Electronic Supplementary Information

Non-symmetric Mechanophores Prepared from Radical-type Symmetric Mechanophores: Bespoken Mechanofunctional Polymers

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Table of Contents

1. General Information

Materials

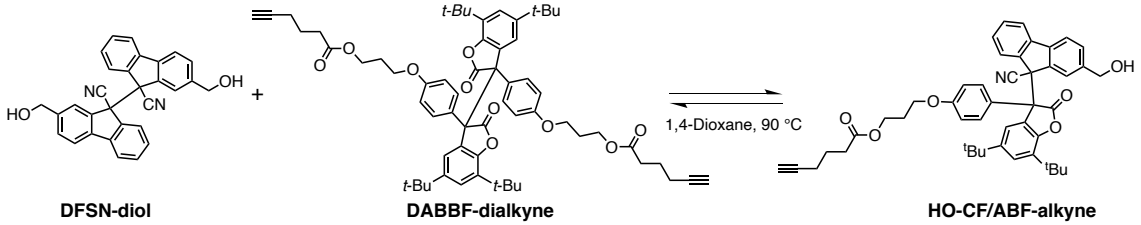
All solvents and reagents from Sigma-Aldrich, Wako Pure Chemical Industries, Tokyo Chemical Industry, and Kanto Chemical were used as received, unless otherwise noted. Copper (I) bromide (CuBr) was washed with acetic acid and then washed with methanol and dried in vacuo. Styrene and 1,4-dioxane were purified by basic alumina column (Merck KGaA) to remove the stabilizer prior to use. **DABBF-diol**,[1] **DABBF-dialkyne**,[1] **PS-DABBF-PS**,[1] **DFSN**,[2] **DFSN-diol**,[2] and 5-hexynoyl chloride[3] were synthesized according to the previously published methods.

Instruments

^{1}H NMR spectroscopic measurements were carried out using 500 MHz Bruker spectrometer with tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) or dimethyl sulfoxide-d_6 (DMSO-d_6). FAB-MS spectrometric measurements were carried out using JEOL JMS-700 MStation (matrix : NBA + Na, solvent : $CHCl_3$). FT-IR spectroscopic measurement was recorded on a JASCO FT/IR-4100 with a KBr plate. UV-vis absorption measurements were carried out on a JASCO V-650 spectrophotometer. Size exclusion chromatography (SEC) measurements were carried out at 40 °C on TOSOH HLC-8320 SEC system equipped with a guard column (TOSOH TSK guard column Super H-L), three columns (TOSOH TSK gel SuperH 6000, 4000, and 2500), a differential refractive index detector. Tetrahydrofuran (THF) was used as the eluent at a flow rate of 0.6 mL/min. Polystyrene (PS) standards (M_n = 4430–3242000; M_w/M_n = 1.03–1.08) were used to calibrate the SEC system. High-performance liquid chromatography (HPLC) analysis was performed at 30 °C on a Shimadzu LC-20AD pump equipped with a guard column (YMC-Guardpack SIL), a column (YMC-Triart C18), and an SPD-20A variable wavelength detector. The pump operated at flow rate of 1.0 mL/min for acetonitrile/water = 97/3 (v/v), and the monitored wavelength was 254 nm. DSC measurements were carried out using a SHIMADZU DSC-60A Plus with a heating rate 10 °C/min.

2. Synthetic Procedure

2-1. Synthesis of HO-CF/ABF-alkyne



DFSN-diol **DABBF-dialkyne** **HO-CF/ABF-alkyne**

In a round-bottomed flask, a solution of **DFSN-diol** (1.00 g, 2.27 mmol), **DABBF-dialkyne** (2.22 g, 2.27 mmol), and 1,4-dioxane (300 mL) was prepared. The mixture was bubbled with nitrogen for 1 h. The reaction mixture was stirred at 90 °C for 3 h. The crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/1, v/v). The solvent was removed and dried in vacuo to give **HO-CF/ABF-alkyne** as white solid (1.67 g, 51.8%). There are two diastereomers in HO-CF/ABF-alkyne, which we named **HO-CF/ABF-alkyne 1** (R_f = 0.40, ethyl acetate / *n*-hexane =1/1) and **HO-CF/ABF-alkyne 2** (R_f = 0.20, ethyl acetate / *n*-hexane =1/1). They were successfully isolated by silica gel column chromatography and confirmed to be diastereomers by ^{1}H NMR and FAB-MS.

HO-CF/ABF-alkyne 1 ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.95 (br, 3H, aromatic), 7.63 (d, *J* = 7.6 Hz, 1H, aromatic), 7.51 (t, *J* = 7.5 Hz, 2H, aromatic), 7.40 (d, *J* = 7.2 Hz, 1H, aromatic), 7.29 (d, *J* = 7.7 Hz, 1H, aromatic), 7.19 (t, *J* = 6.9 Hz, 1H, aromatic), 7.00 (d, *J* = 9.0 Hz, 3H, aromatic), 6.45 (br, 1H, aromatic), 4.62 (m, 2H, C*CH*$_2$OH), 4.32 (t, *J* = 6.3 Hz, 2H, OCH$_2$CH$_2$*CH*$_2$), 4.13 (t, *J* = 6.8 Hz, 2H, O*CH*$_2$CH$_2$CH$_2$), 2.49 (t, *J* = 7.4 Hz, 2H, OC(O)*CH*$_2$CH$_2$CH$_2$), 2.27 (dt, *J* = 2.5 and 6.9 Hz, 2H, *CH*$_2$CCH), 2.18 (quin, 2H, *J* = 6.2 Hz, OCH$_2$*CH*$_2$CH$_2$), 1.97 (t, *J* = 2.5 Hz,1H, CH), 1.87 (quin, *J* = 7.3 Hz, 2H, OC(O)CH$_2$*CH*$_2$CH$_2$), 1.70 (t, *J* = 5.9 Hz, 1H, OH), 1.18 (br, 9H, CH_3), 1.03 (br, 9H, CH_3).
^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 173.13, 159.36, 148.15, 141.59, 141.42, 140.02,139.80, 139.19, 132.82, 130.80, 130.23, 128.39, 127.61, 126.34, 124.91, 123.56, 120.67, 120.36, 119.98, 118.70, 114.45, 83.22, 69.25, 64.77, 64.50, 61.25, 57.19, 54.88, 34.44, 34.14, 32.88, 31.13, 29.25, 28.60, 23.59, 17.86.
FT-IR (KBr, cm^{-1}): 3513, 3299, 3068, 2960, 2870, 2359, 2237, 2118, 1793, 1733, 1607, 1577, 1511, 1477, 1413, 1395, 1364, 1296, 1272, 1256, 1228, 1187, 1167, 1125, 1089, 1052, 989, 918, 884, 826, 808, 777, 754, 726, 640, 561, 537
FAB-MS (m/z): $[M+Na]^+$ calcd. for $C_{46}H_{47}NO_6Na$, 732.3301; Found, 732.3294.

HO-CF/ABF-alkyne 2 ^{1}H NMR (500 MHz, $CDCl_3$): δ/ppm 7.96 (br, 3H, aromatic), 7.63 (d, *J* = 7.8 Hz, 1H, aromatic), 7.51 (d, *J* = 7.5 Hz, 2H, aromatic), 7.40 (d, *J* = 6.9 Hz, 1H,

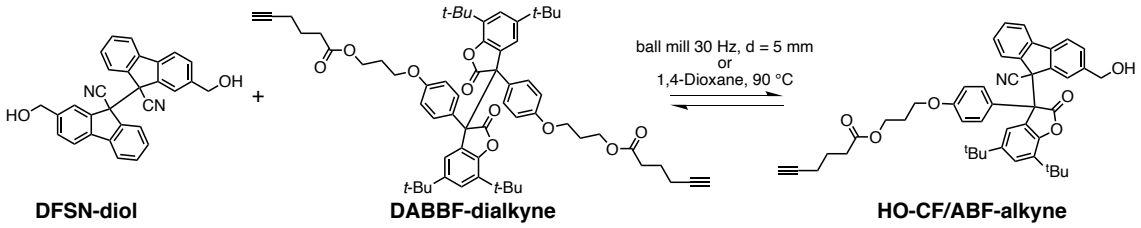
aromatic), 7.23 (t, J = 7.5 Hz, 1H, aromatic), 7.14 (t, J = 7.6 Hz,1H, aromatic), 7.00 (d, 3H, J = 8.9 Hz, aromatic), 6.37 (br, 1H, aromatic), 4.57 (m, 2H, CCH_2OH), 4.32 (m, 2H, $OCH_2CH_2CH_2$), 4.13 (t, J = 6.0 Hz, 2H, $OCH_2CH_2CH_2$), 2.49 (t, J = 7.4 Hz, 2H, $OC(O)CH_2CH_2CH_2$), 2.27 (dt, J = 2.5 and 6.9 Hz, 2H, CH_2CCH_2), 2.18 (quin, 2H, J = 6.2 Hz, $OCH_2CH_2CH_2$), 1.97 t, J = 2.6 Hz, 1H, CH), 1.87 (quin, J = 7.2 Hz, 2H, $OC(O)CH_2CH_2CH_2$), 1.79 (br, 1H, OH), 1.18 (br, 9H, CH_3), 1.05 (br, 9H, CH_3).

FAB-MS (m/z): $[M+Na]^+$ calcd. for $C_{46}H_{47}NO_6Na$, 732.3301; Found, 732.3294.

^{13}C NMR (125 MHz, $CDCl_3$): δ/ppm 173.24, 159.41, 148.20, 141.16, 140.87, 140.21, 139.84, 139.35, 132.95, 130.77, 129.72, 128.75, 128.16, 124.94, 123.60, 120.52, 120.35, 119.84, 118.67, 114.43, 83.24, 69.26, 64.75, 64.52, 61.22, 57.20, 55.02, 34.45, 34.13, 32.90, 31.16, 29.32, 28.60, 23.59, 17.85.

FT-IR (KBr, cm^{-1}): 3506, 3296, 3049, 2959, 2871, 2239, 2118, 1793, 1733, 1607, 1576, 1511, 1477, 1413, 1394, 1364, 1296, 1272, 1256, 1229, 1187, 1167, 1124, 1090, 1051, 924, 888, 866, 825, 779, 752, 724, 665, 636, 562, 539

2-3. Evaluation of generation ratio of HO-CF/ABF-Alkynes by heating and ball milling using HPLC measurement.



DFSN-diol **DABBF-dialkyne** **HO-CF/ABF-alkyne**

Heating process

In a round-bottomed flask, a solution of **DFSN-diol** (0.100 g, 0.227 mmol), **DABBF-dialkyne** (0.222 g, 0.227 mmol), and 1,4-dioxane (22.7 mL) was prepared. The mixture was bubbled with nitrogen for 30 min. The reaction mixture was stirred at 90 °C for 360 min. The crude products were evaluated by HPLC measurement at 0, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 300, and 360 min after reaction (eluent: 0–10 min: acetonitrile/water = 85/15, 10–20 min: acetonitrile/water = 100/0).

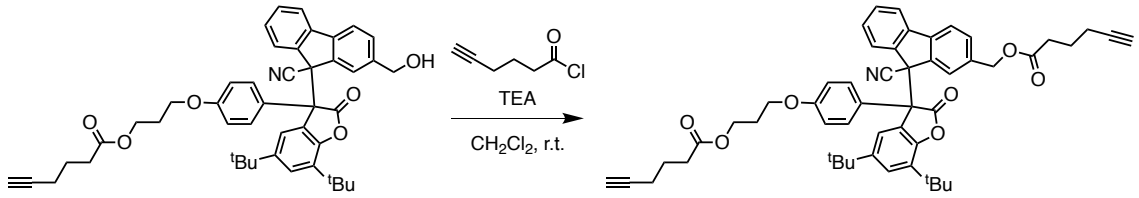
Ball milling process

Powder of **DFSN-diol** (0.0300 g, 0.0681 mmol), **DABBF-dialkyne** (0.0667 g, 0.0681 mmol) and a stainless ball (d = 5 mm) were placed in the grinding jar and ball-milled at 30 Hz at room temperature. Each milling has performed in 10-minute intervals to prevent the temperature of the jar from rising. The crude products were evaluated by HPLC measurement at 0, 10, 20, 30, 40, 50, 60, 90, 120, 150, 180, 210, 240, 300, and 360 min

after milling (eluent: 0–10 min: acetonitrile/water = 85/15, 10-20 min: acetonitrile/water = 100/0).

The generation ratio of HO-CF/ABF-alkyne was calculated by calibration curve (**Figure S7**)

2-4. Synthesis of alkyne-CF/ABF-alkyne

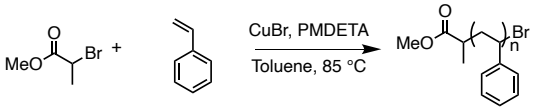


HO-CF/ABF-alkyne **alkyne-CF/ABF-alkyne**

In a round-bottomed flask, a solution of **HO-CF-AF-alkyne** (0.340 g, 0.479 mmol), triethylamine (TEA, 0.280 mL, 2.00 mmol), and dry CH_2Cl_2 (20.0 mL) was prepared. The solution was cooled in ice bath and 5-hexynoyl chloride (0.240 mL, 2.00 mmol) was added dropwise. Once the addition was complete, the mixture was allowed to stir for 2 h as it warmed to r.t. and then the reaction was quenched with water in ice bath. The resulting mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ water and brine and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/4, v/v) and dried in vacuo to give **alkyne-CF/ABF-alkyne** as colorless liquid (0.313 g, 75.1%).

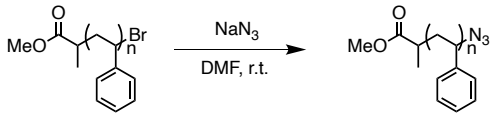
^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 7.95 (br, 3H, aromatic), 7.64 (t, J = 7.3 Hz, 1H, aromatic), 7.51 (t, J = 7.6 Hz, 2H, aromatic), 7.40 (d, J = 6.2 Hz, 1H, aromatic), 7.22 (d, J = 7.3 Hz, 1H, aromatic), 7.17 (t, J = 7.6 Hz, 1H, aromatic), 7.00 (t, J = 8.6 Hz, 3H, aromatic), 6.43 (br, 1H, aromatic), 4.95–5.07 (m, 2H, C*CH*$_2$OH), 4.31 (dt, J = 2.0 and 6.1 Hz, 2H, OCH$_2$CH$_2$*CH*$_2$), 4.13 (dt, J = 2.8 and 6.0 Hz, 2H, O*CH*$_2$CH$_2$CH$_2$), 2.46–2.54 (m, 4H, OC(O)*CH*$_2$CH$_2$CH$_2$), 2.25–2.31 (m, 4H, *CH*$_2$CCH), 2.17 (m, 2H, OCH$_2$*CH*$_2$CH$_2$), 1.99 (t, J = 2.5 Hz, 1H, CH), 1.97 (t, J = 2.5 Hz, 1H, CH), 1.85–1.92 (m, 4H, OC(O)CH$_2$*CH*$_2$CH$_2$), 1.18 (br, 9H, CH_3), 1.03 (br, 9H, CH_3). ^{13}C NMR (125 MHz, DMSO-d_6): δ / ppm 172.92, 172.65, 172.40, 159.69, 147.83, 138.80, 131.25, 130.97, 130.62, 130.29, 128.62, 123.96, 121.86, 121.66, 121.32, 120.70, 115.26, 84.08, 84.02, 83.97, 72.19, 72.10, 72.07, 72.00, 65.42, 65.24, 65.07, 61.32, 57.05, 57.02, 54.53, 34.50, 34.17, 34.15, 32.90, 32.76, 32.70, 31.18, 29.49, 29.43, 28.45, 23.97, 23.92, 23.87, 17.61, 17.57. FT-IR (KBr, cm^{-1}): 3294, 2960, 1794, 1735, 1608, 1577, 1543, 1510, 1458, 1364, 1255, 1158, 1091, 827, 777, 754, 640, 536, 465, 450, 432, 407

2-5. Synthesis of bromine-terminated polystyrene (PS-Br)



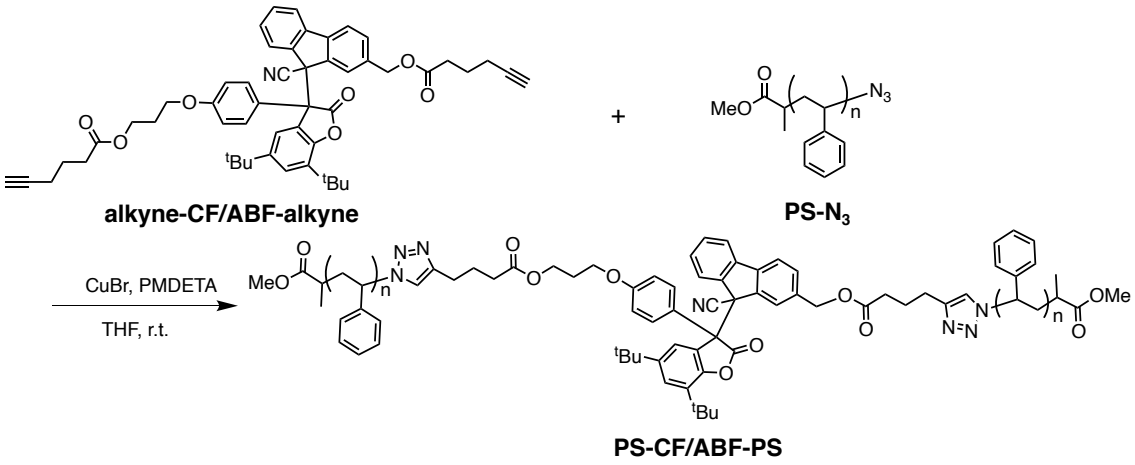
In a round-bottomed flask, a solution of styrene (92.0 mL, 800 mmol) and toluene (30.0 mL) was prepared. The solution was bubbled with nitrogen for 30 minutes, CuBr (0.290 g, 2.00 mmol) was added. After the solution was bubbled with nitrogen for another 20 minutes, *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA) (0.420 mL, 2.00 mmol) was added. After the solution was bubbled with nitrogen for another 10 minutes, methyl 2-bromopropionate (0.223 mL, 2.00 mmol) was added. The mixture was bubbled with nitrogen for 10 minutes, and the resulting solution was allowed to stir at 85 °C for 4 h. The reaction was stopped via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation and precipitation into methanol, the resulting polymer was filtrated and dried in vacuo to give bromo-terminated polystyrene (PS-Br) as a white powder (19.2 g, 20.9%). The M_n and M_w/M_n values were determined by analytical SEC with polystyrene standards. M_n = 8100 g mol^{-1}, M_w/M_n = 1.12. ^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 6.27–7.26 (br, aromatic), 4.35–4.59 (br, CHBr), 3.37–3.54 (s, OCH_3), 1.84 (br, CH_2), 1.43 (br, CHPh).

2-6. Synthesis of azide-terminated polystyrene (PS-N_3)



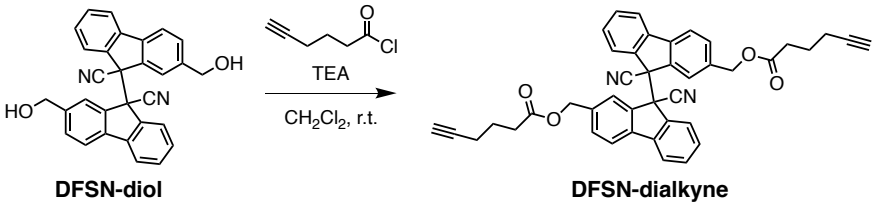
In a round-bottomed flask, a solution of PS-Br (8100 g mol^{-1}, M_w/M_n = 1.12, 19.0 g, 2.34 mmol) in DMF (190 mL) was prepared. Sodium azide (1.64 g, 25.3 mmol) was added into the solution and the mixture was allowed to stir at room temperature for 24 h. After precipitation into water, the resulting precipitate was filtrated and dried in vacuo to give azido-terminated polystyrene (PS-N_3) as a white powder (18.5 g, 97.3%). The M_n and M_w/M_n values were determined by analytical SEC with polystyrene standards. M_n = 8000 g mol^{-1}, M_w/M_n = 1.13. ^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 6.28–7.35 (br, aromatic), 3.93 (m, CHN_3), 3.39–3.49 (m, OCH_3), 1.84 (br, CH_2), 1.44 (br, CHPh)

2-7. Synthesis of linear polystyrene with CF/ABF functionality in the center of polystyrene (PS-CF/ABF-PS)



In a round-bottomed flask, a solution of **alkyne-CF/ABF-alkyne** (60.0 mg, 0.0750 mmol), **PS-N$_3$** (8000 g mol^{-1}, M_w/M_n = 1.13, 1.06 g, 0.133 mmol), CuBr (128 mg, 0.896 mmol), and THF (15 mL) was prepared. After the mixture was bubbled with nitrogen for 1 h, PMDETA (0.190 mL, 0.900 mmol) was added and the resulting solution was allowed to stir at r.t. for 2 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation, the target polymer was isolated by preparative HPLC. The objective polymer was precipitated to methanol, filtrated, and dried in vacuo to give **PS-CF/ABF-PS** as a white powder (329 mg, 31%). M_n and M_w/M_n values were determined by analytical SEC with polystyrene standards. M_n = 16800 g mol^{-1}, M_w/M_n = 1.09. ^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 7.93 (br, 3H, aromatic), 7.61 (d, 1H, aromatic), 7.50 (br, 2H, aromatic), 7.24–6.28 (br, aromatic), 5.12–4.87 (br, 4H, PhCH, CCHOC(O)), 4.26 (br, 2H, $OCH_2CH_2CH_2$), 4.08 (br, 2H, $OCH_2CH_2CH_2$), 3.53–3.38 (br, 6H, OCH_3), 2.41–2.27 (br, 6H, CH_2, NCH), 2.15–1.19 (br, backbone), 0.94–0.90 (br, 8H, $CHCH_3$).

2-8. Synthesis of DFSN-dialkyne

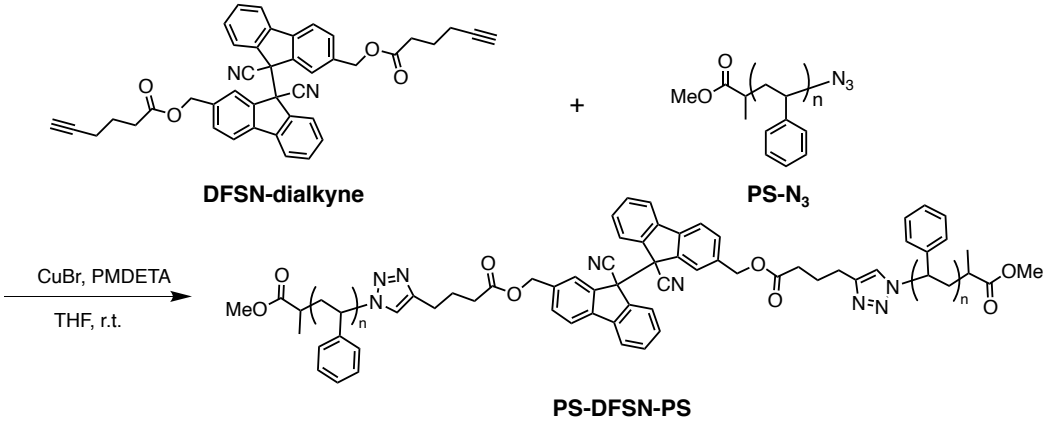


In a round-bottomed flask, a solution of **DFSN-diol** (0.660 g, 1.50 mmol), triethylamine (TEA, 0.836 mL, 6.00 mmol), and dry CH_2Cl_2 (15.0 mL) was prepared. The solution was cooled in ice bath and 5-hexynoyl chloride (0.719 mL, 6.00 mmol) was added dropwise.

Once the addition was complete, the mixture was allowed to stir for 2 h as it warmed to r.t. and then the reaction was quenched with water in ice bath. The resulting mixture was extracted with CH_2Cl_2. The organic layer was washed with saturated $NaHCO_3$ water and brine and dried over anhydrous $MgSO_4$. After filtration and evaporation, the crude product was purified by silica gel column chromatography eluting with ethyl acetate / *n*-hexane (1/4, v/v) and dried in vacuo to give **DFSN-dialkyne** as colorless liquid (0.729 g, 77.3%). ^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 7.75–7.12 (br, 7H, aromatic), 5.13–4.85 (br, 4H, CCHC(O)O), 2.53 (m, 4H, OC(O)CH_2CH$_2$), 2.30–2.27 (m, 4H, CH_2CCH), 1.99 (t, J = 2.6 Hz, 2H, CH), 1.89 (quin, J = 7.0 Hz, 4H, OC(O)CH$_2$$CH_2CH_2$). ^{13}C NMR (125 MHz, DMSO-d_6): δ / ppm 178.39, 172.69, 140.96, 140.54, 137.82, 135.79, 130.62, 130.23, 128.12, 125.15, 124.64, 120.14, 118.19, 83.23, 69.34, 65.49, 53.54, 32.81, 23.52, 17.77,

FT-IR (KBr, cm^{-1}): 3271, 2945, 1731, 1543, 1508, 1499, 1456, 1417, 1391, 1364, 1319, 1232, 1167, 1074, 1024, 999, 875, 827, 775, 753, 719, 669, 485, 434, 413

2-9. Synthesis of linear polystyrene with DFSN functionality in the center of polystyrene (PS-DFSN-PS)



In a round-bottomed flask, a solution of **DFSN-dialkyne** (40.0 mg, 0.0640 mmol), **PS-N$_3$** (8000 g mol^{-1}, M_w/M_n = 1.13, 1.06 g, 0.133 mmol), CuBr (109 mg, 0.763 mmol), and THF (15 mL) was prepared. After the mixture was bubbled with nitrogen for 1 h, PMDETA (0.160 mL, 0.760 mmol) was added and the resulting solution was allowed to stir at r.t. for 2 h. The reaction was quenched via exposure to air and diluted with THF. The solution was filtered through a column filled with neutral alumina in order to remove the copper complex. After evaporation, the target polymer was isolated by preparative HPLC. The objective polymer was precipitated to methanol, filtrated, and dried in vacuo to give **PS-DFSN-PS** as a white powder (313 mg, 28.4%). M_n and M_w/M_n values were

determined by analytical SEC with polystyrene standards. M_n = 16200 g mol^{-1}, M_w/M_n = 1.05. ^{1}H NMR (500 MHz, $CDCl_3$): δ / ppm 7.49–6.25 (br, aromatic), 5.04 (br, 2H, PhCH), 4.95 (br, 2H, $CCH_2OC(O)$), 4.89–5.12 (br, 2H, Ph-CH), 4.13–4.28 (br, 4H, OCH2), 3.91–4.05 (br, 4H, OCH2), 3.53–3.38 (br, 6H, OCH_3), 2.43–2.31 (br, 6H, CH_2, NCH), 2.15–1.22 (br, backbone), 0.99–0.84 (br, 8H, $CHCH_3$).

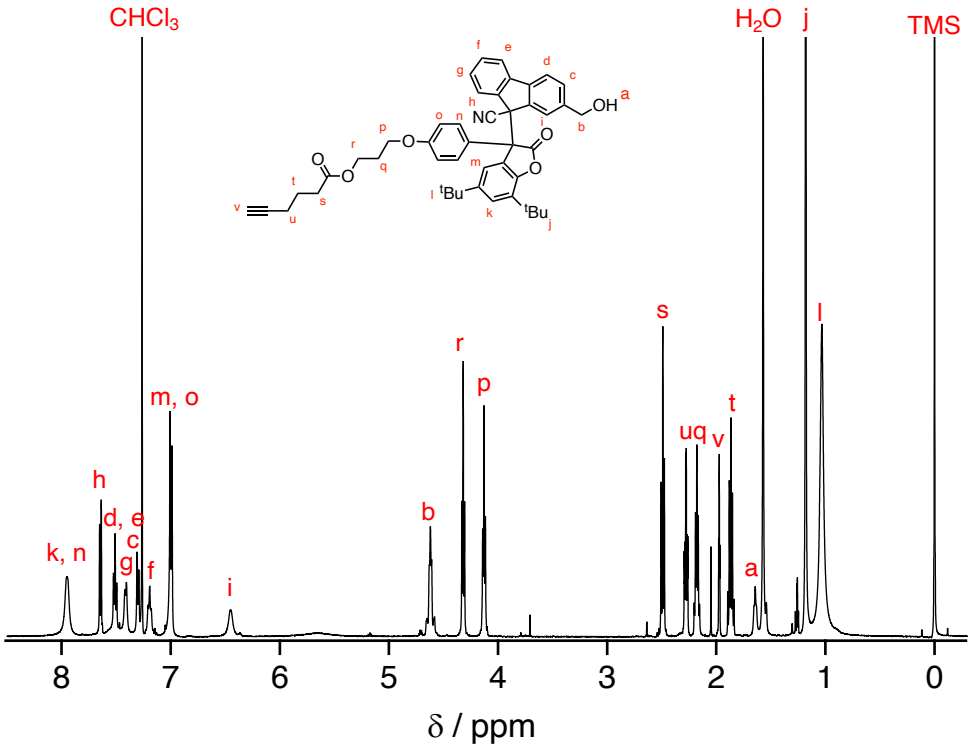


Figure S1. ^{1}H NMR spectrum of **HO-CF/ABF-alkyne 1** ($CDCl_3$, 500 MHz).

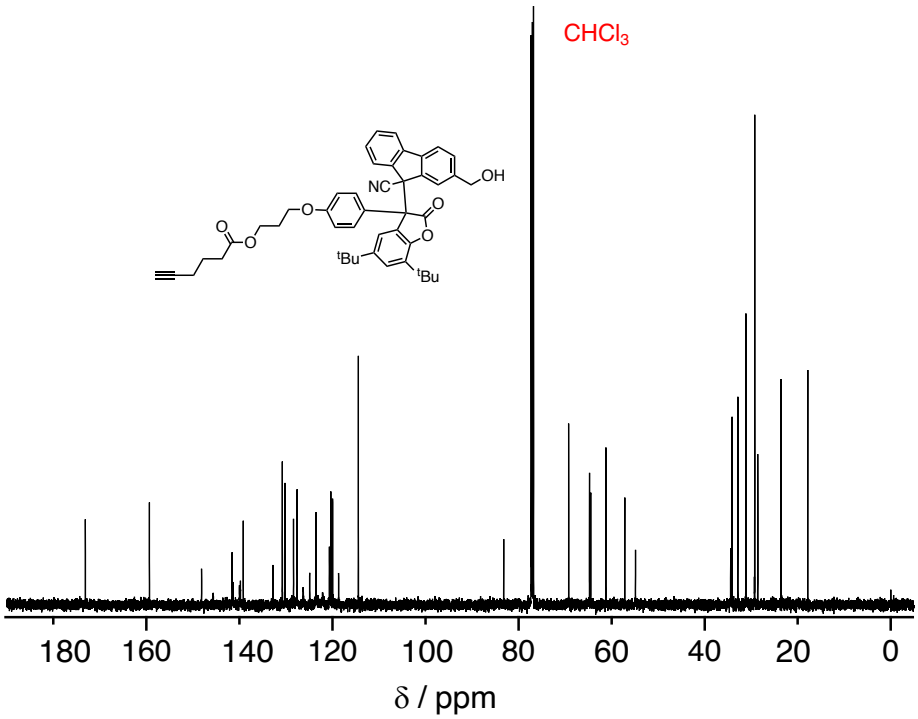


Figure S2. ^{13}C NMR spectrum of **HO-CF/ABF-alkyne1** ($CDCl_3$, 125 MHz).

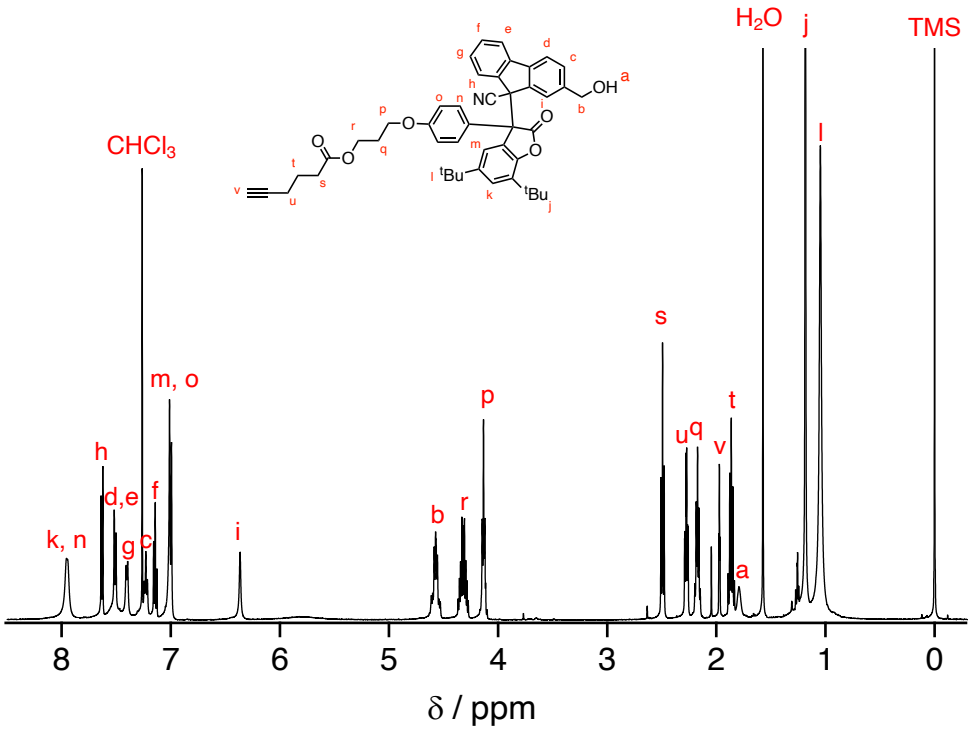


Figure S3. ^{1}H NMR spectrum of **HO-CF/ABF-alkyne 2** ($CDCl_3$, 500 MHz).

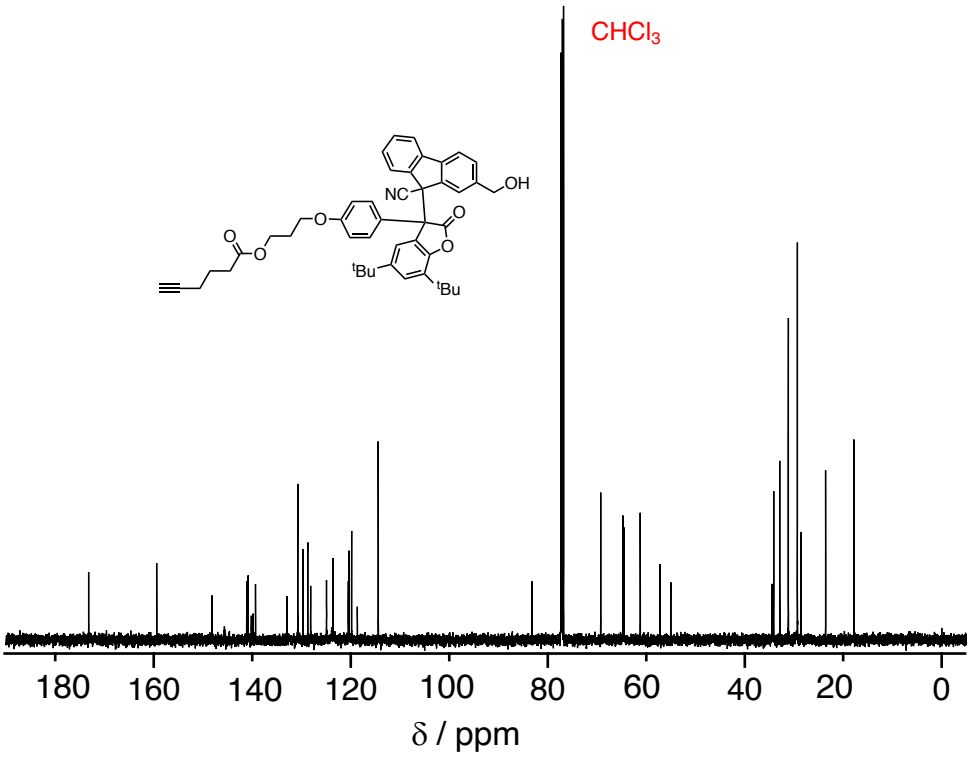


Figure S4. ^{13}C NMR spectrum of **HO-CF/ABF-alkyne1** ($CDCl_3$, 125 MHz).

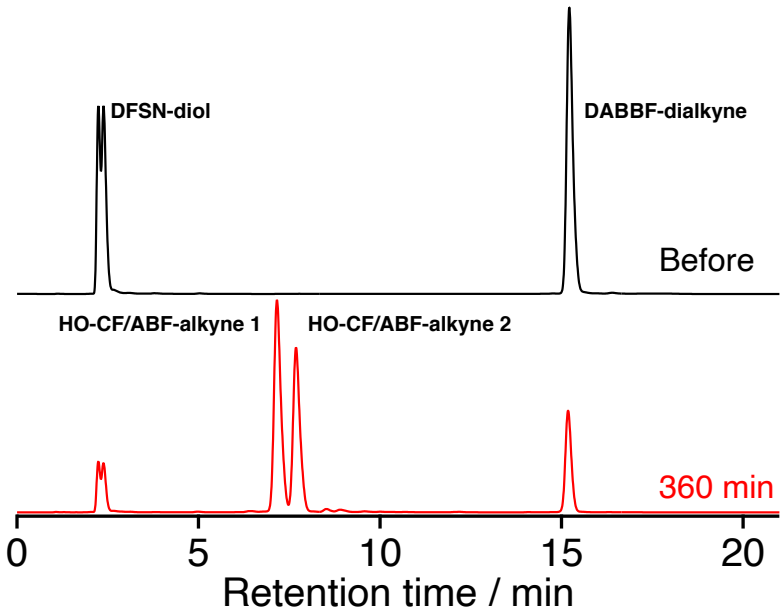


Figure S5. HPLC profiles of before (black) and after 360 min (red) radical exchange reaction between **DFSN-diol** and **DABBF-dialkyne** in 1,4-dioxane at 90 °C. The reaction reached equilibrium in 180 min, and the formation ratio at equilibrium (**DFSN-diol** : **DABBF-dialkyne** : **HO-CF/ABF-alkyne** = 1 : 1 : 4.6).

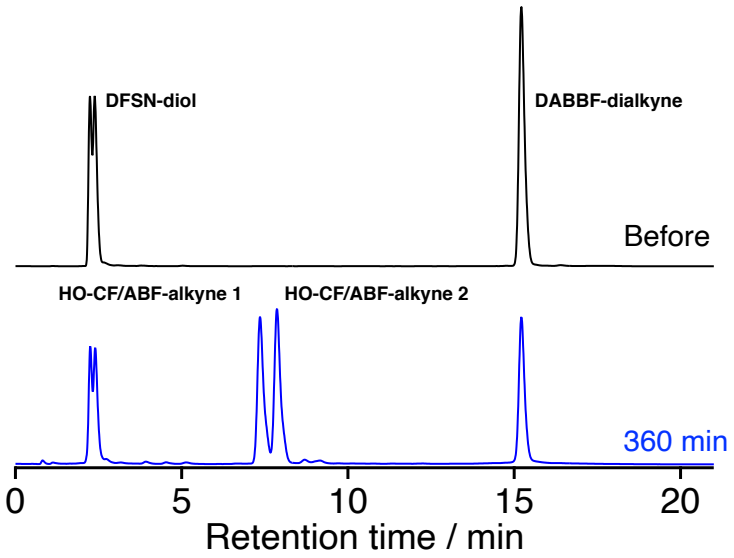


Figure S6. HPLC profiles of before (black) and after (blue) radical exchange reaction between **DFSN-diol** and **DABBF-dialkyne** by ball milling. The reaction reached equilibrium in 360 min, and the formation ratio at equilibrium (**DFSN-diol** : **DABBF-dialkyne** : **HO-CF/ABF-alkyne** = 1 : 1 : 2).

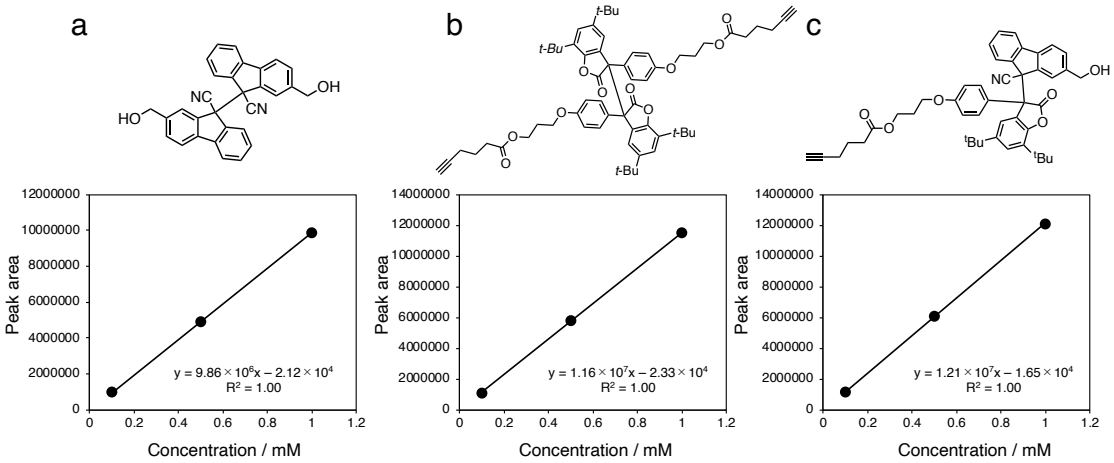


Figure S7. Calibration curves of a) **DFSN-diol**, b) **DABBF-dialkyne**, and c) **HO-CF/ABF-alkyne**.

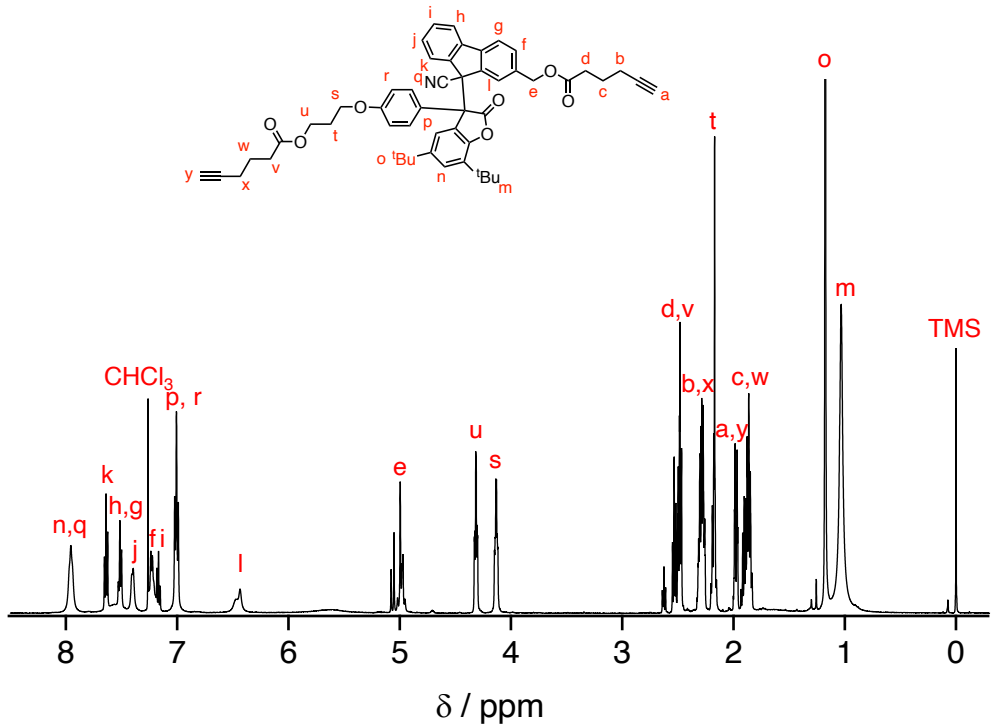


Figure S8. ^{1}H NMR spectrum of **alkyne-CF/ABF-alkyne** ($CDCl_3$, 500 MHz).

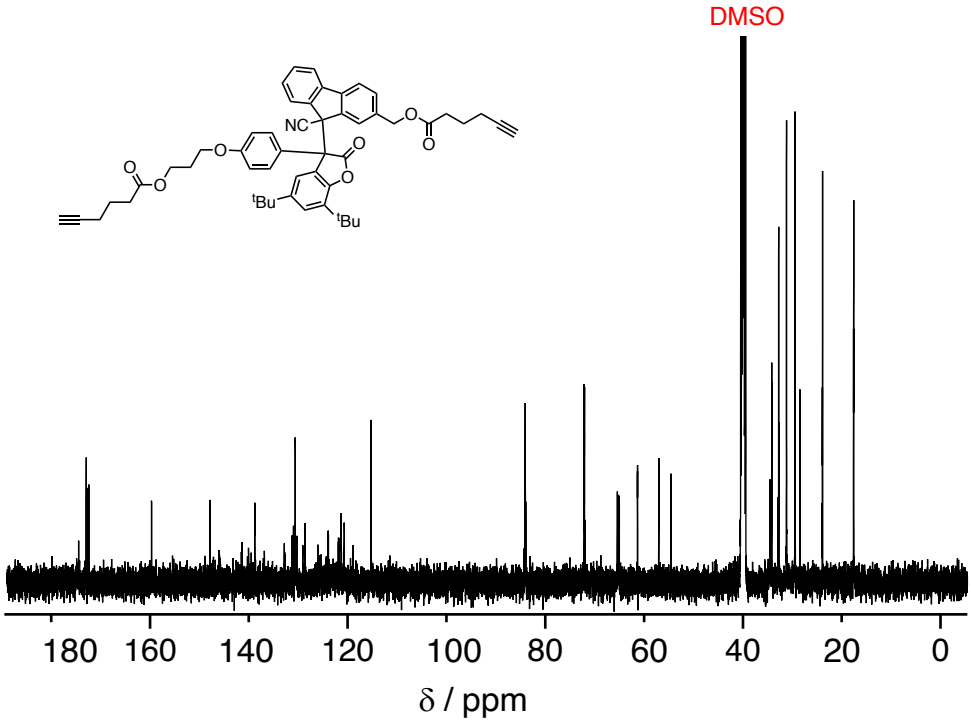


Figure S9. ^{13}C NMR spectrum of **alkyne-CF/ABF-alkyne** (DMSO-d_6, 125 MHz).

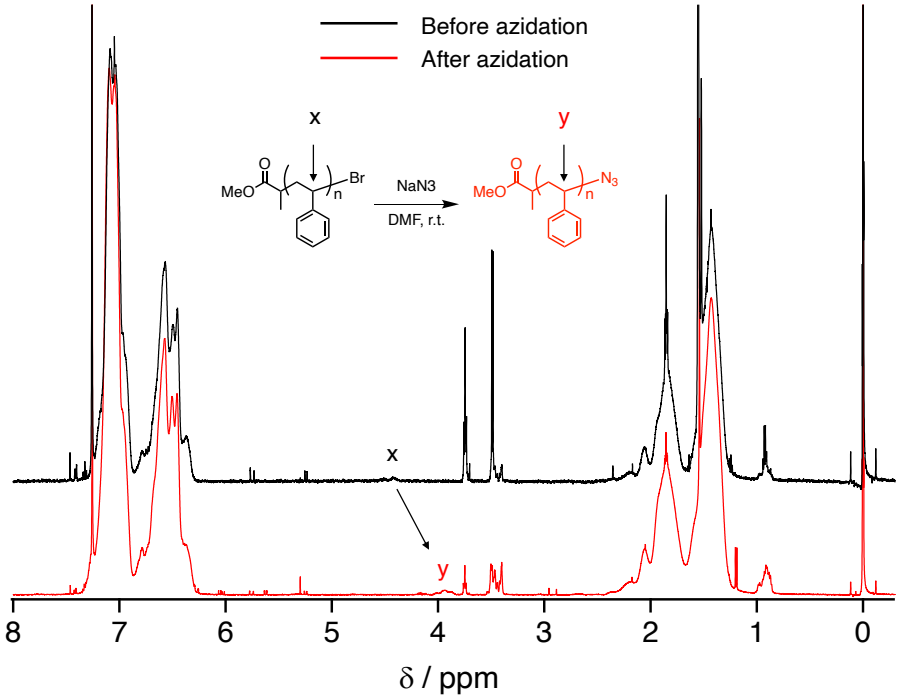


Figure S10. ^{1}H NMR spectra of **PS-Br** (M_n = 8100) (black) and **PS-N$_3$** (M_n = 8000) (red) in the chemical shift range from 4.41 to 3.94 ppm ($CDCl_3$, 500 MHz).

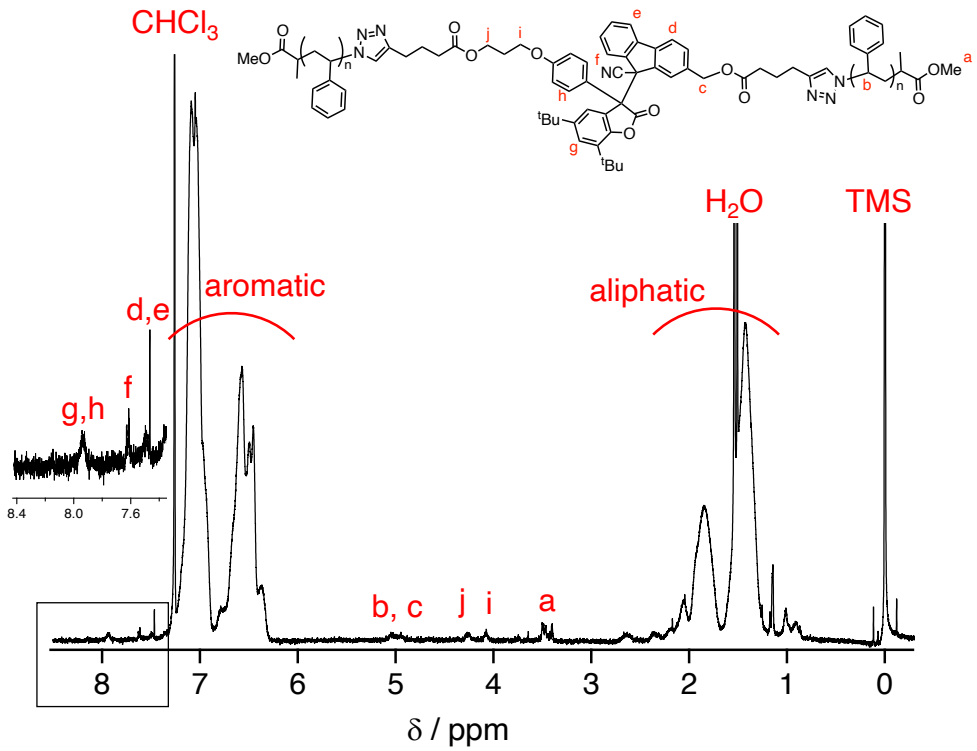


Figure S11. ^{1}H NMR spectrum of **PS-CF/ABF-PS** ($CDCl_3$, 500 MHz).

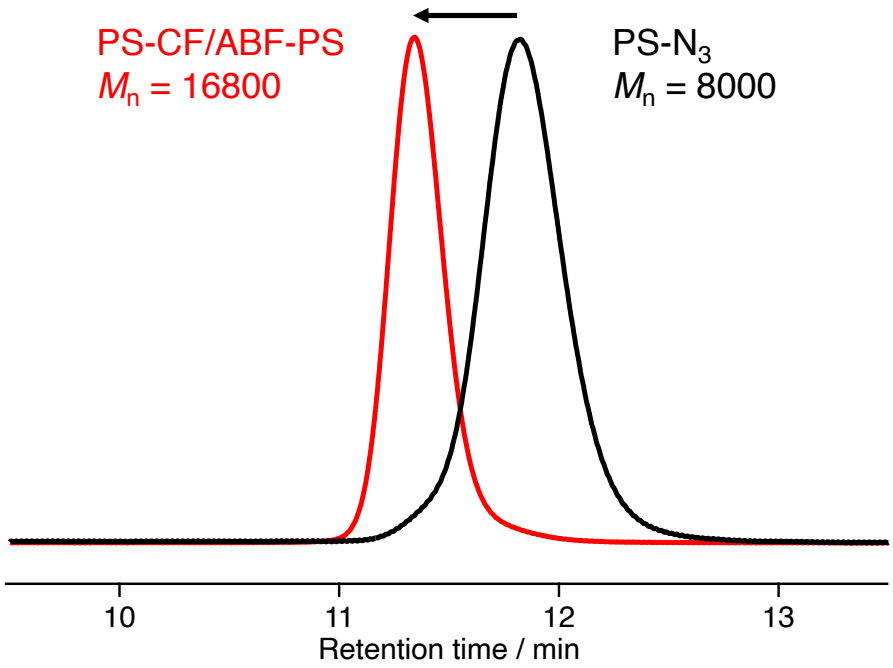


Figure S12. SEC profiles of **PS-N₃** (M_n = 8000) (black) and **PS-CF/ABF-PS** (M_n = 16800) (red).

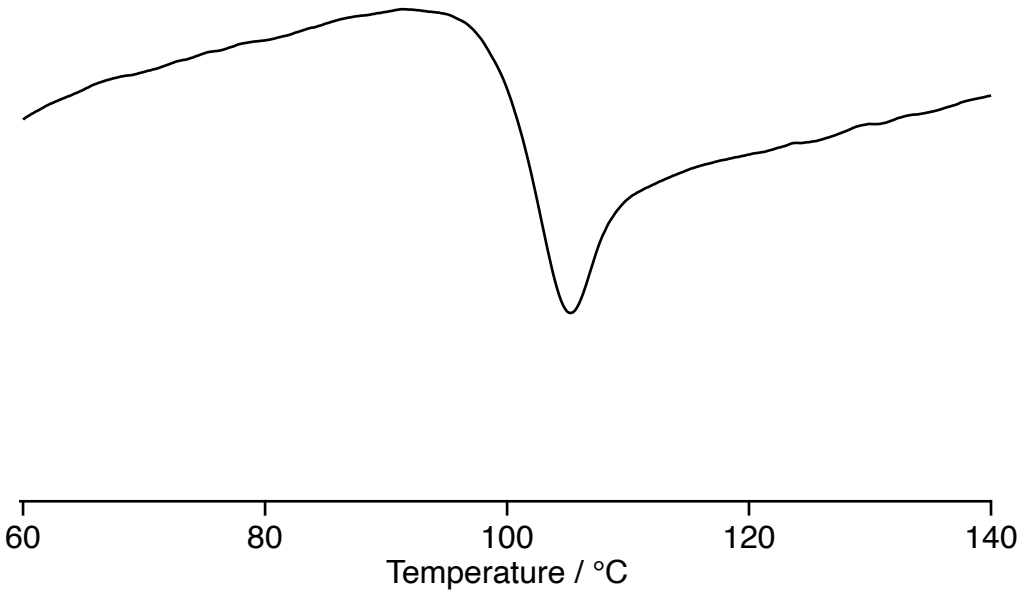


Figure S13. DSC profile of **PS-CF/ABF-PS**.

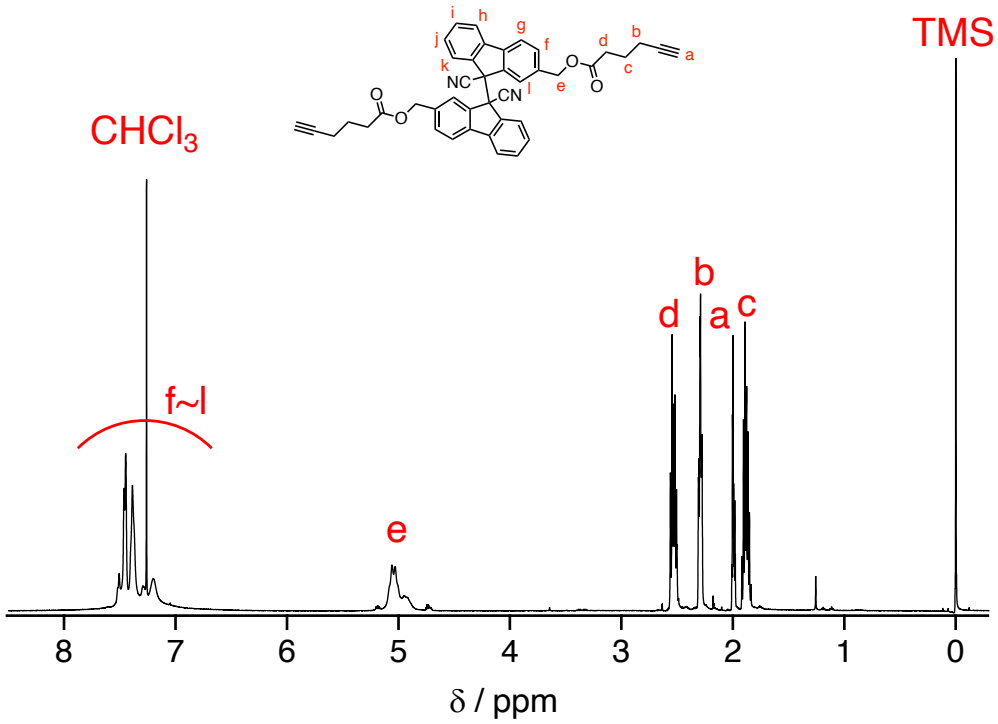


Figure S14. ^{1}H NMR spectrum of **DFSN-dialkyne** ($CDCl_3$, 500 MHz).

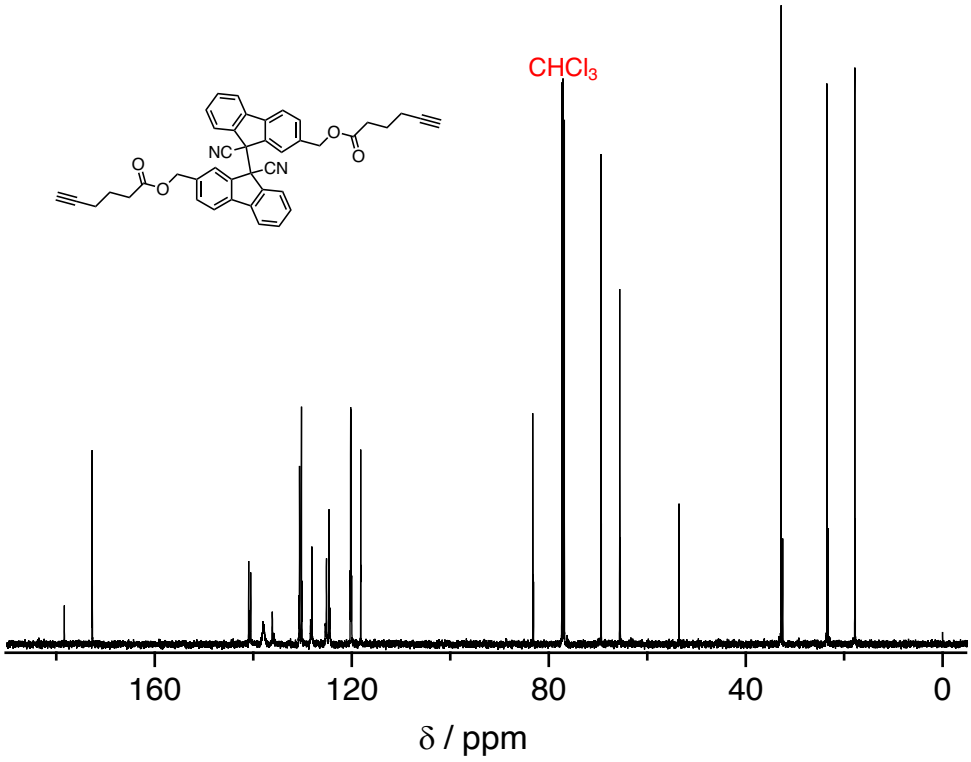


Figure S15. ^{13}C NMR spectrum of **DFSN-dialkyne** ($CDCl_3$, 125 MHz).

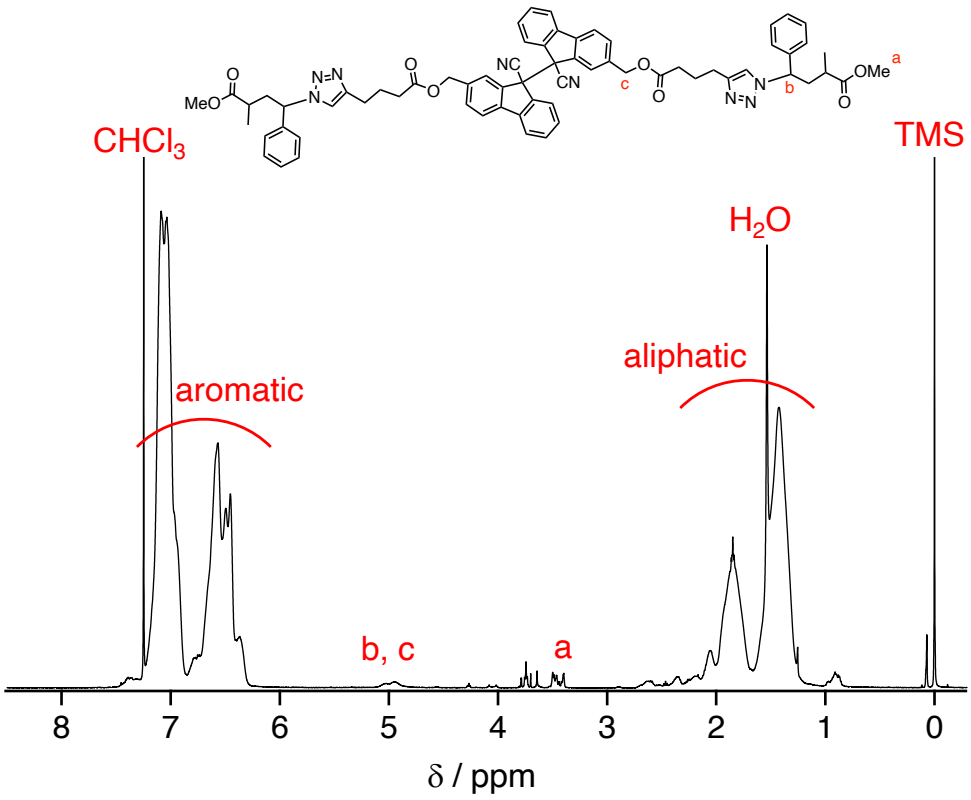


Figure 16. ^{1}H NMR spectrum of **PS-DFSN-PS** ($CDCl_3$, 500 MHz).

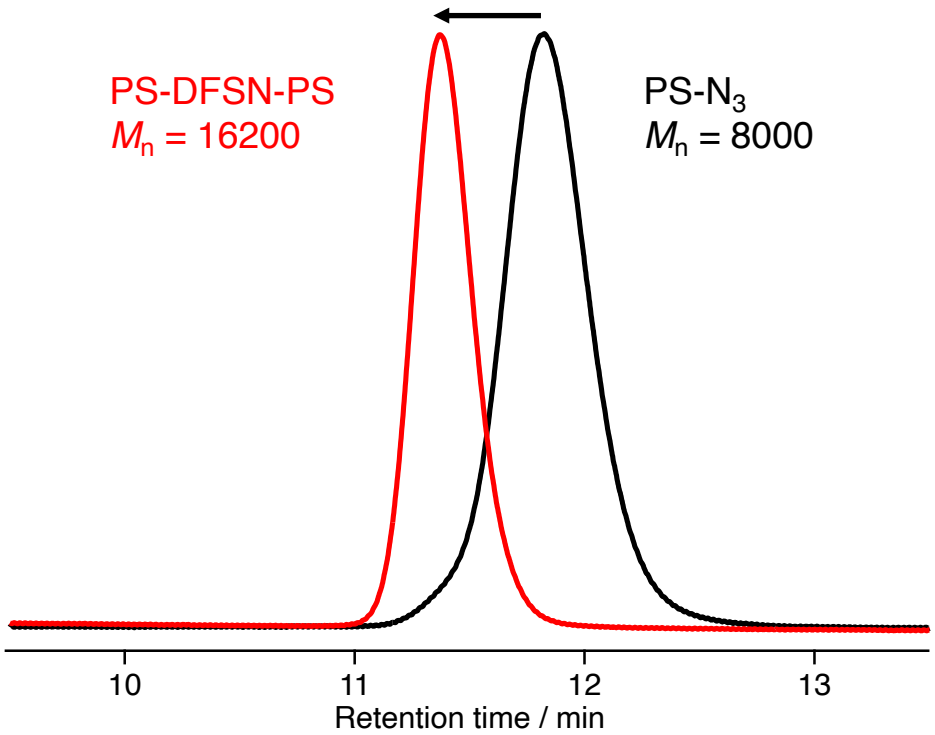


Figure S17. SEC profiles of **PS-N$_3$** (M_n = 8000) (black) and **PS-DFSN-PS** (M_n = 16200) (red).

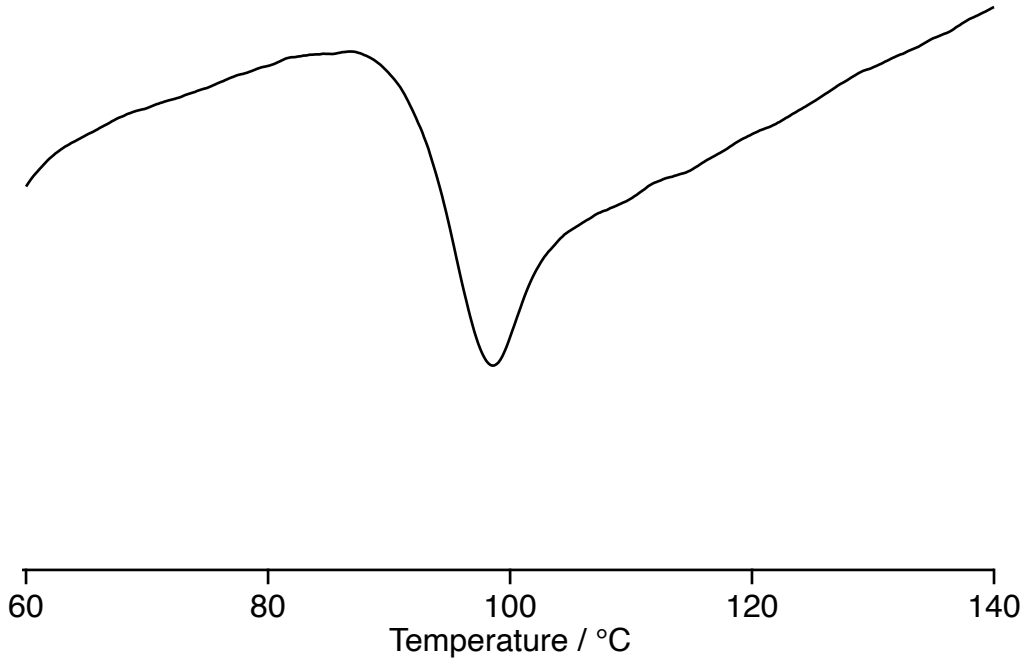


Figure S18. DSC profile of **PS-DFSN-PS**.

3. Electron Paramagnetic Resonance (EPR) Study in Solutions

Variable-temperature EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller.

Anisole solutions of **DABBF-diol** (25 mM), **DFSN** (25 mM), and **HO-CF/ABF-alkyne** (25 mM) were contained in 5 mm glass capillaries to be more than 43.5 mm height, which is the effective measuring range, and the capillaries were sealed after being degassed. Their spectra were measured using a microwave power of 0.10 mW and field modulation of 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.125 mT/s during the heating process from 0 to 120 °C. The concentration of the radicals formed from the cleavage of DABBF, DFSN, and CF/ABF was determined by comparing the area of the observed integral spectrum with a 0.01 mM solution of 4-hydroxy-2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPOL) in benzene under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The *g* value was calculated according to the following equation: $g = h\nu/\beta H$ where *h* is the Planck constant, ν is the microwave frequency, β is the Bohr magneton, and *H* is the magnetic field.

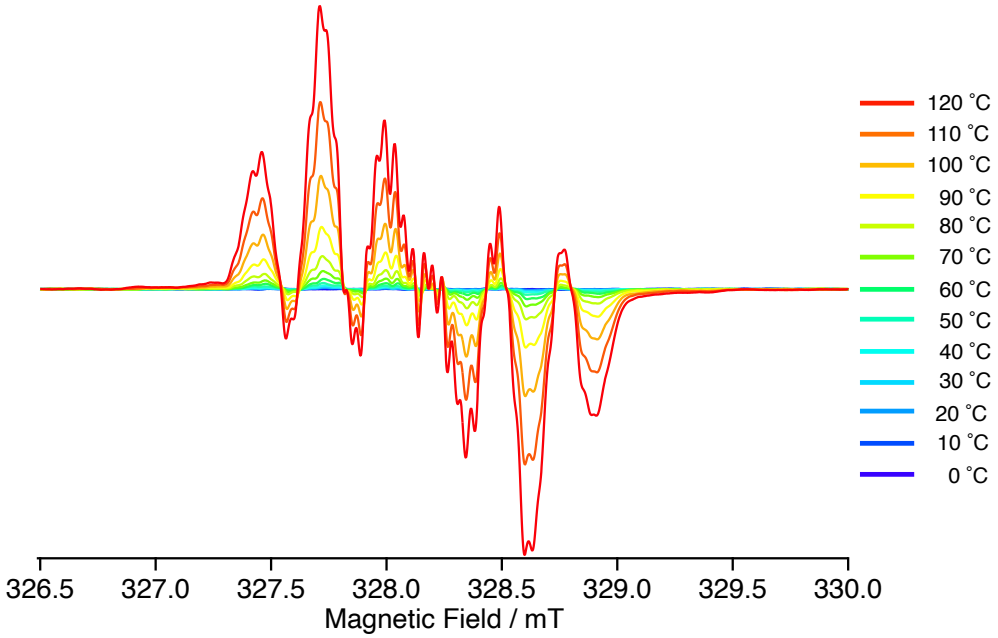


Figure S19. EPR spectra of **HO-CF/ABF-alkyne** in anisole at various temperatures in anisole (25 mM).

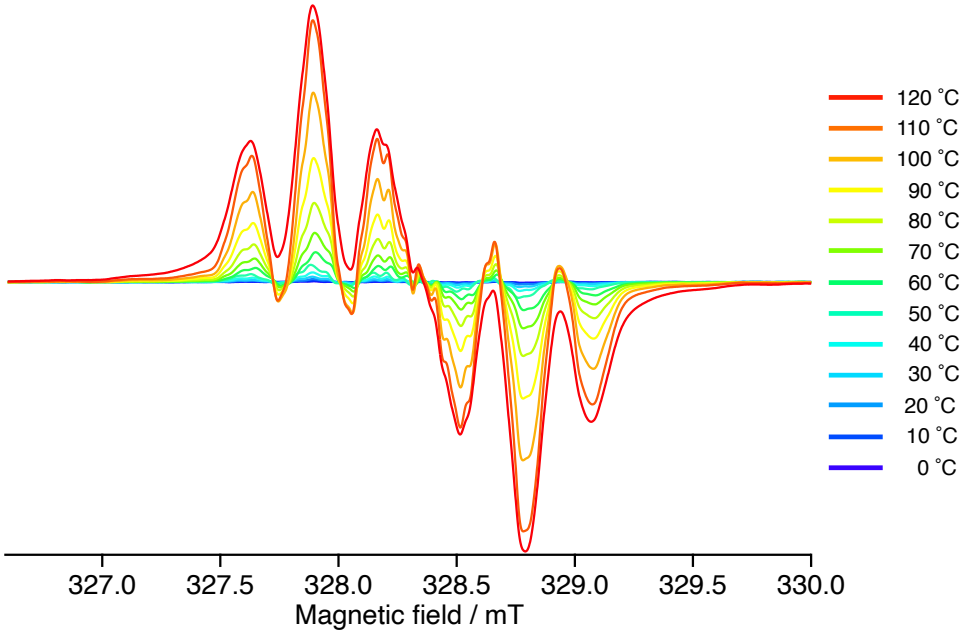


Figure S20. EPR spectra of **DABBF-diol** in anisole at various temperatures in anisole (25 mM).

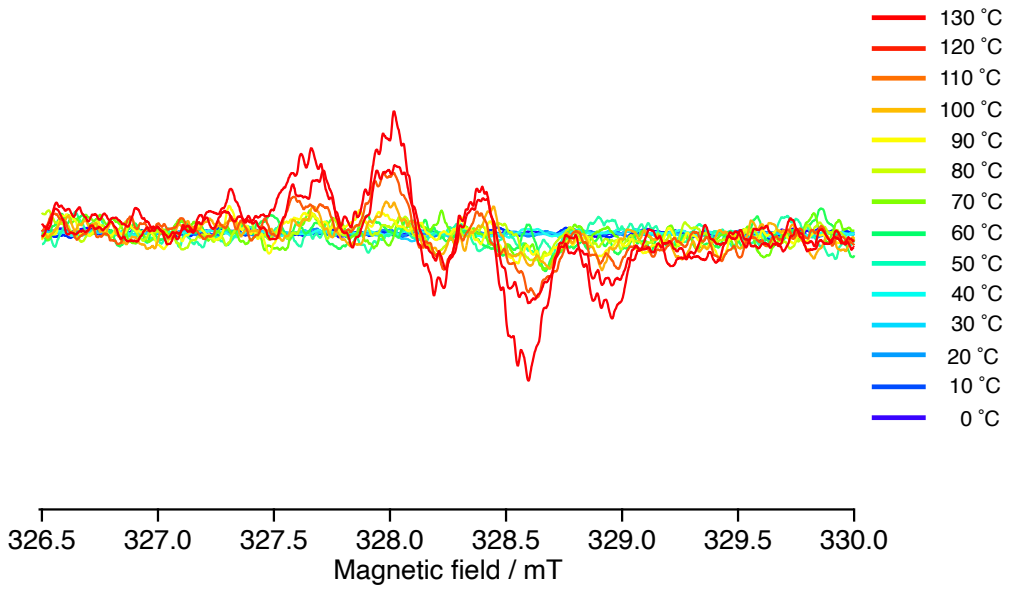


Figure S21. EPR spectra of **DFSN** in anisole at various temperatures in anisole (25 mM).

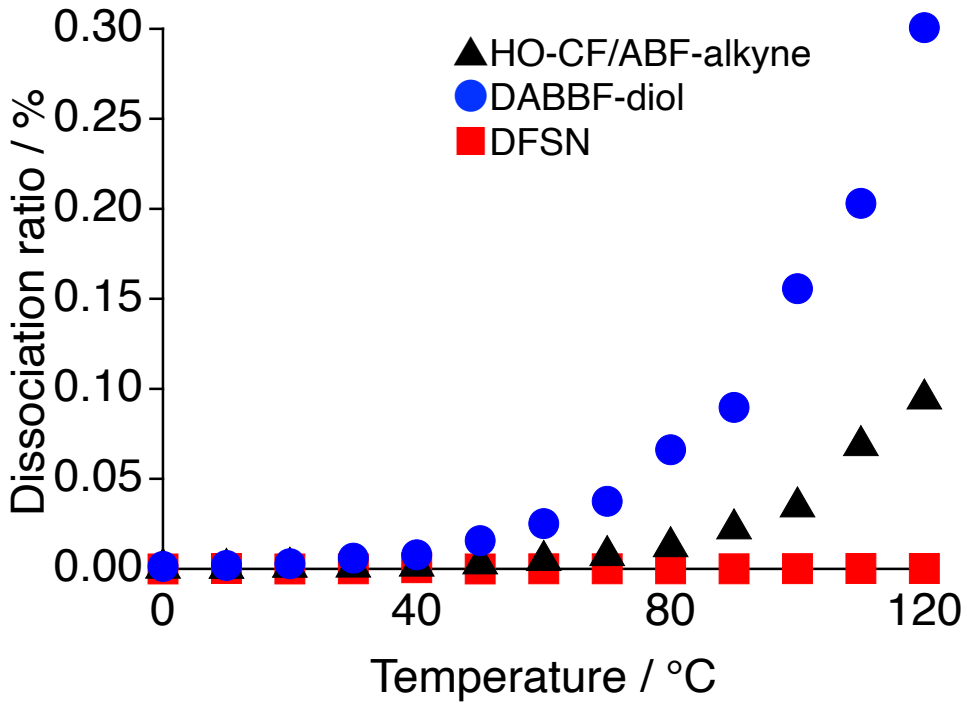
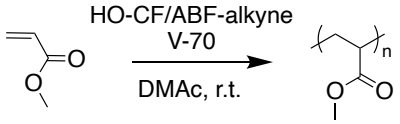


Figure S22. Dissociation ratio of **HO-CF/ABF-alkyne**, **DABBF-diol**, and **DFSN** estimated from EPR measurements at various temperatures in anisole (25 mM).

4. Stability test (polymerization of methyl acrylate)

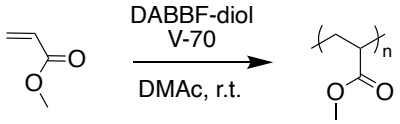
The stability evaluation of CF/ABF at room temperature was carried out by free radical polymerization of methyl acrylate (MA) using the following procedure. Since the ABF radical acts as a radical polymerization inhibitor, polymerization does not proceed when ABF radical is generated.

4-1. Polymerization of MA in the presence of HO-CF/ABF-alkyne



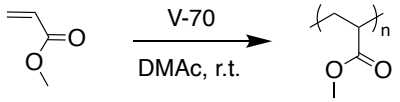
In a round-bottomed flask, a solution of **HO-CF/ABF-alkyne** (11.0 mg, 0.0150 mmol), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 18.8 mg, 0.0600 mmol), methyl acrylate (1.05 g, 12.2 mmol), and *N,N*-dimethylacetamide (DMAc, 1 mL) was prepared. The mixture was bubbled with nitrogen for 30 h. The reaction mixture was stirred at 25 °C for 2 h. The crude product was analyzed by SEC.

4-2. Polymerization of MA in the presence of DABBF-diol



In a round-bottomed flask, a solution of **DABBF-diol** (11.0 mg, 0.0139 mmol), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 18.8 mg, 0.0600 mmol), methyl acrylate (1.05 g, 12.2 mmol), and *N,N*-dimethylacetamide (DMAc, 1 mL) was prepared. The mixture was bubbled with nitrogen for 30 h. The reaction mixture was stirred at 25 °C for 2 h. The crude product was analyzed by SEC.

4-3. Polymerization of MA in the absence of RM (control)



In a round-bottomed flask, 2,2'- azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 18.8 mg, 0.0600 mmol), methyl acrylate (1.05 g, 12.2 mmol), and *N,N*-dimethylacetamide (DMAc, 1 mL) was prepared. The mixture was bubbled with nitrogen for 30 h. The reaction mixture was stirred at 25 °C for 2 h. The crude product was analyzed by SEC.

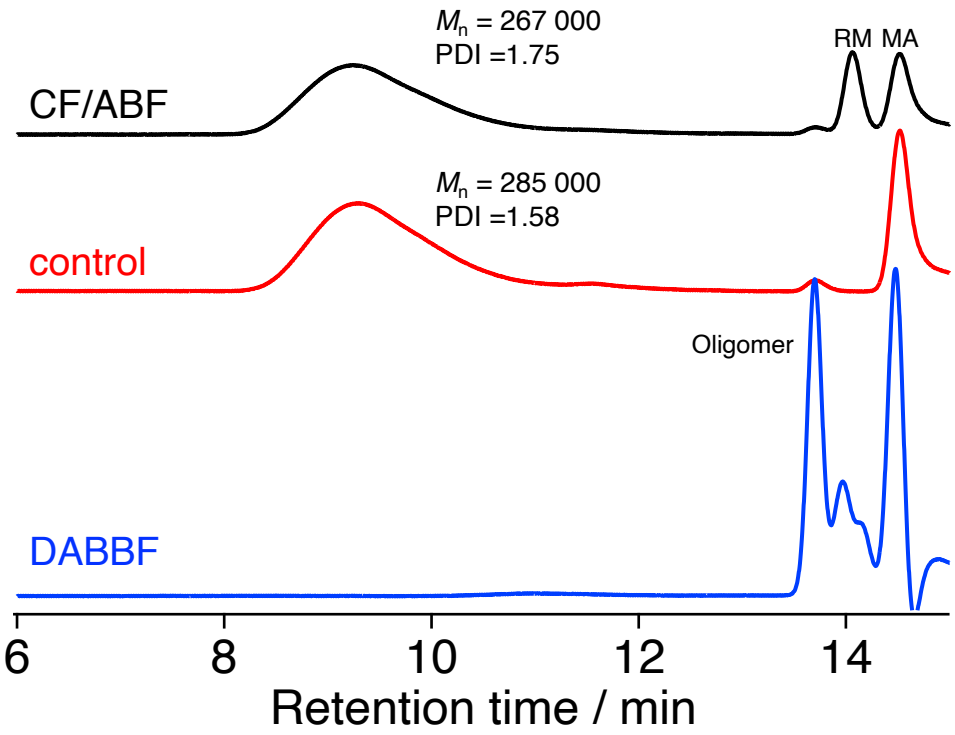


Figure S23. SEC profiles of the reaction mixtures after free radical polymerization of poly (methyl acrylate) in the presence of **HO-CF/ABF-alkyne** (black), **DABBF-diol** (blue), and no RM (red).

5. Grinding Tests and EPR Study in Solid States

Grinding tests of **PS-DABBF-PS**, **PS-DFSN-PS**, **PS-CF/ABF-PS**, and blend of **PS-DABBF-PS** and **PS-DFSN-PS** (1:1, w/w) were performed on a Retsch Mixer Mill MM 400. The mechanical energy was controlled by vibrational frequency and grinding time. A powdered sample (50 mg) and a stainless ball (d = 5 mm) were placed in the grinding jar and ball-milled for 10 min at 30 Hz. The ground samples were transferred into an EPR 5 mm glass capillary, and the capillary was sealed after being degassed. EPR measurements were carried out on a JEOL JES-X320 X-band EPR spectrometer equipped with a JEOL DVT temperature controller. The spectra of the ground samples were measured using a microwave power of 0.1 mW and field modulation of 0.1 mT with a time constant of 0.03 s and a sweep rate of 0.125 mT/s at r.t. The concentration of the radicals formed from the cleavage of DABBF, DFSN, and CF/ABF was determined by comparing the area of the observed integral spectrum with a 0.05 mM solution of TEMPOL in benzene under the same experimental conditions. The Mn^{2+} signal was used as an auxiliary standard. The g value was calculated according to the following equation: $g = h\nu/\beta H$ where h is the Planck constant, ν is the microwave frequency, β is the Bohr magneton, and H is the magnetic field.

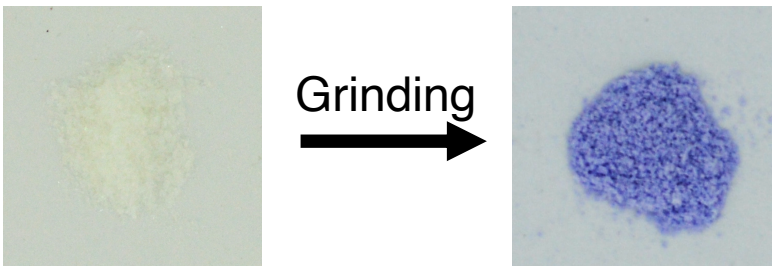


Figure S24. Photographs of the polymer blend of **PS-DABBF-PS** and **PS-DFSN-PS** (1:1, w/w) before and after grinding.

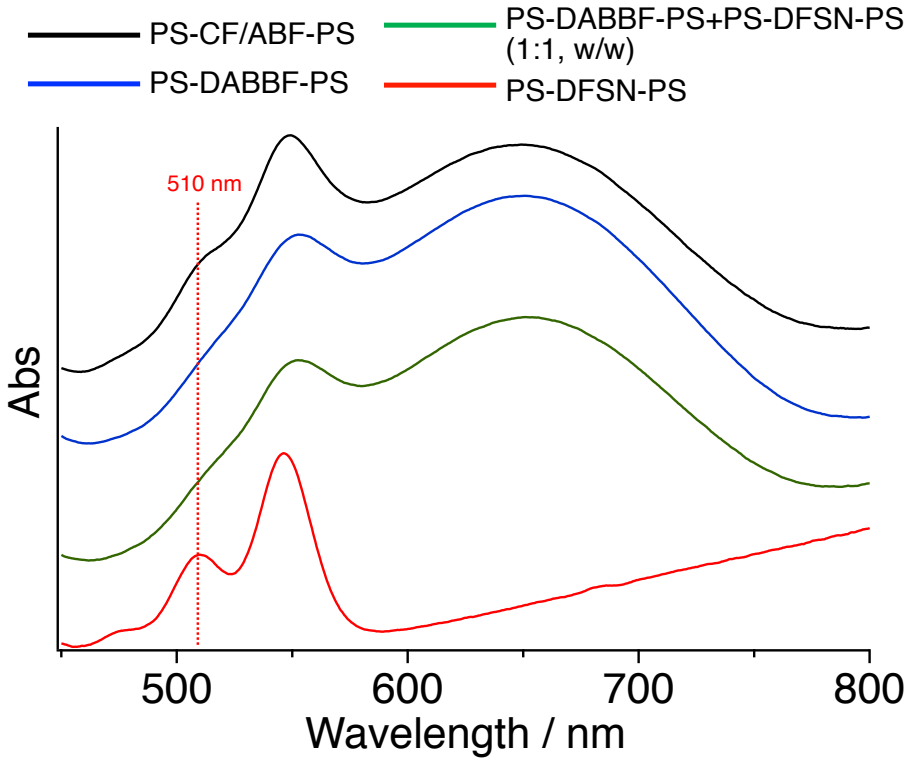


Figure S25. UV-vis spectra of **PS-CF/ABF-PS** (black), **PS-DABBF-PS** (blue), **PS-DFSN-PS** (red), and polymer blend of **PS-DABBF-PS** and **PS-DFSN-PS** (green) after grinding. The characteristic peak overlap at 510 nm seen in **PS-CF/ABF-PS** is not observed in the polymer blend.

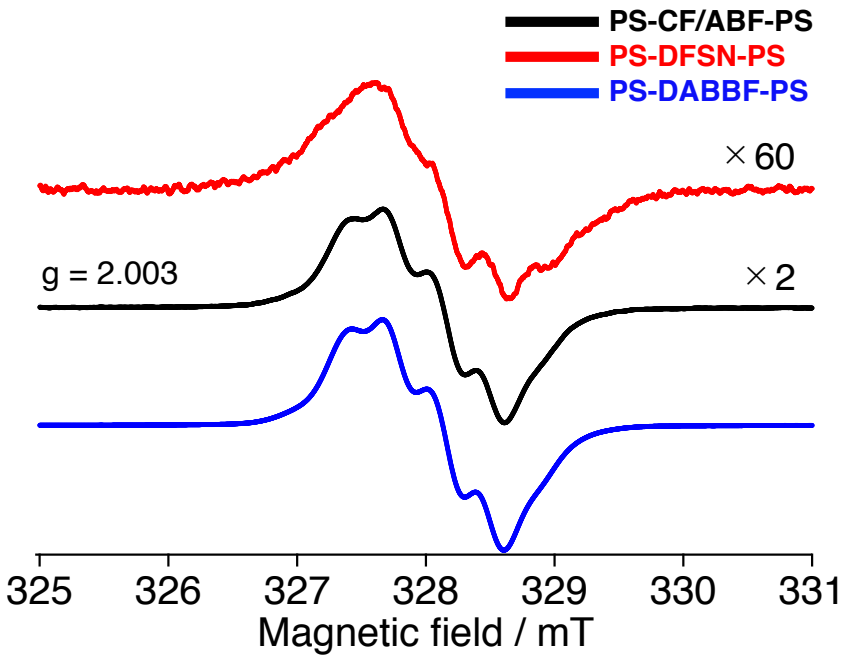


Figure S26. EPR spectra of **PS-DFSN-PS** (red), **PS-CF/ABF-PS** (black), and **PS-DABBF-PS** (blue) after grinding.

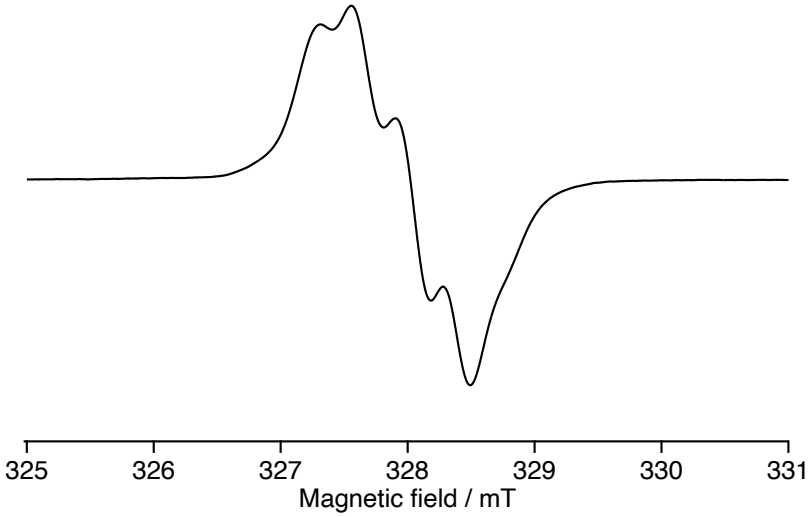


Figure S27. EPR spectrum of polymer blend of P**S-DABBF-PS** and **PS-DFSN-PS** (1:1, w/w) after grinding.

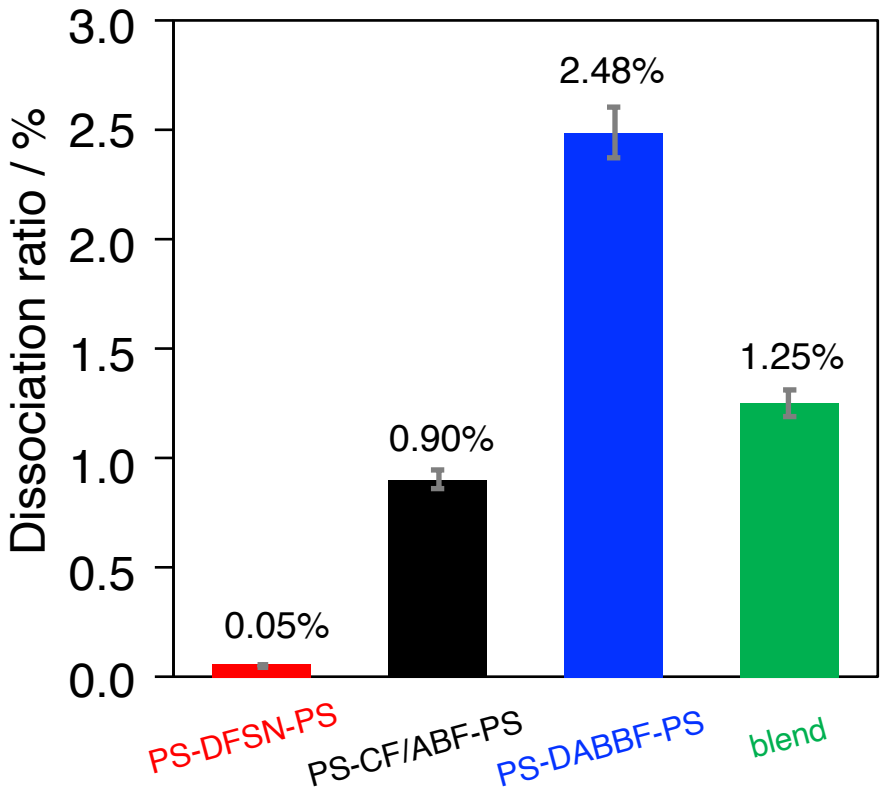


Figure S28. Percentage of dissociated ratio of **PS-CF/ABF-PS** (black), **PS-DABBF-PS** (blue), **PS-DFSN-PS** (red), and polymer blend of **PS-DABBF-PS** and **PS-DFSN-PS** (1:1, w/w) after grinding.

6. Computational details

All computations were performed using Gaussian 16 program package.[4] Geometry optimizations, vibrational analyses of all local equilibrium structures were performed using unrestricted cam-B3LYP. For the calculation, 6-31G(d,p) basis set was used. All stationary points were optimized without any symmetry assumptions and were characterized by normal coordinate analysis at the same level of theory (number of imaginary frequencies, NIMAG, 0 for minima). Cartesian coordinates and energies of the computed structures are listed on pages S28–S47.

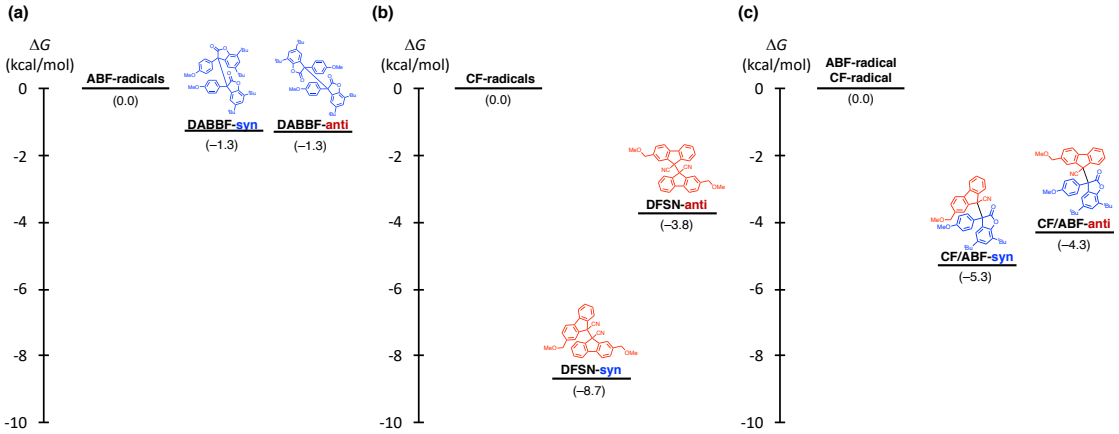


Figure S29. Energy diagram of the mechanophores and their radicals: (a) DABBF, (b) DFSN and (c) CF/ABF.

7. References

(1) Oka, H.; Imato, K.; Sato, T.; Ohishi, T.; Goseki, R.; Otsuka, H. Enhancing Mechanochemical Activation in the Bulk State by Designing Polymer Architectures. *ACS Macro Lett.* **2016**, *5*, 1124–1127.

(2) Sakai, H.; Sumi, T.; Aoki, D.; Goseki, R.; Otsuka, H. Thermally Stable Radical-Type Mechanochromic Polymers Based on Difluorenylsuccinonitrile. *ACS Macro Lett.* **2018**, *7*, 1359–1363.

(3) Earl, R. A.; Vollhardt, K. P. C. The Preparation of 2(1*H*)-Pyridinones and 2,3-Dihydro-5(1*H*)-Indolizinones via Transition Metal Mediated Cocyclization of Alkynes and Isocyanates. A Novel Construction of the Antitumor Agent Camptothecin. *J. Org. Chem.* **1984**, *49*, 4786–4800.

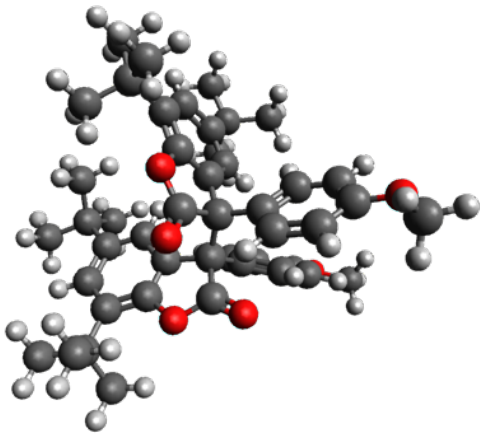
(4) Gaussian 16, Revision C.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.

8. Appendix

Optimized geometries and cartesian coordination

The geometries were given by ball and stick type model (atom color: gray = carbon, blue = nitrogen, red = oxygen, white = hydrogen).

DABBF-syn



E = -2235.680469 a.u.

Zero point energy = -2234.768177 a.u.

Thermal free energy = -2234.850922 a.u.

C	-0.2143790000	-2.7642880000	-0.5471370000
C	0.0717970000	-0.2682140000	-2.1932140000
C	-0.7847210000	-0.2657550000	-0.9148670000
C	-0.5693750000	1.1640960000	-0.4563360000
C	0.0910120000	1.8474870000	-1.4671220000
O	0.4350490000	1.0059710000	-2.5167950000
C	-0.1830580000	-1.3492580000	0.0874150000
C	1.3171050000	-1.1644300000	0.2518360000
C	1.9537190000	-2.3115430000	-0.1978590000
O	1.0536430000	-3.2577820000	-0.6501850000
C	-0.9205340000	1.8395740000	0.6992410000
C	0.0164120000	3.8426300000	-0.2401250000
C	0.3920890000	3.2010860000	-1.4288800000
C	2.0829640000	-0.1149410000	0.7343430000
C	3.4759570000	-0.2368050000	0.7878430000
C	4.0575060000	-1.4160050000	0.3190390000
C	3.3290860000	-2.4943740000	-0.1978240000

H	5.1327590000	-1.5081760000	0.3532160000
H	1.6033420000	0.7926500000	1.0778220000
O	-1.1596530000	-3.4245640000	-0.8646590000
O	0.4015930000	-1.2067410000	-2.8607790000
C	-0.6157630000	3.2002100000	0.8268160000
H	-1.4155380000	1.3116330000	1.5043450000
H	0.2316120000	4.8968950000	-0.1503690000
C	3.9819230000	-3.7733920000	-0.7309260000
C	5.5099170000	-3.7238260000	-0.6159570000
H	5.9375650000	-2.8985880000	-1.1925650000
H	5.9301990000	-4.6527200000	-1.0104930000
H	5.8406020000	-3.6279480000	0.4224600000
C	3.4816670000	-4.9865810000	0.0750290000
H	3.7408810000	-4.8843410000	1.1330660000
H	3.9509830000	-5.9013260000	-0.3001990000
H	2.4004920000	-5.1047710000	-0.0040570000
C	3.6179450000	-3.9489730000	-2.2172080000
H	3.9902860000	-3.1082290000	-2.8094180000
H	2.5393730000	-4.0148290000	-2.3641040000
H	4.0727480000	-4.8655140000	-2.6060840000
C	4.3068130000	0.9176650000	1.3660810000
C	5.8090500000	0.6115200000	1.3742340000
H	6.0429050000	-0.2669440000	1.9823550000
H	6.3528950000	1.4600910000	1.7982590000
H	6.1962180000	0.4440400000	0.3652400000
C	3.8680490000	1.1864730000	2.8169900000
H	4.0159060000	0.3003070000	3.4409080000
H	2.8132010000	1.4671600000	2.8776750000
H	4.4536150000	2.0055140000	3.2464040000
C	4.0819960000	2.1855720000	0.5243490000
H	4.3995950000	2.0246180000	-0.5095850000
H	4.6606900000	3.0206160000	0.9323440000
H	3.0307070000	2.4843940000	0.5075490000
C	1.0558760000	3.9272260000	-2.6041300000
C	0.1644680000	3.7854850000	-3.8523860000
H	0.0331960000	2.7404130000	-4.1364150000

H	0.6203900000	4.3108040000	-4.6972480000
H	-0.8235240000	4.2209800000	-3.6769740000
C	1.2414910000	5.4220120000	-2.3184830000
H	0.2876930000	5.9270690000	-2.1408060000
H	1.7097670000	5.8979130000	-3.1840920000
H	1.8912220000	5.5968940000	-1.4560630000
C	2.4411330000	3.3190770000	-2.8884720000
H	3.1052590000	3.4478980000	-2.0296660000
H	2.8978380000	3.8227600000	-3.7461300000
H	2.3760510000	2.2544990000	-3.1162960000
C	-0.9936240000	3.9310320000	2.1228140000
C	-0.2779460000	3.2633920000	3.3112690000
H	-0.5519900000	2.2101530000	3.4128820000
H	-0.5426260000	3.7669010000	4.2463340000
H	0.8085850000	3.3204210000	3.1935120000
C	-2.5158270000	3.8460690000	2.3351010000
H	-2.8571220000	2.8115660000	2.4229300000
H	-3.0531600000	4.3086150000	1.5022980000
H	-2.8008490000	4.3666260000	3.2546180000
C	-0.5977440000	5.4117420000	2.0973750000
H	0.4813500000	5.5432410000	1.9768550000
H	-0.8830240000	5.8826450000	3.0419600000
H	-1.1022570000	5.9552500000	1.2934340000
C	-0.9598550000	-1.4169280000	1.4119680000
C	-2.2476120000	-0.4979340000	-1.3520670000
C	-3.3034740000	0.1964730000	-0.7497120000
C	-4.6154950000	-0.0091390000	-1.1320450000
C	-4.9174970000	-0.9185230000	-2.1461540000
C	-3.8824840000	-1.6091700000	-2.7692040000
C	-2.5676150000	-1.3941910000	-2.3709940000
C	-0.4041050000	-0.9806950000	2.6200820000
C	-1.1213370000	-1.0252400000	3.8027850000
C	-2.4246400000	-1.5234410000	3.8168870000
C	-2.9868550000	-1.9875650000	2.6310170000
C	-2.2549580000	-1.9348660000	1.4490620000
H	-2.6990620000	-2.3302900000	0.5461260000

H	0.6114270000	-0.6085440000	2.6476070000
H	-0.6837330000	-0.6896620000	4.7362740000
H	-3.9873440000	-2.4000360000	2.6089640000
O	-3.0491280000	-1.5247130000	5.0220340000
H	-1.7846780000	-1.9472840000	-2.8711060000
H	-4.0786810000	-2.3169560000	-3.5640650000
H	-3.1052400000	0.9188030000	0.0302840000
H	-5.4280790000	0.5317540000	-0.6605540000
O	-6.2324790000	-1.0523940000	-2.4544220000
C	-6.5861120000	-1.9597600000	-3.4769420000
H	-6.1406970000	-1.6782560000	-4.4380290000
H	-7.6718990000	-1.9164000000	-3.5596070000
H	-6.2841430000	-2.9839330000	-3.2297760000
C	-4.3602500000	-2.0441800000	5.0910590000
H	-4.3923230000	-3.0990590000	4.7954280000
H	-5.0537950000	-1.4754940000	4.4608640000
H	-4.6680660000	-1.9548430000	6.1325970000

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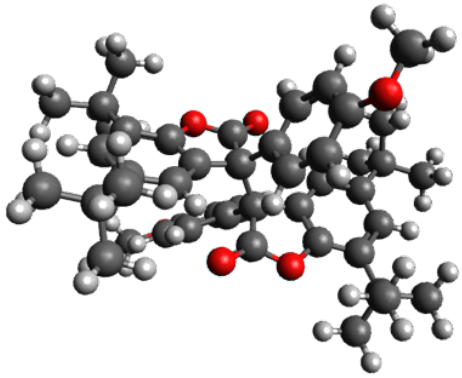


E = -2235.678308 a.u.

Zero point energy = -2234.766434 a.u.

Thermal free energy = -2234.850920 a.u.

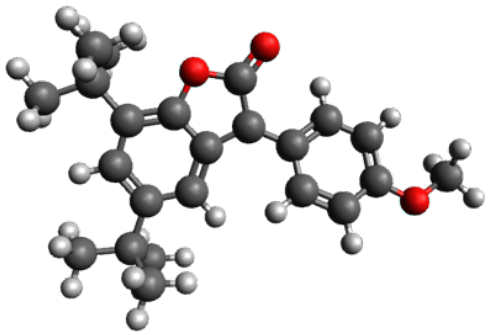
C	0.7027680000	0.3990190000	-1.8069780000
C	-0.3446760000	0.1107030000	1.9396230000
C	-0.3107050000	0.6423190000	0.4863690000
C	-1.8026720000	0.8122640000	0.2328800000
C	-2.4845830000	0.5087540000	1.4001210000

O	-1.6188930000	0.1173110000	2.4129860000
C	0.3796260000	-0.4046530000	-0.5212210000
C	1.7867440000	-0.8474790000	-0.1351940000
C	2.6866640000	-0.2983300000	-1.0340670000
O	2.0429380000	0.4591210000	-2.0033000000
C	-2.5314460000	1.1716480000	-0.8884170000
C	-4.5529590000	0.9395250000	0.3912880000
C	-3.8626870000	0.5566480000	1.5476440000
C	2.2645160000	-1.6946480000	0.8483630000
C	3.6363110000	-1.9405250000	0.9512020000
C	4.4948900000	-1.3310910000	0.0338790000
C	4.0592580000	-0.4932750000	-0.9996050000
H	5.5549580000	-1.5195560000	0.1168740000
H	1.5854080000	-2.1497400000	1.5531760000
O	-0.0481370000	0.9316370000	-2.5764810000
O	0.5617430000	-0.2433550000	2.6409780000
C	-3.9264410000	1.2387080000	-0.8192430000
H	-2.0140990000	1.3713680000	-1.8156130000
H	-5.6301350000	0.9945850000	0.4429910000
C	5.0057100000	0.1633570000	-2.0097960000
C	6.4702570000	-0.1961780000	-1.7333070000
H	6.7936840000	0.1371290000	-0.7429850000
H	7.1078760000	0.2972470000	-2.4717200000
H	6.6495540000	-1.2723860000	-1.8102010000
C	4.6581720000	-0.3116050000	-3.4328510000
H	4.7637150000	-1.3972820000	-3.5160460000
H	5.3371110000	0.1499740000	-4.1567080000
H	3.6376610000	-0.0435820000	-3.7088760000
C	4.8647520000	1.6947260000	-1.9247750000
H	5.1207010000	2.0517980000	-0.9227110000
H	3.8489190000	2.0209980000	-2.1510250000
H	5.5428390000	2.1725860000	-2.6388700000
C	4.1426540000	-2.8510350000	2.0783190000
C	5.6606510000	-3.0582700000	2.0278760000
H	5.9777340000	-3.5252460000	1.0907680000
H	5.9670970000	-3.7168680000	2.8451730000

H	6.2052150000	-2.1169420000	2.1444680000
C	3.4708380000	-4.2313370000	1.9676050000
H	3.7065490000	-4.7056260000	1.0106320000
H	2.3833180000	-4.1648710000	2.0479650000
H	3.8218090000	-4.8888500000	2.7690430000
C	3.7873810000	-2.2156690000	3.4351170000
H	4.2900830000	-1.2514300000	3.5542440000
H	4.1047380000	-2.8671780000	4.2557000000
H	2.7139430000	-2.0398830000	3.5362760000
C	-4.5592020000	0.2026730000	2.8657370000
C	-4.0638900000	1.1399940000	3.9825480000
H	-2.9875650000	1.0515490000	4.1355010000
H	-4.5613320000	0.8926870000	4.9256050000
H	-4.2924800000	2.1828190000	3.7439760000
C	-6.0817460000	0.3505370000	2.7619790000
H	-6.3777590000	1.3753260000	2.5200560000
H	-6.5345860000	0.0950030000	3.7236930000
H	-6.5080680000	-0.3186430000	2.0091980000
C	-4.2457270000	-1.2587960000	3.2372860000
H	-4.5924260000	-1.9409690000	2.4556020000
H	-4.7541530000	-1.5245940000	4.1694270000
H	-3.1758530000	-1.4164100000	3.3794530000
C	-4.7107350000	1.6220590000	-2.0816460000
C	-4.4119630000	0.5986320000	-3.1923150000
H	-3.3483120000	0.5700810000	-3.4406890000
H	-4.9622110000	0.8546640000	-4.1034270000
H	-4.7093940000	-0.4079990000	-2.8844580000
C	-4.2761840000	3.0217610000	-2.5514060000
H	-3.2096830000	3.0568090000	-2.7868440000
H	-4.4762810000	3.7721290000	-1.7809860000
H	-4.8246660000	3.3078560000	-3.4544460000
C	-6.2253330000	1.6460250000	-1.8469300000
H	-6.6061150000	0.6670100000	-1.5420610000
H	-6.7351300000	1.9234080000	-2.7736760000
H	-6.5083600000	2.3773000000	-1.0842510000
C	-0.5312840000	-1.6025020000	-0.8107290000

C	0.4729690000	1.9711840000	0.5179290000
C	-0.0137290000	3.1223970000	-0.1113770000
C	0.7132220000	4.2977060000	-0.1184800000
C	1.9575520000	4.3605440000	0.5095260000
C	2.4544100000	3.2296000000	1.1513490000
C	1.7127330000	2.0524840000	1.1517510000
C	-0.9122440000	-2.4559700000	0.2343210000
C	-1.7172130000	-3.5557350000	0.0124510000
C	-2.1676600000	-3.8491290000	-1.2762770000
C	-1.7985520000	-3.0189880000	-2.3279480000
C	-0.9914940000	-1.9087640000	-2.0863870000
H	-0.7397570000	-1.2725040000	-2.9248440000
H	-0.5803820000	-2.2689400000	1.2486650000
H	-2.0112480000	-4.2085600000	0.8263540000
H	-2.1303590000	-3.2148910000	-3.3394980000
O	-2.9509650000	-4.9517030000	-1.3956740000
H	2.1064550000	1.1916320000	1.6758960000
H	3.4094070000	3.2480430000	1.6605420000
H	-0.9780940000	3.1055410000	-0.6012010000
H	0.3340780000	5.1874420000	-0.6079160000
O	2.5956770000	5.5566390000	0.4475870000
C	3.8641700000	5.6661540000	1.0566220000
H	3.8114330000	5.4841120000	2.1362940000
H	4.1978330000	6.6888810000	0.8826190000
H	4.5861090000	4.9713640000	0.6117230000
C	-3.4331290000	-5.2869920000	-2.6790540000
H	-2.6135320000	-5.4938500000	-3.3770450000
H	-4.0632640000	-4.4916290000	-3.0939550000
H	-4.0318290000	-6.1888000000	-2.5533300000

ABF radical



E = -1117.8233099 a.u.

Zero point energy = -1117.369796 a.u.

Thermal free energy = -1117.424436 a.u.

C	-2.9220890000	0.6230860000	-0.0070100000
C	-1.9238030000	1.6097600000	0.0466940000
C	-0.5929690000	1.2092080000	0.0528280000
C	-0.2755430000	-0.1543200000	-0.0059750000
C	-1.3249160000	-1.0930510000	-0.0250310000
C	-2.6688960000	-0.7547110000	-0.0344200000
H	-3.9536770000	0.9414110000	-0.0152890000
H	0.1957270000	1.9458540000	0.1303430000
C	-3.7751800000	-1.8138360000	-0.0641270000
C	-5.1713110000	-1.1812450000	-0.0871120000
H	-5.3621100000	-0.5756180000	0.8036320000
H	-5.9246710000	-1.9729560000	-0.1133390000
H	-5.3224240000	-0.5537400000	-0.9703500000
C	-3.6206800000	-2.6827140000	-1.3260130000
H	-3.7077460000	-2.0735180000	-2.2305520000
H	-4.4075570000	-3.4428180000	-1.3542180000
H	-2.6565750000	-3.1923140000	-1.3463490000
C	-3.6693170000	-2.7007200000	1.1903450000
H	-3.7911210000	-2.1042620000	2.0993460000
H	-2.7064380000	-3.2105550000	1.2402540000
H	-4.4566740000	-3.4607950000	1.1774200000
C	-2.2591290000	3.1078390000	0.1105250000

C	-1.6237610000	3.8274930000	-1.0924520000
H	-2.0066770000	3.4263980000	-2.0350620000
H	-0.5361220000	3.7210180000	-1.1020220000
H	-1.8517540000	4.8974370000	-1.0602180000
C	-3.7687750000	3.3743920000	0.0786060000
H	-4.2816850000	2.9215500000	0.9317870000
H	-4.2302600000	2.9989790000	-0.8391820000
H	-3.9500210000	4.4517810000	0.1208930000
C	-1.6973100000	3.7021600000	1.4143830000
H	-1.9241400000	4.7712210000	1.4742850000
H	-0.6123000000	3.5890930000	1.4791380000
H	-2.1361680000	3.2119680000	2.2879140000
O	-0.8396130000	-2.3748200000	-0.0134970000
C	0.5487170000	-2.3117520000	0.0268200000
O	1.2028560000	-3.3254370000	0.0620400000
C	0.9430440000	-0.8991220000	0.0025140000
C	2.3135700000	-0.4592180000	-0.0453310000
C	2.6629200000	0.8266210000	-0.5136030000
C	3.9733240000	1.2463020000	-0.5485640000
C	4.9981410000	0.3961040000	-0.1154750000
C	4.6828230000	-0.8867970000	0.3344880000
C	3.3620250000	-1.3047690000	0.3612450000
H	1.8938730000	1.4846520000	-0.8970650000
H	4.2416880000	2.2284080000	-0.9206940000
H	5.4570910000	-1.5670100000	0.6653130000
H	3.1253390000	-2.3048000000	0.6997810000
O	6.2506640000	0.9029570000	-0.1818270000
C	7.3293460000	0.0840240000	0.2240600000
H	7.2421720000	-0.2016360000	1.2782040000
H	8.2302620000	0.6811570000	0.0874490000
H	7.3993480000	-0.8209090000	-0.3895250000

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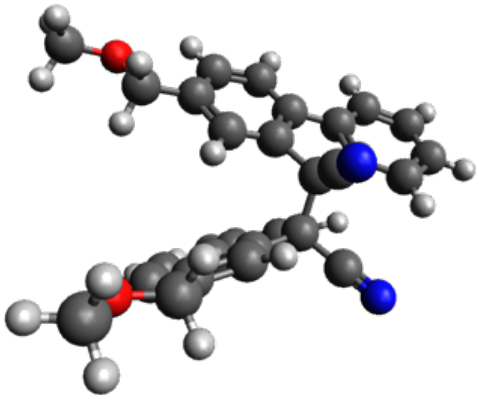

E = -1492.9937504 a.u.

Zero point energy = -1492.512572 a.u.

Thermal free energy = -1492.575782 a.u.

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C	1.1517830000	-0.7495280000	1.6692480000
C	0.8888760000	-1.4187930000	0.4692170000
C	-0.6232240000	-1.5284820000	0.2515030000
C	-1.1704190000	-0.9521080000	1.5611400000
C	-0.3719780000	0.1199650000	3.5777990000
C	-1.6879870000	0.2044320000	4.0199160000
C	-2.7298460000	-0.3029090000	3.2489000000
C	-2.4788300000	-0.8909130000	2.0106130000
C	1.9174090000	-1.8655000000	-0.3401950000
C	3.2380840000	-1.6085440000	0.0380550000
C	3.4988110000	-0.9153970000	1.2193210000
C	2.4619870000	-0.4880240000	2.0429870000
H	2.6815540000	0.0350000000	2.9683300000
H	4.5301600000	-0.7204560000	1.4864730000
H	1.7104930000	-2.4003480000	-1.2612980000
H	0.4402270000	0.4967400000	4.1908980000
H	-1.9033720000	0.6588160000	4.9814450000
H	-3.7489800000	-0.2460490000	3.6159200000
H	-3.2936600000	-1.2959390000	1.4225140000
C	4.3631790000	-2.1219080000	-0.8239590000
O	5.5609750000	-1.4646420000	-0.4963530000
H	4.1165600000	-1.9740550000	-1.8874330000
H	4.4746260000	-3.2095580000	-0.6755510000

C	6.6598290000	-1.9496170000	-1.2262510000
H	6.8324320000	-3.0189670000	-1.0368550000
H	7.5381130000	-1.3870300000	-0.9064490000
H	6.5215870000	-1.8094360000	-2.3079050000
C	-1.1174320000	-0.6908510000	-1.0146680000
C	-1.0082370000	-2.9374440000	0.0927180000
N	-1.3051660000	-4.0467670000	-0.0324870000
C	-2.6425390000	-0.6870410000	-1.1601250000
C	-3.1358230000	0.6114340000	-0.9881060000
C	-2.0081220000	1.5299940000	-0.8039450000
C	-0.8137680000	0.8024600000	-0.8602460000
C	-3.4945810000	-1.7463780000	-1.4256520000
C	-4.8653200000	-1.4974830000	-1.4796380000
C	-5.3625530000	-0.2116870000	-1.2834950000
C	-4.5016300000	0.8545120000	-1.0432610000
C	-1.9748500000	2.9064690000	-0.6409160000
C	-0.7435790000	3.5479900000	-0.5484080000
C	0.4457800000	2.8279750000	-0.6305410000
C	0.4102140000	1.4406310000	-0.7929220000
H	1.3365630000	0.8807850000	-0.8671290000
H	-2.8935730000	3.4824230000	-0.5945700000
H	-0.6904160000	4.6216750000	-0.4184270000
H	-6.4325580000	-0.0374430000	-1.3304570000
H	-4.8920510000	1.8581260000	-0.9096200000
H	-3.1132360000	-2.7482180000	-1.5846550000
H	-5.5484950000	-2.3150290000	-1.6828500000
C	-0.4978570000	-1.2291490000	-2.2335940000
N	-0.0099290000	-1.6513990000	-3.1918240000
C	1.7846850000	3.5183200000	-0.5681780000
O	1.6214490000	4.8682300000	-0.2192300000
H	2.2892240000	3.4356690000	-1.5458760000
H	2.4317400000	3.0051900000	0.1622680000
C	2.8384710000	5.5689120000	-0.1849520000
H	3.5306330000	5.1435430000	0.5561560000
H	2.6142530000	6.5999880000	0.0920840000
H	3.3376370000	5.5633480000	-1.1648170000

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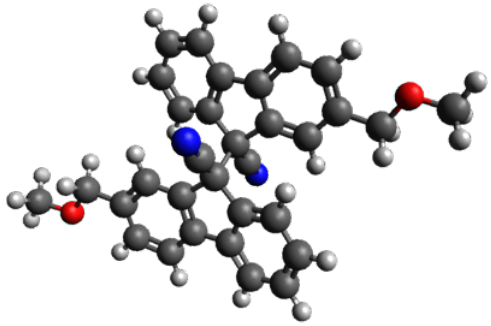

E = -1492.9828018 a.u.

Zero point energy = -1492.501927 a.u.

Thermal free energy = -1492.567868 a.u.

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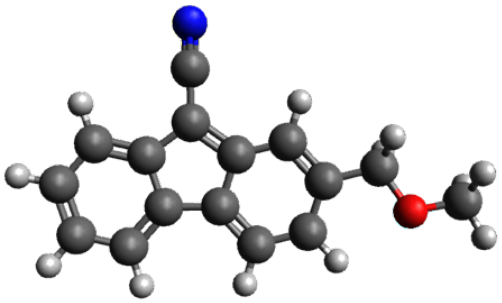
C	-1.9687350000	-2.0666350000	-0.1770060000
C	-1.8040680000	-0.7610090000	0.3021740000
C	-0.3202950000	-0.4866720000	0.5652420000
C	0.2592300000	-1.9030020000	0.4889930000
C	-0.3757610000	-4.1099740000	-0.2738090000
C	0.8803970000	-4.5723810000	0.1061020000
C	1.7947110000	-3.7202760000	0.7181490000
C	1.4870950000	-2.3751170000	0.9195490000
C	-2.8975730000	0.0543840000	0.5188660000
C	-4.1726820000	-0.4079740000	0.1785540000
C	-4.3251450000	-1.6809930000	-0.3640280000
C	-3.2286860000	-2.5226060000	-0.5302070000
H	-3.3689870000	-3.5308150000	-0.9062250000
H	-5.3207200000	-2.0158390000	-0.6266760000
H	-2.7759530000	1.0363850000	0.9635980000
H	-1.1055000000	-4.7886630000	-0.7027760000
H	1.1375410000	-5.6152780000	-0.0475100000
H	2.7511800000	-4.1068170000	1.0538140000
H	2.1891100000	-1.7205470000	1.4220030000
C	-5.3625400000	0.4831100000	0.4325350000
O	-6.5330050000	-0.1147700000	-0.0576110000
H	-5.2025030000	1.4641830000	-0.0460250000

H	-5.4546050000	0.6757070000	1.5148860000
C	-7.6782700000	0.6651280000	0.1741840000
H	-7.8453710000	0.8309690000	1.2483080000
H	-8.5309740000	0.1232990000	-0.2371930000
H	-7.6078180000	1.6454390000	-0.3191560000
C	0.3202590000	0.4861630000	-0.5645670000
C	-0.1040620000	0.1223900000	1.8800330000
N	0.0549660000	0.5899810000	2.9239710000
C	-0.2593780000	1.9024530000	-0.4884580000
C	0.6887990000	2.7747130000	0.0607420000
C	1.9685070000	2.0662980000	0.1777610000
C	1.8039890000	0.7606210000	-0.3013550000
C	-1.4872300000	2.3744470000	-0.9191930000
C	-1.7949660000	3.7195970000	-0.7179140000
C	-0.8807850000	4.5718090000	-0.1058160000
C	0.3753640000	4.1095200000	0.2742670000
C	3.2283940000	2.5224320000	0.5309420000
C	4.3249450000	1.6808900000	0.3649450000
C	4.1726350000	0.4078420000	-0.1775810000
C	2.8975930000	-0.0546340000	-0.5180270000
H	2.7761190000	-1.0365830000	-0.9629230000
H	3.3685920000	3.5307170000	0.9067960000
H	5.3204910000	2.0159140000	0.6274650000
H	-1.1380200000	5.6146990000	0.0476930000
H	1.1050090000	4.7882940000	0.7032610000
H	-2.1891490000	1.7197980000	-1.4216770000
H	-2.7514240000	4.1060430000	-1.0537240000
C	0.1041780000	-0.1229850000	-1.8793410000
N	-0.0547240000	-0.5906910000	-2.9232470000
C	5.3624430000	-0.4835860000	-0.4306030000
O	6.5341300000	0.1183170000	0.0515910000
H	5.4505970000	-0.6827620000	-1.5120710000
H	5.2051820000	-1.4618640000	0.0546050000
C	7.6790690000	-0.6626060000	-0.1783380000
H	7.6106630000	-1.6394970000	0.3220290000
H	8.5327750000	-0.1174970000	0.2265780000

H	7.8429060000	-0.8358260000	-1.2517970000

CF radical



E = -746.474468 a.u.

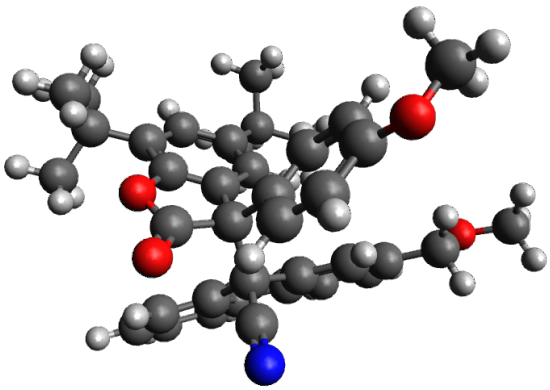
Zero point energy = -746.236653 a.u.

Thermal free energy = -746.280943 a.u.

C	1.3018310000	1.2851330000	0.0007290000
C	2.3942180000	0.3435400000	-0.0085980000
C	1.8468530000	-0.9645730000	0.0047340000
C	0.3819310000	-0.8388010000	0.0233180000
C	0.0652110000	0.5425650000	0.0210370000
C	-1.2561660000	0.9745550000	0.0317360000
C	-2.2782840000	0.0251450000	0.0507510000
C	-1.9621340000	-1.3334470000	0.0534150000
C	-0.6341080000	-1.7721580000	0.0376700000
C	2.6831790000	-2.0639760000	-0.0009170000
C	4.0660360000	-1.8584940000	-0.0197200000
C	4.6031790000	-0.5718380000	-0.0327160000
C	3.7724090000	0.5437650000	-0.0272770000
H	5.6796820000	-0.4402010000	-0.0472640000
H	4.1843490000	1.5477110000	-0.0374450000
H	2.2809590000	-3.0720010000	0.0089610000
H	4.7319040000	-2.7151050000	-0.0243190000
H	-2.7738900000	-2.0499370000	0.0612560000
H	-0.4168900000	-2.8357170000	0.0367010000
H	-1.4857720000	2.0368730000	0.0234090000
C	1.4196520000	2.6852160000	-0.0078880000
N	1.5137880000	3.8441010000	-0.0145050000
C	-3.7130930000	0.4880270000	0.0910500000

O	-4.5792520000	-0.5934780000	-0.1326470000
H	-3.8716360000	1.2733870000	-0.6660840000
H	-3.9259020000	0.9491900000	1.0705920000
C	-5.9336800000	-0.2249010000	-0.0679130000
H	-6.1969470000	0.1803410000	0.9198830000
H	-6.5253590000	-1.1227460000	-0.2515130000
H	-6.1851980000	0.5287720000	-0.8279380000

CF/ABF-syn



E = -1864.3369407 a.u.

Zero point energy = -1863.640282 a.u.

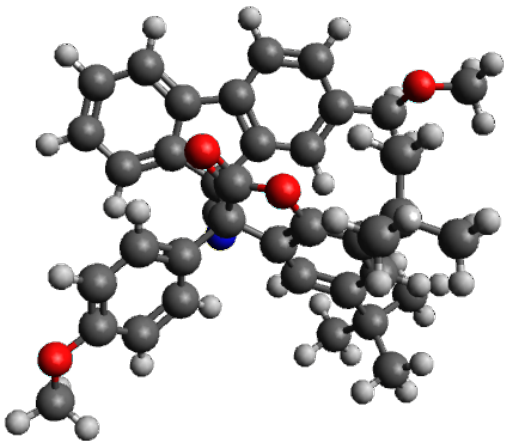
Thermal free energy = -1863.713852 a.u.

C	0.7384190000	1.8550270000	2.3196720000
C	-0.5739190000	2.0930960000	1.7102240000
C	-1.2173660000	0.8647790000	1.5219220000
C	-0.3010370000	-0.2836340000	1.9481890000
C	0.9051510000	0.4788800000	2.5128850000
C	1.7219430000	2.7458820000	2.7272600000
C	2.8659810000	2.2454430000	3.3406590000
C	3.0154550000	0.8785560000	3.5569750000
C	2.0297090000	-0.0191730000	3.1500770000
C	-2.5026640000	0.8030900000	1.0157380000
C	-3.1509470000	1.9888020000	0.6608710000
C	-2.4999980000	3.2109140000	0.8250000000
C	-1.2143020000	3.2719630000	1.3543870000
H	1.5981700000	3.8142420000	2.5816530000
H	3.6431720000	2.9288390000	3.6668030000

H	3.9031160000	0.5056950000	4.0566010000
H	2.1408790000	-1.0794620000	3.3476500000
H	-3.0065370000	-0.1503340000	0.8973610000
H	-3.0195140000	4.1162910000	0.5358270000
H	-0.7281600000	4.2323870000	1.4941140000
C	-4.5664940000	1.9283050000	0.1468300000
O	-4.8890800000	3.1196010000	-0.5248300000
H	-5.2595730000	1.7702030000	0.9907100000
H	-4.6839870000	1.0603910000	-0.5222010000
C	-6.2271850000	3.1543190000	-0.9515530000
H	-6.3851740000	4.1095350000	-1.4543100000
H	-6.9254120000	3.0762450000	-0.1055820000
H	-6.4495140000	2.3404140000	-1.6569580000
C	-0.9518430000	-1.0469560000	3.0228410000
C	0.1080280000	-1.2055100000	0.7114820000
N	-1.4895170000	-1.5834720000	3.8929120000
C	0.9181170000	-0.4267920000	-0.3067290000
C	2.1744200000	-0.9966320000	-0.3916170000
O	2.3152450000	-2.0734340000	0.4736900000
C	1.1657560000	-2.2215580000	1.1912630000
O	1.0718720000	-3.0373430000	2.0621130000
C	0.6179050000	0.6811600000	-1.0900190000
C	1.5863890000	1.1955450000	-1.9506460000
C	2.8401900000	0.5716040000	-1.9933740000
C	3.1904560000	-0.5383680000	-1.2239470000
H	-0.3576330000	1.1405080000	-1.0205500000
H	3.5869420000	0.9800700000	-2.6614650000
C	1.3298080000	2.4257560000	-2.8321560000
C	-0.1044760000	2.9494060000	-2.6931240000
H	-0.8420150000	2.1994820000	-2.9938180000
H	-0.2401780000	3.8206250000	-3.3398150000
H	-0.3325630000	3.2589060000	-1.6697210000
C	1.5646910000	2.0656840000	-4.3097950000
H	0.8895930000	1.2666360000	-4.6292450000
H	2.5884830000	1.7306580000	-4.4931000000
H	1.3831940000	2.9377220000	-4.9456550000

C	2.2941210000	3.5530320000	-2.4214380000
H	2.1448650000	3.8295550000	-1.3739210000
H	2.1253450000	4.4423290000	-3.0368210000
H	3.3393790000	3.2575870000	-2.5426050000
C	4.5725160000	-1.1968940000	-1.2678820000
C	5.5005890000	-0.5039520000	-2.2721760000
H	5.1060220000	-0.5470900000	-3.2914960000
H	6.4704950000	-1.0081880000	-2.2730940000
H	5.6751700000	0.5442720000	-2.0130320000
C	4.4301820000	-2.6719560000	-1.6863340000
H	3.9818220000	-2.7523260000	-2.6809460000
H	3.8115300000	-3.2326760000	-0.9845850000
H	5.4159780000	-3.1458480000	-1.7215230000
C	5.2244330000	-1.1119660000	0.1250060000
H	5.3393530000	-0.0698870000	0.4371490000
H	6.2178900000	-1.5704010000	0.0999360000
H	4.6313950000	-1.6307130000	0.8791550000
C	-1.0765710000	-1.9854420000	0.1195450000
C	-1.6724900000	-3.0346130000	0.8367280000
C	-1.5947680000	-1.6858340000	-1.1363960000
C	-2.6851080000	-2.3729590000	-1.6639530000
C	-3.2762380000	-3.3953220000	-0.9280840000
C	-2.7556660000	-3.7228280000	0.3255140000
H	-3.2141520000	-4.5322510000	0.8818140000
H	-1.1453770000	-0.9063920000	-1.7368930000
H	-3.0508610000	-2.1047980000	-2.6468680000
H	-1.2759880000	-3.3256740000	1.8000460000
O	-4.3402890000	-4.1287080000	-1.3409260000
C	-4.8863910000	-3.8533830000	-2.6127430000
H	-5.2655870000	-2.8265900000	-2.6761290000
H	-5.7148200000	-4.5487520000	-2.7451680000
H	-4.1518970000	-4.0126480000	-3.4106850000

CF/ABF-anti



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Zero point energy = -1863.639339 a.u.

Thermal free energy = -1863.712280 a.u.

C	-1.4136890000	3.4918360000	-0.4256850000
C	0.0327530000	3.2801450000	-0.5385960000
C	0.2724840000	1.9437650000	-0.8700410000
C	-1.0463680000	1.1588980000	-0.8680400000
C	-2.0696560000	2.2781750000	-0.6603630000
C	-2.1400480000	4.6514010000	-0.1966320000
C	-3.5293110000	4.5860690000	-0.2237230000
C	-4.1783110000	3.3843350000	-0.4916230000
C	-3.4511390000	2.2169840000	-0.7171940000
C	1.5587620000	1.4956710000	-1.1275460000
C	2.6255680000	2.3854800000	-1.0160540000
C	2.3849610000	3.7105090000	-0.6456870000
C	1.0950670000	4.1681290000	-0.4143270000
H	-1.6364440000	5.5945860000	-0.0114480000
H	-4.1127450000	5.4841140000	-0.0488570000
H	-5.2619840000	3.3542970000	-0.5302590000
H	-3.9619380000	1.2875310000	-0.9381570000
H	1.7451190000	0.4679280000	-1.4170350000
H	3.2278660000	4.3853440000	-0.5396920000
H	0.9216900000	5.2053180000	-0.1467570000
C	4.0293760000	1.9284580000	-1.3055170000
O	4.8572700000	2.2304650000	-0.2020710000
H	4.4170340000	2.4348780000	-2.2051290000

H	4.0406030000	0.8477410000	-1.5134780000
C	6.2078660000	1.9220900000	-0.4440100000
H	6.7695240000	2.1935470000	0.4509000000
H	6.6047610000	2.4863660000	-1.3006400000
H	6.3518270000	0.8500640000	-0.6427100000
C	-1.2698370000	0.5041870000	-2.1624800000
C	-1.0607360000	0.0461630000	0.2876200000
N	-1.4380600000	-0.0185230000	-3.1793470000
C	0.0859840000	-0.9389640000	0.1258260000
C	0.9467010000	-0.7831660000	1.1969360000
O	0.5030460000	0.1852540000	2.0820530000
C	-0.6370400000	0.7514580000	1.5961390000
O	-1.1701210000	1.6581830000	2.1660600000
C	0.4150670000	-1.8384050000	-0.8819880000
C	1.5973330000	-2.5716230000	-0.7905910000
C	2.4258560000	-2.3691120000	0.3216780000
C	2.1467490000	-1.4704240000	1.3516390000
H	-0.2162190000	-1.9379070000	-1.7517290000
H	3.3445200000	-2.9379150000	0.3802710000
C	2.0229260000	-3.5731370000	-1.8733730000
C	0.9932530000	-3.6748250000	-3.0051030000
H	0.0221410000	-4.0210000000	-2.6395770000
H	1.3392850000	-4.3957870000	-3.7507060000
H	0.8446380000	-2.7188100000	-3.5147670000
C	2.1857640000	-4.9696990000	-1.2474280000
H	1.2452470000	-5.3117510000	-0.8065470000
H	2.9456880000	-4.9799320000	-0.4621400000
H	2.4869570000	-5.6944010000	-2.0101950000
C	3.3639960000	-3.1290290000	-2.4845320000
H	3.2726290000	-2.1434420000	-2.9505310000
H	3.6849640000	-3.8380030000	-3.2539900000
H	4.1558130000	-3.0733420000	-1.7332000000
C	3.0764300000	-1.2346480000	2.5460910000
C	4.3405090000	-2.0974590000	2.4574270000
H	4.1099650000	-3.1668800000	2.4530190000
H	4.9711870000	-1.9009070000	3.3283010000

H	4.9303100000	-1.8665450000	1.5654410000
C	2.3364320000	-1.5982590000	3.8467740000
H	2.0400490000	-2.6514160000	3.8467540000
H	1.4414610000	-0.9892230000	3.9826440000
H	2.9916890000	-1.4314340000	4.7072510000
C	3.5065590000	0.2443920000	2.5916570000
H	4.0109980000	0.5512450000	1.6710020000
H	4.1996570000	0.3981190000	3.4249360000
H	2.6532210000	0.9065100000	2.7401410000
C	-2.4365610000	-0.6168800000	0.4536860000
C	-3.3553520000	-0.1928510000	1.4234420000
C	-2.8257100000	-1.6582860000	-0.3857720000
C	-4.0748340000	-2.2614370000	-0.2810930000
C	-4.9695980000	-1.8297180000	0.6940070000
C	-4.5960530000	-0.7906490000	1.5462390000
H	-5.3006380000	-0.4613930000	2.3014550000
H	-2.1571530000	-2.0228730000	-1.1523930000
H	-4.3292180000	-3.0640410000	-0.9611650000
H	-3.1041820000	0.6250550000	2.0850910000
O	-6.2075820000	-2.3483760000	0.8906280000
C	-6.6302210000	-3.4007950000	0.0496240000
H	-6.6588590000	-3.0910040000	-1.0014130000
H	-7.6374200000	-3.6623320000	0.3729440000
H	-5.9821210000	-4.2795320000	0.1461050000