

New norbornadiene-tethered fulleropyrrolidines**Arslan R. Akhmetov, Airat R. Tuktarov, Zarema R. Sadretdinova,
Leonard M. Khalilov and Usein M. Dzhemilev****Table of Contents**

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General information

All reactions were performed under an argon atmosphere and in anhydrous solvent. The solvents and reagents were dried or refined according to the literature procedures. Commercially available fullerene C₆₀ (99.5% pure, Sigma-Aldrich) was used. The reaction products were analyzed on a HPLC chromatograph Shimadzu SPD-20A (Japan) equipped with the UV detector at 313 or 340 nm. The mixtures were separated on a metal preparative column Cosmosil Buckyprep Waters (250×10 mm) at ~20 °C. Toluene was used as eluent, the flow rate was 3.0 ml•min⁻¹. The ¹H and ¹³C NMR spectra were run on a Bruker Avance-500 spectrometer at 500.17 and 125.78 MHz, respectively. A mixture of CDCl₃ and CS₂ (1:3) was used as a solvent. The chemical shifts are reported as δ values in parts per million relative to internal standard Me₄Si. The coupling constants (*J*) are reported in Hertz. The mass spectra were obtained on an UltraFlex III TOF/TOF (Bruker Daltonik GmbH, Germany) operating in linear (TOF) and reflection (TOF/TOF) positive and negative ion modes. S₈ were used as the matrix. For the application on a metal target, toluene solutions of the samples were used. Photoisomerization of norbornadiene derivatives into quadricyclic derivatives was carried out using a HAMAMATSU LC 8 irradiator at 360 nm.

Norbornadiene-containing fulleropyrrolidines (general procedure).

A 50 ml glass reactor was charged with C₆₀ (100 mg, 0.139 mmol) in *o*-xylene (20 ml), corresponding norbornadiene aldehyde (0.695 mmol) and sarcosine (62 mg, 0.695 mmol) at 80 °C. The resulting reaction mixture was stirred for 2 h and filtered out. The reaction products and the starting fullerene C₆₀ were separated by the semi-preparative HPLC, using toluene as eluent. The samples were washed with hexane and Et₂O before NMR analysis.

Quadricyclanes 3a-c, 5a-c (general procedure).

The corresponding norbornadiene derivative (0.3 g) in 2-propanol (7 ml) was dissolved in a 10 ml quartz cuvette. Acetophenone (10 μ l) was added as a sensitizer. The mixture was irradiated with ultraviolet light, with vigorous stirring with a wavelength of $\lambda = 360$ nm for 8 hours. The solvent was evaporated under reduced pressure to give the corresponding quadricyclane in quantitative yield, and the crude material was used in the reaction with fullerene without further purification. The formation of quadricyclane was determined by the disappearance of the signals of hydrogen atoms at the double bond of norbornadiene in the ¹H NMR spectrum in the region of 6.8 ppm.

Selected data

3-Butylbicyclo[2.2.1]hepta-2,5-diene-2-carbaldehyde 1b: ^1H NMR, δ : 0.88 (t, 3H, CH_3 , J 7.4 Hz), 1.26 (m, 2H, CH_2), 1.52 (m, 2H, CH_2), 1.97 (dd, 2H, CH_2 , J 6.7, 6.7 Hz), 2.63 (t, 2H, CH_2 , J 7.4 Hz), 3.53 (s, 1H, CH), 3.96 (s, 1H, CH), 6.64 (dd, 1H, CH, J 5.0, 3.0 Hz), 6.77 (dd, 1H, CH, J 5.0, 3.0 Hz), 9.79 (s, 1H, CH). ^{13}C NMR, δ : 13.72, 22.25, 28.84, 29.07, 47.31, 55.83, 70.35, 140.57, 143.74, 148.56, 181.13, 184.75.

***N*-Methyl-2-(bicyclo[2.2.1]hepta-2,5-dien-2-yl)-3,4-fulleropyrrolidine 2a:** ^1H NMR, δ : 1.34 (d, 1H, CH, J 8 Hz), 1.53 (d, 1H, CH, J 8 Hz), 1.64 (dt, 1H, CH, J 1.8 Hz), 1.65 (dt, 1H, CH, J 1.8 Hz), 2.05 (m, 2H, CH_2), 2.19 (m, 2H, CH_2), 2.20 (m, 1H, CH), 2.34 (m, 2H, CH_2), 2.66 (s, 3H, CH_3), 2.79 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 2.89 (s, 3H, CH_3), 3.25 (m, 2H, CH_2), 3.63 (m, 2H, CH_2), 3.68 (m, 2H, CH_2), 4.08 (m, 2H, CH_2), 4.09 (m, 2H, CH_2), 4.12 (m, 1H, CH), 4.75 (s, 1H, CH), 4.76 (s, 1H, CH), 4.89 (m, 2H, CH_2), 4.90 (m, 2H, CH_2), 5.47 (m, 1H, CH), 5.92 (m, 1H, CH), 5.96 (m, 1H, CH), 6.38 (m, 1H, CH), 6.59 (m, 1H, CH), 6.89 (m, 1H, CH), 7.05 (m, 1H, CH), 7.10 (m, 1H, CH). ^{13}C NMR, δ : 35.09, 40.48, 41.06, 41.60, 45.65, 46.62, 50.70, 51.11, 51.78, 52.29, 55.12, 69.76, 70.13, 74.81, 75.53, 80.02, 127.68, 130.60, 132.07, 132.29, 132.33, 135.40, 135.56, 135.61, 135.75, 135.81, 136.08, 136.79, 136.96, 137.10, 139.30, 139.52, 140.17, 140.23, 140.35, 140.38, 141.58, 141.73, 141.88, 141.98, 142.07, 142.17, 142.26, 142.34, 142.69, 142.76, 143.04, 143.13, 143.17, 143.26, 143.59, 143.64, 143.66, 143.75, 144.42, 144.49, 144.73, 144.81, 145.22, 145.28, 145.37, 145.47, 145.54, 145.60, 145.62, 145.75, 145.88, 145.97, 146.04, 146.15, 146.18, 146.22, 146.27, 146.37, 146.71, 146.85, 147.12, 147.31, 153.57, 153.67, 154.01, 154.05, 154.43, 154.67, 154.80, 155.45, 155.98. IR (KBr, ν/cm^{-1}): 2878, 1455, 1179, 902, 757, 729, 695, 525. UV (CHCl_3), $\lambda_{\text{max}}/\text{nm}$: 425, 323, 256. Mass spectrum (MALDI TOF), found: m/z 867.8598 $[\text{M}]^+$; $\text{C}_{70}\text{H}_{13}\text{N}$; calculated: $M = 867.8589$ m/z $\text{C}_{70}\text{H}_{13}\text{N}$. Retention time τ , 5.3 min. Yield 40 %.

***N*-Methyl-2-(3-butylbicyclo[2.2.1]hepta-2,5-dien-2-yl)-3,4-fulleropyrrolidine 2b:** ^1H NMR, δ : 0.92-0.96 (m, 3H, CH_3), 1.01-1.05 (m, 3H, CH_3), 1.35 (m, 1H, CH), 1.48 (m, 1H, CH), 1.69 (m, 1H, CH), 1.76 (m, 1H, CH), 1.92 (m, 1H, CH), 2.31 (m, 2H, CH_2), 2.39 (m, 2H, CH_2), 2.60 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 2.86 (s, 3H, CH_3), 3.05 (s, 3H, CH_3), 3.07 (s, 3H, CH_3), 3.25 (s, 3H, CH_3), 3.31 (s, 3H, CH_3), 3.50 (m, 1H, CH), 3.68 (m, 1H, CH), 3.84 (m, 1H, CH), 4.09 (m, 1H, CH), 4.12 (m, 1H, CH), 4.14 (m, 1H, CH), 4.23 (m, 1H, CH), 4.35 (d, 1H, CH, J 11 Hz), 4.71 (m, 2H, CH_2), 4.80 (m, 2H, CH_2), 4.83 (m, 2H, CH_2), 4.88 (m, 2H, CH_2), 4.90 (m, 2H, CH_2), 4.99 (m, 2H, CH_2), 5.49 (m, 2H, CH_2), 5.59 (t, 2H, CH_2 , J 7 Hz), 5.96 (m, 2H, CH_2), 6.22 (m, 1H, CH), 6.33 (m, 1H, CH), 6.50 (m, 1H, CH), 6.65 (m, 1H, CH), 6.86 (m, 1H, CH), 7.08 (m, 1H, CH). ^{13}C NMR, δ : 14.58, 14.66, 22.99, 23.05, 23.12, 23.24, 27.80, 29.47, 29.64, 32.91,

33.05, 35.15, 40.46, 41.07, 41.67, 44.29, 45.06, 46.26, 46.99, 47.24, 47.67, 50.18, 50.75, 51.37, 51.67, 52.57, 54.37, 54.52, 69.29, 69.67, 69.89, 70.26, 70.94, 72.26, 72.49, 73.37, 78.12, 80.90, 83.58, 130.61, 132.31, 135.01, 136.18, 136.52, 136.66, 139.48, 140.18, 140.42, 141.89, 142.20, 142.56, 142.71, 143.18, 143.42, 143.52, 144.45, 144.74, 145.35, 145.51, 145.62, 145.80, 146.03, 146.15, 146.27, 146.37, 146.76, 147.27, 154.14, 154.54, 154.88, 155.69, 156.27. IR (KBr, ν/cm^{-1}): 2902, 1499, 1180, 907, 748, 732, 698, 526. UV (CHCl_3), $\lambda_{\text{max}}/\text{nm}$: 426, 325, 256. Mass spectrum (MALDI TOF), found: m/z 923.9660 $[\text{M}]^+$; $\text{C}_{74}\text{H}_{21}\text{N}$; calculated: $M = 923.9652$ m/z $\text{C}_{74}\text{H}_{21}\text{N}$. Retention time τ , 4.3 min. Yield 44 %.

***N*-Methyl-2-(3-phenylbicyclo[2.2.1]hepta-2,5-dien-2-yl)-3,4-fulleropyrrolidine 2c:** ^1H NMR, δ : 2.07 (s, 3H, CH_3), 2.28 (m, 2H, CH_2), 2.39 (s, 3H, CH_3), 2.50 (s, 3H, CH_3), 2.57 (m, 2H, CH_2), 2.89 (s, 3H, CH_3), 2.98 (s, 3H, CH_3), 3.81 (s, 1H, CH), 3.87 (s, 1H, CH), 4.11 (m, 2H, CH_2), 4.16 (m, 2H, CH_2), 4.44 (m, 2H, CH_2), 4.89 (m, 2H, CH_2), 6.35 (m, 1H, CH), 6.70 (m, 1H, CH), 6.92 (m, 1H, CH), 6.96 (m, 1H, CH), 7.05 (m, 1H, CH), 7.18 (m, 1H, CH), 7.33 (m, 1H, CH), 7.38 (m, 1H, CH), 7.45 (m, 1H, CH). ^{13}C NMR, δ : 40.24, 40.48, 40.94, 41.55, 52.88, 54.16, 56.92, 57.06, 57.62, 69.58, 69.97, 70.10, 70.23, 70.63, 71.53, 73.62, 76.31, 76.64, 76.90, 77.42, 125.41, 125.86, 126.47, 126.99, 127.08, 127.26, 127.30, 127.70, 128.32, 128.41, 128.48, 128.60, 128.78, 129.09, 129.57, 129.73, 130.58, 135.59, 135.71, 136.70, 136.99, 140.90, 141.76, 142.02, 142.13, 142.24, 142.34, 142.69, 143.16, 143.73, 144.36, 144.68, 144.80, 145.24, 145.37, 145.43, 145.59, 145.87, 146.06, 146.19, 146.25, 146.40, 146.58, 147.35, 153.54, 153.91, 154.16, 154.80, 156.12, 156.82, 156.99. IR (KBr, ν/cm^{-1}): 2851, 1427, 1178, 903, 758, 729, 694, 526. UV (CHCl_3), $\lambda_{\text{max}}/\text{nm}$: 430, 326, 256. Mass spectrum (MALDI TOF), found: m/z 943.9539 $[\text{M}]^+$; $\text{C}_{76}\text{H}_{17}\text{N}$; calculated: $M = 943.9548$ m/z $\text{C}_{76}\text{H}_{17}\text{N}$. Retention time τ , 4.7 min. Yield 60 %.

Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1-carbaldehyde 3a: ^1H NMR, δ : 1.42 (m, 2H, CH_2), 1.55 (m, 1H, CH), 1.86 (m, 1H, CH), 2.04 (m, 1H, CH), 2.13 (m, 1H, CH), 2.24 (d, 1H, CH, J 5.0 Hz), 9.50 (s, 1H, CH). ^{13}C NMR, δ : 20.56, 21.20, 22.07, 23.03, 24.53, 26.51, 28.47, 210.63.

5-Butyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1-carbaldehyde 3b: ^1H NMR, δ : 0.78 (t, 3H, CH_3 J 6.6 Hz), 1.12-1.05 (m, 2H, 3 CH_2), 1.19 (m, 2H, CH_2), 1.39-1.51 (m, 2H, CH_2), 1.85 (d, 1H, CH J 9.8 Hz), 2.06 (m, 1H, CH), 9.52 (s, 1H, CH). ^{13}C NMR, δ : 13.81, 22.07, 22.57, 23.07, 26.17, 28.45, 29.45, 31.68, 35.42, 44.94, 210.78.

5-Phenyltetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptane-1-carbaldehyde 3c: ^1H NMR, δ : 1.13 (m, 1H, CH), 1.73 (m, 1H, CH), 1.91 (m, 1H, CH), 2.05 (m, 1H, CH), 2.22 (m, 1H, CH), 2.67 (m, 1H, CH), 3.66 (m, 1H, CH), 7.10-7.25 (m, 5H, 5CH), 9.78 (s, 1H, CH). ^{13}C NMR, δ : 22.35, 23.14, 24.52, 26.47, 27.69, 28.62, 41.60, 126.96, 128.11, 129.66, 134.96, 203.49.

2-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)acetaldehyde 4a: ^1H NMR, δ : 1.98 (dd, 2H, CH_2 , J 4.5, 4.5 Hz), 2.44 (m, 1H, CH), 3.30 (d, 2H, CH_2 , J 6.5 Hz), 6.28 (d, 1H, CH, J 1.0 Hz), 6.75 (d, 1H,

CH, J 6.0 Hz), 9.65 (s, 1H, CH). ^{13}C NMR, δ : 47.34, 50.25, 53.46, 73.71, 136.65, 142.37, 144.19, 154.97, 205.20.

3-(Bicyclo[2.2.1]hepta-2,5-dien-2-yl)propanal 4b: ^1H NMR, δ : 1.87 (m, 2H, CH_2), 2.45 (m, 4H, 2CH_2), 3.21 (d, 1H, CH, J 6.0 Hz), 3.42 (d, 1H, CH, J 6.0 Hz), 6.08 (d, 1H, CH, J 7.5 Hz), 6.67 (dd, 2H, 2CH, J 11.0, 8.5 Hz), 9.64 (s, 1H, CH). ^{13}C NMR, δ : 24.09, 41.19, 50.03, 53.50, 73.36, 134.44, 141.95, 143.77, 156.79, 201.97.

2-(Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1-yl)acetaldehyde 5a: ^1H NMR, δ : 1.05 (m, 1H, CH), 1.32 (d, 2H, CH, J 5.0 Hz), 1.43 (m, 1H, CH), 1.63 (m, 1H, CH), 1.76 (m, 1H, CH), 2.40 (dd, 2H, CH_2 , J 11.0, 11.0 Hz), 9.61 (s, 1H, CH). ^{13}C NMR, δ : 13.51, 17.22, 17.96, 24.34, 27.58, 31.82, 32.07, 43.47, 206.60.

3-(Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1-yl)propanal 5b: ^1H NMR, δ : 1.10 (m, 1H, CH), 1.32-1.45 (m, 1H, CH), 1.52-1.62 (m, 1H, CH), 1.76 (m, 1H, CH), 1.92 (m, 1H, CH), 2.40 (m, 1H, CH), 3.82 (m, 2H, CH_2), 3.98 (m, 2H, CH_2), 9.74 (s, 1H, CH). ^{13}C NMR, δ : 13.32, 17.24, 18.17, 22.54, 23.38, 24.42, 31.99, 33.13, 41.92, 202.91.

4-(Tetracyclo[3.2.0.0^{2,7}.0^{4,6}]heptan-1-yl)butanal 5c: ^1H NMR, δ : 1.07 (m, 1H, CH), 1.31-1.42 (m, 1H, CH), 1.52-1.60 (m, 1H, CH), 1.82-1.93 (m, 1H, CH), 2.15 (m, 2H, CH_2), 2.39 (m, 1H, CH), 3.80 (m, 2H, CH_2), 3.95 (m, 2H, CH_2), 9.69 (s, 1H, CH). ^{13}C NMR, δ : 13.36, 17.09, 18.29, 20.02, 23.37, 24.41, 27.77, 28.34, 31.94, 43.48, 202.75.

***N*-Methyl-2-[(bicyclo[2.2.1]hepta-2,5-dien-2-yl)methyl]-3,4-fulleropyrrolidine 6a:** ^1H NMR, δ : 1.28-1.37 (m, 1H, CH), 1.51-1.78 (m, 1H, CH), 2.04-2.15 (m, 2H, CH_2), 2.39-2.59 (m, 2H, CH_2), 2.79 (s, 3H, CH_3), 2.84 (s, 3H, CH_3), 2.91 (s, 3H, CH_3), 3.08 (s, 3H, CH_3), 3.40 (d, 1H, CH, J 11.8 Hz), 4.10 (t, 1H, CH, J 10 Hz), 4.14 (m, 1H, CH), 4.45 (m, 1H, CH), 4.84 (m, 1H, CH), 5.95 (m, 1H, CH), 6.22 (m, 1H, CH), 6.26 (m, 1H, CH), 7.17 (m, 1H, CH), 7.25 (m, 1H, CH). ^{13}C NMR, δ : 30.00, 32.59, 32.70, 39.92, 40.08, 42.14, 42.23, 49.97, 50.82, 51.49, 51.58, 69.71, 69.76, 78.72, 78.98, 117.37, 117.87, 125.40, 134.16, 134.75, 135.80, 136.51, 136.86, 136.91, 139.55, 139.80, 140.19, 140.21, 140.28, 141.70, 141.81, 142.11, 142.21, 142.35, 142.65, 142.74, 143.03, 143.08, 143.19, 143.22, 144.44, 144.75, 145.24, 145.35, 145.57, 145.93, 146.00, 146.21, 146.36, 146.57, 147.31, 149.71, 149.97, 150.56, 150.61, 153.48, 153.53, 154.03, 154.17, 154.20, 154.25, 154.35, 156.19, 156.28, 156.38. IR (KBr, ν/cm^{-1}): 2919, 1511, 1178, 900, 766, 721, 574, 526. UV (CHCl_3), $\lambda_{\text{max}}/\text{nm}$: 431, 329, 257. Mass spectrum (MALDI TOF), found: m/z 881.8863 [M] $^+$; $\text{C}_{71}\text{H}_{15}\text{N}$; calculated: $M = 881.8855$ m/z $\text{C}_{71}\text{H}_{15}\text{N}$. Retention time τ , 4.6 min. Yield 50 %.

***N*-Methyl-2-[2-(bicyclo[2.2.1]hepta-2,5-dien-2-yl)ethyl]-3,4-fulleropyrrolidine 6b:** ^1H NMR, δ : 1.29 (m, 1H, CH), 2.00 (m, 2H, CH_2), 2.02 (m, 2H, CH_2), 2.04 (m, 2H, CH_2), 2.09 (d,

1H, CH, *J* 5.7 Hz), 2.53 (m, 2H, CH₂), 2.67 (m, 1H, CH), 2.85 (m, 2H, CH₂), 3.01 (s, 3H, CH₃), 3.02 (s, 3H, CH₃), 3.35 (s, 1H, CH), 3.54 (s, 1H, CH), 3.95 (dd, 1H, CH, *J* 9.7; 5.0 Hz), 4.20 (d, 1H, CH, *J* 10 Hz), 4.83 (d, 1H, CH, *J* 3.0 Hz), 6.27 (s, 3H, CH₃), 6.76 (s, 1H, CH), 6.78 (s, 1H, CH). ¹³C NMR, δ: 28.57, 28.61, 29.33, 29.40, 40.07, 50.52, 53.86, 53.94, 70.14, 70.28, 70.44, 73.77, 76.22, 76.28, 77.40, 134.62, 134.76, 135.60, 135.88, 135.91, 136.34, 137.31, 137.36, 139.73, 139.77, 139.91, 140.31, 140.39, 141.77, 141.82, 141.94, 142.09, 142.12, 142.17, 142.24, 142.71, 142.74, 142.78, 143.15, 143.27, 144.01, 144.43, 144.49, 144.66, 144.82, 145.27, 145.34, 145.45, 145.51, 145.61, 145.86, 146.03, 146.05, 146.11, 146.17, 146.23, 146.26, 146.33, 146.38, 146.49, 146.53, 146.72, 146.73, 147.25, 147.29, 153.31, 153.36, 154.35, 154.44, 154.47, 154.52, 156.49, 157.53, 157.56. IR (KBr, ν/cm^{-1}): 2923, 1558, 1426, 1185, 766, 692, 573, 526. UV (CHCl₃), $\lambda_{\text{max}}/\text{nm}$: 431, 327, 256. Mass spectrum (MALDI TOF), found: *m/z* 895.9109 [M]⁺; C₇₂H₁₇N; calculated: M = 895.9120 *m/z* C₇₂H₁₇N. Retention time τ , 4.7 min. Yield 52 %.

***N*-Methyl-2-[3-(bicyclo[2.2.1]hepta-2,5-dien-2-yl)propyl]-3,4-fulleropyrrolidine 6c:** ¹H NMR, δ: 1.97 (m, 2H, CH₂), 2.00 (m, 2H, CH₂), 2.06 (m, 2H, CH₂), 2.34 (m, 2H, CH₂), 2.41 (m, 2H, CH₂), 2.47 (m, 2H, CH₂), 2.98 (s, 3H, CH₃), 2.99 (s, 3H, CH₃), 3.29 (s, 3H, CH₃), 3.50 (s, 3H, CH₃), 3.90 (m, 1H, CH), 4.13 (m, 2H, CH₂), 4.18 (d.d., 2H, CH₂, *J* 9.5, 3.0 Hz), 4.81 (d, 2H, CH₂, *J* 9.5 Hz), 6.20 (s, 1H, CH), 6.73 (m, 1H, CH), 6.76 (m, 1H, CH). ¹³C NMR, δ: 25.39, 30.85, 30.89, 32.24, 40.05, 50.46, 53.69, 53.72, 70.12, 70.50, 73.72, 73.77, 76.29, 78.22, 78.32, 134.62, 134.67, 135.60, 135.93, 136.35, 137.30, 139.66, 139.79, 139.84, 140.30, 140.37, 141.75, 141.81, 142.16, 142.24, 142.71, 142.74, 142.78, 143.13, 143.27, 143.91, 144.43, 144.49, 144.67, 144.83, 145.26, 145.35, 145.42, 145.52, 145.62, 145.87, 146.02, 146.04, 146.12, 146.17, 146.23, 146.26, 146.33, 146.38, 146.86, 147.25, 147.29, 153.39, 153.45, 154.35, 154.38, 154.47, 154.51, 156.52, 157.48, 157.54. IR (KBr, ν/cm^{-1}): 2922, 1508, 1384, 1180, 766, 691, 552, 525. UV (CHCl₃), $\lambda_{\text{max}}/\text{nm}$: 430, 323, 255. Mass spectrum (MALDI TOF), found: *m/z* 909.9394 [M]⁺; C₇₃H₁₉N; calculated: M = 909.9386 *m/z* C₇₃H₁₉N. Retention time τ , 4.8 min. Yield 50 %.

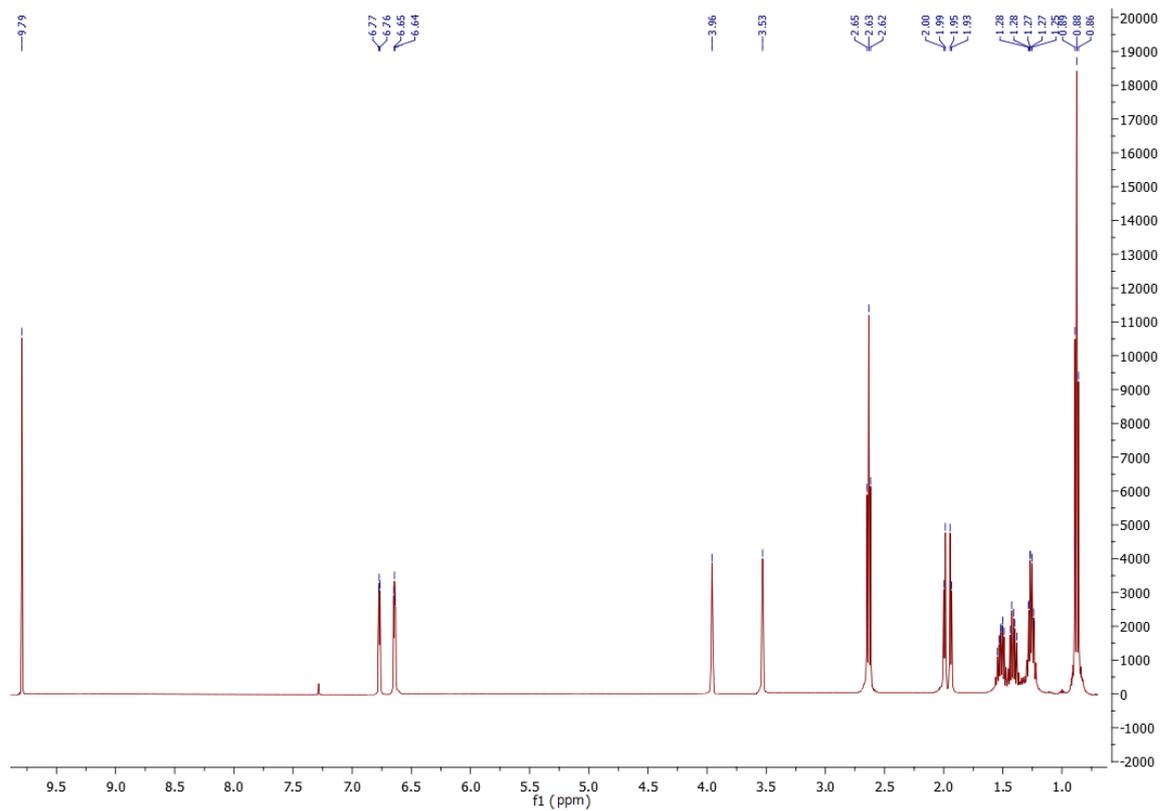


Figure S1. Copy of ¹H NMR spectrum of compound **1b**

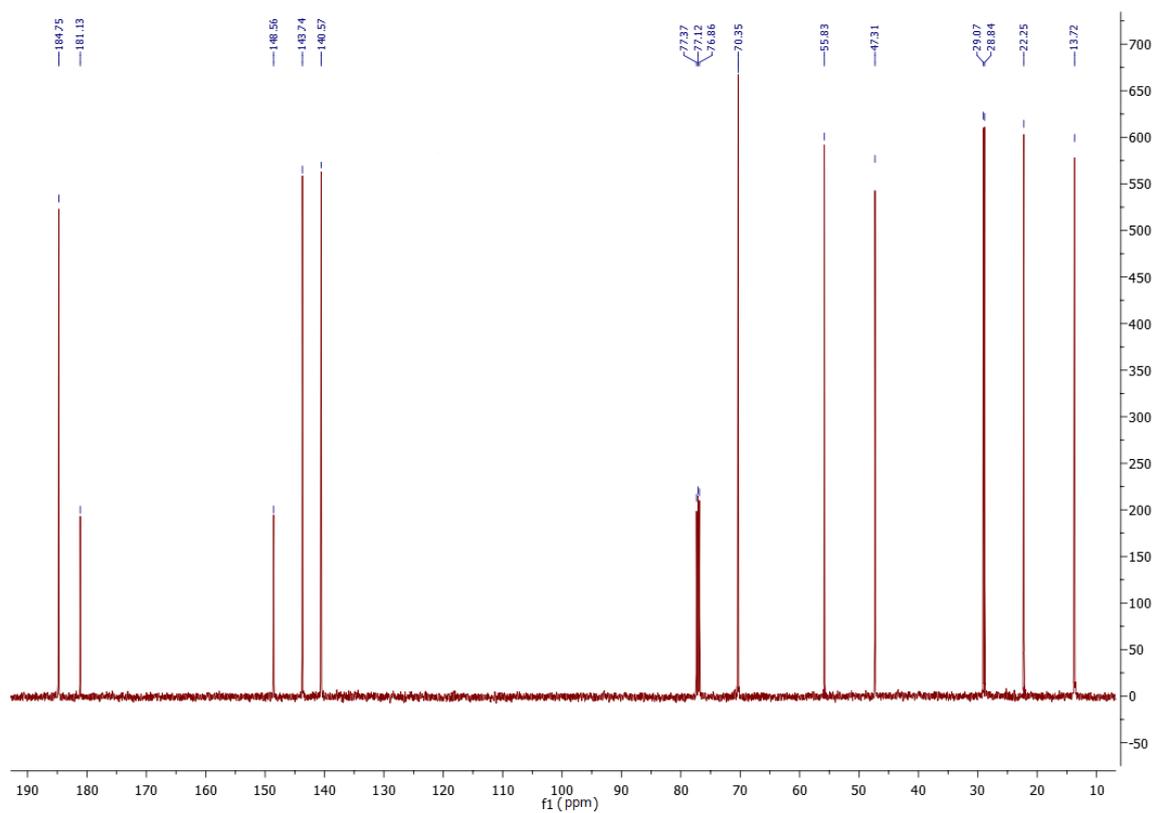


Figure S2. Copy of ¹³C NMR spectrum of compound **1b**

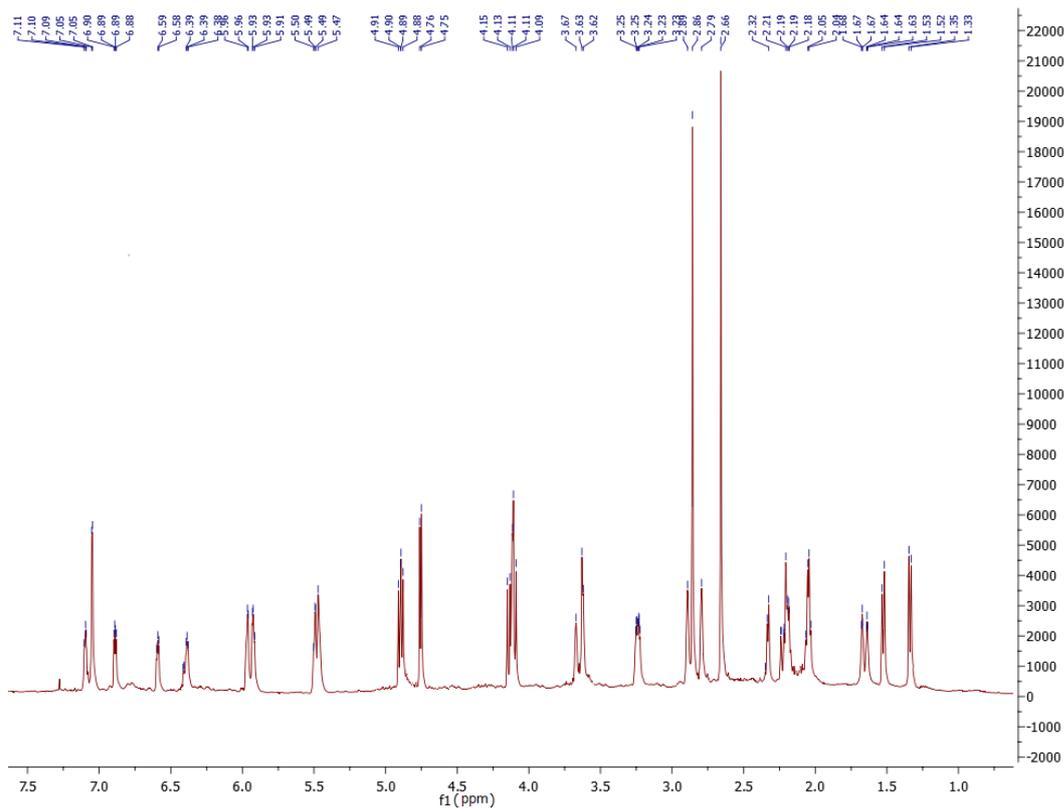


Figure S3. Copy of ^1H NMR spectrum of compound **2a**

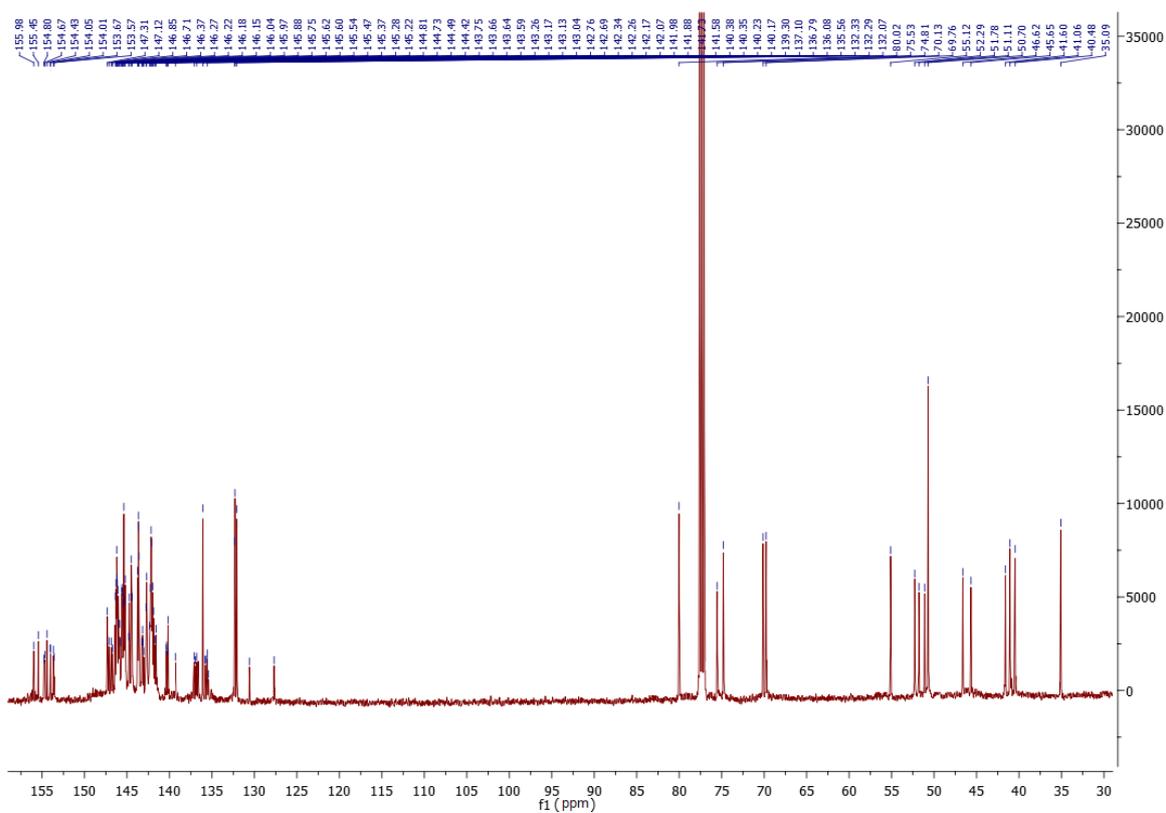


Figure S4. Copy of ^{13}C NMR spectrum of compound **2a**

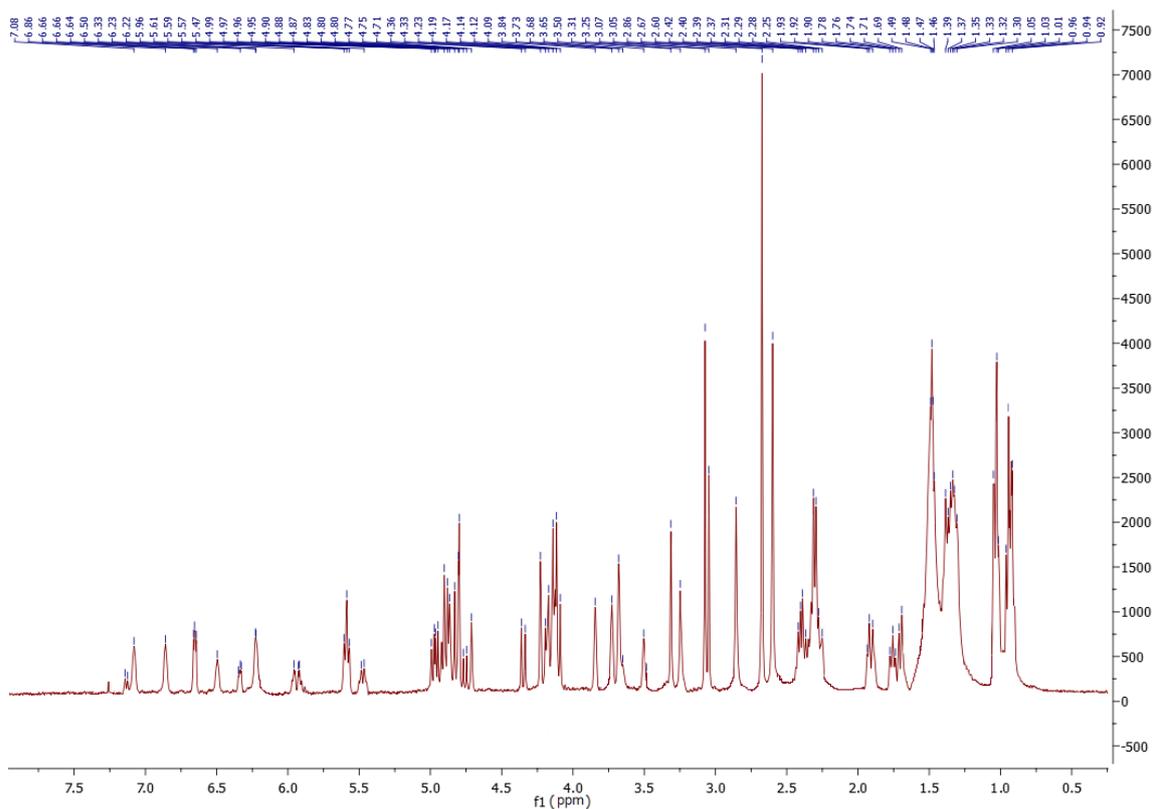


Figure S5. Copy of ^1H NMR spectrum of compound **2b**

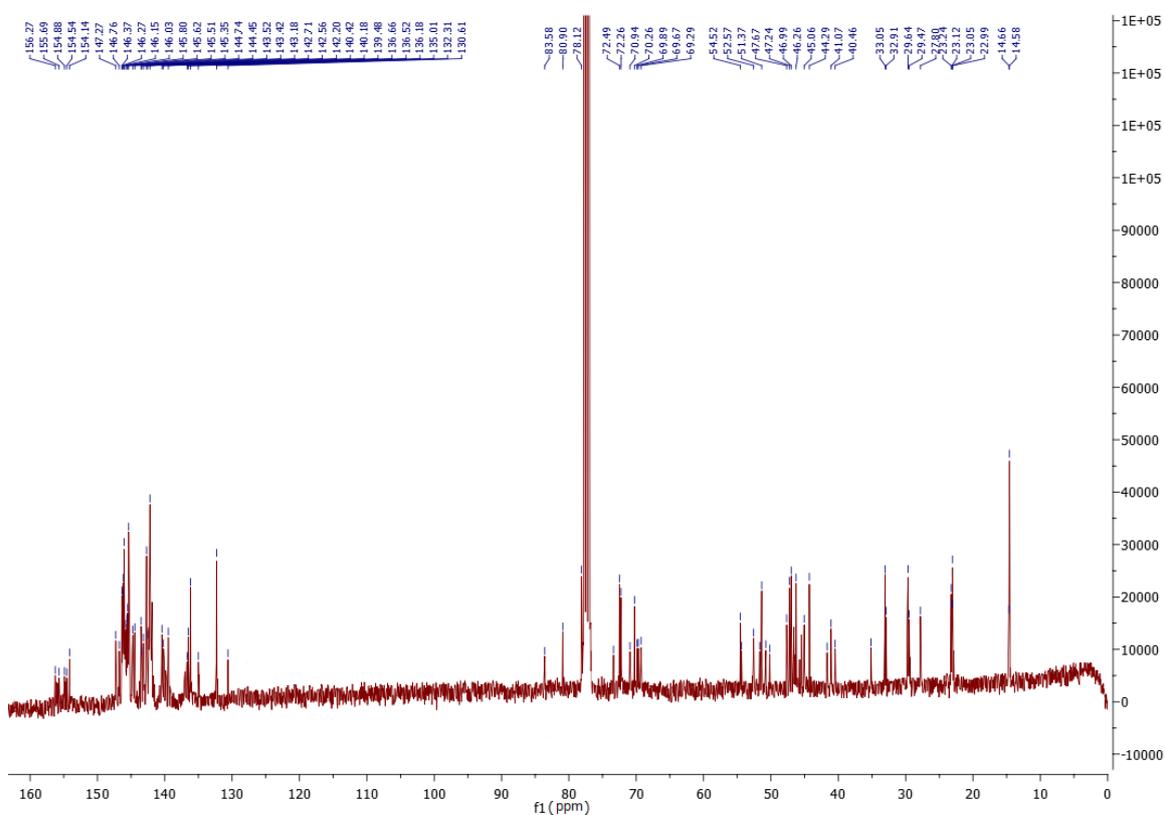


Figure S6. Copy of ^{13}C NMR spectrum of compound **2b**

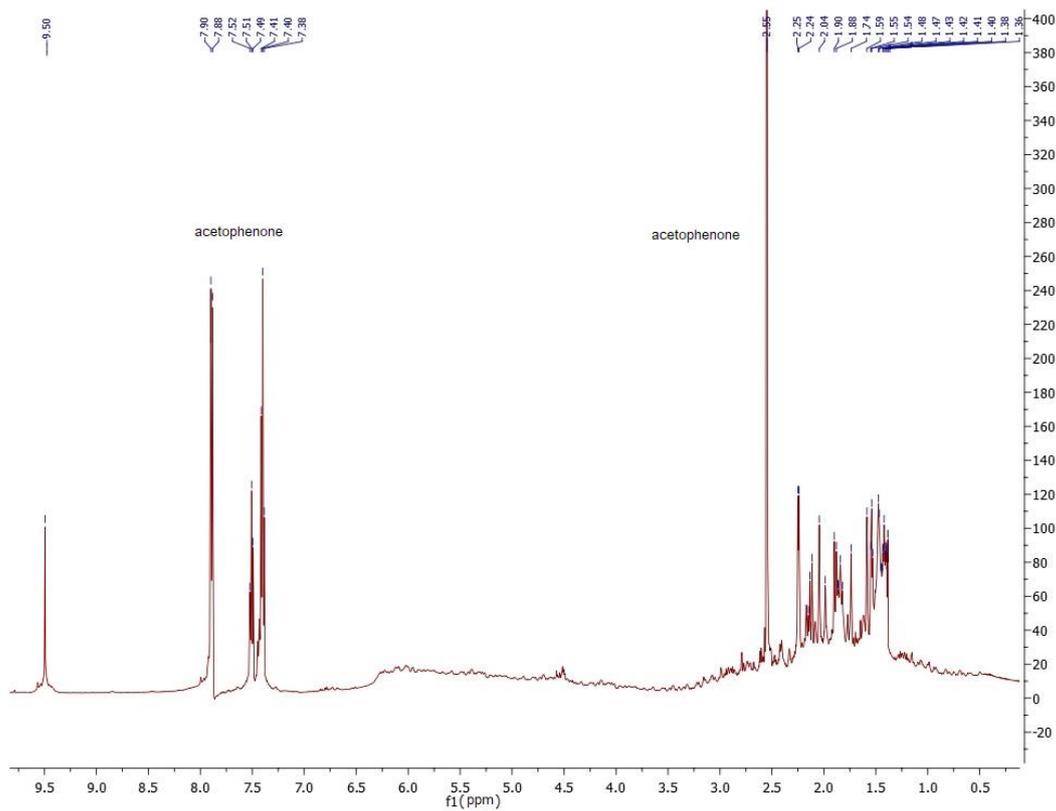


Figure S9. Copy of ¹H NMR spectrum of compound 3a

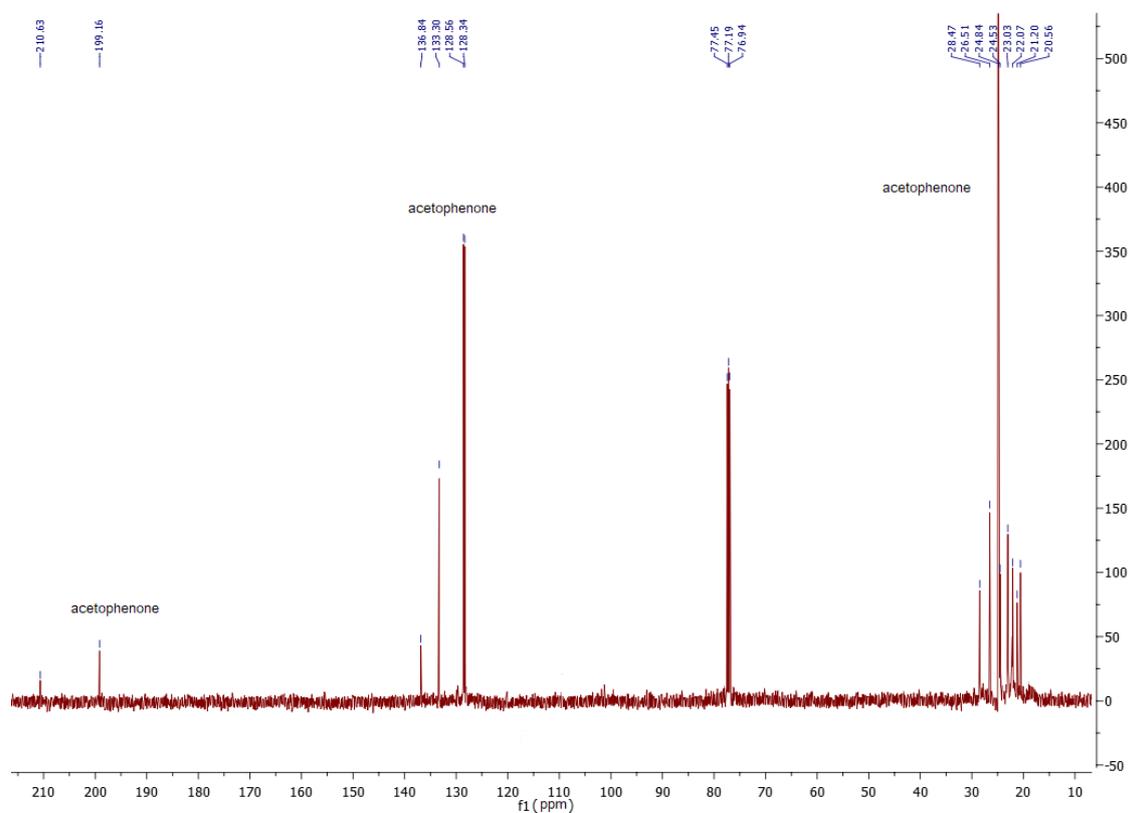


Figure S10. Copy of ¹³C NMR spectrum of compound 3a

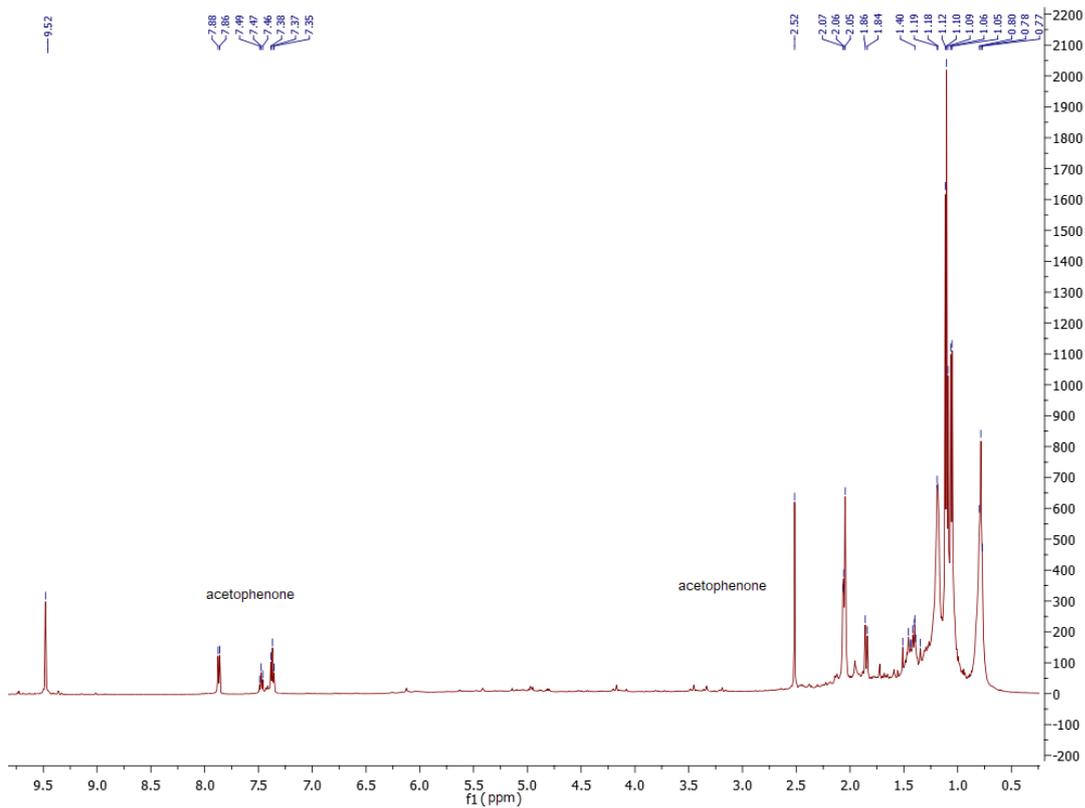


Figure S11. Copy of ^1H NMR spectrum of compound 3b

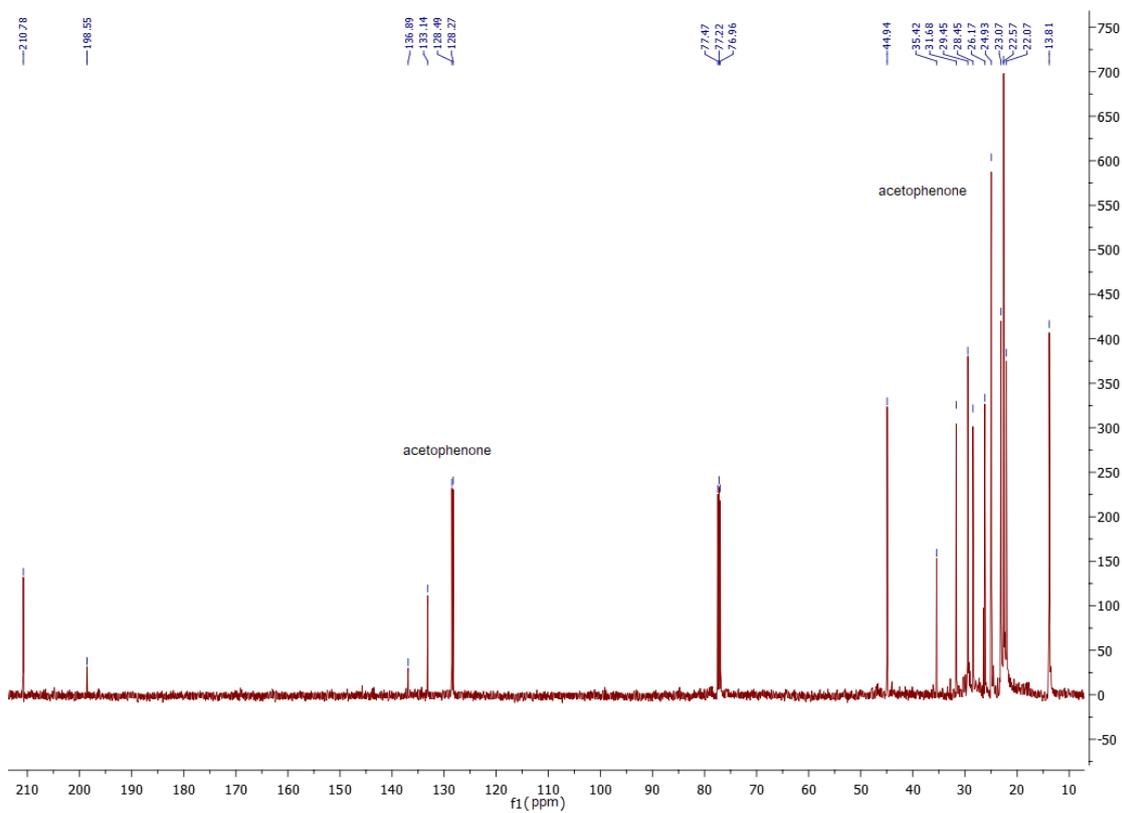


Figure S12. Copy of ^{13}C NMR spectrum of compound 3b

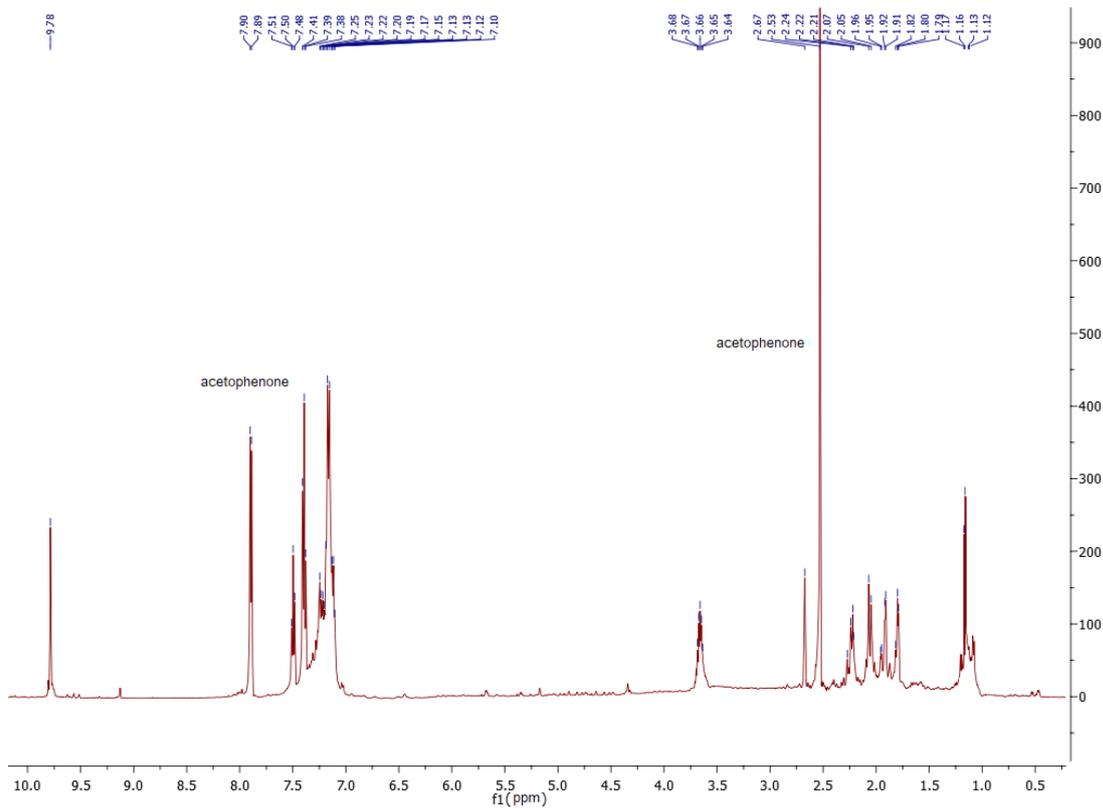


Figure S13. Copy of ¹H NMR spectrum of compound **3c**

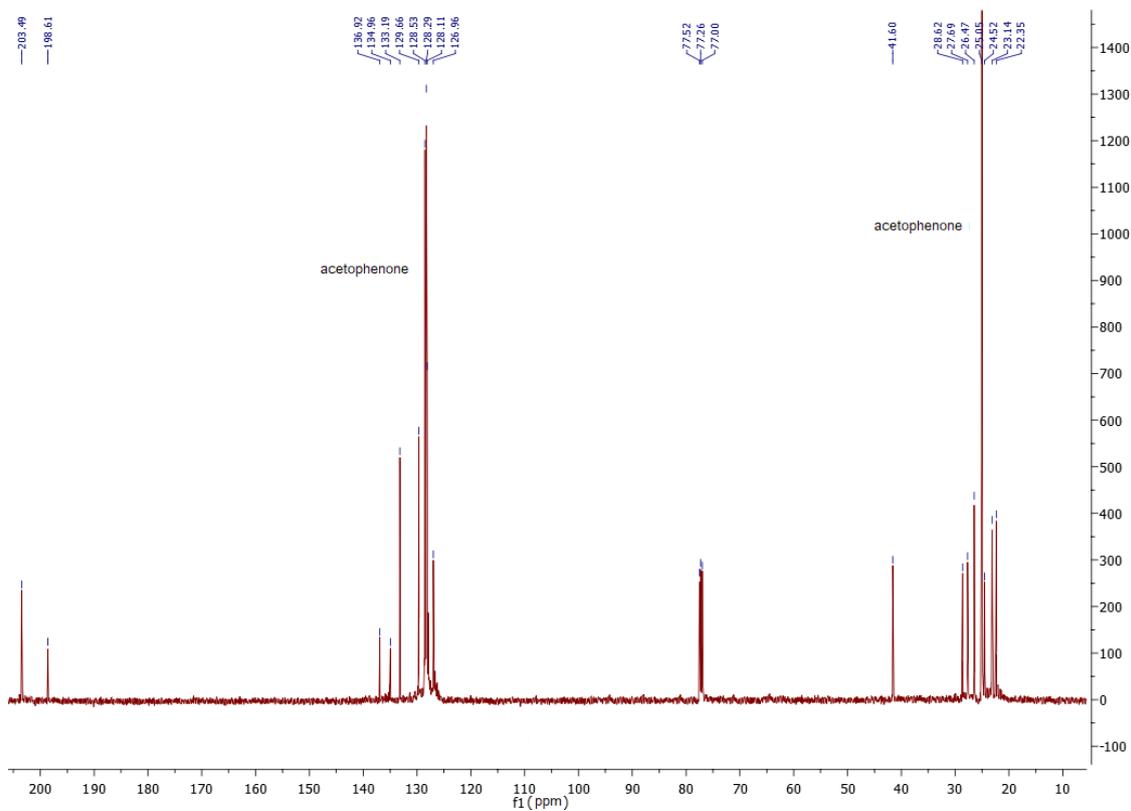


Figure S14. Copy of ¹³C NMR spectrum of compound **3c**

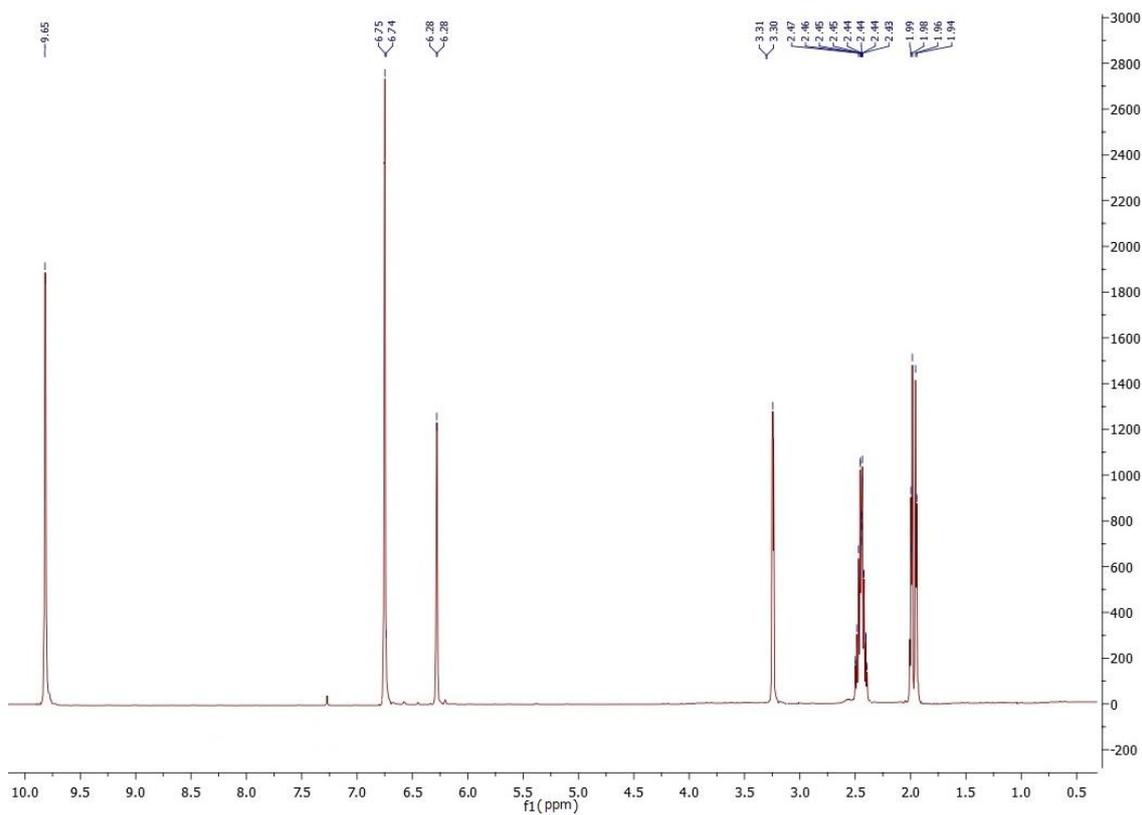


Figure S15. Copy of ^1H NMR spectrum of compound 4a

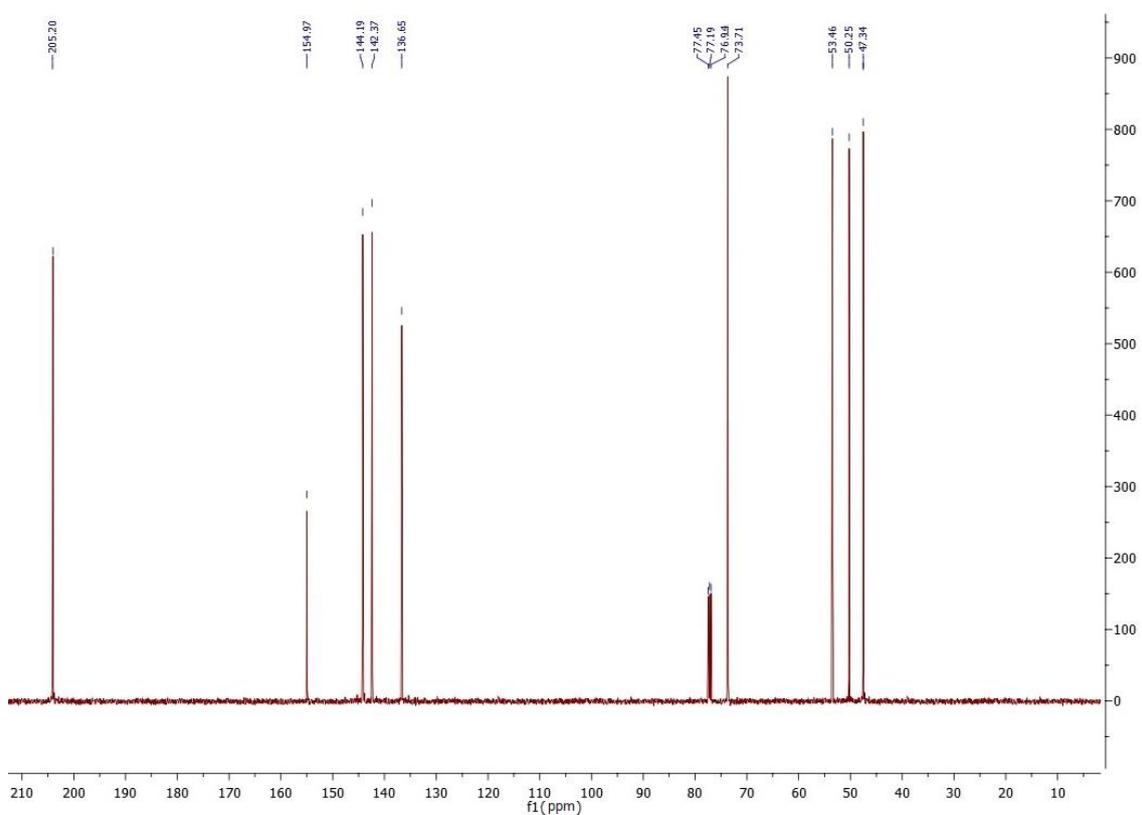


Figure S16. Copy of ^{13}C NMR spectrum of compound 4a

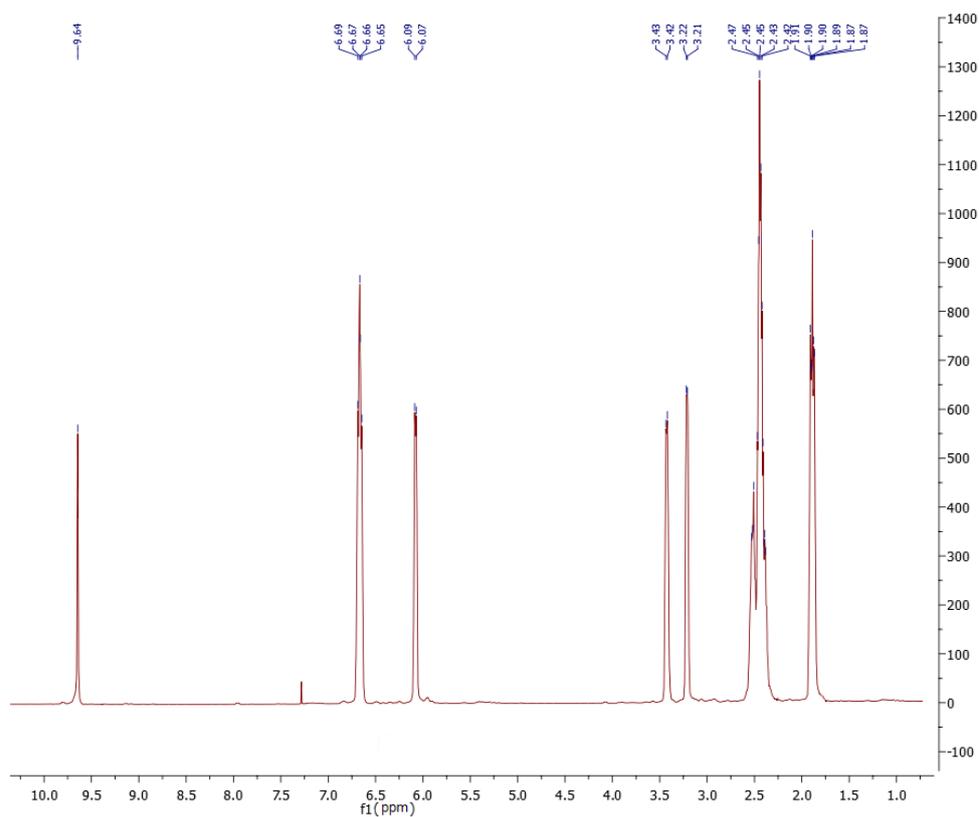


Figure S17. Copy of ¹H NMR spectrum of compound 4b

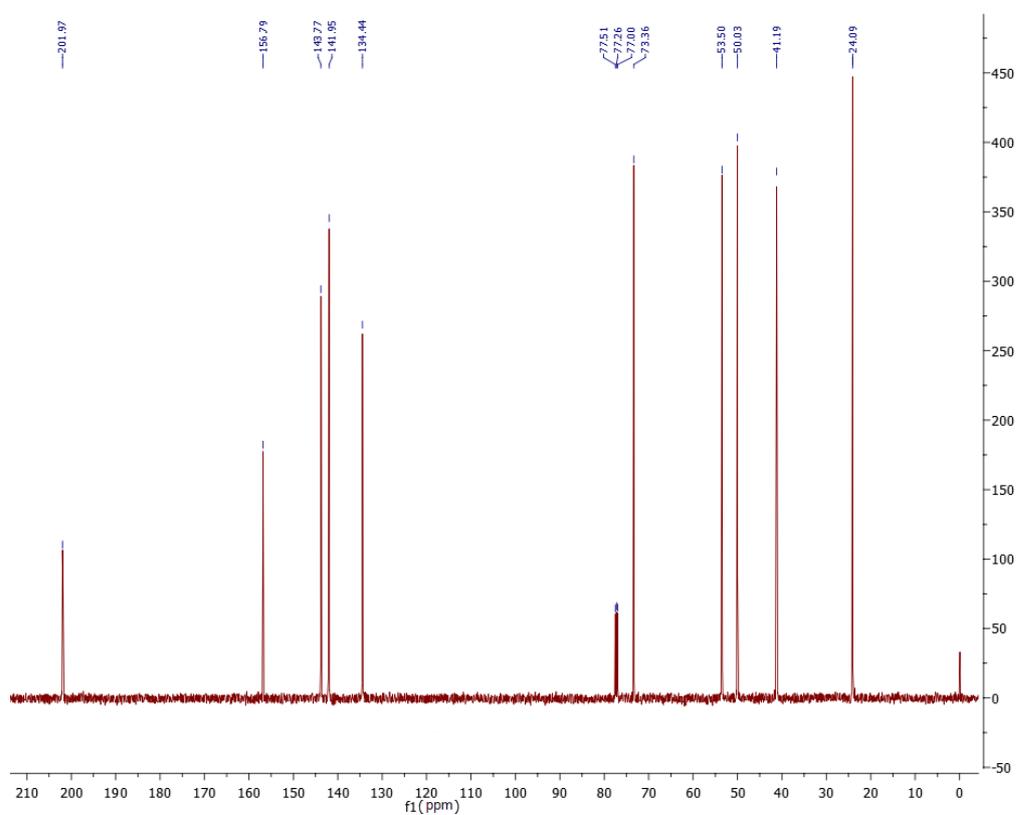


Figure S18. Copy of ¹³C NMR spectrum of compound 4b

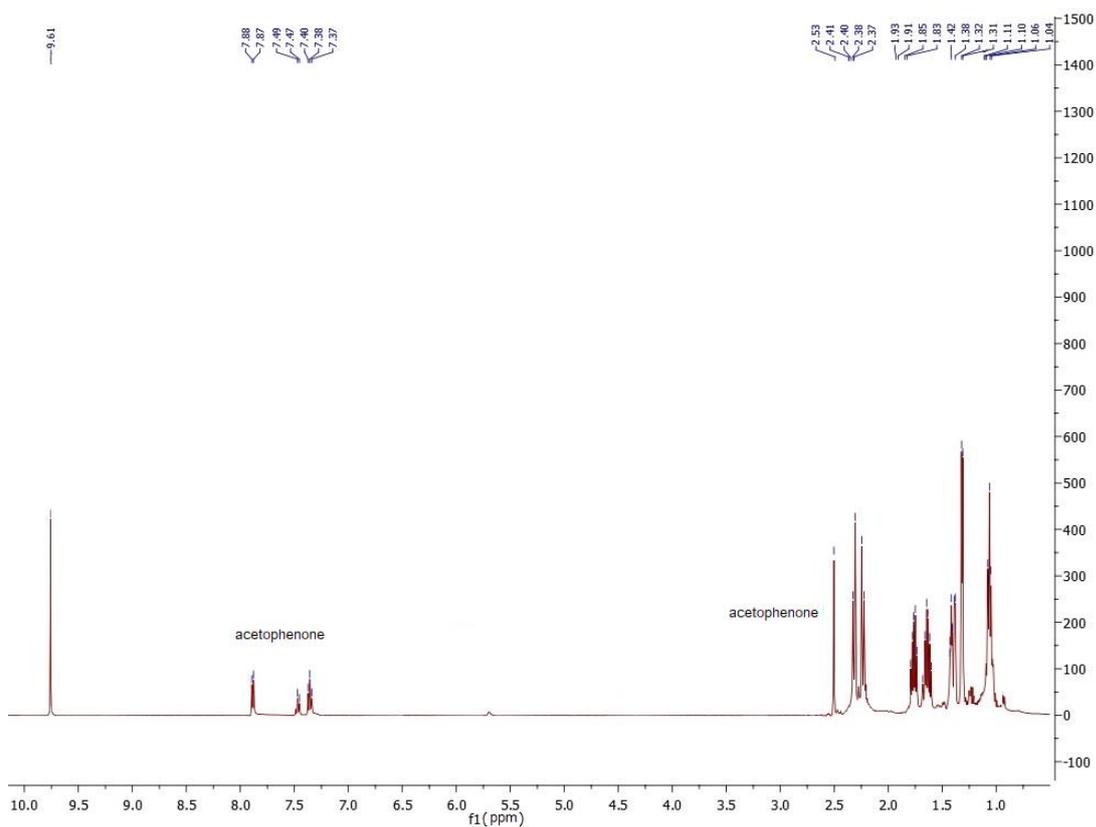


Figure S19. Copy of ¹H NMR spectrum of compound 5a

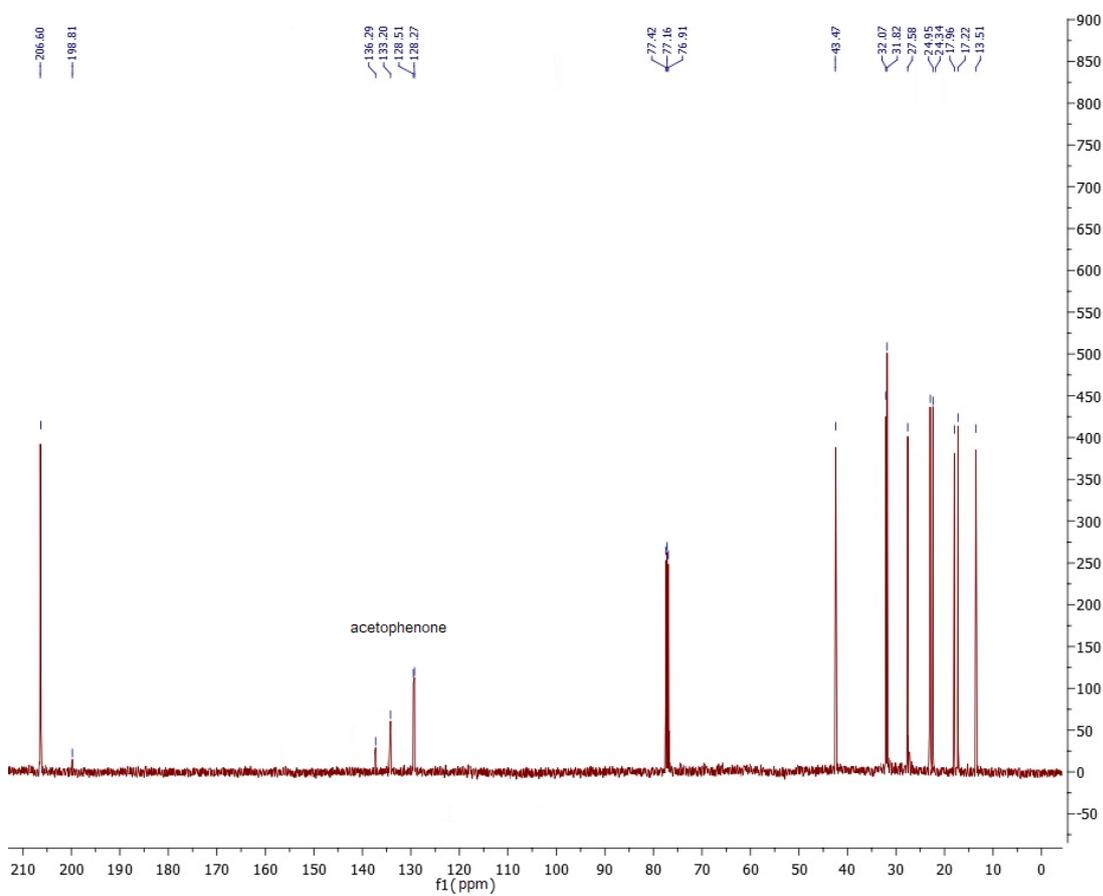


Figure S20. Copy of ¹³C NMR spectrum of compound 5a

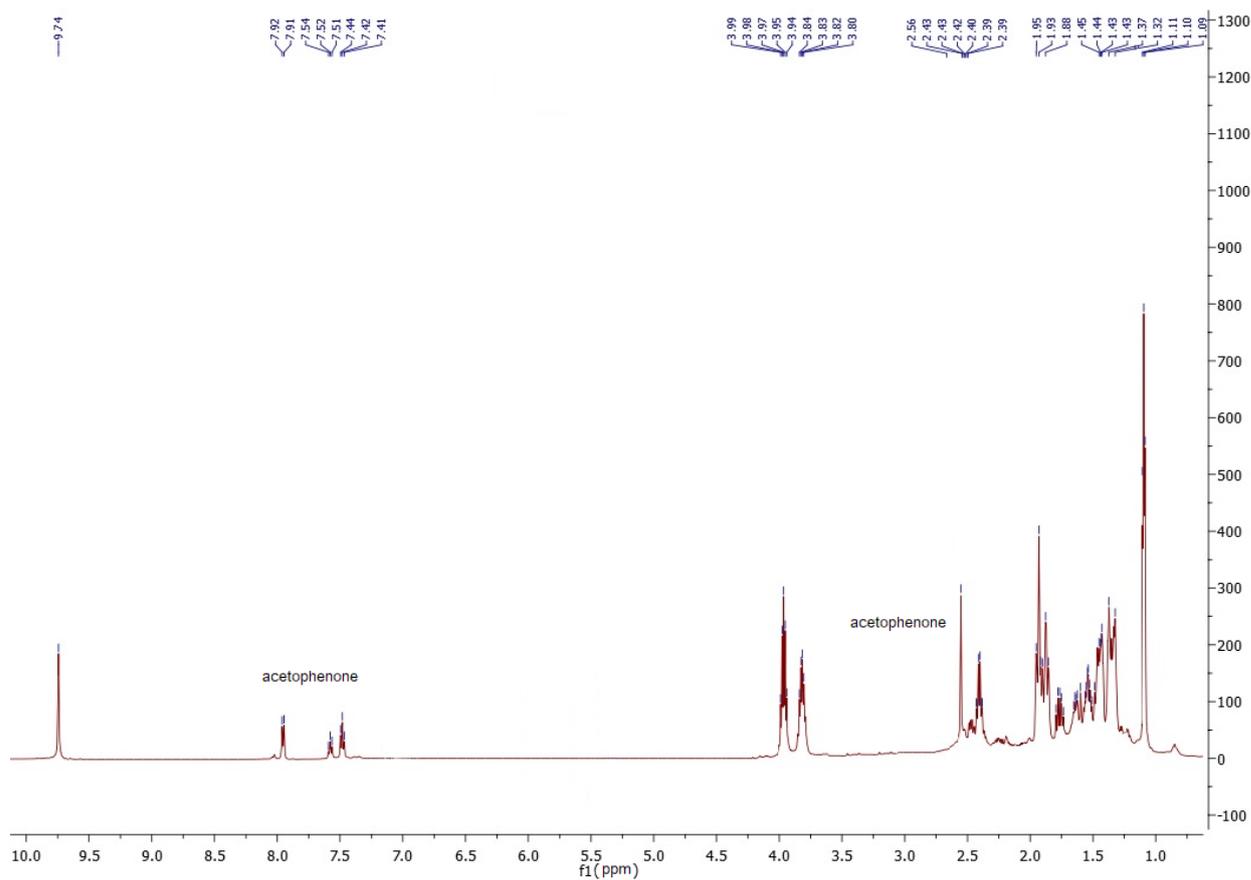


Figure S21. Copy of ¹H NMR spectrum of compound **5b**

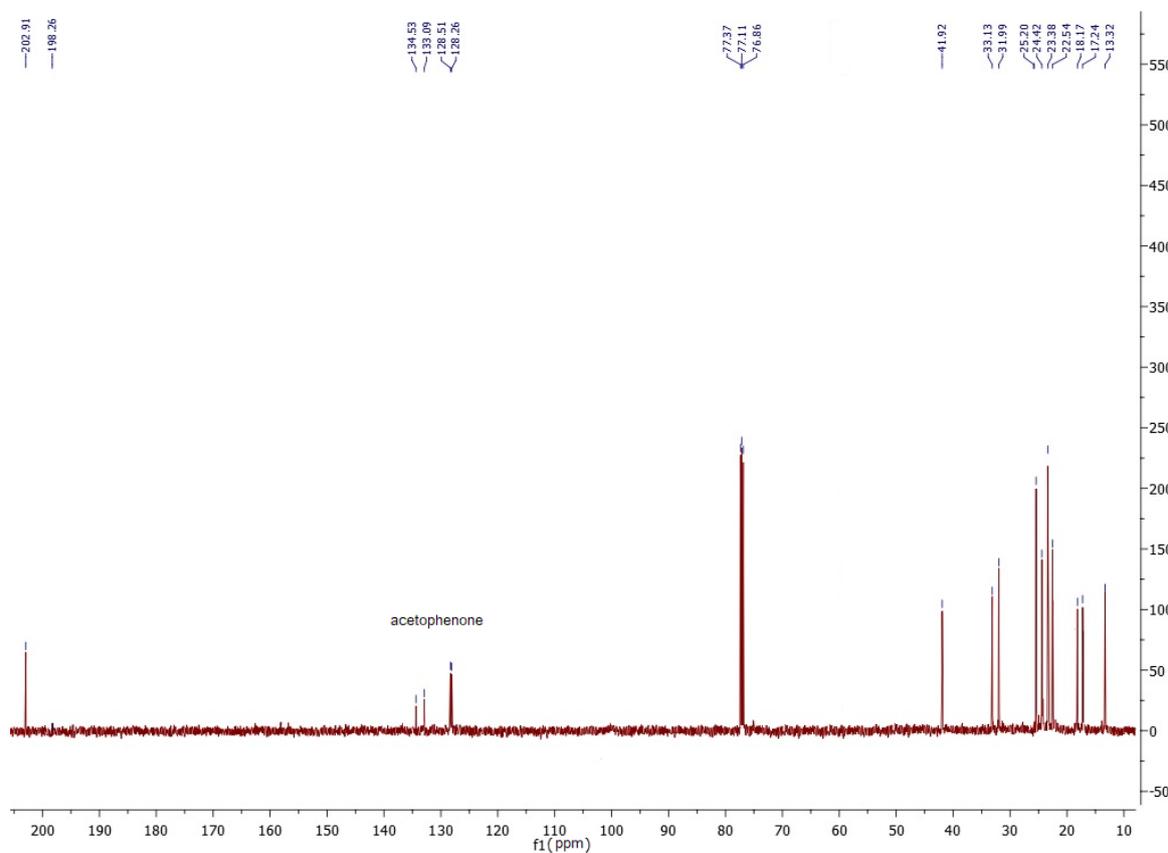


Figure S22. Copy of ¹³C NMR spectrum of compound **5b**

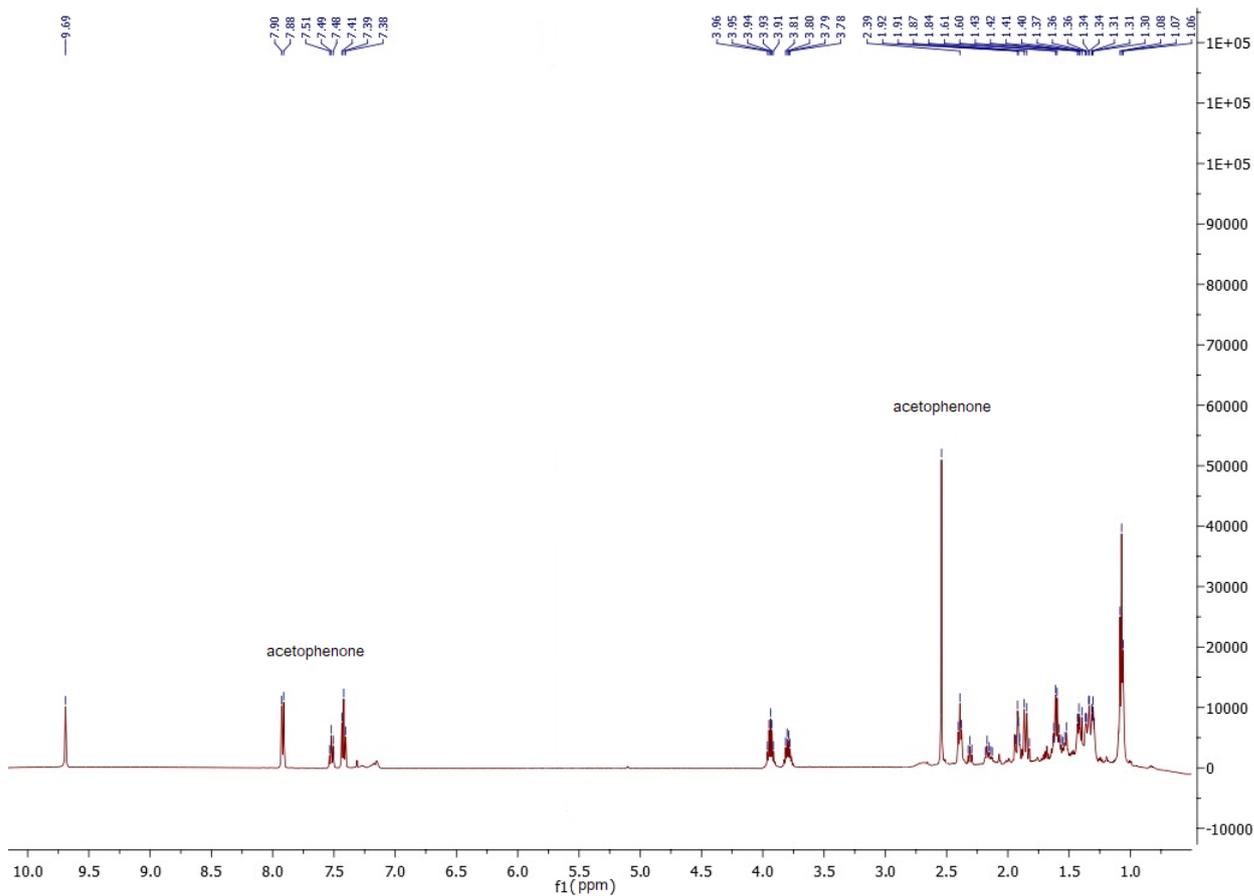


Figure S23. Copy of ¹H NMR spectrum of compound 5c

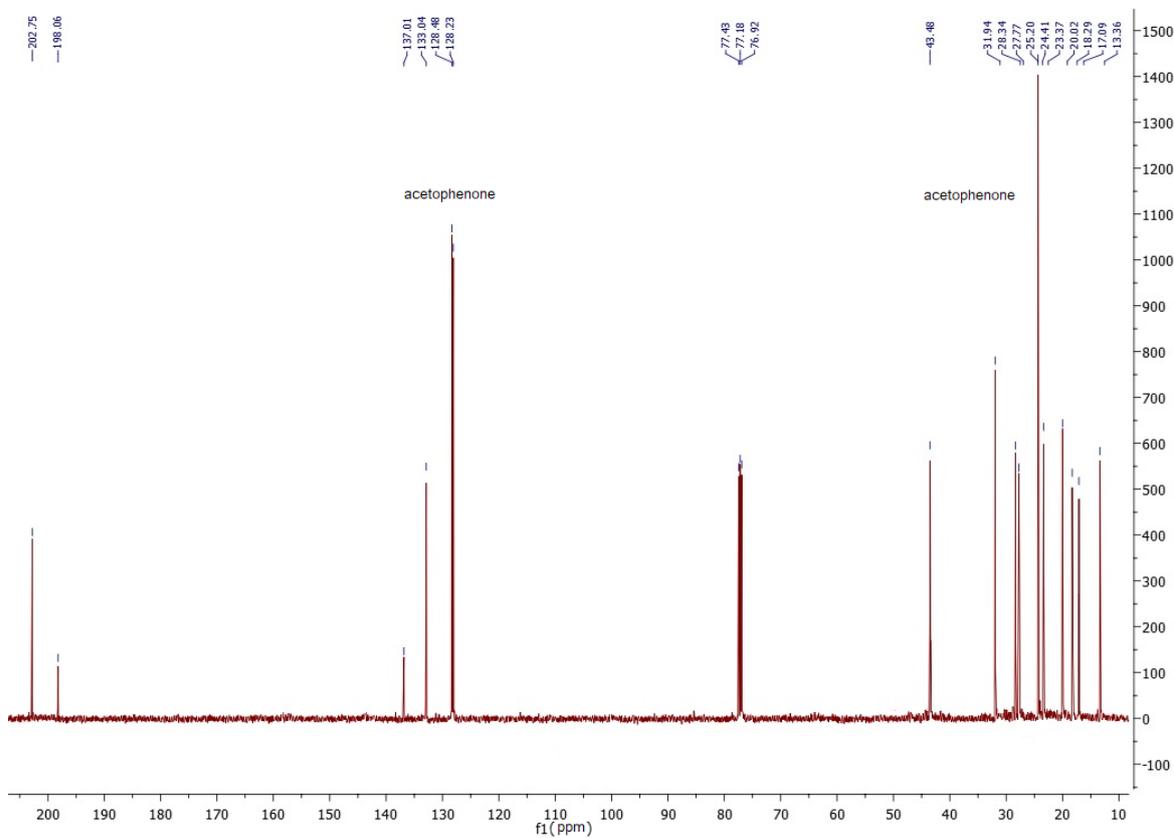


Figure S24. Copy of ¹³C NMR spectrum of compound 5c

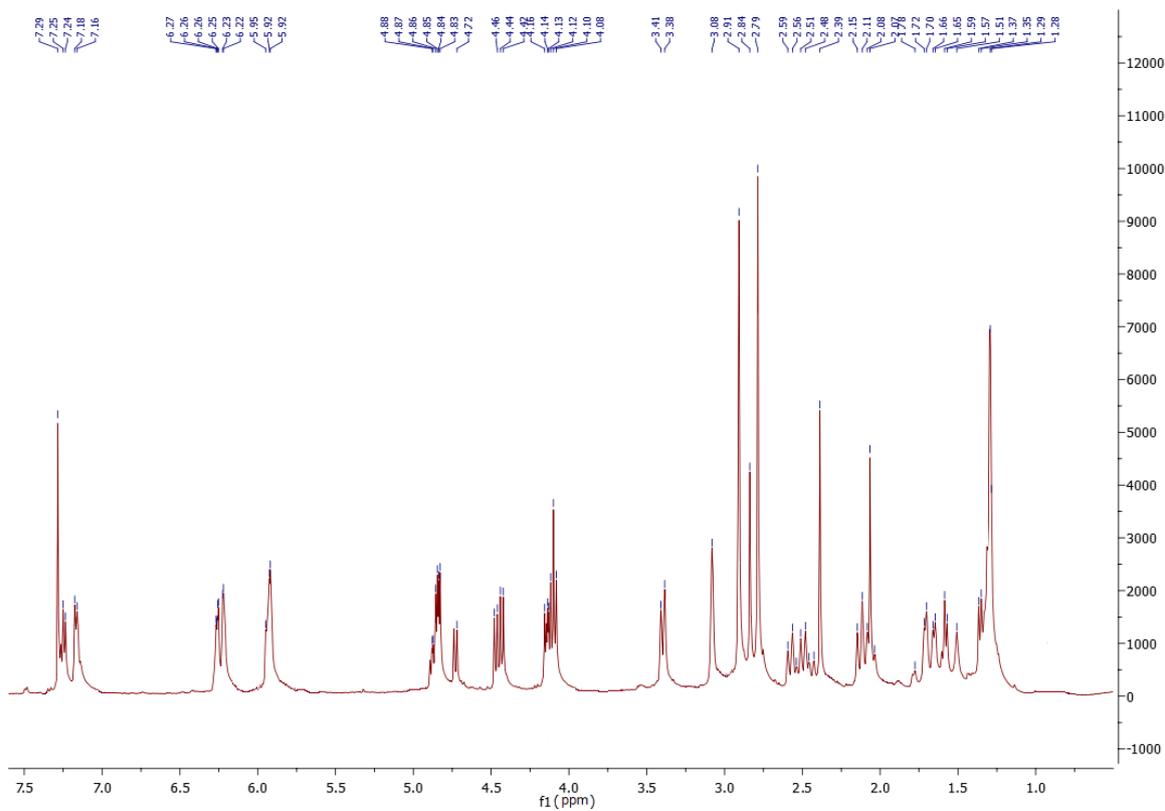


Figure S25. Copy of ^1H NMR spectrum of compound **6a**

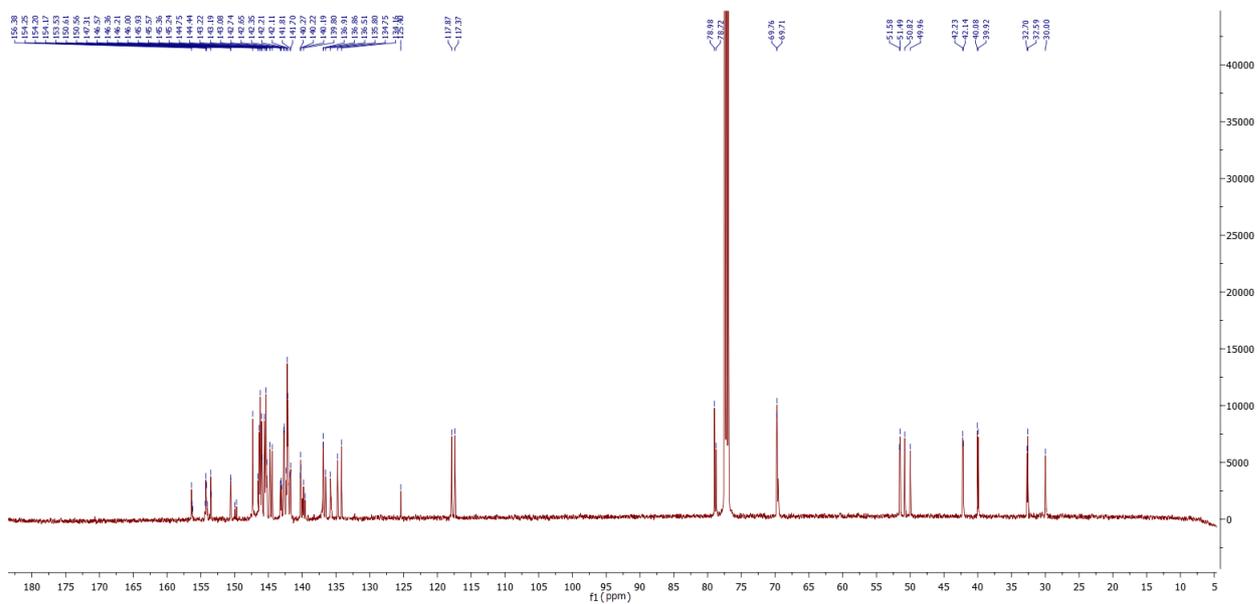


Figure S26. Copy of ^{13}C NMR spectrum of compound **6a**

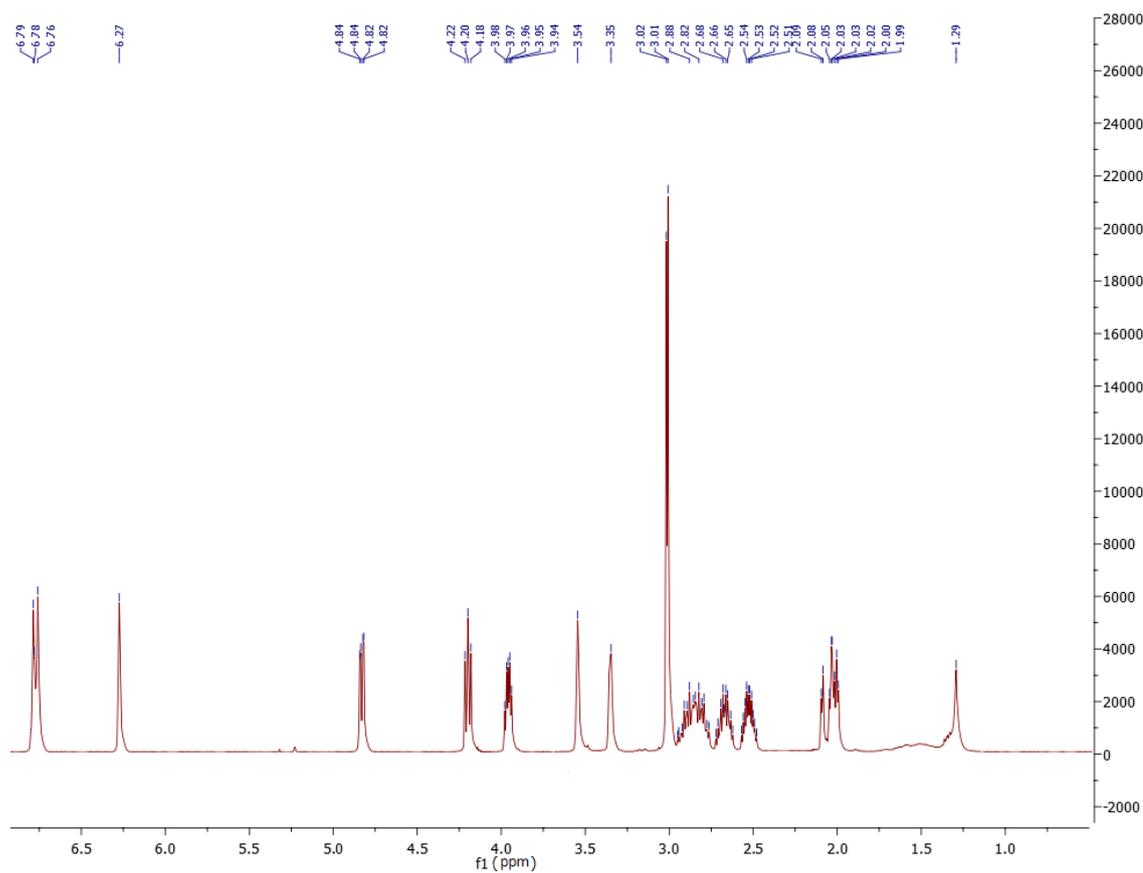


Figure S27. Copy of ¹H NMR spectrum of compound **6b**

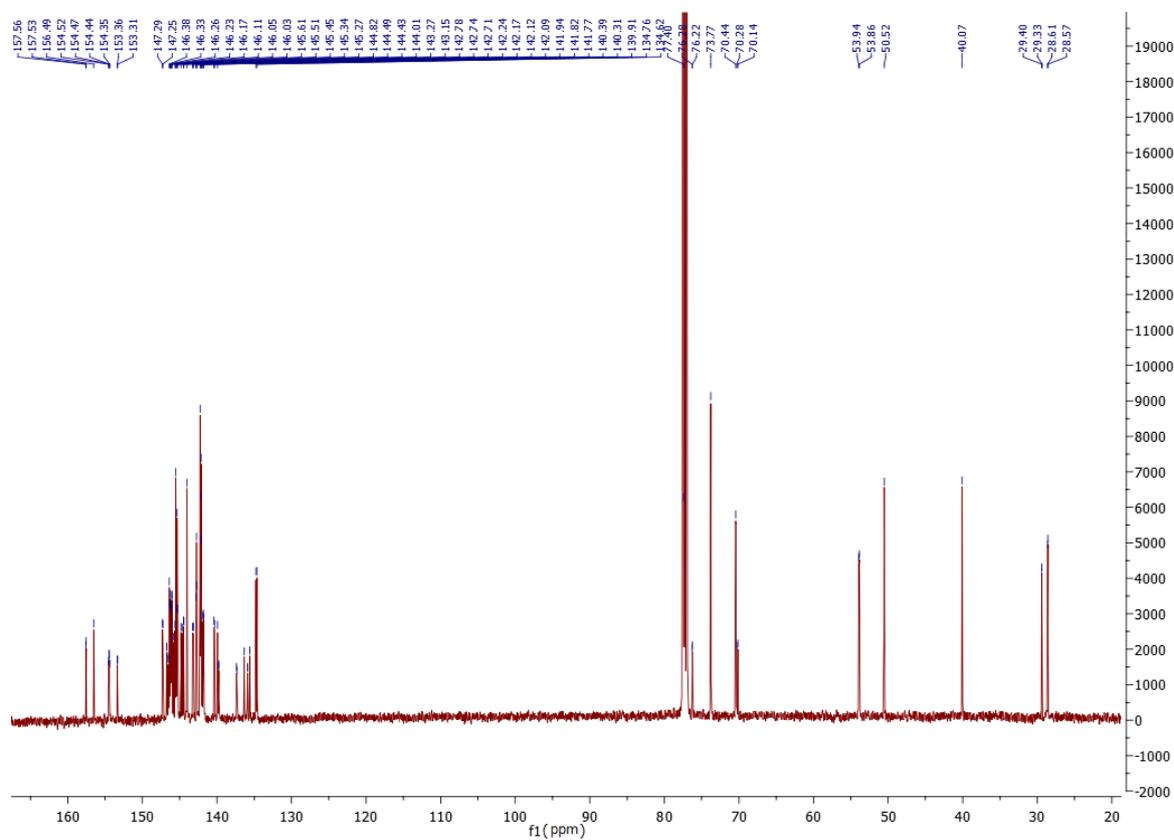


Figure S28. Copy of ¹³C NMR spectrum of compound **6b**

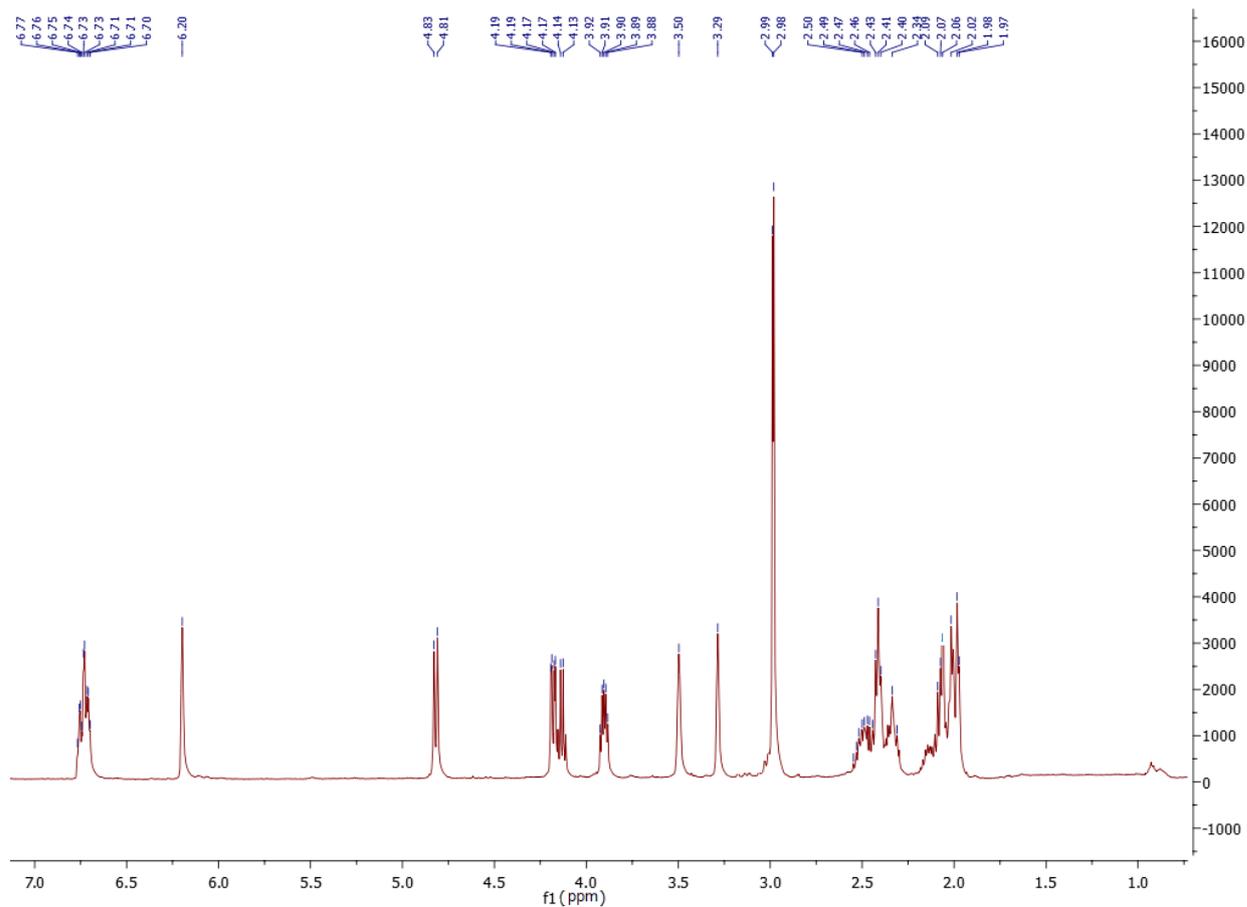


Figure S29. Copy of ^1H NMR spectrum of compound **6c**

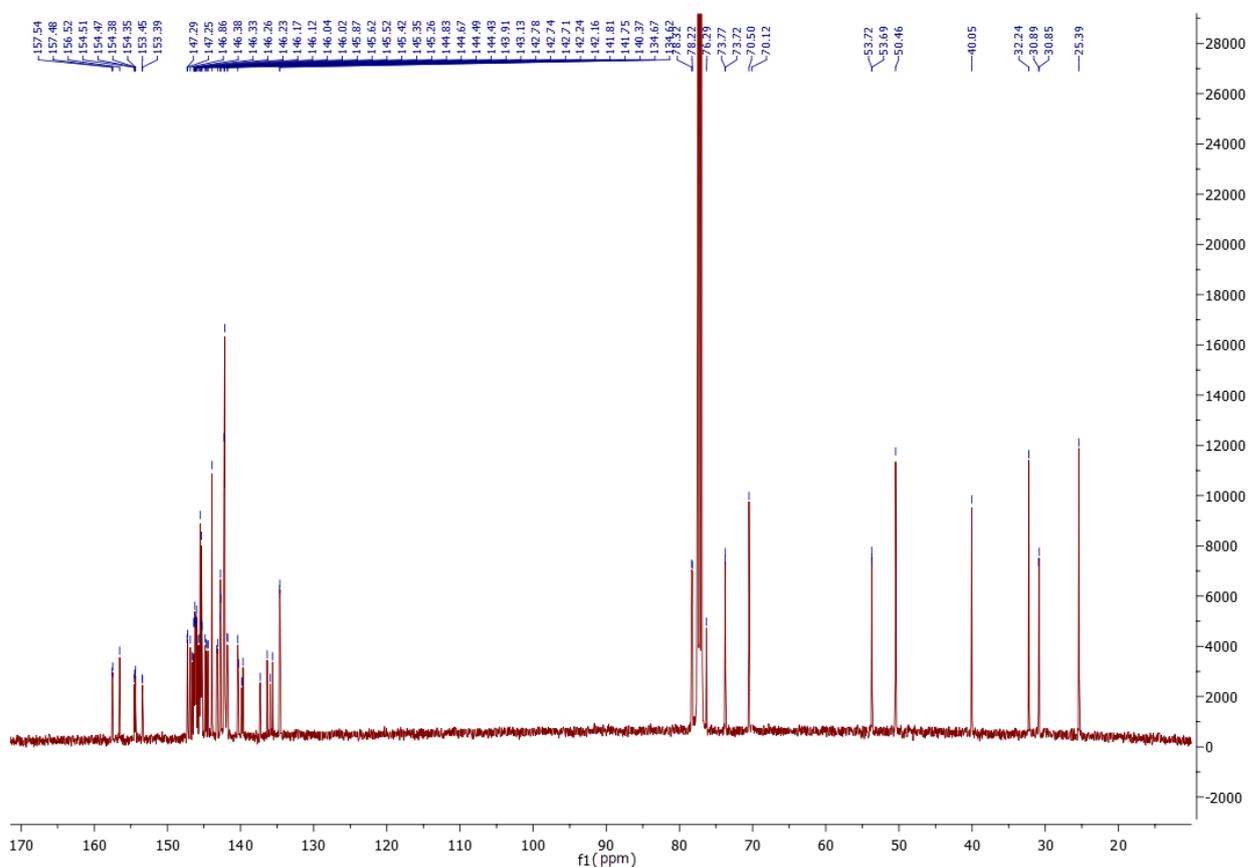


Figure S30. Copy of ^{13}C NMR spectrum of compound **6c**

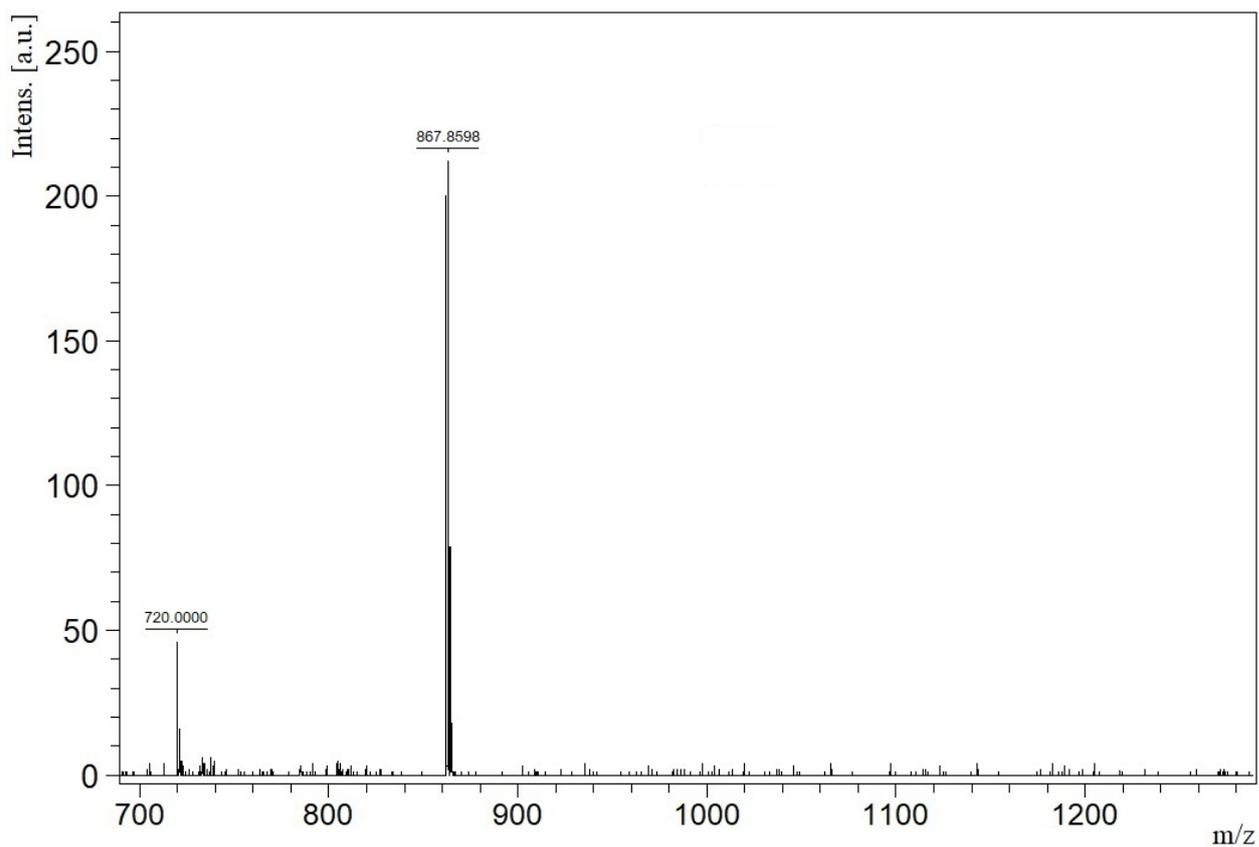


Figure S31. MALDI-TOF mass spectrum of compound **2a**

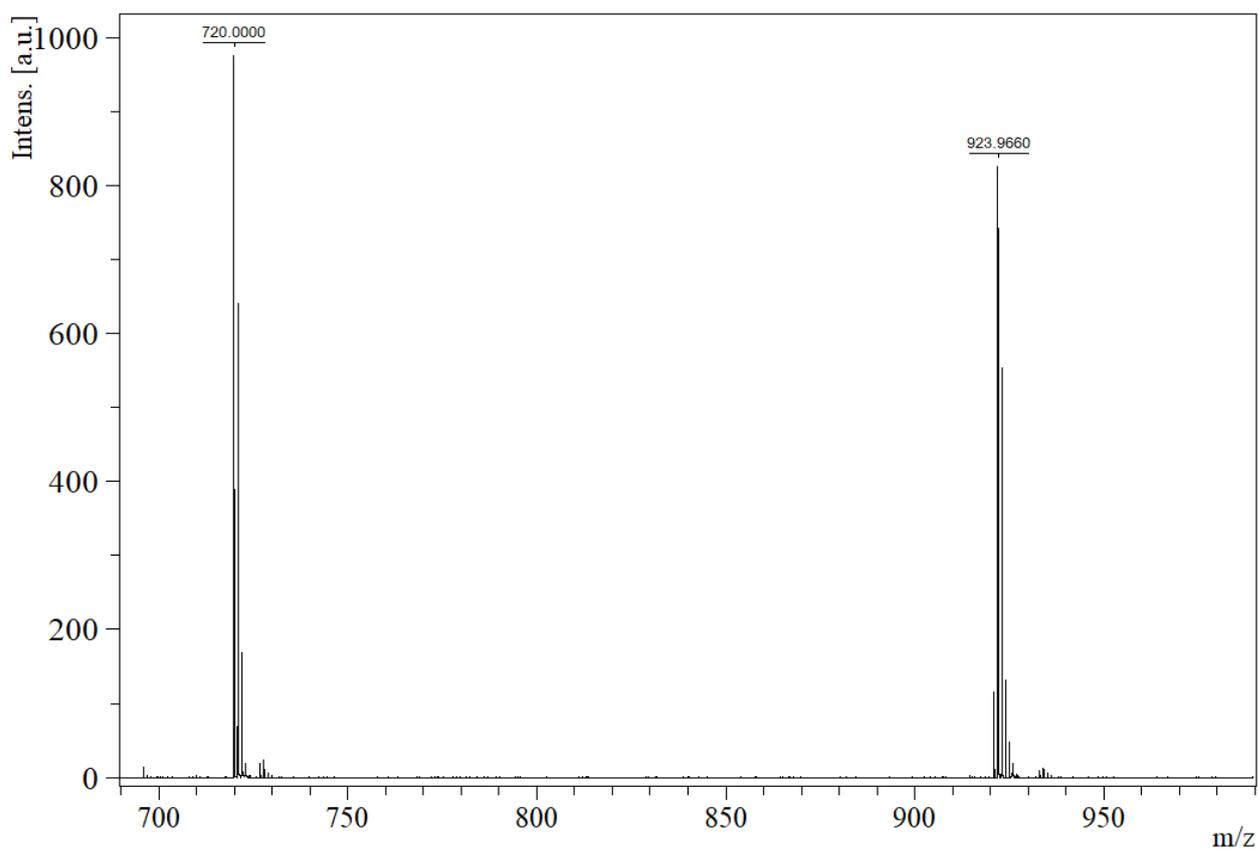


Figure S32. MALDI-TOF mass spectrum of compound **2b**

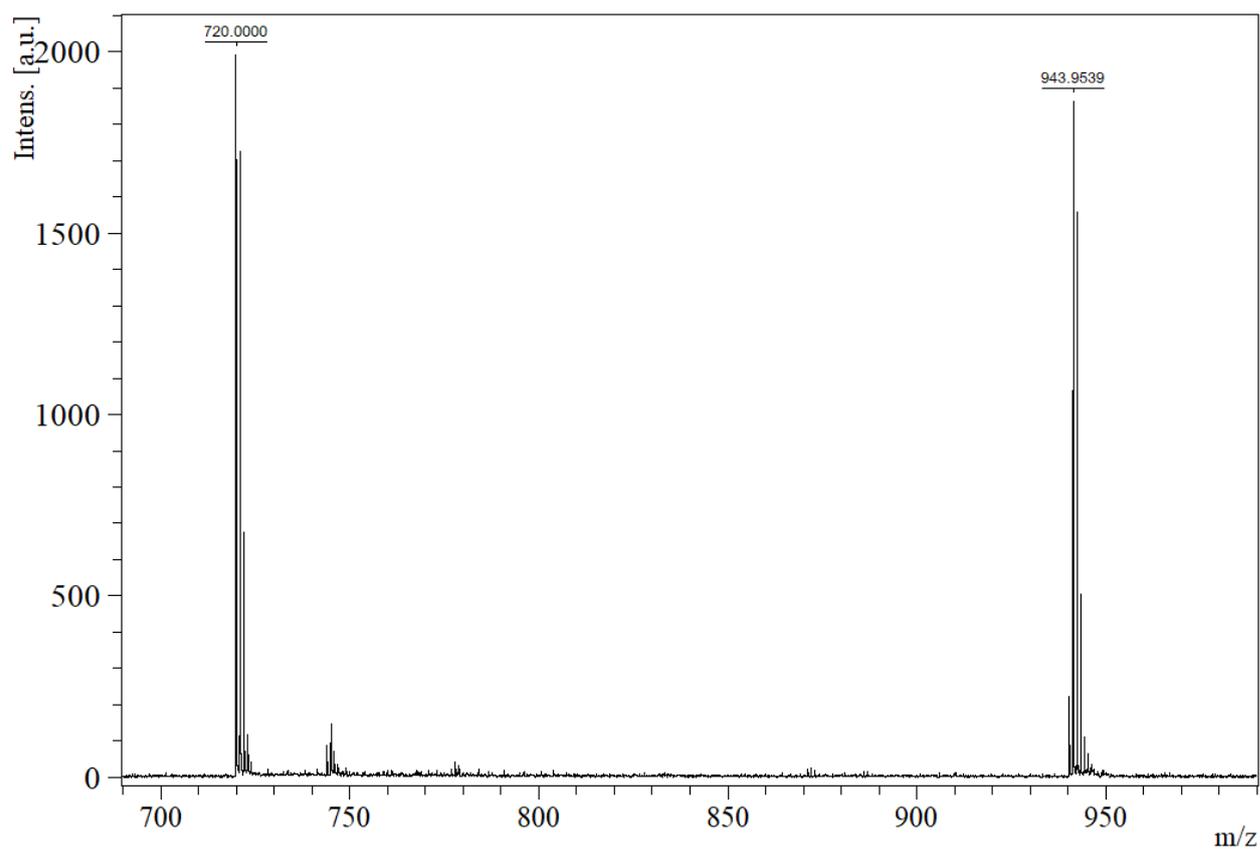


Figure S33. MALDI-TOF mass spectrum of compound **2c**

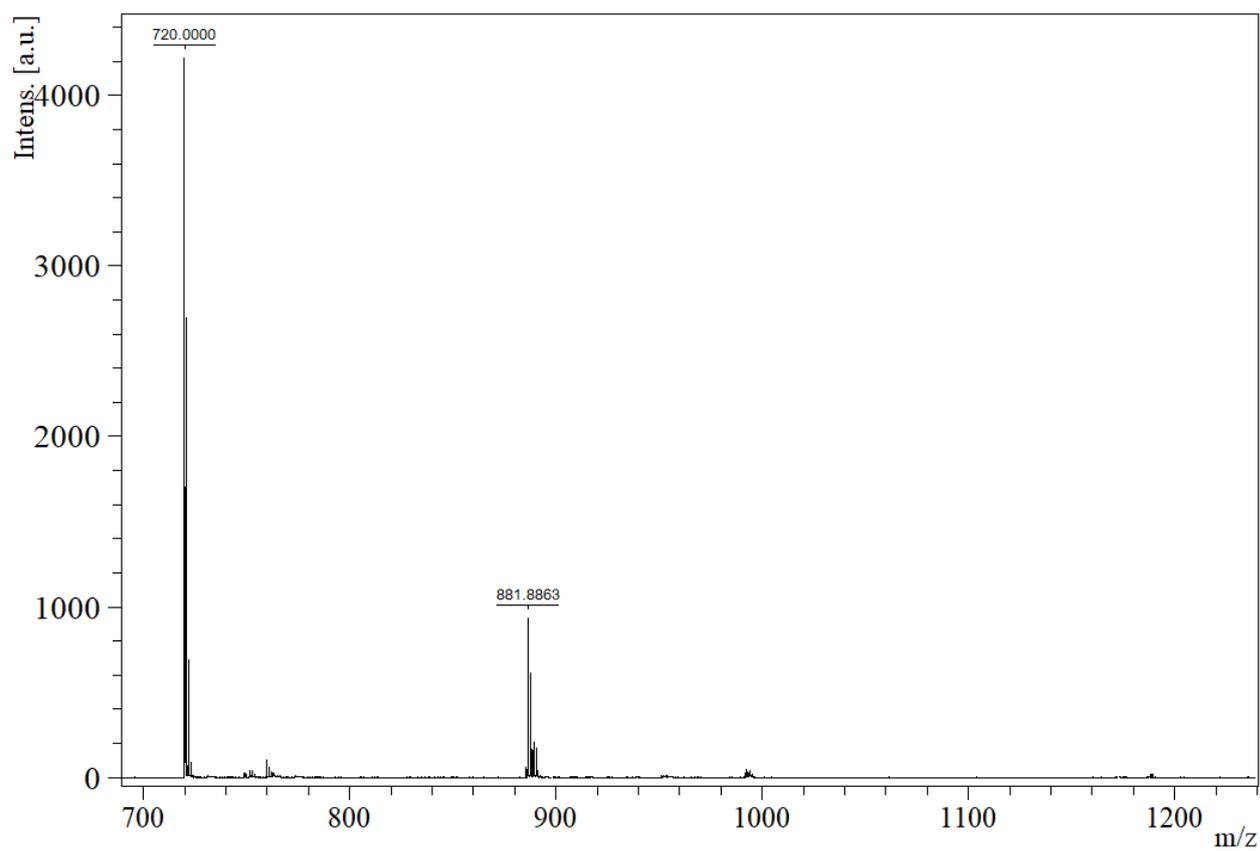


Figure S34. MALDI-TOF mass spectrum of compound **6a**

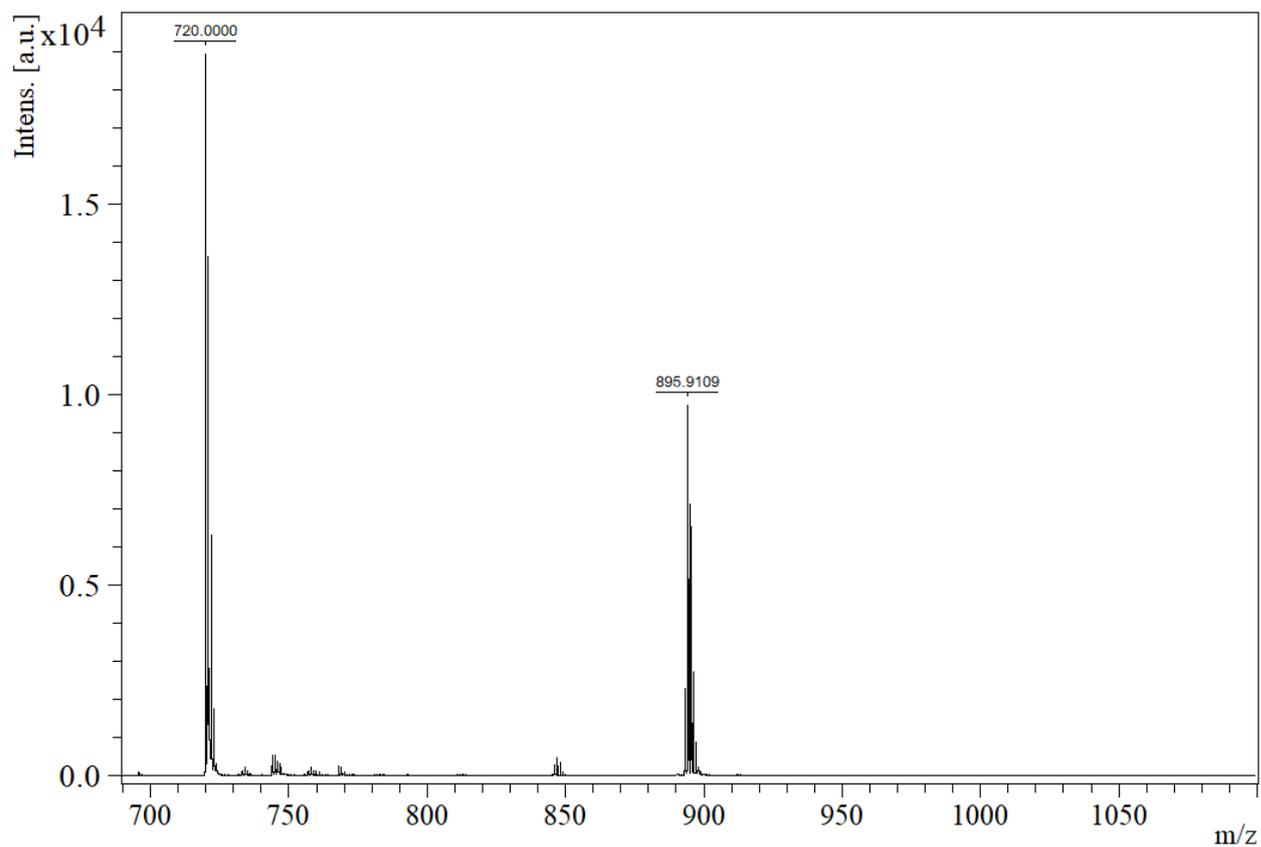


Figure S35. MALDI-TOF mass spectrum of compound **6b**

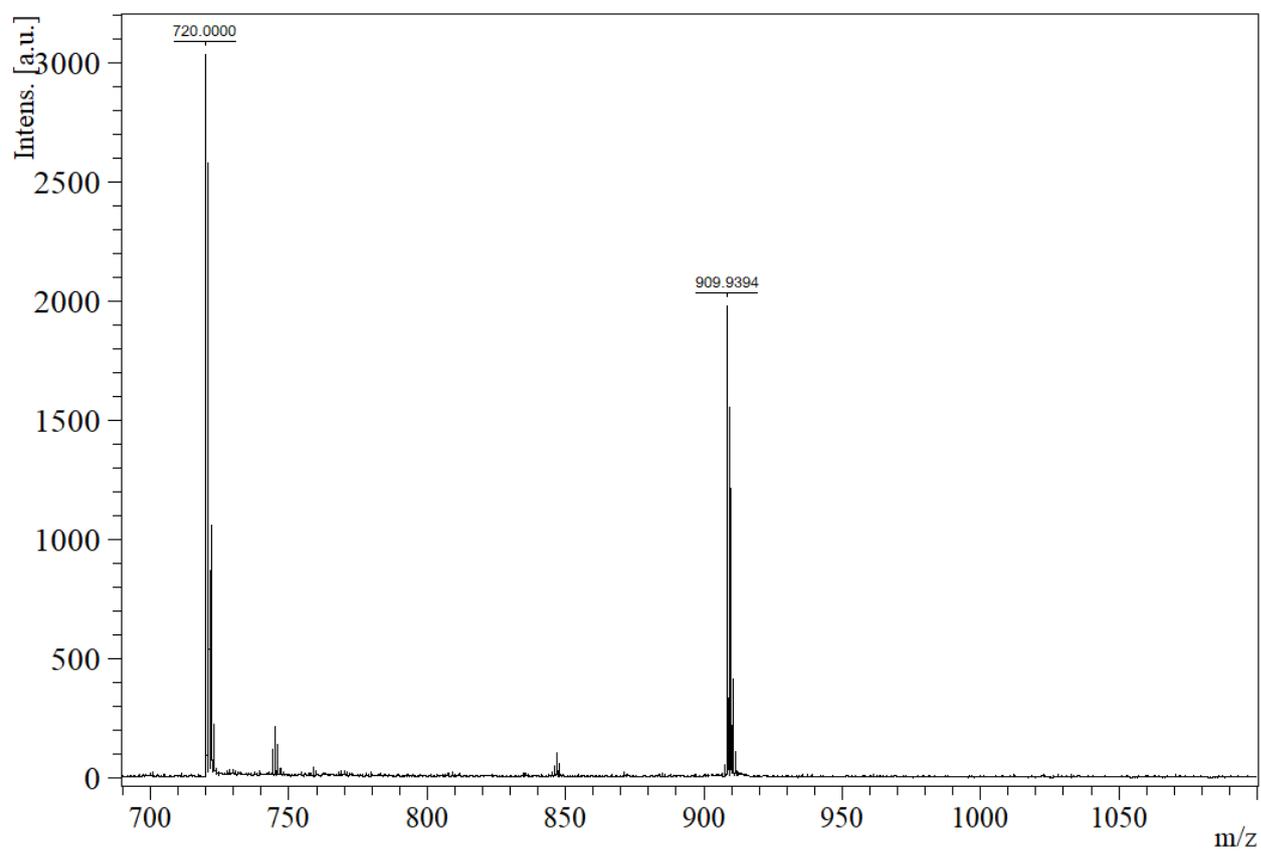


Figure S36. MALDI-TOF mass spectrum of compound **6c**