Supplementary Materials

# Effect of Chain Structure on the Various Properties of the Copolymers of Fluorinated Norbornenes with Cyclooctene

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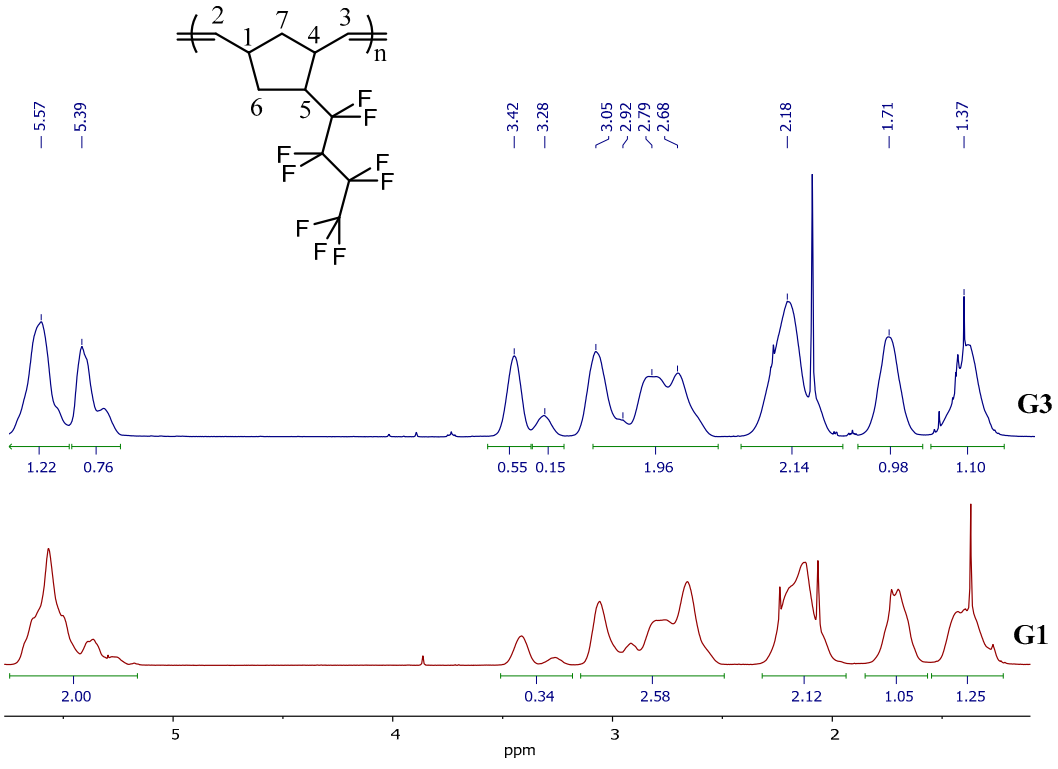


**Figure S1.** $^{1}$H NMR spectra of poly(5-perfluorobutyl-2-norbornene) (PNBF) obtained on the G1 and G3 catalysts at room temperature.

$^{1}$H NMR (400.1 MHz, $CDCl_3/C_6F_6$) δ, ppm: 5.57 (CH=CH, *trans*), 5.39 (CH=CH, *cis*), 3.42 ($HC^5$, *cis*, *endo*), 3.28 ($HC^5$, *cis*, *exo*), 3.05 ($HC^5$, *trans*, *endo*), 2.92 ($HC^5$, *trans*, *exo*), 2.79 ($HC^{1,4}$, *cis*), 2.68 ($HC^{1,4}$, *trans*), 2.18 ($H_2C^6$), 1.71–1.37 ($H_2C^7$).

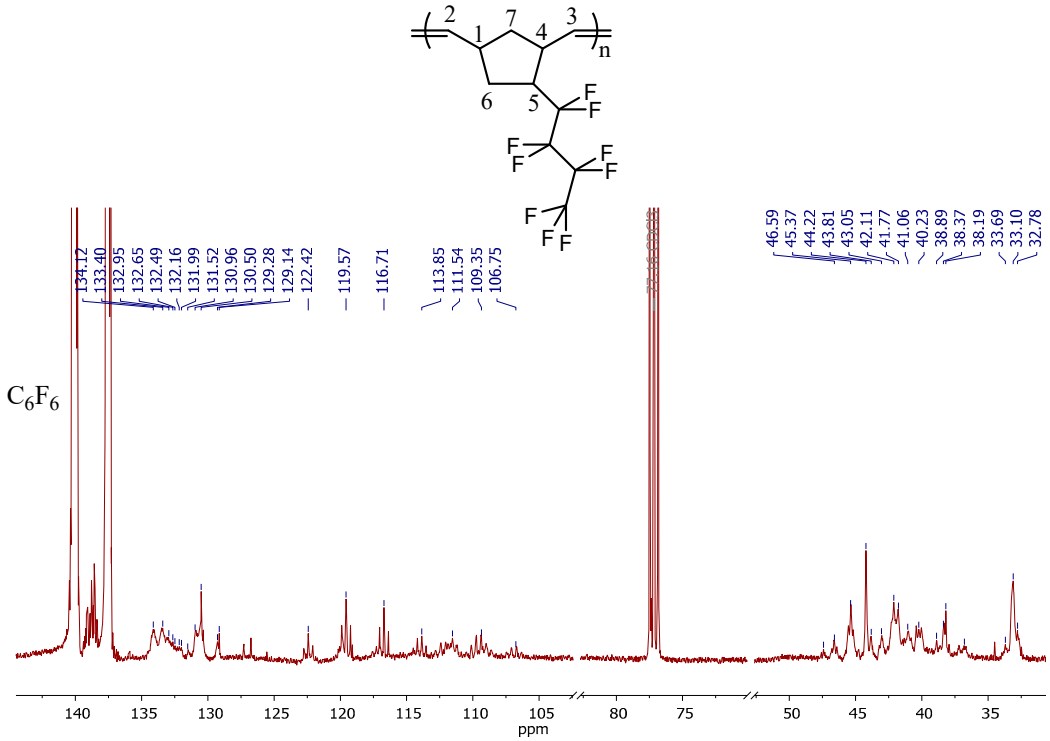


**Figure S2.** $^{13}$C NMR spectrum of poly(5-perfluorobutyl-2-norbornene) (PNBF) at room temperature.

$^{13}$C NMR (100.6 MHz, $CDCl_3/C_6F_6$) δ, ppm: 134.12–132.16 (C=C, *cis/trans*), 131.99–130.96 (C=C), 130.50 ($C^3$, *trans*), 129.28, 129.14 ($C^3$, *cis*), 122.42, 119.57, 116.71, 113.85, 111.54, 109.35, 106.75 (CF), 47.41 ($C^5$, *exo, cis*) 46.59 ($C^5$, *exo*, *trans*), 45.37 ($C^5$, *endo, cis/trans*), 44.22, 43.81 ($C^1$), 43.05 ($C^7$), 42.11, 41.77, 41.06, 40.23 ($C^4$, $C^7$), 38.89, 38.37, 38.19, 36.78 ($C^1$, $C^4$), 33.69–32.78 ($C^6$).

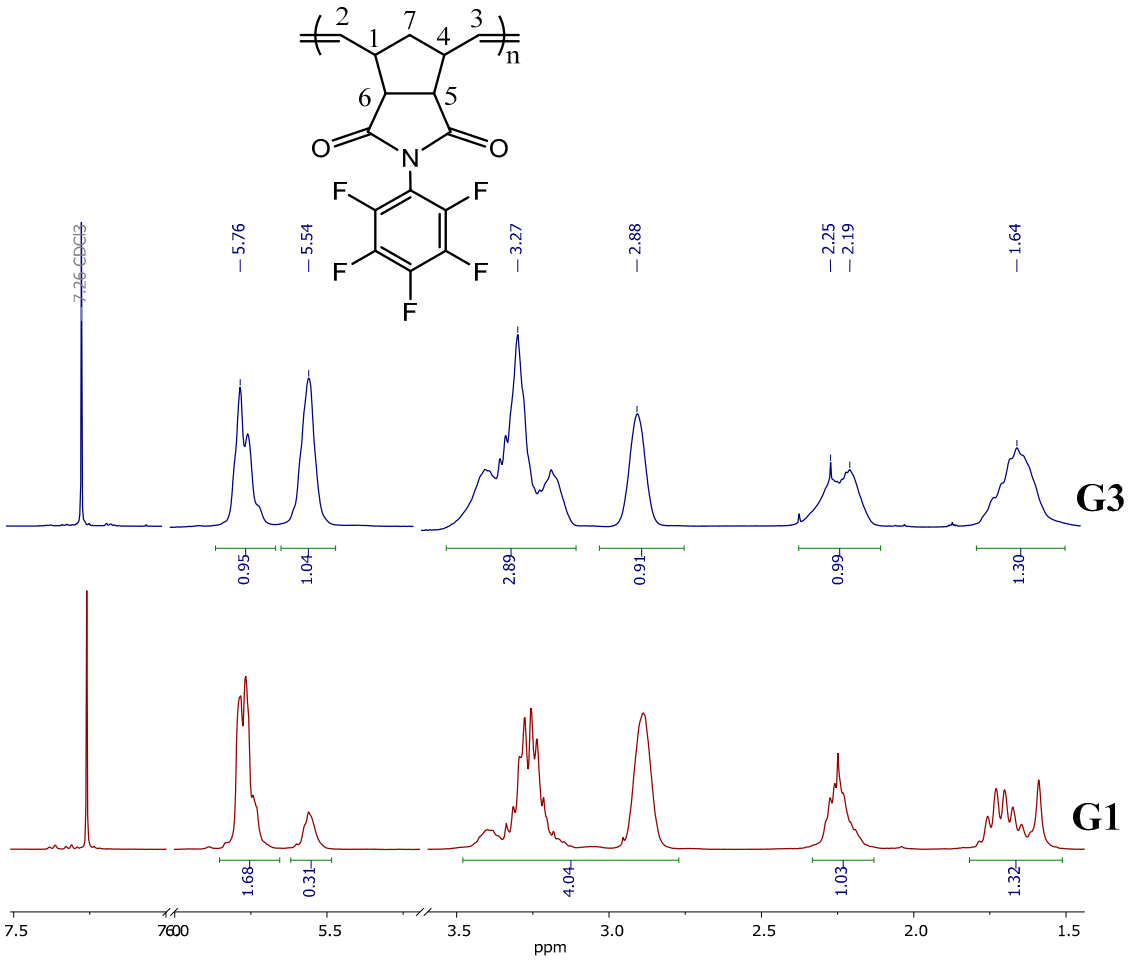


**Figure S3.** $^{1}$H NMR spectra of poly(pentafluorophenyl-norbornene-5,6-dicarboximide) (PNBFD) obtained on the G1 and G3 catalysts at room temperature.

$^{1}$H NMR (400.1 MHz, $CDCl_3$) δ, ppm: 5.76 (CH=CH, *trans*), 5.54 (CH=CH, *cis*), 3.27 (3H), 2.88 (1H), 2.25, 2.19 (1H), 1.64 (1H).

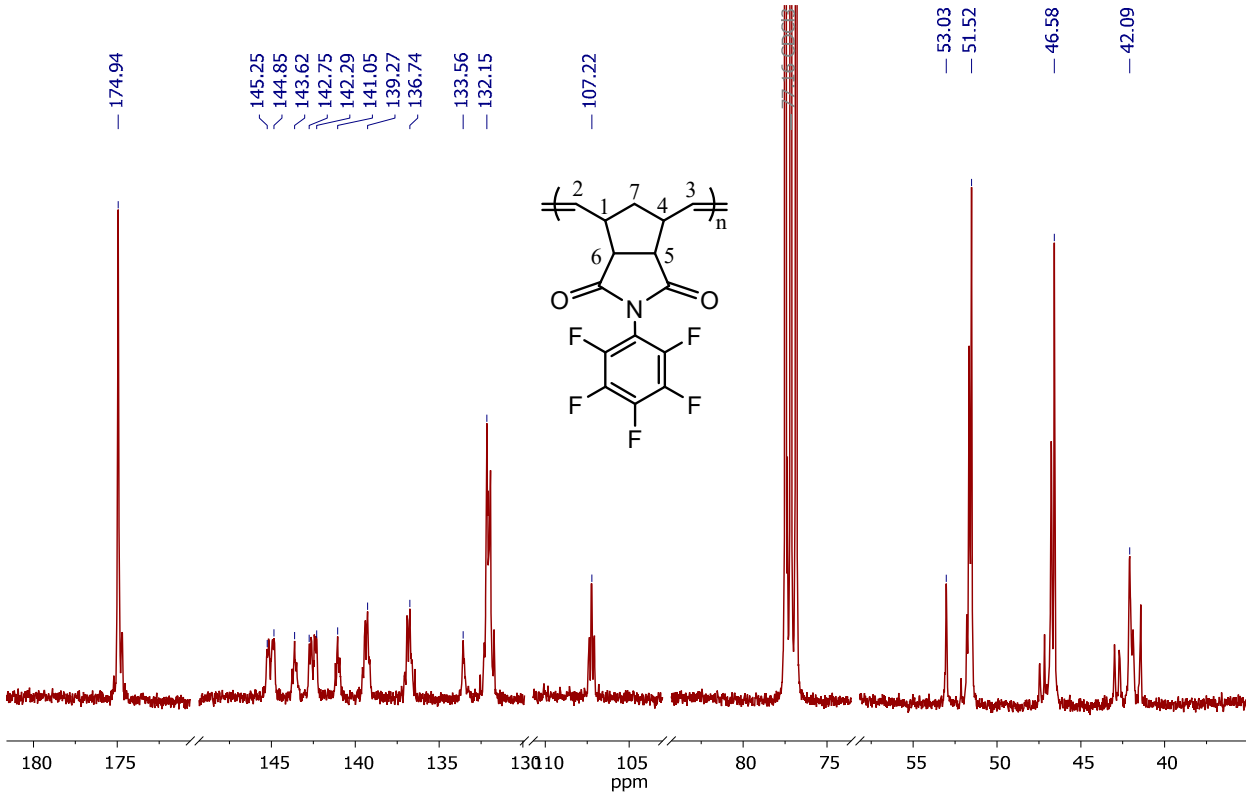


**Figure S4.** $^{13}C$ NMR spectrum of poly(pentafluorophenyl-norbornene-5,6-dicarboximide) (PNBFD) at room temperature.

$^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ, ppm: 174.94 (C=O), 145.25, 144.85, 143.62, 142.75, 142.29, 141.05, 139.27, 136.74 (CF), 133.56 (C=C, *cis*), 132.15 (C=C, *trans*), 107.22 (C-N), 53.03 ($C^{1,4}$, *cis*) 51.52 ($C^{1,4}$, *trans*), 46.58, 42.09.

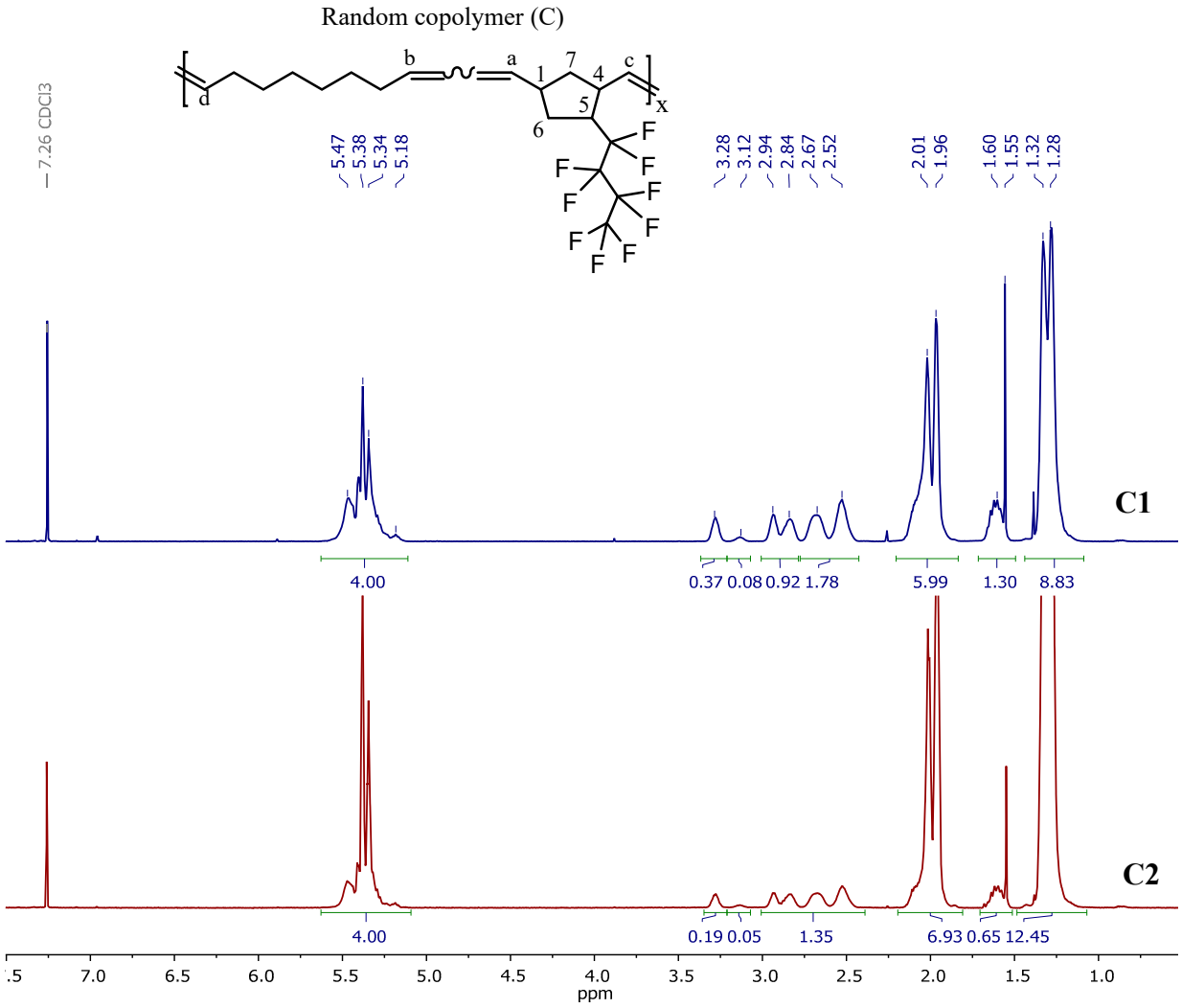


**Figure S5.** $^{1}$H NMR spectra of NBF–COE random C1 and C2 copolymers at room temperature.

$^{1}$H NMR (400.1 MHz, $CDCl_3$) δ, ppm: 5.47, 5.38, 5.34, 5.18 (HC=CH, PNBF, PCOE), 3.28 ($HC^5$, *cis*, *endo,* PNBF), 3.12 ($HC^5$, *cis*, *exo,* PNBF), 2.94 ($HC^5$, *trans*, *endo,* PNBF), 2.84 ($HC^5$, *trans*, *exo,* PNBF), 2.67 ($HC^{1,4}$, *cis*, PNBF), 2.52 ($HC^{1,4}$, *trans,* PNBF), 2.01, 1.96 (($H_2C^6$, PNBF; 4H, PCOE), 1.60, 1.55 ($H_2C^7$, PNBF), 1.32, 1.28 ($H_2C^7$, PNBF; 8H, PCOE).

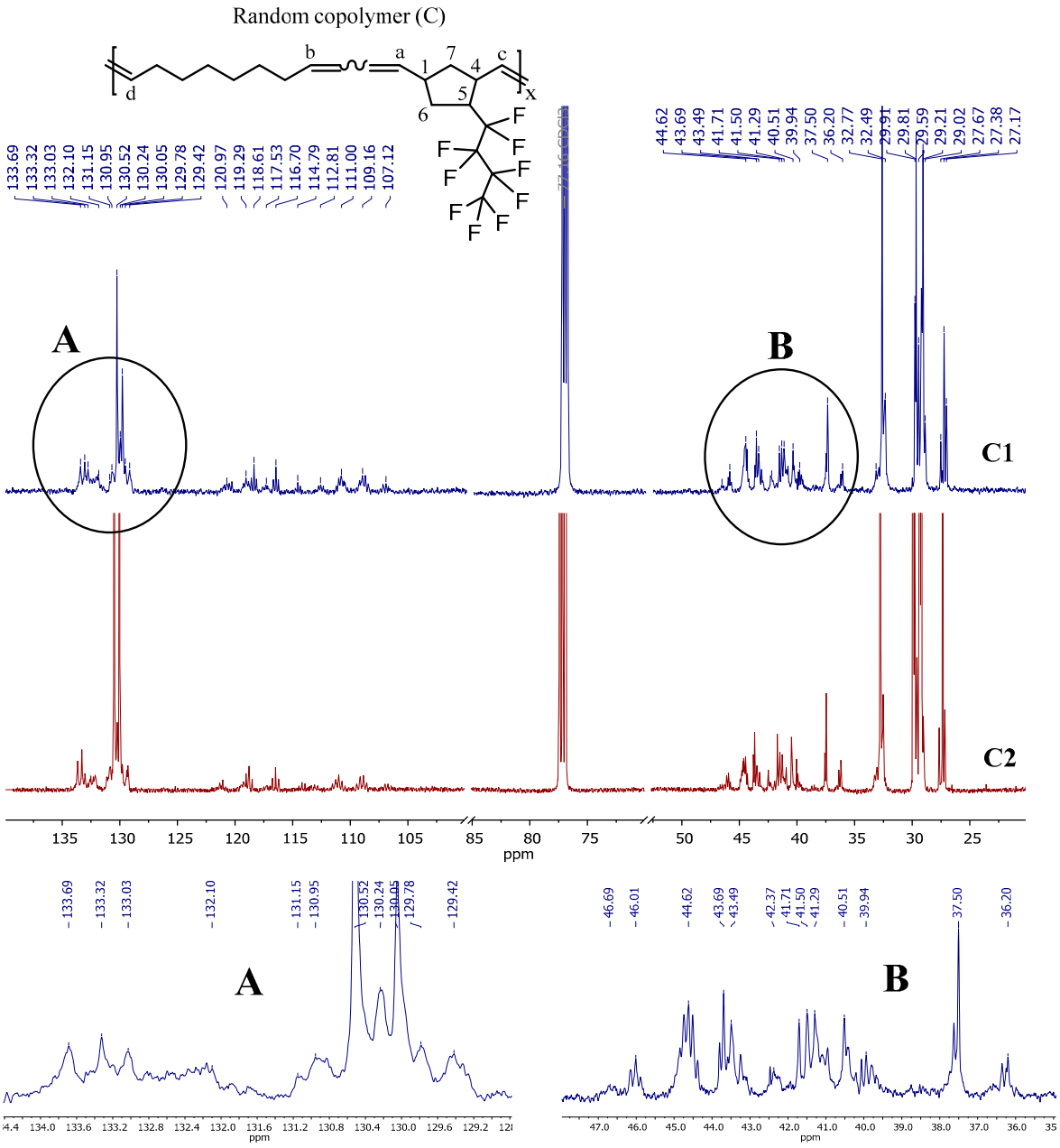


**Figure S6.** $^{13}C$ NMR spectra of NBF–COE random C1 and C2 copolymers at room temperature.

$^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ, ppm: 133.69, 133.32, 133.03, 132.10, 131.15, 130.95 (C=C, PNBF), 130.52 (C=C *trans*, PCOE), 130.24 (C=C, PNBF), 130.05 (C=C *cis*, PCOE), 129.78, 129.42 (C=C, PNBF), 120.97, 119.29, 118.61, 117.53, 116.70, 114.79, 112.81, 111.00, 109.16, 107.12 (C-F), 46.69 ($C^5$, *exo*, *cis*, PNBF), 46.01 ($C^5$, *exo*, *trans*, PNBF), 44.62 ($C^5$, *endo*, *cis/trans*, PNBF), 43.69, 43.49 ($C^1$, PNBF), 42.37, 41.47, 41.50, 41.29, 40.51, 39.94 ($C^{4,7}$, PNBF), 37.50, 36.20 ($C^{1,4}$, PNBF), 32.77, 32.49 ($C^6$, PNBF; $CH_2$, PCOE), 29.91, 29.81, 29.59, 29.21, 29.02, 27.67, 27.38, 27.17 ($CH_2$, PCOE).

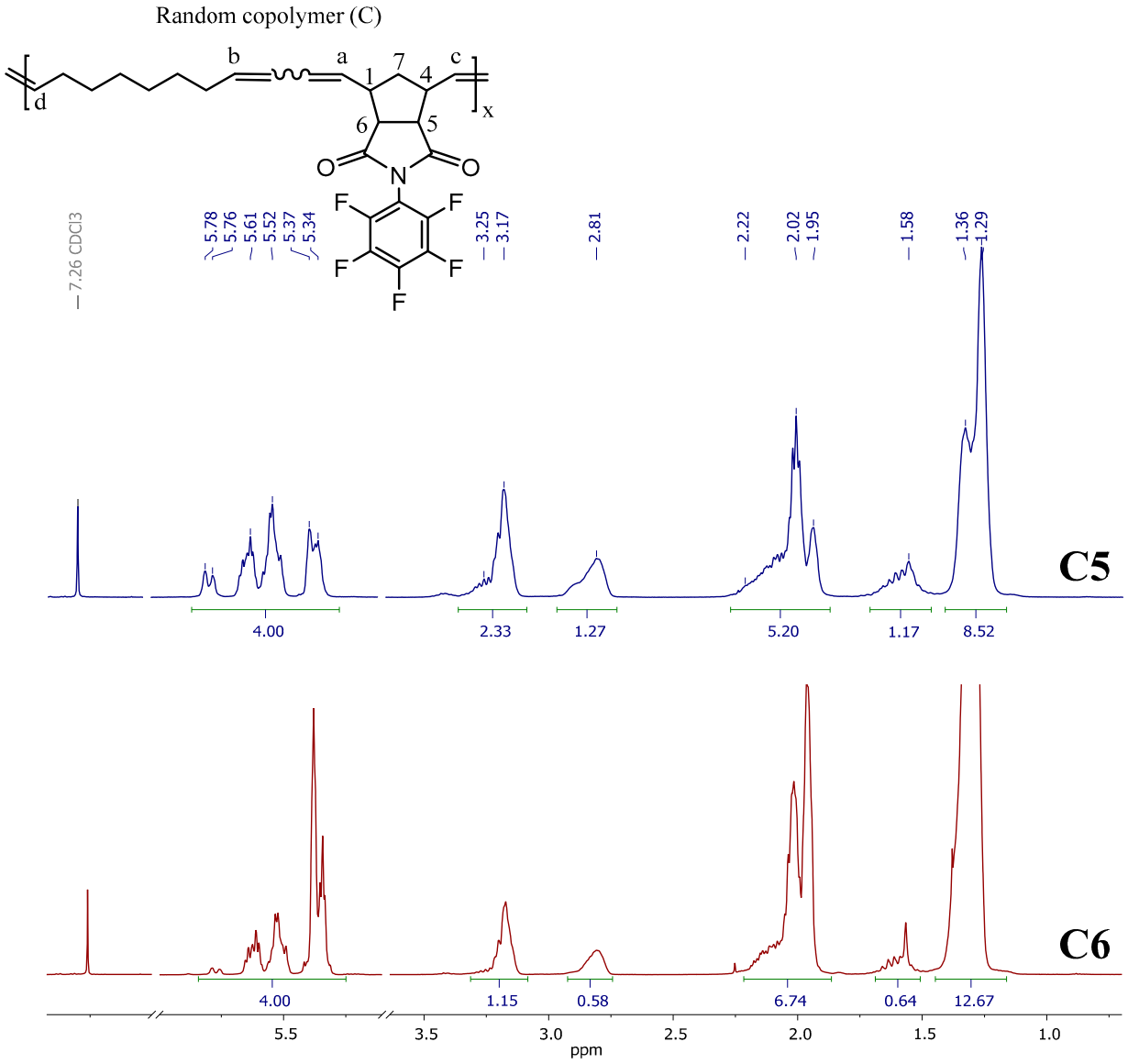


**Figure S7.** $^{1}$H NMR spectra of NBFD–COE random C5 and C6 copolymers at room temperature.

$^{1}$H NMR (400.1 MHz, $CDCl_3$) δ, ppm: 5.78 ($HC^{a}$=$C^{c}$H *trans*, PNBFD), 5.61 (heterodyad **$HC^{a}$**=$C^{b}$H), 5.52 ($HC^{a}$=$C^{c}$H *cis*, PNBFD; heterodyad $HC^{a}$=**$C^{b}$H**), 5.37 ($HC^{b}$=$C^{d}$H *trans*, PCOE), 5.34 ($HC^{b}$=$C^{d}$H *cis*, PCOE), 3.25-3.17 (PNBFD), 2.81 (PNBFD), 2.22, 2.02 (PNBFD), 1.95 (PCOE), 1.58 (PNBFD), 1.36, 1.29 (PCOE, PNBFD).

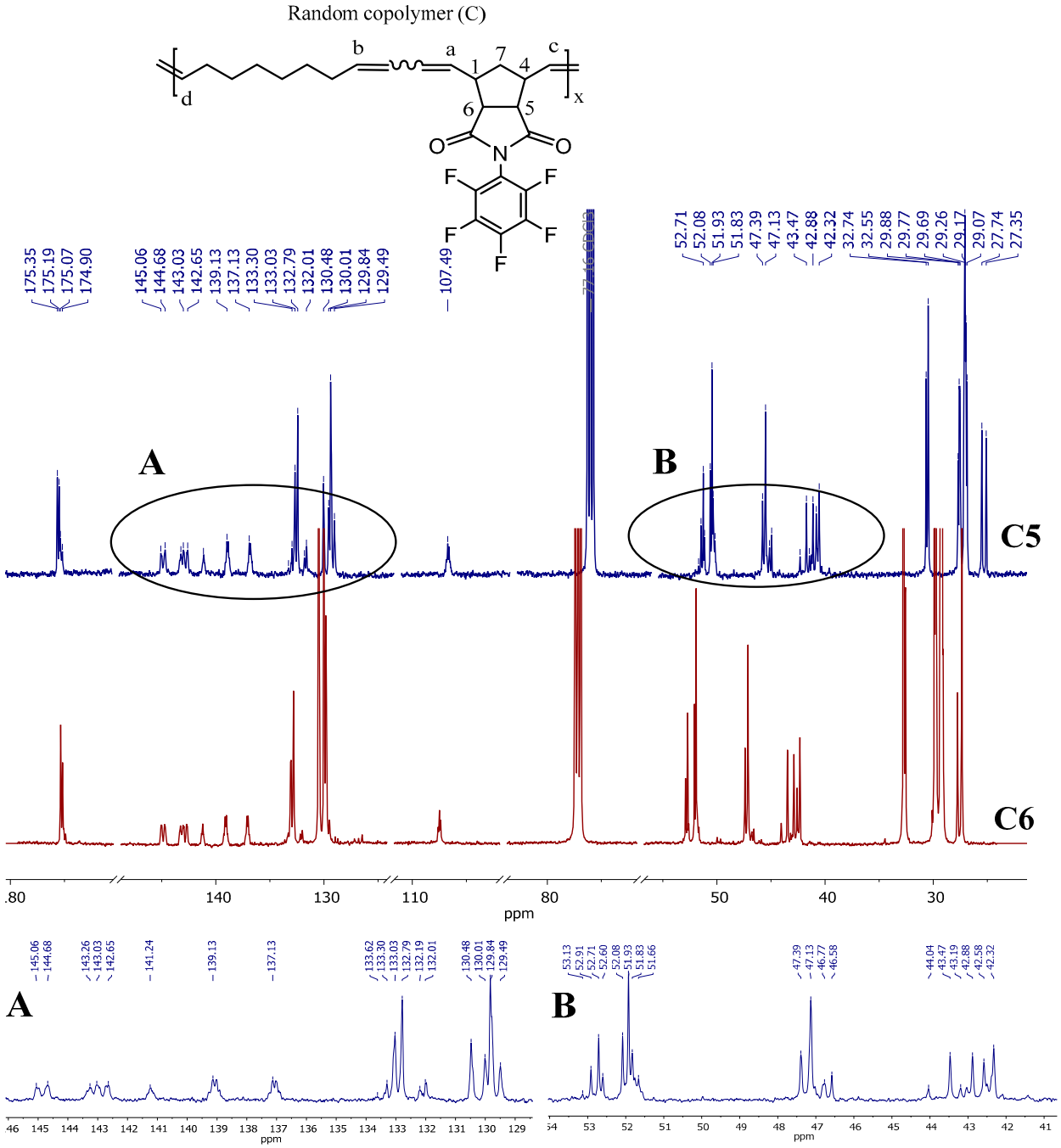


**Figure S8.** $^{13}$C NMR spectra of NBFD–COE random C5 and C6 copolymers at room temperature.

$^{13}$C NMR (100.6 MHz, $CDCl_3$) δ, ppm: 175.35, 175.19, 175.07, 174.90 (C=O), 145.06, 144.68, 143.26, 143.03, 142.65, 141.24, 139.13, 137.13 (C-F), 133.62 ($HC^a$=$C^cH$ *cis*, PNBFD), 133.30, 133.03, 132.79 (heterodyad **$C^a$**=$C^b$), 132.19, 132.01 ($HC^a$=$C^cH$ *trans*, PNBFD), 130.48 ($HC^b$=$C^dH$ *trans*, PCOE), 130.01 ($HC^b$=$C^dH$ *cis*, PCOE), 129.84, 129.49 (heterodyad $C^a$=**$C^b$**), 107.49 (C-N), 53.13, 52.91, 52.71, 52.60 ($C^{1,4}$, *cis,* PNBFD*)*, 52.08, 51.93, 51.83, 51.66 ($C^{1,4}$, *trans*, PNBFD), 47.39, 47.13, 46.77, 46.58, 44.04, 43.47, 43.19, 42.88, 42.58, 42.32 ($C^{5,6,7}$, PNBFD), 32.74 , 32.55, 29.88, 29.77, 29.69, 29.26, 29.17, 29.07, 27.74, 27.35 ($CH_2$, PCOE).

The average lengths of NBFD and COE blocks in the copolymers, $L_{NBFD}$ and $L_{COE}$, were calculated from the integral intensities of homo- (NBFD–NBFD (133.62, 132.19, 132.01 ppm), COE–COE

(130.48, 130.01 ppm)) and hetero- (NBFD–COE (133.30, 133.03, 132.79 ppm), COE–NBFD (129.84, 129.49)) dyad signals in $^{13}C$ NMR spectra:

$$L_{NBFD} = \frac{I\,(C = C_{NBFD-COE}) + I(C = C_{NBFD-NBFD})}{I(C = C_{NBFD-COE})}$$

$$L_{COE} = \frac{I\,(C = C_{COE-NBFD}) + I(C = C_{COE-COE})}{I(C = C_{COE-NBFD})}$$

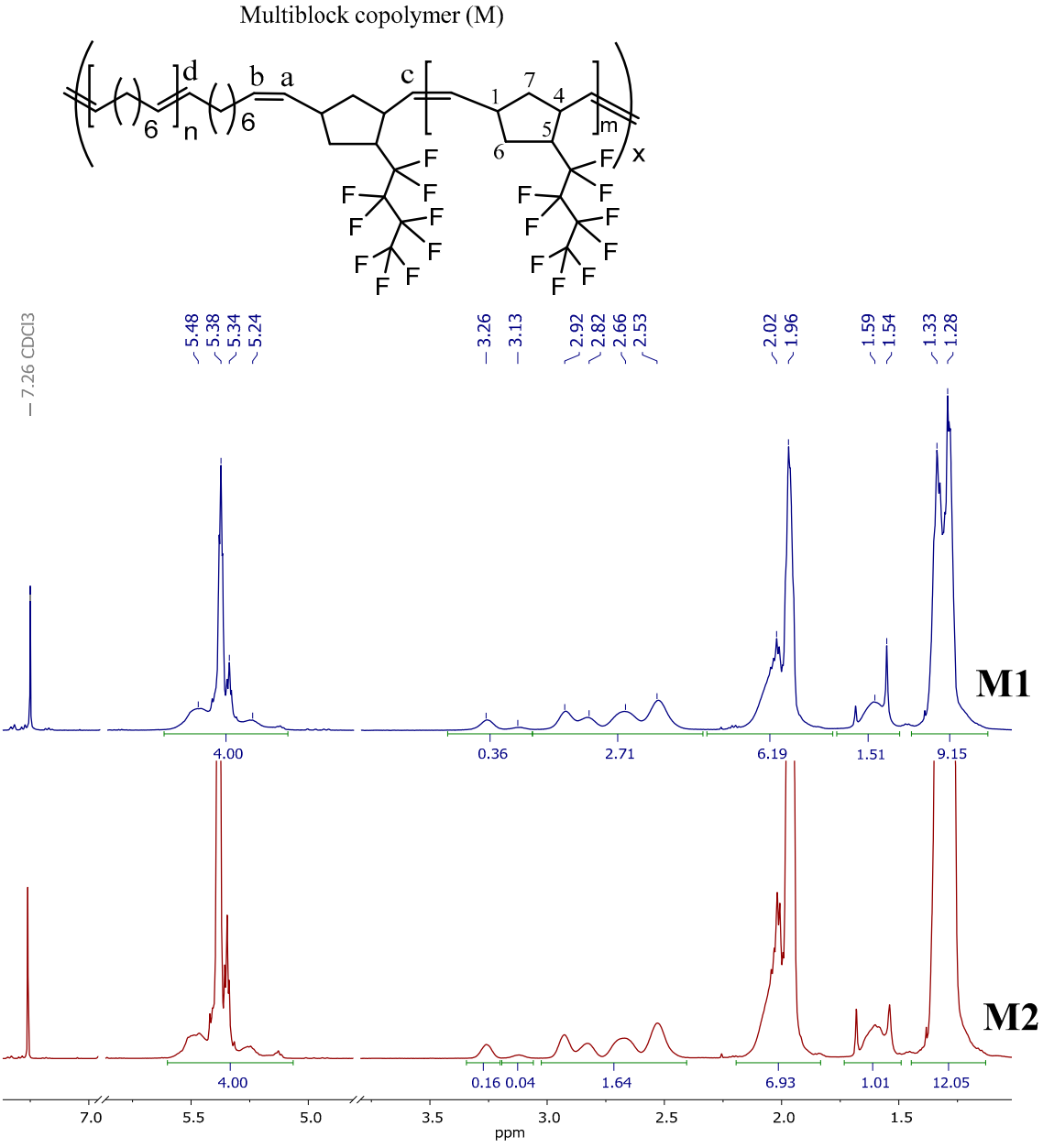


**Figure S9.** $^{1}H$ NMR spectra of NBF–COE multiblock M1 and M2 copolymers at room temperature.

$^{1}H$ NMR (400.1 MHz, CDCl3) δ, ppm: 5.48, 5.38, 5.34, 5.24 (HC=CH, PNBF, PCOE), 3.26 ($HC^{5}$, *cis*, *endo*, PNBF), 3.13 ($HC^{5}$, *cis*, *exo*, PNBF), 2.92 ($HC^{5}$, *trans*, *endo*, PNBF), 2.82 ($HC^{5}$, *trans*, *exo*, PNBF), 2.66 ($HC^{1,4}$, *cis*, PNBF), 2.53 ($HC^{1,4}$, *trans*, PNBF), 2.02, 1.96 (($H_2C^{6}$, PNBF; 4H, PCOE), 1.59, 1.54 ($H_2C^{7}$, PNBF), 1.33, 1.28 ($H_2C^{7}$, PNBF; 8H, PCOE).

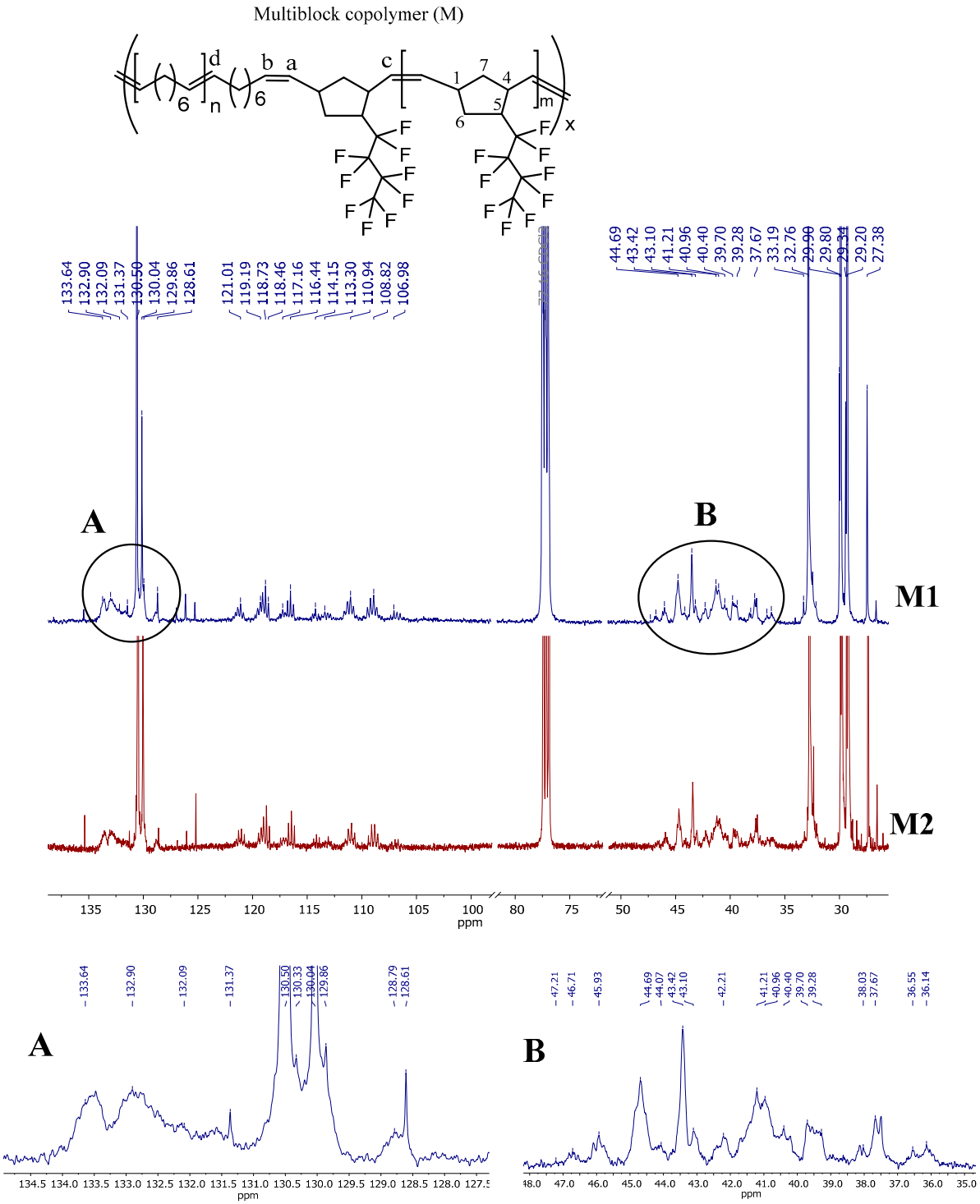


**Figure S10.** $^{13}C$ NMR spectra of NBF–COE multiblock M1 and M2 copolymers at room temperature.

$^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ, ppm: 133.64, 132.90, 132.09, 131.37 (C=C, PNBF), 130.50 (C=C *trans*, PCOE), 130.33 (C=C, PNBF), 130.04 (C=C *cis*, PCOE), 129.86, 128.79, 128.61 (C=C, PNBF), 121.01, 119.19, 118.73, 118.46, 117.16, 116.44, 114.15, 113.30, 110.94, 108.82, 106.98 (C-F), 47.21 ($C^5$, *exo, cis,* PNBF), 46.71 ($C^5$, *exo*, *trans,* PNBF), 45.93 ($C^5$, *endo, cis/trans,* PNBF), 44.69, 44.07 ($C^1$, PNBF), 43.42, 43.10 ($C^7$, PNBF), 42.21, 41.21, 40.96, 40.40, 39.70, 39.28 ($C^{4,7}$, PNBF), 38.03, 37.67, 36.55, 36.14 ($C^{1,4}$, PNBF), 33.19, 32.76, 32.05 ($C^6$, PNBF; $CH_2$, PCOE), 29.90, 29.80, 29.34, 29.20, 27.38 ($CH_2$, PCOE).

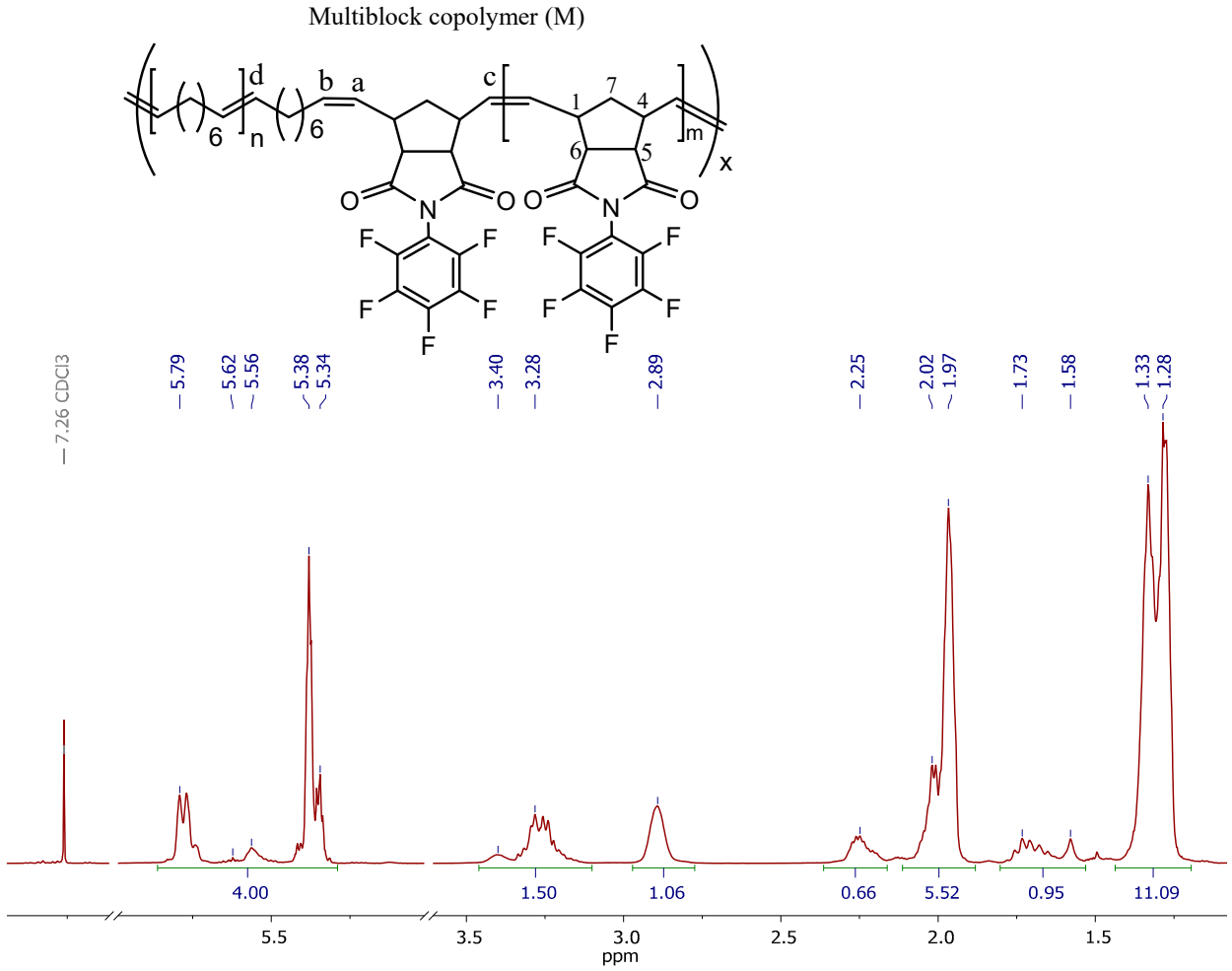


**Figure S11.** $^{1}$H NMR spectrum of NBFD–COE multiblock M4 copolymer at room temperature.

$^{1}$H NMR (400.1 MHz, CDCl3) δ, ppm: 5.79 ($HC^{a}$=$C^{c}H$ *trans*, PNBFD), 5.62 (heterodyad **$HC^{a}$**=$C^{b}H$), 5.56 ($HC^{a}$=$C^{c}H$ *cis*, PNBFD; heterodyad $HC^{a}$=**$C^{b}H$**), 5.38 ($HC^{b}$=$C^{d}H$ *trans*, PCOE), 5.34 ($HC^{b}$=$C^{d}H$ *cis*, PCOE), 3.40, 3.28, 2.89 (PNBFD), 2.25, 2.02 (PNBFD), 1.97 (PCOE), 1.73, 1.58 (PNBFD), 1.33, 1.28 (PCOE, PNBFD).

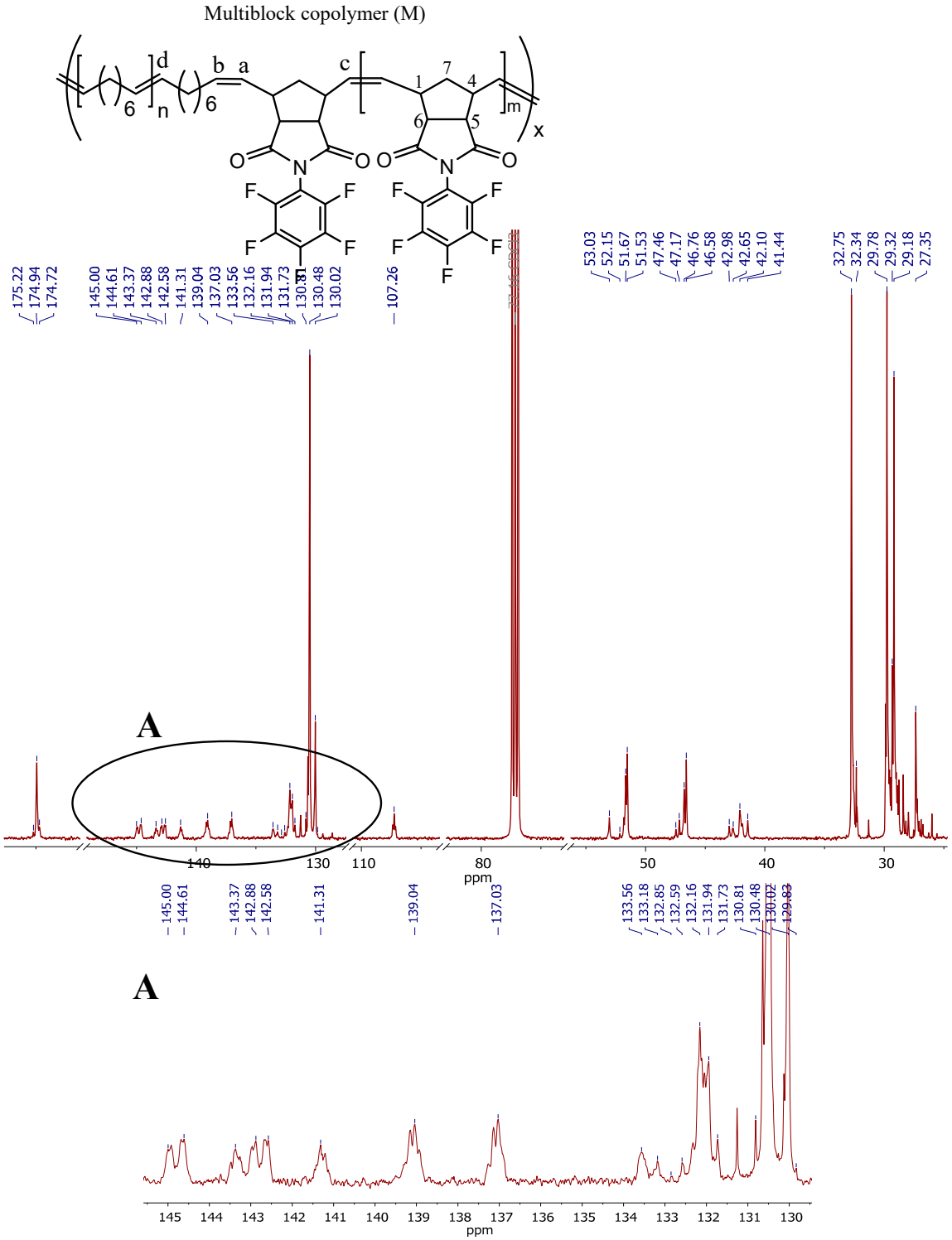


**Figure S12.** $^{13}$C NMR spectrum of NBFD–COE multiblock M4 copolymer at room temperature.

$^{13}$C NMR (100.6 MHz, $CDCl_3$) δ, ppm: 175.22, 174.94, 174.72 (C=O), 145.00, 144.61, 143.37, 142.88, 142.58, 141.31, 139.04, 137.03 (C-F), 133.56, 133.18 ($HC^a$=$C^cH$ *cis*, PNBFD), 132.85 (heterodyad **$C^a$**=$C^b$), 132.59, 132.16, 131.94, 131.73 ($HC^a$=$C^cH$ *trans*, PNBFD), 130.48 ($HC^b$=$C^dH$ *trans*, PCOE), 130.02 ($HC^b$=$C^dH$ *cis*, PCOE), 129.83 (heterodyad $C^a$=**$C^b$**), 107.26 (C-N), 53.03 ($C^{1,4}$, *cis,* PNBFD), 52.15, 51.67, 51.53 ($C^{1,4}$, *trans*, PNBFD), 47.46, 47.17, 46.76, 46.58, 42.98, 42.65, 42.10, 41.44 ($C^{5,6,7}$, PNBFD), 32.75, 32.34, 29.78, 29.32, 29.18, 28.77, 27.35 ($CH_2$, PCOE).

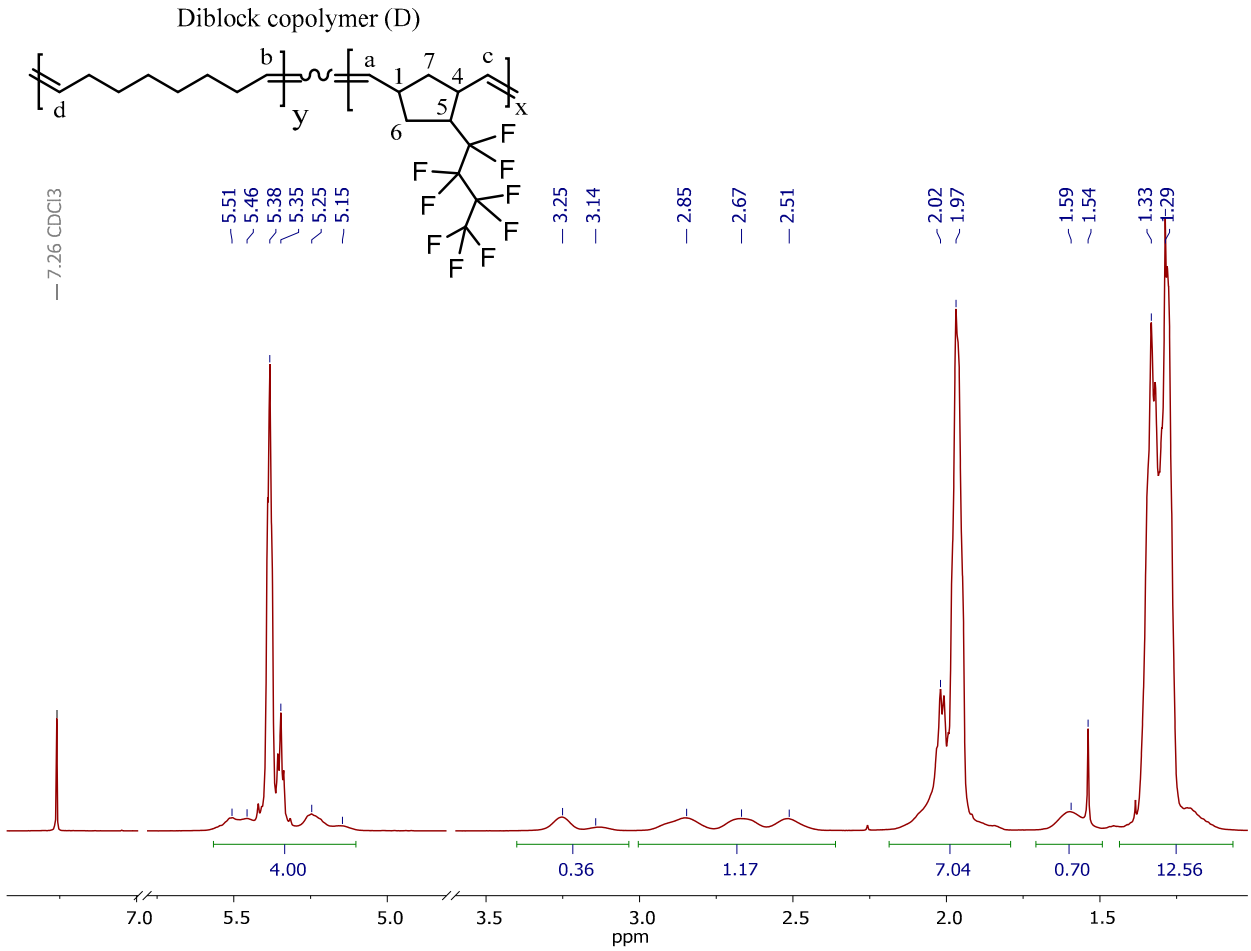


**Figure S13.** $^{1}$H NMR spectrum of NBF–COE diblock D1 copolymer at room temperature.

$^{1}$H NMR (400.1 MHz, CDCl3) δ, ppm: 5.51, 5.46, 5.38, 5.35, 5.25, 5.15 (HC=CH, PNBF, PCOE), 3.25 ($HC^{5}$, *cis*, *endo,* PNBF), 3.14 ($HC^{5}$, *cis*, *exo,* PNBF), 2.85 ($HC^{5}$, *trans*, *endo/exo,* PNBF*)*, 2.67 ($HC^{1,4}$, *cis*, PNBF), 2.51 ($HC^{1,4}$, *trans,* PNBF), 2.02, 1.97 (($H_2C^{6}$, PNBF; 4H, PCOE), 1.59, 1.54 ($H_2C^{7}$, PNBF), 1.33, 1.29 ($H_2C^{7}$, PNBF; 8H, PCOE).

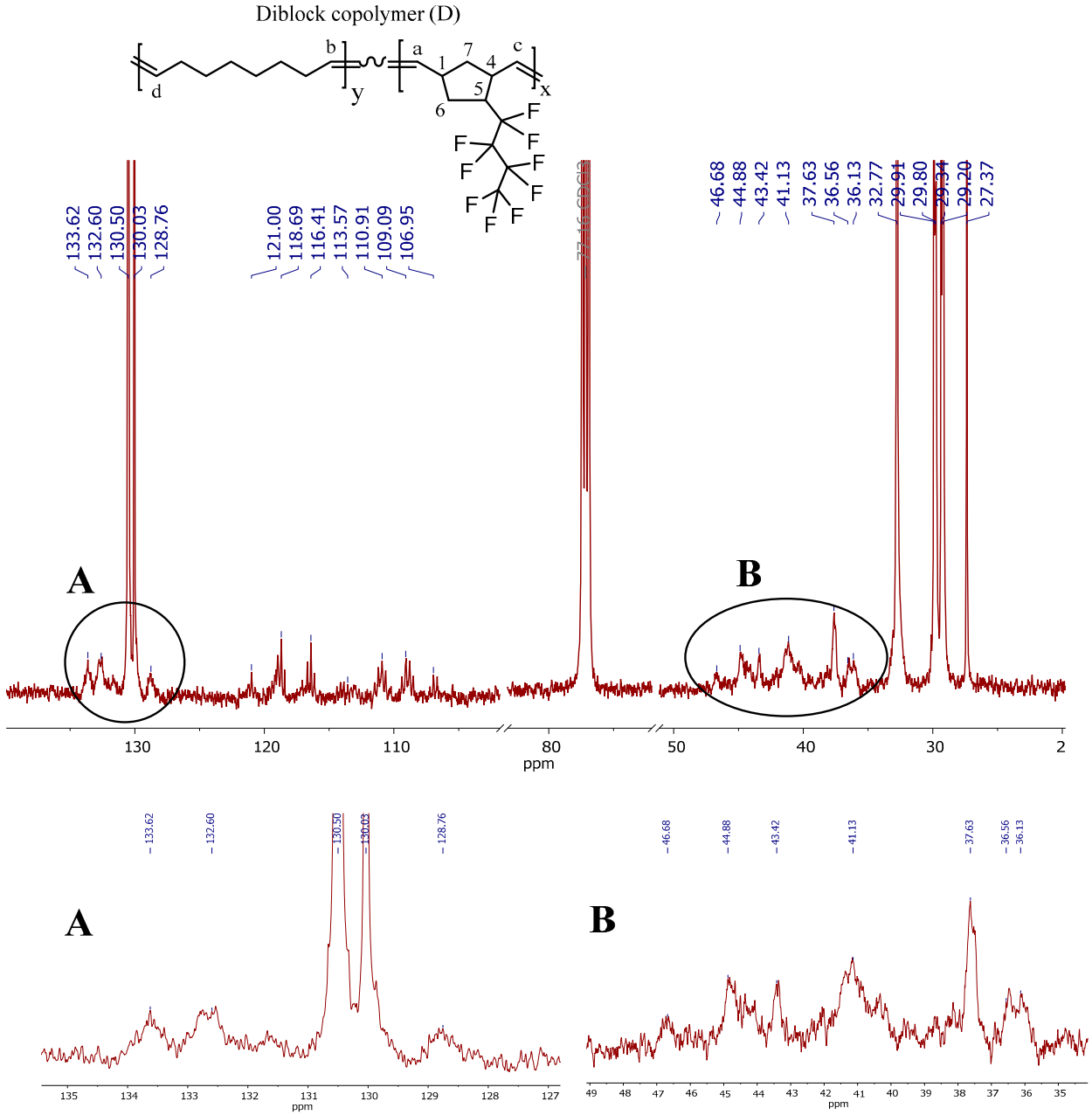


**Figure S14.** $^{13}C$ NMR spectrum of NBF–COE diblock D1 copolymer at room temperature.

$^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ, ppm: 133.62, 132.60 (C=C, PNBF), 130.50 (C=C *trans*, PCOE), 130.03 (C=C *cis*, PCOE), 128.76 (C=C, PNBF), 121.00, 118.69, 116.41, 113.57, 110.91, 109.09, 106.95 (C-F), 46.68 ($C^5$, *exo*, *trans,* PNBF), 44.88, 43.42 ($C^{1,5,7}$, PNBF), 41.13 ($C^{4,7}$, PNBF), 37.63, 36.56, 36.13 ($C^{1,4}$, PNBF), 32.77 ($C^6$, PNBF; $CH_2$, PCOE), 29.91, 29.80, 29.34, 29.20, 27.37 ($CH_2$, PCOE).

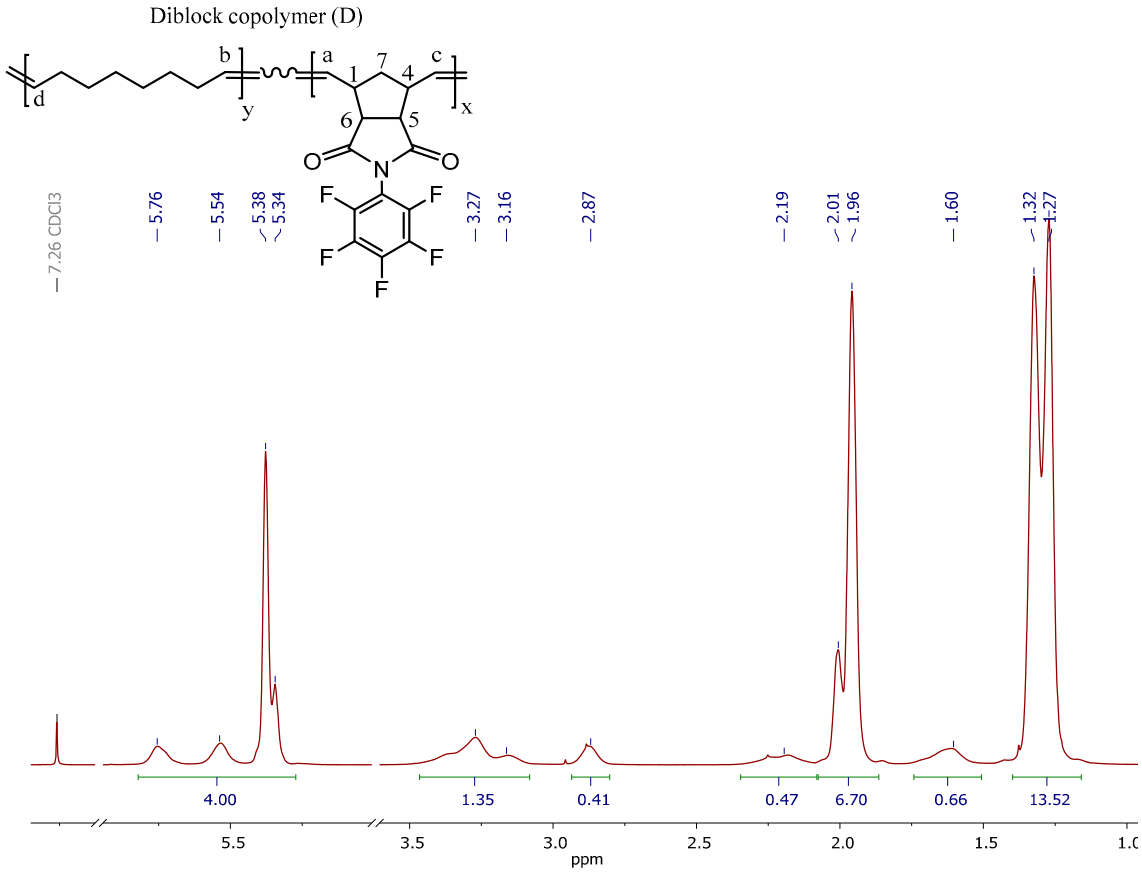


**Figure S15.** $^{1}$H NMR spectrum of NBFD–COE diblock D2 copolymer at room temperature.

$^{1}$H NMR (400.1 MHz, CDCl3) δ, ppm: 5.76 ($HC^{a}$=$C^{c}H$ *trans*, PNBFD), 5.54 ($HC^{a}$=$C^{c}H$ *cis*, PNBFD), 5.38 ($HC^{b}$=$C^{d}H$ *trans*, PCOE), 5.34 ($HC^{b}$=$C^{d}H$ *cis*, PCOE), 3.27, 3.16, 2.87 (PNBFD), 2.19, 2.01 (PNBFD), 1.96 (PCOE), 1.60 (PNBFD), 1.32, 1.27 (PCOE, PNBFD).

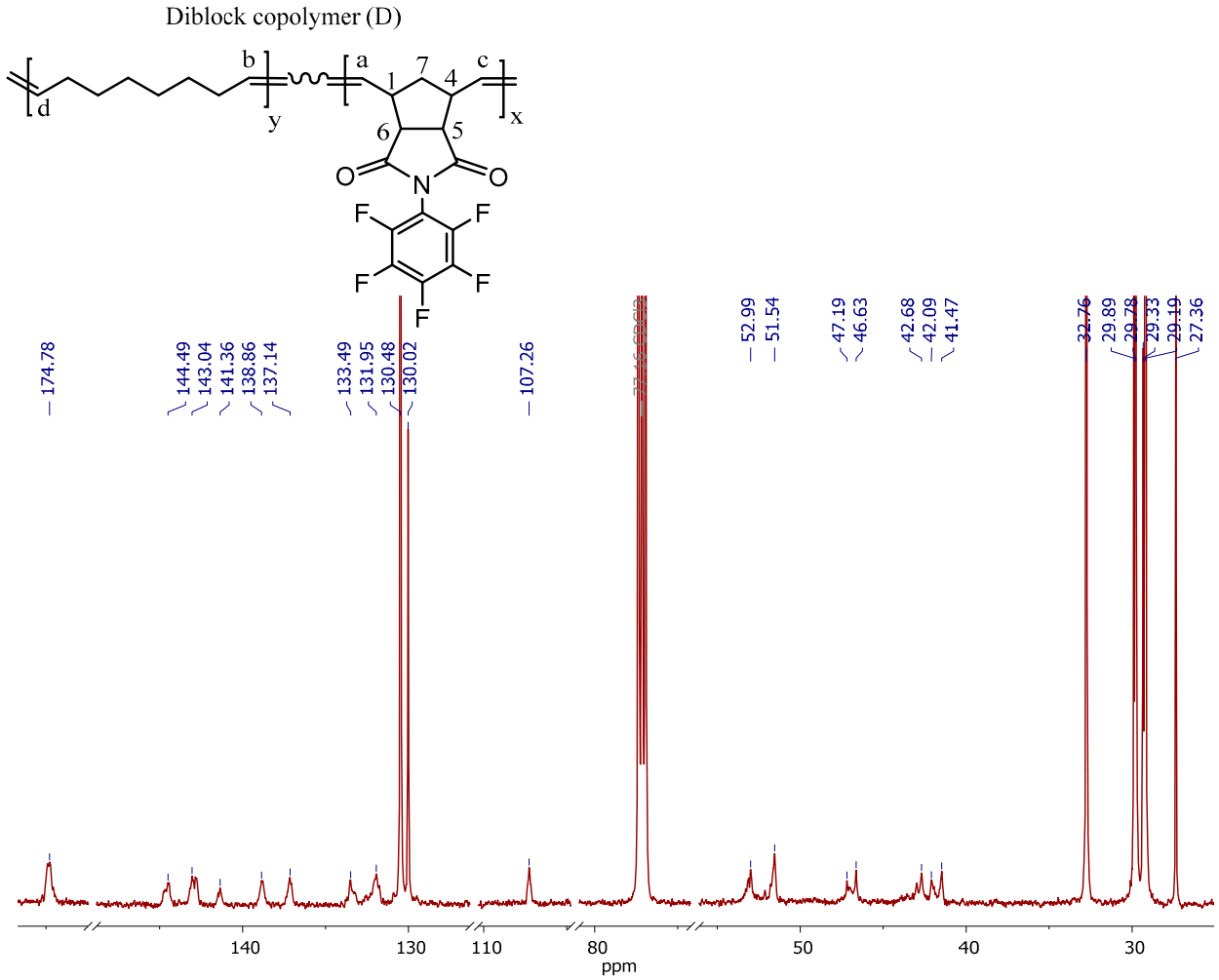


**Figure S16.** $^{13}C$ NMR spectrum of NBFD–COE diblock D2 copolymer at room temperature.

$^{13}C$ NMR (100.6 MHz, $CDCl_3$) δ, ppm: 174.78 (C=O), 144.49, 143.04, 141.36, 138.86, 137.14 (C-F), 133.49 ($HC^a=C^cH$ *cis*, PNBFD), 131.95 ($HC^a=C^cH$ *trans*, PNBFD), 130.48 ($HC^b=C^dH$ *trans*, PCOE), 130.02 ($HC^b=C^dH$ *cis*, PCOE), 107.26 (C-N), 52.99 ($C^{1,4}$, *cis,* PNBFD), 51.54 ($C^{1,4}$, *trans*, PNBFD), 47.19, 46.63, 42.68, 42.09, 41.47 ($C^{5,6,7}$, PNBFD), 32.76, 29.89, 29.78, 29.33, 29.19, 27.36 ($CH_2$, PCOE).

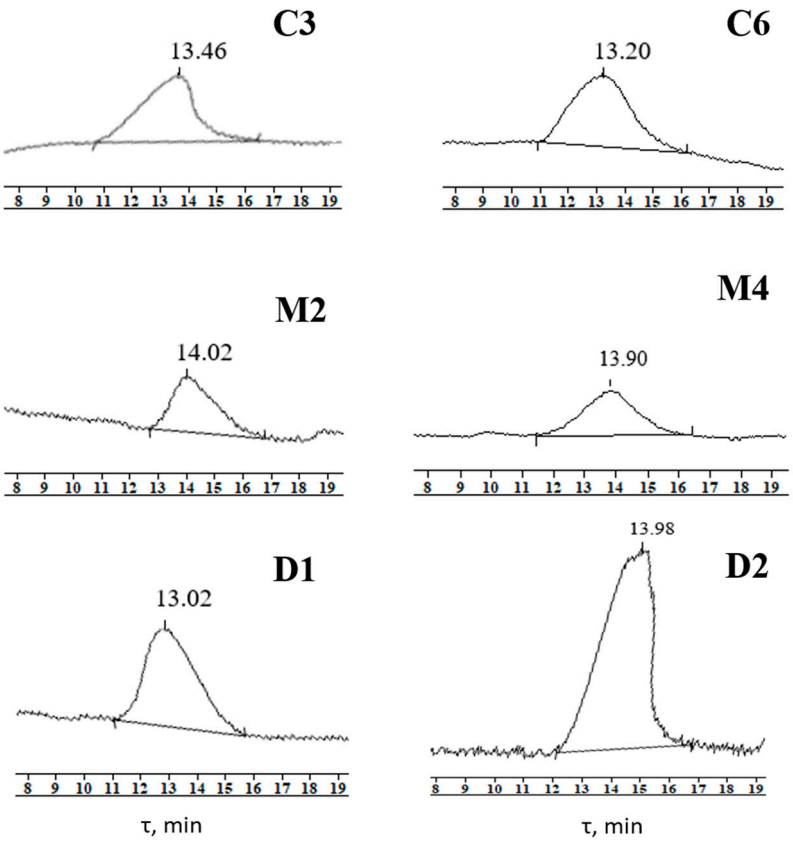


**Figure S17.** GPC curves of different copolymers NBF and NBFD with COE (copolymer D2 was analyzed from a solution in chloroform).