Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

Redox Reaction between Benzyl Azides and Aryl aAzides: Concerted Synthesis of Aryl Nitriles and Anilines

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Contents

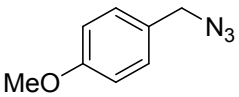
1. General Information

Air-sensitive manipulations were carried out with standard Schlenk techniques under argon atmosphere. Commercial chemicals used without further purification. Flash column chromatography was carried out on silica gel (230-400 mesh) as the stationary phase. ^{1}H and ^{13}C NMR spectra were recorded with Bruker AVANCE III 300MHZ FT-NMR spectrometer and chemical shift are given in δ ppm. ^{1}H NMR spectra were referenced to tetramethylsilane (TMS, 0 ppm). ^{13}C NMR spectra were referenced to $CDCl_3$ (77.23 ppm) as an internal standard. Infrared spectra were recorded on a Shimadzu IR-470 spectrometer with NaCl pellet. Mass spectral data were obtained from the Korea Basic Science Institute (Daegu) on a Jeol JMS 700 high resolution mass spectrometer. Ruthinum complex **1**[1] and **11**[2] were synthesized according to the literature procedure.

2. Synthesis of Benzyl Azides

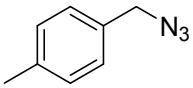
2-a. Synthesis of benzyl azides (2a~2m)

A solution of benzyl bromide (or benzyl chloride) (3.0 mmol) and sodium azide (2.0 equiv, 6.0 mmol) in DMF (20 mL) was stirred for 12 h at room temperature. After completion of the reaction, the mixture was dilluted in H_2O (30 mL) and extracted with diethyl ether (3 x 20 mL). The oragnic layer was washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the benzyl azides.



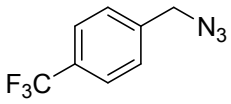
1-(azidomethyl)-4-methoxybenzene (2a)[3]

Yield: 99%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.25-7.22 (m, 2H), 6.92-6.89 (m, 2H), 4.26 (s, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.8, 129.9, 127.6, 114.4, 55.5, 54.6.



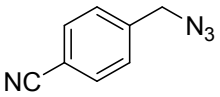
1-(azidomethyl)-4-methylbenzene (2b)[3]

Yield: 93%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.23-7.16 (m, 4H), 4.27 (s, 2H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.3, 132.5, 129.7, 128.5, 54.8, 21.3.



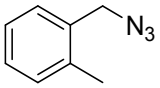
1-(azidomethyl)-4-(trifluoromethyl)benzene (2c)[4]

Yield: 82%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.66-7.63 (m, 2H), 7.64-7.43 (m, 2H), 4.43 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 139.6, 128.5, 126.1, 126.05, 126.0, 125.95, 122.4, 54.3.



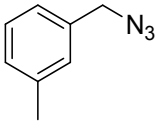
4-(azidomethyl)benzonitrile (2d)[3]

Yield: 89%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.70-7.67 (m, 2H), 7.45-7.43 (m, 2H), 4.45 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 141.0, 132.8, 128.7, 118.6, 112.4, 54.2.



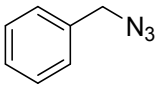
1-(azidomethyl)-2-methylbenzene (2e)[3]

Yield: 96%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.28-7.17 (m, 5H), 4.33 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.0, 133.6, 130.9, 129.5, 128.8, 126.4, 53.2, 19.2.



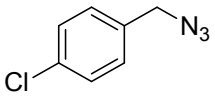
1-(azidomethyl)-3-methylbenzene (2f)[3]

Yield: 95%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.29-7.24 (m, 1H), 7.16-7.09 (m, 3H), 4.29 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.8, 135.5, 129.3, 129.1, 128.9, 125.5, 55.0, 21.6.



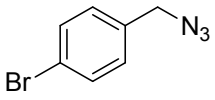
(azidomethyl)benzene (2g)[3]

Yield: 95%; Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.40-7.27 (m, 5H), 4.30 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 135.6, 129.0, 128.5, 128.4, 54.9.



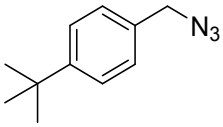
1-(azidomethyl)-4-chlorobenzene (2h)[3]

Yield: 99%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.33 (m, 2H), 7.27-7.23 (m, 2H), 4.31 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 134.4, 134.1, 129.7, 129.2, 54.2.



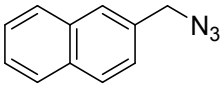
1-(azidomethyl)-4-bromobenzene (2i)[3]

Yield: 93%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.53-7.49 (m, 2H), 7.21-7.19 (m, 2H), 4.30 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 134.6, 132.2, 130.0, 122.6, 54.3.



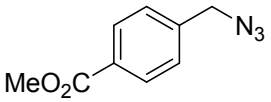
1-(azidomethyl)-4-*tert*-butylbenzene (2j)[5]

Yield: 95%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.42-7.39 (m, 2H), 7.26-7.24 (m, 2H), 4.30 (s, 2H), 1.32 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 151.6, 132.6, 128.2, 126.0, 54.8, 34.8, 31.5.



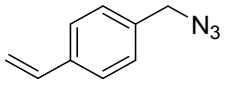
2-(azidomethyl)naphthalene (2k)[6]

Yield: 99%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87-7.81 (m, 3H), 7.76 (s, 1H), 7.52-7.46 (m, 2H), 7.43-7.39 (m, 1H), 4.48 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 133.5, 133.3, 133.0, 129.0, 128.1, 128.0, 127.4, 126.7, 126.5, 126.1, 55.2.



Methyl 4-(azidomethyl)benzoate (2l)[3]

Yield: 94%; Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.07-8.04 (m, 2H), 7.41-7.38 (m, 2H), 4.42 (s, 2H), 3.92 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.8, 140.6, 130.3, 128.1, 54.5, 52.4.

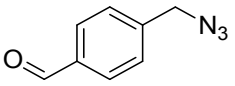


1-(azidomethyl)-4-vinylbenzene (2m)[7]

Yield: 90%; Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.44-7.41 (m, 2H), 7.29-7.25 (m, 2H), 6.72 (dd, *J* = 10.9 Hz, *J* = 17.6 Hz, 1H), 5.77 (d, *J* = 17.7 Hz, 1H), 5.28 (d, *J* = 10.9 Hz, 1H), 4.32 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 137.9, 136.4, 135.0, 128.7, 126.9, 114.7, 54.8.

2-b. Synthesis of 4-(azidomethyl)benzaldehyde (2n)

4-(azidomethyl)benzaldehyde was synthesized accroding to the literature procedure.[8] 4-(bromomethyl)benzonitrile (3.0 mmol) in dry toluene (25 mL), diisobutylaluminum hydride (1.5 equiv, 7.5 mmol, 1.0 M in dichloromethane) was added dropwise at 0 ^{o}C then stirred for 3 h at room temperature. After consumption of starting material, 10% HCl (25 mL) was added dropwise at 0 ^{o}C and stirred for 1 h at 0 ^{o}C. The reaction mixture was extracted with diethyl ether (3 x 30 mL), wash with H_2O (2 x 50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure to afford 4-(bromomethyl)benzaldehye. The crude mixture was directly used for next step without purification. A solution of 4-(bromomethyl)benzaldehyde and sodium azide (2.0 equiv, 6.0 mmol) in DMF (20 mL) was stirred for 12 h at room temperature. After completion of the reaction, the mixture was dilluted in H_2O (30 mL) and extracted with diethyl ether (3 x 20 mL). The oragnic layer was washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford 4-(azidomethyl)benzaldehyde **2n**

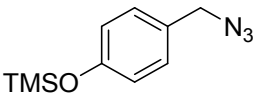


4-(azidomethyl)benzaldehyde (2n)[8]

Yield: 98% (2 steps); Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.0 (s, 1H), 7.92-7.89 (m, 2H), 7.51-7.48 (m, 2H), 4.46 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 191.8, 142.3, 136.4, 130.4, 128.7, 54.5.

2-c. Synthesis of (4-(azidomethyl)phenoxy)(*tert*-butyl)dimethylsilane (2o)

4-(azidomethyl)phenol was synthesized accroding to the literature procedure.[9] A mixture of 4-hydroxy benzylalcohol (5.0 mmol), sodium azide (1.2 equiv, 10.0 mmol) and triphenylphosphine (1.0 equiv, 5.0 mmol) in a mixture of CCl_4 and DMF (1:4, 10 mL) was stirred at 90 ^{o}C reflux for 5 h. After the completion of the reaction, the reaction mixture extracted with diethyl ether (3 x 20 mL). The oragnic layer was washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (1:5 EtOAc:n-hexane) to afford the 4-(azidomethyl)phenol as pale yellow liquid (65%). To a solution of 4-(azidomethyl)phenol (2.0 mmol) and imidazole (2.5 equiv, 5.0 mmol) in DMF (10 mL), tert-butyldimethylsilyl chloride (TBSCl) (1.2 equiv, 2.4 mmol) was added and stirred at room temeparture for 12 h. After the completion of the reaction, the reaction mixture was quenched with H_2O, extracted with diethyl ether (3 x 20 mL). The oragnic layer was washed with water (2 x 50 mL) and brine (50 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (n-hexane) to afford (4-(azidomethyl)phenoxy)(tert-butyl)dimethylsilane **2q**.



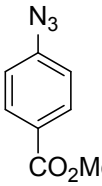
(4-(azidomethyl)phenoxy)(*tert*-butyl)dimethylsilane (2o)

Yield: 67% (2 steps); Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.19-7.15 (m, 2H), 6.86-6.82 (m, 2H), 4.26(s, 2H), 0.98 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ =

156.0, 129.9, 128.3, 120.6, 54.7, 25.9, 18.4, -4.2; IR(NaCl): ν = 3050, 2957, 2931, 2886, 2859, 2097, 1610, 1512 cm^{-1}; HRMS (FAB): m/z calcd. for $C_{13}H_{21}N_3OSi$: 263.1454; found: 263.1453.

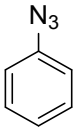
3. Synthesis of Aryl azides

To a solution of methyl 4-aminobenzoate (7.0 mmol) in water (40 mL), aqueous hydrochloric acid (35%, 12 mL) is added. The mixture was cooled to 0 °C then a solution of sodium nitrite (1.1 equiv, 7.7 mmol) in water (10 mL) is added. After stirring for 20 min at 0 °C. Sodium azide (1.2 equiv, 8.4 mmol) was added portionwise. The reaction mixture was stirred at room temperature for 4 h. After completion of the reaction, the mixture was extracted with diethyl ether (3 x 40 mL). The oragnic layer was washed with saturated $NaHCO_3$ aqueous solution (100 mL), H_2O (100 mL) and brine (100 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to afford the aryl azides.



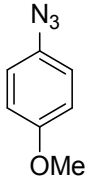
Methyl 4-azidobenzoate (4a)[10]

Yield: 90%; Pale yellow soild; ^1H NMR (300 MHz, $CDCl_3$) δ = 8.05-8.01 (m, 2H), 7.09-7.04 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 166.5, 144.9, 131.6, 126.9, 119.0, 52.3.



Azidobenzene (4b)[10]

Yield: 85%; Pale yellow liquid; ^1H NMR (300 MHz, $CDCl_3$) δ = 7.38-7.31 (m, 2H), 7.16-7.10 (m, 1H), 7.05-7.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 140.2, 130.0, 125.1, 119.2.

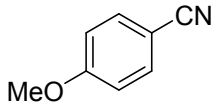


1-azido-4-methoxybenzene (4c)[10]

Yield: 93%; Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.96-6.92 (m, 2H), 6.90-6.86 (m, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 157.2, 132.5, 120.2, 115.3, 55.7.

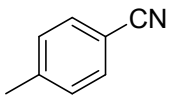
4. Synthesis of nitriles and anilines

The ruthenium catalyst **1** (2.0 mol%, 0.005 mmol) was added to a flame-dried J-Young flask filled with argon. The dry THF (1.0 mL) and benzyl azide (0.25 mmol) were added under a stream of argon. The reaction mixture was stirred for 2 h at room temperature with a household 30W fluorescent light. After the accumulation of N-H aldimine, aryl azide (1.0 equiv, 0.25 mmol) was added then stirred at 70 ^{o}C for 2 h. After completion of the reaction, solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel to afford corresponding nitrile and aniline.



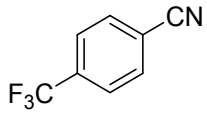
4-methoxybenzonitrile (5a)[11]

Yield: 98%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61-7.58 (m, 2H), 6.98-6.94 (m, 2H), 3.86 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 163.0, 134.2, 119.4, 114.9, 104.2, 55.7.



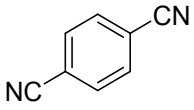
4-methylbenzonitrile (5b)[12]

Yield: 99%; ^{1}H NMR (300 MHz, $CDCl_3$, in crude mixture with an internal standard (CH_2Br_2)) δ = 7.55-7.52 (m, 2H), 7.28-7.25 (m, 2H), 2.41 (s, 3H).



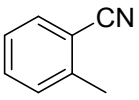
4-(trifluoromethyl)benzonitrile (5c)[12]

Yield: 98%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.82 (d, *J* = 8.3 Hz, 2H), 7.77 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 135.0, 134.5, 132.9, 126.44, 126.40, 126.34, 126.29, 125.1, 121.4, 117.6, 116.3.



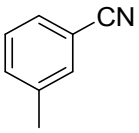
Terephthalonitrile (5d)[13]

Yield: 98%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.80 (s, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 133.0, 117.2, 116.9.



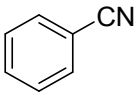
2-methylbenzonitrile (5e)[12]

Yield: 99%; ^{1}H NMR (300 MHz, $CDCl_3$, in crude mixture with an internal standard (CH_2Br_2)) δ = 7.60-7.57 (m, 1H), 7.50-7.44 (m, 1H), 7.32-7.23 (m, 2H), 2.54 (s, 3H).



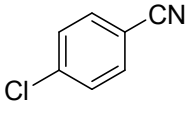
3-methylbenzonitrile (5f)[14]

Yield: 99%; ^{1}H NMR (300 MHz, $CDCl_3$, in crude mixture with an internal standard (CH_2Br_2)) δ = 7.46-7.31 (m, 4H), 2.38 (s, 3H).



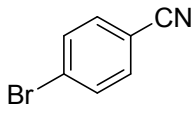
Benzonitrile (5g)

Yield: 90%; ^{1}H NMR (300 MHz, THF-d8, in crude mixture with an internal standard (CH_3NO_2)) δ = 7.71-7.68 (m, 2H), 7.65-7.59 (m, 1H), 7.52-7.47 (m, 2H).



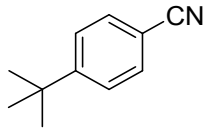
4-chlorobenzonitrile (5h)[11]

Yield: 99%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.63-7.59 (m, 2H), 7.49-7.45 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 139.7, 133.5, 129.8, 118.1, 110.9.



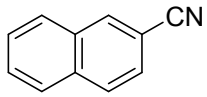
4-bromobenzonitrile (5i)[13]

Yield: 99%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.66-7.62 (m, 2H), 7.55-7.51 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 133.6, 132.8, 128.1, 118.2, 111.4.



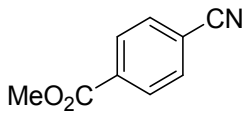
4-*tert*-butylbenzonitrile (5j)[11]

Yield: 99%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.60-7.57 (m, 2H), 7.50-7.46 (m, 2H), 1.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 156.8, 132.2, 126.4, 119.3, 109.5, 35.5, 31.1.



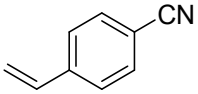
2-naphthonitrile (5k)[11]

Yield: 96%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.22 (s, 1H), 7.92-7.87 (m, 3H), 7.67-7.57 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 134.8, 134.3, 132.4, 129.4, 129.2, 128.6, 128.2, 127.8, 126.5, 119.4, 109.6.



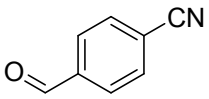
Methyl 4-cyanobenzoate (5l)[11]

Yield: 99%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 8.16-8.13 (m, 2H), 7.76-7.74 (m, 2H), 3.97 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 165.6, 134.1, 132.4, 130.3, 118.2, 116.6, 52.9.



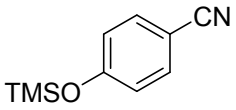
4-vinylbenzonitrile (5m)[15]

Yield: 96%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.61 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H), 6.72 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.87 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 142.1, 135.6, 132.6, 126.9, 119.1, 117.9, 111.3.



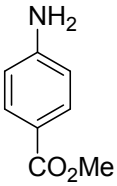
4-formylbenzonitrile (5n)[12]

Yield: 90%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 10.10 (s, 1H), 8.03-7.99 (m, 2H), 7.87-7.84 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 190.8, 138.9, 133.1, 130.1, 117.9, 117.8.



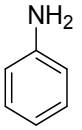
4-(tert-butyldimethylsilyloxy)benzonitrile (5o)[16]

Yield: 99%; Colorless liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.56-7.51 (m, 2H), 6.91-6.87 (m, 2H), 0.98 (s, 9H), 0.23 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 159.9, 134.2, 121.0, 119.4, 104.8, 25.7, 18.4, -4.2.



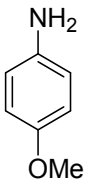
Methyl 4-aminobenzoate (6a)[17]

Yield: 99%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.87-7.82 (m, 2H), 6.65-6.61 (m, 2H), 4.09 (br s, 2H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 167.4, 151.1, 131.8, 119.9, 114.0, 51.8.



Aniline (6b)[18]

Yield: 99%; Yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.18-7.11 (m, 2H), 6.76-7.73 (m, 1H),6.65-6.63 (m, 2H), 3.58 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 146.6, 129.5, 118.7, 115.3.

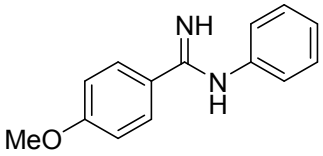


4-methoxyaniline (6c)[17]

Yield: 99%; Brown solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 6.75-6.70 (m, 2H), 6.63-6.57 (m, 2H), 3.71 (s, 3H), 3.41 (br s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 152.8, 140.1, 116.4, 114.9, 55.8.

5. Synthesis of amidine 7

The ruthenium catalyst **1** was added to a flame-dried J-Young flask filled with argon. The dry THF (1.0 mL) and **2a** (0.25 mmol) were added under a stream of argon. The reaction mixture was stirred for 2 h at room temperature with a household 30W fluorescent light. After the accumulation of **3a**, **4a** (1.0 equiv, 0.25 mmol) was added then stirred at 70 °C for 2 h. The reaction mixture was cooled to room temperature then NaH (1.5 equiv, 0.375 mmol) is added at 0 °C and stirred at room temperature for 12h. After completion of the reaction, the reaction mixture was quenched with water at 0 °C, extracted with diethyl ether (3 x 5 mL). The oragnic layer was washed with H_2O (2 x 30 mL), brine (30 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was recrystallized at -20°C (n-hex:dichloromethane = 2:1) to afford amidine **7**.



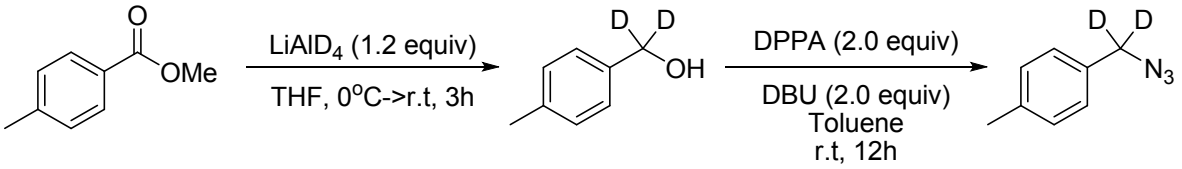
4-methoxy-N-phenylbenzimidamide (7)[19]

Yield: 92%; White solid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.78 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.06-7.01 (m, 1H), 6.97-6.90 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 161.7, 154.9, 149.6, 129.6, 128.6, 123.1, 122.0, 113.9, 55.6.

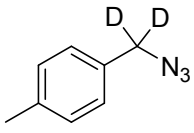
6. Mechanistic investigation

6-a. The reaction using deuterated benzyl azide

6-a-1. Synthesis of 1-(azidomethyl-*d2*)-4-methylbenzene 8



To a solution of methyl 4-methylbenzoate (5.0 mmol) THF (10 mL), lithium aluminum deteride (1.2 equiv, 6.0 mmol) was added at 0 °C. The reaction mixture was stirred at room temperature for 3 h. After completion of the reaction, the mixture was quenched with 1 N HCl (10 mL), extracted with ethyl acetate (3 x 10 mL). The oragnic layer was washed with H_2O (30 mL) and brine (30 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The crude residue was directly used for next step without further purification. To a solution of *p*-tolylmethanol-*d2* and diphenyl phosphoryl azide (DPPA) (2.0 equiv, 10 mmol) in toluene (15 mL), Diazabicyclo[5.4.0]undec-7-ene (DBU) (2.0 equiv, 10 mmol) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature for 12 h and quenched with water (30 mL). The solution was extracted with dichloromethane (3 x 20 mL). The organic was washed with H_2O (2 x 30 mL) brine (30 mL), dried over anhydrous sodium sulfate, concentrated under reduced pressure. The residue was purified by flash column chromatography to afford the deuterated azide **8**.

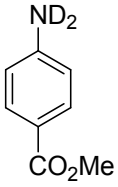


1-(azidomethyl-*d2*)-4-methylbenzene (8)

Yield: 60% (2 steps); Pale yellow liquid; ^{1}H NMR (300 MHz, $CDCl_3$) δ = 7.26-7.18 (m, 4H), 2.37 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ = 138.3, 132.3, 129.6, 128.4, 54.46, 54.29, 54.11, 53.94, 21.3; IR(NaCl): ν = 3026, 3001, 2924, 2868, 2495, 2106, 1907, 1615, 1516 cm^{-1}; HRMS (EI): m/z calcd. for $C_8H_7D_2N_3$: 149.0922; found: 149.0921.

6-a-2. Synthesis of nitrile and methyl-4-amino-*d2*-benzoate

The ruthenium catalyst **1** (2.0 mol%, 0.0025 mmol) was added to a flame-dried NMR reaction J-young tube and filled with argon. The THF-d8 (0.6 mL) and **8** (0.125 mmol) were added under a stream of argon. The reaction mixture was stirred for 2 h at room temperature with a household 30W fluorescent light. After the accumulation of N-H aldimine, **4a** (1.0 equiv, 0.125 mmol) was added then stirred at 70 °C for 2 h.

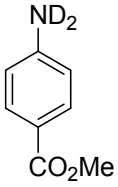


Methyl 4-amino(*d*-2)benzoate (10)

^{1}H NMR (300 MHz, THF-d8, in crude mixture) δ = 7.73-7.68 (m, 2H), 6.55-6.51 (m, 2H), 3.73 (3H).

6-a-3. Synthesis of nitrile and methyl-4-amino-*d2*-benzoate for deuterium NMR

The ruthenium catalyst **1** (2.0 mol%, 0.0025 mmol) was added to a flame-dried NMR reaction J-young tube and filled with argon. The THF (0.6 mL) and **8** (0.125 mmol) were added under a stream of argon. The reaction mixture was stirred for 2 h at room temperature with a household 30W fluorescent light. After the accumulation of N-H aldimine, aryl azide (1.0 equiv, 0.125 mmol) was added then stirred at 70 °C for 2 h. The yield of methyl 4-amino-*d2*-benzoate **10** was determined by deterium NMR using THF-d8 as an internal standard.

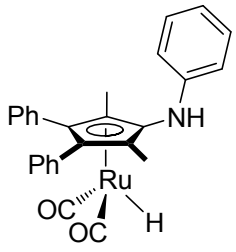


Methyl 4-amino(*d*-2)benzoate (10)

^{2}D NMR (500 MHz, THF-d8, in crude mixture with an internal standard (THF-d8)) δ = 5.16 (s, 2D)

6-b. The reaction using Ru-H 12 as a catalyst

To a solution of the ruthenium chloride **11** (0.02 mmol) in THF (1.0 mL), tributyltin hydride (0.02 mmol) was added. The reaction mixture was stirred for 3 h at room temperature with a 12W blue LED to generate the ruthenium hydride **12** (The generation of **12** was checked by ^{1}H and ^{13}C NMR using THF-d8 as a NMR solvent.[1]). After generation of **12**, **2a** (0.25 mmol) and **4a** (0.25 mmol) were added and stirred at 70 ^{o}C for 16 h under illumination with a household 30 W fluorescent light. After completion of the reaction, solvent was removed under reduced pressure. The yield of **5a** and **6a** was determined by ^{1}H NMR using dibromomethane as an internal standrad.



Ruthenium hydride 12[1]

^{1}H NMR (300 MHz, THF-d8, in crude mixture) δ = 7.32-7.27 (m, 4H), 7.23-7.11 (m, 9H), 6.95 (s, 1H), 6.72-6.65 (m, 3H), 2.04 (s, 6H), -10.08 (s, 1H); ^{13}C NMR (75 MHz, THF-d8, in crude mixture) δ = 202.9, 148.4, 133.0, 132.9, 129.7, 128.4, 128.0, 118.6, 113.9, 110.0, 106.3, 102.2, 11.3.

8. References

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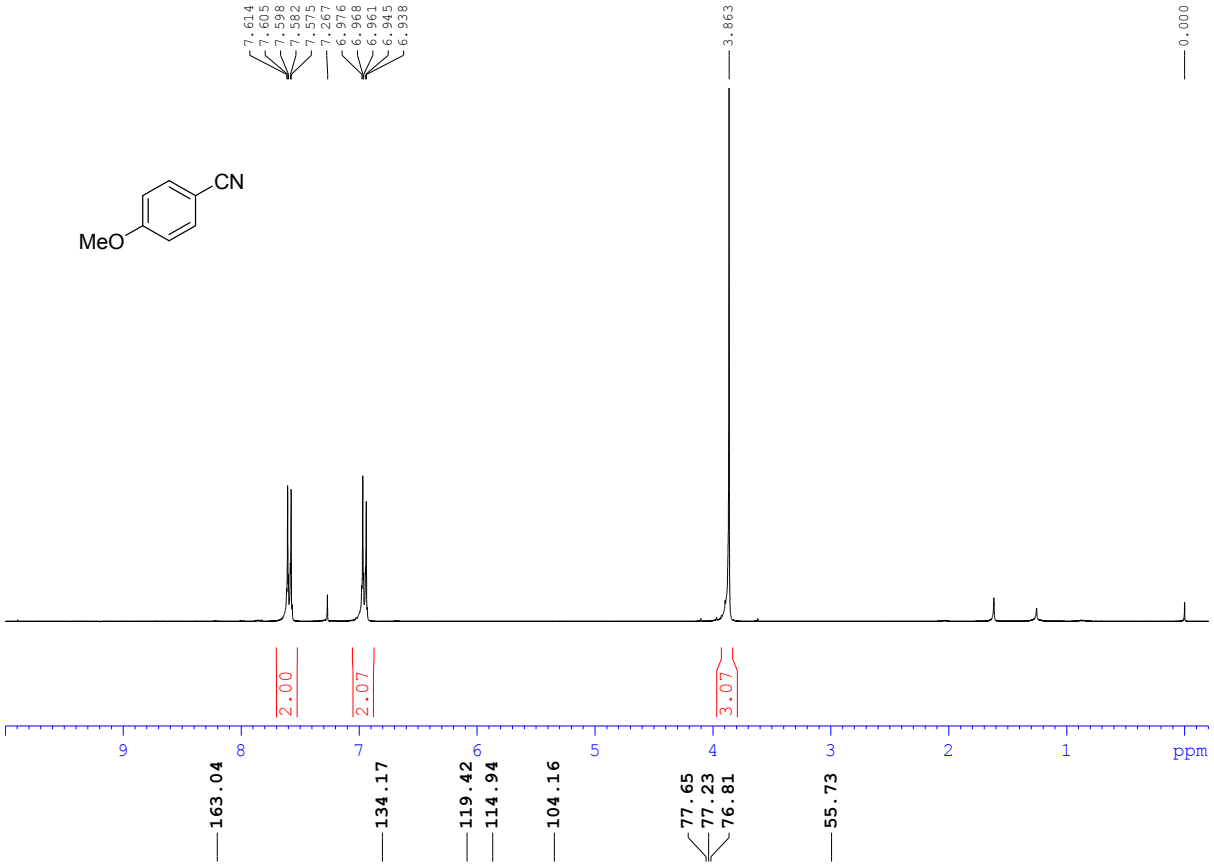
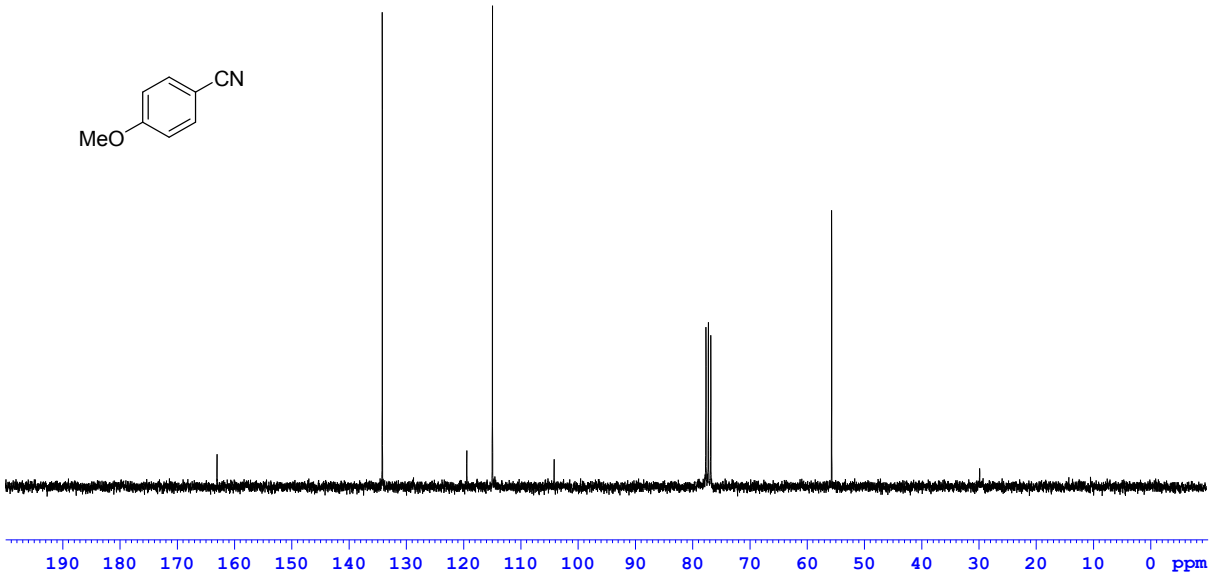
8. NMR Data

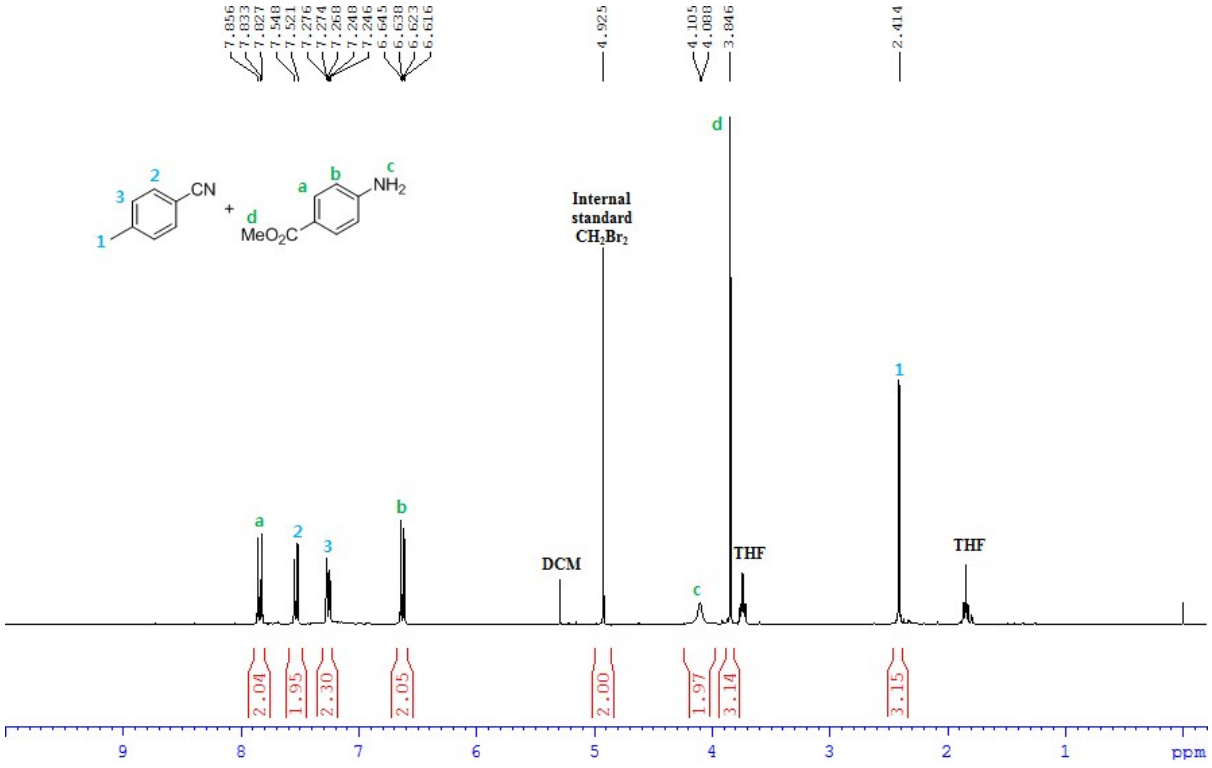
8-a. NMR spectrum of nitriles

^{1}H and ^{13}C NMR spectrum of **5a**

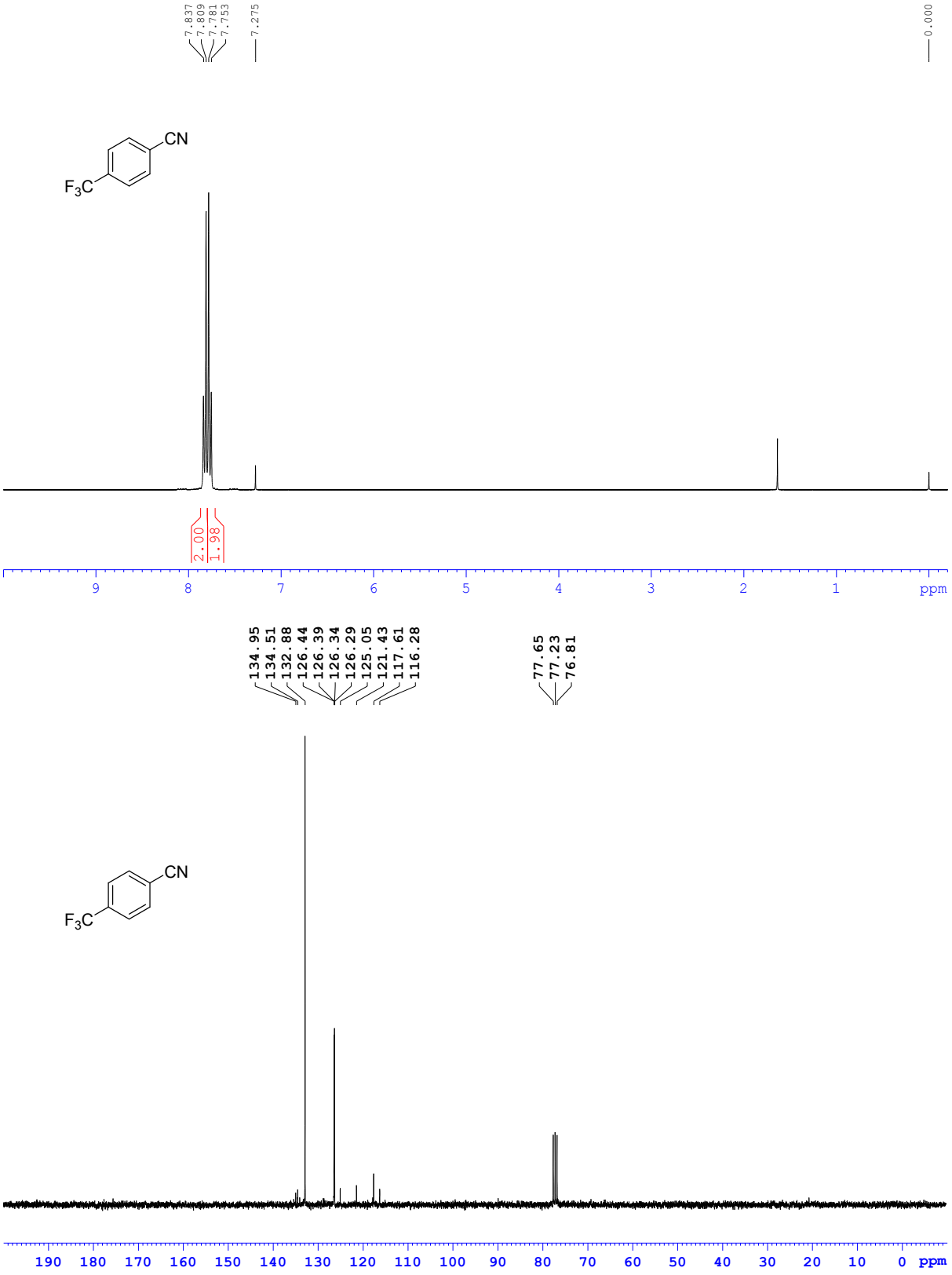




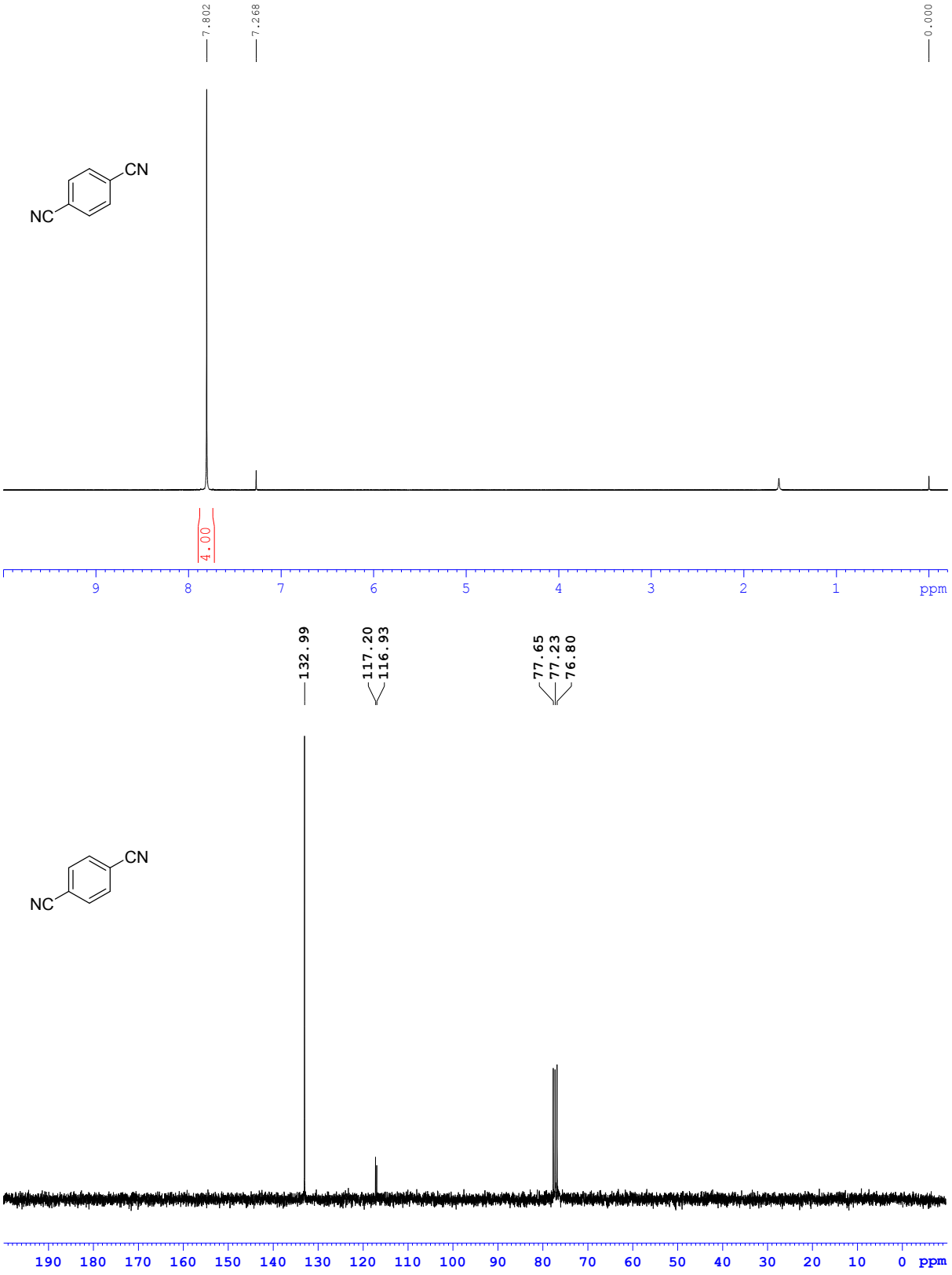
^{1}H spectrum of **5b (crude)**



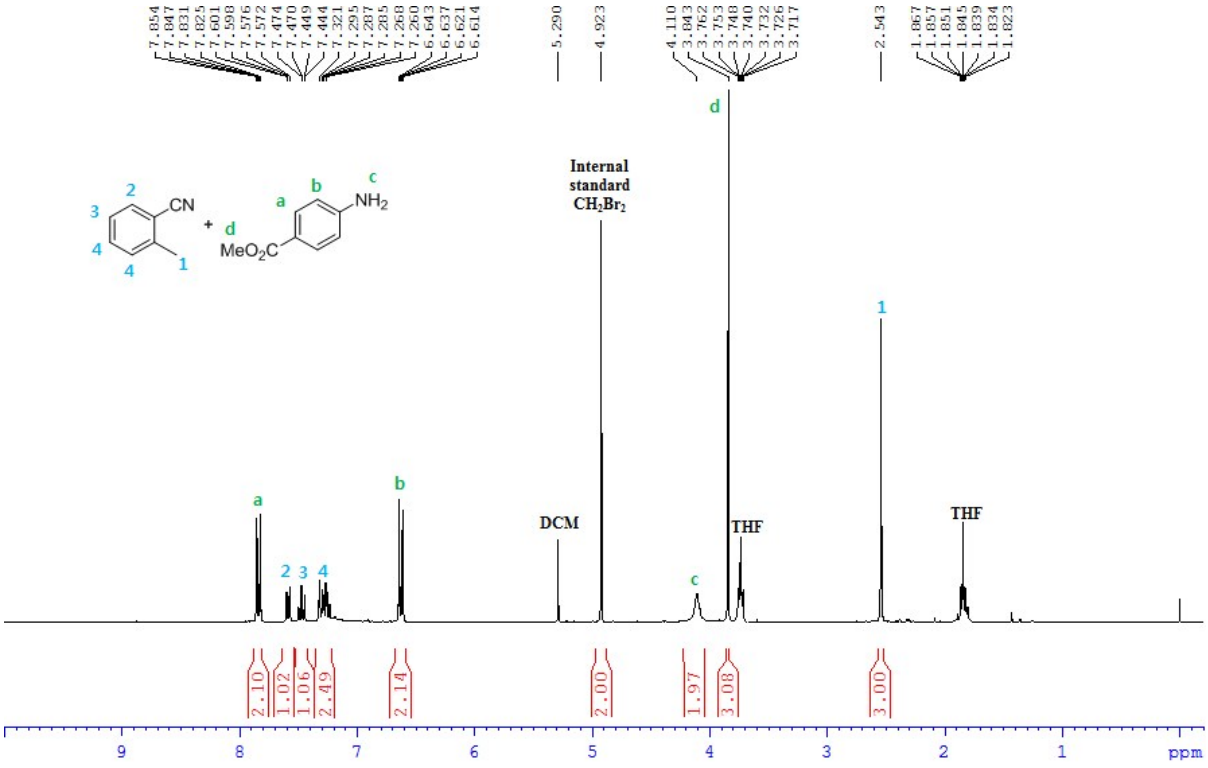
^{1}H and ^{13}C NMR spectrum of **5c**



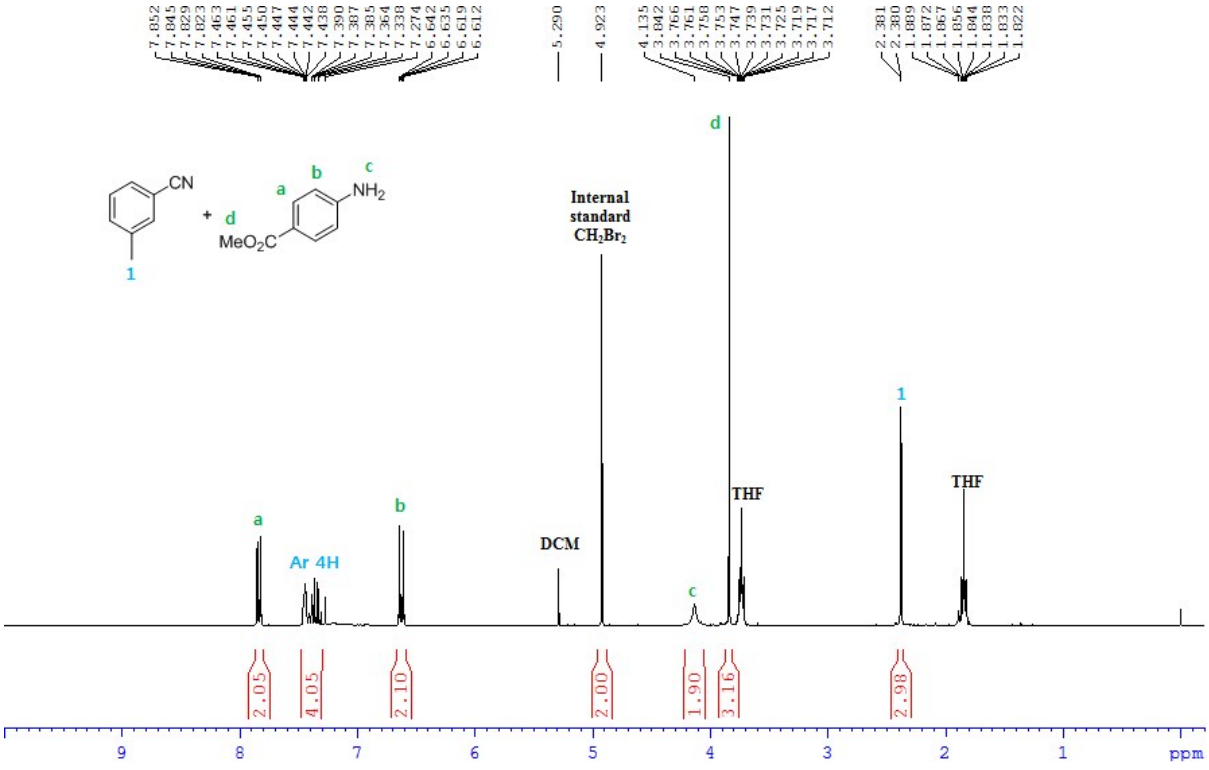
^{1}H and ^{13}C NMR spectrum of **5d**



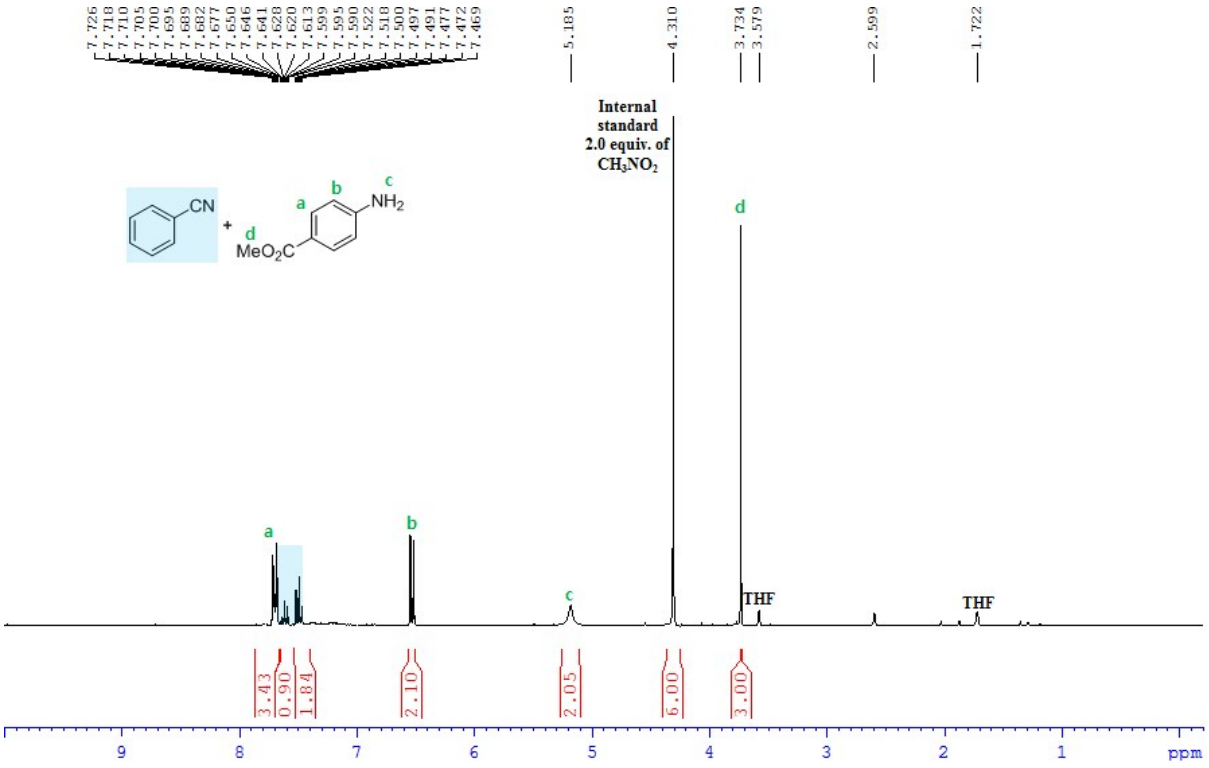
^{1}H NMR spectrum of **5e (crude)**



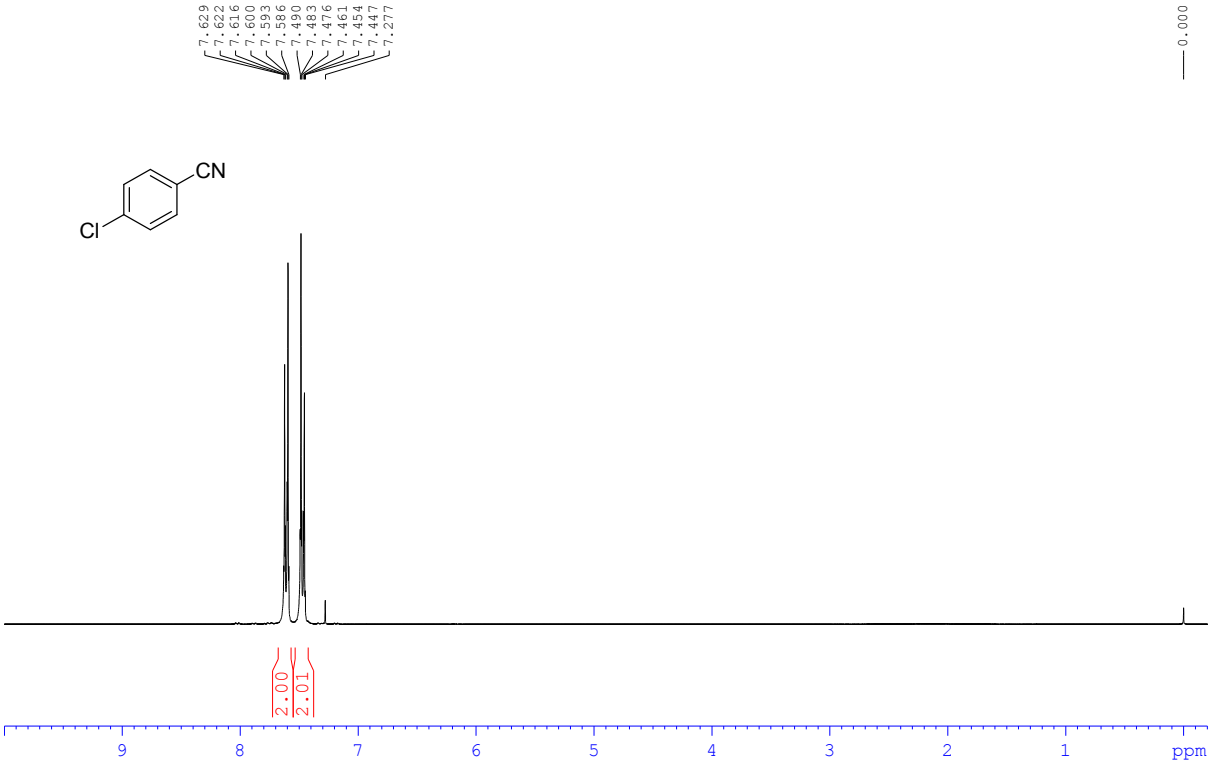
^{1}H NMR spectrum of **5f (crude)**

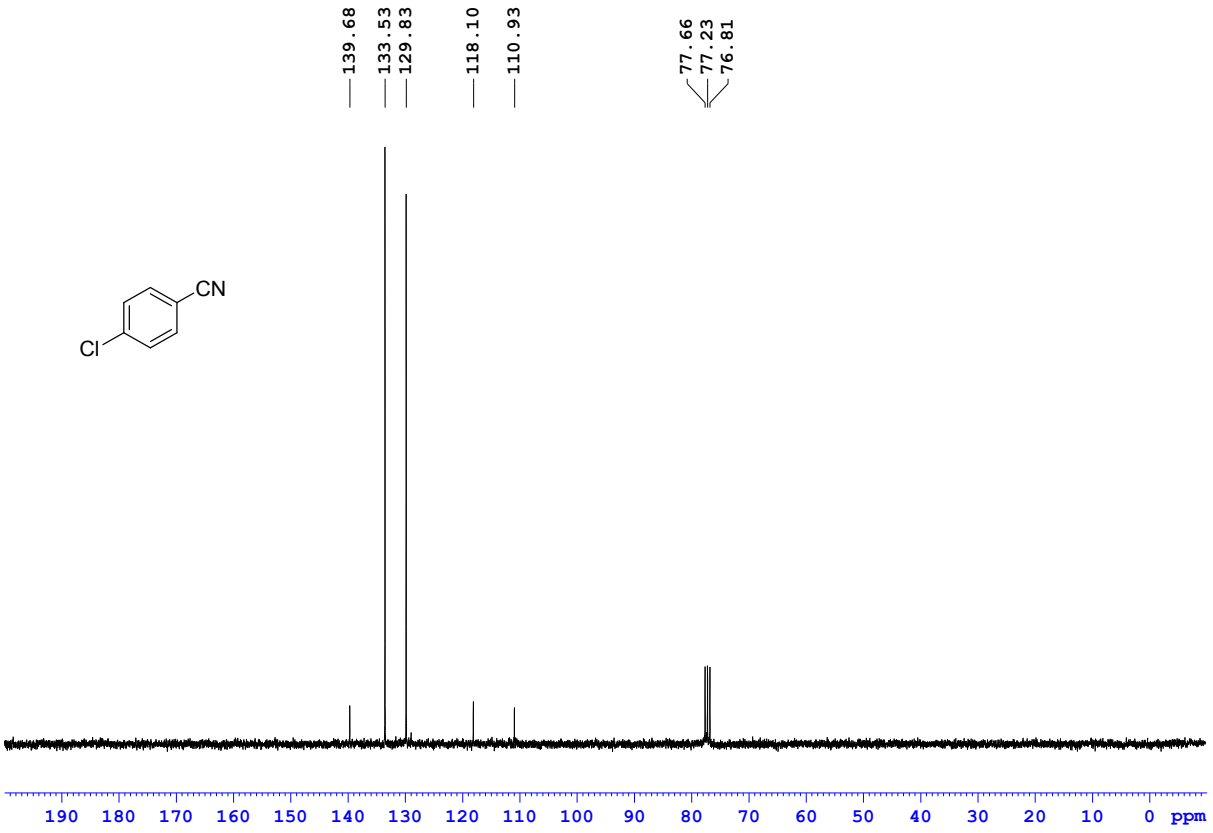


^{1}H NMR spectrum of **5g (crude)**

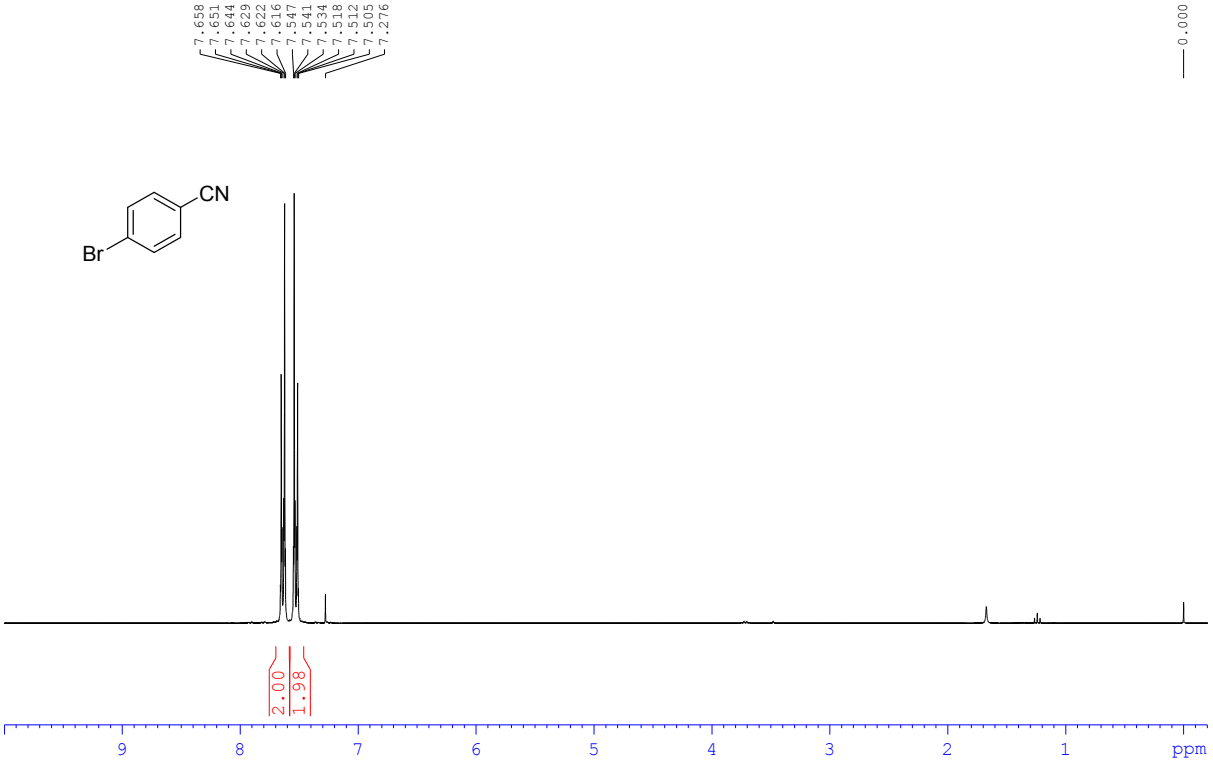


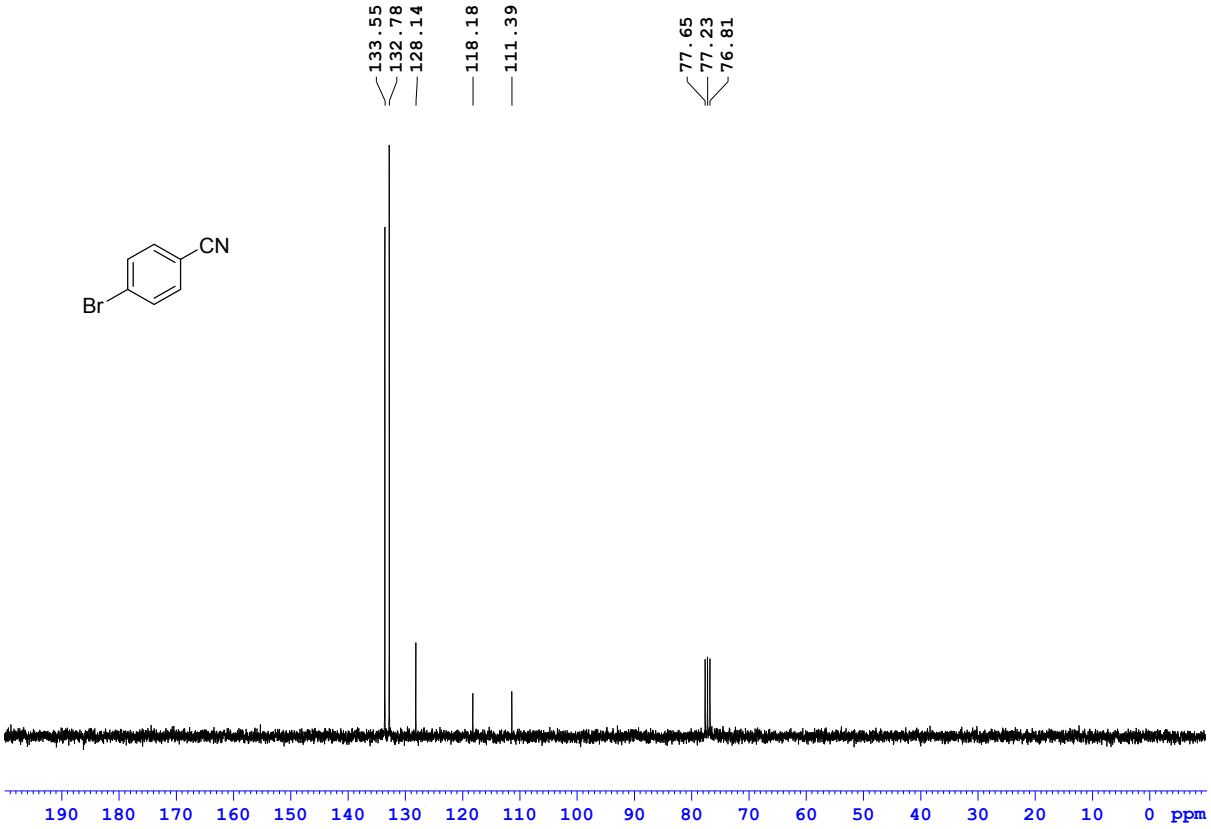
^{1}H and ^{13}C NMR spectrum of **5h**



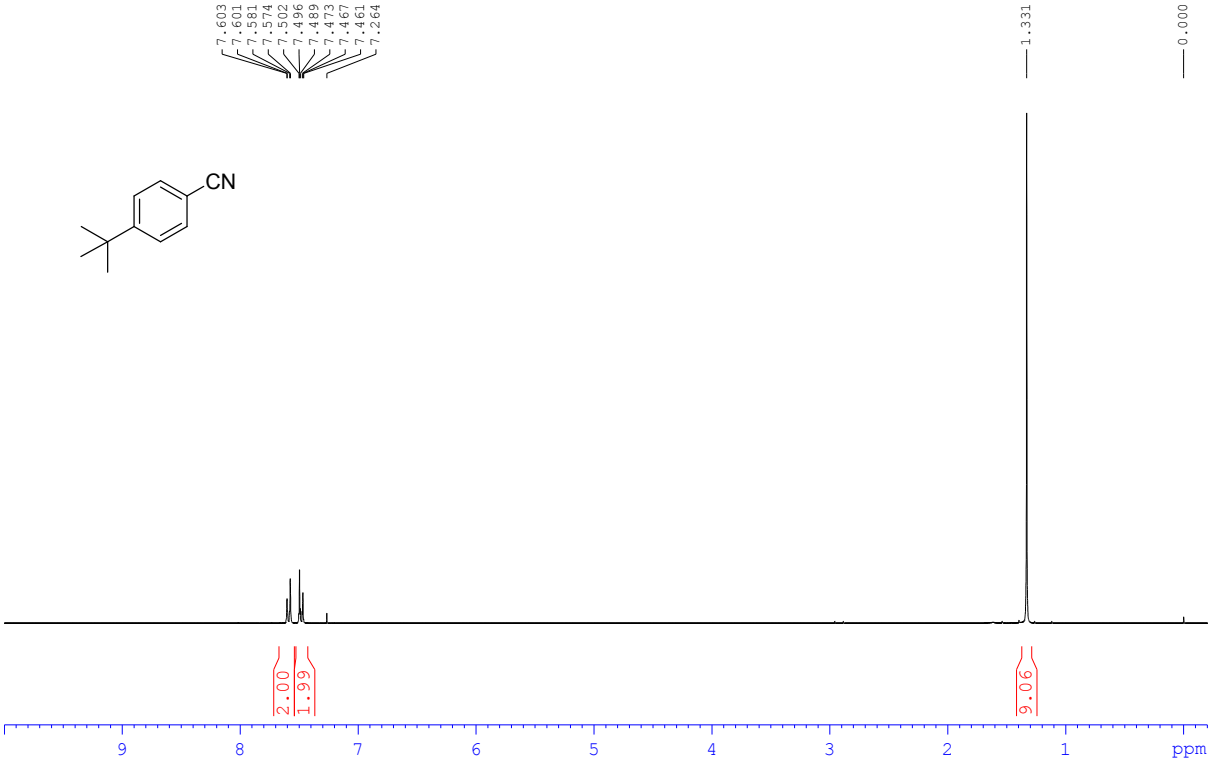


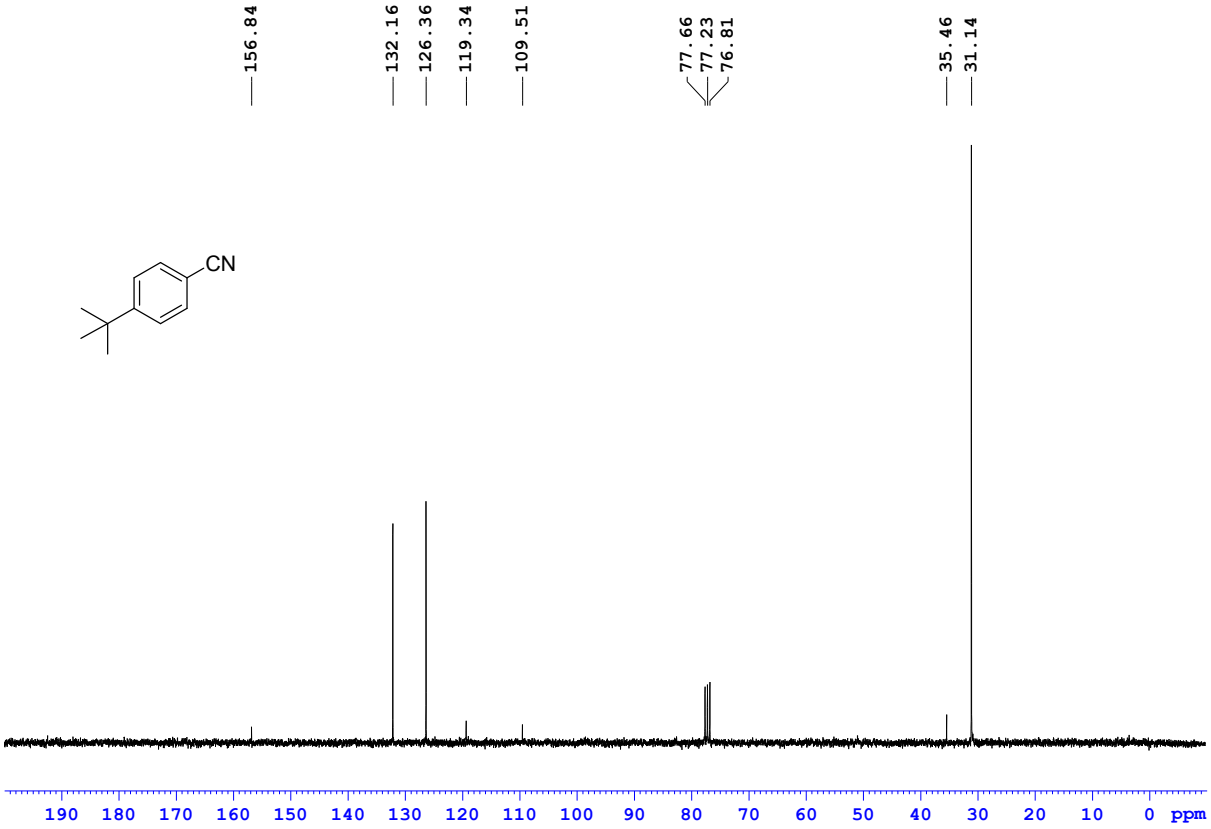
^{1}H and ^{13}C NMR spectrum of **5i**



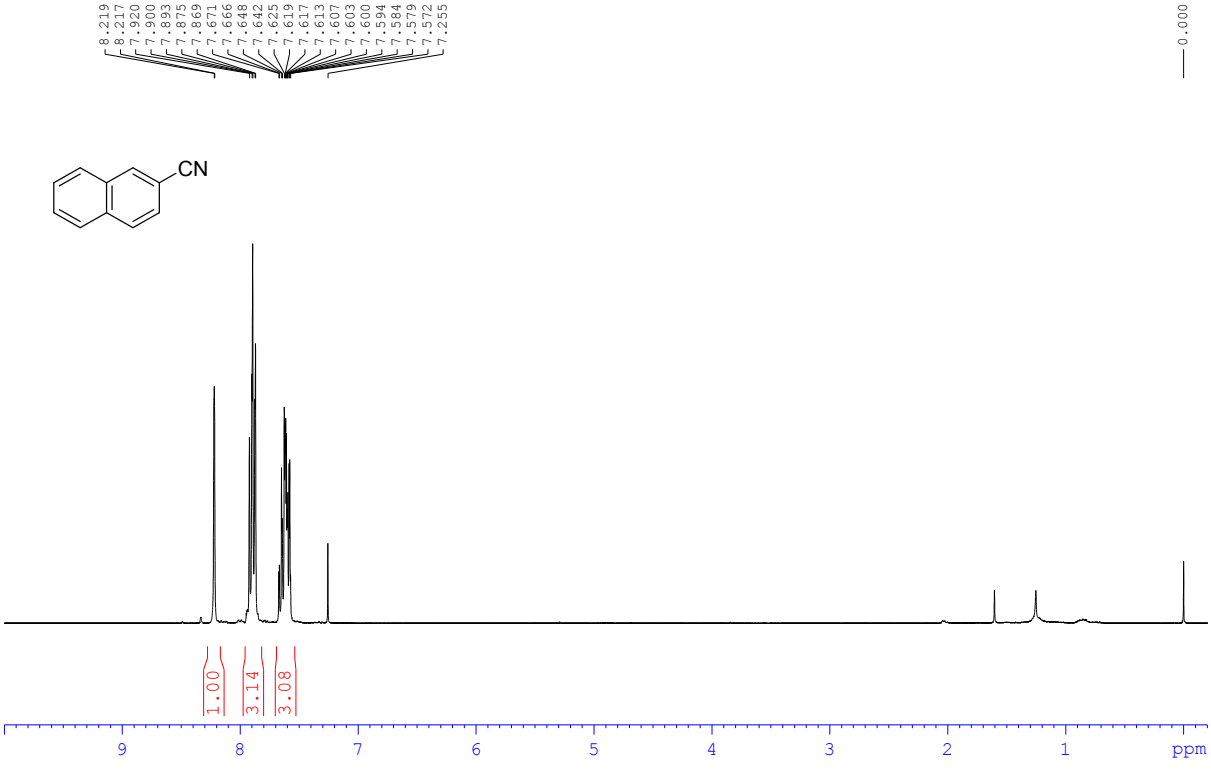


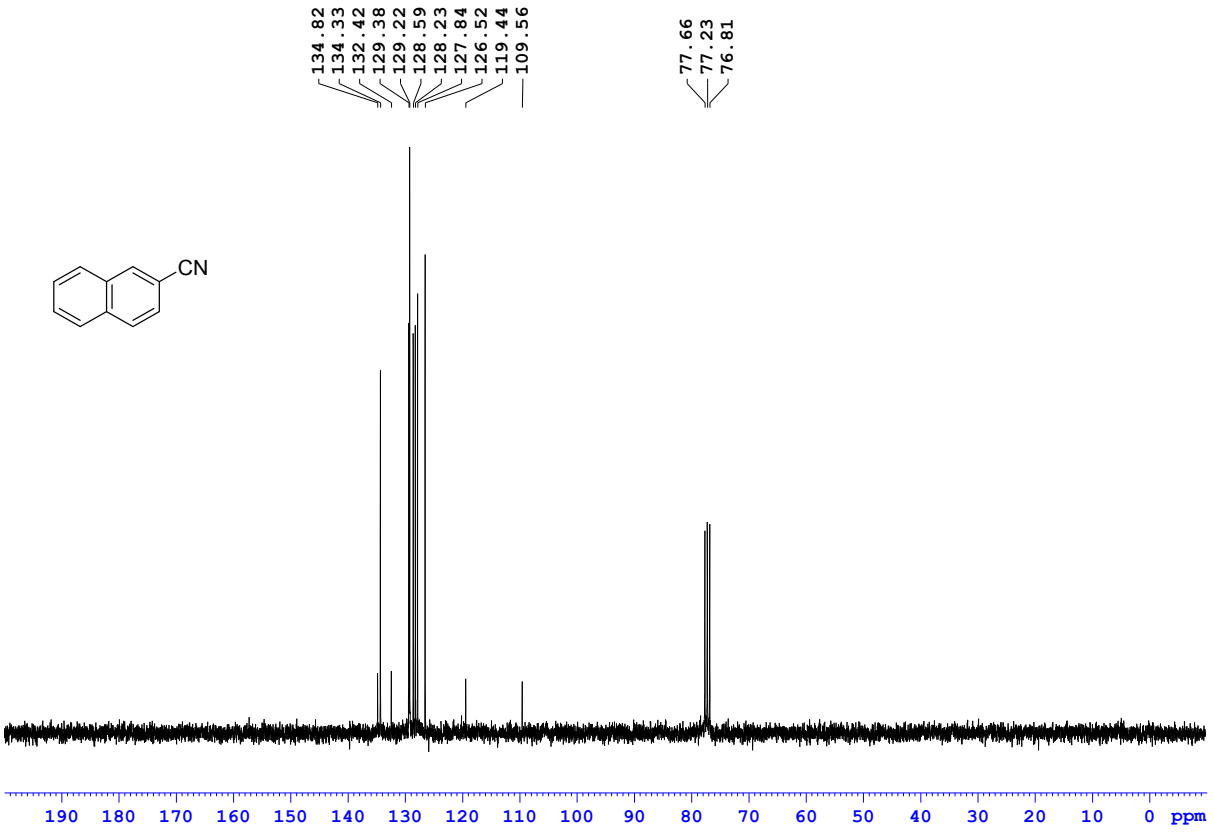
^{1}H and ^{13}C NMR spectrum of **5j**



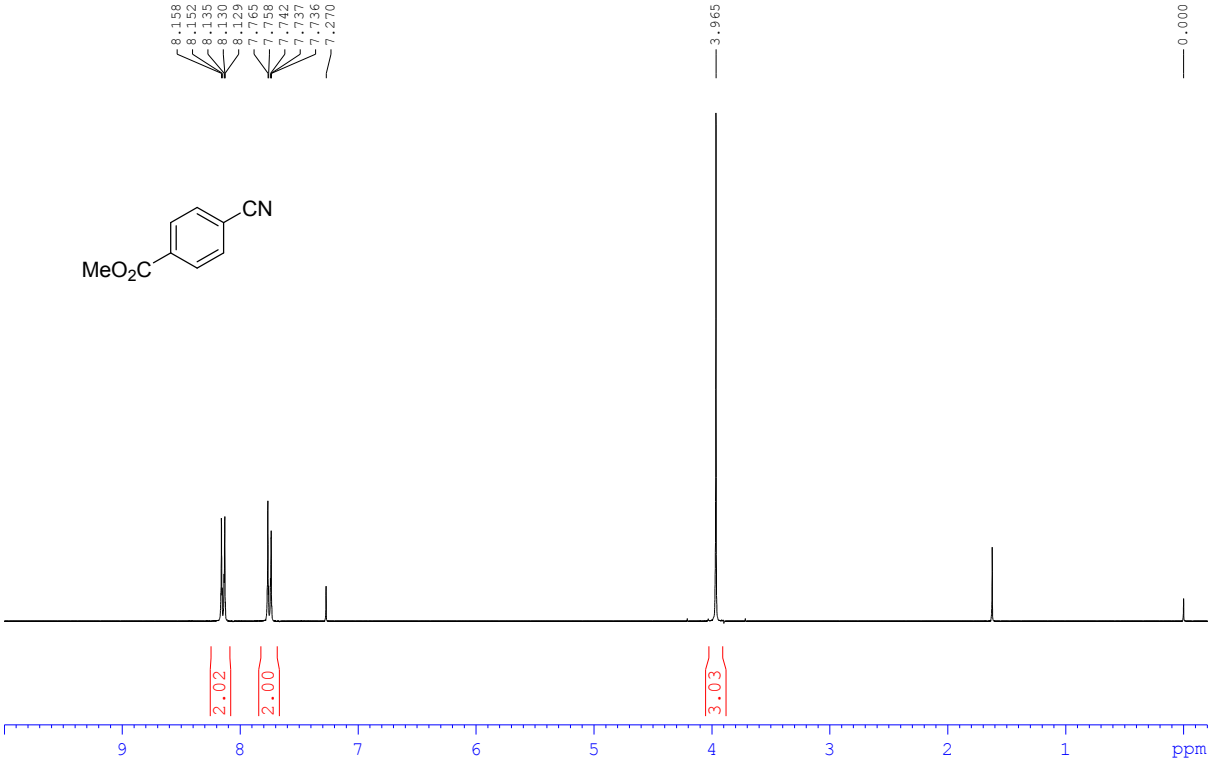


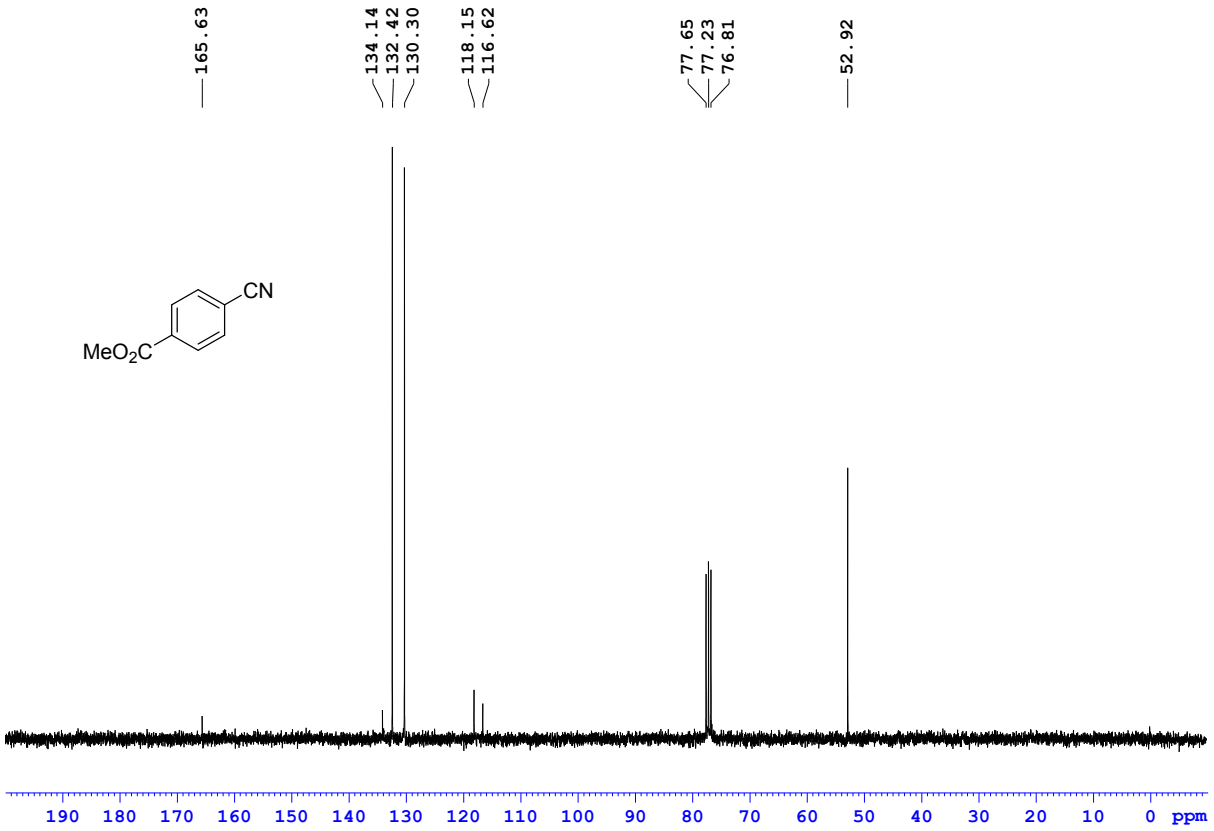
^{1}H and ^{13}C NMR spectrum of **5k**



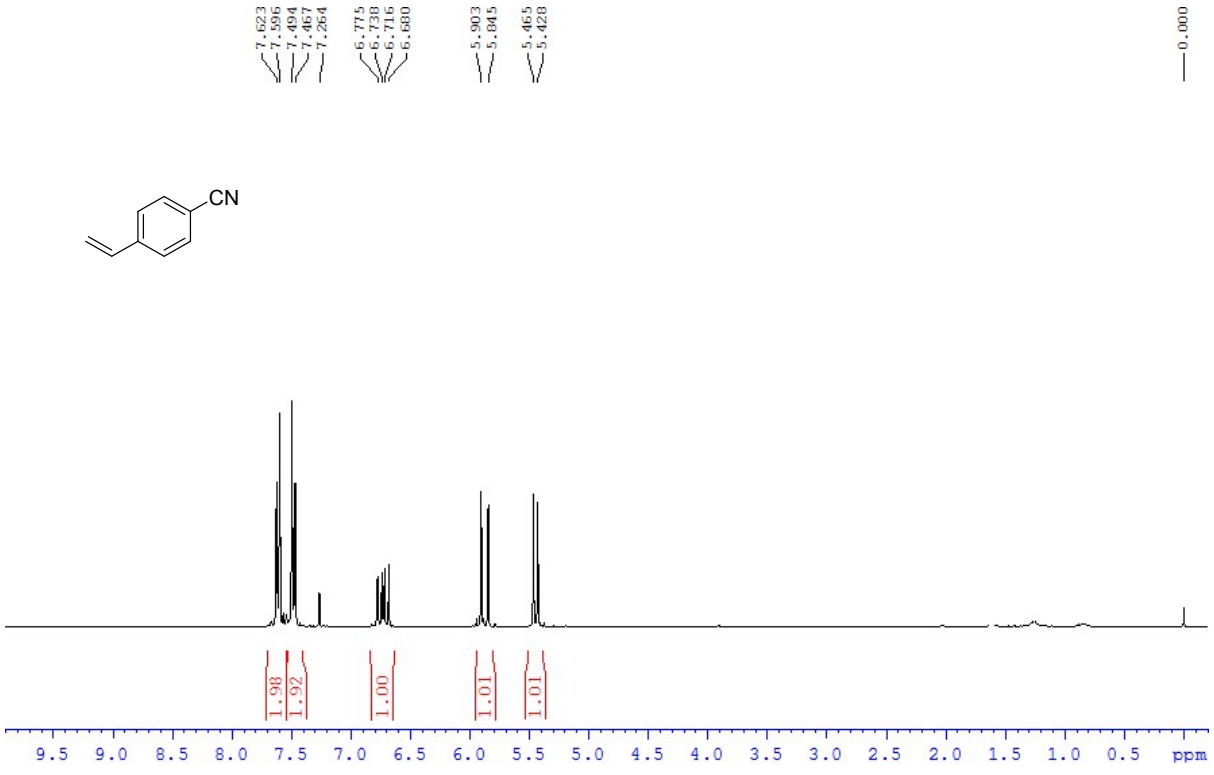


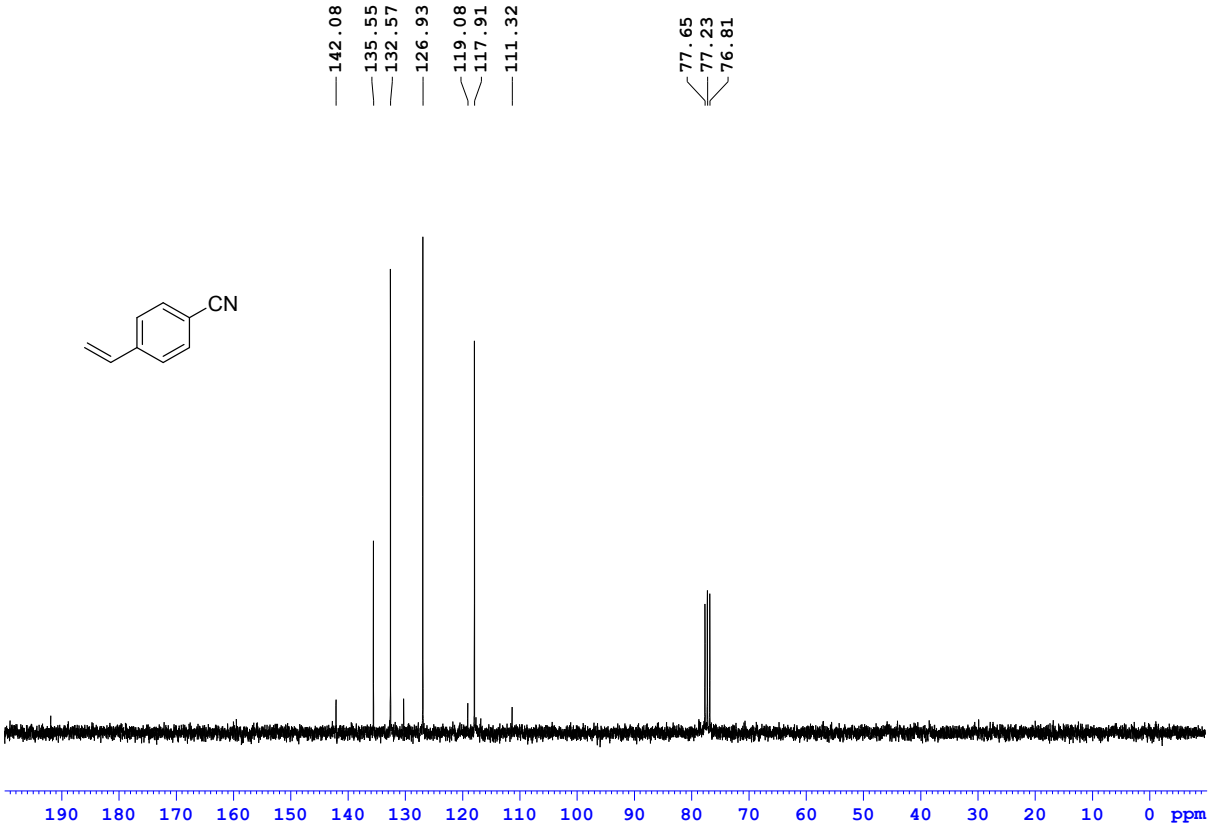
^{1}H and ^{13}C NMR spectrum of **5l**



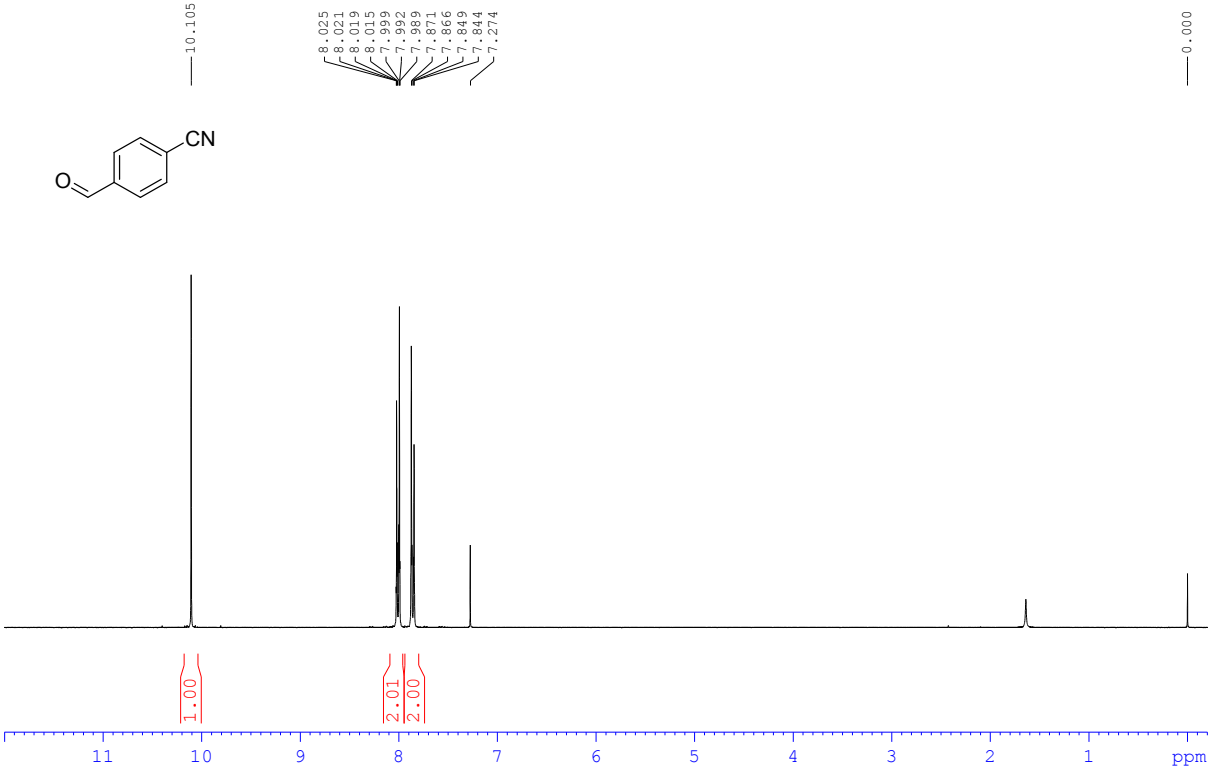


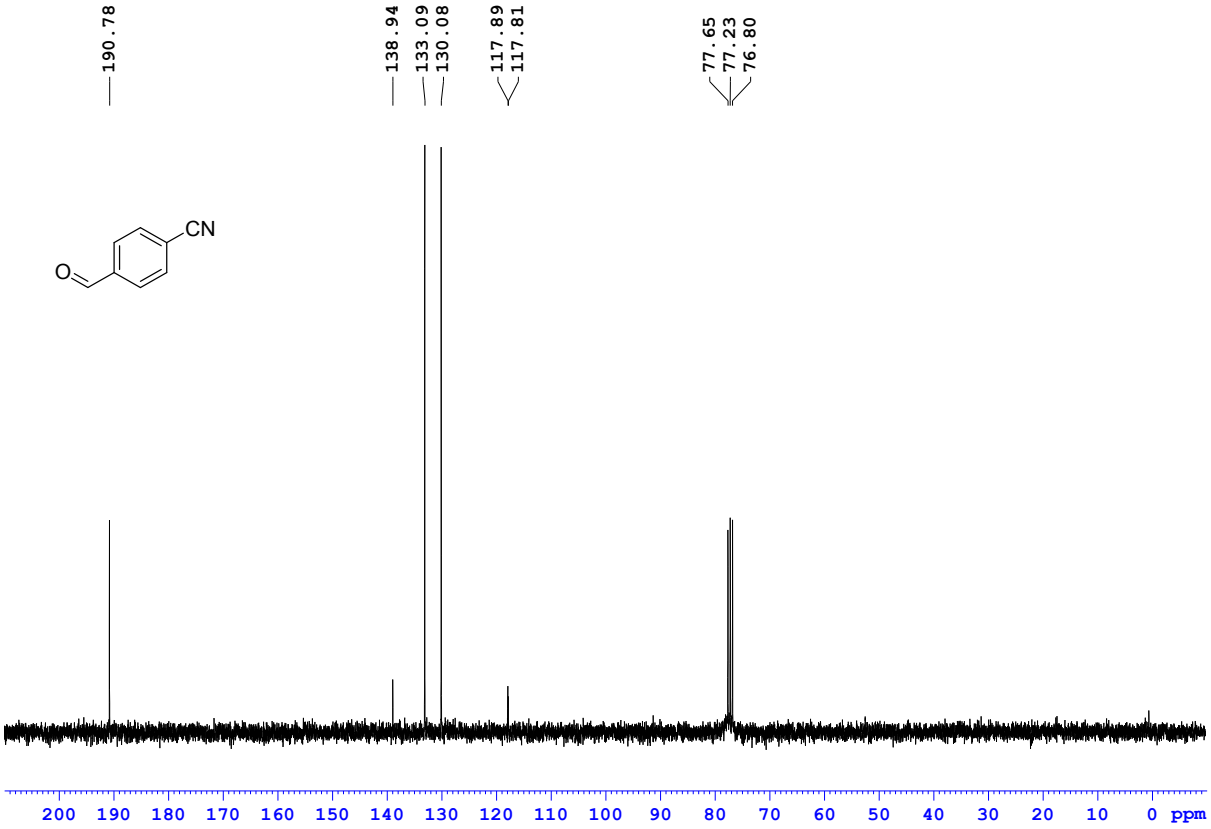
^{1}H and ^{13}C NMR spectrum of **5m**



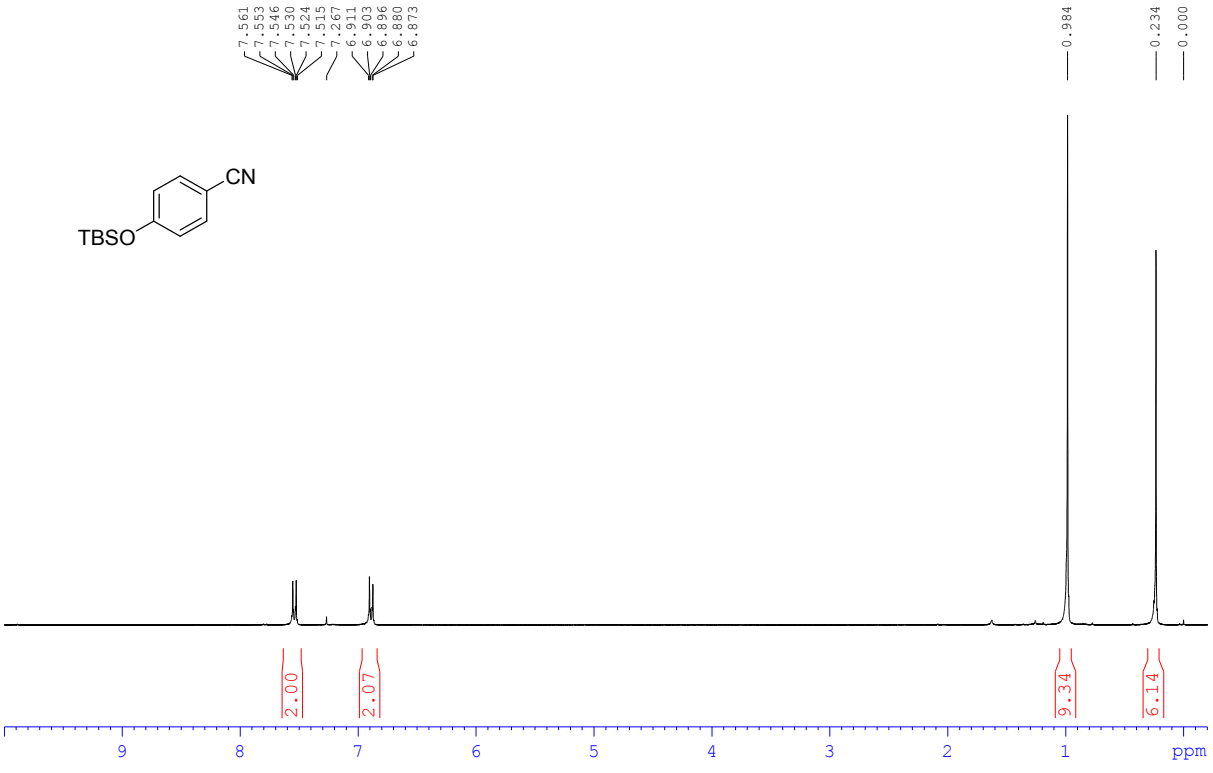


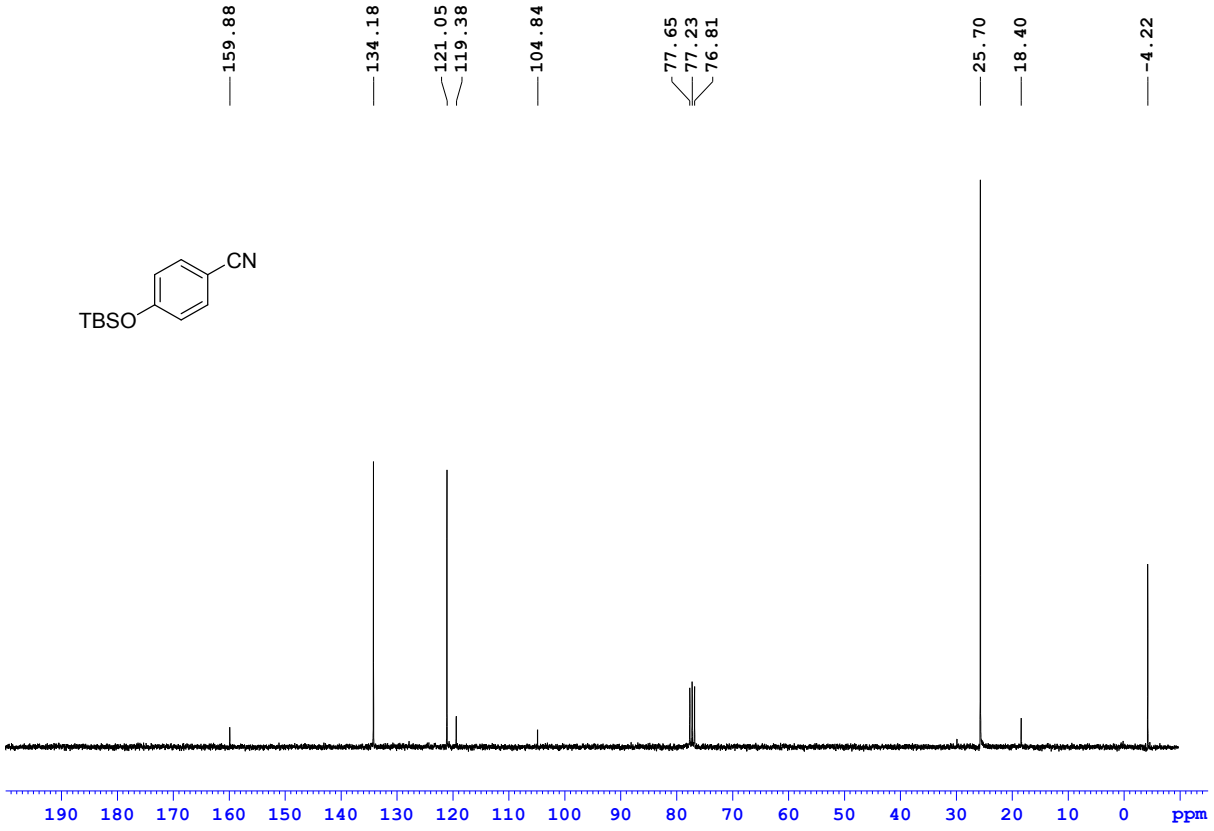
^{1}H and ^{13}C NMR spectrum of **5n**



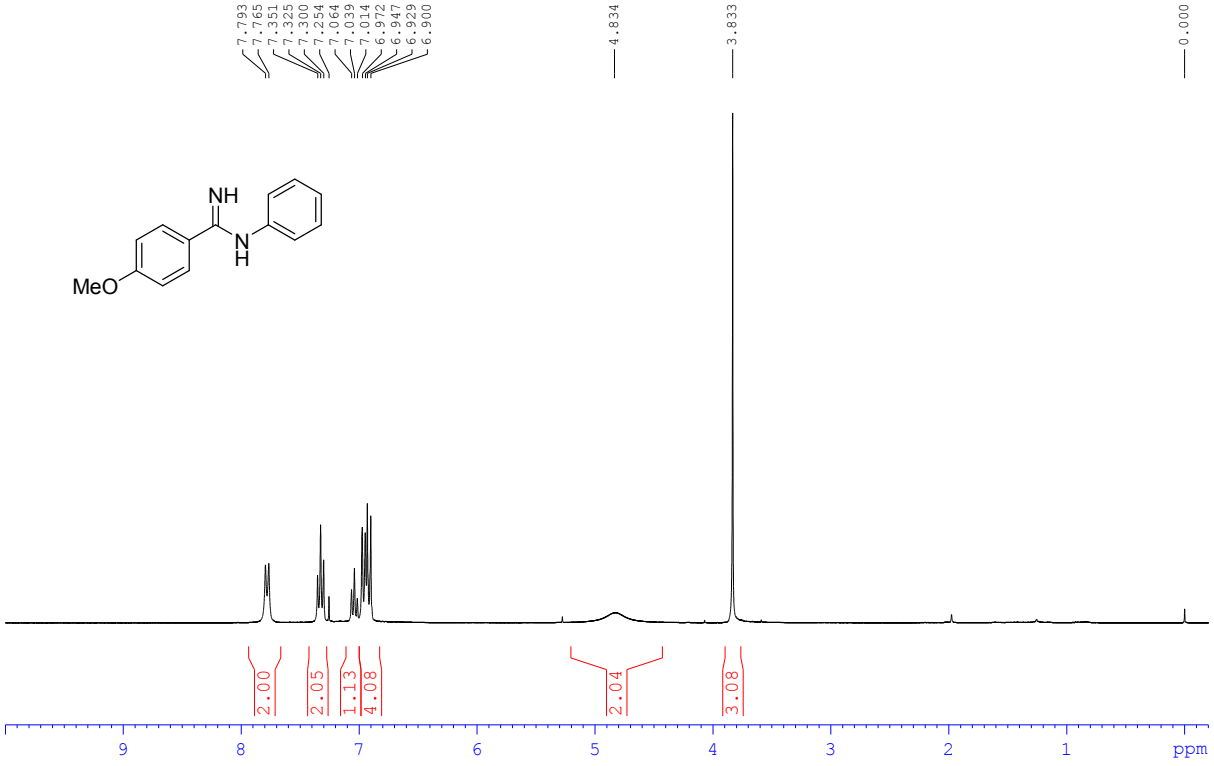


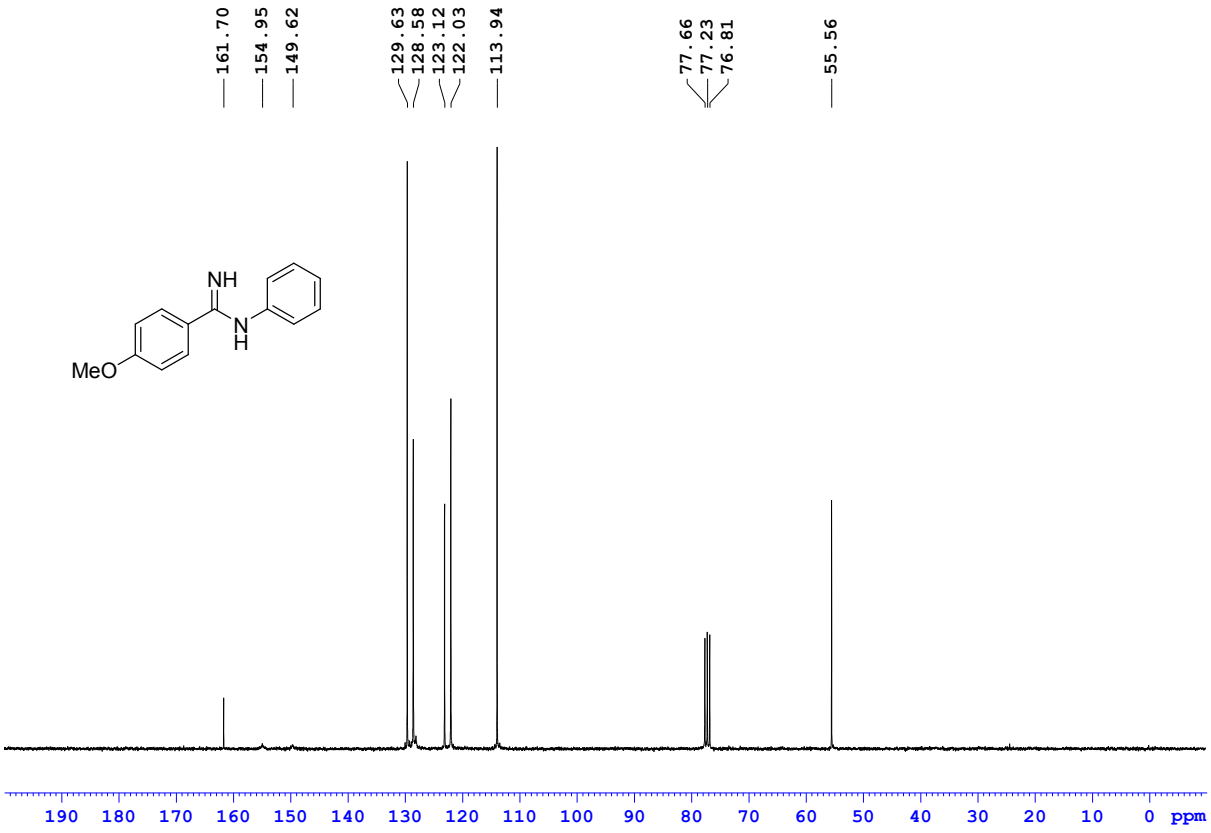
^{1}H and ^{13}C NMR spectrum of **5o**



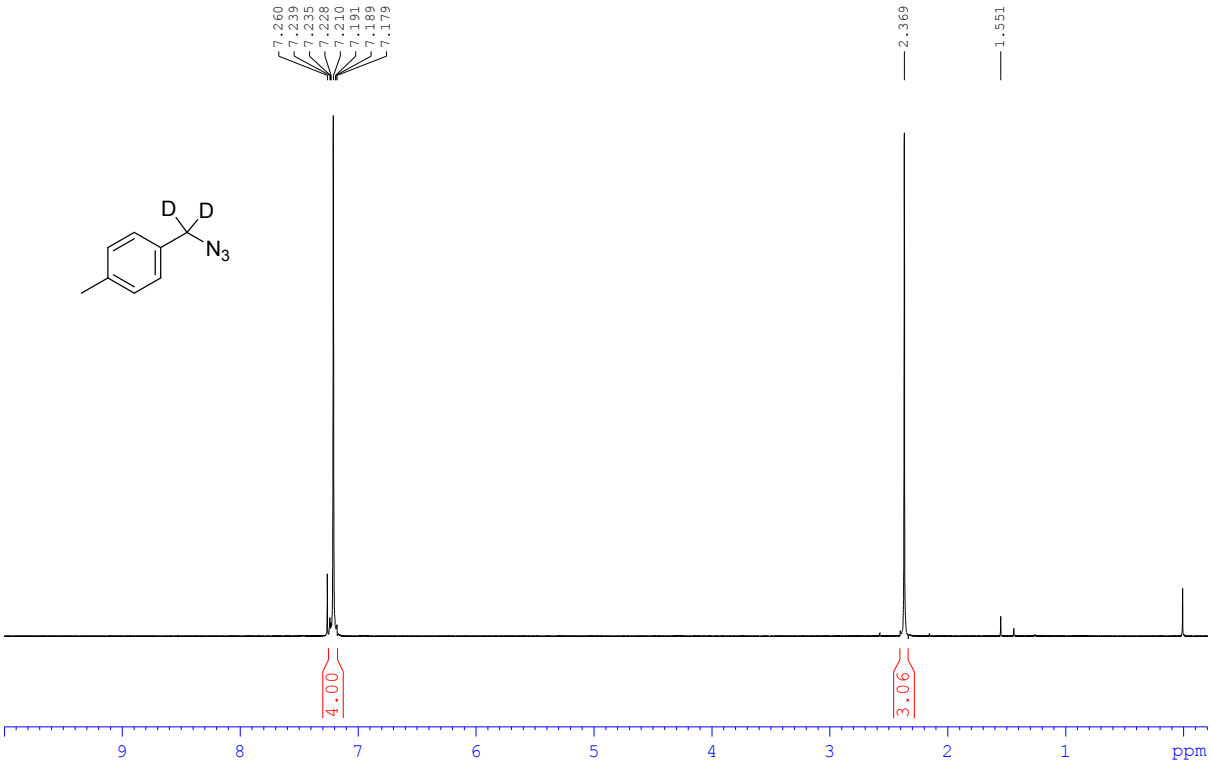


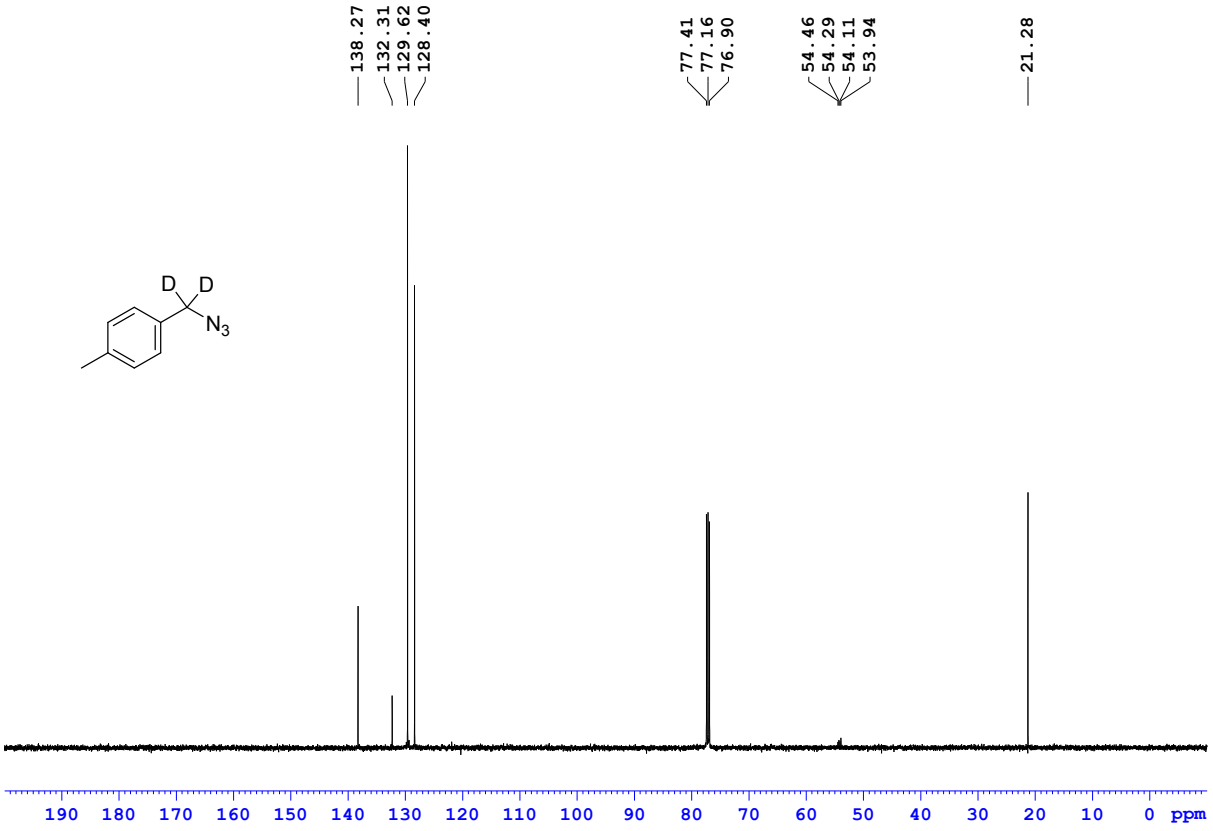
^{1}H and ^{13}C NMR spectrum of **7**



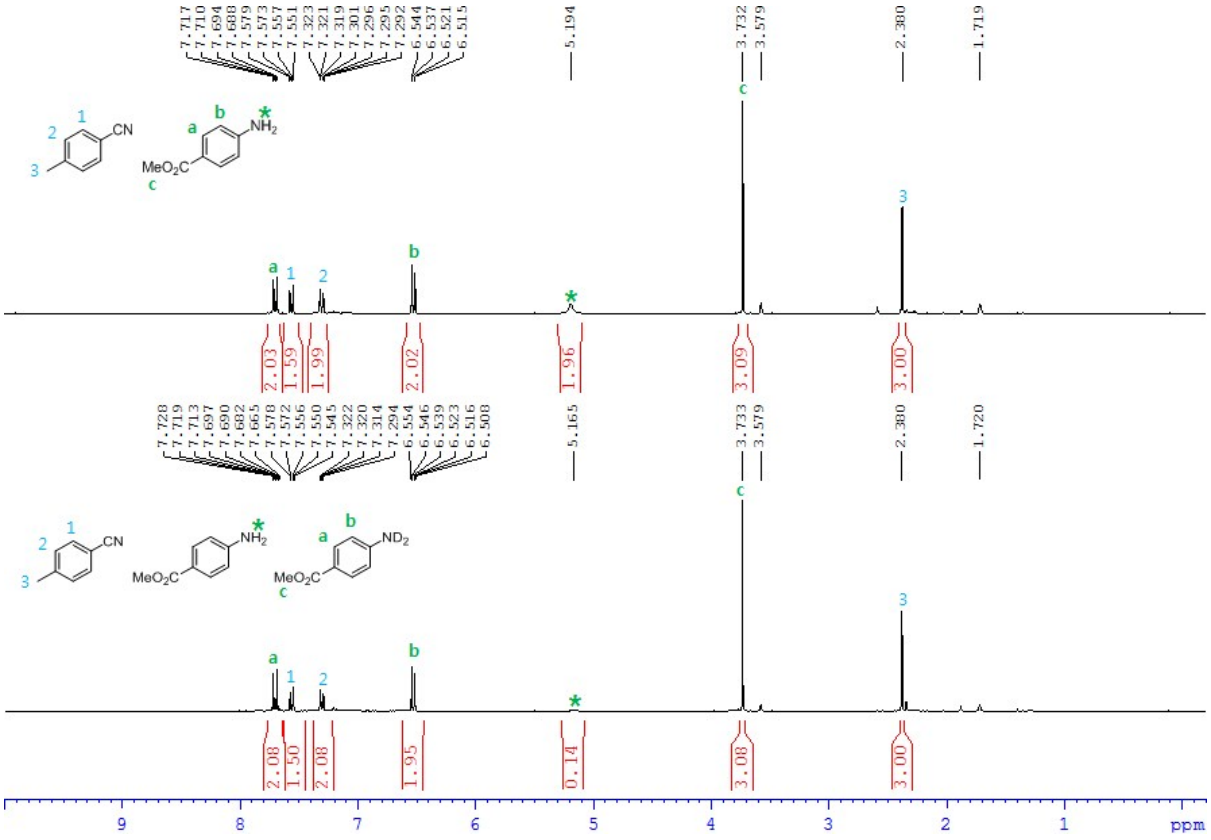


^{1}H and ^{13}C NMR spectrum of **8**

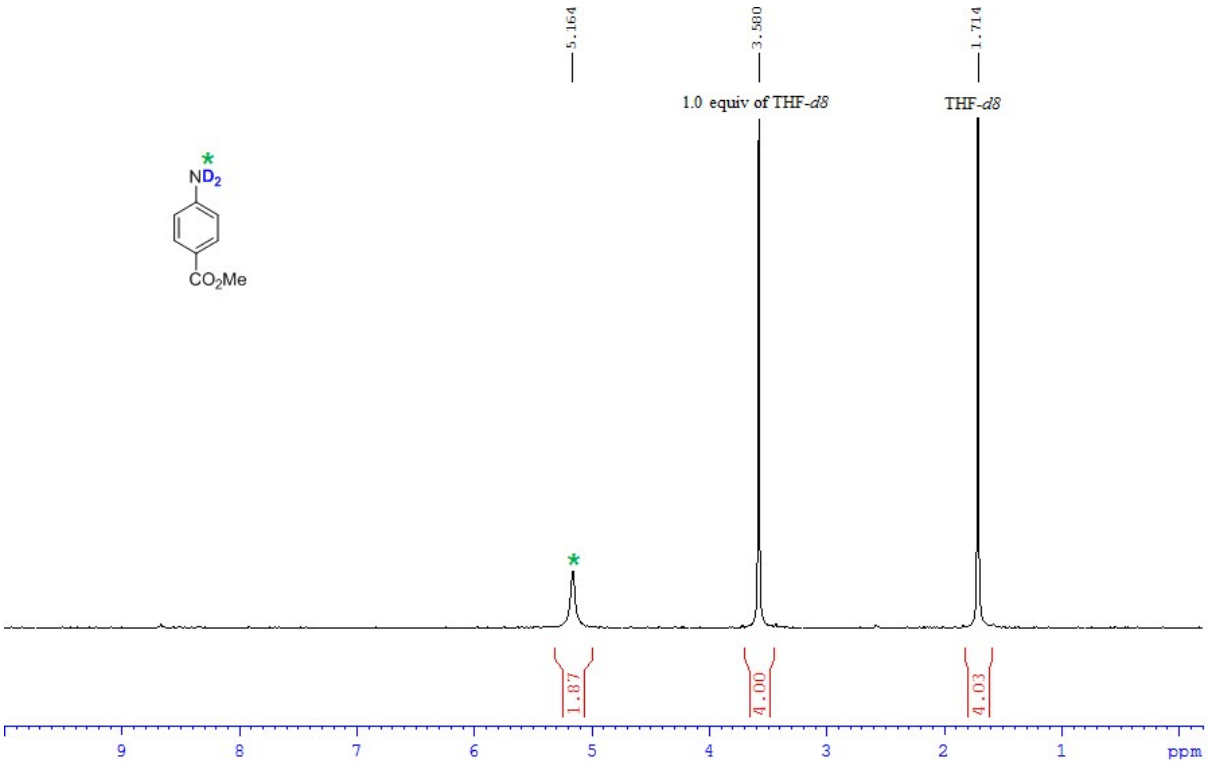




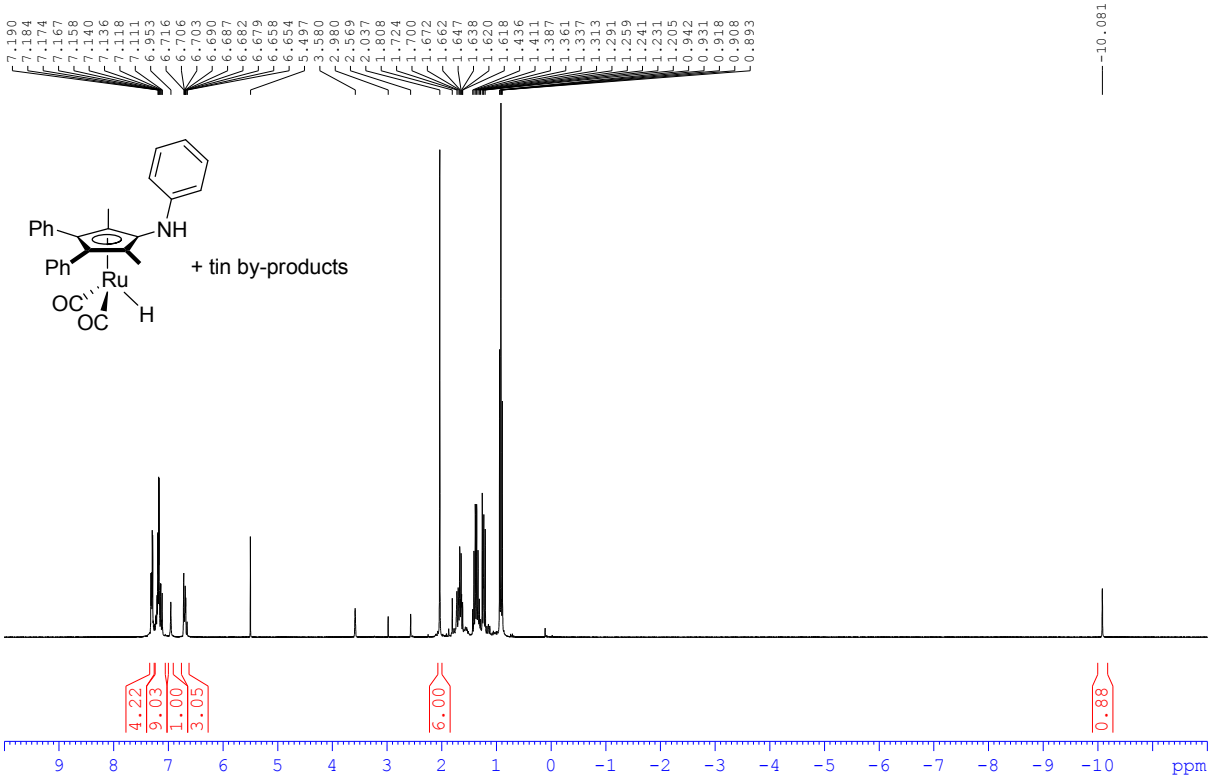
^{1}H NMR spectrum of **5b** and **10**



Deuterium NMR spectrum of **5b** and **10**



^{1}H and ^{13}C NMR spectrum of **12** and tin mixture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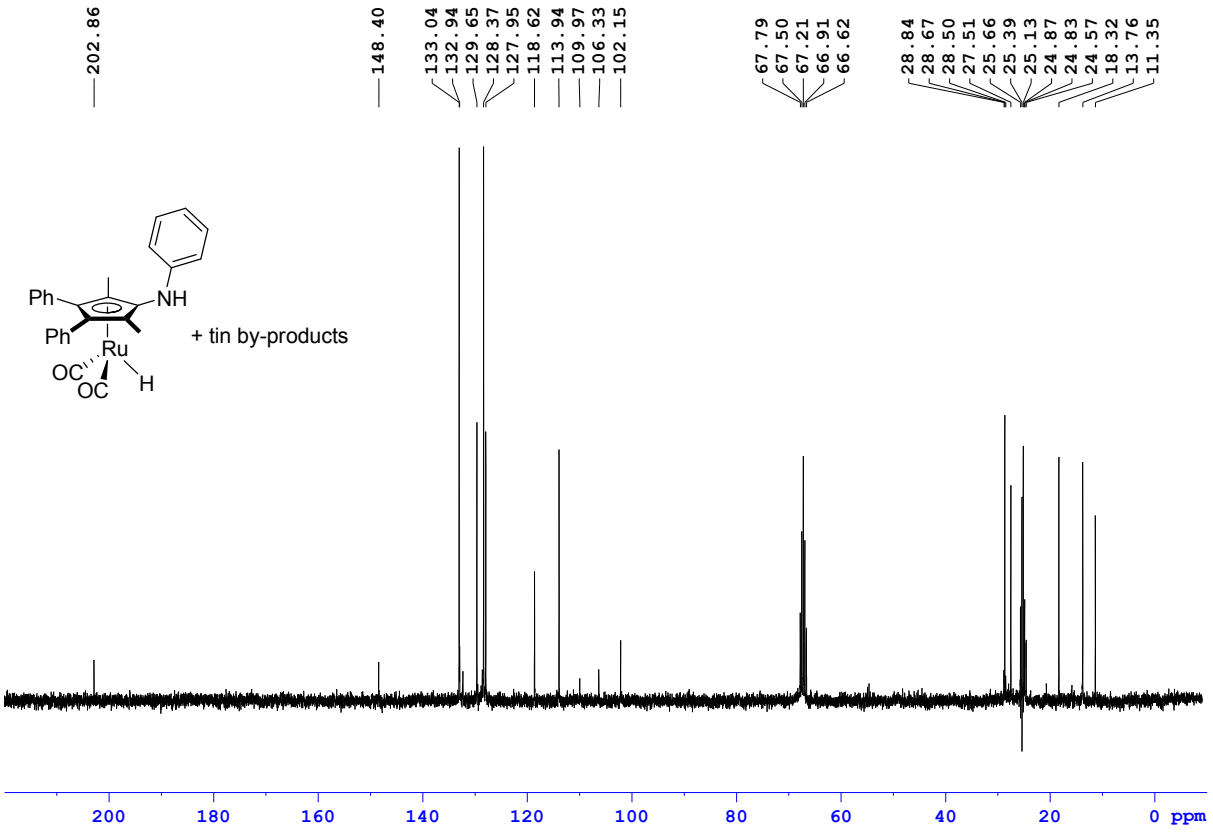
7.184
7.174
7.167
7.158
7.140
7.136
7.118
7.111
6.953
6.716
6.706
6.703
6.690
6.687
6.682
6.679
6.658
6.654
5.497
3.580
2.980
2.569
2.037
1.808
1.724
1.700
1.672
1.662
1.647
1.638
1.620
1.618
1.436
1.411
1.387
1.361
1.337
1.313
1.291
1.259
1.241
1.231
1.205
0.942
0.931
0.918
0.908
0.893
-10.081
Ph
NH
Ph
Ru
OC
OC
H
+ tin by-products
4.22
9.03
1.00
3.05
6.00
0.88
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
ppm


202.86
148.40
133.04
132.94
129.65
128.37
127.95
118.62
113.94
109.97
106.33
102.15
67.79
67.50
67.21
66.91
66.62
28.84
28.67
28.50
27.51
25.66
25.39
25.13
24.87
24.83
24.57
18.32
13.76
11.35
Ph
NH
Ph
Ru
OC
OC
H
+ tin by-products
200
180
160
140
120
100
80
60
40
20
0 ppm