Synthesis of Carbinoxamine via α-C(sp^3)-H 2-pyridylation of *O*, *S* or *N*-containing compounds enabled by non-D-A-type super organoreductant and sulfoxide- or sulfide-HAT-reagents

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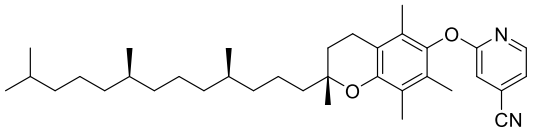
1. General Information

All reactions were carried out under atmospheric pressure. Solvents were pre-dried over activated 4Å molecular sieves and heated to reflux over calcium hydride or Mg turnings and iodine crystals (PhCN, CH_3CN, DCM, Et_3N, THF, DMF, PhCl, DMSO, MeOH) under argon atmosphere and collected by distillation. Aldehydes were used with purification as commercially available. Aldehydes, ketones, imines and other chemicals without notes in experimental section were purchased from commercial sources. All reactions were performed with SemiLEDs lamps (C35LU-60), the glass reaction tube was placed 5 cm away from LEDs. All reactions were monitored by thin layer chromatography. Purification of reaction products were carried out by flash chromatography on silica gel or aluminum oxide active neutral. Chemical yields refer to pure isolated substances. All work-up and purification procedures were carried out with reagent-grade solvents in air. ^{1}H, ^{19}F decoupled, $^{13}C\{^{1}H\}$ NMR spectra were recorded on a Bruker 400/500 spectrometer; Chemical shifts are reported in δ units relative to $CDCl_3$ [^{1}H δ = 7.26, ^{13}C δ = 77.16] and d^6-DMSO [^{1}H δ = 2.50, ^{13}C δ = 39.50]. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF (Waters Corporation). Fluorescence Spectrum was recorded on an F-4600 spectrometer.

2. Experimental procedures

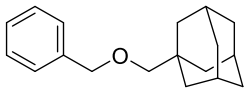
2.1 Synthesis and Characterization of 1p, 2g, 2h, 4a-d_6 and 4q-d_2

Compounds **1p**, **2g** and **2h** were synthesized according to literature procedures.[1]



2-(((*R*)-2,5,7,8-Tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)isonicotinonitrile (1p)

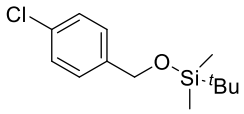
To a suspension of NaH (60% in minerals oil) (20 mmol, 2 equiv) in DMF (15 mL) at 0 °C was added Vitamin E (11 mmol, 1.1 equiv) under an argon atmosphere. After stirring for 5 min, a solution of 2-bromoisonicotinonitrile (10 mmol, 1 equiv) in DMF (10 mL) was added dropwise. After heating up to 80 °C the reaction mixer was further stirred at the same temperature for 14 h and quenched by adding saturated aq. $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the product as a yellow oil (3.7 g, 70%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.33 (d, J = 5.10 Hz, 1H), 7.14-7.12 (m, 1H), 6.99 (s, 1H), 2.61 (t, J = 6.70 Hz, 2H), 2.11 (s, 3H), 1.98 (s, 3H), 1.94 (s, 3H), 1.88-1.75 (m, 2H), 1.60-1.04 (m, 24H), 0.87-0.84 (m, 12H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.5, 149.7, 149.7, 142.0, 127.4, 125.7, 123.7, 123.3, 118.7, 118.0, 116.6, 112.4, 75.3, 40.3, 39.5, 37.6, 37.6, 37.4, 33.0, 32.9, 31.1, 28.1, 25.0, 24.6, 24.1, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.2, 12.3, 12.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{35}H_{53}N_2O_2^+$ 533.4102, found 533.4102.



1-((Benzyloxy)methyl)adamantane (2g)

To a suspension of NaH (60% in minerals oil) (20 mmol, 2 equiv) in DMF (15 mL) at 0 °C was added 1-adamantanemethanol (11 mmol, 1.1 equiv) under an argon atmosphere. After stirring for 5 min, a solution of (bromomethyl)benzene (10 mmol, 1 equiv) in DMF (10 mL) was added dropwise. After heating up to 80 °C the reaction mixer was further stirred at the same temperature for 14 h and quenched by adding saturated *aq.* $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the product as a yellow oil (1.9 g, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36-7.27 (m, 5H), 4.50 (s, 2H), 3.03 (s, 2H), 1.97 (s, 3H), 1.73-1.57 (m, 12H).

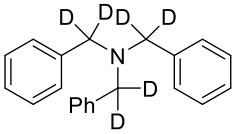
$^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 139.3, 128.4, 127.4, 127.4, 81.4, 73.3, 39.9, 37.7, 34.2, 28.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{25}O^+$ 257.1905, found 257.1910.



***tert*-Butyl((4-chlorobenzyl)oxy)dimethylsilane (2h)**[2]

To a suspension of NaH (60% in minerals oil) (20 mmol, 2 equiv) in DMF (15 mL) at 0 °C was added 4-chlorobenzyl alcohol (11 mmol, 1.1 equiv) under an argon atmosphere. After stirring for 5 min, a solution of TBSCl (10 mmol, 1 equiv) in DMF (10 mL) was added dropwise. After heating up to 80 °C the reaction mixer was further stirred at the same temperature for 14 h and quenched by adding saturated aq. $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the product as a yellow oil (1.9 g, 74%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.24 (m, 4H), 4.70 (s, 2H), 0.94 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 140.1, 132.6, 128.5, 127.5, 64.4, 26.1, 18.5, -5.1.

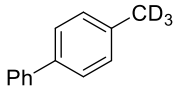
Compounds **4a-*d*$_6$** and **4q-*d*$_2$** were synthesized according to literature procedures.[3-4]



tris(phenylmethyl-d_2)amine

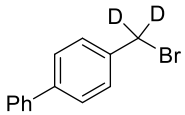
***tris*(Phenylmethyl-*d*$_2$)amine (4a-*d*$_2$)**

To a clarified of ^{t}BuOK (22.5 mmol, 1.5 equiv) in DMSO-d_6 (20 mL) was added tribenzylamine (15 mmol, 1.0 equiv) under an argon atmosphere. After heating up to 30 ^{o}C the reaction mixer was further stirred at the same temperature for 6 h and quenched by adding saturated *aq*. $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the product as white solid (4.3 g, 99%) yield, 94% D-rate[1]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42-7.41 (m, 6H), 7.34-7.31 (m, 6H), 7.25-7.22 (m, 3H), 3.57-3.52 (m, 0.4H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 139.7, 128.9, 128.4, 127.0, 57.7-57.0 (m). HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{16}D_6N^+$ 294.2129, found 294.2132.



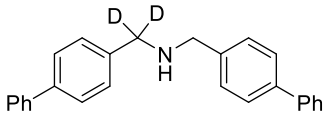
4-(Methyl-*d*$_3$)-1,1'-biphenyl (13)

To a clarified of ^{t}BuOK (22.5 mmol, 1.5 equiv) in DMSO-d_6 (20 mL) was added 4-methyl-1,1'-biphenyl (15 mmol, 1.0 equiv) under an argon atmosphere. After heating up to 30 ^{o}C the reaction mixer was further stirred at the same temperature for 6 h and quenched by adding saturated *aq*. $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the desired product as white solid (2.6 g, 99%) yield, 97% D-rate[1]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.60 (d, *J* = 8.20 Hz, 2H), 7.52 (d, *J* = 8.25 Hz, 2H), 7.45 (t, *J* = 7.50 Hz, 2H), 7.34 (t, *J* = 7.35 Hz, 1H), 7.27 (d, *J* = 8.20 Hz, 2H), 2.39-2.38 (m, 0.1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.3, 138.5, 137.1, 129.7, 128.9, 127.1(3C), 20.6-20.1 (m).



4-(Bromomethyl-*d*$_2$)-1,1'-biphenyl (14)

To a clarified of 4-(methyl-d_3)-1,1'-biphenyl (14.8 mmol, 1 equiv) in CCl_4 (30 mL) was added NBS (16.3 mmol, 1.1 equiv), $(PhCO_2)_2$ (14.8 mmol, 1.0 equiv) under an argon atmosphere. After heating up to 76 ^{o}C the reaction mixer was further stirred at the same temperature for 3 h and quenched by adding saturated aq. $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the desired product as white solid (1.8 g, 70%)[4]. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.59-7.57 (m, 4H), 7.48-7.43 (m, 4H), 7.38-7.34 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.5, 140.6, 136.8, 129.6, 129.0, 127.7, 127.3.



1-([1,1'-Biphenyl]-4-yl)-*N*-([1,1'-biphenyl]-4-ylmethyl)methan-*d*$_2$-amine (4q-*d*$_2$)

To a suspension of 4-(bromomethyl-d_2)-1,1'-biphenyl (10 mmol, 1.0 equiv) and [1,1'-biphenyl]-4-ylmethanamine (10 mmol, 1.0 equiv) in DCM (30 mL) was added Et_3N (20 mmol, 2.0 equiv). After heating up to 37 ^{o}C the reaction mixer was further stirred at the same temperature for 8 h and quenched by adding saturated *aq*. $NaHCO_3$. The crude product was extracted with AcOEt (3 × 20 mL). The combined organic extracts

were washed with brine, dried over Na_2SO_4 and concentrated by rotary evaporator. The residue was purified by flash column chromatography to afford the desired product as white solid (2.4 g, 67%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.61-7.57 (m, 8H), 7.46-7.43 (m, 8H), 7.34 (t, J = 7.35 Hz, 2H), 3.89 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 141.2 (2C), 140.0 (2C), 139.6 (2C), 139.5, 128.9 (2C), 128.8 (2C), 128.7 (2C), 127.3 (2C), 127.2, 52.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{26}H_{22}D_2N^+$ 352.2034, found 352.2028.

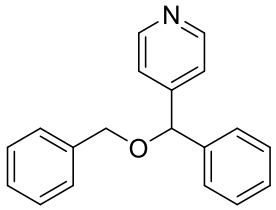
2.2 Synthesis and Characterization of 5-7

General Procedure 1 for the synthesis of 5-6 in CH_3CN:

CBZ6 (3 mol%, 3.9 mg), phenyl sulfoxide (1.2 mmol, 4 equiv) and compound **1** (0.3 mmol, 1 equiv) were weighed into an oven-dried 25 mL Schlenk tube. The reaction tube was purged with argon. Ethers or amine (1.5 mmol, 5 equiv) and dry MeCN (3 mL) were added sequentially in the Schlenk tube via syringe. Then the tube was placed 5 cm away from LED column (18 W = 3 W×6), and stirred under the irradiation of 407 nm light. Upon consumption of nitrile (monitored by TLC), the reaction mixture was concentrated by rotavapor and purified by flash column chromatography on silica gel (PE/EA/DCM 3/1/1 to 1/1/1) to afford the pure product.

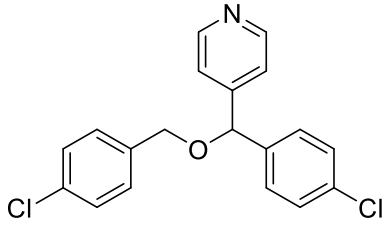
General Procedure 2 for the synthesis of 7 in DMSO without phenyl sulfoxide:

CBZ6 (1 mol%, 1.3 mg) and compound **1** (0.3 mmol, 1 equiv) were weighed into an oven-dried 25 mL Schlenk tube. The reaction tube was purged with argon. Ether or amine (0.75 or 1.8 mmol) and dry DMSO (1.2 mL) were added sequentially via syringe. Then the tube was placed 5 cm away from LED column (18 W = 3 W×6), and stirred under the irradiation of 407 nm light. Upon consumption of nitrile (monitored by TLC), the reaction mixture was concentrated by rotavapor and purified by flash column chromatography on silica gel (PE/EA/DCM 3/1/1 to 1/1/1) to afford the pure product.



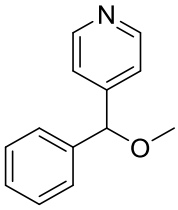
4-((Benzyloxy)(phenyl)methyl)pyridine (5a)

This compound was prepared according to the General Procedure 1 for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product, as a yellow oil (66.9 mg, 81%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (s, 2H), 7.39-7.30 (m, 12H), 5.40 (s, 1H), 4.52 (d, J = 11.90 Hz, 1H), 4.51 (d, J = 11.95 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.3, 149.9, 140.6, 137.9, 128.9, 128.6, 128.4, 128.0, 127.9, 127.5, 121.8, 81.3, 70.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NOS^+$ 276.1383, found 276.1392.



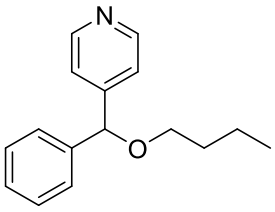
4-(((4-Chlorobenzyl)oxy)(4-chlorophenyl)methyl)pyridine (5b)

This compound was prepared according to the General Procedure 1 for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (74.3 mg, 72%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 4.55, 1.50 Hz, 2H), 7.35-7.32 (m, 4H), 7.28-7.26 (m, 6H), 5.35 (s, 1H), 4.48 (dd, *J* = 25.60, 12.00 Hz, 2H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 150.5, 150.2, 138.9, 136.1, 134.4, 133.9, 129.2,129.2, 128.9, 128.8, 121.6, 80.7, 70.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{15}Cl_2NONa^+$ 366.0428, found 366.0425.



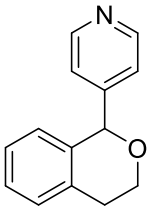
4-(Methoxy(phenyl)methyl)pyridine (5c)[5]

This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (44.8 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 4.55, 1.55 Hz, 2H), 7.37-7.30 (m, 5H), 7.28 (d, *J* = 6.00 Hz, 2H), 5.20 (s, 1H), 3.39 (s, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 151.1, 150.0, 140.5, 128.9, 128.3, 127.3, 121.6, 84.2, 57.2.



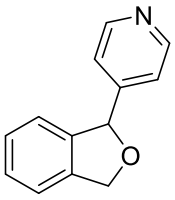
4-(Butoxy(phenyl)methyl)pyridine (5d)

This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (52.9 mg, 73%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.85 Hz, 2H), 7.36-7.34 (m, 1H), 7.33-7.30 (m, 3H), 7.30-7.27 (m, 3H), 5.29 (s, 1H), 3.48-3.41(m, 2H), 1.66-1.60 (m, 2H), 1.46-1.39 (m, 2H), 0.91 (t, J = 7.35 Hz, 3H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 151.7, 150.0, 141.2, 128.8, 128.2, 127.3, 121.7, 82.5, 69.2, 32.0, 19.6, 14.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{20}NO^+$ 242.1545, found 242.1556.



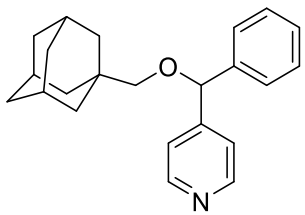
4-(Isochroman-1-yl)pyridine (5e)

This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (52 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.60 (d, J = 5.55 Hz, 2H), 7.27 (s, 2H), 7.23-7.18 (m, 2H), 7.12-7.09 (m, 1H), 6.74 (d, J = 7.75 Hz, 1H), 5.71 (s, 1H), 4.19-4.14 (m, 1H), 3.96-3.91 (m, 1H), 3.16-3.09 (m, 1H), 2.87-2.82 (m, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 150.7, 150.2, 135.6, 133.8, 129.2, 127.3, 126.7, 126.3, 123.7, 78.3, 64.0, 28.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{14}H_{14}NO^+$ 212.1075, found 212.1071.



4-(1,3-Dihydroisobenzofuran-1-yl)pyridine (5f)

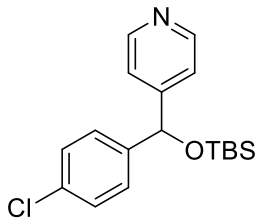
This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (44.4 mg, 75%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.59 (dd, J = 4.50, 1.55 Hz, 2H), 7.31-7.30 (m, 4H), 7.25-7.24 (m, 1H), 7.08 (d, J = 7.55 Hz, 1H), 6.15 (s, 1H), 5.37 (dd, J = 12.25, 2.65 Hz, 1H), 5.26 (dd, J = 12.10, 1.15 Hz, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 151.2, 150.2, 140.6, 138.8, 128.3, 127.9, 122.1, 121.4, 121.3, 84.7, 73.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{12}NO^+$198.0919, found 198.0927.



4-((Adamantan-1-ylmethoxy)(phenyl)methyl)pyridine (5g)

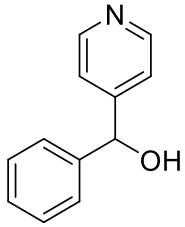
This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (62 mg, 62%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 4.50, 1.60 Hz, 2H), 7.36-7.31 (m, 4H), 7.29-7.27 (m, 3H), 5.21 (s, 1H), 3.00 (dd, J = 14.15, 8.6 Hz, 2H), 1.98 (s, 3H), 1.74-1.65 (m, 6H), 1.59 (d, J =

1.56 Hz, 6H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 152.0, 149.9, 141.4, 128.7, 128.0, 127.2, 121.7, 82.4, 80.0, 39.9, 37.3, 34.3, 28.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{27}NONa^+$356.1990, found 356.1975.



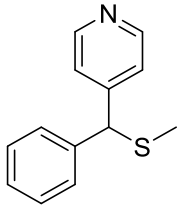
4-(((*tert*-Butyldimethylsilyl)oxy)(4-chlorophenyl)methyl)pyridine (5h)

This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (83.1 mg, 83%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 2H), 7.370-7.25 (m, 6H), 5.66 (s, 1H), 0.91 (s, 9H), 0.02 (s, 3H), -0.04 (s, 3H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 153.5, 150.0, 142.3, 133.6, 128.9, 127.9, 121.0, 75.2, 25.9, 18.4, -4.7, -4.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{18}H_{25}ClNOSi^+$334.1394, found 334.1390.



Phenyl(pyridin-4-yl)methanol (5i)

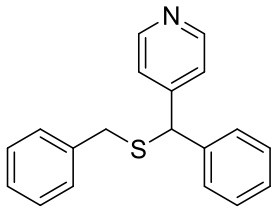
This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** and 0.15 mol of 1-dodecanethiol for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (42.8 mg, 77%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 4.60 Hz, 2H), 7.37-7.33 (m, 4H), 7.33-7.28 (m, 3H), 7.26 (s, 1H), 5.79 (s, 1H), 3.28(s, 1H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 152.8, 149.8, 142.9, 129.0, 128.4, 127.0, 121.4, 75.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{12}H_{12}NO^+$186.0919, found 186.0912.



4-((Methylthio)(phenyl)methyl)pyridine (6a)

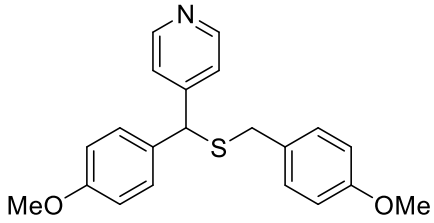
This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (48.4 mg, 75%). ^1H NMR (500 MHz,

$CDCl_3$) δ 8.56 (d, *J* = 2.85 Hz, 2H), 7.38-7.32 (m, 6H), 7.29-7.27 (m, 1H), 4.99 (s, 1H), 2.00 (s, 3H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 150.2, 139.7, 129.2, 128.9, 128.4, 127.9, 123.5, 55.3, 15.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}NS^+$216.0847, found 216.0813.



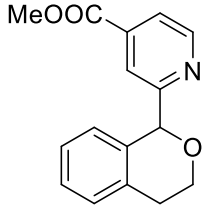
4-((Benzylthio)(phenyl)methyl)pyridine (6b)

This compound was prepared according to the General Procedure 1 for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (74.3 mg, 85%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 6.10 Hz, 2H), 7.31 (d, *J* = 4.35 Hz, 4H), 7.30-7.24 (m, 6H), 7.19 (d, *J* = 7.00 Hz, 2H), 4.83 (s, 1H), 3.56 (s, 2H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 150.2, 150.2, 139.5, 137.5, 129.1, 128.9, 128.7, 128.6, 127.9, 127.4, 123.6, 52.3, 36.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NS^+$ 292.1154, found 292.1170.



4-(((4-Methoxybenzyl)thio)(4-methoxyphenyl)methyl)pyridine (6c)

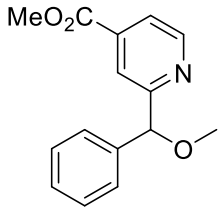
This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (84.4 mg, 80%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 2.85 Hz, 2H), 7.38-7.32 (m, 6H), 7.29-7.27 (m, 2H), 4.99 (s, 1H), 2.00 (s, 3H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 150.2, 139.7, 129.2, 128.9, 128.4, 127.9, 123.5, 55.3, 15.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{22}NO_2S^+$ 352.1371, found 352.1372.



Methyl 2-(isochroman-1-yl)isonicotinate (5j)

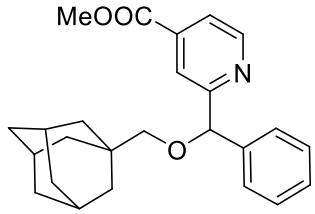
This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM

10/1/1 to 3/1/1) to give the product as a yellow oil (48.8 mg, 60%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (dd, *J* = 5.10, 0.80 Hz, 2H), 7.90 (dd, *J* = 1.40, 0.85 Hz, 1H), 7.78 (dd, *J* = 5.05, 1.60 Hz, 1H), 7.18 (d, *J* = 3.85 Hz, 2H), 7.10-7.06 (m, 1H), 6.92 (d, *J* = 7.65 Hz, 1H), 5.96 (s, 1H), 4.35-4.31 (m, 1H), 4.03-3.97 (m, 1H), 3.91 (s, 3H), 3.29-3.22 (m, 1H), 2.80 (dt, *J* = 16.35, 2.75 Hz, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 165.7, 163.0, 149.8, 138.4, 135.9, 133.6, 129.2, 127.1, 126.5, 126.3, 122.2, 122.0, 80.3, 64.6, 52.8, 28.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_3^+$ 270.1130, found 270.1123.



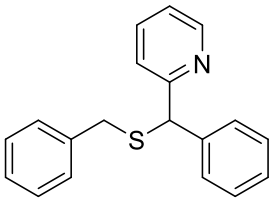
Methyl 2-(methoxy(phenyl)methyl)isonicotinate (5k)

This compound was prepared according to the General Procedure 1 for 48 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (69.5 mg, 90%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.67 (d, *J* = 5.00 Hz,1H), 8.07 (s, 1H), 7.70 (dd, *J* = 5.05 Hz, 1.55 Hz, 1H), 7.43 (d, *J* = 8.70 Hz, 2H), 7.43 (d, *J* = 7.25 Hz, 2H), 7.34-7.31 (m, 2H), 7.27-7.24 (m, 1H), 5.43 (s, 1H), 3.94 (s, 3H), 3.44 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.8, 163.1, 150.0, 140.5, 138.4, 128.7, 128.1, 127.1, 121.7, 119.9, 86.3, 57.3, 52.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{16}NO_3^+$ 258.1130, found 258.1135.



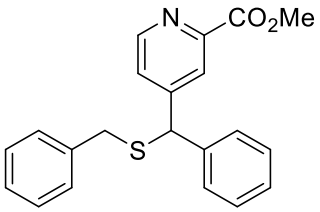
Methyl 2-((adamantan-1-ylmethoxy)(phenyl)methyl)isonicotinate (5l)

This compound was prepared according to the General Procedure 1 for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (82.2 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.65 (dd, *J* = 5.05 Hz, 0.6 Hz,1H), 8.10 (s, 1H), 7.68 (dd, *J* = 5.05 Hz, 1.60 Hz, 1H), 7.44 (d, *J* = 7.25 Hz, 2H), 7.31 (t, *J* = 7.35 Hz, 2H), 7.25-7.22 (m, 1H), 5.46 (s, 1H), 3.95 (s, 3H), 3.10 (d, *J* = 8.75 Hz, 1H), 3.03 (d, *J* = 8.75 Hz, 1H), 1.98 (s, 1H), 1.74-1.66 (m, 7H), 1.62 (d, *J* = 1.65 Hz, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.9, 164.1, 149.7, 141.4, 138.3, 128.5, 127.7, 126.9, 121.5, 119.9, 84.7, 80.2, 52.8, 39.9, 37.3, 34.3, 28.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{25}H_{30}NO_3^+$ 392.2226, found 392.2220.



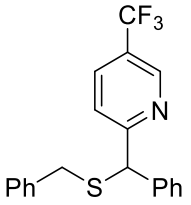
2-((Benzylthio)(phenyl)methyl)pyridine (6d)

This compound was prepared according to the General Procedure 1 using 5 mol% of **CBZ6** for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (34.9 mg, 40%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.70 Hz, 1H), 7.61 (td, *J* = 7.75, 1.60 Hz, 1H), 7.45 (d, *J* = 7.60 Hz, 2H), 7.39 (d, *J* = 7.90 Hz, 2H), 7.33-7.21 (m, 7H), 7.15-7.12 (m, 1H), 5.11 (s, 1H), 3.64 (d, *J* = 13.35 Hz, 1H), 3.58 (d, *J* = 13.35 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 160.8, 149.4, 140.3, 138.0, 136.9, 129.2, 128.8, 128.7, 128.6, 127.6, 127.1, 122.8, 122.2, 55.4, 36.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}NS^+$ 292.1154, found 292.1160.



Methyl 4-((benzylthio)(phenyl)methyl)picolinate (6e)

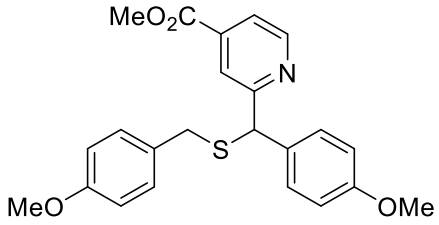
This compound was prepared according to the General Procedure 1 for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (88.1 mg, 84%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.70 (dd, *J* = 5.05 Hz, 0.55 Hz, 1H), 7.93 (s, 1H), 7.46-7.44 (m, 2H), 7.34-7.27 (m, 4H), 7.25-7.21 (m, 4H), 5.12 (s, 1H), 3.93 (s, 3H), 3.61 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.6, 162.1, 150.2, 139.8, 138.2, 137.8, 129.1, 128.9, 128.6, 128.6, 127.8, 127.2, 122.2, 121.4, 55.2, 52.8, 36.6. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}NO_2S^+$ 350.1215, found 350.1218.



2-((Benzylthio)(phenyl)methyl)-5-(trifluoromethyl)pyridine (6f)

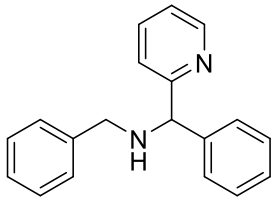
This compound was prepared according to the General Procedure 1 for 48 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (69.0 mg, 64%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.81 (s, 1H), 7.81 (dd, *J* = 8.30, 2.05 Hz, 1H), 7.50 (d, *J* = 8.30 Hz, 1H), 7.43 (d, *J* = 7.30 Hz, 2H), 7.34-7.21 (m, 8H), 5.15 (s, 1H), 3.68-3.60 (m, 2H). ^{13}C NMR (125 MHz,

$CDCl_3$): δ 164.9, 145.3 (q, *J* = 3.89 Hz), 139.4, 137.6, 134.0 (q, *J* = 3.55 Hz), 129.1, 129.0, 128.7, 128.6, 128.0, 127.3, 125.1 (q, *J* = 32.88 Hz), 123.6 (q, *J* = 271.09 Hz), 122.6, 55.2, 36.7. ^{19}F NMR (471 MHz, $CDCl_3$): δ -62.35. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{17}NF_3S^+$ 360.1034, found 360.1030.



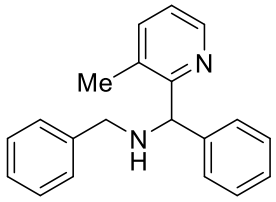
Methyl 2-(((4-methoxybenzyl)thio)(4-methoxyphenyl)methyl)isonicotinate (6g)

This compound was prepared according to the General Procedure 1 for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 3/1/1) to give the product as a yellow oil (73.7 mg, 60%). ^1H NMR (500 MHz, $CDCl_3$): δ 8.69 (d, *J* = 5.05 Hz,1H), 7.90 (s, 1H), 7.66 (dd, *J* = 5.05 Hz, 1.50 Hz, 1H), 7.36 (d, *J* = 8.70 Hz, 2H), 7.12 (d, *J* = 8.65 Hz, 2H), 6.85 (d, *J* = 8.75 Hz, 2H), 6.80 (d, *J* = 8.65 Hz, 2H), 5.11 (s, 1H), 3.93 (s, 3H), 3.79 (s, 3H), 3.78 (s, 3H), 3.56 (dd, *J* = 25.75 Hz, 13.45 Hz, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.7, 162.4, 159.1, 158.7, 138.2, 131.9, 130.2, 129.8, 129.7, 122.1, 121.3, 114.2, 114.0, 55.4, 54.5, 52.8, 36.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{24}NO_4S^+$ 410.1426, found 410.1433.



***N*-Benzyl-1-phenyl-1-(pyridin-2-yl)methanamine (7b)**

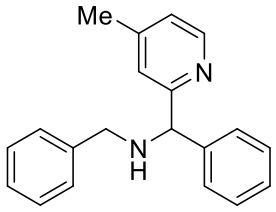
This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (67.5 mg, 82%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.56 (d, *J* = 4.10 Hz, 1H), 7.61-7.11 (m, 13H), 4.98 (s, 1H), 3.79 (d, *J* = 13.20 Hz, 1H), 3.74 (d, *J* = 13.20 Hz, 1H), 2.33 (brs, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 162.7, 149.3, 142.7, 140.4, 136.7, 128.7, 128.5, 128.4, 127.9, 127.5, 127.1, 122.1, 122.1, 67.6, 51.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}N_2^+$ 275.1543, found 275.1548.



***N*-Benzyl-1-(3-methylpyridin-2-yl)-1-phenylmethanamine (7c)**

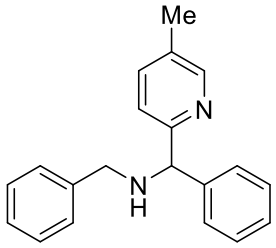
This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 21 h. The product was purified on silica gel chromatography (PE/EA/DCM

3/1/1 to 1/1/1) to give the product as a yellow oil (46.7 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.55 Hz, 1H), 7.38-7.07 (m, 12H), 4.99 (s, 1H), 3.71 (d, *J* = 13.00 Hz, 1H), 3.67 (d, *J* = 13.00 Hz, 1H), 2.17 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.5, 146.9, 142.0, 140.5, 138.1, 131.2, 128.6, 128.5, 128.4, 128.3, 127.2, 126.9, 122.0, 61.1, 51.3, 18.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_2^+$ 289.1699, found 289.1701.



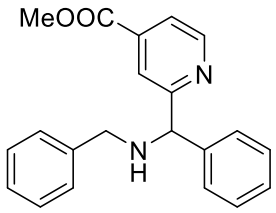
***N*-Benzyl-1-(4-methylpyridin-2-yl)-1-phenylmethanamine (7d)**

This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (68.3 mg, 79%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 5.00 Hz, 1H), 7.47 (d, *J* = 7.55 Hz, 2H), 7.35-7.23 (m, 8H), 7.13 (s, 1H), 6.94 (d, *J* = 4.95 Hz, 1H), 4.94 (s, 1H), 3.78 (d, *J* = 13.20 Hz, 1H), 3.73 (d, *J* = 13.20 Hz, 1H), 2.29 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.4, 149.0, 147.8, 142.7, 140.5, 128.7, 128.5, 128.4, 127.9, 127.4, 127.0, 123.2, 122.8, 67.5, 51.9, 21.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_2^+$ 289.1699, found 289.1702.



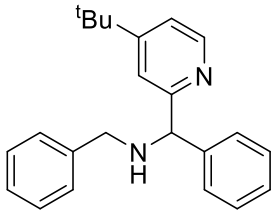
***N*-Benzyl-1-(5-methylpyridin-2-yl)-1-phenylmethanamine (7e)**

This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (54.5 mg, 63%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.46 (d, *J* = 7.50 Hz, 2H), 7.41-7.21 (m, 10H), 4.95 (s, 1H), 3.77 (d, *J* = 13.20 Hz, 1H), 3.73 (d, *J* = 13.20 Hz, 1H), 2.50 (brs, 1H), 2.28 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 159.7, 149.6, 142.8, 140.4, 137.4, 131.5, 128.7, 128.5, 128.4, 127.9, 127.4, 127.0, 121.6, 67.3, 51.9, 18.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{21}N_2^+$ 289.1699, found 289.1702.



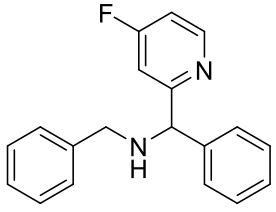
Methyl 2-((benzylamino)(phenyl)methyl)isonicotinate (7f)

This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 24 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (67.8 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 5.00 Hz, 1H), 7.94 (s, 1H), 7.68 (dd, *J* = 5.00, 1.45 Hz, 1H), 7.47 (d, *J* = 7.25 Hz, 2H), 7.35-7.25 (m, 8H), 5.05 (s, 1H), 3.92 (s, 1H), 3.79 (d, *J* = 13.15 Hz, 1H), 3.74 (d, *J* = 13.15 Hz, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 165.9, 164.0, 150.1, 142.2, 140.2, 138.1, 128.8, 128.5, 128.4, 127.8, 127.7, 127.1, 121.4, 121.3, 67.5, 52.8, 51.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{21}N_2O_2^+$ 333.1598, found 333.1604.



***N*-Benzyl-1-(4-(tert-butyl)pyridin-2-yl)-1-phenylmethanamine (7g)**

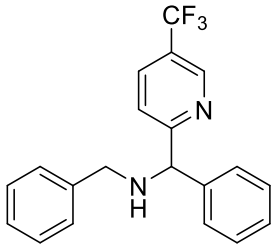
This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (92.2 mg, 93%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.25 Hz, 1H), 7.48 (d, *J* = 7.60 Hz, 2H), 7.35-7.12 (m, 10H), 4.96 (s, 1H), 3.78 (d, *J* = 13.15 Hz, 1H), 3.73 (d, *J* = 13.15 Hz, 1H), 2.55 (brs, 1H), 1.27 (s, 9H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 162.3, 160.7, 149.2, 142.8, 140.5, 128.6, 128.5, 128.5, 127.9, 127.4, 127.0, 119.3, 119.0, 67.8, 51.9, 34.8, 30.7. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{27}N_2^+$ 331.2169, found 331.2175.



***N*-Benzyl-1-(4-fluoropyridin-2-yl)-1-phenylmethanamine (7h)**

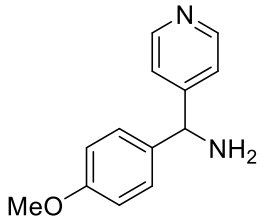
This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (57.0 mg, 65%). ^{1}H NMR (500 MHz,

$CDCl_3$) δ 8.51 (dd, *J* = 8.45, 2.80 Hz, 1H), 7.45 (d, *J* = 7.40 Hz, 2H), 7.36-7.14 (m, 9H), 6.87 (td, *J* = 5.70, 2.30 Hz, 1H), 4.98 (s, 1H), 3.79 (d, *J* = 13.15 Hz, 1H), 3.74 (d, *J* = 13.15 Hz, 1H), 2.49 (brs, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 170.4, 168.3, 166.5 (d, *J* = 6.13 Hz), 151.7 (d, *J* = 6.76 Hz), 141.1 (d, *J* = 232.30 Hz), 128.9, 128.6, 128.4, 127.8, 127.8, 127.2, 110.2 (d, *J* = 16.55 Hz), 109.6 (d, *J* = 17.25 Hz), 67.6 (d, *J* = 2.68 Hz), 51.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -102.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{18}FN_2^+$ 293.1449, found 293.1457.



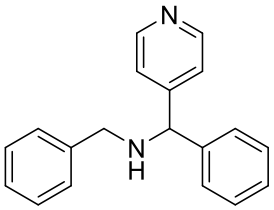
***N*-Benzyl-1-phenyl-1-(5-(trifluoromethyl)pyridin-2-yl)methanamine (7i)**

This compound was prepared according to the General Procedure 2 using 2 mol% of **CBZ6** and 1.8 mmol amine for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (71.9 mg, 70%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.82 (s, 1H), 7.84 (dd, *J* = 8.25, 2.15 Hz, 1H), 7.52 (d, *J* = 8.25 Hz, 1H), 7.44 (d, *J* = 7.25 Hz, 2H), 7.36-7.27 (m, 8H), 5.04 (s, 1H), 3.80 (d, *J* = 13.25 Hz, 1H), 3.73 (d, *J* = 13.25 Hz, 1H). $^{13}C\{^1H\}$ NMR (125 MHz, $CDCl_3$) δ 166.7, 146.3 (q, *J* = 3.69 Hz), 141.8, 140.0, 133.9 (q, *J* = 4.76 Hz), 129.0, 128.6, 128.4, 127.9, 127.9, 127.3, 125.1 (q, *J* = 32.7 Hz), 123.7 (q, *J* = 272.81 Hz), 121.7, 67.5, 51.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{18}F_3N_2^+$ 343.1417, found 343.1425.



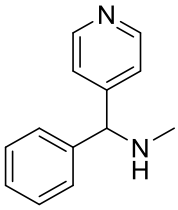
(4-Methoxyphenyl)(pyridin-4-yl)methanamine (7j)

This compound was prepared according to the General Procedure 2 using 2 mol% of **CBZ6** for 36 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (54.6 mg, 85%). ^1H NMR (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 4.55, 1.50 Hz, 2H), 7.31 (d, *J* = 5.90 Hz, 2H), 7.24 (d, *J* = 8.70 Hz, 2H), 6.87-6.84 (m, 2H), 5.14 (s, 1H), 3.79(s, 3H), 1.72 (brs, 2H). $^{13}C\{1H\}$ NMR (125 MHz, $CDCl_3$) δ 159.1, 154.5, 150.0, 136.5, 128.2, 122.0, 114.2, 58.5, 55.4. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{15}N_2O^+$ 215.1184, found 215.1178.



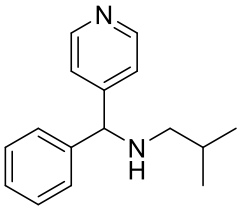
***N*-Benzyl-1-phenyl-1-(pyridin-4-yl)methanamine (7a)**

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (80.7 mg, 98%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 5.20 Hz, 2H), 7.39-7.26 (m, 12H), 4.83 (s, 1H), 3.74 (s, 2H), 1.91 (brs, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 152.8, 150.1, 142.6, 140.0, 128.9, 128.6, 128.3, 127.8, 127.5, 127.3, 122.6, 65.7, 51.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{19}H_{19}N_2^+$ 275.1543, found 275.1551.



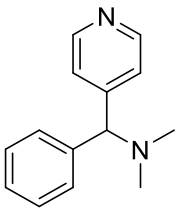
***N*-Methyl-1-phenyl-1-(pyridin-4-yl)methanamine (7k)**

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (51.7 mg, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 4.55, 1.50 Hz, 2H), 7.35-7.30 (m, 6H), 7.25-7.23 (m, 1H), 4.67 (s, 1H), 2.41 (s, 3H), 1.65(brs, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 152.8, 150.1, 142.6, 128.9, 127.8, 127.4, 122.5, 68.8, 35.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{14}N_2Na^+$ 221.1055, found 221.1076



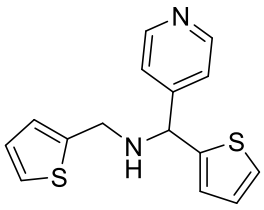
2-Methyl-*N*-(phenyl(pyridin-4-yl)methyl)propan-1-amine (7l)

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (66.3 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 5.65 Hz, 2H), 7.36-7.24 (m, 7H), 4.75 (s, 1H), 2.42-2.32 (m, 2H), 1.80-1.72 (m, 1H), 1.63 (brs, 1H), 0.92 (dd, *J* = 8.70, 6.55 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 153.4, 150.0, 143.1, 128.8, 127.7, 127.4, 122.6, 67.0, 56.3, 28.8, 20.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{16}H_{21}N_2^+$ 241.1705, found 241.1707.



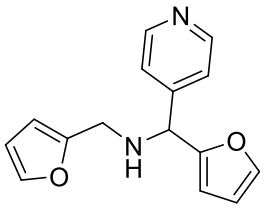
***N,N*-Dimethyl-1-phenyl-1-(pyridin-4-yl)methanamine (7m)**[6]

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (56 mg, 88%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (dd, *J* = 4.55, 1.55 Hz, 2H), 7.37-7.20 (m, 7H), 4.07 (s, 1H), 2.19 (s, 6H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 152.5, 150.1, 141.6, 128.8, 128.0, 127.7, 123.0, 77.0, 44.6.



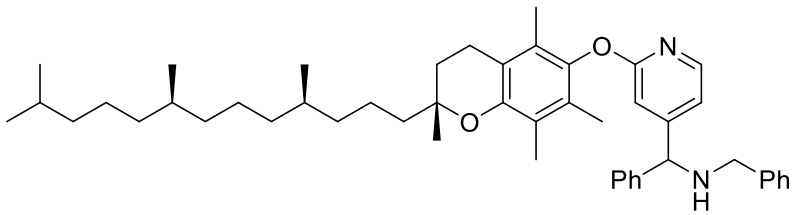
1-(Pyridin-4-yl)-1-(thiophen-2-yl)-*N*-(thiophen-2-ylmethyl)methanamine (7n)

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (73.1 mg, 85%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 4.50 Hz, 1.60 Hz, 2H), 7.38 (dd, *J* = 4.65 Hz, 1.45 Hz, 2H), 7.26-7.24 (m, 2H), 6.97-6.93 (m, 2H), 6.91-6.89 (m, 2H), 5.12 (s, 1H), 3.97 (s, 2H), 1.71 (brs, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.8, 150.3, 146.6, 143.3, 126.9, 126.9, 125.5, 125.5, 125.2, 124.9, 122.5, 60.5, 46.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}O_2S_2^+$ 287.0677, found 287.0696.



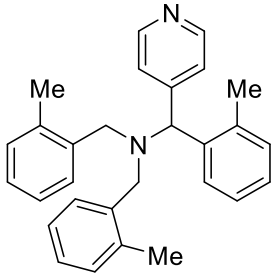
1-(Furan-2-yl)-*N*-(furan-2-ylmethyl)-1-(pyridin-4-yl)methanamine (7o)

This compound was prepared according to the General Procedure 2 using 2 mol% of **CBZ6** for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (59.9 mg, 78%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 5.90 Hz, 2H), 7.38-7.35 (m, 4H), 6.32-6.31 (m, 2H), 6.17-6.15 (m, 2H), 4.86 (s, 1H), 3.73 (d, *J* = 1.55 Hz, 2H), 1.89 (brs, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 154.3, 153.1, 150.2, 149.7, 142.6, 142.3, 122.9, 110.4, 110.3, 107.7, 58.7, 44.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{15}H_{15}N_2O_2^+$ 255.1134, found 255.1138.



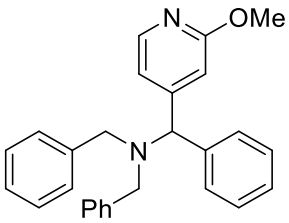
***N*-Benzyl-1-phenyl-1-(2-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)methyl)pyridin-4-yl)methanamine (7p)**

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (113.9 mg, 54%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 5.2 Hz, 1H), 7.39 (d, *J* = 7.39 Hz, 2H), 7.35-7.26 (m, 8H), 6.96 (d, *J* = 5.25 Hz, 1H), 6.92 (s, 1H), 4.80 (s, 1H), 3.74 (s, 2H), 2.61 (t, *J* = 6.65 Hz, 2H), 2.12 (s, 3H), 2.00 (s, 3H), 1.95 (s, 3H), 1.86-1.76 (m, 3H), 1.60-1.29 (m, 13H), 1.25-1.07 (m, 10H), 0.89-0.86 (m, 12H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.7, 156.5, 149.1, 148.2, 142.8, 142.6, 140.1, 128.8, 128.6, 128.3, 127.9, 127.8, 127.6, 127.3, 126.0, 123.2, 117.6, 116.6, 108.0, 75.1, 65.7, 52.0, 40.4, 39.5, 37.6, 37.6, 37.6, 37.4, 32.9, 32.9, 31.2, 28.1, 24.9, 24.6, 24.1, 22.9, 22.8, 21.2, 20.8, 19.9, 19.8, 13.3, 12.4, 12.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{48}H_{67}N_2O_2^+$ 703.5197, found 703.5198.



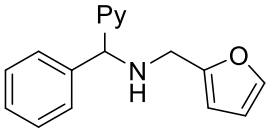
***N,N*-Bis(2-methylbenzyl)-1-(pyridin-4-yl)-1-(o-tolyl)methanamine (7q)**

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow solid (115.9 mg, 95%). m.p. 96-97 ºC. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.52 (d, *J* = 5.55 Hz, 2H), 7.62 (d, *J* = 7.45 Hz, 2H), 7.49 (d, *J* = 7.20 Hz, 1H), 7.30 (d, *J* = 5.65 Hz, 2H), 7.25-7.08 (m, 9H), 5.35 (s, 1H), 3.79 (d, *J* = 15.10 Hz, 2H), 3.75 (d, *J* = 15.10 Hz, 2H), 2.07 (s, 6H), 1.92 (s, 3H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 151.2, 149.8, 137.7, 137.6, 137.2, 136.4, 131.0, 130.3, 129.1, 127.9, 127.6, 126.7, 126.1, 126.1, 124.2, 63.5, 52.5, 19.6, 19.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{29}H_{31}N_2^+$ 407.2482, found 407.2486.

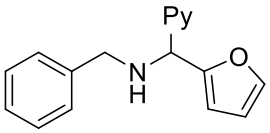


***N,N*-Dibenzyl-1-(2-methoxypyridin-4-yl)-1-phenylmethanamine (7r)**

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (112.4 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.15-8.14 (m, 1H), 7.47-7.27 (m, 15 H), 6.99 (s, 1H), 6.91 (d, *J* = 3.15 Hz, 1H), 4.93 (s, 1H), 3.97 (s, 3H), 3.71 (d, *J* = 14.10 Hz, 2H), 3.50 (d, *J* = 14.10 Hz, 2H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 164.7, 153.3, 146.7, 139.1, 138.0, 129.6, 128.7, 128.6, 128.5, 127.7, 127.2, 117.5, 111.0, 66.4, 53.8, 53.5. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{27}H_{27}N_2O^+$ 395.2118, found 395.2019.

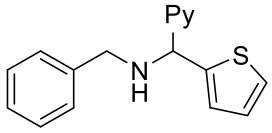


***N*-(Furan-2-ylmethyl)-1-phenyl-1-(pyridin-2-yl)methanamine (7s)**

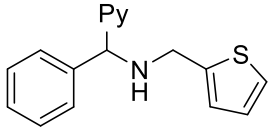


***N*-Benzyl-1-(furan-2-yl)-1-(pyridin-2-yl)methanamine (7s')**

This compound was prepared according to the General Procedure 2 for 24 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 1/1/1) to give the product as a yellow oil (77.7 mg, 98%, 1:1.1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, *J* = 5.75 Hz, 1H), 8.52 (d, *J* = 5.65 Hz, 0.95H), 7.37-7.25 (m, 7H), 6.32 (s, 1H), 6.17 (d, *J* = 3.20 Hz, 0.51H), 6.13 (d, *J* = 3.00 Hz, 0.45H), 4.86 (s, 0.51H), 4.79 (s, 0.45H), 3.76-3.73 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 154.6, 153.5, 152.5, 150.1, 142.5, 142.3, 142.2, 139.6, 129.0, 128.7, 128.3, 127.9, 127.6, 127.4, 122.9, 122.6, 110.4, 110.3, 107.7, 107.5, 65.2, 58.9, 51.6, 44.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}N_2O^+$ 265.1341, found 265.1340.

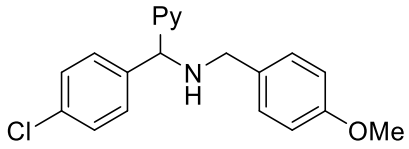


***N*-Benzyl-1-(pyridin-2-yl)-1-(thiophen-2-yl)methanamine (7t)**

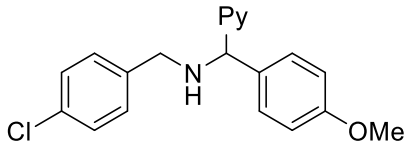


1-Phenyl-1-(pyridin-2-yl)-*N*-(thiophen-2-ylmethyl)methanamine (7t')

This compound was prepared according to the General Procedure 2 for 24 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 1/1/1) to give the product as a yellow oil (83.3 mg, 99%, 1:1.7). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (d, *J* = 4.85 Hz, 0.74H), 8.53 (d, *J* = 5.05 Hz, 1.23 H), 7.39 (m, 7H), 6.97-6.88 (m, 2H), 5.07 (s, 0.32H), 4.88 (s, 0.57H), 3.93 (s, 1.21H), 3.78 (s, 0.75H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 152.6, 152.2, 150.3, 150.1, 147.0, 143.7, 142.2, 139.6, 129.0, 128.7, 128.3, 127.9, 127.6, 127.4, 126.9, 126.8, 125.3, 125.3, 125.0, 124.8, 122.6, 122.5, 65.1, 61.1, 51.7, 46.3. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{17}H_{17}N_2S^+$ 281.1112, found 281.1115.

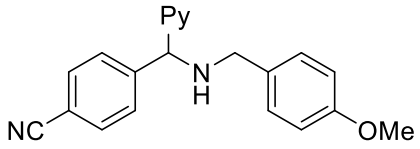


1-(4-Chlorophenyl)-*N*-(4-methoxybenzyl)-1-(pyridin-2-yl)methanamine (7u)

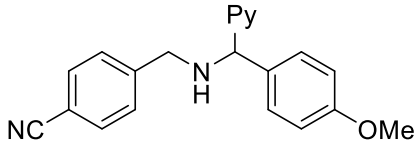


***N*-(4-Chlorobenzyl)-1-(4-methoxyphenyl)-1-(pyridin-2-yl)methanamine (7u')**

This compound was prepared according to the General Procedure 2 for 24 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 1/1/1) to give the product as a yellow oil (86.4 mg, 85%, 1:1). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.52 (s, 2H), 7.35-7.20 (m, 8H), 6.86 (t, *J* = 9.50 Hz, 2H), 4.77 (s, 0.46H), 4.74 (s, 0.48H), 3.81 (s, 1.38H), 3.78 (s, 1.36H), 3.69 (s, 1.10H), 3.65 (s, 0.88H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.3, 159.0, 153.0, 152.4, 150.3, 150.1, 141.1, 138.5, 134.4, 133.5, 133.0, 131.9, 129.6, 129.4, 129.1, 128.9, 128.7, 128.5, 122.4, 122.4, 114.3, 114.0, 64.9, 64.8, 55.4, 55.4, 51.2, 51.1. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{20}H_{20}ClN_2O^+$ 339.1264, found 339.1260.

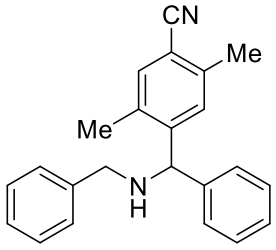


4-(((4-methoxybenzyl)amino)(pyridin-2-yl)methyl)benzonitrile (7v)



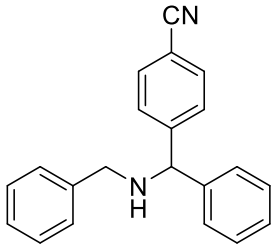
4-((((4-methoxyphenyl)(pyridin-2-yl)methyl)amino)methyl)benzonitrile (7v')

This compound was prepared according to the General Procedure 2 for 24 h. The product was purified on silica gel chromatography (PE/EA/DCM 10/1/1 to 1/1/1) to give the product as a yellow oil (59.3 mg, 60%, 1:1.3). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.55-8.53 (m, 2H), 7.62 (d, *J* = 7.15 Hz, 2H), 7.52 (d, *J* = 8.25 Hz, 0.91H), 7.45 (d, *J* = 8.10 Hz, 1.18H), 7.35-7.19 (m, 4H), 6.87 (t, *J* = 7.70 Hz, 2H), 4.85 (s, 0.46H), 4.75 (s, 0.57H), 3.81-3.65 (m, 5H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 159.4, 159.1, 152.7, 151.5, 150.4, 150.2, 147.8, 145.7, 134.1, 132.8, 132.4, 131.5, 129.4, 128.8, 128.6, 128.3, 122.4, 119.0, 118.7, 114.4, 114.1, 111.7, 111.1, 65.2, 65.2, 55.4, 55.4, 51.4, 51.2. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{20}N_3O^+$ 330.1606, found 330.1610.



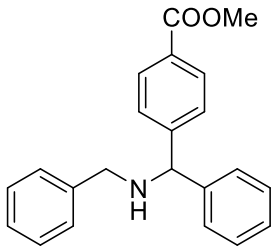
4-((Benzylamino)(phenyl)methyl)-2,5-dimethylbenzonitrile (11a)

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow solid (85.2 mg, 87%). m.p. 67-68 °C ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.36-7.25 (m, 11H), 4.99 (s, 1H), 3.77 (d, *J* = 13.25 Hz, 1H), 3.71 (d, *J* = 13.25 Hz, 1H), 2.55 (s, 3H), 2.16 (s, 3H), 1.76 (brs, 1H). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$) δ 146.6, 141.8, 140.1, 139.8, 134.4, 134.3, 128.9, 128.6, 128.6, 128.3, 128.1, 127.7, 127.3, 118.6, 111.0, 62.1, 52.2, 20.4, 18.9. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{23}H_{23}N_2^+$ 327.1856, found 327.1859.



4-((Benzylamino)(phenyl)methyl)benzonitrile (11b)

This compound was prepared according to the General Procedure 2 for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow oil (85.0 mg, 95%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61-7.60 (m, 4H), 7.39-7.27 (m, 10H), 4.90 (s, 1H), 3.74 (s, 2H), 1.83 (brs, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 149.5, 142.8, 140.0, 132.5, 129.0, 128.6, 128.2, 128.2, 127.8, 127.4, 127.3, 119.1, 111.0, 66.3, 52.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{21}H_{19}N_2^+$ 299.1543, found 299.1544.



Methyl 4-((benzylamino)(phenyl)methyl)benzoate (12)

This compound was prepared according to the General Procedure 2 using 1.8 mmol amine for 18 h. The product was purified on silica gel chromatography (PE/EA/DCM 3/1/1 to 1/1/1) to give the product as a yellow solid (80.5 mg, 81%), m.p. 99-100 °C. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, J = 8.25 Hz, 2H), 7.46 (d, J = 8.25 Hz, 2H), 7.34 (d, J = 7.35 Hz, 2H), 7.27-7.16 (m, 8H), 4.84 (s, 1H), 3.82 (s, 3H), 3.68 (s, 2H), 1.84 (brs, 1H). $^{13}C\{^{1}H\}$ NMR (125 MHz, $CDCl_3$) δ 167.1, 149.3, 143.4, 140.2, 130.0, 129.0, 128.8, 128.6, 128.3, 127.5, 127.5, 127.2, 66.3, 52.2, 52.0. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{22}H_{22}NO_2^+$ 332.1645, found 332.1648.

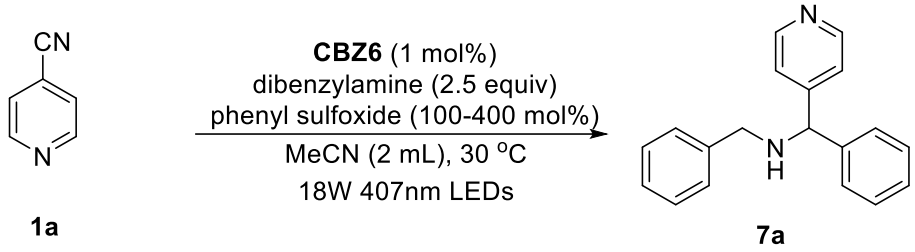
2.3 Synthesis of Carbinoxamine

CBZ6 (5 mol%, 80 mg), phenyl sulfoxide (15 mmol, 4 equiv) and 2-cyanopyridine (3.8 mmol, 1 equiv) were added in an oven-dried 100 mL Schlenk tube. The reaction tube was purged with argon. Then *tert*-butyl((4-chlorobenzyl)oxy)dimethylsilane (11.5 mmol, 3 equiv) and dry MeCN (30 mL) were added sequentially via syringe. The reaction tube was placed 5 cm away from 36 W LED column (3 W×12), and stirred vigorously under the irradiation of 407 nm light. Upon consumption of cyanopyridines (about 48 h, monitored by TLC), the reaction mixture was concentrated by rotavapor and purified by column chromatography on silica gel (PE/EA/DCM 10/1/1 to 5/1/1) to afford the 2-(((*tert*-butyldimethylsilyl)oxy)(4-chlorophenyl)methyl)pyridine (**5m**) in 60%. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (m, 1H), 7.65 (td, *J* = 7.75 Hz, 1.75 Hz, 1H), 7.55 (d, *J* = 7.90 Hz, 1H),7.40 (m, *J* = 8.45 Hz, 2H), 7.26-7.24 (m, 2H), 7.13-7.10 (m, 1H), 5.84 (s, 1H), 0.92 (s, 9H), 0.00 (d, *J* = 5.95 Hz, 6H). ^{13}C{^{1}H} NMR (125 MHz, *d*-DMSO) δ 164.0, 148.7, 142.6, 137.0, 133.0, 128.5, 127.7, 122.3, 120.1, 26.0, 25.9, 19.4, -4.7, -4.8. HRMS (ESI-TOF) m/z: $[M+H]^+$ calcd for $C_{13}H_{22}ClOSi^+$ 257.1128, found 257.1134.

To the ice-bath cooled (0 °C) solution of compound **5m** (2.3 mmol, 1 equiv) in dry THF (15 mL) in a Schlenk tube was dropwise added TBAF in THF (7 mmol, 3 equiv) via syringe under argon atmosphere. The reaction mixture was remained stirring at 0 °C for 5 hours. The reaction was quenched by saturated *aq.* $NaHCO_3$, extracted with ethyl acetate, and purified by flash column chromatography on silica gel (PE/EA/DCM 5/1/1 to 3/1/1) to afford **5n** (86%, 2 mmol). ^{1}H NMR (500 MHz, $CDCl_3$)[7] δ 8.54 (d, *J* = 4.80 Hz, 1H), 7.62 (td, *J* = 7.70, 1.60 Hz, 1H), 7.32-7.28 (m, 4H), 7.21-7.18 (m, 1H), 7.13 (d, *J* = 7.90 Hz, 1H), 5.72 (s, 1H), 5.41 (brs, 1H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 160.6, 148.0, 141.8, 137.1, 133.6, 128.8, 128.5, 122.7, 121.3, 74.4.

Compound **5n** and ^{t}BuONa (4.4 mmol, 2.2 equiv) were added in an oven-dried 100 mL Schlenk tube. The reaction tube was vacuumed by the pump and refilled with argon for three times. Then 2-chloro-*N*,*N*-dimethylethan-1-amine (2.2 mmol, 1.1 equiv) and dry toluene (20 mL) were added sequentially in the Schlenk tube via syringe under argon atmosphere. Then the tube was stirred at 110 °C. Upon consumption of (4-chlorophenyl)(pyridin-2-yl)methanol (about 12 h), the tube was removed from oil bath. The crude product residue was purified by flash column chromatography on silica gel (PE/EA/DCM 5/1/1 to 1/1/1) to afford the **Carbinoxamine**[5] (0.48 g, 44% for 3 steps). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 4.80 Hz, 1H), 7.66 (dt, *J* = 7.70, 1.60 Hz, 1H), 7.50 (d, *J* = 7.95 Hz, 1H), 7.37 (d, *J* = 8.50 Hz, 2H), 7.27 (d, *J* = 8.40 Hz, 2H), 7.16-7.14 (m, 1H), 5.46 (s, 1H), 3.63-3.56 (m, 2H), 2.60 (t, *J* = 5.85 Hz, 2H), 2.26 (s, 6H). ^{13}C{1H} NMR (125 MHz, $CDCl_3$) δ 161.4, 149.2, 139.8, 137.1, 133.6, 128.7, 128.5, 122.7, 120.7, 84.6, 67.8, 59.1, 46.1.

3. Kinetic study



All data was collected on NMR using methyl benzoate as the internal standard. The initial rates were calculated as the slopes of time zero on the curves of **7a** against time.

The kinetic study on the dependence of the initial rate on phenyl sulfoxide

General procedure: Phenyl sulfoxide (100-400 mol %, 62-247 mg), **1a** (33 mg) and **CBZ6** (1.3 mg) were weighed directly into a 25 mL Schlenk tube and dried under high vacuum for 15 mins, purged with argon 3 times. Dibenzylamine (0.15 mL) and methyl benzoate (0.3 mmol, 0.038 mL) (as internal standard) were then added. The resulting reaction mixture was stirred at 30 ˚C under the irradiation of 18 W (3 W × 6) 407 nm LEDs. At each sampling time 20 μL reaction mixture was extracted and examined by NMR. The results were demonstrated in **Figures S1-5** and **Table S1**.

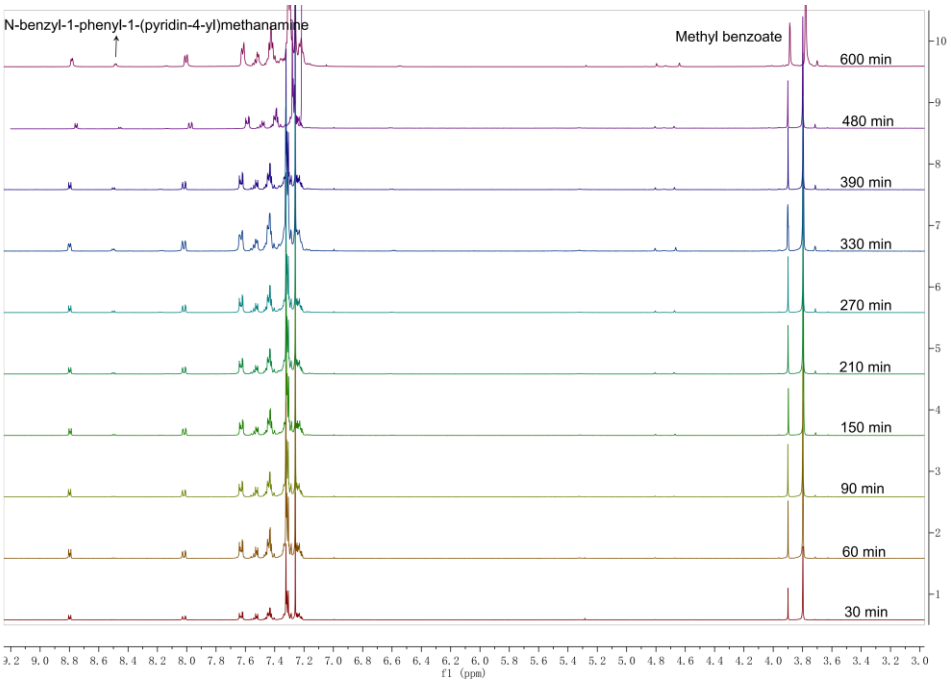


Figure S1. Conditions: **1a** (4-cyanopyridine) = 0.15 M (0.3 mmol, 32 mg), **CBZ6** (1.3 mg), **phenyl sulfoxide** (100 mol %, 62 mg), dibenzylamine (2 equiv, 0.15 mL), MeCN (2 mL), 18 W 407 nm LEDs, 32 ˚C, methyl benzoate (0.3 mmol, 0.038 mL) as internal

standard.

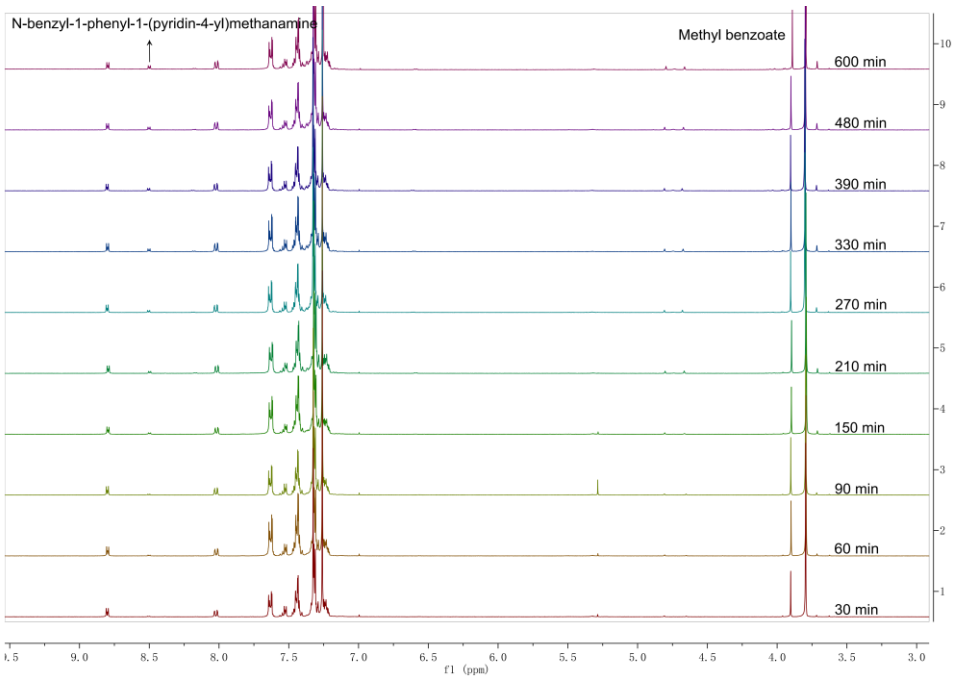


Figure S2. Conditions: **1a** (4-cyanopyridine) = 0.15 M (0.3 mmol, 32 mg), **CBZ6** (1.3 mg), phenyl sulfoxide (200 mol %, 125 mg), dibenzylamine (2 equiv, 0.15 mL), MeCN (2 mL), 18 W 407 nm LEDs, 30 ˚C, methyl benzoate (0.3 mmol, 0.038 mL) as internal standard.

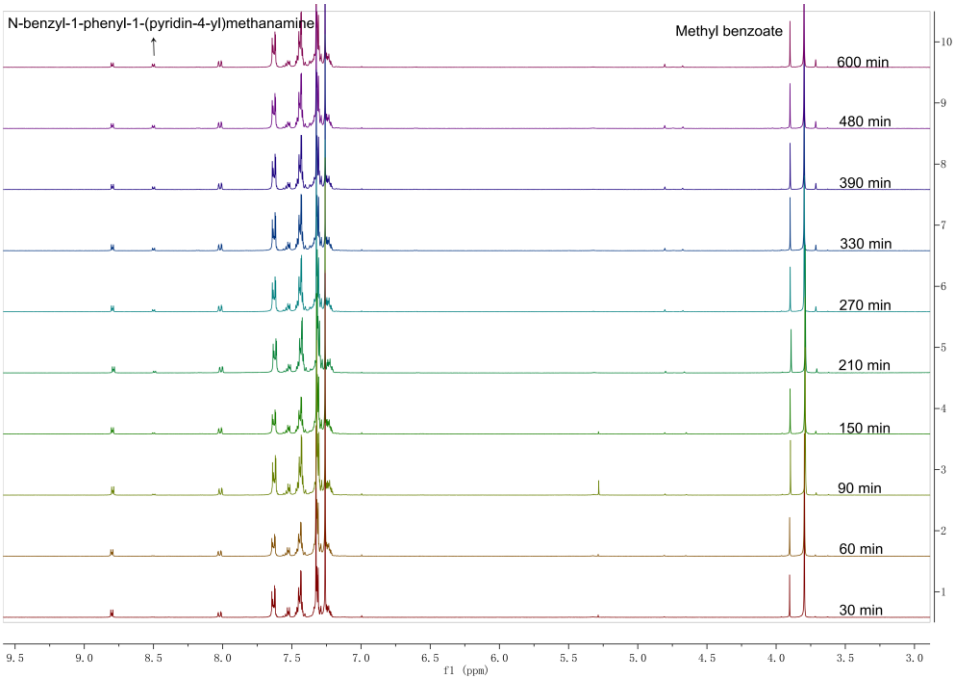


Figure S3. Conditions: **1a** (4-cyanopyridine) = 0.15 M (0.3 mmol, 32 mg), **CBZ6** (1.3 mg), phenyl sulfoxide (300 mol %, 185 mg), dibenzylamine (2 equiv, 0.15 mL), MeCN (2 mL), 18 W 407 nm LEDs, 30 ˚C, methyl benzoate (0.3 mmol, 0.038 mL) as internal standard.

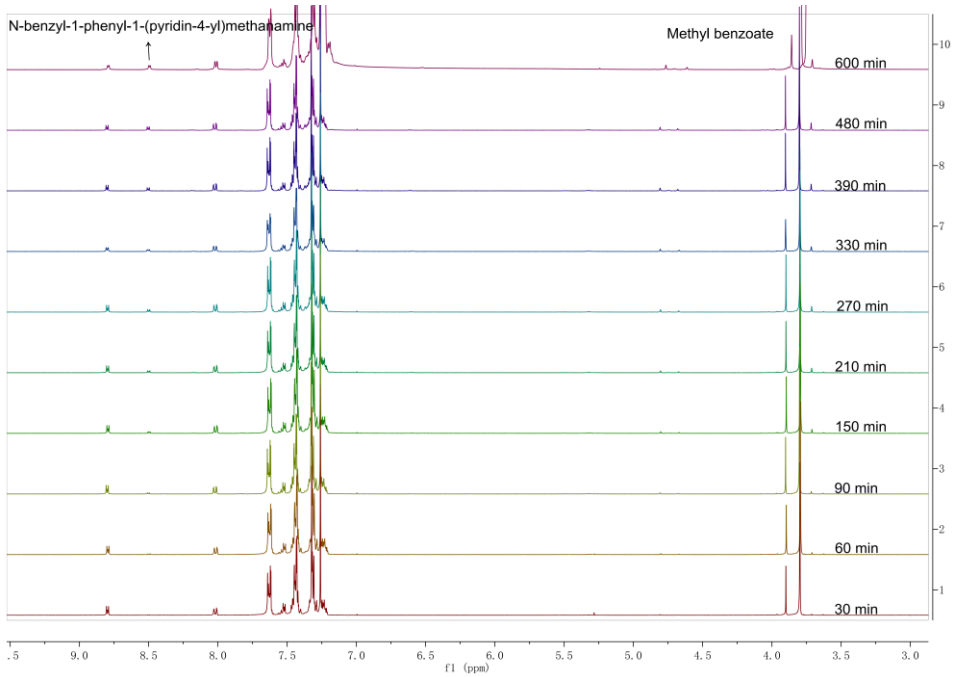


Figure S4. Conditions: **1a** (4-cyanopyridine) = 0.15 M (0.3 mmol, 32 mg), **CBZ6** (1.3 mg), phenyl sulfoxide (400 mol %, 247 mg), dibenzylamine (2 equiv, 0.15 mL), MeCN

(2 mL), 18 W 407 nm LEDs, 30 ˚C, methyl benzoate (0.3 mmol, 0.038 mL) as internal standard.

Table S1. Dependence of phenyl sulfoxide (mol %): *N*-benzyl-1-phenyl-1-(pyridin-4-yl)methanamine v.s. time.

Time (min)	*N*-benzyl-1-phenyl-1-(pyridin-4-yl)methanamine			
	100 mol%	200 mol%	300 mol%	400 mol%
0	0	0	0	0
30	2	3	4	4
60	5	6	7	9
90	7	9	10	14
150	10	14	16	20
210	15	18	22	27
270	18	23	28	32
330	21	27	33	37
390	23	30	36	43
480	25	35	42	50
600	29	40	48	58

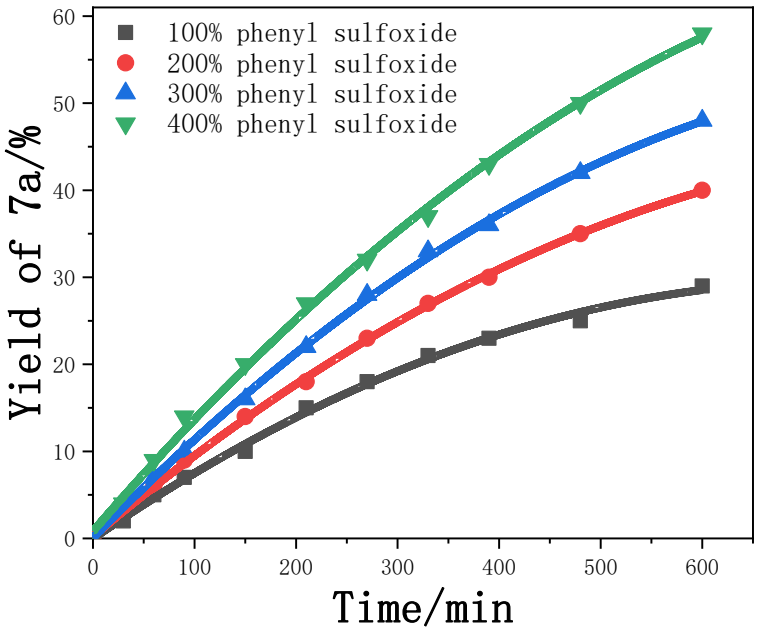
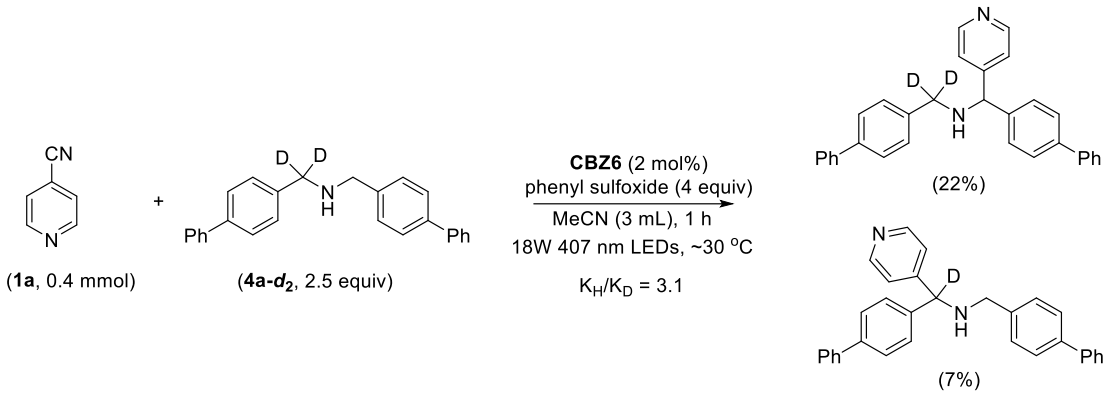
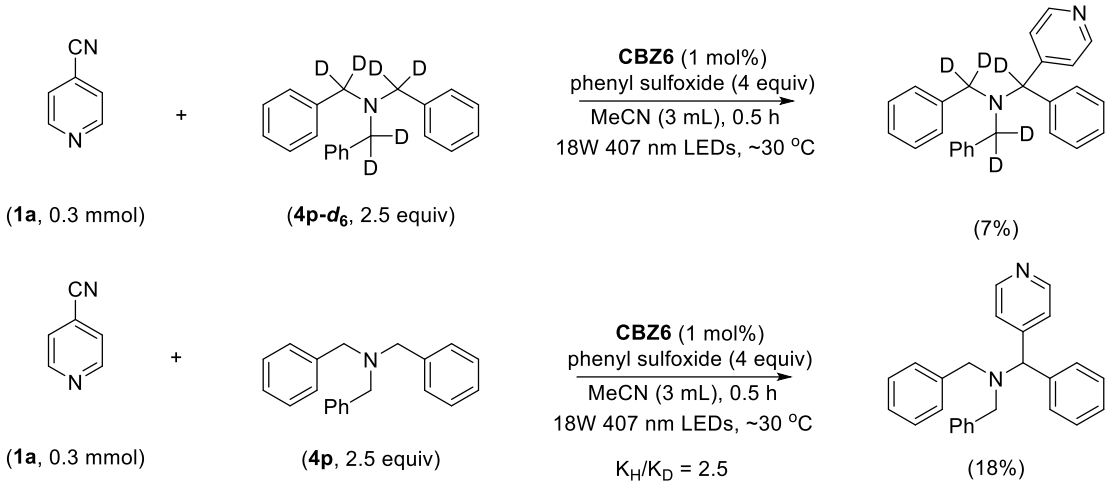


Figure S5. Dependence of the initial rate on phenyl sulfoxide: plots of **7a** [*N*-benzyl-1-phenyl-1-(pyridin-4-yl)methanamine] v.s. time.

4. KIE Experiments



CBZ6 (2 mol%, 3.5 mg), phenyl sulfoxide (1.2 mmol, 4 equiv) and 4-cyanopyridine (0.4 mmol, 1 equiv) were weighed into an oven-dried 25 mL Schlenk tube. The reaction tube was purged with argon. Then 1-([1,1'-biphenyl]-4-yl)-N-([1,1'-biphenyl]-4-ylmethyl)methan-d2-amine (1 mmol, 2.5 equiv,) and dry MeCN (3 mL) were added sequentially in the Schlenk tube via syringe. Then the tube was placed 5 cm away from LED column (18 W = 3 W×6), and stirred under the irradiation of 407 nm light for 1 hours. At last, the reaction mixture was extracted and examined by NMR.



CBZ6 (1 mol%, 1.3 mg), phenyl sulfoxide (1.2 mmol, 4 equiv) and 4-cyanopyridine (0.3 mmol, 1 equiv) were weighed into an oven-dried 25 mL Schlenk tube. The reaction tube was purged with argon. Deuterated tribenzylamine (0.75 mmol, 2.5 equiv) and dry MeCN (3 mL) were added sequentially in the Schlenk tube via syringe. Then the tube was placed 5 cm away from LED column (18 W = 3 W×6), and stirred under the irradiation of 407 nm light for 0.5 hours. At last, the reaction mixture was extracted and examined by NMR.

CBZ6 (1 mol%, 1.3 mg), phenyl sulfoxide (1.2 mmol, 4 equiv) and 4-cyanopyridine (0.3 mmol, 1 equiv) were weighed into an oven-dried 25 mL Schlenk tube. The reaction tube was purged with argon. Tribenzylamine (0.75 mmol, 2.5 equiv) and dry MeCN (3 mL) were added sequentially in the Schlenk tube via syringe. Then the tube was placed 5 cm away from LED column (18 W = 3 W×6), and stirred under the irradiation of 407 nm light for 0.5 hours. At last, the reaction mixture was extracted and examined by NMR.

5. Fluorescence and Luminescence Experiments

Test conditions for quenching reaction:

CBZ6: 4.3 mg dissolved in 10 mL DCM (0.001 M)

Quencher: 104 mg of 4-Cyanopyridine dissolved in 5 mL DCM (0.2 M).

General procedure:

0.5 mL of prepared solution containing **CBZ6** was added to a cuvette, keep the total volume at 2 mL, 4-cyanopyridine and DCM were added as the following table:

Entry	**CBZ6**	4-Cyanopyridine	DCM	Total volume
1	0.5 mL (2.5×10^{-4} M)	0 mL (0 M)	1.5 mL	2 mL
2	0.5 mL (2.5×10^{-4} M)	0.1 mL (10 mM)	1.4 mL	2 mL
3	0.5 mL (2.5×10^{-4} M)	0.2 mL (20 mM)	1.3 mL	2 mL
4	0.5 mL (2.5×10^{-4} M)	0.3 mL (30 mM)	1.2 mL	2 mL
5	0.5 mL (2.5×10^{-4} M)	0.5 mL (50 mM)	1 mL	2 mL

Excitation wavelength: 330 nm

Make and model of fluorescence spectrophotometer:

Make: Hitachi High-Technologies Corporation, Tokyo, Japan

Model: F-4600

Test conditions for quenching reaction:

1,4-Dicyanobenzene: 13 mg dissolved in 10 mL MeCN (0.01 M)

Quencher: 207 mg of dibenzylamine dissolved in 5 mL MeCN (0.2 M).

General procedure:

0.5 mL of prepared solution containing **1,4-Dicyanobenzene** was added to a cuvette, keep the total volume at 2mL, dibenzylamine and MeCN were added as the following table:

Entry	1,4-Dicyanobenzene	Dibenzylamine	MeCN	Total volume
1	0.5 mL ($2.5\text{x}10^{-3}$ M)	0 mL (0 M)	1.5 mL	2 mL
2	0.5 mL ($2.5\text{x}10^{-3}$ M)	0.2 mL (40 mM)	1.3 mL	2 mL
3	0.5 mL ($2.5\text{x}10^{-3}$ M)	0.4 mL (60 mM)	1.1 mL	2 mL
4	0.5 mL ($2.5\text{x}10^{-3}$ M)	0.8 mL (80 mM)	0.7 mL	2 mL

Excitation wavelength: 290 nm

Make and model of fluorescence spectrophotometer:

Make: Hitachi High-Technologies Corporation, Tokyo, Japan

Model: F-4600

6. X-ray molecular structures

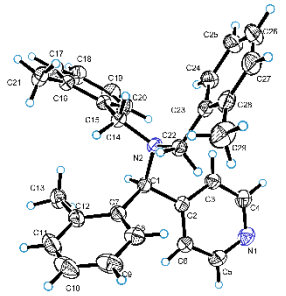


Figure S6. Crystal data and structure refinement for **7q**

Empirical formula	$C_{29}H_{30}N_2$
Formula weight	406.24
Temperature/K	293(2)
Crystal system	monoclinic
Space group	I2/a
a/Å	22.0567(3)
b/Å	7.51330(10)
c/Å	32.5379(6)
α/°	90
β/°	109.612(2)
γ/°	90
Volume/Å^3	5079.32(15)
Z	8
ρ_{calc}g/cm^3	1.174
μ/mm^{-1}	1.458
F(000)	1912.0
Crystal size/mm^3	0.25 × 0.21 × 0.2
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	8.512 to 140.136
Index ranges	-26 ≤ h ≤ 24, -9 ≤ k ≤ 6, -39 ≤ l ≤ 37
Reflections collected	9093
Independent reflections	4699 [R_{int} = 0.0183, R_{sigma} = 0.0176]
Data/restraints/parameters	4699/6/298
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0655, wR_2 = 0.1823
Final R indexes [all data]	R_1 = 0.0732, wR_2 = 0.1908
Largest diff. peak/hole / e Å^{-3}	0.69/-0.84

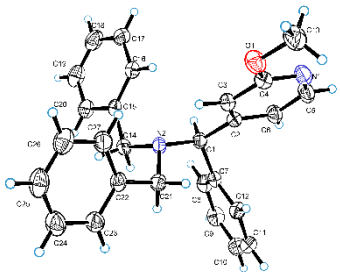


Figure S7. Crystal data and structure refinement for **7r**

Empirical formula	$C_{27}H_{26}N_2O$
Formula weight	394.50
Temperature/K	293(2)
Crystal system	triclinic
Space group	P-1
a/Å	7.8864(3)
b/Å	9.9577(4)
c/Å	15.3148(4)
α/°	75.304(3)
β/°	85.678(3)
γ/°	67.535(4)
Volume/Å^3	1074.74(7)
Z	2
ρ_{calc}g/cm^3	1.219
μ/mm^{-1}	0.576
F(000)	420.0
Crystal size/mm^3	0.23 × 0.22 × 0.18
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.912 to 140.106
Index ranges	-9 ≤ h ≤ 8, -12 ≤ k ≤ 11, -13 ≤ l ≤ 18
Reflections collected	7116
Independent reflections	3956 [R_{int} = 0.0171, R_{sigma} = 0.0202]
Data/restraints/parameters	3956/0/273
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0407, wR_2 = 0.1111
Final R indexes [all data]	R_1 = 0.0432, wR_2 = 0.1142
Largest diff. peak/hole / e Å^{-3}	0.17/-0.15

7. References

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2. N. Murai, M. Yonaga and K. Tanaka, *Org. Lett.* 2012, **14**, 1278-1281.

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7. Y.-H. Liu, Y. Yu, C.-Y. Sun, Y.-W. Fu, Z.-G. Mang, L. Shi and H. Li, *Org. Lett*. 2020, **22**, 8127-8131.

8. NMR Spectra

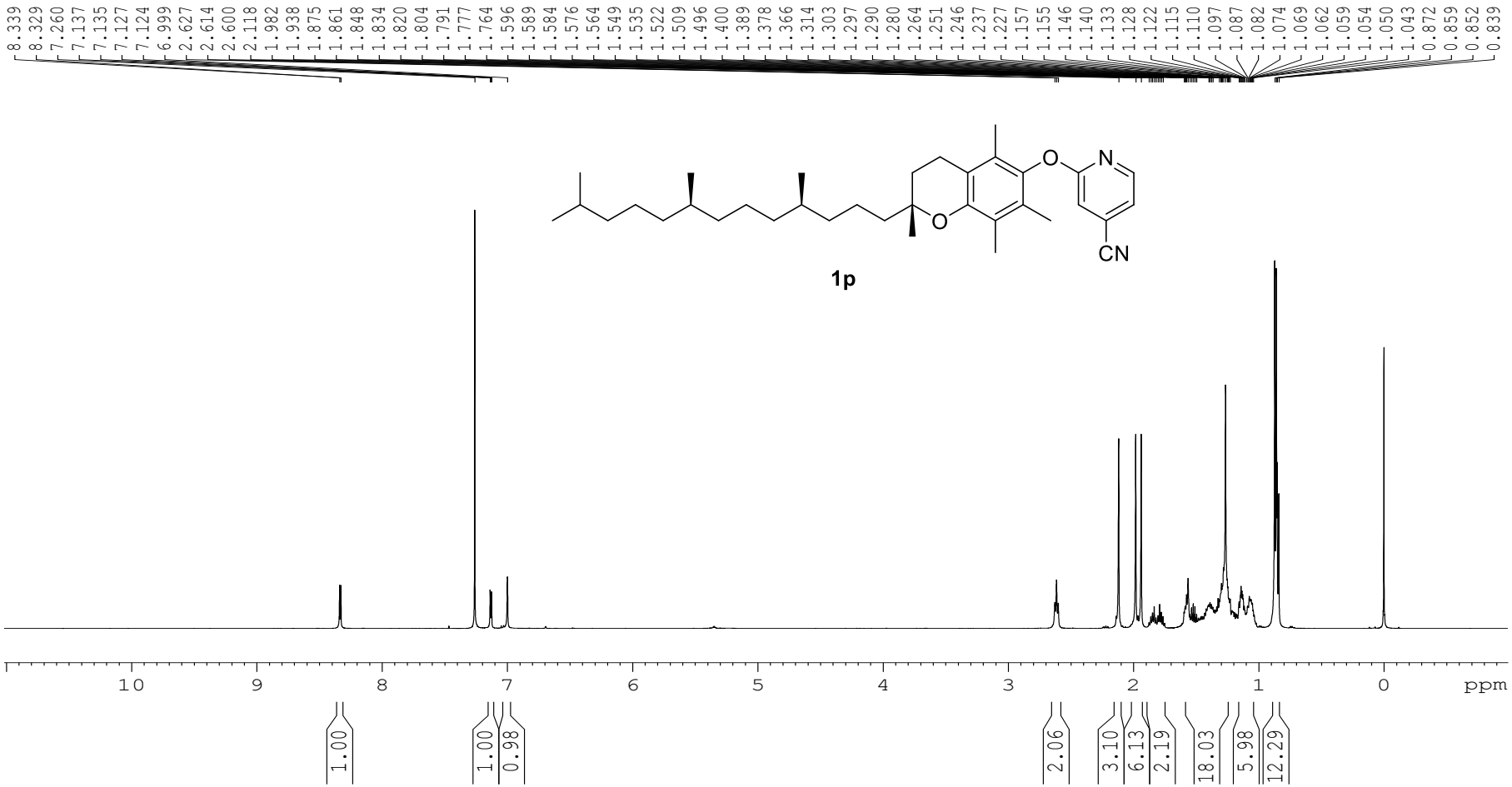

Figure S8. ^{1}H NMR spectra of **1p** ($CDCl_3$, 500M).

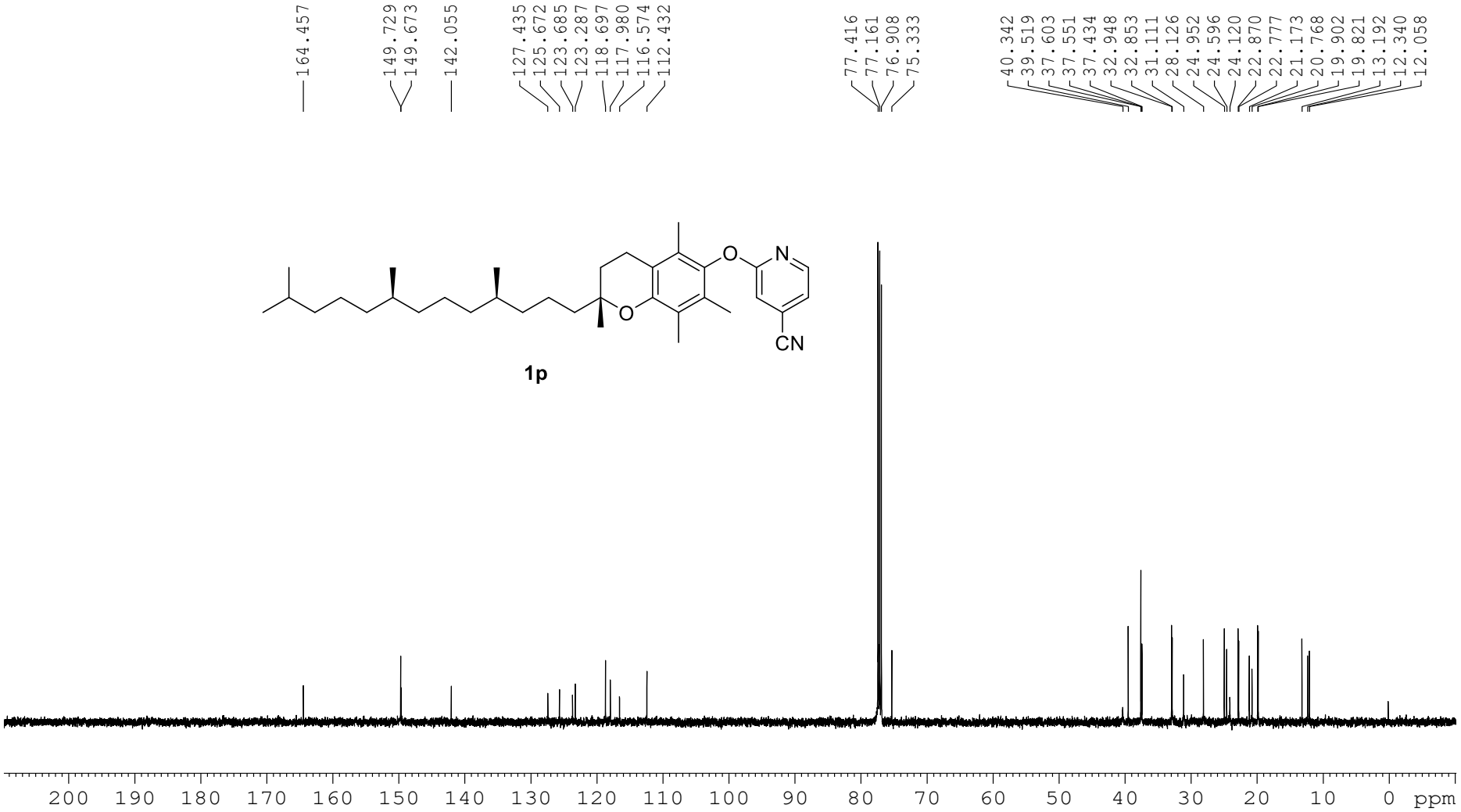

Figure S9. ^{13}C NMR spectra of **1p** ($CDCl_3$, 125M).

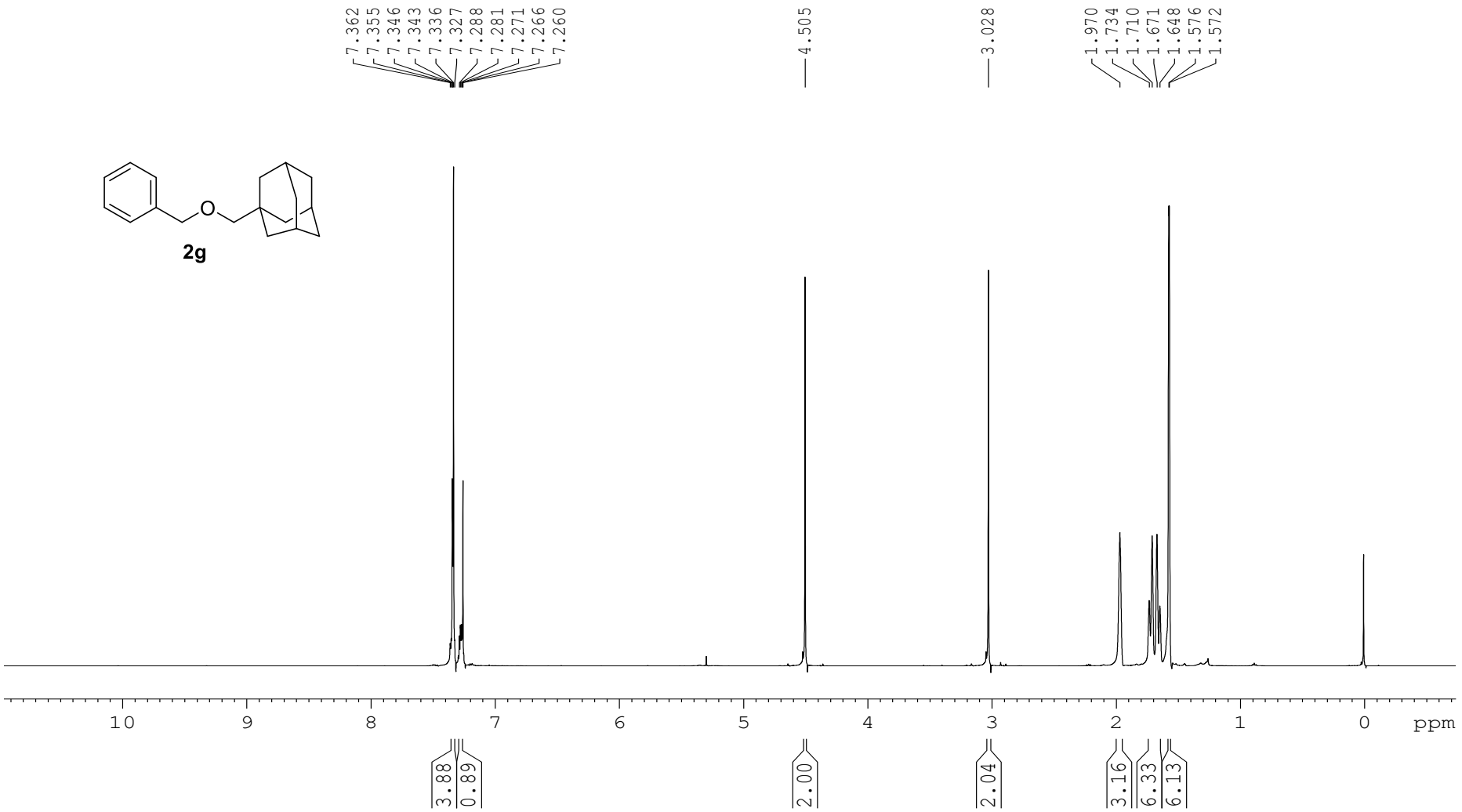

Figure S10. ^{1}H NMR spectra of **2g** ($CDCl_3$, 500M).

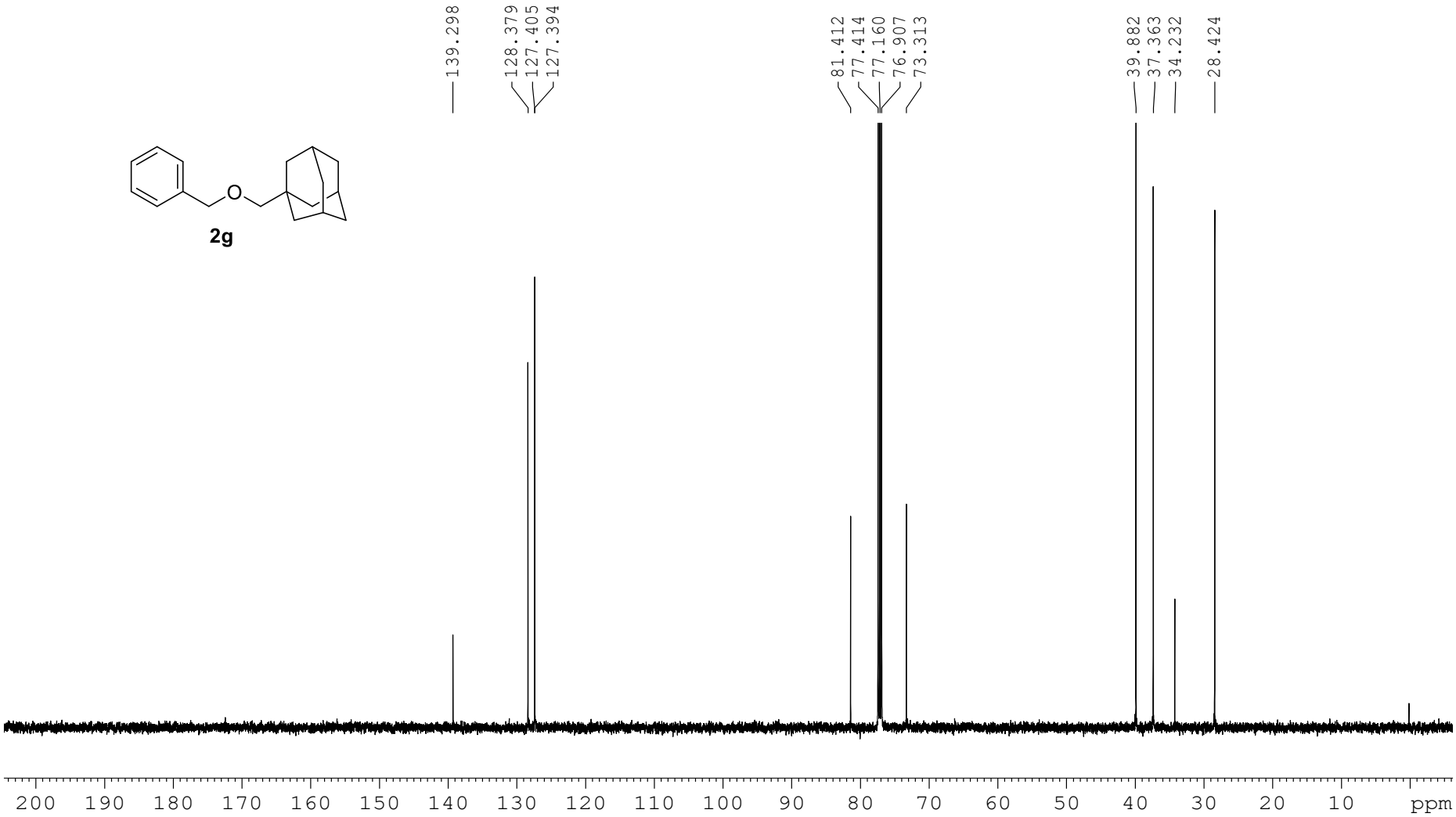

Figure S11. ^{13}C NMR spectra of **2g** ($CDCl_3$, 125M).

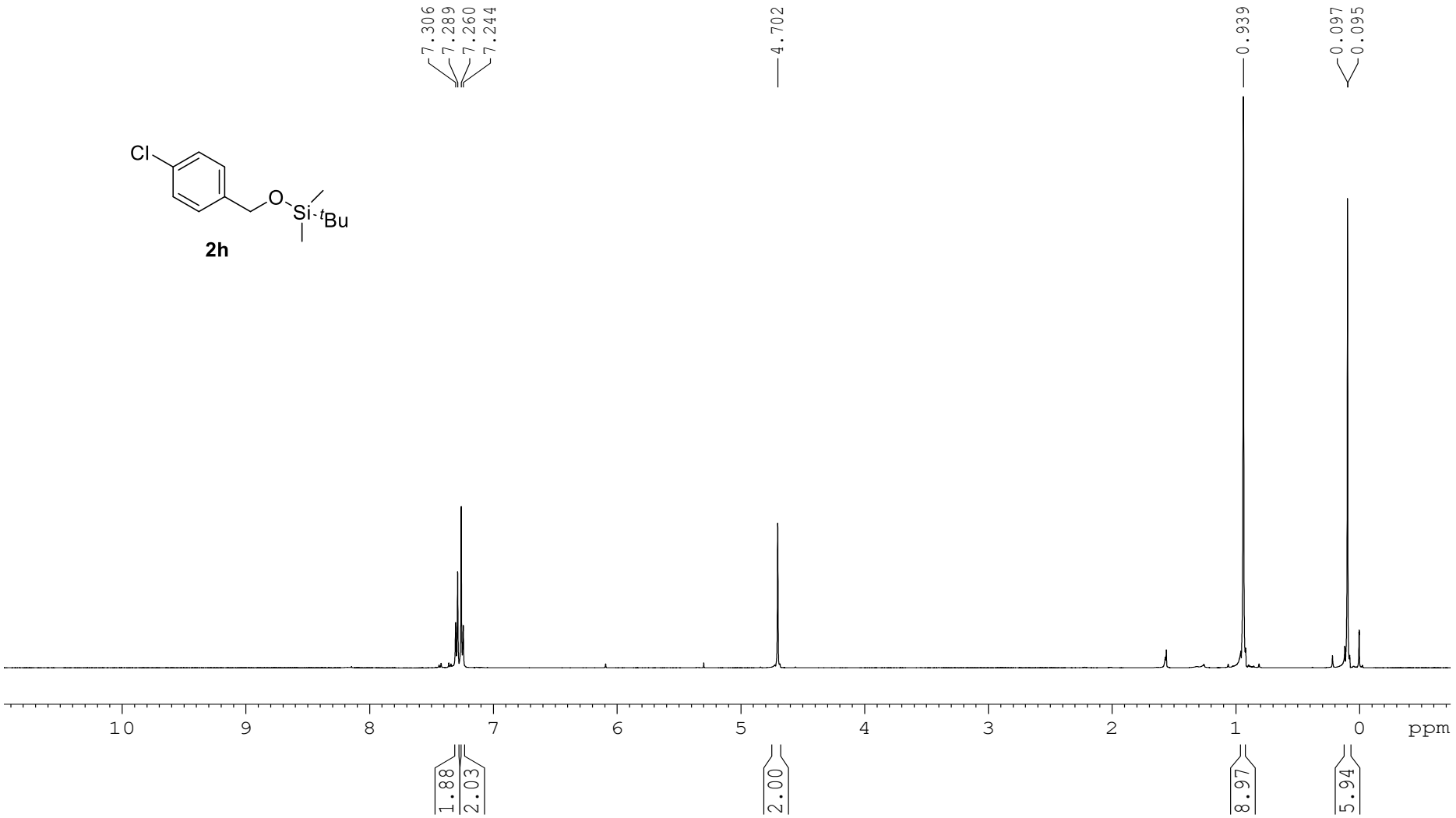

Figure S12. ^{1}H NMR spectra of **2h** ($CDCl_3$, 500M).

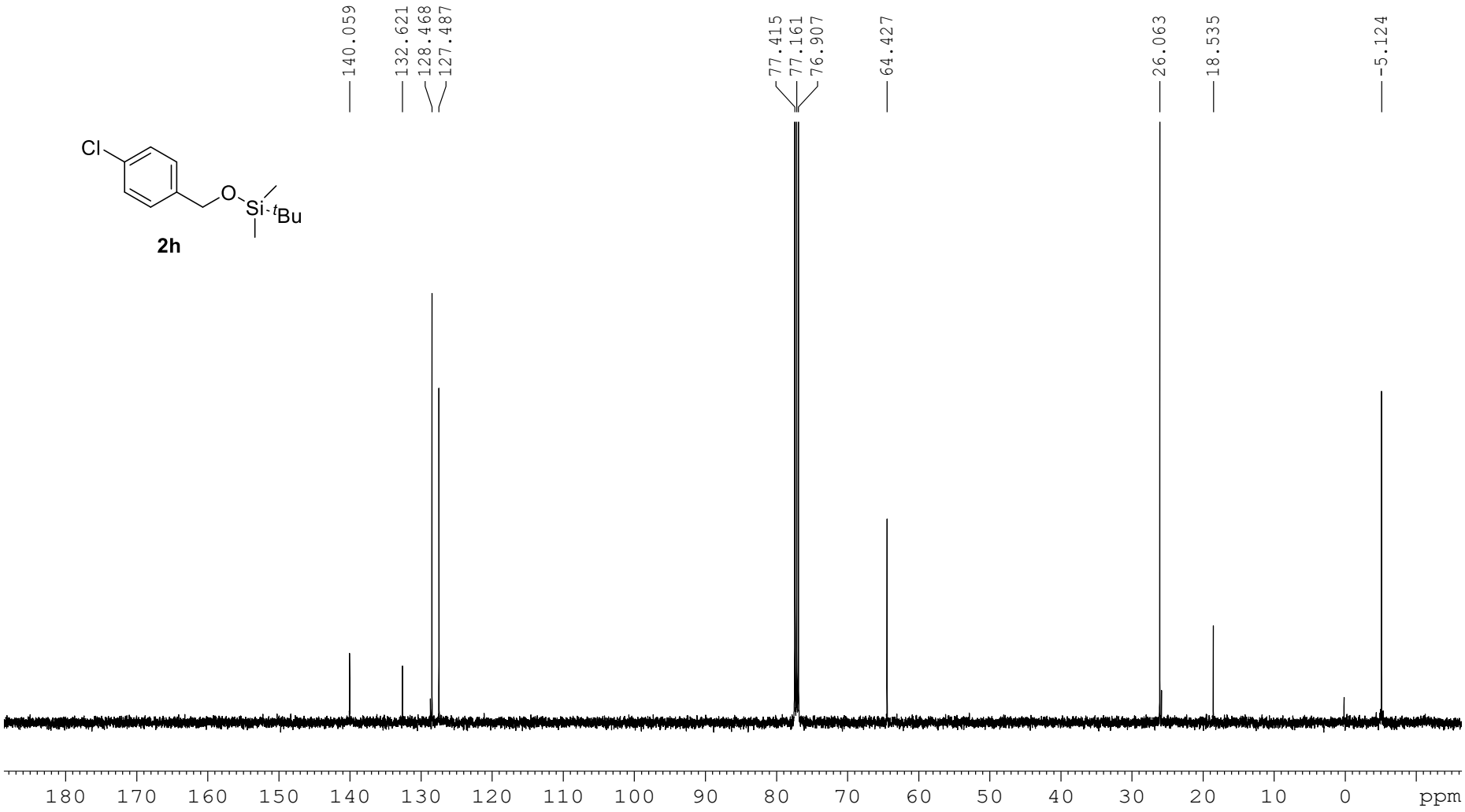

Figure S13. ^{13}C NMR spectra of **2h** ($CDCl_3$, 125M).

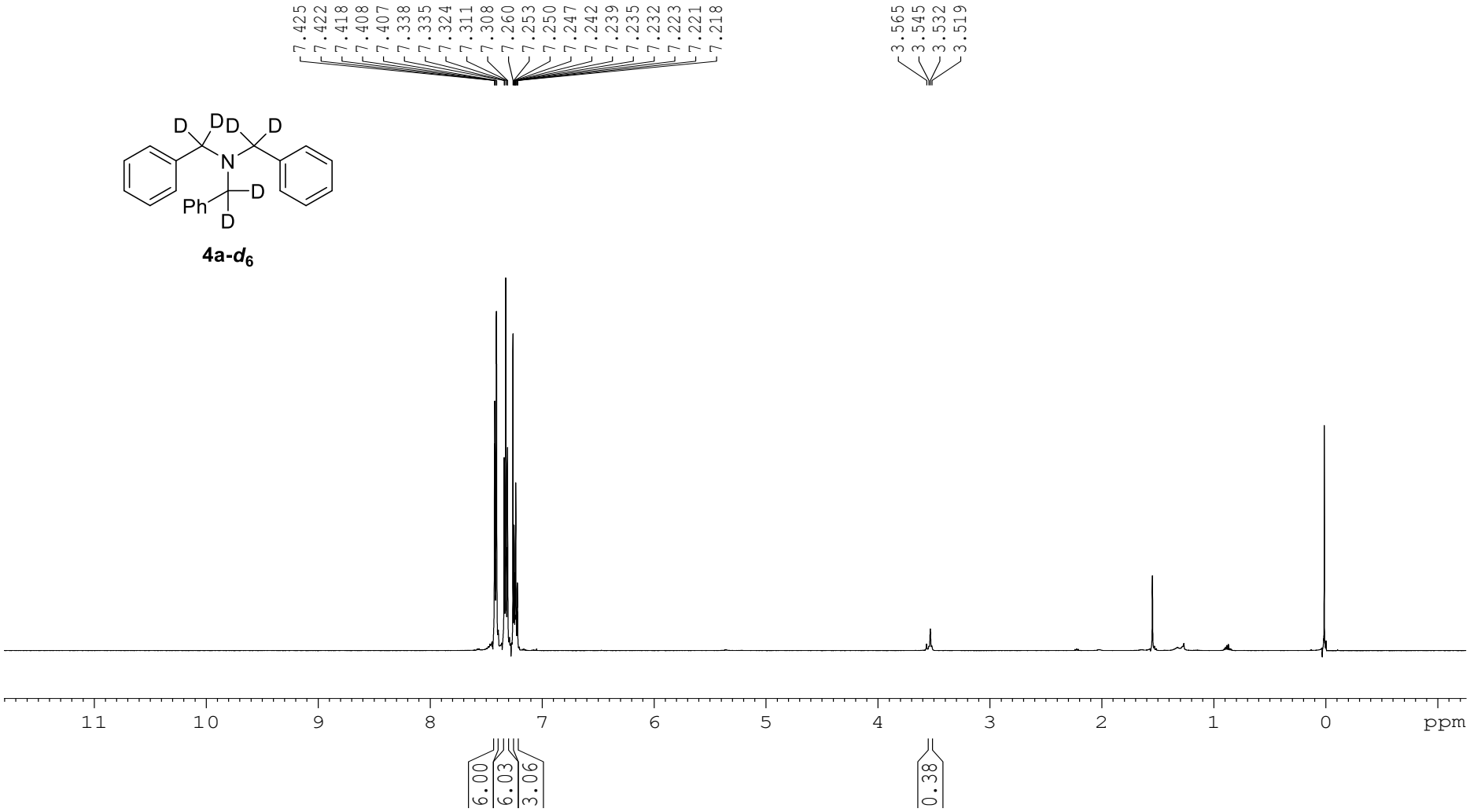

Figure S14. ^{1}H NMR spectra of **4a-*d*$_6$** ($CDCl_3$, 500M).

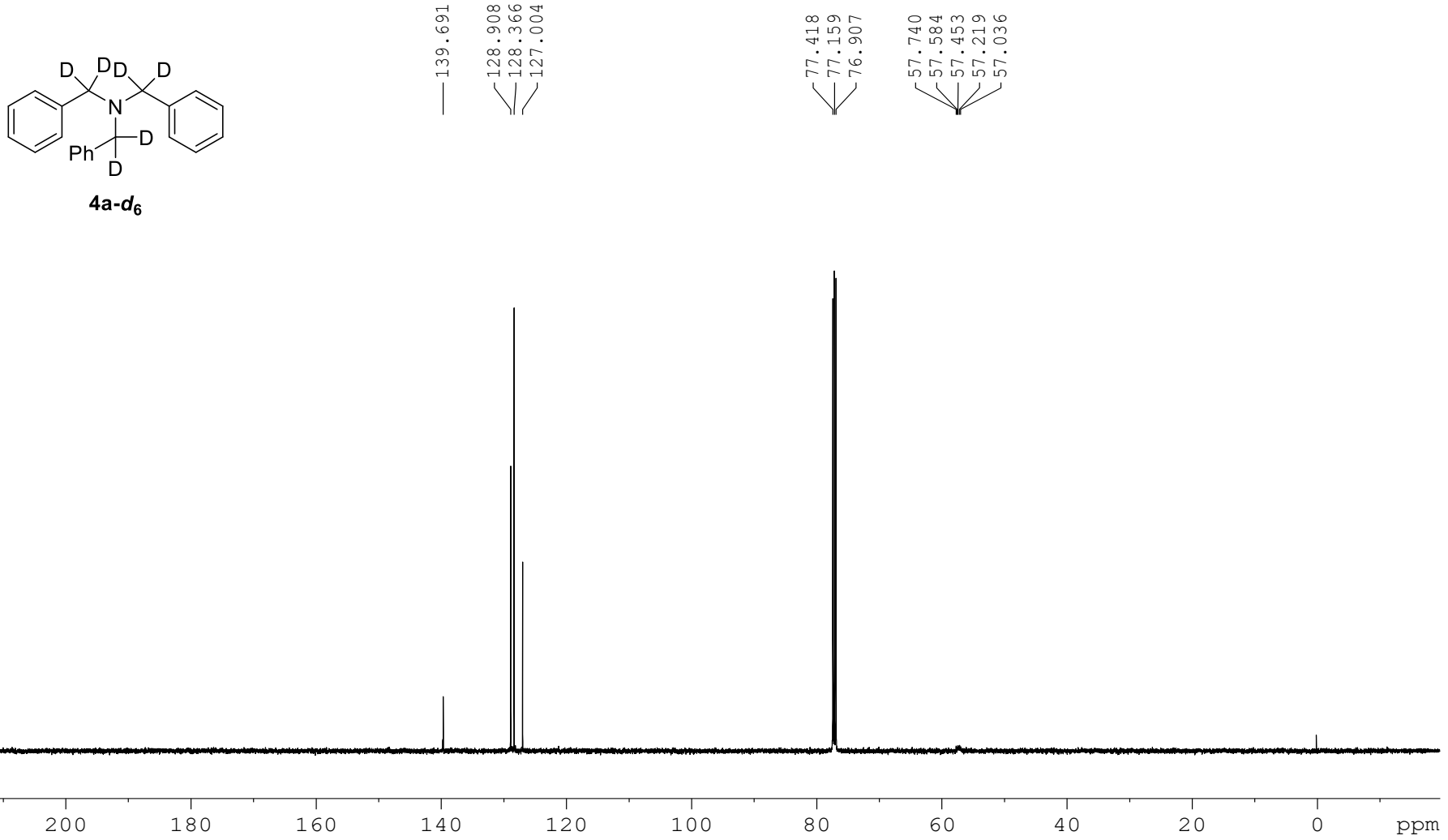

Figure S15. ^{13}C NMR spectra of **4a-*d*$_6$** ($CDCl_3$, 125M).

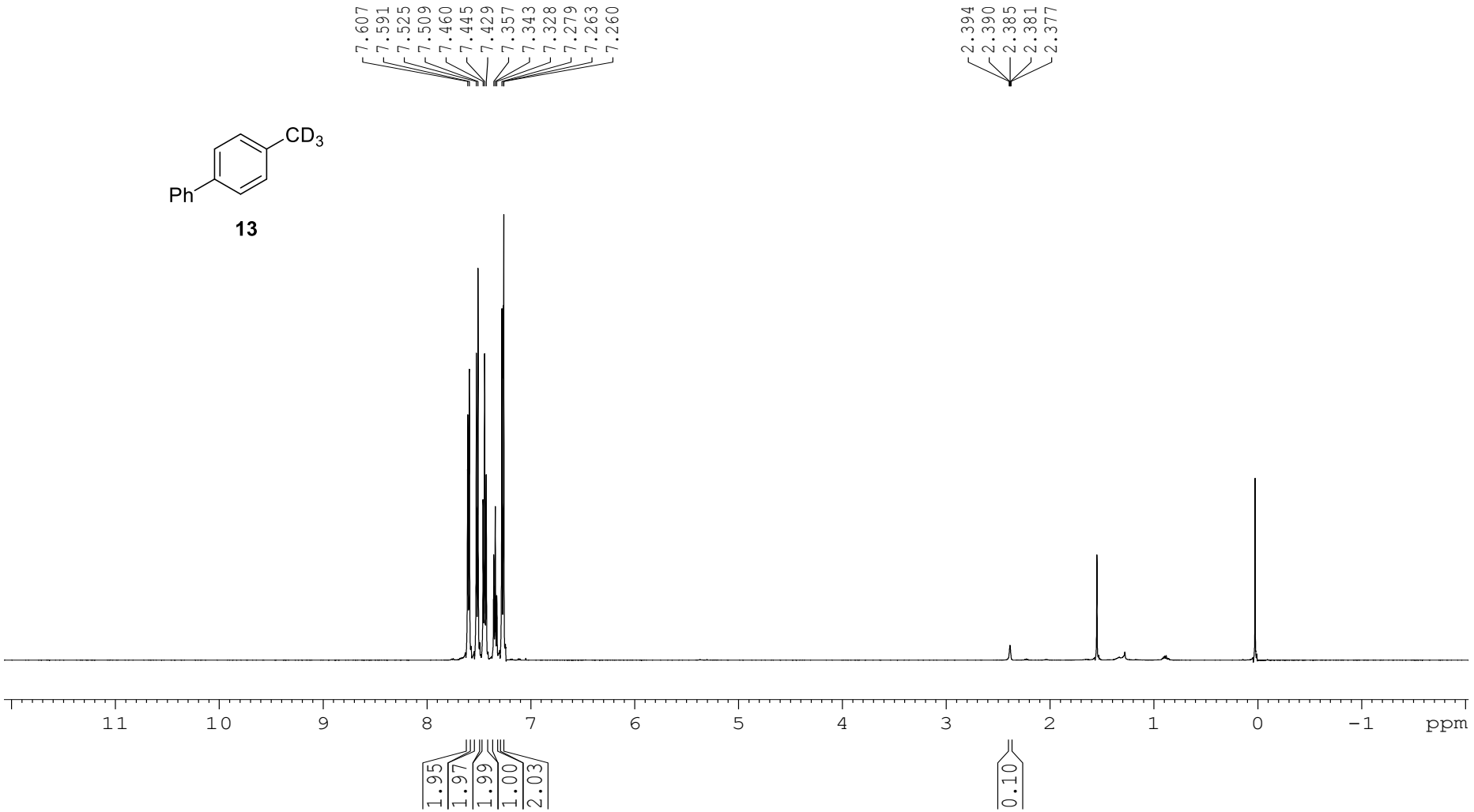

Figure S16. ^{1}H NMR spectra of **13** ($CDCl_3$, 500M).

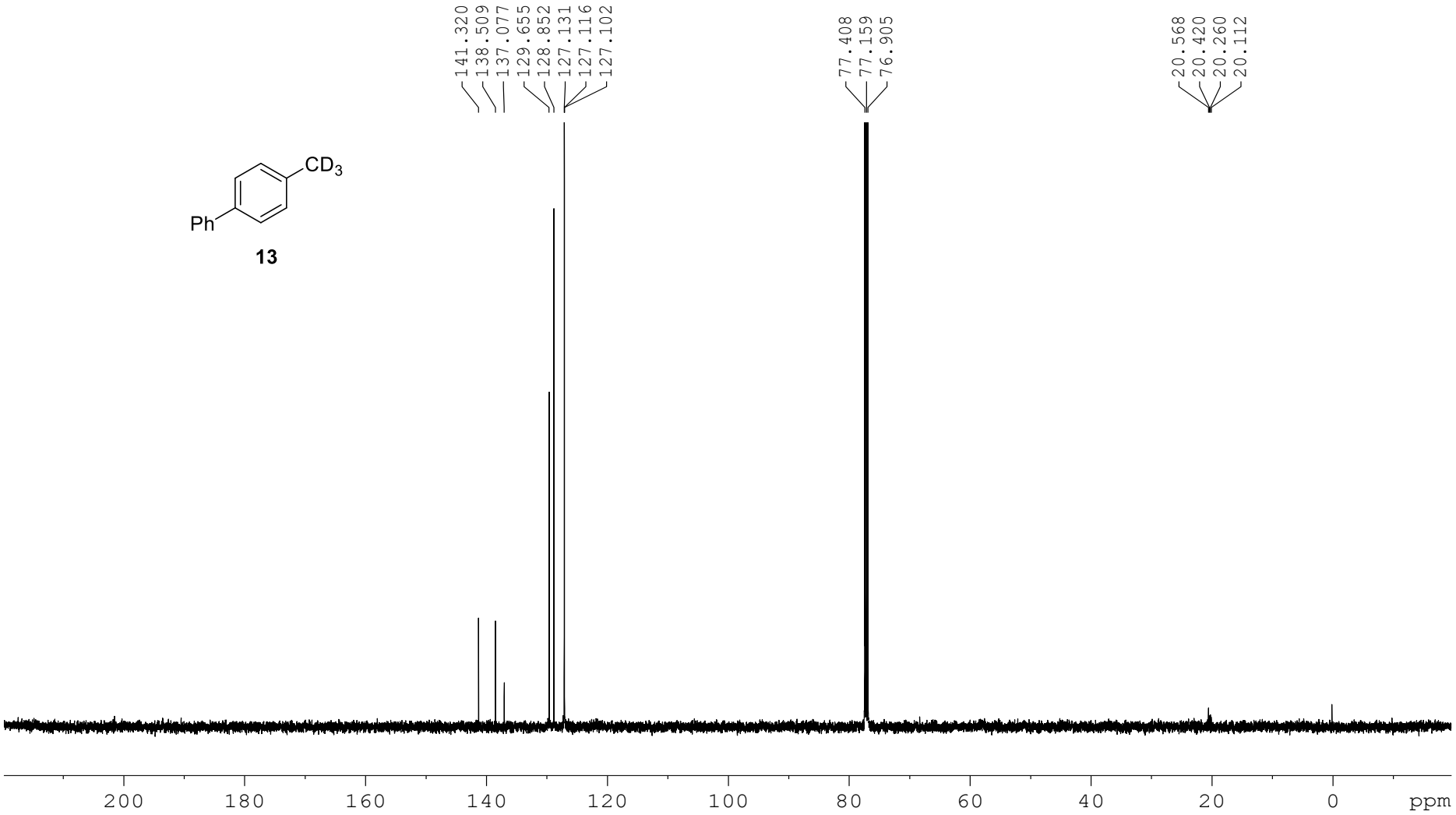

Figure S17. ^{13}C NMR spectra of **13** ($CDCl_3$, 125M).

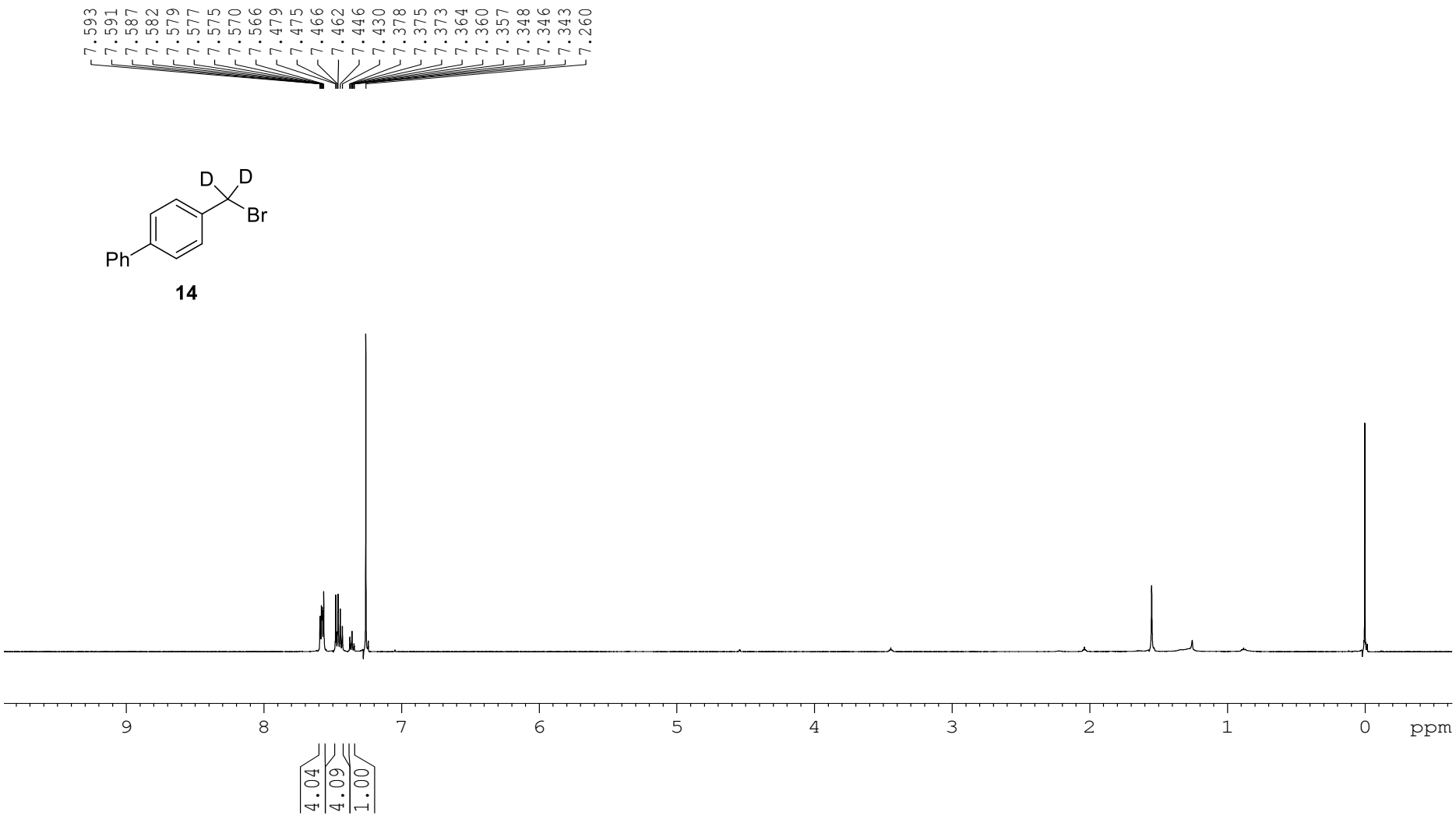

Figure S18. ^{1}H NMR spectra of **14** ($CDCl_3$, 500M).

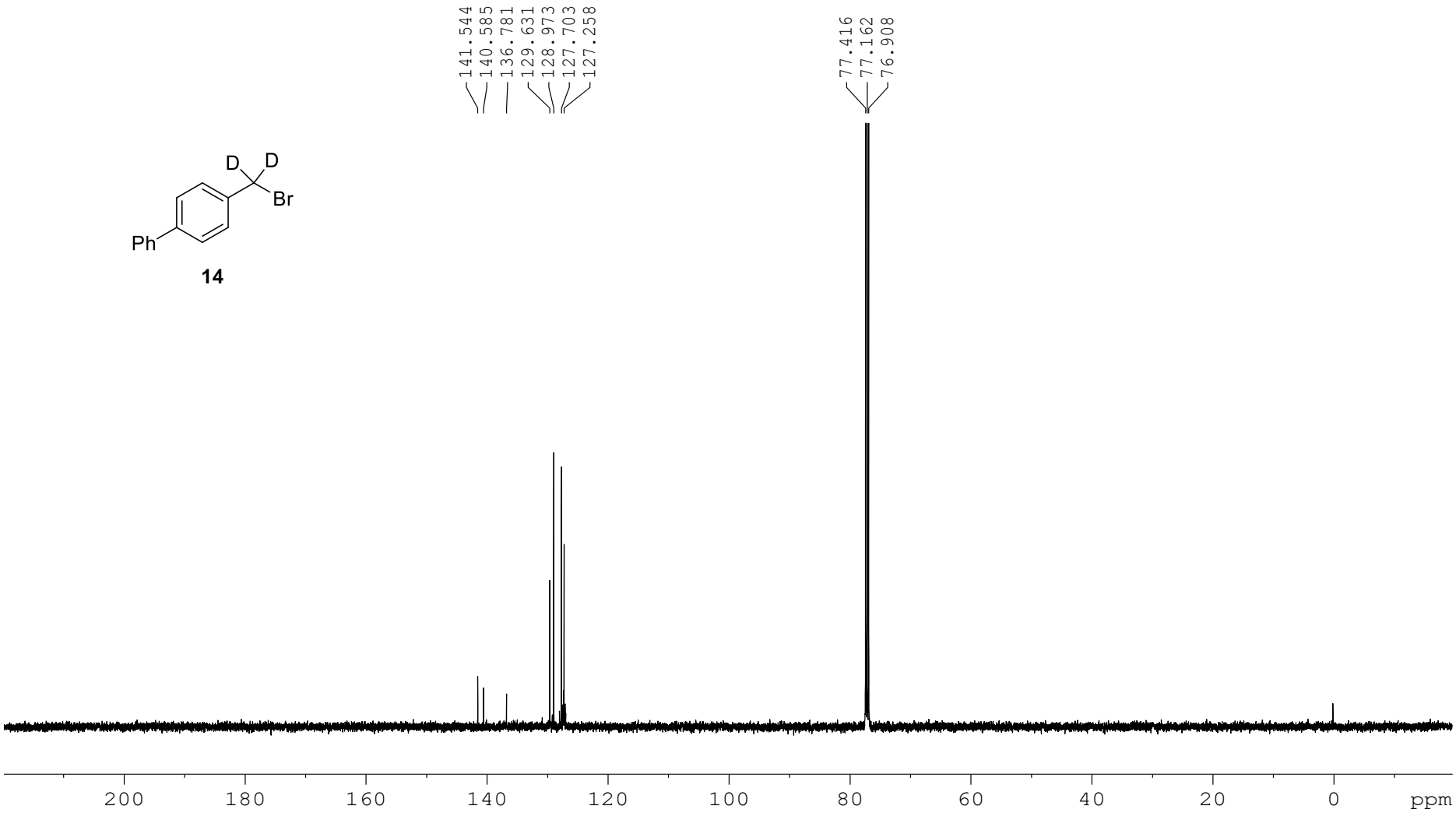

Figure S19. ^{13}C NMR spectra of **14** ($CDCl_3$, 125M).

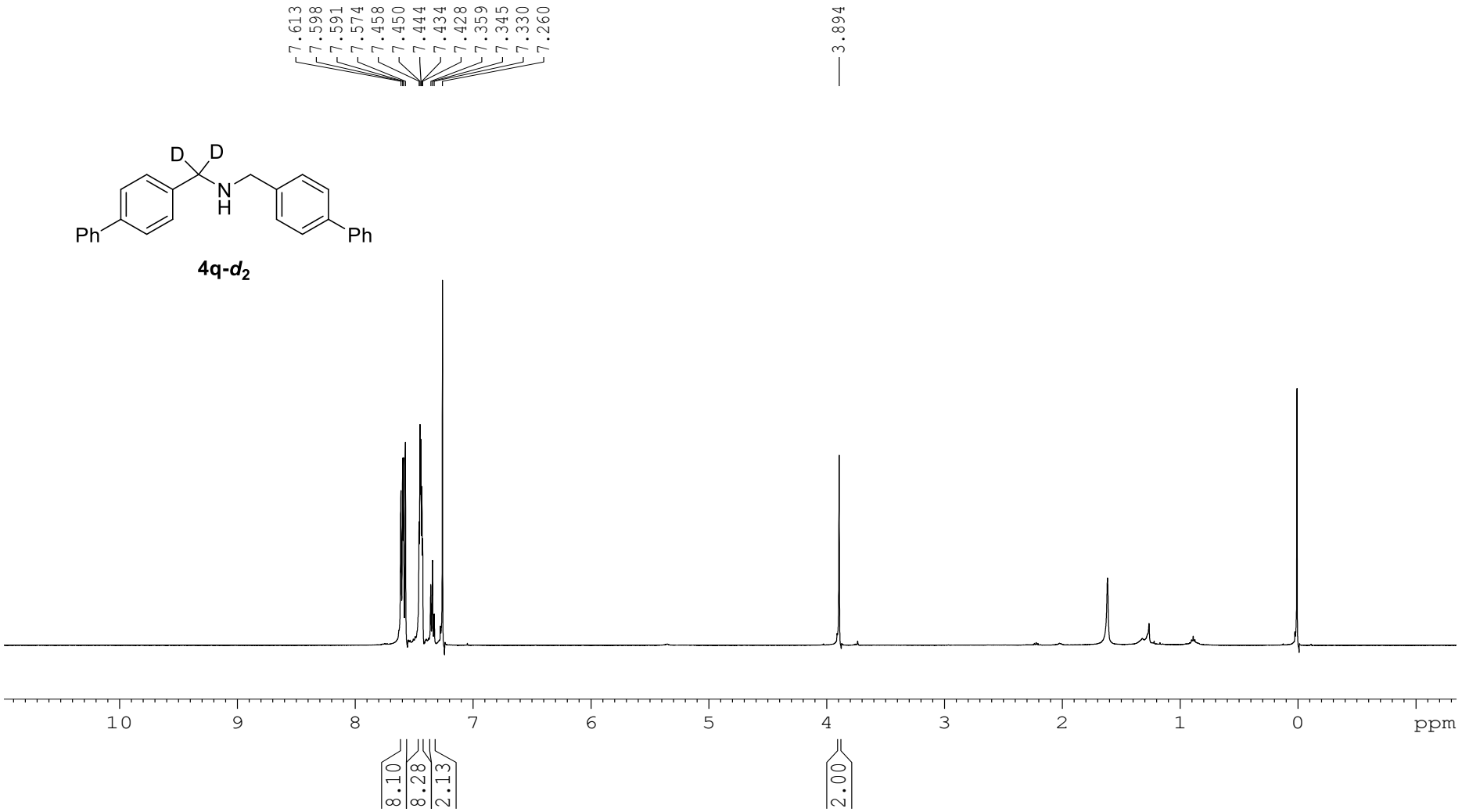

Figure S20. ^{1}H NMR spectra of **4q-*d*$_2$** ($CDCl_3$, 500M).

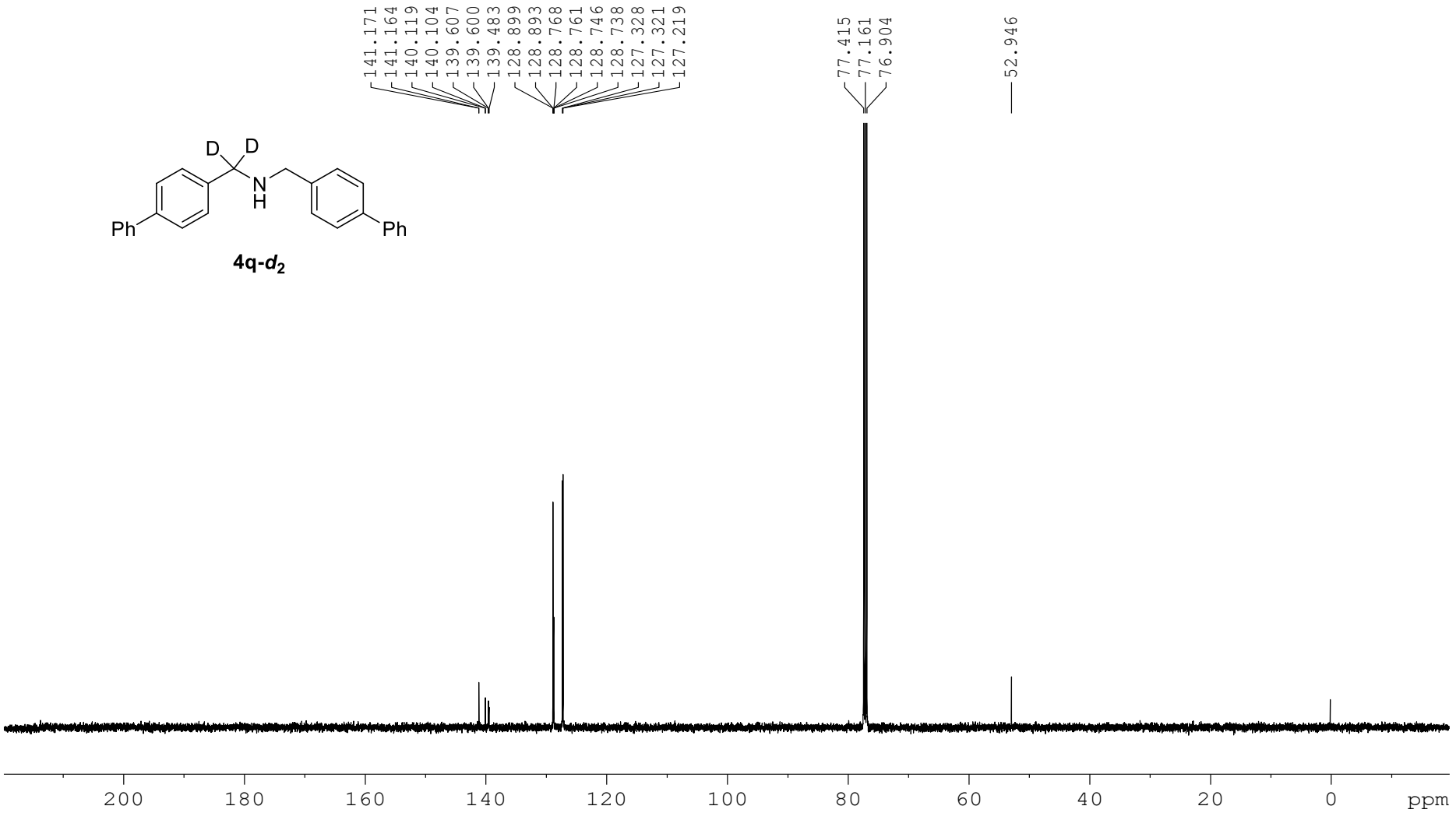

Figure S21. ^{13}C NMR spectra of **4q-*d*2** ($CDCl_3$, 125M).

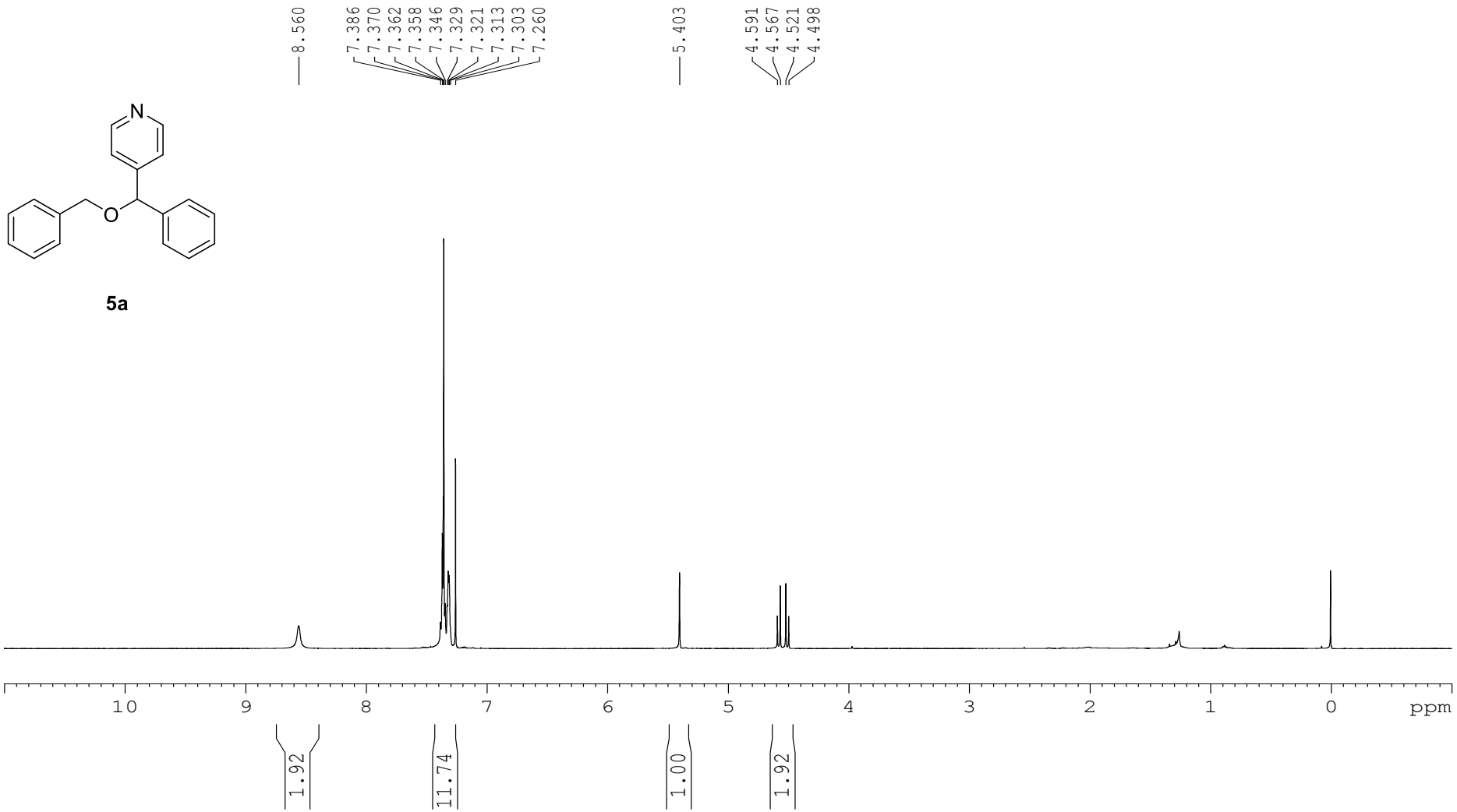

Figure S22. ^{1}H NMR spectra of **5a** ($CDCl_3$, 500M).

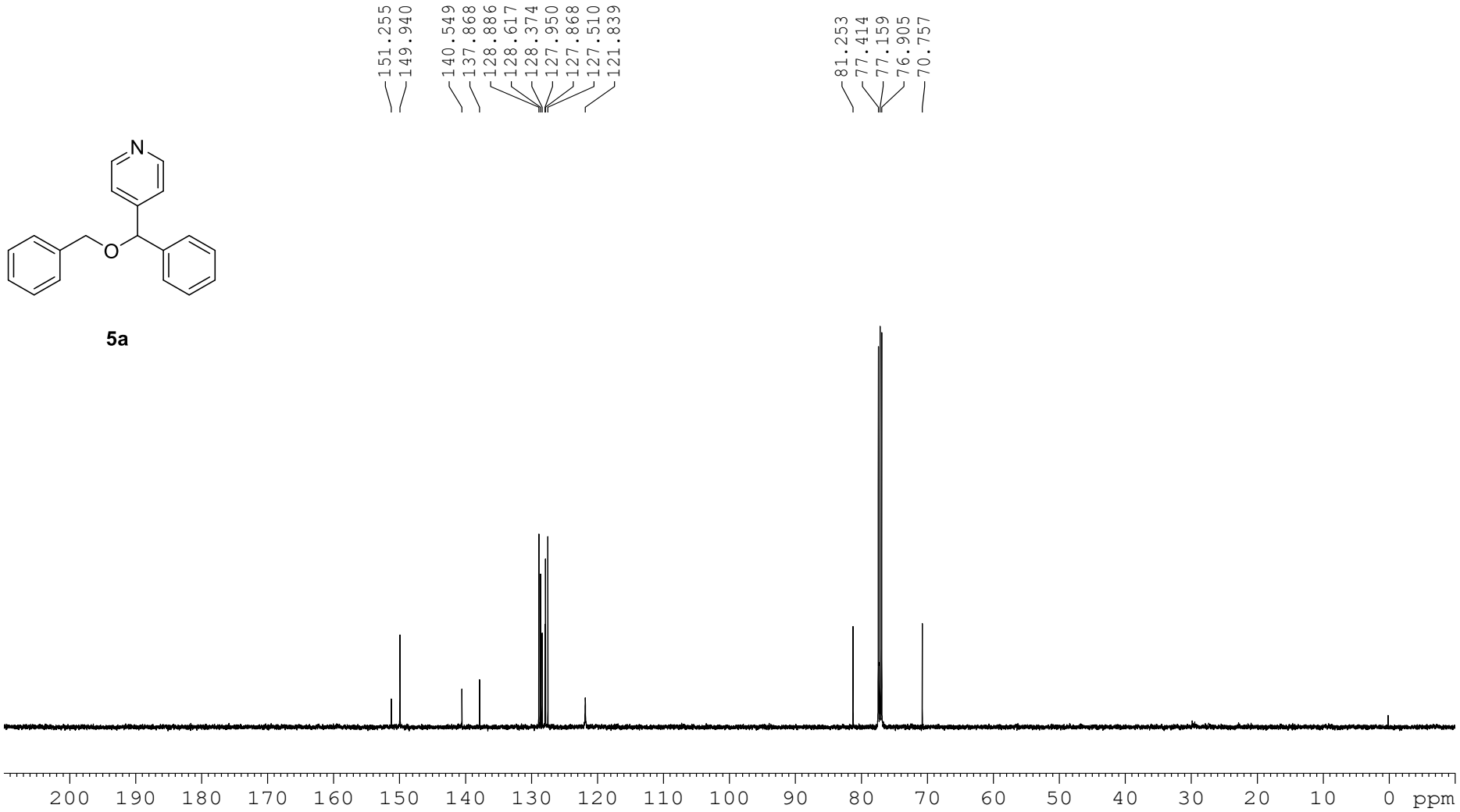

Figure S23. ^{13}C NMR spectra of **5a** ($CDCl_3$, 125M).

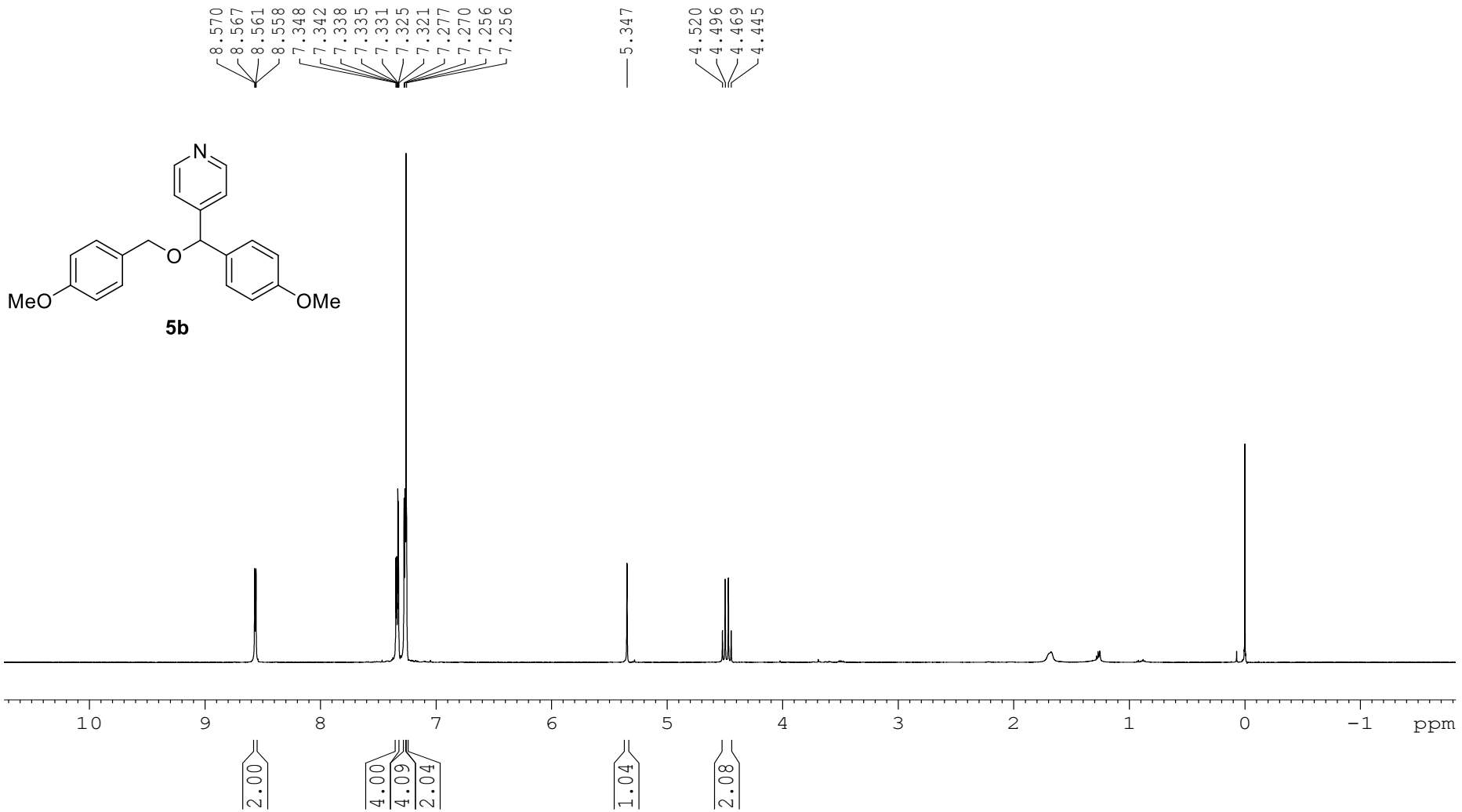

Figure S24. ^{1}H NMR spectra of **5b** ($CDCl_3$, 500M).

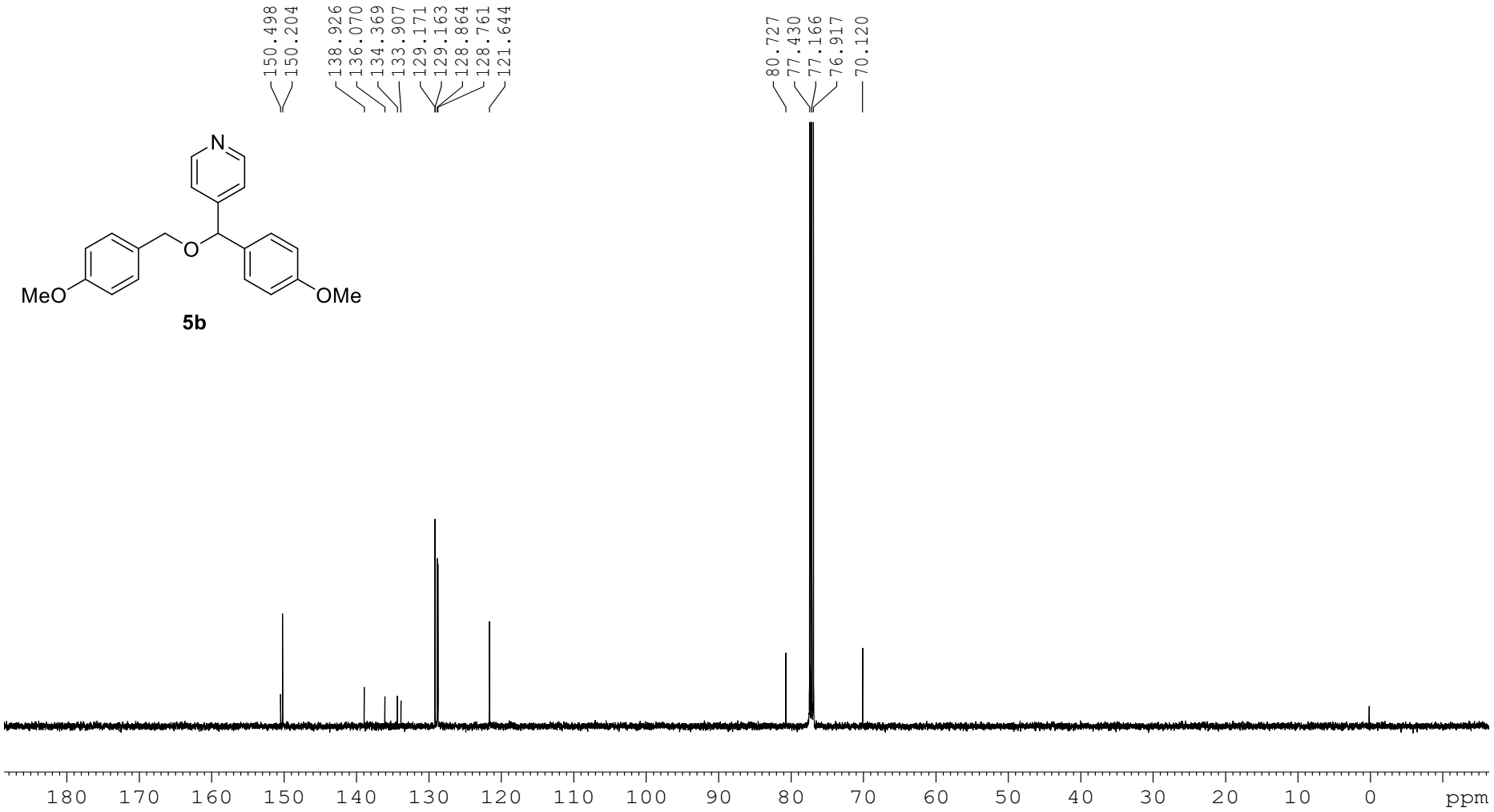

Figure S25. ^{13}C NMR spectra of **5b** ($CDCl_3$, 125M).

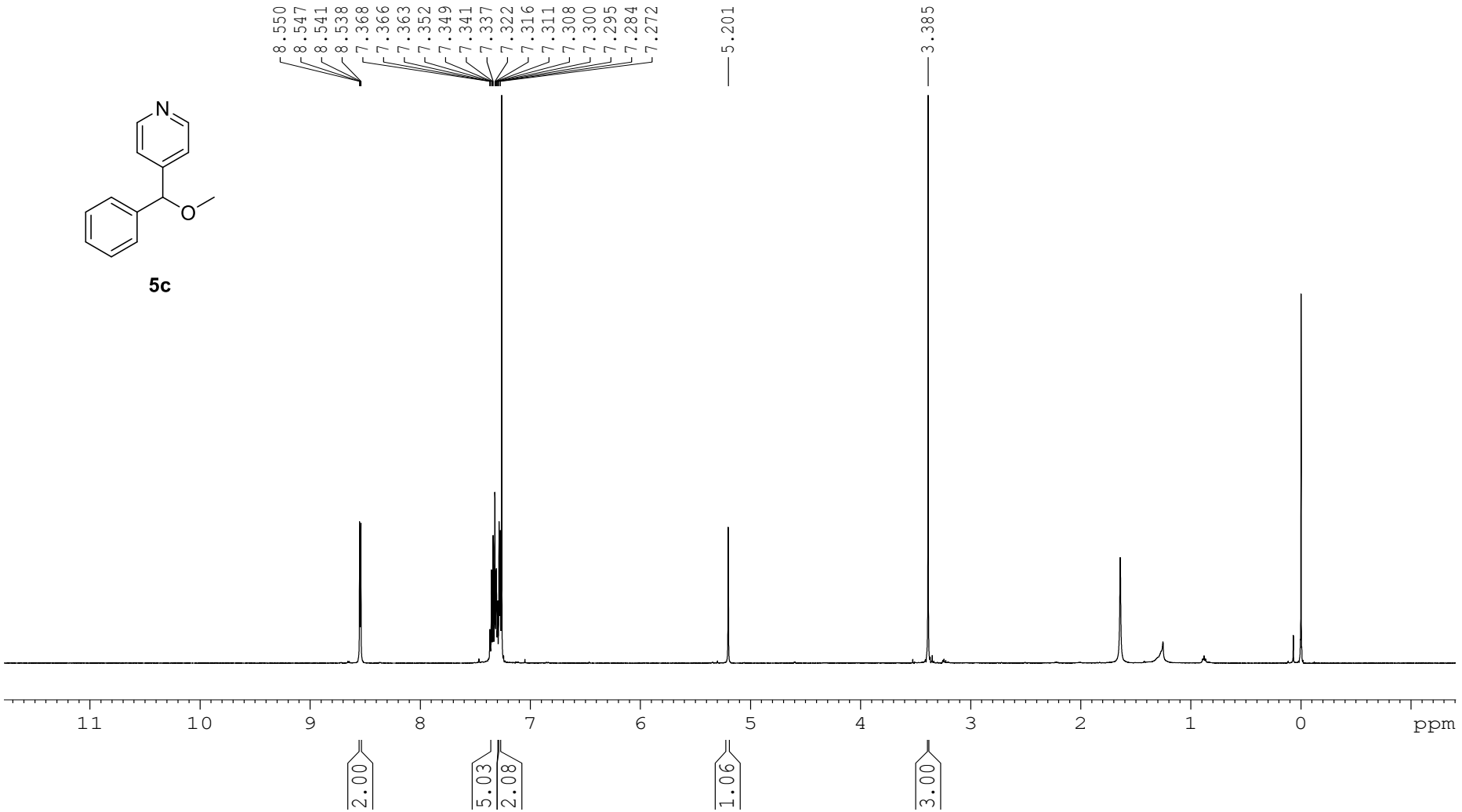

Figure S26. ^{1}H NMR spectra of **5c** ($CDCl_3$, 500M).

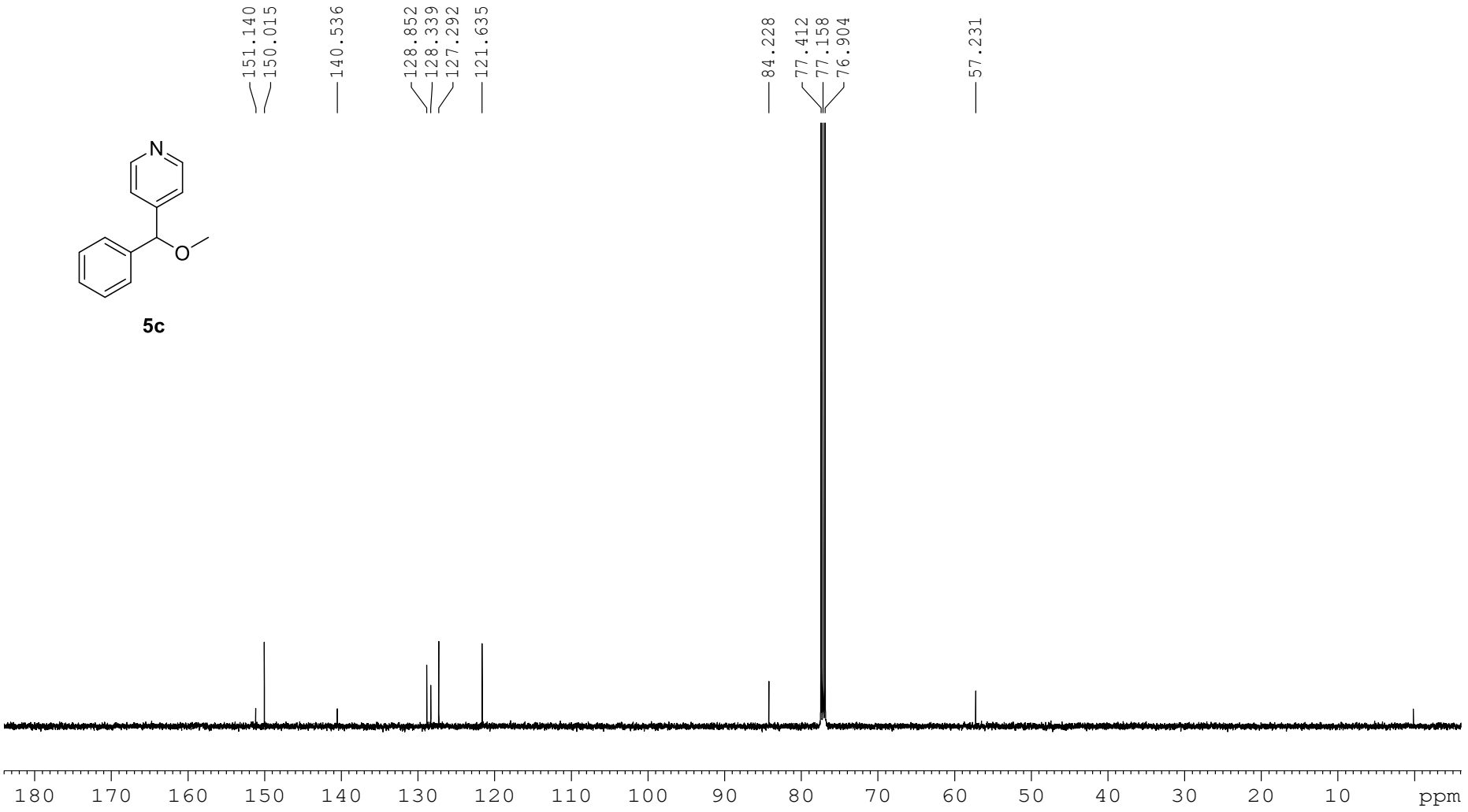

Figure S27. ^{13}C NMR spectra of **5c** ($CDCl_3$, 125M).

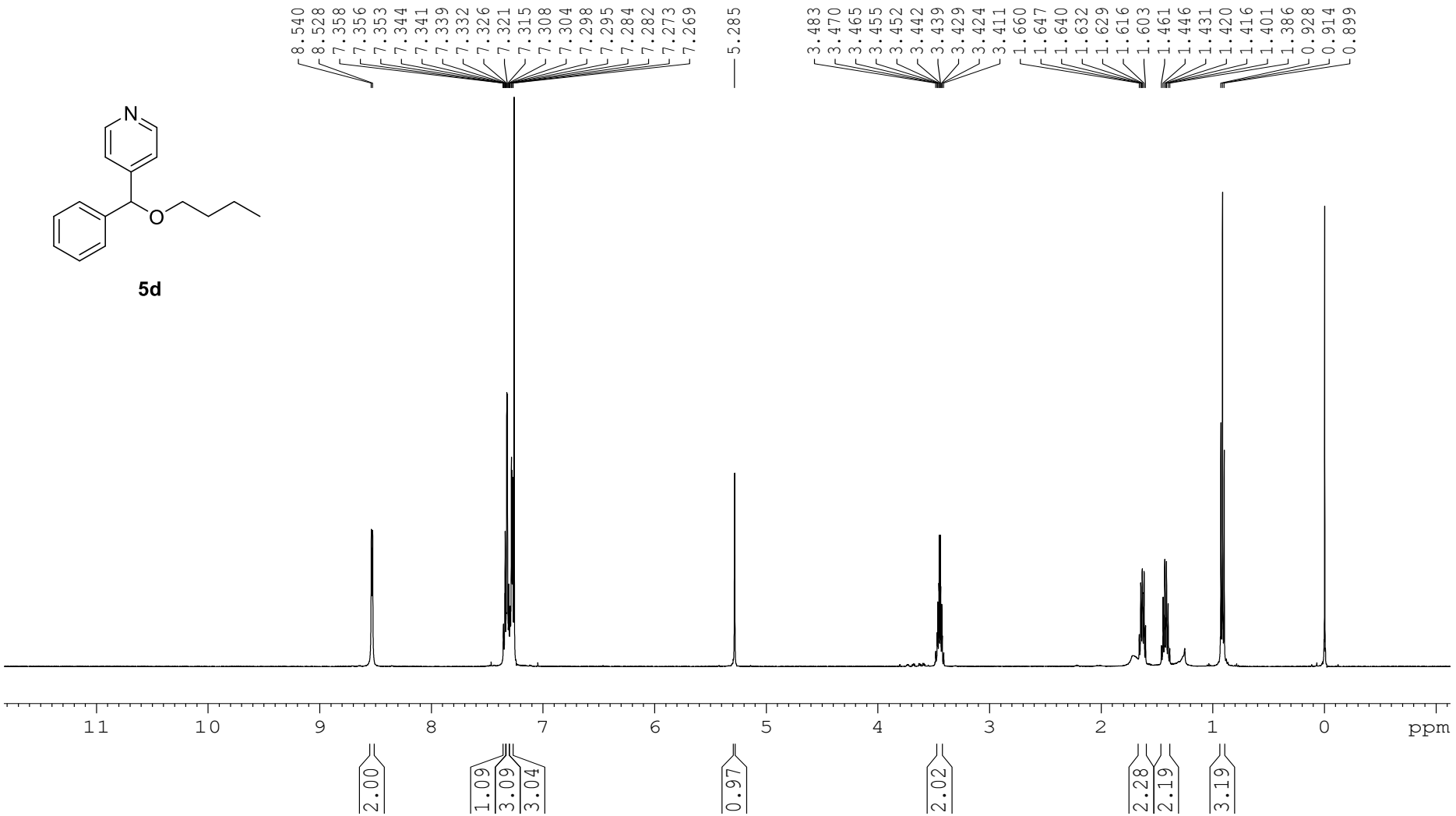

Figure S28. ^{1}H NMR spectra of **5d** ($CDCl_3$, 500M).

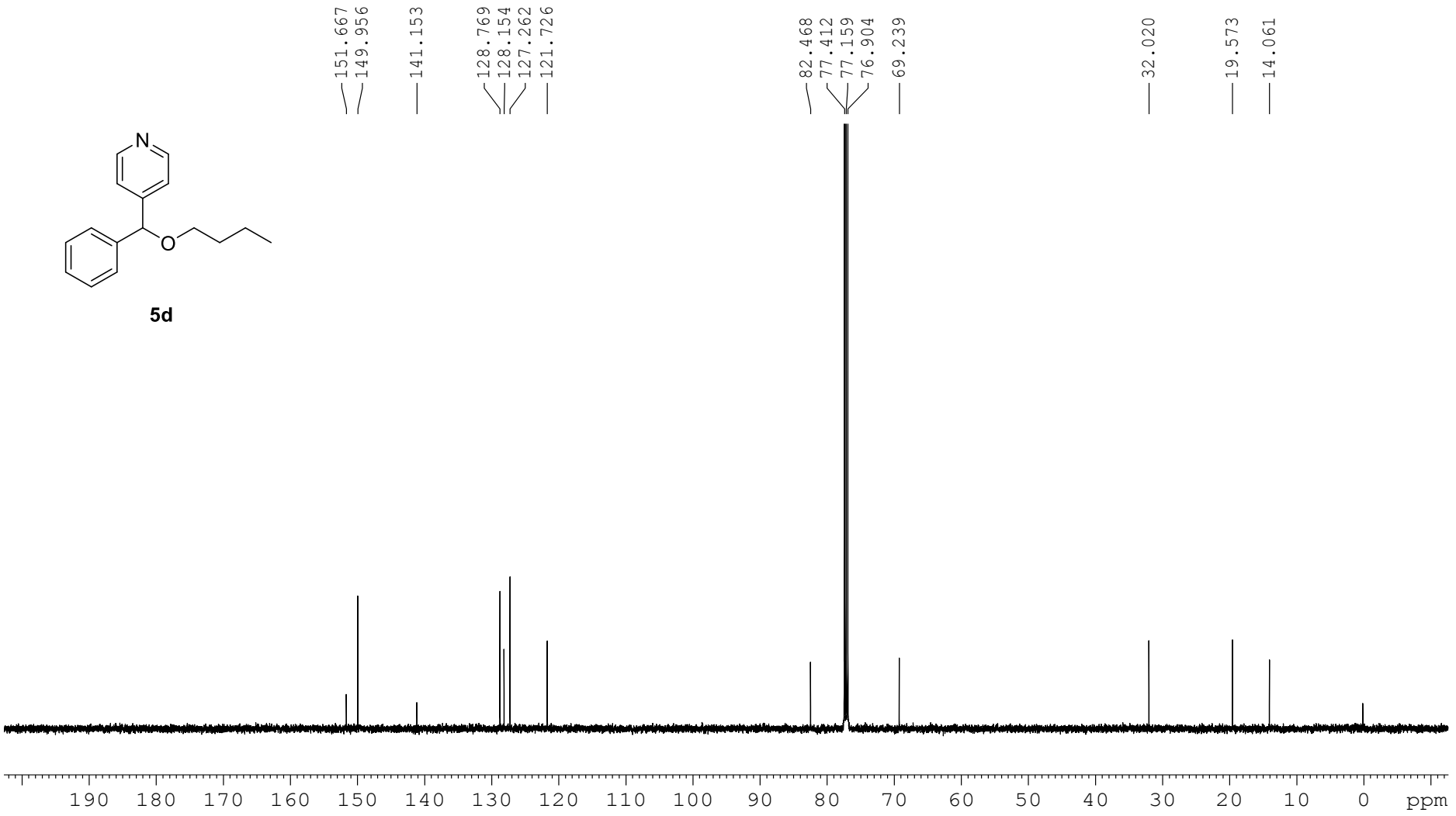

Figure S29. ^{13}C NMR spectra of **5d** ($CDCl_3$, 125M).

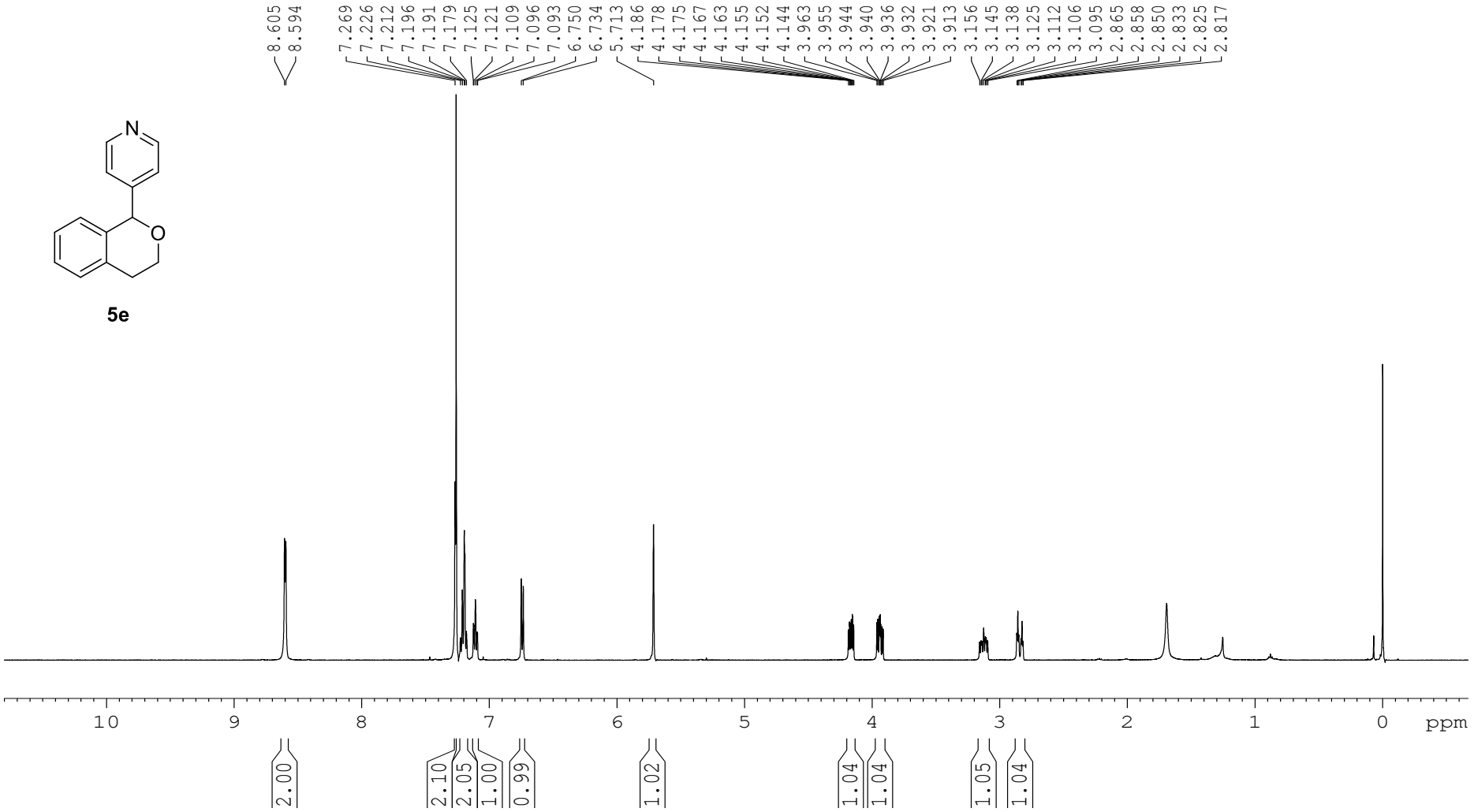

Figure S30. ^{1}H NMR spectra of **5e** ($CDCl_3$, 500M).

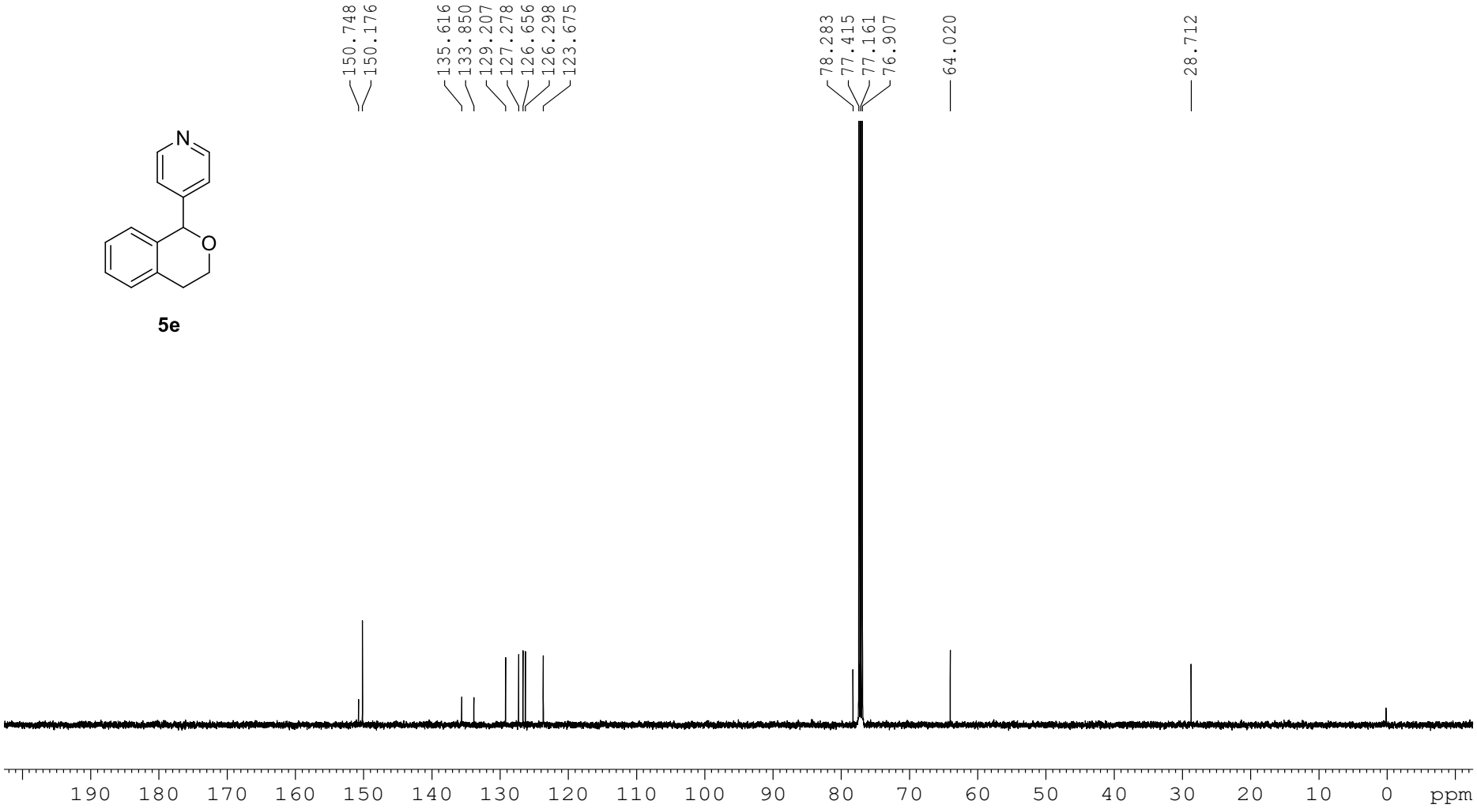

Figure S31. ^{13}C NMR spectra of **5e** ($CDCl_3$, 125M).

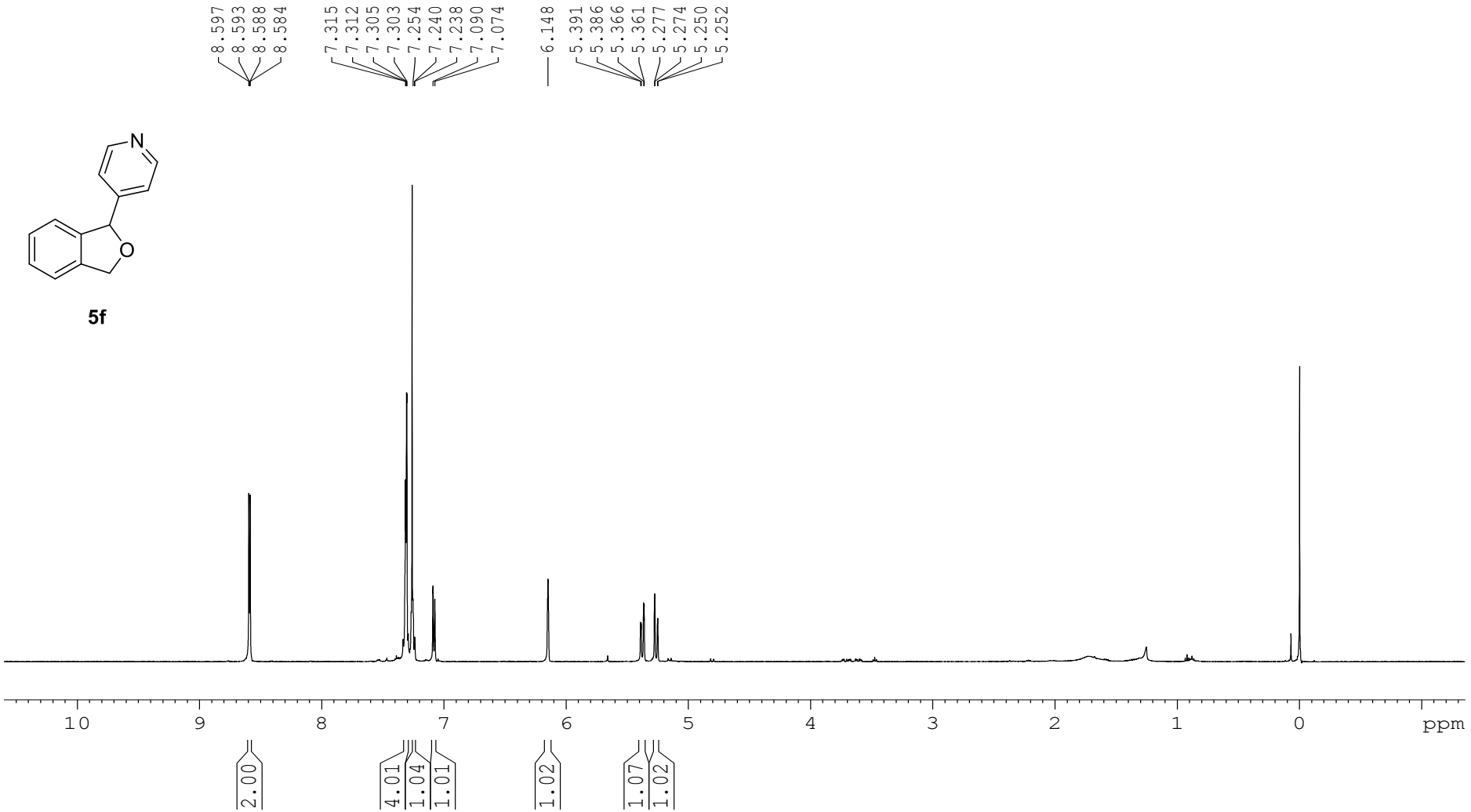

Figure S32. ^{1}H NMR spectra of **5f** ($CDCl_3$, 500M).

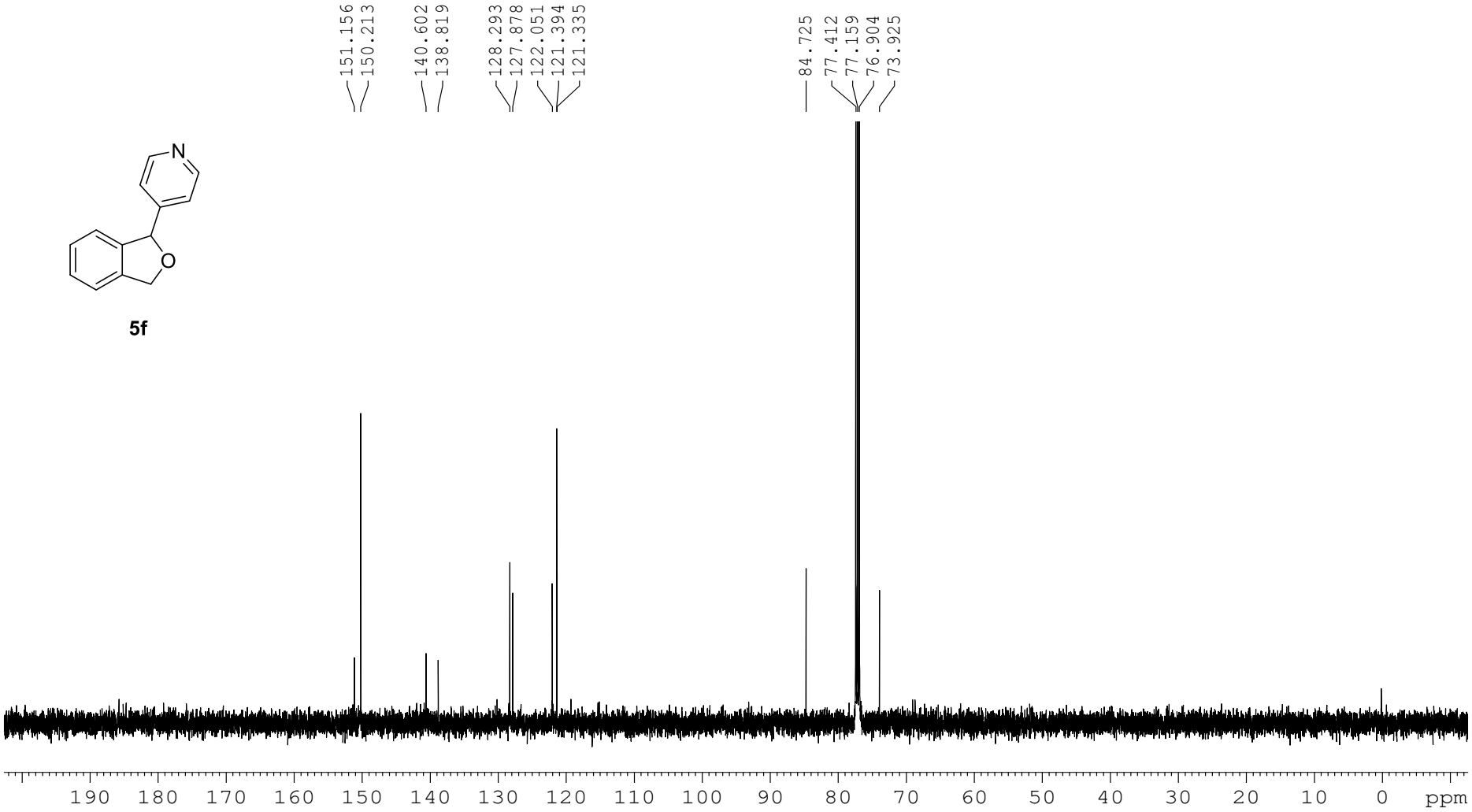

Figure S33. ^{13}C NMR spectra of **5f** ($CDCl_3$, 125M).

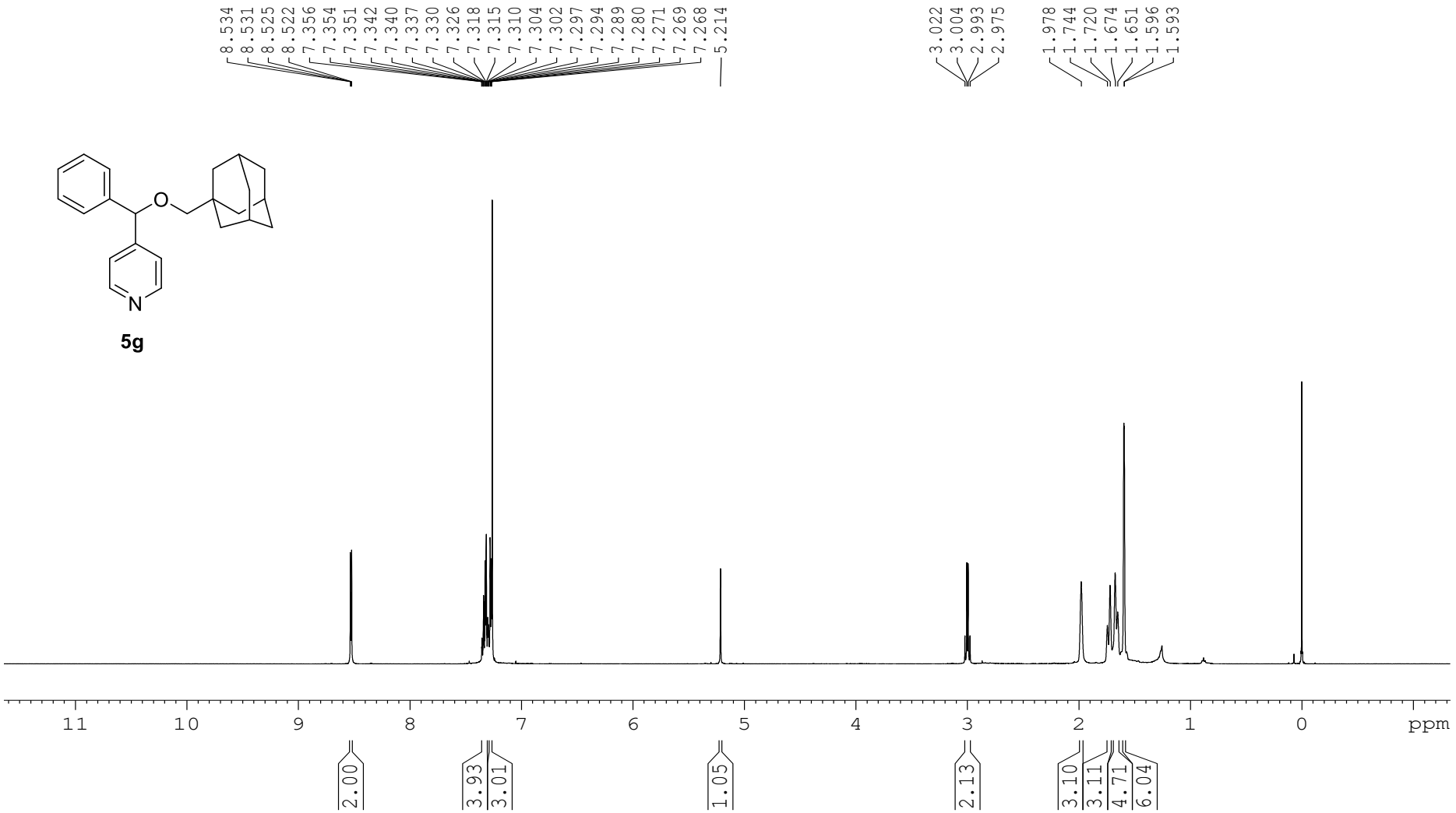

Figure S34. ^{1}H NMR spectra of **5g** ($CDCl_3$, 500M).

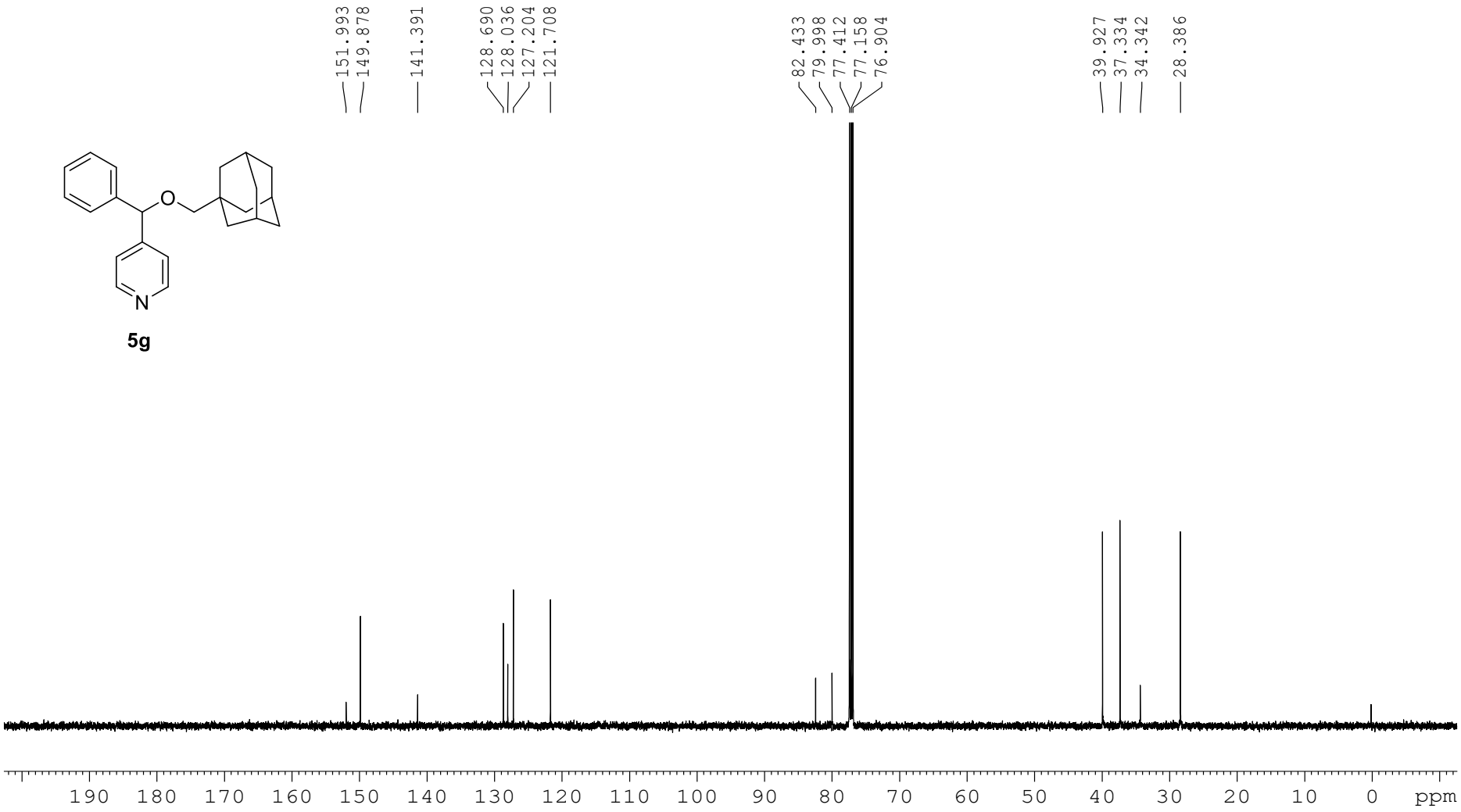

Figure S35. ^{13}C NMR spectra of **5g** ($CDCl_3$, 125M).

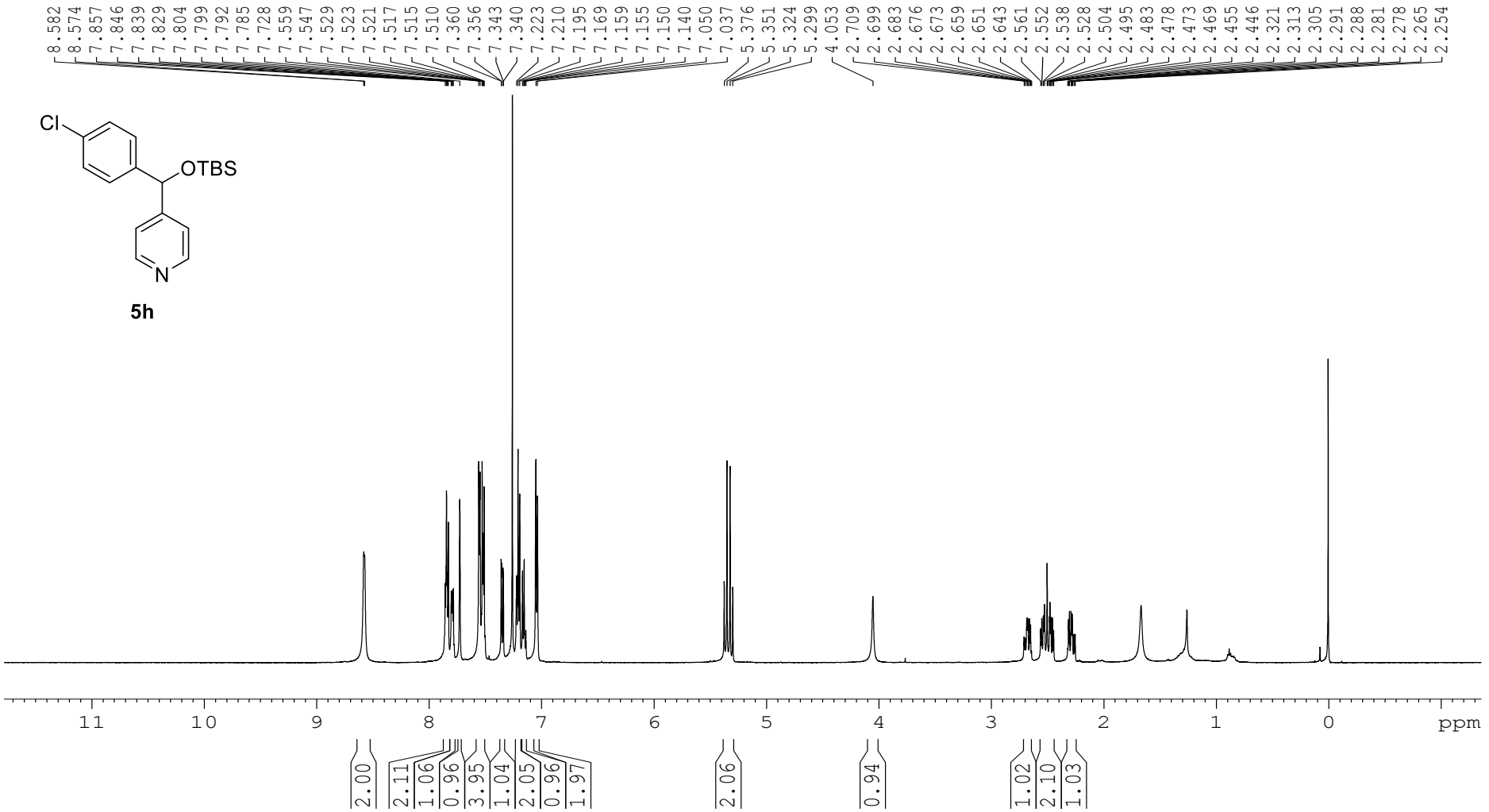

Figure S36. ^{1}H NMR spectra of **5h** ($CDCl_3$, 500M).

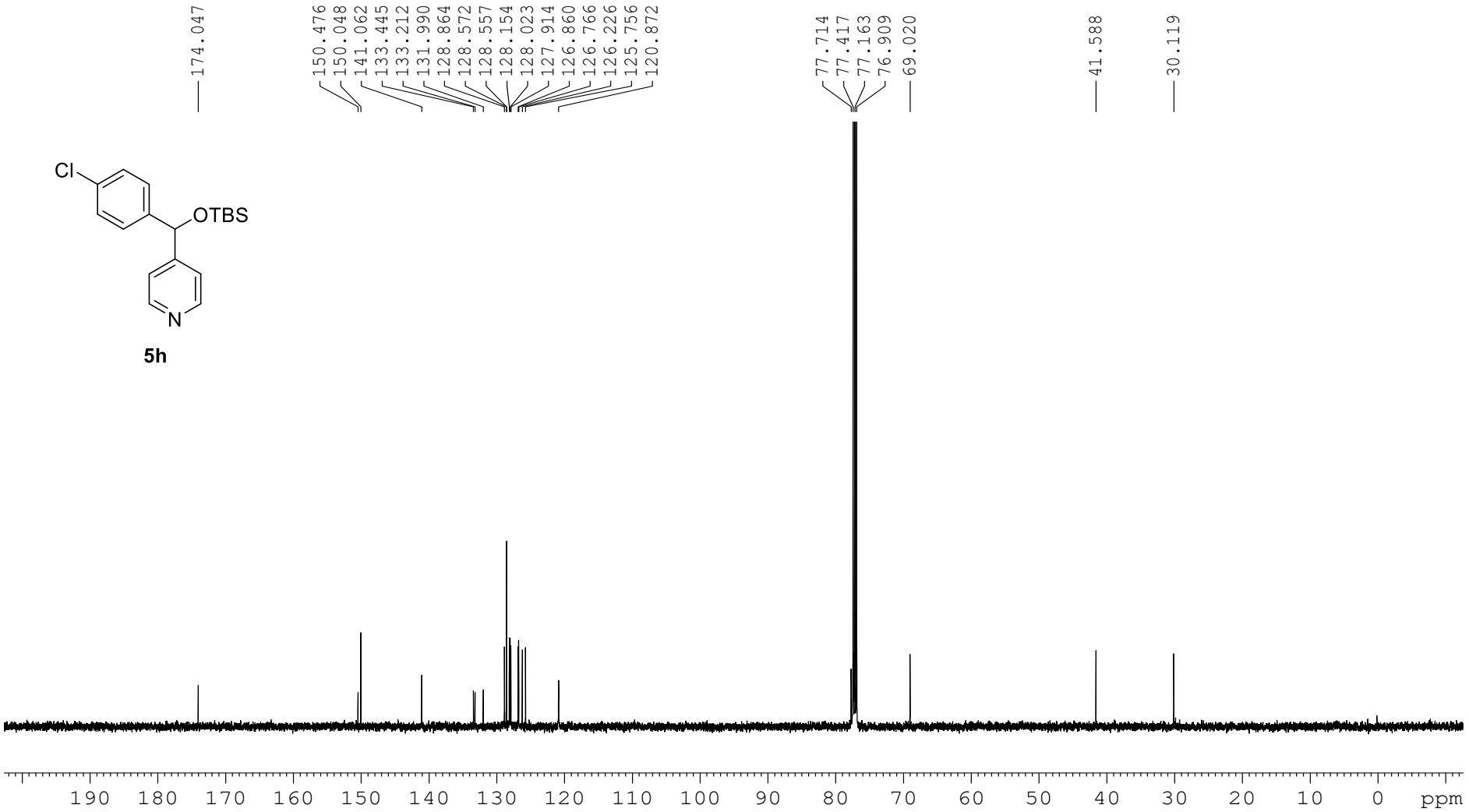

Figure S37. ^{13}C NMR spectra of **5h** ($CDCl_3$, 125M).

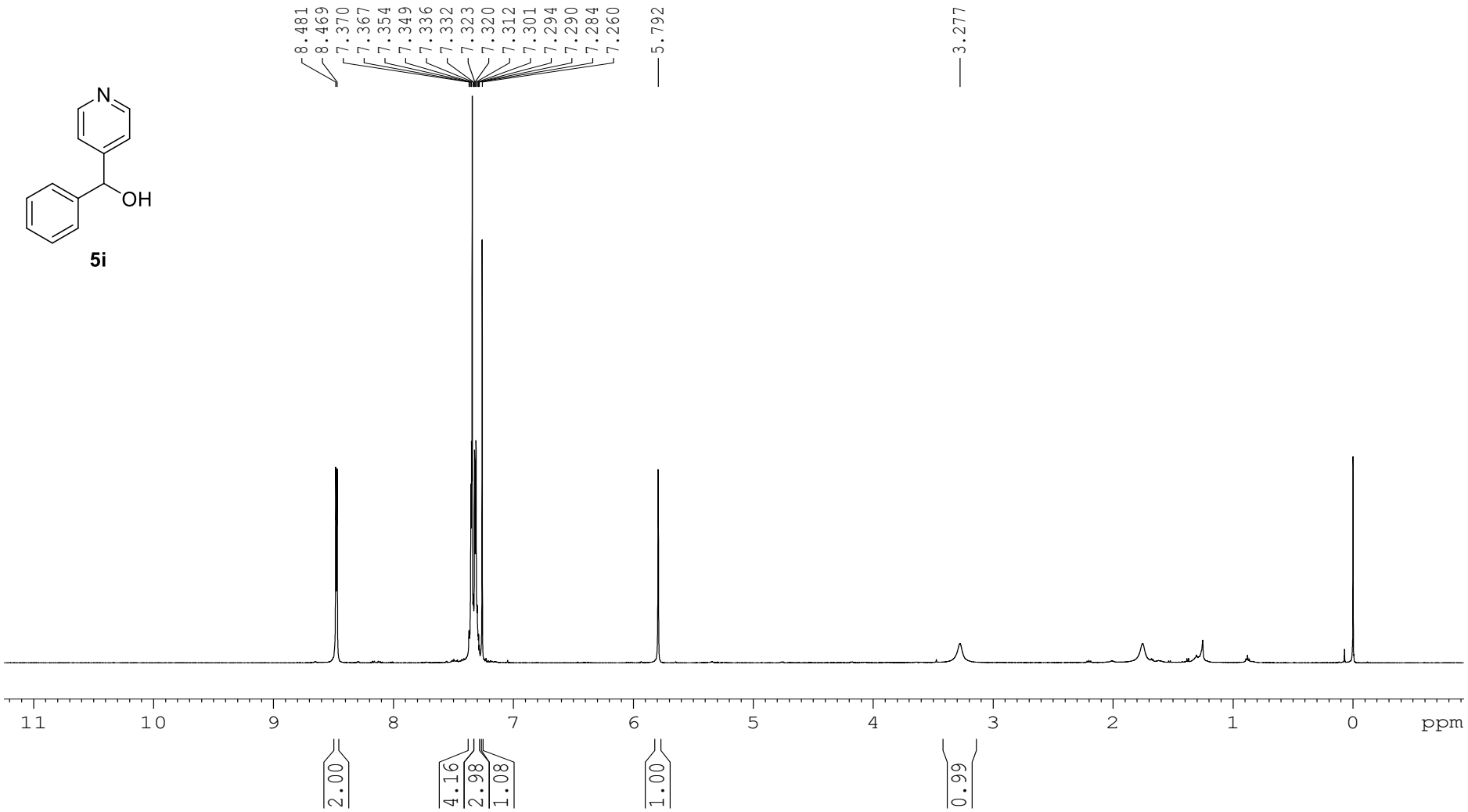

Figure S38. ^{1}H NMR spectra of **5i** ($CDCl_3$, 500M).

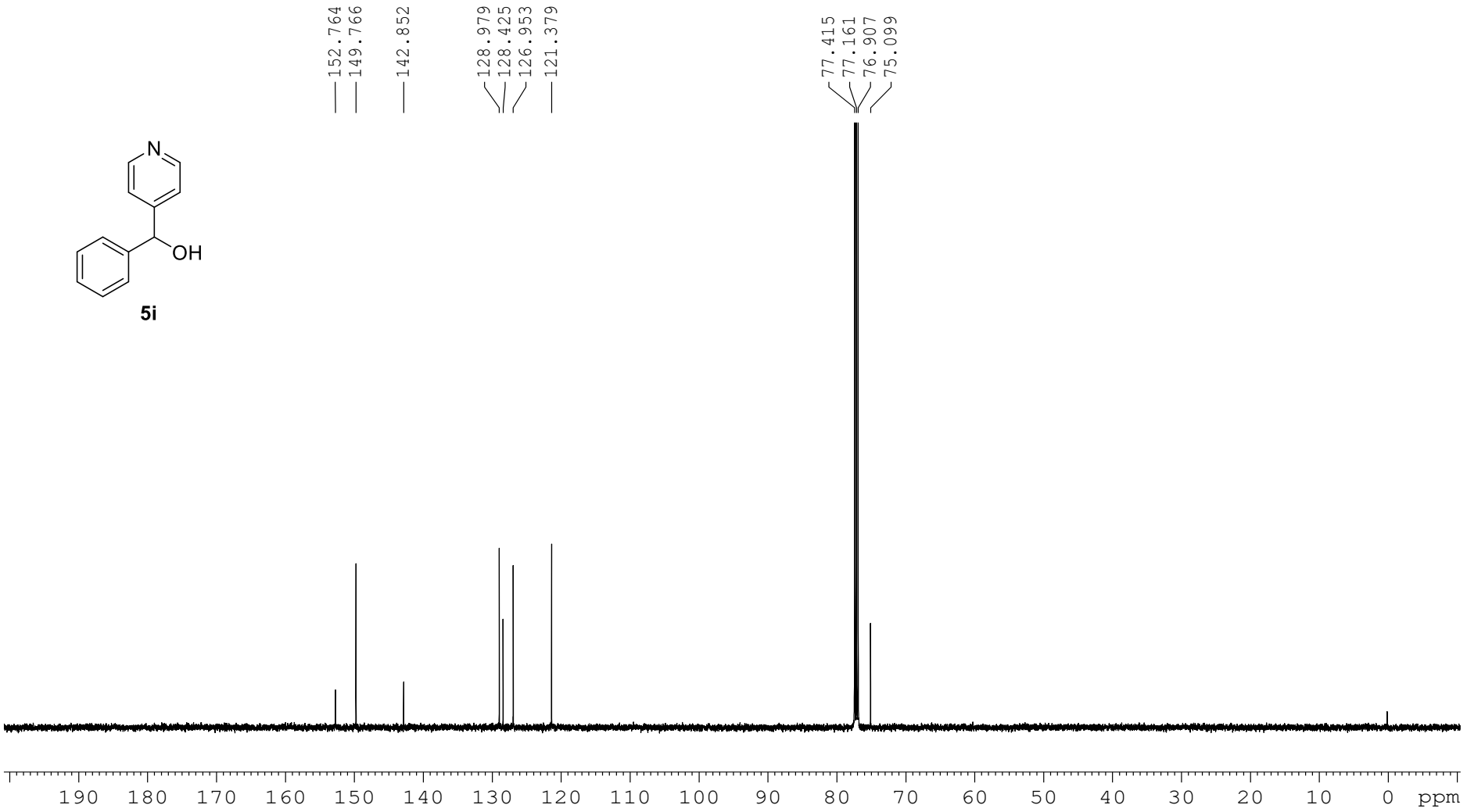

Figure S39. ^{13}C NMR spectra of **5i** ($CDCl_3$, 125M).

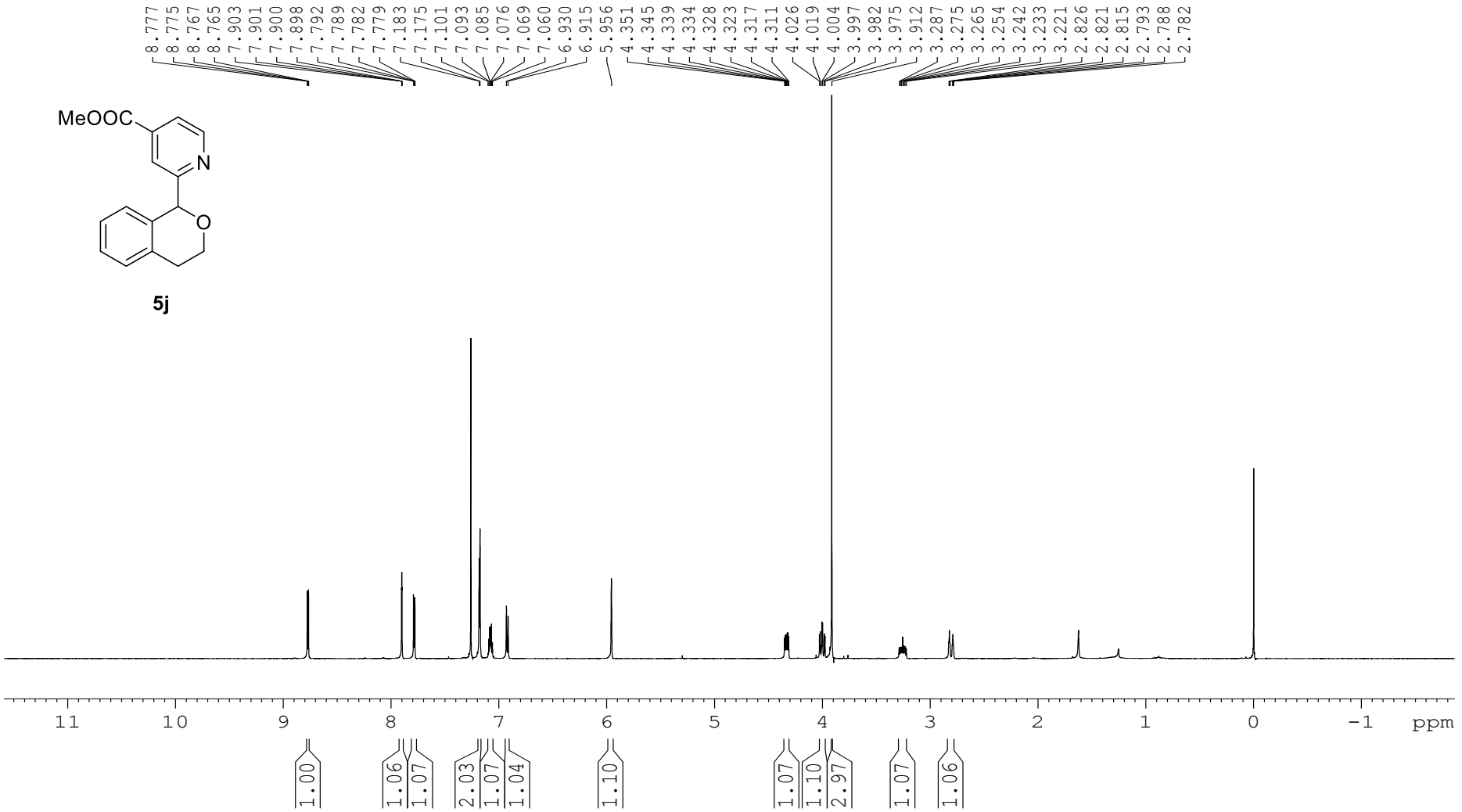

Figure S40. ^{1}H NMR spectra of **5j** ($CDCl_3$, 500M).

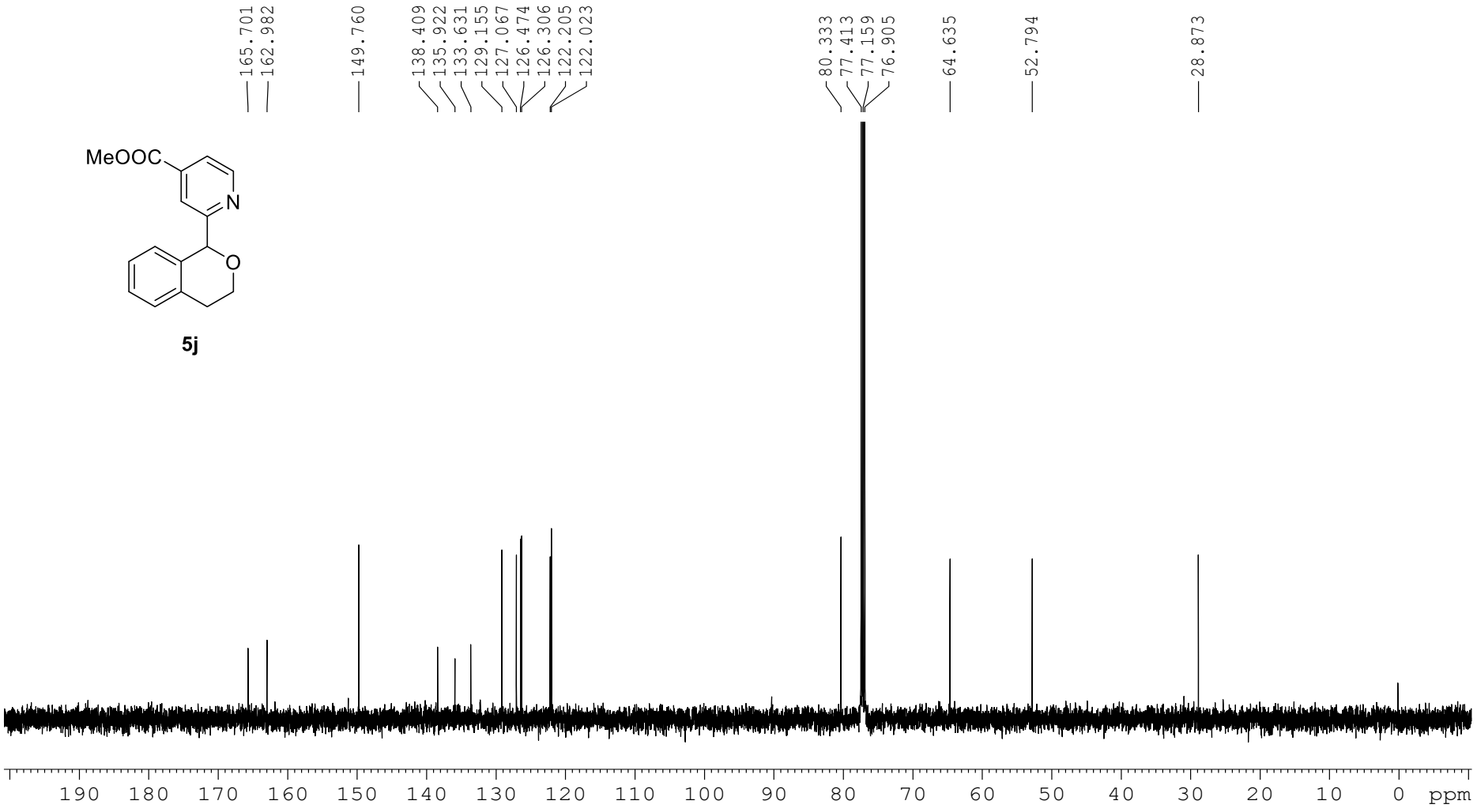

Figure S41. ^{13}C NMR spectra of **5j** ($CDCl_3$, 125M).

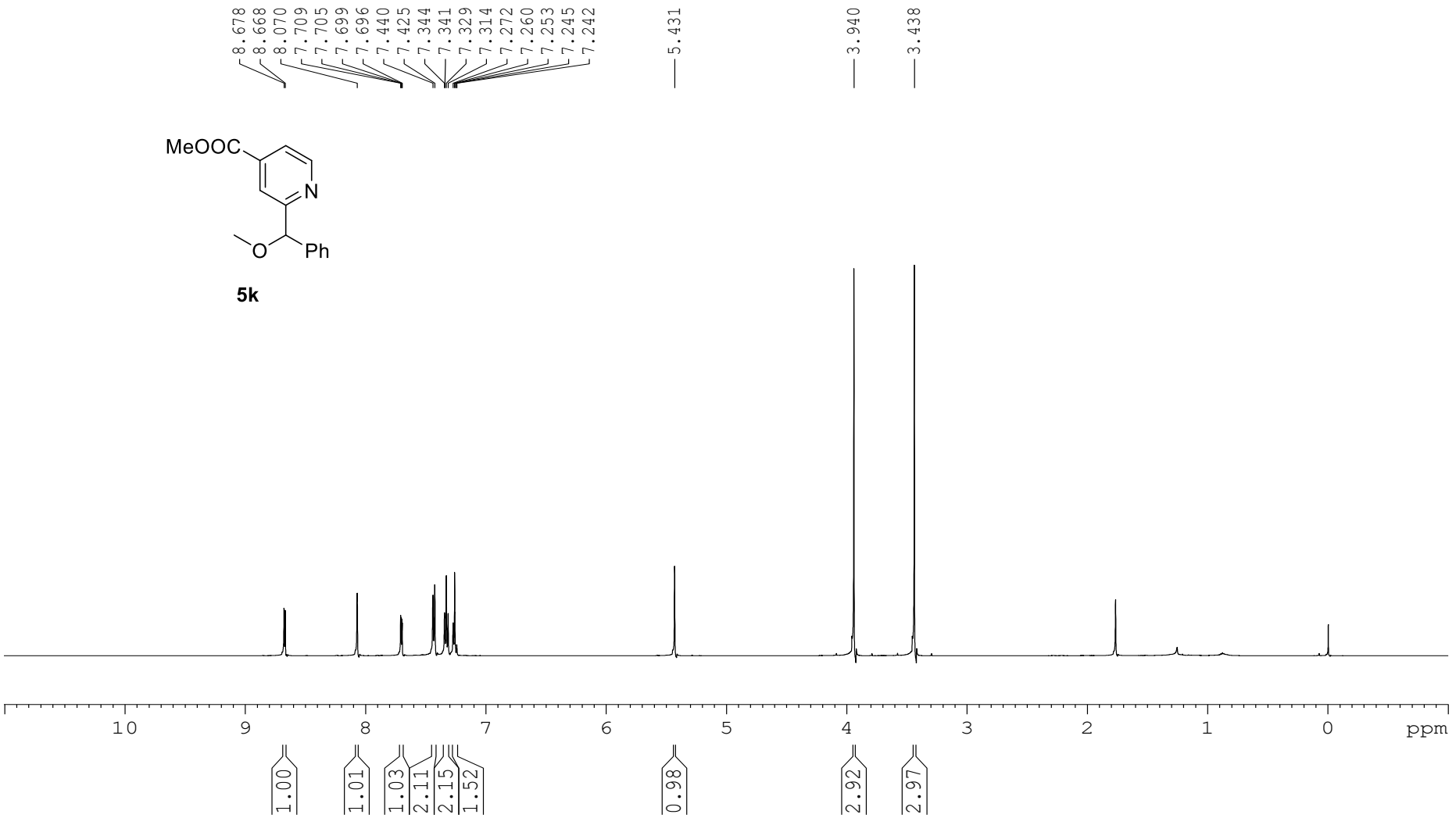

Figure S42. ^{1}H NMR spectra of **5k** ($CDCl_3$, 500M).

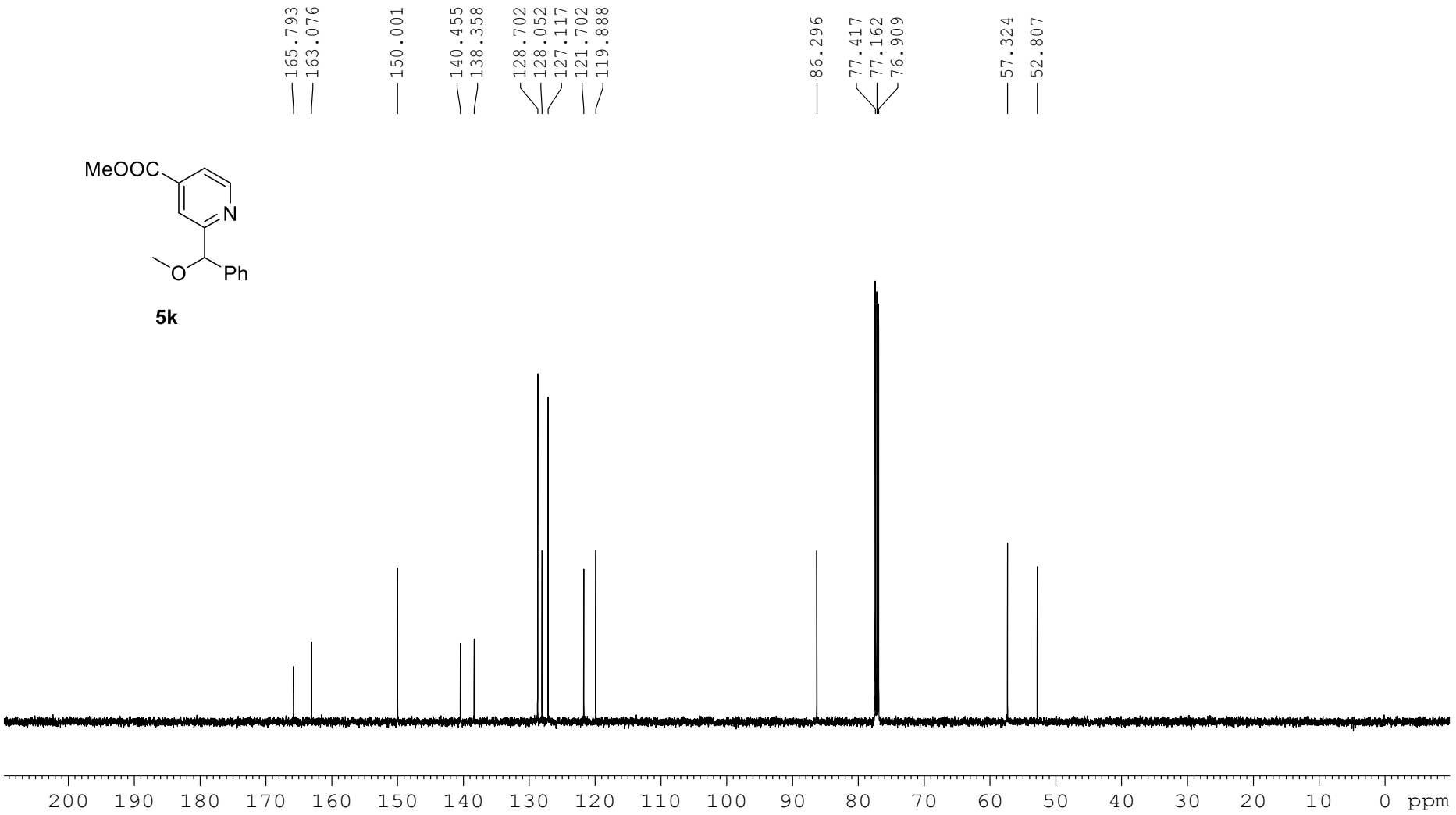

Figure S43. ^{13}C NMR spectra of **5k** ($CDCl_3$, 125M).

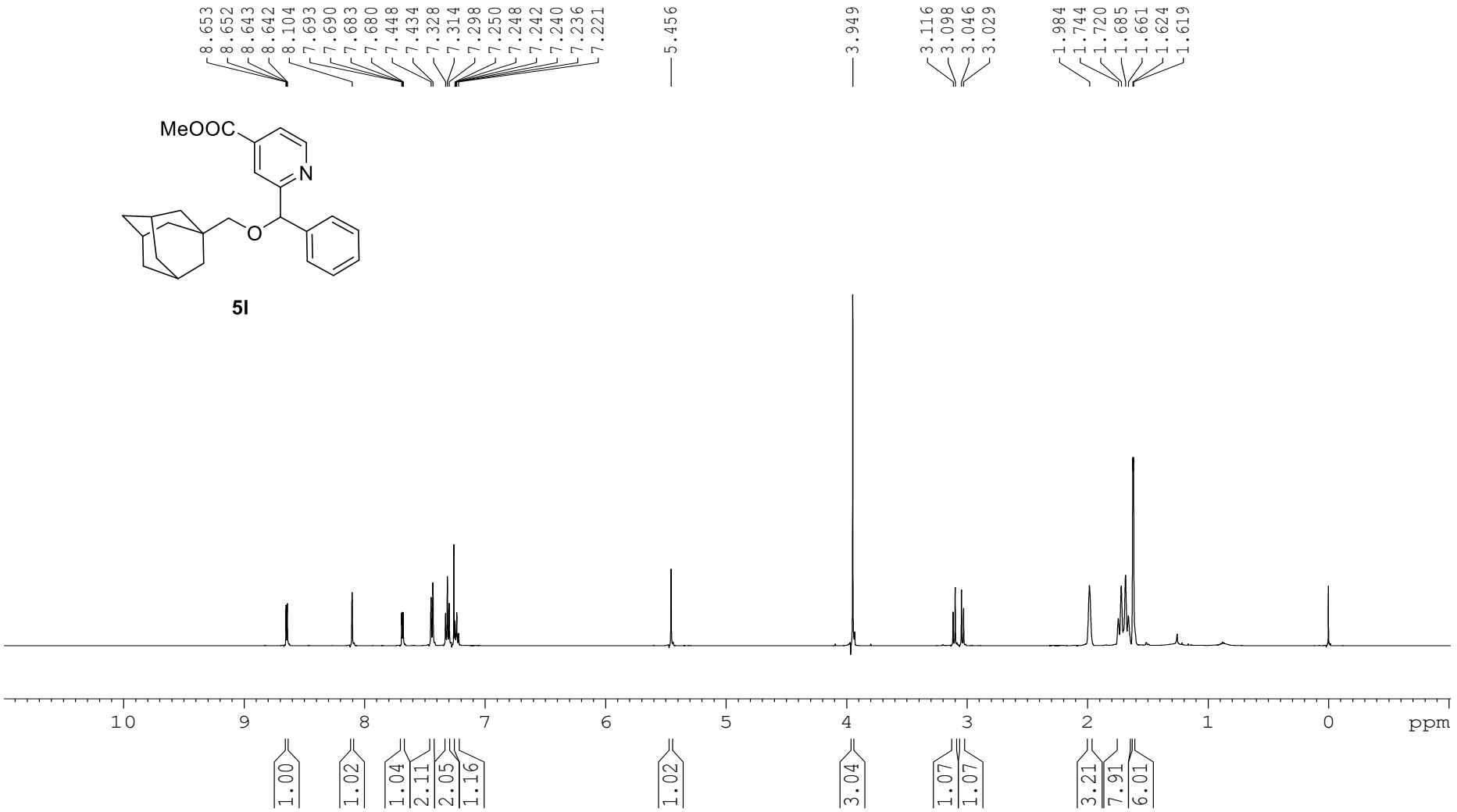

Figure S44. ^{1}H NMR spectra of **5l** ($CDCl_3$, 500M).

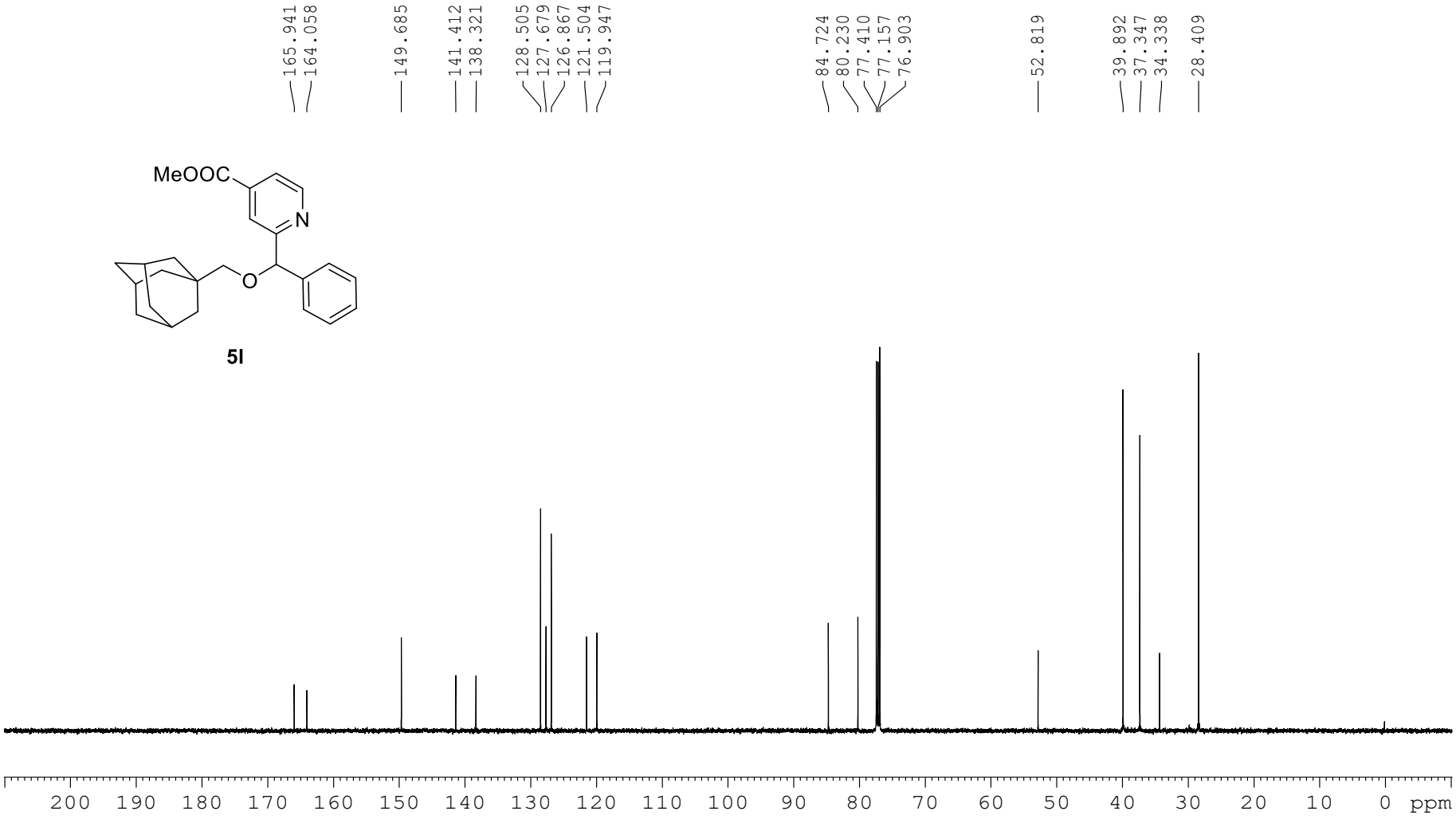

Figure S45. ^{13}C NMR spectra of **5l** ($CDCl_3$, 125M).

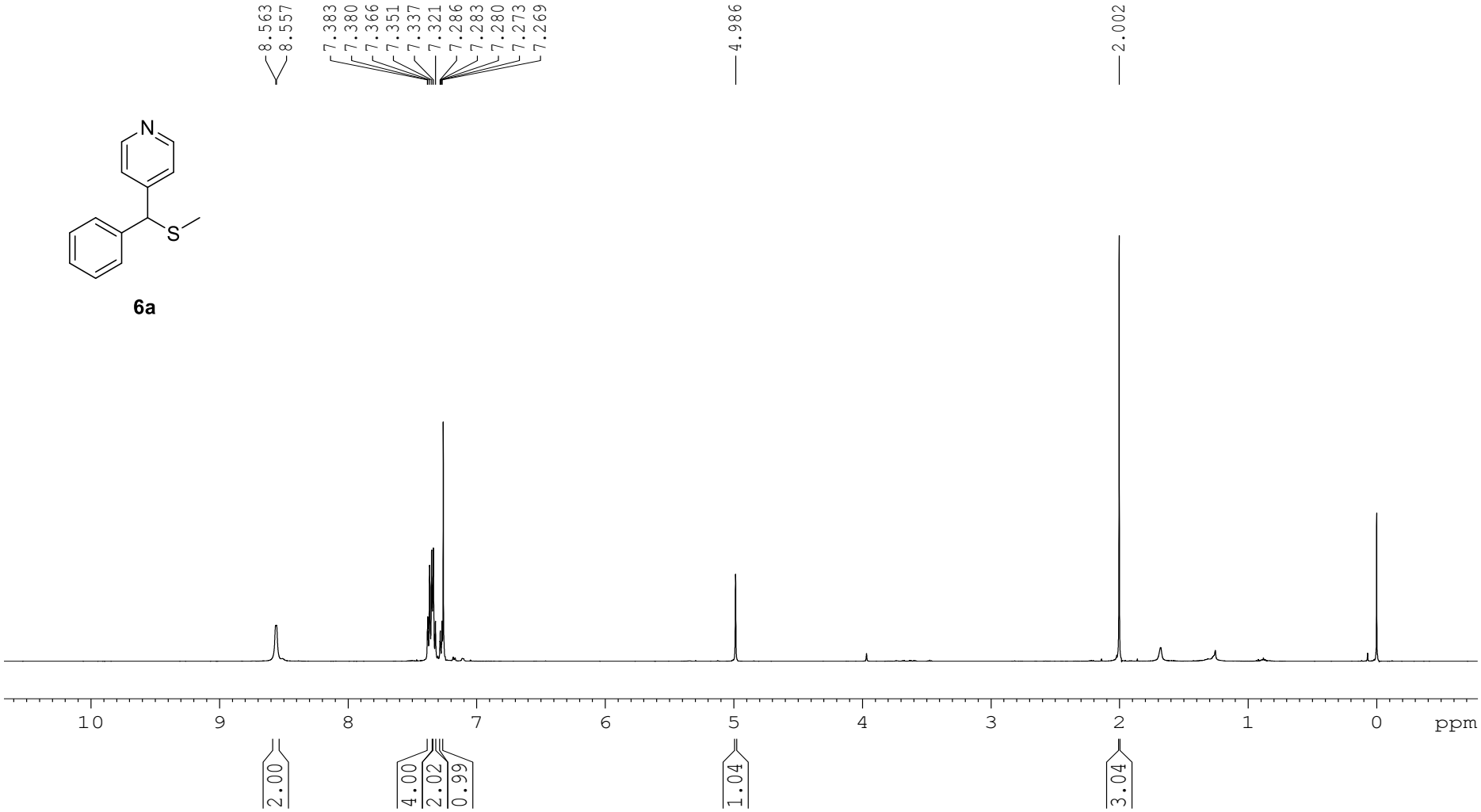

Figure S46. ^{1}H NMR spectra of **6a** ($CDCl_3$, 500M).

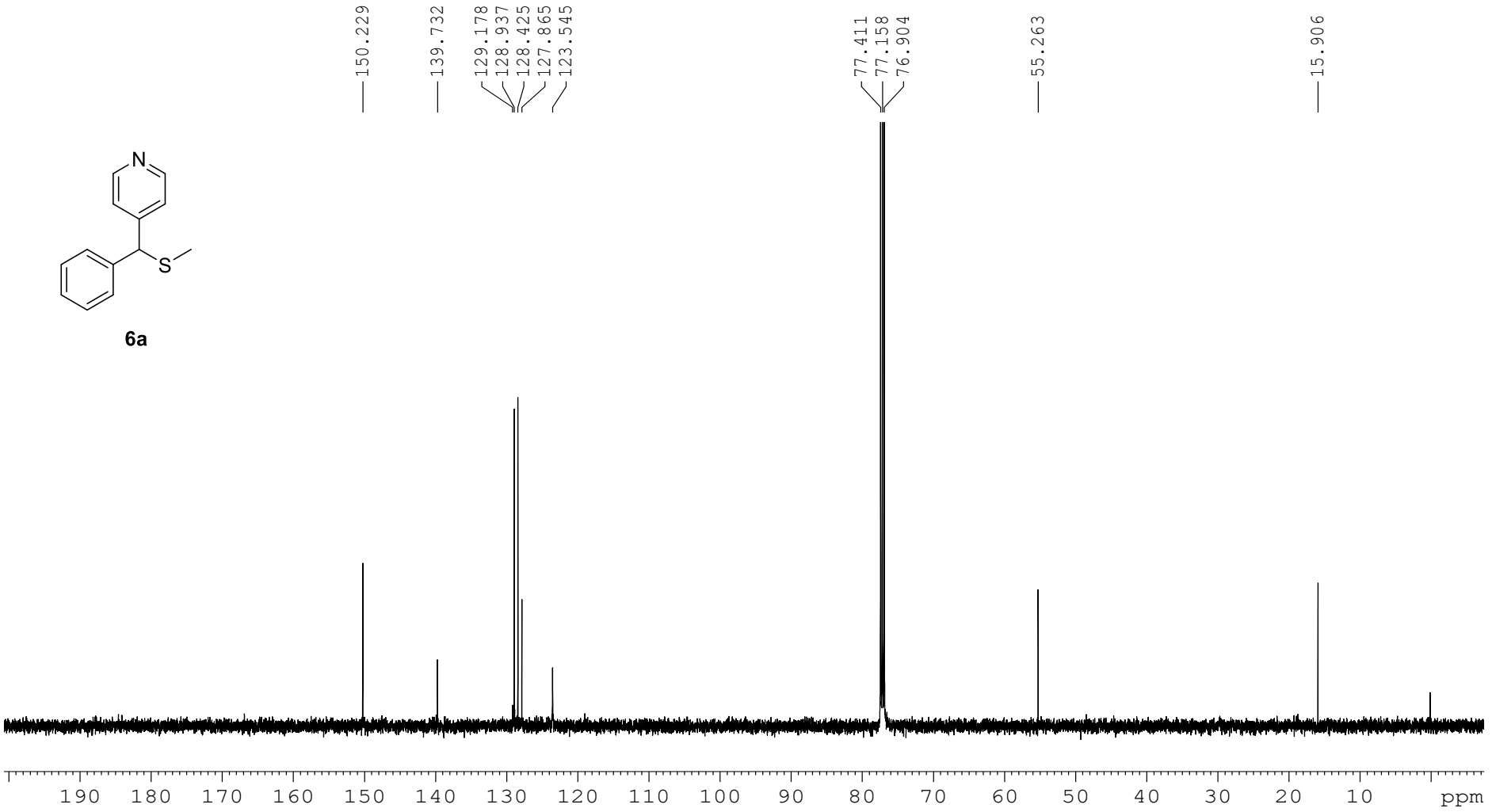

Figure S47. ^{13}C NMR spectra of **6a** ($CDCl_3$, 125M).

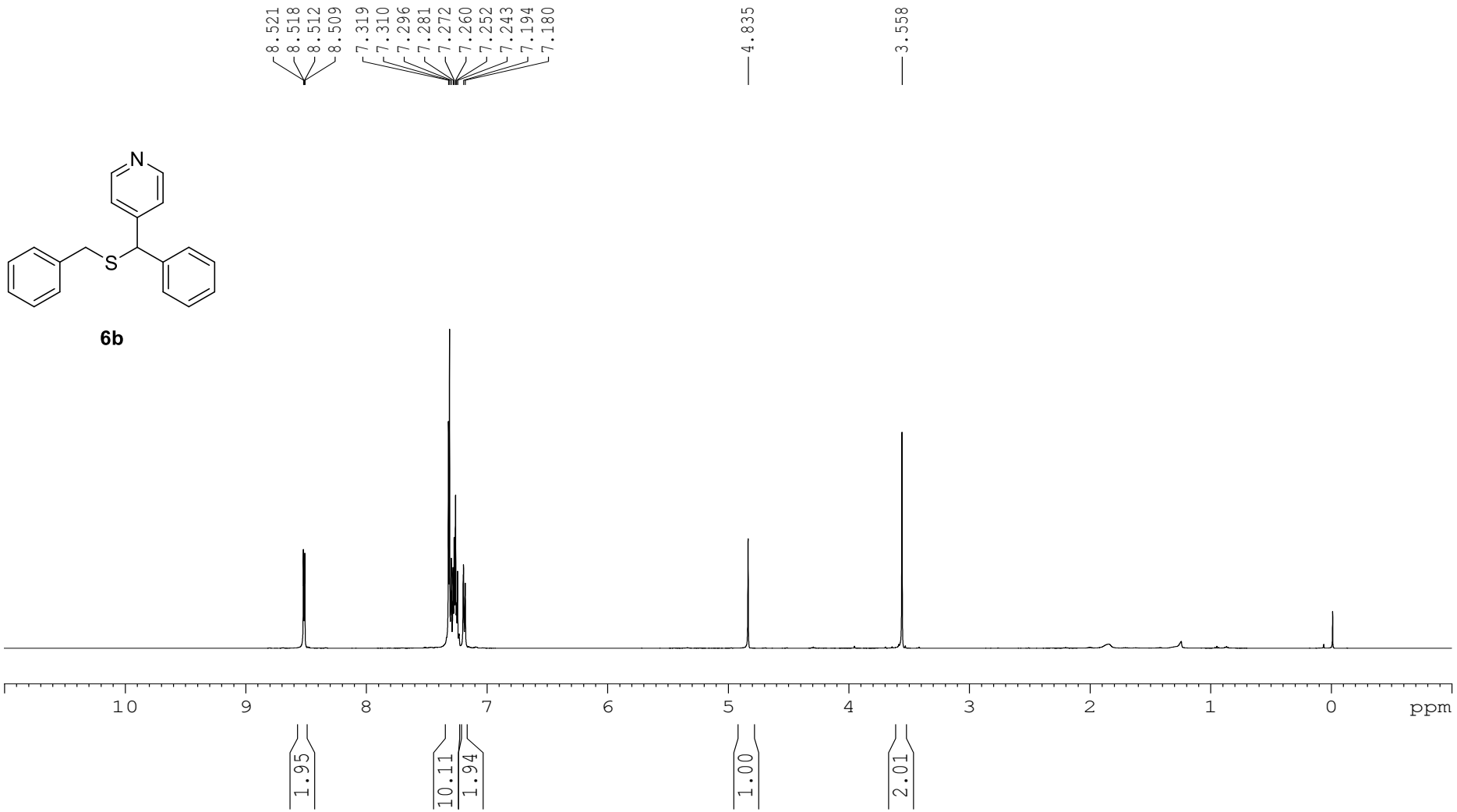

Figure S48. ^{1}H NMR spectra of **6b** ($CDCl_3$, 500M).

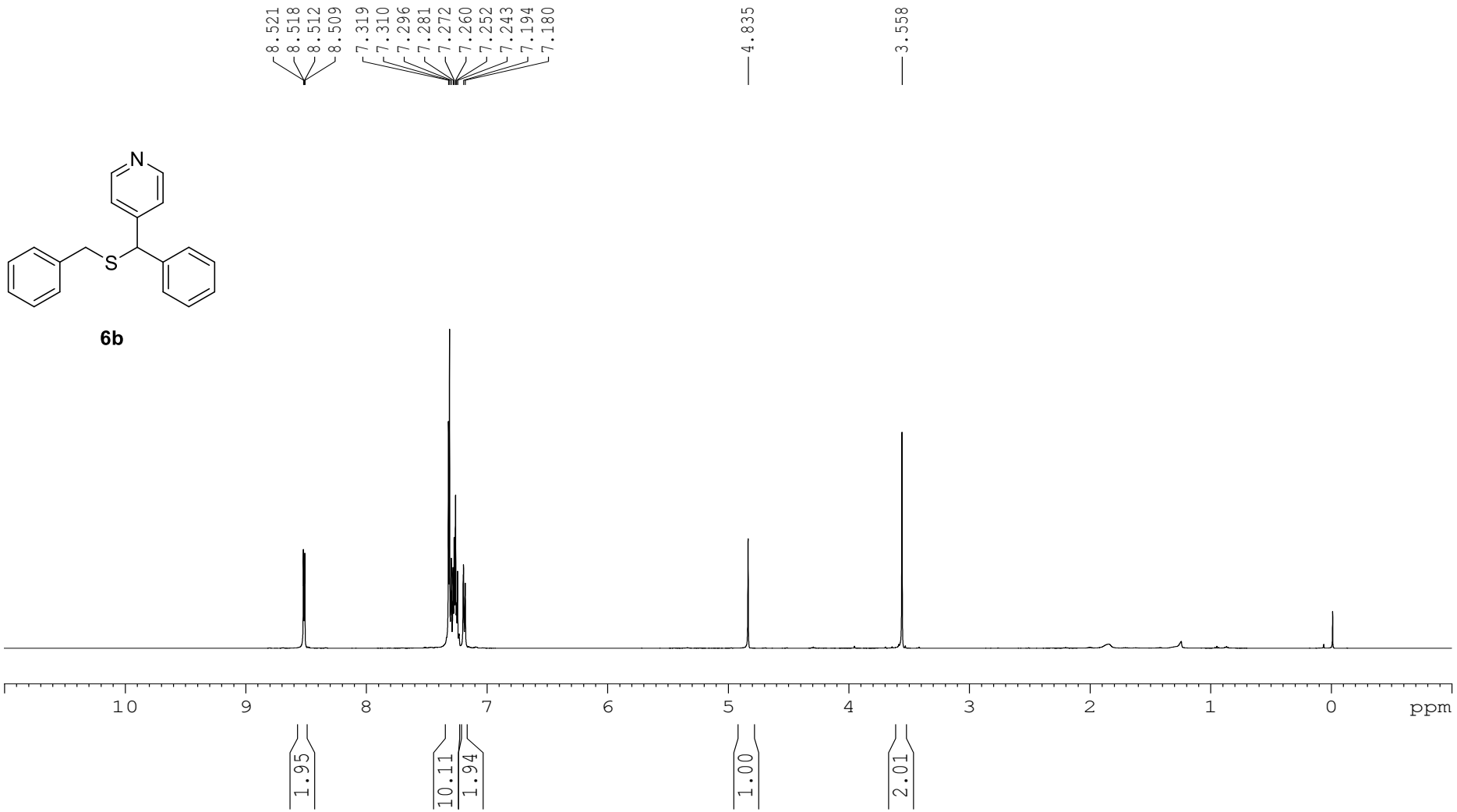

Figure S49. ^{13}C NMR spectra of **6b** ($CDCl_3$, 125M).

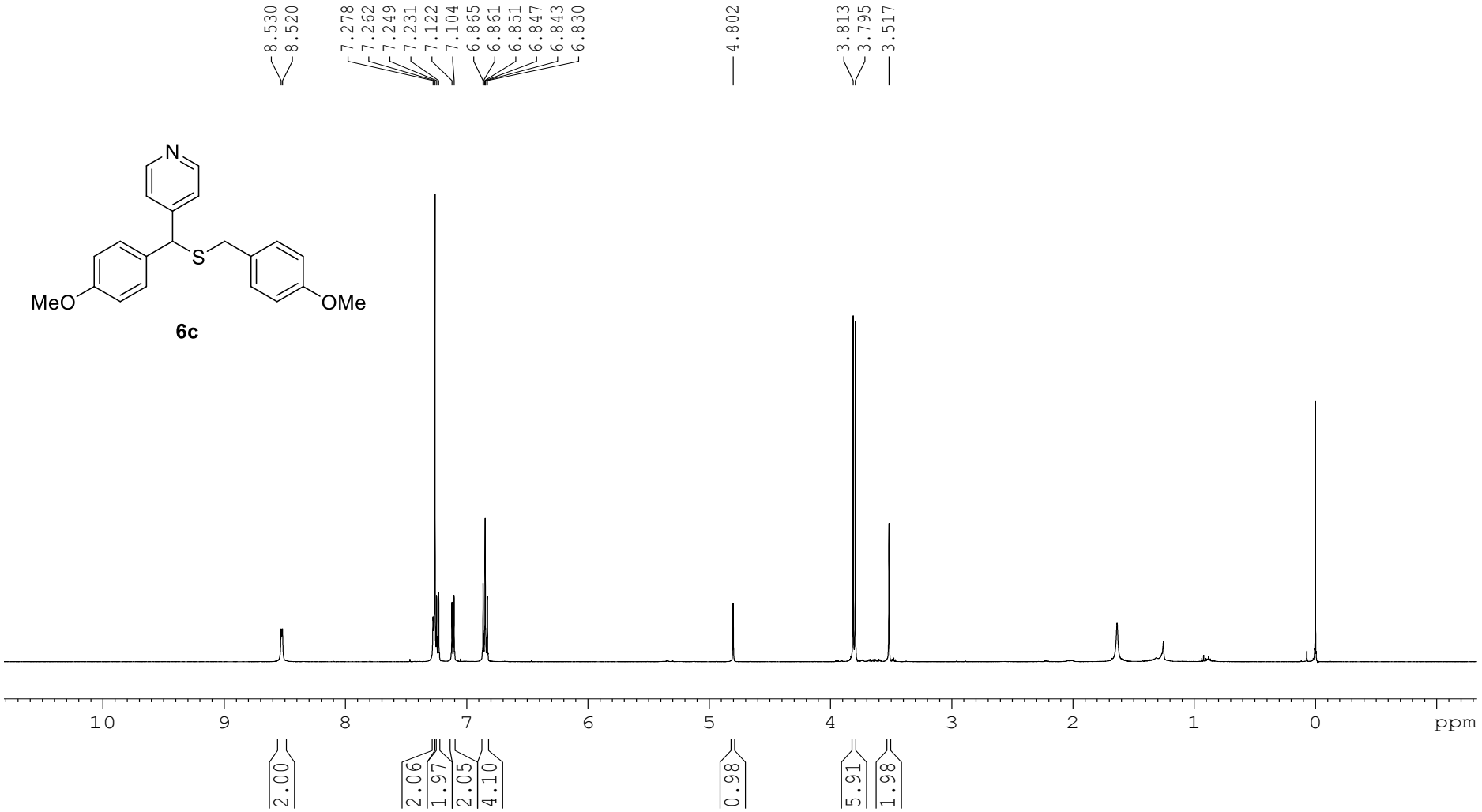

Figure S50. ^{1}H NMR spectra of **6c** ($CDCl_3$, 500M).

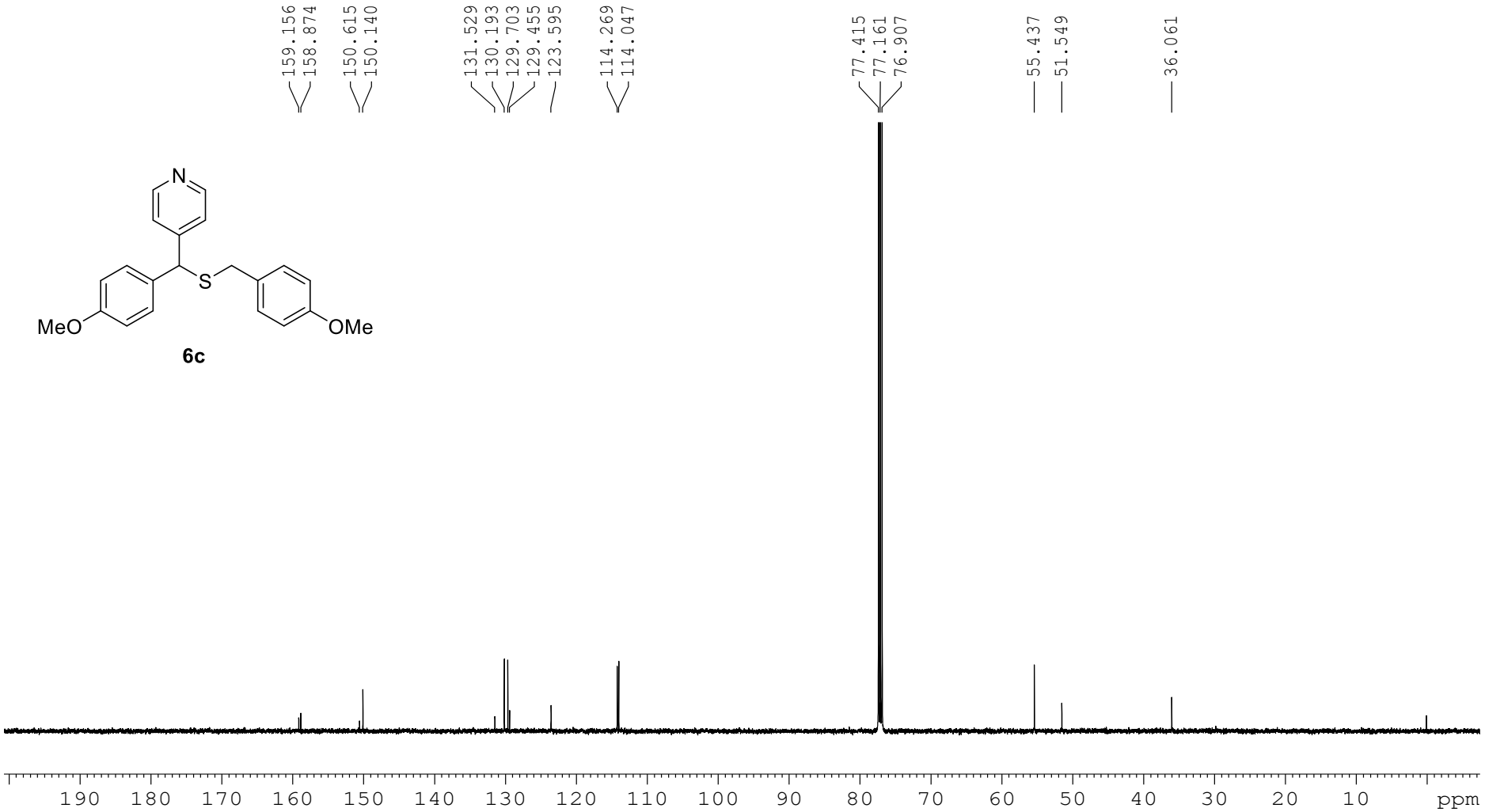

Figure S51. ^{13}C NMR spectra of **6c** ($CDCl_3$, 125M).

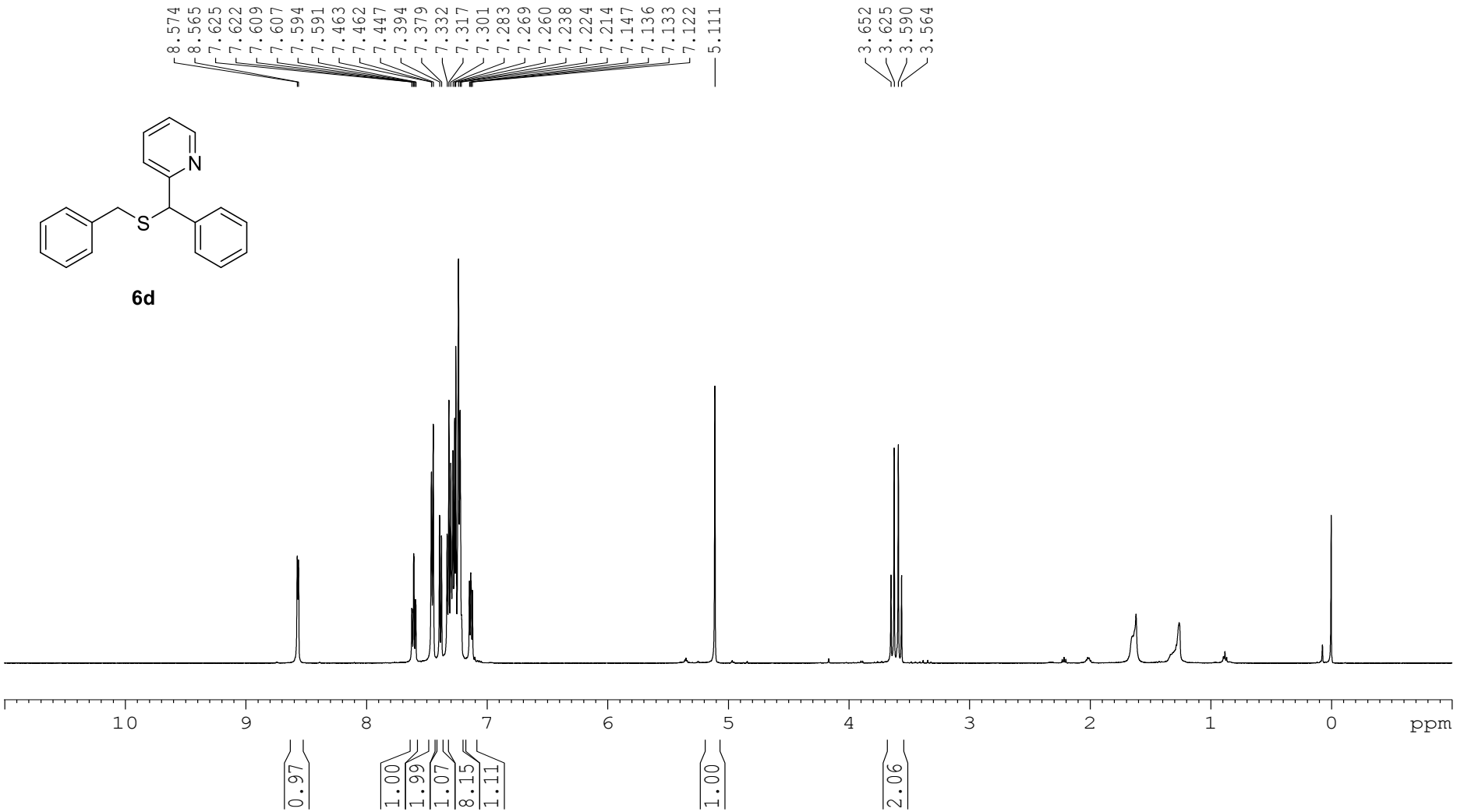

Figure S52. ^{1}H NMR spectra of **6d** ($CDCl_3$, 500M).

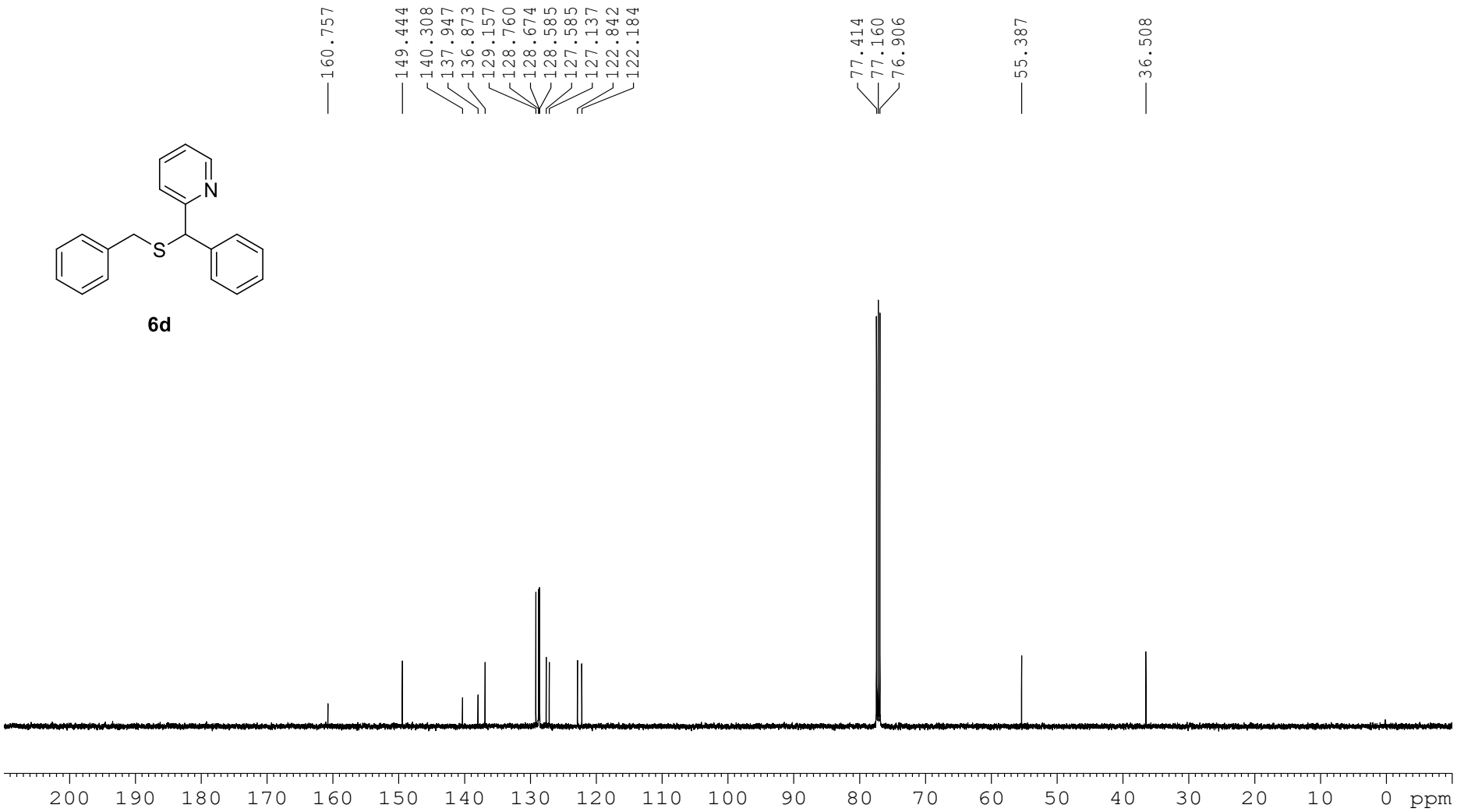

Figure S53. ^{13}C NMR spectra of **6d** ($CDCl_3$, 125M).

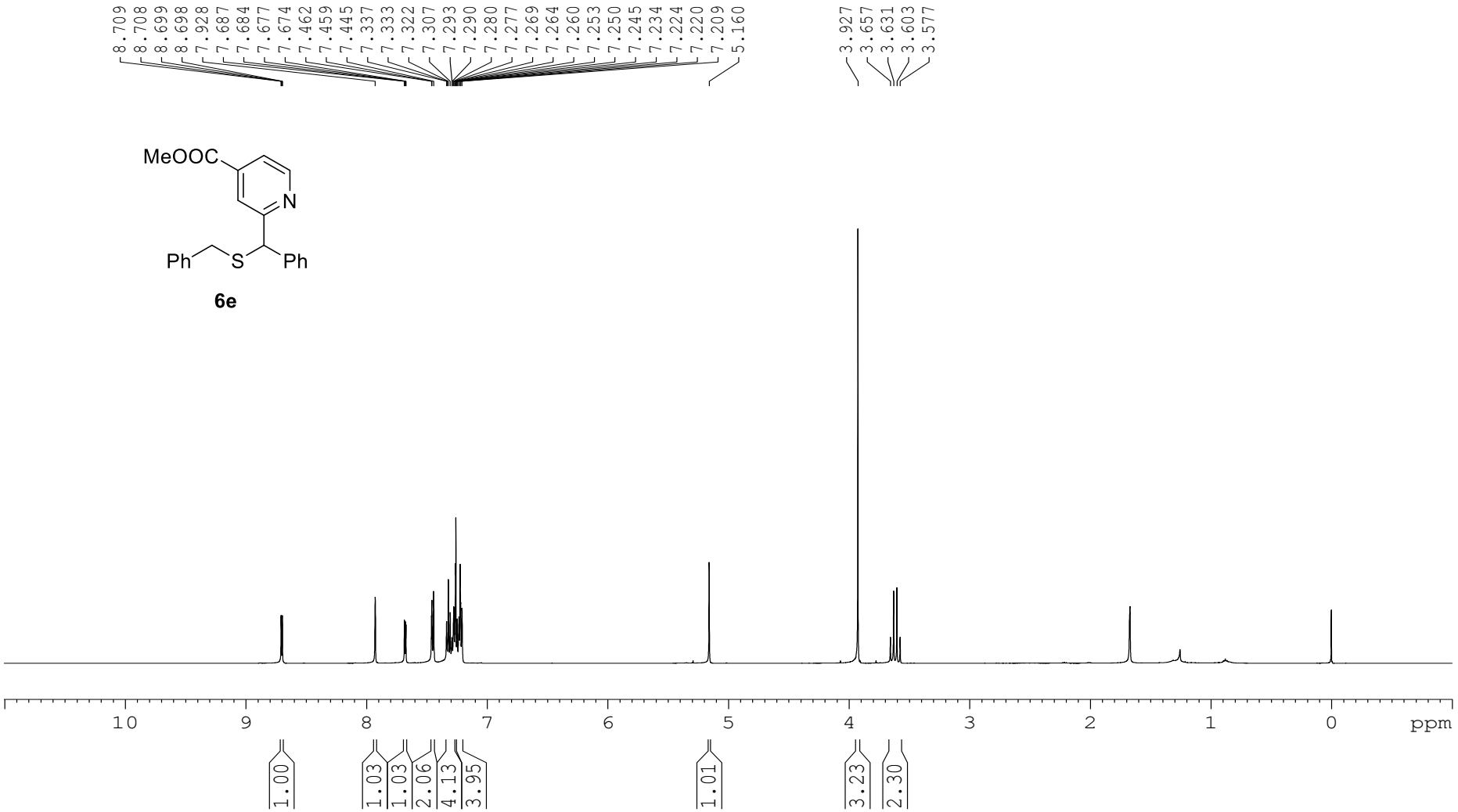

Figure S54. ^{1}H NMR spectra of **6e** ($CDCl_3$, 500M).

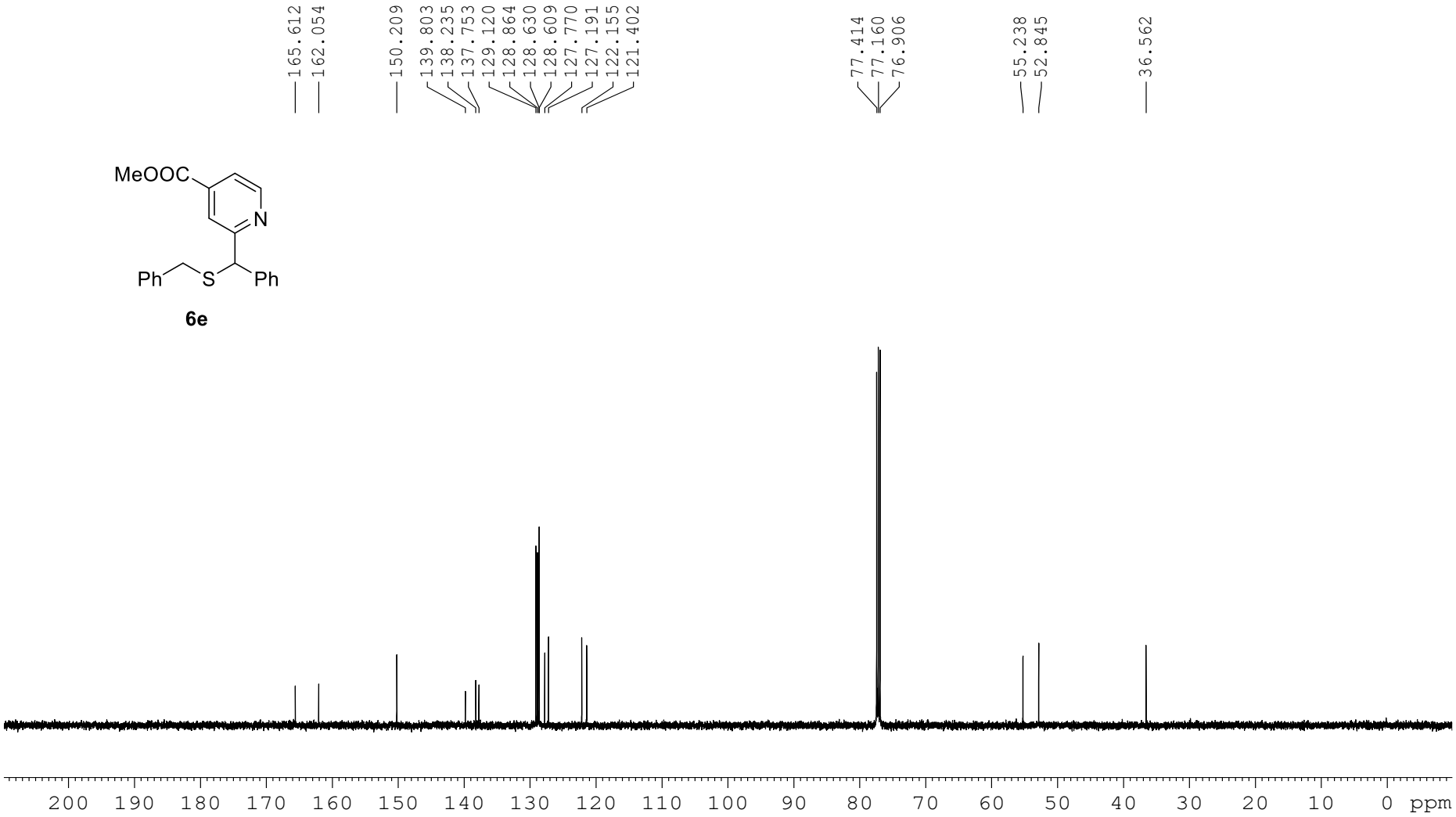

Figure S55. ^{13}C NMR spectra of **6e** ($CDCl_3$, 125M).

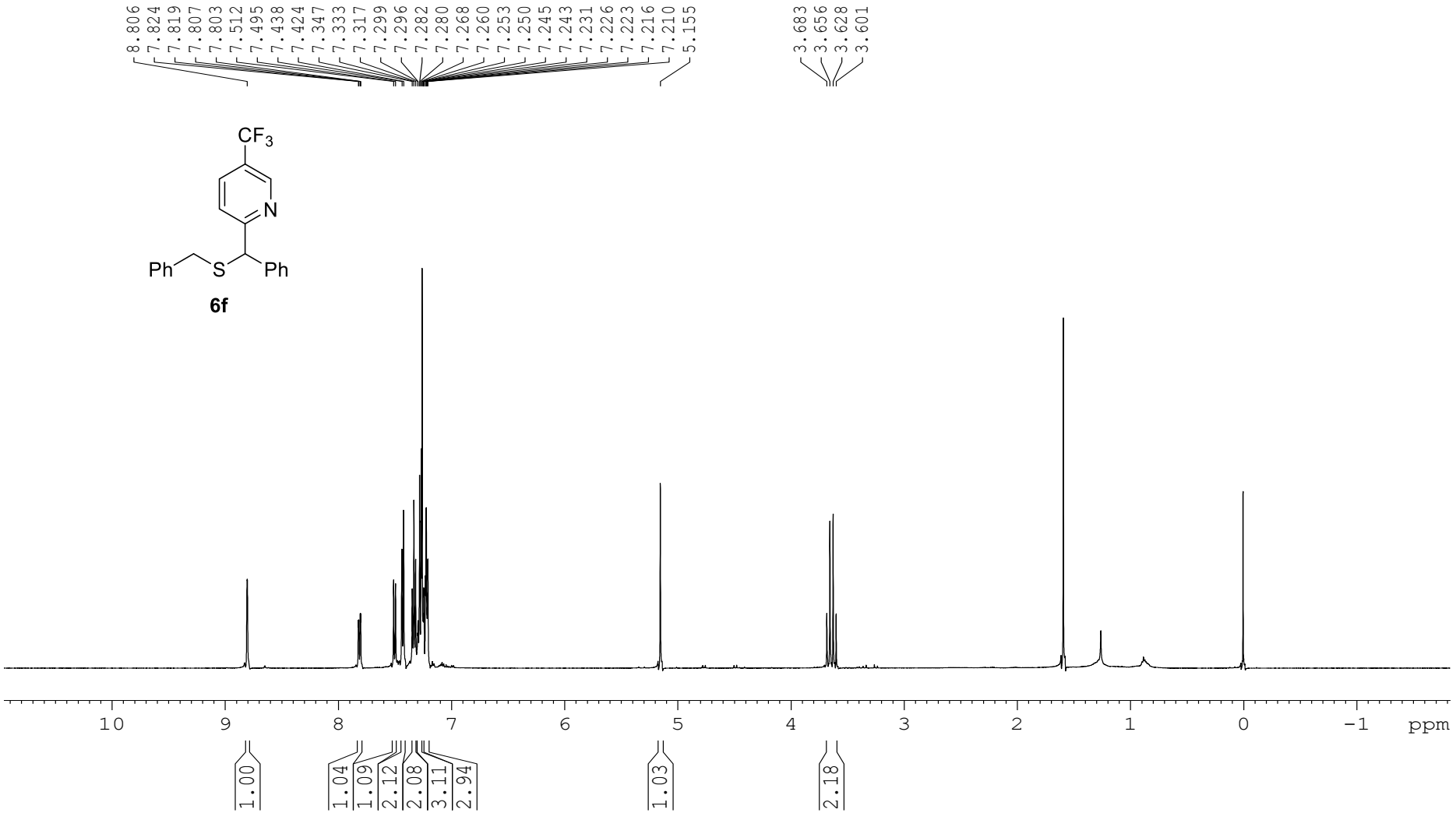

Figure S56. ^{1}H NMR spectra of **6f** ($CDCl_3$, 500M).

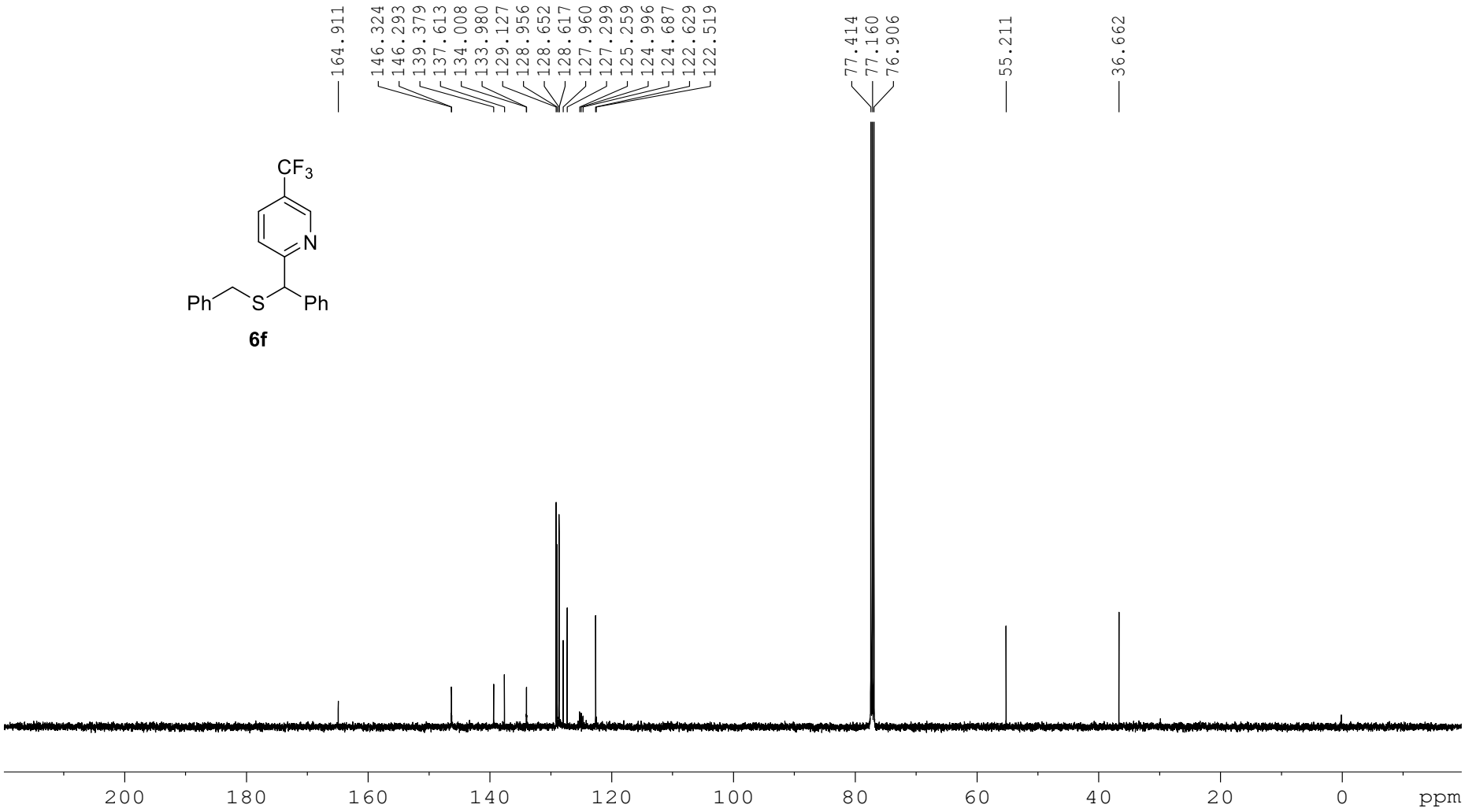

Figure S57. ^{13}C NMR spectra of **6f** ($CDCl_3$, 125M).

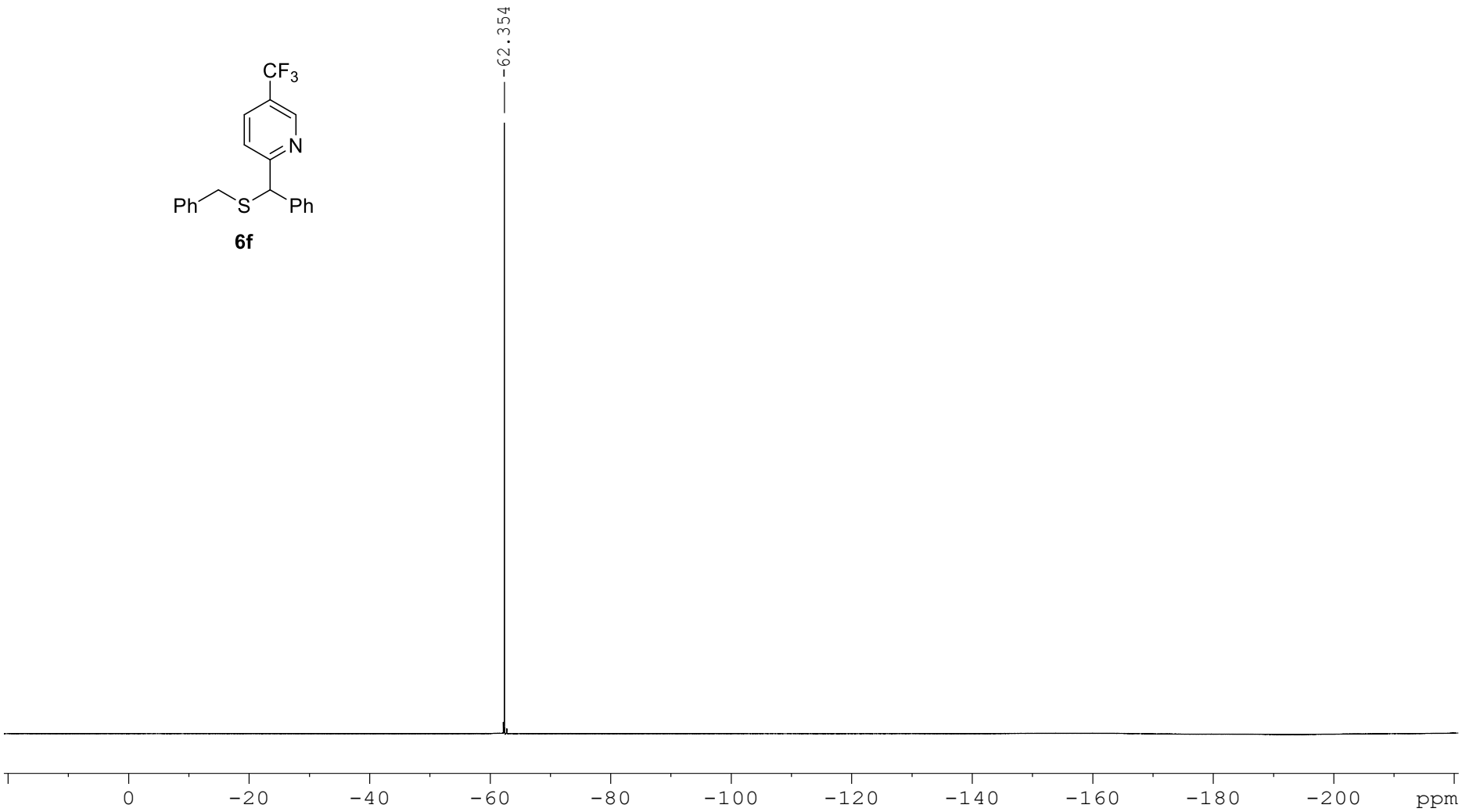

Figure S58. ^{19}F NMR spectra of **6f** ($CDCl_3$, 471M).

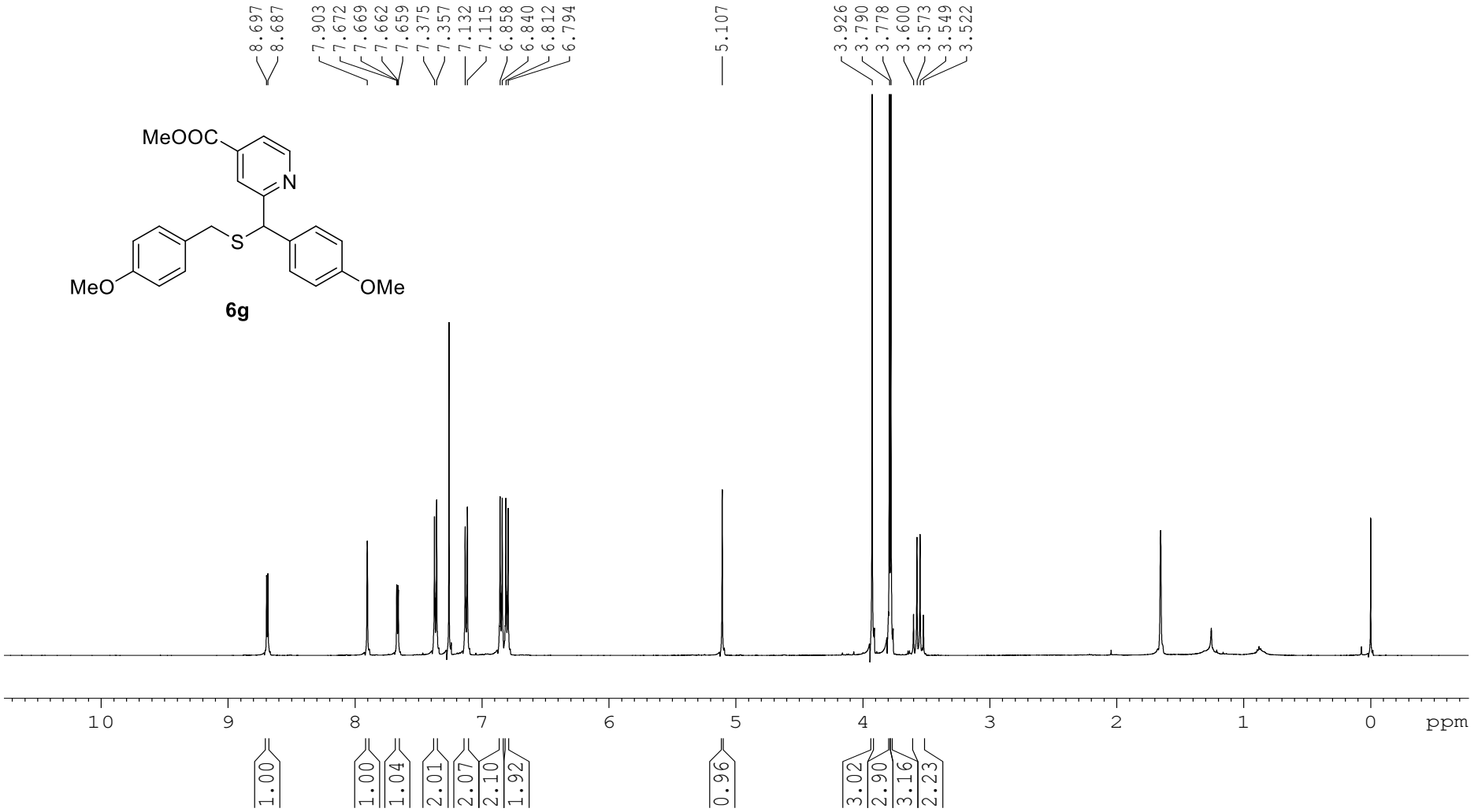

Figure S59. ^{1}H NMR spectra of **6g** ($CDCl_3$, 500M).

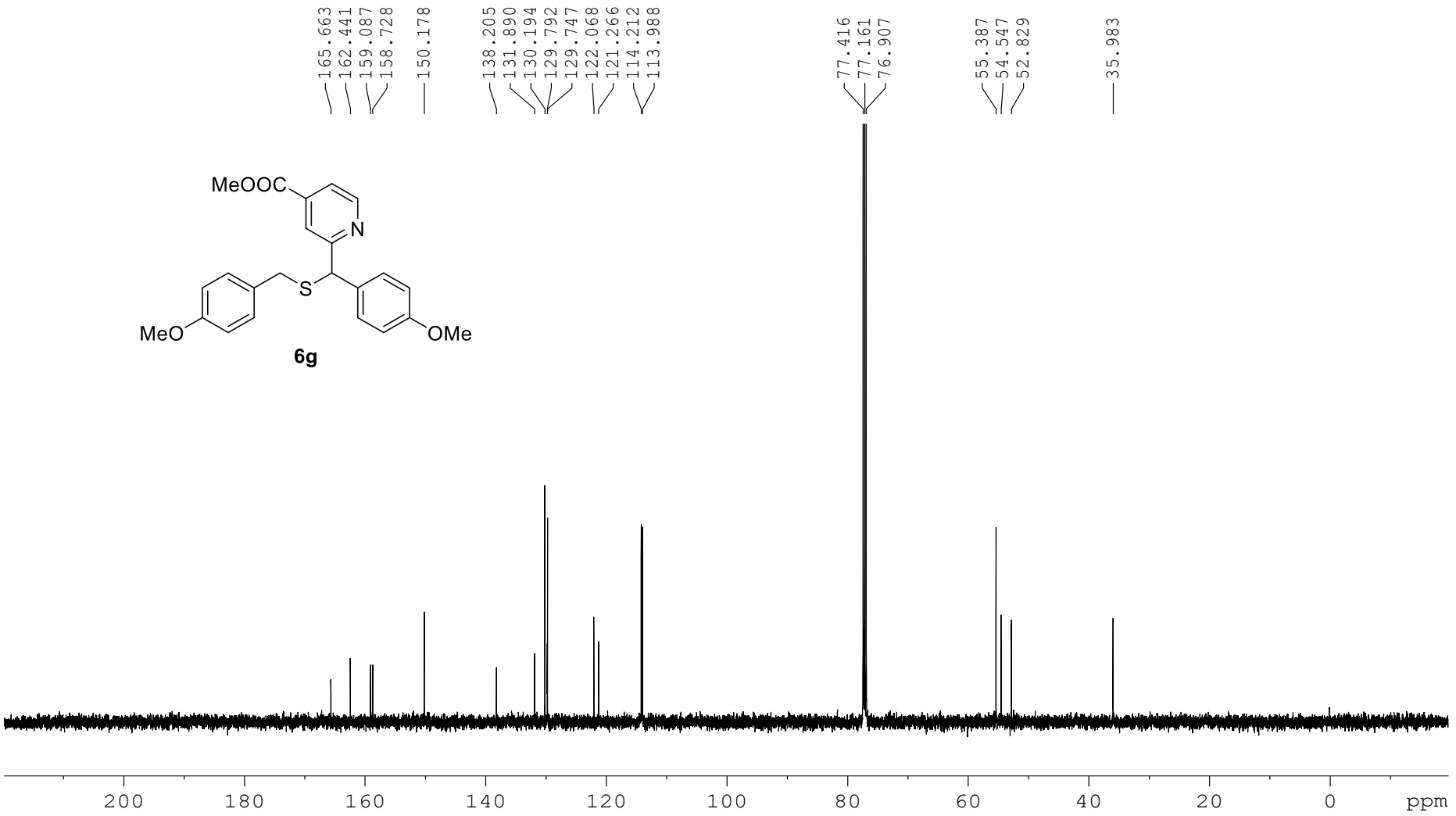

Figure S60. ^{13}C NMR spectra of **6g** ($CDCl_3$, 125M).

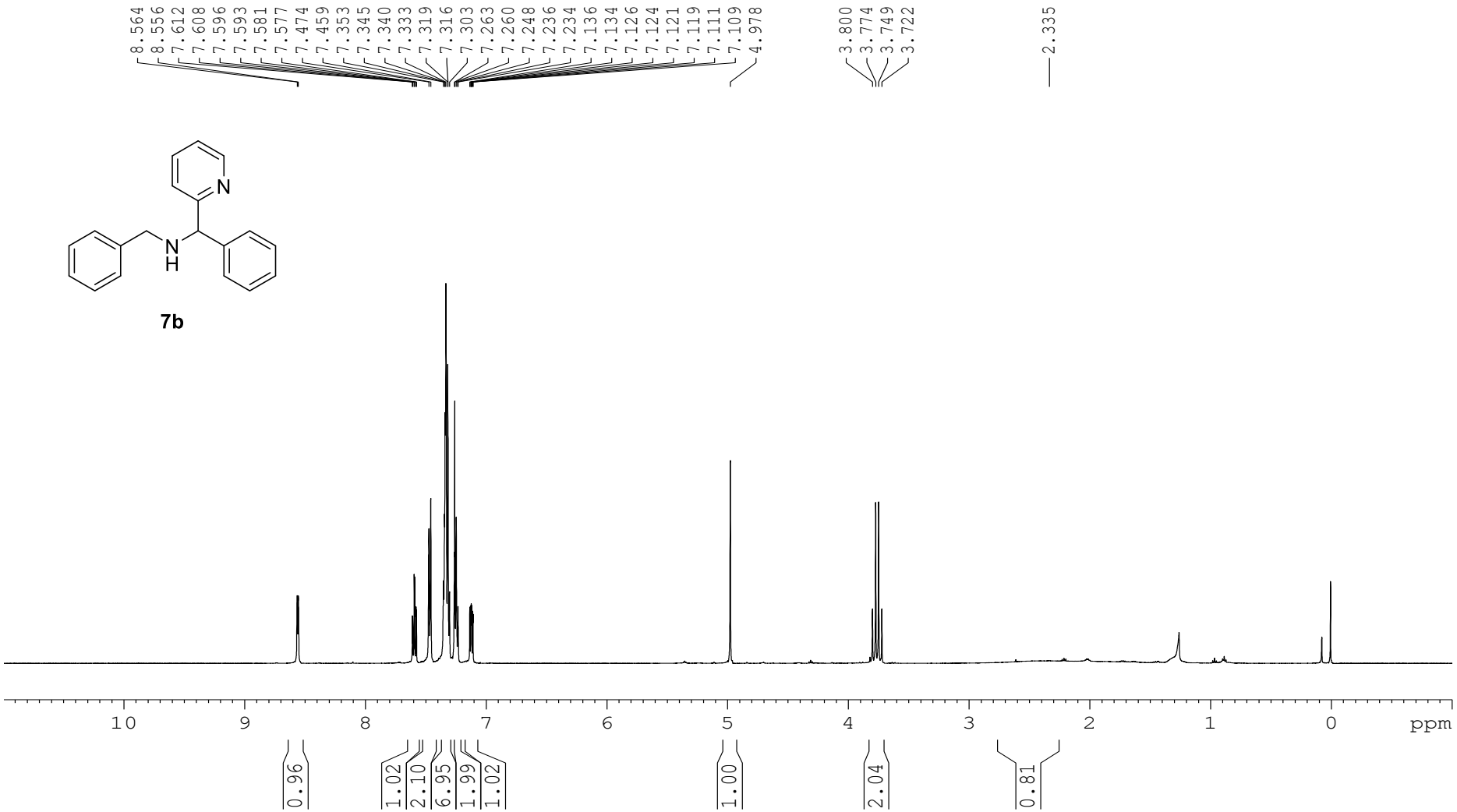

Figure S61. ^{1}H NMR spectra of **7b** ($CDCl_3$, 500M).

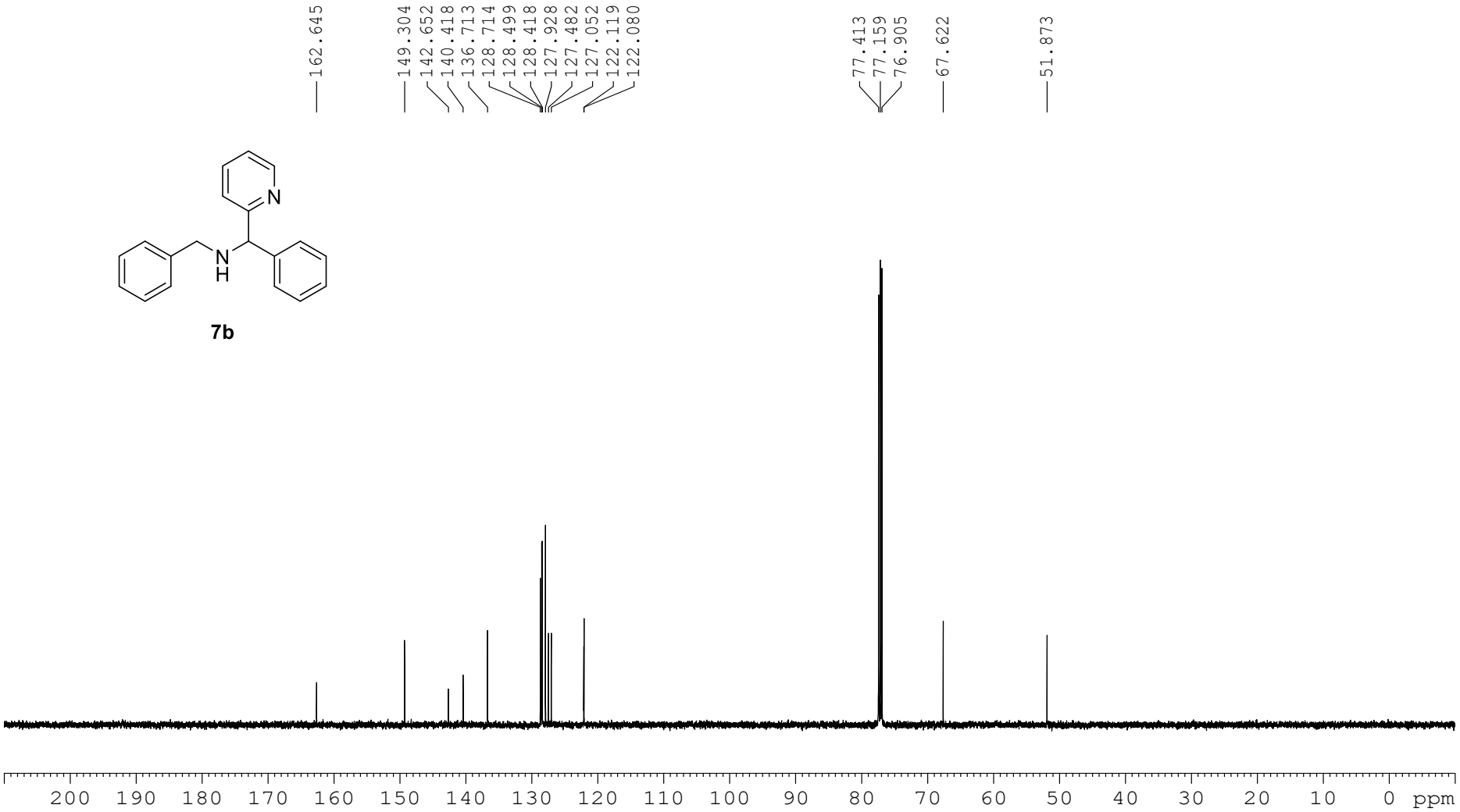

Figure S62. ^{13}C NMR spectra of **7b** ($CDCl_3$, 125M).

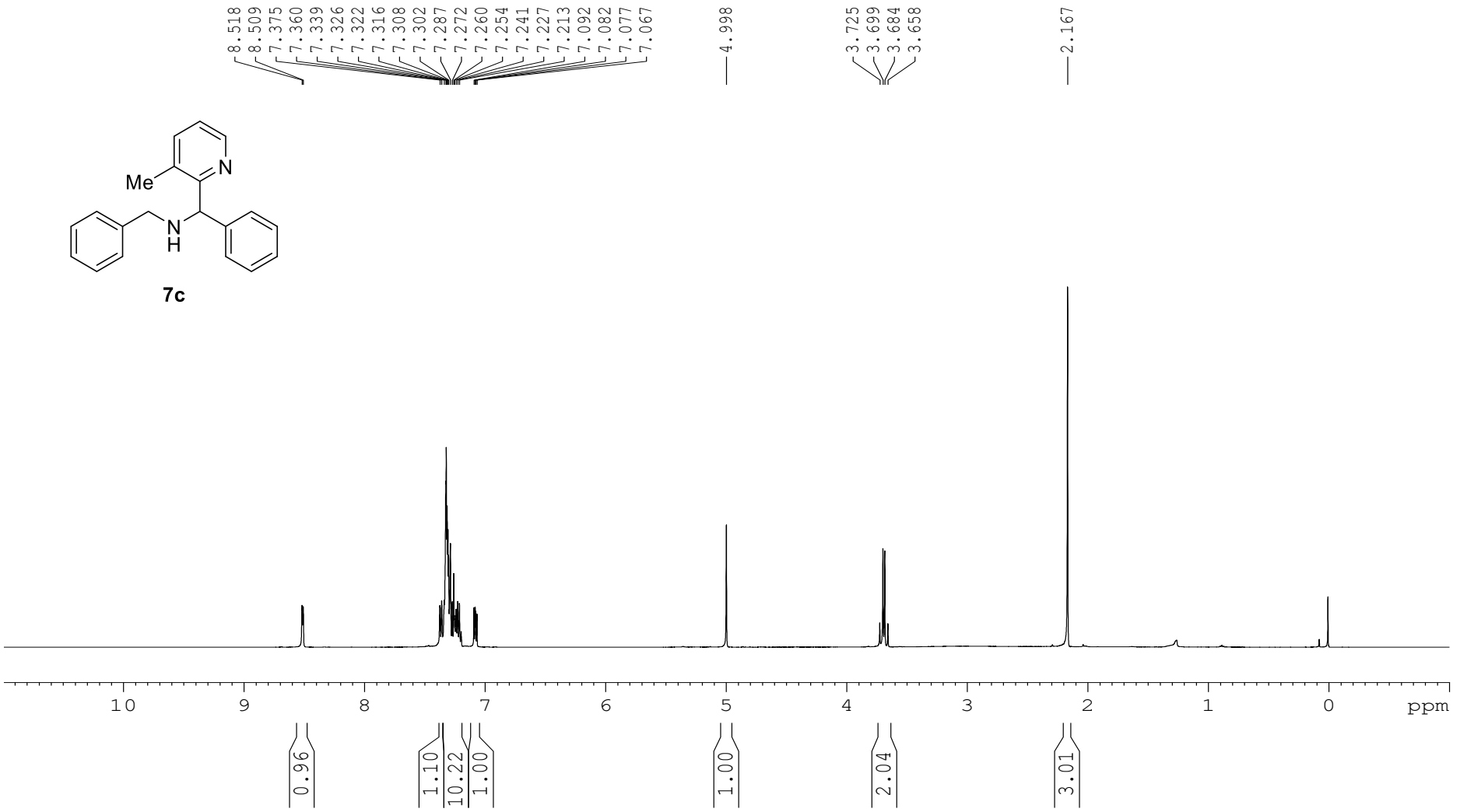

Figure S63. ^{1}H NMR spectra of **7c** ($CDCl_3$, 500M).

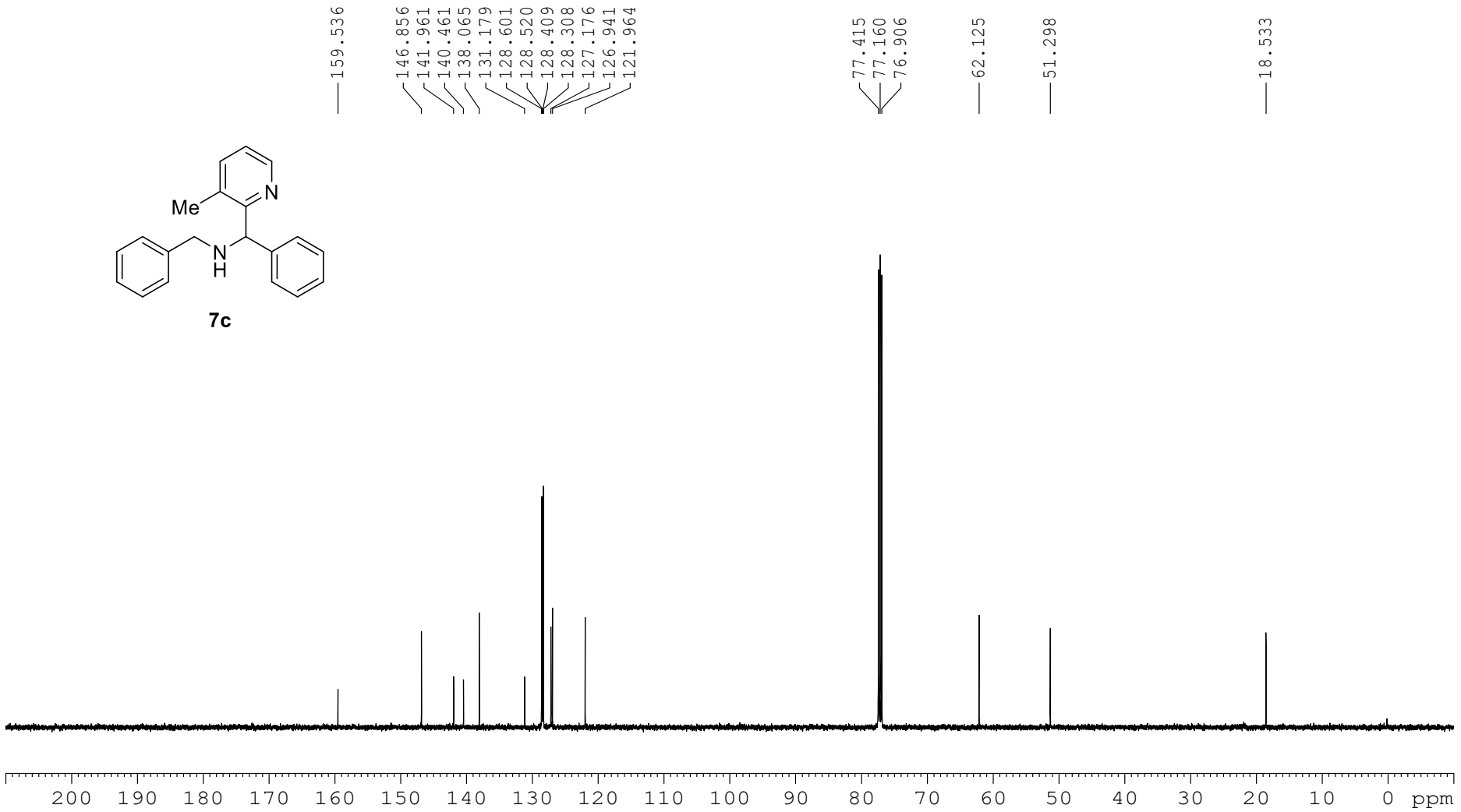

Figure S64. ^{13}C NMR spectra of **7c** ($CDCl_3$, 125M).

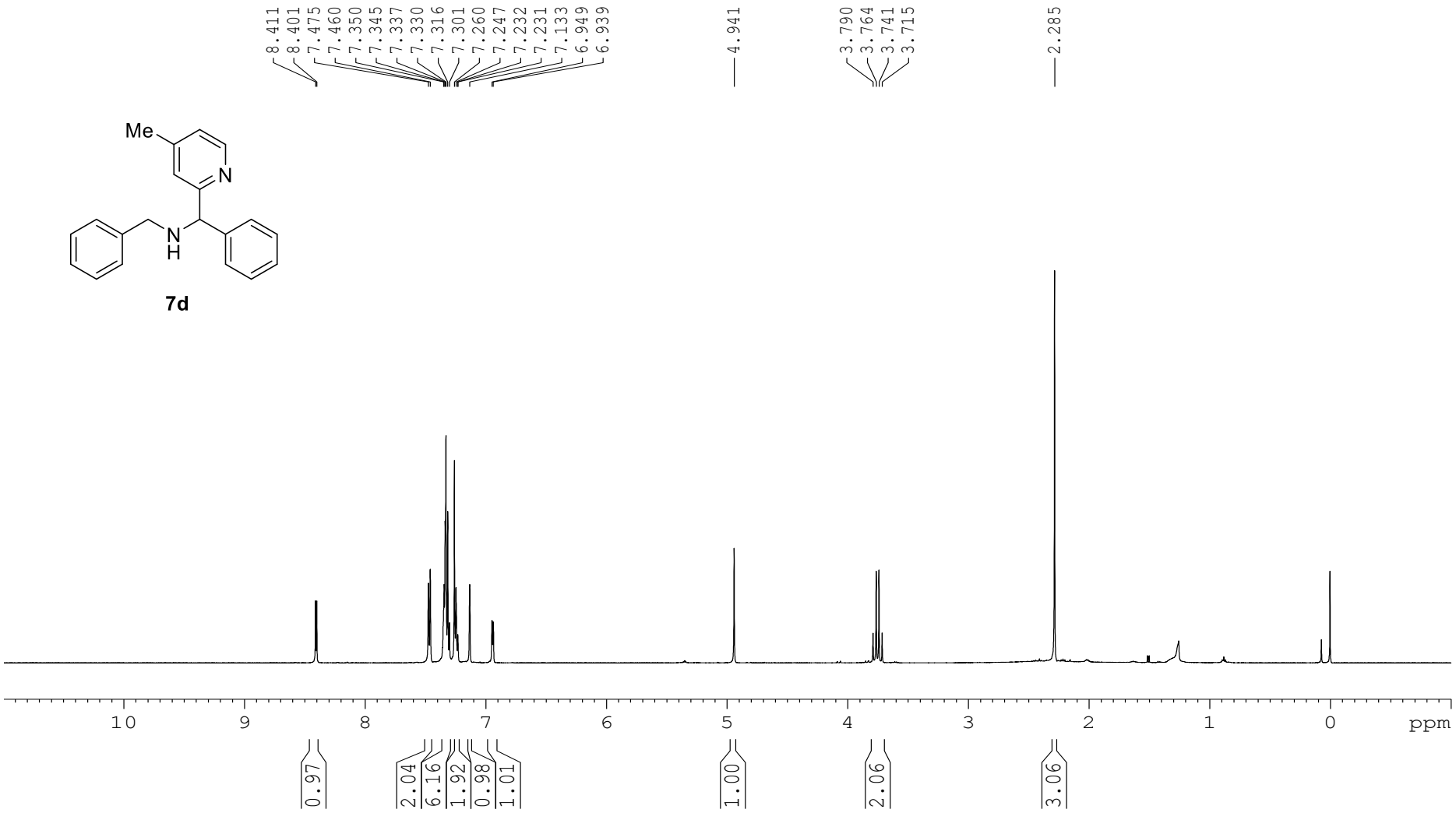

Figure S65. ^{1}H NMR spectra of **7d** ($CDCl_3$, 500M).

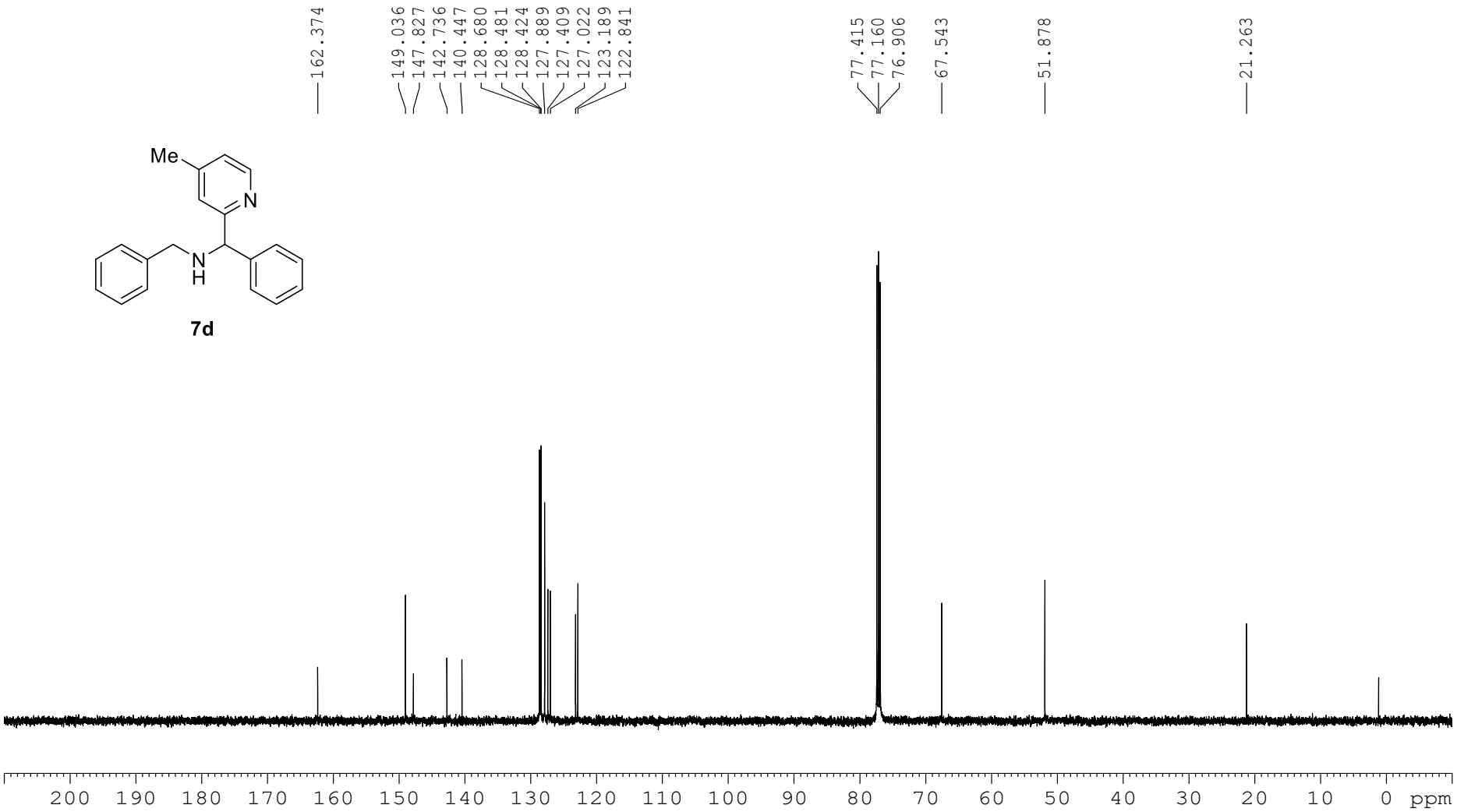

Figure S66. ^{13}C NMR spectra of **7d** ($CDCl_3$, 125M).

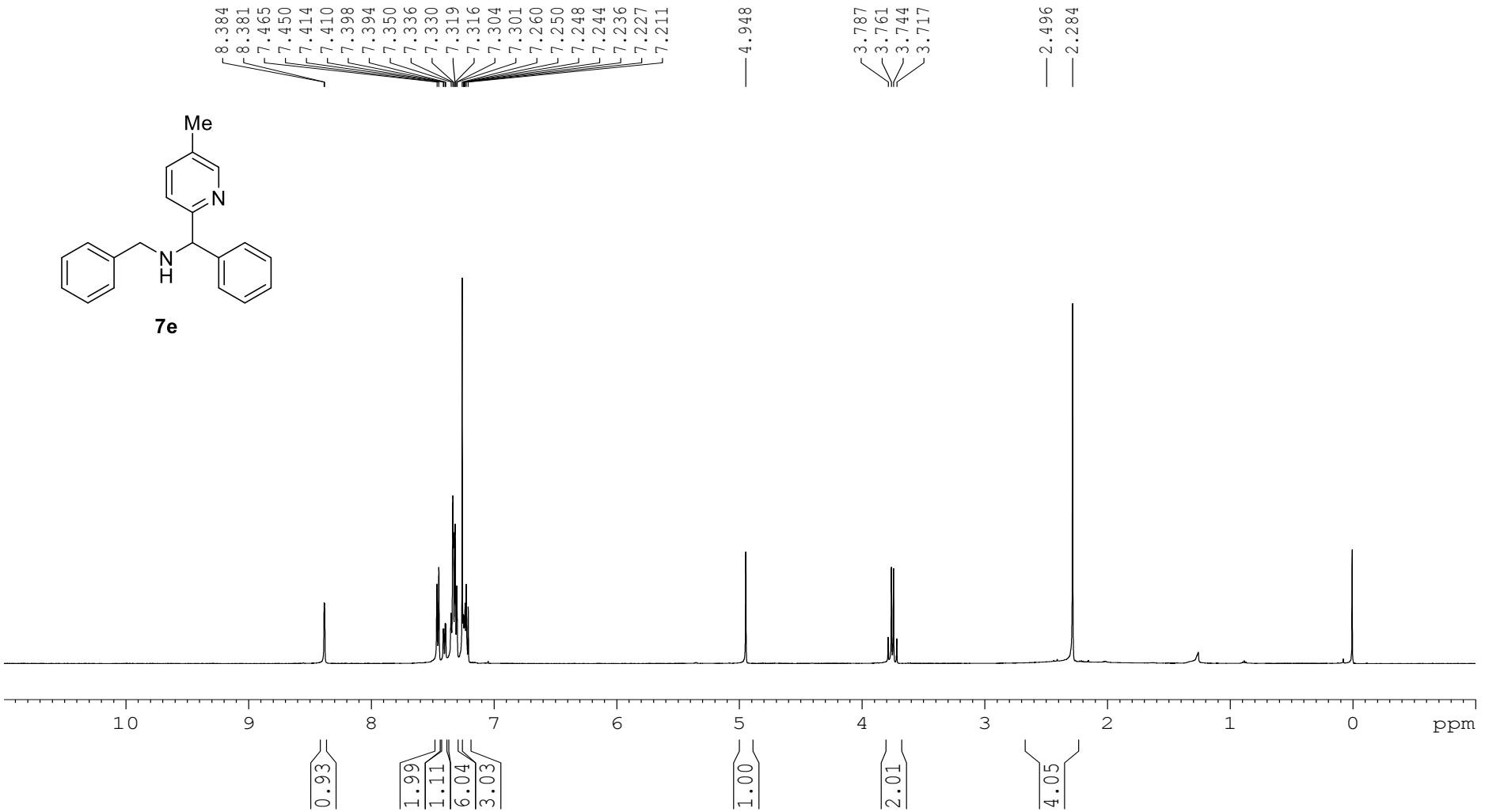

Figure S67. ^{1}H NMR spectra of **7e** ($CDCl_3$, 500M).

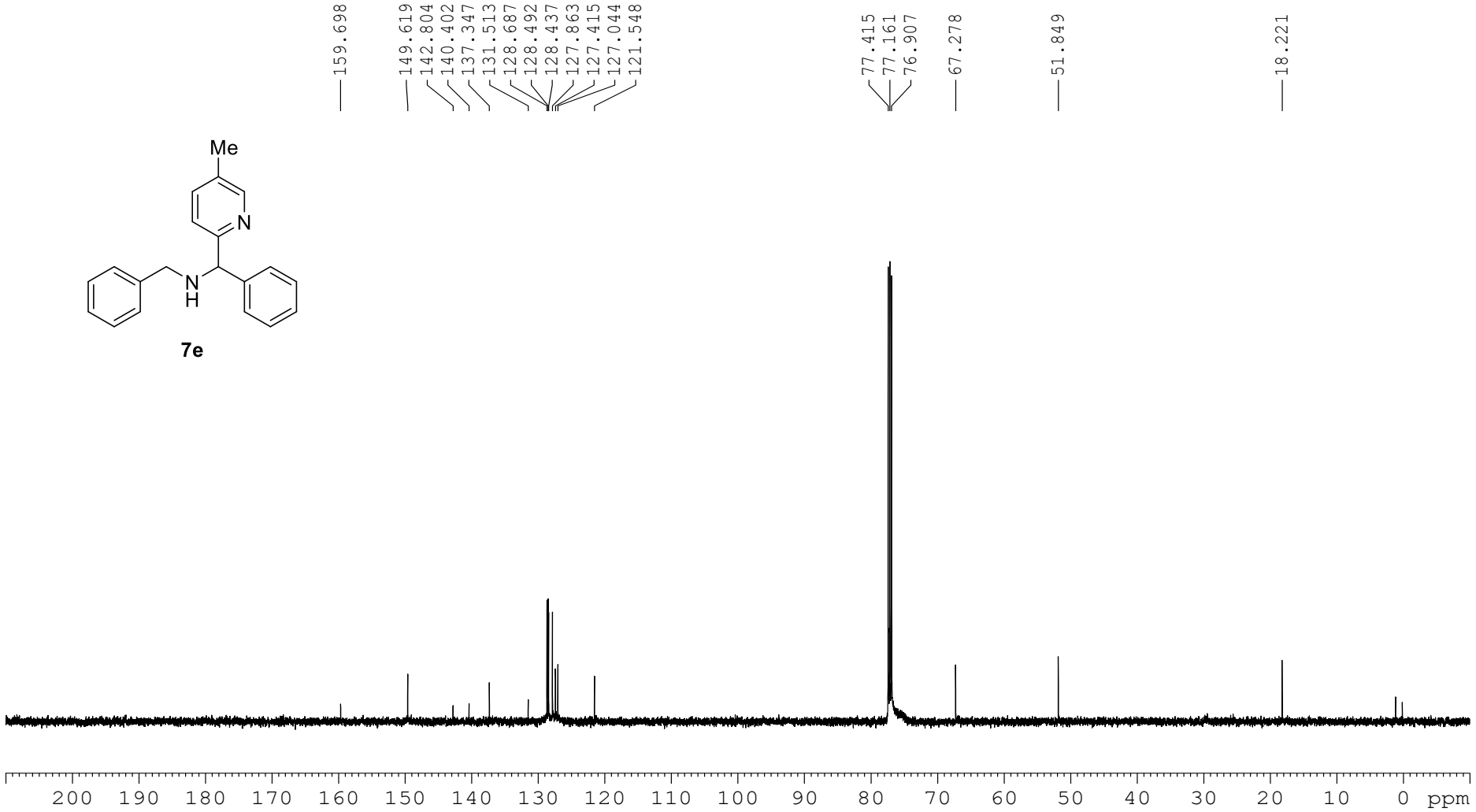

Figure S68. ^{13}C NMR spectra of **7e** ($CDCl_3$, 125M).

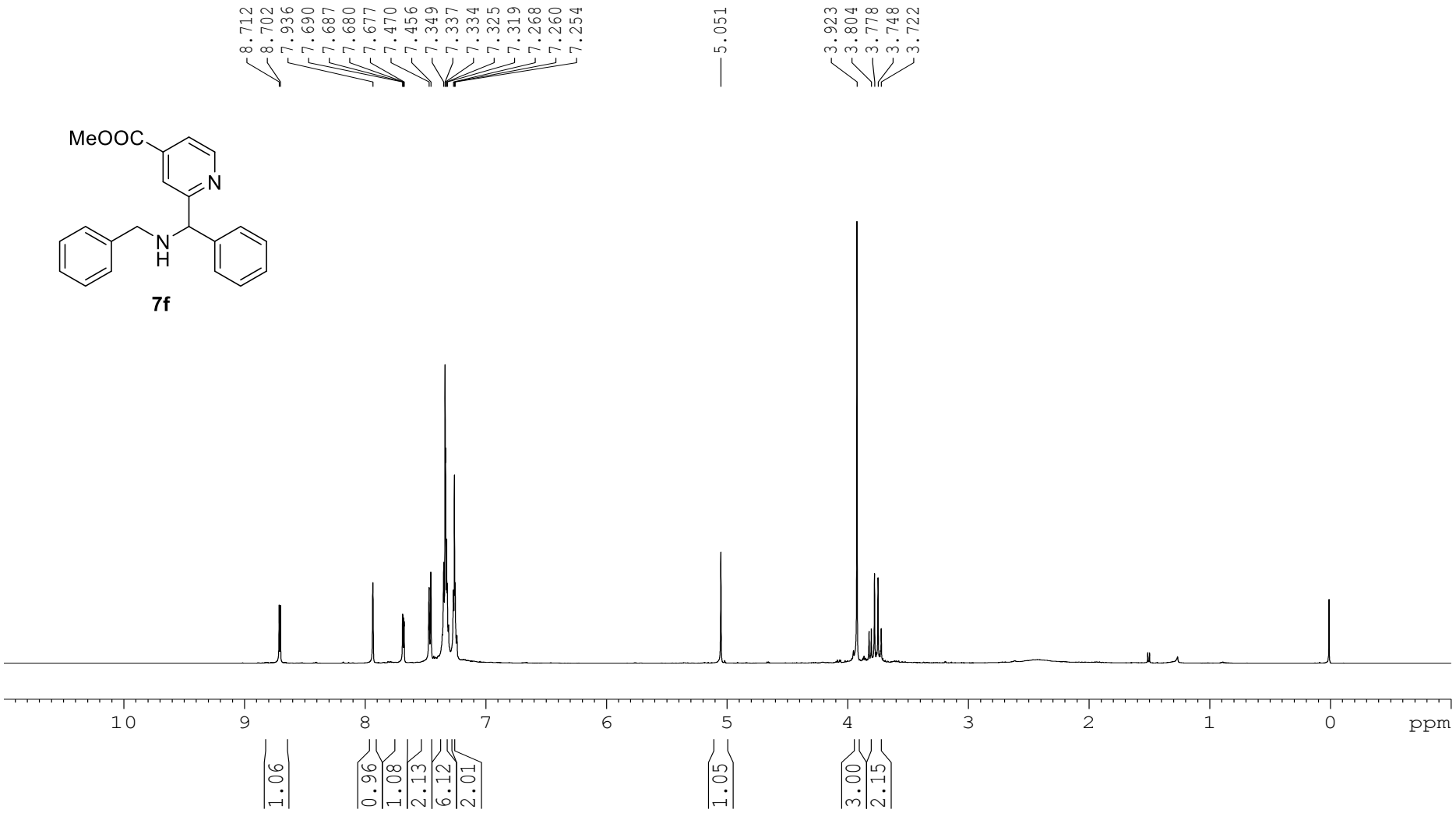

Figure S69. ^{1}H NMR spectra of **7f** ($CDCl_3$, 500M).

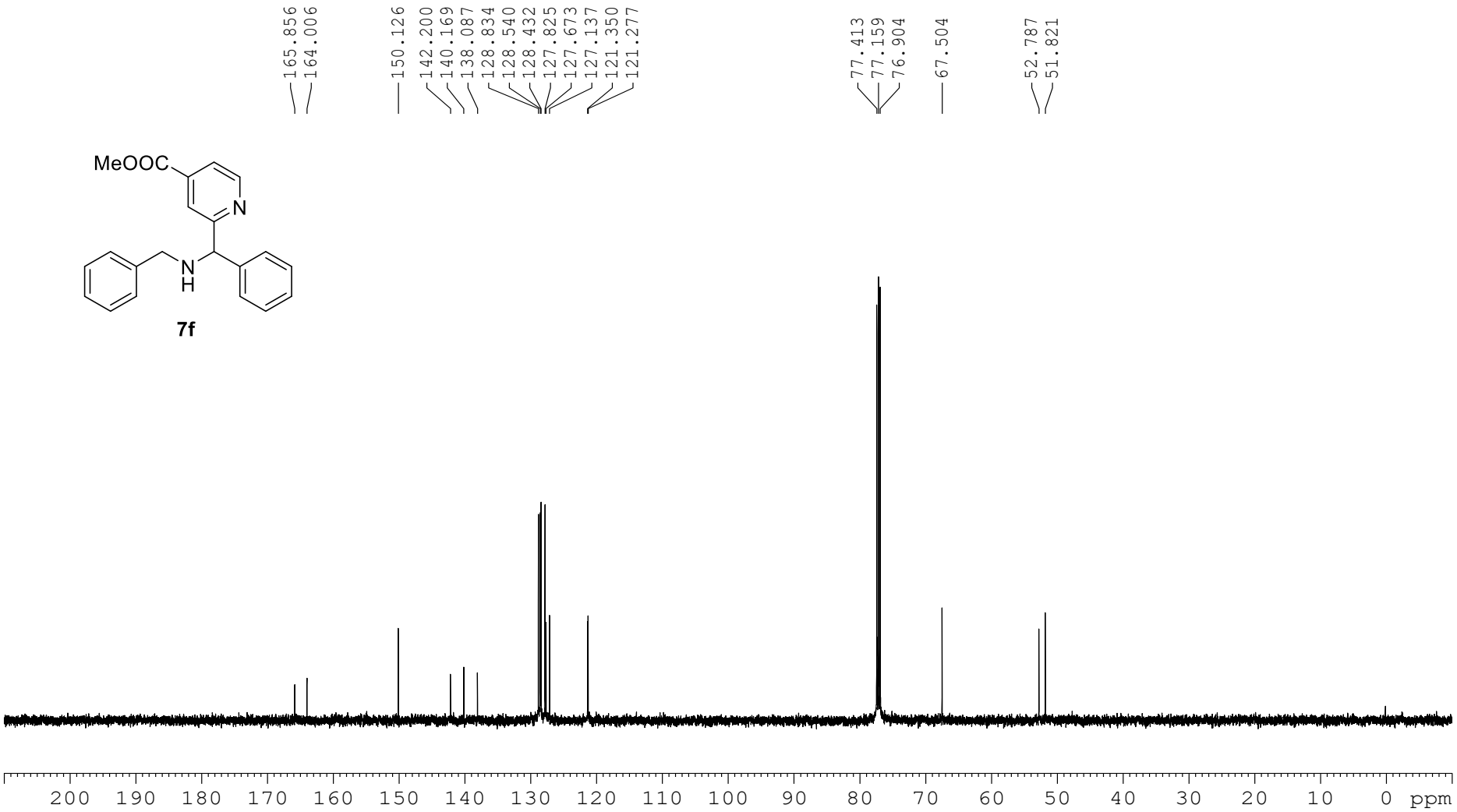

Figure S70. ^{13}C NMR spectra of **7f** ($CDCl_3$, 125M).

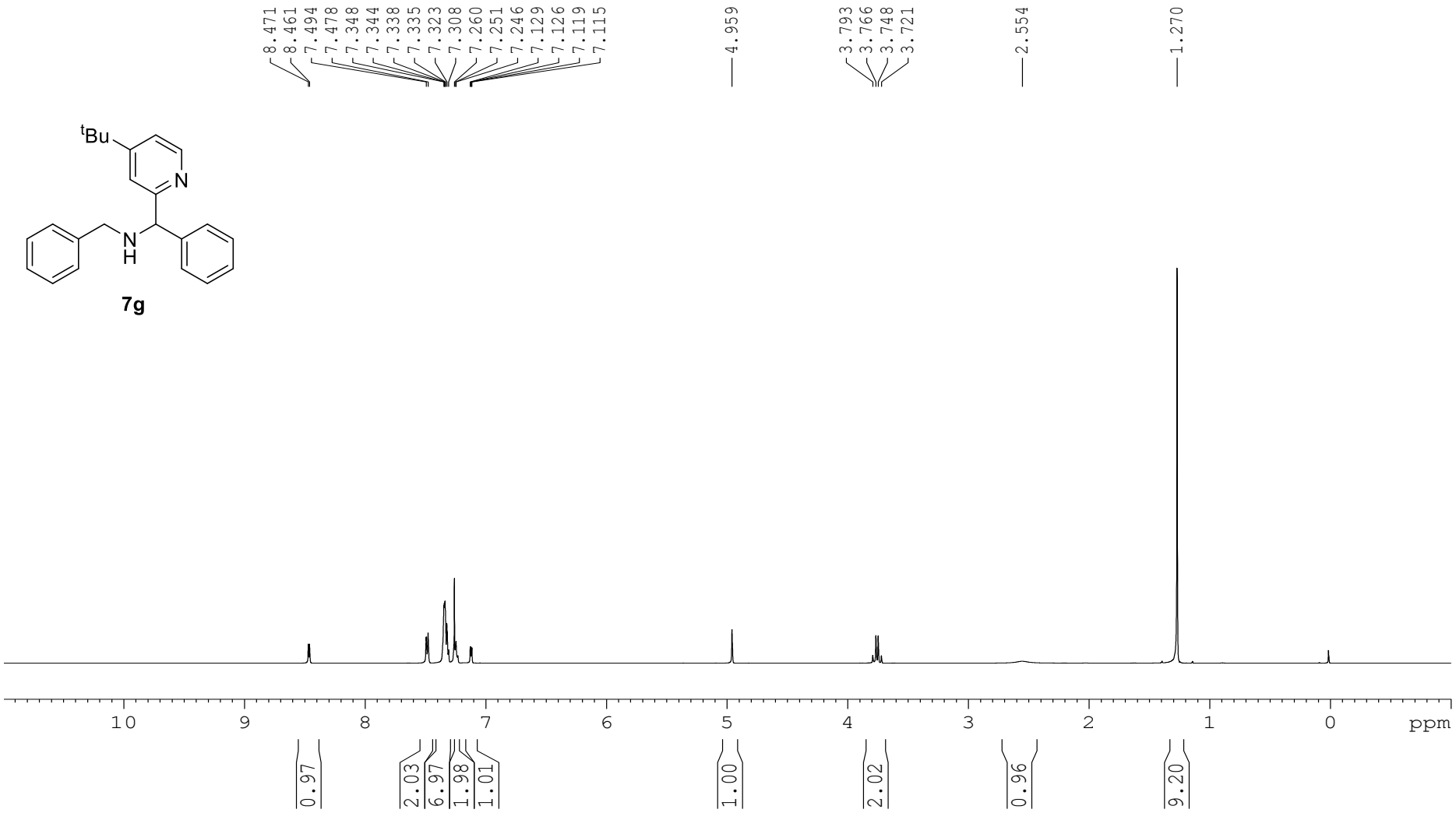

Figure S71. ^{1}H NMR spectra of **7g** ($CDCl_3$, 500M).

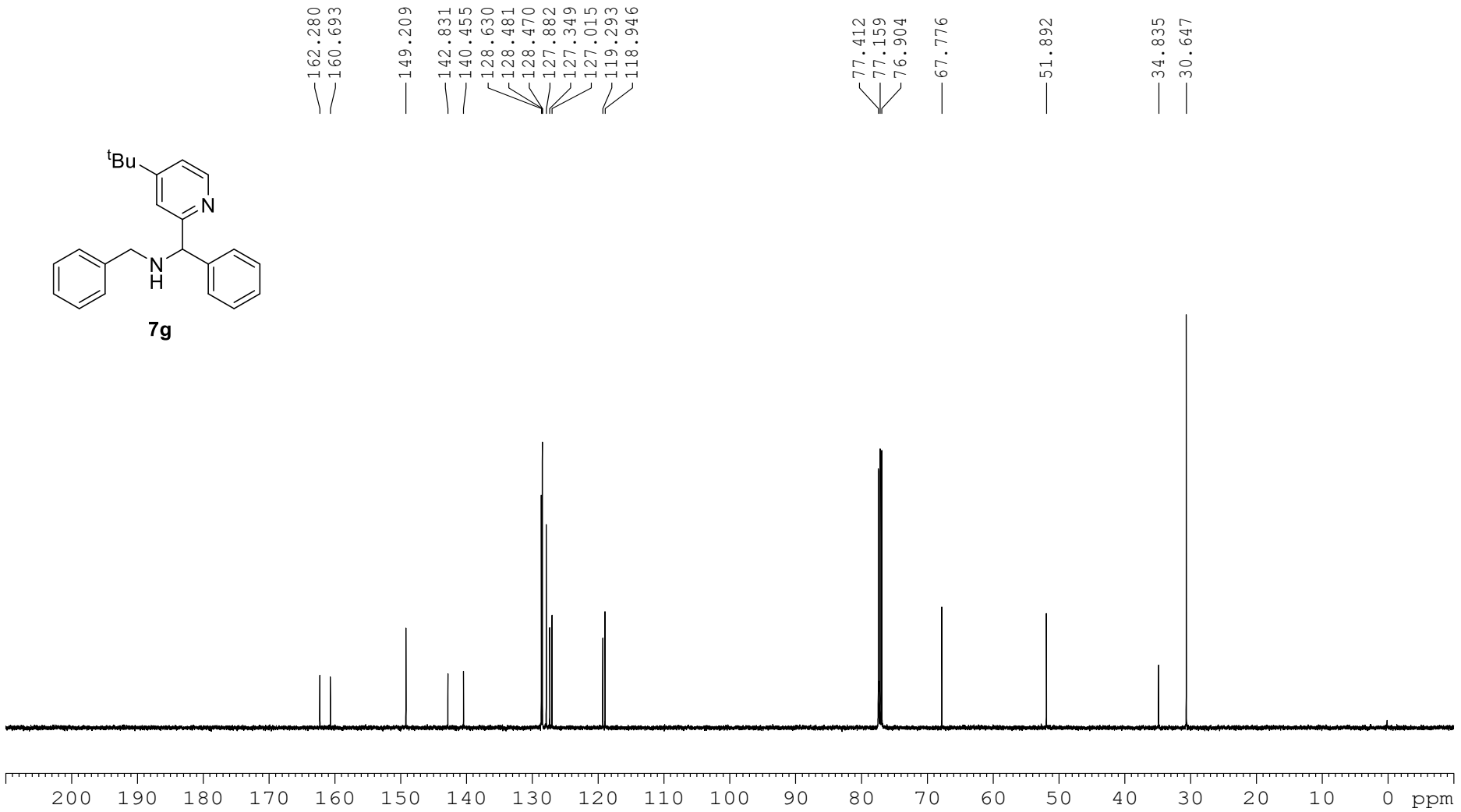

Figure S72. ^{13}C NMR spectra of **7g** ($CDCl_3$, 125M).

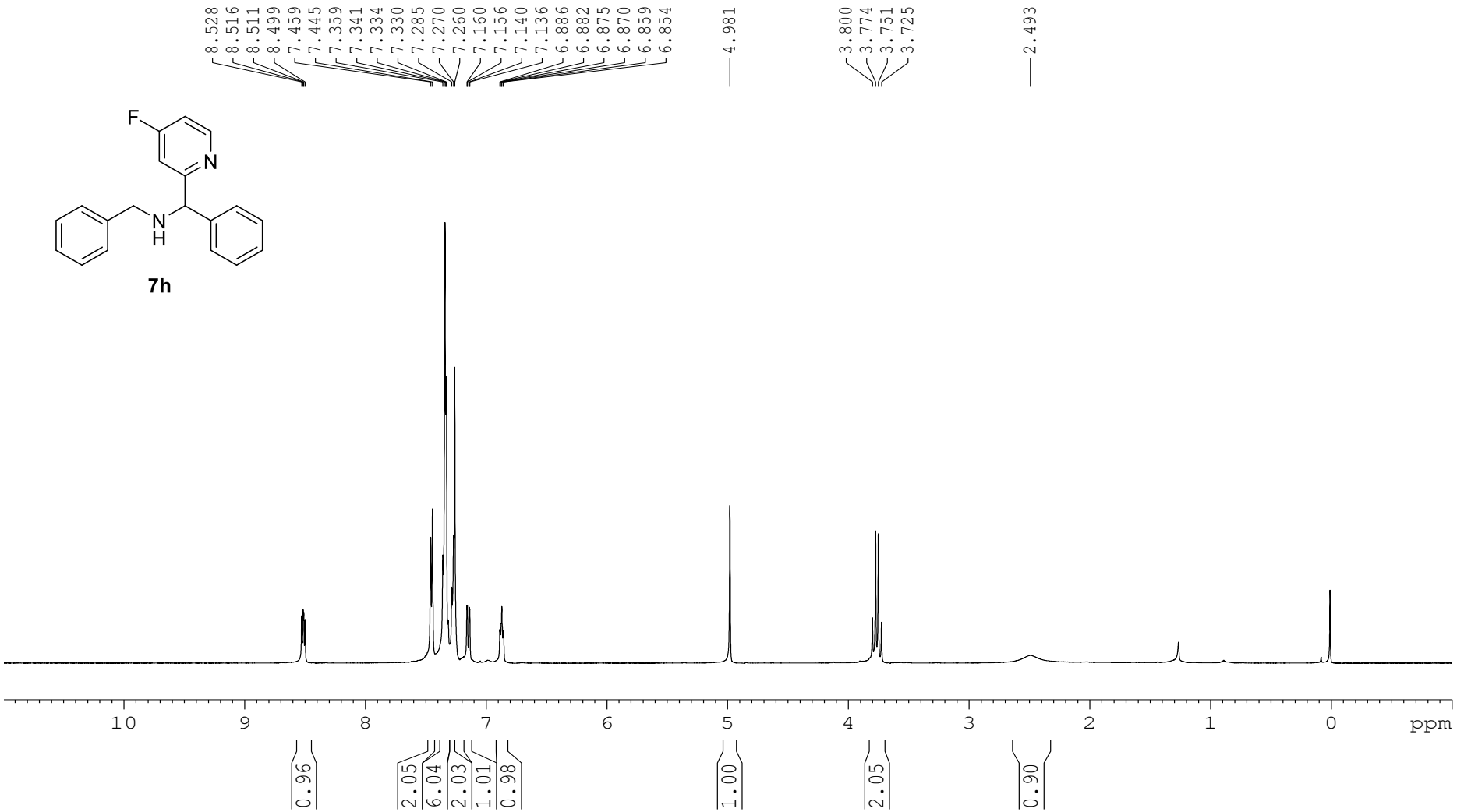

Figure S73. ^{1}H NMR spectra of **7h** ($CDCl_3$, 500M).

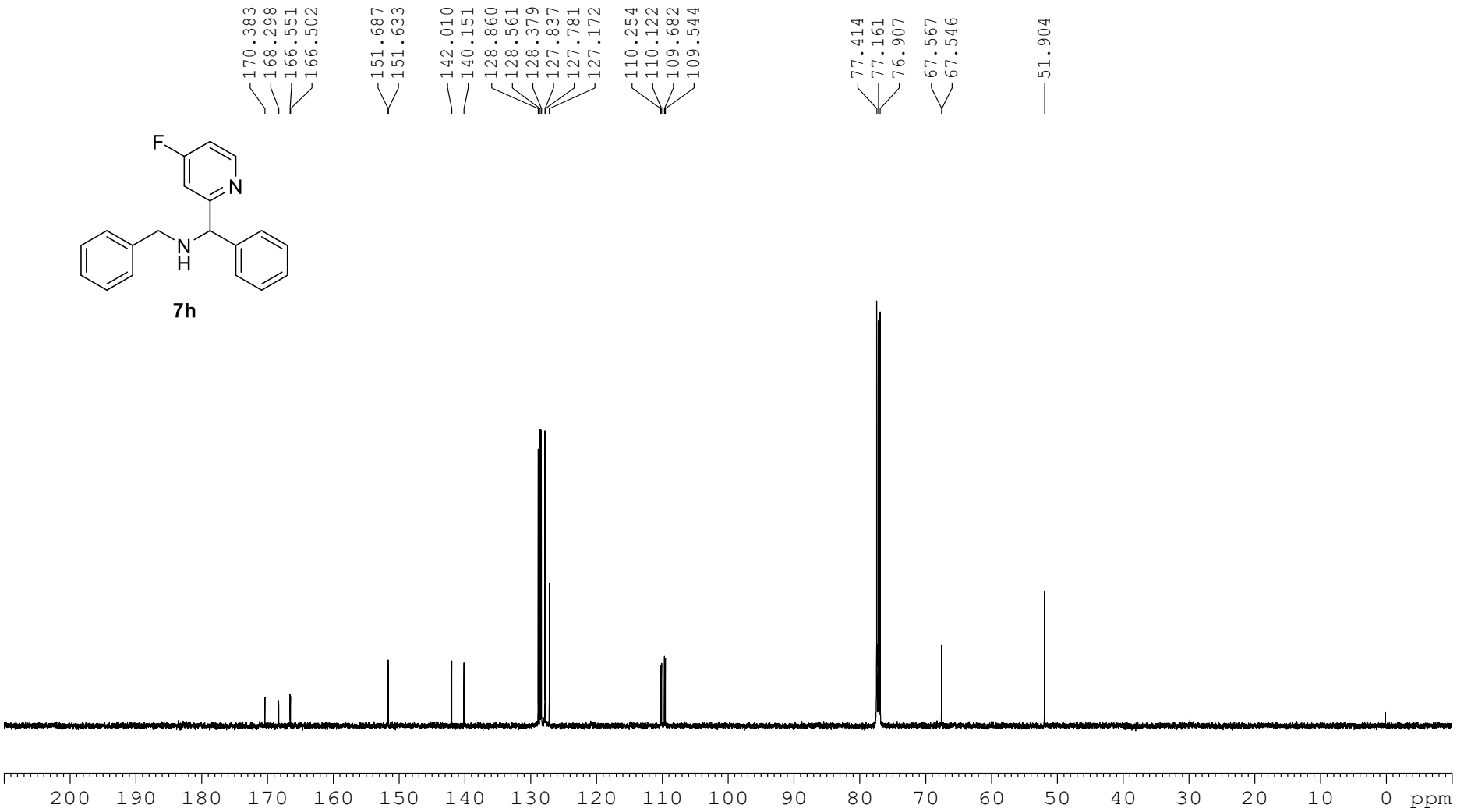

Figure S74. ^{13}C NMR spectra of **7h** ($CDCl_3$, 125M).

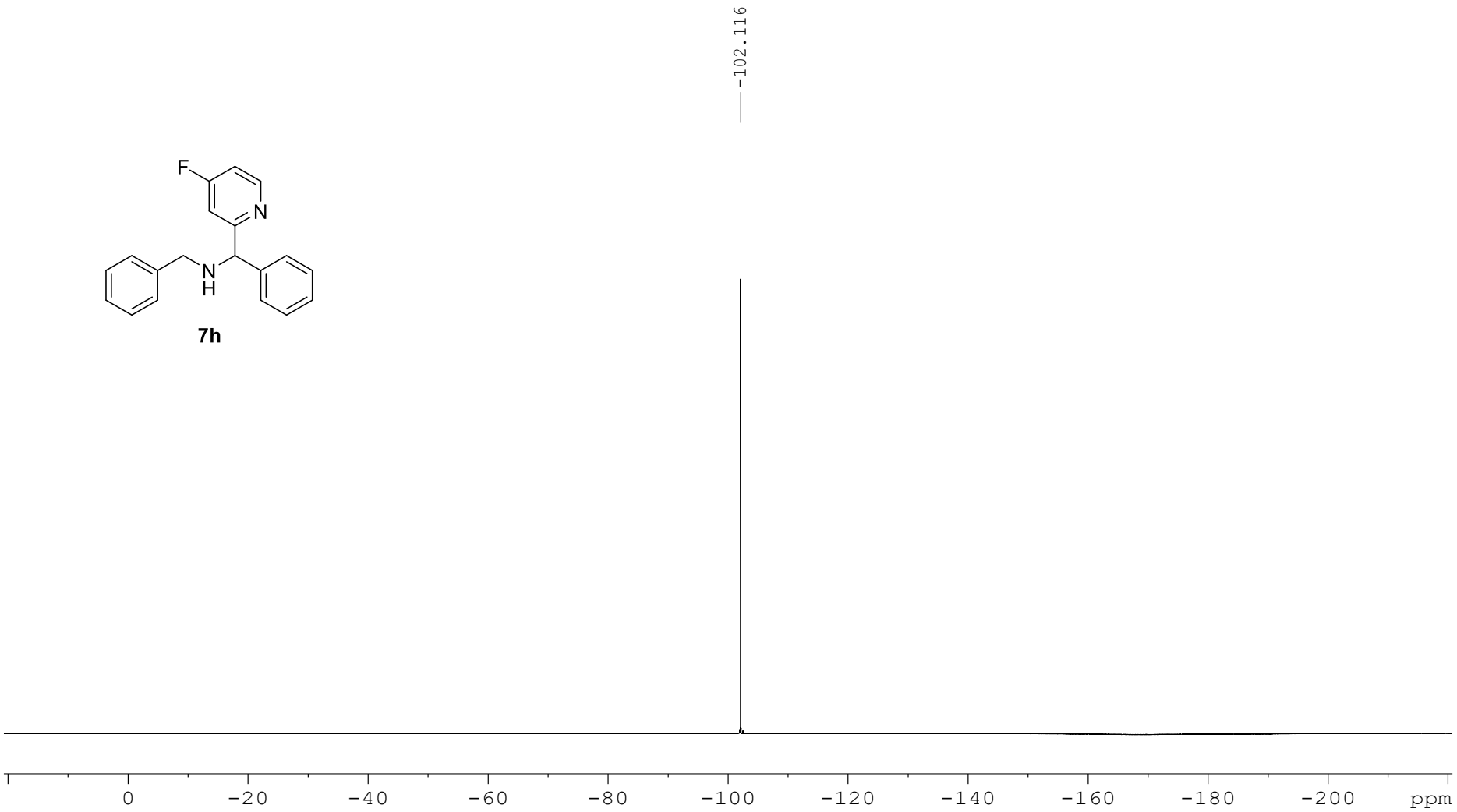

Figure S75. [19] F NMR spectra of **7h** ($CDCl_3$, 471M).

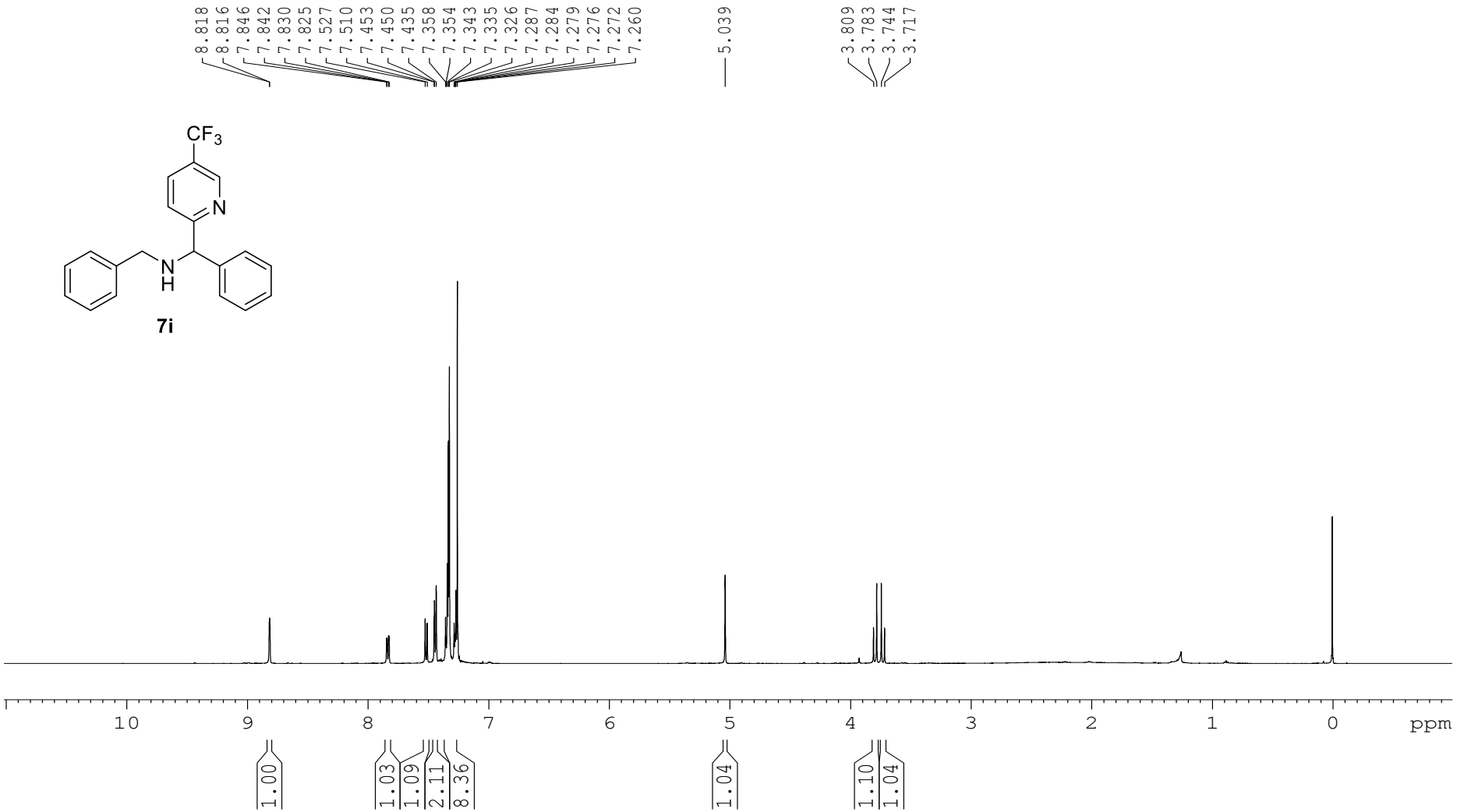

Figure S76. ^{1}H NMR spectra of **7i** ($CDCl_3$, 500M).

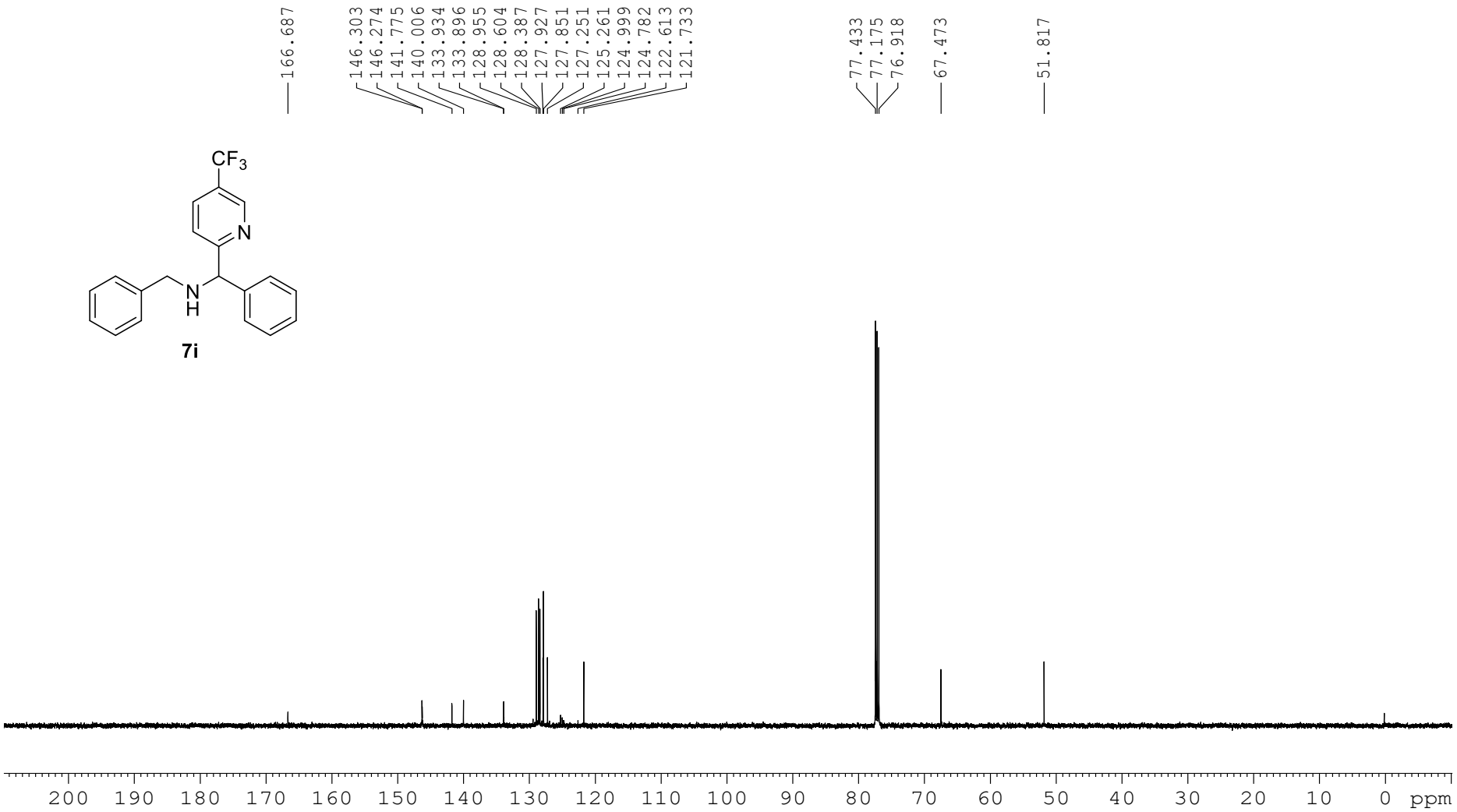

Figure S77. ^{13}C NMR spectra of **7i** ($CDCl_3$, 125M).

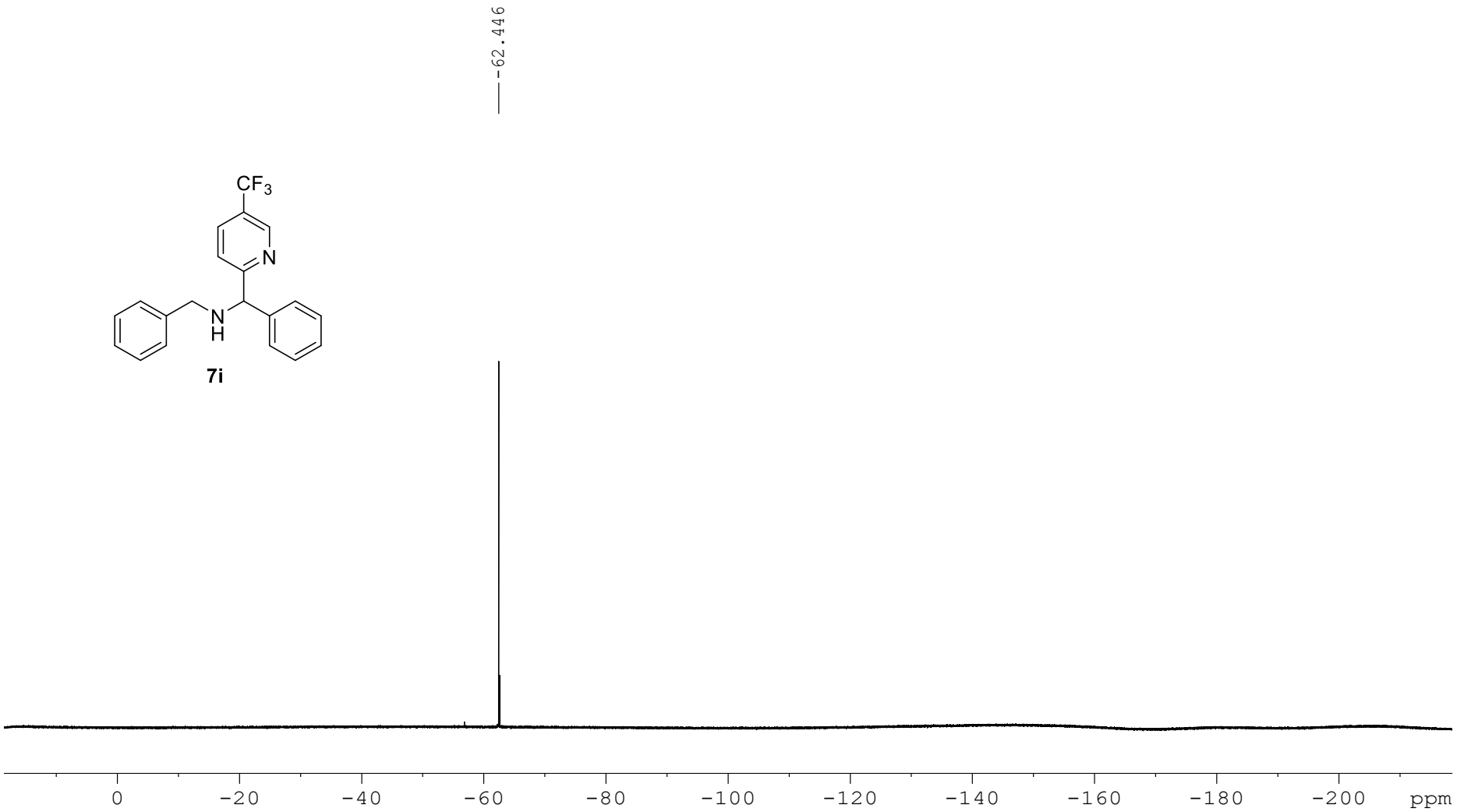

Figure S78. [19] F NMR spectra of **7i** ($CDCl_3$, 471M).

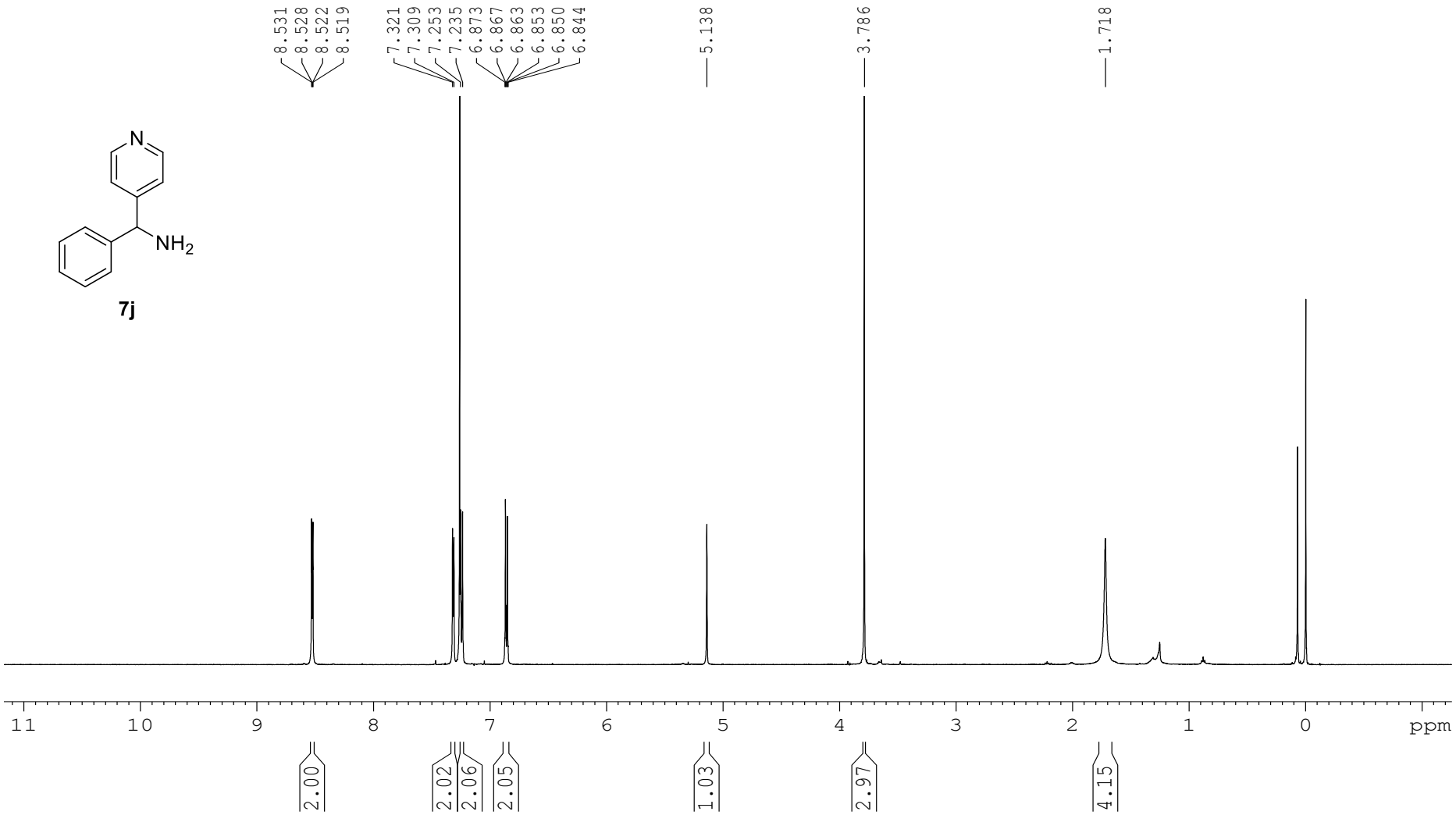

Figure S79. ^{1}H NMR spectra of **7j** ($CDCl_3$, 500M).

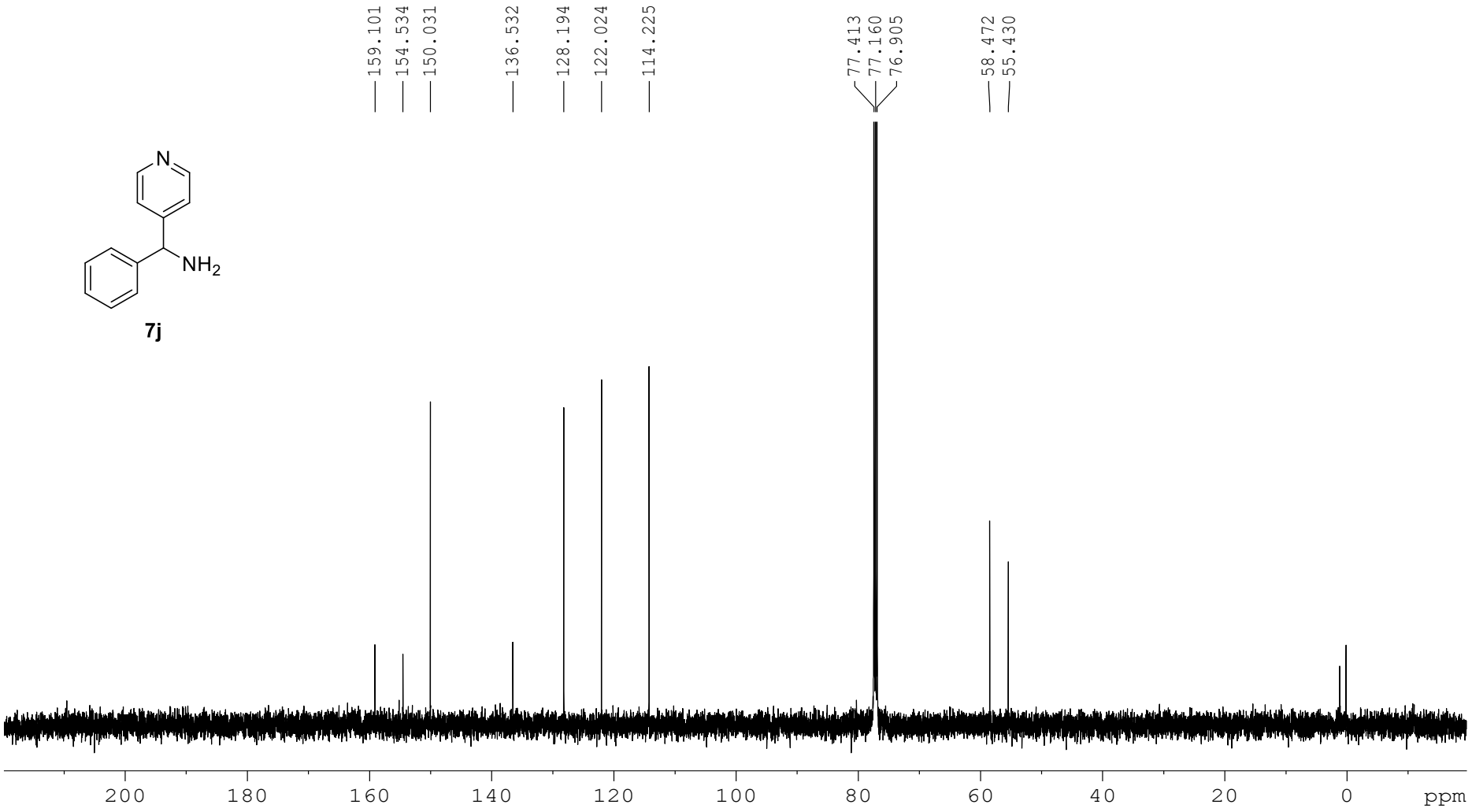

Figure S80. ^{13}C NMR spectra of **7j** ($CDCl_3$, 125M).

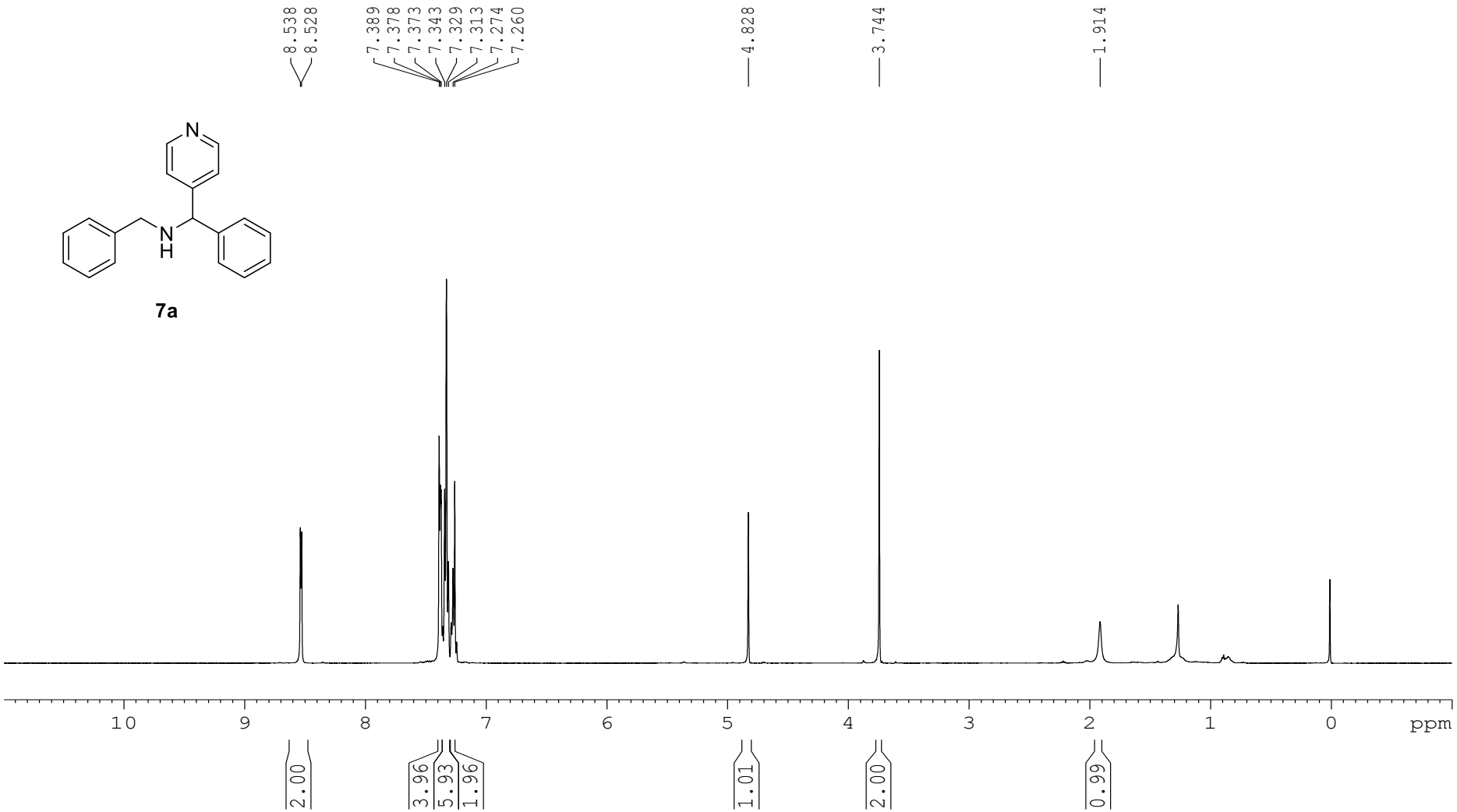

Figure S81. ^{1}H NMR spectra of **7a** ($CDCl_3$, 500M).

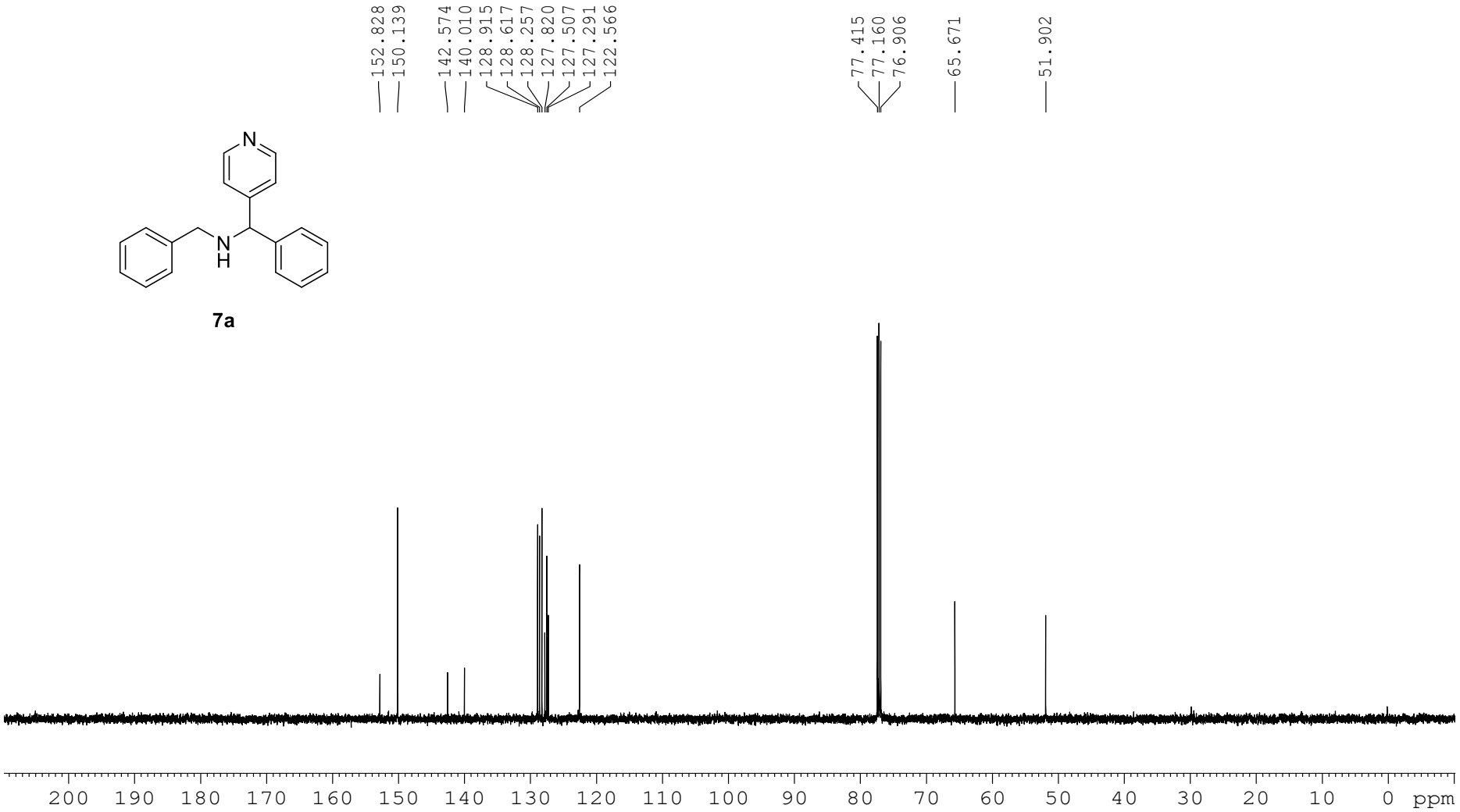

Figure S82. ^{13}C NMR spectra of **7a** ($CDCl_3$, 125M).

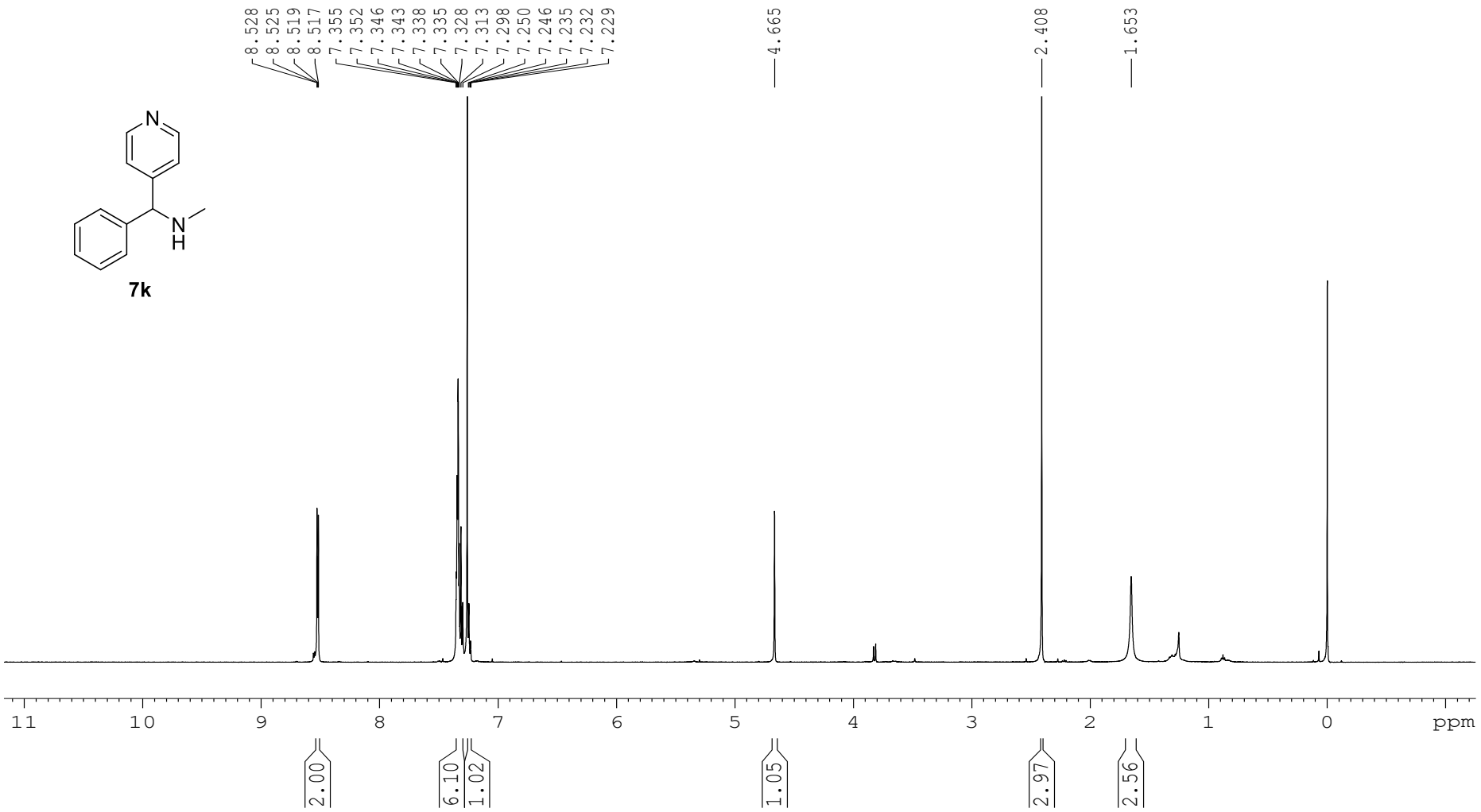

Figure S83. ^{1}H NMR spectra of **7k** ($CDCl_3$, 500M).

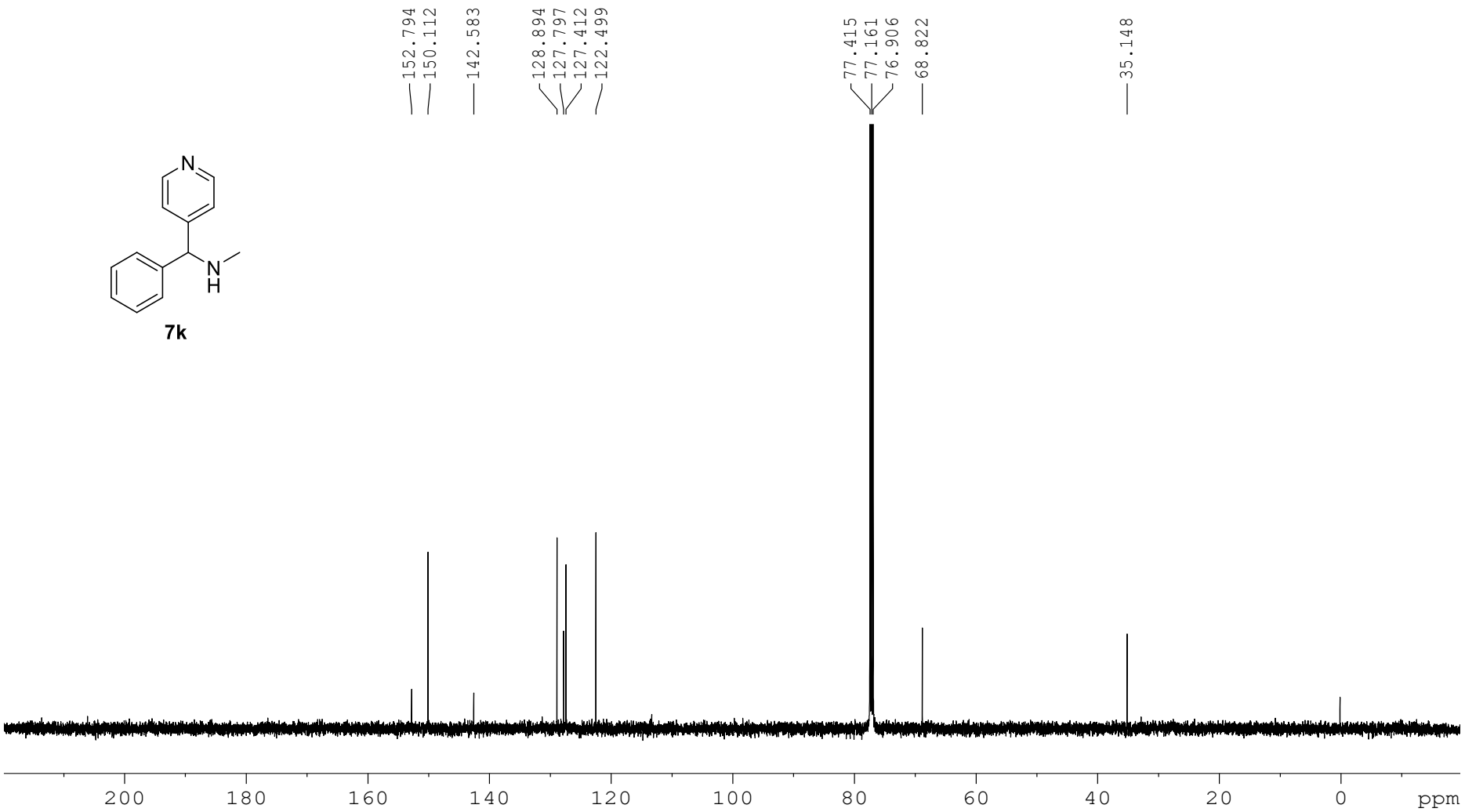

Figure S84. ^{13}C NMR spectra of **7k** ($CDCl_3$, 125M).

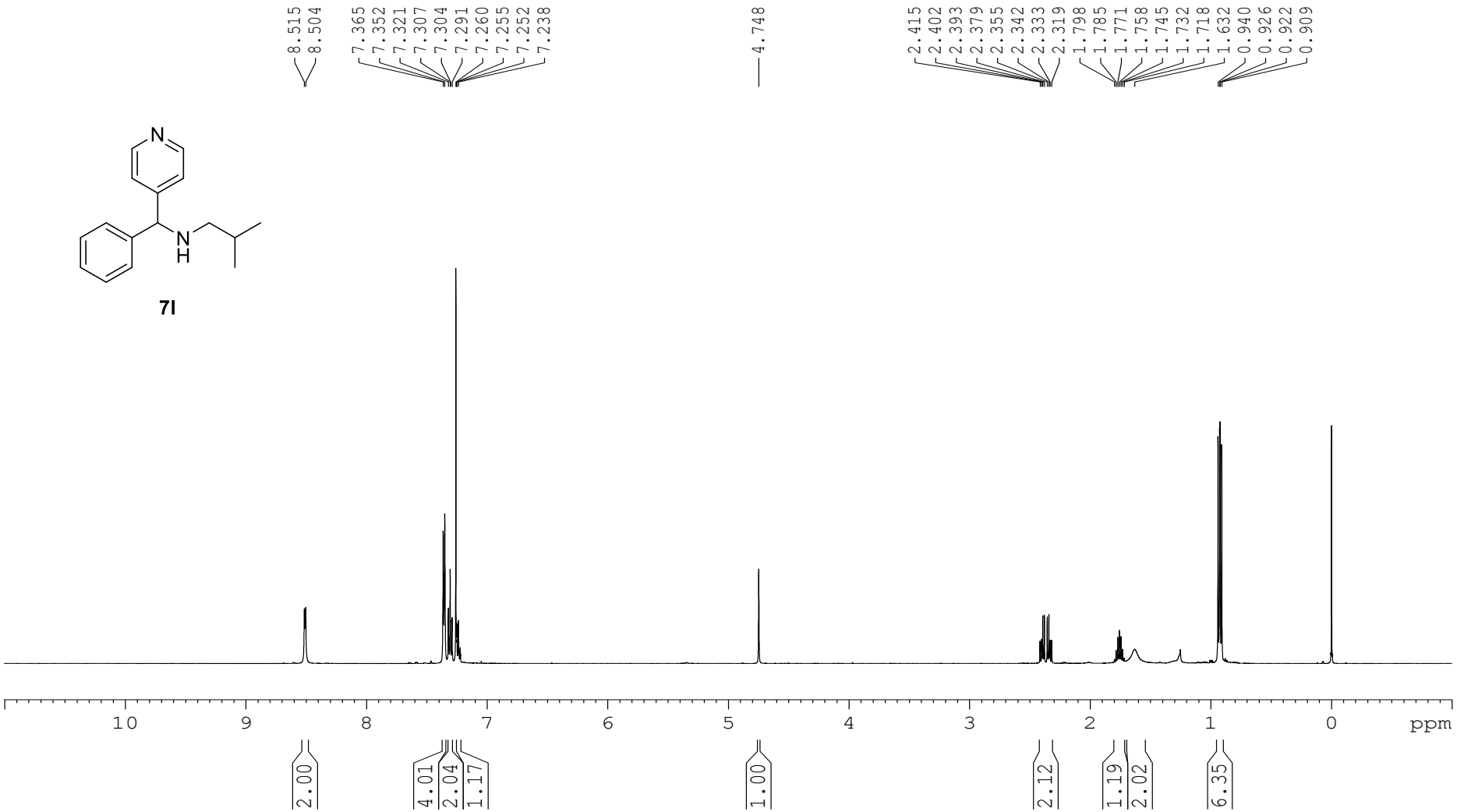

Figure S85. ^{1}H NMR spectra of **7l** ($CDCl_3$, 500M).

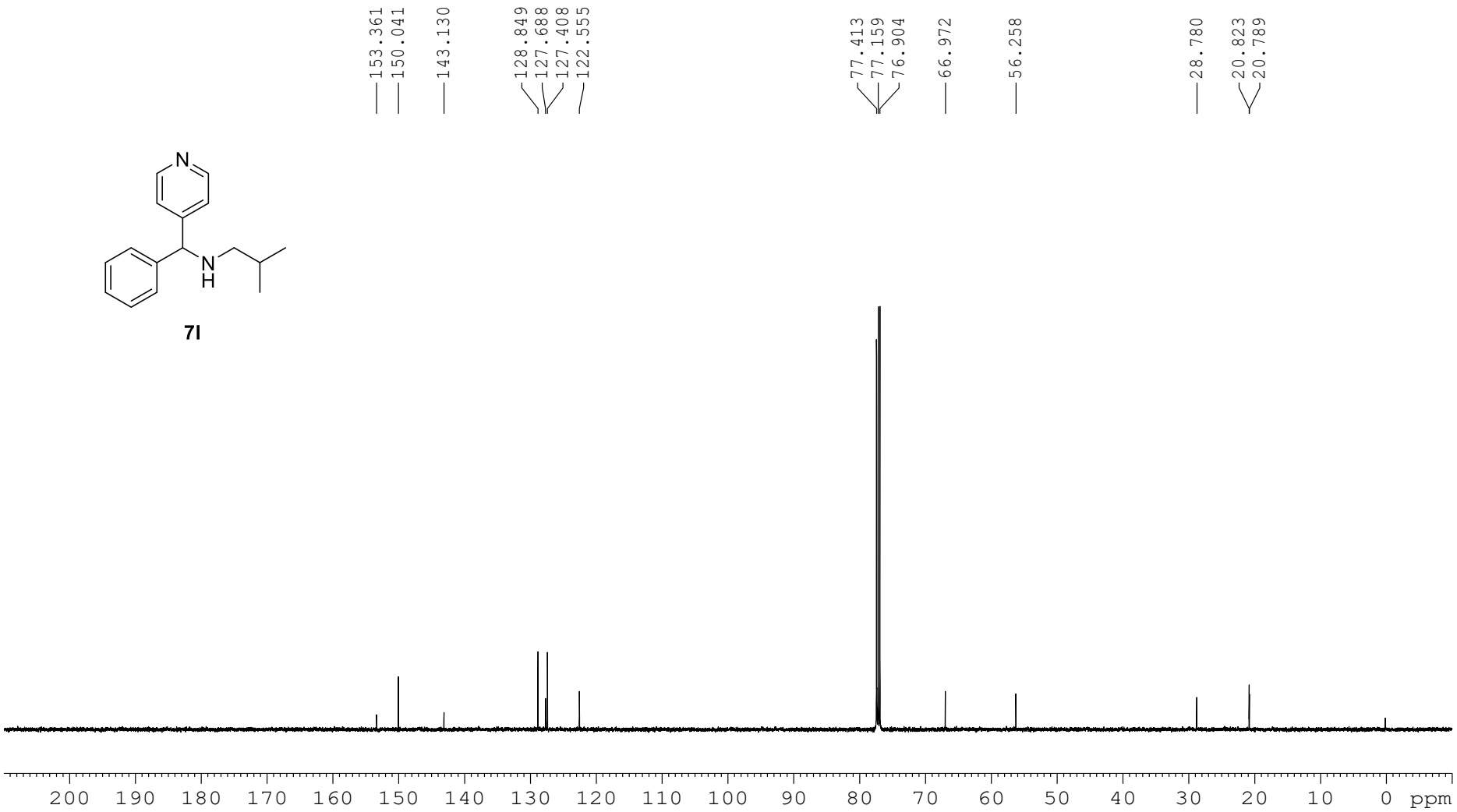

Figure S86. ^{13}C NMR spectra of **7l** ($CDCl_3$, 125M).

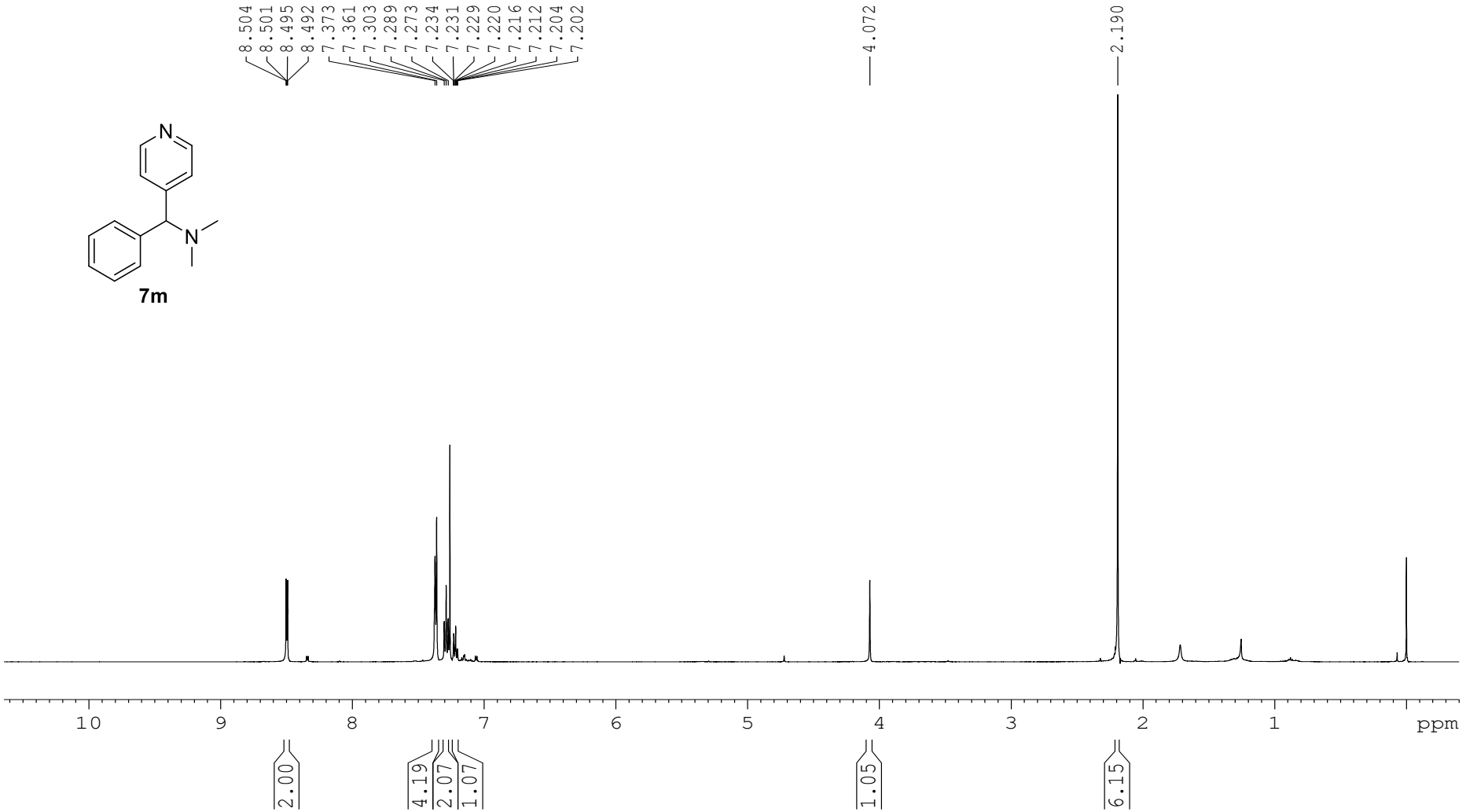

Figure S87. ^{1}H NMR spectra of **7m** ($CDCl_3$, 500M).

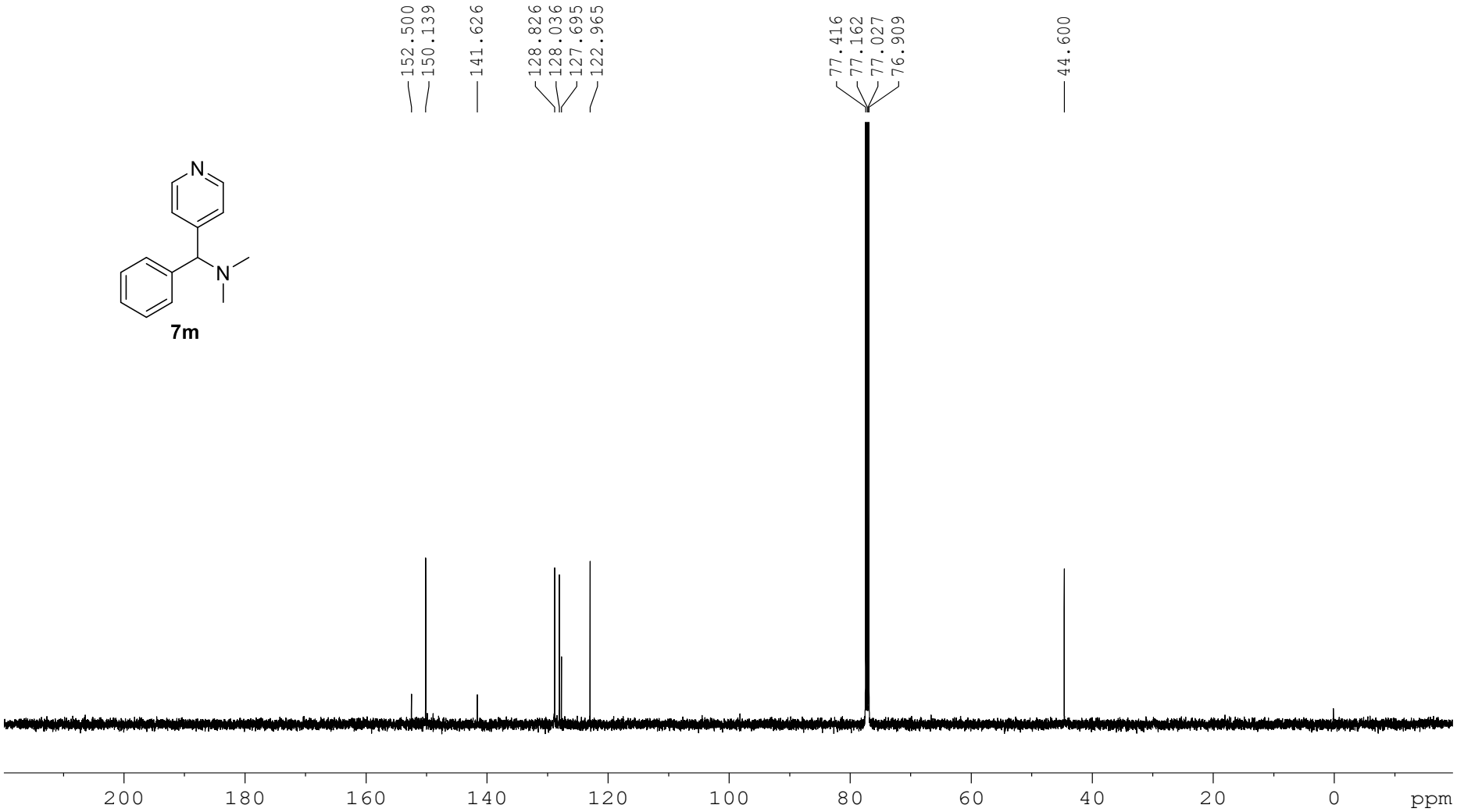

Figure S88. ^{13}C NMR spectra of **7m** ($CDCl_3$, 125M).

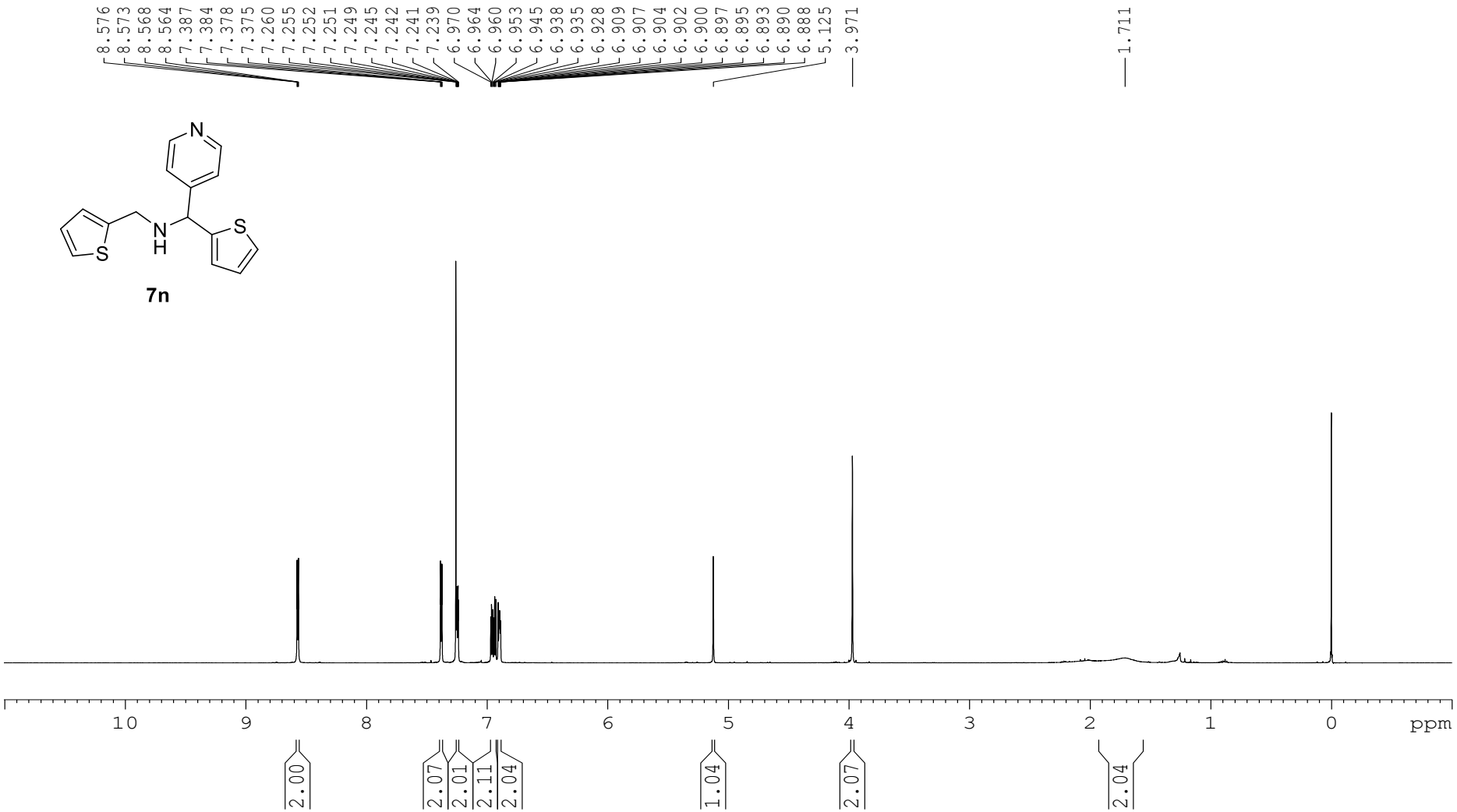

Figure S89. ^{1}H NMR spectra of **7n** ($CDCl_3$, 500M).

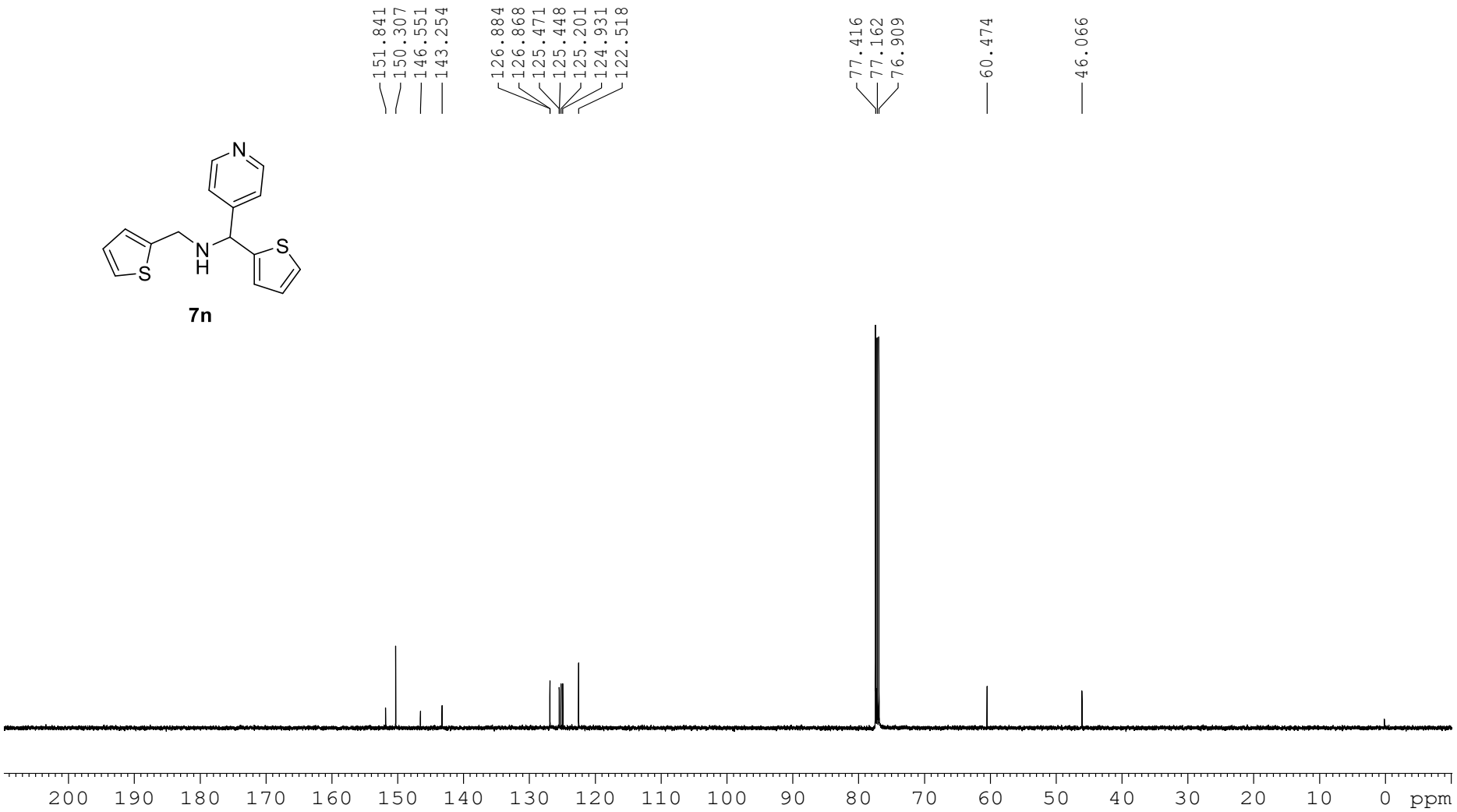

Figure S90. ^{13}C NMR spectra of **7n** ($CDCl_3$, 125M).

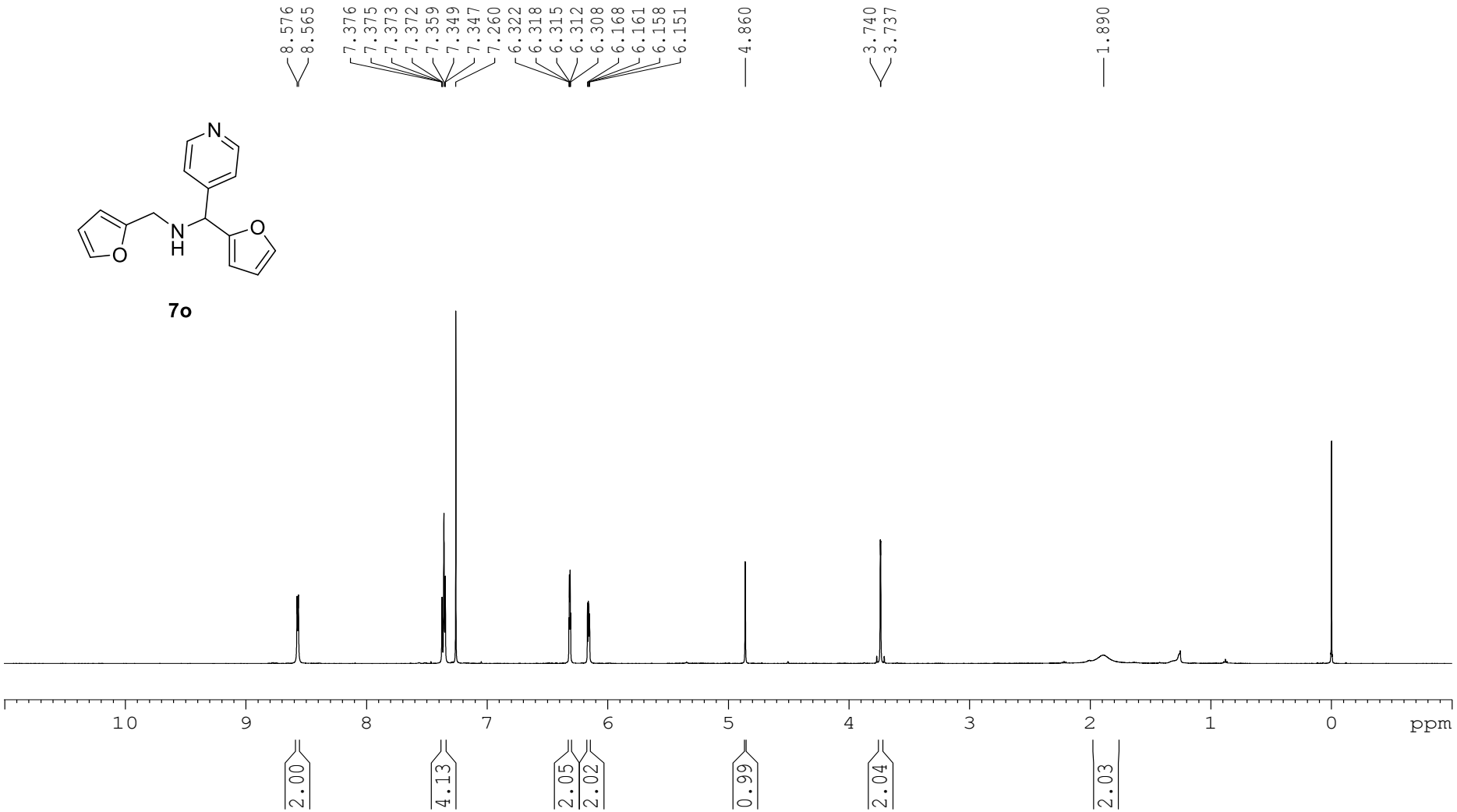

Figure S91. ^{1}H NMR spectra of **7o** ($CDCl_3$, 500M).

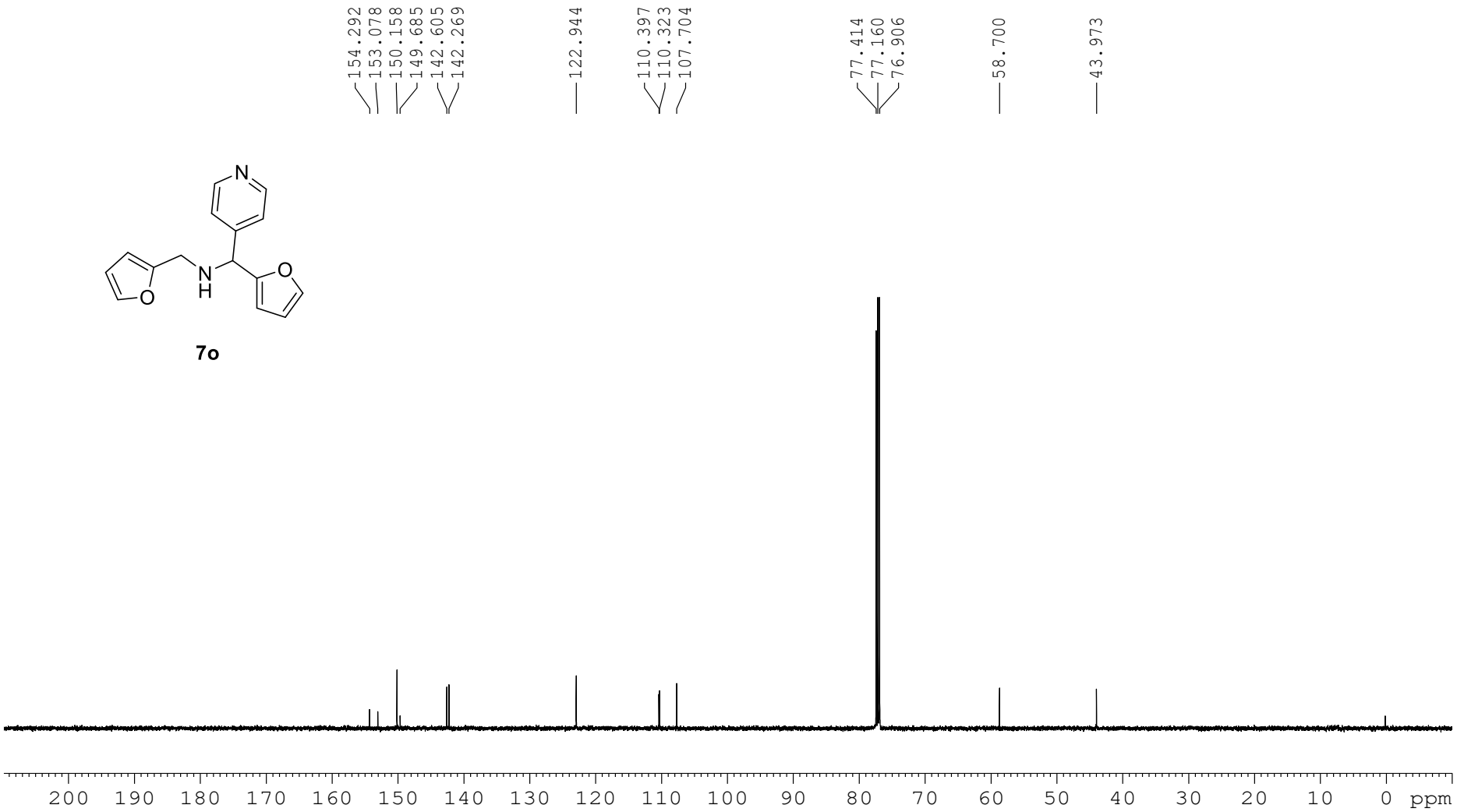

Figure S92. ^{13}C NMR spectra of **7o** ($CDCl_3$, 125M).

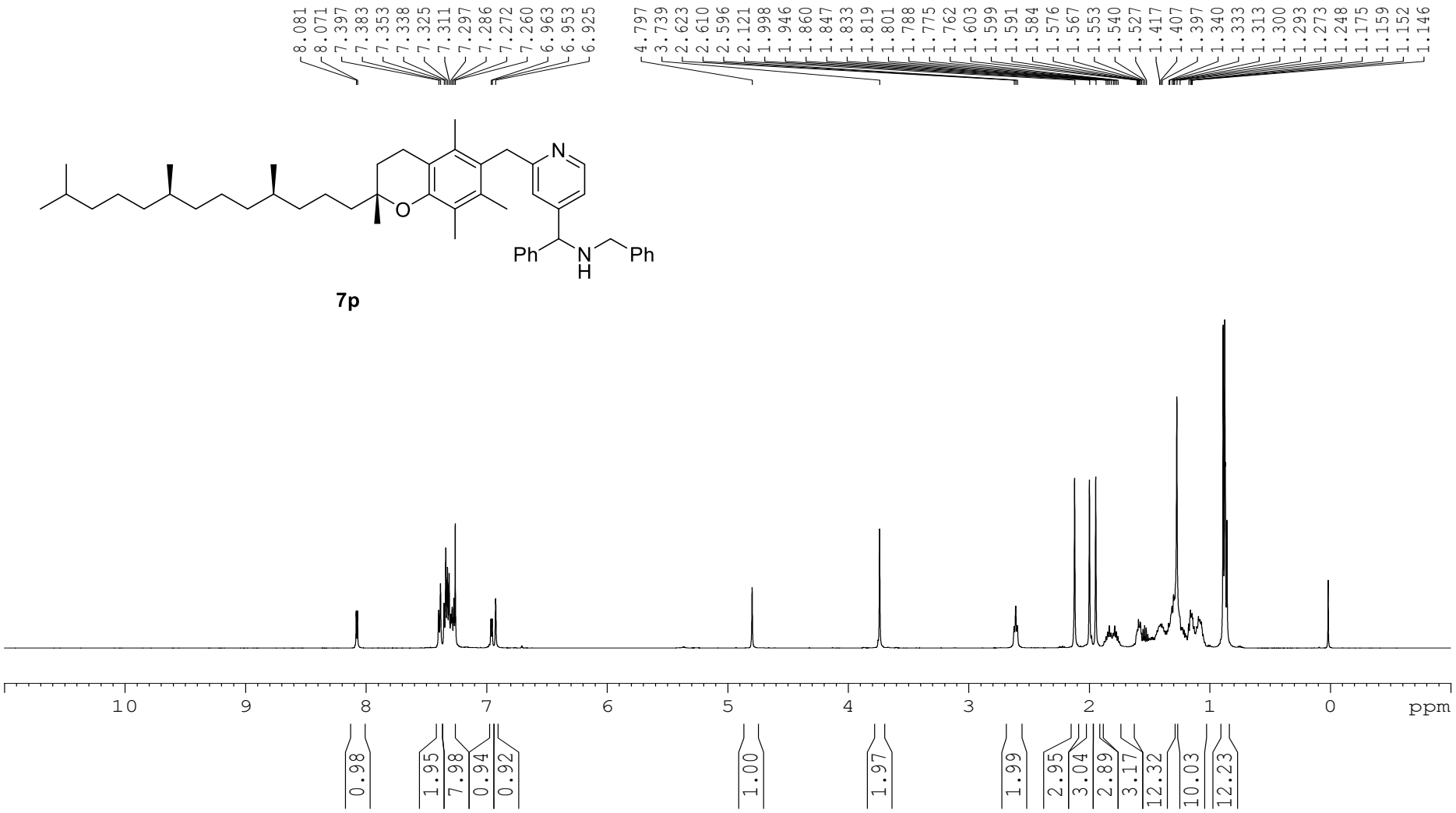

Figure S93. ^{1}H NMR spectra of **7p** ($CDCl_3$, 500M).

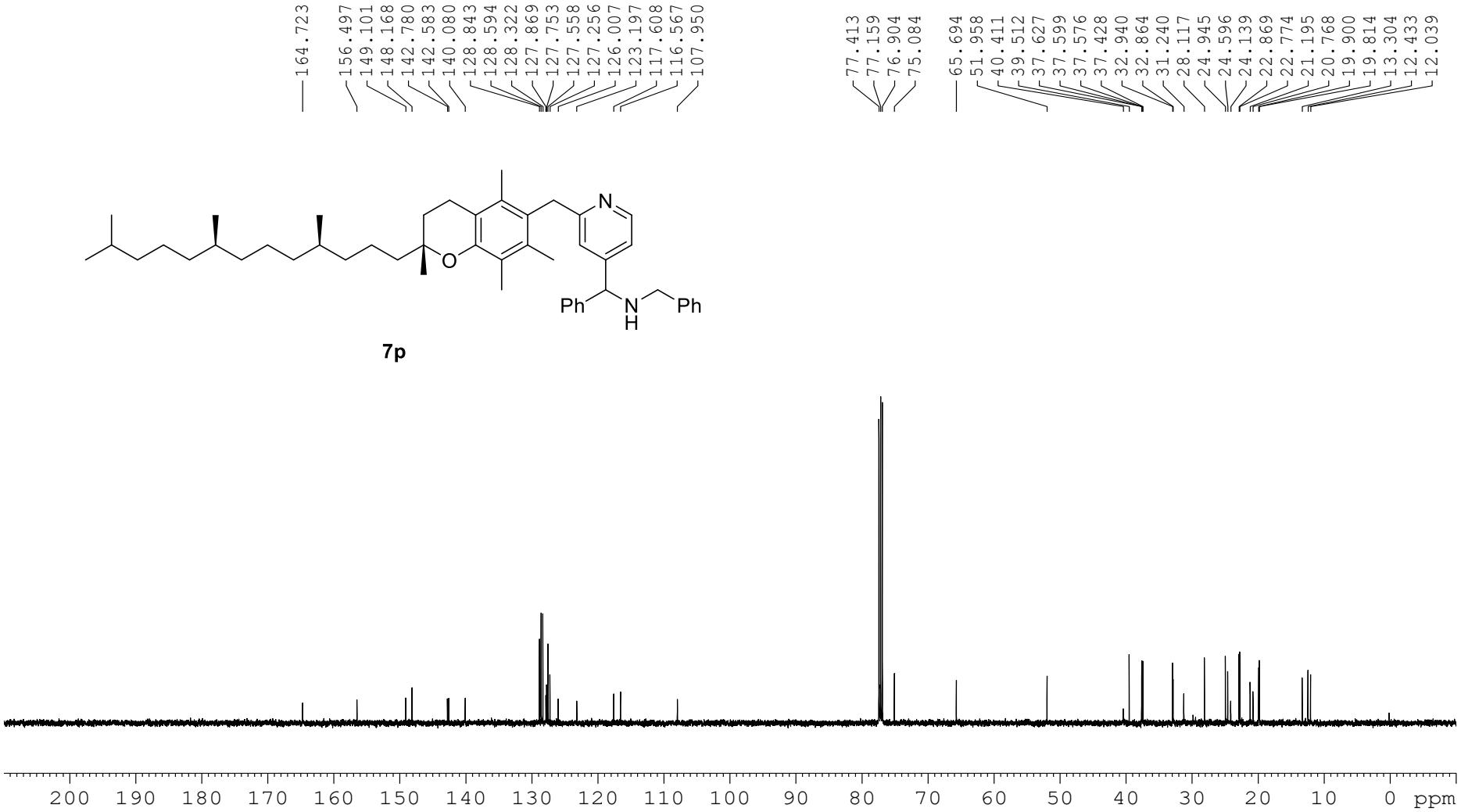

Figure S94. ^{13}C NMR spectra of **7p** ($CDCl_3$, 125M).

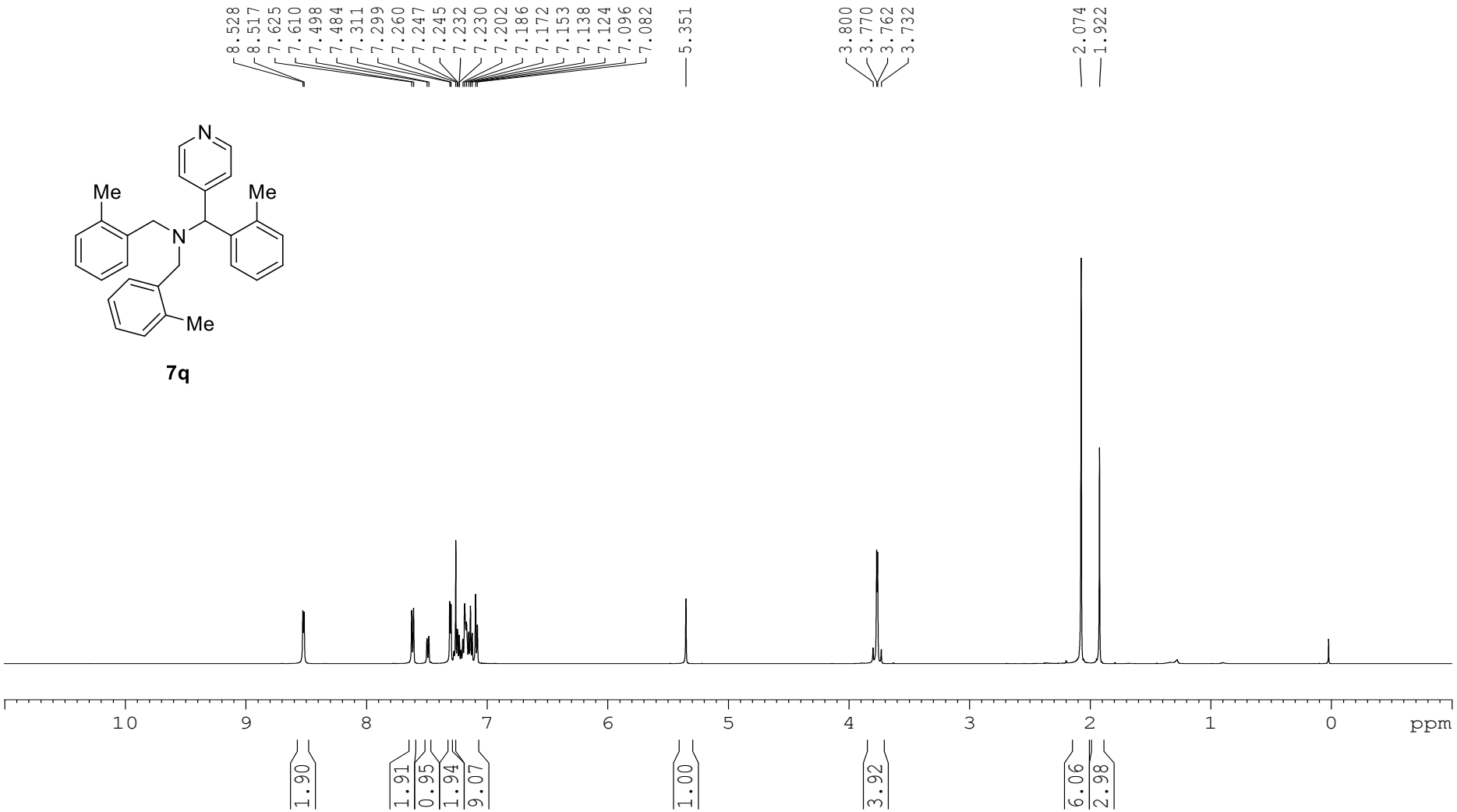

Figure S95. ^{1}H NMR spectra of **7q** ($CDCl_3$, 500M).

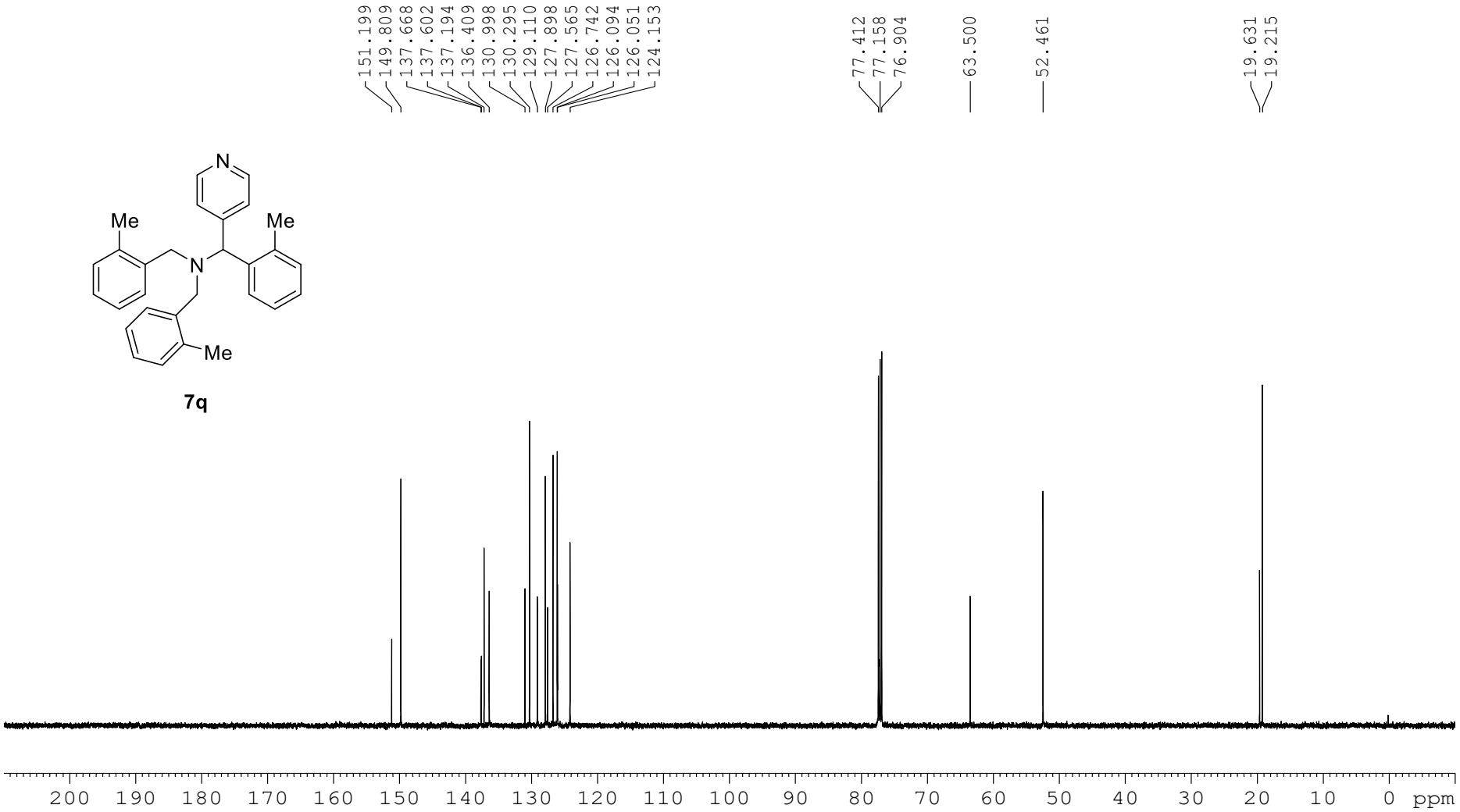

Figure S96. ^{13}C NMR spectra of **7q** ($CDCl_3$, 125M).

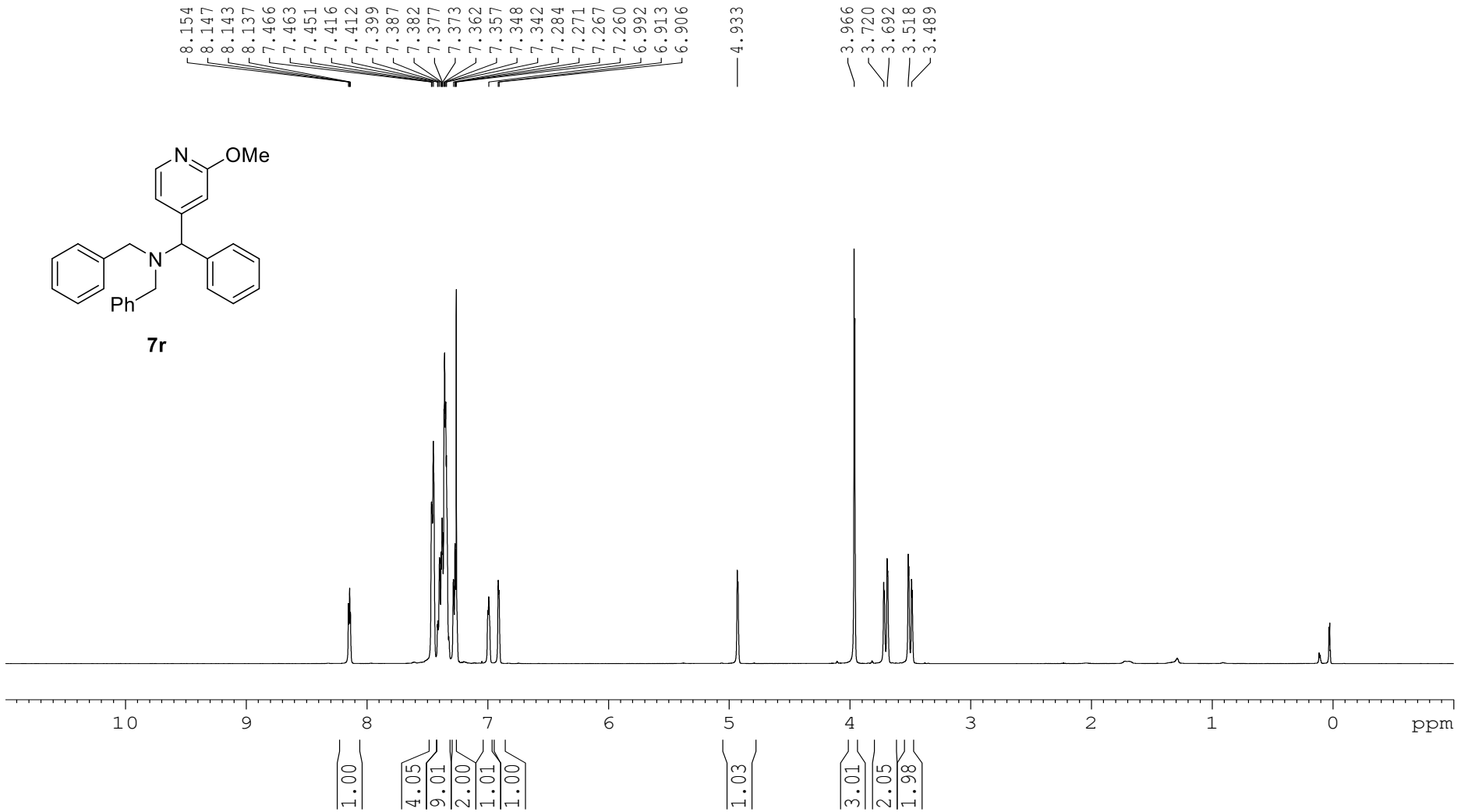

Figure S97. ^{1}H NMR spectra of **7r** ($CDCl_3$, 500M).

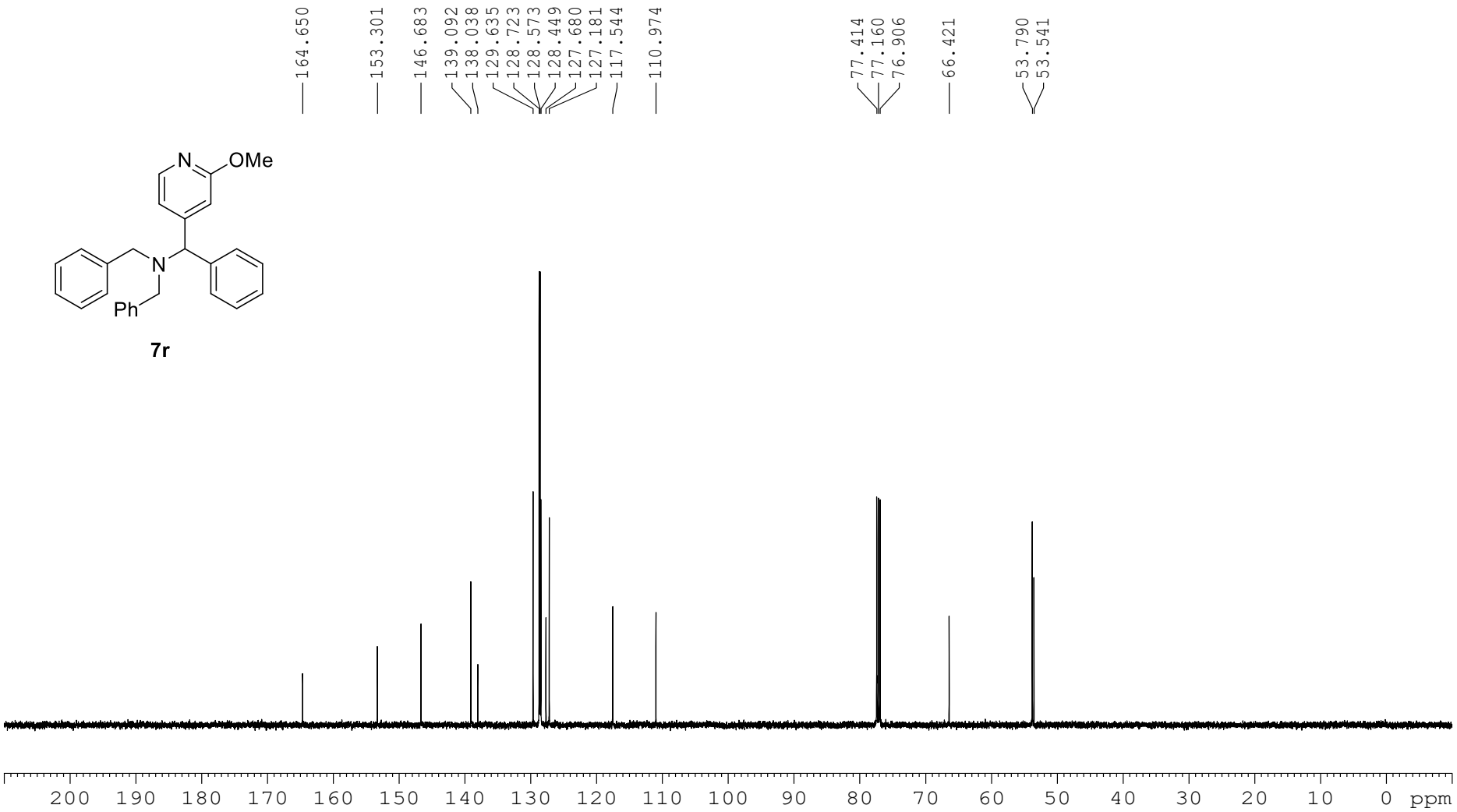

Figure S98. ^{13}C NMR spectra of **7r** ($CDCl_3$, 125M).

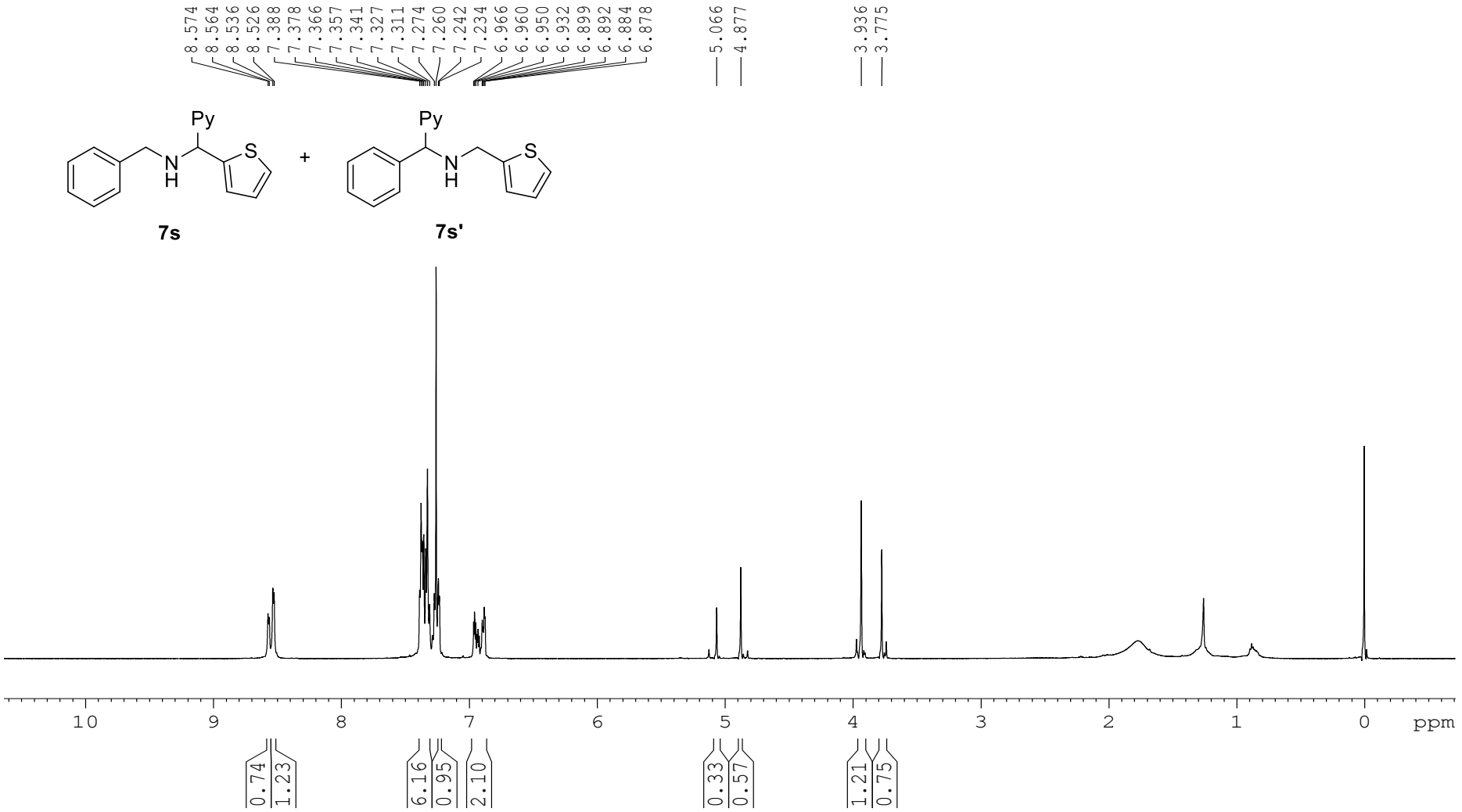

Figure S99. ^{1}H NMR spectra of **7s and 7s'** ($CDCl_3$, 500M).

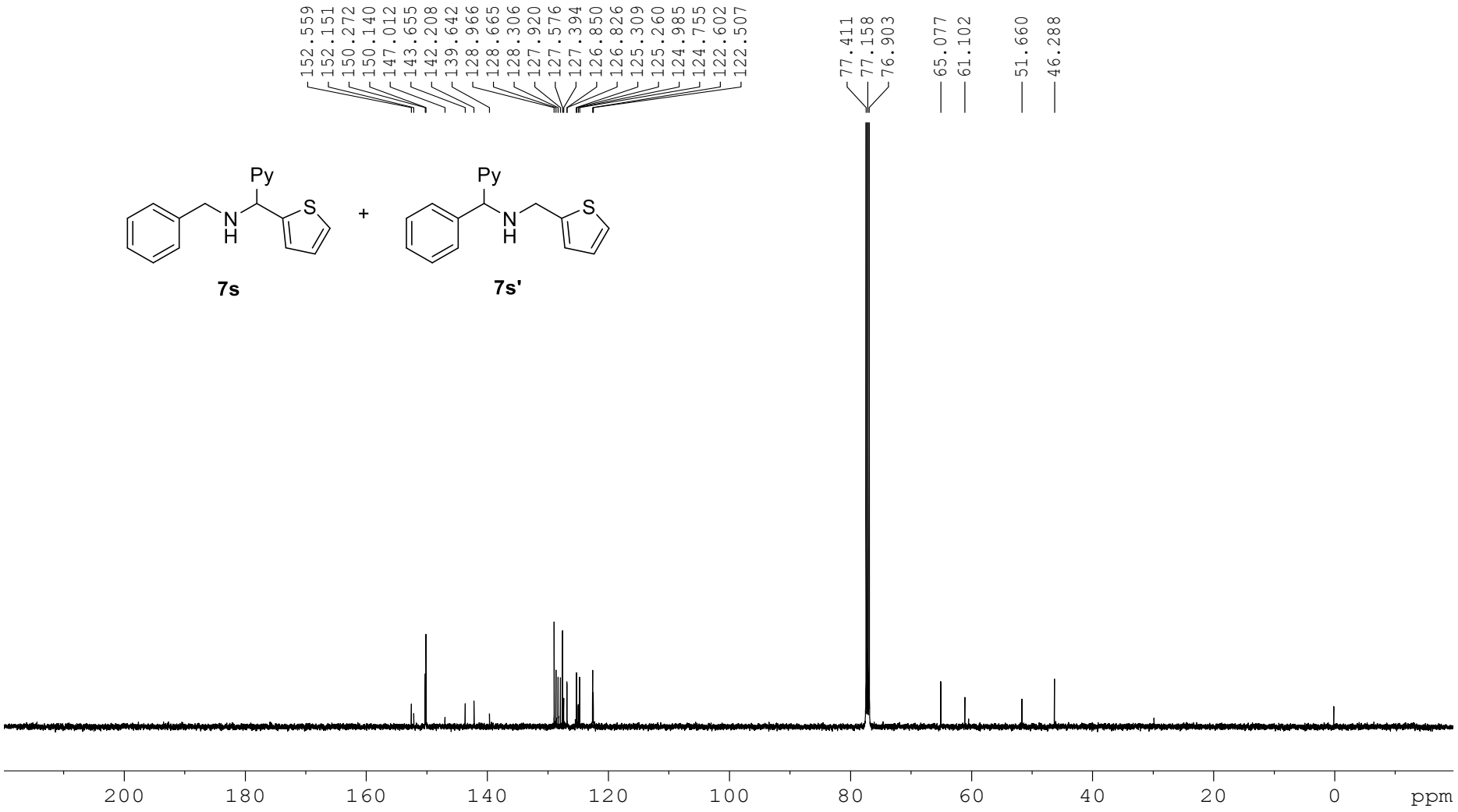

Figure S100. ^{13}C NMR spectra of **7s and 7s'** ($CDCl_3$, 125M).

Figure S101. ^{1}H NMR spectra of **7t and 7t'** ($CDCl_3$, 500M).

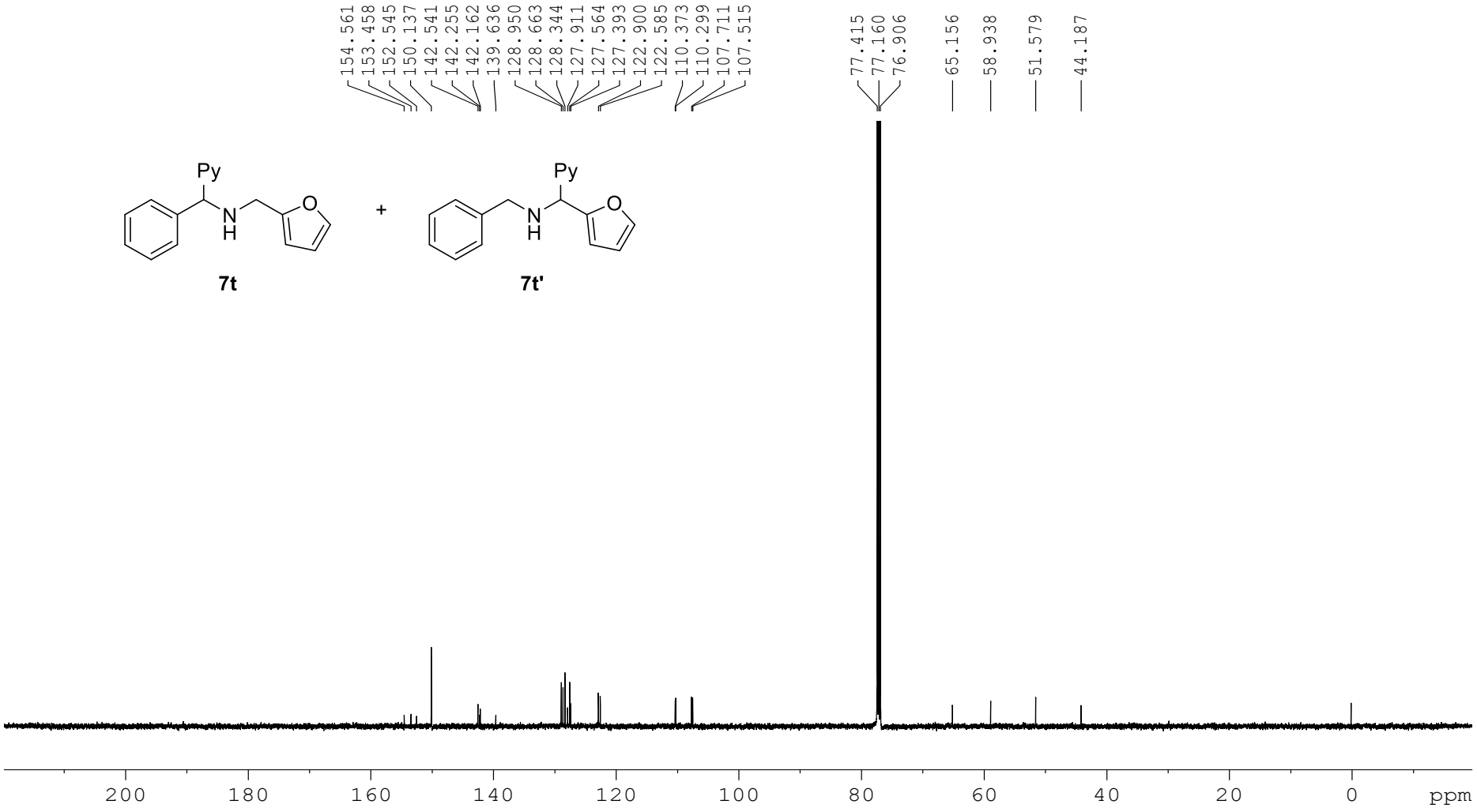

Figure S102. ^{13}C NMR spectra of **7t and 7t'** ($CDCl_3$, 125M).

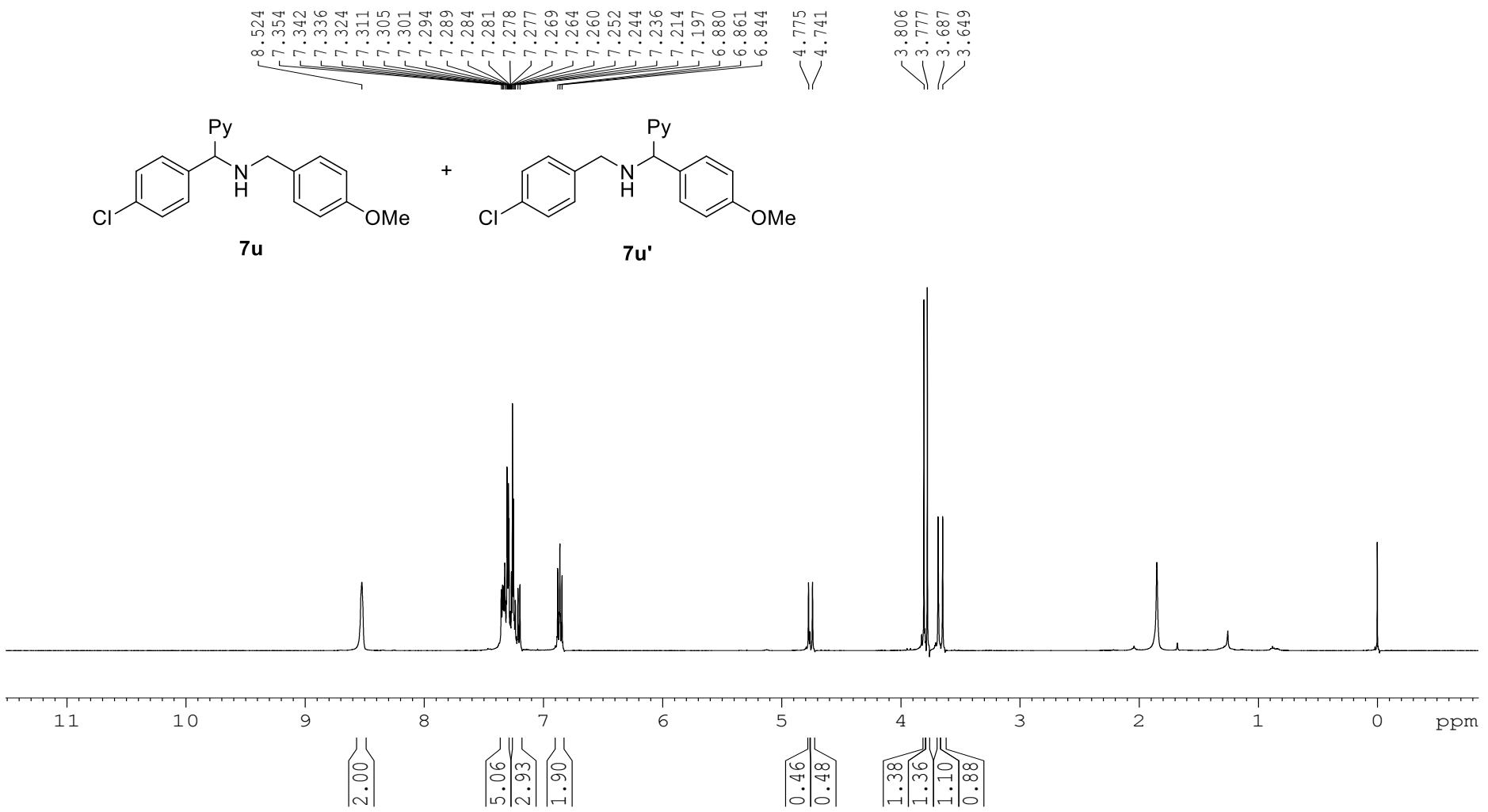

Figure S103. ^{1}H NMR spectra of **7u and 7u'** ($CDCl_3$, 500M).

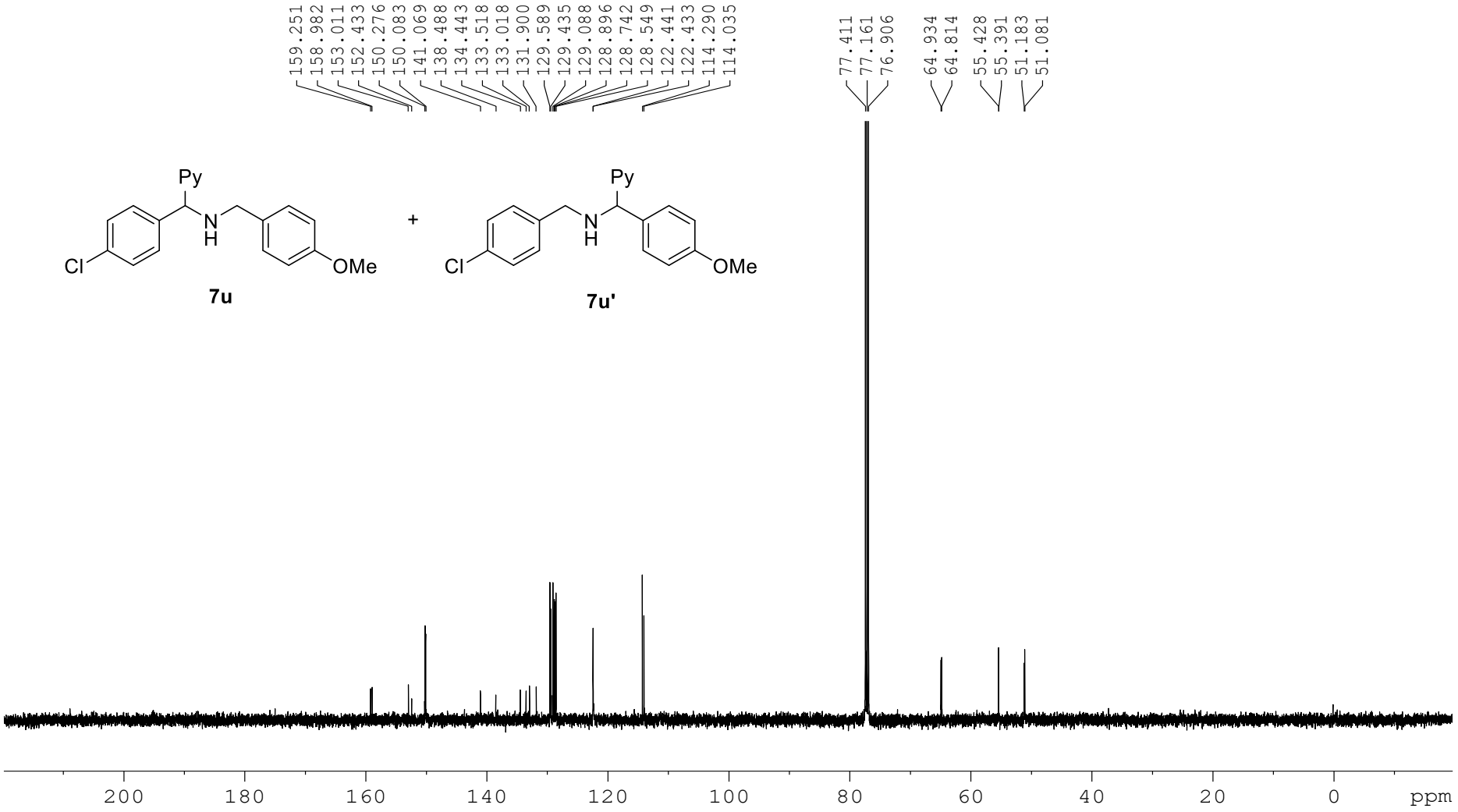

Figure S104. ^{13}C NMR spectra of **7u and 7u'** ($CDCl_3$, 125M).

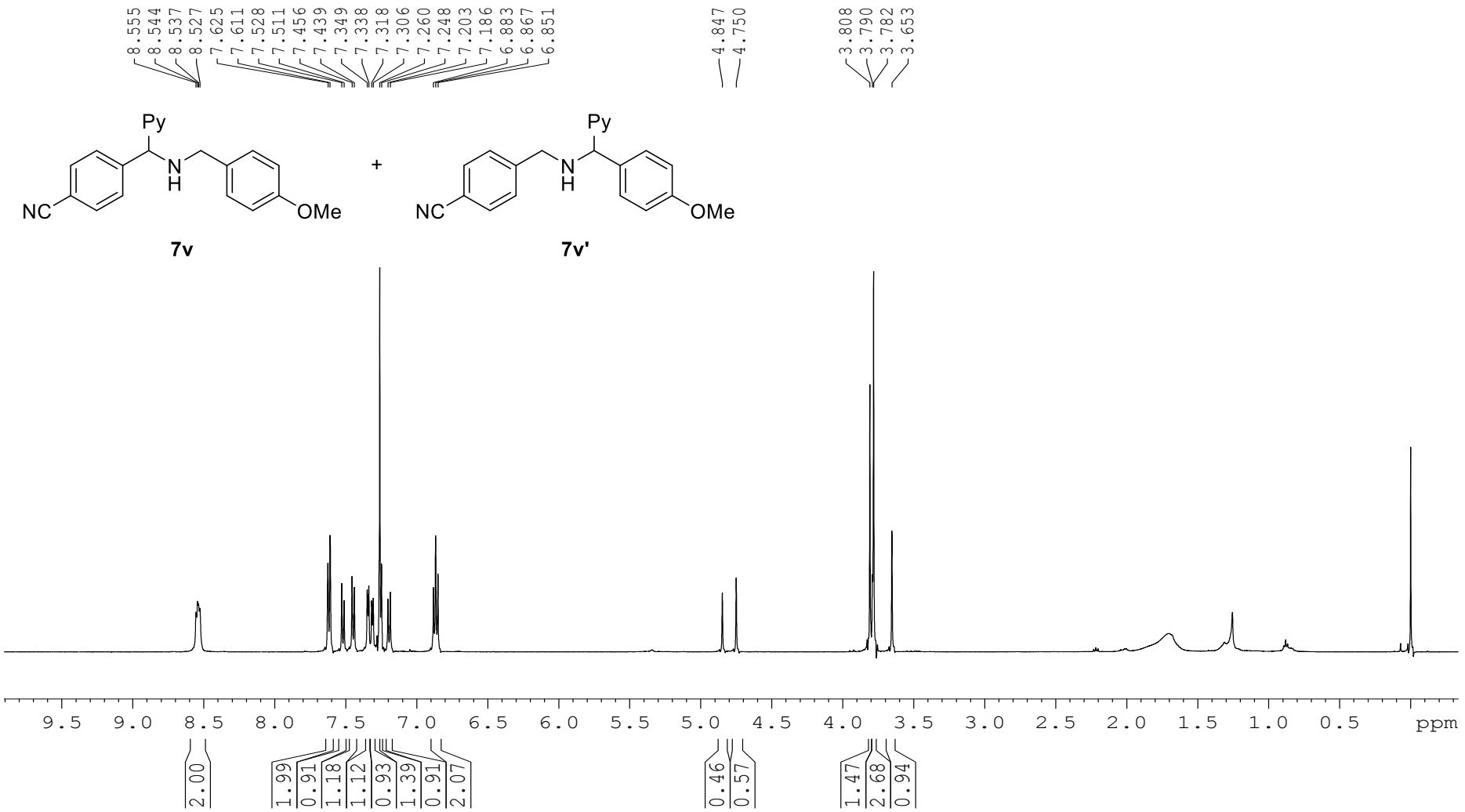

Figure S105. ^{1}H NMR spectra of **7v and 7v'** ($CDCl_3$, 500M).

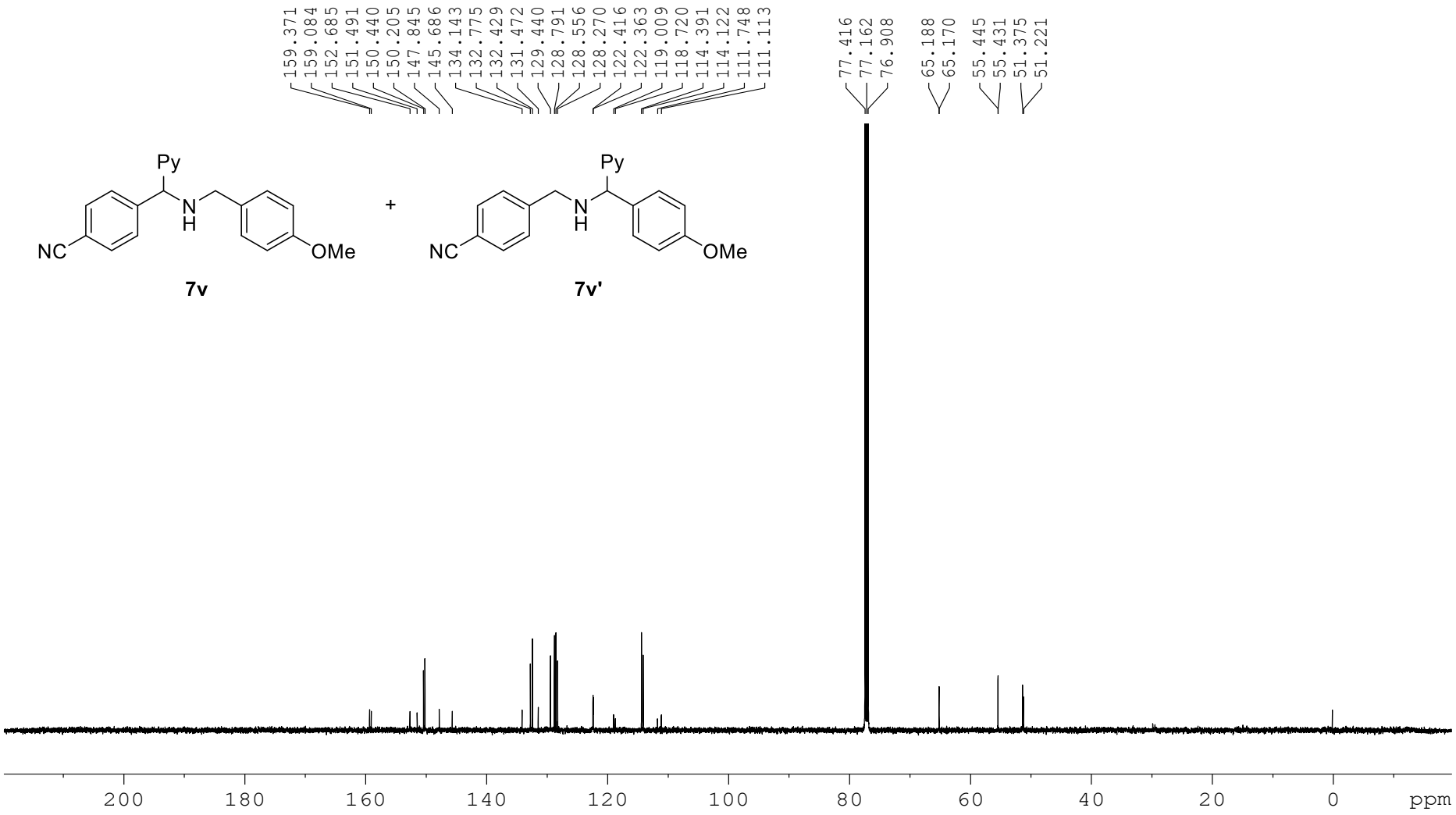

Figure S106. ^{13}C NMR spectra of **7v and 7v'** ($CDCl_3$, 125M).

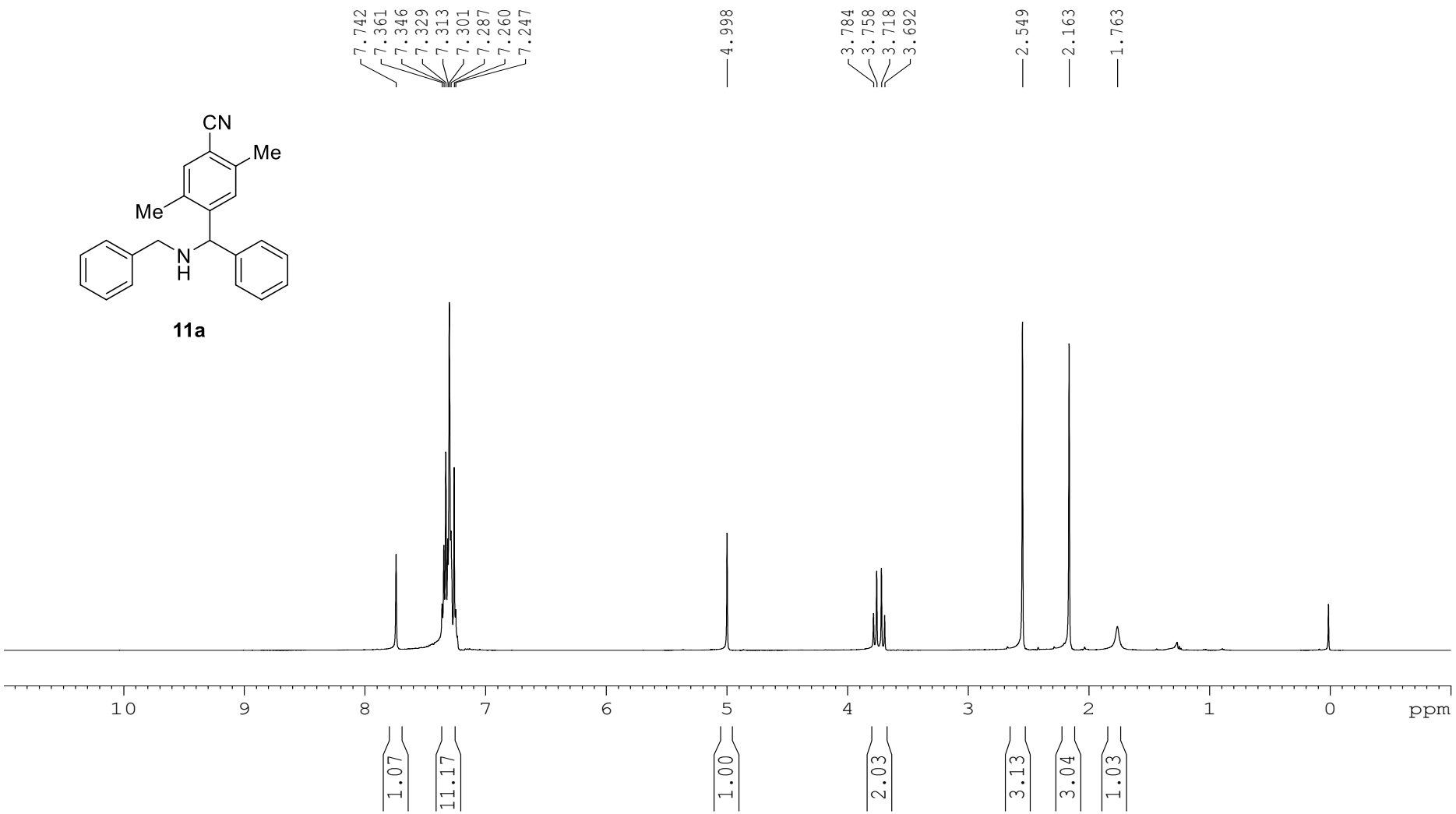

Figure S107. ^{1}H NMR spectra of **11a** ($CDCl_3$, 500M).

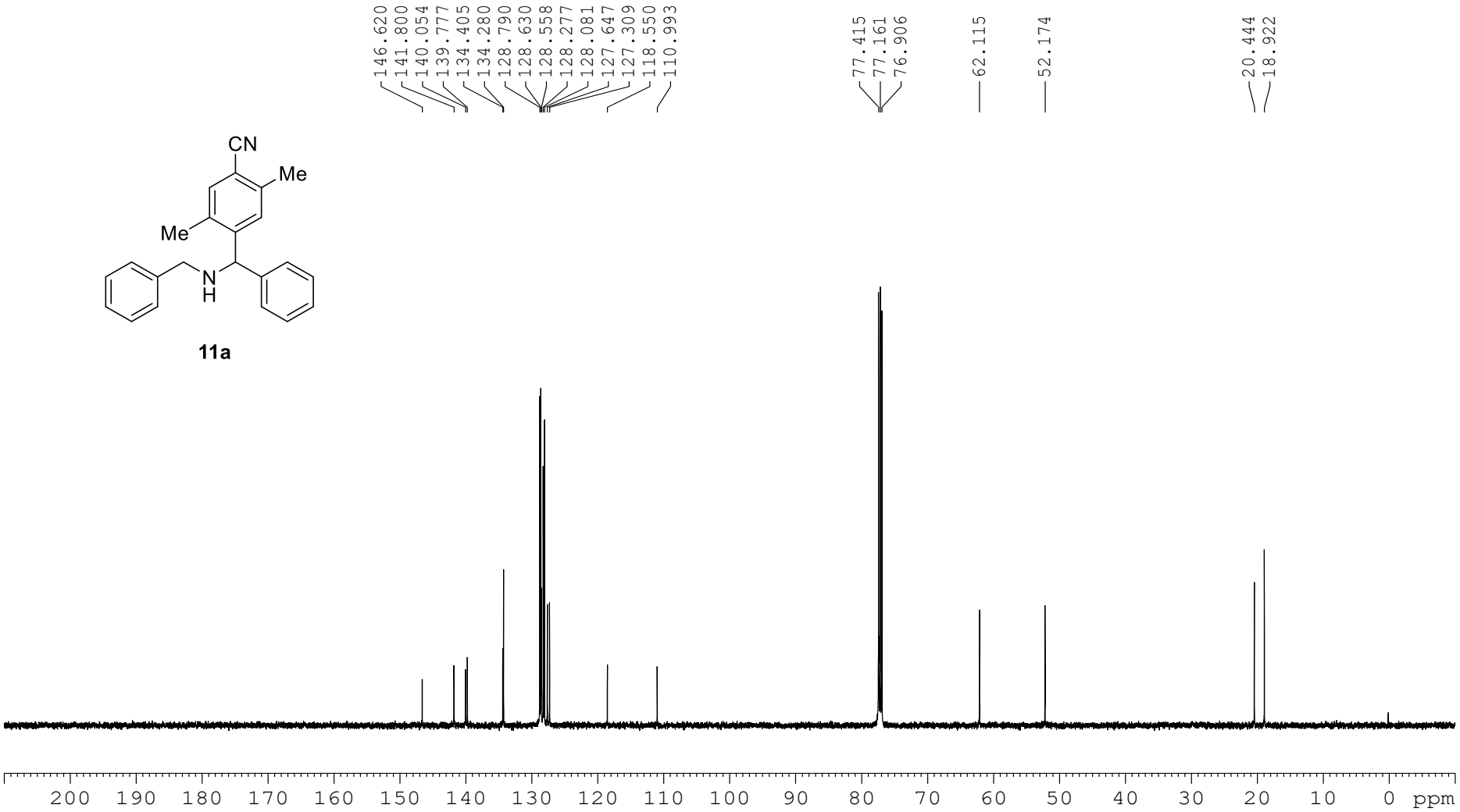

Figure S108. ^{13}C NMR spectra of **11a** ($CDCl_3$, 125M).

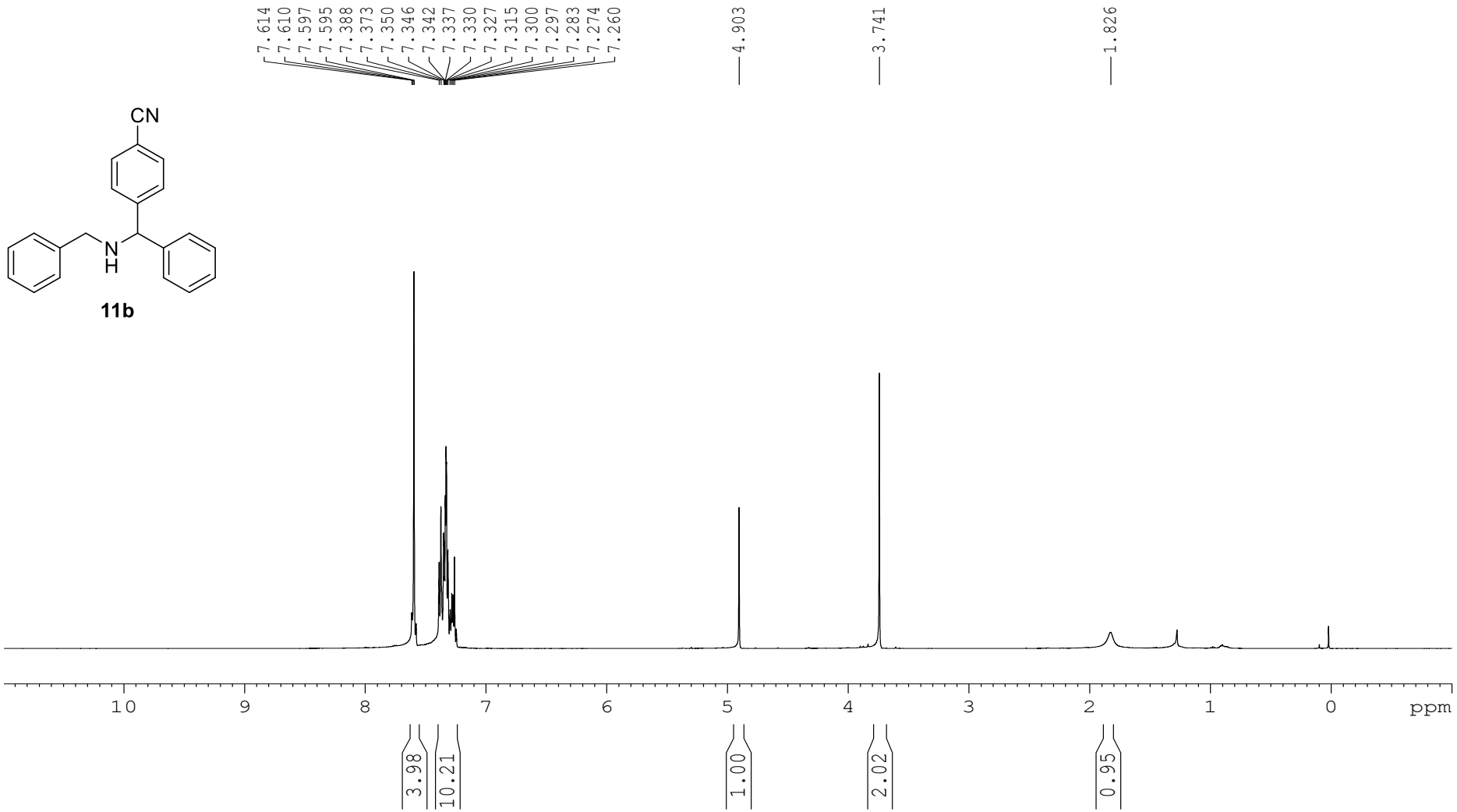

Figure S109. ^{1}H NMR spectra of **11b** ($CDCl_3$, 500M).

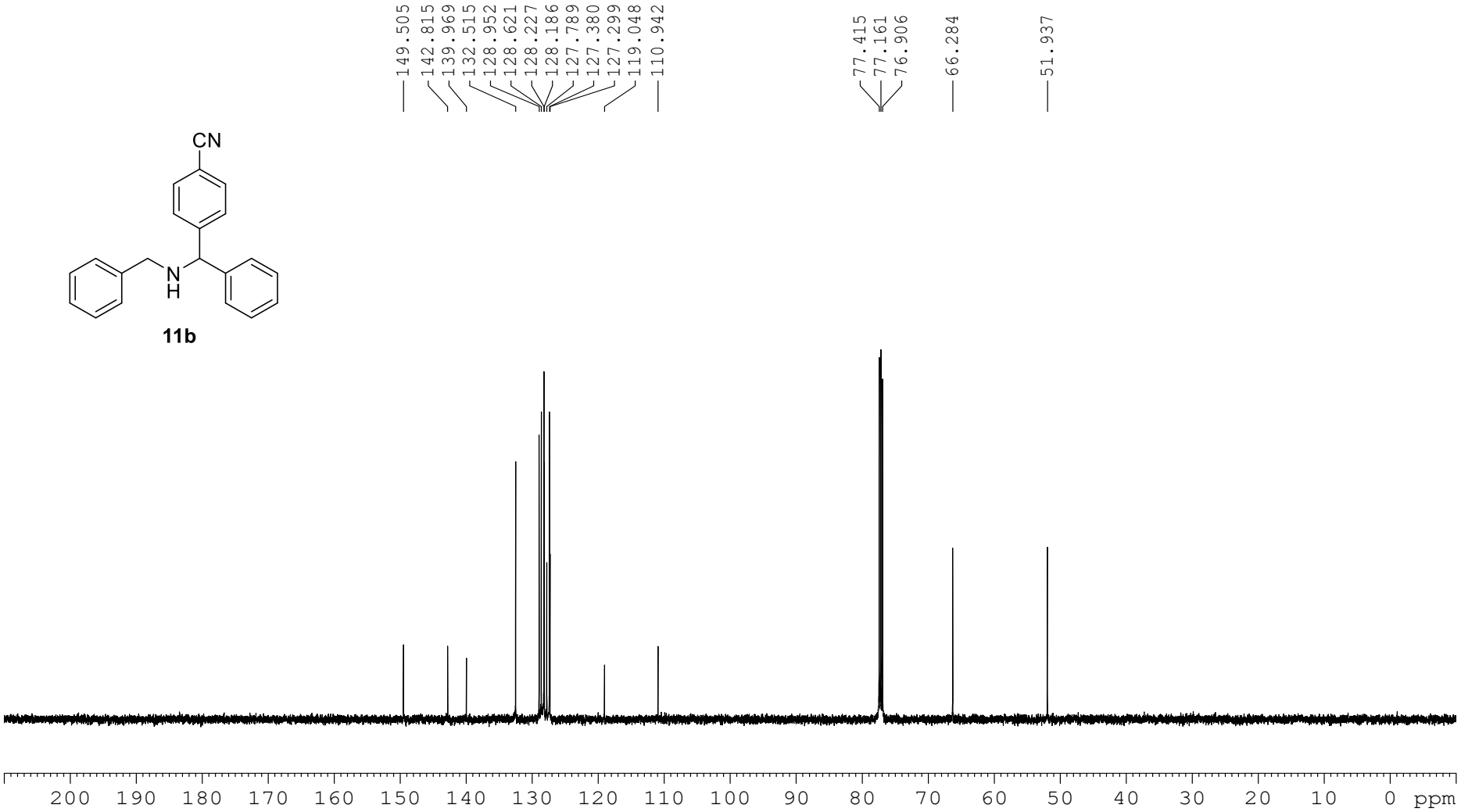

Figure S110. ^{13}C NMR spectra of **11b** ($CDCl_3$, 125M).

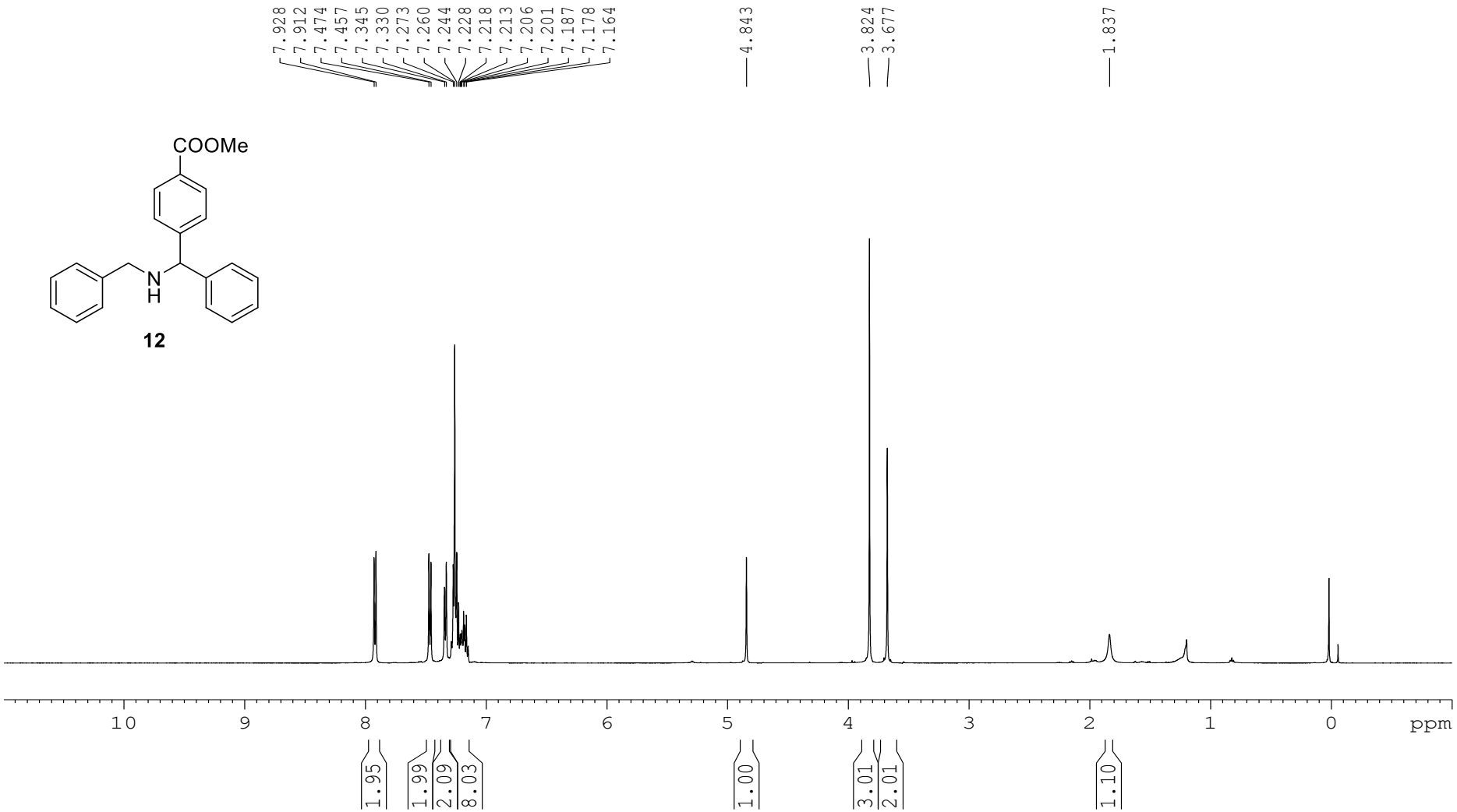

Figure S111. ^{1}H NMR spectra of **12** ($CDCl_3$, 500M).

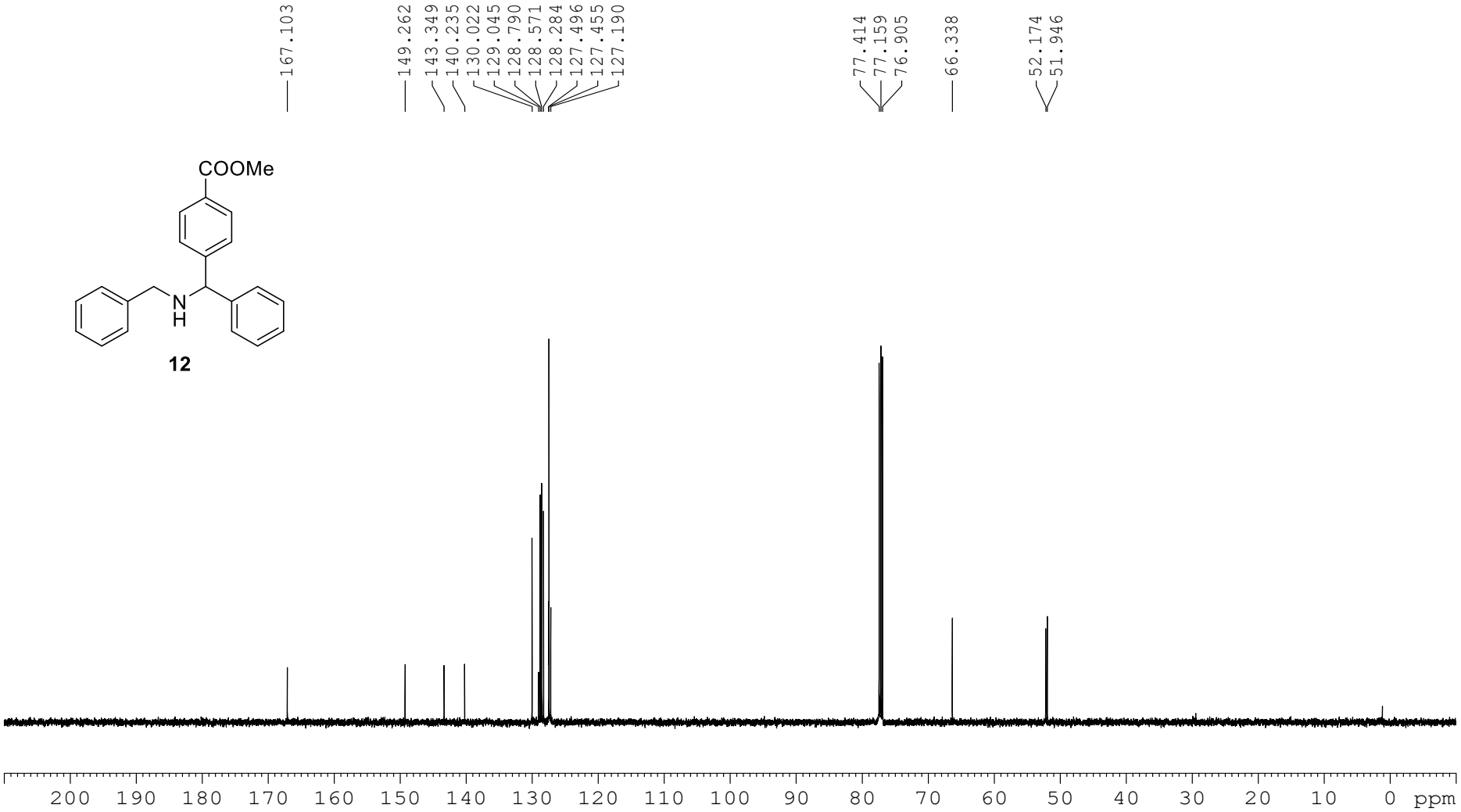

Figure S112. ^{13}C NMR spectra of **12** ($CDCl_3$, 125M).

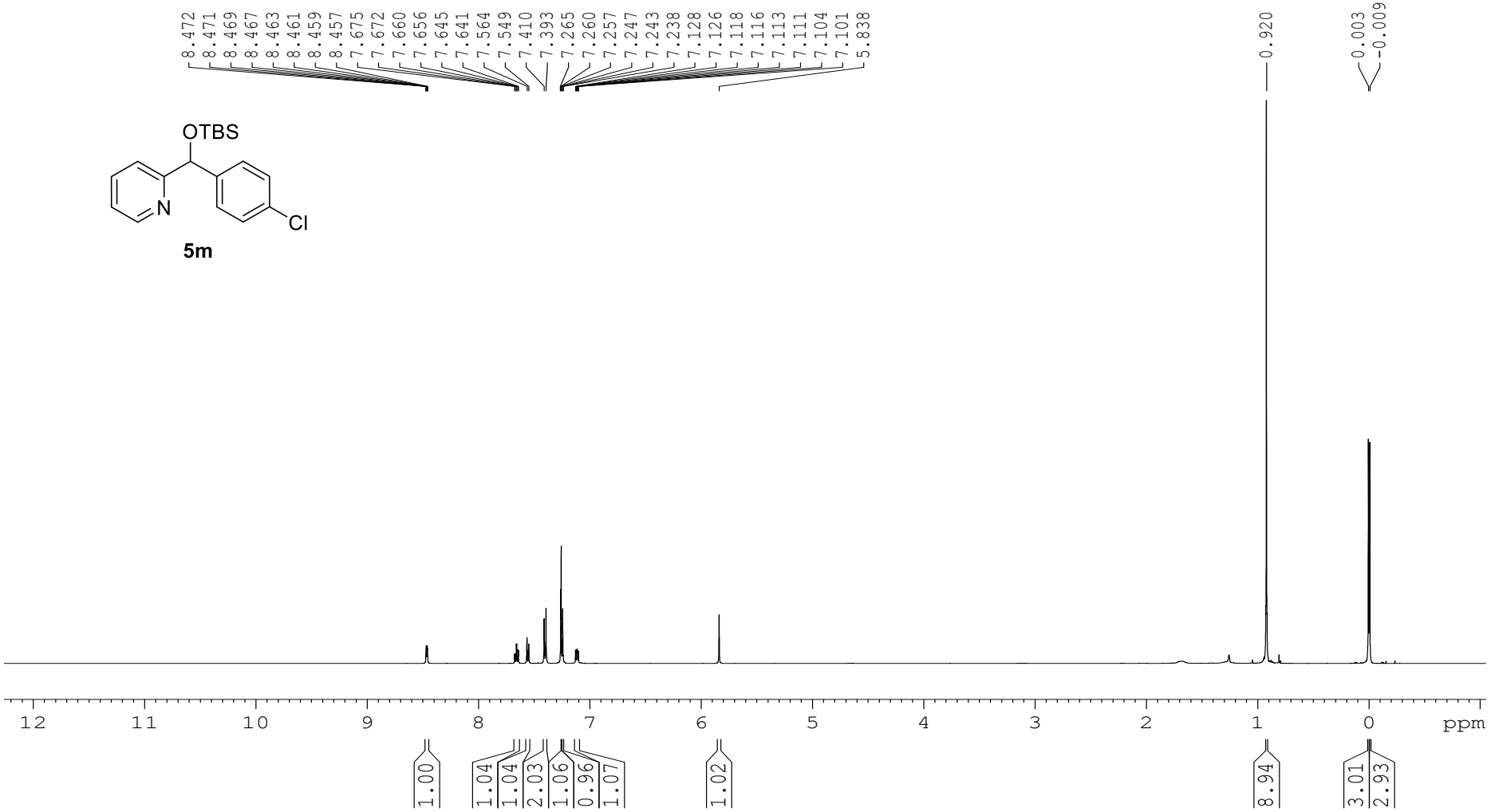

Figure S113. ^{1}H NMR spectra of **5m** ($CDCl_3$, 500M).

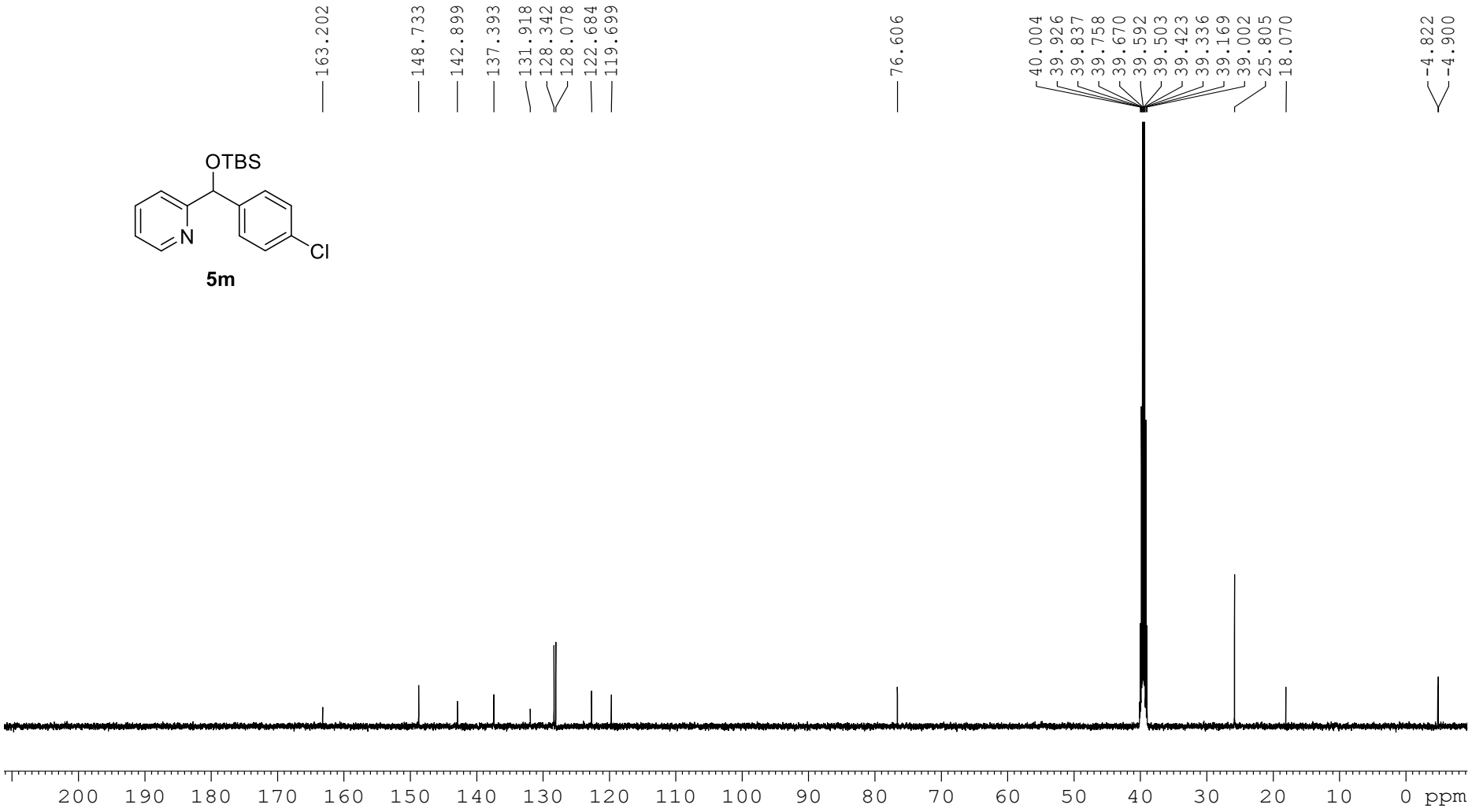

Figure S114. ^{13}C NMR spectra of **5m** (*d*-DMSO, 125M).

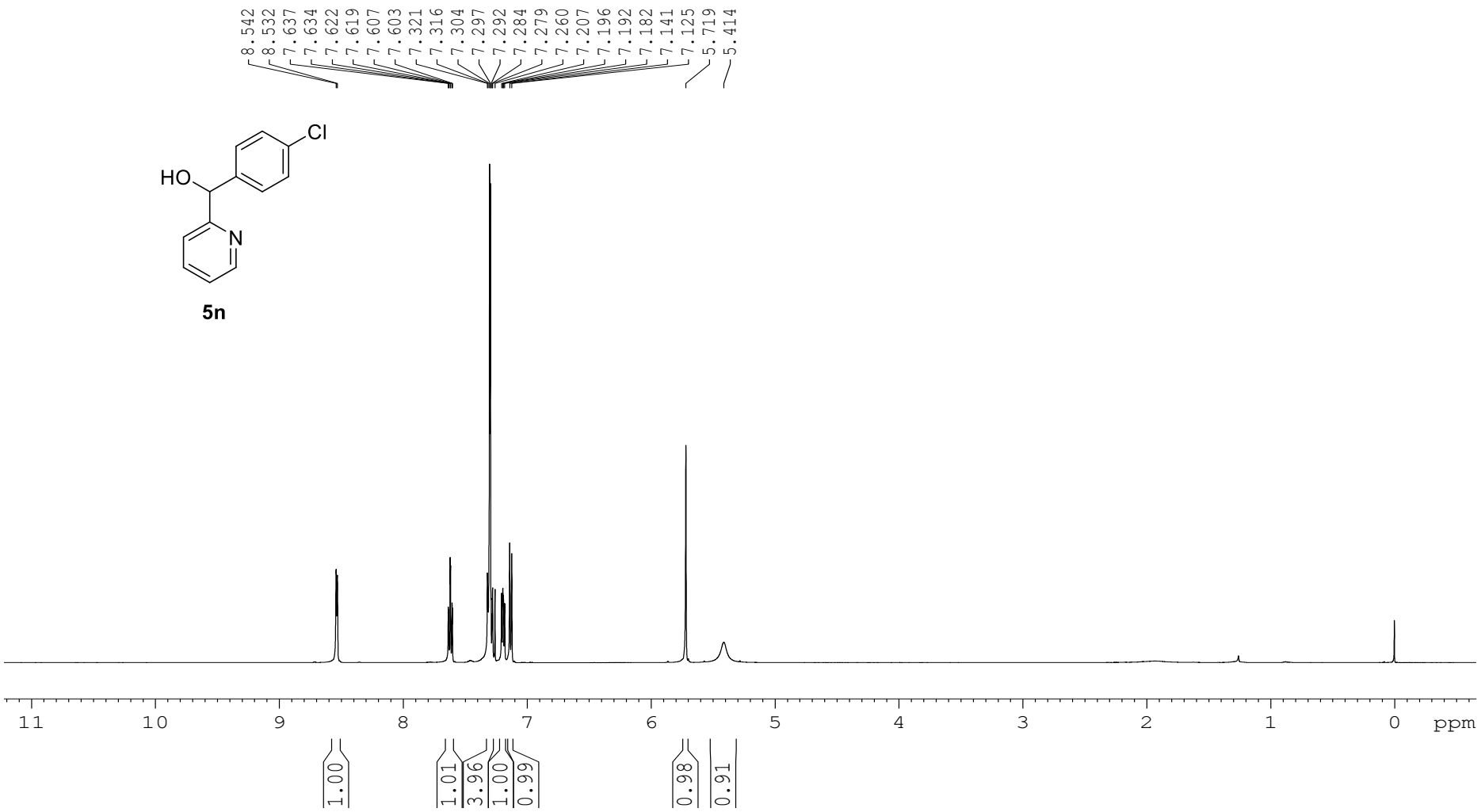

Figure S115. ^{1}H NMR spectra of **5n** ($CDCl_3$, 500M).

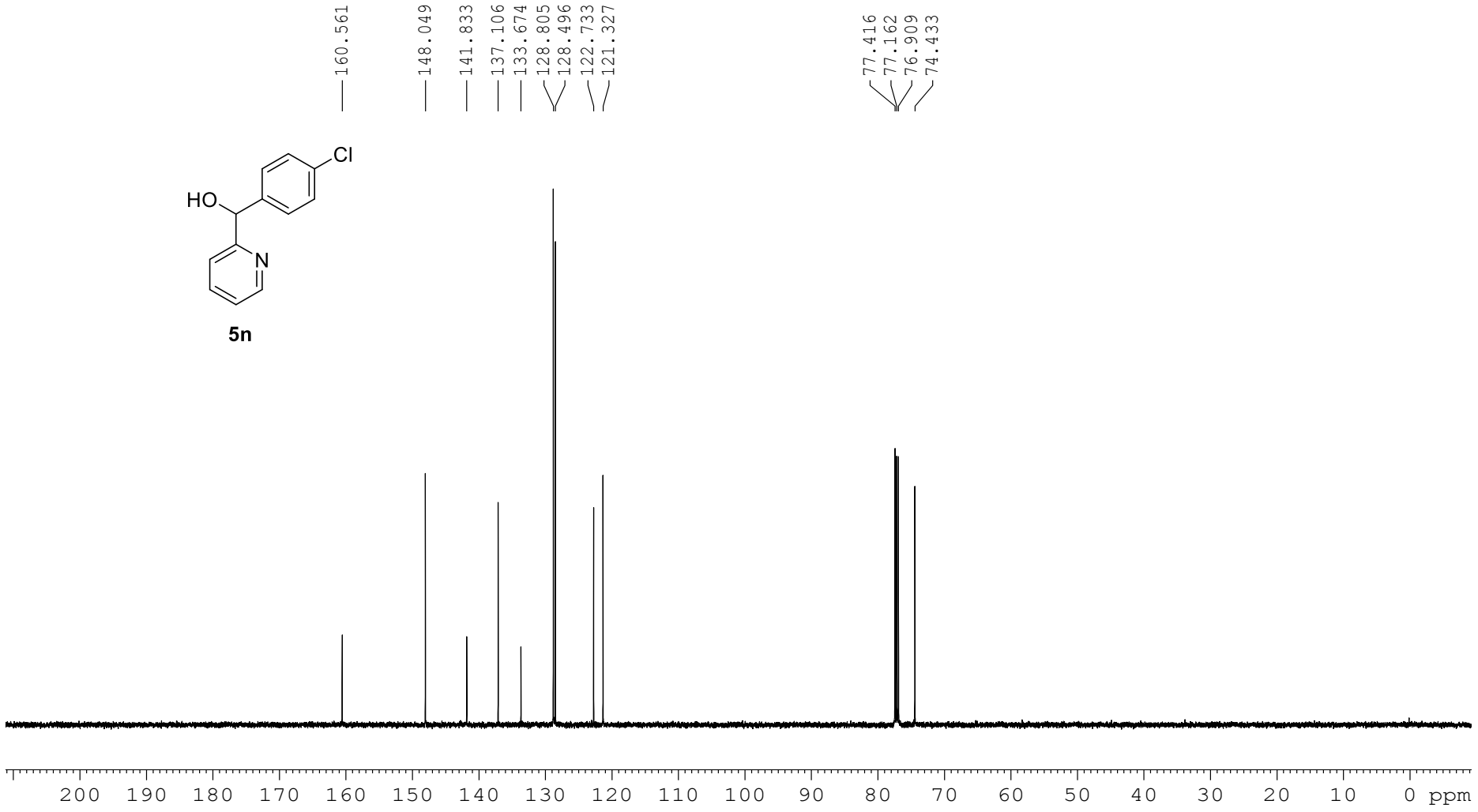

Figure S116. ^{13}C NMR spectra of **5n** ($CDCl_3$, 125M).

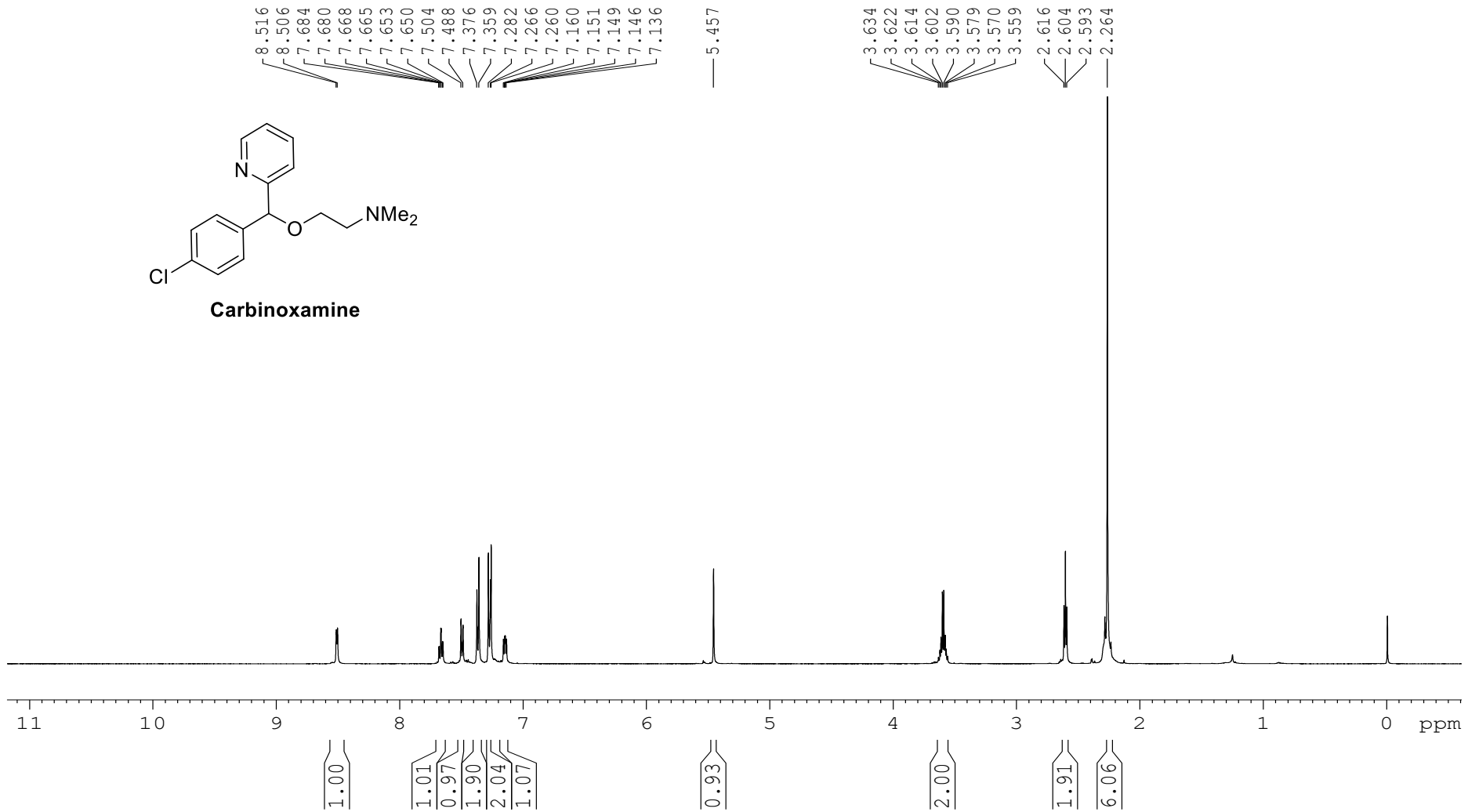

Figure S117. ^{1}H NMR spectra of **Carbinoxamine** ($CDCl_3$, 500M).

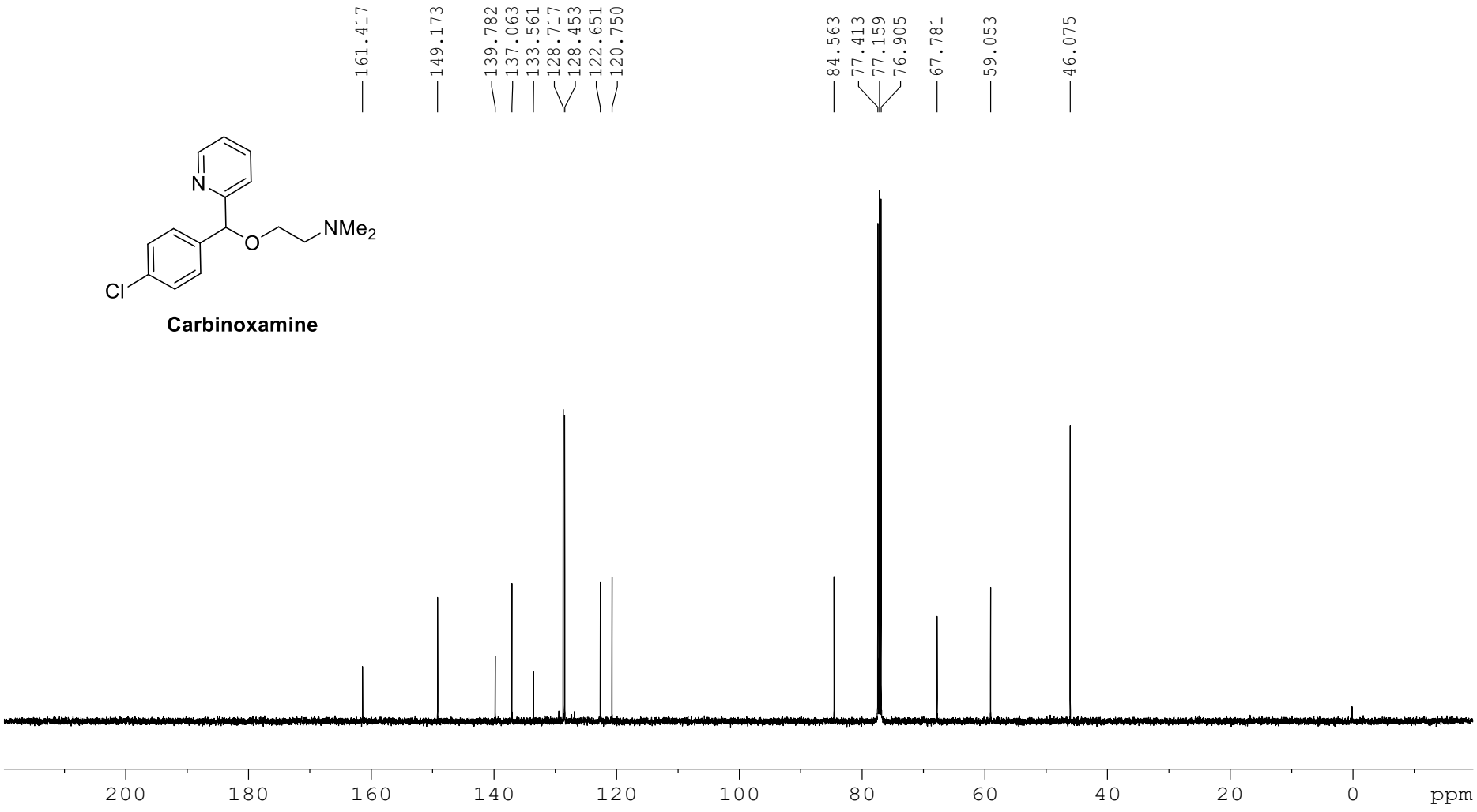

Figure S118. ^{13}C NMR spectra of **Carbinoxamine** ($CDCl_3$, 125M).