Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information for

N-Heterocyclic Carbene-Mediated Redox Condensation of Alcohols

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Experimental Section

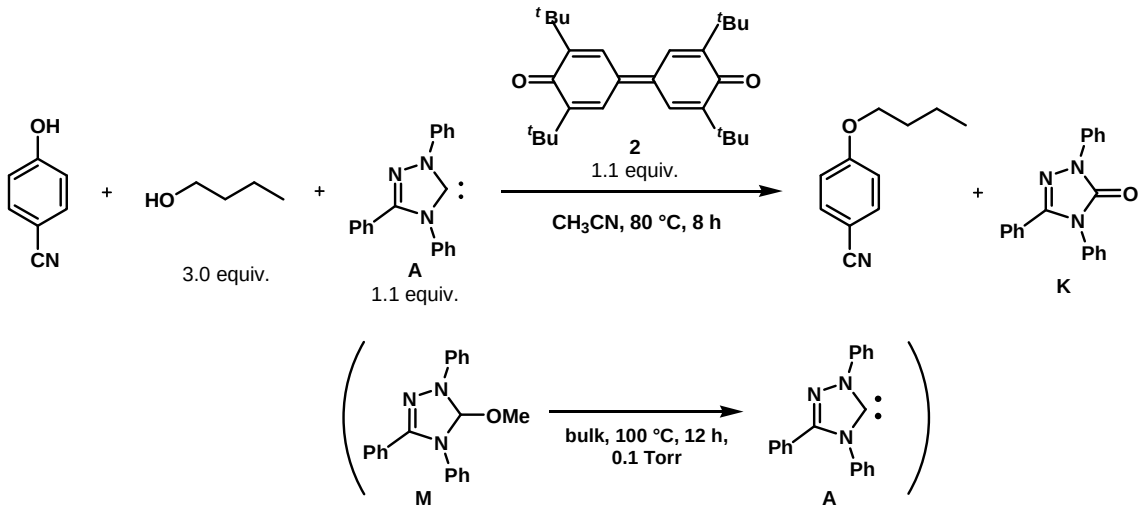
General

All reactions were performed under nitrogen atmosphere. NHC precursors were prepared according to the previous literatures (**A**,[1] **B**,[1] **C**,[2] **D**,[3] **E**,[4] **F**,[4] **G**,[4] **H**,[5] **I**,[6] **J**,[7] **M**[1]). 3',5,5'-Tetra-*t*-butyl-4,4'-diphenoquinone, **2,** was prepared according to the previous literature.[8] *n*-Butanol, phenethyl alcohol, *N*,*N*-diisopropylethylamine, and 1,2-dichloroethane were distilled from CaH_2 under reduced pressure. *t*-Butanol, isopropyl alcohol, 1,4-dioxane, 1,2-dimethoxyethane, toluene and acetonitrile were distilled from CaH_2. *m*-Cresol, benzyl alcohol and propionic acid were distilled under reduced pressure before use. Hydroquinone was purified by sublimation. Anhydrous tetrahydrofuran and ethanol were purchased from KANTO CHEMICAL CO., INC. (*R*)-(+)-1-Phenylethyl alcohol was purchased from Tokyo Chemical Industry Co., Ltd. and its optical purity was determined to be 95% by HPLC analysis (Chiralpak IA column, hexane: *i*-PrOH= 95: 5, 1.0 mL/min, 254 nm). Other reagents were used as received. Kugelrohr distillations were carried out under reduced pressure (2.0 mmHg) at 110 °C ~ 220 °C.

^1H and ^{13}C NMR spectra were recorded on Bruker Avance III HD (400 MHz for ^1H, 100 MHz for ^{13}C) NMR spectrometers. Chemical shift values in ^1H and ^{13}C NMR spectra are relative to the internal TMS standard (0.0 ppm for ^1H) or $CDCl_3$ resonance (77.16 ppm for ^{13}C). Electrospray ionization mass spectrometry (ESI-MS) was performed in methanol or acetonitrile solutions on a Waters Synapt G2 HDMS tandem quadrupole orthogonal acceleration time-of-flight instrument equipped with a Z-spray nanoelectrospray ionization source. Infrared spectra were obtained on a JASCO FT/IR-460 Plus spectrometer. Thin layer chromatography was performed on TLC Silica gel 60 F_{254} Merck KGaA. Microwave irradiation experiments were carried out in a Biotage Initiator microwave reactor. The reaction temperature was measured by a surface sensor. The enantiomeric excesses were determined by the HPLC analysis, which was performed on a JASCO UV-2089 intelligent pump (1.0 mL/min) equipped with a JASCO UV-2075 detector (254 nm) and a Daicel CHIRALPAK IA column (0.46 cm (i.d.) × 25 cm).

Experimental Procedure and Compound Characterization Data

The typical procedure for redox condensation of *n*-butanol with 4-cyanophenol mediated by NHC A and oxidant 2 (table 2, entry 5).

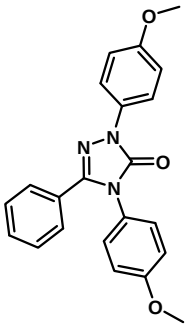


In a two-necked flask equipped with a three way stopcock, NHC precursor **M** (80 mg, 0.24 mmol) was heated at 100 °C for 12 h under 0.1 Torr to generate NHC **A**. To this flask, acetonitrile (0.6 mL), *n*-butanol (49 mg, 0.65 mmol), and 4-cyanophenol (26 mg, 0.22 mmol) were added. After stirring for a few mins at room temperature, 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone, **2,** (98 mg, 0.24 mmol) was added and the mixture was heated at 80 °C for 8 h. The precipitated byproduct, **K**, was removed by filtration with hexane. The filtrate was subjected to silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.1) as the eluent to give 4-butoxybenzonitrile (35 mg, 0.20 mmol, transparent liquid) in 89% yield. For the ^{1}H and ^{13}C NMR data of 4-butoxybenzonitrile, see ref 9.

In the case of the purification of **K**, the crude reaction mixture was subjected to the silica gel column chromatography using dichloromethane (R_f = 0.6) as the eluent to give **K** (60 mg, 0.19 mmol, white solid) in 80% yield. For the ^{1}H and ^{13}C NMR data of **K**, see ref 10.

In the case of the purification of **L**, methanol (20 mL) was added to the reaction mixture and stirred for 5 min. The precipitate was collected by filtration and subjected to silica gel column chromatography using dichloromethane/methanol (100/ 0 to 30/1) as the eluent to give **L** (56 mg, 0.15 mmol, white solid) in 62% yield.

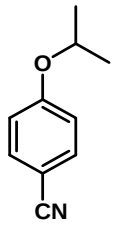
2,4-Bis(4-methoxyphenyl)-5-phenyl-3*H*-2,4-dihydro-1,2,4-triazol-3-one (L)



mp = 201.9-203.2 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.84 (s, 6H, -OCH_3), 6.95 (d, 2H, *J* = 9.0 Hz, *Ph*), 6.98 (d, 2H, *J* = 9.2 Hz, *Ar*), 7.21 (d, 2H, *J* = 9.3 Hz, *Ar*), 7.30-7.33 (m,2H, *Ar*), 7.36-7.43 (m, 3H, *Ar*), 7.98 (d, 2H, *J*= 9.3 Hz, *Ar*), ^{13}C NMR (100 MHz, $CDCl_3$); δ: 55.6, 55.7, 114.3, 114.9, 120.8, 126.4, 126.6, 128.1, 128.7, 128.8, 130.3, 131.4, 145.1, 152.2, 157.5, 159.8. HRMS (ESI) *m*/*z*: calcd for $C_{22}H_{19}N_3O_3$ $[M+Na]^+$ 396.1324, found 396.1311. IR (KBr, cm^{-1}): 3437, 3051, 2995, 2962, 2934, 2840, 1701, 1510, 1452, 1300, 1255, 1154, 1031, 831, 741.

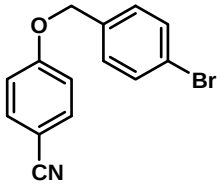
4-Isopropoxybenzonitrile



27 mg, 0.17 mmol, 76% isolated yield, transparent liquid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.1) as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.36 (d, 6H, *J* = 6.0 Hz, CH_3), 4.62 (sept, 1H, *J* = 6.0 Hz, C*H*), 6.91 (d, 2H, *J* = 8.9, *Ar*), 7.57 (d, 2H, *J* = 8.9, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 21.9, 70.5, 103.4, 116.1, 119.5, 134.1, 161.5. HRMS (ESI) *m*/*z*: calcd for $C_{10}H_{11}NO$ $[M+Na]^+$ 184.0733, found 184.0738. IR (NaCl, cm^{-1}): 2963, 2224, 1605, 1506, 1260, 1103, 1260, 799, 702.

4-(4-Bromobenzyloxy)benzonitrile

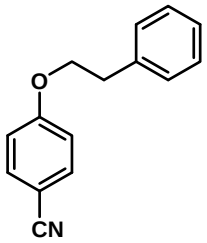


39 mg, 0.14 mmol, 61% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.

mp = 114.7-115.3 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 5.06 (s, 2H, C*H*$_2$), 6.99 (d, 2H, *J* = 8.8 Hz, *Ar*-CN), 7.28 (d, 2H, *J*= 8.2 Hz, *Ar*-Br), 7.53 (d, 2H, *J* = 8.2 Hz, *Ar*-Br), 7.59 (d, 2H, *J* = 8.8 Hz, *Ar*-CN). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 69.6, 104.5, 115.6, 119.2, 122.5, 129.2, 132.0, 134.2, 134.8, 161.7. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{10}BrNO$ $[M+Na]^+$ 309.9843, found 309.9859. IR (KBr, cm^{-1}): 2925, 2853, 2223, 1604, 1507, 1241, 1172, 1039, 1101, 835, 812.

4-Phenethyloxybenzonitrile



31mg, 0.14 mmol, 63% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/ 20, R_f = 0.1) as the eluent.

mp = 58.2-59.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 3.12 (t, 2H, *J* = 7.2 Hz, Ph-C*H*$_2$-), 4.21 (t, 2H, *J* = 7.2 Hz, -O-C*H*$_2$-), 6.93 (d, 2H, *J* = 8.8 Hz, *Ar*-CN), 7.24-7.35 (m, 5H, *Ph*), 7.57 (d, 2H, *J* = 8.8 Hz, *Ar*-CN). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 35.6, 69.1, 104.0, 115.3, 119.3, 126.8, 128.7, 129.1, 134.1, 137.6, 162.2. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{13}NO$ $[M+Na]^+$ 246.0895, found 246.0900. IR (KBr, cm^{-1}): 3061, 3028, 2947, 2876, 2219, 1607, 1509, 1303, 1258, 1020, 836, 749, 698.

4-Benzyloxybenzonitrile[10]

36 mg, 0.17 mmol, 78% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.

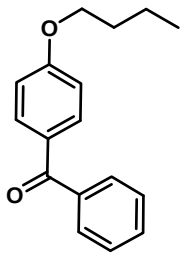
4-(Prop-2-en-1-yloxy)benzonitrile[10]

32 mg, 0.20 mmol, 93% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.

4-(Prop-2-yn-1-yloxy)benzonitrile[10]

15 mg, 0.09 mmol, 43% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.

4-Butoxybenzophenone

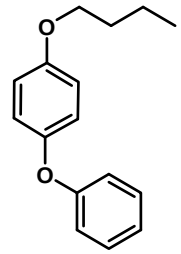


54 mg, 0.21 mmol, 96% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.

mp= 31.1-31.5 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, 3H, *J* = 7.6 Hz, -C*H*$_3$), 1.46-1.53 (m, 2H, -C*H*$_2$-CH$_3$), 1.76-1.83 (m, 2H, -O-CH$_2$-C*H*$_2$-), 4.04 (t, 2H, *J* = 6.6 Hz, -O-C*H*$_2$-), 6.94 (d, 2H, *J* = 8.8 Hz, *Ar*), 7.45-7.48 (m, 2H, *Ar*), 7.54-7.58 (m, 1H, *Ar*), 7.74 (d, 2H, *J* = 7.0 Hz, *Ar*), 7.81 (d, 2H, *J* = 8.8 Hz, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 13.9, 19.3, 31.2, 68.0, 114.1, 128.3, 129.8, 129.9, 131.9, 132.7, 138.4, 163.0, 195.7. HRMS (ESI) *m*/*z*: calcd for $C_{17}H_{18}O_2$ $[M+Na]^+$ 277.1205, found 277.1212. IR (KBr, cm^{-1}): 2955, 2933, 2873, 1643, 1603, 1576, 1308, 1290, 1252, 1177, 1150, 847, 693.

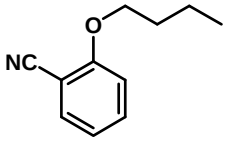
1-Butoxy-4-phenoxybenzene



30 mg, 0.12 mmol, 56% isolated yield, yellow liquid, purified by silica gel column chromatography using ethyl acetate/hexane (1/ 20, R_f = 0.5) as the eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, 3H, *J* = 7.3 Hz, -C*H*$_3$), 1.45-1.54 (m, 2H, -C*H*$_2$-CH$_3$), 1.73-1.80 (m, 2H, -O-CH$_2$-C*H*$_2$-), 3.94 (t, 2H, *J* = 6.5 Hz, -O-C*H*$_2$-), 6.86-7.05 (m, 7H, *Ar*), 7.27-7.31 (m, 2H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 14.0. 19.4, 31.5, 68.3, 115.6, 117.7, 121.0, 122.5, 129.7, 150.0, 155.6, 158.7. IR (NaCl, cm^{-1}): 3042, 2959, 2934, 2872, 1778, 1590, 1505, 1489, 1287, 1225, 1071, 869, 843, 750, 691.

2-Butoxybenzonitrile



16 mg, 0.09 mmol, 41% isolated yield, transparent liquid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.
^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.98 (t, 3H, *J* = 7.4 Hz, -C*H*$_3$), 1.49-1.58 (m, 2H, -C*H*$_2$-CH_3), 1.79-1.86 (m, 2H, -O-CH_2-C*H*$_2$-), 4.07 (t, 2H, *J* = 6.4 Hz, -O-C*H*$_2$-), 6.93-6.99 (m, 2H, *Ph*) 7.48-7.55 (m, 2H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 13.9, 19.3, 31.0, 68.8, 102.1, 112.3, 116.7, 120.6, 133.9, 134.4, 161.0. HRMS (ESI) *m*/*z*: calcd for $C_{11}H_{13}NO$ $[M+Na]^+$ 198.0895, found 198.0891. IR (NaCl, cm^{-1}): 2960, 2874, 2227, 1599, 1579, 1494, 1471, 1451, 1289, 1260, 1165, 1110, 755.

4-Butoxybenzoic acid methyl ester[11]

38 mg, 0.18 mmol, 84% isolated yield, white solid, purified by silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent.

1-Bromo-4-butoxybenzene[12]

Purified by Kugelrohr distillation to give 34 mg of the crude mixture. The product 1-bromo-4-butoxybenzene (57% ^{1}H NMR yield) and the unreacted 4-bromophenol (15%) were obtained.

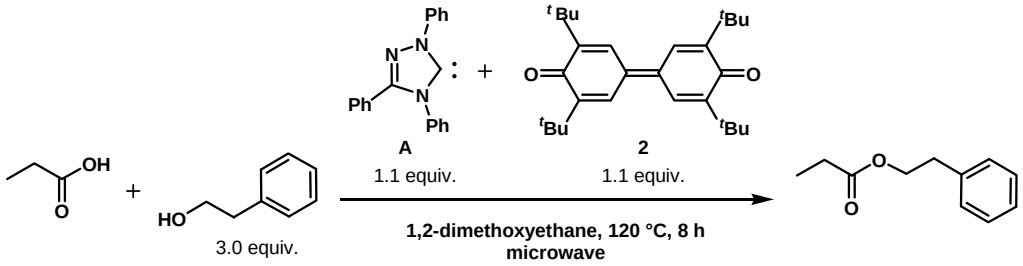
1-Butoxy-4-methoxybenzene[13]

13 mg, 0.07 mmol, 33% isolated yield, transparent liquid, purified by Kugelrohr distillation.

1-Butoxy-3-methylbenzene[14]

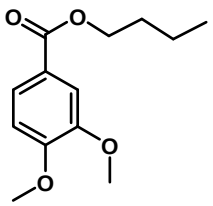
Purified by Kugelrohr distillation to give 18 mg of the crude mixture. The product 1-butoxy-3-methylbenzene (24% ^{1}H NMR yield) and unreacted *m*-cresol (38%) were obtained.

Esterification of propionic acid with 2-phenylethyl alcohol mediated by NHC and 2 (Scheme 2).



In a two-necked flask equipped with a three way stopcock, NHC **A** (72 mg, 0.24 mmol), 1,2-dimethoxyethane (0.6 mL), and 2-phenylethyl alcohol (79 mg, 0.65 mmol) were added. After stirring for a few mins at room temperature, the mixture was transferred by a microsyringe into a 2.0 mL microwave vial. To this vial, propionic acid (16 mg, 0.22 mmol) and 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone, **2,** (98 mg, 0.24 mmol) were added. The vial was then sealed and heated with microwave irradiation at 120 °C for 8 h. Ethyl acetate (20 mL) and hexane (20 mL) were added to the reaction mixture and washed with water. The organic layer was dried over $MgSO_4$, followed by filtration and concentration. The Kugelrohr distillation gave propionic acid 2-phenylethyl ester (25 mg, 0.14 mmol, transparent liquid) in 66% yield. For the ^1H and ^{13}C NMR data of propionic acid 2-phenylethyl ester, see ref 15.

3,4-Dimethoxybenzoic acid butyl ester



32 mg, 0.13 mmol, 62% isolated yield, transparent liquid, purified by Kugelrohr distillation. ^1H NMR (400 MHz, $CDCl_3$) δ: 0.97 (t, 3H, *J* = 7.4 Hz, -CH_2-C*H*$_3$), 1.42-1.51 (m, 2H, -C*H*$_2$-CH_3), 1.71-1.78 (m, 2H, -O-CH_2-C*H*$_2$-), 3.93 (s, 6H, -OC*H*$_3$) , 4.30 (t, 2H, *J* = 6.6 Hz, -O-C*H*$_2$-), 6.88 (d, 1H, *J* = 8.4 Hz, *Ar*), 7.54 (d, 1H, *J* = 2.0 Hz, *Ar*), 7.68 (dd, 1H, *J* = 2.0 Hz, 8.4 Hz, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 30.9, 56.1, 64.8, 110.3, 112.0, 148.6, 152.9, 166.6. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{18}O_4$ $[M+Na]^+$ 261.1103, found 261.1101. IR (NaCl, cm^{-1}): 2959, 2873, 2839, 1711, 1601, 1515, 1465, 1417, 1291, 1272, 1223, 1177, 1026, 765.

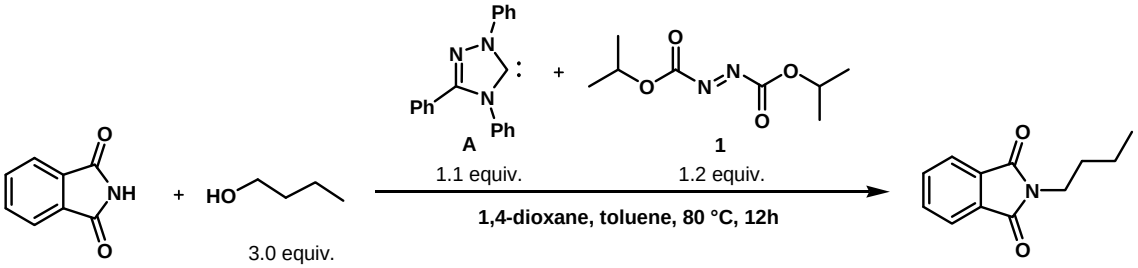
Benzoic acid butyl ester[16]

20 mg, 0.11 mmol, 52% isolated yield, transparent liquid, purified by Kugelrohr distillation.

4-Cyanobenzoic acid ethyl ester[17]

14 mg, 0.08 mmol, 38% isolated yield, transparent liquid, purified by Kugelrohr distillation.

***N*-Alkylation of phthalimide mediated by NHC A and oxidant 1 (Scheme 3).**



In a two-necked flask equipped with a three way stopcock, NHC **A** (72 mg, 0.24 mmol), 1,4-dioxane (0.46 mL) , phthalimide (32 mg, 0.22 mmol), and *n*-butanol (49 mg, 0.65 mmol), diisopropyl azodicarboxylate (0.14 mL, 1.9 mol/L in toluene, 0.26 mmol) were added and stirred at 80 °C for 12 h. After the volatiles were removed under reduced pressure, the crude mixture was subjected to silica gel column chromatography using dichloromethane (R_f= 0.6) as the eluent to give *N*-butylphthalimide (33 mg, 0.16 mmol, pale yellow liquid) in 76% isolated yield. For the ^{1}H and ^{13}C NMR data of *N*-butyl phthalimide, see ref 18.

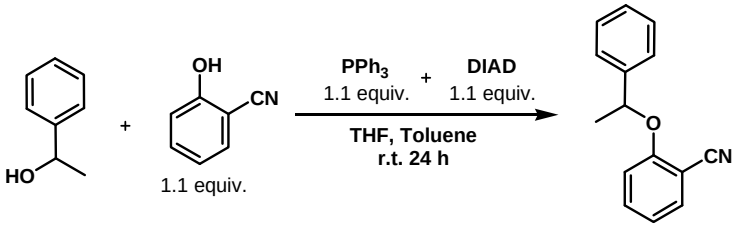
***N*-Benzylphthalimide**[18]

41 mg, 0.17 mmol. 79% isolated yield, white solid, purified by silica gel column chromatography using dichloromethane (R_f = 0.5) as the eluent.

***N*-Isopropylphthalimide**[18]

26 mg, 0.14 mmol, 63% isolated yield, purified by silica gel column chromatography using dichloromethane (R_f = 0.6) as the eluent.

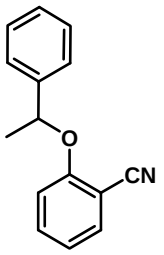
Condensation of 1-phenylethyl alcohol with 2-cyanophenol mediated by PPh_3 and DIAD 1. The absolute configuration was assigned by the model compounds prepared by the Mitsunobu reaction.



In a two-necked flask equipped with a three way stopcock, triphenylphosphine (0.22 g, 0.84 mmol), 2-cyanophenol (0.10 g, 0.84 mmol), (±)-1-phenylethyl alcohol (86 mg, 0.70 mmol), and tetrahydrofuran (0.5 mL) were added. Diisopropyl azodicarboxylate (0.44 mL, 1.9 mol/L in toluene, 0.84 mmol) was added dropwise at 0 °C and stirred at room temperature for 24 h. The reaction mixture was subjected to silica gel column chromatography using ethyl acetate/hexnane (1/5, R_f= 0.6) to give 2-(1-phenylethoxy)benzonitrile (78 mg, 0.35 mmol, transparent liquid) in 50% yield. HPLC analysis of the product showed the two peaks assignable to the isomers at retention times of 12.1 min and 12.8 min.

The same procedure was performed using (*R*)-(+)-1-phenylethyl alcohol (95% ee) in place of (±)-1-phenylethyl alcohol. The product (0.10 g, 0.45 mmol, transparent liquid) was obtained in 64% yield and was subjected to the HPLC analysis. A major peak detected at a retention time of 13.0 min was identified as (*S*)-2-(1-Phenylethoxy)benzonitrile (80% ee). HPLC analysis: Chiralpak IA column, hexane/*i*-PrOH (99/1), R_t = 12.2 min (minor), R_t= 13.0 min (major).

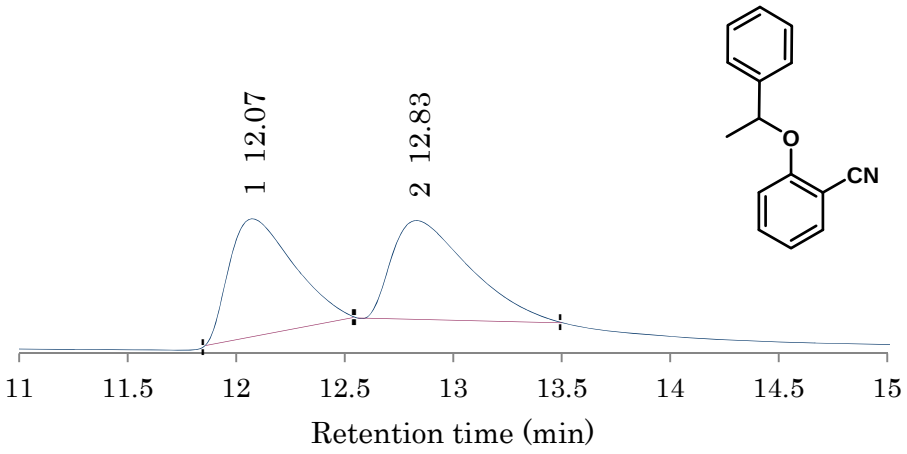
2-(1-Phenylethoxy)benzonitrile (racemic)



^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.70 (d, 3H, *J* = 6.4 Hz, -C*H*$_3$), 5.40 (q, 1H, *J* = 6.4 Hz, -C*H*-), 6.80 (d, 1H, *J* = 8.6 Hz, *Ar*), 6.91 (t, 1H, *J* = 7.6 Hz, *Ar*), 7.25-7.29 (m, 1H, *Ar*), 7.32-7.40 (m, 5H, *Ar*), 7.52-7.54 (m, 1H, *Ar*). ^{13}C NMR (100 MHz, $CDCl_3$); δ: 24.6, 77.6, 102.9, 114.3, 116.8, 120.8, 125.6, 128.0, 129.0, 133.9, 134.1, 141.9, 159.8. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{13}NO$ $[M+Na]^+$ 246.0895, found 246.0896. IR (NaCl, cm^{-1}): 3064, 3033, 2981, 2226, 1598, 1578, 1488, 1450, 1288, 1256, 1165, 1108, 1066, 932, 756, 701.

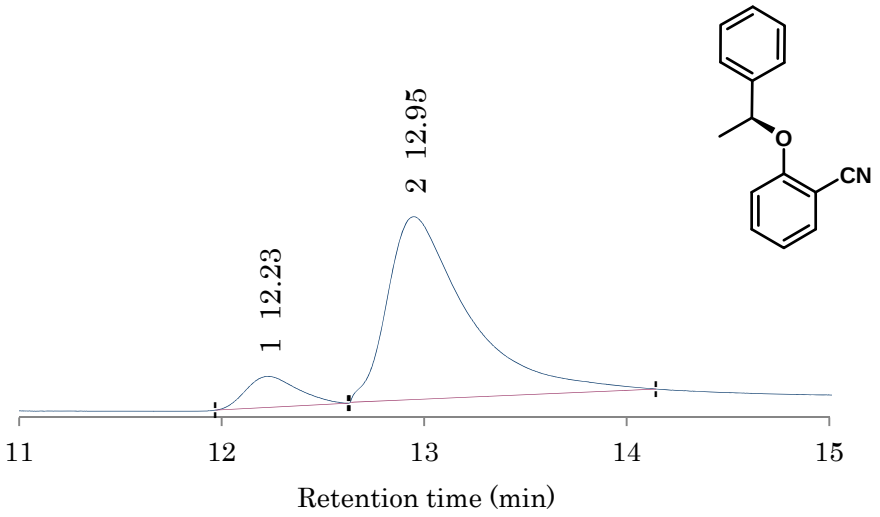
HPLC Charts of model compounds

2-(1-Phenylethoxy)benzonitrile (racemic)



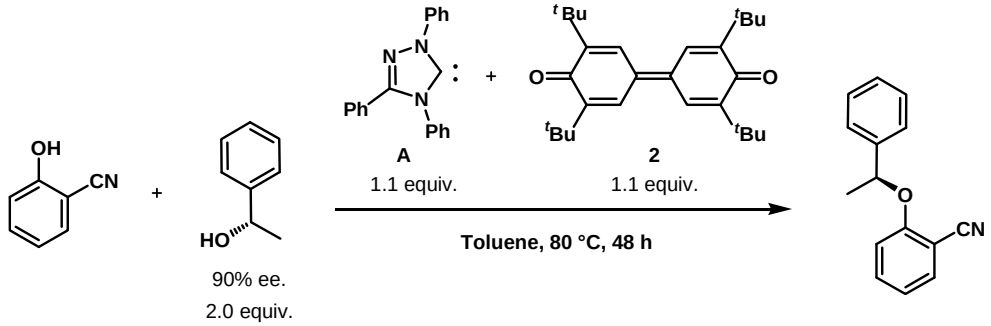
No.	Retention Time (min)	Area	Area %	Height
1	12.07	578764.8	49.60	28125
2	12.83	588212.2	50.40	23561
Total		1166977	100	51686

(*S*)-2-(1-Phenylethoxy)benzonitrile (80% ee)



No.	Retention Time (min)	Area	Area %	Height
1	12.23	21956	9.79	1232
2	12.95	202210.1	90.21	7265
Total		224166.1	100	8497

Condensation of (*R*)-(+)-1-phenylethyl alcohol with 2-cyanophenol mediated by NHC A and oxidant 2 (Scheme 4).



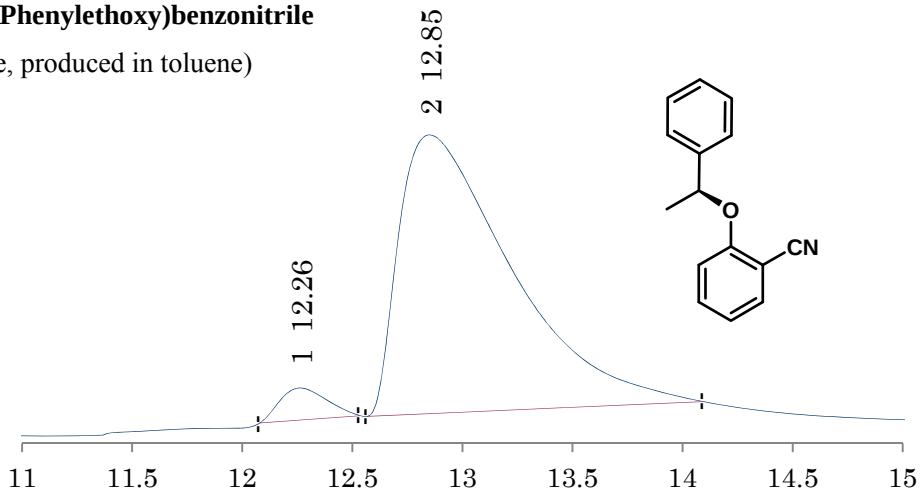
In a two-necked flask equipped with a three way stopcock, NHC **A** (72 mg, 0.24 mmol), toluene (0.6 mL) , 2-cyanophenol (26 mg, 0.22 mmol), (*R*)-(+)-1-phenylethyl alcohol (54mg, 0.44 mmol), and 3,3',5,5'-tetra-*t*-butyl-4,4'-diphenoquinone **2** (98 mg, 0.24 mmol) were added and stirred at 80 °C for 48 h. The crude mixture was subjected to silica gel column chromatography using ethyl acetate/hexane (1/20, R_f = 0.2) as the eluent to give (*S*)-2-(1-phenylethoxy)benzonitrile (17 mg, 0.08 mmol, transparent liquid) in 36% yield with 90% ee. HPLC analysis: Chiralpak IA column, hexane/*i*-PrOH (99/1), R_t = 12.3 min (minnor), R_t= 12.9 min (major).

In the case of CH_3CN as the solvent, (*S*)-2-(1-phenylethoxy)benzonitrile (6.8 mg, 0.03 mmol, yellow liquid) was obtained in 14% yield with 54% ee. HPLC analysis: Chiralpak IA column, hexane/*i*-PrOH (99/1), R_t = 12.3 min (minor), R_t= 13.0 min (major).

HPLC charts of the products

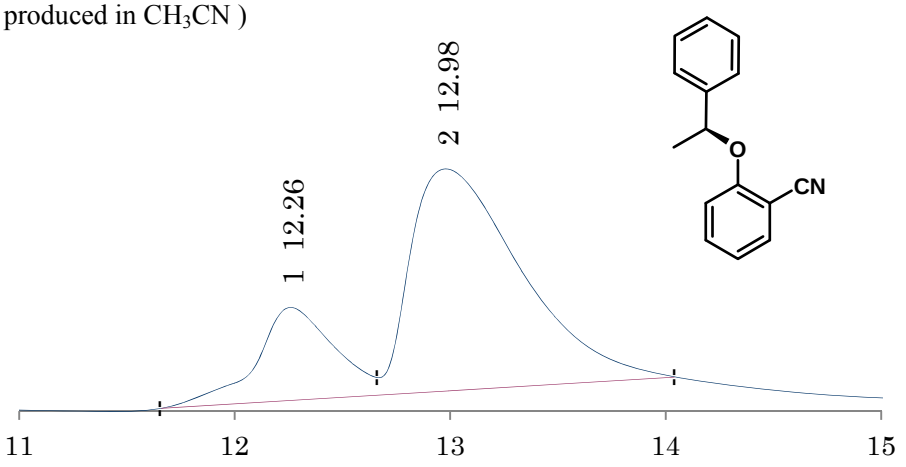
(S)-2-(1-Phenylethoxy)benzonitrile

(90% ee, produced in toluene)



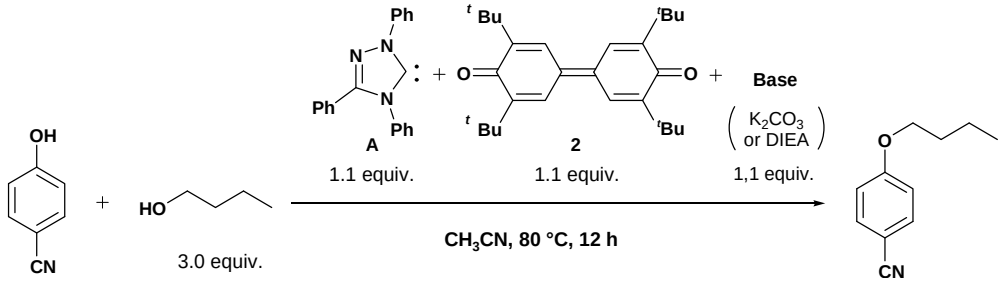
No.	Retention Time (min)	Area	Area %	Height
1	12.26	81589.1	4.72	5340
2	12.85	1648732.8	95.28	44540
Total		1730321.9	100	49880

(54% ee, produced in CH_3CN)



No.	Retention Time (min)	Area	Area %	Height
1	12.26	474000.878	22.92	18783
2	12.98	1594083.322	77.08	44827
Total		2068084.2	100	63610

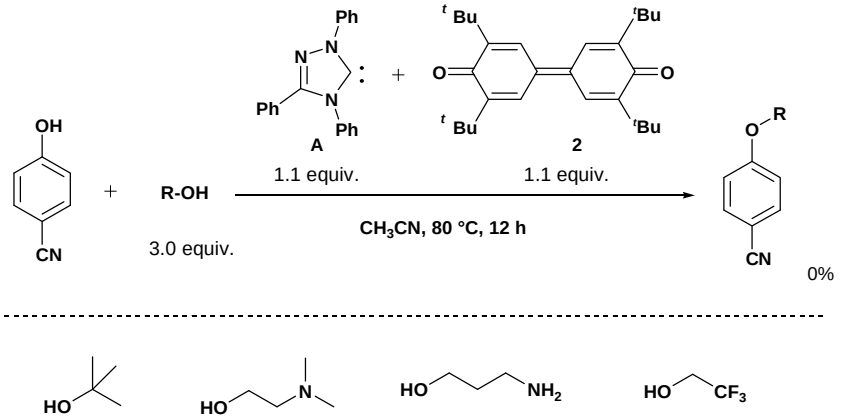
Table S1. Condensation of 4-cyanophenol with *n*-butanol in the presence of bases.



entry	base	Isolated yield (%)
1	K_2CO_3	66
2	DIEA	67
3	-	89

*These results shows the product yields were not significantly affected by K_2CO_3 and DIEA.

Scheme S1. Alcohols that did not undergo the condensation by NHC **A** and oxidant **2**



Scheme S2. Pronucleophiles that did not undergo the condensation by NHC **A** and oxidant **2**

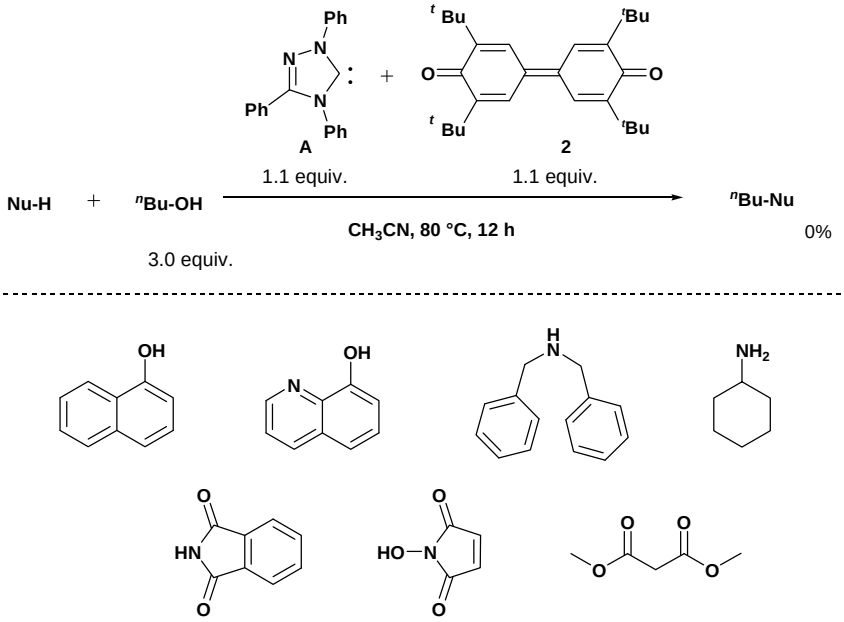
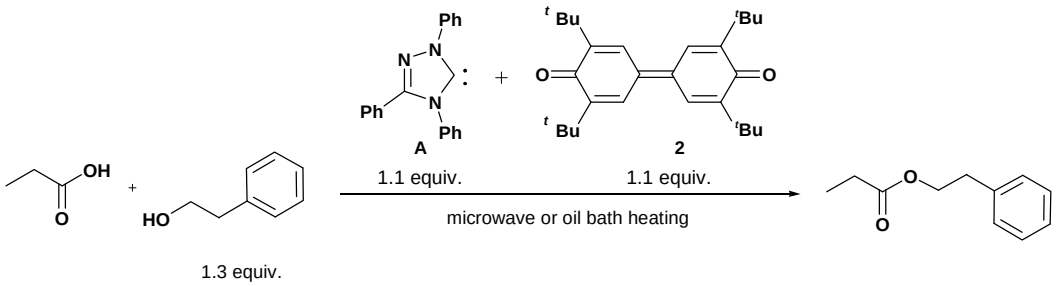


Table S2. Esterification of propanoic acid with phenethyl alcohol promoted by NHC **A** and oxidant **2**



entry	solvent	temp. (°C)	time (h)	Heating method[a]	yield[b]
1	CH_3CN	80	12	OB	50
2	CH_3CN	150	2	MW	41
3	CH_3CN	120	6	MW	48
4	1,4-dioxane	120	12	MW	60

[a] OB: oil bath heating, WM: microwave irradiation.

[b] Isolated yield.

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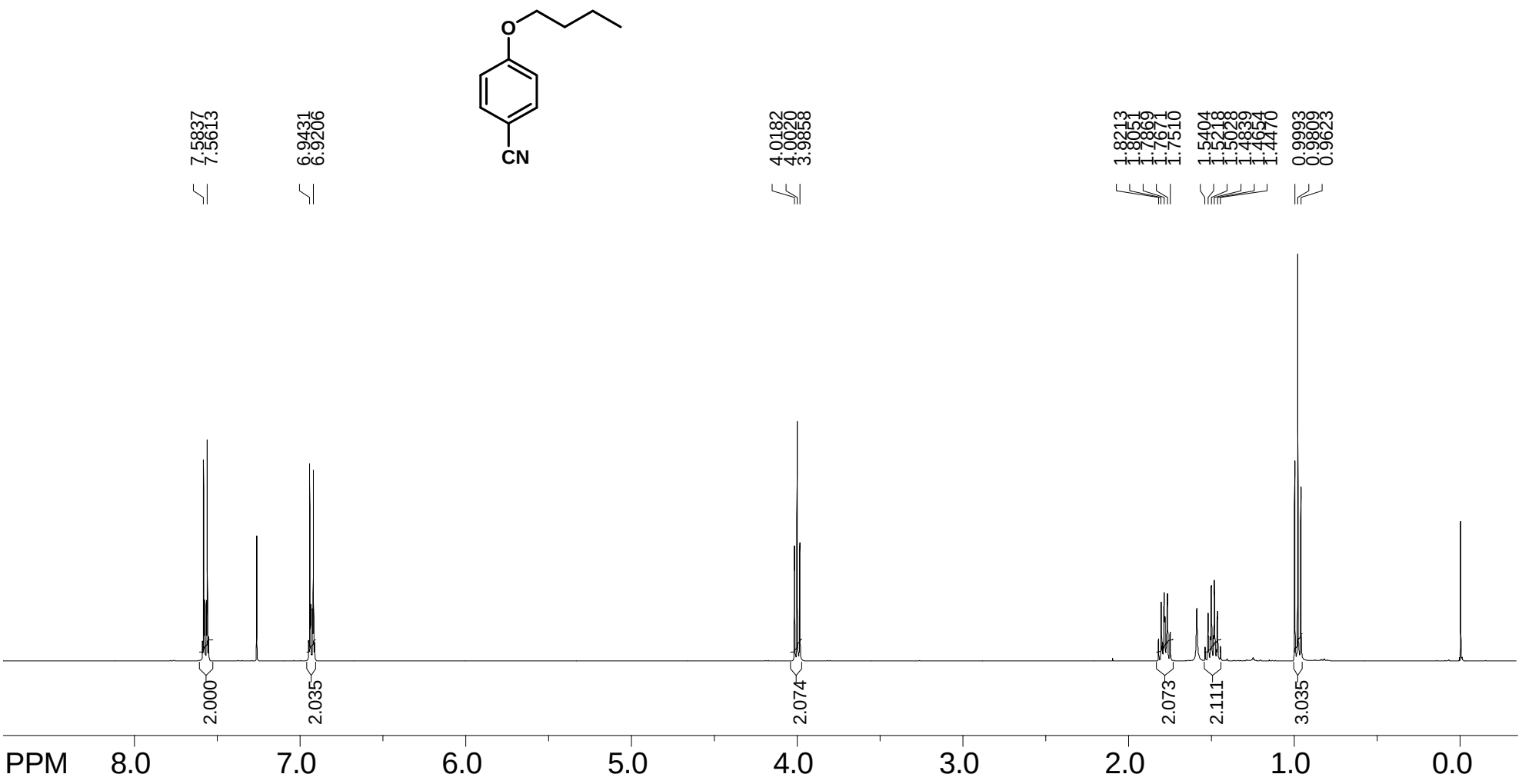

Figure S1. ^{1}H NMR spectrum of 4-butoxybenzonitrile ($CDCl_3$)

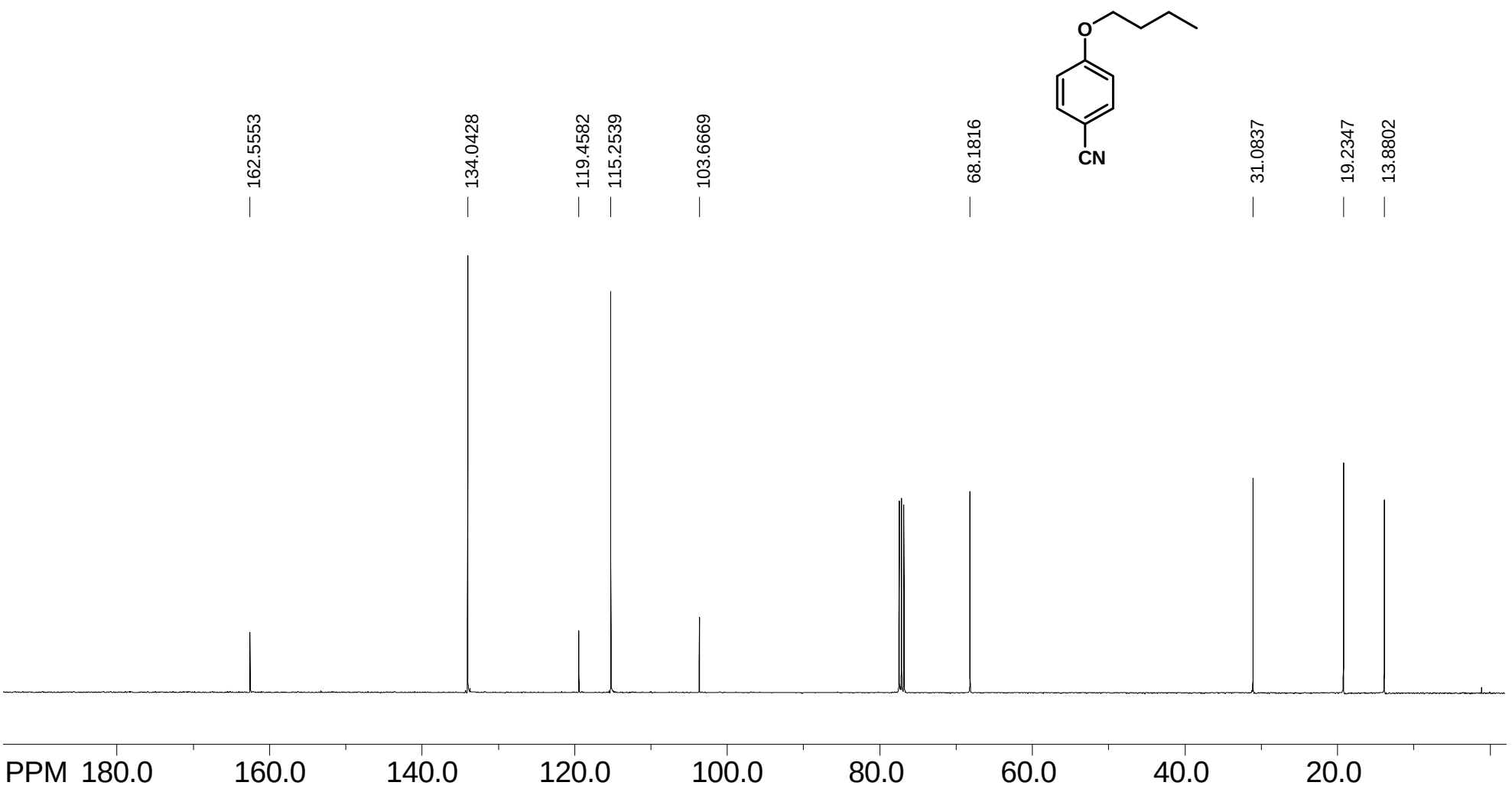

Figure S2. ^{13}C NMR spectrum of 4-butoxybenzonitrile ($CDCl_3$)

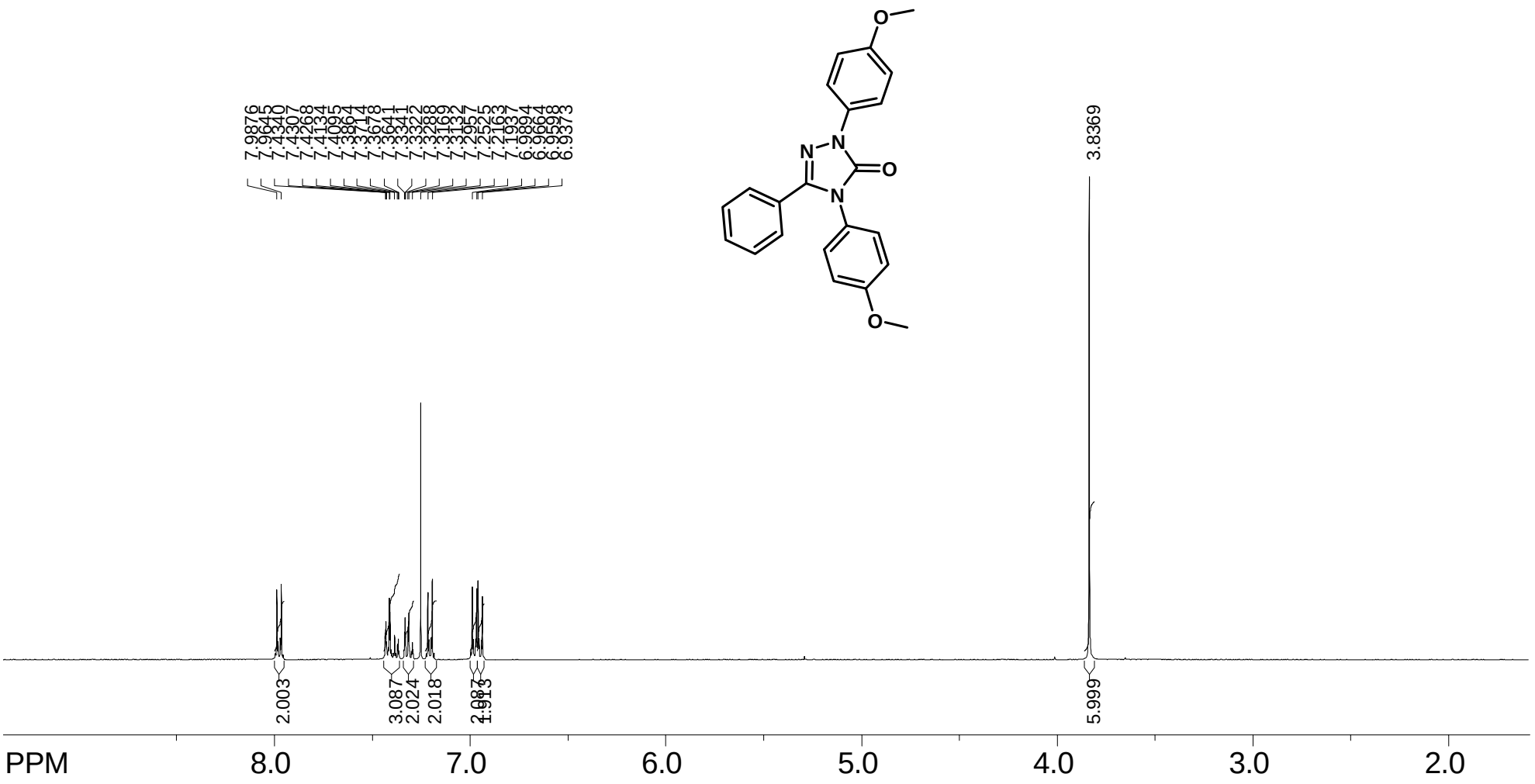

Figure S3. ^{1}H NMR spectrum of compound **L** ($CDCl_3$)

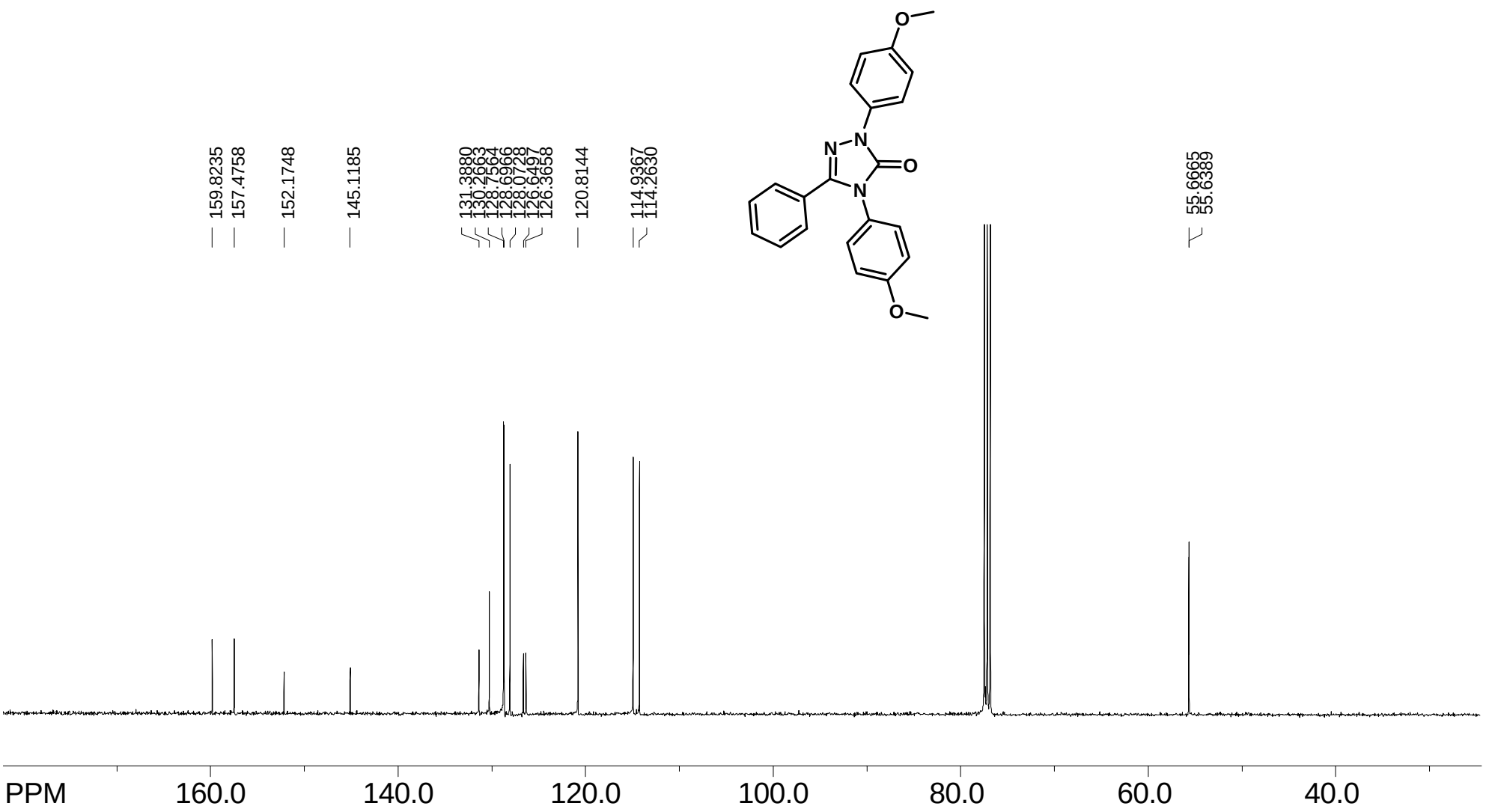

Figure S4. ^{13}C NMR spectrum of compound **L** ($CDCl_3$)

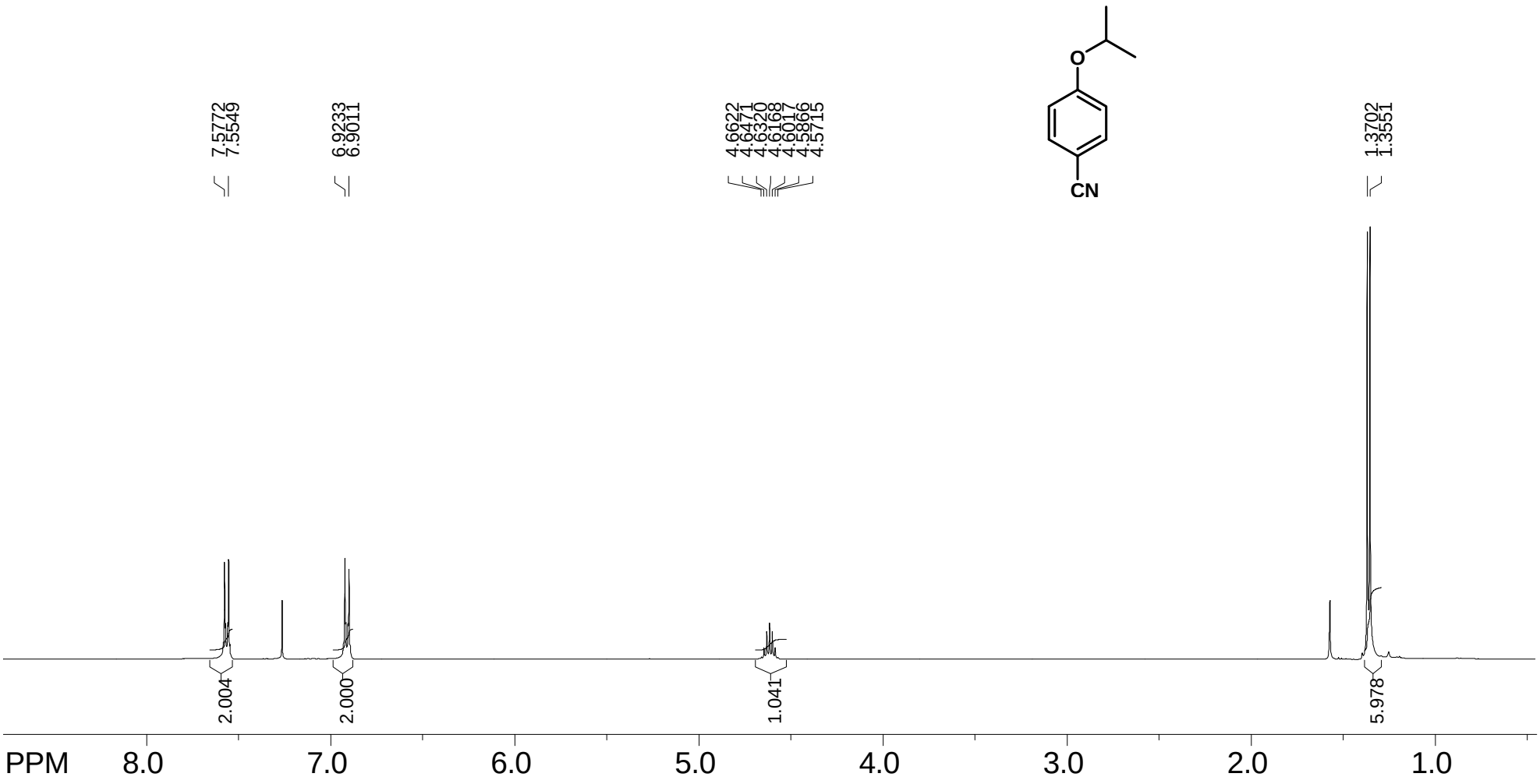

Figure S5. ^{1}H NMR spectrum of 4-isopropoxybenzonitrile ($CDCl_3$)

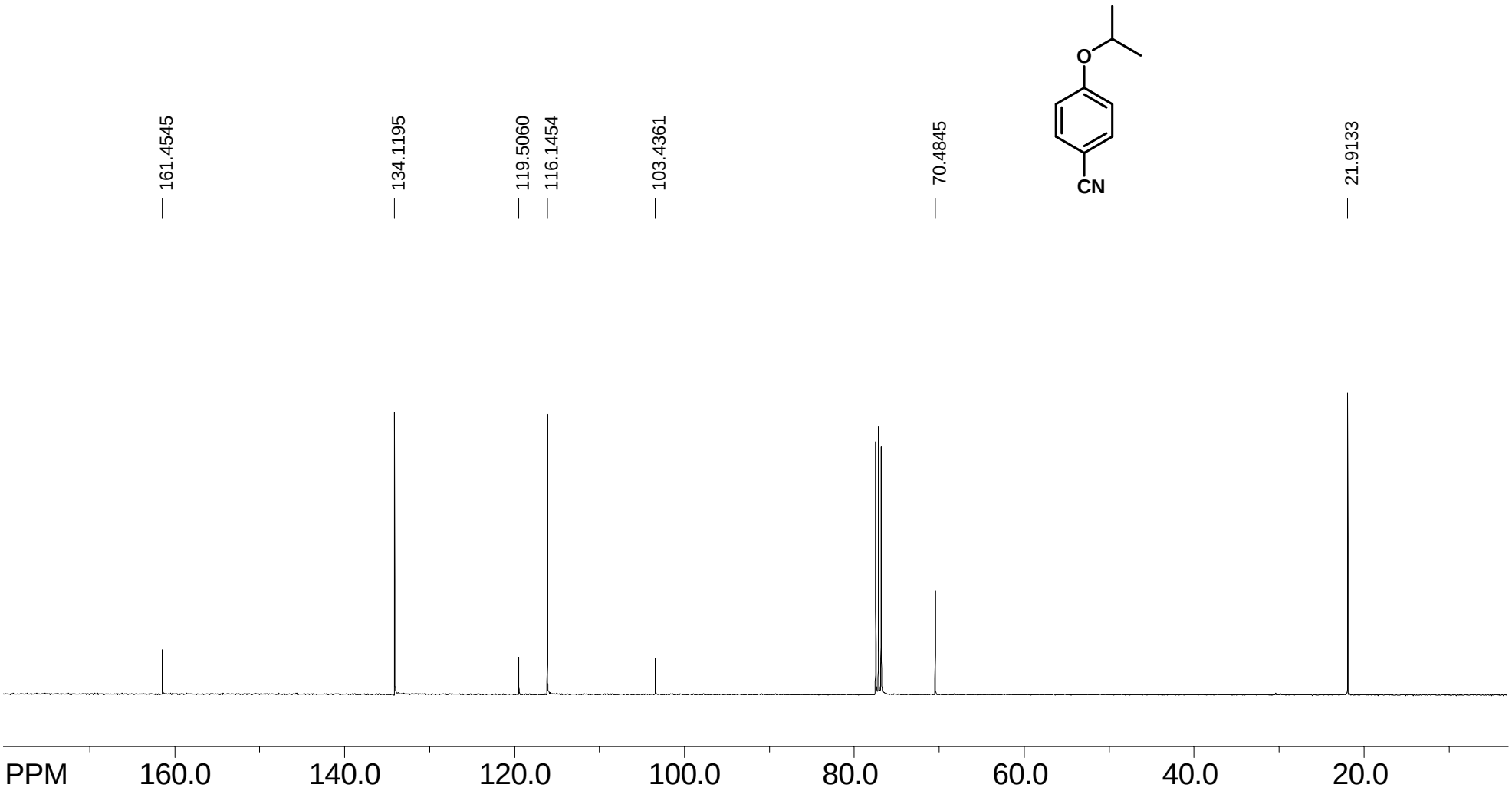

Figure S6. ^{13}C NMR spectrum of 4-isopropoxybenzonitrile ($CDCl_3$)

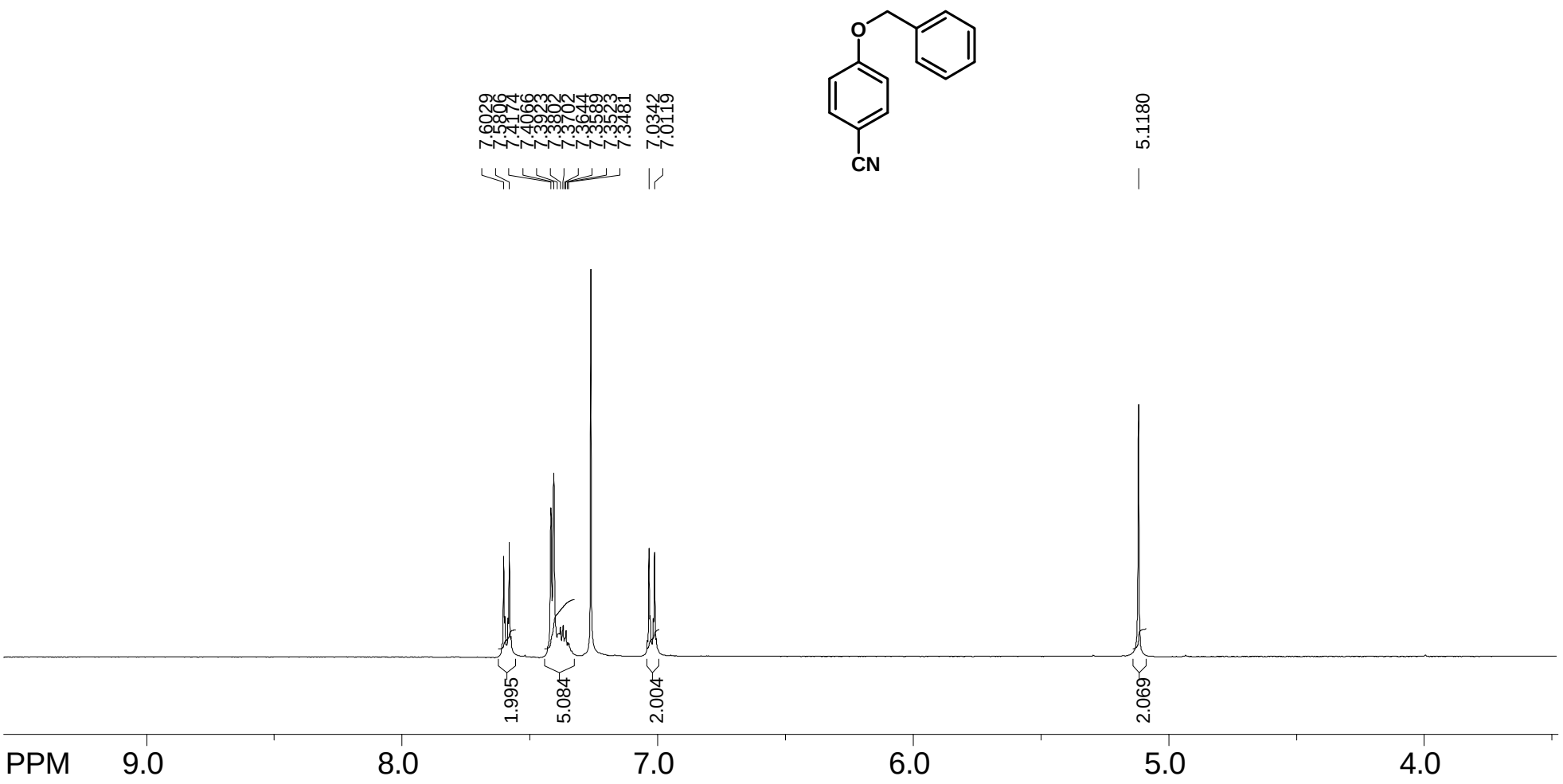

Figure S7. ^{1}H NMR spectrum of 4-benzoxybenzonitrile ($CDCl_3$)

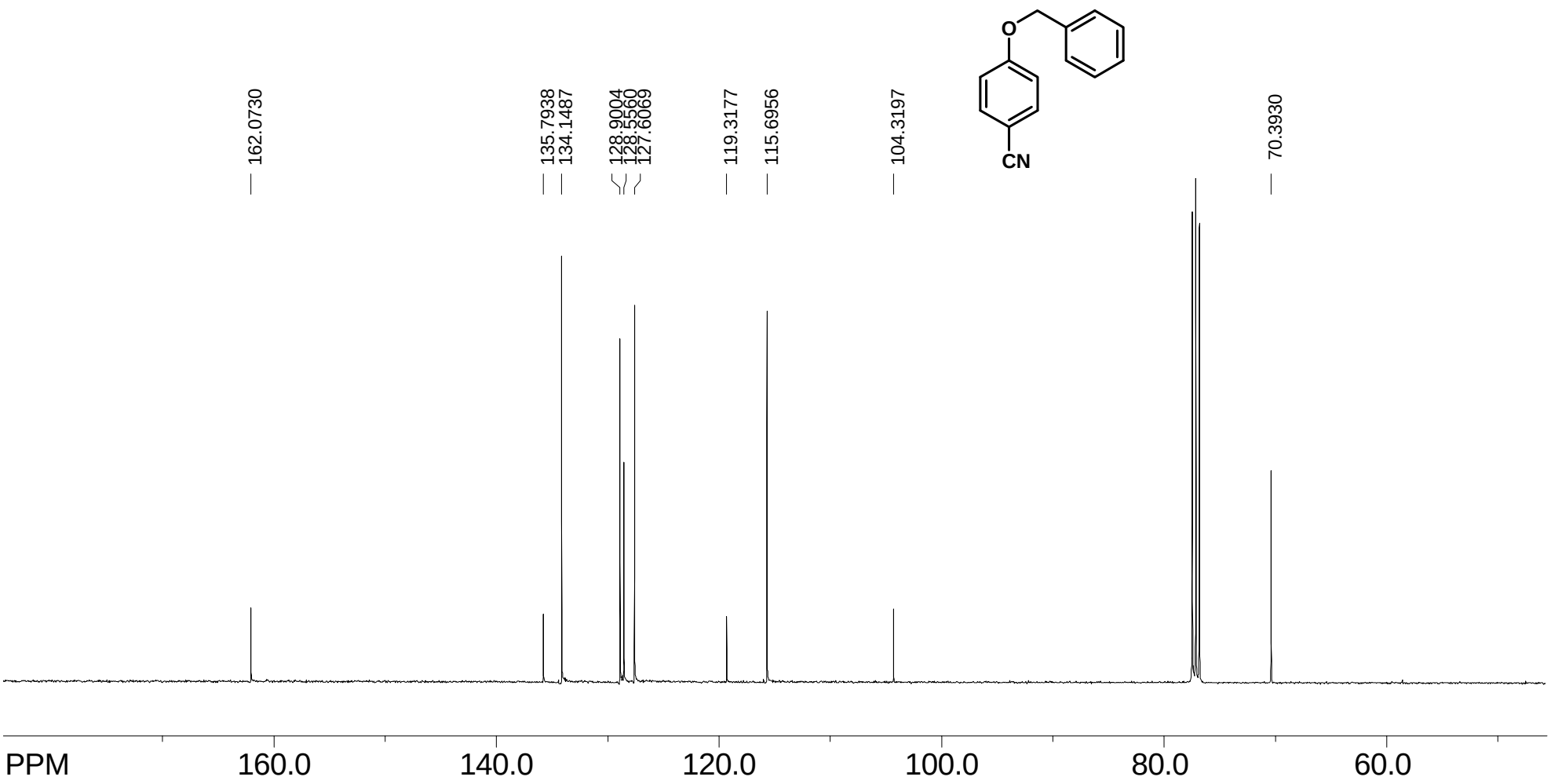

Figure S8. ^{13}C NMR spectrum of 4-benzyloxybenzonitrile ($CDCl_3$)

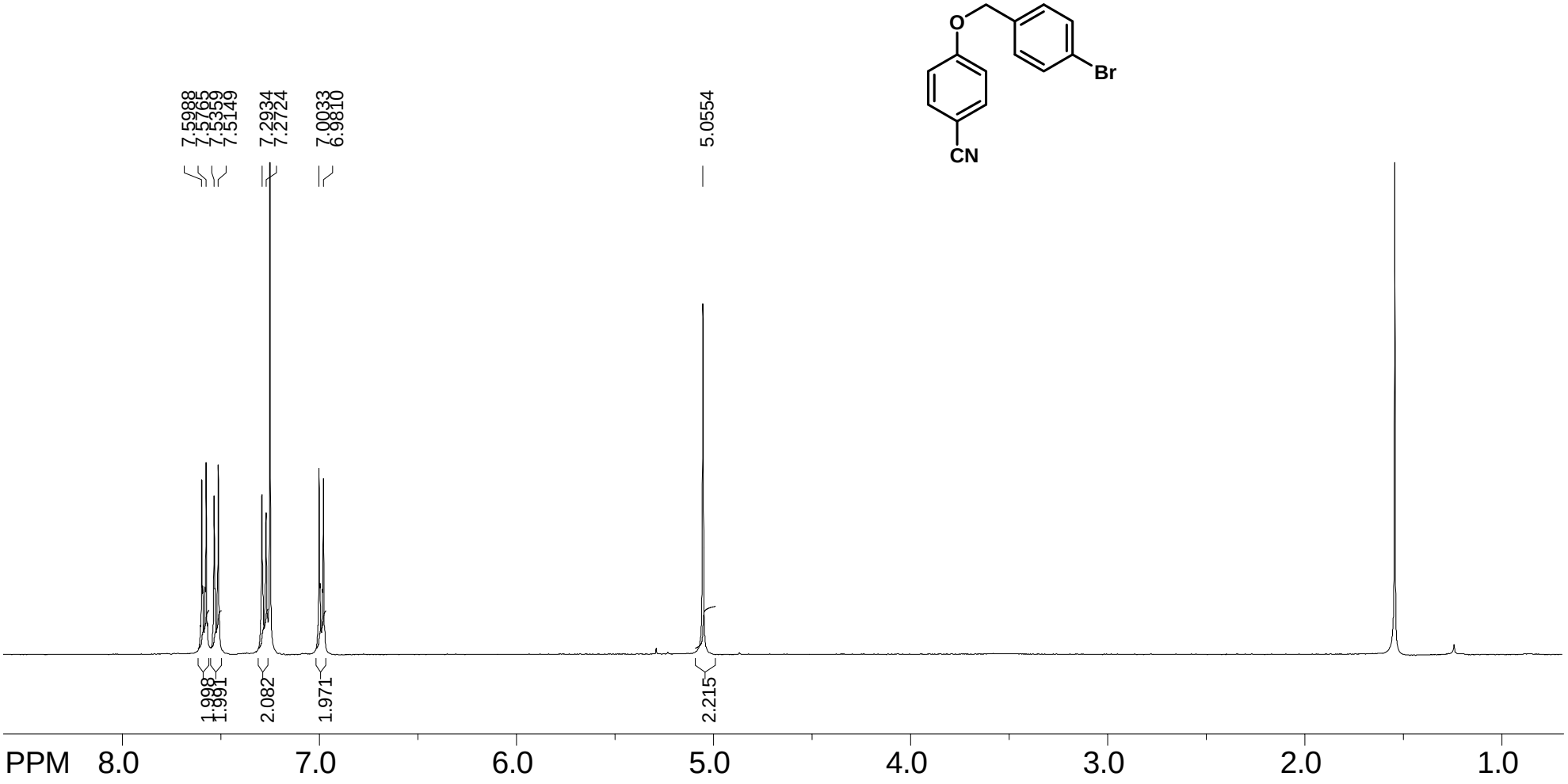

Figure S9. ^{1}H NMR spectrum of 4-(4-bromobenzyloxy)benzonitrile ($CDCl_3$)

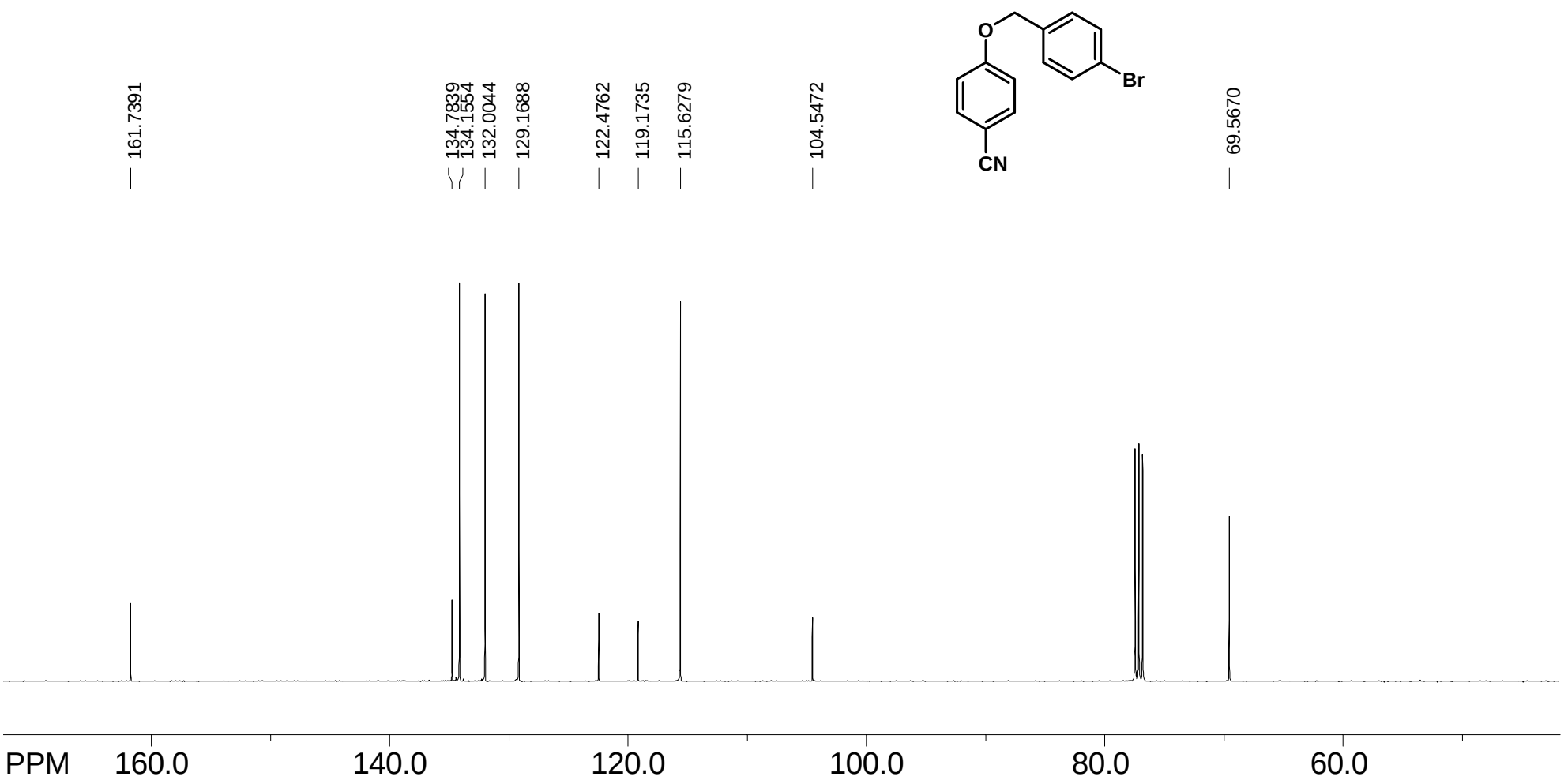

Figure S10. ^{13}C NMR spectrum of 4-(4-bromobenzyloxy)benzonitrile ($CDCl_3$)

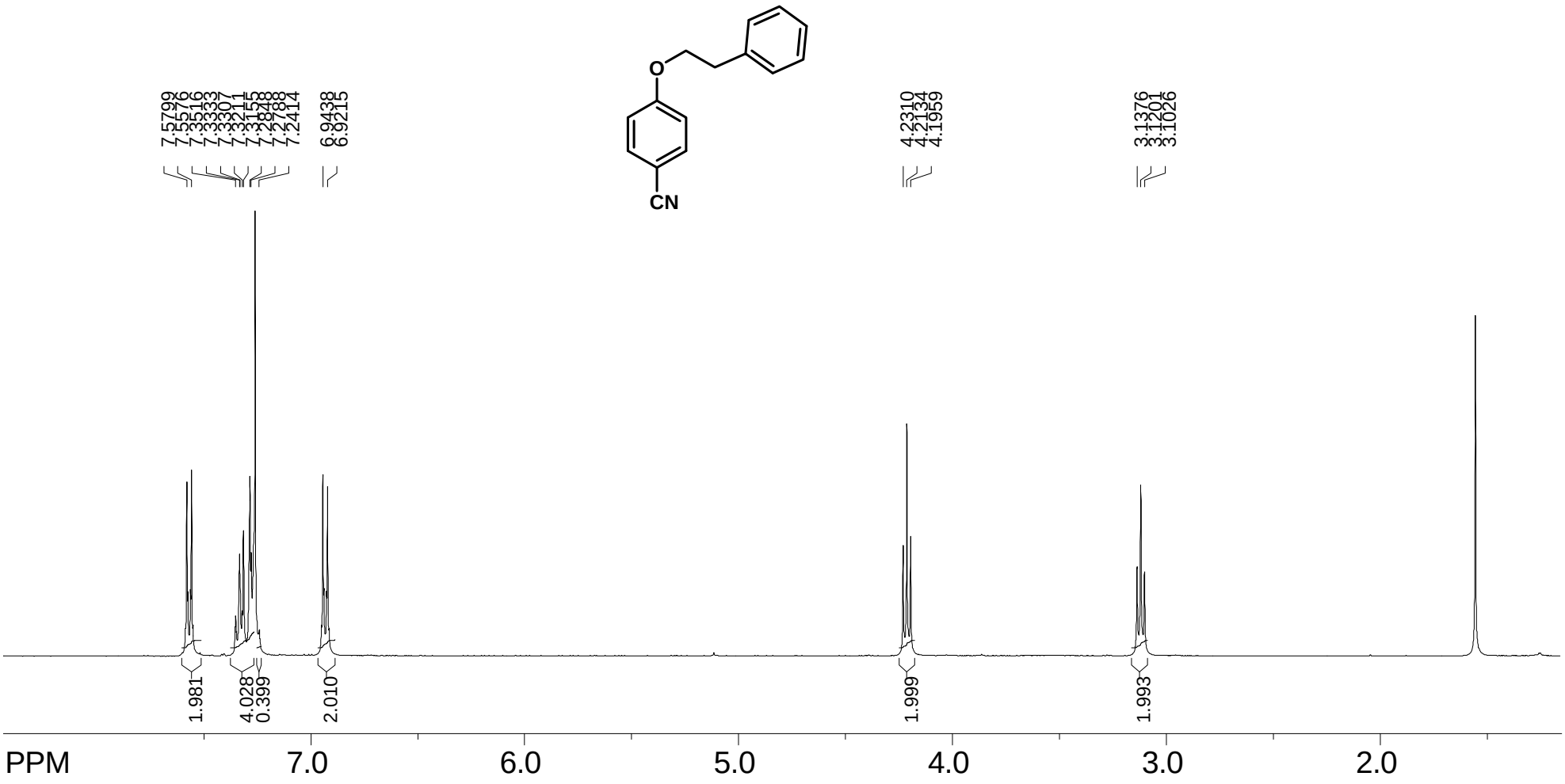

Figure S11. ^{1}H NMR spectrum of 4-phenethyloxybenzonitrile ($CDCl_3$)

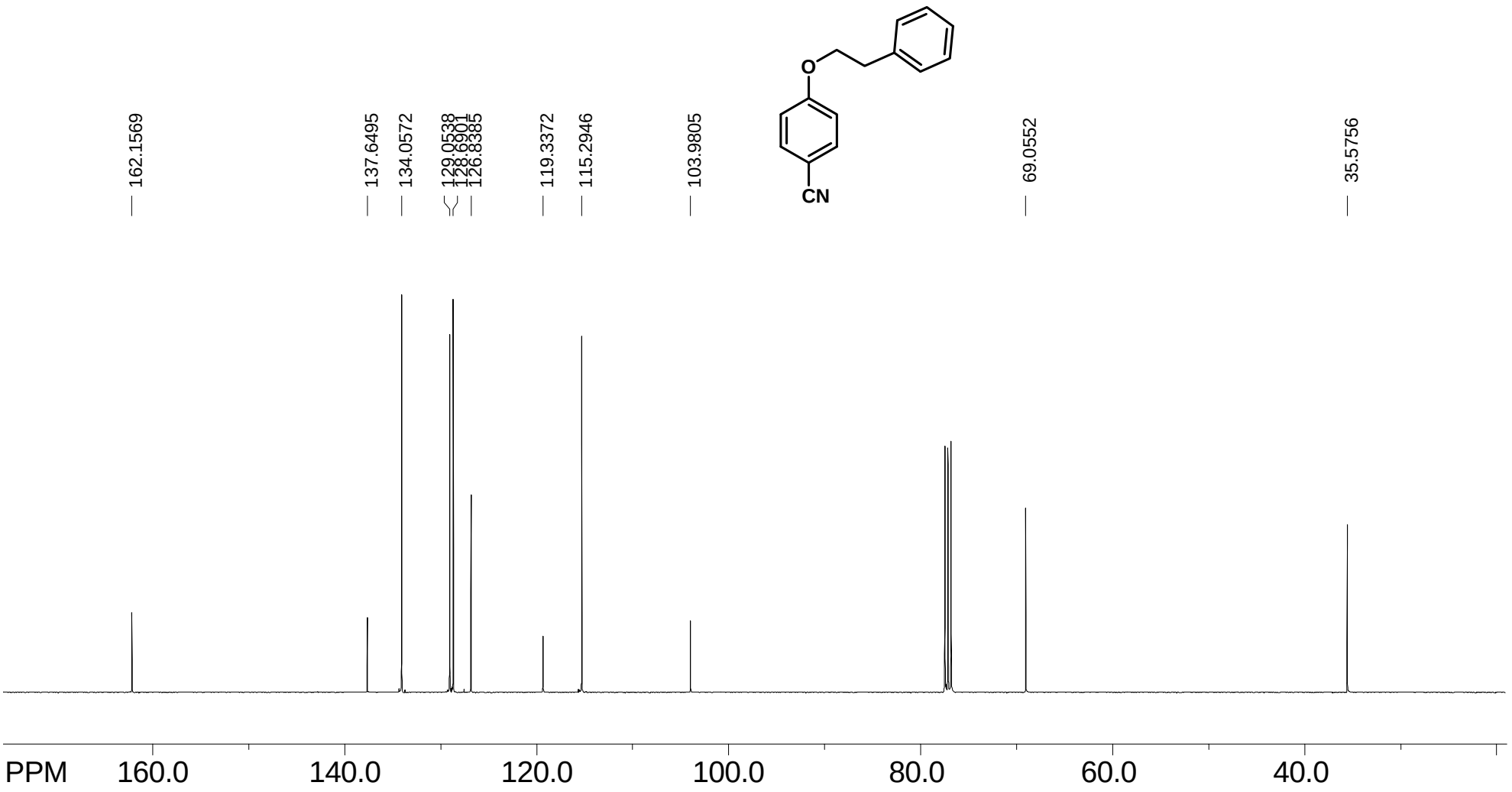

Figure S12. ^{13}C NMR spectrum of 4-phenethyloxybenzonitrile ($CDCl_3$)

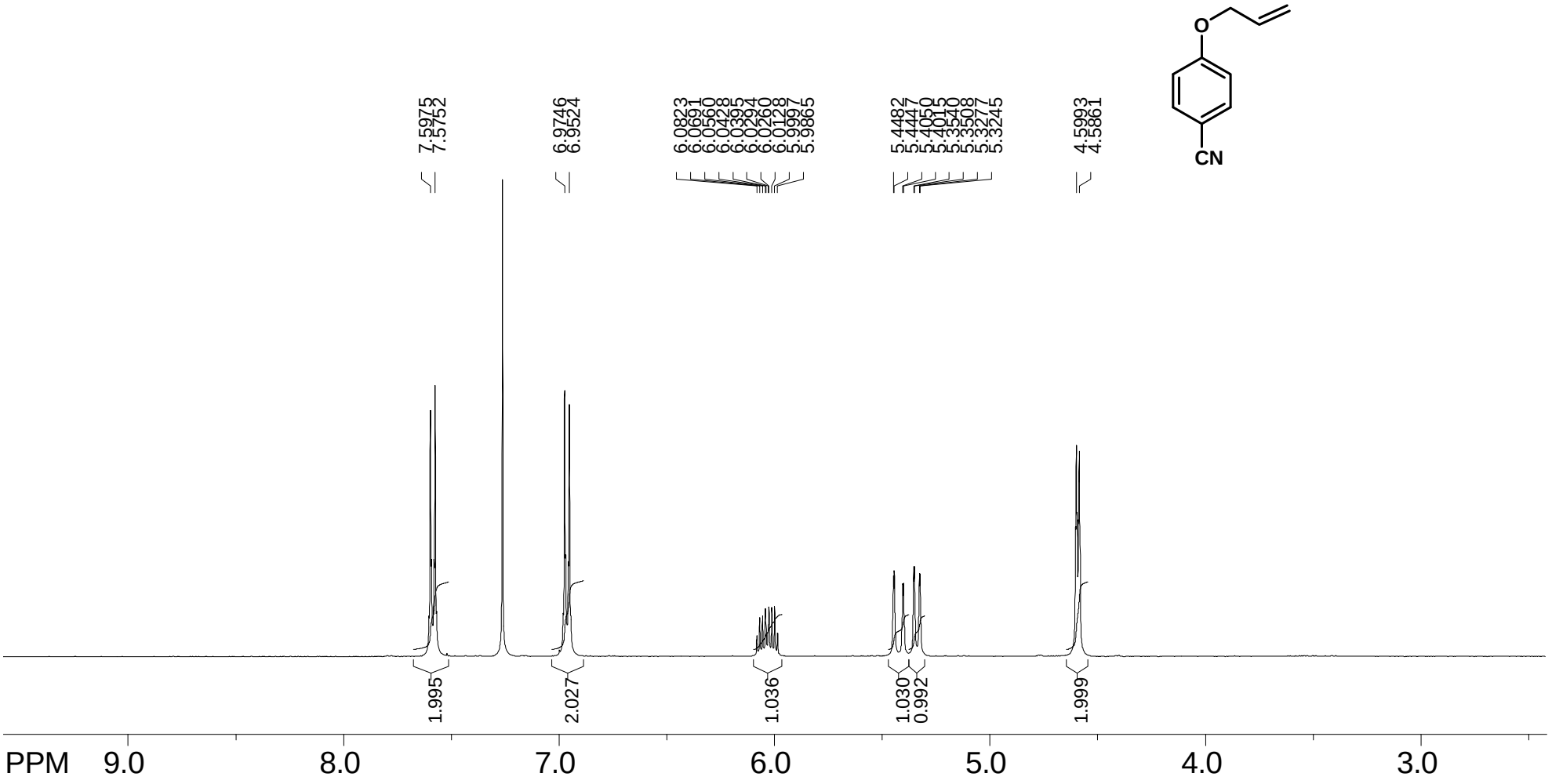

Figure S13. ^{1}H NMR spectrum of 4-(prop-2-en-1-yloxy)benzonitrile ($CDCl_3$)

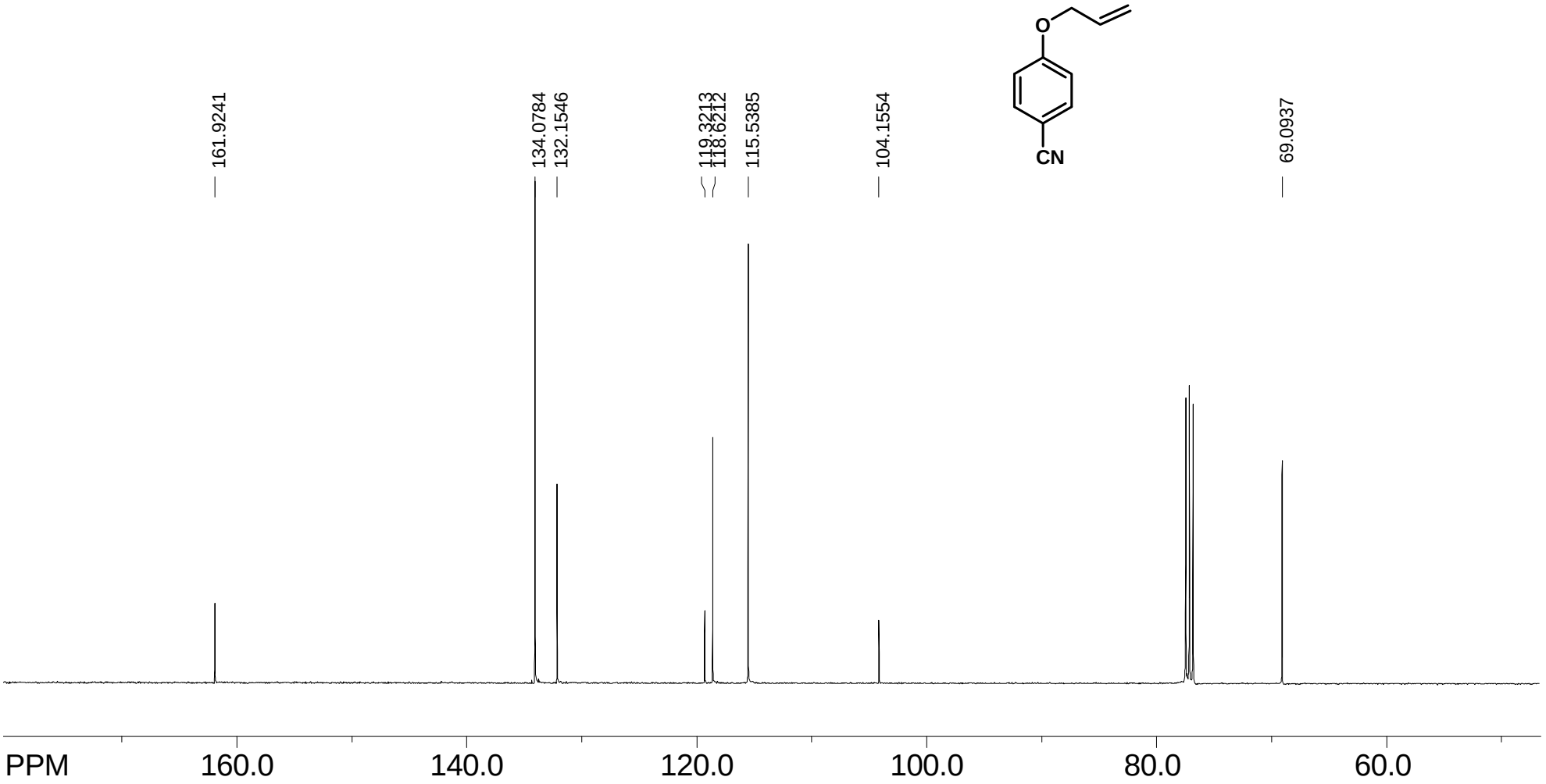

Figure S14. ^{13}C NMR spectrum of 4-(prop-2-en-1-yloxy)benzonitrile ($CDCl_3$)

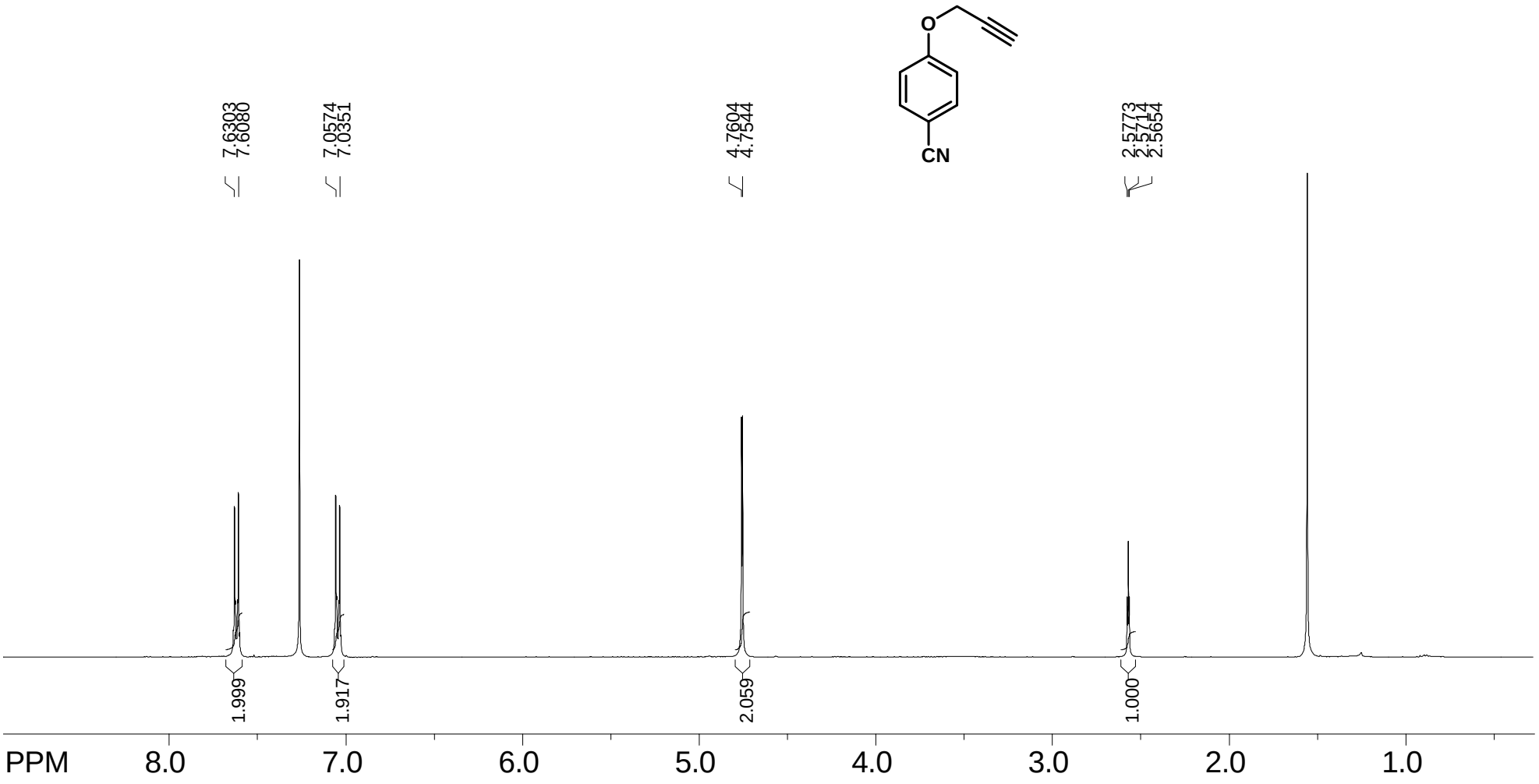

Figure S15. ^{1}H NMR spectrum of 4-(prop-2-yn-1-yloxy)benzonitrile ($CDCl_3$)

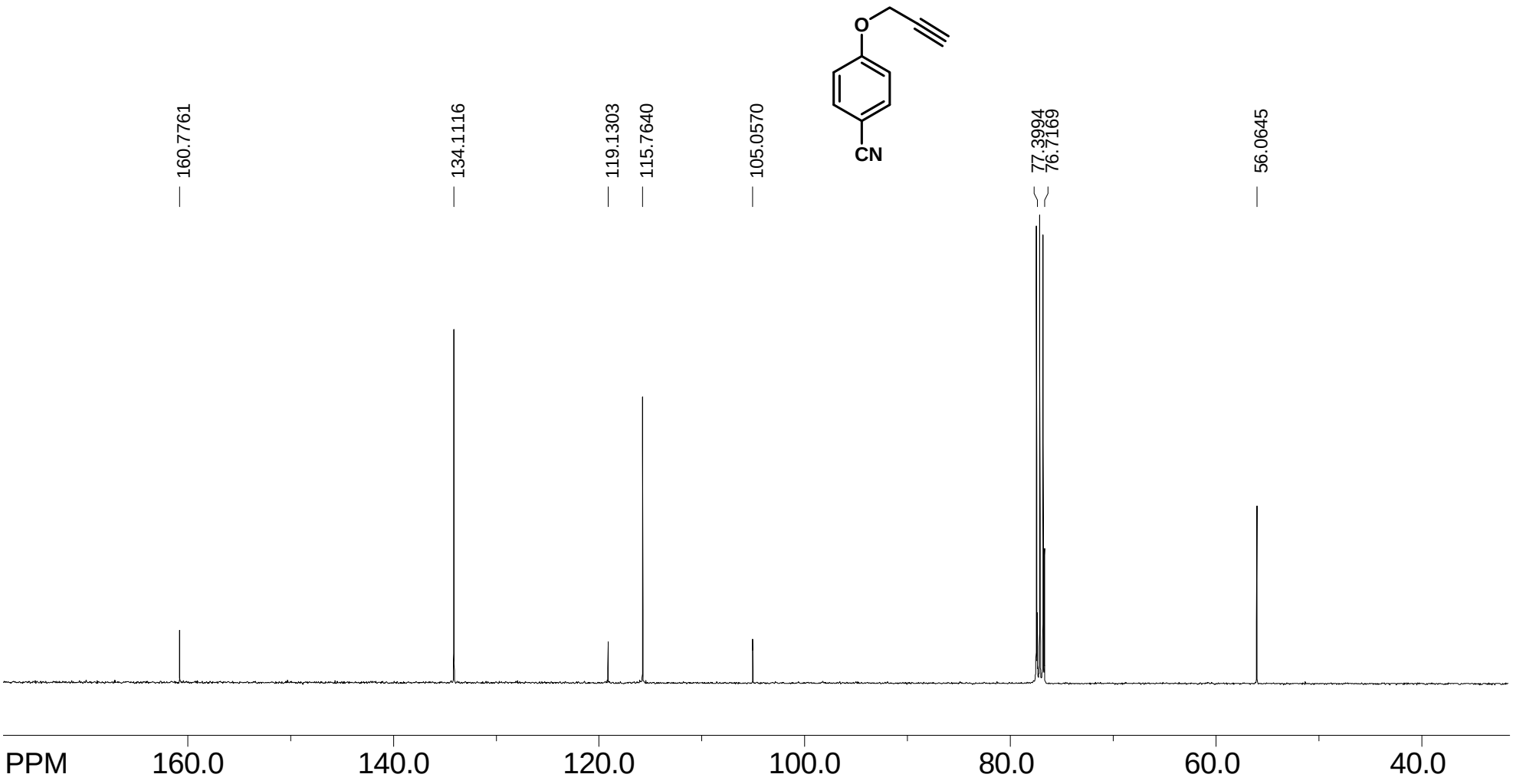

Figure S16. ^{13}C NMR spectrum of 4-(prop-2-yn-1-yloxy)benzonitrile ($CDCl_3$)

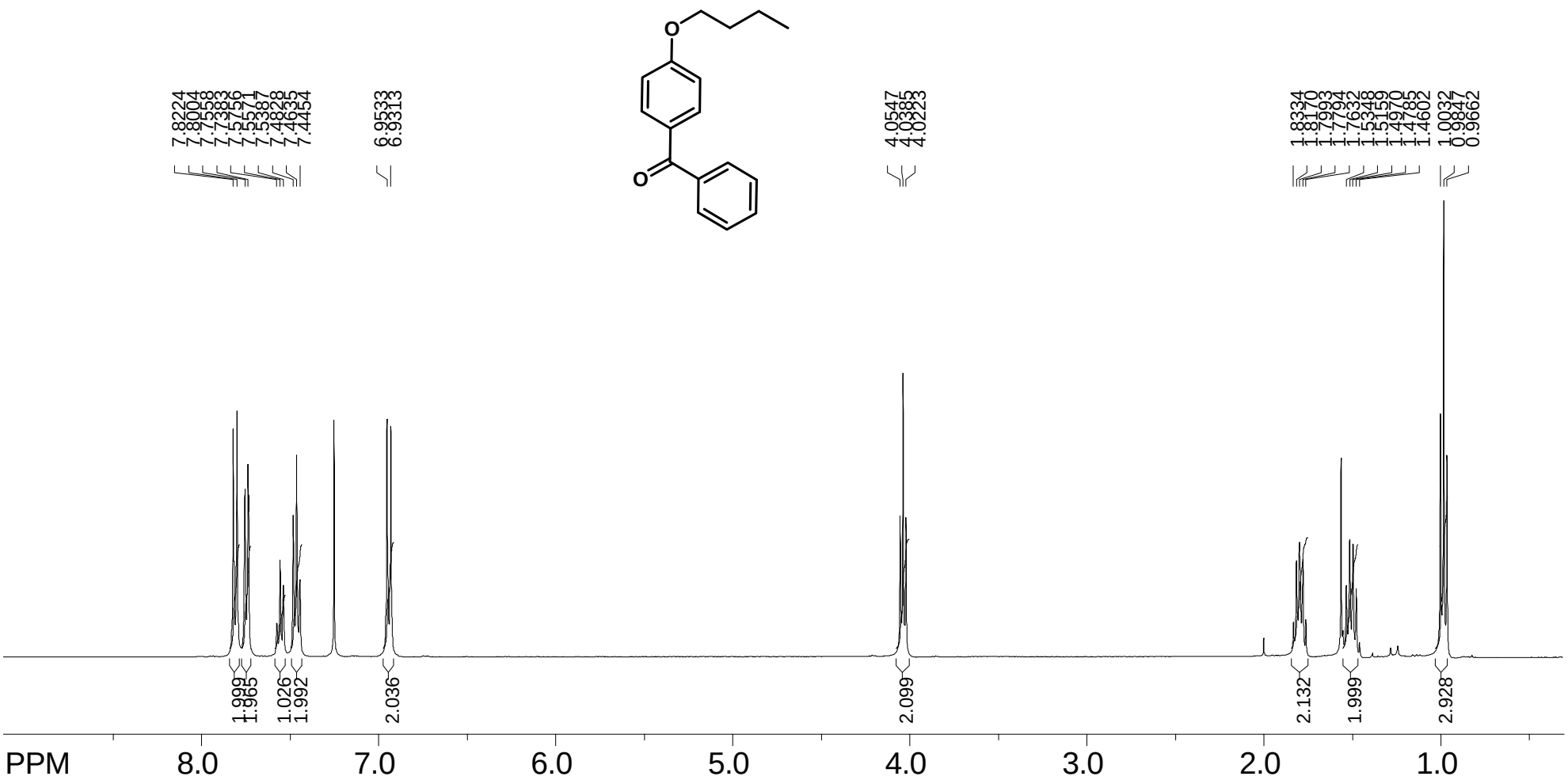

Figure S17. ^{1}H NMR spectrum of 4-butoxybenzophenone ($CDCl_3$)

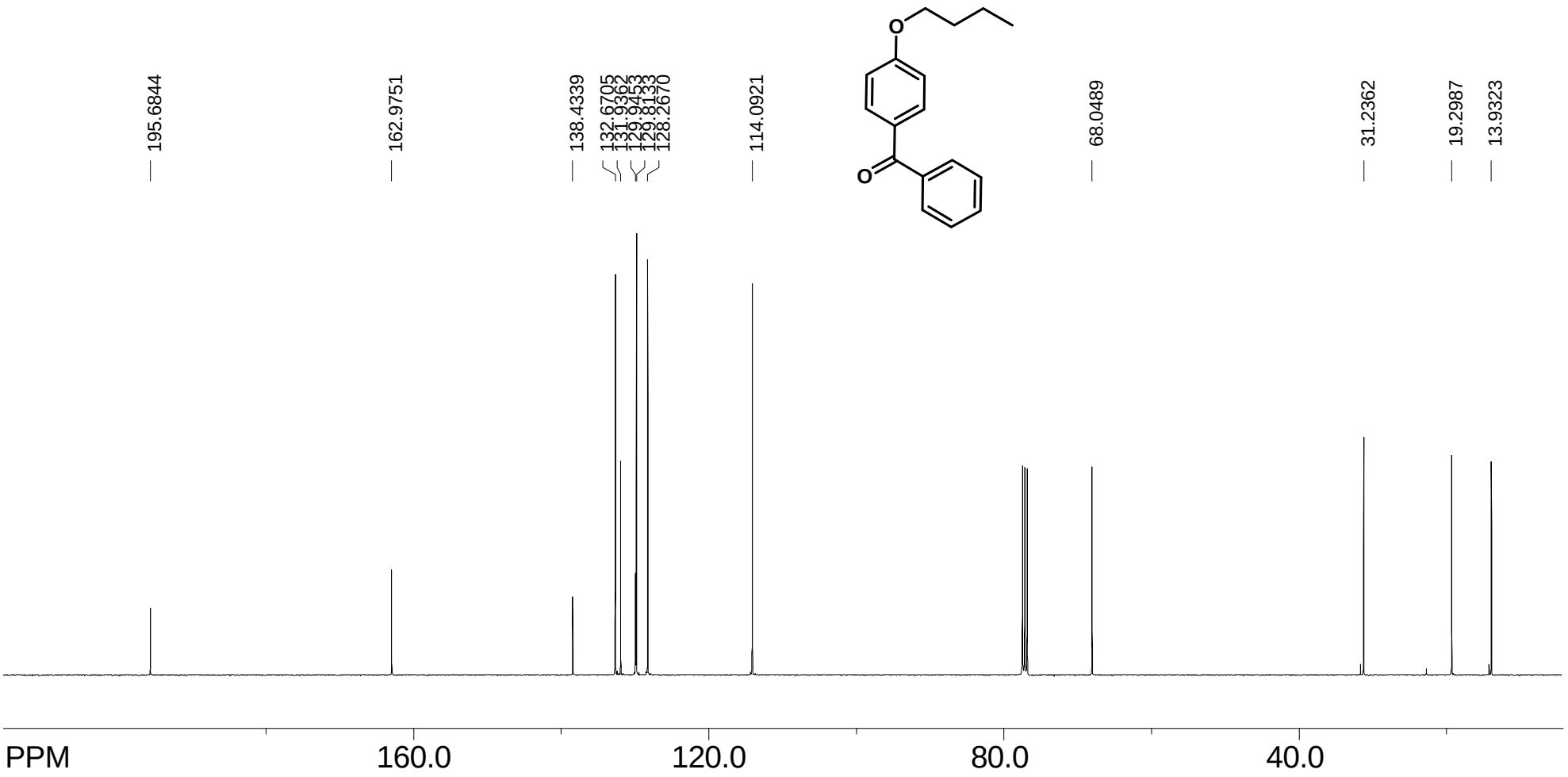

Figure S18. ^{13}C NMR spectrum of 4-butoxybenzophenone ($CDCl_3$)

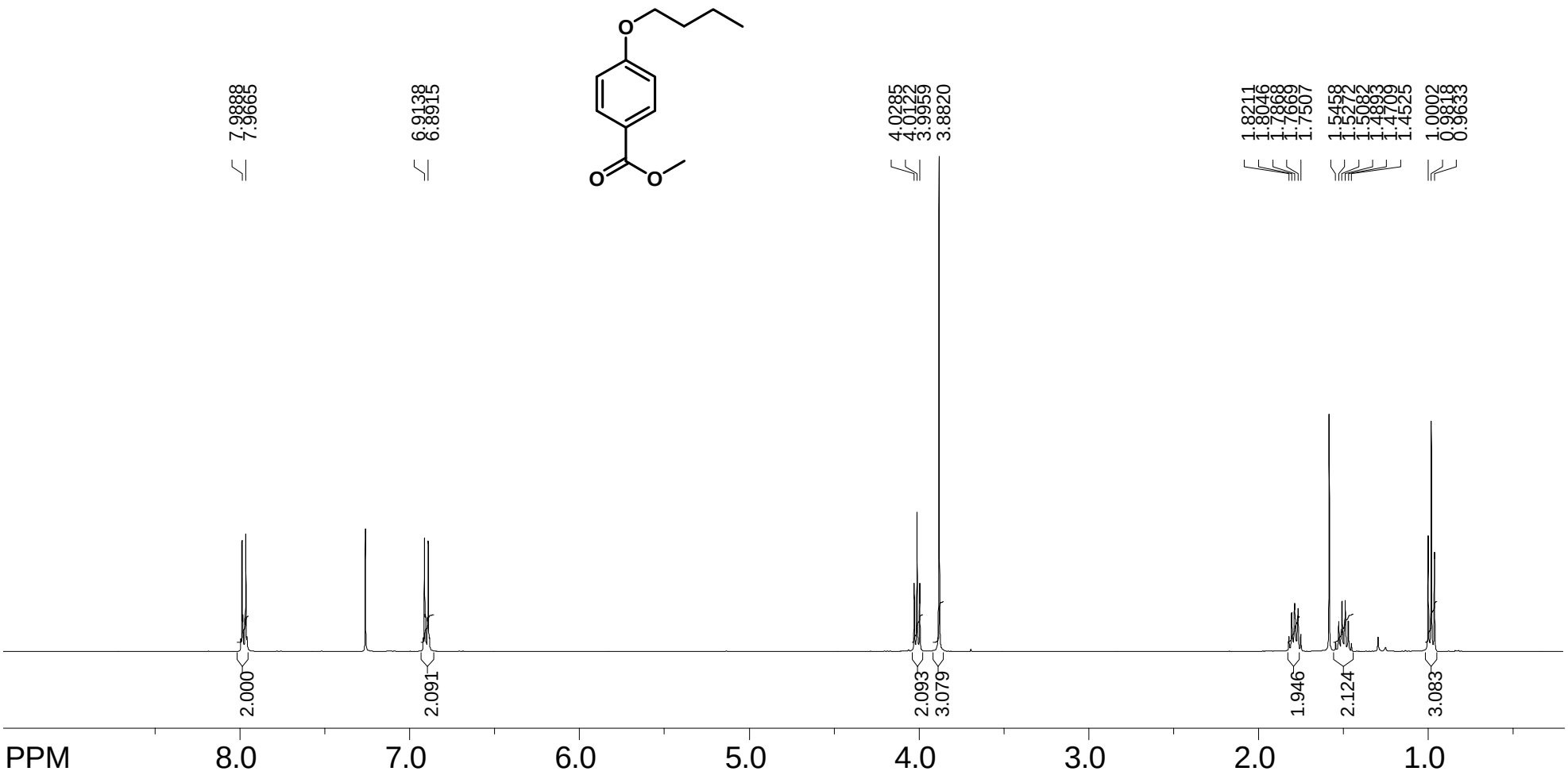

Figure S19. ^{1}H NMR spectrum of 4-butoxybenzoic acid methyl ester ($CDCl_3$)

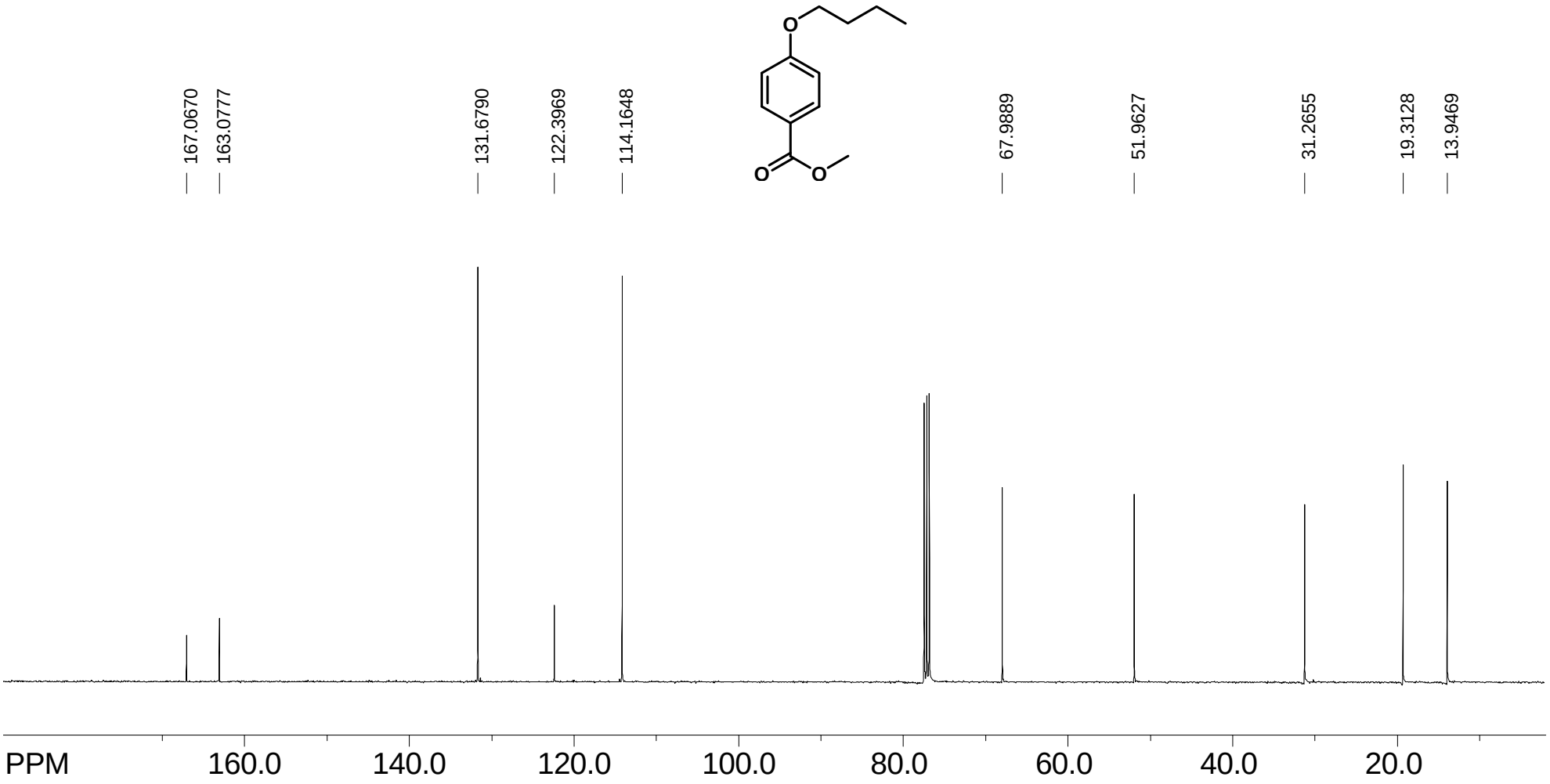

Figure S20. ^{13}C NMR spectrum of 4-butoxybenzoic acid methyl ester ($CDCl_3$)

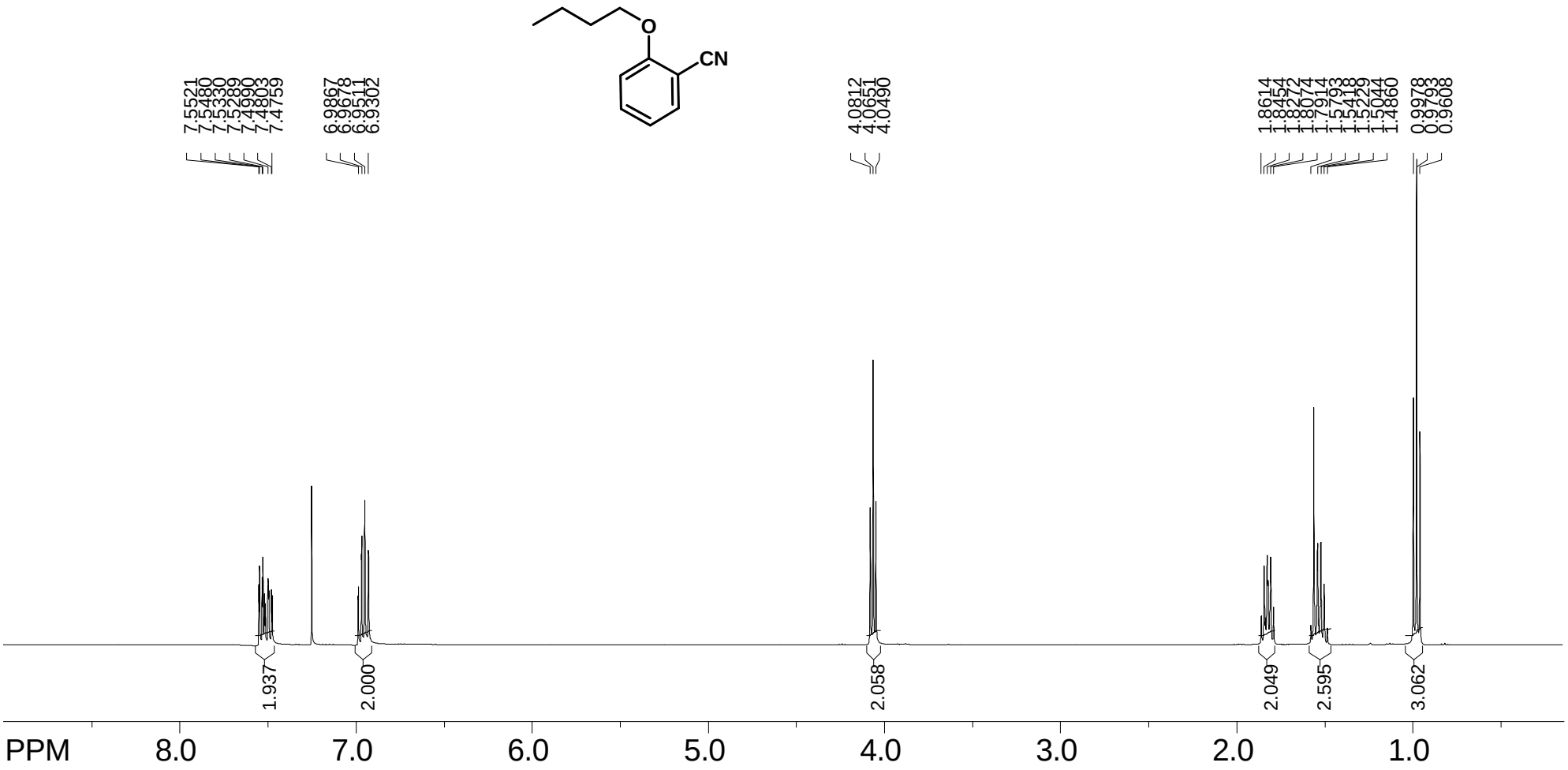

Figure S21. ^{1}H NMR spectrum of 2-butoxybenzonitrile ($CDCl_3$)

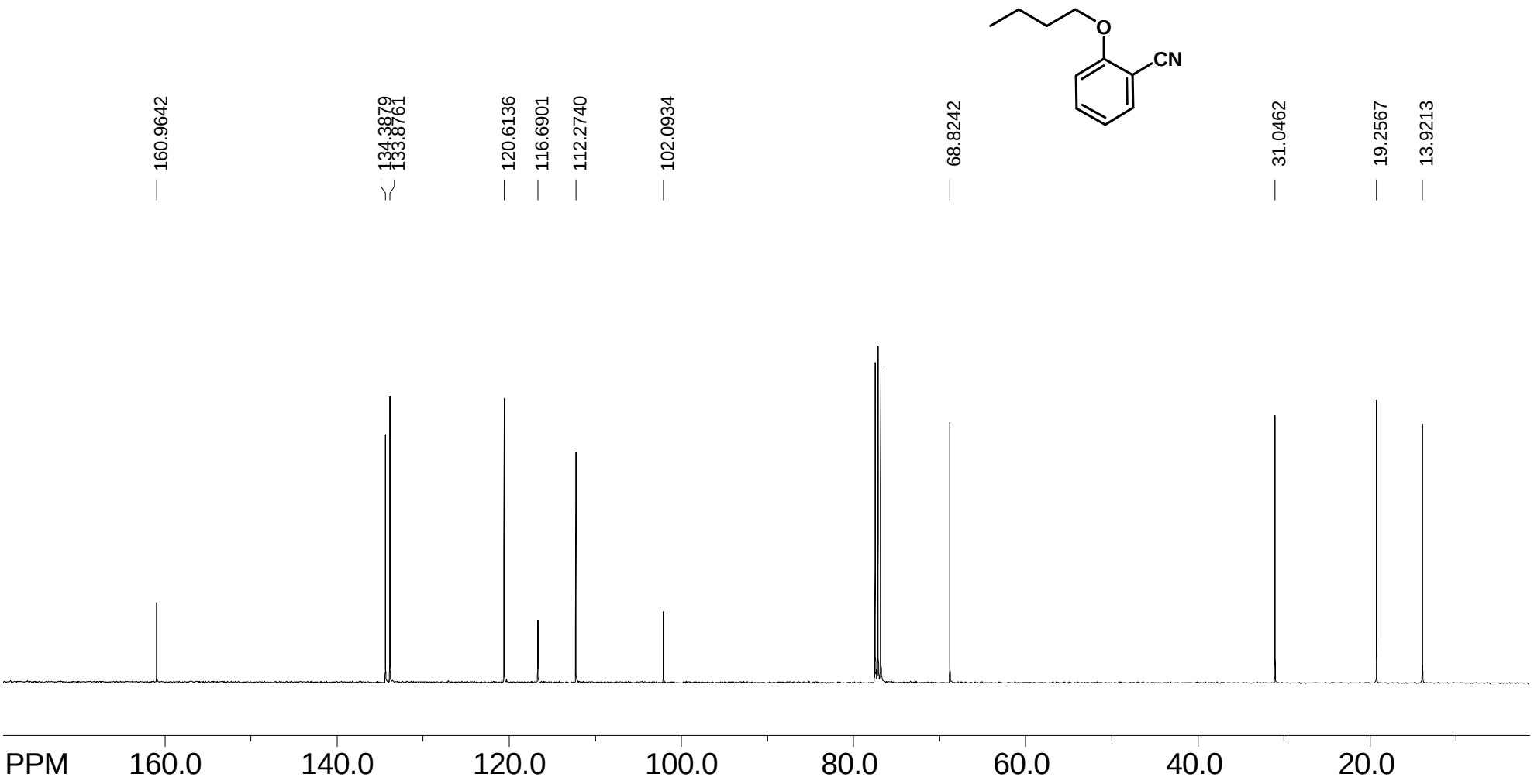

Figure S22. ^{13}C NMR spectrum of 2-butoxybenzonitrile ($CDCl_3$)

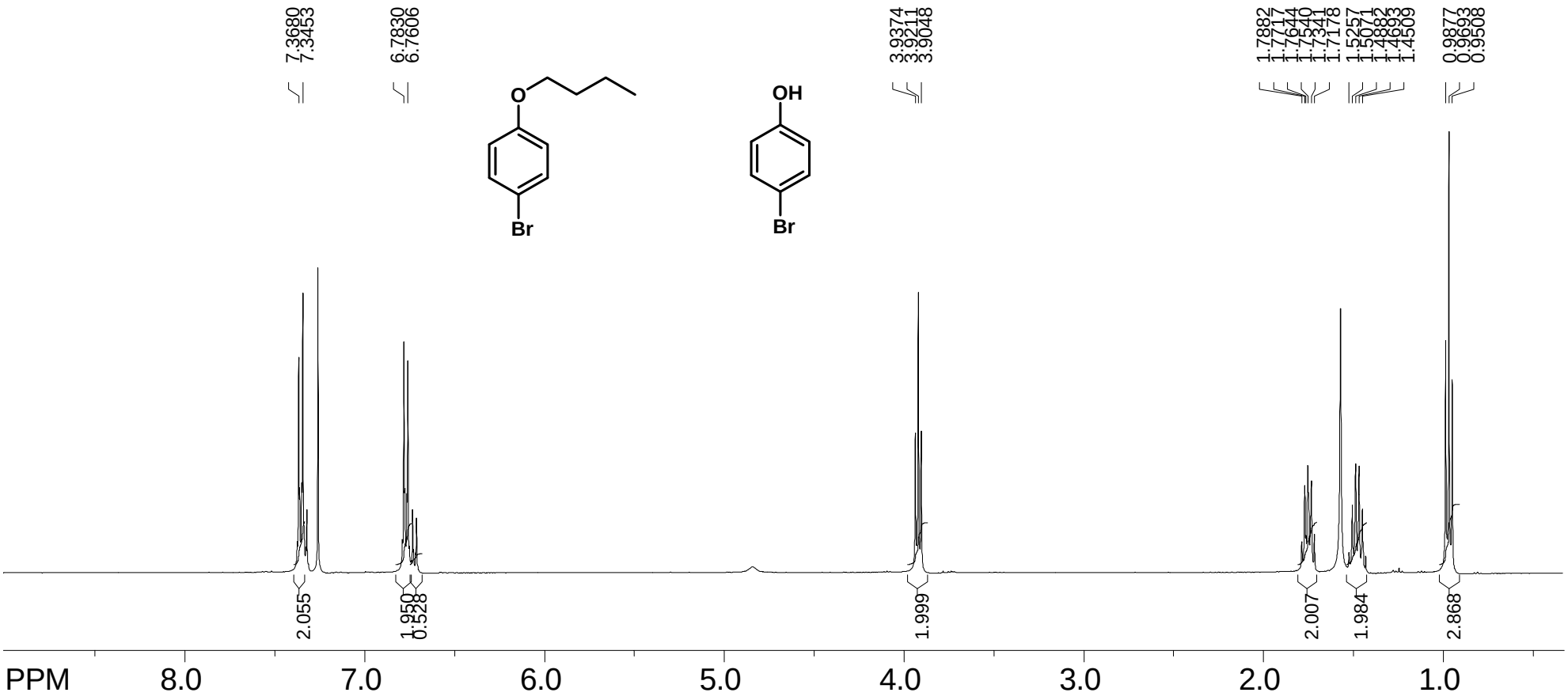

Figure S23. ^{1}H NMR spectrum of the mixture; ptoduct1-bromo-4-butoxybenzene and unreacted 4-bromophenol ($CDCl_3$)

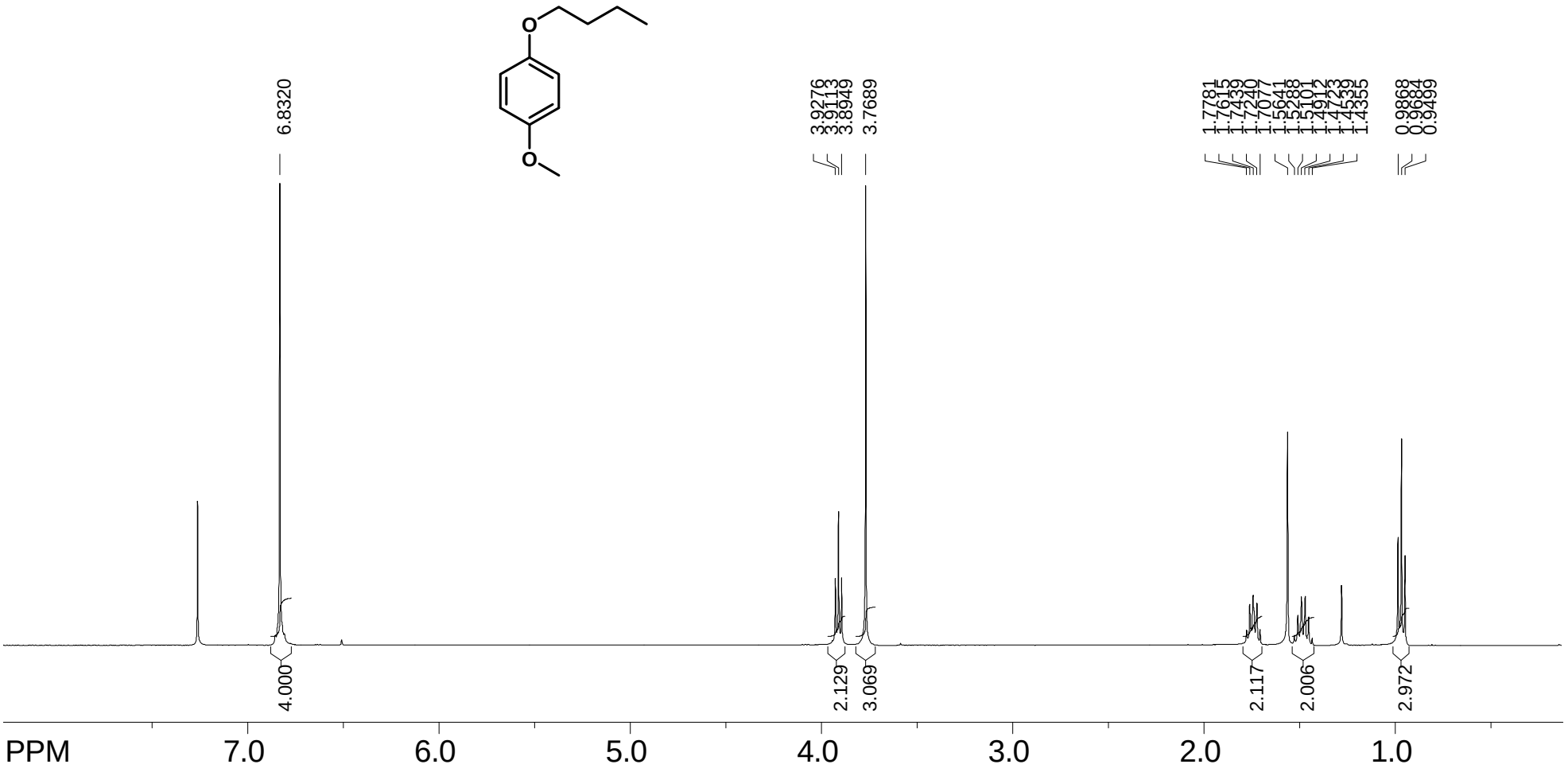

Figure S24. ^{1}H NMR spectrum of 1-butoxy-4-methoxybenzene ($CDCl_3$)

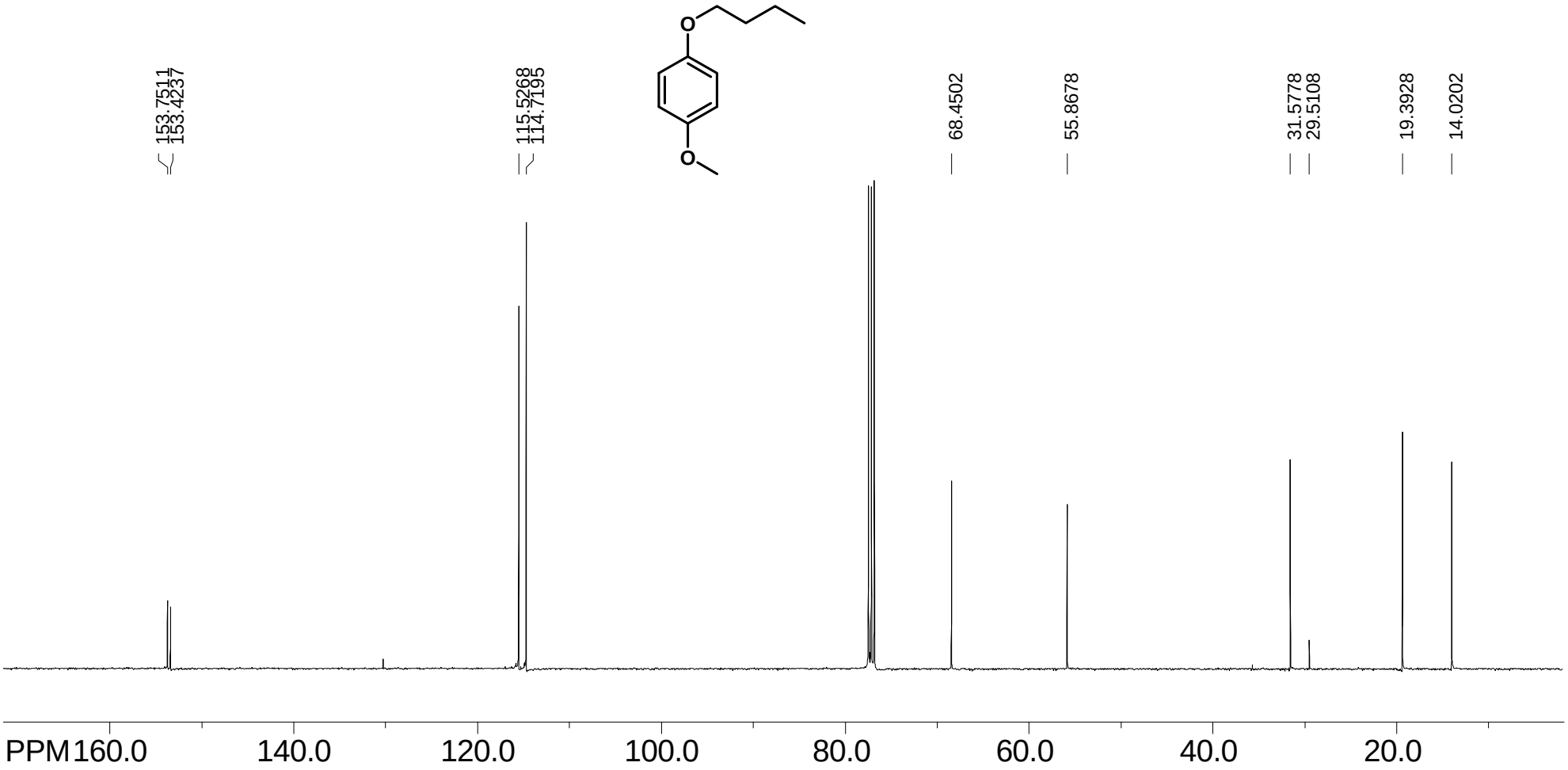

Figure S25. ^{13}C NMR spectrum of 1-butoxy-4-methoxybenzene ($CDCl_3$)

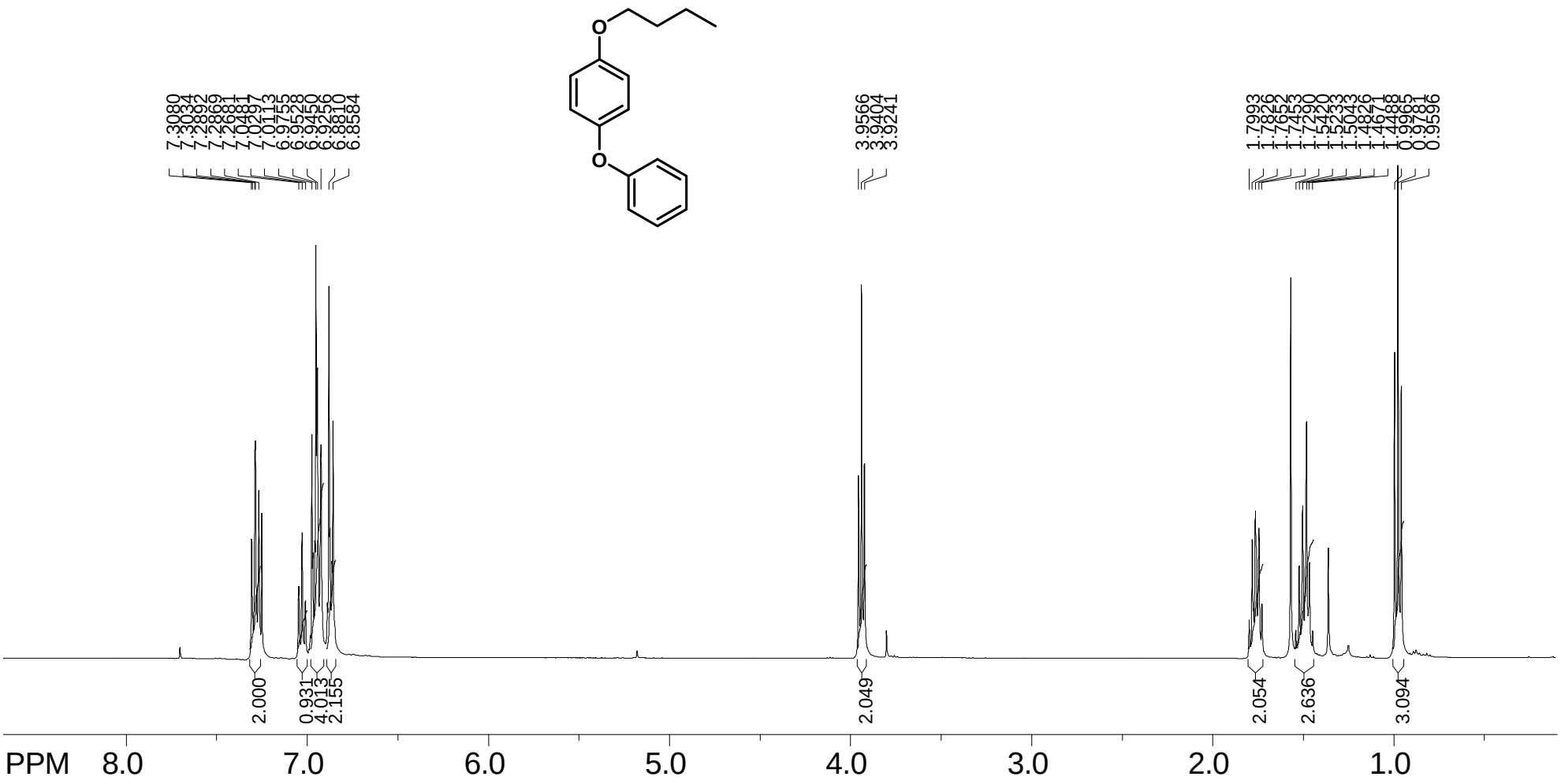

Figure S26. ^{1}H NMR spectrum of 1-butoxy-4-phenoxybenzene ($CDCl_3$)

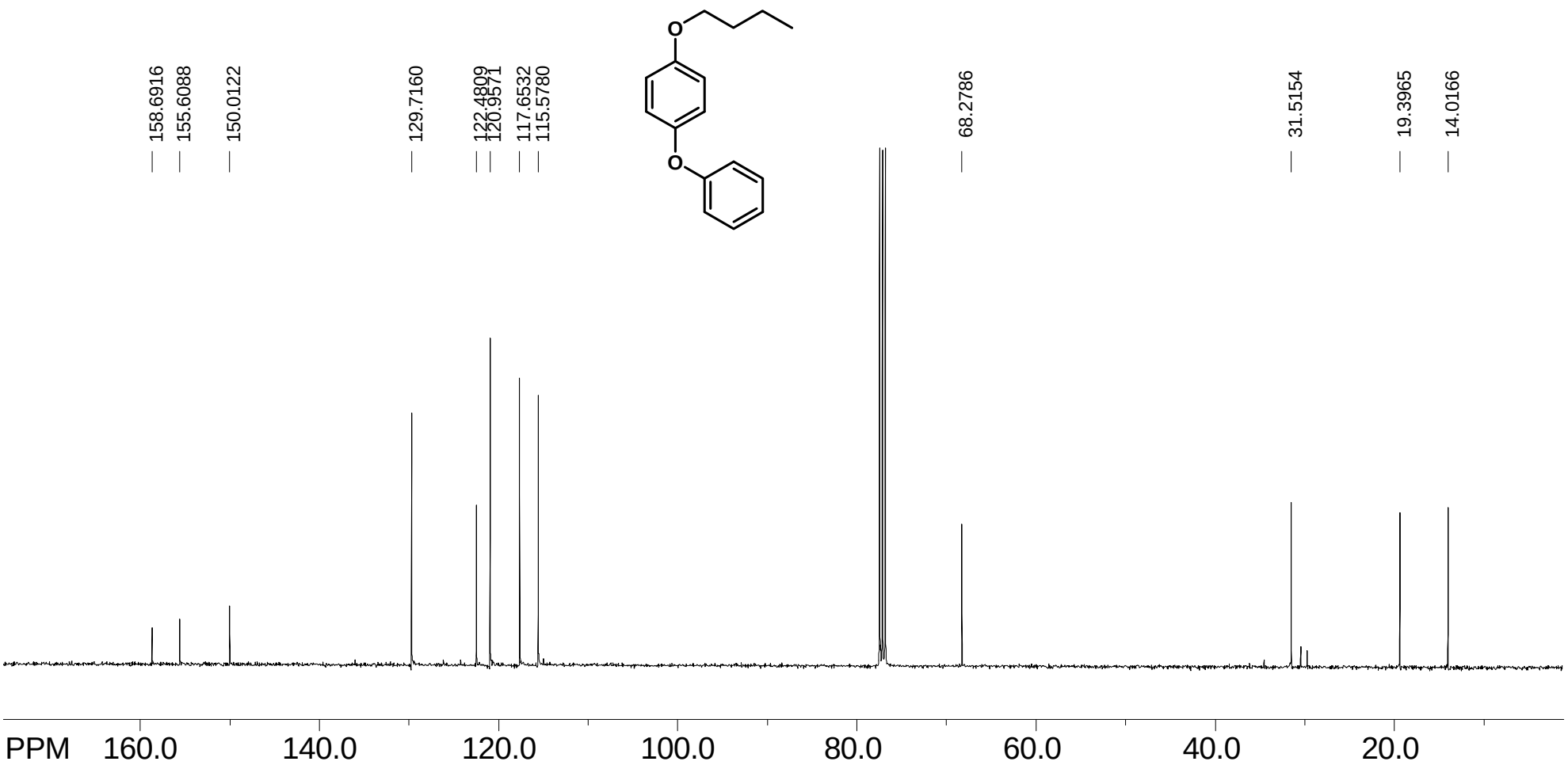

Figure S27. ^{13}C NMR spectrum of 1-butoxy-4-phenoxybenzene ($CDCl_3$)

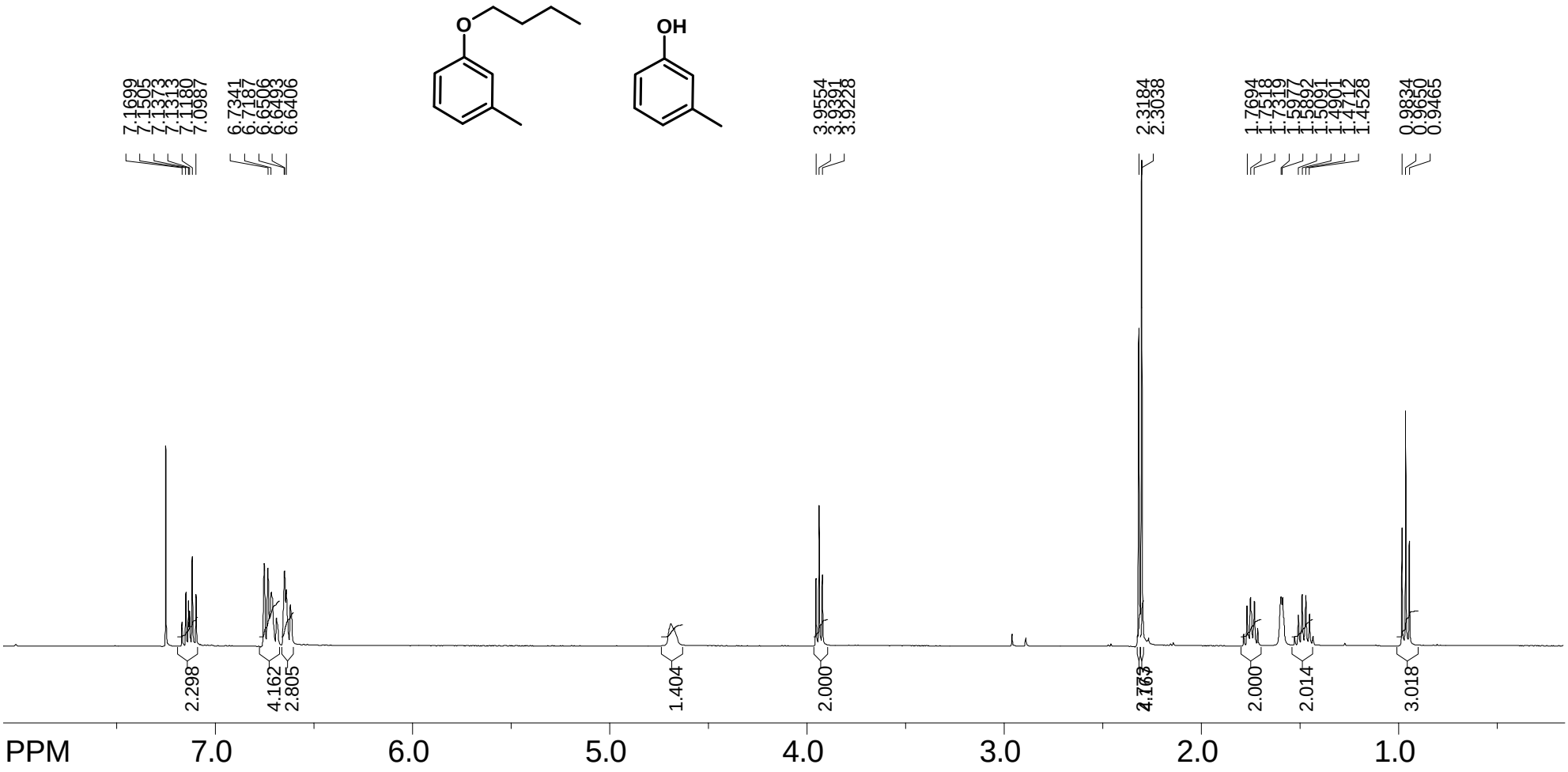

Figure S28. ^{1}H NMR spectrum of the mixture; product 1-butoxy-3-methylbenzene and unreacted *m*-cresol ($CDCl_3$)

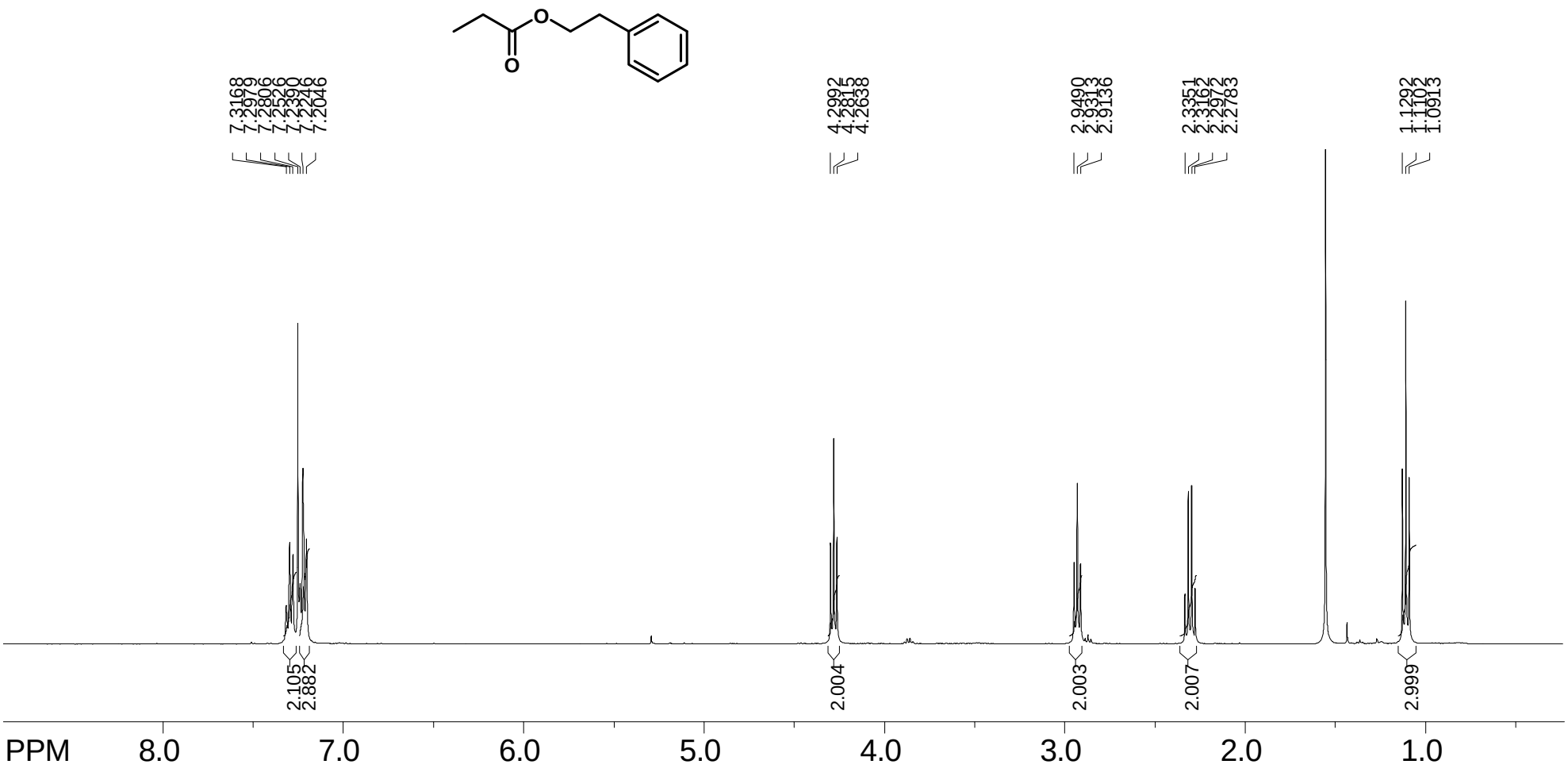

Figure S29. ^{1}H NMR spectrum of propionic acid 2-phenylethyl ester ($CDCl_3$)

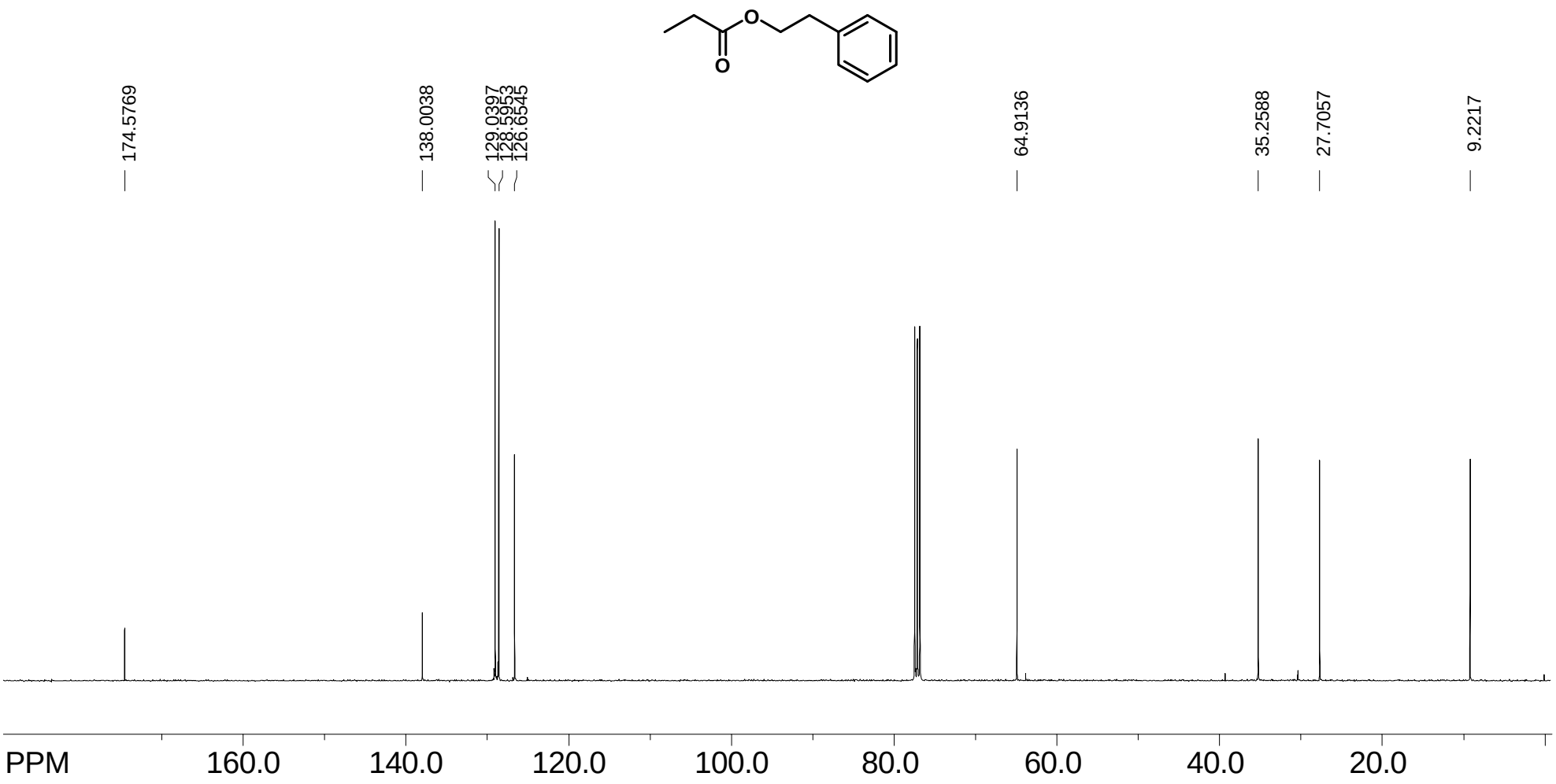

Figure S30. ^{13}C NMR spectrum of propionic acid 2-phenylethyl ester ($CDCl_3$)

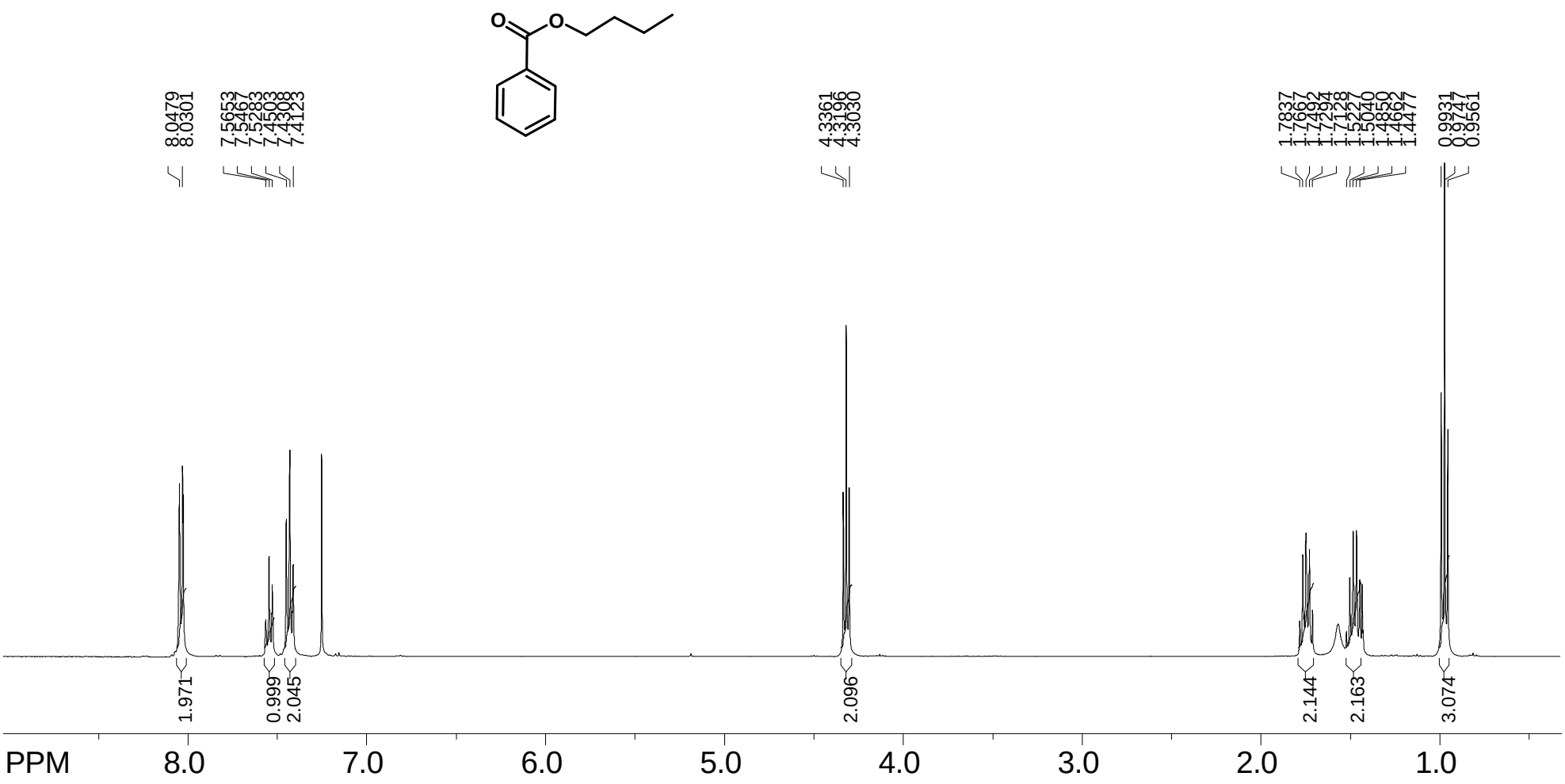

Figure S31. ^{1}H NMR spectrum of benzoic acid butyl ester ($CDCl_3$)

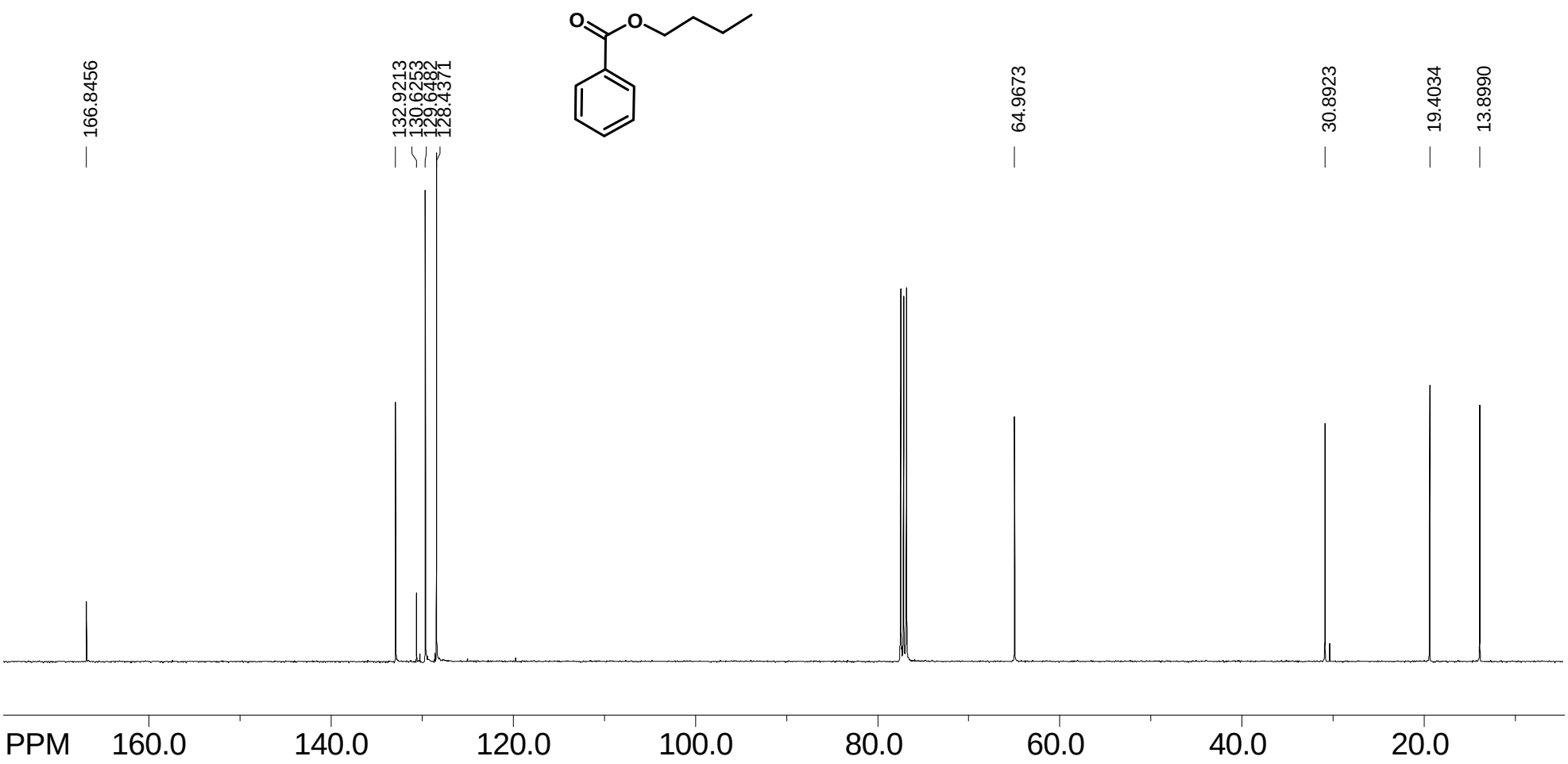

Figure S32. ^{13}C NMR spectrum of benzoic acid butyl ester ($CDCl_3$)

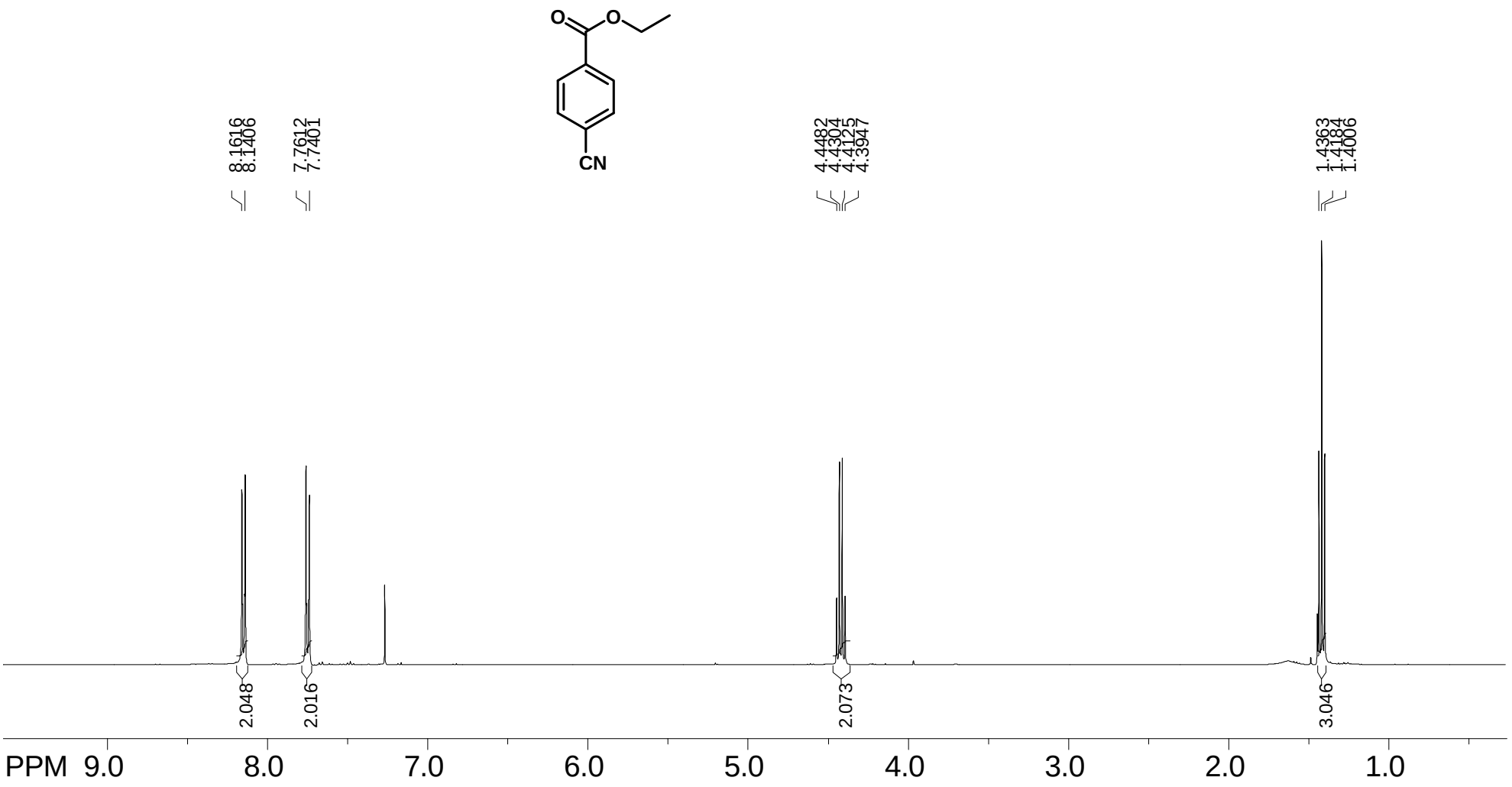

Figure S33. ^{1}H NMR spectrum of 4-cyanobenzoic acid ethyl ester ($CDCl_3$)

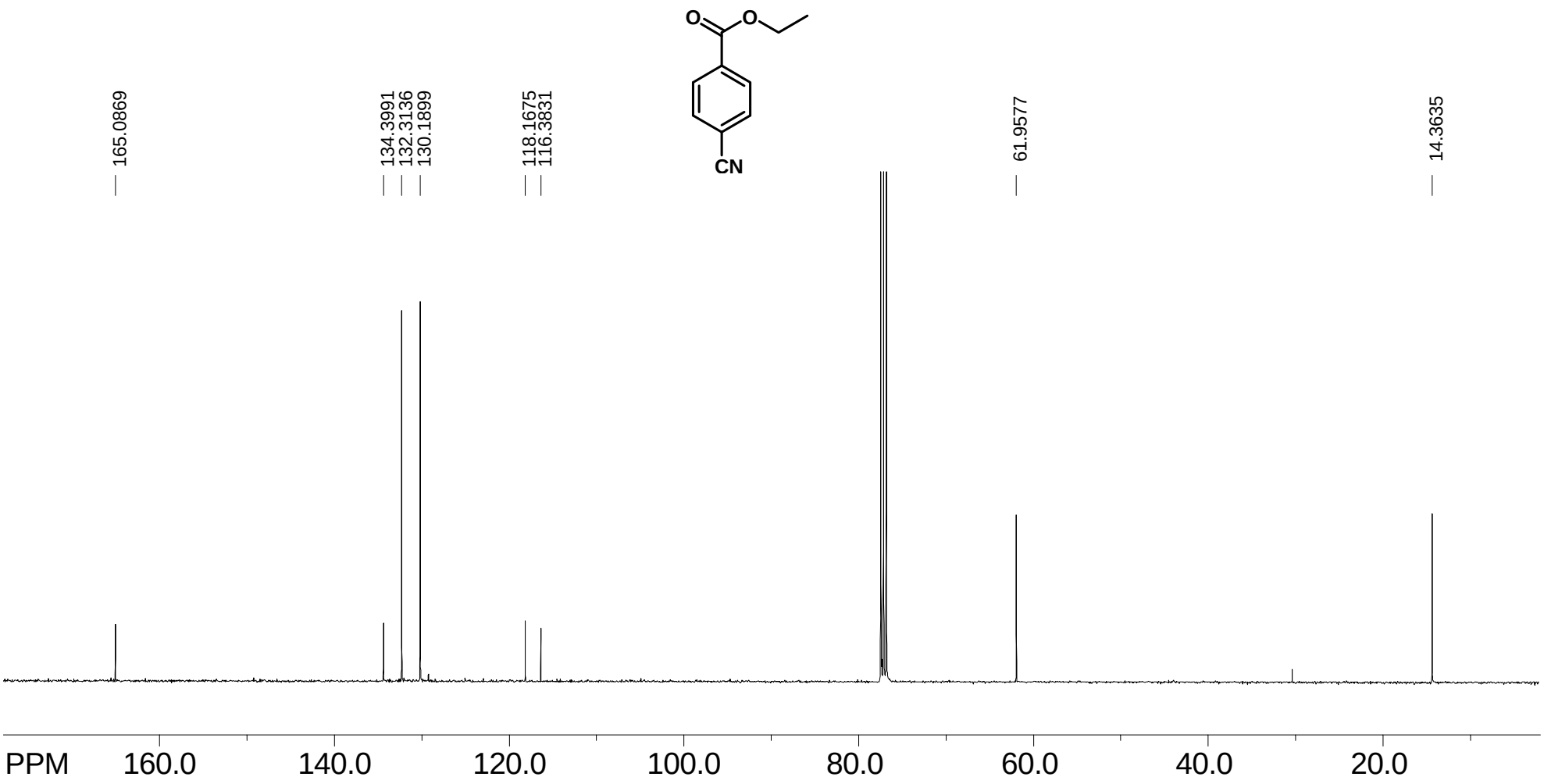

Figure S34. ^{13}C NMR spectrum of 4-cyanobenzoic acid ethyl ester ($CDCl_3$)

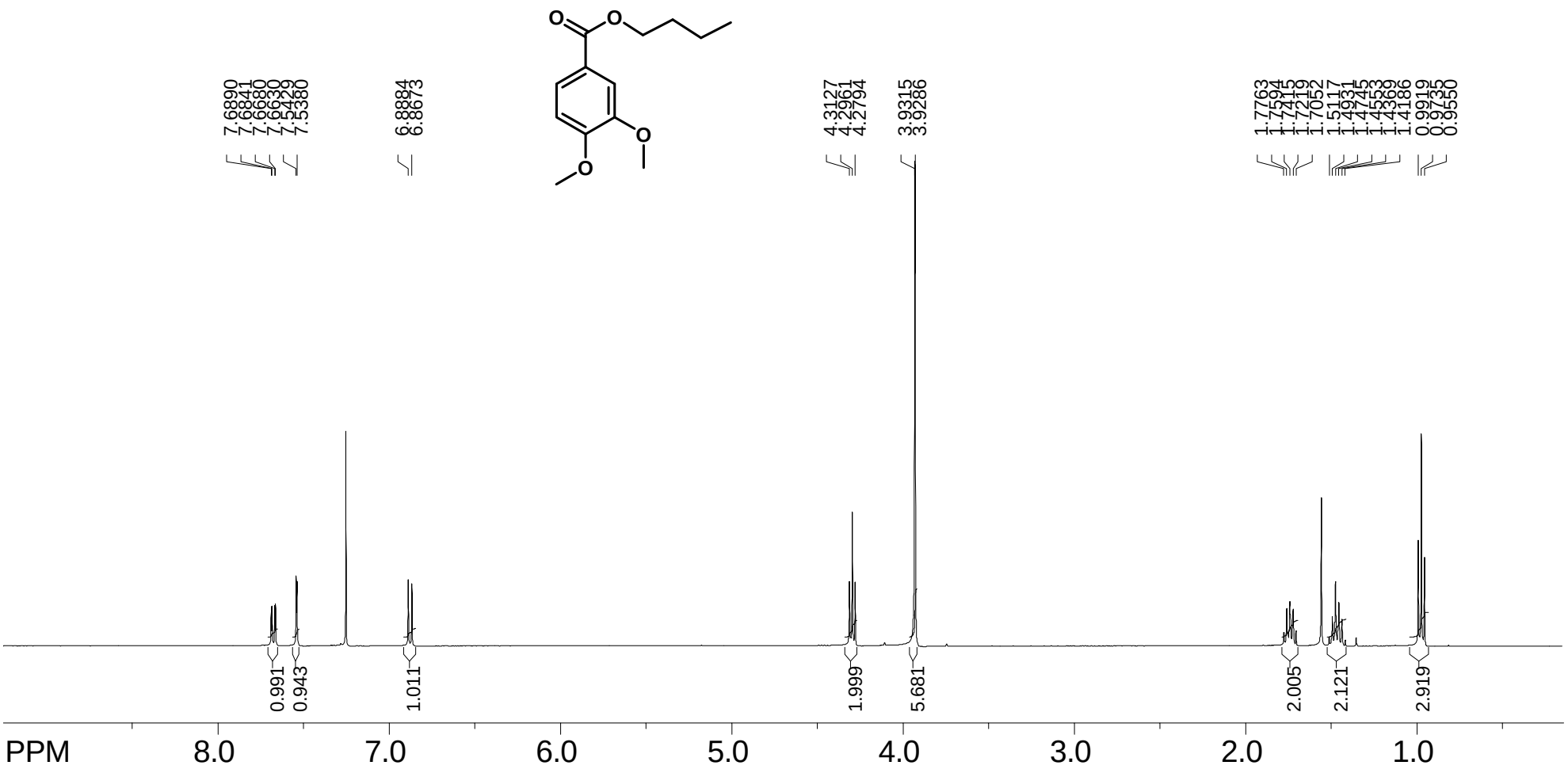

Figure S35. ^{1}H NMR spectrum of 3,4-dimethoxybenzoic acid butyl ester ($CDCl_3$)

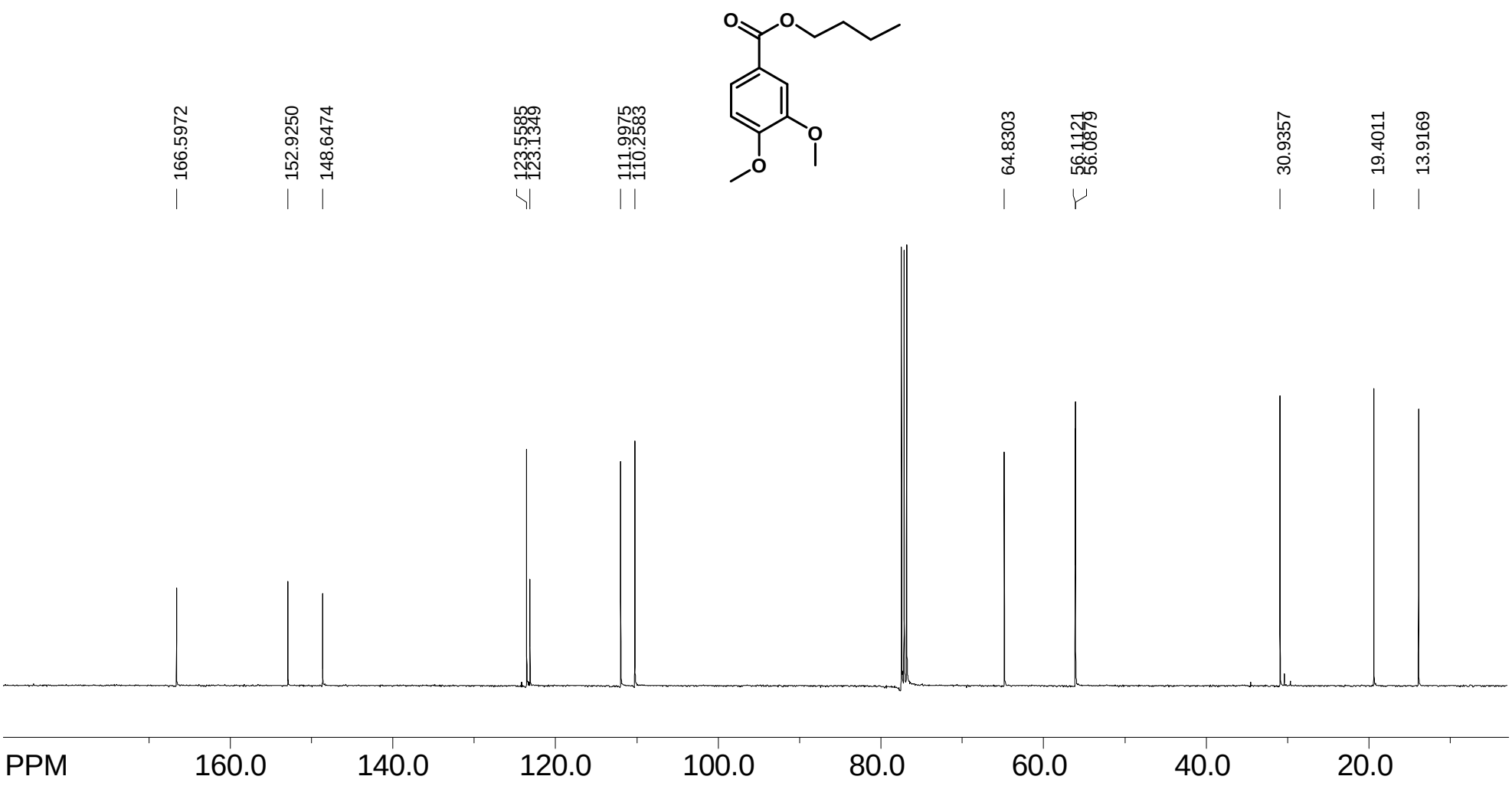

Figure S36. ^{13}C NMR spectrum of 3,4-dimethoxybenzoic acid butyl ester ($CDCl_3$)

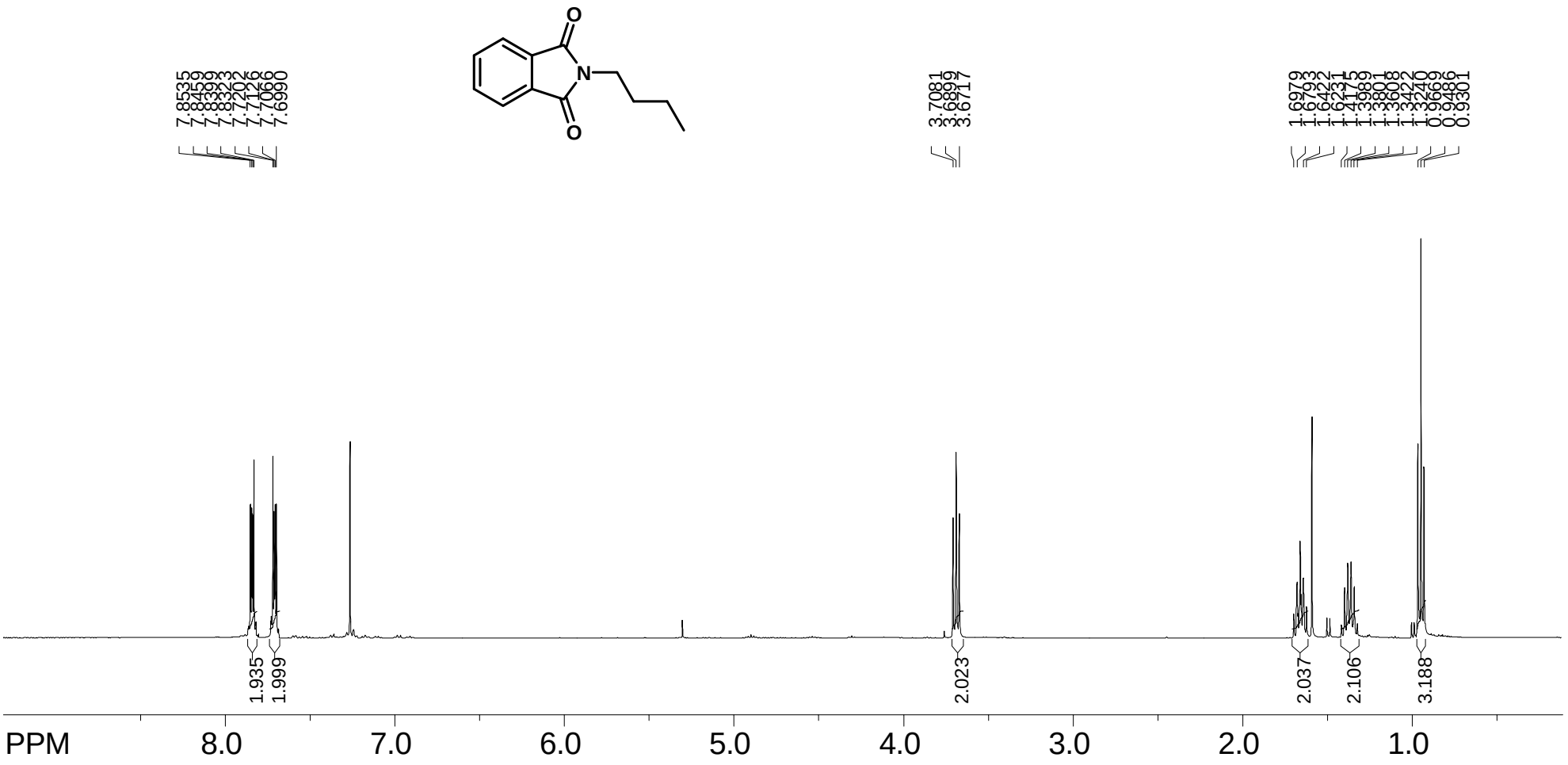

Figure S37. ^{1}H NMR spectrum of *N*-butylphthalimide ($CDCl_3$)

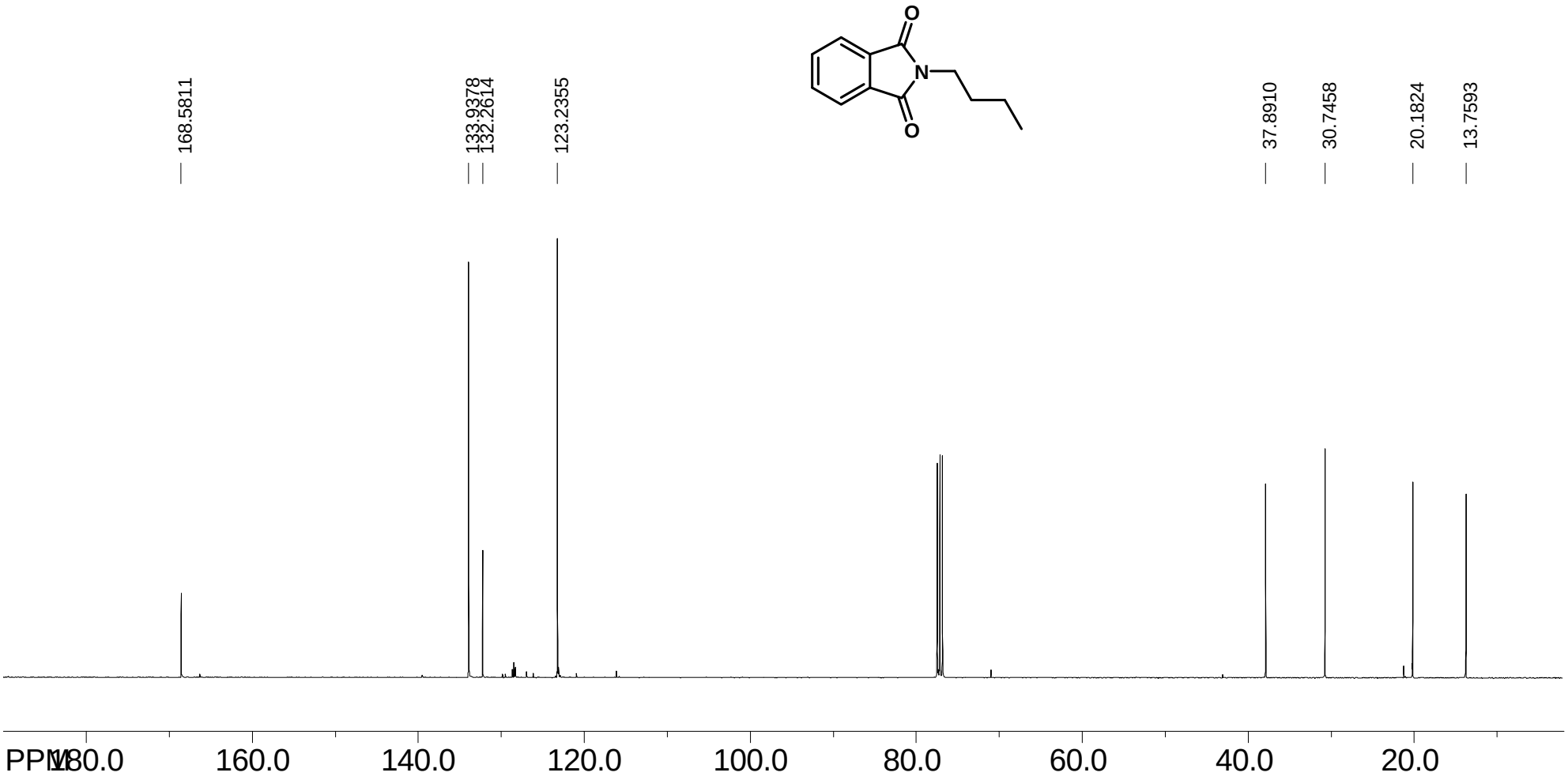

Figure S38. ^{13}C NMR spectrum of *N*-butylphthalimide ($CDCl_3$)

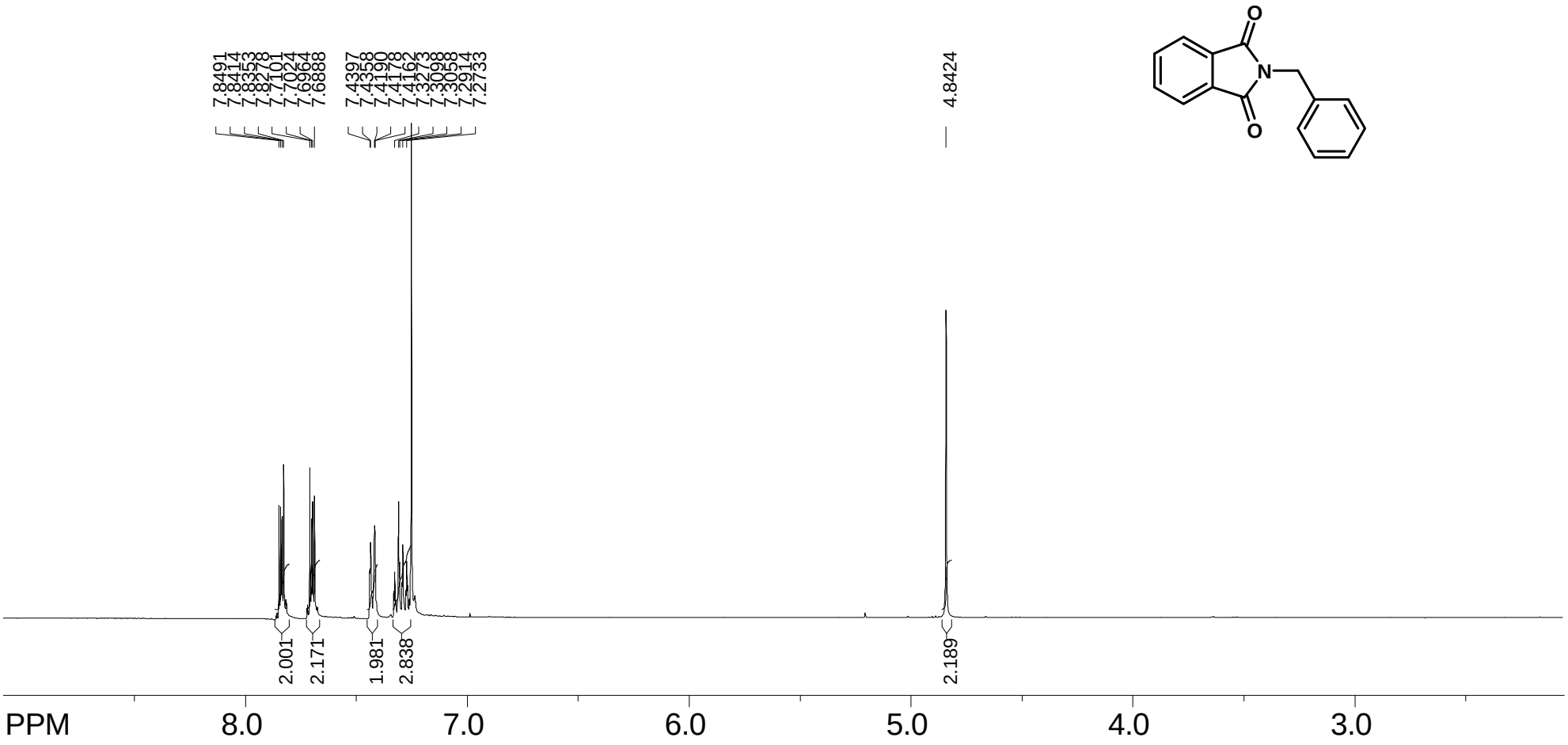

Figure S39. ^{1}H NMR spectrum of *N*-benzylphthalimide ($CDCl_3$)

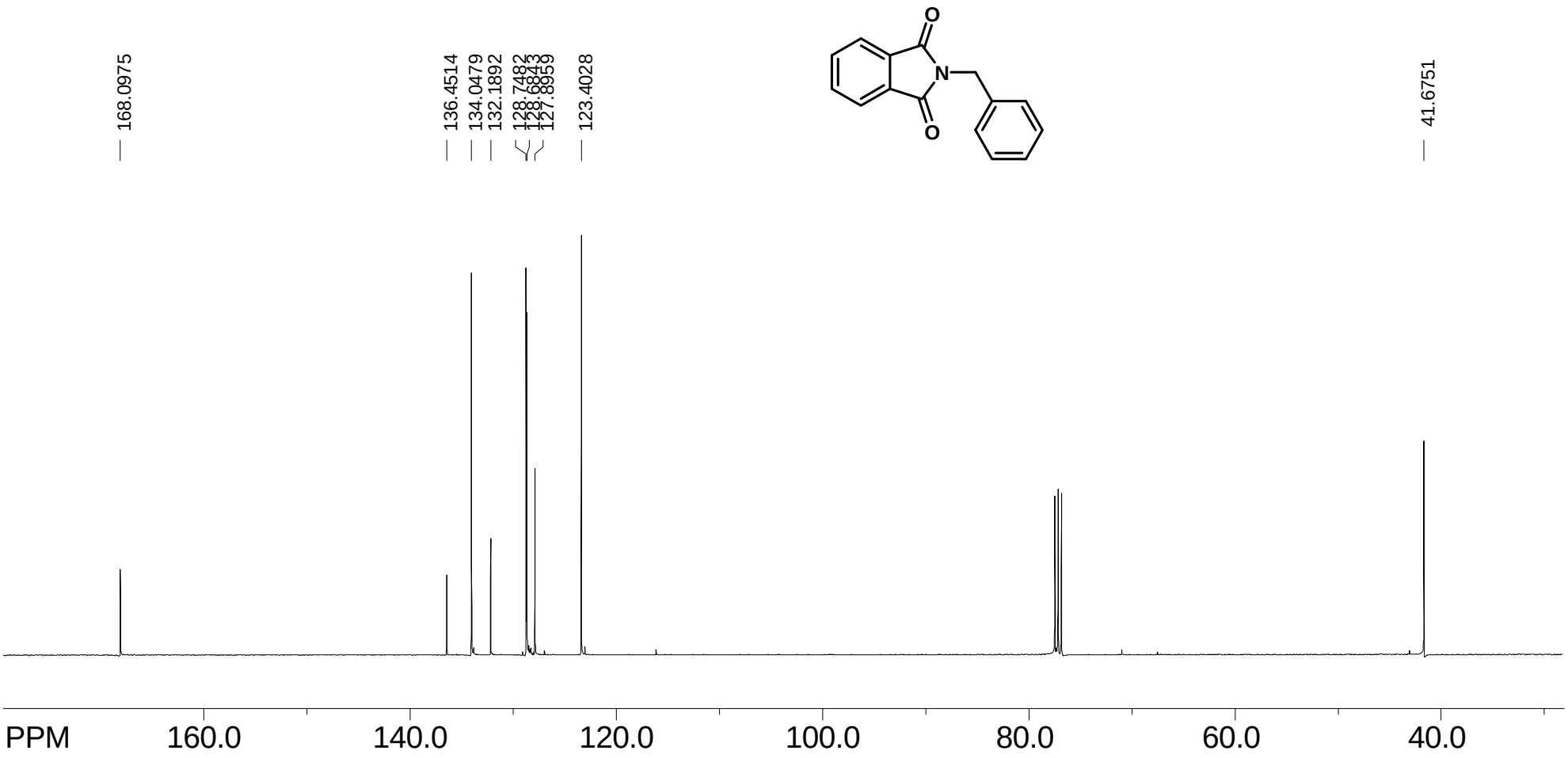

Figure S40. ^{13}C NMR spectrum of *N*-benzylphthalimide ($CDCl_3$)

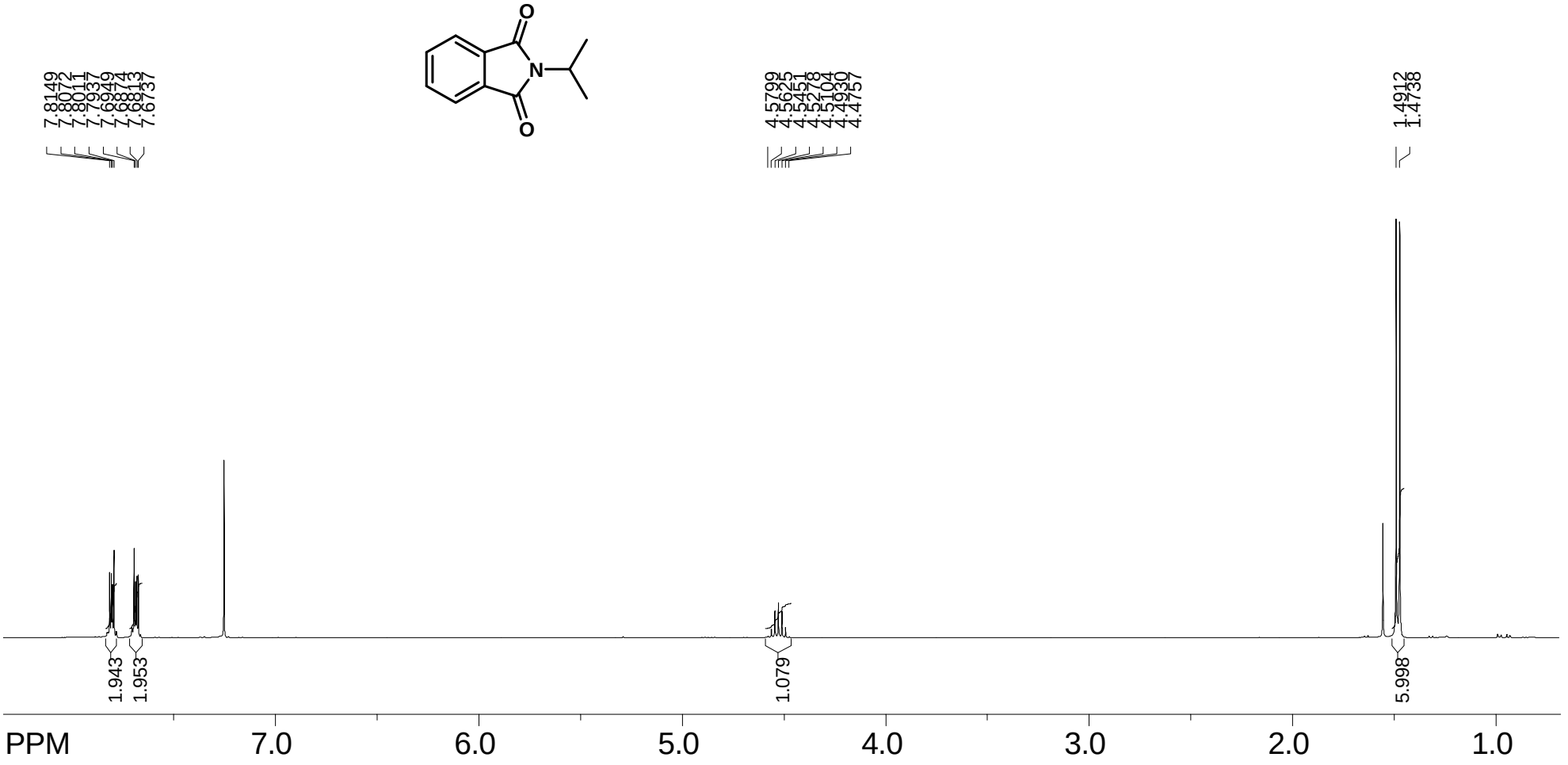

Figure S41. ^{1}H NMR spectrum of *N*-isopropylphthalimide ($CDCl_3$)

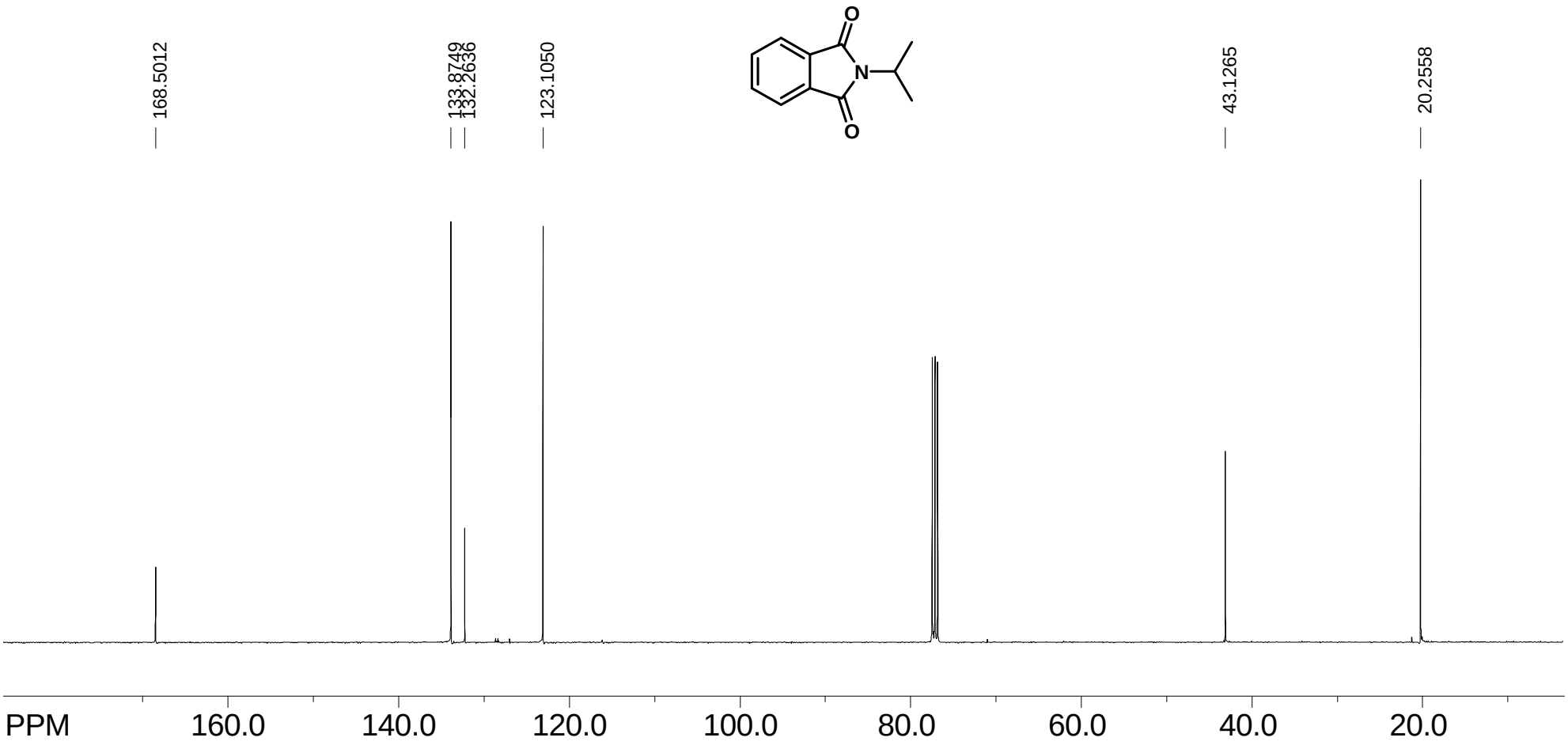

Figure S42. ^{1}H NMR spectrum of *N*-isopropylphthalimide ($CDCl_3$)

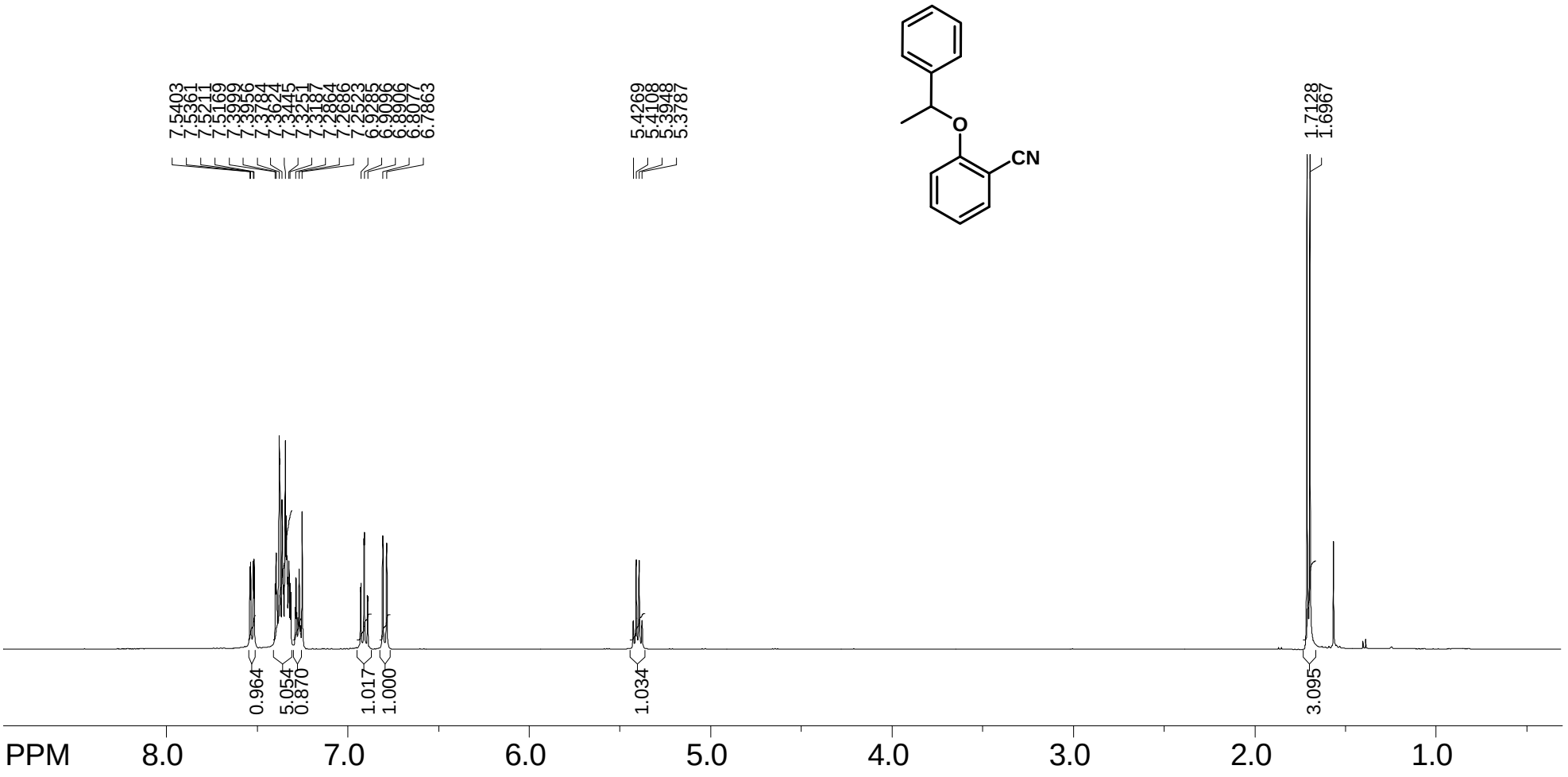

Figure S43. ^{1}H NMR spectrum of 2-(1-phenylethoxy)benzonitrile ($CDCl_3$)

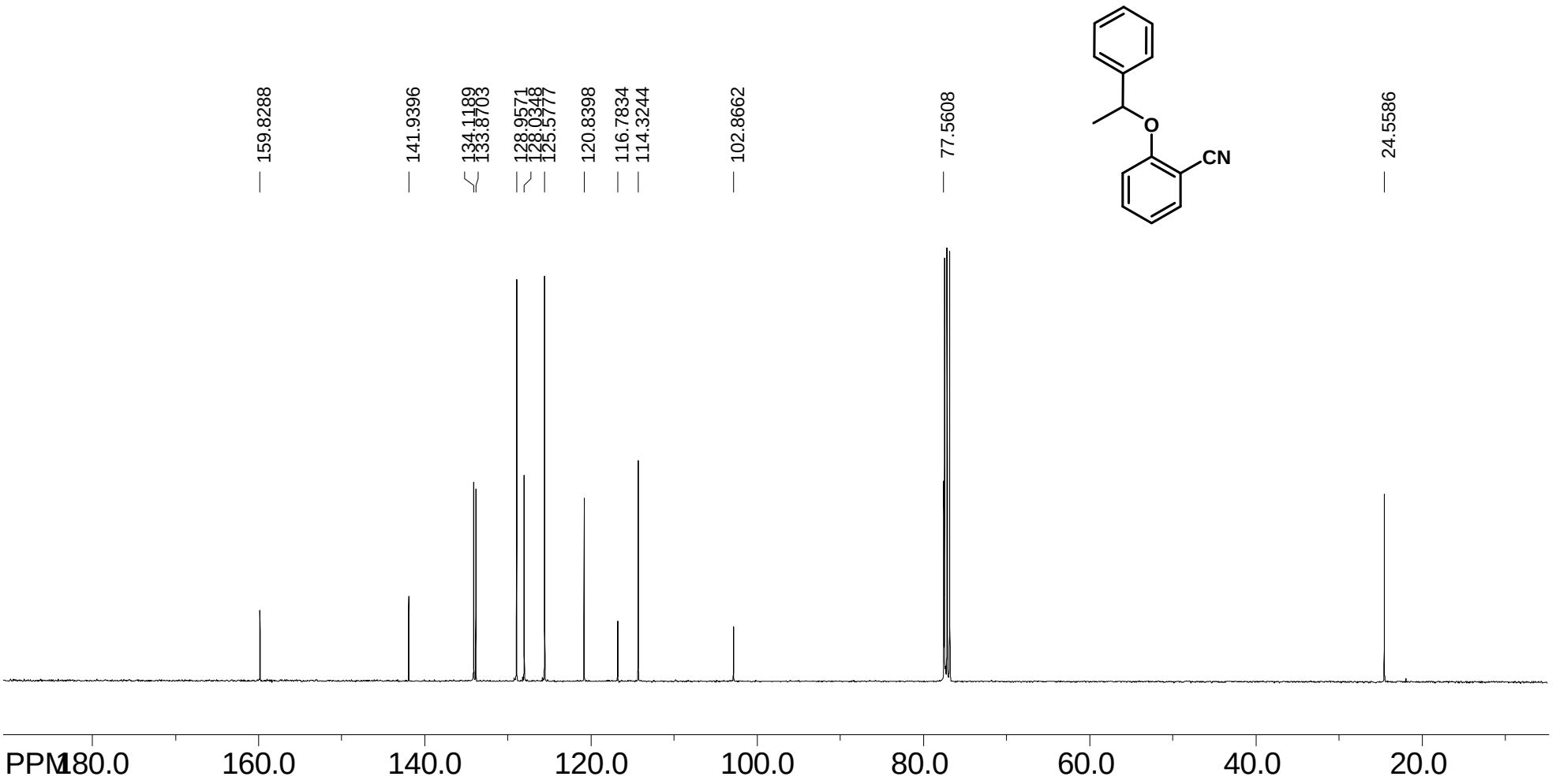

Figure S44. ^{1}H NMR spectrum of 2-(1-phenylethoxy)benzonitrile ($CDCl_3$)