A Metal-free Hydrosilylation for the Reduction of Aromatic Nitriles

Christoph Bornschein, Svenja Werkmeister, Kathrin Junge, and Matthias Beller[a*]
Leibniz-Insitut für Katalyse e.V., Albert-Einstein-Straße 29a, 18059 Rostock, Germany
E-mail: matthias.beller@catalysis.de

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1. Experimental Section – General Information

Unless otherwise stated, all reactions were run under an argon atmosphere with exclusion of moisture from reagents and glassware using standard techniques for manipulating air-sensitive compounds. All isolated compounds were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy and high resolution mass spectrometry (HRMS). NMR spectra were recorded on Bruker AV 300 or AV 400. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are related to the solvent peaks (DMSO), respectively. All measurements were carried out at room temperature unless otherwise stated. Mass spectra were in general recorded on a Finnigan MAT 95-XP (Thermo Electron) or on a 6210 Time-of-Flight LC/MS (Agilent). Gas chromatography was performed on a HP 6890 with a HP5 column.

Reagents: Unless otherwise stated, commercial reagents were used without purification.

2a. Hydrosilylation of Nitriles

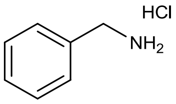
General procedure: A 10 mL Schlenk tube was charged with dry toluene (2.0 mL), nitrile (1.0 mmol) and phenylsilane (1.3 mmol) and stirred for 10 min. To start the reaction tetra-*n*-butylammonium fluoride (0.05 mmol), 1 M solution in THF, was added under an argon atmosphere. After stirring 60 min at room temperature 1 mL of a 1 M HCl-Solution in MeOH was carefully added to the coloured reaction mixture.* After completion of the hydrolysis (ca. 90 min) hexadecane was added as an internal standard and the yield determined by GC (30 m HP Agilent Technologies column, 50–300 °C, benzonitrile: 7.08 min, benzylamine: 7.60 min). For isolation of the products the reaction mixture was concentrated to dryness. The hydrochloride salt of the amine was washed with Et_2O and ethyl acetate to gain the pure product as white crystals.

* We advise to ensure for sufficient gas exchange in the reaction vessel to avoid the formation of inflammable silanes.

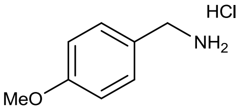
2b. Hydrosilylation of other Carbonyl Compounds

General procedure: A 10 mL Schlenk tube was charged with dry toluene (2.0 mL), carbonyl substrate (1.0 mmol) and phenylsilane (1.3 mmol) and stirred for 10 min. To start the reaction tetra-*n*-butylammonium fluoride (0.05 mmol), 1 M solution in THF, was added under an argon atmosphere. After stirring 2 hours at room temperature 1 mL of a 1 M HCl-Solution in MeOH was carefully added to the coloured reaction mixture. After completion of the hydrolysis (ca. 90 min) the reaction mixture was concentrated to dryness. The crude residue was neutralized and extracted with ethyl acetate. After washing with brine the combined organic layer were dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by column chromatography (eluent: pentane/ethyl acetate; 1:3) to yield the pure product.

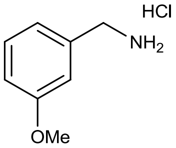
3. Analytical Data



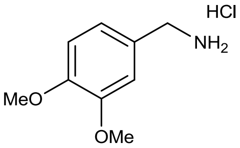
Phenylmethanamine hydrochloride (1b). ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.53 (s, 3H), 7.51 – 7.37 (m, 2H), 7.37 – 7.22 (m, 3H), 3.91 (s, 2H). **^{13}C NMR** (75 MHz, DMSO-*d*$_6$) δ 134.15, 128.89, 128.48, 128.30, 42.1. **HRMS** (ESI-TOF, m/z) calc. for $C_7H_{10}N$ $(M+H)^+$, 108.0808; found 108.0809.



(4-Methoxyphenyl)methanamine hydrochloride (1c). ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.45 (s, 3H), 7.45 – 7.28 (m, 2H), 6.95 – 6.77 (m, 2H), 3.84 (s, 2H), 3.67 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-*d*$_6$) δ 159.24, 130.52, 125.94, 113.81, 55.14, 41.55. **HRMS** (EI, m/z) calc. for $C_8H_{10}NO$ $(R{=}NH_2)^+$, 136.0757; found 136.0757.

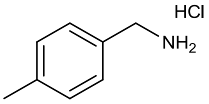


(3-Methoxyphenyl)methanamine hydrochloride (1d). ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.57 (s, 3H), 7.22 (dd, *J* = 8.2, 7.5 Hz, 1H), 7.11 (dd, *J* = 2.6, 1.5 Hz, 1H), 6.98 (ddd, *J* = 7.6, 1.7, 0.9 Hz, 1H), 6.84 (ddd, *J* = 8.4, 2.6, 0.9 Hz, 1H), 3.89 (s, 2H), 3.68 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-*d*$_6$) δ 159.22, 135.51, 129.57, 120.91, 114.43, 113.87, 55.14, 41.99. **HRMS** (ESI-TOF, m/z) calc. for $C_8H_{12}NO$ $(M+H)^+$, 138.0913; found 138.0915.

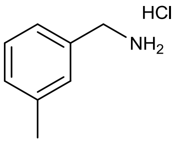


(3,4-Dimethoxyphenyl)methanamine hydrochloride (1e). ^{1}H NMR (300 MHz, DMSO-*d*$_6$) δ 8.42 (s, 3H), 7.17 (d, *J* = 1.9 Hz, 1H), 6.96 – 6.82 (m, 2H), 3.84 (s, 2H), 3.68 (s, 3H), 3.66 (s, 3H). **^{13}C NMR** δ (75 MHz, DMSO-*d*$_6$) δ 148.75, 148.52, 126.24, 121.37, 112.86, 111.46, 55.51, 41.98. **HRMS**

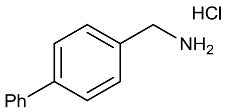
(ESI-TOF, m/z) calc. for $C_9H_{14}NO_2$ $(M+H)^+$, 168.1019; found 168.1018, calc. for $C_9H_{14}NNaO_2$ $(M+Na)^+$, 190.0839; found 190.0839.



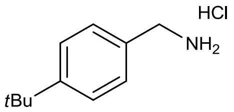
***p*-Tolylmethanamine hydrochloride (1f).** **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.62 – 8.25 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 3.86 (s, 2H), 2.22 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 137.65, 131.02, 128.99, 128.92, 128.89, 41.81, 20.71. **HRMS** (ESI-TOF, m/z) calc. for $C_8H_{12}N$ $(M+H)^+$, 122.0964, found 122.0966.



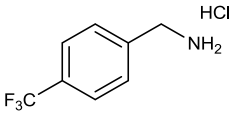
***m*-Tolylmethanamine hydrochloride (1g).** **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.43 (s, 3H), 7.29 – 7.14 (m, 3H), 7.16 – 7.00 (m, 1H), 3.87 (s, 2H), 2.23 (s, 3H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 137.65, 133.95, 129.45, 128.90, 128.44, 125.92, 42.04, 40.27, 20.91. **HRMS** (ESI-TOF, m/z) calcc. for $C_8H_{12}N$ $(M+H)^+$, 122.0964, found 122.0964.



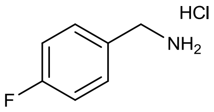
Biphenyl-4-ylmethanamine hydrochloride (1h). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.53 (s, 3H), 7.70 – 7.56 (m, 4H), 7.56 – 7.47 (m, 2H), 7.45 – 7.34 (m, 2H), 7.34 – 7.21 (m, 1H), 3.97 (s, 2H).; **^{13}C NMR** (75 MHz, DMSO-d_6) δ140.12, 139.47, 133.24, 129.56, 128.94, 127.63, 126.71, 126.64, 41.76, 38.61. **HRMS** (ESI-TOF, m/z) calc. for $C_{13}H_{14}N$ $(M+H)^+$, 184.1121, found 184.1120.



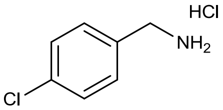
(4-*Tert*-butylphenyl)methanamine hydrochloride (1i). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.44 (s, 3H), 7.34 (s, 4H), 3.87 (s, 2H), 1.19 (s, 9H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 150.88, 131.10, 128.72, 125.25, 41.74, 34.29, 31.02. **HRMS** (ESI-TOF, m/z) calc. for $C_{11}H_{18}N$ $(M+H)^+$, 164.1434, found 164.1431.



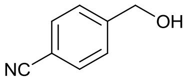
(4-(Trifluoromethyl)phenyl)methanamine hydrochloride (1j). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.67 (s, 3H), 7.87 – 7.51 (m, 4H), 4.04 (s, 2H). **^{13}C NMR** (75 MHz, DMSO-d_6) δ 138.78, 129.75, 129.40, 128.98, 128.56, 128.14, 125.88, 125.35, 125.30, 125.25, 125.20, 122.27, 41.49, 38.59. **HRMS** (ESI-TOF, m/z) calc. for $C_8H_9F_3N$ $(M+H)^+$, 176.0682, found 176.0680.



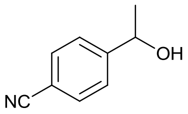
(4-Fluorophenyl)methanamine hydrochloride (1k). **^{1}H NMR** (300 MHz, DMSO-d_6) δ 8.44 (s, 3H), 7.55 – 7.42 (m, 2H), 7.23 – 7.10 (m, 2H), 3.92 (s, 2H).^{13}C **NMR** (75 MHz, DMSO-*d*$_6$) δ 163.61, 160.37, 131.40, 131.29, 130.37, 130.33, 115.41, 115.12, 41.29. **HRMS** (EI, m/z) calc. for C_7H_8NF (M)$^+$, 125.0636, found 125.0626.



(4-Chlorophenyl)methanamine hydrochloride (1l). ^{1}**H NMR** (300 MHz, DMSO-*d*$_6$) δ 8.53 (s, 3H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 2H). ^{13}**C NMR** (75 MHz, DMSO-*d*$_6$) δ 133.07, 133.04, 130.95, 128.43, 41.32, 38.61. **HRMS** (ESI-TOF, m/z) calc. for C_7H_9ClN (M+H)$^+$, 142.0418 + 144.0389, found 142.0418 + 144.0387.



4-(Hydroxymethyl)benzonitrile (2a). ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 7.62 – 7.46 (m, 2H), 7.45 – 7.32 (m, 2H), 4.68 (s, 2H), 2.42 (s, 1H). ^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 146.43, 132.31, 127.04, 118.93, 110.94, 64.10. **HRMS** (EI, m/z) calc. for C_8H_7NO (M)$^+$, 133.0522, found 133.0518.

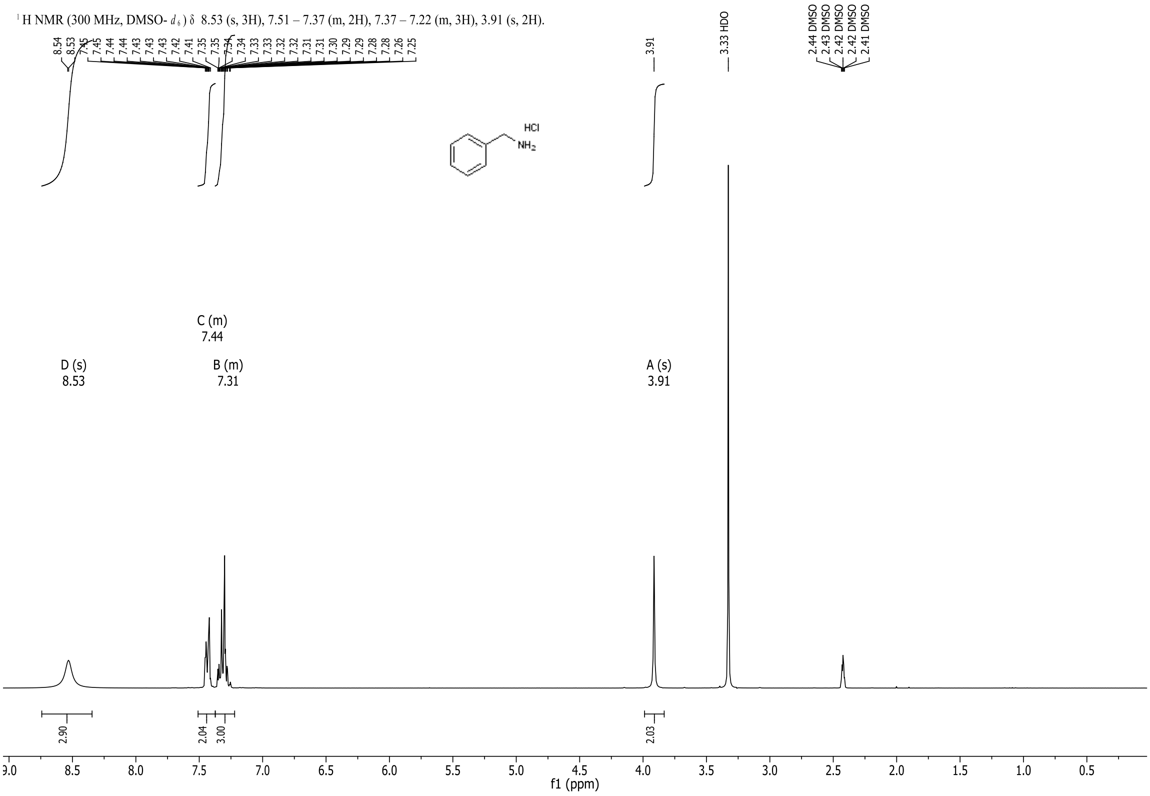


4-(1-Hydroxyethyl)benzonitrile (2b). ^{1}**H NMR** (300 MHz, Chloroform-*d*) δ 7.57 – 7.48 (m, 2H), 7.44 – 7.34 (m, 2H), 4.85 (q, *J* = 6.5 Hz, 1H), 2.65 – 2.54 (m, 1H), 1.39 (d, *J* = 6.5 Hz, 3H). ^{13}**C NMR** (75 MHz, Chloroform-*d*) δ 51.37, 132.31, 126.12, 118.94, 110.77, 69.52, 25.38. **HRMS** (ESI-TOF, m/z) calc. for $C_9H_{10}NO$ (M+H)$^+$, 148.0757, found 148.0755; C_9H_9NONa (M+Na)$^+$, 170.0576, found 170.0572.

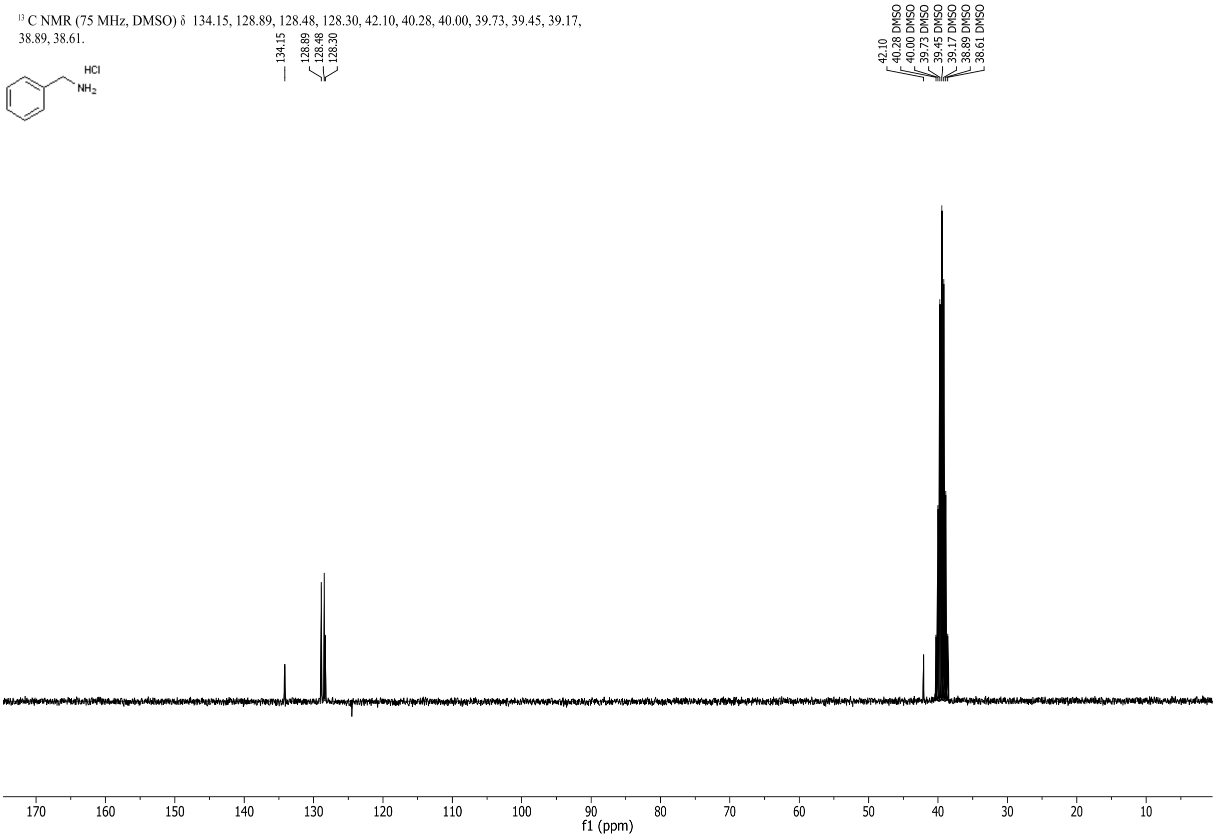
4. Copies of ^{1}H NMR and ^{13}C NMR

Phenylmethanamine hydrochloride (1b)

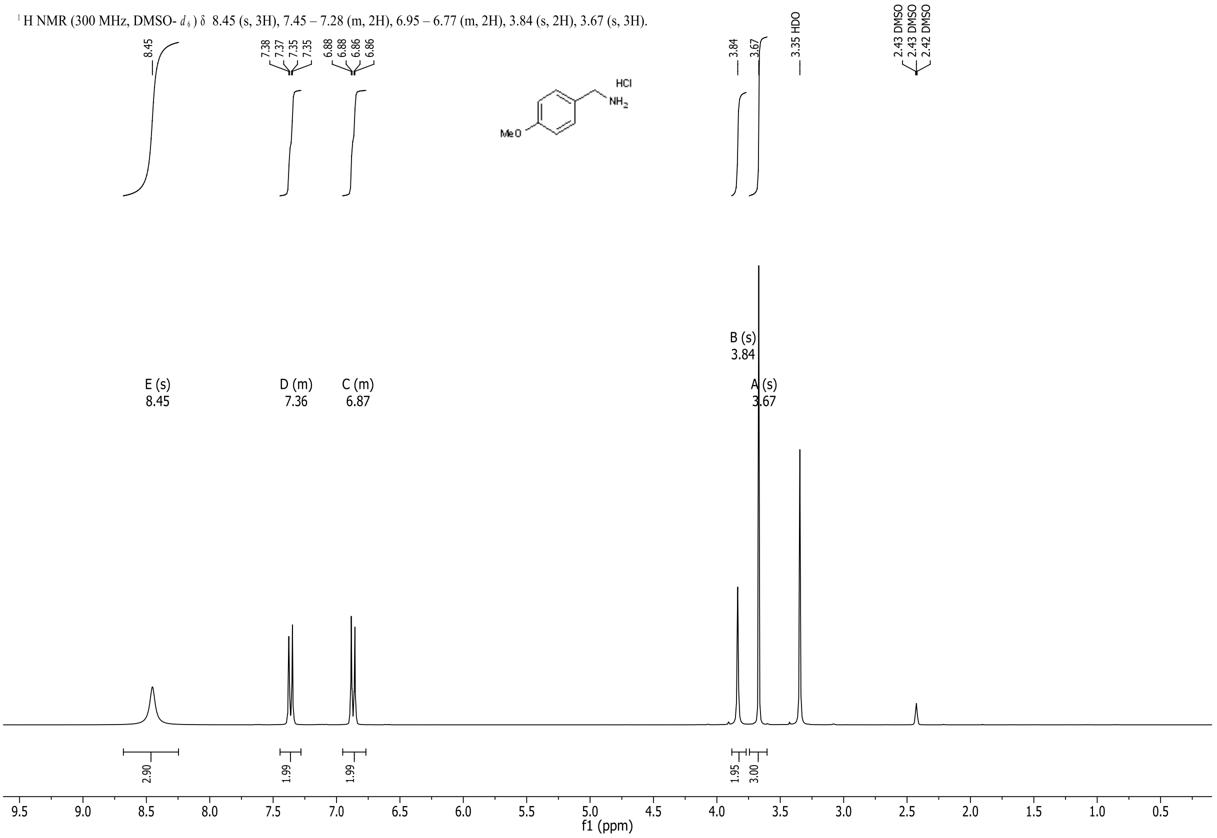
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.53 (s, 3H), 7.51 – 7.37 (m, 2H), 7.37 – 7.22 (m, 3H), 3.91 (s, 2H).



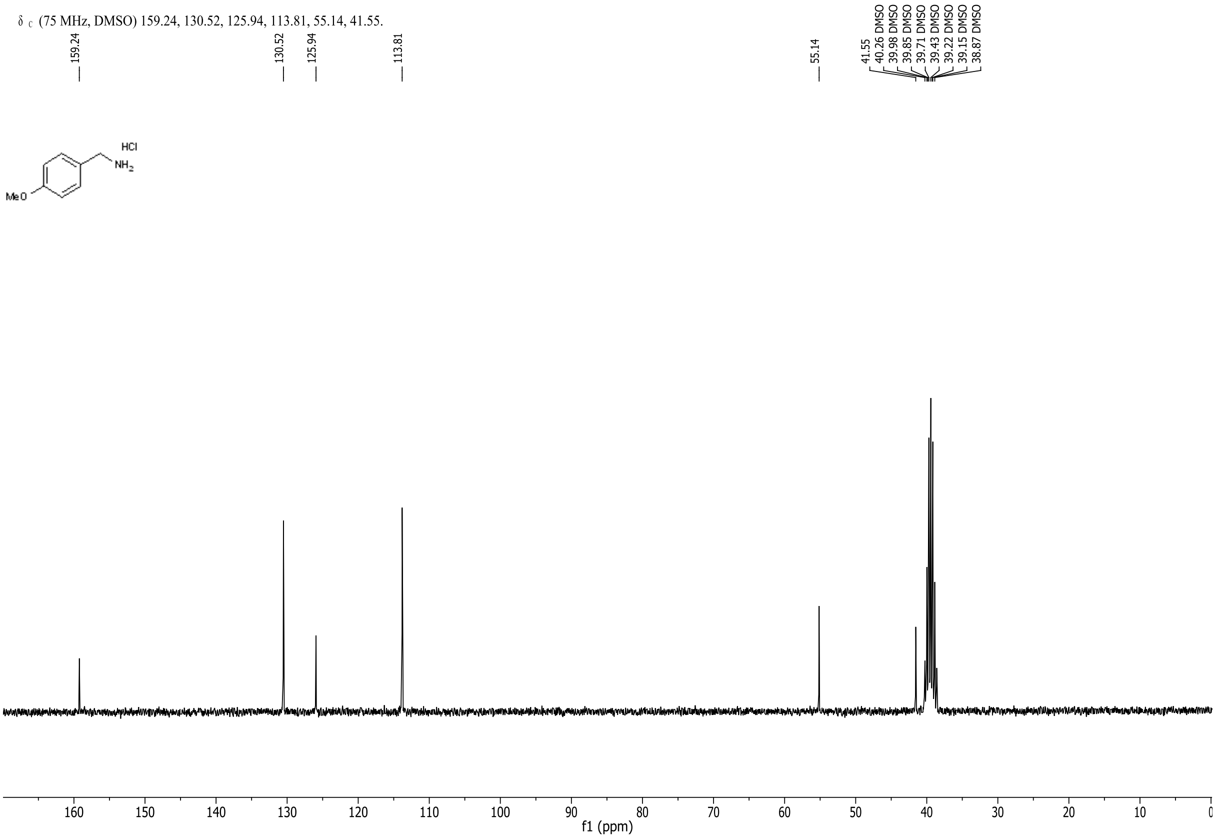
^{13}C NMR (75 MHz, DMSO) δ 134.15, 128.89, 128.48, 128.30, 42.10, 40.28, 40.00, 39.73, 39.45, 39.17, 38.89, 38.61.



(4-Methoxyphenyl)methanamine hydrochloride (1c)



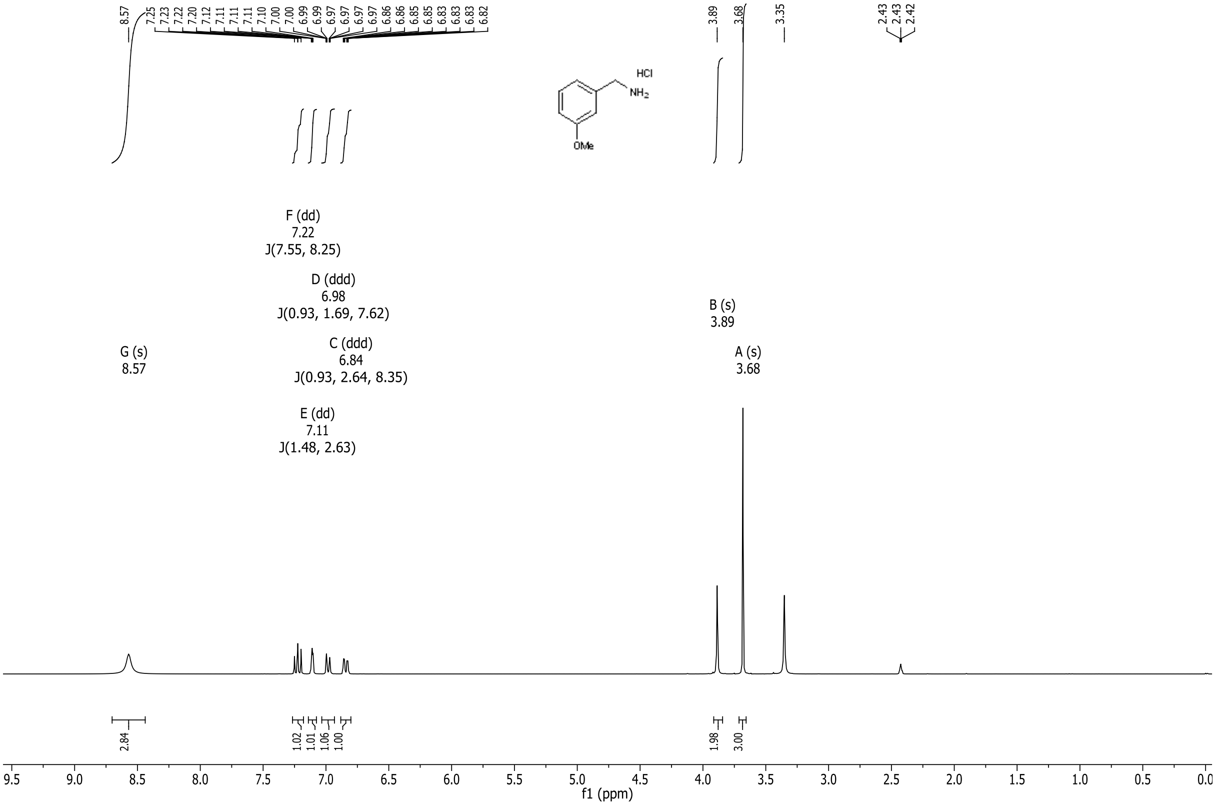
^{1}H NMR (300 MHz, DMSO-d_6) δ 8.45 (s, 3H), 7.45 – 7.28 (m, 2H), 6.95 – 6.77 (m, 2H), 3.84 (s, 2H), 3.67 (s, 3H).



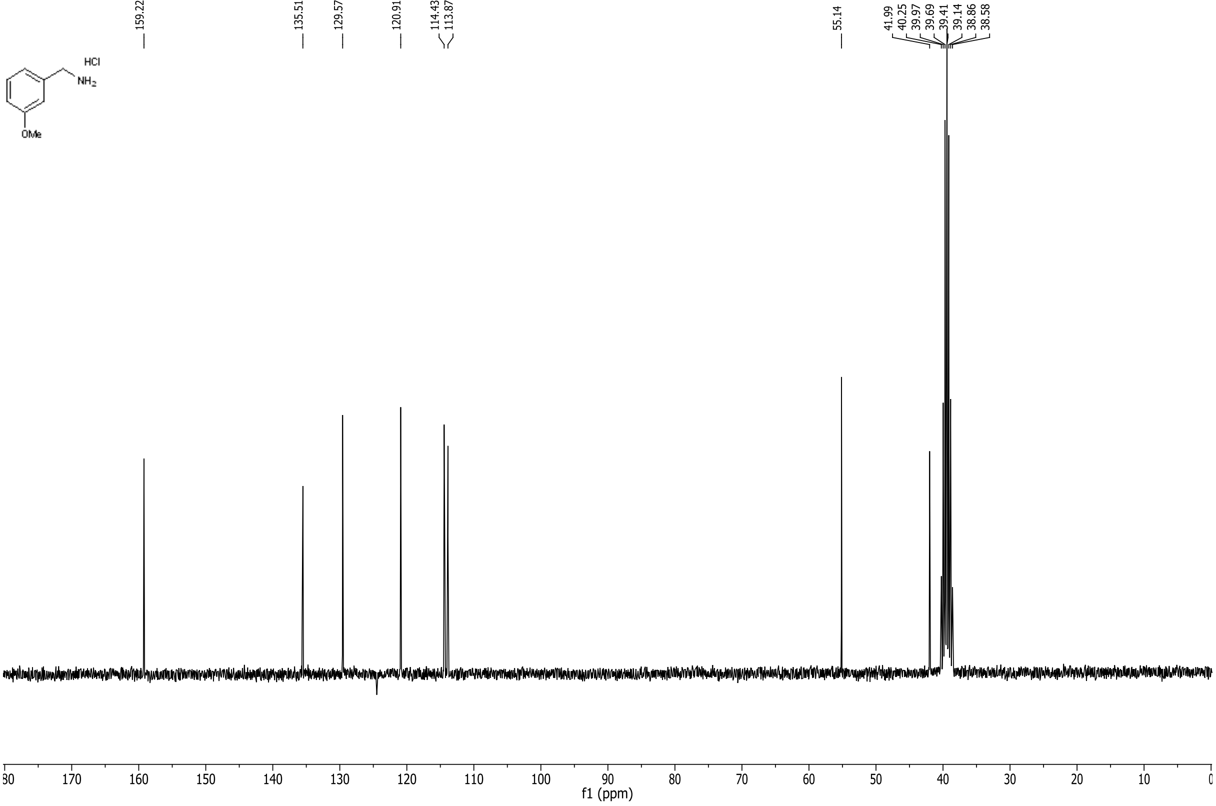
δ$_C$ (75 MHz, DMSO) 159.24, 130.52, 125.94, 113.81, 55.14, 41.55.

(3-Methoxyphenyl)methanamine hydrochloride (1d).

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.57 (s, 3H), 7.22 (dd, J = 8.2, 7.5 Hz, 1H), 7.11 (dd, J = 2.6, 1.5 Hz, 1H), 6.98 (ddd, J = 7.6, 1.7, 0.9 Hz, 1H), 6.84 (ddd, J = 8.4, 2.6, 0.9 Hz, 1H), 3.89 (s, 2H), 3.68 (s, 3H).

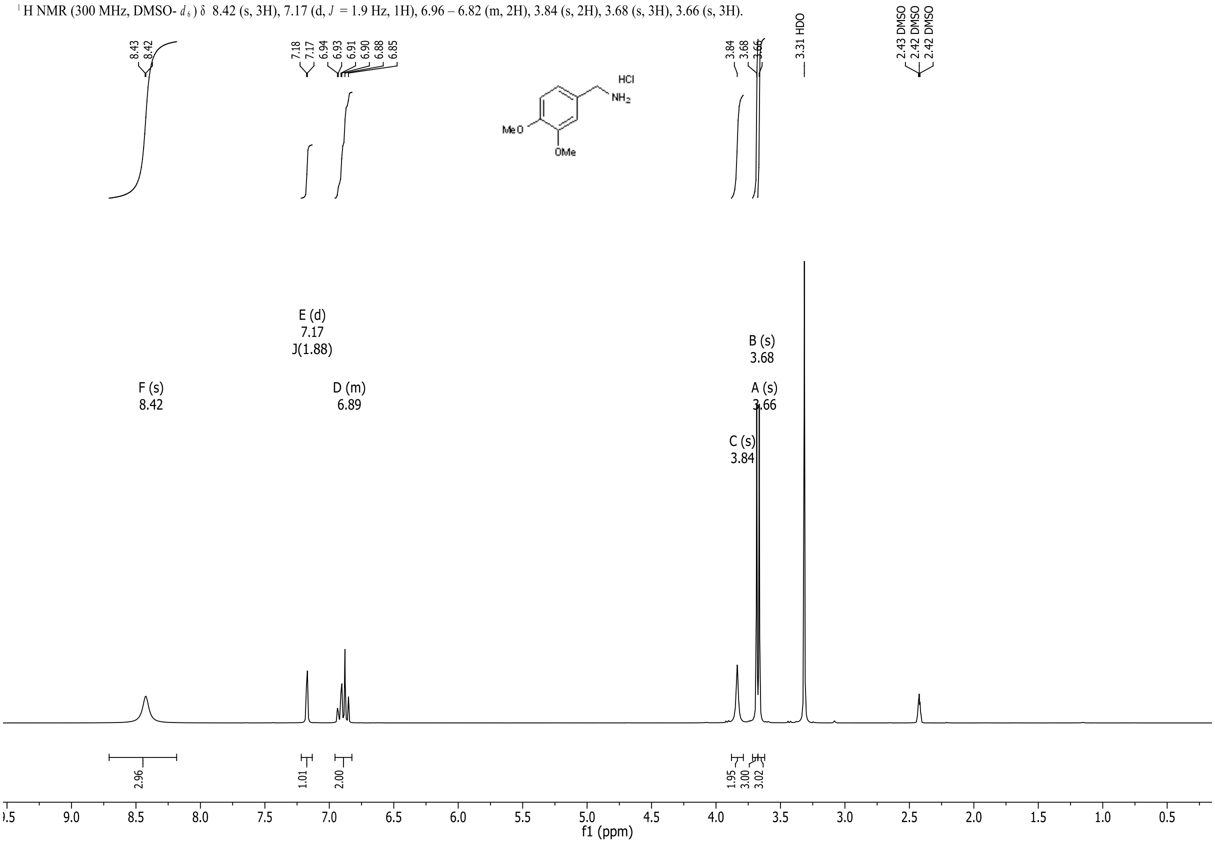


δ$_C$ (75 MHz, DMSO) 159.22, 135.51, 129.57, 120.91, 114.43, 113.87, 55.14, 41.99.

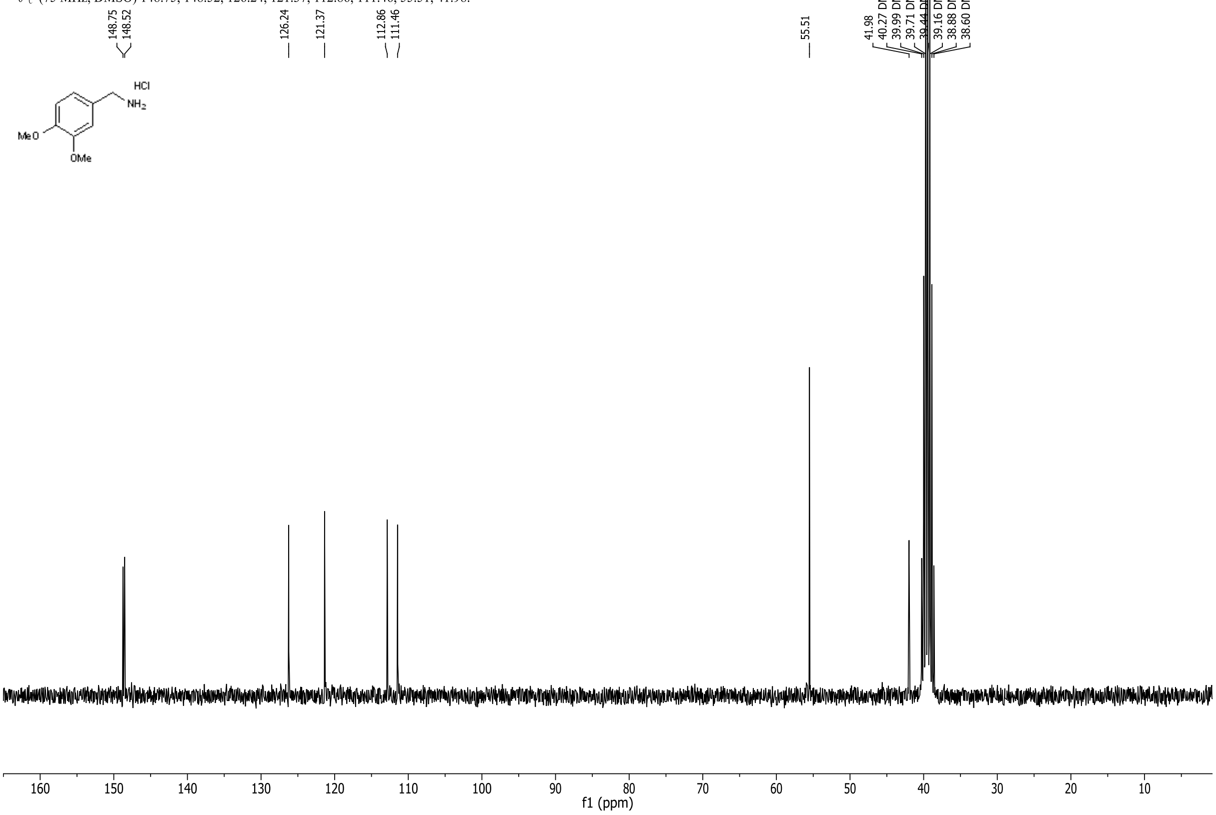


(3,4-Dimethoxyphenyl)methanamine hydrochloride (1e)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.42 (s, 3H), 7.17 (d, J = 1.9 Hz, 1H), 6.96 – 6.82 (m, 2H), 3.84 (s, 2H), 3.68 (s, 3H), 3.66 (s, 3H).

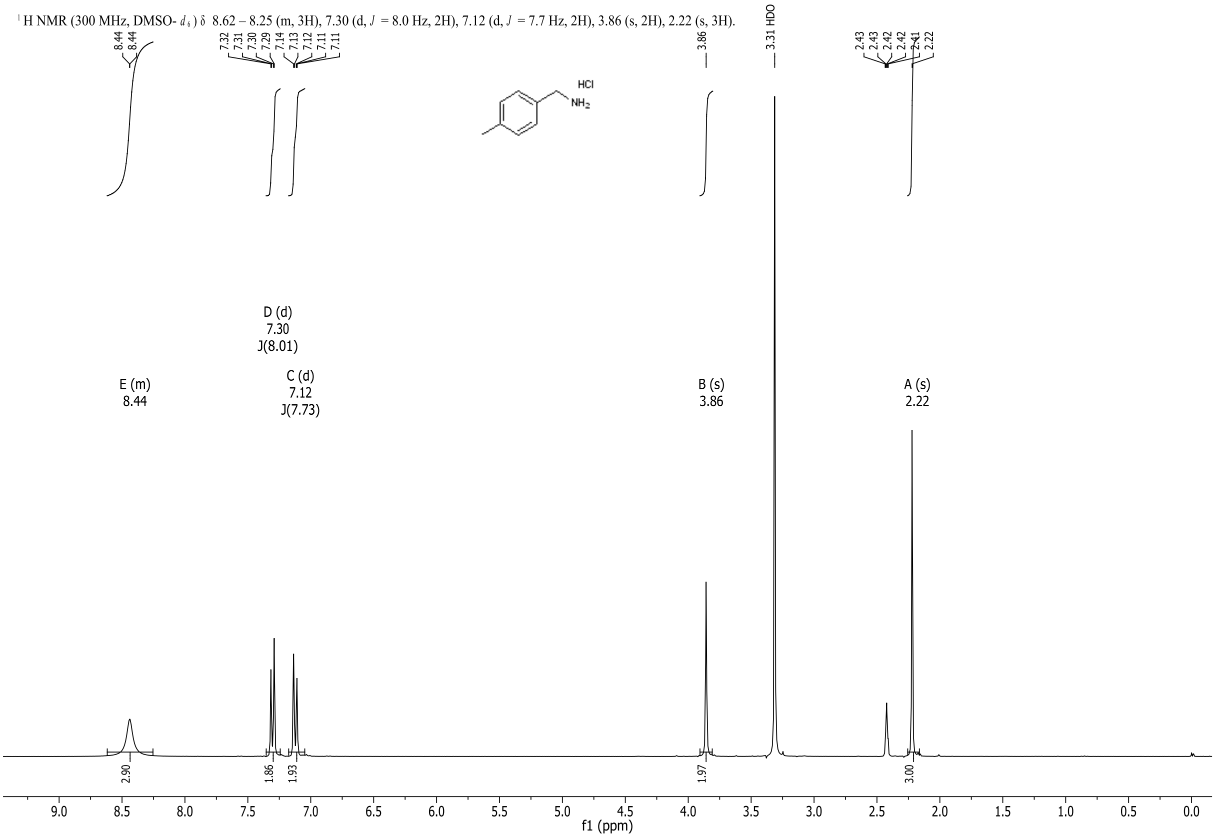


δ$_C$ (75 MHz, DMSO) 148.75, 148.52, 126.24, 121.37, 112.86, 111.46, 55.51, 41.98.

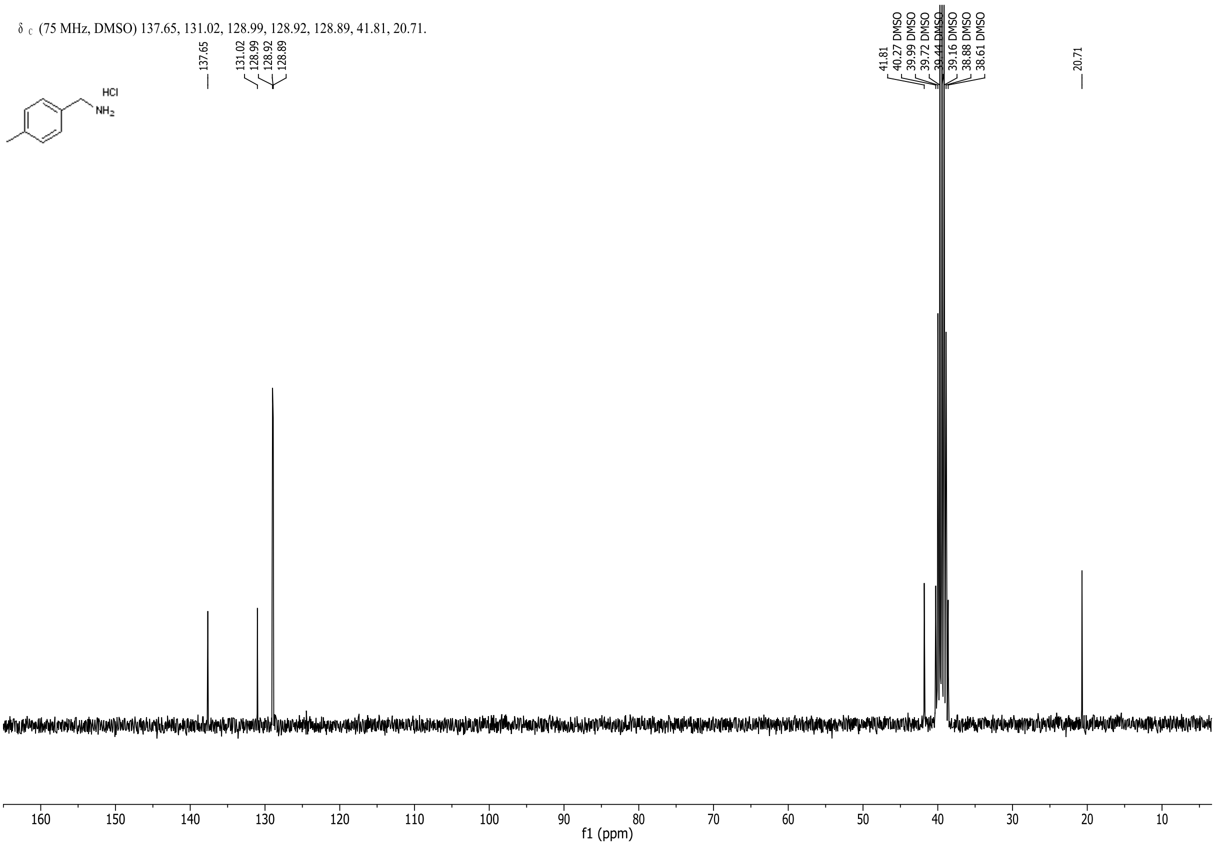


p-Tolylmethanamine hydrochloride (1f).

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.62 – 8.25 (m, 3H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.7 Hz, 2H), 3.86 (s, 2H), 2.22 (s, 3H).

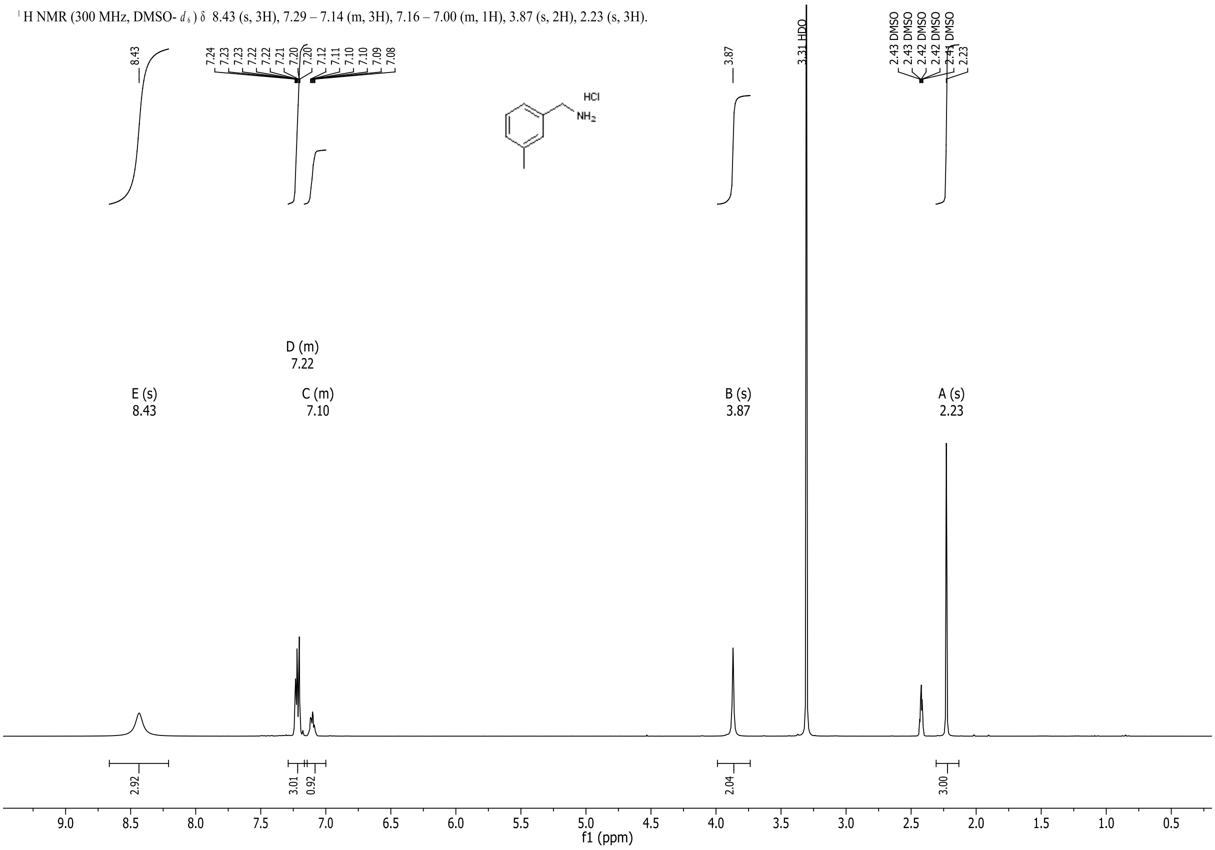


δ$_C$ (75 MHz, DMSO) 137.65, 131.02, 128.99, 128.92, 128.89, 41.81, 20.71.

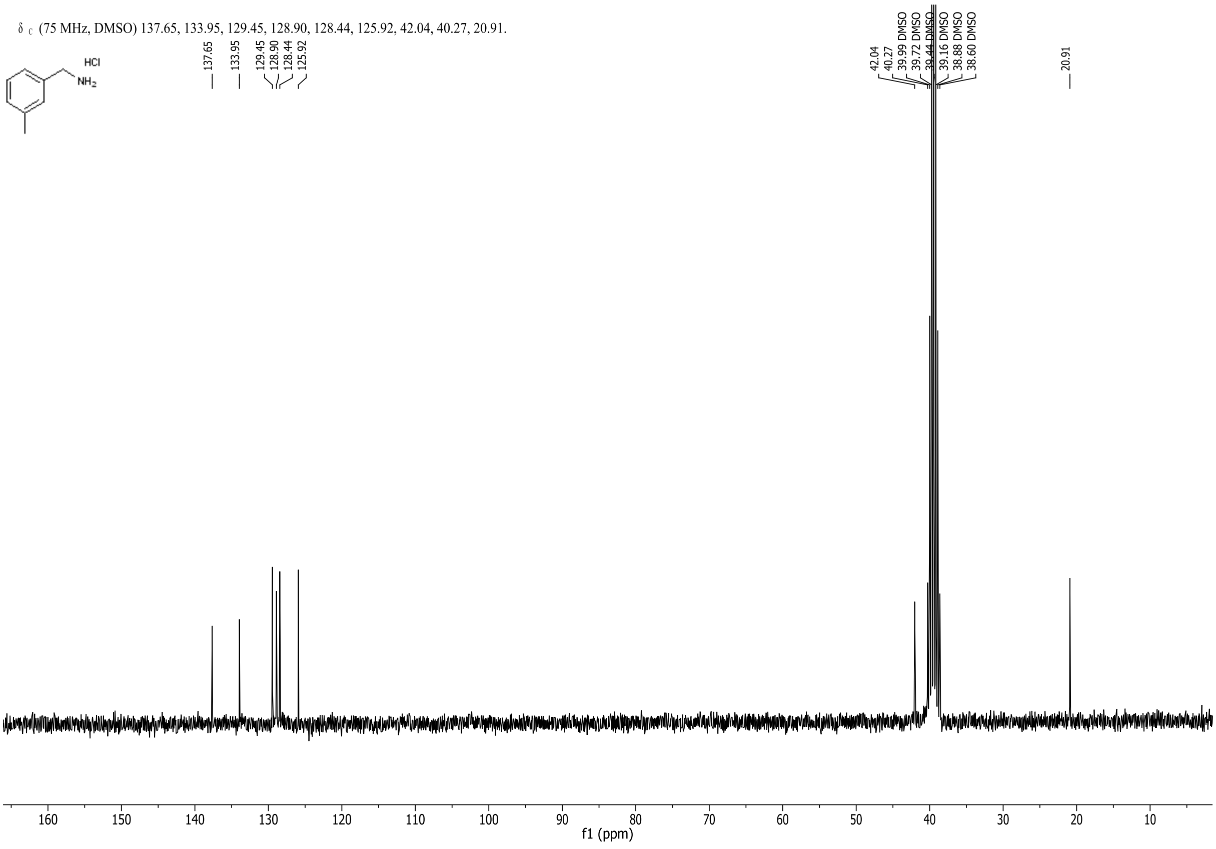


m-Tolylmethanamine hydrochloride (1g)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.43 (s, 3H), 7.29 – 7.14 (m, 3H), 7.16 – 7.00 (m, 1H), 3.87 (s, 2H), 2.23 (s, 3H).

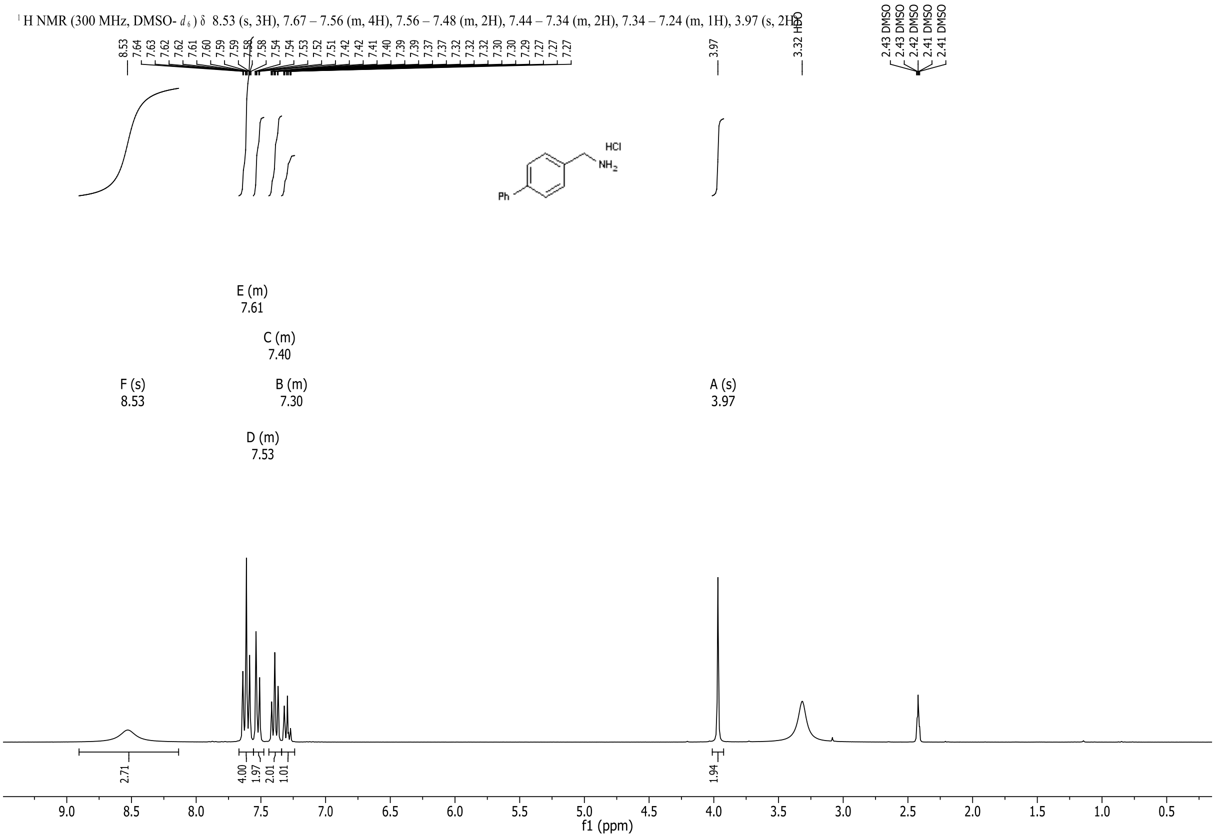


δ$_C$ (75 MHz, DMSO) 137.65, 133.95, 129.45, 128.90, 128.44, 125.92, 42.04, 40.27, 20.91.

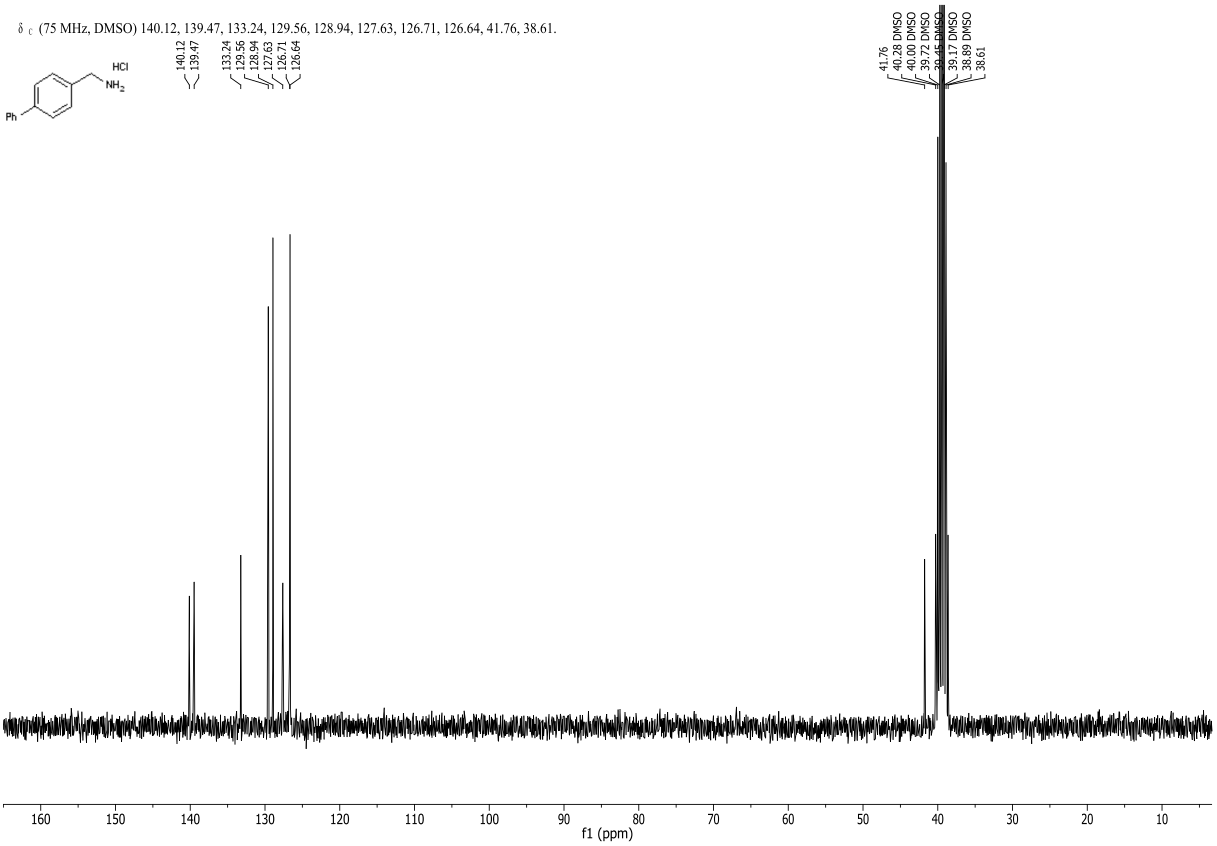


Biphenyl-4-ylmethanamine hydrochloride (1h).

^{1}H NMR (300 MHz, DMSO- d_6) δ 8.53 (s, 3H), 7.67 – 7.56 (m, 4H), 7.56 – 7.48 (m, 2H), 7.44 – 7.34 (m, 2H), 7.34 – 7.24 (m, 1H), 3.97 (s, 2H)

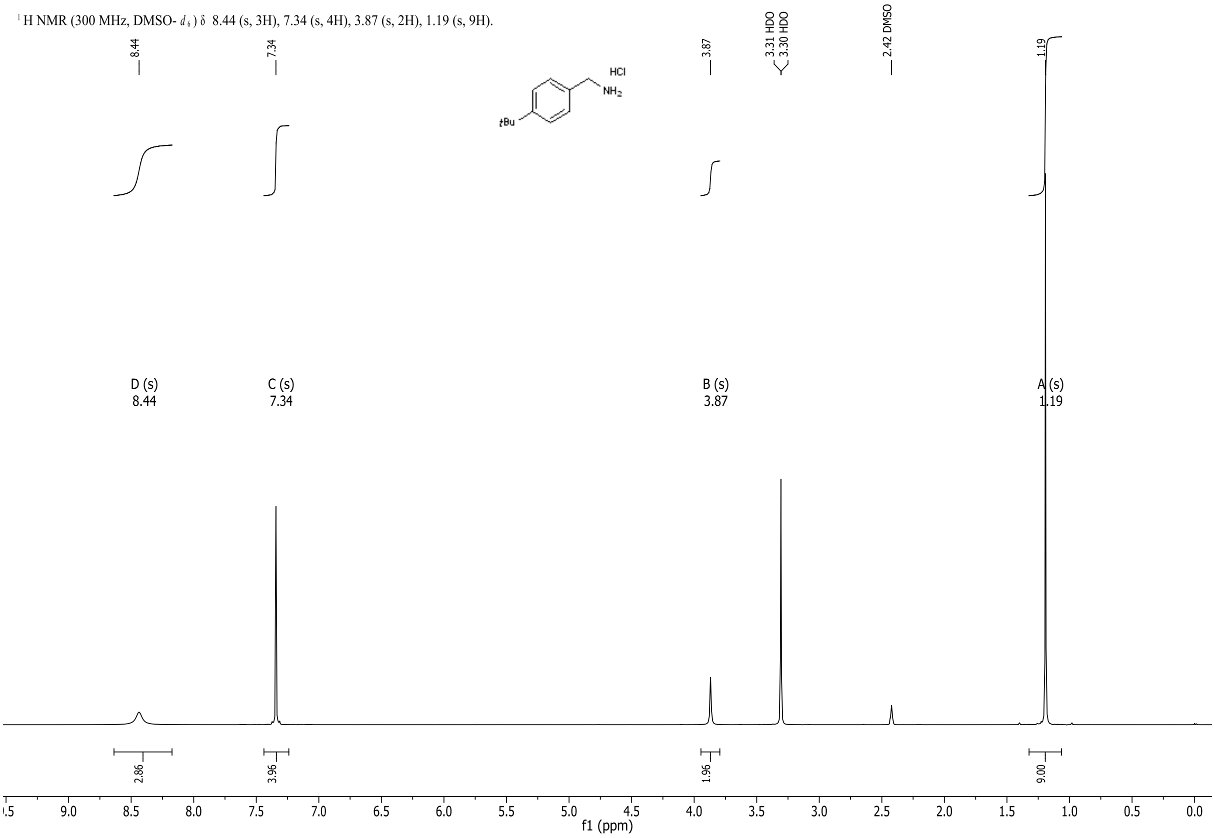


δ C (75 MHz, DMSO) 140.12, 139.47, 133.24, 129.56, 128.94, 127.63, 126.71, 126.64, 41.76, 38.61.

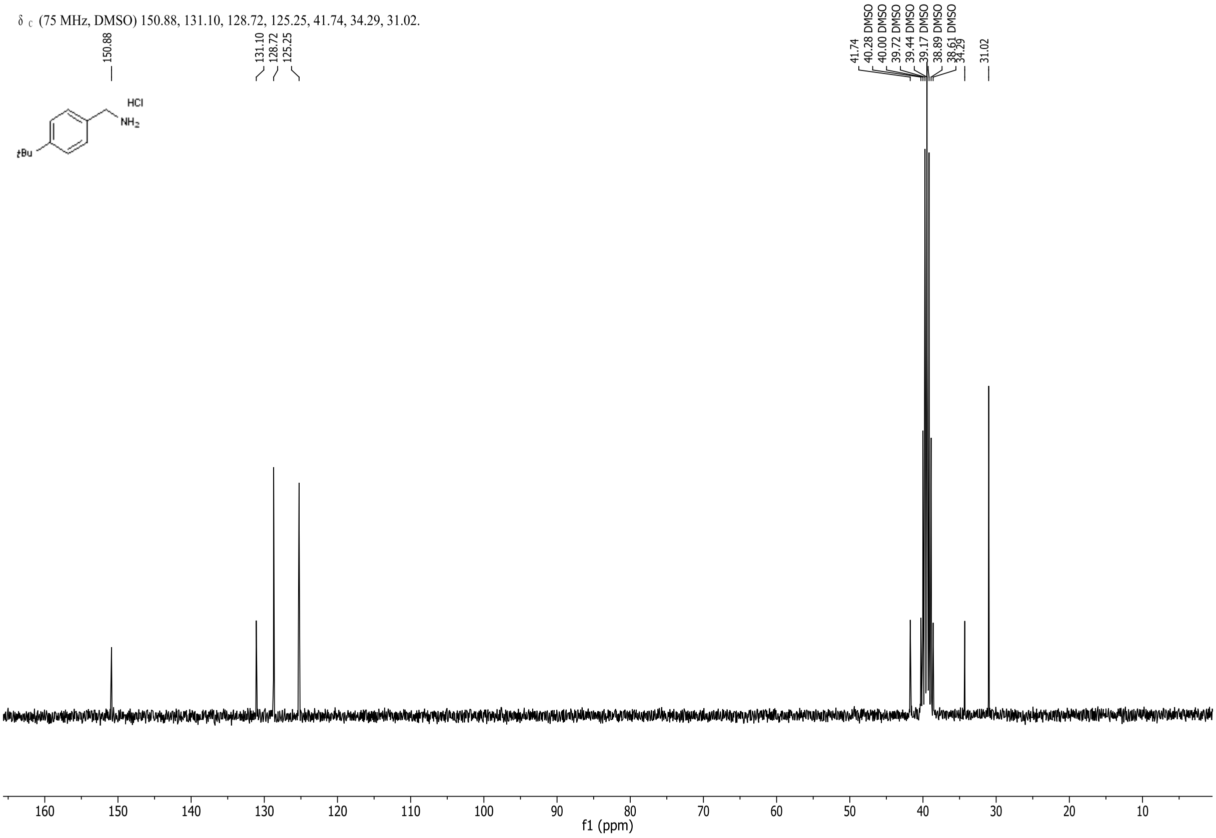


(4-*Tert*-butylphenyl)methanamine hydrochloride (1i)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.44 (s, 3H), 7.34 (s, 4H), 3.87 (s, 2H), 1.19 (s, 9H).

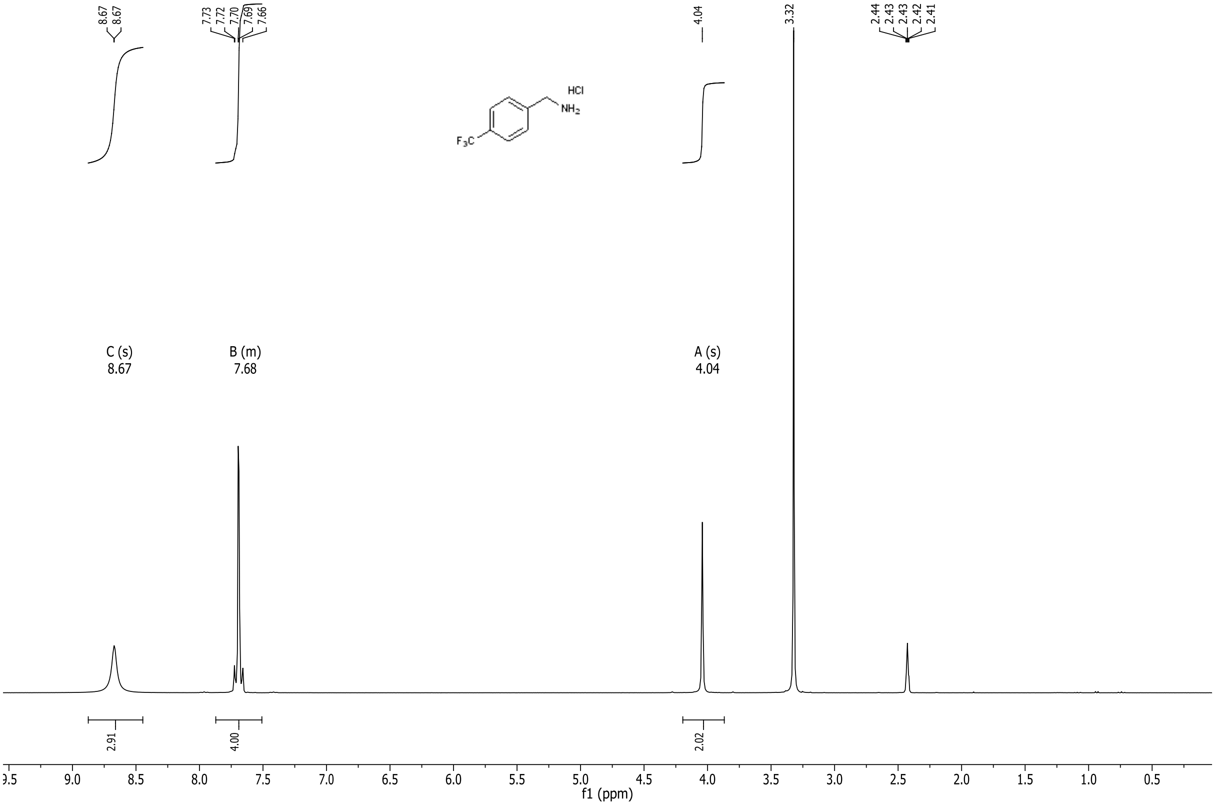


δ$_C$ (75 MHz, DMSO) 150.88, 131.10, 128.72, 125.25, 41.74, 34.29, 31.02.

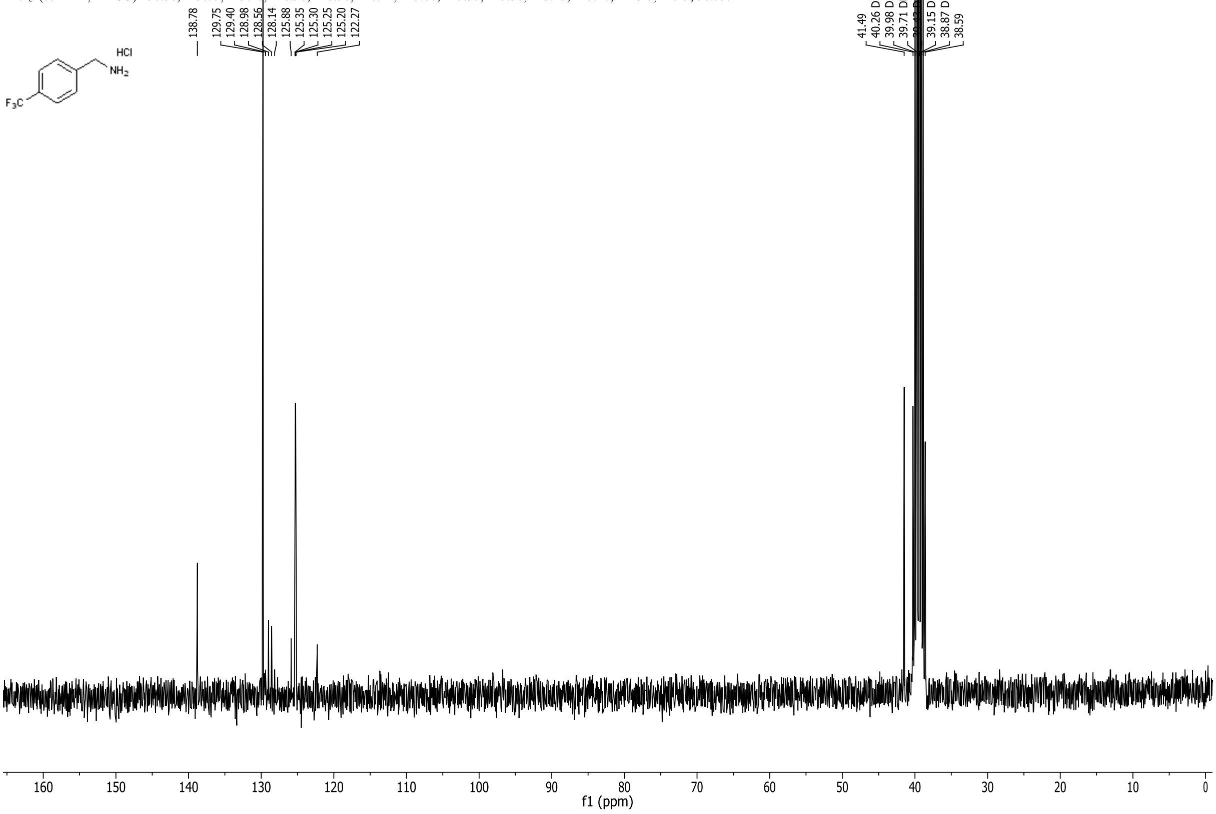


(4-(Trifluoromethyl)phenyl)methanamine hydrochloride (1j)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.67 (s, 3H), 7.87 – 7.51 (m, 4H), 4.04 (s, 2H).

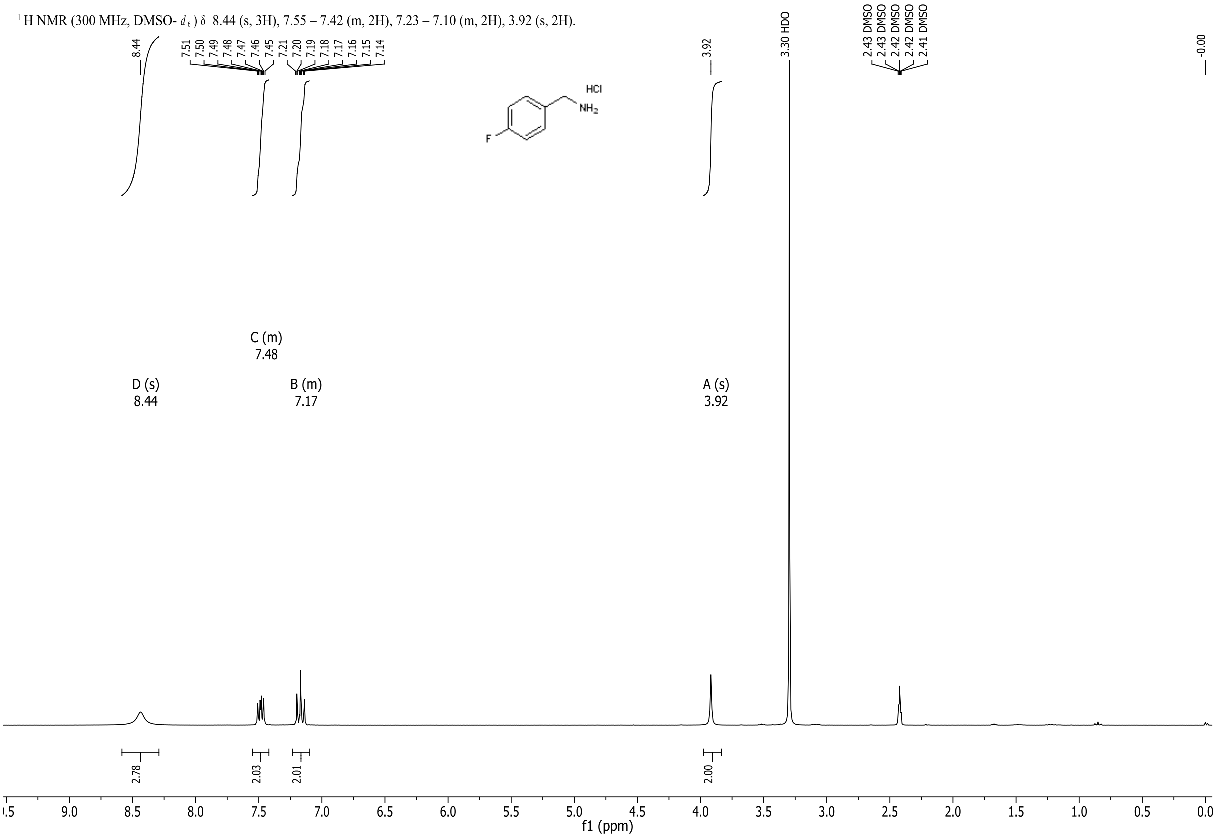


δ$_C$ (75 MHz, DMSO) 138.78, 129.75, 129.40, 128.98, 128.56, 128.14, 125.88, 125.35, 125.30, 125.25, 125.20, 122.27, 41.49, 38.59.

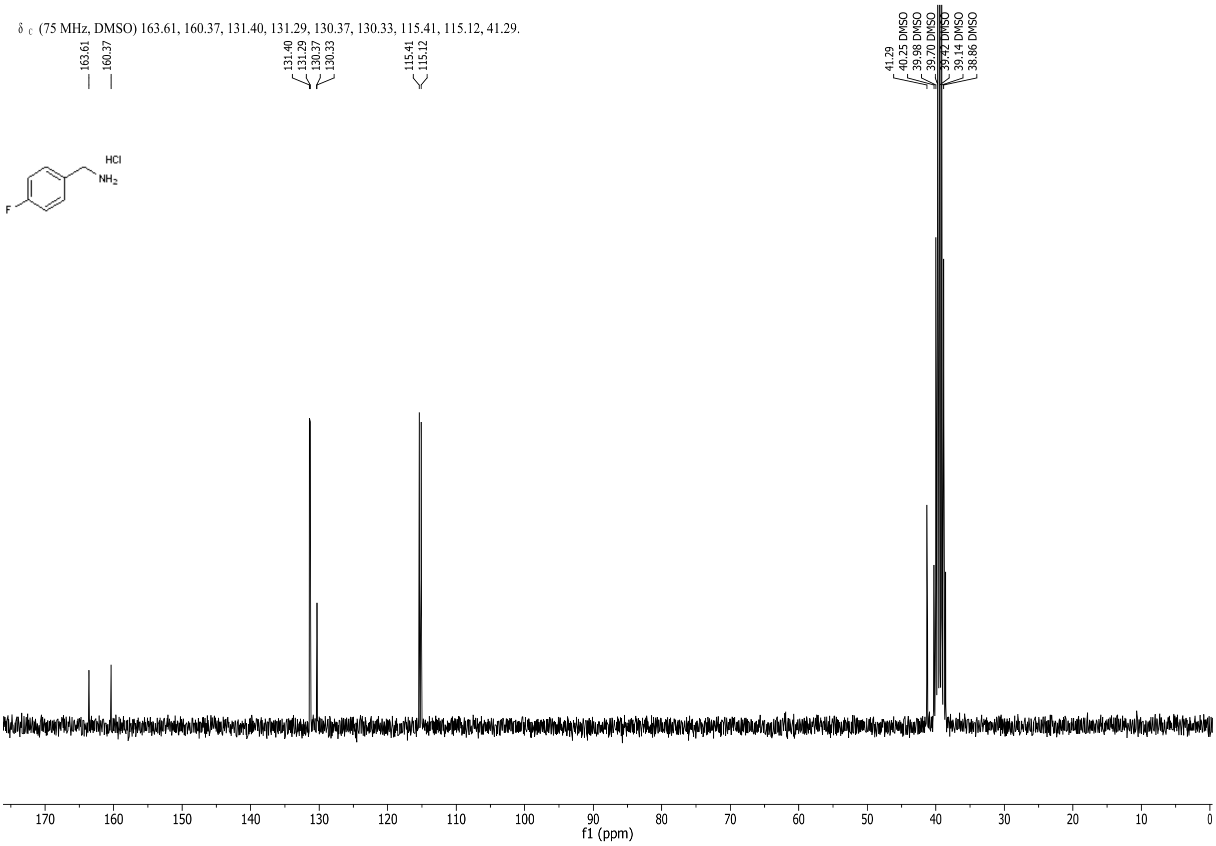


(4-Fluorophenyl)methanamine hydrochloride (1k).

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.44 (s, 3H), 7.55 – 7.42 (m, 2H), 7.23 – 7.10 (m, 2H), 3.92 (s, 2H).

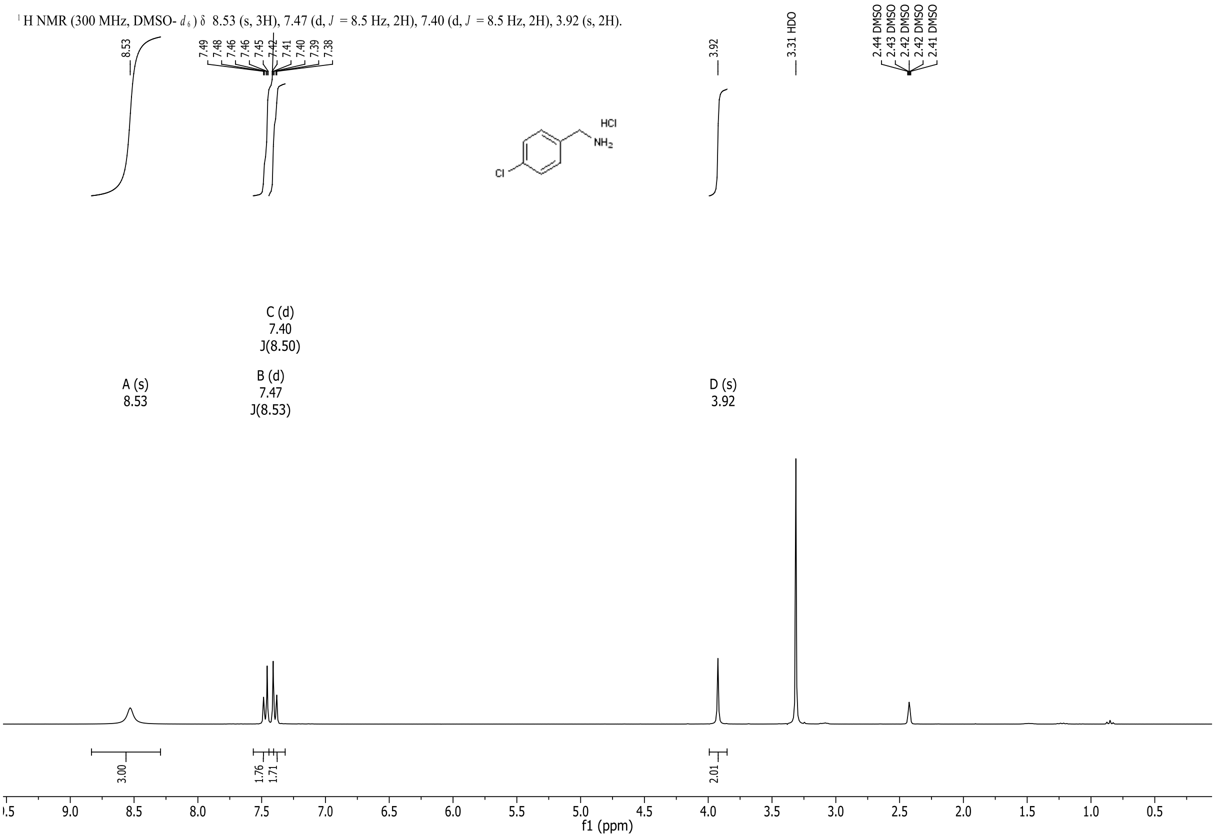


δ C (75 MHz, DMSO) 163.61, 160.37, 131.40, 131.29, 130.37, 130.33, 115.41, 115.12, 41.29.

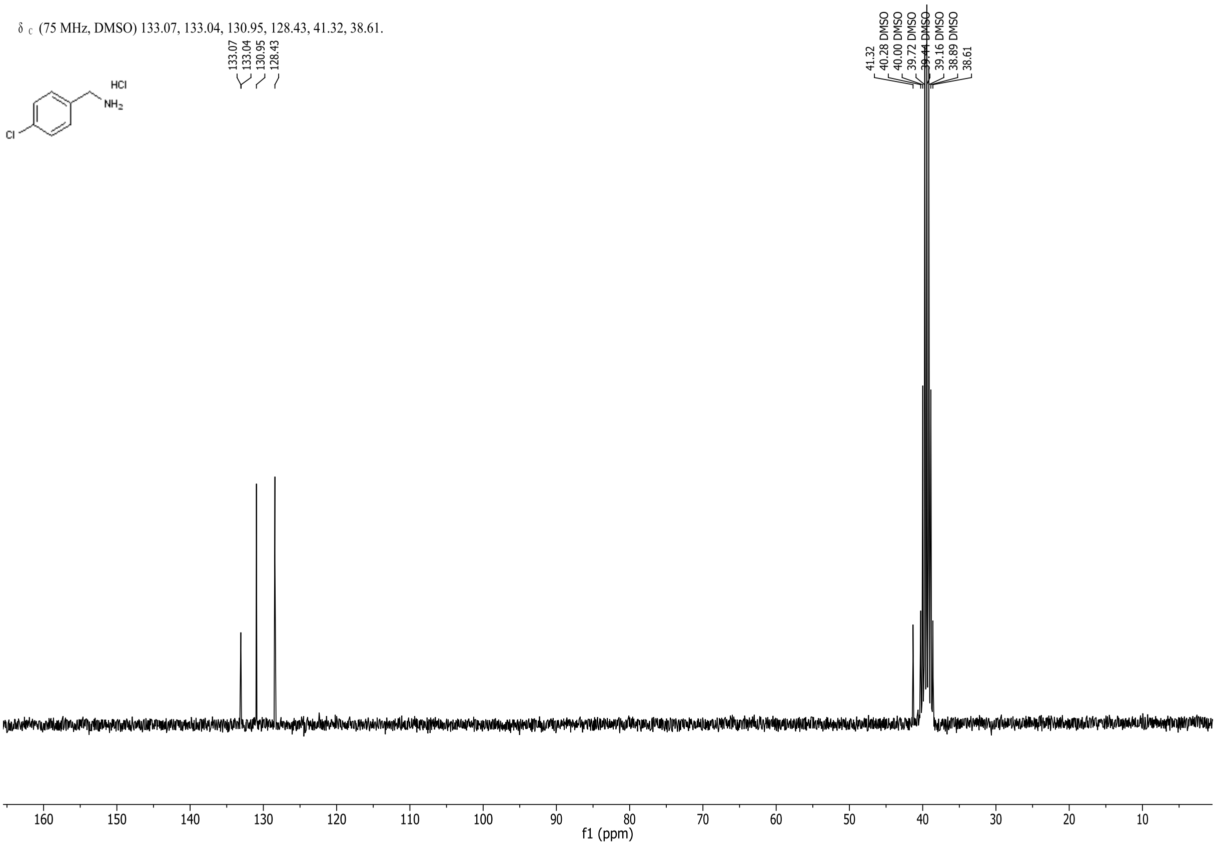


(4-Chlorophenyl)methanamine hydrochloride (1l)

^{1}H NMR (300 MHz, DMSO-d_6) δ 8.53 (s, 3H), 7.47 (d, J = 8.5 Hz, 2H), 7.40 (d, J = 8.5 Hz, 2H), 3.92 (s, 2H).

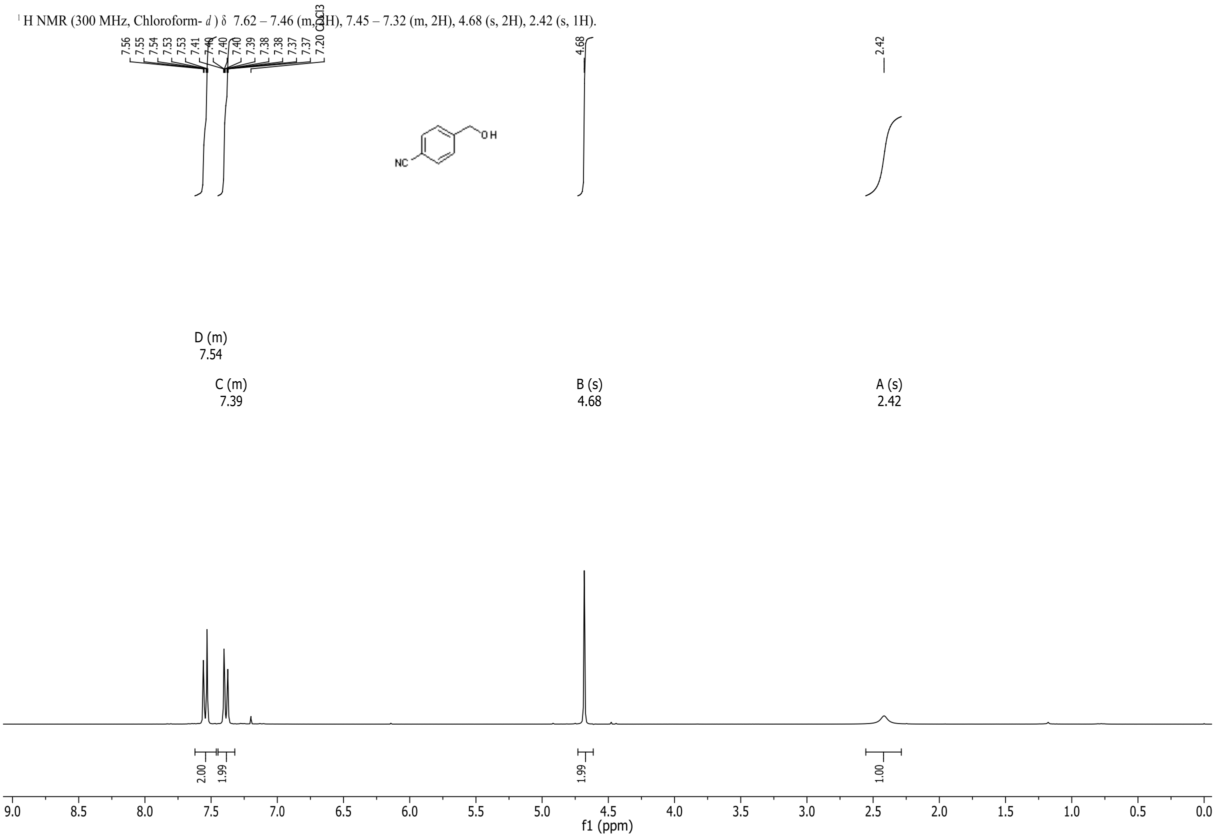


δ$_C$ (75 MHz, DMSO) 133.07, 133.04, 130.95, 128.43, 41.32, 38.61.

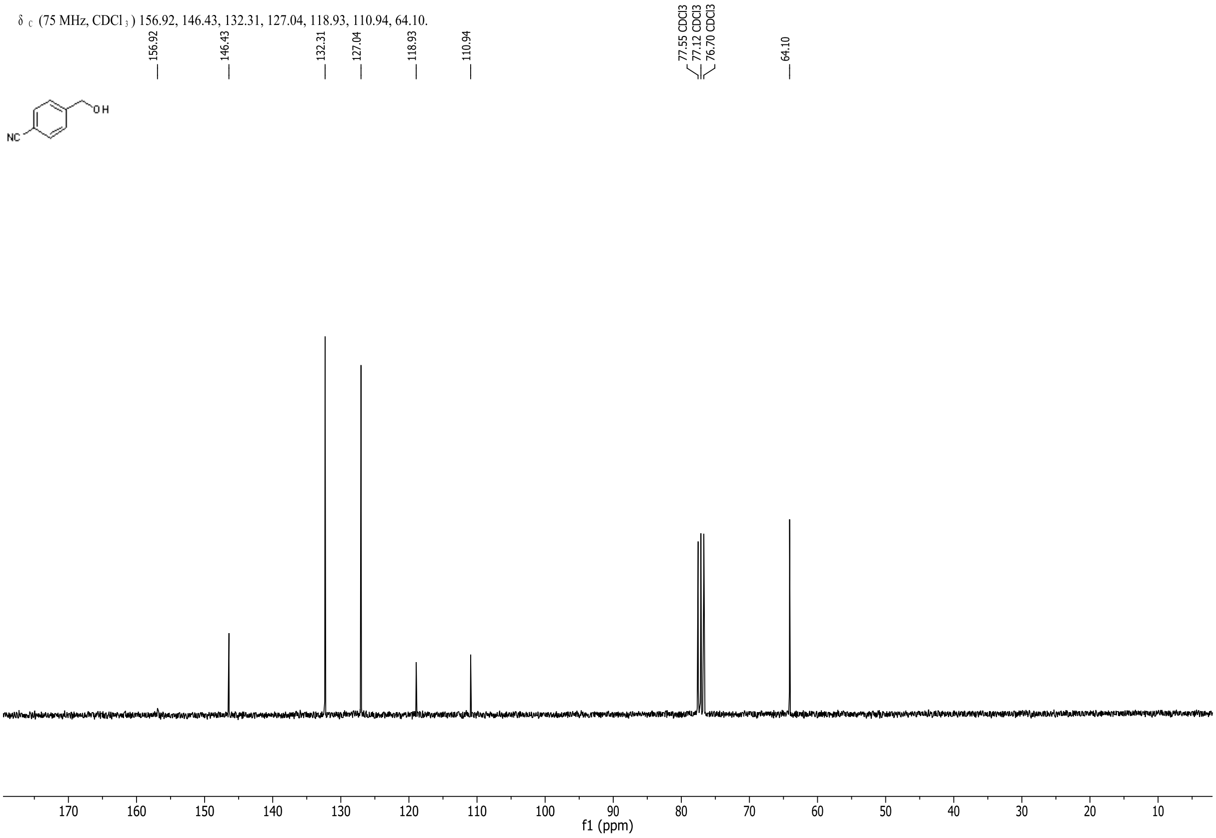


4-(Hydroxymethyl)benzonitrile (2a)

^1H NMR (300 MHz, Chloroform-d) δ 7.62 – 7.46 (m, 2H), 7.45 – 7.32 (m, 2H), 4.68 (s, 2H), 2.42 (s, 1H).

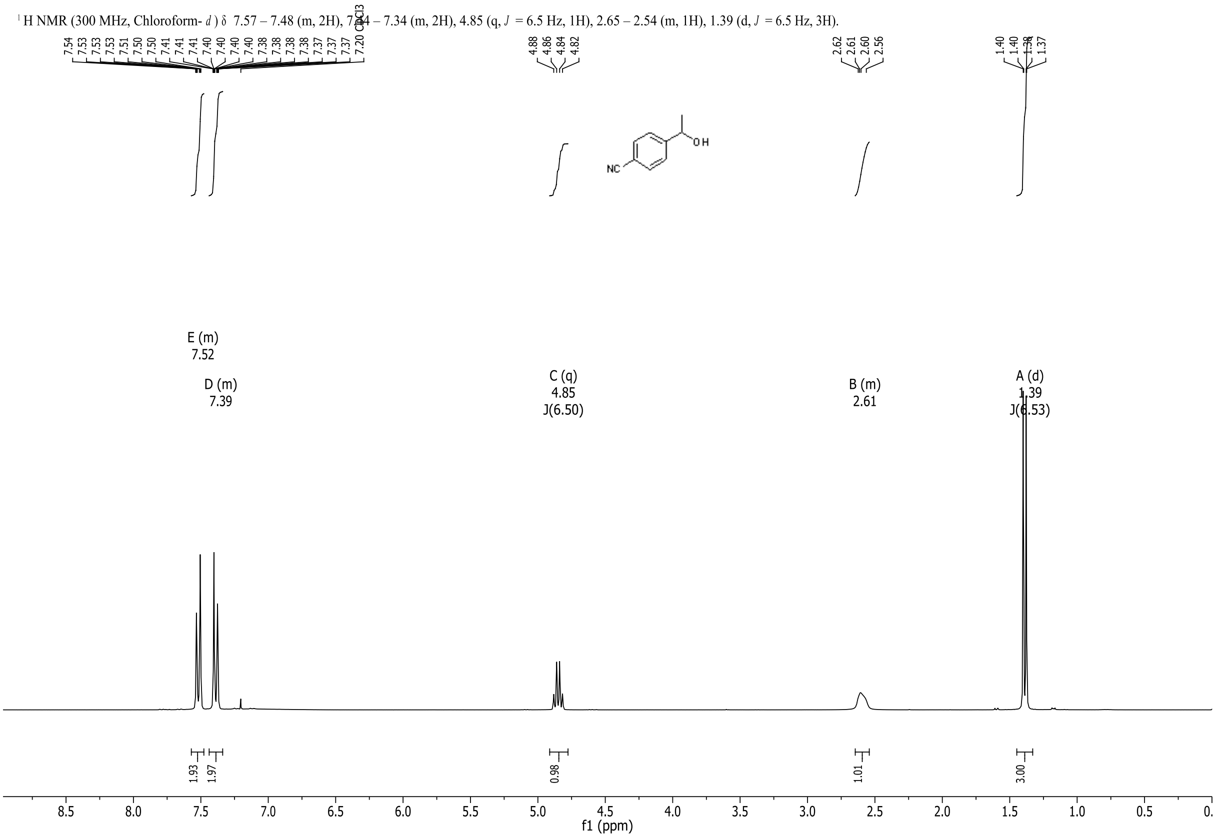


δ$_C$ (75 MHz, CDCl$_3$) 156.92, 146.43, 132.31, 127.04, 118.93, 110.94, 64.10.



4-(1-Hydroxyethyl)benzonitrile (2b)

^{1}H NMR (300 MHz, Chloroform-d) δ 7.57 – 7.48 (m, 2H), 7.44 – 7.34 (m, 2H), 4.85 (q, J = 6.5 Hz, 1H), 2.65 – 2.54 (m, 1H), 1.39 (d, J = 6.5 Hz, 3H).



δ$_C$ (75 MHz, CDCl$_3$) 151.37, 132.31, 126.12, 118.94, 110.77, 69.52, 25.38.