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Benzylamine imines as versatile precursors to azomethine and nitrile ylides in the [2 + 3] cycloaddition reactions with [60]fullerene

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Experimental

1. The assignment of the structure of 3b based on ^{1}H NMR data

Low solubility of **3b** (below 3-4 mg/ml) did not allow us to permit 2D NOESY NMR experiments to prove unambiguously the position of the double bond in the pyrroline ring of this compound. However, a comparison of the ^{1}H NMR spectra of **3a** and **3b** was decisive for the structural assignment (Figure 1). The imine double bond in the pyrroline ring is conjugated with the adjacent aryl group that results in the down-field shielding of aromatic protons. Therefore, the up-fielded set of resonances in the spectrum of **3a** corresponds to the phenyl ring that is non-adjacent to C=N and *vice versa*. The signals due to the phenyl ring protons in the spectrum of **3b** have very similar chemical shifts with the up-fielded set of resonances from phenyl unit in **3a** (marked with "*" in figure 1). At the same time, down-fielded phenyl signals of **3a** meet minor peaks in the spectrum corresponding to **3b1** (denoted by "#"). Therefore, the phenyl group is non-adjacent with C=N in **3b**, but it is adjacent in the case of **3b1**.

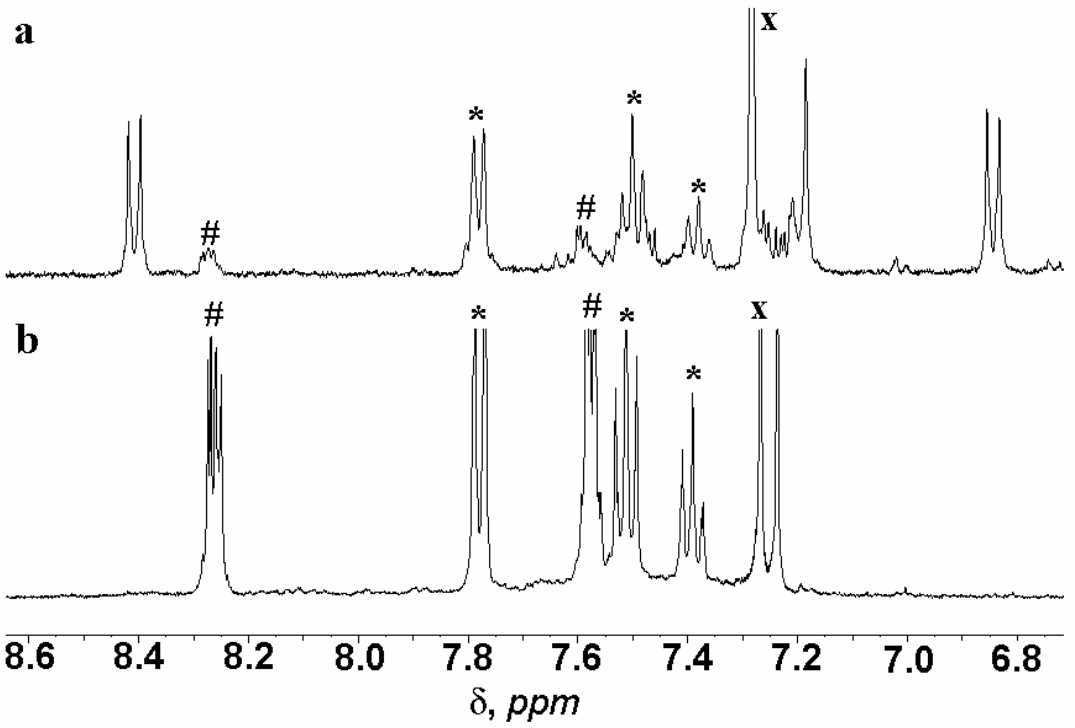


Figure 1 Selected frames of the ^{1}H NMR spectra of **3b** (a) and **3a** (b) that illustrate correlations between chemical shifts of the phenyl protons. Symbol "*" denotes resonances of non-adjacent to C=N phenyl units; symbol "#" denotes signals of phenyl groups low-filed shielded because of conjugation with C=N; symbol "x" denotes $CHCl_3$ in $CDCl_3$

2. Experimental procedures and spectral data

Synthesis of 2a and 3a in argon atmosphere

Imine **1a** (50.7 mg, 0.26 mmol), C_{60} (105 mg, 0.15 mmol) and butyric acid (1.2 ml) were heated at reflux in 1,2-dichlorobenzene (50 ml) in argon atmosphere. The course of the reaction was monitored by TLC; the synthesis was stopped after 10 h when fullerene conversion was ca. 70%. Then the reaction mixture was cooled down to the room temperature, solvent was removed at the rotary evaporator. The residue was dissolved in CCl_4 (200-300 ml) and poured at the top of silica gel column (40-60 μ, 60Å, Acros Organics). Pyrrolidinofullerene **2a** was eluted with CCl_4-toluene 2:1 – 1:1 mixture; pyrrolinofullerene **3a** was washed out with CCl_4-toluene 1:8 – pure toluene.

Synthesis of 3a in air atmosphere

Imine **1a** (50.7, 0.26 mmol), C_{60} (105 mg, 0.15 mmol) and butyric acid (1.2 ml) were heated at reflux in 1,2-dichlorobenzene (50 ml) in air atmosphere; reverse condenser was protected from the

top with a tube filled with anhydrous $CaCl_2$. Conventional 60W light bulb was used to irradiate the reaction mixture. Workup and chromatographic separation were done as described above.

Synthesis of 3b

Imine **1b** (95.2 mg, 0.40 mmol), C_{60} (210 mg, 0.30 mmol) and butyric acid (4 ml) were heated at reflux in 1,2-dichlorobenzene (50 ml) in air atmosphere without additional irradiation for 12 h. Application of irradiation has no pronounced effect on the product yield. Then the reaction mixture was cooled down and solvent was removed. The residue was dissolved in pure toluene (400 ml), then diluted with 300 ml of hexane and chromatographed to give a distinct fraction of **3b** eluted with toluene.

Reaction of C_{60} with imine 1c

The reagent ratios, synthesis and workup procedures were the same as described above for preparation of **3a** in air. The residue formed after removal of the solvent was dissolved in 400 ml of CCl_4 and the resulting solution was diluted with ca. 200 ml of hexane. Elution with pure CCl_4 – CCl_4-toluene 9:1 mixture afforded mixture of **3a** with 4-nitrobenzaldehyde. Following elution with CCl_4-toluene 2:1 – CCl_4-toluene 1:1 yielded mixture of **2c** and **3c1**.

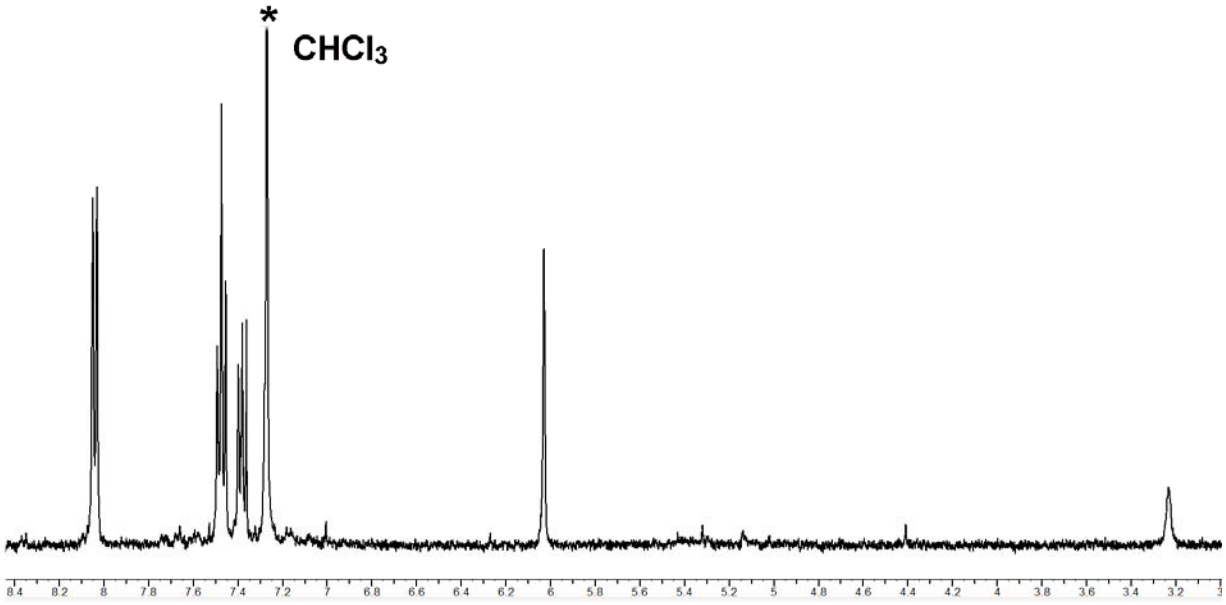
Pyrrolidinofullerene **2a**. ^{1}H NMR (400 MHz, $CDCl_3$), δ= 3.23 (1H, broad s), 6.03 (2H, s), 7.38 (2H, t), 7.47 (4H, t), 8.04 (4H, d) ppm. ^{13}C NMR (100 MHz, CS_2-C_6D_{12} 10:1): δ = 75.10, 76.32, 128.64, 128.68, 128.86, 136.07, 137.06, 138.14, 139.44, 140.02, 141.54, 141.99, 142.04, 142.09, 142.22, 142.31, 142.60, 142.67, 144.38, 144.68, 145.16, 145.24, 145.27, 145.57, 145.87, 146.12, 146.26, 146.29, 146.94, 147.24, 153.46, 153.72 ppm.

Pyrrolidinofullerene **2c** ^{1}H NMR (600 MHz, CS_2-$(CD_3)_2CO$ 10:1), δ= 6.16 (1H, s), 7.22 (1H, s), 7.40 (1H, t), 7.49 (2H, t), 7.70 (2H, d), 8.38 (2H, d), 8.51 (2H, d) ppm. ^{13}C NMR (150 MHz, CS_2-$(CD_3)_2CO$ 10:1): δ = 74.17, 75.61, 77.41, 77.97 ppm; sp^2 carbon signals cannot be confidently distinguished among the peaks of **3c1**.

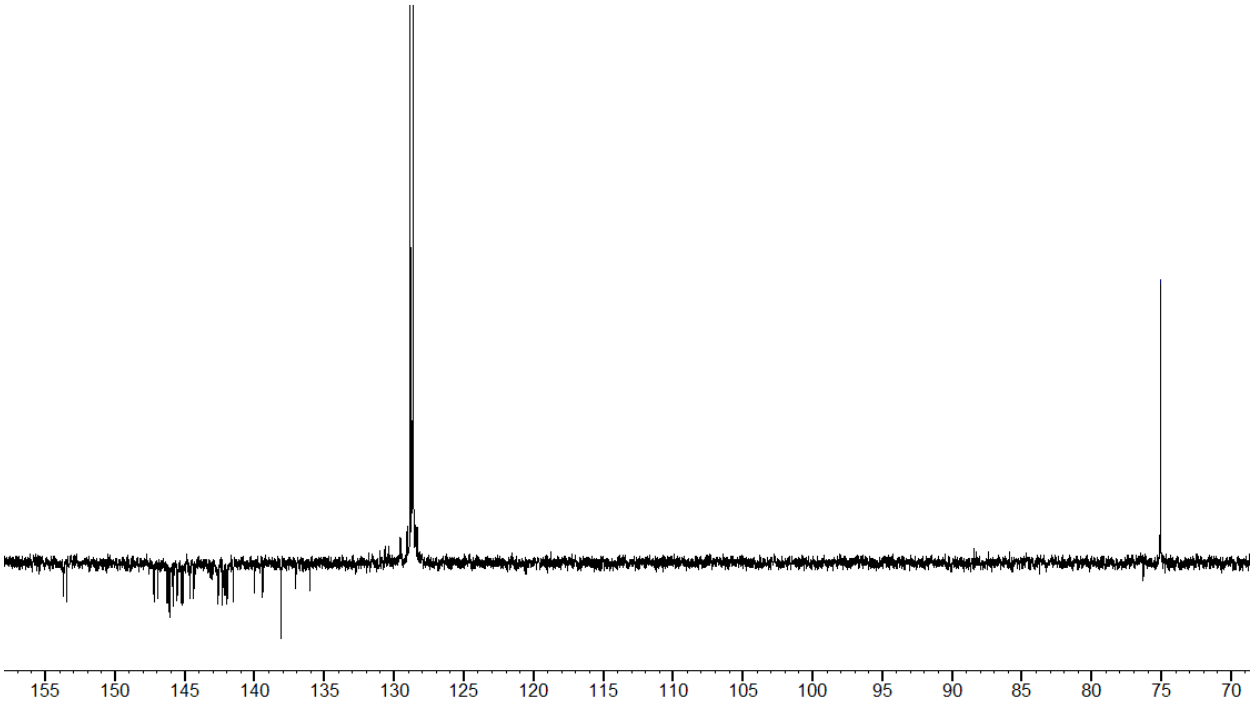
Pyrrolinofullerene **3a**. ^{1}H NMR (400 MHz, $CDCl_3$), δ= 7.23 (1H, s), 7.39 (1H, t), 7.51 (2H, t), 7.57 (3H, m), 7.78 (2H, d), 8.26 (2H, dd) ppm. ^{13}C NMR (100 MHz, CS_2-C_6D_{12} 10:1): δ= 78.04, 88.40, 128.39, 128.48, 128.76, 129.11, 129.58, 130.71, 134.02, 134.69, 134.97, 136.39, 136.42, 139.88, 139.92, 140.20, 140.27, 140.64, 141.73, 141.83, 141.91, 141.98, 142.10, 142.14, 142.24, 142.28, 142.36, 142.39, 142.62, 142.73, 142.79, 142.80, 142.85, 143.25, 143.28, 144.11, 144.14, 144.44, 144.52, 145.00, 145.09, 145.12, 145.17, 145.28, 145.41, 145.44, 145.60, 145.70, 145.77, 145.79, 145.86, 145.97, 146.05, 146.40, 1
6.46, 146.69, 147.01, 147.03, 147.34, 147.88, 148.98, 152.86, 155.41, 170.12 ppm.

Pyrrolinofullerene **3b**. ^{1}H NMR (600 MHz, CS_2-$(CD_3)_2CO$ 10:1), δ= 3.11 (6H, s), 6.76 (2H, d) 7.10 (1H, s), 7.34 (1H, t), 7.45 (2H, t), 7.70 (2H, d), 8.32 (2H, d) ppm. ^{13}C NMR (150 MHz, CS_2-$(CD_3)_2CO$ 10:1): δ= 40.07, 78.50, 84.43, 87.97, 111.74, 122.13, 125.46, 125.55, 127.86, 128.26, 128.43, 128.98, 129.23, 129.58, 130.65, 131.53, 133.94, 134.98, 136.26, 139.56, 139.90, 139.93, 140.66, 140.79, 141.64, 141.74, 141.94, 142.06, 142.34, 142.37, 142.39, 142.62, 142.72, 142.78, 142.82, 143.18, 143.26, 144.12, 144.16, 144.48, 144.56, 144.76, 144.89, 145.07, 145.26, 145.35, 145.36, 145.37, 145.49, 145.78, 145.87, 145.92, 146.02, 146.35, 146.38, 147.14, 147.71, 148.83, 149.87, 151.55, 153.37, 155.94, 168.51 ppm.

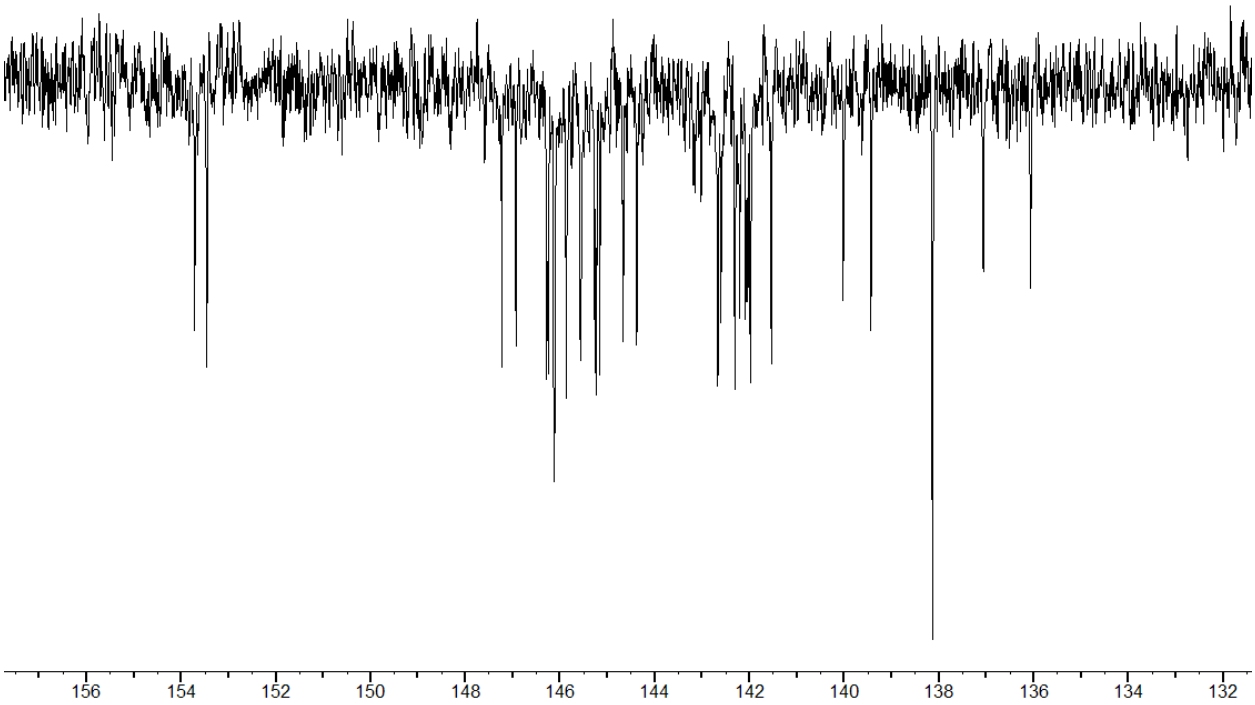
Pyrrolinofullerene **3c1**. ^{1}H NMR (600 MHz, CS_2-$(CD_3)_2CO$ 10:1), δ= 7.30 (1H, s), 7.56 (2H, d), 7.96 (2H, d), 8.26 (2H, d), 8.33 (2H, d) ppm. ^{13}C NMR (150 MHz, CS_2-$(CD_3)_2CO$ 10:1): δ = 84.87, 87.41, 88.62, 124.14, 128.87, 129.07, 129.55, 130.50, 131.02, 134.20, 134.31, 135.19, 136.10, 136.35, 140.06, 140.12, 140.29, 140.75, 141.80, 141.83, 141.85, 142.04, 142.08, 142.13, 142.19, 142.30, 142.32, 142.35, 142.49, 142.81, 142.88, 142.90, 143.18, 143.31, 143.34, 144.12, 144.18, 144.35, 144.48, 145.20, 145.30, 145.38, 145.47, 145.50, 145.60, 145.66, 145.71, 145.94, 146.05, 146.13, 146.15, 146.45, 146.48, 147.03, 147.07, 147.09, 147.12, 147.34, 147.86, 148.35, 151.46, 154.64, 171.69 ppm.



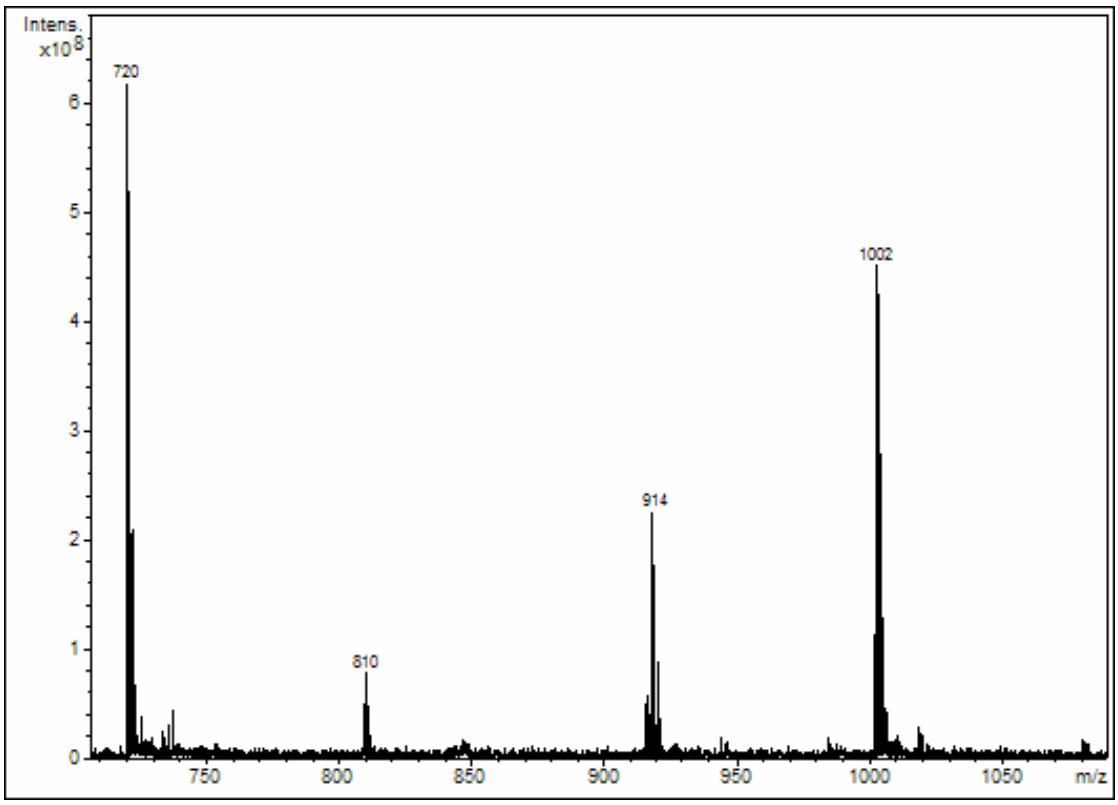
^{1}H NMR spectrum of **2a**



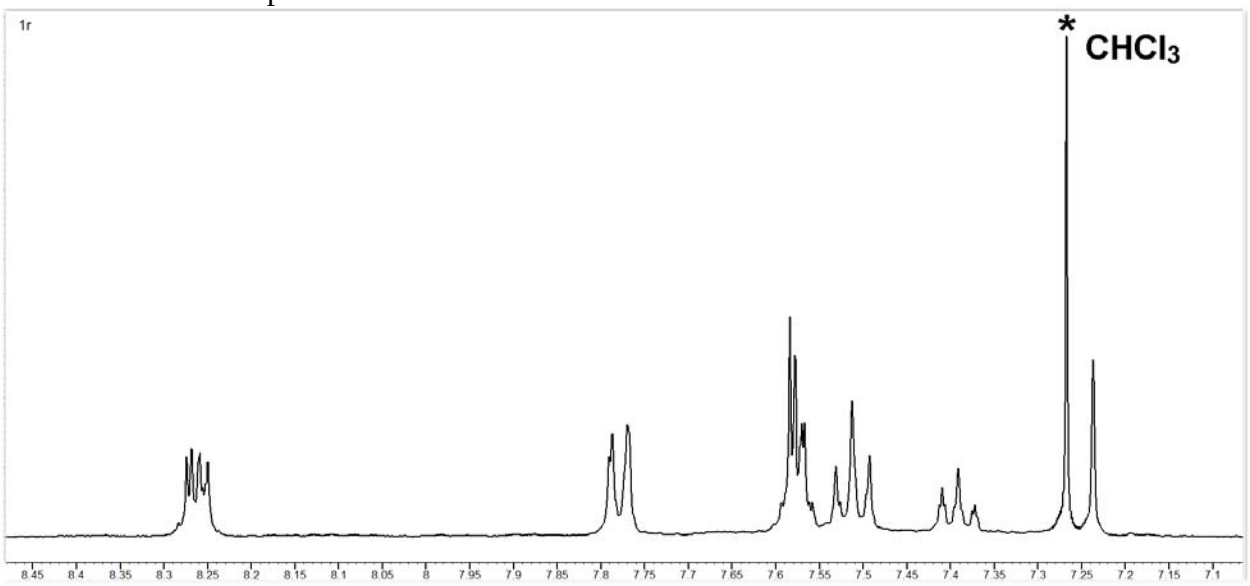
^{13}C NMR spectrum of **2a** (APT mode)



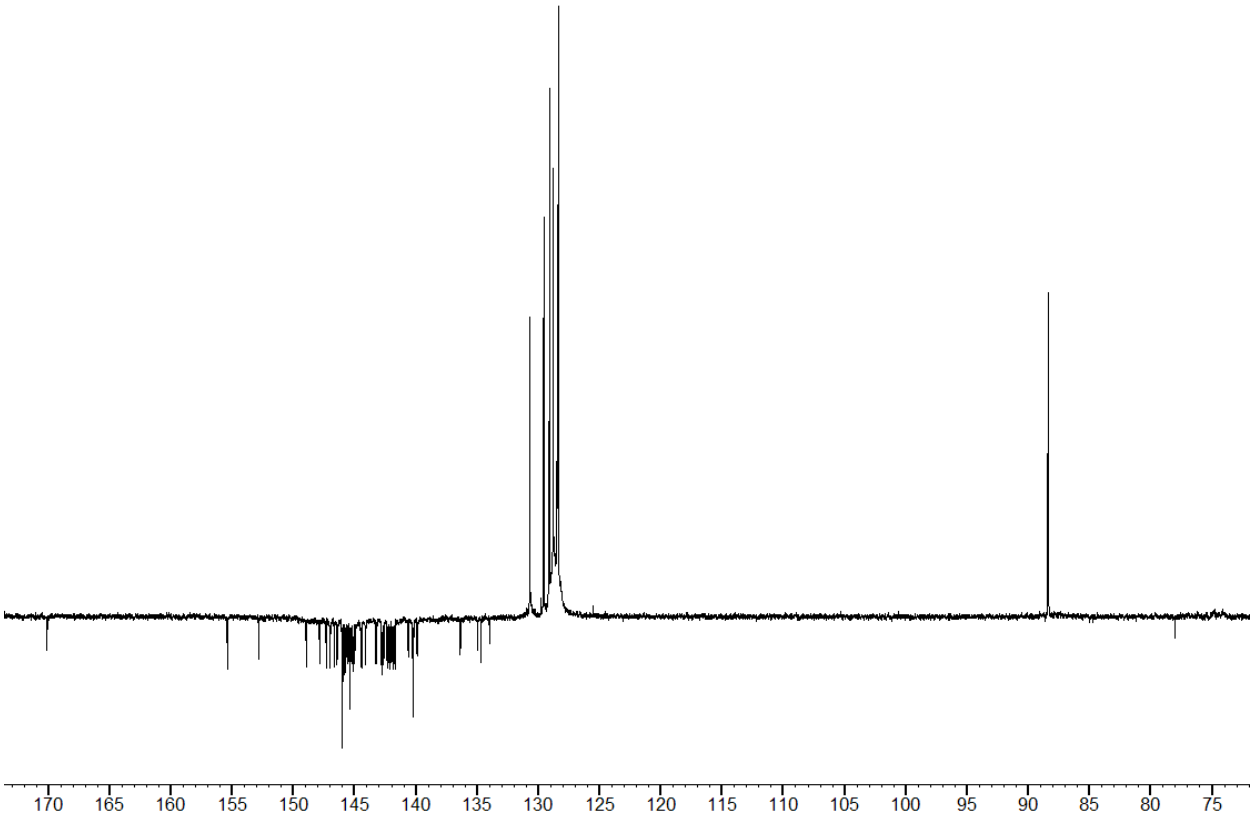
The part of the ^{13}C NMR spectrum of **2a** (APT mode)



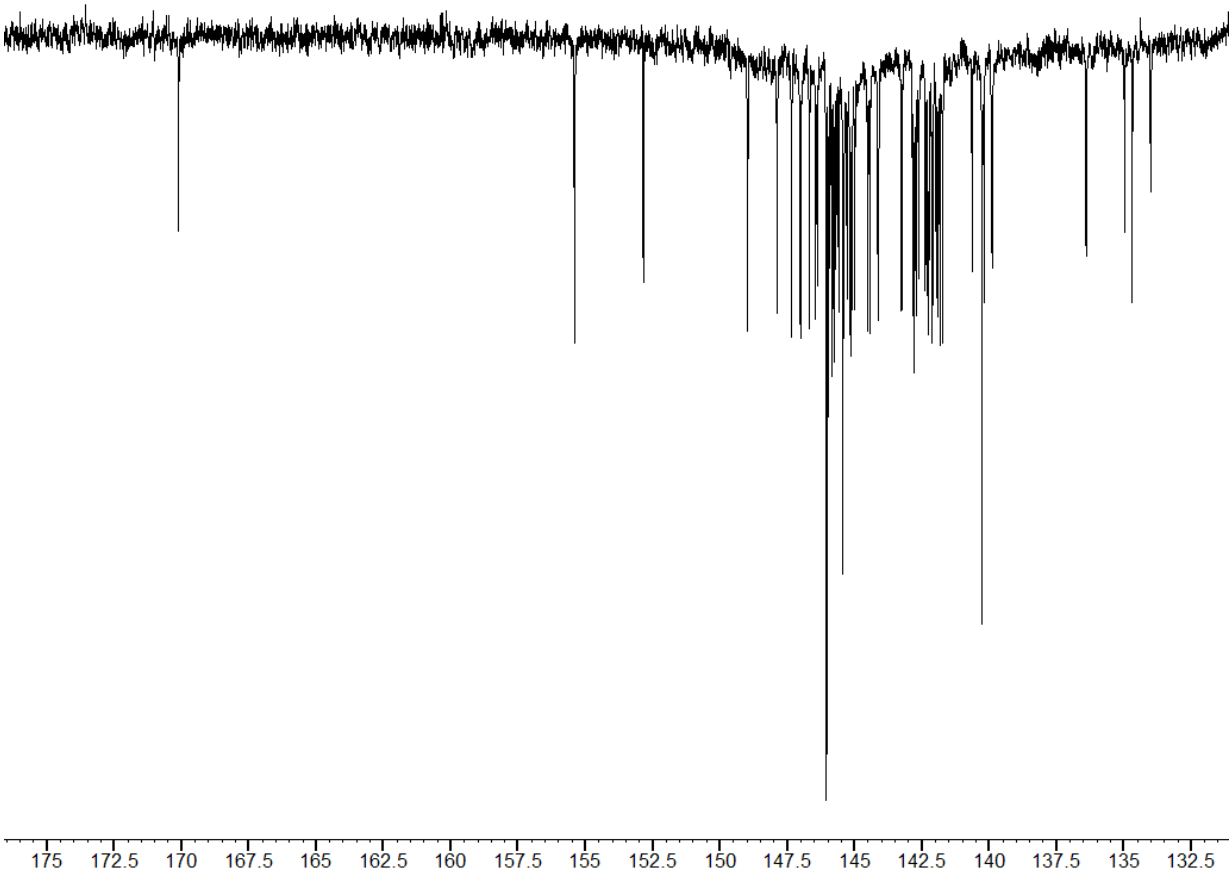
MALDI TOF mass spectrum of **2a**



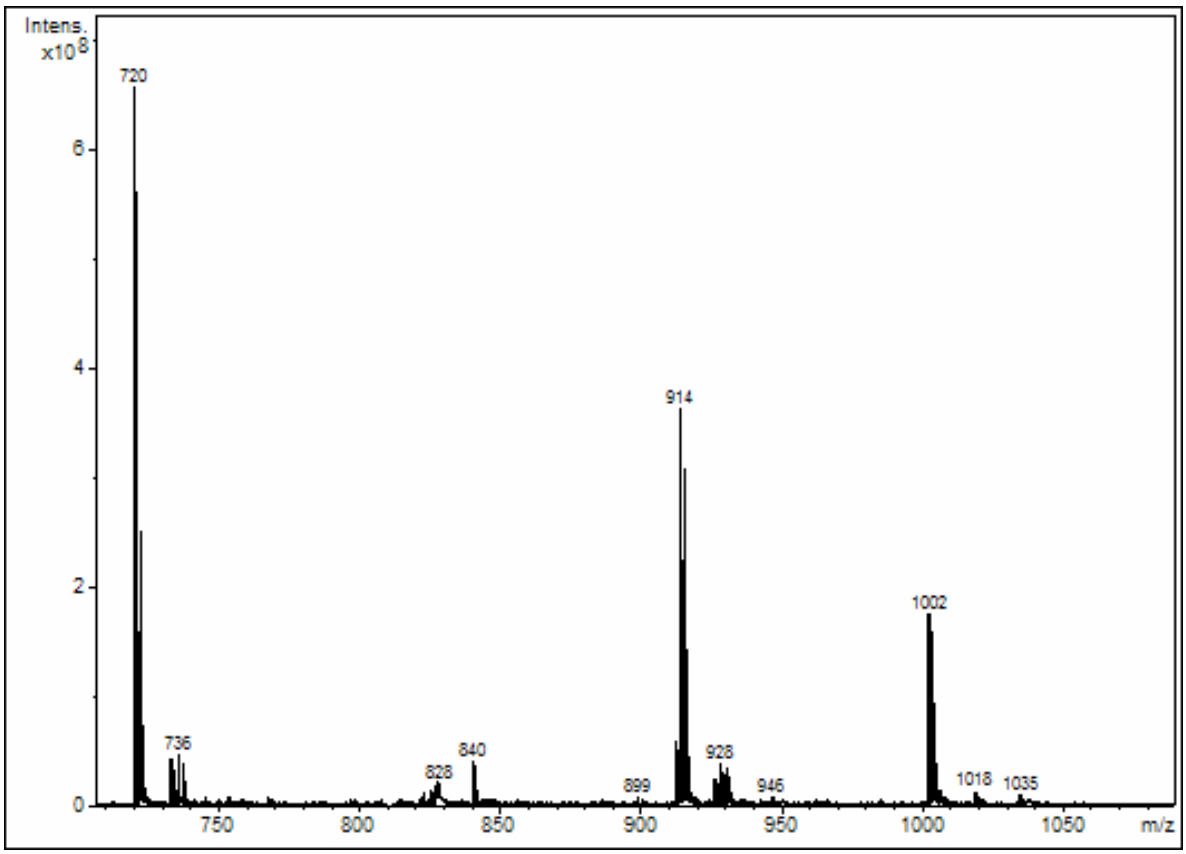
^{1}H NMR spectrum of **3a**



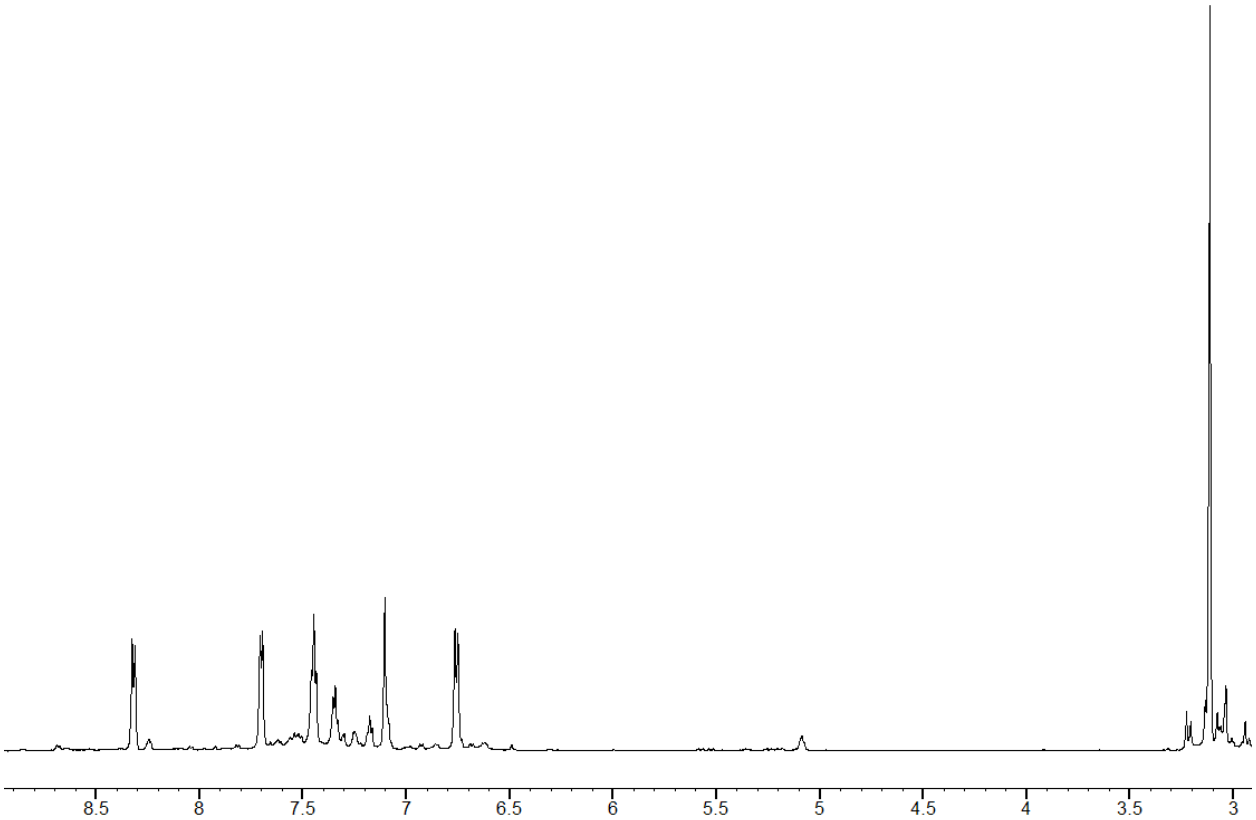
^{13}C NMR spectrum of **3a** (APT mode)



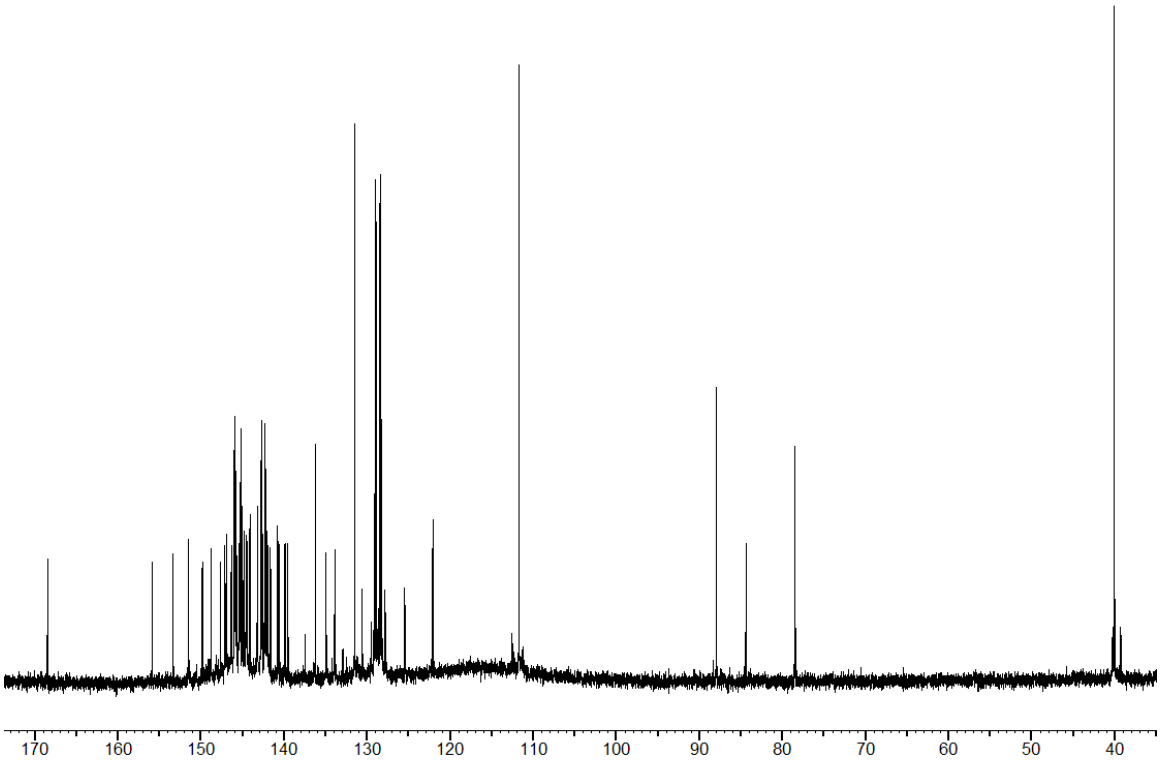
The part of the ^{13}C NMR spectrum of **3a** (APT mode)



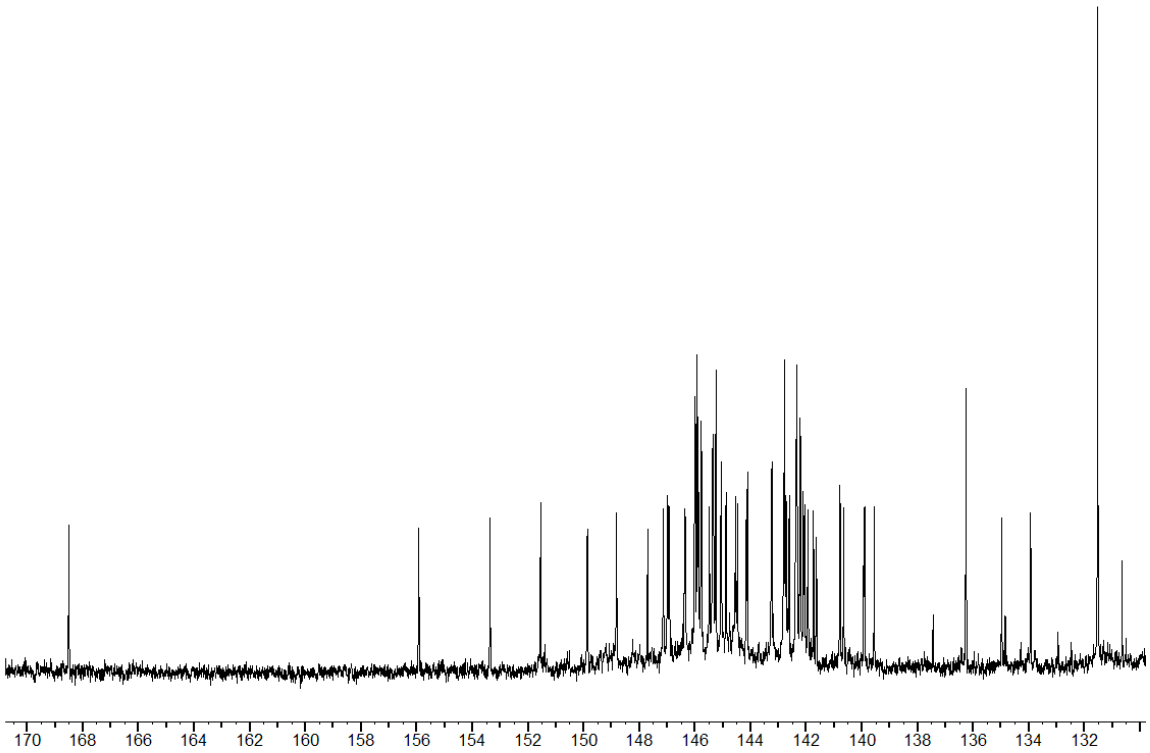
MALDI TOF mass spectrum of **3a**



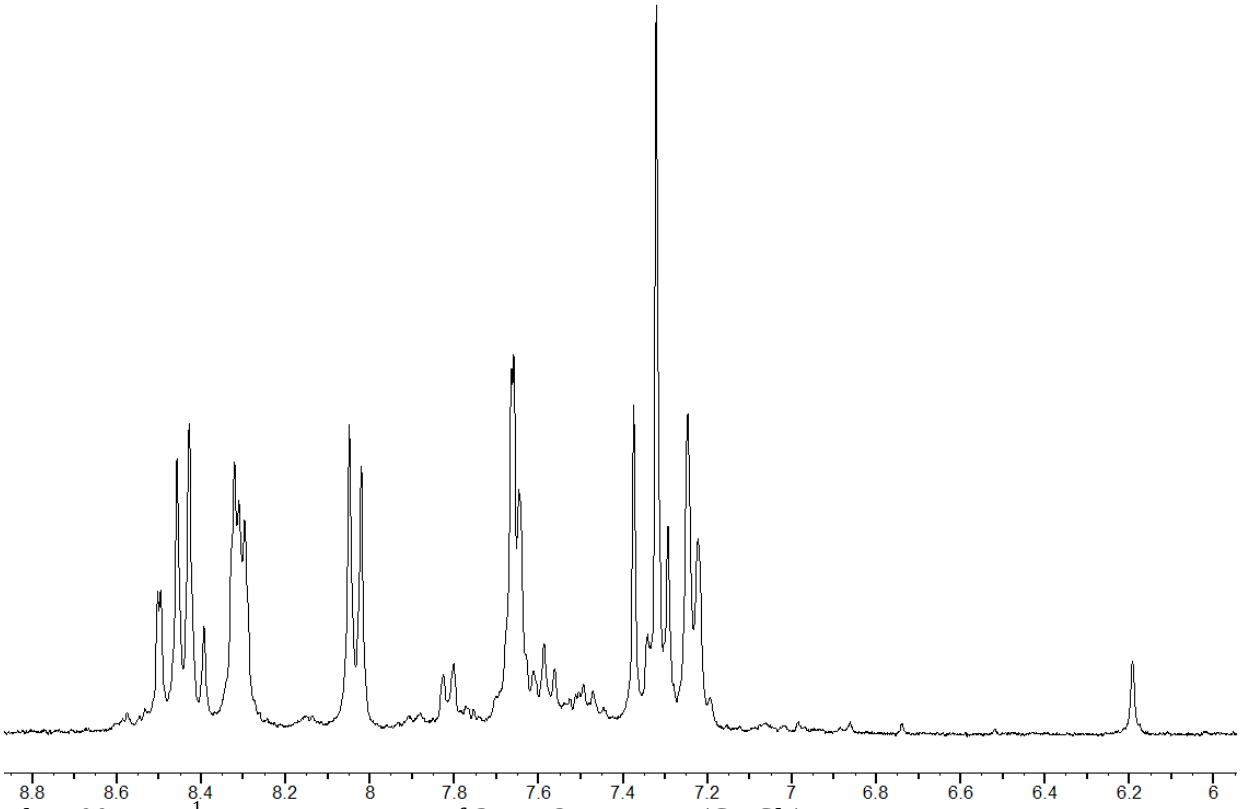
^{1}H NMR spectrum of **3b**



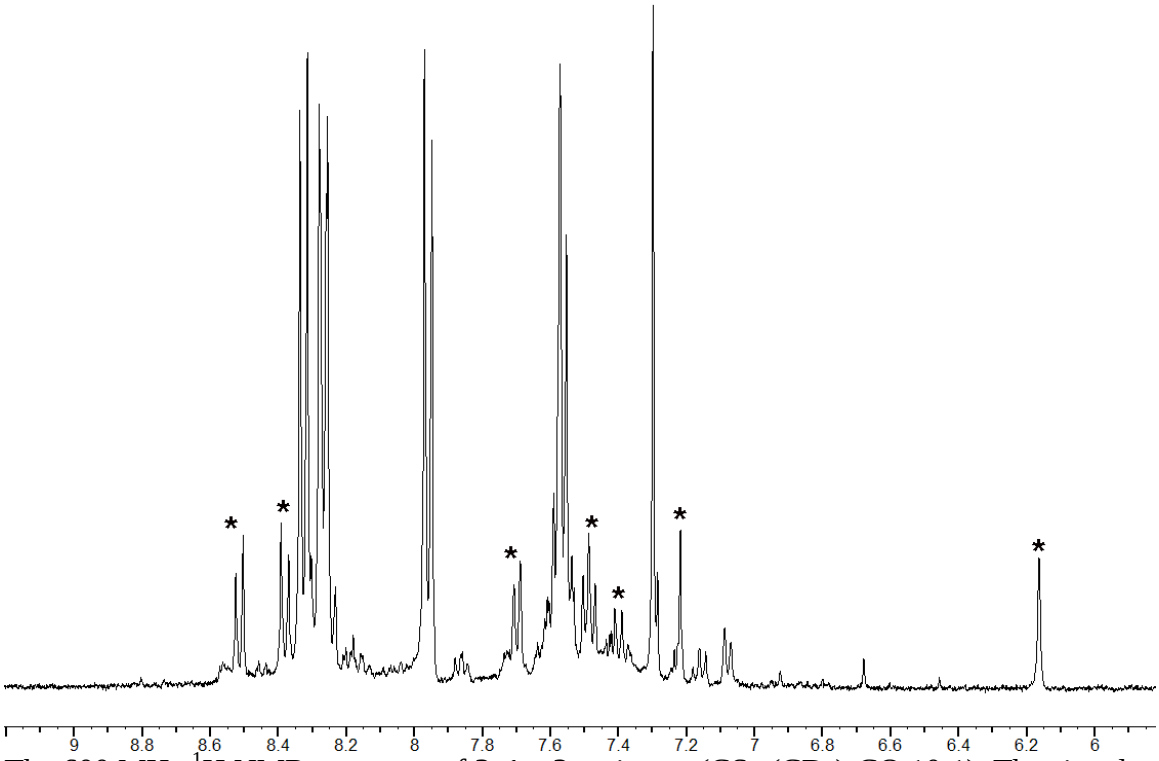
^{13}C NMR spectrum of **3b**



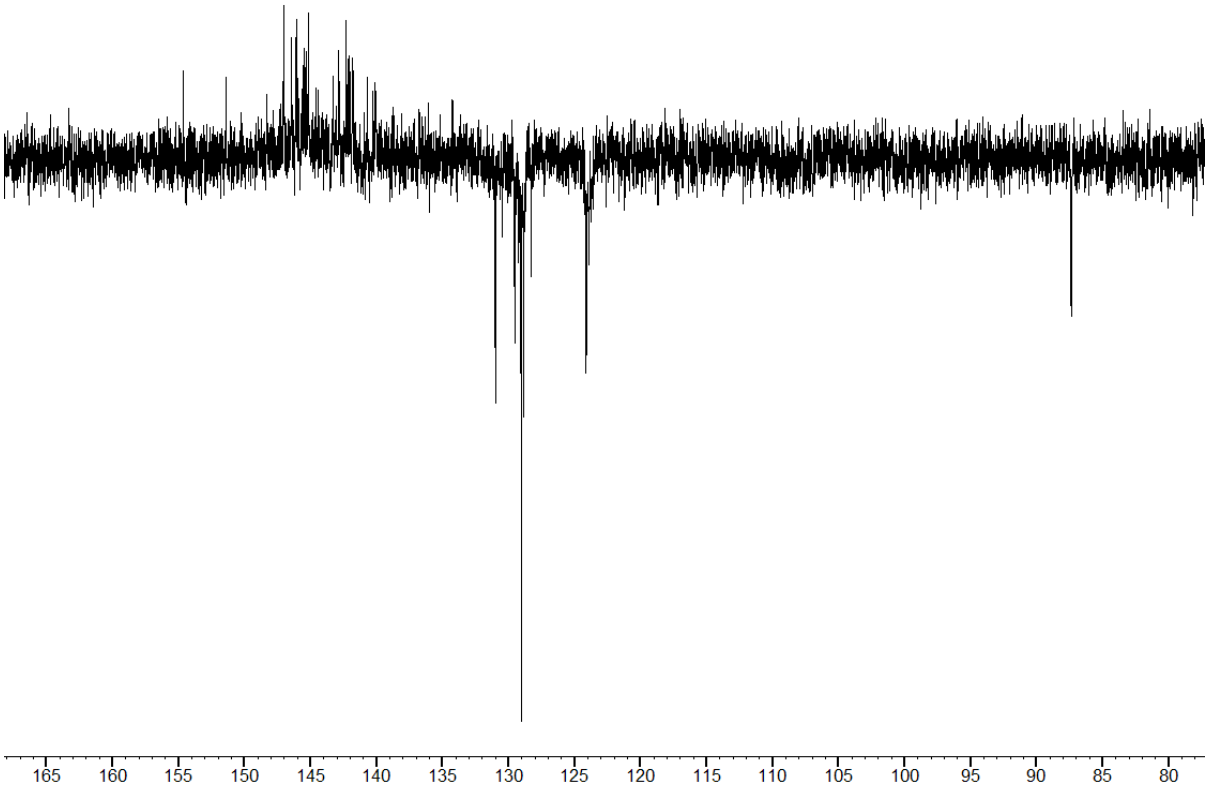
The part of the ^{13}C NMR spectrum of **3b**



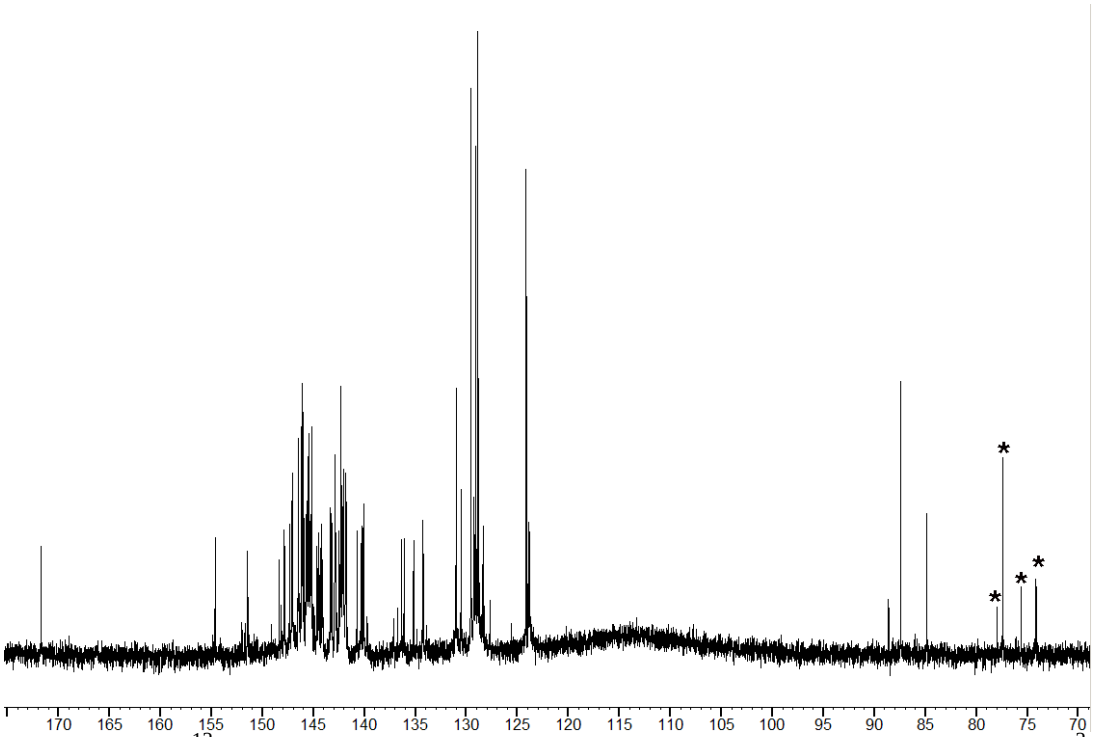
The 400 MHz ^{1}H NMR spectrum of **3c1 – 2c** mixture ($CDCl_3$).



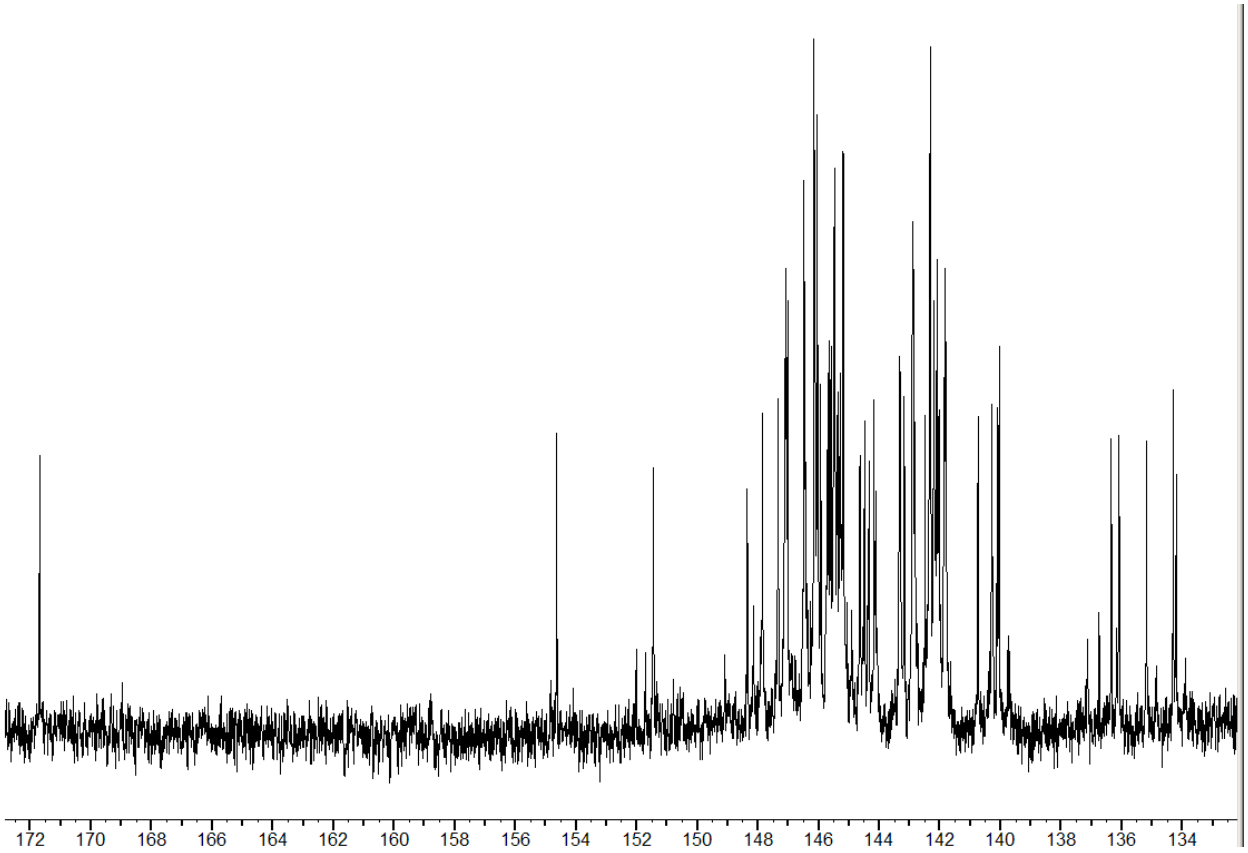
The 600 MHz ^{1}H NMR spectrum of **3c1 – 2c** mixture (CS_2-$(CD_3)_2CO$ 10:1). The signals assigned to **2c** are marked with symbol "*".



The 100 MHz ^{13}C NMR spectrum of **3c1-2c** mixture (APT mode)



The 150 MHz ^{13}C NMR spectrum of **3c1-2c** mixture. The signals assigned to the sp^3 carbons of **2c** are marked with symbol "*".



The part of the 150 MHz ^{13}C NMR spectrum of **3c1-2c** mixture