Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting information

Synthesis of Chain End Acyl-Functionalized Polymers by Living Anionic Polymerization: Versatile Precursor for H-Shaped Polymers

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Contents

Synthesis of chain end acyl-functionalized PIsp.

A difunctional living PIsp was obtained by the anionic polymerization of Isp (0.43 g, 6.25 mmol) with K-Naph (0.147 mmol) in THF at –78 °C for 4 h (**Table 1**, run 9). DPE (0.265 mmol, 1.6 equivalent) in THF (2 mL) was added at –78 °C and reacted for 15 min. A THF solution (6 mL) of **1** (0.286 mmol, 1.9 equivalent) was then added at –78 °C to the solution of DPE-capped living PIsp and reacted for 2 h. Finally, the end-functionalization was terminated with degassed AcOH. A white polymer (0.51 g, 96%) was obtained by pouring reaction solution into MeOH. The resulting PIsp was purified by reprecipitation in MeOH and freeze-drying from the benzene solution.

^{1}H NMR (400 MHz; $CDCl_3$; ppm) δ = 1.20-2.35 (br, main chain), 1.72 (br, 24H, adamantyl), 1.95-2.03 (br, 36H, adamantyl), 3.74 (s, 2H, terminal C*H*), 4.69-5.74 (br, olefin protons, 7.05-7.41 (br, aromatic).

^{13}C NMR (100 MHz; $CDCl_3$; ppm): δ = 16.5-42.4 (-CH_3), 28.3 (adamantyl), 36.7 (adamantyl), 40.2 (adamantyl), 36.7-50.0 (main chain), 47.0 (adamantyl), 110.6-111.6 (=CH_2), 126.0-128.3 (Ar), 136-139 (-CH=CH_2), 147.2-148.9 (-C(CH_3)=CH_2), 209.1 (C=O).

IR (KBr; cm^{-1}): 3072, 2923, 2362, 1780, 1668 (C=O), 1644 (=CH_2), 1602, 1448, 1411, 1374, 885, 699.

Synthesis of H-shaped block copolymer of St and 2VP.

A living P2VP anion was firstly prepared by the polymerization of 2VP (0.98 g, 9.31 mmol) with *sec*-BuLi (0.0892 mmol) and DPE (0.161 mmol) in THF at –78 °C. Then, to the solution of the P2VP anion, a THF solution of chain end acyl tetra-functionalized PSt (M_n = 3.9 kg/mol, 0.0181 mmol) was added at –78 °C and reacted for 24 h. During the reaction, the red coloration of the living P2VP was maintained. Finally, the reaction was terminated with MeOH. A polymer of white powder was obtained by pouring reaction solution to hexane. A bimodal GPC curve of the reaction system was obtained, which was corresponding to the objective H-shaped block copolymer and the excess amount of P2VP branch. The H-shaped block copolymer was isolated in 39% yield by repeating fractional precipitations (ethanol/hexane), and purified by freeze-drying from the benzene solution.

^{1}H NMR (400 MHz; $CDCl_3$; ppm) δ = 0.58-0.72 (m, 24H, C*H*$_3$CH$_2$CHC*H*$_3$-), 0.98-2.41 (br, backbone and adamantyl), 3.75 (s, 2H, terminal CH), 6.15-7.25 (br, Ar), 8.06-8.43 (br, 6-position in pyridine ring).

IR (KBr; cm^{-1}) 3004, 2930, 1590, 1567, 1473, 1433, 1148, 747, 700.

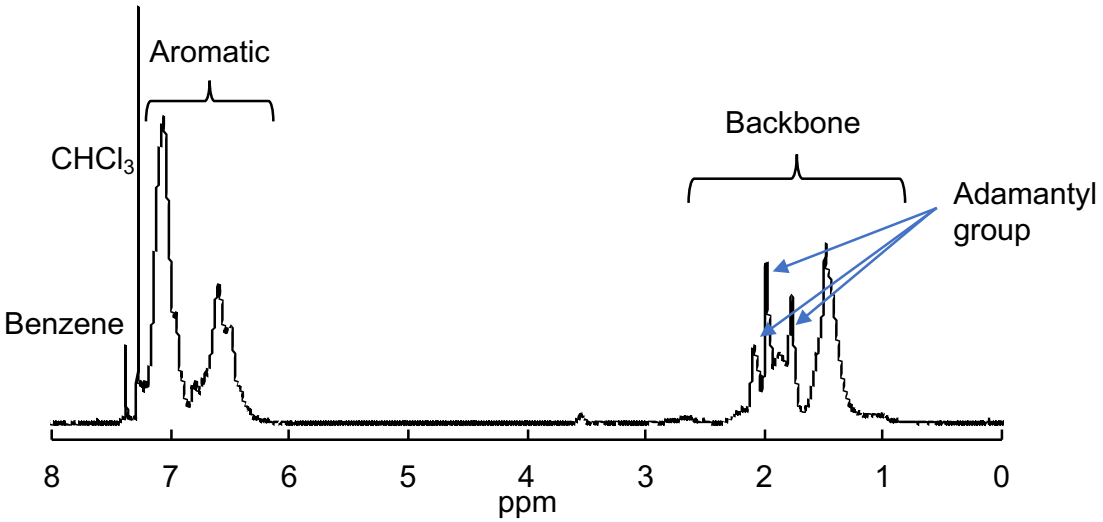

Figure S1. ^{1}H NMR spectrum of run 2.

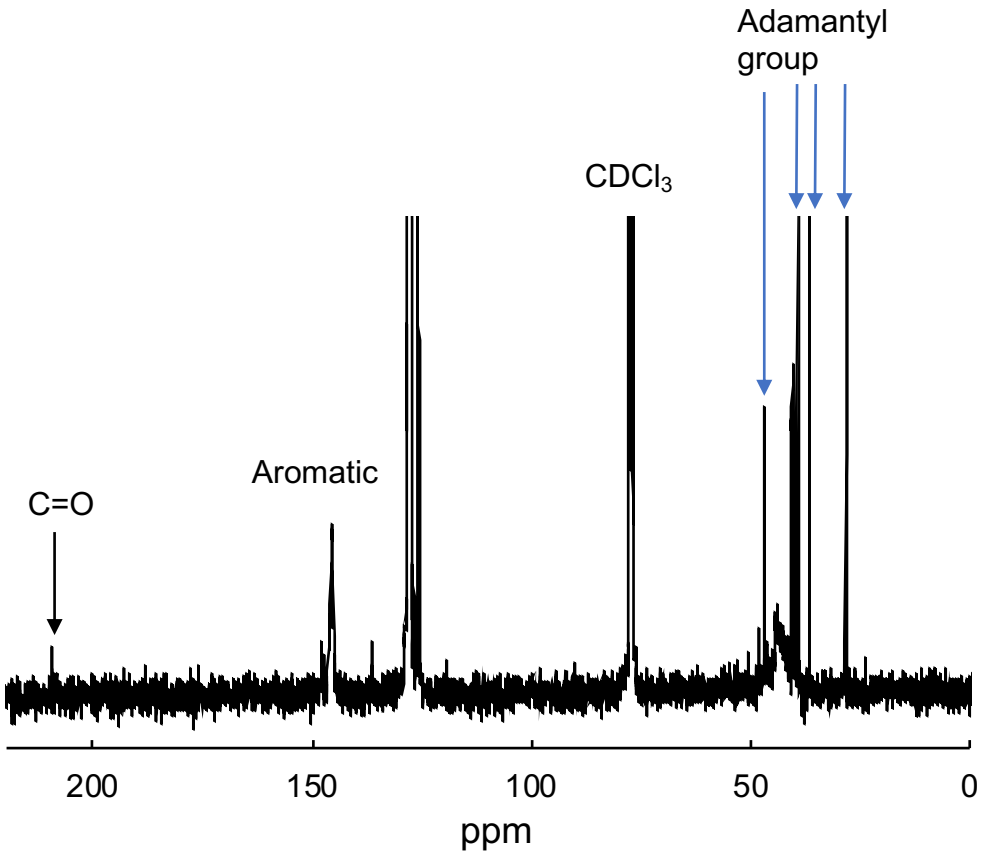

Figure S2. ^{13}C NMR spectrum of run 2.

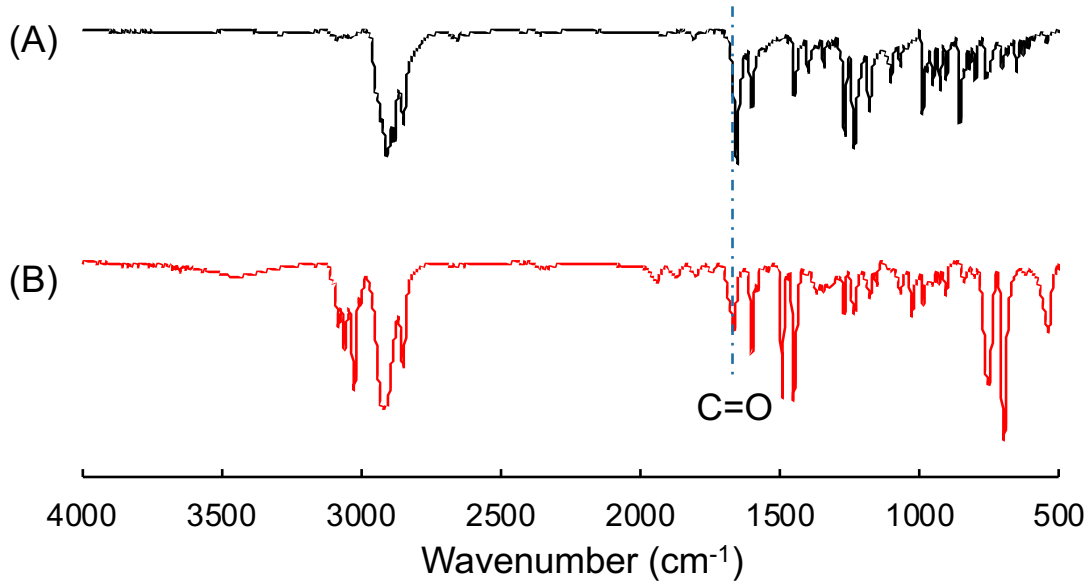

Figure S3. FT-IR spectra of **1** (A) and run 2 (B).

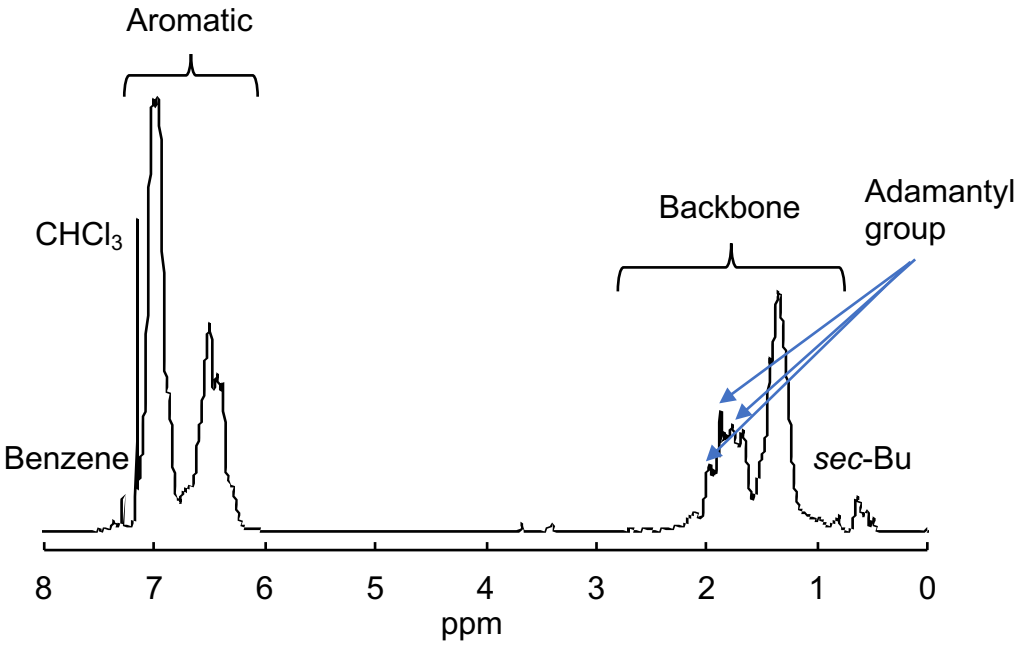

Figure S4. ^{1}H NMR spectrum of run 8.

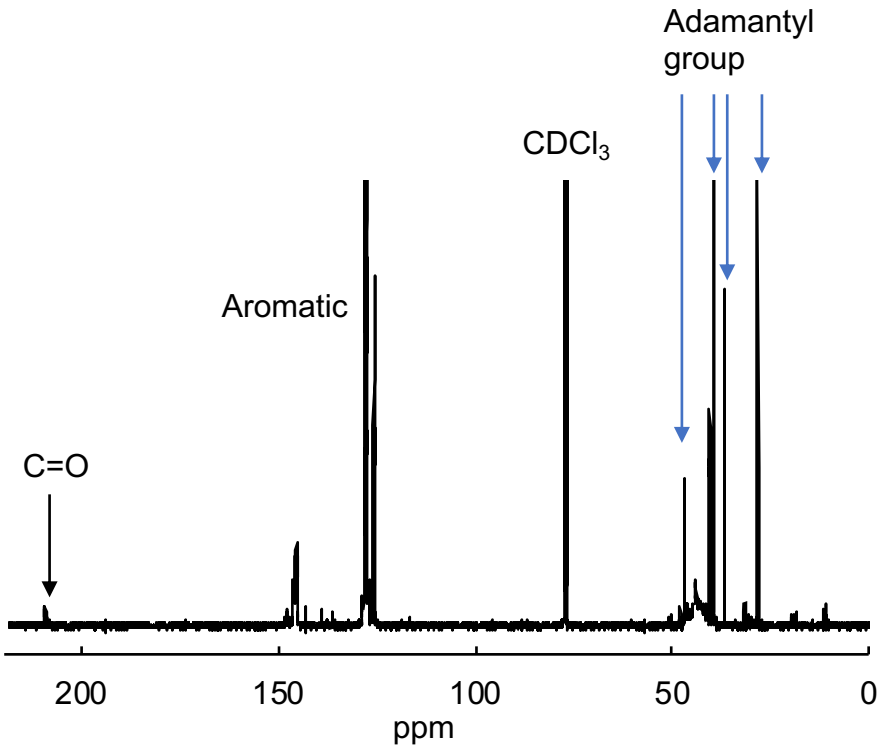

Figure S5. ^{13}C NMR spectrum of run 8.

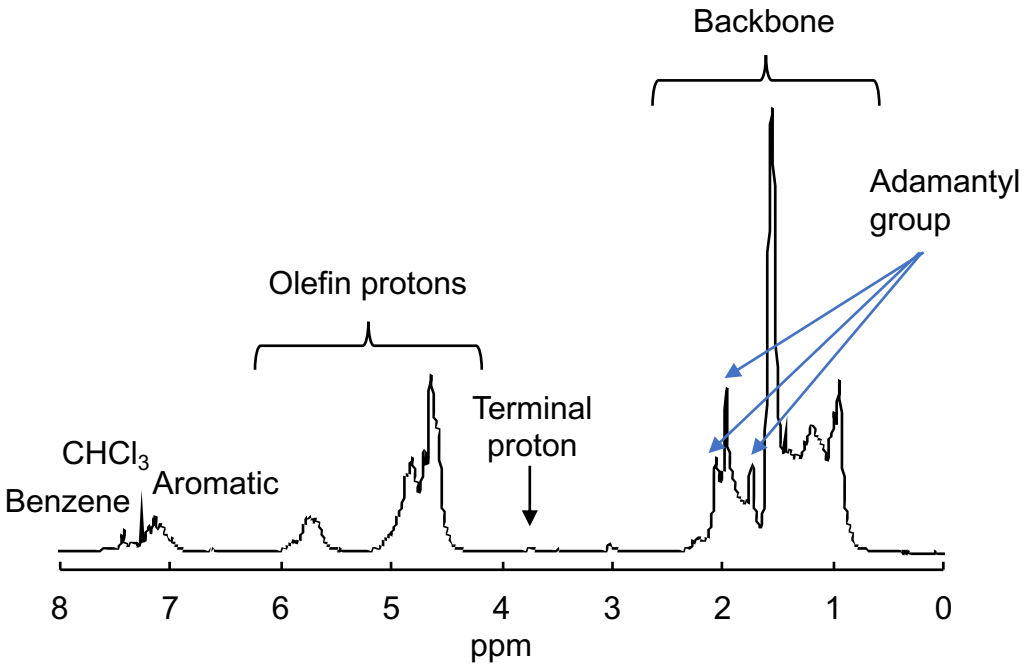

Figure S6. ^{1}H NMR spectrum of run 9.

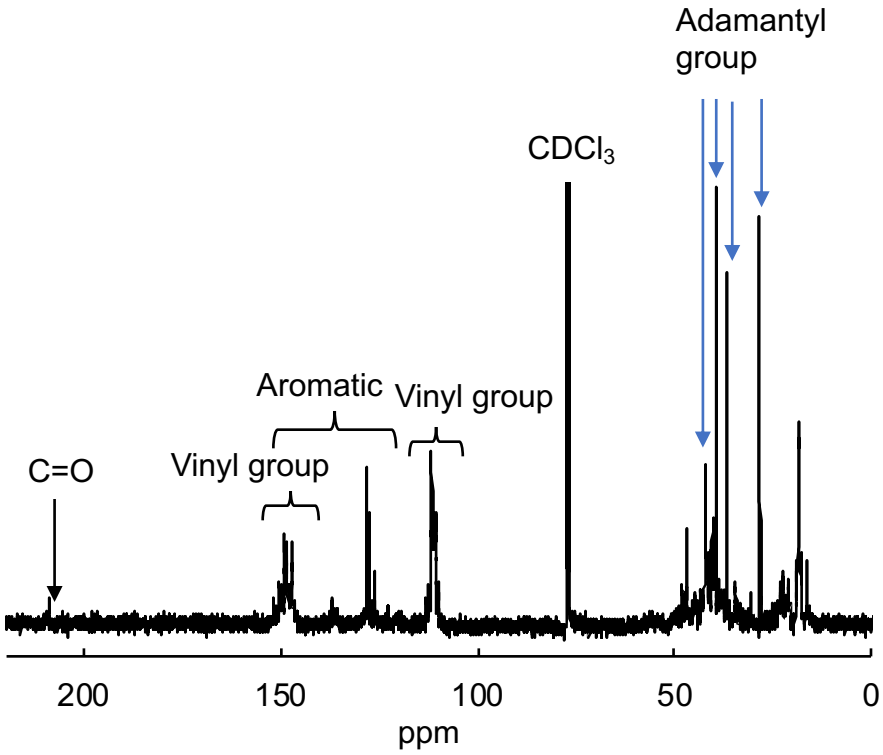

Figure S7. ^{13}C NMR spectrum of run 9.

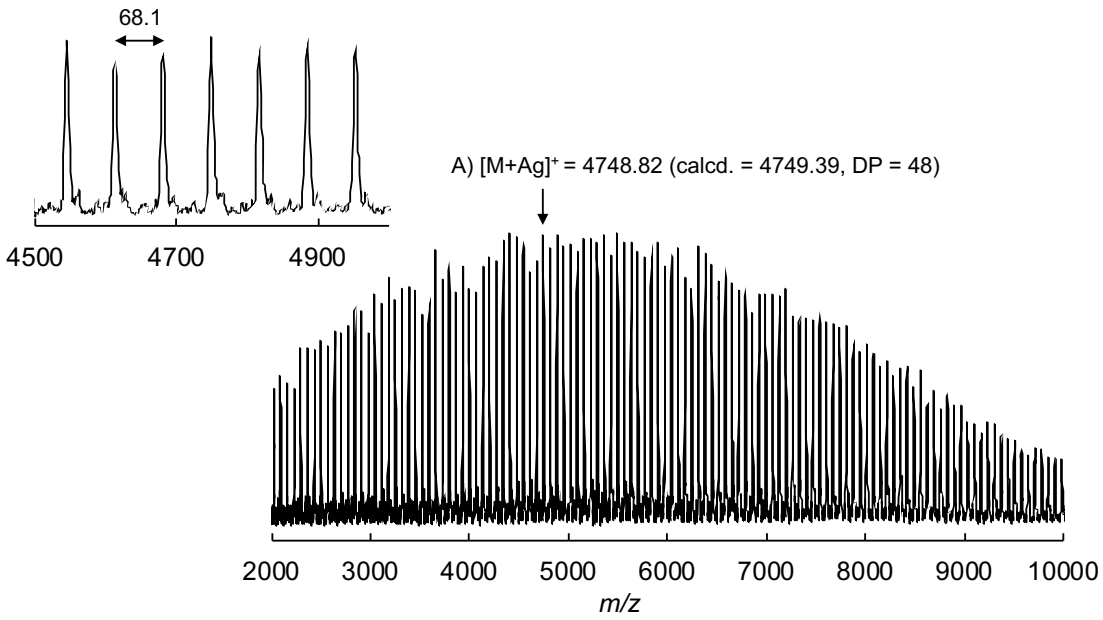

Figure S8. MALDI-TOF-MS spectrum of run 9.

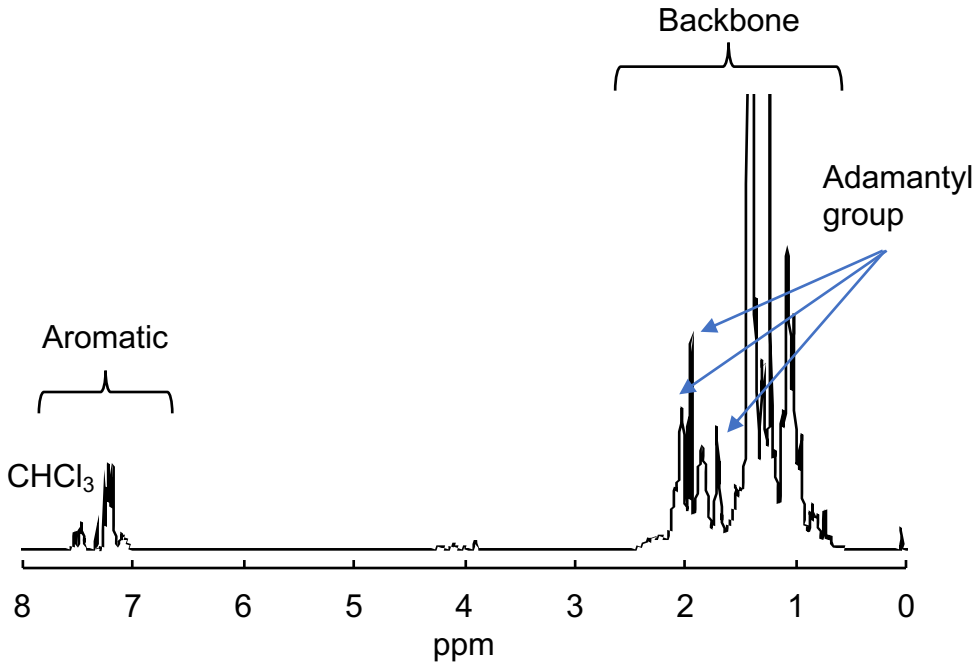

Figure S9. ^{1}H NMR spectrum of run 10.

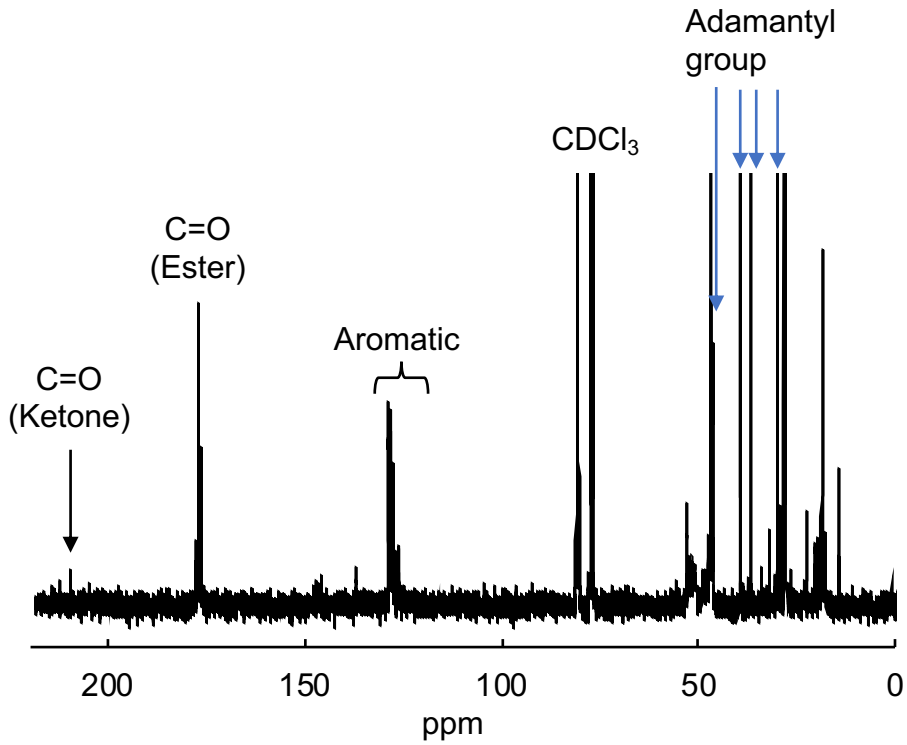

Figure S10. ^{13}C NMR spectrum of run 10.

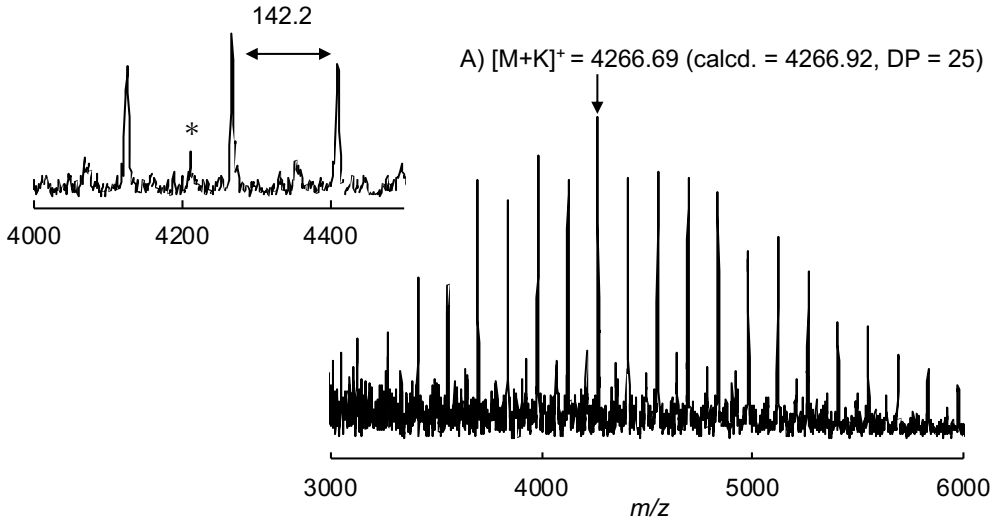

Figure S11. MALDI-TOF-MS spectrum of run 10.

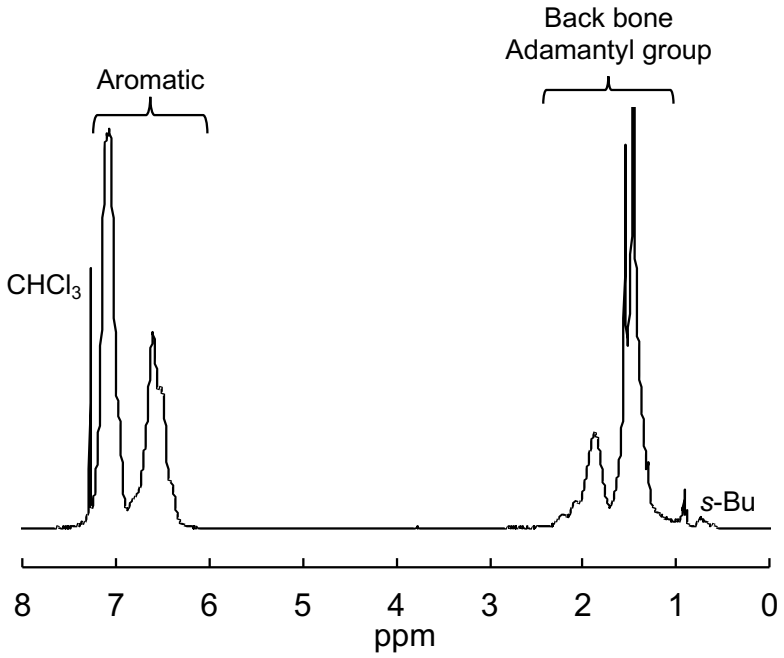

Figure S12. ^{1}H NMR spectrum of H-shaped PSt.

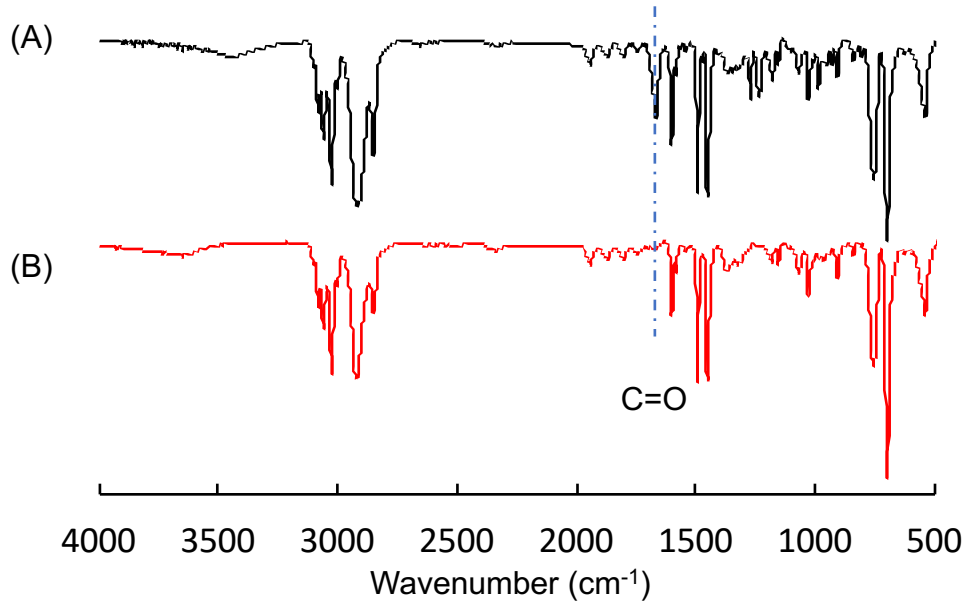

Figure S13. IR spectra of starting acyl end-functionalized telechelic PSt (A), and H-shaped PSt (B).

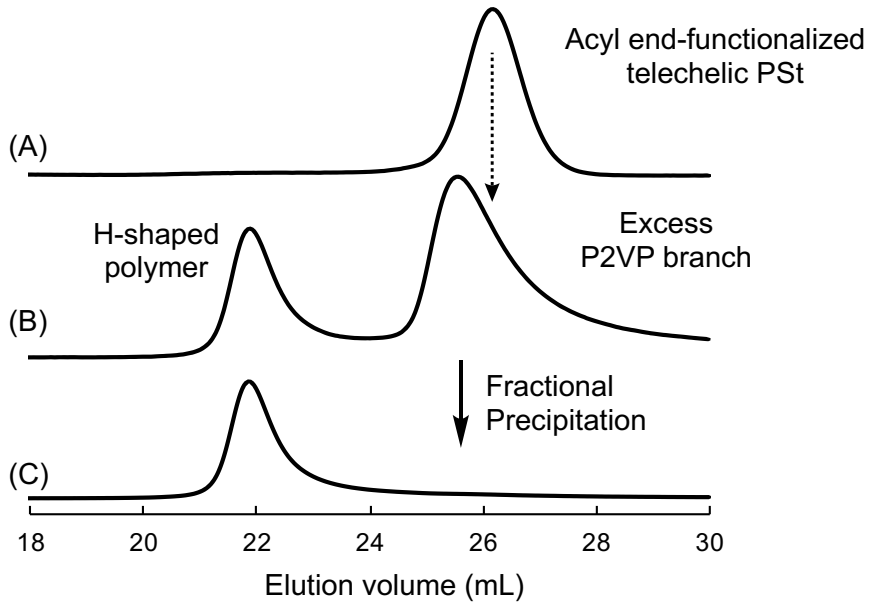

Figure S14. GPC curves of starting acyl end-functionalized telechelic PSt (A), the crude product after the grafting reaction (B), and the isolated H-shaped block copolymer with St and 2VP (C).

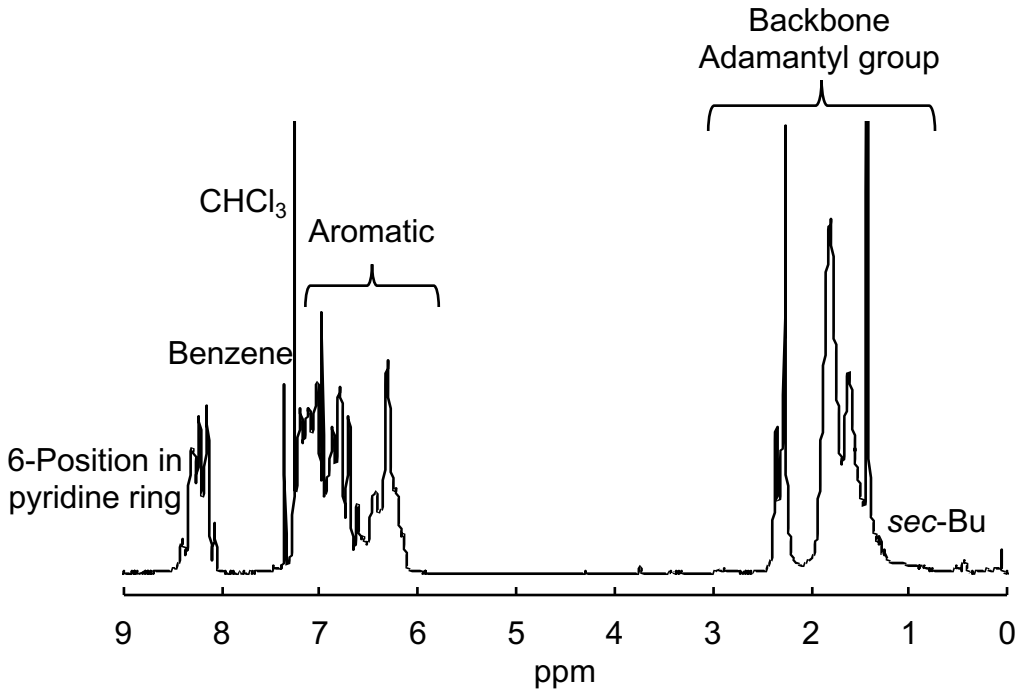

Figure S15. ^{1}H NMR spectrum of H-shaped copolymer with St and 2VP.

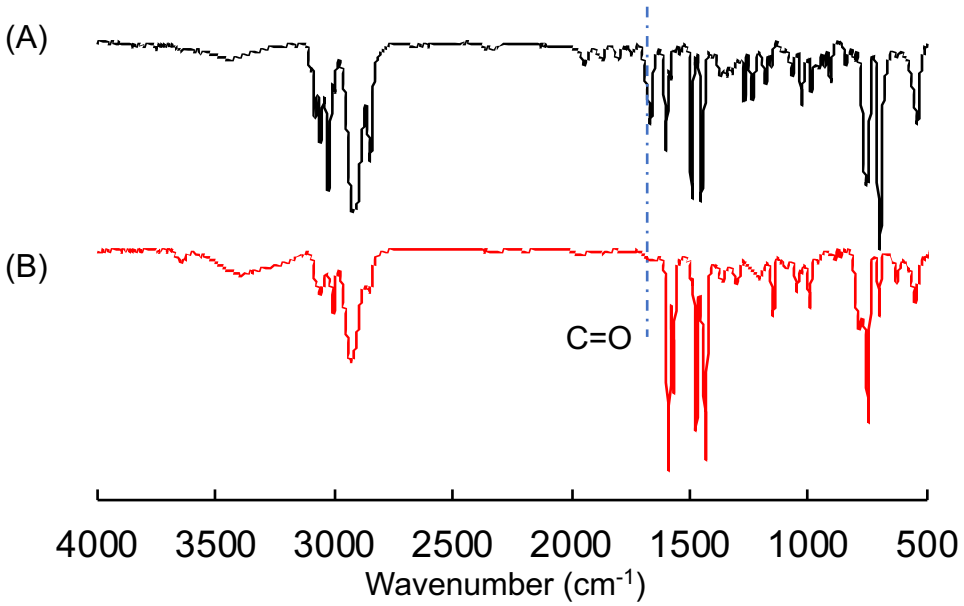

Figure S16. IR spectra of starting acyl end-functionalized telechelic PSt (A), and H-shaped copolymer with St and 2VP (B).

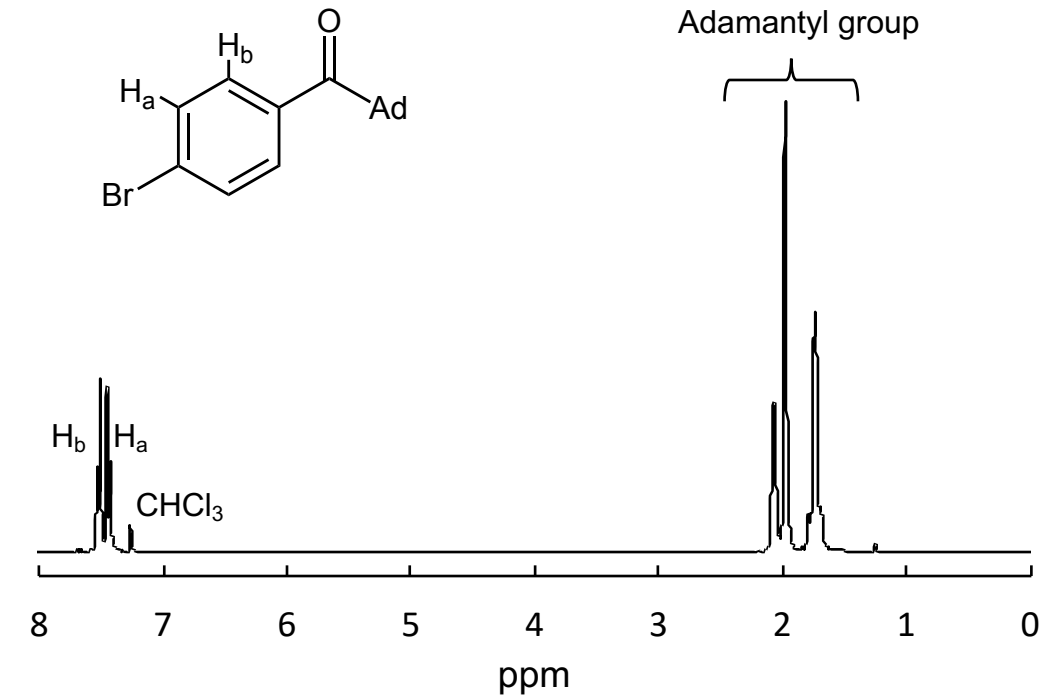

Figure S17. ^{1}H NMR spectrum of 1-adamantanyl 4-bromophenyl ketone.

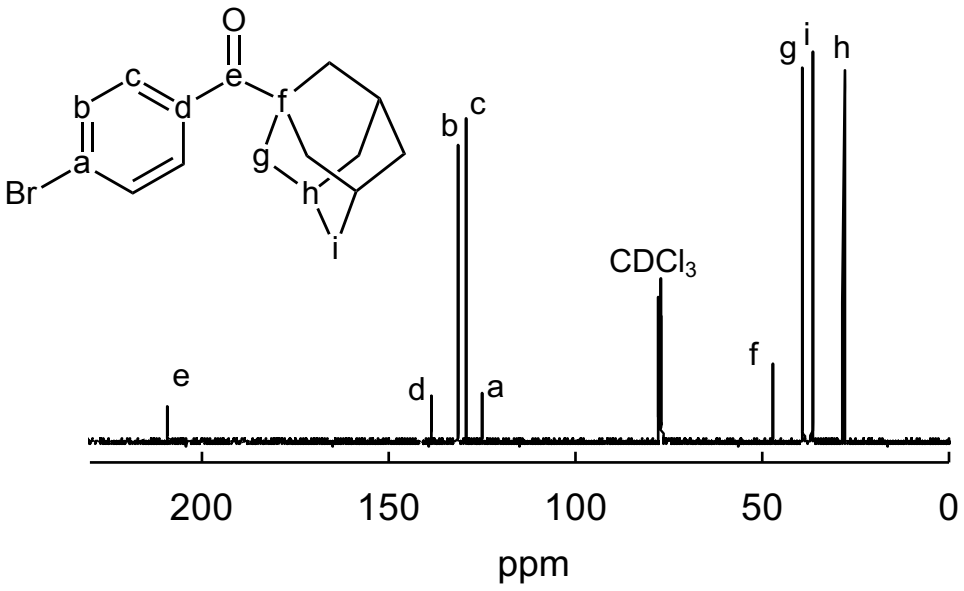

Figure S18. ^{13}C NMR spectrum of 1-adamantanyl 4-bromophenyl ketone.

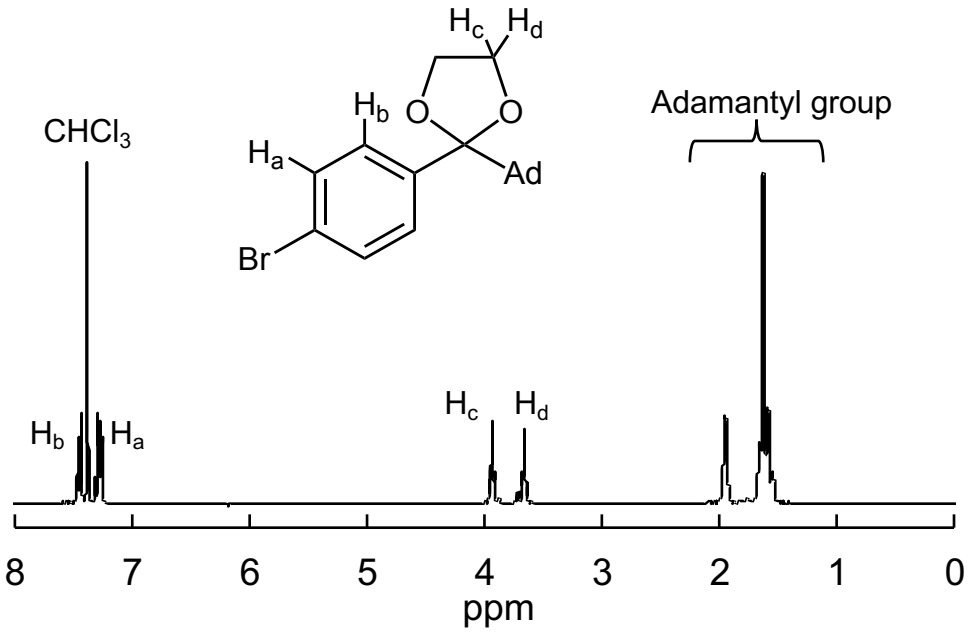

Figure S19. ^{1}H NMR spectrum of 2-(1-adamantyl)-2-(4-bromophenyl)-1,3-dioxolane.

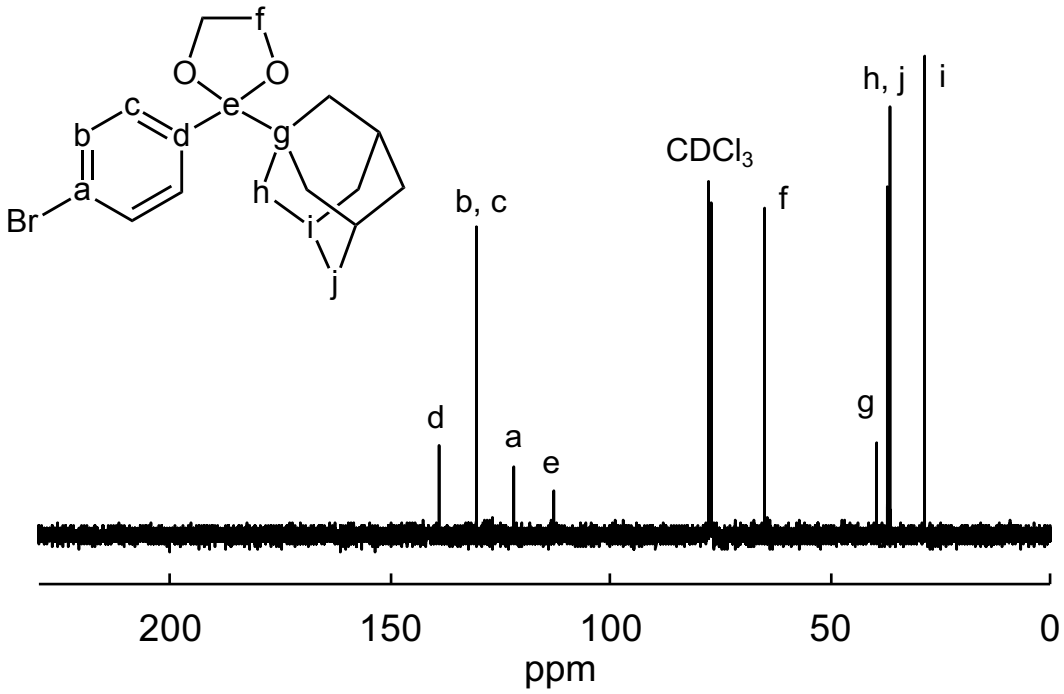

Figure S20. ^{13}C NMR spectrum of 2-(1-adamantyl)-2-(4-bromophenyl)-1,3-dioxolane.

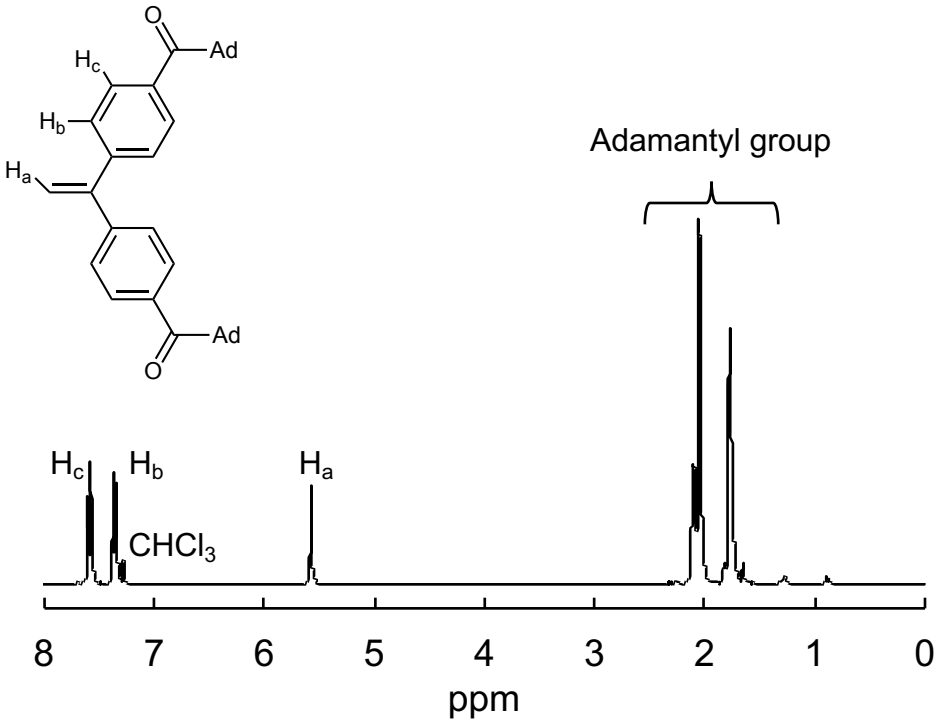

Figure S21. ^{1}H NMR spectrum of **1**.

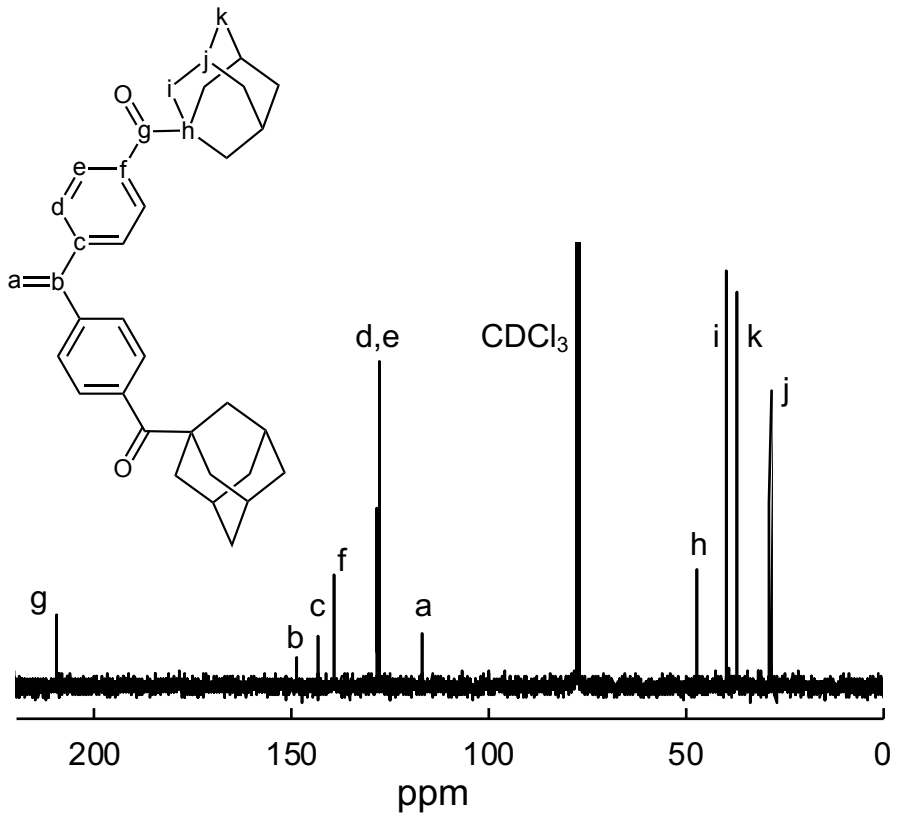

Figure S22. ^{13}C NMR spectrum of **1**.