Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Water-soluble Superbulky (η^6-*p*-cymene) Ruthenium(II) Amine: Active Catalyst in Oxidative Homocoupling of Arylboronic Acids and Hydration of Organonitriles

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Table of contents Page. No

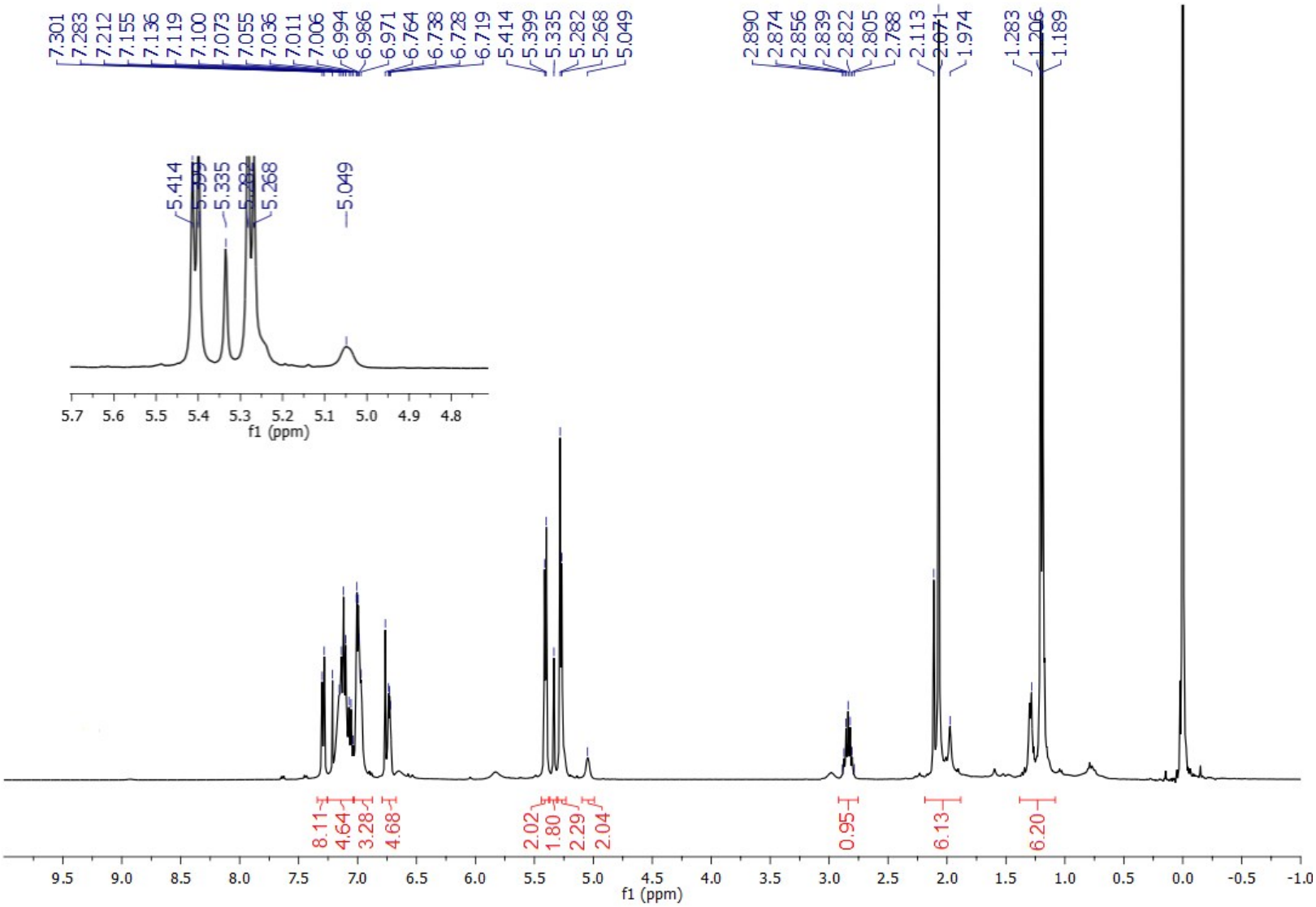


Figure S1. ^{1}H NMR spectrum of [(η^{6}-*p*-cymene)-$RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)$] complex (**2**) in $CDCl_3$ at 27°C.

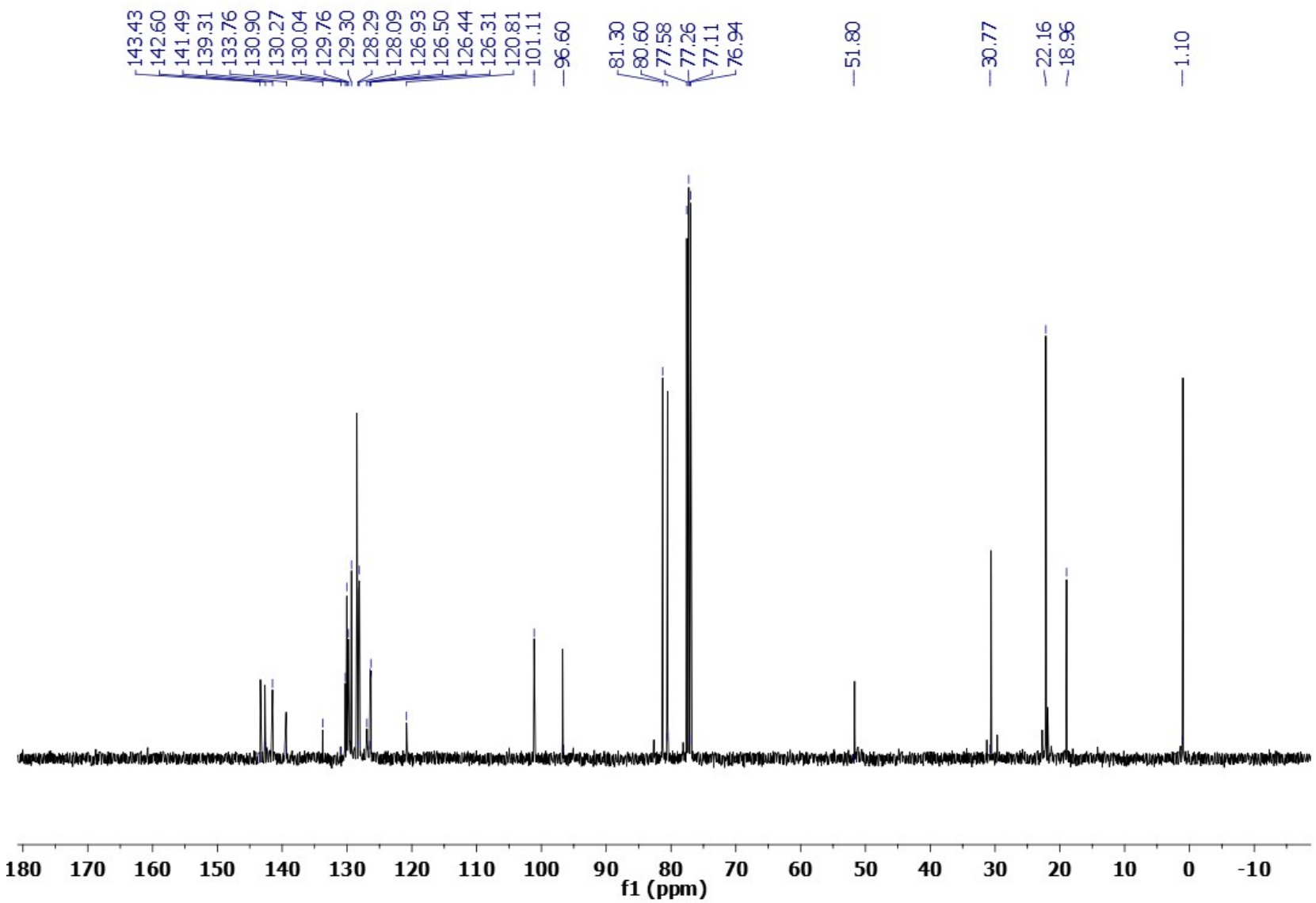


Figure S2. ^{13}C NMR spectrum of [(η^6-*p*-cymene)-$RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)$] complex (**2**) in $CDCl_3$ at 27°C.

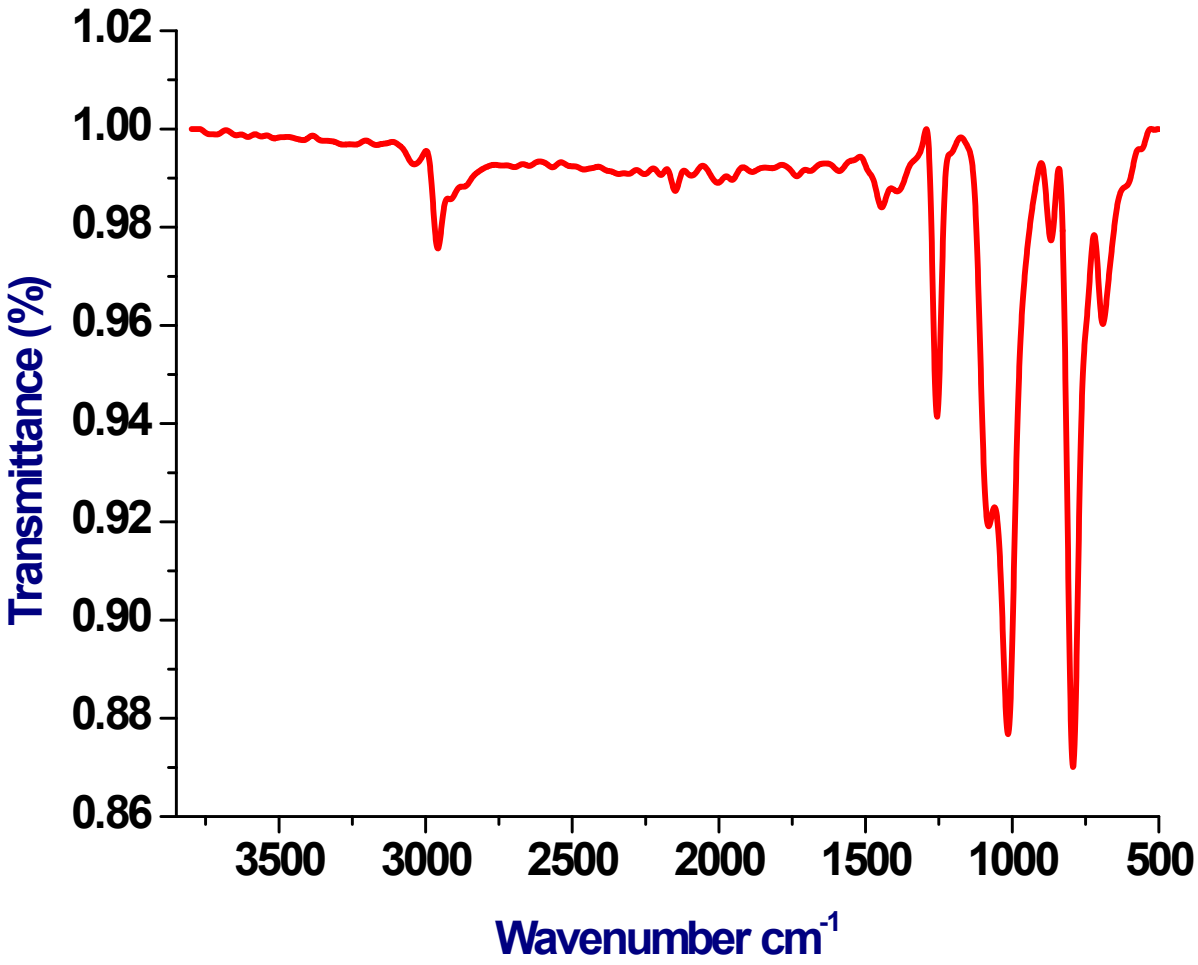


Figure S3. IR spectrum of [(η^6-*p*-cymene)-$RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)$] complex (**2**).

2. Catalysis:

2.1 General Experimental Procedure:

General procedure for the homocoupling of arylboronic acids to form biaryls

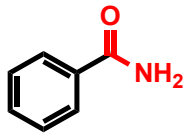
The arene-ruthenium- catalyzed homocoupling of arylboronic acids was carried out according to the previously reported method [19a]. Arylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) was added to a reaction tube containing water (5 mL) and [Ru]-catalyst **2** (0.029 g, 4 mol %). The reaction mixture was stirred for the preferred reaction time at room temperature. The procession of reaction was examined by thin layer chromatography (TLC). After completion of the reaction, it was extracted with ethyl acetate (3 × 10 mL). The organic layer was alienated and dried with anhydrous Na_2SO_4 to expel moisture. The solvent was evaporated under reduced pressure to get the desired product. The product formation was identified by ^1H NMR. Isolated yield was computed by using column chromatography with Hexane: EtOAc (99:1 or 95:5 v/v) as eluent.

General procedure for the hydration of nitriles

To a stirred solution of ruthenium(II) complex [(η^6-*p*-cymene)-$RuCl_2(C_6H_2(C_6H_5)_4CH_3NH_2)$] (**2**) (0.029 g, 0.04 mmol, 4 mol %, dissolved in 5 ml of water) in a round bottom flask, was added a nitrile (1 mmol) under open air conditions. The reaction mixture was stirred at room temperature for a pertinent period of time. After culmination of the reaction, the reaction mixture was extracted with dichloromethane. The organic layer was alienated and dried with sodium sulfate to expel moisture. The product was filtered and evaporated under reduced pressure. The crude reaction mixture was purified by column chromatography using diethyl ether as eluent. The identity of the resulting amides was assessed by ^1H NMR spectroscopy.

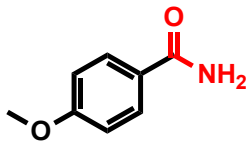
2.2 Characterization data of amide compounds Chart 1, Entry 1- 12

Benzamide (Chart 1, Entry 1)



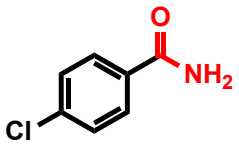
The reaction of benzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 98 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.87 – 7.85 (m, 2H, ArH), 7.71- 7.48 (m, 3H, ArH), 6.33 (brs, 2H, NH_2).

4-methoxybenzamide (Chart 1, Entry 2)



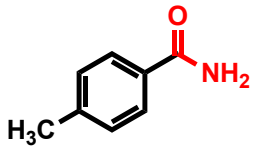
The reaction of 4-methoxybenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 82 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.93 – 7.77 (m, 3H, ArH), 7.18 (brs, 2H, NH_2), 6.93-6.91 (d, 2H, J = 8 Hz, ArH), 3.77 (s, 3H, -OCH_3).

4-chlorobenzamide (Chart 1, Entry 3)



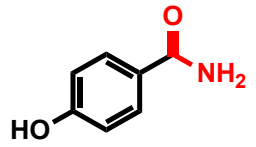
The reaction of 4-chlorobenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 99 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.10 (brs, 2H, NH_2), 7.91 – 7.90 (m, 1H, ArH), 7.86-7.85 (d, 1H, J = 1.6 Hz, ArH), 7.85-7.69 (m, 1H, ArH).

4-methylbenzamide (Chart 1, Entry 4)



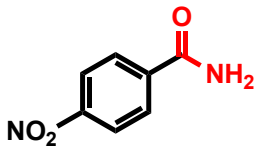
The reaction of 4-methylbenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 87 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.89-7.87 (m, 1H, ArH), 7.76 – 7.29 (m, 1H, ArH), 7.69-7.66 (m, 2H, ArH), 6.17 (brs, 2H, NH_2), 2.37 (s, 3H, $-CH_3$).

4-hydroxybenzamide (Chart 1, Entry 5)



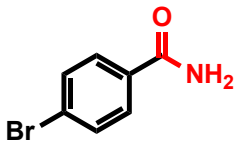
The reaction of 4-hydroxybenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 87 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 12.94 (s, 1H, -OH), 8.41 (brs, 2H, NH_2), 7.84-7.71 (m, 2H, ArH), 7.62 – 7.59 (m, 1H, ArH).

4-nitrobenzamide (Chart 1, Entry 6)



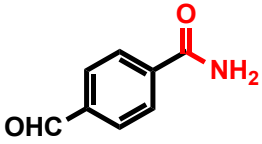
The reaction of 4-nitrobenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 99 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.29 (d, 2H, J = 7.2 Hz, ArH), 8.09 (d, 2H, J = 6.9 Hz, ArH), 7.89 (brs, 2H, NH_2).

4-bromobenzamide (Chart 1, Entry 7)



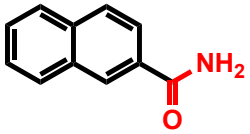
The reaction of 4-bromobenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 99 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.12 (brs, 2H, NH_2), 7.82 -7.79 (m, 2H, ArH), 7.52 (m, 2H, ArH).

4-formylbenzamide (Chart 1, Entry 8)



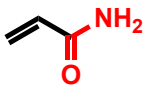
The reaction of 4-formylbenzonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 95 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.88 (s, 1H, -CHO), 8.43-8.22 (m, 2H, ArH), 8.12-8.07 (m, 2H, ArH), 7.43 (brs, 2H, NH_2).

2-naphthamide (Chart 1, Entry 9)



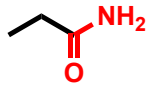
The reaction of 2-naphthonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 74 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.01-7.98 (m, 2H, ArH), 7.84-7.59 (m, 4H, ArH), 7.50 (brs, 2H, NH_2).

Acrylamide (Chart 1, Entry 10)



The reaction of acrylonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 71 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 6.52-6.21 (m, 2H, ArH), 6.19 (m, 1H, ArH), 6.97 (brs, 2H, NH_2).

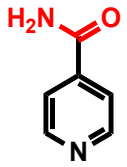
Propionamide (Chart 1, Entry 11)



The reaction of propionitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 96 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.29 (brs, 1H, NH_2), 5.98 (brs, 1H, NH_2), 2.19 (q, 2H, -CH_2), 1.09 (t, 3H, -CH_3).

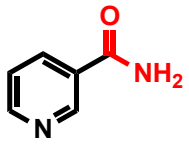
2.3 Characterization data of amide compounds Chart 2, Entry 1- 7

Isonicotinamide (Chart 2, Entry 1)



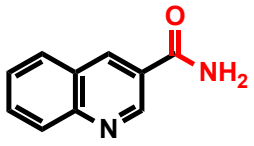
The reaction of isonicotinonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 97 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.34-8.32 (s, 1H, J = 8.4 Hz, ArH), 8.16-8.14 (d, J = 8 Hz, ArH), 7.86-7.62 (m, 2H, ArH), 7.53 (brs, 2H, NH_2).

Nicotinamide (Chart 2, Entry 2)



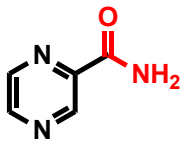
The reaction of nicotinonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 99 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.29-8.02 (s, 1H, J = 7.8 Hz, ArH), 7.94-7.83 (d, J = 6.2 Hz, ArH), 7.59 -7.44 (m, 2H, ArH), 7.12 (brs, 2H, NH_2).

Quinoline-3-carboxamide (Chart 2, Entry 3)



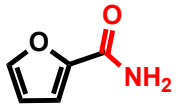
The reaction of nicotinonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 93 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.19 (s, 1H, ArH), 8.27-8.18 (m, 4H, ArH), 7.69 (brs, 2H, NH_2), 7.65 – 7.03 (m, 2H, ArH).

Pyrazin-2-carboxamide (Chart 2, Entry 4)



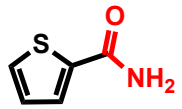
The reaction of pyrazine-2-carbonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 96 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.87 (s, 1H, ArH), 9.03-8.94 (m, 2H, ArH), 8.21 (brs, 2H, NH_2).

Furan-2-carboxamide (Chart 2, Entry 5)



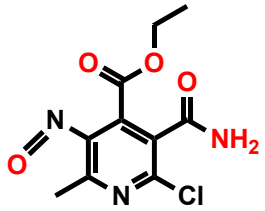
The reaction of furan-2-carbonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a brown solid in 96 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.57-7.55 (d, J = 8.8 Hz, 1H, ArH), 7.26 (s, 1H, -CH), 6.95-6.86 (m, 1H, ArH), 6.41 (brs, 2H, NH_2).

Thiophene-2-carboxamide (Chart 2, Entry 6)



The reaction of thiophene-2-carbonitrile (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 98 % yield. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.15 (brs, 2H, NH_2), 7.86-7.53 (m, 3H, ArH), 7.52 (brs, 2H, NH_2).

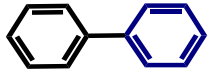
2-Chloro-4-(ethoxycarbonyl)-6-methyl-5-nitroso-3-pyridine carboxamide (Chart 2, Entry 7)



The reaction of ethyl 2-chloro-3-cyano-6-methyl-5-nitrosoisonicotinate (1 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O under aerobic conditions. The title compound was recovered as a white solid in 79 % yield. ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.89 (brs, 1H, NH_2), 7.64 (brs, 1H, NH_2), 4.43-4.383 (m, 2H, CH_2), 2.67 (s, 3H, CH_3), 1.34 (s, 3H, CH_3).

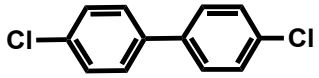
2.4 Characterization data of compounds Chart 3, Entry 1- 10

Biphenyl (Chart 3, Entry 1)



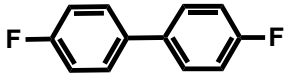
The reaction of phenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as a white crystalline solid in 92 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.59 – 7.56 (m, 4H, ArH), 7.45- 7.40 (m, 4H, ArH), 7.35 – 7.31 (m, 2H, ArH).

4,4'-dichloro-1,1'-biphenyl (Chart 3, Entry 2)



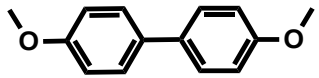
The reaction of 4-chlorophenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as a white crystalline solid in 69 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.47 – 7.44 (m, 4H, ArH), 7.41- 7.37 (m, 4H, ArH).

4,4'-difluoro-1,1'-biphenyl (Chart 3, Entry 3)



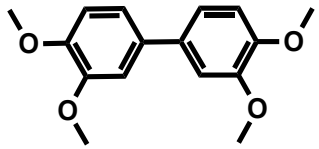
The reaction of 4-fluorophenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as colorless oil in 79 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.41 – 7.38 (m, 2H, ArH), 7.29- 7.01 (m, 3H, ArH), 6.89-6.87 (m, 3H, ArH).

4,4'-dimethoxy-1,1'-biphenyl (Chart 3, Entry 4)



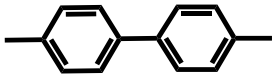
The reaction of 4-methoxyphenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as a white crystalline solid in 92 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.41 – 7.17 (m, 4H, ArH), 6.89- 6.70 (m, 2H, ArH), 6.69-6.67 (m, 2H, ArH), 3.76 (s, 3H, $-OCH_3$), 3.68 (s, 3H, $-OCH_3$).

3,3',4,4'-tetramethoxy-1,1'-biphenyl (Chart 3, Entry 5)



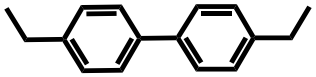
The reaction of 3,4-dimethoxyphenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as colorless oil in 84 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 6.83 – 6.80 (m, 3H, ArH), 6.79- 6.76 (m, 3H, ArH), 3.85 (s, 3H, $-OCH_3$), 3.81 (s, 6H, $-OCH_3$), 3.77 (s, 3H, $-OCH_3$).

4,4'-dimethyl-1,1'-biphenyl (Chart 3, Entry 6)



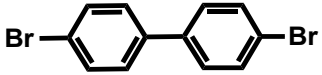
The reaction of 4-methylphenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as a white crystalline solid in 79 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.40– 7.28 (m, 3H, ArH), 7.19- 7.06 (m, 5H, ArH), 2.30 (s, 3H, $-CH_3$), 2.18 (s, 3H, $-CH_3$).

4,4'-diethyl-1,1'-biphenyl (Chart 3, Entry 7)



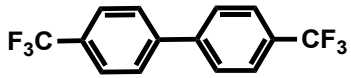
The reaction of 4-ethylphenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as colorless oil in 82 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.42– 7.40 (m, 2H, ArH), 7.30- 7.28 (m, 3H, ArH), 7.17-7.05 (m, 3H, ArH), 2.26-2.56 (q, 2H, $-CH_2$), 2.50-2.44 (q, 2H, $-CH_2$), 1.20 (s, 3H, $-CH_3$), 1.18 (s, 3H, $-CH_3$).

4,4'-dibromo-1,1'-biphenyl (Chart 3, Entry 8)



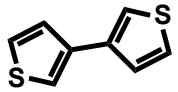
The reaction of 4-bromophenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as colorless oil in 61 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.53 – 7.39 (m, 5H, ArH), 7.32- 7.27 (m, 3H, ArH).

4,4'-bis(trifluoromethyl)-1,1'-biphenyl (Chart 3, Entry 9)



The reaction of 4-(trifluoromethyl)phenylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as a white crystalline solid in 84 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.34 – 7.26 (m, 4H, ArH), 7.17- 7.15 (m, 2H, ArH), 7.09-7.00 (m, 2H, ArH).

3,3'-bithiophene (Chart 3, Entry 10)



The reaction of 3-thienylboronic acid (1 mmol) with tri-potassium phosphate (0.425 g, 2 mmol) and $Cu(OAc)_2$ (0.300 g, 1.5 mmol) and catalyst **2** (0.029 g, 4 mol %) in 5mL of H_2O in presence of air. The title compound was recovered as a white crystalline solid in 69 % yield. ^1H NMR ($CDCl_3$, 400 MHz): δ 7.38 – 7.37 (m, 2H, ArH), 7.36- 7.26 (m, 2H, ArH).

2.6 Representative ^{1}H NMR spectra for amide products

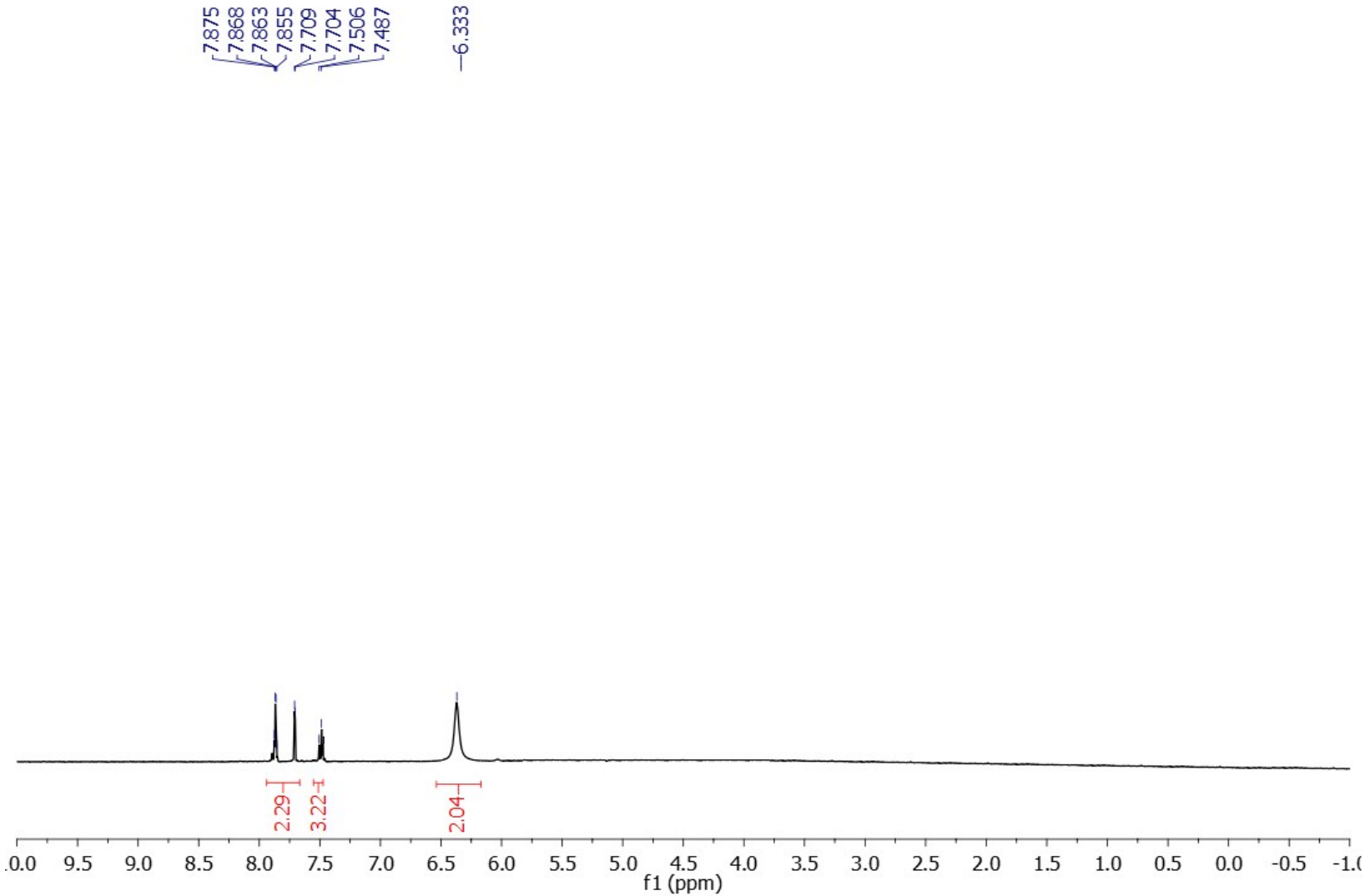


Figure S4:[1]H NMR spectrum of benzamide

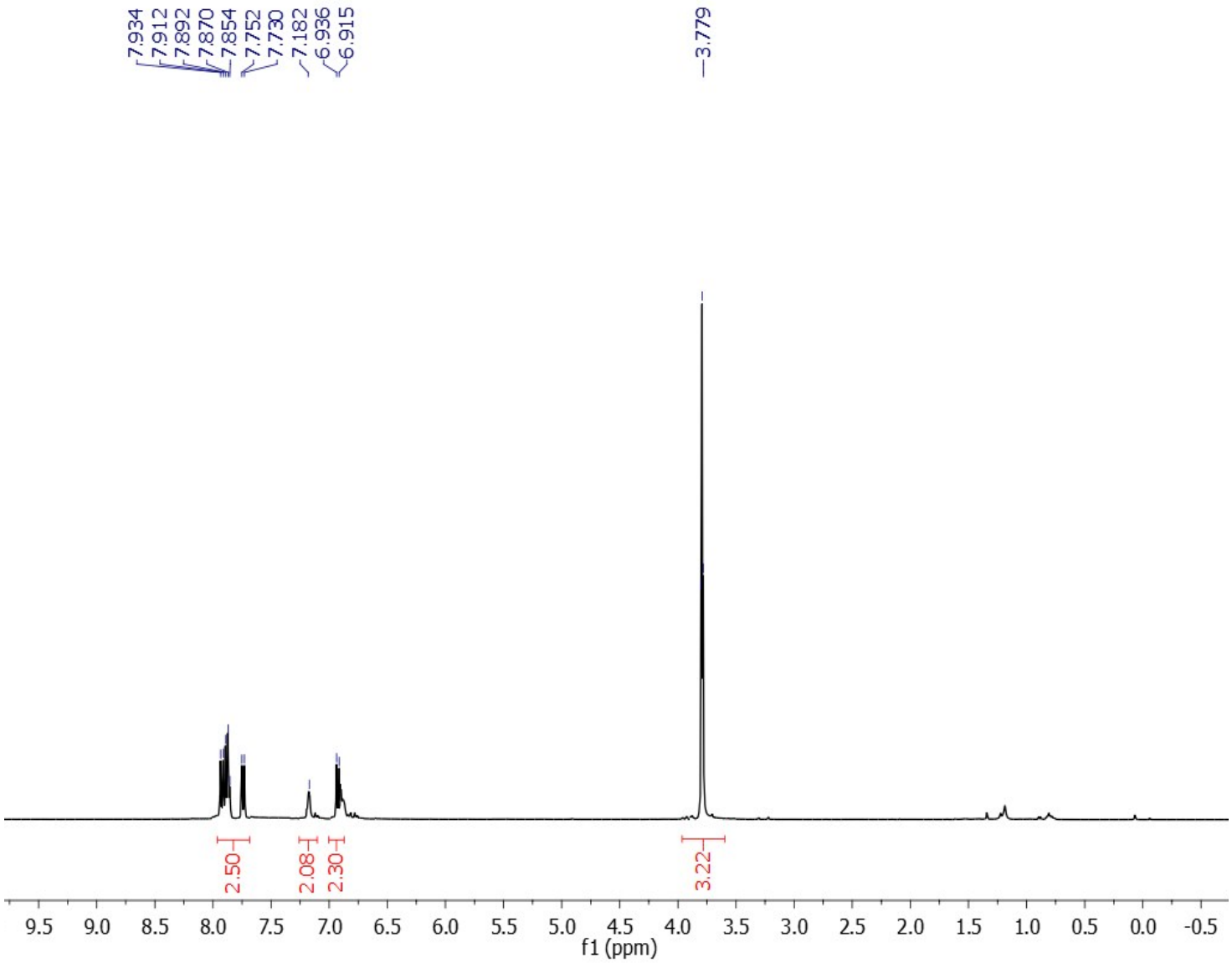


Figure S5:[1]H NMR spectrum of 4-methoxybenzamide

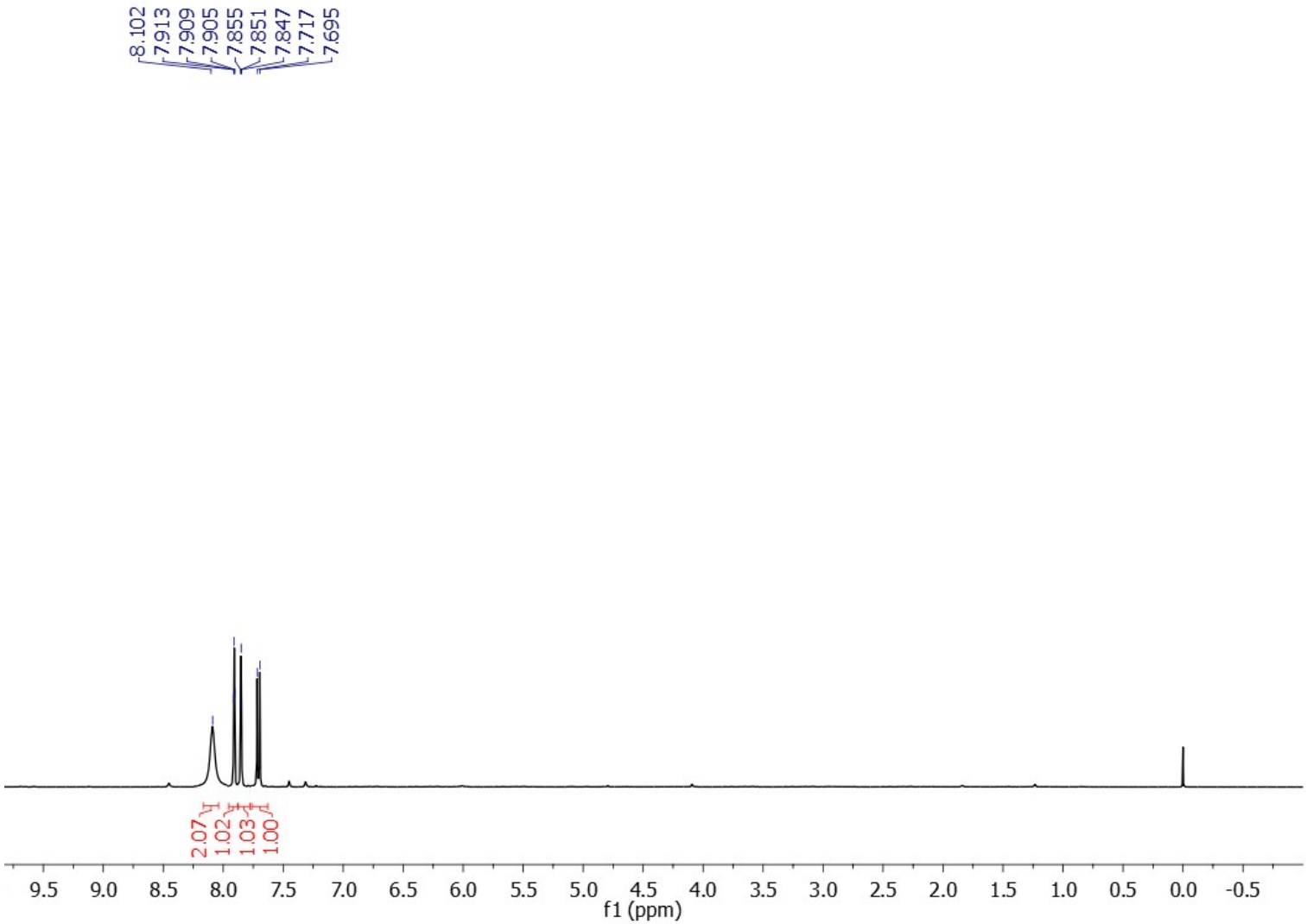


Figure S6:[1]H NMR spectrum of 4-chlorobenzamide

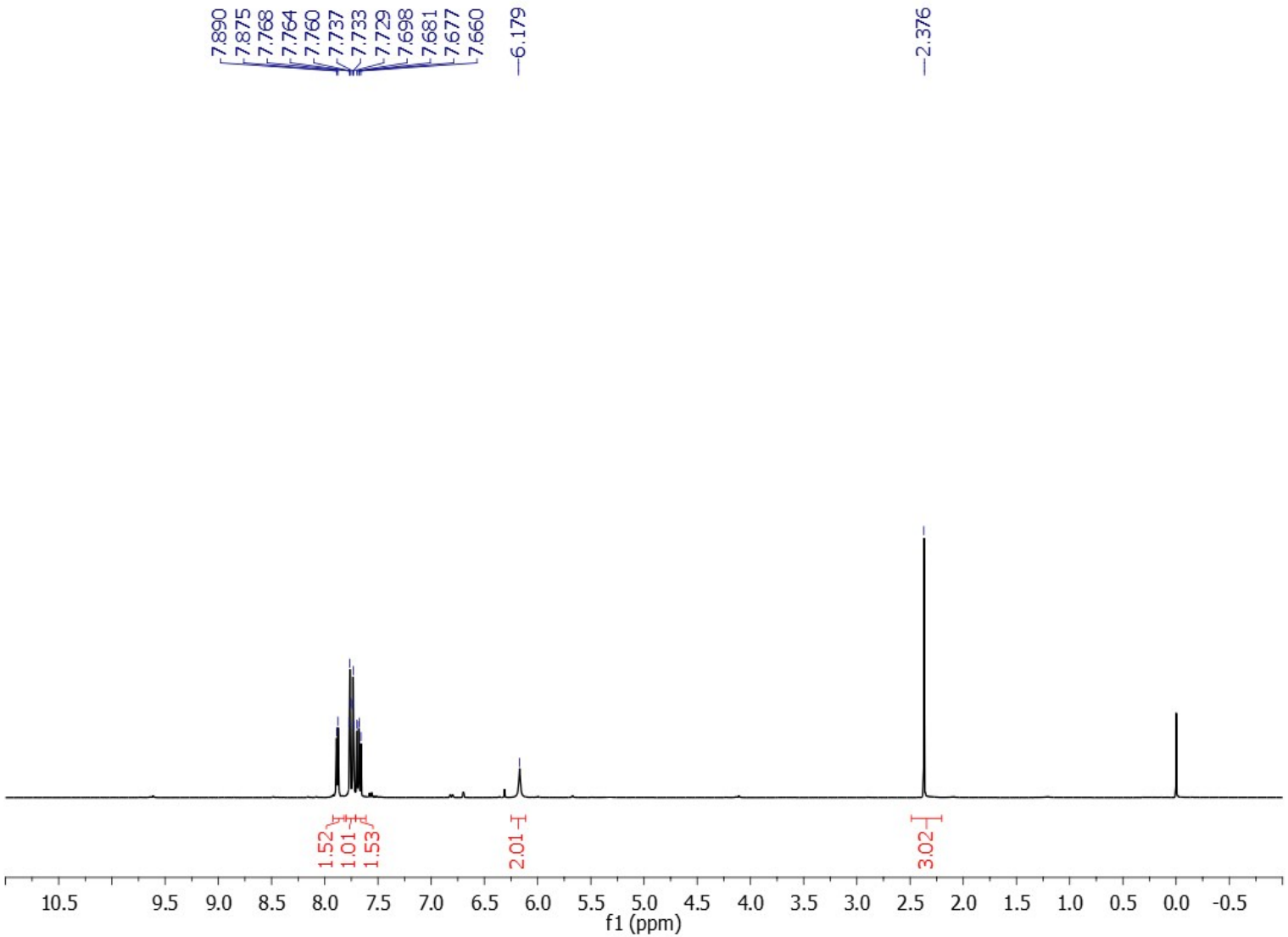


Figure S7:[1]H NMR spectrum of 4-methylbenzamide

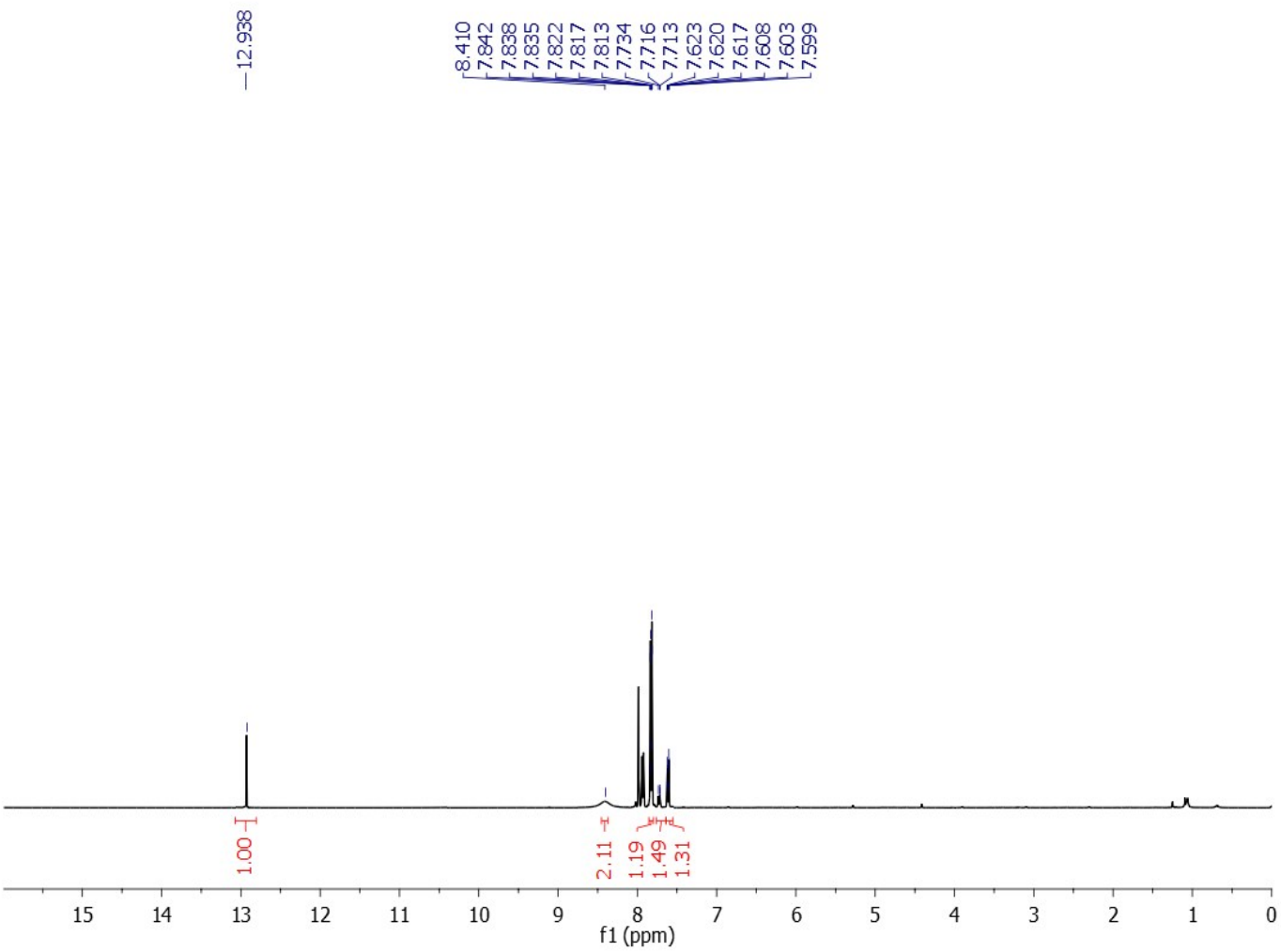


Figure S8:[1]H NMR spectrum of 4-hydroxybenzamide

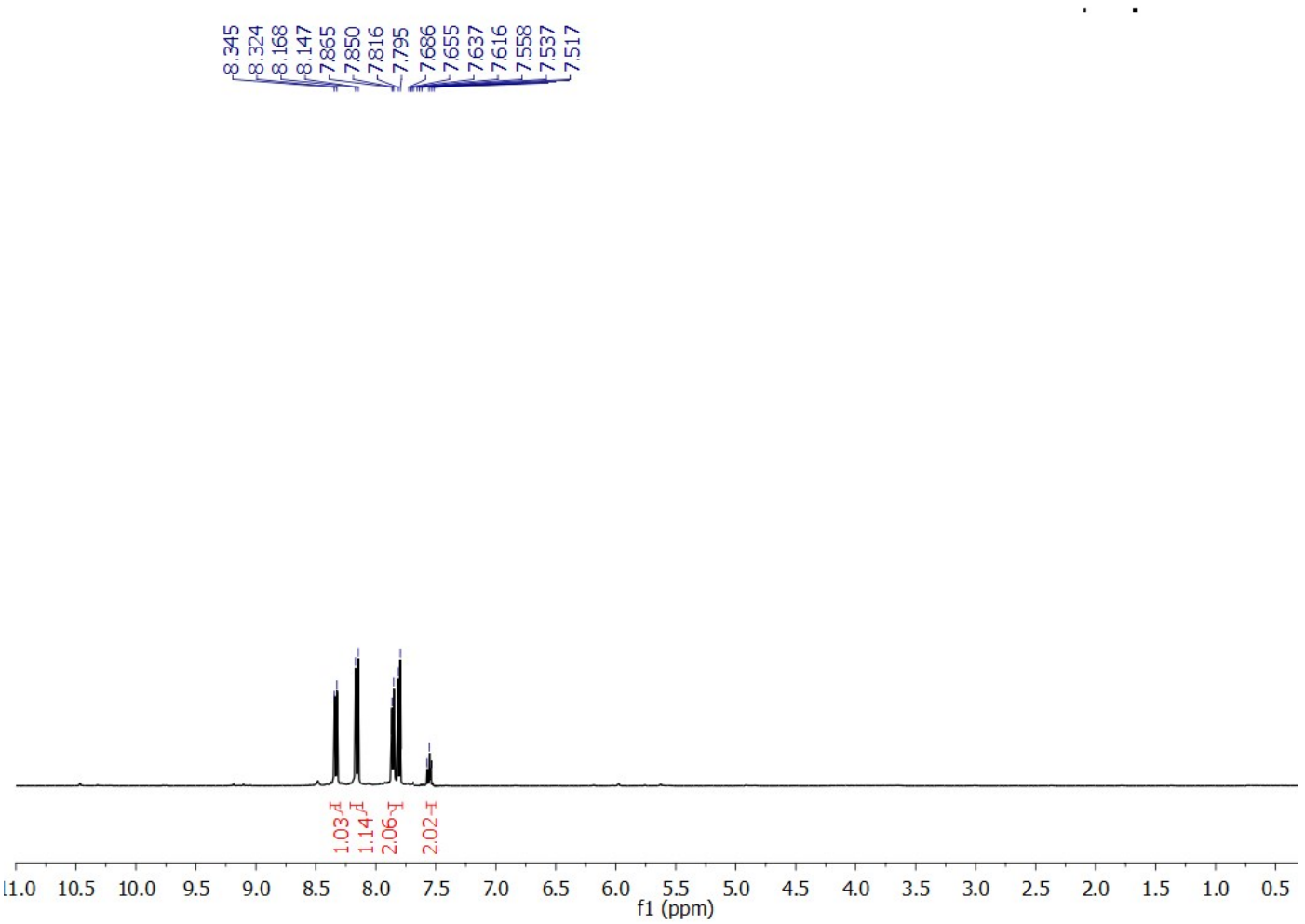


Figure S9:[1]H NMR spectrum of isonicotinamide

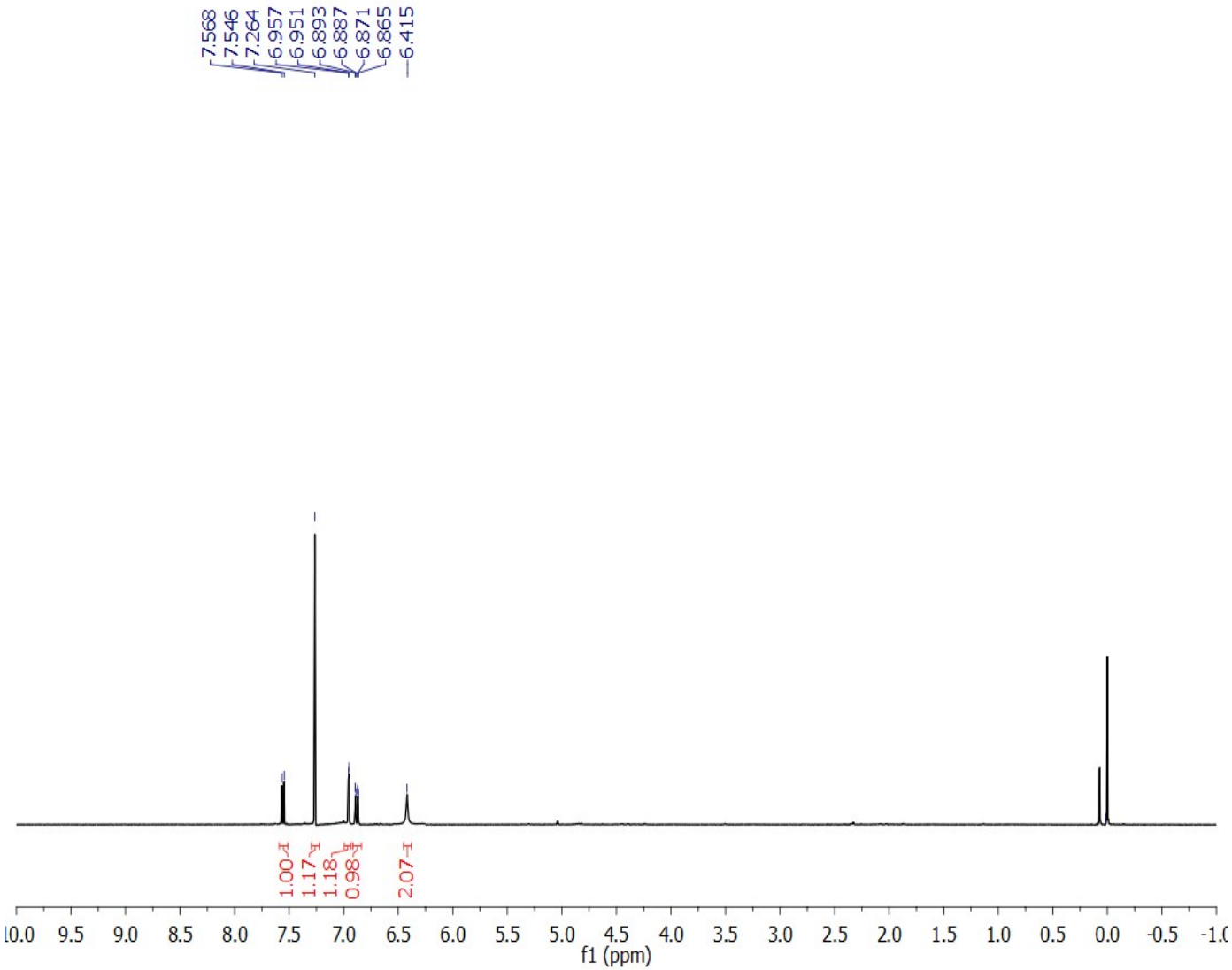


Figure S10:[1]H NMR spectrum of furan-2-carboxamide

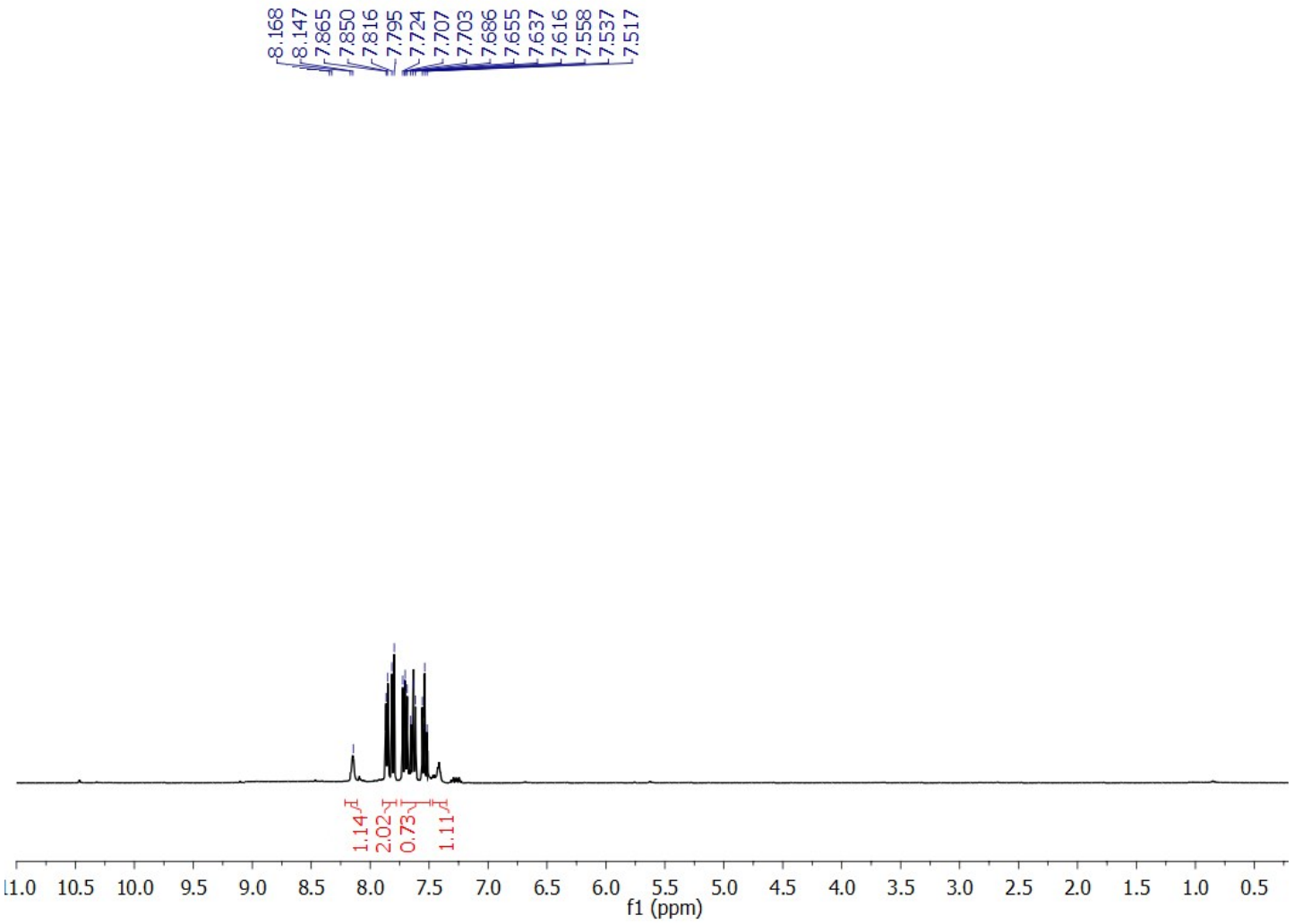


Figure S11:[1]H NMR spectrum of thiophene-2-carboxamide

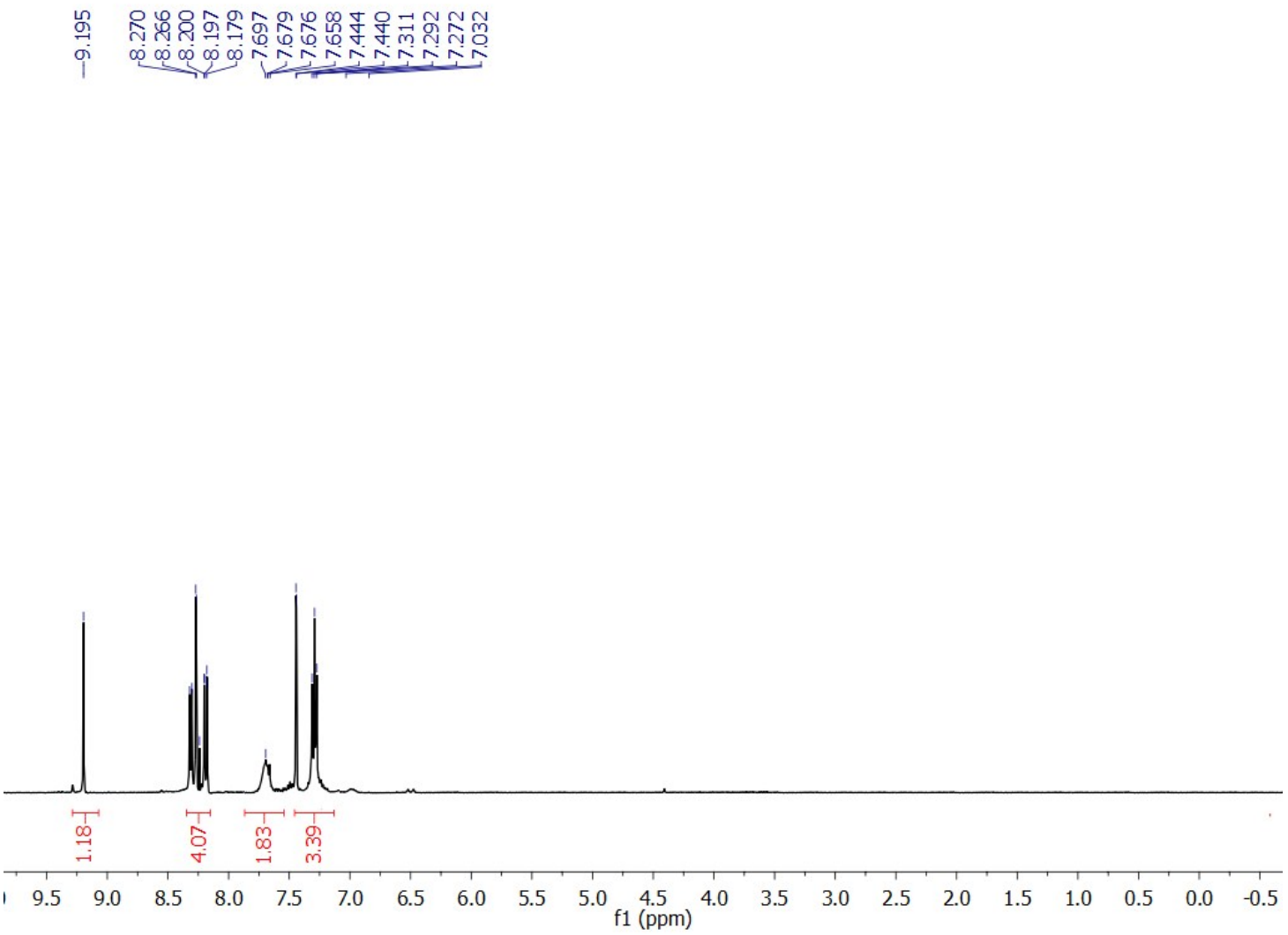


Figure S12:[1]H NMR spectrum of quinoline-3-carboxamide

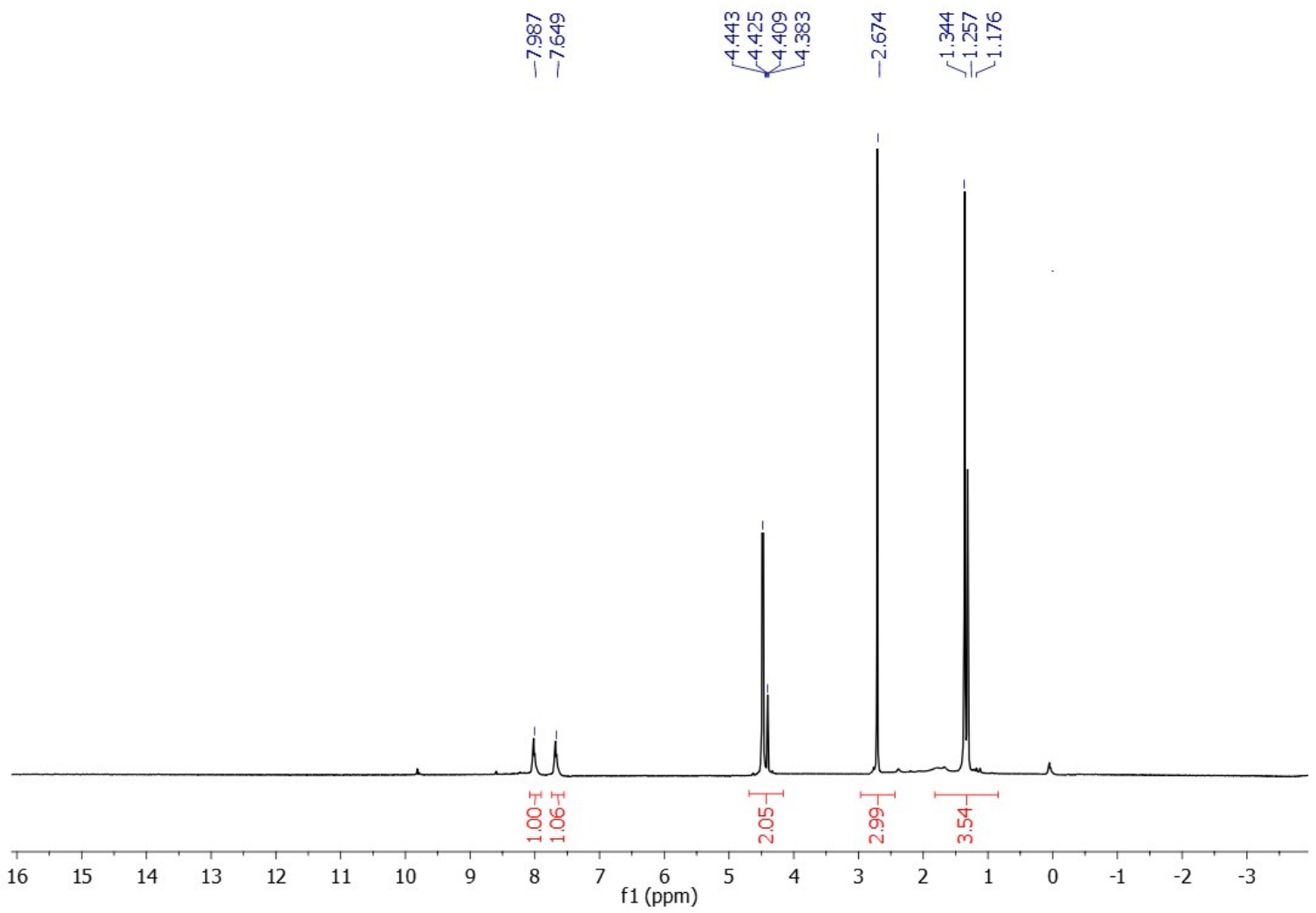


Figure S13:[1]H NMR spectrum of 2-chloro-4-(ethoxycarbonyl)-6-methyl-5-nitroso-3-pyridine carboxamide

2.7 Representative ^{1}H NMR spectra for homocoupled prodcuts

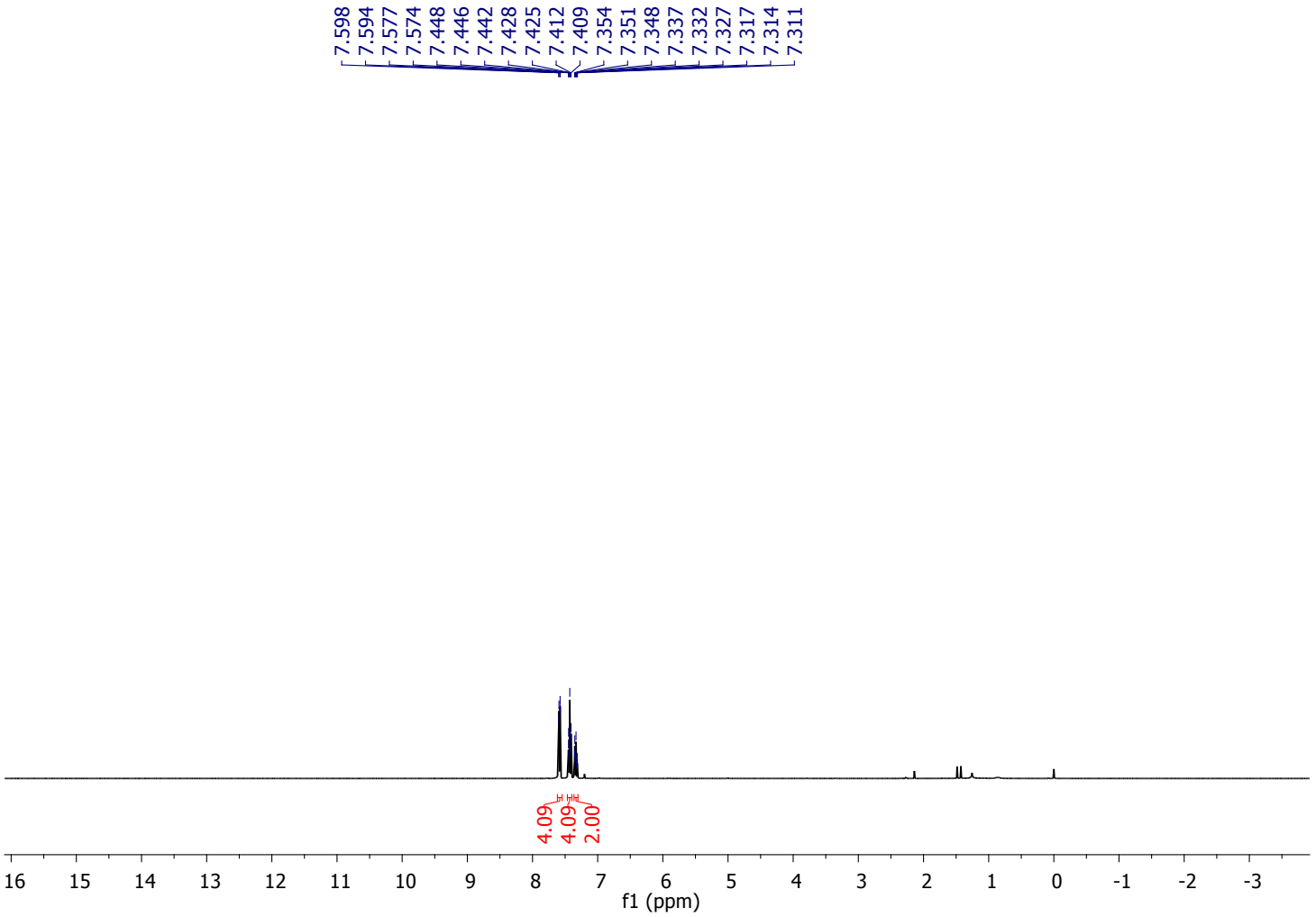


Figure S14:^{1}H NMR spectrum of Biphenyl

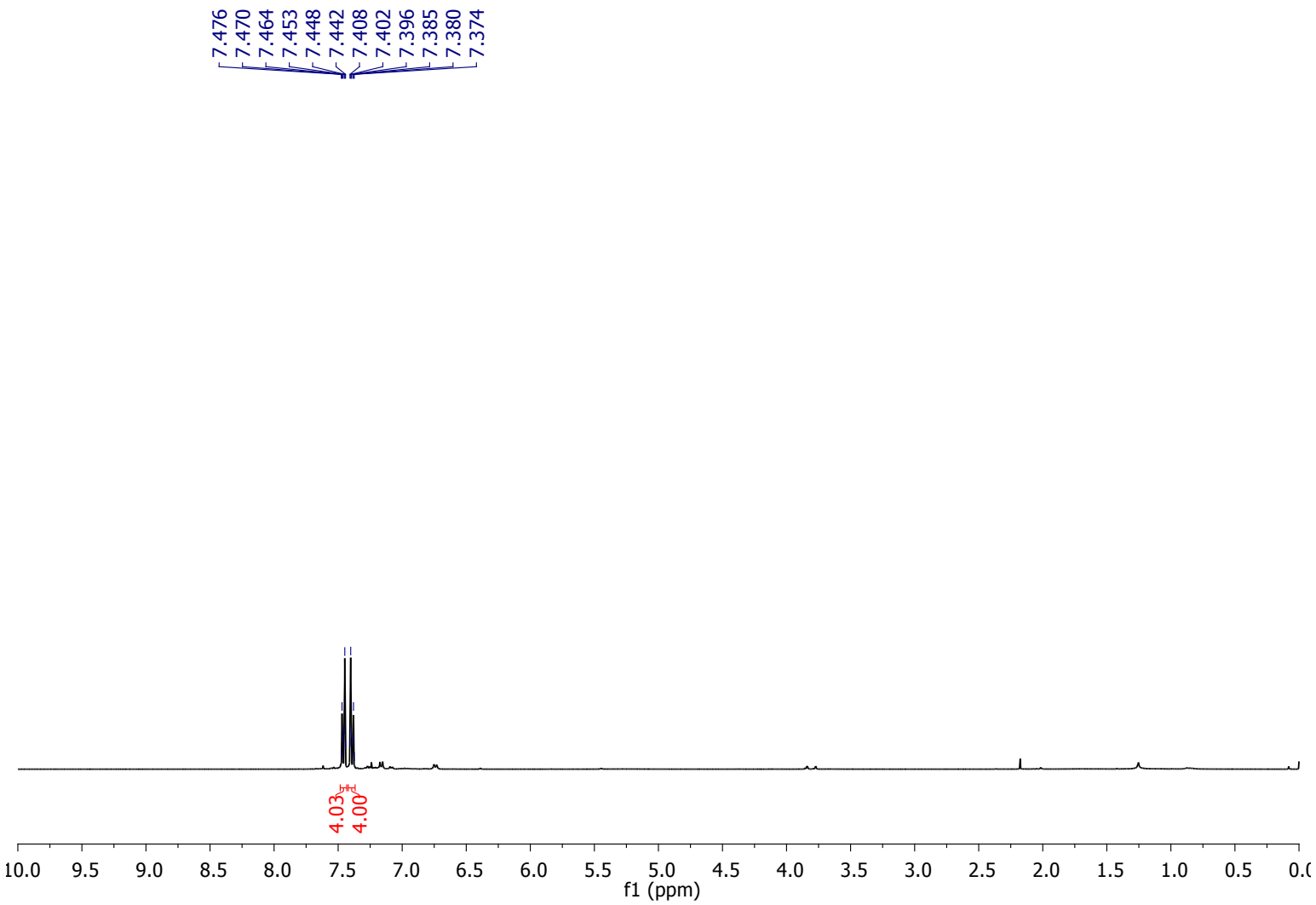


Figure S15:[1]H NMR spectrum of 4,4'-dichloro-1,1'-biphenyl

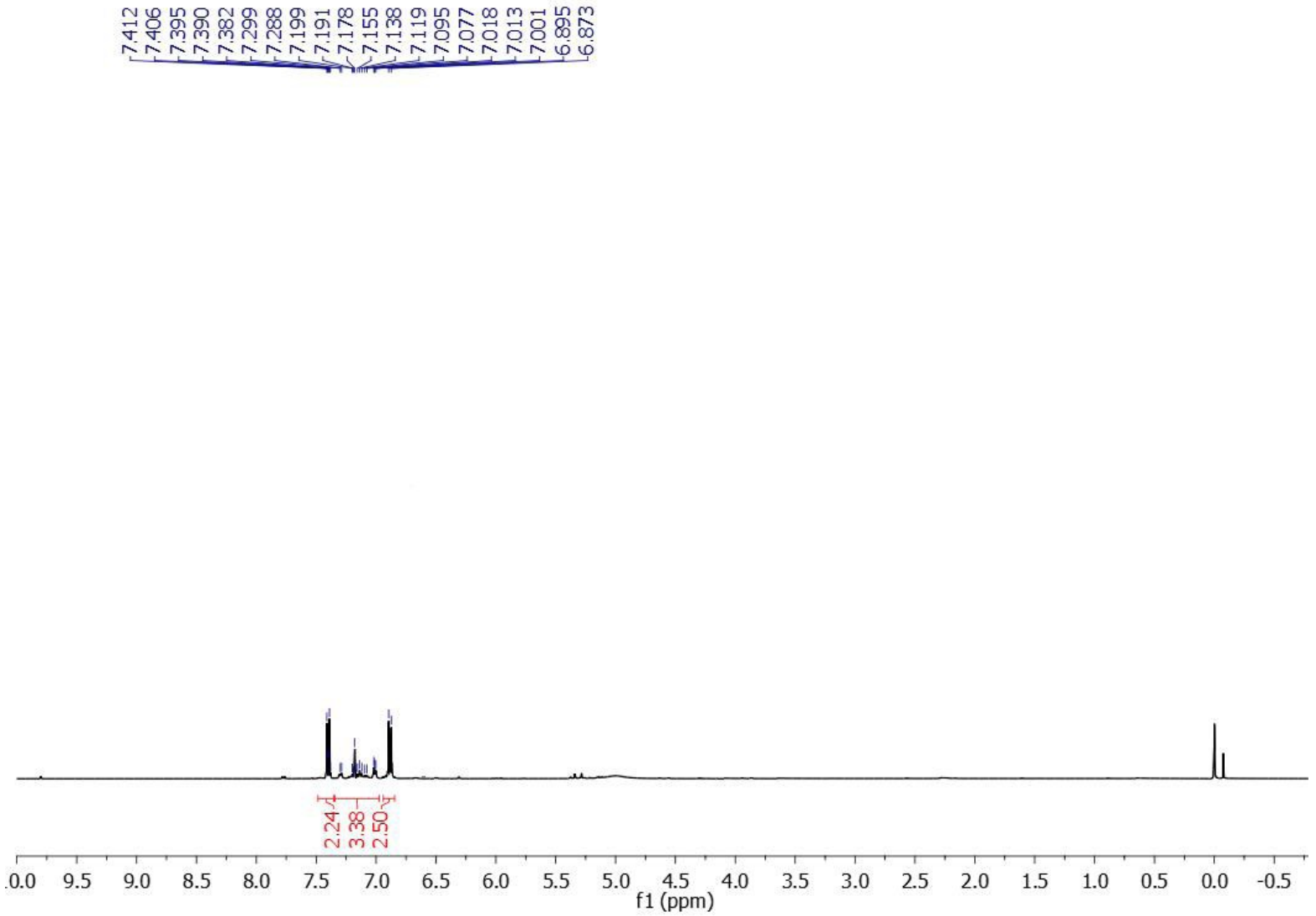


Figure S16:[1]H NMR spectrum of 4,4'-difluoro-1,1'-biphenyl

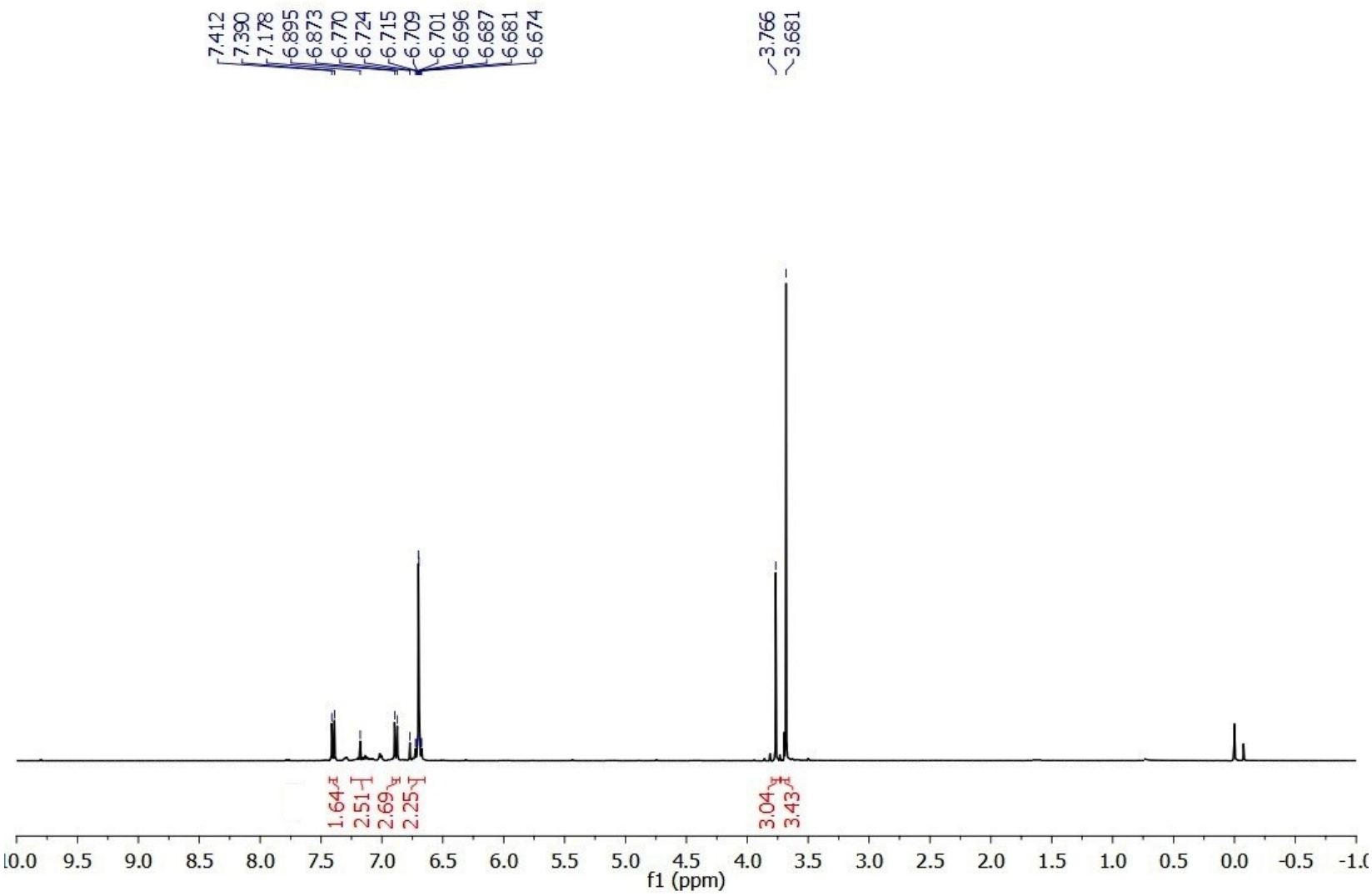


Figure S17:[1]H NMR spectrum of 4,4'-dimethoxy-1,1'-biphenyl

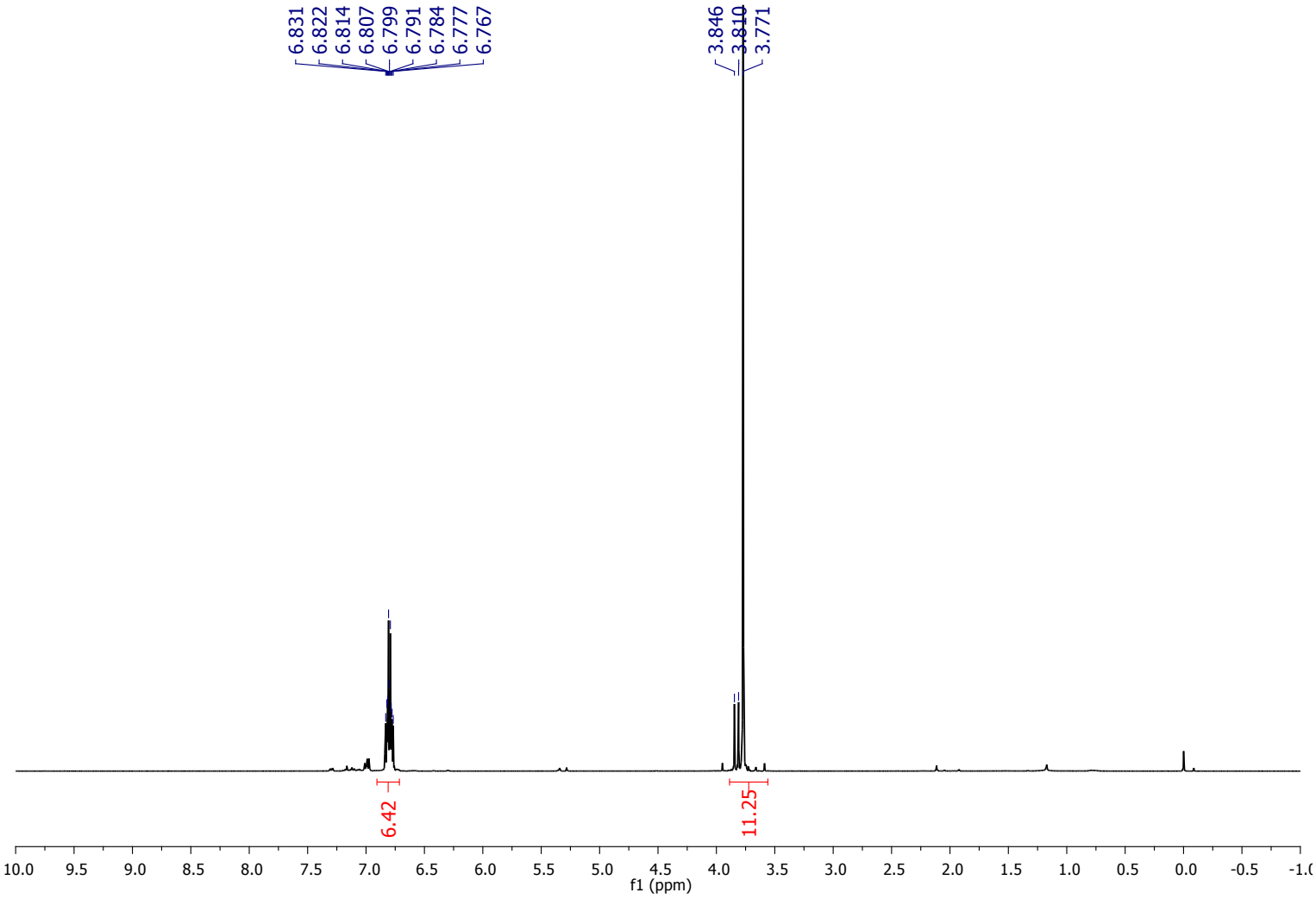


Figure S18:[1]H NMR spectrum of 3,3',4,4'-tetramethoxy-1,1'-biphenyl

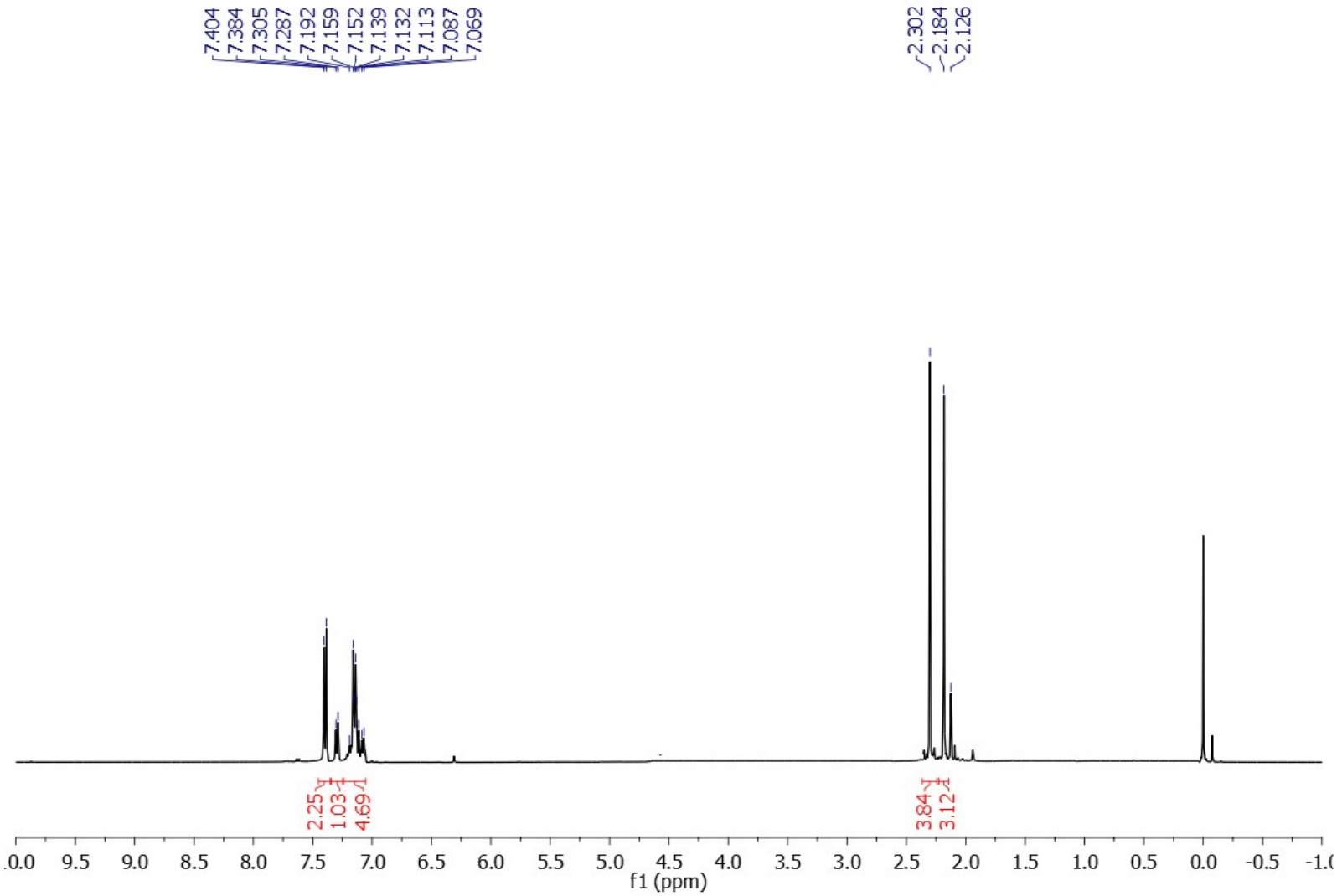


Figure S19:[1]H NMR spectrum of 4,4'-dimethyl-1,1'-biphenyl

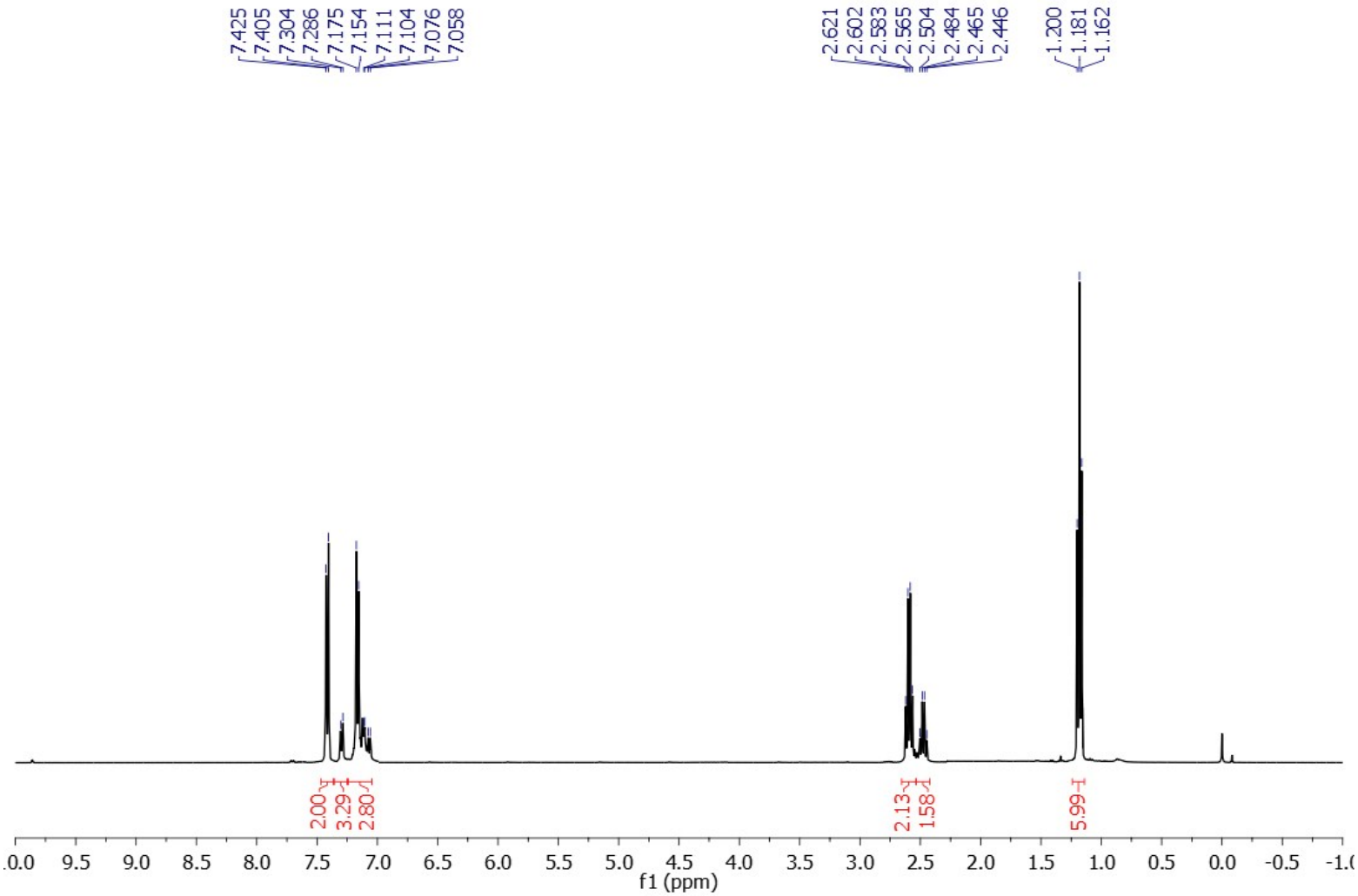


Figure S20:[1]H NMR spectrum of 4,4'-diethyl-1,1'-biphenyl

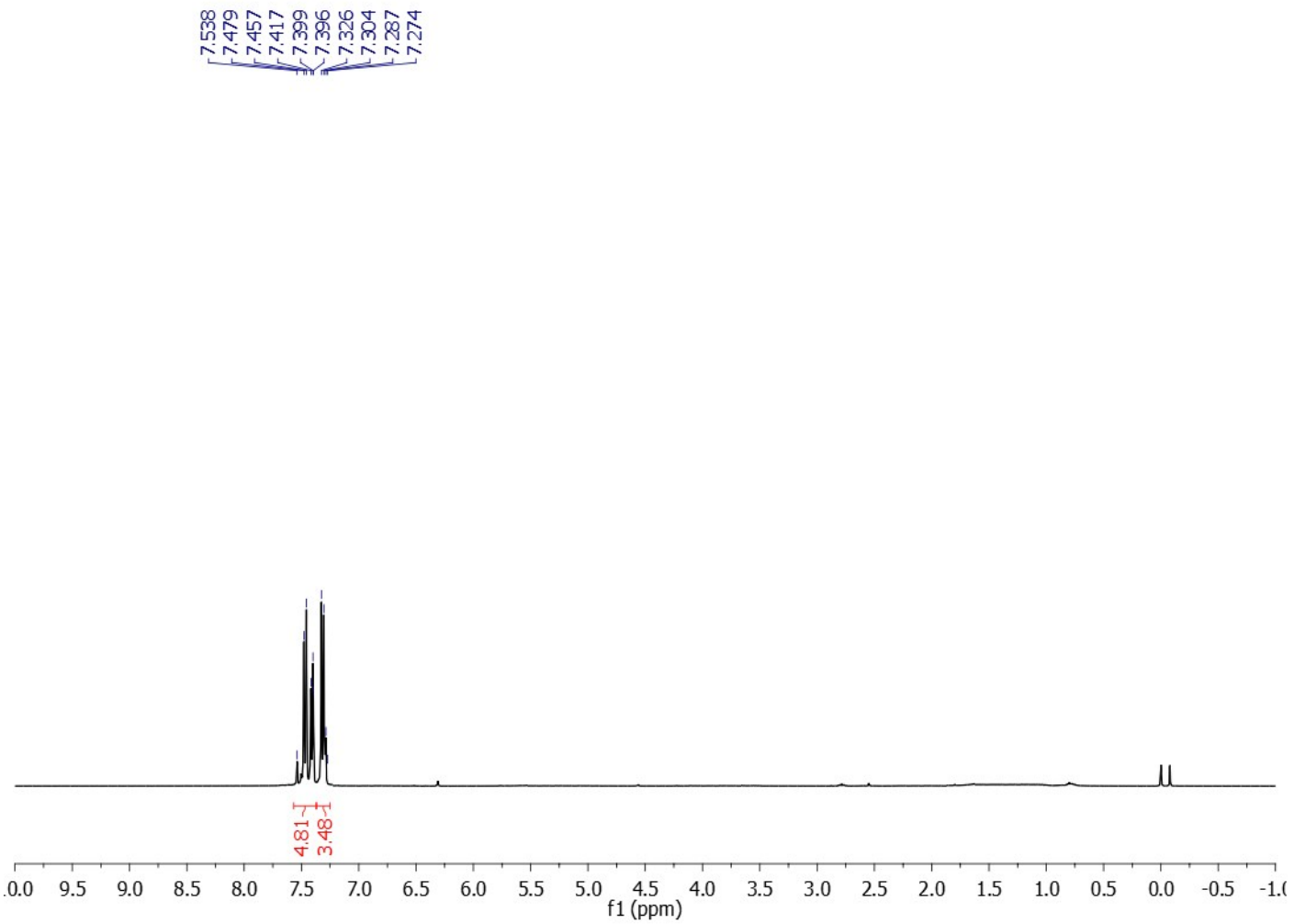


Figure S21:[1]H NMR spectrum of 4,4'-dibromo-1,1'-biphenyl

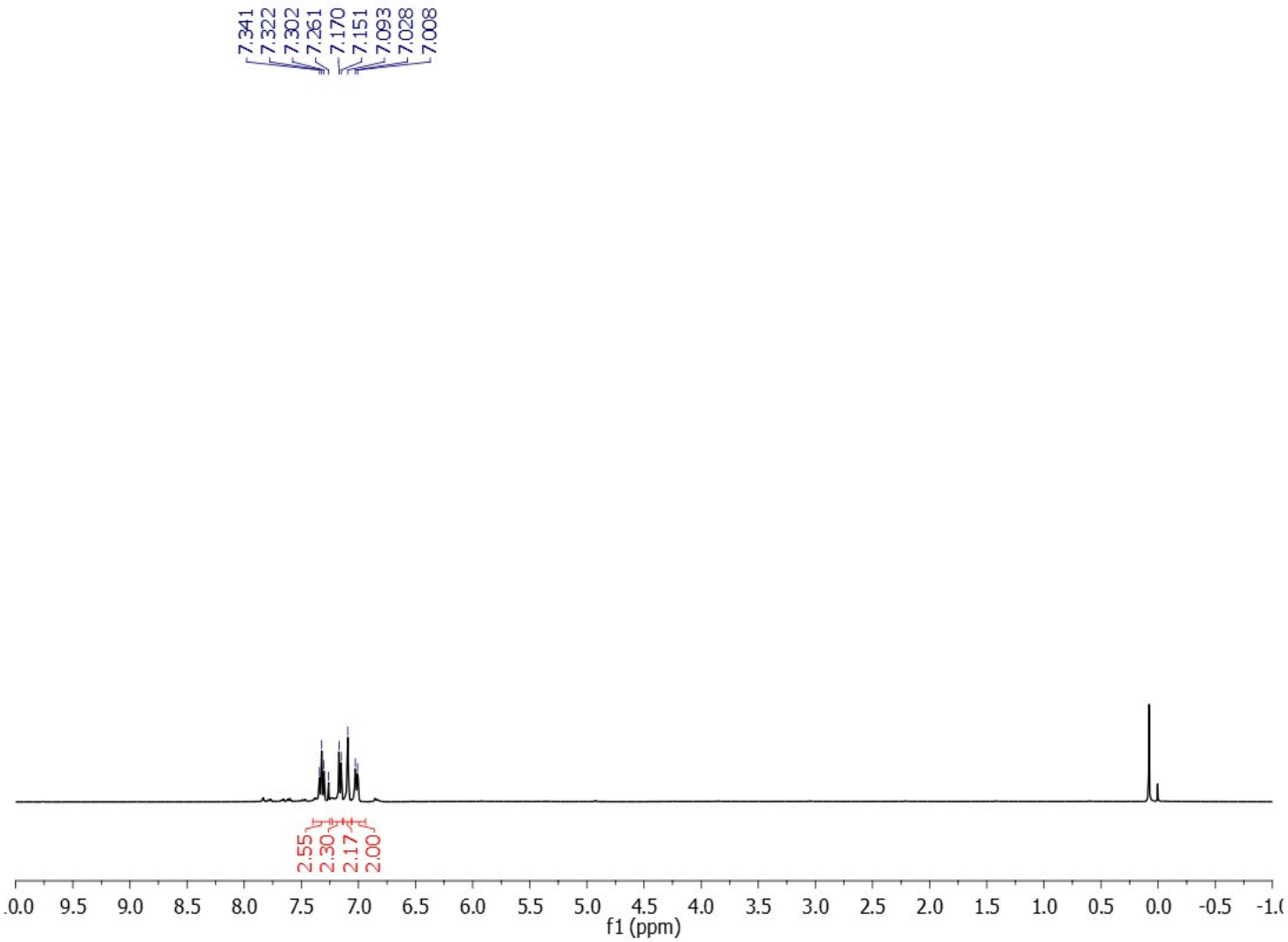


Figure S22:[1]H NMR spectrum of 4,4'-bis(trifluoromethyl)-1,1'-biphenyl

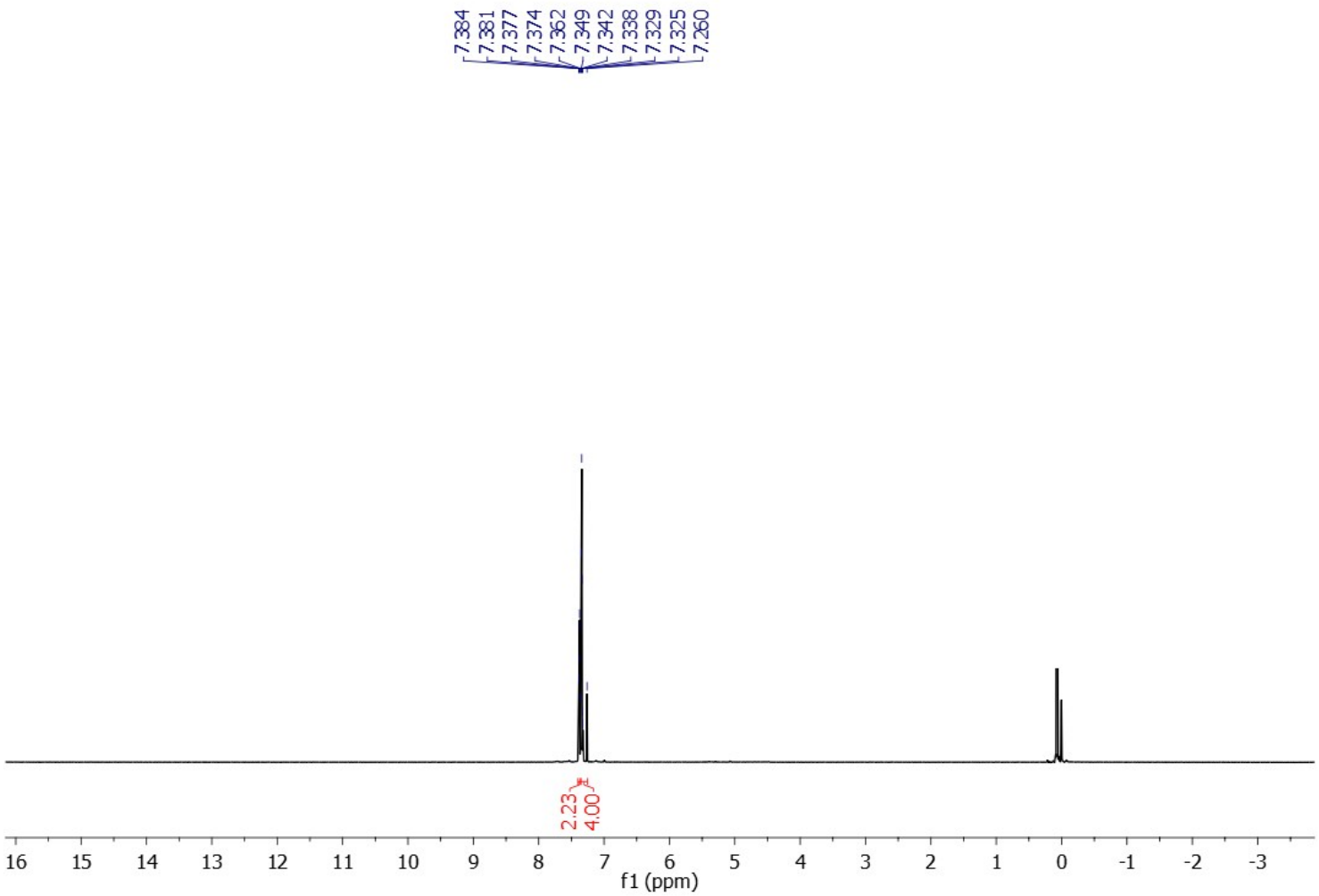


Figure S23:[1]H NMR spectrum of 3,3'-bithiophene