Rh(III)-Catalyzed Synthesis of Amino-Side-Chained Poly(Phenylene Vinylene) via C-H Bond Olefination

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1. General Consideration

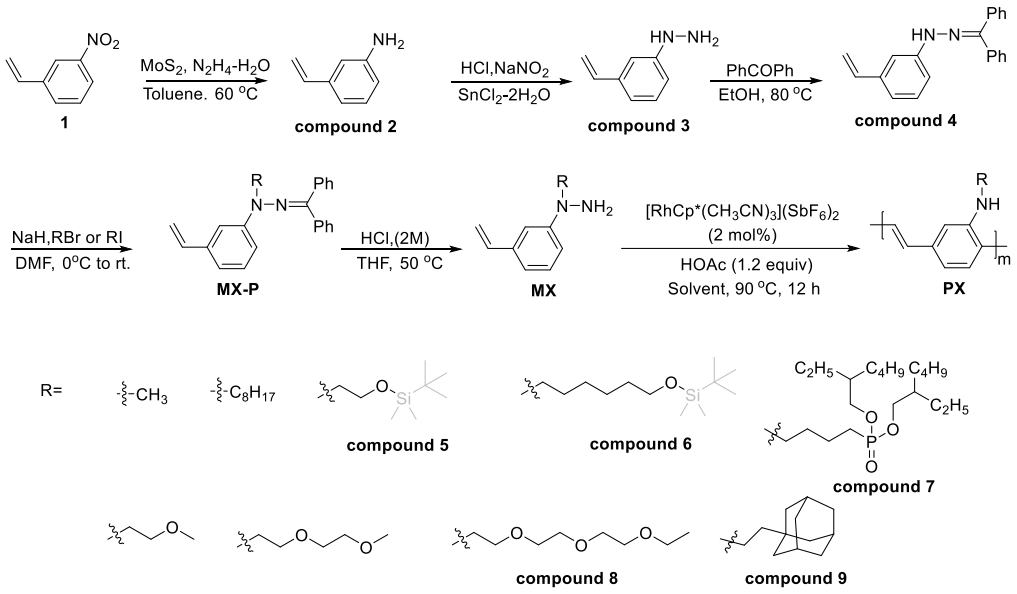
Gel permeation chromatography (GPC) data were measured using a Polymer Laboratories PL-GPC 50 instrument equipped with a 10 μm mixed-B columns, a 5 μm mixed-D columns and a refractive index (RI) detector (from Agilent Technology) or 10 μm Olexis columns and a refractive index (RI) detector (from Agilent Technology). HPLC grade *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) were used as an eluent at a flow rate of 1 mL/min. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) data are reported relative to polystyrene (DMF) and poly(methyl methacrylate) (DMSO) standards. For the reported M_n in the range of approximately 4 kDa or lower, the value is not considered to be accurate since the GPC trace has already approached the solvent regime. The ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 400 MHz or 500 MHz spectrometer {H}. The chemical shifts are expressed in ppm in reference to the residual deuterated solvent and the coupling constants are given in Hz. Data for ^{1}H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), coupling constant (Hz) and integration. Data for ^{13}C NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectrometric data were obtained using Bruker Apex IV RTMS. UV-vis absorption spectra were measured using Shanghai Metash Instruments UV-8000S UV-Vis-NIR spectrophotometer. Photoluminescence (PL) measurements were carried out on HORIBA Fluolog3 spectrophotometer, the absolute photoluminescence quantum yields (Φ_F) were measured with HORIBA FL3 fluorescence spectrometer. The prompt and decay lifetimes of the samples were measured with Edinburgh Instruments FLS980 spectrometer. Thermal gravimetric analysis (TGA) was performed by an SDT851e/SF/1100 ^{o}C TGA instrument under nitrogen flow at a heating rate of 10 ^{o}C min^{-1} from 25 to 600 ^{o}C. Differential scanning calorimeter (DSC) was performed on a Q2000 DSC system in nitrogen atmosphere. An indium standard was used for temperature and enthalpy calibrations. All the samples were first heated from -30 to 200 ^{o}C at a rate of 30 ^{o}C min^{-1} and held at this temperature for 2 min to eliminate the thermal history, then they were cooled to -30 ^{o}C and heated again from -30 to 200 ^{o}C at a heating or cooling rate of 10 ^{o}C min^{-1}.

2. Materials

All commercial reagents were used without additional purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040-0.063 mm). Visualization on TLC was achieved by use of UV light (254 nm) or iodine.

3. Synthesis of monomers and polymers

Scheme S1. Synthesis of monomers



Synthesis of ***2***[1]: The round-bottom flask with a stir bar was flushed with N_2 more than three times to remove the air, and filled with N_2. Then, 3-Nitrophenylethene (17.4 mmol), hydrazine monohydrate (52.0 mmol), MoS_2 (0.28 g 0.1 mmol) and toluene (30.0 mL) were added into flask. After the tube closed, the reaction was kept at 60 °C for 12 h with continuously stirring. After the reaction was completed, The MoS_2 catalyst was filtrated off and washed with ethanol (3×2.0 mL). The organic layer was dried over anhydrous sodium sulphate, concentrated and subjected for column chromatography (ethyl acetate/hexane = 8:1 to 4:1) to obtain corresponding pure substituted **2** as a yellowish oil. (1.8 g, 87%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 - 7.18 (m, 1H, ArH), 6.95 - 6.91 (m, 1H, ArH), 6.79 - 6.69 (m, 2H, Ar), 6.66 - 6.64 (m, 1H, -CH=CH_2), 5.80 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.31 (dd, J = 2.5 Hz 1H, -CH=CH_2), 3.68 (br, 1H, NH_2). ^{13}C NMR (125 MHz, $CDCl_3$), δ 146.67, 138.69, 127.10, 129.49, 116.92, 114.86, 113.71. 112.79.

Synthesis of ***3***[2]: Substituted aniline **2** (50 mmol) was dissolved in the 50 mL HCl (18%, aqueous) in the ice bath. $NaNO_2$ (50 mmol) dissolved in 50 mL water was added dropwise. The reaction mixture was stirred for 1 h to obtain a clear solution. Then the solution of $SnCl_2$(0.1 mol) in 30 mL of concentrated HCl was added dropwise at 0 °C. The mixture was stirred at room temperature for 2 h. After wards, the mixture was extracted with 50 mL EtOAc (EA) and the organic impurities were discarded. Then the solution was basified with NaOH (40%, aqueous) until it reached about pH 7.0. The reaction mass was extracted with EtOAc three times. Finally, substituted **3** was afforded after being vapored under reduced pressure in 70% yield. ^{1}H NMR (500 MHz, DMSO) δ 7.11 - 7.07 (m, 1H, ArH), 6.84 - 6.92 (br, 1H, NH), 6.75 - 6.67 (m, 3H, Ar), 6.63 (t, J = 2.5 Hz 1H, -CH=CH_2), 5.73 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.71 (dd, J = 2.5 Hz 1H, -CH=CH_2), 3.95 (br, 1H, NH_2). ^{13}C NMR (125 MHz, DMSO), δ 153.31, 137.59, 128.75, 115.21, 113.17, 111.67, 108.82.

Synthesis of ***4***[3] : 4-Methylbenzenesulfonic acid (0.1 eq) was added to a mixture of diphenylmethanone (1.82 g 10 mmol) and Compound **3** (2.98 g 10 mmol) in ethanol (40 mL). Stir the reaction mixture under reflux for overnight. After completion of the reaction, the solvent was removed, the residue was purified by silica gel chromatography (PE) to obtain corresponding pure substituted **4** as a yellowish oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 - 7.76 (m, 6H, Ar), 7.47 - 7.34 (m, 6H, Ar), 7.17 - 7.16 (m, 2H, Ar), 6.83 (t, J = 7.5 Hz 1H, -CH=CH_2), 5.88 (dd, J = 3.75 Hz 1H, -CH=CH_2), 5.37 (dd, J = 2.5 Hz 1H, -CH=CH_2). ^{13}C NMR (125 MHz, $CDCl_3$), δ 144.93, 144.43, 138.72, 138.45, 137.17, 132.88, 129.82, 129.47, 129.38, 129.26, 128.31, 128.17, 126.63, 118.36, 113.96, 112.71, 110.74. HRMS (ESI) Calcd. for $C_{21}H_{19}N_2$: [M+H]+, 299.1543. Found: m/z 299.1542.

Compound **5,** Compound **6,** Compound **7,** Compound **8**, and Compound **9** were prepared according to the reported literatures[4-7] and the structures were confirmed by ^{1}H NMR.

Compound **5**[4]: Compound **5** as colorless liquid, yield = 90.5%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.89 (t, J = 2.5 Hz 2H, OCH_2), 3.39 (t, J = 3.75 Hz 2H, $BrCH_2$), 0.9 (s, 9H, $C(CH_3)_3$), 0.09 (s, 6H, $Si(CH_3)_2$), ^{13}C NMR (125 MHz, $CDCl_3$), δ 63.67, 33.41, 25.97, 18.47, -5.13.

Compound **6**[4]: Compound **6** as colorless liquid, yield = 92.1%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.60 (t, J = 2.5 Hz 2H, OCH_2), 3.40 (t, J = 3.75 Hz 2H, $BrCH_2$), 1.89 - 1.83 (m, 2H, $BrCH_2CH_2$), 1.55 - 1.49 (m, 2H, $BrCH_2CH_2CH_2CH_2CH_2CH_2O$), 1.47 - 1.41 (m, 2H, $BrCH_2CH_2CH_2CH_2CH_2CH_2O$), 1.38 - 1.32 (m, 2H, $BrCH_2CH_2CH_2CH_2CH_2CH_2O$), 0.89 (s, 9H, $C(CH_3)_3$), 0.04 (s, 6H, $Si(CH_3)_2$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 63.00, 33.82, 32.82, 32.61, 27.98, 25.97, 25.03, 18.35, -5.28.

Compound **7**[5]: Compound **7** as colorless liquid, yield = 68.2%, ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.97 - 3.89 (m, 4H, OCH_2), 3.46 - 3.42 (m, 2H, $BrCH_2$), 2.05 - 2.02 (m, 2H, $BrCH_2CH_2CH_2CH_2$), 1.99 - 1.93 (m, 2H, $BrCH_2CH_2$), 1.80 - 1.73 (m, 2H, $BrCH_2CH_2CH2$), 1.59 - 1.51 (m, 2H, CH), 1.34 - 1.28 (m, 16H, $CH(CH_2CH_2CH_2CH_3)(CH_2CH_3)$), 0.92 - 0.88 (m, 12H, $CH(CH_2CH_2CH_2CH_3)(CH_2CH_3)$). ^{13}C NMR (100 MHz, $CDCl_3$), δ 67.79, 67.72, 40.37, 40.31, 33.31, 33.15, 32.81, 32.57, 31.99, 31.06, 30.09, 29.00, 25.27, 23.87, 23.47, 23.44, 23.10, 21.44, 21.39, 14.15, 11.05.

Compound **8**[6]: Compound **8** as colorless liquid, yield = 68.2%, ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.71 (t, J = 3.75 Hz 2H, $BrCH_2CH_2$), 3.59 - 3.53 (m, 6H, $BrCH_2CH_2OCH_2CH_2OCH_2CH_2OCH_2CH_3$), 3.48 (dd,

J = 1.25 Hz 2H, $BrCH_2CH_2OCH_2CH_2OCH_2\underline{CH_2}OCH_2CH_3$), 3.42 (q, *J* = 1.25 Hz 2H, $Br\underline{CH_2}CH_2OCH_2CH_2OCH_2CH_2O\underline{CH_2}CH_3$), 3.37 (t, *J* = 2.5 Hz 2H, $OCH_2\underline{CH_3}$). ^{13}C NMR (125 MHz, $CDCl_3$), *δ* 71.13, 70.66, 70.54, 70.46, 69.75, 66.51, 30.28, 15.11.

Compound **9**[7]: Compound **9** as white solid, yield = 77.4%, ^{1}H NMR (500 MHz, $CDCl_3$), *δ* 3.19 - 3.16 (m, 2H, ICH_2), 1.97 - 1.94 (m, 3H, $\underline{CH}$ $(CH_2)_3$, 1.81 - 1.77 (m, 2H, $ICH_2\underline{CH_2}$), 1.72 - 1.68 (m, 3H, $CH\underline{CH_2}CH$), 1.64 - 1.60 (m, 3H, $CH\underline{CH_2}CH$), 1.50 - 1.49 (m, 6H, $C\underline{CH_2}CH$). ^{13}C NMR (125 MHz, $CDCl_3$), *δ* 49.90, 41.85, 41.84, 37.02, 35.38, 28.53, 1.13.

General Procedures for Preparation of **MX-P**. The mixture of **4** (2.98 g 10 mmol) and NaH (1.5 eq) in DMF (40 mL) was stirred vigorously, and the temperature was maintained at 0 ºC by adding ice. The RBr or RI (15 mmol) in DMF (15 mL) was added drop by drop to the reaction mixture stirring overnight at 25 °C. After quenching of the reaction by the addition of water, it was extracted with EA. The combined organic phase was then washed with brine, dried over Na_2SO_4, and evaporated to dryness to give a crude product. This material was further purified by silica gel column chromatography.

M1-P: **M1-P** as yellow oil, yield = 52.7%. ^{1}H NMR (500 MHz, $CDCl_3$), *δ* 7.72 - 7.71 (m, 2H，ArH), 7.51 - 7.40 (m, 8H，ArH), 7.32 (t, *J* = 3.75 Hz 1H，ArH), 7.27 (t, *J* = 1.25 Hz 1H, ArH), 7.16 - 7.14 (m, 2H, ArH), 6.80 (dd, *J* = 2.5 Hz 1H, -$\underline{CH}$=CH_2), 5.82 (dd, *J* = 3.75 Hz 1H, -CH=$\underline{CH_2}$), 5.30 (dd, *J* =2.5 Hz 1H, -CH=$\underline{CH_2}$), 2.98 (s, 3H, CH_3).^{13}C NMR (125 MHz, $CDCl_3$), *δ* 156.76, 150.65, 139.56, 138.29, 137.60, 137.37, 129.32, 129.25, 129.07, 128.78, 128.59, 128.39, 128.18, 117.77, 114.23, 113.67, 112.63, 41.62. HRMS (ESI) Calcd. for $C_{22}H_{20}N_2$: [M+H]+, 321.1621. Found: m/z 321.1625.

M2-P: **M2-P** as yellow oil, yield = 92.8%, ^{1} H NMR (500 MHz, $CDCl_3$) , *δ* 7.75 - 7.74 (m, 2H, ArH), 7.50 - 7.42 (m, 6H, ArH), 7.38 - 7.36 (m, 2H, ArH), 7.28 - 7.25 (m, 1H, ArH), 7.17 - 7.16 (br, 1H, ArH), 7.05 - 7.02 (m, 2H, ArH), 6.77 (dd, *J* = 2.5 Hz 1H, -$\underline{CH}$=CH_2), 5. 80 (d, *J* = 5 Hz 1H, -CH=$\underline{CH_2}$), 5.29 (dd, *J* = 2.5 Hz 1H, -CH=$\underline{CH_2}$), 3.46 (t, *J* = 3.75 Hz 2H, N$\underline{CH_2}CH_2$-), 1.59 - 1.53 (m, 2H, $NCH_2\underline{CH_2}$-), 1.42 - 1.41 (m, 10H, -$\underline{(CH_2)_5}$-CH_3), 1.00 - 0.97 (m, 3H, CH_3). ^{13}C NMR (125MHz, $CDCl_3$), *δ* 160.05, 150.64, 139.35, 138.14, 137.50, 137.21, 129.42, 128.90, 128.80, 128.60, 128.35, 128.28, 128.17, 118.32, 116.67, 115.23, 113.49, 54.84, 31.90, 29.40, 29.34, 27.11, 26.50, 22.74, 14.22. HRMS (ESI) Calcd. for $C_{29}H_{32}N_2$: [M+H]+, 411.2795. Found: m/z 411.2795.

M3-P: **M3-P** as yellow oil, yield = 86.4%. ^{1} H NMR (500 MHz, $CDCl_3$), *δ* 7.73 - 7.66 (m, 2H, ArH), 7.48 - 7.29 (m, 8H, ArH), 7.17 (t, *J* = 3.75 Hz 1H, ArH), 7.09 (t, *J* = 1.25 Hz 1H, ArH), 6.98 - 6.95 (m, 2H, ArH), 6.68 (dd, *J* = 2.5 Hz 1H, -$\underline{CH}$=CH_2), 5.72 (dd, *J* = 1.25 Hz 1H, -CH=$\underline{CH_2}$), 5.22 (dd, *J* = 1.25 Hz 1H, -CH=$\underline{CH_2}$), 3.73 - 3.57 (m, 4H, N$\underline{CH_2}\underline{CH_2}$), 0.92 (s, 9H, -C$\underline{(CH_3)_3}$), 0.06 (s, 6H, -Si$\underline{(CH_3)_2}$). ^{13}C NMR (125 MHz, $CDCl_3$), *δ* 161.87, 150.41, 139.07, 138.06, 137.41, 136.73, 129.68, 128.90, 128.84, 128.75, 128.42, 128.31, 128.21, 118.54, 116.75, 115.12, 113.54, 60.16, 57.80, 26.03, 18.37, -5.18. HRMS (ESI) Calcd. for $C_{29}H_{37}ON_2Si$: [M+H]+, 457.2670. Found: m/z 457.2672.

M4-P: **M4-P** as yellow oil, yield = 88.7%. ^{1} H NMR (500 MHz, $CDCl_3$), *δ* 7.68 - 7.66 (m, 2H, ArH), 7.44 - 7.34 (m, 6H, ArH), 7.30 - 7.28 (m, 2H, ArH),7.19 (t, *J* = 3.75 Hz 2H, ArH), 7.08 (t, *J* = 1.25 Hz 1H, ArH), 6.98 - 7.93(m, 2H, ArH), 6.70 (dd, *J* = 2.5 Hz 1H, -$\underline{CH}$=CH_2), 5.72 (dd, *J* = 3.75 Hz 1H, -CH=$\underline{CH_2}$), 5.22 (dd, *J* = 2.5 Hz 1H, -CH=$\underline{CH_2}$), 3.60 (t, *J* = 2.5 Hz 2H, -$\underline{CH_2}$O),3.40 - 3.37 (m, 2H, -

N$\underline{CH_2}$), 1.53 - 1.46 (m, 4H, NCH$_2\underline{CH_2}$CH$_2$CH$_2\underline{CH_2}$CH$_2$O), 1.31 - 1.14 (m, 4H, NCH$_2$CH$_2\underline{CH_2}\underline{CH_2}CH_2CH_2$O), 0.93 (s, 3H, -C$\underline{(CH_3)_3}$), 0.08 (s, 6H, -Si$\underline{(CH_3)_2}$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 160.30, 150.64, 139.30, 138.16, 137.50, 137.19, 129.48, 128.92, 128.81, 128.63, 128.36, 128.30, 128.19, 118.37, 116.72, 115.29, 113.53, 63.26, 54.90, 32.92, 26.98, 26.59, 26.12, 25.70, 18.48, -5.12, -5.13. HRMS (ESI) Calcd. for $C_{33}H_{45}ON_2Si$: [M+H]+, 513.3296. Found: m/z 513.3301.

M5-P: **M5-P** as orange yellow oil, yield = 72.1%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.64 (dd, J = 6.9 Hz 2H, ArH), 7.43 - 7.31 (m, 6H, ArH), 7.25 - 7.23 (m, 2H, ArH), 7.15 (t, J = 3.75 Hz 1H, ArH), 7.02 - 6.88 (m, 3H, ArH), 6.65 (dd, J = 2.5 Hz 1H, -$\underline{CH}$=CH$_2$), 5.68 (d, J = 5 Hz 1H, -CH=$\underline{CH_2}$), 5.20 (d, J = 2.5Hz 1H, -CH=$\underline{CH_2}$), 3.95 - 3.89 (m, 4H, OCH$_2$), 3.39 (t, J = 3.75 Hz 2H, NCH$_2$), 1.62 - 1.50 (m, 6H, NCH$_2\underline{CH_2}$CH$_2\underline{CH_2}$), 1.36 - 1.30 (m, 18H, -CH and -$\underline{CH_2}$CH$_2\underline{CH_2}$CH$_3$ and -$\underline{CH_2}$CH$_3$), 0.95 - 0.89 (m, 18H, -CH$_2$CH$_2$CH$_2\underline{CH_3}$ and -CH$_2\underline{CH_3}$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 160.57, 150.60, 138.99, 138.10, 137.23, 136.95, 129.49, 128.83, 128.65, 128.52, 128.23, 128.19, 128.11, 118.74, 117.26, 115.85, 113.53, 67.60, 67.57, 67.54, 67.52, 65.17, 54.97, 42.00, 40.24, 40.19, 30.18, 30.00, 29.96, 29.16, 28.91, 28.88, 27.80, 27.67, 25.81, 24.69, 23.39, 23.34, 23.32, 23.30, 23.13, 23.00, 20.24, 20.20, 14.07, 14.06, 10.94. HRMS (ESI) Calcd. for $C_{41}H_{60}O_3N_2P$: [M+H]+, 659.4336. Found: m/z 659.4339.

M6-P: **M6-P** as yellow oil, yield = 95.6%. ^{1} H NMR (500 MHz, $CDCl_3$), δ 7.68 - 7.66 (m, 2H, ArH), 7.45 - 7.42 (m, 1H, ArH), 7.68 - 7.66 (m, 2H, ArH),7.40 - 7.36 (m, 2H, ArH), 7.36 - 7.32 (m, 3H, ArH), 7.28 - 7.26 (m, 2H, ArH), 7.16 (t, J = 3.75 Hz 1H, ArH), 7.04 (t, J = 1.25 Hz 1H, ArH), 6.96 - 6.92 (m, 2H, ArH), 6.66 (dd, J = 2.5 Hz 1H, -$\underline{CH}$=CH$_2$), 5.59 (dd, J = 3.75 Hz 1H, -CH=$\underline{CH_2}$), 5.21 (dd, J = 2.5 Hz 1H, -CH=$\underline{CH_2}$), 3.63 (t, J = 3.75 Hz 2H, NCH$_2\underline{CH_2}$-), 3.41 (t, J = 3.75 Hz 2H, N$\underline{CH_2}$CH$_2$-). 3.30 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 150.52, 138.96, 138.16, 137.35, 136.75, 129.79, 128.93, 128.84, 128.74, 128.45, 128.33, 128.25, 118.80, 116.96, 115.45, 113.67, 69.55, 58.92, 55.24. HRMS (ESI) Calcd. for $C_{24}H_{25}ON_2$: [M+H]+, 357.1961. Found: m/z 357.1960.

M7-P: **M7-P** as yellow oil, yield = 93.1%. ^{1} H NMR (500 MHz, $CDCl_3$), δ 7.67 - 7.65 (m, 2H, ArH), 7.45 - 7.40 (m, 1H, ArH), 7.39 - 7.37 (m, 2H, ArH),7.36 - 7.34 (m, 2H, ArH), 7.34 - 7.31 (m, 3H, ArH), 7.15 (t, J = 3.75 Hz 1H, ArH), 7.05 (t, J = 1.25 Hz 1H, ArH), 6.95 - 6.92 (m, 2H, ArH), 6.65 (dd, J = 2.5 Hz 1H, -$\underline{CH}$=CH$_2$), 5.69 (dd, J = 2.5 Hz 1H, -CH=$\underline{CH_2}$), 5.20 (dd, J = 2.5 Hz 1H, -CH=$\underline{CH_2}$), 3.66 (t, J = 2.5 Hz 2H, NCH$_2\underline{CH_2}$-), 3.53 - 3.48 (m, 6H, N$\underline{CH_2}$CH$_2$- and -O$\underline{CH_2}\underline{CH_2}$O-). 3.37 (s, 3H, CH$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 162.64, 150.44, 138.90, 138.11, 137.33, 136.67, 129.78, 128.88, 128.85, 128.73, 128.56, 128.44, 128.29, 128.21, 127.14, 126.64, 118.69, 116.87, 115.32, 113.62, 71.97, 70.43, 68.09, 59.15, 55.16. HRMS (ESI) Calcd. for $C_{26}H_{29}O_2N_2$: [M+H]+, 401.2224 Found: m/z 401.2224.

M8-P: **M8-P** as yellow oil, yield = 94.3%. ^{1} H NMR (500 MHz, $CDCl_3$), δ 7.65 - 7.63 (m, 2H, ArH), 7.43 - 7.40 (m, 1H, ArH), 7.37 - 7.36 (m, 2H, ArH),7.35 - 7.30 (m, 3H, ArH), 7.26 - 7.24 (m, 2H, ArH), 7.13 (t, J = 3.75 Hz 1H, ArH), 7.03 (m, 1H, ArH), 6.93 - 6.90 (m, 2H, ArH), 6.63 (dd, J = 2.5 Hz 1H, -$\underline{CH}$=CH$_2$), 5.67 (dd, J = 5 Hz 1H, -CH=$\underline{CH_2}$), 5.18 (dd, J = 2.5 Hz 1H, -CH=$\underline{CH_2}$), 3.64 - 3.47 (m, 14H, -CH$_2$), 1.21 (t, J = 3.75 Hz 3H, CH$_3$). ^{13}C NMR (125 MHz, $CDCl_3$), δ 162.42, 150.47, 138.93, 138.09, 137.34, 136.70, 129.75, 128.86, 128.84, 128.72, 128.42, 128.30, 128.21, 118.68, 116.90, 115.36, 113.61, 70.80, 70.65, 70.58, 69.91, 68.12, 66.72, 55.17, 15.26. HRMS (ESI) Calcd. for $C_{29}H_{35}O_3N_2$: [M+H]+, 459.2642. Found: m/z 459.2641.

M9-P: **M9-P** as orange yellow needle-like solid, yield = 69.5%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.67 - 7.65 (m, 2H, ArH), 7.44 - 7.36 (m, 8H, ArH), 7.22 (t, J = 3.75 Hz 1H, ArH), 7.10 (t, J = 2.5 Hz 1H, ArH), 6.98 - 6.96 (m, 2H, ArH), 6.71 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.73 (dd, J = 3.75 Hz 1H, -CH=CH_2), 5.22 (dd, J = 2.5 Hz 1H, -CH=CH_2), 3.44 - 3.31 (m, 2H, NCH_2), 1.92 - 1.91 (m, 3H, -CH$(CH_2)_3$), 1.71 - 1.68 (m, 3H, -CHCH_2CH-), 1.61 - 1.58 (m, 3H, -CHCH_2CH-), 1.40-1.39 (m, 6H, CCH_2CH-), 1.26 - 1.13 (m, 2H, -NCH_2CH_2). ^{13}C NMR (125 MHz, $CDCl_3$), δ 160.68, 150.32, 139.33, 138.18, 137.61, 137.15, 129.53, 128.97, 128.87, 128.77, 128.51, 128.36, 128.19, 118.13, 116.20, 114.57, 113.47, 48.51, 42.30, 39.28, 37.20, 31.85, 28.70, 28.68. HRMS (ESI) Calcd. for $C_{33}H_{37}N_2$: [M+H]+, 461.2951. Found: m/z 461.2947.

*General Procedures for Preparation of **MX***. The mixture of **MX-P** (10 mmol) and THF (50 mL) was stirred vigorously, then the 5N HCl (5.0 mL) was added drop by drop to the reaction mixture stirring overnight at 50 °C. Then the solution was basified with NaOH (40%, aqueous) until it reached pH > 7.0. The reaction mass was extracted with EA three times. The combined organic phase was then washed with brine, dried over Na_2SO_4, the solvent was removed, the residue was purified by silica gel chromatography to obtain corresponding pure **MX**.

M1: M1 as yellow oil, yield = 62.7%. ^{1}H NMR (500 MHz, DMSO), δ 7.13 (t, J = 5 Hz 1H, ArH), 7.08 - 7.07 (br, 1H, ArH), 6.89 (dd, J = 2.5 Hz 1H, ArH), 6.79 (d, J = 1.25 Hz 2H, ArH), 6.70 - 6.64 (m, 1H, -CH=CH_2), 5.75 (dd, J = 3.75 Hz 1H, -CH=CH_2), 5.20 (dd, J = 2.5 Hz 1H, -CH=CH_2),4.38 (s, 2H, NH_2), 3.03 (s, 3H, CH_3). ^{13}C NMR (125 MHz, DMSO), δ 153.76, 138.12, 137.74, 129.13, 115.51, 113.78, 113.40, 111.44, 44.18. HRMS (ESI) Calcd. for $C_9H_{13}N_2$: [M+H]+, 149.1073. Found: m/z 149.1074.

M2: M2 as yellow oil, yield = 69.4%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.21 (t, J = 3.75 Hz 1H, ArH), 7.04 (t, J = 1.25 Hz 1H, ArH), 6.89 - 6.85 (m, 2H, ArH), 6.70 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.74 (dd, J = 5 Hz 1H, -CH=CH_2), 5.23 (dd, J = 2.5 Hz 1H, -CH=CH_2), 3.39 (t, J = 3.75 Hz 2H, -NCH_2), 1.76 - 1.63 (m, 2H, -NCH_2CH_2), 1.36 - 1.27 (m, 10H, -$(CH_2)_5CH_3$), 0.89, (t, J = 2.5 Hz 3H, -CH_3), ^{13}C NMR (125 MHz, $CDCl_3$), δ 152.04, 138.50, 137.67, 129.28, 116.28, 113.63, 113.04, 111.33, 56.05, 31.97, 29.65, 29.44, 27.21, 25.92, 22.80, 14.24. HRMS (ESI) Calcd. for $C_{16}H_{27}N_2$: [M+H]+, 247.2169. Found: m/z 247.2170.

M3: M3 as yellow oil, yield = 62.4%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.26 (q, J = 1.25 Hz 1H, ArH), 7.04 - 7.00 (m, 1H, ArH), 6.96 (d, J = 1.25 Hz 1H, ArH), 6.88 (dd, J = 1.25 Hz 1H, ArH), 6.72 (dd, J = 2.5 Hz 1H, CH=CH_2), 5.77 (d, J = 5 Hz 1H, CH=CH_2), 5.27 (d, J = 3.75 Hz 1H, CH=CH_2), 3.98 (t, J = 2.5 Hz 2H, CH_2OH), 3.65(s, 2H, NH_2), 3.48 (t, J = 1.25 Hz 2H, NCH_2). ^{13}C NMR (125 MHz, $CDCl_3$), δ 152.78, 139.18, 137.26, 129.19, 117.61, 114.14, 113.22, 111.54, 61.61, 56.64. HRMS (ESI) Calcd. for $C_{10}H_{15}ON_2$: [M+H]+, 179.1179. Found: m/z 179.1180.

M4: M4 as yellow oil, yield = 64.5%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.23 (t, J = 3.75 Hz 1H, ArH), 7.04 (s, 1H, ArH), 6.89 - 6.87 (m, 2H, ArH), 6.72 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.77 (d, J = 3.75 Hz 1H, -CH=CH_2), 5.25 (d, J = 2.5 Hz 1H, -CH=CH_2), 3.65 (t, J = 3.75 Hz 2H, NH_2), 3.41 (t, J = 3.75 Hz 2H, -CH_2OH), 3.00 (s, 2H, NCH_2), 1.71 - 1.42 (m, 8H, -$CH_2CH_2CH_2CH_2CH_2CH_2$OH). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.99, 138.42, 137.57, 129.23, 116.22, 113.62, 112.92, 111.22, 62.79, 55.78, 32.73, 26.88, 25.87, 25.72. HRMS (ESI) Calcd. for $C_{14}H_{23}ON_2$: [M+H]+, 235.1805. Found: m/z 235.1806.

M5: M5 as yellow oil, yield = 48.1%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.17 (t, J = 3.75 Hz 1H, ArH), 6.97 (s, 1H, ArH), 6.85 - 6.81 (m, 2H, ArH), 6.67 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.71 (d, J = 5 Hz 1H, -CH=CH_2), 5.20 (d, J = 2.5 Hz 1H, -CH=CH_2), 3.95 - 3.85 (m, 4H, -OCH_2), 3.37 (t, J = 3.75 Hz 2H, -NCH_2), 1.81 - 1.65 (m, 6H, -$NCH_2CH_2CH_2CH_2$), 1.55 - 1.48 (m, 2H, -OCH_2CH-), 1.40 - 1.27 (m, 16H), 0.87 (t, J = 3.75 Hz 12H). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.98, 138.44, 137.51, 129.22, 116.32, 113.61, 112.85, 111.17, 67.69, 67.67, 67.64, 67.62, 55.16, 40.29, 40.24, 30.01, 28.94, 28.92, 27.07, 26.95, 25.84, 24.72, 23.39, 23.36, 23.04, 20.28, 20.24, 14.10, 10.98. HRMS (ESI) Calcd. for $C_{28}H_{52}O_3N_2P$: [M+H]+, 495.3710. Found: m/z 495.3713.

M6: M6 as yellow oil, yield = 69.7%. ^{1} H NMR (500 MHz, $CDCl_3$), δ 7.21 (t, J = 2.5 Hz 1H, ArH), 7.06 (t, J = 1.25 Hz 1H, ArH), 6.90 - 6.86 (m, 2H, ArH), 6.70 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.74 (dd, J = 5 Hz 1H, -CH=CH_2), 5.22 (dd, J = 3.57 Hz 1H, -CH=CH_2), 3.70 (t, J = 2.5 Hz 2H, -CH_2OCH_3), 3.63 (t, J = 2.5 Hz 2H, -NCH_2CH_2), 3.37 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.72, 137.60, 129.23, 116.30, 113.62, 112.88, 111.26, 70.78, 59.17, 55.40. HRMS (ESI) Calcd. for $C_{11}H_{17}ON_2$: [M+H]+, 193.1335. Found: m/z 193.1337.

M7: M7 as yellow oil, yield = 70.5%. ^{1} H NMR (500 MHz, $CDCl_3$), δ 7.19 (t, J = 3.75 Hz 1H, ArH), 7.06 (t, J = 1.25 Hz 1H, ArH), 6.89 - 6.84 (m, 2H, ArH), 6.68 (dd, J = 3.75 Hz 1H, -CH=CH_2), 5.73 (dd, J = 5 Hz 1H, -CH=CH_2), 5.21 (dd, J = 2.5 Hz 1H, -CH=CH_2), 3.79 (t, J = 2.5 Hz 2H, -NCH_2OCH_2), 3.71 - 3.69 (m, 2H, NH_2),3.65 (t, J = 2.5 Hz 2H, -OCH_2CH_2O), 3.62 - 3.60 (m, 2H, -OCH_2CH_2O), 3.52 - 3.50 (m, 2H, -NCH_2), 3.36 (s, 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.60, 138.35, 137.58, 129.14, 116.13, 113.51, 112.84, 112.81, 111.20, 71.95, 70.53, 69.19, 59.07, 55.24. HRMS (ESI) Calcd. for C16H19O3N4: [M+H]+, 315.1452. Found: m/z 315.1449.

M8: M8 as yellow oil, yield = 73.3%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.17 (t, J = 3.75 Hz 1H, ArH), 7.06 (t, J = 1.25 Hz 1H, ArH), 6.88 - 6.82 (m, 2H, ArH), 6.68 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.72 (dd, J = 5 Hz 1H, -CH=CH_2), 5.20 (dd, J = 2.5 Hz 1H, -CH=CH_2), 3.78 (t, J = 2.5 Hz 2H, -NCH_2OCH_2), 3.64 - 3.59 (m, 8H, O$CH_2CH_2OCH_2CH_2$O),3.57 - 3.55 (m, 2H, -OCH_2CH_3), 3.51 (dd, 2H, -NCH_2CH_2O), 1.20 (t, J = 3.75 Hz 3H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.59, 138.29, 137.58, 129.09, 116.00, 113.42, 112.78, 111.16, 70.67, 70.58, 70.56, 69.84, 69.13, 66.64, 55.16, 15.19. HRMS (ESI) Calcd. for $C_{13}H_{21}O_2N_2$: [M+H]+, 237.1598. Found: m/z 237.1598.

M9: M9 as orange-red liquid, yield = 57.3%. ^{1}H NMR (500 MHz, $CDCl_3$), δ 7.29 (t, J = 3.75 Hz 1H, ArH), 7.09 (t, J = 1.25 Hz 1H, ArH), 6.94 - 6.91 (m, 2H, ArH), 6.79 (dd, J = 2.5 Hz 1H, -CH=CH_2), 5.83 (dd, J = 3.75 Hz 1H, -CH=CH_2), 5.31 (dd, J = 2.5Hz 1H, -CH=CH_2), 3.58 (s, 2H, NH_2), 3.53 - 3.50 (m, 2H, NCH_2), 2.09 - 2.06 (m, 3H, -CH $(CH_2)_3$)), 1.85 - 1.81 (m, 3H, -CHCH_2CH), 1.78 - 1.74 (m, 3H, -CHCH_2CH-), 1.66 - 1.65 (m, 6H, -CCH_2CH), 1.47 - 1.44 (m, 2H, -NCH_2CH_2). ^{13}C NMR (125 MHz, $CDCl_3$), δ 151.58, 138.24, 137.61, 129.10, 115.85, 113.32, 112.78, 111.06, 49.89, 42.41, 38.41, 37.11, 31.67, 28.63. HRMS (ESI) Calcd. for $C_{20}H_{28}N_2$: [M+H]+, 296.2247. Found: m/z 296.2249.

General Procedures for Preparation of ***PX:*** A 10 mL sized screw-cap vial with septum and a magnetic bar were dried in oven for 1 h. Under an atmosphere of nitrogen, and loaded with monomers (0.5 mmol), $[RhCp^*(CH_3CN)_3](SbF_6)_2$ (2.0 mol %), HOAc (1.2 eq) 2 mL of solvent was injected into the test tube via syringe. The reaction mixtures were then stirred for 12 h at 90 °C. When the reaction

reaches the time. The crude residue of polymer was precipitated by hexane at room temperature; collected by centrifugation, washed with hexane, and dried under vacuum to afford polymers. The M_n and M_w/M_n of these polymers were characterized by SEC.

P1. 61.2% yield. SEC: M_n = 10.6 kDa, M_w/M_n = 1.41. Td = 245 °C, Tg = 100 °C. ^{1}H NMR (500 MHz, CD_2Cl_2, 25 °C): δ 7.43 - 7.42 (br, -CH), 7.23 - 7.17 (br, ArH), 7.02 - 6.95 (m, ArH), 6.81 - 6.72 (m, CH-), 4.19 - 3.95 (br, -NH), 2.97 - 2.90 (m, $-CH_3$).

P2. 63.4% yield. SEC: M_n = 17.6 kDa, M_w/M_n = 1.33. Td = 263 °C, Tg = 126 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.44 - 7.42 (m, -CH), 7.12 - 7.07 (br, ArH), 7.02 - 6.97 (m, ArH), 6.91 - 6.73 (m, CH-), 3.79 - 3.76 (m, NH), 3.27 - 3.18 (m, $-CH_2$), 1.48 - 1.28 (m, $-C_6H_{12}$-), 0.93 - 0.89 (m, $-CH_3$).

P3. 74.3% yield. SEC: M_n = 18.4 kDa, M_w/M_n = 1.41. Td = 234 °C, Tg = 107 °C. ^{1}H NMR (500 MHz, CF_3COOD, 25 °C): δ 7.96 - 7.78 (m, -CH and ArH), 7.62 - 7.54 (m, ArH), 7.38 - 7.30 (m, CH-), 4.32 - 4.26 (br, $-NCH_2$), 3.99 - 3.88 (m, $-NCH_2\underline{CH_2}OH$).

P4. 82.9% yield. SEC: M_n = 28.0 kDa, M_w/M_n = 1.39. Td = 249 °C, Tg = 105 °C. ^{1}H NMR (500 MHz, DMF-d_7, 25 °C): δ 7.57 - 7.54 (br, -CH and ArH), 7.11 - 6.91 (m, ArH and CH-), 3.56 - 3.54 (br, $-\underline{CH_2}OH$), 3.30 - 3.28 (br, $-NCH_2$-), 1.79 - 1.72 (m, $-NCH_2\underline{CH_2}$), 1.57 - 1.41 (m, $-NCH_2\underline{CH_2}CH_2\underline{CH_2}\underline{CH_2}CH_2OH$-).

P5. 43.2% yield. SEC: M_n = 8.3 kDa, M_w/M_n = 1.42. Td = 281 °C, Tg = 81 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.40 - 7.34 (br, -CH), 7.13 - 7.07 (m, ArH), 6.98 - 6.91 (br, ArH), 6.76 - 6.69 (br, CH-), 3.96 - 3.88 (br, $-O\underline{CH_2CH}$-), 3.31 - 3.18 (br, $-NCH_2$-), 1.84 - 1.80 (br, $-NCH_2\underline{CH_2}$- and -CH-), 1.54 - 1.19 (br, $-NCH_2CH_2CH_2\underline{CH_2}$-).1.40 - 1.19 (br, $-CH\underline{C_3H_6}$- and $-CH\underline{CH_2}CH_3$-), 0.86 - 0.82 (br, $-CH_3$).

P6. 77.3% yield. SEC: M_n = 13.9 kDa, M_w/M_n = 1.32. Td = 233 °C, Tg = 110 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.47 - 7.37 (br, -CH), 7.18 - 7.12 (br, ArH), 7.01 - 6.98 (m, ArH), 6.81 - 6.78 (m, CH-), 3.73 - 3.67 (m, CH_2), 3.44 - 3.38 (m, CH_2 and CH_3).

P7. 84.7% yield. SEC: M_n = 25.6 kDa, M_w/M_n = 1.51. Td = 255 °C, Tg = 124 °C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.44 - 7.43 (m, -CH), 7.19 - 7.11 (m, ArH), 7.00 - 6.97 (m, ArH), 6.81 - 6.80 (m, CH-), 3.83 - 3.78 (m, $-NCH_2\underline{CH_2}O$-), 3.70 - 3.66 (m, $-O\underline{CH_2}CH_2O$-), 3.58 - 3.54 (m, $-OCH_2\underline{CH_2}O$-), 3.47 - 3.47 (m, $-N\underline{CH_2}$-), 3.35 - 3.32 (m, $-OCH_3$).

P8. 82.1% yield. SEC: M_n = 17.9 kDa, M_w/M_n = 1.57. Td = 257 °C, Tg = 83°C. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.43 - 7.36 (m, -CH), 7.20 - 7.12 (m, ArH), 6.99 - 6.93 (m, ArH), 6.79 - 6.71 (m, CH-), 4.39 - 4.29 (br, -NH), 3.81 - 3.39 (m, $-N\underline{CH_2CH_2}O\underline{CH_2CH_2}O\underline{CH_2CH_2}O\underline{CH_2}$-), 1.12 - 1.15 (m, $-OCH_3$).

P9. 57.8% yield. SEC: M_n = 11.3 kDa, M_w/M_n = 1.27. Td = 275 °C, Tg = 123°C.^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ 7.41 - 7.35 (m, -CH), 7.13 - 7.05 (m, ArH), 7.00 - 6.93 (m, ArH), 6.77 - 6.68 (m, CH-), 3.88 - 3.62 (br, -NH), 3.24 - 3.15 (m, $-NCH_2$), 1.99 (br, $-\underline{CH}(CH_2)_3$), 1.75 - 1.73 (m, $-CH\underline{CH_2}CH$-), 1.69 - 1.67 (m, $-CH\underline{CH_2}CH$-), 1.61 - 1.58 (br, $-C\underline{CH_2}CH$-), 1.52 - 1.47 (m, $-NCH_2\underline{CH_2}$-).

References

(1) H, Lei.; P, Luo.; M, Xiong.; R, Chen.; Y, Wang.; W, Xing.; J. Huang.; Selective Reduction of Nitroarenes with Molybdenum Disulfide. *Chin. J. Chem.* **2013**, *31*, 987 - 991.

(2) X, Wang; Y.-F., ioo Chen.; Yan, W.; L.-L.; Cao.; Y.-H. Ye. Synthesis and Biological Evaluation of Benzimidazole Phenylhydrazone Derivatives as Antifungal Agents against Phytopathogenic Fungi. *Molecules* **2016**, *21*, 1574 - 1588.

(3) Mo, Zhang.; Z.-Re., Shang.; X.-T., Li.; J.-N., Zhang.; Y, Wang.; K, Li.; Y.-Y., Li.; Z.-H., Zhang. Simple and efficient approach for synthesis of hydrazones from carbonyl compounds and hydrazides catalyzed by meglumine. *Synthetic Communications.* **2017**, *47*, 1532 - 2432.

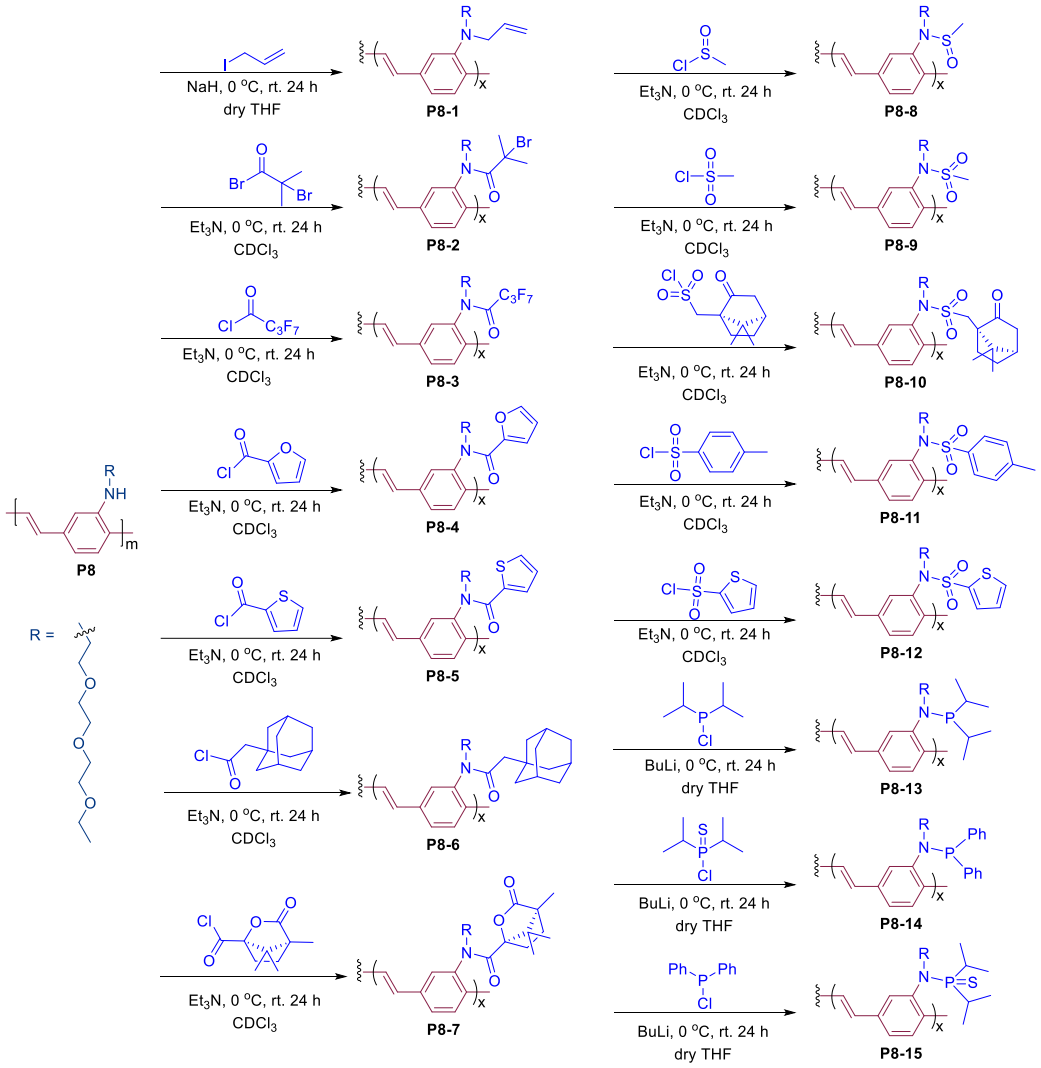
(4) S.-I, Kuwabe.; K. E., Torraca.; S. L., Buchwald. PalladiumCatalyzed Intramolecular C-O Bond Formation. *J. Am. Chem. Soc.* **2001**, *123*, 12202 - 12206.

(5) S.-H, Kang.; D, Lee.; H, Kim.; W, Choi.; J, Oh.; J. H., Oh.; C, Yang. Effects of the Polarity and Bulkiness of End-Functionalized Side Chains on the Charge Transport of Dicyanovinyl-End-Capped Diketopyrrolopyrrole-Based *n*-Type Small Molecules. *ACS Appl. Mater. Interfaces* **2021**, *13*, 52840 - 52849.

(6) X, Zhao.; G, Xue.; G, Qu.; V, Singhania.; Y, Zhao.; K, Butrouna.; A, Gumyusenge.; Y, Diao.; K. R., Graham; H, Li.; J. Mei. Complementary Semiconducting Polymer Blends: Influence of Side Chains of Matrix Polymers. *Macromolecules* **2017**, *50*, 6202 - 6209.

(7) Y, Naeem.; M, Doré.; C, Joud.; M, Visser.; C, Springer.; X, Xie.; K, Herlihy.; D, Porter.; B. B., Touré. Lipophilic Isosteres of a π–π Stacking Interaction: New Inhibitors of the Bcl-2-Bak Protein–Protein Interaction. *ACS Medicinal Chemistry Letters* **2012**, *3*, 579 - 583.

Scheme S2. Reaction conditions for different post-functionalization of P8.



*General Procedures for Preparation of post-functionalization of **P8***: Add different bases (10 equiv, 5 mmol, equivalent to repeat unit) to a stirred solution of **P8** (150 mg, 0.5 mmol) in $CDCl_3$ or THF (5 mL) at 0 °C. Stir the mixture for 30 minutes. Add modified unit (5.0 equiv, 2.5 mmol) dropwise to the mixture. Stir the reaction mixture at room temperature for 24 h. Add a large amount of saturated aqueous ammonium chloride solution, extracted with DCM, the combined organic phase was then washed with brine, dried over Na_2SO_4, and evaporated to dryness, and finally add appropriate $CHCl_3$ to dissolve and precipitate with n-hexane, and dried under vacuum to afford target polymer.

4. Figure S1-S74 Characterization data for monomers and polymers

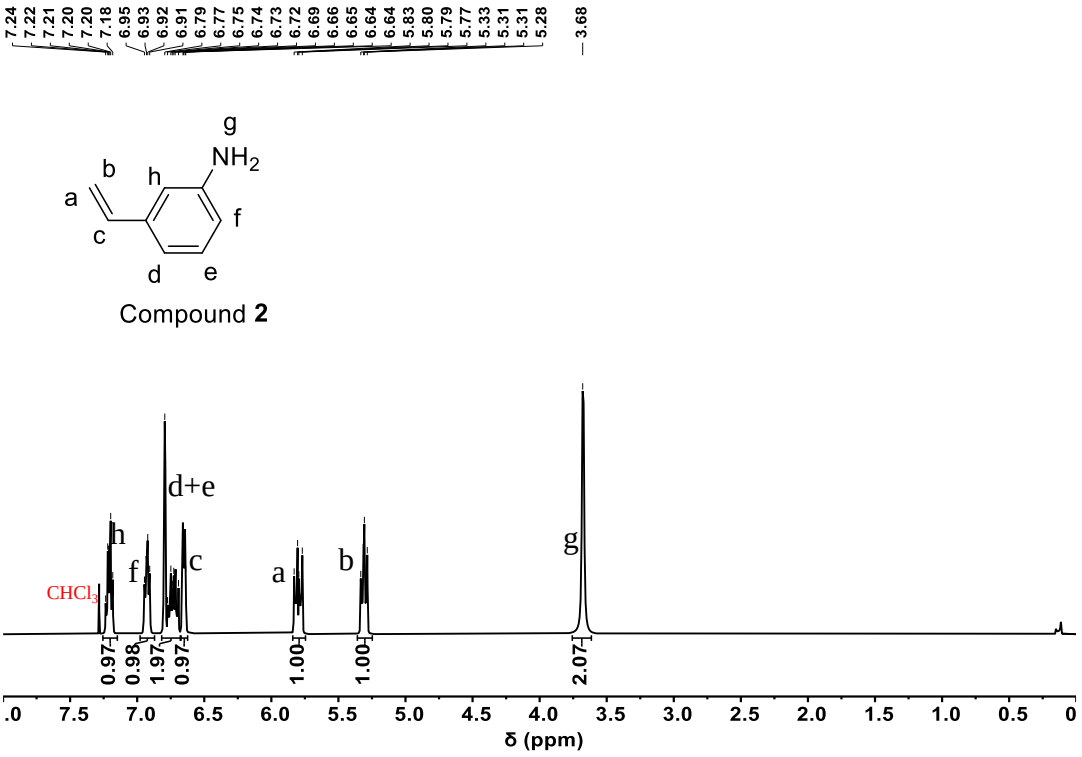


Figure S1. ^{1}H NMR (500 MHz) spectrum of Compound **2** measured in $CDCl_3$ at 25 °C.

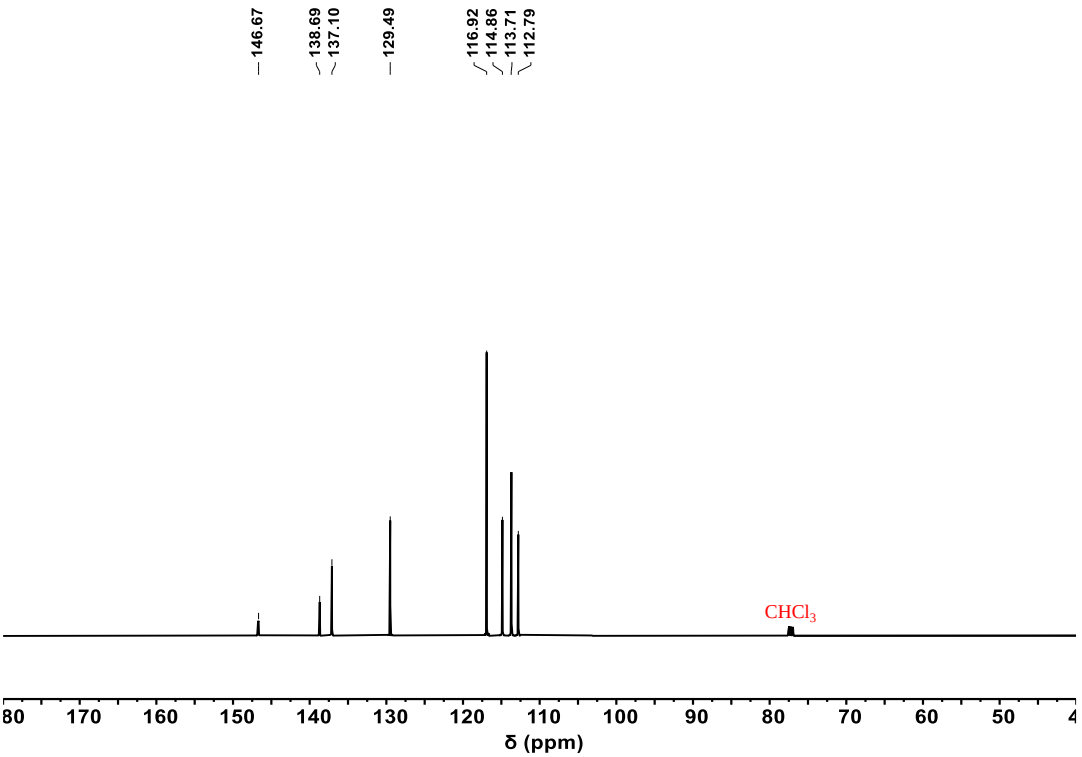


Figure S2. ^{13}C NMR (125 MHz) spectrum of Compound **2** measured in $CDCl_3$ at 25 °C.

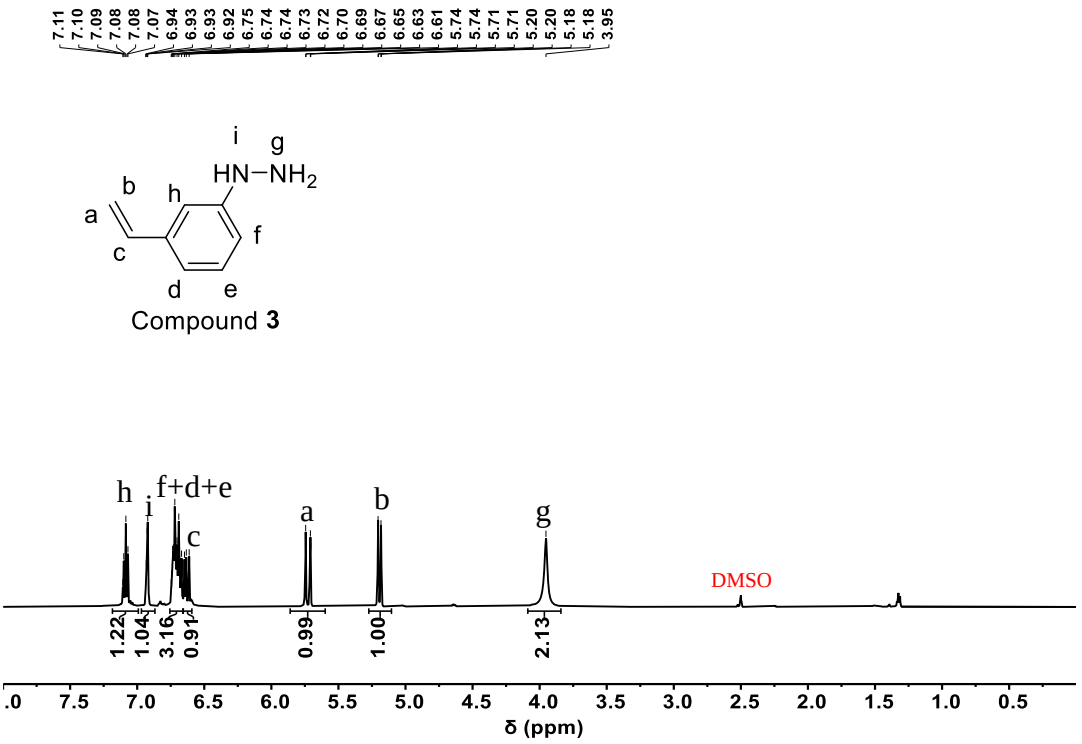


Figure S3. [1]H NMR (500 MHz) spectrum of Compound **3** measured in DMSO at 25 °C

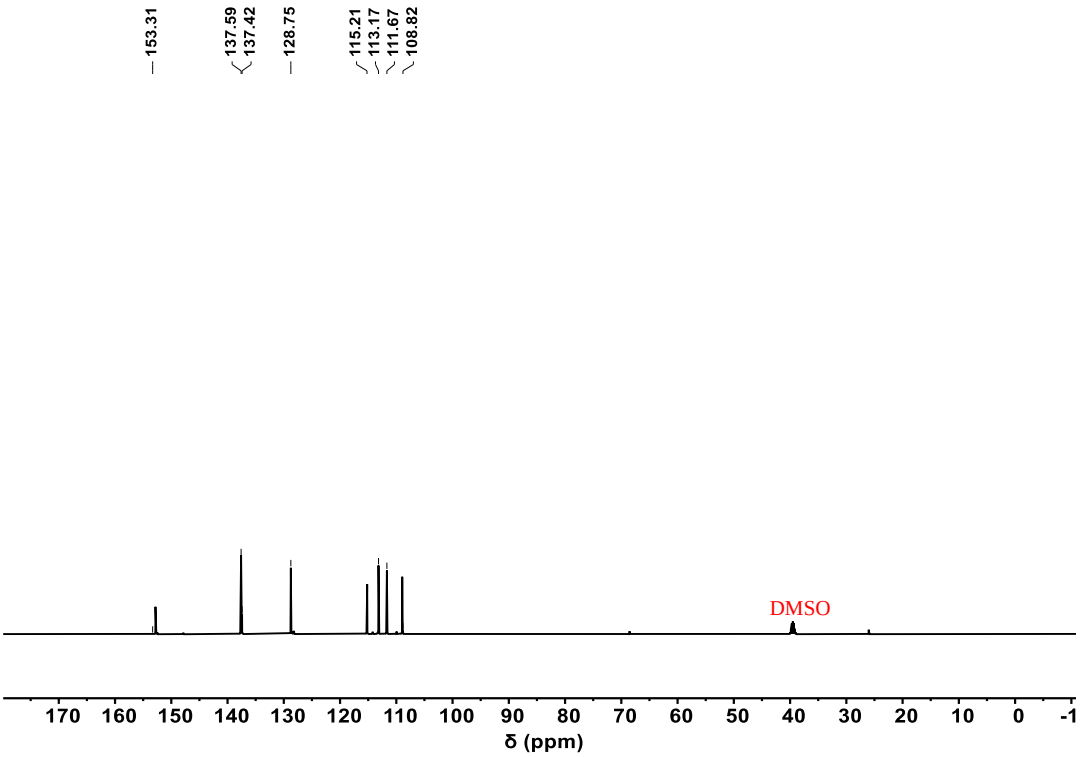


Figure S4. [13]C NMR (125 MHz) spectrum of Compound **3** measured in DMSO at 25 °C.

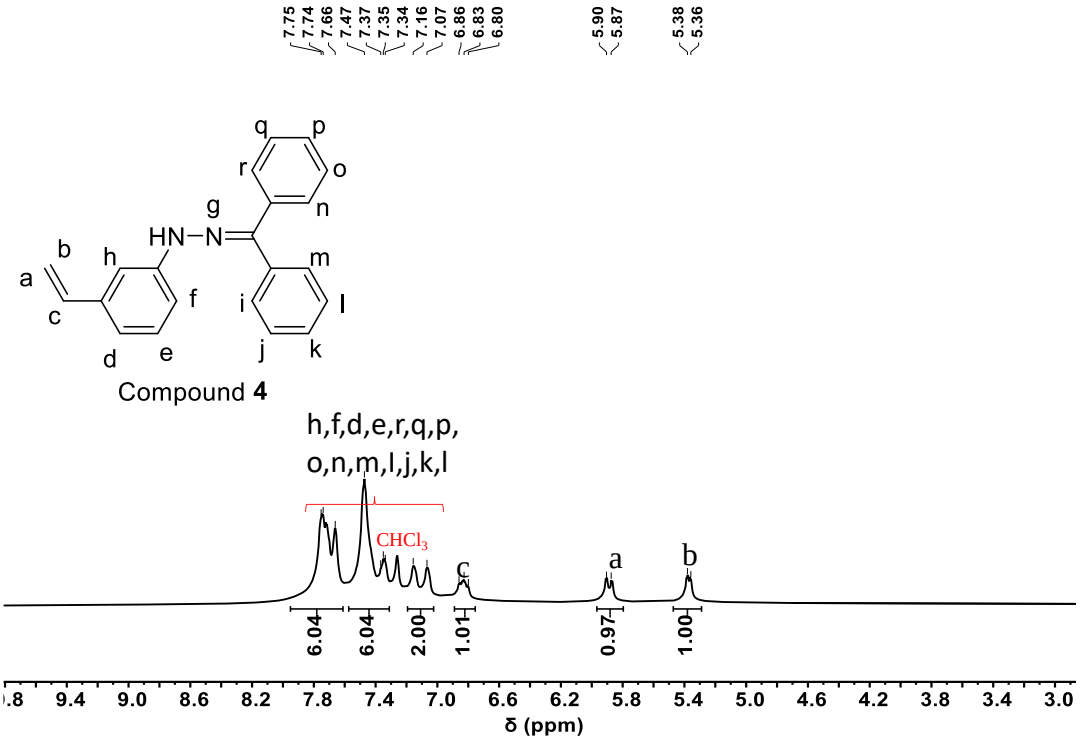


Figure S5. ^{1}H NMR (500 MHz) spectrum of Compound **4** measured in $CDCl_3$ at 25 °C.

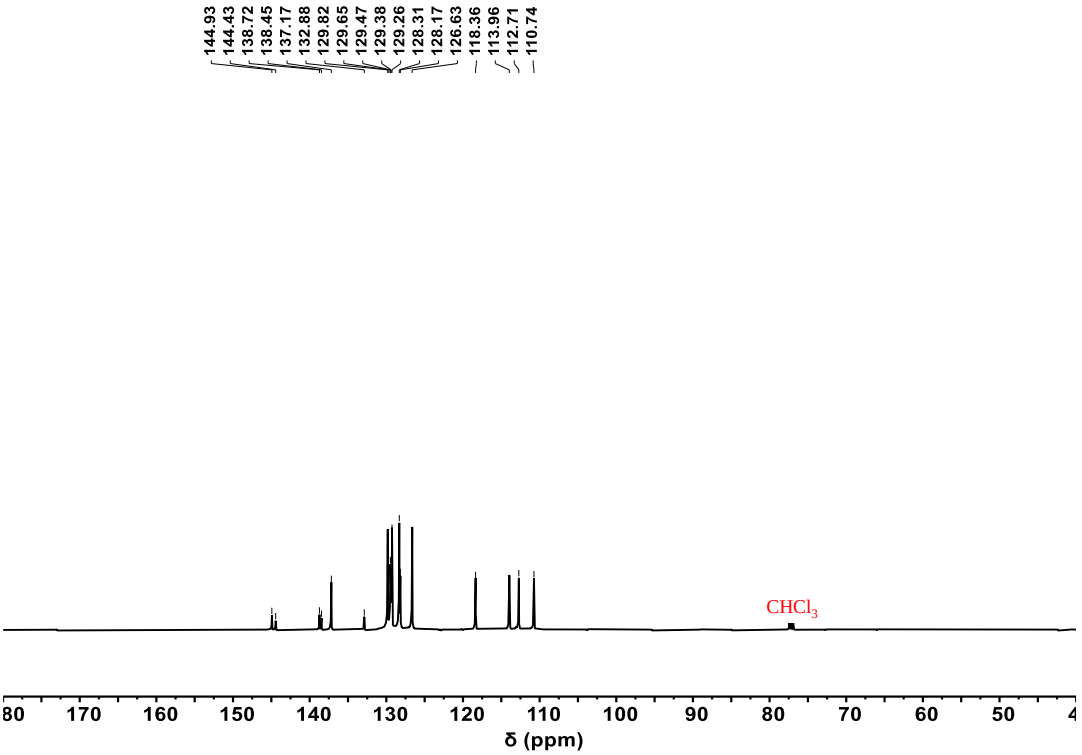


Figure S6. ^{13}C NMR (125 MHz) spectrum of Compound **4** measured in $CDCl_3$ at 25 °C.

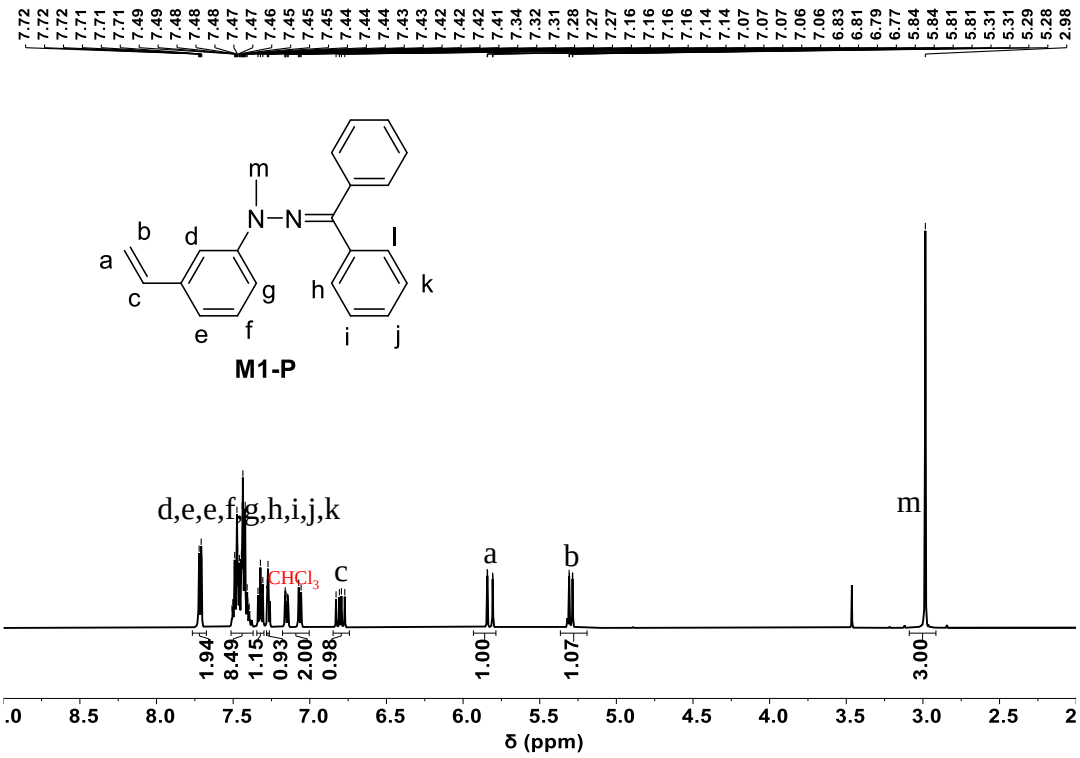


Figure S7. ^{1}H NMR (500 MHz) spectrum of Compound **M1-P** measured in $CDCl_3$ at 25 °C.

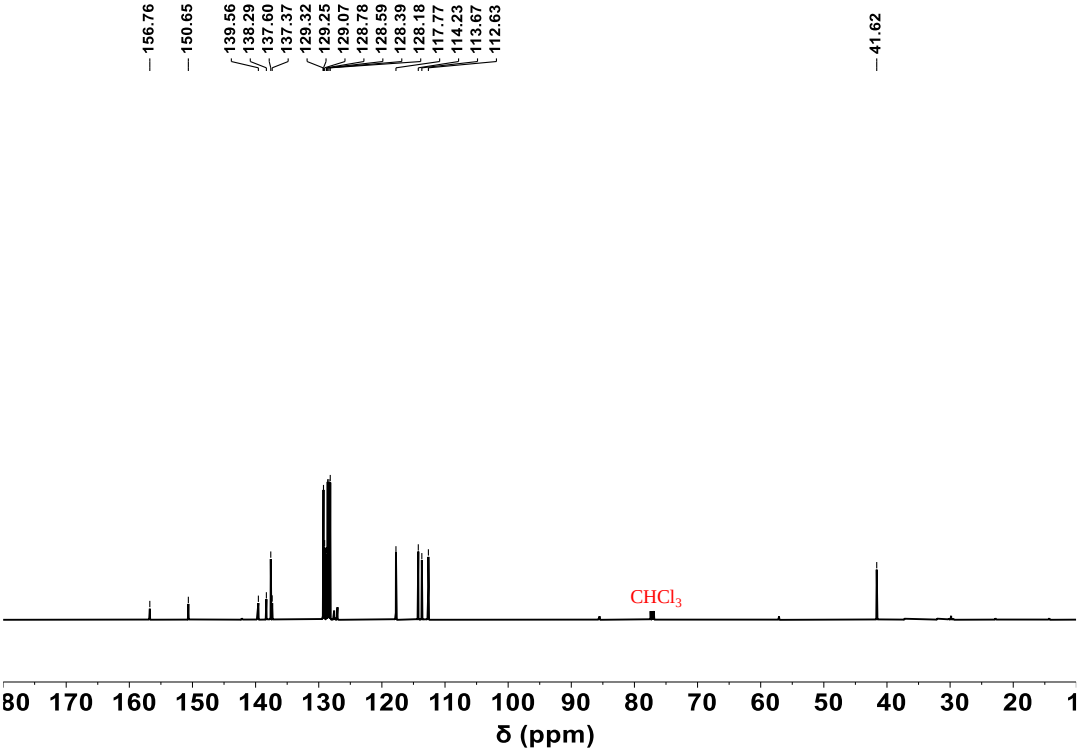


Figure S8. ^{13}C NMR (125 MHz) spectrum of Compound **M1-P** measured in $CDCl_3$ at 25 °C.

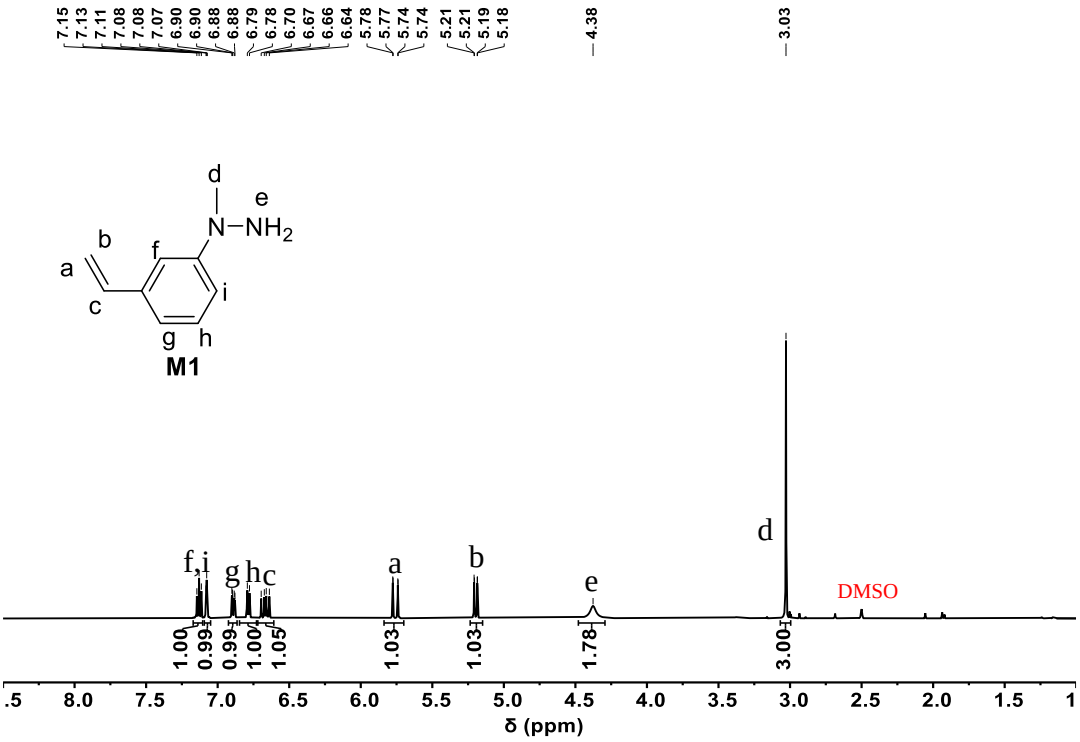


Figure S9. [1]H NMR (500 MHz) spectrum of **M1** measured in DMSO at 25 °C.

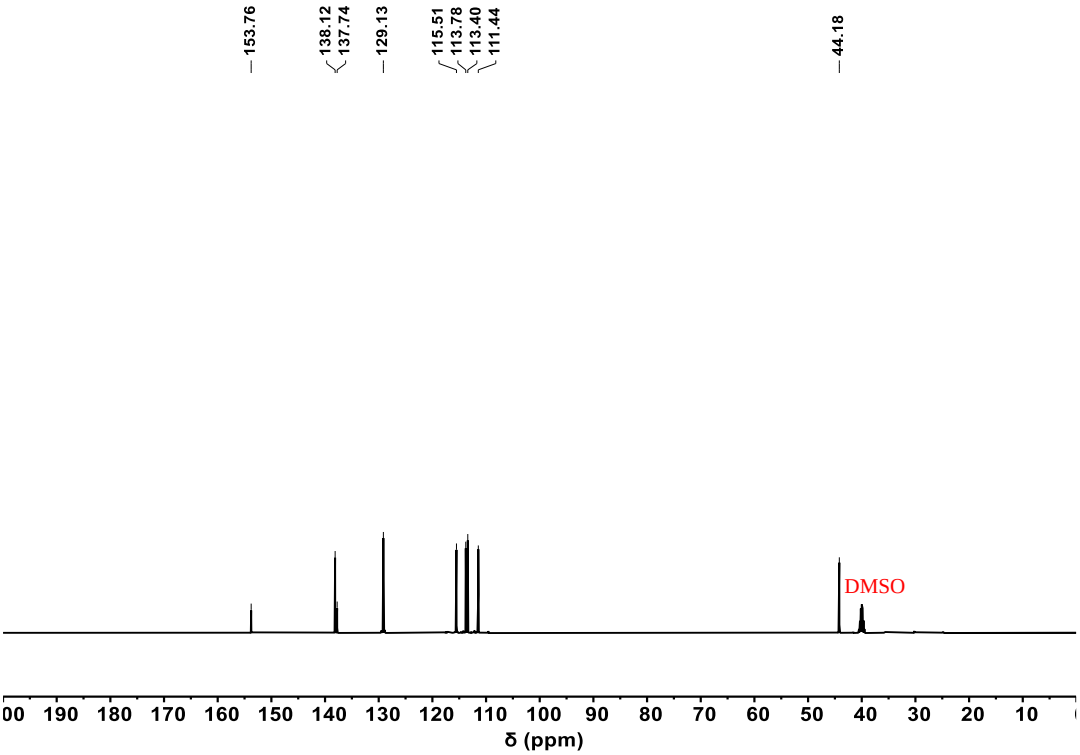


Figure S10. [13]C NMR (125 MHz) spectrum of **M1** measured in DMSO at 25 °C.

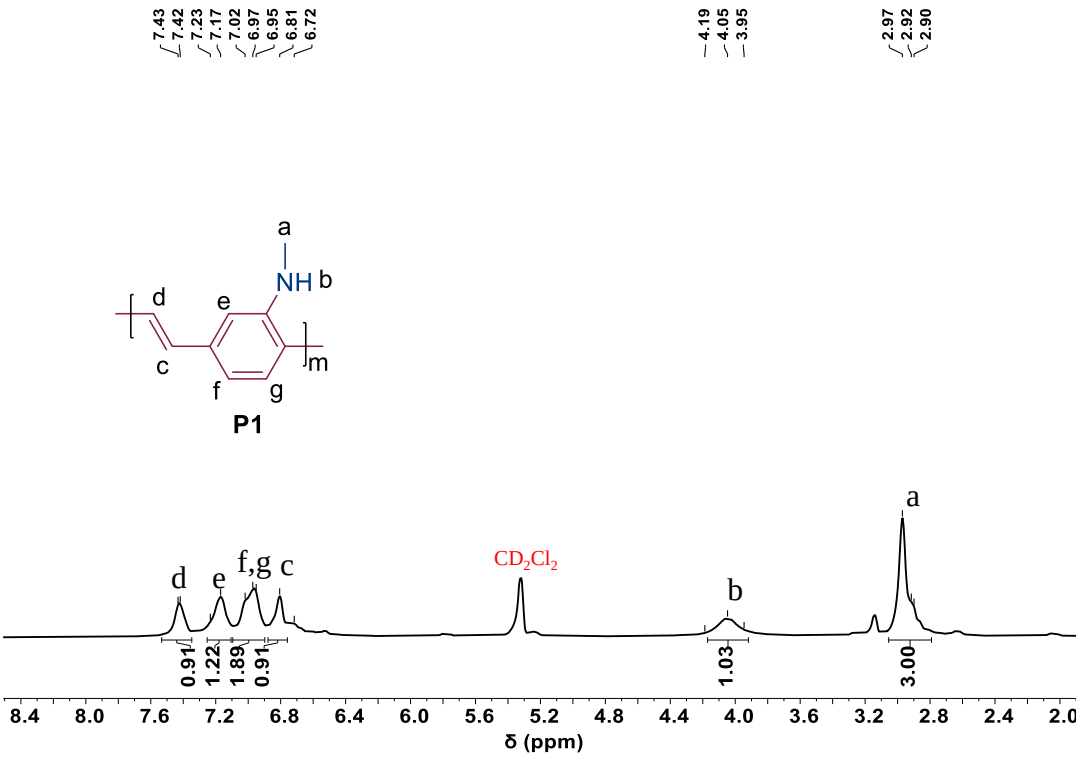


Figure S11. ^{1}H NMR (500 MHz) spectrum of **P1** measured in CD_2Cl_2 at 25 °C.

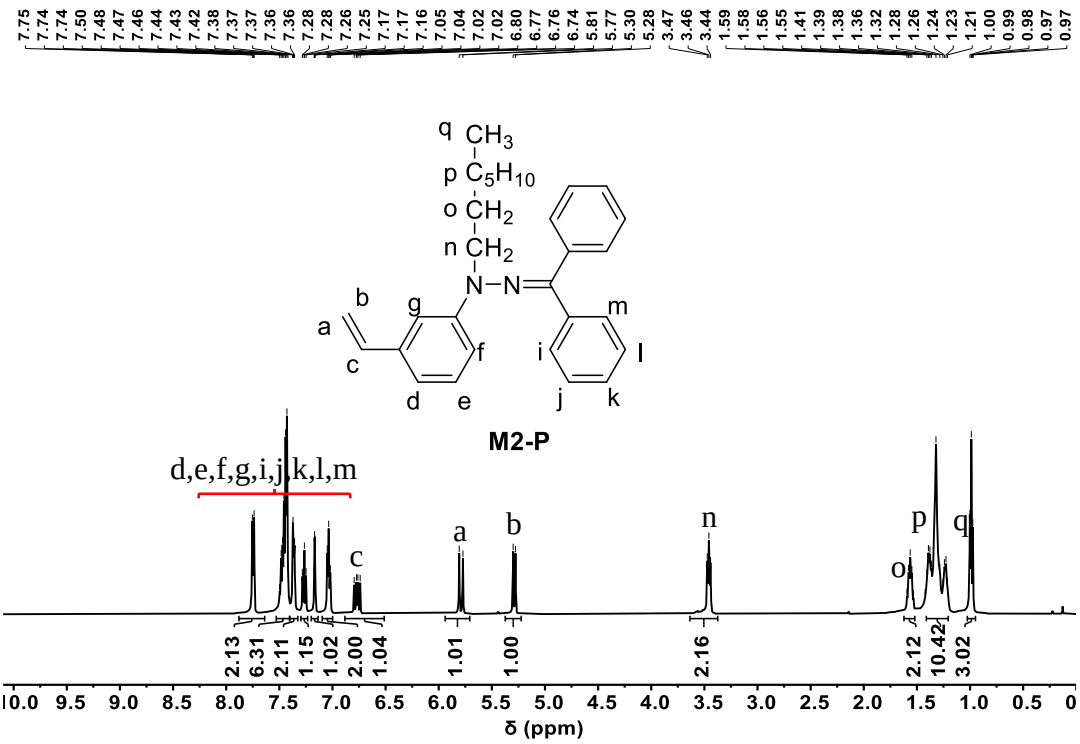


Figure S12. ^{1}H NMR (500 MHz) spectrum of Compound **M2-P** measured in $CDCl_3$ at 25 °C.

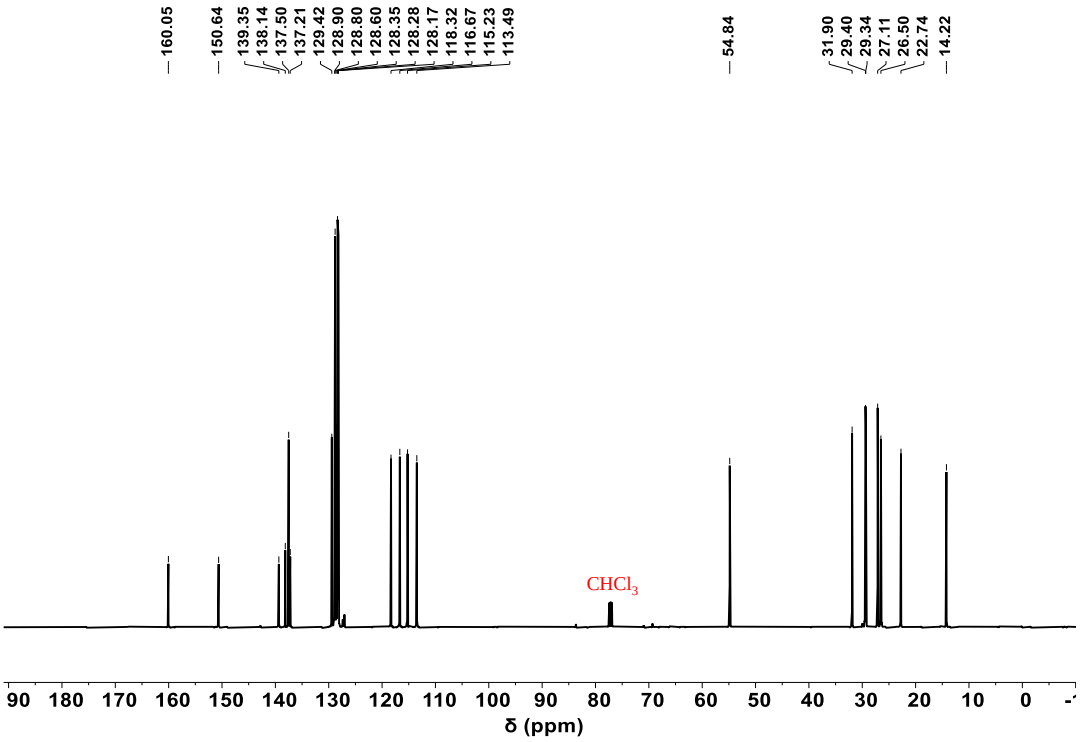


Figure S13.[13]C NMR (125 MHz) spectrum of Compound **M2-P** measured in $CDCl_3$ at 25 °C.

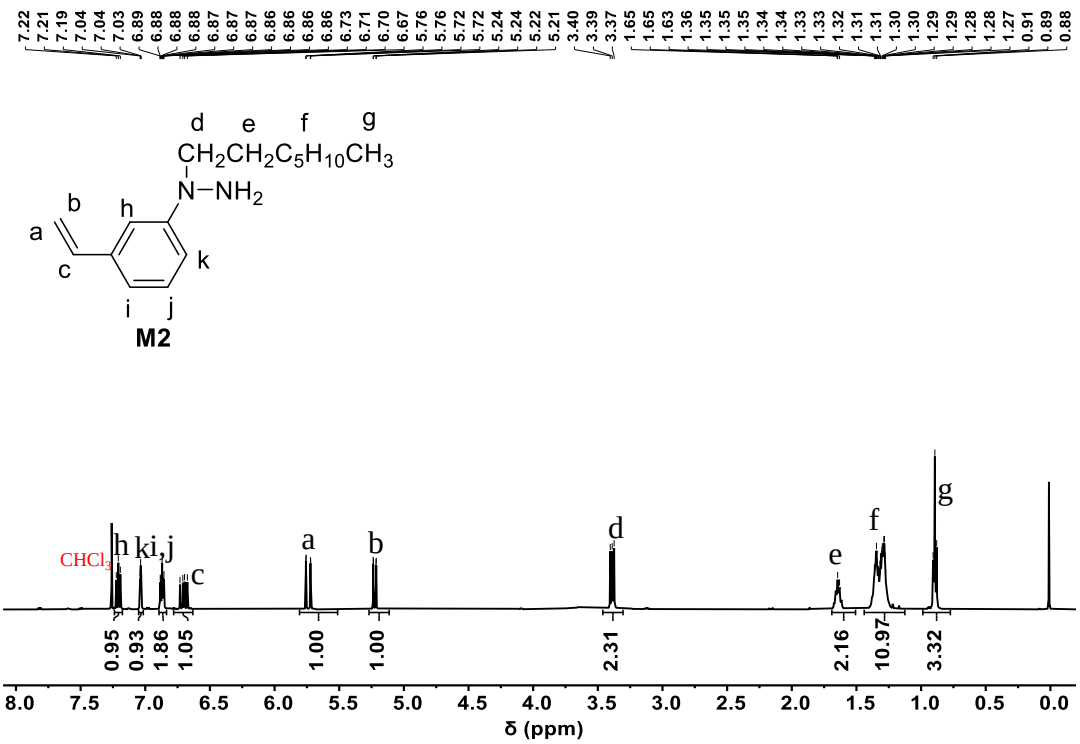


Figure S14. [1]H NMR (500 MHz) spectrum of **M2** measured in $CDCl_3$ at 25 °C.

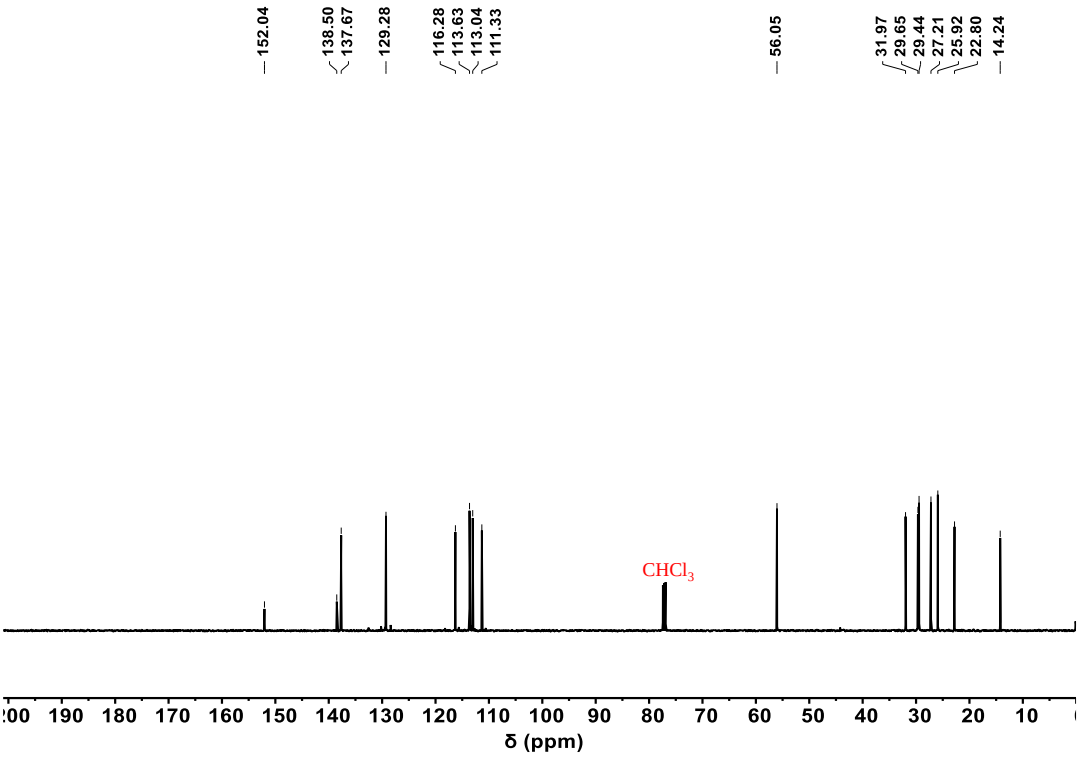


Figure S15. ^{13}C NMR (125 MHz) spectrum of **M2** measured in $CDCl_3$ at 25 °C.

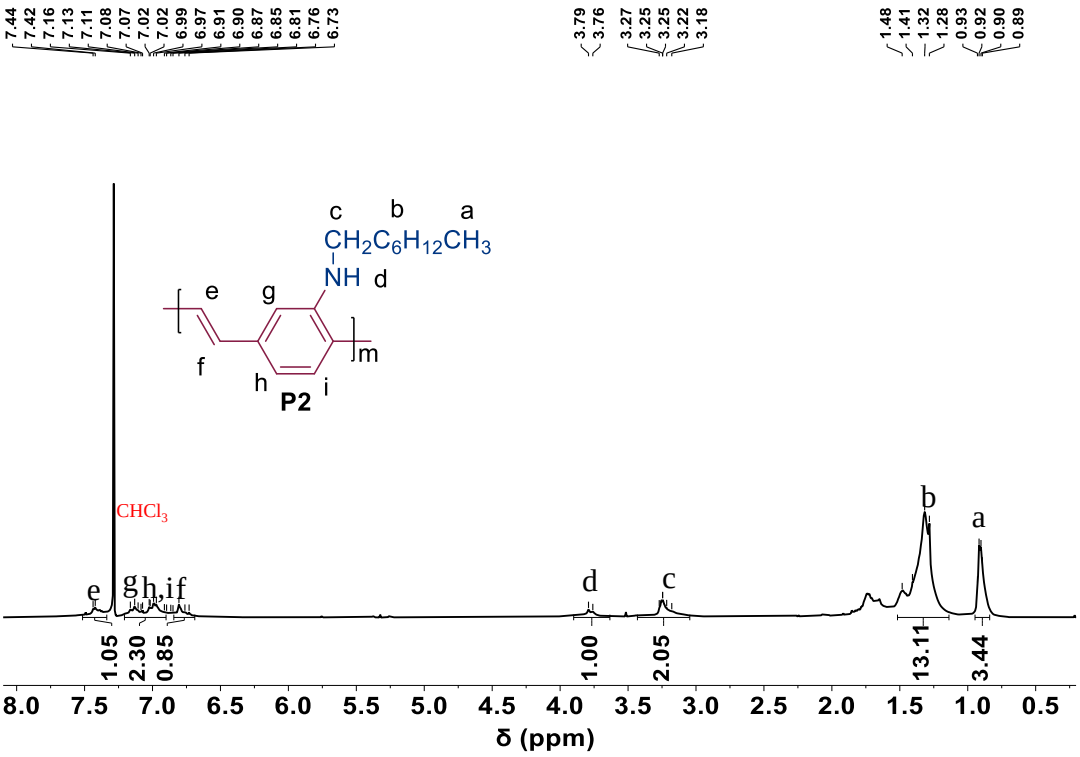


Figure S16. ^{1}H NMR (500 MHz) spectrum of **P2** measured in $CDCl_3$ at 25 °C.

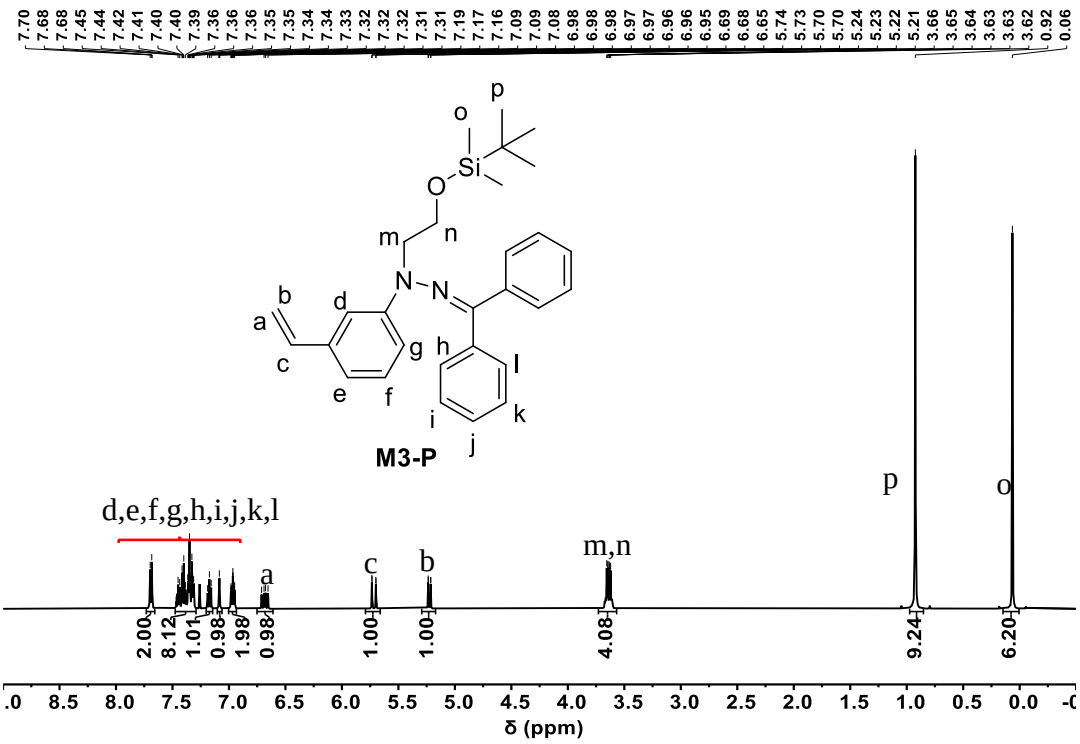


Figure S17. ^{1}H NMR (500 MHz) spectrum of Compound **M3-P** measured in $CDCl_3$ at 25 °C.

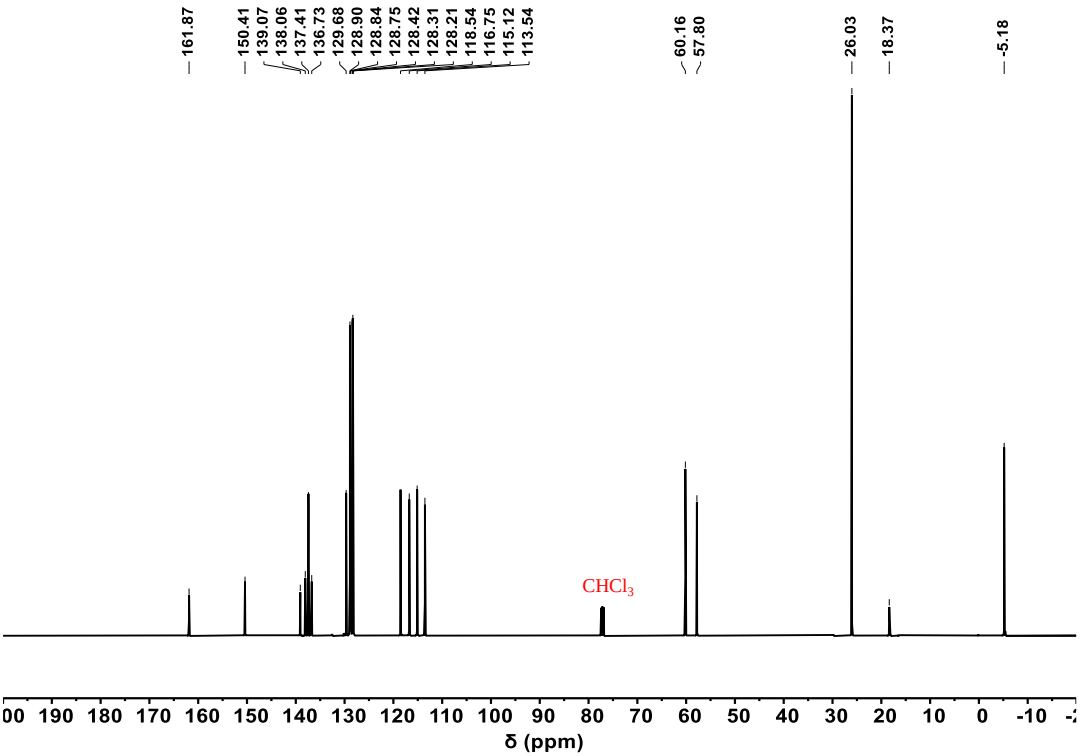


Figure S18. ^{13}C NMR (125 MHz) spectrum of Compound **M3-P** measured in $CDCl_3$ at 25 °C.

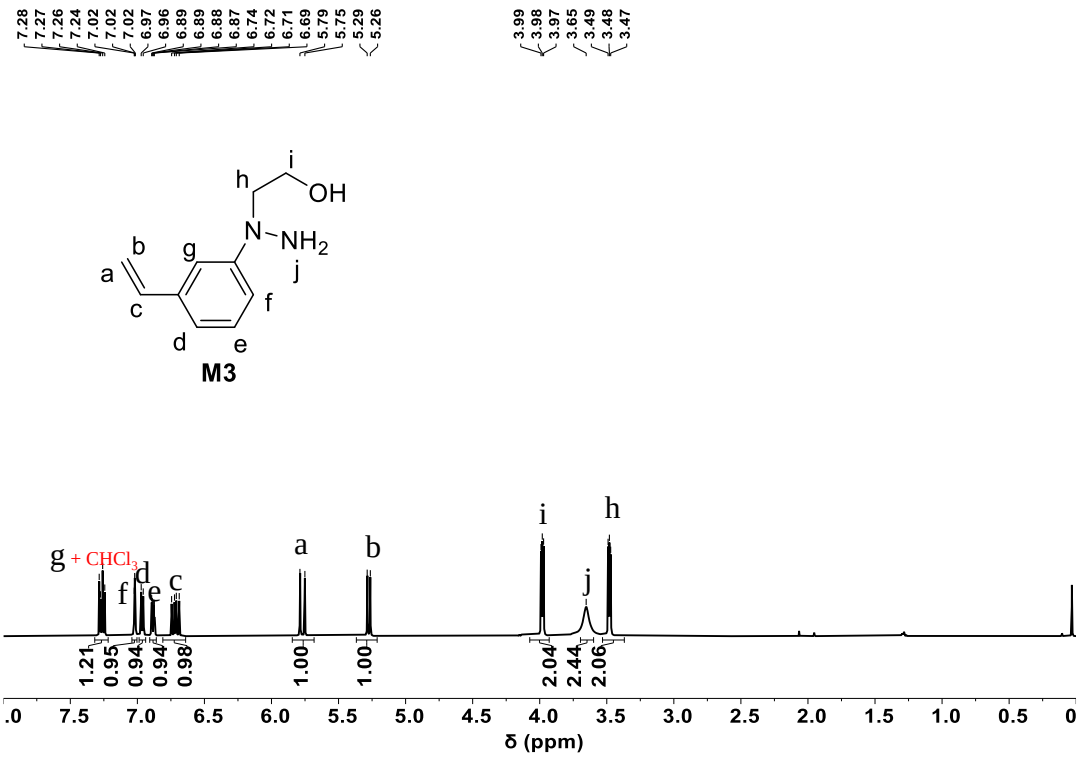


Figure S19. ^{1}H NMR (500 MHz) spectrum of **M3** measured in $CDCl_3$ at 25 °C.

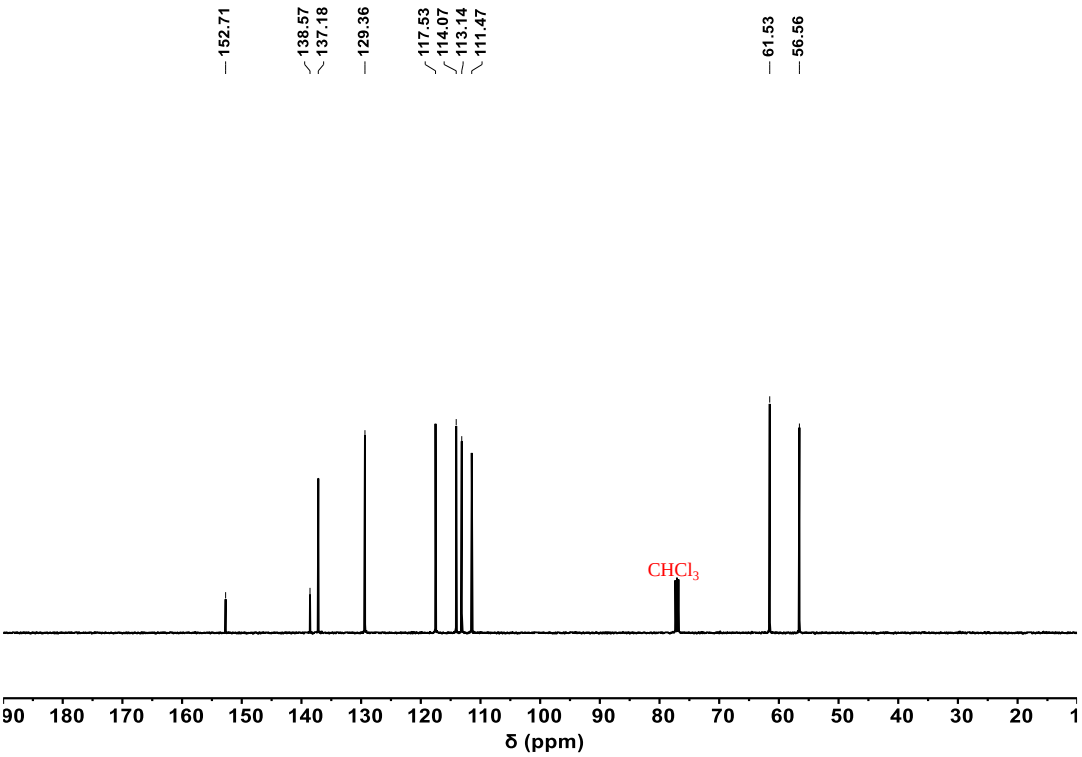


Figure S20. ^{13}C NMR (125 MHz) spectrum of **M3** measured in $CDCl_3$ at 25 °C.

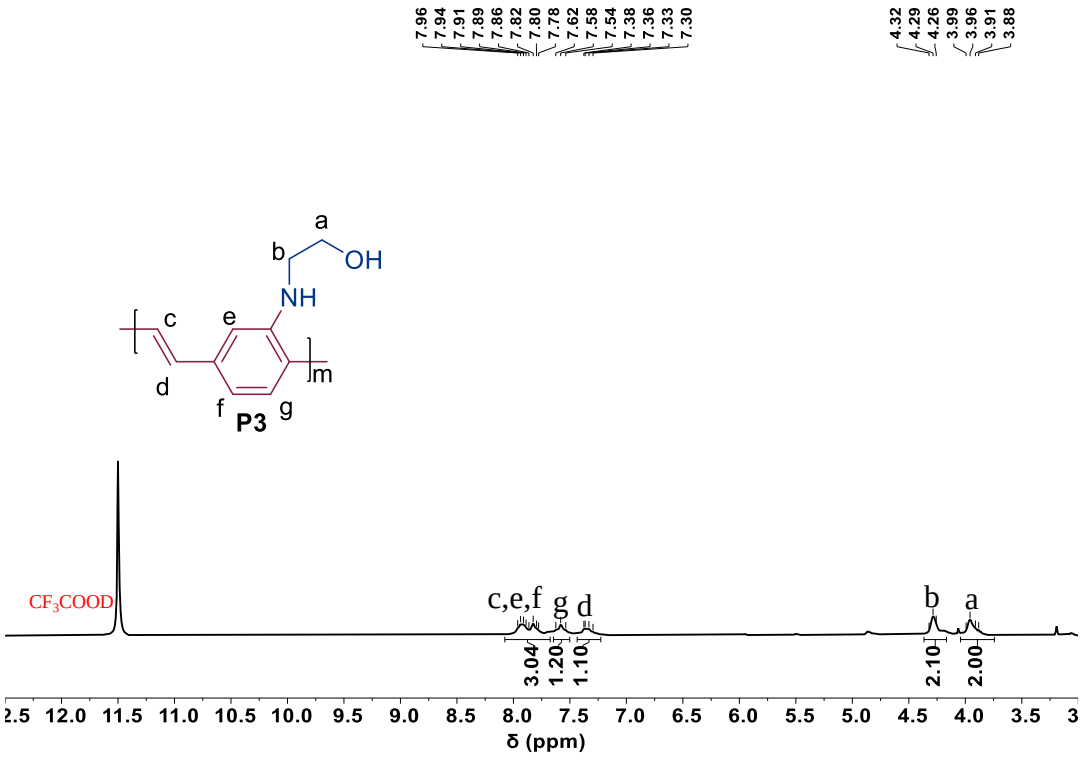


Figure S21. ^{1}H NMR (500 MHz) spectrum of **P3** measured in in CF_3COOD at 25 °C.

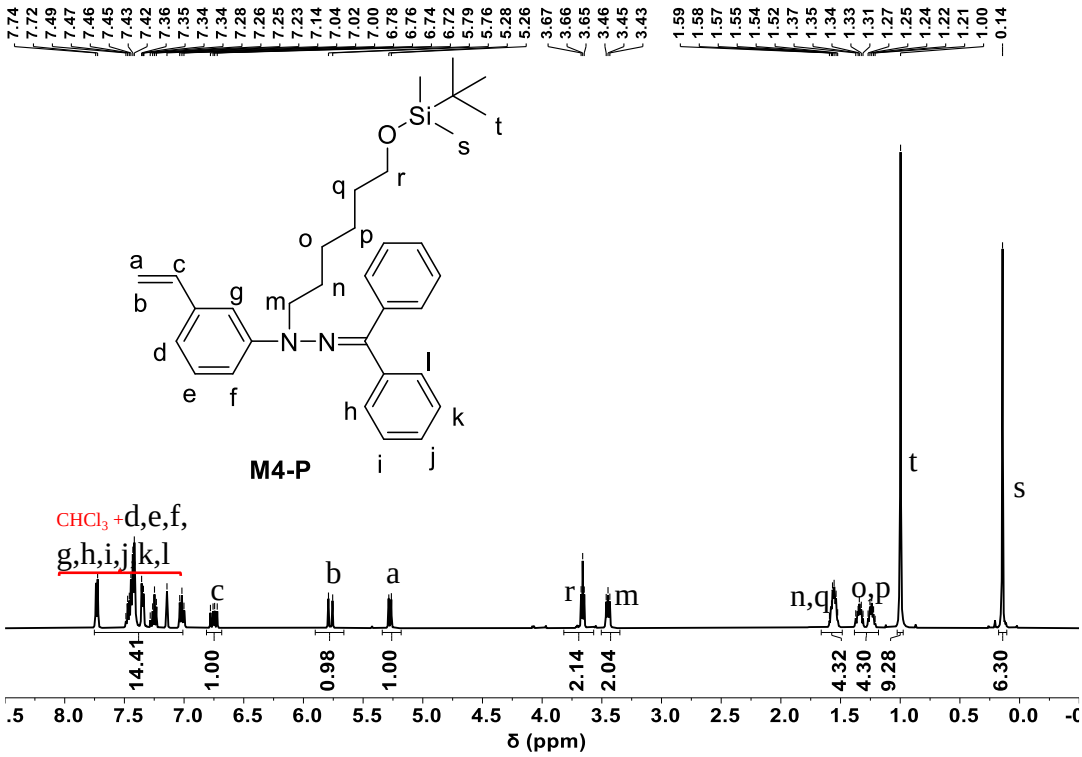


Figure S22. ^{1}H NMR (500 MHz) spectrum of Compound **M4-P** measured in $CDCl_3$ at 25 °C.

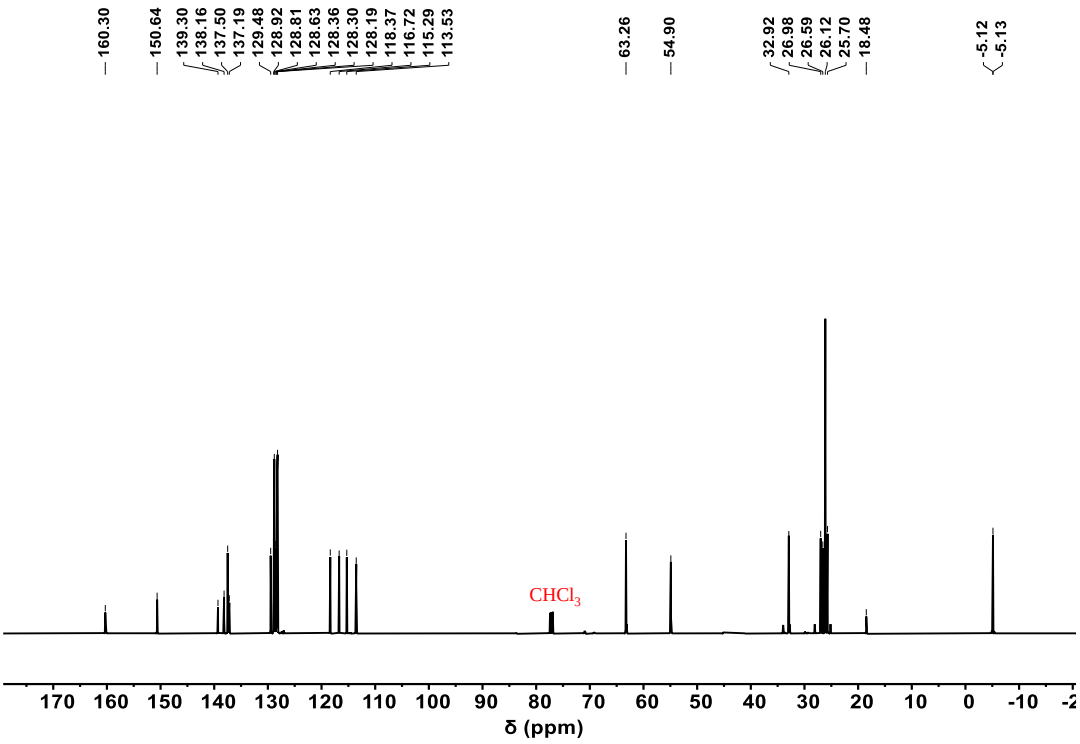


Figure S23. ^{13}C NMR (125 MHz) spectrum of Compound **M4-P** measured in $CDCl_3$ at 25 °C.

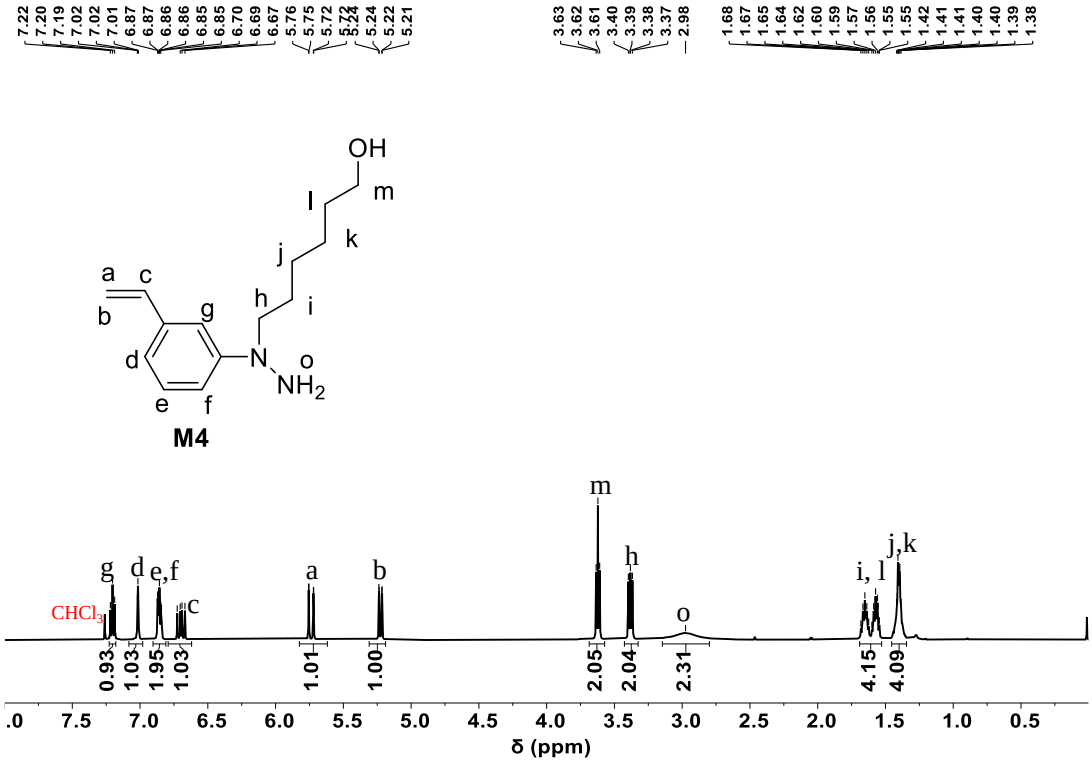


Figure S24. ^{1}H NMR (500 MHz) spectrum of **M4** measured in $CDCl_3$ at 25 °C.

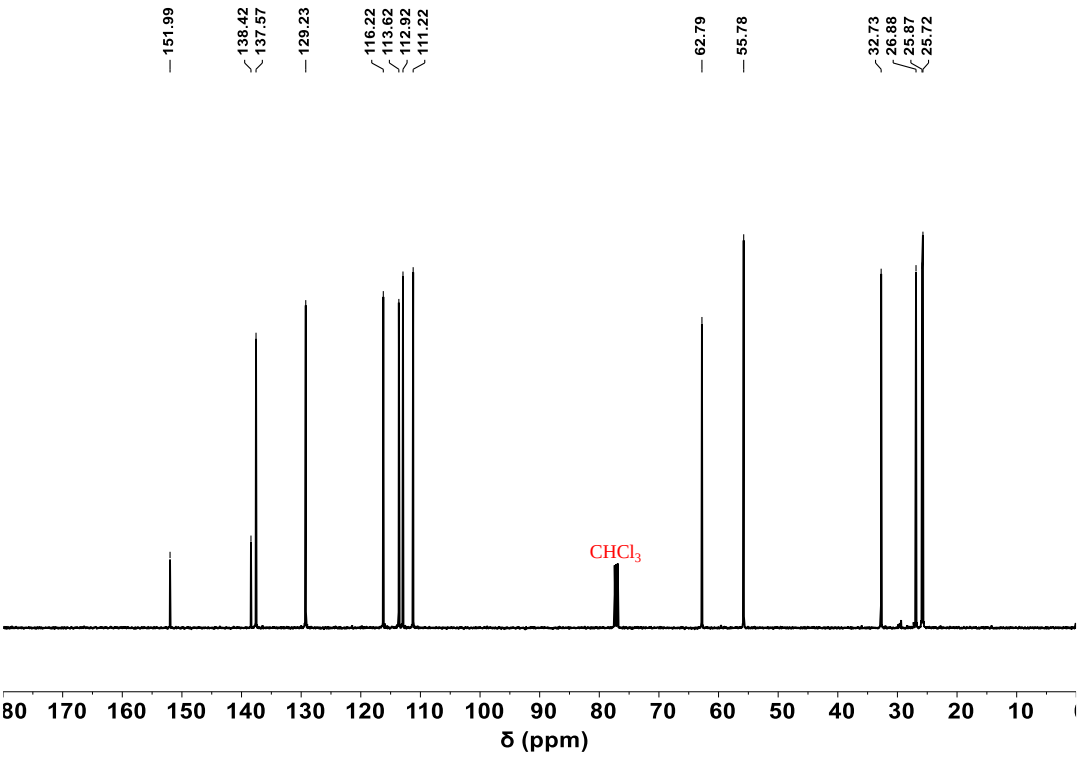


Figure S25. ^{13}C NMR (125 MHz) spectrum of **M4** measured in $CDCl_3$ at 25 °C.

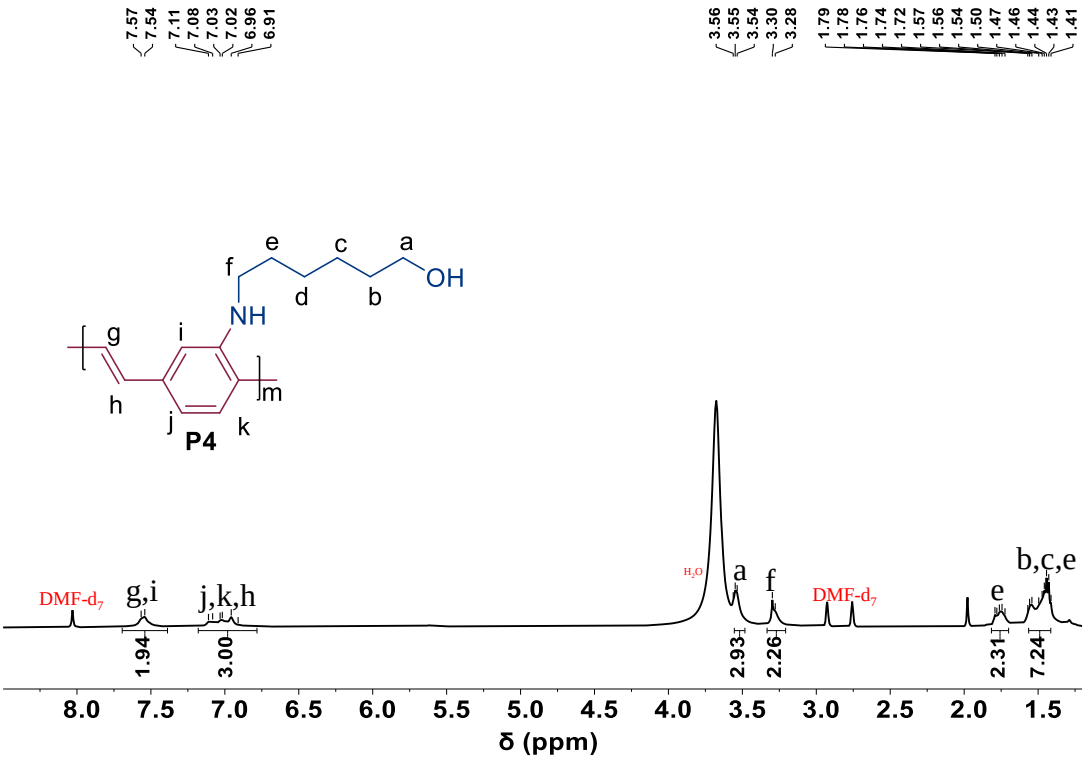


Figure S26. ^{1}H NMR (500 MHz) spectrum of **P4** measured in in DMF-d_7 at 25 °C.

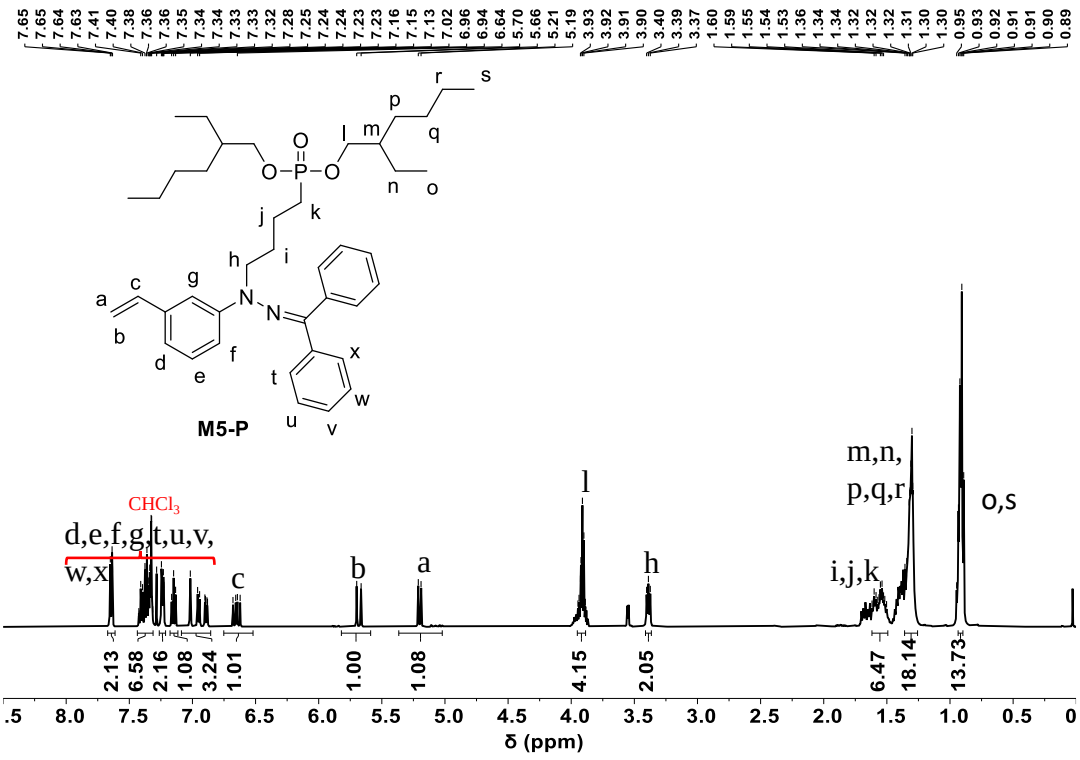


Figure S27. ^{1}H NMR (500 MHz) spectrum of Compound **M5-P** measured in $CDCl_3$ at 25 °C.

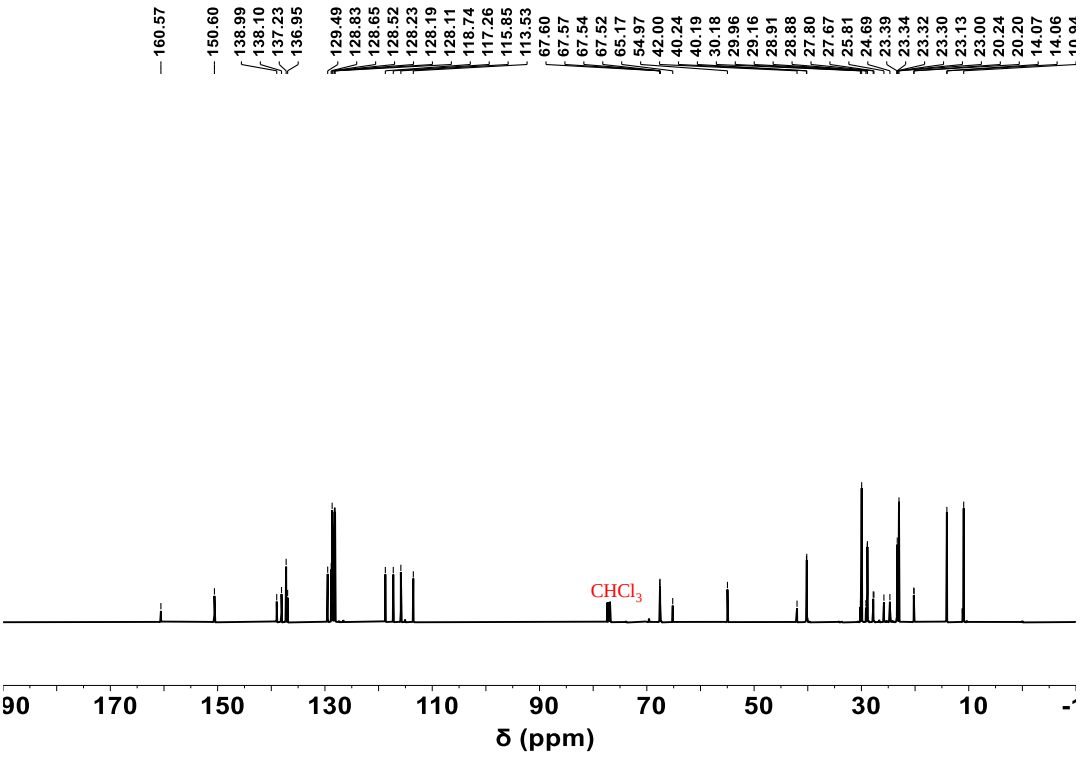


Figure S28. ^{13}C NMR (125 MHz) spectrum of Compound **M5-P** measured in $CDCl_3$ at 25 °C.

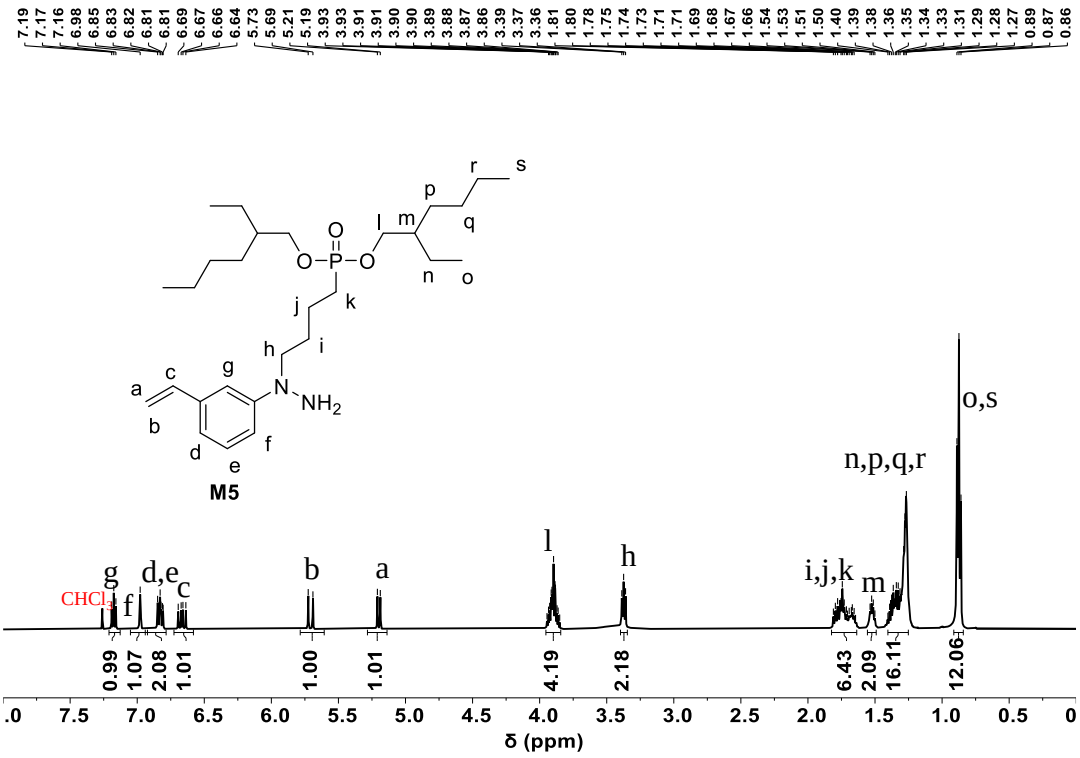


Figure S29. ^{1}H NMR (500 MHz) spectrum of **M5** measured in $CDCl_3$ at 25 °C.

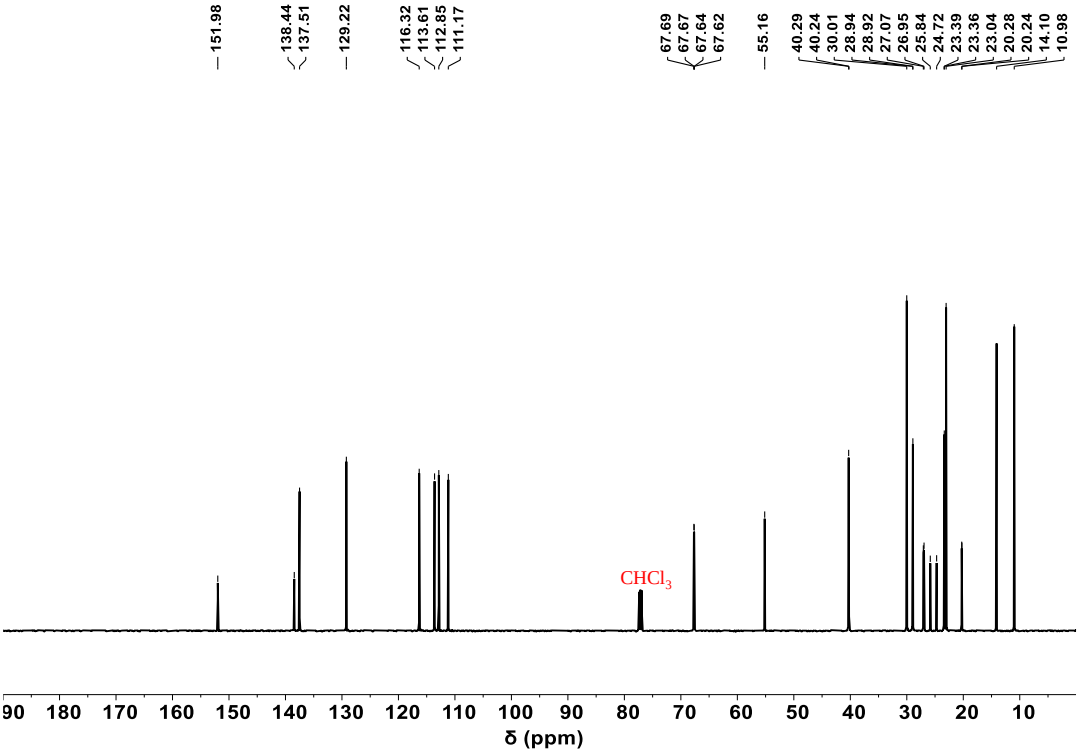


Figure S30. ^{13}C NMR (125 MHz) spectrum of **M5** measured in $CDCl_3$ at 25 °C.

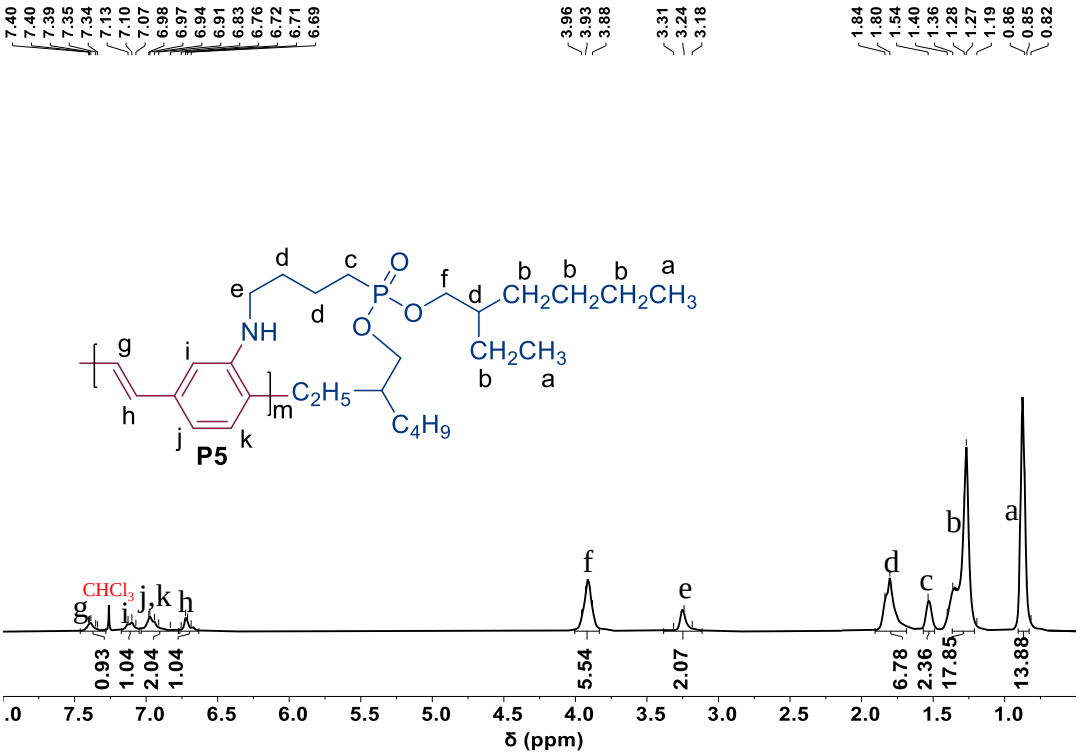


Figure S31. ^{1}H NMR (500 MHz) spectrum of **P5** measured in in $CDCl_3$ at 25 °C.

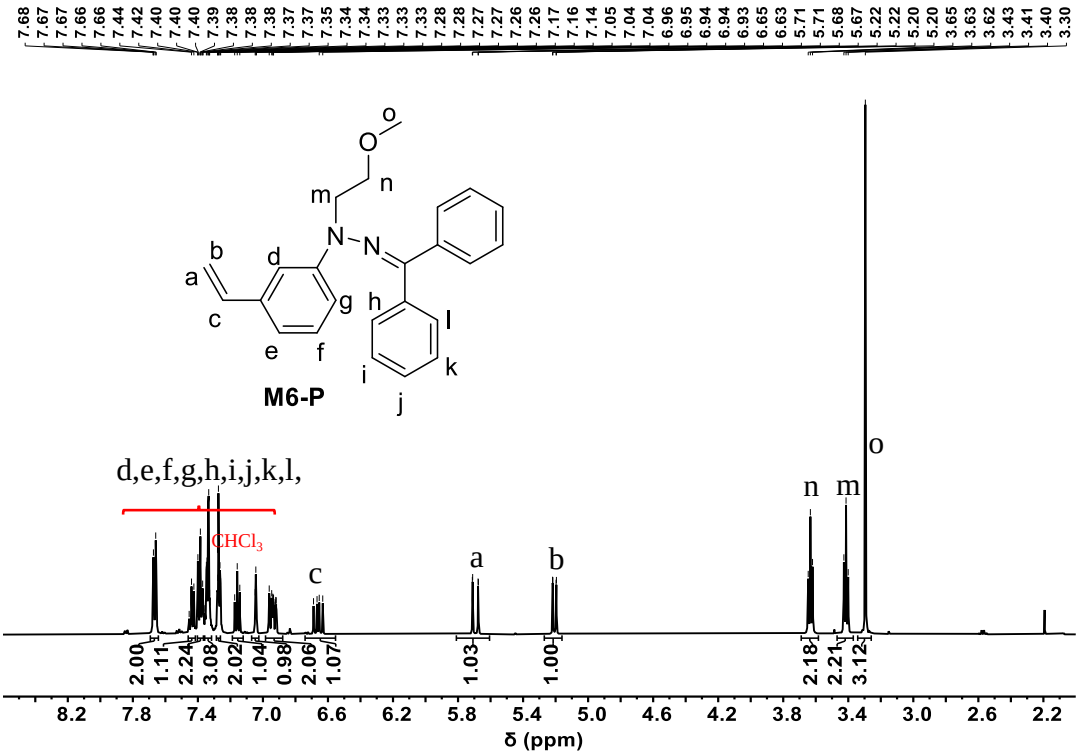


Figure S32. ^{1}H NMR (500 MHz) spectrum of Compound **M6-P** measured in $CDCl_3$ at 25 °C.

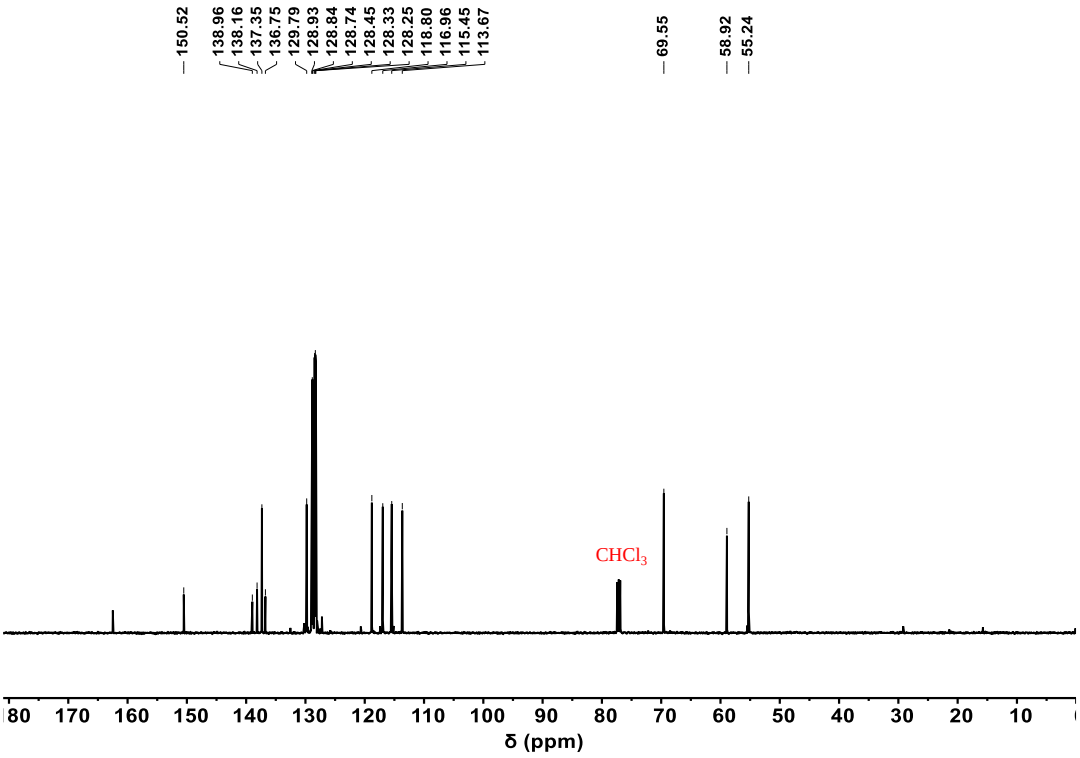


Figure S33. ^{13}C NMR (125 MHz) spectrum of Compound **M6-P** measured in $CDCl_3$ at 25 °C.

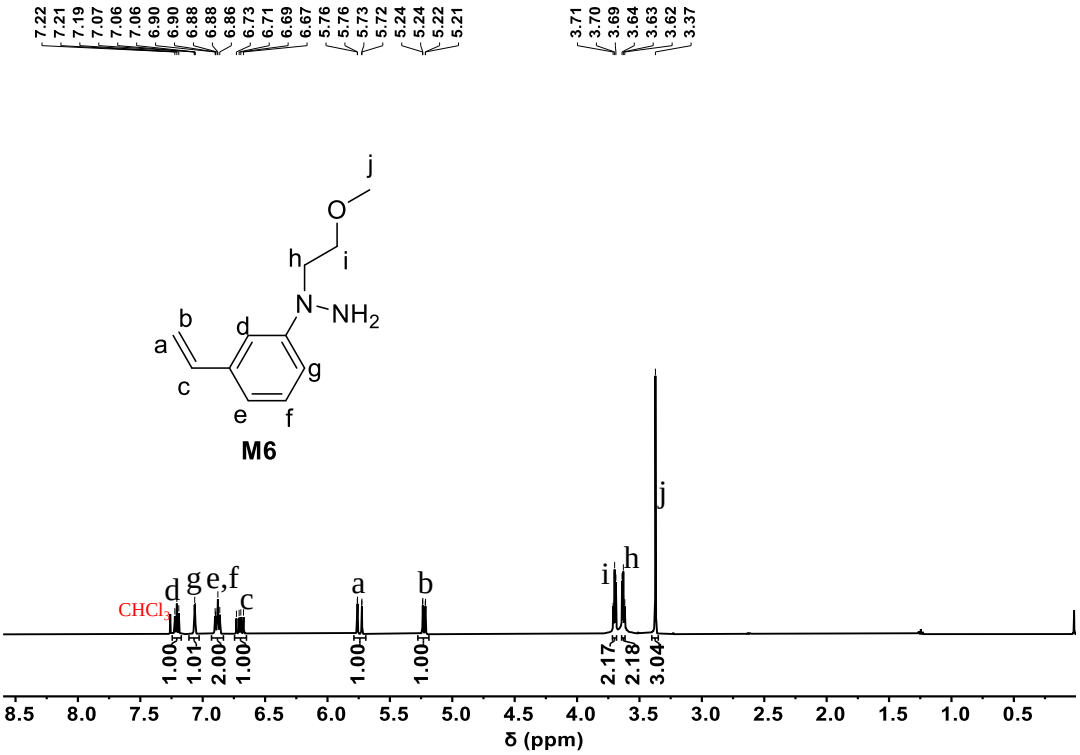


Figure S34. ^{1}H NMR (500 MHz) spectrum of **M6** measured in $CDCl_3$ at 25 °C.

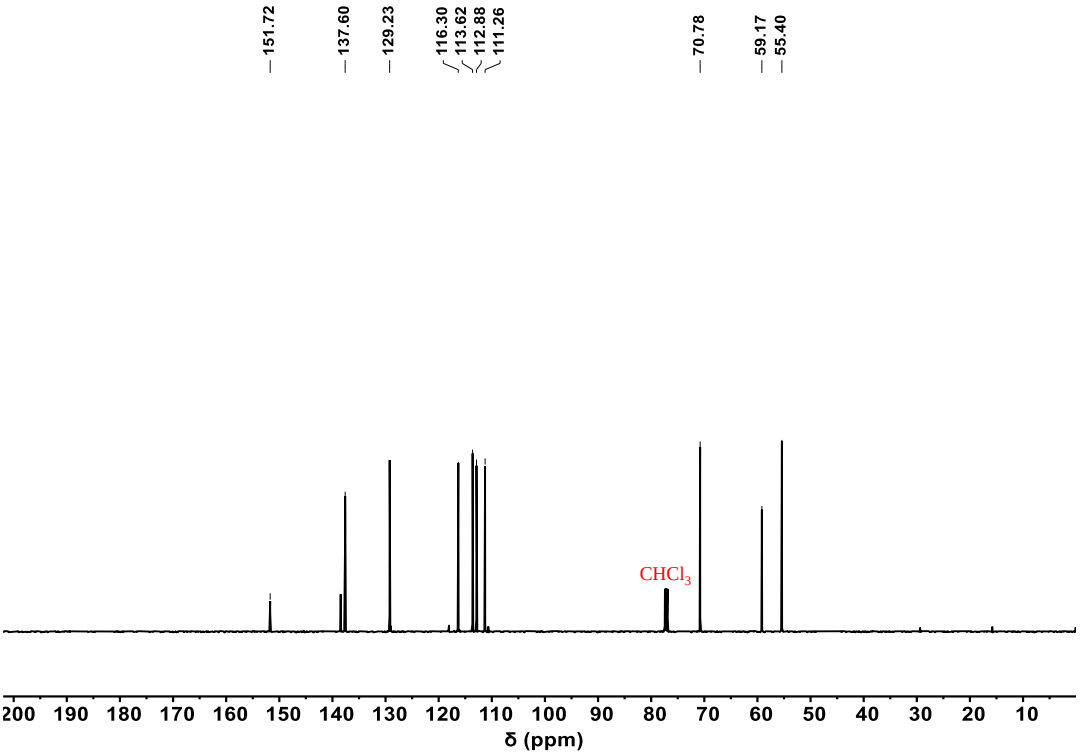


Figure S35. ^{13}C NMR (125 MHz) spectrum of **M6** measured in $CDCl_3$ at 25 °C.

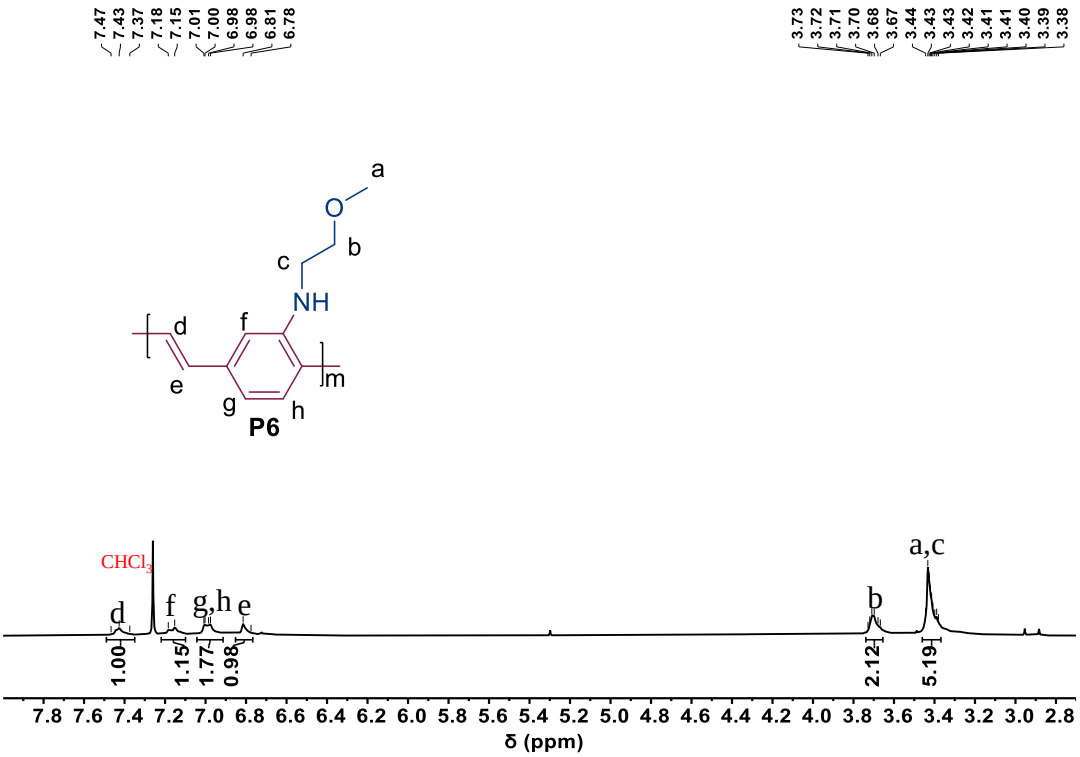


Figure S36. ^{1}H NMR (500 MHz) spectrum of **P6** measured in $CHCl_3$ at 25 °C.

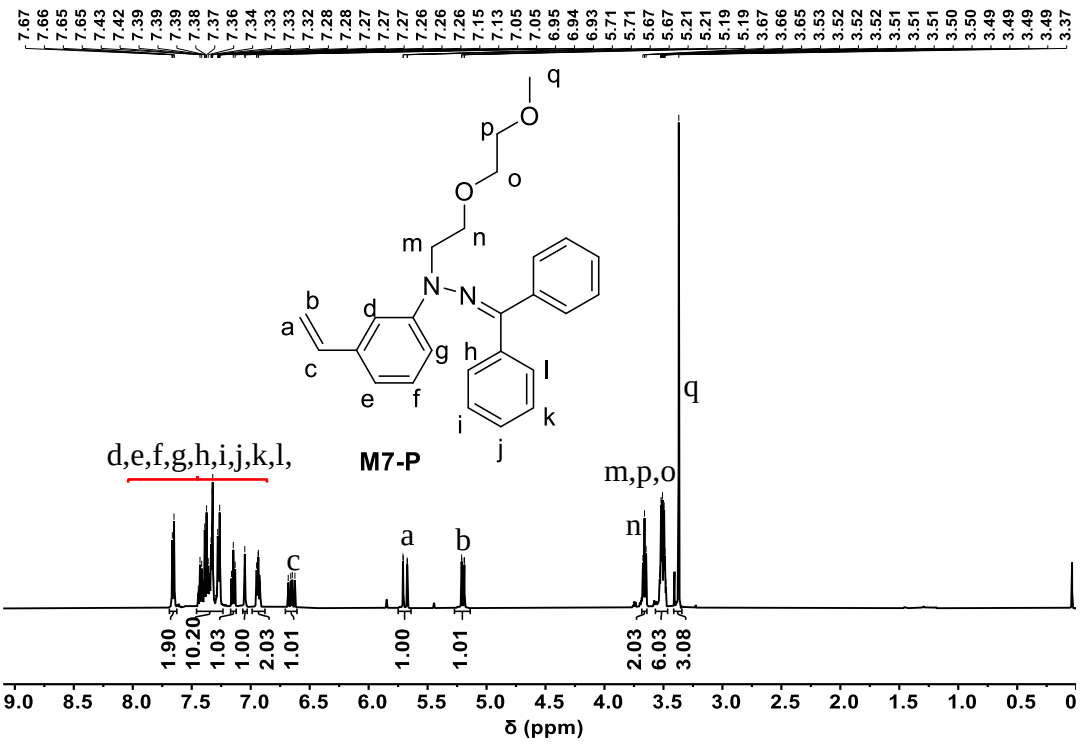


Figure S37. [1]H NMR (500 MHz) spectrum of Compound **M7-P** measured in $CDCl_3$ at 25 °C.

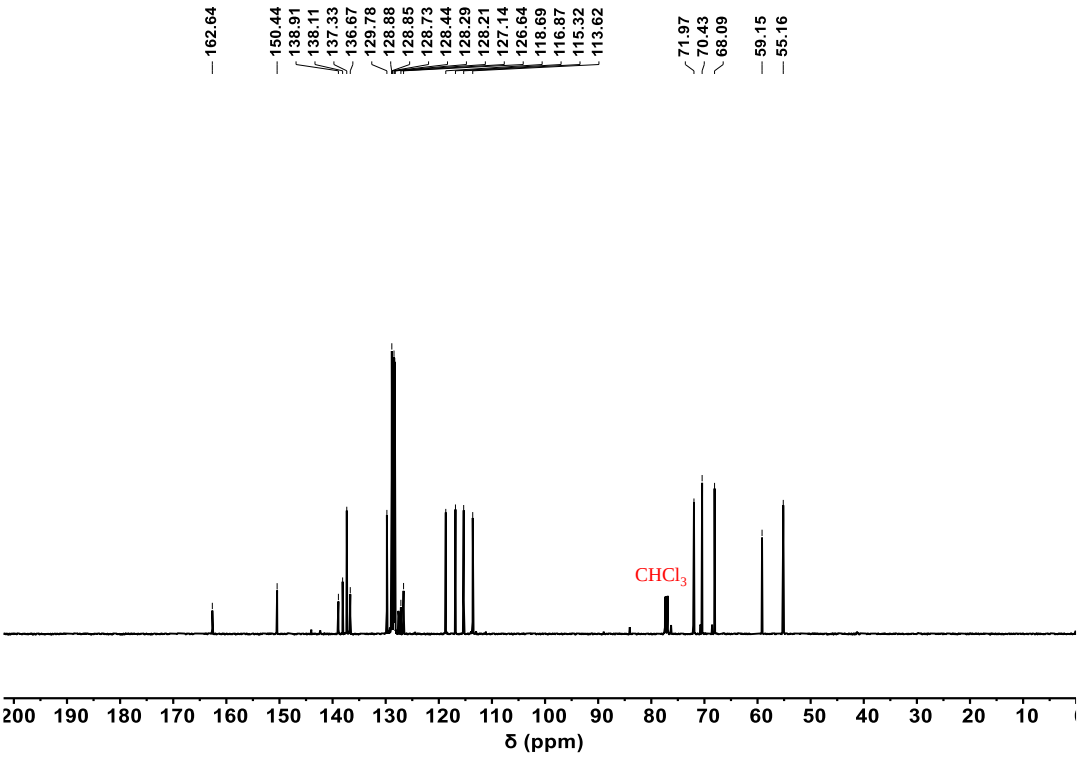


Figure S38. [13]C NMR (125 MHz) spectrum of Compound **M7-P** measured in $CDCl_3$ at 25 °C.

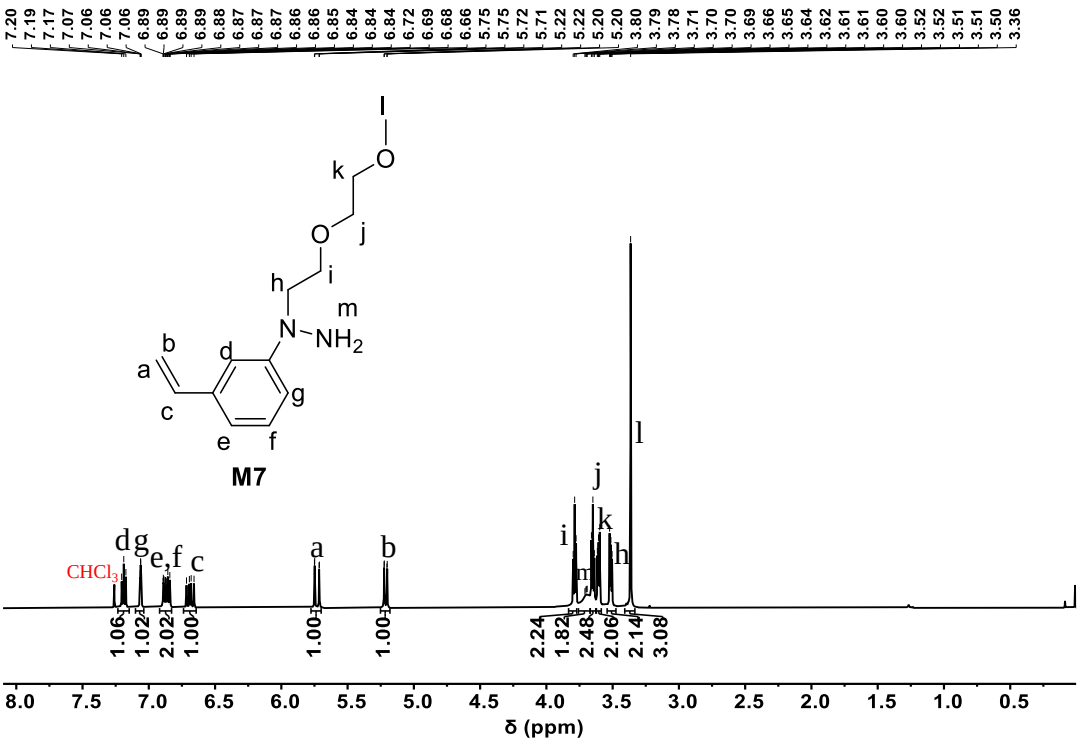


Figure S39. ^{1}H NMR (500 MHz) spectrum of **M7** measured in $CDCl_3$ at 25 °C.

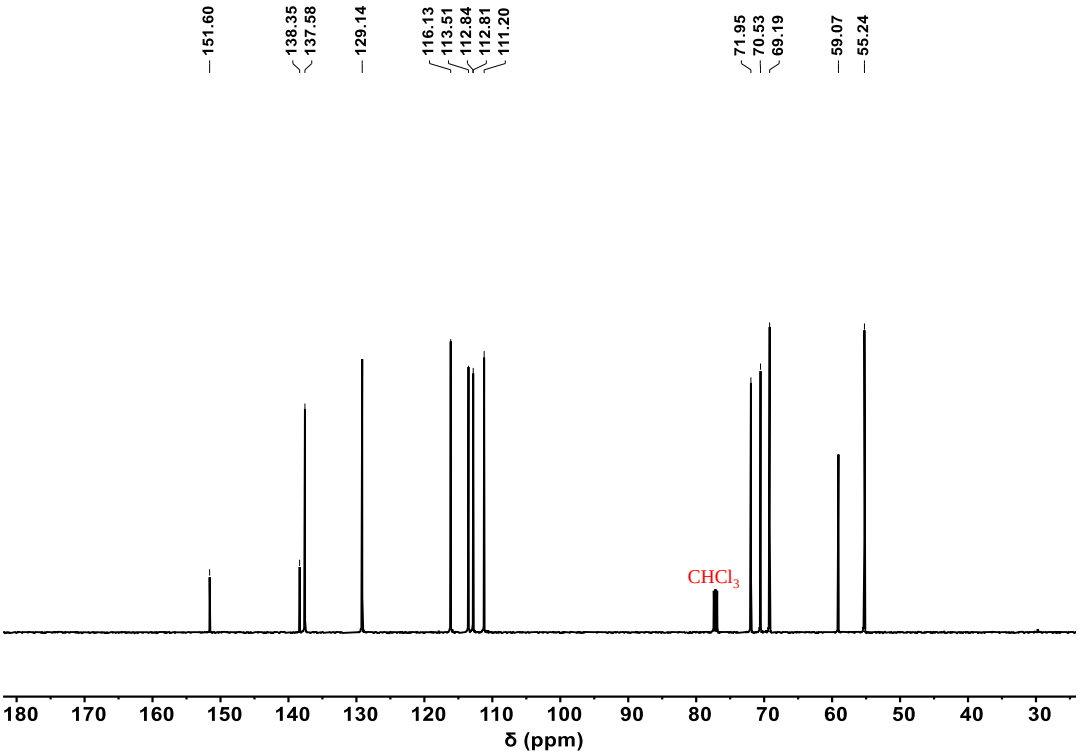


Figure S40. ^{13}C NMR (125 MHz) spectrum of **M7** measured in $CDCl_3$ at 25 °C.

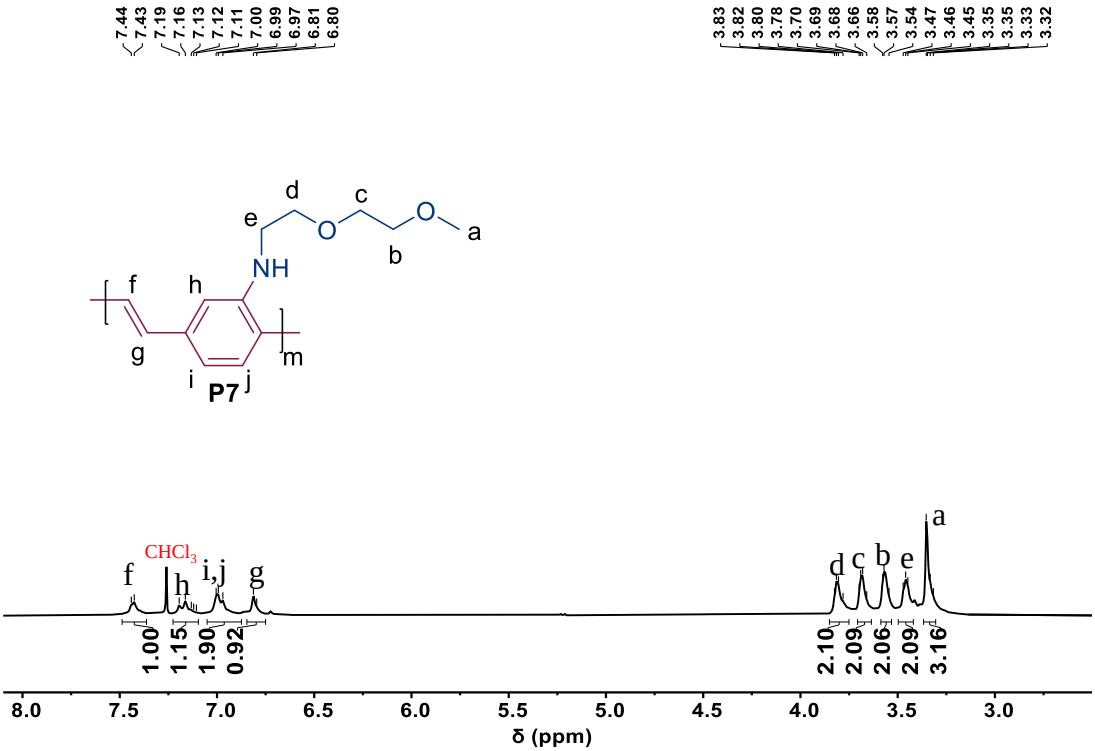


Figure S41. ^{1}H NMR (500 MHz) spectrum of **P7** measured in $CDCl_3$ at 25 °C.

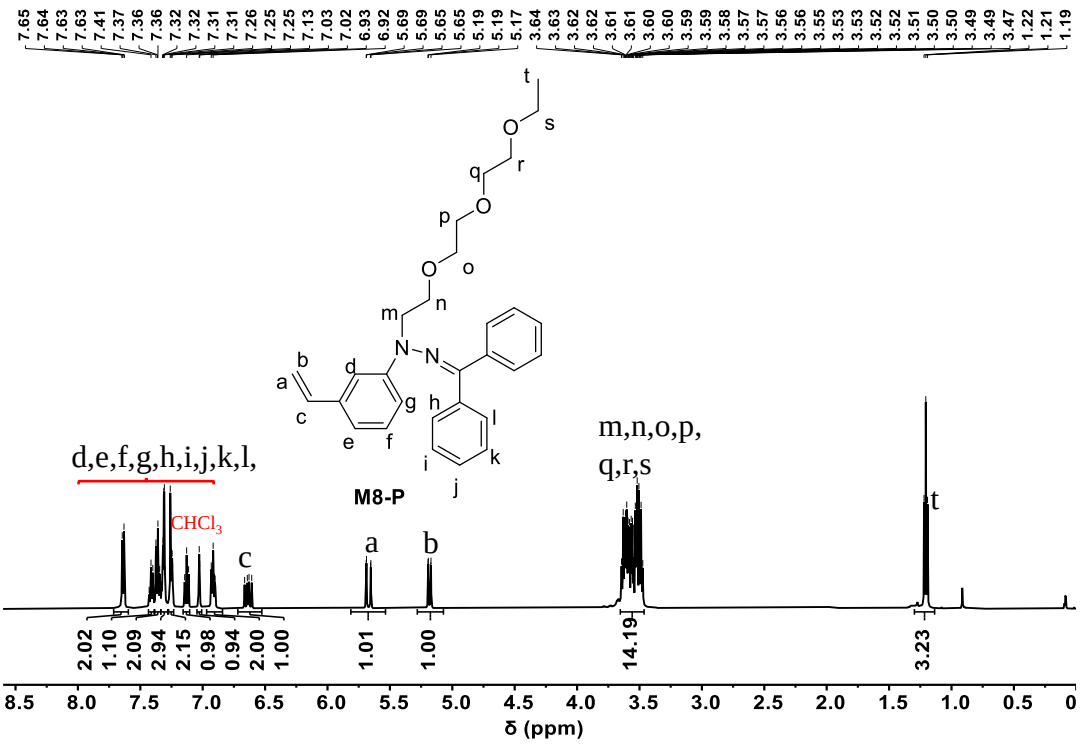


Figure S42. ^{1}H NMR (500 MHz) spectrum of Compound **M8-P** measured in $CDCl_3$ at 25 °C.

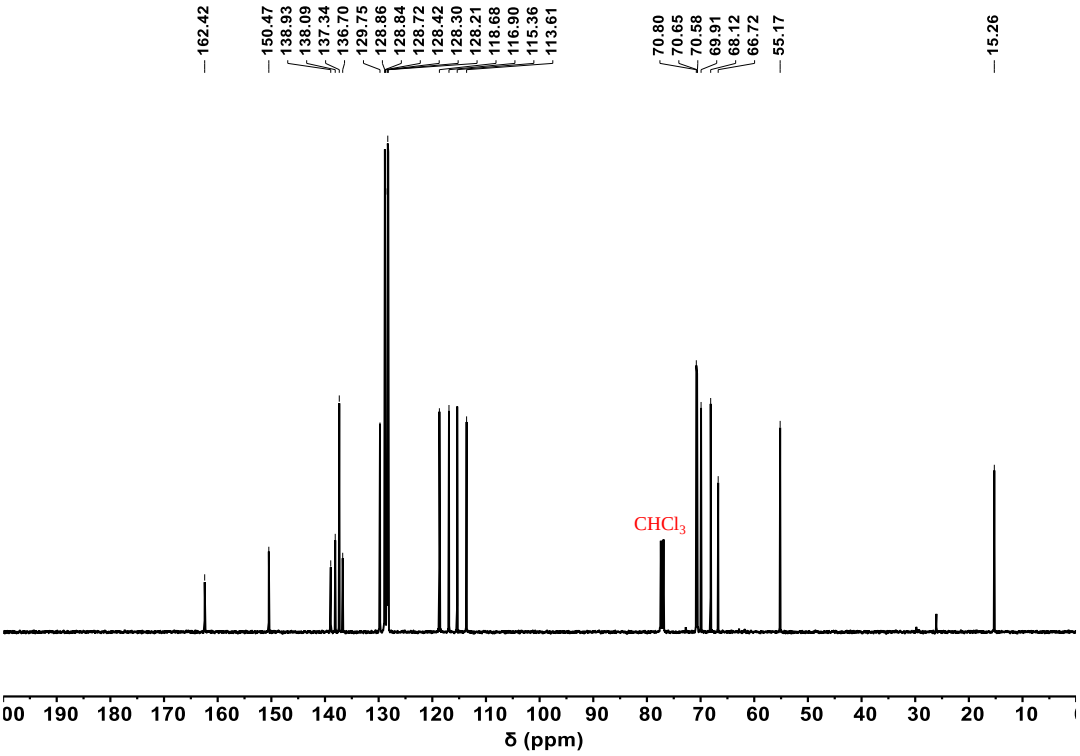


Figure S43. ^{13}C NMR (125 MHz) spectrum of Compound **M8-P** measured in $CDCl_3$ at 25 °C.

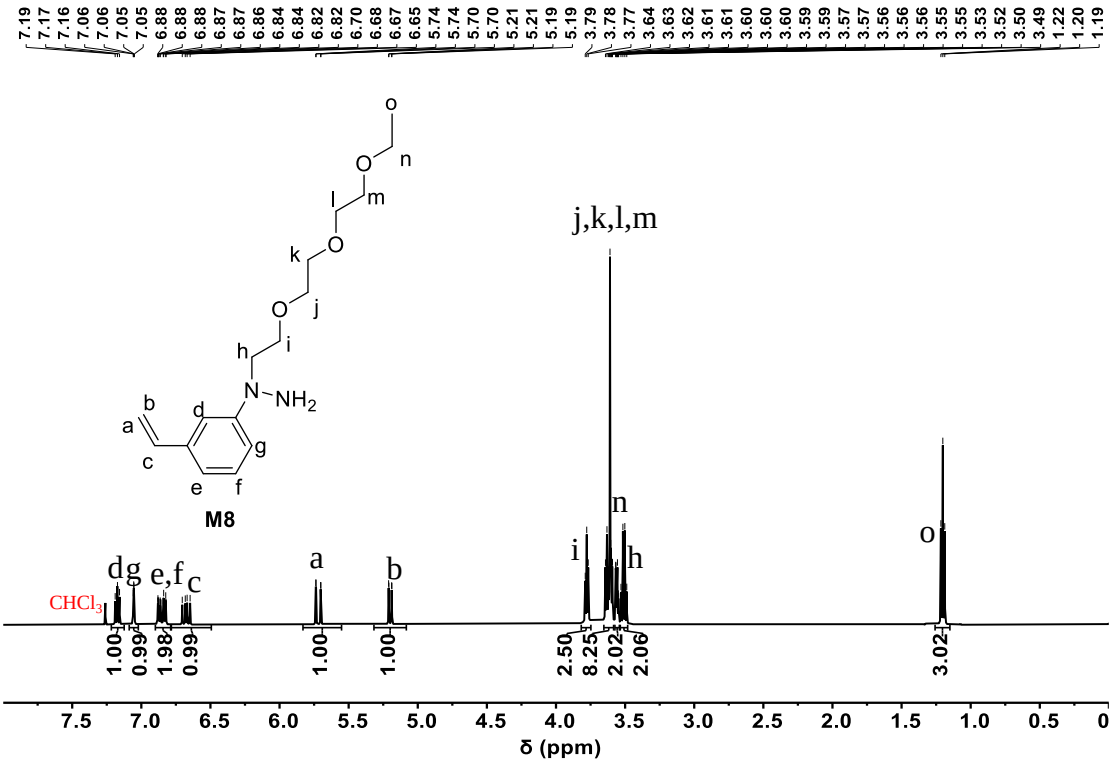


Figure S44. ^{1}H NMR (500 MHz) spectrum of **M8** measured in $CDCl_3$ at 25 °C.

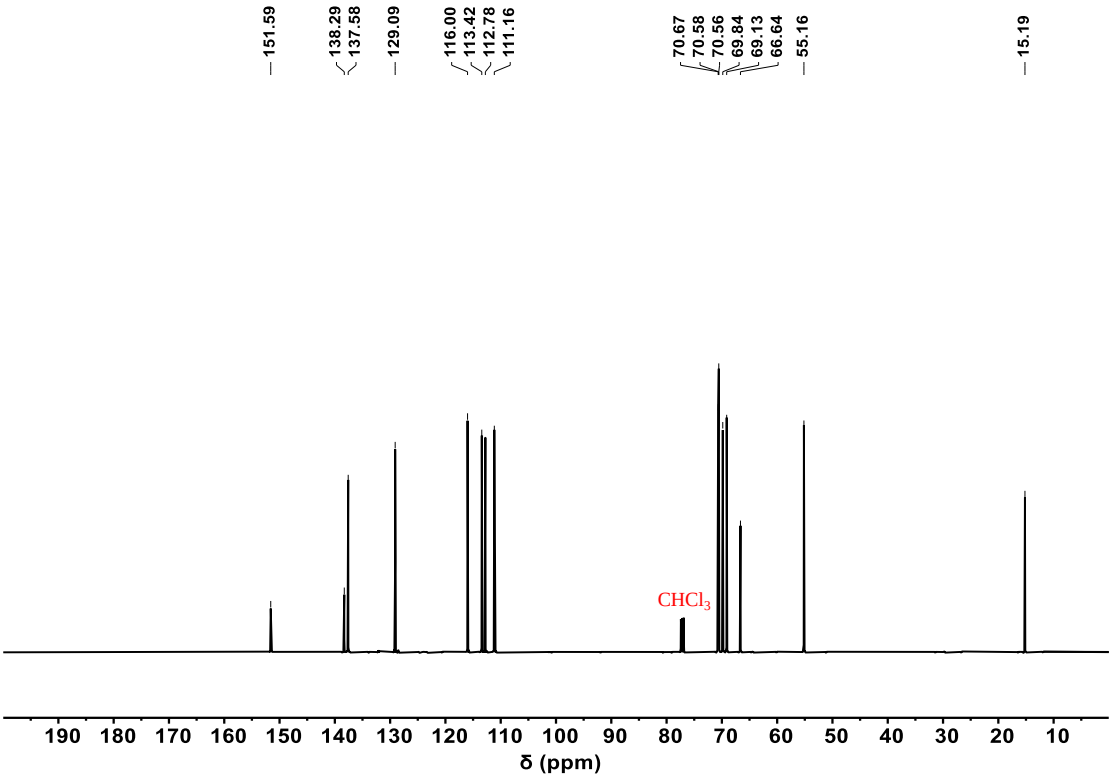


Figure S45. ^{13}C NMR (125 MHz) spectrum of Compound **M8** measured in $CDCl_3$ at 25 °C.

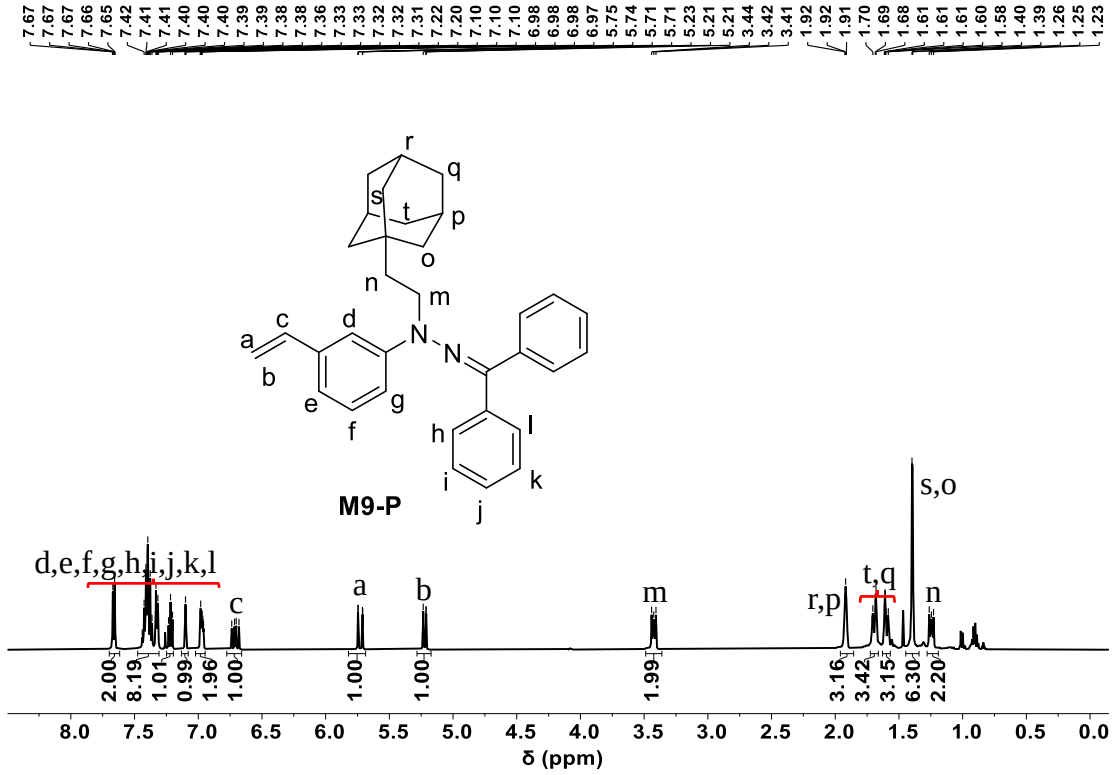


Figure S46. ^{1}H NMR (500 MHz) spectrum of Compound **M9-P** measured in $CDCl_3$ at 25 °C.

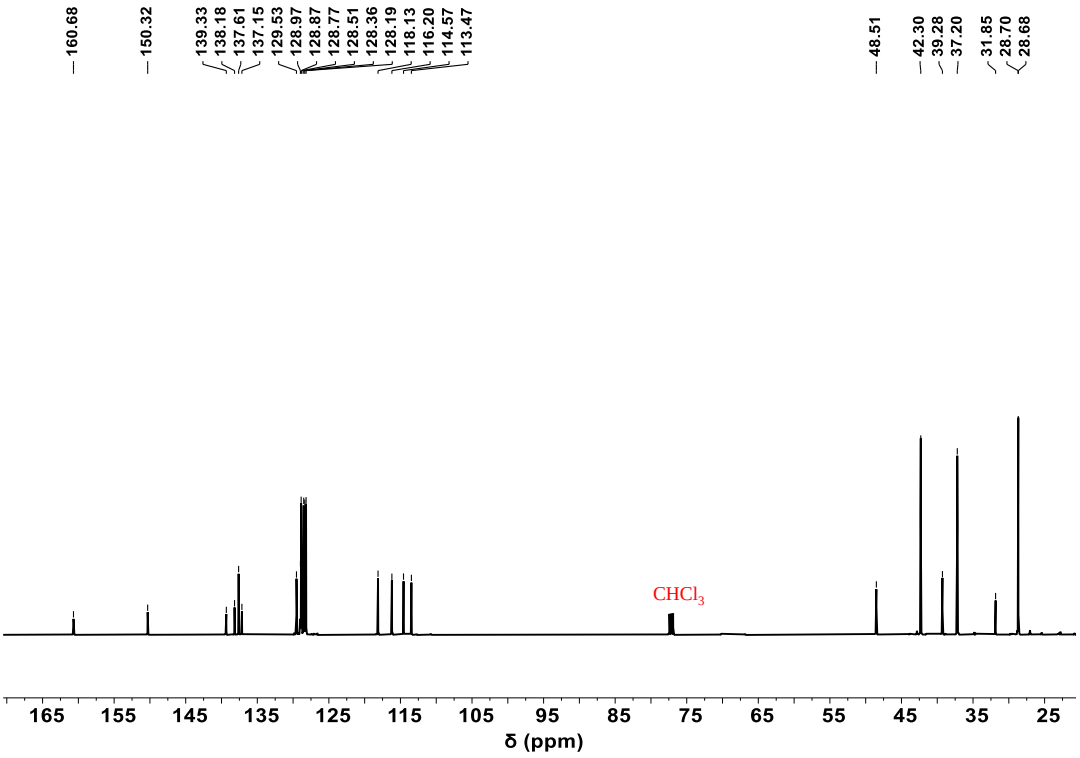


Figure S47. ^{13}C NMR (125 MHz) spectrum of **M9-P** measured in $CDCl_3$ at 25 °C.

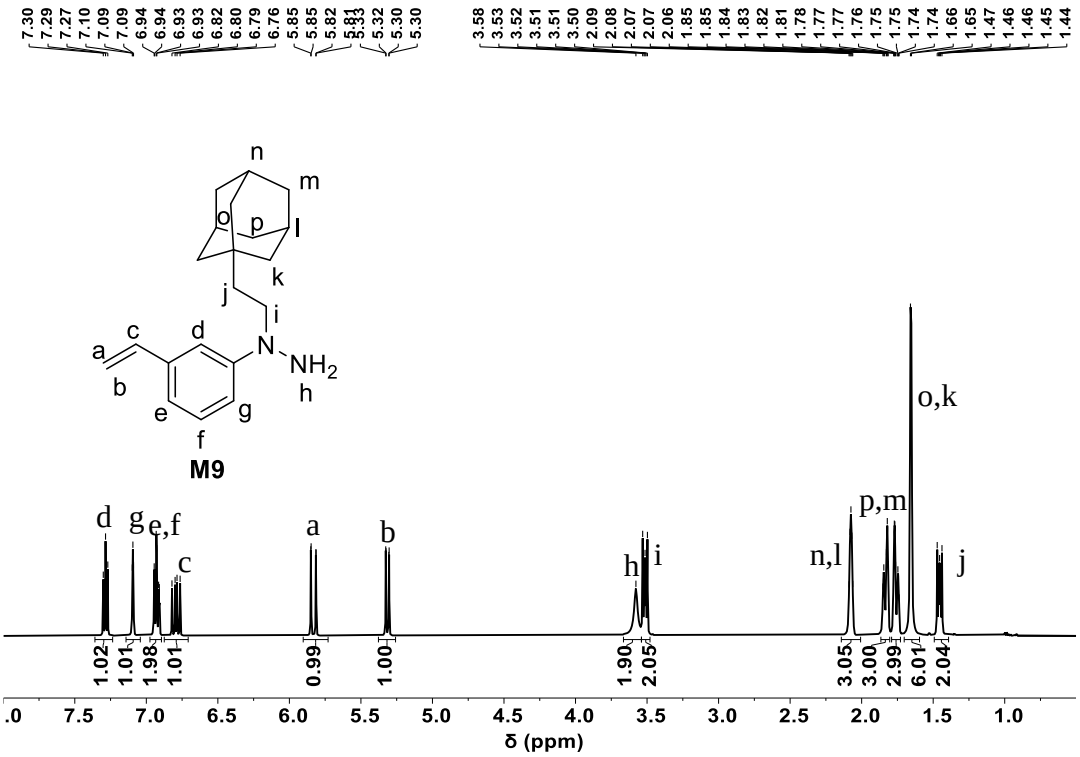


Figure S48. ^{1}H NMR (500 MHz) spectrum of **M9** measured in $CDCl_3$ at 25 °C.

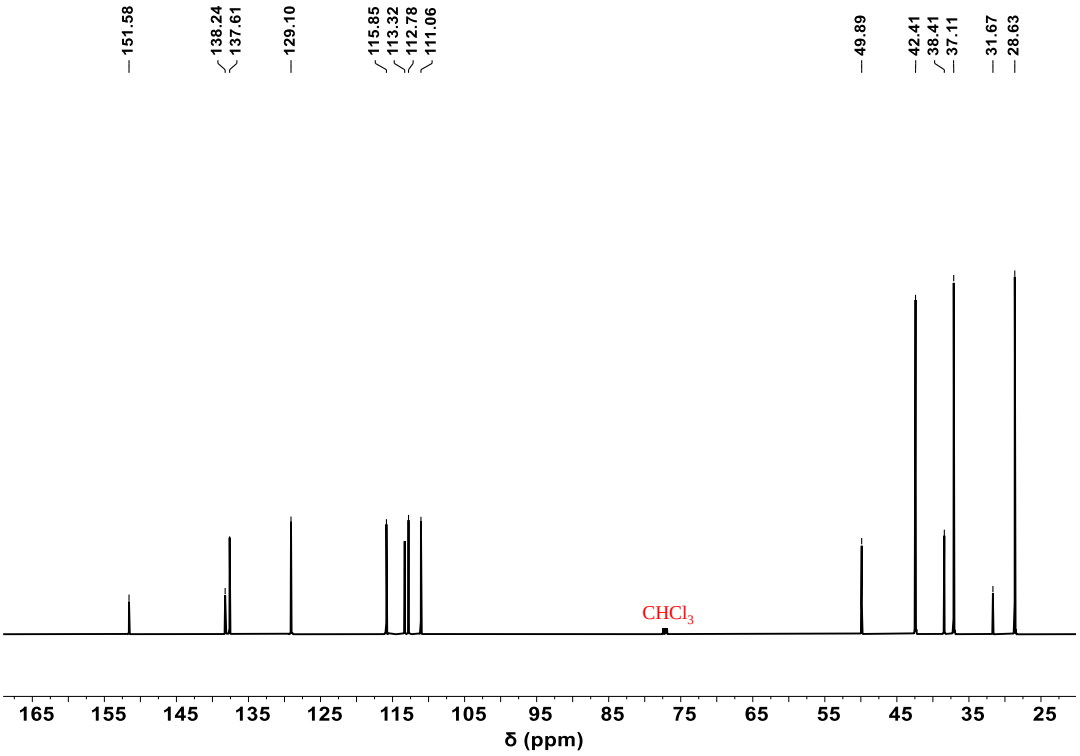


Figure S49. ^{13}C NMR (125 MHz) spectrum of **M9** measured in $CDCl_3$ at 25 °C.

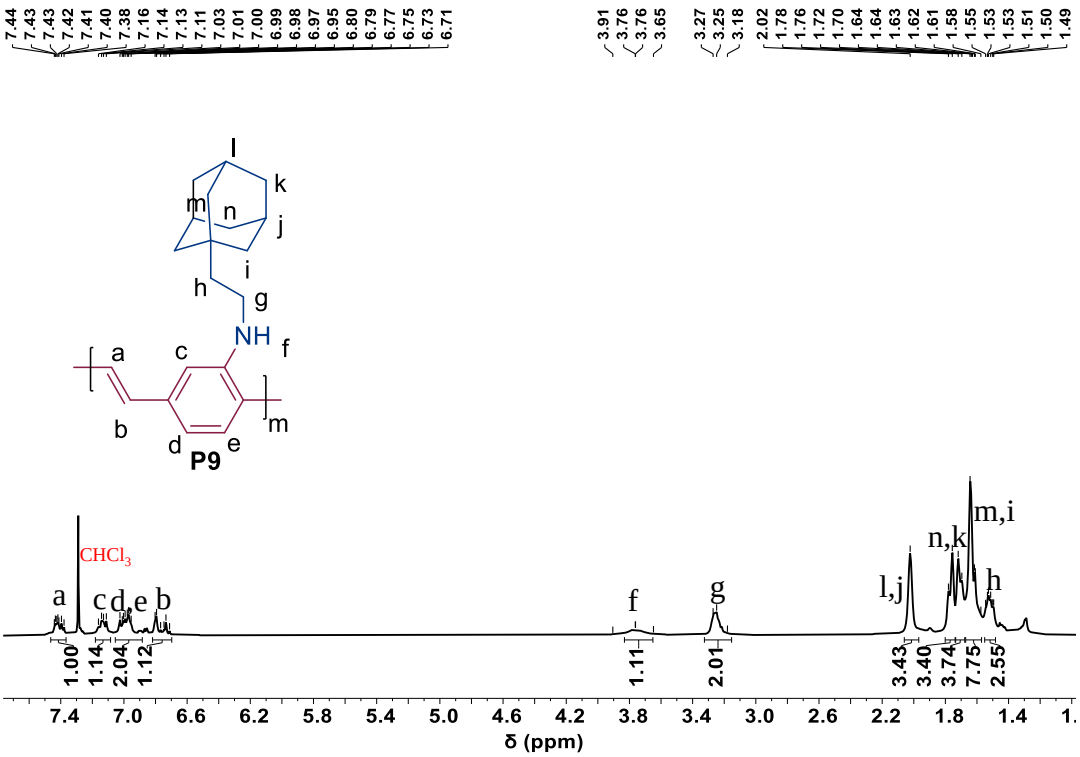


Figure S50. ^{1}H NMR (500 MHz) spectrum of **P9** measured in $CDCl_3$ at 25 °C.

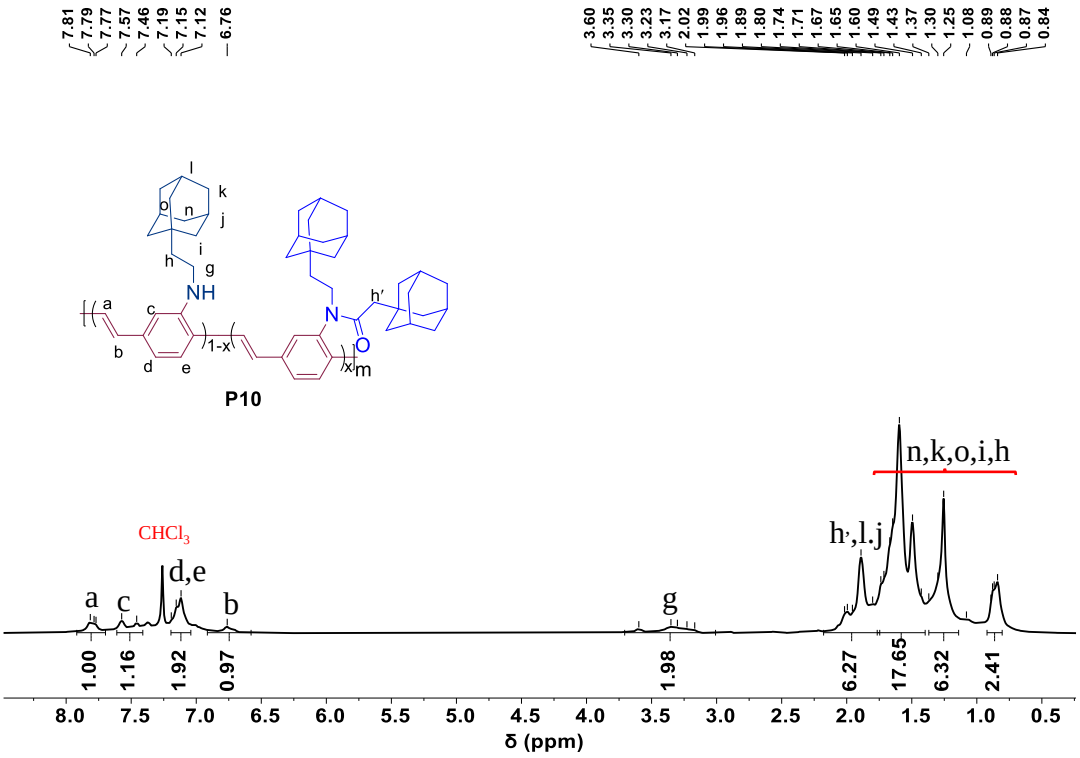


Figure S51. ^{1}H NMR (400 MHz) spectrum of **P10** measured in $CDCl_3$ at 25 °C.

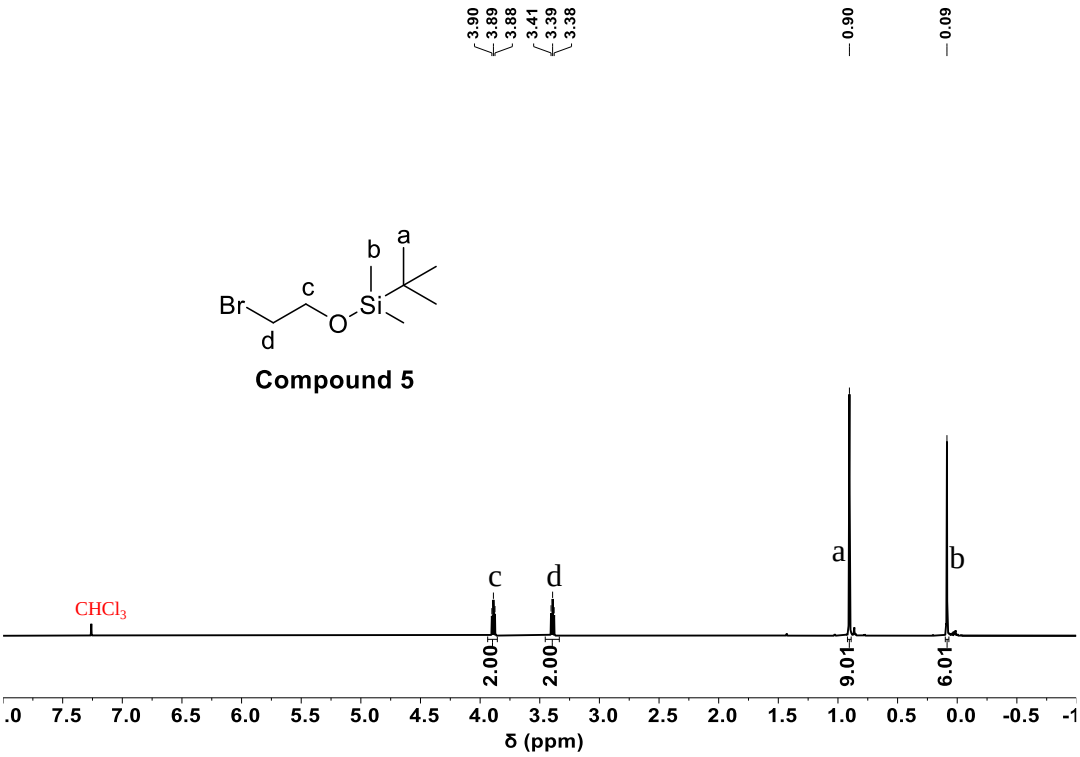


Figure S52. ^{1}H NMR (500 MHz) spectrum of Compound **5** measured in $CDCl_3$ at 25 °C.

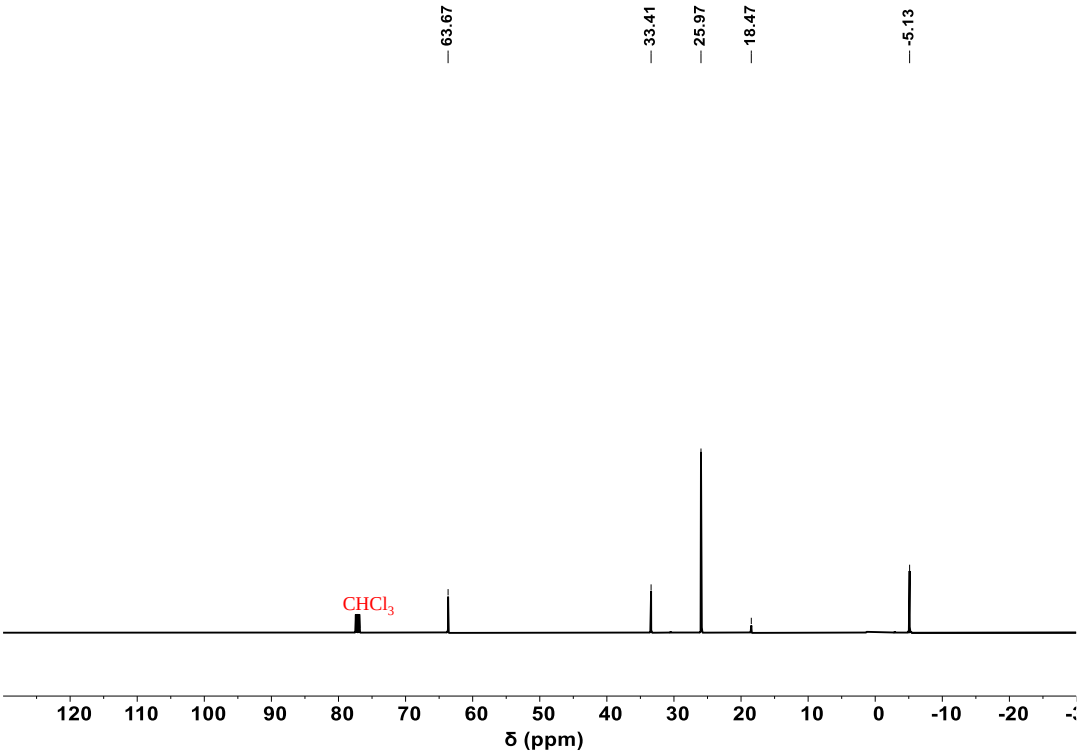


Figure S53. ^{13}C NMR (125 MHz) spectrum of Compound **5** measured in $CDCl_3$ at 25 °C.

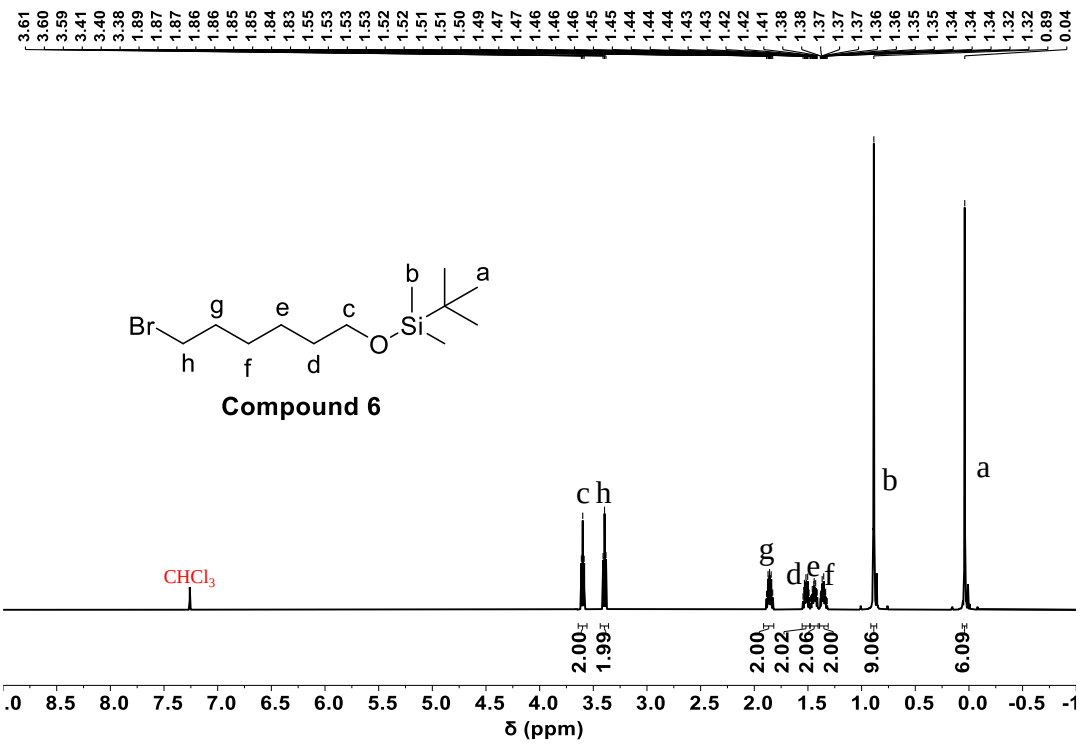


Figure S54. ^{1}H NMR (500 MHz) spectrum of Compound **6** measured in $CDCl_3$ at 25 °C.

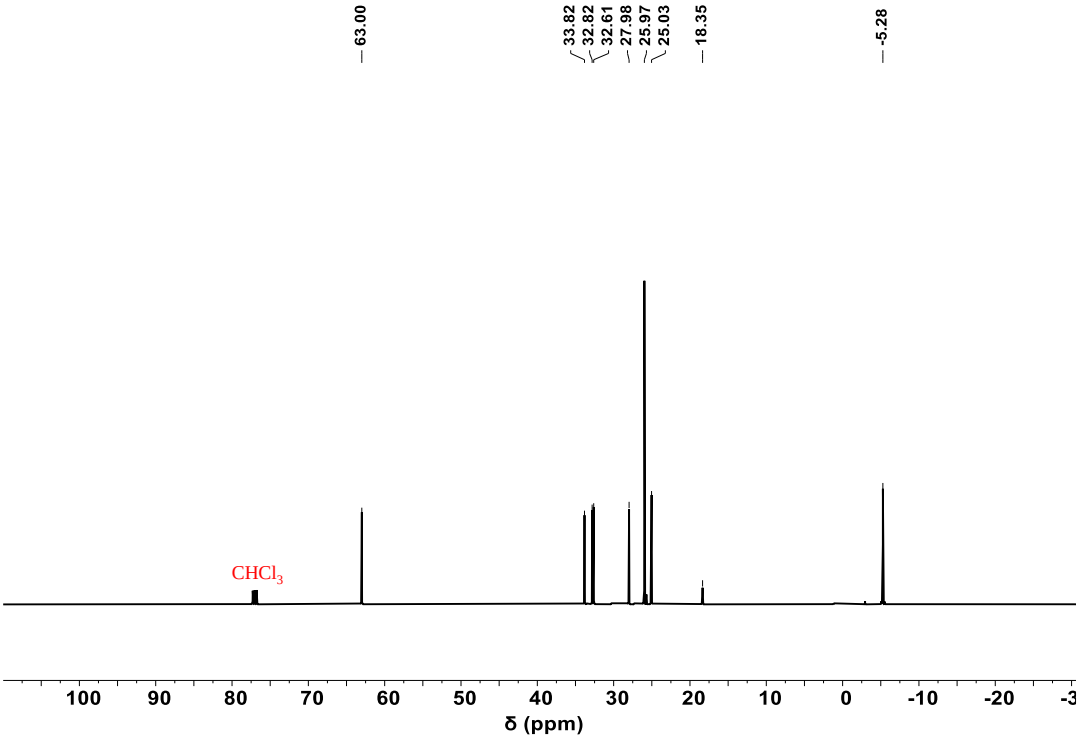


Figure S55. ^{13}C NMR (125 MHz) spectrum of Compound **6** measured in $CDCl_3$ at 25 °C.

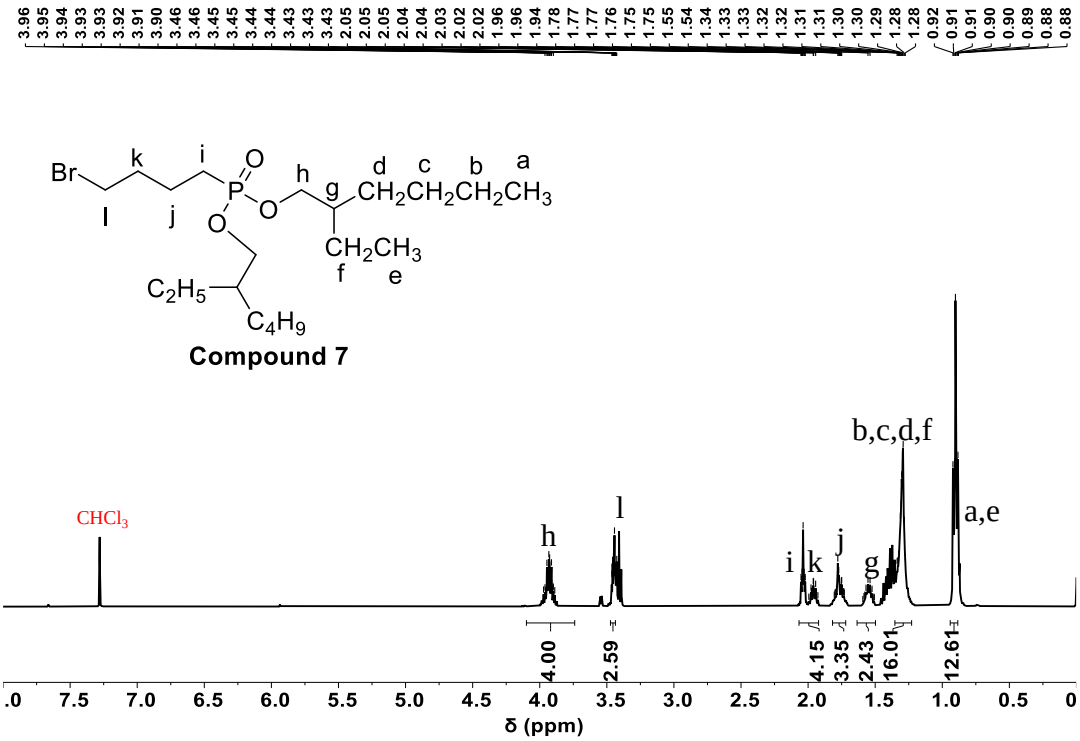


Figure S56.^{1}H NMR (400 MHz) spectrum of Compound **7** measured in $CDCl_3$ at 25 °C.

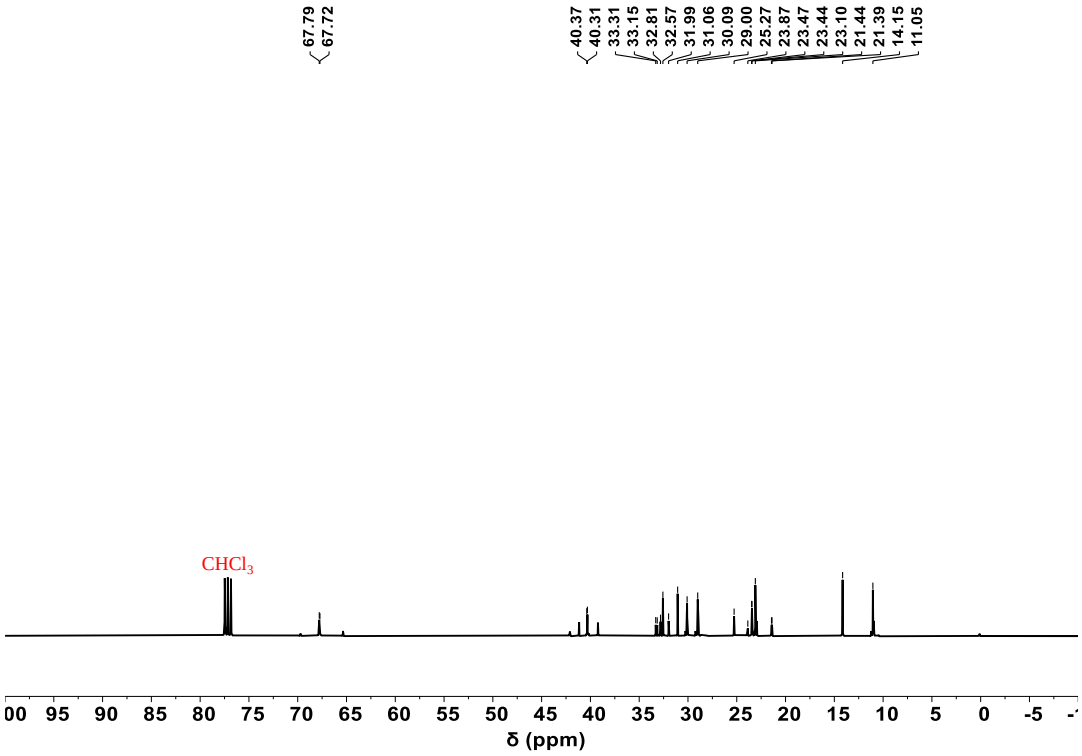


Figure S57. ^{13}C NMR (100 MHz) spectrum of Compound **7** measured in $CDCl_3$ at 25 °C.

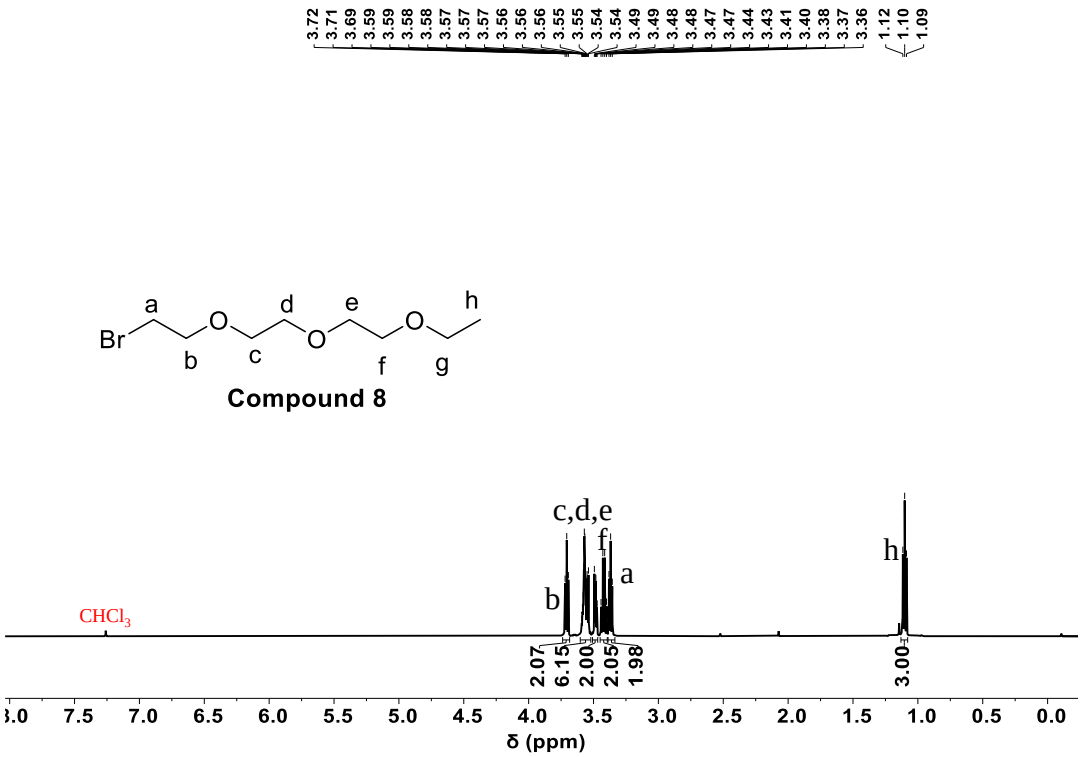


Figure S58. ^{1}H NMR (500 MHz) spectrum of Compound **8** measured in $CDCl_3$ at 25 °C.

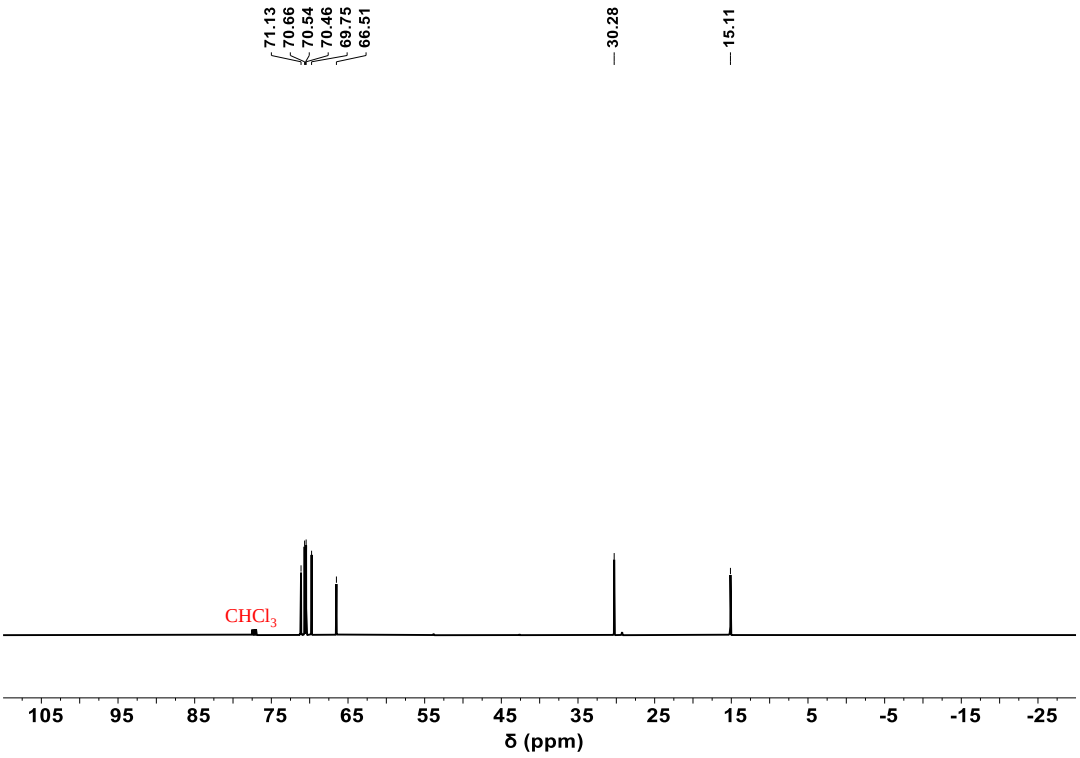


Figure S59. ^{13}C NMR (125 MHz) spectrum of Compound **8** measured in $CDCl_3$ at 25 °C.

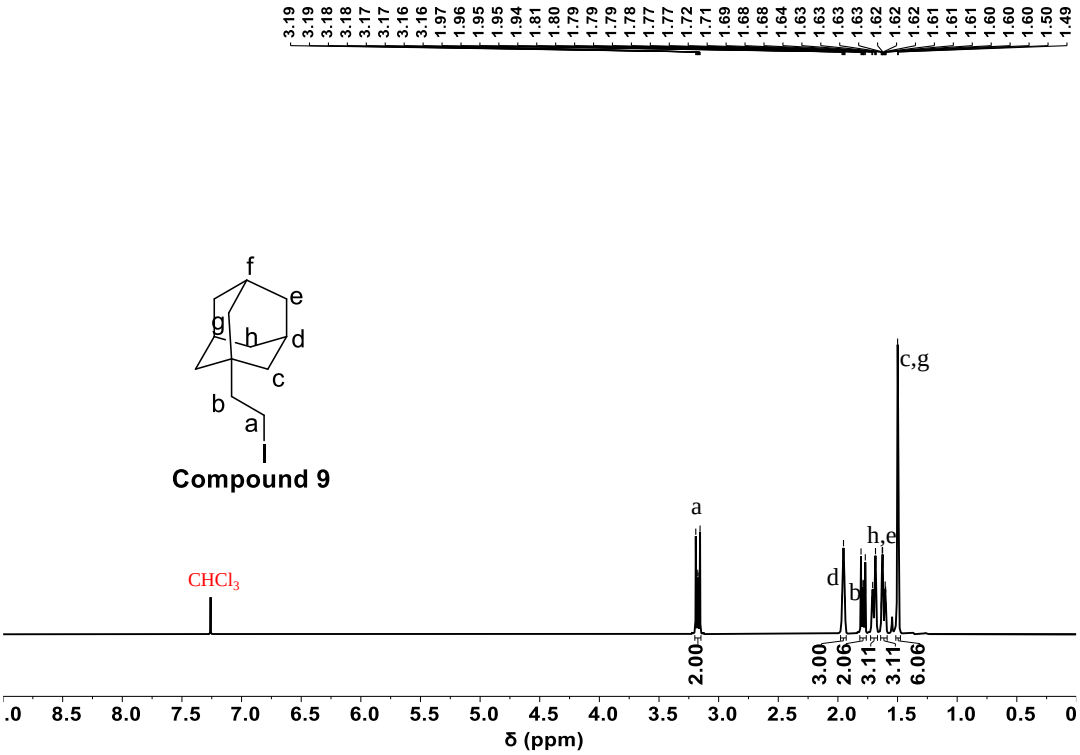


Figure S60. ^{1}H NMR (500 MHz) spectrum of Compound **9** measured in $CDCl_3$ at 25 °C.

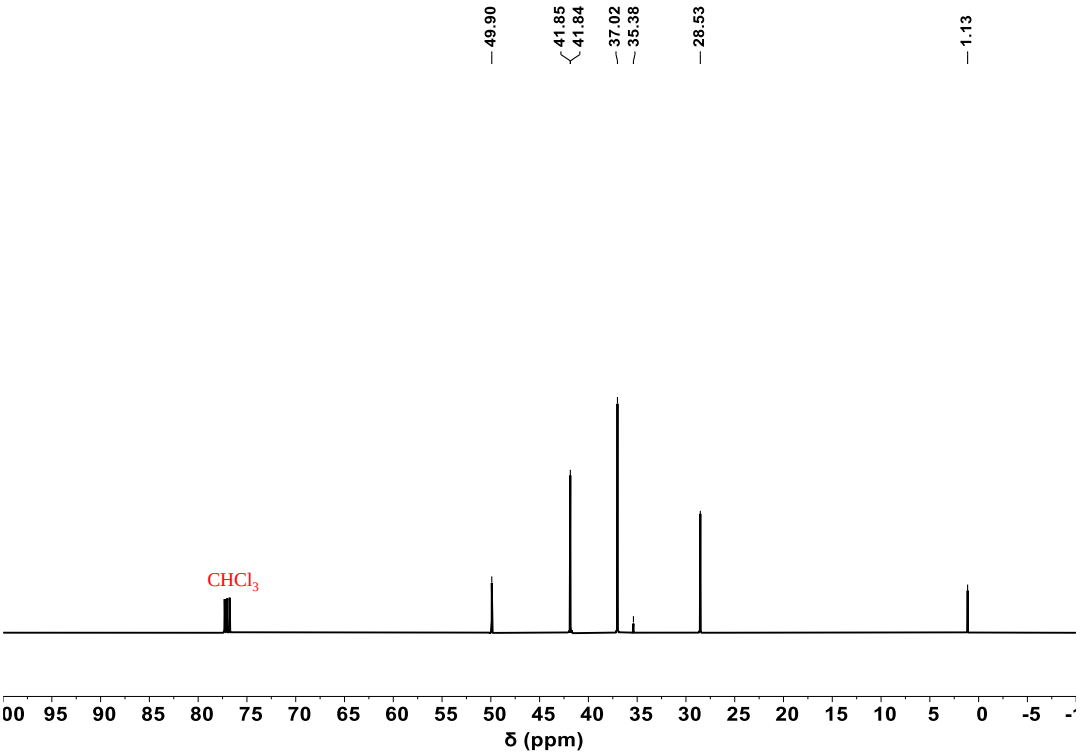


Figure S61. ^{13}C NMR (125 MHz) spectrum of Compound **9** measured in $CDCl_3$ at 25 °C.

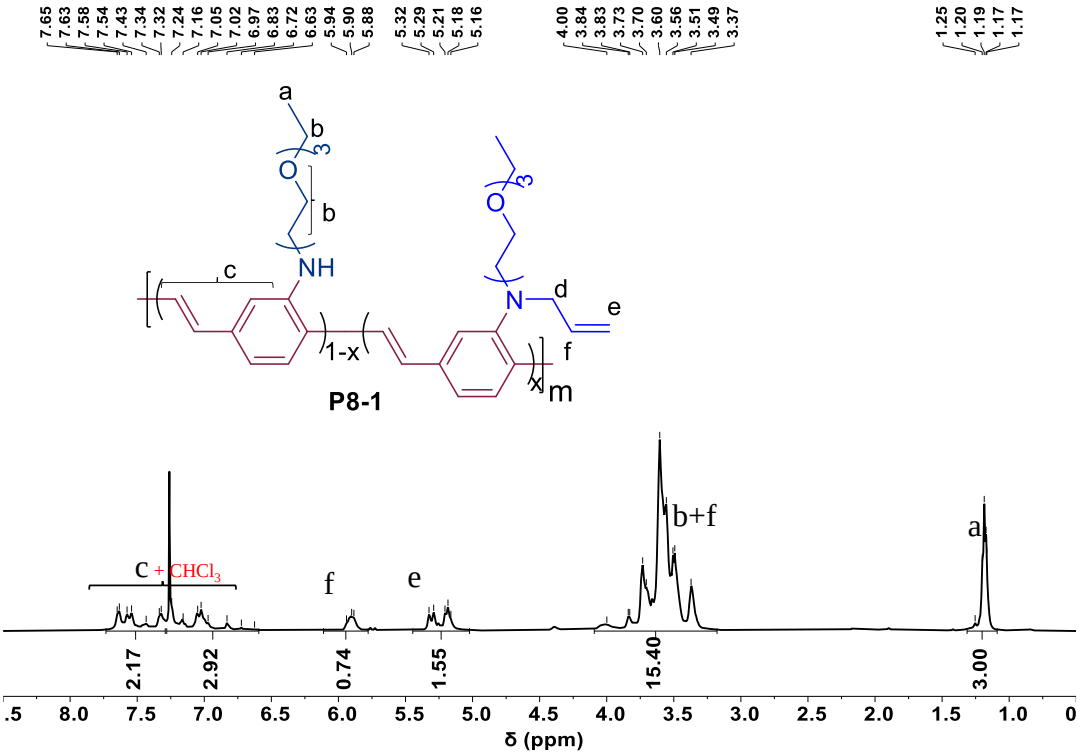


Figure S62. ^{1}H NMR (500 MHz) spectrum of **P8-1** measured in $CDCl_3$ at 25 °C.

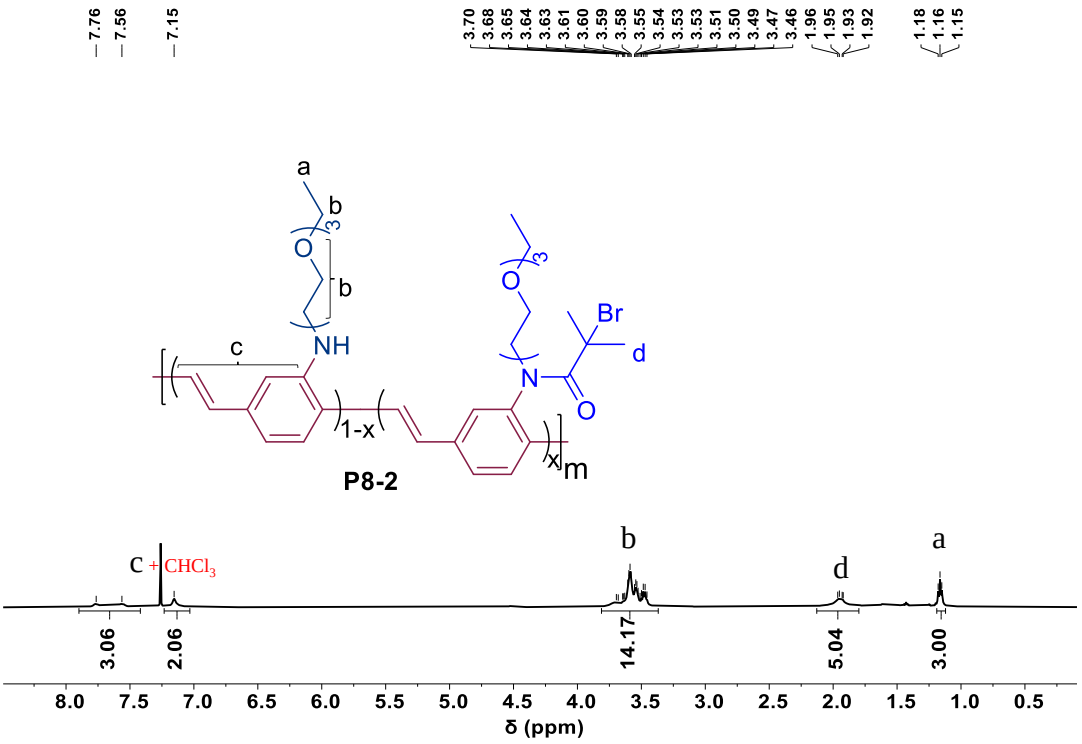


Figure S63. ^{1}H NMR (500 MHz) spectrum of **P8-2** measured in $CDCl_3$ at 25 °C.

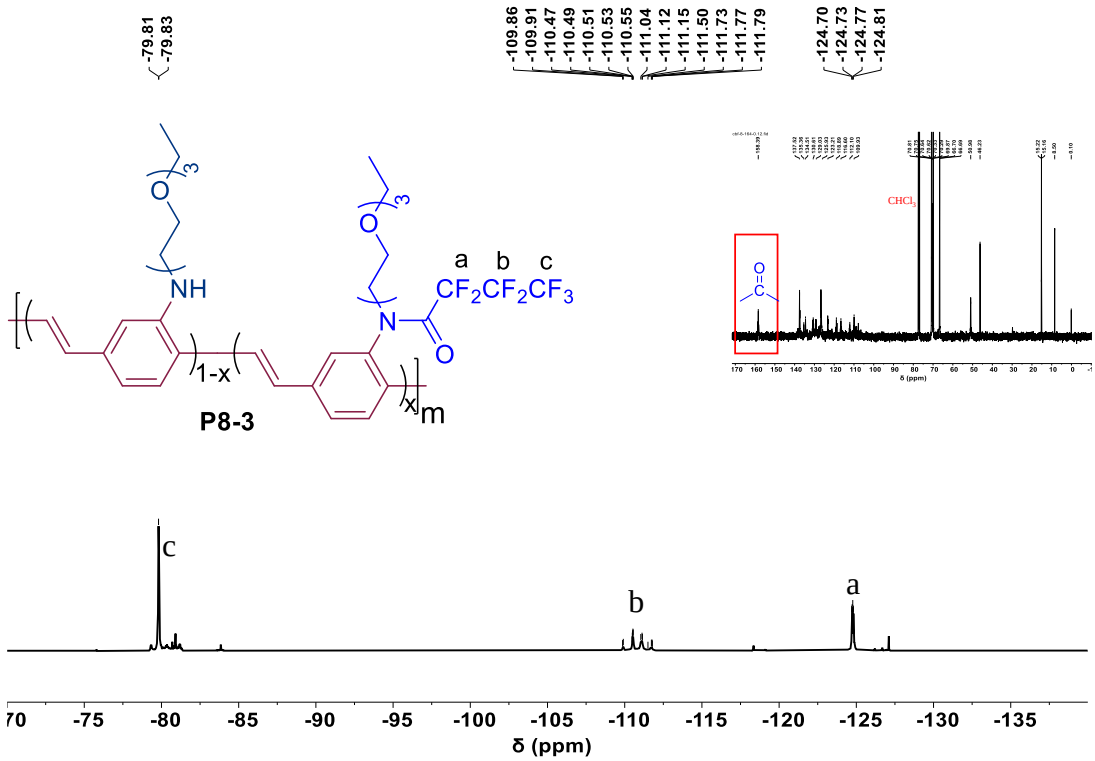


Figure S64. ^{19}F NMR (500 MHz) and ^{13}C NMR (125 MHz) spectrum of **P8-3** measured in $CDCl_3$ at 25 °C

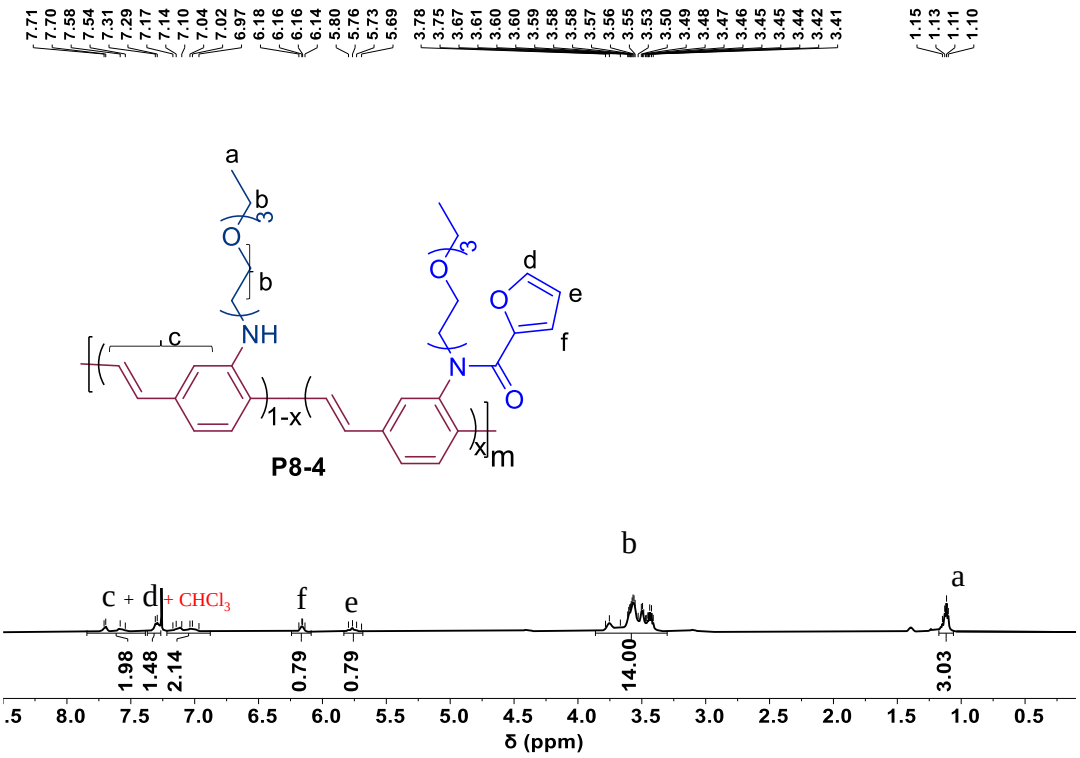


Figure S65. ^{1}H NMR (500 MHz) spectrum of **P8-4** measured in $CDCl_3$ at 25 °C.

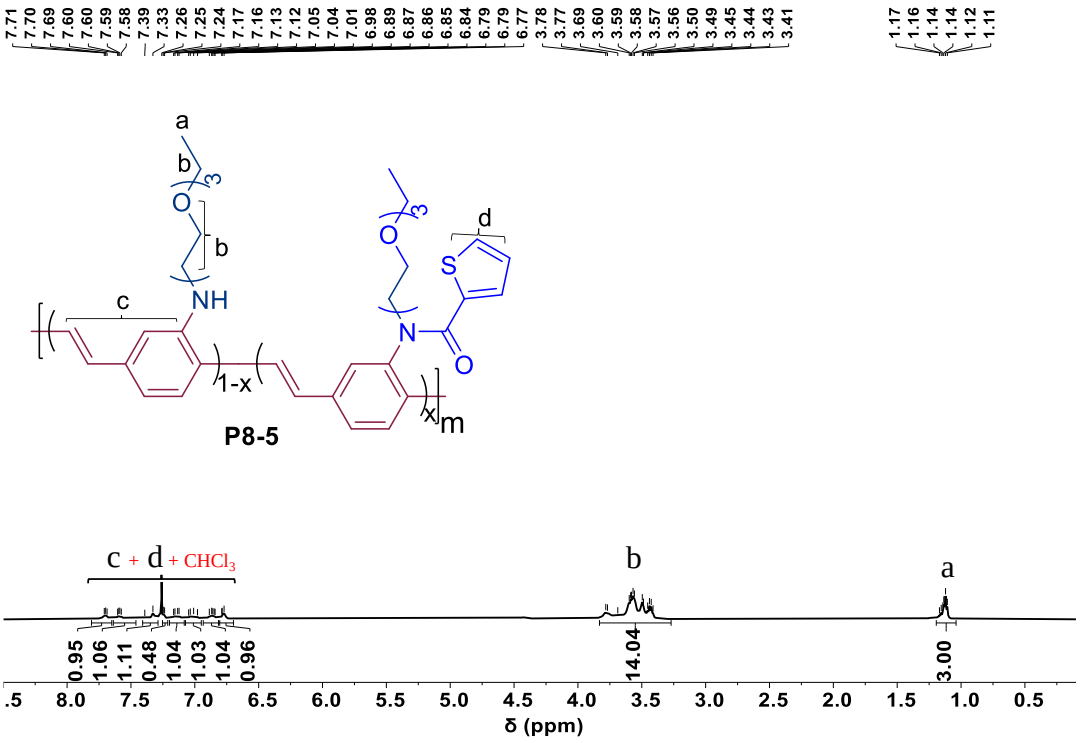


Figure S66. ^{1}H NMR (500 MHz) spectrum of **P8-5** measured in $CDCl_3$ at 25 °C.

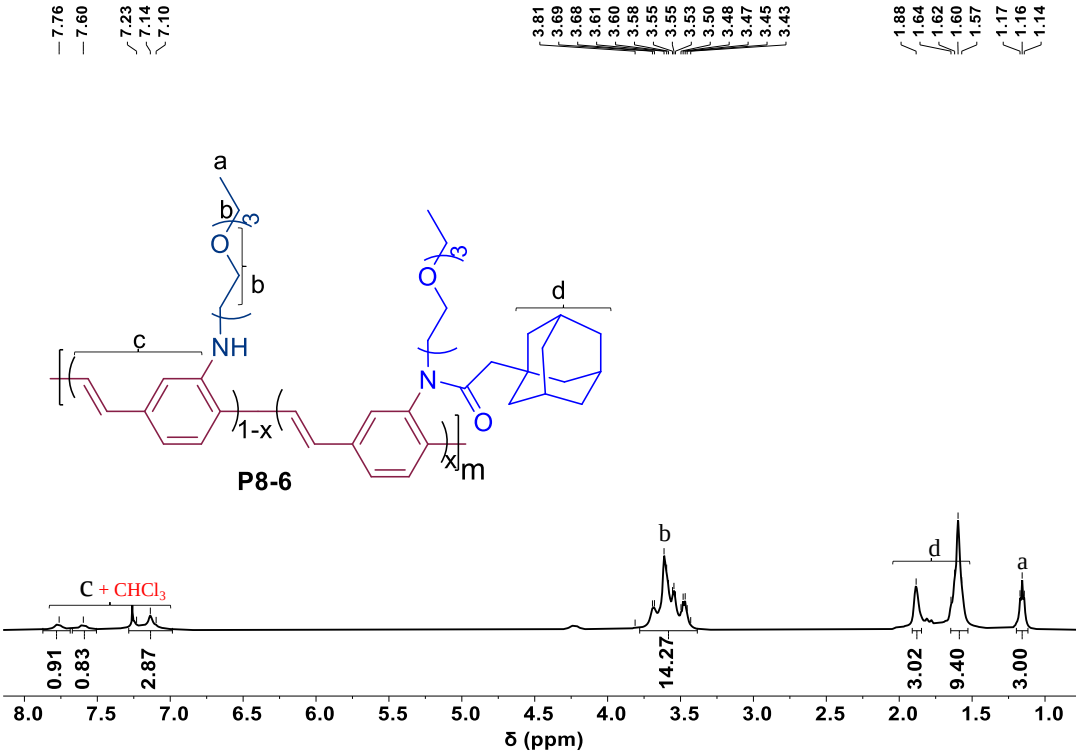


Figure S67. ^{1}H NMR (500 MHz) spectrum of **P8-6** measured in $CDCl_3$ at 25 °C.

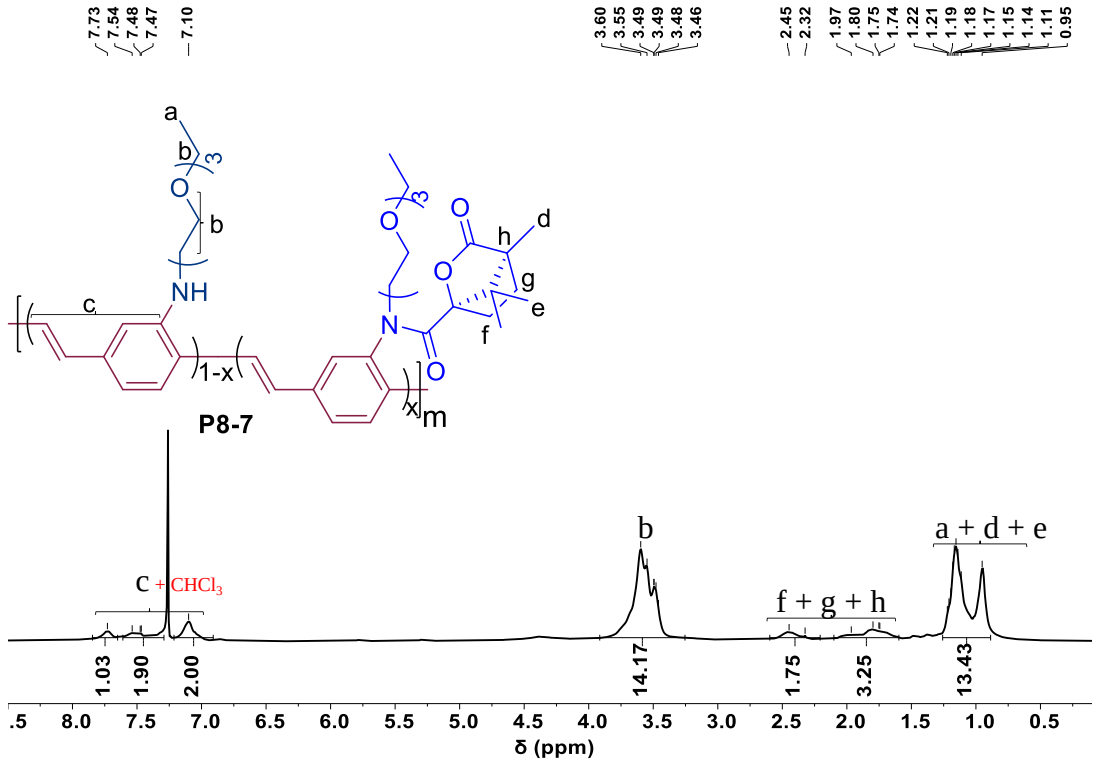


Figure S68. ^{1}H NMR (500 MHz) spectrum of **P8-7** measured in $CDCl_3$ at 25 °C.

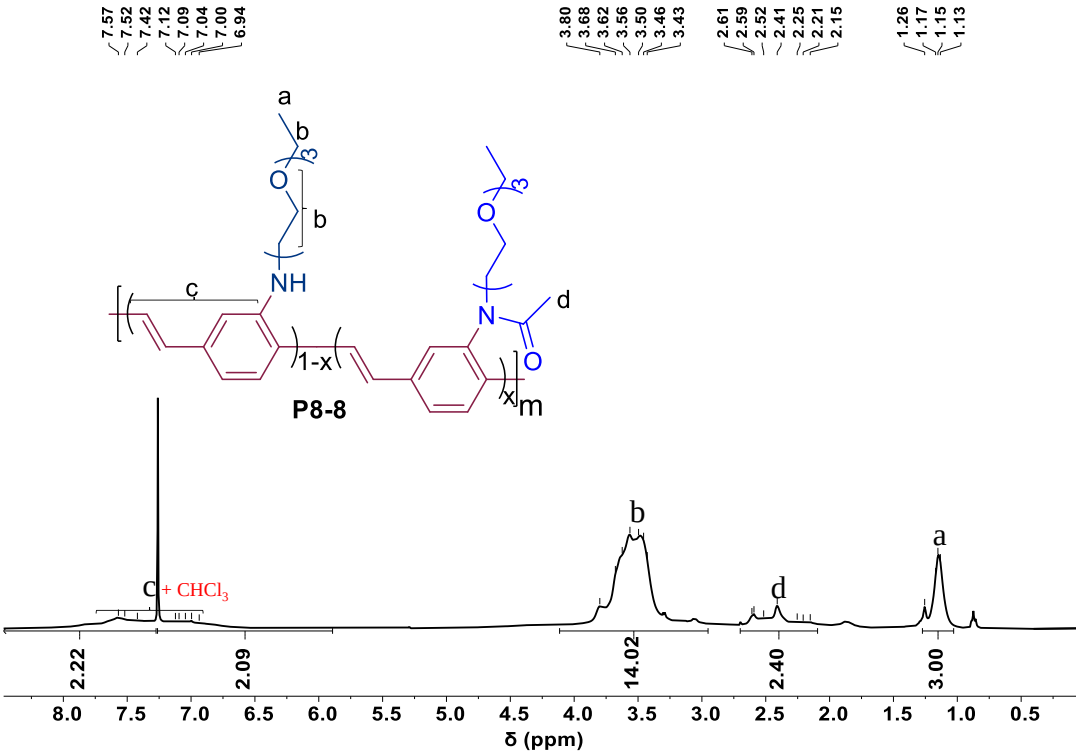


Figure S69. ^{1}H NMR (500 MHz) spectrum of **P8-8** measured in $CDCl_3$ at 25 °C.

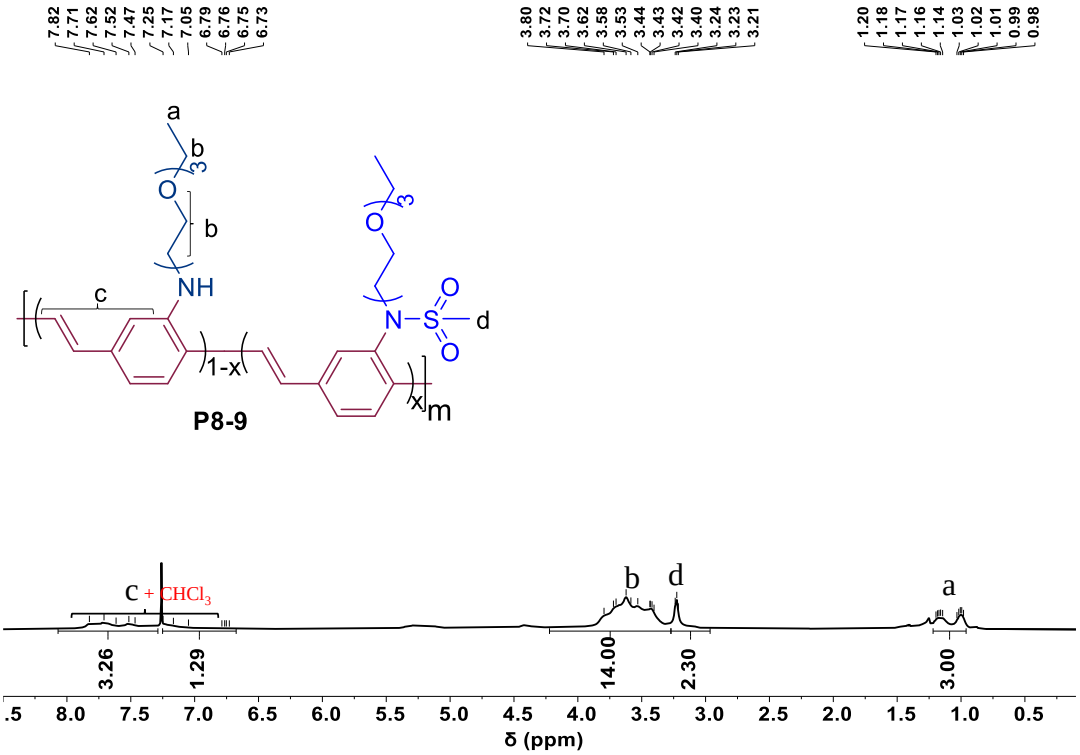


Figure S70. ^{1}H NMR (500 MHz) spectrum of **P8-9** measured in $CDCl_3$ at 25 °C.

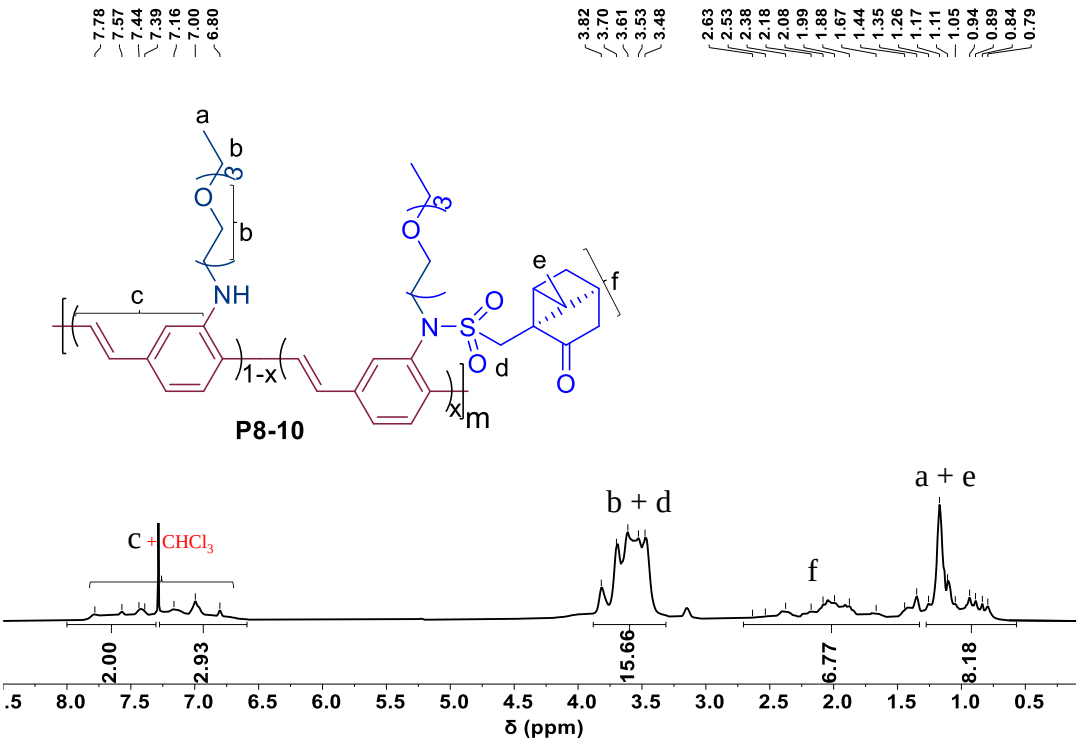


Figure S71. ^{1}H NMR (500 MHz) spectrum of **P8-10** measured in $CDCl_3$ at 25 °C.

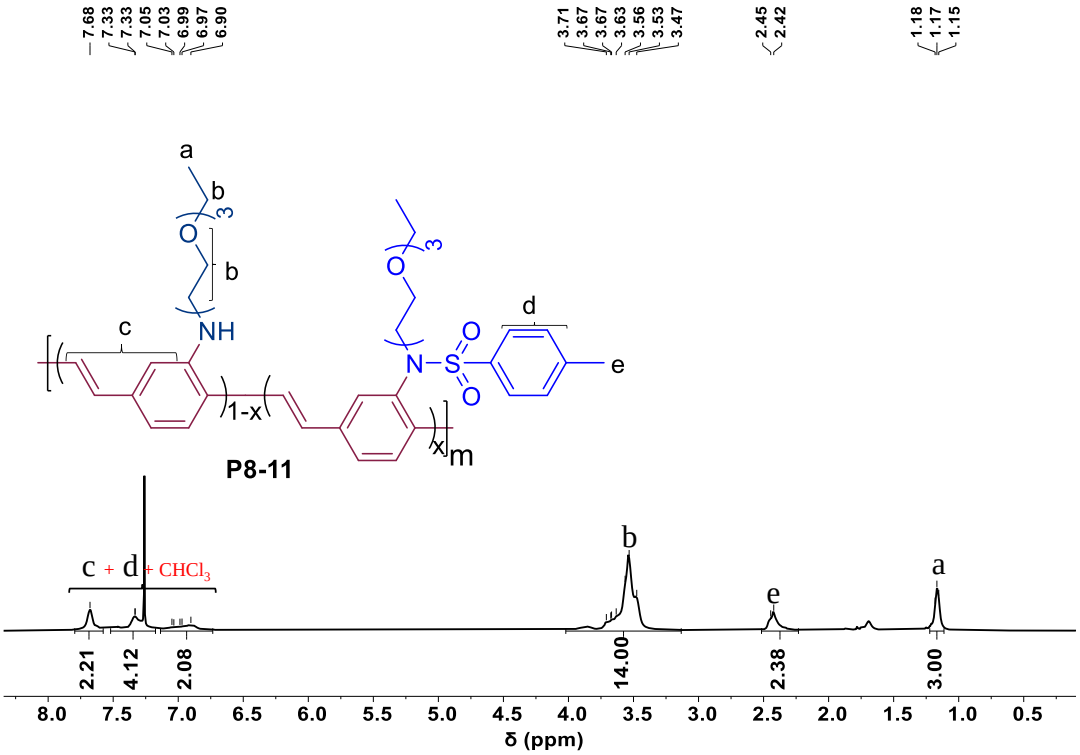


Figure S72. ^{1}H NMR (500 MHz) spectrum of **P8-11** measured in $CDCl_3$ at 25 °C.

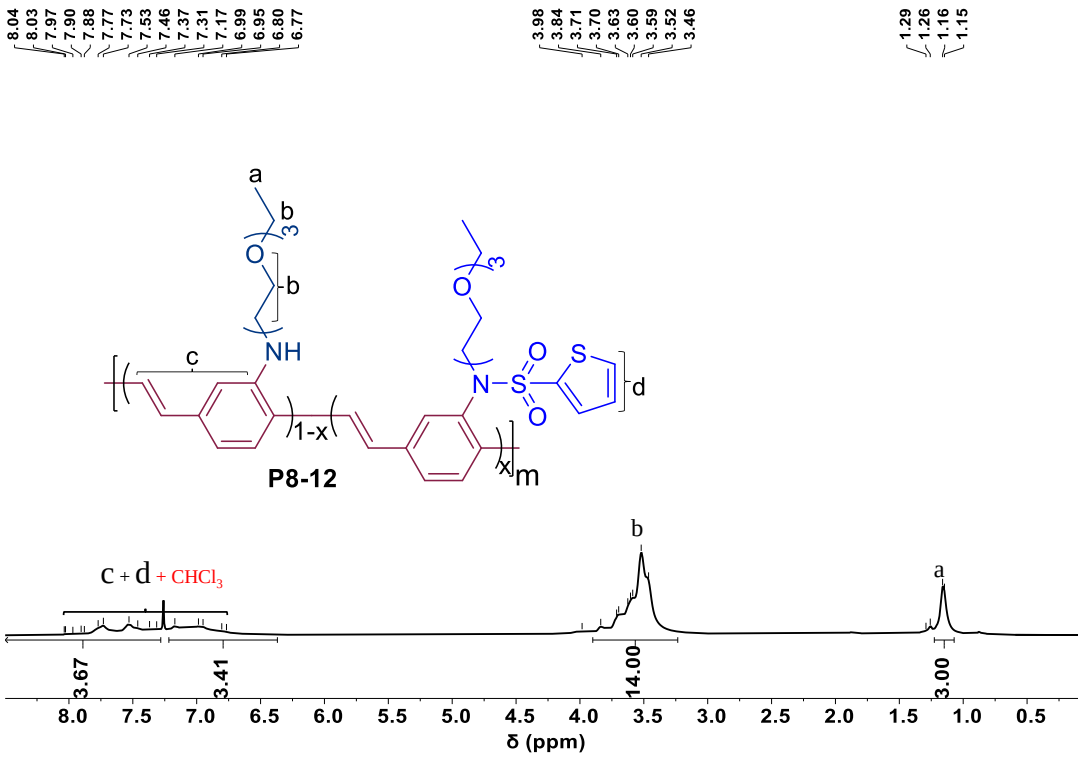


Figure S73. ^{1}H NMR (500 MHz) spectrum of **P8-12** measured in $CDCl_3$ at 25 °C.

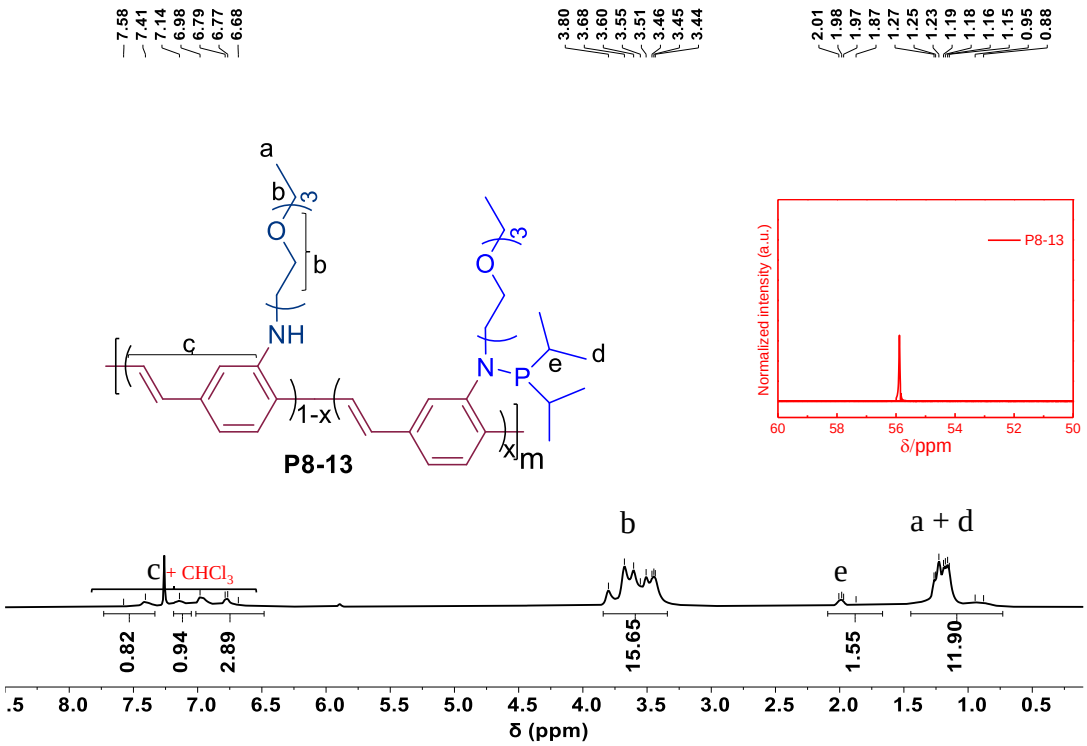


Figure S74. ^{1}H NMR (500 MHz) and ^{31}P NMR (400 MHz, decoupled to ^{1}H) spectrum of **P8-13** measured in $CDCl_3$ at 25 °C.

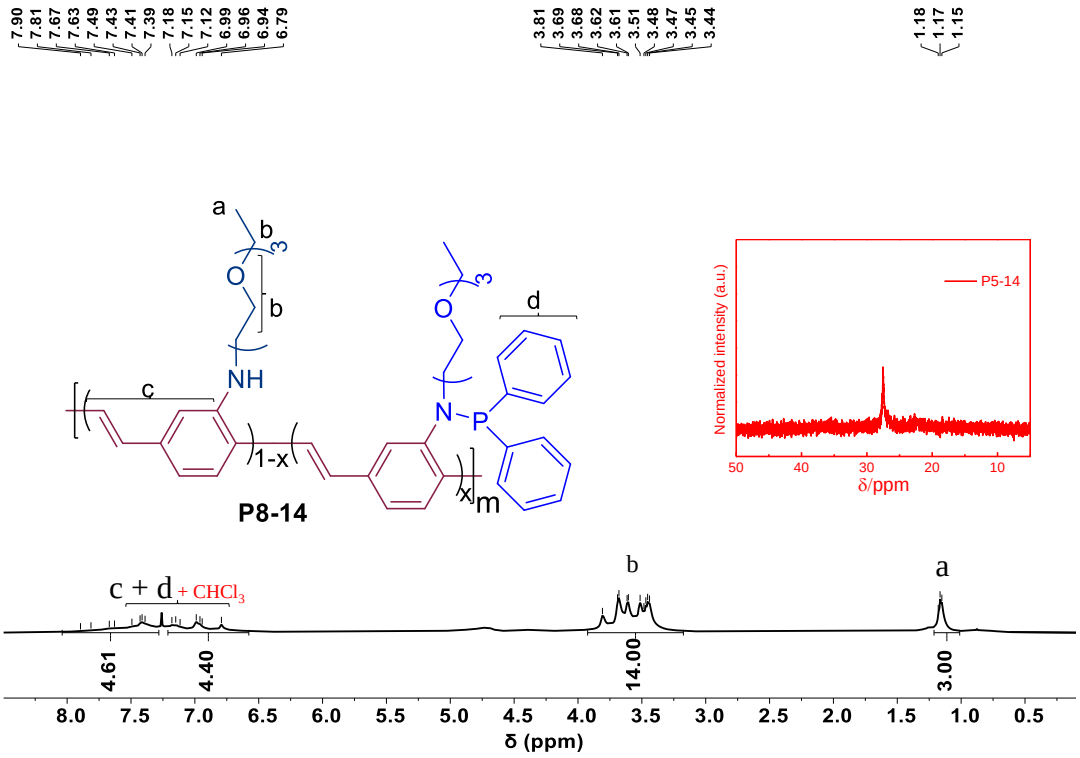


Figure S75. ^{1}H NMR (500 MHz) and ^{31}P NMR (400 MHz, decoupled to ^{1}H) spectrum of **P8-14** measured in $CDCl_3$ at 25 °C.

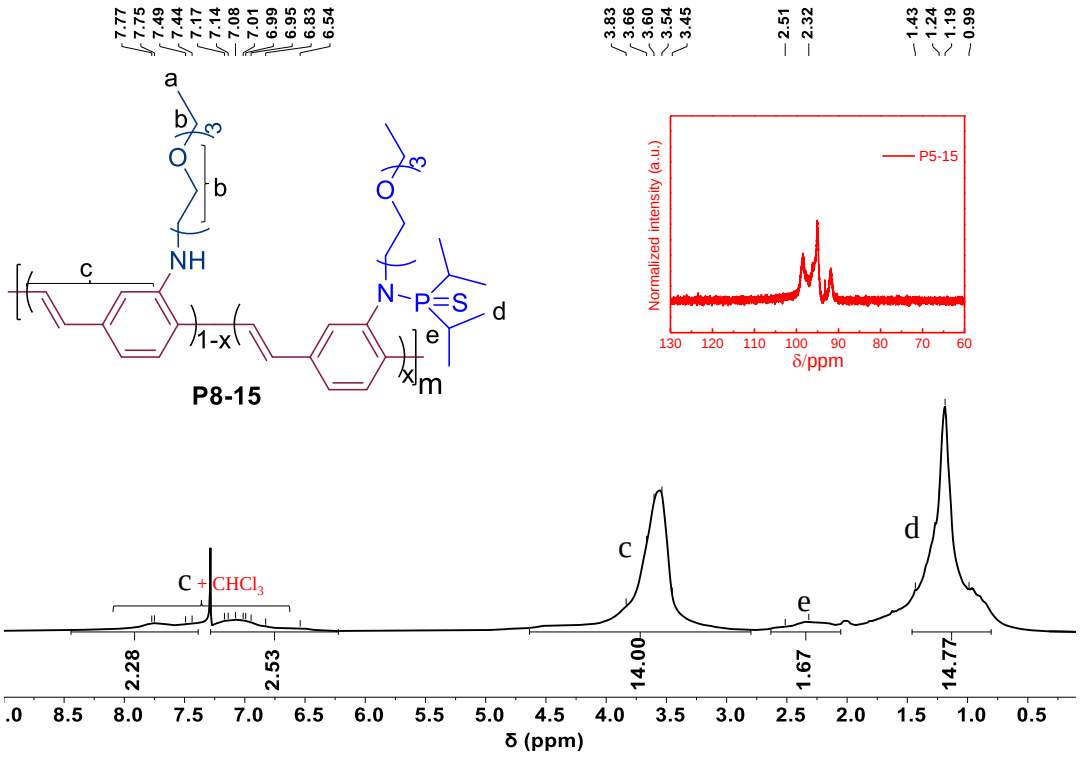


Figure S76. ^{1}H NMR (500 MHz) and ^{31}P NMR (400 MHz, decoupled to ^{1}H) spectrum of **P8-15** measured in $CDCl_3$ at 25 °C.

Table S1. Polymerization of **P8** by using different solvent.

Entry	solvent	M_n[a]	$Đ$[a]	Yield (%)[b]
1	THF	6.3 kDa	1.26	61.3
2	THP	6.8 kDa	1.24	68.1
3	^{t}AmOH	8.1 kDa	1.23	58.2
4	Toluene	9.5 kDa	1.44	78.6
5	CH_3OH: ^{t}AmOH=1:1	8.2 kDa	1.38	73.3
6	CH_3OH: THP=1:1	13.4 kDa	1.43	78.2
7	CH_3OH: THP=2:1	14.3 kDa	1.41	80.3
8	CH_3OH: THP=3:1	17.9 kDa	1.57	82.1
9	CH_3OH	30.1 kDa	1.50	84.7

[a]Determind by DMF size-exclusion chromatography (SEC) calibrated by using polystyrene (PS) standards. [b]Isolated yield after purification by hexane from THF.

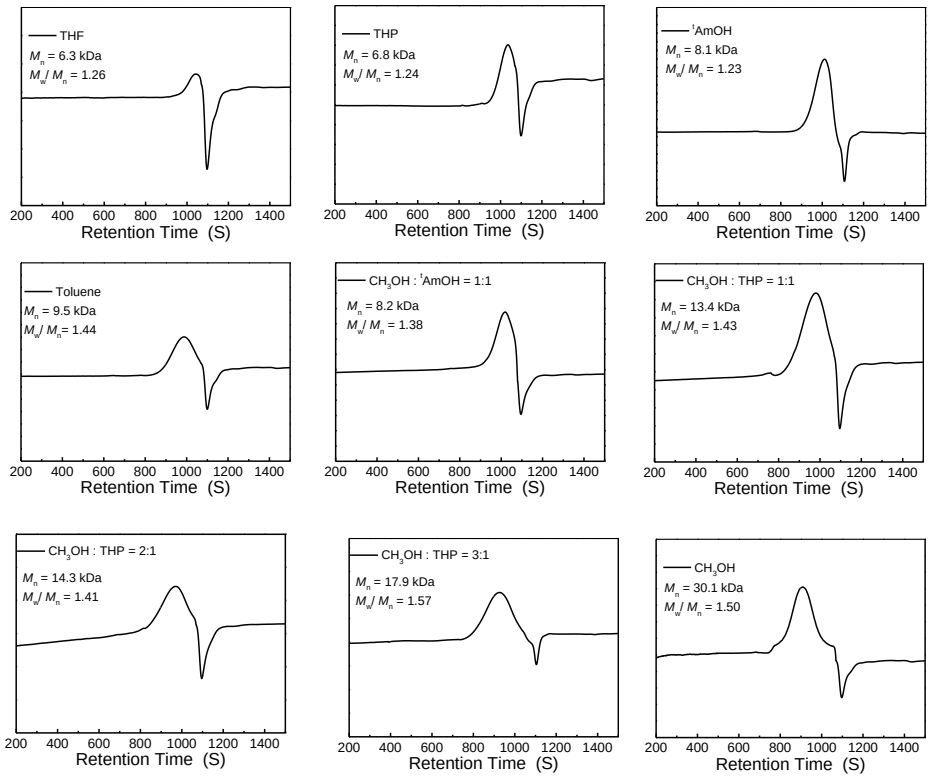


Figure S77. SEC chromatograms of the polymerization of **P8** pared by using different solvents.

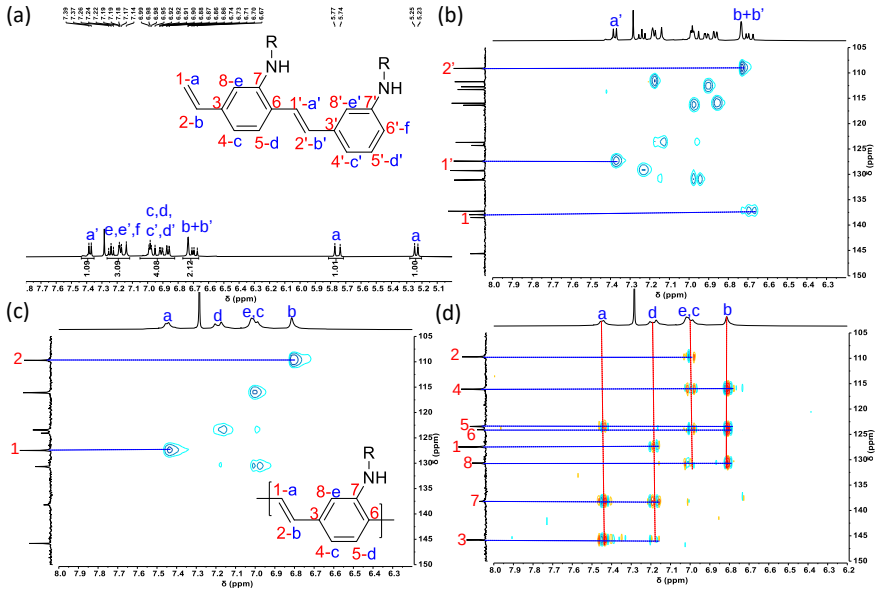


Figure S78.H NMR spectra of Dimer of **M8** (a), HSQC(b); ^{1}H NMR spectra of **P8** HSQC (c), (d) HMBC.

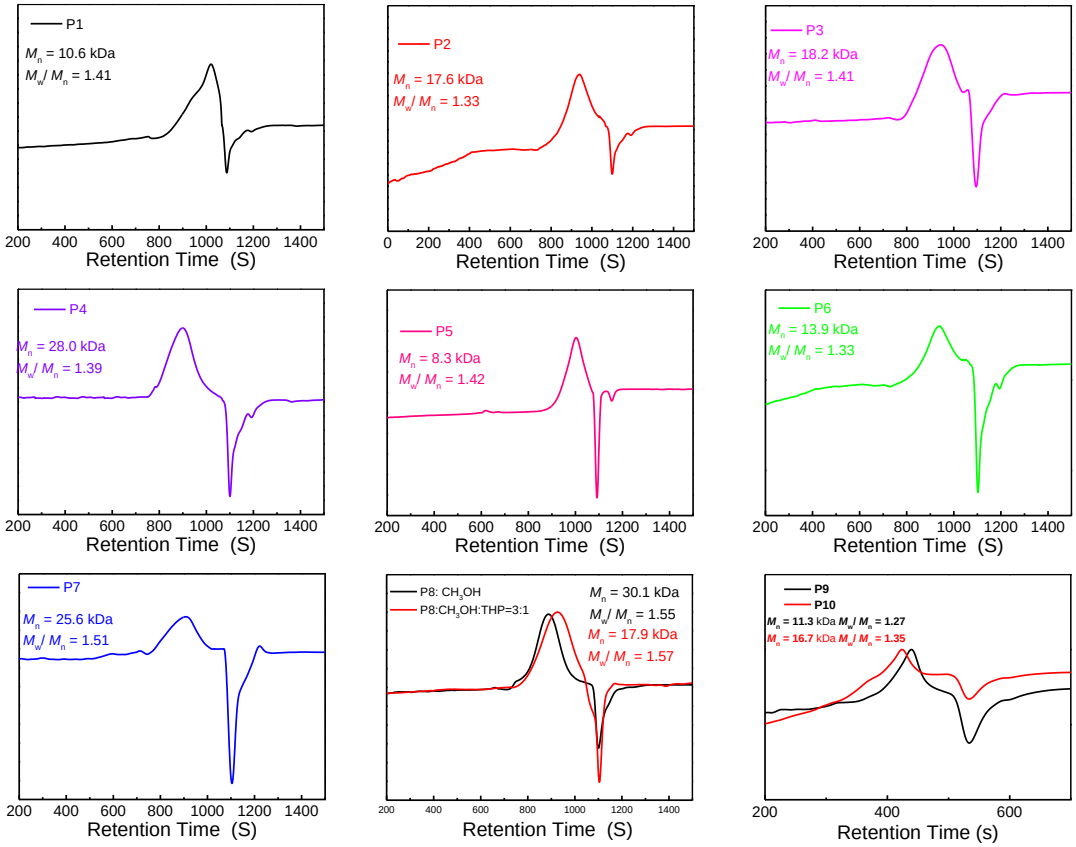


Figure S79. SEC chromatograms of the polymerization of **P1-P8** pared by using different solvents (**P1-P8**: SEC conditions: eluent = DMF; temperature= 35 °C; **P9** and **P10**: SEC conditions: eluent = DMSO; temperature= 50 °C; Notes: Part of **P9** can precipitate during the polymerization process; **P9** and **P10** failed to pass 0.22 μm filter membrane before the test, and a small amount of chloroform and DMSO was used to dissolve the sample before injection).

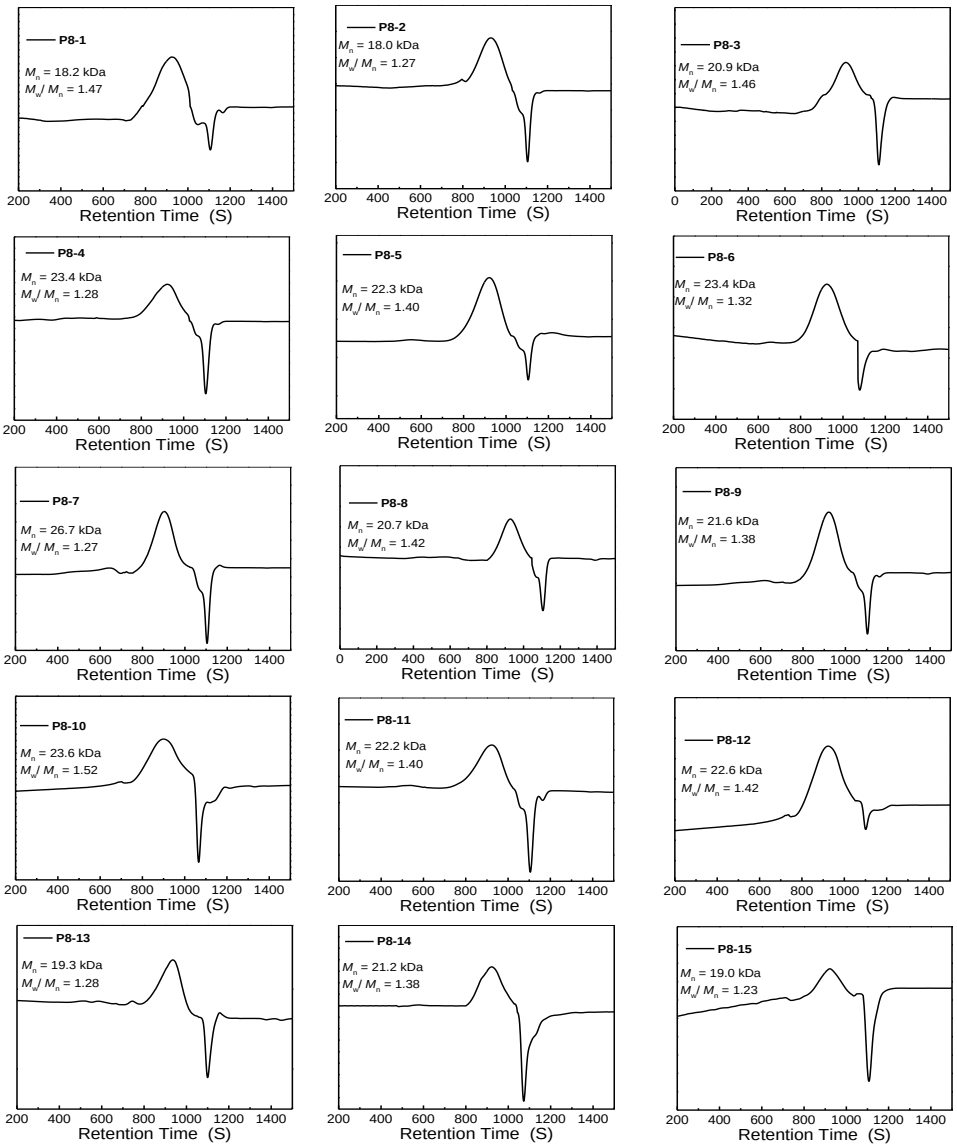


Figure S80. SEC chromatograms of the **P8-N** (SEC conditions: eluent = DMF; temperature= 35 °C).

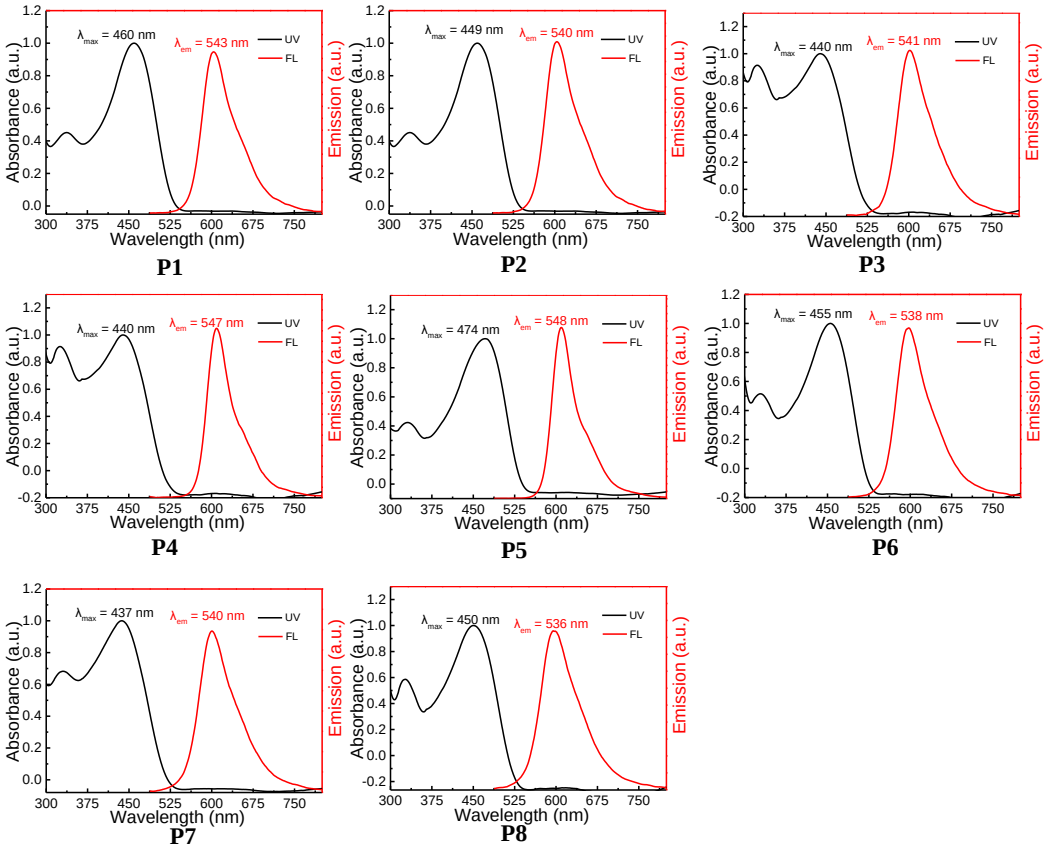


Figure S81. UV−vis absorption and emission spectral measured in THF solution of **P1-P8** (c = 0.1 g/L; excitation wavelength: 440 nm) at 25 °C.

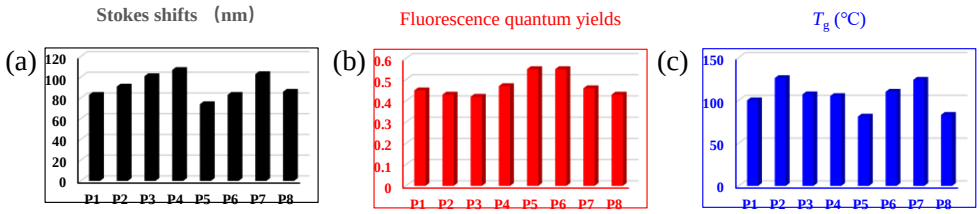


Figure S82. The graph representation of Stokes shifts, fluorescence quantum yields, and T_g of **P1-P8**.

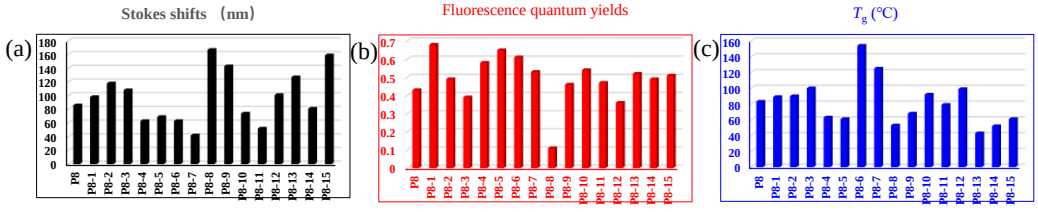


Figure S83. The graph representation of Stokes shifts, fluorescence quantum yields, and T_g of **P8-N**.

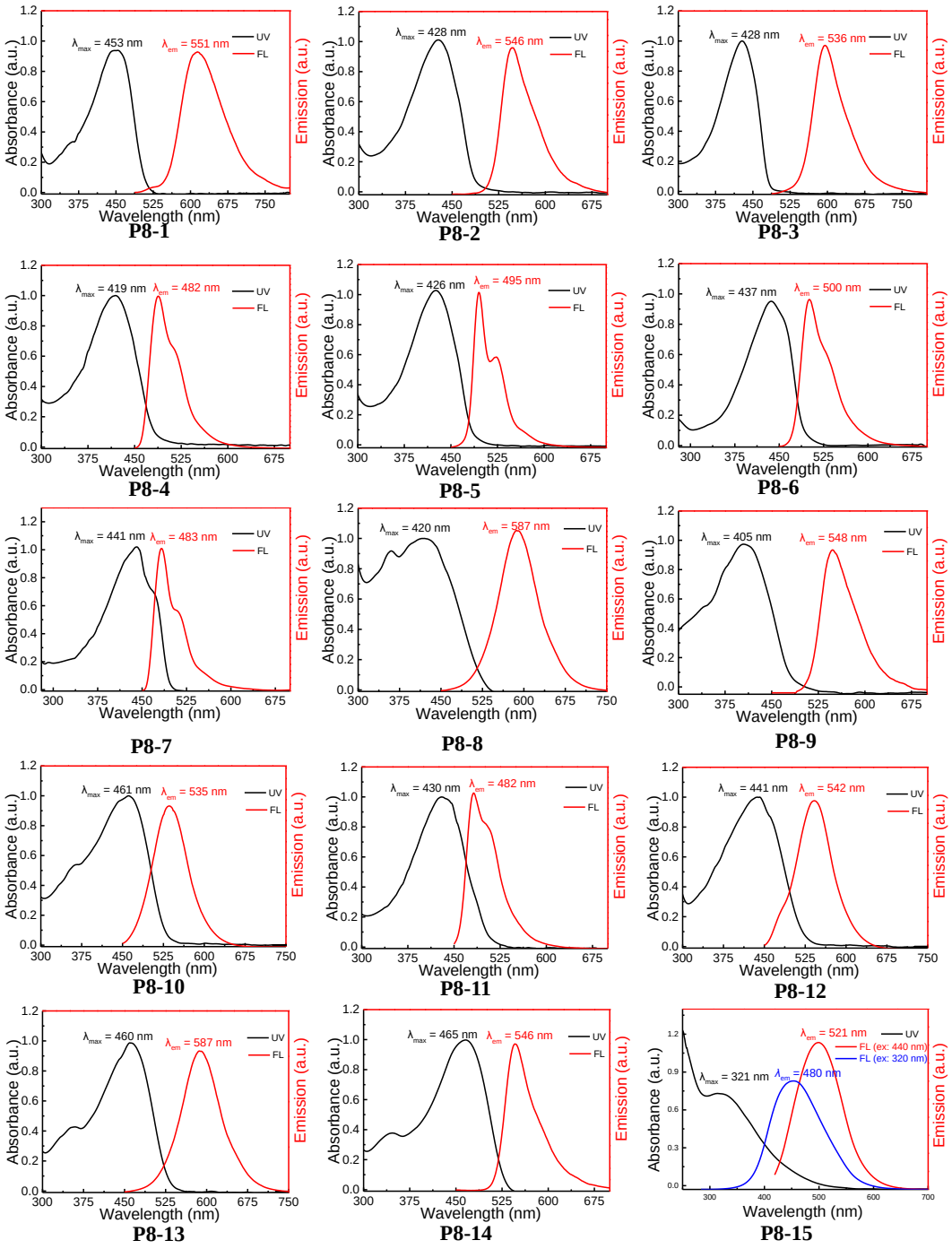


Figure S84. UV−vis absorption and emission spectral measured in THF solution of **P8-N** (c = 0.1 g/L; excitation wavelength: 440 nm) at 25 °C.

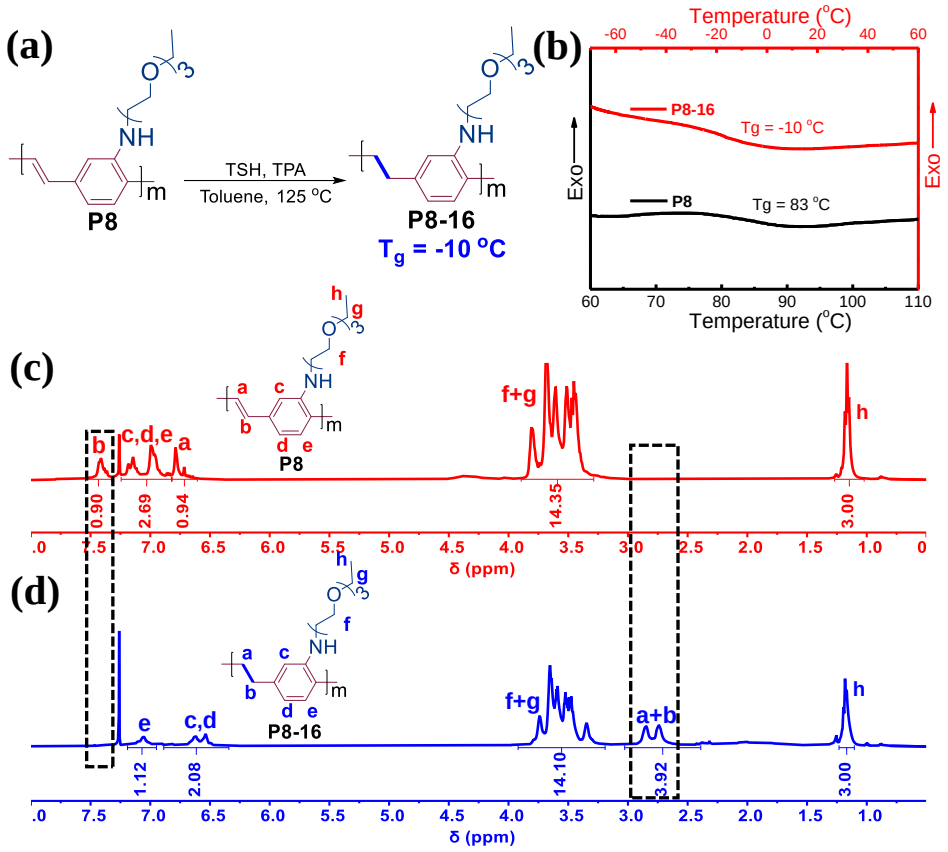


Figure S85 (a) Hydrogenation of **P8** for the synthesis of **P8-16** (TSH: *p*-toluenesulfonyl hydrazide; TPA: tripropylamine). (b) DSC trace of **P8** and **P8-16**. ^{1}H NMR spectra of **P8** (c) and **P8-16** (d) in $CDCl_3$.

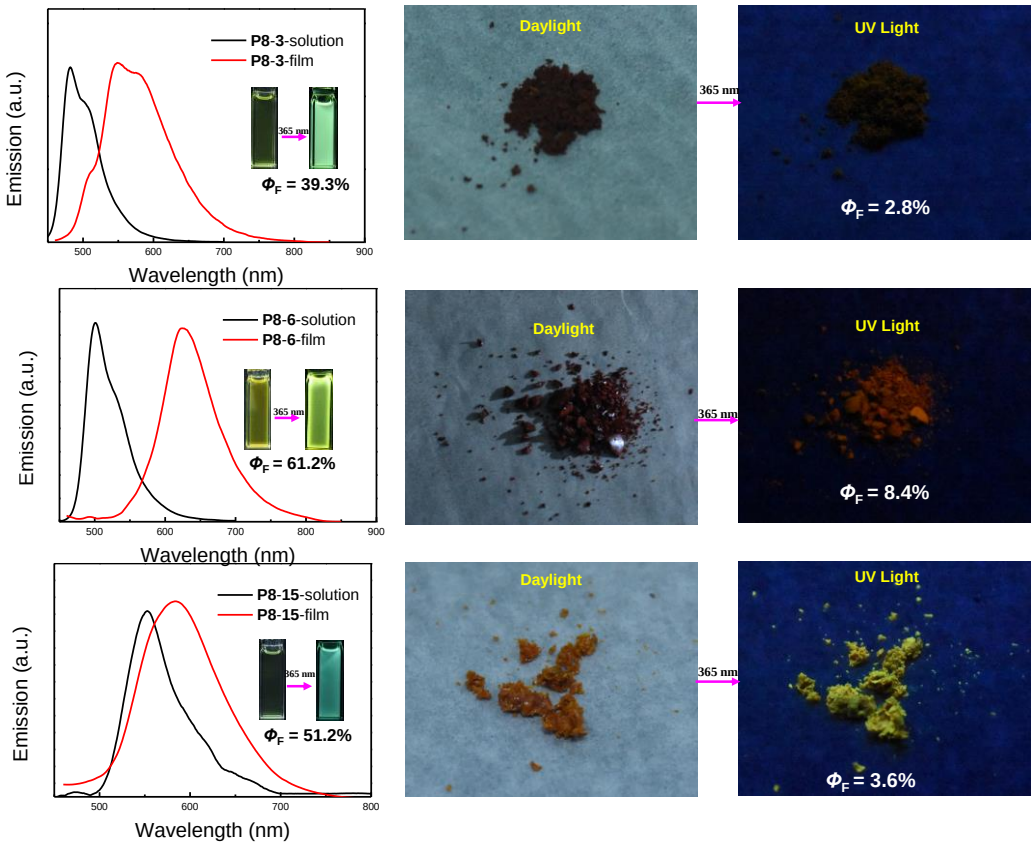


Figure S86. The emission spectral and visual images of **P8-3**, **P8-6**, **P8-15**.

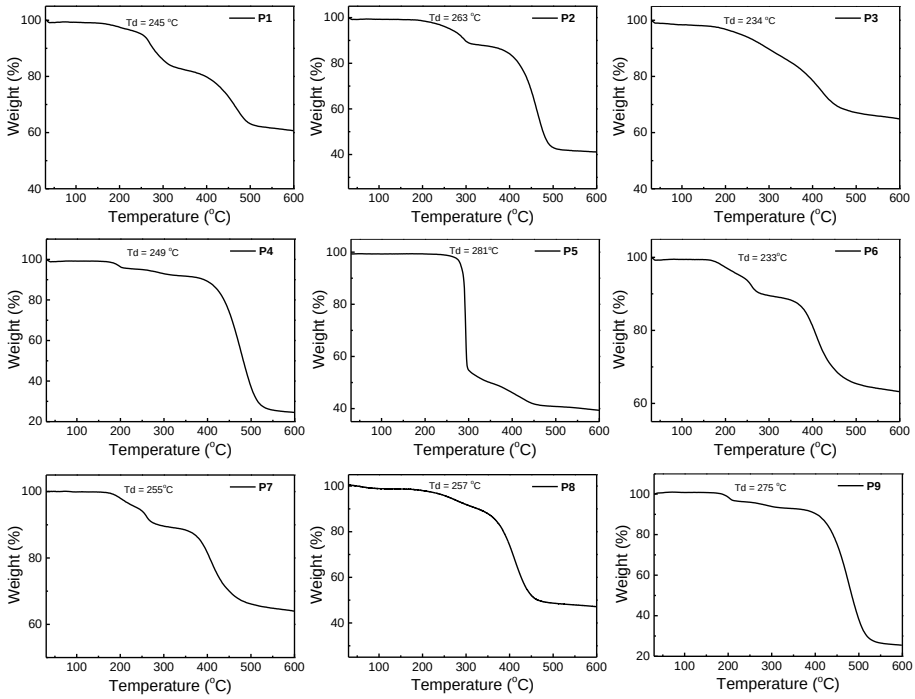


Figure S87. TGA trace of **P1-P9**;

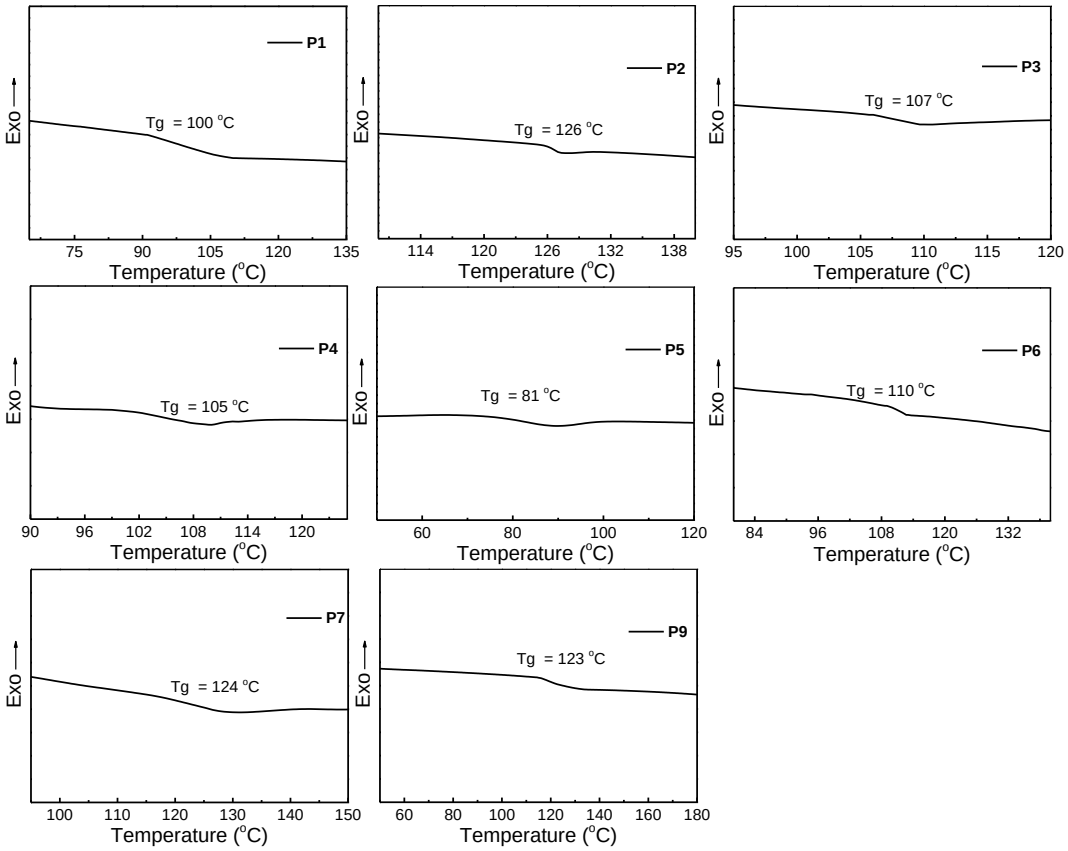


Figure S88. DSC trace of the **P1-P7** and **P9** from the second heating scan (10 °C min^{-1})

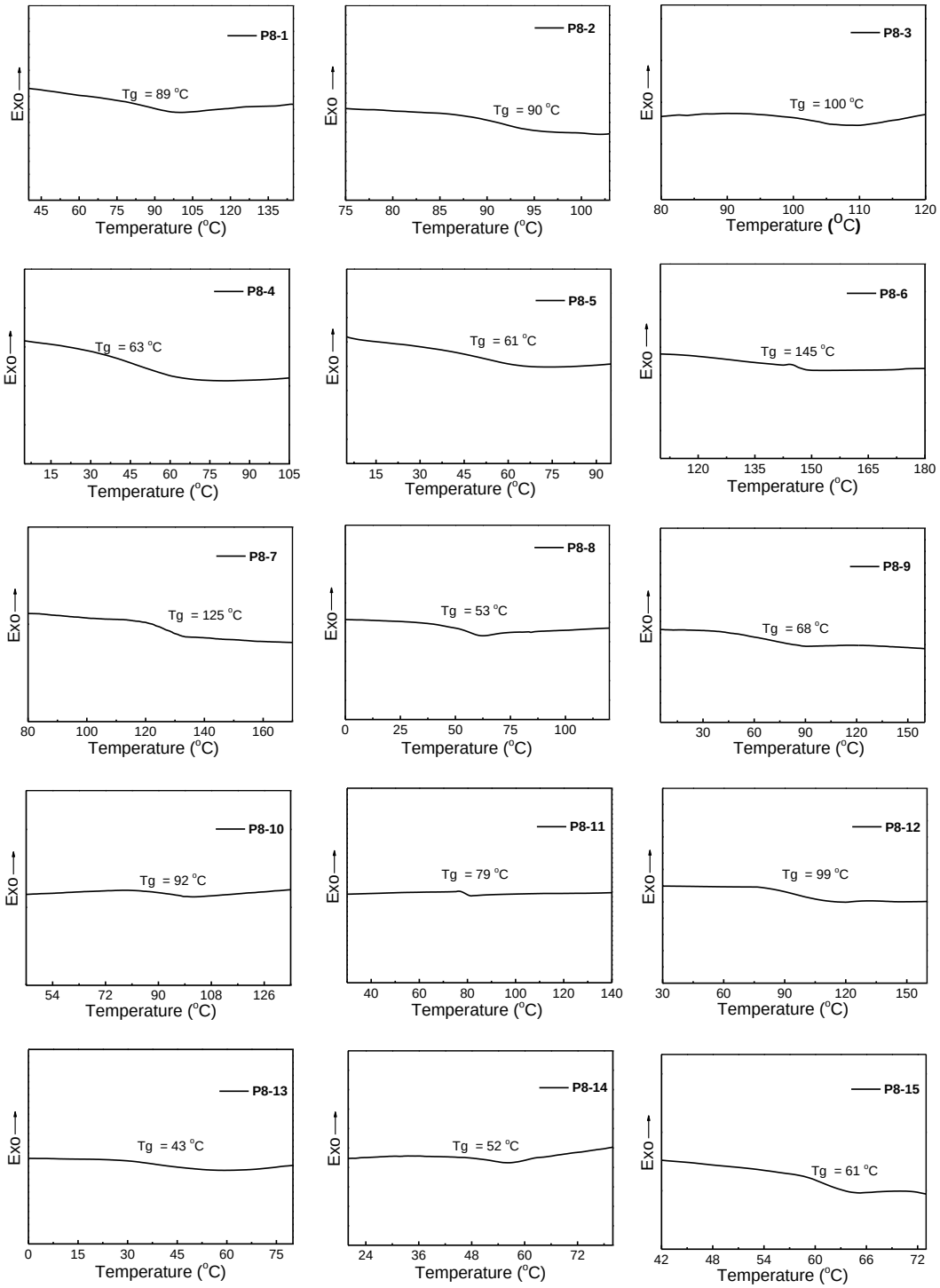


Figure S89. DSC trace of the post-functionalization of **P8-N** from the second heating scan (10 °C min^{-1})

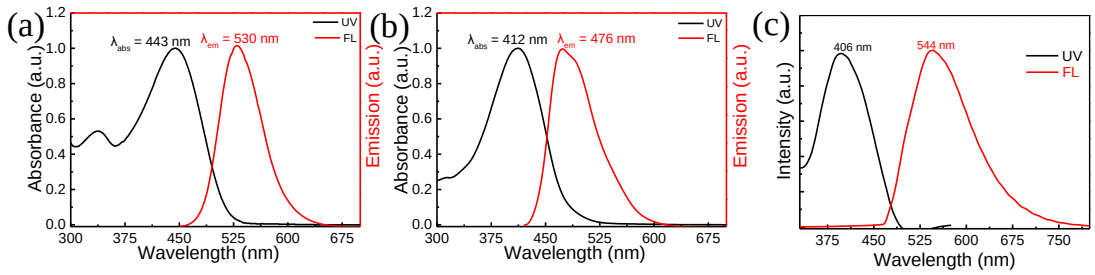


Figure S90. The UV−vis absorption and emission spectra of **P9** (a), **P10** (b); The UV−vis absorption and Emission spectra measured in film of **P10** (The spin-coated films from $CHCl_3$/toluene (3:1) solutions (15 mg/mL) on quartz plates (1 cm × 3 cm) (1000 N/s, 30 s).