

# Suzuki–Miyaura Coupling Using Monolithic Pd Reactors and Scaling-up by Series Connection of the Reactors

Aiichiro Nagaki, Katsuyuki Hirose, Yuya Moriwaki, Masahiro Takumi, Yusuke Takahashi, Koji Mitamura, Kimihiro Matsukawa, Norio Ishizuka, and Jun-ichi Yoshida

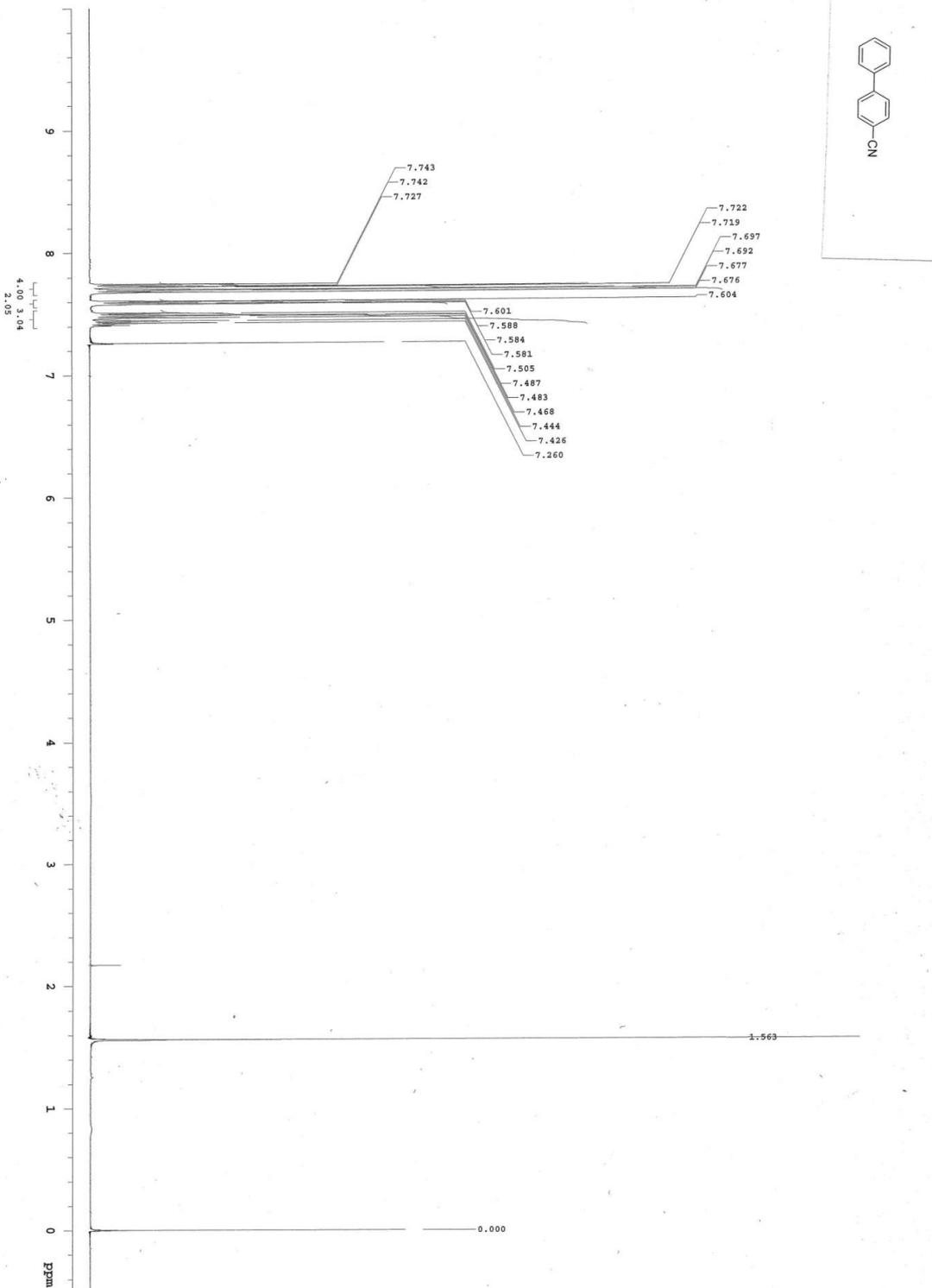


Figure S1. <sup>1</sup>H NMR spectrum of biphenyl-4-carbonitrile

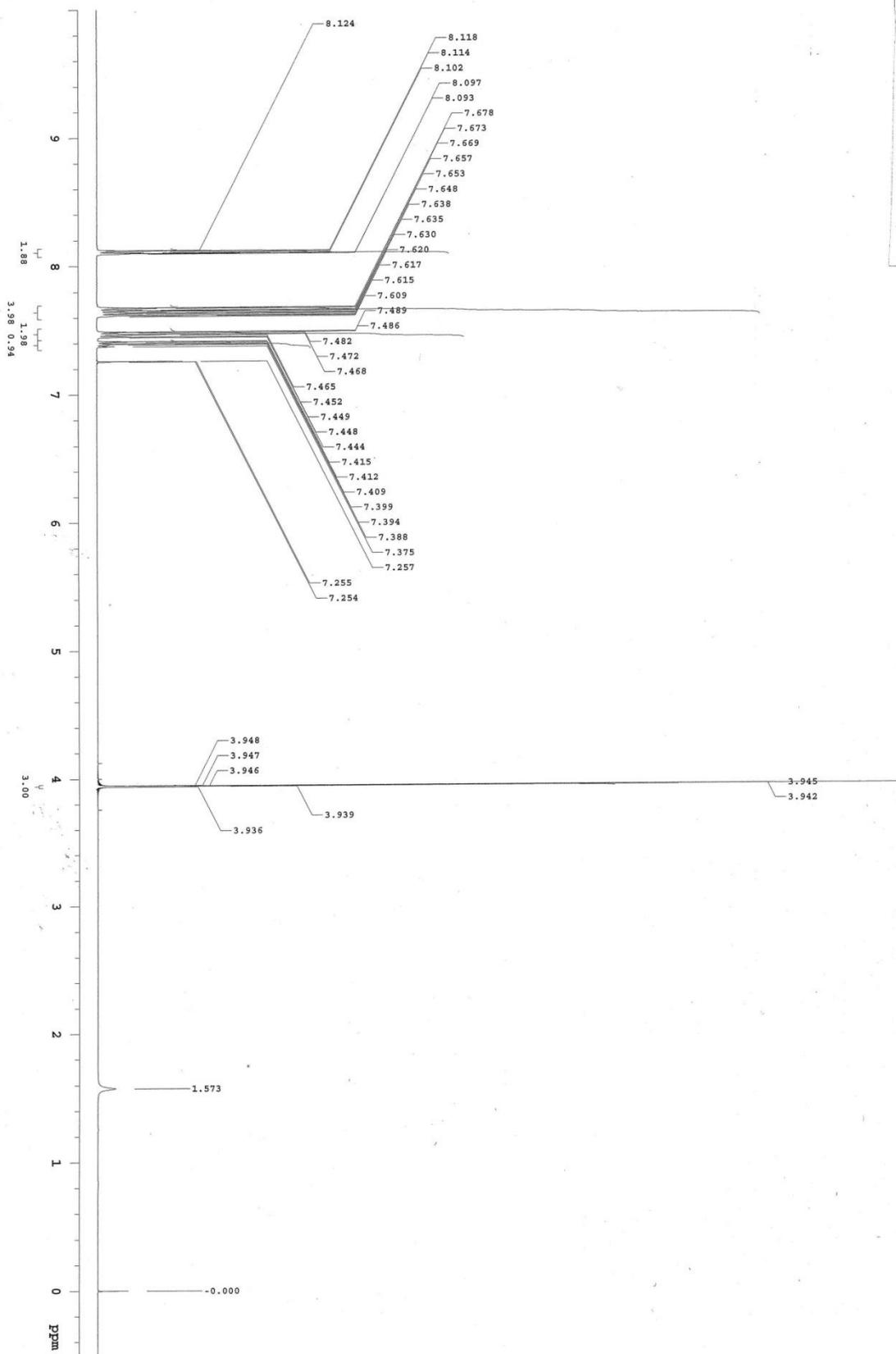


Figure S2.  $^1\text{H}$  NMR spectrum of methyl 4-phenylbenzoate

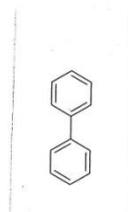
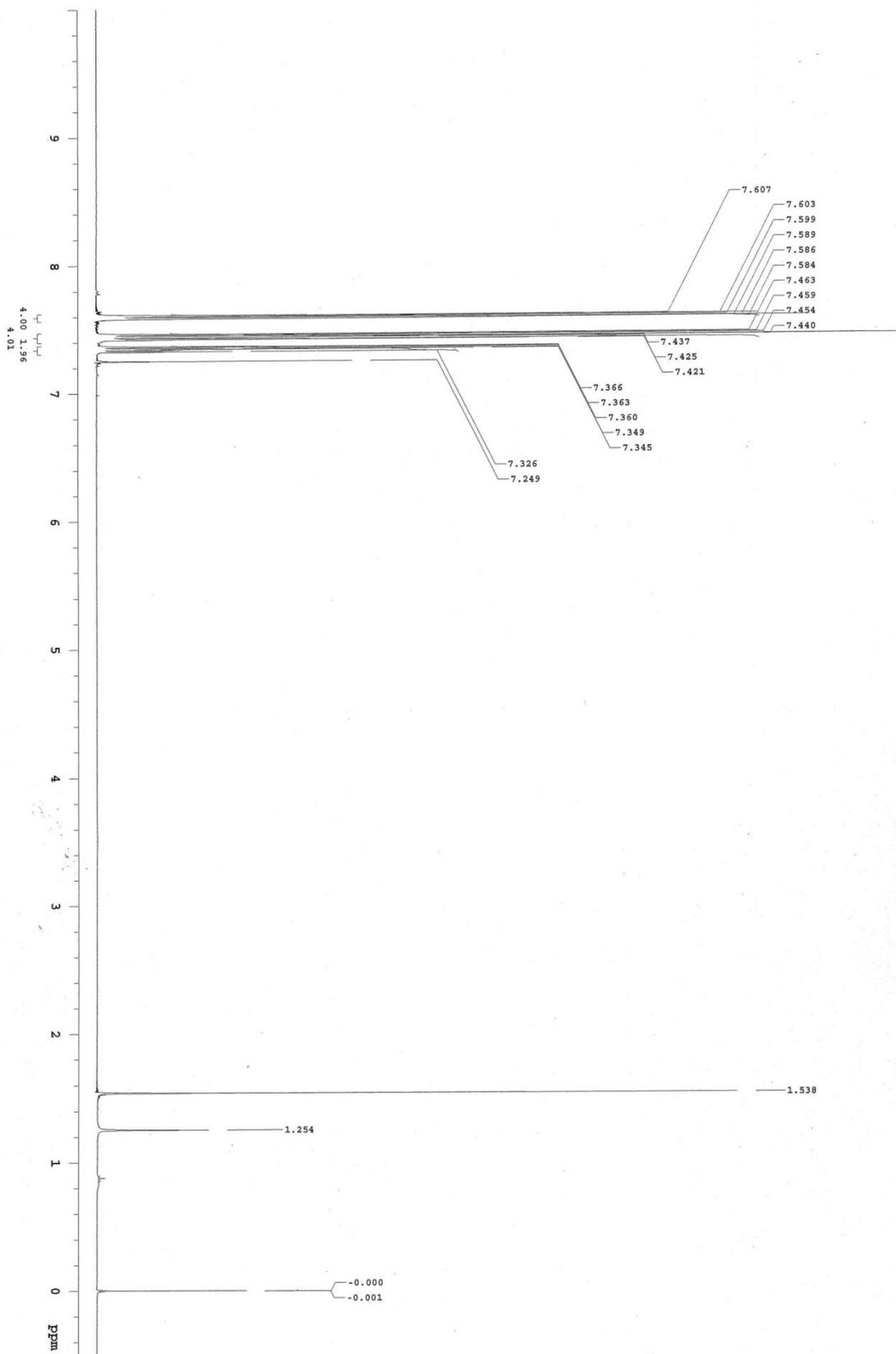


Figure S3. <sup>1</sup>H NMR spectrum of biphenyl

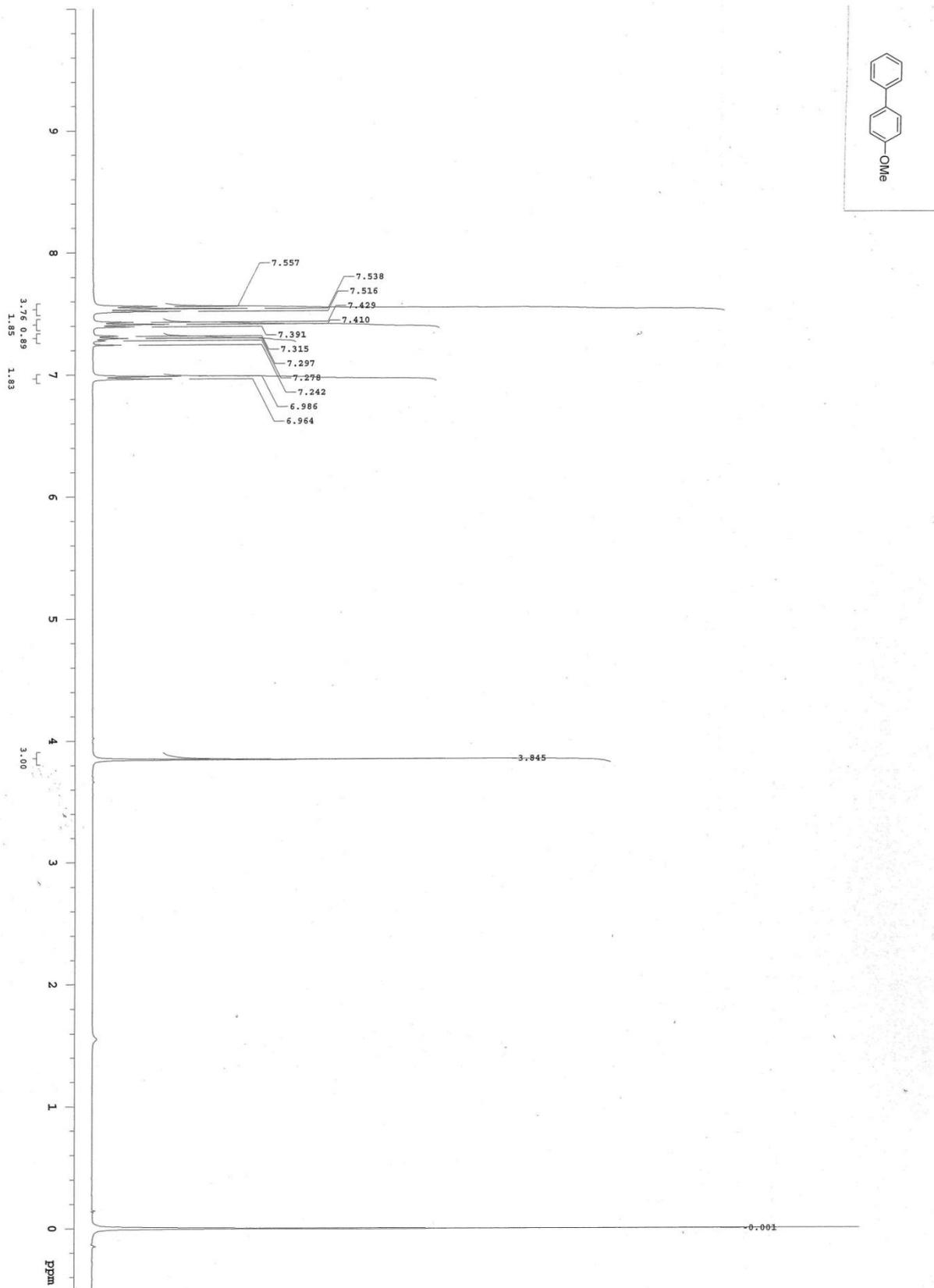


Figure S4. <sup>1</sup>H NMR spectrum of 4-methoxybiphenyl

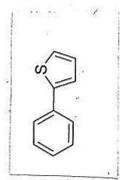
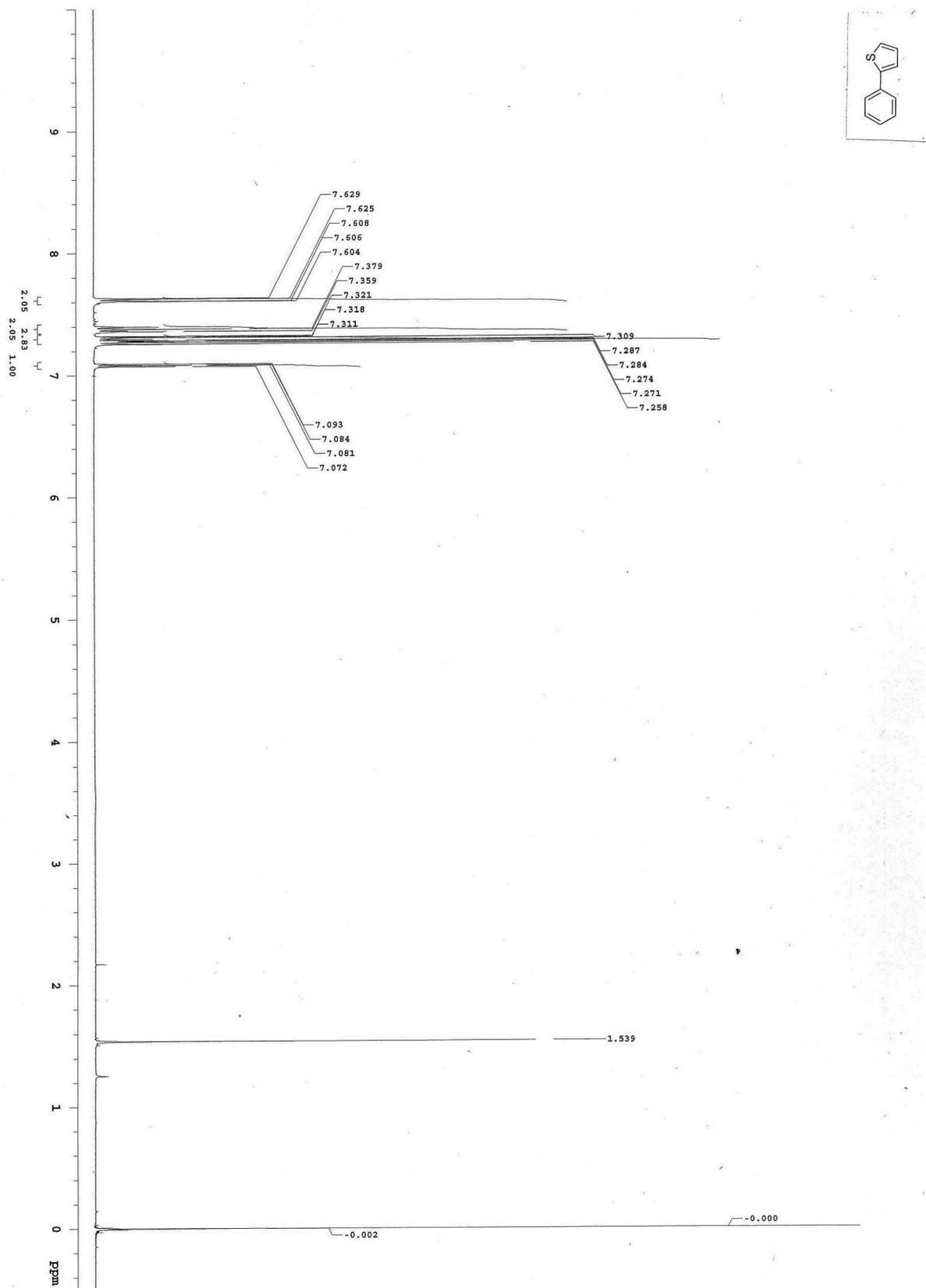


Figure S5.  $^1\text{H}$  NMR spectrum of 2-phenylthiophene

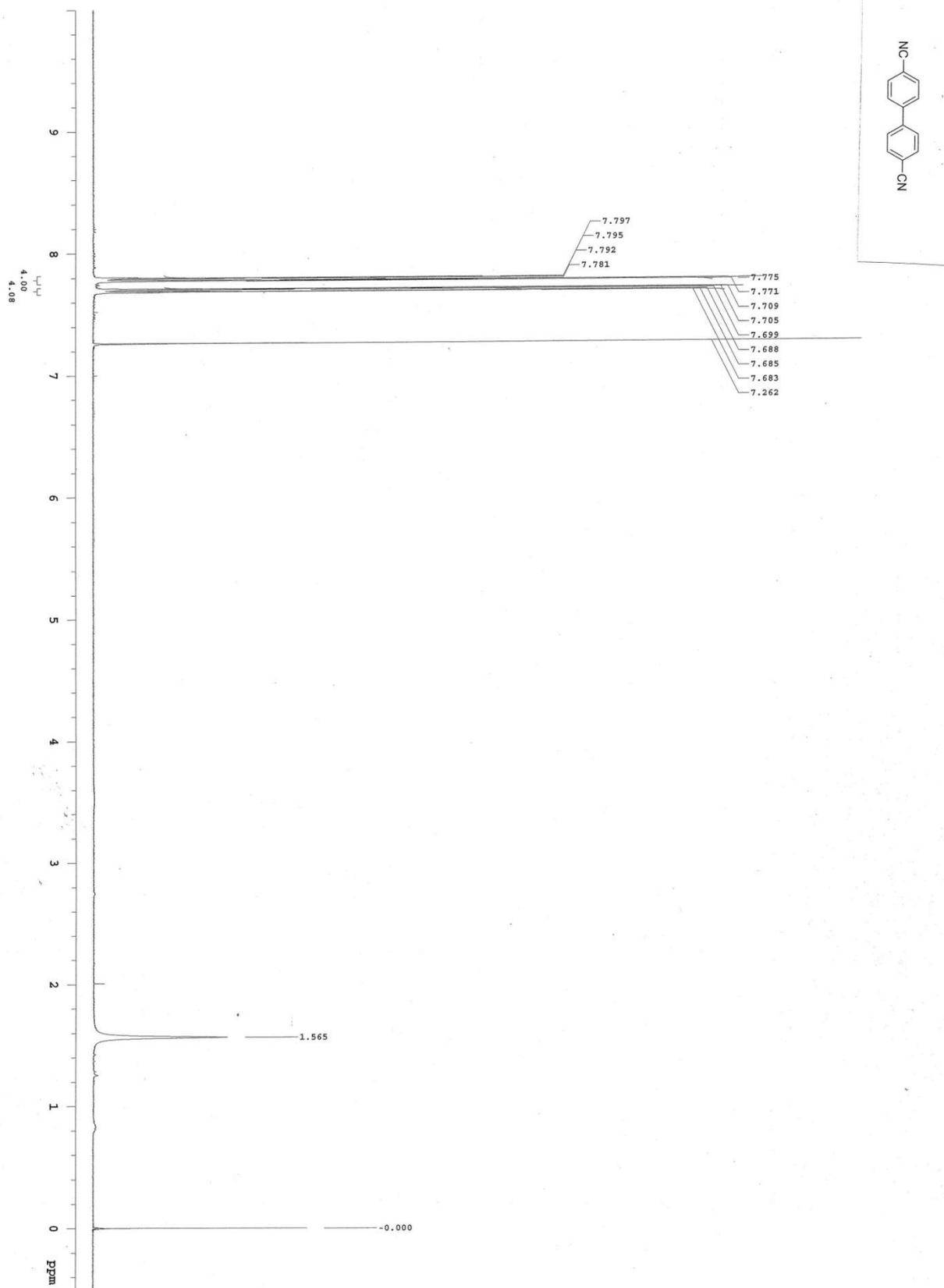


Figure S6.  $^1\text{H}$  NMR spectrum of 4,4'-dicyanobiphenyl

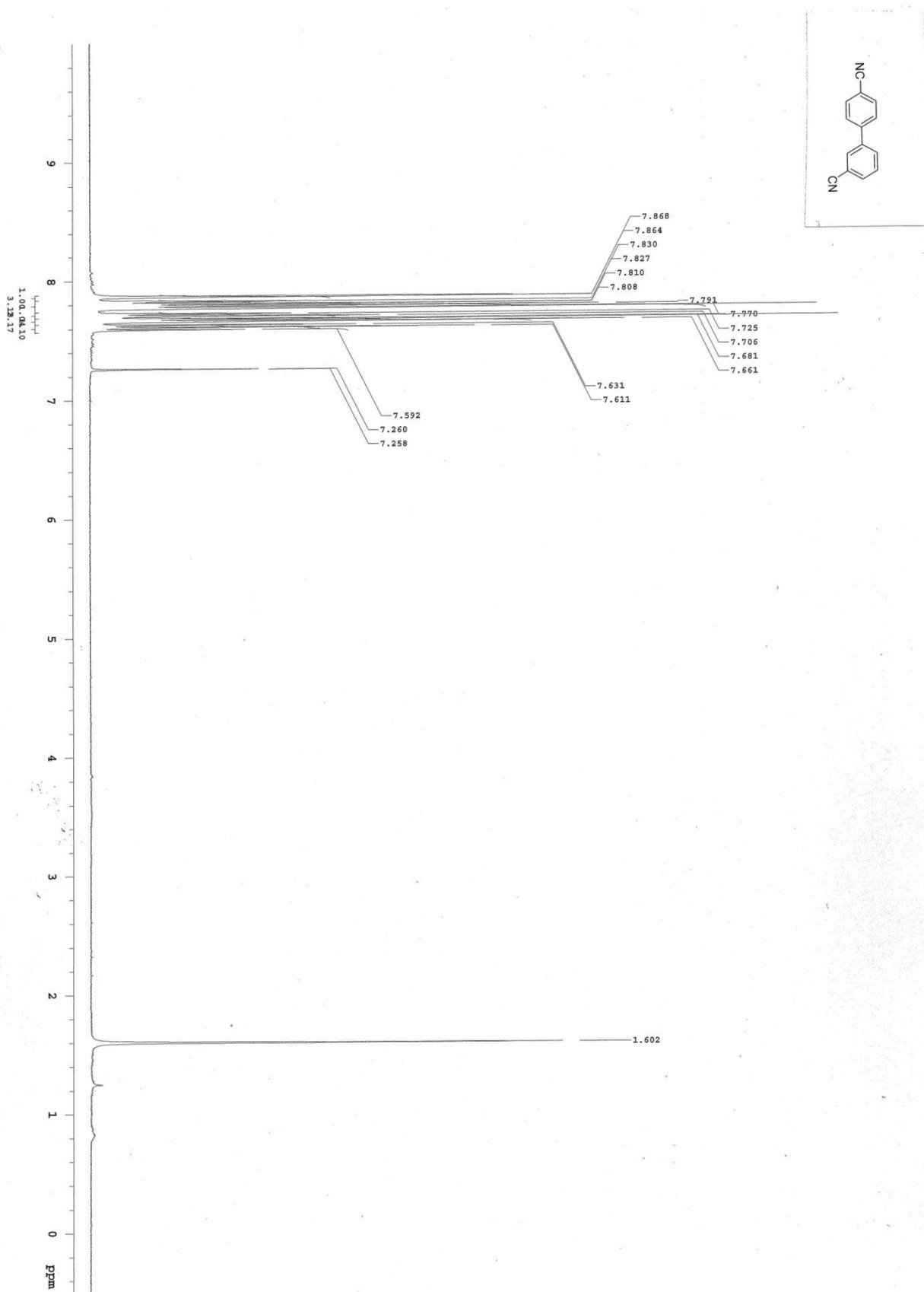


Figure S7.  $^1\text{H}$  NMR spectrum of 3,4'-dicyanobiphenyl

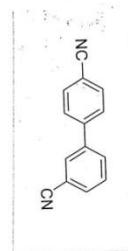
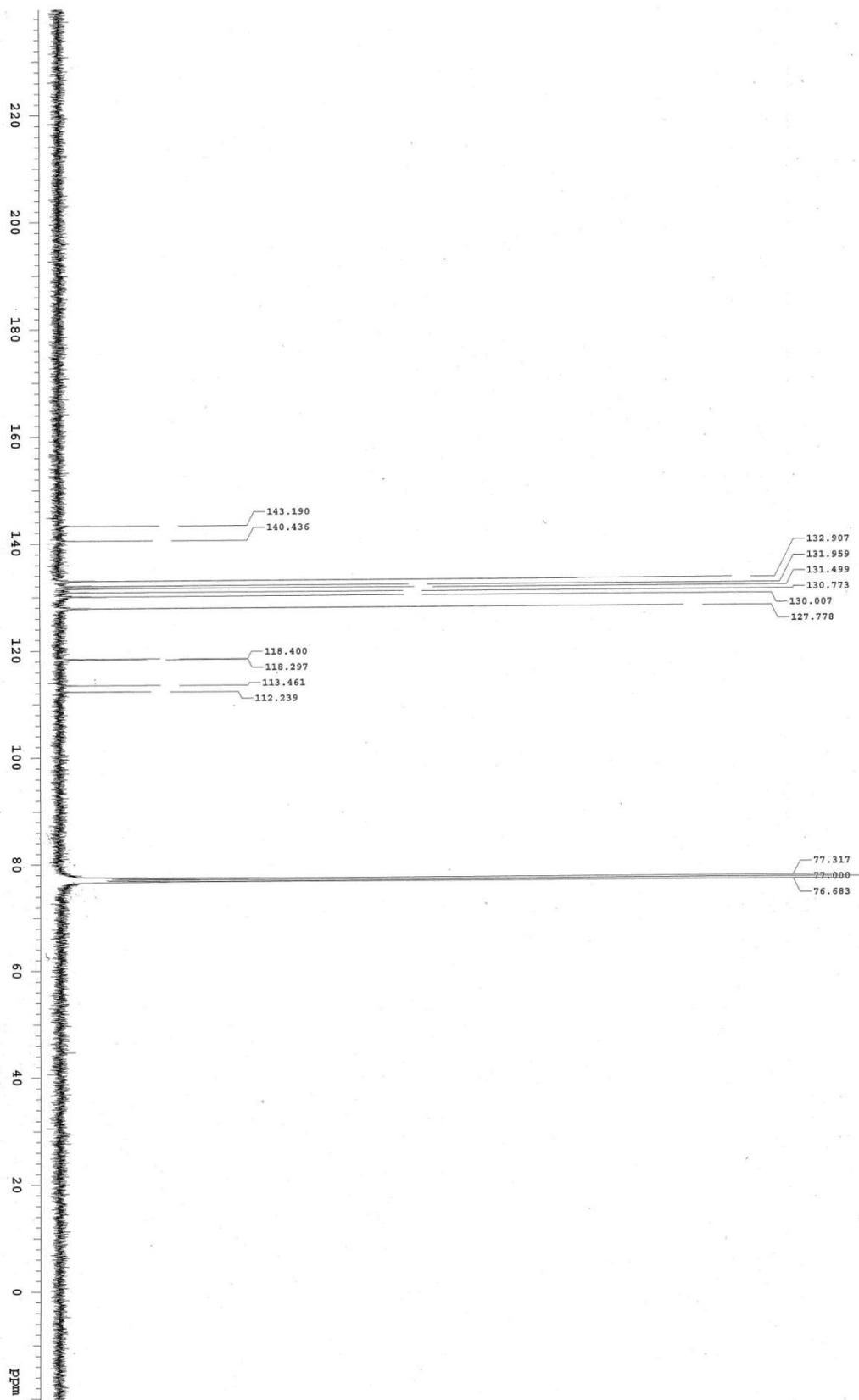


Figure S8. <sup>13</sup>C NMR spectrum of 3,4'-dicyanobiphenyl

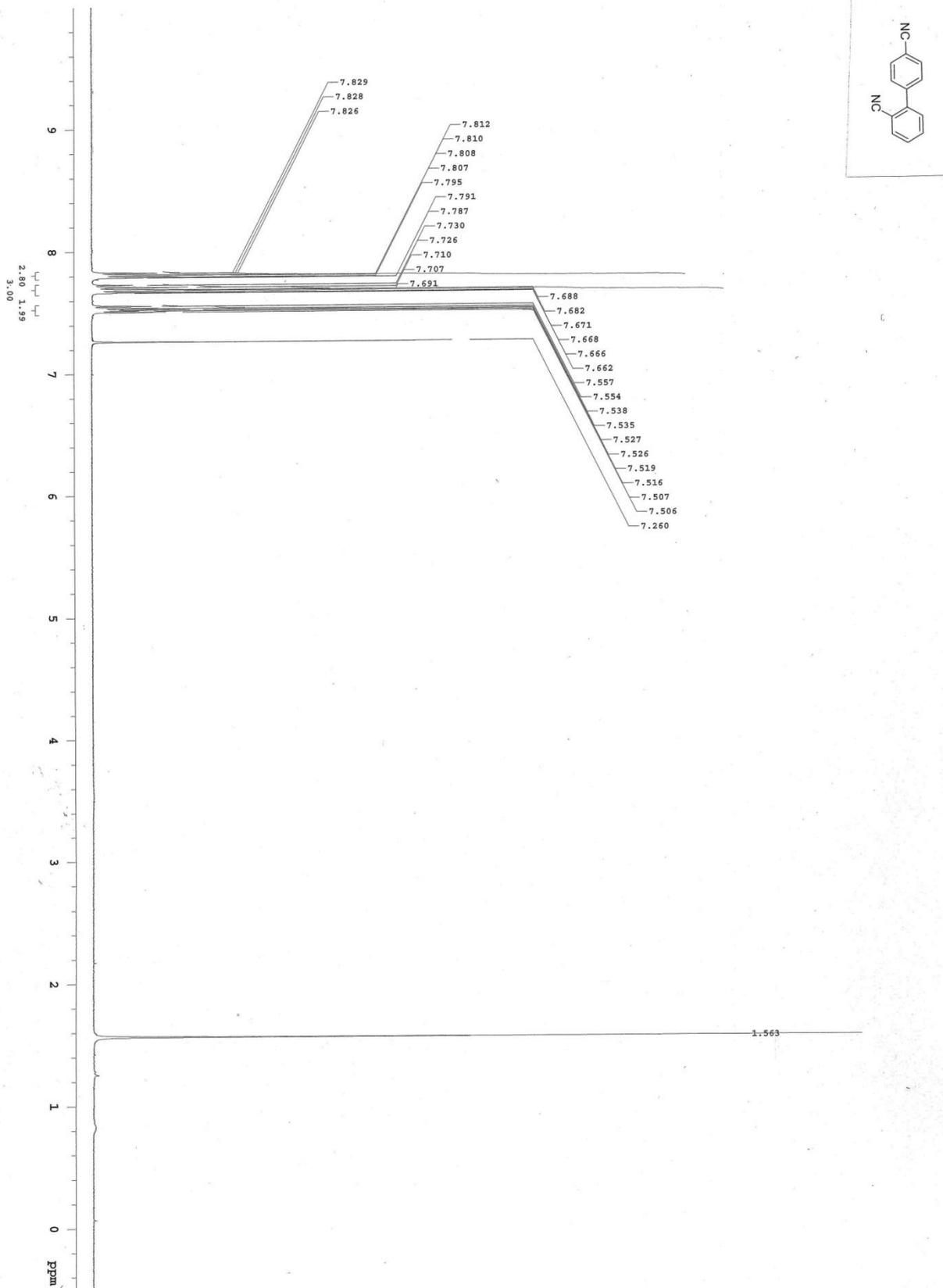


Figure S9. <sup>1</sup>H NMR spectrum of 2,4'-dicyanobiphenyl

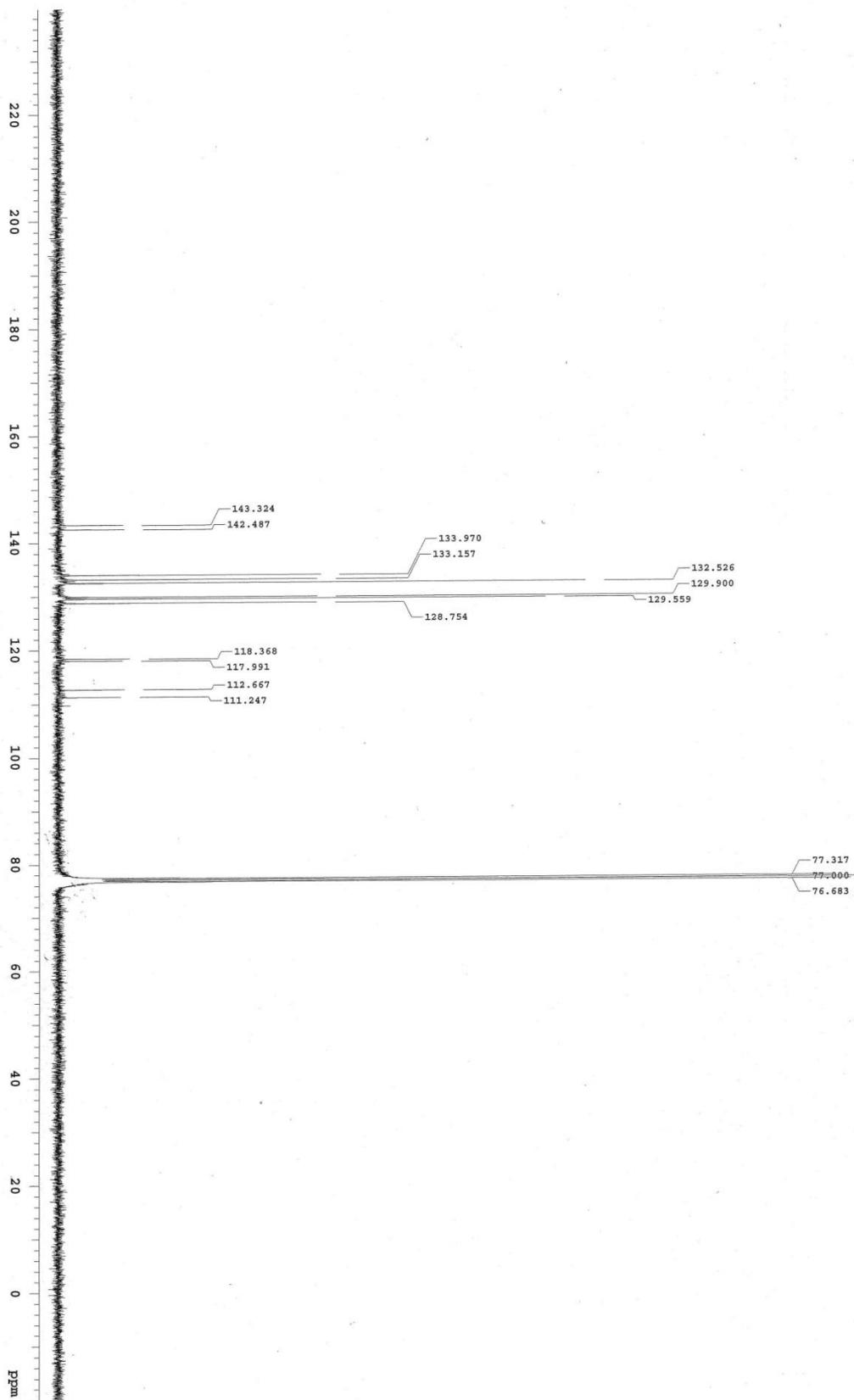


Figure S10.  $^{13}\text{C}$  NMR spectrum of 2,4'-dicyanobiphenyl

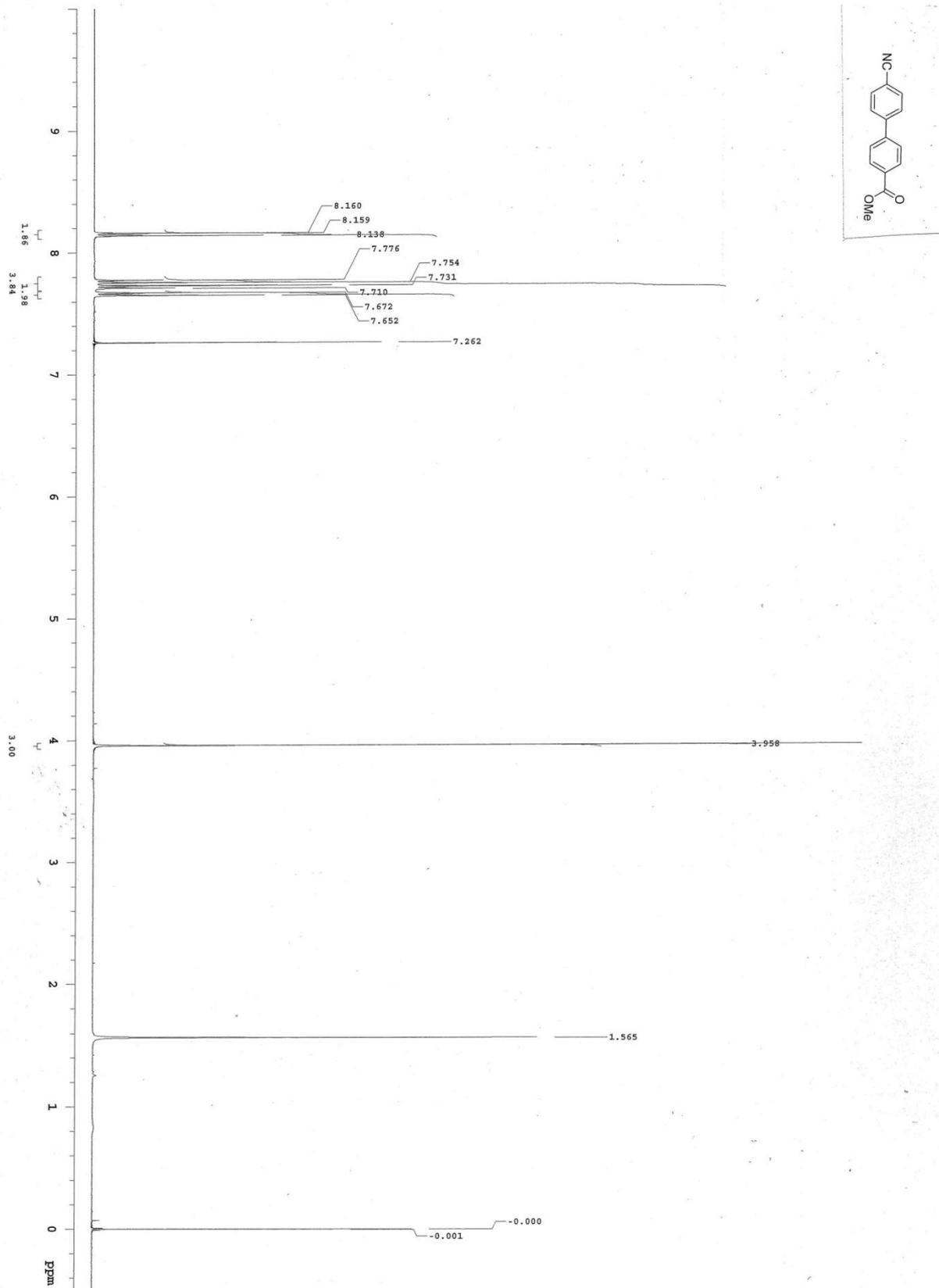


Figure S11. <sup>1</sup>H NMR spectrum of methyl 4-(4-cyanophenyl)benzoate

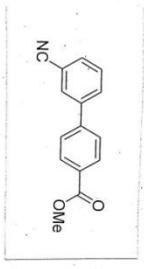
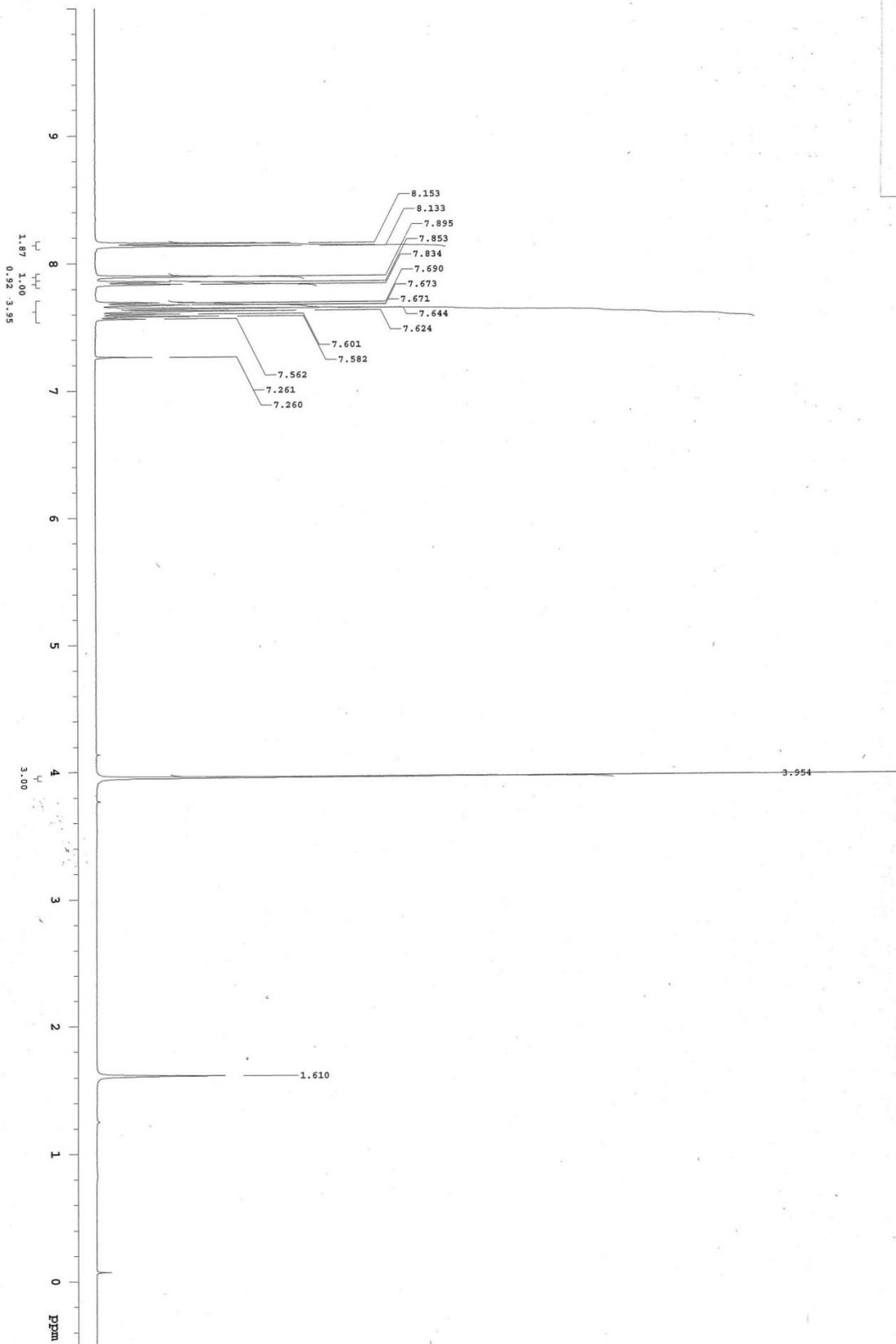


Figure S12. <sup>1</sup>H NMR spectrum of methyl 4-(3-cyanophenyl)benzoate

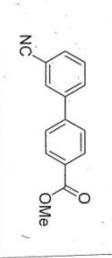
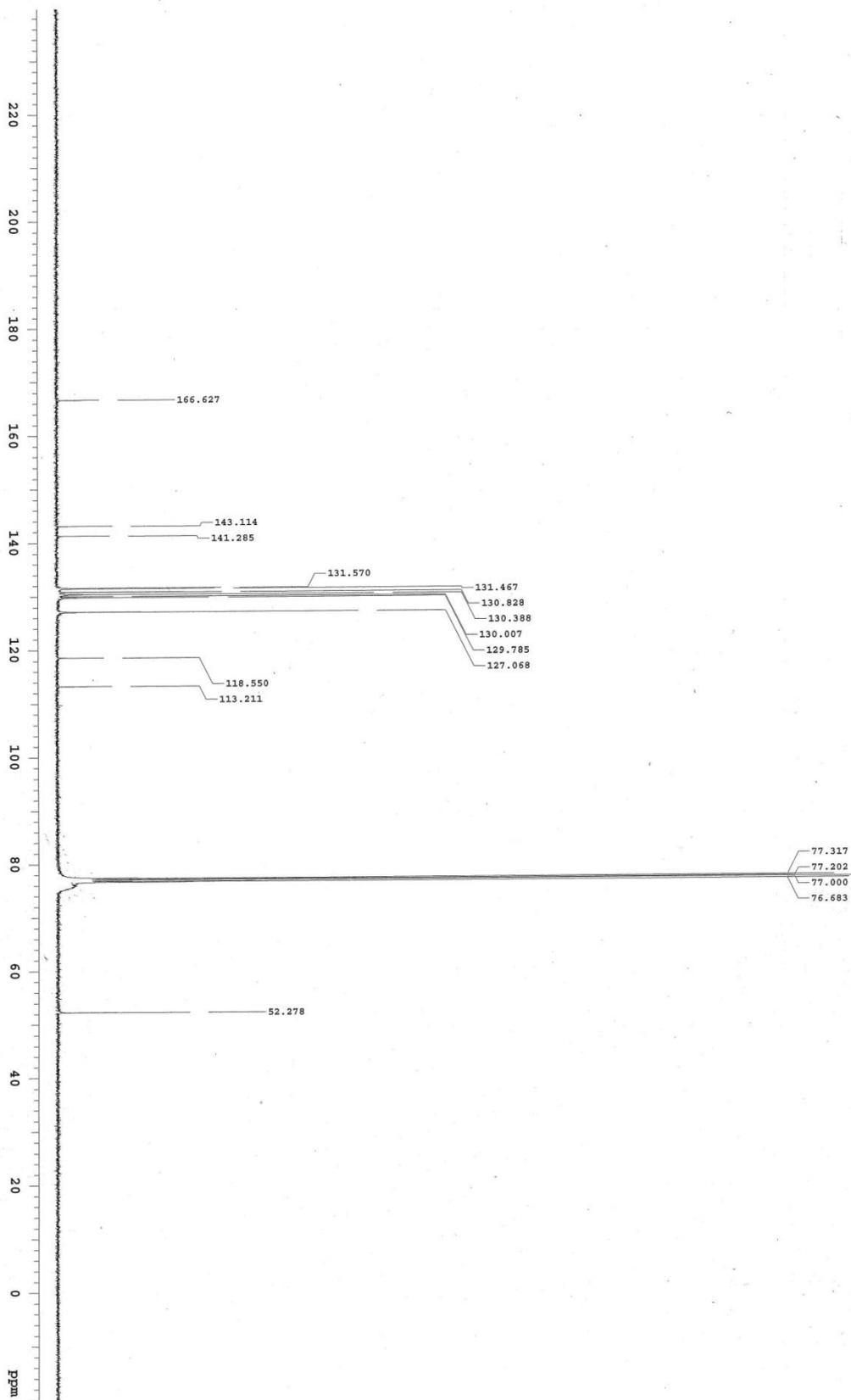


Figure S13. <sup>13</sup>C NMR spectrum of methyl 4-(3-cyanophenyl)benzoate

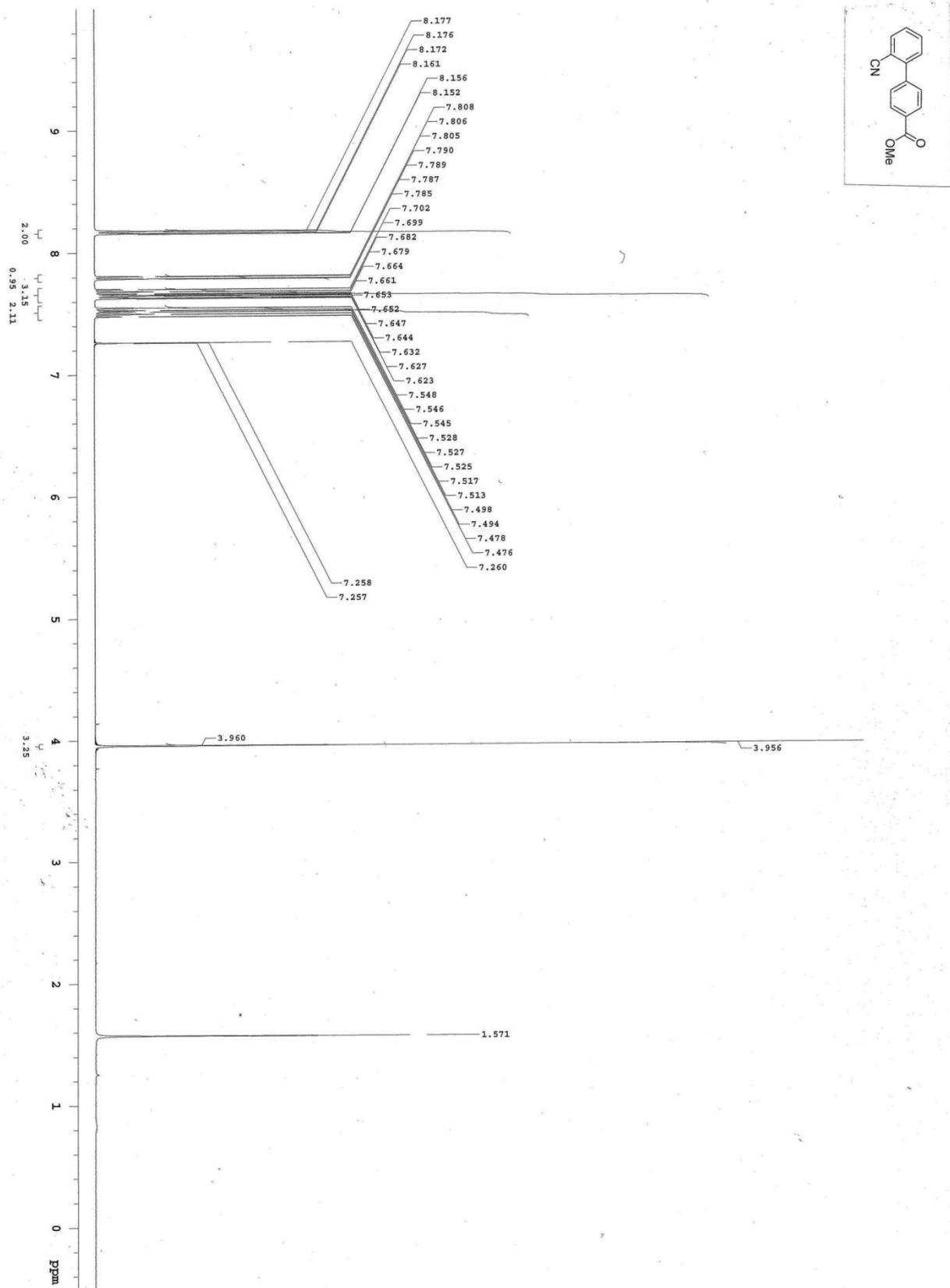


Figure S14. <sup>1</sup>H NMR spectrum of methyl 4-(2-cyanophenyl)benzoate

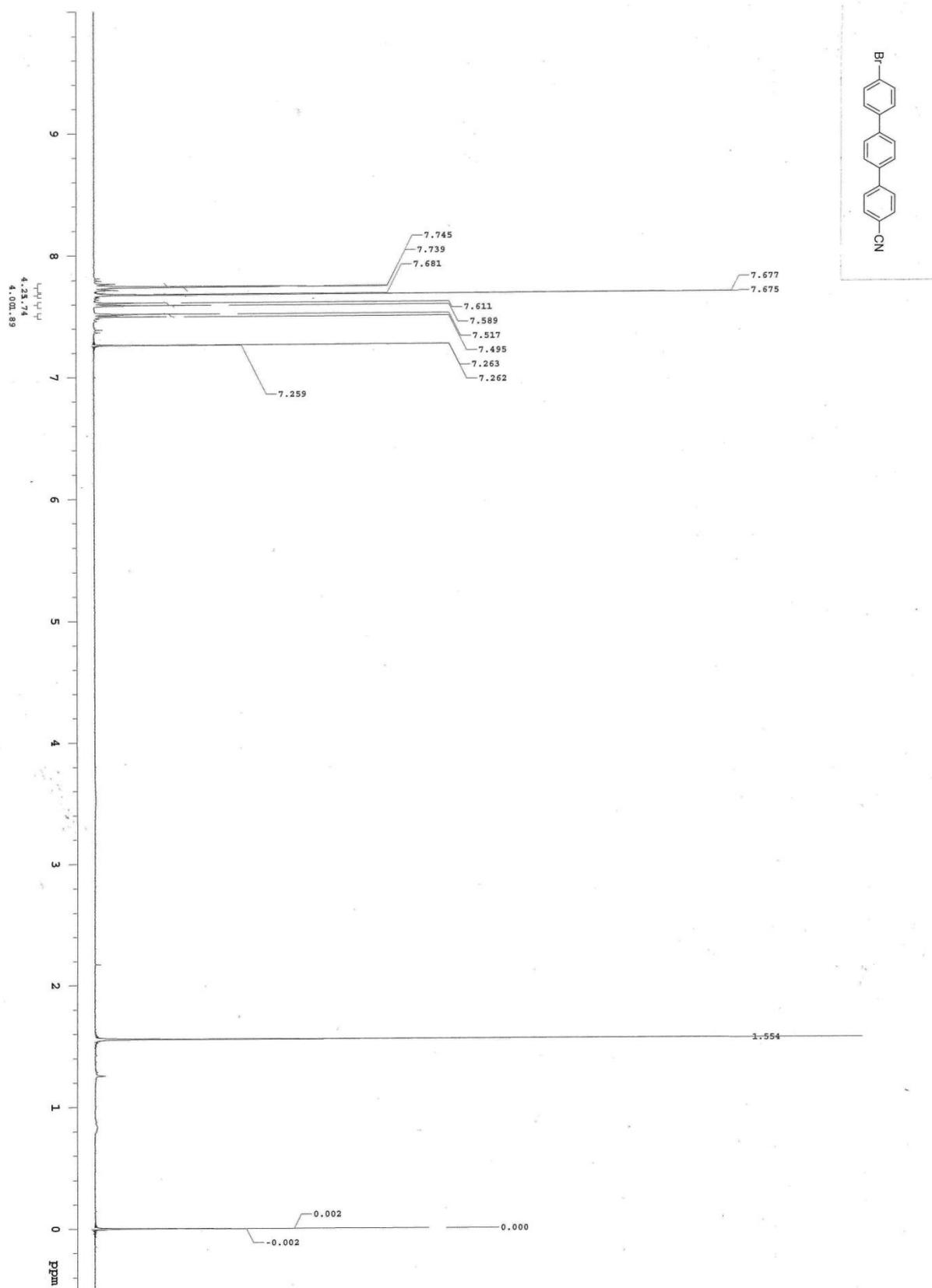


Figure S15.  $^1\text{H}$  NMR spectrum of 1-cyano-4'-bromo-4,1':4',1''-terphenylene

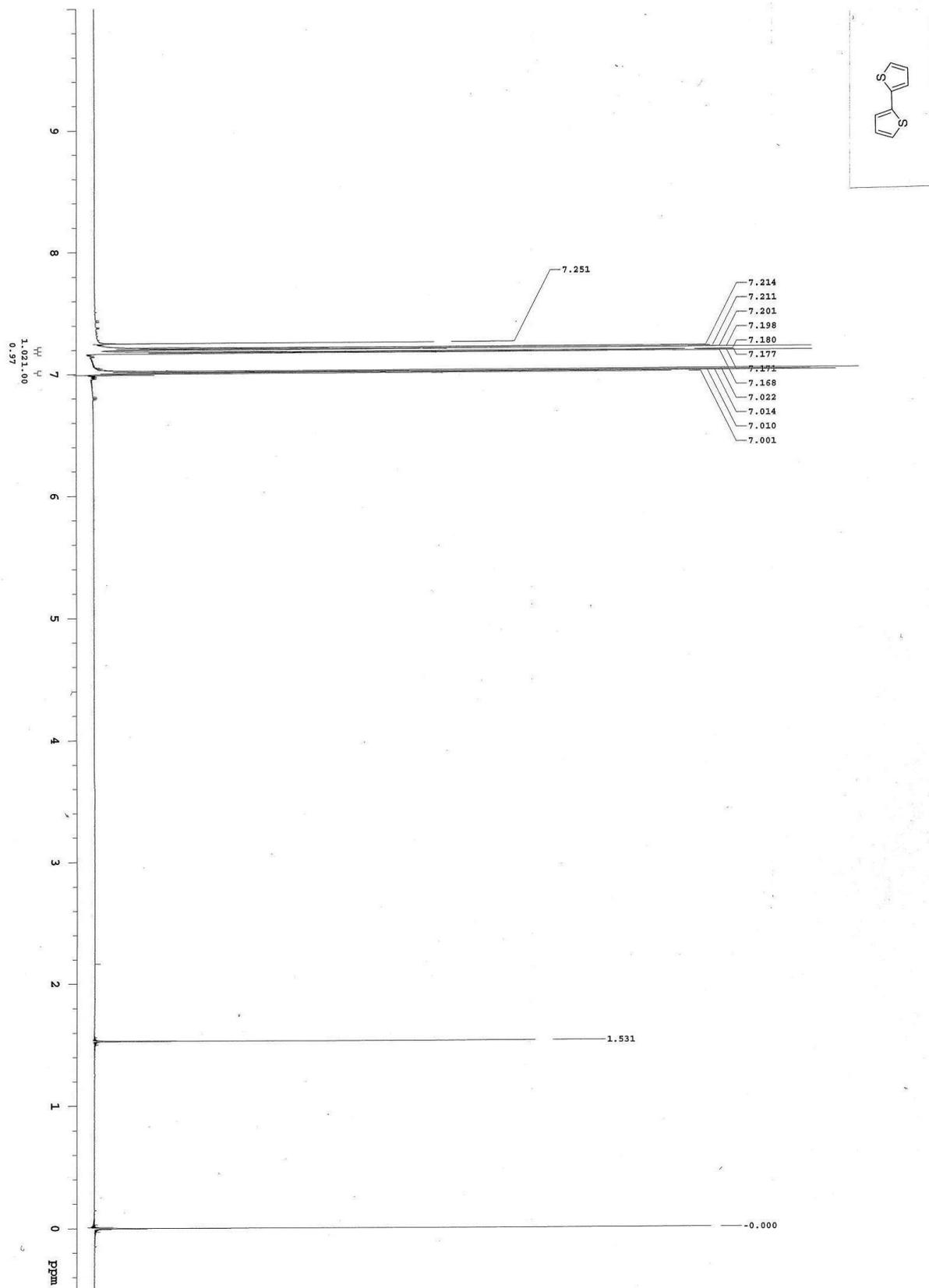


Figure S16.  $^1\text{H}$  NMR spectrum of 2,2'-bithiophene

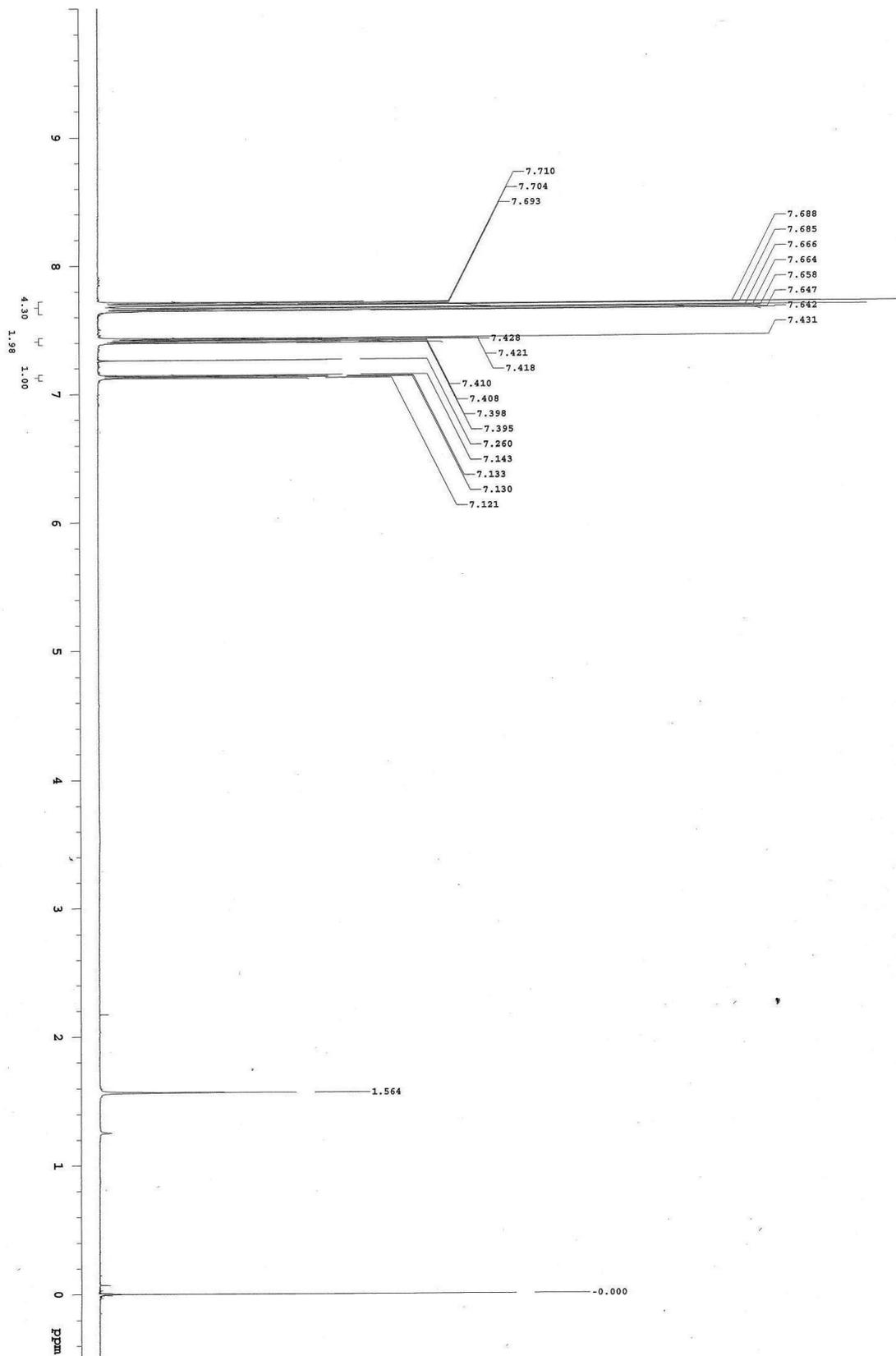


Figure S17.  $^1\text{H}$  NMR spectrum of 4-(thiophen-2-yl)benzonitrile

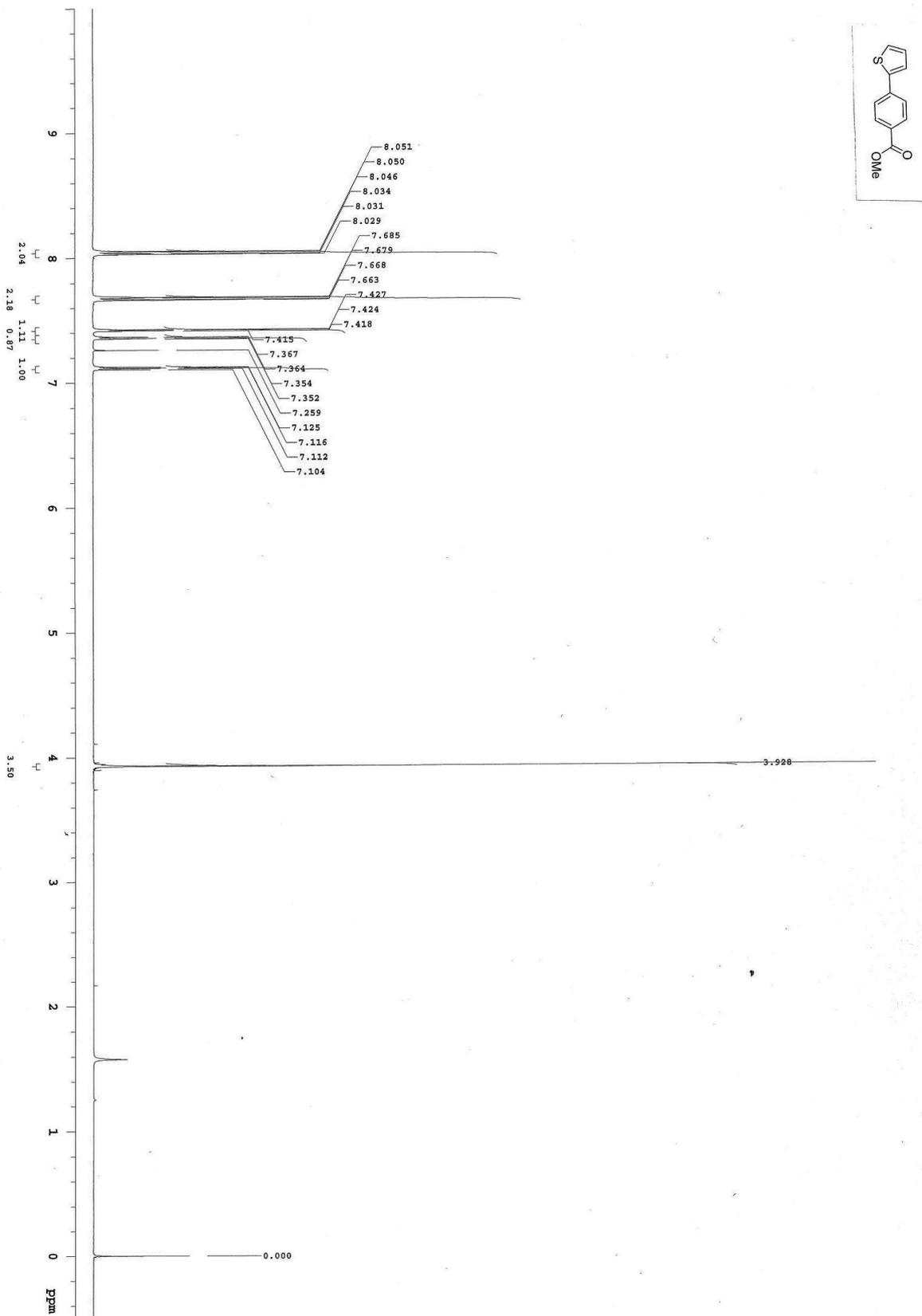


Figure S18. <sup>1</sup>H NMR spectrum of methyl 4-(thiophen-2-yl)benzoate

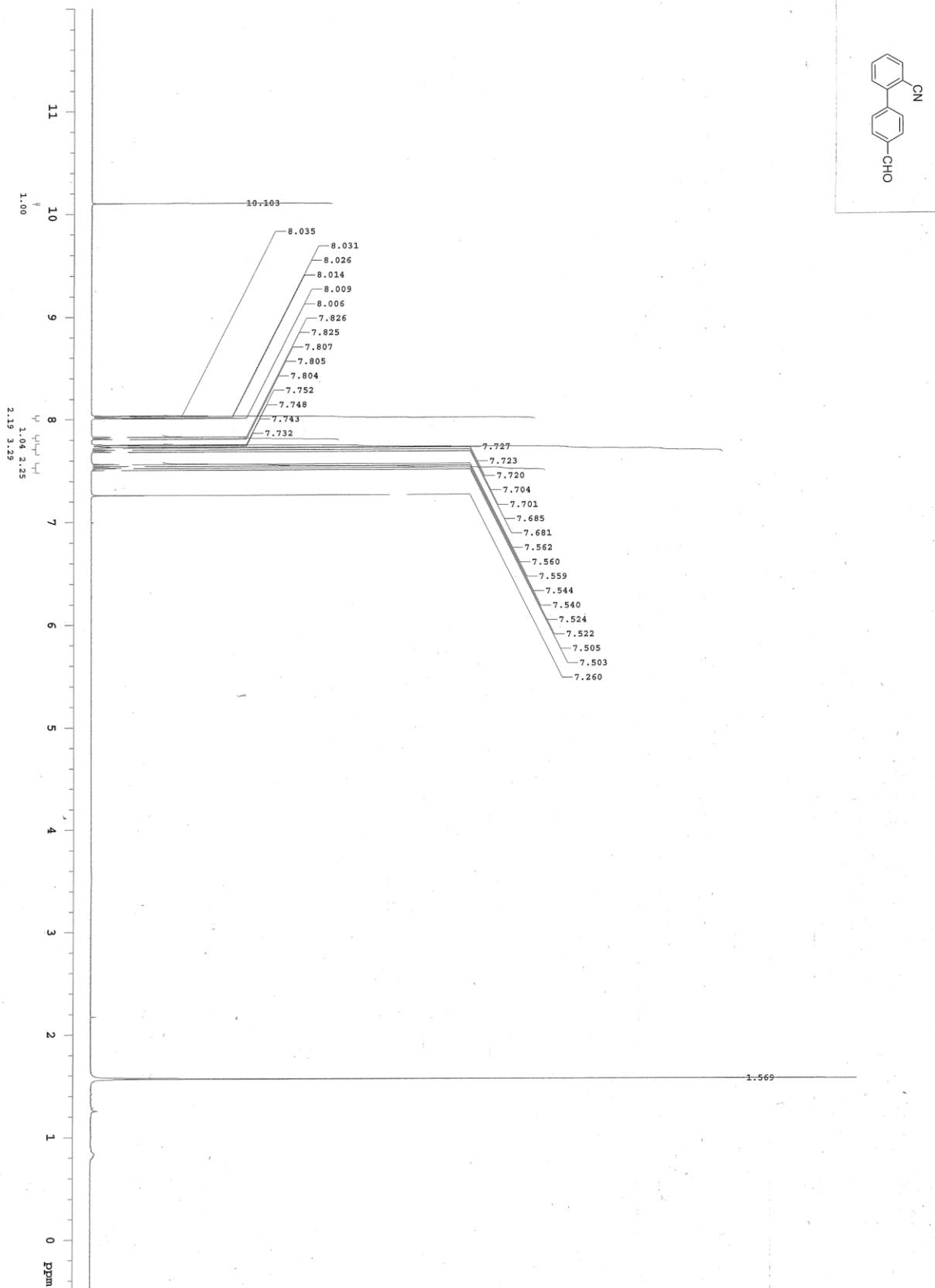


Figure S19. <sup>1</sup>H NMR spectrum of 2-Cyano-4'-formylbiphenyl

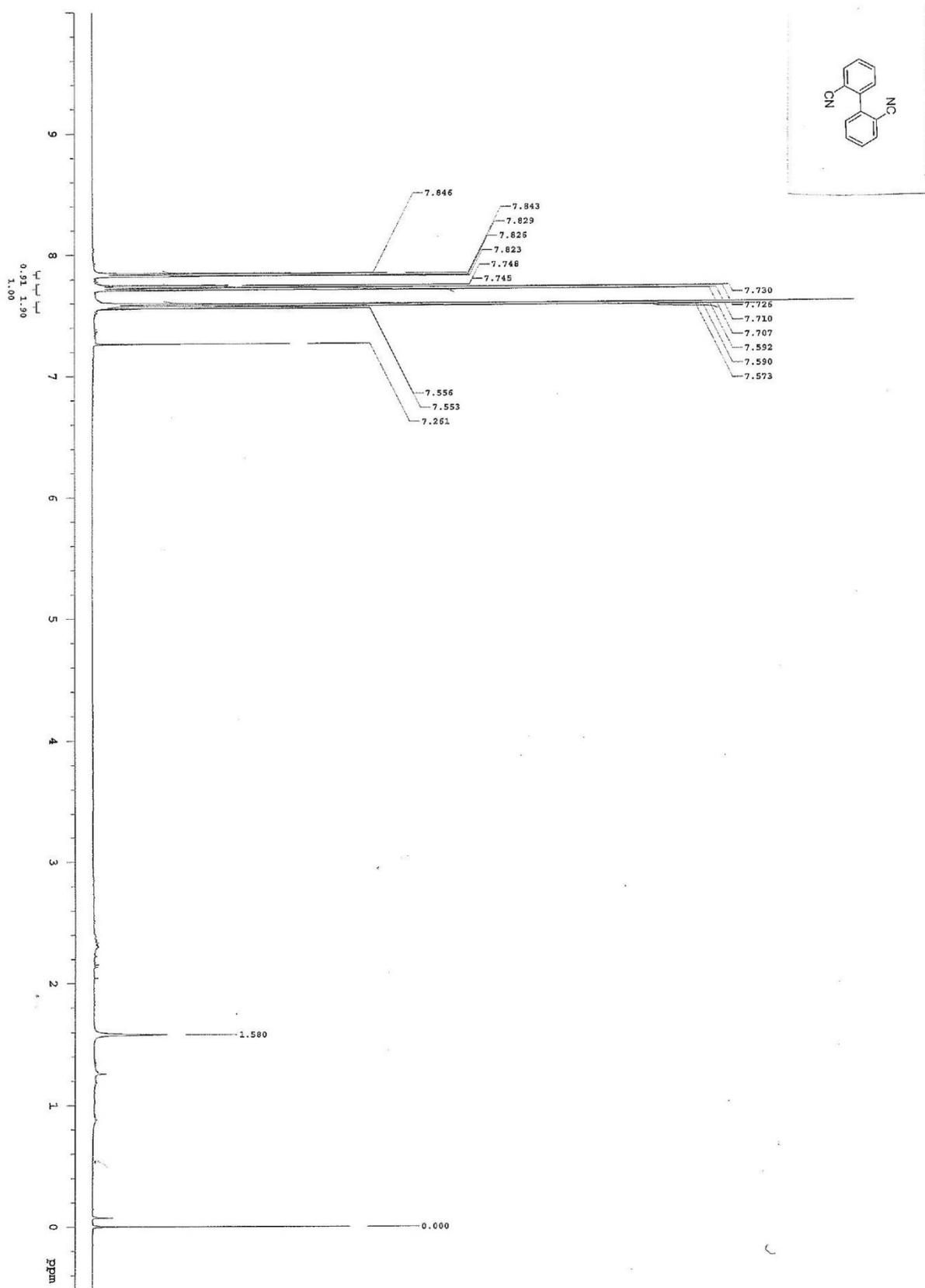


Figure S20. <sup>1</sup>H NMR spectrum of 2,2'-Dicyanobiphenyl

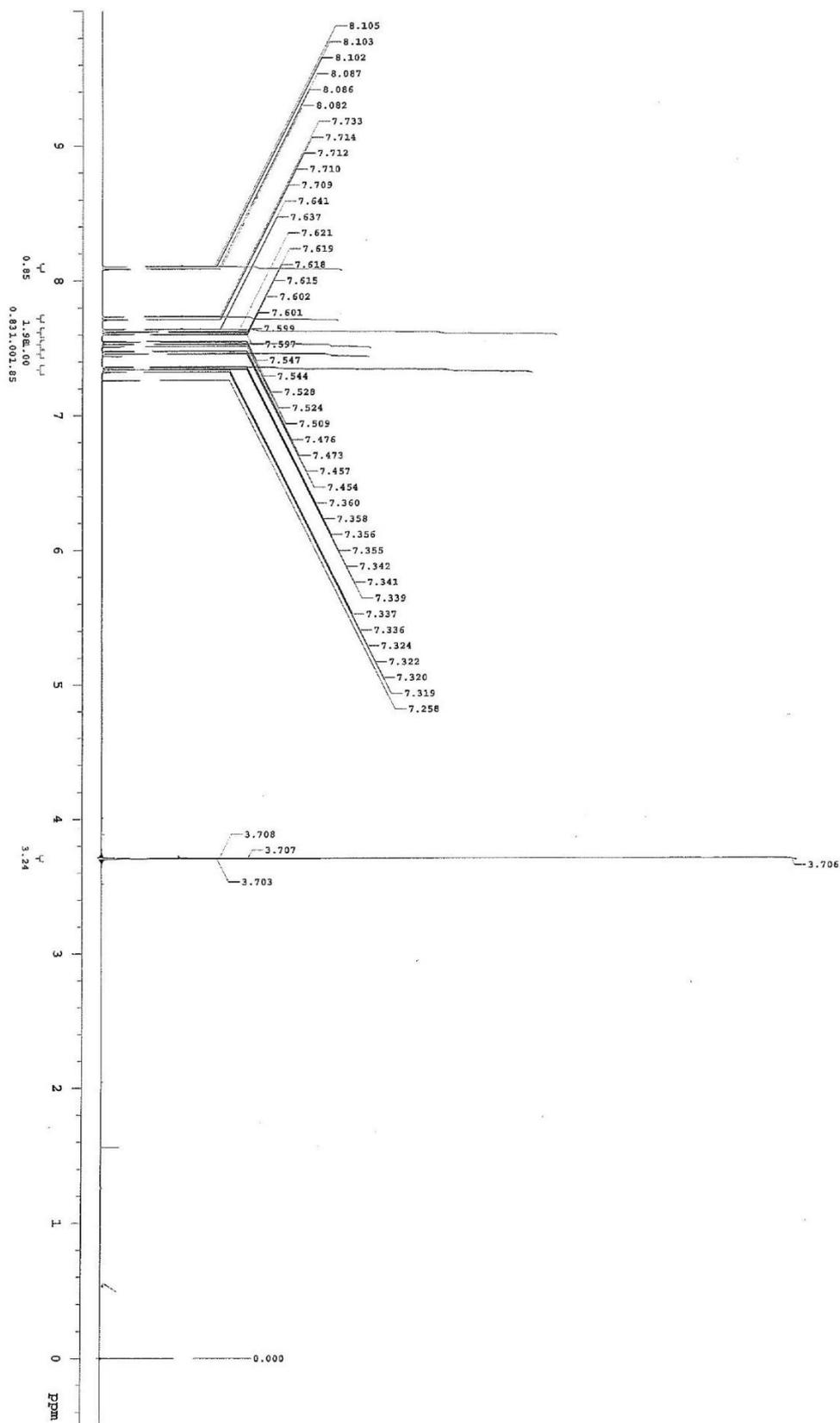


Figure S21. <sup>1</sup>H NMR spectrum of Methyl 2-(2-Cyanophenyl)benzoate

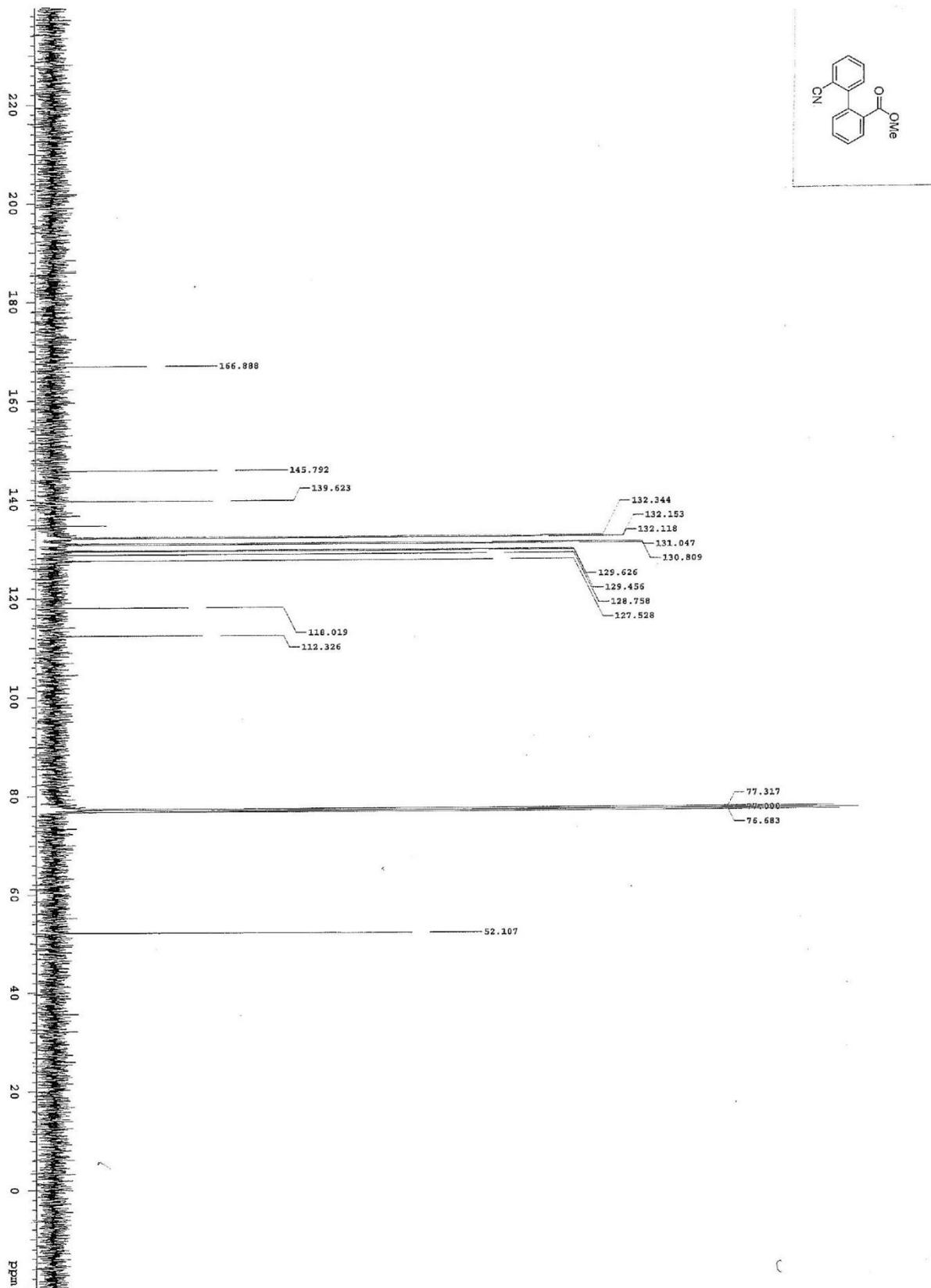


Figure S22.  $^{13}\text{C}$  NMR spectrum of Methyl 2-(2-Cyanophenyl)benzoate

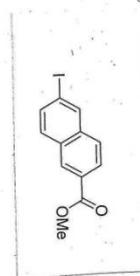
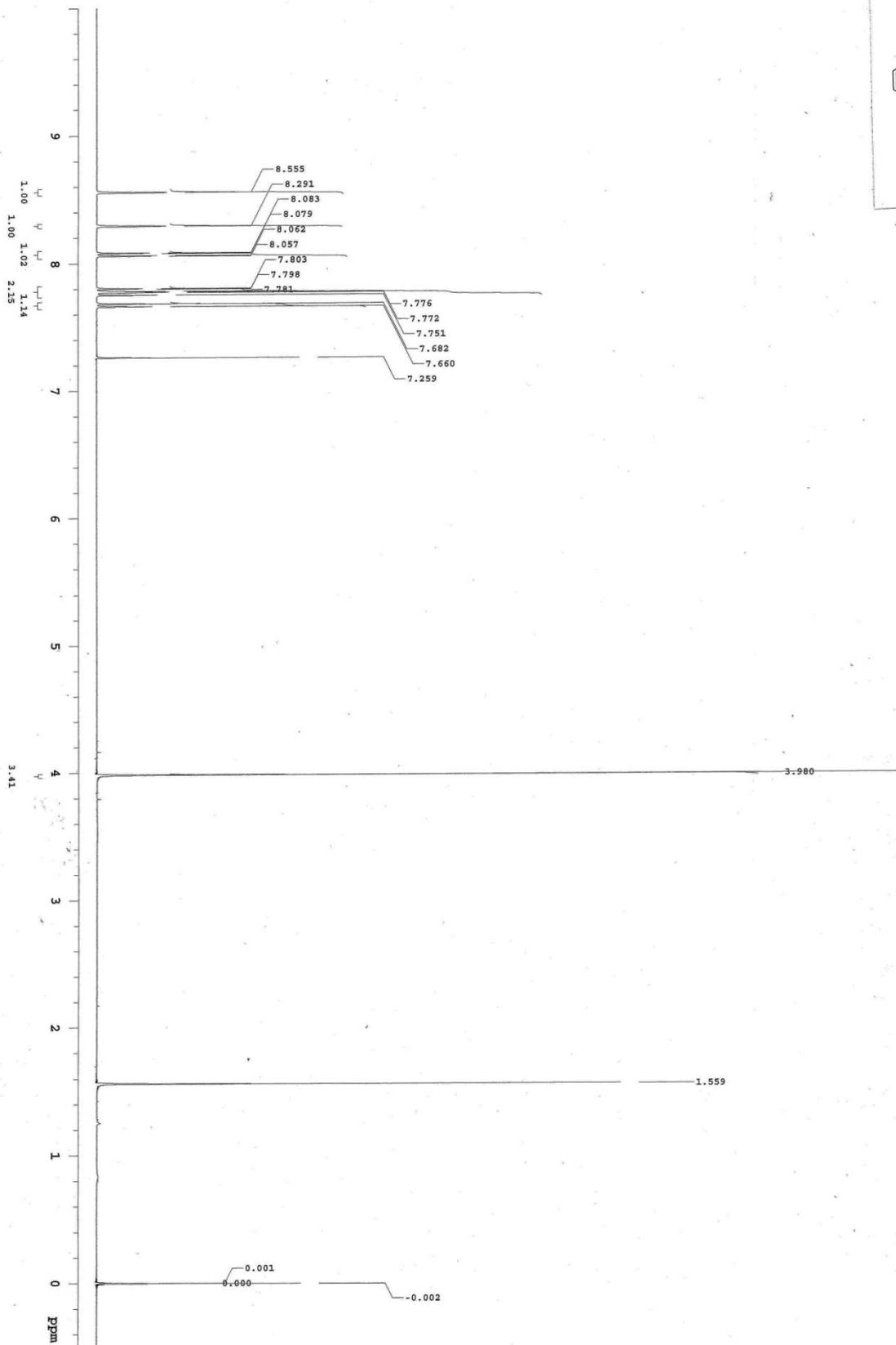


Figure S23. <sup>1</sup>H NMR spectrum of methyl 6-iodo-2-naphthoate

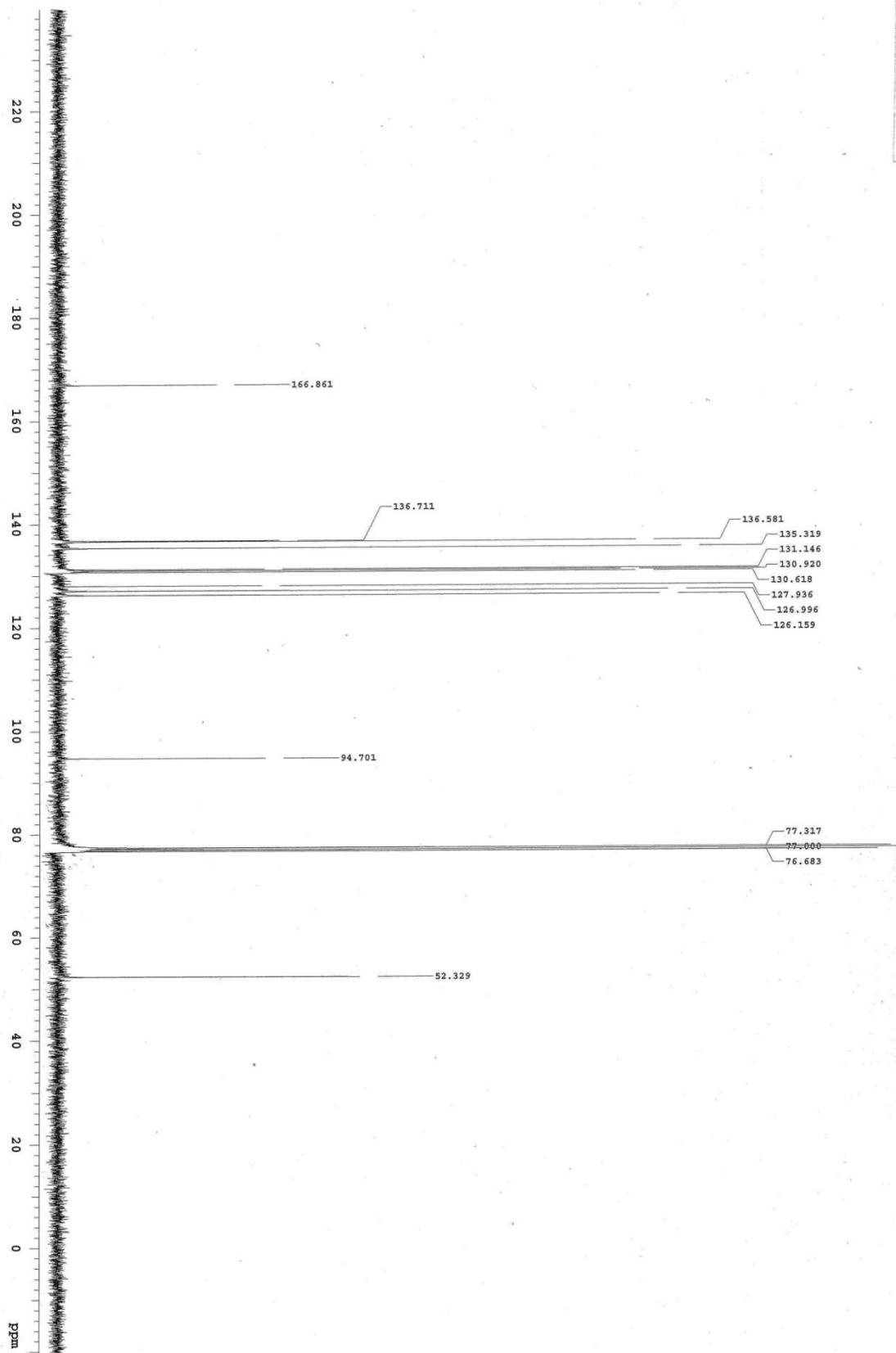


Figure S24.  $^{13}\text{C}$  NMR spectrum of methyl 6-iodo-2-naphthoate



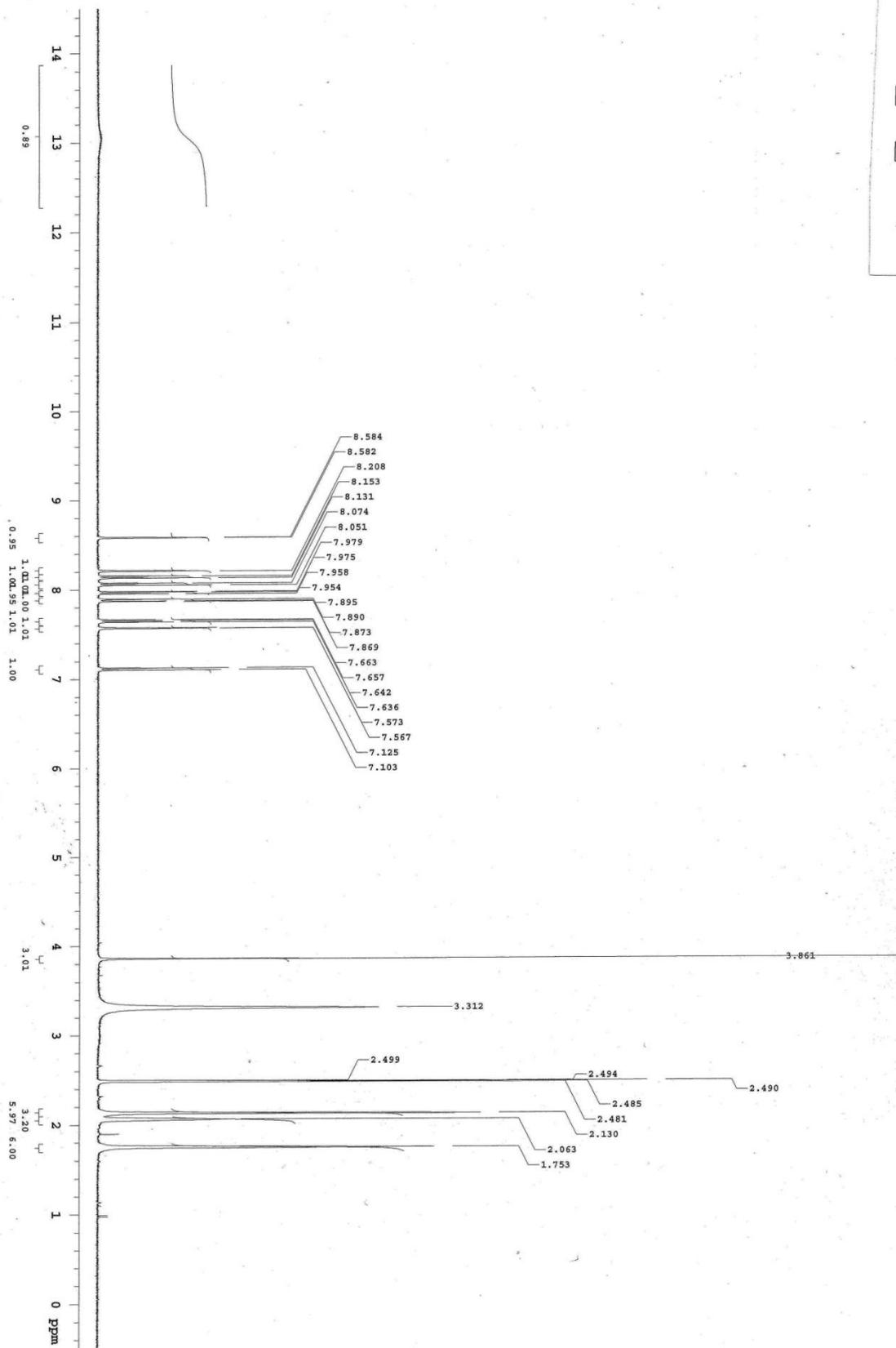


Figure S26. <sup>1</sup>H NMR spectrum of 6-(3-(1-adamantyl)-4-methoxyphenyl)-2-naphthoic acid (Adapalene)

### General Procedure of GC Analysis

GC analysis was performed on a SHIMADZU GC-2014 gas chromatograph equipped with a flame ionization detector using a fused silica capillary column (column, CBPI; 0.25 mm x 25 m; initial oven temperature, 50 °C; rate of temperature increase, 10 °C/min; final oven temperature, 250 °C keeping time after reaching final oven temperature, 10 min). GC yield was calculated by using an internal standard (tetradecane).

**Table S1. Retention Time List of Products obtained by Cross-Coupling Reaction in GC Analysis**

<b>Cross-Coupling Products</b>	<b>Retention Time in GC Analysis (min)</b>
Biphenyl-4-carbonitrile	21.4
Methyl 4-Phenylbenzoate	22.9
Biphenyl	17.0
4-Methoxybiphenyl	20.7
2-Phenylthiophene	25.6
4,4'-Dicyanobiphenyl	25.4
3,4'-Dicyanobiphenyl	25.2
2,4'-Dicyanobiphenyl	24.2
Methyl 4-(4-Cyanophenyl)benzoate	26.5
Methyl 4-(3-Cyanophenyl)benzoate	26.3
Methyl 4-(2-Cyanophenyl)benzoate	25.6
2,2'-Bithiophene	25.6
4-(Thiophen-2-yl)benzotrile	25.6
Methyl 4-(Thiophen-2-yl)benzoate	25.6
2-Cyano-4'-formylbiphenyl	24.0
2,2'-Dicyanobiphenyl	22.8
Methyl 2-(2-Cyanophenyl)benzoate	23.3