Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Recyclable Polyisobutylene (PIB)-bound Organic Photoredox Catalyst Catalyzed Polymerization Reactions

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General Information

Vinyl terminated PIB (Glissopal 1000) with molecular weight of 1000 Da was provided by BASF.[1] Methyl acrylate, 2-ethoxyethyl methacrylate, and benzyl methacrylate were passed through a plug of basic alumina before use. Other reagents and solvents were purchased from commercial suppliers and used without further purification unless otherwise stated. All glassware was oven-dried or flame-dried before use. ^{1}H NMR and ^{13}C NMR spectra were obtained on either an Inova 300 spectrometer operating at 299.91 MHz for proton and 75.41for carbon nuclei, or an Inova 500 spectrometer operating at 499.95 MHz for proton and 125.72 MHz for carbon nuclei at room temperature. Chemical shifts are reported in ppm and referenced to the residual proton in $CDCl_3$, and spin multiplicities are indicated by the following symbols: s (singlet), d (doublet), t (triplet), dd (doublet of doublet) and m (multiplet). A Viscotek gel permeation chromatograph (GPC) that was calibrated with polystyrene standards was used to analyze the molecular weight of the polymer products. PIB-OH **2**[2] was prepared following the literature procedures.

Synthesis of PIB-bound Iodide (3). A 250-mL round-bottomed flask equipped with a magnetic stir bar was charged with triphenylphosphine (3.64 g, 13.9 mmol), iodine (3.55 g, 28 mmol), imidazole (0.92 g, 13.5 mmol) and these reagents were dissolved in 100 mL of dichloromethane. After stirring for 10 min, a solution of PIB-bound alcohol **2** (14.7 g, 10.8 mmol) in 25 mL of dichloromethane was added dropwise to the reaction mixture. The reaction mixture was then allowed to stir at room temperature for 20 h. At this point, the solvent was removed under reduced pressure. The resulting residue was dissolved in 250 mL of hexane, and the hexane layer was extracted with 90% ethanol/water (50 mL x 2), DMF (25 mL x 3), and brine (50 mL). Then the hexane phase was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to afford the product **3** (16.1 g, 9.1 mmol, 84% yield) as colorless viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 3.28 (dd, 1 H), 3.14 (dd, 1 H), 2.05-0.85 (m).

Synthesis of PIB-bound Triphenylphosphonium Iodide (4). A 50-mL pressure vessel equipped with a magnetic stir bar was charged with PIB-bound iodide **3** (7.22 g, 4.1 mmol) and triphenylphosphine (4.0 g, 15.2 mmol) and 15 mL of toluene and 15 mL DMF were introduced. The vessel was sealed with a rubber septum and N_2 was bubbled through the reaction mixture for 15 min. At this point, the rubber septum was replaced with the pressure vessel lid and closed tightly. The reaction mixture was allowed to stir at 160 °C for 48 h. Then the reaction mixture was allowed to cool to room temperature and diluted with 250 mL of hexane. The solution was transferred to a separatory funnel and was extracted with DMF (25 mL x 3), and brine (50 mL). Then the hexane layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by a neutral alumina column using dichloromethane/methanol (19:1, v/v) as the eluent to afford the desired product **4** (5.54 g, 3.6 mmol, 80% yield) as light yellow viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.81 (m, 16 H), 4.32 (m, 1 H), 3.17 (m, 1 H), 1.75-0.75 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.0, 133.8, 133.7, 132.1, 132.0, 131.9, 130.5, 130.4, 128.5, 128.4, 119.2, 118.6, 59.5-23.8 (multiple peaks).

Synthesis of PIB-bound Bromobenzene (5). A 100-mL round-bottomed flask equipped with a magnetic stir bar was sealed with a rubber septum. Then a solution of PIB-bound triphenylphosphonium iodide **4** (5.33 g, 3.5 mmol) in 50 mL distilled anhydrous THF was transferred into the flask by forced siphon and cooled to -78 °C. Then 2.3 mL of a 1.6M solution of *n*-BuLi in hexane (3.68 mmol) was added to the flask by syringe, and the reaction mixture was allowed to stir at -78 °C. After stirring for 2 h, a solution of 4-bromobenzylaldehyde (0.9 g, 4.86 mmol) in 10 mL of THF was added to the flask via cannula. This reaction mixture was allowed to stir at -78 °C and slowly warmed to room temperature for 72 h. Then the reaction was quenched by methanol, and the solvent was removed under reduced pressure. The resulting crude materials were dissolved in 200 mL of hexane and were extracted with 50 mL of 90% ethanol/water for three times. Then the hexane layer was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane as the eluent to afford the product **5** (3.64 g, 2.6 mmol, 74% yield) as colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.48 (d, 2 H), 7.43 (d, 1 H), 7.22 (d, 1 H), 7.16 (d, 1H), 6.19 (m, 2H), 5.58 (dd, 1H), 2.89 (m), 2.53 (m), 1.95-0.75 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.5, 140.1, 137.0, 131.5, 131.3, 127.4, 125.9, 124.6, 120.2, 59.5-14.1 (multiple peaks).

Synthesis of PIB-bound Bromobenzene (6). A 50-mL Schlenk flask equipped charged with a magnetic stir bar was charged with PIB-bound bromobenzene **5** (3.60 g, 2.57 mmol), 10 wt.% palladium on carbon (54.1 mg), 20 mL heptane and 20 mL ethyl acetate. Then this Schlenk tube was connected to a balloon filled with hydrogen, and the reaction mixture was allowed to stir for 48 h at room temperature. At this point, the reaction mixture was filtered through Celite, and the solvent was removed under reduced pressure to afford the product **6** (3.59 g, 2.54 mmol, 99% yield) as colorless viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.40 (d, 2 H), 7.07 (d, 2 H), 2.57 (m), 1.65-0.85 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 142.0, 131.3, 130.1, 119.2, 59.5-14.1 (multiple peaks).

Synthesis of PIB-bound PTH (7). A 100-mL round bottom flask equipped with a magnetic stir bar was charged with PIB-bound bromobenzene **6** (3.46 g, 2.45 mmol), phenothiazine (0.69 mg, 3.46 mmol), sodium *tert*-butoxide (0.46 g, 4.78 mmol), RuPhos (33.2 mg, 0.07 mmol), RuPhos precatalyst (62.5 mg, 0.08 mmol), and 50 mL of dioxane and was sealed with a rubber septum. The reaction mixture was allowed to stir at 110 °C for 20 h at which point the reaction was allowed to cool to room temperature. At this point, 150 mL of hexane was added, and the non-polar phase was extracted with water (30 mL), acetonitrile (30 mL x 3), and brine (30 mL). Then the hexane phase was dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure. The crude product was purified by silica gel column chromatography using hexane as the eluent to obtain the product **7** (3.42 g, 1.96 mmol, 80% yield) as a light yellow viscous oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.42 (d, 2 H), 7.30 (d, 2 H), 7.01 (d, 2 H), 6.81 (m, 4 H), 6.20 (dd, 2 H), 2.71 (m), 1.95-0.85 (m); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.5, 143.4, 138.2, 130.8, 130.7, 126.8, 126.6, 122.2, 119.7, 115.7, 59.5-11.4 (multiple peaks).

Procedure for Polymerization of 9 Catalyzed by 7 Using DMA/heptane Solvent Mixture. A 20-mL vial equipped with a magnetic stir bar was charged with PIB-bound PTH **7** (26.5 mg, 15 μmol), methyl methacrylate (1 mL, 9.3 mmol) in 1.75 mL of heptane and 0.25 mL DMA and was sealed with a copper wired rubber septum. The mixture was degassed by freeze-pump-thaw for 3 cycles, and then ethyl 2-bromoisobutyrate (30 μL, 0.24 mmol) was injected via syringe. The reaction mixture was allowed to stir under the irradiation of a 23 W household fluorescent bulb at ambient temperature for 15 h. After the reaction, 1.5 mL of heptane was added to the vial followed by adding 1.5 mL of DMA to insure that the catalyst and polymer were soluble in their respective phases. The mixture was centrifuged, and the DMA phase was removed. Then another 0.5 mL of DMA was added to extract any remaining polymer from the heptane phase. This DMA phase was separated from the heptane solution of **7** by centrifugation. The two DMA phases were combined and diluted with 2.5 mL of dichloromethane, and the polymer was precipitated by adding this solution to 100 mL of heptane. The polymer precipitate was isolated by vacuum filtration to afford the product **10** as a white solid (0.18 g/cycle). The catalyst containing heptane phase was concentrated under reduced pressure, and the recovered catalyst was reused for the following cycle by dissolving in 1.75 mL of heptane with 0.25 mL DMA, fresh monomer and initiator added. The product PMMA polymer **10** was characterized by NMR spectroscopy. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 3.61 (bs, $-OCH_3$), 1.83 (m, $-CH_2-$), 1.24 (m, isotactic methyl groups), 1.03 (bs, heterotactic methyls group), 0.86 (bs, syndiotactic methyl groups); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 178.1, 177.8, 177.0, 54.4, 54.2, 51.8, 44.9, 44.5, 31.9, 22.7, 18.7, 16.5, 14.1. The PMMA product **10** was dissolved in THF and analyzed using a Viscotek gel permeation chromatography that was calibrated with polystyrene standards to give the molecular weight (M_n) and molecular weight distribution (M_w/M_n) data of **10** shown in Table 1.

Procedure for Polymerization of 11 Catalyzed by 7 Using a DMA/heptane Solvent Mixture. A 20-mL vial equipped with a magnetic stir bar was charged with PIB-bound PTH **7** (25.2 mg, 14.4 μmol), 2-ethoxyethyl methacrylate (1.6 mL, 9.8 mmol) in 2.1 mL of heptane and 0.3 mL DMA. The mixture was degassed by freeze-pump-thaw for 3 cycles, and ethyl 2-bromoisobutyrate (30 μL, 0.24 mmol) were injected via syringe. The reaction mixture was allowed to stir under the irradiation of a 23 W compact fluorescent bulb at room temperature for 15 hours. After the reaction, 2 mL of heptane was added to the vial followed by adding 2 mL of DMA to dissolve the polymer. The mixture was centrifuged, and the DMA phase was removed. Then another 1 mL of DMA was added to extract the polymer and removed after centrifugation. The DMA phases were combined and diluted with 2.5 mL of dichloromethane, and the precipitation was achieved by adding 70 mL of heptane. The supernatant was removed and the polymer precipitates were dried under vacuum to afford the product **12** as a waxy gel (1.01 g/cycle). The catalyst containing heptane phase was concentrated under reduced pressure, and the recovered catalyst was reused for the following cycle by dissolving it in 2.1 mL of heptane with 0.3 mL DMA, fresh monomer and initiator added. The product polymer 12 was characterized by NMR spectroscopy and GPC. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm): 4.09 (bs, $-OCH_2-$), 3.62 (bs, $-OCH_2-$), 3.52 (bs, $-OCH_2-$), 2.14-1.84 (m, $-CH_2-$), 1.22 (b, $-CH_2\underline{CH_3}$), 1.07 and 0.92 (bs, stereoisomeric methyl groups); ^{13}C NMR

(125 MHz, $CDCl_3$) δ (ppm): 177.7, 177.3, 176.6, 67.9, 67.7, 66.5, 64.0, 54.2, 45.1, 44.7, 15.2. The PEEMA product **12** was dissolved in THF and analyzed using a Viscotek gel permeation chromatograph that was calibrated with polystyrene standards to give the molecular weight (M_n) and molecular weight distribution (M_w/M_n) data of **12** shown in Table 1.

Kinetic Study of Light-Mediated Polymerization Catalyzed by 7. A 20 mL vial equipped with a magnetic stir bar was charged with benzyl methacrylate (1.7 mL, 10 mmol), PIB-bound PTH **7** (26.1 mg, 15 μmol), and 2 mL of THF and sealed with a copper wired rubber septum. The reaction mixture was degassed by freeze-pump-thaw for 3 cycles, and ethyl α-bromophenylacetate (35 μL, 0.2 mmol) were injected via syringe. The reaction mixture was allowed to stir under the irradiation of a 23 W compact fluorescent bulb at room temperature. Aliquots of the reaction mixture were removed from the vial by syringe at different time points and were analyzed by ^1H NMR spectroscopy to determine the conversions of the monomer. The PBnMA product **14** was dissolved in THF and analyzed using a Viscotek gel permeation chromatograph that was calibrated with polystyrene standards to give the molecular weight (M_n) and molecular weight distribution (M_w/M_n) data of **14** at different conversions that are shown in Figure 3. The PBnMA product **14** was also characterized by NMR spectroscopy. ^1H NMR (500 MHz, $CDCl_3$) δ (ppm): 7.28 (bs, phenyl), 4.90 (bs, $-OCH_2-$), 1.96 (m, $-CH_2-$), 0.94 and 0.75 (stereoisomeric methyl groups); ^{13}C NMR (125 MHz, $CDCl_3$) δ (ppm): 177.4, 177.1, 176.4, 136.4, 135.1, 128.5, 128.4, 128.2, 66.8, 45.1, 44.7.

^{1}H NMR Spectroscopic Analysis for Contamination of 7 in PMMA, PEEMA, and PBnMA Polymer Products. As shown in Figure S19, PIB_{1000} has a broad singlet at 1.14 δ for the 102 protons of the 34 methyl groups of the repeating subunits in this polymer. Figure S20 shows the same ^1H NMR spectral region of PMMA. There is a miniscule peak at 1.14 δ whose area integration is 1 which represent 102 protons per mole of PIB. There are peaks ta 1.03 and 0.87 δ for the methyl groups of PMMA.[3] These peaks have a total integral of 224. The M_n value for this PMMA product was 3300 Da. Thus, the degree of polymerization is 33 and these signals with an integral of 224 correspond to 99 protons per mole of PMMA. The relative area of the signals due to the moles of PMMA and the moles of PIB is 2.26/0.01, and the calculated mol% of PIB present in this PMMA product is 0.44 mol% which corresponds to 0.17 wt% of PIB in the

PMMA product. A similar calculation for the PEEMA product and the PBnMA product shows that PIB contamination in those products was 0.48 wt% and 0.11 wt% respectively.

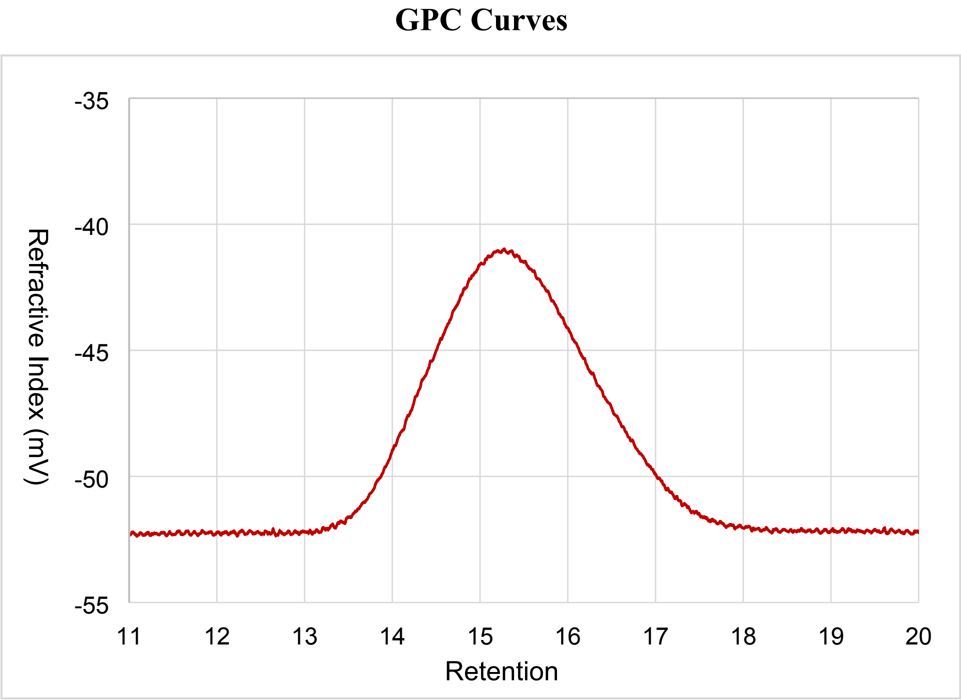

Figure S1. GPC trace of polymer product **12** (PEEMA).

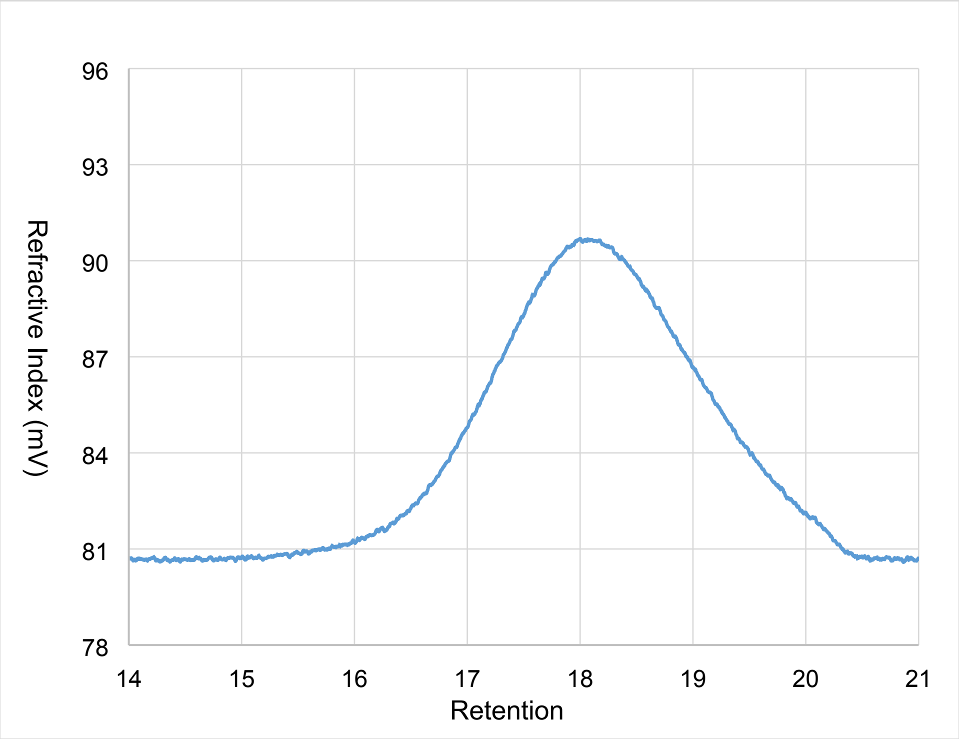

Figure S2. GPC trace of PIB.

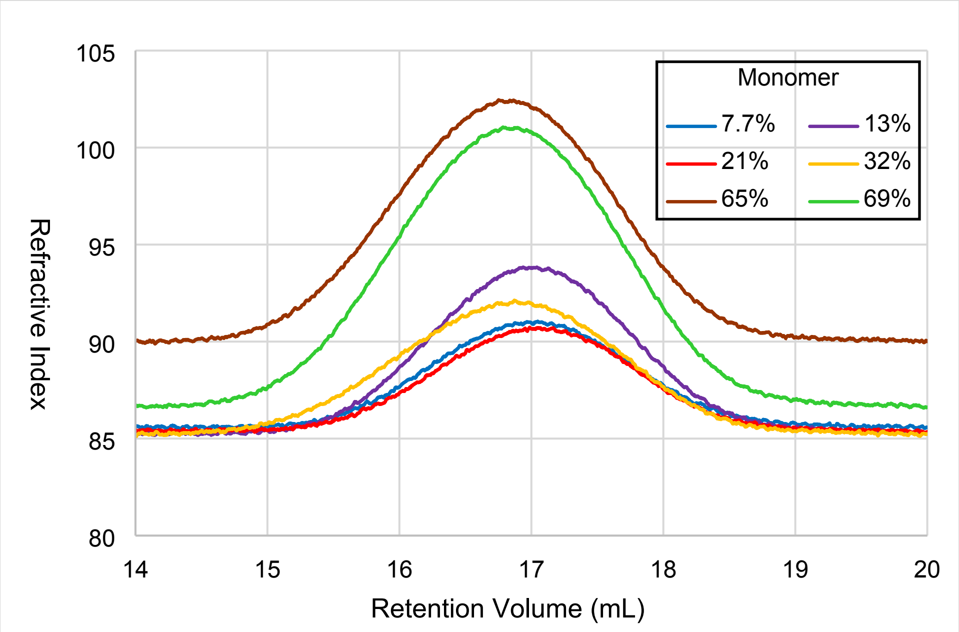

Figure S3. GPC trace of polymer product **14** PBnMA at different conversions.

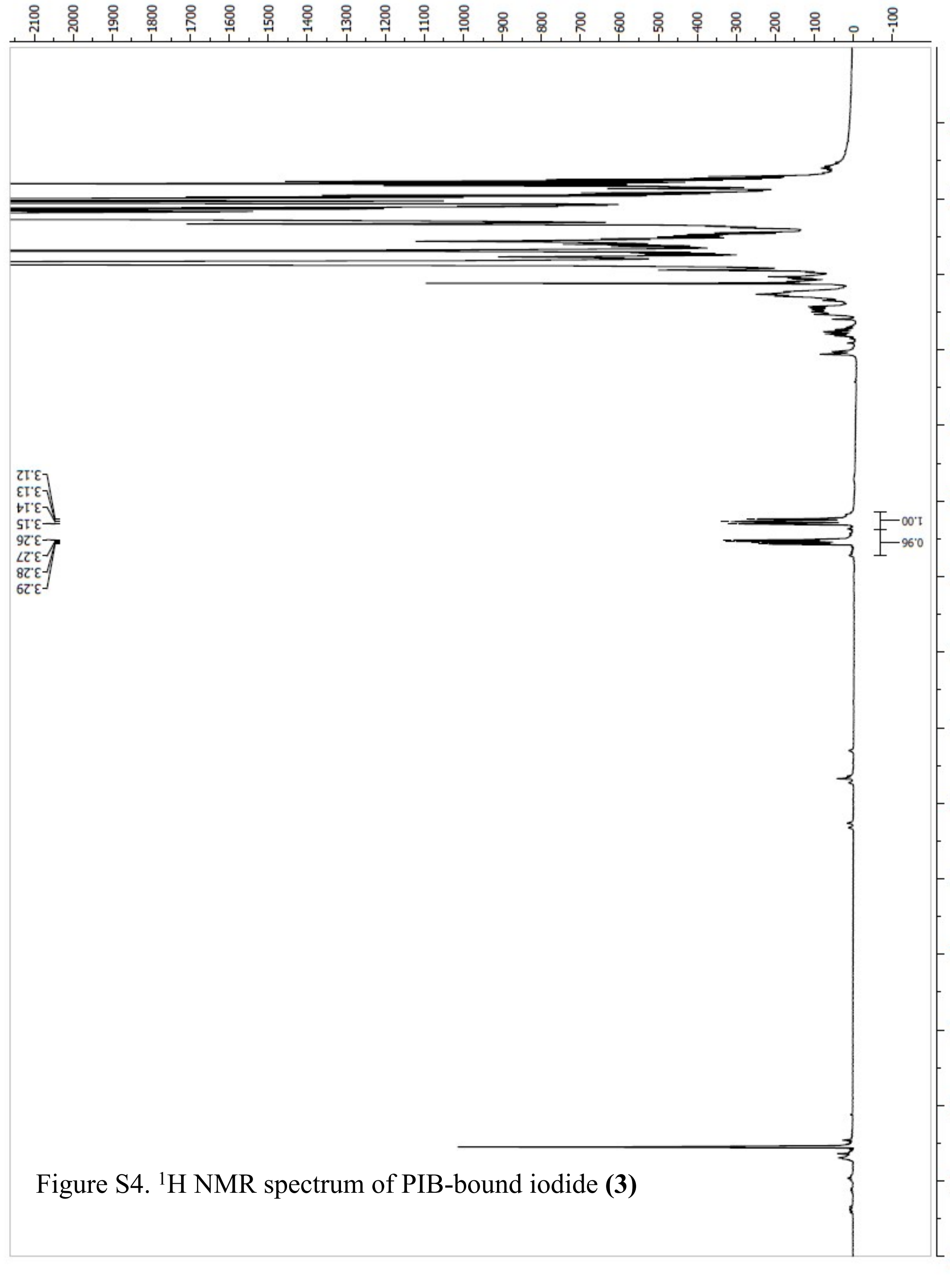

Figure S4. ^{1}H NMR spectrum of PIB-bound iodide **(3)**

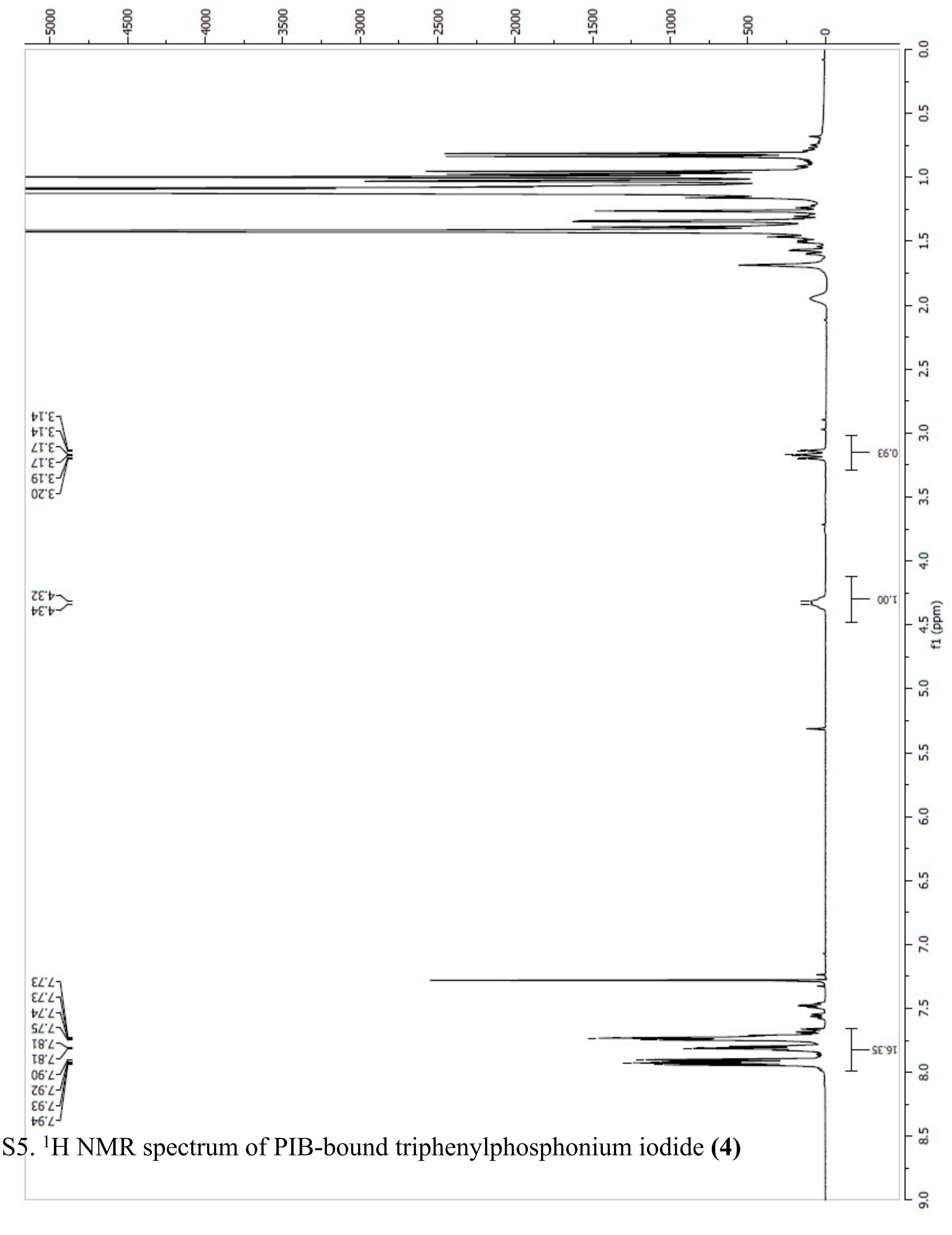

Figure S5. ^{1}H NMR spectrum of PIB-bound triphenylphosphonium iodide **(4)**

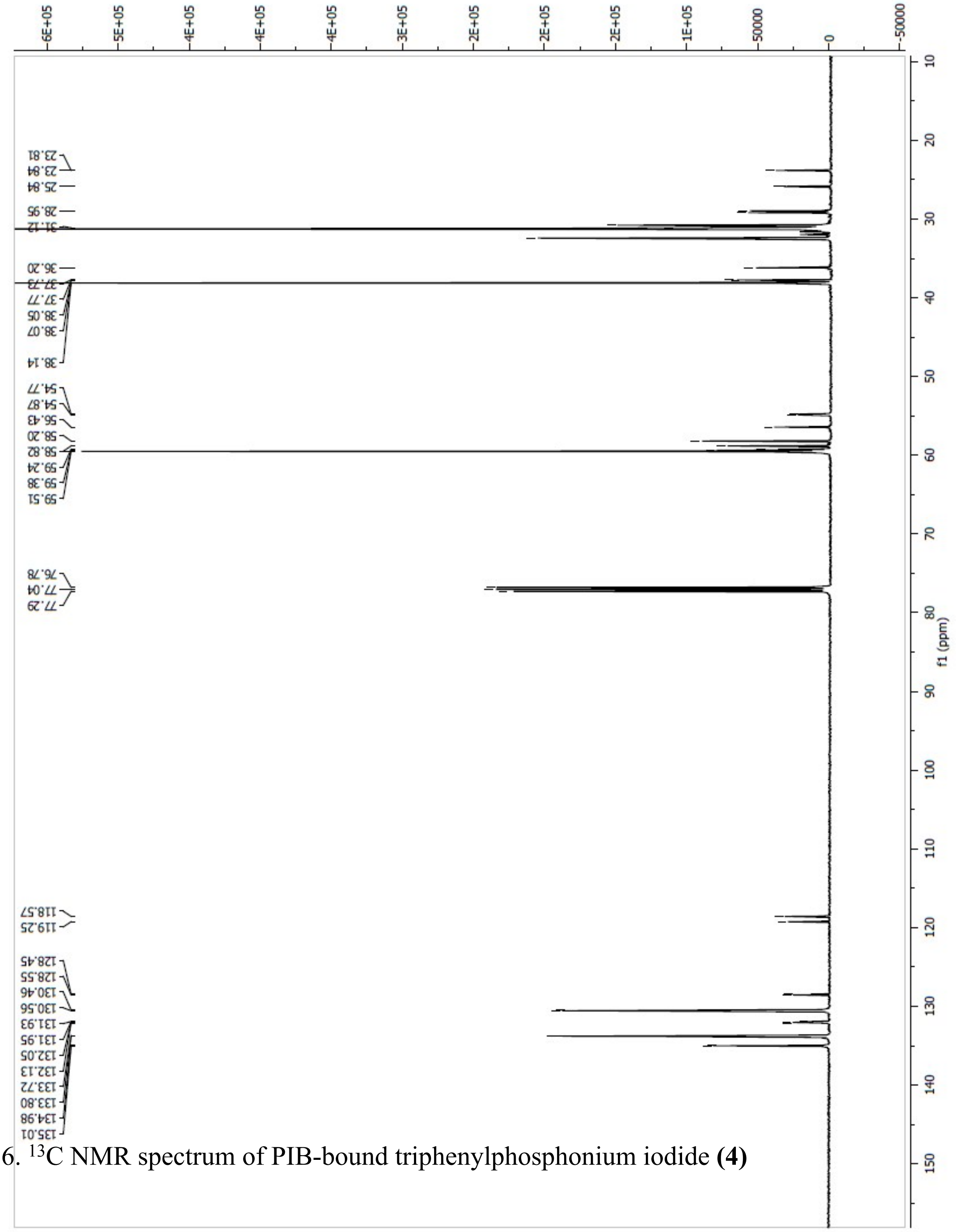

Figure S6. ^{13}C NMR spectrum of PIB-bound triphenylphosphonium iodide **(4)**

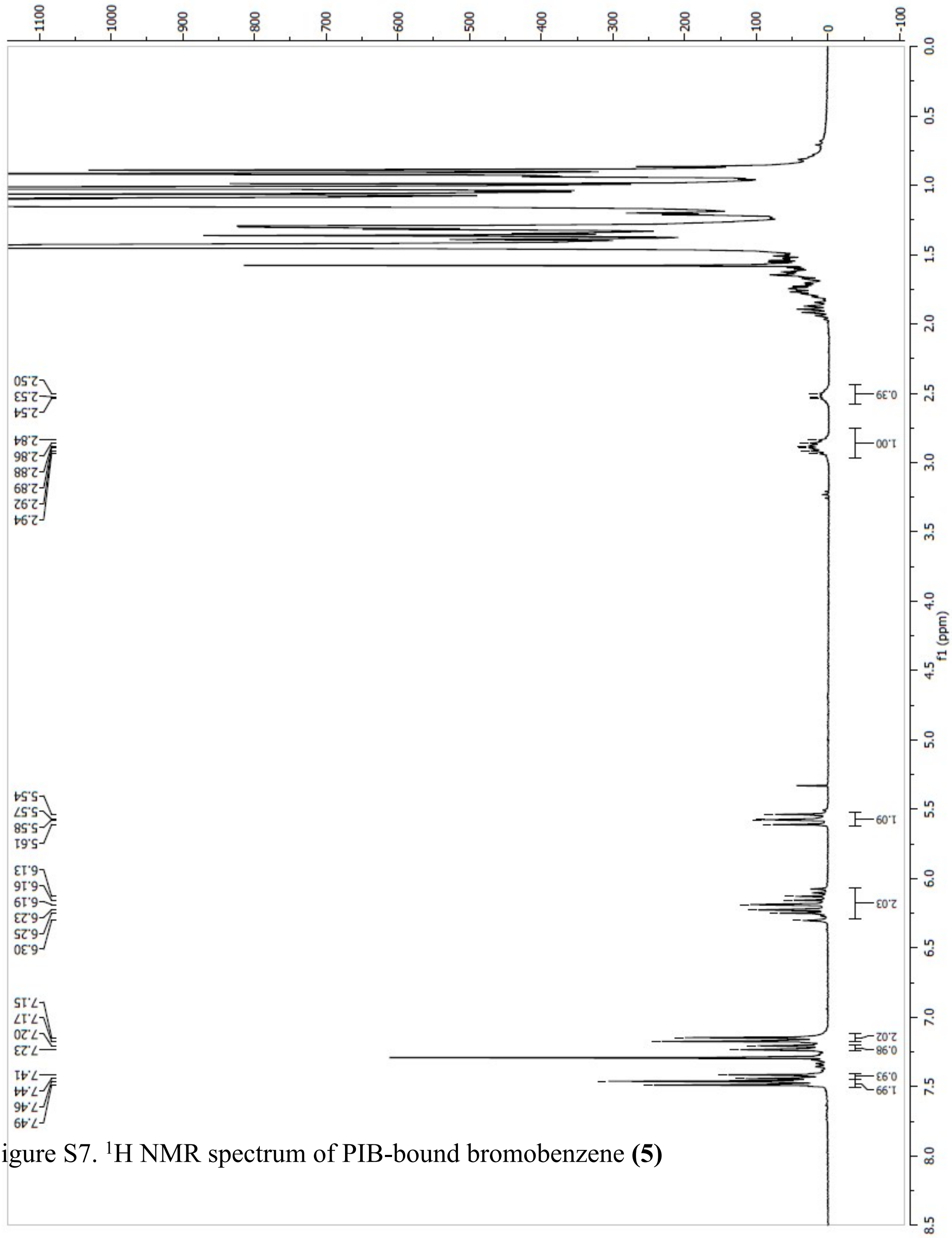

Figure S7. ^{1}H NMR spectrum of PIB-bound bromobenzene **(5)**

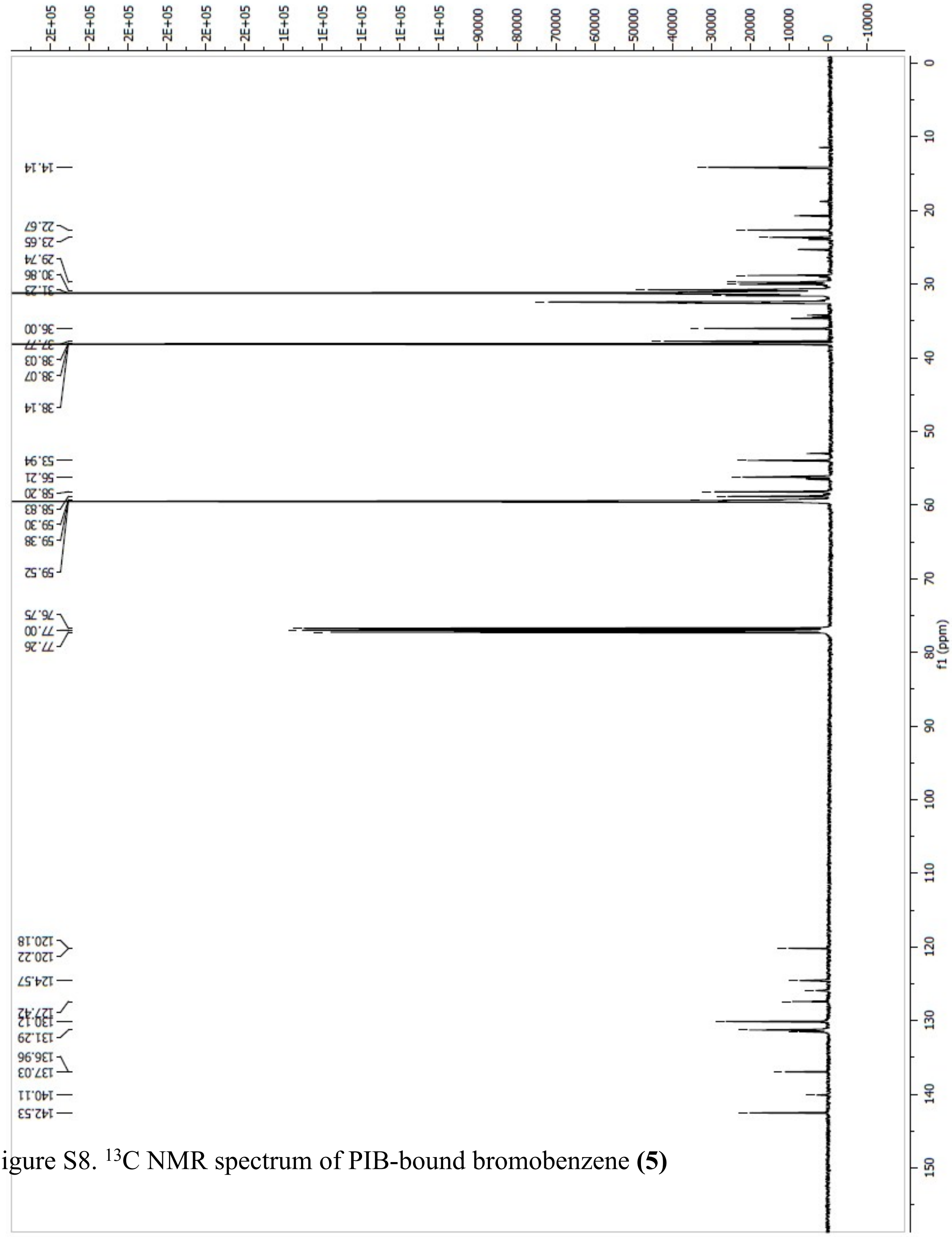

Figure S8. ^{13}C NMR spectrum of PIB-bound bromobenzene **(5)**

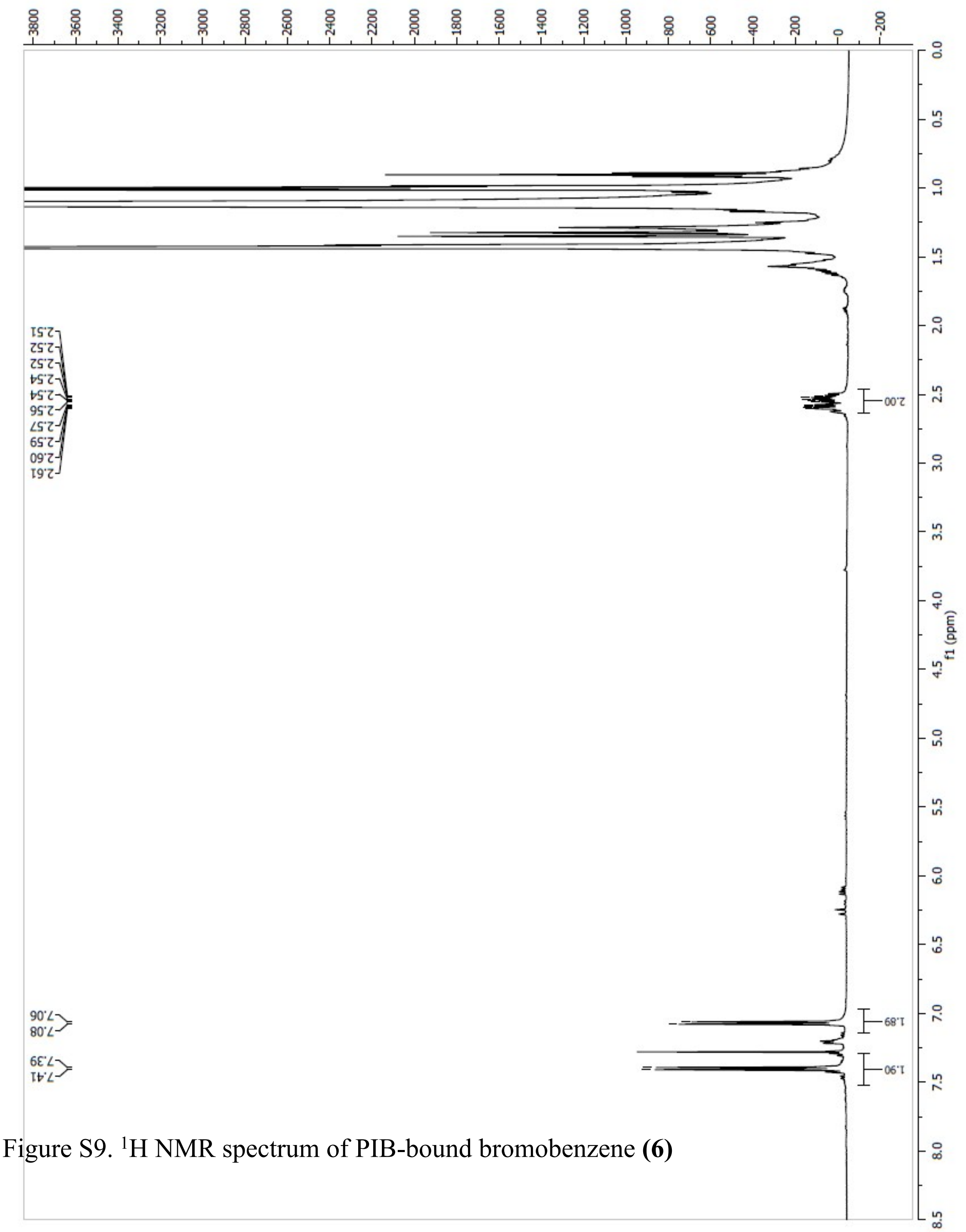

Figure S9. ^{1}H NMR spectrum of PIB-bound bromobenzene **(6)**

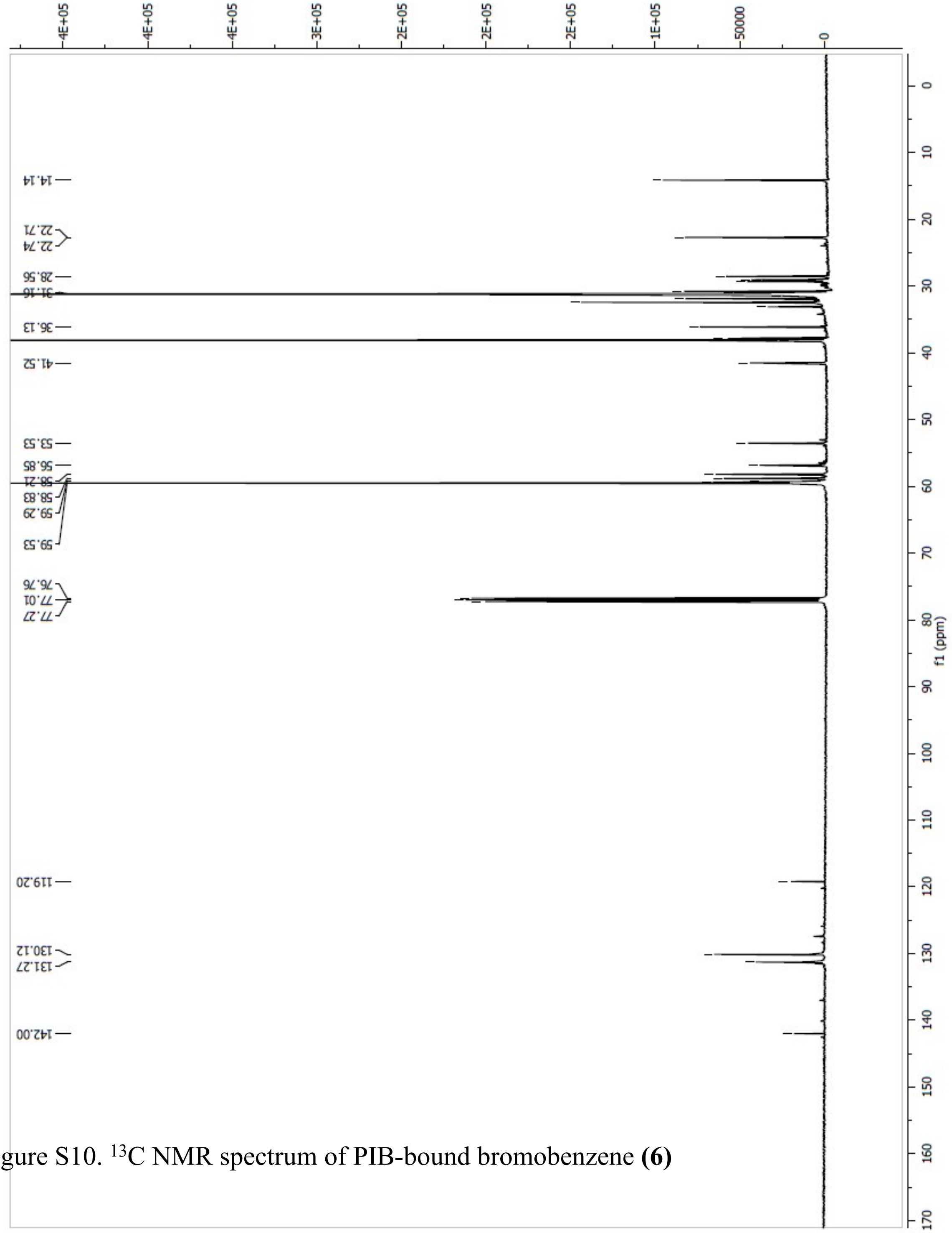

Figure S10. ^{13}C NMR spectrum of PIB-bound bromobenzene **(6)**

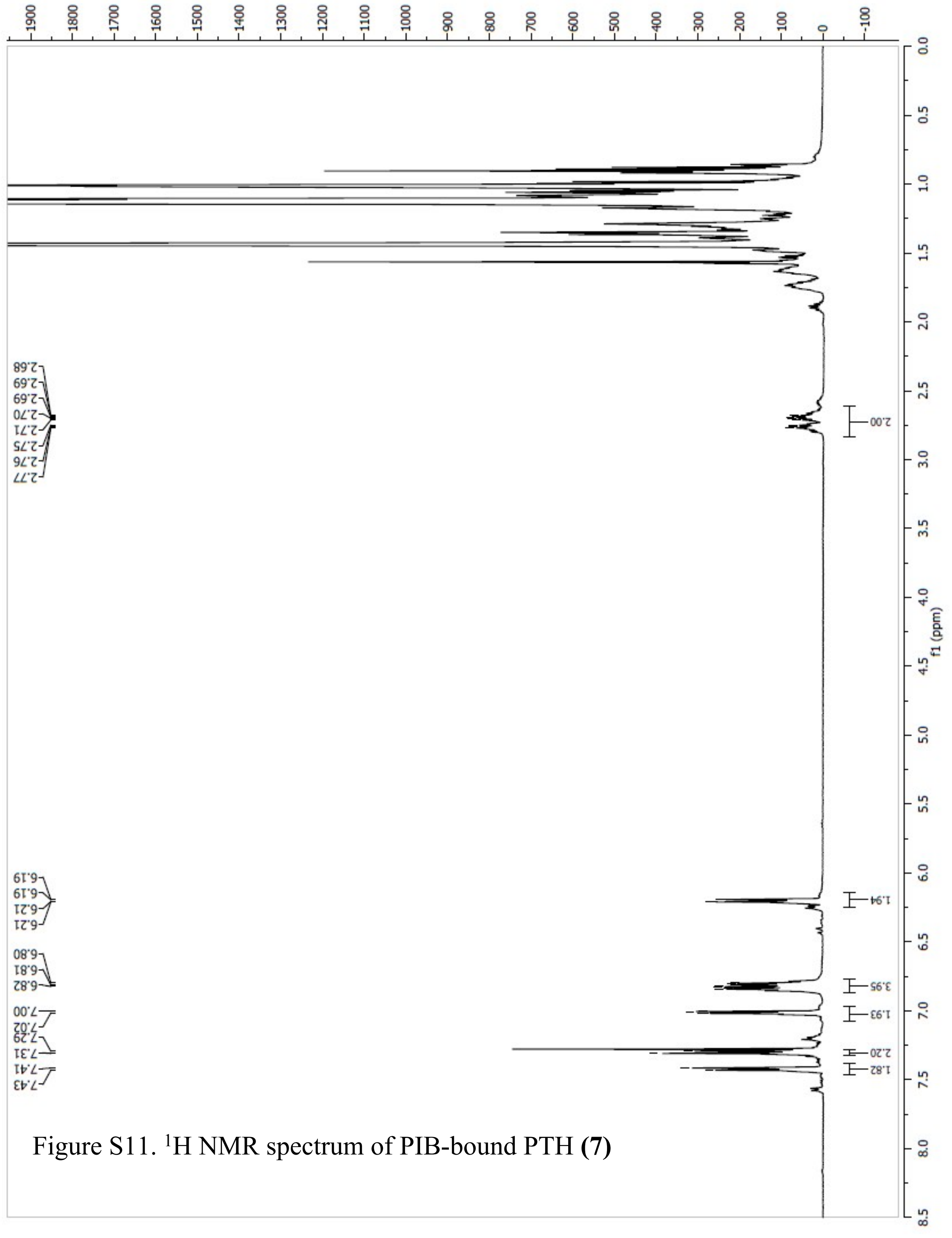

Figure S11. ^{1}H NMR spectrum of PIB-bound PTH **(7)**

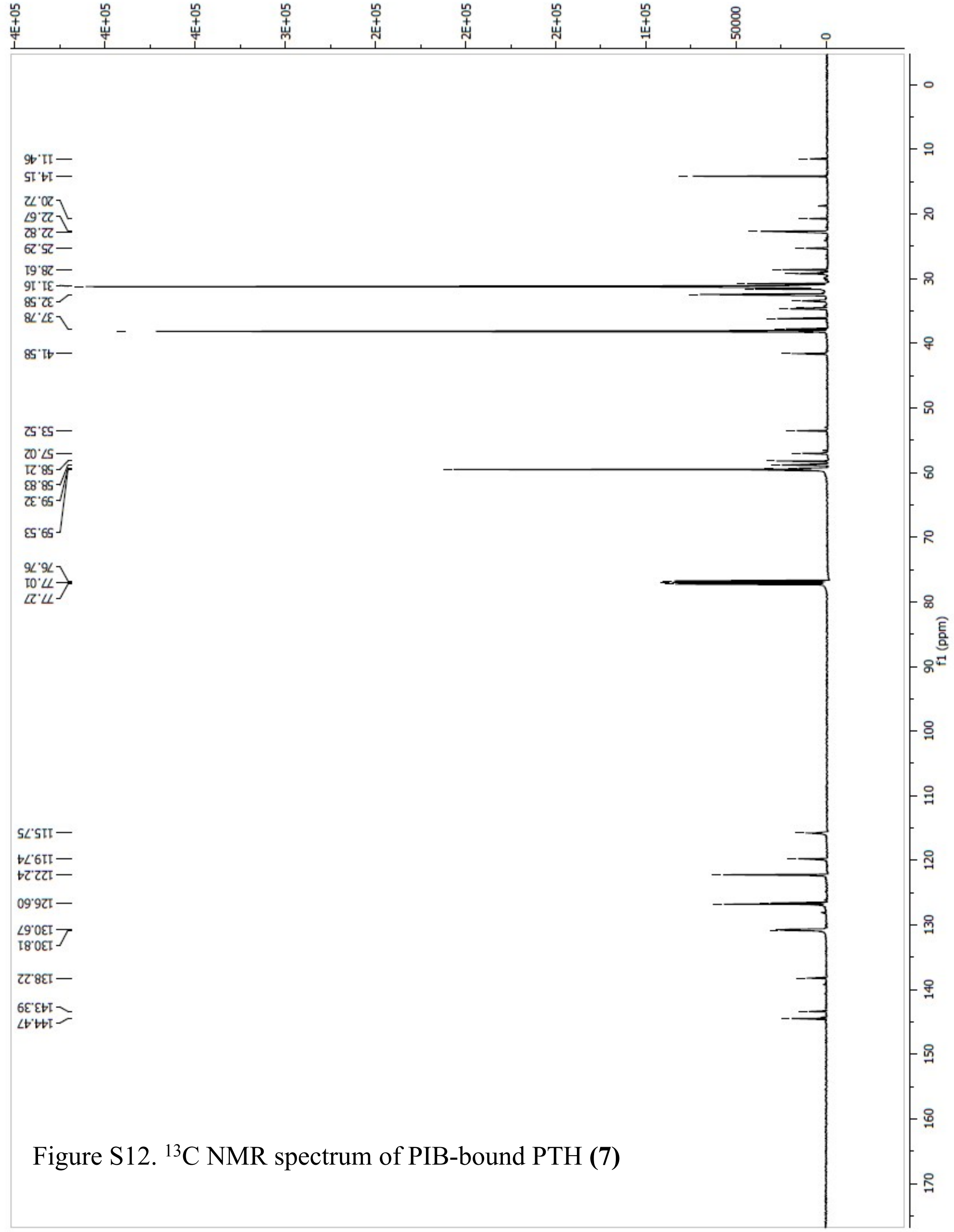

Figure S12. ^{13}C NMR spectrum of PIB-bound PTH **(7)**

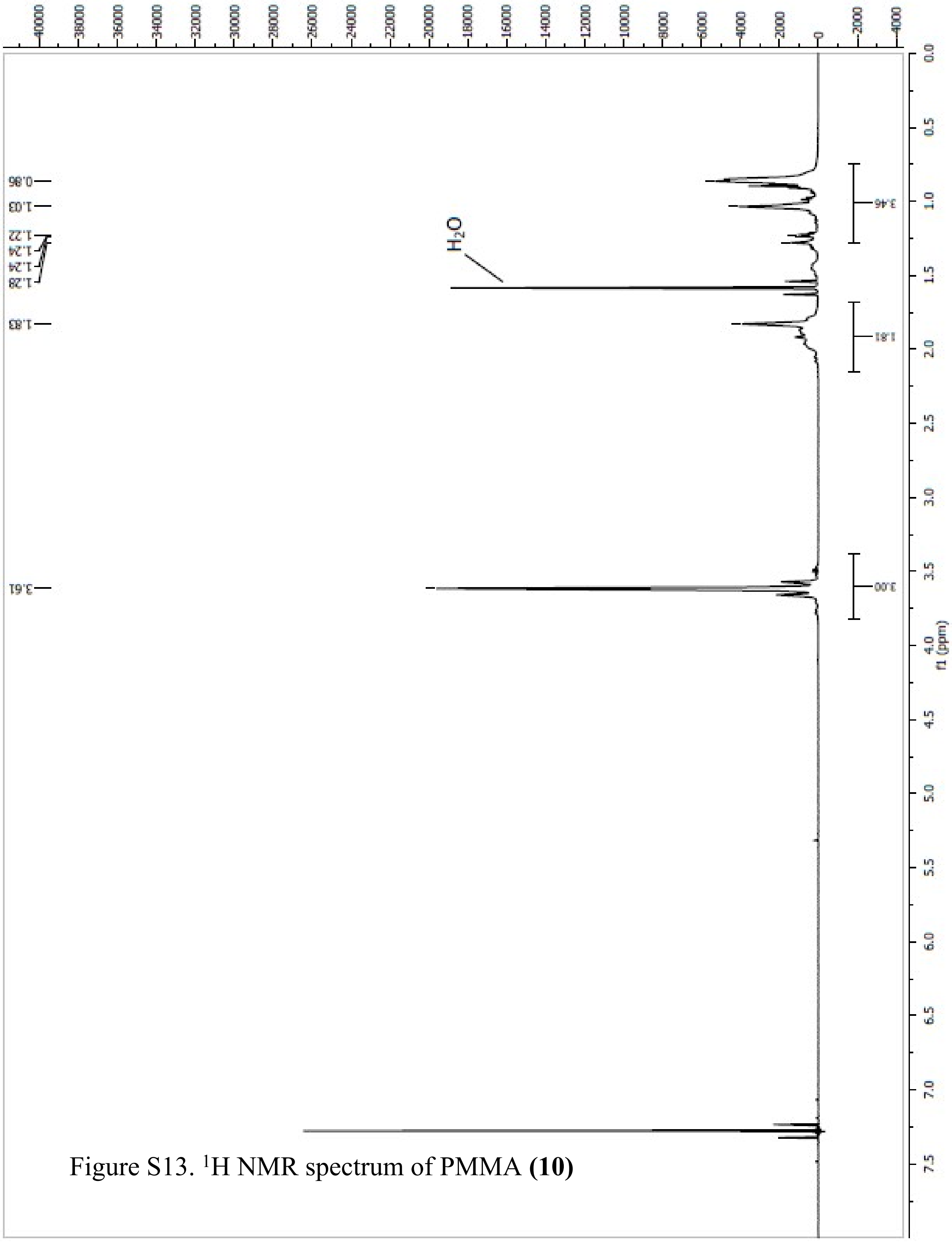

Figure S13. ^1H NMR spectrum of PMMA **(10)**

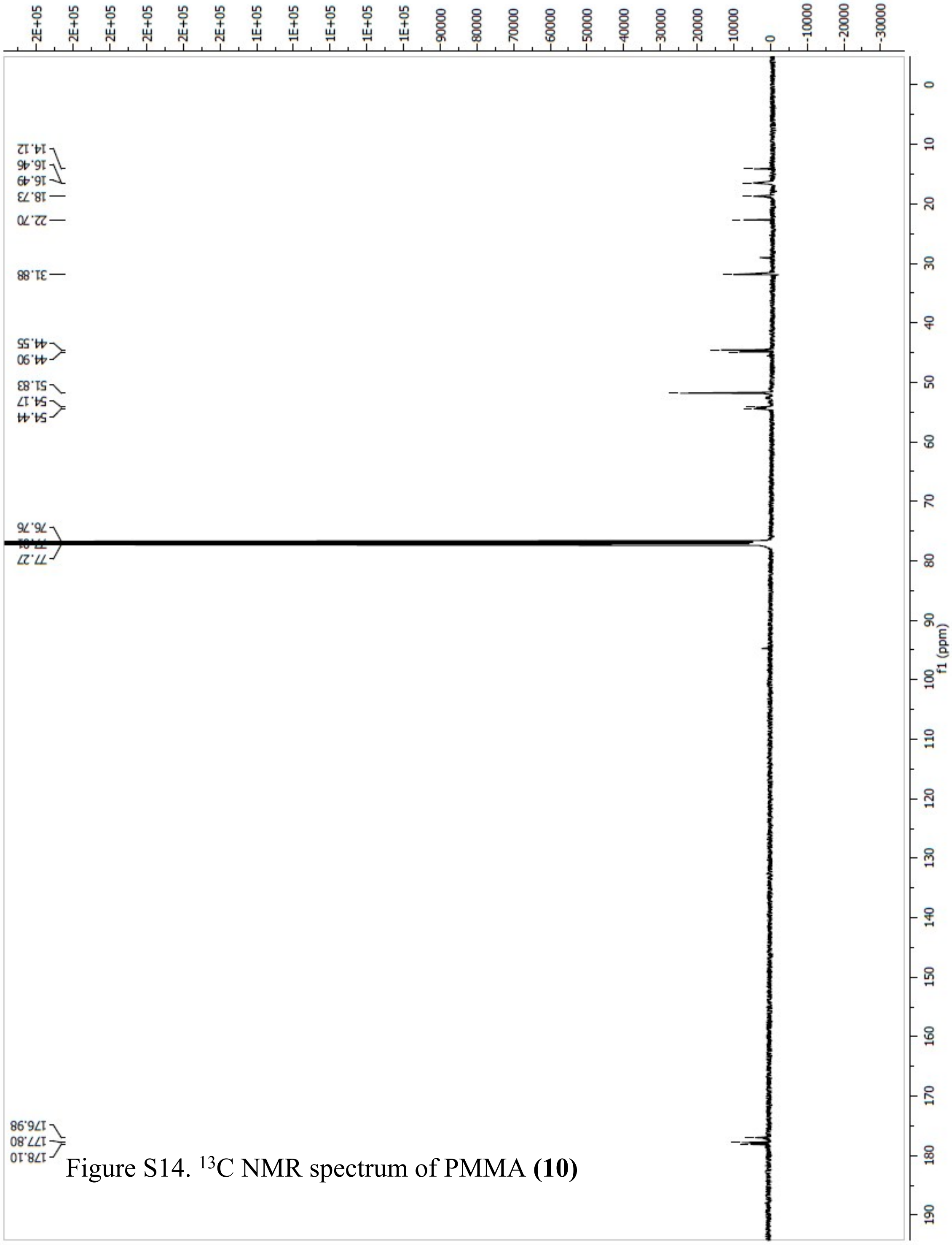

Figure S14. ^{13}C NMR spectrum of PMMA **(10)**

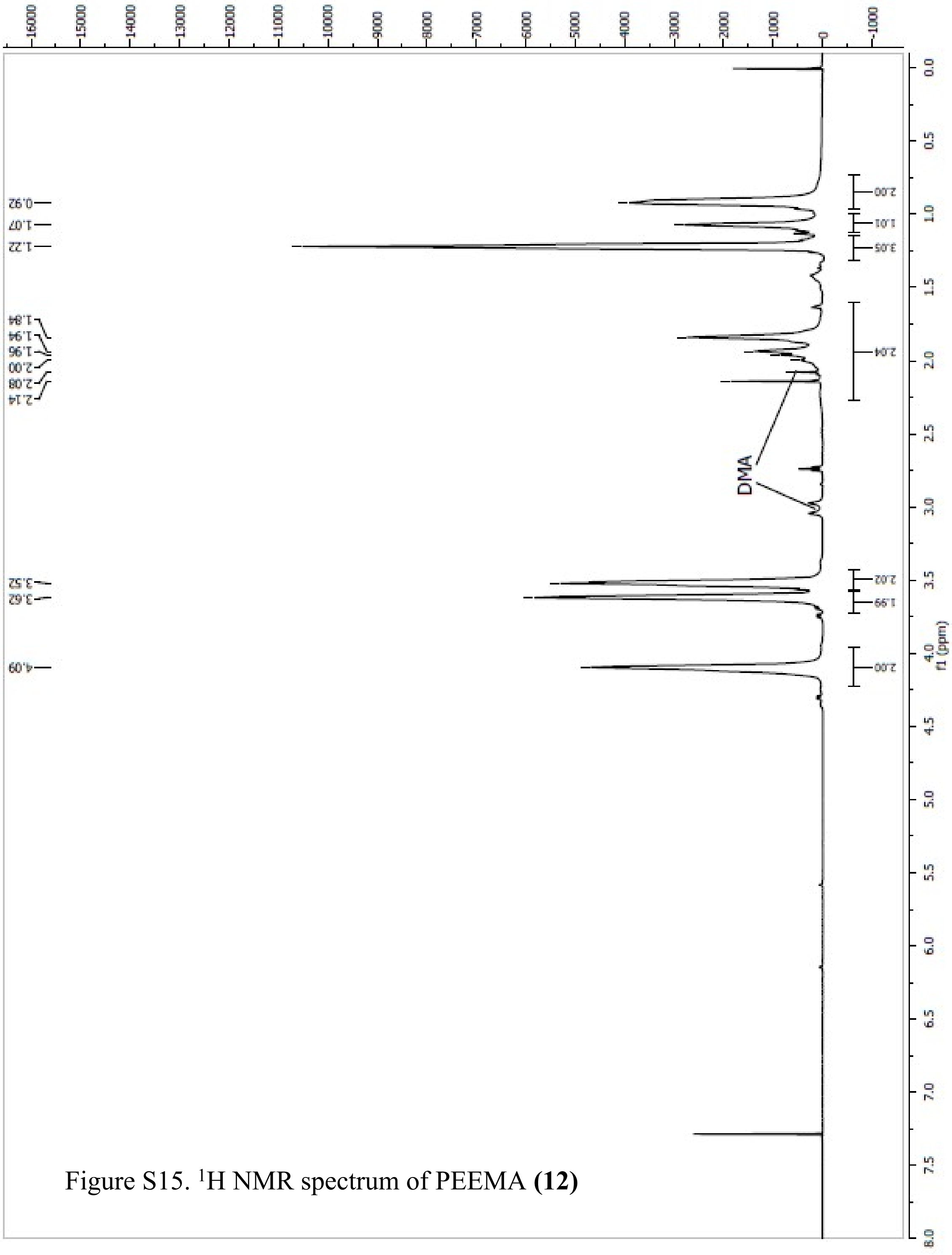

Figure S15. ${}^{1}H$ NMR spectrum of PEEMA **(12)**

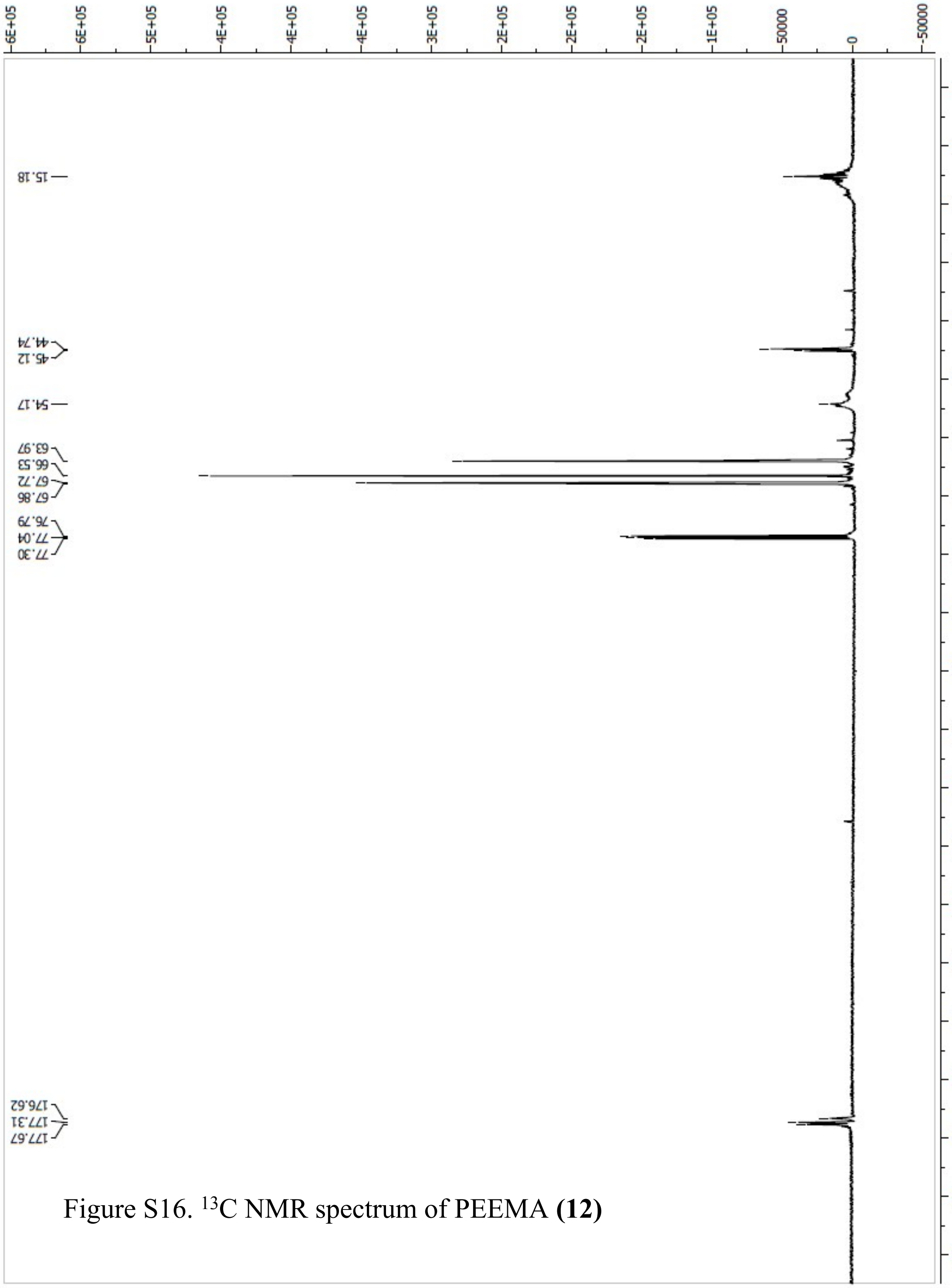

Figure S16. ^{13}C NMR spectrum of PEEMA **(12)**

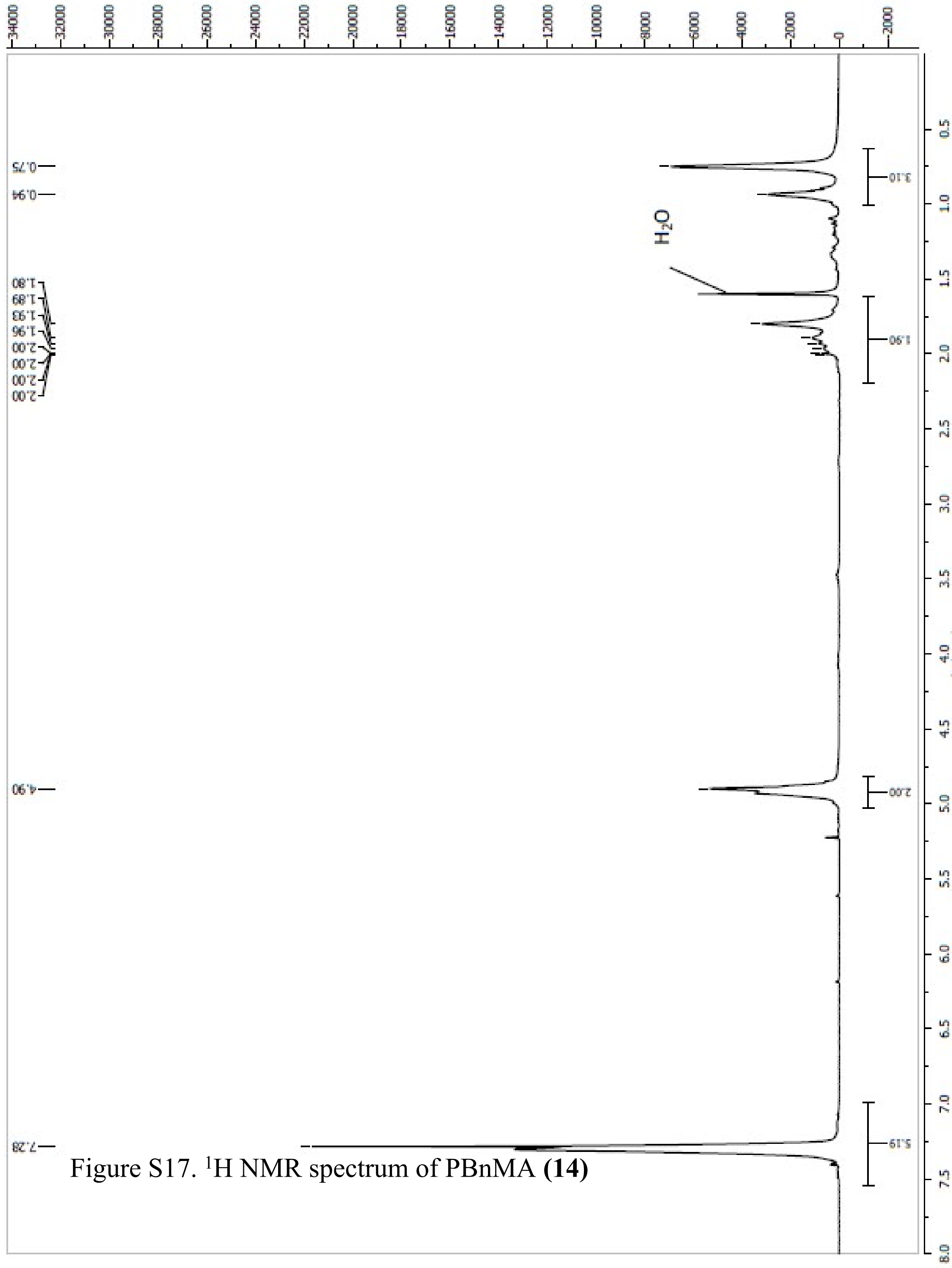

Figure S17. ^{1}H NMR spectrum of PBnMA **(14)**

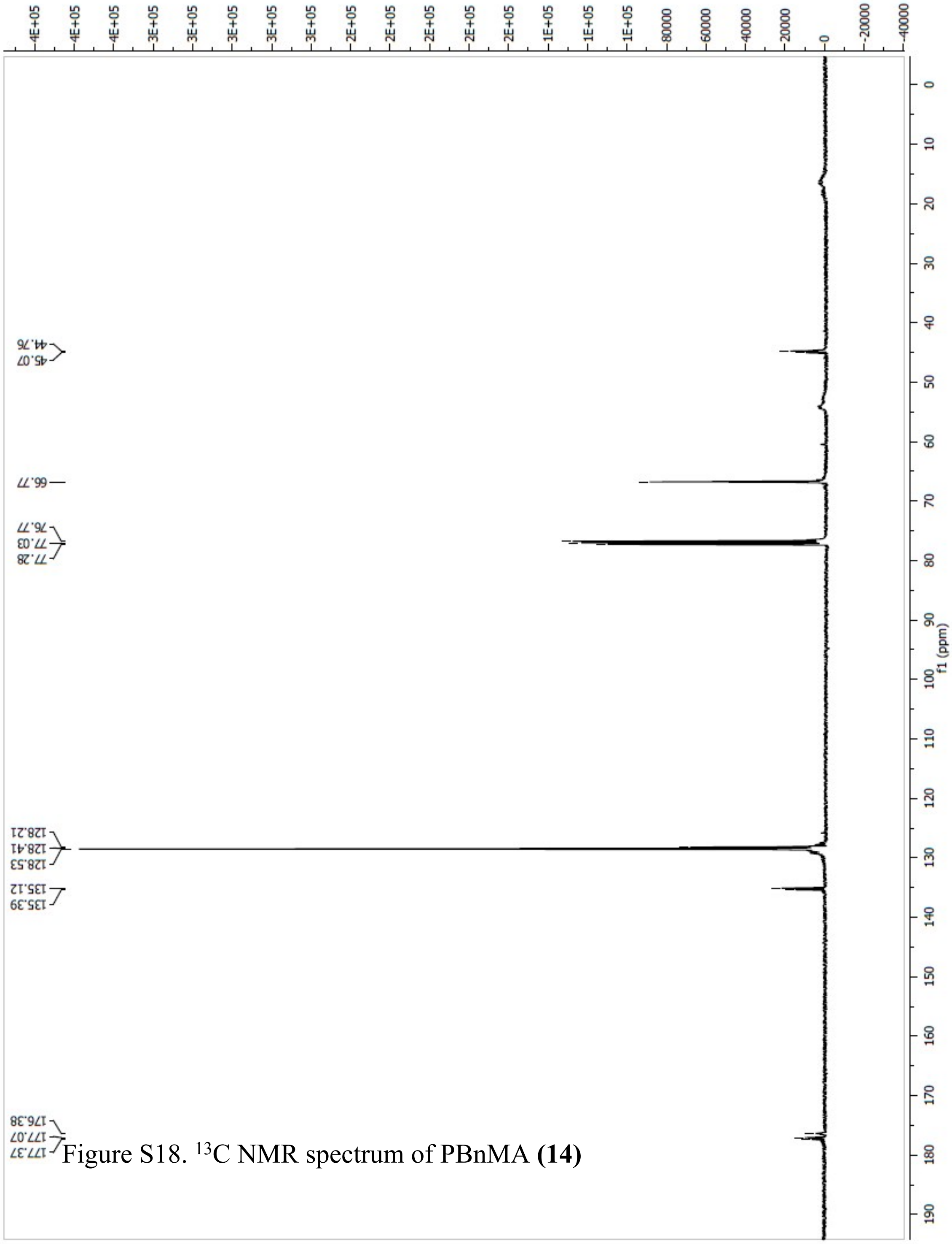

Figure S18. ^{13}C NMR spectrum of PBnMA **(14)**

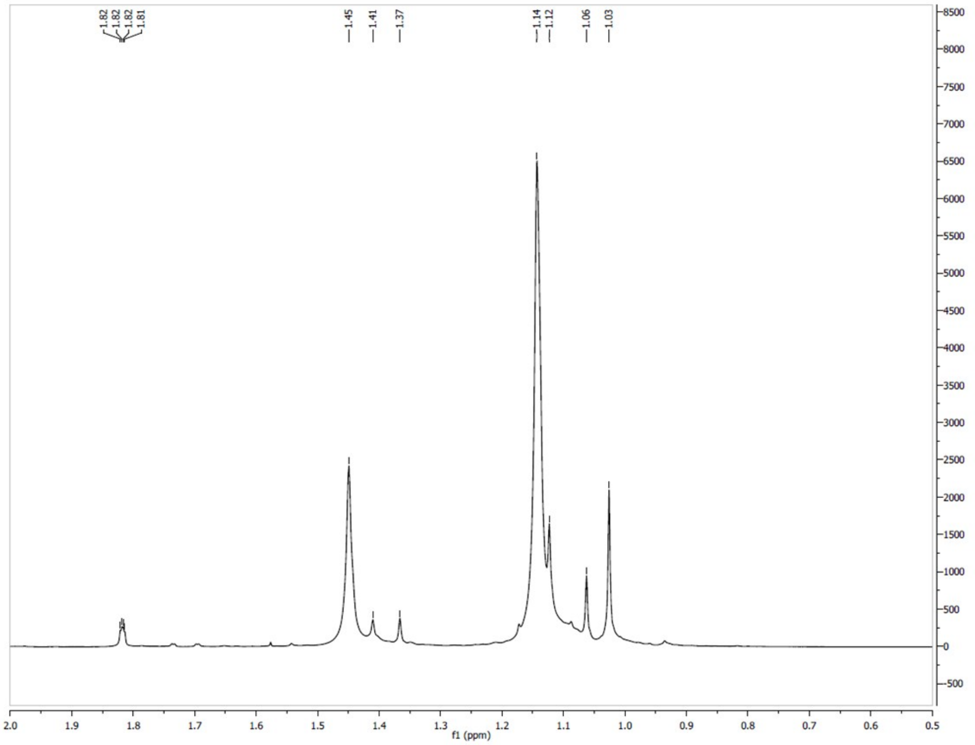

Figure S19. ^{1}H NMR spectrum of PIB$_{1000}$ from 2.0 ppm to 0.5 ppm

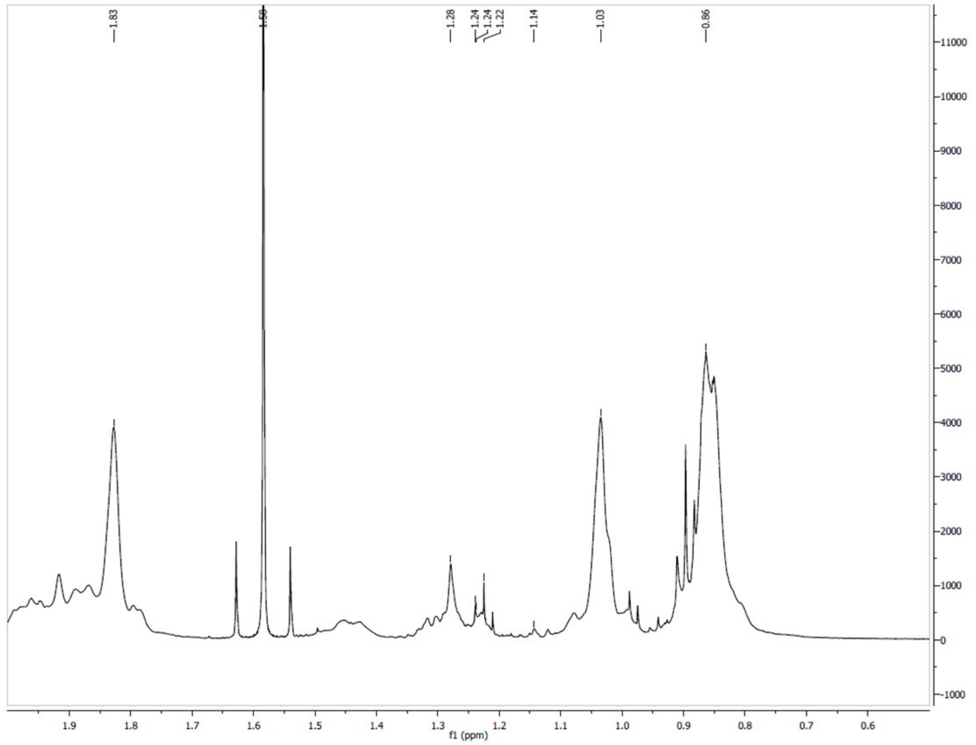

Figure S20. ^{1}H NMR spectrum of PMMA from 2.0 ppm to 0.5 ppm

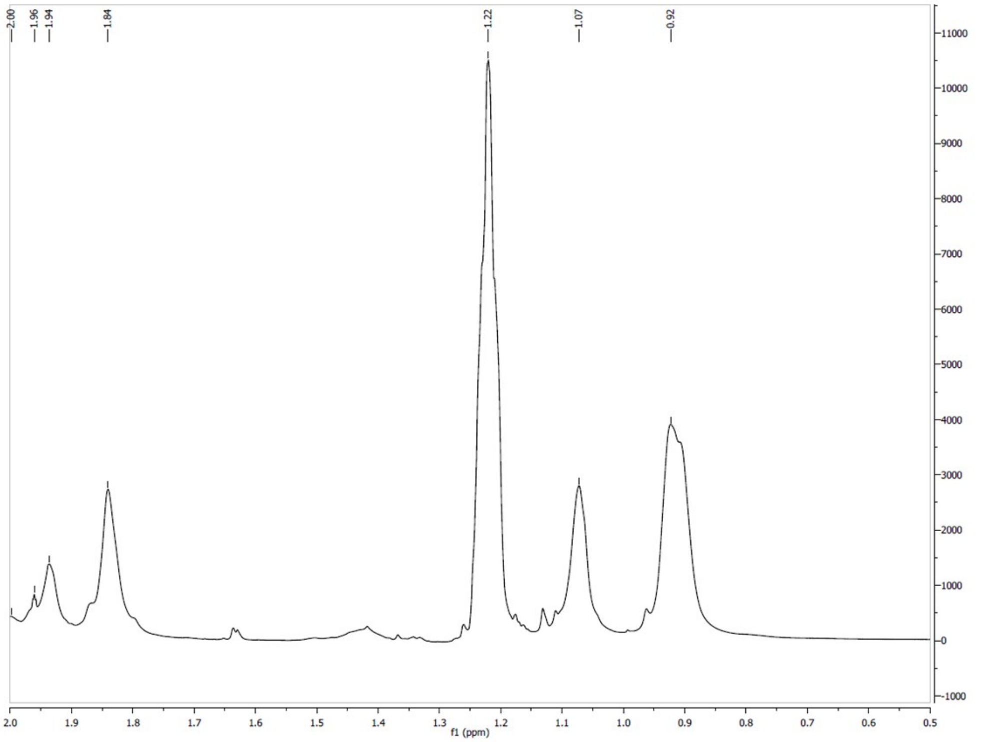

Figure S21. ^{1}H NMR spectrum of PEEMA from 2.0 ppm to 0.5 ppm

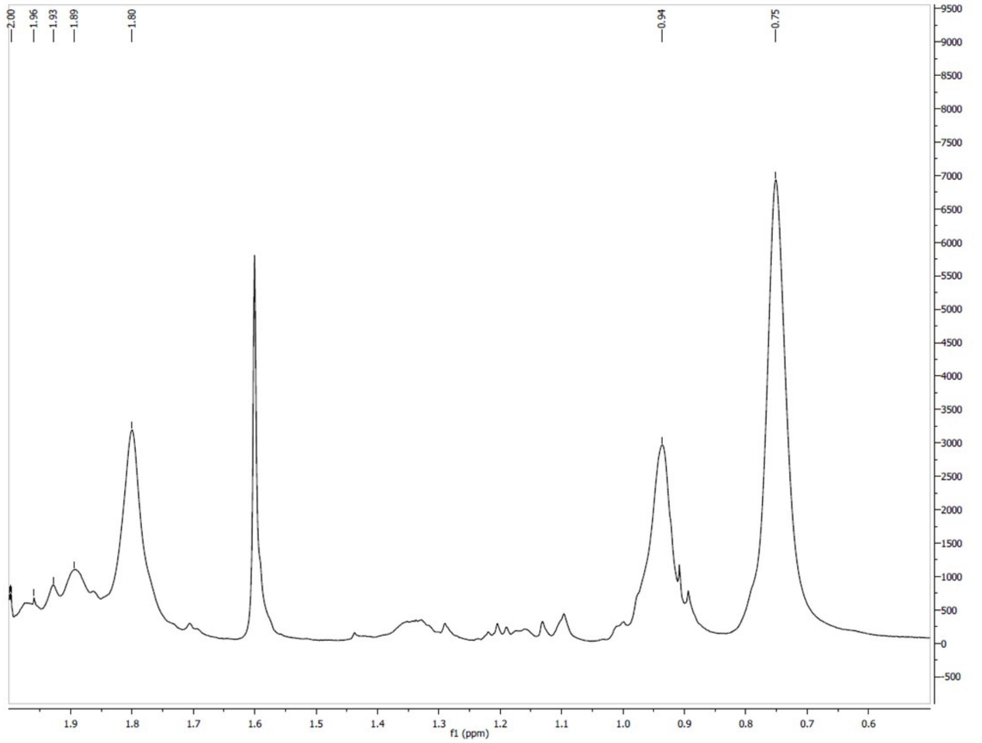

Figure S22. ^{1}H NMR spectrum of PBnMA from 2.0 ppm to 0.5 ppm

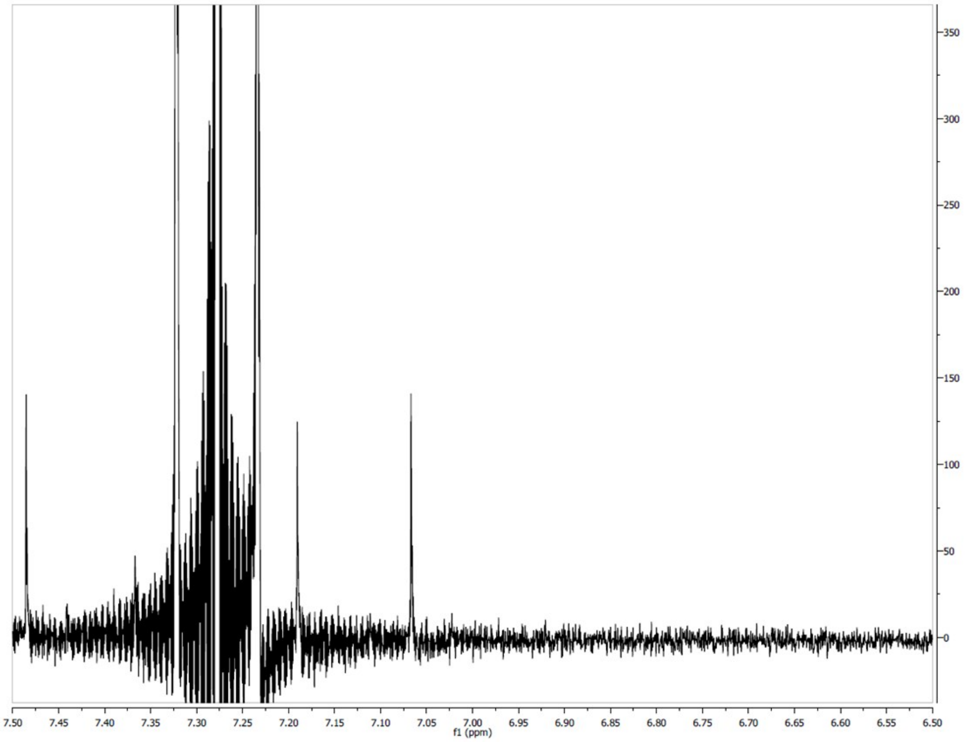

Figure S23. ^{1}H NMR spectrum of PMMA from 6.5 ppm to 7.5 ppm

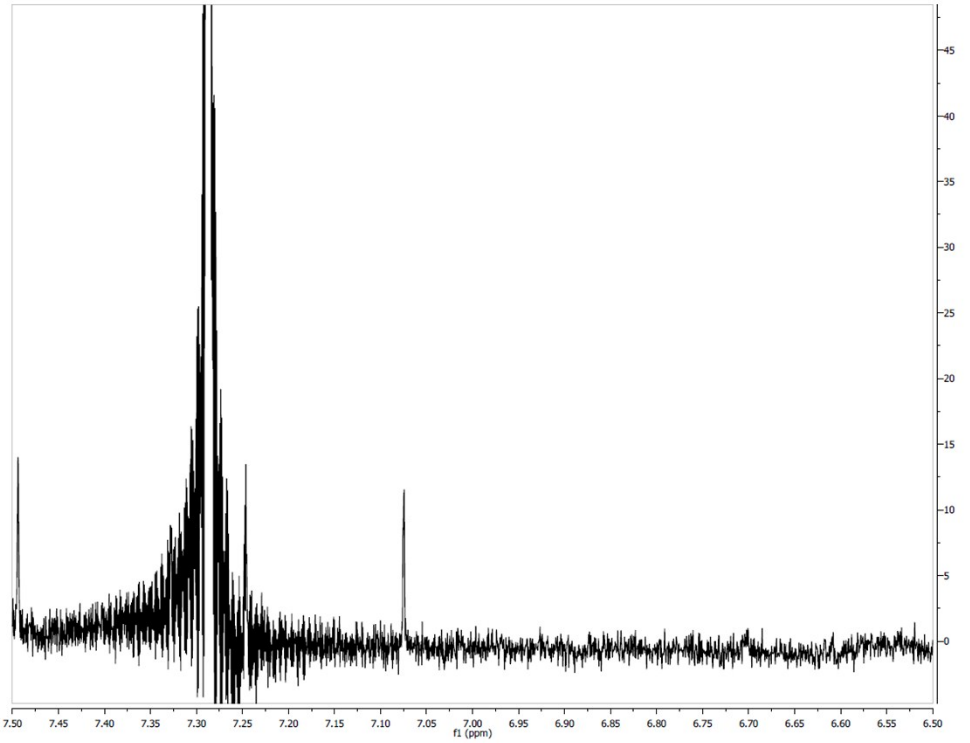

Figure S24. ^{1}H NMR spectrum of PEEMA from 6.5 ppm to 7.5 ppm

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3. Q. Li, Y. Bao, H. Wang, F. Du, Q. Li, B. Jin and R. Bai, *Polym. Chem.,* 2013, **4***,* 2891-2897.