Recoverable Reusable Polyisobutylene (PIB)-Bound Ruthenium Bipyridine ($Ru(PIB\text{-}bpy)_3Cl_2$) Photoredox Polymerization Catalysts

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General Procedures: Vinyl terminated PIB (Glissopal 2300) with M_n value of 2300 Da, was provided by BASF. Ethyl methacrylate (99%) was obtained from Aldrich and purified by passing through a basic alumina oxide column. This purified monomer was stored at -20 $^{\circ}$C. $RuCl_3$: xH_2O was dried at 120 °C in the oven for 12 h. Other reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated. ^{1}H NMR spectra were recorded on an Inova 500 spectrometer operating at 499.95 MHz or on an Inova 300 spectrometer operating at 299.91 MHz. ^{13}C NMR spectra were recorded on an Inova 500 or Inova 300 spectrometers operating at 125.72 MHz or 75.41 MHz respectively. Chemical shifts are reported in ppm and referenced to the residual protons resonances in $CDCl_3$. Coupling constants (*J* values) are reported in Hertz (Hz), and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), dd (doublet of doublet) and m (multiplet). A NexION 300D Inductively Coupled Plasma-Mass Spectrometer (ICP-MS) was used to determine Ru metal content in polymer products. Gel permeation chromatrography (GPC) data were collected using a Viscotek I-MBMMW-3078 which was calibrated with polystyrene standards using DMF and THF solvents. UV-Vis spectra were recorded on a Cary 100 UV-Vis spectrometer. All reactions were carried out under nitrogen atmosphere unless otherwise noted. PIB-CH_2OH **1**, PIB-CH_2-OMs **2**,[1] PIB-CH_2-Br 3[1] and the Ru complexes $Ru(bpy)_3(PF_6)_2$ **9**[2] and $Ru(Mbpy)_3(PF_6)_2$ **10**[2] were synthesized following published procedures.[2]

ICP-MS analysis procedure: Polymer products that were precipitated from methanol were filtered under vacuum to obtain solid samples. These samples (~100 mg) were digested in 2 mL of concentrated nitric acid by heating at 120 °C for 24 h. The solutions that formed were cooled to room temperature and 2 mL of concentrated sulfuric acid was added. These solutions were heated to 120 °C for 48 h. At this point, the concentrated acid solution was diluted with 1% nitric acid solution and filtered through celite. These diluted samples were then analyzed for Ru content by ICP-MS.

Synthesis of polyisobutylene (PIB)-bipyridine ligands (5 and 6): To a 50-mL round-bottomed flask was added 5 mL of freshly distilled anhydrous tetrahydrofuran (THF). The flask was sealed with a rubber septum. Then this solution was cooled to -78 °C in a Dry Ice/acetone bath for 10 min. A syringe was used to add diisopropylamine (0.35 mL, 2.5 mmol). This was followed by addition of *n*-butyllithium (1.62 mL, 2.5 mmol) in hexane. After stirring for 40 min, a solution of 4,4'dimethyl-2,2'-bipyridine (0.184 g, 1mmol) in 5 mL of THF was added to the reaction flask. The reaction temperature was maintained at -78 °C for another 2 h. The formation of bipyridyl anions was inferred by the color change of the reaction solution which changed from light yellow to dark brown-black. After 2 h of stirring, the flask was charged with polyisobutyl bromide (5.0 g, 2,.3 mmol) in 10 mL of THF. This solution was allowed to warm to room temperature and stir overnight at room temperature. At this point 5 mL of water was added to reaction mixture and THF was removed under reduced pressure. The resulting viscous oil like material was dissolved in 50 mL of hexane. The organic phase was washed with 3 30-mL portions of 10% aq. ethanol and 1 50-mL portion of brine. Then the organic layer was dried with anhydrous sodium sulfate and the hexane solvent was evaporated under reduced pressure to obtain PIB-bipyridine ligand **5** along with a greater portion of the product in the form of **6**. This mixture of mono and disubstituted products

was obtained in 80% yield based on the amount of starting 4,4'dimethyl-2,2'-bipyridine **4**. While this mixture was generally used in the reactions below, it was possible to separate the dipolyisobutylated **5** from the monopolyisobutylated product by silica column chromatography using hexane/ethyl acetate as the eluent. However, while this chromatography afforded pure **5**, it was relatively inefficient. Since the Ru complex containing at least one PIB group per Ru was as phase selectively soluble as the Ru complex containing two PIB groups per Ru, the mixture of **5** and **6** was generally used in the reactions below.

Polyisobutylene (PIB)-bipyridine ligand (5): ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.56 (d, 2 H), 8.24 (s, 2 H), 7.14 (d, 2 H), 2.69 (m, 2 H), 1.71 – 0.68 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.8, 153.5, 149.4, 124.3, 121.8, 60.40, 41.3-15.0 (multiple peaks).

Synthesis of $Ru(PIB\text{-}bpy)_3Cl_2$ catalyst (7). A solution of PIB-bipyridine ligand **5** (8 mmol) in 2 mL of heptane and a solution of anhydrous $RuCl_3$ (2.07 mg, 2 mmol) in ethanol were mixed in a pressure vessel and closed with a rubber septum. This solution was bubbled with N_2 stream for 15 minutes. Then the rubber septum was quickly replaced with the pressure vessel lid and closed tightly. This reaction vessel was heated to 90 °C for 12 h at which point the reaction mixture turned to a dark orange red color. Then the reaction solution was cooled to room temperature and poured in to 250-mL separatory funnel to which 5 mL of water was added. The solution was separated into two phases, upper heptane layer and lower aq. layer. Another 100 mL of hexane was added to the funnel and organic phase was washed with 3 50-mL portions of 10% aq. ethanol. Then the organic layer was dried with anhydrous sodium sulfate and evaporated under reduced pressure. This bright red color crude product was purified by a neutral alumina column and dichloromethane: methanol (10:1, v/v) as the eluent to obtain the catalyst in 61 % yield. UV-Vis (hexane) λ_{max} 463 nm, ε =

15500 $M^{-1}cm^{-1}$; ^1H NMR (300 MHz, $CDCl_3$) δ: 8.47 (m, 2 H), 7.65 (m, 2 H), 7.37 (m, 2 H), 2.85 (bs), 1.8 – 0.5 (m).

Synthesis of Ru(PIB-bpy)$_3$Cl$_2$ catalyst (8); The procedure used above to prepare **7** was used to prepare **8**. The starting mixture of polyisobutylated ligands varied in different preparations of **8** but typically contained a ca. 2/1 ratio of **5**/**6**. The product **8** contained a 2/1 ratio of polyisobutyl/methyl groups on the Ru(PIB-bpy)$_3$Cl$_2$ complex based on integration of the PIBCH_2Ar and CH_3Ar peaks at 2.86 and 2.66 δ in the ^1H NMR spectrum of the Ru(PIB-bpy)$_3$Cl$_2$ complex **8** which was otherwise nearly identical to that of **7** with very slight (<0.04 ppm) differences in the ^1H NMR chemical shifts. ^1H NMR (300 MHz, $CDCl_3$) δ: 8.47 (m, 2 H), 7.67 (m, 2 H), 7.33 (m, 2 H), 2.86 (m), 2.66 (bs, 3 H), 1.8-0.8 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.6, 156.2, 154.7, 150.8, 150.6, 129.1, 127.9, 125.1, 124.1, 59.0-57.0 (multiple peaks), 38.0 – 21.5 (multiple peaks).

Synthesis of Ru(bpy)$_3$(PF$_6$)$_2$ and Ru(Mbpy)$_3$(PF$_6$)$_2$ (9 and 10). A 25-mL round-bottomed flask equipped with a stir bar was charged with 4,4'dimethyl-2,2'-bipyridine or bipyridine (4.3 mmol) dissolved in ethanol (15 mL) and $RuCl_3$ (0.18 g, 0.86 mmol). This solution was purged with N_2 for 10 minutes and then refluxed 24 h upon which a dark reddish orange solution was obtained. This solution was cooled to room temperature and added a saturated aq. solution of KPF_6 (10 mL). At this point dark orange red solid precipitated. This solid was isolated by filtration and was washed with diethyl ether (2 3 mL portions) and dried at reduced pressure to obtain the product in 80% yield.

Ru(bpy)$_3$(PF$_6$)$_2$ (9).[3] : UV-vis (CH_3CN) λ_{max}: 453 nm (ε = 14000 $M^{-1}cm^{-1}$) , 280 nm; ^1H NMR (300 MHz, CD_3OD) δ: 8.85 (m, 6 H), 8.17 (m, 6 H), 7.73 (m, 6 H), 7.53 (t, 6 H), 2.49; ^{13}C NMR (125 MHz, DMSO) δ:156.7, 151.2, 138.2, 128.2, 124.8.

$Ru(Mbpy)_3(PF_6)_2$ (10).[3] UV-vis (CH_3CN) λ_{max} : 457 nm, (ε = 15300 $M^{-1}cm^{-1}$) ; ^1H NMR (300 MHz, DMSO) δ: 8.52 (bs,, 2 H), 7.58 (d, J = 7.2 , 2 H), 7.28 (bs 2 H), 2.04 (s, 6 H).

General Procedure for Photocatalyzed polymerization and recycling of the catalyst 8: A 10-mL Schlenk tube equipped with a stir bar was charged with 0.01 mol% of $Ru(PIB\text{-}bpy)_3Cl_2$ **8** dissolved in 2.5 mL of heptane and ethyl methacrylate (2.5 mL, 20 mmol). Since 8 typically contained a 2/1 ratio of **5**/**6** with PIB groups whose molecular weight could have changed due to fractionation in the various synthesis steps, the amount of **8** used was based on analysis of the Ru content in the mixture of **8** that was used for the photopolymerization. This solution was purged with N_2 for 15 min and then degassed three times using the freeze pump thaw method. At this point *N*,*N*-diisopropylethylamine (170 μL, 1mmol) and ethyl 2-bromoisobutyrate (75 μL, 0.5 mmol) were added. Then the reaction tube was irradiated with a 30W household fluorescent bulb for 24 h at which point the solid polymer had precipitated from the heptane solution of **8**. Then the supernatant liquid containing was transferred by forced siphon to another Schlenk tube with fresh monomer substrate. The volume was adjusted to 5 mL by adding heptane and this second solution was degassed three times using the freeze pump thaw method. Fresh ethyl 2-bromoisobutyrate initiator and additional iPr$_2$NEt was added and this subsequent polymerization cycle commenced. The precipitated solid polymer from the original reaction flask was dissolved in 5 mL of *N*,*N*-dimethylformamamide (DMF) and precipitated in 70 mL of methanol. This polymer product precipitate was isolated by vacuum filtration. The solid was then dried in vacuum overnight to obtain the product polymer. Typical isolated yields were in 70 – 80 % range. Yields for each reaction are listed in Table 1 in the manuscript. The product polymers were collected and then analyzed by GPC to determine the M_n and PDI using DMF as the solvent for PEMA and THF as the solvent for PEEMA and PGMA.

Poly(ethyl methacrylate) PEMA (**12**).[4] ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm): 4.03 (q, 2H), 1.96-1.70 (m, 2H), 1.60 (m, 0.3H), 1.45 (m, 0.22 H), 1.03 (s, 1H), 0.88 (bs, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.8, 177.5, 176.8, 60.8, 54.1, 44.7, 31.4, 18.5, 16.6, 13.8.

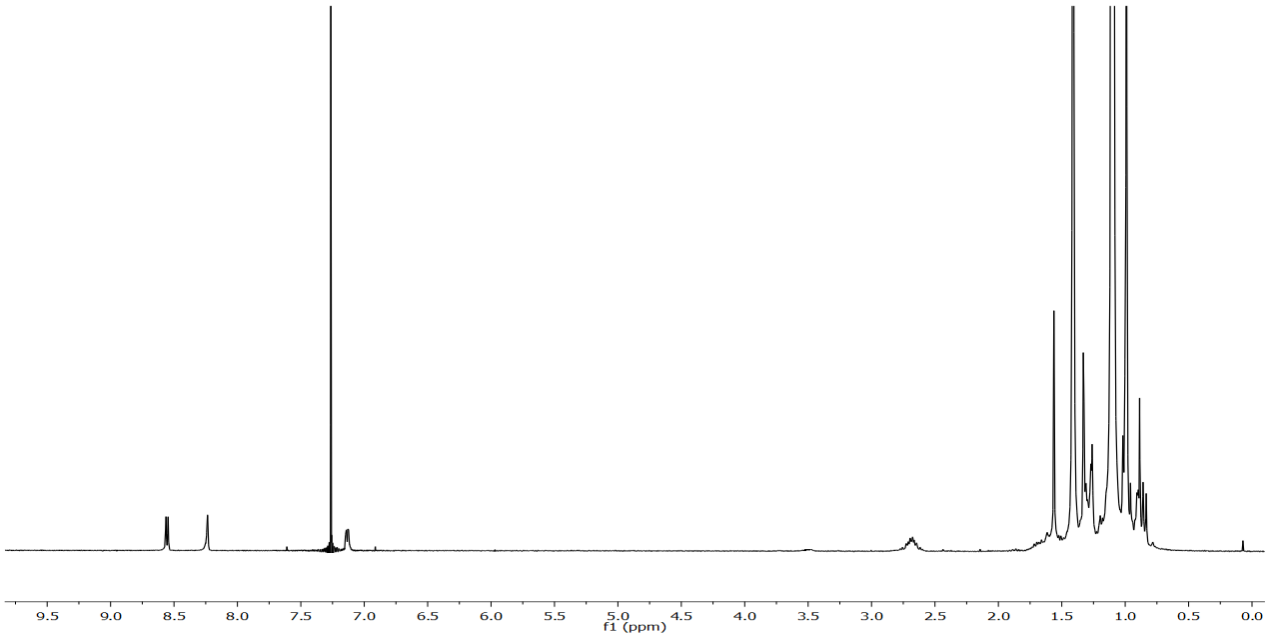
Poly(ethoxyethyl methacrylate) PEEMA (**14**).[4] The reaction was carried out in a 20 mmol scale and polymer was isolated as 77% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.09 (t, 2 H), 3.53 (t, 2 H), 3.50 (t, 2 H), 1.84-2.02 (m, 2 H), 1.22 (t, 3 H), 0.92 (t, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.6, 67.7, 66.5, 63.9, 54.1, 17.3, 13.4.

Poly(glycidyl methacrylate) PGMA (**16**).[4] The reaction was carried out in a 20 mmol scale and polymer was isolated as 72% yield. ^{1}H NMR (300 MHz, $CDCl_3$) δ (ppm):3.80 – 4.30 (br d, J = 7.0 Hz, 2 H), 3.18 – 3.24 (m, 1H), 2.60-2.85 (br d, 2 H), 1.88 – 2.00 (m, 2 H), 0.92 – 1.07 (t, *J* = 7.0 Hz, 3 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 177.0, 65.1, 62.2 50.5, 49.0, 45.0, 18.3.

Procedure for kinetic study of photocatalyzed polymerization of ethyl methacrylate: A 10-mL Schlenk tube was equipped with a magnetic stir bar and sealed with a rubber septum. Ethyl methacrylate (2.5 mL, 20 mmol), **8** (13.8 mg, 0.01 mol %) dissolved in 2.5 mL of toluene was added to the tube. The reaction mixture was degassed by 3 freeze pump-thaw cycles. Then the tube was filled with nitrogen, and both *N*,*N*-diisopropylethylamine (170 μL, 1mmol) and ethyl 2-bromoisobutyrate (75 μL, 0.5 mmol) were injected via syringe. The reaction was stirred under irradiation of a household lamp at ambient temperature and aliquots (50 μL) of reaction mixture were removed from the reaction mixture via syringe at different time points. A known amount of 1,1,2,2-tetrachloroethane (~0.5 mmol was added to each sample as an internal standard, and each sample was analyzed by ^{1}H NMR to determine the conversion and the concentration of the monomer. After the NMR analysis, methanol was added to each sample in order to precipitate out the polymer products which were analyzed by GPC.

^{1}H and ^{13}C NMR spectra

PIB-bipyridine (5) – ^{1}H NMR



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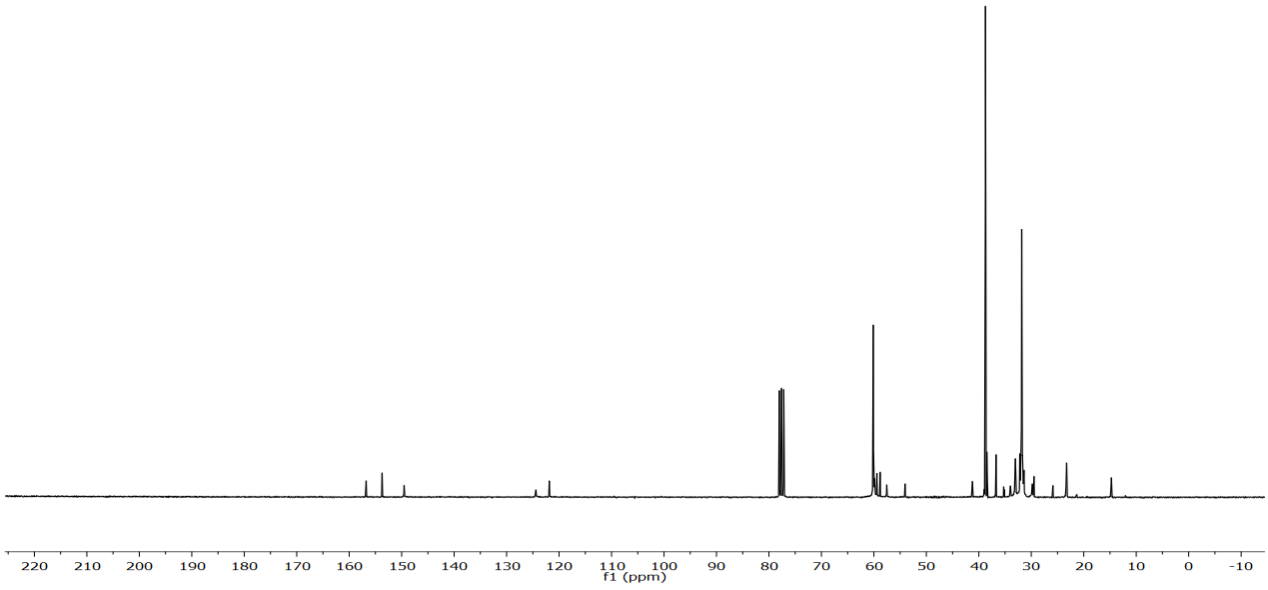
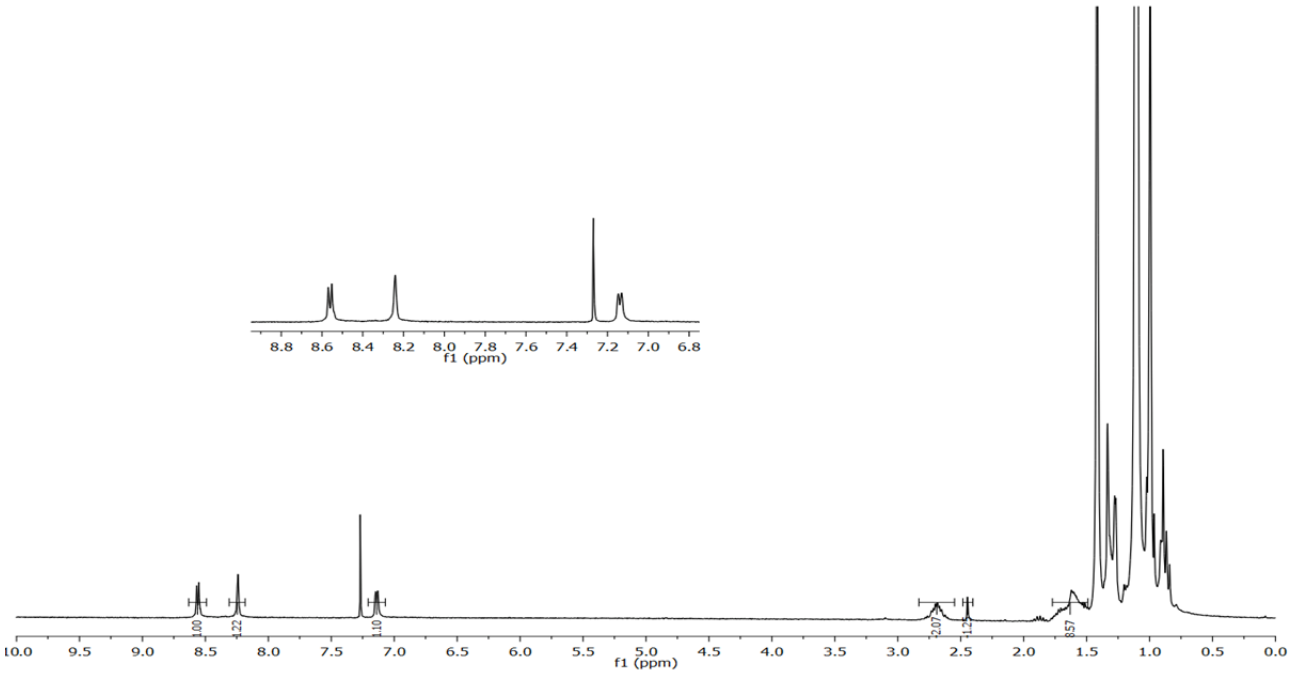
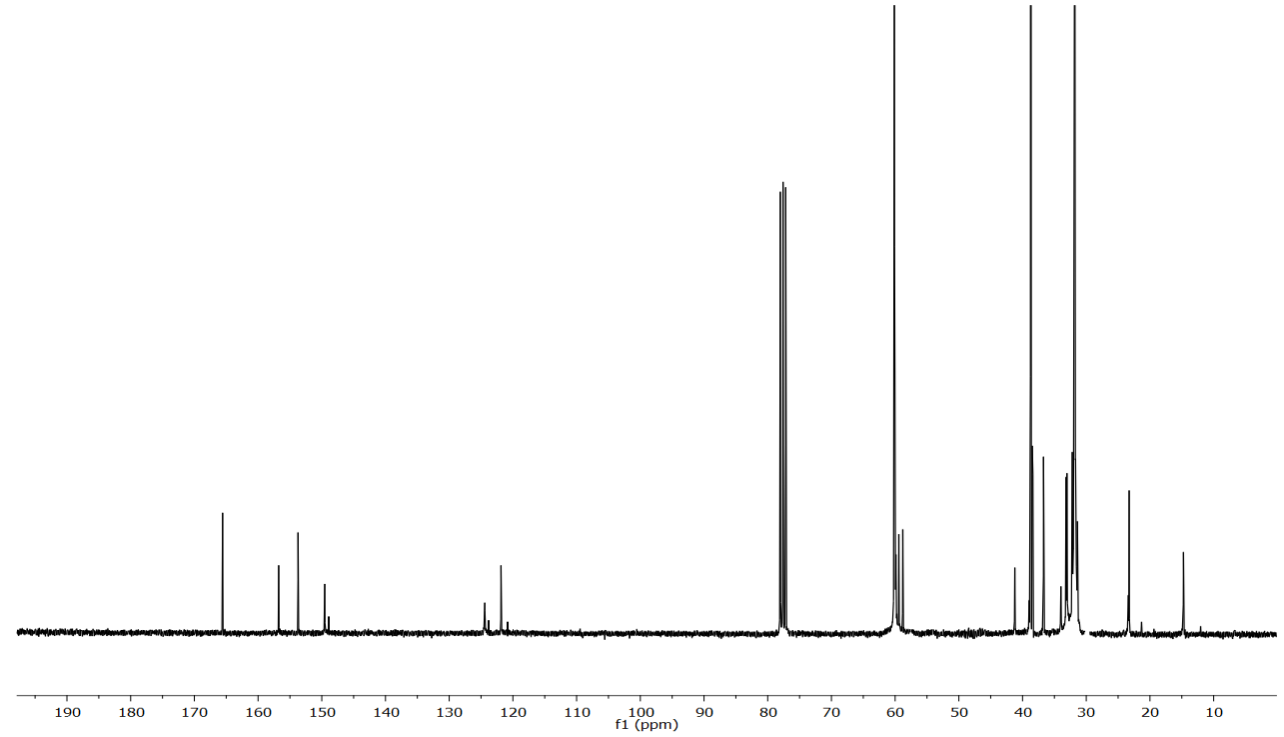


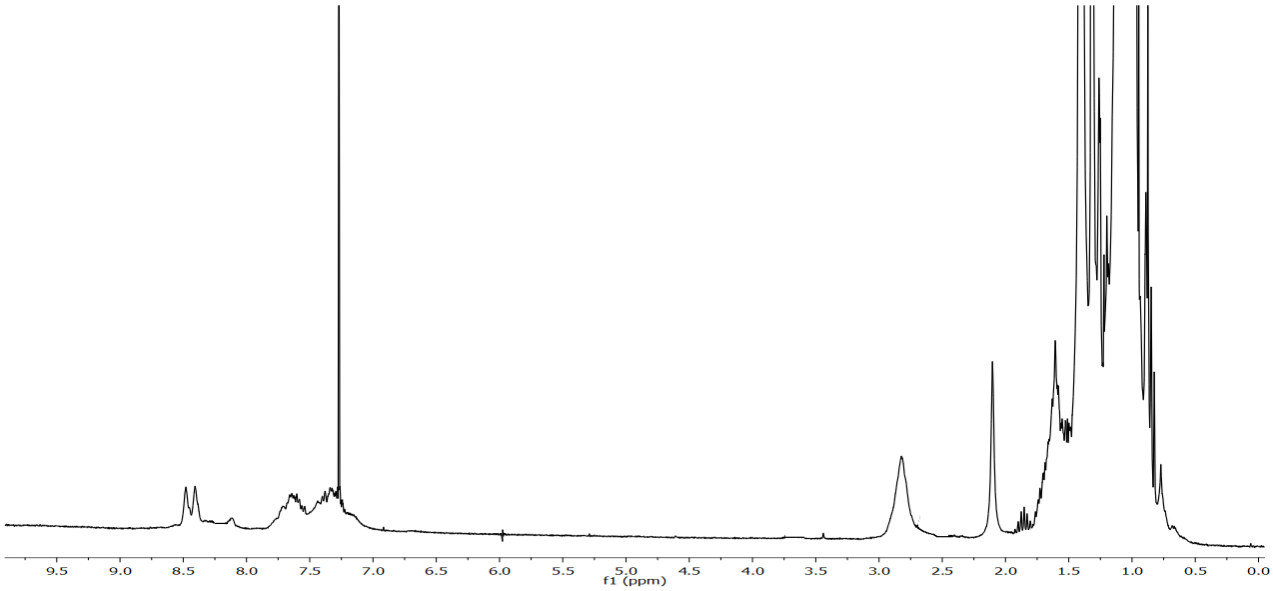
PIB-bipyridine (5 and 6) mixture - ^{1}H NMR



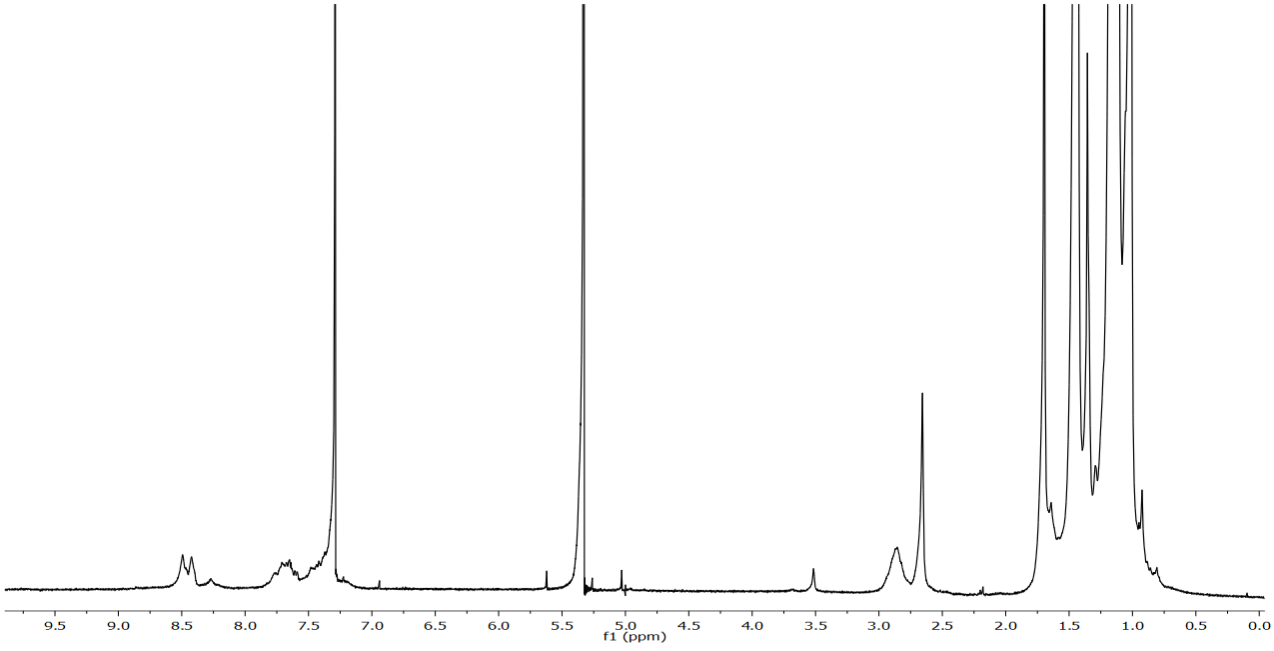
PIB-bipyridine (5 and 6) mixture – ^{13}C NMR



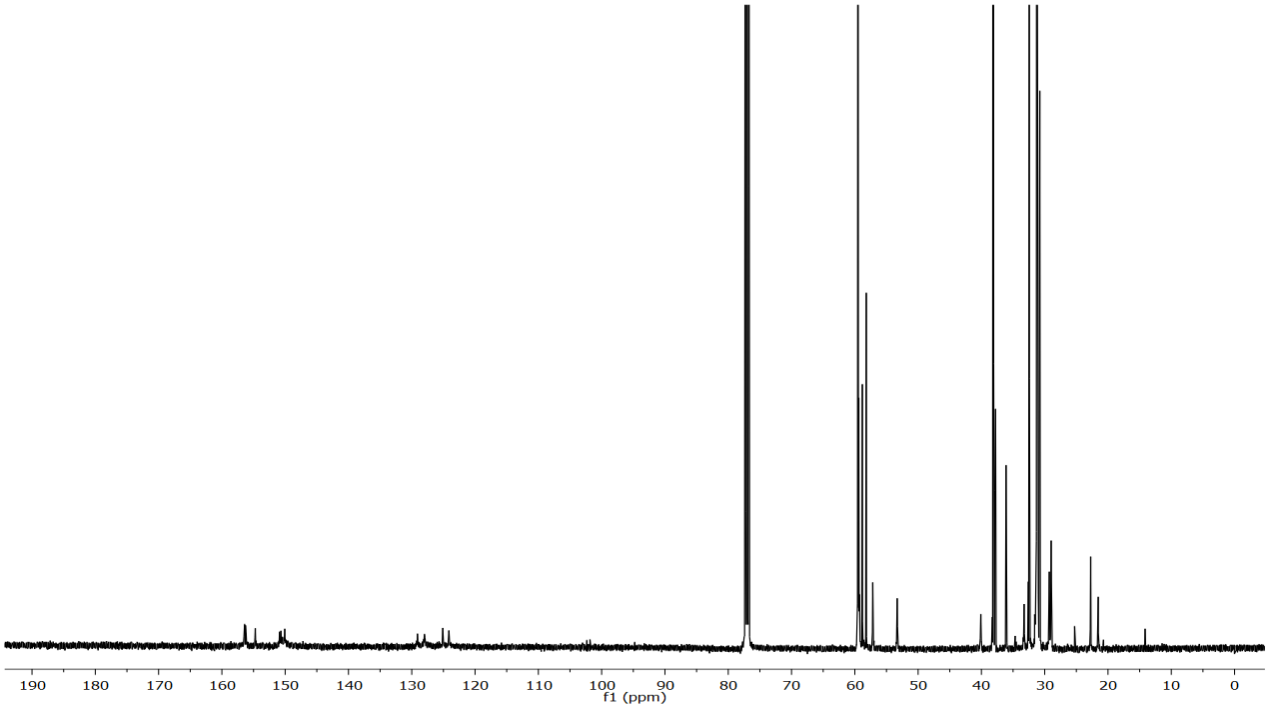
Ru(PIB-bpy)$_3$Cl$_2$ (7) – ^{1}H NMR



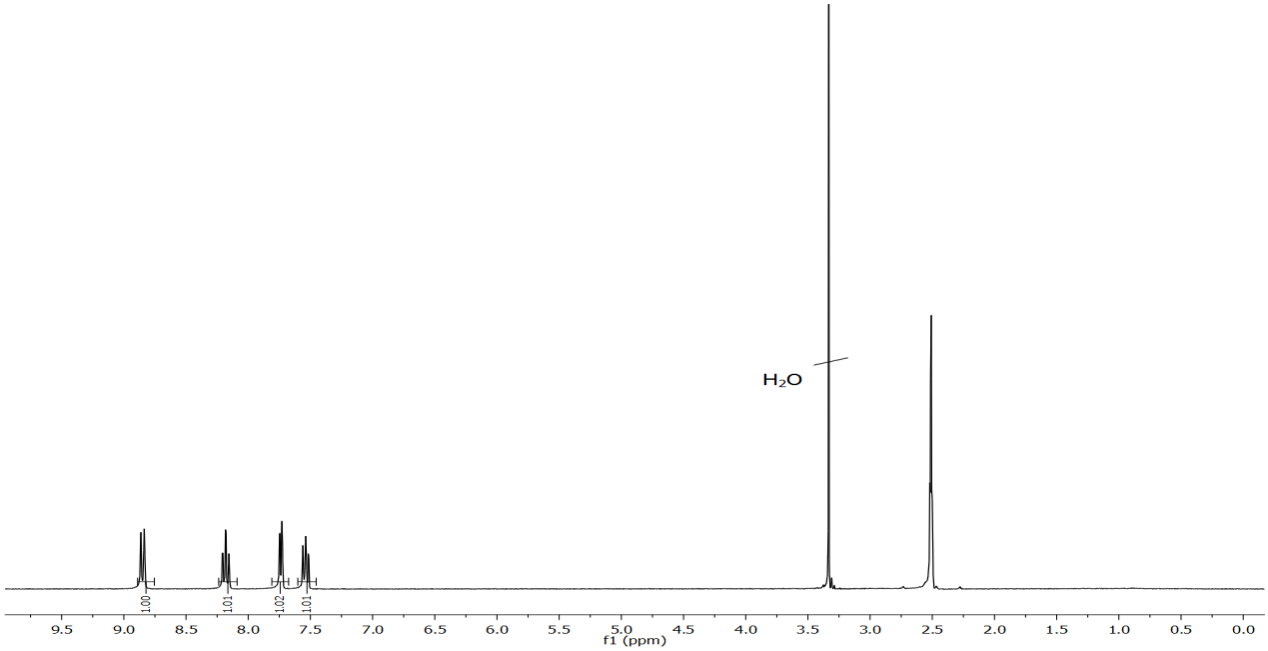
Ru(PIB-bpy)$_3$Cl$_2$ (8) – ^{1}H NMR



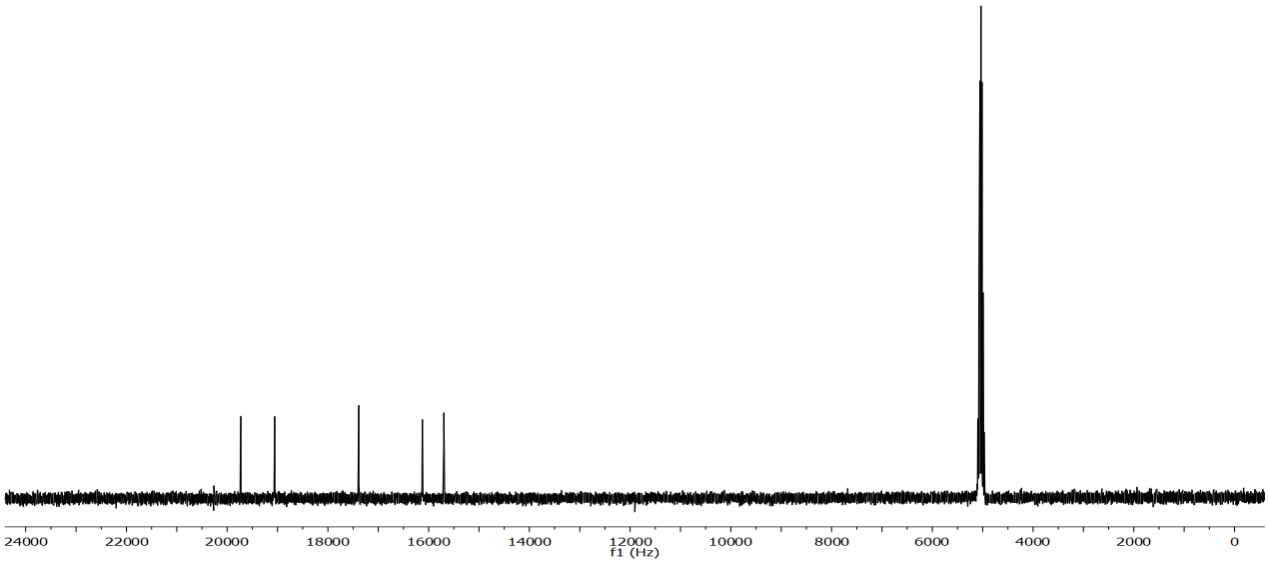
$Ru(PIB\text{-}bpy)_3Cl_2$ (8) – ^{13}C NMR



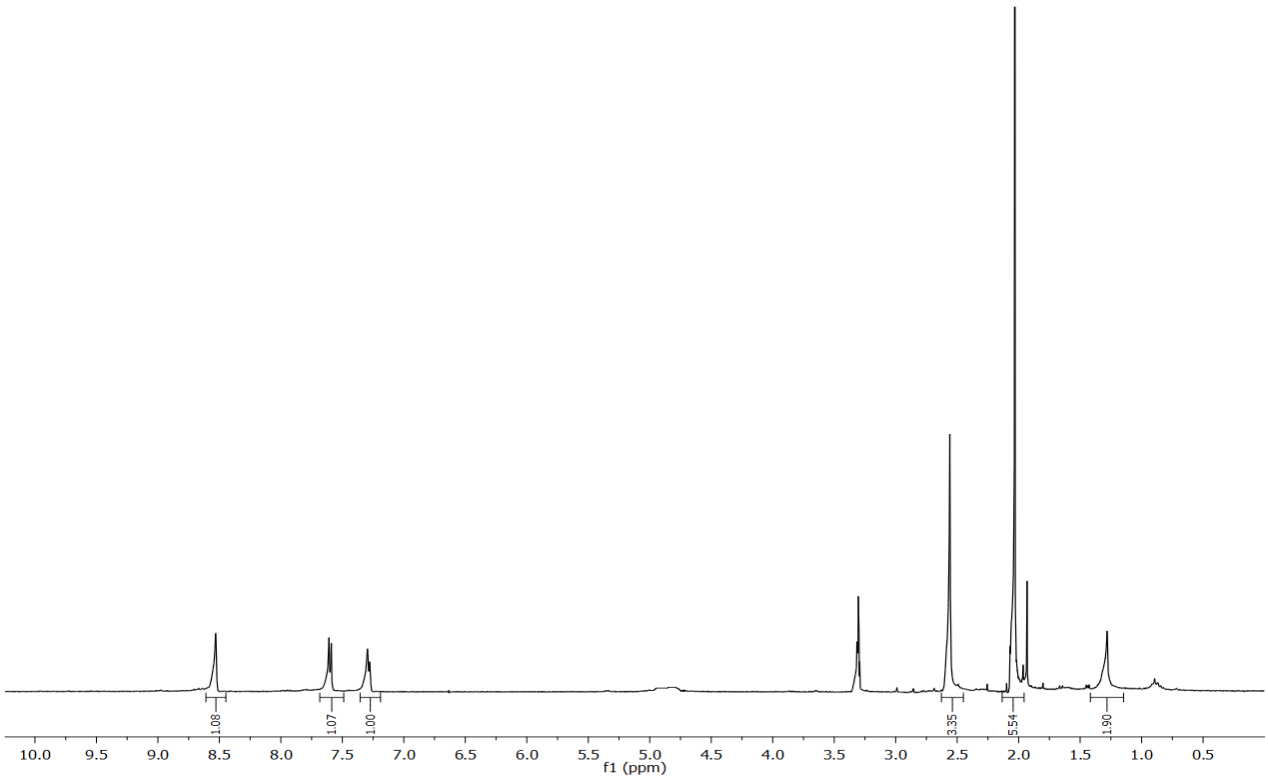
$Ru(bpy)_3(PF_6)_2$ (9) – ^{1}H NMR



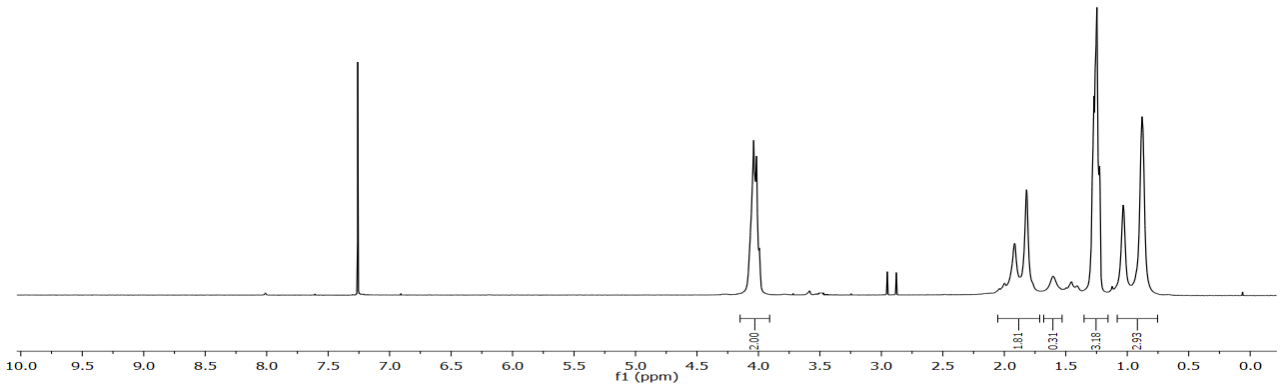
$Ru(bpy)_3(PF_6)_2$ (9) –13C NMR



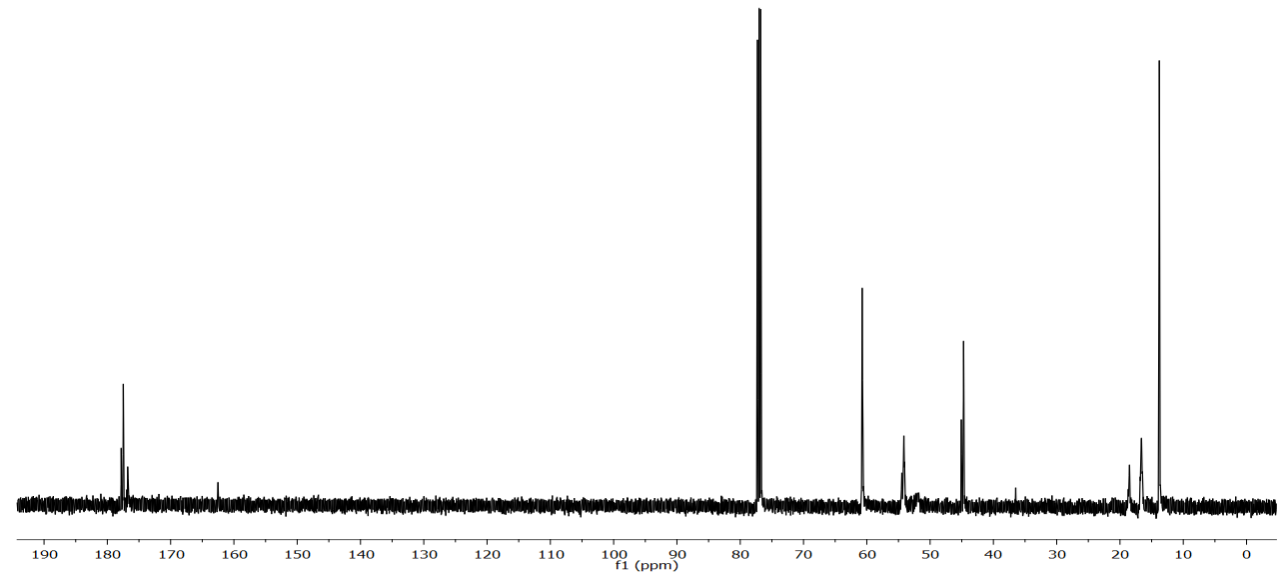
$Ru(bpy)_3(PF_6)_2$ (10) – ^{1}H NMR



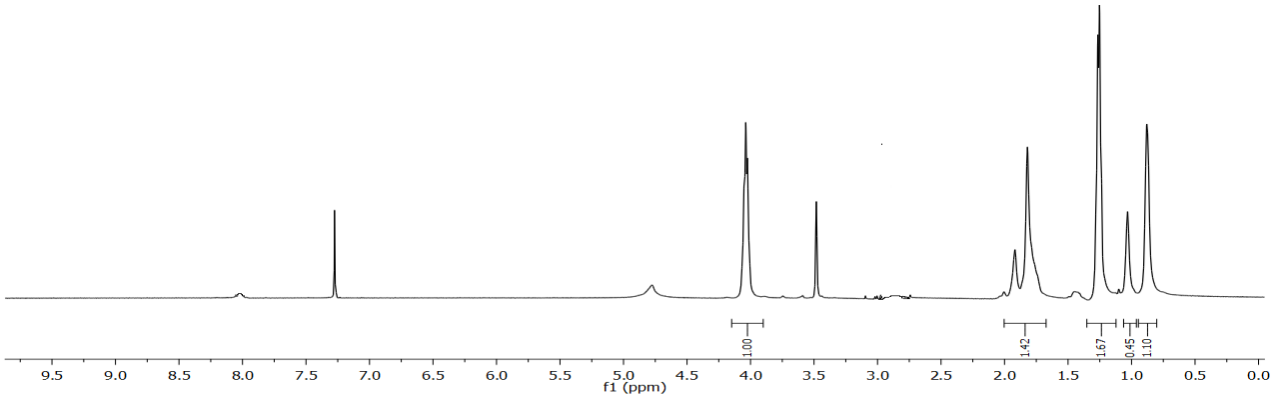
(PEMA) ^{1}H NMR (13)



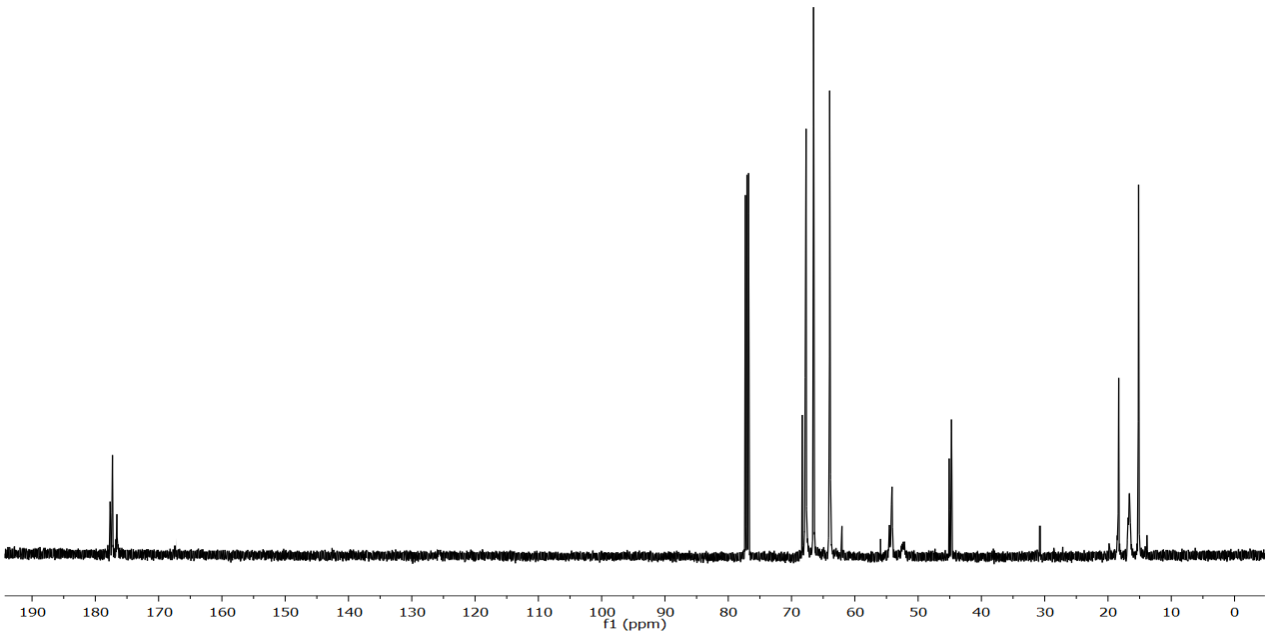
(PEMA) ^{13}C NMR (13)



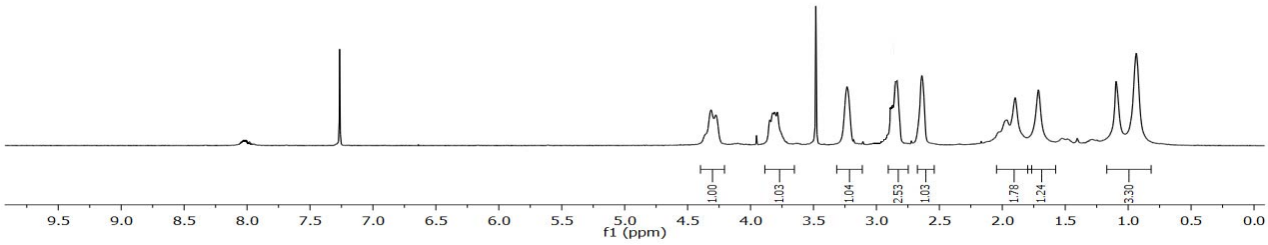
PEEMA ^{1}H NMR (15)



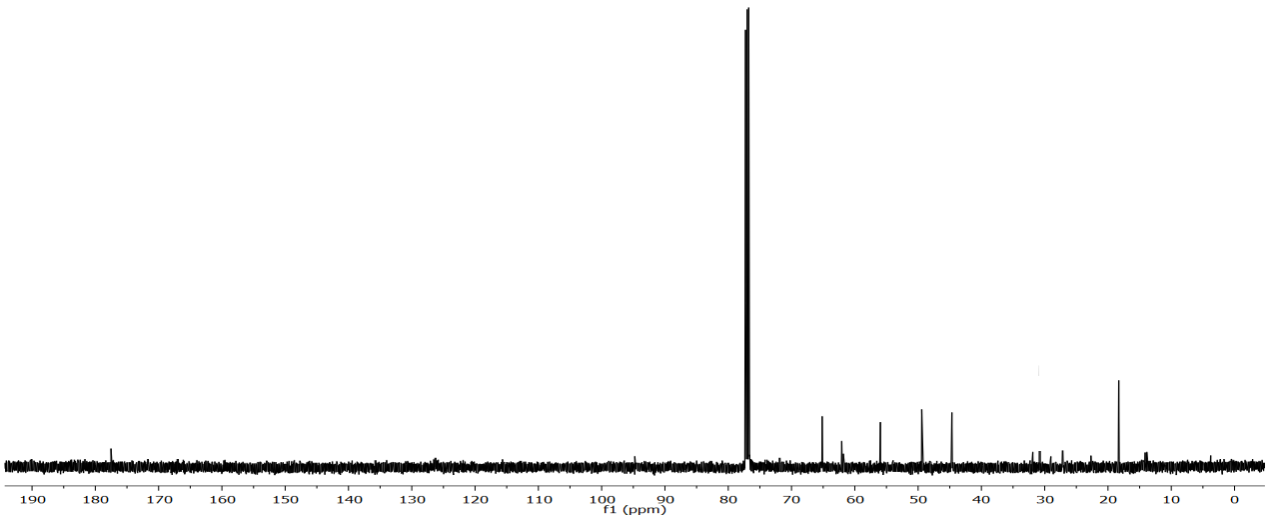
PEEMA ^{13}C NMR (15)



PGMA ^{1}H NMR (17)



PGMA ^{13}C NMR (17)



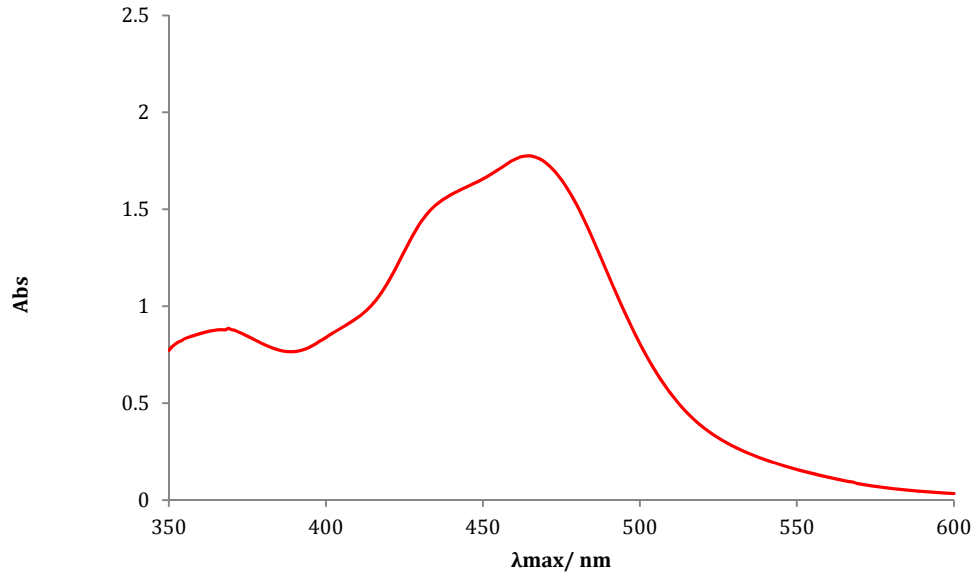


Figure S1. The UV-visible spectrum of the PIB-bound catalyst **8** as a 2×10^{-4} M solution in hexane.

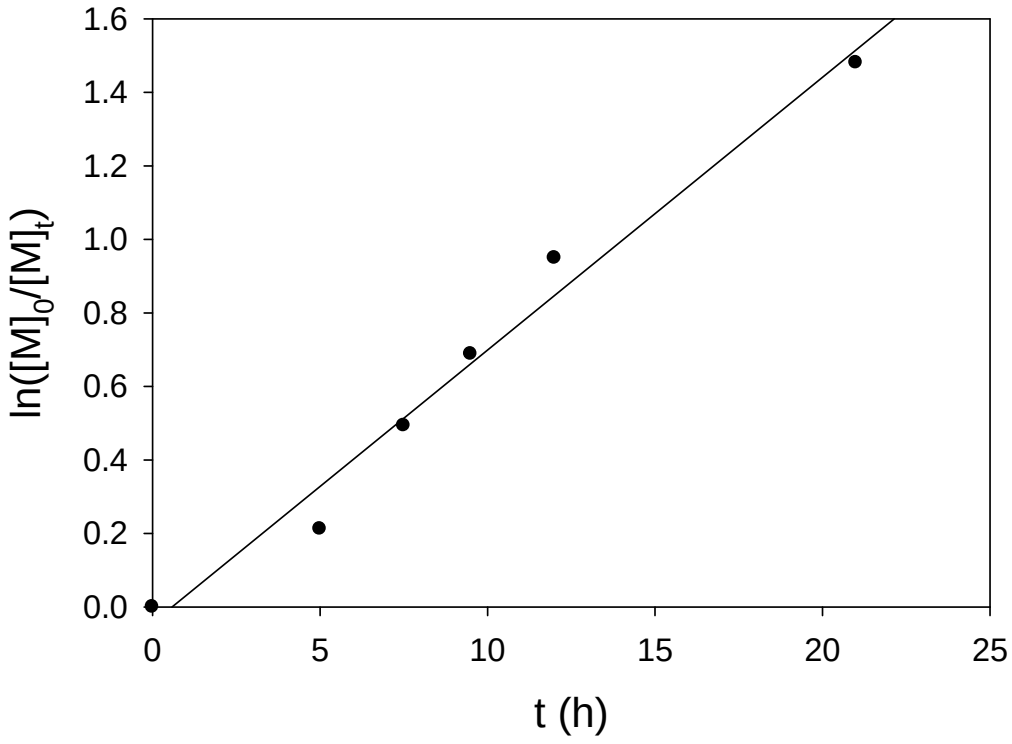


Figure S2. Semilogarithmic kinetic plot for polymerization of 12 in toluene (1:1, vol:vol) using **8** as a catalyst.

Supporting Information References

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