Supporting Information for

Alternating ROMP copolymers containing charge-transfer units

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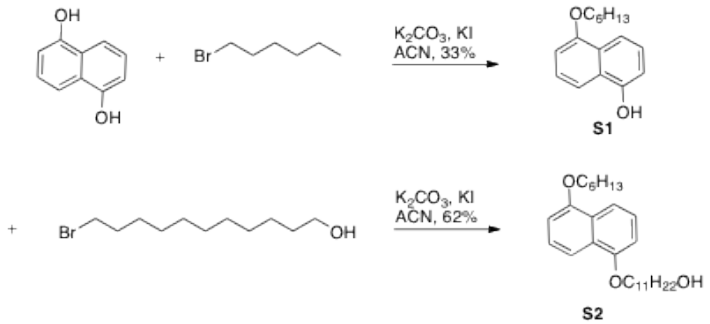
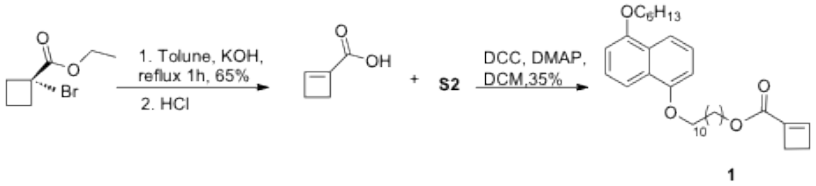
Materials and Methods

All reagents were purchased either from Acros Organics, Sigma-Aldrich, EMD Chemicals, or Alfa Aesar Chemicals and used without further purification. . ^{1}H NMR and ^{13}C NMR spectra were recorded at 25°C on a Bruker AC 400 (^{1}H: 400.1 MHz) spectrometer. ^{1}H NMR spectra were reported as chemical shift in ppm (multiplicity, coupling constant in Hz, and integration). ^{13}C NMR spectra were reported as chemical shift in ppm. The residual solvent nuclei in deuterated solvents was used as an internal reference. Molecular weights and polydispersity indices were measured using a Shimadzu pump coupled to a Shimadzu UV detector with CH_2Cl_2 as the eluent and a flow rate of 0.700 mL/min on American Polymer Standards column (Phenogel 5 μ MXL GPC column, Phenomenex). All GPCs were calibrated using poly(styrene) standards and carried out at 30 °C. M_w, M_n, and PDI represent the weight-average molecular weight, number-average molecular weight, and polydispersity index, respectively. All polymerization reactions were performed under an N_2 or Ar atmosphere. CH_2Cl_2 was dried by the solvent dispensing system and bubbled with N_2 right before use. CD_2Cl_2, $CDCl_3$ were degassed before use for reactions. 2nd generation Grubbs catalyst and ethyl 1-bromocyclobutanecarboxylate were purchased from Sigma-Aldrich (Milwaukee, WI). Precatalyst $(H_2IMes)(3\text{-Br-Py})_2(Cl)_2Ru{=}CHPh$ (**4**) was generated following the procedures published by Love, J.A. *et al.*[17] Aluminum TLC (thin layer chromatography) plates were silica gel 60 (F_{254}). Mallinckrodt silica gel 60 (230-400 mesh) and Combiflash chromatography system (Teledyne Isco, Inc, Lincoln NE) were used for column chromatography.



11-((5-(hexyloxy)naphthalen-1-yl)oxy)undecan-1-ol (S2). To a solution of 11-bromo-1-undecanol (2.57 g, 10.2 mmol) and **S1** (2.50 g, 10.2 mmol) in acetonitrile (50 mL) were added K_2CO_3 (3.66 g, 25.4 mmol) and KI (cat). The mixture was stirred under reflux for 18 h and then cooled to rt. The solid was filtered and the solution concentrated under reduced pressure. The crude residue was purified by column chromatography (1:3/Ethyl acetate (EtOAc):Hexanes) to afford **S2** in 62% yield. ^{1}H-NMR ($CDCl_3$): δ = 7.85 (d, 2H), 7.35 (t, 2H), 6.83 (d, 2H), 4.12 (t, 4H), 3.64 (t, 2H), 1.92 (quintet, 4H), 1.56 (dt, 6H), 1.41-1.32 (m, 19H), 0.94 (d, 3H); ^{13}C NMR ($CDCl_3$): δ 154.71, 126.84, 125.06, 114.08, 105.28, 68.21, 63.11, 34.06, 32.86, 32.82, 31.67, 29.59, 29.55, 29.48, 29.45, 29.34, 28.78, 28.19, 26.28, 25.98, 25.76, 22.66, 14.08. HRMS calcd for $C_{27}H_{42}O_3$ (MH)+ 415.31) found 416.55.

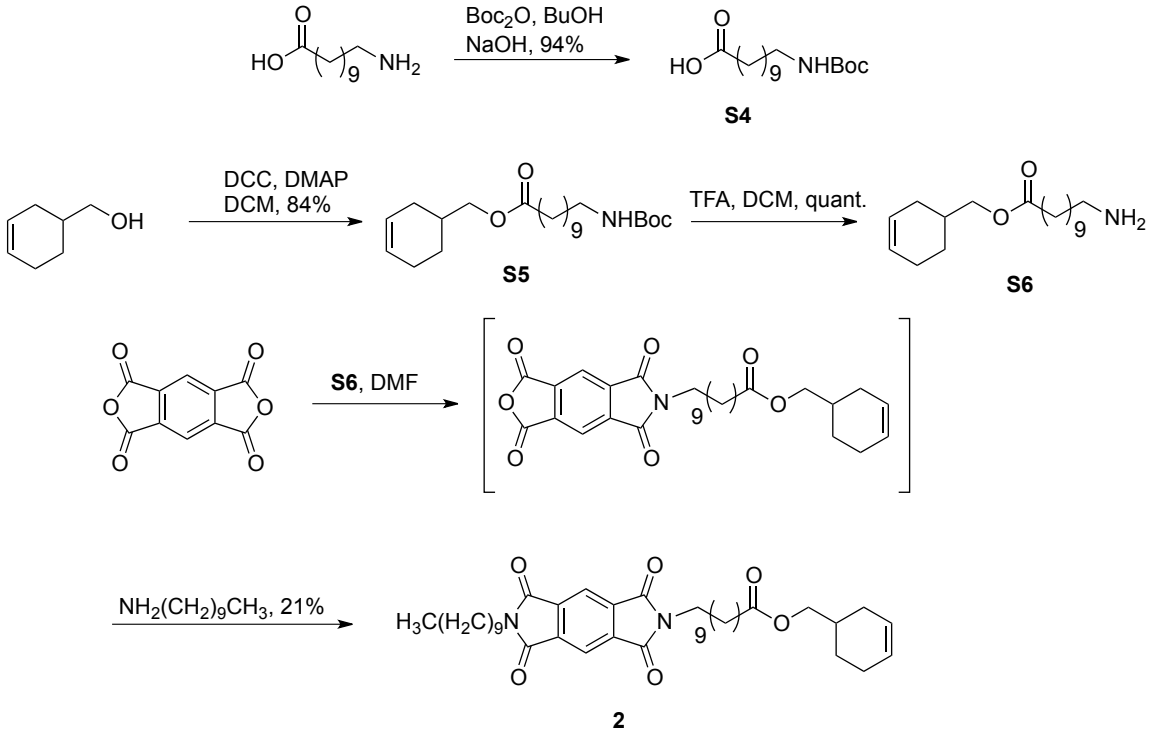


1

Cyclobut-1-enecarboxylic acid. Cyclobut-1-enecarboxylic acid was prepared according to the procedure for the preparation of 3,3-dimethylcylobutene carboxylic acid as described by Campbell et al.[18] and modified as previously reported.[12] ^{1}H-NMR (400 MHz, $CDCl_3$) δ 10.23 (bs, 1H), 6.94 (t, J = 1.2 Hz, 1H), 2.76 (t, J = 3.2 Hz, 2H), 2.51 (td, J = 3.2 Hz, 1.2 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 150.1, 138.4, 29.1, 27.5.

11-(5-(hexyloxy)naphthalen-1-yloxy)undecyl cyclobut-1-enecarboxylate (1). To a solution of cyclobut-1-enecarboxylic acid (190 mg, 1.94 mmol) and dicyclohexylcarbodiimide (DCC) (417 mg, 2.04 mmol) in CH_2Cl_2 (10 mL) stirred at 0°C for 30 minutes, S**2** (400 mg, 0.97 mmol) and a catalytic amount of dimethylaminopyridine (DMAP) were added. The mixture was allowed to warm to rt over 12 h. CH_2Cl_2 was evaporated under reduced pressure and the crude product was purified by flash chromatography (1:1/Hexanes:CH_2Cl_2) to afford **1** in 35% yield: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d,

J = 8.2 Hz, 2H), 7.36 (t, J = 7.6 Hz, 2H), 6.84 (d, J = 7.2 Hz, 2H), 6.80 (s, 1H), 4.10 (m, 6H), 2.74 (s, 1H), 2.47 (s, 1H), 1.93 (d, J = 6.3 Hz, 2H), 1.67 (d, J = 6.4 Hz, 1H), 1.58 (d, J = 5.7 Hz, 2H), 1.36 (d, J = 45.9 Hz, 8H), 0.94 (s, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.3, 154.6, 154.6, 146.1, 146.1, 138.8, 126.7, 124.9, 113.9, 113.9, 105.1, 68.0, 64.2, 64.2, 33.9, 32.7, 31.6, 29.5, 29.4, 29.4, 29.4, 29.3, 29.2, 29.0, 28.7, 28.6, 25.9, 25.8, 22.6, 14.0.



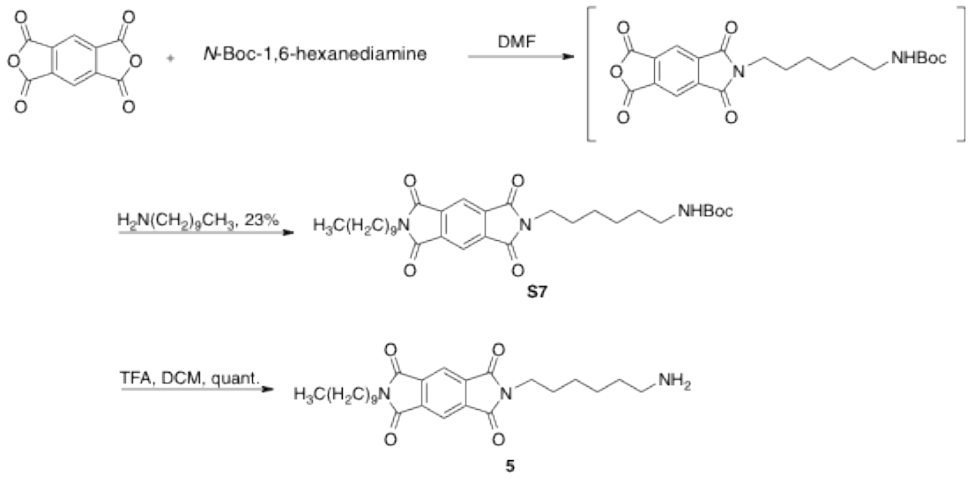
Cyclohex-3-en-1-ylmethyl 3-aminopropanoate (S6). A solution of **S4** (1.0 g, 3.31 mmol) and DCC (821.4 mg, 3.98 mmol) in CH_2Cl_2 (10 mL) were stirred at 0 °C for 30 min under Ar gas. 3-Cyclohexene-1-methanol (4.65 mL, 3.98 mmol) and a catalytic amount of DMAP were added to the mixture. This was allowed to warm to rt over 12 h. The CH_2Cl_2 was evaporated under reduced pressure and the crude product was purified by column chromatography (5:95/ EtOAc/CH_2Cl_2) to afford **S5** in 84% yield. Compound **S5** was then dissolved in a 1:1 trifluoroacetic acid:CH_2Cl_2 mixture and stirred at rt for one h. The solution was neutralized with 2M potassium hydroxide, followed by extraction into CH_2Cl_2 and dried over magnesium sulfate. The solution was concentrated to afford **S6** in quantitative yield. ^{1}H-NMR

($CDCl_3$): δ 5.71-5.64 (m, 2H), 4.49 (s, 1H), 3.99-3.96 (m, 2H), 3.10 (dd, J = 11.5, 5.6, 2H), 2.31 (t, J = 7.5, 2H), 2.07 (d, J = 7.4, 2H), 1.97-1.93 (m, 1H), 1.79 (d, J = 11.9, 2H), 1.63-1.56 (m, 13H), 1.45 (s, 7H), 1.28 (s, 11H). ^{13}C NMR ($CDCl_3$): δ 173.8, 166.5, 126.9, 125.4, 68.4, 34.2, 33.0, 30.8, 29.6, 29.5, 29.3, 29.2, 29.1, 28.1, 27.5, 25.2, 24.9, 24.3. HRMS $[M + H]^+$ calcd for $C_{18}H_{33}NO_2$ 295.25; found, 296.27.

Cyclohex-3-en-1-ylmethyl 3-(6-decyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-f] isoindol-2(1H, 3H, 5H)-yl)propanoate (2). Pyromellitic dianhydride (370.0 mg, 1.69 mmol) was dissolved and stirred in 10 mL DMF at 150 °C. To this mixture, a solution of **S6** (500.0 mg, 1.69 mmol) in 10 mL DMF was added dropwise and the solution was heated at reflux for 12 h. Decylamine (0.4 mL, 2.03 mmol) was added and the mixture was heated at reflux for an additional 12 h. The solution was cooled to rt and concentrated under reduced pressure. The residue was dissolved in dichloromethane (30 mL) and washed with distilled water (3 x 30 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (1:3/EtOAc:CH_2Cl_2) to afford **2** in 21% yield. ^{1}H-NMR ($CDCl_3$): δ = 8.26 (s, 2H), 5.68-5.65 (m, 2H), 3.97 (d, J = 6.7, 2H), 3.73 (t, J = 7.3, 4H), 2.30 (t, J = 7.5, 2H), 2.13 (s, 1H), 2.07 (dd, J = 6.4, 4.1, 3H), 1.94 (dt, J = 14.3, 7.3, 2H), 1.77 (dt, J = 10.5, 5.2, 2H), 1.71-1.67 (m, 4H), 1.63-1.59 (m, 2H), 1.29 (dd, J = 21.7, 8.1, 25H), 0.87 (t, J = 6.7, 3H). ^{13}C NMR ($CDCl_3$): δ 174.0, 166.3, 137.2, 127.0, 125.5, 118.1, 68.5, 40.0, 38.7, 38.7, 34.3, 34.3, 33.0, 31.8, 29.5, 29.4, 29.3, 29.3, 29.3, 29.2, 29.2, 29.1, 29.1, 29.1, 29.0, 28.9, 28.4, 28.2, 26.8, 26.8, 25.3, 25.0, 25.0, 24.4, 22.6, 14.1. HRMS $[M + H]^+$ calcd for $C_{38}H_{54}N_2O_6$ 635.40; found 635.41.

3

2,5-dioxopyrrolidin-1-yl cyclohex-3-enecarboxylate (3). 3-Cyclohexene-1-carboxylic acid (100 mg, 0.79 mmol), N-hydroxysuccinimide (100 mg, 0.87 mmol), and ethyl, dimethylaminopropyl carbodiimide hydrochloride (EDC•HCl) (182 mg, 0.95 mmol) were dissolved in CH_2Cl_2 and cooled in an ice bath. Then DIEA was added to adjust the pH to 8-9. The reaction was stirred for 16 h and washed with 5% Na_2CO_3 (50 mL). The organic phase was dried and condensed, followed by flash chromatography, eluted with 100% CH_2Cl_2 to yield a white solid in 80% yield: ^{1}H NMR (600 MHz, $CDCl_3$) δ 5.88 – 5.44 (m, 2H), 3.01 – 2.80 (m, 1H), 2.76 (s, 4H), 2.42 – 2.22 (m, 2H), 2.17 – 1.92 (m, 3H), 1.90 – 1.62 (m, 1H). ^{13}C NMR ($CDCl_3$) δ 170.6, 169.2, 126.6, 124.0, 36.6, 26.9, 25.4, 24.6, 23.6.



2-(6-aminohexyl)-6-decylpyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetraone (5)

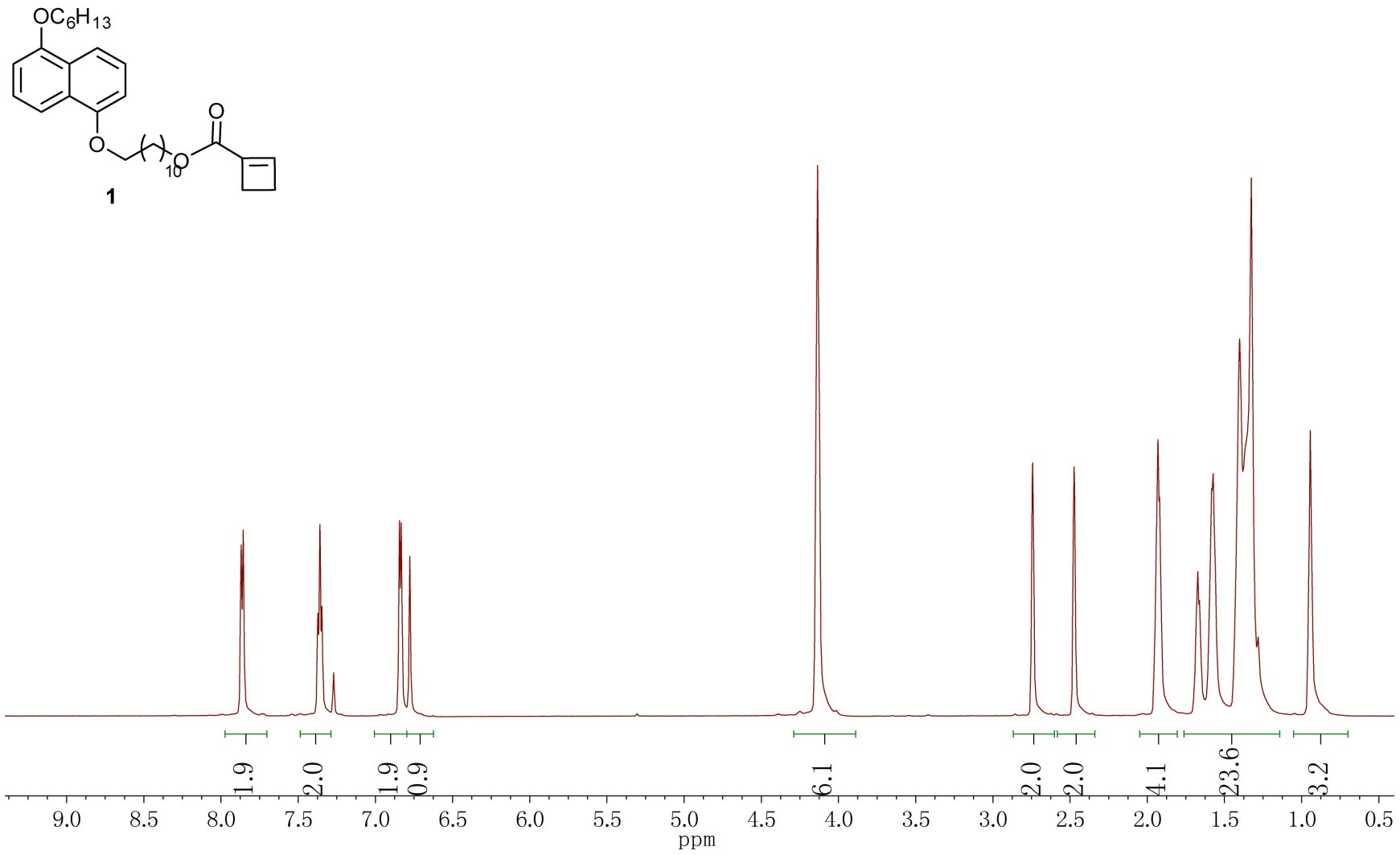
Pyromellitic dianhydride (370.0 mg, 1.69 mmol) was dissolved and stirred in 10 mL DMF at 150 °C. To this mixture, *N*-Boc-1,6-hexanediamine (365.3 mg, 1.69 mmol) was added dropwise and the solution was heated at reflux for 12 h. Decylamine (0.4 mL, 2.03 mmol) was added dropwise and the mixture was heated at reflux for an additional 12 h. The solution was cooled to rt and concentrated under reduced pressure. The residue was dissolved in dichloromethane (30 mL) and washed with distilled water (3 x 30 mL). The organic layer was dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by column chromatography (1:3/EtOAc:CH_2Cl_2) to afford *tert*-butyl (6-(6-decyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-*f*]isoindol-2(1*H*,3*H*,5*H*)-yl)hexyl)carbamate in 23% yield. ^{1}H-

NMR ($CDCl_3$): δ 8.16 (s, 2H), 3.64 (t, J = 7.3, 4H), 3.00 (q, J = 6.4, 2H), 1.60 (d, J = 8.9, 4H), 1.33 (s, 9H), 1.28-1.15 (m, 21H), 0.77 (t, J = 6.8, 3H). ^{13}C NMR ($CDCl_3$): δ 166.3, 137.2, 118.1, 38.7, 38.5, 31.8, 29.5, 29.4, 29.2, 29.1, 28.4, 28.3, 26.8, 26.4, 26.2, 22.6, 14.1. HRMS $[M + Na]^+$ calcd for $C_{31}H_{45}N_3O_6$ 578.33; found, 578.32. The intermediate compound was then dissolved in a 1:1 trifluoroacetic acid:CH_2Cl_2 mixture and stirred at rt for 1 h. The solution was neutralized with 2M potassium hydroxide, followed by extraction into CH_2Cl_2 and dried over magnesium sulfate. The solution was concentrated to afford **5** in quantitative yield. ^{1}H-NMR ($CDCl_3$): δ 8.18 (s, 2H), 3.65 (td, J = 7.2, 2.9, 4H), 2.59 (t, J = 6.7, 2H), 1.62 (dq, J = 14.0, 7.0, 4H), 1.40-1.32 (m, 6H), 1.29 (dd, J = 7.1, 3.1, 3H), 1.24 (t, J = 5.7, 6H), 1.20 (s, 15H), 0.78 (t, J = 6.8, 3H). ^{13}C NMR ($CDCl_3$): δ 166.3, 137.2, 118.1, 42.0, 38.7, 38.6, 33.6, 31.8, 29.5, 29.4, 29.2, 29.1, 28.4, 28.4, 26.8, 26.6, 26.3, 22.6, 14.1.

poly(1-*alt*-2)$_5$. The reaction was monitored by ^{1}H NMR. The NMR tube was evacuated under high vacuum for 15 min, and then was purged with N_2 gas for another 15 min. Under an N_2 atmosphere, a solution of monomer **1 (**29.6 mg**,** 0.060 mmol**)** in CD_2Cl_2 (300 μL) was added to the NMR tube. Then a solution of catalyst $(H_2IMes)(3\text{-Br-Py})_2(Cl)_2Ru{=}CHPh$ (**4**, 5.3 mg, 6.0 μmol) in CD_2Cl_2 (300 μL) was added to the NMR tube. After complete mixing of the solution, the NMR tube was spun for 60 min at an elevated temperature 37 °C until the precatalyst had reacted as can be observed by disappearance of ruthenium alkylidene proton at 19 ppm. Monomer **2** (19.5 mg, 0.030 mmol) in CD_2Cl_2 (100 μL) was added to the NMR tube. The reaction was quenched in 8 h with ethyl vinyl ether (50 μL) and the resulting solution was stirred for another 1 h. The mixture was condensed to give a dark brown oil which was further purified by column chromatography (100:1/CH_2Cl_2:MeOH (methanol)) to yield an orange solid in 55% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 – 7.92 (m, 8H), 7.83-7.74 (m, 10H), 7.42 – 7.20 (m, 10H), 6.93 – 6.62 (m, 15H), 5.66 – 5.17 (m, 8H), 4.30 – 3.91 (m, 41H), 3.72 (m, 16H), 3.41 – 3.03 (m, 6H), 2.65 – 1.02 (m, 382H), 0.99 – 0.62 (m, 34H). Mn^{cal}=5748, Mn^{GPC}=3291, Mw^{GPC}=4252, PDI=1.29.

poly(1-*alt*-5)$_{10}$. The reaction was monitored by ^{1}H NMR. The NMR tube was evacuated under high vacuum for 15 min, and then was purged with N_2 gas for another 15 min. Under an N_2 atmosphere, a

solution of monomer **1 (**29.6 mg**,** 0.060 mmol**)** in CD_2Cl_2 (300 µL) was added to the NMR tube. Then a solution of catalyst $(H_2IMes)(3\text{-Br-Py})_2(Cl)_2Ru{=}CHPh$ (**4**, 5.3 mg, 6.0 µmol) in CD_2Cl_2 (300 µL) was added to the NMR tube. After complete mixing of the solution, the NMR tube was spun for 60 min at 25 °C until the precatalyst had reacted as can be observed by disappearance of ruthenium alkylidene proton at 19 ppm. Monomer **3** (26.8 mg, 0.120 mmol) in CD_2Cl_2 (100 µL) was added to the NMR tube. The reaction was quenched in 6 h with ethyl vinyl ether (50 µL) and the resulting solution was stirred for another 1 h. The mixture was condensed to give a dark brown oil which was further purified by column chromatography (100:1/CH_2Cl_2:MeOH) to yield an orange solid in 75% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (m, 20H), 7.32 (m, 20H), 6.98 – 6.56 (m, 30H), 5.33 (m, 13H), 4.11 (s, 3H), 292 – 1.25 (m, 366H), 0.95 (m, 30H). The resulting polymer poly(**1**-*alt*-**3**)$_{10}$ (27.2 mg, 3.7 µmol) was dissolved in dry THF and cooled in an ice bath. EDC•HCl (7.1 mg, 37 µmol), DIEA (9.7 mg, 74 µmol), and 2-(6-aminohexyl)-6-decylpyrrolo[3,4-*f*]isoindole-1,3,5,7(2*H*,6*H*)-tetraone **(5)** (34 mg, 74 µmol) were added. The mixture was stirred for 2 days and then filtered, followed by column chromatography (5:95/acetone/CH_2Cl_2) to yield an orange solid in 20% yield. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 – 7.92 (m, 9H), 7.80 (dd, J = 14.4, 6.1 Hz, 20H), 7.42 – 7.18 (m, 20H), 6.93 – 6.62 (m, 30H), 5.66 – 5.17 (m, 12H), 4.30 – 3.91 (m, 59H), 3.72 (dd, J = 14.7, 7.1 Hz, 15H), 3.41 – 3.03 (m, 6H), 2.65 – 0.99 (m, 545H), 0.99 – 0.62 (m, 86H). Mn^{Cal}=10948, Mn^{GPC}=7966, Mw^{GPC}=10221, PDI=1.28.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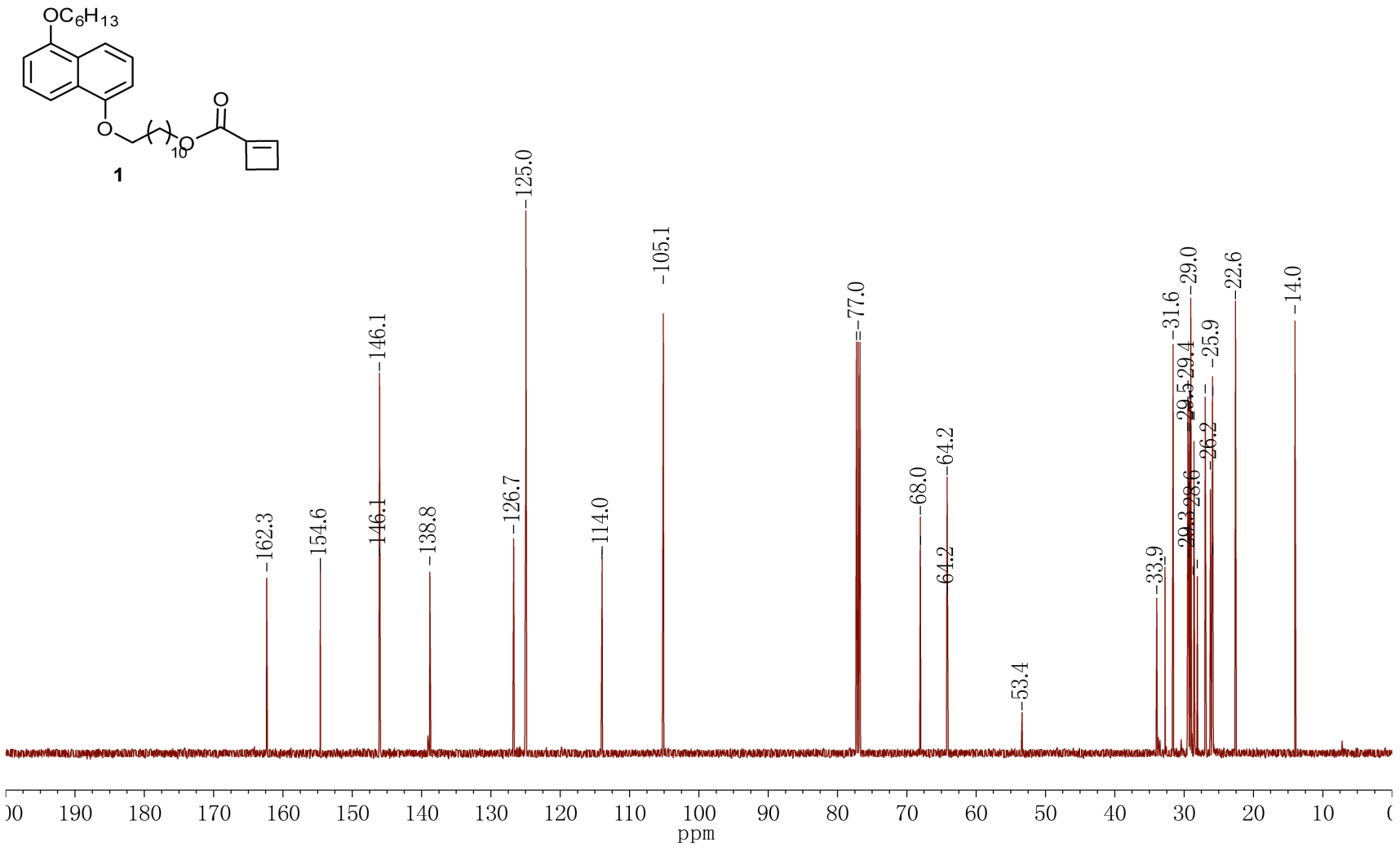
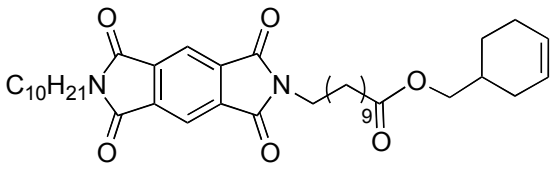


Figure S2. ^{13}C-NMR spectrum of 11-(5-(hexyloxy)naphthalen-1-yloxy)undecyl cyclobut-1-enecarboxylate (**1**)



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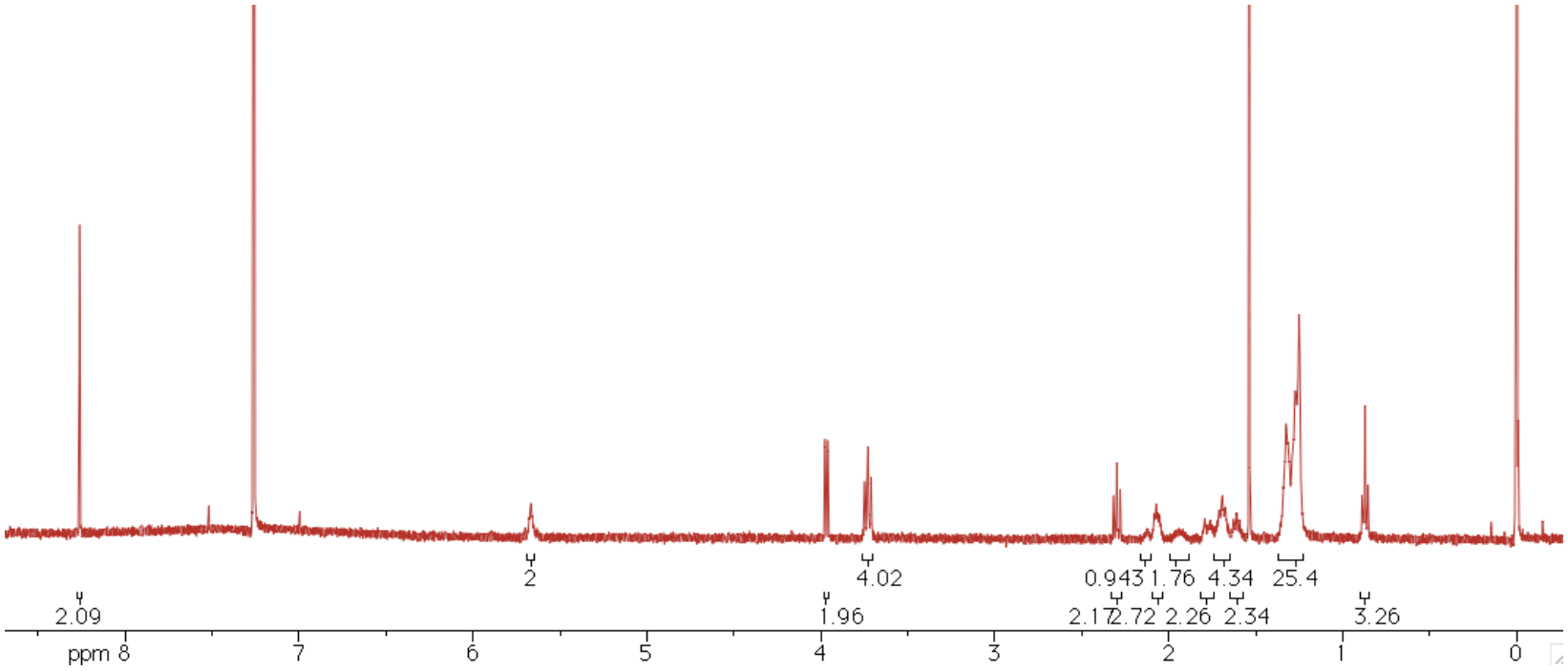
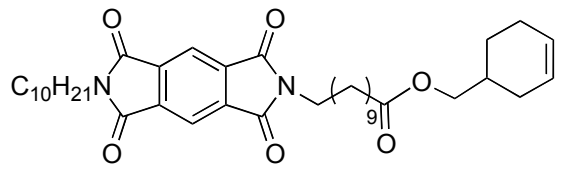


Figure S3. ^{1}H-NMR spectrum of Cyclohex-3-en-1-ylmethyl 3-(6-decyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-f] isoindol-2(1H, 3H, 5H)-yl)propanoate (**2**)



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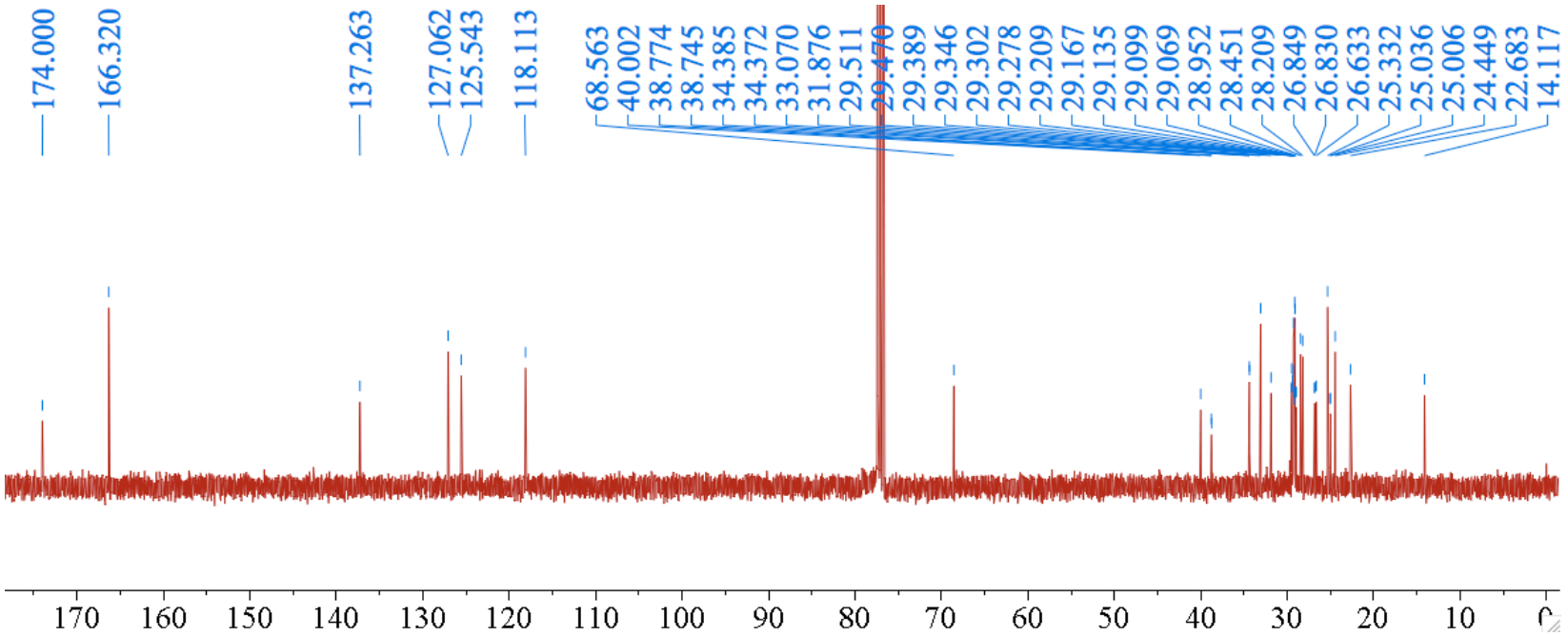

Figure S4. ^{13}C-NMR spectrum of Cyclohex-3-en-1-ylmethyl 3-(6-decyl-1,3,5,7-tetraoxo-6,7-dihydropyrrolo[3,4-f] isoindol-2(1H, 3H, 5H)-yl)propanoate (**2**)

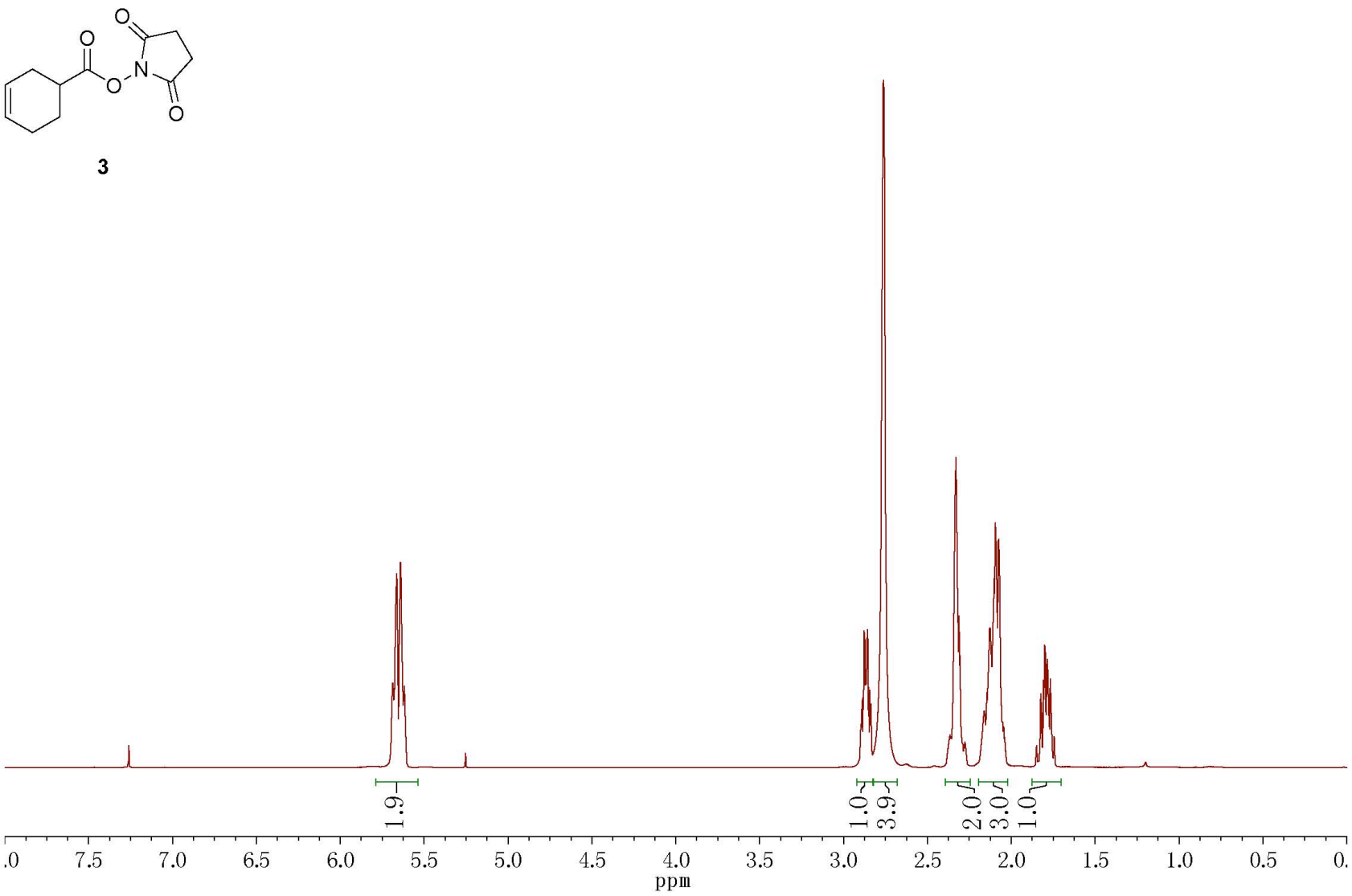

Figure S5. ^{1}H-NMR spectrum of 2,5-dioxopyrrolidin-1-yl cyclohex-3-enecarboxylate (**3**).

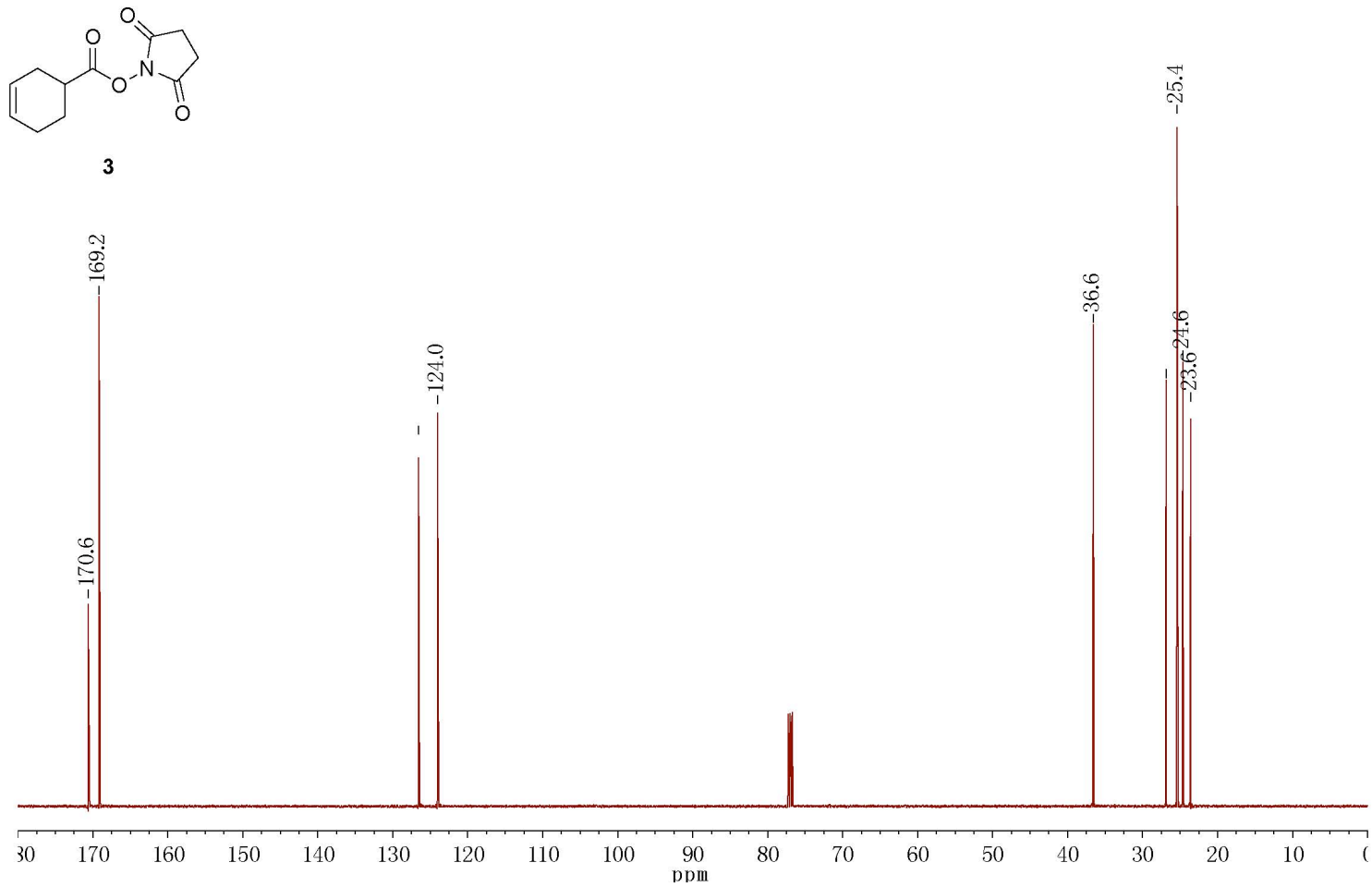

Figure S6. ^{13}C-NMR spectrum of 2,5-dioxopyrrolidin-1-yl cyclohex-3-enecarboxylate (**3**).

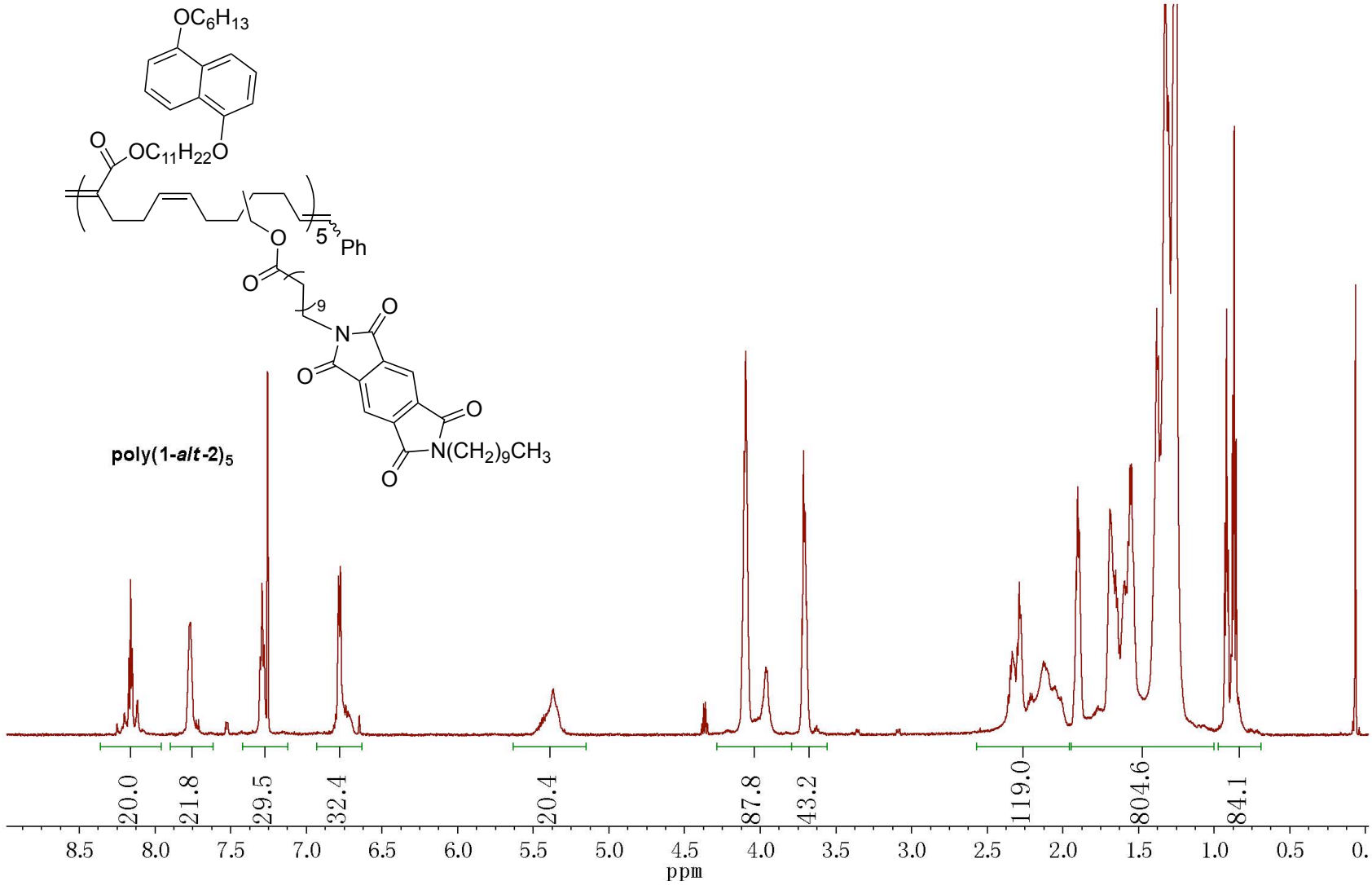

Figure S7. ^{1}H-NMR spectrum of poly(**1**-*alt*-**2**)$_5$.

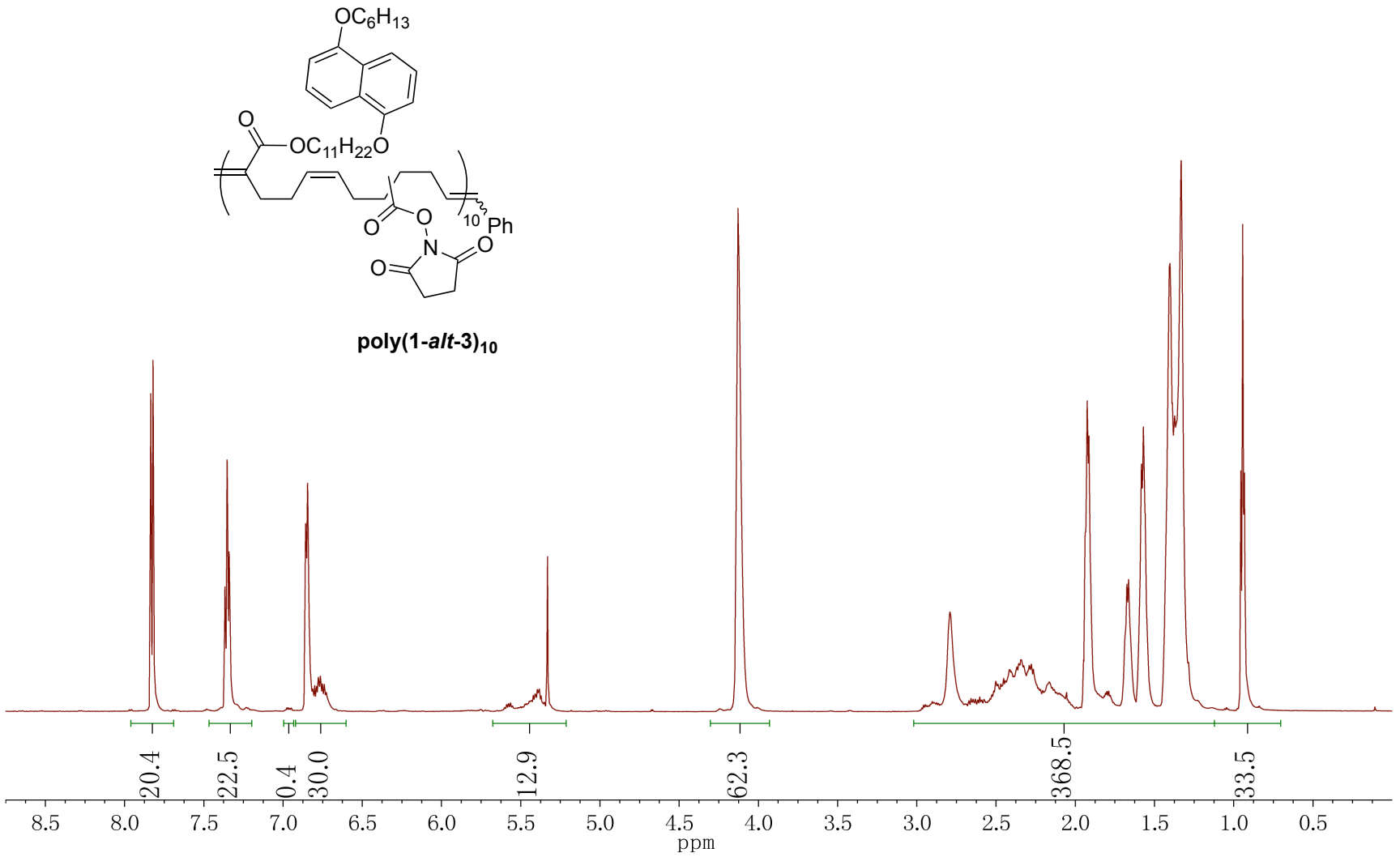

Figure S8. ^{1}H-NMR spectrum of poly(**1**-*alt*-**3**)$_{10}$

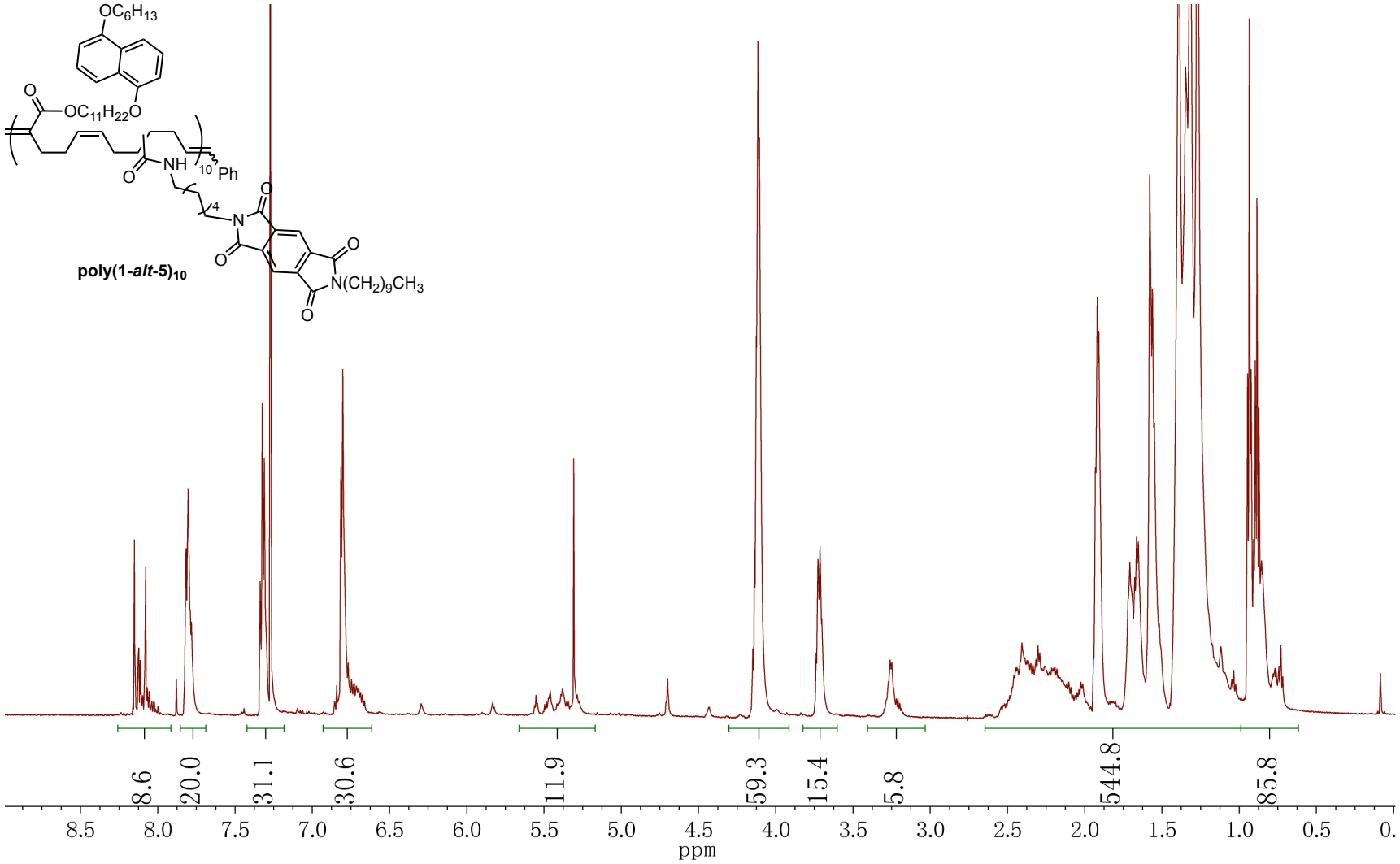

Figure S9. ^{1}H-NMR spectrum of poly(**1**-*alt*-**5**)$_{10}$.

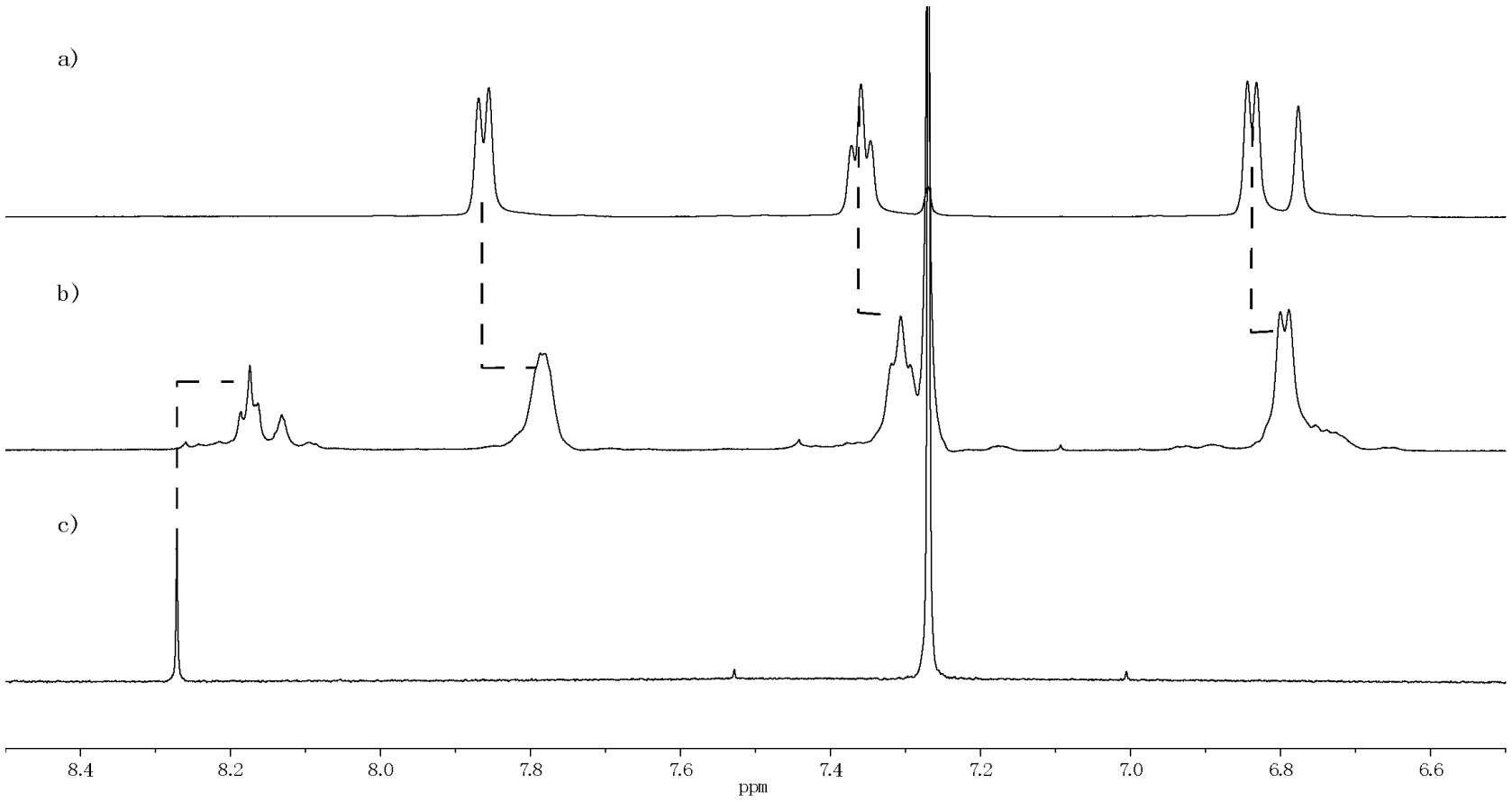

Figure S10. Partial ^{1}H-NMR spectrum of a) **1**; b) poly(**1**-*alt*-**2**)$_5$; and c) **2**.

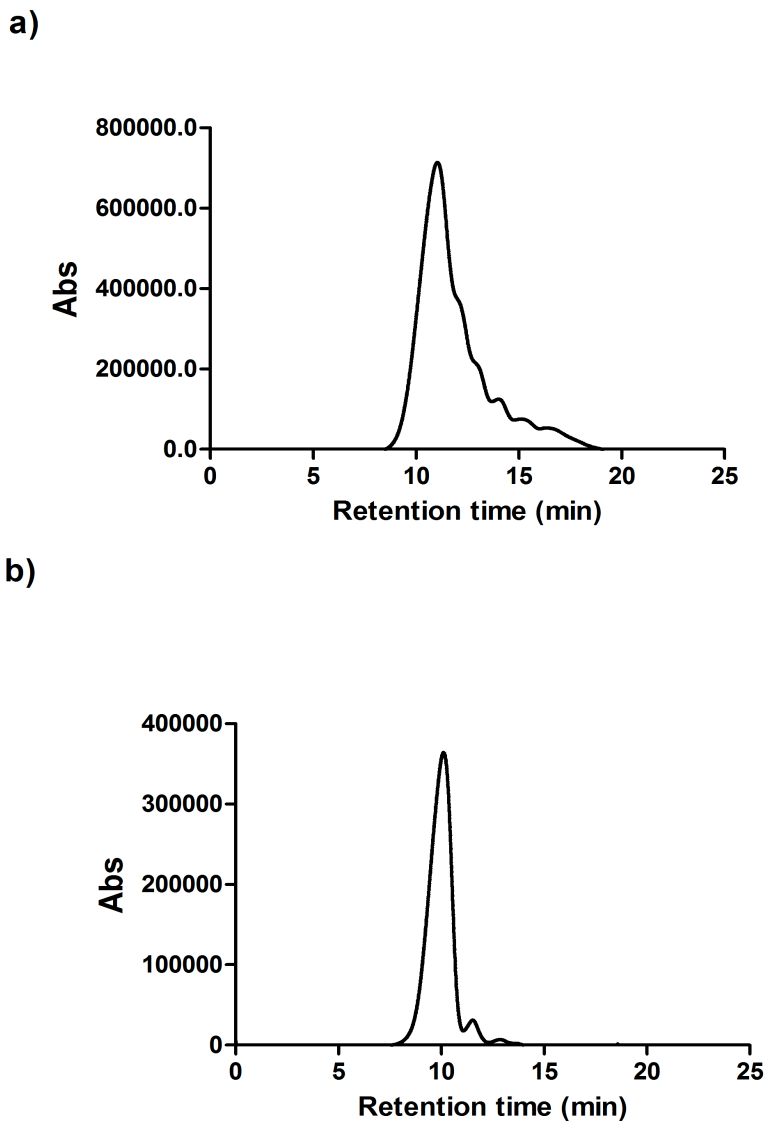

Figure S11. GPC traces of alternating copolymers. a) poly(**1**-*alt*-**2**)$_5$; b) poly(**1**-*alt*-**5**)$_{10}$, polystyrene standard was used for calibration.