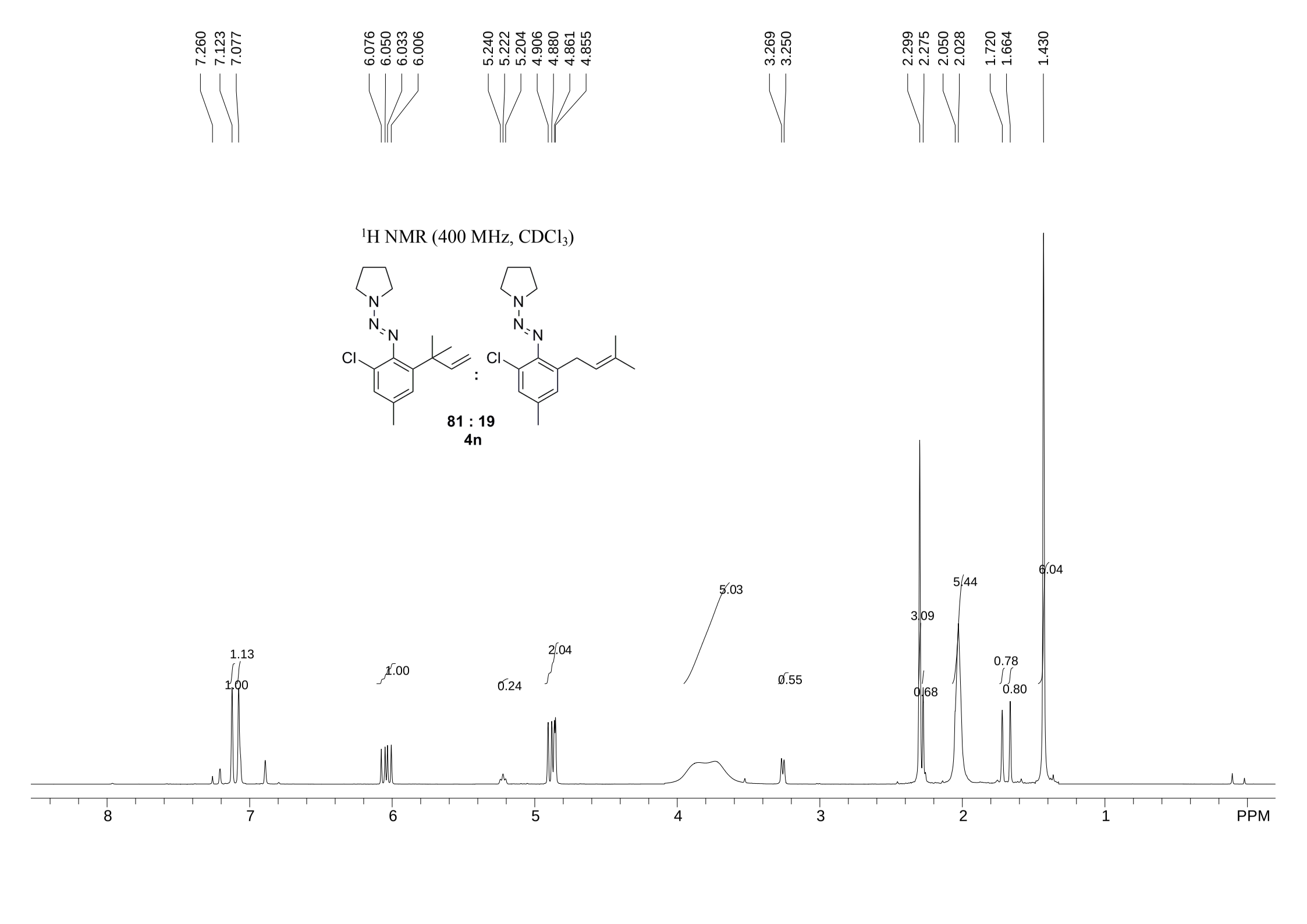
149.495
147.428
140.759
138.229
133.511
131.827
128.725
125.373
114.939
108.400
77.318
77.000
76.682
41.084
36.630
28.427
23.924
21.187

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

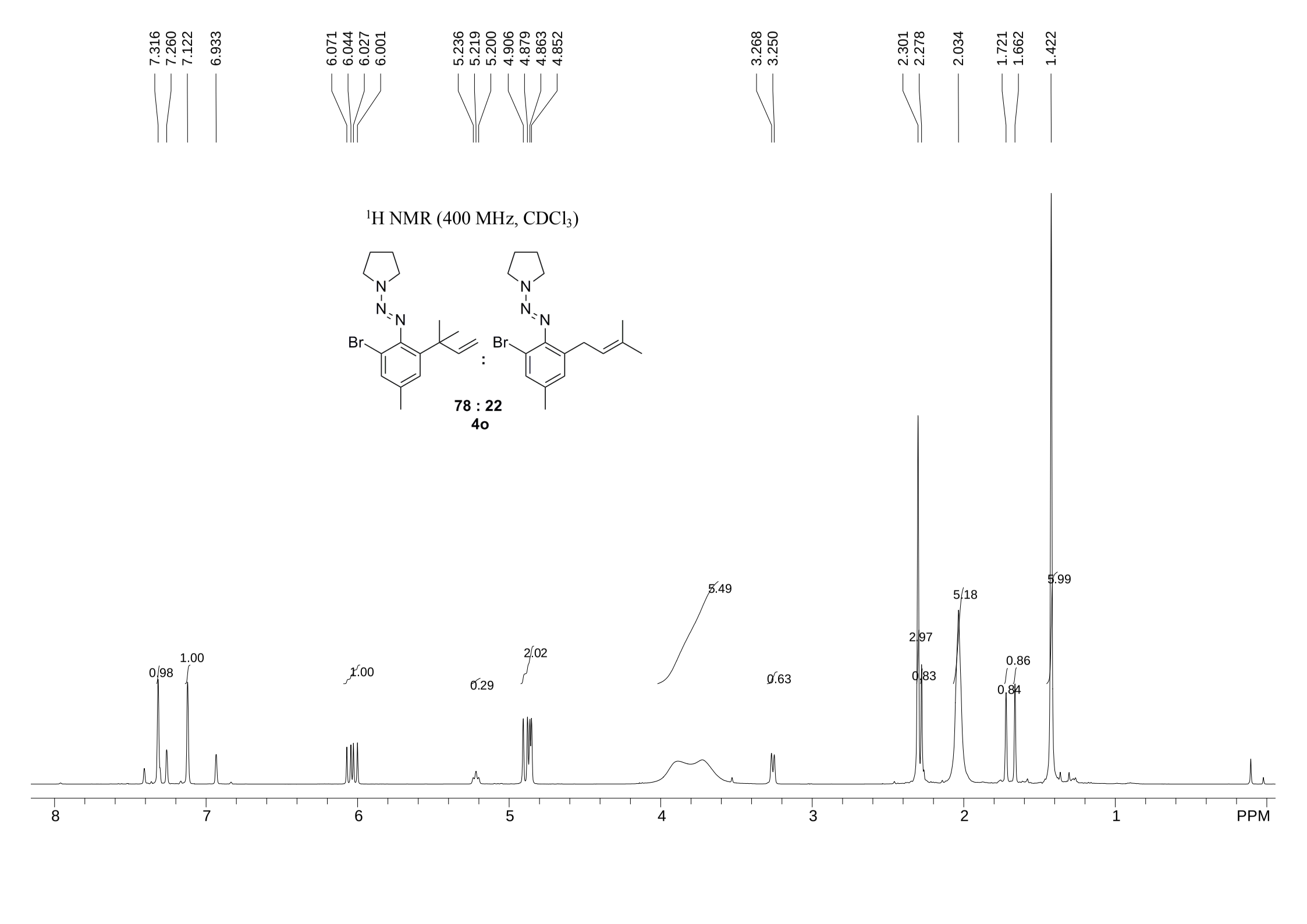


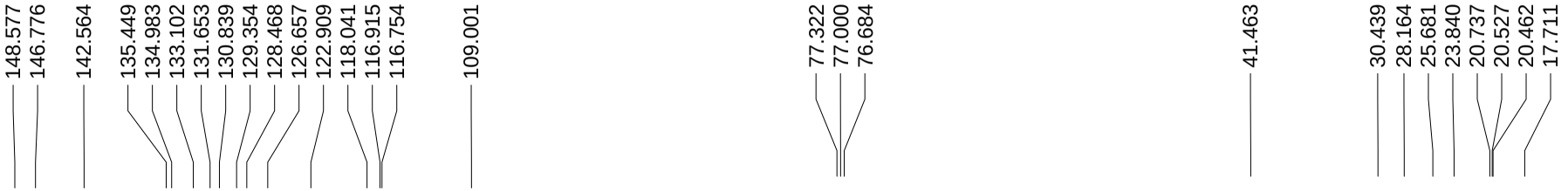
88 : 12
4m



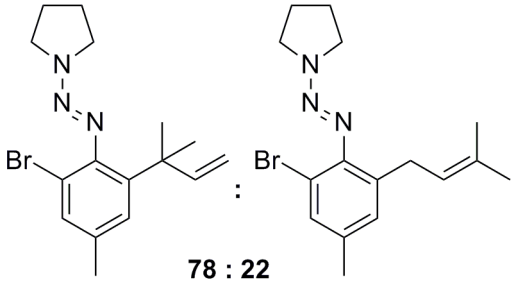

7.260
7.123
7.077
6.076
6.050
6.033
6.006
5.240
5.222
5.204
4.906
4.880
4.861
4.855
3.269
3.250
2.299
2.275
2.050
2.028
1.720
1.664
1.430
1H NMR (400 MHz, CDCl3)
Cl
N
N
N
:
81 : 19
4n
1.13
1.00
1.00
0.24
2.04
5.03
0.55
3.09
0.68
5.44
0.78
0.80
6.04
8
7
6
5
4
3
2
1
PPM

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


7.316
7.260
7.122
6.933
6.071
6.044
6.027
6.001
5.236
5.219
5.200
4.906
4.879
4.863
4.852
3.268
3.250
2.301
2.278
2.034
1.721
1.662
1.422
^{1}H NMR (400 MHz, $CDCl_3$)
Br
Br
78 : 22
4o
0.98
1.00
1.00
0.29
2.02
5.49
0.63
2.97
0.83
5.18
0.84
0.86
5.99
8
7
6
5
4
3
2
1
PPM

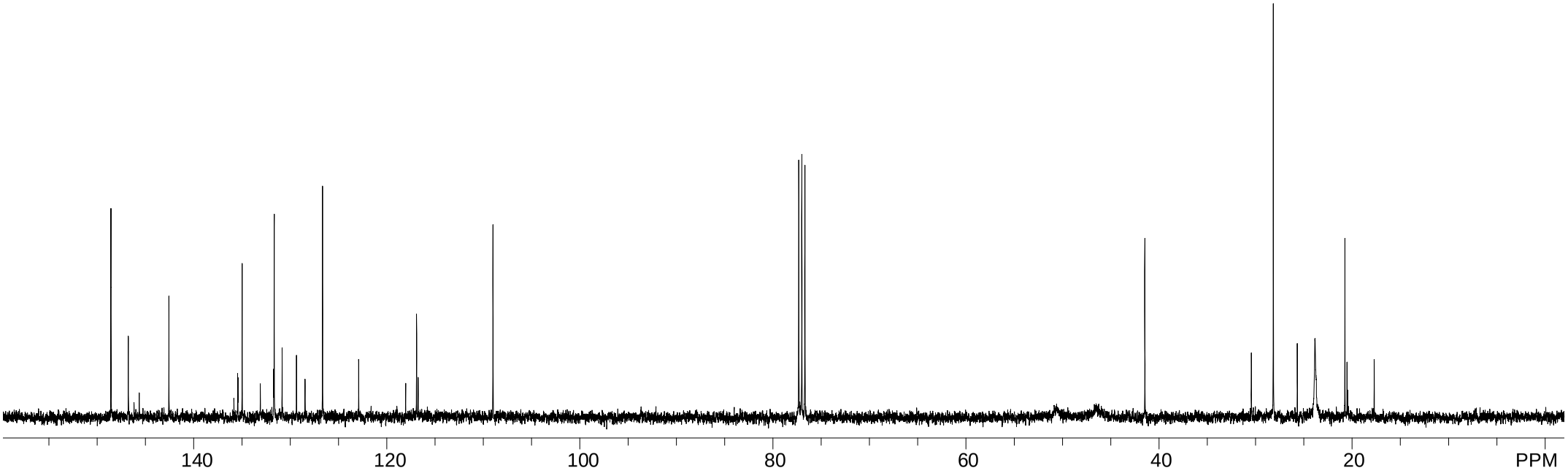


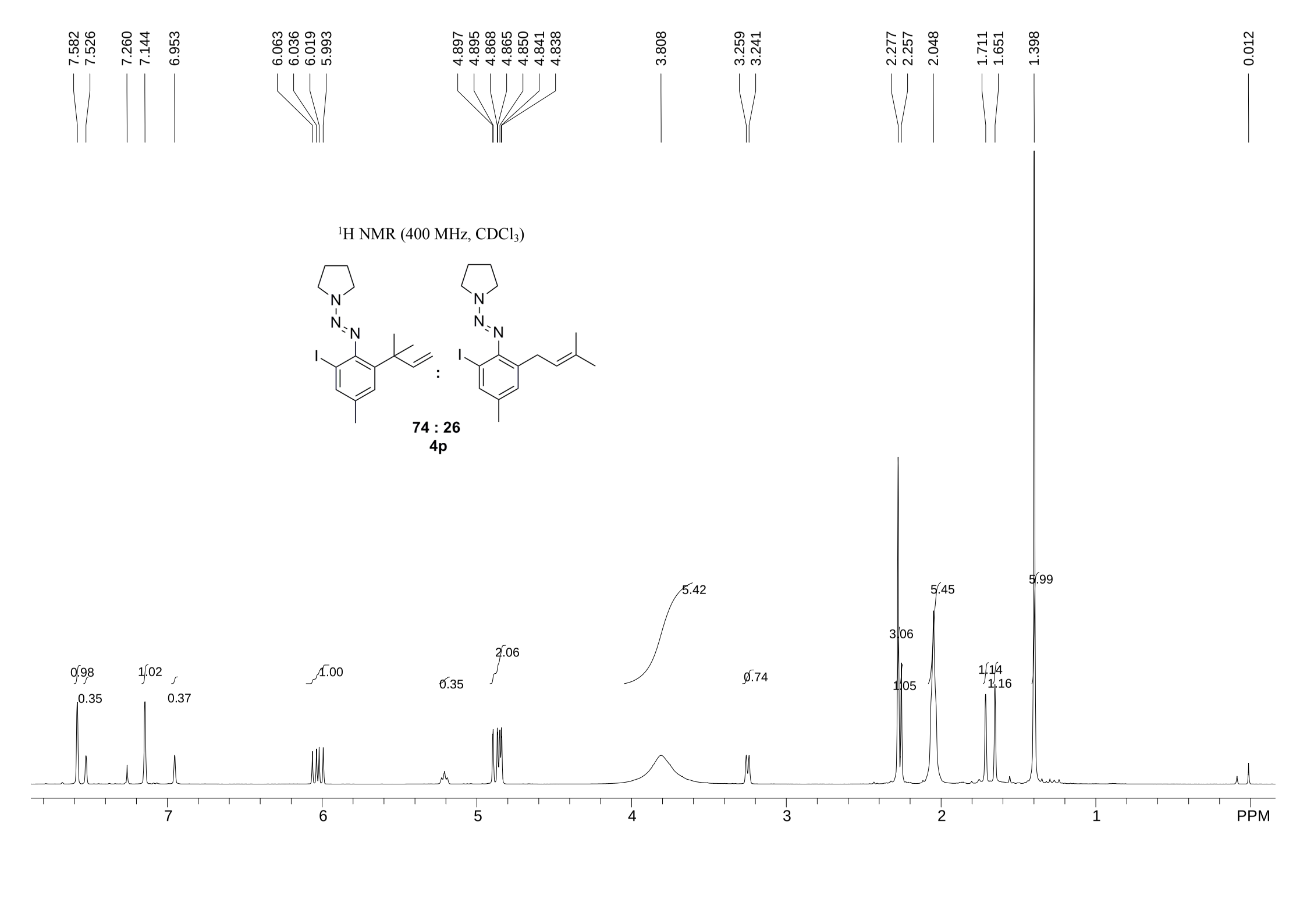
^{13}C NMR (100 MHz, $CDCl_3$)



78 : 22

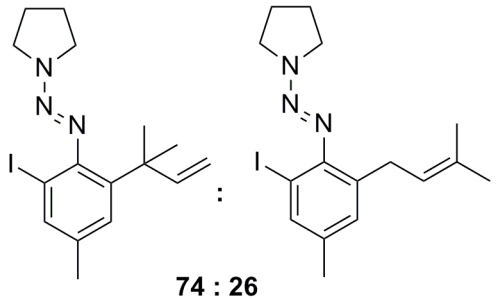
4o



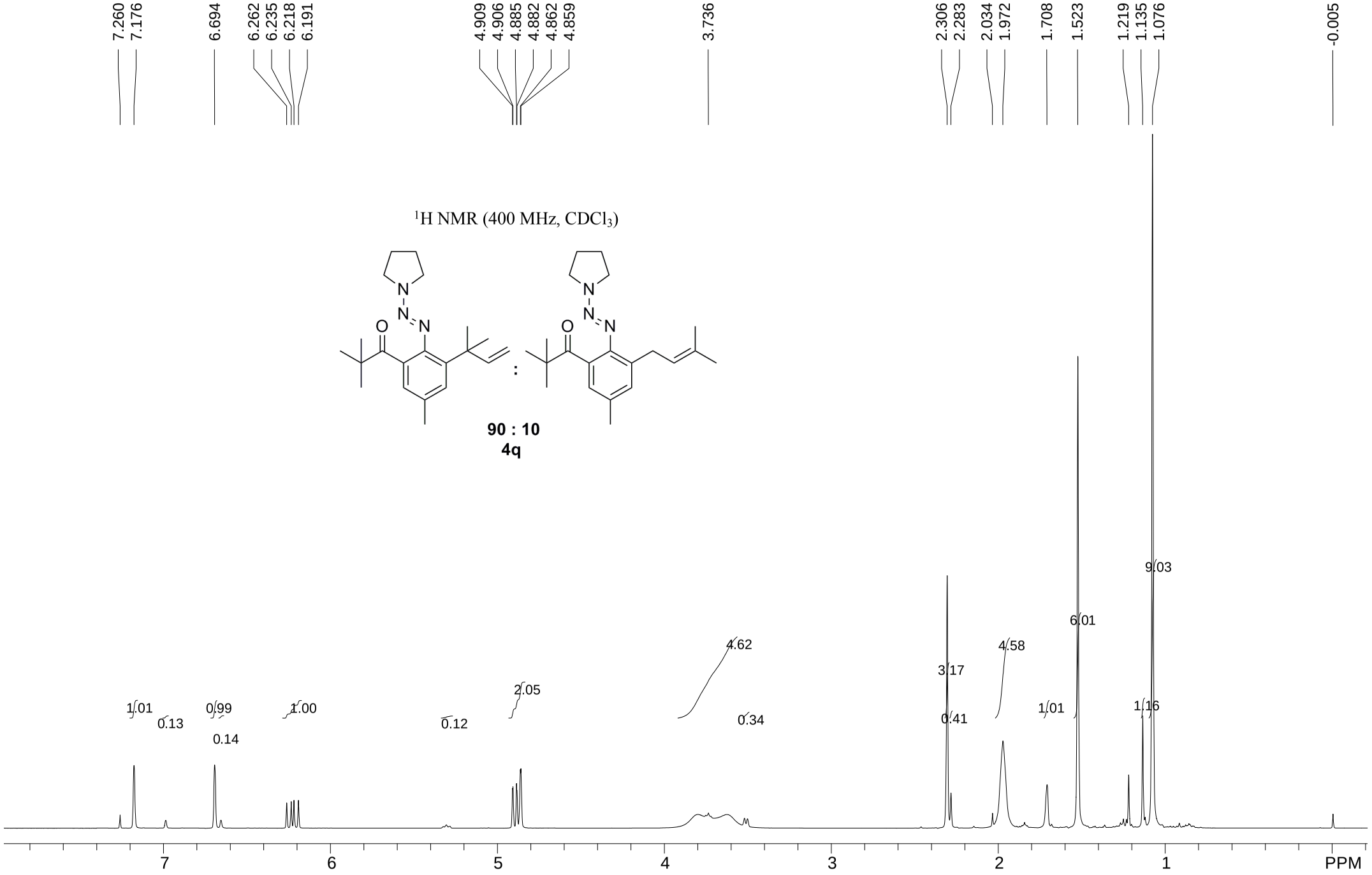

7.582
7.526
7.260
7.144
6.953
6.063
6.036
6.019
5.993
4.897
4.895
4.868
4.865
4.850
4.841
4.838
3.808
3.259
3.241
2.277
2.257
2.048
1.711
1.651
1.398
0.012
^{1}H NMR (400 MHz, CDCl$_3$)
74 : 26
4p
0.98
0.35
1.02
0.37
1.00
0.35
2.06
5.42
0.74
3.06
1.05
5.45
1.14
1.16
5.99
7
6
5
4
3
2
1
PPM

149.229
148.758
148.013
141.759
138.081
137.111
136.058
135.709
134.289
131.767
130.645
127.933
123.086
109.017
93.181
92.957
77.317
77.000
76.685
41.646
30.774
28.305
25.720
23.973
23.858
20.514
20.323
17.792

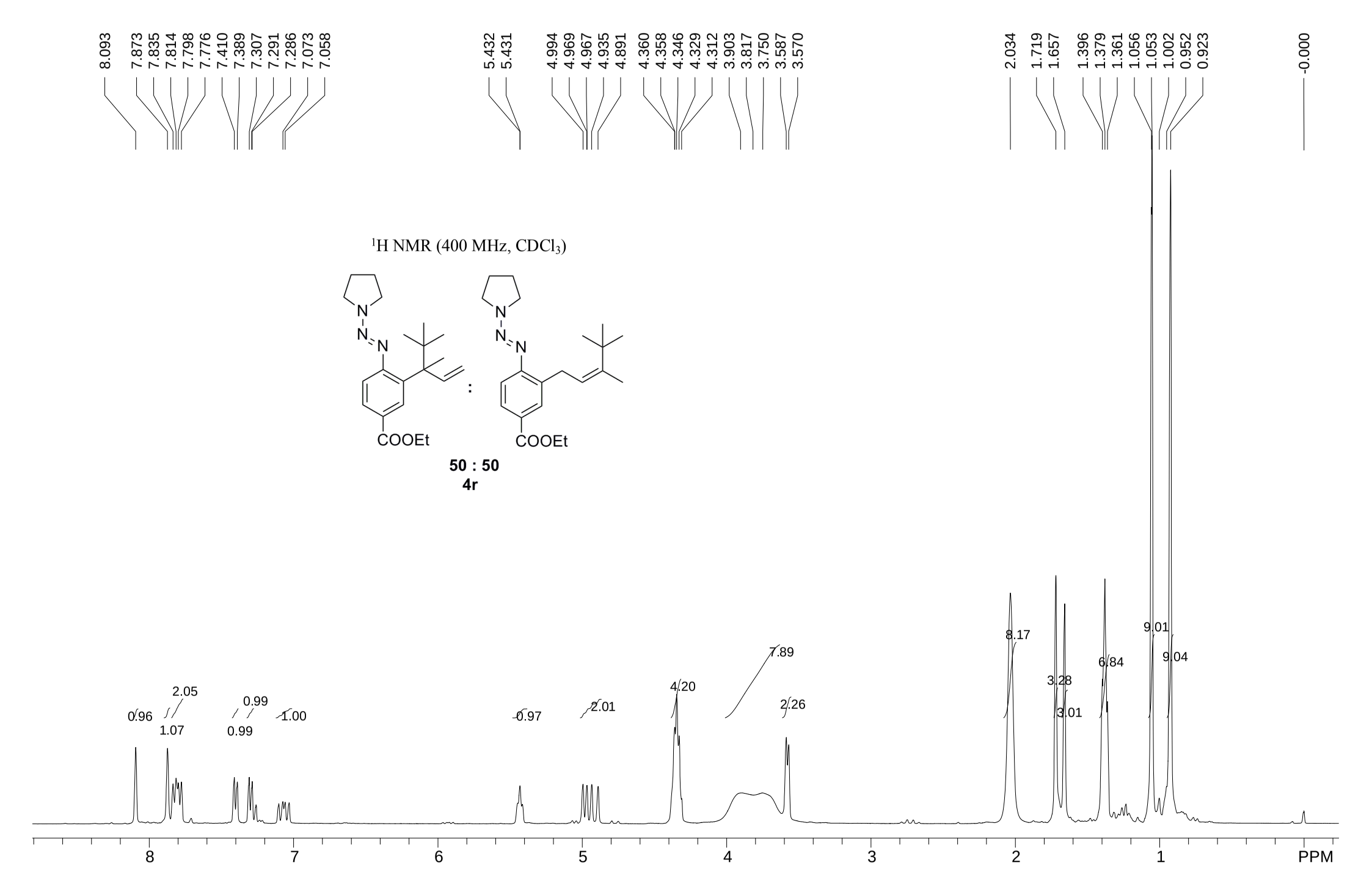
^{13}C NMR (100 MHz, $CDCl_3$)

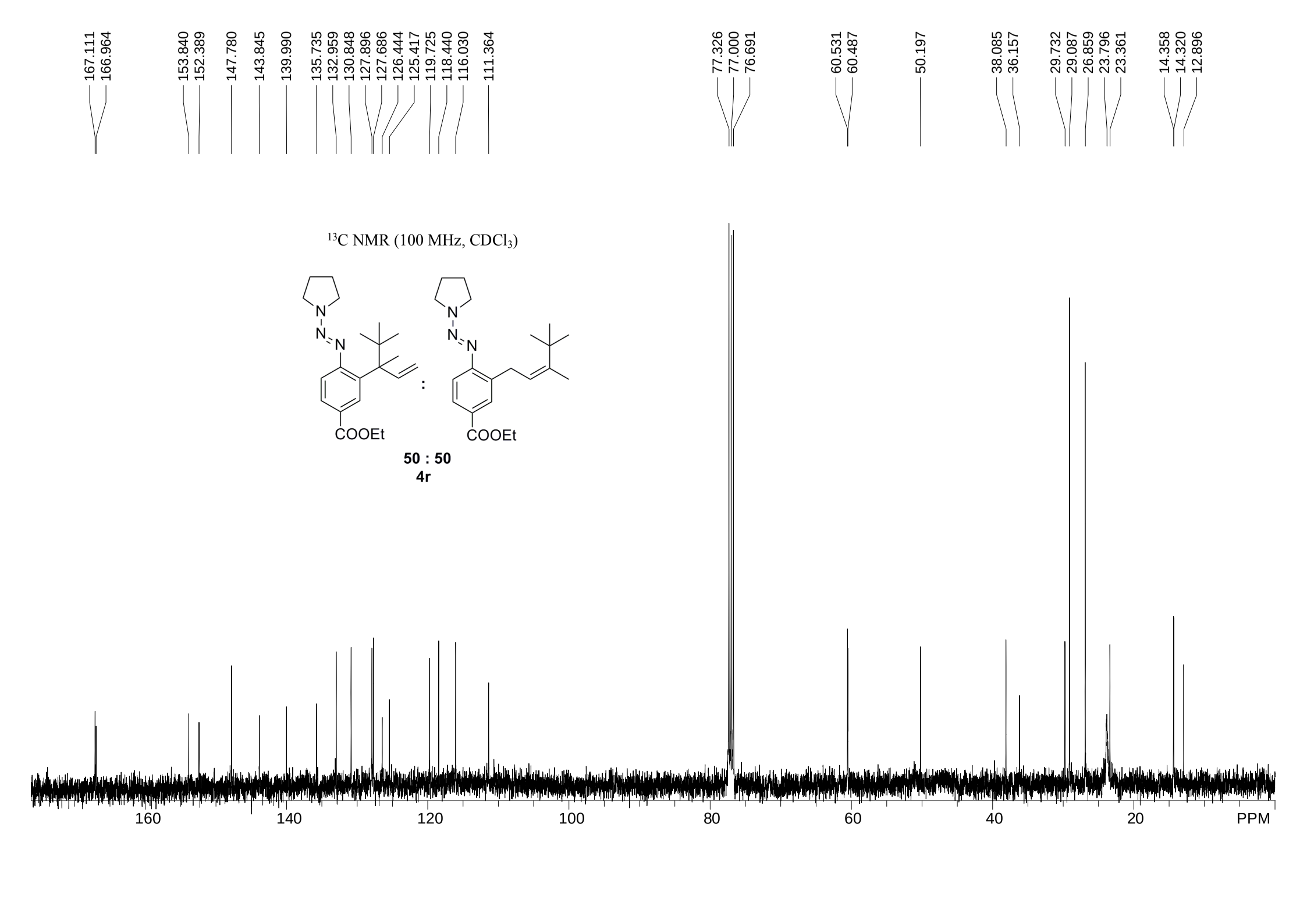


74 : 26
4p


7.260
7.176
6.694
6.262
6.235
6.218
6.191
4.909
4.906
4.885
4.882
4.862
4.859
3.736
2.306
2.283
2.034
1.972
1.708
1.523
1.219
1.135
1.076
-0.005
1H NMR (400 MHz, CDCl3)
90 : 10
4q
1.01
0.13
0.99
0.14
1.00
0.12
2.05
4.62
0.34
3.17
0.41
4.58
1.01
6.01
1.16
9.03
7
6
5
4
3
2
1
PPM

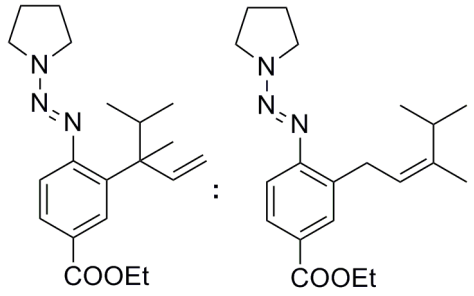
215.564
149.189
143.611
142.181
133.689
132.519
127.863
125.730
109.166
77.309
77.000
76.677
44.312
41.377
28.386
27.540
21.127
200
150
100
50
PPM
90 : 10
4q
^{13}C NMR (100 MHz, CDCl$_3$)


8.093
7.873
7.835
7.814
7.798
7.776
7.410
7.389
7.307
7.291
7.286
7.073
7.058
5.432
5.431
4.994
4.969
4.967
4.935
4.891
4.360
4.358
4.346
4.329
4.312
3.903
3.817
3.750
3.587
3.570
2.034
1.719
1.657
1.396
1.379
1.361
1.056
1.053
1.002
0.952
0.923
-0.000
^{1}H NMR (400 MHz, $CDCl_3$)
COOEt
COOEt
50 : 50
4r
0.96
2.05
1.07
0.99
0.99
1.00
0.97
2.01
4.20
7.89
2.26
8.17
3.28
3.01
6.84
9.01
9.04
8
7
6
5
4
3
2
1
PPM


167.111
166.964
153.840
152.389
147.780
143.845
139.990
135.735
132.959
130.848
127.896
127.686
126.444
125.417
119.725
118.440
116.030
111.364
77.326
77.000
76.691
60.531
60.487
50.197
38.085
36.157
29.732
29.087
26.859
23.796
23.361
14.358
14.320
12.896
13C NMR (100 MHz, CDCl3)
COOEt
COOEt
50 : 50
4r
160
140
120
100
80
60
40
20
PPM

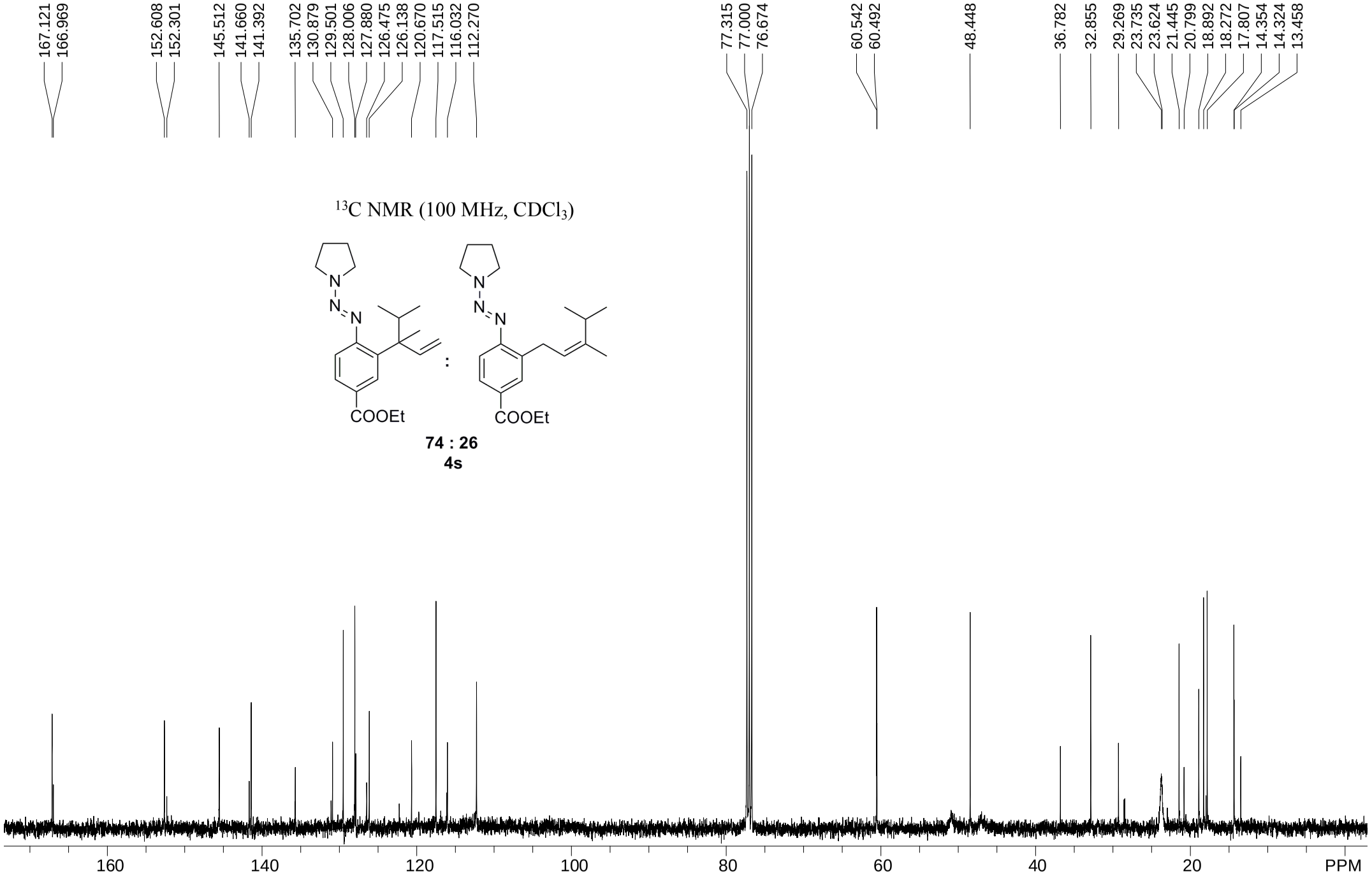
8.017
8.013
7.880
7.829
7.825
7.807
7.804
7.393
7.372
7.260
5.100
5.098
5.073
5.070
5.016
5.012
4.971
4.969
4.375
4.357
4.339
4.321
3.586
3.569
3.046
2.053
1.683
1.639
1.479
1.401
1.396
1.383
1.378
1.365
1.018
1.002
0.816
0.799
0.671
0.654
0.000

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



74 : 26

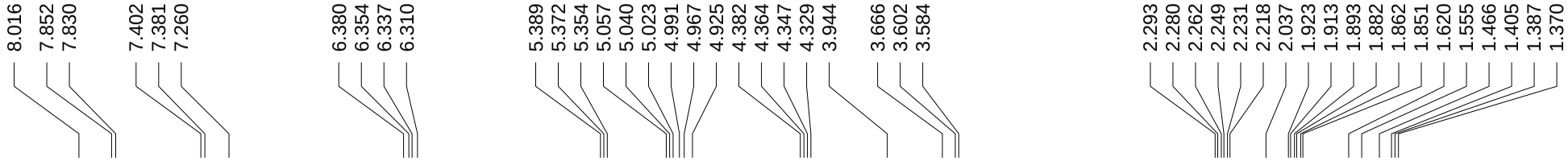
4s



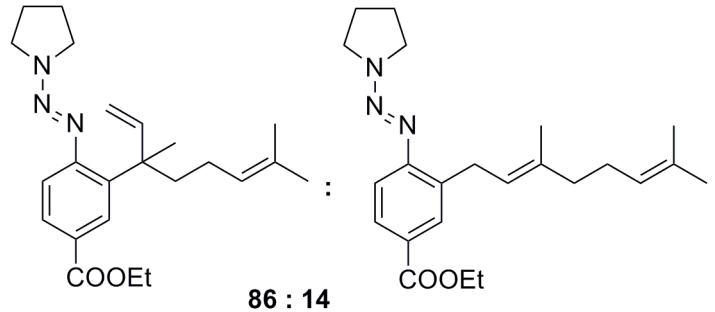
^{13}C NMR (100 MHz, $CDCl_3$)

74 : 26

4s

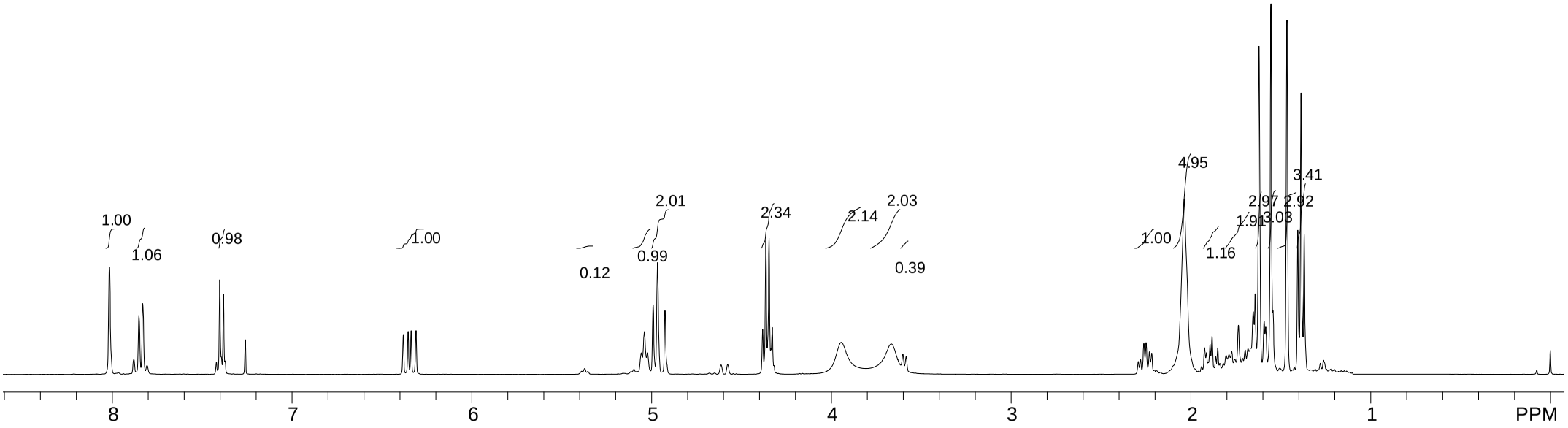


^{1}H NMR (400 MHz, $CDCl_3$)



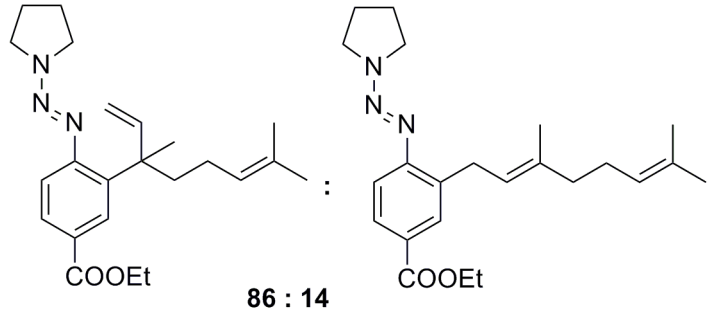
86 : 14

4t

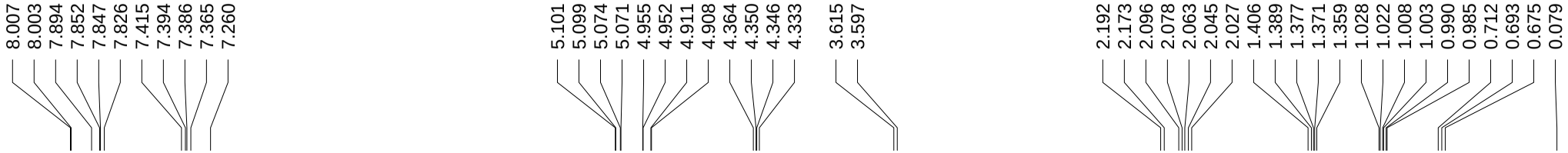


167.079
152.934
147.782
139.869
130.799
129.443
128.282
126.085
125.062
117.278
110.295
77.327
77.000
76.689
60.560
44.733
39.737
25.643
25.271
23.692
17.463
14.364

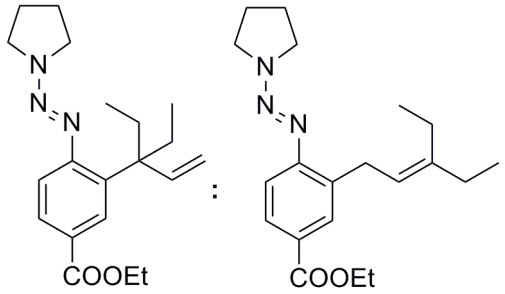
^{13}C NMR (100 MHz, $CDCl_3$)



86 : 14
4t

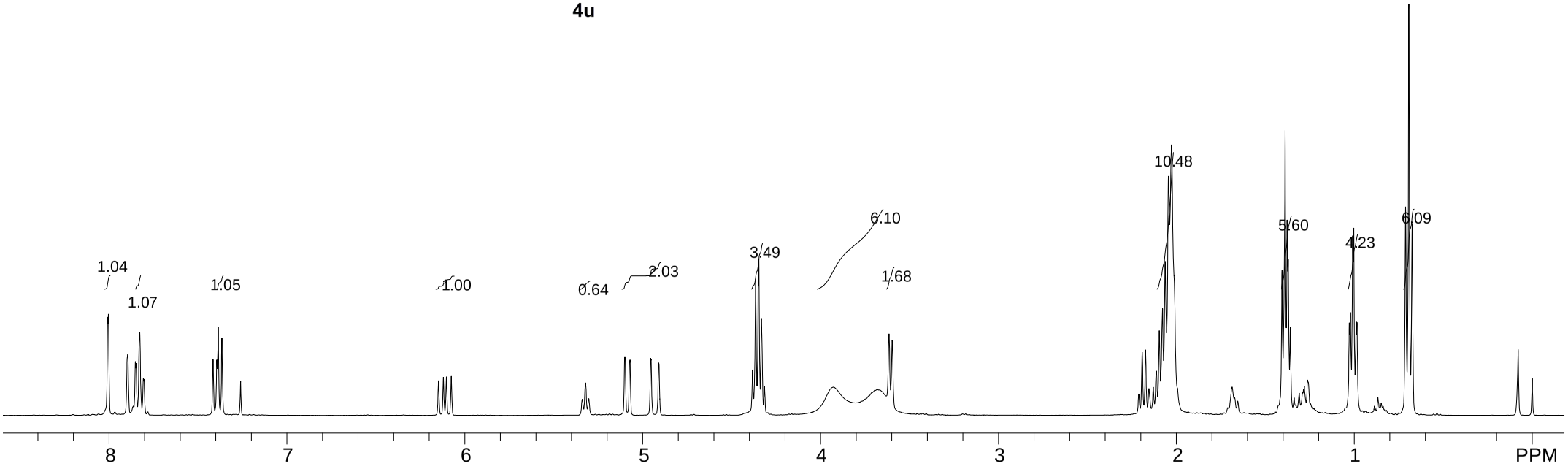


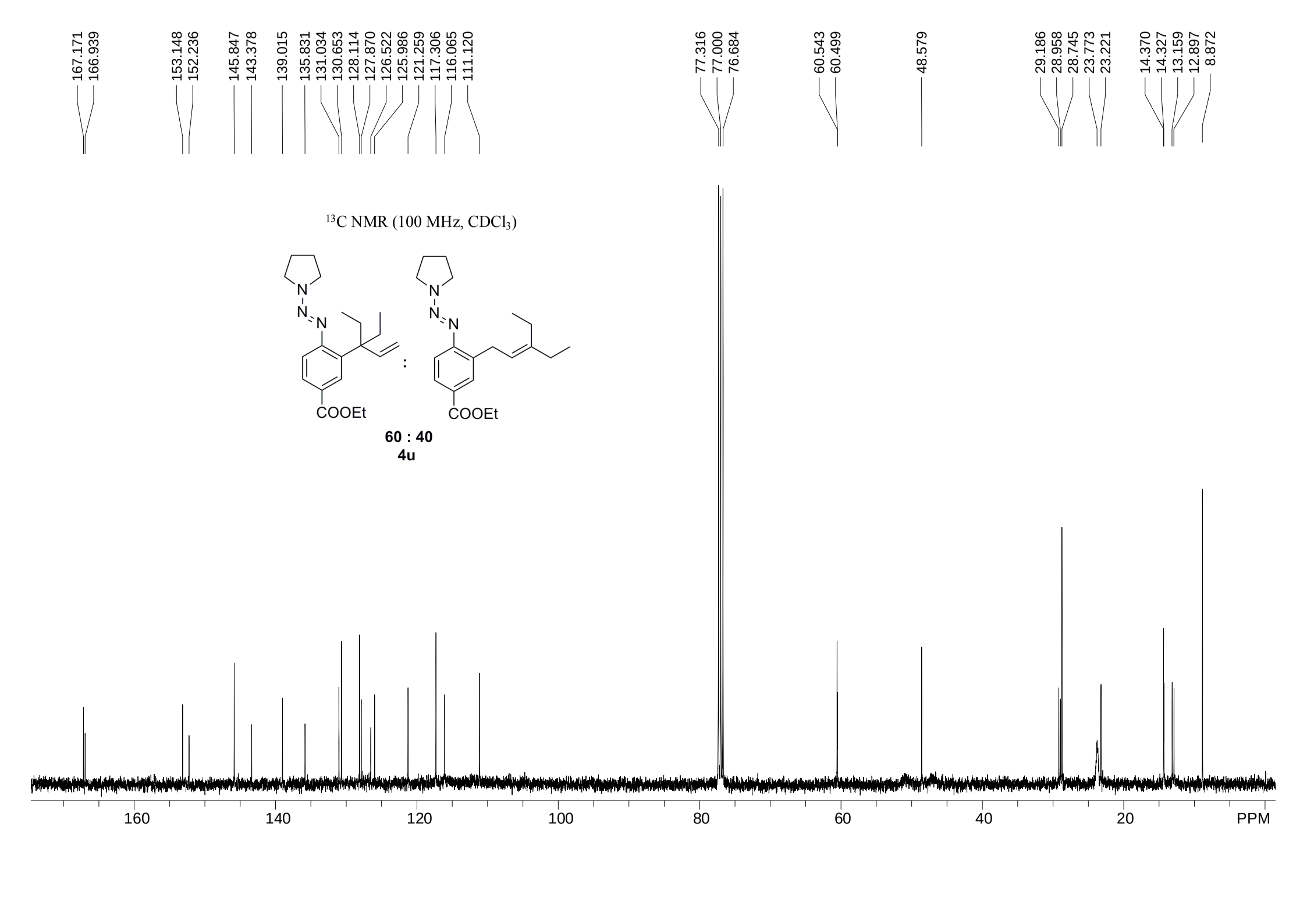
^{1}H NMR (400 MHz, $CDCl_3$)

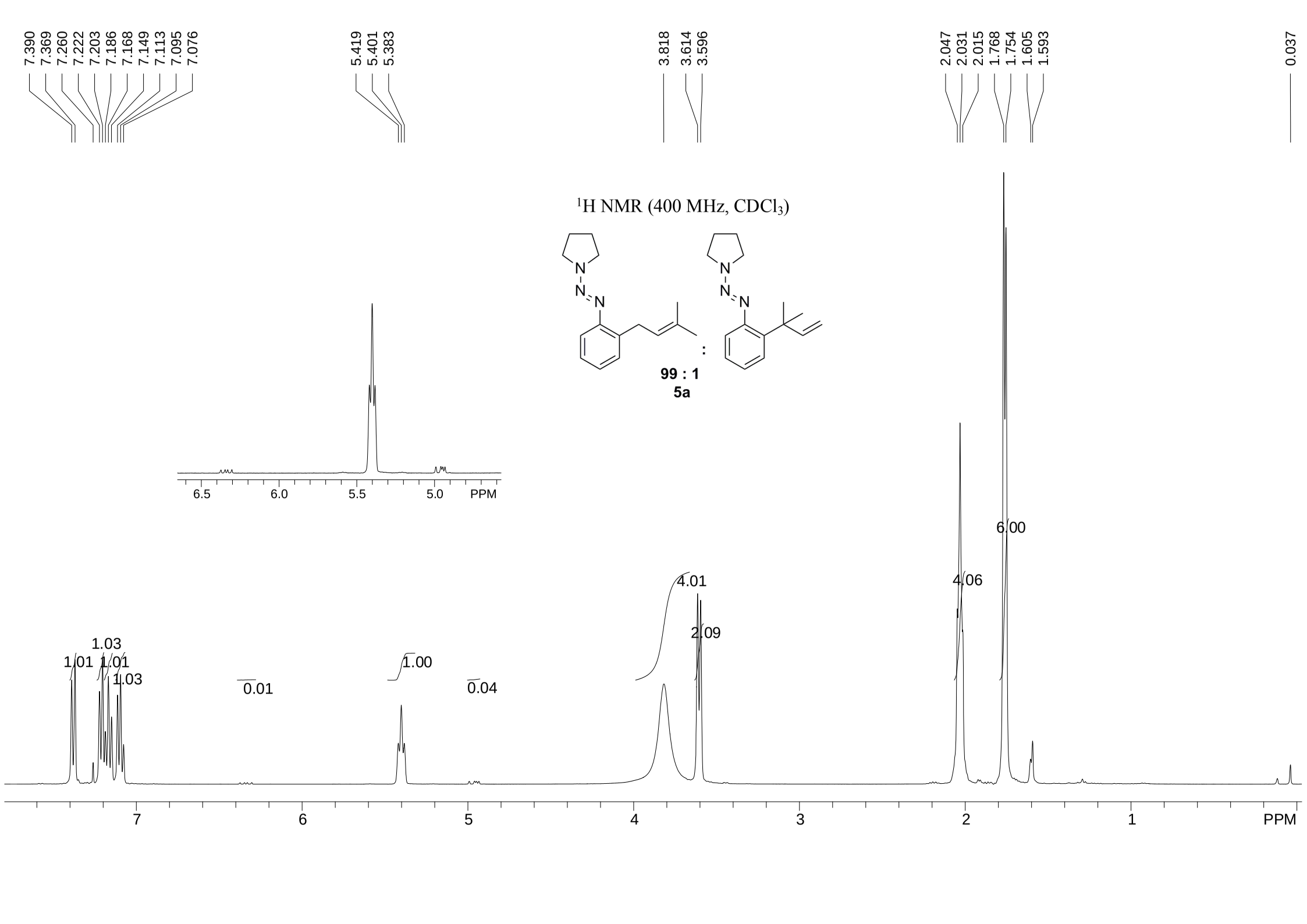


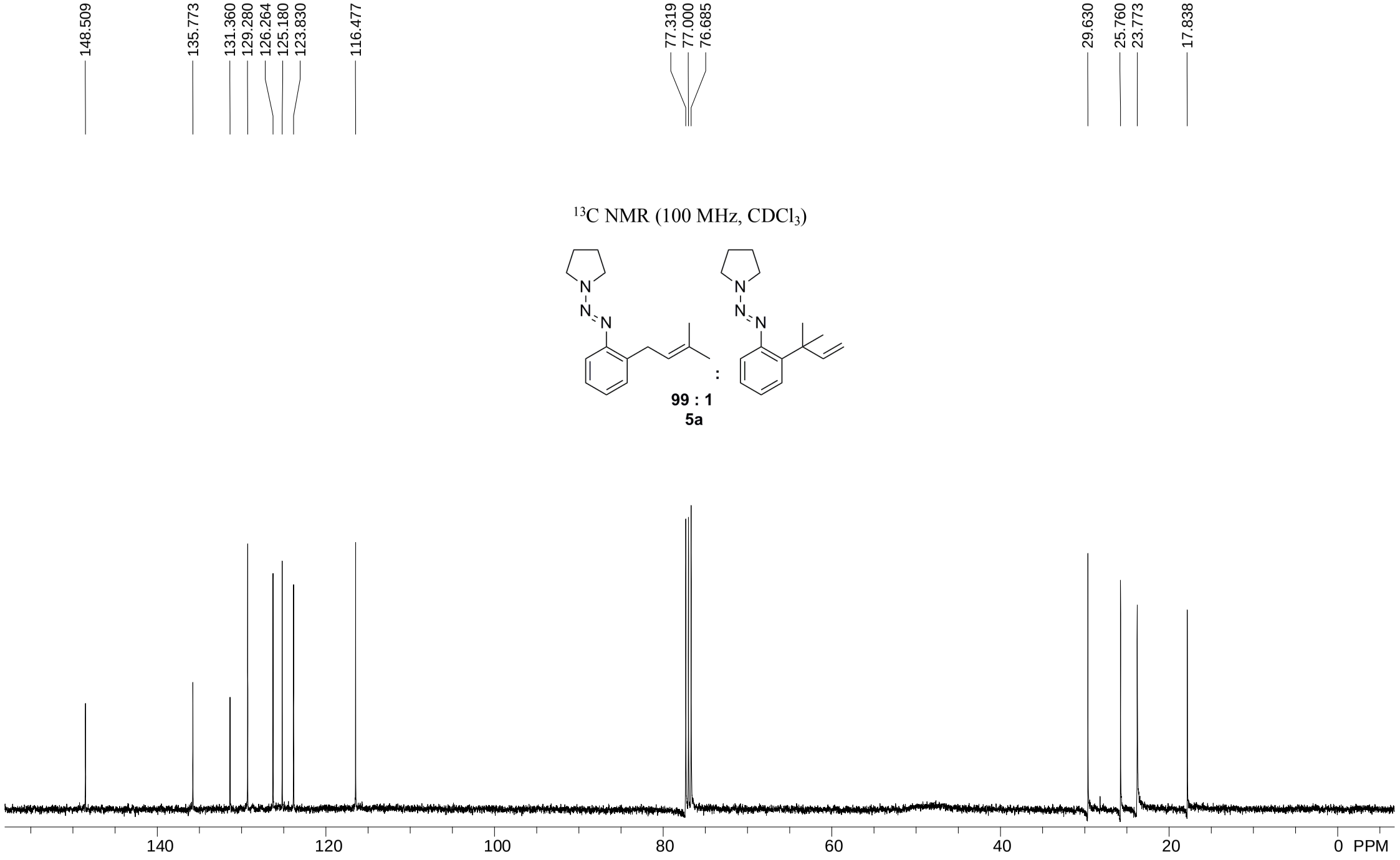
60 : 40

4u




167.171
166.939
153.148
152.236
145.847
143.378
139.015
135.831
131.034
130.653
128.114
127.870
126.522
125.986
121.259
117.306
116.065
111.120
77.316
77.000
76.684
60.543
60.499
48.579
29.186
28.958
28.745
23.773
23.221
14.370
14.327
13.159
12.897
8.872
13C NMR (100 MHz, CDCl3)
COOEt
COOEt
60 : 40
4u
160
140
120
100
80
60
40
20
PPM

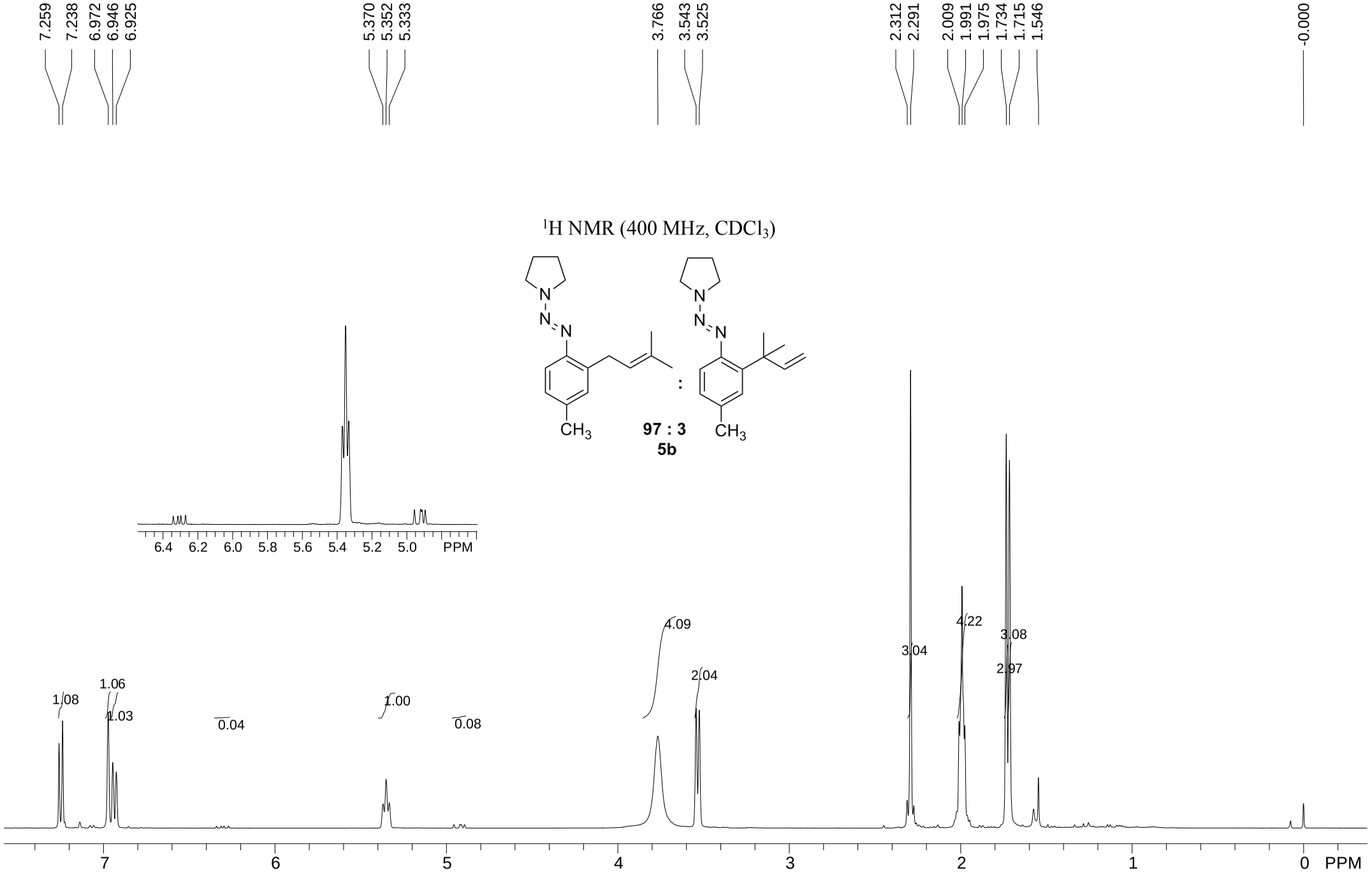

7.390
7.369
7.260
7.222
7.203
7.186
7.168
7.149
7.113
7.095
7.076
5.419
5.401
5.383
3.818
3.614
3.596
2.047
2.031
2.015
1.768
1.754
1.605
1.593
0.037
^{1}H NMR (400 MHz, $CDCl_3$)
99 : 1
5a
6.5
6.0
5.5
5.0
PPM
1.01
1.03
1.01
1.03
0.01
1.00
0.04
4.01
2.09
4.06
6.00
7
6
5
4
3
2
1
PPM



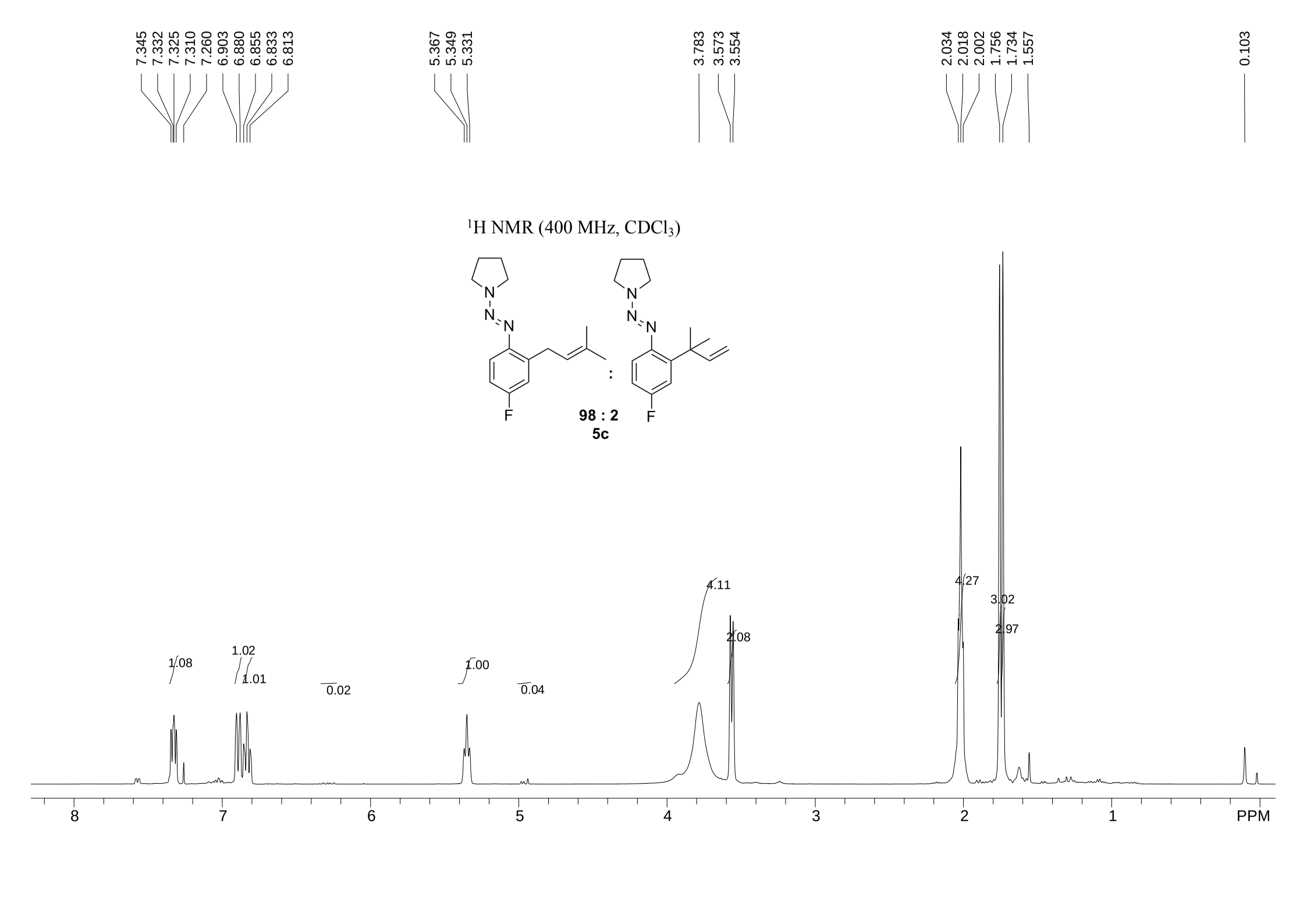
^{13}C NMR (100 MHz, $CDCl_3$)

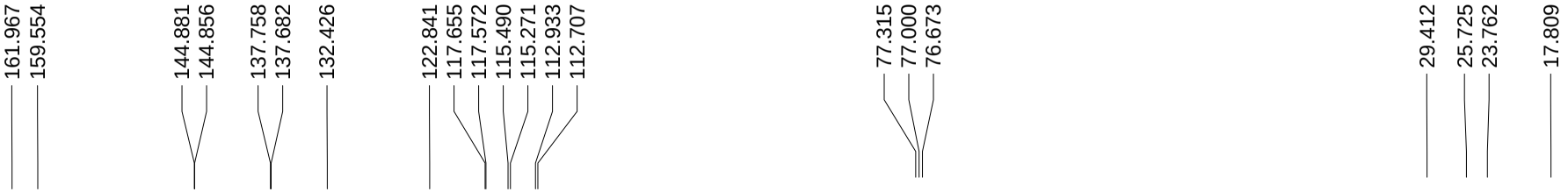
99 : 1

5a

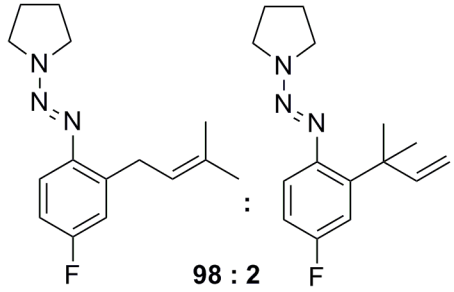

7.259
7.238
6.972
6.946
6.925
5.370
5.352
5.333
3.766
3.543
3.525
2.312
2.291
2.009
1.991
1.975
1.734
1.715
1.546
-0.000
1H NMR (400 MHz, CDCl3)
CH3
97 : 3
5b
CH3
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 PPM
1.08
1.06
1.03
0.04
1.00
0.08
4.09
2.04
3.04
4.22
3.08
2.97
7 6 5 4 3 2 1 0 PPM

^{13}C NMR (100 MHz, $CDCl_3$)
146.251
135.633
134.715
131.195
129.925
127.018
124.029
116.317
77.314
77.000
76.681
29.616
25.790
23.794
21.033
17.853
97 : 3
5b
CH_3
CH_3
140
120
100
80
60
40
20
PPM


7.345
7.332
7.325
7.310
7.260
6.903
6.880
6.855
6.833
6.813
5.367
5.349
5.331
3.783
3.573
3.554
2.034
2.018
2.002
1.756
1.734
1.557
0.103
1H NMR (400 MHz, CDCl3)
N
N
N
F
:
98 : 2
5c
1.08
1.02
1.01
0.02
1.00
0.04
4.11
2.08
4.27
3.02
2.97
8
7
6
5
4
3
2
1
PPM

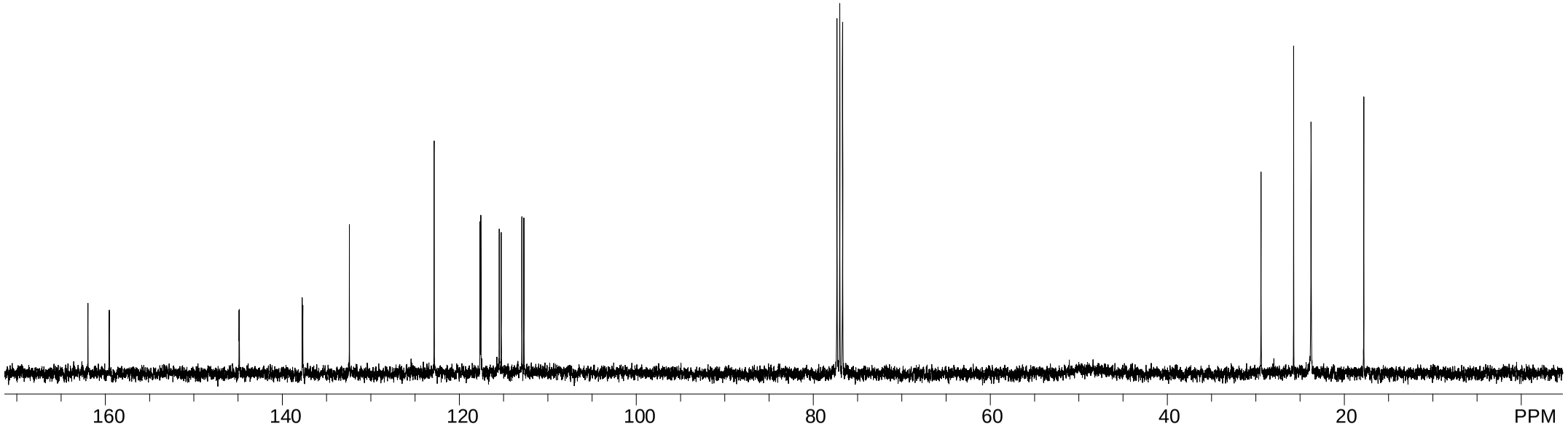


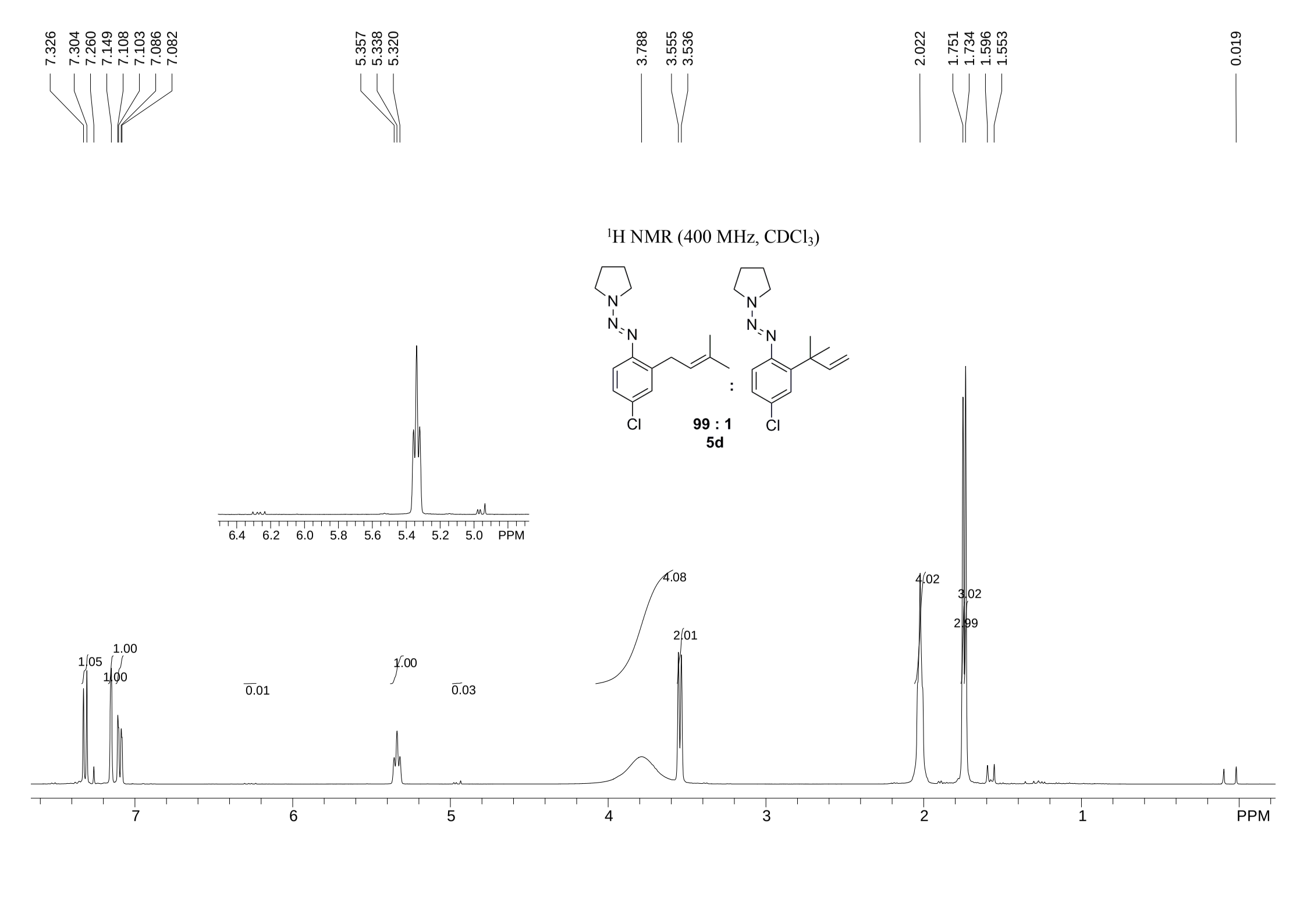
^{13}C NMR (100 MHz, $CDCl_3$)



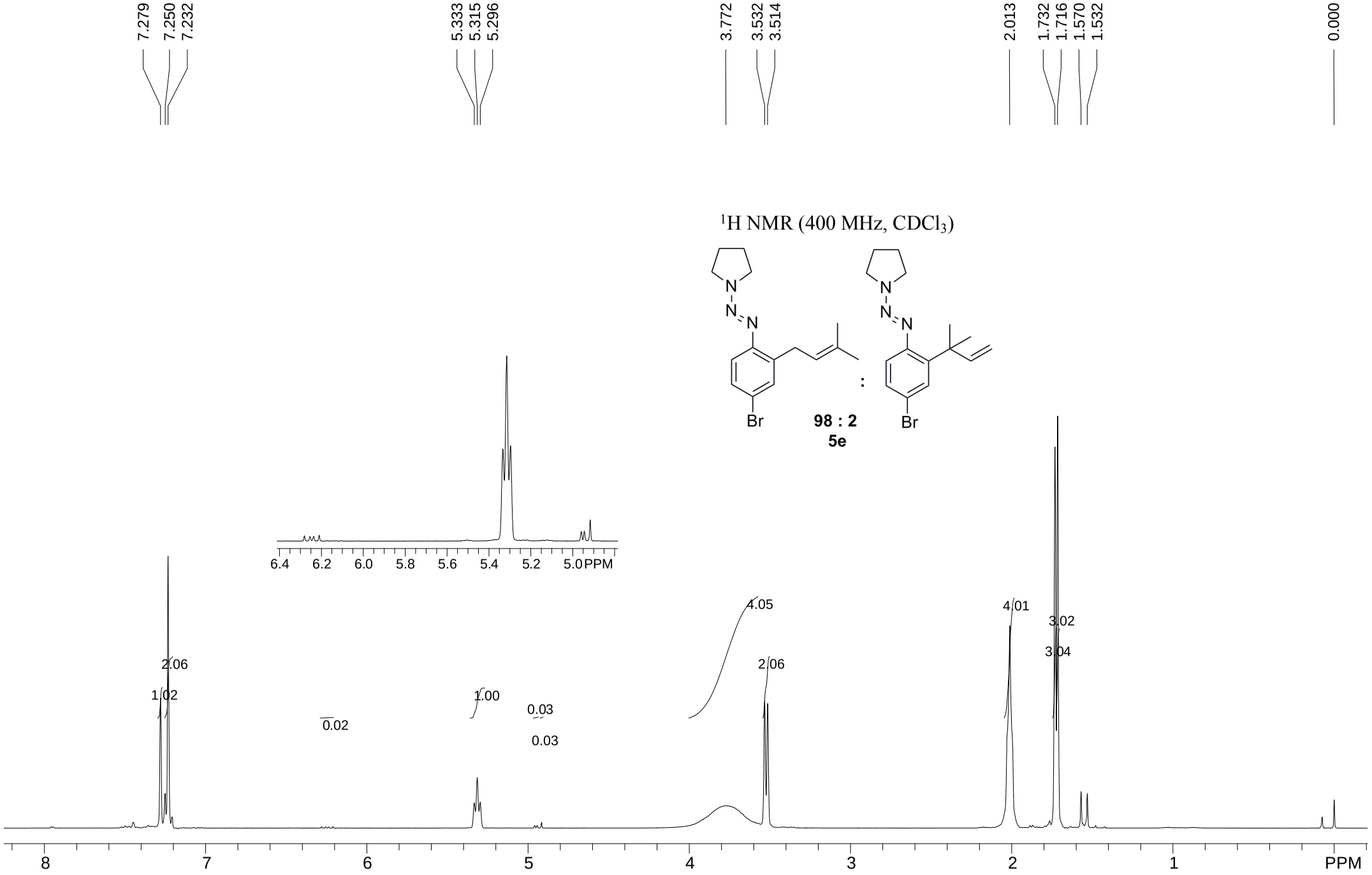
98 : 2

5c

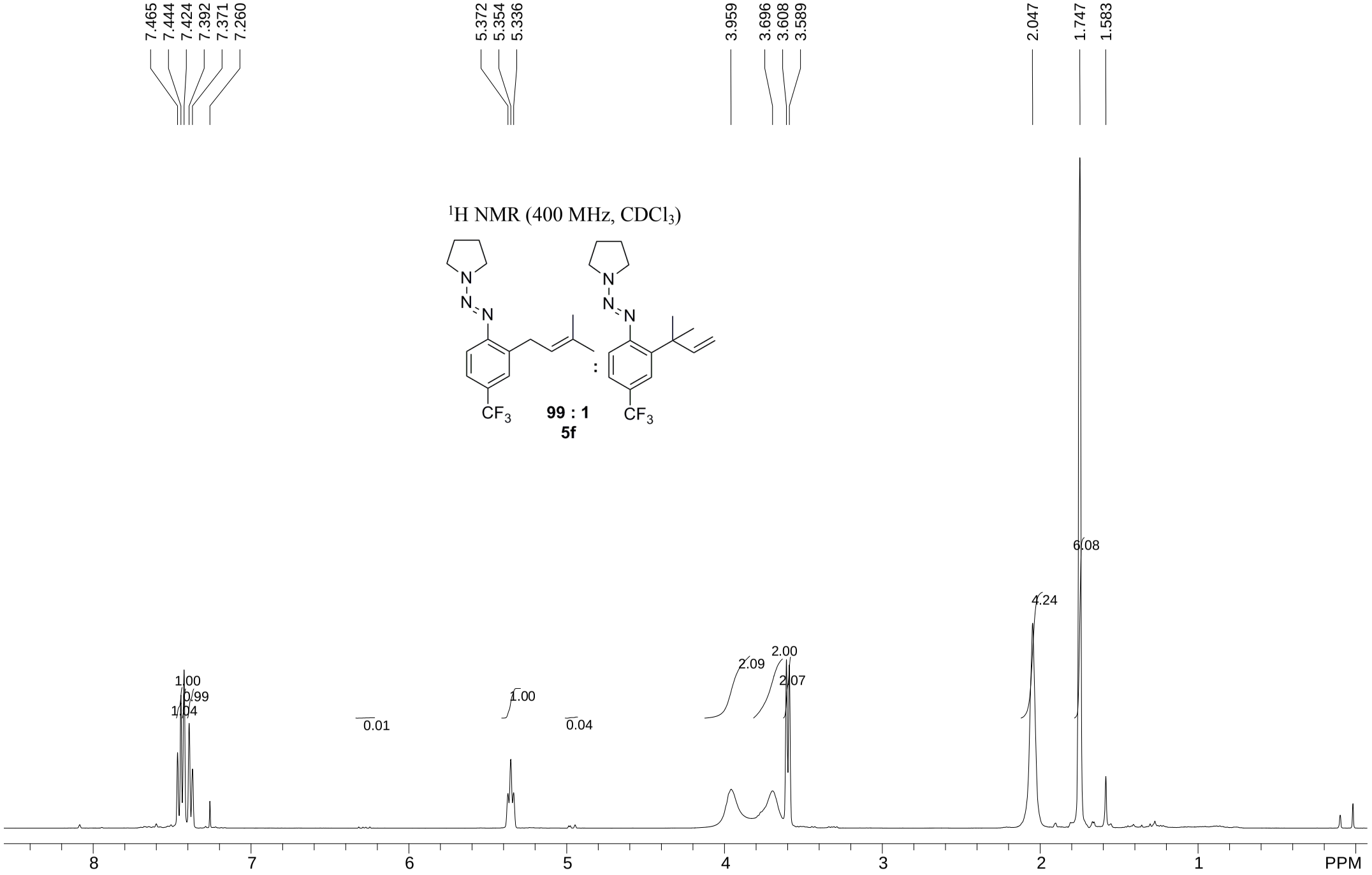


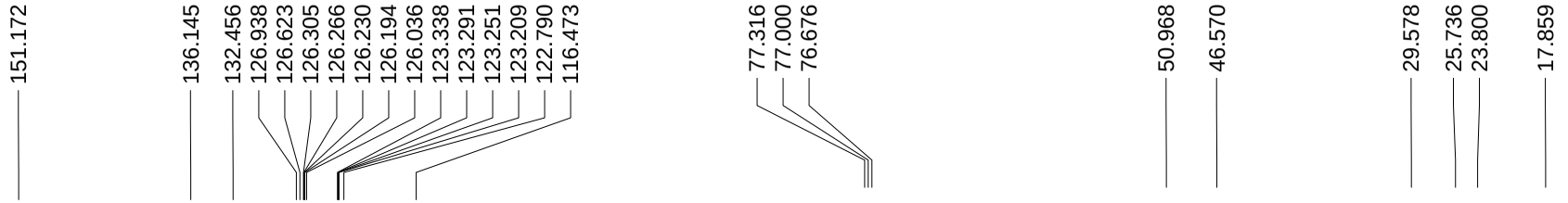

7.326
7.304
7.260
7.149
7.108
7.103
7.086
7.082
5.357
5.338
5.320
3.788
3.555
3.536
2.022
1.751
1.734
1.596
1.553
0.019
1H NMR (400 MHz, CDCl3)
N
N
N
Cl
:
99 : 1
5d
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 PPM
1.05
1.00
1.00
0.01
1.00
0.03
4.08
2.01
4.02
3.02
2.99
7 6 5 4 3 2 1 PPM

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

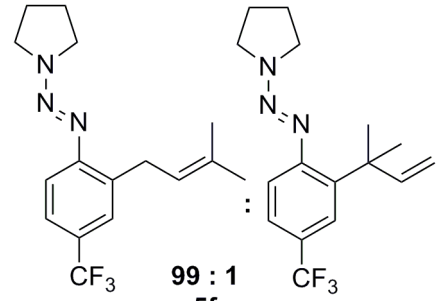

7.279
7.250
7.232
5.333
5.315
5.296
3.772
3.532
3.514
2.013
1.732
1.716
1.570
1.532
0.000
^{1}H NMR (400 MHz, $CDCl_3$)
Br
98 : 2
5e
Br
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 PPM
2.06
1.02
0.02
1.00
0.03
0.03
4.05
2.06
4.01
3.02
3.04
8 7 6 5 4 3 2 1 PPM

^{13}C NMR (100 MHz, $CDCl_3$)
147.528
137.900
132.338
131.915
129.185
122.860
118.253
118.015
77.314
77.000
76.681
29.324
25.769
23.747
17.857
140
120
100
80
60
40
20
PPM
Br
N
N
N
98 : 2
5e
Br
N
N
N

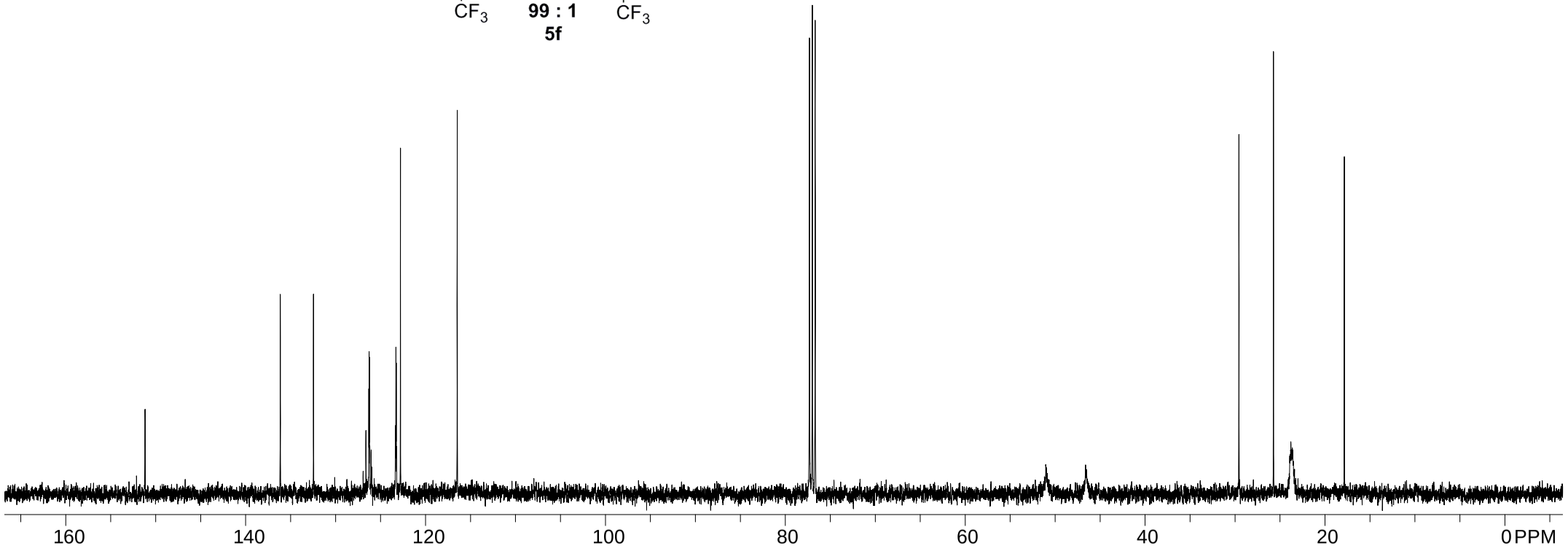

7.465
7.444
7.424
7.392
7.371
7.260
5.372
5.354
5.336
3.959
3.696
3.608
3.589
2.047
1.747
1.583
^{1}H NMR (400 MHz, $CDCl_3$)
99 : 1
5f
1.00
0.99
1.04
0.01
1.00
0.04
2.09
2.00
2.07
4.24
6.08
8
7
6
5
4
3
2
1
PPM

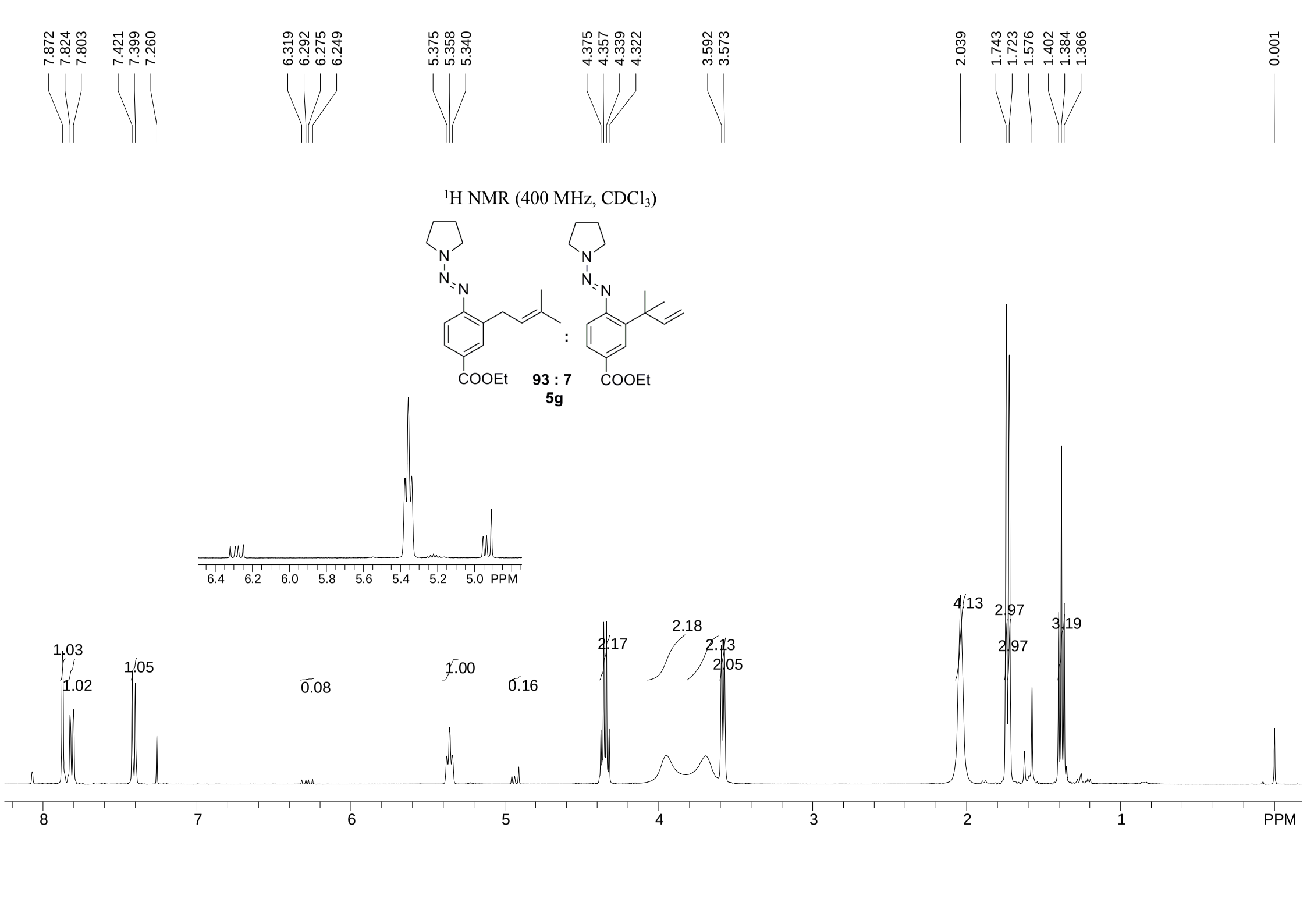


^{13}C NMR (100 MHz, $CDCl_3$)



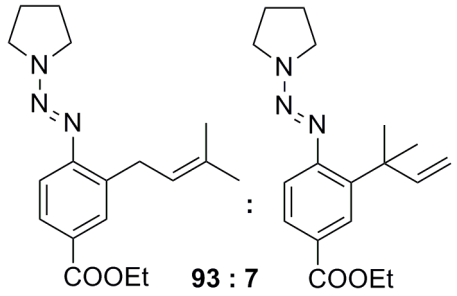
5f




7.872
7.824
7.803
7.421
7.399
7.260
6.319
6.292
6.275
6.249
5.375
5.358
5.340
4.375
4.357
4.339
4.322
3.592
3.573
2.039
1.743
1.723
1.576
1.402
1.384
1.366
0.001
^{1}H NMR (400 MHz, $CDCl_3$)
COOEt
93 : 7
COOEt
5g
6.4 6.2 6.0 5.8 5.6 5.4 5.2 5.0 PPM
1.03
1.02
1.05
0.08
1.00
0.16
2.17
2.18
2.13
2.05
4.13
2.97
2.97
3.19
8 7 6 5 4 3 2 1 PPM

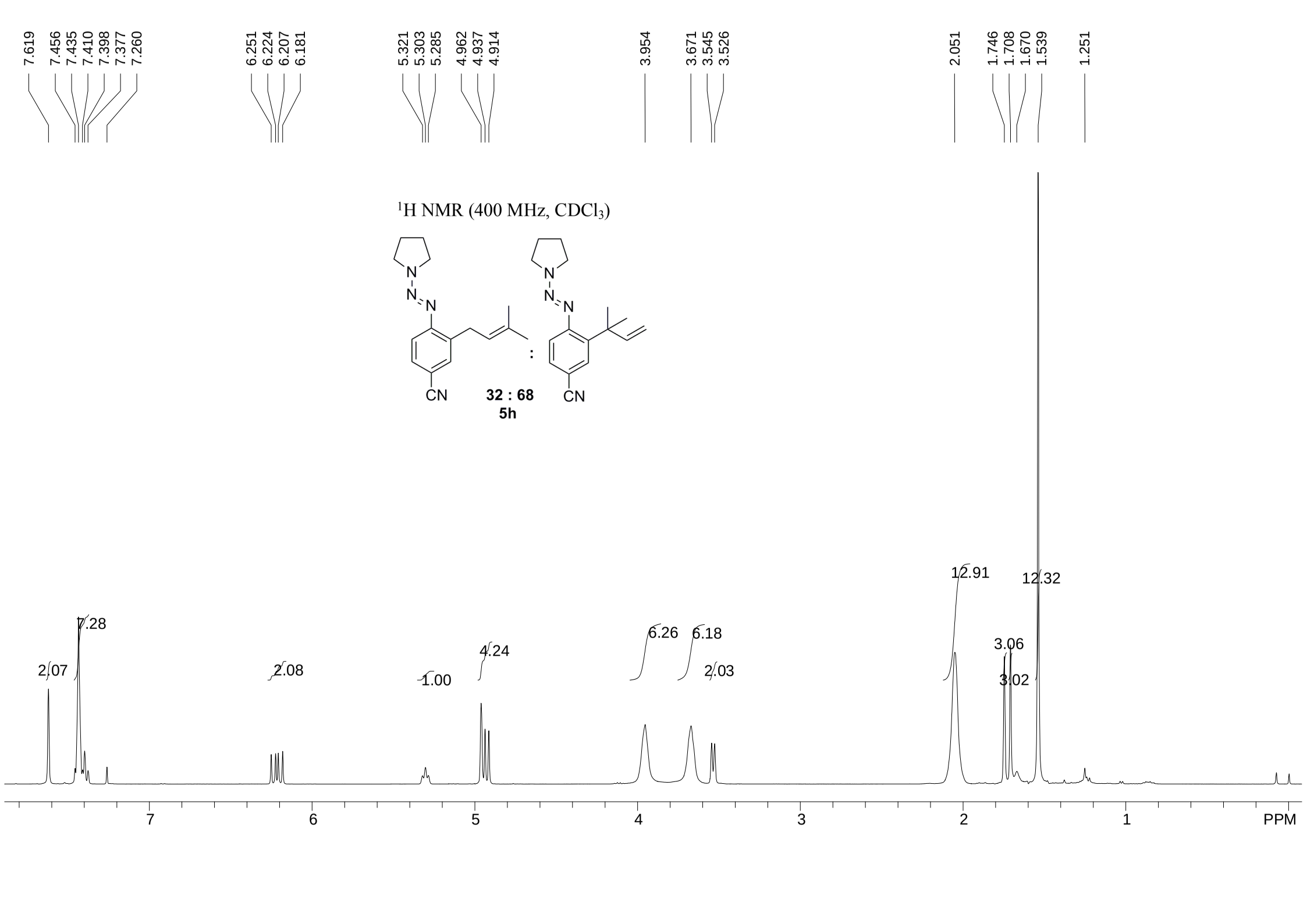
166.954
152.156
135.701
131.882
131.058
127.907
126.517
123.299
116.064
77.318
77.000
76.685
60.543
29.689
25.757
17.913
14.359

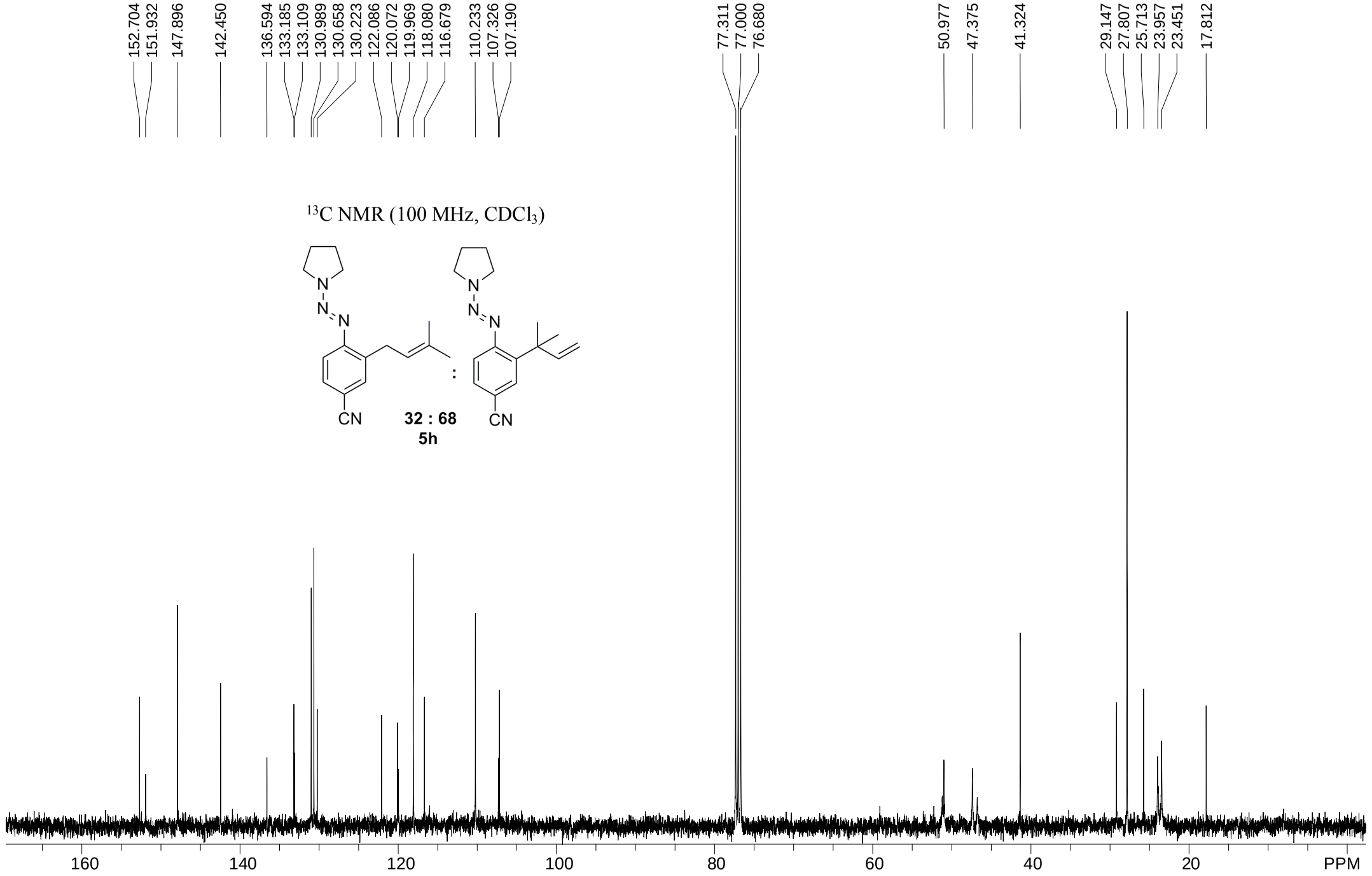
^{13}C NMR (100 MHz, $CDCl_3$)

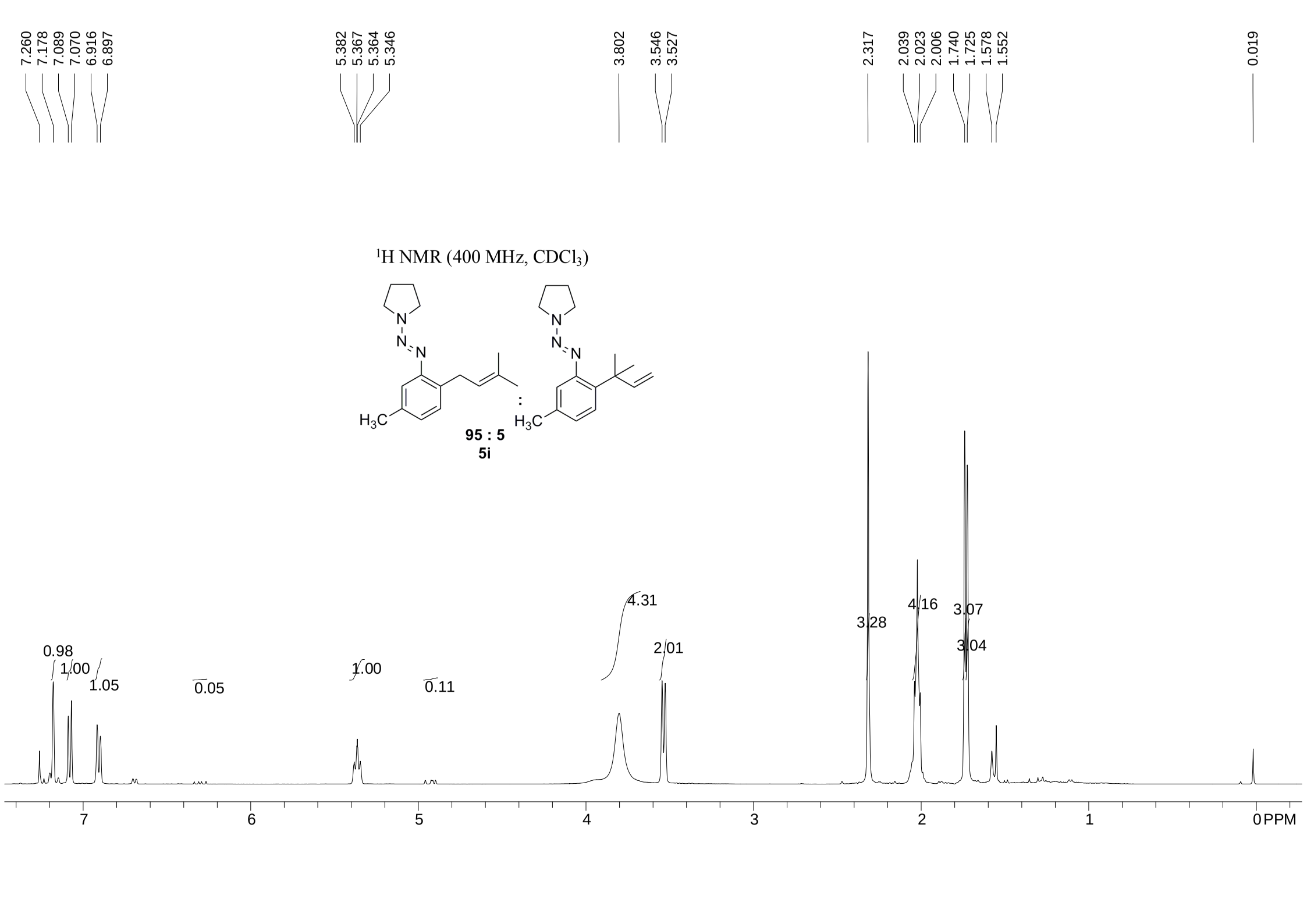


93 : 7

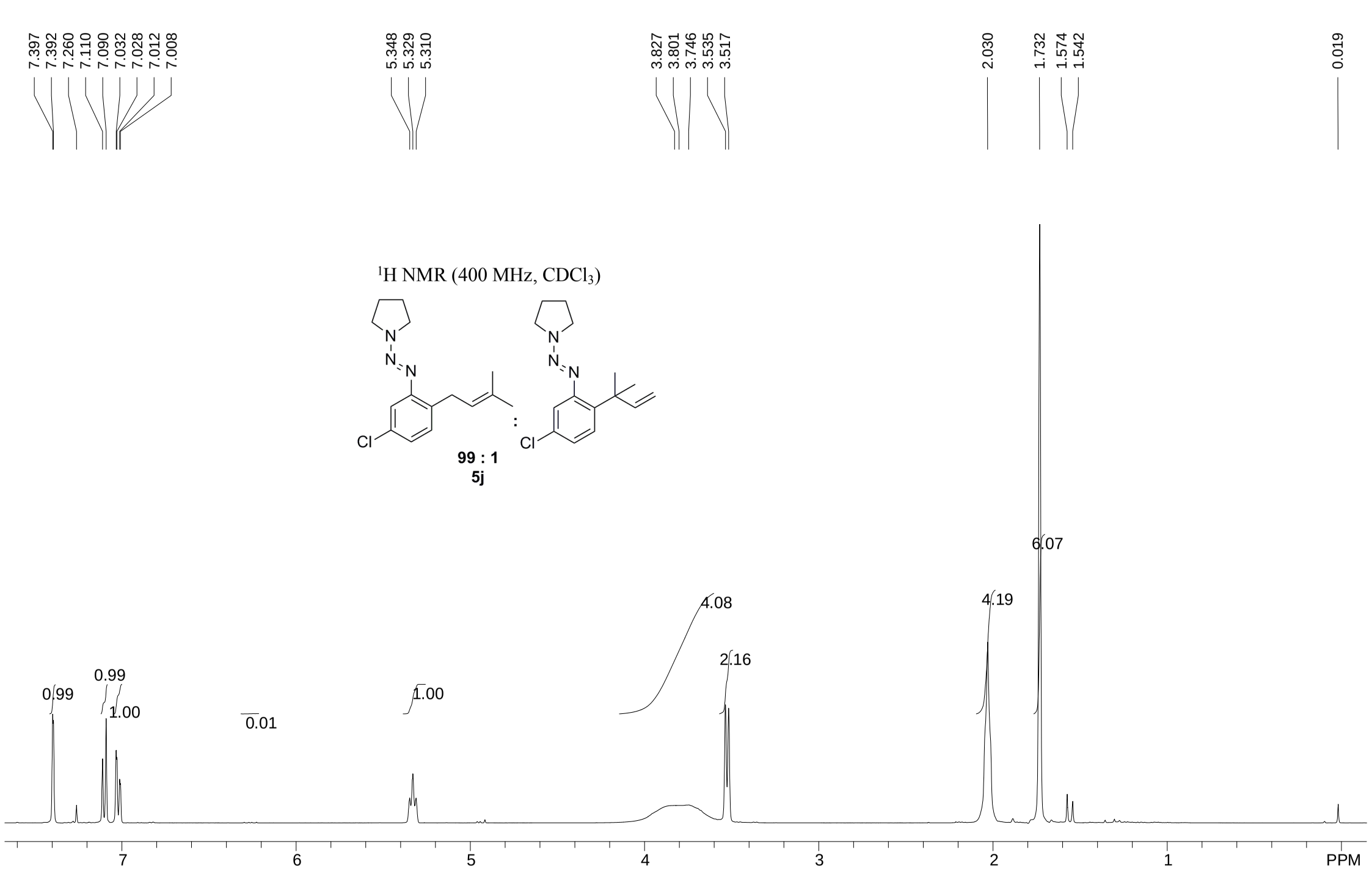
5g


7.619
7.456
7.435
7.410
7.398
7.377
7.260
6.251
6.224
6.207
6.181
5.321
5.303
5.285
4.962
4.937
4.914
3.954
3.671
3.545
3.526
2.051
1.746
1.708
1.670
1.539
1.251
1H NMR (400 MHz, CDCl3)
CN
32 : 68
5h
CN
2.07
7.28
2.08
1.00
4.24
6.26
6.18
2.03
12.91
12.32
3.06
3.02
7
6
5
4
3
2
1
PPM

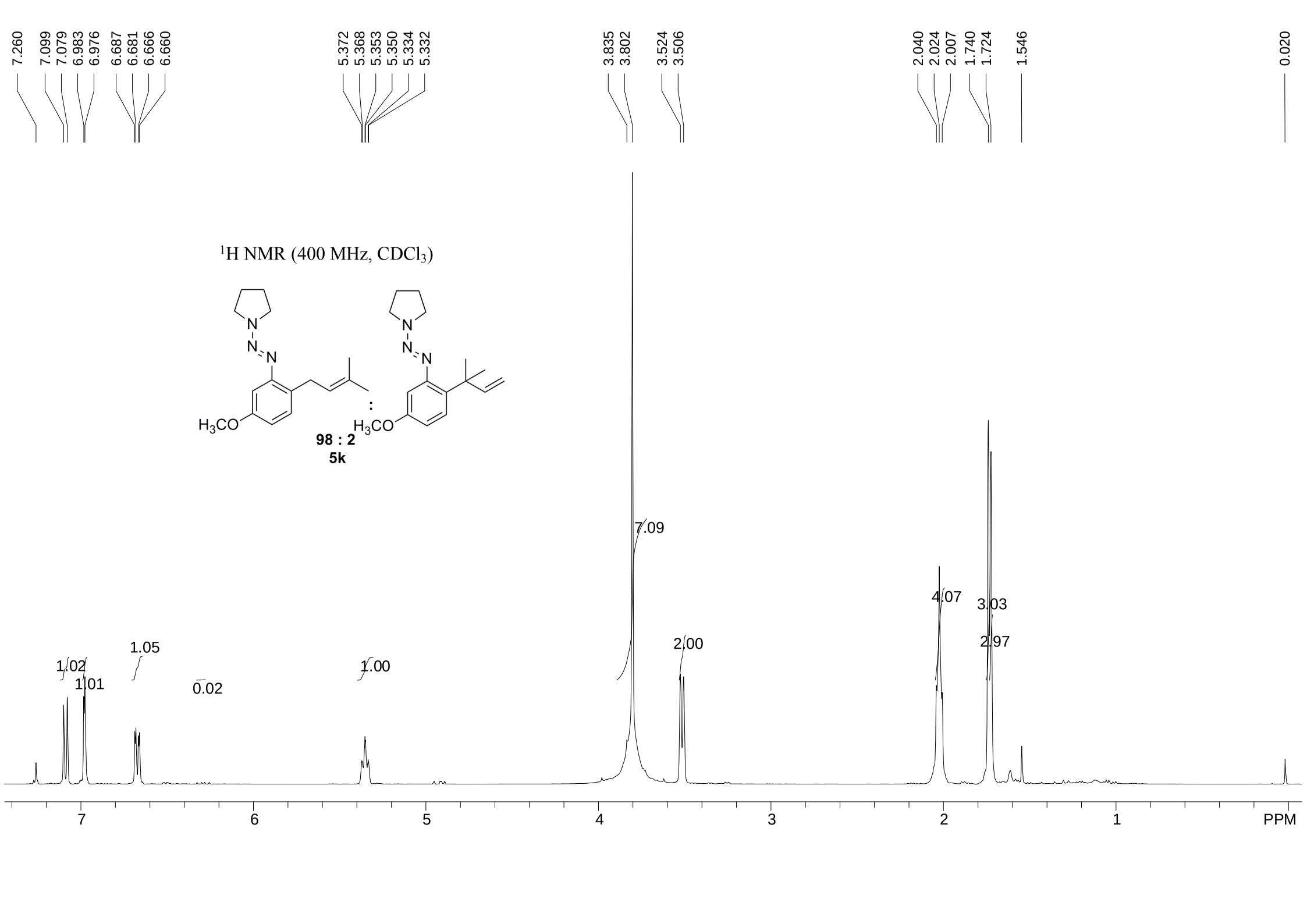

152.704
151.932
147.896
142.450
136.594
133.185
133.109
130.989
130.658
130.223
122.086
120.072
119.969
118.080
116.679
110.233
107.326
107.190
77.311
77.000
76.680
50.977
47.375
41.324
29.147
27.807
25.713
23.957
23.451
17.812
^{13}C NMR (100 MHz, $CDCl_3$)
CN
32 : 68
5h
CN
160
140
120
100
80
60
40
20
PPM


7.260
7.178
7.089
7.070
6.916
6.897
5.382
5.367
5.364
5.346
3.802
3.546
3.527
2.317
2.039
2.023
2.006
1.740
1.725
1.578
1.552
0.019
^{1}H NMR (400 MHz, $CDCl_3$)
95 : 5
5i
0.98
1.00
1.05
0.05
1.00
0.11
4.31
2.01
3.28
4.16
3.07
3.04
7
6
5
4
3
2
1
0 PPM

^{13}C NMR (100 MHz, CDCl$_3$)
95 : 5
5i
148.289
135.783
132.883
131.121
129.155
126.055
124.108
117.049
77.315
77.000
76.683
29.268
25.753
25.740
23.796
21.102
17.820
140
120
100
80
60
40
20
PPM

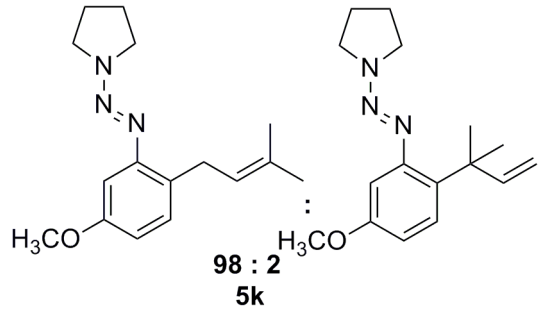

7.397
7.392
7.260
7.110
7.090
7.032
7.028
7.012
7.008
5.348
5.329
5.310
3.827
3.801
3.746
3.535
3.517
2.030
1.732
1.574
1.542
0.019
^{1}H NMR (400 MHz, $CDCl_3$)
99 : 1
5j
0.99
0.99
1.00
0.01
1.00
4.08
2.16
4.19
6.07
7
6
5
4
3
2
1
PPM

^{13}C NMR (100 MHz, CDCl$_3$)
99 : 1
5j
149.380
134.222
131.880
131.847
130.348
124.705
123.278
116.425
77.316
77.000
76.681
29.121
25.727
23.723
17.837
160
140
120
100
80
60
40
20
PPM


7.260
7.099
7.079
6.983
6.976
6.687
6.681
6.666
6.660
5.372
5.368
5.353
5.350
5.334
5.332
3.835
3.802
3.524
3.506
2.040
2.024
2.007
1.740
1.724
1.546
0.020
^{1}H NMR (400 MHz, $CDCl_3$)
98 : 2
5k
1.02
1.01
1.05
0.02
1.00
7.09
2.00
4.07
3.03
2.97
7
6
5
4
3
2
1
PPM

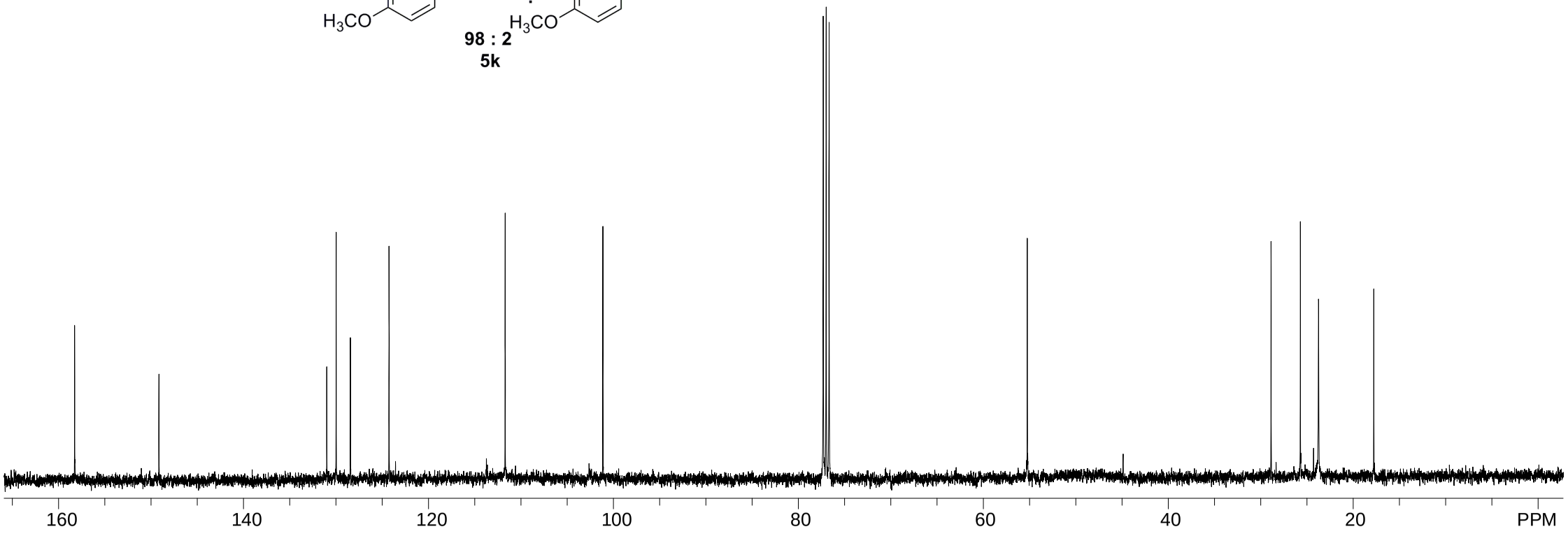
158.263
149.141
130.993
129.974
128.436
124.260
111.706
101.141
77.319
77.000
76.684
55.263
28.908
25.738
23.774
17.795

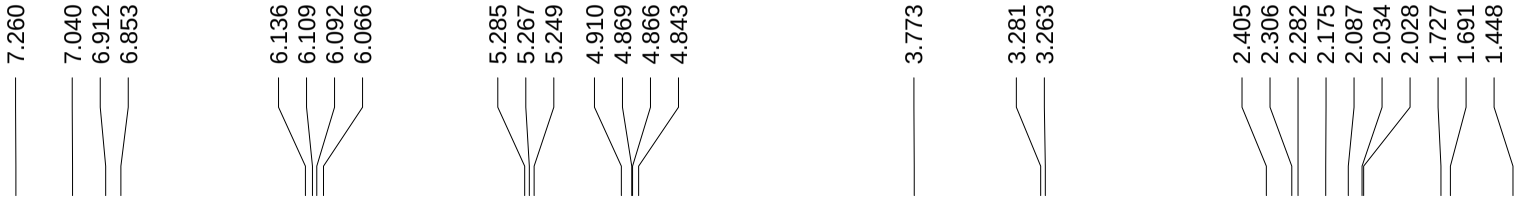
^{13}C NMR (100 MHz, $CDCl_3$)



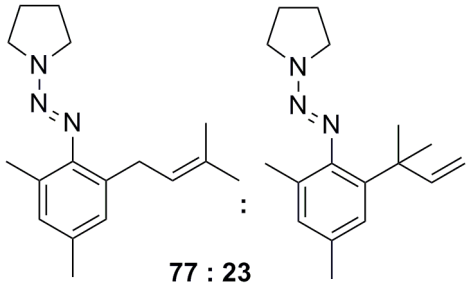
98 : 2

5k



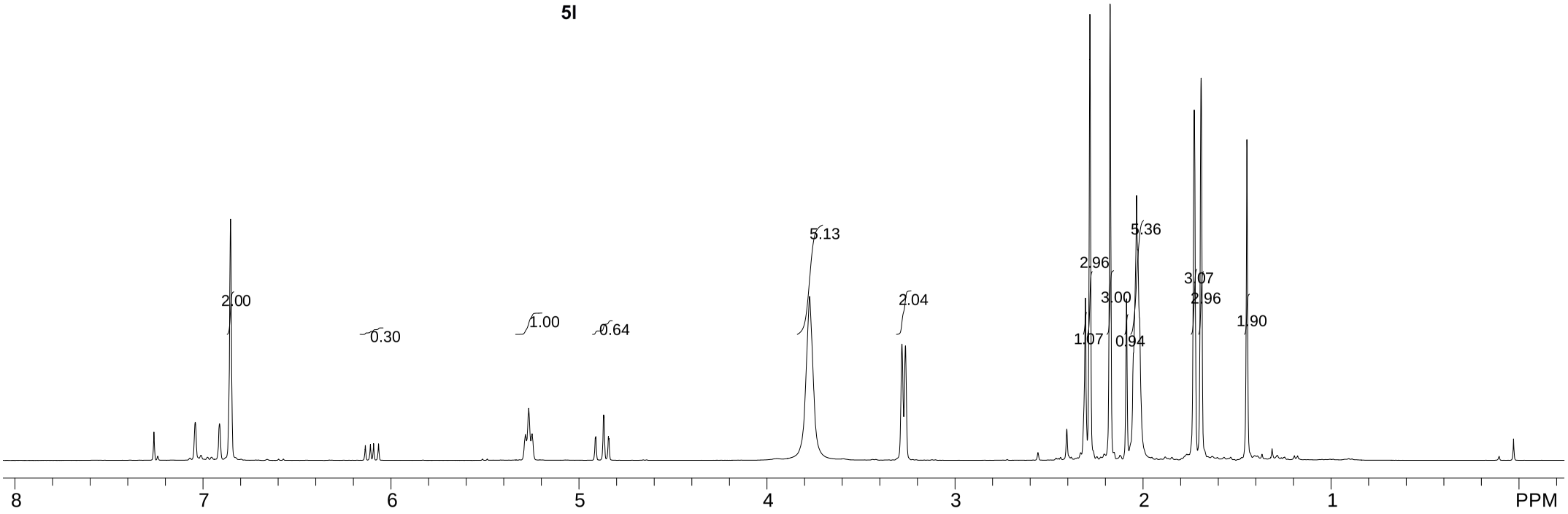


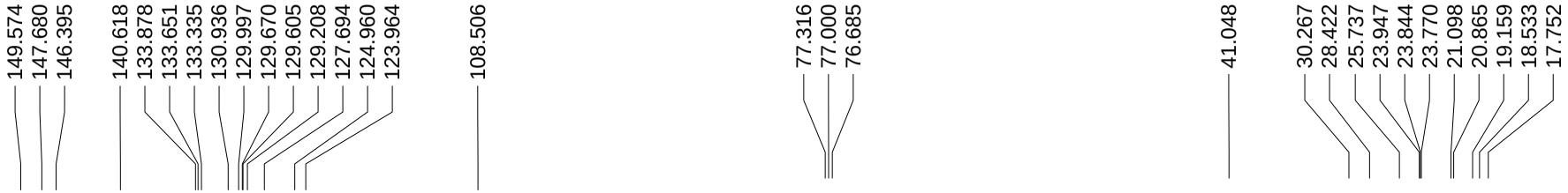
^{1}H NMR (400 MHz, $CDCl_3$)



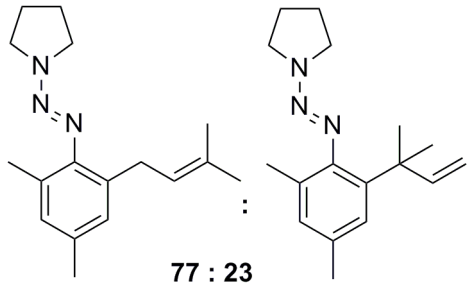
77 : 23

5l



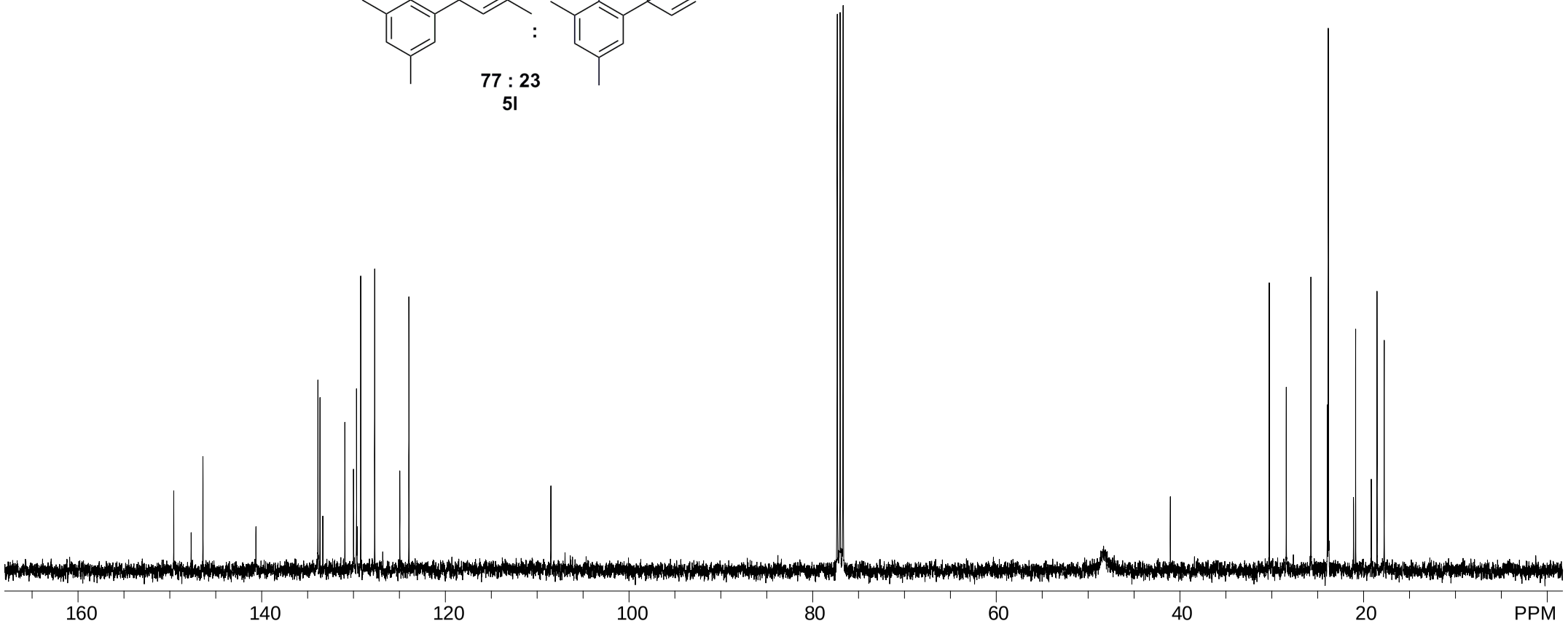


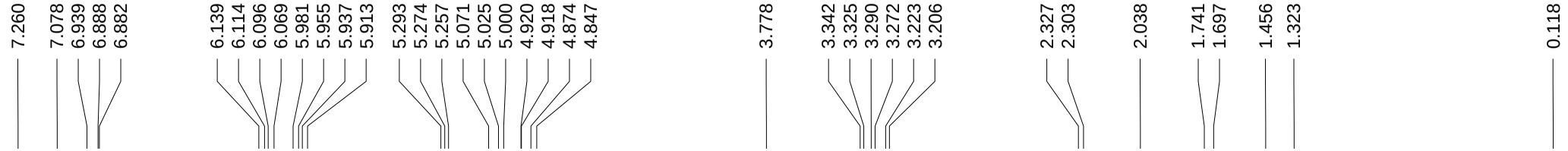
^{13}C NMR (100 MHz, $CDCl_3$)



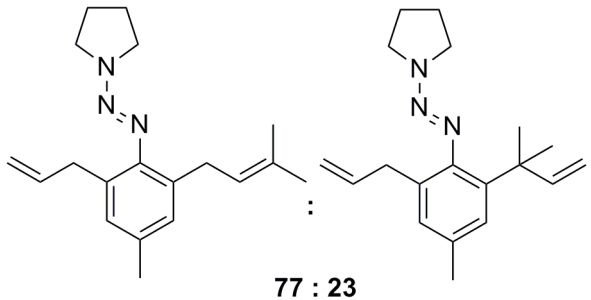
77 : 23

5l





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



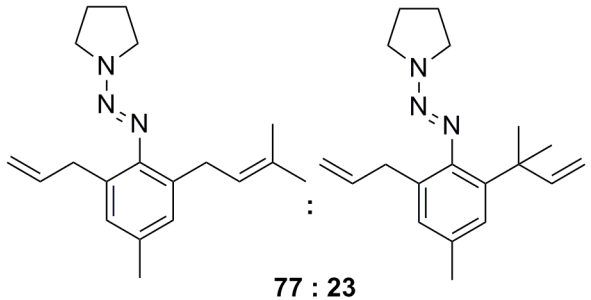
77 : 23
5m

149.490
147.419
146.039
138.218
140.752
138.041
134.084
133.619
133.499
131.921
131.814
131.069
128.710
128.182
128.061
125.359
123.784
114.919
114.816
108.385

77.311
77.000
76.679

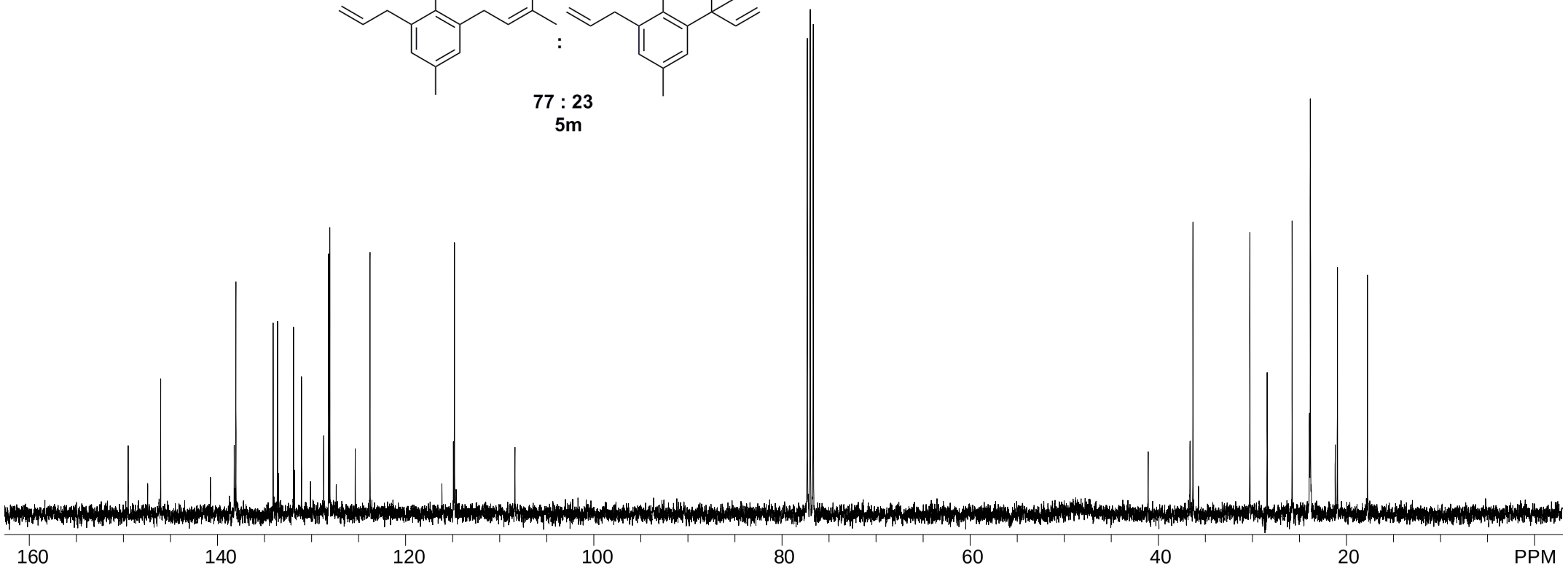
41.071
36.613
36.300
30.248
28.415
25.756
23.916
23.818
21.163
20.934
17.741

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

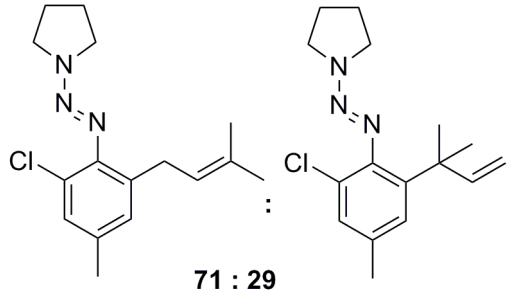


77 : 23

5m



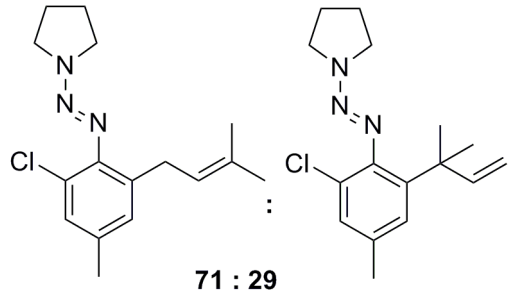
^{1}H NMR (400 MHz, $CDCl_3$)



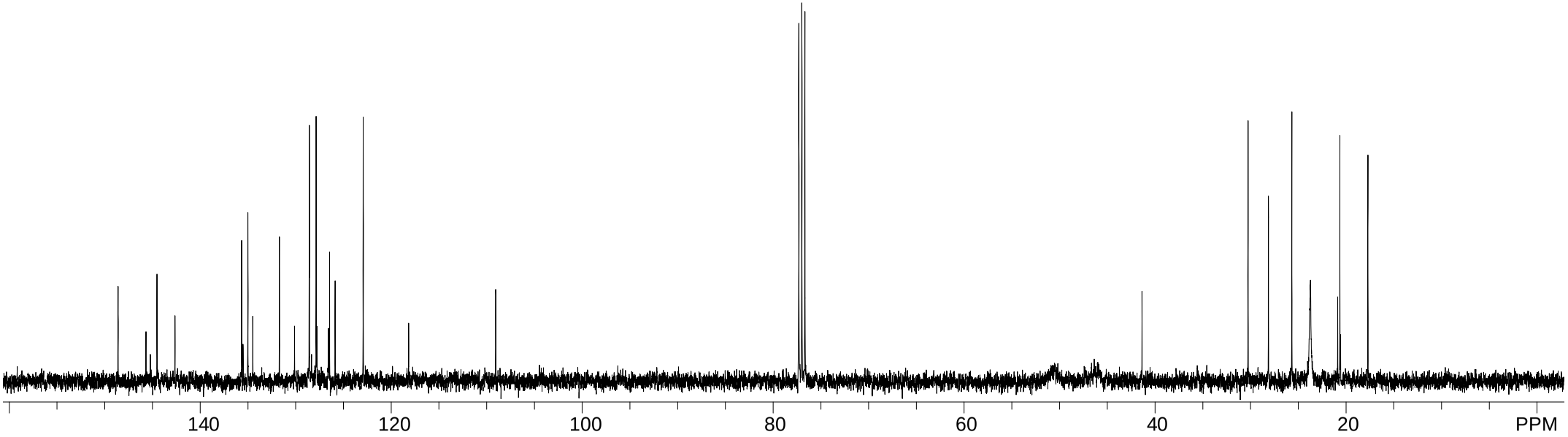
71 : 29
5n

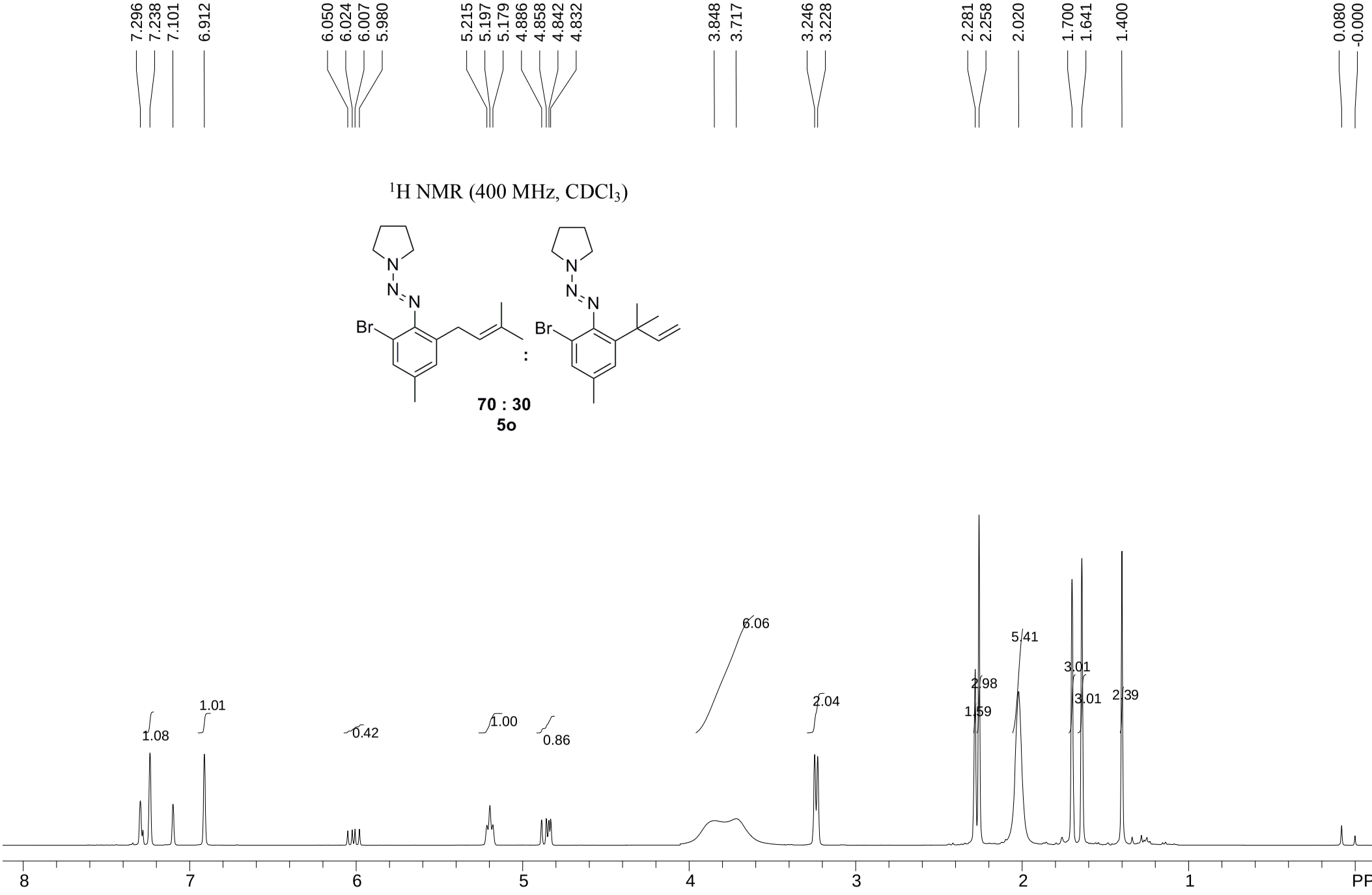
148.605
145.682
144.527
142.641
135.651
135.004
134.487
131.699
130.120
128.563
127.857
126.453
125.867
122.929
118.167
109.048
77.313
77.000
76.682
41.371
30.260
28.127
25.670
23.727
20.870
20.642
20.565
17.700

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



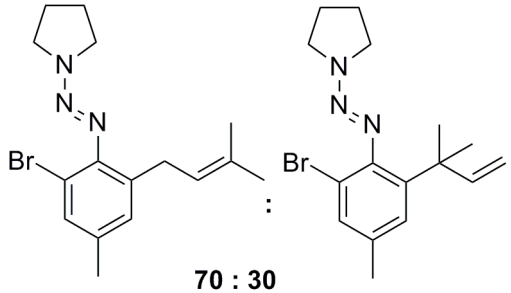
71 : 29
5n




7.296
7.238
7.101
6.912
6.050
6.024
6.007
5.980
5.215
5.197
5.179
4.886
4.858
4.842
4.832
3.848
3.717
3.246
3.228
2.281
2.258
2.020
1.700
1.641
1.400
0.080
-0.000
1H NMR (400 MHz, CDCl3)
Br
Br
70 : 30
5o
1.08
1.01
0.42
1.00
0.86
6.06
2.04
2.98
1.59
5.41
3.01
3.01
2.39
8
7
6
5
4
3
2
1
PPM

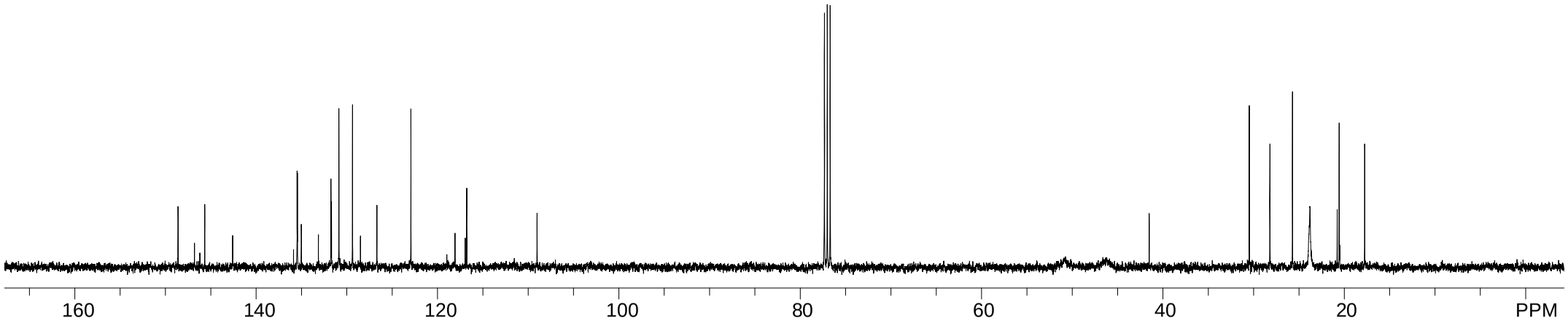
148.611
145.664
142.592
135.481
135.018
133.130
131.742
131.683
130.871
129.376
128.490
126.681
122.930
118.065
116.765
109.013
77.311
77.000
76.680
41.493
30.456
28.180
25.695
23.767
20.761
20.545
17.726

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



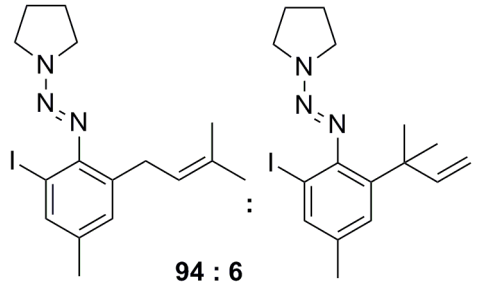
70 : 30

5o

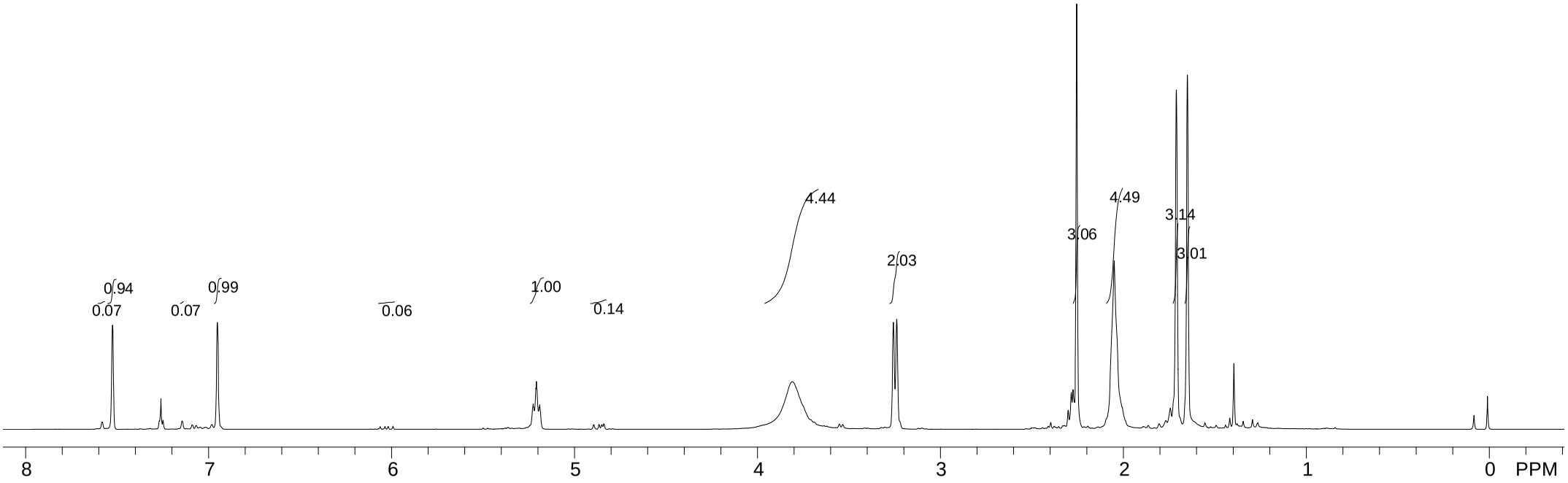


7.524 7.260 6.951 5.226 5.223 5.211 5.208 5.193 5.189 3.810 3.257 3.239 2.285 2.275 2.255 2.051 2.006 1.711 1.650 1.396 0.010

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

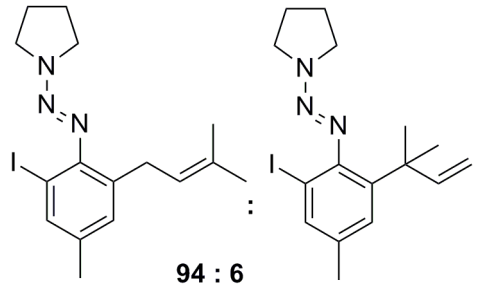


94 : 6
5p

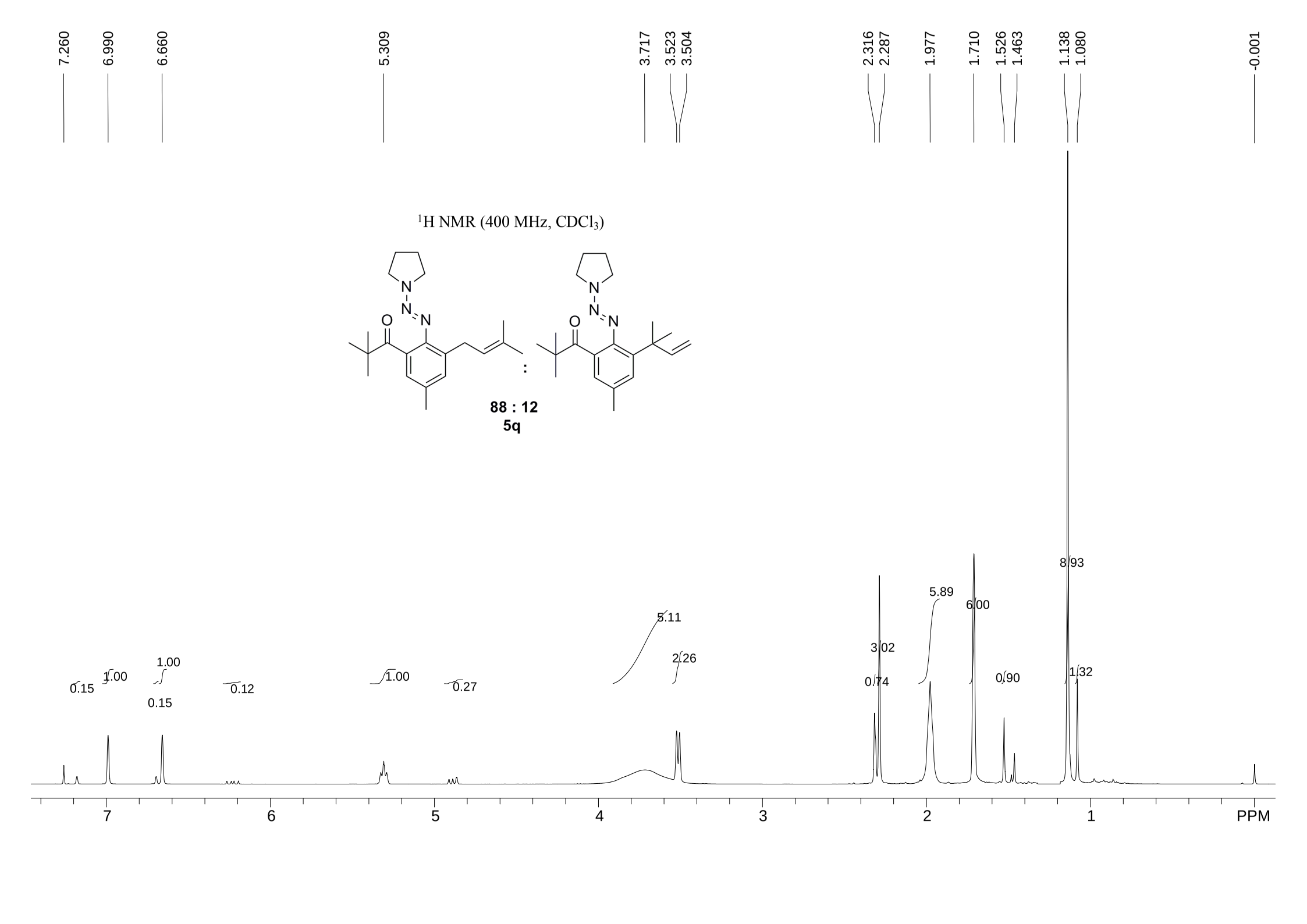


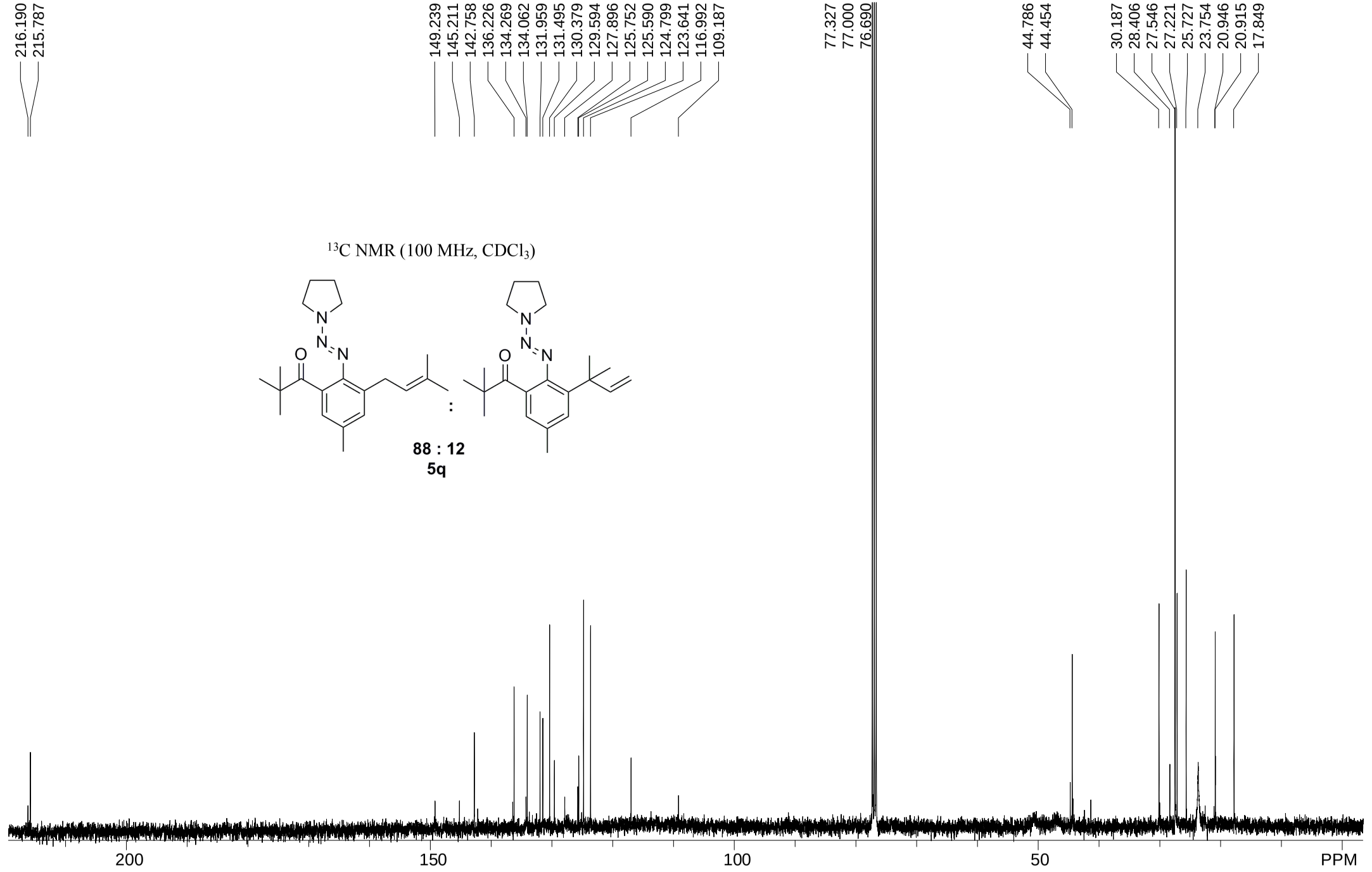
148.037
137.136
136.076
134.312
131.799
130.667
123.109
93.201
77.326
77.000
76.693
30.786
25.721
23.877
20.334
17.804

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



94 : 6
5p

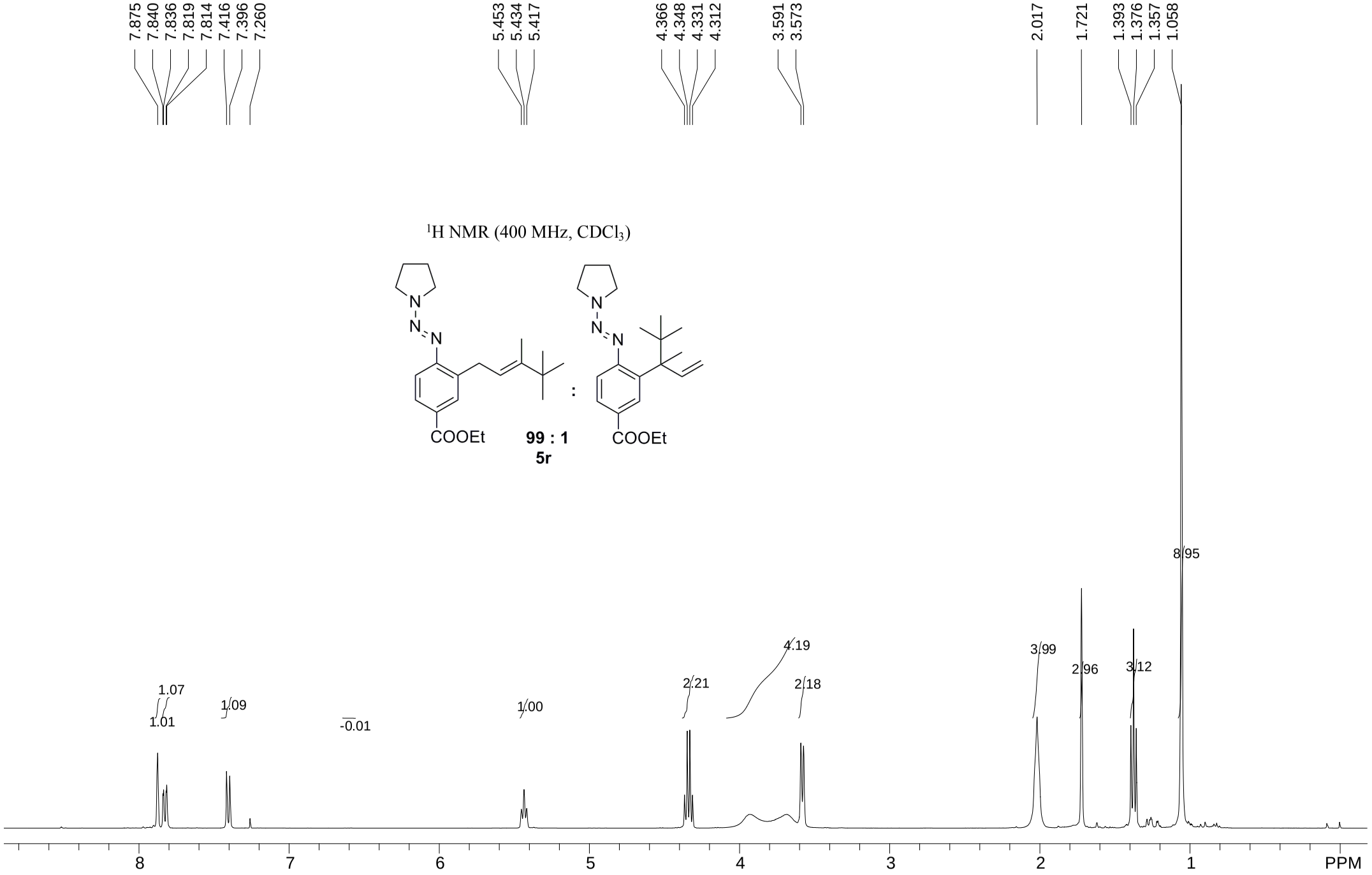

7.260
6.990
6.660
5.309
3.717
3.523
3.504
2.316
2.287
1.977
1.710
1.526
1.463
1.138
1.080
-0.001
^{1}H NMR (400 MHz, $CDCl_3$)
88 : 12
5q
0.15
1.00
1.00
0.15
0.12
1.00
0.27
5.11
2.26
3.02
0.74
5.89
6.00
0.90
8.93
1.32
7
6
5
4
3
2
1
PPM



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

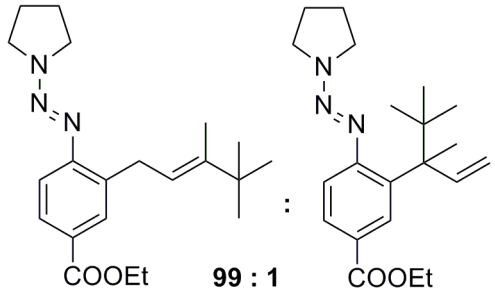
88 : 12

5q


7.875
7.840
7.836
7.819
7.814
7.416
7.396
7.260
5.453
5.434
5.417
4.366
4.348
4.331
4.312
3.591
3.573
2.017
1.721
1.393
1.376
1.357
1.058
1H NMR (400 MHz, CDCl3)
COOEt
99 : 1
5r
COOEt
1.07
1.01
1.09
-0.01
1.00
2.21
4.19
2.18
3.99
2.96
3.12
8.95
8
7
6
5
4
3
2
1
PPM

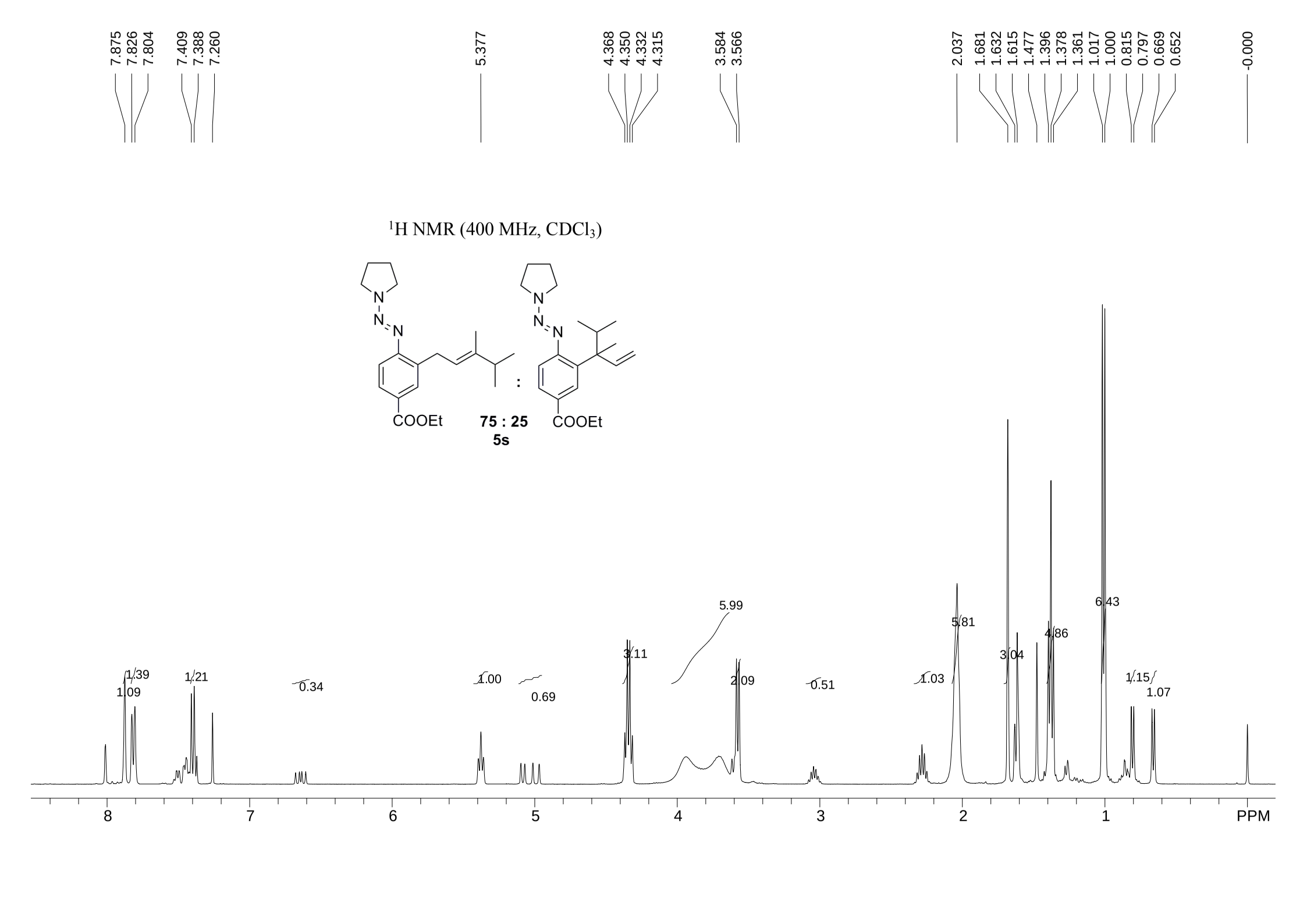
166.899
152.345
143.787
135.682
130.796
127.840
126.376
119.680
115.982
77.327
77.000
76.689
60.452
50.917
46.423
36.135
29.705
29.068
23.964
23.712
14.300
12.881

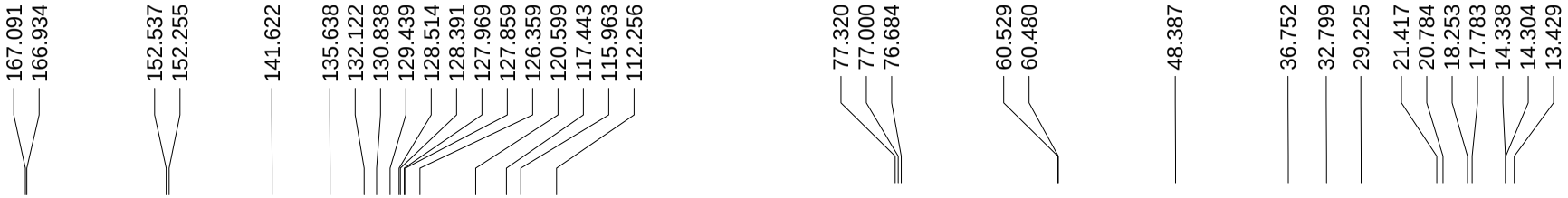
^{13}C NMR (100 MHz, $CDCl_3$)



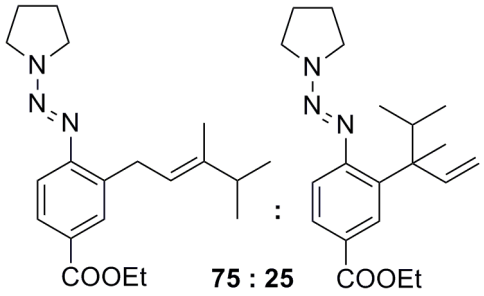
99 : 1

5r


7.875
7.826
7.804
7.409
7.388
7.260
5.377
4.368
4.350
4.332
4.315
3.584
3.566
2.037
1.681
1.632
1.615
1.477
1.396
1.378
1.361
1.017
1.000
0.815
0.797
0.669
0.652
-0.000
1H NMR (400 MHz, CDCl3)
COOEt
75 : 25
5s
COOEt
1.09
1.39
1.21
0.34
1.00
0.69
3.11
5.99
2.09
0.51
1.03
5.81
3.04
4.86
6.43
1.15
1.07
8
7
6
5
4
3
2
1
PPM

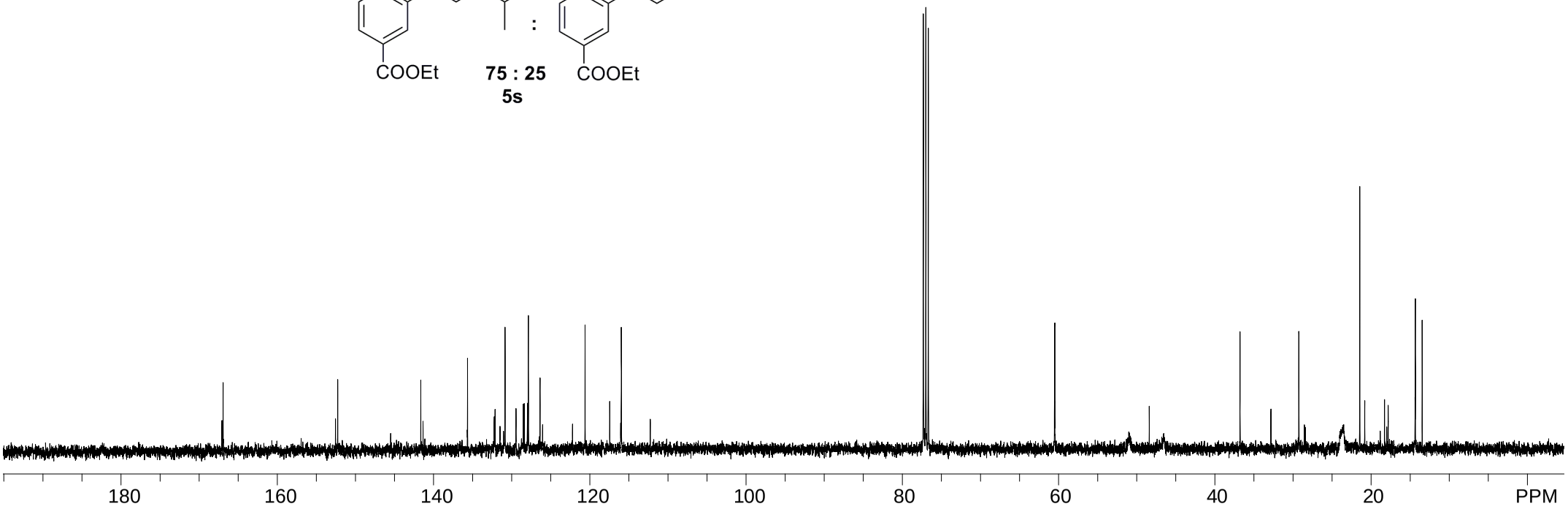


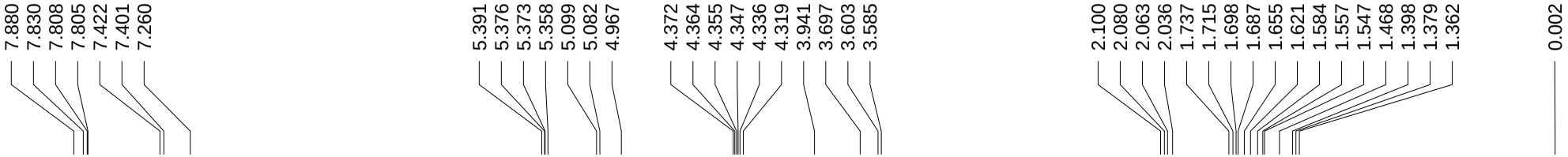
^{13}C NMR (100 MHz, $CDCl_3$)



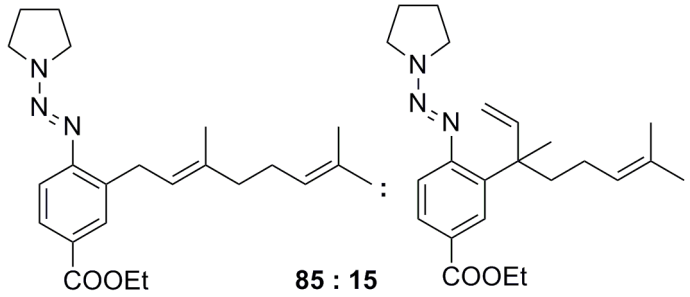
75 : 25

5s





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

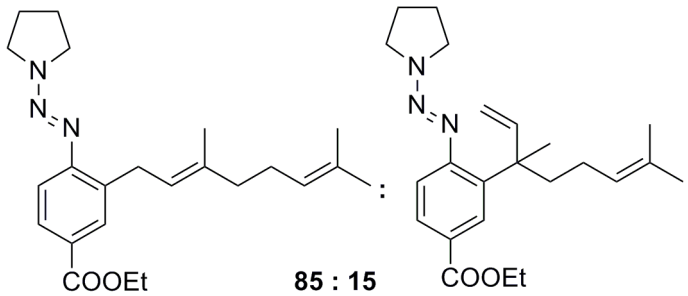


85 : 15

5t

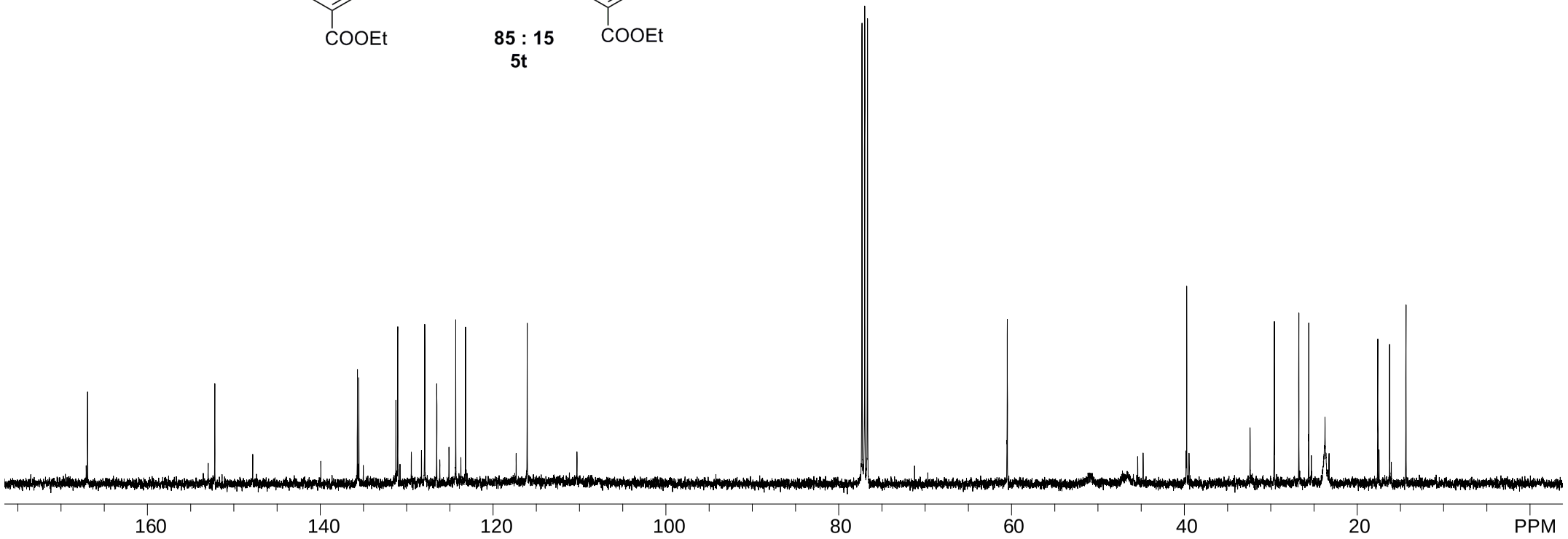
166.930
152.207
135.704
135.527
131.237
131.025
127.906
126.519
124.319
123.180
116.050
77.310
77.000
76.678
60.503
39.733
32.393
29.579
26.741
25.625
25.587
23.718
17.604
16.238
14.338

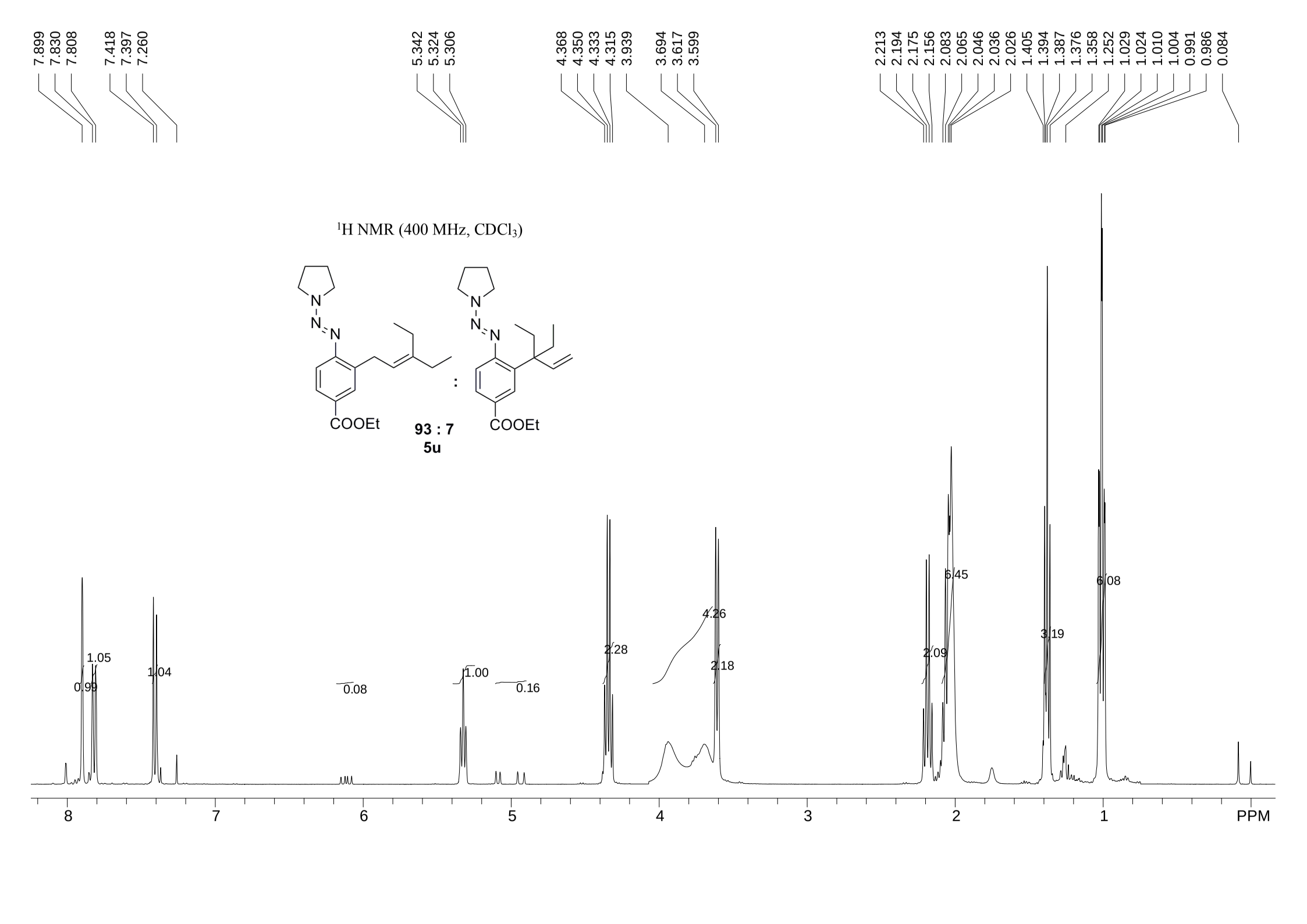
^{13}C NMR (100 MHz, $CDCl_3$)



85 : 15

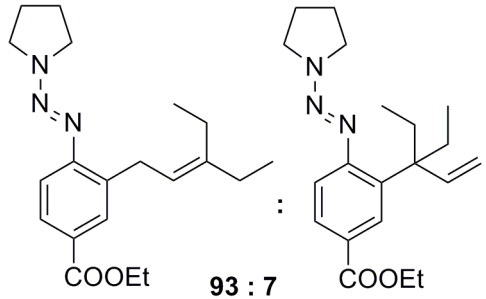
5t




7.899
7.830
7.808
7.418
7.397
7.260
5.342
5.324
5.306
4.368
4.350
4.333
4.315
3.939
3.694
3.617
3.599
2.213
2.194
2.175
2.156
2.083
2.065
2.046
2.036
2.026
1.405
1.394
1.387
1.376
1.358
1.252
1.029
1.024
1.010
1.004
0.991
0.986
0.084
1H NMR (400 MHz, CDCl3)
N
N
N
COOEt
:
COOEt
93 : 7
5u
1.05
0.99
1.04
0.08
1.00
0.16
2.28
4.26
2.18
2.09
6.45
3.19
6.08
8
7
6
5
4
3
2
1
PPM

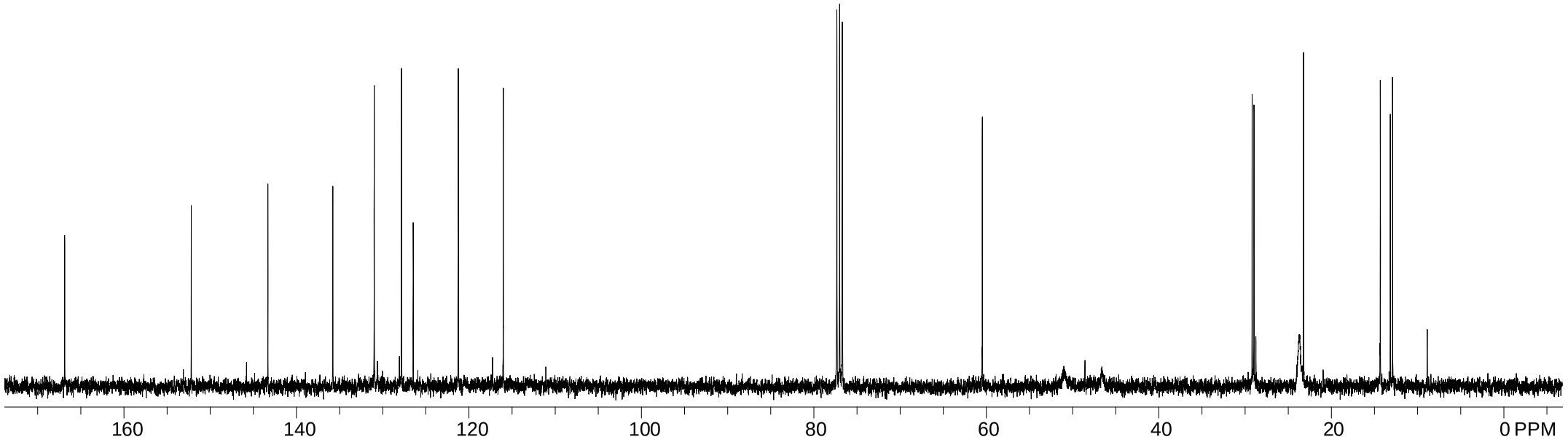
166.873
152.199
143.310
135.781
130.976
127.822
126.460
121.228
116.013
77.320
77.000
76.683
60.436
29.144
28.926
23.684
23.542
23.185
14.280
13.109
12.856

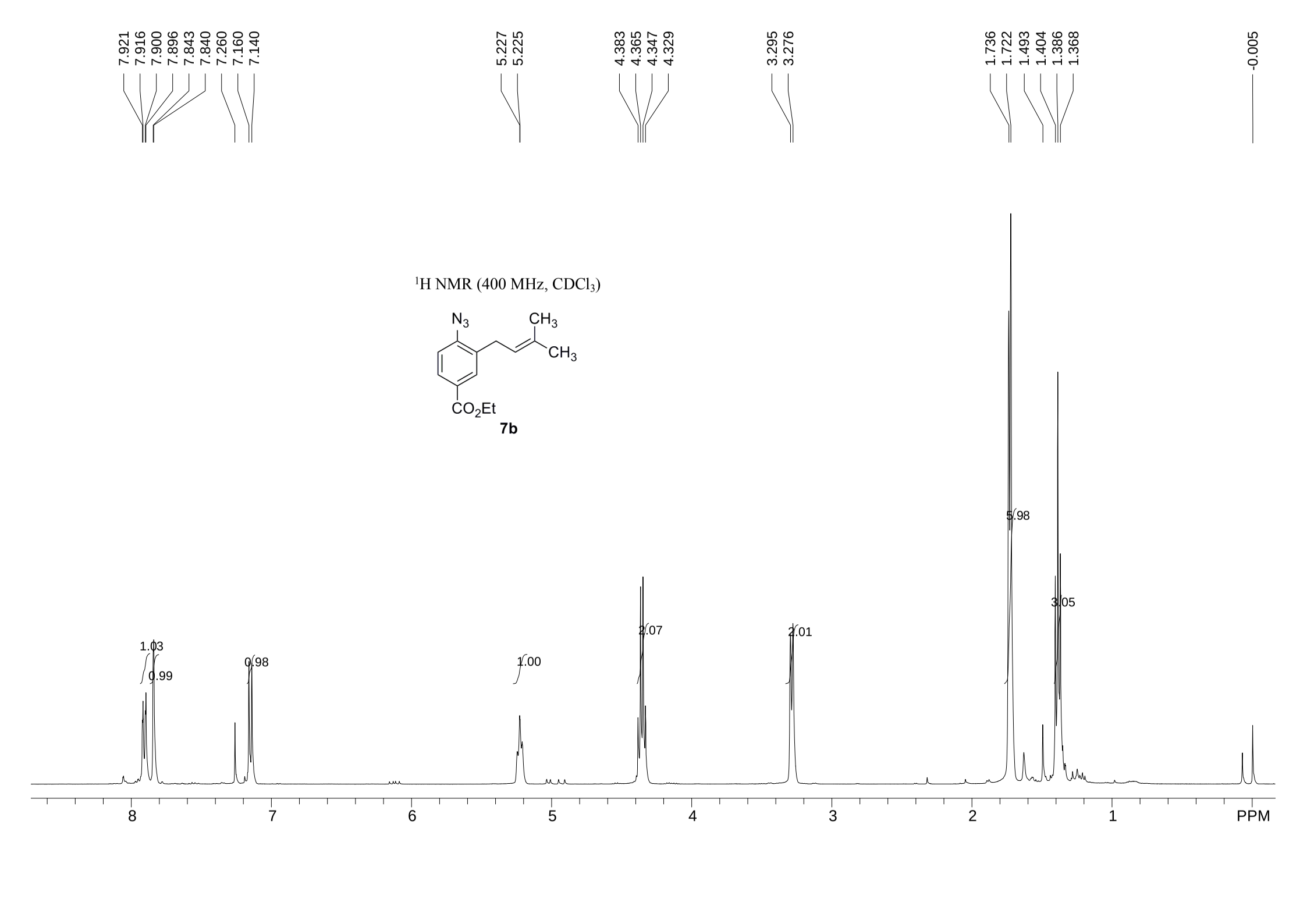
^{13}C NMR (100 MHz, $CDCl_3$)

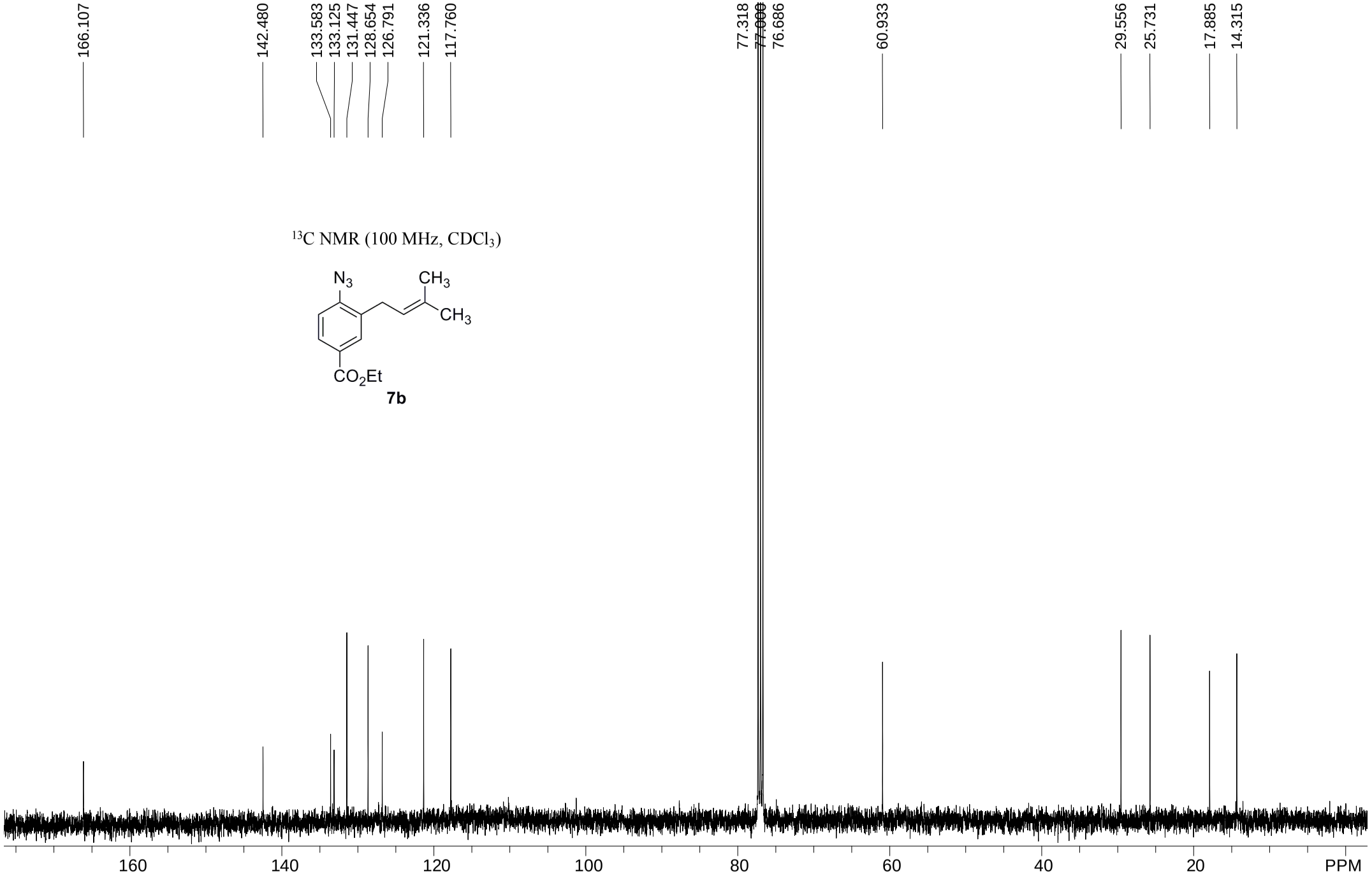


93 : 7

5u

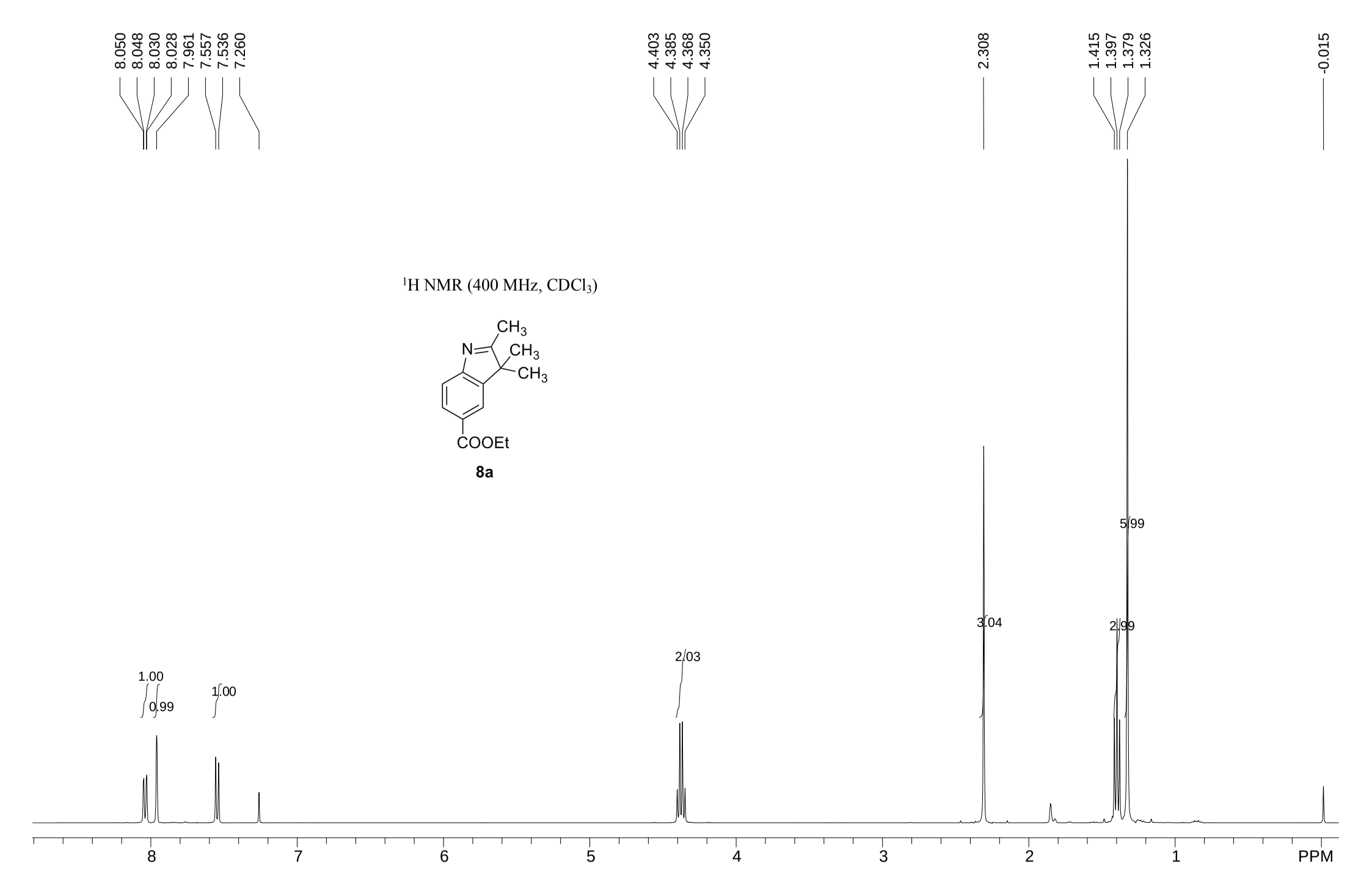


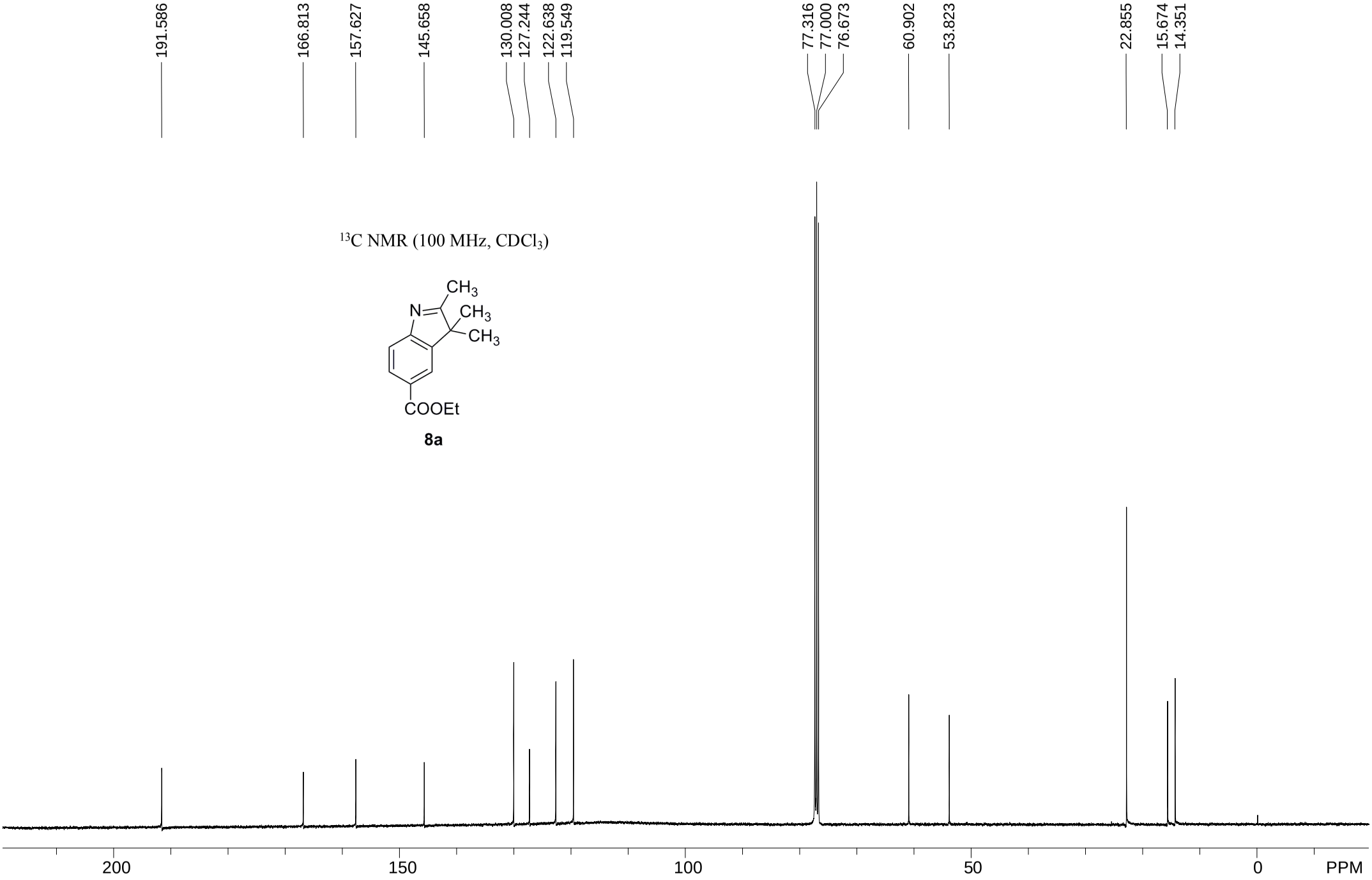

7.921
7.916
7.900
7.896
7.843
7.840
7.260
7.160
7.140
5.227
5.225
4.383
4.365
4.347
4.329
3.295
3.276
1.736
1.722
1.493
1.404
1.386
1.368
-0.005
1H NMR (400 MHz, CDCl3)
N3
CH3
CH3
CO2Et
7b
1.03
0.99
0.98
1.00
2.07
2.01
5.98
3.05
8
7
6
5
4
3
2
1
PPM

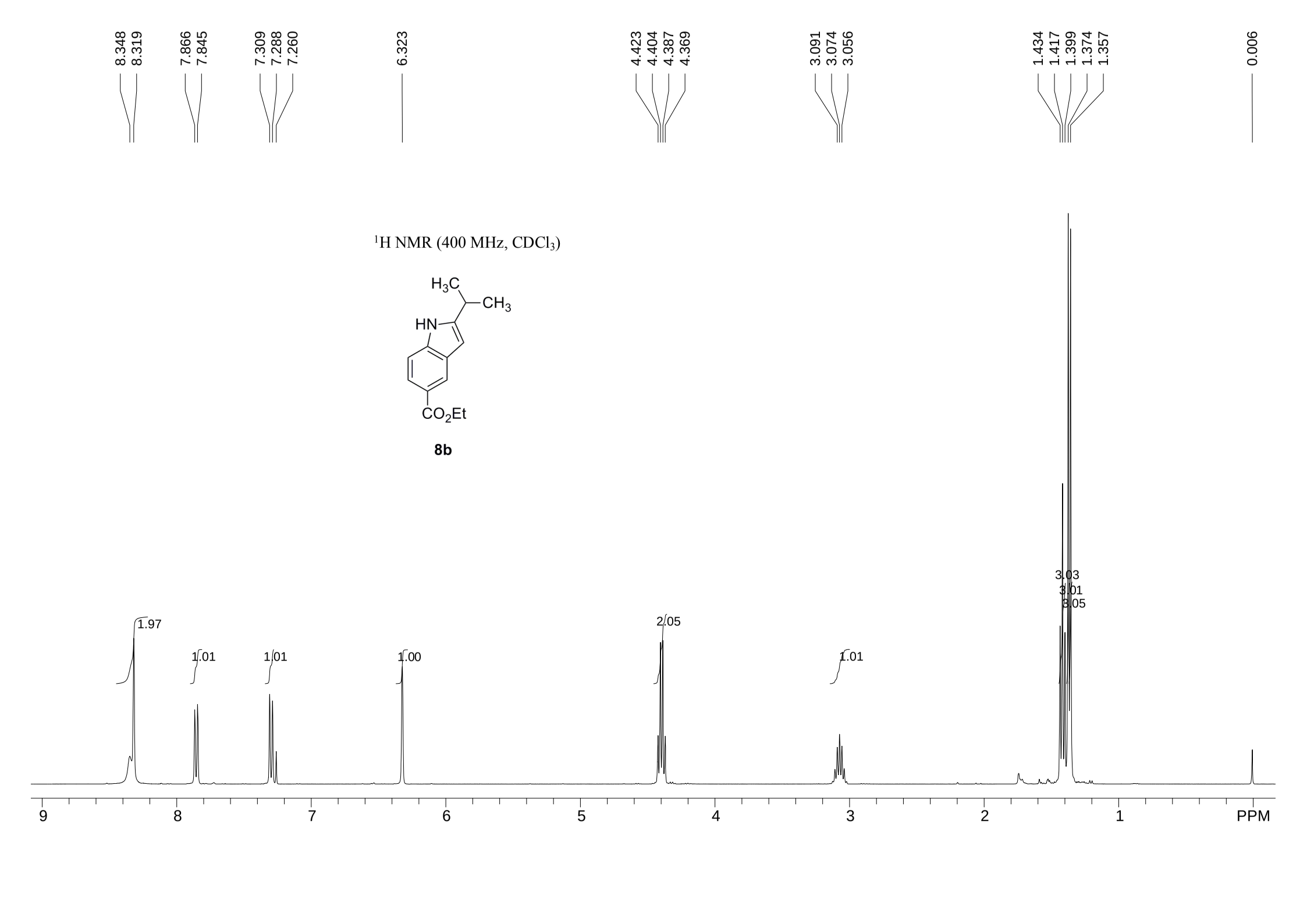


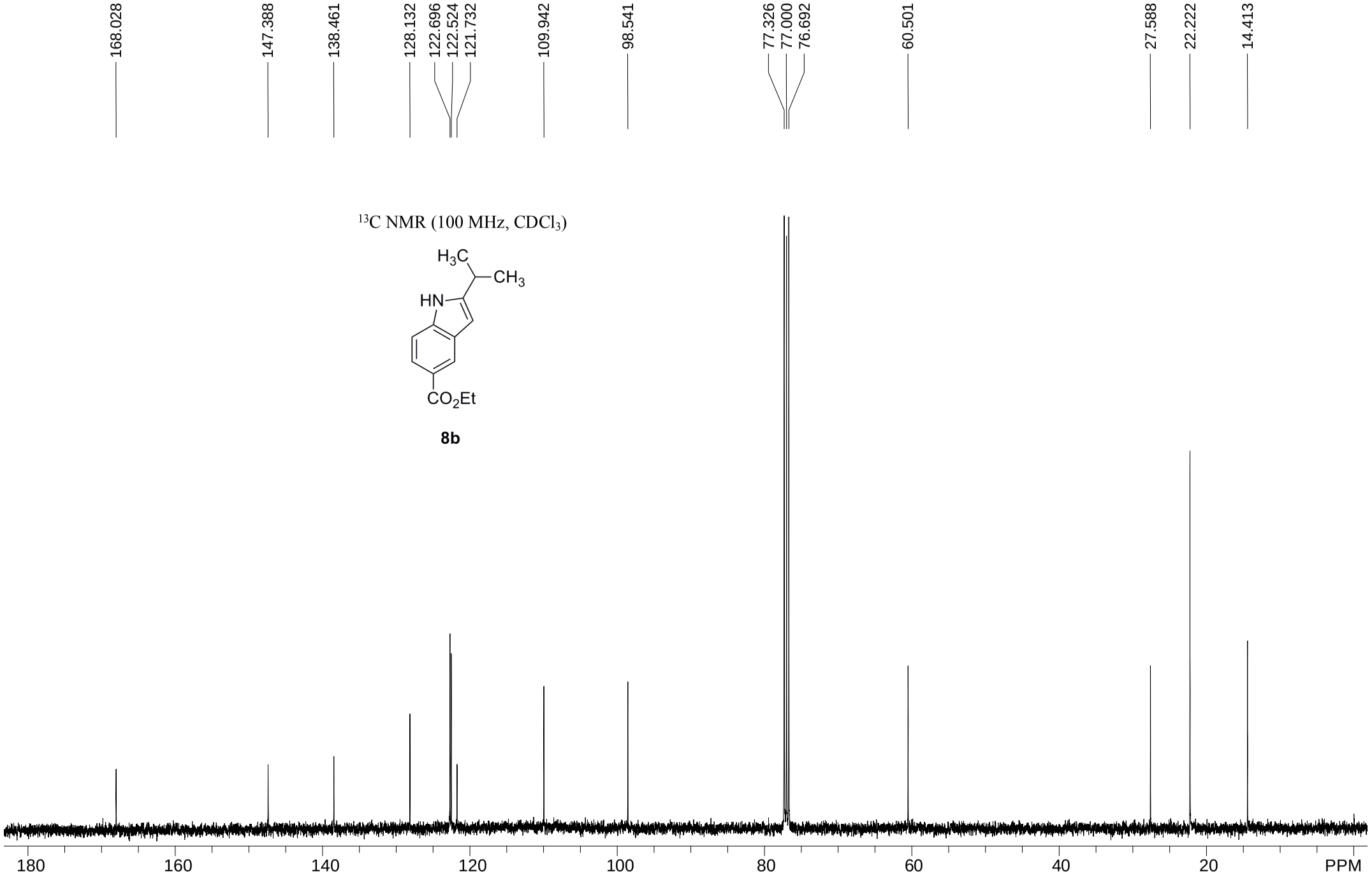
^{13}C NMR (100 MHz, $CDCl_3$)

7b


8.050
8.048
8.030
8.028
7.961
7.557
7.536
7.260
4.403
4.385
4.368
4.350
2.308
1.415
1.397
1.379
1.326
-0.015
1H NMR (400 MHz, CDCl3)
CH3
N
CH3
CH3
COOEt
8a
1.00
0.99
1.00
2.03
3.04
2.99
5.99
8
7
6
5
4
3
2
1
PPM


191.586
166.813
157.627
145.658
130.008
127.244
122.638
119.549
77.316
77.000
76.673
60.902
53.823
22.855
15.674
14.351
^{13}C NMR (100 MHz, $CDCl_3$)
CH_3
N
CH_3
CH_3
COOEt
8a
200
150
100
50
0
PPM


8.348
8.319
7.866
7.845
7.309
7.288
7.260
6.323
4.423
4.404
4.387
4.369
3.091
3.074
3.056
1.434
1.417
1.399
1.374
1.357
0.006
^{1}H NMR (400 MHz, $CDCl_3$)
H_3C
CH_3
HN
CO_2Et
8b
1.97
1.01
1.01
1.00
2.05
1.01
3.03
3.01
3.05
9
8
7
6
5
4
3
2
1
PPM


168.028
147.388
138.461
128.132
122.696
122.524
121.732
109.942
98.541
77.326
77.000
76.692
60.501
27.588
22.222
14.413
^{13}C NMR (100 MHz, $CDCl_3$)
H_3C
CH_3
HN
CO_2Et
8b
180
160
140
120
100
80
60
40
20
PPM