Photoinduced Arylation of Chloroarenes in Flow: Synthesis of Unsymmetrical Biaryls

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Supporting Information

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General Information

All reactions were conducted under air if not specifically stated. Solvent acetonitrile was purified by passing through activated alumina with a commercial solvent purification system. Other solvents (ACS grade) and commercially available reagents were used as received with no further purification. Thin layer chromatography (TLC) analysis with silica gel 60 Å F254 plates and visualized by 254 nm UV lamp. Flash chromatography was performed on 230-400 mesh silica gel with indicated eluents. The photoflow reactor was made of coiled FEP tubing and a germicidal UV lamp (G10T8; 10 W); one layer of FEP tubing (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) was wrapped around a quartz cylinder (4.5 mm O.D., 4.0 mm I.D), and the germicidal UV lamp was placed at the center of the quartz cylinder. The germicidal UV lamps (G10T8; 10 W) were purchased from SANKYO DENKI Co. [Warning: Germicidal UV lamps pose imminent danger if used without taking the proper precautions] Fluorinated ethylene propylene (FEP) tubing was purchased from mK Company Ltd. Syringe pumps (NE-1000) were purchased from New Era Pump System. Nuclear Magnetic resonance (NMR) spectra were recorded on Agilent 400-MR DD2 (400 MHz) in indicated deuterated solvents. Chemical shifts were recorded in ppm relative to residual non-deuterated solvent (δ 7.26 ppm for ^{1}H NMR and 77.16 for ^{13}C NMR in $CDCl_3$). Coupling constants were recorded in hertz (Hz) and multiplicities were abbreviated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad). IR spectra were recorded on Thermo Nicolet iS5 FT-IR spectrometer with ATR sampling technique and were reported in wave number (cm^{-1}). High-resolution mass spectroscopy was performed on TOF instrument with EI and ESI.

Experimental Procedures and Characterization Data

General Procedure A (Phenylation of Electron-rich Chloroarenes): The aryl chloride (0.2 mmol) was dissolved in a cosolvent mixture of benzene and 2,2,2-trifluoroethanol (20 mL; v/v = 1/1). The syringe pump was used to deliver the resultant solution to the photoflow reactor (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) covered by aluminum foil. The flow rates were determined based on the indicated residence time. When the initial 4.0 mL of reaction solution had expelled, a sample of photosylate (12.5 mL) was collected and concentrated under reduced pressure. The resultant residual was purified by flash chromatography (hexanes/EtOAc) to give the corresponding biphenyl products.

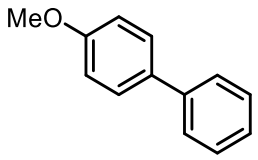
General Procedure B (Phenylation of Electron-deficient Chloroarenes): The aryl chloride (0.2 mmol) and tetrabutylammonium iodide (TBAI; 15 mol%, 0.03 mmol, 11 mg) was dissolved in a cosolvent mixture of benzene and acetone (20 mL; v/v = 4/1). The syringe pump was used to deliver the resultant solution to the photoflow reactor (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) covered by aluminum foil. The flow rates were determined based on the indicated residence time. When the initial 4.0 mL of reaction solution had expelled, a sample of photosylate (12.5 mL) was collected and concentrated under reduced pressure. The resultant residual was purified by flash chromatography (hexanes/EtOAc) to give the corresponding biphenyl products.

General Procedure C (Arylation of Electron-rich Chloroarenes with Polysubstituted Benzenes): The aryl chloride (0.3 mmol) and the polysubstituted benzenes (6.0 mmol) was dissolved in 2,2,2-trifluoroethanol (30 mL). The syringe pump was used to deliver the resultant solution to the photoflow reactor (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) covered by aluminum foil. The residence time was 10 minutues. When the initial 3.0 mL of reaction solution had expelled, a sample of

photosylate (25 mL) was collected and concentrated under reduced pressure. The resultant residual was purified by flash chromatography (hexanes/EtOAc) to give the corresponding biphenyl products.

General Procedure D (Arylation of Electron-deficient Chloroarenes with Polysubstituted Benzenes): The aryl chloride (0.2 mmol), the polysubstituted benzenes (4.0 mmol) and tetrabutylammonium iodide (TBAI; 15 mol%, 0.03 mmol, 11 mg) was dissolved in a cosolvent mixture of acetonitrile and acetone (20 mL; v/v = 4/1). The syringe pump was used to deliver the resultant solution to the photoflow reactor (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) covered by aluminum foil. The residence time was 20 minutes. When the initial 4.0 mL of reaction solution had expelled, a sample of photosylate (12.5 mL) was collected and concentrated under reduced pressure. The resultant residual was purified by flash chromatography (hexanes/EtOAc) to give the corresponding biphenyl products.

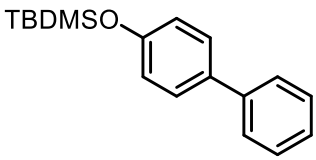
4-Methoxylbiphenyl (1a)[1]



1a

Following General Procedure A, 4-chloroanisole was used as the starting material, and the residence time was 10 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1a** (21 mg, 93%) as white solid. R_f: 0.3 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.57-7.53 (m, 4H), 7.42-7.40 (m, 2H), 7.33-7.29 (m, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 3.86 (s, 3H).

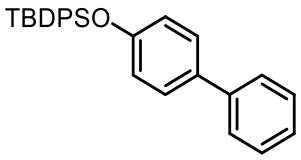
4-(*tert*-Butyldimethylsiloxy)biphenyl (1b)[2]



1b

Following General Procedure A, 1-(*tert*-butyldimethylsilyloxy)-4-chlorobenzene was used as the starting material, and the residence time was 30 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1b** (28 mg, 83%) as white solid. R_f : 0.4 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.56 (d, J = 7.3 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 7.42 (t, J = 7.3 Hz, 2H), 7.30 (t, J = 7.3 Hz, 1H), 6.92 (d, J = 8.5 Hz, 2H), 1.02 (s, 9H), 0.25 (s, 6H). **IR** (film): 2955, 2927, 2856, 1607, 1518, 1486, 1471, 1256, 1169, 915, 838, 807, 781, 763, 696 cm^{-1}.

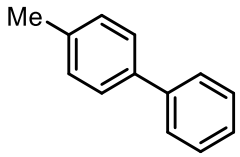
([1,1'-Biphenyl]-4-yloxy)(*tert*-butyl)diphenylsilane (1c)[3]



1c

Following General Procedure A, *tert*-butyl-4-chlorophenoxy-diphenylsilane was used as the starting material, and the retention time was 30 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1c** (25 mg, 52%) as white solid. R_f : 0.3 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.77 (m, 4H), 7.51-7.49 (m, 2H), 7.47 – 7.32 (m, 10H), 7.30 – 7.25 (m, 1H), 6.85 (d, J = 8.7 Hz, 2H), 1.14 (s, 9H).

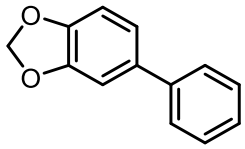
4-Methylbipheny (1d)[1]



1d

Following General Procedure A, 4-chlorotoluene was used as the starting material, and the residence time was 10 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1d** (11 mg, 50%) as white solid. R_f: 0.4 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.62-7.57 (m, 2H), 7.53-7.49 (m, 2H), 7.48-7.40 (m, 2H), 7.37-7.32 (m, 1H), 7.29-7.26 (m, 2H), 2.42 (s, 3H).

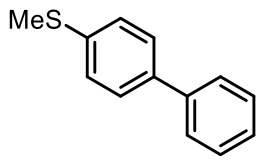
5-Phenyl-1,3-benzodioxole (1e)[4]



1e

Following General Procedure A, 5-chloro-1,3-benzodioxole was used as the starting material, and the residence time was 10 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1e** (23 mg, 95%) as white solid. R_f: 0.2 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.57 (d, J = 7.6 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.36 (t, J = 7.6 Hz, 1H), 7.15 – 7.08 (m, 2H), 6.93 (d, J = 8.0 Hz, 1H), 6.02 (s, 2H).

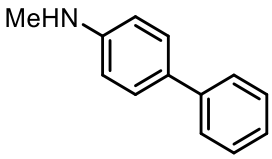
4-Phenylthioanisole (1f)[5]



1f

Following General Procedure A, 4-chlorophenyl methyl sulfide was used as the starting material, and the residence time was 10 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1f** (24 mg, 99%) as yellow solid. R_f : 0.3 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.44 (m, 2H), 7.35 (m,3H), 2.53 (s, 3H).

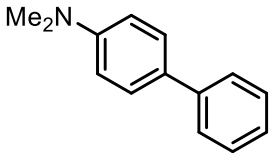
***N*-Methyl-4-phenylaniline (1g)**[6]



1g

Following General Procedure A, 4-chloro-*N*-methylaniline was used as the starting material, and the residence time was 10 minutes. The crude product was purified by flash column chromatography (hexanes to hexane/EtOAc = 4/1) furnishing **1g** (12 mg, 55%) as white solid. R_f : 0.5 (hexanes/ EtOAc = 4/1). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.56 (d, J = 7.6 Hz, 2H), 7.47 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 7.6 Hz, 2H), 7.26 (t, J = 7.6 Hz, 1H), 6.70 (d, J = 8.5 Hz, 2H), 2.82 (s, 3H).

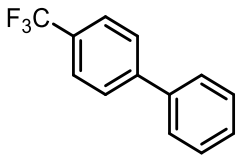
***N,N*-dimethyl-4-biphenylamine (1h)**[7]



1h

Following General Procedure A, 4-chloro-*N,N*-dimethylaniline was used as the starting material, and the residence time was 10 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1h** (24 mg, 99%) as white solid. R_f: 0.3 (hexane/ EtOAc = 20/1). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.3 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.29 – 7.23 (m, 1H), 6.82 (d, *J* = 8.7 Hz, 2H), 3.00 (s, 6H).

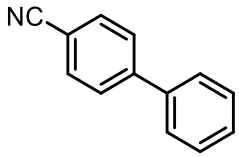
4-(Trifluoromethyl)-1,1'-biphenyl (1i)[8]



1i

Following General Procedure B, 4-chlorobenzotrifluoride was used as the starting material, and the residence time was 20 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1i** (22 mg, 80%) as white solid. (R_f: 0.5 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.70 (s, 4H), 7.61 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.3 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 1H).

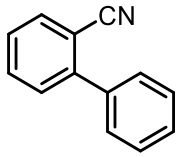
4-Cyanobiphenyl (1j)[8]



1j

Following General Procedure B, 4-chlorobenzonitrile was used as the starting material, and the residence time was 20 minutes. The crude product was purified by flash column chromatography (hexanes/EtOAc = 40/1 to hexanes/EtOAc = 25/1) furnishing **1j** (19 mg, 85%) as white solid. R_f: 0.2 (hexanes/ EtOAc = 20/1). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.49 (t, *J* = 7.4 Hz, 2H), 7.43 (m, 1H).

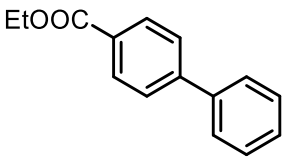
2-Cyanobiphenyl (1k)[9]



1k

Following General Procedure B (Note: 20 mol% of TBAI (15 mg) was added in this case), 2-chlorobenzonitrile was used as the starting material, and the residence time was 20 minutes. The crude product was purified by flash column chromatography (hexanes to hexanes/EtOAc = 4/1) furnishing **1k** (11 mg, 46%) as yellow solid. R_f: 0.4 (hexanes/ EtOAc = 4/1). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.77 (d, *J* = 9.0 Hz, 1H), 7.65 (m, 1H), 7.60 – 7.41 (m, 7H).

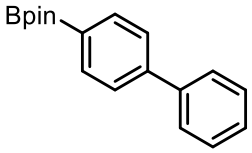
Ethyl 4-phenylbenzoate (1l)[8]



1l

Following General Procedure B, ethyl 4-chlorobenzoate was used as the starting material, and the residence time was 60 minutes. The crude product was purified by flash column chromatography (hexanes to hexanes/EtOAc = 30/1) furnishing **1l** (19 mg, 67%) as white solid. R_f : 0.3 (hexanes/ EtOAc = 20/1). **^{1}H NMR** (400MHz, $CDCl_3$): δ 8.12 (d, *J* = 8.5 Hz, 2H), 7.69 – 7.60 (m, 4H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.40 (t, *J* = 7.4 Hz, 1H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.42 (t, *J* = 7.1 Hz, 3H).

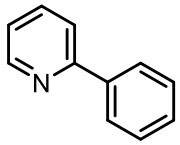
4-Biphenylboronic acid pinacol ester (1m)[10]



1m

Following General Procedure B, 4-chlorophenylboronic acid pinacol ester was used as the starting material, and the residence time was 30 minutes. The crude product was purified by flash column chromatography (hexanes to hexanes/EtOAc = 30/1) furnishing **1m** (24 mg, 68%) as white solid. R_f : 0.2 (hexanes/ EtOAc = 20/1). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.90 (d, J = 7.5 Hz, 2H), 7.68 – 7.59 (m, 4H), 7.45 (t, J = 7.5 Hz, 2H), 7.41 – 7.32 (m, 1H), 1.37 (s, 12H).

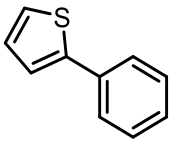
2-Phenylpyridine (1n)[11]



1n

Following General Procedure B, 2-chloropyridine was used as the starting material, and the residence time was 20 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1n** (6 mg, 28%) as white solid. R_f: 0.5 (hexanes). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.73 – 8.67 (m, 1H), 7.99 (d, J = 7.0 Hz, 2H), 7.78-7.71 (m, 2H), 7.52 – 7.45 (m, 2H), 7.45 – 7.39 (m, 1H), 7.23 (ddd, J = 6.5, 4.8, 2.0 Hz, 1H).

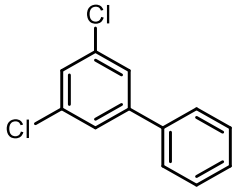
2-Phenylthiophene (1o)[12]



1o

Following General Procedure B (Note: 20 mol% of TBAI (15 mg) was added in this case), 2-chlorothiophene was used as the starting material, and the residence time was 20 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1o** (11 mg, 56%) as yellow solid. R_f : 0.5 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.68 – 7.63 (m, 2H), 7.44 – 7.27 (m, 5H), 7.10 (dd, J = 5.1, 3.6 Hz, 1H).

3,5-Dichlorobiphenyl (1p)[13]

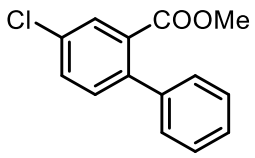


1p

Following General Procedure A, 1,3,5-trichlorobenzene was used as the starting

material, and the residence time was 20 minutes. The crude product was purified by flash column chromatography (hexanes) furnishing **1p** (26 mg, 94%) as white solid. R_f: 0.4 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.56 – 7.52 (m, 2H), 7.49 – 7.43 (m, 4H), 7.43 – 7.39 (m, 1H), 7.34 (t, *J* = 1.9 Hz, 1H).

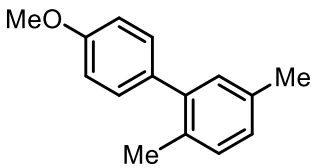
Methyl 4-chloro-[1,1'-biphenyl]-2-carboxylate (1q)[14]



1q

Following General Procedure B, methyl 2,5-dichlorobenzoate was used as the starting material, and the residence time was 40 minutes. The crude product was purified by flash column chromatography (hexanes to hexanes/EtOAc = 30/1) furnishing **1q** (23 mg, 73%) as white solid. R_f: 0.2 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.81 (d, *J* = 2.3 Hz, 1H), 7.48 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.42 – 7.34 (m, 3H), 7.30 (d, *J* = 8.3, 1H), 7.28 – 7.23 (m, 2H), 3.63 (s, 3H).

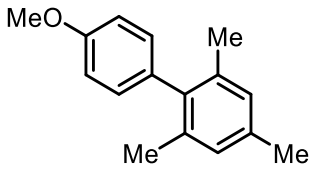
4'-Methoxy-2,5-dimethylbiphenyl (1r)[15]



1r

Following General Procedure C, 4-chloroanisole and *p*-xylene was used as the starting materials. The crude product was purified by flash column chromatography (hexanes) furnishing **1r** (52 mg, 97%) as yellow solid. R_f: 0.2 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.08 (m, 2H), 6.98 (m, 4H), 3.88 (s, 3H), 2.35 (s, 3H), 2.04 (s, 6H).

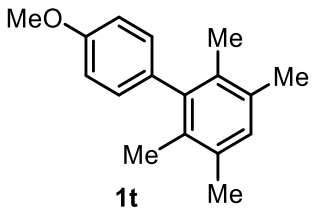
4-Mesitylanisole (1s)[16]



1s

Following General Procedure C, 4-chloroanisole and mesitylene were used as the starting materials. The crude product was purified by flash column chromatography (hexanes) furnishing **1s** (37 mg, 66%) as yellow solid. R_f : 0.2 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.08 (m, 2H), 7.18 (m, 4H), 3.88 (s, 3H), 2.35 (s, 3H), 2.04 (s, 6H).

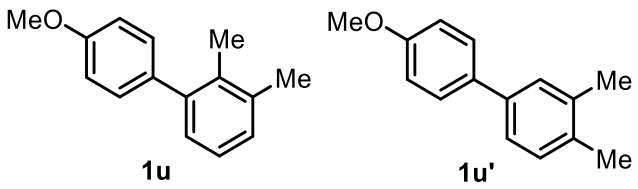
2,3,5,6-Tetramethyl-4'-methoxybiphenyl (1t)



1t

Following General Procedure C, 4-chloroanisole and 1,2,4,5-tetramethylbenzene were used as the starting materials. The crude product was purified by flash column chromatography (hexanes) furnishing **1t** (39 mg, 65%) as yellow solid. R_f : 0.2 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.05 – 7.01 (m, 2H), 7.00 (s, 1H), 6.97 (d, m Hz, 1H), 6.96 – 6.95 (m, 1H), 3.87 (s, 3H), 2.27 (s, 6H), 1.91 (s, 6H). **^{13}C** (100MHz, $CDCl_3$): δ 158.22, 141.86, 134.81, 133.59, 132.60, 130.48, 128.85, 113.82, 55.36, 20.37, 17.37. **IR** (film): 2935, 1608, 1574, 1509, 1464, 1382, 1284, 1243, 1175, 1104, 1036, 814, 778, 637, 581 cm^{-1}. **HRMS** (EI, $[M]^+$) for $C_{17}H_{20}O$ calcd. 240.1580, found 240.1587.

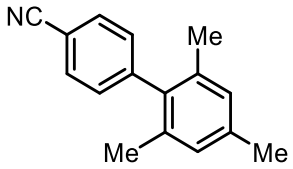
4'-Methoxy-2,3-dimethylbiphenyl (1u) and 4'-methoxy-3,4-dimethylbiphenyl (1u')[17]



1u **1u'**

Following General Procedure C, 4-chloroanisole and *o*-xylene were used as the starting materials. The crude product was purified by flash column chromatography (hexanes) giving an inseparable mixture of 4'-methoxy-2,3-dimethylbiphenyl (**1u**) and 4'-methoxy-3,4-dimethylbiphenyl (**1u'**) (42 mg, 80% combined yield; ratio = 1/1 as judged by ^{1}H NMR analysis) as yellow solid. R_f : 0.2 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$) for the mixture of **1u** and **1u'**: δ 7.56 – 7.51 (m, 2H), 7.37 – 7.26 (m, 3H), 7.25 – 7.08 (m, 5H), 7.02 – 6.95 (m, 4H), 3.88 (s, 3H), 3.87 (s, 3H), 2.36 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 2.19 (s, 3H).

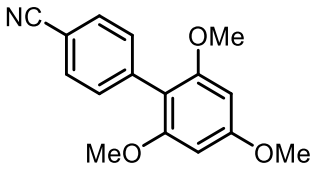
2',4',6'-Trimethyl-[1,1'-biphenyl]-4-carbonitrile (1v)[18]



1v

Following General Procedure D, 4-chlorobenzonitrile and mesitylene were used as the starting materials. The crude product was purified by flash column chromatography (hexanes) furnishing product **1v** (16 mg, 54%) as white solid. R_f : 0.2 (hexanes). **^{1}H** NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 8.3 Hz, 2H), 7.27 (d, J = 8.3 Hz, 2H), 6.95 (s, 2H), 2.34 (s, 3H), 1.97 (s, 6H).

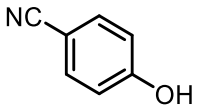
2',4',6'-Trimethoxy-[1,1'-biphenyl]-4-carbonitrile (1w)[19]



1w

Following General Procedure D, 4-chlorobenzonitrile and 1,3,5-trimethoxybenzene were used as the starting materials. The crude product was purified by flash column chromatography (hexanes) furnishing **1w** (18 mg, 52%) as white solid. R_f : 0.2 (hexanes). **^{1}H NMR** NMR (400 MHz, $CDCl_3$) δ7.64 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 6.22 (s, 2H), 3.87 (s, 3H), 3.73 (s, 6H).

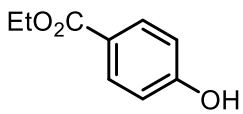
4-Cyanophenol (2a)[20]



2a

4-Chlorobenzonitrile (0.3 mmol, 41 mg), (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO; 0.3 mmol, 67 mg) and tetrabutylammonium iodide (TBAI; 15 mol%, 0.045 mmol, 17 mg) were dissolved in a cosolvent mixture of acetonitrile and acetone (30 mL; v/v = 4/1). The syringe pump was used to deliver the resultant solution to the photoflow reactor (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) covered by aluminum foil. The residence time was 10 minutes. When the initial 4.0 mL of reaction solution had expelled, a sample of photosylate (23.0 mL) was collected and concentrated under reduced pressure. The resultant residual was purified by flash chromatography (hexanes) furnishing **3a** (10 mg, 38%) as white solid. R_f: 0.1 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.56 (t, *J* = 8.8 Hz, 4H), 6.91 (t, *J* = 8.8 Hz, 2H), 5.67 (bs, 1H).

Ethyl parahydroxybenzoate (2b)[20]



2b

Ethyl 4-chlorobenzoate (0.3 mmol, 54 mg), (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO; 0.3 mmol, 67 mg) and tetrabutylammonium iodide (TBAI; 15 mol%, 0.045 mmol, 17 mg) were dissolved in a cosolvent mixture of acetonitrile and acetone (30 mL; v/v = 4/1). The syringe pump was used to deliver the resultant solution to the photoflow reactor (I.D. = 1.0 mm, 3.5 m in length; volume = 2.5 mL) covered by aluminum foil. The residence time was 20 minutes. When the initial 4.0 mL of reaction solution had expelled, a sample of photosylate (23.0 mL) was collected and concentrated under reduced pressure. The resultant residual was purified by flash chromatography (hexanes) furnishing **3b** (11 mg, 35%) as white solid. R_f: 0.1 (hexanes). **^{1}H NMR** (400MHz, $CDCl_3$): δ 7.96 (d, *J* = 8.7 Hz, 2H), 6.87 (d, *J* = 8.7 Hz, 2H), 5.89 (bs, 1H), 4.35 (q, *J* = 7.1 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

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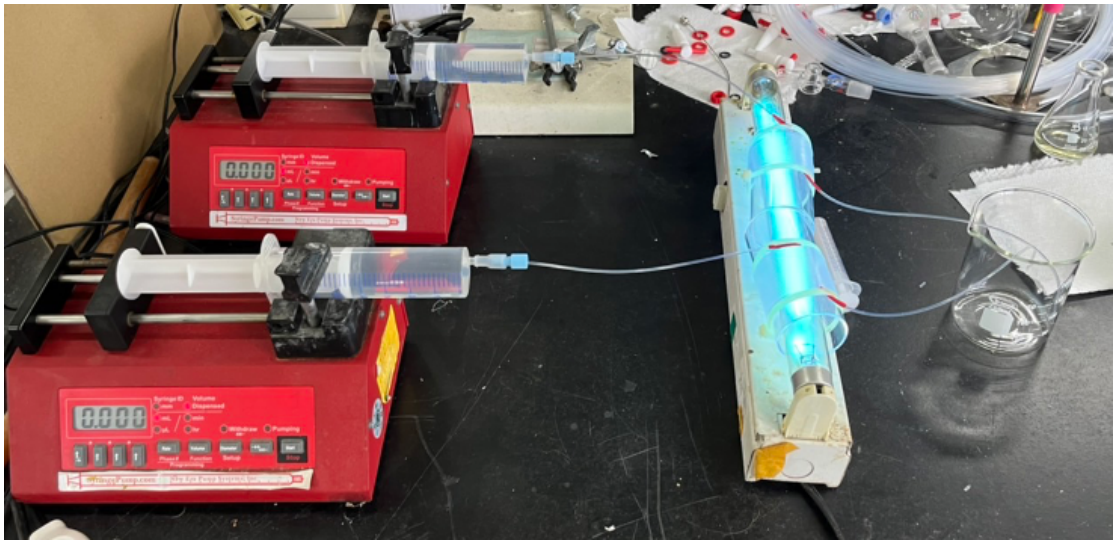
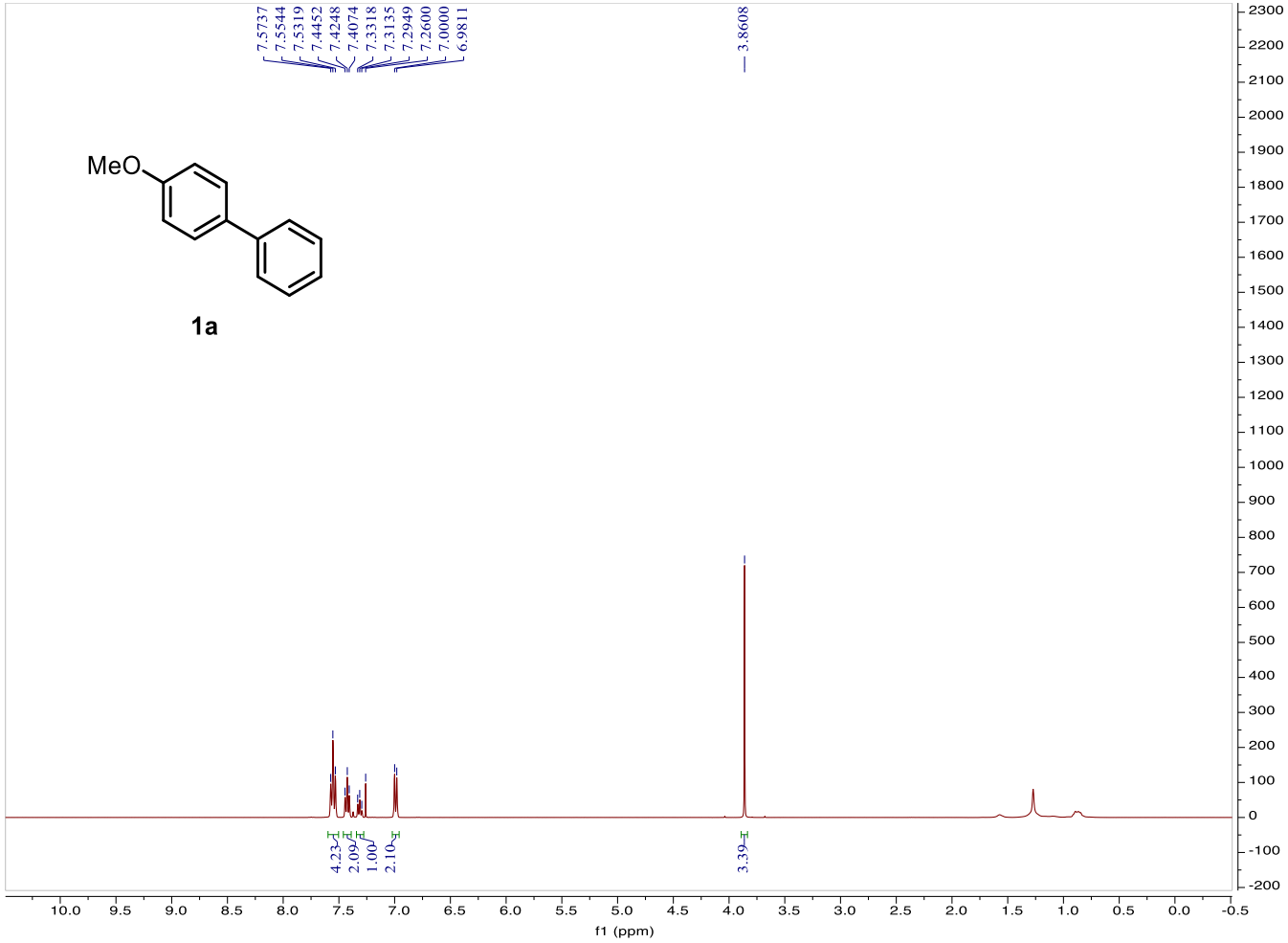
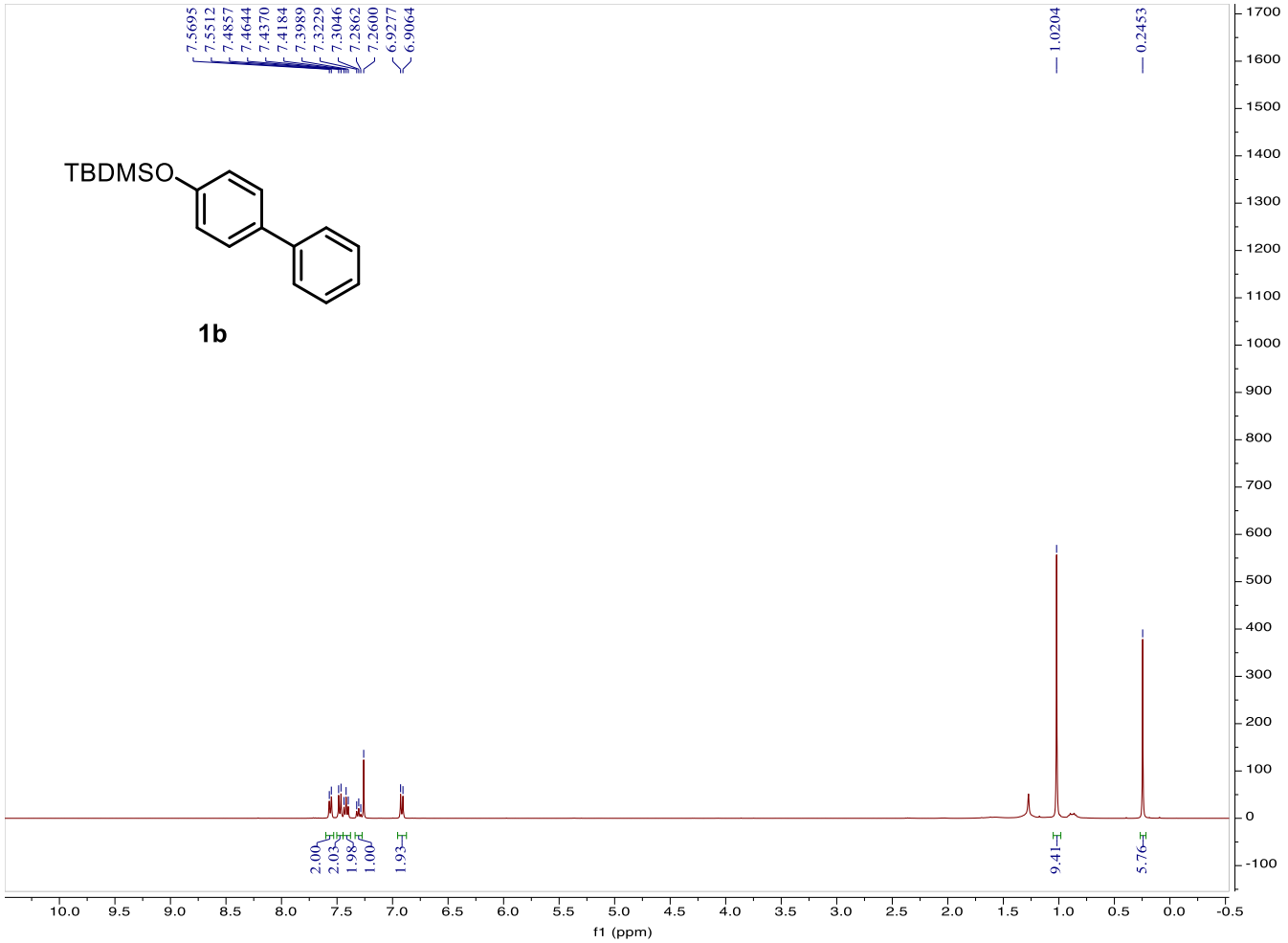
Figure S1. Synthesis of **1j** using two parallel flow reactors.

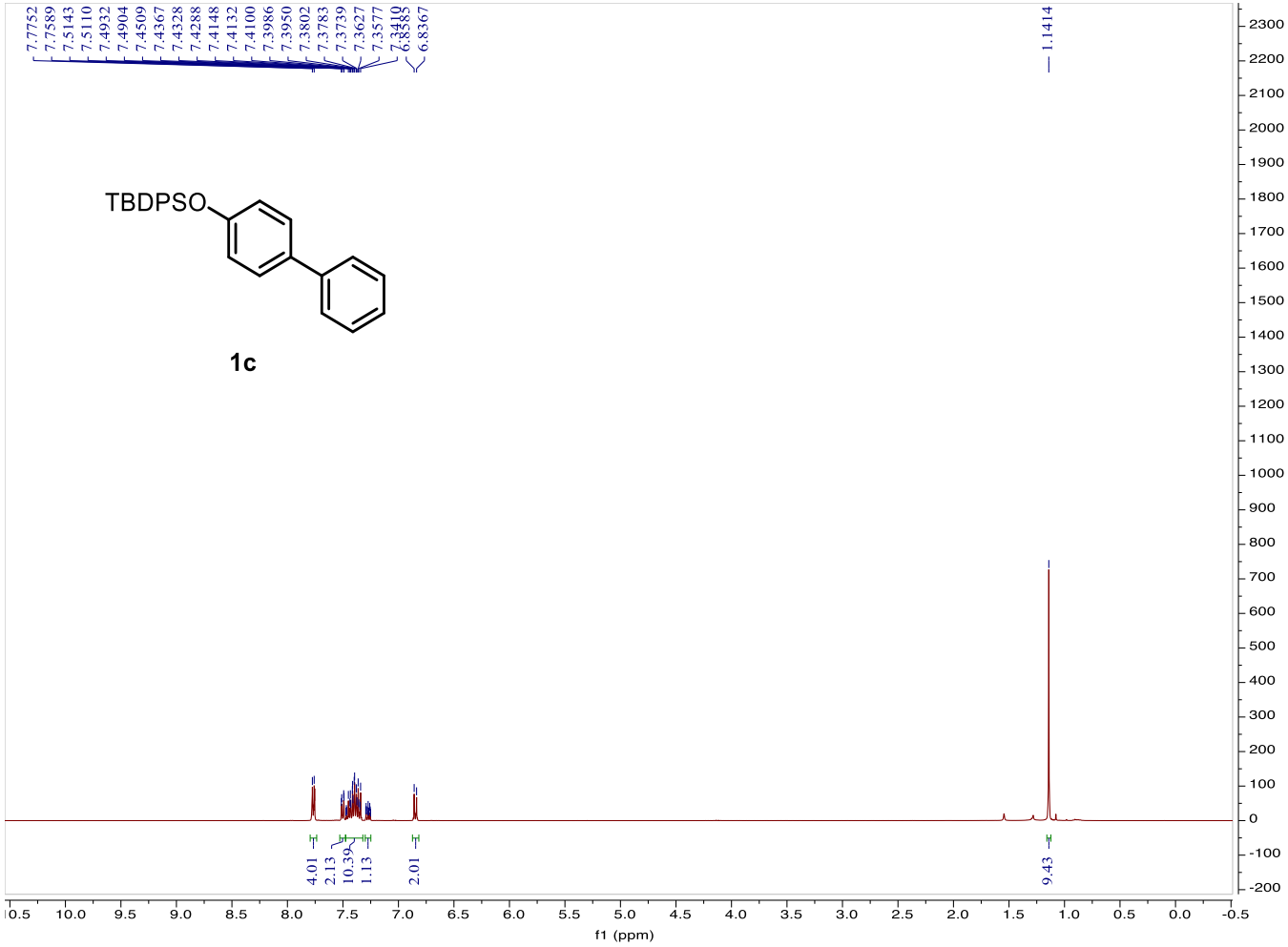




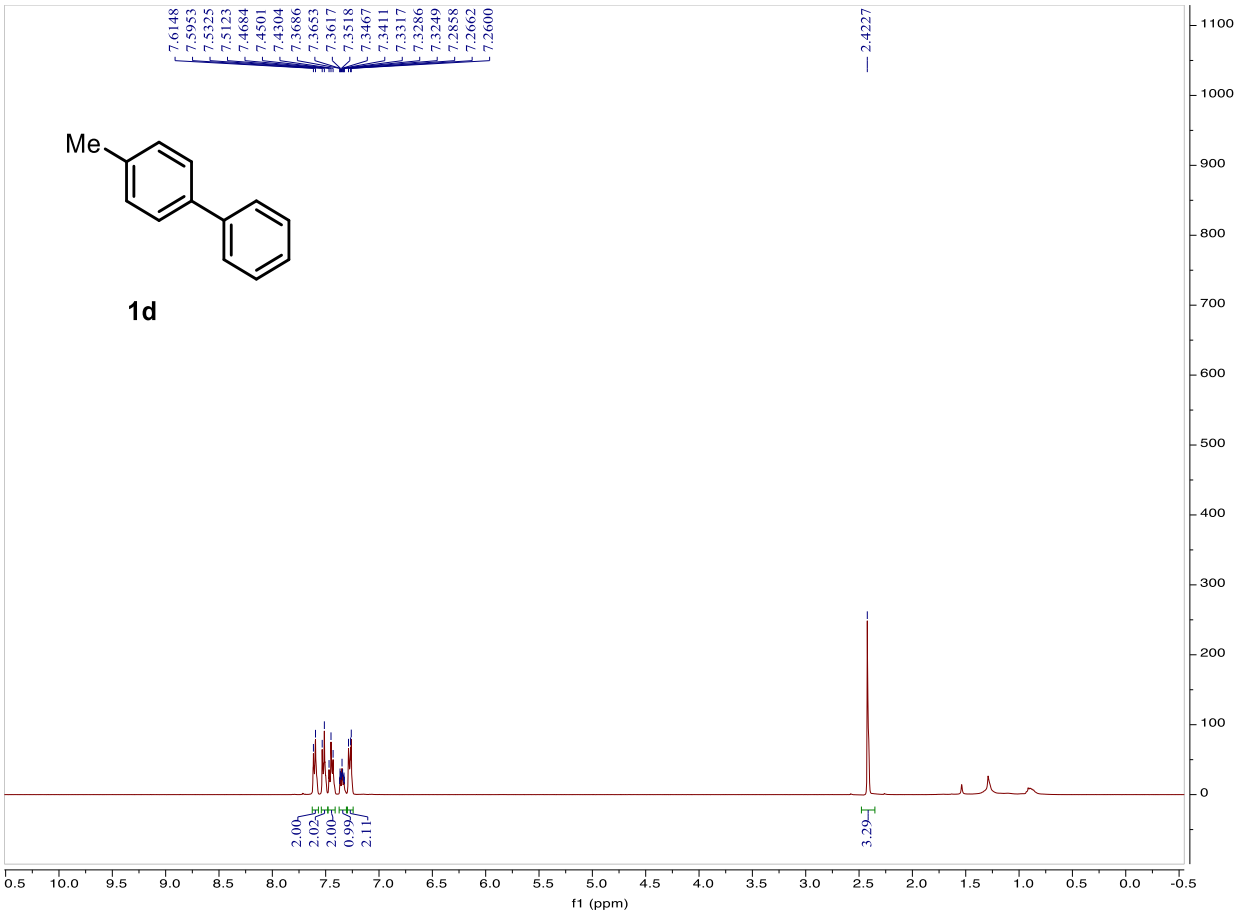
^{1}H NMR spectrum of compound 1a



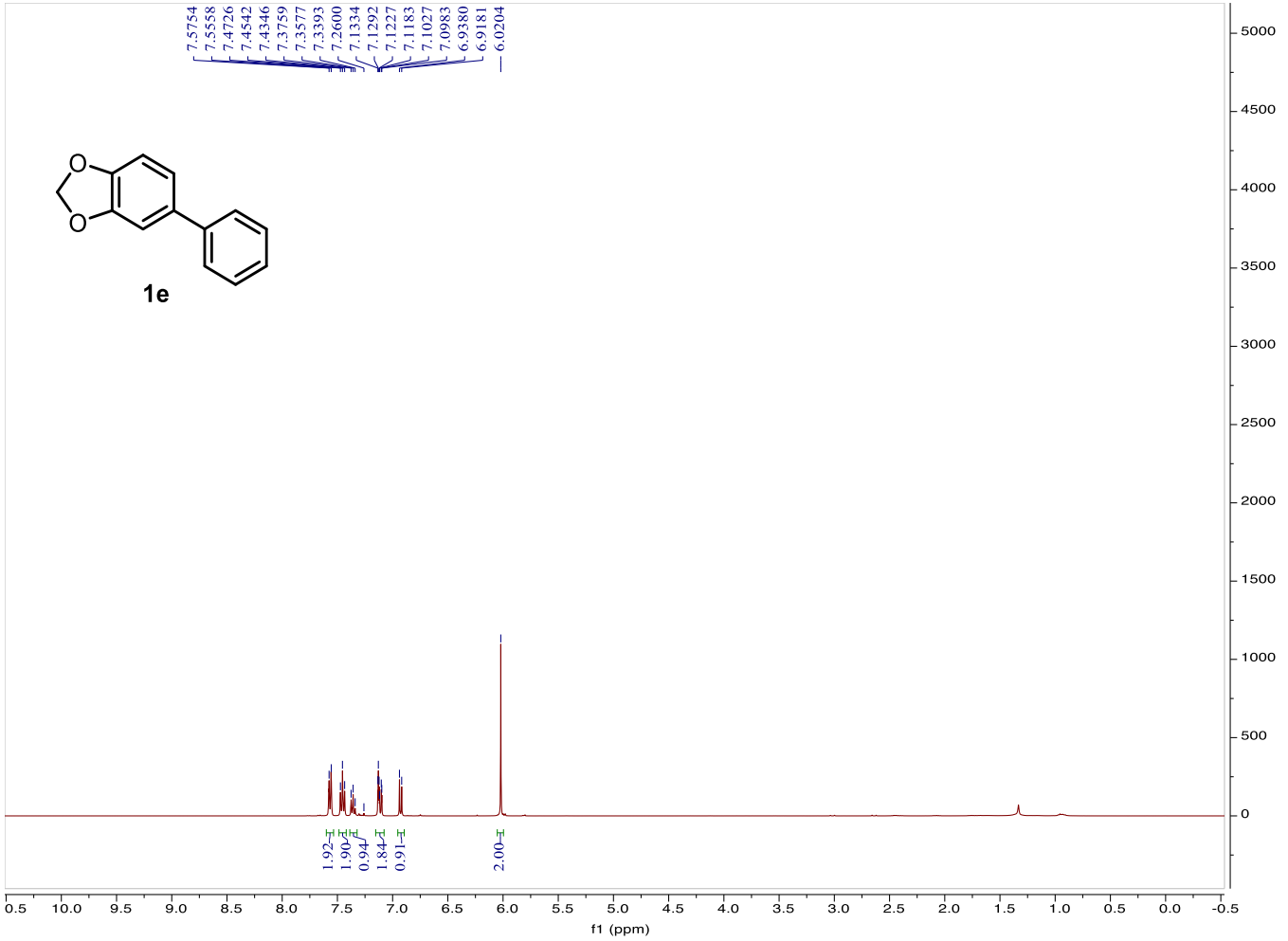
^{1}H NMR spectrum of compound 1b



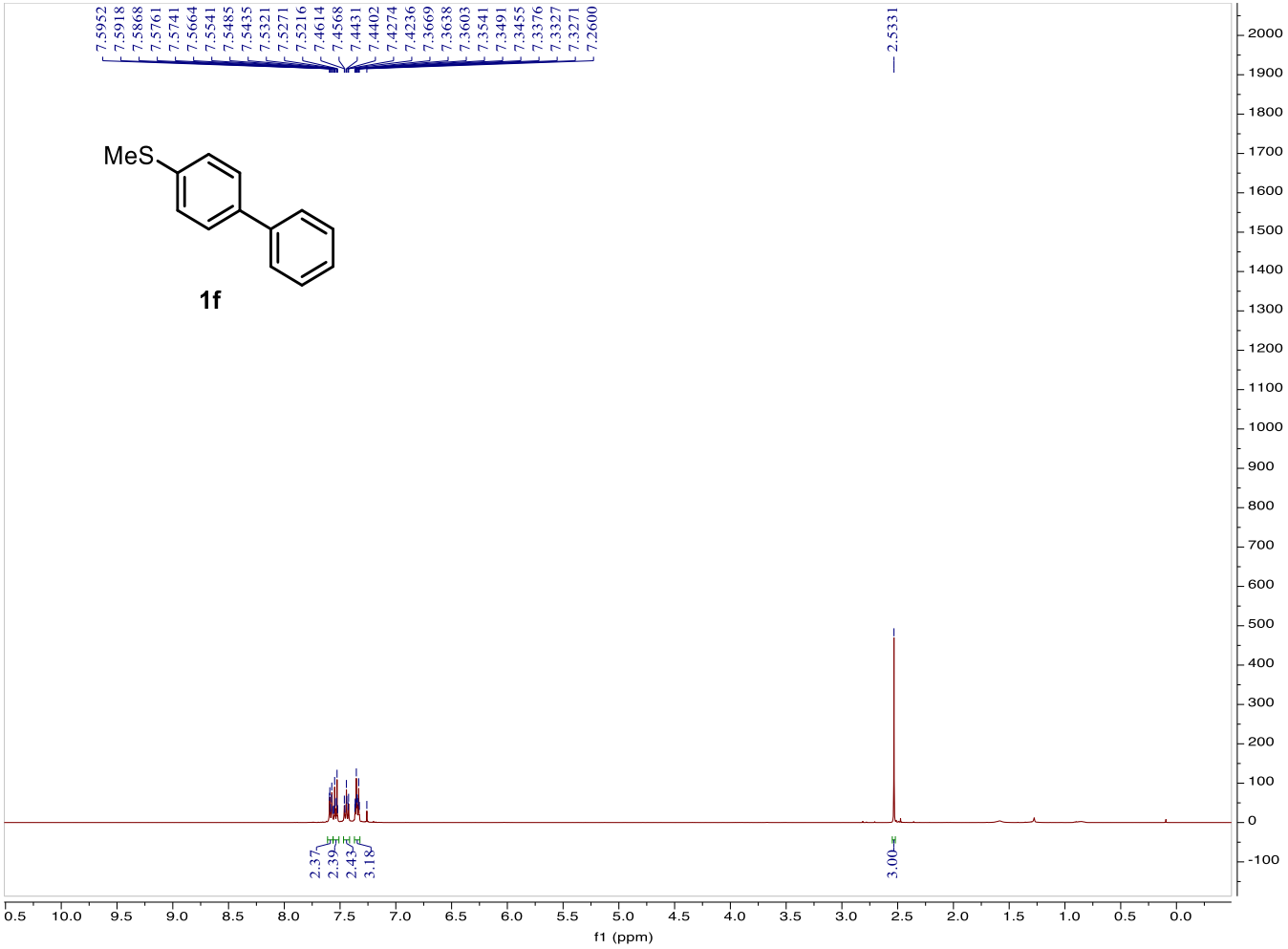
^{1}H NMR spectrum of compound 1c



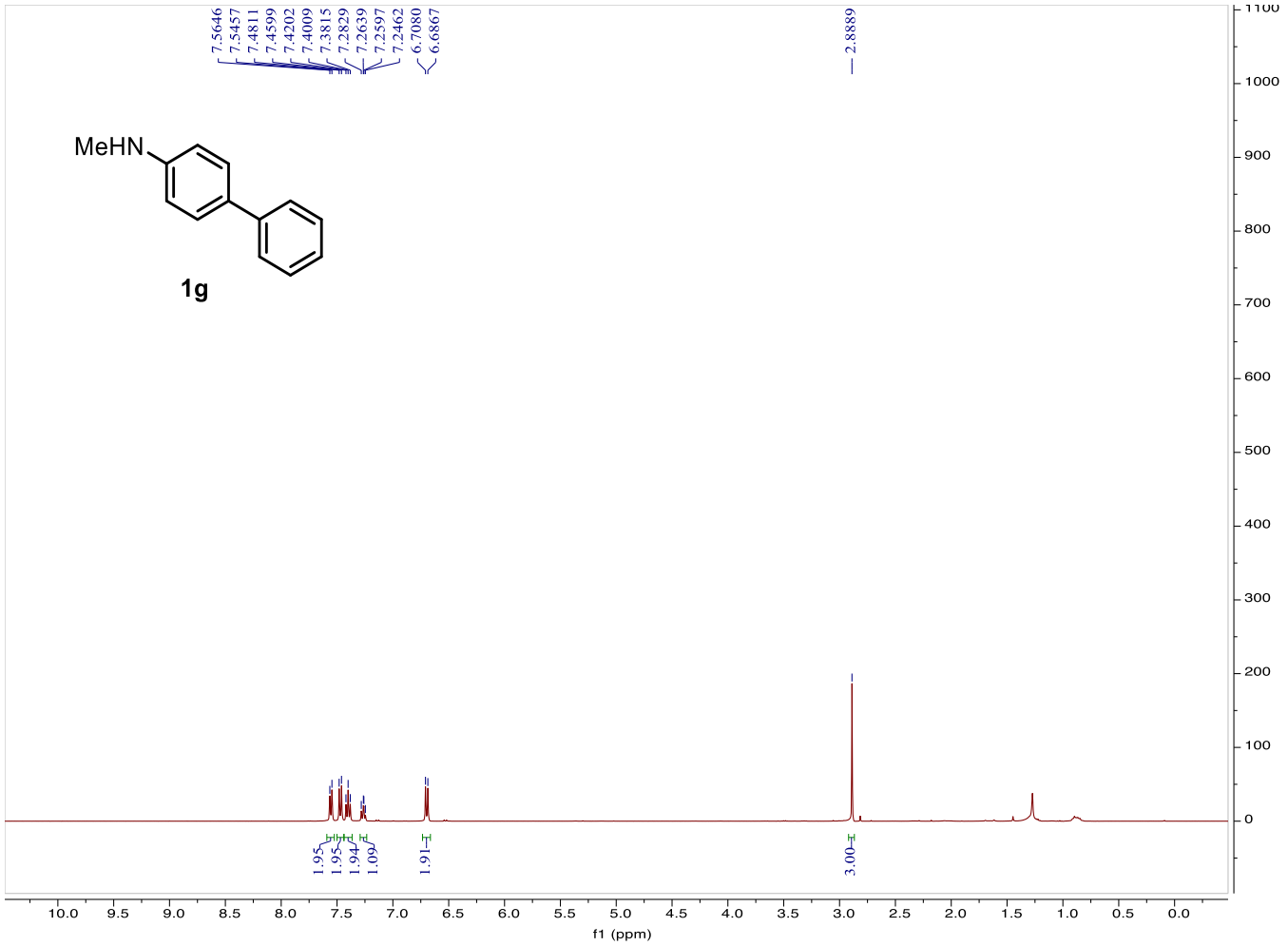
^{1}H NMR spectrum of compound 1d



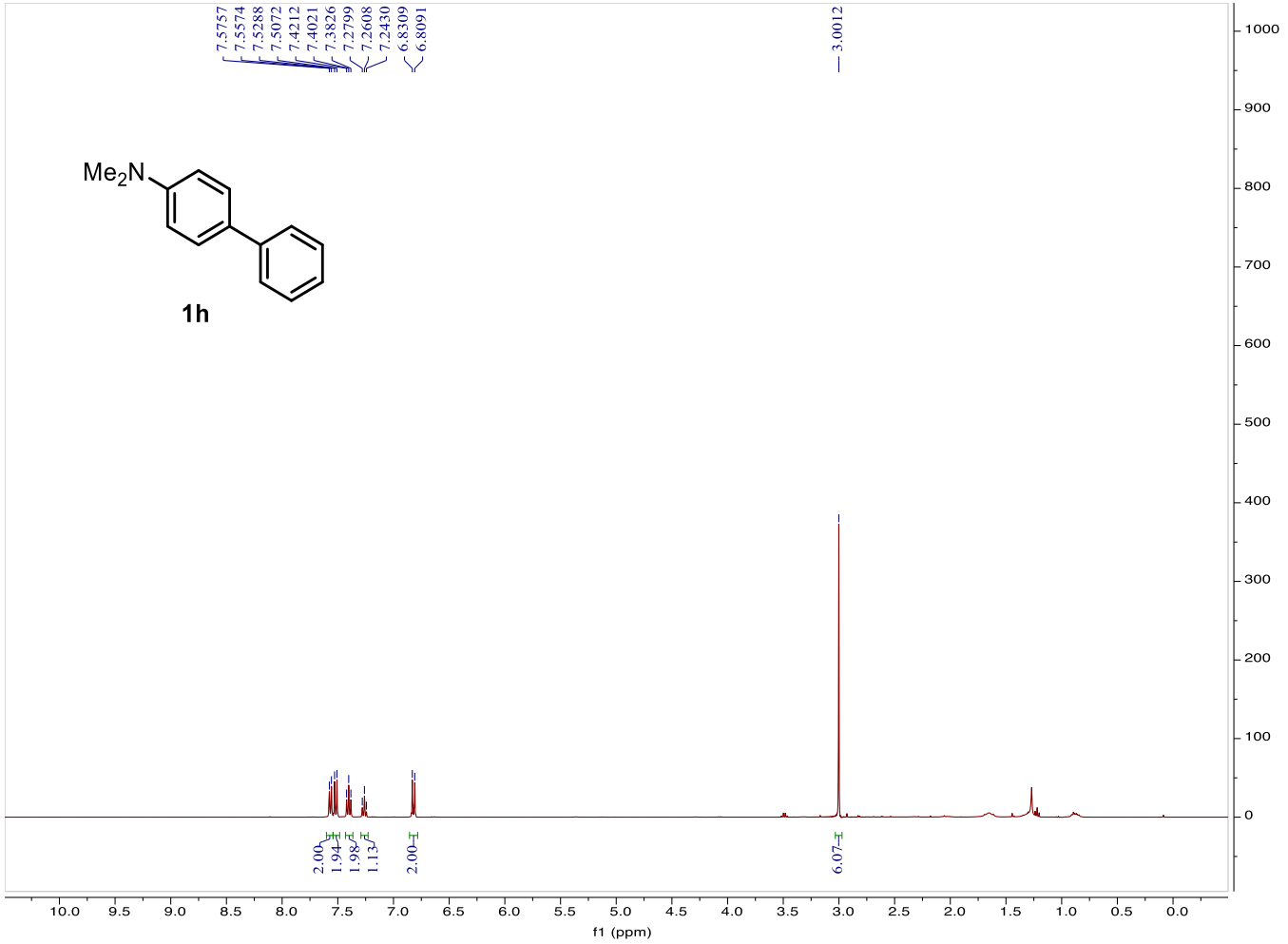
^{1}H NMR spectrum of compound 1e



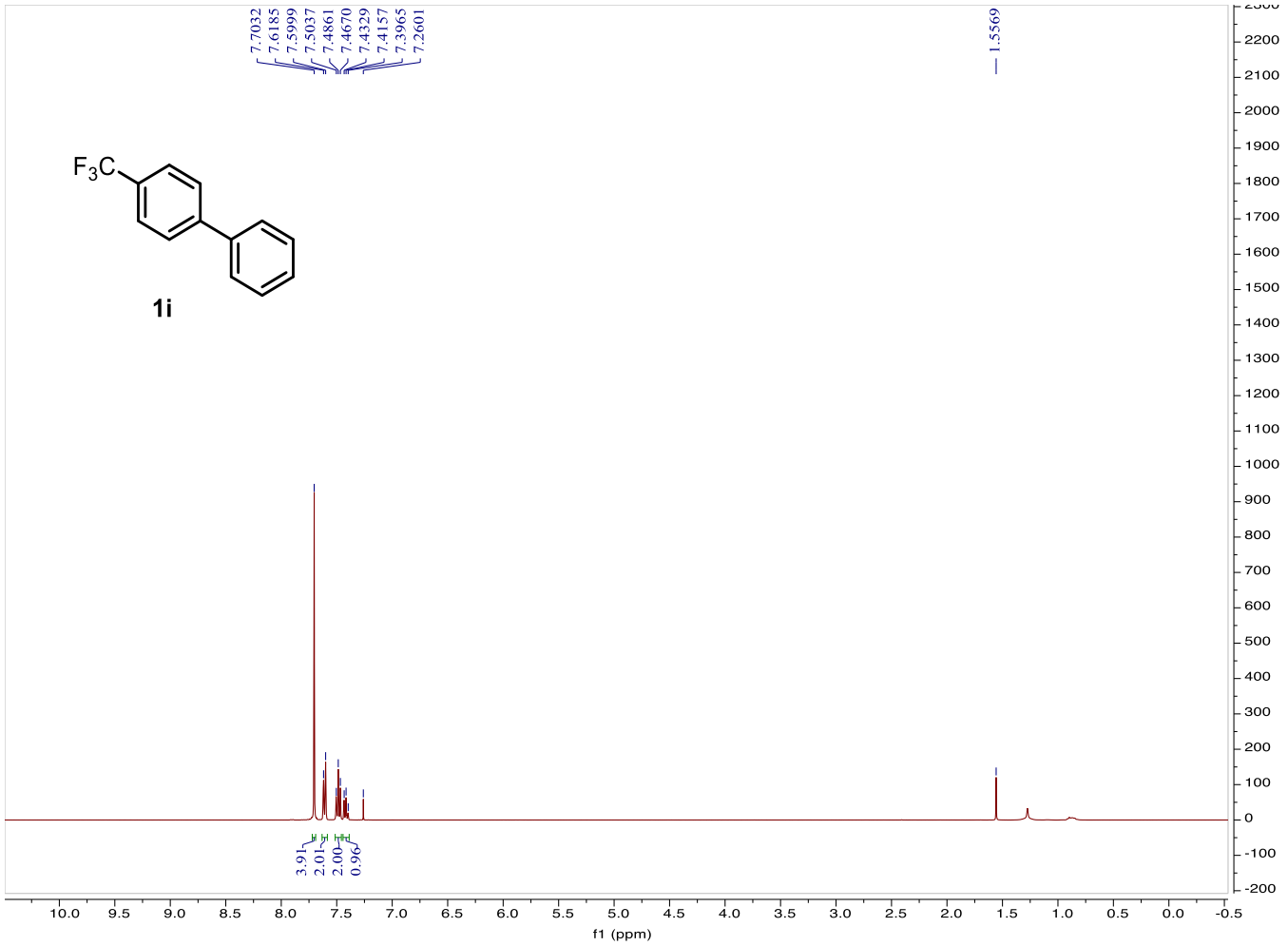
^{1}H NMR spectrum of compound 1f



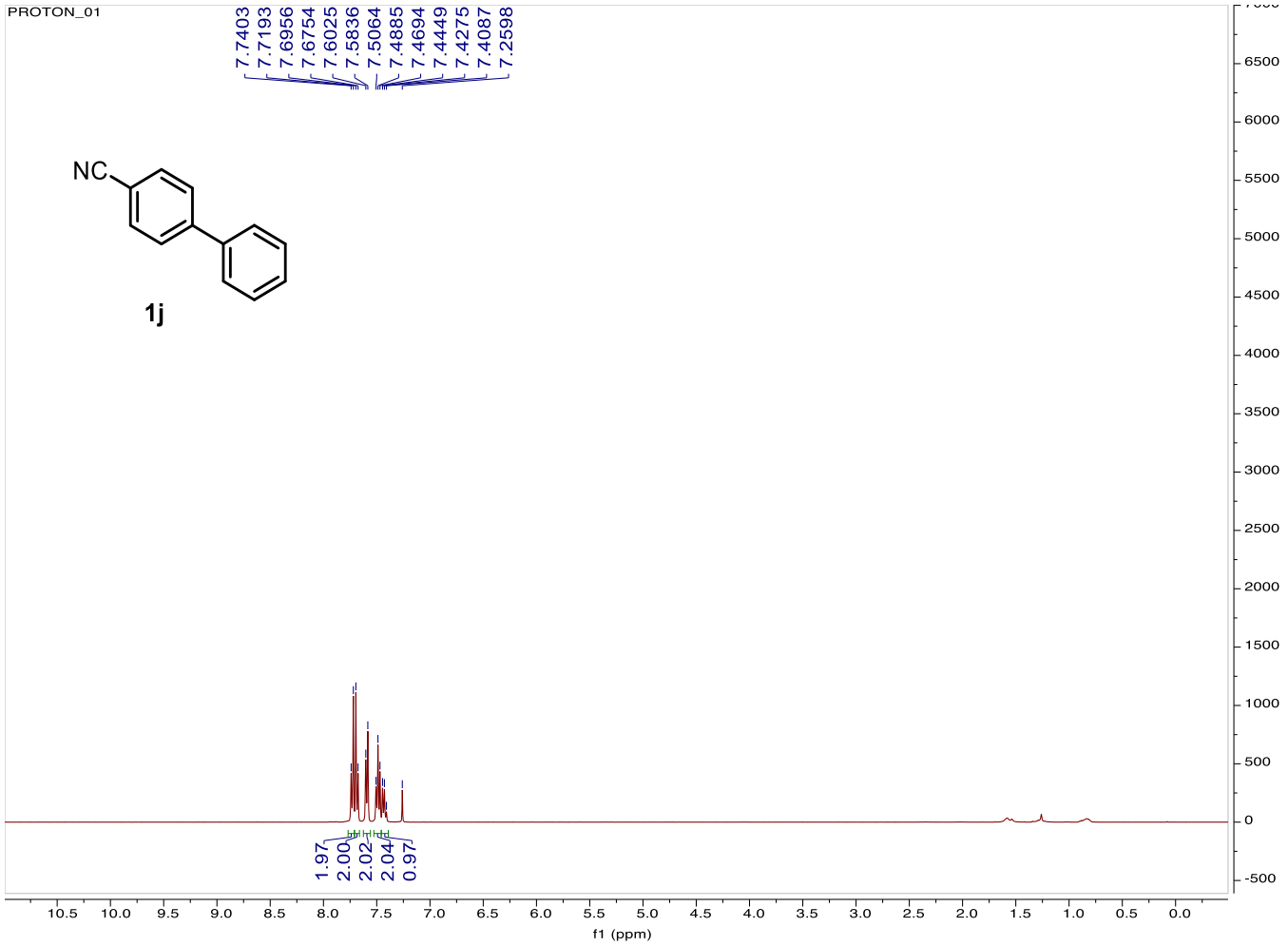
^{1}H NMR spectrum of compound 1g



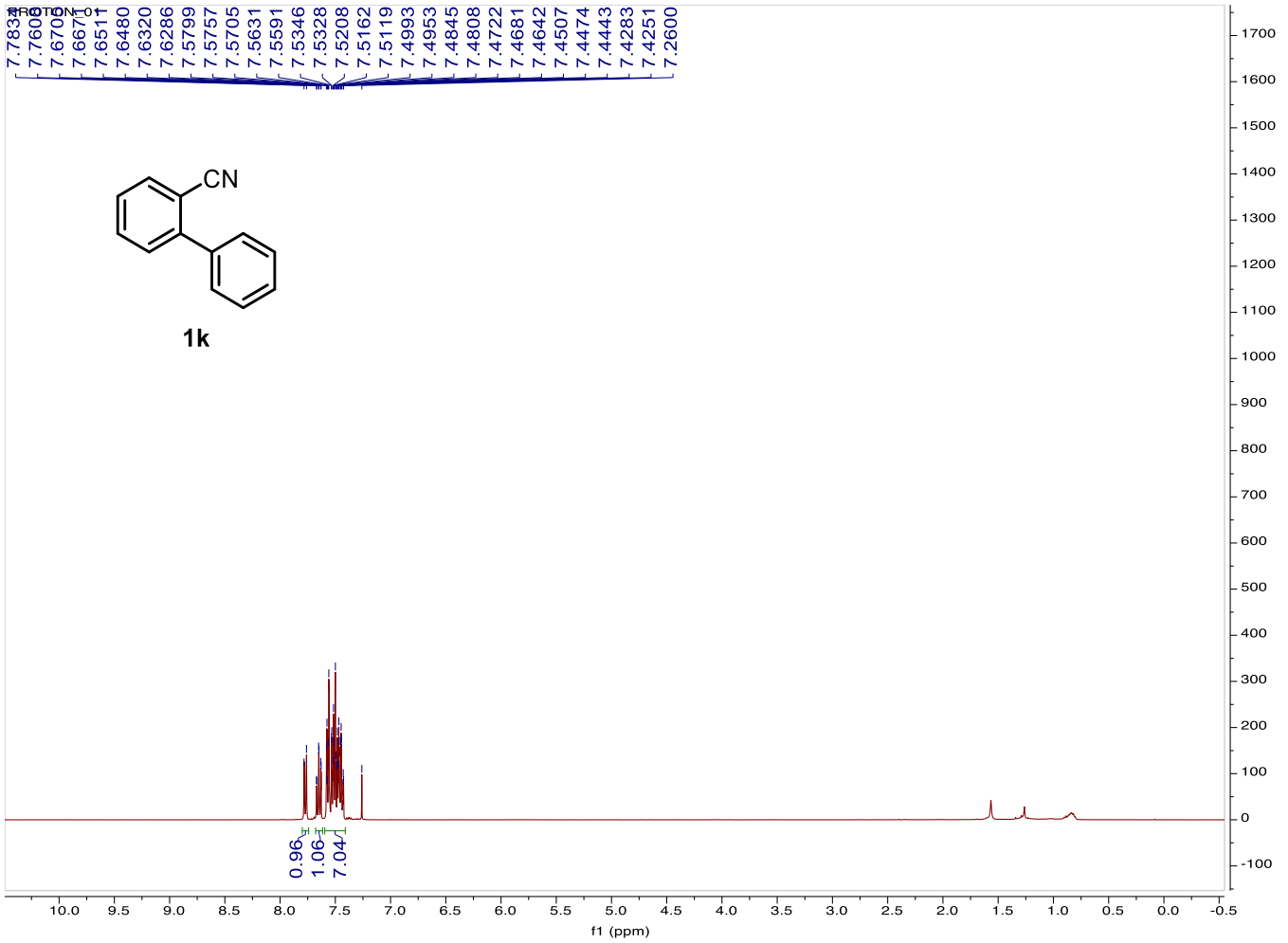
^{1}H NMR spectrum of compound 1h



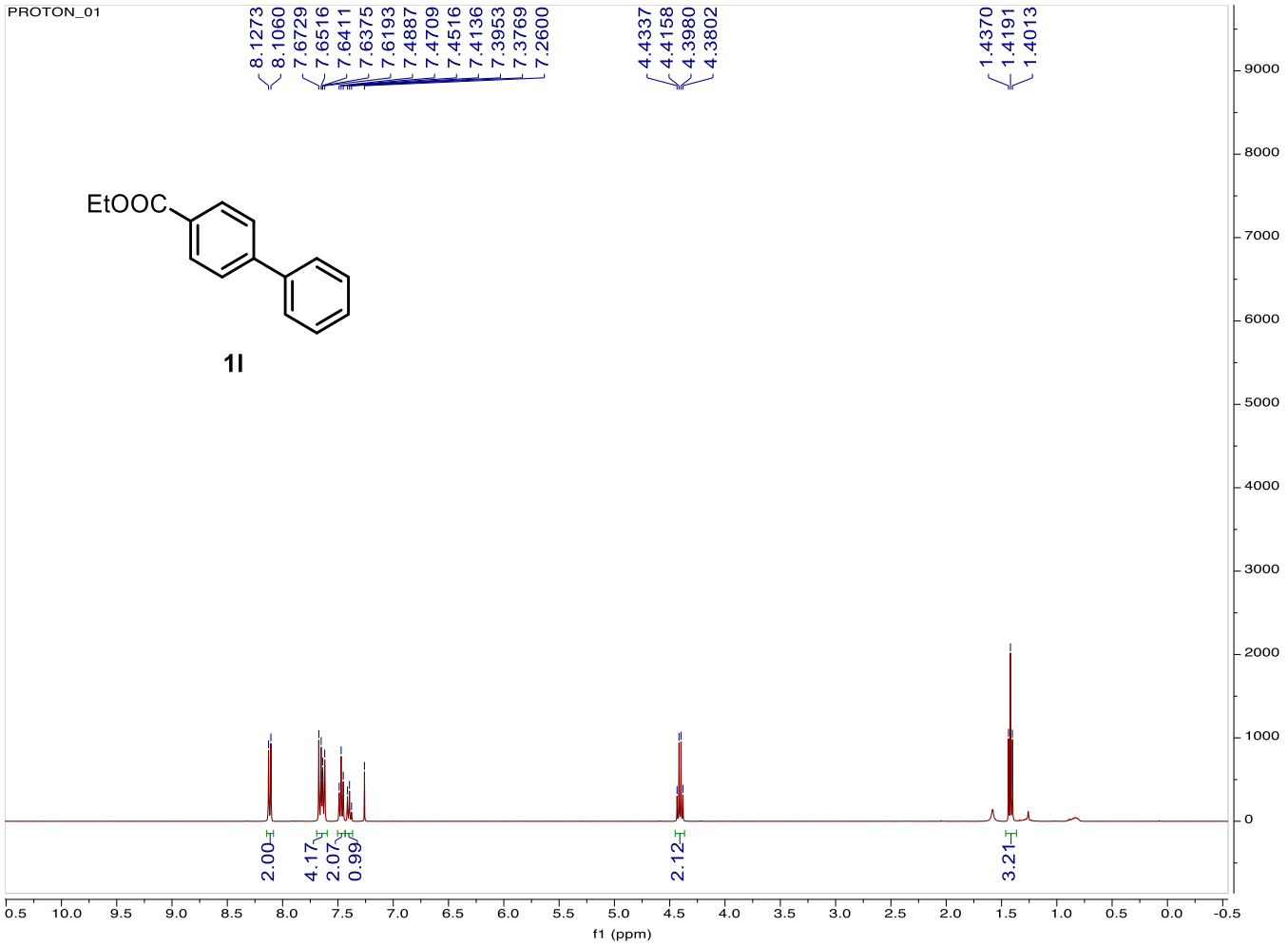
^{1}H NMR spectrum of compound 1i



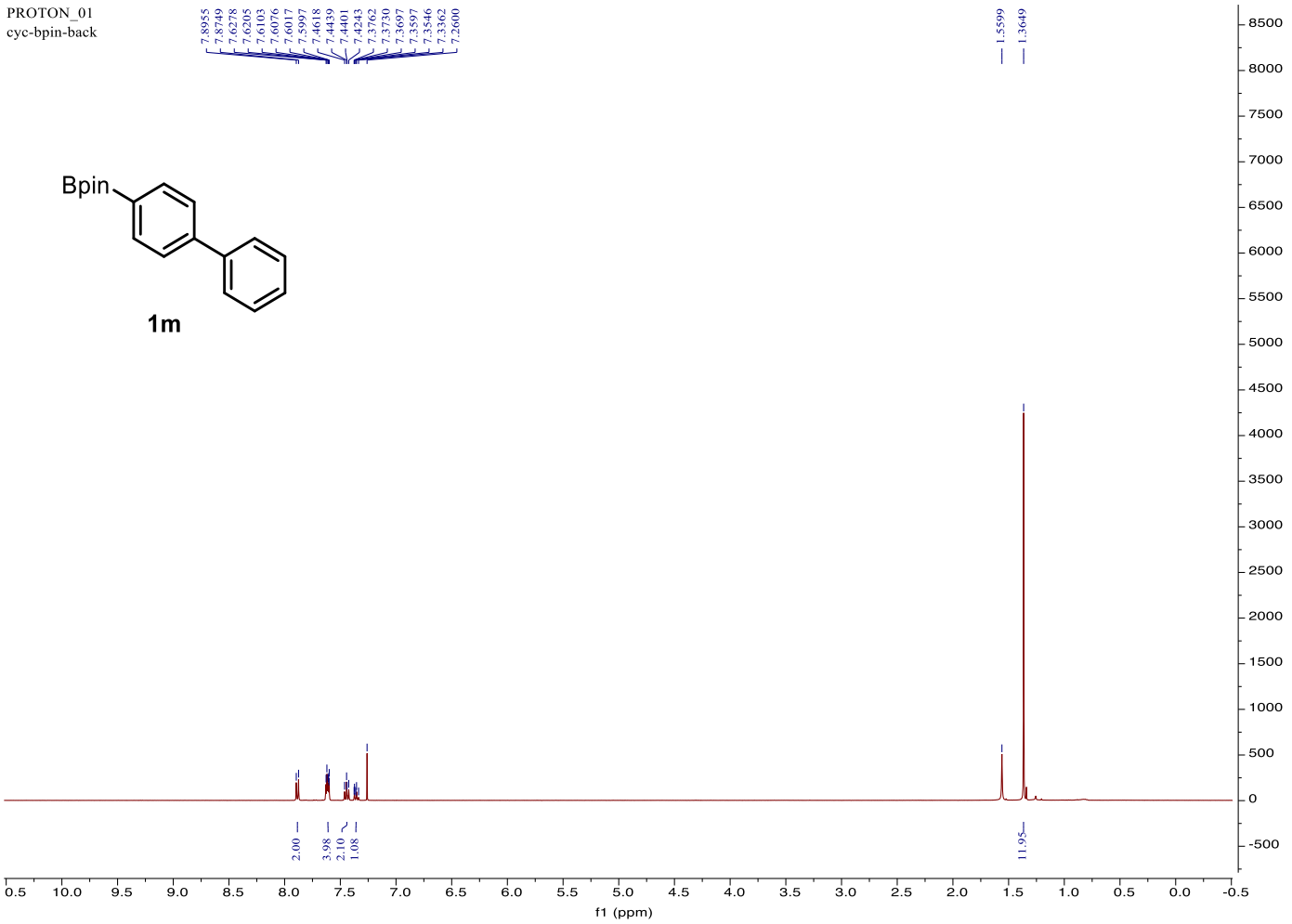
^{1}H NMR spectrum of compound 2j



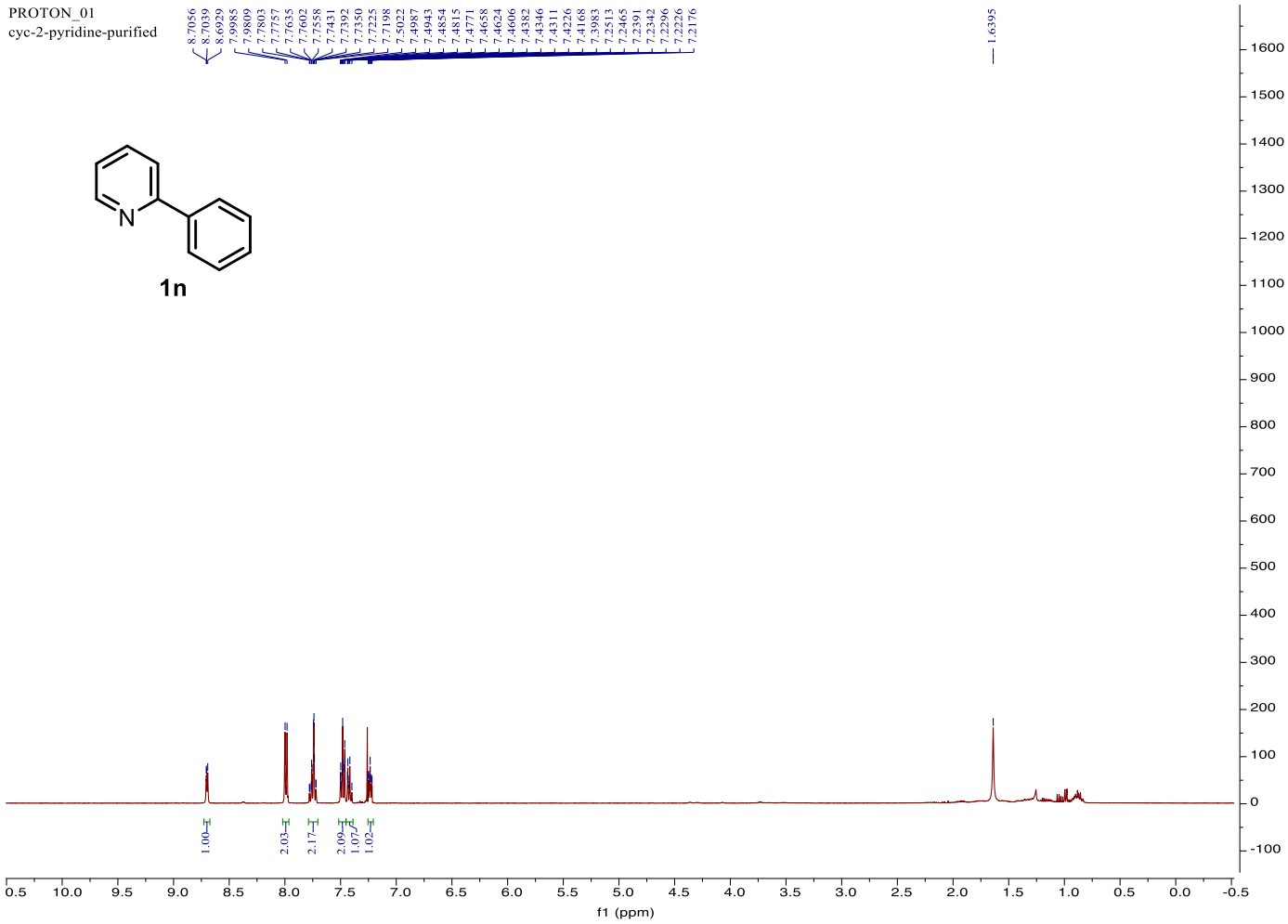
^{1}H NMR spectrum of compound 1k



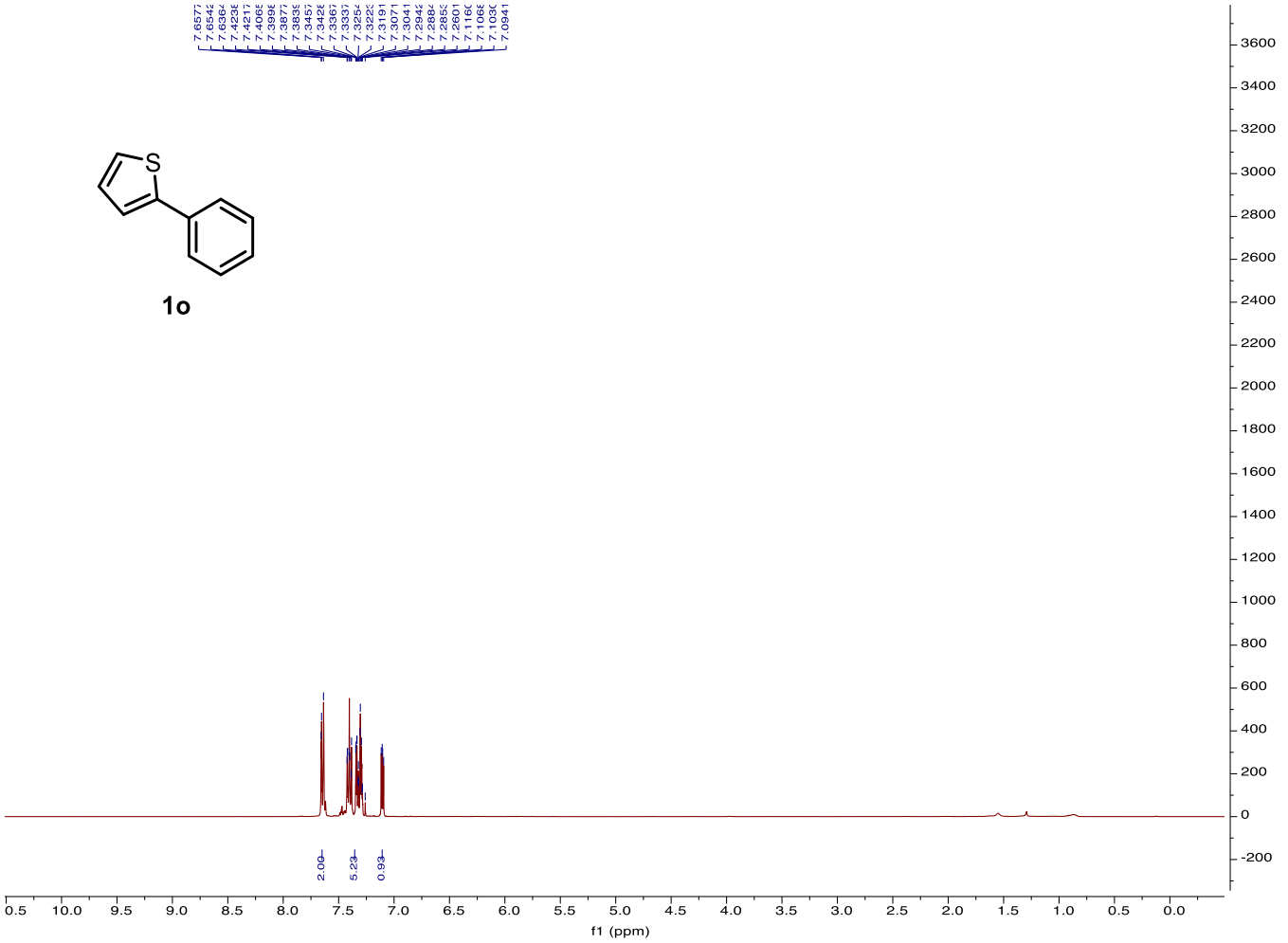
^{1}H NMR spectrum of compound 1l



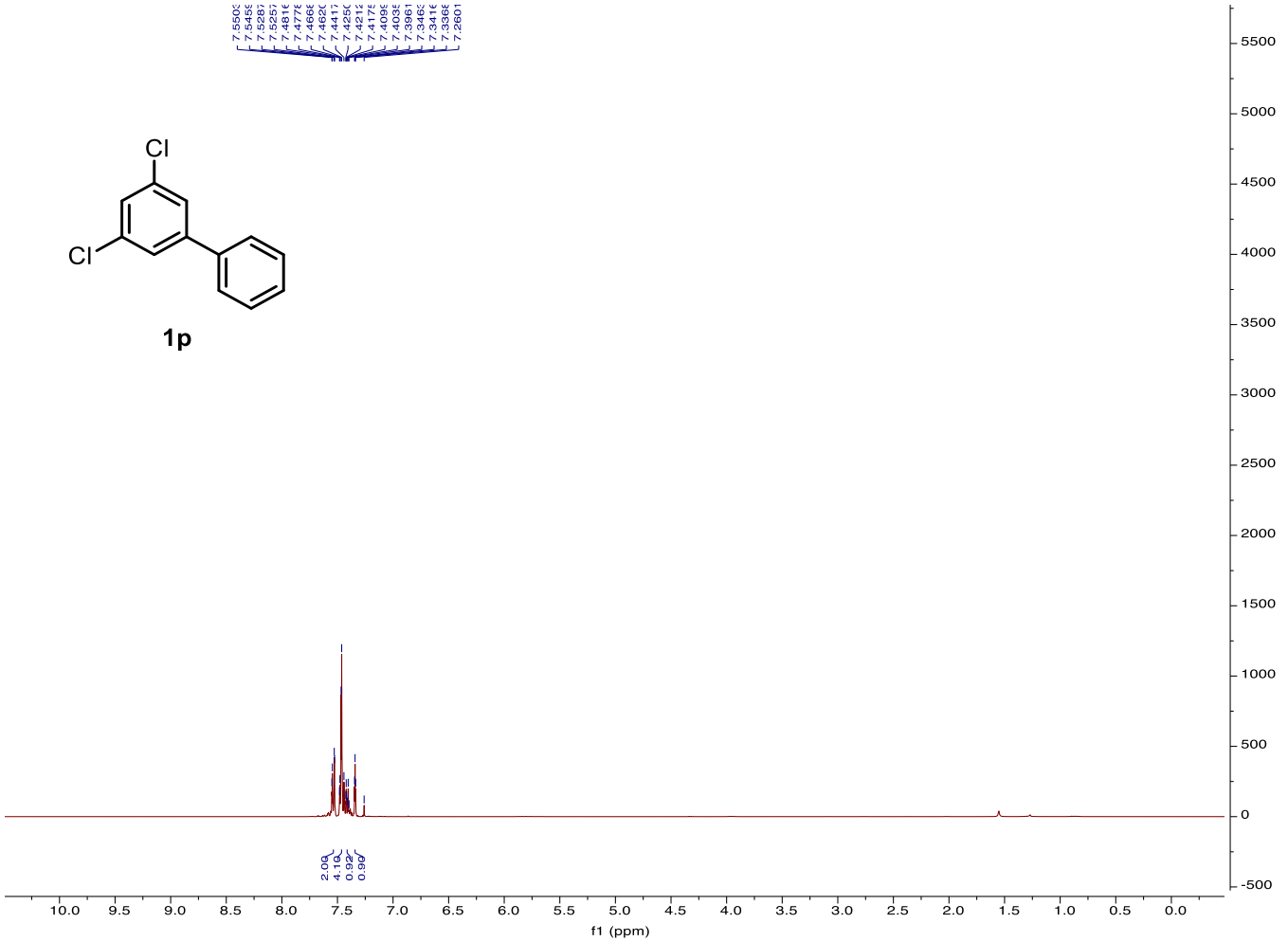
^{1}H NMR spectrum of compound 1m



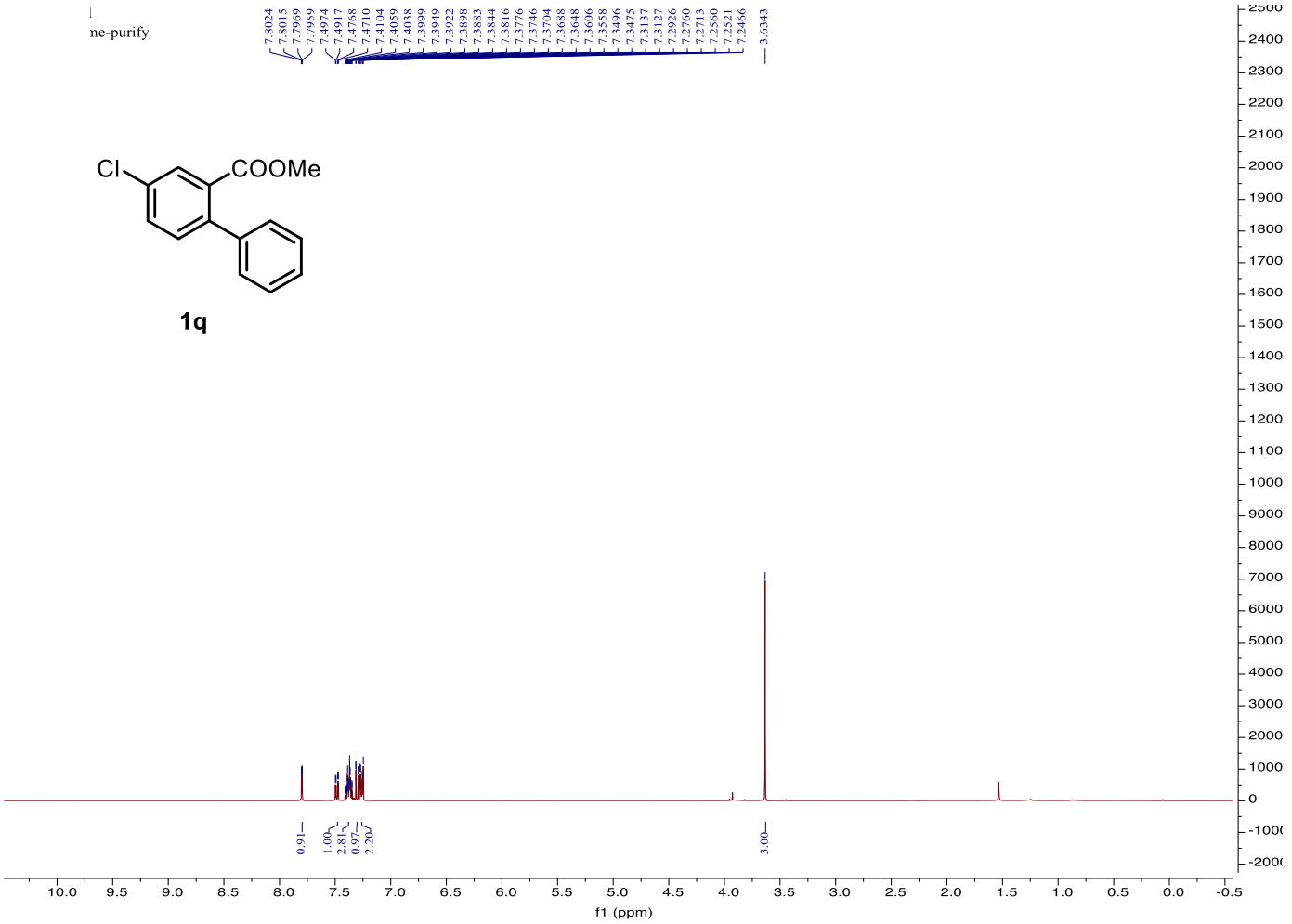
^{1}H NMR spectrum of compound 1n



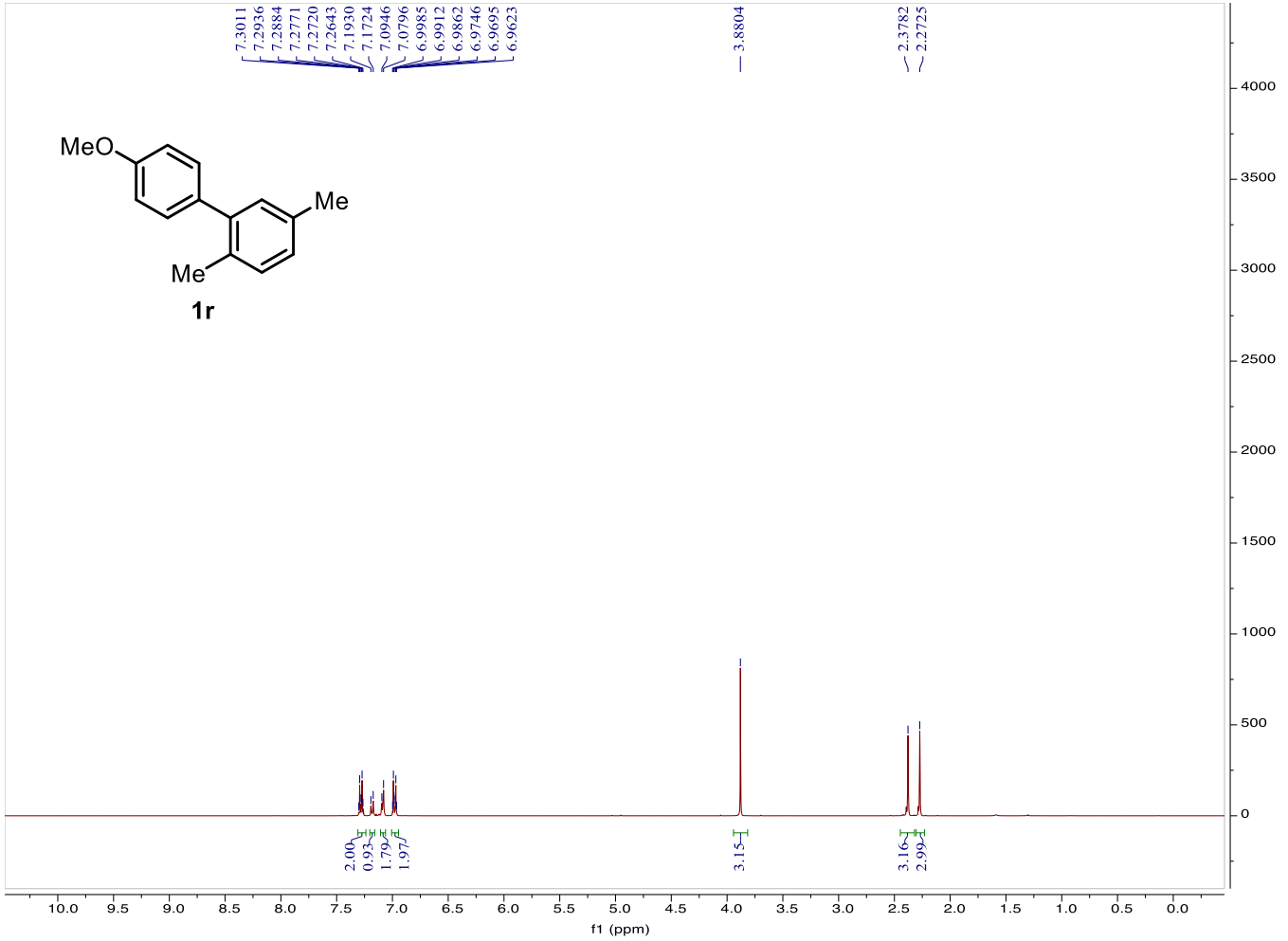
^{1}H NMR spectrum of compound 1o



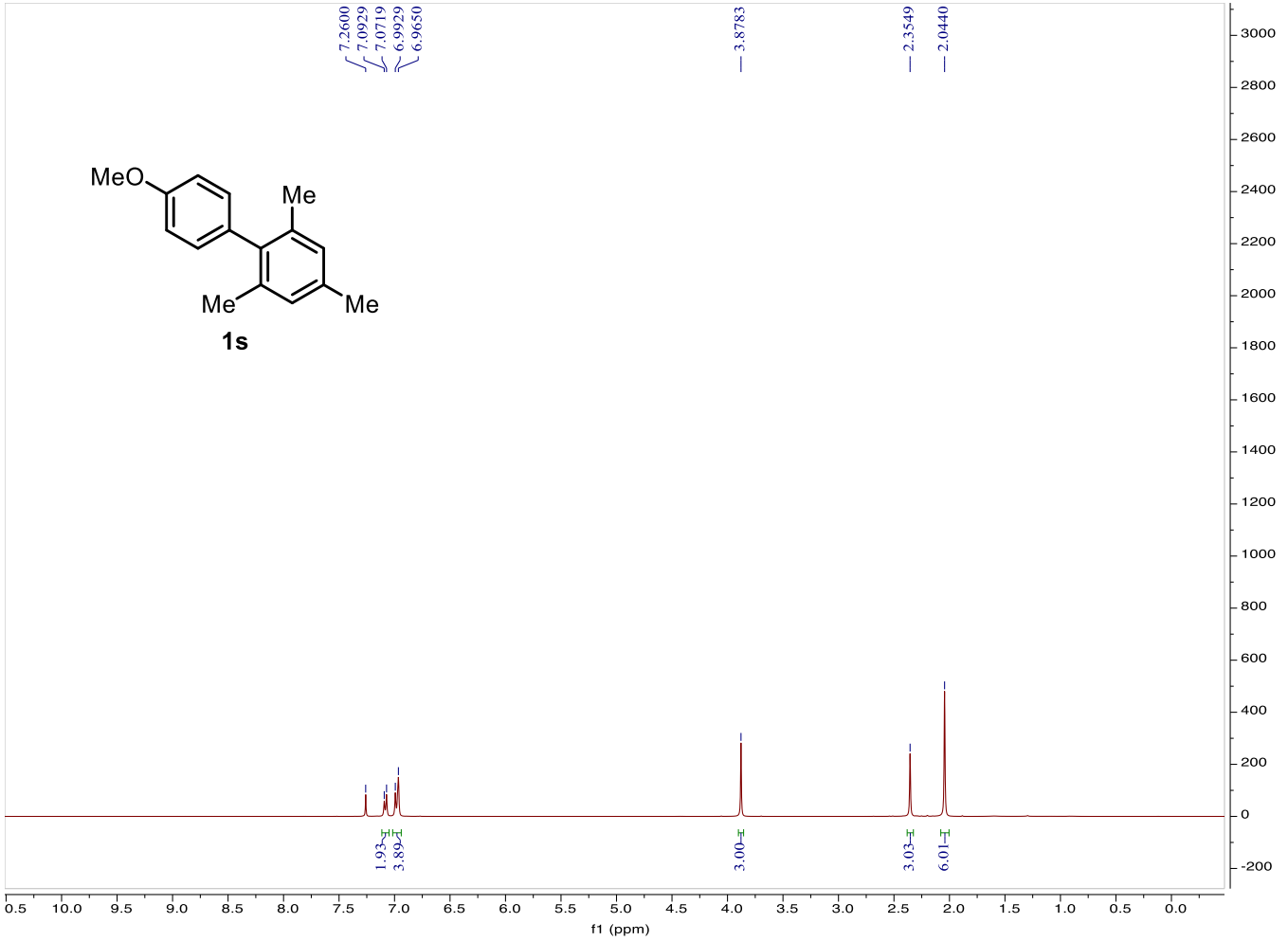
^{1}H NMR spectrum of compound 1p



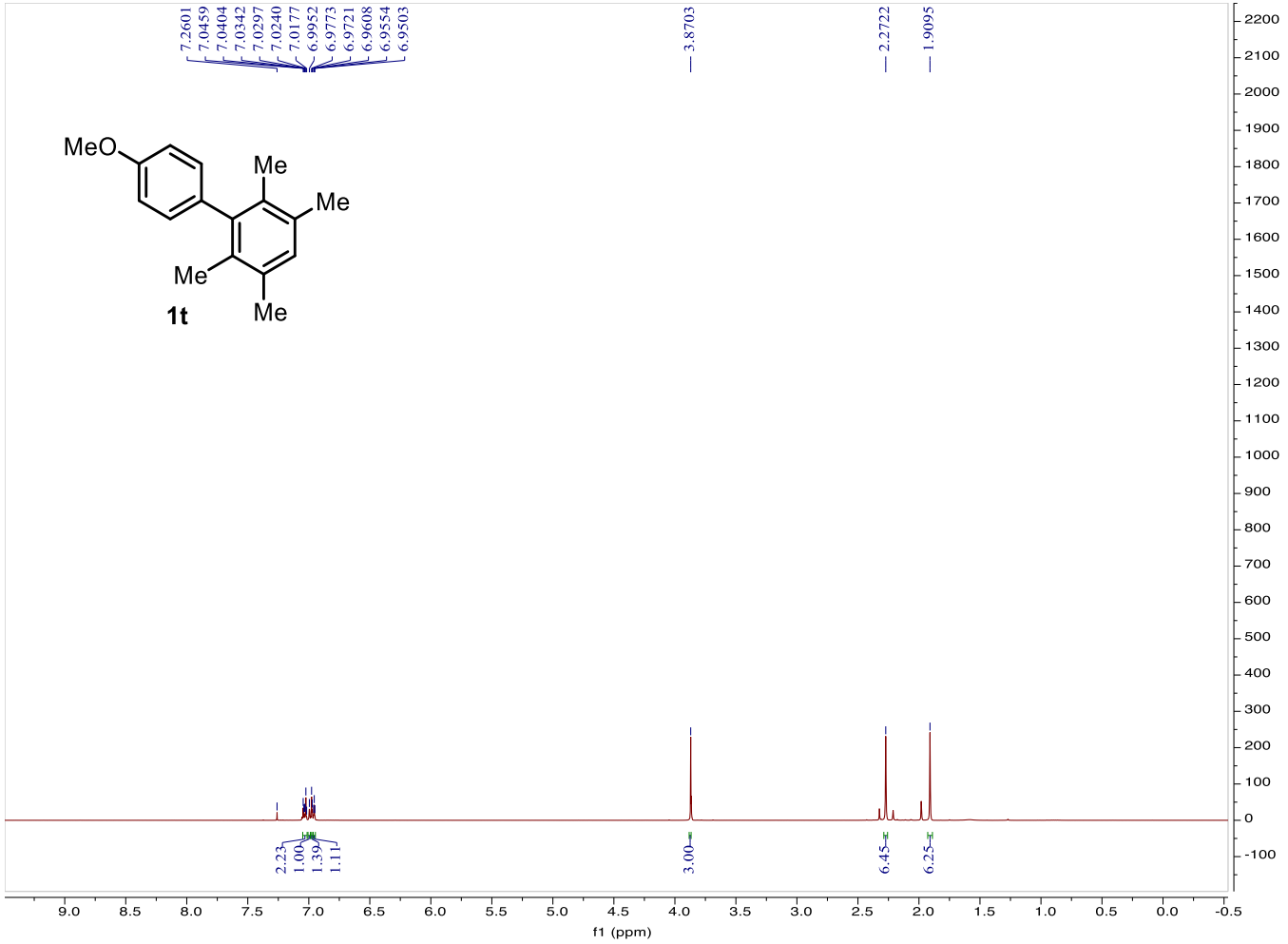
^{1}H NMR spectrum of compound 1q



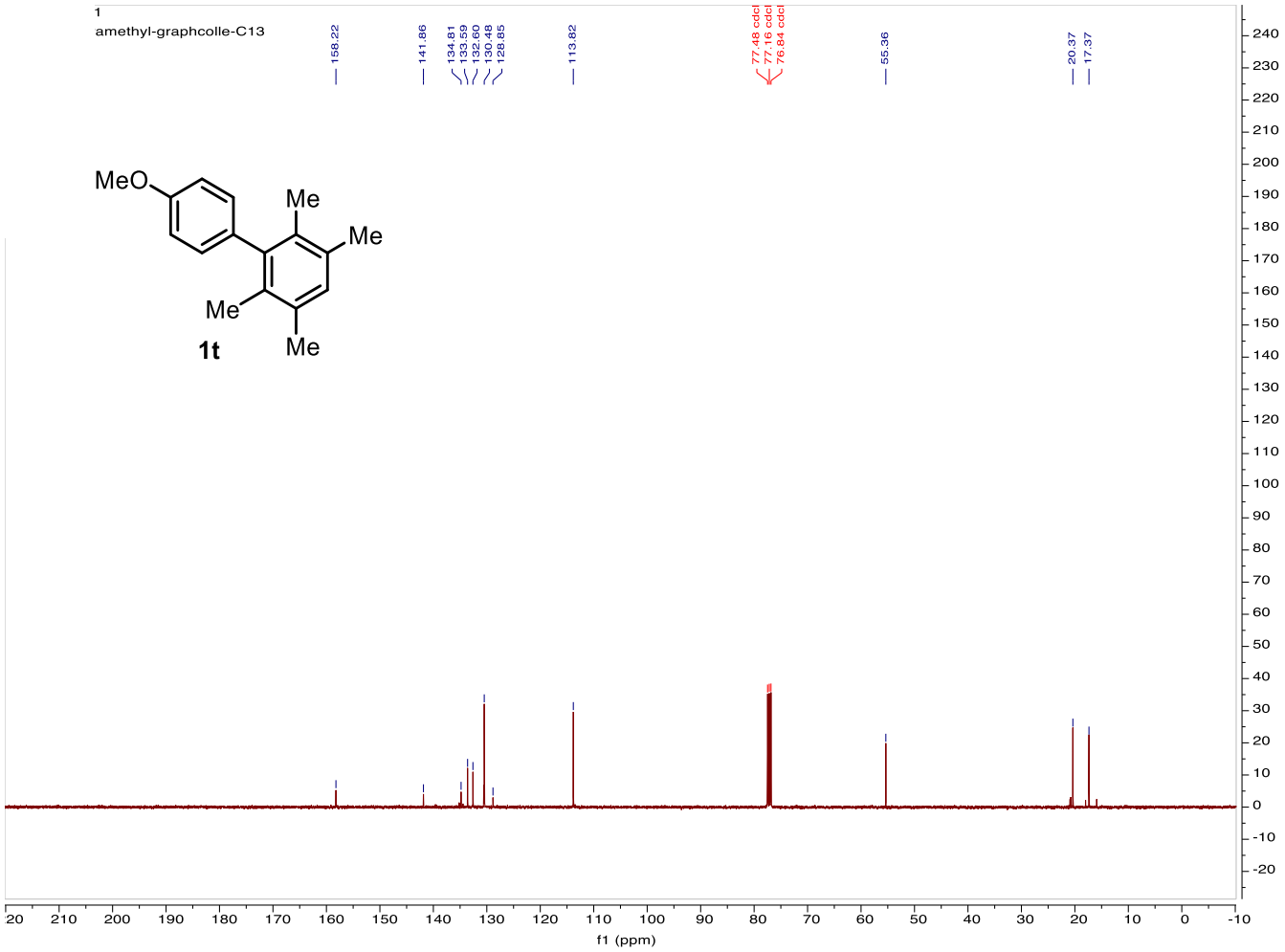
^{1}H NMR spectrum of compound 1r



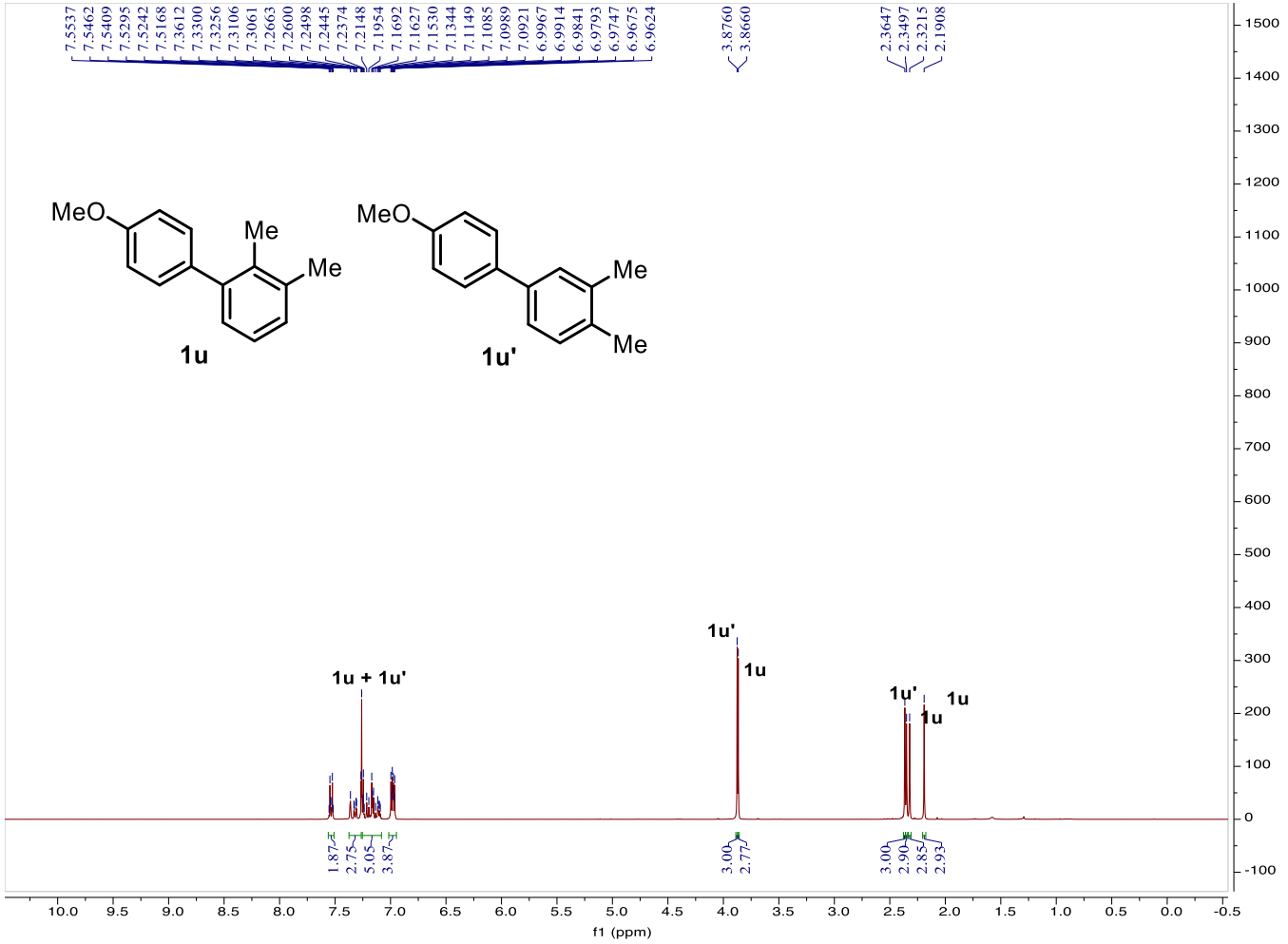
^{1}H NMR spectrum of compound 1s



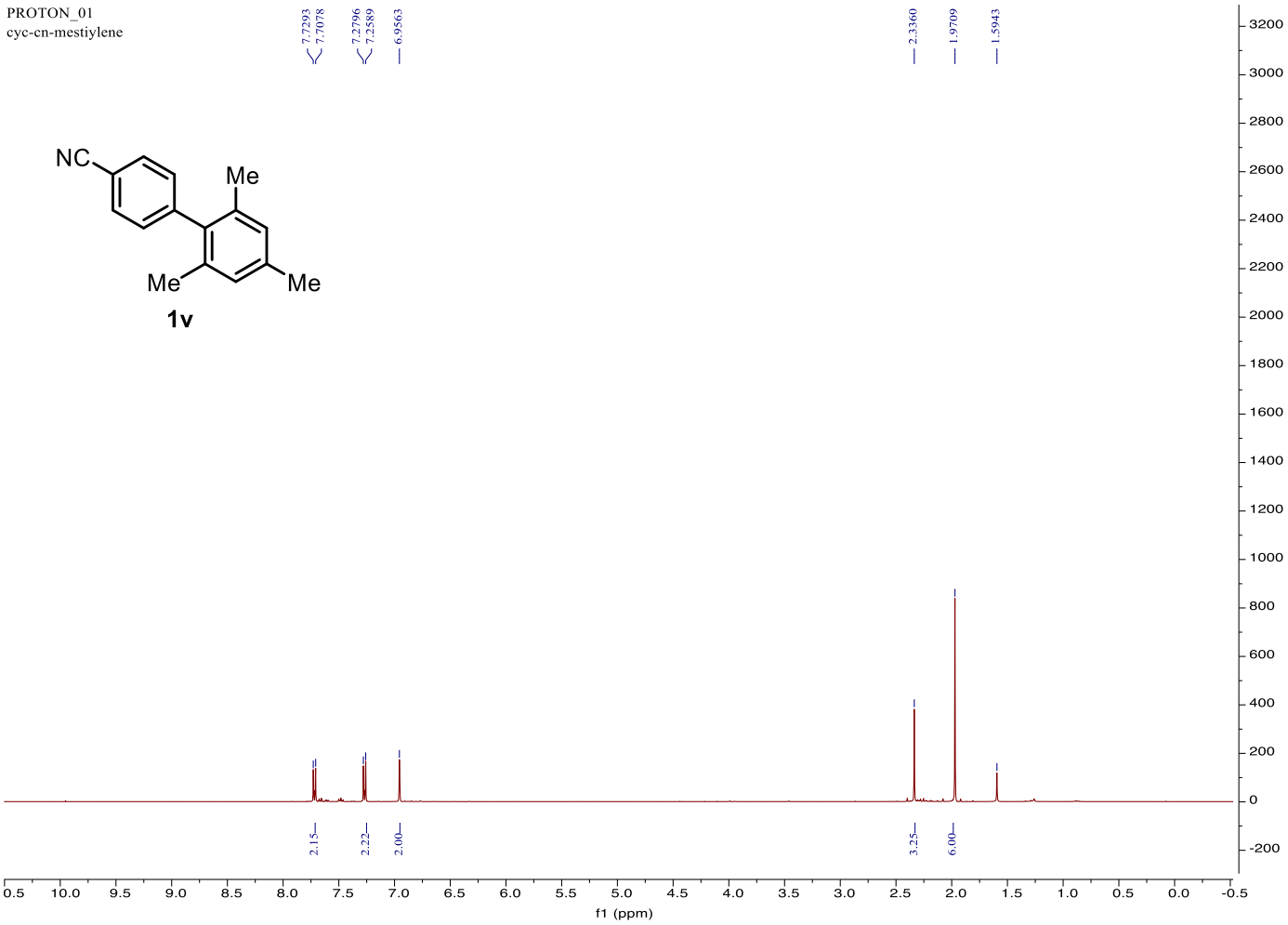
^{1}H NMR spectrum of compound 1t



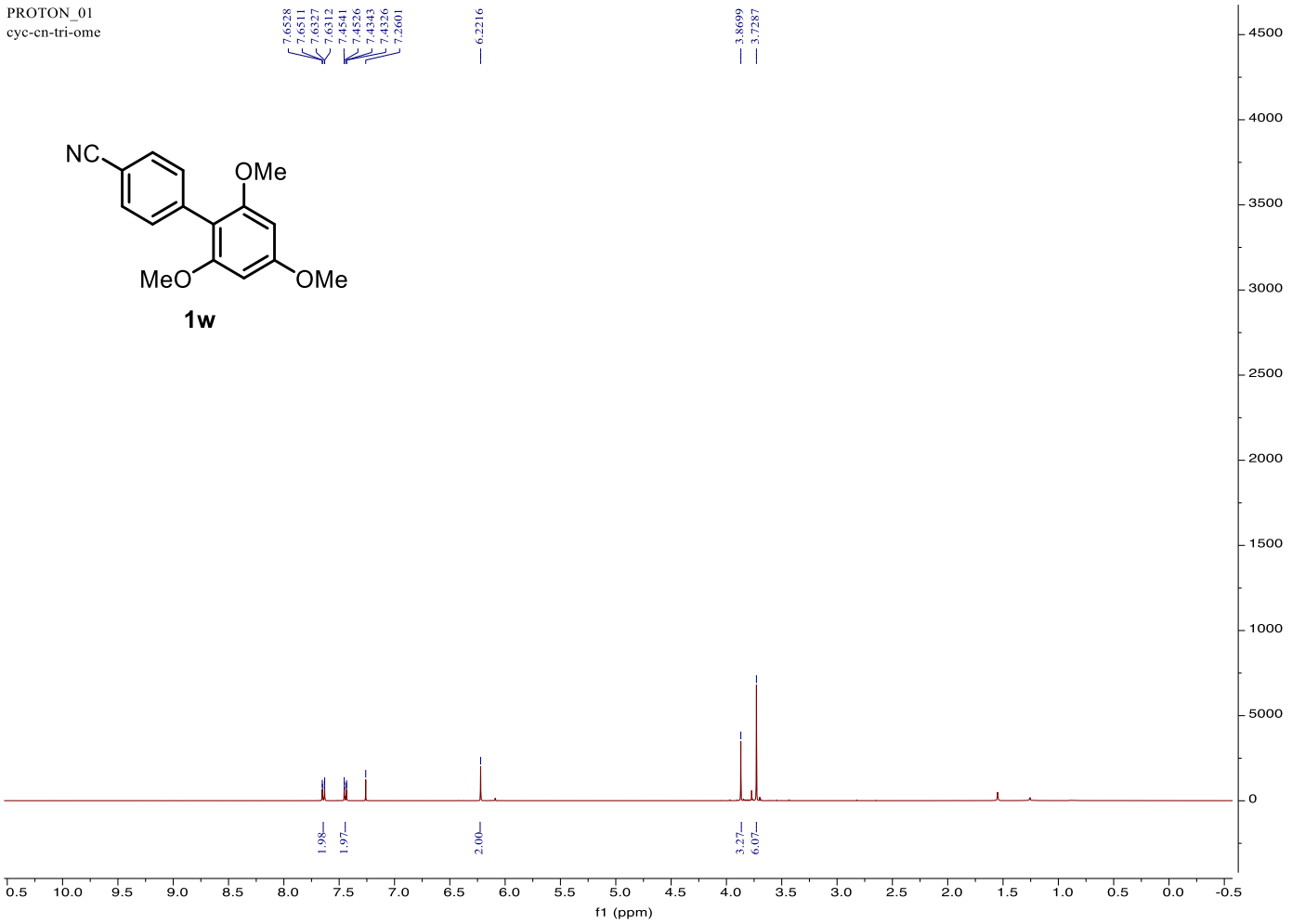
^{13}C NMR spectrum of compound 1t



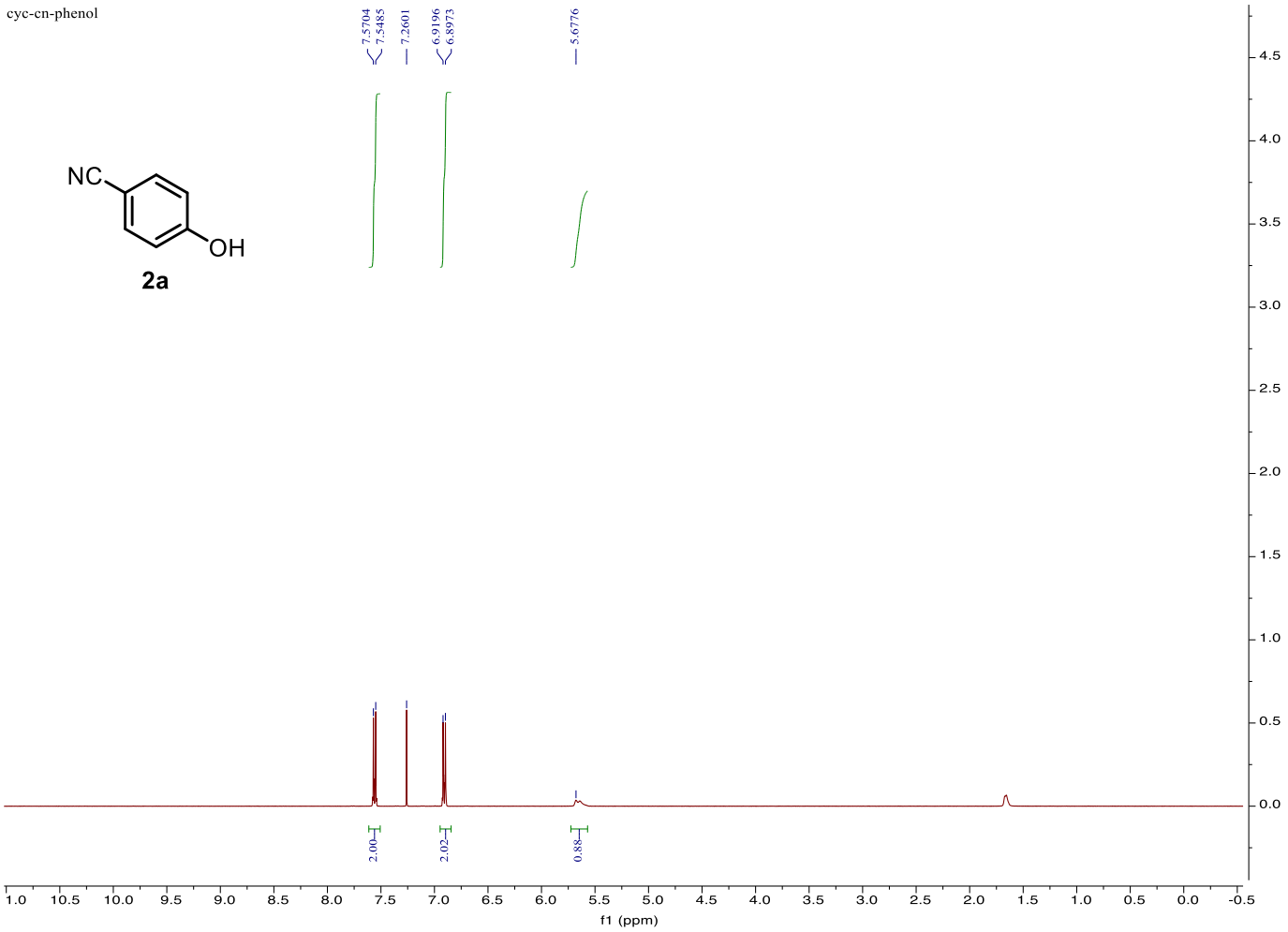
^{1}H NMR spectrum of compound 1u and 1u'



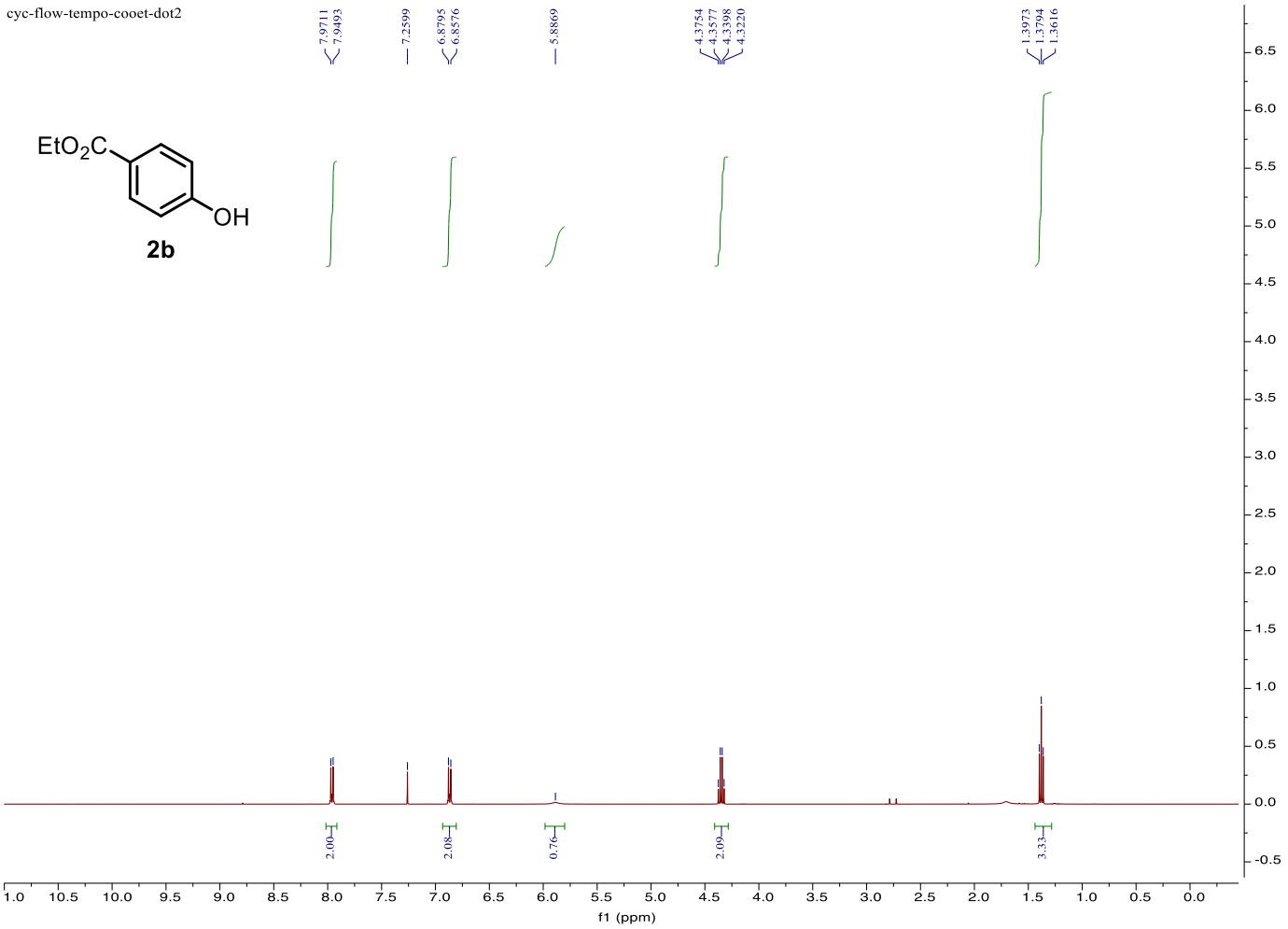
^{1}H NMR spectrum of compound 1v



^{1}H NMR spectrum of compound 1w



^{1}H NMR spectrum of compound 2a



^{1}H NMR spectrum of compound 2b