Electronic Supplementary Material (ESI) for Chemical Communications

Polymer Nitrile *N*-Oxide Directed toward Catalyst- and Solvent-Free Click Grafting

Supporting Information

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Contents

1. Experimental Section

Equipment

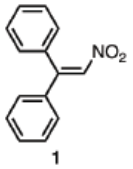
^{1}H NMR (400 MHz) and ^{13}C NMR spectra (100 MHz) were recorded on a JEOL AL-400 spectrometer using $CDCl_3$, DMSO–d_6, and toluene-d_8 as the solvents, calibrated using residual undeuterated solvent or tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO FT/IR-230 spectrometer. FAB HR-MS were taken by JEOL JMS700 mass spectrometer at the Center for Advanced Materials Analysis, Tokyo Institute of Technology on request. Melting points were measured on a MELTING POINT APPARATUS SMP3 (Stuart Scientific) instrument. SEC analyses using DMF as eluent were carried out on JASCO PU-2080 plus pump with a JASCO UV-1570 (UV detector) JASCO RI-1530 (RI detector) equipped with a consecutive linear polystyrene gel columns TOSO TSK gel GMHXL and G5000HXL at 30 °C. SEC analyses using THF as eluent were carried out with a Tosoh high-speed liquid chromatograph HLC-8120 equipped with refractive index (RI) and UV detectors, which was operated with three TSK gel columns, GMHXL×2 and G2000HXL at 40 °C. The absolute molecular weight was calculated by gel permeation chromatography using a Shodex GPC-101 system with Minidawn (Wyatt Technology) as a light scattering detector (GPC-MALS) and Shodex KF-803L and 804L columns using THF as an eluent. TGA analyses were carried out on a Shimadzu TGA-50 instrument under N_2 atmosphere (flow rate of 50 mL/min) to determine 5% and 10% weight decomposition temperatures (T_{d5} and T_{d10}) at which 5% and 10% weight loss was observed. DSC analyses were carried out with a Shimadzu DSC-60 instrument at N_2 atmosphere (flow rate of 50 mL/min) with liquid N_2 as a refrigerant to determine a glass transition temperature (T_g). Preparative GPC were carried out using a HPLC LC-918 instrument by Japan Analysis Kogyo with a Megapak-Gel 201CP (Guard Column), a Megapak-Gel 201C, and a JAIGEL-H.

Materials

Tetrahydrofuran (THF) was freshly distilled in the presence of sodium and benzophenone under argon atmosphere prior to use. Monomers were purchased from Wako Pure Chemical Industries Co. Ltd. and purified by a general distillation technique under reduced pressure to remove the polymerization inhibitor. For the NMR analysis, deuterated solvents from Acros Organics were used. Other reagents and solvents commercially available were used without further purification unless otherwise noted.

2. Chemical Synthesis

Synthesis of 1-nitro-2,2-diphenylethene **1**.



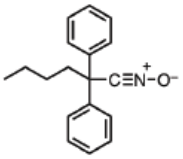
1

Method 1.[1] To a solution of bis(trimethylsilyl)amine (HMDS, 3.23 g, 20.0 mmol) in THF (10.0 mL) was added *n*-butyllithium (2.60 M in hexane, 7.96 mL, 20 mmol) at 0 °C under Ar atmosphere and the mixture was stirred for 30 min. Then, benzophenone (1.82 g, 10.0 mmol) was added to the mixture. The mixture was warmed to room temperature, stirred for 1 d, and evaporated to give the crude. Nitromethane (40 mL) was added to the crude residue and the mixture was sonicated for 30 min, and filtrated. The filtrate was refluxed for 3 d until the disappearance of the spot of the benzophenone imine derivative on TLC plate. After cooling to room temperature, the mixture was evaporated and recrystallized from hexane/ethyl acetate. The solids were collected by filtration and dried *in vacuo* to give 1-nitro-2,2-diphenylethene **1** (1.64 g, 7.3 mmol, 73%) as pale yellow plates.

Method 2. [2] Benzophenone imine (0.91 g, 5.00 mmol) and nitromethane (1.22 g, 20.0 mmol) were placed in a 5 mL

flask and the mixture was refluxed for 3 h. After cooling to room temperature, the reaction mixture was evaporated and purified by a silica gel column chromatography (eluent: hexane/ethyl acetate: 5/1). The crude was recrystallized from toluene to obtain 1-nitro-2,2-diphenylethene **1** (0.65 g, 2.88 mmol, 58%) as pale yellow plates; mp 86.2–87.2 ºC (lit. 86–87 °C)[1]; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.51–7.35 (m, 7H), 7.32–7.21 (m, 4H) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 150.6, 137.2, 135.6, 134.5, 131.0, 129.5, 129.0, 128.9, 128.9, 128.6 ppm; IR (KBr) υ 1658 (C=C), 1610 (C=C, Ar), 1516 (N=O), 1445 (C=C, Ar), 1339 (N=O) cm^{-1}; FAB-HRMS (m/z) calc'd for $C_{14}H_{12}NO_2^+$ $[M+H]^+$, 226.0868; found, 226.0872.

Synthesis of 1,1-diphenylhexylnitrile *N*-oxide **2**.[3]



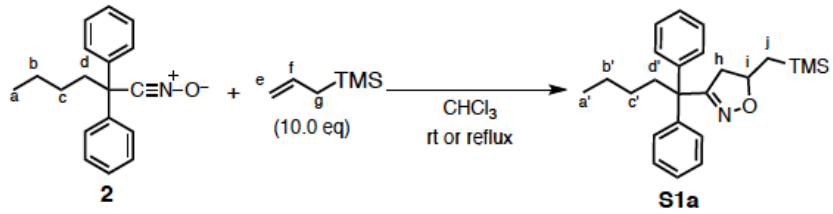
2

1-Nitro-2,2-diphenylethene **1** (0.901 g, 4.0 mmol) was dissolved in THF (80 mL) under argon atmosphere and cooled to –78 °C. *n*-Butyllithium (2.60 M in hexane, 3.08 mL, 8.0 mmol) was added into the solution and the mixture was stirred for 30 min at the same temperature. To the reaction mixture was added conc. H_2SO_4 (>95%, 3.92 g, 40 mmol) and the mixture was warmed to 0 °C and stirred for 30 min. The mixture was diluted with dichloromethane (100 mL), washed with water, dried over anhydrous magnesium sulfate, filtered, and evaporated. The crude was purified by a silica gel column chromatography (eluent: hexane/ethyl acetate: 5/1) to obtain **2** in 95% yield (1.01 g, 3.82 mmol) as a deep red oil; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.37–7.23 (m, 10H, Ph–H), 2.38 (t, *J* = 6.8 Hz, 2H, Ph_2C–CH_2–), 1.38–1.31 (m, 4H, –CH_2–), 0.88 (t, *J* = 6.8 Hz, 3H, –CH_3) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 141.8, 128.8, 127.9, 126.7, 53.2, 40.6, 28.0, 22.6, 13.8 ppm; IR (KBr) υ 2289 (C≡N$^+$–O$^-$), 1598 (C=C, Ar), 1448 (C=C, Ar) cm^{-1}; FAB-HRMS (*m/z*) calc'd for $C_{18}H_{20}NO^+$ $[M+H]^+$, 226.1545; found, 226.1540.

Evaluation of the reactivity of 1,1-diphenylhexanenitrile *N*-oxide 2 with various unsaturated bonds.

To confirm the reactivity of aliphatic nitrile *N*-oxide **2** to unsaturated bonds, the cycloaddition reactions of **2** were performed by using various dipolarophiles such as allyltrimethylsilane (monosubstituted olefin), *trans*-4-octene (disubstituted olefin), 2-methyl-2-butene (trisubstituted olefin), and isobutyronitrile (nitrile group). The conversions of each reaction were estimated from the time-dependent ^{1}H NMR spectra by comparing the integrals between newly appeared peaks and the peaks of original aliphatic protons. Assuming that the reaction at the initial stage obeyed the first-order kinetics, the plots were fit by a line and the slope was calculated by least squares approximation to determine the reaction kinetic constants. The half-lives τ were estimated from the following equation (τ = 1n2/*k*). The reaction rate constants and the half-lives of **2** of above experiments were summarized in **Table S1**. As a result, it turned out that both electronic and steric factors of dipolarophiles are densely related to the reactivity of cycloaddition reaction with **2**.

Evaluation of the reactivity of 1,1-diphenylhexylnitrile *N*-oxide 2 with allyltrimethylsilane.



Scheme S1

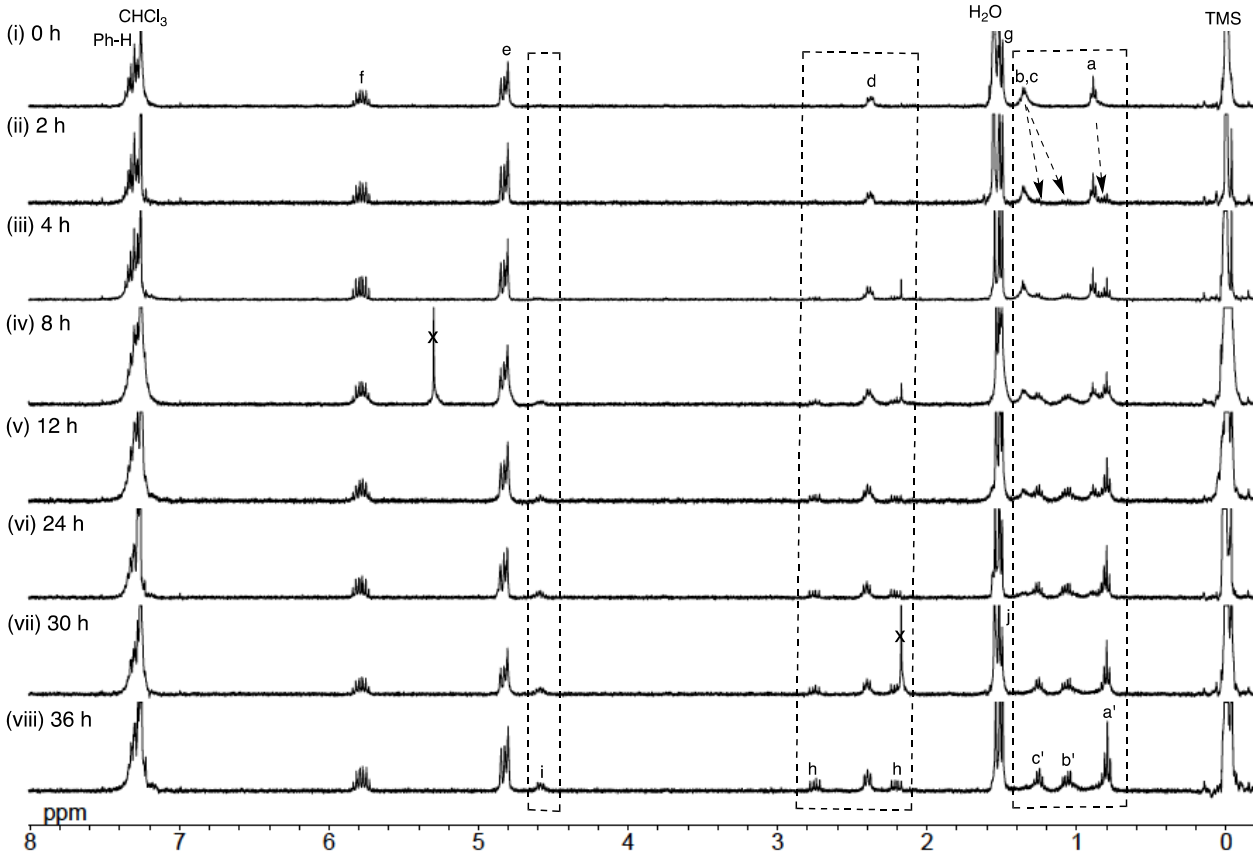


Figure S1. Time-dependent ^{1}H NMR spectra of a mixture of **2** and allyltrimethylsilane to give **S1a** at room temperature in $CDCl_3$ (400 MHz, 298 K, $CDCl_3$).

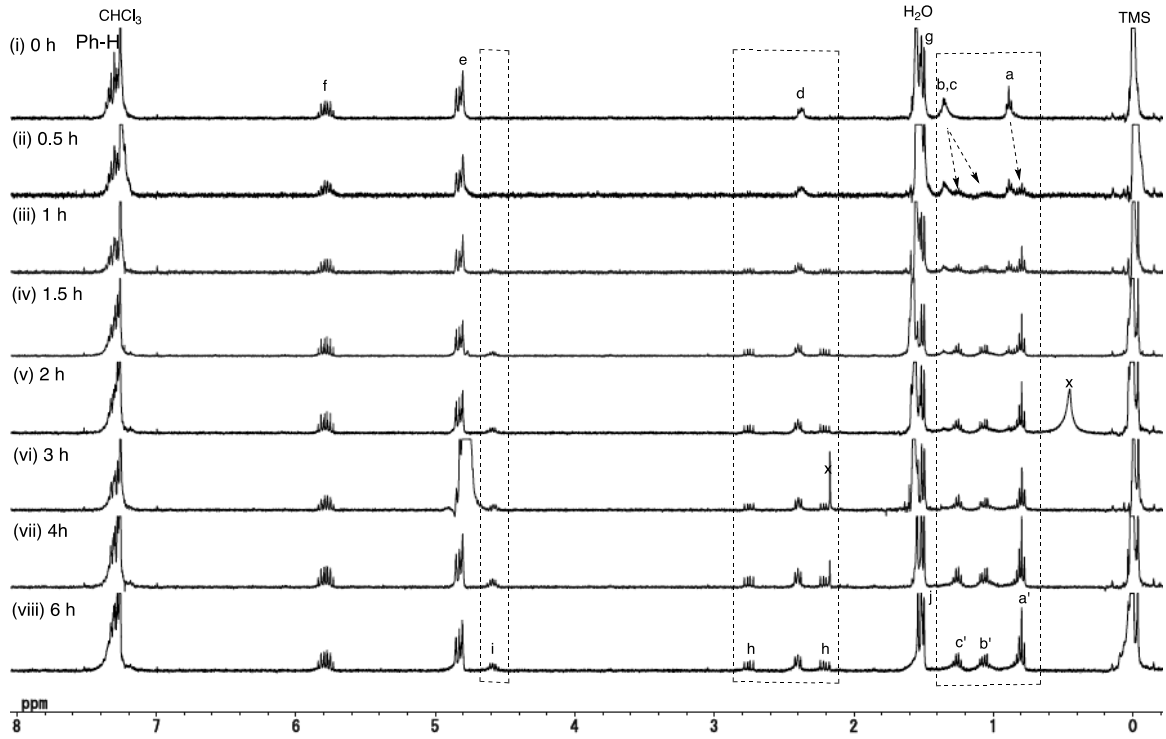


Figure S2. Time-dependent ^{1}H NMR spectra of a mixture of **2** and allyltrimethylsilane to give **S1a** in refluxed $CDCl_3$ (400 MHz, 298 K, $CDCl_3$).

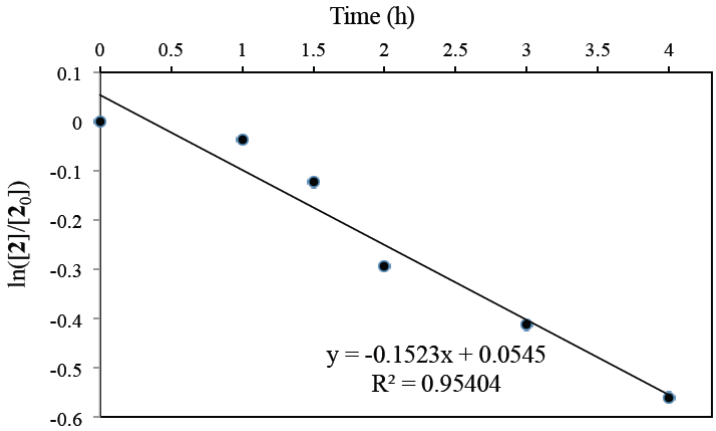


Figure S3. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to allyltrimethylsilane in $CHCl_3$ at room temperature.

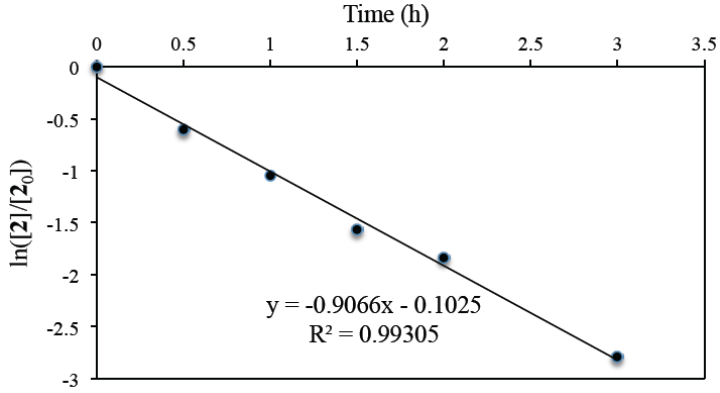
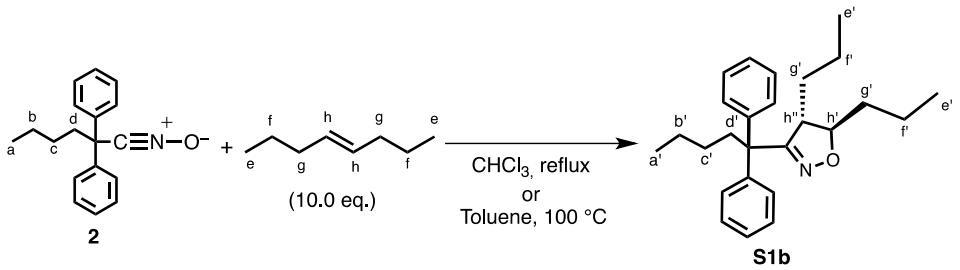


Figure S4. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to allyltrimethylsilane in $CHCl_3$ under reflux.

Evaluation of the reactivity of 1,1-diphenylhexylnitrile *N*-oxide 2 with *trans*-4-octene.



Scheme **S2**

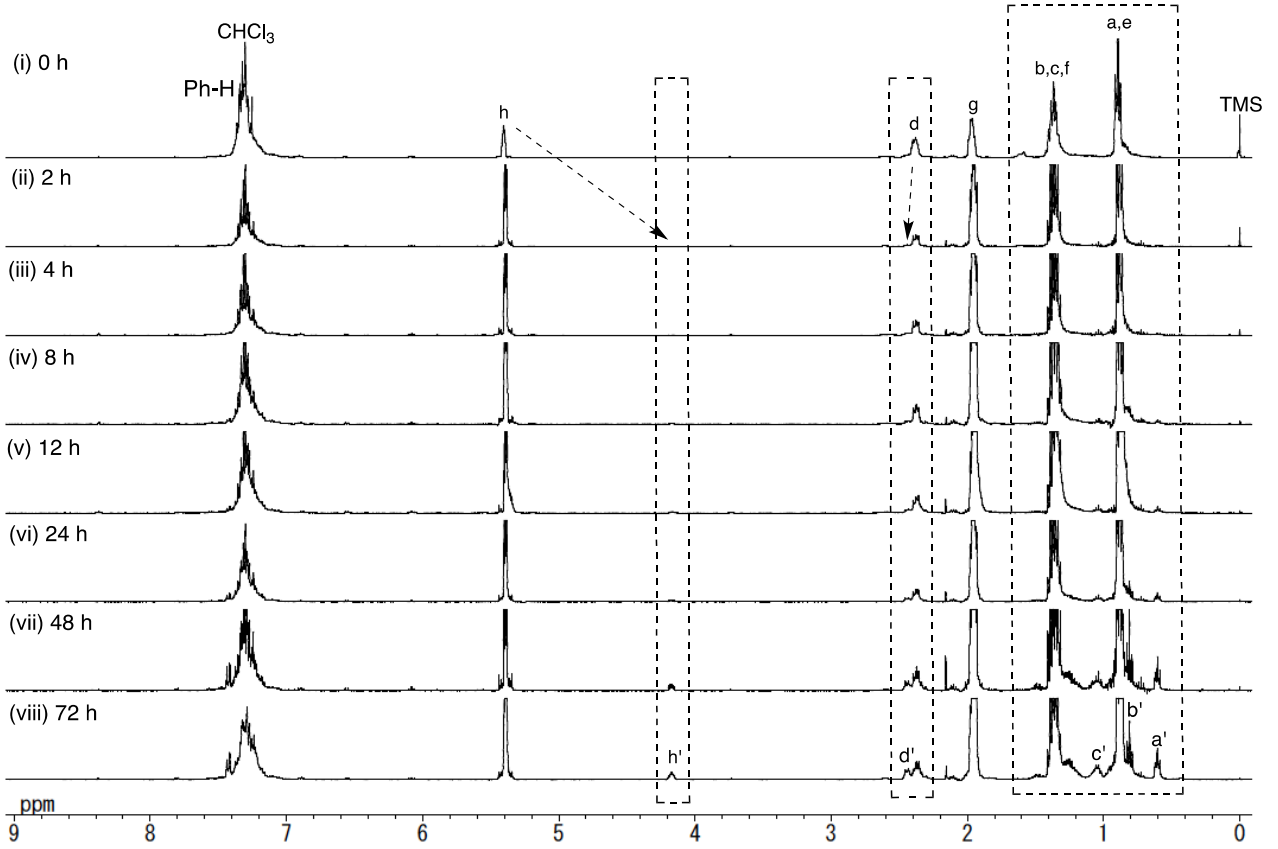


Figure S5. Time-dependent ^{1}H NMR spectra of a mixture **2** and *trans*-4-octene to give **S1b** in refluxed $CDCl_3$ (400 MHz, 298 K, $CDCl_3$).

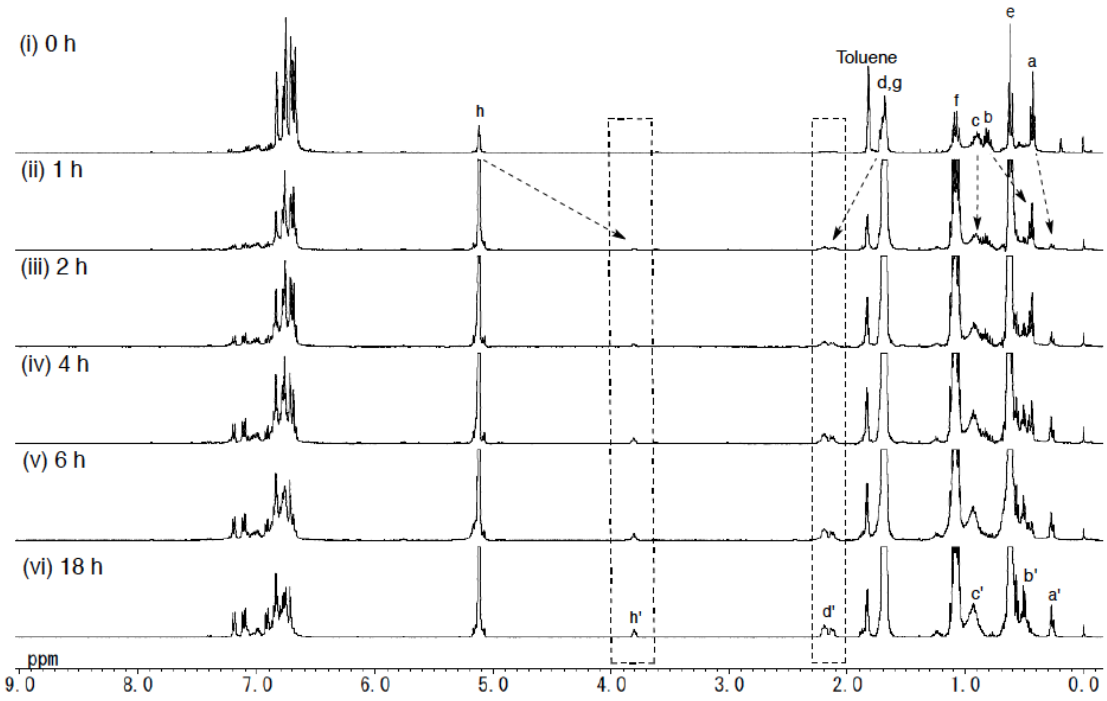


Figure S6. Time-dependent ^{1}H NMR spectra of a mixture **2** and *trans*-4-octene to give **S1b** at 100 °C in toluene-d_8 (400 MHz, 298 K, toluene-d_8).

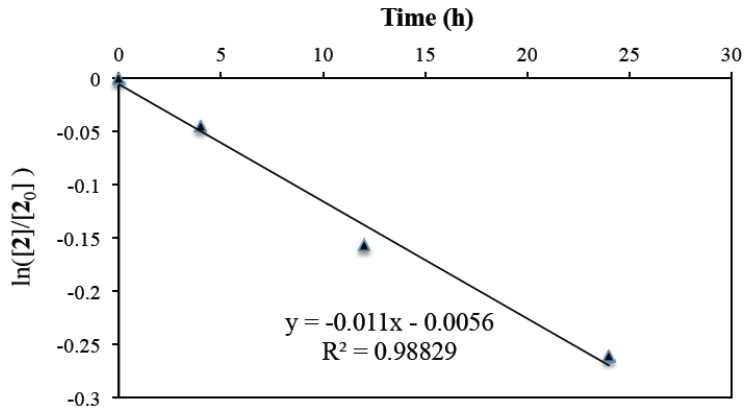


Figure S7. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to *trans*-4-octene in $CHCl_3$ under reflux.

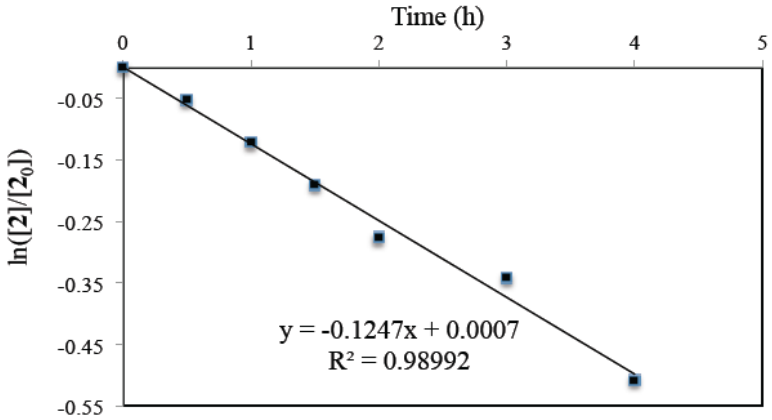
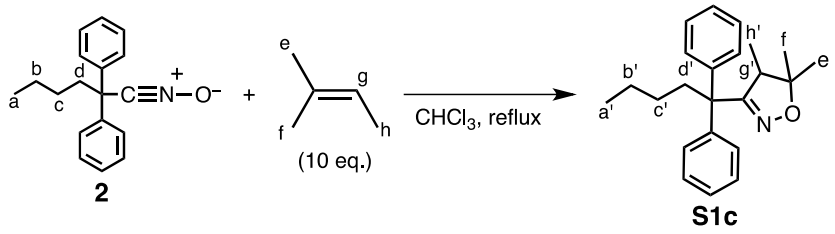


Figure S8. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to *trans*-4-octene in toluene at 100 °C.

Evaluation of the reactivity of 1,1-diphenylhexylnitrile *N*-oxide with 2-methyl-2-butene.



Scheme S3

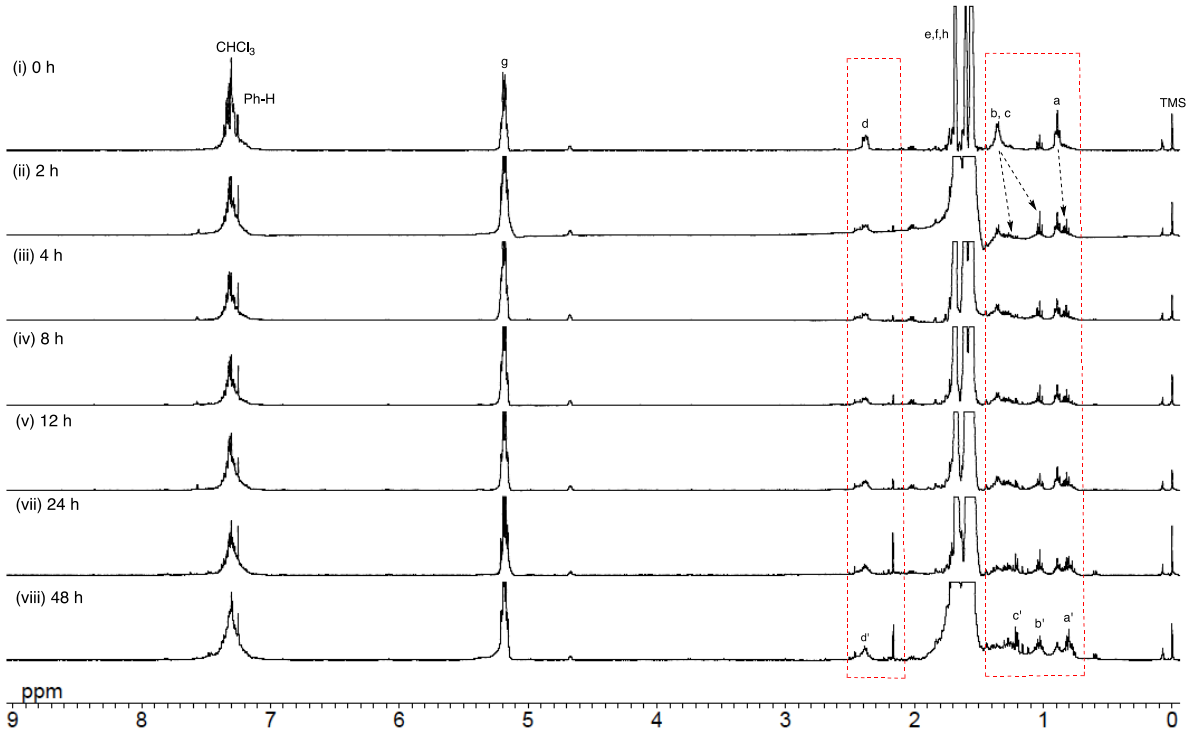


Figure S9. Time-dependent ^{1}H NMR spectra of a mixture of **2** and 2-methyl-2-butene to give **S1c** in refluxed $CDCl_3$ (400 MHz, 298 K, $CDCl_3$).

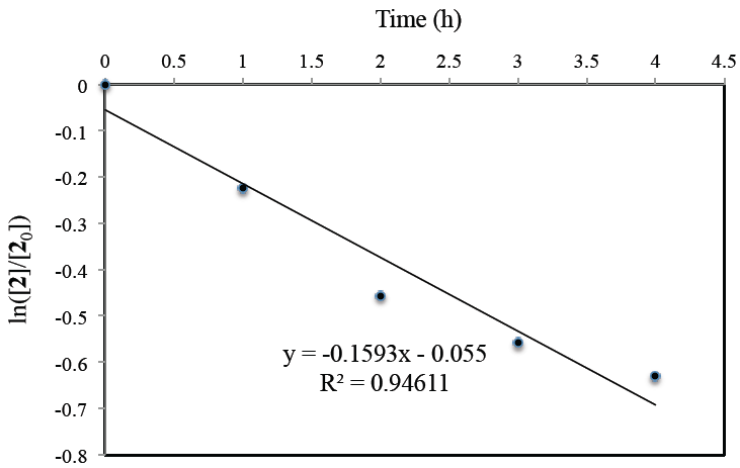
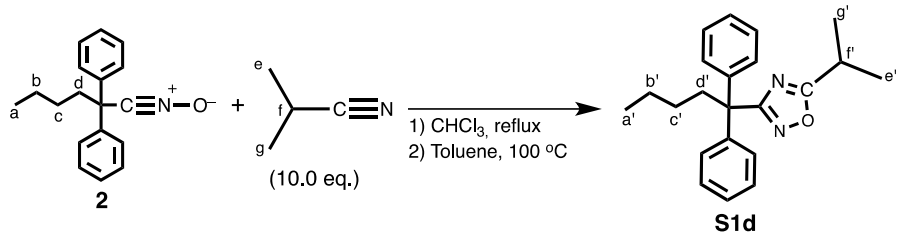


Figure S10. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to 2-methyl-2-butene in $CHCl_3$ under reflux.

Evaluation of the reactivity of 1,1-diphenylhexylnitrile *N*-oxide 2 with isobutyronitrile.



Scheme S4

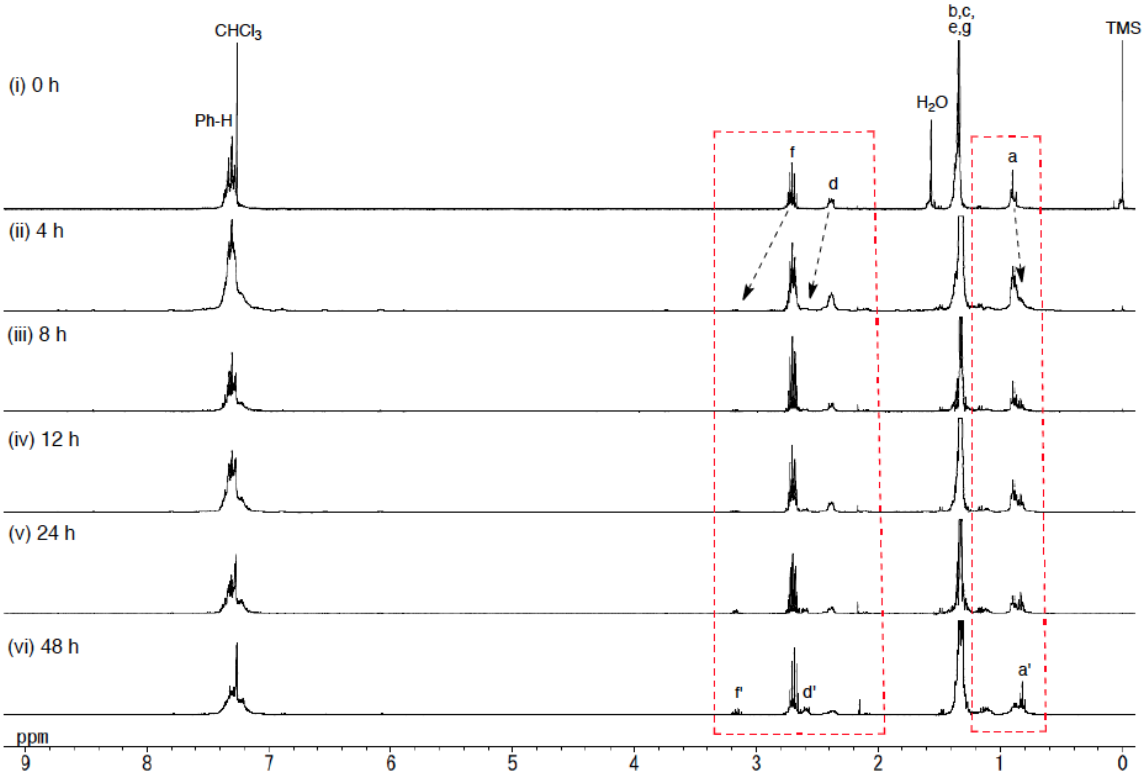


Figure S11. Time-dependent ^{1}H NMR spectra of a mixture of **2** and isobutyronitrile to give generating **S1d** in refluxed $CDCl_3$ (400 MHz, 298 K, $CDCl_3$).

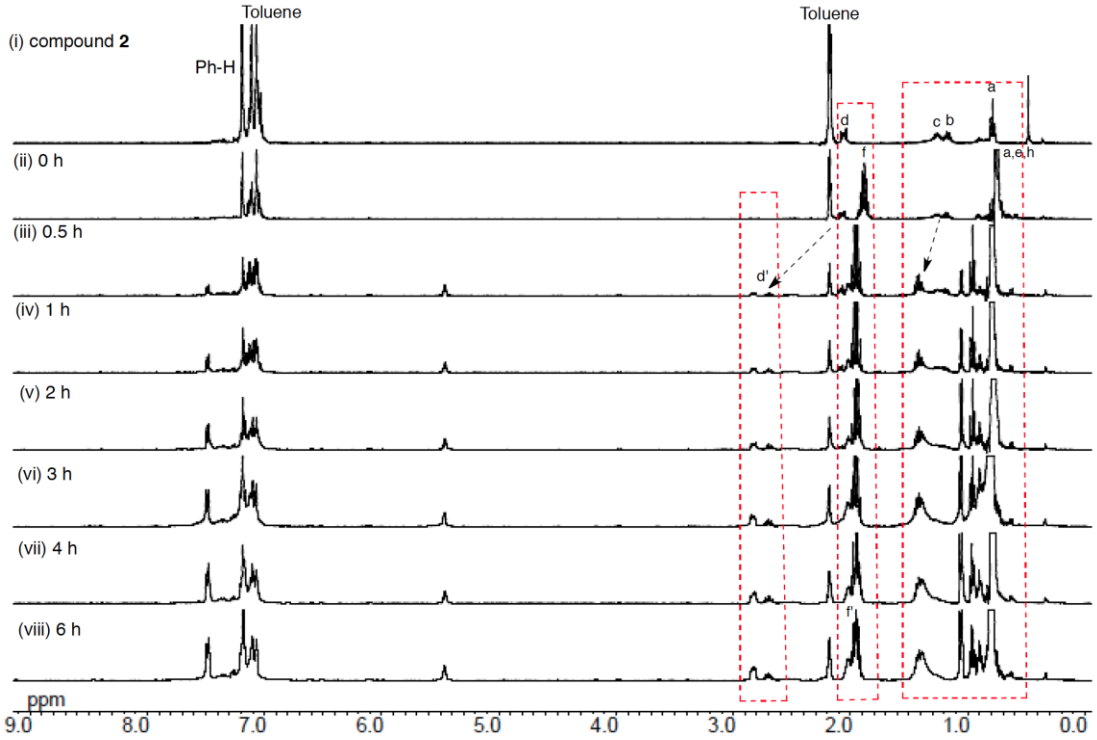


Figure S12. Time-dependent ^{1}H NMR spectra of a mixture of **2** and isobutyronitrile to give **S1d** at 100 °C in toluene-d_8 (400 MHz, 298 K, toluene-d_8).

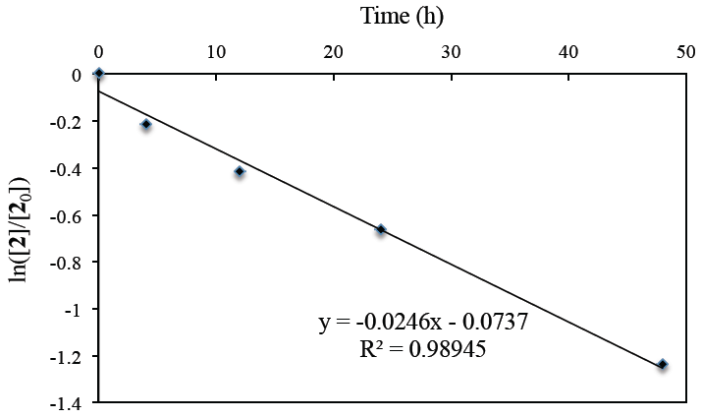


Figure S13. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to isobutyronitrile in $CHCl_3$ under reflux.

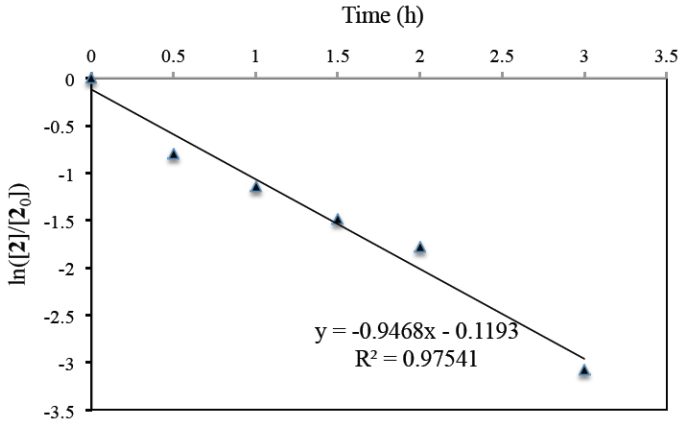
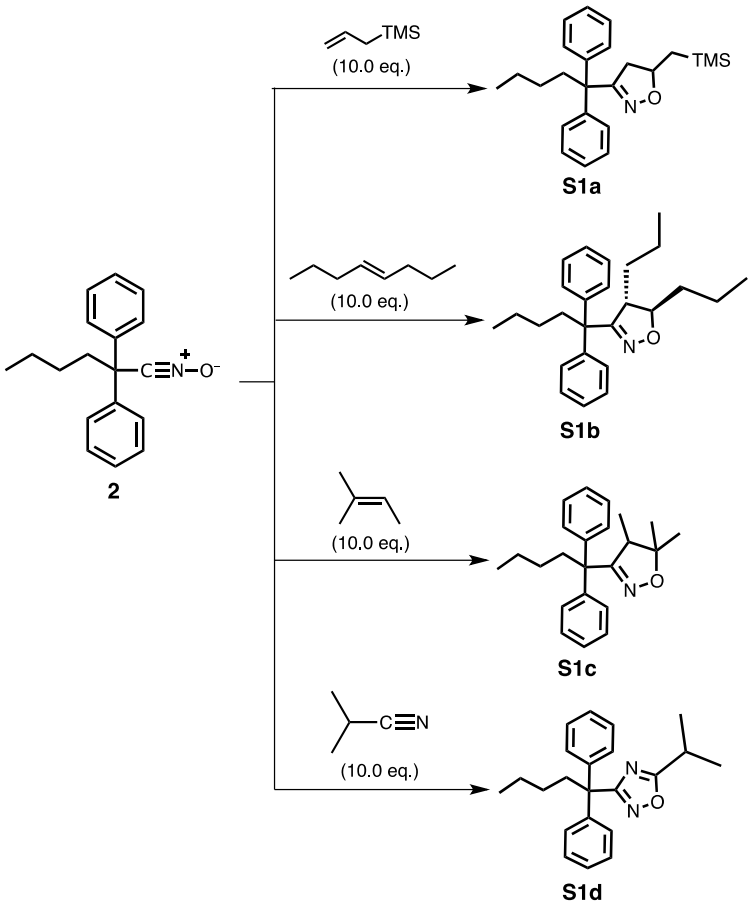


Figure S14. Pseudo-first-order kinetic plots for the cycloaddition of nitrile *N*-oxide **2** to isobutyronitrile in toluene at 100 °C.

Table S1. Reaction rate constants and half-lives of cycloaddition using 1,1-diphenylhexylnitrile *N*-oxide **2**.

Reactant	Solvent	Temp. (°C)	Reaction rate constant **k** (h^{-1})[a]	Half-lives τ of **2** (h)[b]
AllyTMS	$CHCl_3$	rt	0.152	4.56
AllyTMS	$CHCl_3$	Reflux	0.907	0.76
trans-4-Octene	$CHCl_3$	Reflux	0.011	63.01
trans-4-Octene	Toluene	100	0.125	5.55
2-Methyl-2-butene	$CHCl_3$	Reflux	0.159	4.35
Isobutyronitrile	$CHCl_3$	Reflux	0.025	27.73
Isobutyronitrile	Toluene	100	0.947	0.73

[a] Obtained from pseudo-first-order kinetic model. [b] Calculated by the following equation: $\tau = \ln(2)/k$.



Scheme S5

Synthesis of isoxazoline **S1a.** 1,1-Diphenylhexylnitrile *N*-oxide **2** (100 mg, 0.377 mmol) and allyltrimethylsilane (431 mg, 3.77 mmol) were dissolved in $CHCl_3$ (2.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to

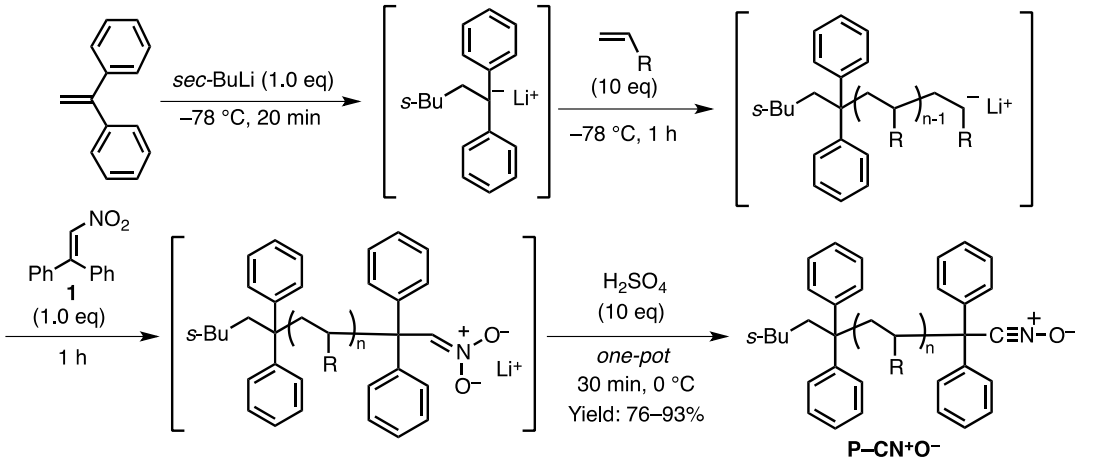
room temperature, the reaction mixture was evaporated and dried *in vacuo* to give the isoxazoline **S1a** in 90% yield (129 mg, 0.34 mmol) as an orange oil; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.35–7.28 (m, 10H, Ph–H), 4.63–4.55 (m, 1H, –CH–CH_2–TMS), 2.79–2.72 (m, 1H, –CH_2–CH–CH_2), 2.46–2.42 (m, 2H, –CH_2–CPh_2), 2.24–2.18 (m, 1H, –CH_2–CH–CH_2), 1.31–1.21 (m, 2H, –CH_2–), 1.11–1.05 (m, 2H, –CH_2–), 1.02–0.97 (m, 1H, –CH_2–TMS), 0.90–0.84 (m, 1H, –CH_2–TMS), 0.80 (t, *J* = 7.1 Hz, 3H, –CH_3), 0.00 (s, 9H, –Si–$(CH_3)_3$) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 163.5, 143.0, 129.2, 128.2, 126.8, 79.4, 54.5, 43.4, 38.6, 27.2, 24.0, 23.3, 14.1, –0.92 ppm; IR (NaCl) υ 1661 (C=N), 1598 (C=C), 1494 (C=C), 1250 (Si–C) cm^{-1}; FAB-HRMS (*m/z*) calc'd for $C_{24}H_{34}NOSi^+$ $[M+H]^+$, 380.2410; found, 380.2412.

Synthesis of isoxazoline **S1b.** 1,1-Diphenylhexylnitrile *N*-oxide **2** (100 mg, 0.377 mmol) and *trans*-4-octene (423 mg, 3.77 mmol) were dissolved in $CHCl_3$ (2.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was evaporated and purified by HPLC to give the isoxazoline **S1b** in 72% yield (106 mg, 2.71 mmol) as an yellow oil; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.43–7.23 (m, 10H, Ph–H), 4.20–4.15 (m, 1H, –CH–O), 2.46–2.42 (m, 1H, –CH–C–N), 2.40–2.32 (m, 2H, –CH_2–CPh_2), 1.37–1.17 (m, 4H, –CH_2–), 1.10–1.02 (m, 2H, –CH_2–), 0.98–0.88 (m, 2H, –CH_2–), 0.88 (t, *J* = 7.1 Hz, 3H, –CH_3), 0.81 (t, *J* = 7.1 Hz, 3H, –CH_3), 0.61 (t, *J* = 7.1 Hz, 3H, –CH_3) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 164.7, 143.4, 143.3, 129.4, 129.0, 128.0, 127.2, 126.7, 126.5, 85.5, 54.2, 54.0, 39.5, 37.3, 33.3, 27.1, 23.1, 20.3, 18.4, 14.0,13.9, 13.4 ppm; IR (NaCl) υ 1685 (C=N), 1598 (C=C), 1494 (C=C) cm^{-1}; FAB-HRMS (*m/z*) calc'd for $C_{26}H_{36}NO^+$ $[M+H]^+$, 378.2797; found, 378.2808.

Synthesis of isoxazoline **1c.** 1,1-Diphenylhexylnitrile *N*-oxide **2** (100 mg, 0.377 mmol) and 2-methyl-2-butene (264 mg, 3.77 mmol) were dissolved in $CHCl_3$ (2.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was evaporated and purified by HPLC to give the isoxazoline **S1c** in 45% yield (56.9 mg, 0.17 mmol) as an yellow oil; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.34–7.24 (m, 10H, Ph–H), 2.42–2.37 (m, 3H, –CH_2–CPh_2), 1.29–1.16 (m, 6H, –CH_3), 1.10–0.99 (m, 4H, –CH_2–), 0.83–0.76 (m, 3H, –CH_3), 0.61–0.59 (m, 3H, –CH_3) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 166.8, 162.5, 142.9, 129.5, 129.0, 128.0, 127.5, 126.6, 126.4, 86.5, 54.4, 45.6, 38.5, 32.7, 27.0, 25.1, 23.2, 20.8, 14.0 ppm; IR (NaCl) υ 1685 (C=N), 1598 (C=C), 1494 (C=C) cm^{-1}; FAB-HRMS (*m/z*) calc'd for $C_{23}H_{30}NO^+$ $[M+H]^+$, 336.2327; found, 336.2328.

Synthesis of oxadiazole **S1d.** 1,1-Diphenylhexylnitrile *N*-oxide **2** (100 mg, 0.377 mmol) and isobutyronitrile (260 mg, 3.77 mmol) were dissolved in $CHCl_3$ (2.0 mL) and the reaction mixture was refluxed for 24 h. After cooling to room temperature, the reaction mixture was evaporated and purified by HPLC to give the oxadiazole **S1d** in 64% yield (81 mg, 2.41 mmol) as an yellow oil; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.35–7.28 (m, 10H, Ph–H), 3.21–3.11 (m, 1H,–CH–$(CH_3)_2$), 2.60–2.56 (m, 2H, –CH_2–CPh_2), 1.35–1.27 (m, 6H, ,–CH–$(CH_3)_2$), 1.13–1.05 (m, 4H, –CH_2–), 0.82 (t, *J* = 7.3 Hz, 3H, –CH_3) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 183.0, 174.7, 144.3, 129.1, 127.8, 126.7, 53.2, 38.6, 27.6, 27.4, 23.3, 20.3 14.1 ppm; IR (KBr) υ 1578 (C=C), 1494 (C=C) cm^{-1}; FAB-HRMS (*m/z*) calc'd for $C_{22}H_{27}N_2O^+$ $[M+H]^+$, 335.2123; found, 335.2131.

Synthesis of polymer nitrile *N*-oxide **(Polymer–CN$^+$O$^-$)**



P1: PMMA–CN$^+$O$^-$, M_n 2200; PDI 1.23
P2: PMMA–CN$^+$O$^-$, M_n 5900; PDI 1.25
P3: PDMAAm–CN$^+$O$^-$, M_n 3300; PDI 1.21

Scheme S6

Synthesis of nitrile *N*-oxide-terminated poly(methyl methacrylate) **(PMMA–CN$^+$O$^-$)**[4]

1,1-Diphenylethylene (721 mg, 4.0 mmol) was dissolved in THF (60 mL) under argon atmosphere and the mixture was cooled to –78 °C. *s*-BuLi (1.02 M in cyclohexane, 3.92 mL, 4.0 mmol) was added into the mixture and the solution was stirred for 20 min. To the reaction mixture was added a solution of methyl methacrylate (4.00 g, 40 mmol) in THF (20 mL) and the mixture was stirred for 60 min. A solution of 1-nitro-2,2-diphenylethene **1** (901 mg, 4.0 mmol) in THF (5 mL) was then added into the mixture and the mixture was warmed to –60 °C. After stirring for 1 h, conc. H_2SO_4 (>95%, 3.92 g, 40 mmol) was added to the mixture. The mixture was warmed to 0 °C, stirred for 30 min, diluted with dichloromethane (100 mL), washed with water, dried over magnesium sulfate, filtered, and evaporated. The crude **PMMA–CN$^+$O$^-$** was dissolved in $CHCl_3$ (20 mL) and precipitated in hexane (500 mL) three times. The precipitates were collected by filtration and dried *in vacuo* to give **PMMA–CN$^+$O$^-$**as an yellow powder.

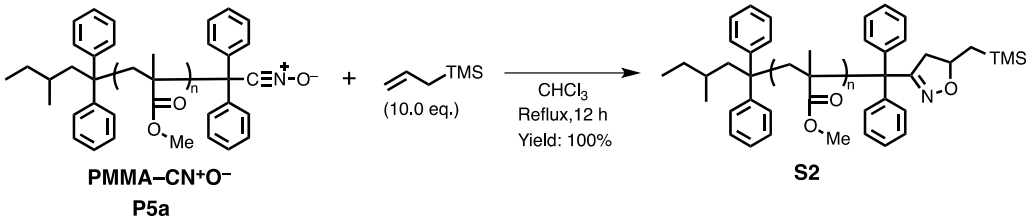
P1: Yield: 76% (4.38 g), M_n 2200; M_w/M_n 1.23 (estimated by SEC based on PMMA standards, eluent: chloroform); M_n 3800; M_w/M_n 1.46 (estimated by SEC-MALS, eluent: THF); T_g 96.0 °C; T_{d5} 324 °C; T_{d10} 348 °C; ^{1}H NMR (400 MHz, 298 K, $CHCl_3$) δ 7.41–6.95 (br, –Ph-H), 3.56 (s, –COOC$\underline{H}_3$), 2.02–1.70 (m, –C$\underline{H}_2$C), 0.95–0.76 (m, –C–C$\underline{H}_3$) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 177.8, 148.9, 147.4, 129.1, 128.7, 128.0, 127.4, 127.3, 125.7, 54.3, 52.7, 51.7, 44.8, 44.4, 30.6, 30.2, 20.7, 18.6, 16.2, 11.0 ppm; IR (KBr) υ 2298 (–C≡N$^+$–O$^-$), 1732 (C=O), 1242 (C–O), 1149 (C–O) cm^{-1}.

P2: To synthesize **P2**, 40.0 equiv of methyl methacrylate was used for the reaction. The reaction was performed in the same manner as the synthesis of **P1**. Yield: 93% (4.16 g), M_n 5700; M_w/M_n 1.27 (estimated by SEC based on PMMA standards, eluent: chloroform); T_g 108.1 °C; T_{d5} 345 °C; T_{d10} 356 °C.

Synthesis of nitrile *N*-oxide-terminated poly(*N*,*N*-dimethylacrylamide) **(PDMMAm–CN$^+$O$^-$, P3)**[5]

1,1-Diphenylethylene (360 mg, 2.0 mmol) was dissolved in dried THF (80 mL) under argon atmosphere and the mixture was cooled to –78 °C. *s*-BuLi (1.02 M in cyclohexane, 1.96 mL, 2.00 mmol) was added into the mixture and the mixture was stirred for 20 min. To the reaction mixture was added a solution of 1.0 M diethylzinc in hexane (24.0 mL, 24 mmol) and the mixture was stirred for 10 min. A solution of dimethylacrylamide (1.98 g, 20 mmol) in THF (10 mL) was added to the mixture with vigorous stirring for 1 h. A solution of 1-nitro-2,2-diphenylethene **1** (450 mg, 2

mmol) in THF (5.0 mL) was then added into the mixture and the mixture was warmed to –50 °C. After stirring for 1 h, conc. H_2SO_4 (>95%, 2.35 mL, 44 mmol) was added to the mixture and the mixture was warmed to 0 °C and stirred for 30 min. The reaction mixture was poured into hexane (1 L) and filtered. The precipitated solids were dissolved in THF/methanol (v/v 5/1, 100 mL) and filtered to remove zinc salts. The filtrate was reprecipitated into THF/Et_2O (v/v 1/1, 500 mL) three times. The precipitates were collected by filtration and dried *in vacuo* to give **PDMMAm–CN^+O^- (P3)** in 86% yield (2.49 g) as a pale yellow powder. M_n 3300; M_w/M_n 1.21 (estimated by SEC based on PMMA standards, eluent: chloroform); T_g 91.9 °C; T_{d5} 250 °C; T_{d10} 270 °C; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 7.29–7.03 (m, Ph–H), 3.74 (s, –N(C<u>H</u>$_3$)$_2$), 3.19 (br, –CH_2–C<u>H</u>–), 2.96–1.09 (m, main chain) ppm; IR (KBr) υ 2278 (–C≡N^+–O^-), 1619 (C=O), 1498 (C=C) cm^{-1}.



Scheme S7

Determination of the termination ratio of nitrile *N*-oxide group of **PMMA–CN^+O^- (P1)**

To determinate the termination ratio of the nitrile *N*-oxide group, **P1** was reacted with excess amount of allyltrimethylsilane to obtain isoxazoline **S2** possessing a TMS group. In comparison with the integral ratio between phenyl protons and TMS protons in the ^{1}H NMR spectrum, it found that the content of the nitrile *N*-oxide group of **P1** was almost 100%, as shown in **Figure S15**.

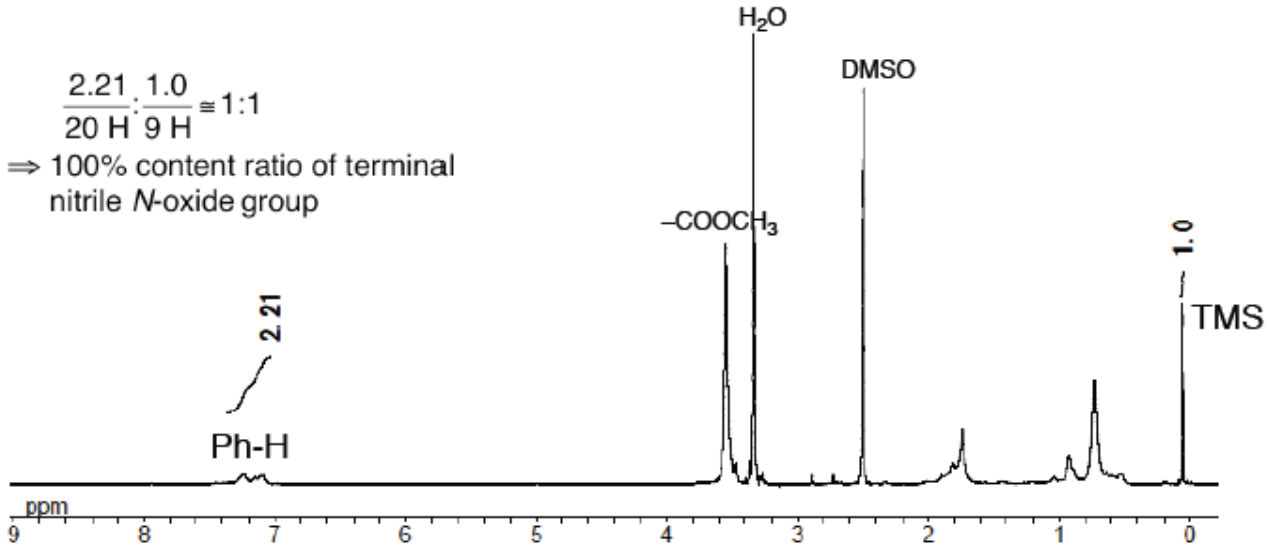
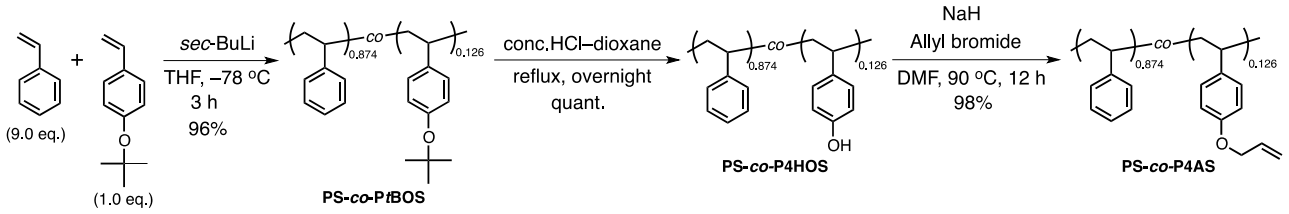


Figure S15. ^{1}H NMR spectrum of **S2**. (400 MHz, 298 K, DMSO-d_6).



Scheme S8

Synthesis of poly(styrene-*co*-4-*tert*-butoxystyrene) **(PS-*co*-P*t*BOS)**[6]

In a round-bottom flask, a mixture of THF (40 mL) and *s*-BuLi (1.02 M in cyclohexane, 1.96 mL, 2.00 mmol) was cooled to –78 °C. When a solution of styrene (9.37 g, 90.0 mmol) and 4-*tert*-butoxystyrene (1.76, 10.0 mmol) in THF (20 mL) was dropped into the mixture, the solution color changed from bright yellow to deep red. After stirring for 3 h at –78 °C, the reaction was terminated with degassed methanol and then poured into methanol to precipitate white solids. The precipitates were collected by filtration and dried *in vacuo* for 24 h to give **PS-*co*-P*t*BOS** in 96% (10.8 g) as a white solid; M_n 4500; M_w/M_n 1.27 (estimated by SEC based on polystyrene standards, eluent: THF); T_g 92.0 °C; T_{d5} 267 °C; T_{d10} 387 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.24–6.38 (m, –Ph–H), 1.62–1.21 (m, main chain), 1.52 (s, –OC(CH_3)$_3$) ppm; IR (KBr) υ 1601 (C=C), 1493 (C=C), 1236 (C–O) 1028 (C–O) cm^{-1}.

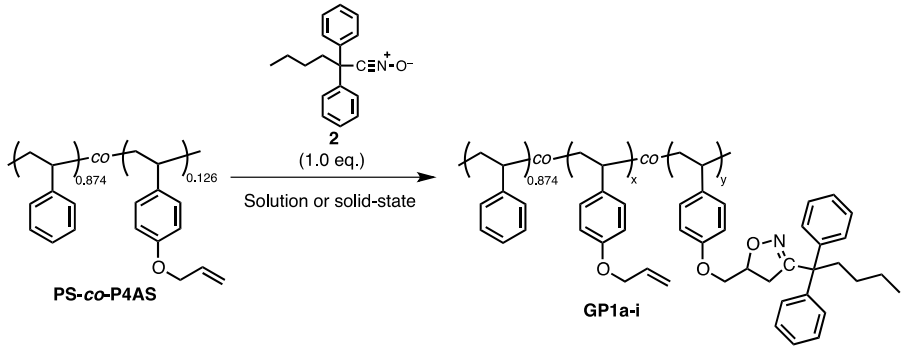
Synthesis of poly(styrene-*co*-4-hydroxystyrene) **(PS-*co*-P4HOS)**[6]

PS-*co*-P*t*BOS (10.0 g) was dissolved in dioxane (150 mL), and 36 wt% HCl (15 mL, 126 mmol) was added to the mixture. The mixture was warmed to 80 °C under an Ar atmosphere, stirred overnight, and then precipitated into water (600 mL). After neutralization with a 5 wt% aq. NaOH solution to a pH value of 6–7, the resulting precipitates were filtered. The obtained polymer was precipitated from THF (50 mL) to 300 mL of methanol/water (1:1) mixture three times. The solids were collected by filtration and dried under vacuum for 2 d to give **PS-*co*-P4HOS** in a quantitative yield (11.58 g) as white solids; M_n 10600; M_w/M_n 1.30 (estimated by SEC based on polystyrene standards, eluent: THF); T_g 99.0 °C; T_{d5} 375 °C; T_{d10} 386 °C; ^{1}H NMR (400 MHz, 323 K, DMSO-d_6) δ 8.10 (br, Ph–OH), 7.43–6.27 (m, Ph–H), 2.53–0.54 (m, main chain) ppm; IR (KBr) υ 3547 (O–H), 1601 (C=C), 1493 (C=C), 1256 (C–O), 1171 (C–O), 1028 (C–O) cm^{-1}.

Synthesis of poly(styrene-*co*-4-allyloxystyrene) **(PS-*co*-P4AS)**

To a solution of **PS-*co*-P4HOS** (6.0 g) in DMF (80 mL) was added NaH (1.20 g, 30.0 mmol, NaH was washed with hexane three times to remove mineral oil before the use) and the reaction was stirred for 20 min at room temperature. A solution of allylbromide (3.63 g, 10.0 mmol) in DMF (10 mL) was added dropwise to the mixture through a dropping funnel. The reaction mixture was warmed to 90 °C and stirred for 12 h. After cooling to room temperature, the reaction mixture was diluted with dichloromethane (200 mL) and then filtered. The solvent was evaporated and the resulting crude was poured into methanol (2 L) to precipitate solids as the crude **PS-*co*-P4AS**. The solids were collected by filtration, dissolved again in $CHCl_3$ (20 mL), and precipitated in methanol (300 mL) three times. The resulting precipitates were collected by filtration and dried *in vacuo* for 2 d to give **PS-*co*-P4AS** in 98% yield (6.06 g) as a white solid. From the ^{1}H NMR spectrum, it turned out that the resulting polymer contained 12.6% of the allyl-functionalized monomer units; M_n 12600; M_w/M_n 1.02 (estimated by SEC-MALS, eluent: THF); T_g 83.9 °C; T_{d5} 404 °C; T_{d10} 412 °C; ^{1}H NMR (400 MHz, 323 K, DMSO-d_6) δ 7.25–6.32 (m, Ph–H), 6.00 (br, –OCCH), 5.44–5.24 (m, C=CH_2), 4.45 (br, –OCH_2), 1.93–0.61 (m, main chain) ppm; ^{13}C NMR (100 MHz, 298 K, $CDCl_3$) δ 156.5, 145.3, 146.1, 133.6, 128.0, 127.9, 127.6, 125.6, 117.4, 114.2, 68.8, 43.9, 40.3 ppm; IR (KBr) υ 1601 (C=C, Ar), 1583 (C=C), 1493 (C=C, Ar), 1240 (C–O), 1028 (C–O) cm^{-1}.

Typical procedure for the modification of **PS-*co*-P4AS** with **2** to give polymer **GP1a-f**



Scheme S9

The reaction of poly(styrene-*co*-4-allyloxystyrene) (**PS-*co*-P4AS**) with **2** was performed under various conditions (Scheme S9). The results demonstrate a positive correlation between the conversion and the reaction temperature, as shown in Table S2. Moreover, it was found that the solvent-free condition accelerates the 1,3-dipolar cycloaddition reaction of **2** to afford higher conversions (Table S2, entries 7–9), in contrast to the cases using solvent (Table S2, entries 1, 3, and 5). The optimal conversion reached 97% under the solid-state reaction condition at 100 °C for 2 h (Table S2, entry 9).

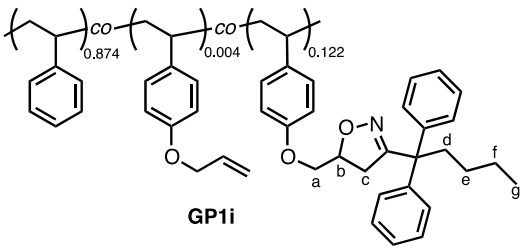
(Solution Reaction) **PS-*co*-P4AS** (100 mg, 7.92 μmol) was dissolved in solvent (2.20 mL) and added 1,1-diphenylhexylnitrile *N*-oxide **2** (29.8 mg, 0.11 mmol) to the mixture. The reaction solution was warmed to the arbitrary temperature and stirred. After cooling to room temperature, the reaction mixture was precipitated into methanol (100 mL) to give solids. The solids were collected by filtration and dried *in vacuo* to give the polymer **GP1a-f** as an yellow solid.

(Solid State Reaction) **PS-*co*-P4AS** (100 mg, 7.92 μmol) was mixed with 1,1-diphenylhexylnitrile *N*-oxide **2** (29.8 mg, 0.11 mmol), warmed to the arbitrary temperature, and ground in a mortar. After 2 h, the mixture was dissolved in $CHCl_3$ (3.0 mL) and precipitated from methanol (100 mL) to give solids. The solids were collected by filtration and dried *in vacuo* to give the polymer **GP1g-i** as an yellow solid. The conversions were calculated from the integral ratio in the ^1H NMR spectra.

Table S2. Results for the click reaction of **PS-*co*-P4AS** with nitrile *N*-oxide **2**.

Entry	Solvent	Temp. (°C)	Time (h)	Conv. (%)[a]	Yield (%)	Polymer
1	$CHCl_3$	rt	2	20	90	**GP1a**
2	$CHCl_3$	rt	48	76	95	**GP1b**
3	$CHCl_3$	Reflux	2	50	91	**GP1c**
4	$CHCl_3$	Reflux	16	81	92	**GP1d**
5	Toluene	100	2	91	89	**GP1e**
6	Toluene	100	8	94	85	**GP1f**
7	–[b]	rt	2	54	84	**GP1g**
8	–[b]	70	2	71	91	**GP1h**
9	–[b]	100	2	97	89	**GP1i**

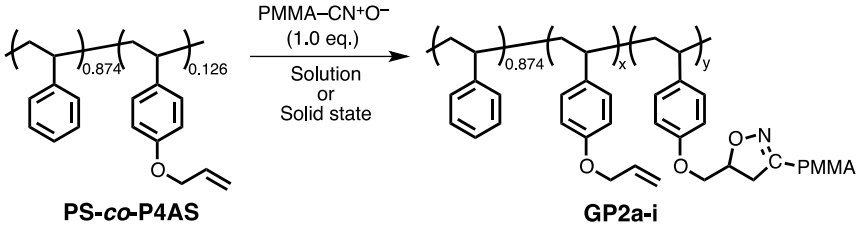
[a] Determined from the ratio of ^1H NMR integrals. [b] Solid-state reaction.



GP1i

GP1i: T_g 71.8 °C; T_{d5} 263 °C; T_{d10} 309 °C; ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.59–6.34 (m, Ph–H), 4.78 (br, –OCCHO–, b), 3.86 (br, –CHCH$_2$C–, c), 2.81 (br, –OCH$_2$–, a), 2.45 (br, –CPh$_2$CH$_2$–, d), 2.04–1.40 (m, main chain), 1.28 (br, –CH$_2$–, e), 1.10 (br, –CH$_2$–, f), 0.81(br, –CH$_3$, g) ppm; IR (KBr) υ 1678 (C=N), 1601 (C=C, Ar), 1583 (C=C), 1493 (C=C), 1261 (C–O), 1028 (C–O) cm^{-1}.

Typical procedure for the grafting reaction of PMMA–CN$^+$O$^-$ onto PS-*co*-P4AS

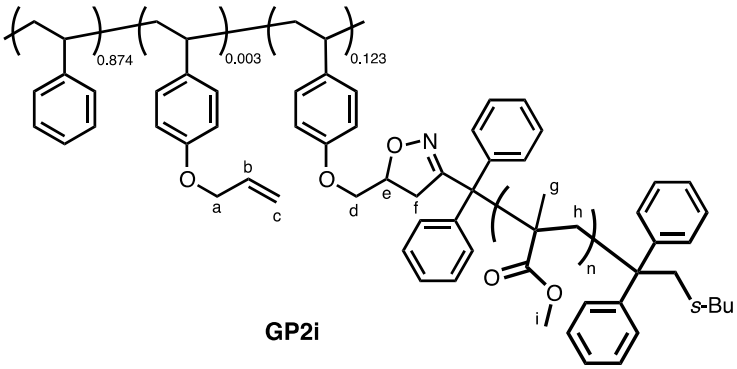


Scheme S10

(Solution Reaction) **PS-*co*-P4AS** (100 mg, 0.01 mmol) was dissolved in mesitylene (2.20 mL) and added **P1** (223 mg, 0.11 mmol). The reaction solution was warmed to the arbitrary temperature and stirred. After cooling to room temperature, the reaction mixture was precipitated from methanol (100 mL) to give solids. The solids were collected by filtration and dried *in vacuo* to give the grafting polymer **GP2a-c** as a brown solid.

(Solid State Reaction) **PS-*co*-P4AS** (100 mg, 0.01 mmol) was mixed with **P1** (223 mg, 0.11 mmol) warmed to the arbitrary temperature and ground in a mortar. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (5.0 mL) and precipitated from methanol (100 mL). The resulting solids were collected by filtration and dried *in vacuo* to give the grafting polymer **GP2d-i** as a brown solid. The conversions were calculated from the integral ratio in the ^{1}H NMR spectra.

(In case of using P2 as a grafting reagent) **PS-*co*-P4AS** (50 mg, 0.005 mmol) was mixed with **P2** (318 mg, 0.055 mmol) warmed to the arbitrary temperature and ground in a mortar. After cooling to room temperature, the mixture was dissolved in $CHCl_3$ (5.0 mL) and precipitated from methanol (100 mL). The resulting solids were collected by filtration and dried *in vacuo* to give the grafting polymer **GP2i** as a brown solid. The conversions were calculated from the integral ratio in the ^{1}H NMR spectra.



GP2i

GP2i: M_n 47800; M_w/M_n 1.58 (estimated by SEC-MALS, eluent: THF); ^{1}H NMR (400 MHz, 298 K, $CHCl_3$) δ 7.27–6.38 (m, –Ph–H), 6.00 (s, –OCCH–, b), 5.38–5.20 (m, C=CH_2, c), 4.92 (s, –OCCH, e), 4.49 (s, –OCH_2–, a), 3.75 (br, –OCH_2–, d), 3.56 (s, –COOCH_3, i), 2.73 (br, –CH_2–, f), 2.02–1.16 (m, –CH_2C–, main chain, h), 0.95–0.5 (m, –C–CH_3, h) ppm; IR (KBr) υ 1731 (C=O), 1602 (C=C, Ar), 1580 (C=C), 1493 (C=C, Ar), 1242 (C–O), 1030 (C–O) cm^{-1}.

Size-exclusion chromatography with multiangle light scattering detection (SEC-MALS) was employed for evaluation of the absolute molecular weight of graft copolymer **GP2i** for proof of the grafting reaction. The peak of the graft copolymer appeared as a monomodal peak at a different elution time to those of starting polymers, indicating a clear structural change from the starting polymers. The later elution time of **GP2i** than that of **PS-*co*-P4AS** is consistent with a stronger interaction between the basic isoxazoline moieties on the resulting graft copolymer and the SEC stationary phase.

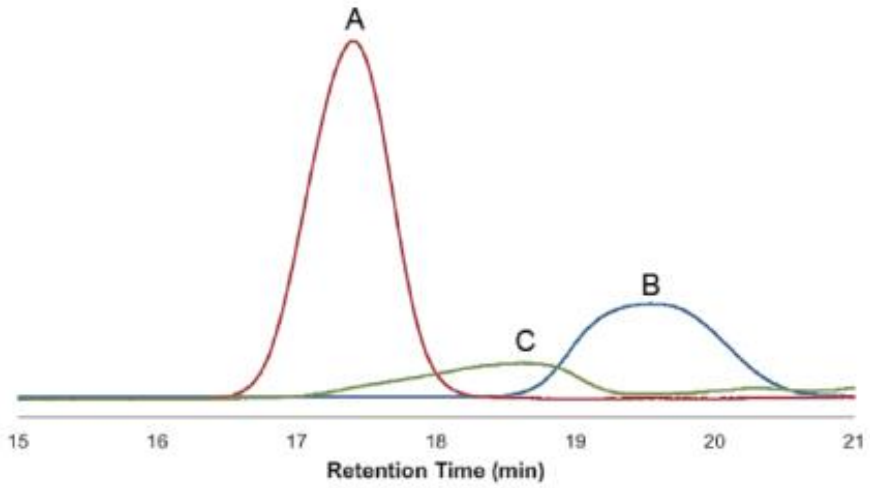
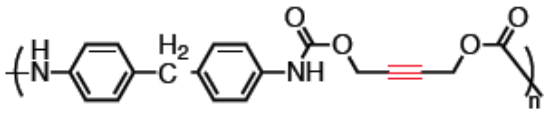


Figure S16. GPC-MALS profiles of **PS-*co*-P4AS** (peak A, M_n 12600; M_w/M_n 1.02), PMMA nitrile *N*-oxide(**P1**, peak B, M_n 3800; M_w/M_n 1.46), and graft polymer **GP2i (**peak C, M_n 47800; M_w/M_n 1.58) using THF as eluent.

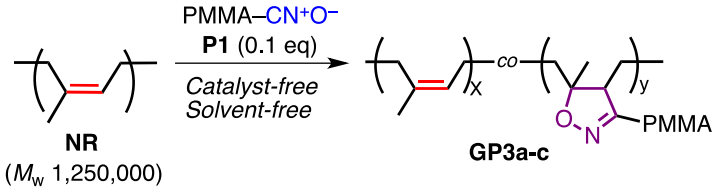
Synthesis of internal-ethynyl-moiety-containing polyurethane **P4**



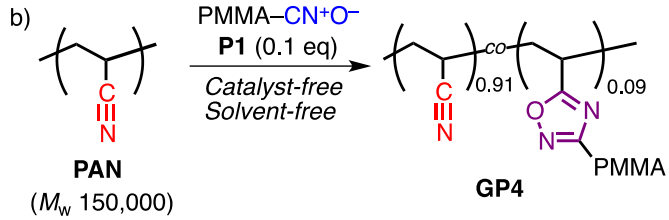
P4

To a solution of 4,4-diphenylmethane diisocyanate (MDI, 300 mg, 1.20 mmol) and 2-butyne-1,4-diol (86.0 μL, 1.20 mmol) in DMF (1.0 mL) was added dibutyltindilaurate (35.5 μL, 0.060 mmol) and the mixture was stirred at room temperature for 1 h. Then, the mixture was stirred at 100 °C for 1 h and at 160 °C for 1 h. The mixture was cooled to room temperature and poured into MeOH to give precipitates. The resulting precipitates were collected by filtration and dried *in vacuo* to give the internal-ethynyl-moiety-containing polyurethane **P4** (393.6 mg, 98%) as a brown solid; M_w 10000; M_w/M_n 1.8 (on the basis of polystyrene standards, eluent: DMF); no T_g was observed in a range from room temperature to 220 °C; T_{d5} 272 °C; ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 9.74 (s, 2H), 7.32 (d, J = 8.4 Hz, 4H), 7.09 (d, J = 8.4 Hz, 4H), 4.80 (s, 4H), 3.78 (s, 2H) ppm; IR (KBr) υ 3322, 3127, 3034, 2940, 1906, 1709, 1599, 1527, 1413, 1367, 1316, 1226, 1154, 1054, 1017, 914, 848, 816, 764, 616, 510 cm^{-1}.

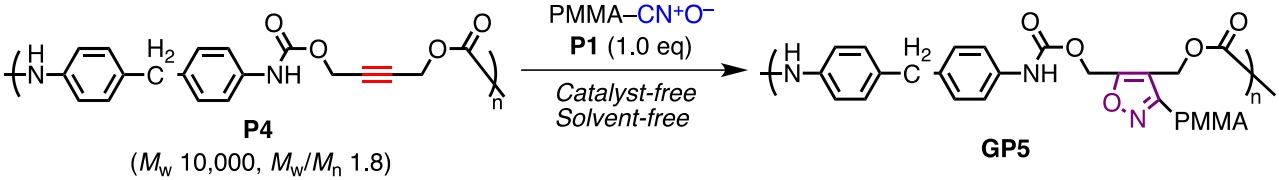
Typical procedure for the grafting reaction of PMMA–CN$^+$O$^-$ (**P1**) onto nature rubber (**NR**), polyacrylonitrile (**PAN**), and internal-ethynyl-moiety-containing polyurethane (**P4**) in solid state.



Scheme S11



Scheme S12



Scheme S13

(Reaction of NR) NR (50 mg, 0.734 mmol of monomeric unit) was mixed with **P1** (147 mg, 0.0734 mmol, 10 mol% of internal alkene) and warmed to arbitrary temperature in a mortar. After grinding for the arbitrary reaction time, the mixture was dissolved in $CHCl_3$ (5 mL) and precipitated into methanol (100 mL). The resulting solids were collected by filtration, washed with acetone for several times, and dried *in vacuo* to give the graft NR **GP3a-c** as a brown oil. Through the comparison of the integral ratio in ^{1}H NMR and the IR spectra between the virgin rubber and the modified materials, the conversions were calculated.

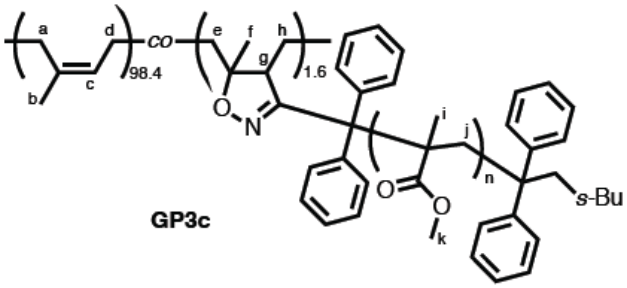
(Reaction of PAN) PAN (50 mg, 0.942 mmol of monomeric unit) was mixed with **P1** (188 mg, 0.0942 mmol, 10 mol% of nitrile group) and warmed to 200 °C in a mortar. After grinding for 2 h, the mixture was dissolved in DMF (5 mL) and precipitated into water (100 mL). The resulting solids were collected by filtration and dried *in vacuo* to give the graft PAN **GP4** as a brown solid.

(Reaction of **P4**) **P4** (30 mg, 0.009 mmol) was mixed with **P1** (303 mg, 0.149 mmol) warmed to 200 °C in a mortar. After grinding for 2 h, the mixture was dissolved in $CHCl_3$ (5 mL) and precipitated into methanol (100 mL). The resulting solids were collected by filtration and dried *in vacuo* to give the graft **GP5** as a brown solid.

Table S3. Grafting reaction of PAN, P4, and NR with P1.

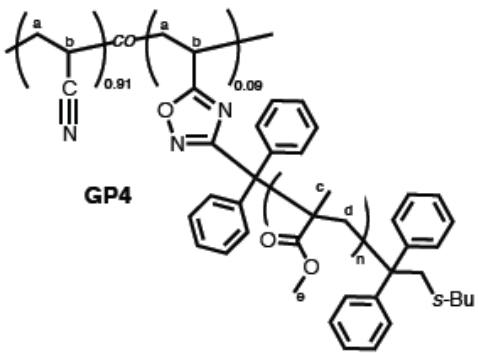
Entry	Polymer	Temp. (°C)	Time (h)	Conv. (%)	Yield (%)[c]	Graft Copolymer
1	NR	180	2	0.7[b]	97	**GP3a**
2	NR	200	0.25	7.4[b]	100	**GP4b**
3	NR	200	0.5	15.6[b]	100	**GP3c**
4	PAN	200	2	90.6[a]	88	**GP4**
5	**P4**	200	2	95.1[b]	100	**GP5**

[a] Determined from the ratio of IR integrals. [b] Determined from the ratio of ^{1}H NMR integrals. [c] Isolated yield after purification by precipitation.

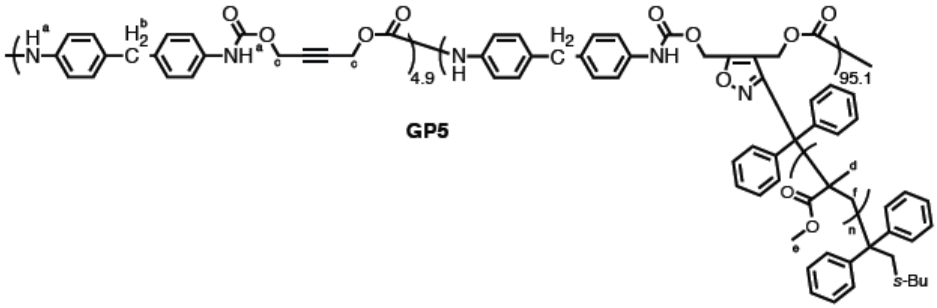


GP3c

GP3c: ^{1}H NMR (400 MHz, 298 K, $CDCl_3$) δ 7.26–7.11 (m, –Ph–H), 5.12 (s, –C=CH, c), 3.60 (br, –COOCH_3, k), 2.68 (br, –CH–, g), 2.17 (s, –C(CH_3), f), 2.04 (s, –C(CH_3), b), 2.02–1.70 (m, –CH_2C–, j), 1,68 (s, –CH_2–, a, d, e, h) 0.95–0.76 (m, –C–CH_3, i) ppm; IR (KBr) υ 1733 (C=O) cm^{-1}.



GP4: ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 7.25–7.11 (m, –Ph-H), 3.55 (br, –COOCH_3, e), 3,15 (br, –CH_2–CHCN, b), 2.04 (br, –CH_2–, a), 2.02–1.70 (m, –CH_2–, d), 1.04–0.54 (m, –CCH_3, c) ppm; IR (KBr) υ 2243 (C≡N), 1732 (C=O), 1619 (C=C, Ar), 1241 (C–O), 1149 (C–O) cm^{-1}.



GP5: ^{1}H NMR (400 MHz, 298 K, DMSO-d_6) δ 9.74 (s, 2H, –NH, a), 7.33–7.11 (m, –Ph-H), 4.80 (s, –OCH_2, c), 3.77 (s, –Ph–CH_2, b), 3.55 (br, –COOCH_3, e), 2.01–1.74 (m, –CH_2–, f), 1.04–0.52 (m, –CCH_3, c) ppm; IR (KBr) υ 1730 (C=O), 1601 (C=C, Ar), 1242 (C–O), 1149 (C–O) cm^{-1}.

3. Spectra Data of Synthesized Compounds

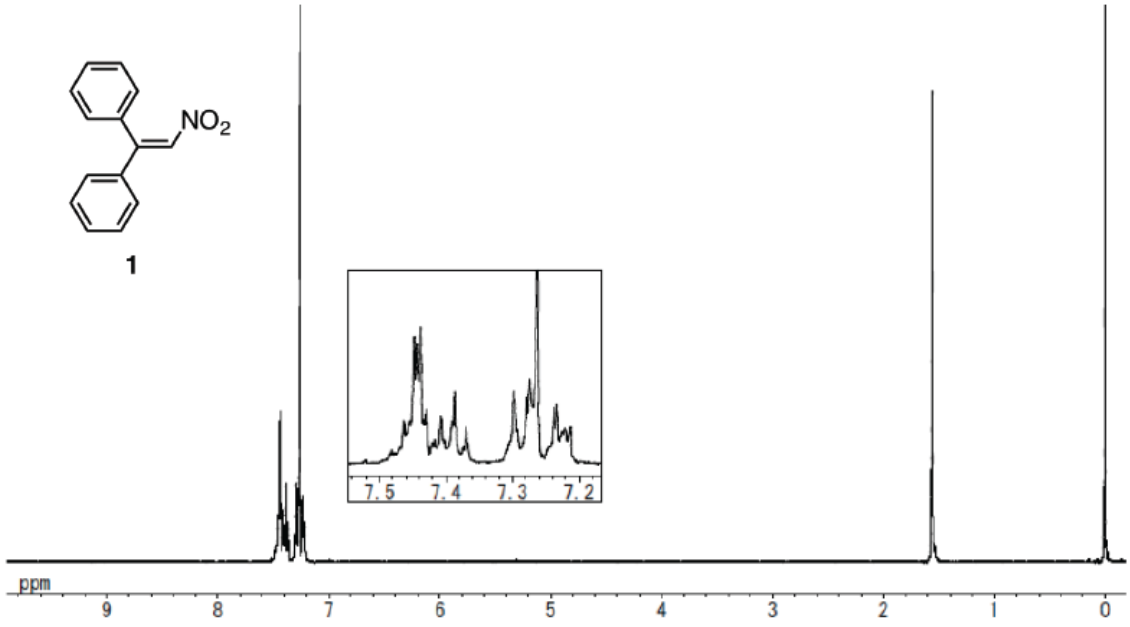


Figure S17. ^{1}H NMR spectrum of **1** (400 MHz, 298 K, $CDCl_3$).

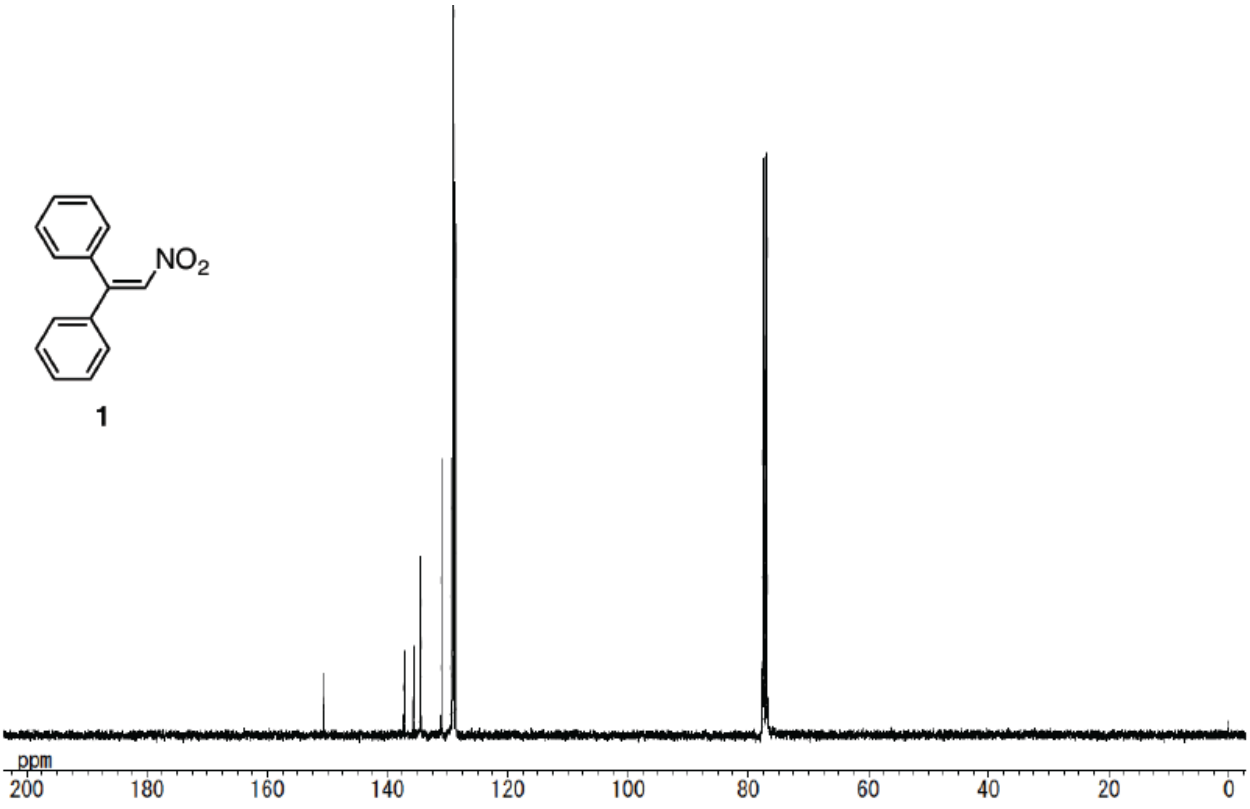


Figure S18. ^{13}C NMR spectrum of **1** (100 MHz, 298 K, $CDCl_3$).

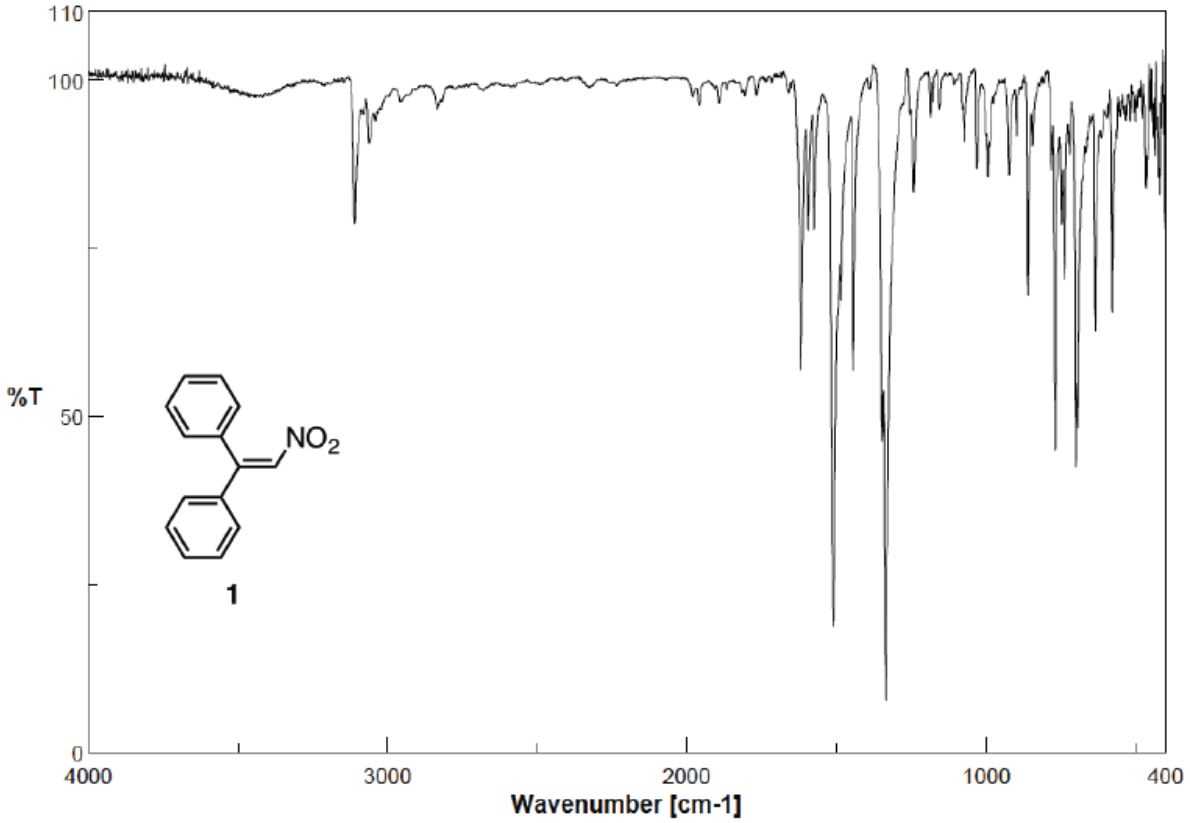


Figure S19. IR spectrum of **1** (KBr).

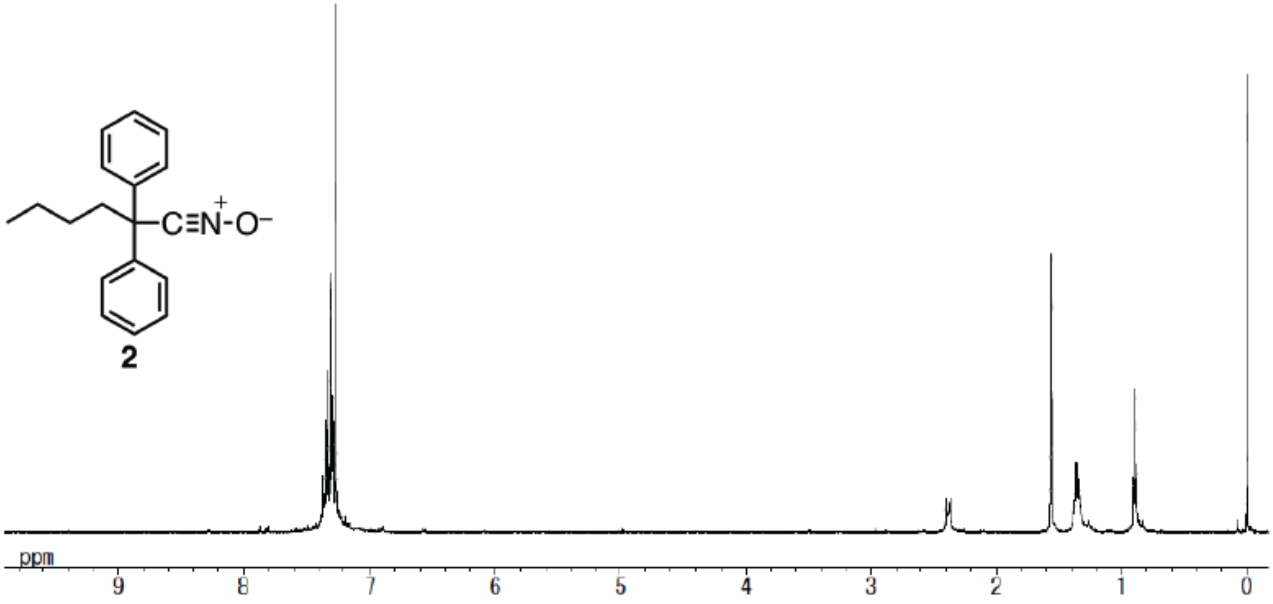


Figure S20. ^{1}H NMR spectrum of **2** (400 MHz, 298 K, $CDCl_3$).

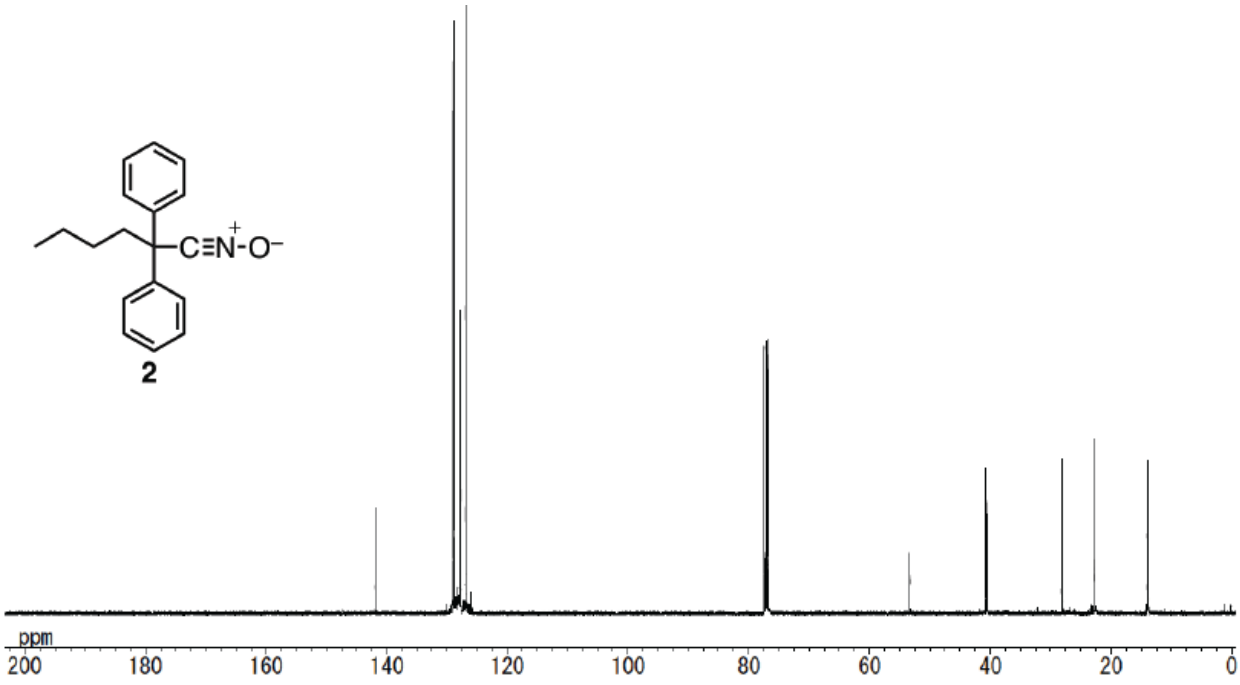


Figure S21. ^{13}C NMR spectrum of **2** (100 MHz, 298 K, $CDCl_3$).

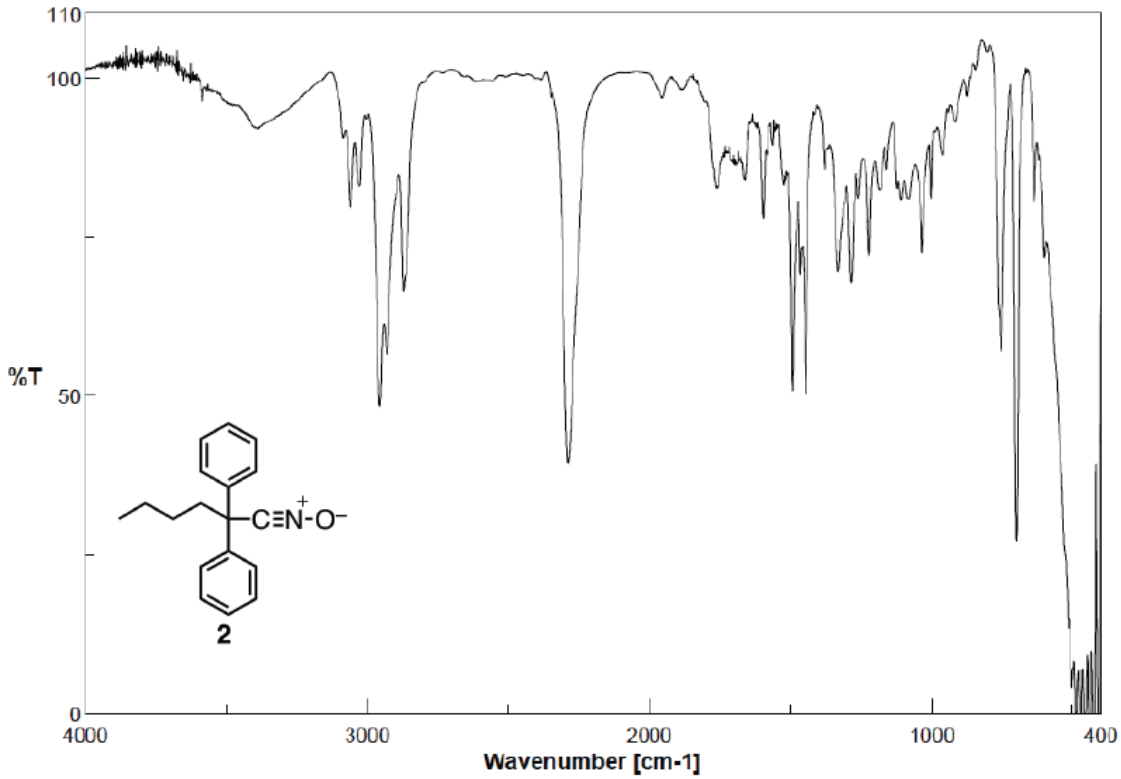


Figure S22. IR spectrum of **2** (NaCl).

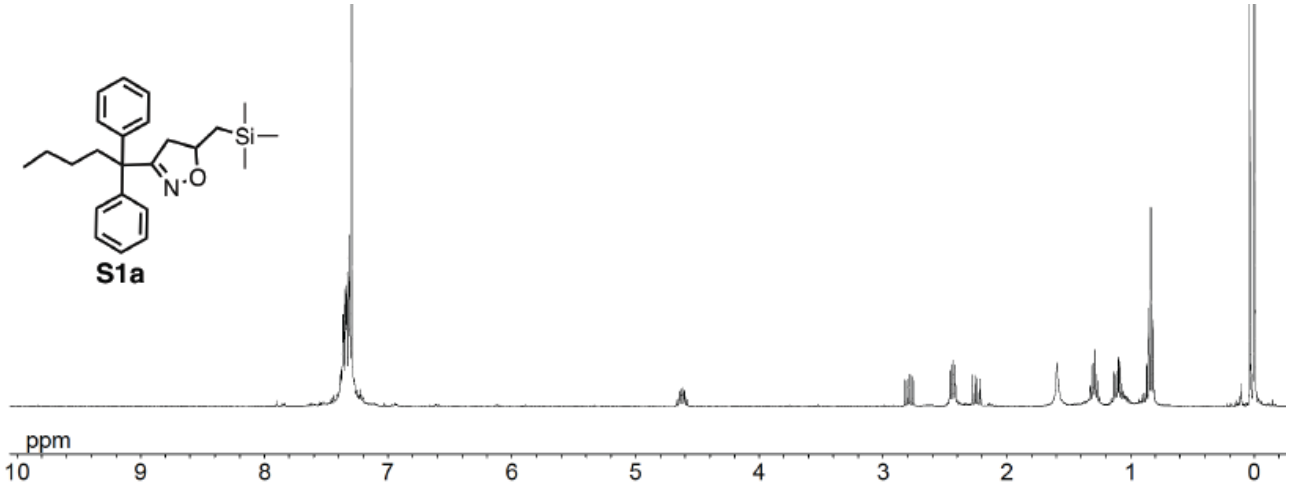


Figure S23. ^{1}H NMR spectrum of **S1a** (400 MHz, 298 K, $CDCl_3$).

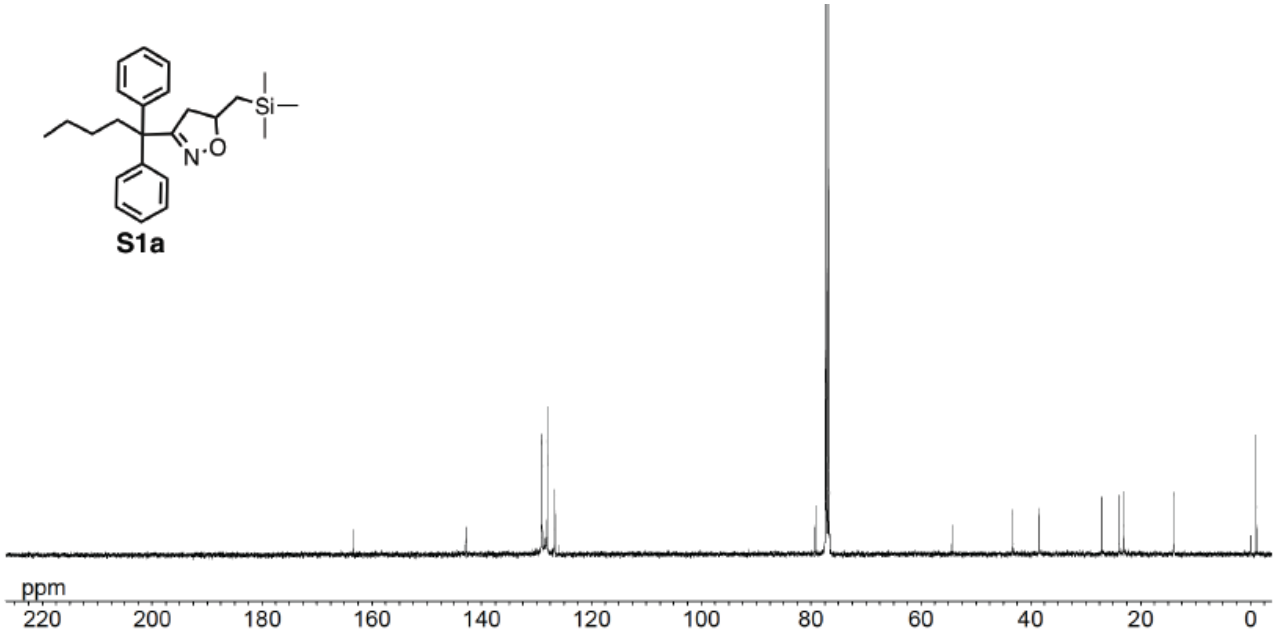


Figure S24. ^{13}C NMR spectrum of **S1a** (100 MHz, 298 K, $CDCl_3$).

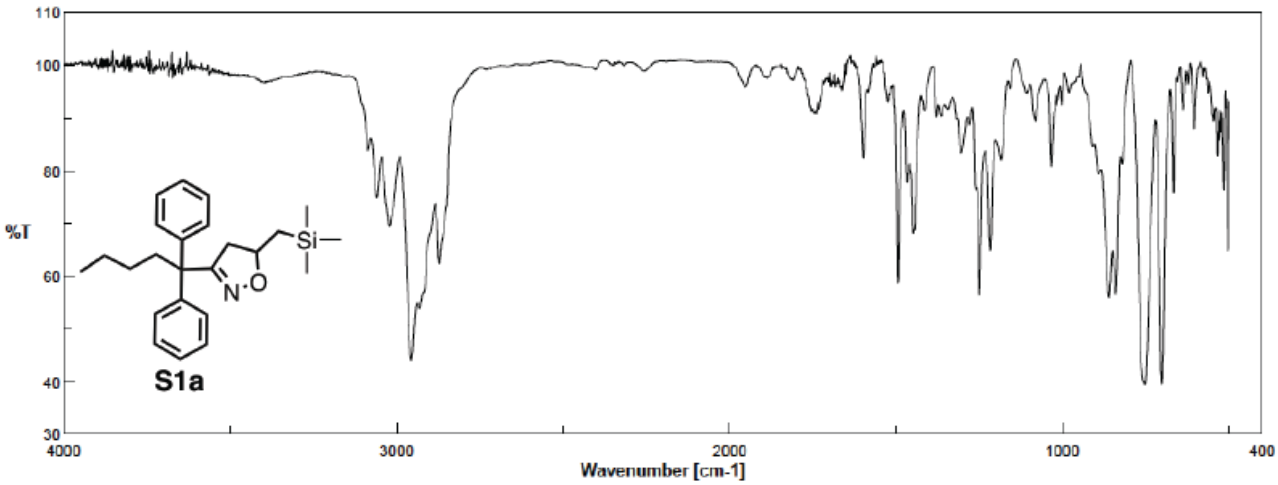


Figure S25. IR spectrum of **S1a** (NaCl).

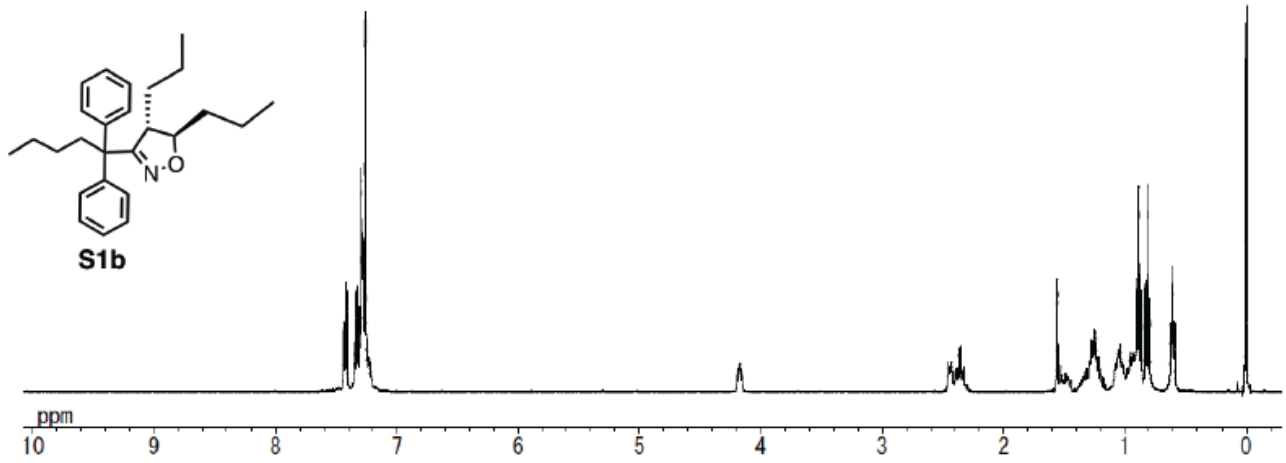


Figure S26. ^{1}H NMR spectrum of **S1b** (400 MHz, 298 K, $CDCl_3$).

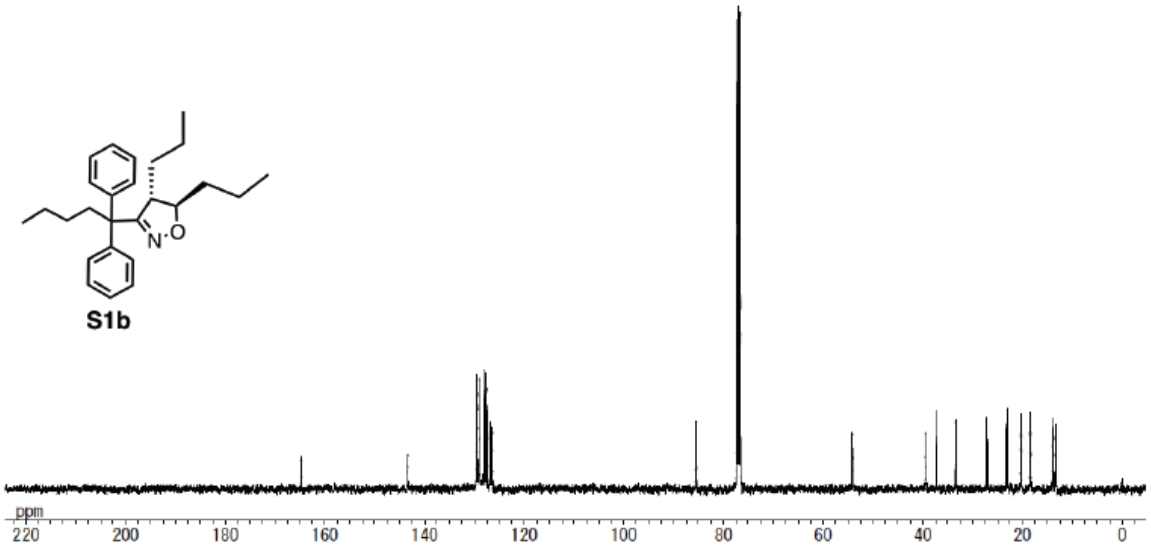


Figure S27. ^{13}C NMR spectrum of **S1b** (100 MHz, 298 K, $CDCl_3$).

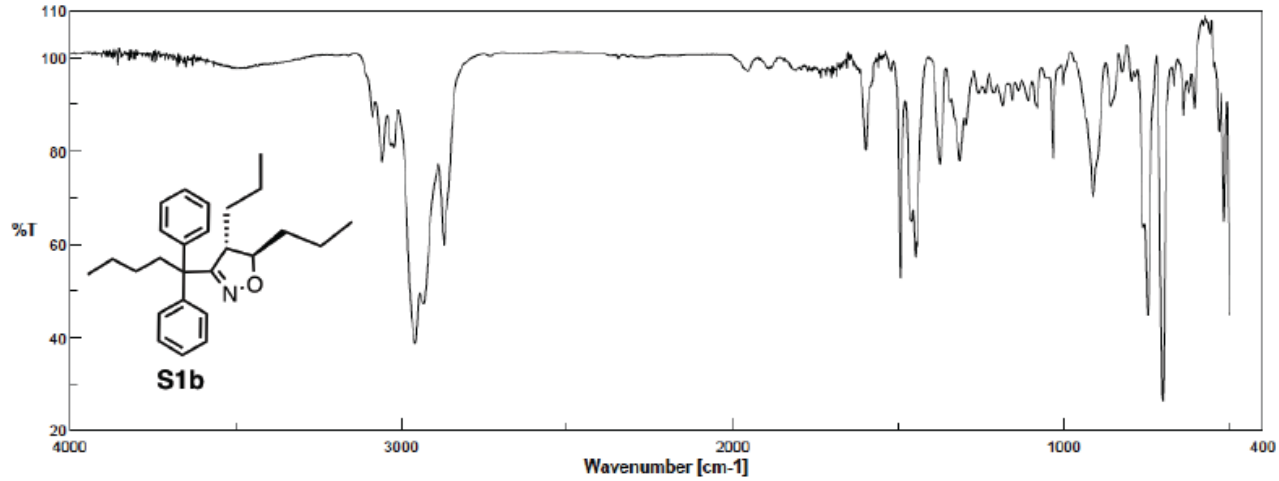


Figure S28. IR spectrum of **S1b** (NaCl).

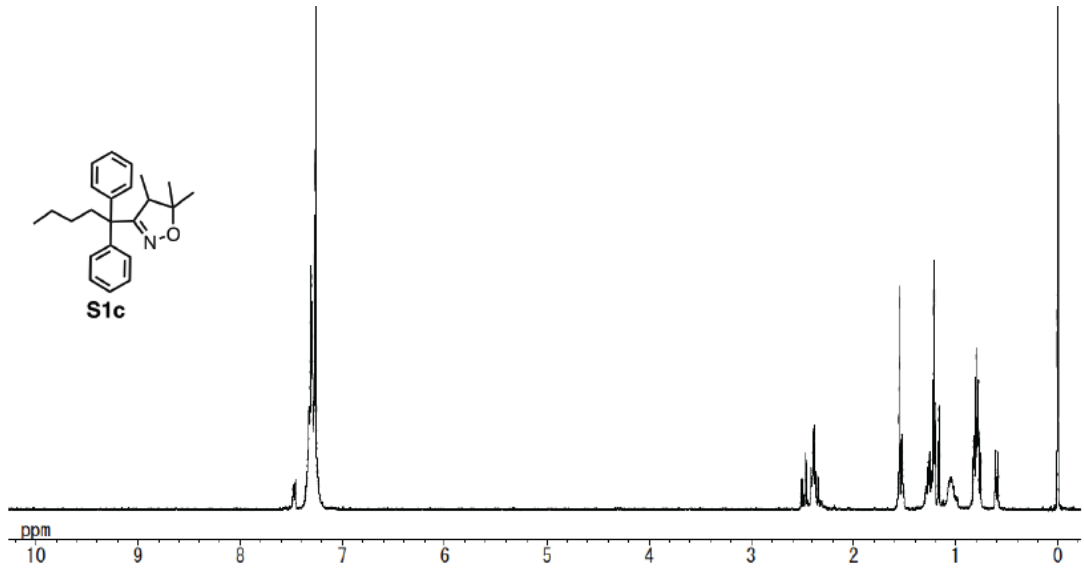


Figure S29. ^{1}H NMR spectrum of **S1c** (400 MHz, 298 K, $CDCl_3$).

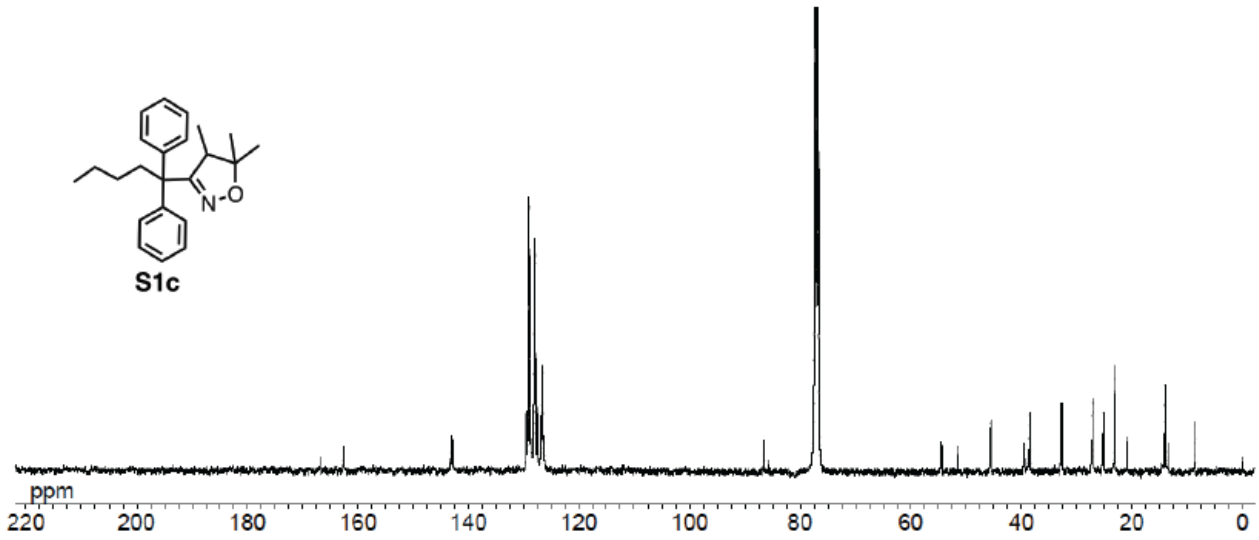


Figure S30. ^{13}C NMR spectrum of **S1c** (100 MHz, 298 K, $CDCl_3$).

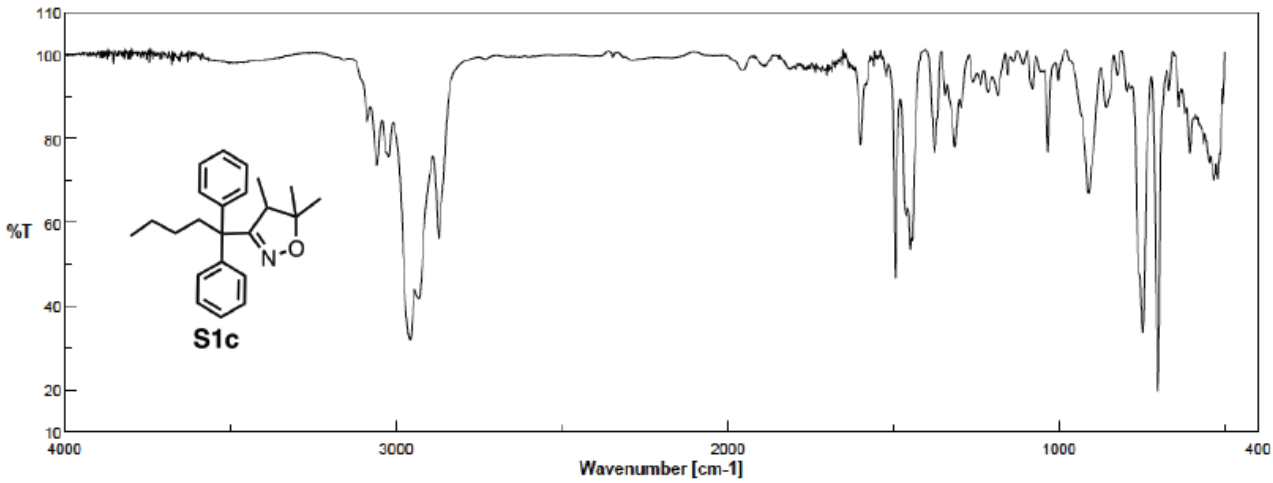


Figure S31. IR spectrum of **S1c** (NaCl).

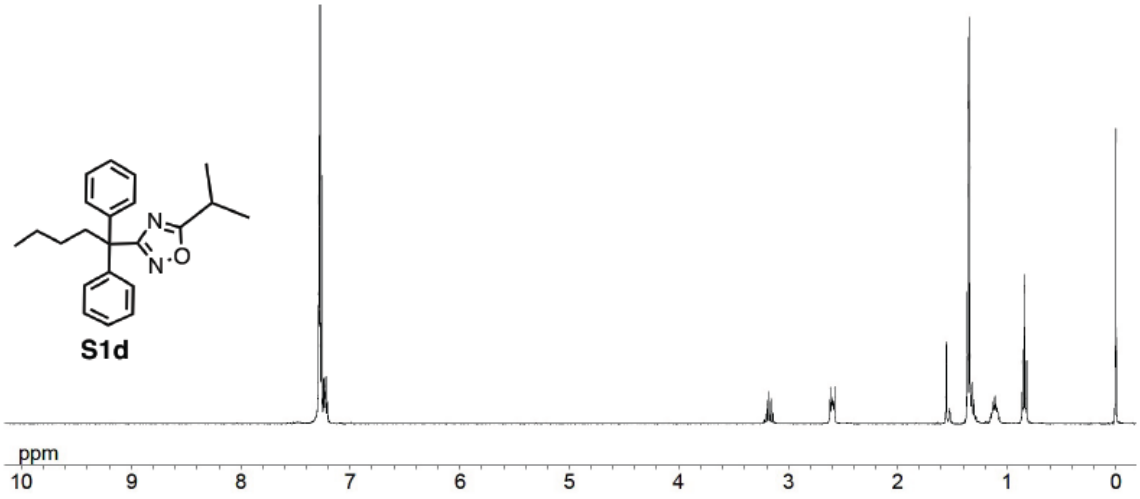


Figure S32. ^{1}H NMR spectrum of **S1d** (400 MHz, 298 K, $CDCl_3$).

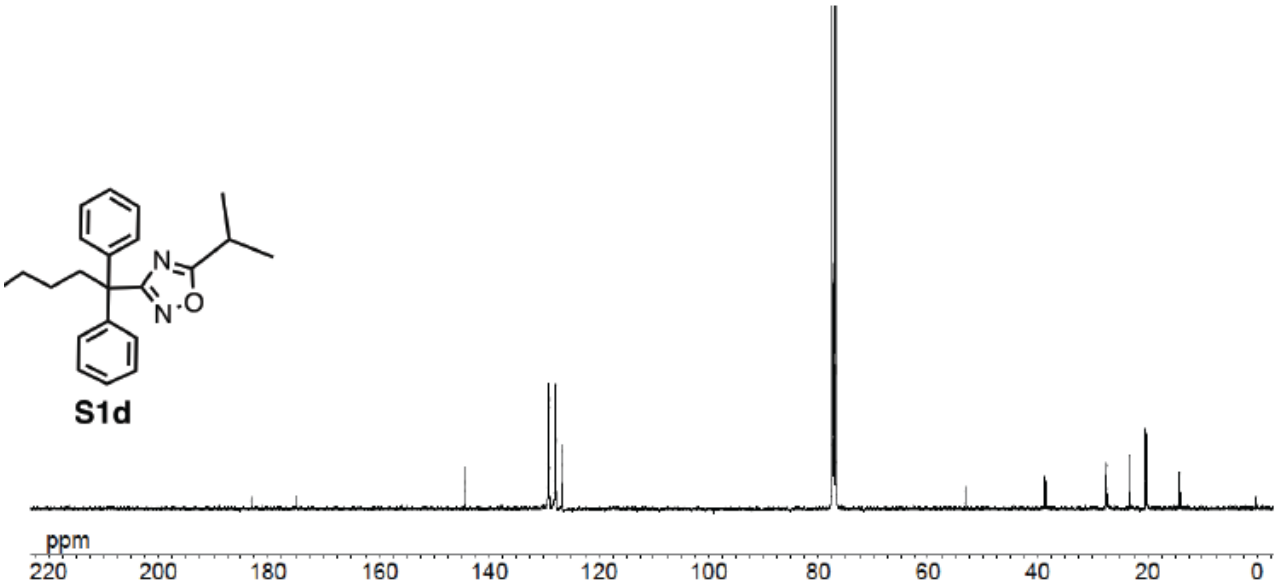


Figure S33. ^{13}C NMR spectrum of **S1d** (100 MHz, 298 K, $CDCl_3$).

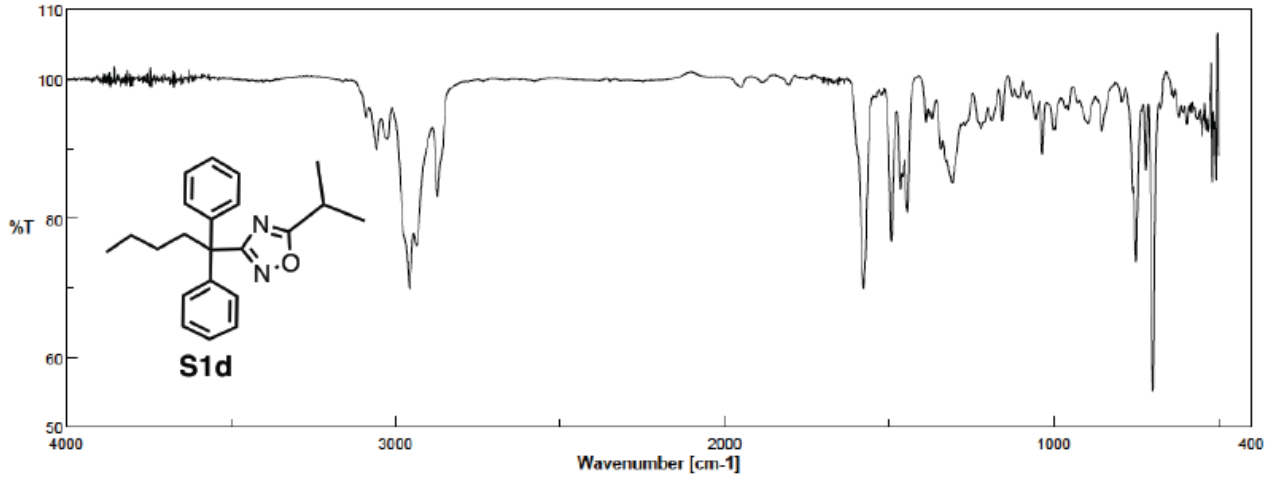


Figure S34. IR spectrum of **S1d** (NaCl).

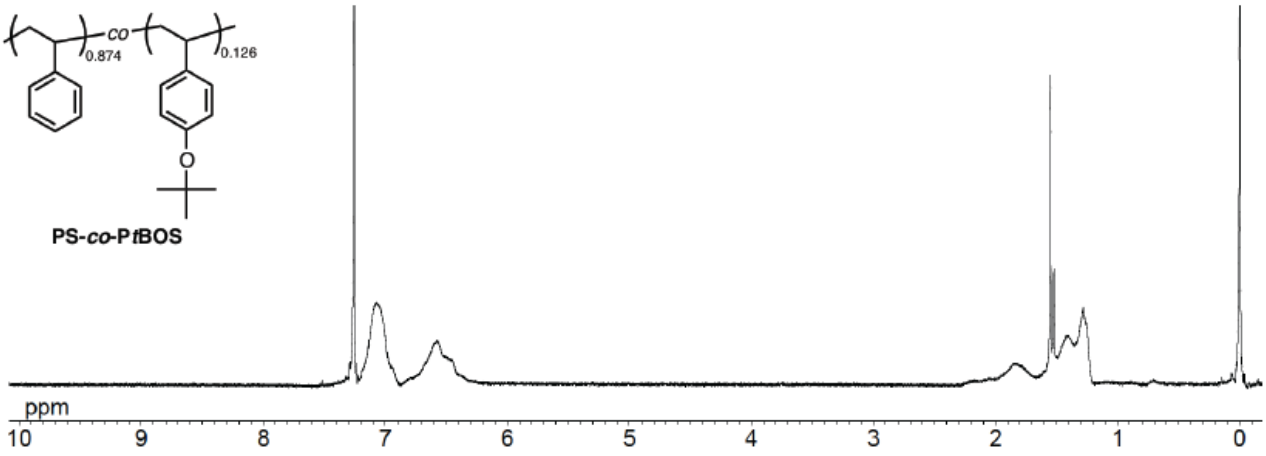


Figure S35. ^{1}H NMR spectrum of **PS-*co*-P*t*BOS** (400 MHz, 298 K, $CDCl_3$).

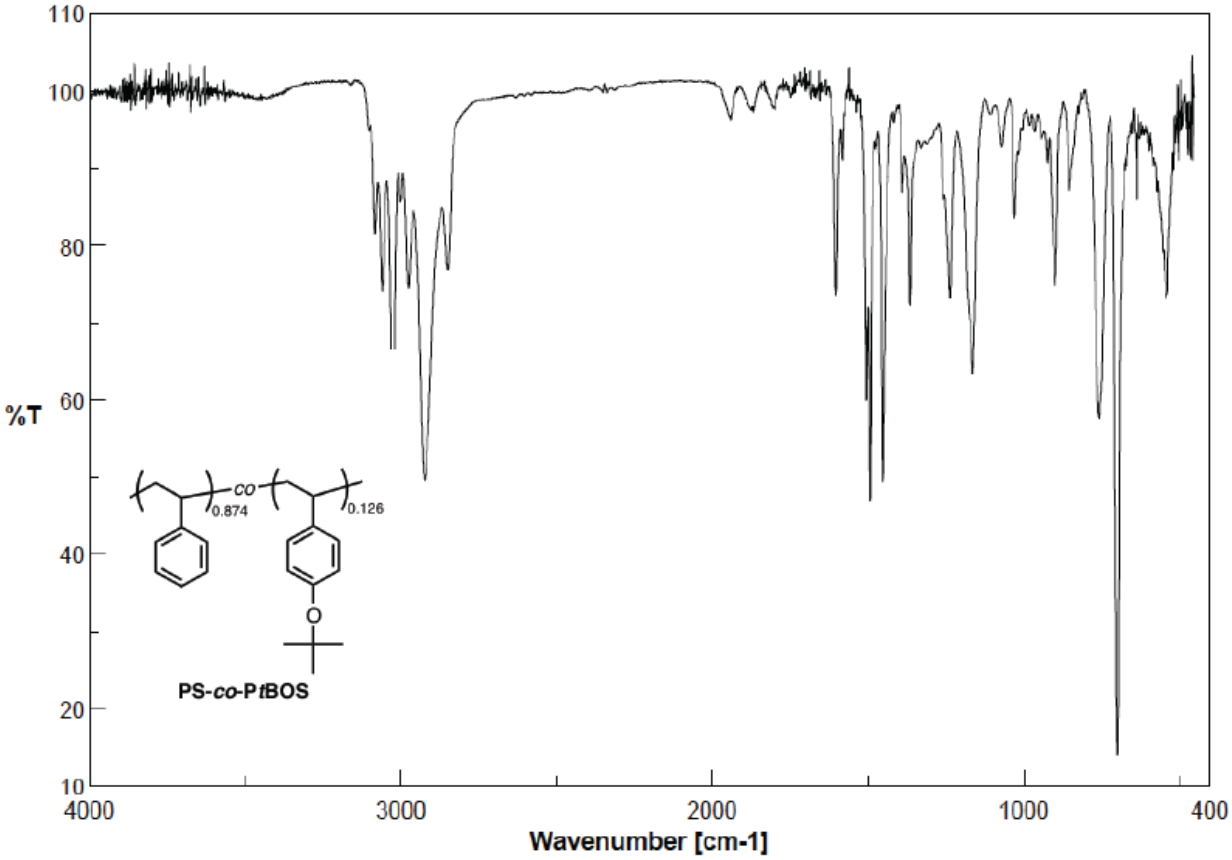


Figure S36. IR spectrum of **PS-*co*-P*t*BOS** (KBr).

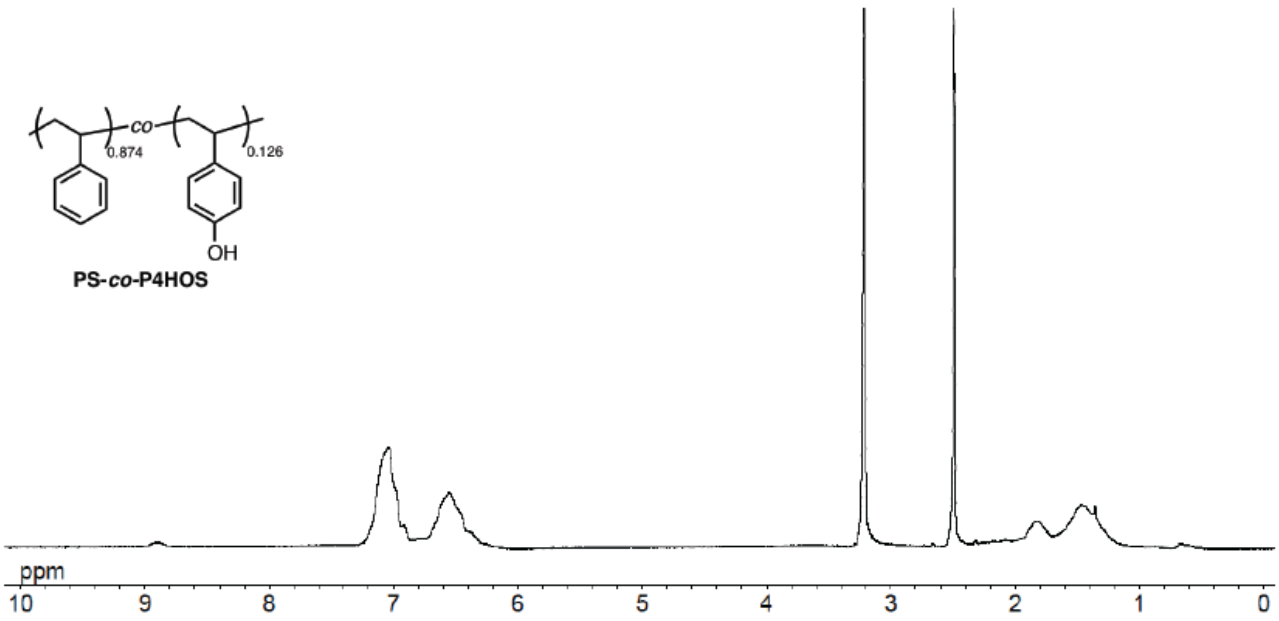


Figure S37. ^{1}H NMR spectrum of **PS-*co*-P4HOS** (400 MHz, 323 K, DMSO-d_6).

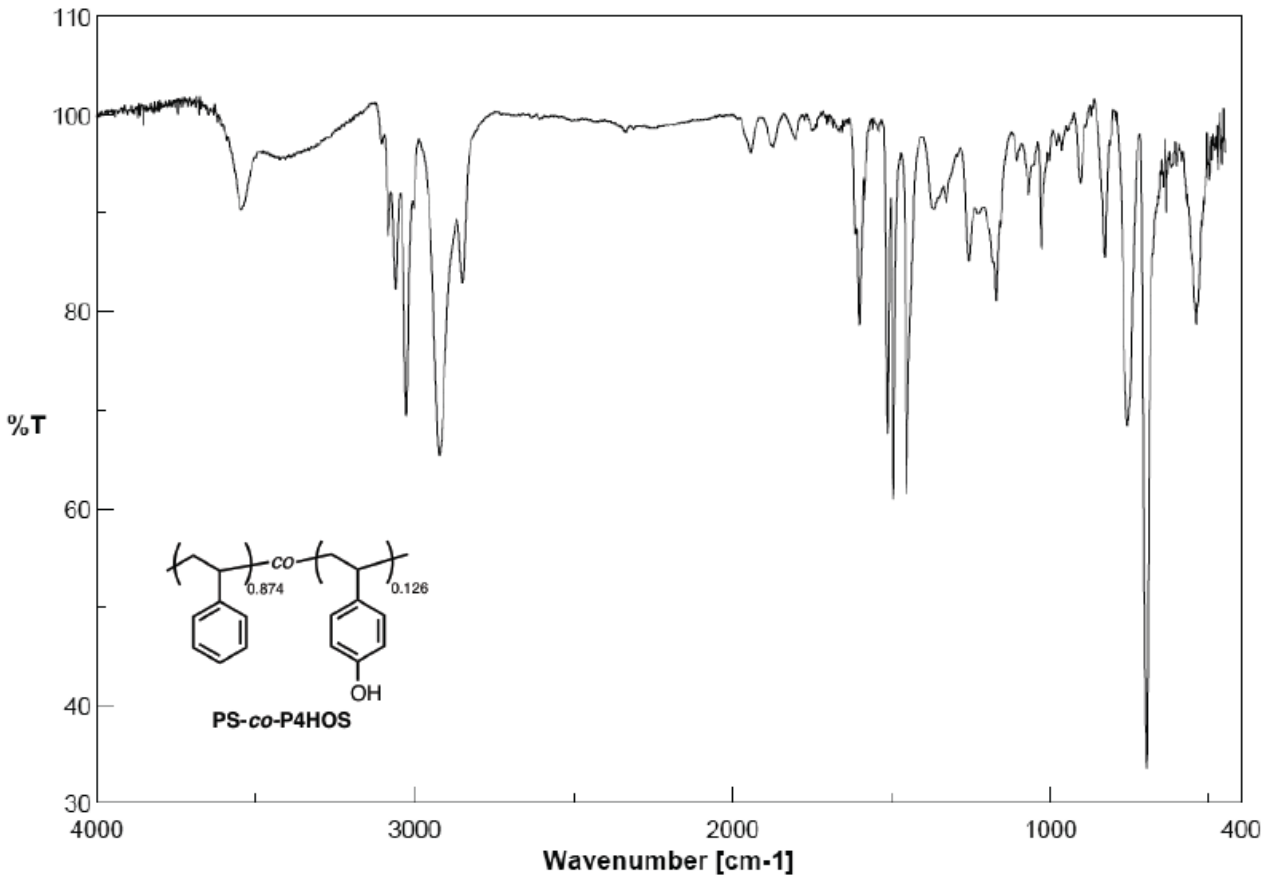


Figure S38. IR spectrum of **PS-*co*-P4HOS** (KBr).

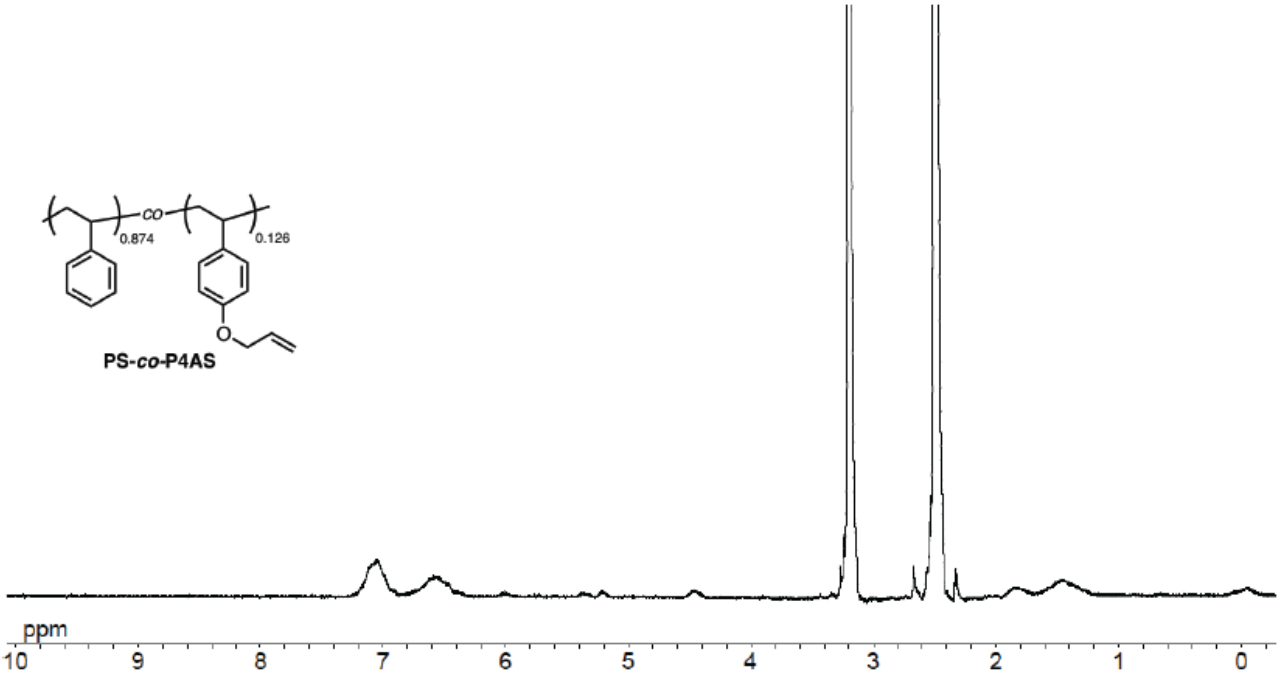


Figure S39. ^{1}H NMR spectrum of **PS-*co*-P4AS** (400 MHz, 323 K, DMSO-d_6).

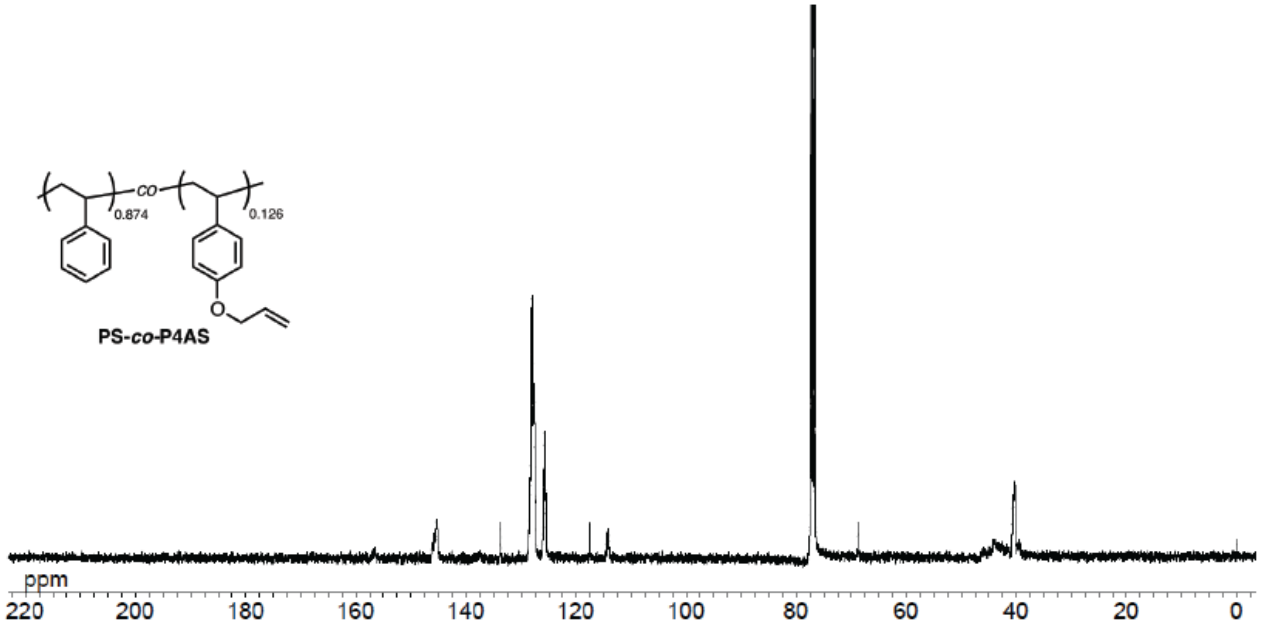


Figure S40. ^{13}C NMR spectrum of **PS-*co*-P4AS** (100 MHz, 298 K, $CDCl_3$).

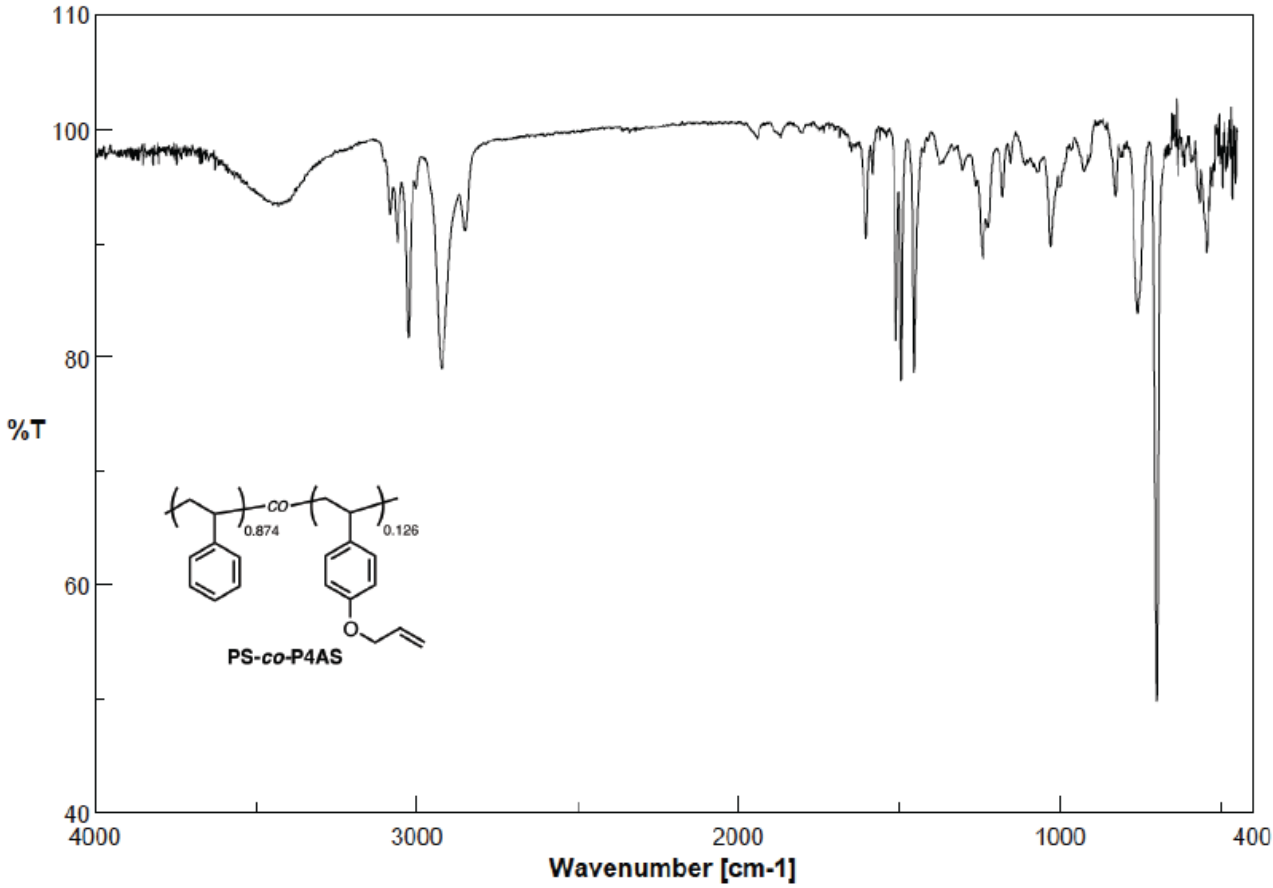


Figure S41. IR spectrum of **PS-*co*-P4AS** (KBr).

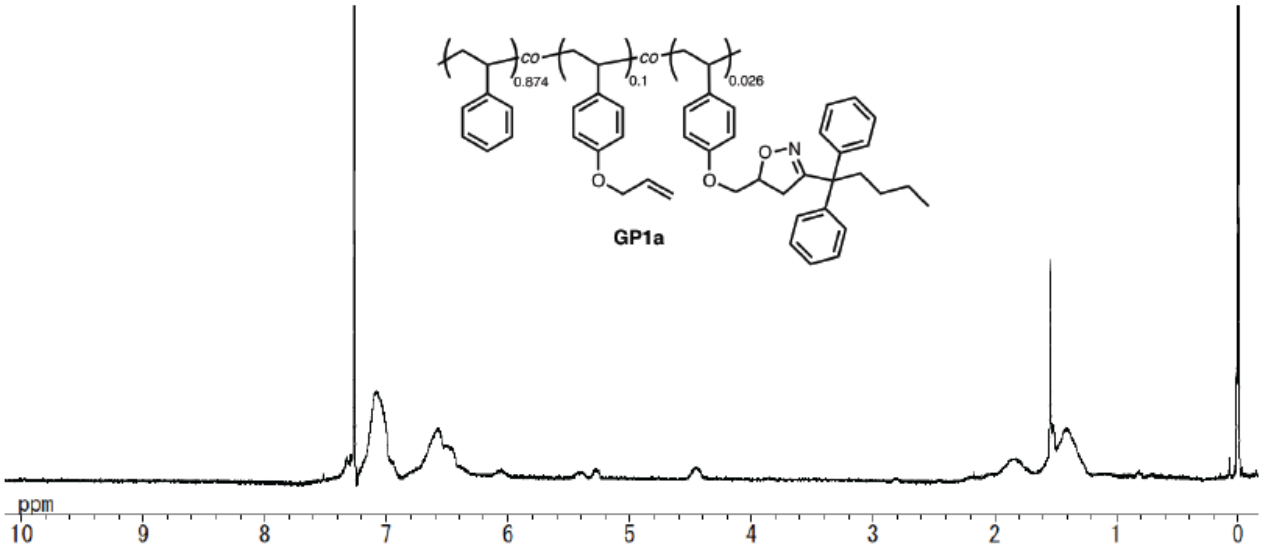


Figure S42. ^{1}H NMR spectrum of **GP1a** (400 MHz, 298 K, $CDCl_3$).

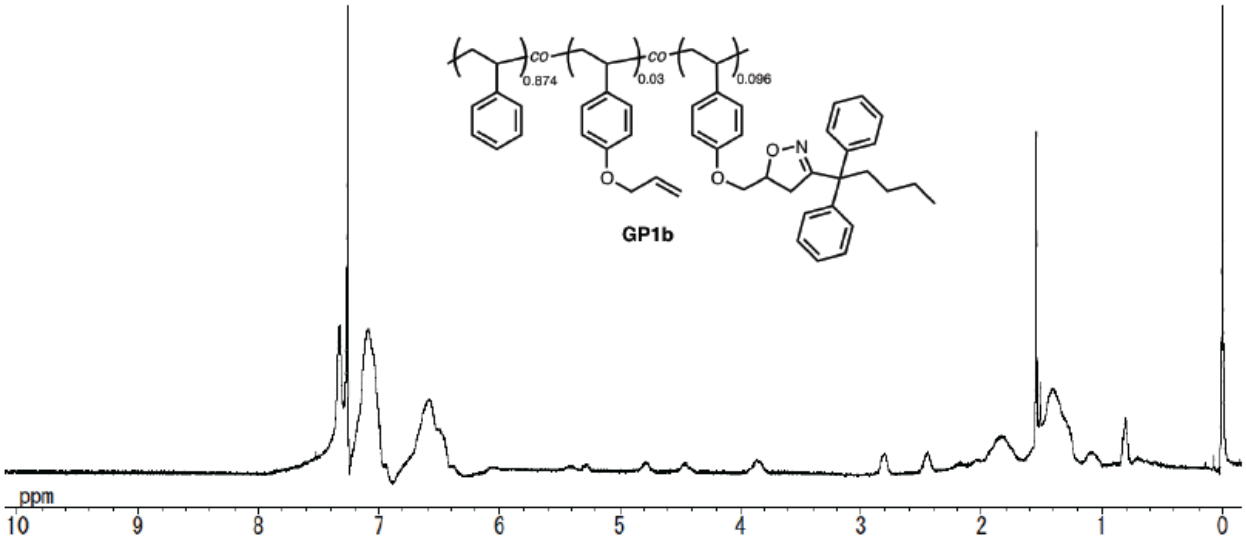


Figure S43. ^{1}H NMR spectrum of **GP1b** (400 MHz, 298 K, $CDCl_3$).

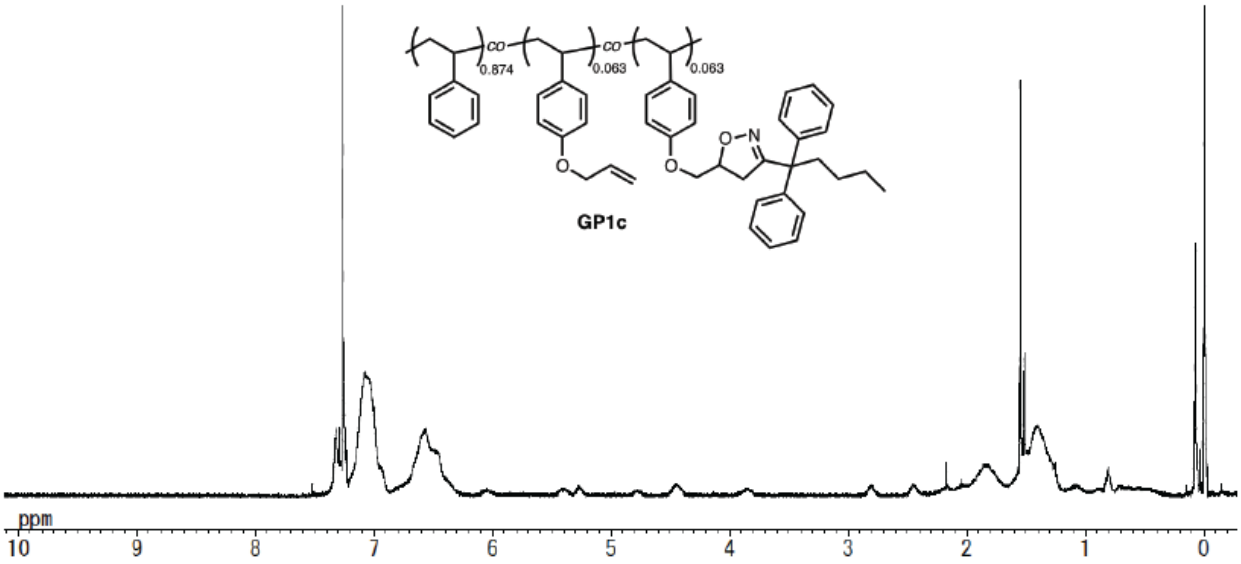


Figure S44. ^{1}H NMR spectrum of **GP1c** (400 MHz, 298 K, $CDCl_3$).

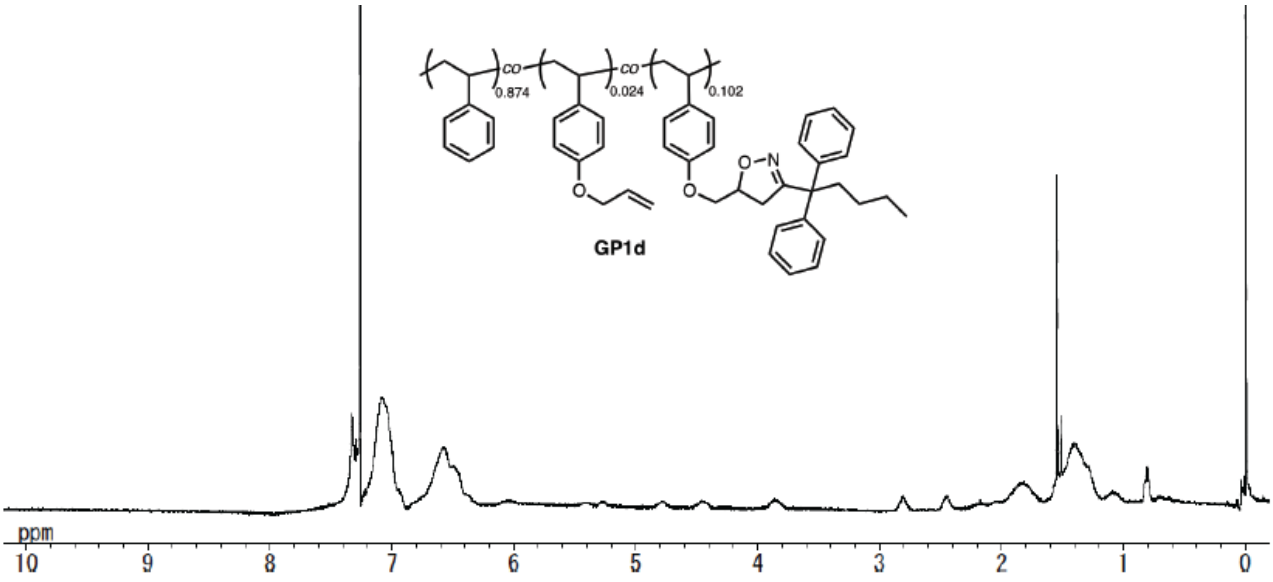


Figure S45. ^{1}H NMR spectrum of **GP1d** (400 MHz, 298 K, $CDCl_3$).

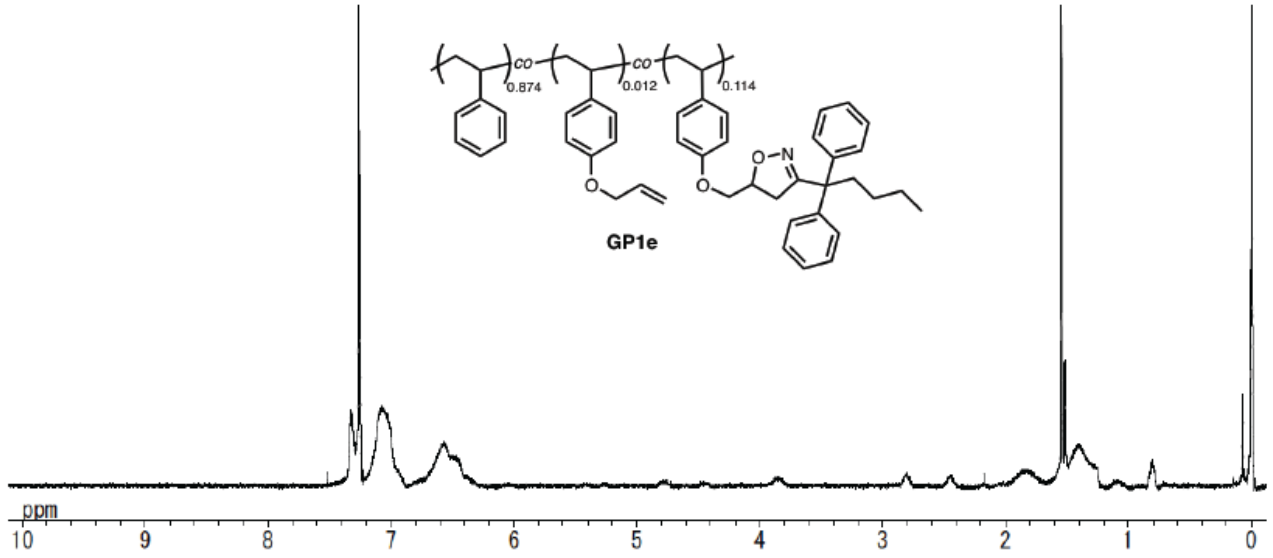


Figure S46. ^{1}H NMR spectrum of **GP1e** (400 MHz, 298 K, $CDCl_3$).

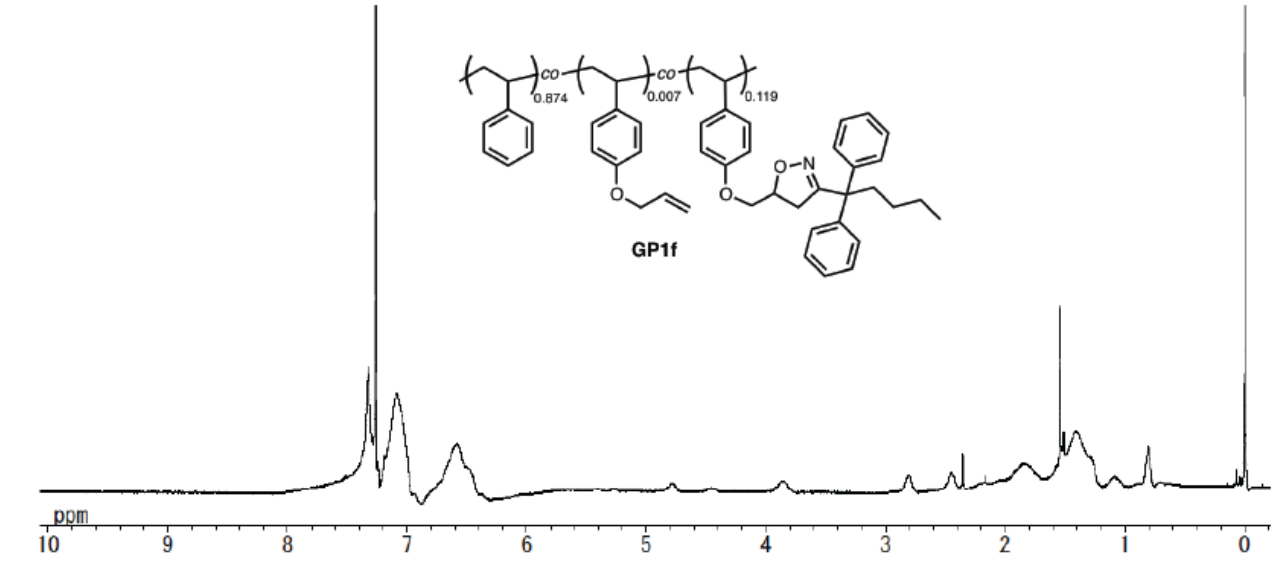


Figure S47. ^{1}H NMR spectrum of **GP1f** (400 MHz, 298 K, $CDCl_3$).

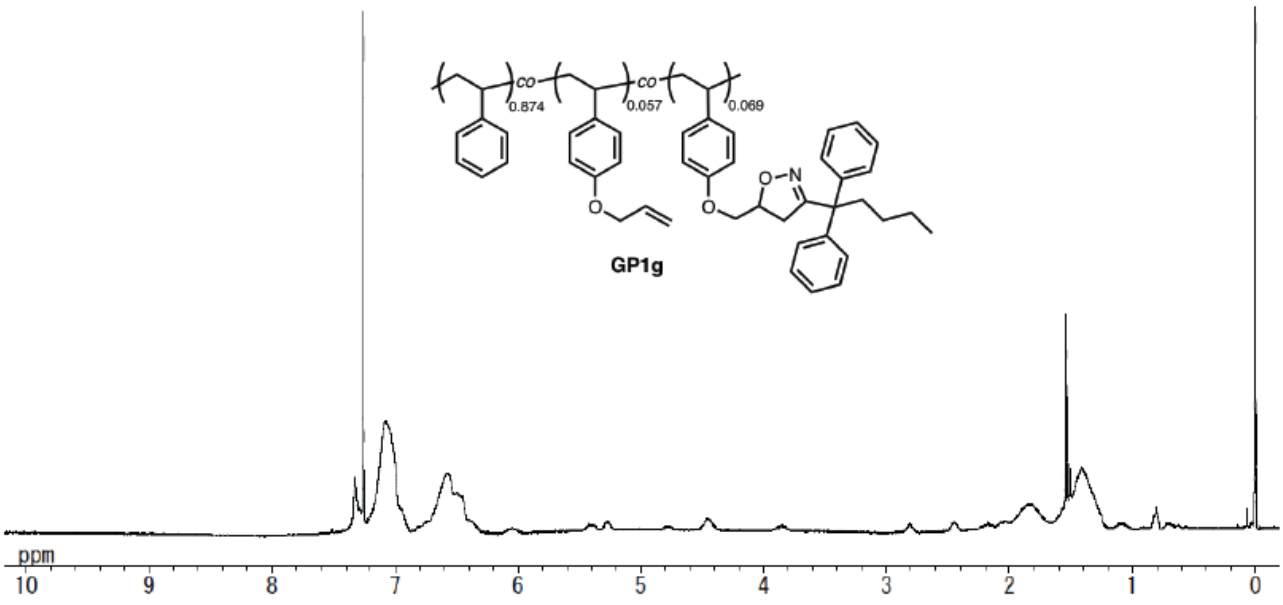


Figure S48. ^{1}H NMR spectrum of **GP1g** (400 MHz, 298 K, $CDCl_3$).

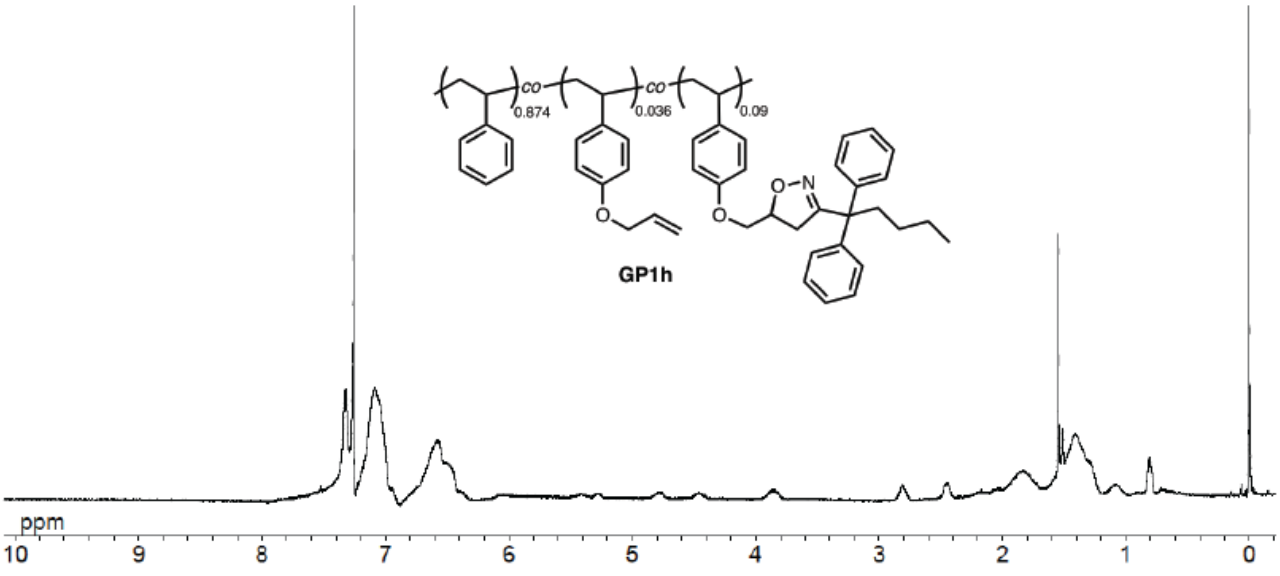


Figure S49. ^{1}H NMR spectrum of **GP1h** (400 MHz, 298 K, $CDCl_3$).

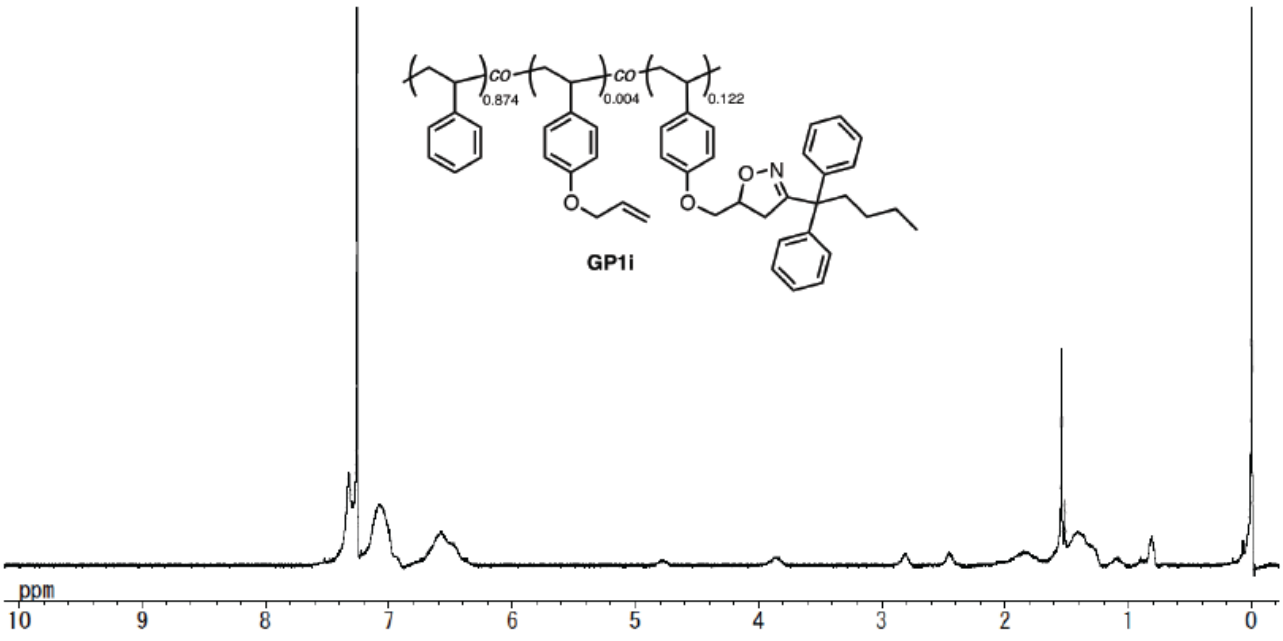


Figure S50. ^{1}H NMR spectrum of **GP1i** (400 MHz, 298 K, $CDCl_3$).

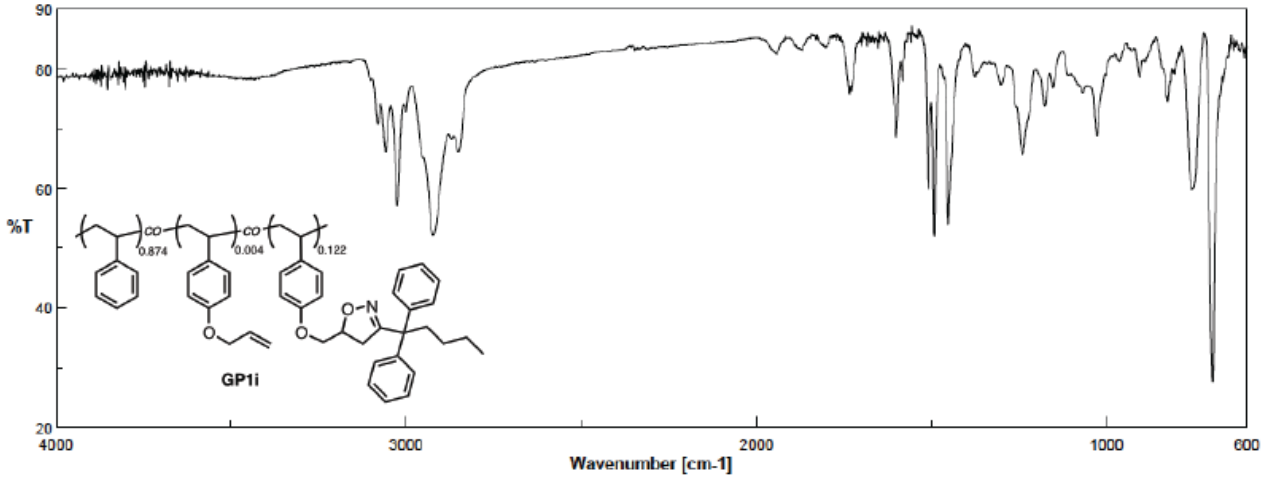


Figure S51. IR spectrum of **GP1i** (KBr).

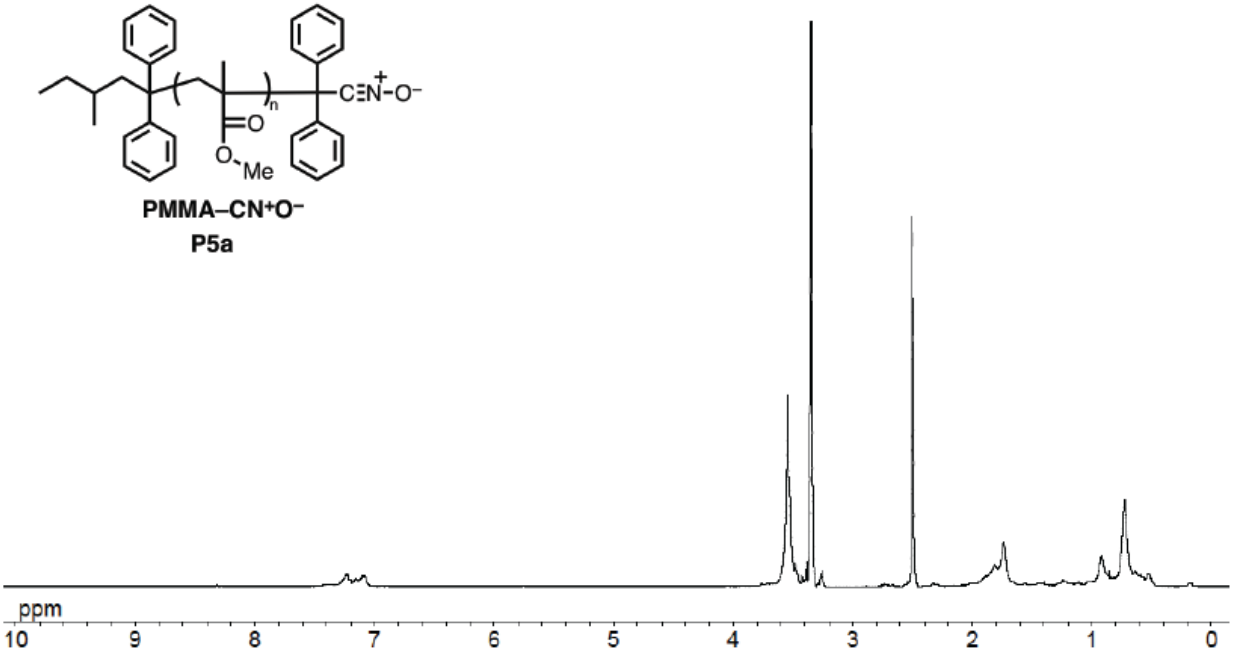


Figure S52. ^{1}H NMR spectrum of **PMMA-CN^{+}O^{-} (P5a)**(400 MHz, 298 K, DMSO-d_6).

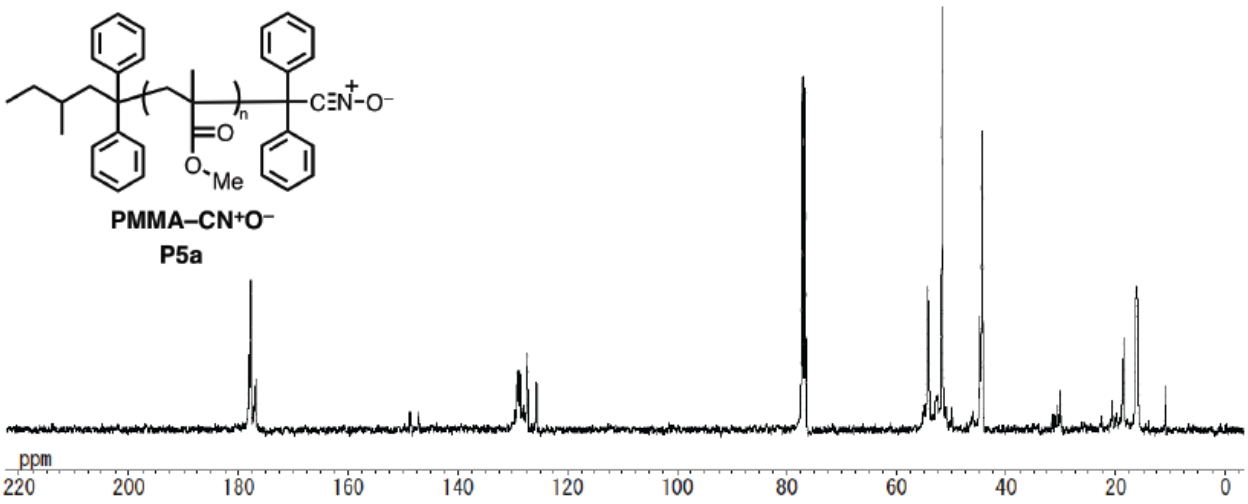


Figure S53. ^{13}C NMR spectrum of **PMMA-CN$^+$O$^-$ (P5a)** (100 MHz, 298 K, $CDCl_3$).

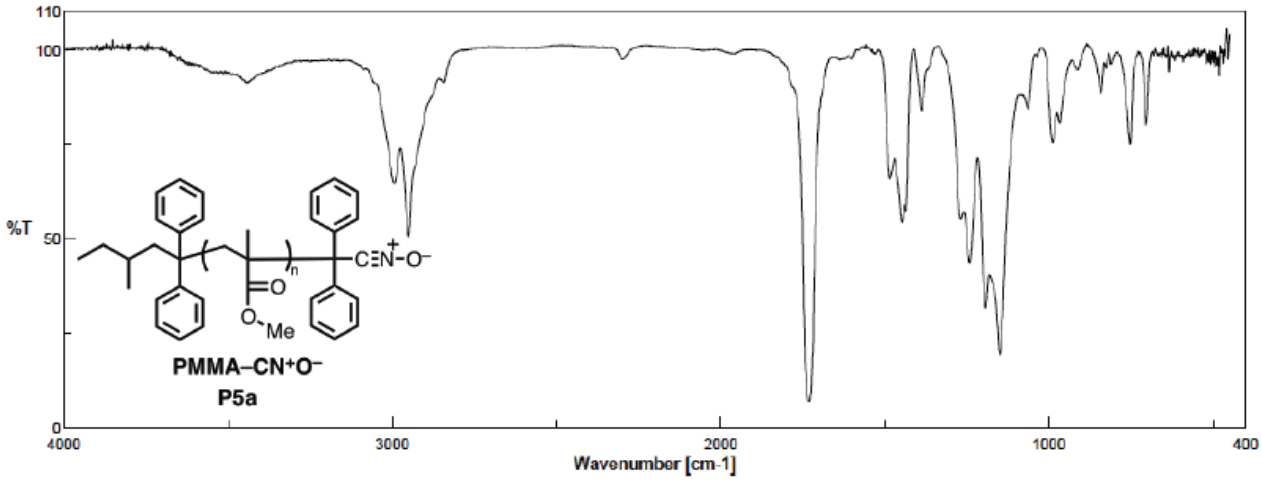


Figure S54. IR spectrum of **PMMA-CN$^+$O$^-$ (P5a)** (KBr).

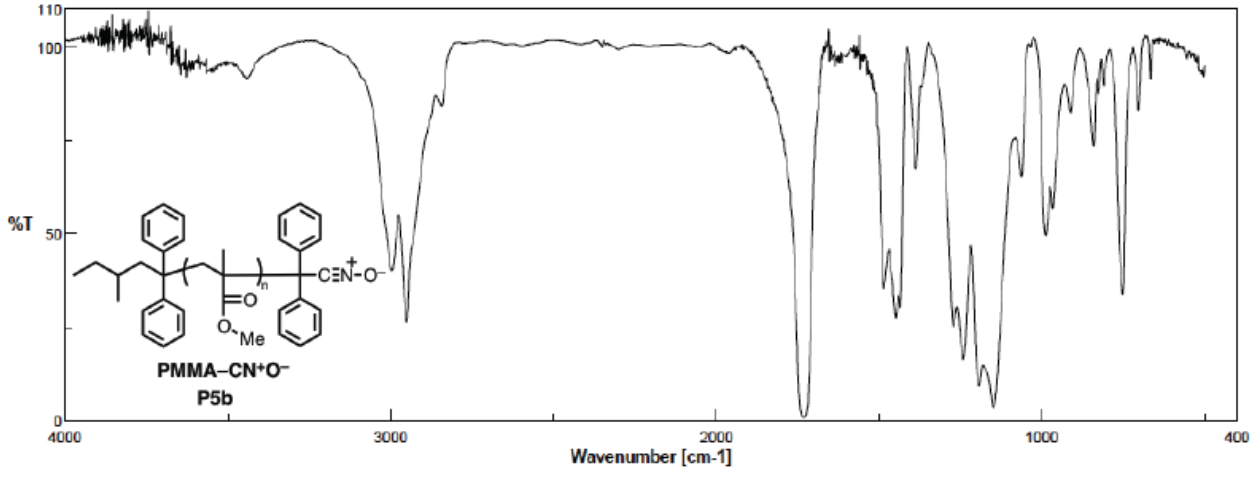


Figure S55. IR spectrum of **PMMA-CN$^+$O$^-$ (P5b)** (KBr).

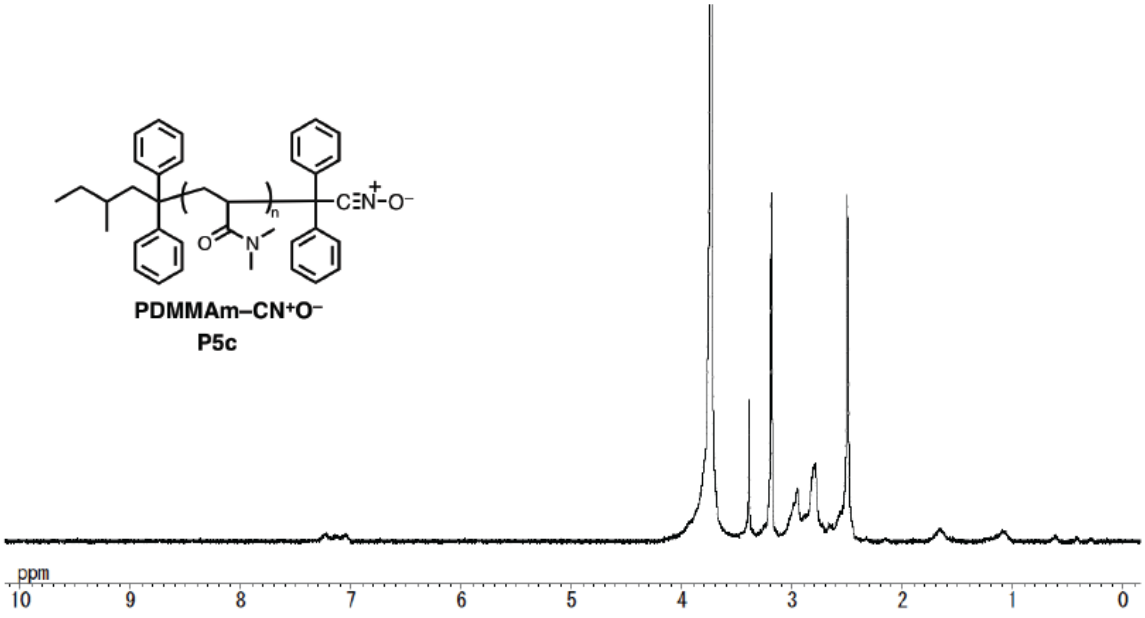


Figure S56. ^{1}H NMR spectrum of **PDMAAm-CN^{+}O^{-} (P5c)** (400 MHz, 298 K, DMSO-d_6).

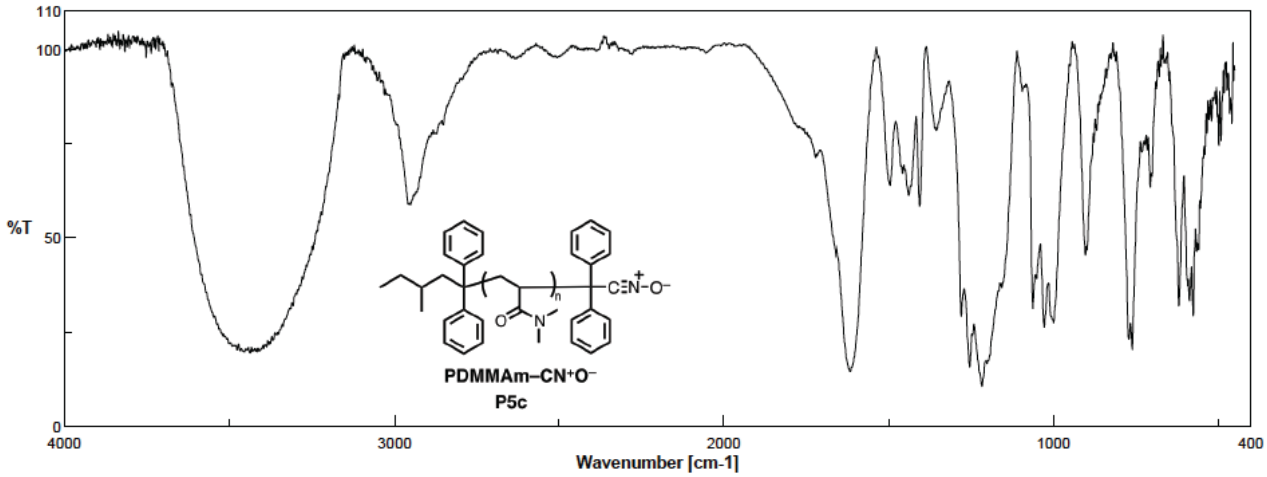


Figure S57. IR spectrum of **PDMAAm-CN^{+}O^{-} (P5c)** (KBr).

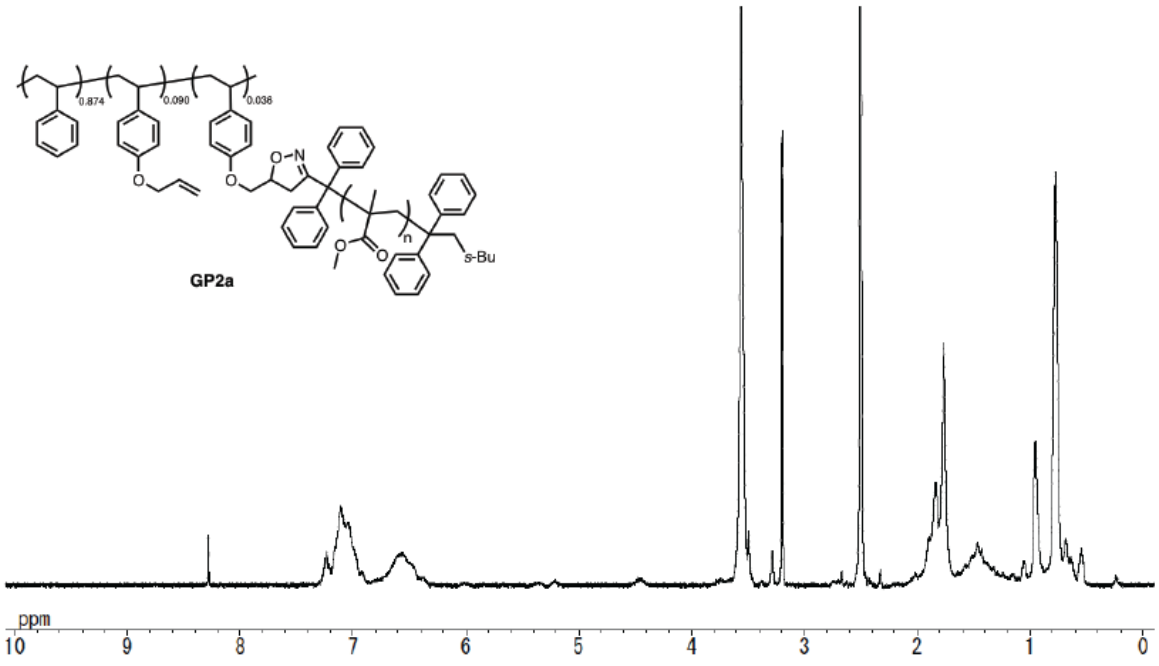


Figure S58. ^{1}H NMR spectrum of **GP2a** (400 MHz, 323 K, DMSO-d_6).

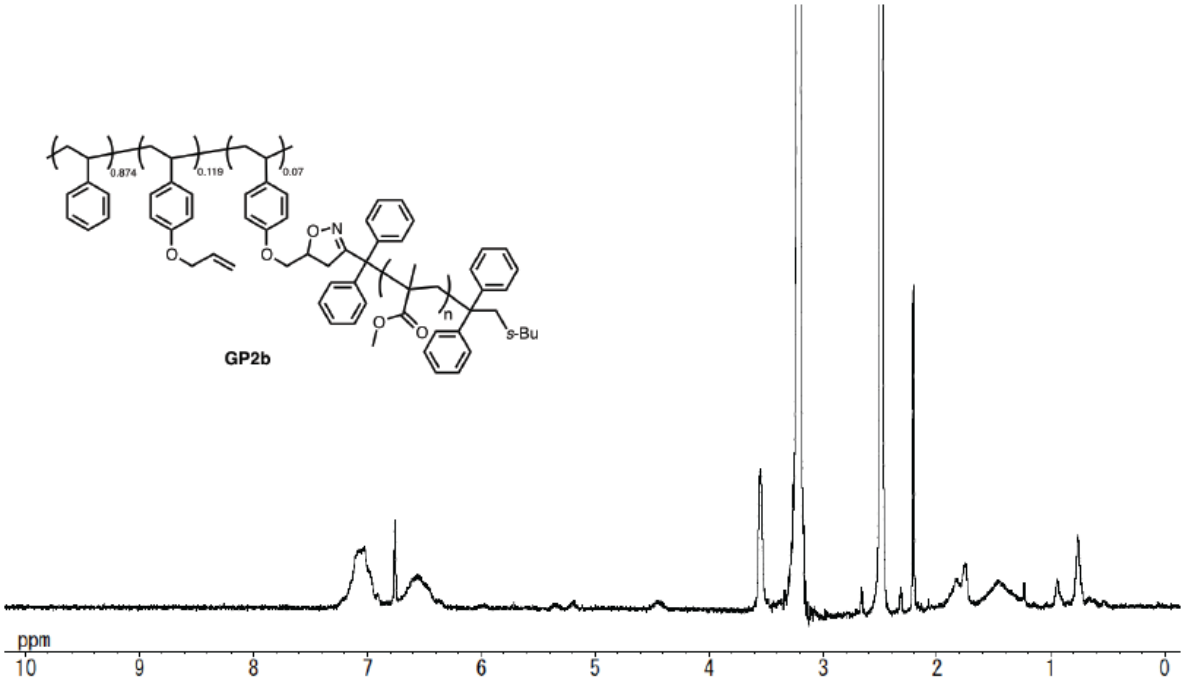


Figure S59. ^{1}H NMR spectrum of **GP2b** (400 MHz, 323 K, DMSO-d_6).

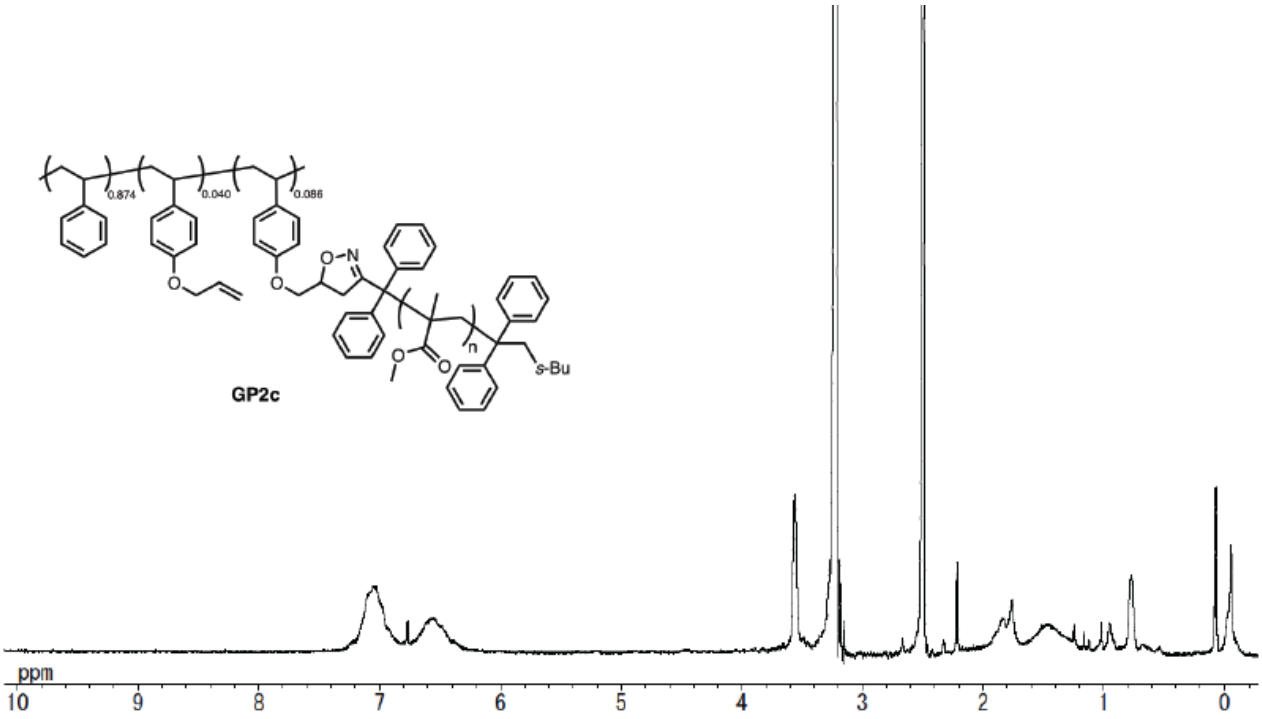


Figure S60. ^{1}H NMR spectrum of **GP2c** (400 MHz, 323 K, DMSO-d_6).

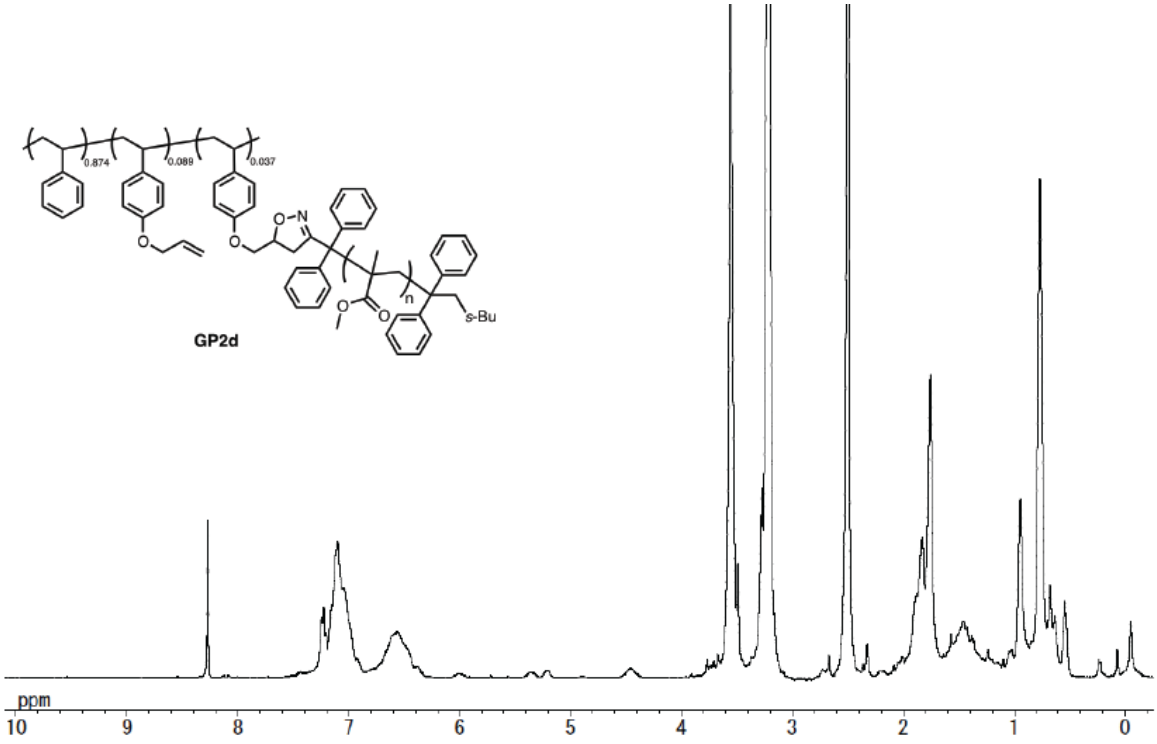


Figure S61. ^{1}H NMR spectrum of **GP2d** (400 MHz, 323 K, DMSO-d_6).

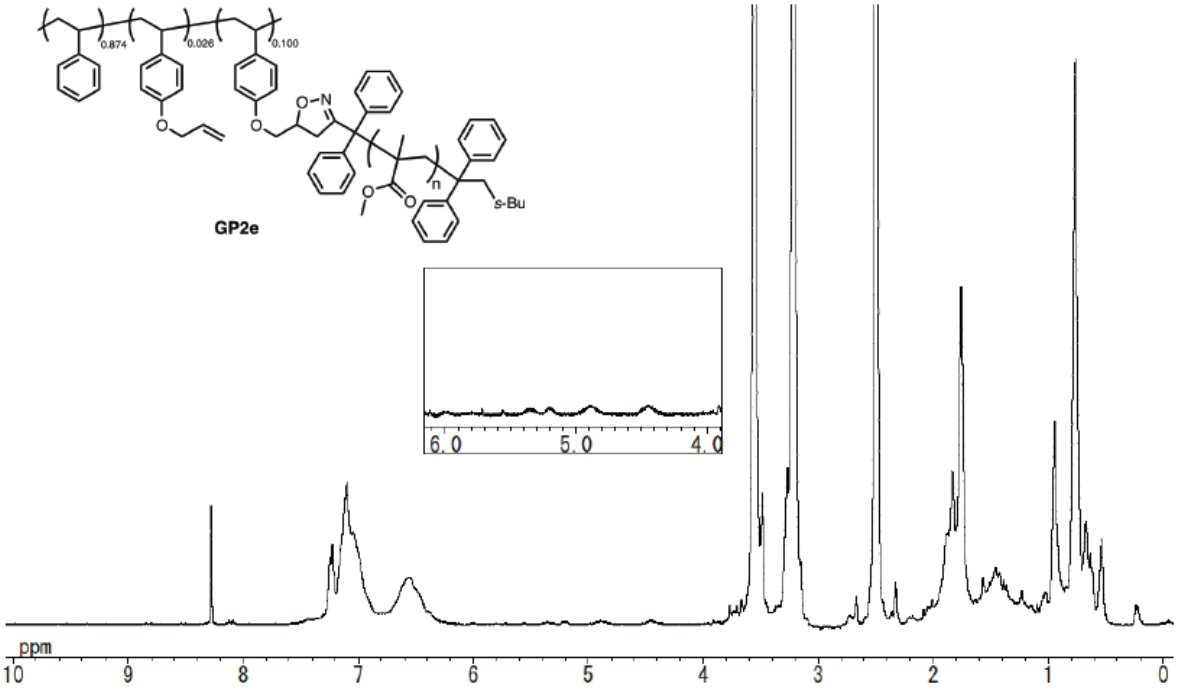


Figure S62. ^{1}H NMR spectrum of **GP2e** (400 MHz, 323 K, DMSO-d_6).

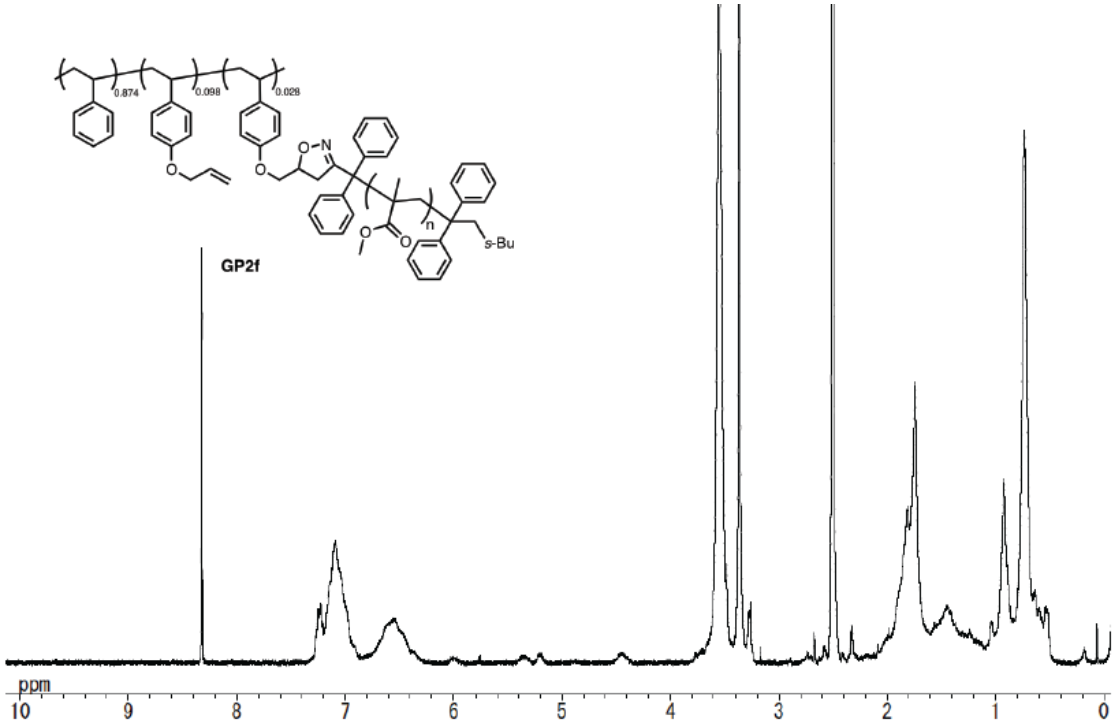


Figure S63. ^{1}H NMR spectrum of **GP2f** (400 MHz, 323 K, DMSO-d_6).

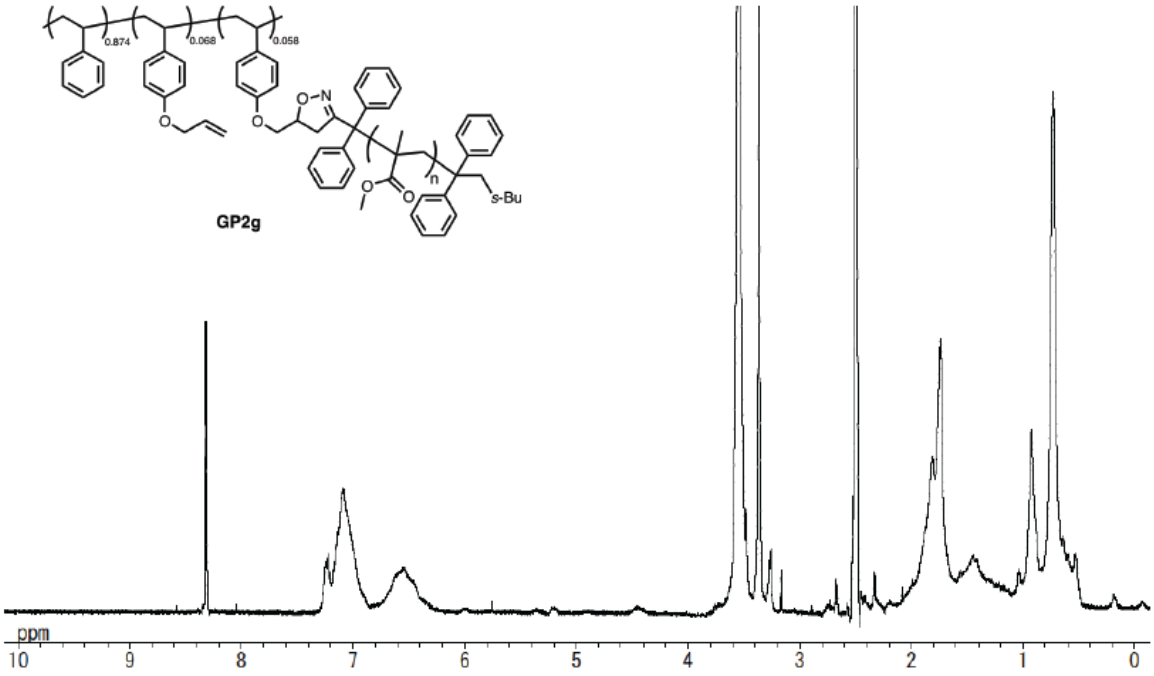


Figure S64. ^{1}H NMR spectrum of **GP2g** (400 MHz, 323 K, DMSO-d_6).

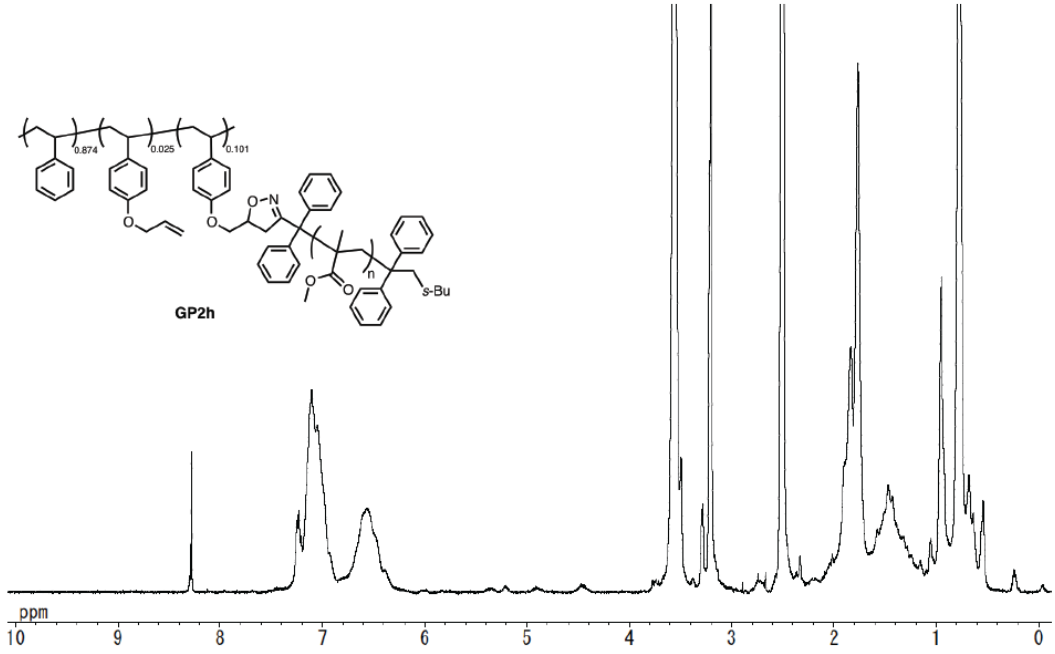


Figure S65. ^{1}H NMR spectrum of **GP2h** (400 MHz, 323 K, DMSO-d_6).

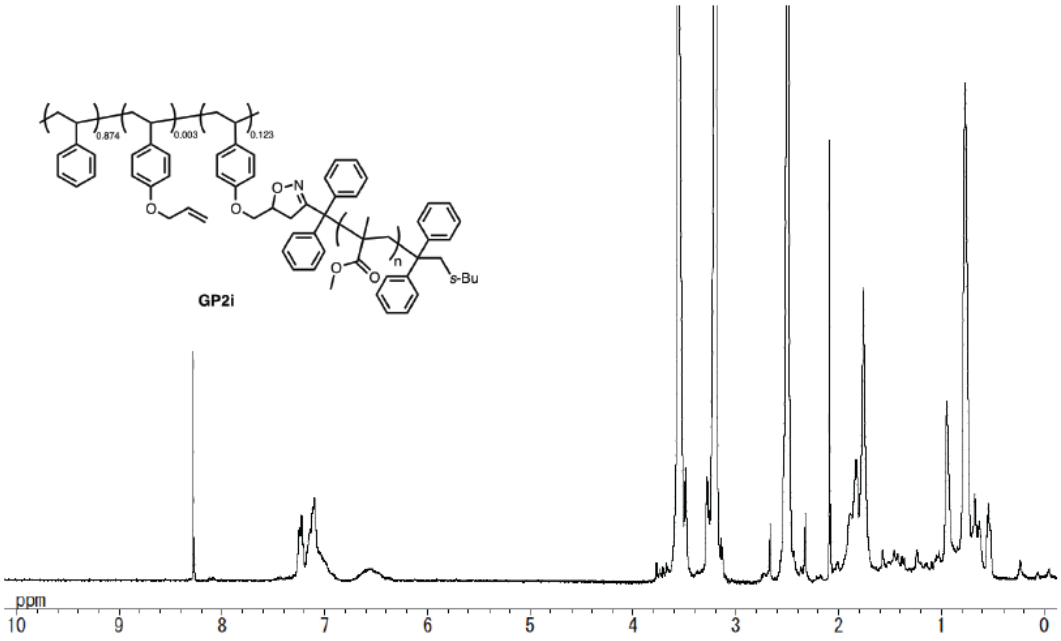


Figure S66. ^{1}H NMR spectrum of **GP2i** (400 MHz, 323 K, DMSO-d_6).

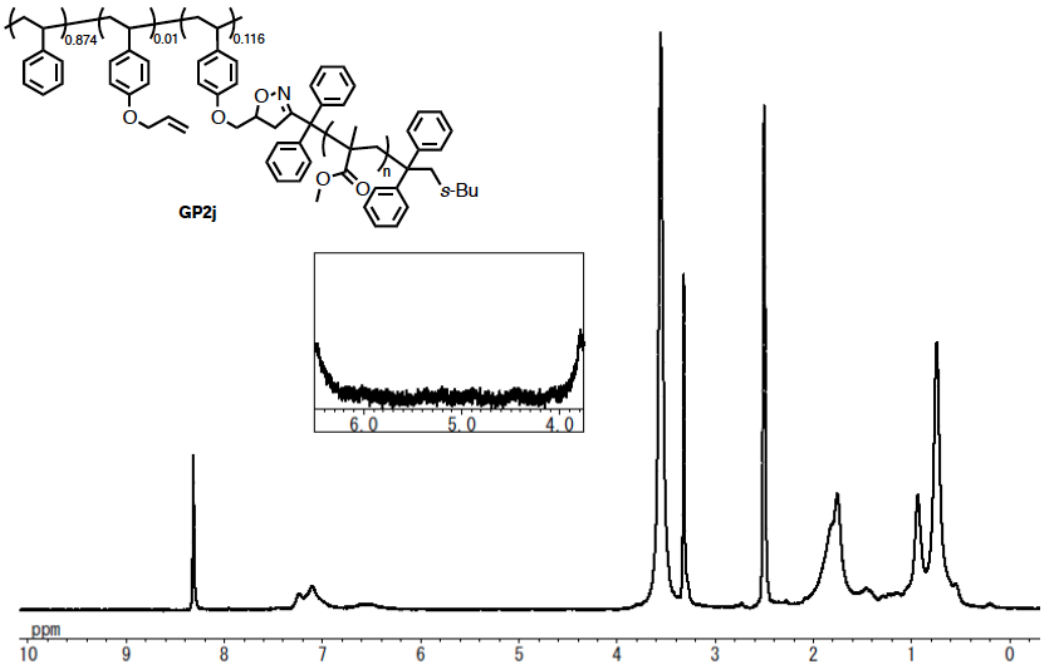


Figure S67. ^{1}H NMR spectrum of **GP2j** (400 MHz, 323 K, DMSO-d_6).

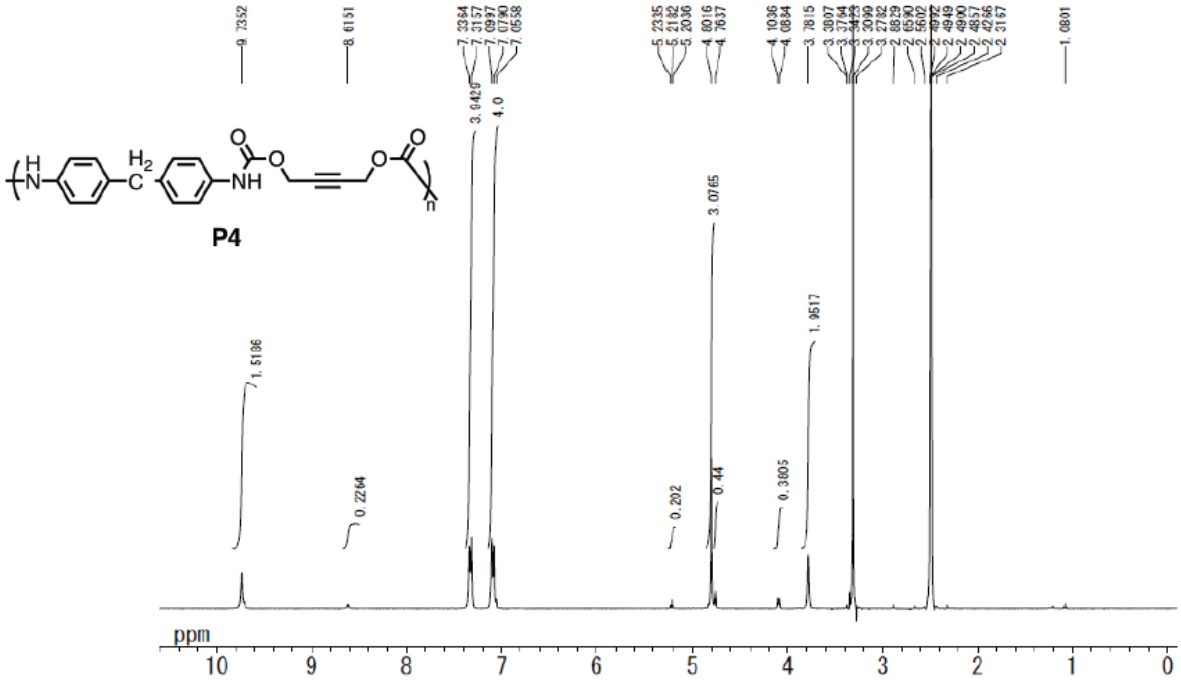


Figure S68. ^{1}H NMR spectrum of internal alkyne-containing polyurethane (400 MHz, DMSO-d_6, 298 K).

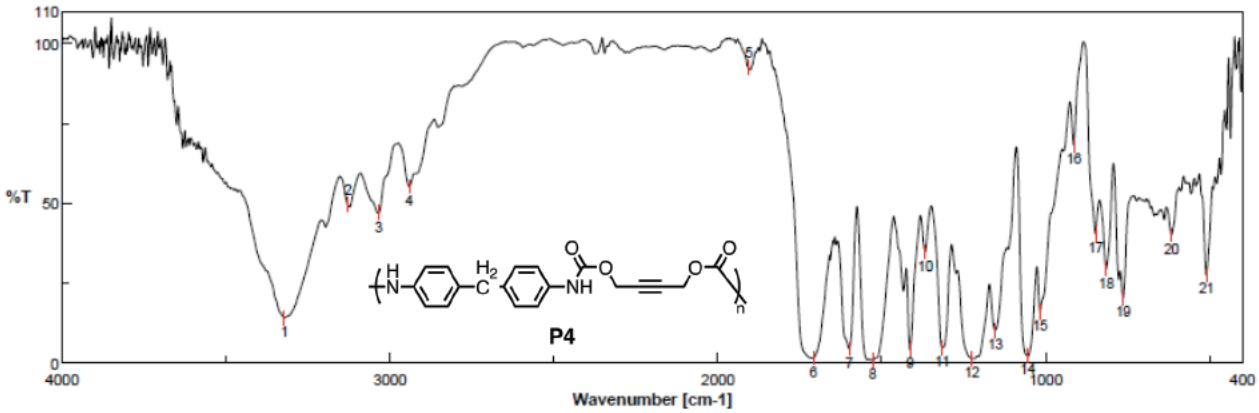


Figure S69. IR spectrum of internal alkyne-containing polyurethane (KBr).

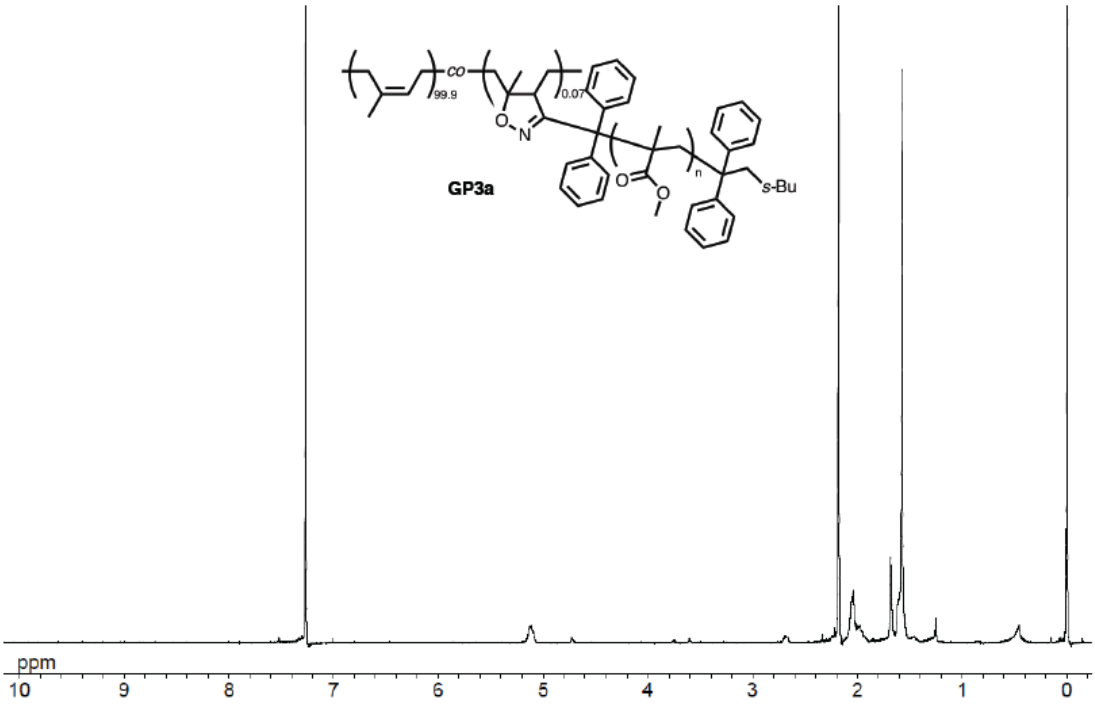


Figure S70. ^{1}H NMR spectrum of **GP3a** (400 MHz, 298 K, $CDCl_3$).

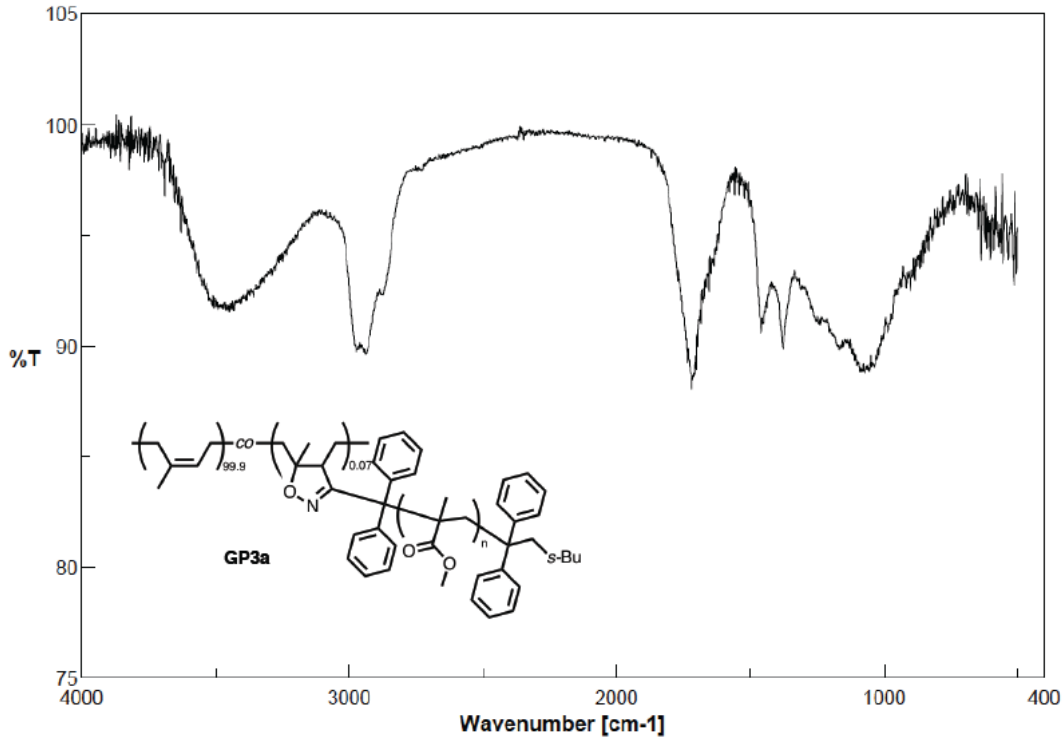


Figure S71. IR spectrum of **GP3a** (KBr).

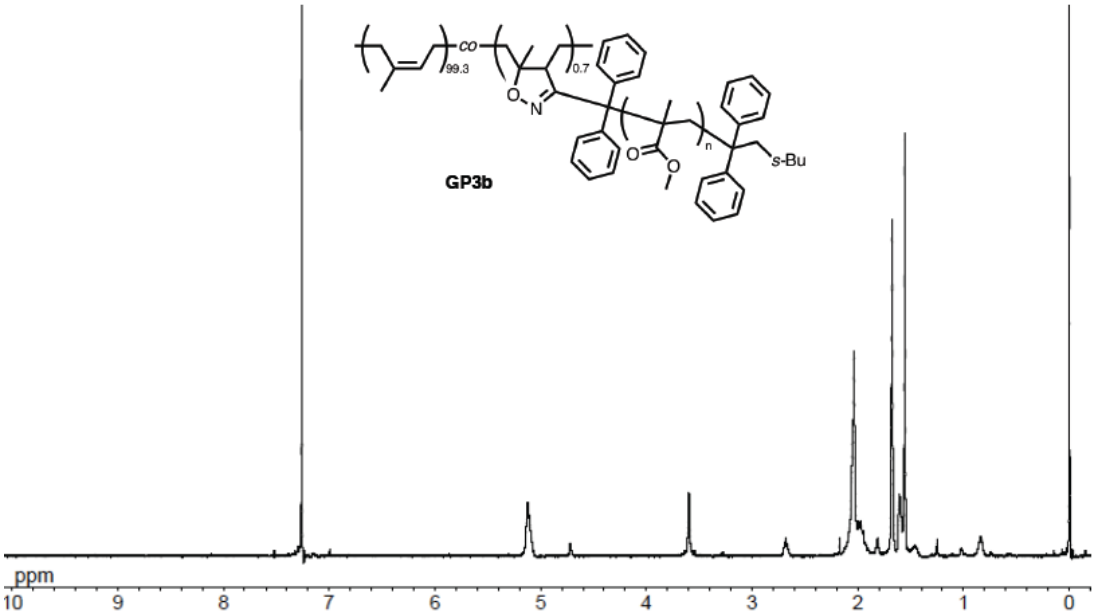


Figure S72. ^{1}H NMR spectrum of **GP3b** (400 MHz, 298 K, $CDCl_3$).

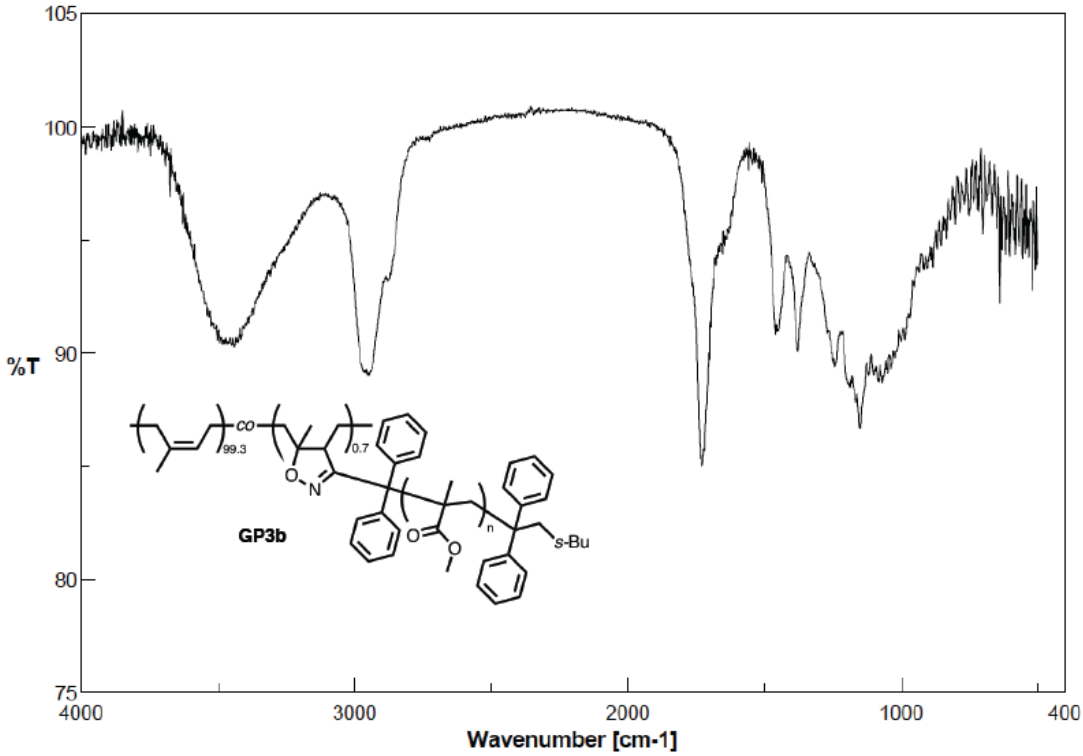


Figure S73. IR spectrum of **GP3b** (KBr).

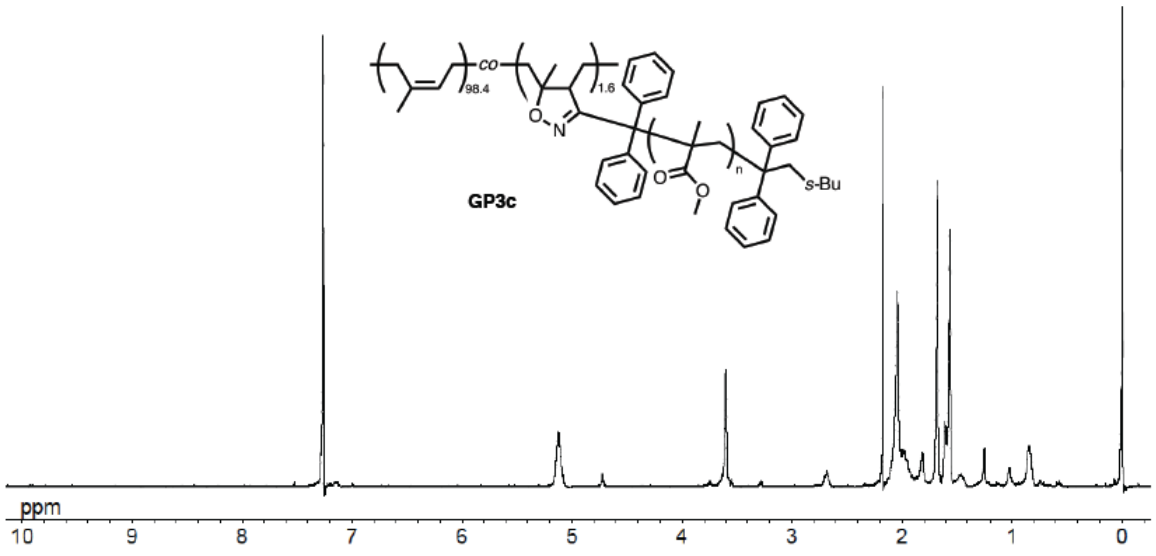


Figure S74. ^{1}H NMR spectrum of **GP3c** (400 MHz, 298 K, $CDCl_3$).

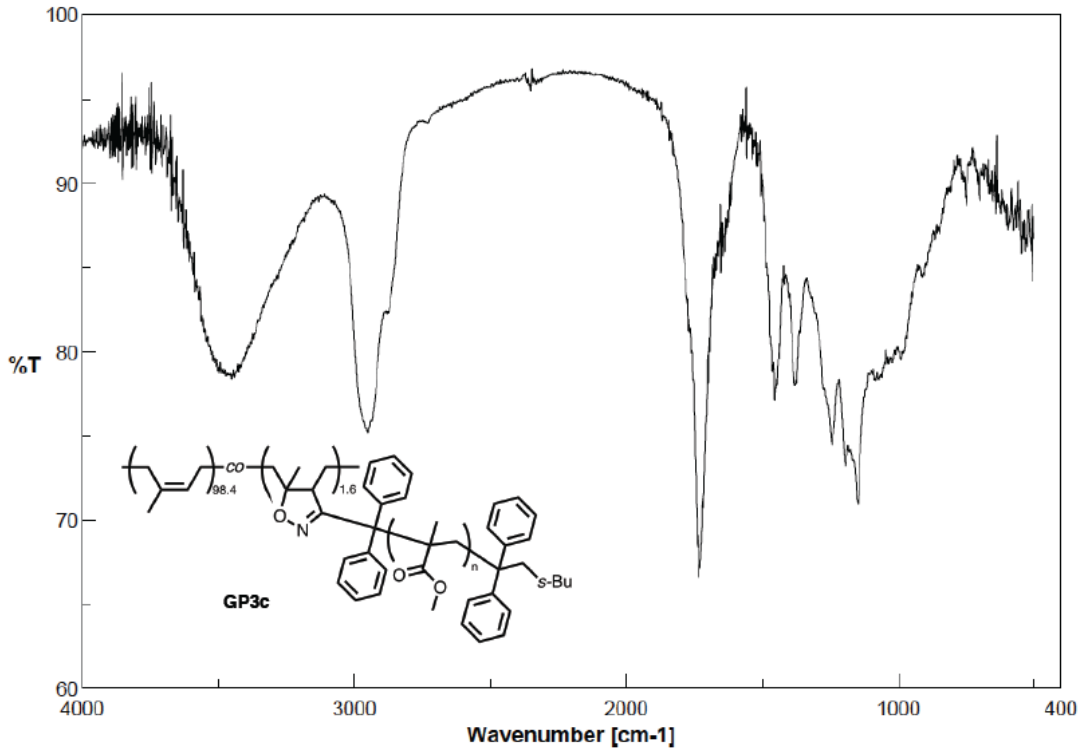


Figure S75. IR spectrum of **GP3c** (KBr).

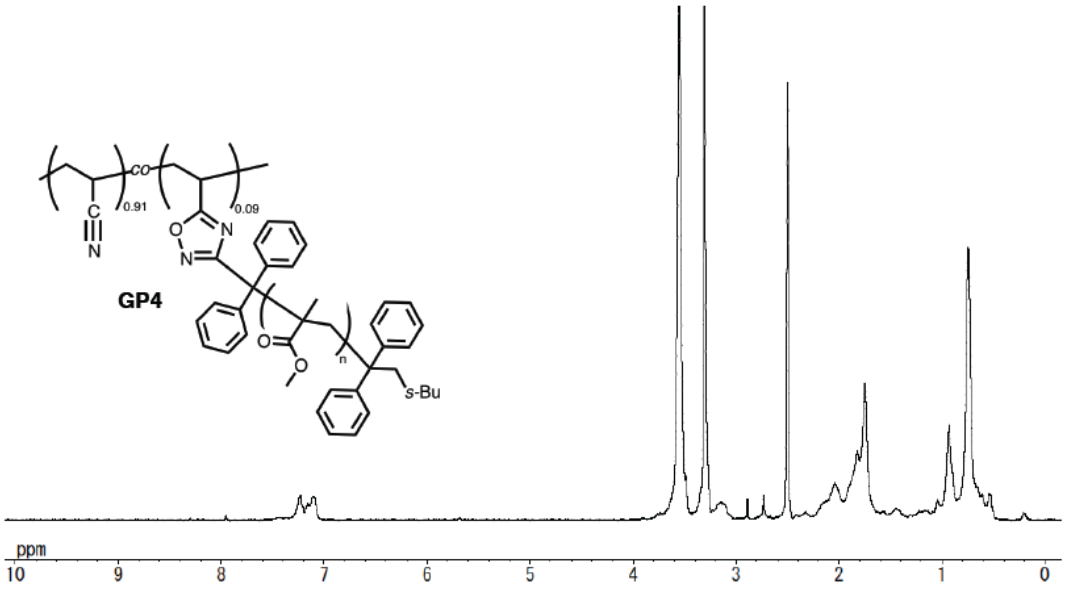


Figure S76. ^{1}H NMR spectrum of **GP4** (400 MHz, 298 K, DMSO-d_6).

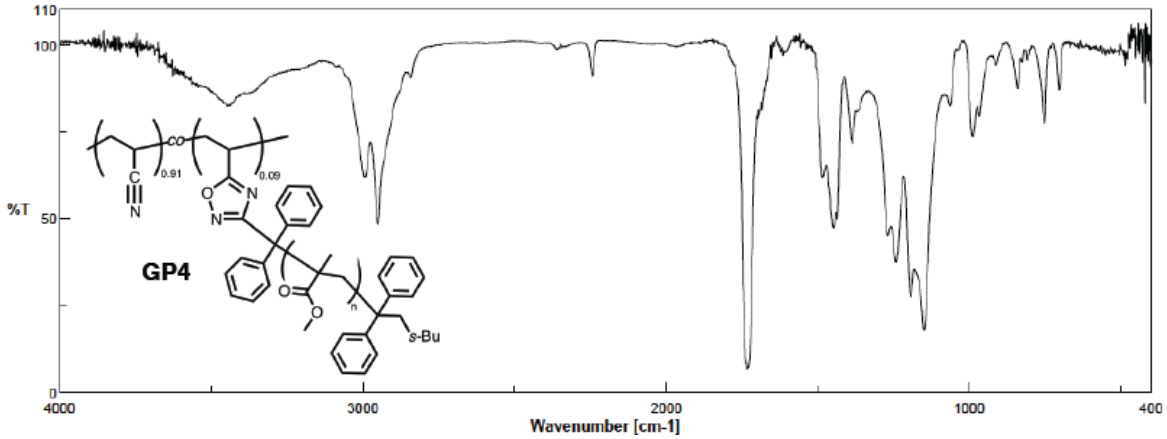


Figure S77. IR spectrum of **GP4** (KBr).

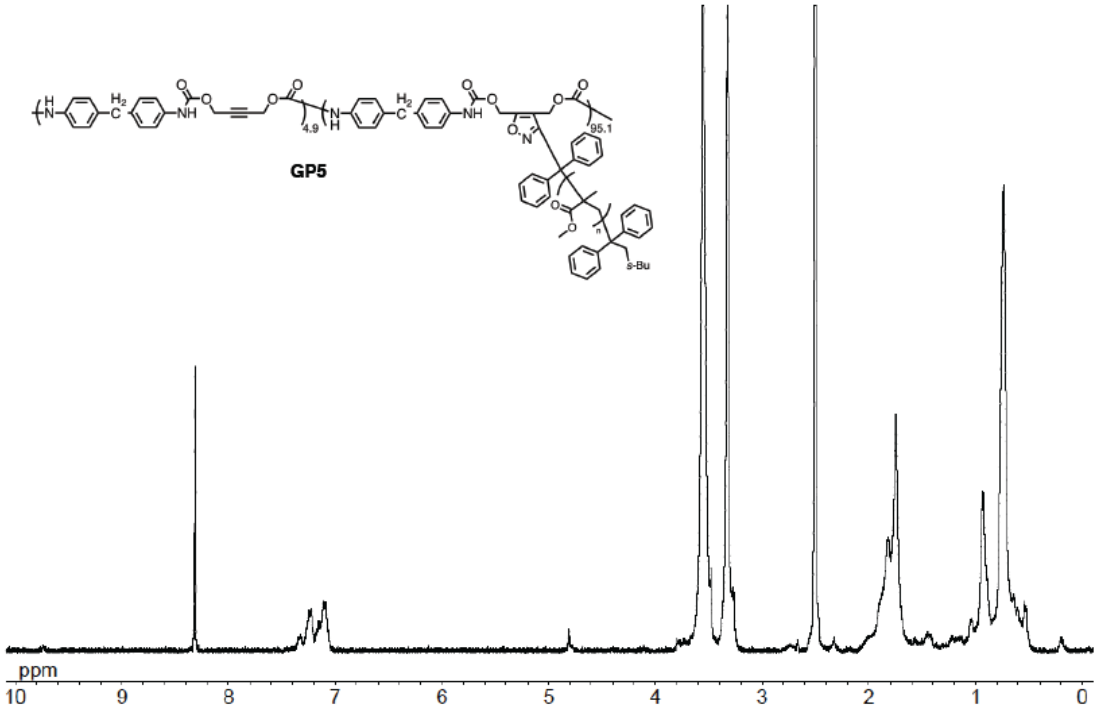


Figure S78. ^{1}H NMR spectrum of **GP5** (400 MHz, 298 K, DMSO-d_6).

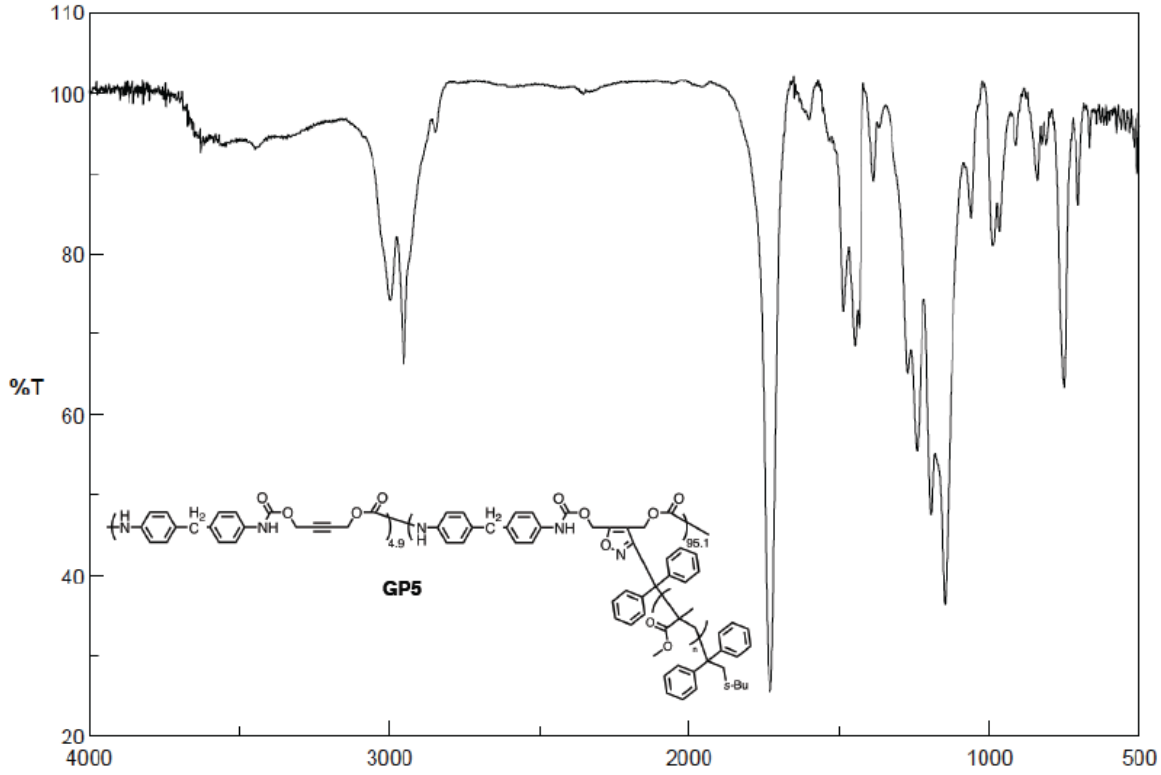
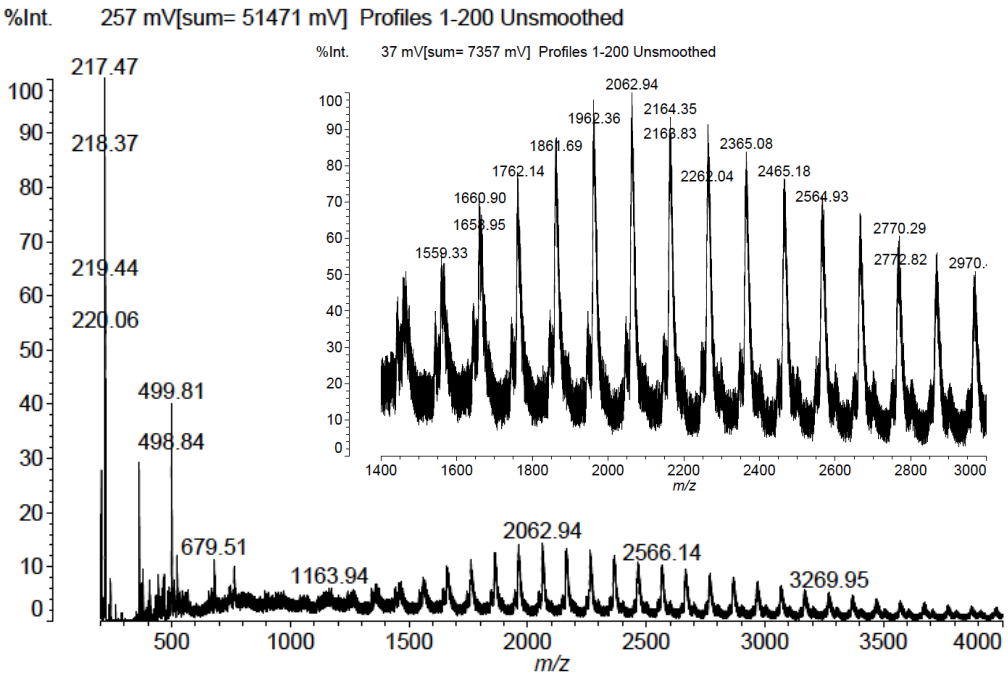
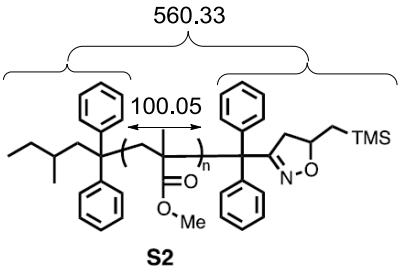


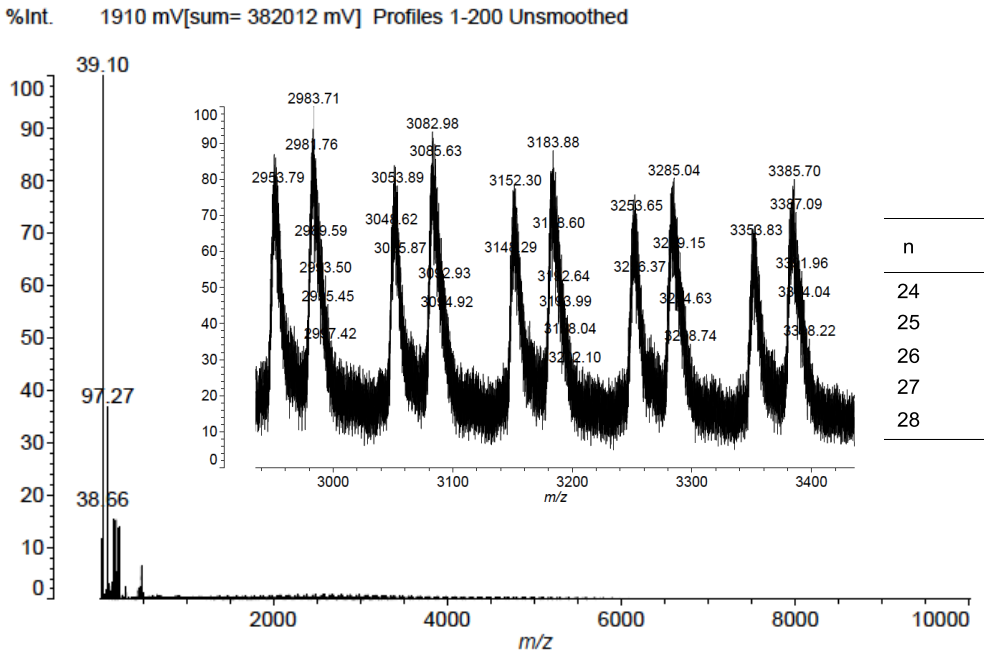
Figure S79. IR spectrum of **GP5** (KBr).





n	theoretical values
11	1660.88
12	1760.93
13	1860.98
14	1961.03
15	2061.08
16	2161.13
17	2261.18

Figure S80. MALDI-TOF MS of the adduct of **P1** to allyltrimethylsilane (**S2**, matrix: dithranol).



n	theoretical values	
	(M+Na$^+$)	(M+Na$^+$–OMe)
24	2984.53	2953.51
25	3084.58	3053.56
26	3184.63	3153.61
27	3284.68	3253.66
28	3384.73	3353.71

Figure S81. MALDI-TOF MS of the adduct of **P2** to allyltrimethylsilane (matrix: dithranol).

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