Supplementary Information

for

n-Butyllithium as a Highly Efficient Precatalyst for Cyanosilylation of Aldehydes and Ketones

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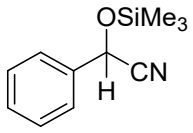
General Information

All manipulations of air-sensitive materials were carried out by using modified Schlenk line under an atmosphere of dry argon or glovebox techniques under nitrogen-atmosphere. Solvents of THF, DME, $CHCl_3$, CH_3CN and toluene were dried and freed of oxygen by refluxing over sodium/benzophenone ketyl and distilled prior to use. Trimethylsilyl cyanide (Me_3SiCN) was purchased from Macklin and used without further purification. All the liquid ketones and aldehydes were dried over CaH_2, freshly distilled, and degassed prior to use. All the solid ketones and aldehydes were degassed prior to use. Mesitylene was used for the clarification of product yield. $CDCl_3$ and THF-d_8 were purchased from TCI and stored over activated 4Å molecular sieves. ^1H and $^{13}C\{^1H\}$ spectra were recorded on Bruker AV-400 MHz and referenced to the resonances of the solvent used. Chemical shifts of the cyanohydrin products were reported as parts per million in δ scale using residual solvent signal as internal standard ($CDCl_3$ referenced at δ 7.26 in ^1H NMR and δ 77.0 for central line of the triplet in ^{13}C NMR) and compared to literature values. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad) and coupling constant (*J*, Hz). Fourier infrared spectroscopy was recorded on Bruker Vertex 70 spectrophotometer. Note: the catalytic cyanosilylation of aldehydes and ketones by *n*-BuLi is an exothermic reaction. Large-scale reactions should be carried out under cooling in an ice bath, and *n*-BuLi should be added in a slow dropwise manner.

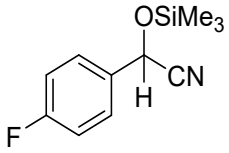
General Catalytic Procedure for the Cyanosilylation of Aldehydes and Ketones

Aldehyde or ketones (1.0 mmol), Me_3SiCN (1.1 mmol) and *n*-BuLi (0.01-0.05 mol %, 0.0367 M) were charged in a Schlenk tube with a magnetic bead inside the glove box. The reaction mixture was allowed to stir at room temperature for 1 hour. Upon completion of reaction, the vial was moved out of the glove box and the reaction was exposed to the air. Subsequently, a drop of solution was added to the above J. Young tap NMR tube. The progress of the reaction was monitored by ^1H and ^{13}C NMR spectroscopy.

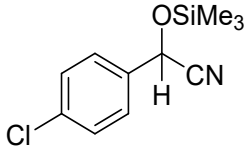
Characterization Data (^{1}H and ^{13}C NMR Spectra) for Corresponding Cyanosilylated Products of Aldehydes and Ketones:



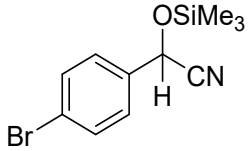
2-phenyl-2-((trimethylsilyl)oxy)acetonitrile(3a)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.43 – 7.28 (m, 5H), 5.42 (s, 1H), 0.16 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 136.35, 129.37, 128.97, 126.39, 63.69, -0.22.



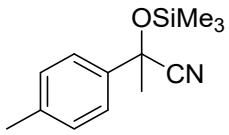
2-(4-fluorophenyl)-2-((trimethylsilyl)oxy)acetonitrile(3b)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (dd, *J* = 8.6, 5.2 Hz, 2H), 7.10 (t, J = 8.6 Hz, 2H), 5.47 (s, 1H), 0.23 (s, 10H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 164.67, 162.20, 132.56, 128.59, 119.26, 116.35, 63.28, 0.00, 0.00.



2-(4-chlorophenyl)-2-((trimethylsilyl)oxy)acetonitrile(3c)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.42 – 7.34 (m, 5H), 5.45 (s, 1H), 0.22 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 135.28, 134.93, 129.15, 127.71, 118.87, 62.97, -0.28.

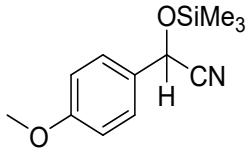


2-(4-bromophenyl)-2-((trimethylsilyl)oxy)acetonitrile(3d)[6]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.35 (d, J = 8.3 Hz, 2H), 5.45 (s, 1H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 132.13, 127.98, 63.04, -0.24.

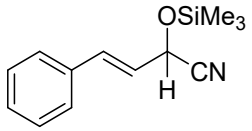


2-(p-tolyl)-2-((trimethylsilyl)oxy)propanenitrile(3e)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 1.83 (s, 3H), 0.15 (s, 9H). ^{13}C NMR ($CDCl_3$,

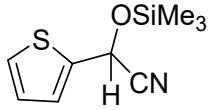
101 MHz): δ 139.57, 133.66, 129.81, 126.62, 119.53, 63.81, 21.42, 0.00.



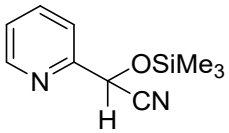
2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)acetonitrile(3f)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.7 Hz, 2H), 5.44 (s, 1H), 3.82 (s, 3H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 160.38, 128.52, 127.97, 119.40, 114.30, 63.38, 55.35, -0.19.



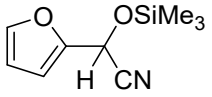
4-phenyl-2-((trimethylsilyl)oxy)but-3-enenitrile(3g)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.44 – 7.29 (m, 5H), 6.82 (d, *J* = 15.8 Hz, 1H), 6.20 (dd, *J* = 15.8, 6.0 Hz, 1H), 5.13 (d, *J* = 6.0 Hz, 1H), 0.27 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 135.10, 133.93, 128.81, 127.03, 123.67, 118.51, 62.27, -0.06.



2-(thiophen-2-yl)-2-((trimethylsilyl)oxy)acetonitrile(3h)[4]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.36 (d, *J* = 5.1 Hz, 1H), 7.19 (d, *J* = 3.6 Hz, 1H), 7.02 – 6.97 (m, 1H), 5.73 (s, 1H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.82, 127.49, 127.20, 126.60, 118.59, 59.87, -0.00.

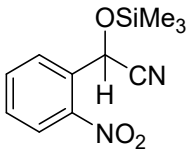


2-(pyridin-2-yl)-2-((trimethylsilyl)oxy)acetonitrile(3i)[9]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.32 (s, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.33 (d, *J* = 7.8 Hz, 1H), 7.04 (d, *J* = 4.4 Hz, 1H), 5.34 (d, *J* = 2.0 Hz, 1H), 0.02 – -0.02 (m, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 155.78, 149.71, 137.84, 124.34, 120.82, 119.05, 65.47, 0.00.

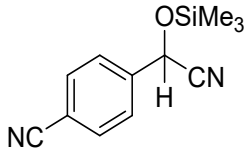


2-(furan-2-yl)-2-((trimethylsilyl)oxy)acetonitrile(3j)[1]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.50 (s, 1H), 6.60 (d, *J* = 3.3 Hz, 1H), 6.46 (s, 1H), 5.58 (s, 1H), 0.28 (s, 9H).

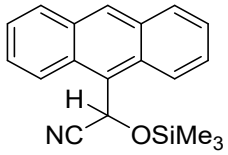
^{13}C NMR ($CDCl_3$, 101 MHz): δ 148.25, 143.91, 117.18, 110.85, 109.78, 57.48, -0.35.



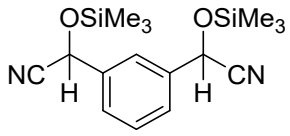
2-(2-nitrophenyl)-2-((trimethylsilyl)oxy)acetonitrile(3k)[6]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.09 (t, *J* = 10.5 Hz, 1H), 7.97 (t, *J* = 8.0 Hz, 1H), 7.73 (q, *J* = 7.7 Hz, 1H), 7.55 (q, *J* = 8.1 Hz, 1H), 6.17 (s, 1H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 146.91, 134.89, 132.60, 130.66, 129.00, 125.77, 118.31, 60.64, 0.00.



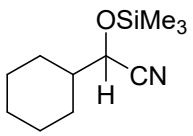
4-(cyano((trimethylsilyl)oxy)methyl)benzonitrile(3l)[2]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, *J* = 5.1 Hz, 2H), 7.56 (d, *J* = 4.8 Hz, 2H), 5.56 (s, 1H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 141.26, 132.70, 126.89, 118.11, 113.22, 67.82, 62.76, 25.56, -0.41.



2-(anthracen-9-yl)-2-((trimethylsilyl)oxy)acetonitrile(3m)[5]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.55 – 8.48 (m, 3H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.59 (m, 2H), 7.55 – 7.48 (m, 2H), 6.94 (s, 1H), 0.11 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 131.66, 130.76, 129.59, 127.38, 126.16, 125.44, 119.95, 58.26, 0.00.

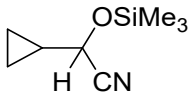


2-(3-((cyano((trimethylsilyl)oxy)methyl)phenyl)-2-((trimethylsilyl)oxy)acetonitrile(3n)[5]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.54 (s, 1H), 7.49 – 7.40 (m, 3H), 5.51 (s, 2H), 0.20 (s, 19H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 137.66, 129.93, 127.44, 124.41, 119.16, 63.53, 0.00.

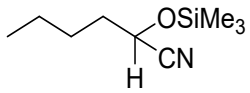


2-cyclohexyl-2-((trimethylsilyl)oxy)acetonitrile(3o)[4]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.15 (s, 1H), 1.90 – 1.75 (m, 4H), 1.72 – 1.59 (m, 2H), 1.25 – 1.05 (m, 4H), 0.36 (s, 1H), 0.19 (s, 9H). ^{13}C

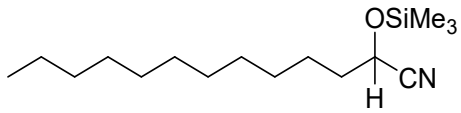
NMR ($CDCl_3$, 101 MHz): δ 119.89, 43.39, 28.59, 28.37, 26.49, 25.98, -0.00.



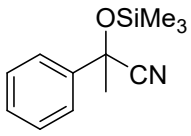
2-cyclopropyl-2-((trimethylsilyl)oxy)acetonitrile(3p): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.07 (d, *J* = 6.8 Hz, 1H), 1.35 – 1.17 (m, 1H), 0.62 (d, *J* = 8.0 Hz, 2H), 0.44 (d, *J* = 4.8 Hz, 2H), 0.17 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 119.45, 64.94, 16.41, 3.88, 2.43, 0.00.



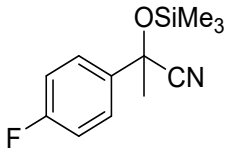
2-((trimethylsilyl)oxy)hexanenitrile(3q): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.37 (t, *J* = 6.6 Hz, 1H), 1.84 – 1.71 (m, 2H), 1.49 – 1.28 (m, 4H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 120.51, 36.36, 27.05, 22.48, 14.23, 0.00.



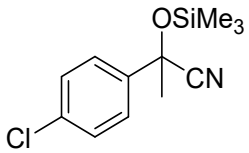
2-((trimethylsilyl)oxy)tridecanenitrile(3r): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 4.37 (t, *J* = 6.6 Hz, 1H), 1.81 – 1.71 (m, 2H), 1.25 (s, 18H), 0.87 (t, *J* = 6.9 Hz, 3H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 120.49, 61.89, 36.65, 32.31, 30.00, 29.88, 29.78, 29.73, 24.96, 23.08, 14.50, 0.00.



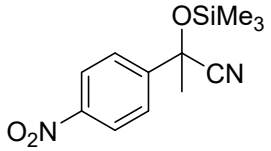
2-phenyl-2-((trimethylsilyl)oxy)propanenitrile(4a)[2]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.43 – 7.32 (m, 3H), 1.87 (s, 3H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ142.03, 128.70, 124.63, 121.64, 71.64, 33.60, 1.09.



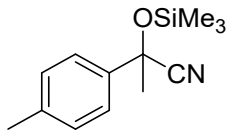
2-(4-fluorophenyl)-2-((trimethylsilyl)oxy)propanenitrile(4b): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.52 (dd, *J* = 8.9, 5.1 Hz, 2H), 7.07 (t, *J* = 8.7 Hz, 2H), 1.84 (s, 3H), 0.18 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 162.88, 160.42, 136.91, 125.52, 120.39, 114.39, 70.00, 32.53, -0.00.



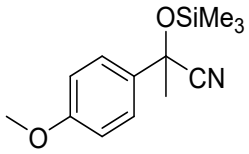
2-(4-chlorophenyl)-2-((trimethylsilyl)oxy)propanenitrile(4c)[9]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.48 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 1.83 (s, 3H), 0.19 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 139.65, 133.54, 127.77, 125.02, 120.18, 70.01, 32.46, 0.00.



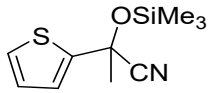
2-(4-nitrophenyl)-2-((trimethylsilyl)oxy)propanenitrile(4d)[2]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.24 (d, *J* = 8.8 Hz, 2H), 7.72 (d, *J* = 8.8 Hz, 2H), 1.85 (s, 3H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 148.94, 147.99, 125.76, 123.93, 120.64, 70.92, 33.31, 1.00.



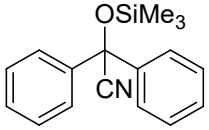
2-(p-tolyl)-2-((trimethylsilyl)oxy)propanenitrile(4e)[2]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.46 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 3.79 (s, 3H), 1.83 (s, 3H), 0.15 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.01, 137.44, 128.18, 127.36, 123.51, 120.68, 70.44, 32.44, 19.98, -0.00.



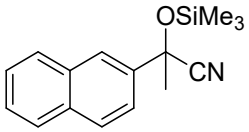
2-(4-methoxyphenyl)-2-((trimethylsilyl)oxy)propanenitrile(4f)[2]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 6.8 Hz, 2H), 6.80 (d, *J* = 8.6 Hz, 3H), 3.73 (s, 3H), 2.41 (s, 3H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 198.35, 165.43, 161.76, 132.44, 127.93, 115.58, 57.29, 28.13, -0.00.



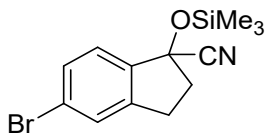
2-(thiophen-2-yl)-2-((trimethylsilyl)oxy)propanenitrile(4g)[7]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.31 – 7.28 (m, 1H), 7.21 – 7.18 (m, 1H), 6.96 (dd, *J* = 5.1, 3.6 Hz, 1H), 1.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 145.50, 125.81, 125.17, 123.90, 120.03, 67.46, 32.61, 0.00.



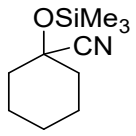
2,2-diphenyl-2-((trimethylsilyl)oxy)acetonitrile(4h)[2]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (d, *J* = 6.9 Hz, 5H), 7.44 – 7.34 (m, 8H), 0.24 (s, 10H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 142.04, 128.65, 125.97, 120.79, 1.03.



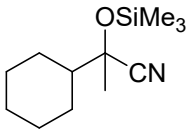
2-(naphthalen-2-yl)-2-((trimethylsilyl)oxy)propanenitrile(4i)[8]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.85 (s, 1H), 7.71 – 7.61 (m, 3H), 7.41 (dd, *J* = 8.7, 1.9 Hz, 1H), 7.35 – 7.28 (m, 2H), 1.73 (s, 3H), -0.00 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 138.14, 132.15, 131.76, 127.68, 127.27, 126.56, 125.63, 125.59, 122.60, 121.26, 120.52, 70.74, 32.37, 0.00.



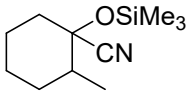
5-bromo-1-((trimethylsilyl)oxy)-2,3-dihydro-1H-indene-1-carbonitrile(4j): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.60 (s, 1H), 7.42 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 8.1 Hz, 1H), 3.07 – 2.86 (m, 2H), 2.70 (ddd, *J* = 13.0, 7.6, 5.3 Hz, 1H), 2.43 – 2.33 (m, 1H), 0.21 (s, 10H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 144.45, 141.28, 133.02, 127.27, 126.78, 120.91, 120.45, 42.97, 29.04, 1.18.



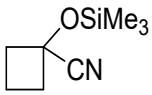
1-((trimethylsilyl)oxy)cyclohexane-1-carbonitrile(4k)[4]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.07 – 1.96 (m, 2H), 1.75 – 1.67 (m, 2H), 1.66 – 1.40 (m, 6H), 0.21 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 121.84, 67.82, 39.32, 24.48, 22.60, 1.35.



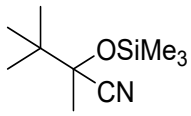
2-cyclohexyl-2-((trimethylsilyl)oxy)propanenitrile(4l)[4]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.24 (s, 1H), 2.02 (s, 3H), 1.73 (d, J = 26.3 Hz, 5H), 1.34 – 0.96 (m, 6H), 0.29 (s, 10H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 213.84, 128.85, 53.22, 30.29, 29.68, 27.74, -0.00.



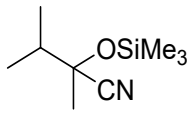
2-methyl-1-((trimethylsilyl)oxy)cyclohexane-1-carbonitrile(4m)[10]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.18 – 2.11 (m, 1H), 1.83 – 1.50 (m, 9H), 1.05 (d, J = 6.6 Hz, 3H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 118.71, 74.58, 41.72, 39.41, 38.29, 30.09, 23.46, 22.31, 18.75, 14.97, -0.00.



1-((trimethylsilyl)oxy)cyclobutane-1-carbonitrile(4n): ^{1}H NMR ($CDCl_3$, 400 MHz): δ 2.62 – 2.51 (m, 2H), 2.37 – 2.24 (m, 2H), 1.92 – 1.78 (m, 2H), 0.20 (d, J = 2.5 Hz, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 122.31, 66.96, 37.96, 12.22, 0.54.

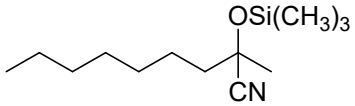


2,3,3-trimethyl-2-((trimethylsilyl)oxy)butanenitrile(4o)[11]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.47 (s, 3H), 0.99 (s, 9H), 0.20 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 121.77, 76.11, 38.77, 24.51, 23.71, 1.08.



2,3-dimethyl-2-((trimethylsilyl)oxy)butanenitrile(4p)[3]: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.86 (p,

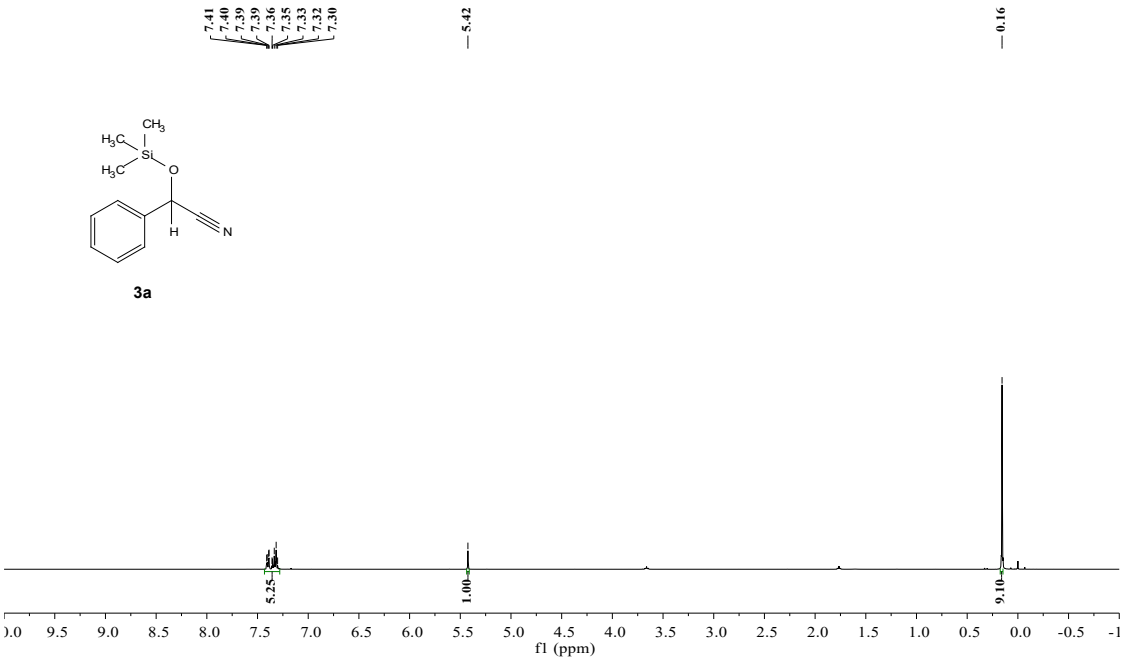
J = 6.8 Hz, 1H), 1.53 (s, 3H), 1.03 (dd, *J* = 6.7, 4.3 Hz, 6H), 0.24 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 121.59, 73.48, 39.10, 17.16, 16.95, 1.20.



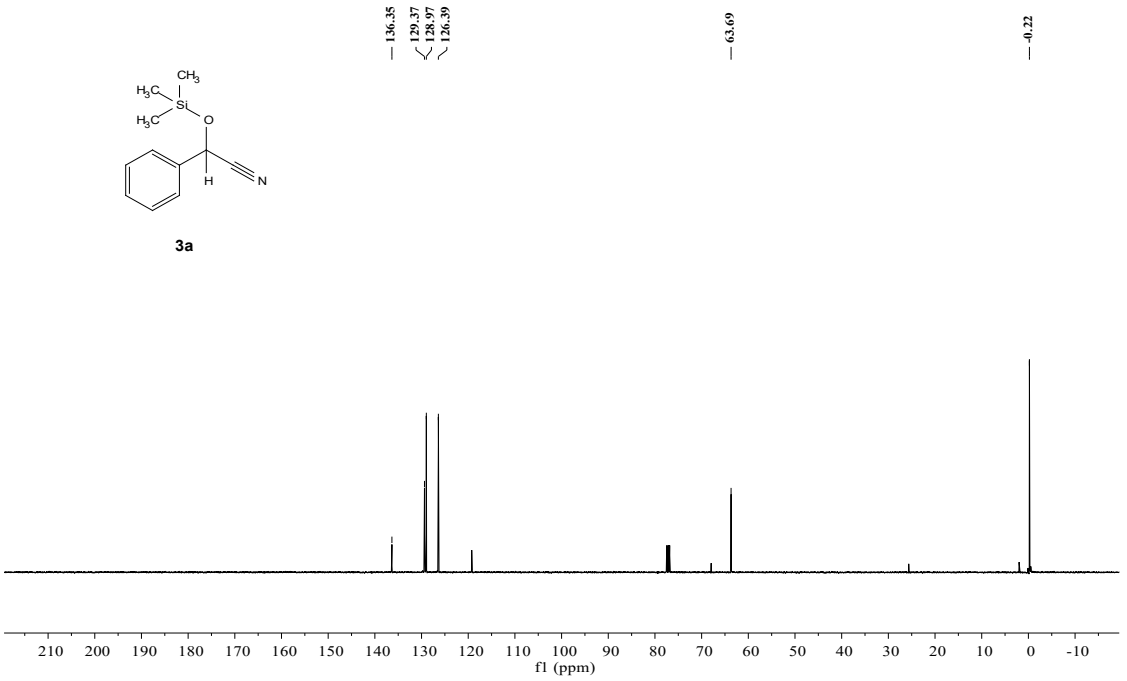
2-methyl-2-((trimethylsilyl)oxy)nonanenitrile(4q): ^{1}H NMR ($CDCl_3$, 400 MHz) δ 6.84 (d, J = 1.3 Hz, 3H), 1.80 – 1.69 (m, 2H), 1.60 (s, 4H), 1.41 – 1.28 (m, 9H), 0.94 (t, J = 6.6 Hz, 3H), 0.28 (s, 9H). ^{13}C NMR ($CDCl_3$, 101 MHz) δ 120.90, 66.64, 42.12, 30.47, 28.03, 27.84, 27.60, 23.02, 21.35, 19.89, 12.78, 0.00.

Copies of NMR Spectra of Cyanohydrin Products

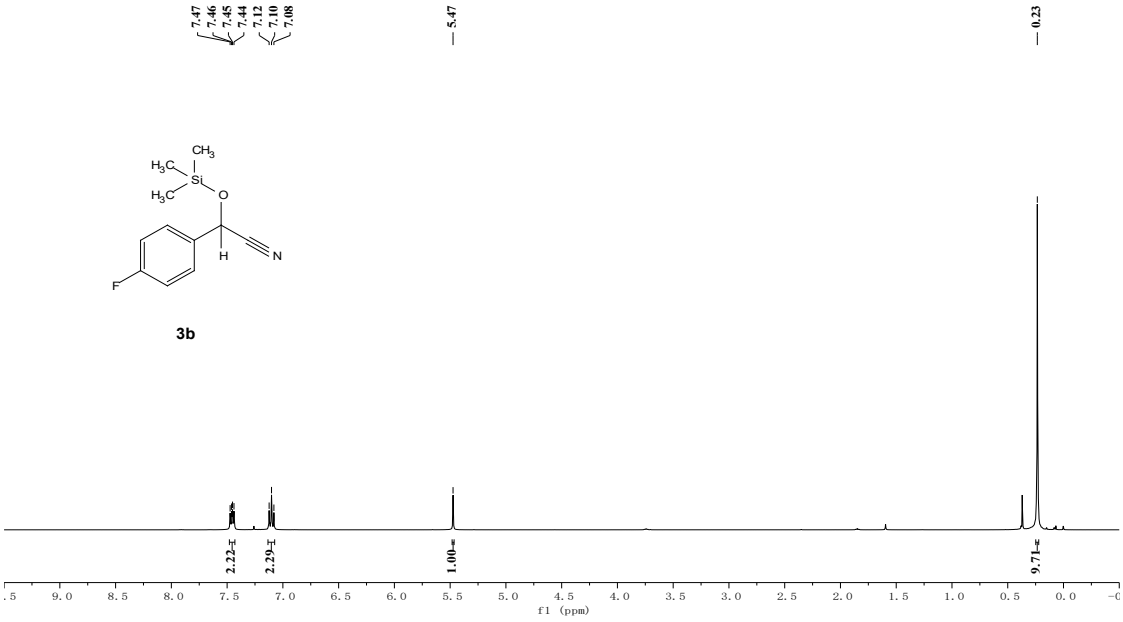
^{1}H NMR spectrum of **3a** in $CDCl_3$ at 400 MHz



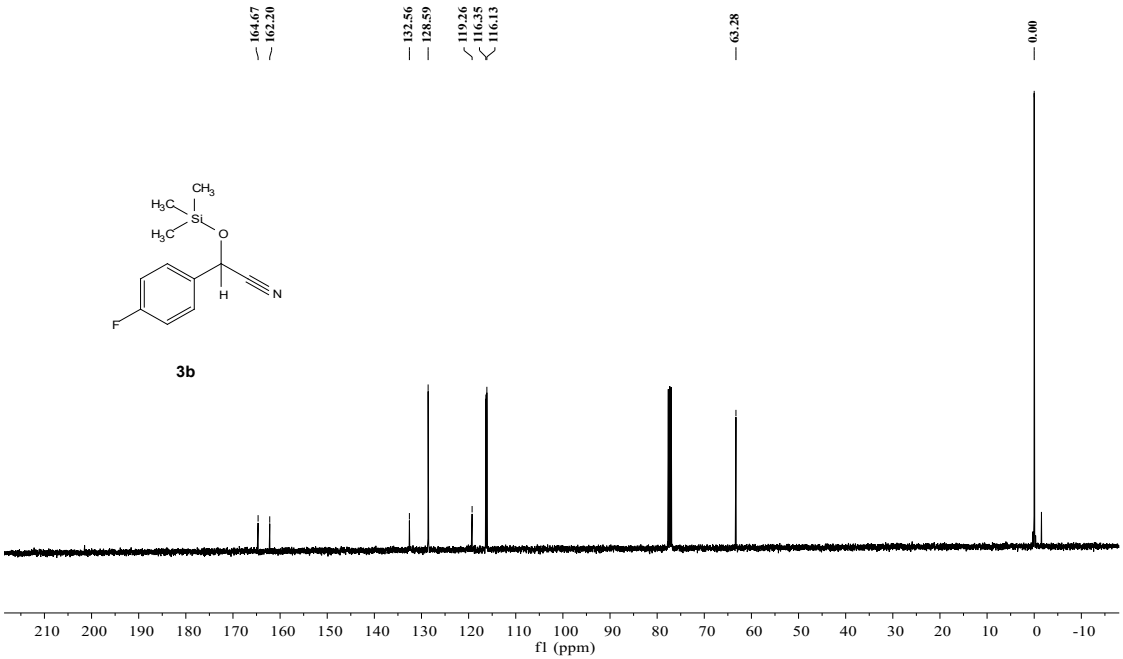
^{13}C NMR spectrum of **3a** in $CDCl_3$ at 101 MHz



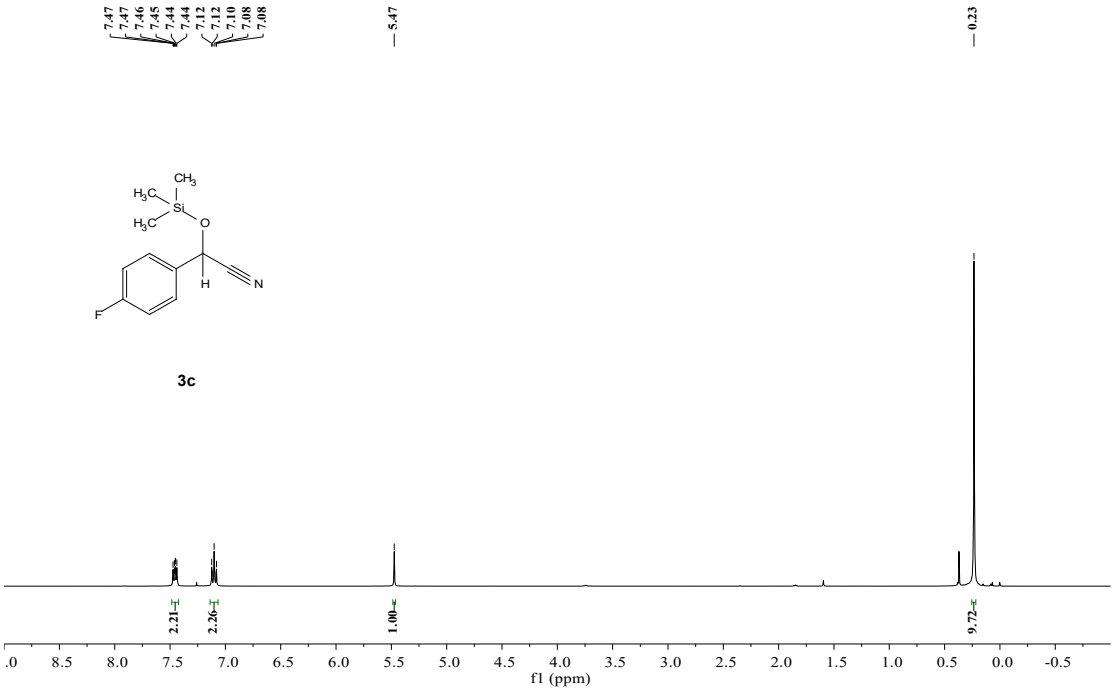
^{1}H NMR spectrum of **3b** in $CDCl_3$ at 400 MHz



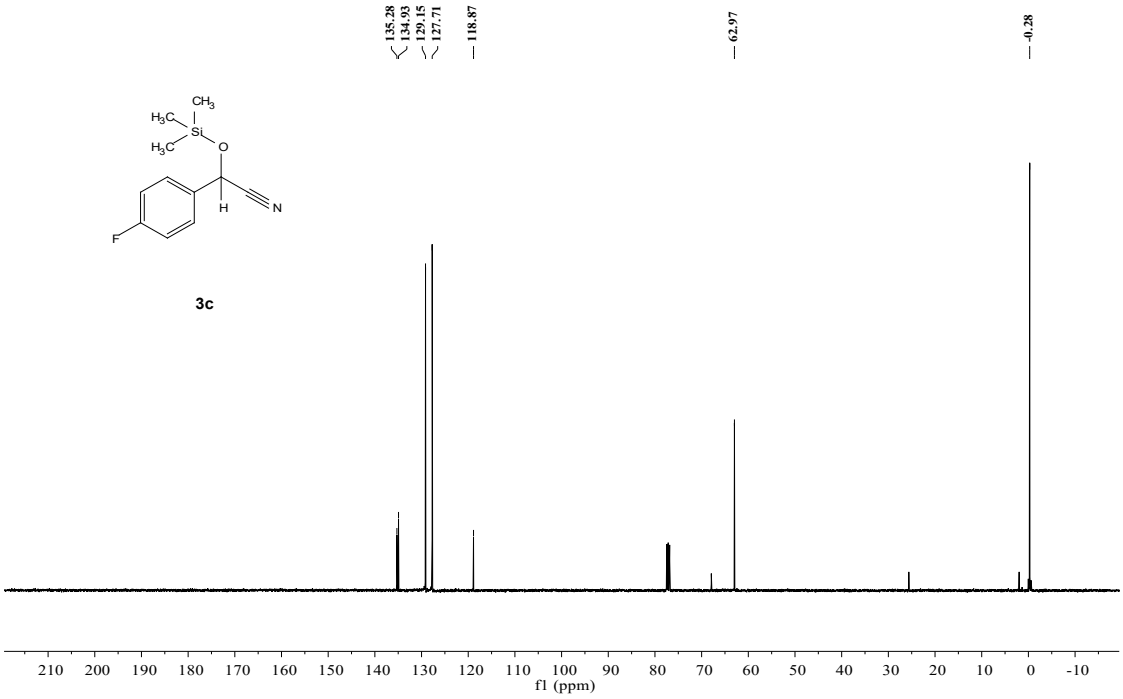
^{13}C NMR spectrum of **3b** in $CDCl_3$ at 101 MHz



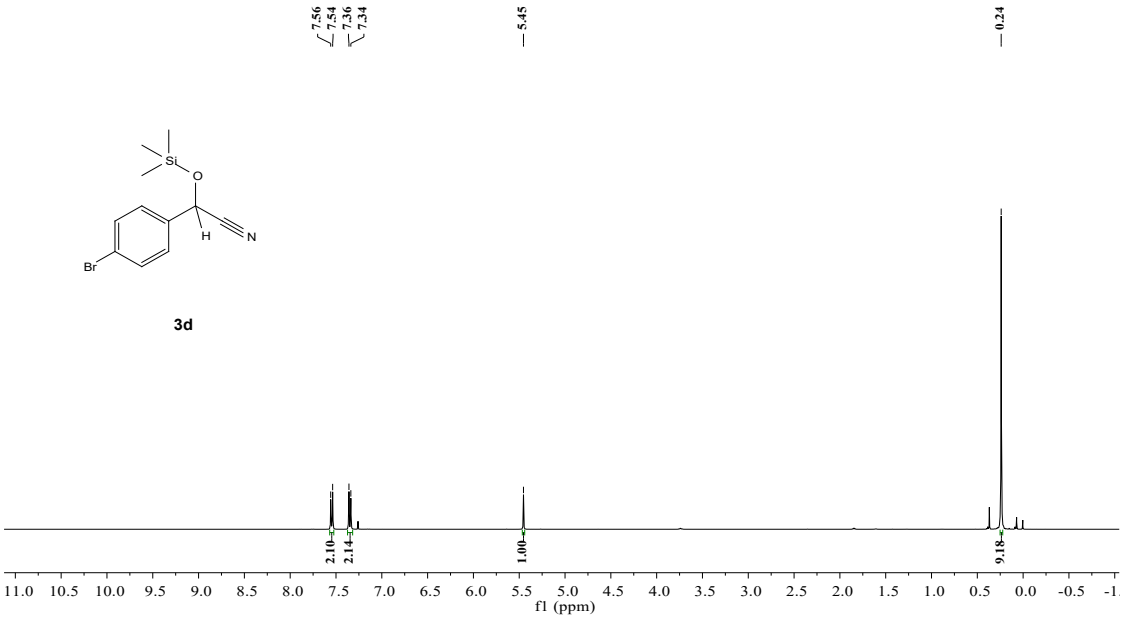
^{1}H NMR spectrum of **3c** in $CDCl_3$ at 400 MHz



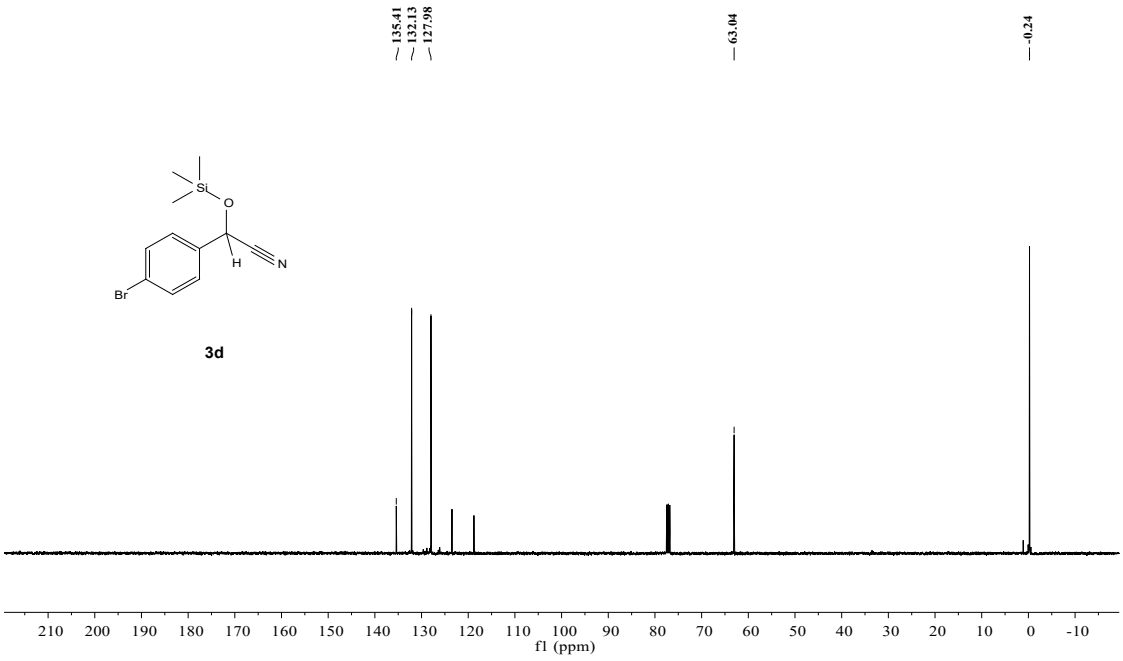
^{13}C NMR spectrum of **3c** in $CDCl_3$ at 101 MHz



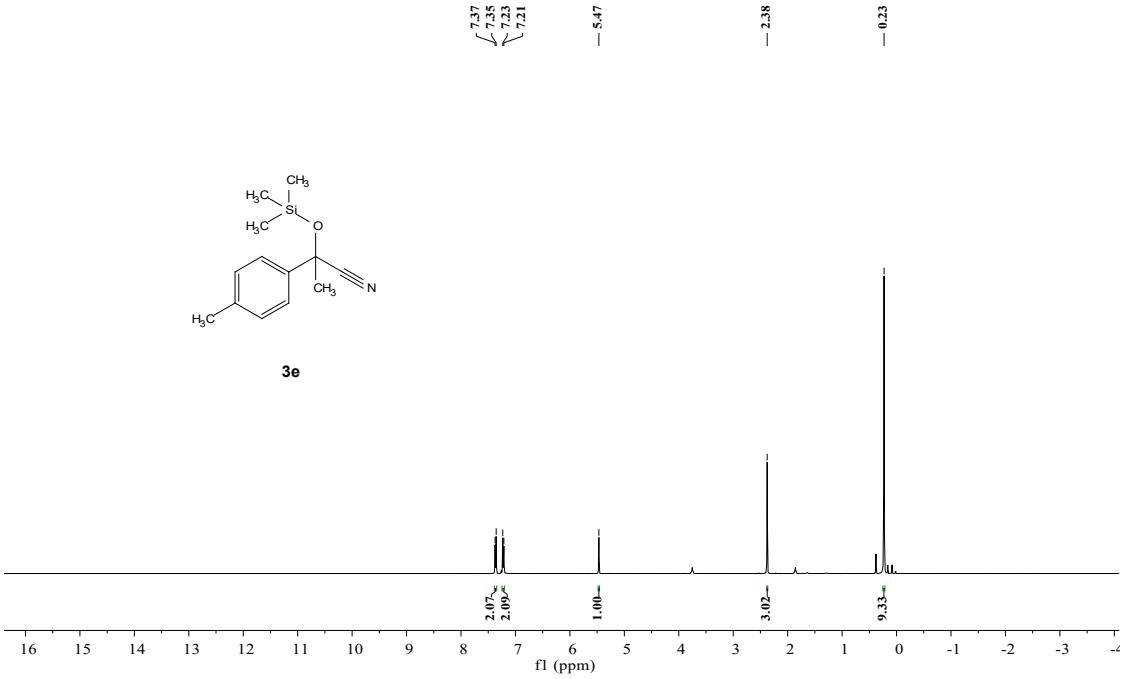
^{1}H NMR spectrum of **3d** in $CDCl_3$ at 400 MHz



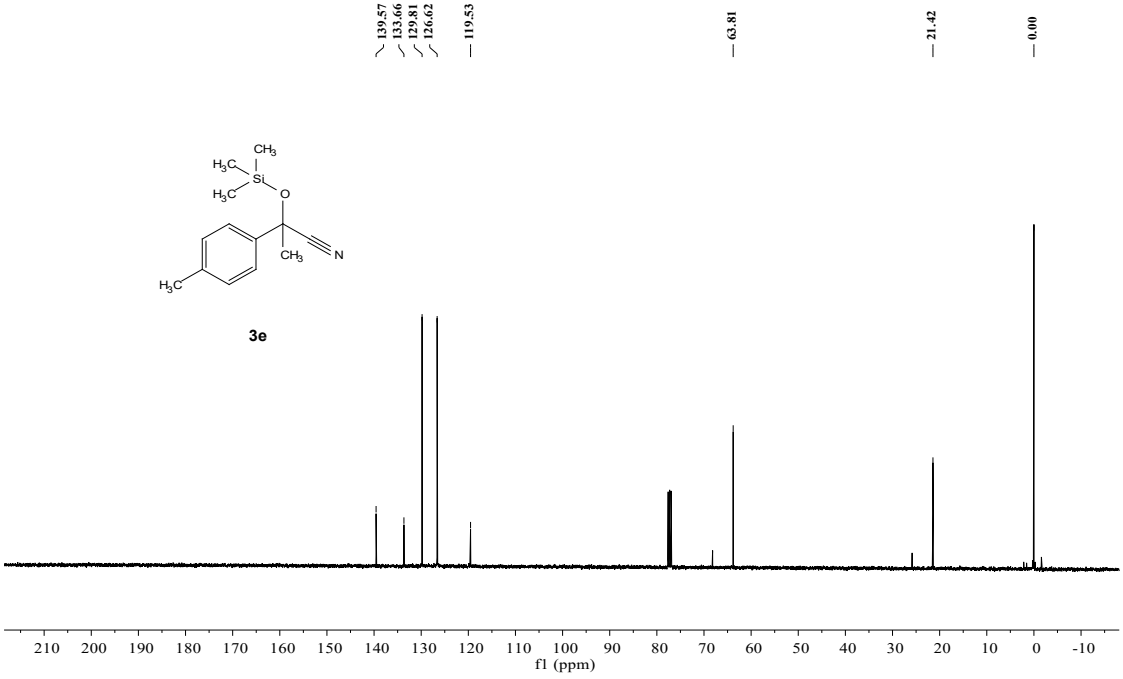
^{13}C NMR spectrum of **3d** in $CDCl_3$ at 101 MHz



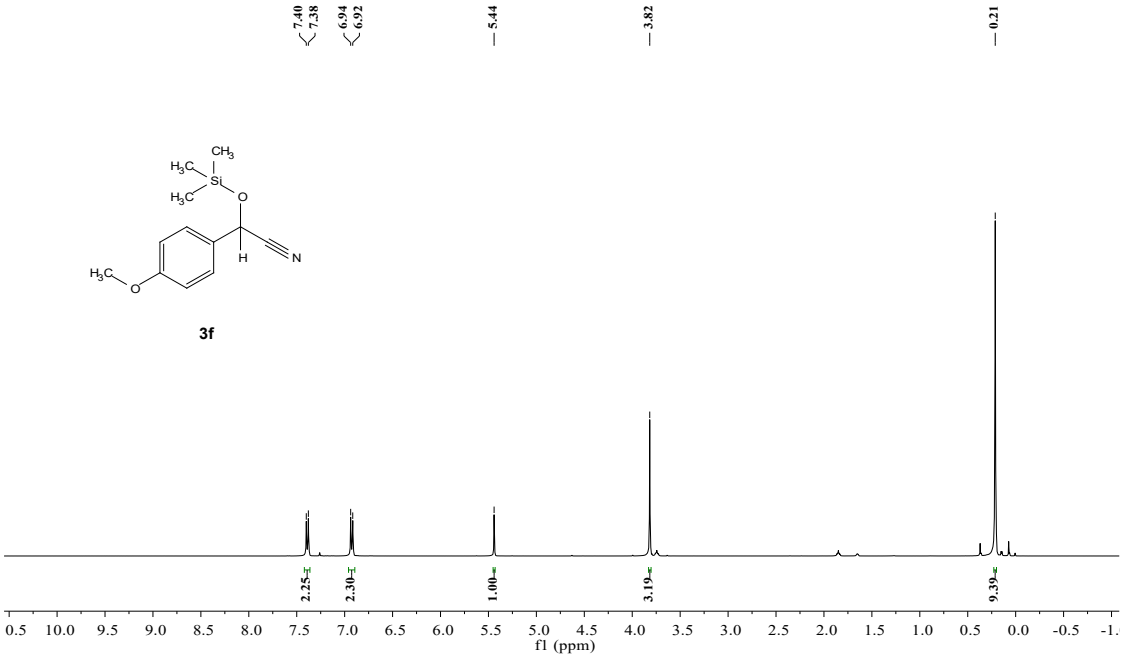
^{1}H NMR spectrum of **3e** in $CDCl_3$ at 400 MHz



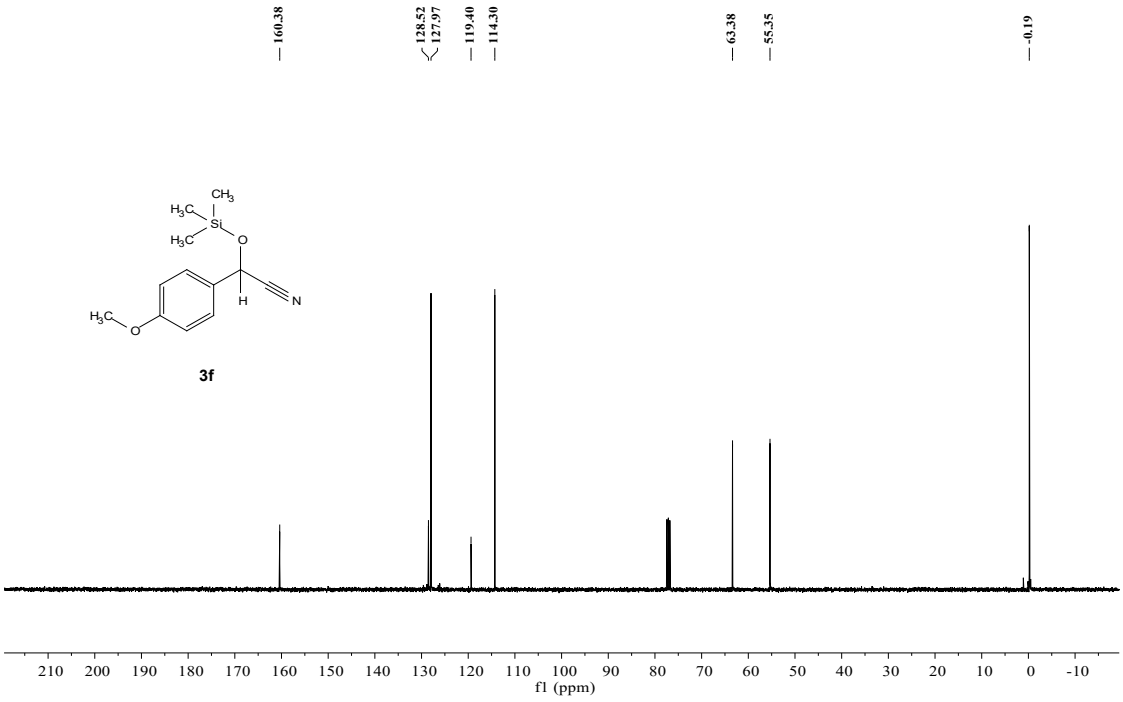
^{13}C NMR spectrum of **3e** in $CDCl_3$ at 101 MHz



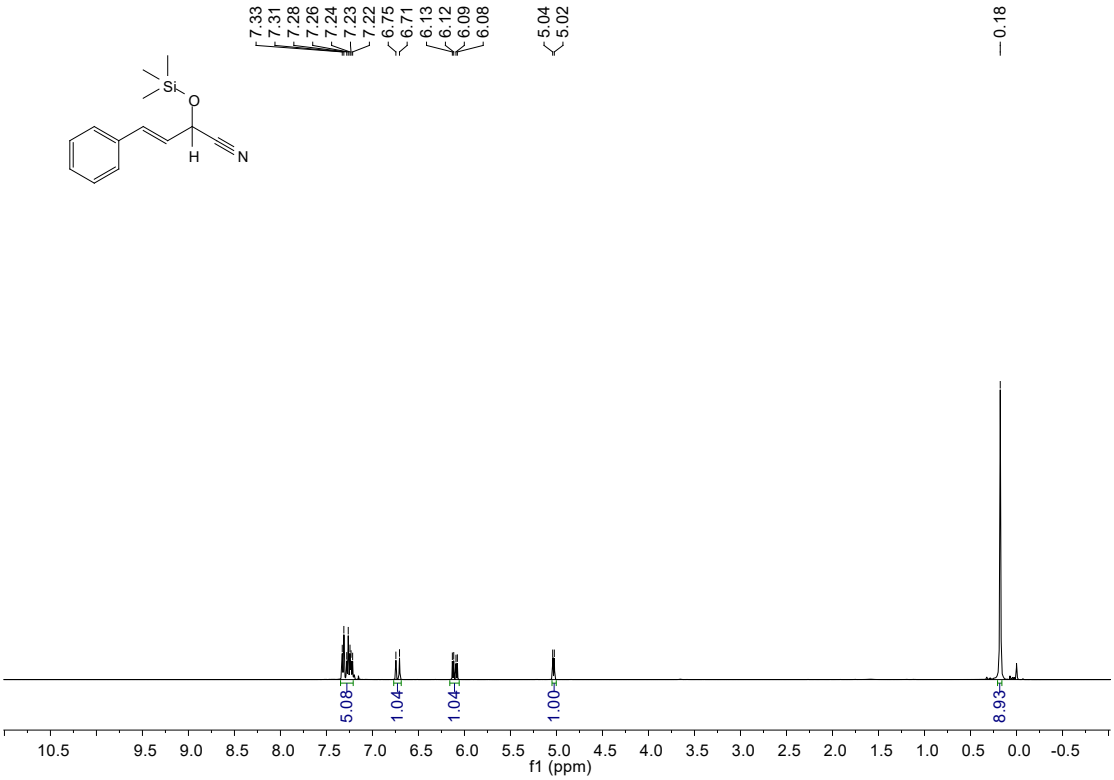
^{1}H NMR spectrum of **3f** in $CDCl_3$ at 400 MHz



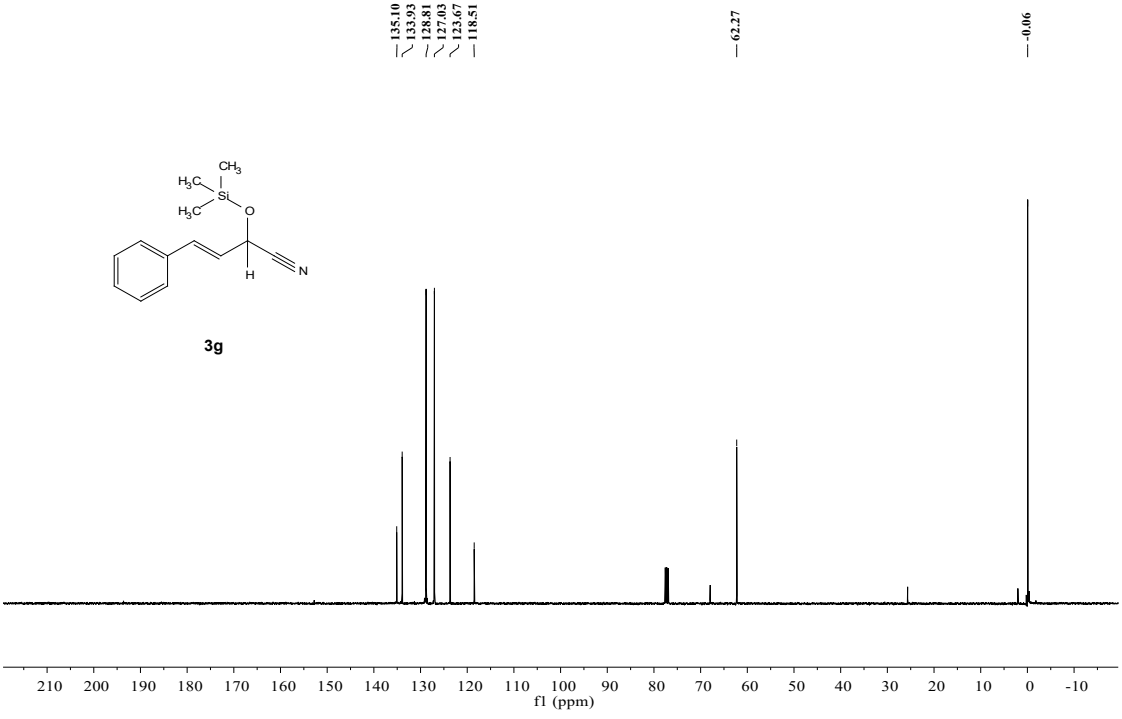
^{13}C NMR spectrum of **3f** in $CDCl_3$ at 101 MHz



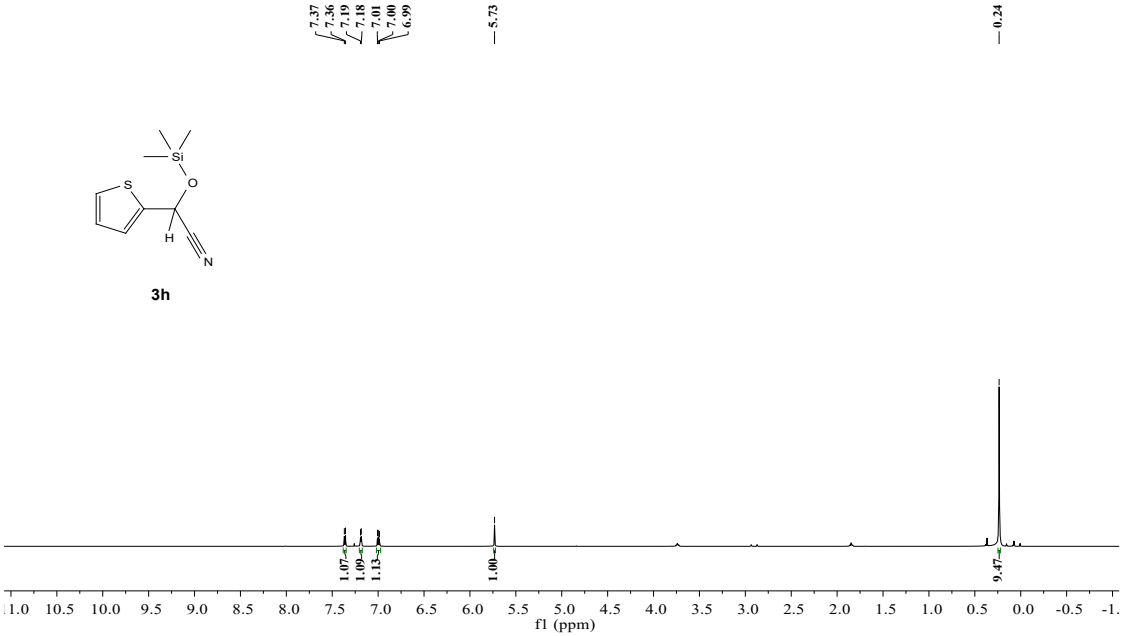
^{1}H NMR spectrum of **3g** in $CDCl_3$ at 400 MHz



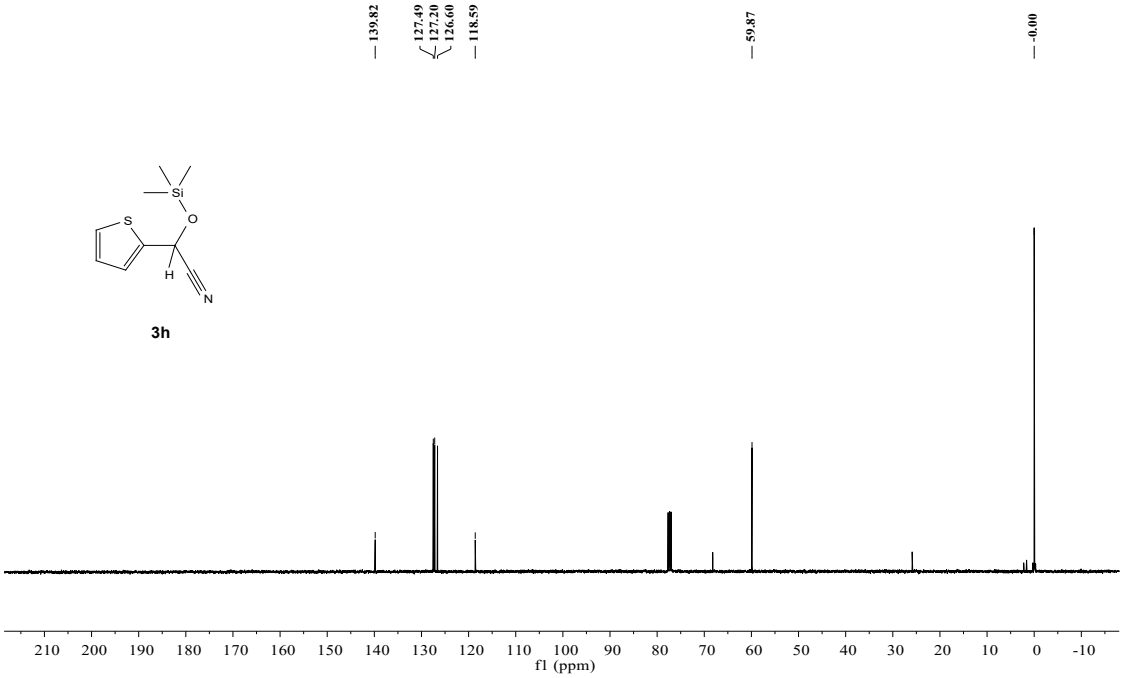
^{13}C NMR spectrum of **3g** in $CDCl_3$ at 101 MHz



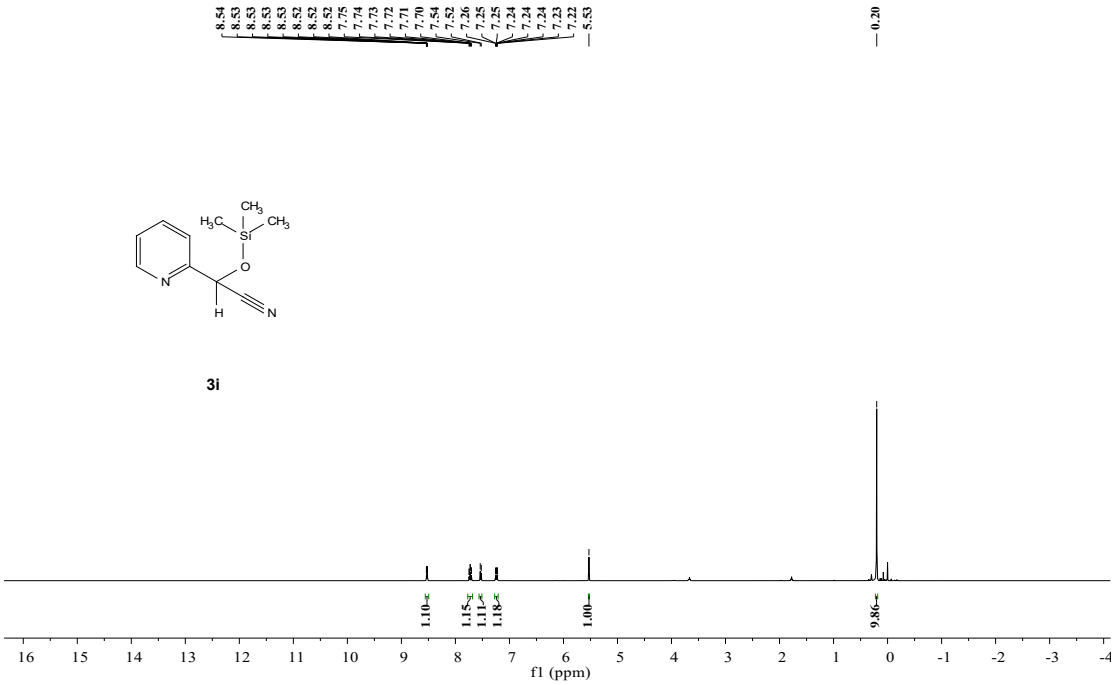
^{1}H NMR spectrum of **3h** in $CDCl_3$ at 400 MHz



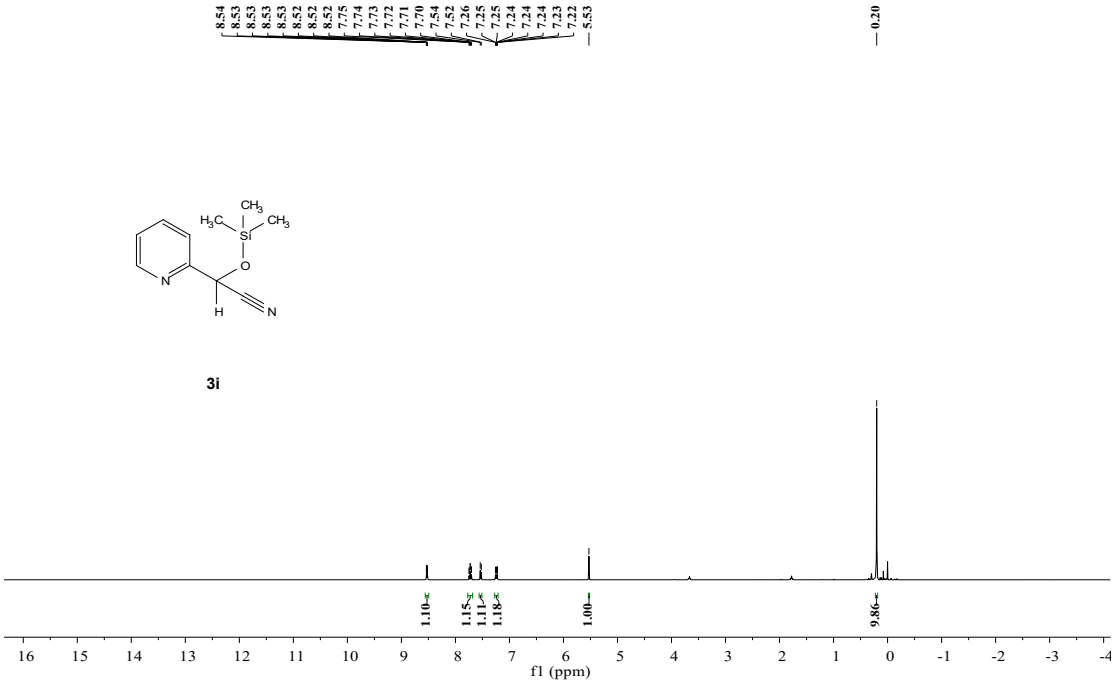
^{13}C NMR spectrum of **3h** in $CDCl_3$ at 101 MHz



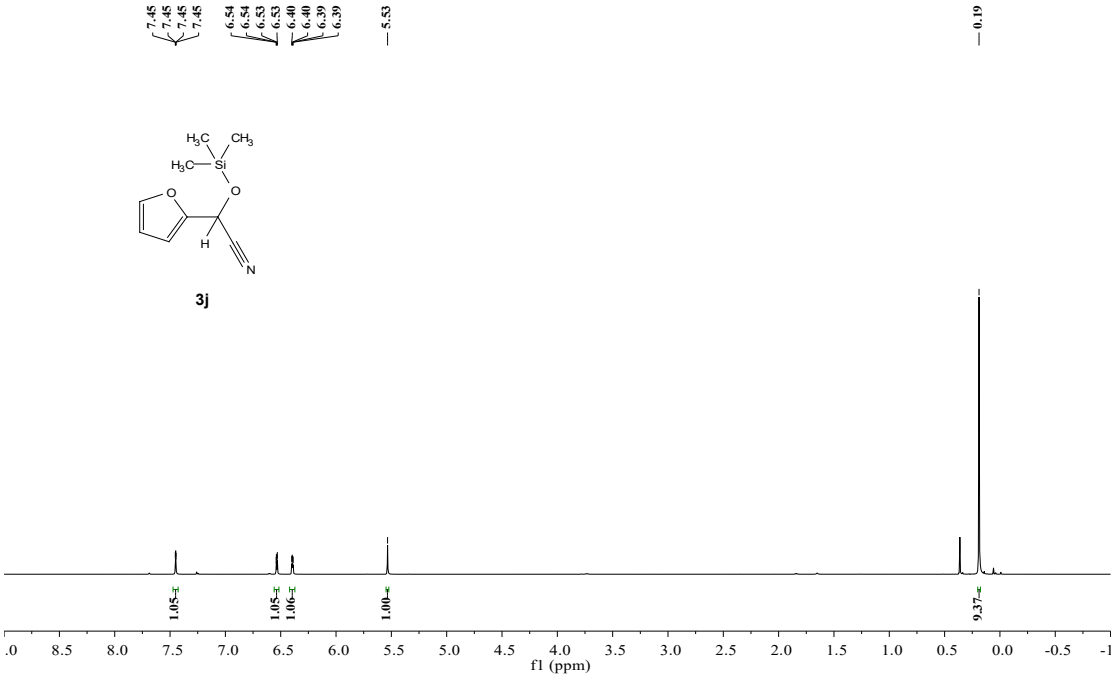
^{1}H NMR spectrum of **3i** in $CDCl_3$ at 400 MHz



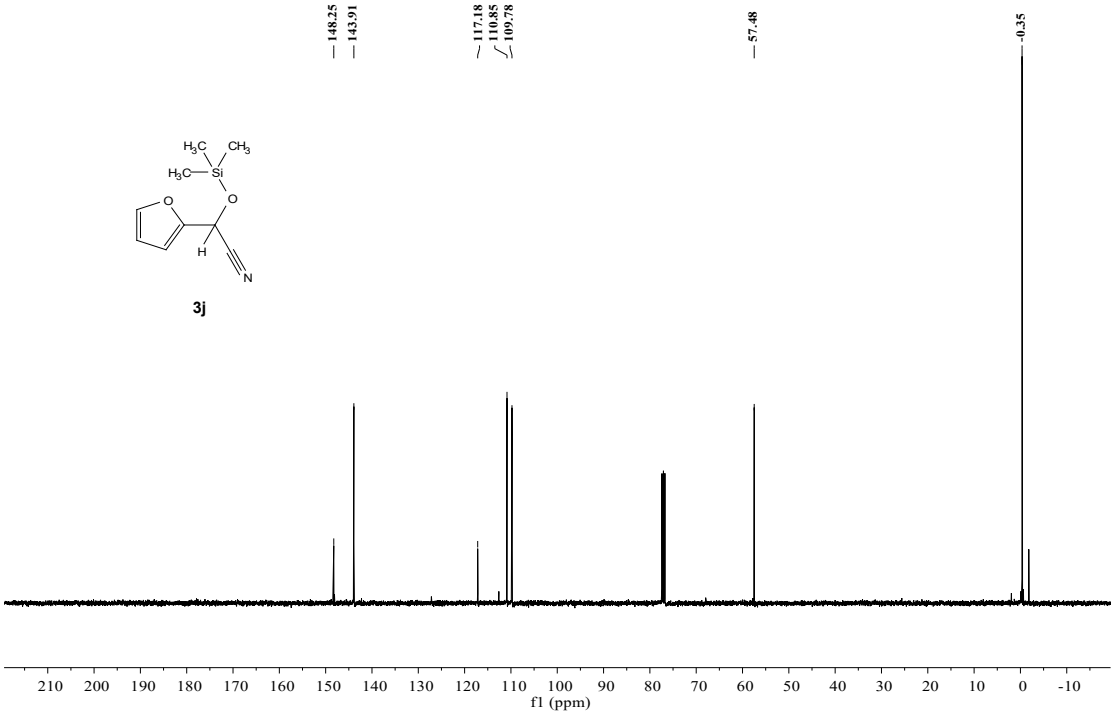
^{13}C NMR spectrum of **3i** in $CDCl_3$ at 101 MHz



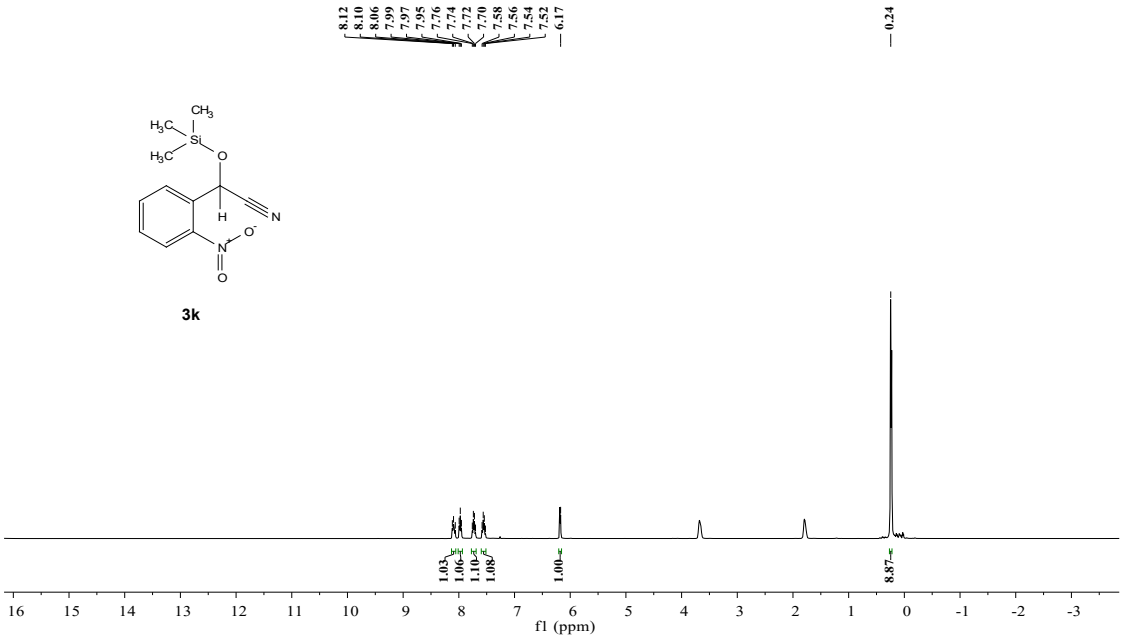
^{1}H NMR spectrum of **3j** in $CDCl_3$ at 400 MHz



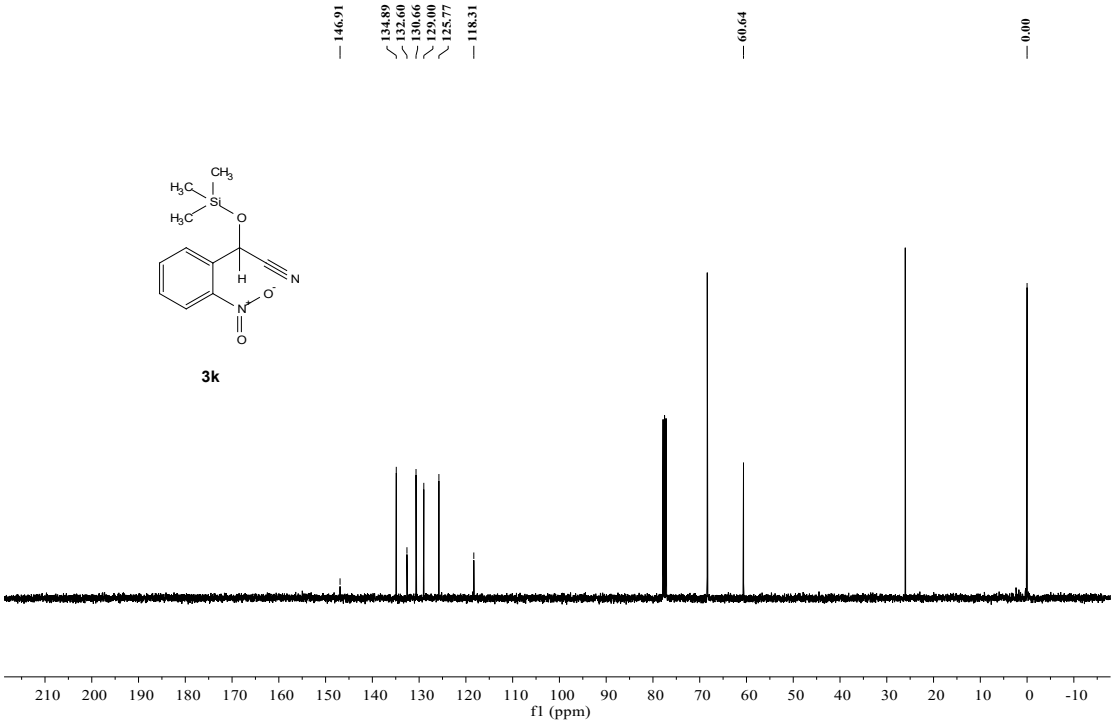
^{13}C NMR spectrum of **3j** in $CDCl_3$ at 101 MHz



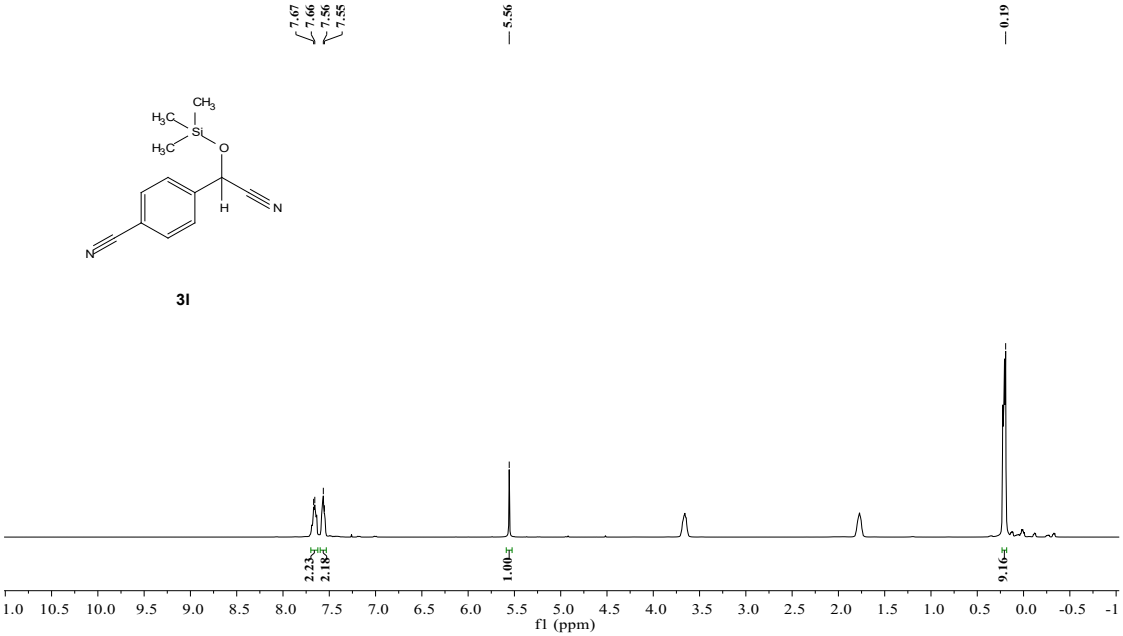
^{1}H NMR spectrum of **3k** in $CDCl_3$ at 400 MHz



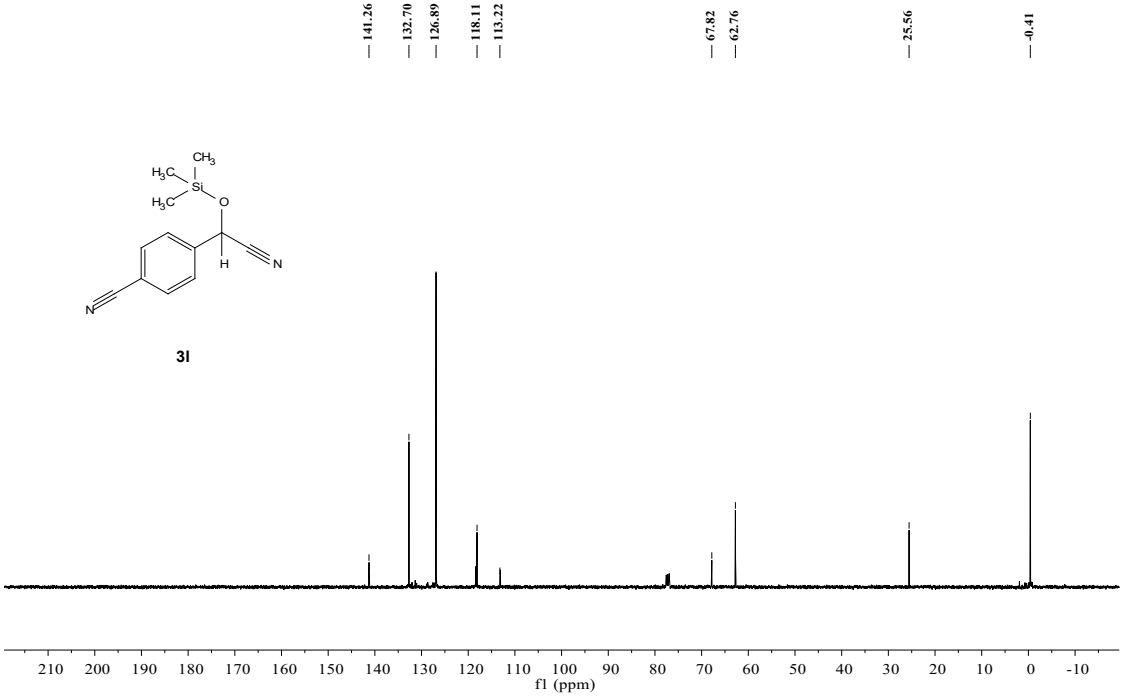
^{13}C NMR spectrum of **3k** in $CDCl_3$ at 101 MHz



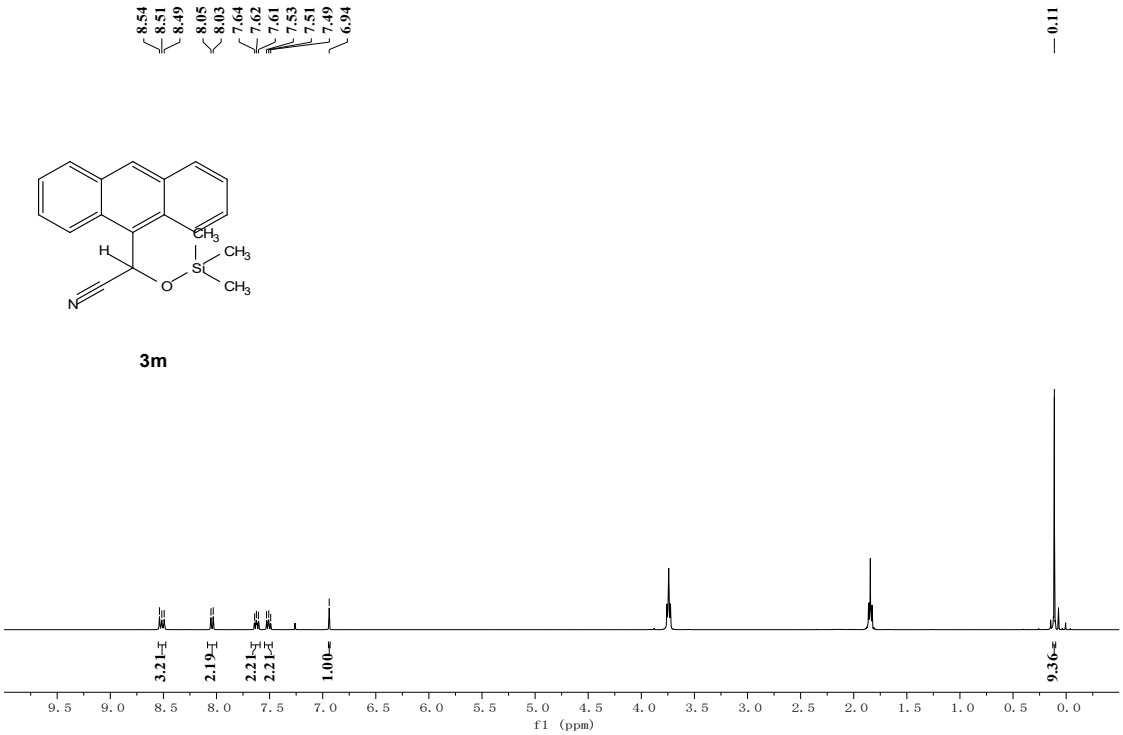
^{1}H NMR spectrum of **3l** in $CDCl_3$ at 400 MHz



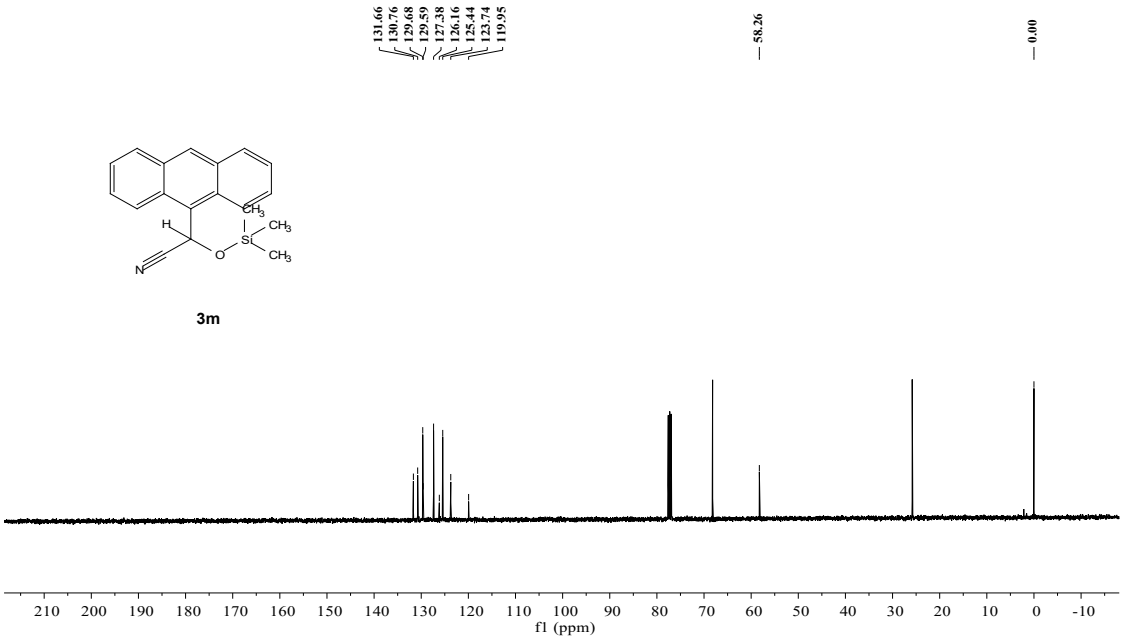
^{13}C NMR spectrum of **3l** in $CDCl_3$ at 101 MHz



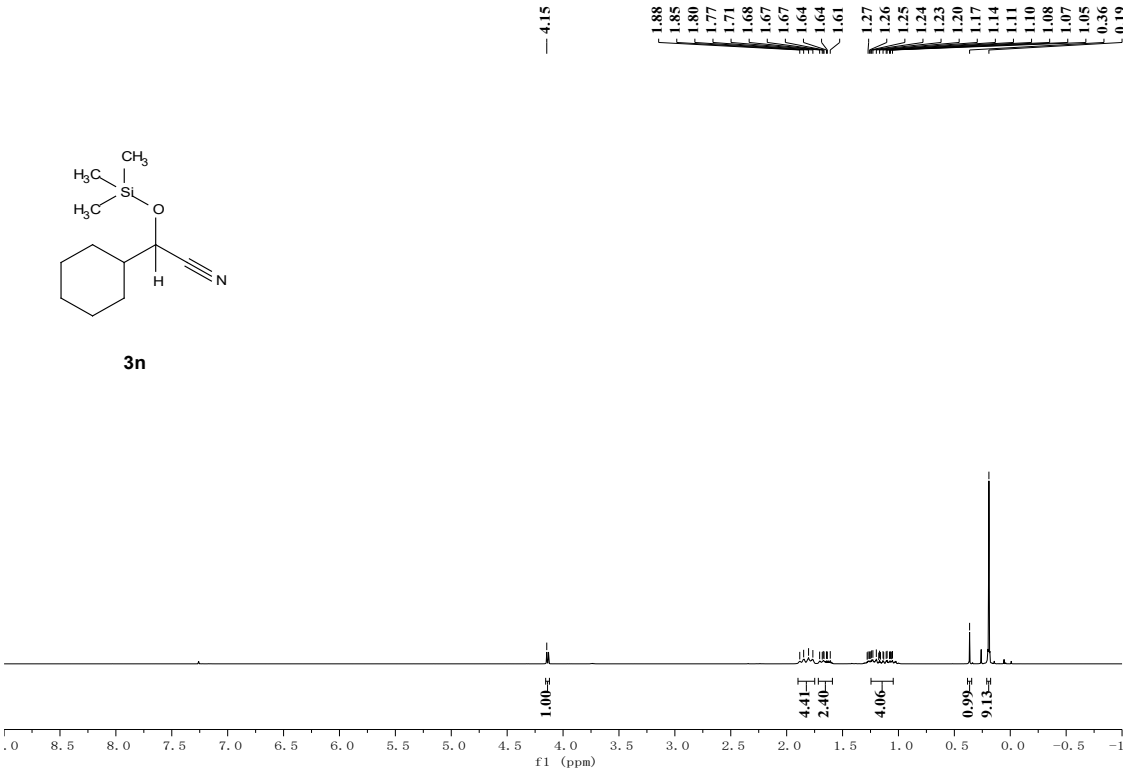
^{1}H NMR spectrum of **3m** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **3m** in $CDCl_3$ at 101 MHz

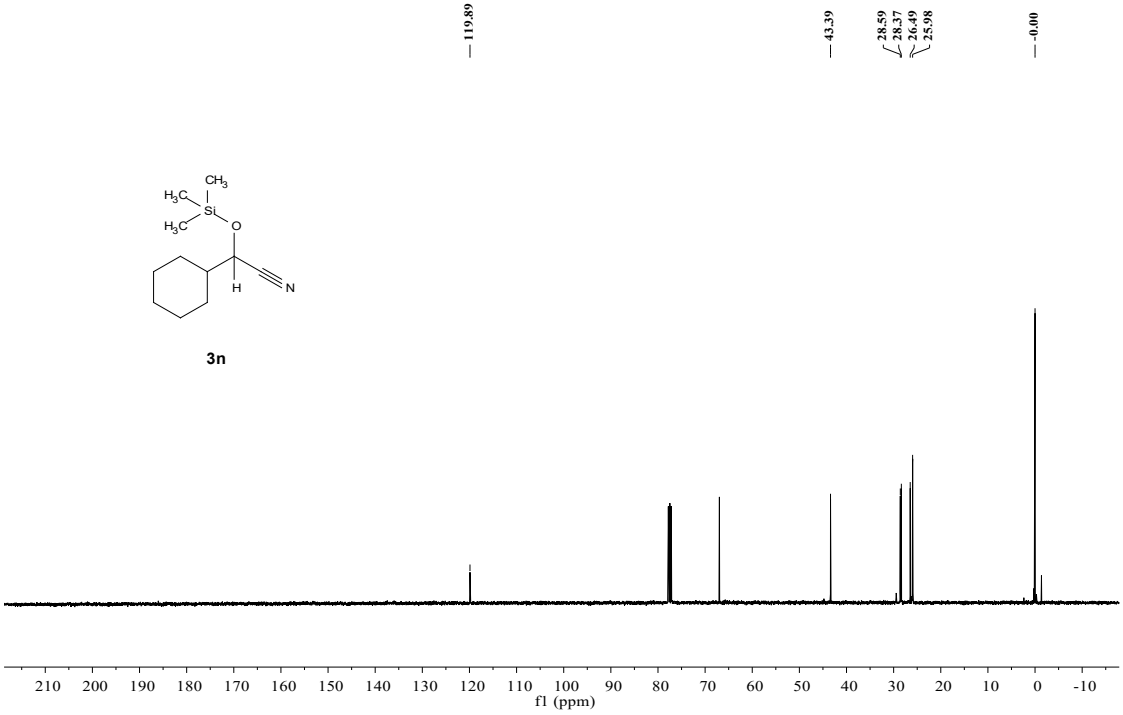


^{1}H NMR spectrum of **3n** in $CDCl_3$ at 400 MHz



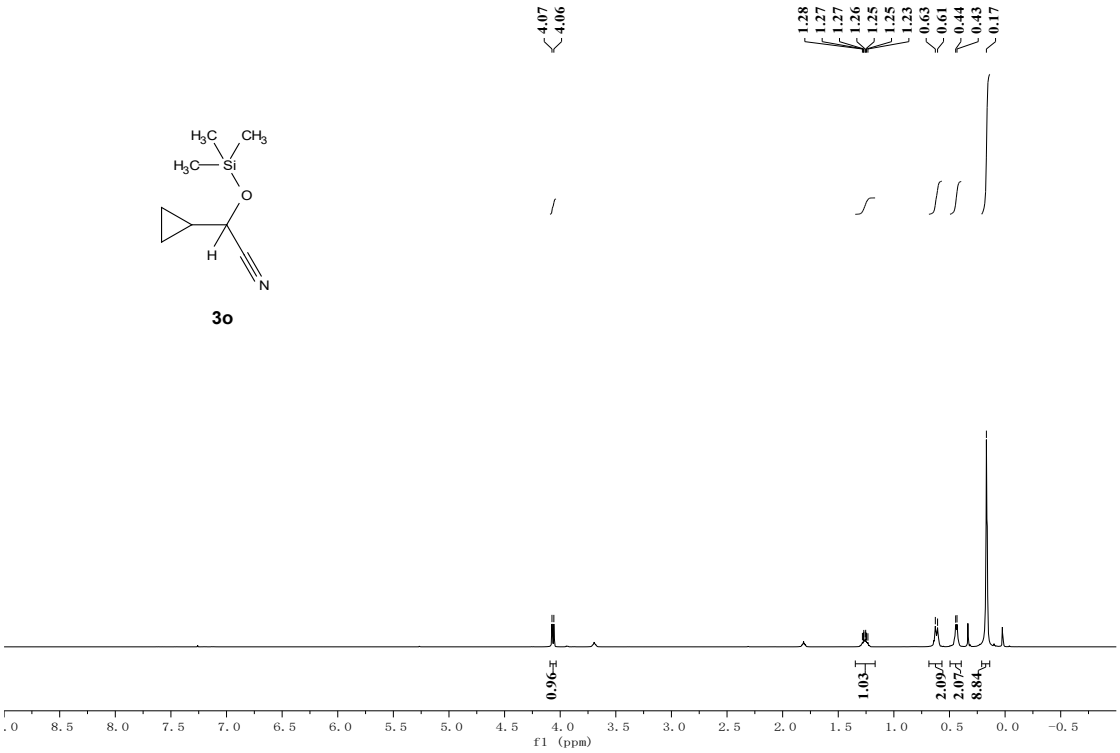
3n

^{13}C NMR spectrum of **3n** in $CDCl_3$ at 101 MHz

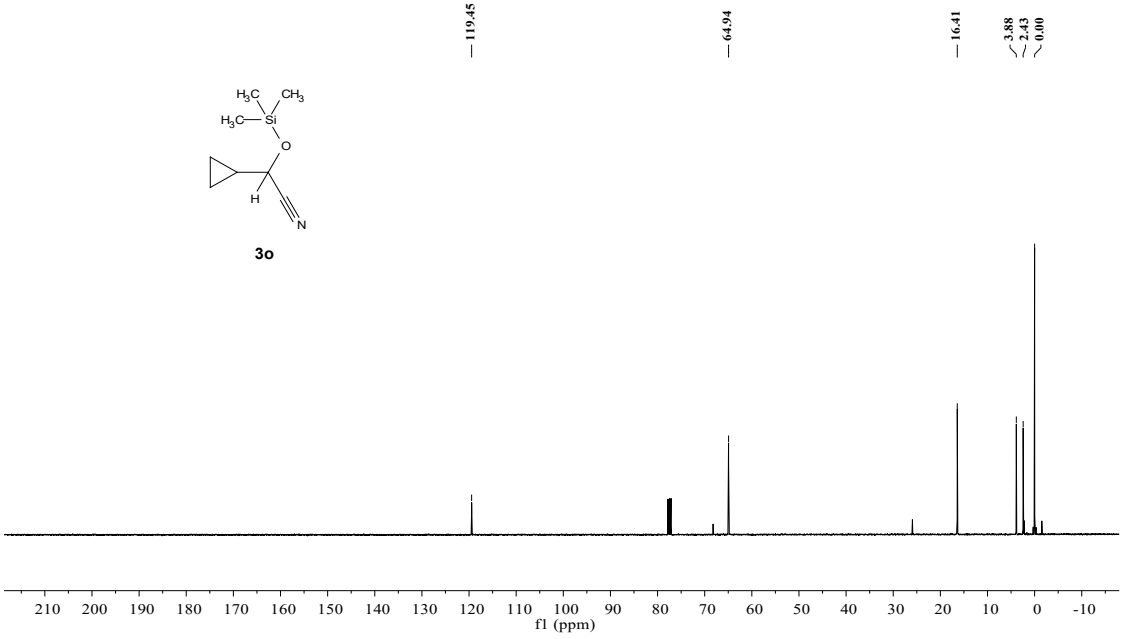


3n

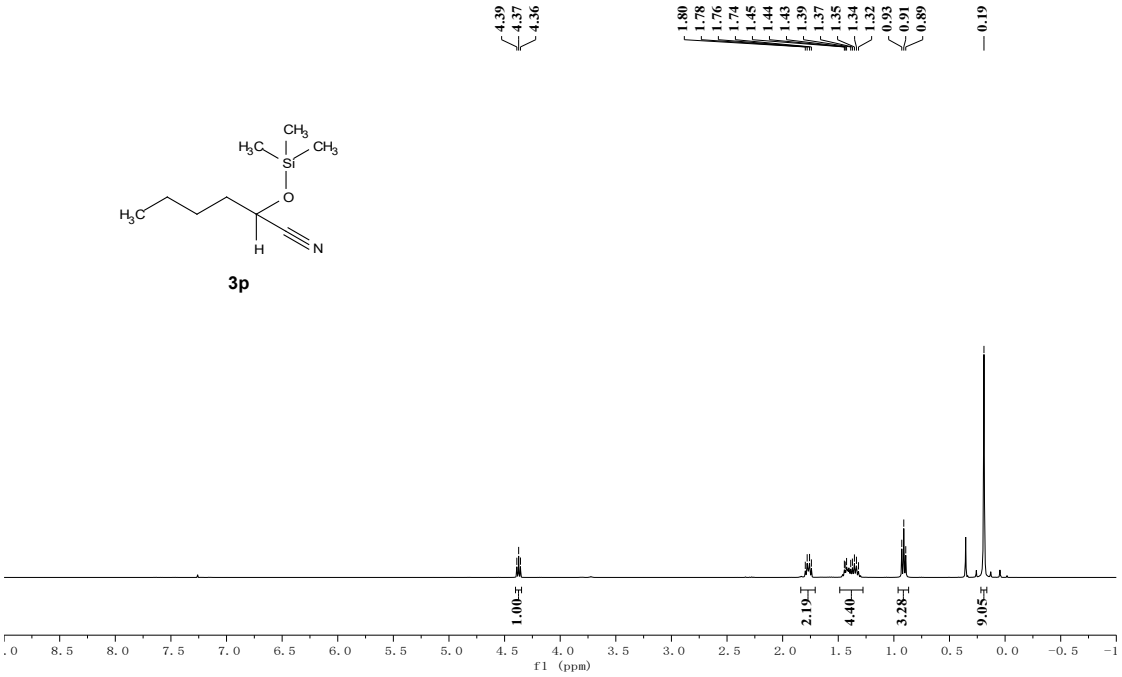
^{1}H NMR spectrum of **3o** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **3o** in $CDCl_3$ at 101 MHz

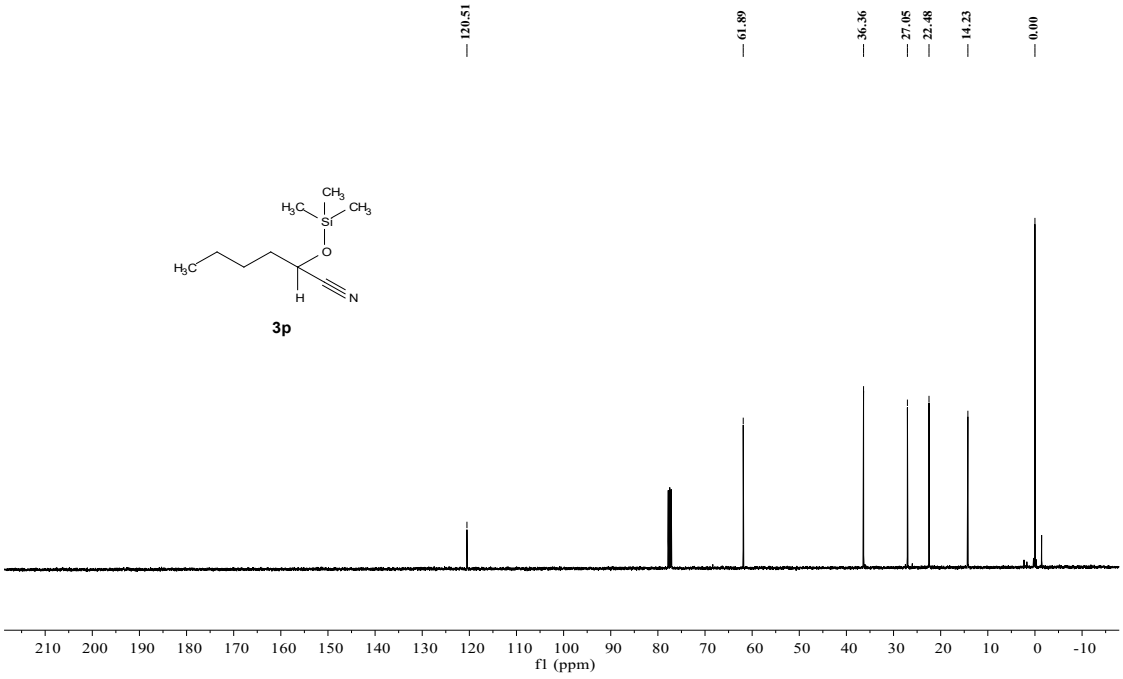


^{1}H NMR spectrum of **3p** in $CDCl_3$ at 400 MHz



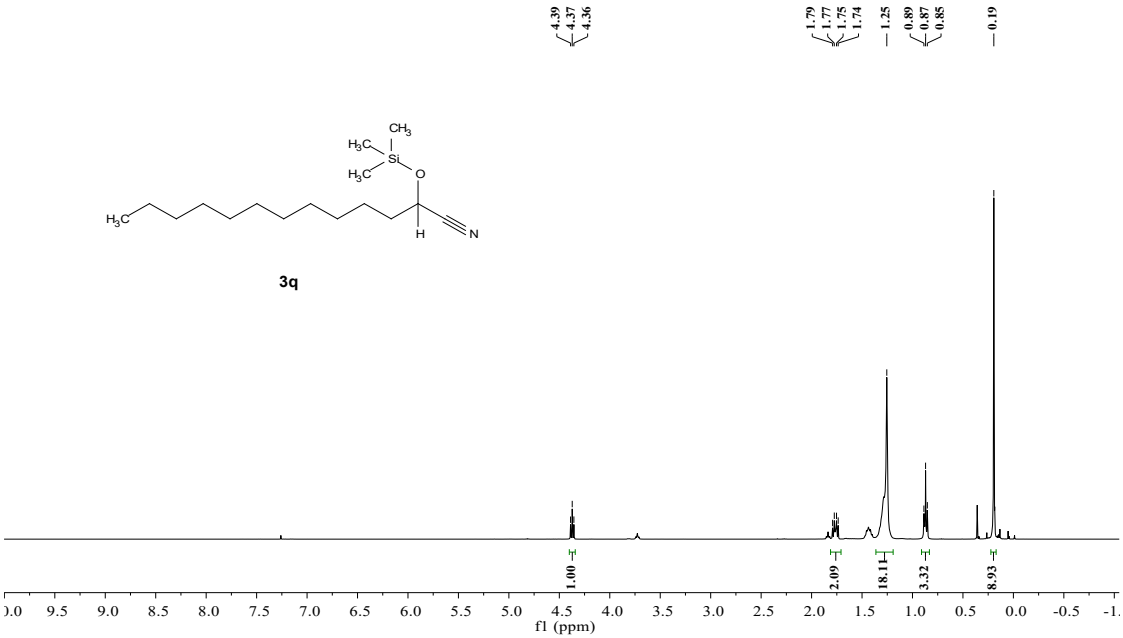
3p

^{13}C NMR spectrum of **3p** in $CDCl_3$ at 101 MHz

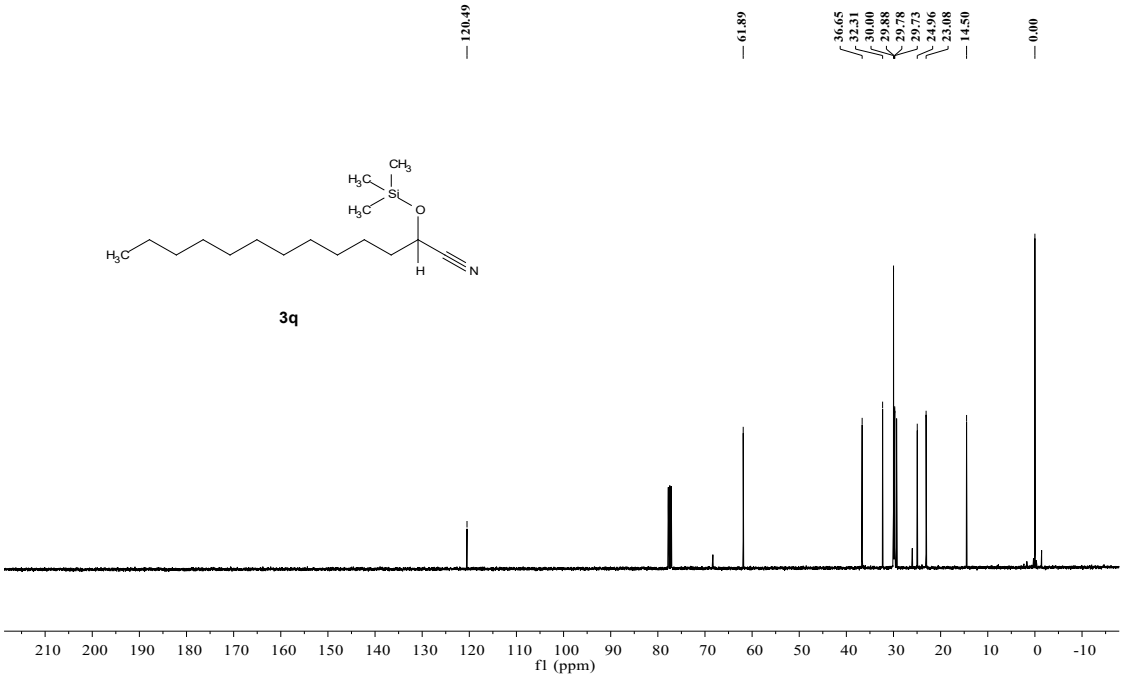


3p

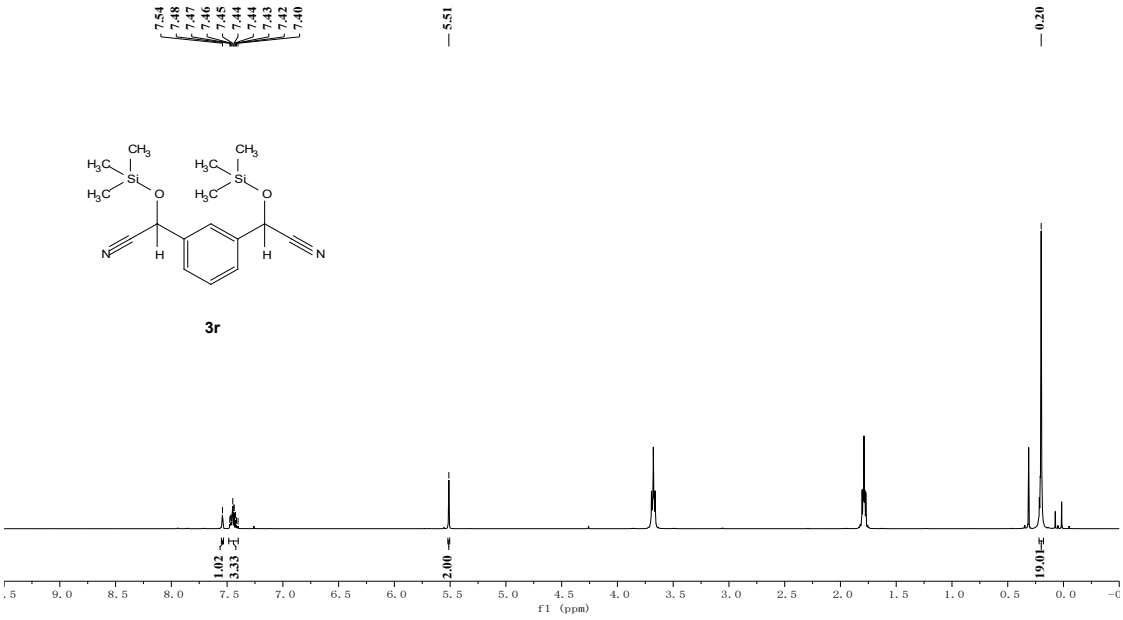
^{1}H NMR spectrum of **3q** in $CDCl_3$ at 400 MHz



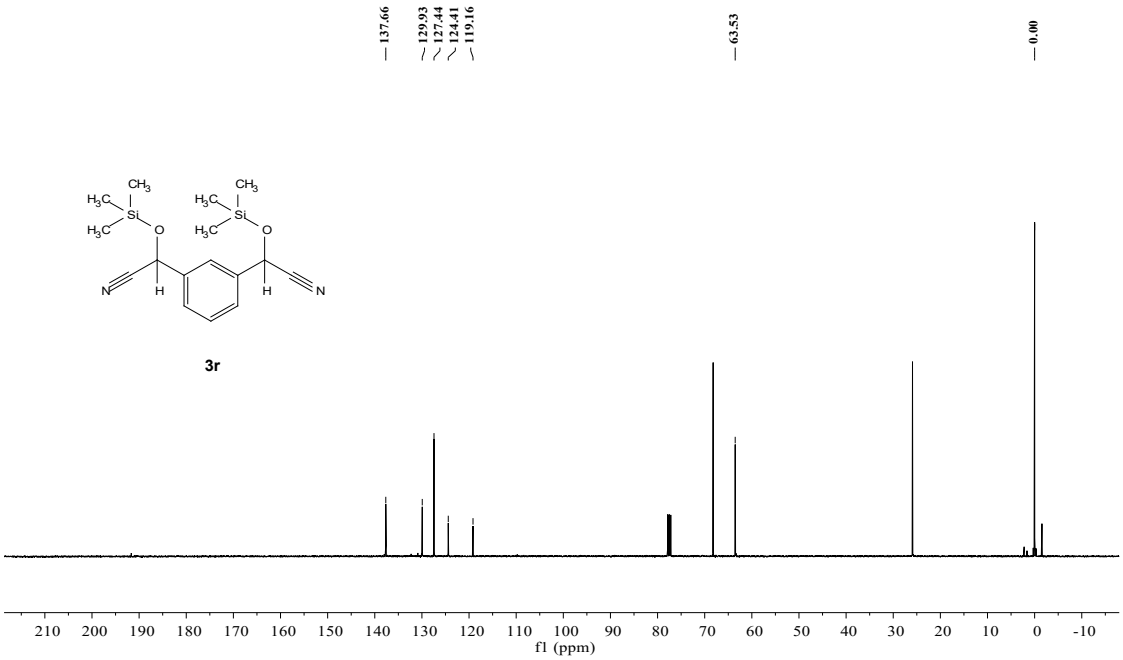
^{13}C NMR spectrum of **3q** in $CDCl_3$ at 101 MHz



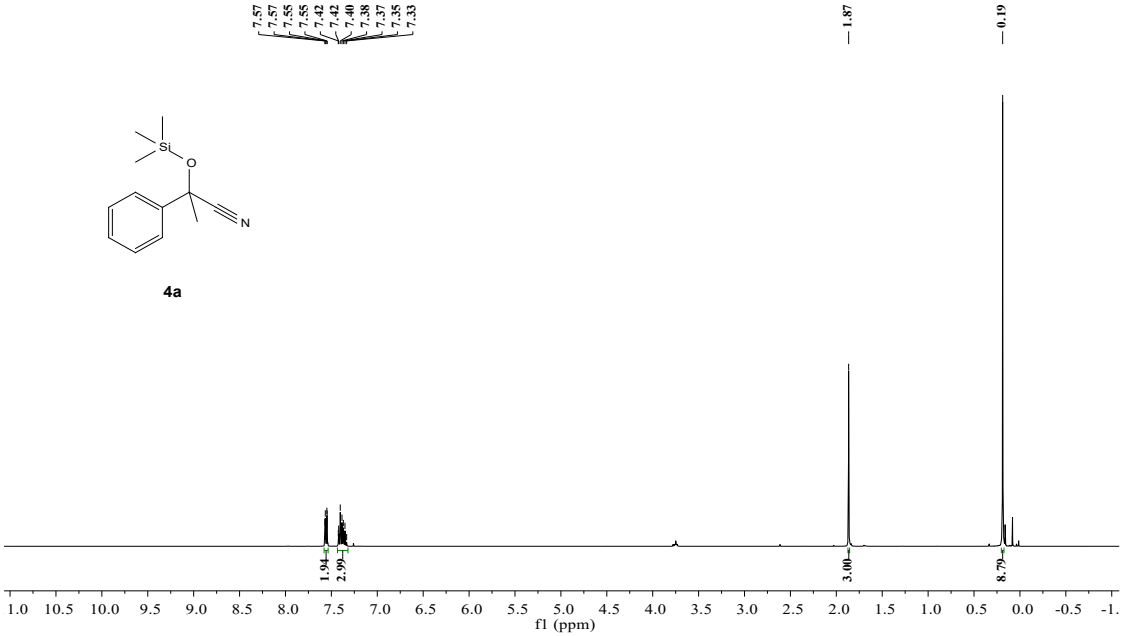
^{1}H NMR spectrum of **3r** in $CDCl_3$ at 400 MHz



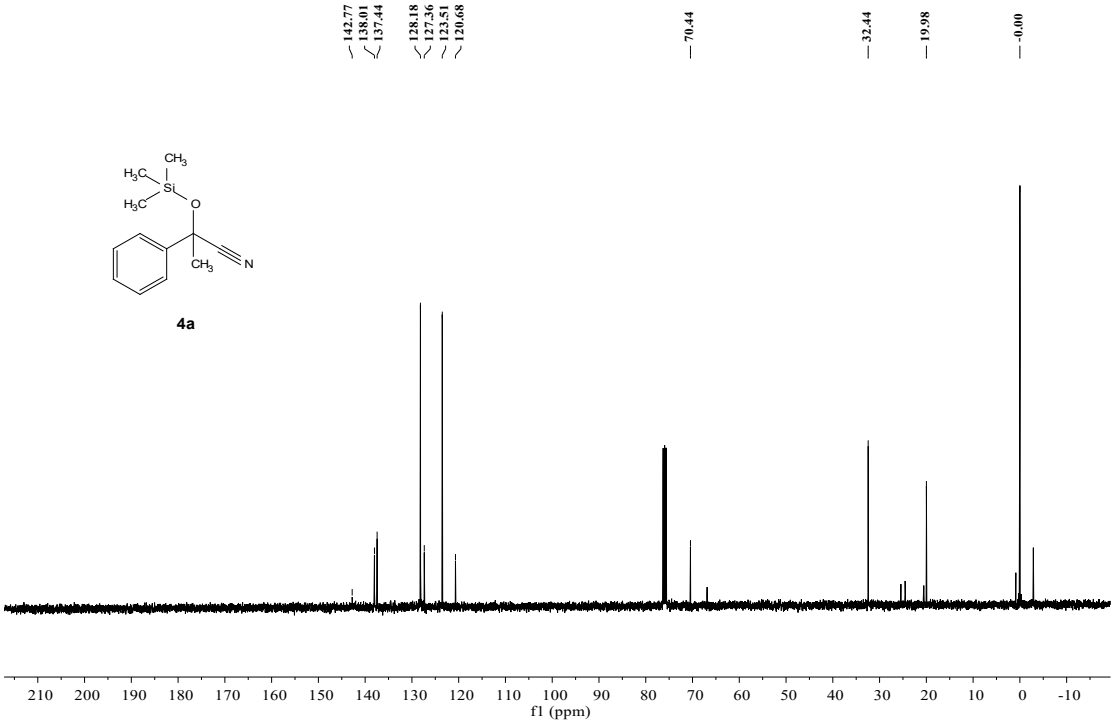
^{13}C NMR spectrum of **3r** in $CDCl_3$ at 101 MHz



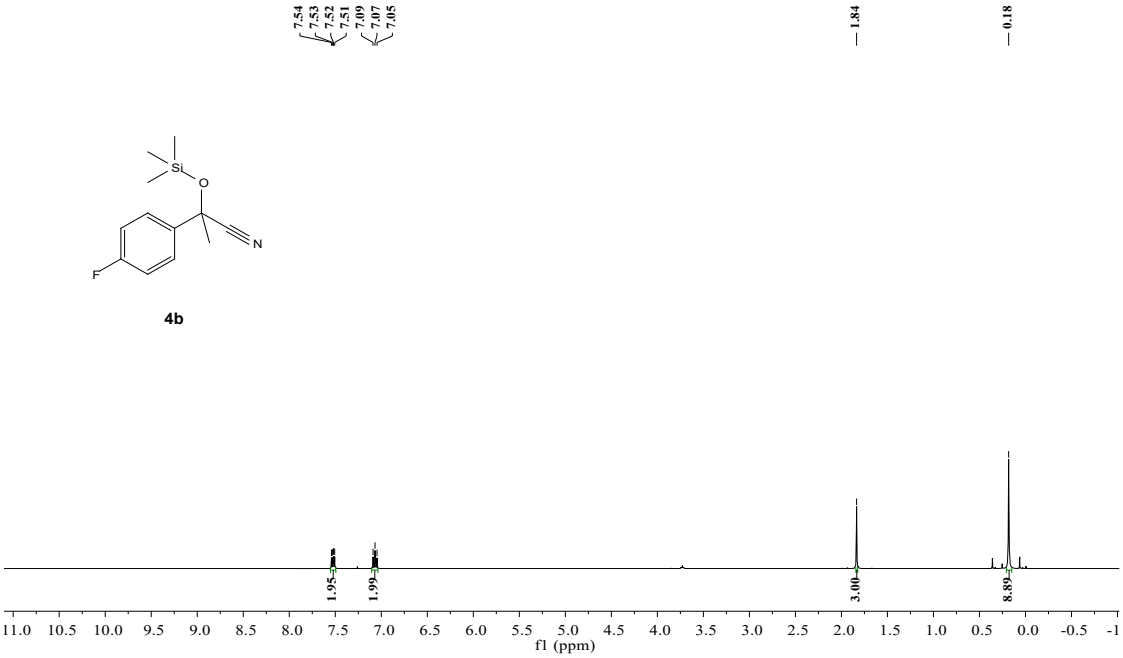
^{1}H NMR spectrum of **4a** in $CDCl_3$ at 400 MHz



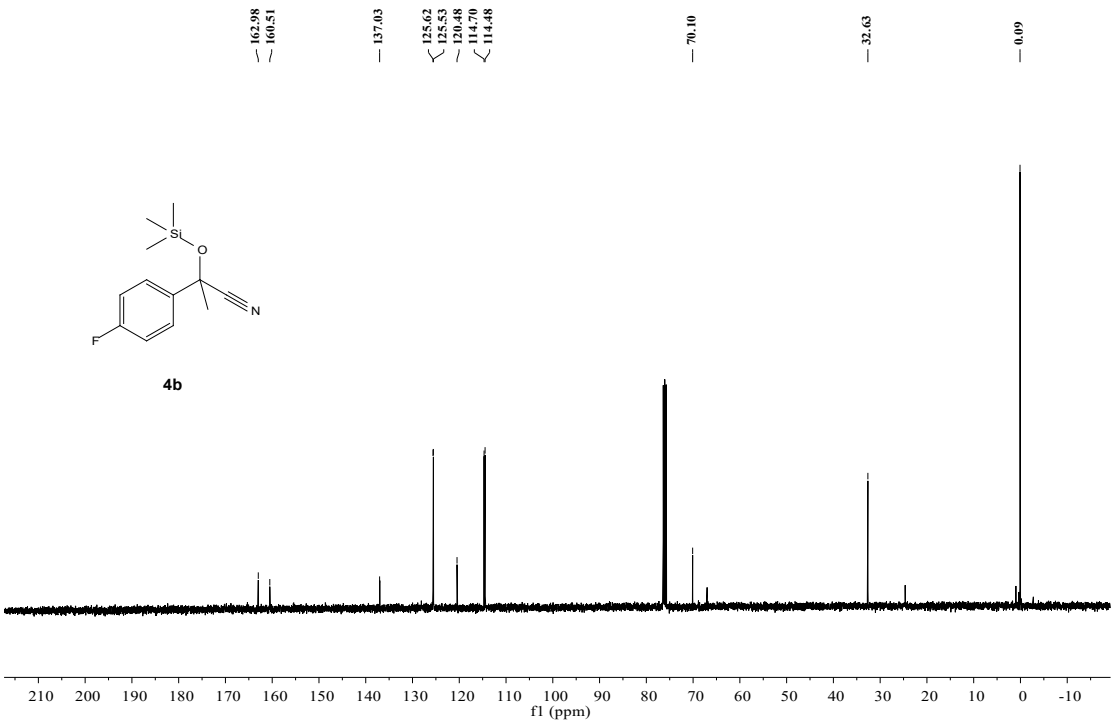
^{13}C NMR spectrum of **4a** in $CDCl_3$ at 101 MHz



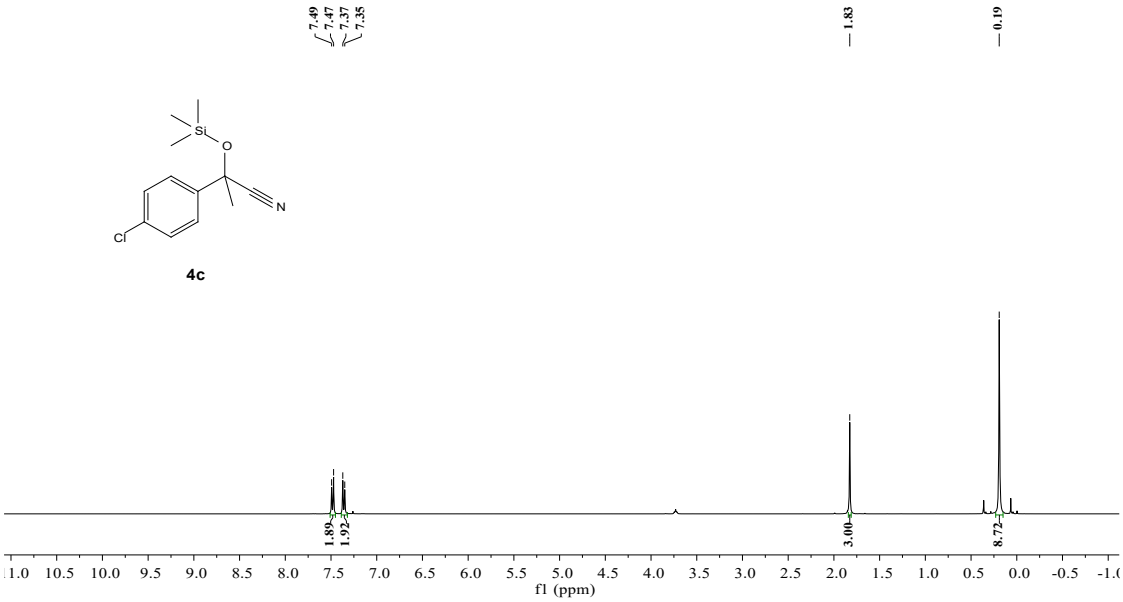
^{1}H NMR spectrum of **4b** in $CDCl_3$ at 400 MHz



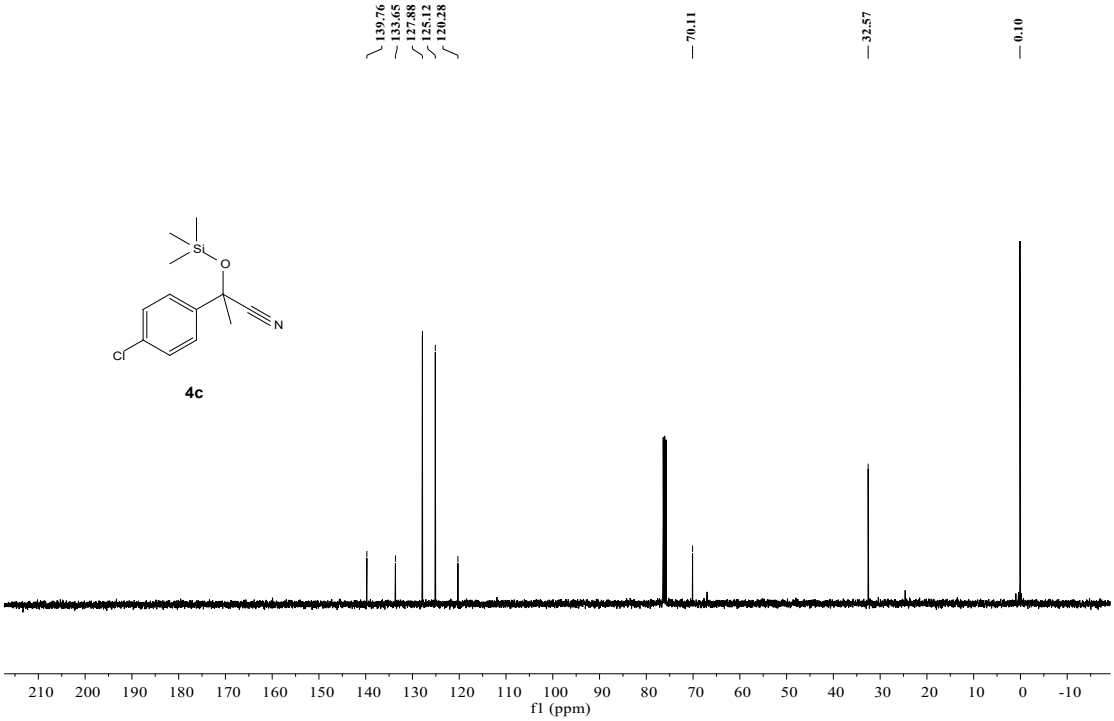
^{13}C NMR spectrum of **4b** in $CDCl_3$ at 101 MHz



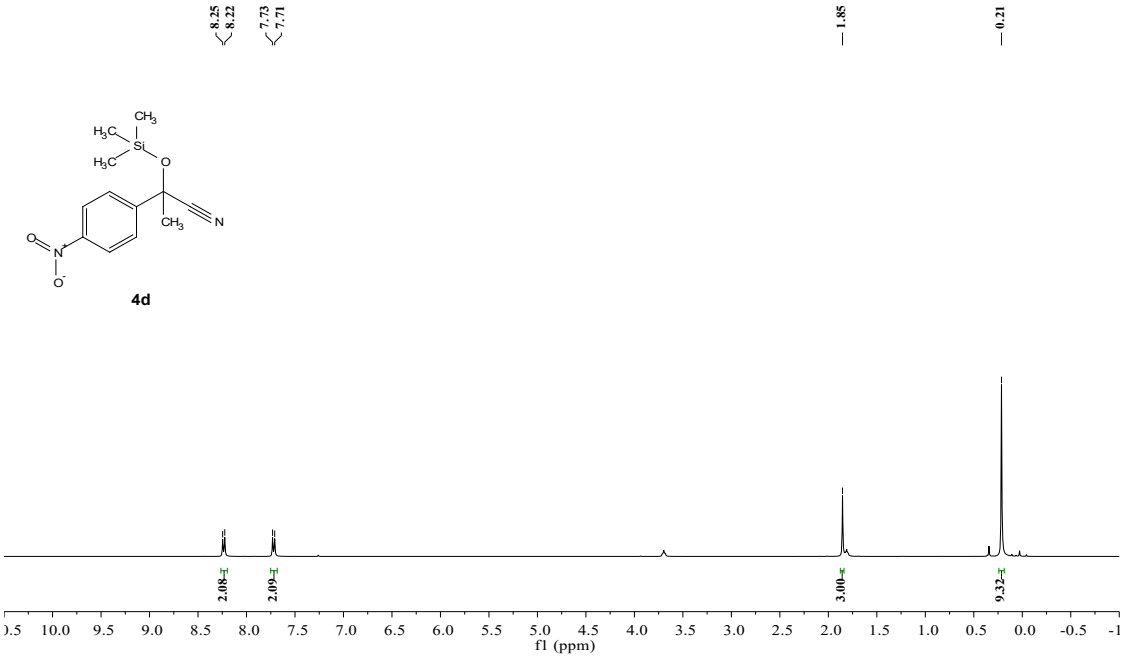
^{1}H NMR spectrum of **4a** in $CDCl_3$ at 400 MHz



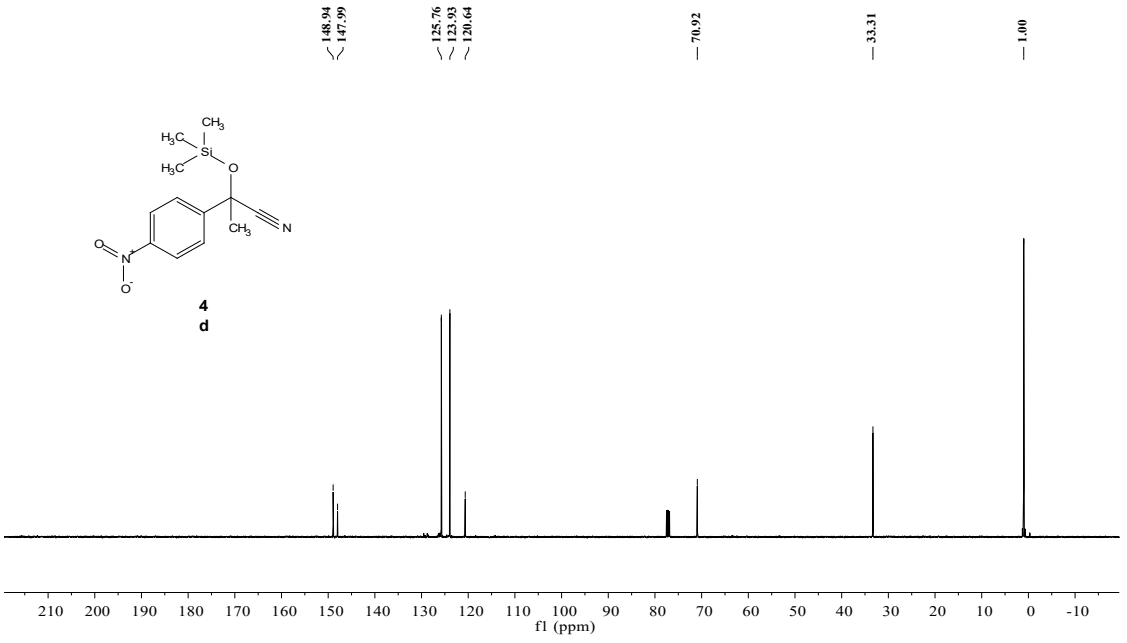
^{13}C NMR spectrum of **4a** in $CDCl_3$ at 101 MHz



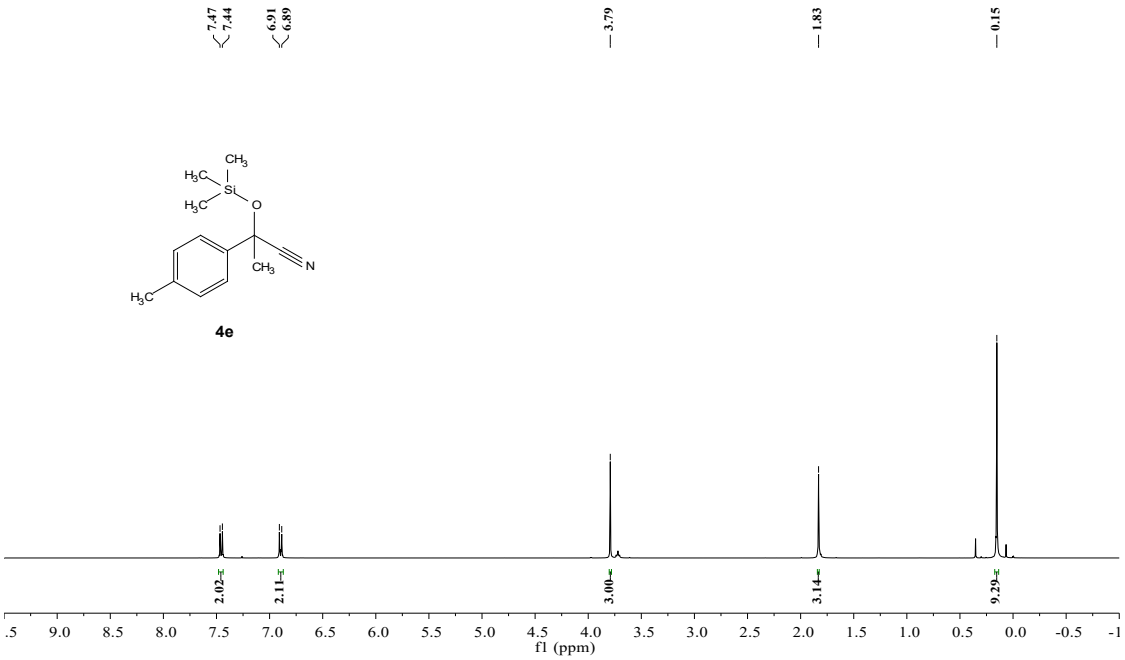
^{1}H NMR spectrum of **4d** in $CDCl_3$ at 400 MHz



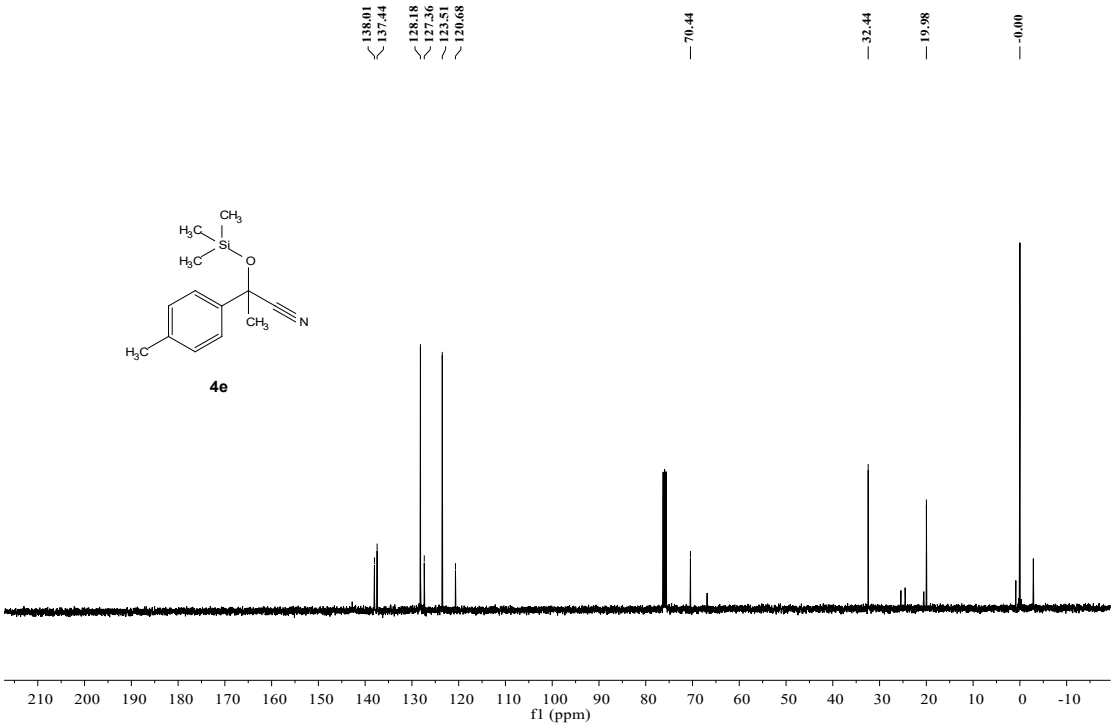
^{13}C NMR spectrum of **4d** in $CDCl_3$ at 101 MHz



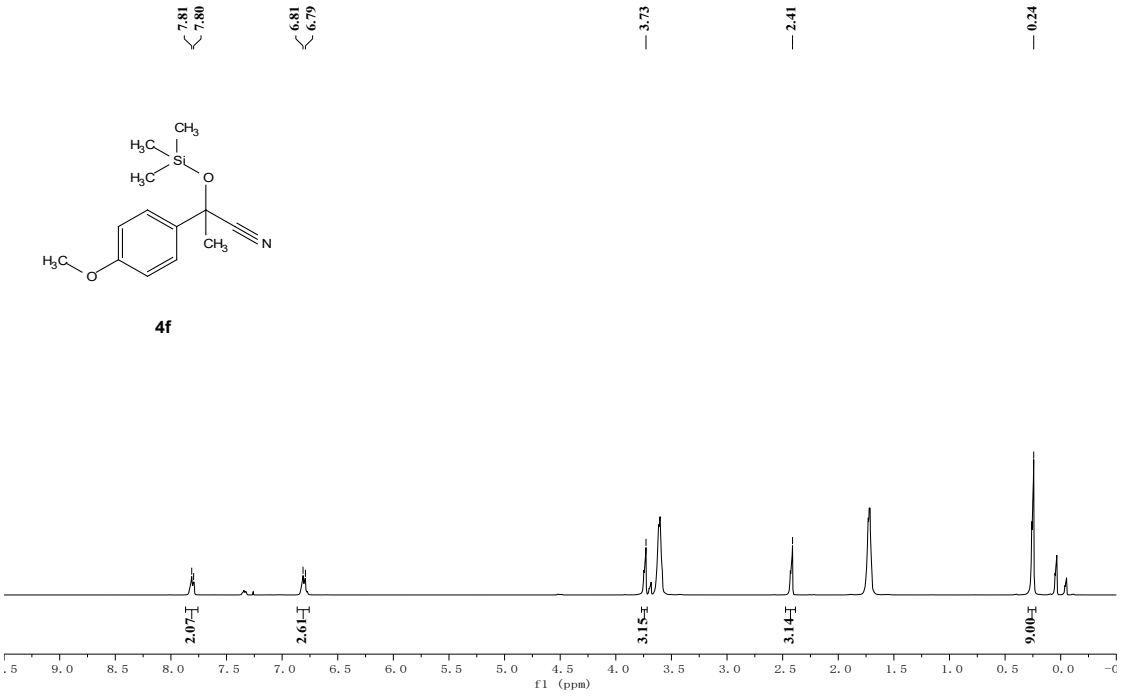
^{1}H NMR spectrum of **4e** in $CDCl_3$ at 400 MHz



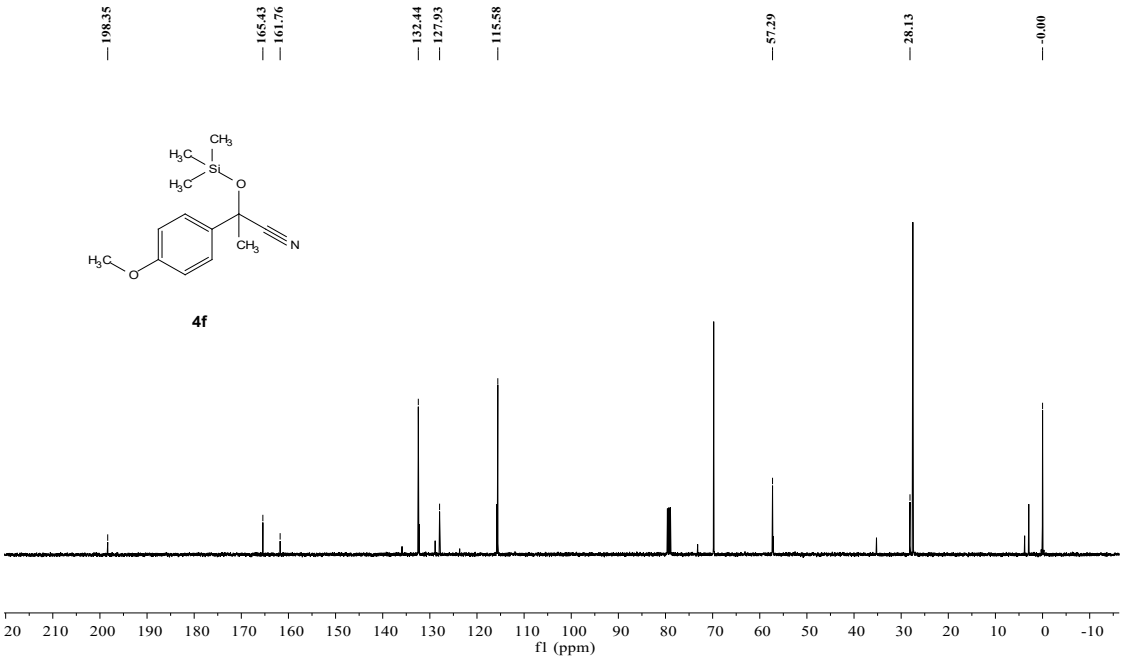
^{13}C NMR spectrum of **4e** in $CDCl_3$ at 101 MHz



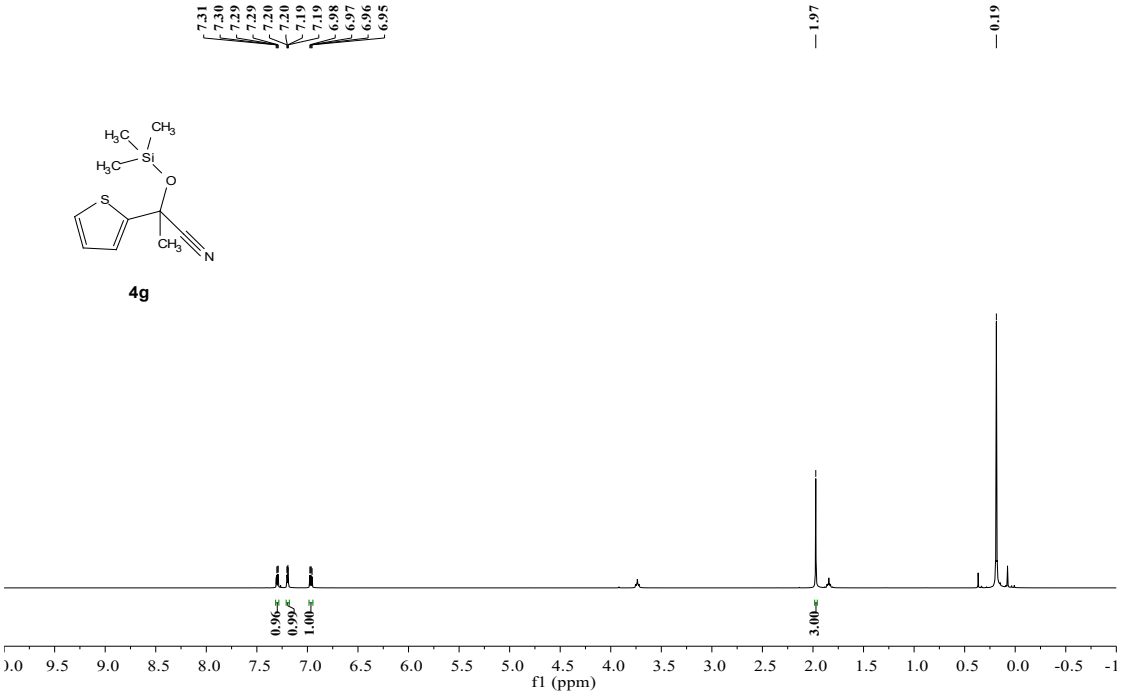
^{1}H NMR spectrum of **4f** in $CDCl_3$ at 400 MHz



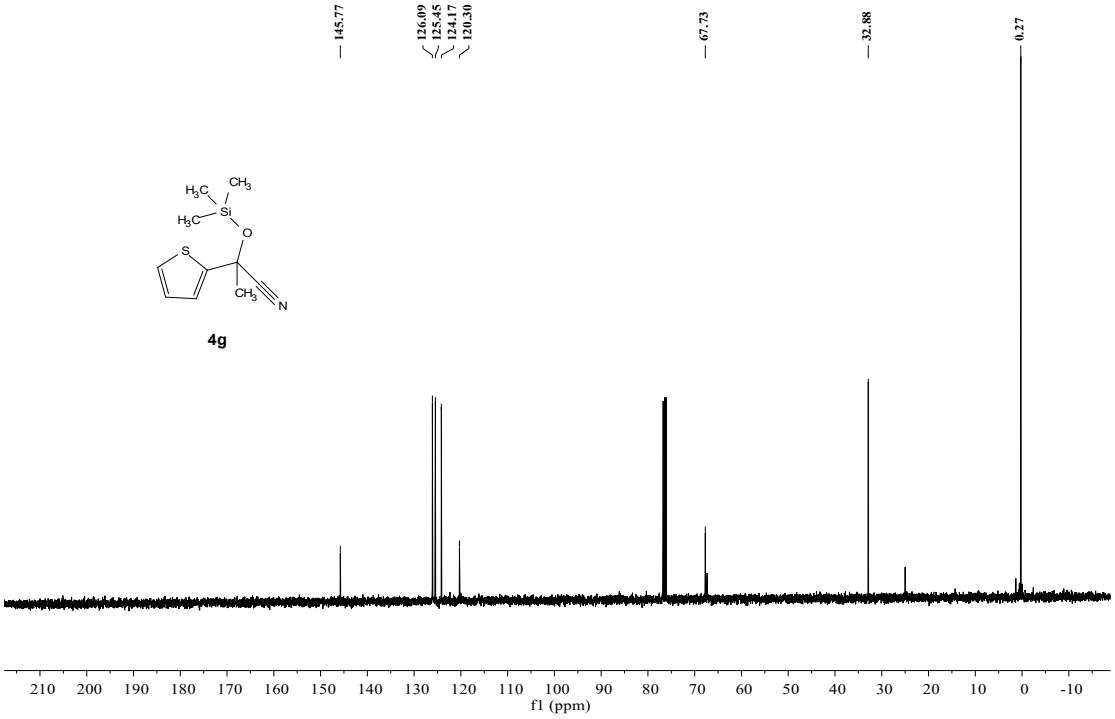
^{13}C NMR spectrum of **4f** in $CDCl_3$ at 101 MHz



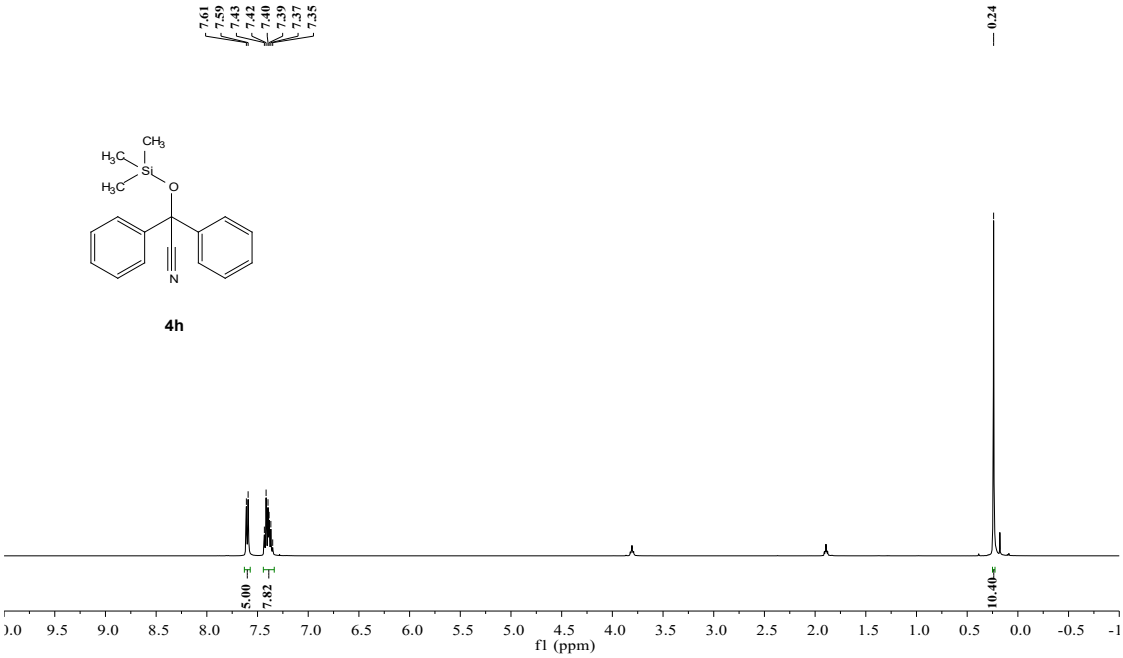
^{1}H NMR spectrum of **4g** in $CDCl_3$ at 400 MHz



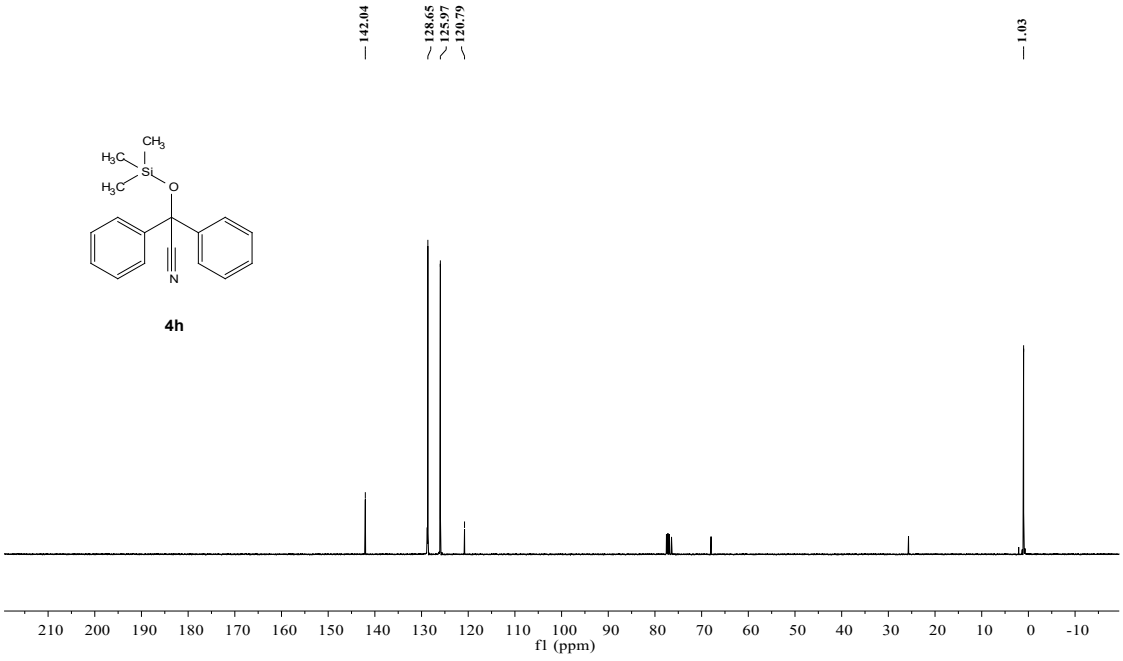
^{13}C NMR spectrum of **4g** in $CDCl_3$ at 101 MHz



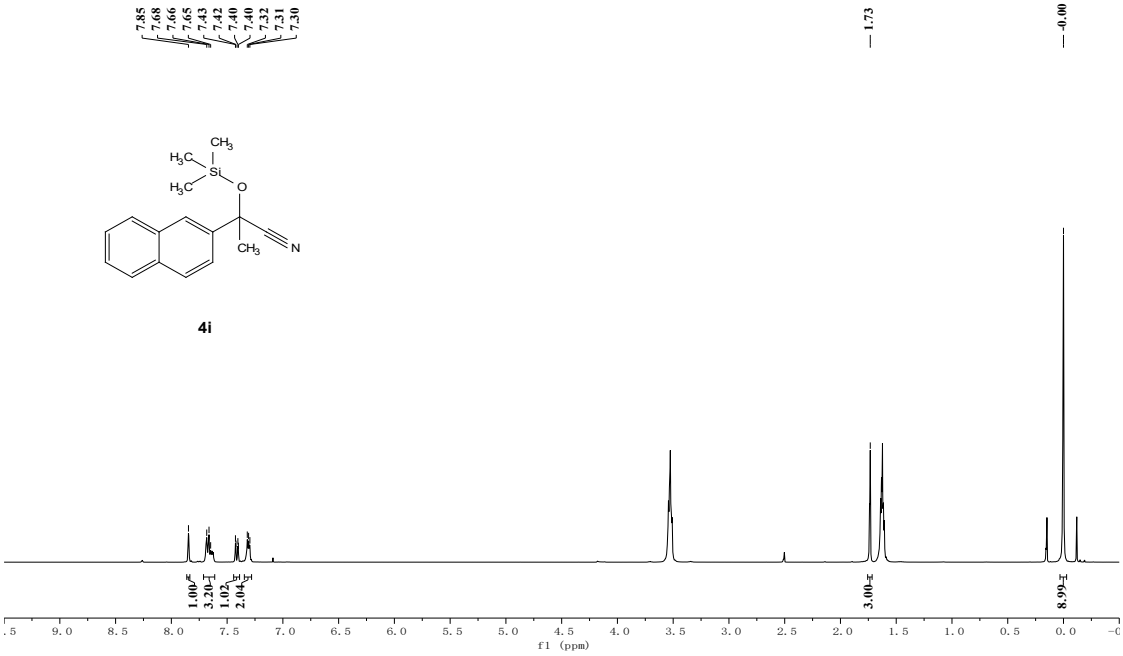
^{1}H NMR spectrum of **4h** in $CDCl_3$ at 400 MHz



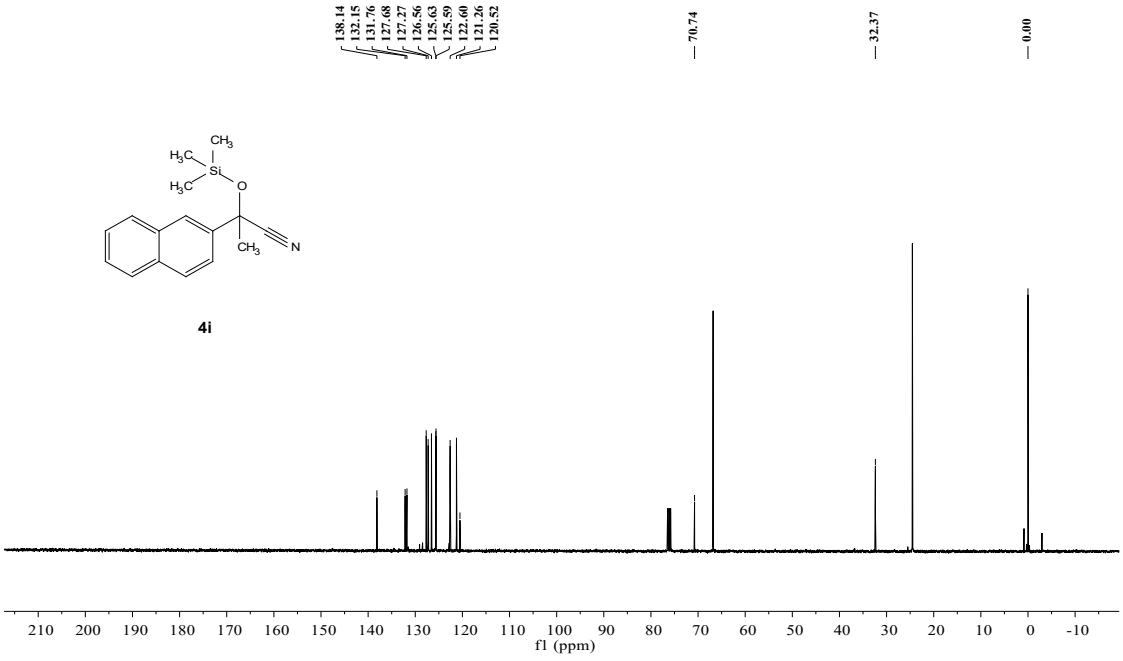
^{13}C NMR spectrum of **4h** in $CDCl_3$ at 101 MHz



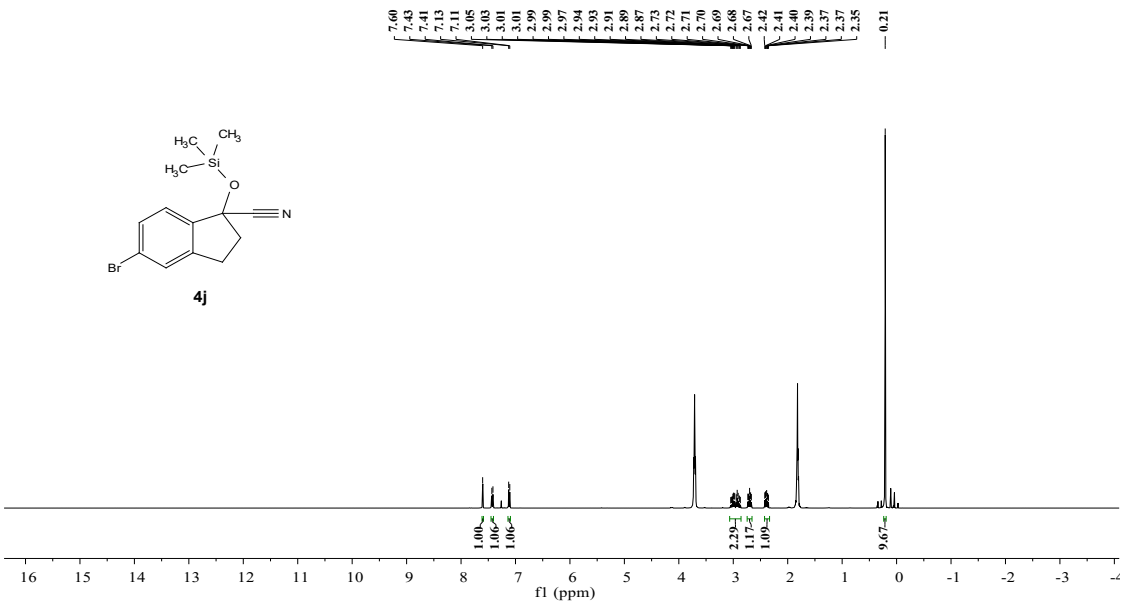
^{1}H NMR spectrum of **4i** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **4i** in $CDCl_3$ at 101 MHz

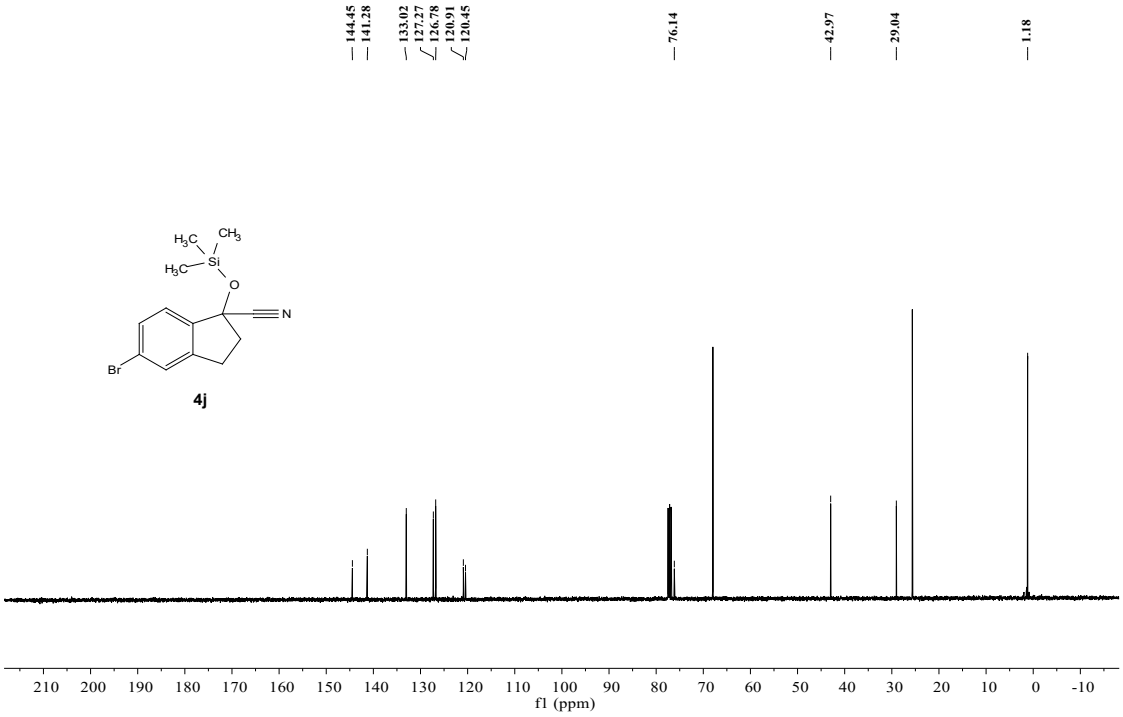


^{1}H NMR spectrum of **4j** in $CDCl_3$ at 400 MHz



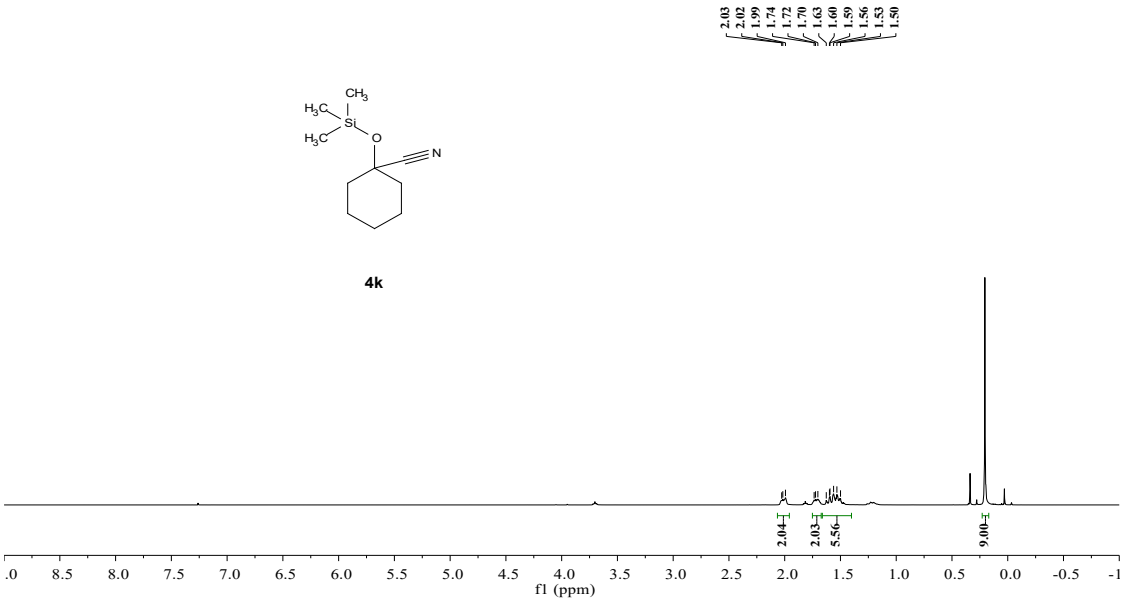
4j

^{13}C NMR spectrum of **4j** in $CDCl_3$ at 101 MHz

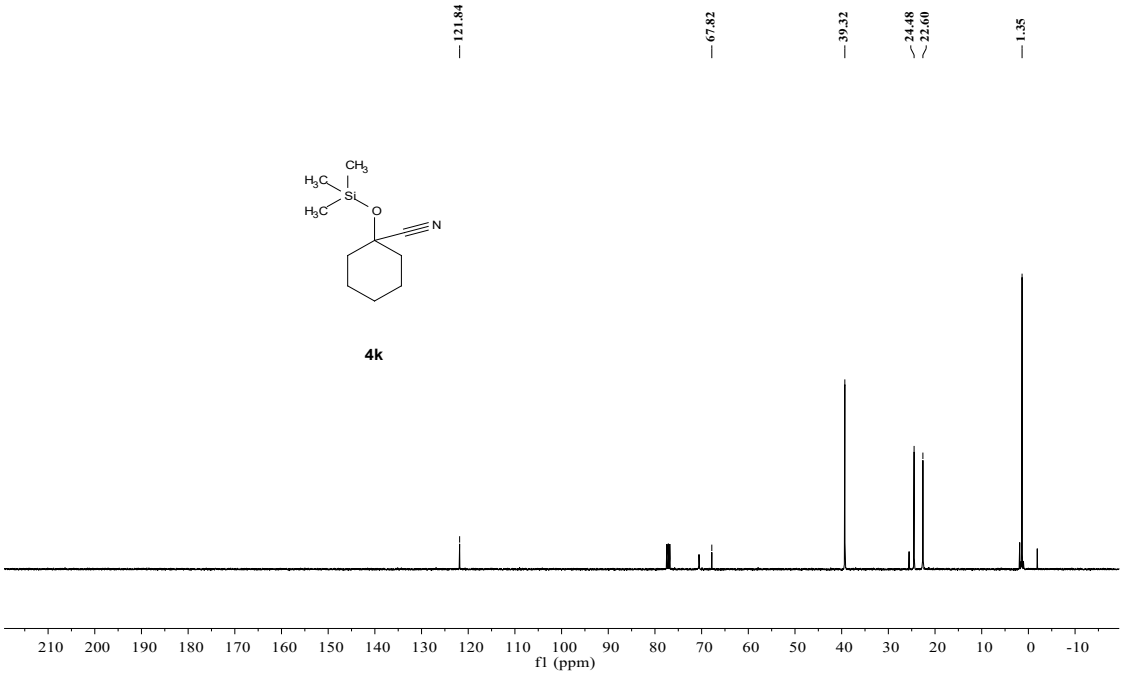


4j

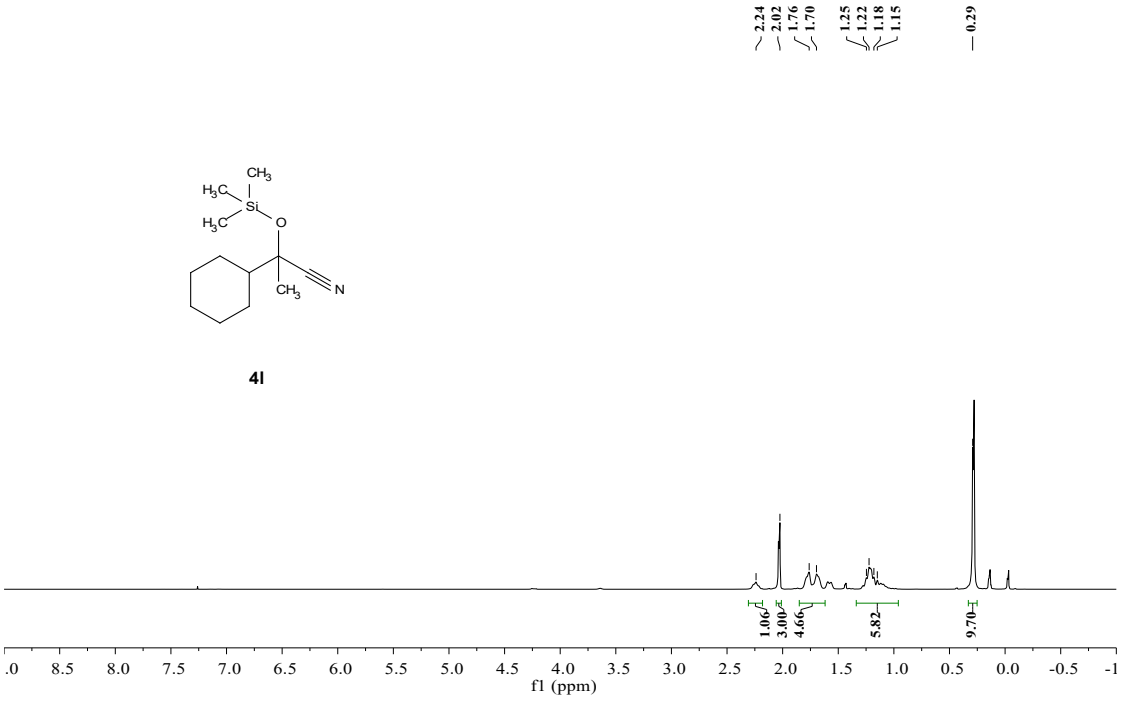
^{1}H NMR spectrum of **4k** in $CDCl_3$ at 400 MHz



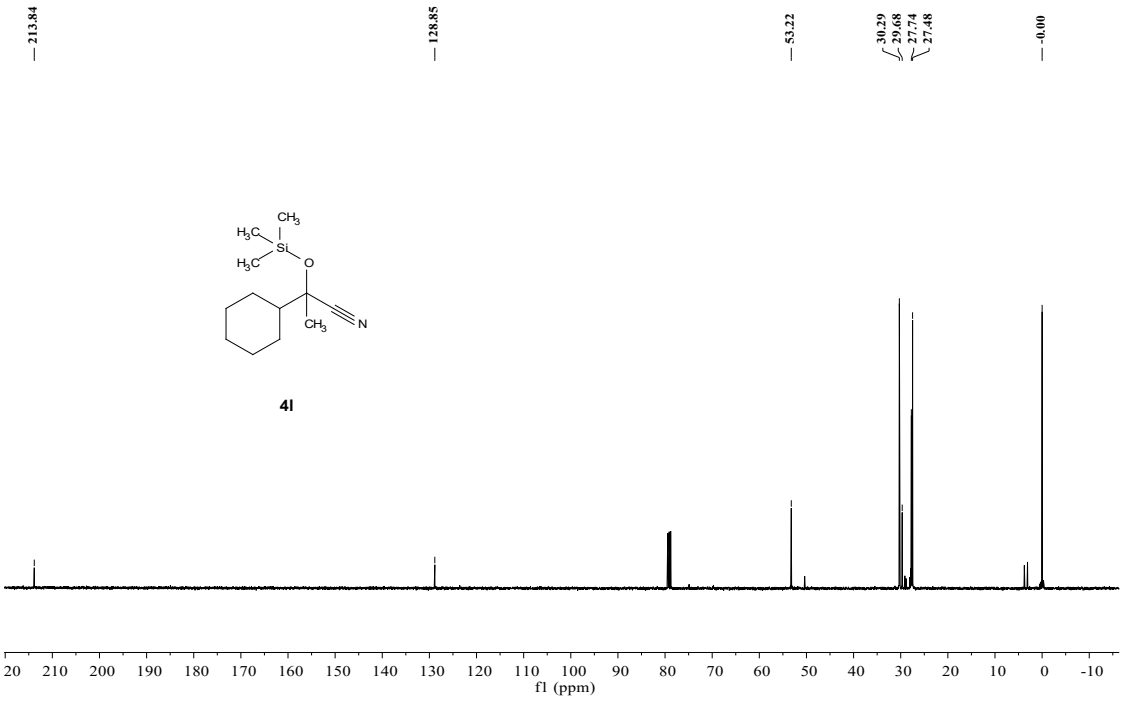
^{13}C NMR spectrum of **4k** in $CDCl_3$ at 101 MHz



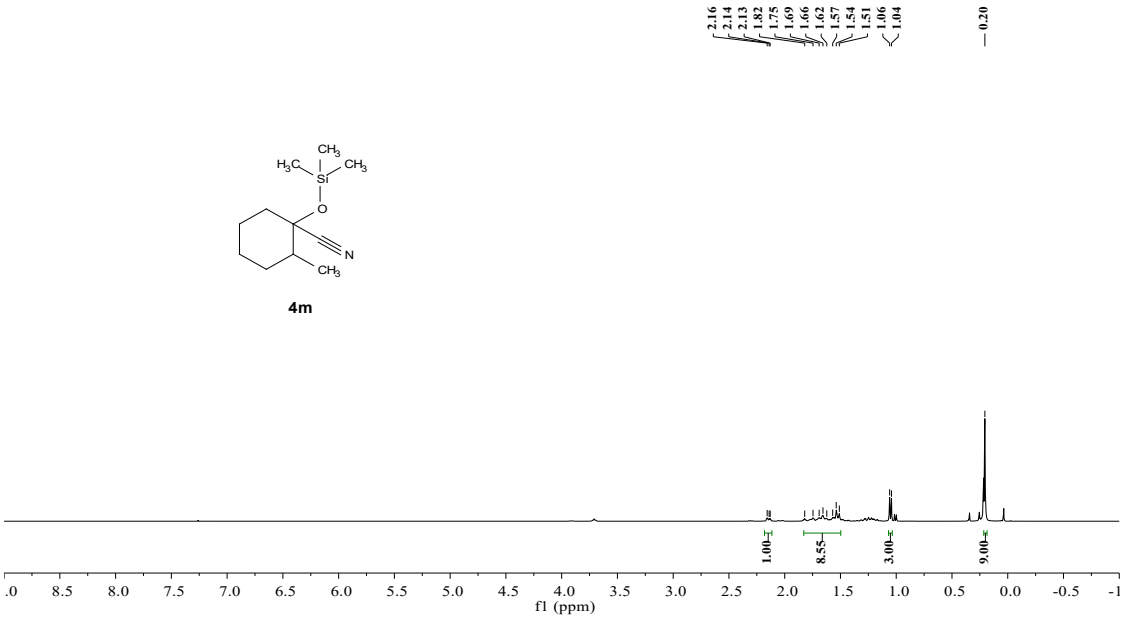
^{1}H NMR spectrum of **4l** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **4l** in $CDCl_3$ at 101 MHz

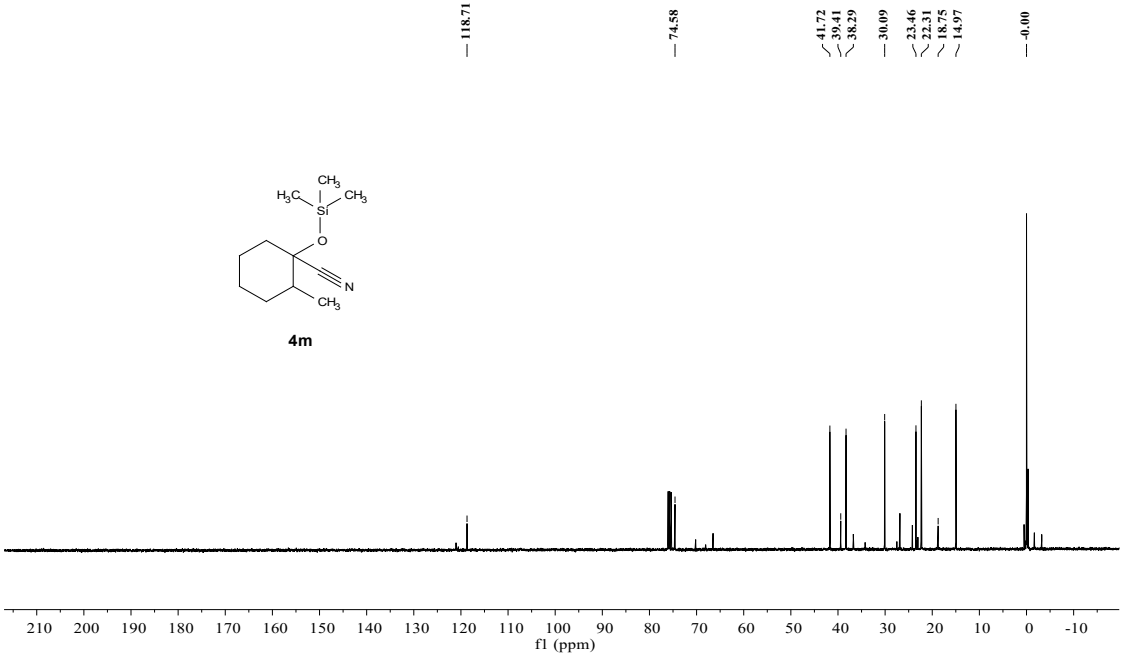


^{1}H NMR spectrum of **4m** in $CDCl_3$ at 400 MHz



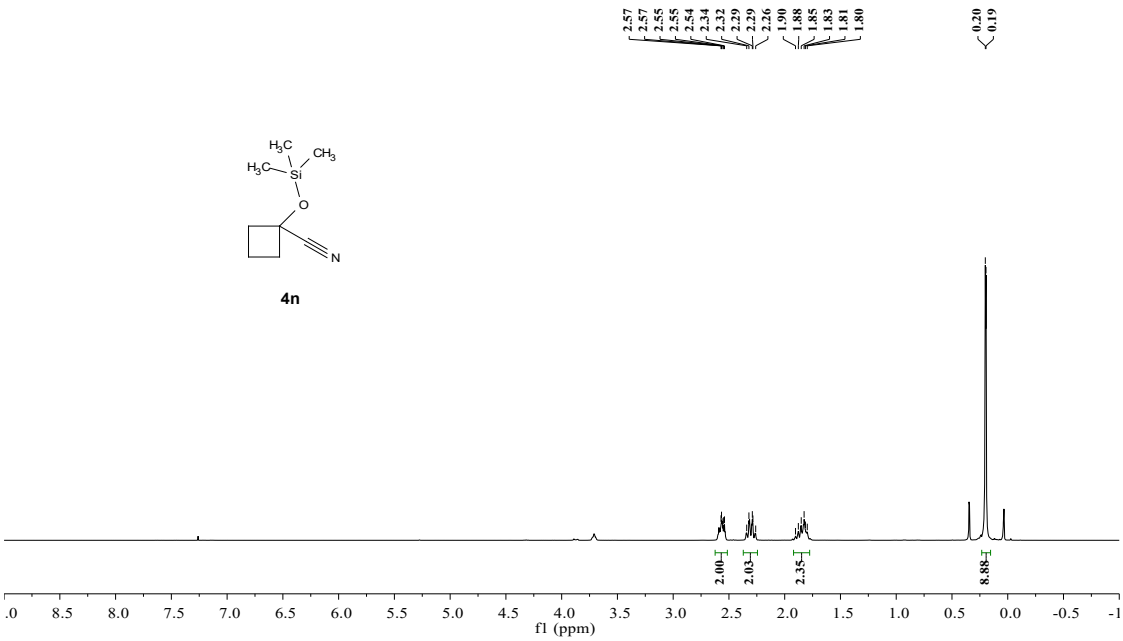
4m

^{13}C NMR spectrum of **4m** in $CDCl_3$ at 101 MHz

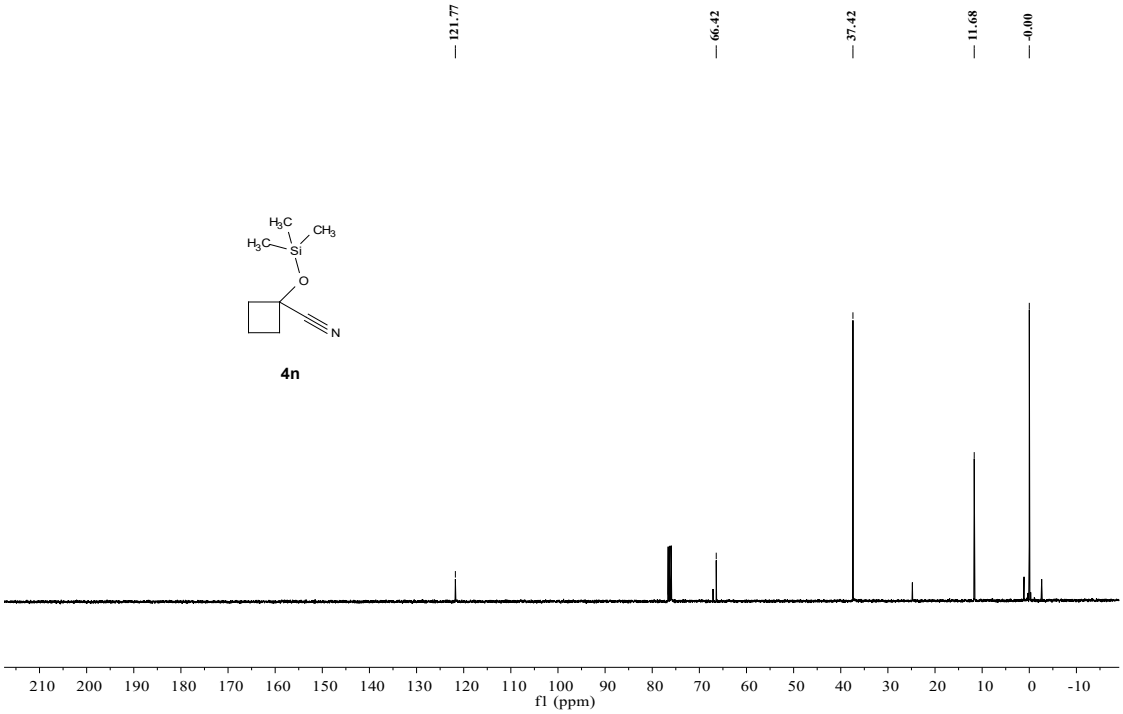


4m

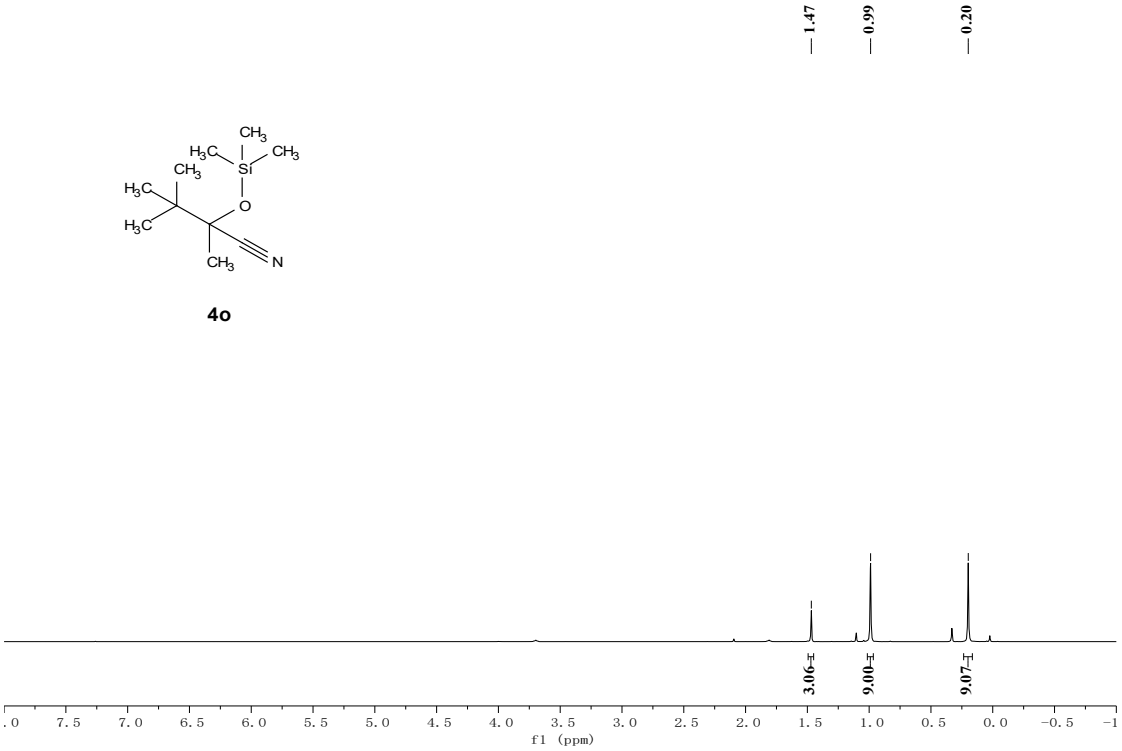
^{1}H NMR spectrum of **4n** in $CDCl_3$ at 400 MHz



^{13}C NMR spectrum of **4n** in $CDCl_3$ at 101 MHz

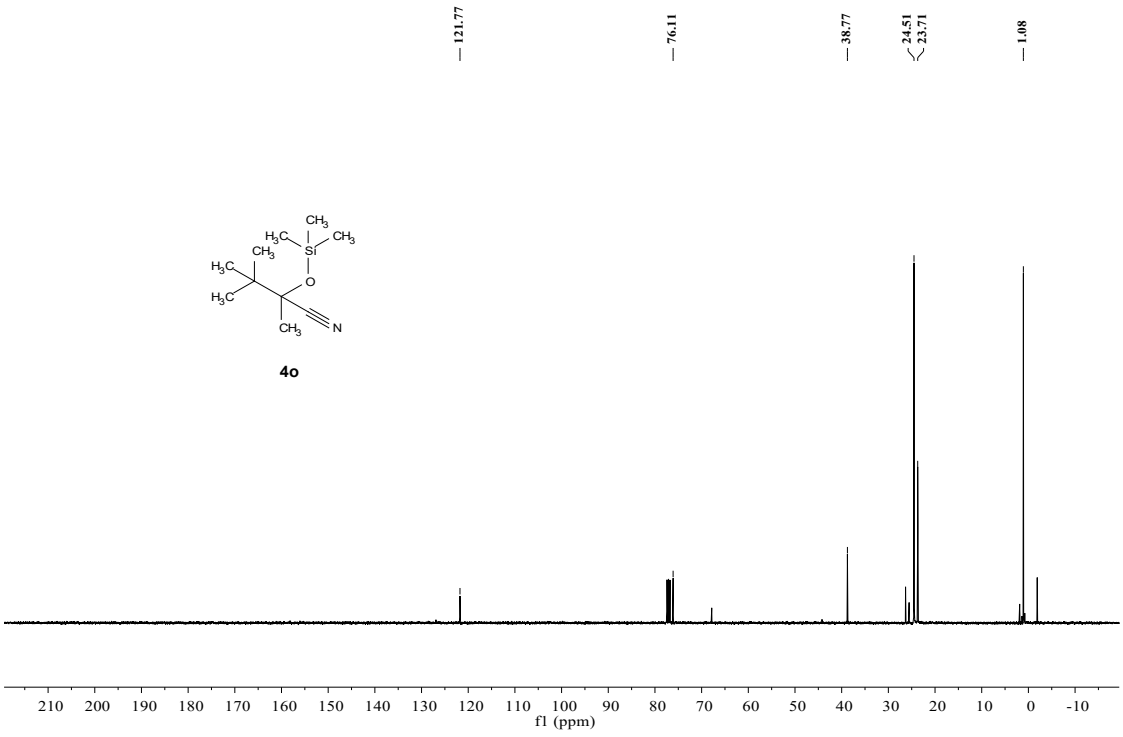


^{1}H NMR spectrum of **4o** in $CDCl_3$ at 400 MHz



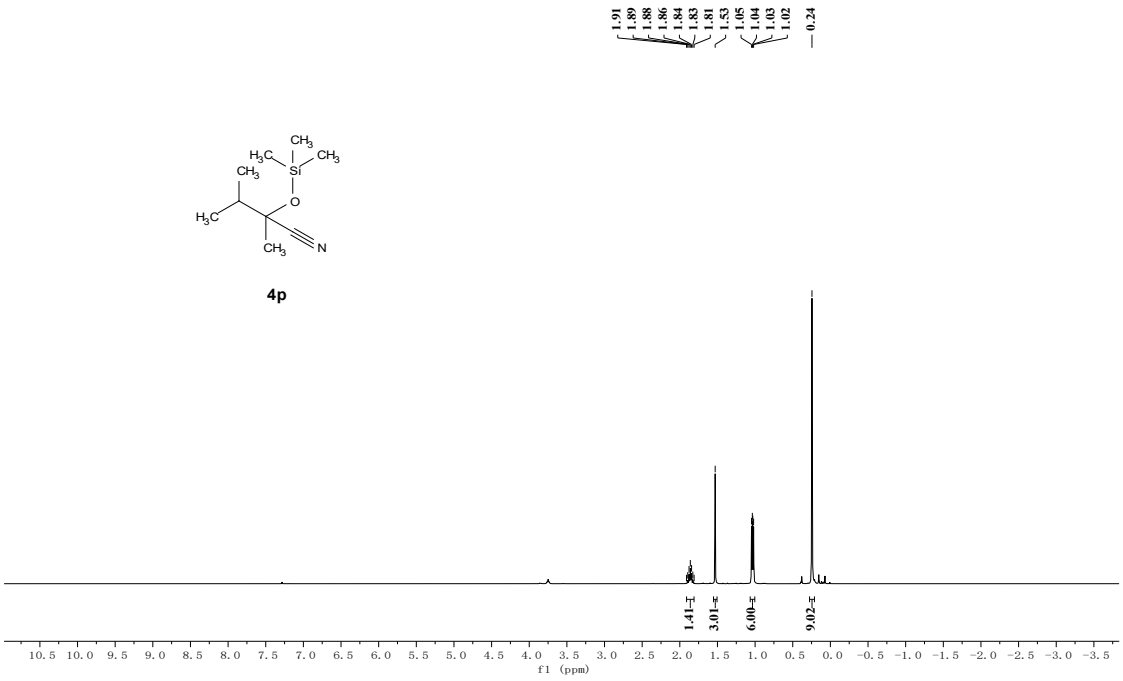
4o

^{13}C NMR spectrum of **4o** in $CDCl_3$ at 101 MHz

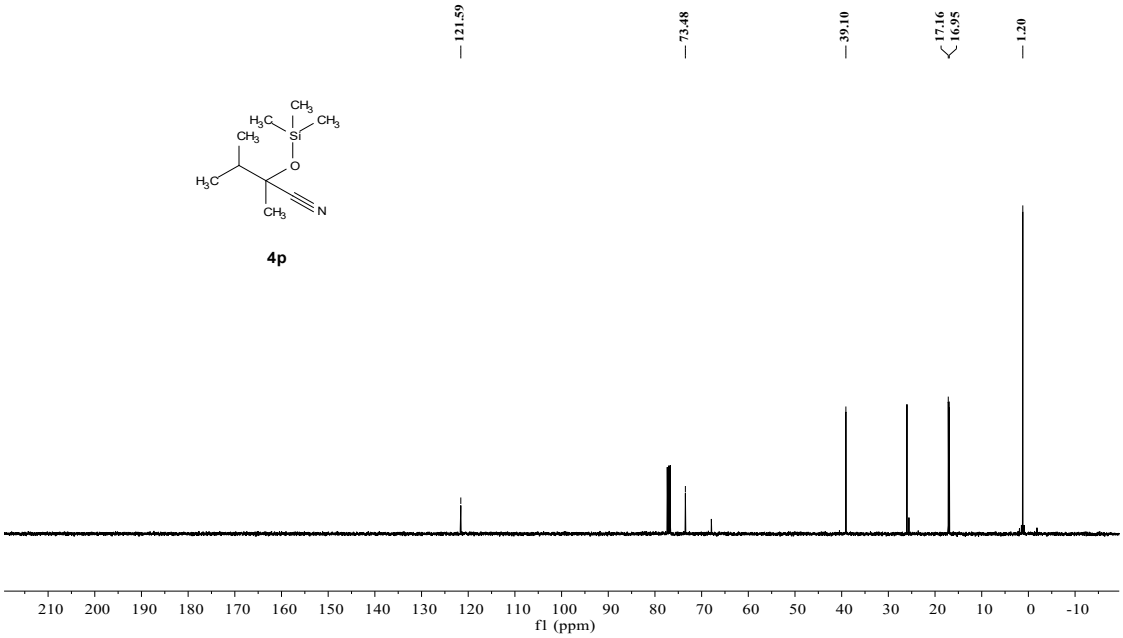


4o

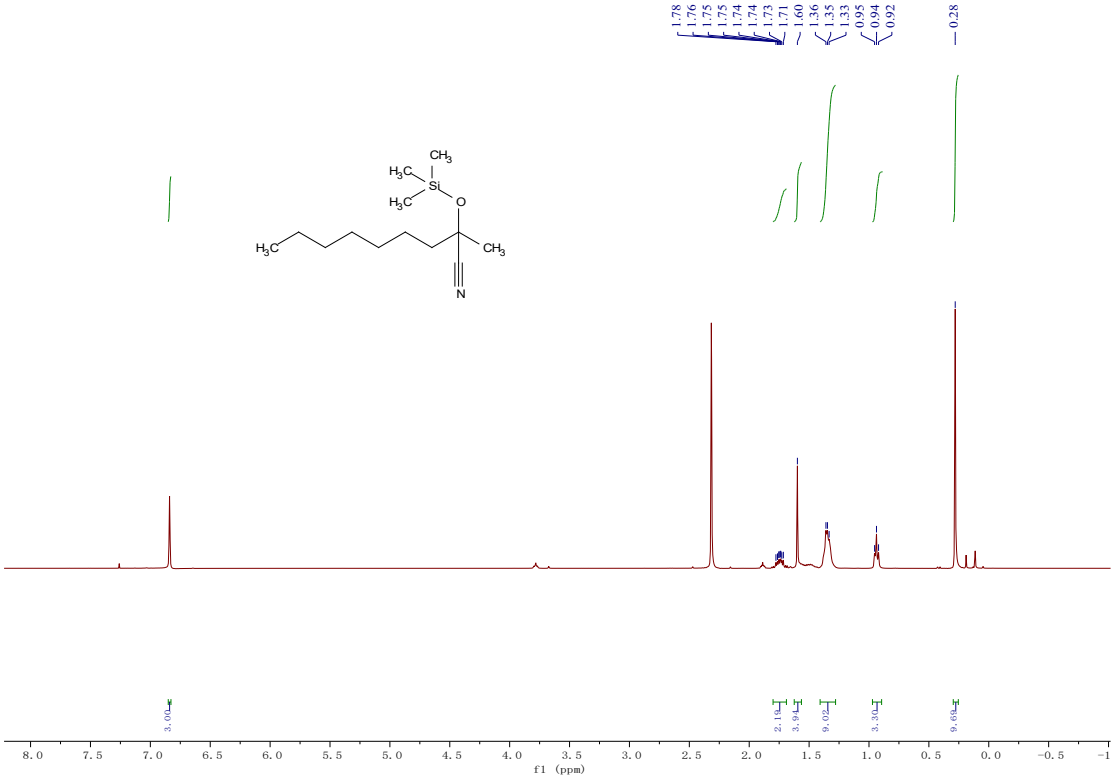
^{1}H NMR spectrum of **4p** in $CDCl_3$ at 400 MHz



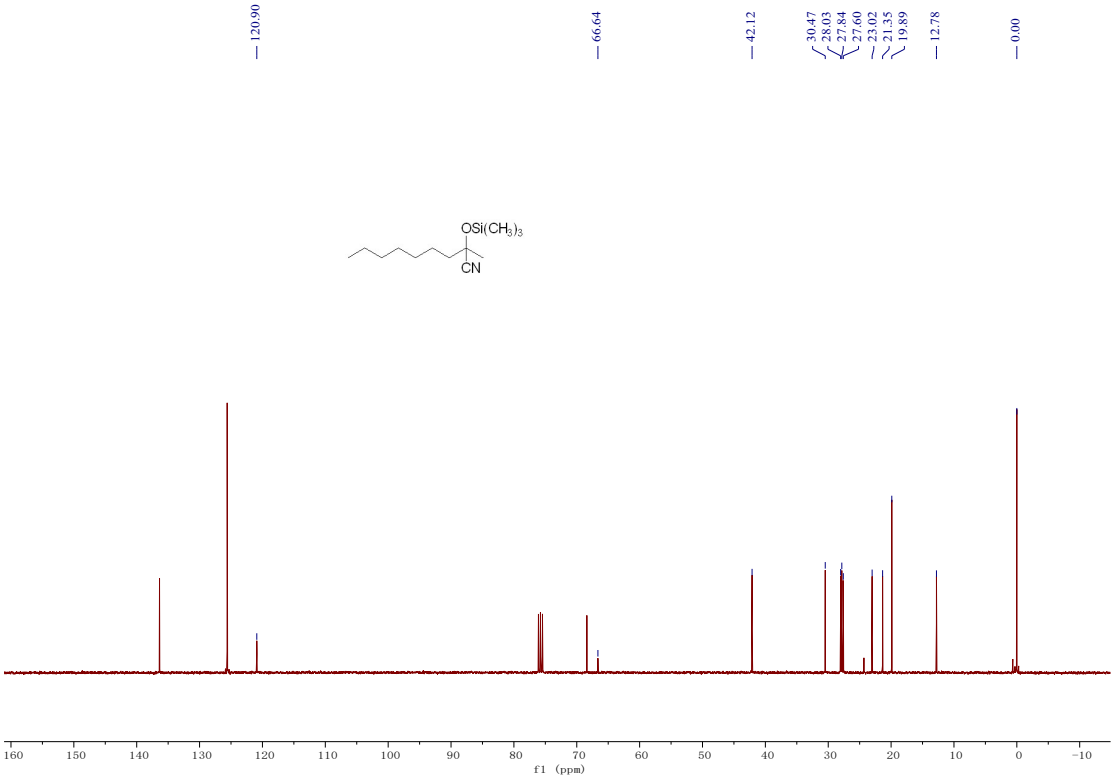
^{13}C NMR spectrum of **4p** in $CDCl_3$ at 101 MHz



^{1}H NMR spectrum of **4q** in $CDCl_3$ at 400 MHz



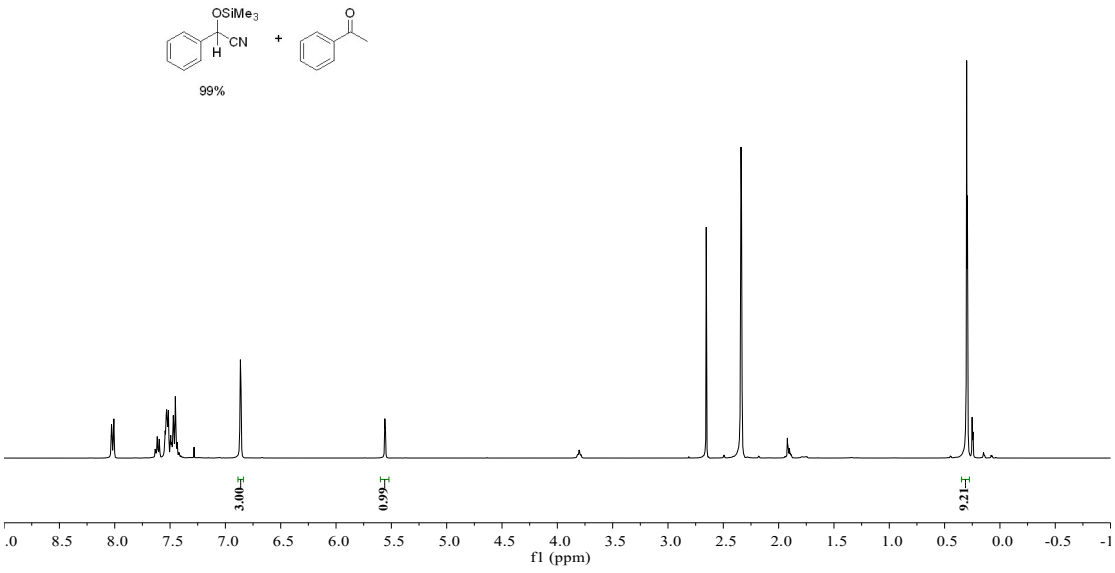
^{13}C NMR spectrum of **4q** in $CDCl_3$ at 101 MHz

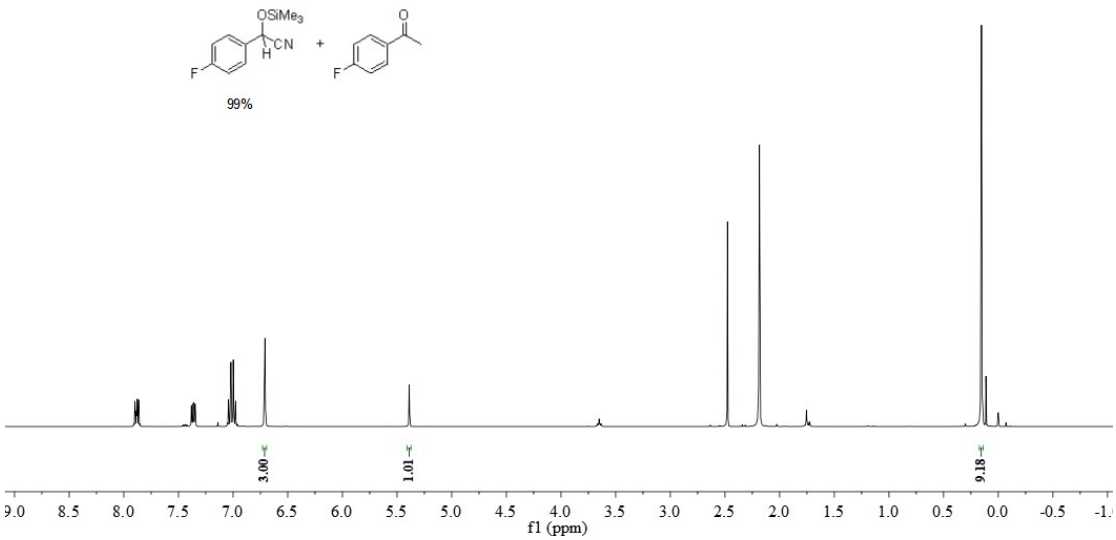


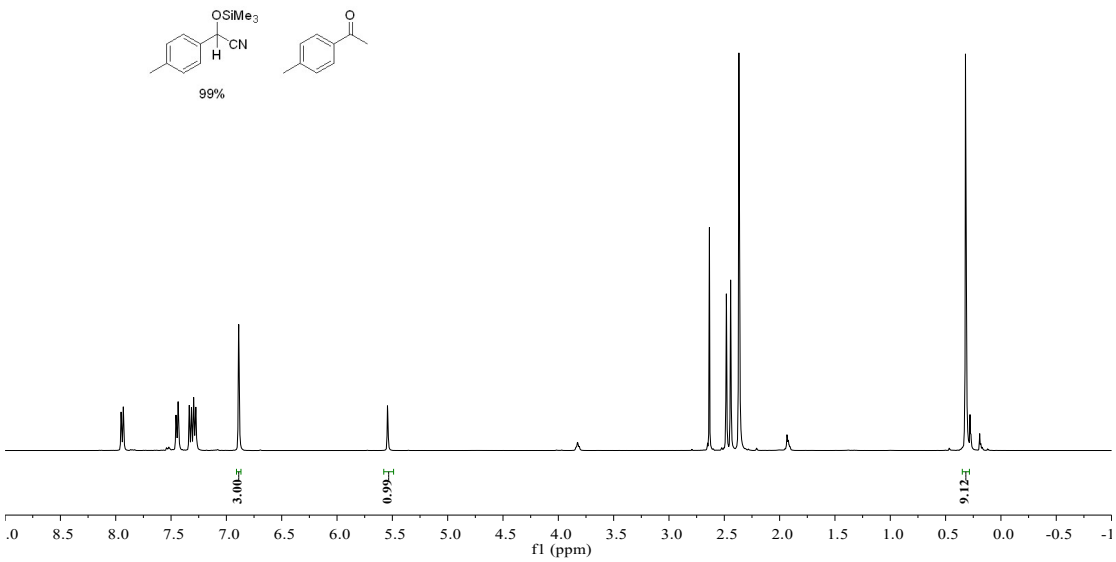
Competing Experiments for Selective Cyanosilylation of Aldehyde *vs* Ketone

Aldehyde (1 mmol), ketone (1 mmol), trimethylsilyl cyanide (1.1 mmol), and *n*-butyllithium (0.01-0.05 mol %) were taken in a screw capped vial equipped with a magnetic bar and the reaction mixture was stirred at room temperature for 1 h. Reaction progress was monitored by ^{1}H NMR, which clearly indicated the complete conversion of an aldehyde to its corresponding cyanohydrin product and predominant presence of the unreacted ketone; final spectra are provided as follows:

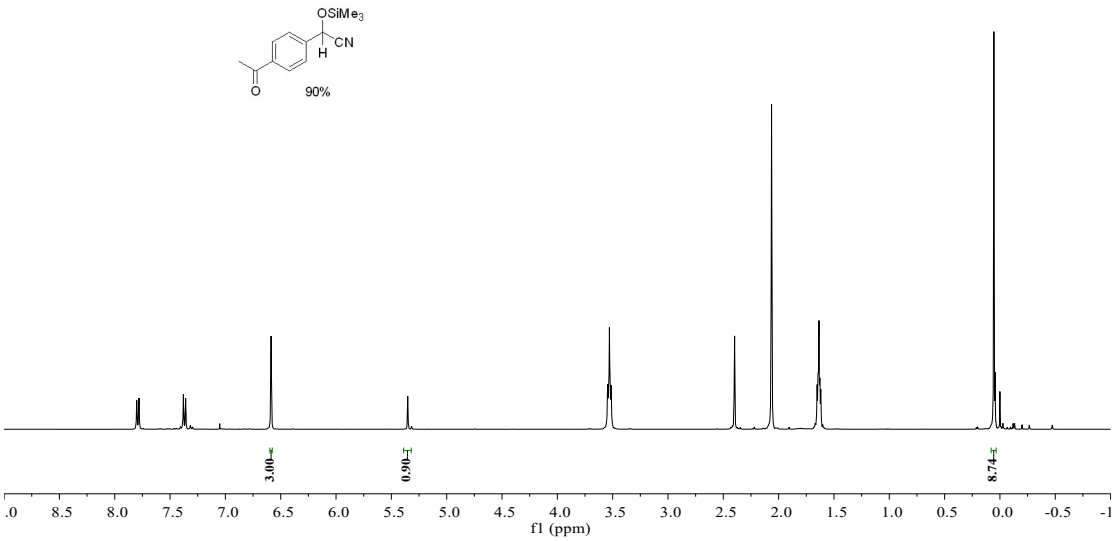
^{1}H NMR Spectra of Intermolecular Cyanosilylation Reactions (400 MHz, $CDCl_3$):

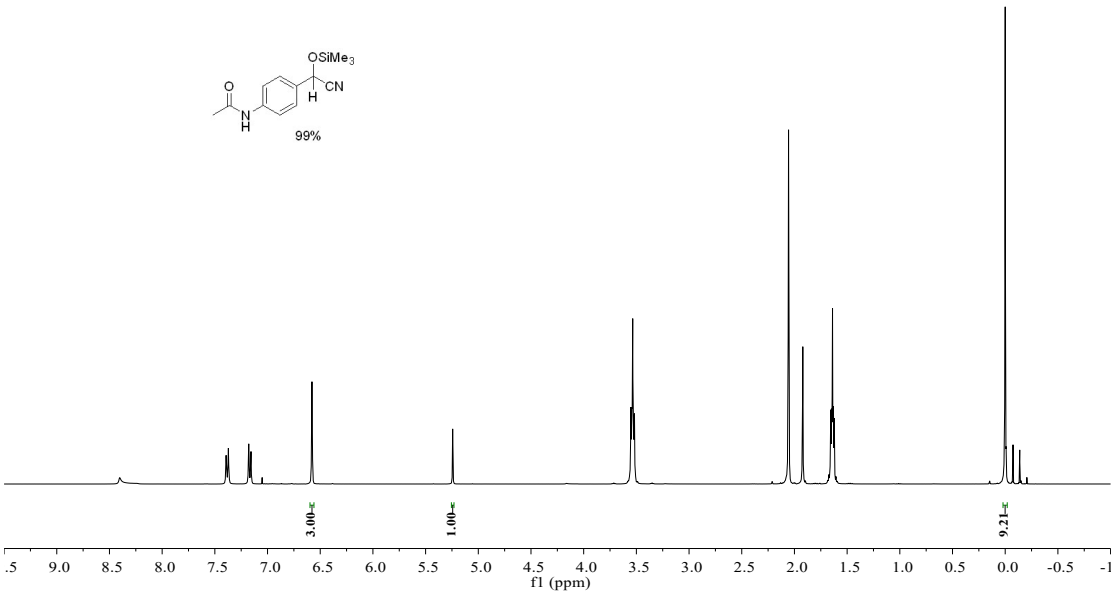


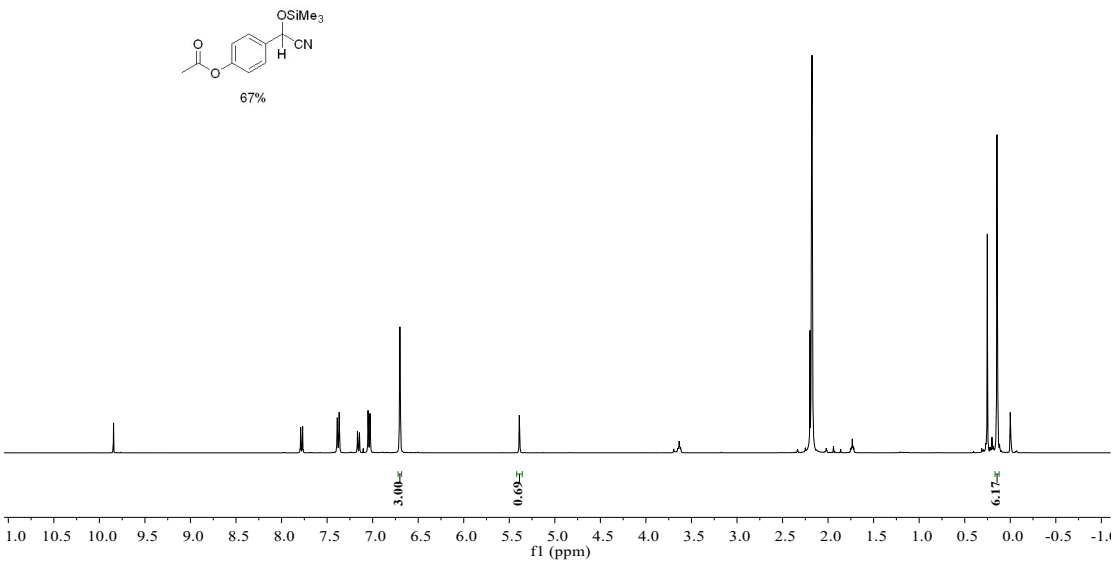

OSiMe3
CN
H
F
+
O
F
99%
3.00
1.01
9.18
f1 (ppm)


OSiMe3
CN
H
O
99%
3.00
0.99
9.12
f1 (ppm)

^{1}H NMR Spectra of Intramolecular Cyanosilylation Reaction (400 MHz, $CDCl_3$):






OSiMe3
CN
H
O
O
67%
3.00
0.69
6.17
1.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

Mechanistic Studies

General Procedure for Stoichiometric Reactions

In a glovebox, benzaldehyde (0.05 mmol) and *n*-BuLi (0.05 mmol) were mixed in the THF-d_8 solvent (0.5 mL) in a NMR tube for 1 h at room temperature. Reaction progress was monitored by ^{1}H NMR. The characteristic H signal of benzaldehyde was still there without change (**Fig. S1**; δ = 10.01 ppm); nevertheless, the H signal of PhCHO was disappeared upon adding Me_3SiCN to the above mixture, subsequently accompanied by the appearance of the newly formed cyanohydrin peak (**Fig. S3**; δ = 4.68 ppm). When stoichiometric reaction of *n*-BuLi (0.05 mmol) with Me_3SiCN (0.05 mmol) was carried out in THF-d_8, however, the peaks were unattributed in the ^{1}H NMR spectra for unclear reasons yet (**Fig. S5**).

Moreover, we also utilized PhNHLi instead of *n*-BuLi to infer the reaction process of *n*-BuLi-catalyzed cyanosilylation. Firstly, The reaction of a 1:1.1 molar ratio of benzaldehyde and Me_3SiCN catalyzed by PhNHLi (0.01 mol %) was carryied out at room temperature under neat conditions. It was recorded that PhNHLi exhibited excellent catalytic activity similar to that of *n*-BuLi (**Fig. SA**). Next, stoichiometric reactions were executed. The procedure was operated in a glovebox by adding 0.05 mmol PhNHLi (4.9 mg in 0.5 mL THF-d_8) and 0.05 mmol PhCHO to a NMR tube, and no reaction occurred as demonstrated by the ^{1}H NMR spectrum as the same as the *n*-BuLi case (**Fig. S2**; δ = 10.01 ppm); subsequently, one equivalent of Me_3SiCN was added to the above mixture, which did lead to the formation of cyanosilylated product (**Fig. 4**; top; δ = 5.52 ppm). Moreover, when 0.05 mmol PhNHLi (4.9 mg in 0.5 mL THF-d_8) was treated with 0.05 mmol Me_3SiCN, it can been clearly seen that a new peak was recorded at δ = 4.41 ppm (**Fig. S6**).

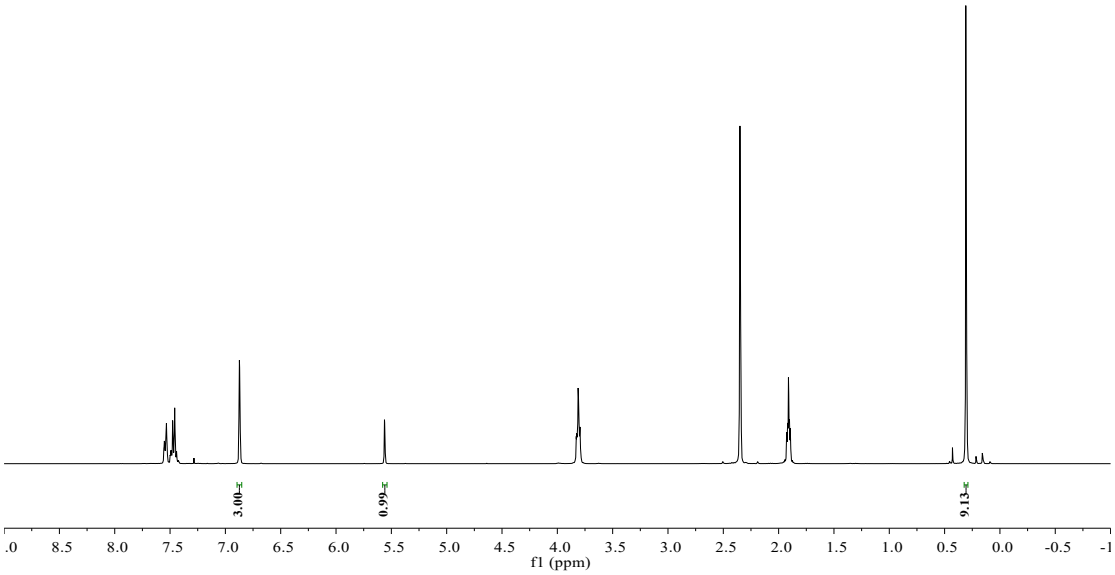


Fig. SA The copy of ^{1}H NMR spectra (400 MHz) with mesitylene as an internal standard of PhNHLi-catalyzed cyanosilylation. Reaction conditions: Benzaldehyde (1 mmol), Me_3SiCN (1.1 mmol) and PhNHLi (0.01 mol %) at 25 ^{o}C; 1 h.

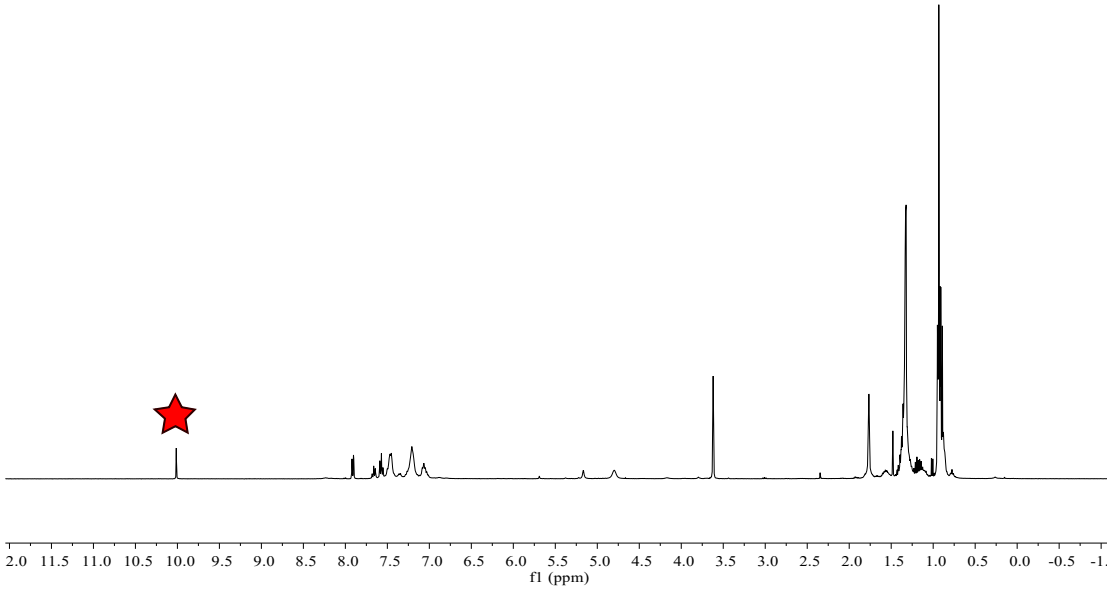


Fig. S1 The copy of ^{1}H NMR spectra (400 MHz) with mesitylene as an internal standard. Reaction conditions: Benzaldehyde (0.05 mmol) and n-BuLi (0.05 mmol) in 0.5 mL THF-d_8 at 25 ^{o}C; 1 h.

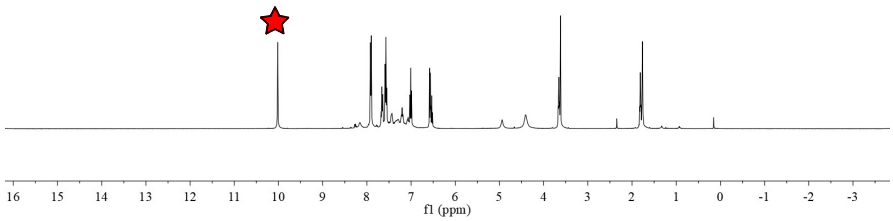


Fig. S2 The copy of ^{1}H NMR spectra (400 MHz) with mesitylene as an internal standard. Reaction conditions: Benzaldehyde (0.05 mmol) and PhNHLi (0.05 mmol) in 0.5 mL THF-d_8 at 25 ^{o}C; 1h.

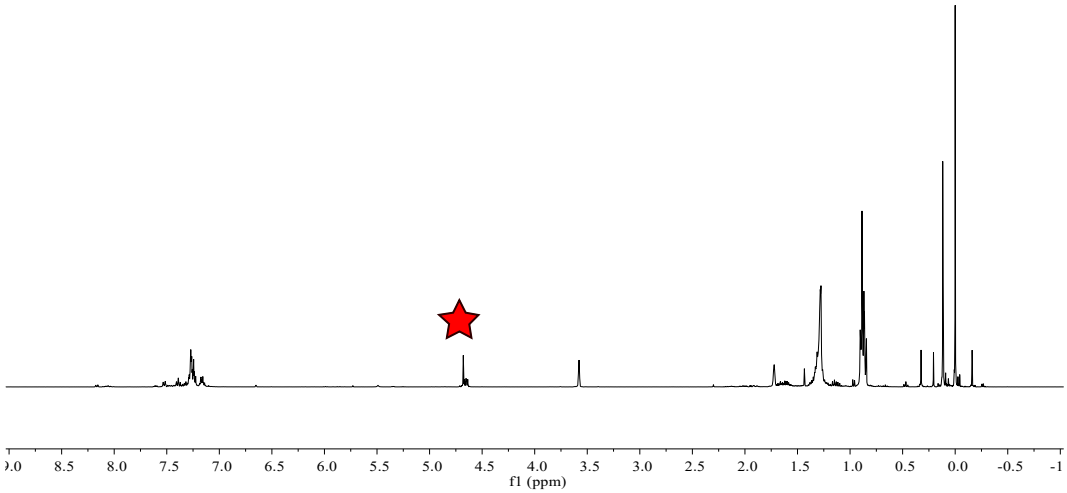


Fig. S3 The copy of ^{1}H NMR spectra of the 1:1:1 mixture of PhCHO, n-BuLi and Me_3SiCN. Reaction conditions: Benzaldehyde (0.05 mmol) and n-BuLi (0.05 mmol) in 0.5 mL THF-d_8 were first mixed at 25 °C for 1 h, then the Me_3SiCN (0.05 mmol) was added to the above mixture in 1 h.

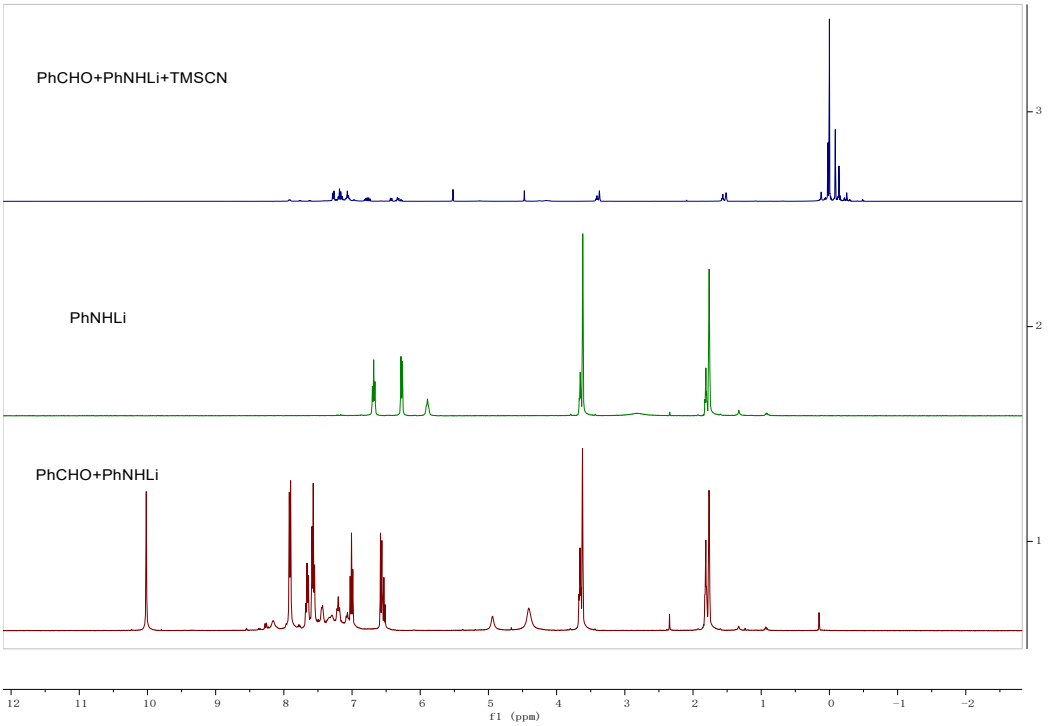


Fig. S4 The copy of ^{1}H NMR spectra of compound PhNHLi (middle, green), the 1:1 mixture of PhCHO and PhNHLi (bottom, red), and the 1:1:1 mixture of PhCHO, PhNHLi and Me_3SiCN (top, blue).

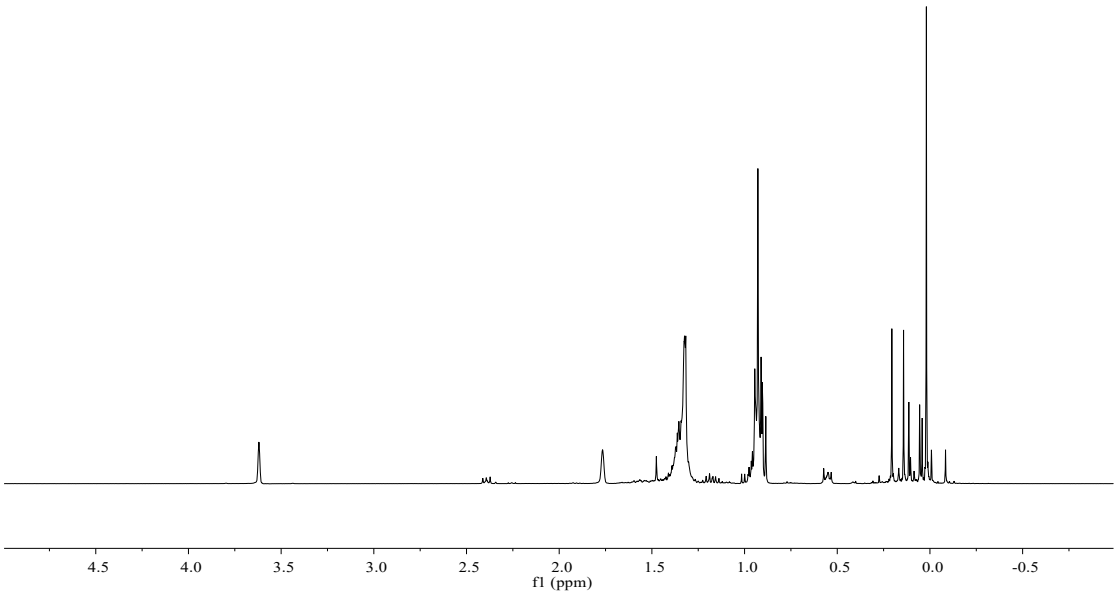


Fig. S5 The copy of ^{1}H NMR spectra of the 1:1 mixture of Me_3SiCN and n-BuLi. Reaction conditions: Me_3SiCN (0.05 mmol) and n-BuLi (0.05 mmol) in 0.5 mL THF-d_8 at 25 ^{o}C; 1 h.

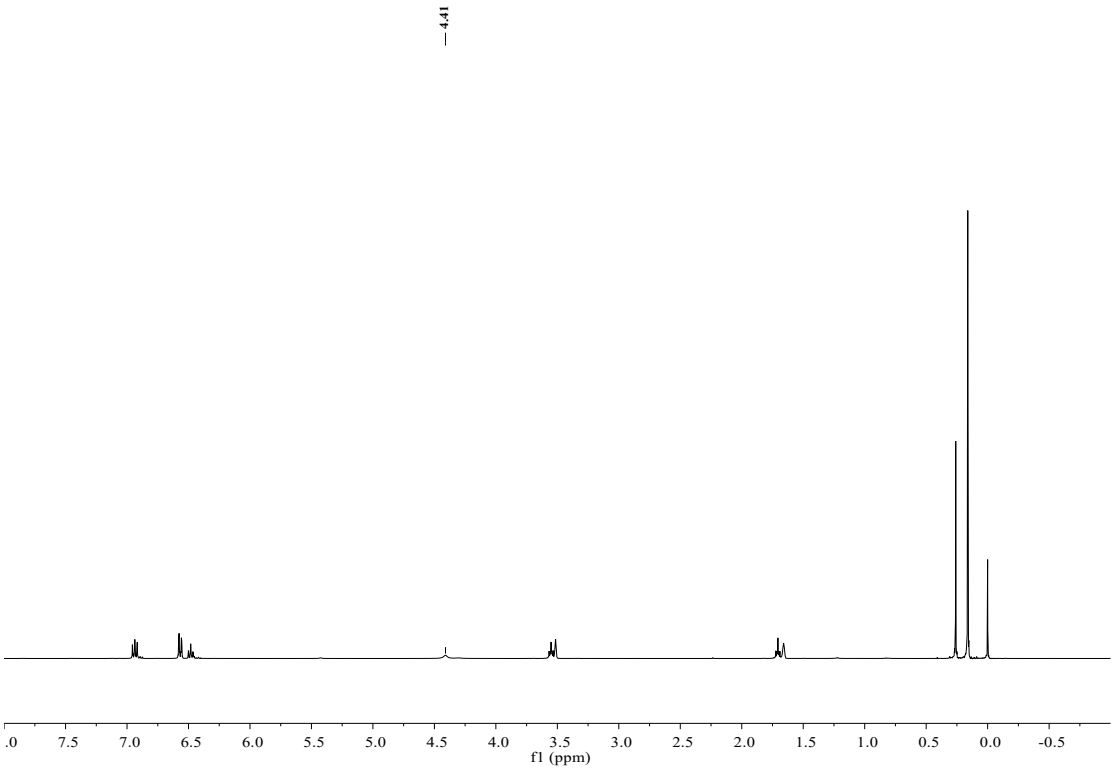
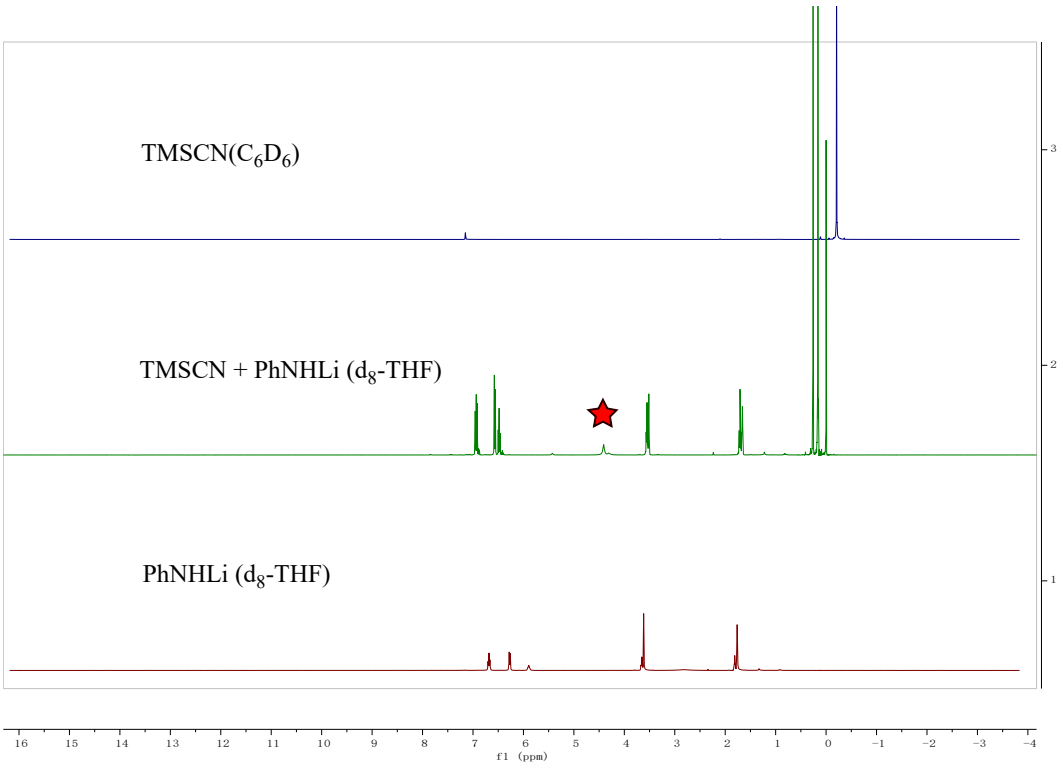


Fig. S6 The copy of ^{1}H NMR spectra (400 MHz) with mesitylene as an internal standard. Reaction conditions: TMSCN (0.05 mmol) and PhNHLi (0.05 mmol) in 0.5 mL THF-d_8 at 25 °C, 1 h; **Fig. S6** corresponding to the middle (green) of the figure below.



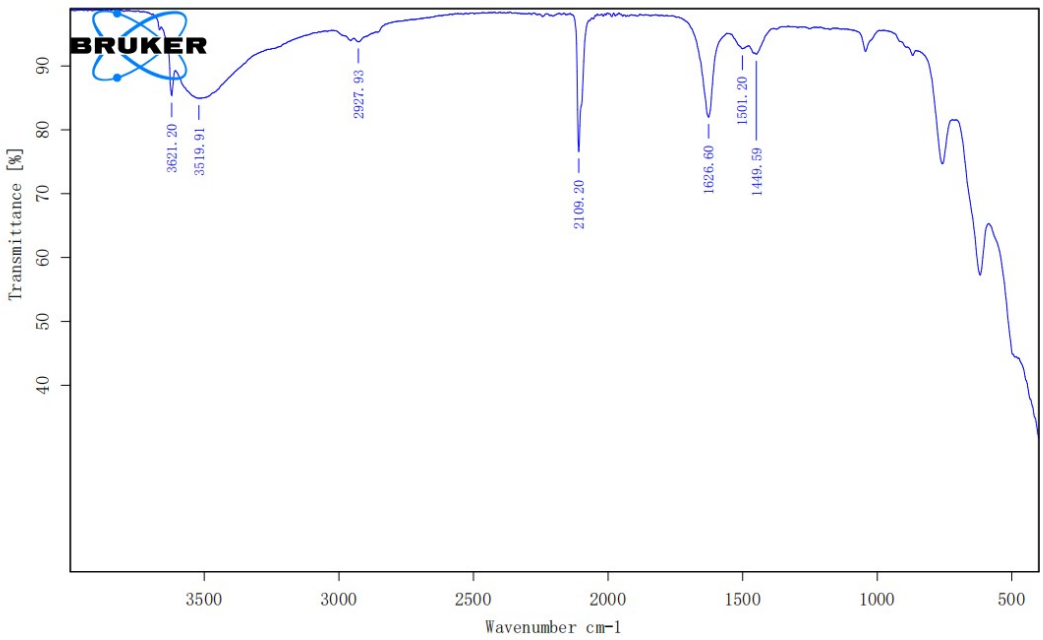
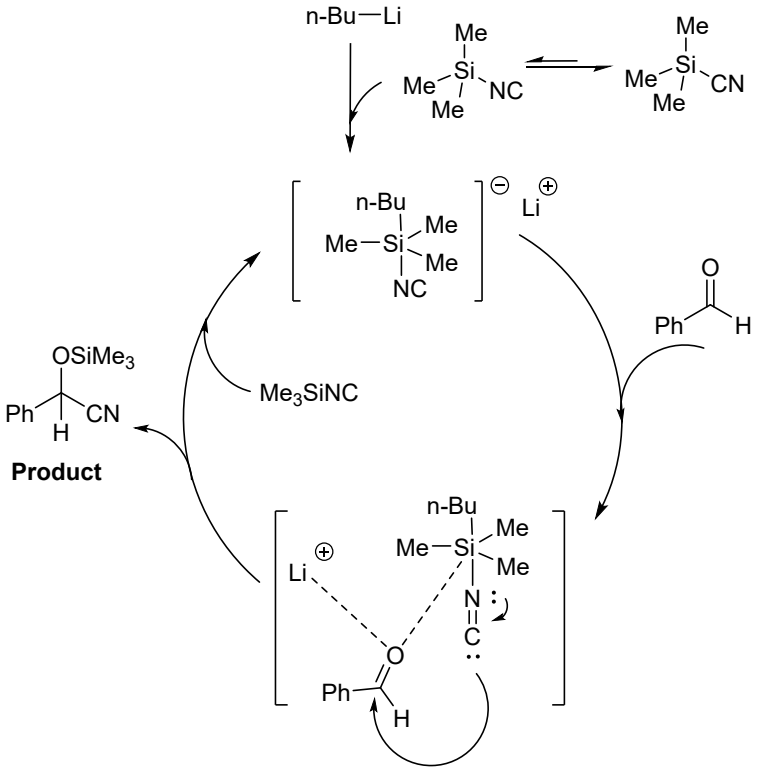


Fig. S7 The IR spectrum of the compound **II**.



Scheme S1 Another Possible Mechanistic Pathway for Cyanosilylation of Carbonyl Compounds Catalyzed by *n*-BuLi.

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