Supporting Information for

Ru-Catalyzed Polycondensation of Dialkyl 1,4-Phenylenebis(diazoacetate) with Dianiline: Synthesis of Well-Defined Aromatic Polyamines Bearing an Alkoxycarbonyl Group at the Adjacent Carbon of Each Nitrogen in the Main Chain Framework

Hiroaki Shimomoto, Hiroto Mukai, Hideaki Bekku, Tomomichi Itoh, and Eiji Ihara*

Department of Materials Science and Biotechnology, Graduate School of Science and Engineering, Ehime University, 3 Bunkyo-cho, Matsuyama 790-8577, Japan

Phone & Fax: +81-89-927-8547; e-mail: ihara@ehime-u.ac.jp (E. I.).

Contents:

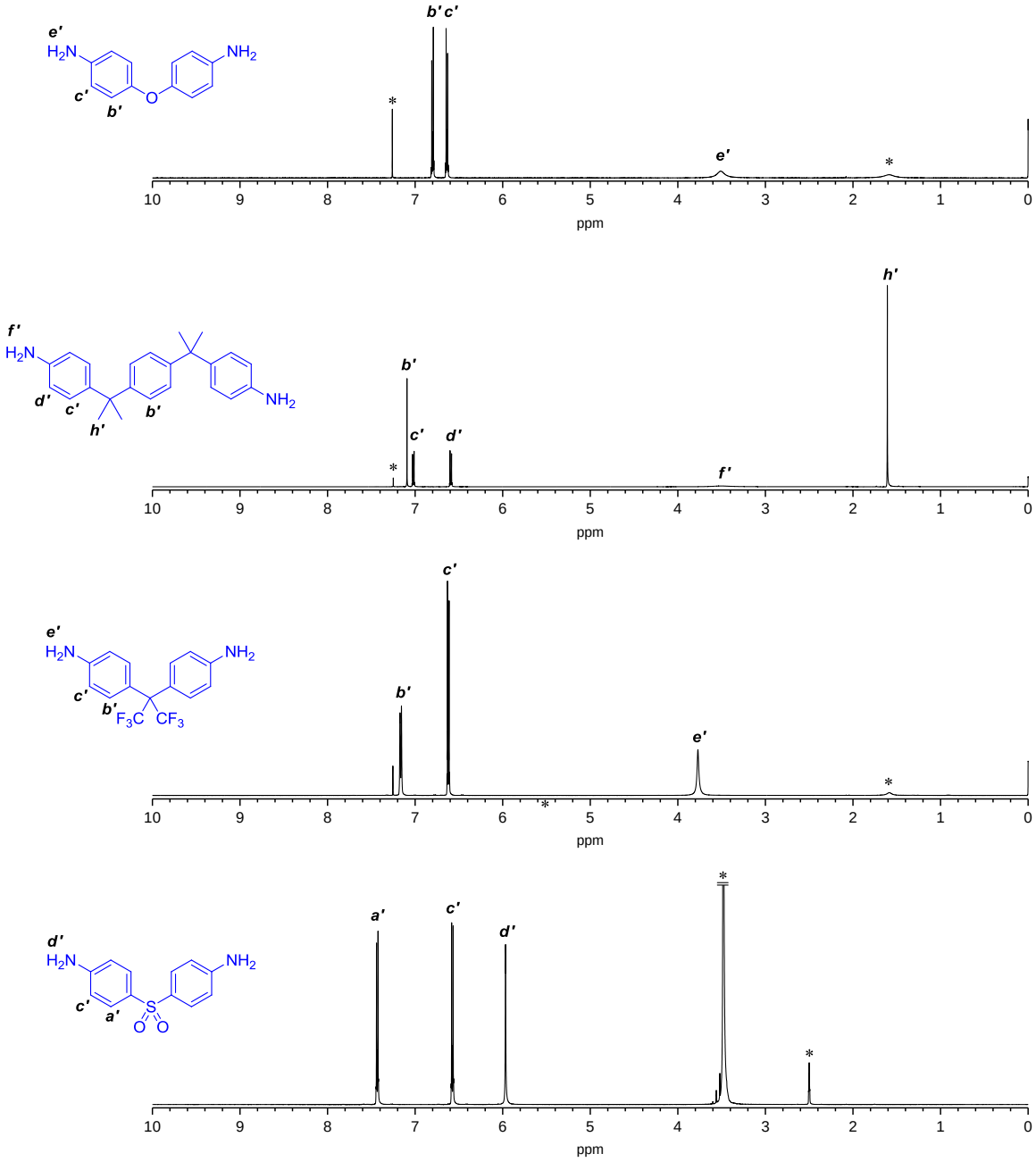

Figure S1. ^{1}H NMR spectra of **3b-3e** recorded in $CDCl_3$ (**3b-3d**) or DMSO-d_6 (**3e**).

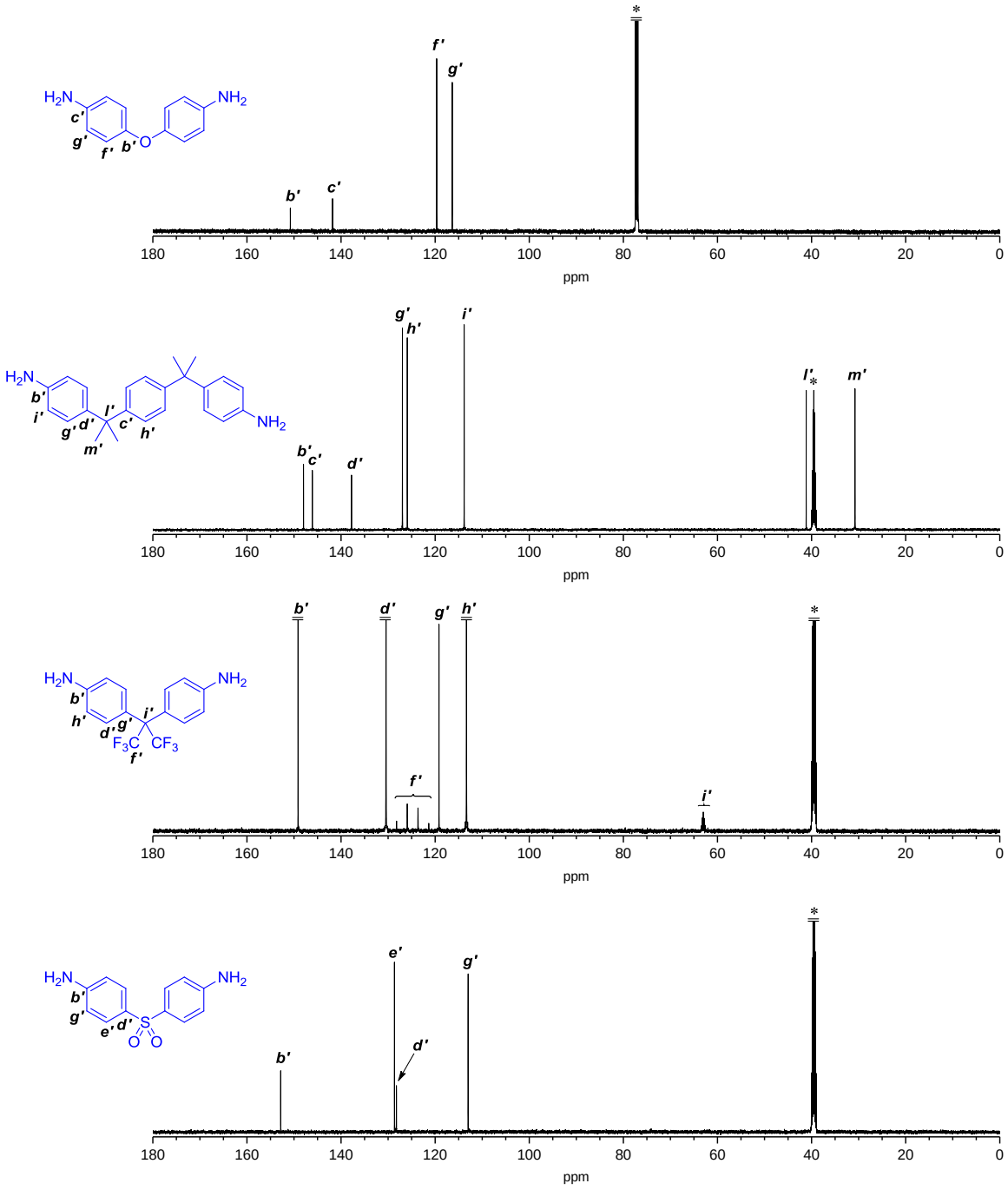

Figure S2. ^{13}C NMR spectra of **3b**-**3e** recorded in $CDCl_3$ (**3b**) or DMSO-d_6 (**3c**-**3e**) .

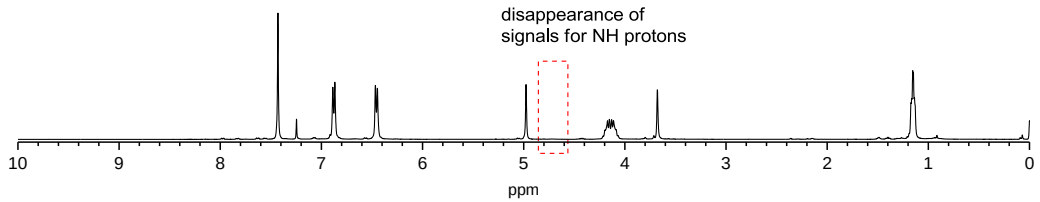

Figure S3. Hydrogen/deuterium exchange ^{1}H NMR spectrum of **4a** (run 2 in Table 1).

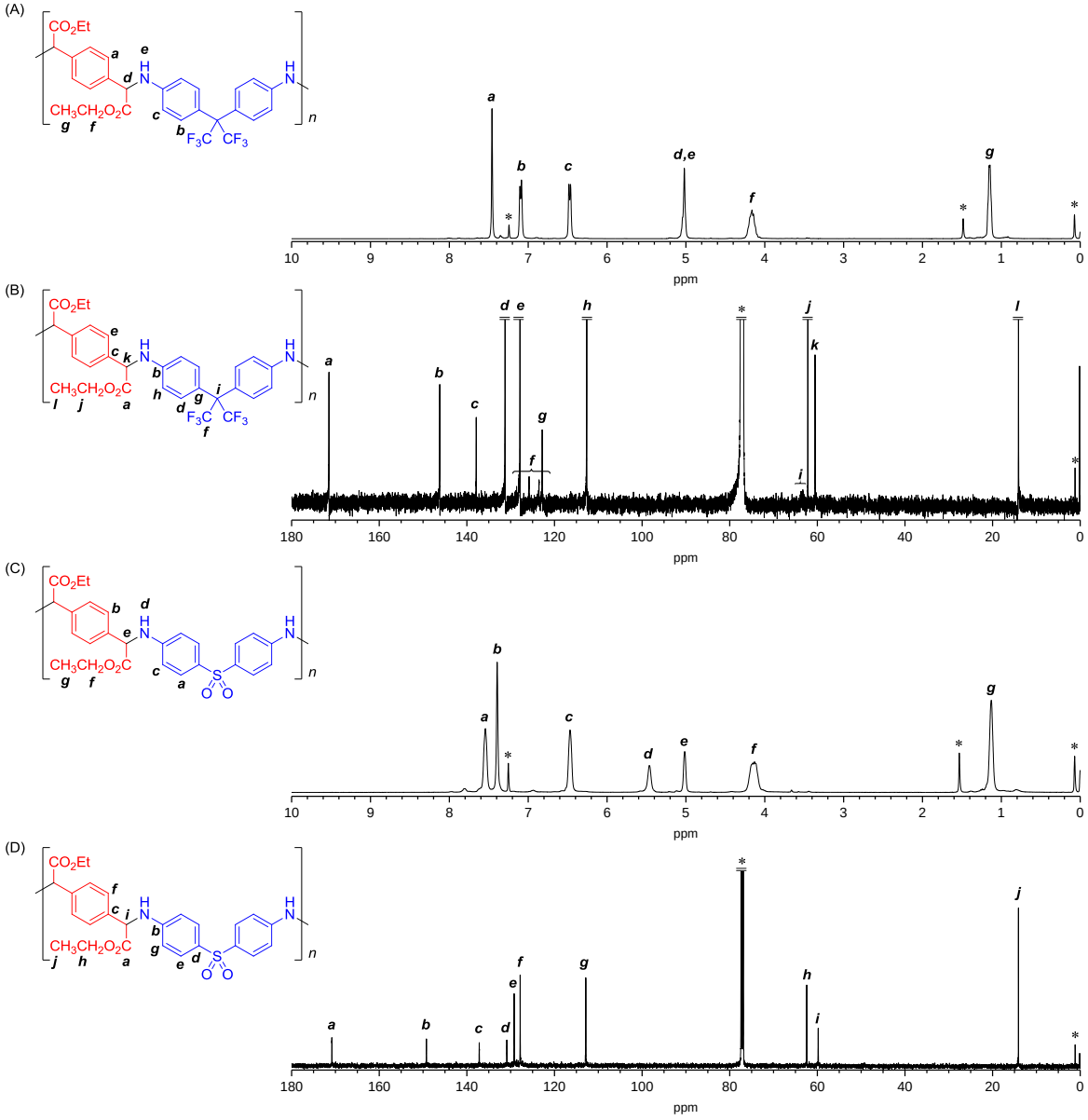

Figure S4. (A) ^{1}H and (B) ^{13}C NMR spectra of **4d** (Table 1, run 7) and (C) ^{1}H and (D) ^{13}C NMR spectra of **4e** (Table 1, run 8) (* solvent, water, or grease).

4a: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.43 (s, 4H, −CH[CO_2Et]−Ph[−*H*]−CH[CO_2Et]−), 6.88 (d, *J* = 8.0 Hz, 4H, −NH−Ph[−*H*]−CH_2−), 6.45 (d, *J* = 8.0 Hz, 4H, −NH−Ph[−*H*]−CH_2−), 4.98 (s, 2H, −Ph−C*H*[CO_2Et]−NH−), 4.72 (s, 2H, −N*H*−), 4.14 (m, 4H, −CO_2C$H_2$$CH_3$), 3.68 (s, 2H, −Ph−C$H_2$−Ph), 1.15 (dt, *J* = 2.4 Hz, 7.0 Hz, 6H, −CO_2CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.9 (−*C*O_2Et), 144.3 (−NH−Ph[−*C*]−CH_2−), 138.0 (−CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 131.6 (−NH−Ph[−*C*]−CH_2−), 129.7 (−NH−Ph[−*C*]−CH_2−), 127.8 (−CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 113.6 (−NH−Ph[−*C*]−CH_2−), 61.9 (CO_2*C*$H_2$$CH_3$), 60.9 (−Ph−*C*H[$CO_2$Et]−NH−), 40.2 (−Ph−*C*$H_2$−Ph), 14.1 ($CO_2CH_2$*C*$H_3$). Anal. Calcd for $(C_{27}H_{28}N_2O_4)_n$: C, 72.95; H, 6.35; N, 6.30. Found: C, 68.25; H, 6.22; N, 5.75.

4b: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.44 (s, 4H, −CH[CO_2Et]−Ph[−*H*]−CH[CO_2Et]−), 6.72 (d, *J* = 8.4 Hz, 4H, −NH−Ph[−*H*]−O−), 6.48 (d, *J* = 8.4 Hz, 4H, −NH−Ph[−*H*]−O−), 4.97 (s, 2H, −Ph−C*H*[CO_2Et]−NH−), 4.67 (s, 2H, −N*H*−), 4.15 (m, 4H, −CO_2C$H_2$$CH_3$), 1.16 (t, *J* = 7.2 Hz, 6H, −CO_2CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 171.9 (−*C*O_2Et), 150.4 (−NH−Ph[−*C*]−CH_2−), 141.9 (−NH−Ph[−*C*]−CH_2−), 138.0 (−CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 127.8 (−NH−Ph[−*C*]−CH_2−), 119.6 (−NH−Ph[−*C*]−CH_2−), 114.6 (−NH−Ph[−*C*]−CH_2−), 62.0 (CO_2*C*$H_2$$CH_3$), 61.3 (−Ph−*C*H[$CO_2$Et]−NH−), 14.2 ($CO_2CH_2$*C*$H_3$). Anal. Calcd for $(C_{26}H_{28}N_2O_5)_n$: C, 69.63; H, 6.29; N, 6.25. Found: C, 67.24; H, 5.71; N, 5.91.

4c: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46 (s, 4H, −CH[CO_2Et]−Ph[−*H*]−CH[CO_2Et]−), 7.04 (s, 4H, −C[CH_3]$_2$−Ph[−*H*]−C[CH_3]$_2$−), 6.97 (d, *J* = 8.4 Hz, 4H, −NH−Ph[−*H*]−C[CH_3]−), 6.46 (d, *J* = 8.4 Hz, 4H, −NH−Ph[−*H*]−C[CH_3]−), 5.00 (s, 2H, −Ph−C*H*[CO_2Et]−NH−), 4.74 (s, 2H, −N*H*−), 4.14 (m, 4H, −CO_2C$H_2$$CH_3$), 1.56 (s, 12H, −Ph−C[C$H_3$]$_2$−Ph−), 1.15 (dt, *J* = 2.8 Hz, 7.0 Hz, 6H, −CO_2CH_2CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.0 (−*C*O_2Et), 148.0 (−NH−Ph[−*C*]−C[CH_3]$_2$−), 143.9 (−C[CH_3]$_2$−Ph[−*C*]−C[CH_3]$_2$−), 140.7 (−NH−Ph[−*C*]−C[CH_3]$_2$−), 138.0 (−CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 127.8 (−CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 127.7 (−NH−Ph[−*C*]−C[CH_3]$_2$−), 126.3 (−C[CH_3]$_2$−Ph[−*C*]−C[CH_3]$_2$−), 113.1 (−C[CH_3]$_2$−Ph[−*C*]−C[CH_3]$_2$−), 61.9 (CO_2*C*$H_2$$CH_3$), 61.3 (−Ph−*C*H[$CO_2$Et]−NH−), 41.8 (−Ph−*C*[$CH_3$]$_2$−Ph−), 31.0 (−Ph−C[*C*$H_3$]$_2$−Ph−), 14.2 ($CO_2CH_2$*C*$H_3$). Anal. Calcd for $(C_{38}H_{42}N_2O_4)_n$: C, 77.26; H, 7.17; N, 4.74. Found: C, 72.73; H, 6.95; N, 4.40.

4d: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.46 (s, 4H, −CH[CO_2Et]−Ph[−*H*]−CH[CO_2Et]−), 7.10 (d, *J* = 8.0 Hz, 4H, −NH−Ph[−*H*]−C[CF_3]$_2$−), 6.47 (d, *J* = 8.0 Hz, 4H, −NH−Ph[−*H*]−C[CF_3]$_2$−), 5.04 (s, 2H, −Ph−C*H*[CO_2Et]−NH−; 2H, −N*H*−), 4.16 (m, 4H, −CO_2C$H_2$$CH_3$), 1.14 (m, 6H, −$CO_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 171.5 (s, −*C*O_2Et), 148.0 (s, −NH−Ph[−*C*]−C[CH_3]$_2$−), 146.2 (s, −NH−Ph[−*C*]−C[CF_3]$_2$−), 137.7 (s, −CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 131.3 (s, −NH−Ph[−*C*]−C[CF_3]$_2$−), 128.1, 125.8, 123.5, and 121.2 (a pair of s, −Ph−C[*C*F_3]$_2$−Ph−), 127.9 (s, −CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 122.8 (s, −NH−Ph[−*C*]−C[CF_3]$_2$−), 112.6 (s, −NH−Ph[−*C*]−C[CF_3]$_2$−), 63.9-63.1 (m, −Ph−*C*[CF_3]$_2$−Ph−), 62.2 (s, CO_2*C*$H_2$$CH_3$), 60.5 (−Ph−*C*H[$CO_2$Et]−NH−), 14.1 ($CO_2CH_2$*C*$H_3$). Anal. Calcd for $(C_{29}H_{32}N_2O_4F_6)_n$: C, 59.38; H, 5.50; N, 4.78. Found: C, 58.65; H, 4.59; N, 4.74.

4e: ^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.54 (s, 4H, −NH−Ph[−*H*]−SO_2−), 7.39 (s, 4H, −CH[CO_2Et]−Ph[−*H*]−CH[CO_2Et]−), 6.47 (s, 4H, −NH−Ph[−*H*]−SO_2−), 5.46 (s, 2H, −N*H*−), 5.02 (s, 2H, −Ph−C*H*[CO_2Et]−NH−), 4.15 (br, 4H, −CO_2C$H_2$$CH_3$), 1.16 (br, 6H, −$CO_2CH_2CH_3$). ^{13}C NMR (126 MHz, $CDCl_3$, δ): 170.8 (−*C*O_2Et), 149.2 (−NH−Ph[−*C*]−SO_2−), 138.0 (−CH[CO_2Et]−Ph[−*C*]−CH[CO_2Et]−), 130.9 (−NH−Ph[−*C*]−SO_2−), 129.2 (−NH−Ph[−*C*]−SO_2−), 127.8 (−NH−Ph[−*C*]−CH_2−), 112.8 (−NH−Ph[−*C*]−SO_2−), 62.0 (CO_2*C*$H_2$$CH_3$), 59.8 (−Ph−*C*H[$CO_2$Et]−NH−), 14.1 ($CO_2CH_2$*C*$H_3$). Anal. Calcd for $(C_{26}H_{26}N_2SO_6)_n$: C, 63.14; H, 5.30; N, 5.66. Found: C, 60.73; H, 5.54; N, 4.61.

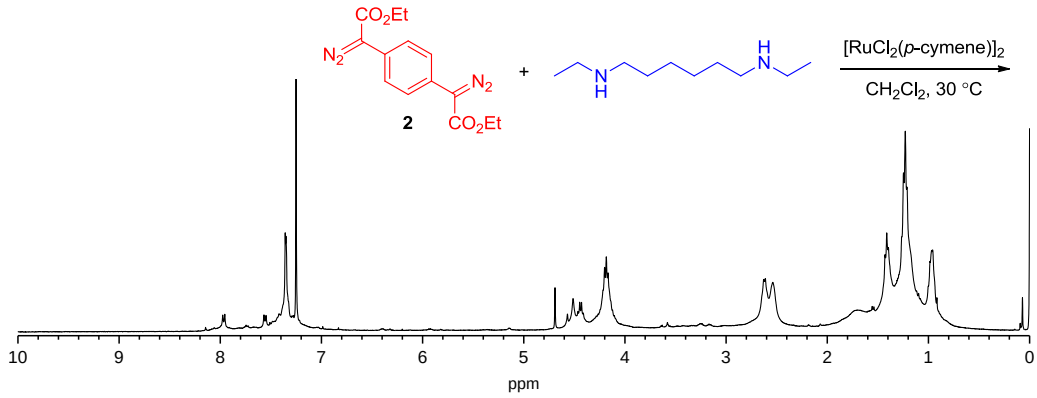

Figure S5. ^{1}H NMR spectrum of the product obtained by polycondensation of **2** with *N,N'*-diethyl-1,6-diaminohexane (yield = 25%, M_n = 250, M_w/M_n = 2.7).

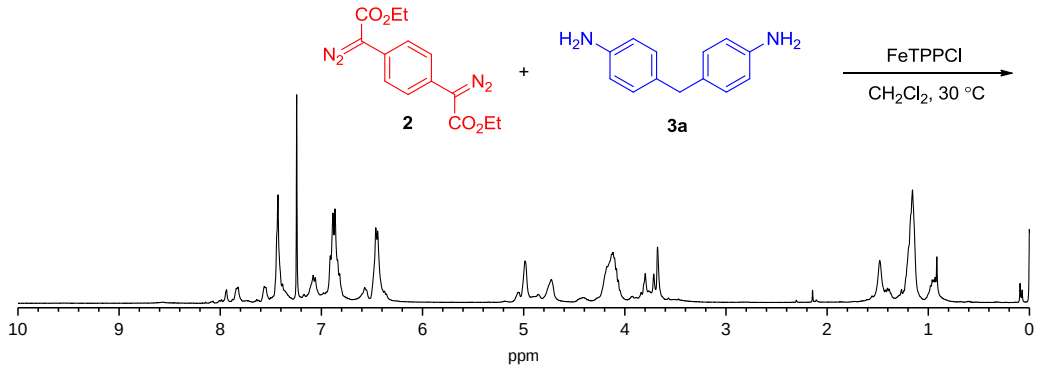

Figure S6. ^{1}H NMR spectrum of the product obtained by polycondensation of **2** with **3a** using FeTPPCl as catalyst (yield = 30%, M_n = 840, M_w/M_n = 8.0).