

Palladium Nanoparticles Supported on Carbon Nanotubes from Solventless Preparations: Versatile Catalysts for Ligand-Free Suzuki Cross Coupling Reactions

Ali R. Siamaki,¹ Yi Lin,² Kendra Woodberry,¹ John W. Connell,³ and B. Frank Gupton¹

¹ *Department of Life Science and Chemical Engineering, Virginia Commonwealth University, Richmond, VA, 23284, USA*

² *National Institute of Aerospace, 100 Exploration Way, Hampton, VA 23666*

³ *Advanced Materials and Processing Branch, NASA Langley Research Center, Hampton, VA, 23681-2199, USA*

Supporting Information

	<u>Page</u>
XRD Spectra of a) (Pd/SWCNT)_M b) (Pd/SWCNT)_T-----	S2
TEM Images of Pd/ MWCNT Prepared at Different Ball-mill Time-----	S2
Spectroscopic Data (¹H, ¹³C NMR)-----	S4
NMR Spectra of the Compounds in Table 2-----	S8

Figure S1. XRD spectra of a) (Pd/SWCNT)_M b) (Pd/SWCNT)_T

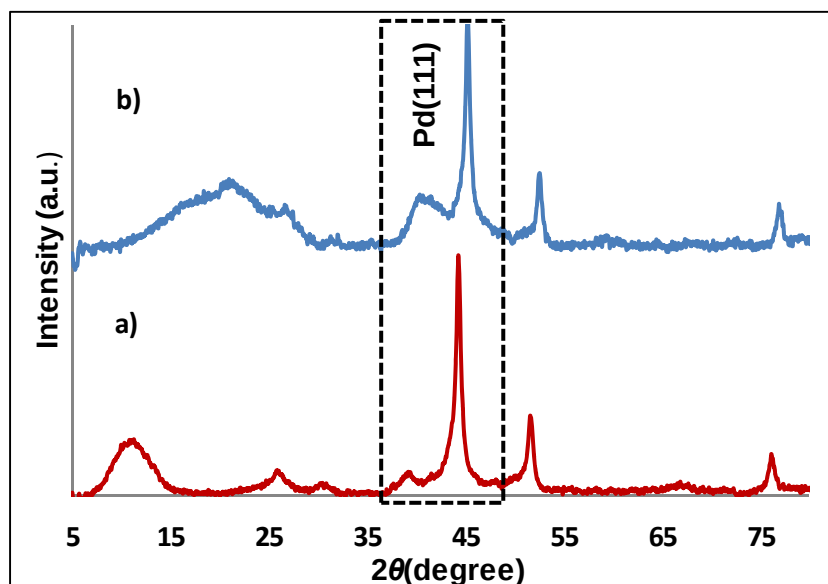
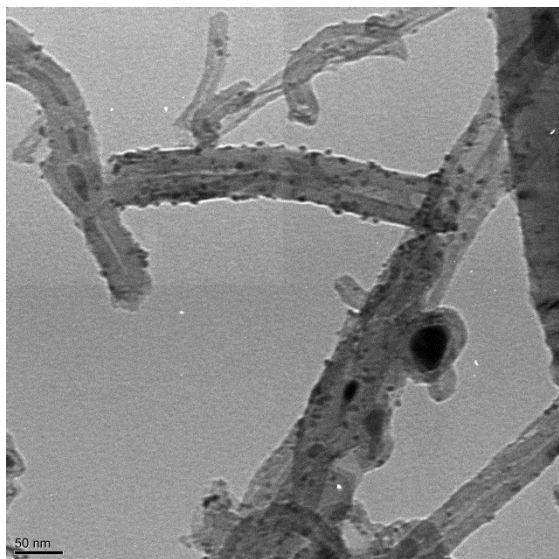
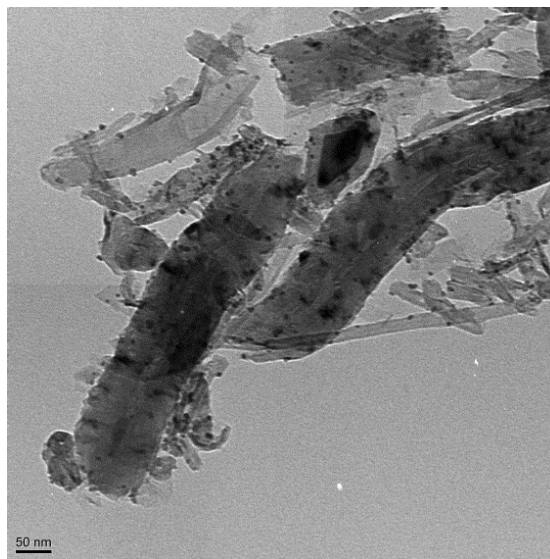


Figure S2: TEM Images of Pd/ MWCNT Prepared at Different Ball-mill Time of a) 10 min, b) 30 min, c) 60 min

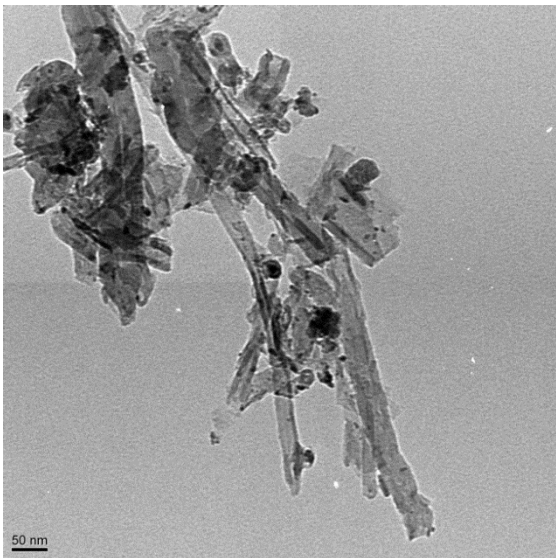
a)



b)



c)



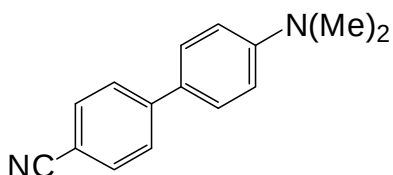
Spectroscopic Data:

Spectroscopic Data on Biphenyl Product in Figure 4:

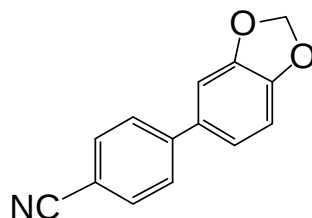
^1H NMR (300 MHz, CDCl_3): δ 7.76-7.73 (m, 2H), 7.61-7.55 (m, 2H), 7.51-7.46 (m, 1H). ^{13}C (75.5 MHz, CDCl_3): δ 141.6, 129.1, 127.6, 127.5. GC-MS (EI, 70 eV): $m/z(\%) = 154$ (100) $[\text{M}^+]$.

Spectroscopic Data on Table 2: Suzuki Cross Coupling

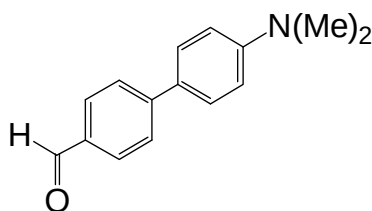
4'-(dimethylamino)-[1,1'-biphenyl]-4-carbonitrile (1a): Isolated yield: 95% ^1H NMR (300 MHz, CDCl_3): δ 7.64 (s, 4H), 7.53-7.50 (d, 2H), 6.81-6.78 (d, 2H), 3.02 (s, 6H). ^{13}C (75.5 MHz, CDCl_3): δ 150.9, 145.8, 132.7, 131.6, 128.1, 126.5, 119.6, 112.7, 109.1, 40.5. HRMS calculated for: $\text{C}_{15}\text{H}_{15}\text{N}_2^+$: 223.1157, Found: 223.1230



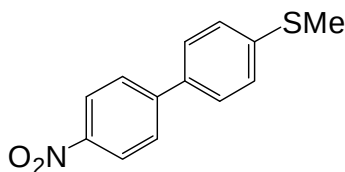
4-(benzo[d][1,3]dioxol-5-yl)benzonitrile (1b): Isolated yield: 92% ^1H NMR (300 MHz, CDCl_3): δ 7.68-7.65 (d, 2H), 7.59-7.56 (d, 2H), 7.07-7.03 (m, 2H), 6.90-6.88 (d, 1H), 6.01 (s, 2H). ^{13}C (75.5 MHz, CDCl_3): δ 48.7, 148.4, 145.4, 133.5, 132.8, 127.5, 121.3, 119.2, 110.6, 109.09, 107.7, 101.7. HRMS calculated for: $\text{C}_{14}\text{H}_{10}\text{NO}_2^+$: 224.0633, Found: 224.0706



4'-(dimethylamino)-[1,1'-biphenyl]-4-carbaldehyde (1c): Isolated yield: 90% ^1H NMR (300 MHz, CDCl_3): δ 10 (s, 1H), 7.90-7.88 (d, 2H), 7.72-7.70 (d, 2H), 7.59-7.56 (d, 2H), 6.81-6.78 (d, 2H), 3.02 (s, 6H). ^{13}C (75.5 MHz, CDCl_3): δ 192.1, 150.9, 147.4, 134.2, 130.6, 128.2, 127.08, 126.4, 112.7, 40.5. HRMS calculated for: $\text{C}_{15}\text{H}_{16}\text{NO}^+$: 226.1154, Found: 226.1223

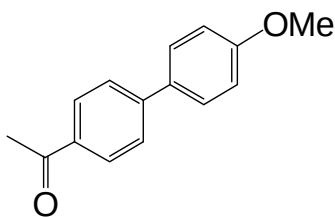


Methyl(4'-nitro-[1,1'-biphenyl]-4-yl)sulfane (1d): Isolated yield: 87% ^1H NMR (300 MHz, CDCl_3): δ 8.29-8.26 (d, 2H), 7.72-7.69 (d, 2H), 7.56-7.53 (d, 2H), 7.36-7.33 (d, 2H), 2.53 (s, 3H). ^{13}C (75.5 MHz, CDCl_3): δ 147.14, 147.11, 140.5, 135.3, 127.8, 127.5, 126.8, 124.4, 15.6. HRMS calculated for: $\text{C}_{13}\text{H}_{12}\text{NO}_2\text{S}^+$: 246.0510, Found: 246.0582

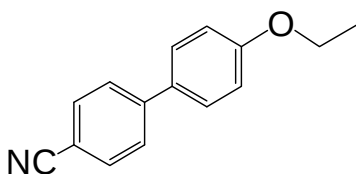


1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (1e): Isolated yield: 90% ^1H NMR (300 MHz, CDCl_3): δ 8.0-7.97 (d, 2H), 7.64-7.61 (d, 2H), 7.58-7.55 (d, 2H), 7.0-6.97 (d, 2H), 3.84 (s, 3H),

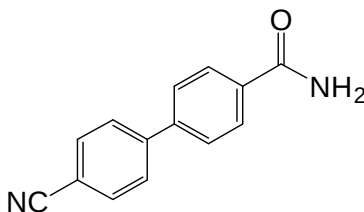
2.61 (s, 3H). ^{13}C (75.5 MHz, CDCl_3): δ 197.9, 160.1, 145.5, 135.4, 132.4, 129.1, 128.5, 126.8, 114.6, 55.6, 26.8. HRMS calculated for: $\text{C}_{15}\text{H}_{15}\text{O}_2^+$: 227.0994, Found: 227.1063



4'-ethoxy-[1,1'-biphenyl]-4-carbonitrile (1f): Isolated yield: 92% ^1H NMR (300 MHz, CDCl_3): δ 7.68-7.60 (q, 4H), 7.53-7.50 (d, 2H), 7.0-6.97 (d, 2H), 4.09-4.06 (d, 2H), 1.47-1.42 (t, 3H). ^{13}C (75.5 MHz, CDCl_3): δ 159.8, 145.4, 132.7, 131.4, 128.5, 127.2, 119.3, 115.2, 110.2, 63.8, 15.05. HRMS calculated for: $\text{C}_{15}\text{H}_{14}\text{NO}^+$: 224.0997, Found: 224.1064

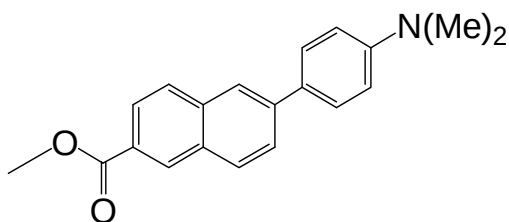


4'-cyano-[1,1'-biphenyl]-4-carboxamide (1g): Isolated yield: 87% ^1H NMR (300 MHz, DMSO-d_6): δ 8.0-7.98 (d, 2H), 7.90 (s, 4H), 7.82-7.79 (d, 2H). ^{13}C (75.5 MHz, DMSO-d_6): δ 168.03, 144.3, 141.4, 134.9, 133.5, 128.9, 128.4, 127.6, 119.4, 111.2. HRMS calculated for: $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}^+$: 223.0793, Found: 223.0862

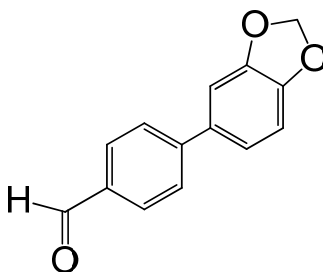


Methyl 6-(4-(dimethylamino)phenyl)-2-naphthoate (1h): Isolated yield: 85% ^1H NMR (300 MHz, CDCl_3): δ 8.59 (s, 1H), 8.065-8.031 (dd, 1H), 8.004 (s, 1H), 7.98-7.95 (d, 1H), 7.89-7.86

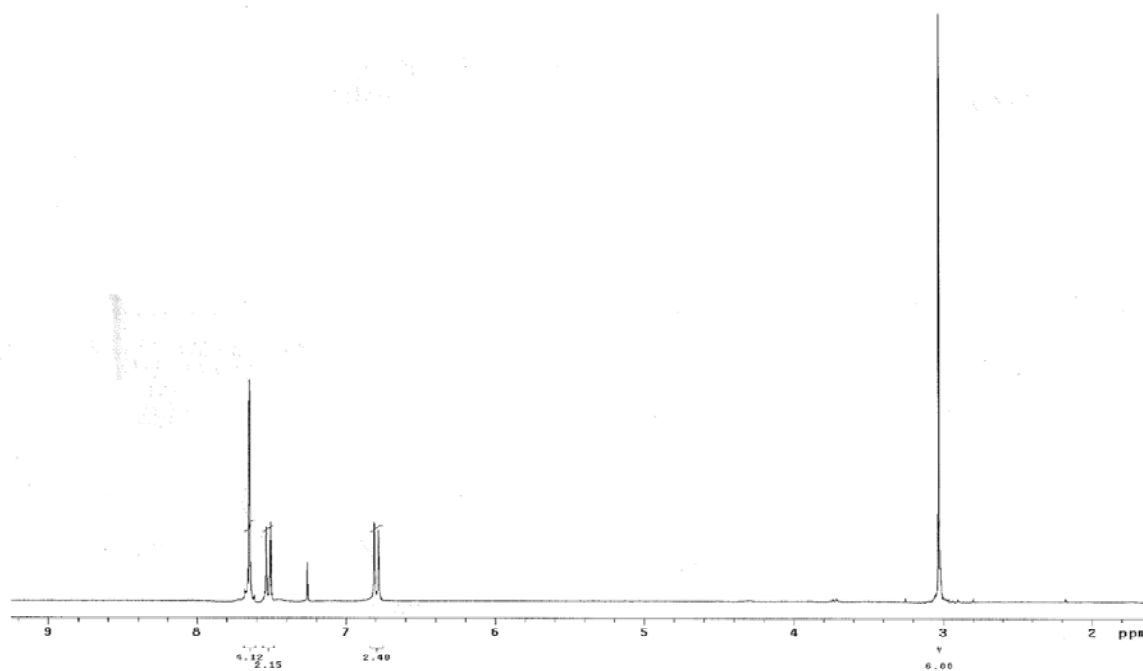
(d, 1H), 7.819-7.813-7.785 (dd, 1H), 7.67-7.64 (d, 2H), 6.86-6.83 (d, 2H), 3.98 (s, 3H), 3.03 (s, 6H). ^{13}C (300 MHz, CDCl_3): δ 167.6, 150.5, 141.2, 136.3, 131.2, 131.05, 130.15, 129.8, 128.31, 128.29, 126.8, 126.2, 125.7, 123.9, 112.9, 52.4, 40.7. HRMS calculated for: $\text{C}_{20}\text{H}_{20}\text{NO}_2^+$: 306.1416, Found: 306.1485



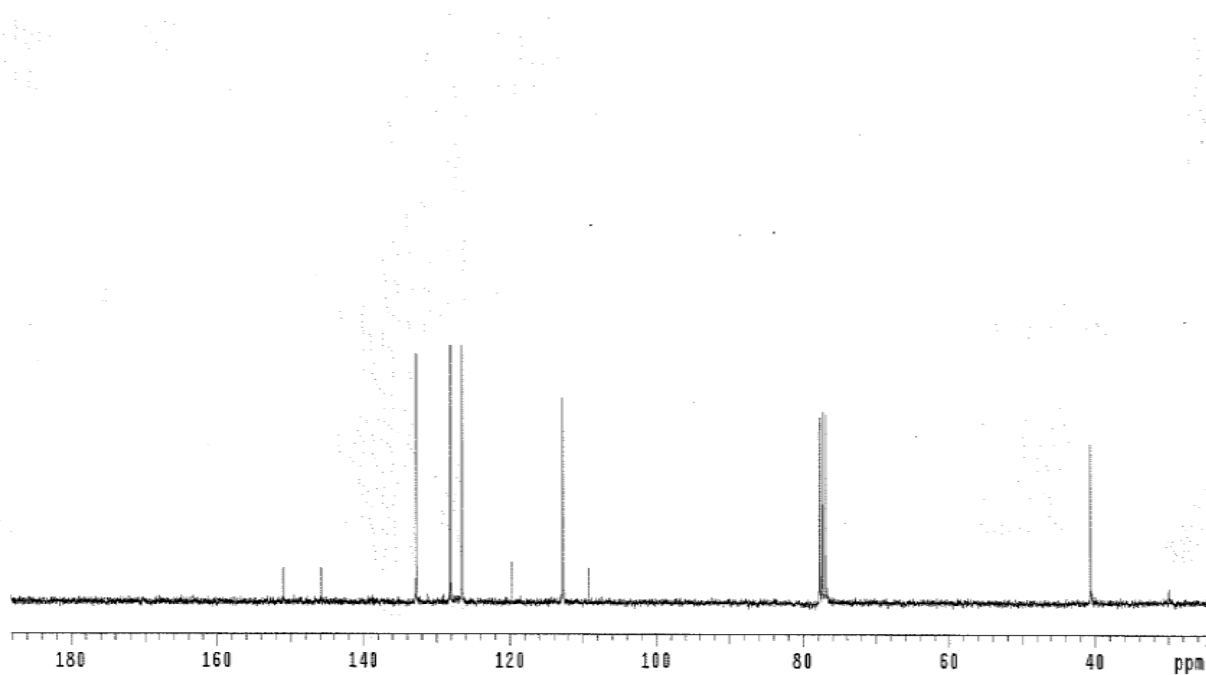
4-(benzo[d][1,3]dioxol-5-yl)benzaldehyde (1i): Isolated yield: 90% ^1H NMR (300 MHz, CDCl_3): δ 10.01 (s, 1H), 7.91-7.88 (d, 2H), 7.66-7.63 (d, 2H), 7.12-7.09 (d, 2H), 6.91-6.88 (d, 1H), 6.01 (s, 2H). ^{13}C (300 MHz, CDCl_3): δ 192.0, 148.6, 148.3, 147.0, 135.09, 134.1, 130.5, 127.4, 121.4, 109.03, 107.8, 101.6. HRMS calculated for: $\text{C}_{14}\text{H}_{11}\text{O}_3^+$: 227.0630, Found: 227.0702



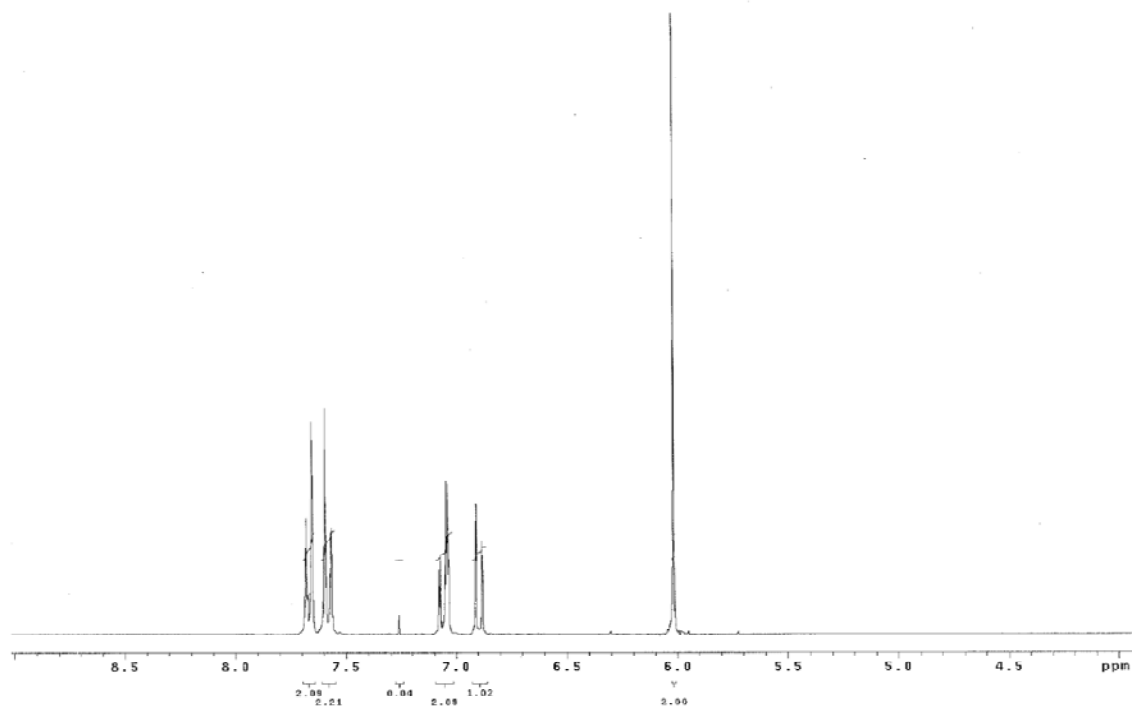
NMR Spectra of the Compounds in Table 2:
4'-(dimethylamino)-[1,1'-biphenyl]-4-carbonitrile (1a)
¹H NMR:



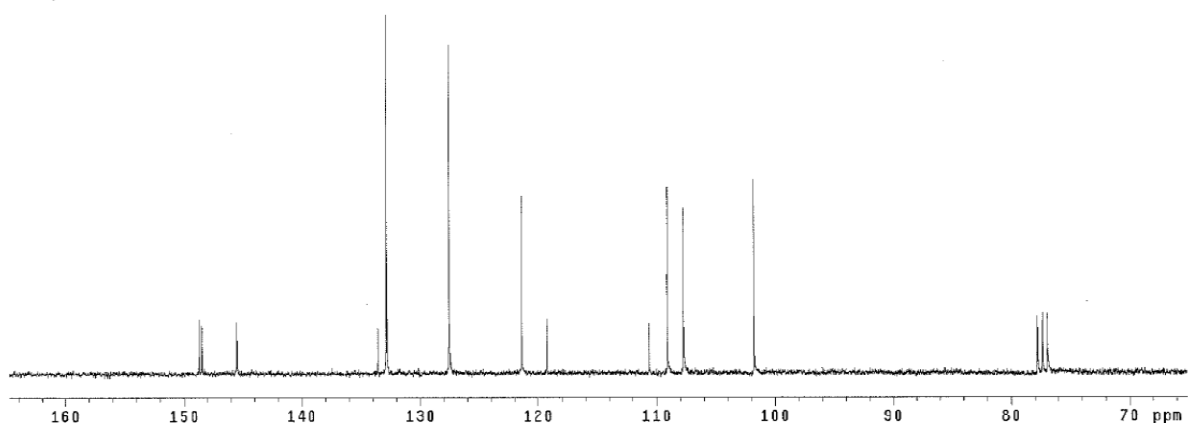
¹³C NMR:



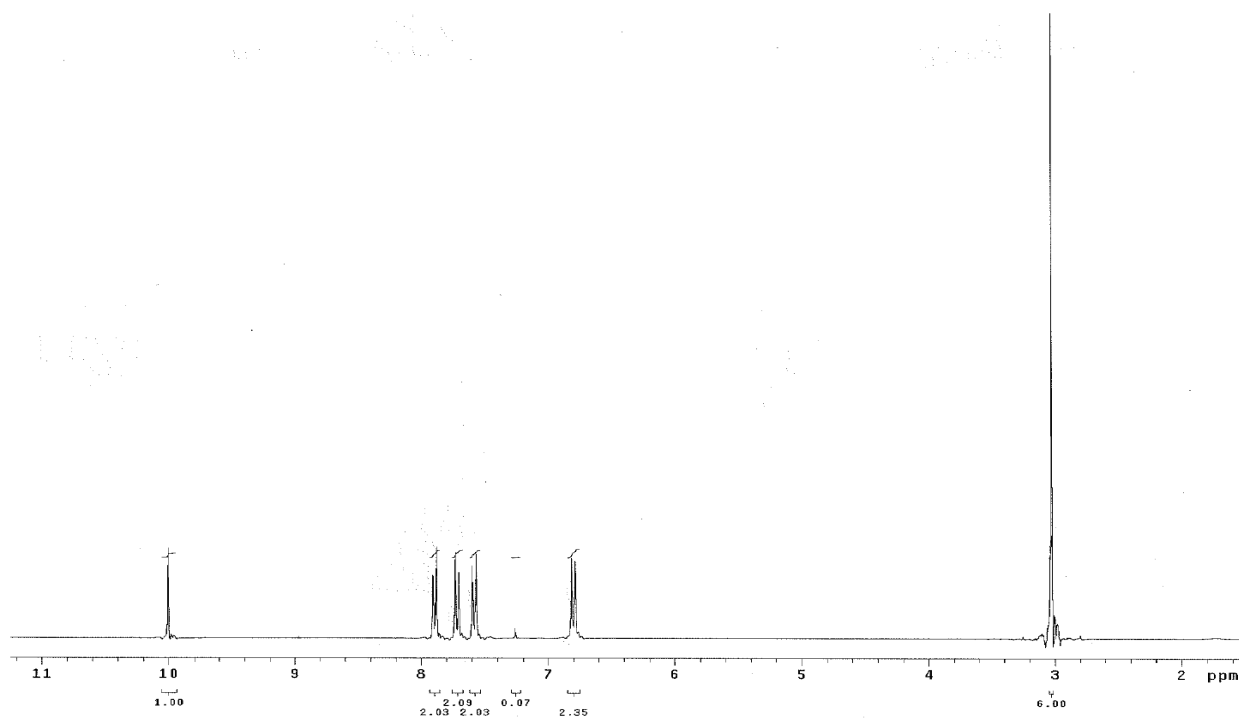
**4-(benzo[d][1,3]dioxol-5-yl)benzonitrile (1b):
¹H NMR:**



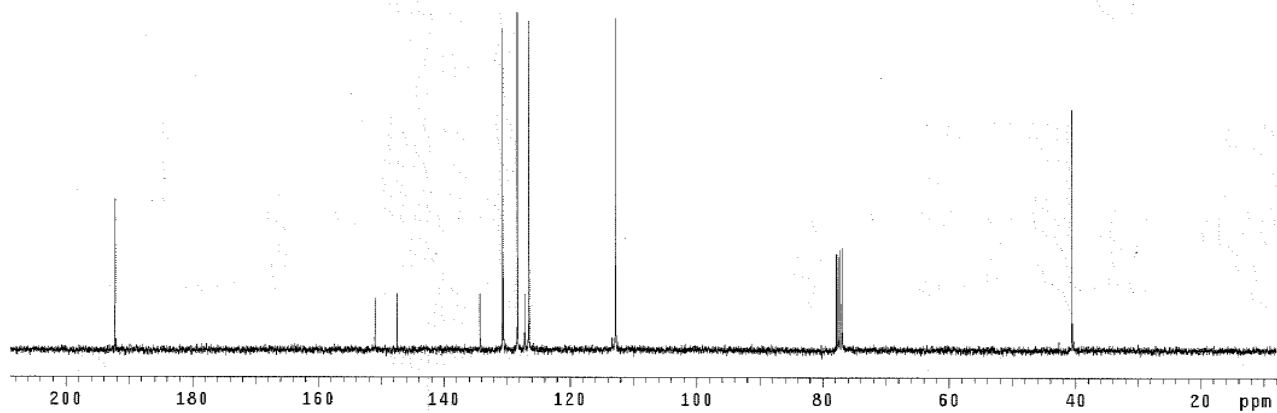
¹³C NMR:



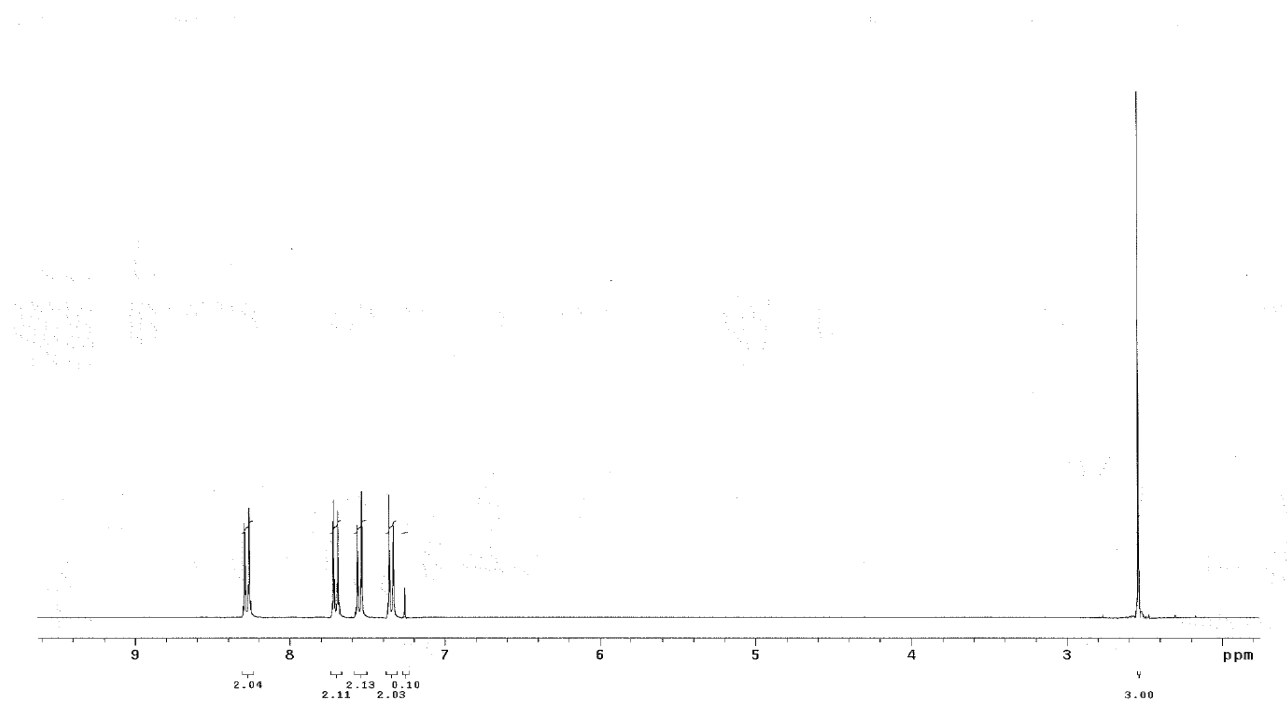
**4'-(dimethylamino)-[1,1'-biphenyl]-4-carbaldehyde (1c):
¹H NMR:**



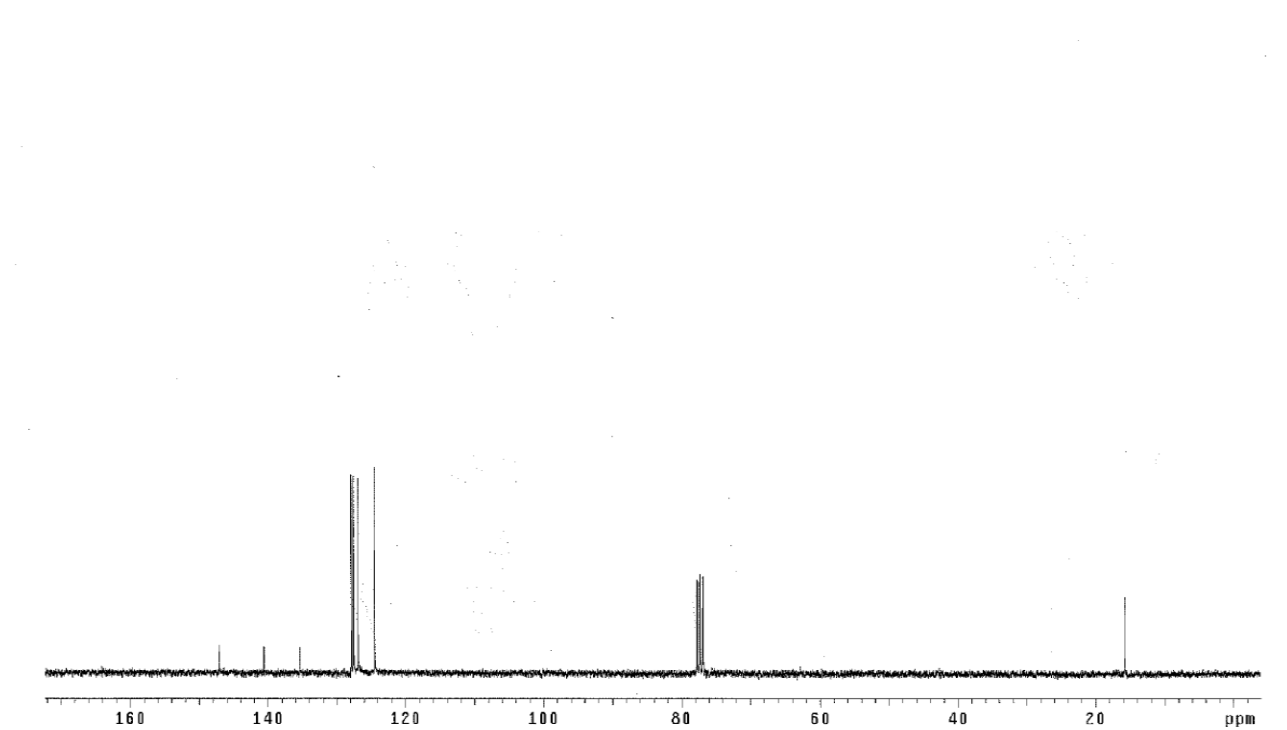
¹³C NMR:



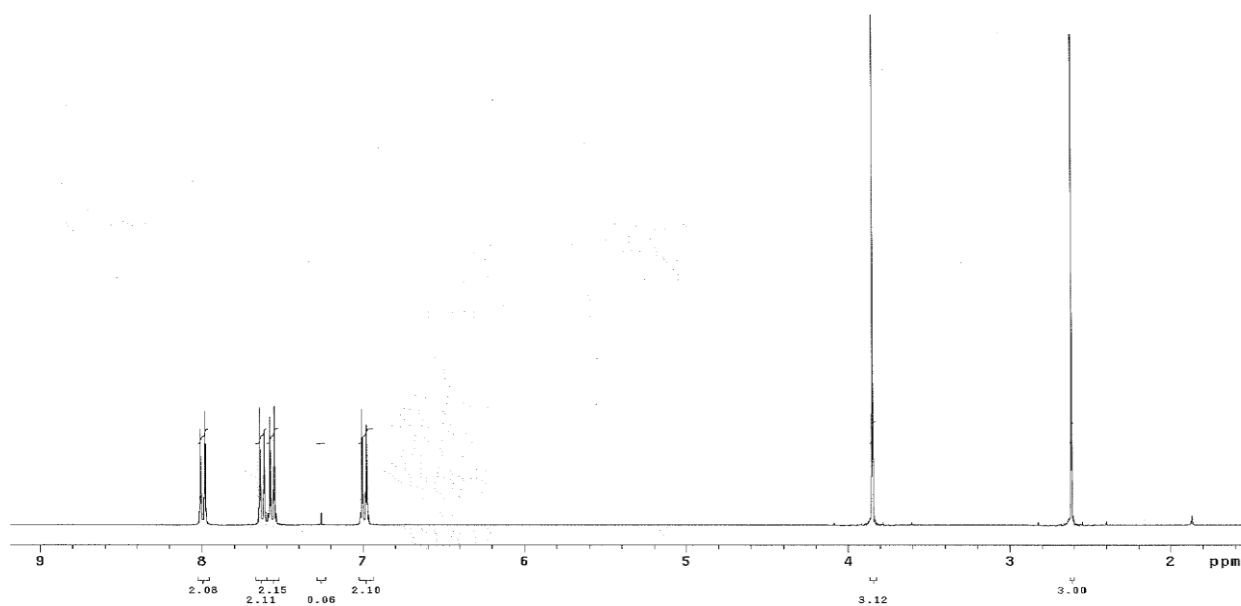
**Methyl(4'-nitro-[1,1'-biphenyl]-4-yl)sulfane (1d):
¹H NMR:**



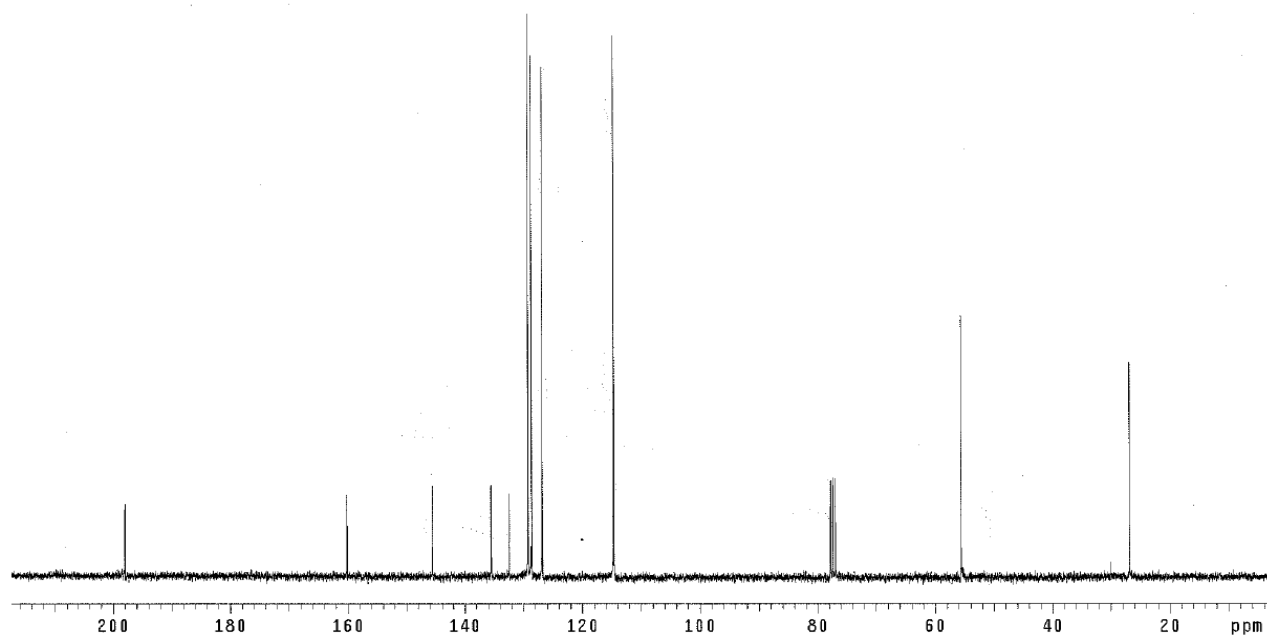
¹³C NMR:



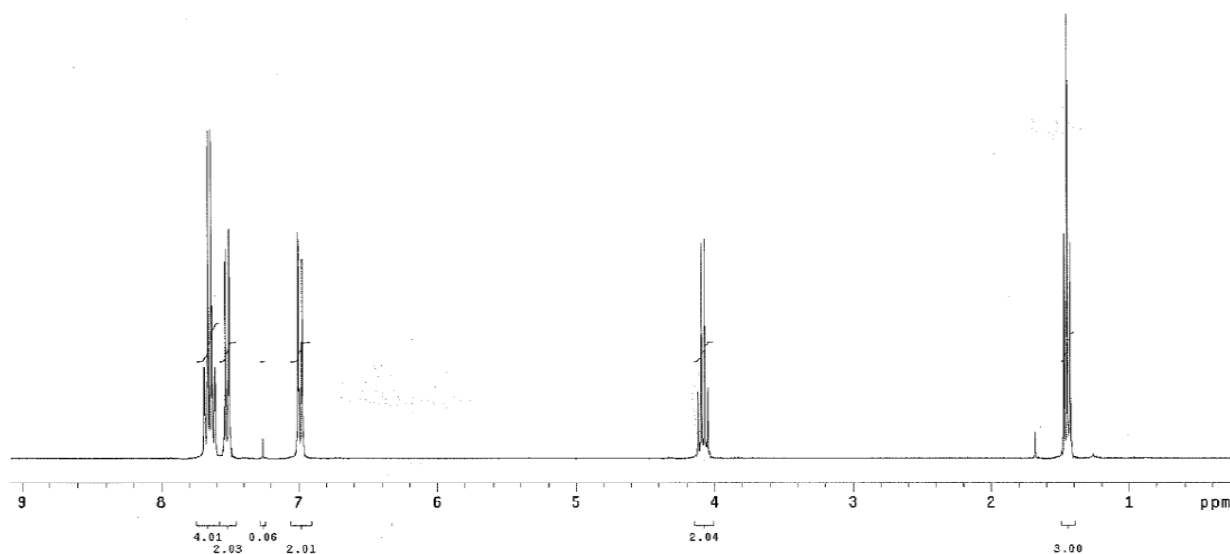
1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethanone (1e):
¹H NMR:



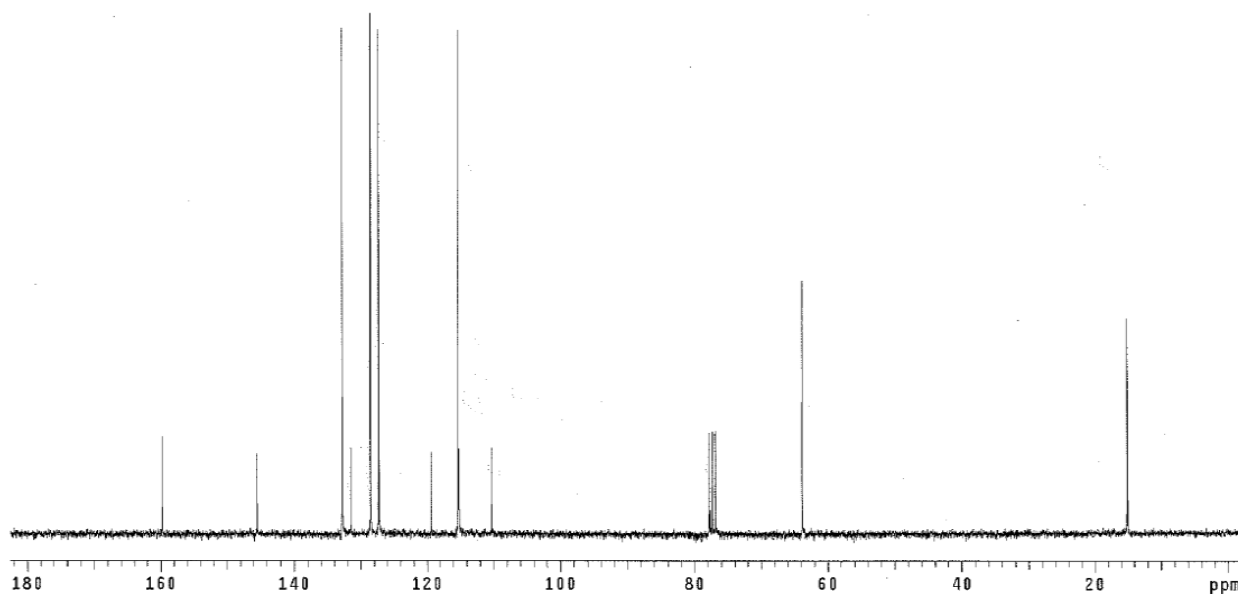
¹³C NMR:



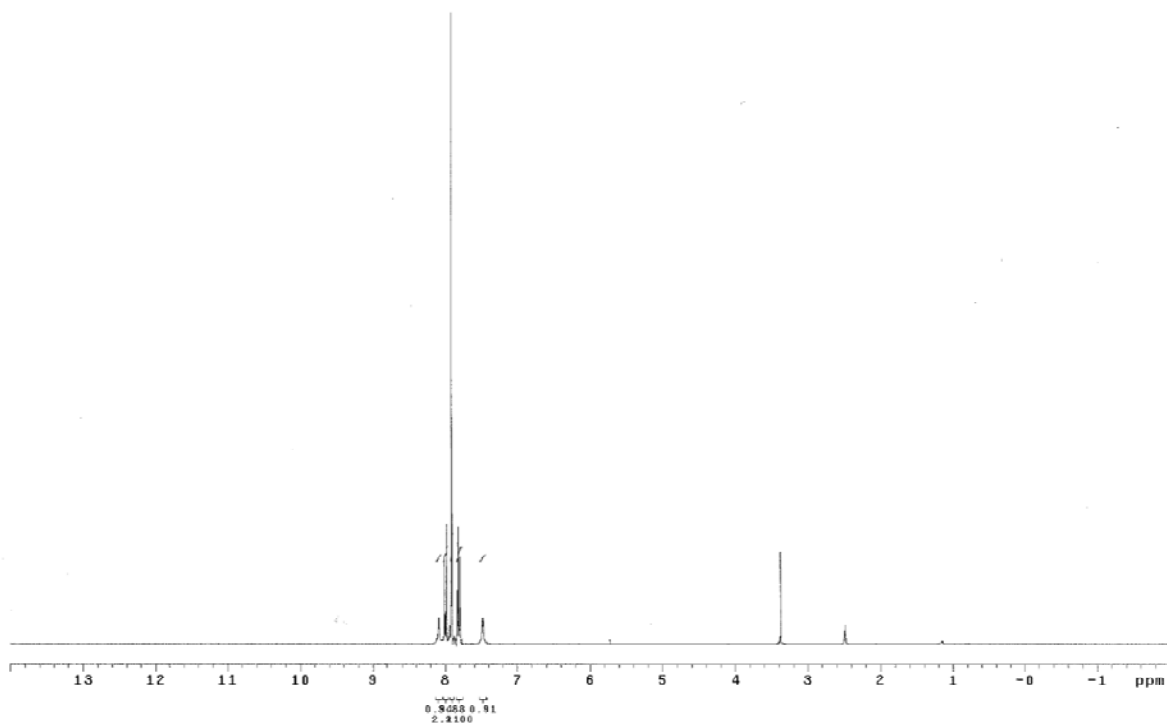
**4'-ethoxy-[1,1'-biphenyl]-4-carbonitrile (1f):
¹H NMR:**



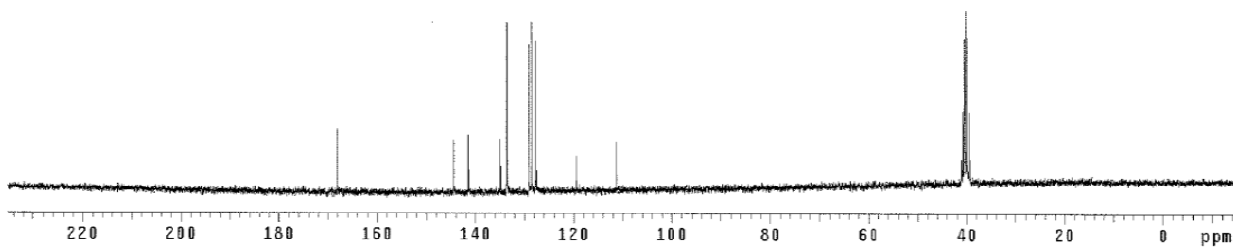
¹³C NMR:



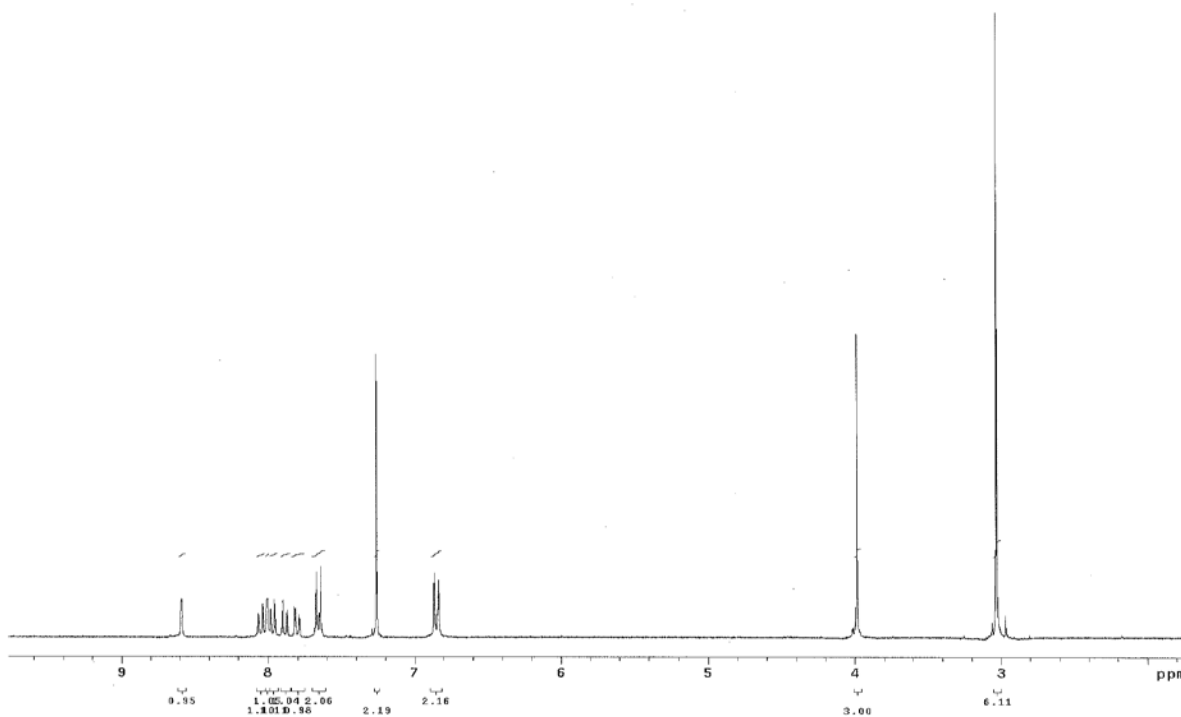
**4'-cyano-[1,1'-biphenyl]-4-carboxamide (1g):
¹H NMR:**



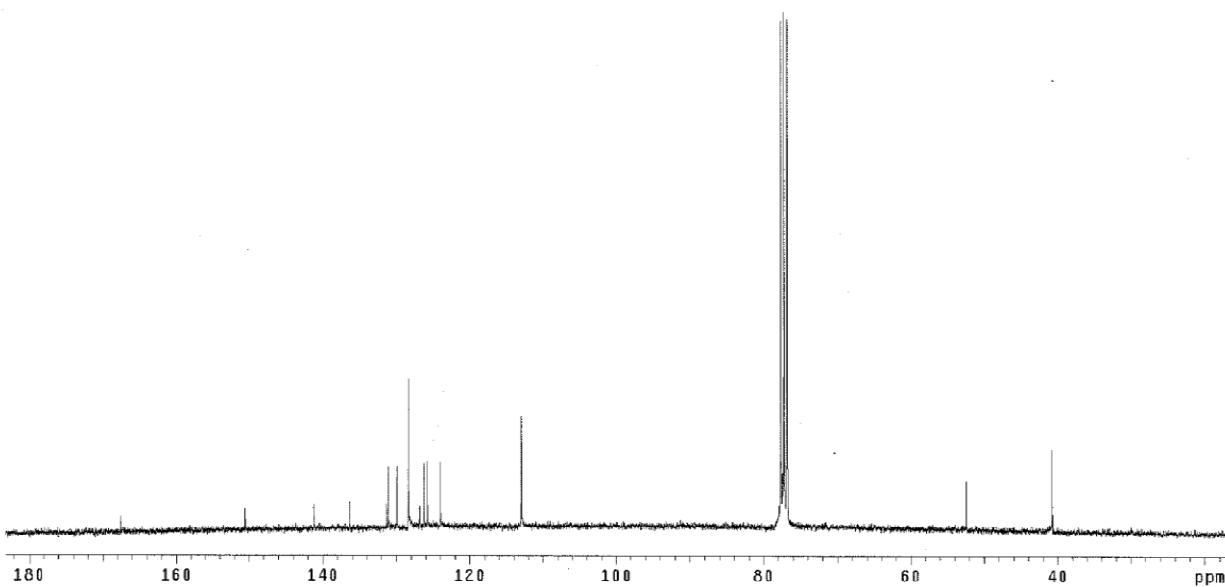
¹³C NMR:



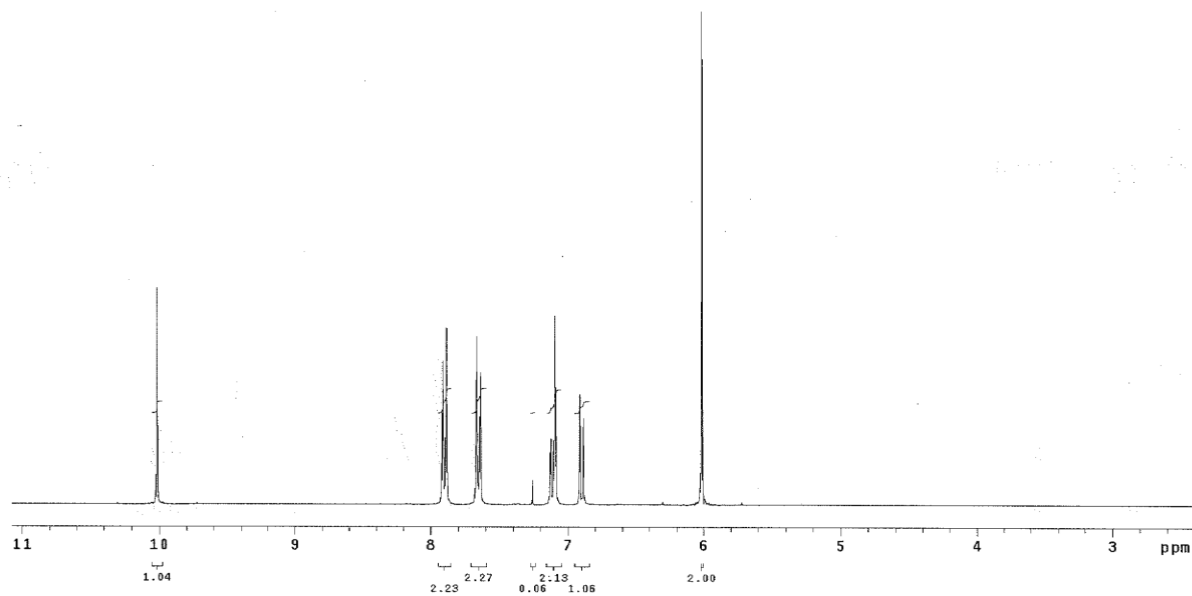
**Methyl 6-(4-(dimethylamino)phenyl)-2-naphthoate (1h):
¹H NMR:**



¹³C NMR:



4-(benzo[d][1,3]dioxol-5-yl)benzaldehyde (1i):
¹H NMR:



¹³C NMR:

