

Supplementary Information

for

Cocatalyst versus Precatalyst impact on the Vinyl-Addition Polymerization of Norbornenes with Polar Groups: Looking at the other Side of the Coin

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General information

Materials

(S)-(+)-1,2,3,4-Tetrahydro-1-naphthylamine, ((η^3 -C₃H₅)PdCl)₂, Na⁺[B(3,5-(CF₃)₂C₆H₅)₄]⁻ (NaBARF) from J&K Scientific, (R)-(-)-1-cyclohexylethylamine from ABCR GmbH, (S)-1-(4-methoxyphenyl)ethylamine, (S)-(-)-1-(4-methylphenyl)ethylamine, AgSbF₆, AgBF₄ from Alfa Aesar, 1,2,4-trichlorobenzene, maleic anhydride, dicyclopentadiene, palladium (II) acetate, Li⁺[B(C₆F₅)₄]⁻ (LiFABA), toluene, methanol from Sigma-Aldrich were used in this study and they were applied as received without a preliminary purification. Methylene chloride, chloroform and 1,2-dichloroethane were distilled over CaH₂ under argon atmosphere and stored over molecular sieves (4 Å). SIMesPd(cinn)Cl, SIPrPd(cinn)Cl,^{1, 2} (η^6 -toluene)Ni(C₆F₅)₂,³ **M1**⁴ and **M6**⁵ were prepared according to the literature procedures.

Methods

NMR-spectra were recorded on a Bruker Ascend™ 400 spectrometer at 400.1 MHz (¹H NMR), 100.6 MHz (¹³C NMR). Chemical shifts δ are reported in parts per million (ppm) relative to the reference (residual CHCl₃ signal) for ¹H, ¹³C NMR. Each sample was dissolved in a solvent (CDCl₃) up to a concentration of 10%.

Specific rotation was measured using KRÜSS P3000 polarimeter in CHCl₃ or THF (HPLC grade).

Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters system with a differential refractometer (Chromatopack Microgel-5; eluent, chloroform; flow rate, 1 ml/min). The molecular weights and polydispersity were calculated by a standard procedure relative to monodispersed polystyrene standards.

Calorimetric measurements were conducted using a “Mettler” TA-4000 differential scanning calorimeter (Giesen, Germany) at a heating rate of 20°C/min under argon. TGA measurements were carried out on "TGA/DSC 1" (Mettler Toledo) in argon and in air at the heating rate of 10 °C/min from 30 to 1000 °C.

Wide-angle X-ray diffraction (WAXD) data were obtained using a two-coordinate AXS detector (Bruker, Bremen, Germany) and Cu K α emission (wavelength of 0.154 nm).

X-ray diffraction experiments for the compounds **M4** and **M5** were carried out at 120 K with a Bruker APEX2 DUO CCD diffractometer, using graphite monochromated Mo-K α (λ = 0.71073 Å). Using Olex2,⁶ the structures were solved with the ShelXT structure solution program⁷ using Intrinsic Phasing and refined against F² in the anisotropic-isotropic approximation with the olex2.refine refinement package⁸ using Gauss-Newton minimization.

The positions of hydrogen atoms were calculated and they were then refined in the isotropic approximation within the riding model.

Circular dichroism (CD) spectra of the vinyl-addition polynorbornenes were measured in chloroform at the concentration of 1 mg/ml. Spectra were recorded with spectropolarimeter J-810 (Jasco, Japan) in the 220–450 nm range (50 nm/min, 1 nm slit width) in the 0.01 cm and 0.1 cm path-length quartz cells with a detachable window (Hellma, Germany). The baseline spectrum was recorded from pure chloroform.

Glove box "M.Braun" and standard Schlenk technique were used for the operations in argon atmosphere.

Experimental data

Synthesis of monomers

The preparation of exo-nadic anhydride (exo-NDA)

Exo-NDA was prepared according to a modified procedure.⁹ A 500 ml two necked round bottom flask was filled with 200 ml of 1,2,4-trichlorobenzene and 59.3 g of maleic anhydride (0.606 mol). The solution was heated to 200°C and then DCPD (40.8 ml, 0.303 mol) was added dropwise over 20 min. The solution acquired a yellow color, which on further heating changed to dark brown. The reaction mixture was stirred for 6 h at 200°C. After that, it was cooled to room temperature and was allowed to stay overnight. The crystal precipitate formed in the flask was separated and recrystallized four times from benzene. *Exo*-NDA was isolated as white crystals (18.2 g, 18% yield, the content of *exo*-isomer was more 98%). M.p. – 146-148°C.

¹H NMR (CDCl₃, δ, ppm): 1.50 (d, 2H, CH₂, ²J = 10.2 Hz); 2.97 (s, 2H); 3.42 (s, 2H); 6.30 (s, 2H, CH=CH).

¹³C NMR (CDCl₃, δ, ppm): 44.07; 46.82; 48.71; 137.91; 171.59.

Synthesis of M2

A 250 ml round bottom flask was fitted with a Dean Stark distillation receiver and was filled with *exo*-NDA (7.00 g, 42.7 mmol), toluene (160 ml), and (S)-1-(4-methoxyphenyl)ethylamine (6.0 g, 44.4 mol). The reaction mixture was refluxed for 6 h and then it was cooled to room temperature. Thereafter, the reaction mixture was washed twice with the solution of 10% HCl (30 ml) and with H₂O (30 ml). The organic layer was dried by Na₂SO₄ and toluene was evaporated using a rotary evaporator. The resulting molten yellow solid was dissolved in CH₂Cl₂ and was filtered through a pad of silica. The final solution was evaporated using a rotary evaporator, and the residue was recrystallized from MeOH and after that from hexane. Monomer **M2** was obtained as a white crystal powder (7.50 g, 63%). [α]_D²⁰ = -25° (THF, C = 1). M. p. 64-66°C.

^1H NMR (CDCl_3 , δ , ppm): 1.07 (d, 1H, $^2J=9.7$ Hz); 1.38 (d, 1H, $^2J=9.7$ Hz); 1.75 (d, 3H, $^3J=7.4$ Hz); 2.29 (s, 3H, Ar-CH₃); 2.52-2.59 (m, 2H); 3.15-3.27 (m, 2H); 5.28-5.38 (m, 1H); 6.20-6.28 (m, 2H, CH=CH); 7.04-7.15 (d, 2H, ArH, $^3J=7.9$ Hz); 7.27-7.35 (d, 2H, ArH, $^3J=7.9$ Hz).

^{13}C NMR (CDCl_3 , δ , ppm): 16.02; 20.64; 42.12; 44.94; 44.99; 46.96; 49.90; 127.01; 128.57; 136.13; 136.93; 137.47; 137.51; 177.33; 177.39.

MS (EI, m/z (intensity, %)): 281 (60%, M⁺), 215 (77%, C₁₃H₁₃NO₂⁺), 66 (62%, C₅H₆⁺).

Synthesis of **M3**

A 250 ml round bottom flask was filled with exo-NDA 8.00 g (0.0488 mol), toluene 160 ml, (S)-1-(4-methoxyphenyl)ethylamine 7.74g (0.0513 mol), magnetic stirring bar, fitted with Dean-Stark apparatus, and refluxed for 6 h. The reaction mixture was cooled to room temperature. Then it was washed twice with the solution of 10% HCl (30 ml) and with H₂O (30 ml). The organic layer was dried by Na₂SO₄. Toluene was evaporated using a rotary evaporator. Molten yellow solid dissolved in CH₂Cl₂ and was filtered through a pad of silica. The final solution was evaporated using a rotary evaporator and the residue was twice recrystallized from MeOH. Monomer **M3** was obtained as a white crystal powder (8.40 g, 58%). $[\alpha]_{\text{D}}^{28}=-62^\circ$ (THF, C=1). M. p. 76-79 °C.

^1H NMR (CDCl_3 , δ , ppm): 1.05 (d, 1H, CH, $^2J=9.54$); 1.37 (d, 1H, CH, $^2J=9.54$); 1.71-1.80 (m, 3H); 2.53-2.61 (m, 2H); 3.14-3.26 (m, 2H); 3.76 (s, 3H, O-CH₃); 5.30-5.39 (m, 1H); 6.20-6.29 (br. s, 2H, R-CH=CH-R); 6.83 (d, 2H, ArH, $^3J=8.53$); 7.37 (d, 2H, ArH, $^3J=8.53$).

^{13}C NMR (CDCl_3 , δ , ppm): 15.71; 42.08; 44.94; 44.98; 46.94; 49.20; 54.72; 128.41; 131.29; 137.47; 137.49; 158.50; 177.37; 177.42.

MS (EI, m/z (intensity, %)): 297 (56%, M⁺), 231 (42%, C₁₃H₁₃NO₃⁺), 66 (62%, C₅H₆⁺).

Synthesis of **M4**

A 250 ml round bottom flask was filled with exo-NDA 6.00 g (0.0365 mol), toluene 120 ml, (R)-1-cyclohexylethylamine 4.65 g (0.0366 mol), magnetic stirring bar, fitted with Dean-Stark apparatus, and refluxed for 6 h. The reaction mixture was cooled to room temperature. Then it was washed twice with the solution of 10% HCl (20 ml) and with H₂O (20 ml). The organic layer was dried by Na₂SO₄. Toluene was evaporated using a rotary evaporator. Molten yellow solid dissolved in CH₂Cl₂ and was filtered through a pad of silica. The final solution was evaporated using a rotary evaporator and the residue was recrystallized from MeOH. Monomer **M4** was obtained as a white crystal powder (7.19 g, 72%). M. p. 98-101 °C. $[\alpha]_{\text{D}}^{20}=-13^\circ$ (THF, C=1).

^1H NMR (CDCl_3 , δ , ppm): 0.75-2.07 (m, 16H); 2.55-2.65 (m, 2H); 3.21-3.28 (br. s, 2H); 3.76-3.85 (m, 1H); 6.20-6.28 (m, 2H, R-CH=CH-R)

APT NMR (CDCl_3 , δ , ppm): 15.71; 25.63; 25.75; 26.09; 30.24; 30.42; 38.80; 42.83; 45.21; 45.32; 47.48; 53.19; 137.9; 178.32.

MS (EI, m/z (intensity, %)): 274 (0.1%, M^+), 164 (100%, $\text{C}_4\text{H}_{10}\text{NO}_2^+$), 62 (66%, C_5H_6^+).

Synthesis of **M5**

A 250 ml round bottom flask was filled with exo-NDA 5.70 g (0.0348 mol), toluene 120 ml, (S)-1,2,3,4-tetrahydro-1-naphthylamine 5.62 g (0.0495 mol), magnetic stirring bar, fitted with Dean-Stark apparatus, and refluxed for 6 h. The reaction mixture was cooled to room temperature. Then it was washed twice with the solution of 10% HCl (20 ml) and with H_2O (20 ml). The organic layer was dried by Na_2SO_4 . Toluene was evaporated using a rotary evaporator. Molten yellow solid dissolved in CH_2Cl_2 and was filtered through a pad of silica. The final solution was evaporated using a rotary evaporator and the residue was recrystallized from MeOH. Monomer **M5** was obtained as a white crystal powder (6.99 g, 74%). $[\alpha]_{\text{D}}^{20} = -70^\circ$ (THF, $\text{C}=1$). M. p. 130-132 $^\circ\text{C}$.

^1H NMR (CDCl_3 , δ , ppm): 1.37 (d, 1H, CH, $^2J=9.70$); 1.53 (d, 1H, CH, $^2J=9.70$); 1.70-1.80 (m, 1H); 1.93-2.00 (m, 1H); 2.00-2.10 (m, 1H); 2.21-2.33 (m, 1H); 2.63-2.70 (m, 1H); 2.70-2.80 (m, 2H); 2.92-3.00 (m, 1H, CH); 3.26(s, 1H, CH); 3.32 (s, 1H, CH); 5.34-5.41 (m, 1H); 6.28-6.33 (br. s, 2H, R-CH=CH-R); 6.88 (d, 1H, ArH, $^3J=7.53$); 7.05-7.16 (m, 3H, ArH).

^{13}C NMR (CDCl_3 , δ , ppm): 21.82; 26.52; 28.90; 42.29; 44.84; 44.92; 47.14; 47.16; 125.29; 125.51; 126.36; 128.71; 133.48; 137.45; 137.52; 137.57; 177.1; 177.16.

MS (EI, m/z (intensity, %)): 293 (3%, M^+), 164 (11%, $\text{C}_9\text{H}_{10}\text{NO}_2^+$), 130 (100%, $\text{C}_{10}\text{H}_{10}^{+2}$), 66 (12%, C_5H_6^+).

Synthesis of **M7**

5-Norbornene-2-methanol (5.0 g, 40 mmol), pyridine (6.3 g, 80 mmol), p-toluenesulfonyl chloride (8.4 g, 43 mmol) and dry dichloromethane (100 ml) were mixed in a two-neck round bottom glass flask (150 ml) equipped with a reflux condenser. The mixture was stirred for 2 h at room temperature. Then the mixture was rinsed with HCl (10% aqueous solution). An organic phase was separated, dried over MgSO_4 , filtered through 2 cm silica gel layer and evaporated under vacuum. The yield of 5-(tosyloxymethyl)norbornene-2 was 10 g (89%).

2-Butoxyethanol (100 ml) was placed in a round bottom flask (250 ml) equipped with a reflux condenser. Metallic sodium (2.5 g, 110 mmol) was added to the flask in small portions. After the complete dissolution of the sodium, 5-(tosyloxymethyl)norbornene (15 g, 54 mmol)

was added to the solution. The solution was refluxed while stirring up to the complete conversion of initial 5-(tosyloxymethyl)norbornene (controlled by GC). Then initial 2-butoxyethanol was distilled off from the reaction mixture under vacuum (0.2-0.5 mm Hg), and the residue was distilled under deeper vacuum (0.05 mm Hg). The product was isolated as a colorless oil (yield – 61%).

^1H NMR (δ , CDCl_3 , ppm): 6.11-6.00 (m, 1.2H, $\text{C}_{2,3}\text{H}$ (*exo+endo*)), 5.93-5.88 (m, 0.8H, $\text{C}_{2,3}\text{H}$ (*endo*)), 3.65-3.41 (m, 6.2H, O-CH_2), 3.38-3.32 (m, 0.2H, O-CH_2 + O-CH_3), 3.20-3.13 (m, 0.8H, O-CH_2 (*endo*)), 3.09-3.02 (m, 0.8H, O-CH_2 (*endo*)), 2.91-2.87 (m, 0.8H, $\text{C}_{1,4}\text{H}$ (*endo*)), 2.79-2.72 (m, 1.2H, $\text{C}_{1,4}\text{H}$ (*exo+endo*)), 2.39-2.29 (m, 0.8H), 1.82-1.74 (m, 0.8H), 1.72-1.64 (m, 0.2H), 1.59-1.49 (m, 2H, $\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 1.41-1.16 (m, 4.2H, $\text{C}_{5,7}\text{H}$ + $\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 1.10-1.04 (m, 0.2H), 0.93-0.86 (t, 3H, $\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 0.50-0.43 (m, 0.8H, C_6H (*endo*)).

^{13}C NMR (δ , CDCl_3 , ppm, *endo*-isomer): 137.08 ($\text{C}_{2,3}$), 132.51 ($\text{C}_{2,3}$), 75.09 (O-CH_2), 71.19 (O-CH_2), 70.26 (O-CH_2), 70.08 (O-CH_2), 49.40, 43.95, 42.20, 38.70, 31.76 ($\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 29.16, 19.29 ($\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 13.93 ($\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$).

^{13}C NMR (δ , CDCl_3 , ppm, *exo*-isomer): 136.64 ($\text{C}_{2,3}$), 136.61 ($\text{C}_{2,3}$), 76.06 (O-CH_2), 74.21 (O-CH_2), 70.31 (O-CH_2), 70.12 (O-CH_2), 44.98, 43.63, 41.53, 38.77, 31.76 ($\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 29.70, 19.29 ($\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$), 13.93 ($\text{O-CH}_2\text{-(CH}_2\text{)}_2\text{-CH}_3$).

MS (EI, m/z (intensity, %)): 224 (1%, M^+), 66 (100%, C_5H_6^+).

Crystallographic data

Crystals of **M4** ($\text{C}_{17}\text{H}_{23}\text{NO}_2$, $M = 273.36$) are monoclinic, space group P2_1 , at 120 K: $a = 6.524(8)$, $b = 8.428(10)$, $c = 13.854(15)$ Å, $\beta = 97.68(3)$, $V = 754.9(15)$ Å³, $Z = 2$, $d_{\text{calc}} = 1.203$ gcm^{-3} , $\mu(\text{MoK}\alpha) = 0.78$ cm^{-1} , $F(000) = 296$.

Crystals of **M5** ($\text{C}_{19}\text{H}_{10}\text{NO}_2$, $M = 293.35$) are orthorhombic, space group $\text{P2}_12_12_1$, at 120 K: $a = 5.48910(10)$, $b = 10.9586(3)$, $c = 24.8426(6)$ Å, $V = 1494.35(6)$ Å³, $Z = 4$, $d_{\text{calc}} = 1.304$ gcm^{-3} , $\mu(\text{CuK}\alpha) = 6.70$ cm^{-1} , $F(000) = 624$.

Intensities of 8149 and 21265 reflections were measured for **M4** and **M5**, respectively, with a Bruker APEX2 DUO CCD diffractometer [$\lambda(\text{MoK}\alpha) = 0.71073$ Å, ω -scans, $2\theta < 60^\circ$ for **M4**; $\lambda(\text{CuK}\alpha) = 1.54178$ Å, ω -scans, $2\theta < 136^\circ$ for **M5**; 4295 and 2704 independent reflections [$R_{\text{int}} 0.0223$ and 0.0350] were used in further refinement. Using Olex2,⁶ the structures were solved with the ShelXT⁷ structure solution program using Intrinsic Phasing and refined with the XL⁷ refinement package using Least-Squares minimisation. Positions of hydrogen atoms were calculated. All hydrogen atoms were refined in the isotropic approximation within the riding

model. For **M4**, the refinement converged to $wR2 = 0.1040$ and $GOF = 1.033$ for all the independent reflections ($R1 = 0.0398$ was calculated against F for 3924 observed reflections with $I > 2\sigma(I)$). For **M5**, the refinement converged to $wR2 = 0.0699$ and $GOF = 1.059$ for all the independent reflections ($R1 = 0.0278$ was calculated against F for 2628 observed reflections with $I > 2\sigma(I)$). CCDC 2095888 and 2095889 contain the supplementary crystallographic information for **M4** and **M5**, respectively.

Vinyl-addition polymerization in the presence of Pd-N-heterocyclic carbene complex

*The example is given for **M1**/SIMesPd(cinn)Cl/AgSbF₆ molar ratio equals to 500/1/1.5*

The solution of the catalyst was prepared by the addition of SIMesPd(cinn)Cl solution in dichloromethane (0.32 ml, $1.94 \cdot 10^{-2}$ mmol, 0.06 M) to AgSbF₆ solution in dichloromethane (10.0 mg, $2.9 \cdot 10^{-2}$ mmol in 0.58 ml of dichloromethane) at stirring. The mixture was stirred for 1 h before the usage and then it was filtered through 0.2 μ m Teflon filter.

Dichloromethane (0.57 ml), **M1** (0.5 g, 1.87 mmol) and decalin (0.25 ml, an internal standard) were placed via a rubber septum into a vial (4 ml) equipped with a magnetic stirrer. The vial was heated to 45°C. The polymerization was initiated by the addition of the solution of the catalyst (0.18 ml) to the solution of **M1** at stirring. The reaction mixture was allowed to stir for the required time at 45°C. The conversion was controlled by GLC chromatography. For this during the polymerization, aliquots (0.04-0.05 ml) were taken off and precipitated in ethanol. The polymer was separated and the filtrate was analyzed with GLC. The conversion of **M1** was 63% after 4 h. The polymer was washed by several portions of ethanol and dried in vacuum (0.05 mm Hg) at 80–90°C to the constant weight. The polymer was purified by double reprecipitation from chloroform solution in methanol. The polymer was isolated as white fibers.

*The example is given for **M1**/SIMesPd(cinn)Cl/NaBARF molar ratio equals to 500/1/1.5*

The solution of the catalyst was prepared by the addition of SIMesPd(cinn)Cl solution in dichloromethane (0.2 ml, $1.71 \cdot 10^{-2}$ mmol, 0.06 M) to NaBARF solution in dichloromethane (0.36 ml, $0.181 \cdot 10^{-2}$ mmol, 0.05 M) at stirring. The mixture was stirred for 1 h before the usage and then it was filtered through 0.2 μ m Teflon filter.

Dichloromethane (0.57 ml), **M1** (0.5 g, 1.87 mmol) and decalin (0.25 ml) were placed into a vial (4 ml) equipped with a magnetic stirrer. The vial was heated to 45°C. The polymerization was initiated by the addition of the solution of the catalyst (0.18 ml) to the solution of **M1** at stirring. The reaction mixture was allowed to stir for the required time at 45°C. The conversion was controlled by GLC chromatography. For this during the polymerization, aliquots (0.04-0.05 ml) were taken off and precipitated in ethanol. The polymer was separated

and the filtrate was analyzed with GLC. The conversion of **M1** was 48% after 4 h. The polymer was washed by several portions of ethanol and dried in vacuum (0.05 mm Hg) at 80–90°C to the constant weight. The polymer was purified by double reprecipitation from chloroform solution in methanol. The polymer was isolated as white fibers.

*The example is given for **M3**/SIMesPd(cinn)Cl/AgSbF₆ molar ratio equals to 3000/1/3*

The catalyst solution was obtained by mixing of SIMesPd(cinn)Cl solution in dichloromethane (2.42 ml, $4.8 \cdot 10^{-3}$ mmol, $2 \cdot 10^{-3}$ M), AgSbF₆ solution in dichloromethane (5.82 ml, $1.4 \cdot 10^{-2}$ mmol, $2.5 \cdot 10^{-3}$ M). The catalyst solution was allowed stirring for 1 h. In a glass vial **M3** (0.5 g, 1.77 mmol) was introduced. The vial was heated in an oven at 45°C. After that, the preliminary prepared catalyst solution (1 ml) was added to the monomer solution at stirring. The reaction mixture was stirred for a minute and the vial with the reaction mixture was stored at 45°C for 24 h. The vial was opened and the polymer was precipitated by ethanol. The polymer was washed by several portions of ethanol and dried in vacuum (0.05 mm Hg) at 80–90°C to the constant weight. The polymer was purified by double reprecipitation from chloroform solution in methanol. The polymer was isolated as white fibers. Yield: 0.44 g (87%). $M_w = 3.02 \cdot 10^6$, $M_w/M_n=1.6$.

Film preparation

The polymer films for investigations were prepared by casting from the 5 wt.% chloroform solution of a polymer. The solution was poured into a 7 cm diameter steel cylinder, having stretched cellophane bottom. The solvent was allowed to evaporate slowly at room temperature to yield the desired polymer films. Once the polymeric film was formed, cellophane was detached, and the obtained film was dried under a vacuum at room temperature up to a constant weight. A thermal treatment was not applied. The thickness of resulted films was in the range of 70-100 μm .

NMR and mass spectra of monomers and catalytic mixtures

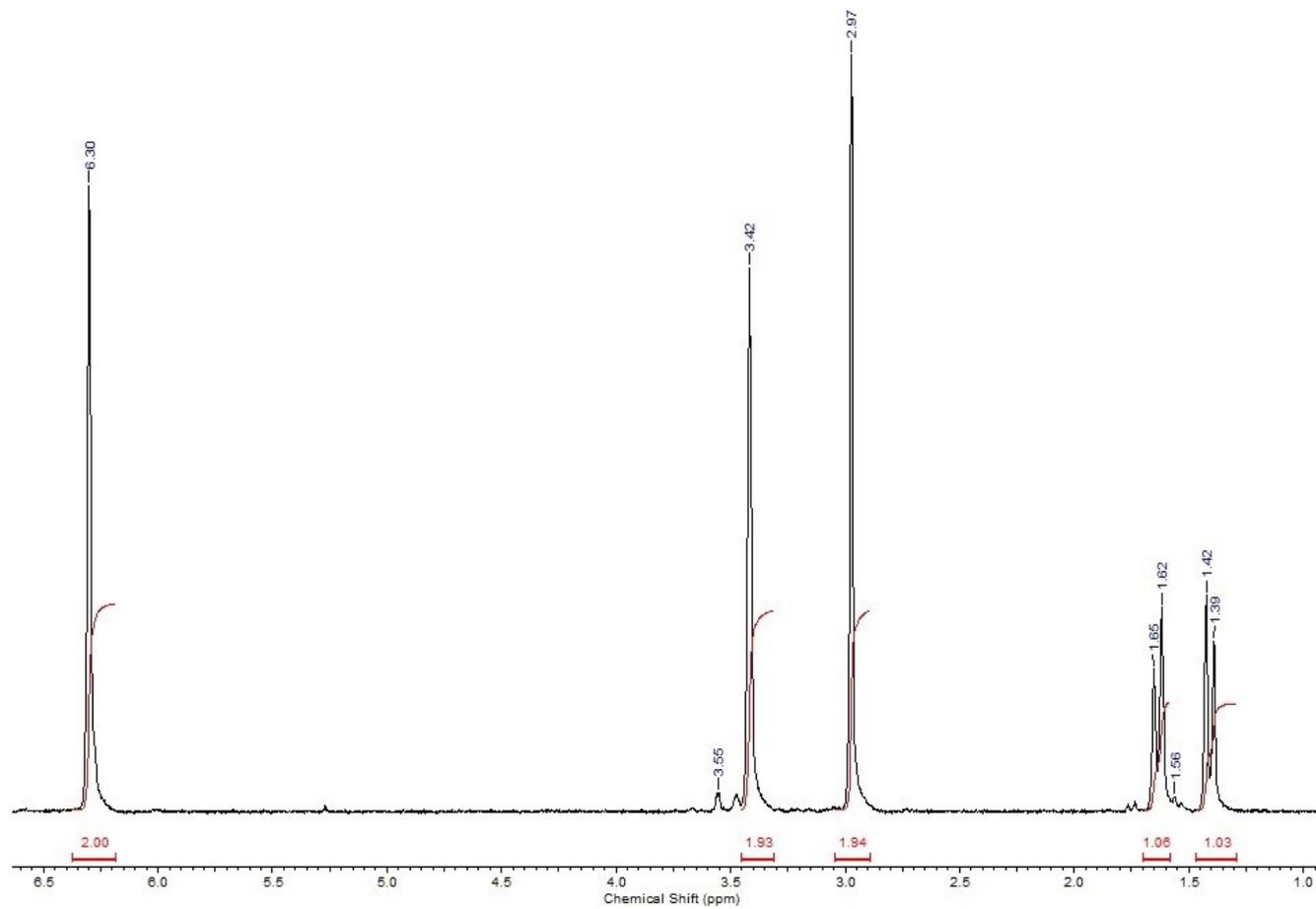


Fig. S1 ^1H NMR spectrum of *exo*-NDA (CDCl_3).

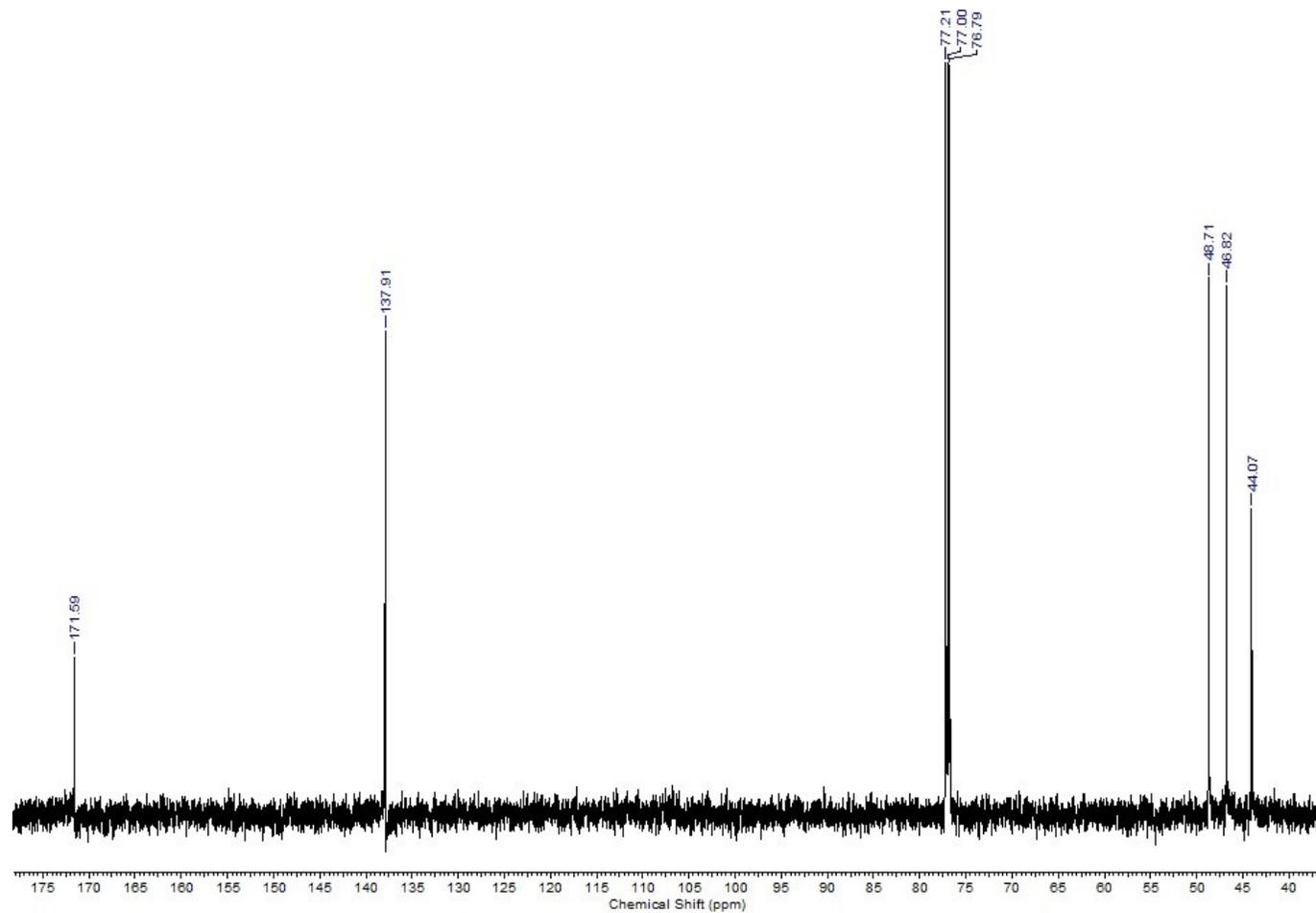


Fig. S2 ^{13}C NMR spectrum of *exo*-NDA (CDCl_3).

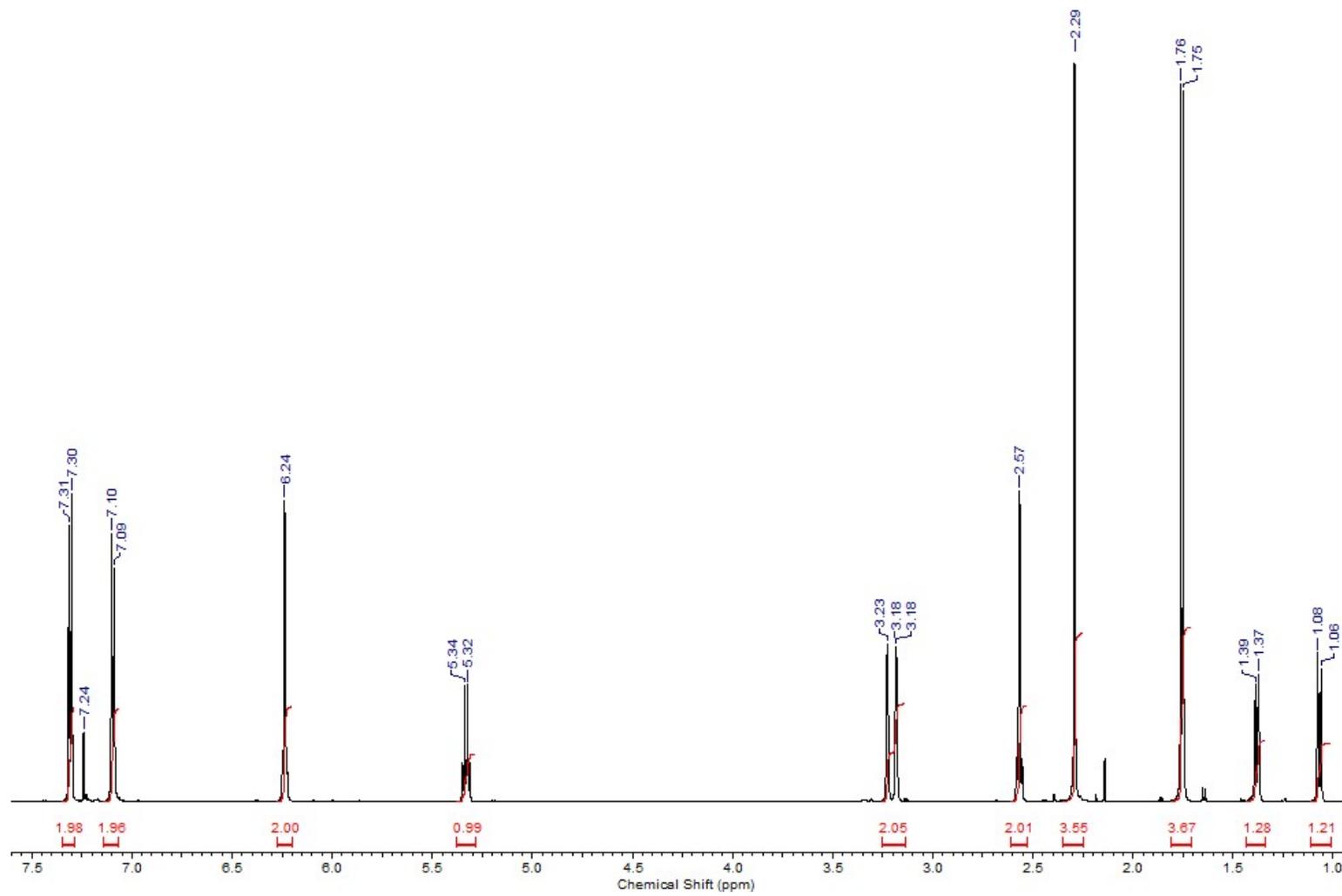


Fig. S3 ^1H NMR spectrum of M2 (CDCl_3).

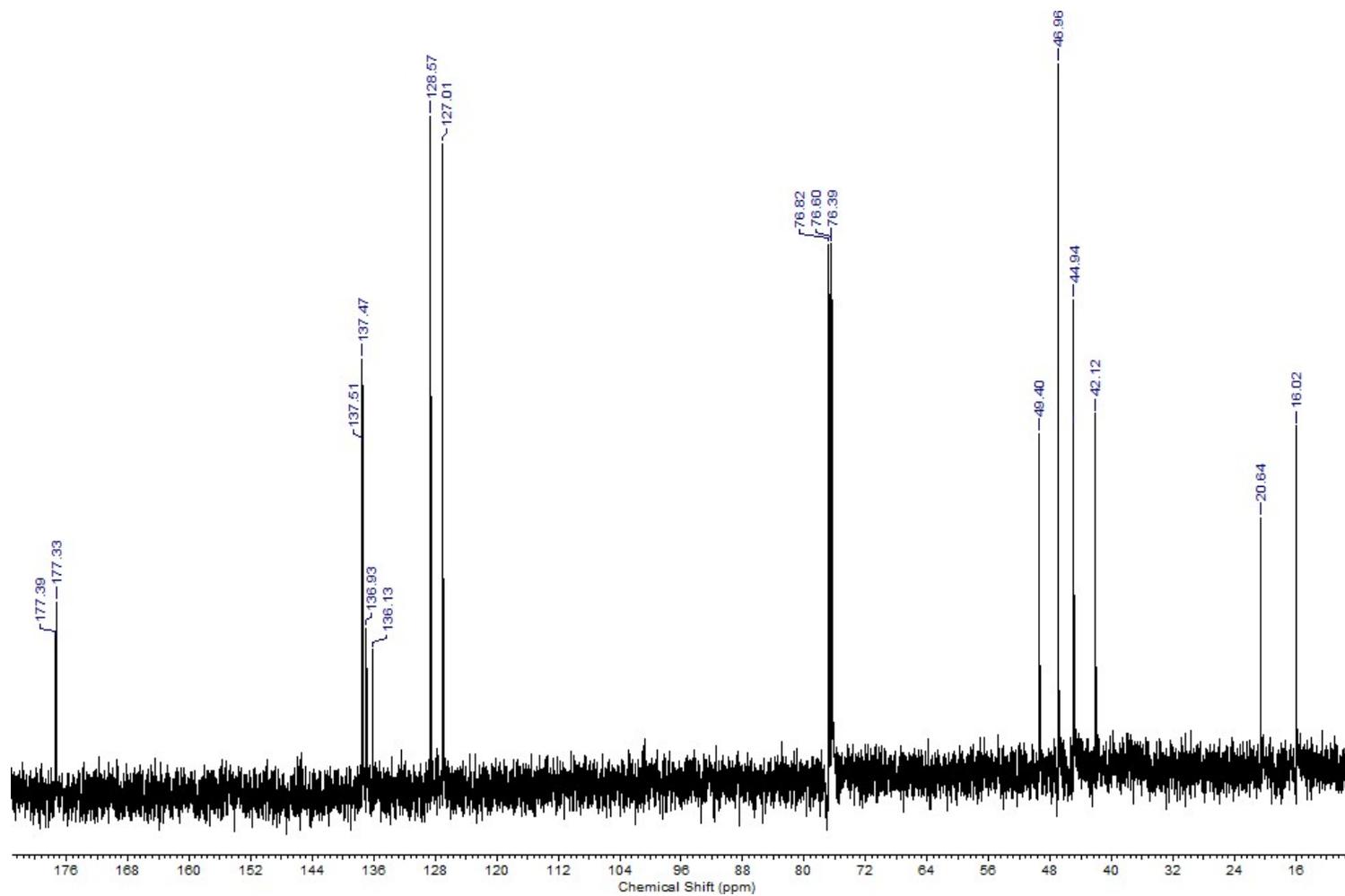


Fig. S4 ^{13}C NMR spectrum of M2 (CDCl_3).

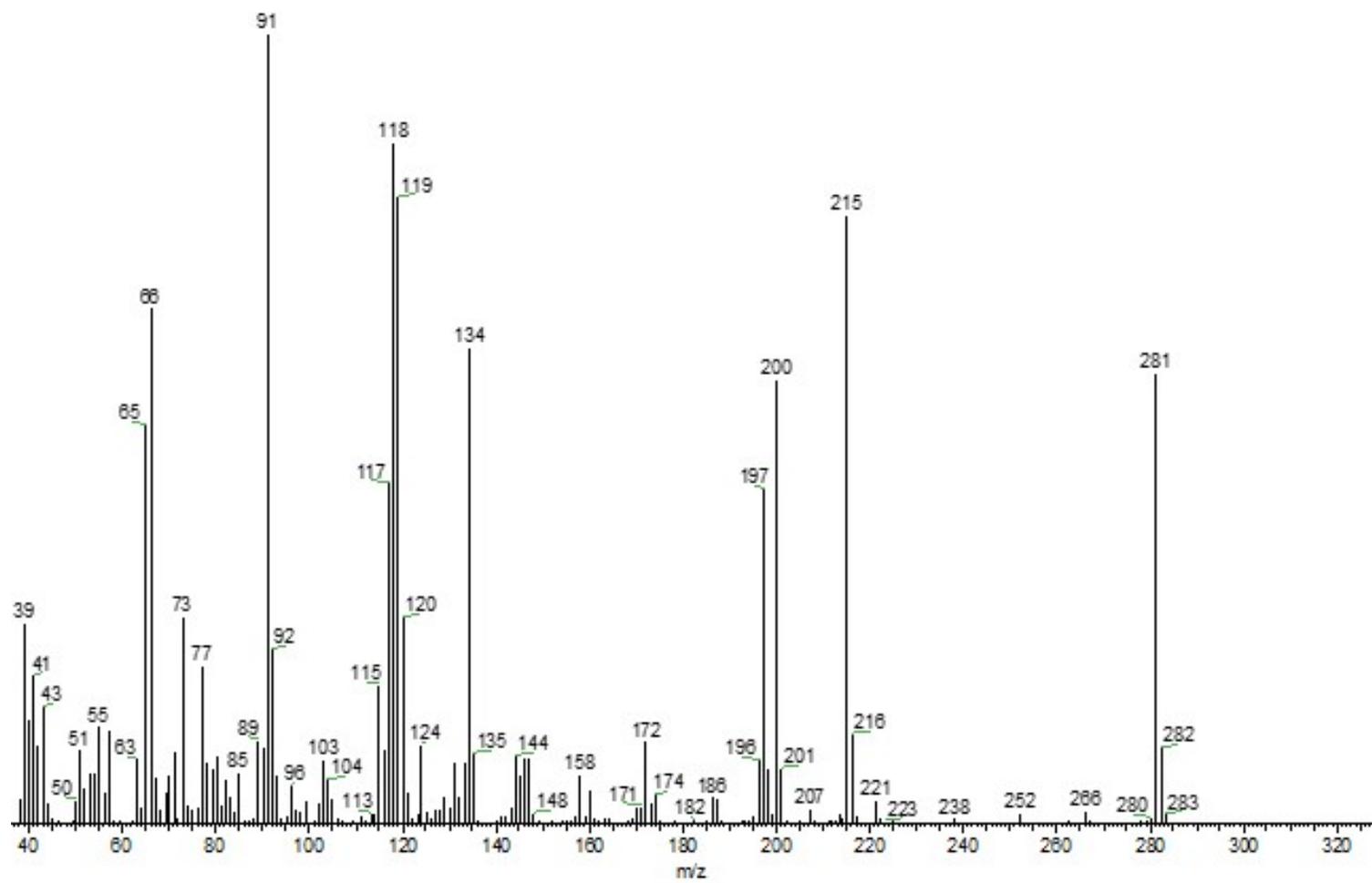


Fig. S5 Mass spectrum of **M2**.

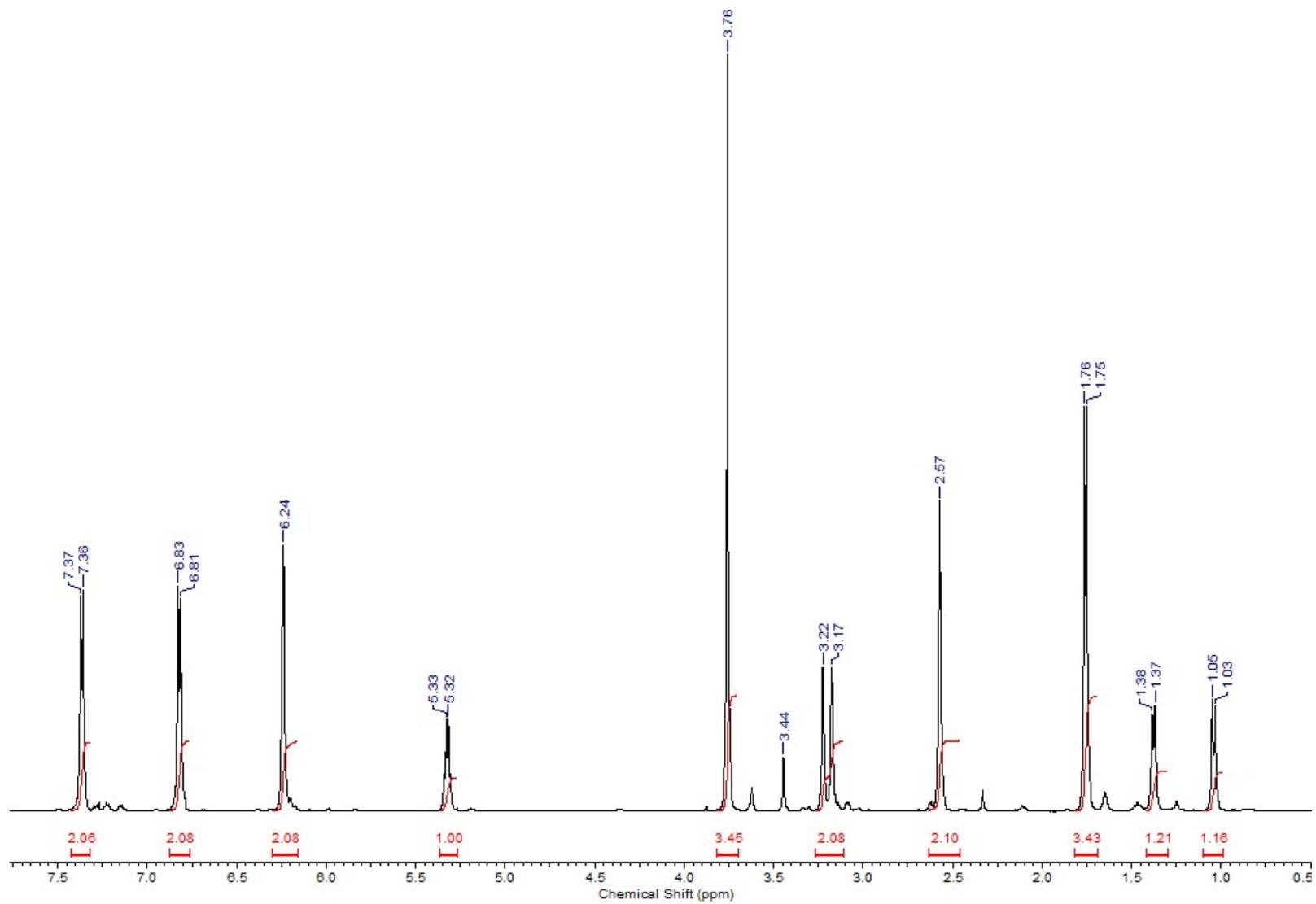


Fig. S6 ^1H NMR spectrum of **M3** (CDCl_3).

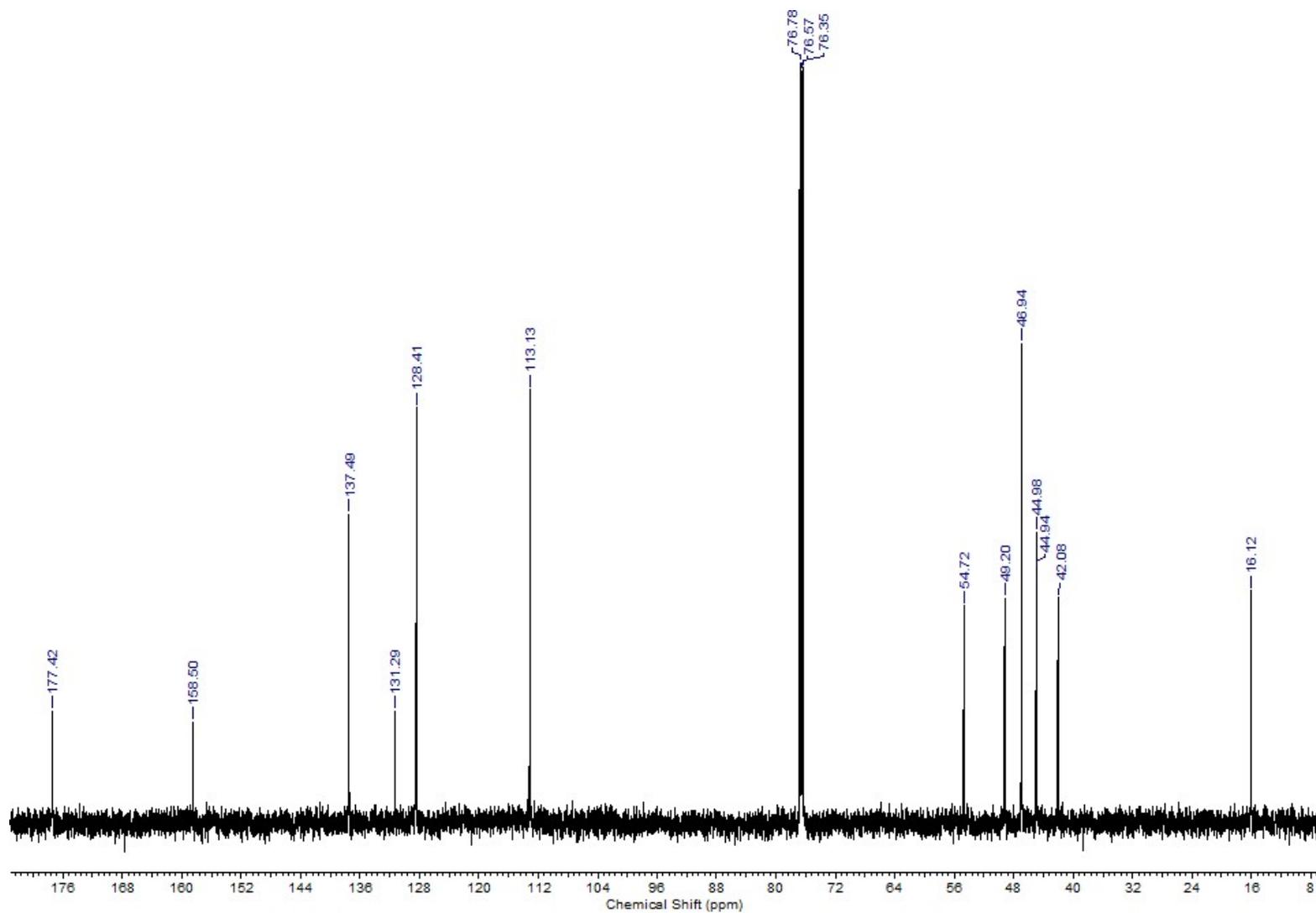


Fig. S7 ^{13}C NMR spectrum of M3 (CDCl_3).

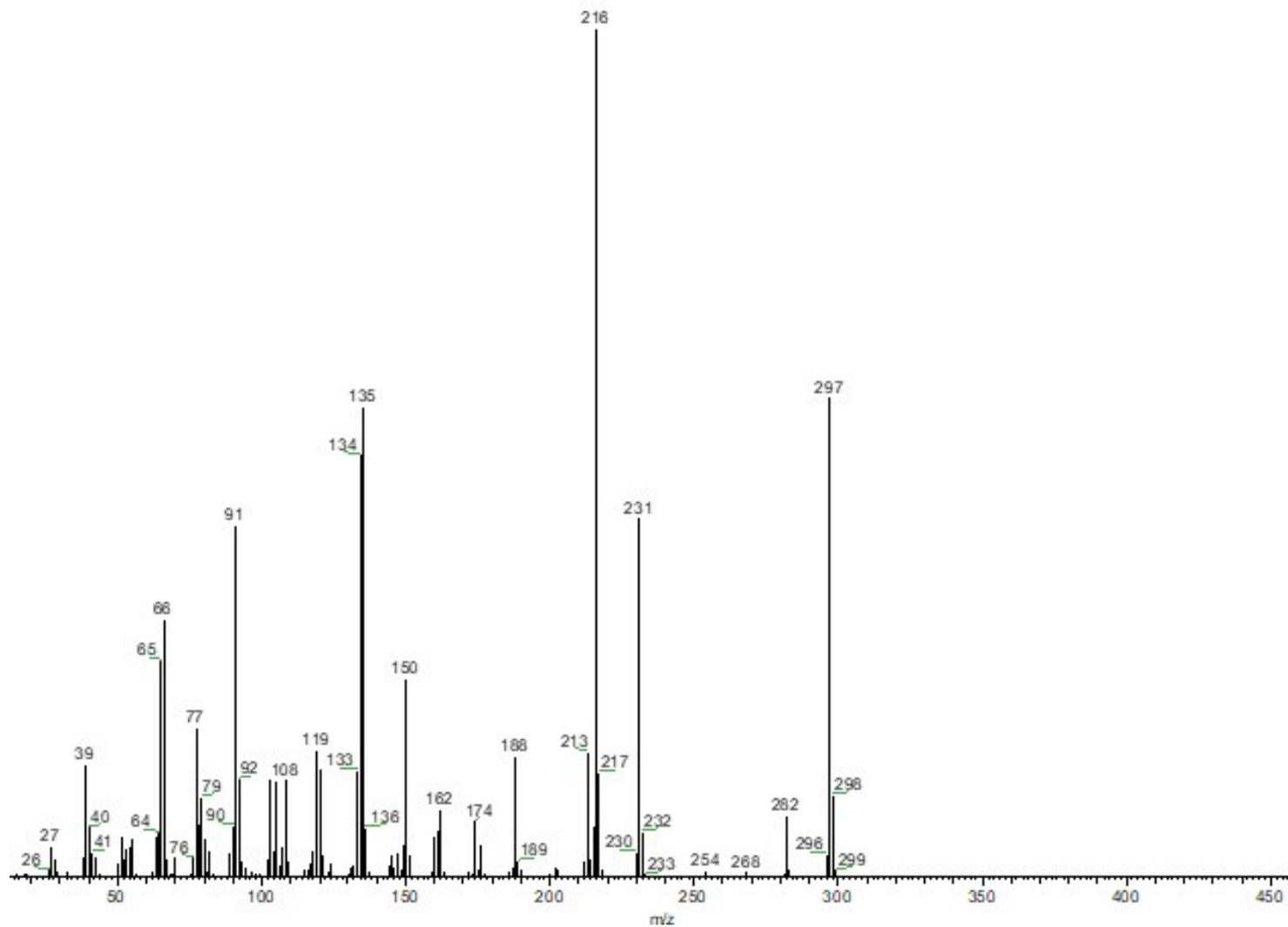


Fig. S8 Mass spectrum of M3.

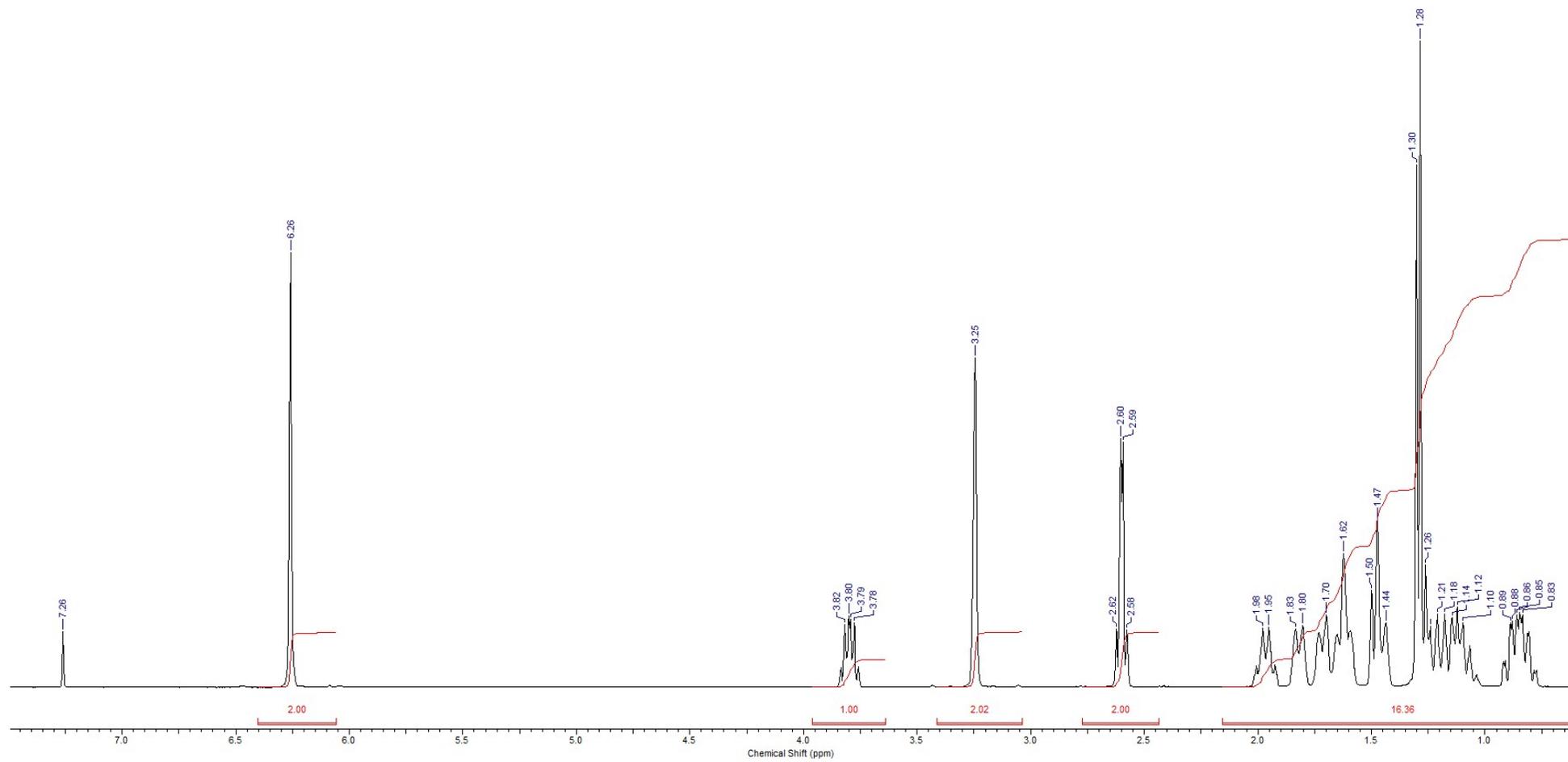


Fig. S9 ^1H NMR spectrum of **M4** (CDCl_3).

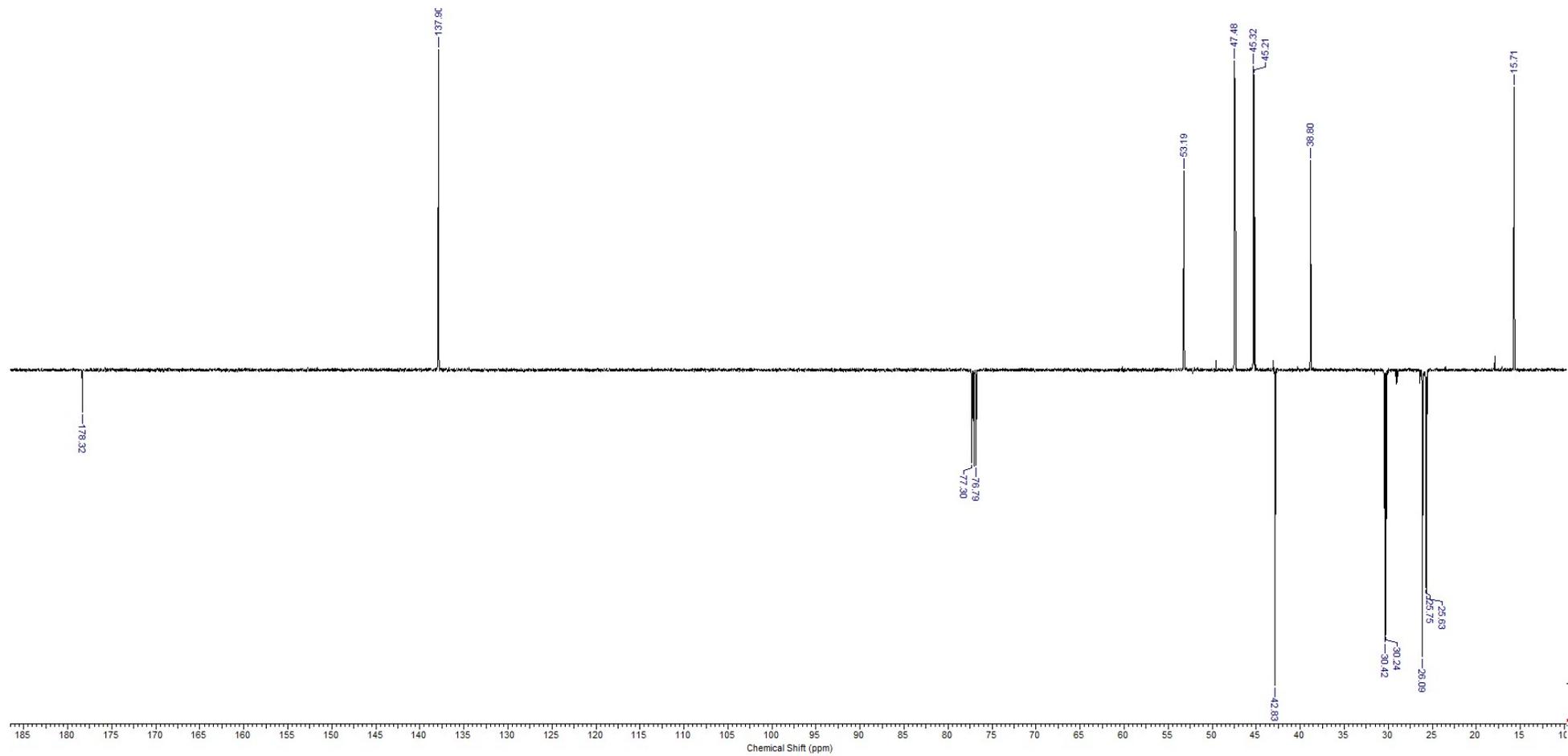


Fig. S10 APT NMR spectrum of **M4** (CDCl₃).

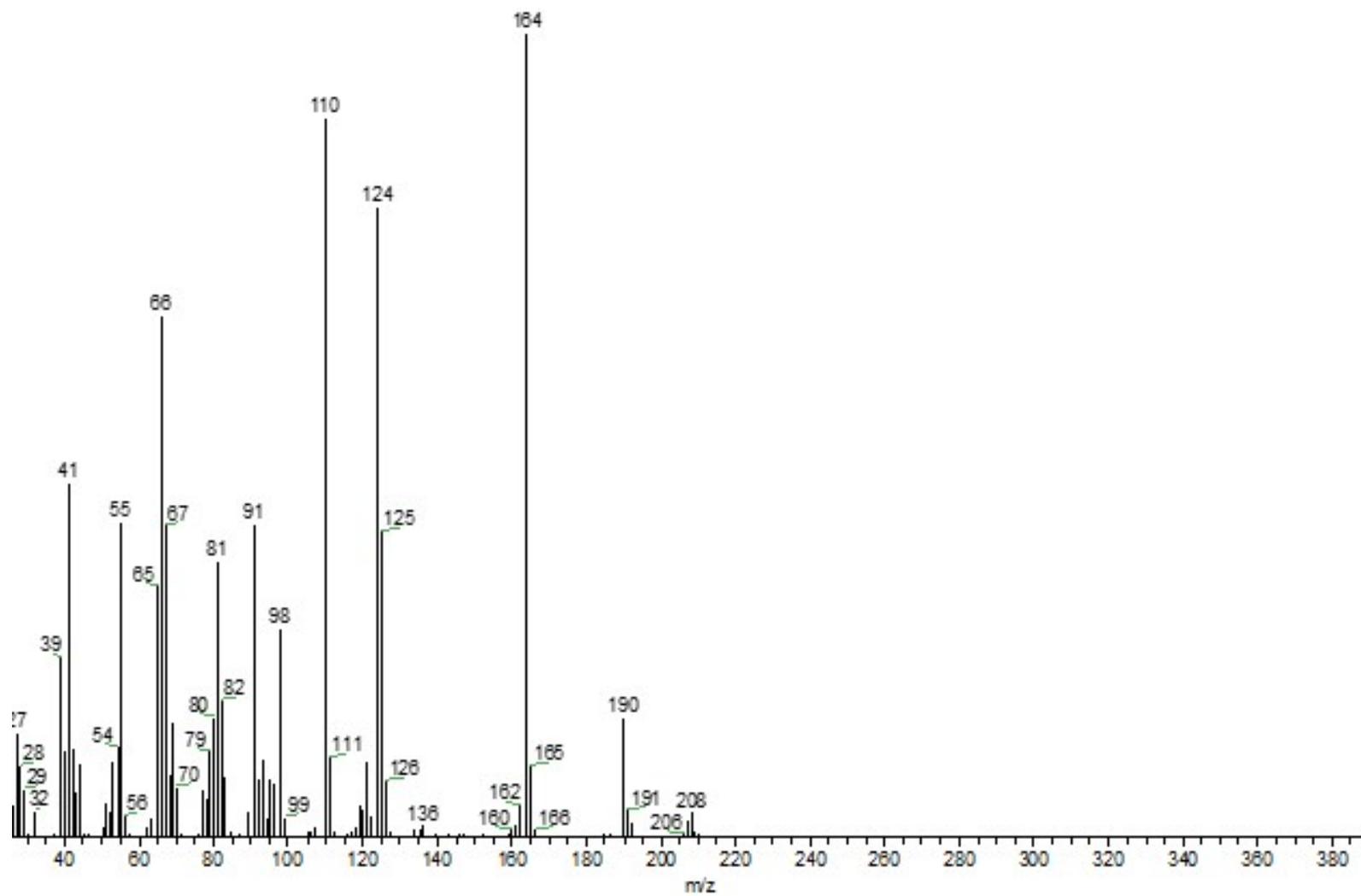


Fig. S11 Mass spectrum of M4.

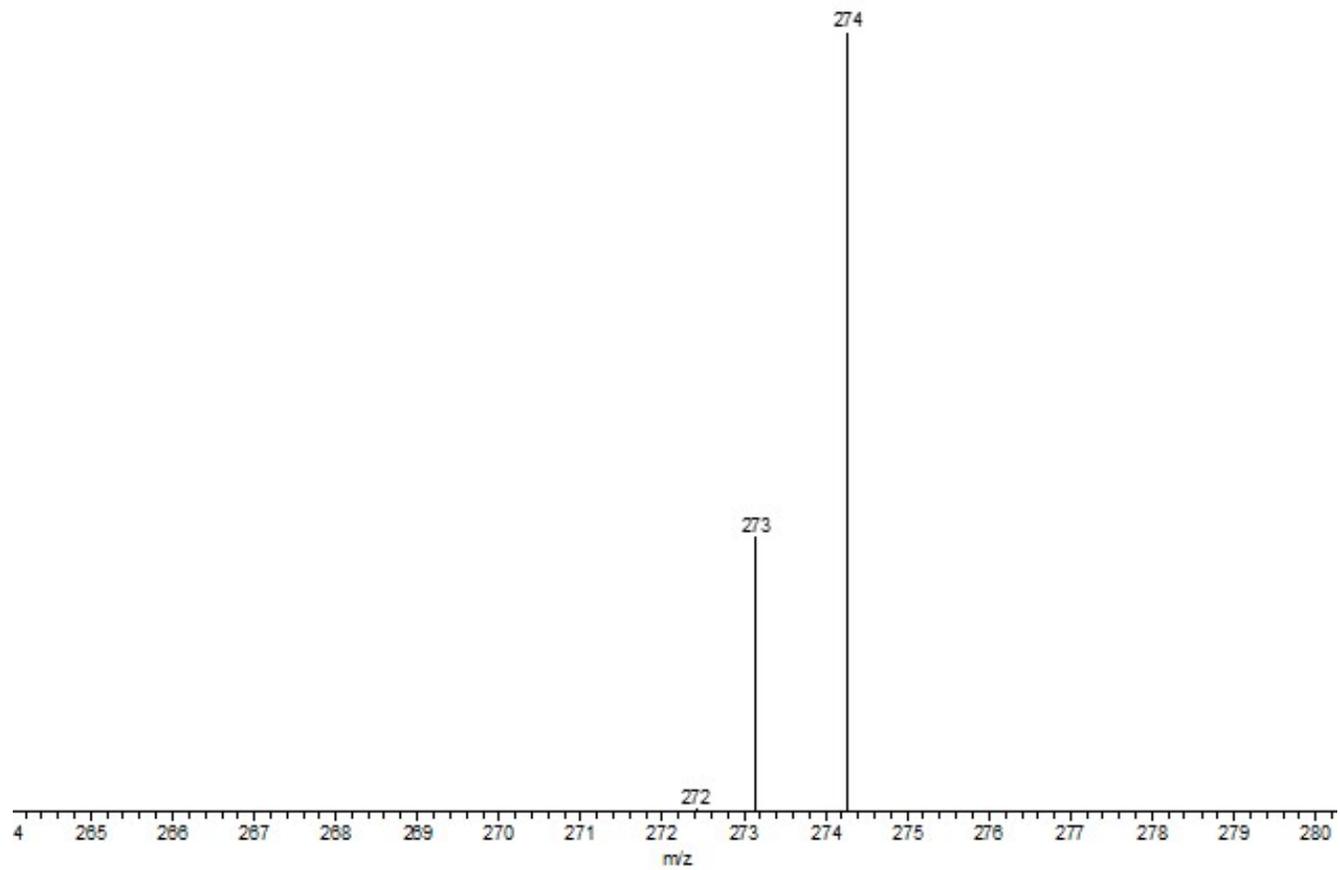


Fig. S12 The section of mass spectrum of **M4**.

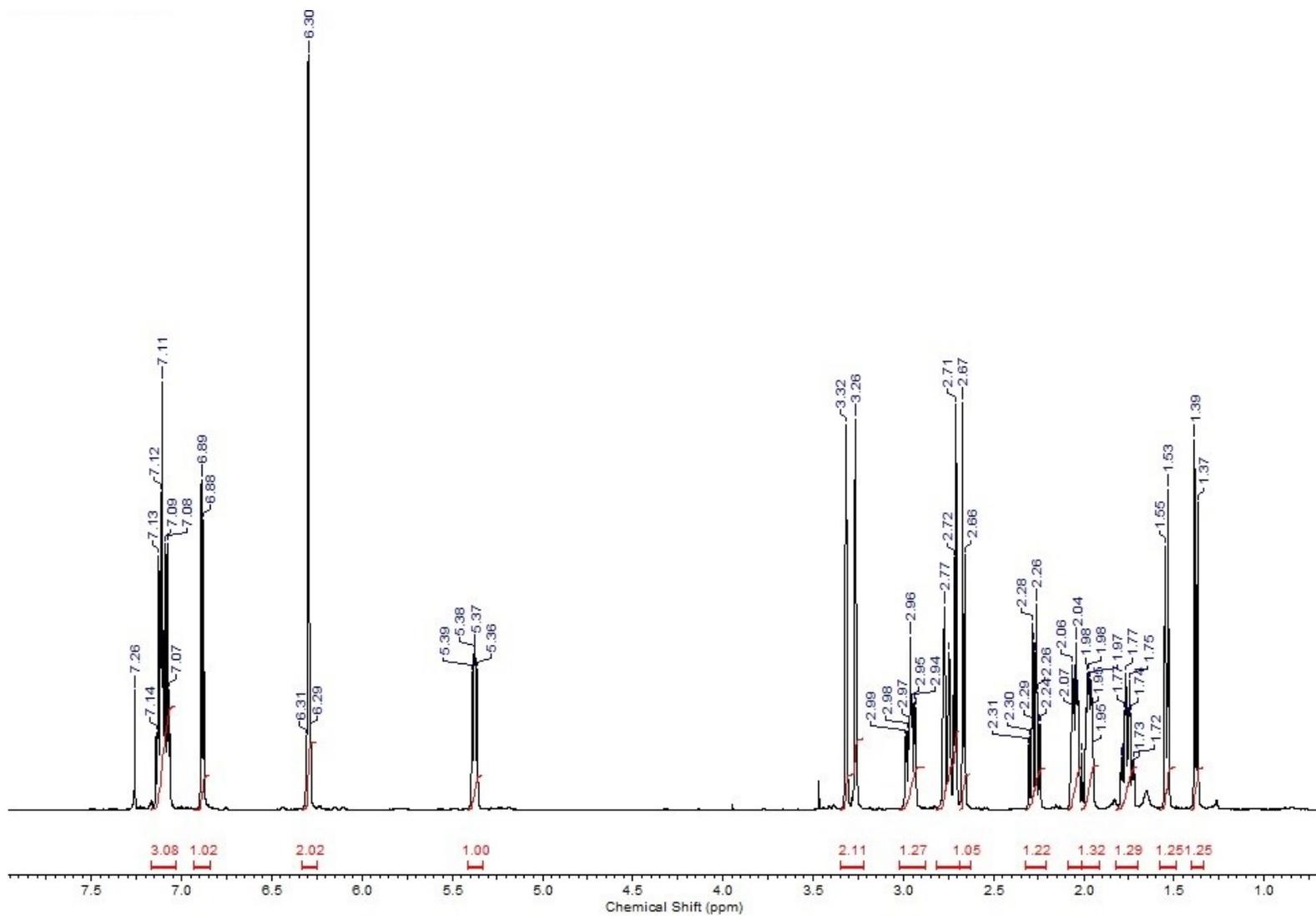


Fig. S13 ¹H NMR spectrum of M5 (CDCl₃).

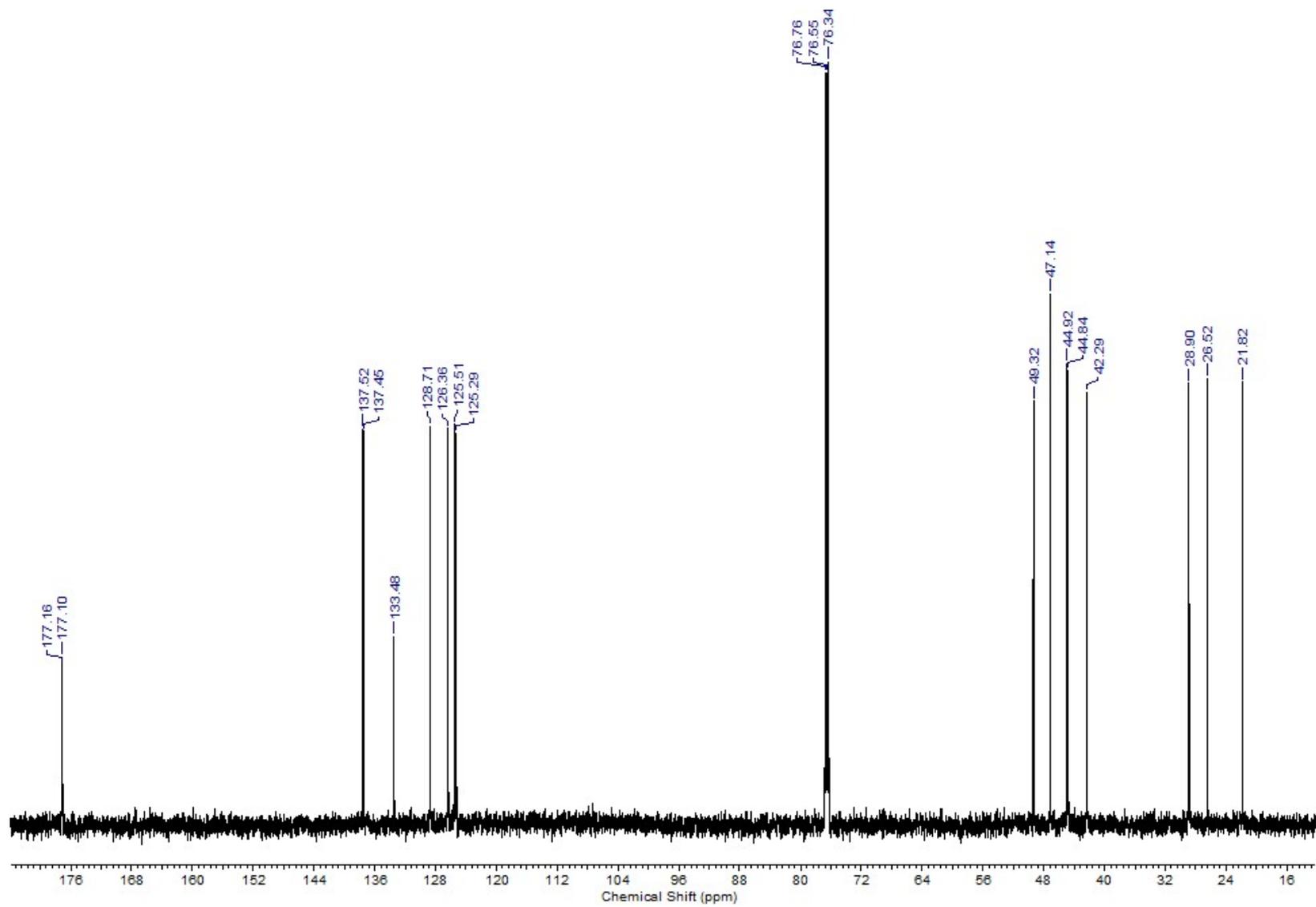


Fig. S14 ^{13}C NMR spectrum of M5 (CDCl_3).

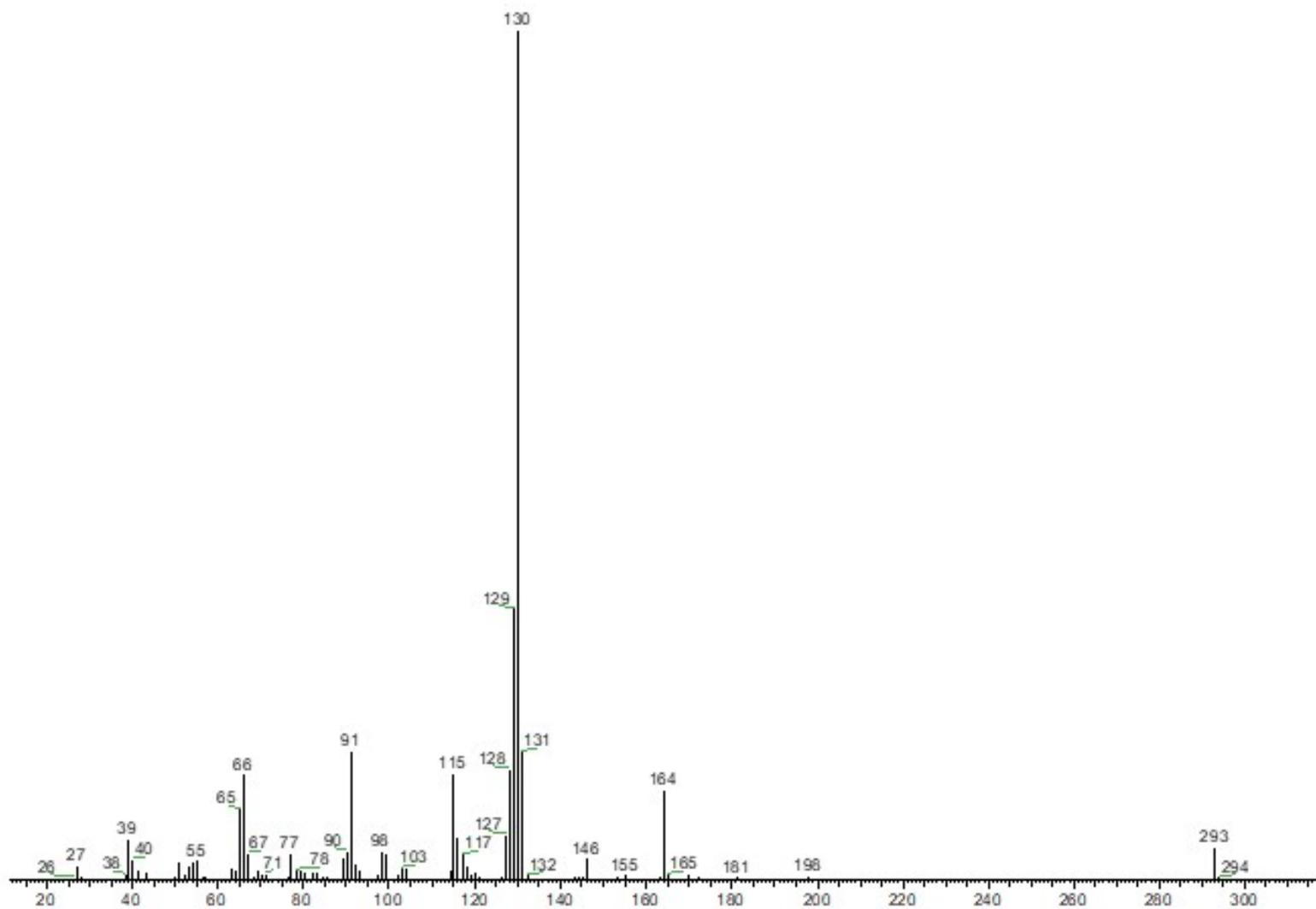
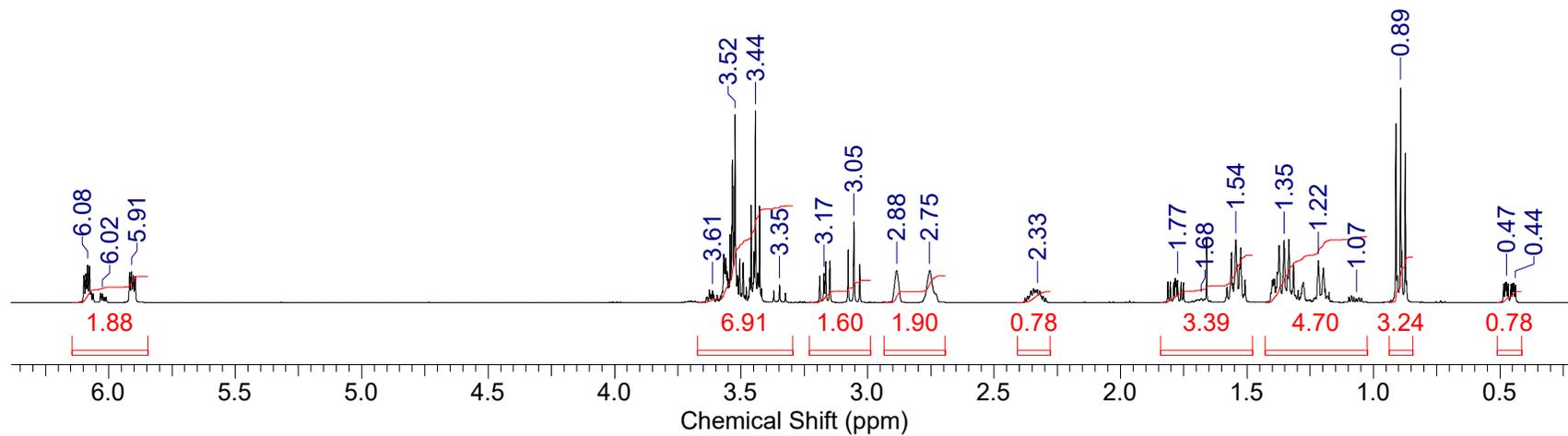
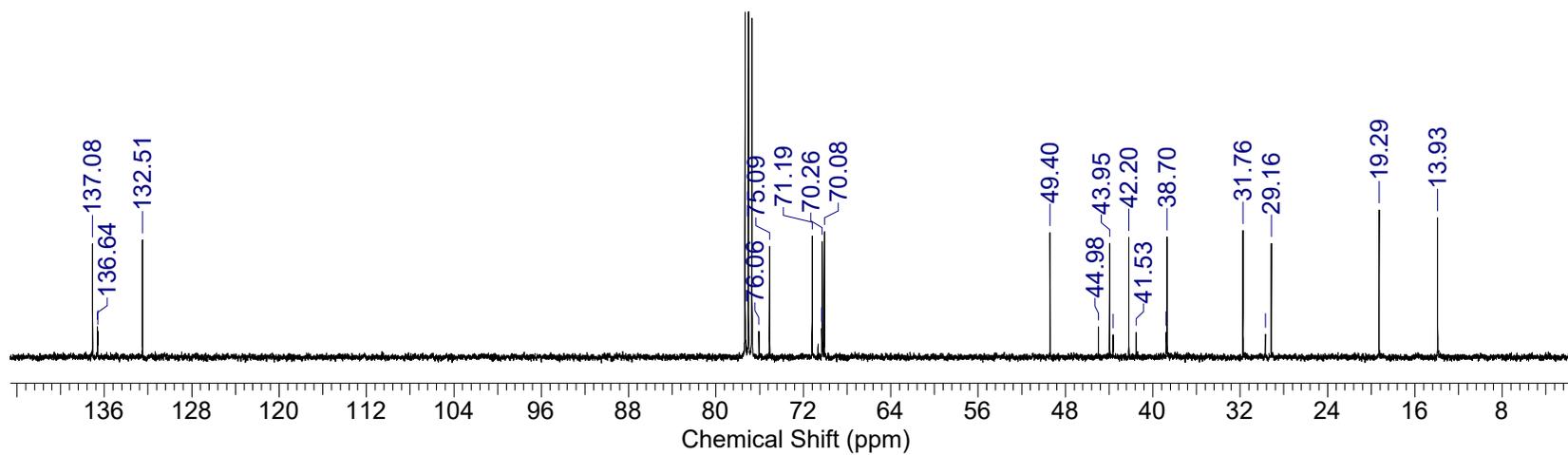


Fig. S15 Mass spectrum of M5.

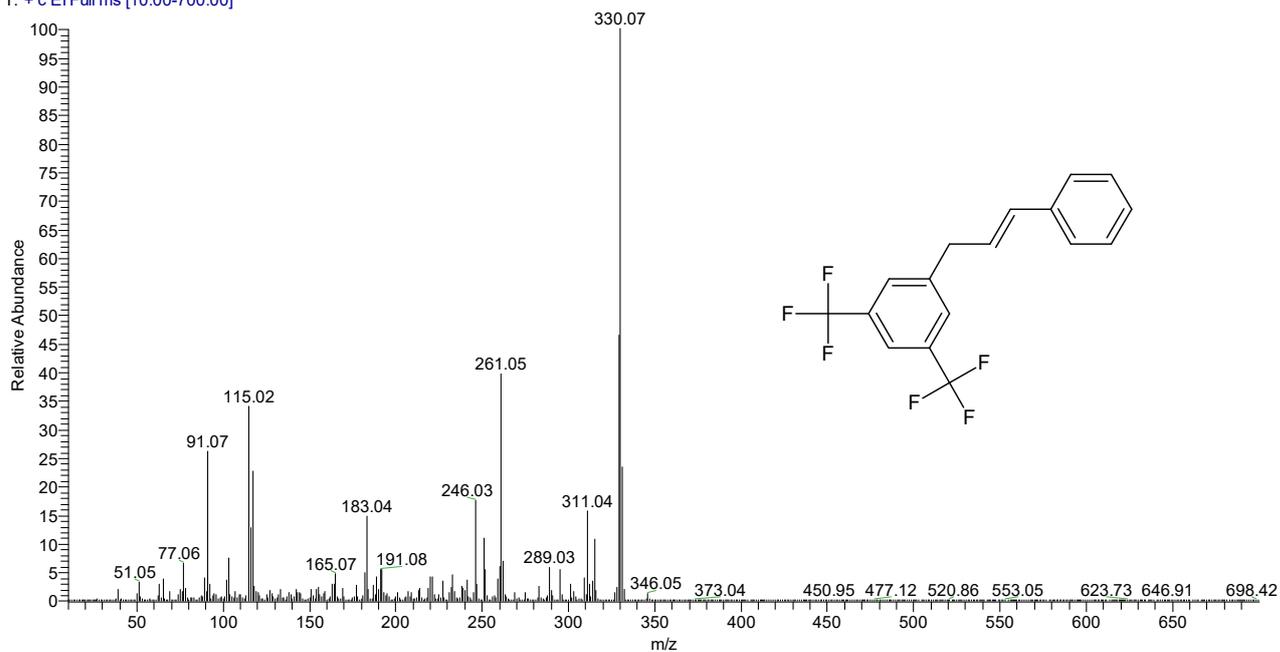


(a)

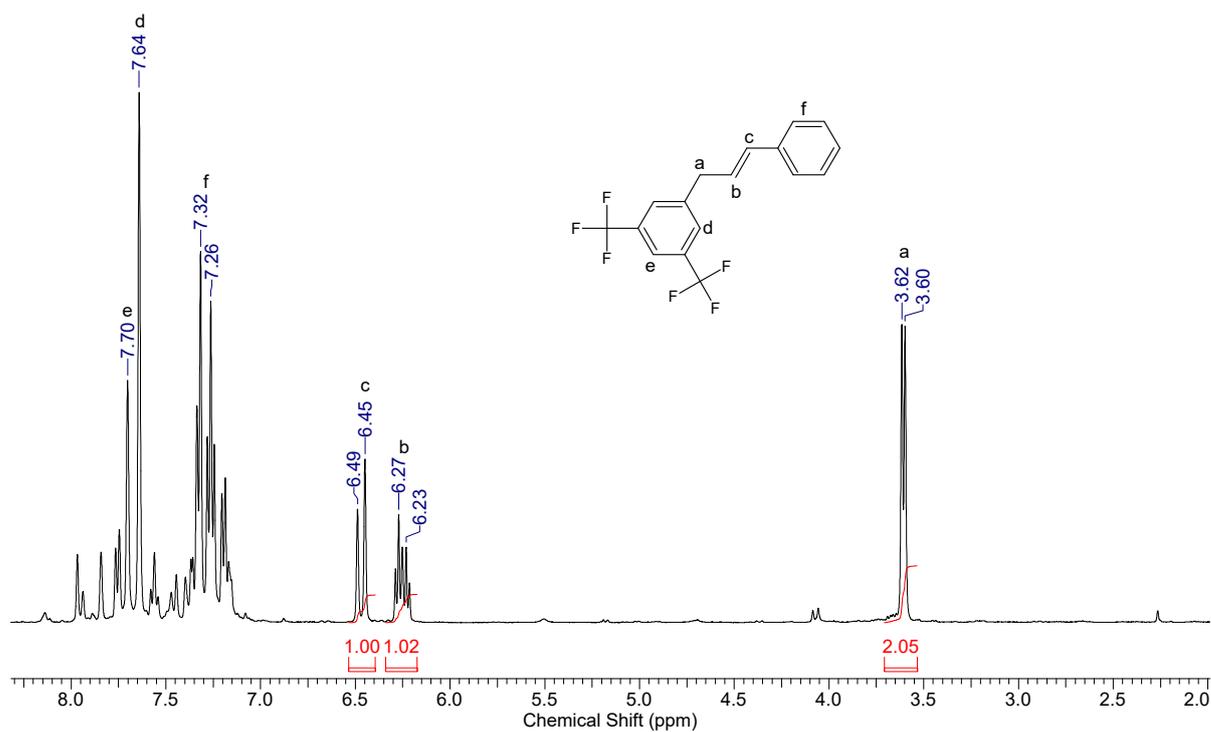


(b)

Fig. S16 (a) ¹H and (b) ¹³C NMR spectrum of M7 (CDCl₃).

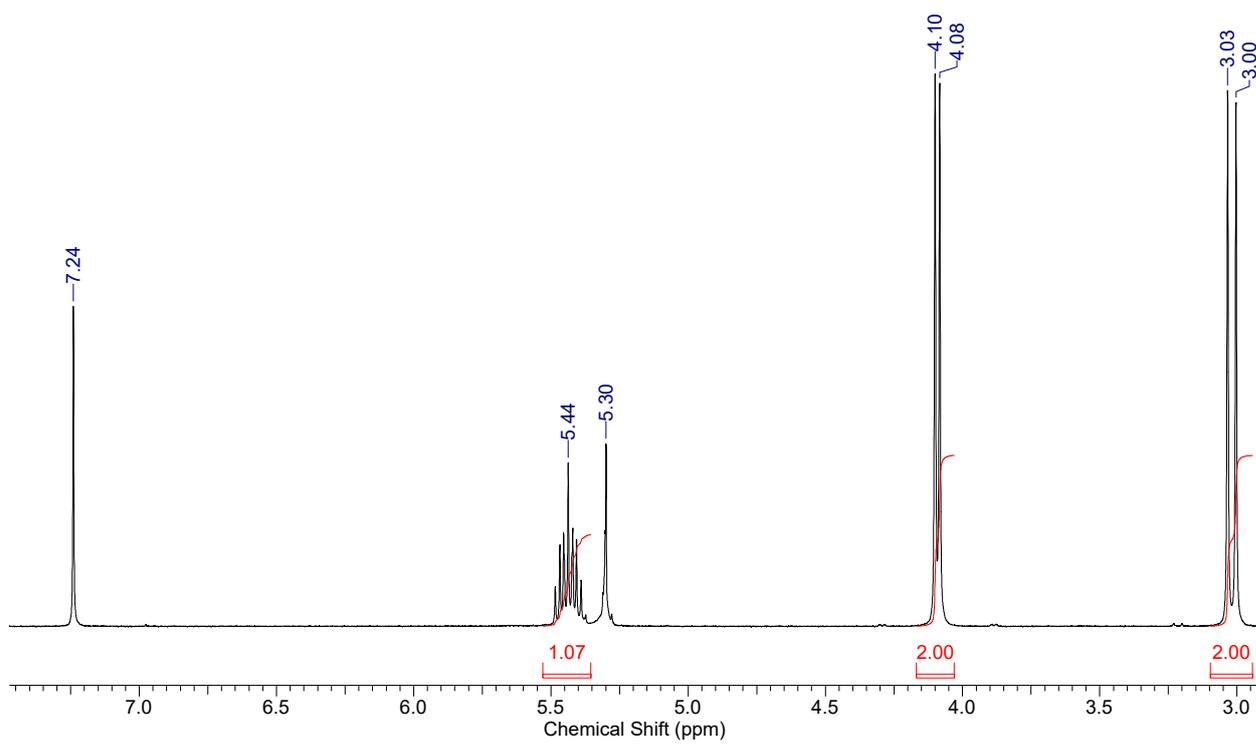


(a)

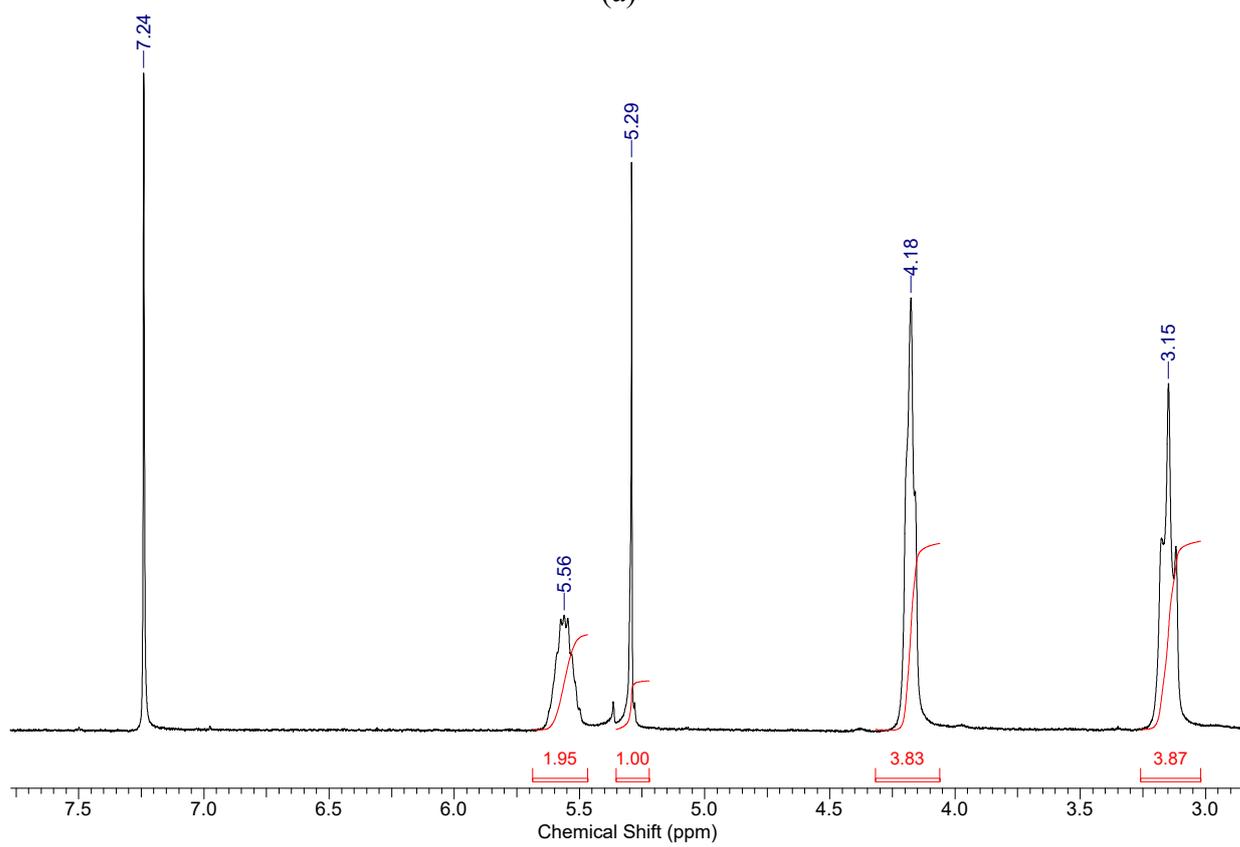


(b)

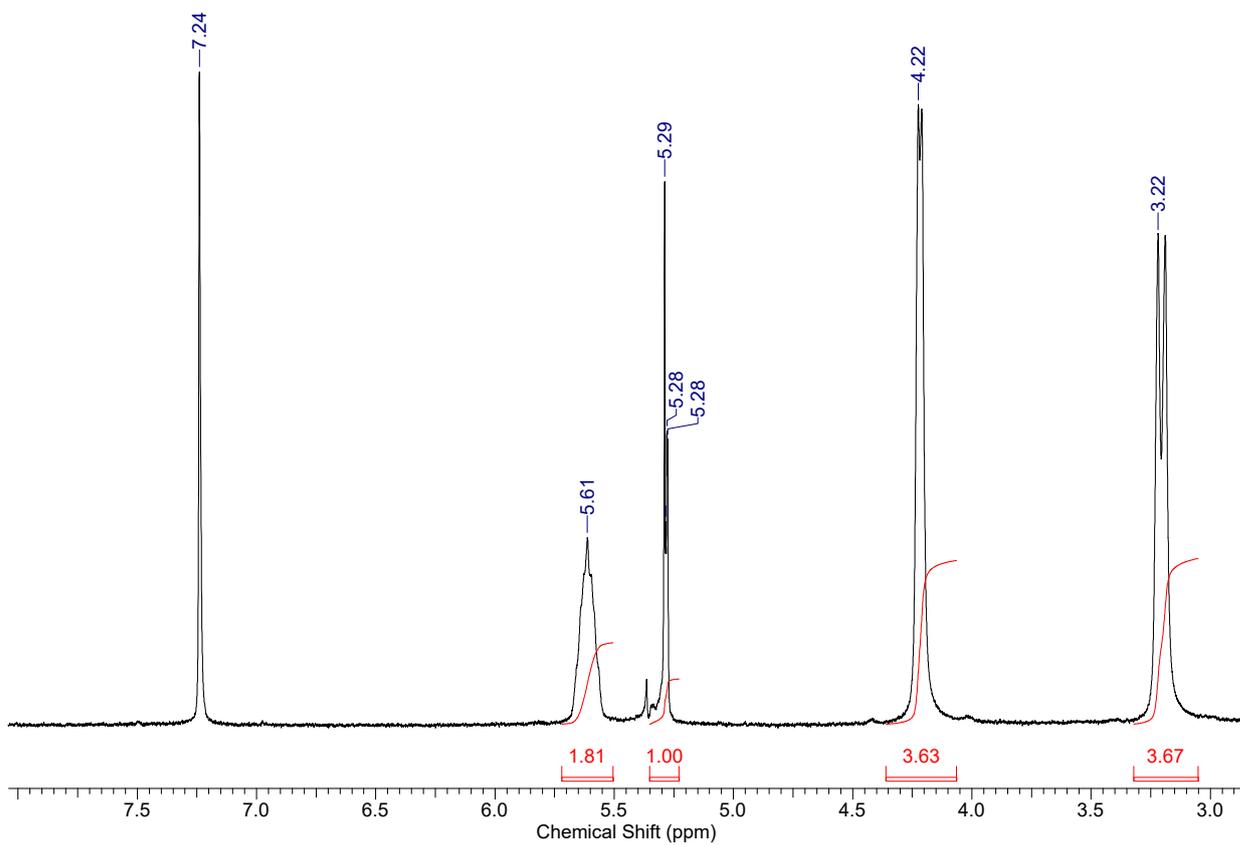
Fig. S17 (a) Mass-spectrum and (b) ¹H NMR spectrum of 1-[3-phenylprop-2-en-1-yl]-3,5-bis(trifluoromethyl)benzene formed in the reaction mixture ($\eta^3\text{-C}_3\text{H}_5\text{PdCl}$)₂/NaBARF in CHCl₃.



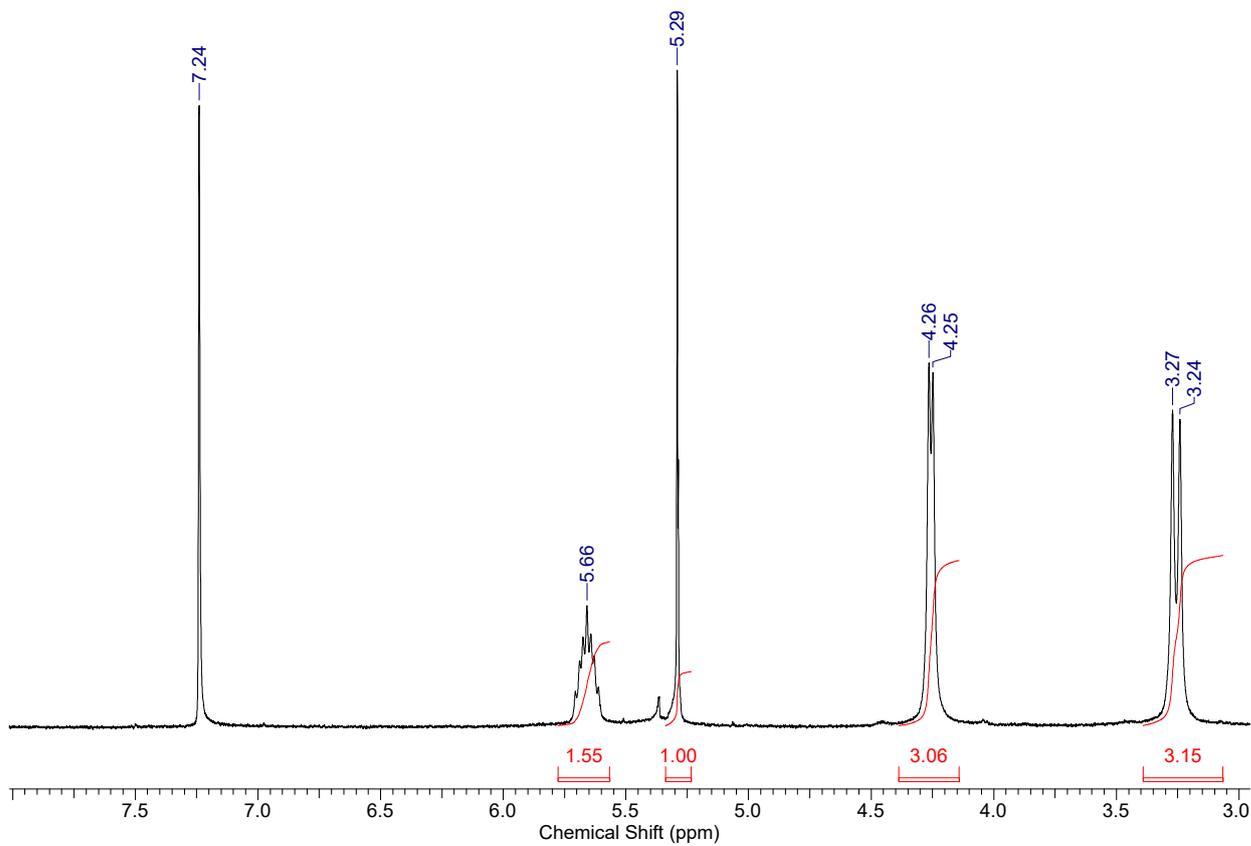
(a)



(b)



(c)



(d)

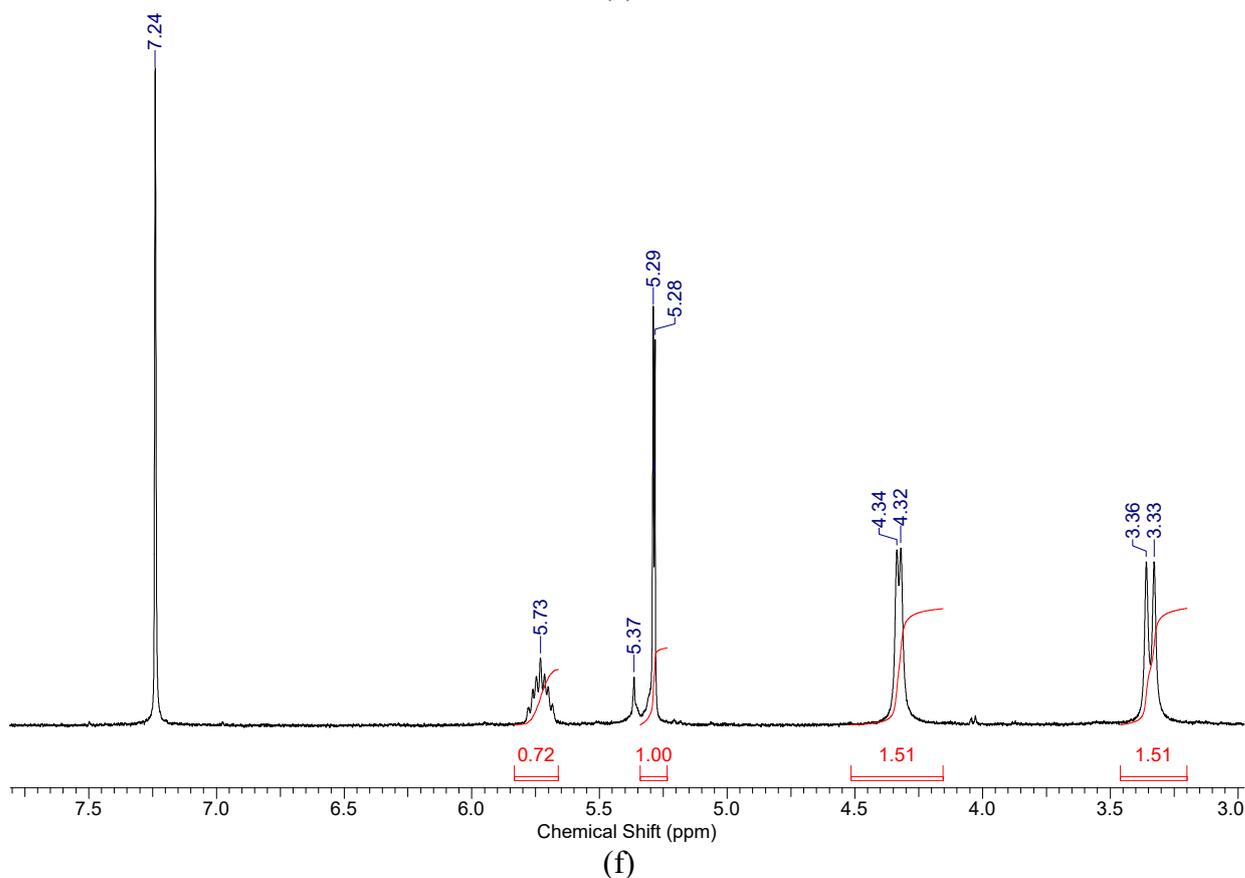
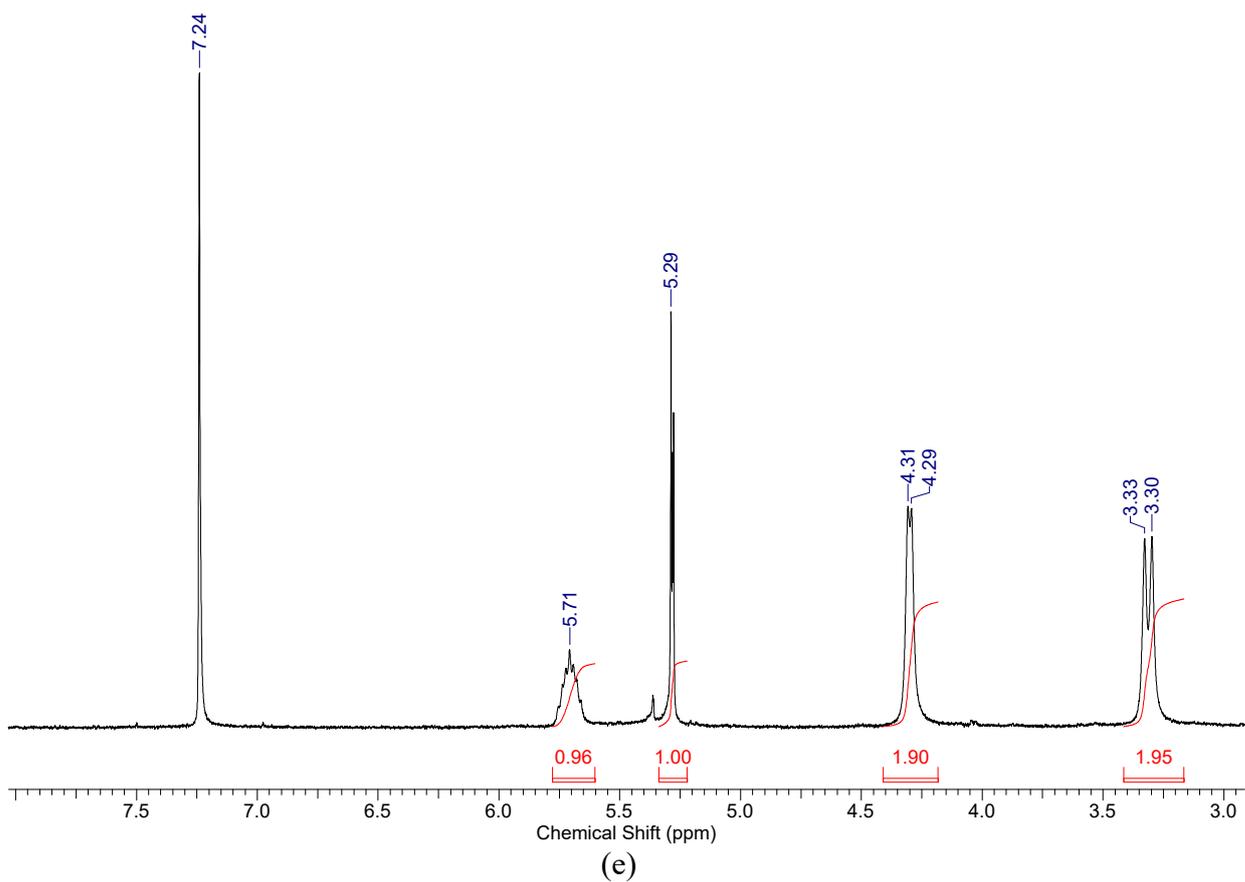
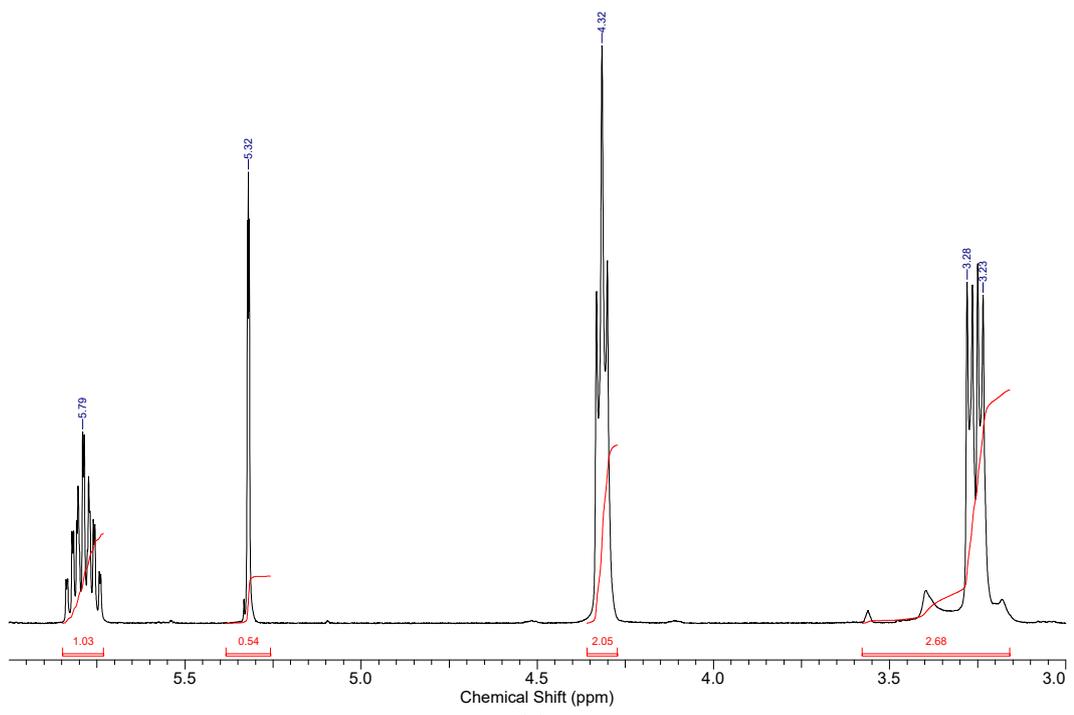
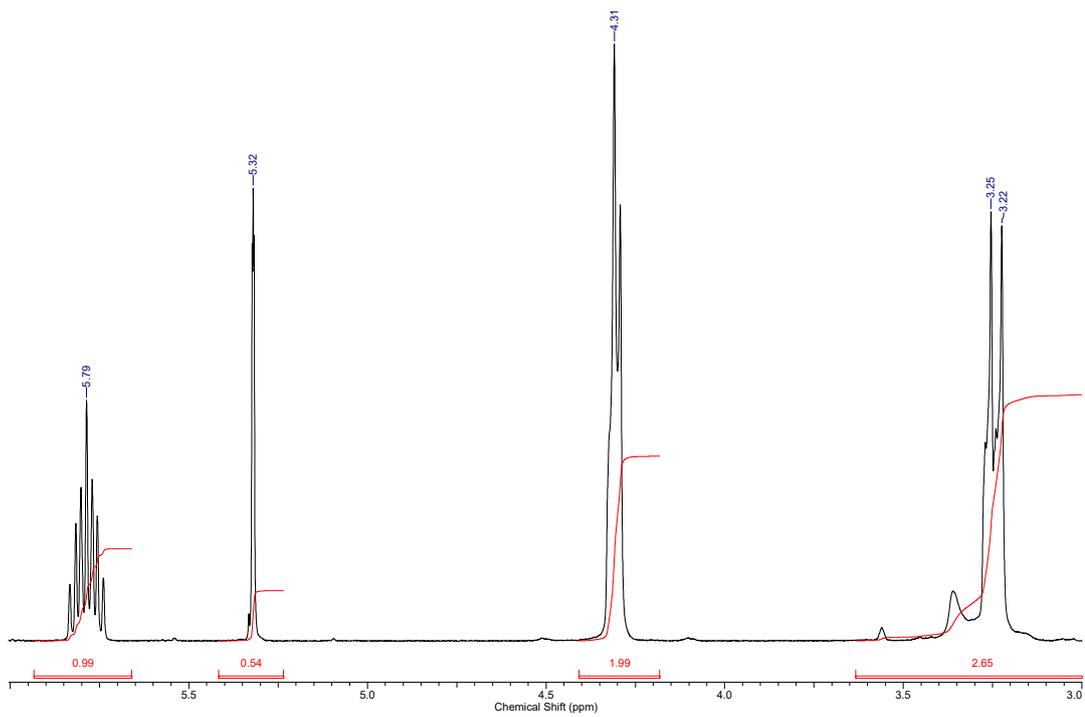


Fig. S18 ^1H NMR spectra of $(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}_2$ complex (a) and $(\eta^3\text{-C}_3\text{H}_5)\text{PdCl}_2/\text{AgSbF}_6$ system in 15 minutes (b), 1 h (c), 2 h (d), 3.5 h (e), 5.5 h (f) after the preparation in CDCl_3 (CH_2Cl_2 sealed in a capillary (5.29-5.30 ppm) was used as an external standard).



(a)



(b)

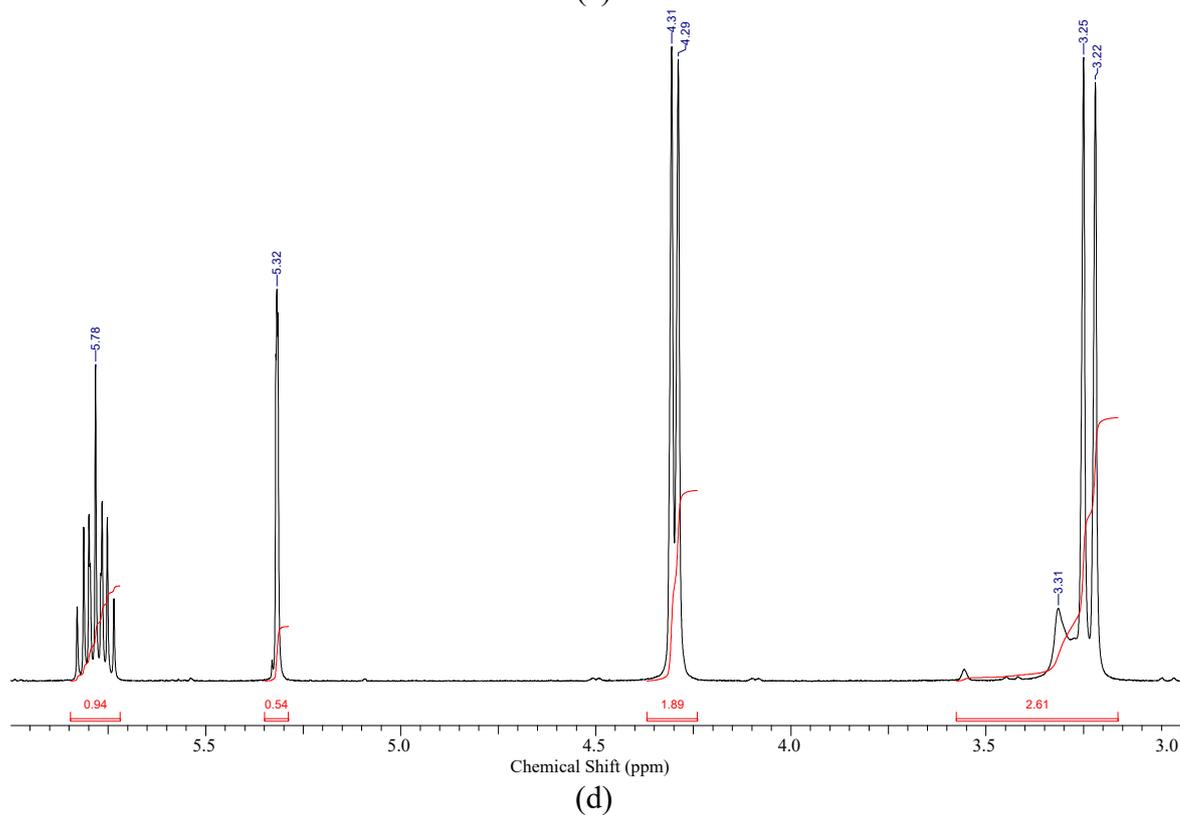
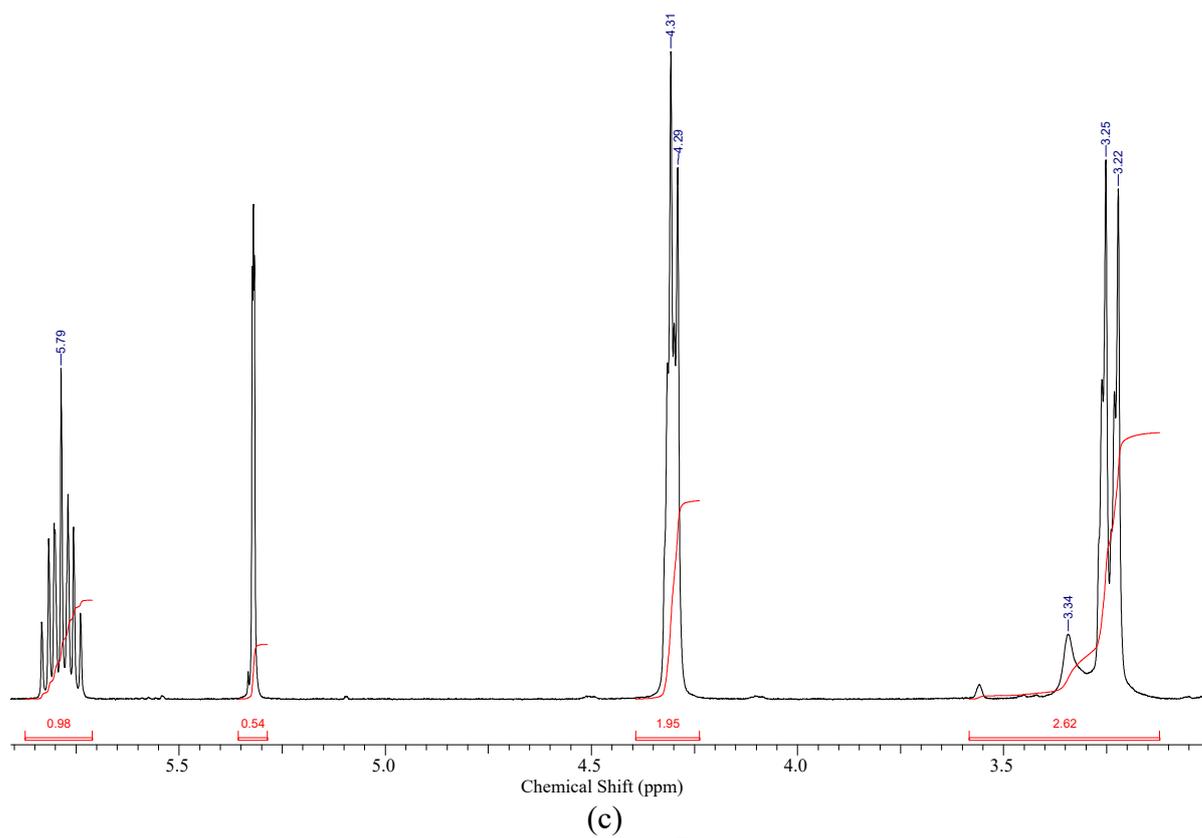
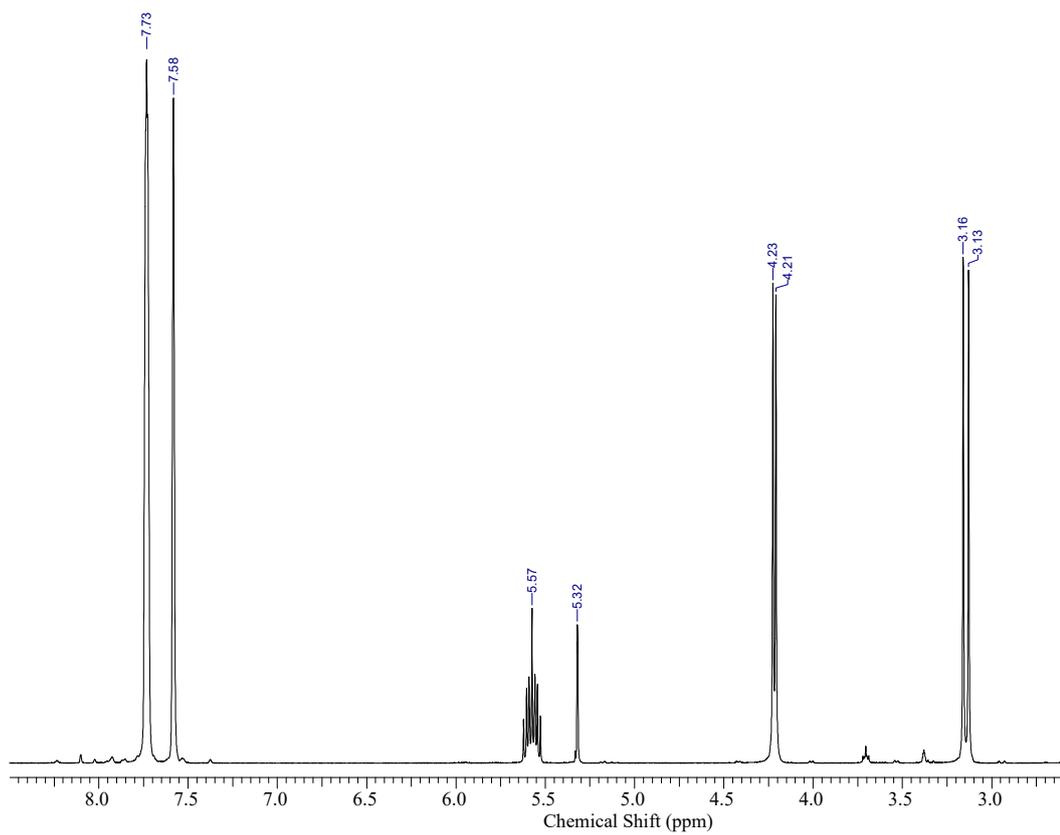
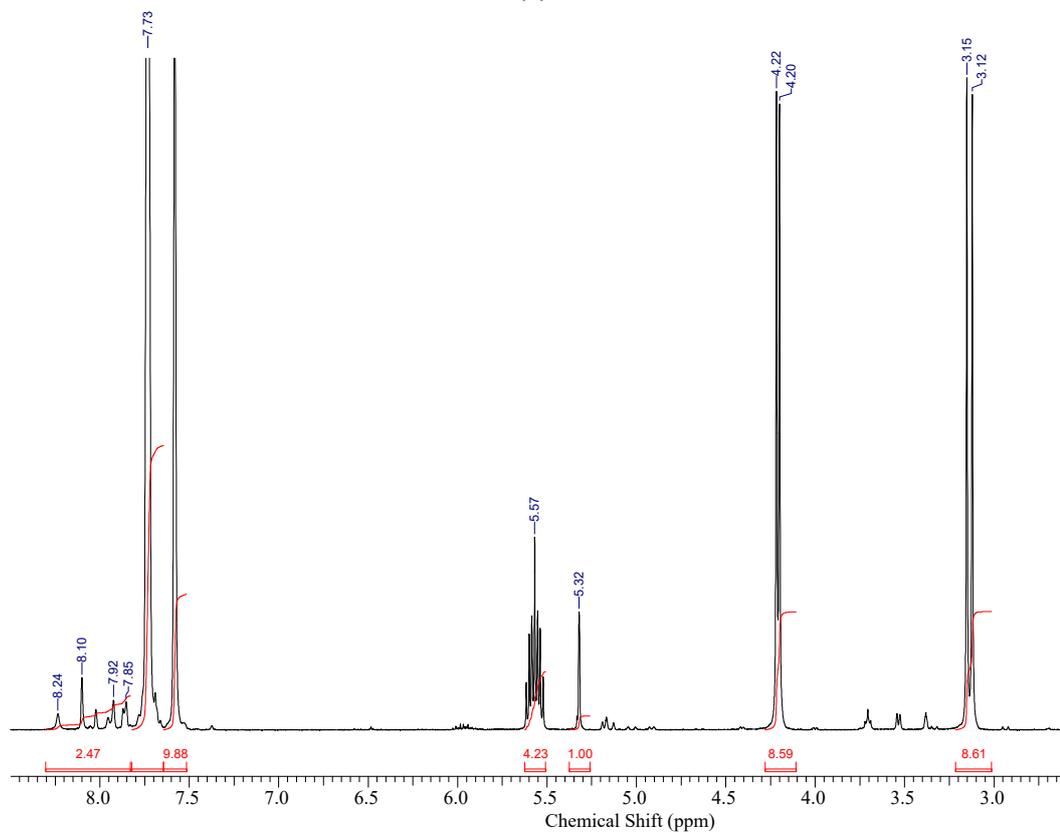


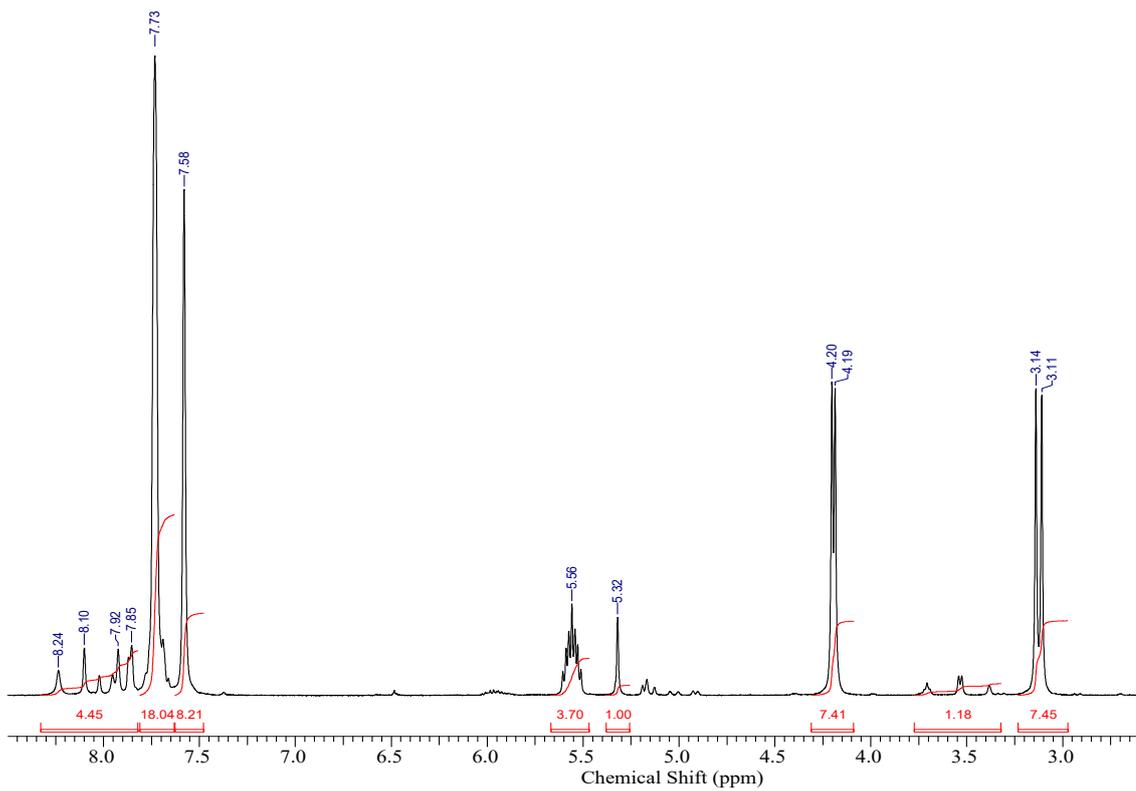
Fig. S19 ^1H NMR spectra of $(\eta^3\text{-C}_3\text{H}_5)_2\text{PdCl}_2/\text{AgSbF}_6$ system in 5 minutes (a), 1 h (b), 2 h (c), 8 h (d) after the preparation in CD_2Cl_2 (the protons of CH_2Cl_2 and CHDCl_2 (5.29-5.30 ppm) were used as a standard).



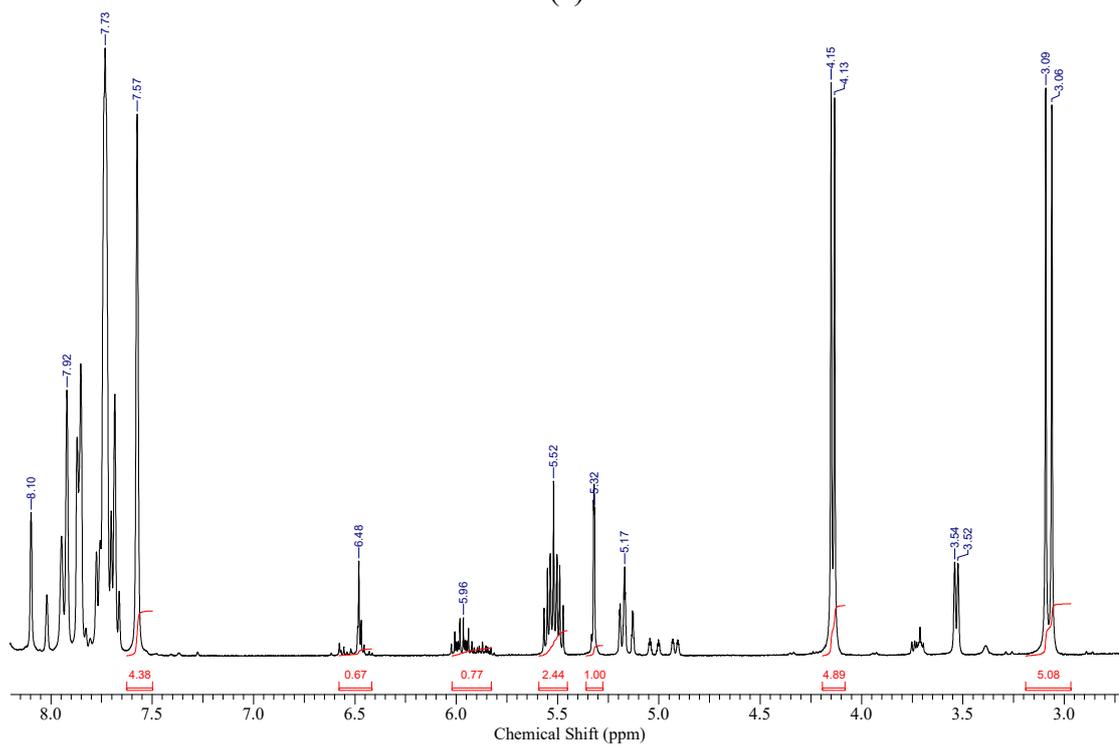
(a)



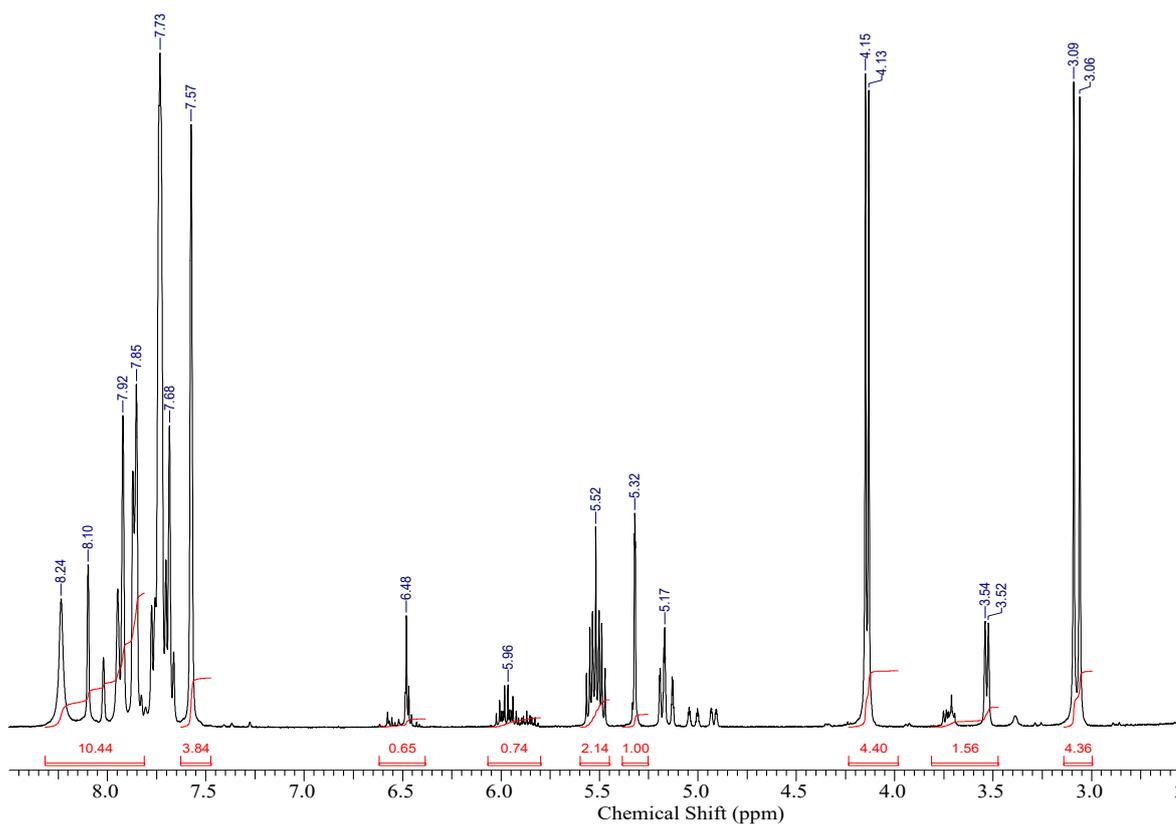
(b)



(c)



(d)



(e)

Fig. S20 ^1H NMR spectra of $((\eta^3\text{-C}_3\text{H}_5)\text{PdCl})_2/\text{NaBARF}$ system in 5 minutes (a), 30 minutes (b), 1h (c), 8h (d) 10h (e) after the preparation in CD_2Cl_2 (the protons of CH_2Cl_2 and CHDCl_2 (5.29-5.30 ppm) were used as a standard).

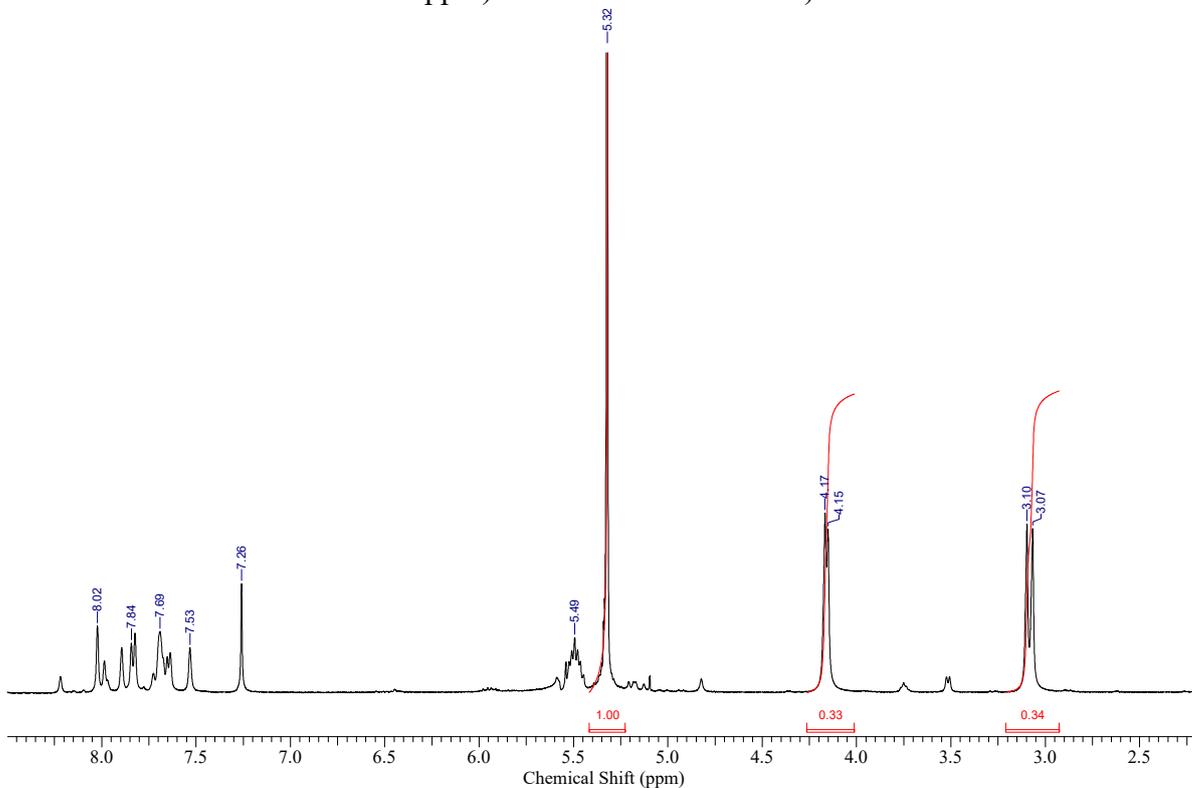


Fig. S21 ^1H NMR spectrum of $((\eta^3\text{-C}_3\text{H}_5)\text{PdCl})_2/\text{NaBARF}$ system in 5 minutes after the preparation in CDCl_3 (CH_2Cl_2 sealed in a capillary (5.29-5.30 ppm) was used as an external standard).

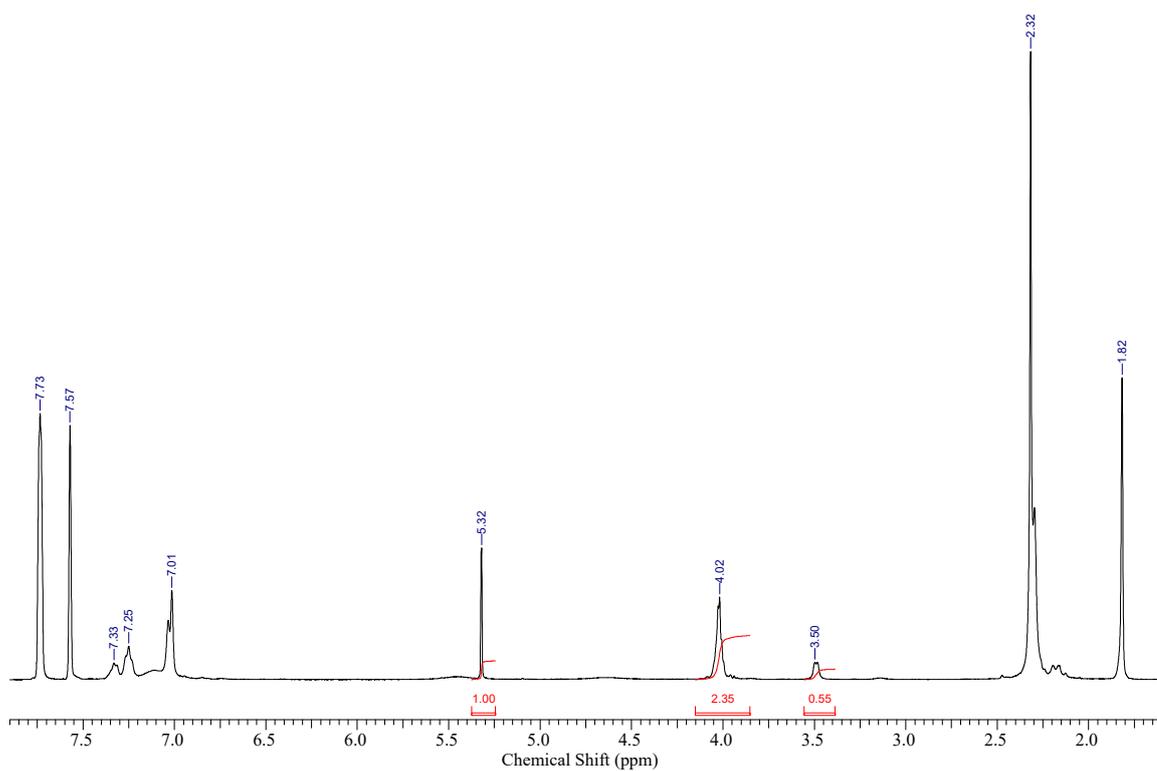
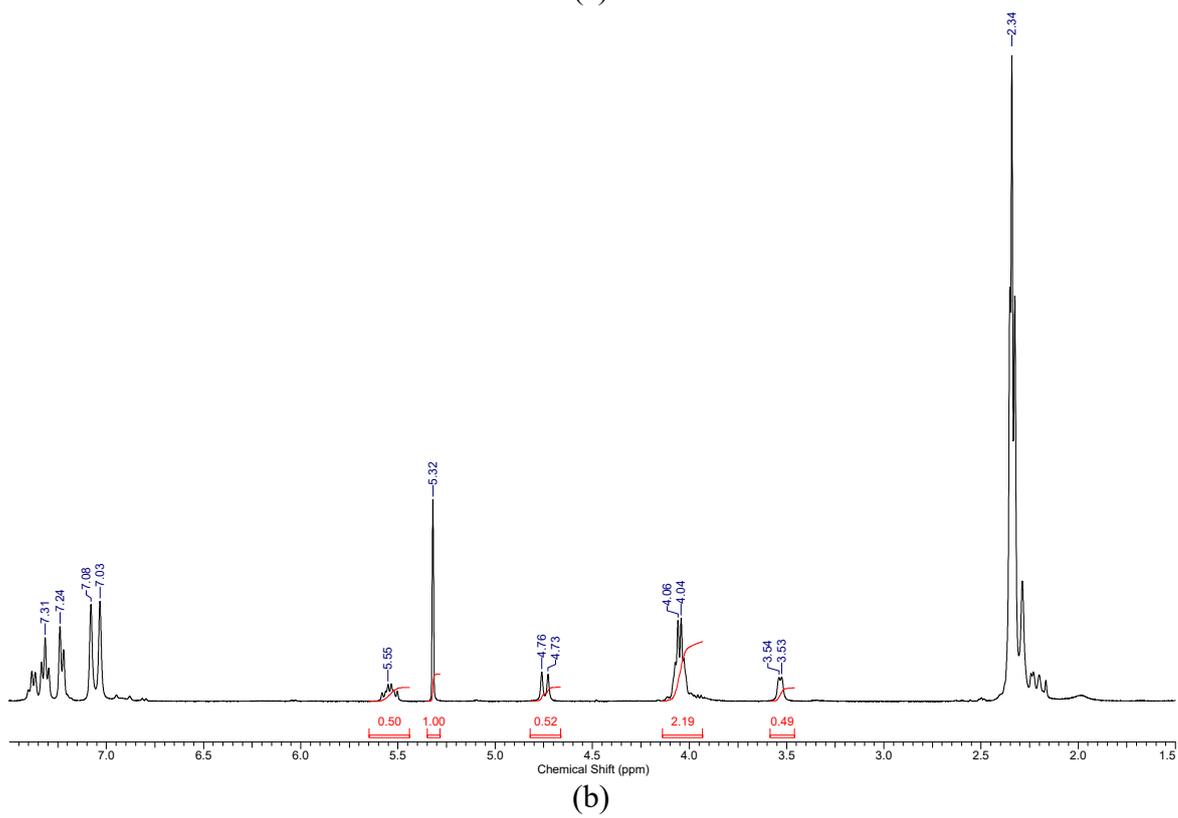
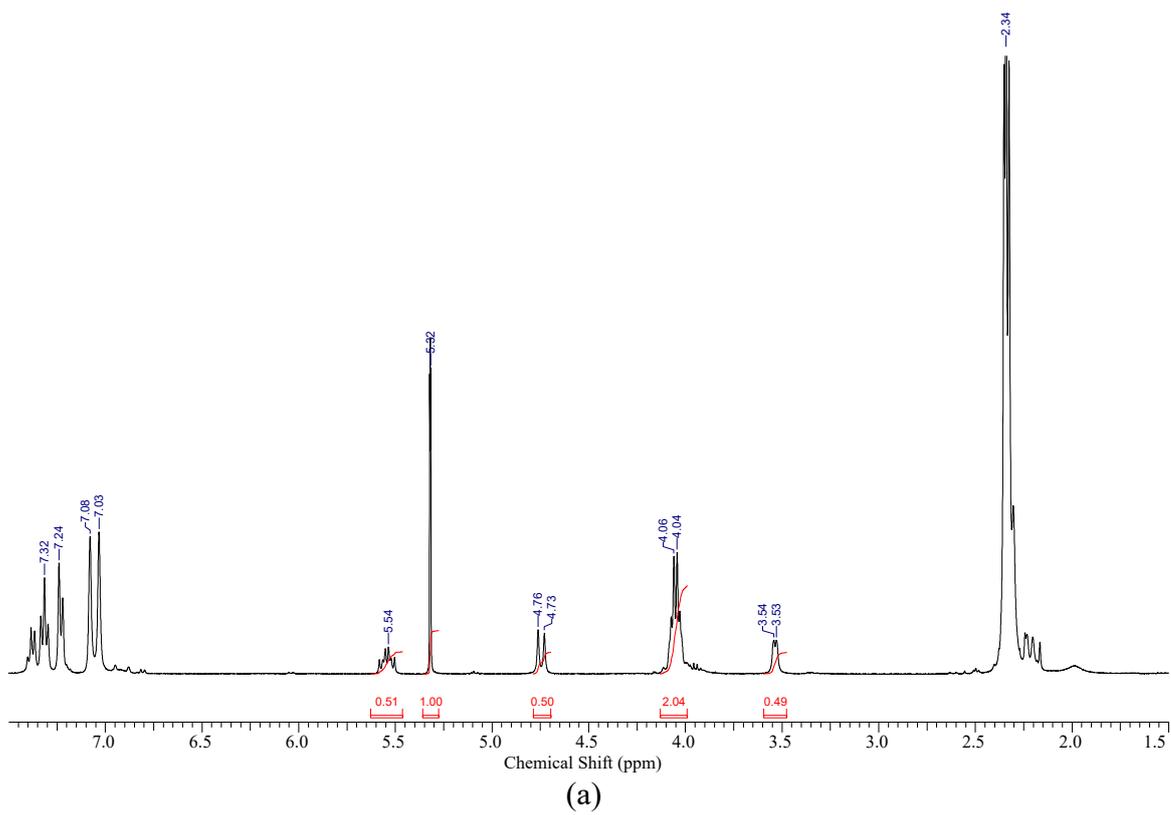


Fig. S22 ^1H NMR spectrum of SIMesPd(cinn)Cl/NaBARF system in 5 minutes after the preparation in CD_2Cl_2 (the protons of CH_2Cl_2 and CHDCl_2 (5.29-5.30 ppm) were used as a standard).



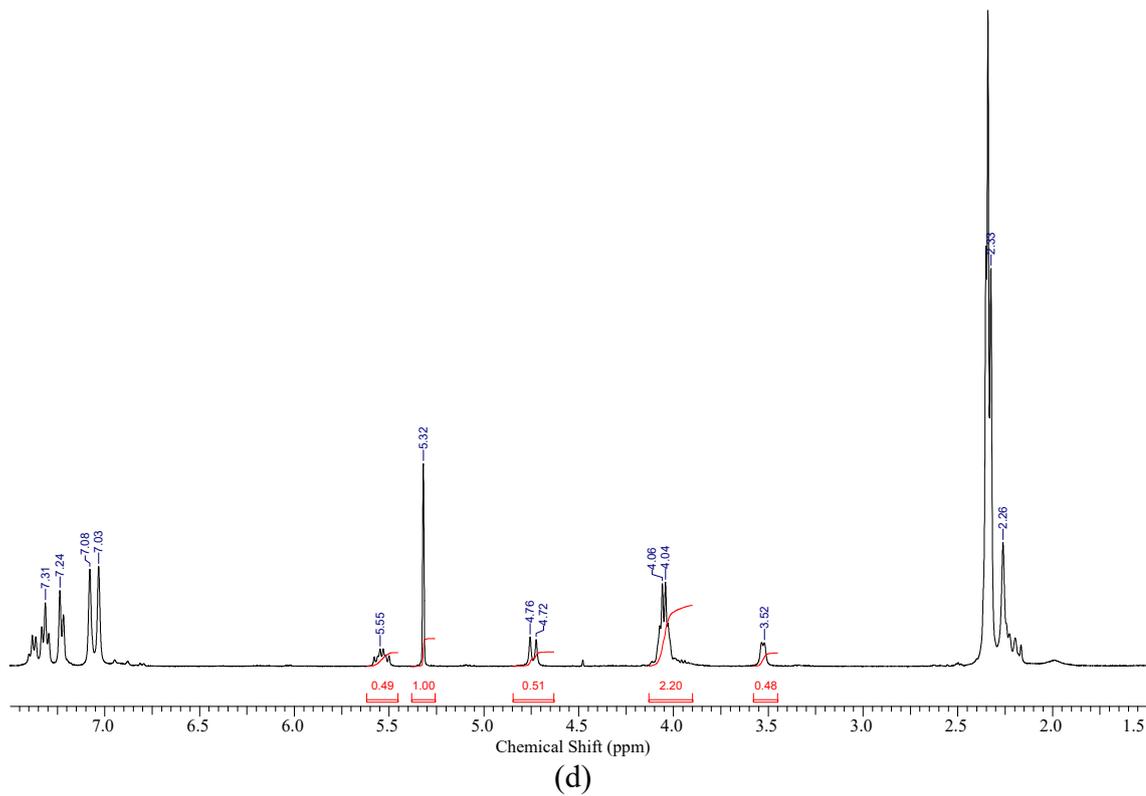
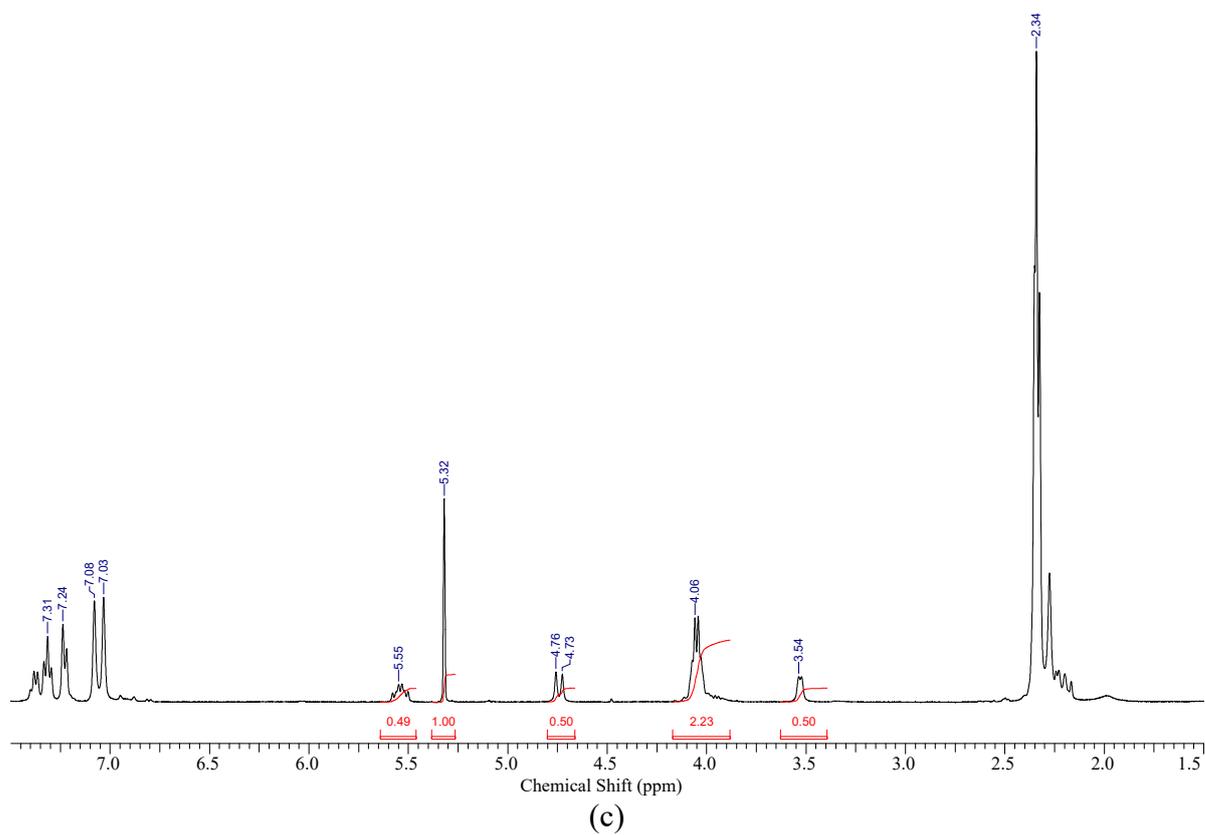
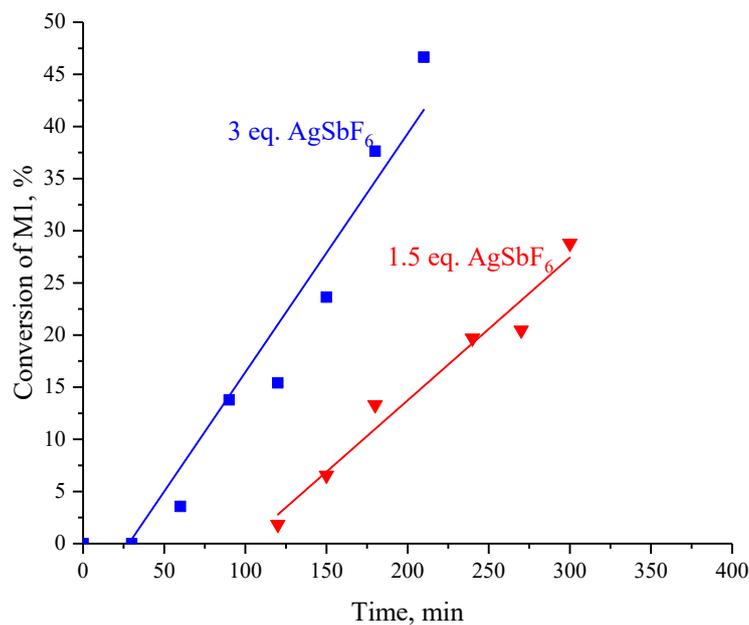
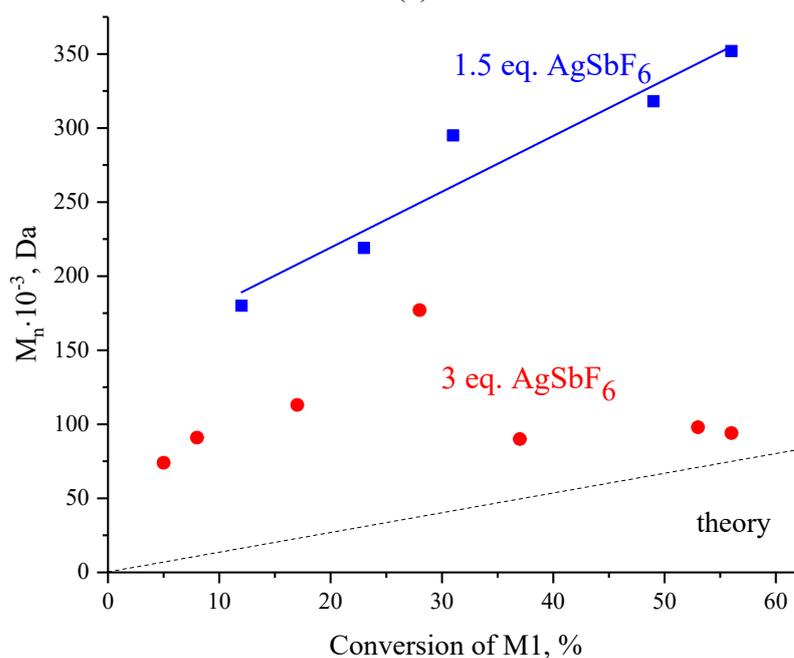


Fig. S23 ^1H NMR spectra of $\text{SIMesPd}(\text{cinn})\text{Cl}/\text{AgSbF}_6$ system in 5 minutes (a), 1 h (b), 4 h (c), 10 h (d) after the preparation in CD_2Cl_2 (the protons of CH_2Cl_2 and CHDCl_2 (5.29-5.30 ppm) were used as a standard).

Additional information about vinyl-addition polymerization of the norbornenes



(a)



(b)

Fig. S24 (a) The effect of the AgSbF₆/SIMesPd(cinn)Cl molar ratio on the conversion of **M1** in vinyl-addition polymerization in the presence of SIMesPd(cinn)Cl as a precatalyst (AgSbF₆/Pd molar ratios of 3/1 and 1.5/1; **M1**/Pd molar ratio of 500/1, [**M1**] = 1.0 M; dichloromethane; 45°C) and (b) the effect of the AgSbF₆/SIMesPd(cinn)Cl molar ratio on the molecular weights of formed poly(**M1**) in vinyl-addition polymerization in the presence of SIMesPd(cinn)Cl as a precatalyst (AgSbF₆/Pd molar ratios of 3/1 and 1.5/1; **M1**/Pd molar ratio of 500/1, [**M1**] = 1.3 M; dichloromethane; 45°C).

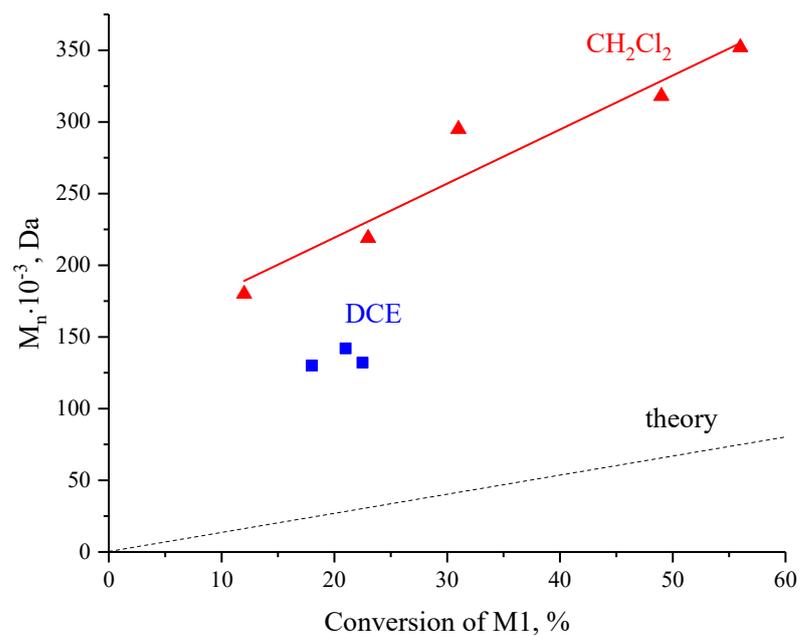


Fig. S25 The influence of a solvent on the molecular weights of vinyl-addition polynorbornene derived from **M1** (AgSbF₆/Pd molar ratio of 1.5/1; precatalyst - SIMesPd(cinn)Cl; [**M1**]/Pd molar ratio of 500/1; [**M1**] = 1.3 M; 45°C).

Table S1 The results of vinyl-addition polymerization of some norbornenes with polar groups^a

Monomer (M)	Catalytic system (Cat)	Molar ratio [M]/[Cat]	[M]	Reaction time, h	Yield, %	M _w ·10 ⁻³ , Da	M _n ·10 ⁻³ , Da	M _w /M _n
M1	Ni-1	100	1.25	78	8	52	26	2.0
M1	Ni-1	200	2.0	78	traces	-	-	-
M1	Pd(OAc) ₂ /NaBARF (1/3 molar ratio)	300	1.3	78	10	-	-	-
M1^b	Pd-3 /AgSbF ₆ (1/3 molar ratio)	100	1.0	48	45	76	26	2.9
M2	SIMesPd(cinn)Cl/AgSbF ₆ (1/3 molar ratio)	3000	0.9	24	65	751	549	1.4
M6	SIMesPd(cinn)Cl/NaBARF (1/3 molar ratio)	1000	1.6	2.5	85	144	86	1.7
M7	SIMesPd(cinn)Cl/NaBARF (1/3 molar ratio)	500	1.67	5	90	86	56	1.7

^a Solvent – CH₂Cl₂; reaction temperature – 45°C.

^b Ivan V. Nazarov, Evgeniya V. Bermesheva, Konstantin V. Potapov, Zoya B. Khesina, Mikhail M. Il'in, Elizaveta K. Melnikova and Maxim V. Bermeshev. Palladium complex with tetrahydronaphthyl-substituted diimine ligand as a catalyst for polymerization of norbornenes and diazoacetates. // *Mendeleev Commun.*, 2021, 31, accepted manuscript.

Table S2 The specific rotation of synthesized optically active nadimides and vinyl-addition polynorbornenes based on the corresponding monomers

	[α] _D	
	Monomer	Polymer
M2	-25° (C = 1, 20°C, THF)	-26° (C = 0.76, 28°C, CHCl ₃)
M3	-62° (C = 1, 20°C, THF)	-83° (C = 1.00, 28°C, CHCl ₃)
M5	-70° (C = 1, 20°C, THF)	-22° (C = 0.90, 28°C, CHCl ₃)

NMR spectra, WAXD patterns, TGA and CD spectra curves of vinyl-addition polynorbornenes

BJ NZR 1352_001001r

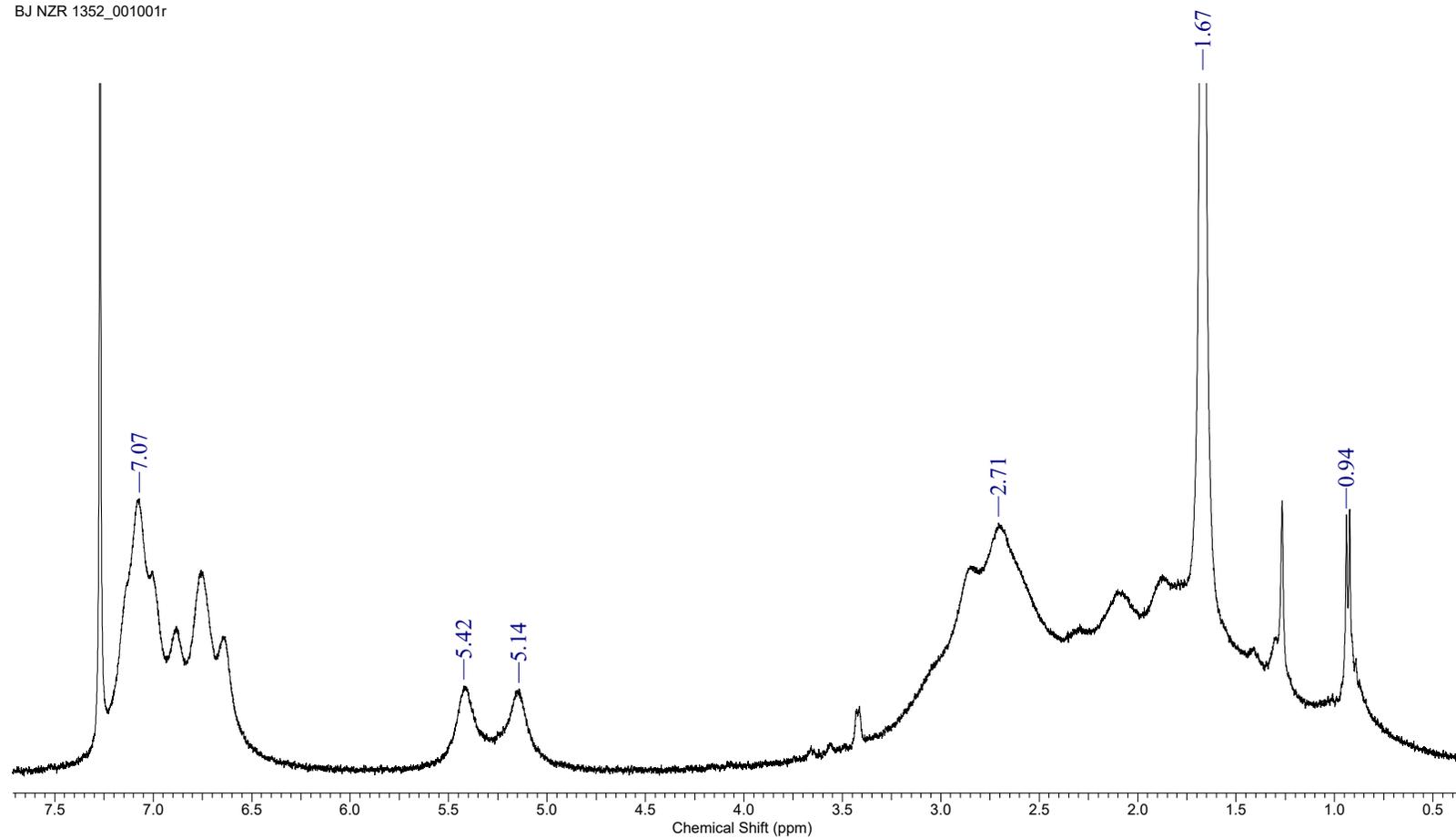


Fig. S26 ¹H NMR spectrum of vinyl-addition polymer based on **M2** (CDCl₃).

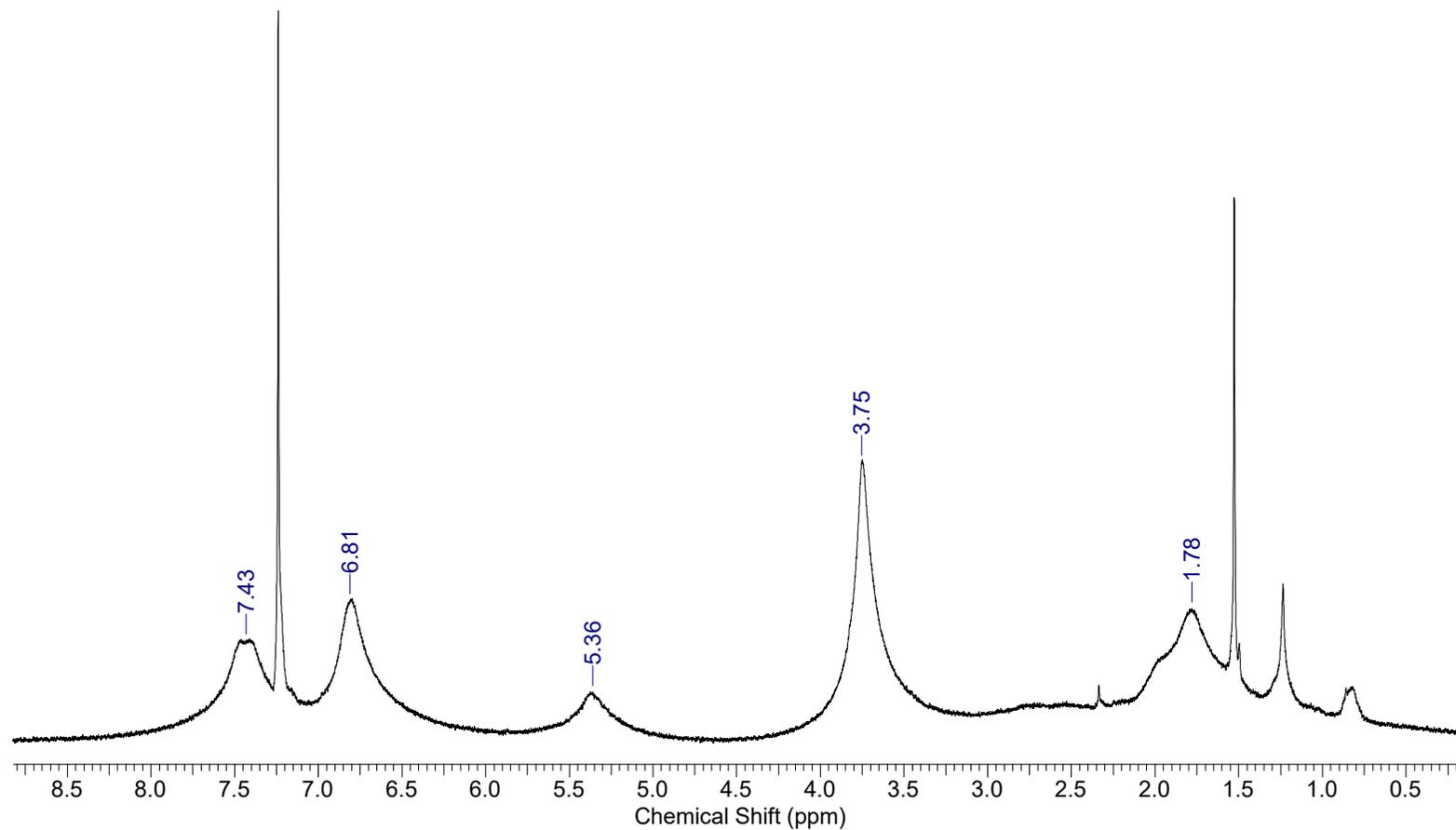


Fig. S27 ¹H NMR spectrum of vinyl-addition polymer based on **M3** (CDCl₃).

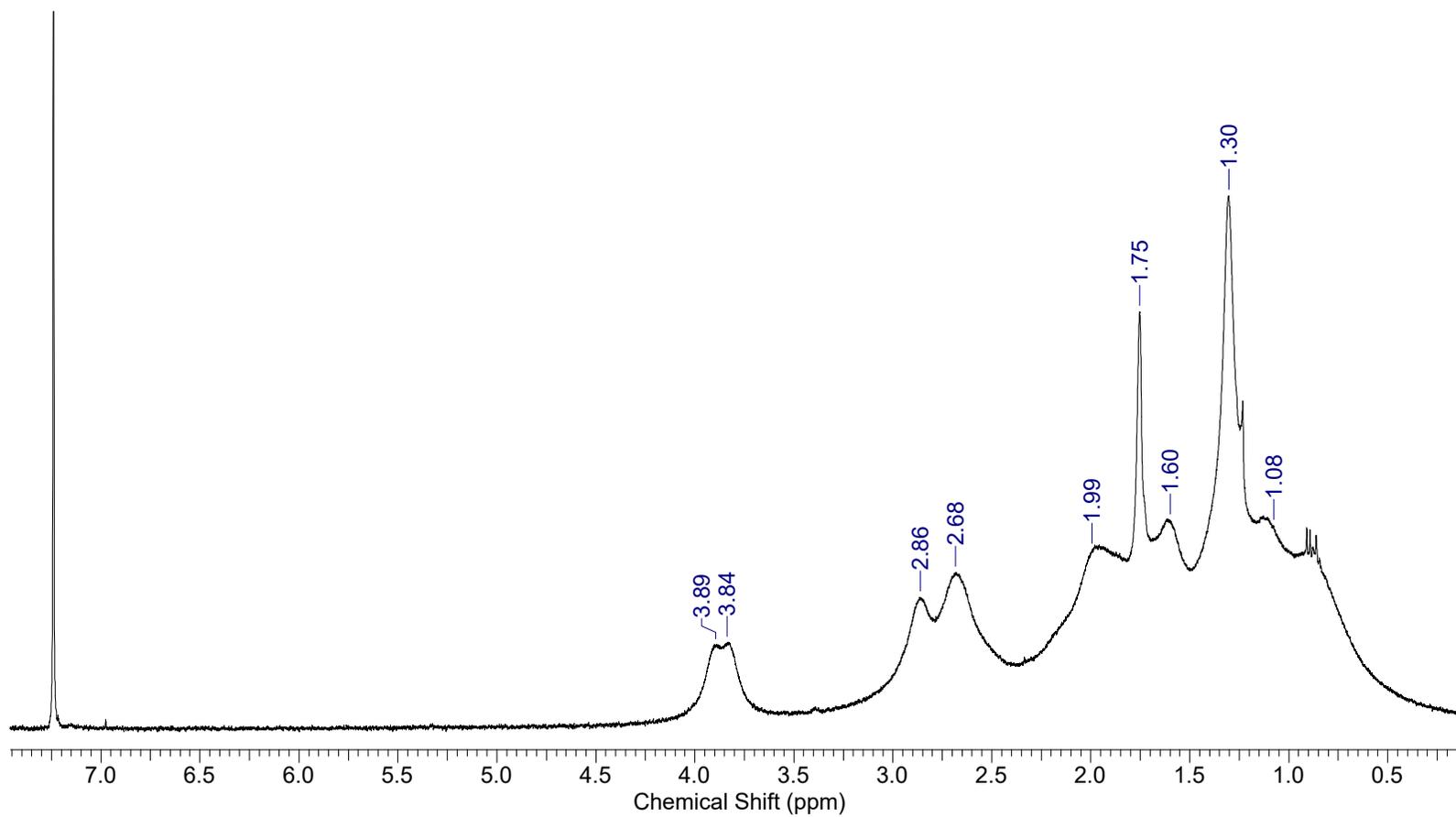


Fig. S28 ¹H NMR spectrum of vinyl-addition polymer based on **M4** (CDCl₃).

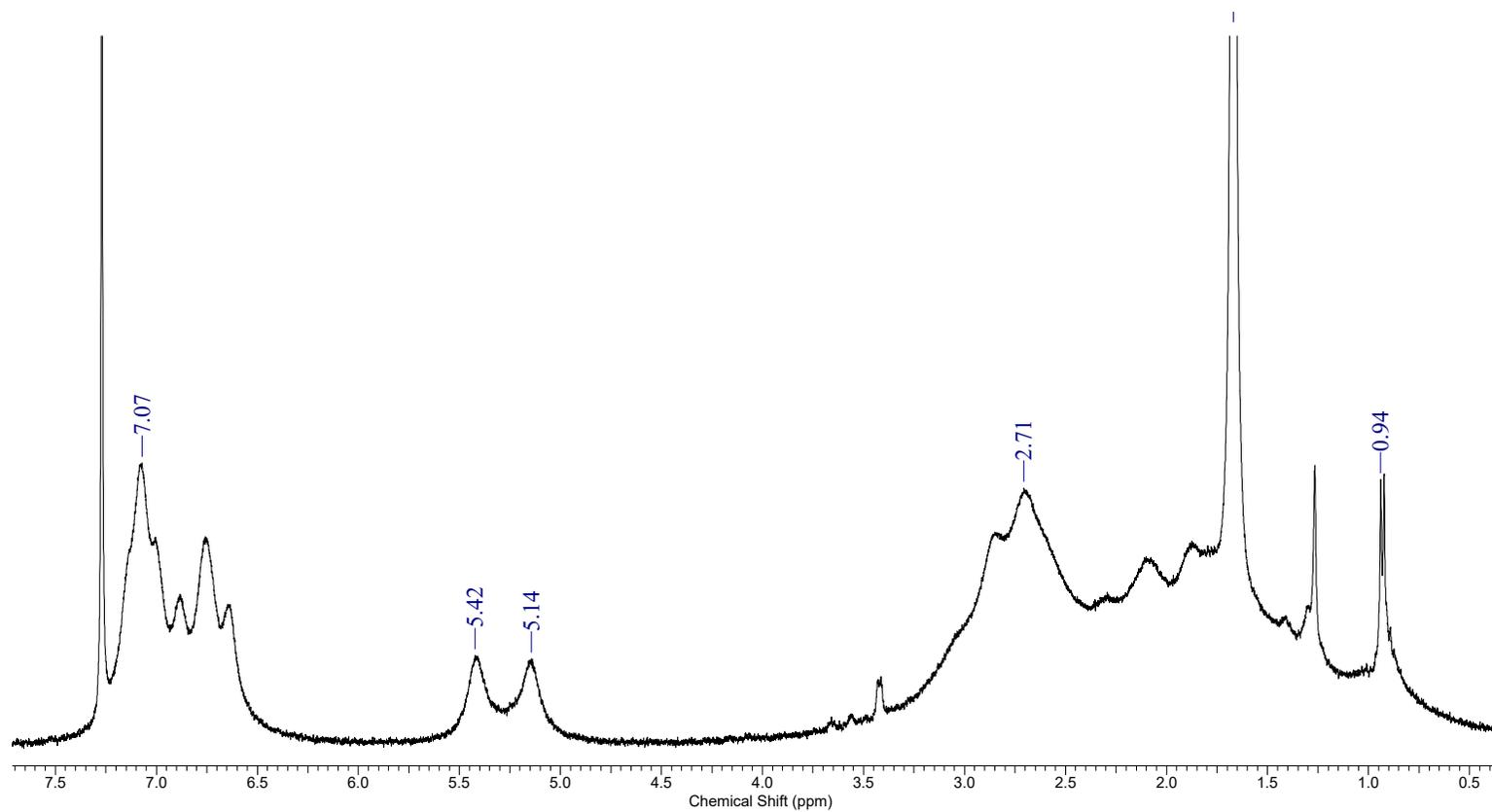


Fig. S29 ^1H NMR spectrum of vinyl-addition polymer based on **M5** (CDCl_3).

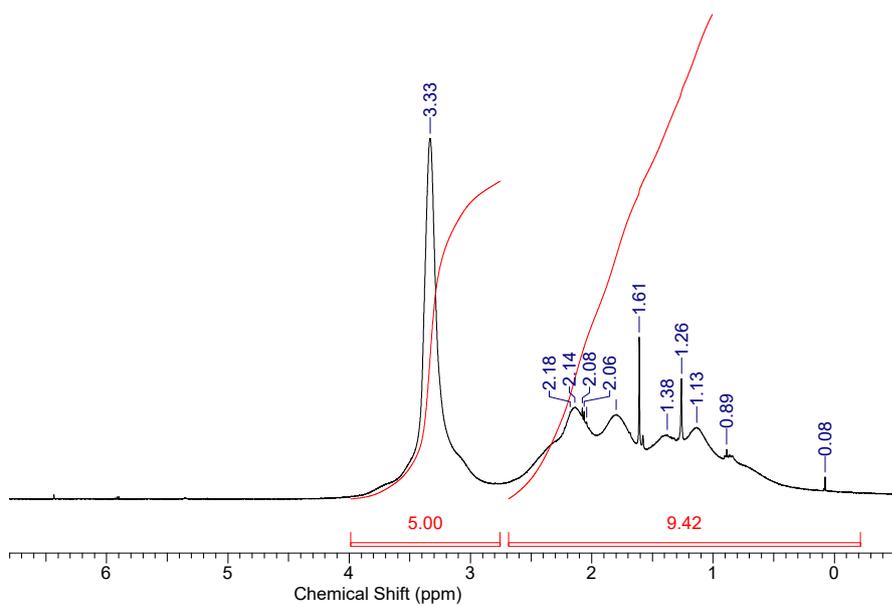


Fig. S30 ^1H NMR spectrum of vinyl-addition polymer based on **M6** (CDCl_3).

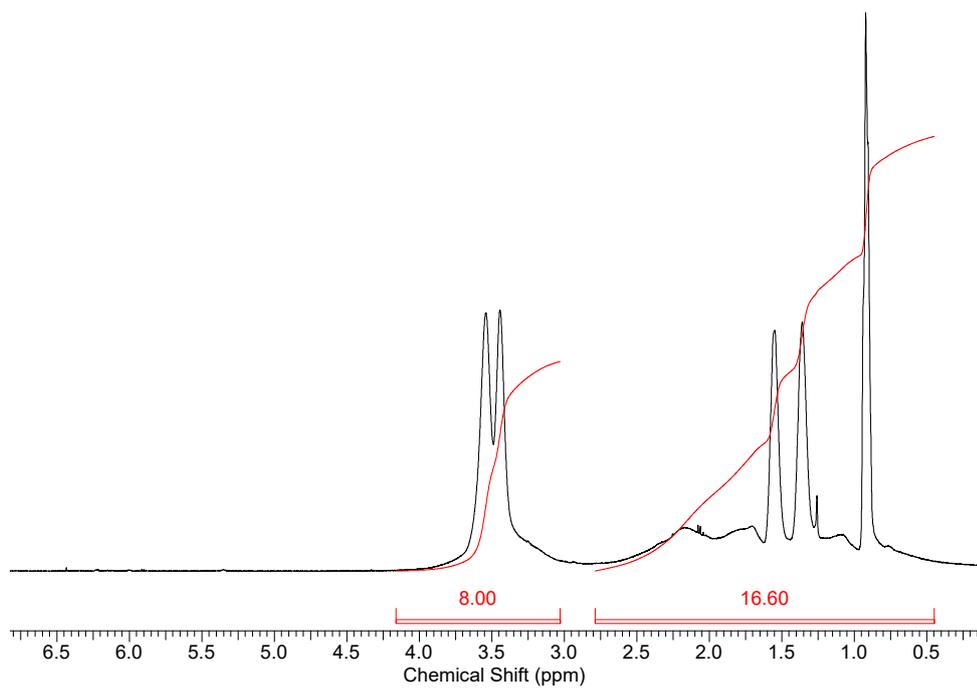
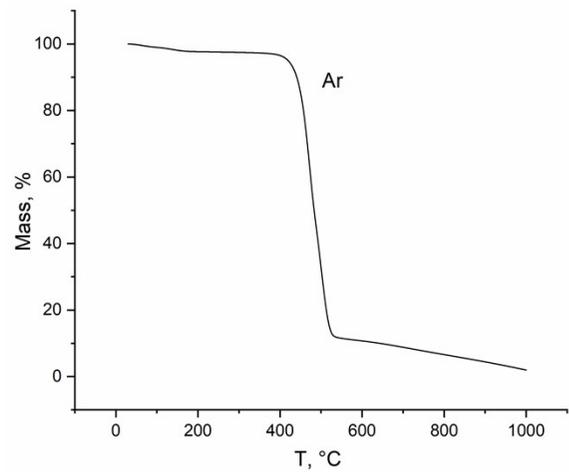
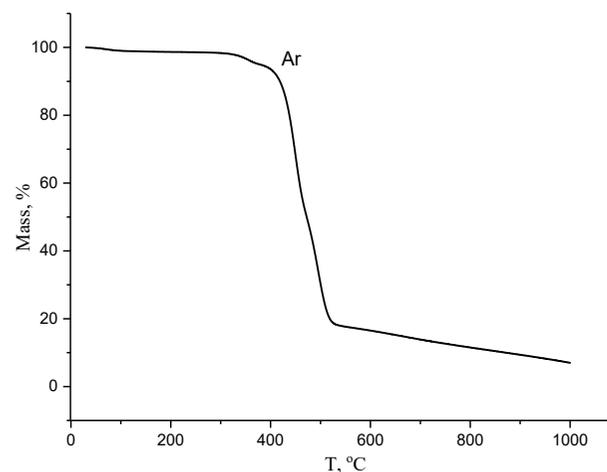


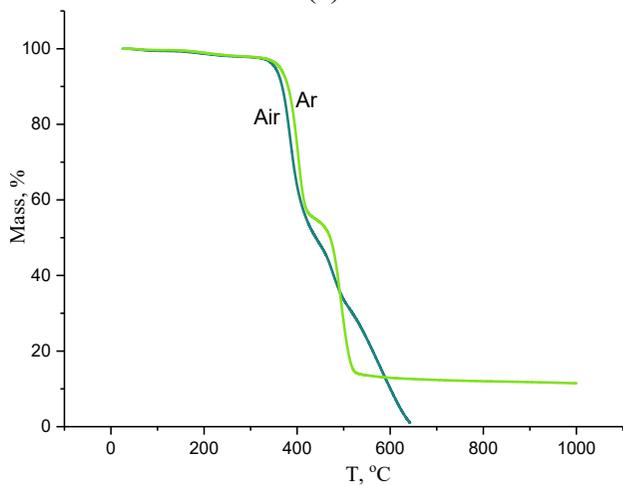
Fig. S31 ^1H NMR spectrum of vinyl-addition polymer based on **M7** (CDCl_3).



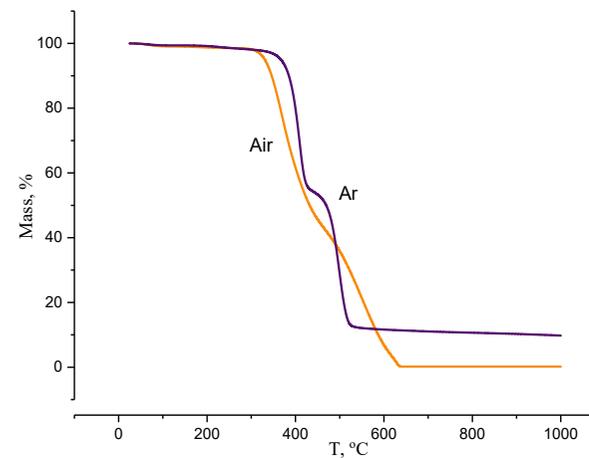
(a)



(b)

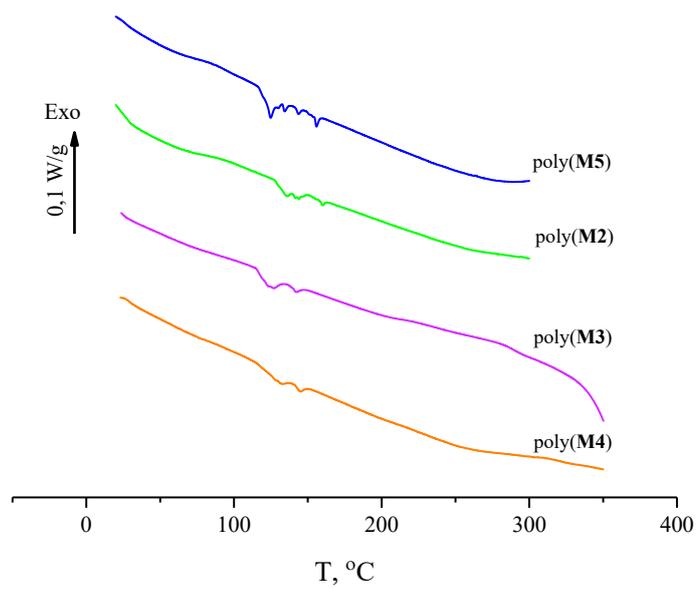


(c)

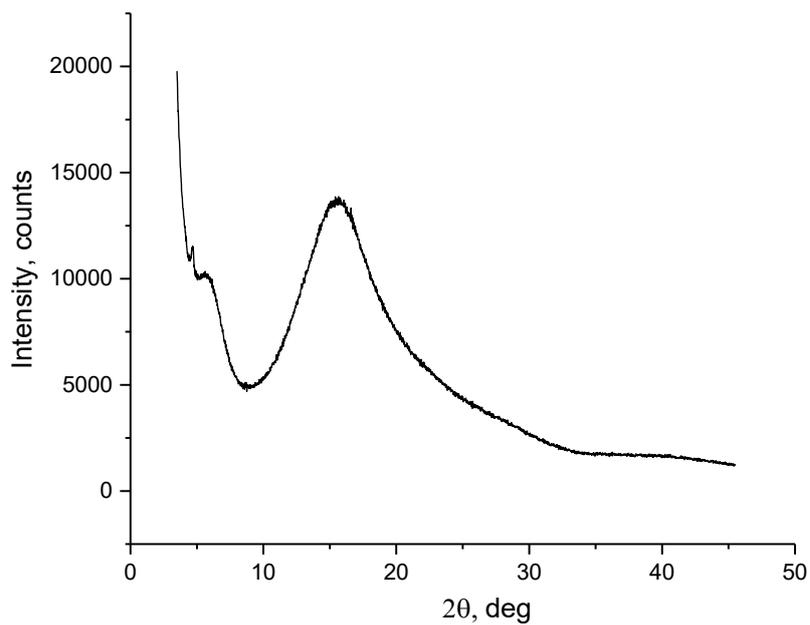


(d)

Fig. S32 TGA curves of vinyl-addition polymer based on **M1** (a), **M2** (a), **M3** (c) and **M5** (d).

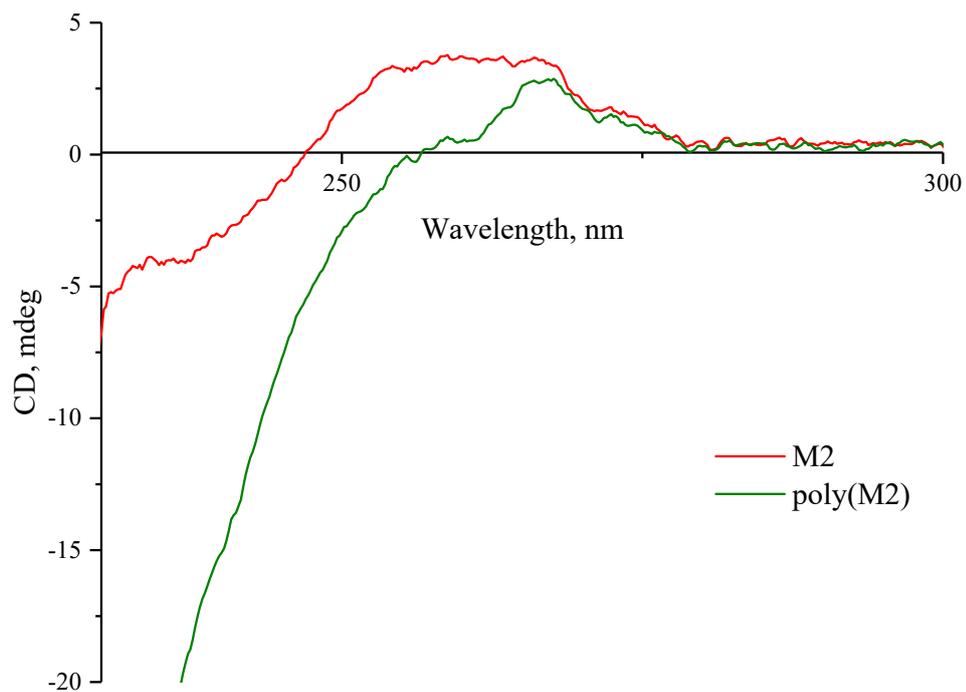


(a)

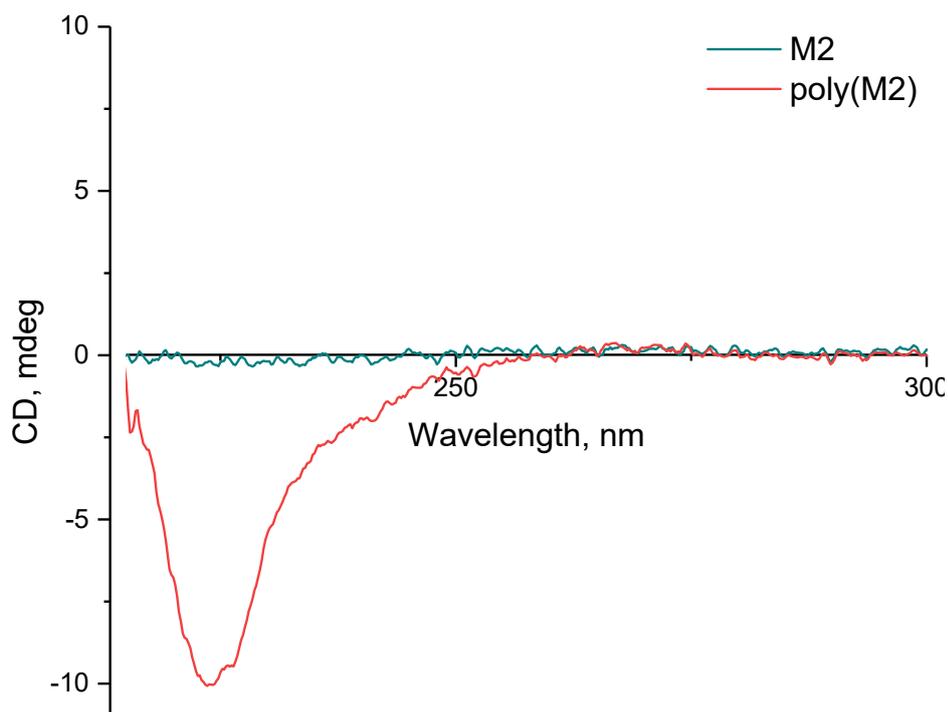


(b)

Fig. S33 (a) DSC curves of vinyl-addition polymers from various N-substituted *exo*-5-norbornene-2,3-dicarboxyimdes and (b) WAXD pattern of vinyl-addition polymer based on **M3**.

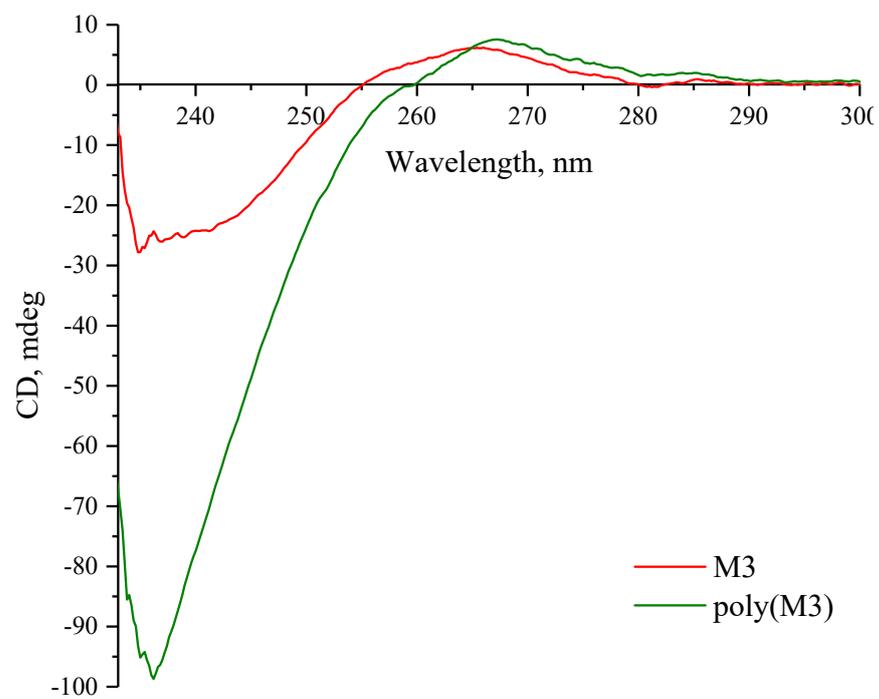


(a)

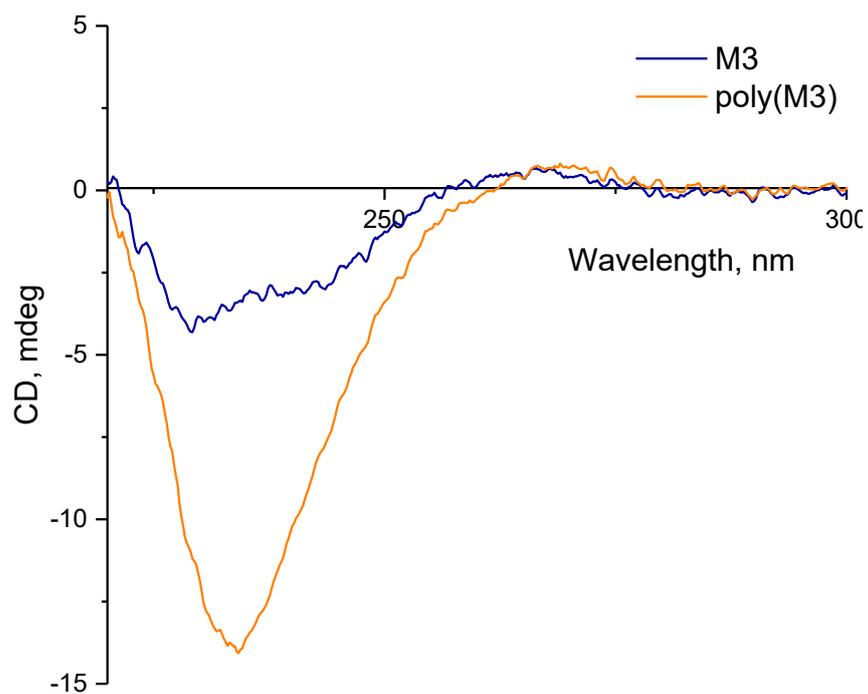


(b)

Fig. S34 Circular dichroism spectra of **M2** and vinyl-addition polymer based on **M2** (poly(**M2**)) in CHCl_3 at 25°C . The concentration of both samples is 1 mg/ml. The measurements were done in the 0.1 cm (a) and 0.01 cm (b) path-length quartz cells with a detachable window.

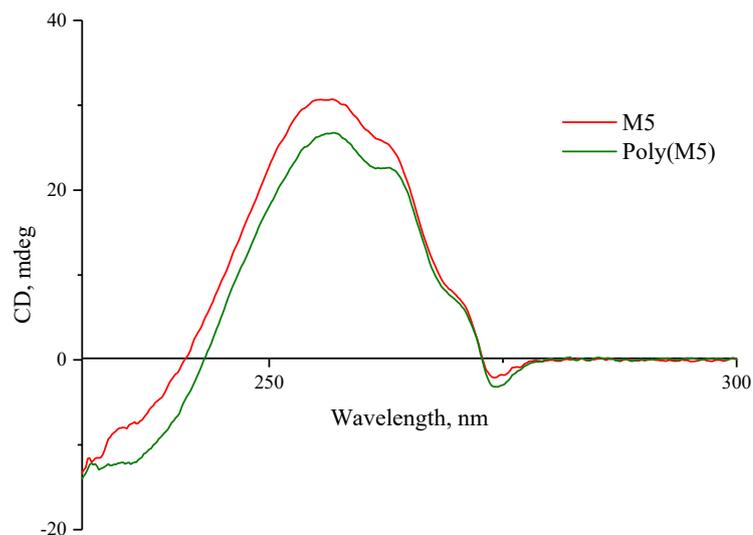


(a)

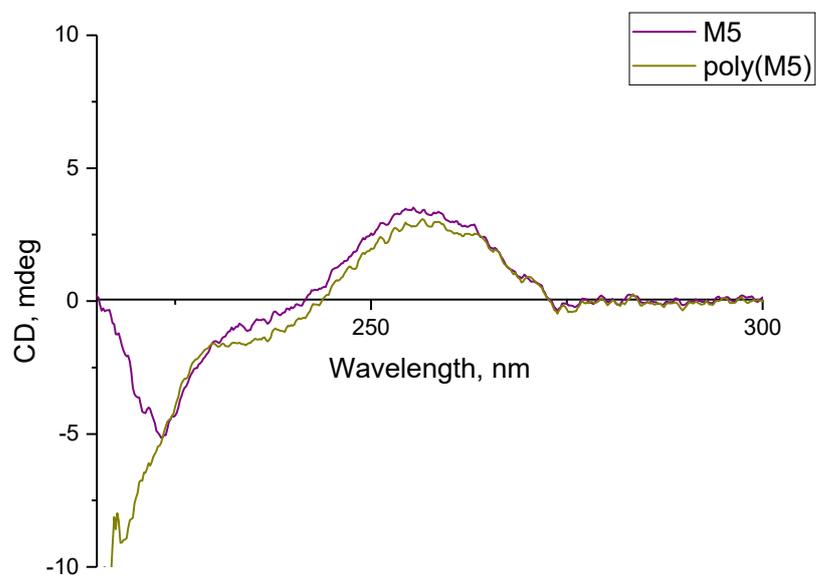


(b)

Fig. S35 Circular dichroism spectra of **M3** and vinyl-addition polymer based on **M3** (poly(**M3**)) in CHCl_3 at 25°C . The concentration of both samples is 1 mg/ml. The measurements were done in the 0.1 cm (a) and 0.01 cm (b) path-length quartz cells with a detachable window.



(a)



(b)

Fig. S36 Circular dichroism spectra of **M5** and vinyl-addition polymer based on **M5** (poly(**M5**)) in CHCl_3 at 25°C . The concentration of both samples is 1 mg/ml. The measurements were done in the 0.1 cm (a) and 0.01 cm (b) path-length quartz cells with a detachable window.

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