Electronic Supplementary Information

Synthesis of Arylacetonitrile Derivatives; Ni-catalyzed Reaction of Benzyl Chlorides and Trimethylsilyl Cyanide under Base-free Conditions

Yasushi Satoh, Yasushi Obora*

Department of Chemistry and Materials Engineering, Faculty of Chemistry, Materials and Bioengineering, Kansai University, Suita, Osaka 564-8680, Japan

Table of Contents

General

GLC analysis was performed with a flame ionization detector using a 0.22 × 25 m capillary column (BP-5). ^{1}H and ^{13}C NMR were measured at 400 and 100 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. The products were characterized by ^{1}H NMR, ^{13}C NMR, HMQC, HMBC.

All reagents were commercially available and used without any purification.

Experimental Section

A typical reaction procedure for the preparation of **3a** (entry 13, Table 1):

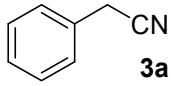
A mixture of phenylacetonitrile (**1a**) (127 mg, 1 mmol), trimethylsilyl cyanide (**2**) (397 mg, 4 mmol), $Ni(cod)_2$ (28 mg, 0.2 mmol), PPh_3 (52 mg, 0.2 mmol), and toluene (1 mL) was stirred for 16 h at 60 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC and **3a** was obtained in 97% yield. The products (**3a**) was isolated by silica gel column chromatography (*n*-hexane:EtOAc=100:0 to 10:1 as eluent) in 83% yield (97 mg) as yellow liquid.

A typical reaction procedure for the preparation of **3a** (Scheme 1):

A mixture of $Ni(\eta^3\text{-}CH_2Ph)(PCy_2Ph)Cl$ (**6**) (182 mg, 0.4 mmol) with TMSCN (**2**) (159 mg, 1.6 mmol) and toluene (3 mL) was stirred for 40 h at 100 °C under Ar. The yields of the products were estimated from the peak areas based on the internal standard technique using GC and **3a** was obtained in 29% yield.

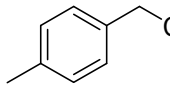
Compounds **3a-3d**[1], **3e**[2], **3g**[1], **3h**[1], **3i**[3], **3j**[3], and **3k**[1] are known compound and reported previously.

3a[1] **:** colorless liguid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 2H), 7.32-7.36 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.4 (CH_2), 117.8 (C), 127.8 (2CH), 128.0 (CH), 129.0 (2CH), 129.8 (C)



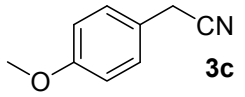
3a

3b[1] : colorless liguid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H), 3.67 (s, 2H), 7.15 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 20.9 (CH_3), 23.1 (CH_2), 118.0 (C), 126.8 (C), 127.7 (2CH), 129.7 (2CH), 137.7 (C)



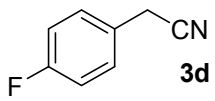
3b

3c[1] :colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 2H), 3.80 (s, 3H), 6.89 (d, J = 8.4 Hz, 2H), 7.23 (d, J = 8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_2), 55.3 (CH_3), 114.4 (2CH), 118.2 (C), 121.7 (C), 129.0 (2CH), 159.3 (C)



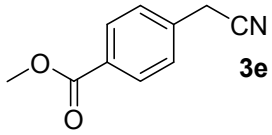
3c

3d[1]: colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.72 (s, 2H), 7.06 (t, J = 8.8 Hz, 2H), 7.29 (dd, J = 5.2, 5.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 22.7 (CH_2), 115.9 (J = 22 Hz, 2CH), 117.7 (C), 125.6 (J = 2.9 Hz, C), 129.5 (J = 8.5 Hz, 2CH), 162.2 (J = 246 Hz, C)



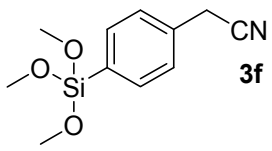
3d

3e[2] : white solid; m.p. 60.9-61.2 ^{o}C (ref[3]. 61-62 ^{o}C), ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.75 (s, 2H), 3.85 (s, 3H), 7.34 (d, J = 7.6 Hz, 2H), 7.97 (d, J = 7.6 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.6 (CH_2), 52.2 (CH_3), 117.1 (C), 127.9 (2CH), 130.3 (2CH), 134.8 (C), 166.3 (C)



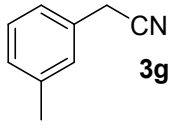
3e

3f : colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.47 (s, 9H), 3.61(s, 2H), 7.22 (d, J = 6.4 Hz, 2H), 7.52 (d, J = 6.8 Hz, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.5 (CH_2), 50.7 (3CH), 117.5 (C), 127.4 (2CH), 129.4 (C), 132.3 (C), 135.4 (2CH); IR (neat, cm^{-1}) 3020, 2250, 1604, 1458, 1124, 797; GC-MS (EI) *m/z* (relative intensity) 237 (9) $[M]^+$, 121 (100), 91 (8), 77 (8), 41 (7); HRMS (EI) *m/z* calcd for $C_{11}H_{15}NO_3Si$, $[M]^+$ 237.0821, found 237.0824



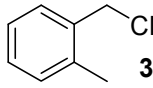
3f

3g[1] : colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 3H), 3.60 (s, 2H), 7.01-7.24 (m, 4H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.3 (CH_3), 23.5 (CH_2), 124.9 (C), 128.6 (CH), 127.7 (CH), 129.0 (CH), 129.7 (CH), 139.0 (C)



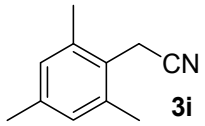
3g

3h[1] : colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 3.59 (s, 2H), 7.00-7.23 (m, 4H);



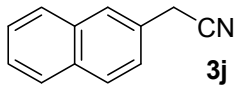
3h ^{13}C-NMR (100 MHz, $CDCl_3$) δ 19.2 (CH_3), 21.8 (CH_2), 117.5 (C), 126.7 (CH), 128.3 (CH), 128.5 (CH), 130.6 (CH), 136.0 (C)

3i[3] : colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.26 (s, 3H), 2.35 (s, 6H), 3.59 (s, 2H), 6.89 (s, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 17.3 (CH_3), 19.9 ($2CH_3$), 20.8 (CH_2), 117.4 (C), 124.4 (C), 129.3 (2CH), 136.4 (C), 137.8 (C)



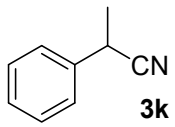
3i

3j[4] : beiji solid; m.p. 78-80 ^{o}C, ^{1}H-NMR (400 MHz, $CDCl_3$) δ 3.68 (s, 2H), 7.17-7.68 (s, 7H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 23.5 (CH_2), 117.8 (C), 125.3 (CH), 126.3 (CH), 126.6 (CH), 126.7 (CH), 127.1 (C), 127.5 (CH), 127.6 (CH), 128.8 (CH), 132.5 (C), 133.1 (C)



3j

3k[1] : colorless liquid; ^{1}H-NMR (400 MHz, $CDCl_3$) δ 1.57 (d, J = 7.6 Hz, 3H), 3.83 (q, J = 7.2 Hz, 1H), 7.27-7.32 (m, 5H); ^{13}C-NMR (100 MHz, $CDCl_3$) δ 21.4 (CH_3), 31.2 (CH), 121.6 (C), 126.7 (CH), 128.0 (CH), 129.1 (2CH), 137.0 (C)



3k

References

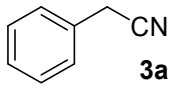
1. Y. Ren, C. Dong, S. Zhao, Y. Sun, J. Wang, J. Ma and C. Hou, *Tetrahedron Lett*., 2012, **53**, 2825.

2. E.G. Sakellriou, *Tetrahedron*, 2013, **59**, 9083.

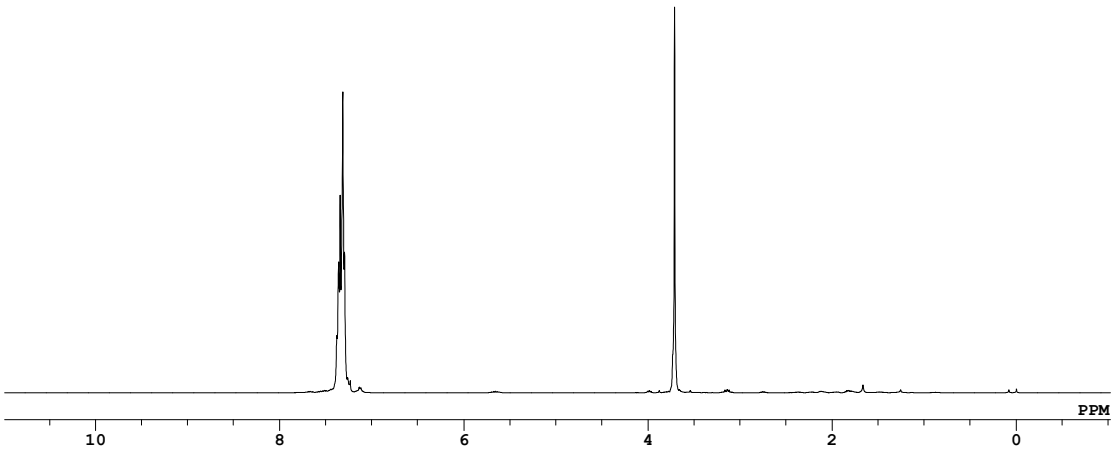
3. Z. Pechlivanidis, H. Hopf and L. Ernst, *Eur. J. Org. Chem.,* 2009, 223.

4. J. Velicky, A. Soicke, R. Steiner and H.-G. Schmalz, *J. Am. Chem. Soc.,* 2011, **133**, 6948.

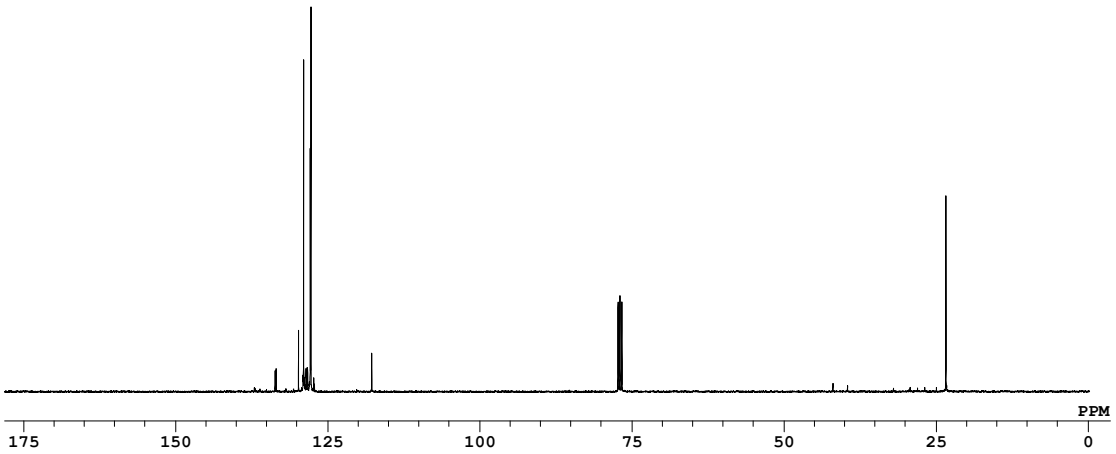
^{1}H NMR



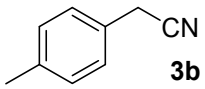
3a



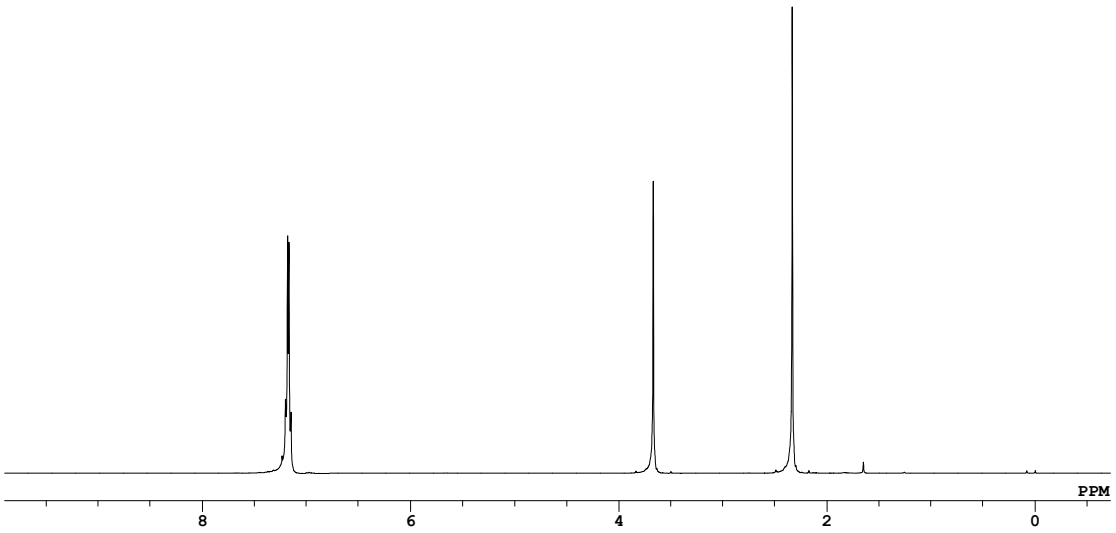
^{13}C NMR



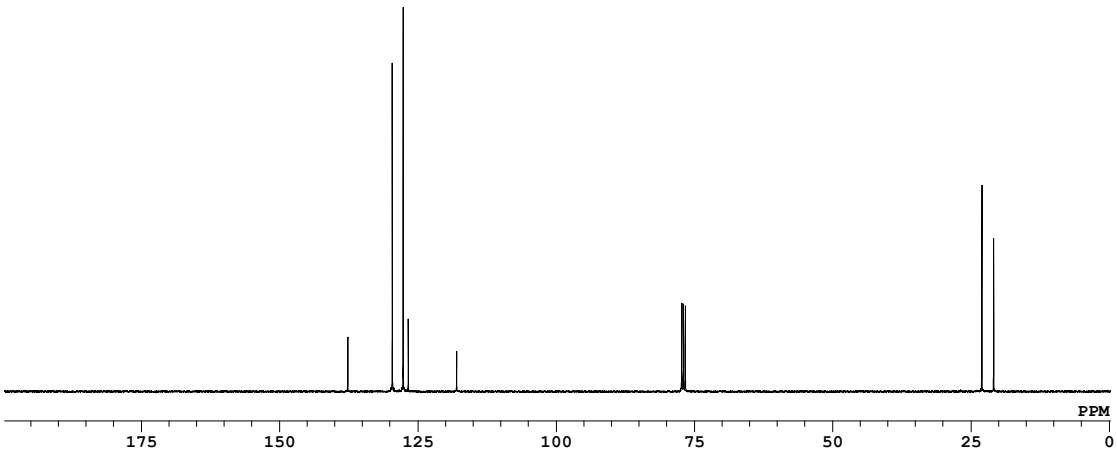
^{1}H NMR



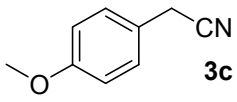
3b



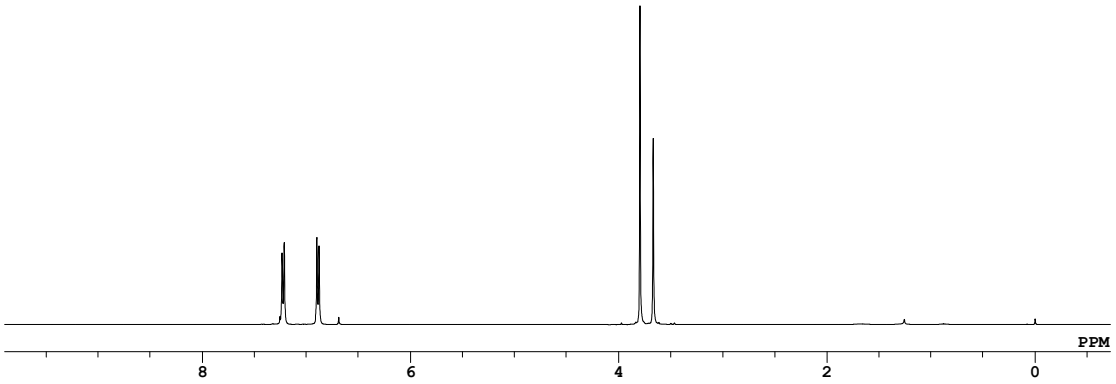
^{13}C NMR



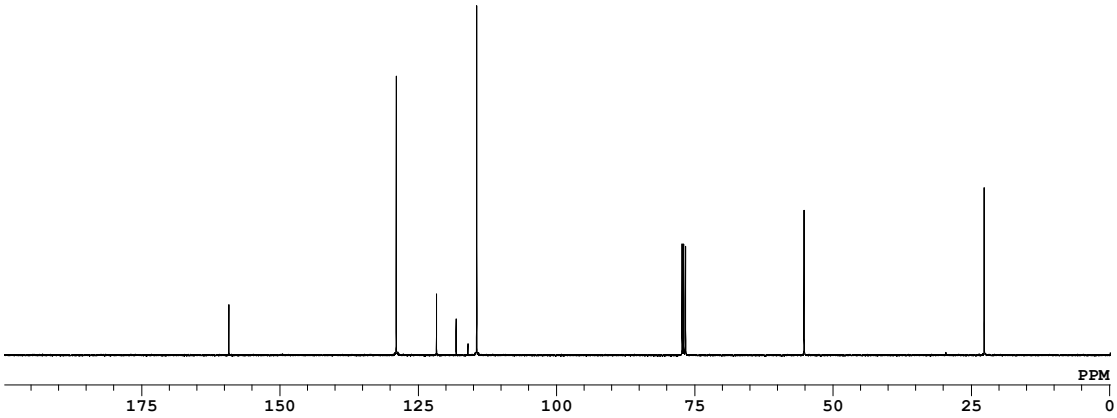
^{1}H NMR



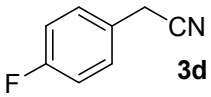
3c



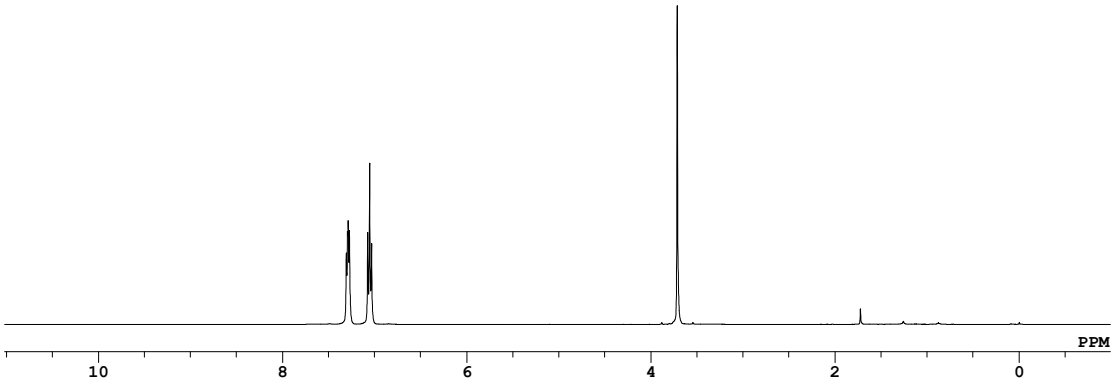
^{13}C NMR



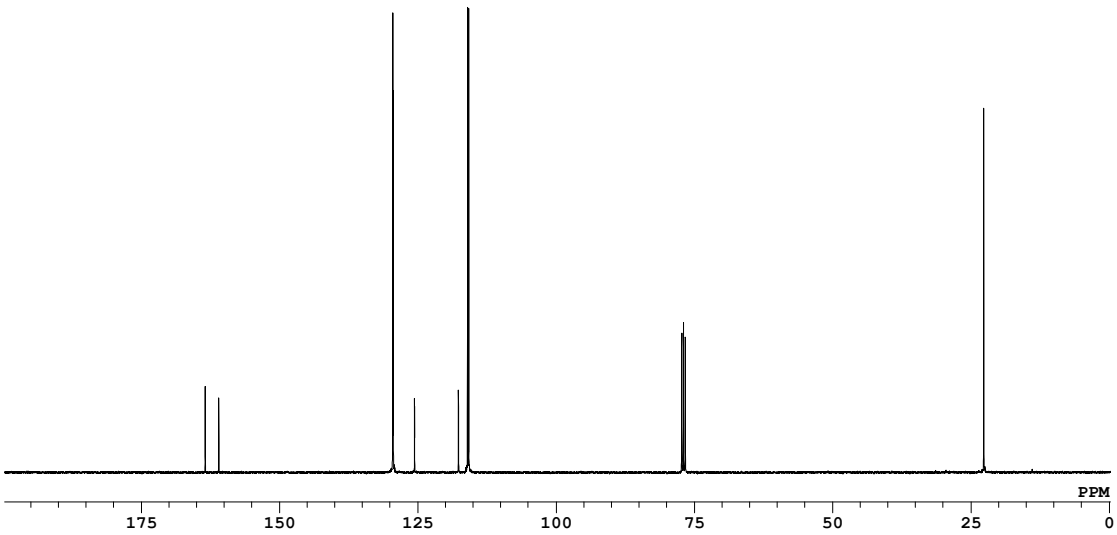
^{1}H NMR



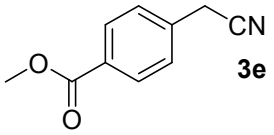
3d



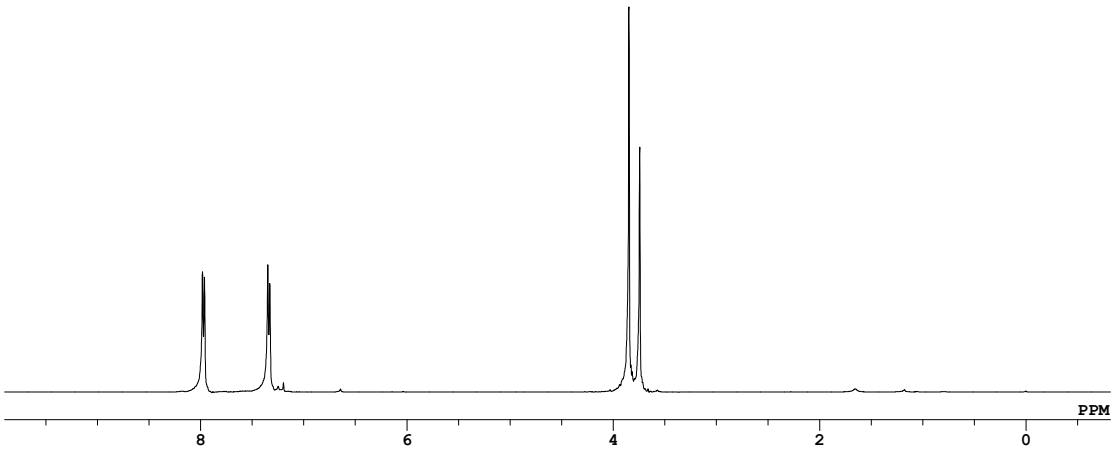
^{13}C NMR



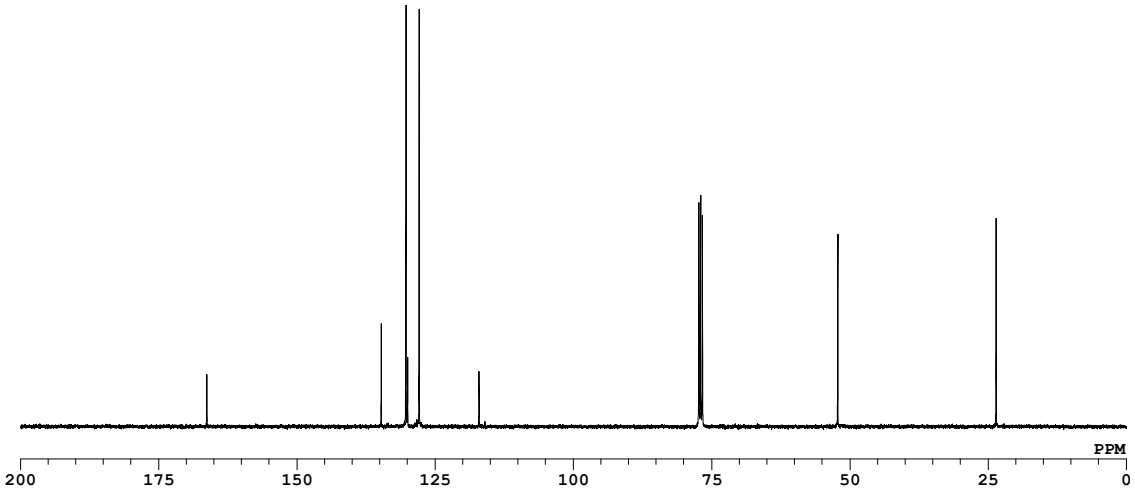
^{1}H NMR



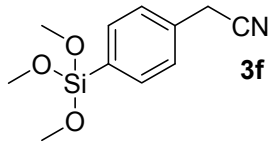
3e



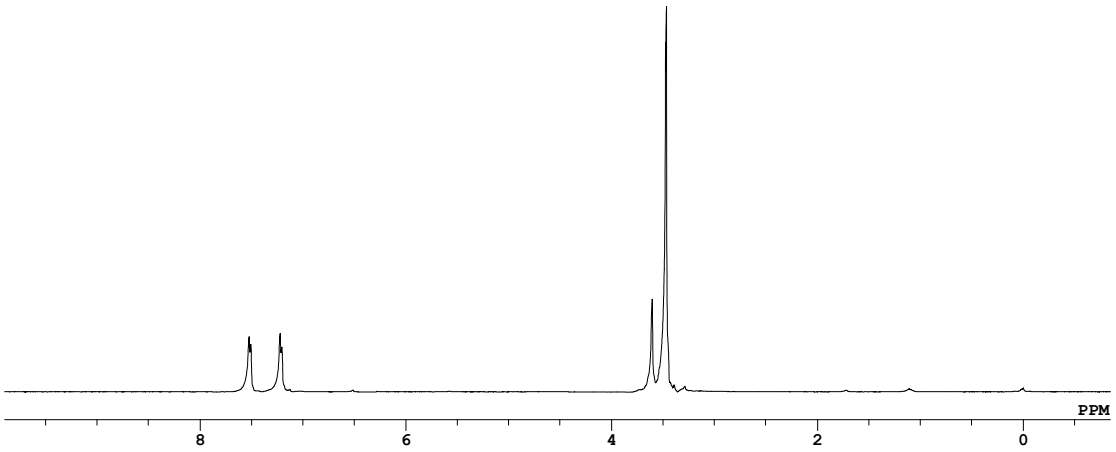
^{13}C NMR



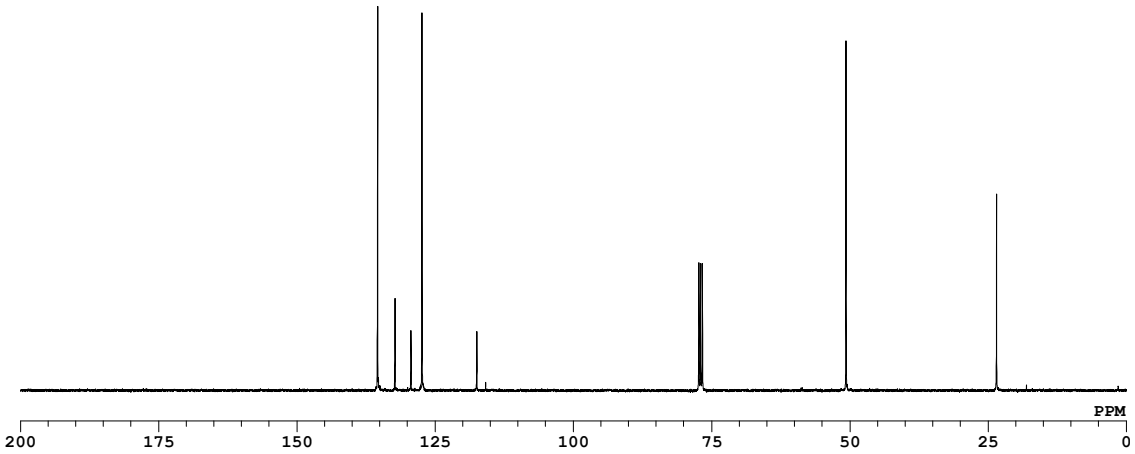
^{1}H NMR



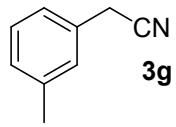
3f



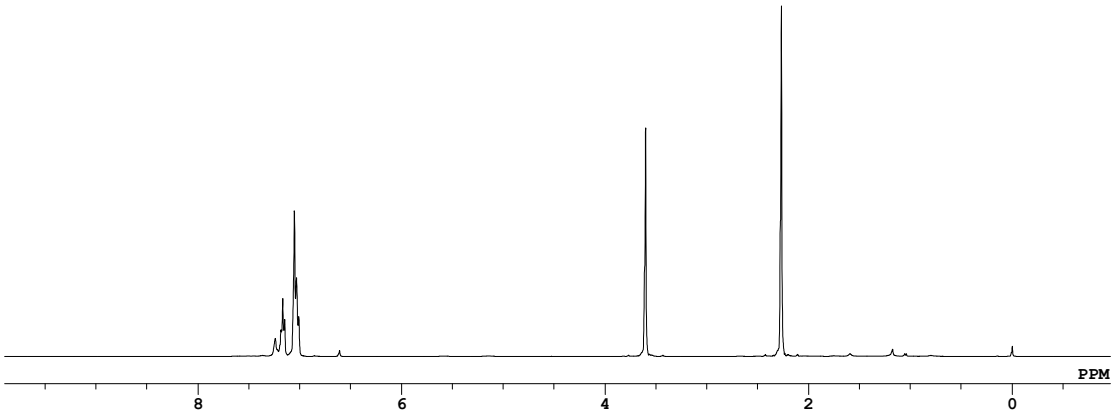
^{13}C NMR



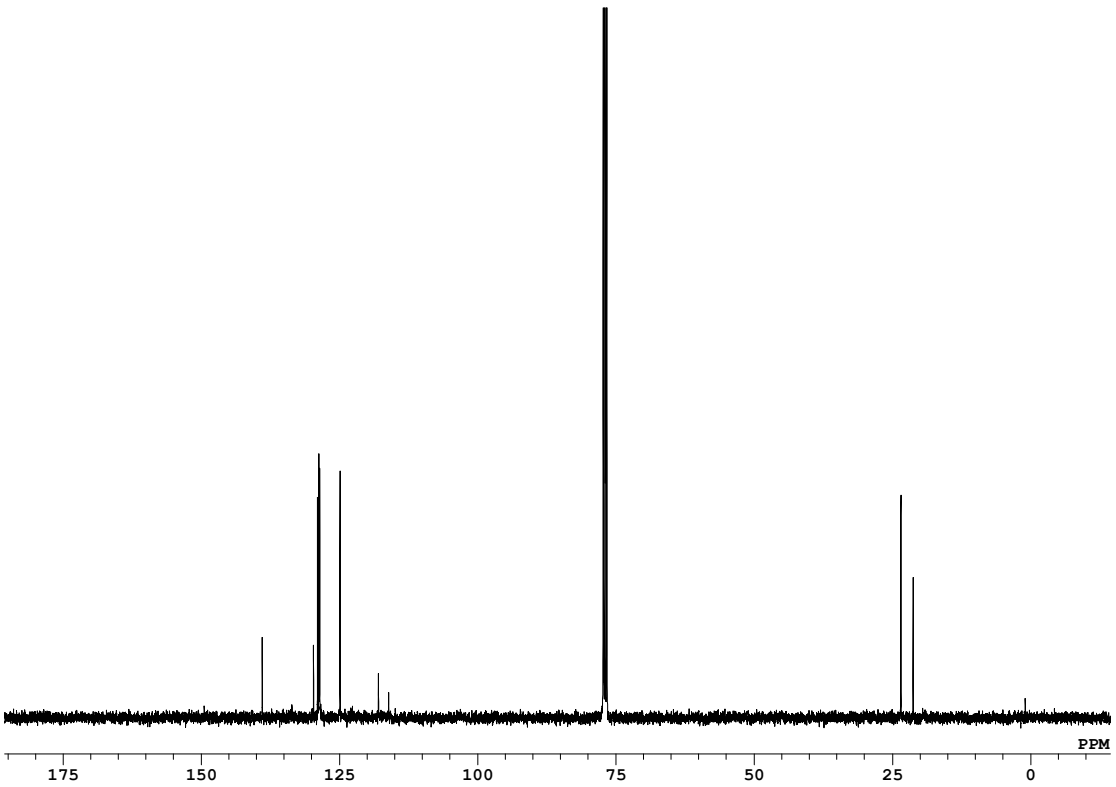
^{1}H NMR



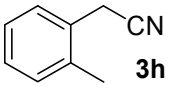
3g



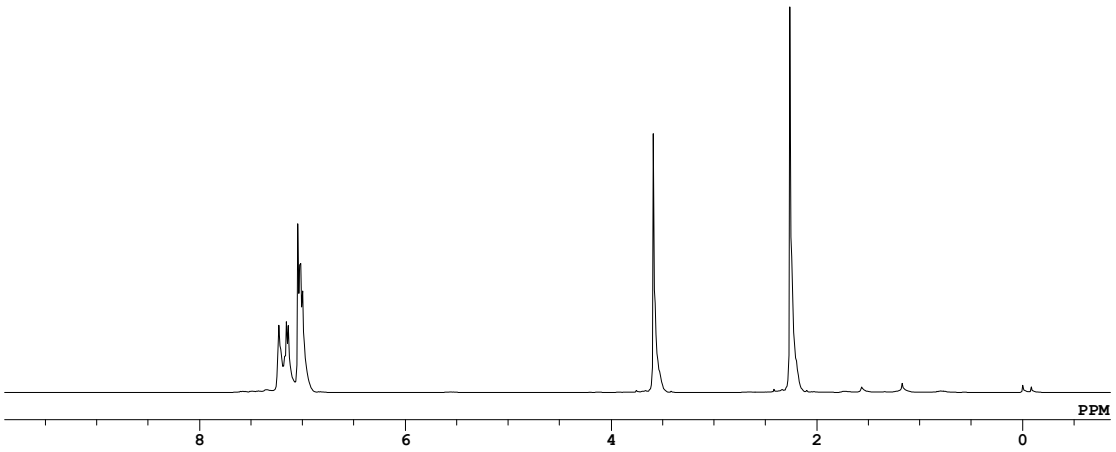
^{13}C NMR



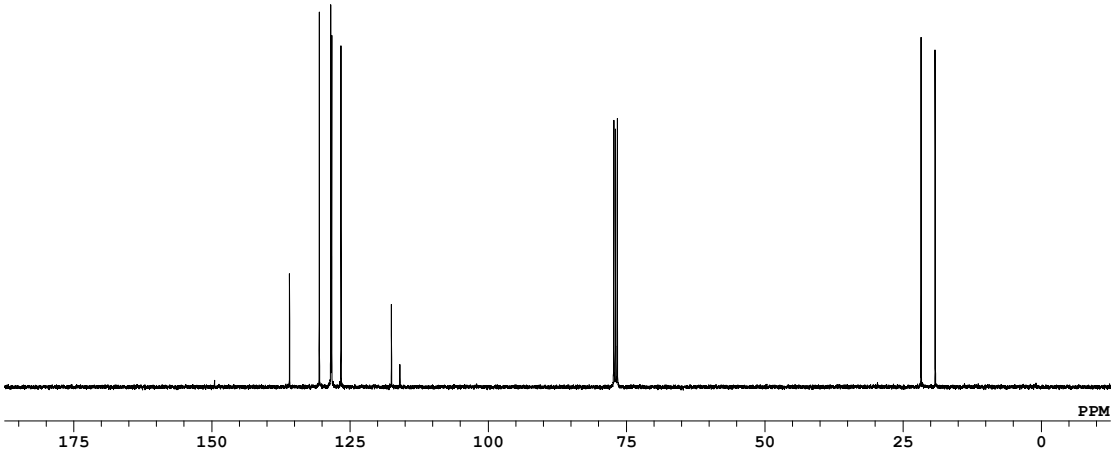
^{1}H NMR



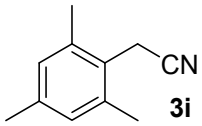
3h



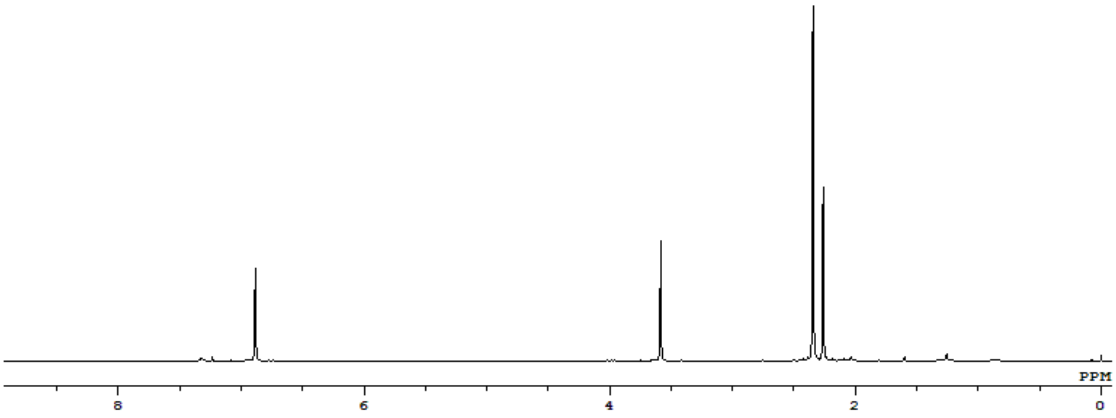
^{13}C NMR



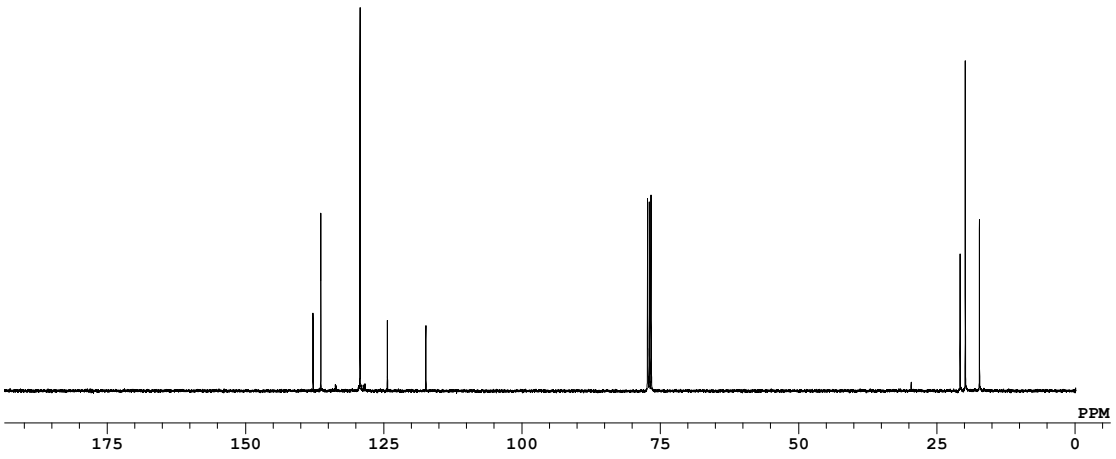
^{1}H NMR



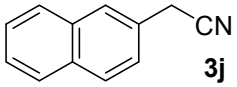
3i



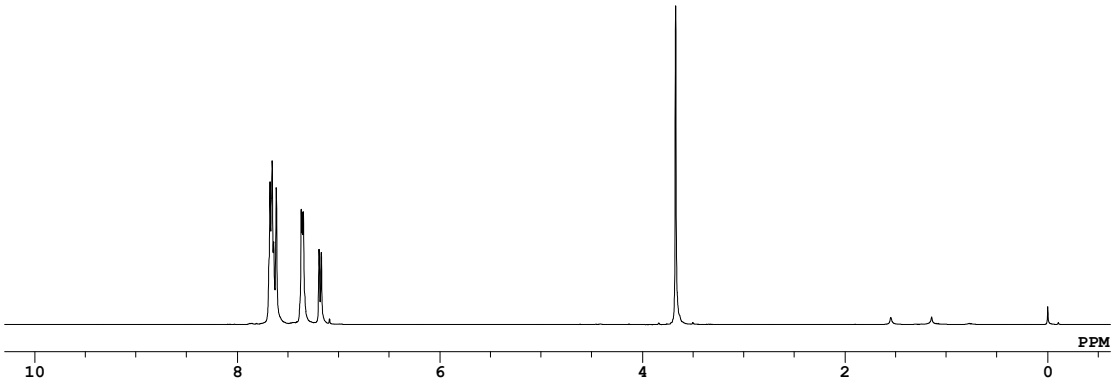
^{13}C NMR



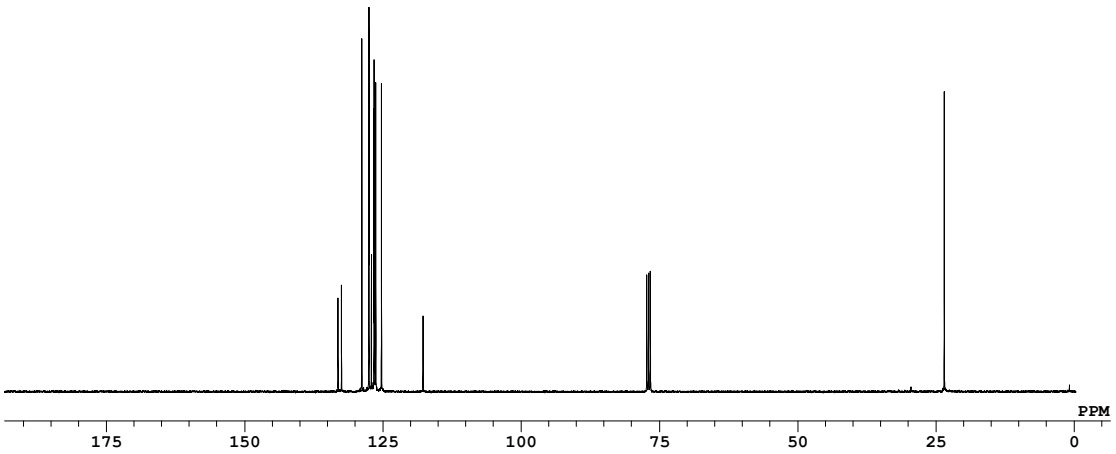
^{1}H NMR



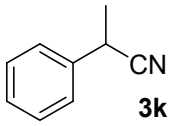
3j



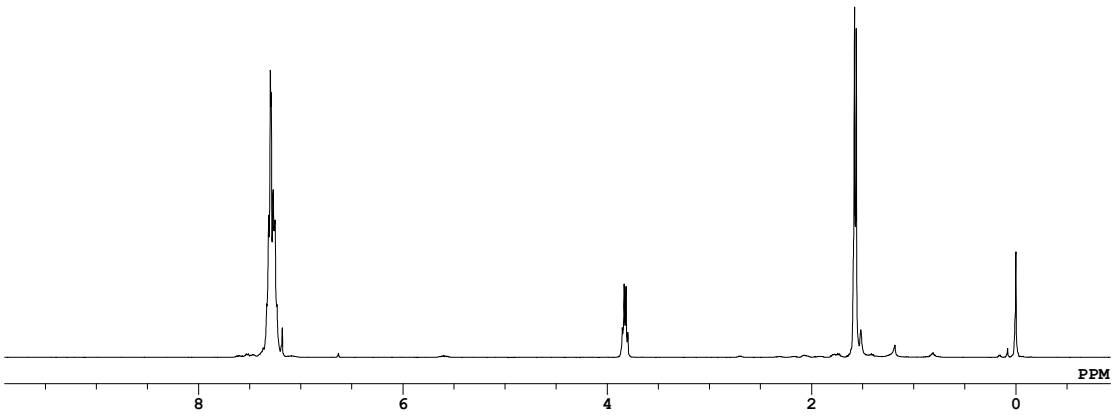
^{13}C NMR



^{1}H NMR



3k



^{13}C NMR