Electronic Supplementary Material (ESI) for Polymer Chemistry.

An efficient and mild route to highly fluorinated polyolefins via copolymerization of ethylene and 5-perfluoroalkylnorbornenes

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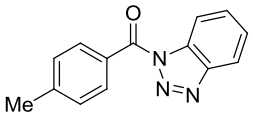
1. General Information

All air or moisture sensitive manipulations were carried out under a high pure nitrogen atmosphere using Schlenk techniques or in a glovebox. ^{1}H NMR, ^{13}C NMR spectra were recorded on Varian Mercury 300 spectrometer, Varian 400 MR spectrometer , Agilent Technologies 600 MR spectrometer, and JEOL 600 NMR spectrometer. Mass spectra were carried out with a HP5989A spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). M_n, M_w, and M_w/M_n values of polymers were determined with Agilent Technologies PL-GPC 220 and CFC- polymer char High Temperature Chromatography at 145℃ (polystyrene calibration, 1,2,4-trichlorobenzene as a solvent at a flow rate of 1.0 mL·min^{-1}). X-Ray crystallographic data were collected using a Bruker AXSD8 X-ray diffractometer. Toluene, hexane, dichloromethane (DCM) were purified by MB SPS-800 system. T_m, T_d values were determined by TA Q 2000 and TA Q 500 respectively. The ligands **3c**-**d** were prepared by treatment of amine with diketones, from $MgBr_2{\cdot}OEt_2$-promoted aldol addition.[1] Compounds **4a**-**4b** were prepared according to the procedures in reference.[2]

2. Typical procedure for synthesis of ligands and complexes

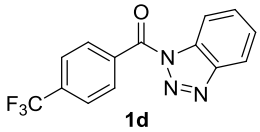
Typical procedure for synthesis of 1

(1H-benzo[d][1,2,3]triazol-1-yl)(p-tolyl)methanone (**1c** as an example)**.** To a solution of 1H-1,2,3-benzotriazole (12 g, 100 mmol) in DCM（200 mL）at 0 ℃, was added Et_3N (17 mL, 120 mmol), followed by addition of 4-methylbenzoyl chloride (15 g, 97 mmol). The reaction mixture was stirred for 11 hours at room temperature and quenched with 10 % aqueous HCl (100 mL) and stirred for 15 min. The organic phase was washed with 10 % aqueous HCl (100 mL) and water (100 mL), dried over sodium sulfate and recrystallized from 2-propanol to give **1c** as a white solid (21 g, 89 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.39 (d, 1H, J = 8.1 Hz, Ar-*H*), 8.16 (m, 3H, Ar-*H*), 7.71 (t, 1H, J = 7.8 Hz, Ar-*H*), 7.55 (t, 1H, J = 7.8 Hz, Ar-*H*), 7.39 (d, 2H, J = 7.8 Hz, Ar-*H*), 2.50 (s, 3H, Ar-CH_3).



1c

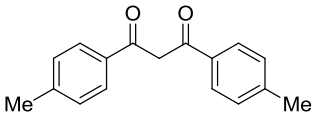
(1H-benzo[d][1,2,3]triazol-1-yl)(4-(trifluoromethyl)phenyl)methanone (**1d**). Yield: (13 g, 90 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.41 (d, 1H, *J* = 8.1 Hz, Ar-*H*), 8.33 (d, 2H, *J* = 7.5 Hz, Ar-*H*), 8.20 (d, 1H, *J* = 8.7 Hz, Ar-*H*),7.86 (d, 2H, *J* = 8.1 Hz, Ar-*H*), 7.76 (t, 1H, *J* = 7.8 Hz, Ar-*H*), 7.59 (d, 1H, *J* = 8.1 Hz, Ar-*H*).



1d

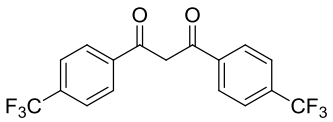
Typical procedure for synthesis of 2

1, 3-di-p-tolylpropane-1, 3-dione (**2c** as an example). To a mixture of **1c** (8.5 g, 36 mmol) and $MgBr_2 \cdot OEt_2$ (19.4 g, 75 mmol) in DCM（50 mL）at room temperature, was added 1-(*p*-tolyl)ethanone (4.0 mL, 30 mmol), followed by addition of *i*-Pr_2NEt (11.7 g, 90 mmol). The resulting suspension was stirred for 13 h and quenched with 10 % aqueous HCl (100 mL) and stirred for 15 min. The organic phase was washed with 10 % aqueous HCl (100 mL) and water (100 mL), dried over sodium sulfate. The residue was purified by flash chromatography on silica gel to give white solid. Yield: 5.3 g (70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 17.00 (s, 1H, CH_2), 7.89 (d, 4H, *J* = 7.8 Hz, Ar-*H*), 7.29 (d, 4H, *J* = 8.1 Hz, Ar-*H*), 6.82 (s, 1H, CH_2), 2.43 (s, 6H, Ar-CH_3).



2c

1,3-bis(4-(trifluoromethyl)phenyl)propane-1,3-dione (**2d**). Yield: 5.9 g (82 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 16.61 (s, 1H, CH_2), 8.10 (d, 4H, *J* = 8.1 Hz, Ar-*H*), 7.77 (d, 4H, *J* = 8.1 Hz, Ar-*H*), 6.89 (s, 1H, CH_2).

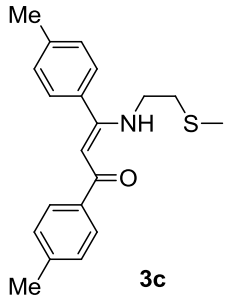


2d

Typical procedure for synthesis of 3

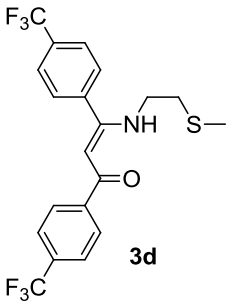
(Z)-3-((2-(methylthio)ethyl)amino)-1,3-di-p-tolylprop-2-en-1-one (**3c**). (**3c** as

an example). To a solution of 1, 3-di-p-tolylpropane-1, 3-dione (4.0 g, 15.9 mmol) and 2-(methylthio)ethanamine (1.74 g, 19.1 mmol) in toluene (60 mL) was added 4-methylbenzenesulfonic acid hydrate (0.091 g, 0.48 mmol) at room temperature. The flask was equipped with a water separator. After refluxing for 2 days, the solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel to give yellow solid. Yield: 3.6 g (70 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.43 (s, 1H, N*H*), 7.80(d, 2H, *J* = 8.1 Hz, Ar-*H*), 7.34-7.18 (m, 6H, Ar-*H*), 5.77 (s, 1H, = C*H*), 3.46-3.39 (m, 2H, NCH_2), 2.63 (t, 2H, *J* = 7.5 Hz, SCH_2), 2.42 (s, 3H, Ar-CH_3), 2.38 (s, 3H, Ar-CH_3), 2.02 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 188.2, 166.2, 140.9, 139.4, 137.3, 132.5, 129.0, 128.7, 127.5, 126.9, 93.5, 43.5, 34.8, 21.3, 21.2, 15.3. IR v(cm $^{-1}$) 2917, 1594, 1577, 1483, 1330, 1302, 1230, 1181, 1143, 1063, 824, 772. MS (ESI, m/z): 325 (M^+). Anal. Calcd for $C_{20}H_{23}NOS$ (325.47): C 73.81; H 7.12; N 4.30. Found: C 73.73; H 7.38; N 4.09.



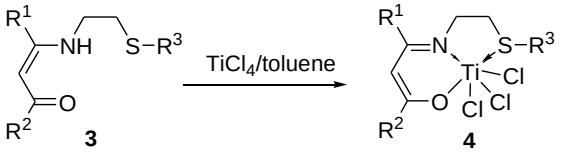
3c

(Z)-3-((2-(methylthio)ethyl)amino)-1,3-bis(4-(trifluoromethyl)phenyl)prop-2-en-1-one (**3d**). Yield: 4.3 g (79 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ 11.51 (s, 1H, N*H*), 7.98 (d, 2H, *J* = 7.8 Hz, Ar-H), 7.77 (d, 2H, *J* = 8.1Hz, Ar-H), 7.66 (d, 2H, *J* = 8.1Hz, Ar-H), 7.58(d, 2H, *J* = 8.1 Hz, Ar-H), 5.75 (s, 1H, =C*H*), 3.45-3.38 (m, 2H, NCH_2), 2.66 (t, 2H, *J* = 6.3 Hz, SCH_2), 2.04 (s, 3H, SCH_3). ^{13}C NMR (75 MHz, $CDCl_3$): δ 187.1, 165.3, 142.8, 138.6, 132.3 (q, *J* = 32.6 Hz), 131.7 (q, *J* = 32.5Hz), 128.2, 127.3, 125.7 (q, *J* = 3.5 Hz), 125.2 (q, *J* = 4.0 Hz), 123.8 (q, *J* = 270.9 Hz), 123.6 (q, *J* = 270.9 Hz), 93.8, 43.6, 34.8, 15.4. ^{19}F NMR (284 MHz, $CDCl_3$) : δ -62.8, -62.9. IR v(cm $^{-1}$) 2919, 1586, 1568, 1320, 1167, 1127, 1066, 1015, 851, 784. MS (ESI, m/z): 433 (M^+). Anal. Calcd for $C_{20}H_{17}F_6NOS$ (433.41): C 55.42; H 3.95; N 3.23. Found: C 55.61; H 4.06; N 3.21.



3d

Synthesis of Titanium Complexes 4c-4d



3 **4**

3c, **4c**. $R^1 = R^2 = p$-MePh, R^3 = Me
3d, **4d**. $R^1 = R^2 = p$-CF_3Ph, R^3 = Me

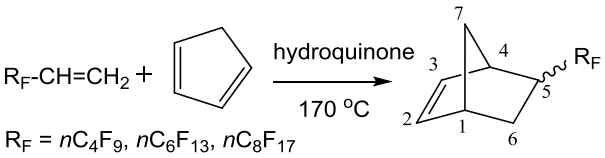
Scheme S1. Synthesis of Titanium Complexes 4

[3-(2-(methylthio)ethylimino)-1,3-di-*p*-tolylprop-1-en-1-olate]Ti(IV)Cl_3 **(4c).** To a stirred solution of $TiCl_4$ (1.5 g, 8.0 mmol) in dry toluene (50 mL) at -78 ℃ was added a solution of **3c** (2.0 g, 6.1 mmol) in dry toluene (10 mL) dropwise over 20 min. The solution was allowed to warm to room temperature and stirred for 16 h. The solvent was removed under vacuum and the residue was redissolved in dried toluene (100 mL). The solution was concentrated under vacuum to about 20 mL and then kept at – 30 ℃ overnight. Reddish black crystals were collected and dried under vacuum, to give complex **4c** (2.54 g) in 87 % yield. ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.71 (d, *J* = 8.1 Hz, 2H; Ar-*H*), 7.33-7.18 (m, 6H, Ar-*H*), 6.35 (s, 1H, =C*H*), 4.20-4.02 (m, 2H, NCH_2), 3.28-3.19 (m, 1H, SCH_2), 2.77 (s, 3H, SCH_3), 2.69-2.65 (m, 1H, SCH_2), 2.43 (s, 3H, CH_3), 2.39 (s, 3H, CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 171.1, 170.0, 142.9, 140.1, 134.7, 129.9, 129.7, 129.3, 127.2, 125.9, 109.2, 56.8, 38.1, 22.4, 21.7, 21.4.Element analysis Anal. calcd for $C_{20}H_{22}Cl_3NOSTi$ (478.69): C 50.18, H 4.63, N 2.93; Found: C 50.03, H 4.62, N 2.95.

[(1Z,3Z)-3-((2-(methylthio)ethyl)imino)-1,3-bis(4-(trifluoromethyl)phenyl)prop-1-en-1-olate]Ti(IV)Cl_3 **(4d).** The same procedures as that for the preparation of **4c**.

Yield: 1.5 g (83 %). ^{1}H NMR(300 MHz, $CDCl_3$, δ): 7.93 (d, *J* = 8.1 Hz, 2 H, Ar-*H*), 7.83 (d, *J* = 8.1 Hz, 2 H, Ar-*H*), 7.69 (d, *J* = 8.1 Hz, 2 H, Ph-*H*), 7.47 (d, *J* = 7.8 Hz, 2 H, Ph-*H*), 6.36 (s, 1 H, =CH), 4.19-3.95 (m, 2 H, NCH_2), 3.32-3.25 (m, 1 H, SCH_2), 2.80 (s, 3 H, SCH_3), 2.75-2.71 (m, 1H, SCH_2); ^{13}C NMR (75 MHz, $CDCl_3$, δ): 169.2, 168.2, 140.7, 135.2, 133.4 (q, *J* = 32.3 Hz), 132.2 (q, *J* = 33.4 Hz), 127.4, 126.6, 126.3, 125.9 (q, *J* = 4.0 Hz), 123.5 (q, *J* = 270.6 Hz), 123.4 (q, *J* = 271.1 Hz), 109.5, 57.0, 37.9, 22.6; ^{19}F NMR (282 MHz, $CDCl_3$, δ): -63.4, -63.5. Element analysis Anal. calcd for $C_{20}H_{16}Cl_3F_6NOSTi$(586.63): C 40.95, H 2.75, N 2.39; Found: C 41.18, H 2.85, N 2.26.

3. General Procedure for Preparing Fluorinated Comonomer NBF*n*



Scheme S2. Synthesis of Fluorinated Comonomers

Three monomers were synthesized utilizing a Diels-Alder reaction described by Perez et al..[3] Briefly, a Parr Instruments high-pressure reaction vessel was charged with 1/1 molar ratios of the 1H,1H,2H-perfluoro-1-alkene and dicyclopentadiene and 0.03 mole fraction of hydroquinone, as a quenching agent. The reaction was held at 170 °C for 72 h. Monomers were purified by vacuum distillation. A DRX-400 Bruker NMR spectrometer equipped with a 9.4 T Oxford magnet was used to confirm the chemical structure and composition of the synthesized 5-(perfluoro-n-alkyl)norbornenes (NBF*n*). The reactions yielded ~3/1 ratio of endo- to exo-isomers of the NBF*n* as determined by GC analysis. The ^{13}C NMR spectra were collected using deuterated chloroform as solvent and are consistent with those reported by Perez et al.

We tried to get pure isomer (exo and endo) to identify the signal of each C and H in both monomers. Consequently, monomer NBF6 (2.0 g, see monomer NMR) was first selected as an example to be separated as exo- and endo- isomer via C18 column using

either CH_3CN/H_2O (9/1, v/v) or methol (100%) as mobile phase. However, the separation was quite difficult because of the existence of perfluoro-alkyl in the molecular, though trace of endo isomer of NBF_6 could be determined by ^1H NMR (see monomer NMR): Consequently, we combine information of ^{13}C NMR dept 135 and H-H Cosy and C-H HSQC C-H HMBC together to identified each C and H on the NBF. For **NBF4**: ^1H NMR δ 6.19 ppm (brs, 1.19 H, exo H2, endo H2, and exo H3), 5.97 ppm (brs, 0.76 H endo H3), 3.18 ppm (brs, 1H, endo H4 and exo H4), 2.98 ppm (brs, 0.21 H, exo H1), 2.94 ppm (brs, 0.78 H, endo H1), 2.74-2.85 ppm (m, 0.8 H, endo H5) 1.95-2.13 ppm (m, 1.0 H, exo H5, endo H5 and endo H6), 1.82-1.85 ppm (m, 0.23 H, exo H6), 1.47-1.55 ppm (m, 1H, exo H7 and endo H7), 1.26-1.42 ppm (m, 2H, exo H7, exo H6, endo H7 and endo H6). ^{13}C NMR (400 MHz, $CDCl_3$) endo isomer (ppm): δ C1 42.17, C2 137.46, C3 131.94, C4 43.79, C5 40.30, C6 27.71, C7 49.84; exo isomer (ppm) δ C1 41.42, C2 138.45, C3 136.51, C4 42.56, C5 41.04, C6 26.94, C7 46.56. ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.0 (m, C*F*$_3$), -116.5 to -111.4 (m, C*F*$_2$), -123.8 to -121.4 (m, C*F*$_2$), -127.1 to -125.1 (m, C*F*$_2$). HRMS (EI^+ m/z) Anal. calcd for NBF4 $[M+H]^+$: found 312.0560. For **NBF6**: ^1H NMR (400 MHz, $CDCl_3$): δ 6.18 ppm (brs, 1.23 H, exo H2, endo H2, and exo H3), 5.96 ppm (brs, 0.77 H endo H3), 3.17 ppm (brs, 1.0 H, endo H4 and exo H4), 2.98 ppm (brs, 0.25 H, exo H1), 2.93 ppm (brs, 0.74 H, endo H1), 2.74-2.87 ppm (m, 0.8 H, endo H5) 1.95-2.12 ppm (m, 1.0 H, exo H5, endo H5 and endo H6), 1.80-1.83 ppm (m, 0.28 H, exo H6), 1.46-1.54 ppm (m, 1H, exo H7 and endo H7), 1.24-1.41 ppm (m, 2H, exo H7, exo H6, endo H7 and endo H6). ^{13}C NMR (400 MHz, $CDCl_3$): for endo isomer (ppm): δ C1 42.22, C2 137.45, C3 131.97, C4 43.85, C5 40.47, C6 27.74, C7 49.84; exo isomer (ppm) δ C1 41.47, C2 138.46, C3 136.53, C4 42.62, C5 41.21, C6 26.97, C7 46.56. HRMS (EI^+ m/z) Anal.calcd for **NBF6** $[M+H]^+$: 412.0497, found 412.0494. ^{19}F NMR (376 MHz, $CDCl_3$): δ -80.9 (m, C*F*$_3$), -116.3 o -111.3 (m, C*F*$_2$), -123.8 to -121.3 (m, C*F*$_2$), -127.1 to -125.3 (m, C*F*$_2$). For **NBF8**: ^1H NMR (400 MHz, $CDCl_3$): δ 6.18 ppm (brs, 1.23 H, exo H2, endo H2, and exo H3), 5.97 ppm (brs, 0.77 H endo H3), 3.17 ppm (brs, 1.0 H, endo H4 and exo H4), 2.97 ppm (brs, 0.23 H, exo H1), 2.93 ppm (brs, 0.76 H, endo H1), 2.72-2.84 ppm (m, 0.8 H, endo H5) 1.94-2.12 ppm (m, 1.0 H, exo

H5, endo H5 and endo H6), 1.81-1.84 ppm (m, 0.26 H, exo H6), 1.46-1.54 ppm (m, 1H, exo H7 and endo H7), 1.24-1.41 ppm (m, 2H, exo H7, exo H6, endo H7 and endo H6). ^{13}C NMR (400 MHz, $CDCl_3$) for endo isomer (ppm): δ C1 42.28, C2 137.42, C3 132.00, C4 43.89, C5 40.55, C6 27.72, C7 49.83; exo isomer (ppm) δ C1 41.52, C2 138.46, C3 136.56, C4 42.86, C5 41.28, C6 26.95, C7 46.56. HRMS (EI^+ m/z) Anal.calcd for NBF8 $[M+H]^+$: 512.0433, found 512.0438. ^{19}F NMR (376 MHz, $CDCl_3$): δ -81.0 (m, C*F*$_3$); -116.4 to -111.4 (m, C*F*$_2$), -123.8 to -121.4 (m, C*F*$_2$), -127.2 to -125.4 (m, C*F*$_2$).

4. General procedure of ethylene/NBF*n* copolymerization

A flame-dried Schlenk flask was charged with ethylene and placed in an oil bath at a desired temperature. A desired amount of toluene was transferred into the flask, and saturated with ethylene. MMAO and comonomer were injected into the flask in sequence via syringe, and the mixture was stirred for 10 min. The polymerization was started by adding a precursor catalyst solution in toluene with a syringe. After a desired time, the copolymerization was quenched with acidified ethanol. And poured into a large amount of acidified ethanol (300 mL, 10 vol.-% HCl in ethanol). The precipitated copolymer was collected, washed with ethanol, and then dried at 60 ℃ under vacuum till a constant weight.

5. NMR spectra of ligands and complexes

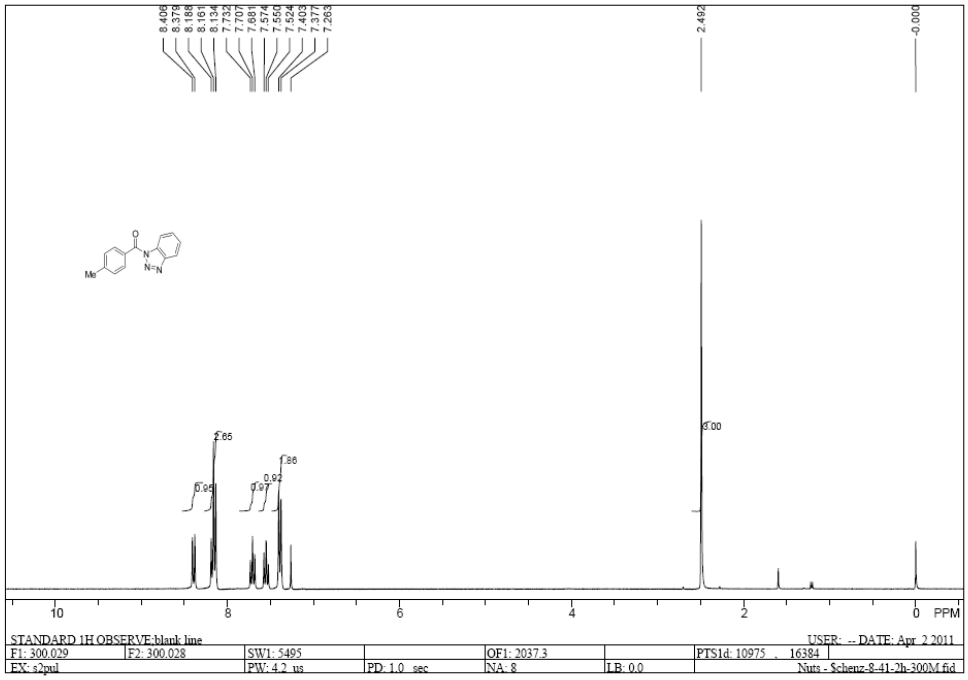


Figure S1 ^{1}H NMR of **1c (** 300 MHz, $CDCl_3$)

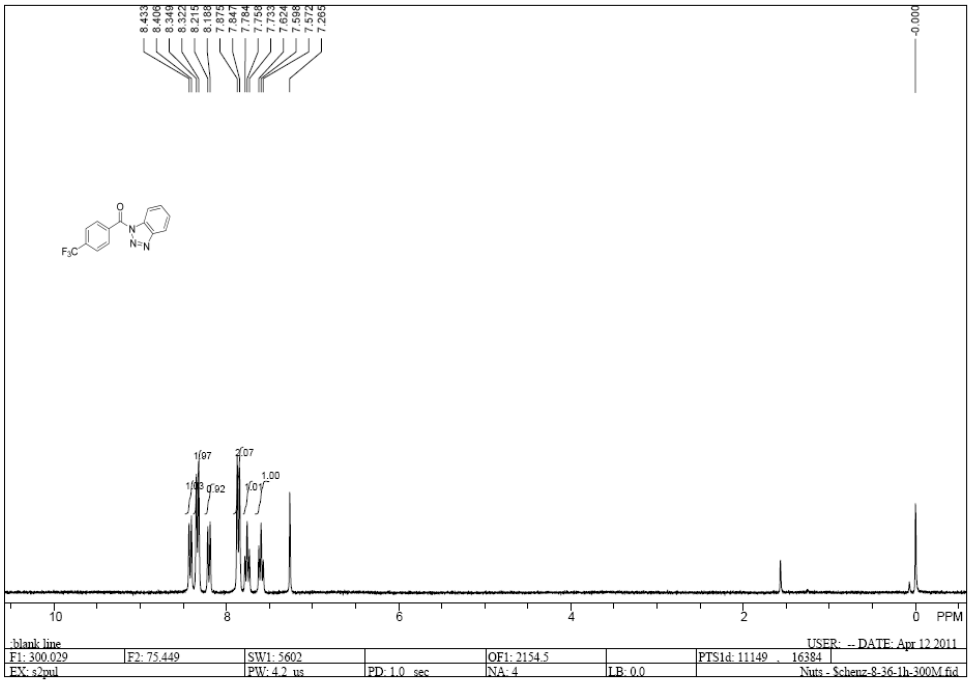


Figure S2 ^{1}H NMR of **1d (** 300 MHz, $CDCl_3$)

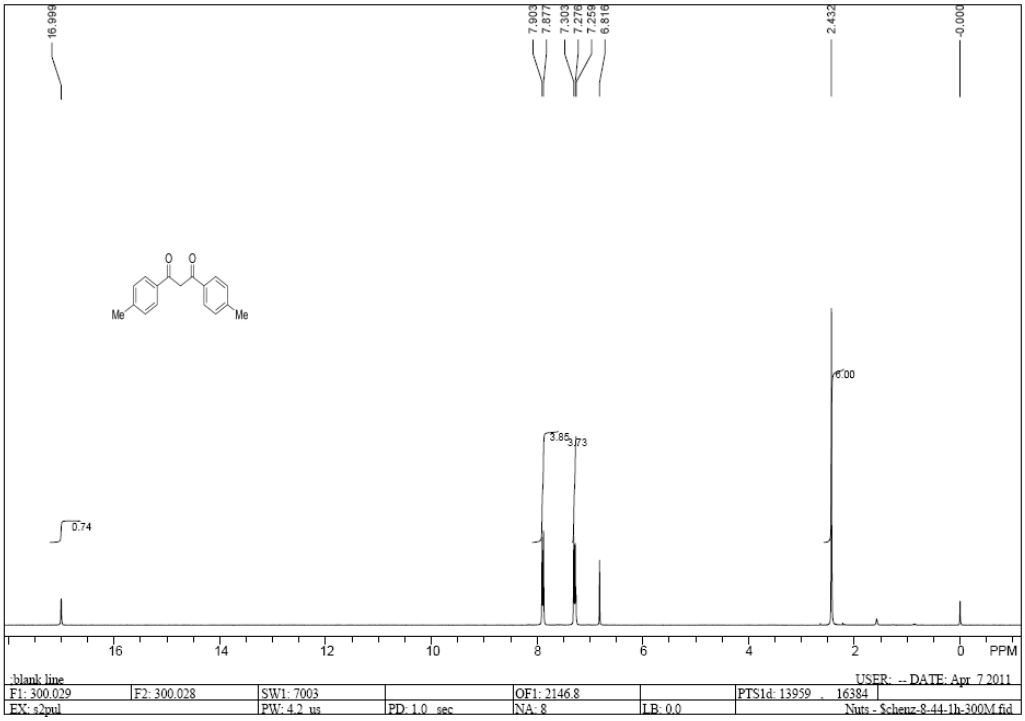


Figure S3 ^{1}H NMR of **2c (** 300 MHz, $CDCl_3$)

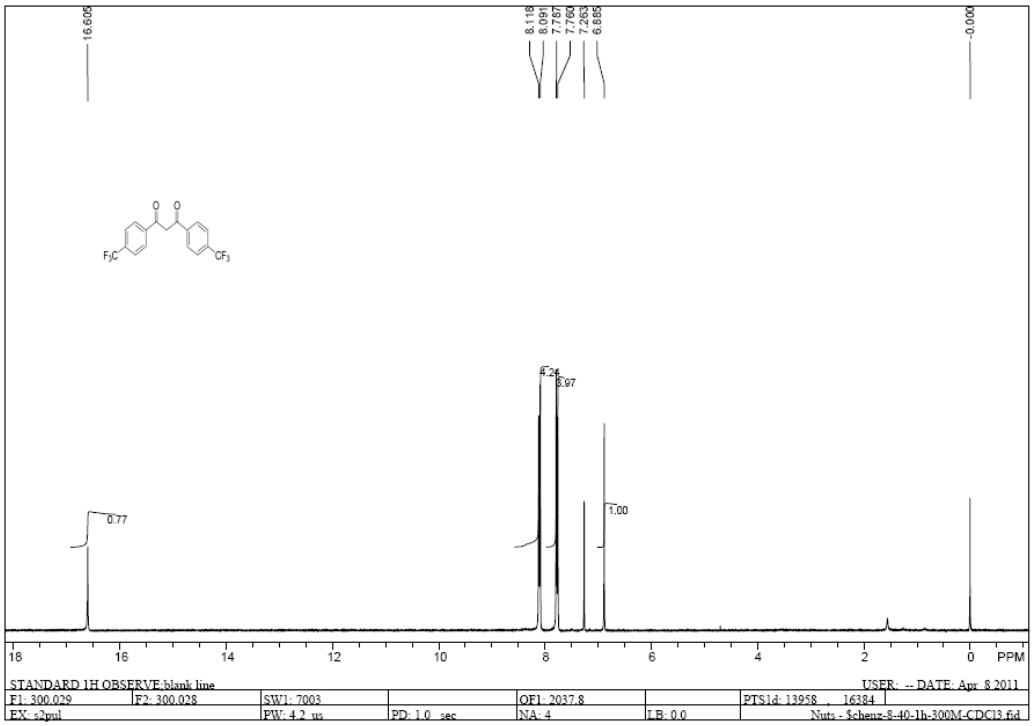


Figure S4 ^{1}H NMR of **2d (** 300 MHz, $CDCl_3$)

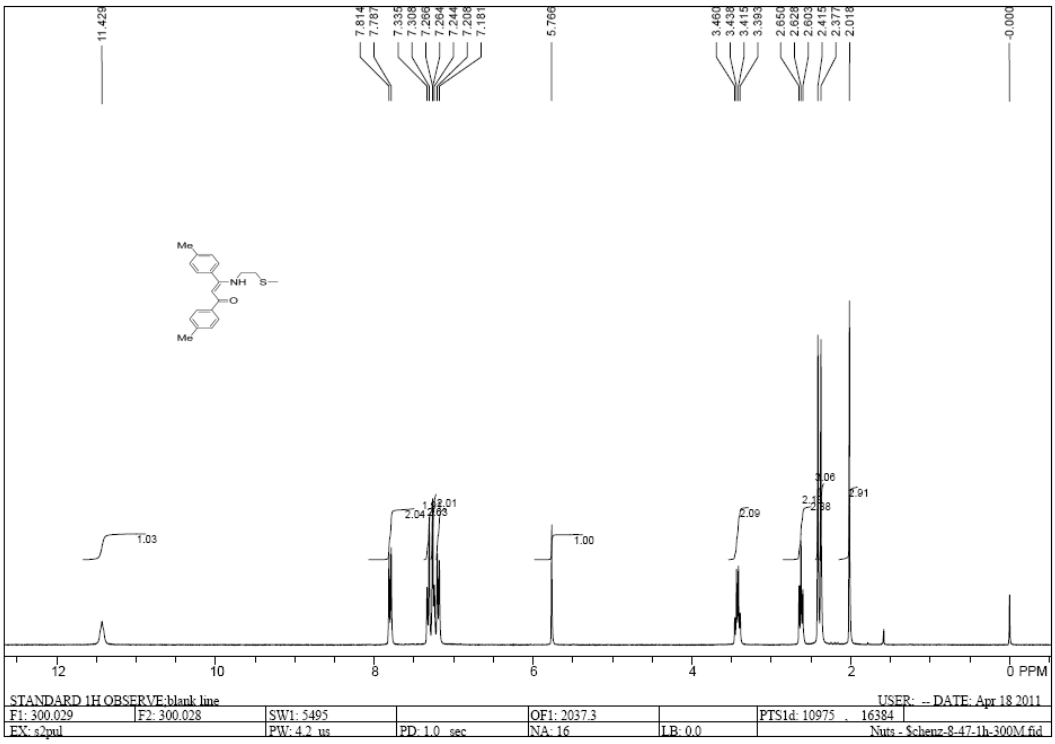


Figure S5 ^{1}H NMR of **3c (** 300 MHz, $CDCl_3$)

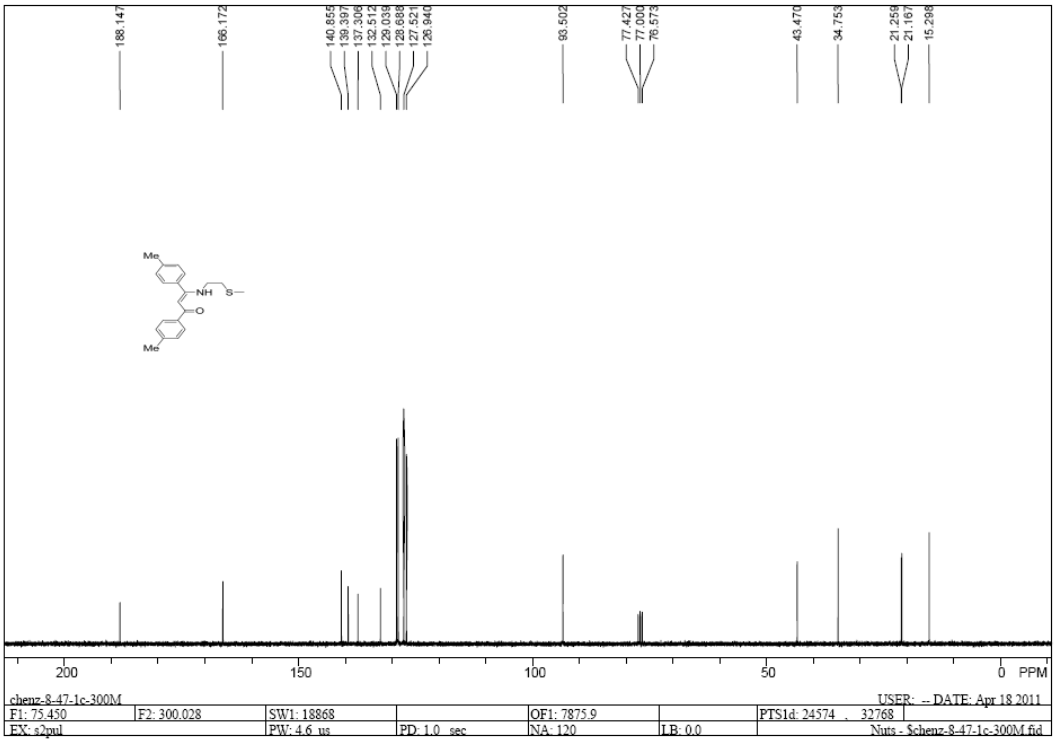


Figure S6 ^{13}C NMR of **3c (** 75 MHz, $CDCl_3$)

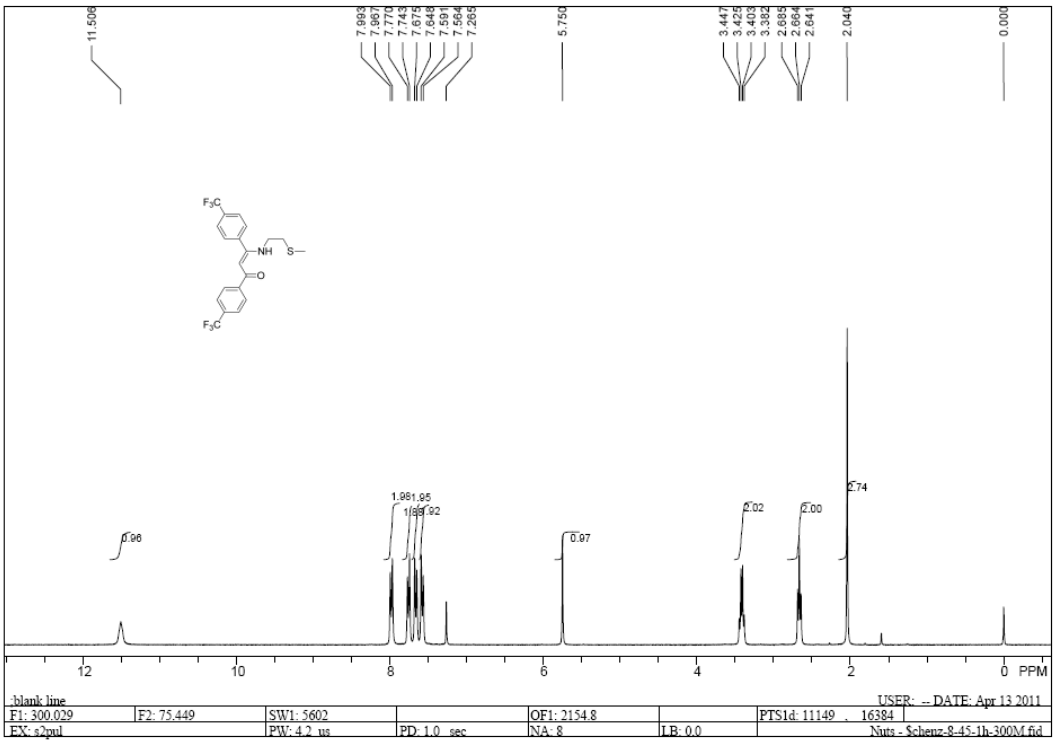


Figure S7 [1] H NMR of **3d (** 300 MHz, $CDCl_3$)

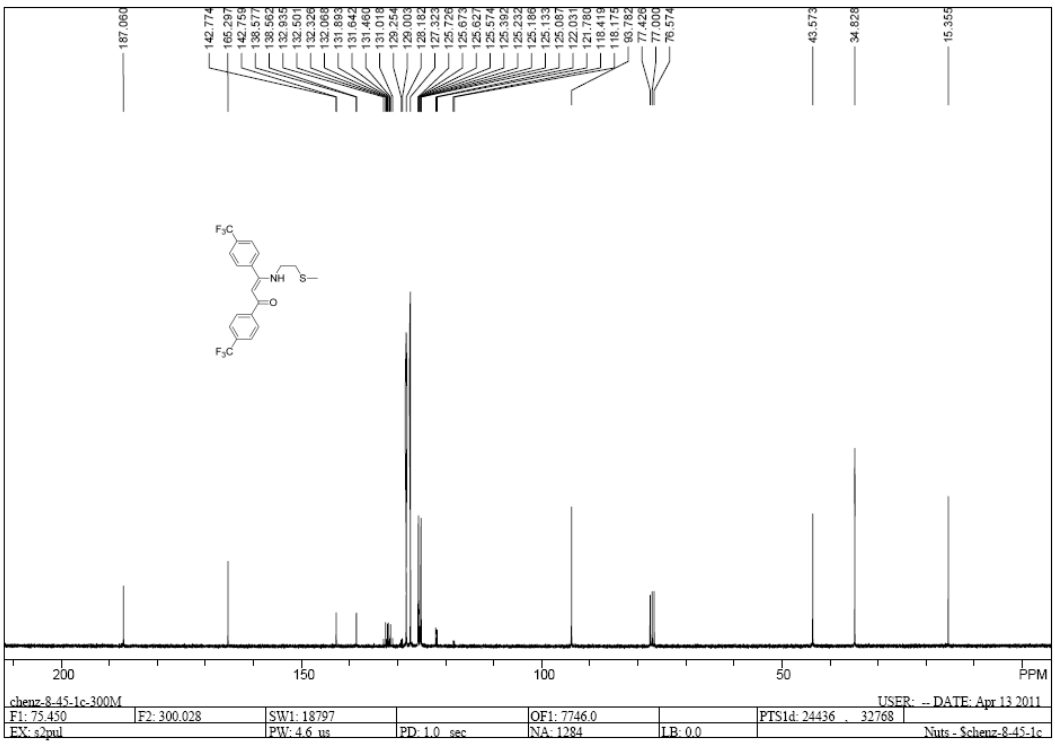


Figure S8 [13] C NMR of **3d (** 75 MHz, $CDCl_3$)

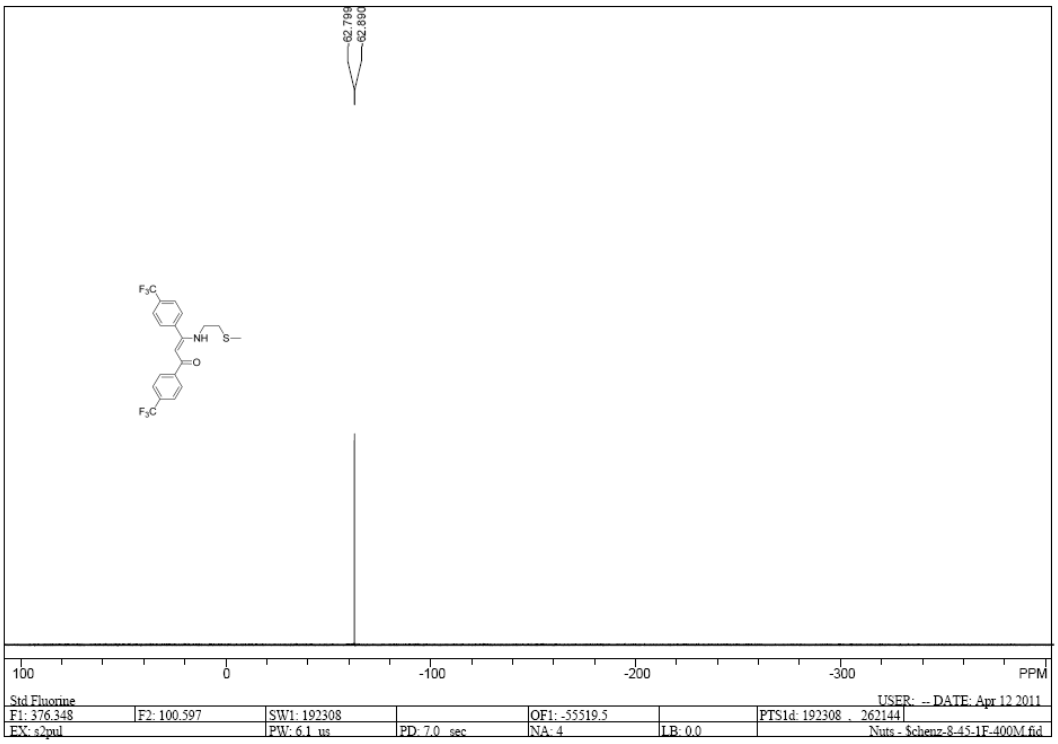


Figure S9 ^{19}F NMR of **3d (** 376 MHz, $CDCl_3$)

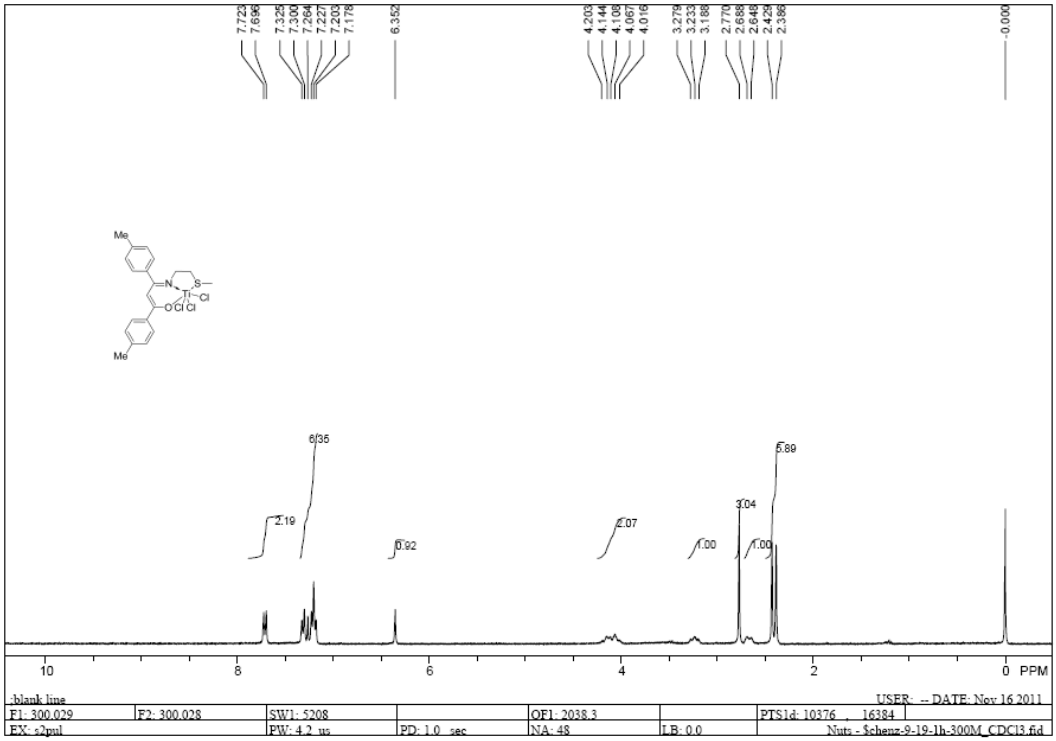


Figure S10 ^{1}H NMR of **4c (** 300 MHz, $CDCl_3$)

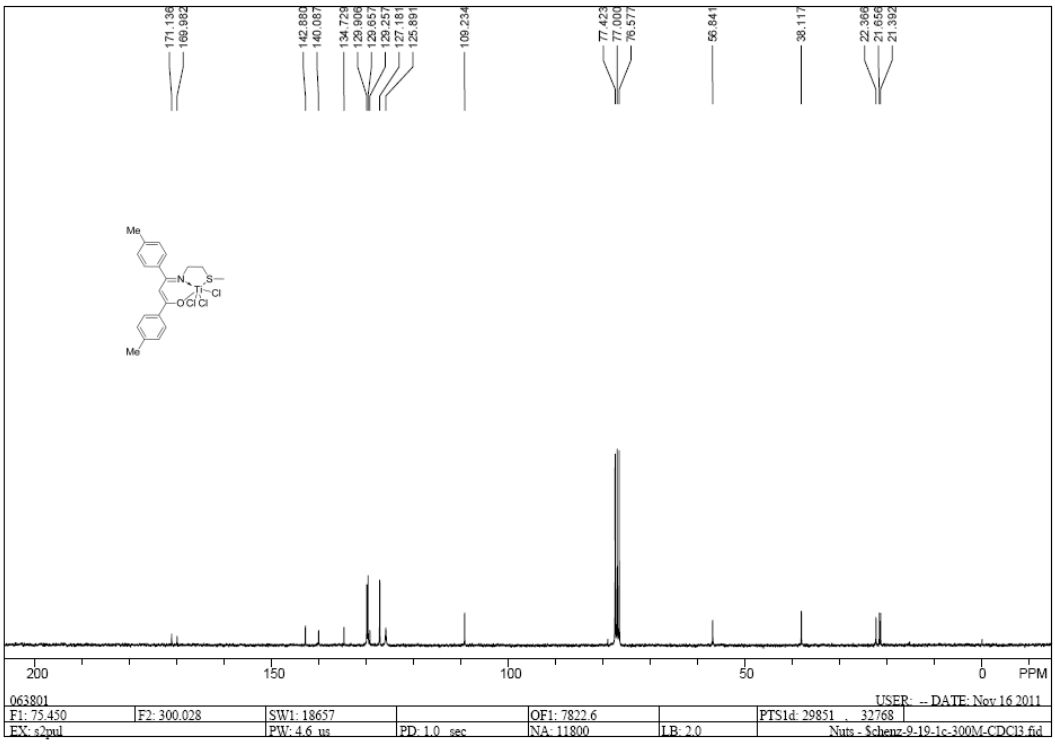


Figure S11 ^{13}C NMR of **4c (** 75 MHz, $CDCl_3$)

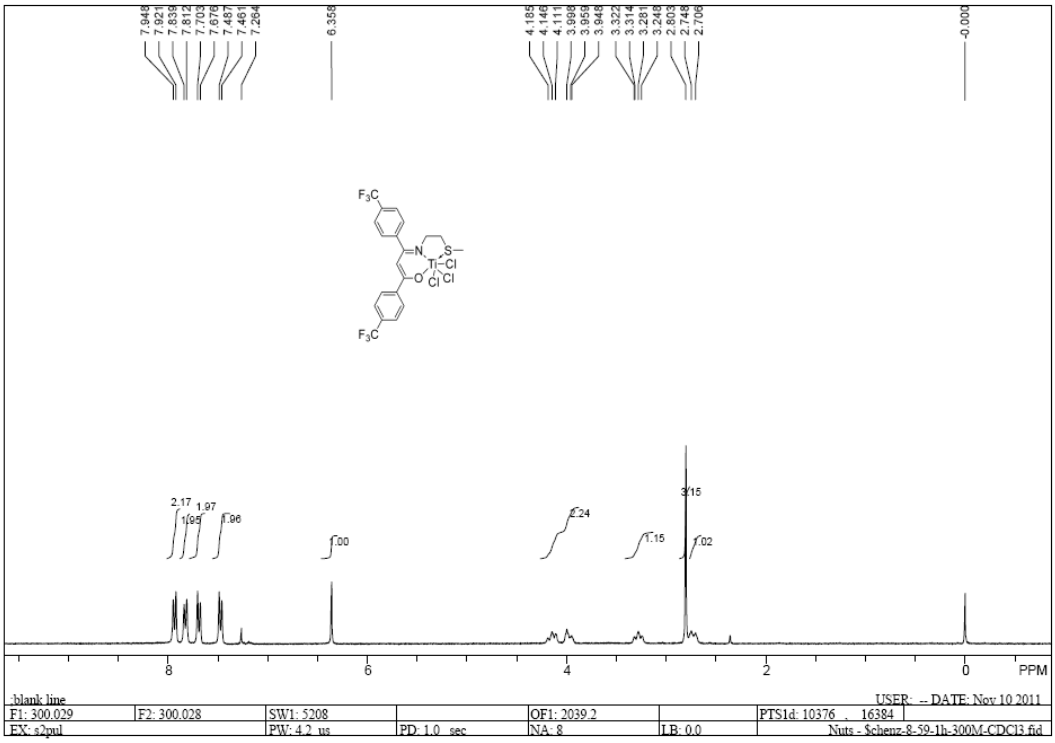


Figure S12 ^{1}H NMR of **4d (** 300 MHz, $CDCl_3$)

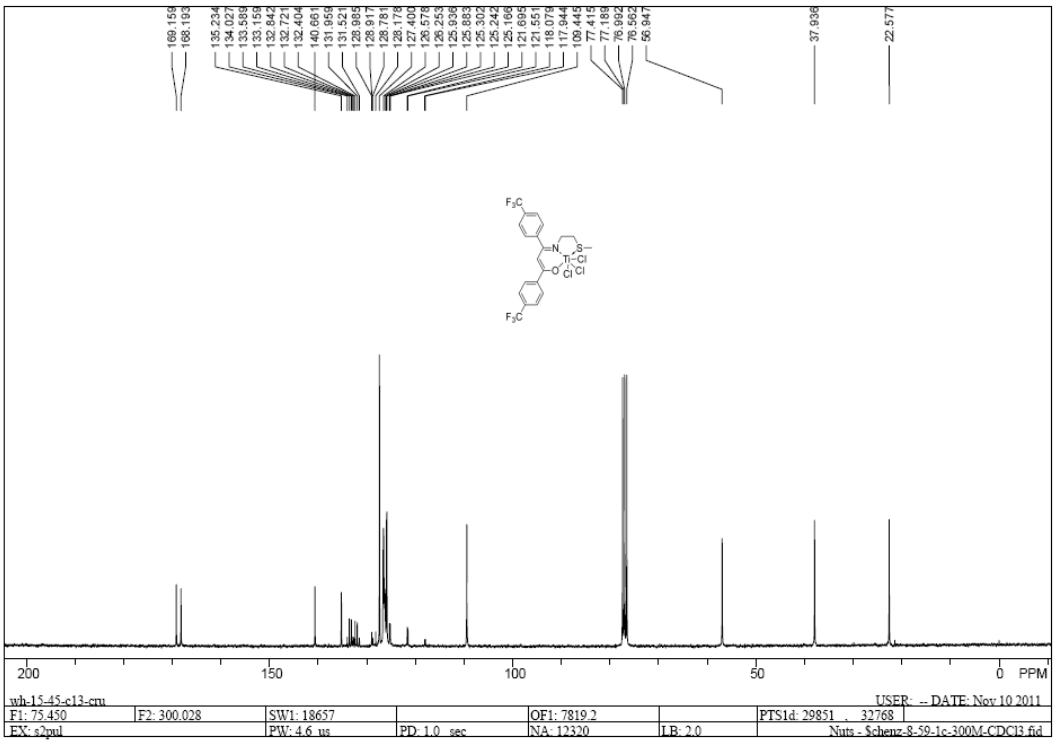


Figure S13 ^{13}C NMR of **4d (** 75 MHz, $CDCl_3$)

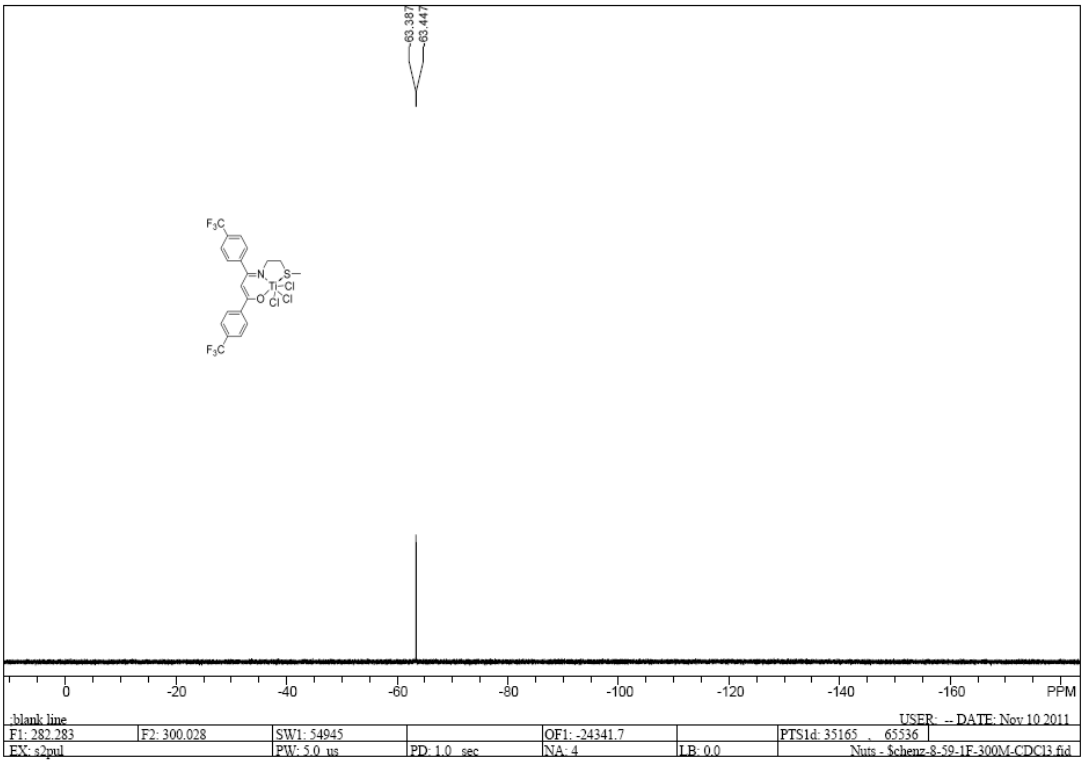


Figure S14 ^{19}F NMR of **4d (** 282 MHz, $CDCl_3$)

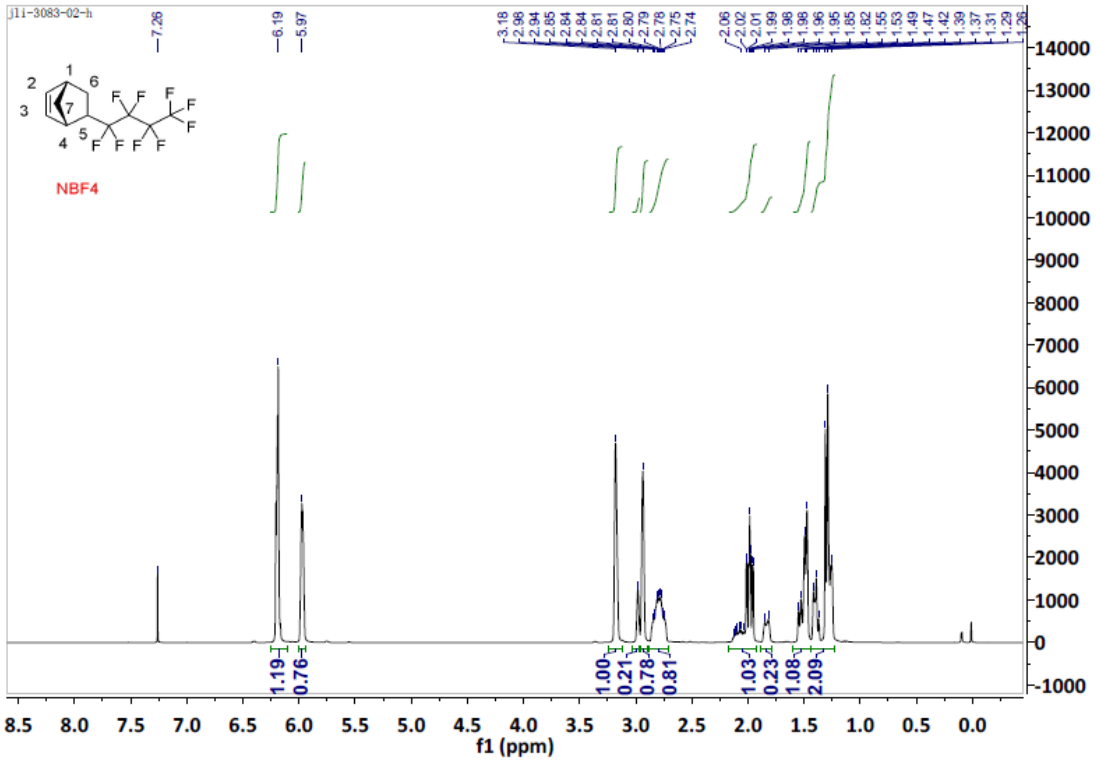


Figure S15 ^{1}H NMR of **NBF4** (400 MHz, $CDCl_3$)

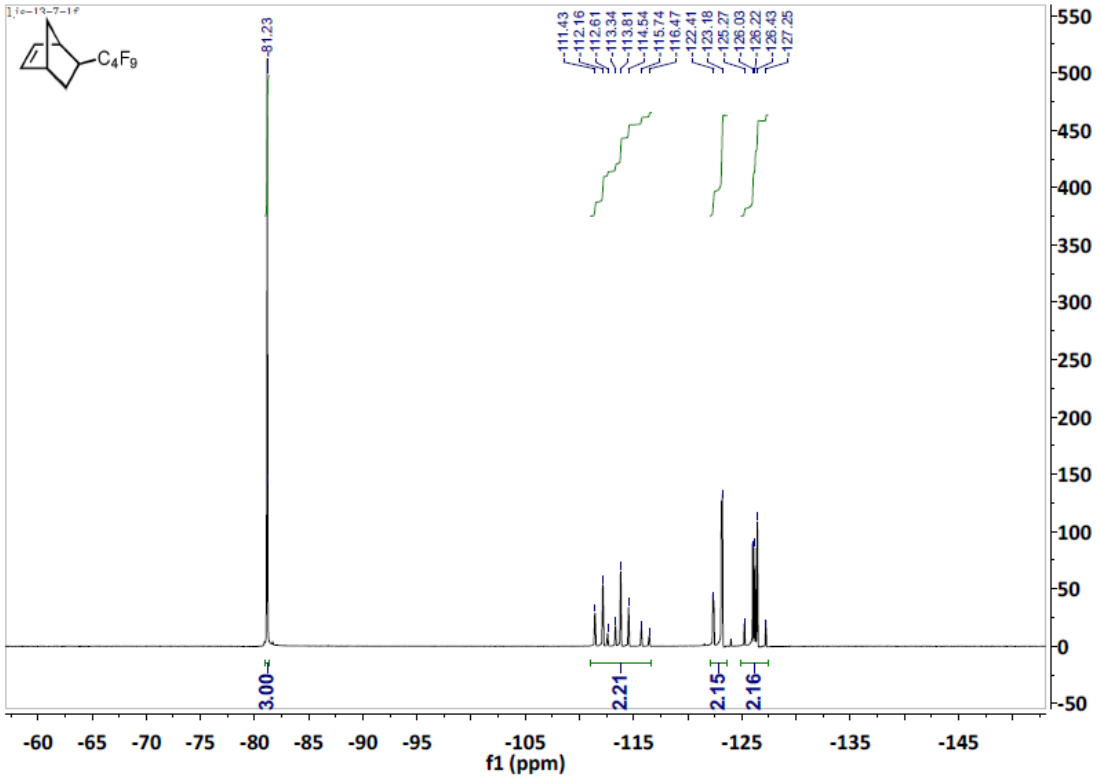


Figure S16 ^{19}F NMR of **NBF4** (376 MHz, $CDCl_3$)

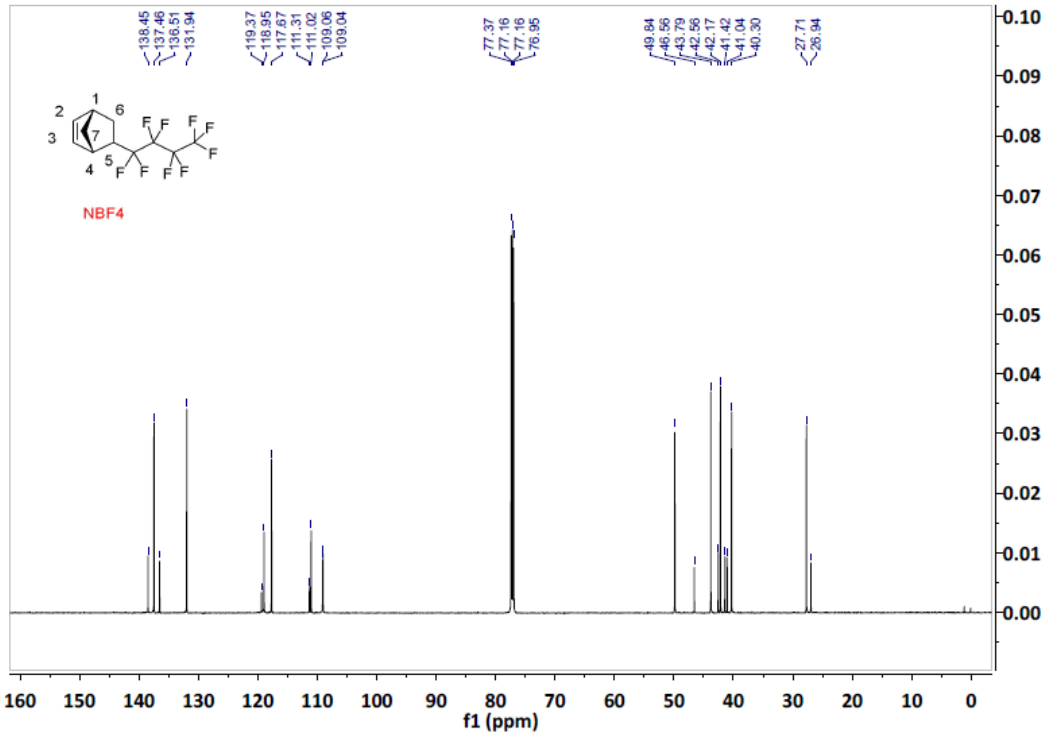


Figure S17 ^{13}C NMR for **NBF4** (exo/endo, 24/76) with H&F decoupling ($CDCl_3$ 600 MHz).

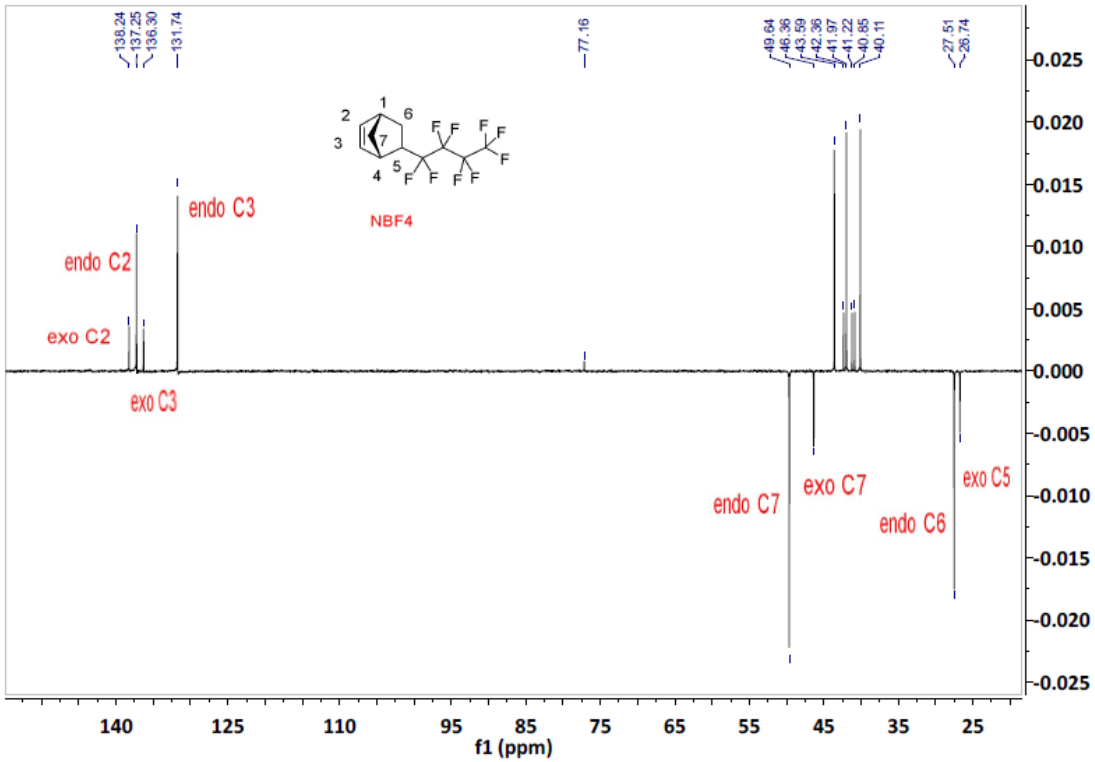


Figure S18 Dept 135 NMR for **NBF4** (exo/endo, 24/76) with H&F decoupling ($CDCl_3$ 600 MHz).

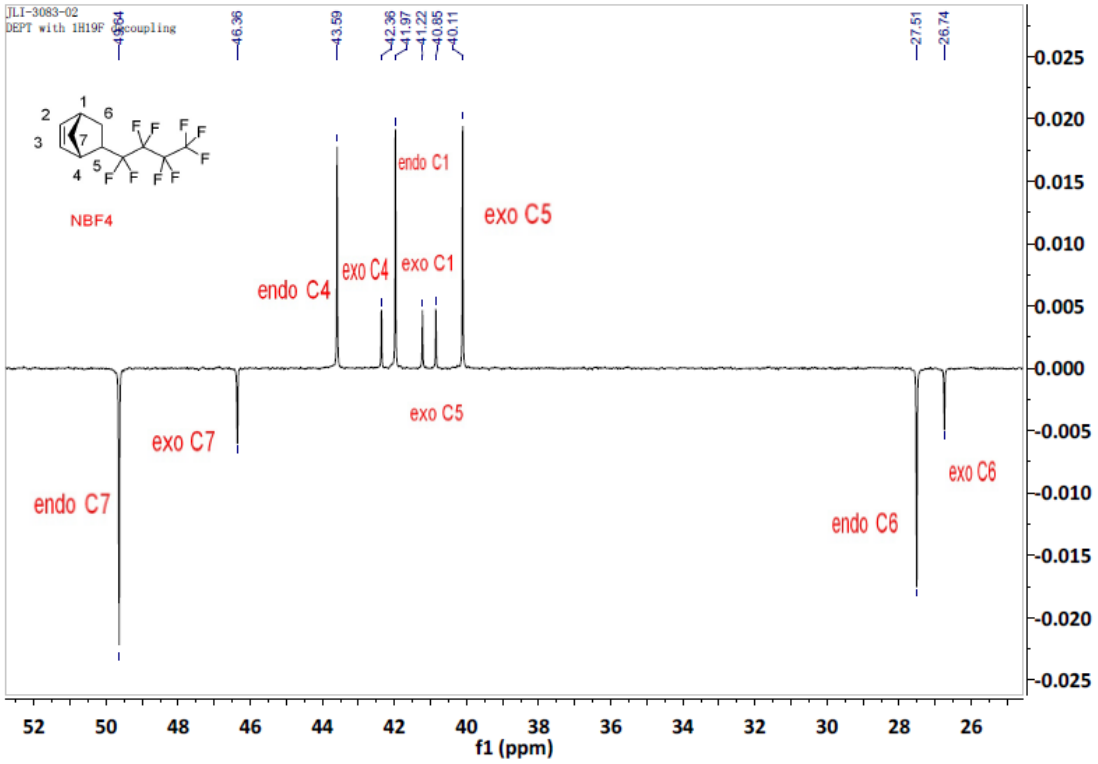


Figure S19 Dept 135 NMR for **NBF4** (exo/endo, 24/76) with H&F decoupling ($CDCl_3$ 600 MHz).

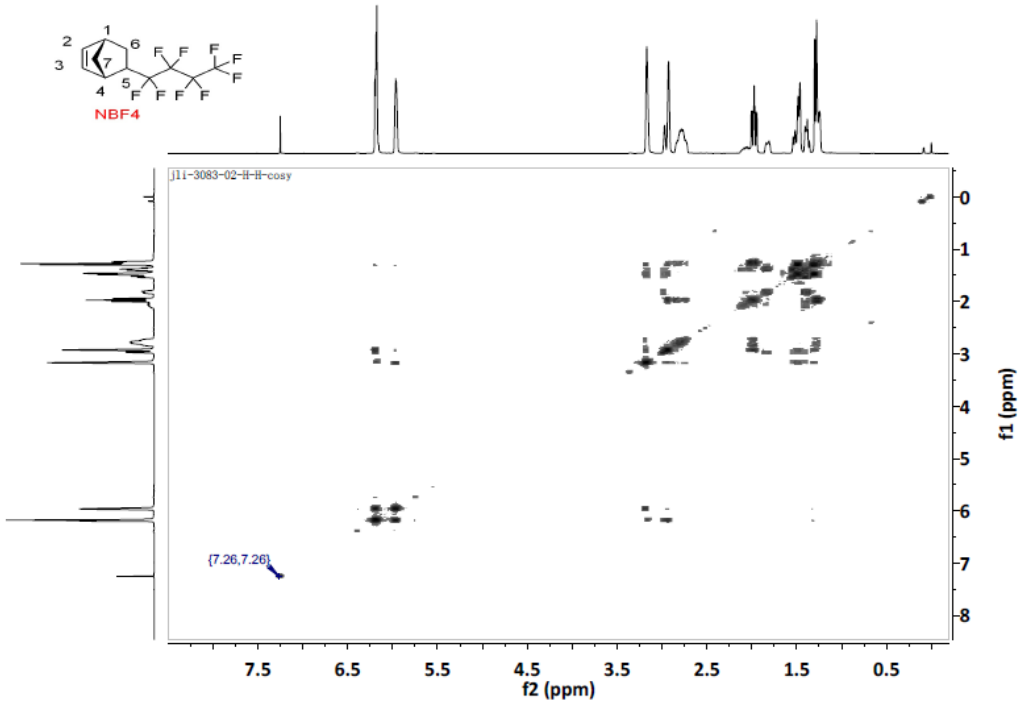


Figure S20 H-H Cosy NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz).

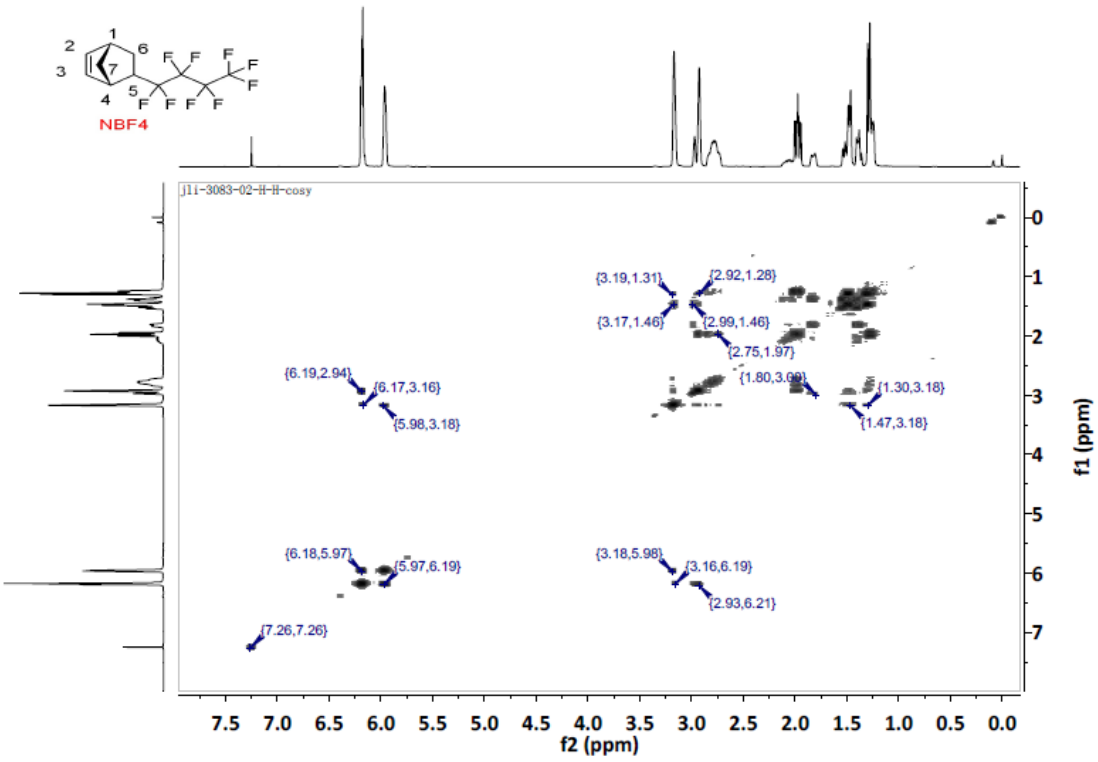


Figure S20a H-H Cosy NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz).

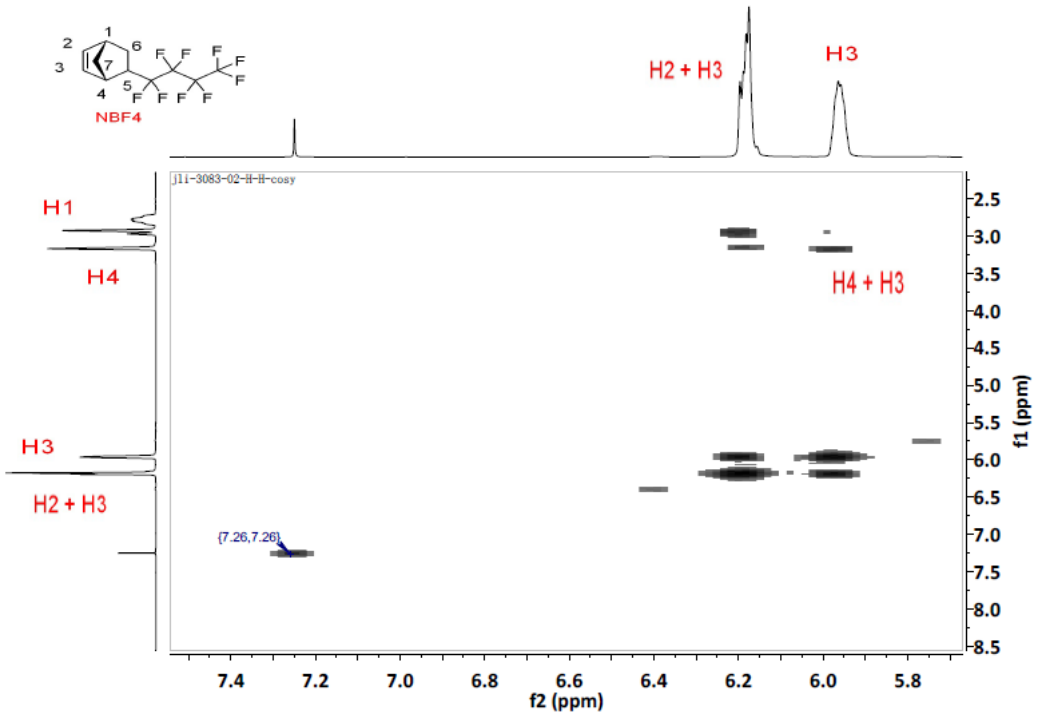


Figure S20b H-H Cosy NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz).

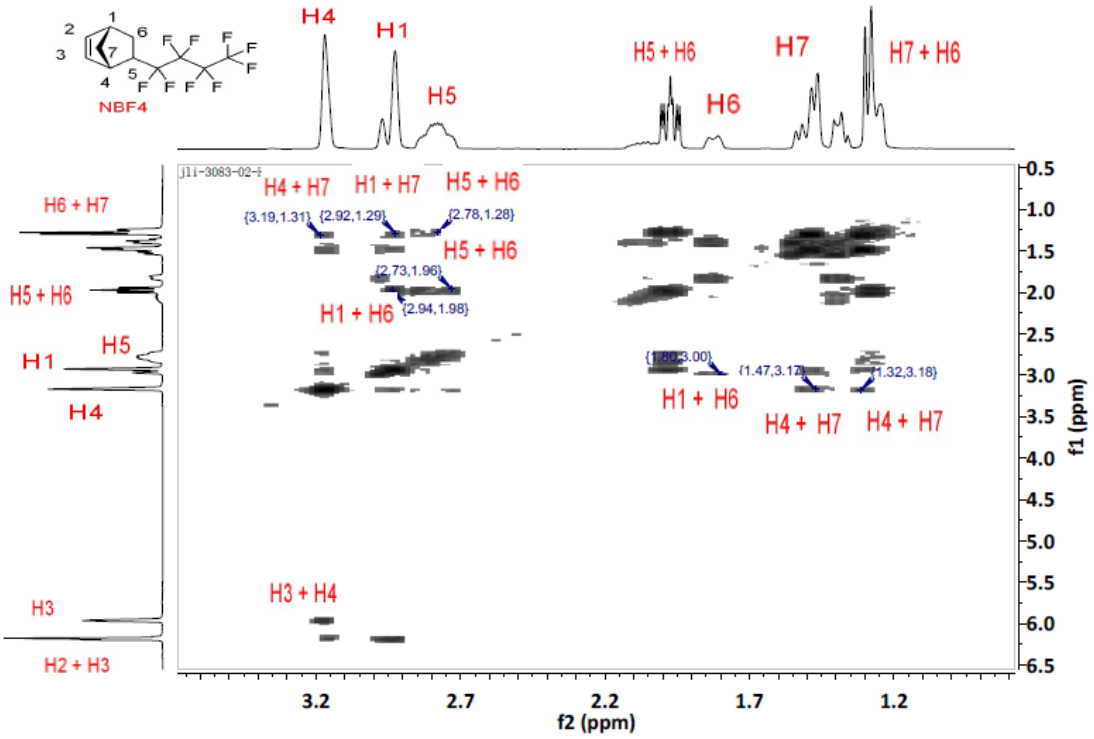


Figure S20c H-H Cosy NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz).

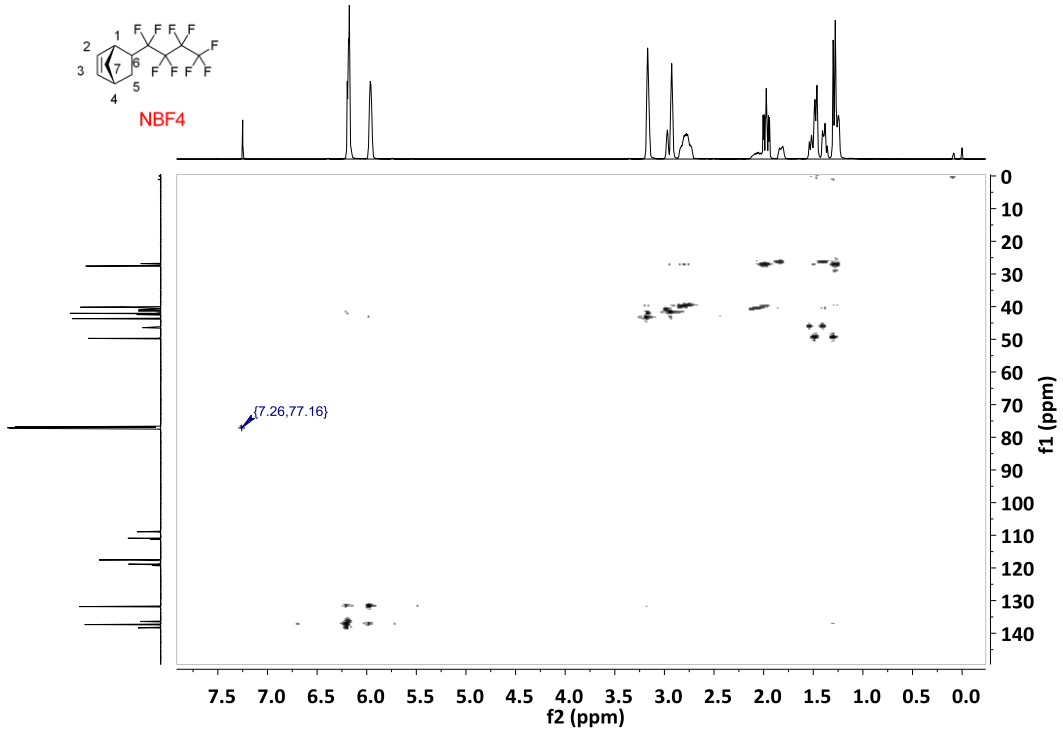


Figure S21 C-H HSQC NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz).

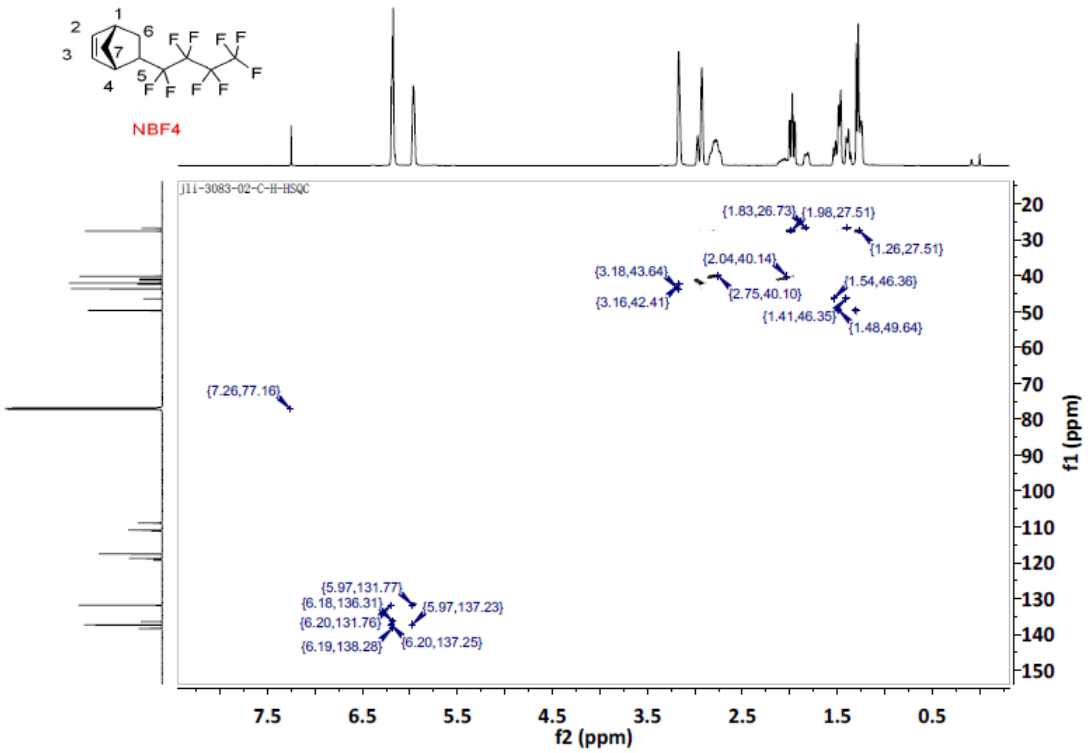


Figure S21a C-H HSQC NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz)

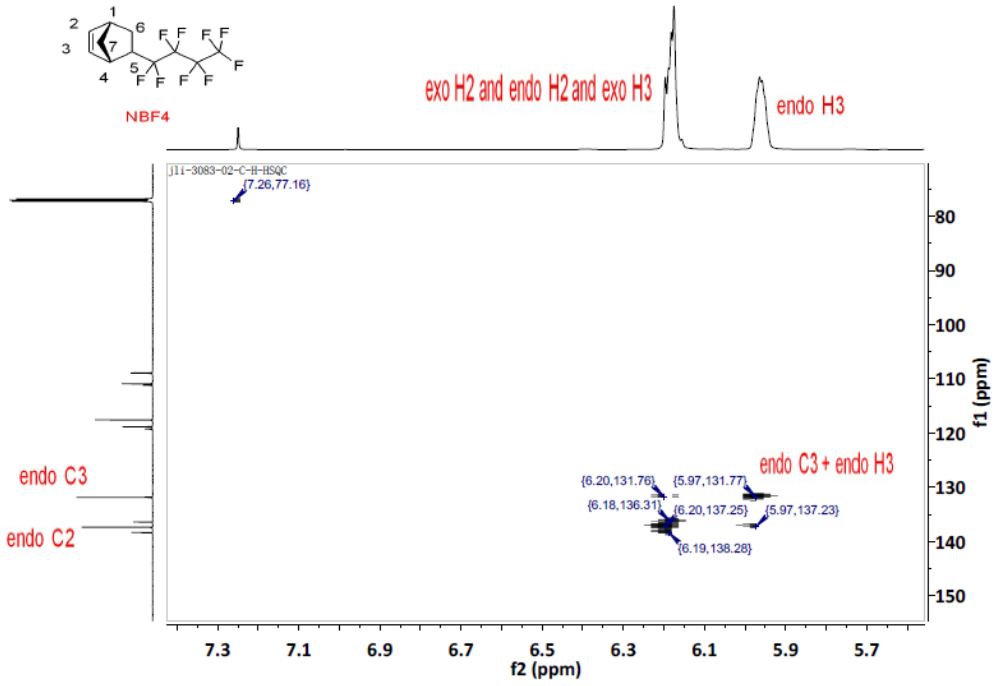


Figure S21b C-H HSQC NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz)

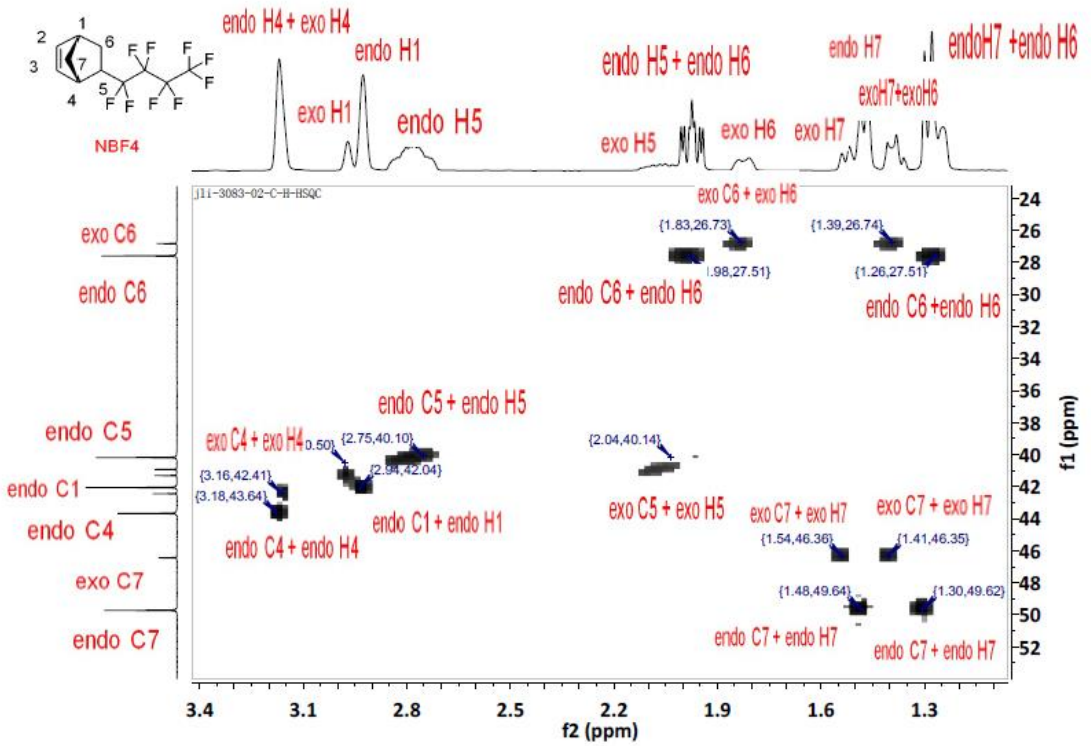


Figure S21c C-H HSQC NMR for **NBF4** (exo/endo, 24/76) ($CDCl_3$ 400 MHz)

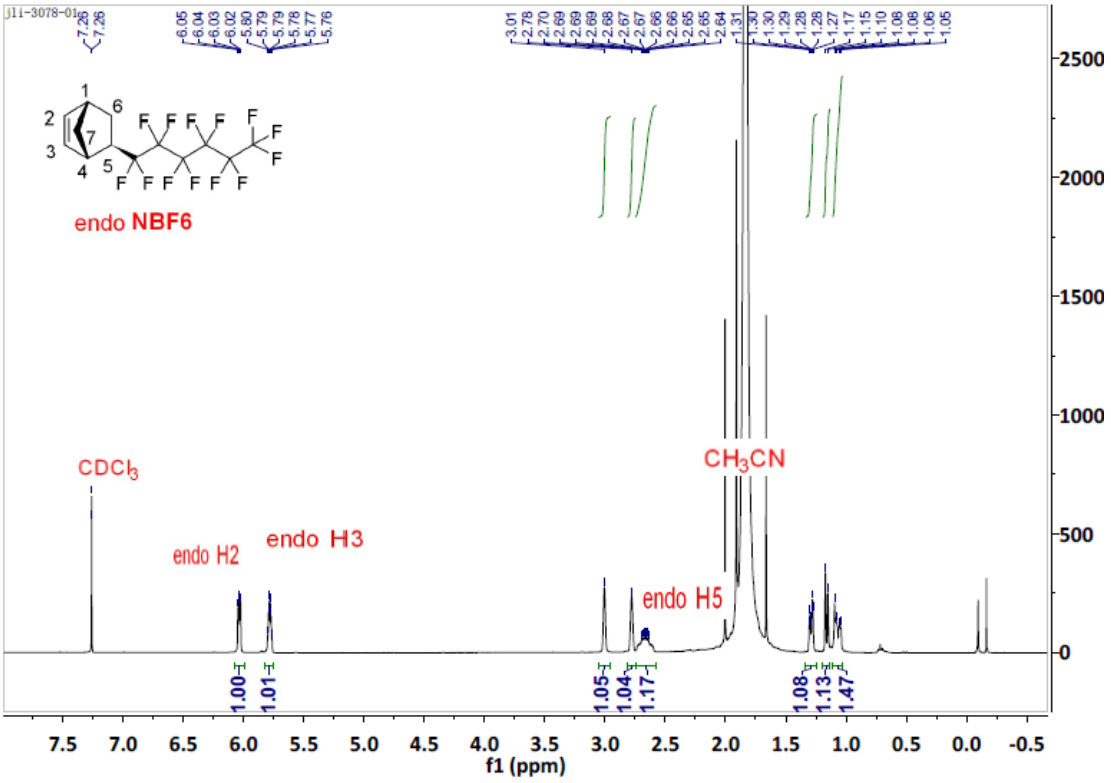


Figure S22 ^{1}H NMR of endo isomer of **NBF6** (400 MHz, $CDCl_3$)

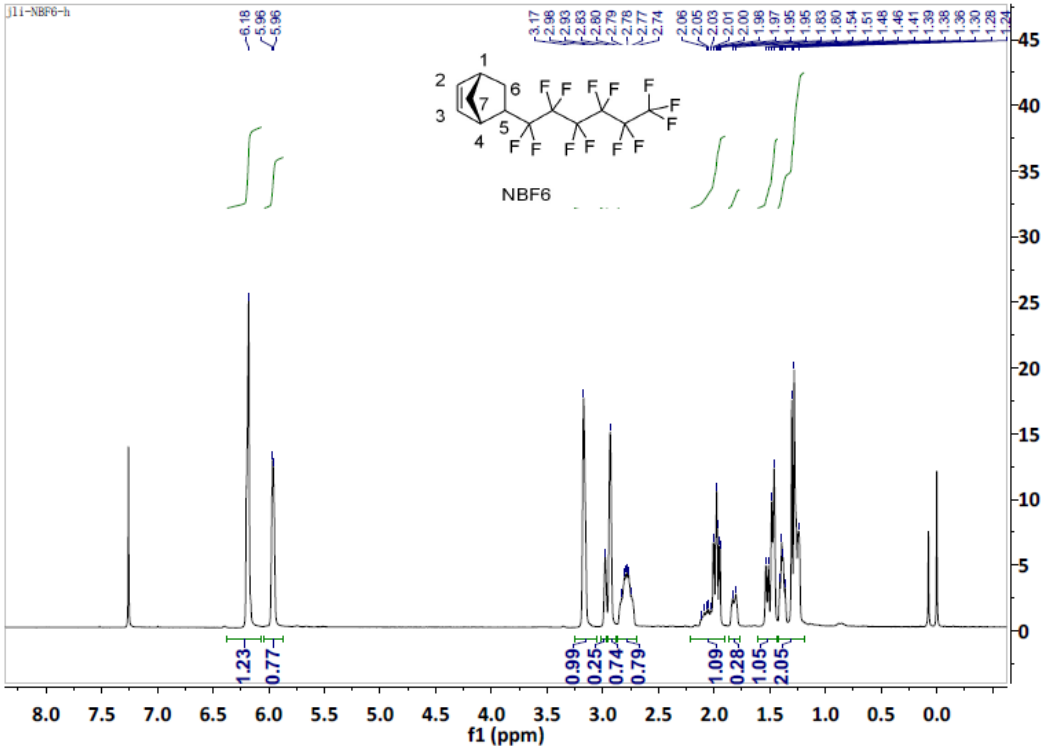


Figure S23 ^{1}H NMR of **NBF6** (400 MHz, $CDCl_3$)

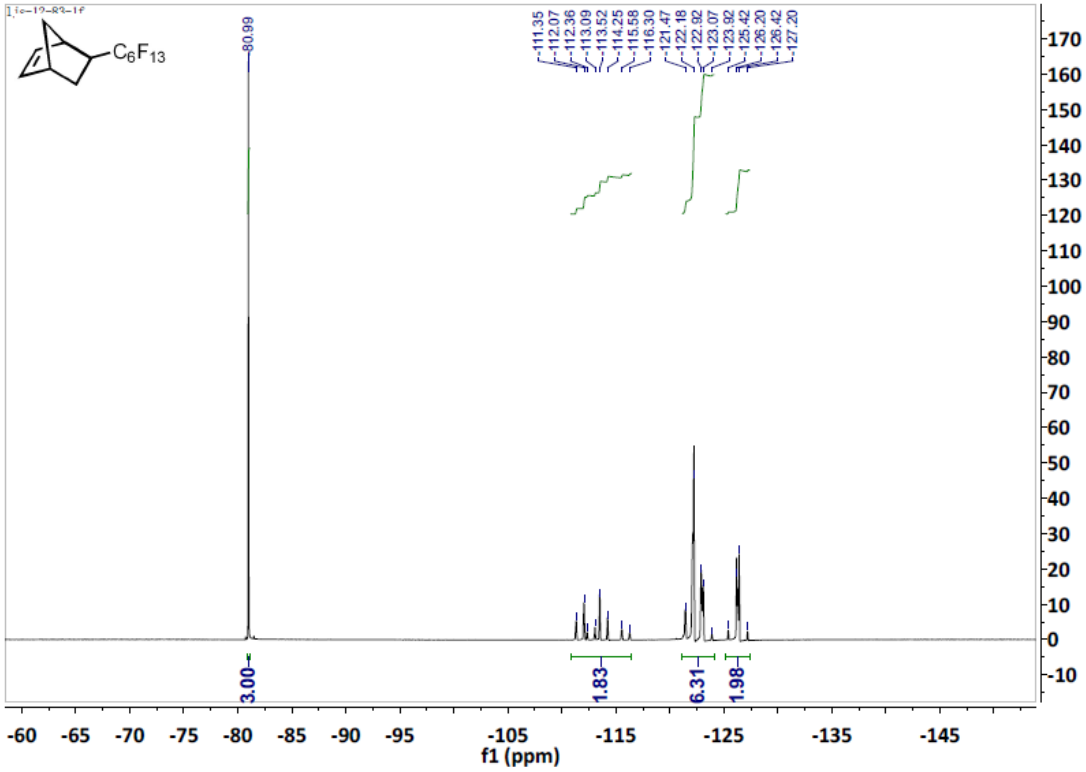


Figure S24 ^{19}F NMR of **NBF6** (376 MHz, $CDCl_3$)

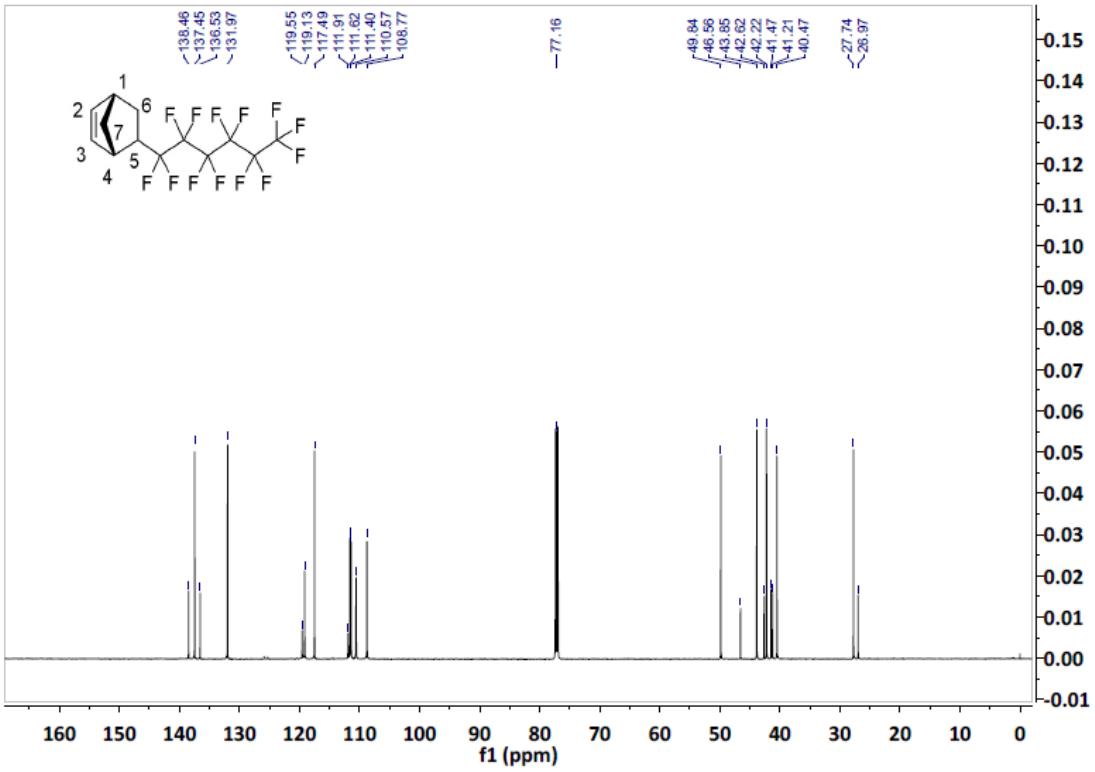


Figure S25 ^{13}C NMR for **NBF6** (exo/endo, 23/77) with H&F decoupling ($CDCl_3$ 600 MHz).

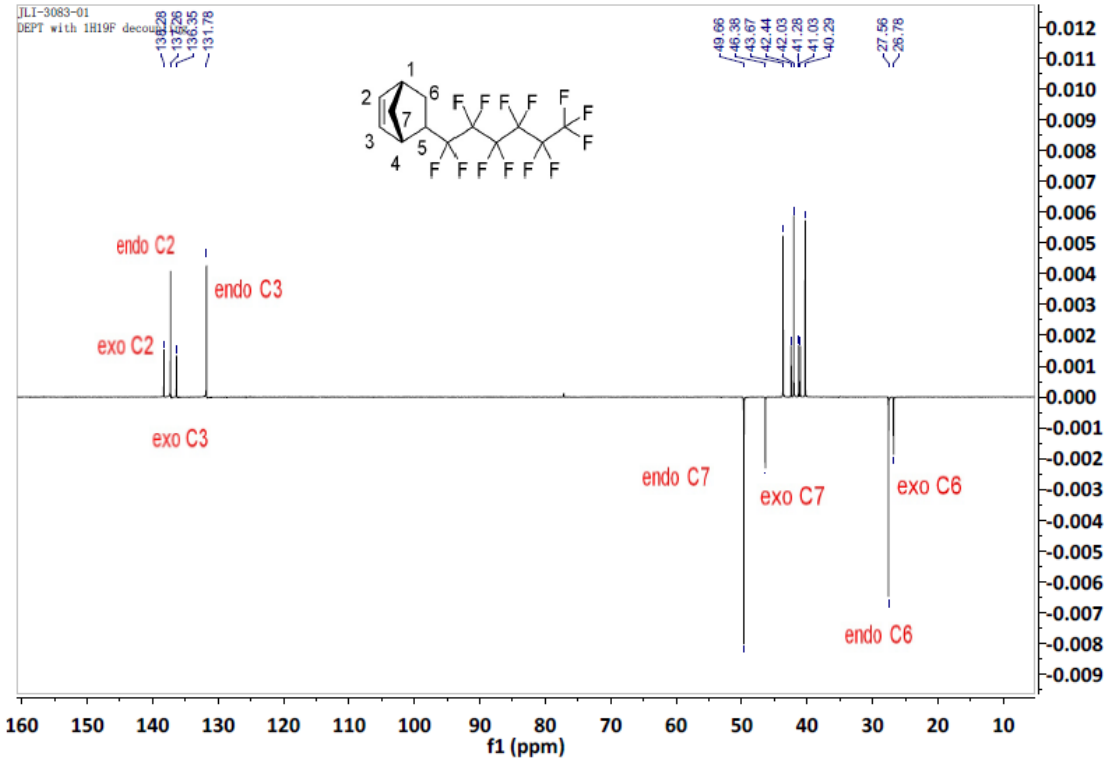


Figure S26 Dept 135 NMR for **NBF6** (exo/endo, 23/77) with H&F decoupling ($CDCl_3$ 600 MHz).

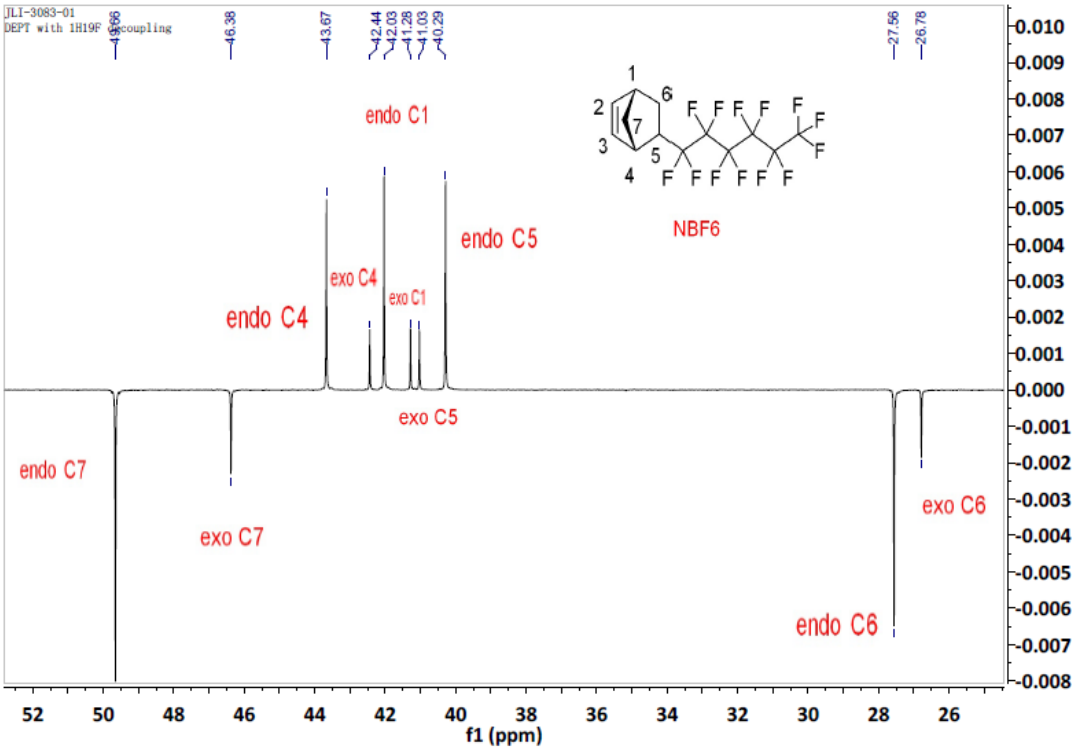


Figure S26a Dept 135 NMR for **NBF6** (exo/endo, 23/77) with H&F decoupling ($CDCl_3$ 600 MHz).

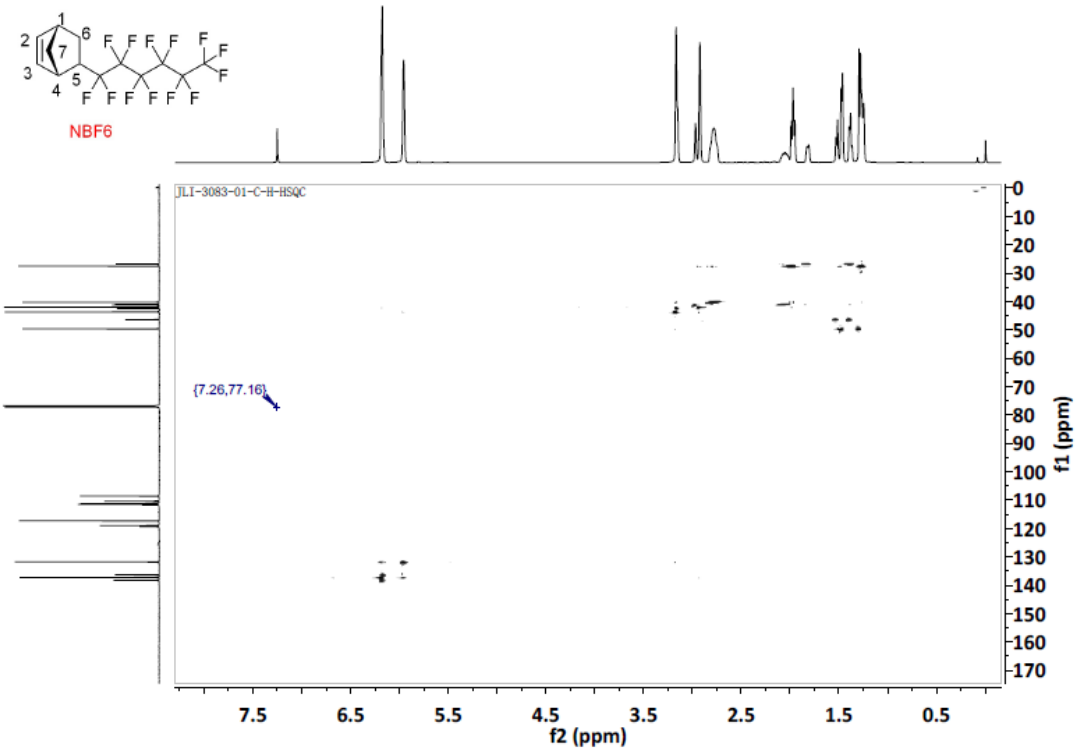


Figure S27 C-H HSQC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

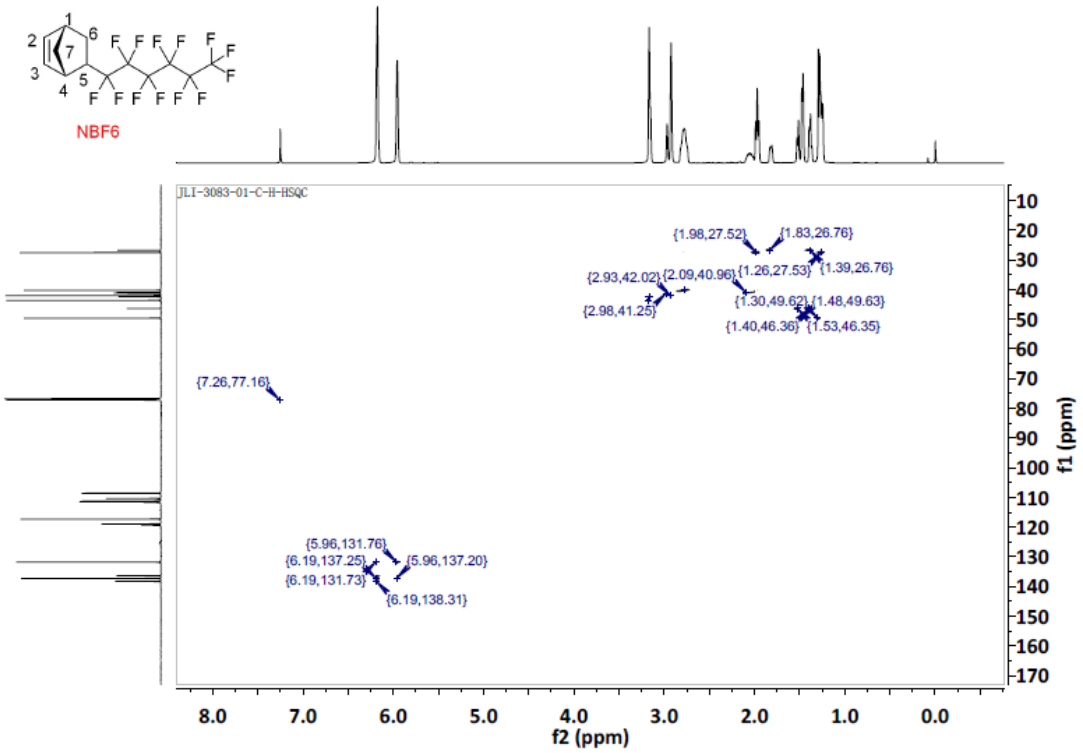


Figure S27a C-H HSQC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

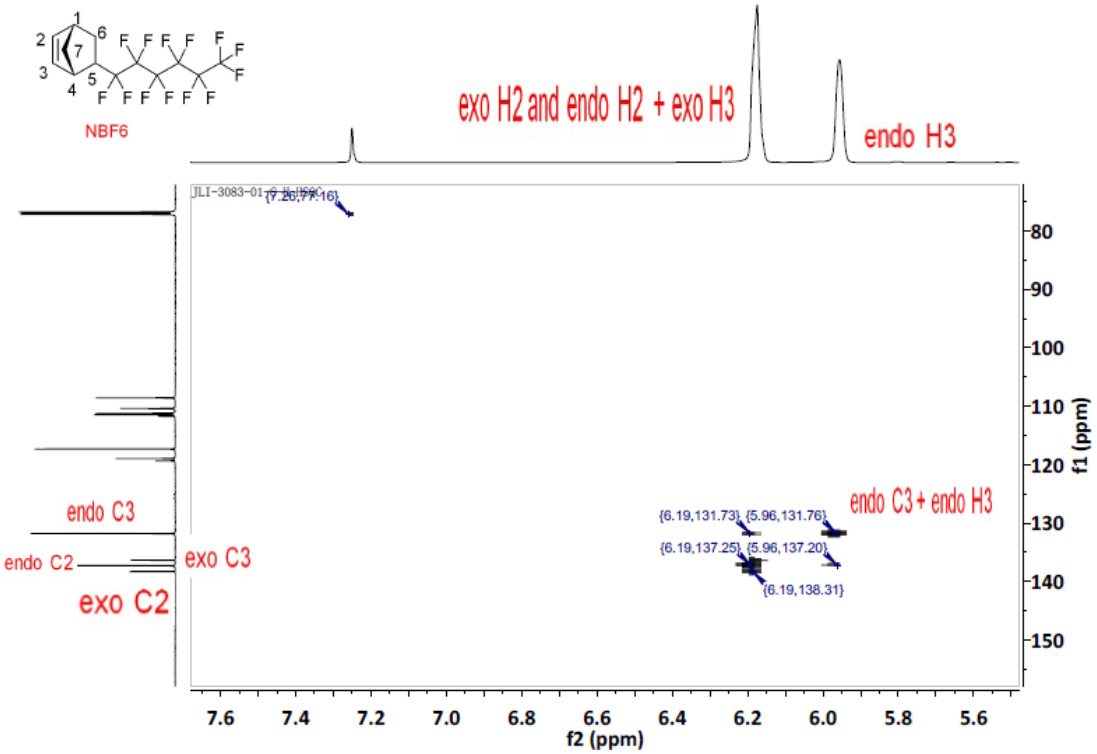
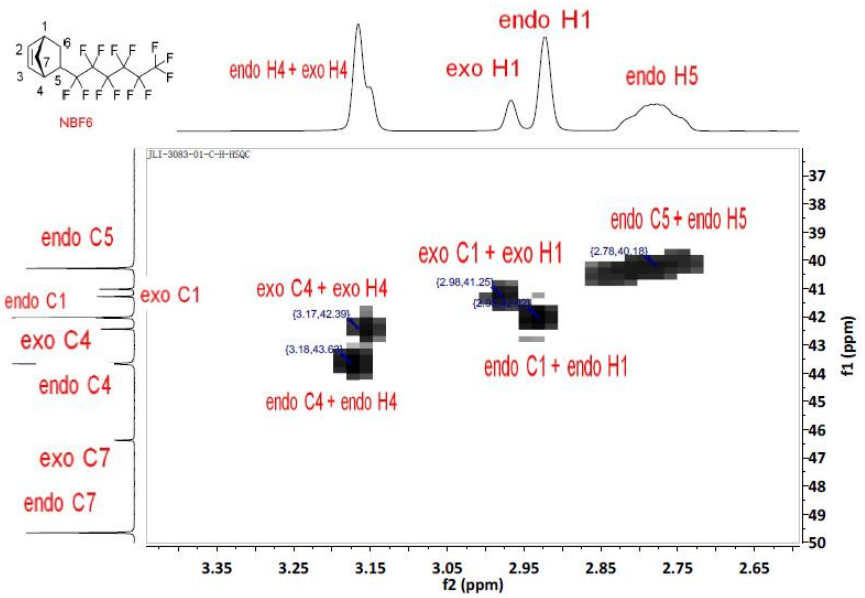
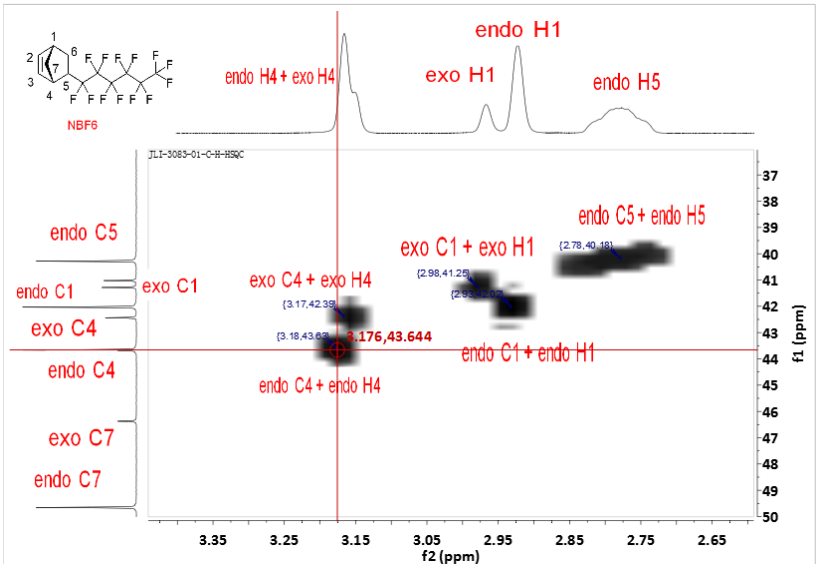
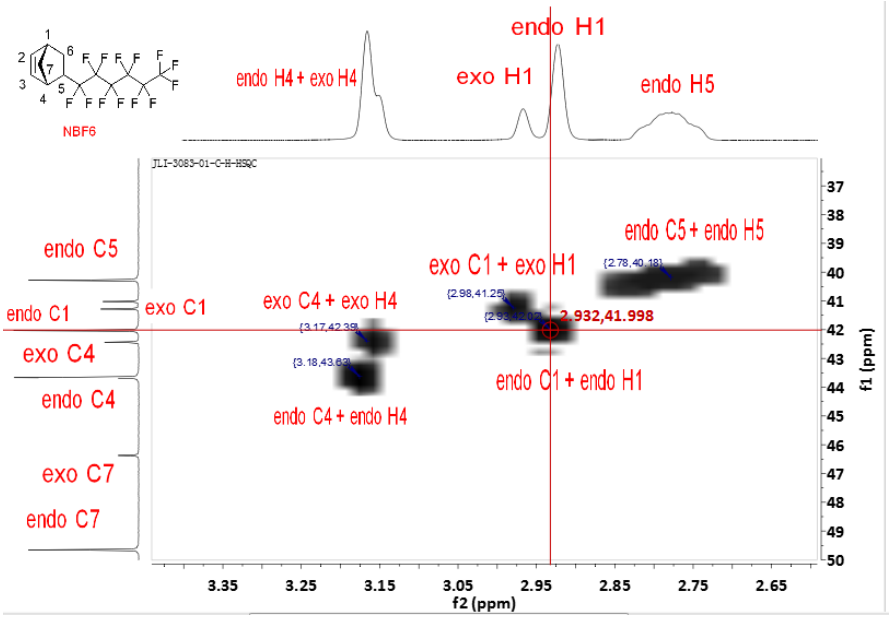


Figure S27b C-H HSQC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).


NBF6
endo H4 + exo H4
exo H1
endo H1
endo H5
JLI-3083-01-C-H-HSQC
endo C5
endo C1
exo C1
exo C4
endo C4
exo C7
endo C7
exo C4 + exo H4
{3.17,42.39}
{3.18,43.69}
endo C4 + endo H4
exo C1 + exo H1
{2.98,41.25}
endo C1 + endo H1
endo C5 + endo H5
{2.78,40.18}
f1 (ppm)
f2 (ppm)


NBF6
endo H4 + exo H4
exo H1
endo H1
endo H5
JLI-3083-01-C-H-HSQC
endo C5
endo C1
exo C1
exo C4
endo C4
exo C7
endo C7
exo C4 + exo H4
{3.17,42.39}
3.176,43.644
endo C4 + endo H4
exo C1 + exo H1
{2.98,41.25}
endo C1 + endo H1
endo C5 + endo H5
{2.78,40.18}
f1 (ppm)
f2 (ppm)


NBF6
endo H4 + exo H4
exo H1
endo H1
endo H5
JLI-3083-01-C-H-HSQC
endo C5
endo C1
exo C1
exo C4
endo C4
exo C7
endo C7
exo C4 + exo H4
{3.17,42.39}
endo C4 + endo H4
exo C1 + exo H1
{2.98,41.25}
2.932,41.998
endo C1 + endo H1
endo C5 + endo H5
{2.78,40.18}
f1 (ppm)
f2 (ppm)

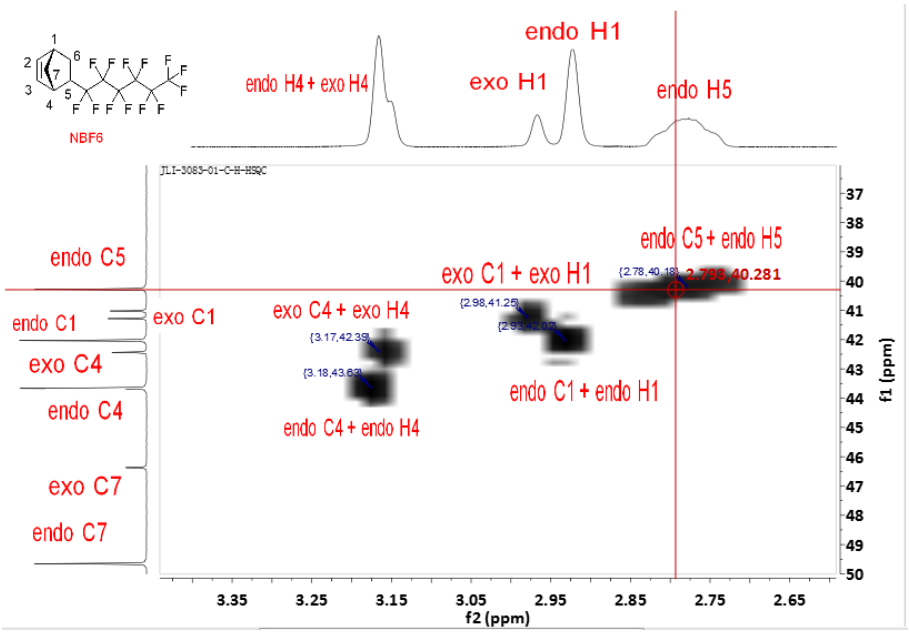


Figure S27c C-H HSQC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

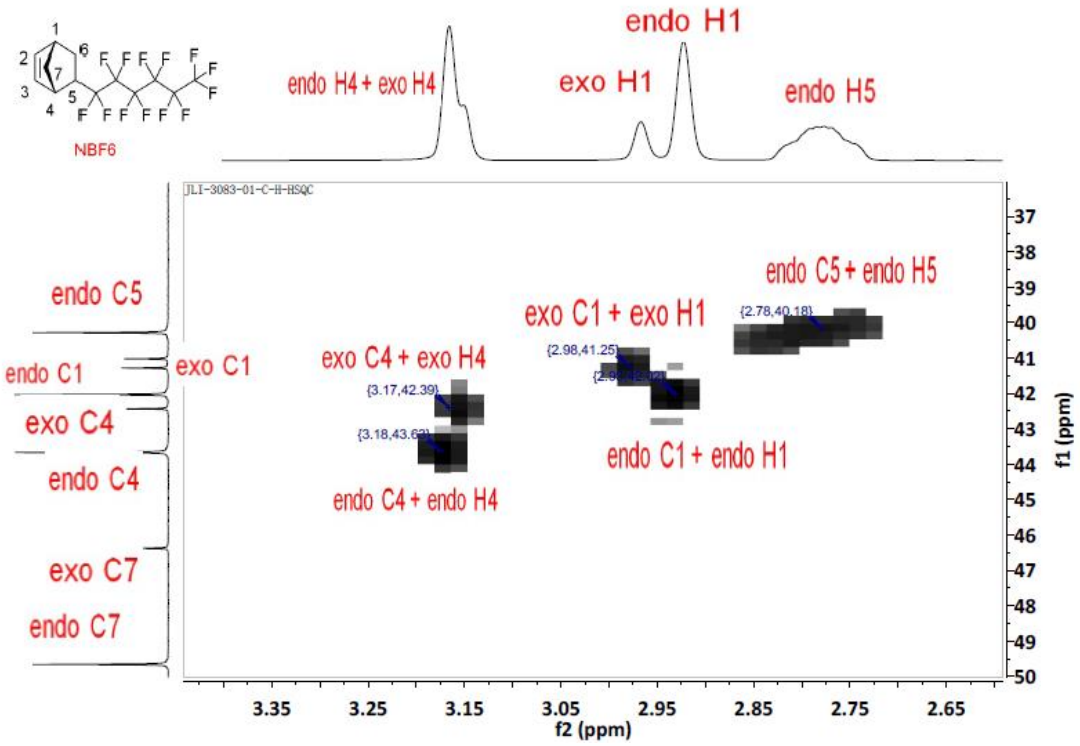


Figure S27d C-H HSQC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

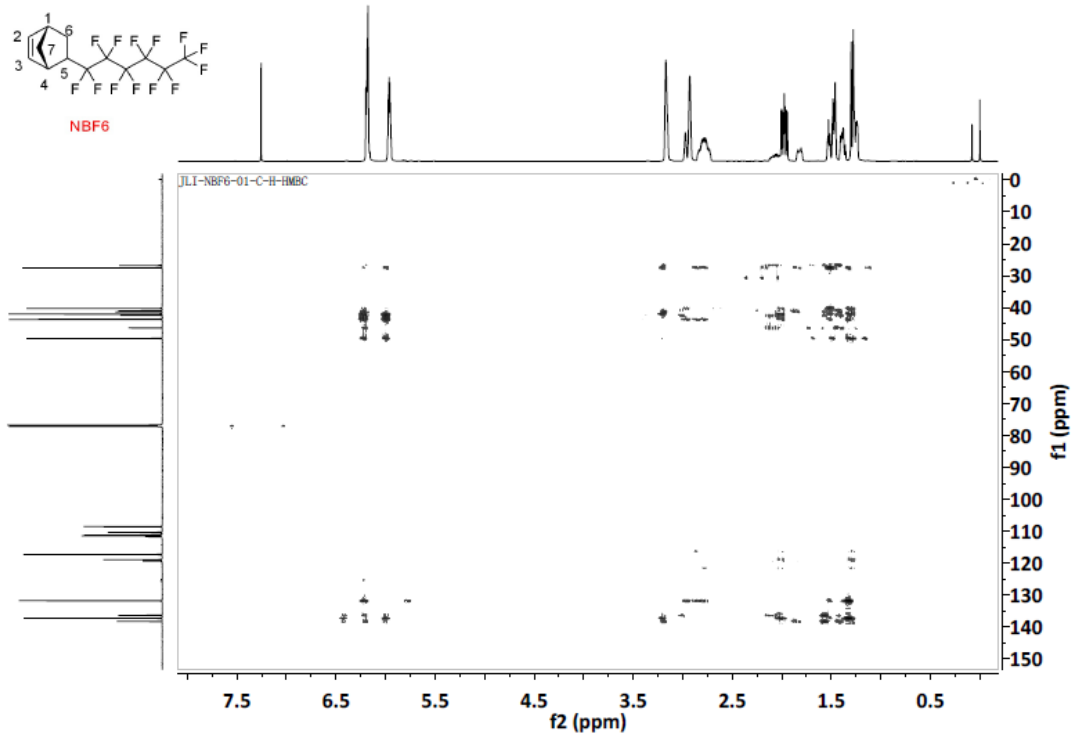


Figure S28 C-H HMBC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

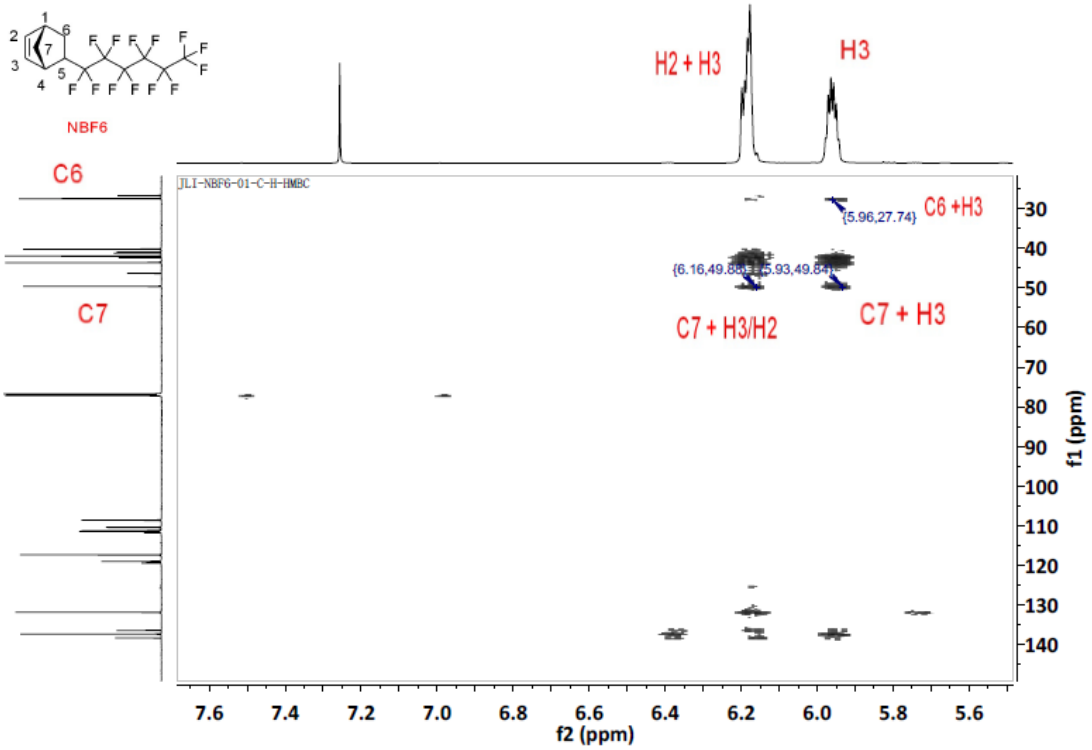


Figure S28a C-H HMBC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

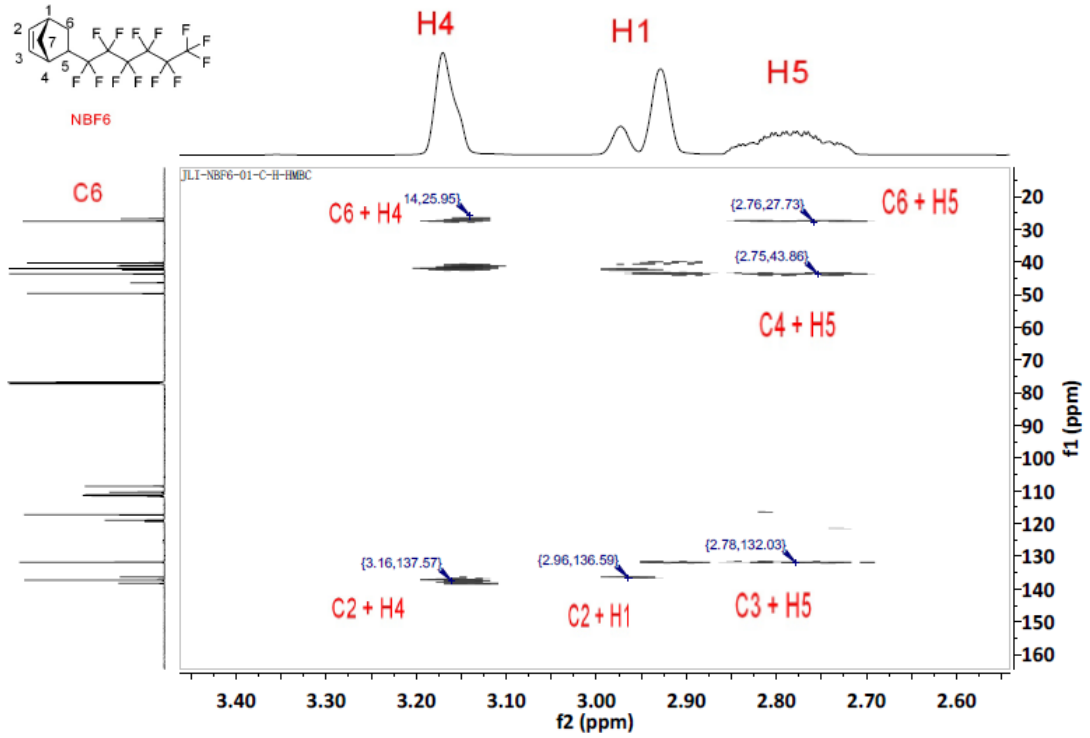


Figure S28b C-H HMBC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

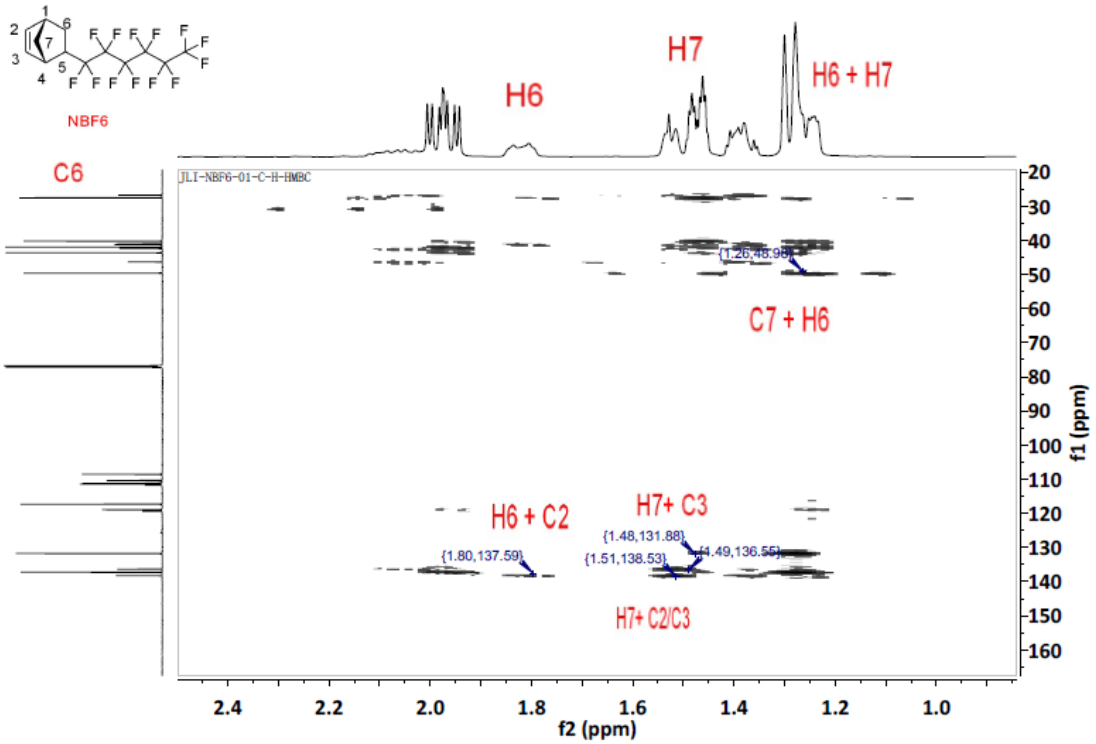


Figure S28c C-H HMBC for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

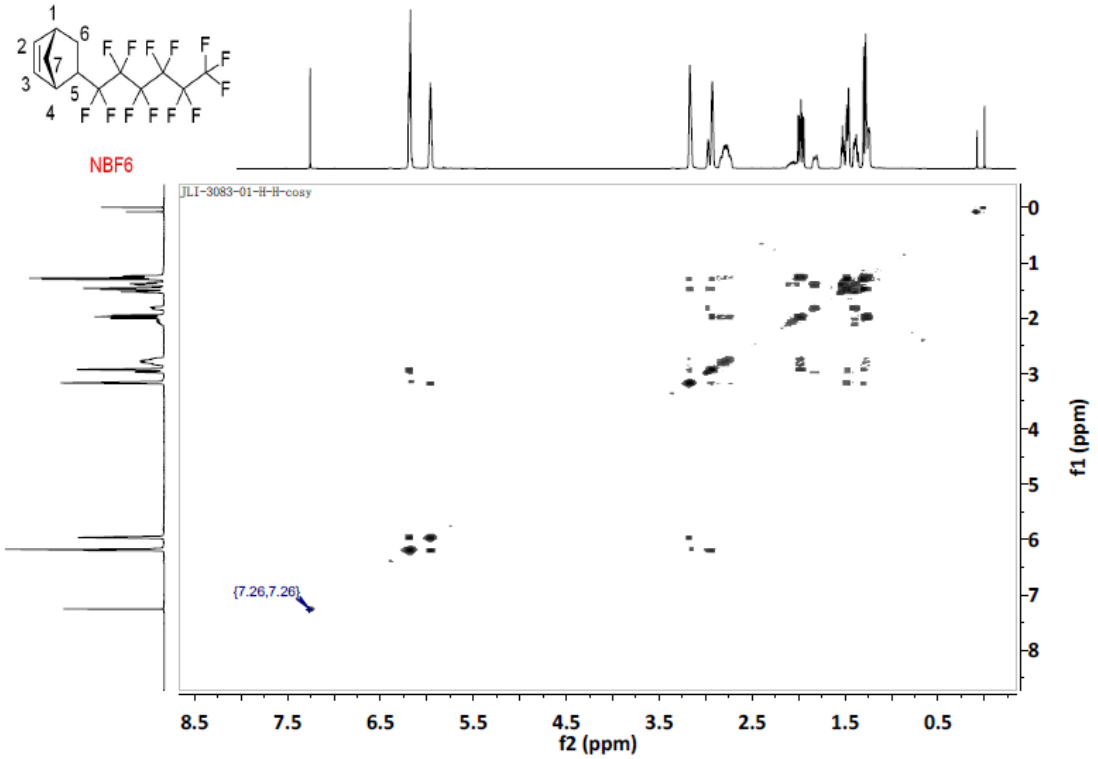


Figure S29 H-H Cosy NMR for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

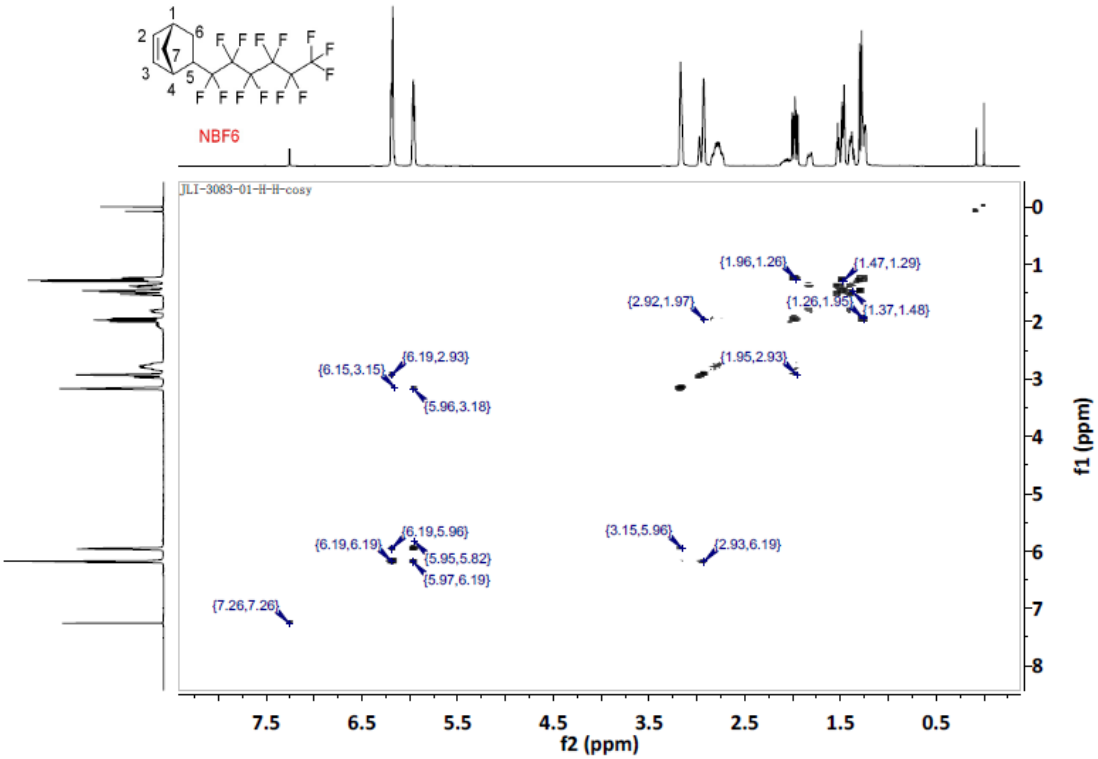


Figure S29a H-H Cosy NMR for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

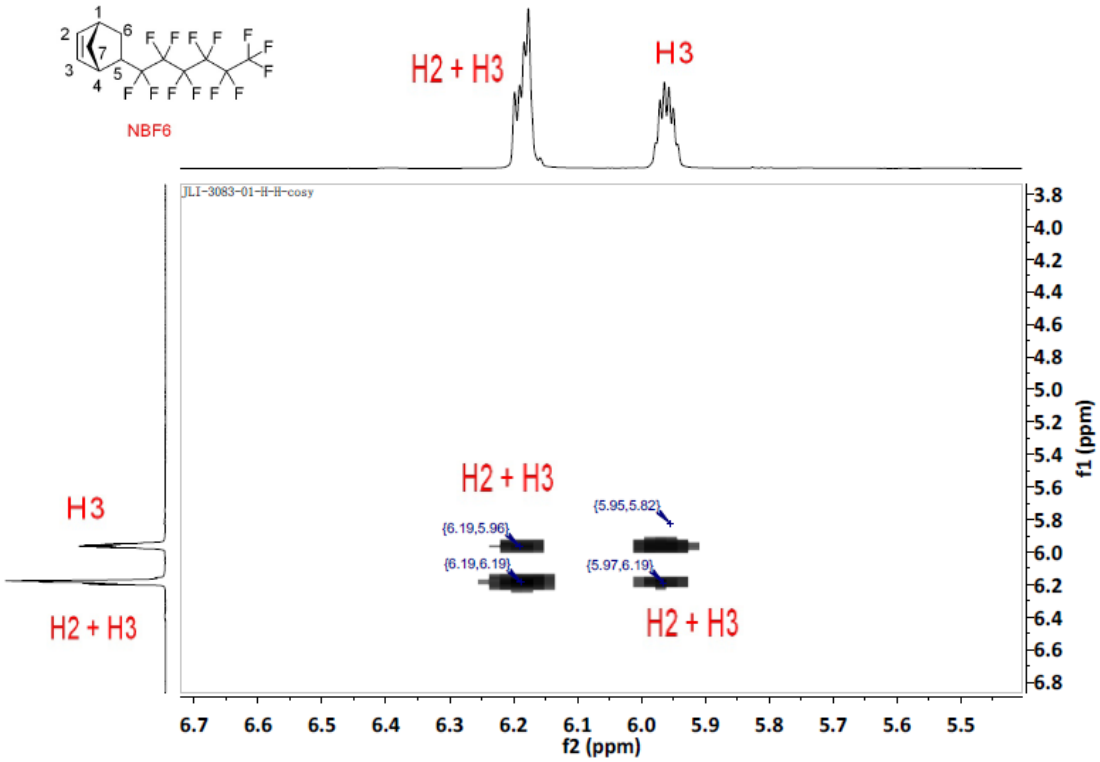


Figure S29b H-H Cosy NMR for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

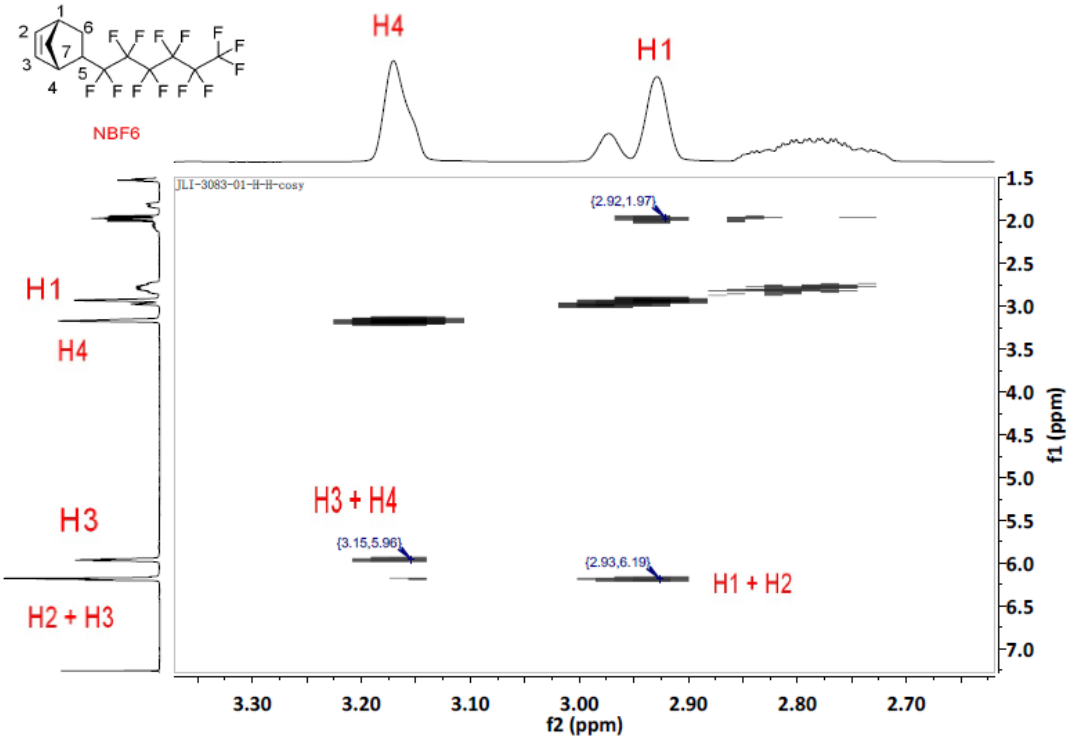


Figure S29c H-H Cosy NMR for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

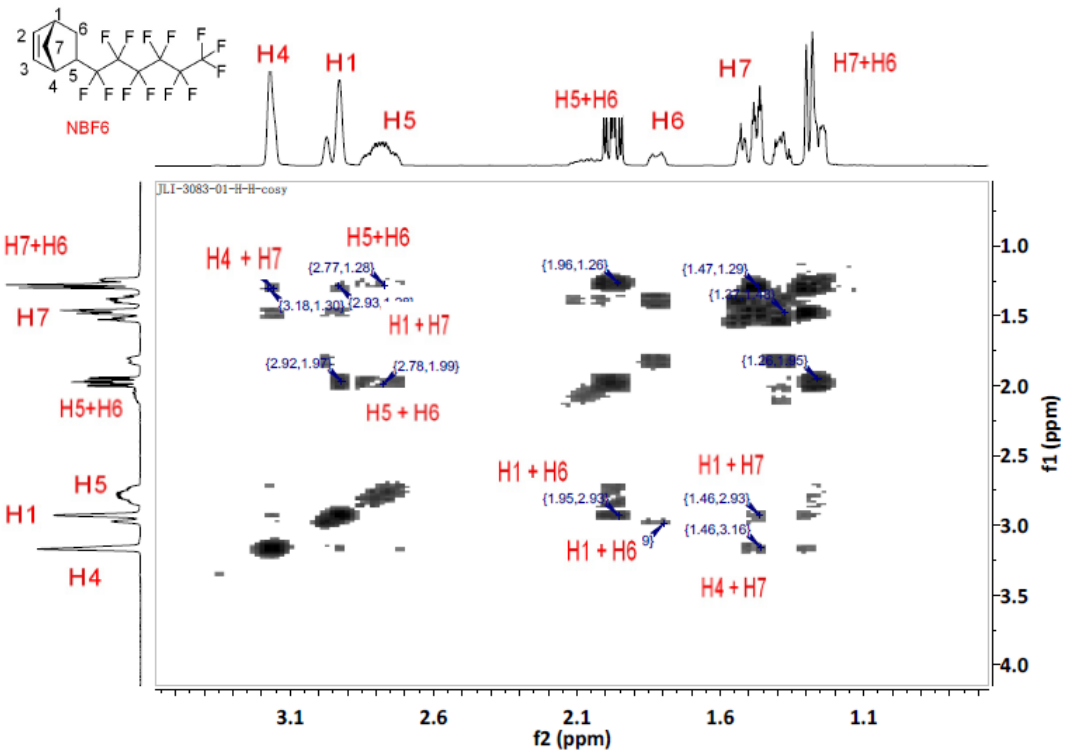


Figure S29d H-H Cosy NMR for **NBF6** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

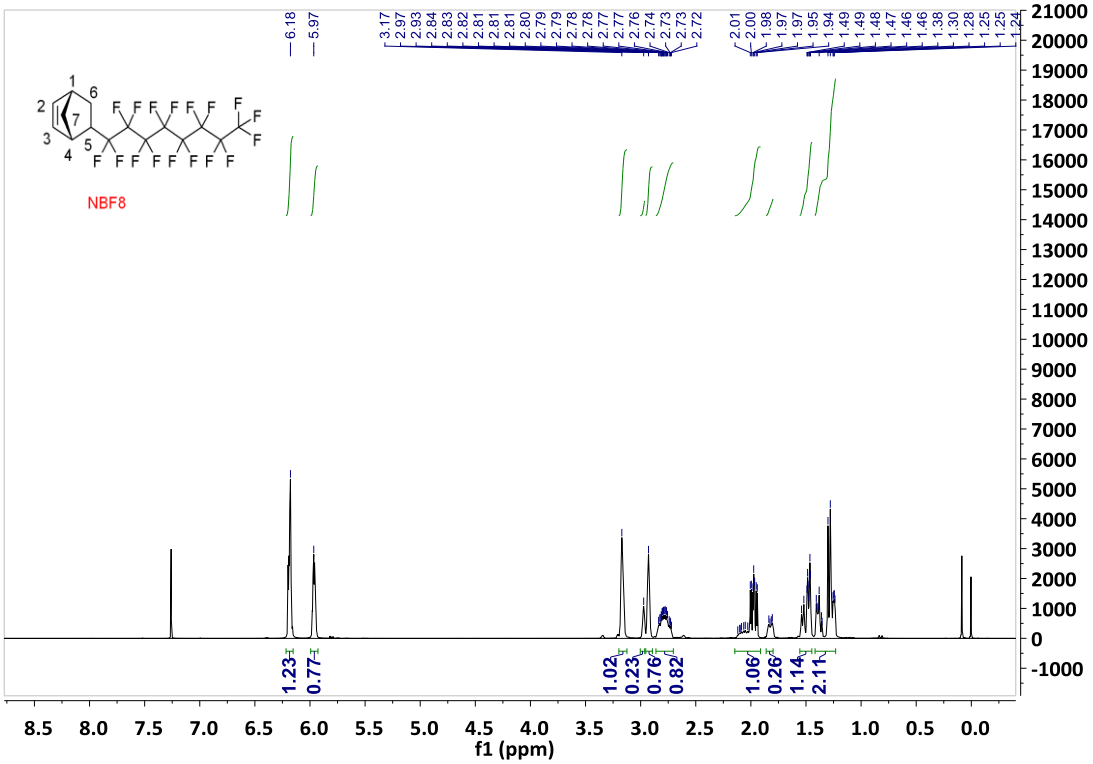


Figure S30 ^{1}H NMR of **NBF8** (400 MHz, $CDCl_3$)

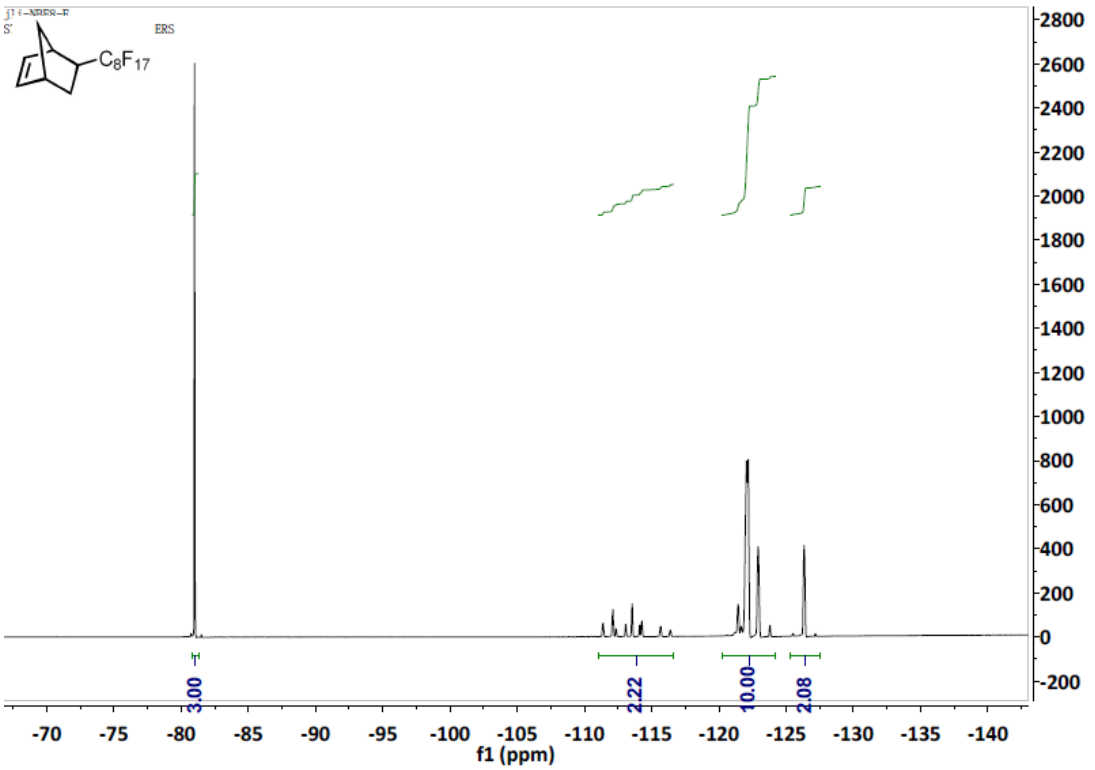


Figure S31 ^{19}F NMR of **NBF8** (376 MHz, $CDCl_3$)

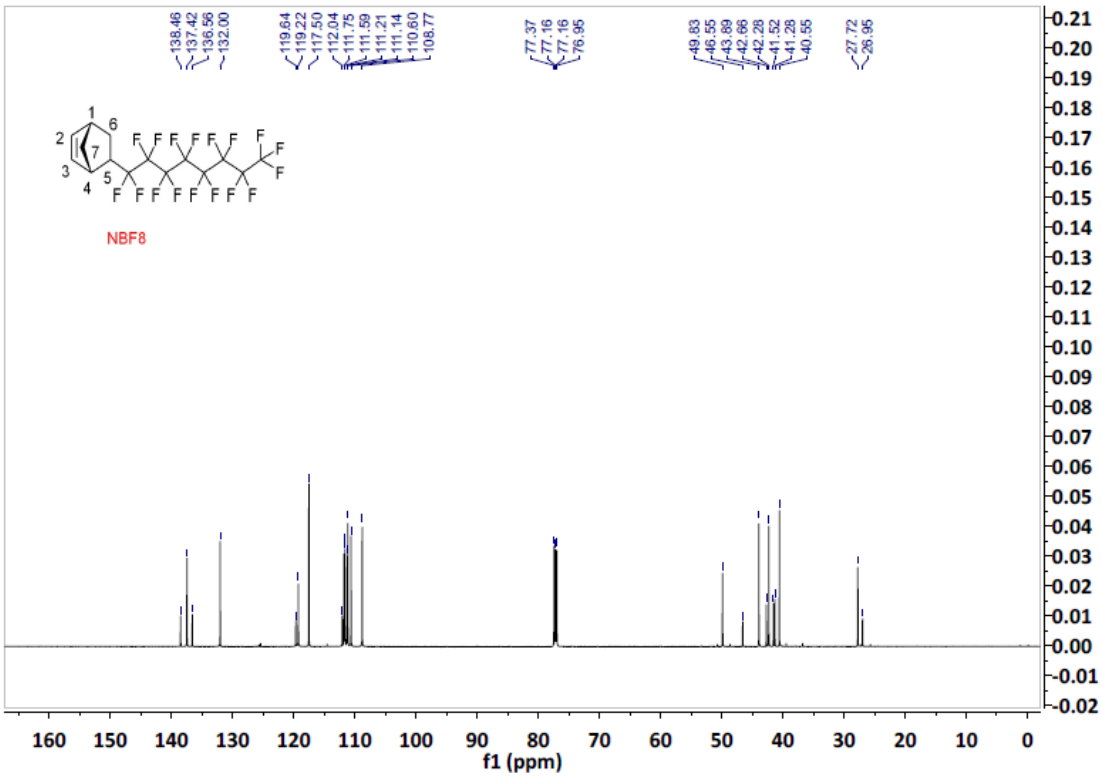


Figure S32 ^{13}C NMR for **NBF8** (exo/endo, 23/77) with H&F decoupling ($CDCl_3$ 600 MHz).

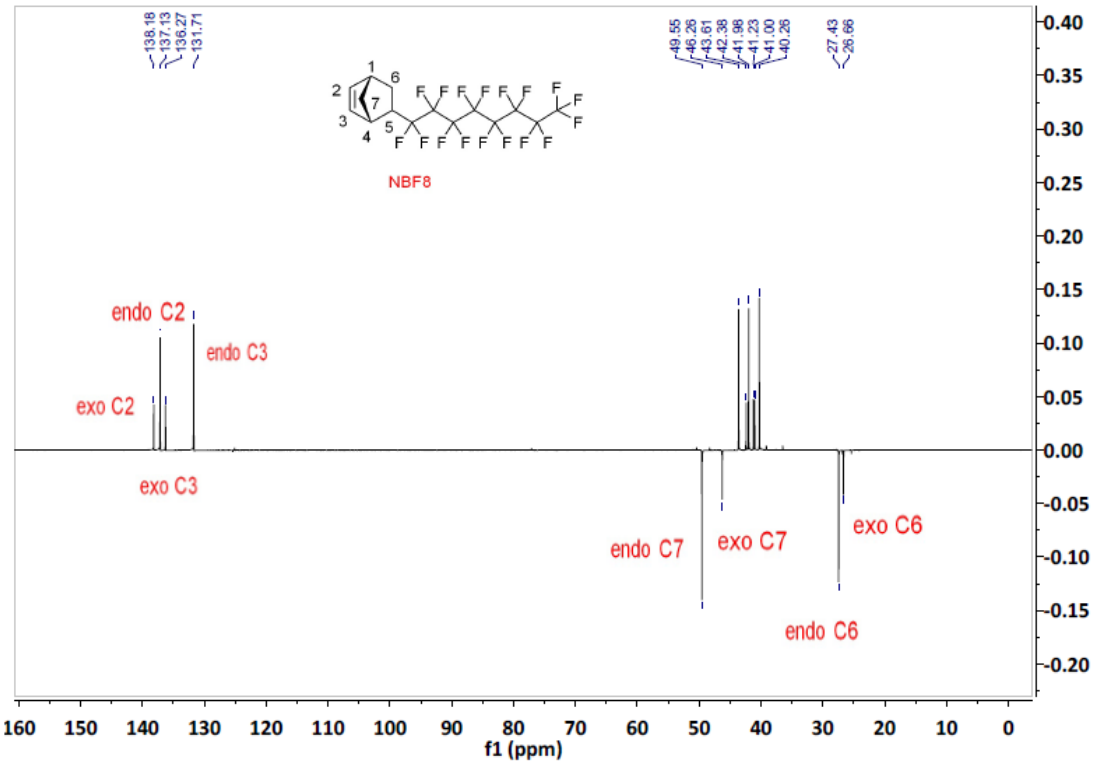


Figure S33 Dept 135 NMR for **NBF8** (exo/endo, 23/77) with H&F decoupling ($CDCl_3$ 600 MHz).

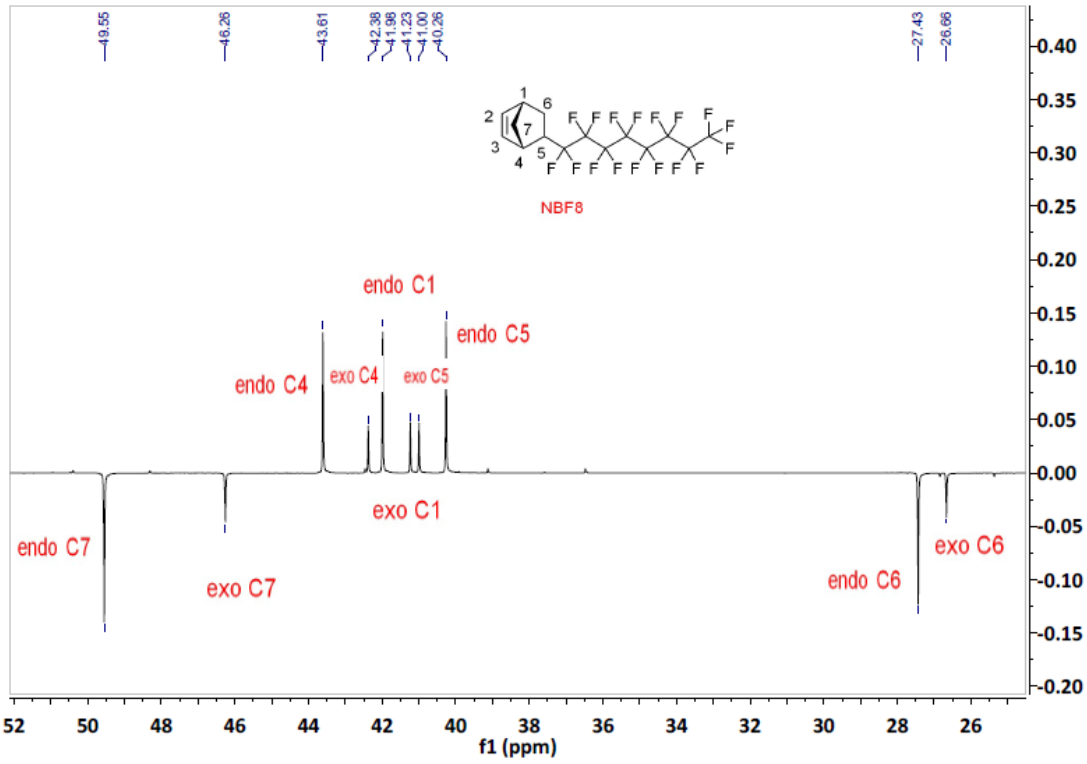


Figure S33a Dept 135 NMR for **NBF8** (exo/endo, 23/77) with H&F decoupling ($CDCl_3$ 600 MHz).

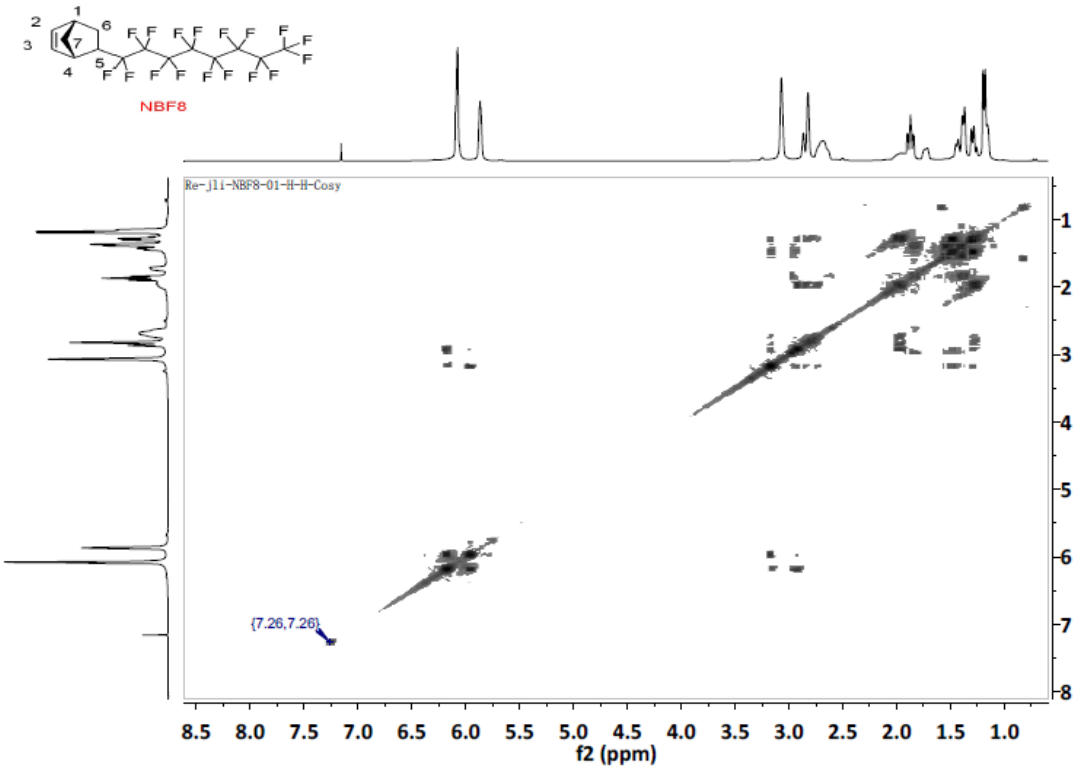


Figure S34 H-H Cosy NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

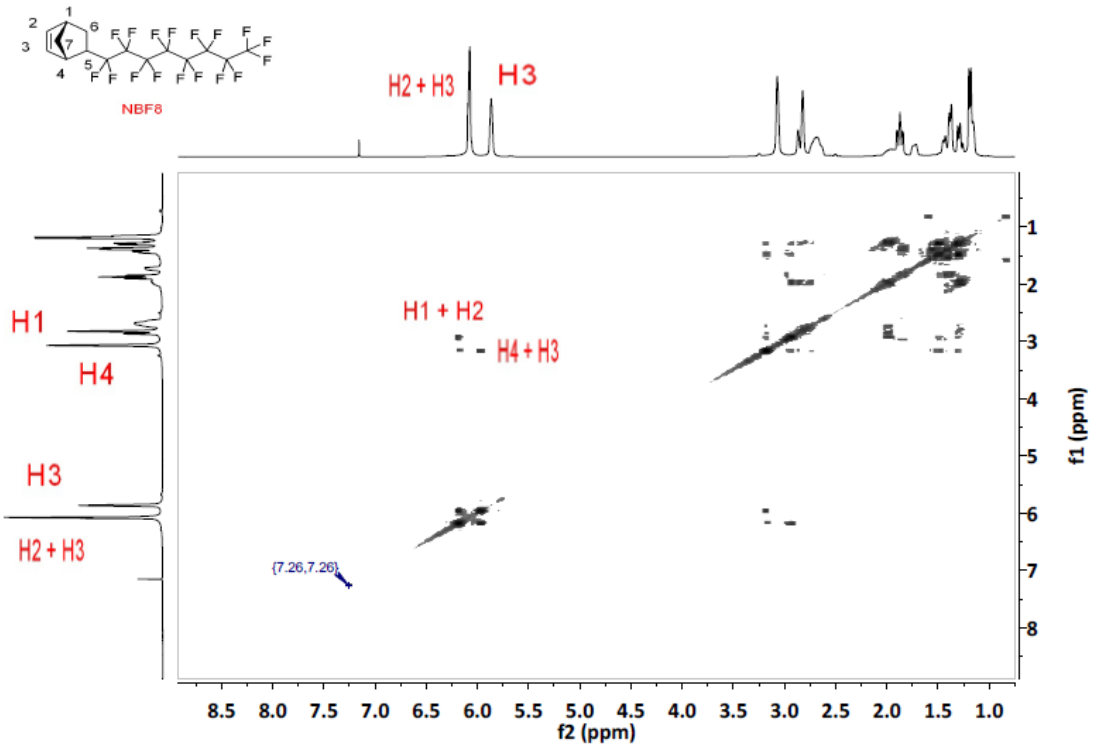


Figure S34a H-H Cosy NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

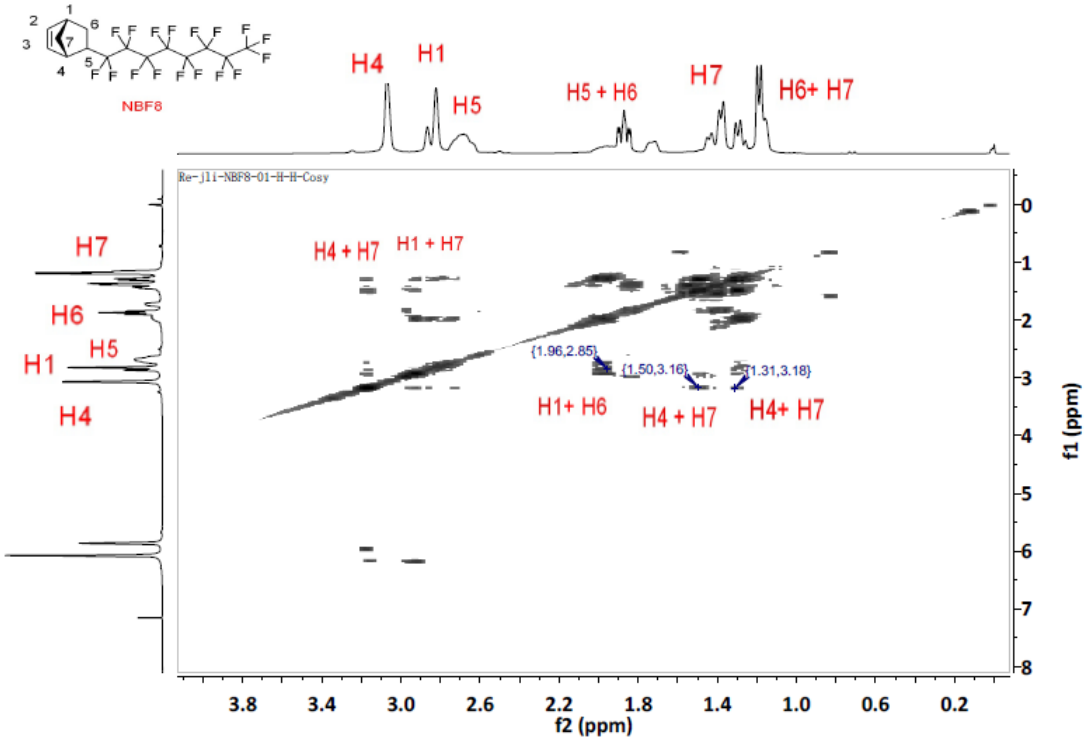


Figure S34b H-H Cosy NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

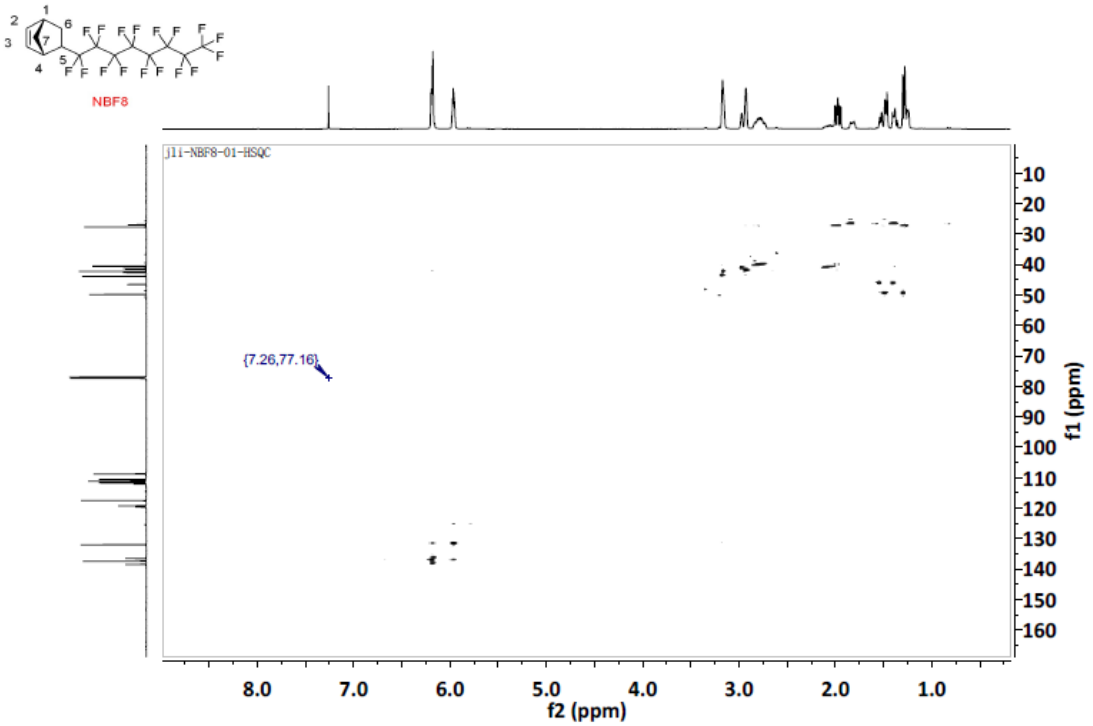


Figure S34c C-H HSQC NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

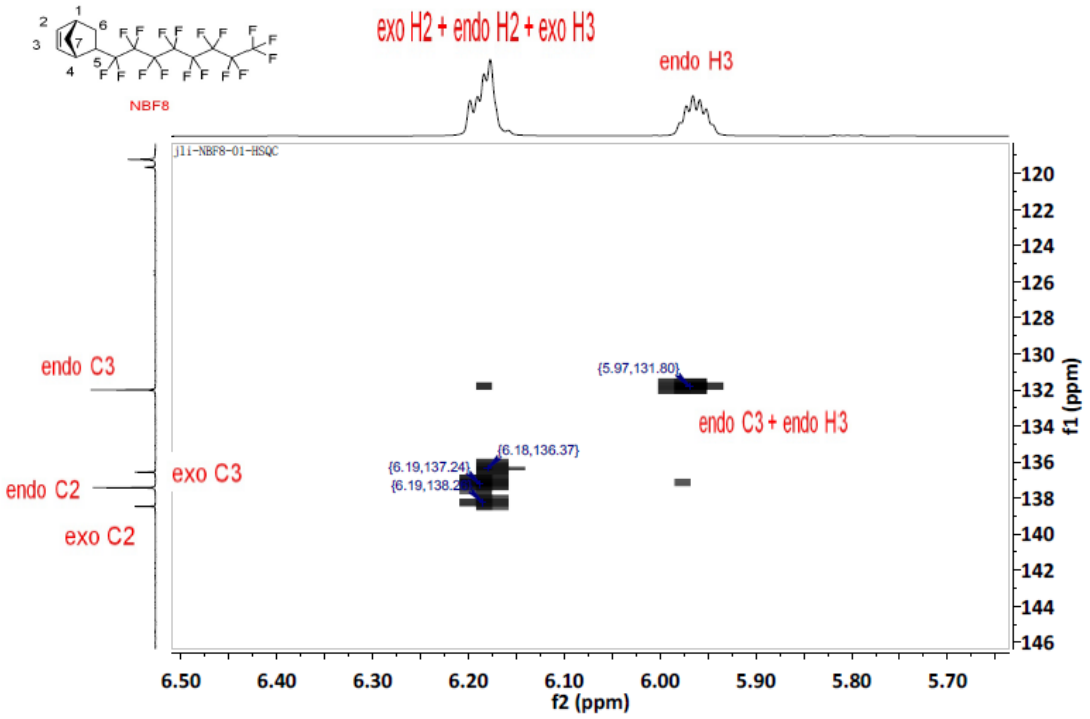


Figure S34d C-H HSQC NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

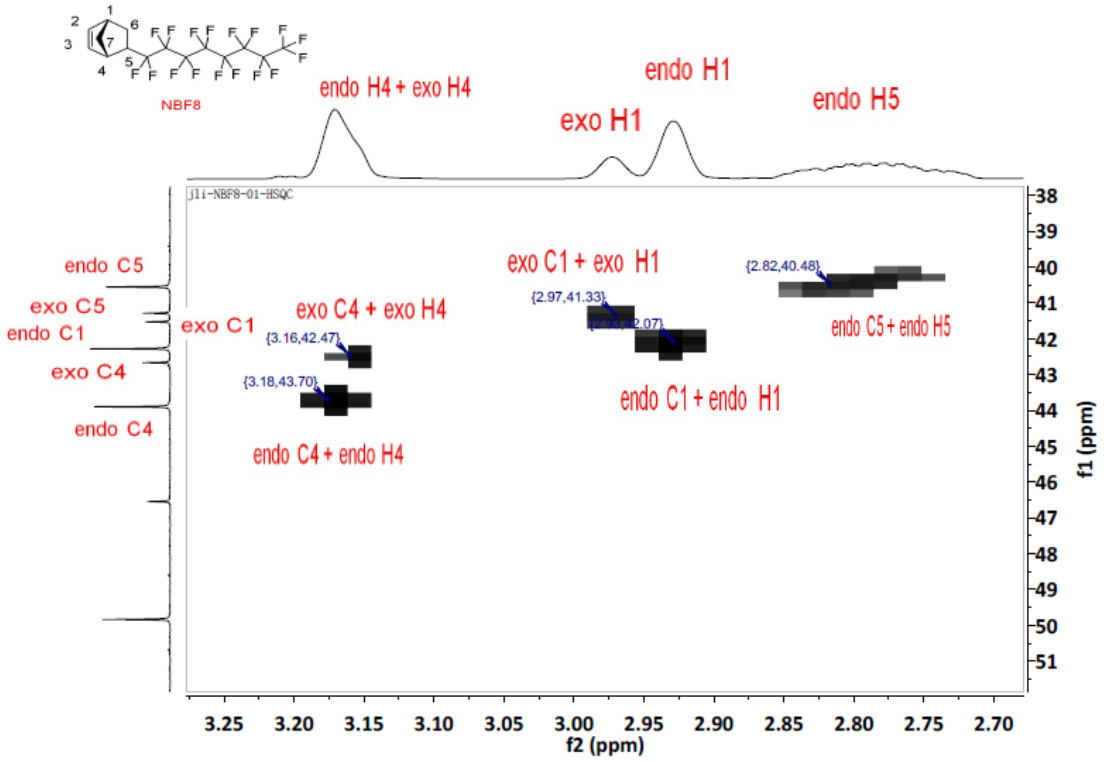


Figure S34e C-H HSQC NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

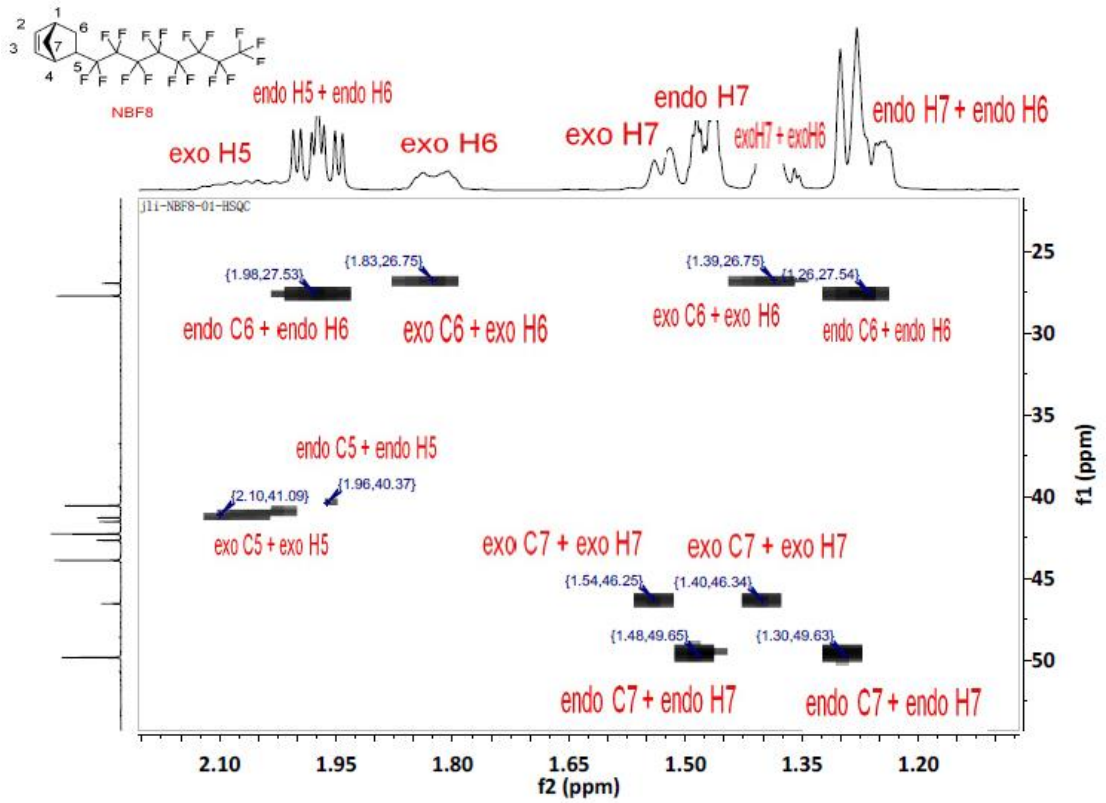


Figure S34f C-H HSQC NMR for **NBF8** (exo/endo, 23/77) ($CDCl_3$ 400 MHz).

6. Characterization of some representative copolymers

MW Averages

Mp: 35245	Mn: 17582	Mv: 51965	Mw: 60799
Mz: 171702	Mz+1: 338324	PD: 3.4580	

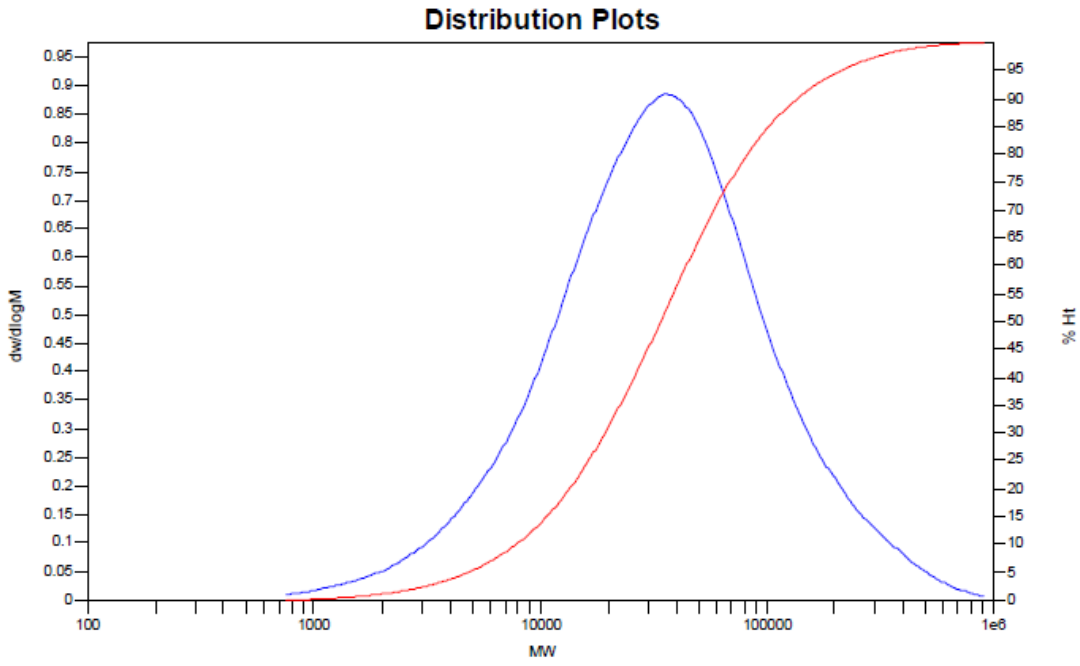


Figure S35. GPC analysis for the **poly(ethylene-*co*-NBE)** sample (entry 9, Table 2)

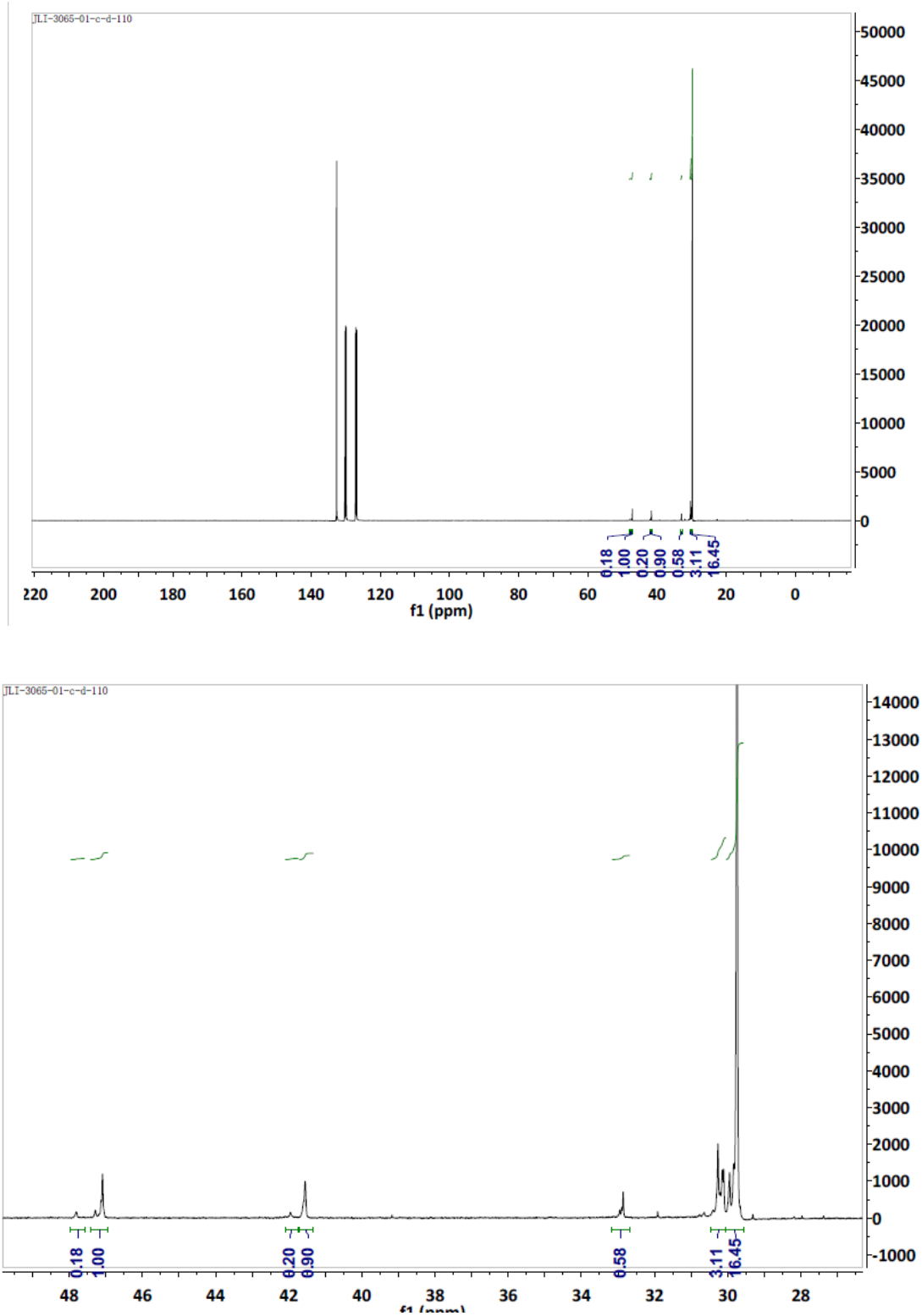


Figure S36. ^{13}C NMR spectrum for the **poly(ethylene-*co*-NBE)** sample (entry 9, Table 2, 1, 2–dichlorobenzene-d_4, 600 MHz, 110 ^{o}C)

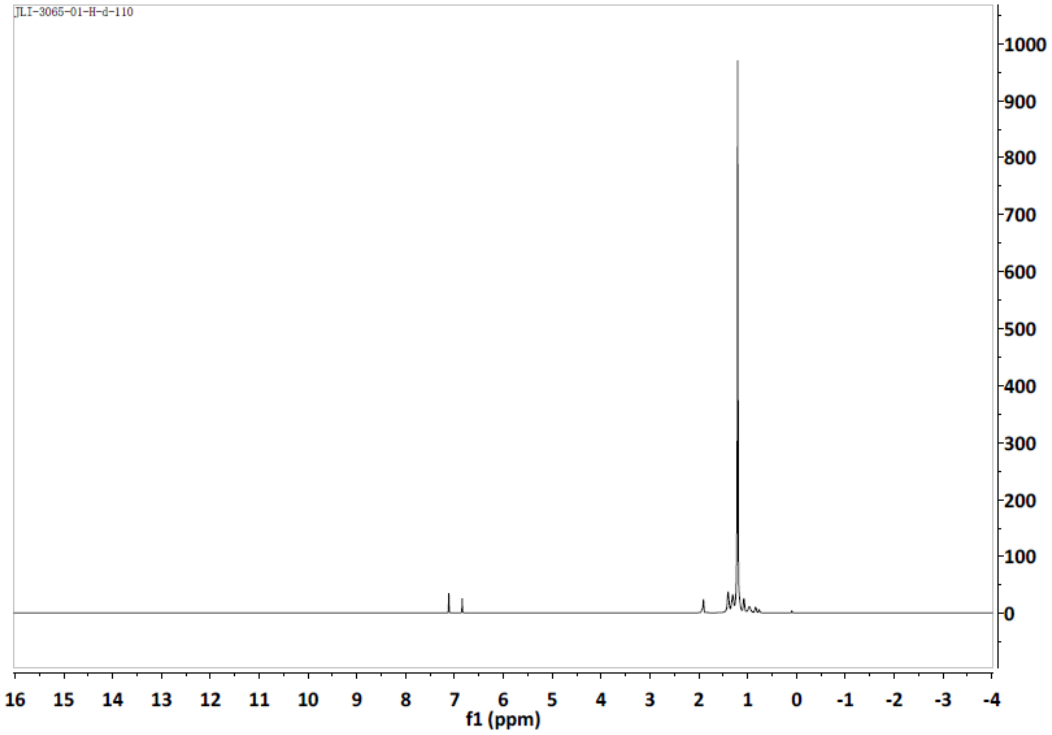


Figure S37. ^{1}H NMR spectrum for the **poly(ethylene-*co*-NBE)** sample (entry 9, Table 2, 1, 2–dichlorobenzene-d_4, 600 MHz, 110 ^{o}C)

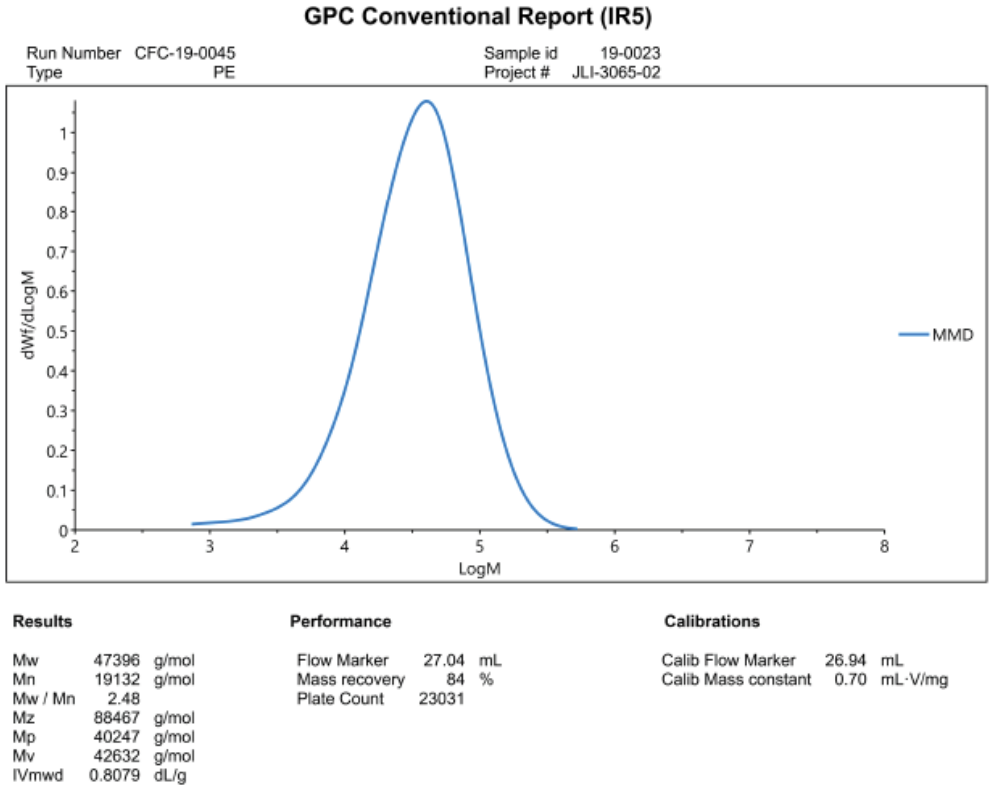
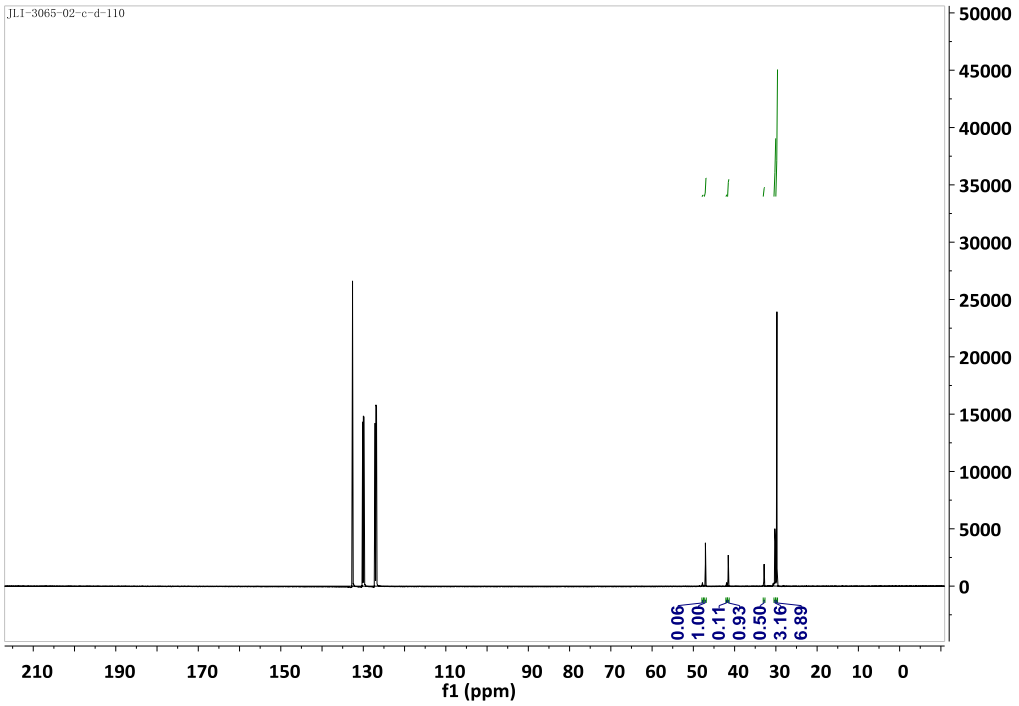


Figure S38. GPC analysis for the **poly(ethylene-*co*-NBE)** sample (entry 10, Table 2)



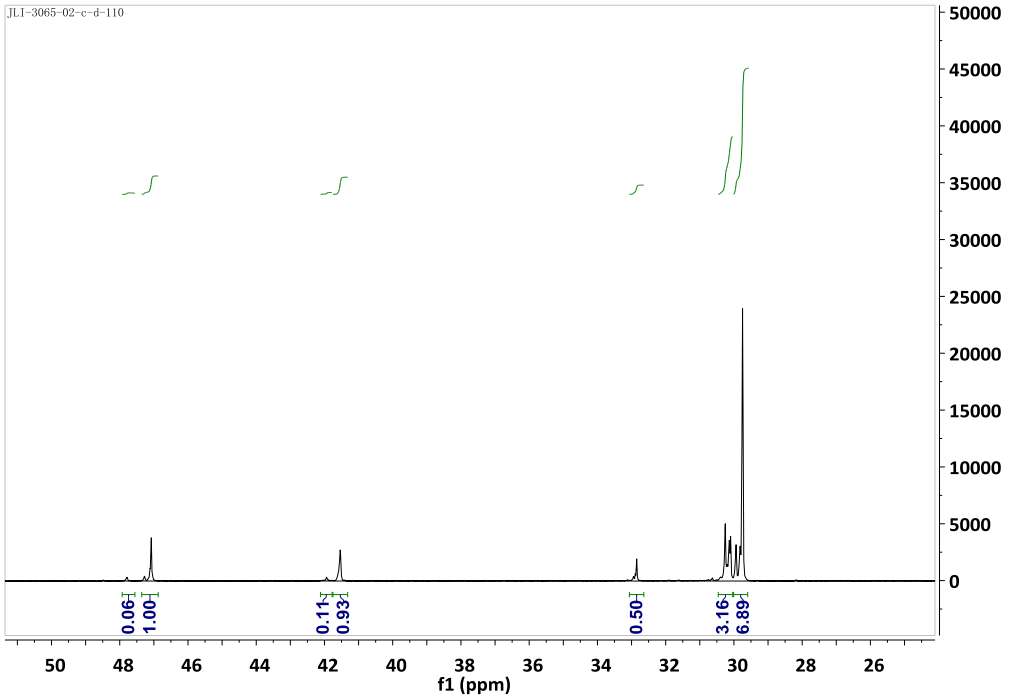


Figure S39. ^{13}C NMR spectrum for the **poly(ethylene-*co*-NBE)** sample (entry 10, Table 2)

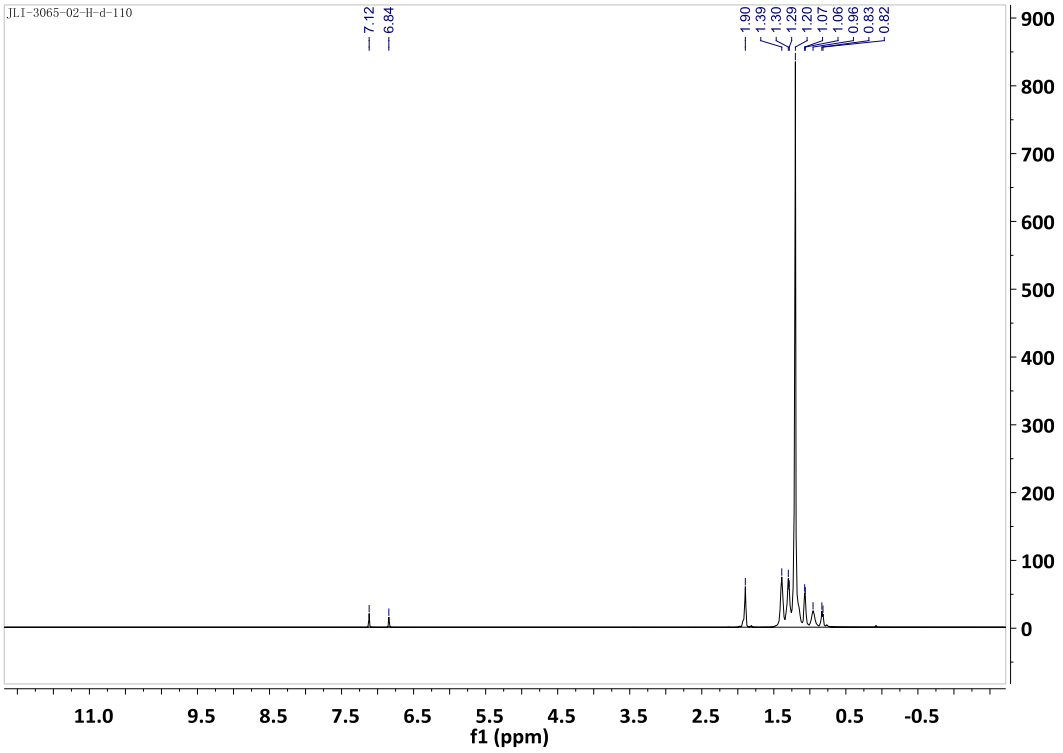


Figure S40. ^{1}H NMR spectrum for the **poly(ethylene-*co*-NBE)** sample (entry 10, Table 2)

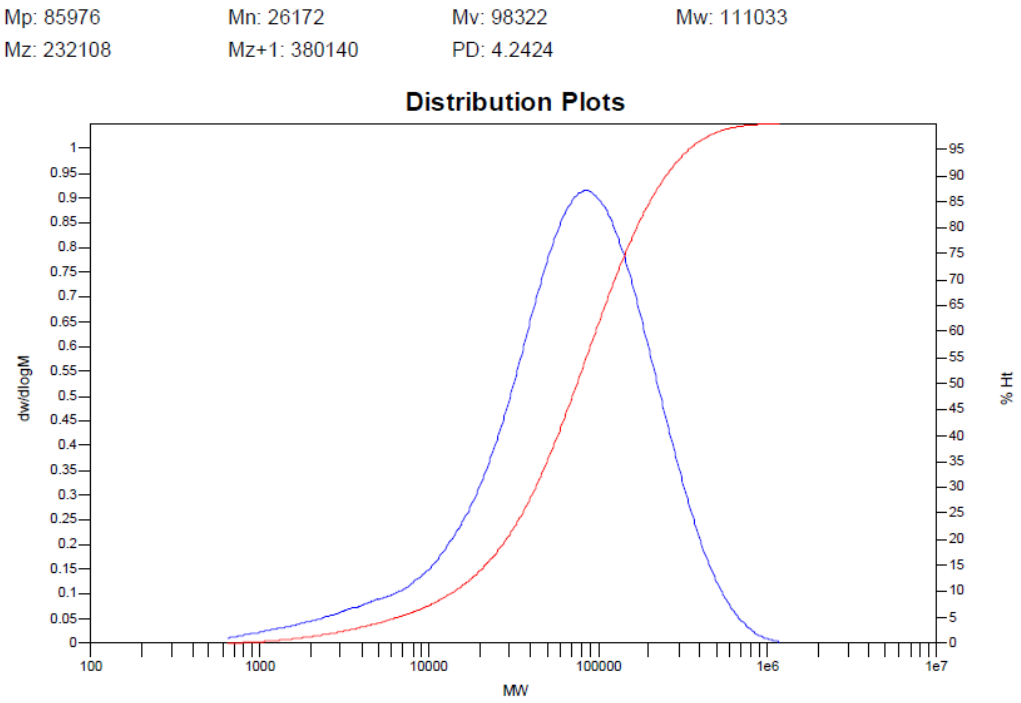


Figure S41. GPC analysis for the **poly(ethylene-*co*-NBF4)** sample (entry 1, Table 3)

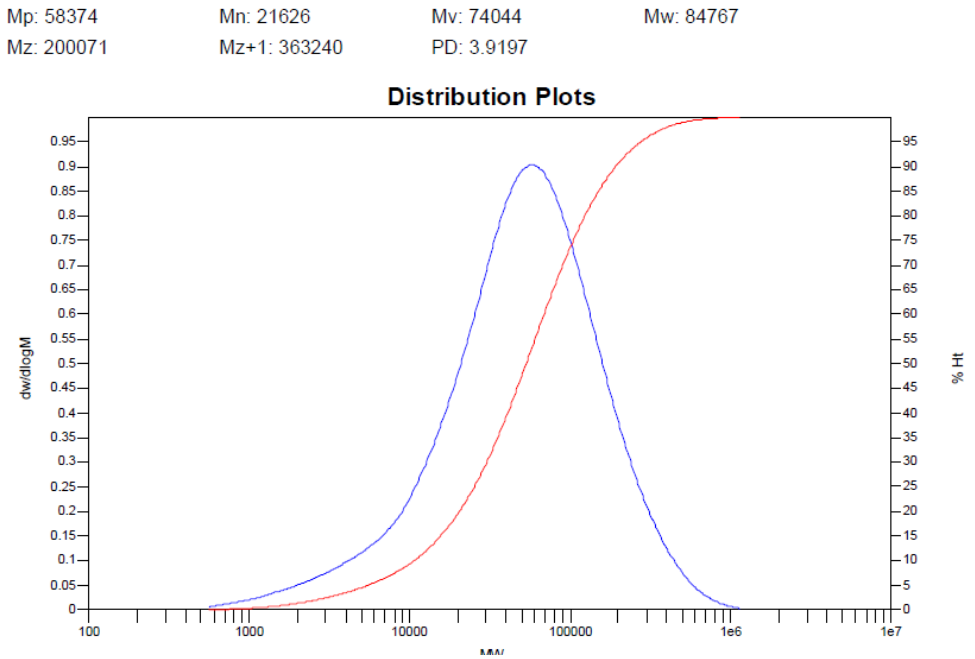


Figure S42. GPC analysis of the **poly(ethylene-*co*-NBF4)** sample (entry 2, Table 3)

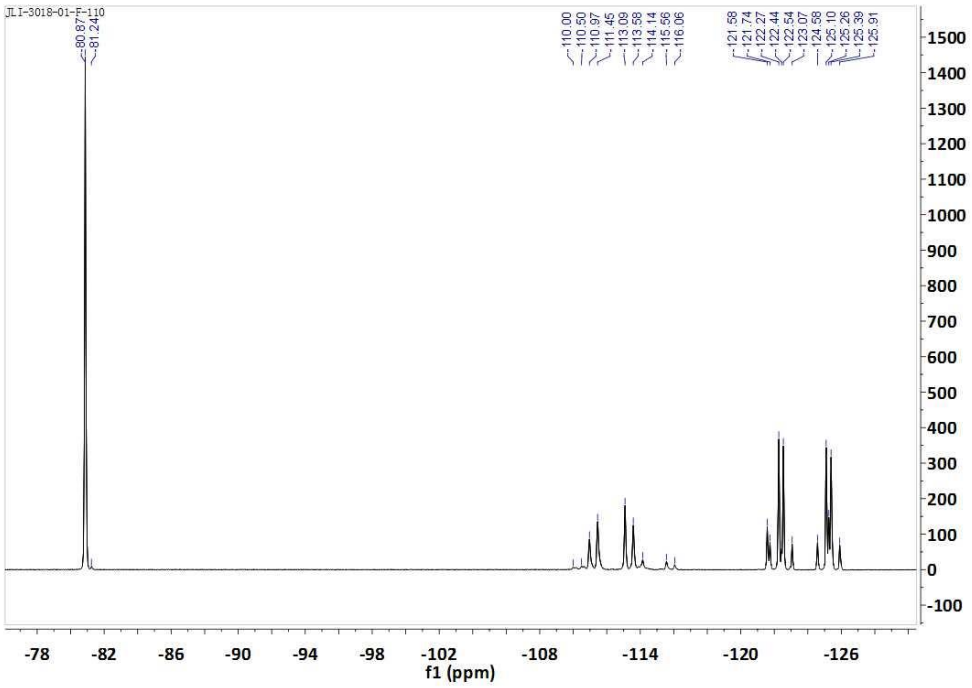


Figure S43. ^{19}F NMR spectrum of the **poly(ethylene-*co*-NBF4)** sample (entry 2 in Table 3)

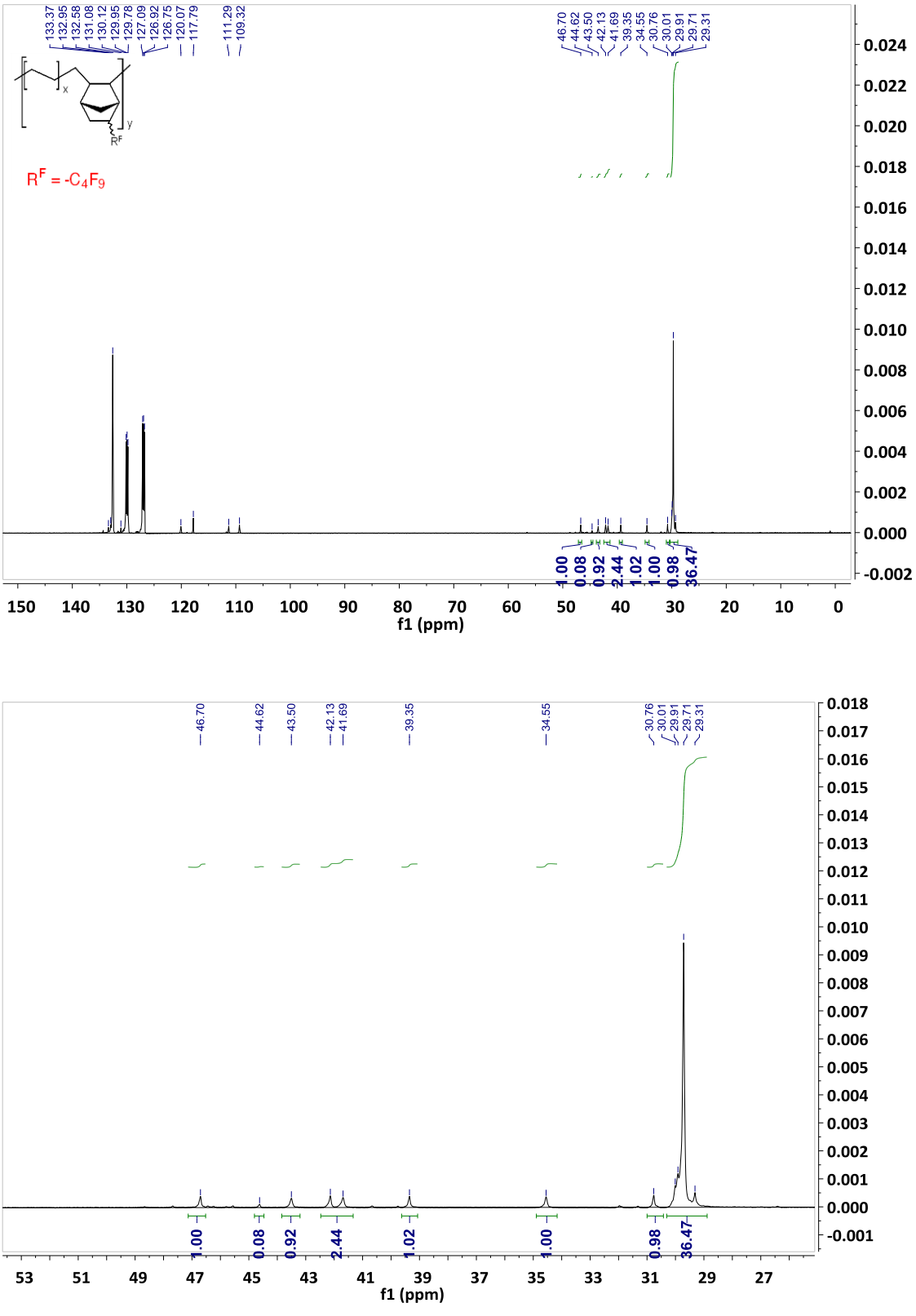


Figure S44. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF4)** with H&F decoupling sample (entry 2 in Table 3, 600 MHz 1,2-dichlorobenzene-d_4 110 °C)

MW Averages

Mp: 82059	Mn: 41815	Mv: 104867	Mw: 117301
Mz: 240353	Mz+1: 402022	PD: 2.8052	

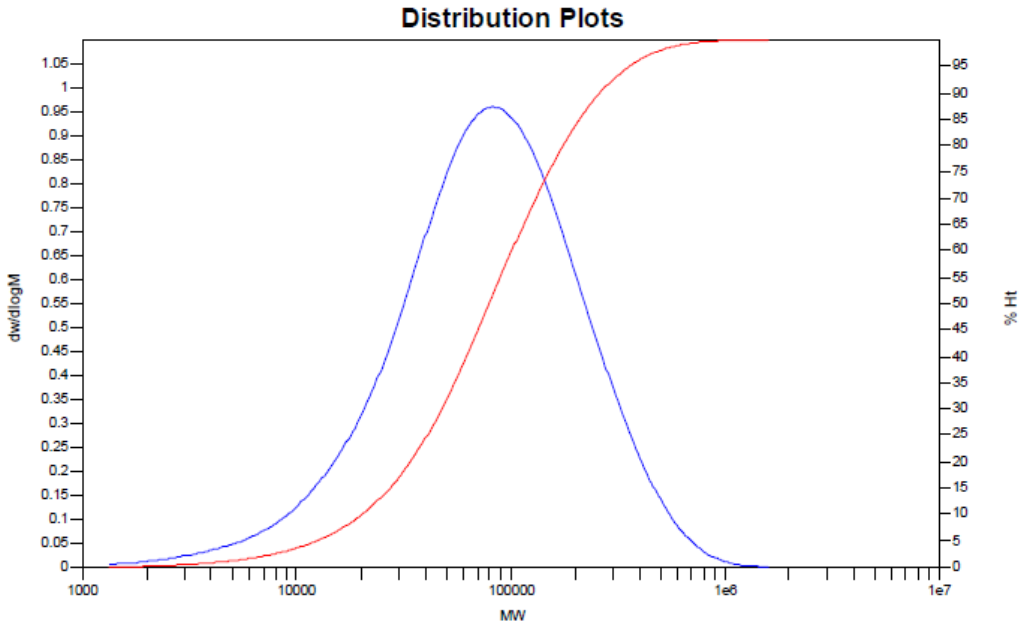


Figure S45. GPC analysis of the **poly(ethylene-*co*-NBF6)** sample (entry 3 in Table 3)

Mp: 20576	Mn: 8002	Mv: 29978	Mw: 35299
Mz: 109289	Mz+1: 265798	PD: 4.4113	

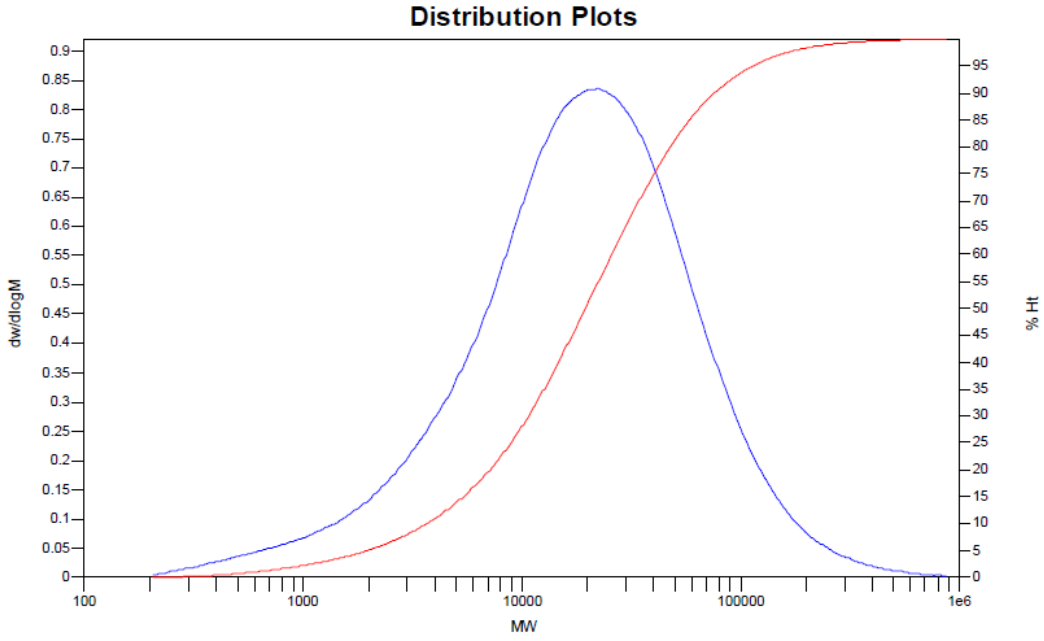


Figure S46. GPC analysis for the **poly(ethylene-*co*-NBF6)** sample (entry 4 in Table 3)

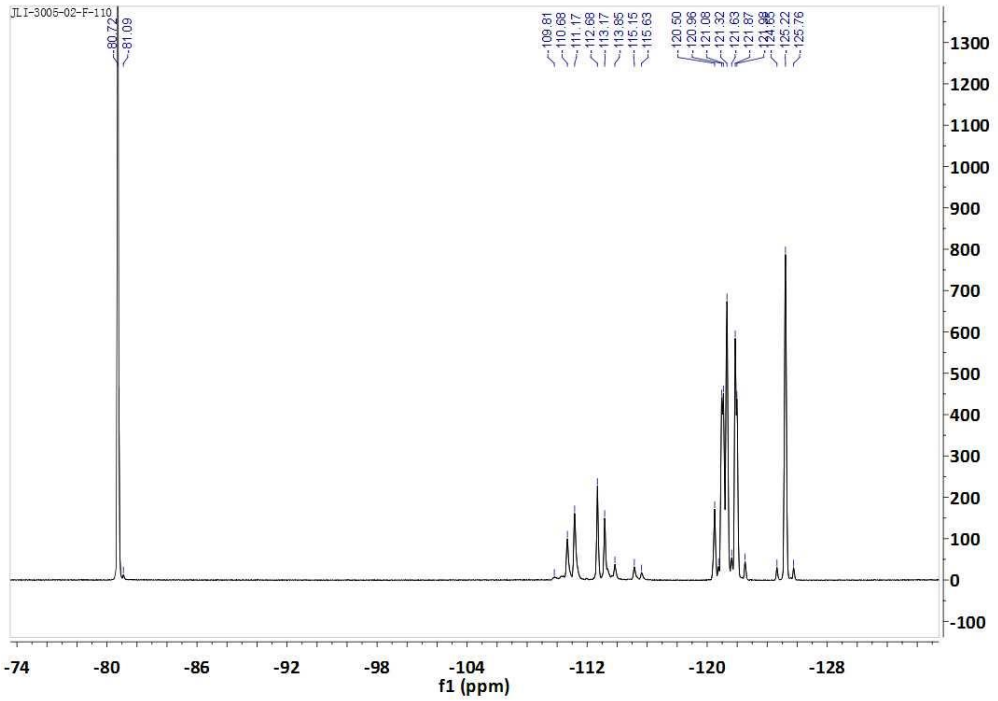


Figure S47. ^{19}F NMR spectrum of the **poly(ethylene-*co*-NBE6)** sample (entry 4 in Table 3)

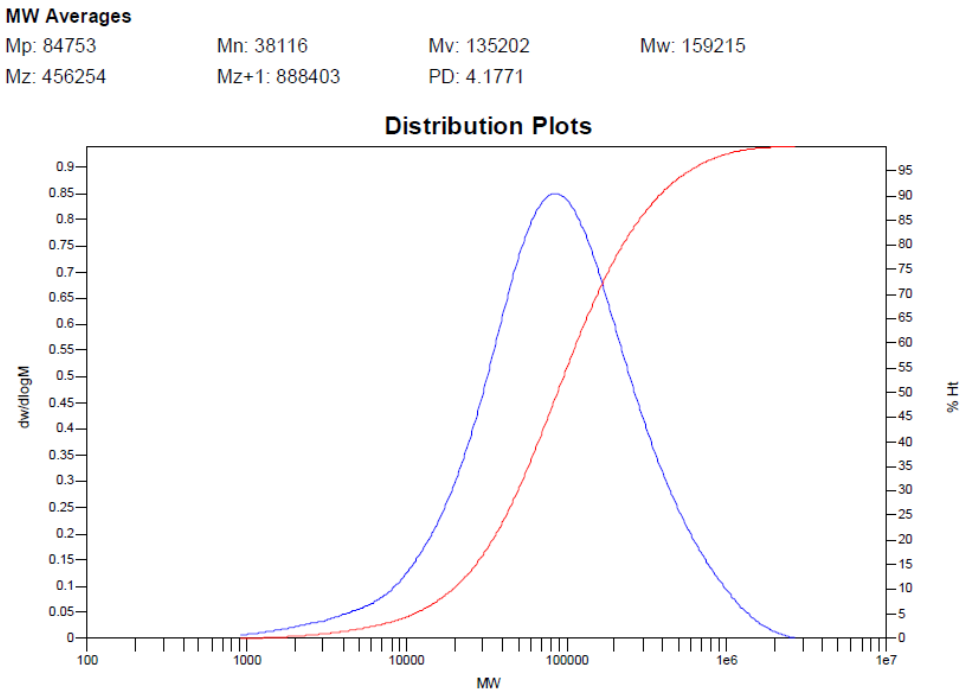


Figure S48. GPC analysis for the **poly(ethylene-*co*-NBF8)** sample (entry 5 in Table 3)

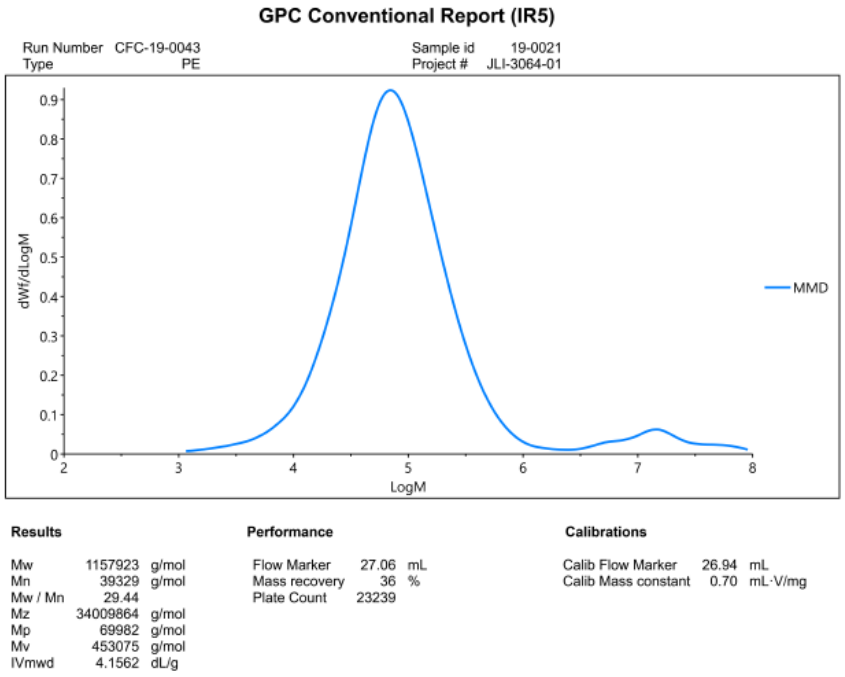


Figure S49. GPC analysis for the **poly(ethylene-*co*-NBF8)** sample (entry 6 in Table 3).

This series copolymer samples were difficult to be dissolved well comparing to the ethylene/norbornene copolymer samples. We think that the appearance of high molecular weight polymer part in the GPC curve (as shown in Figure S49) probably due to the strong fluorine-hydrogen bonding force and the formation of cohesion between fluorinate chains. We have repeated the GPC measurement for the same polymer sample from entry 6 in table 3 using a different instrument (as shown in Figure S49), and clearly observed a minor peak standing for the high molecular weight components in the GPC spectrum.

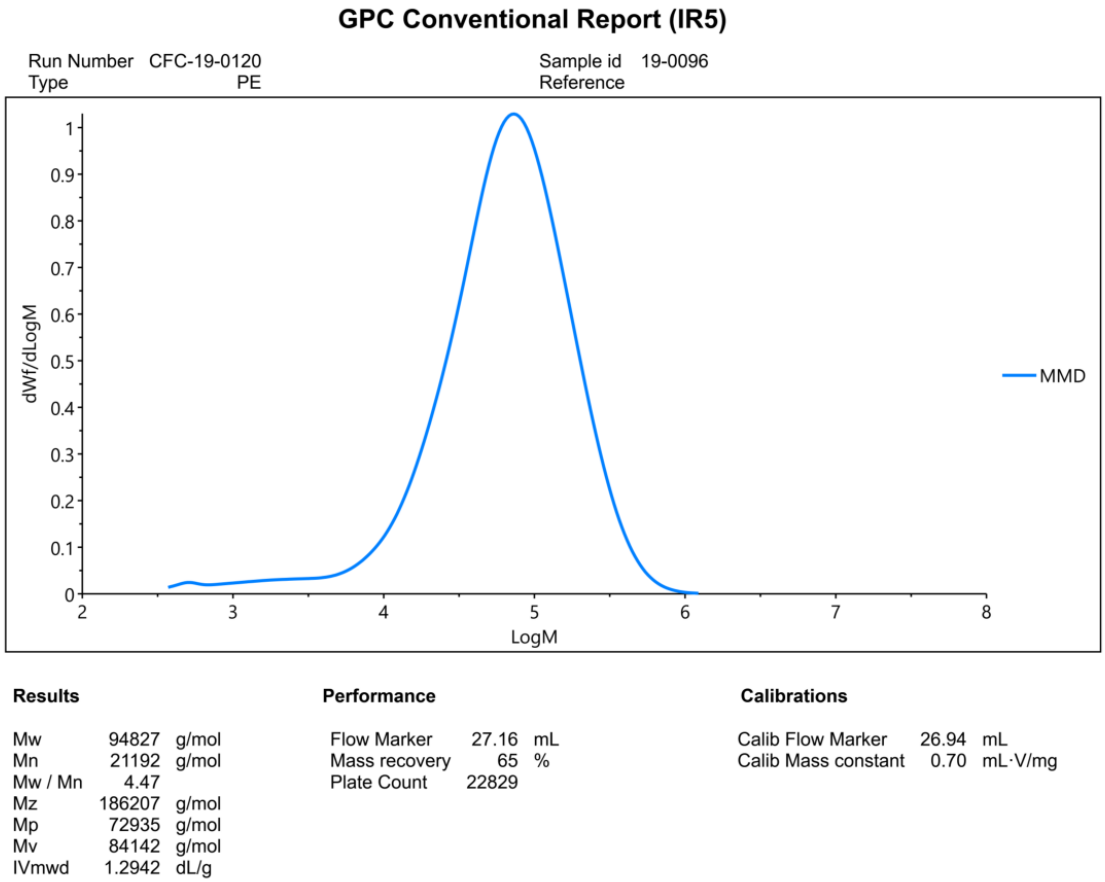


Figure S50. GPC analysis for the **poly(ethylene-*co*-NBF6)** sample (entry 3 in Table 2).

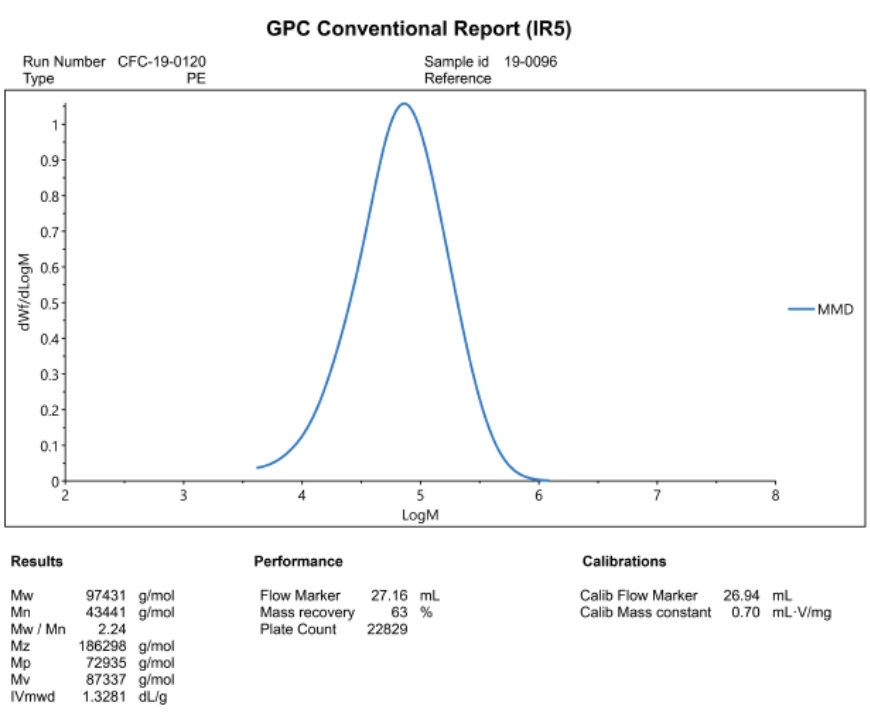


Figure S51. GPC analysis for the **poly(ethylene-*co*-NBF6)** sample based on the main peak by a different instrument (entry 3 in Table 2).

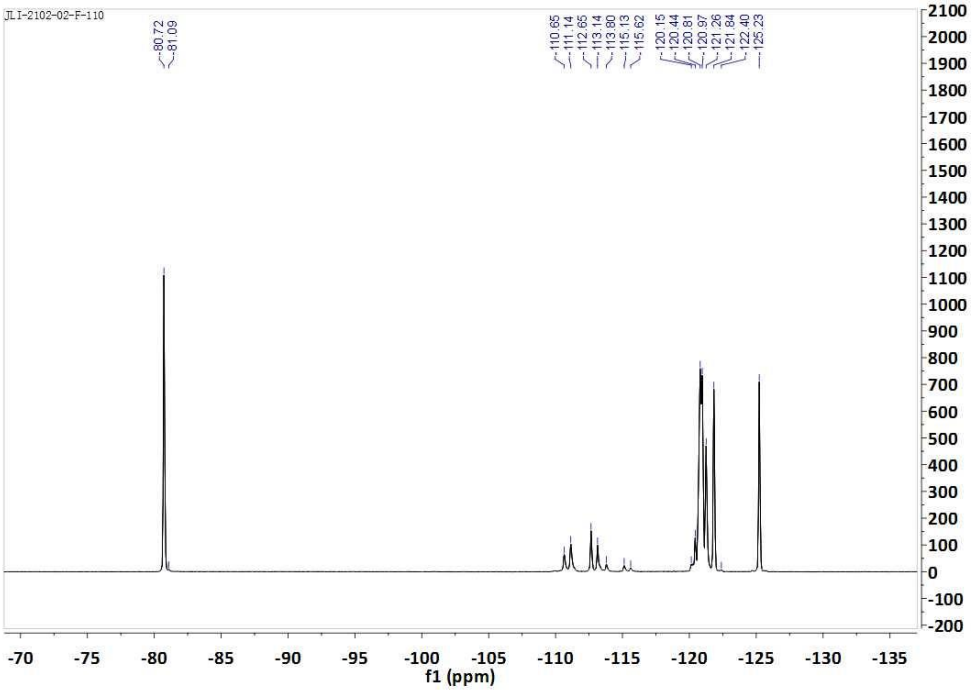


Figure S52. ^{19}F NMR spectrum of the **poly(ethylene-*co*-NBF8)** sample (entry 6 in Table 3).

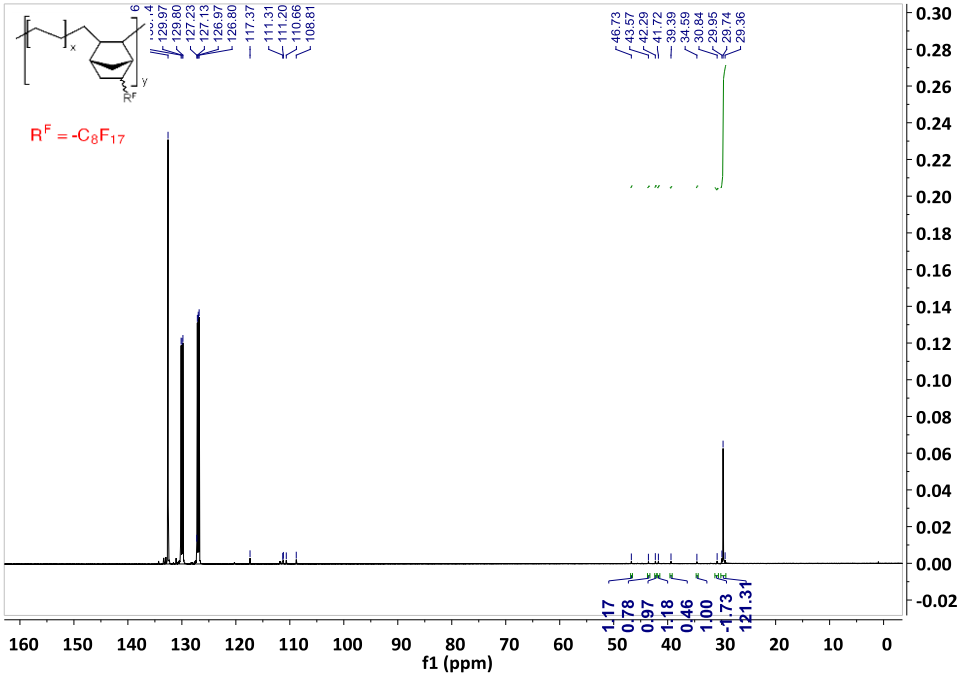


Figure S53. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF8)** with H&F decoupling sample (entry 6 in Table 3) (600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

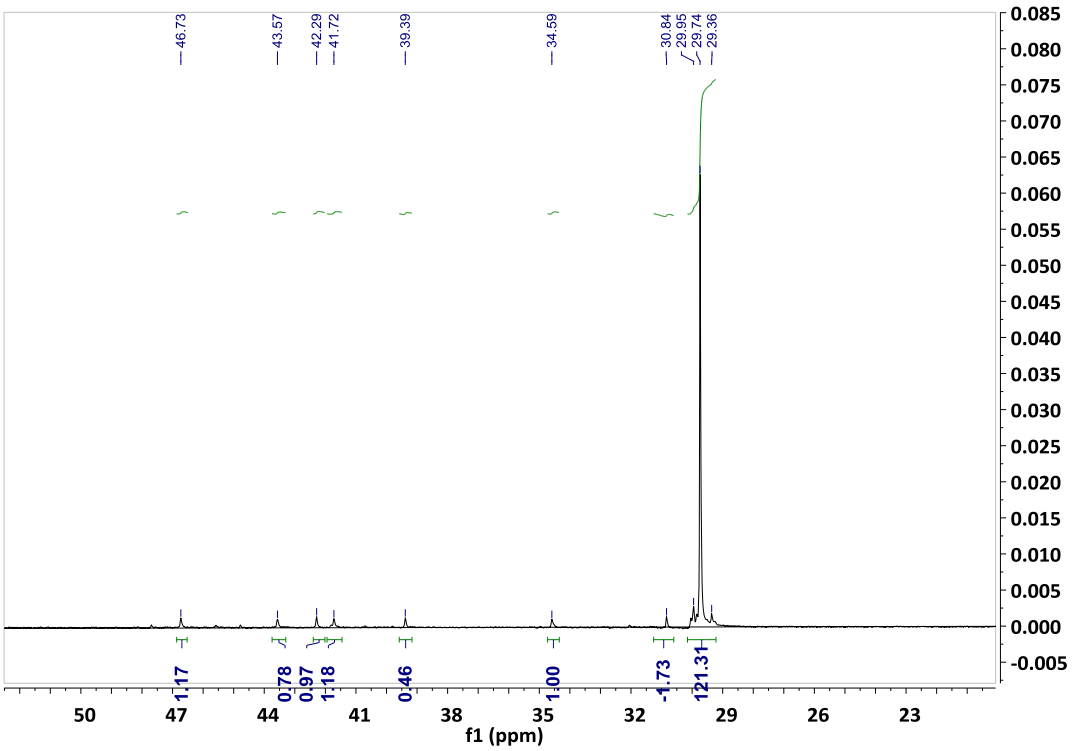


Figure S53a. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF8)** with H&F decoupling sample (entry 6 in Table 3) (600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

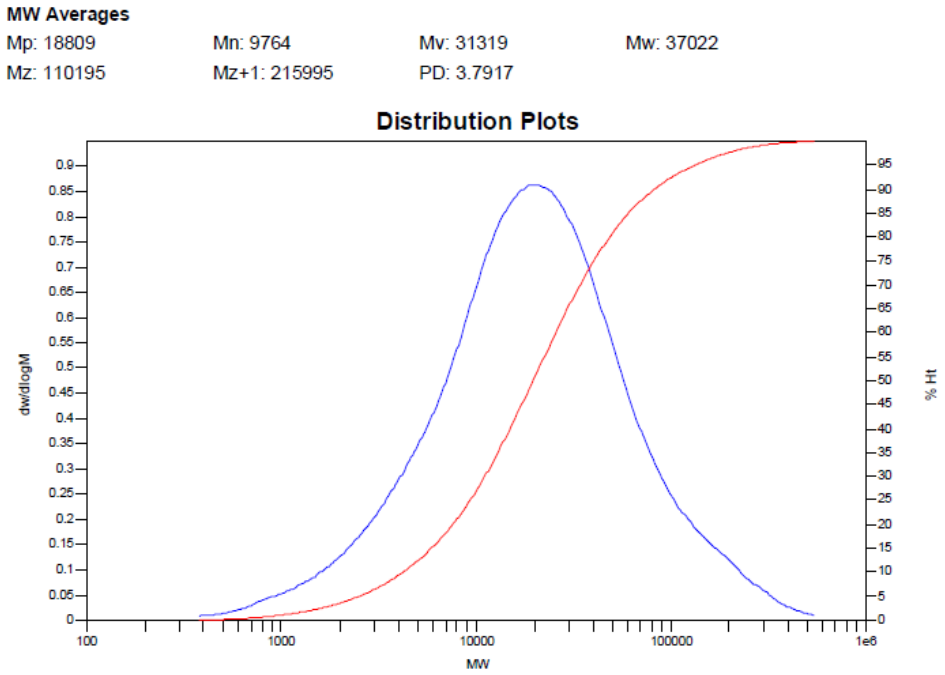


Figure S54. GPC curve of the **poly(ethylene-*co*-NBF6)** sample (entry 7 in Table 3)

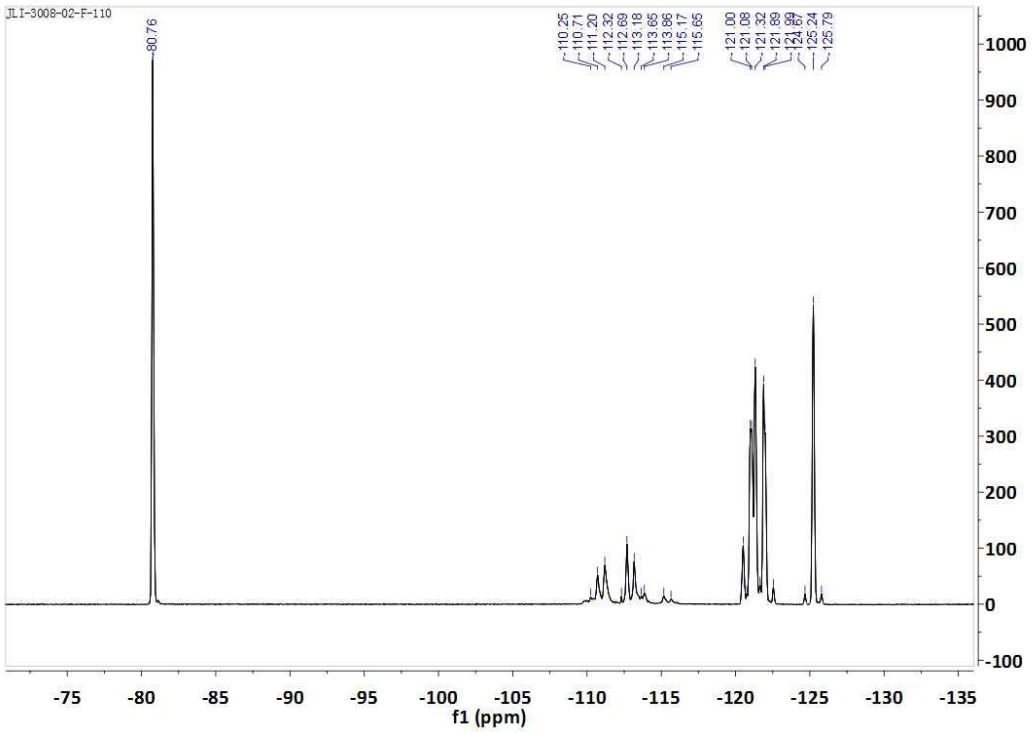


Figure S55. ^{19}F NMR spectrum of the **poly(ethylene-*co*-NBE6)** sample (entry 7 in Table 3).

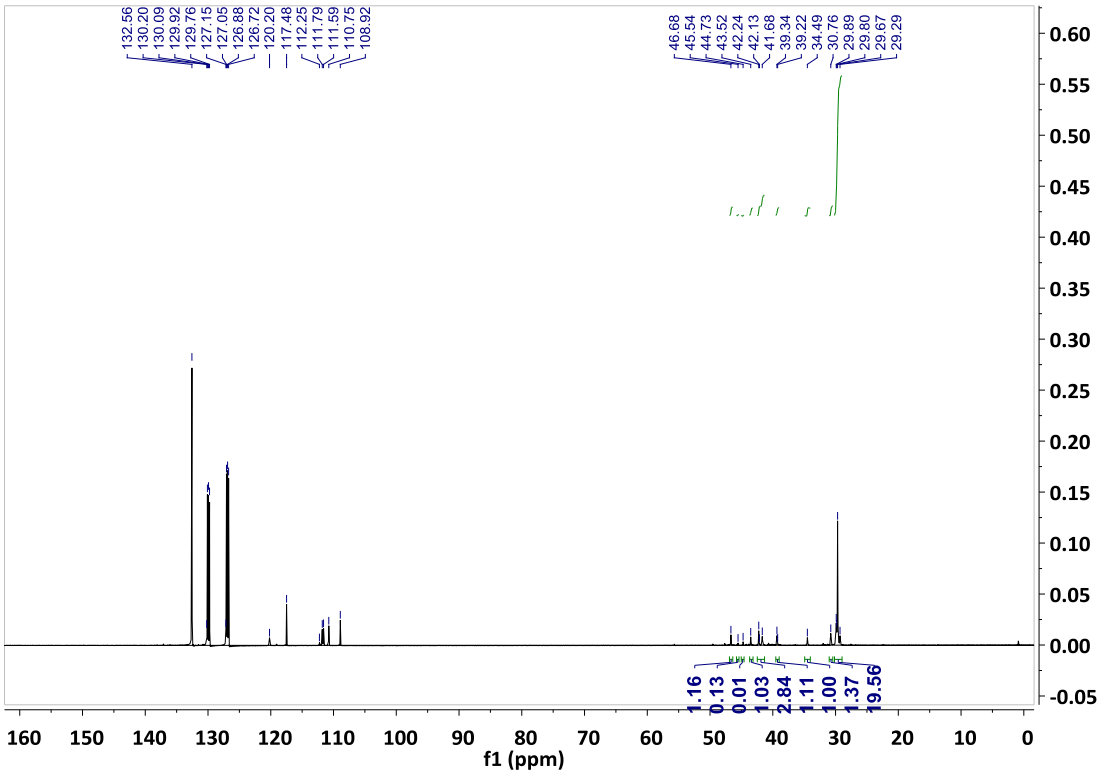


Figure S56a. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF6)** with H&F decoupling sample (entry 7 in Table 3, 600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

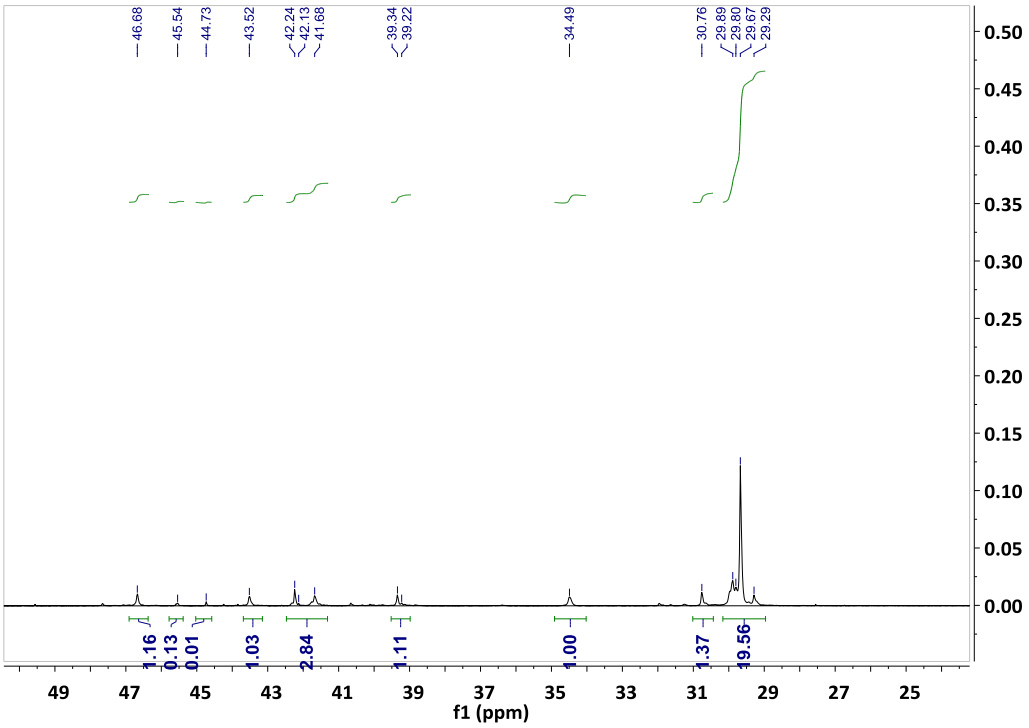


Figure S56b. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF6)** with H&F decoupling sample (entry 7 in Table 3, 600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

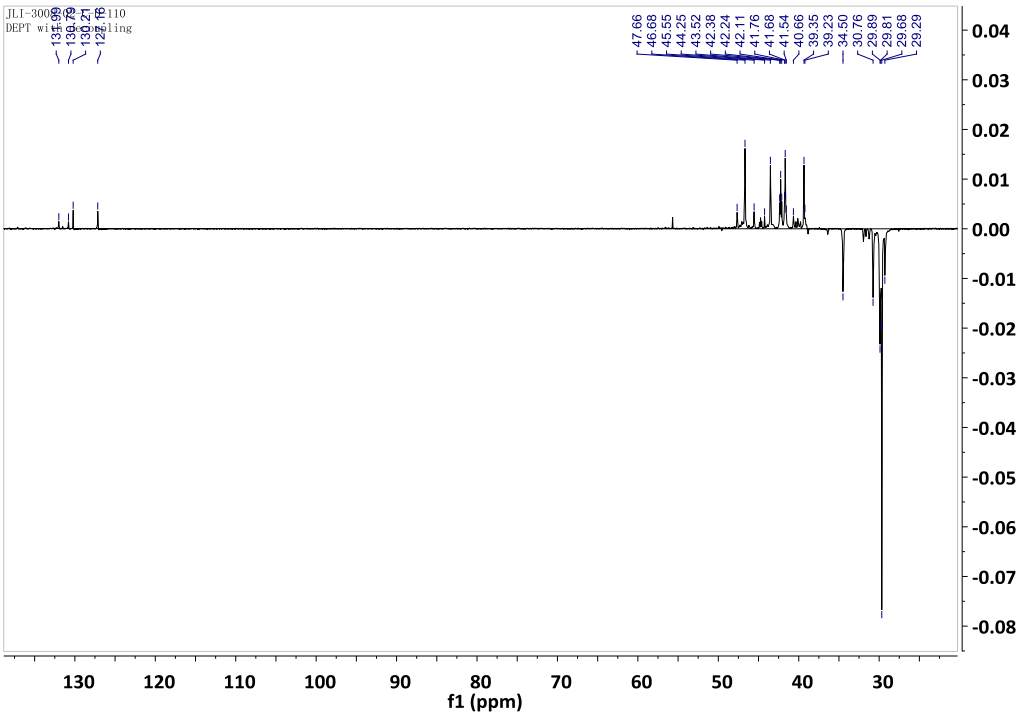


Figure S56c. Dept 135 NMR of copolymer for entry 7 in Table 3 (600 MHz 1,2-dichlorobenzene -d_4 110 ^{o}C).

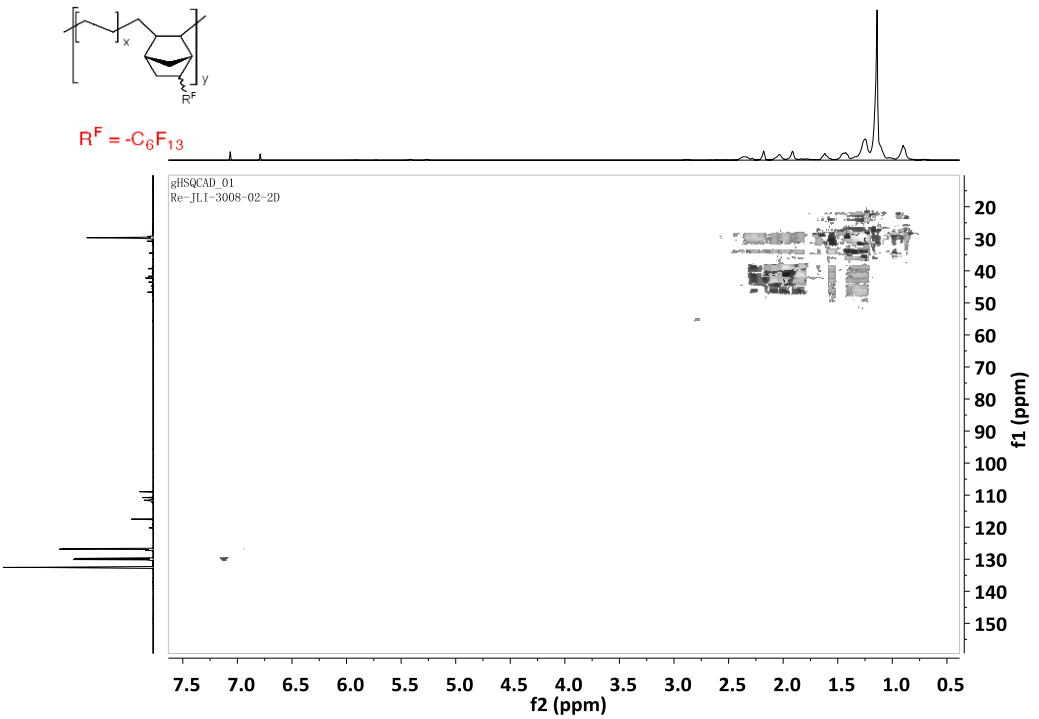


Figure S56d. C-H HSQC NMR of copolymer for entry 7 in table 3 (600 MHz 1,2-dichlorobenzene -d_4 110 ^{o}C).

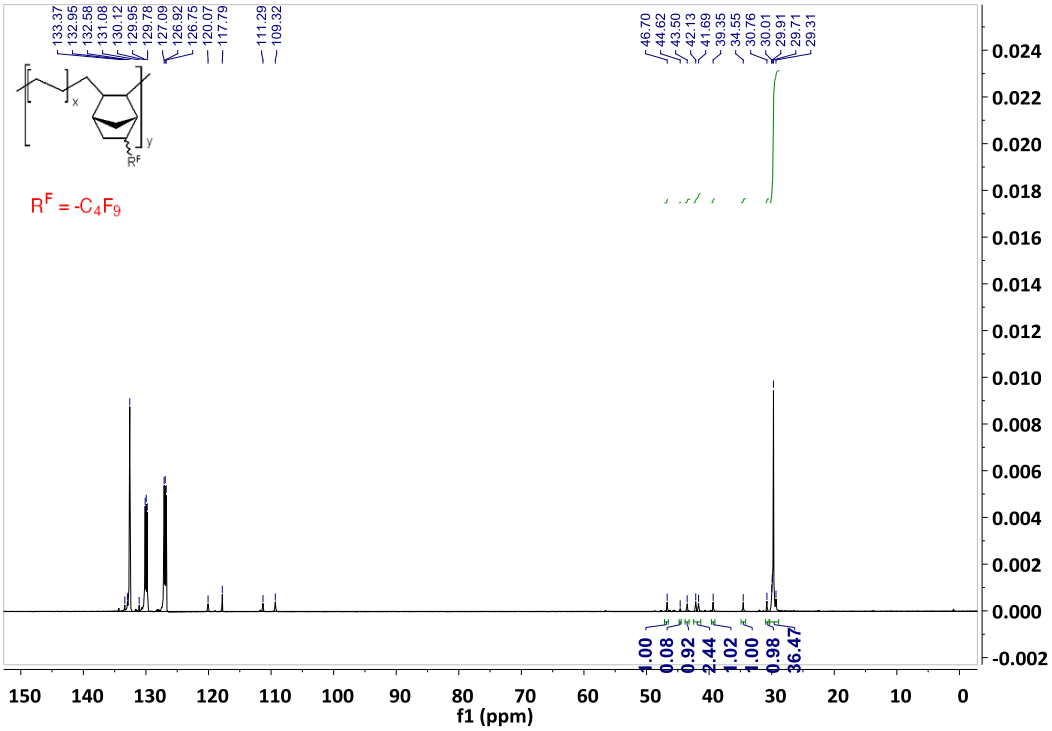


Figure S57a. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF4)** with H&F decoupling sample (entry 2 in Table 3, 600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

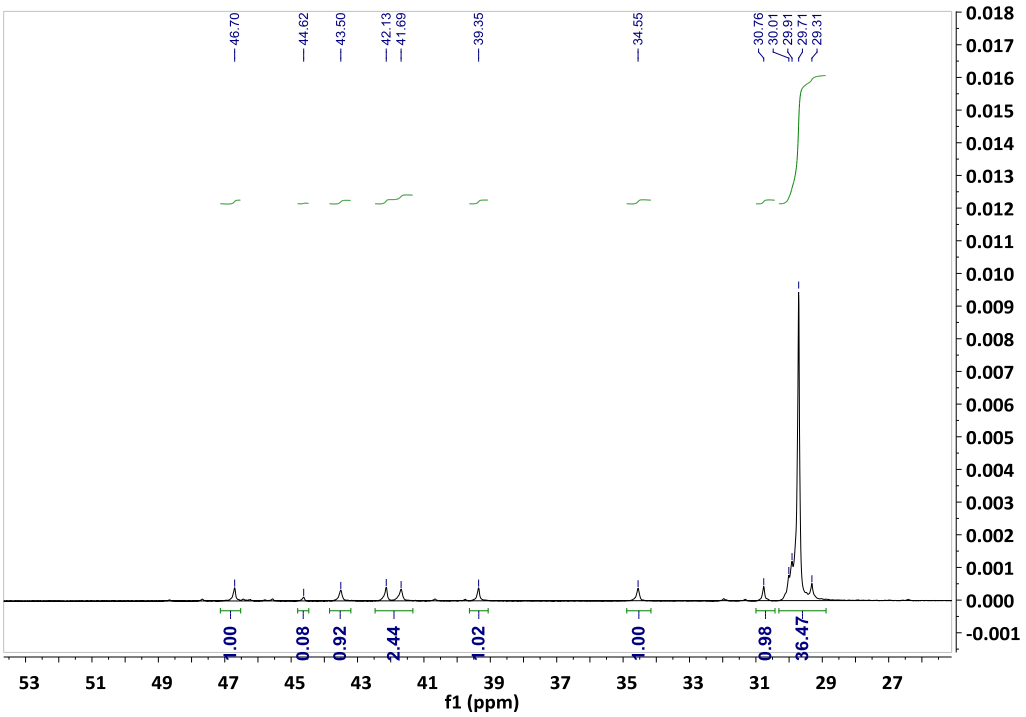


Figure S57b. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF4)** with H&F decoupling sample (entry 2 in Table 3, 600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

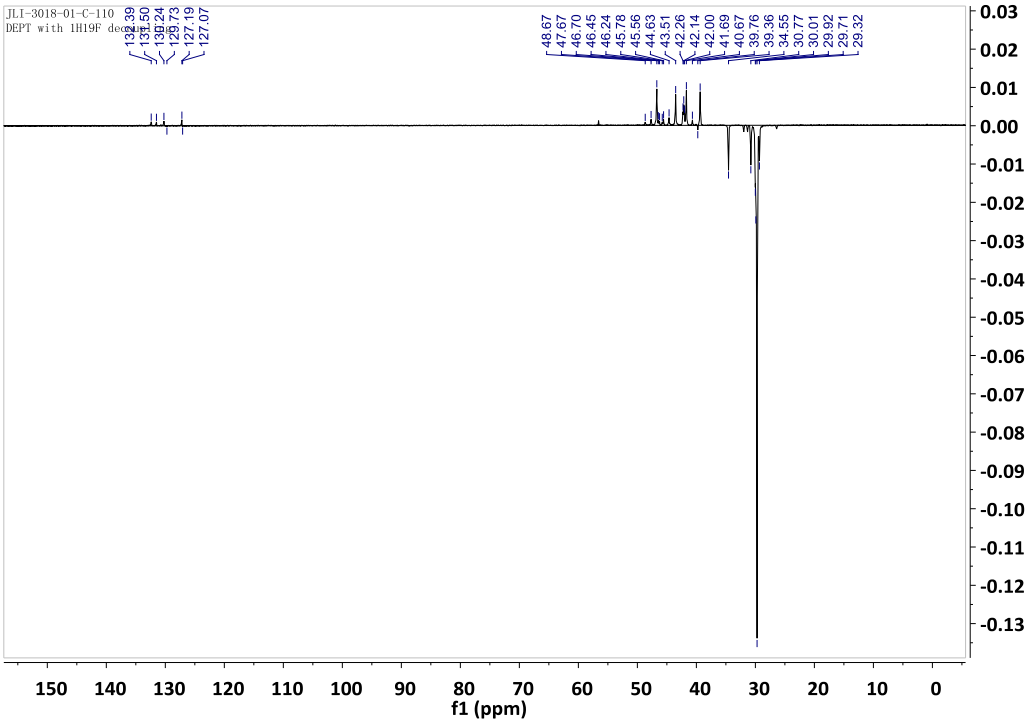


Figure S57c. Dept 135 NMR of copolymer for entry 2 in Table 3 (600 MHz 1,2-dichlorobenzene -d_4 110 ^{o}C).

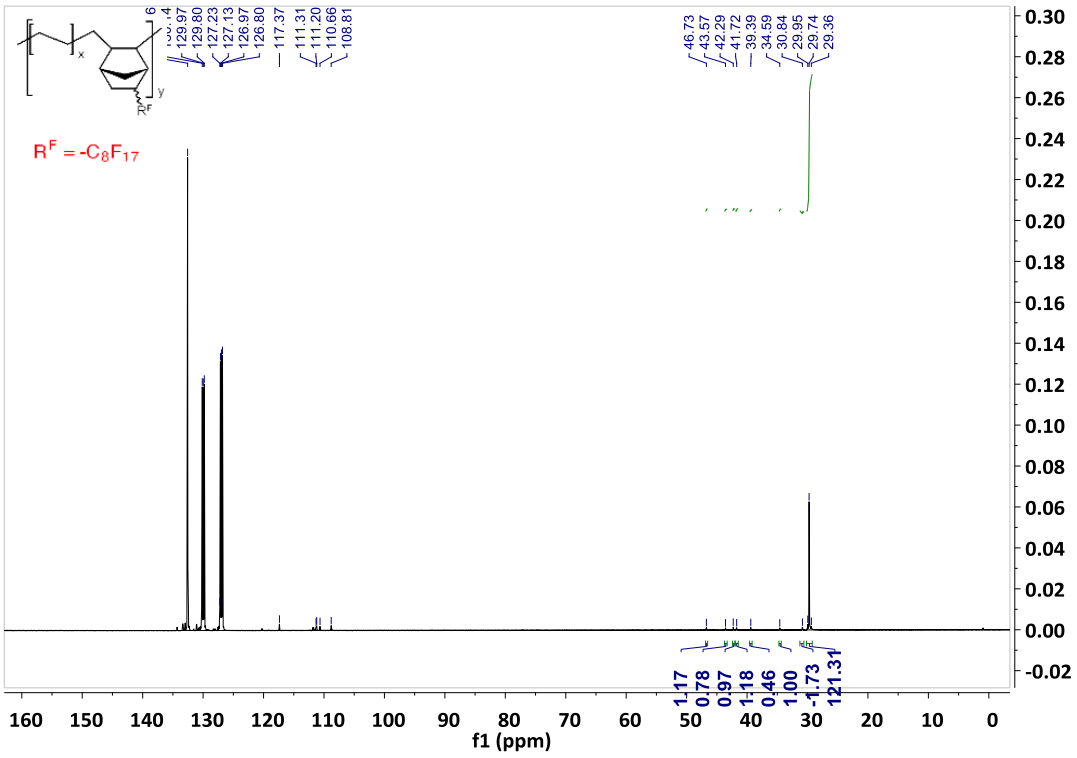


Figure S58a. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF8)** with H&F decoupling sample (entry 6 in Table 3, 600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

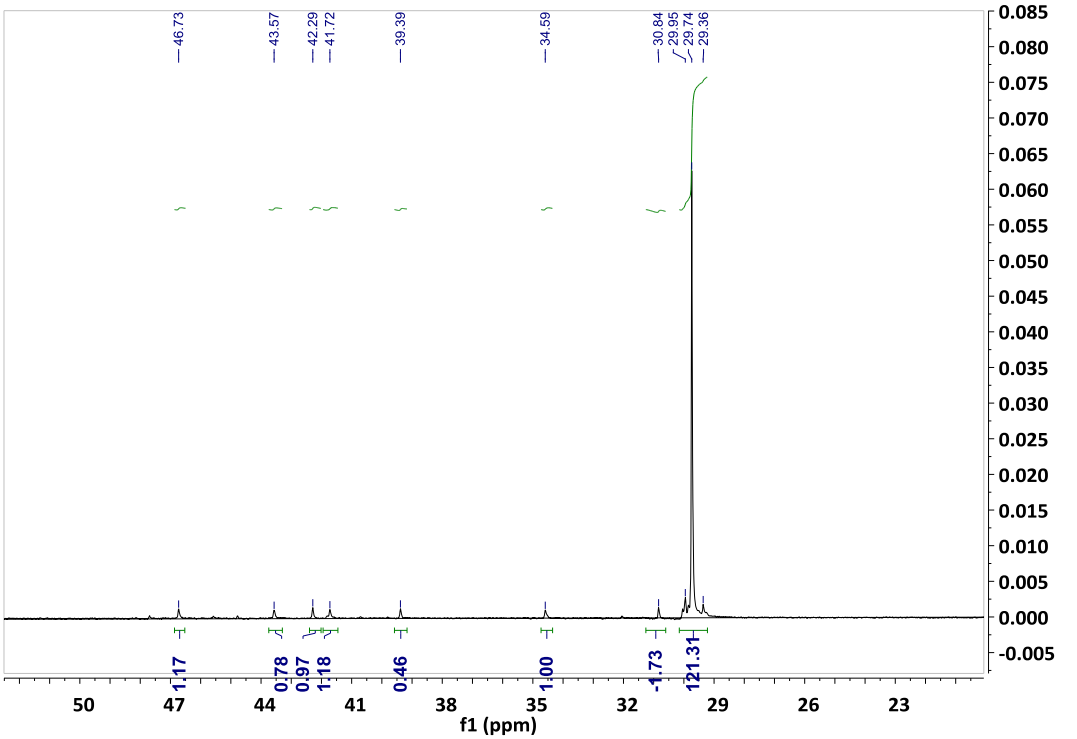


Figure S58b. ^{13}C NMR spectrum of the **poly(ethylene-*co*-NBF8)** with H&F

decoupling sample (entry 6 in Table 3, 600 MHz 1,2- dichlorobenzene -d_4 110 ^{o}C)

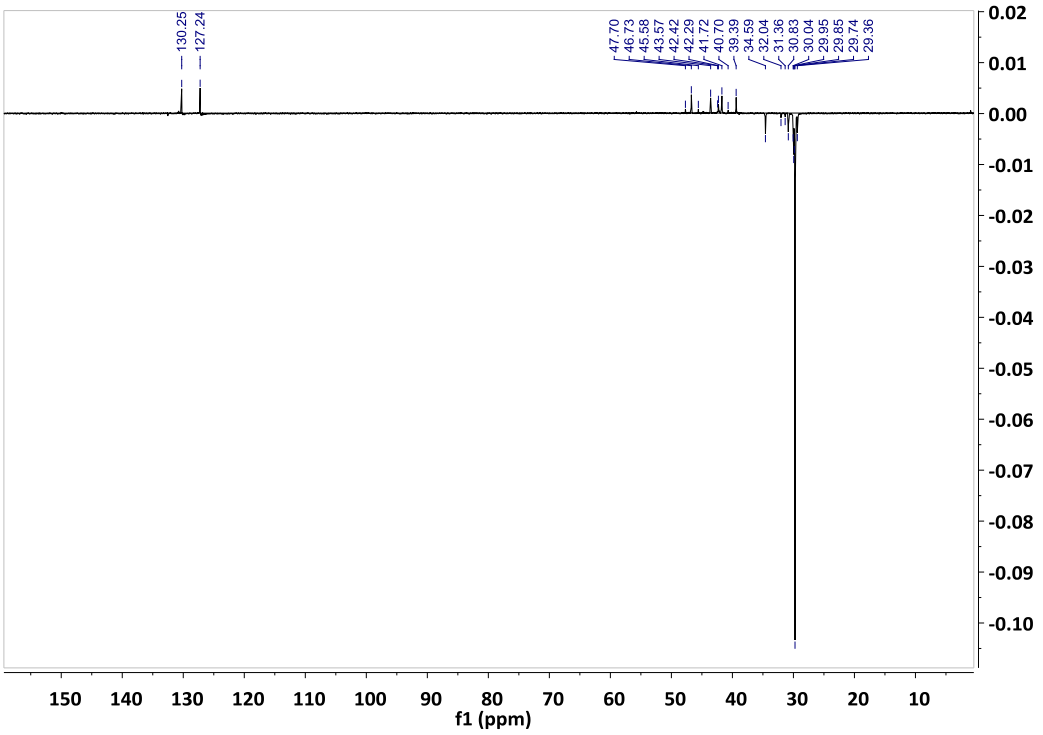


Figure S58c. Dept 135 NMR of copolymer for entry 6 in Table 3 (600 MHz 1,2-dichlorobenzene -d_4 110 ^{o}C).

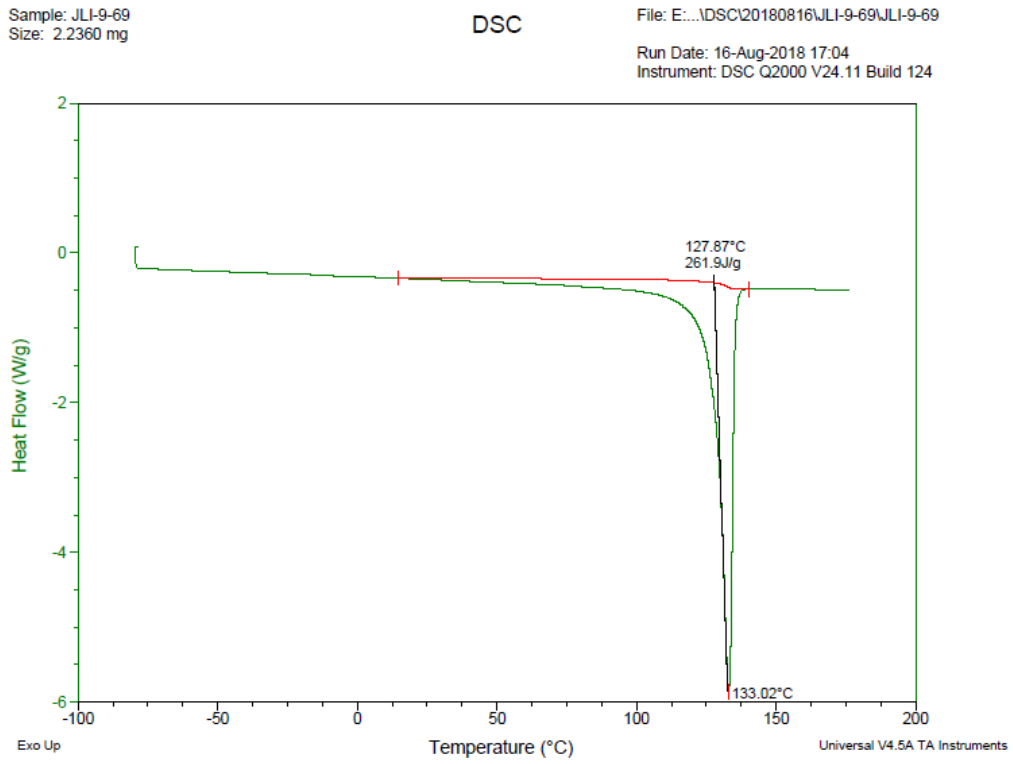


Figure S59. DSC spectrum of the sample from entry 1 in table 1**.**

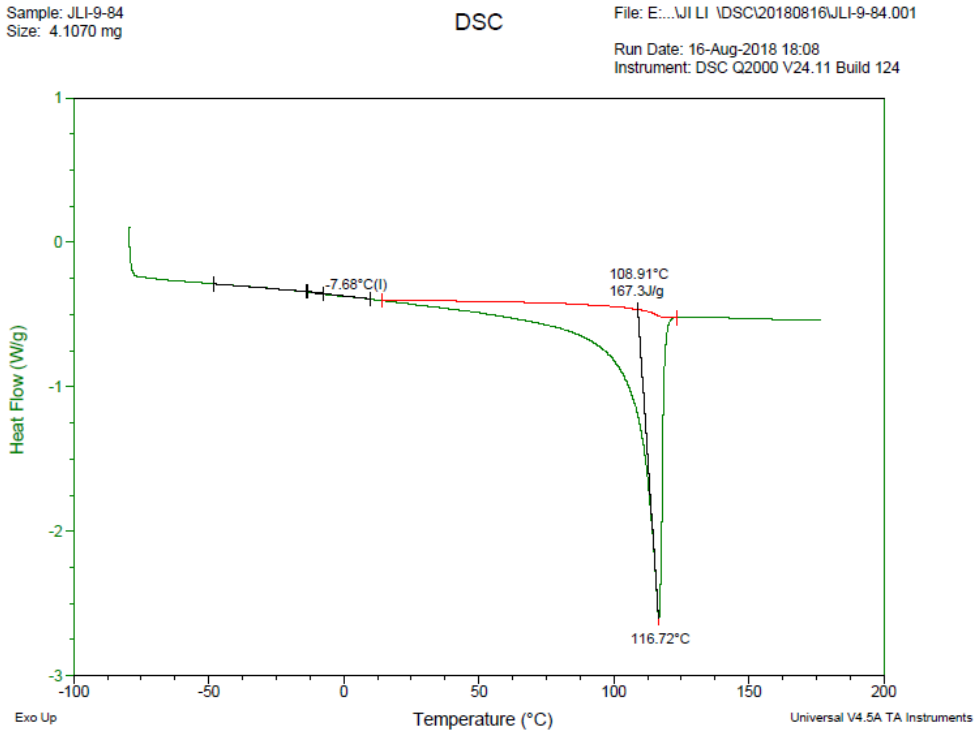


Figure S60. DSC spectrum of the sample from entry 2 in table 1.

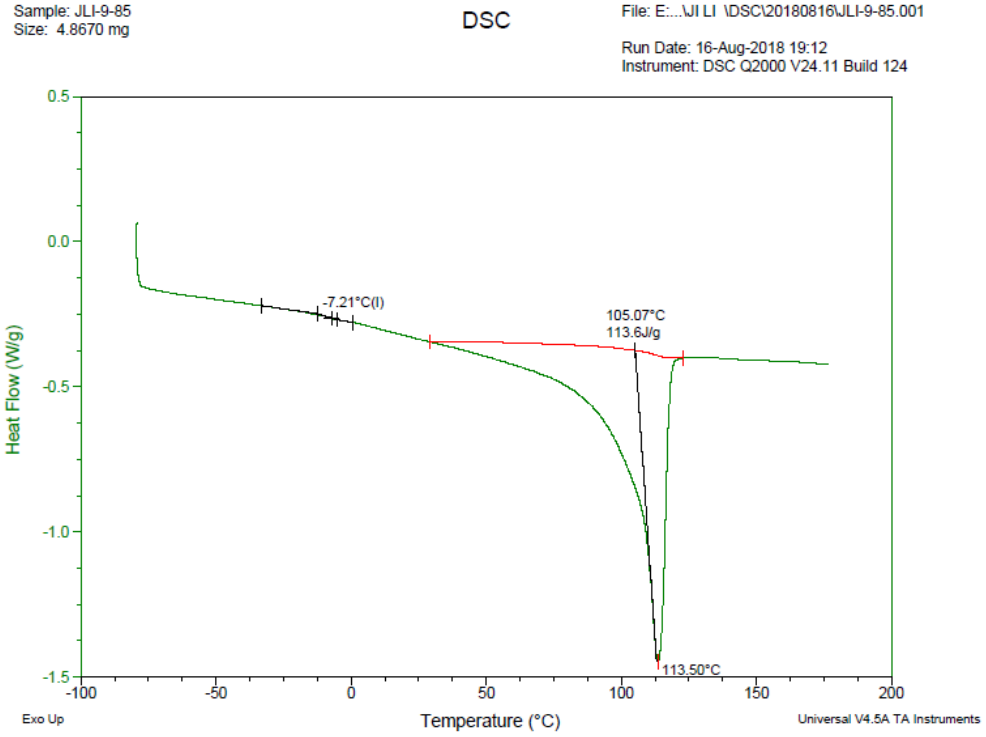


Figure S61. DSC spectrum of the sample from entry 3 in table 1.

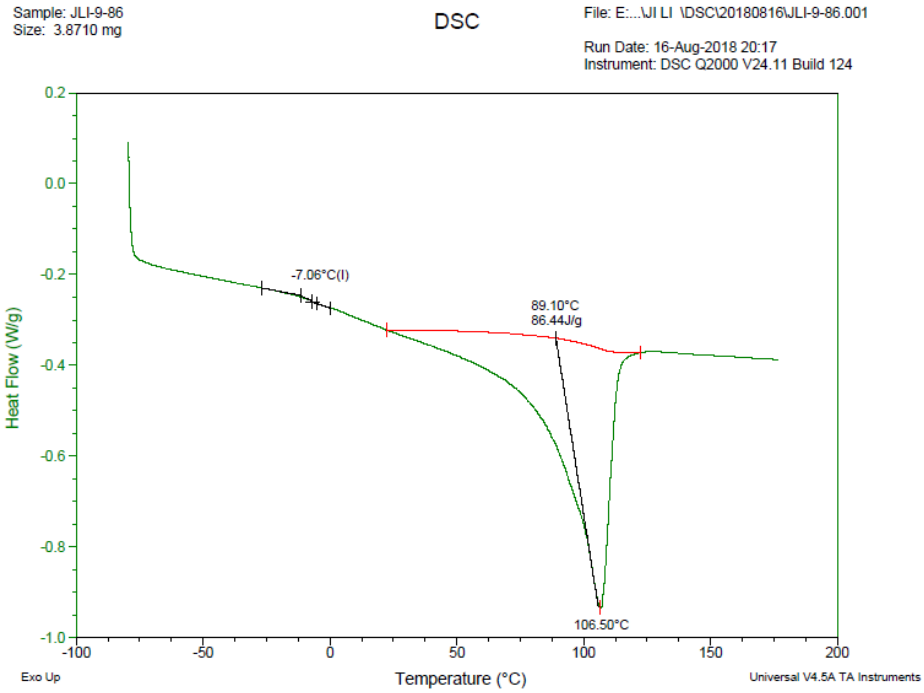


Figure S62. DSC spectrum of the sample from entry 4 in table 1.

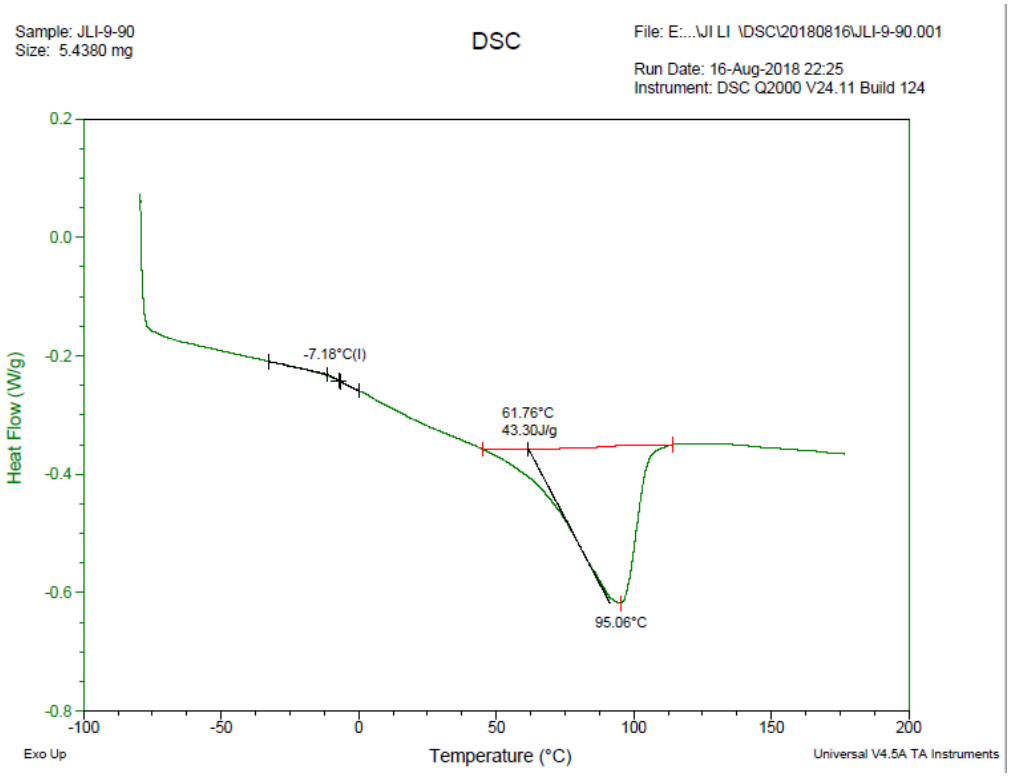


Figure S63. DSC spectrum of the sample from entry 5 in table 1.

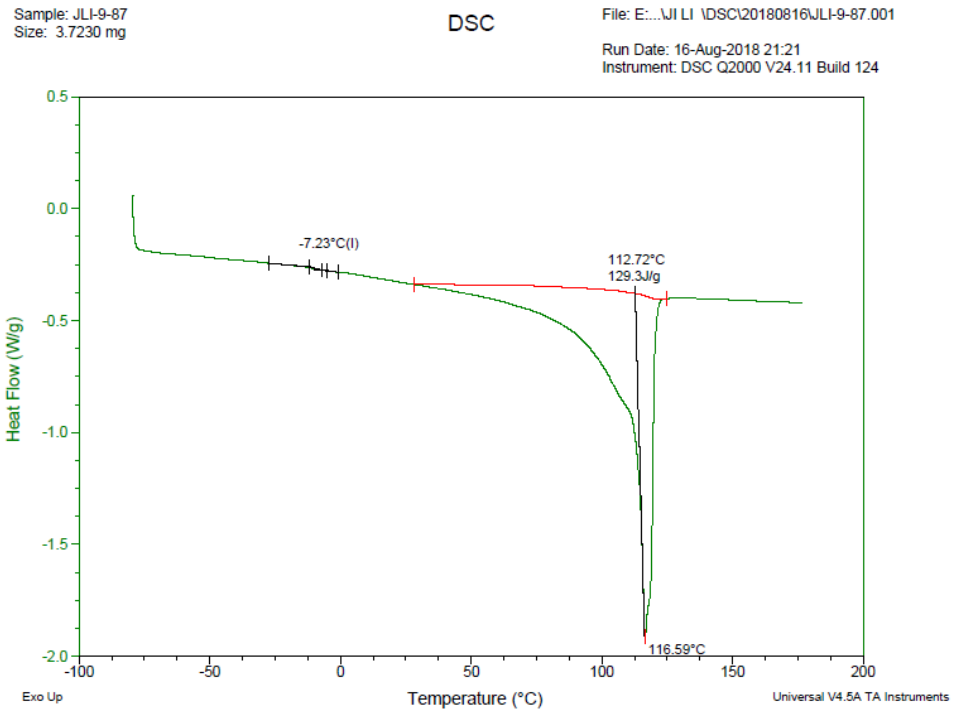


Figure S64. DSC spectrum of the sample from entry 6 in table 1.

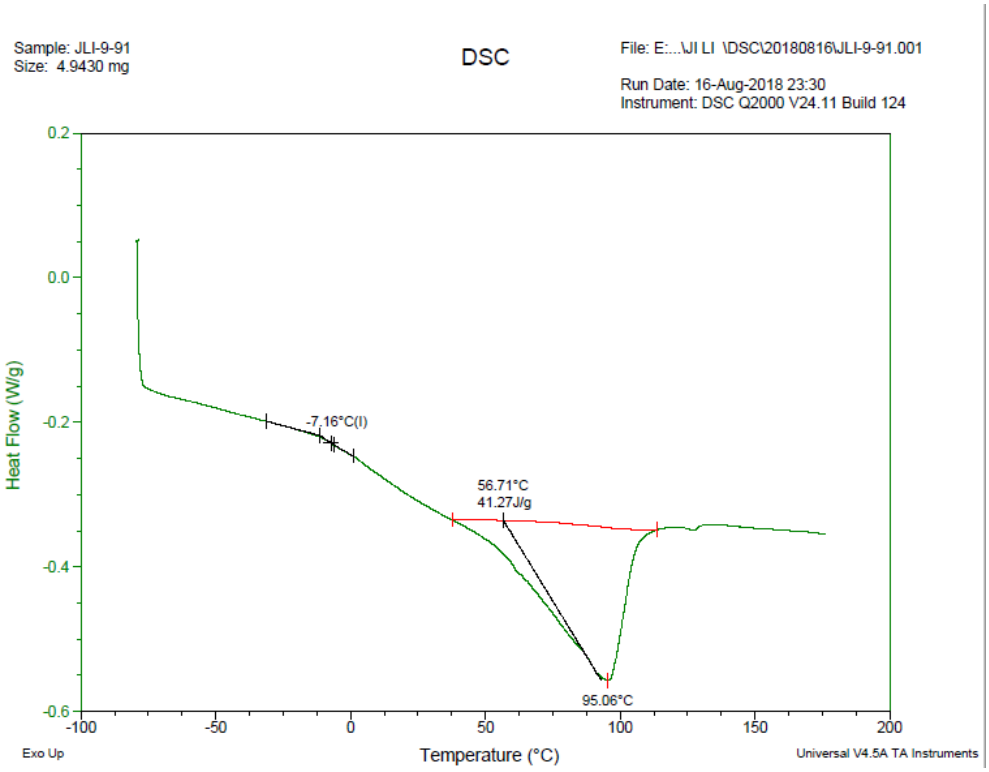


Figure S65. DSC spectrum of the sample from entry 7 in table 1.

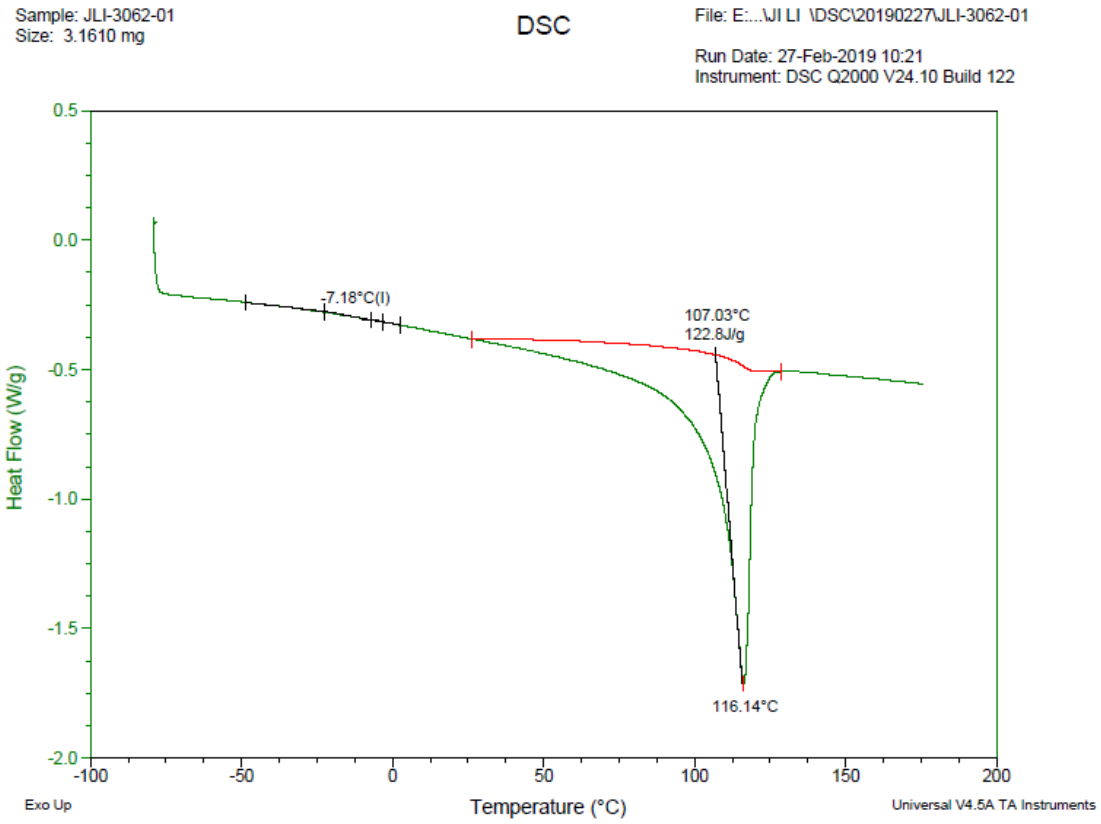


Figure S66. DSC spectrum of the sample from entry 8 in table 1.

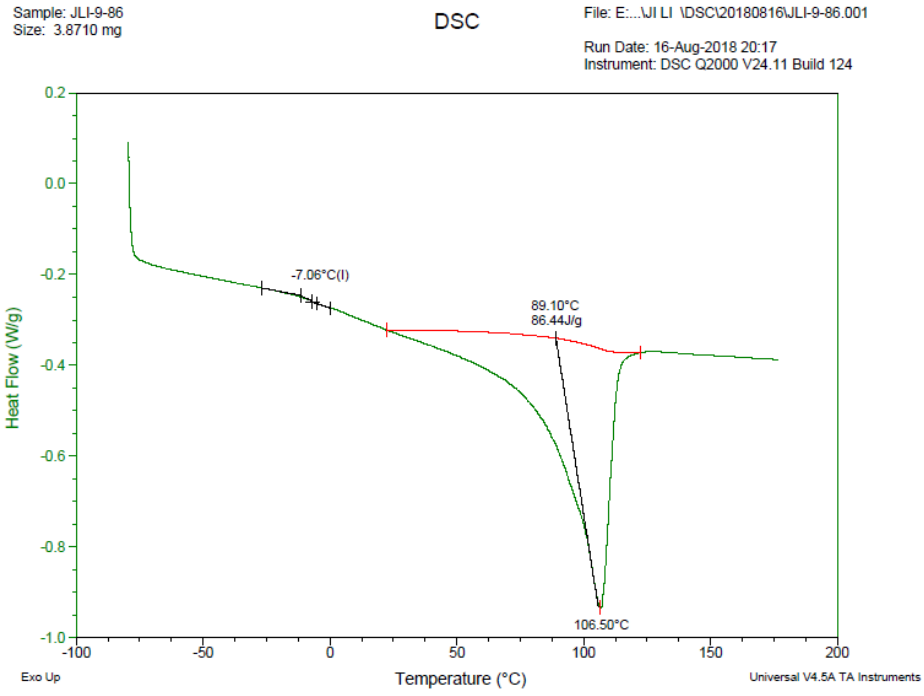


Figure S67. DSC spectrum of the sample from entry 1 in table 2.

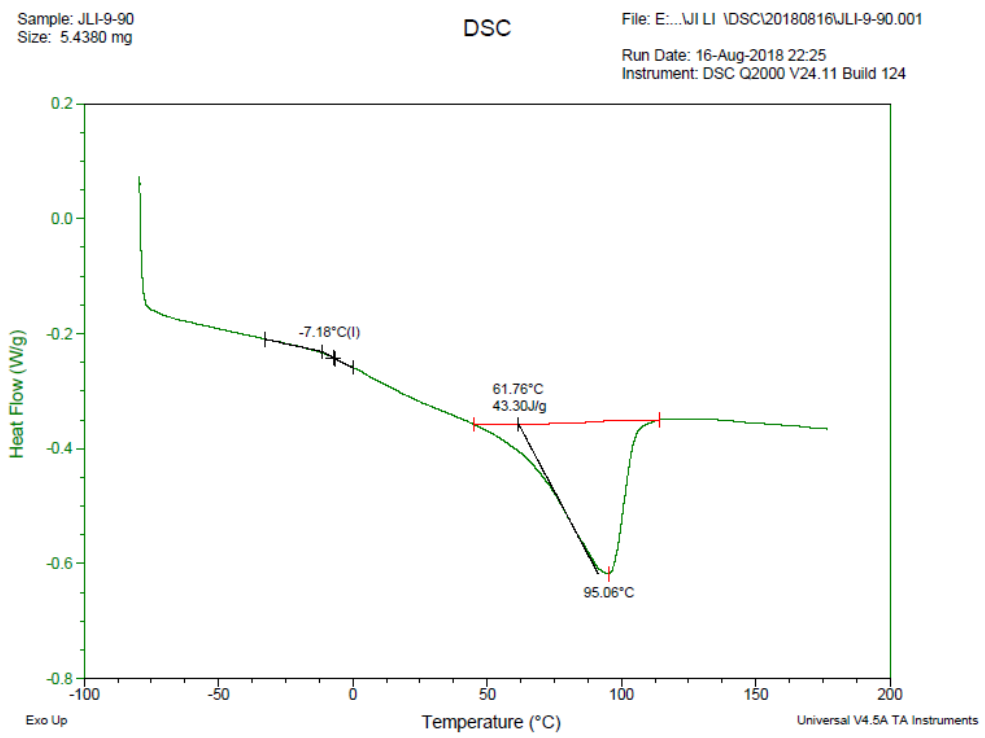


Figure S68. DSC spectrum of the sample from entry 2 in table 2.

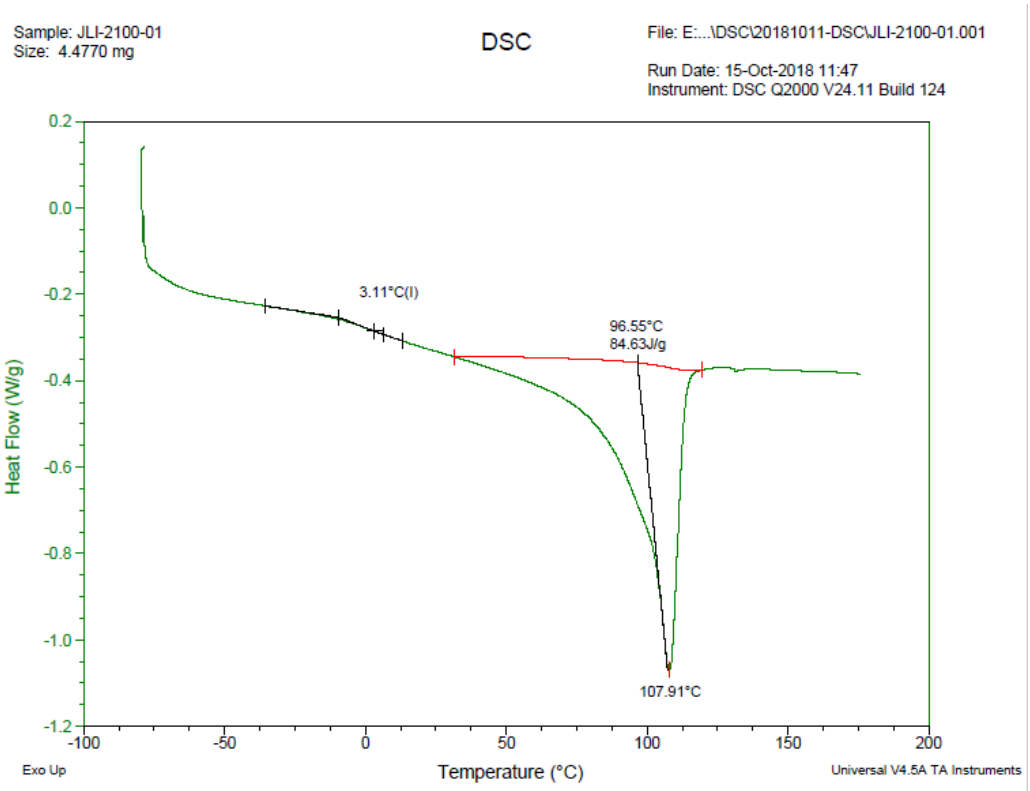


Figure S69. DSC spectrum of the sample from entry 3 in table 2.

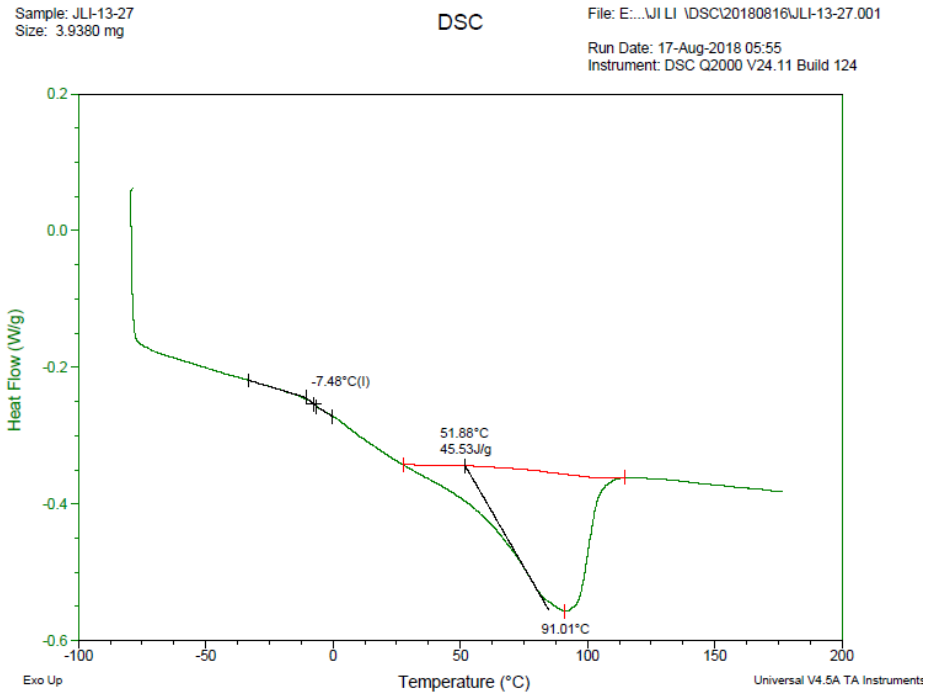


Figure S70. DSC spectrum of the sample from entry 4 in table 2.

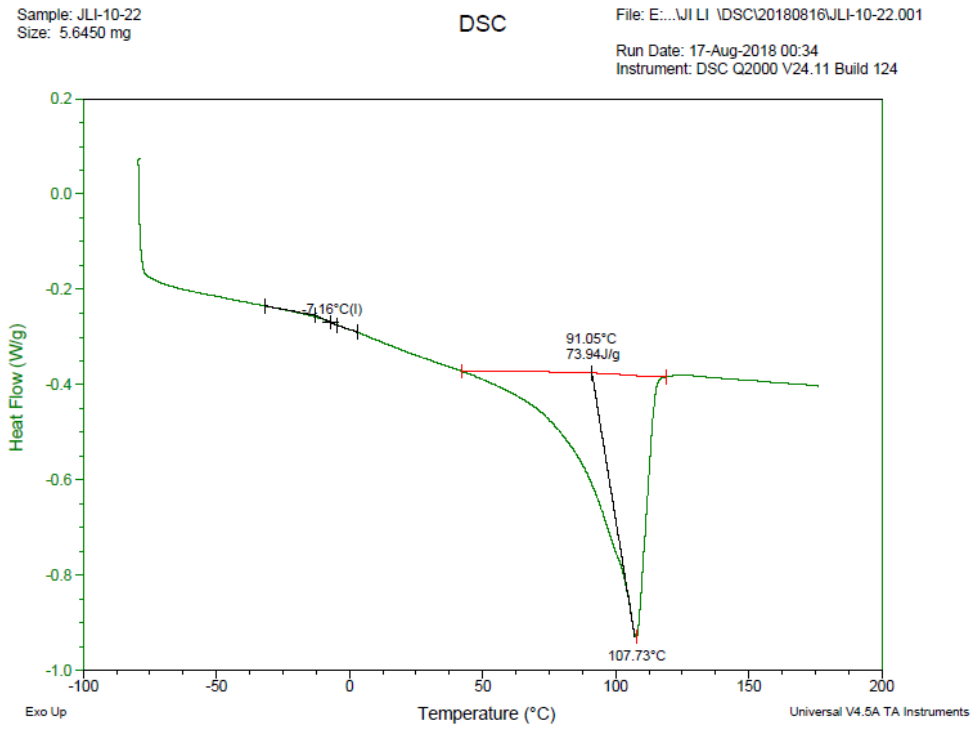


Figure S71. DSC spectrum of the sample from entry 5 in table 2.

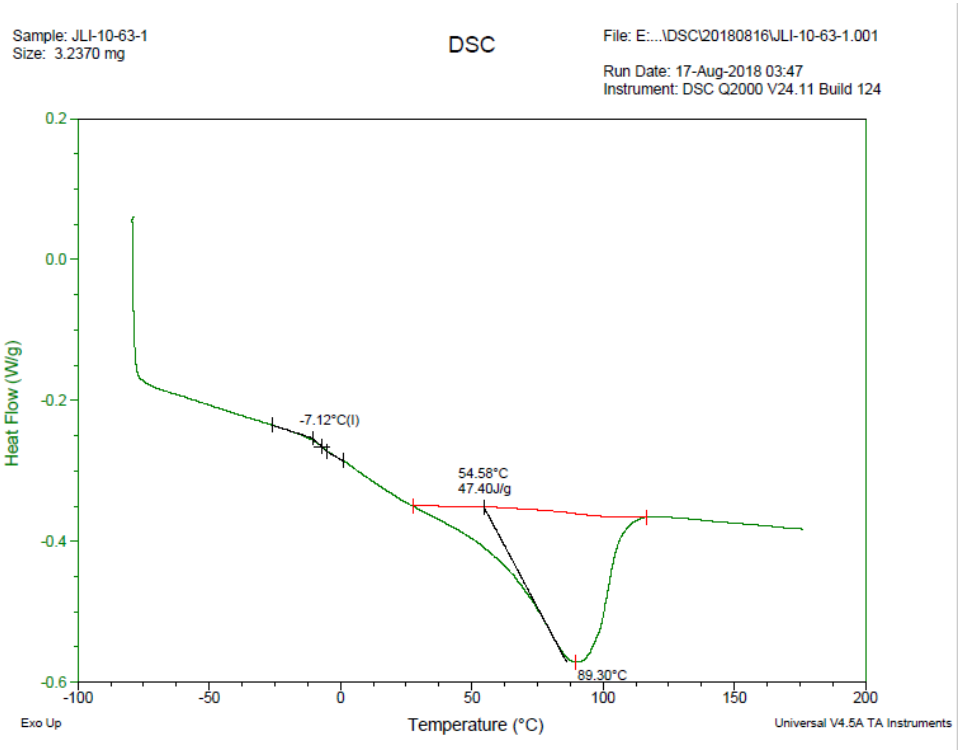


Figure S72. DSC spectrum of the sample from entry 6 in table 2.

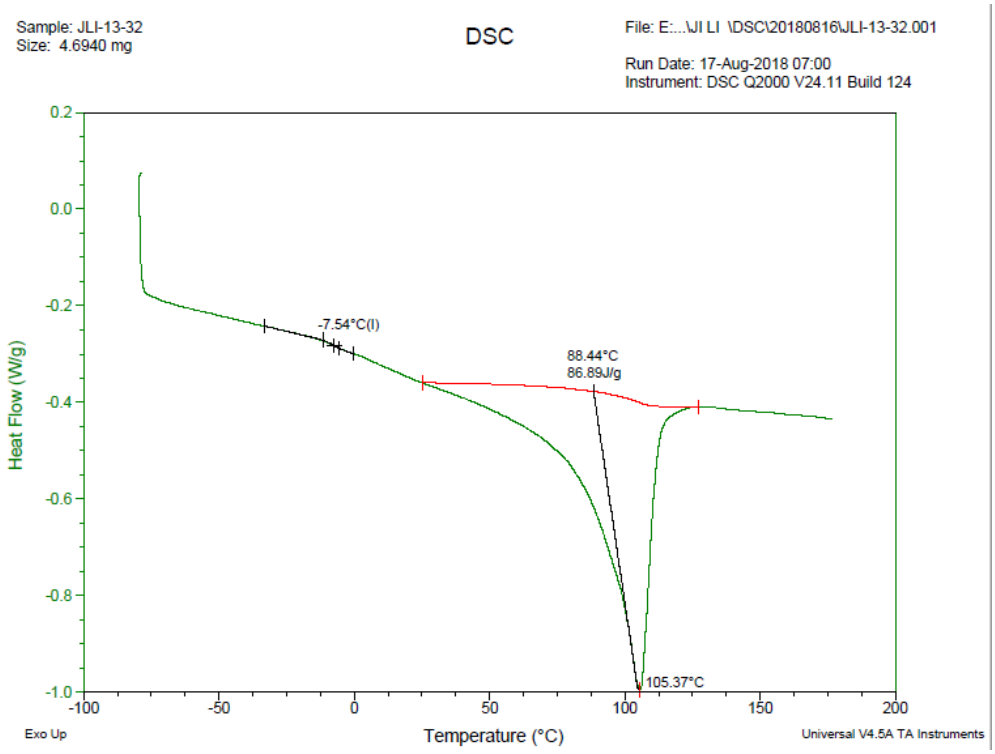


Figure S73. DSC spectrum of the sample from entry 7 in table 2.

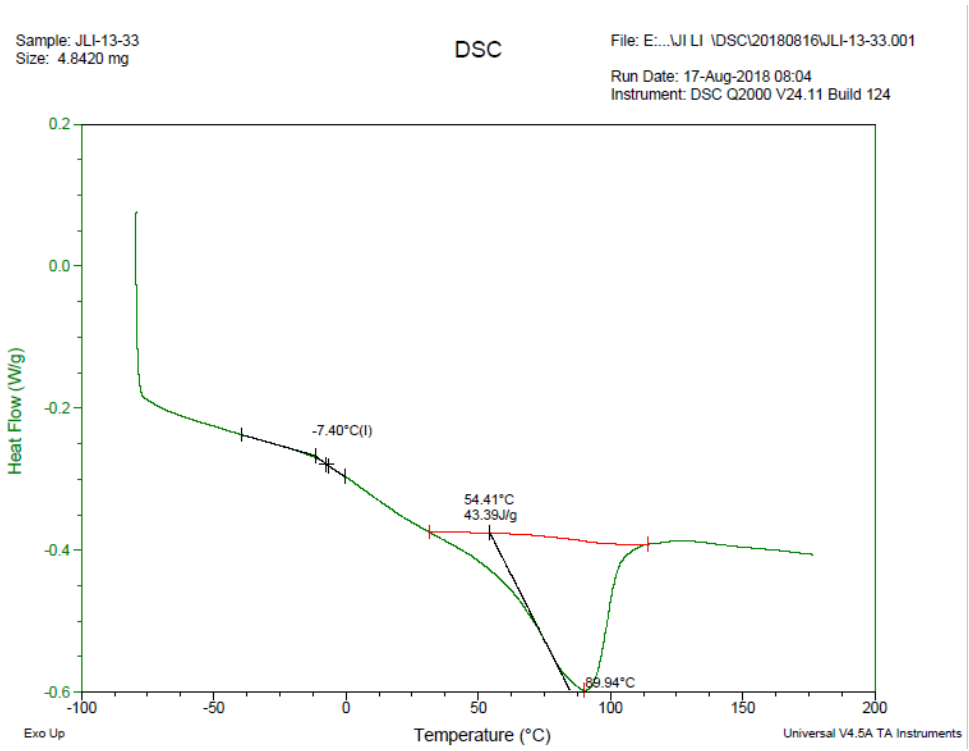


Figure S74. DSC spectrum of the sample from entry 8 in table 2.

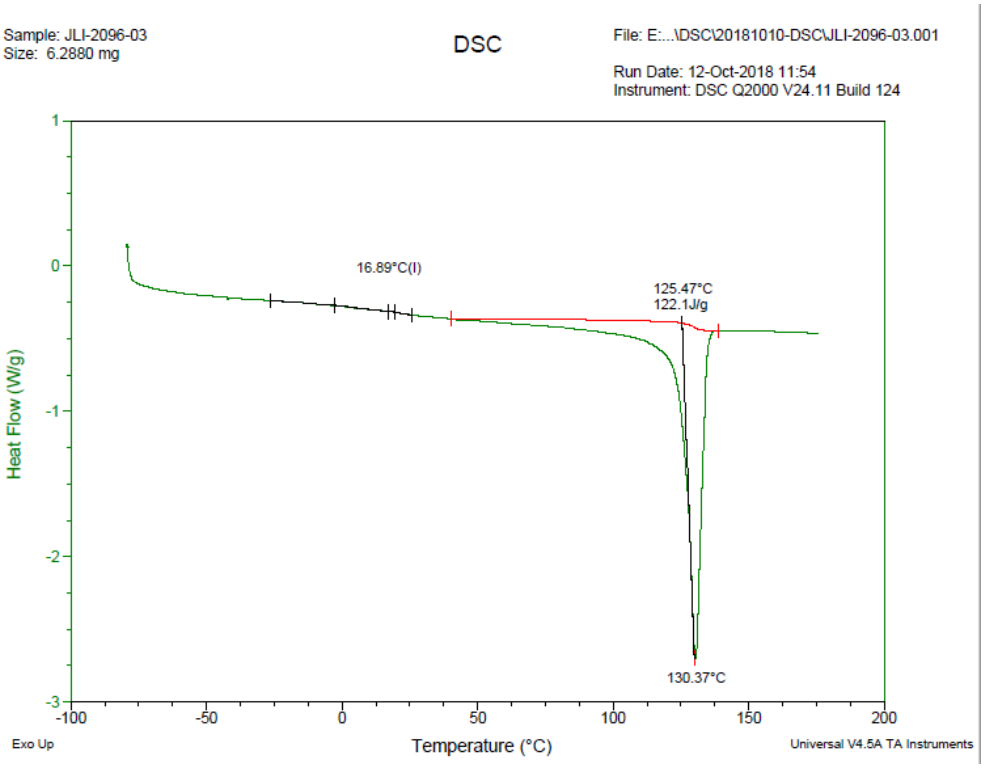


Figure S75. DSC spectrum of the sample from entry 9 in table 2.

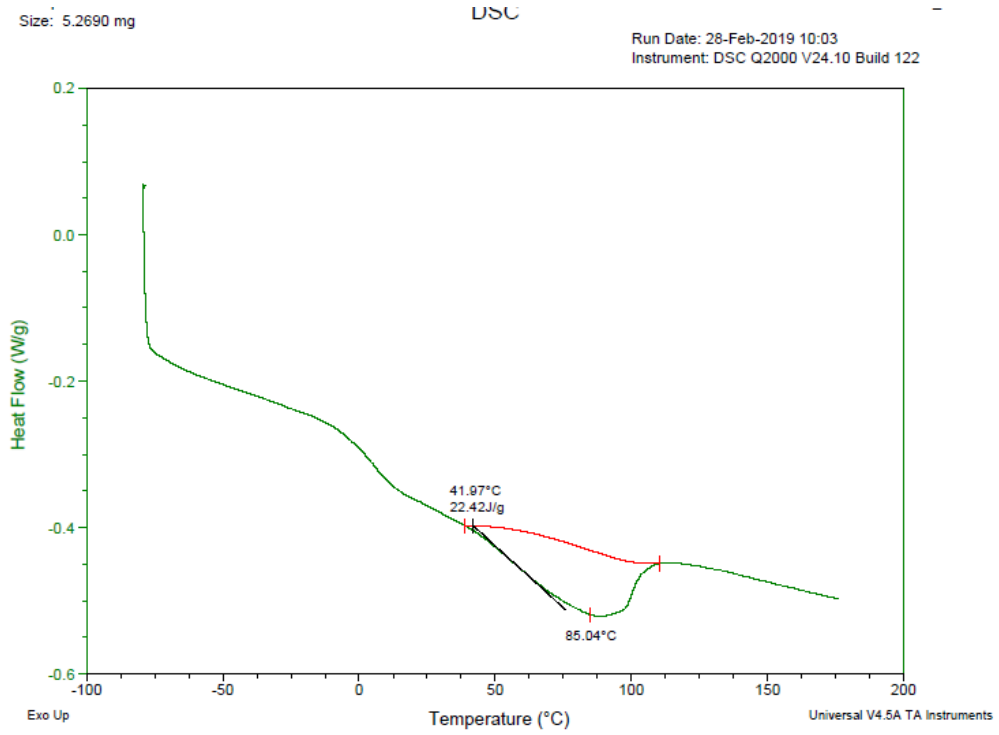


Figure S76. DSC spectrum of the sample from entry 10 in table 2.

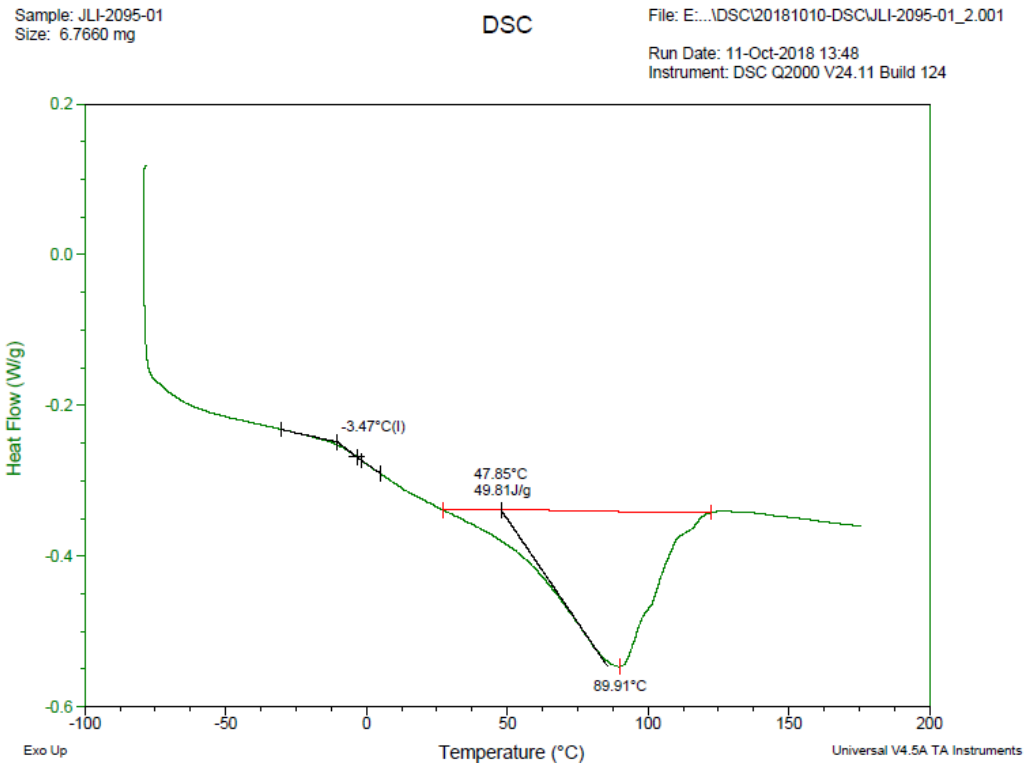


Figure S77. DSC spectrum of the sample from entry 1 in table 3.

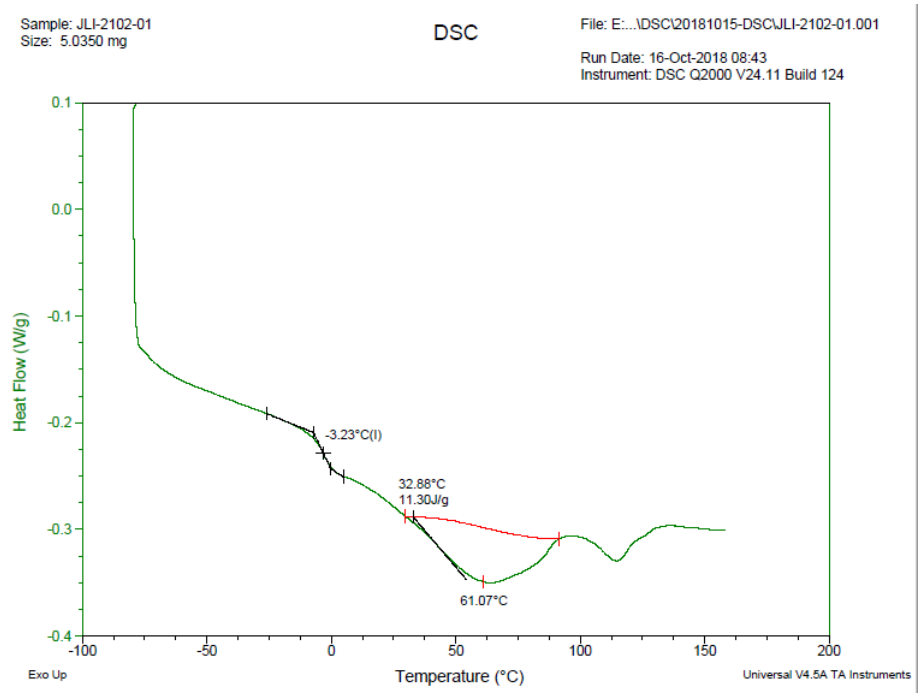


Figure S78. DSC spectrum of the sample from entry 2 in table 3.

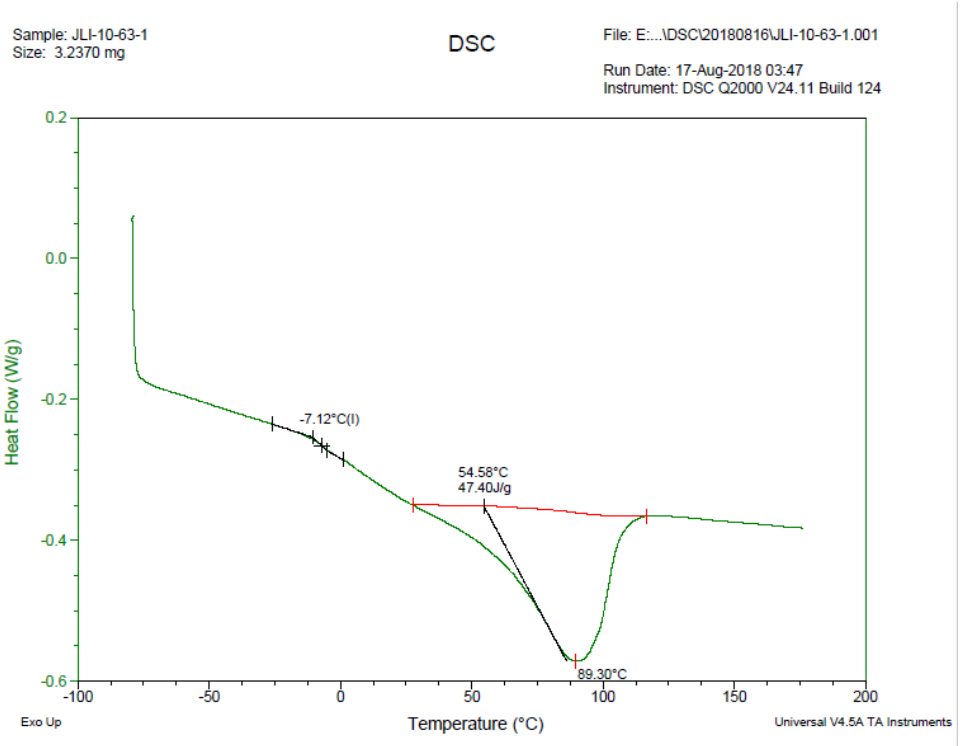


Figure S79. DSC spectrum of the sample from entry 3 in table 3.

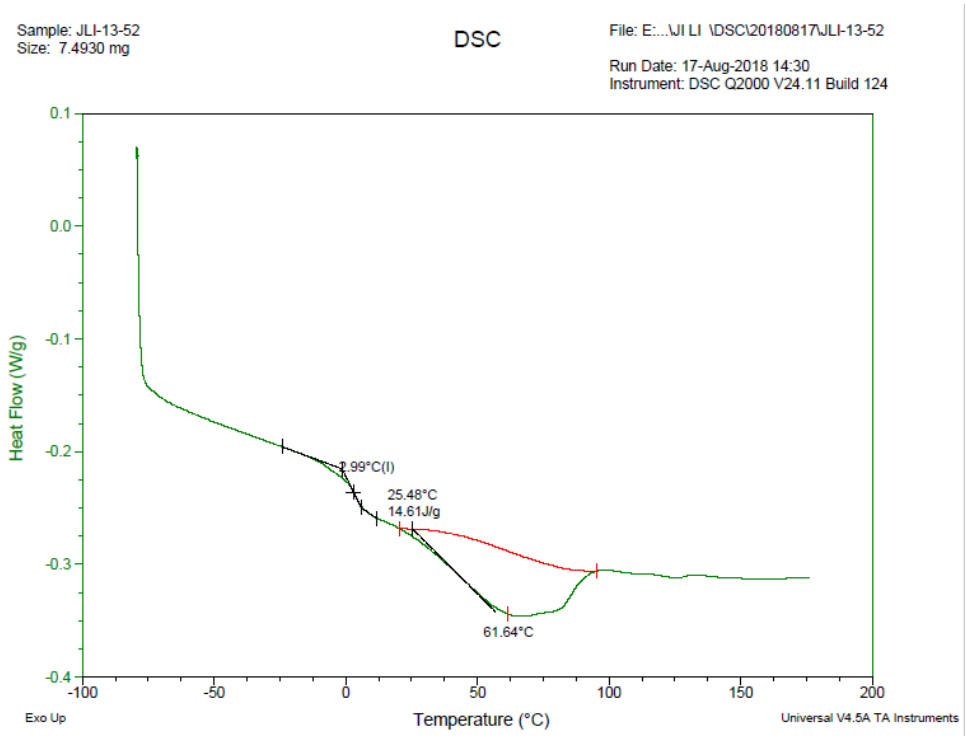


Figure S80. DSC spectrum of the sample from entry 4 in table 3.

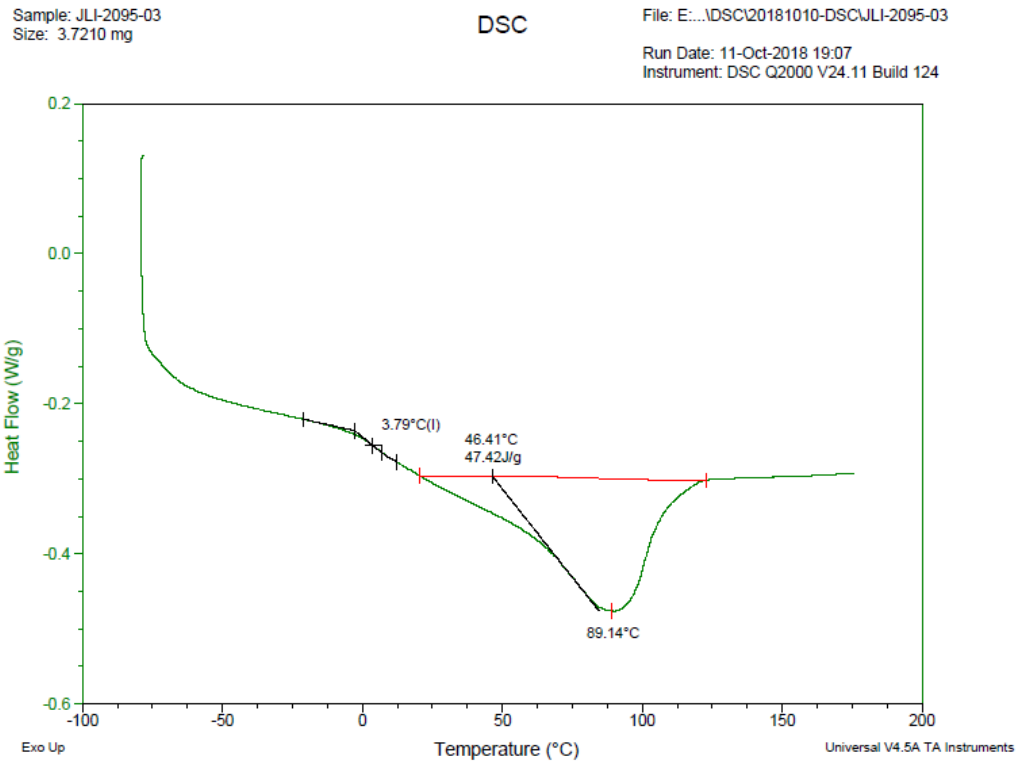


Figure S81. DSC spectrum of the sample from entry 5 in table 3.

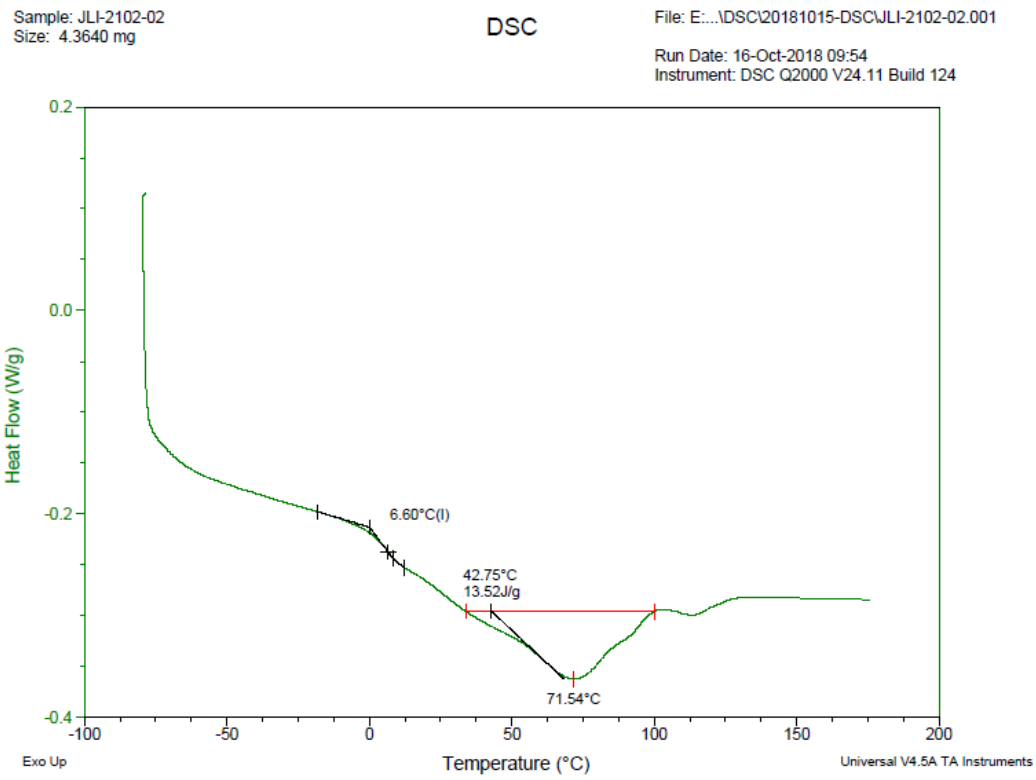


Figure S82. DSC spectrum of the sample from entry 6 in table 3.

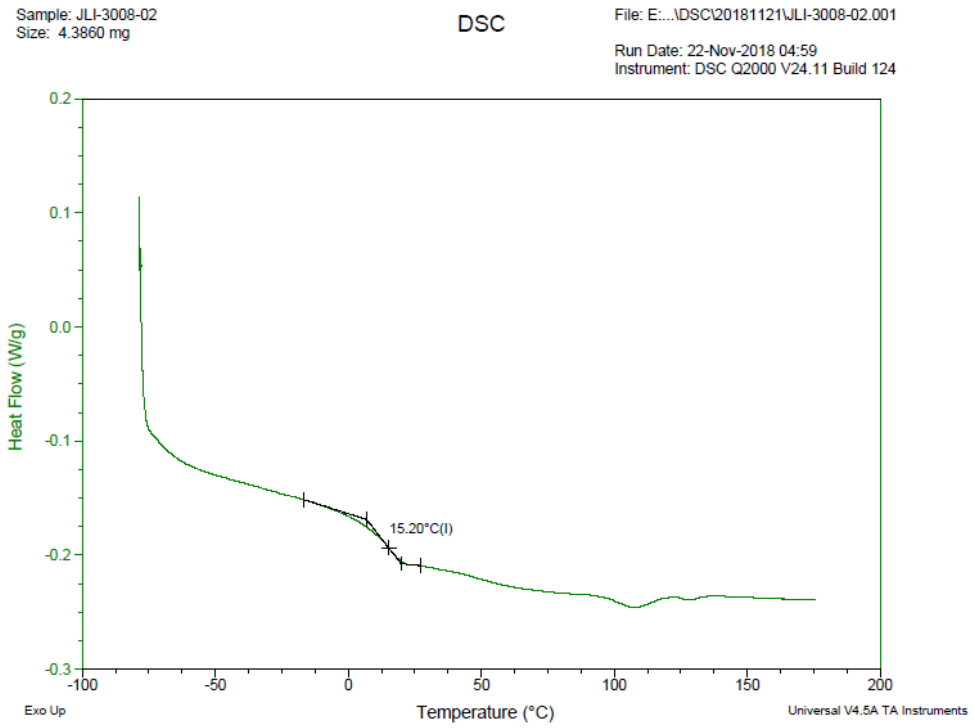


Figure S83. DSC spectrum of the sample from entry 7 in table 3.

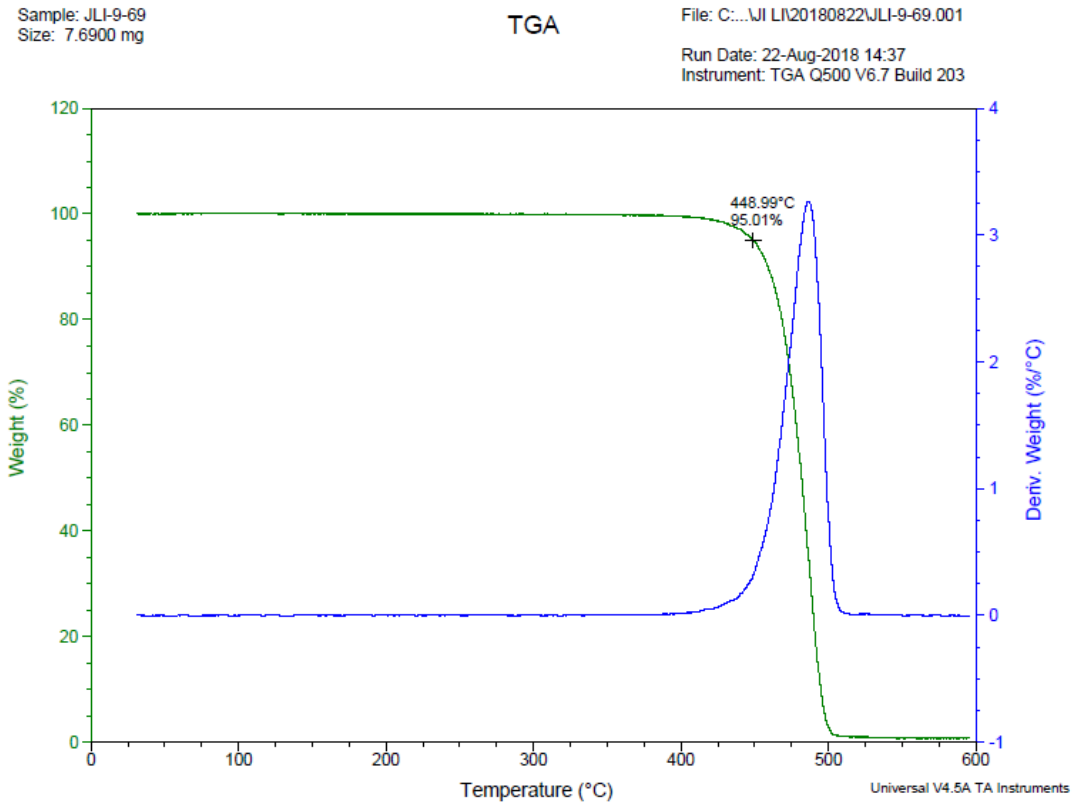


Figure S84. TGA spectrum of the sample from entry 1 in table 1.

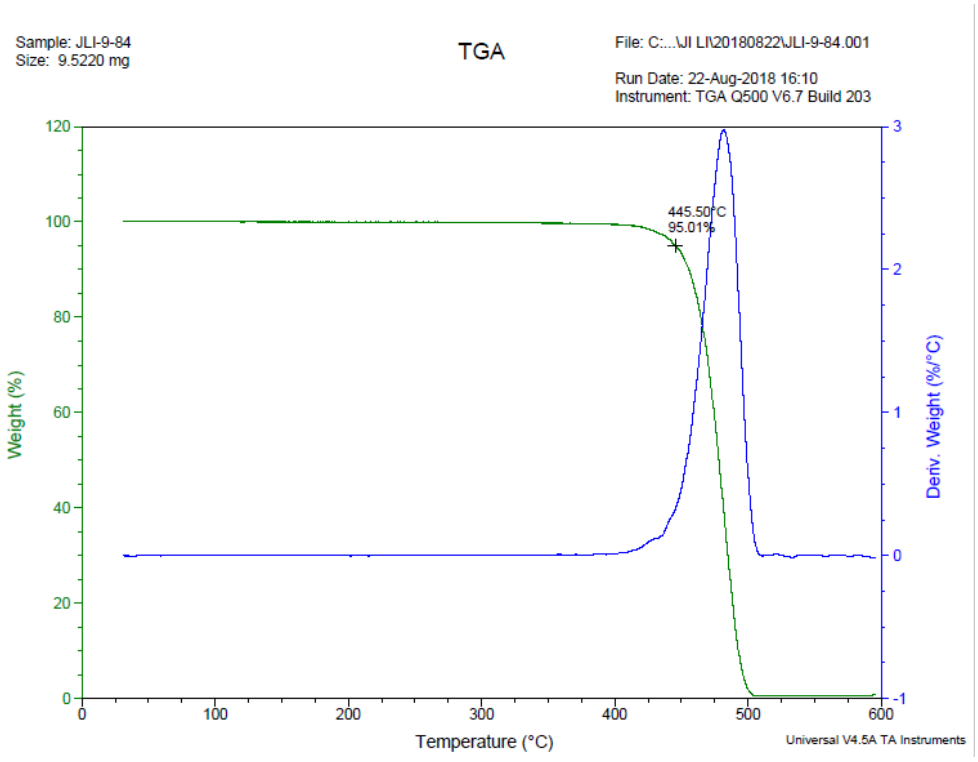


Figure S85. TGA spectrum of the sample from entry 2 in table 1.

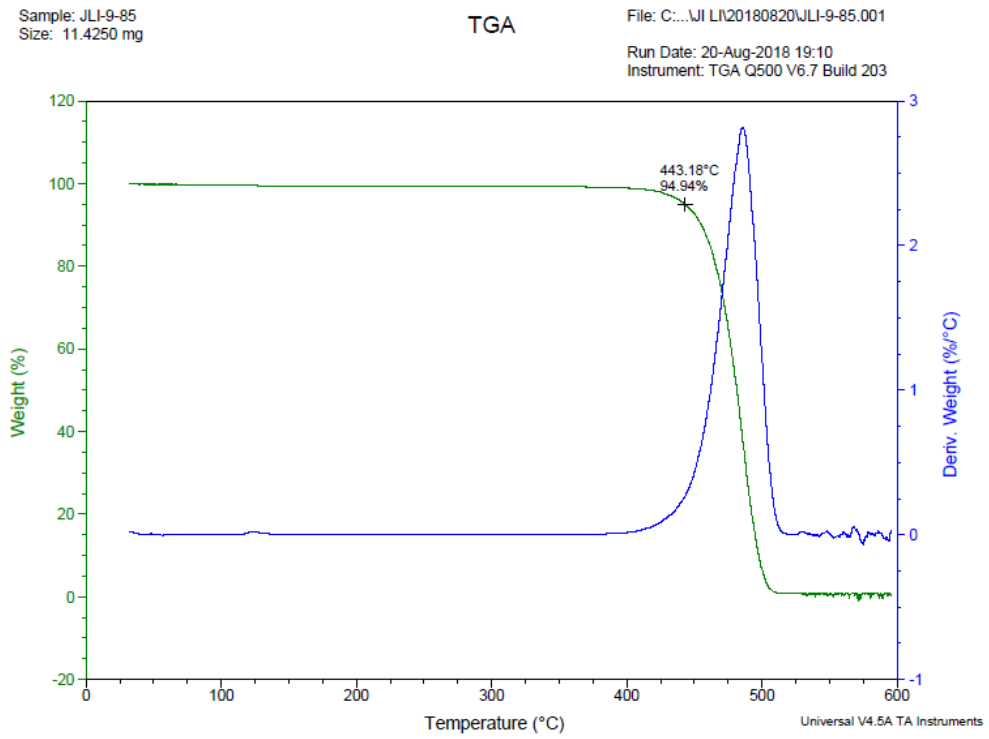


Figure S86. TGA spectrum of the sample from entry 3 in table 1.

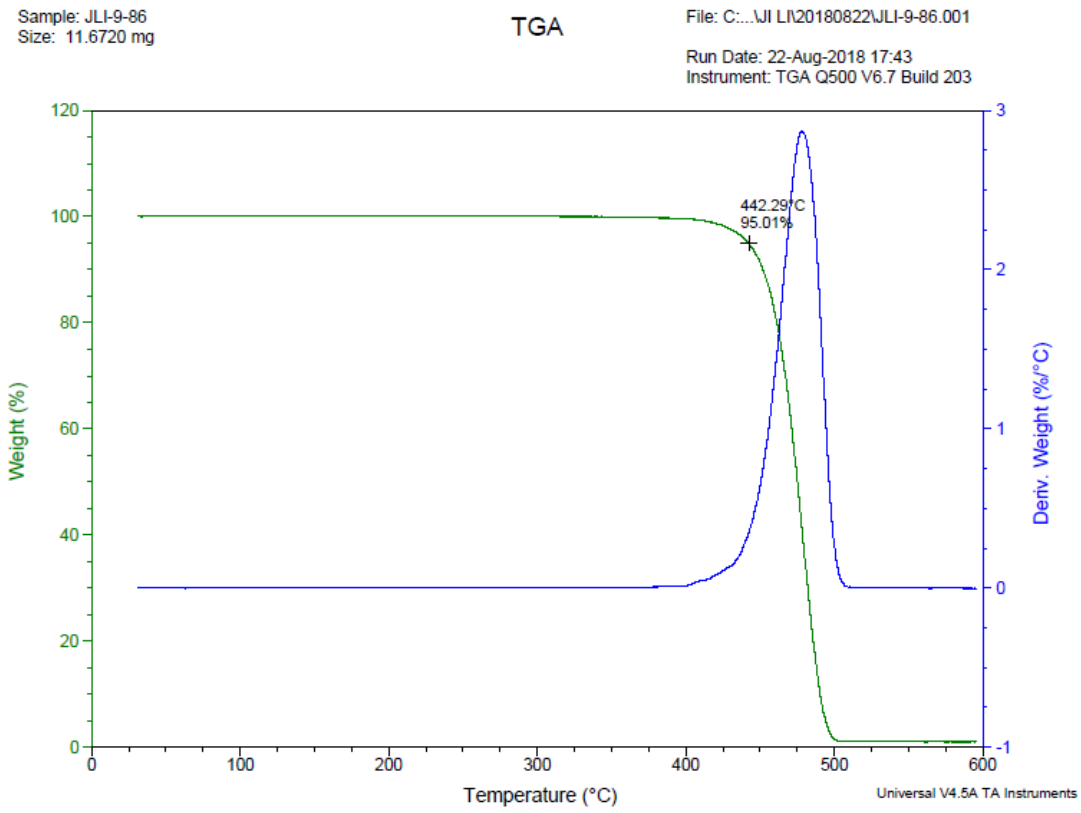


Figure S87. TGA spectrum of the sample from entry 4 in table 1.

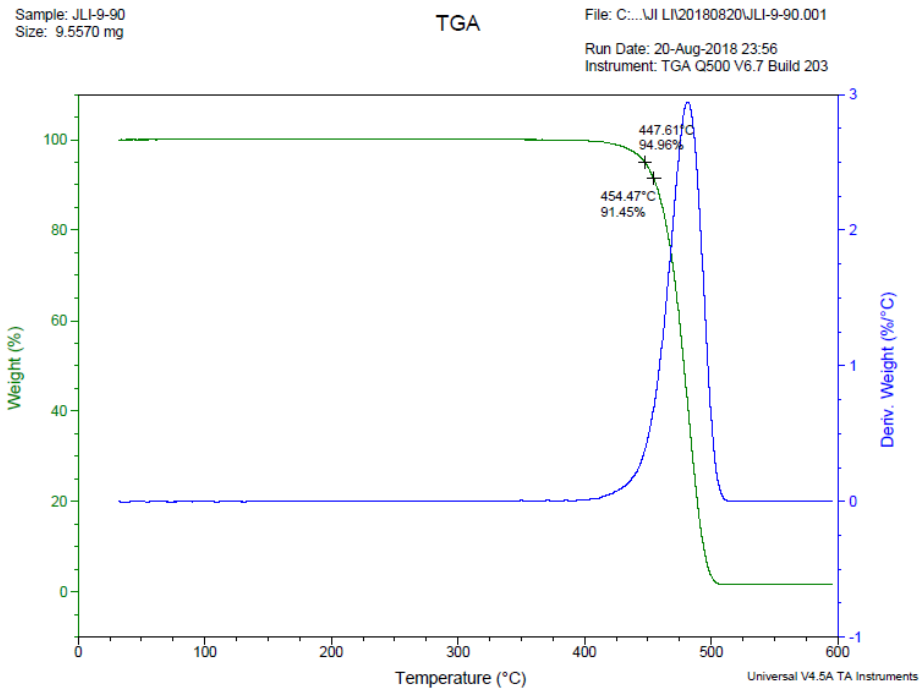


Figure S88. TGA spectrum of the sample from entry 5 in table 1.

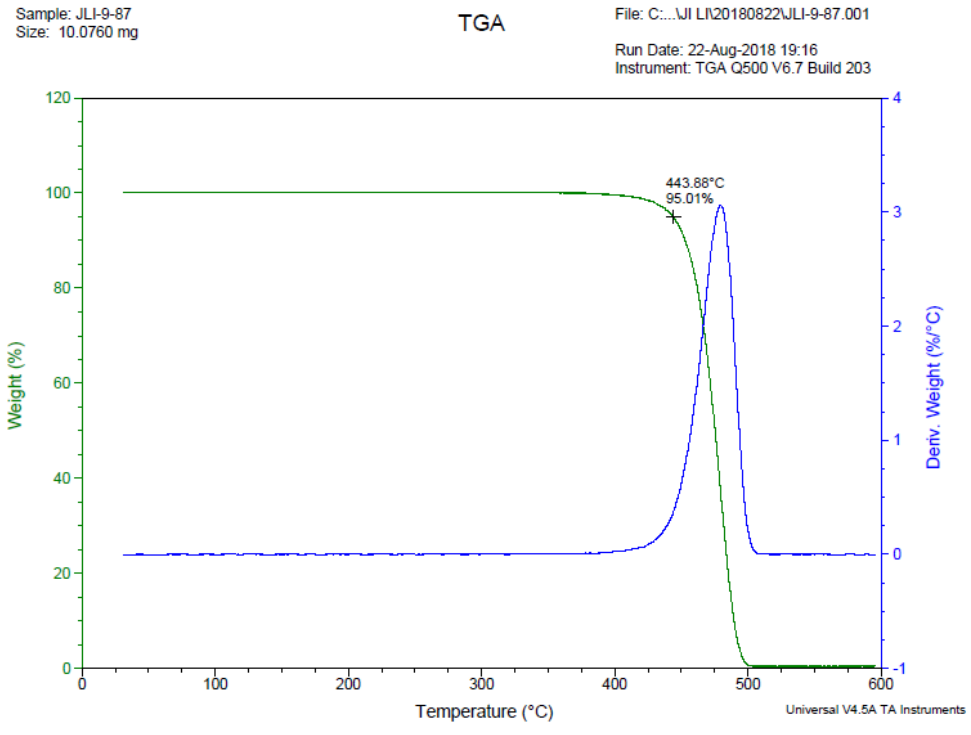


Figure S89. TGA spectrum of the sample from entry 6 in table 1.

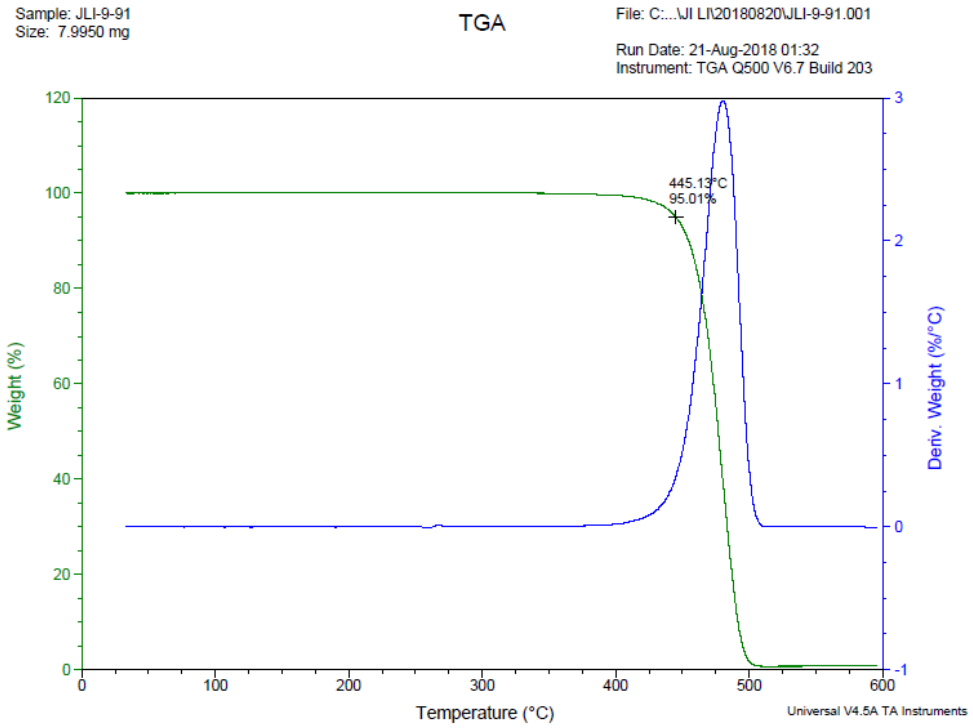


Figure S90. TGA spectrum of the sample from entry 7 in table 1

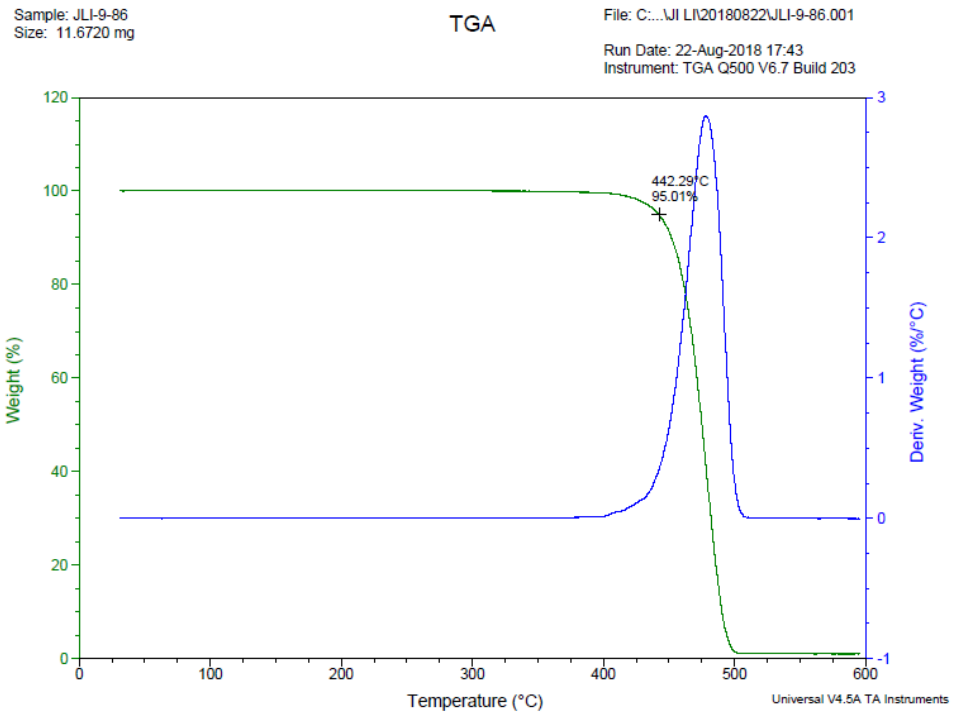


Figure S91. TGA spectrum of the sample from entry 1 in table 2.

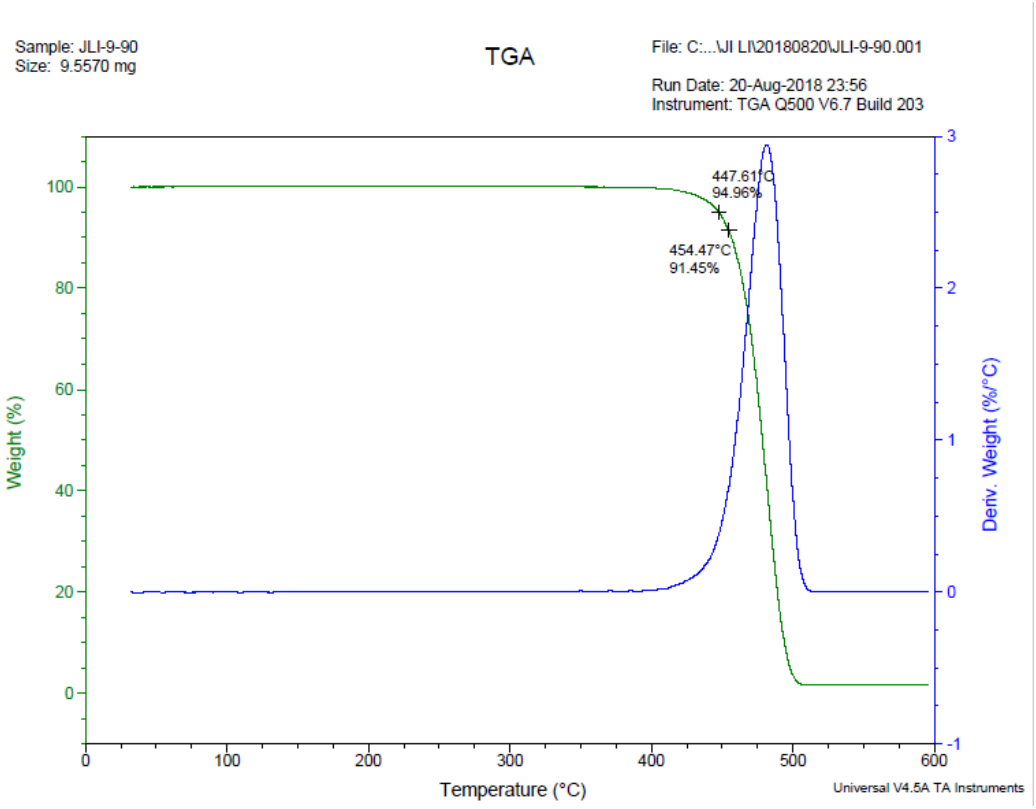


Figure S92. TGA spectrum of the sample from entry 2 in table 2.

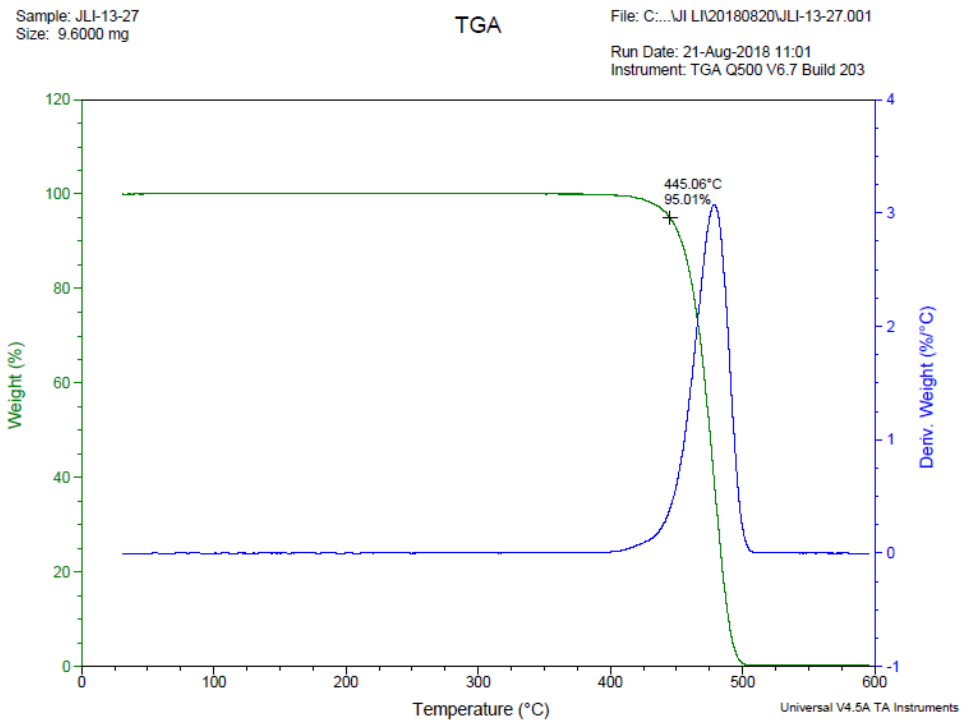


Figure S93. TGA spectrum of the sample from entry 4 in table 2.

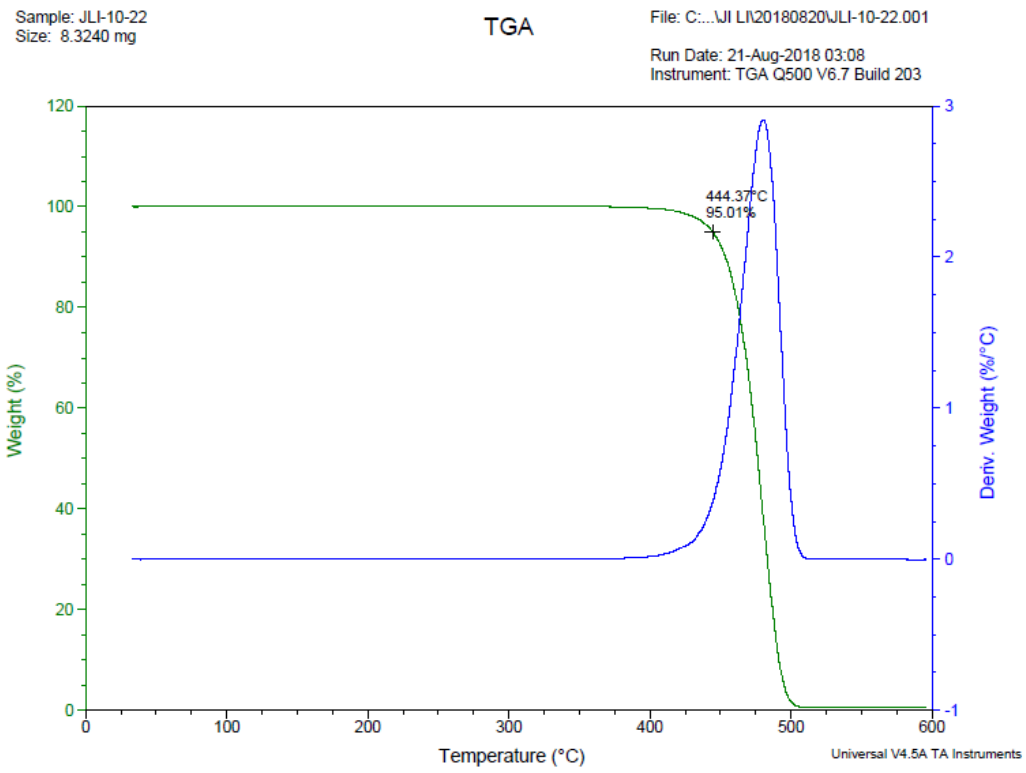


Figure S94. TGA spectrum of the sample from entry 5 in table 2.

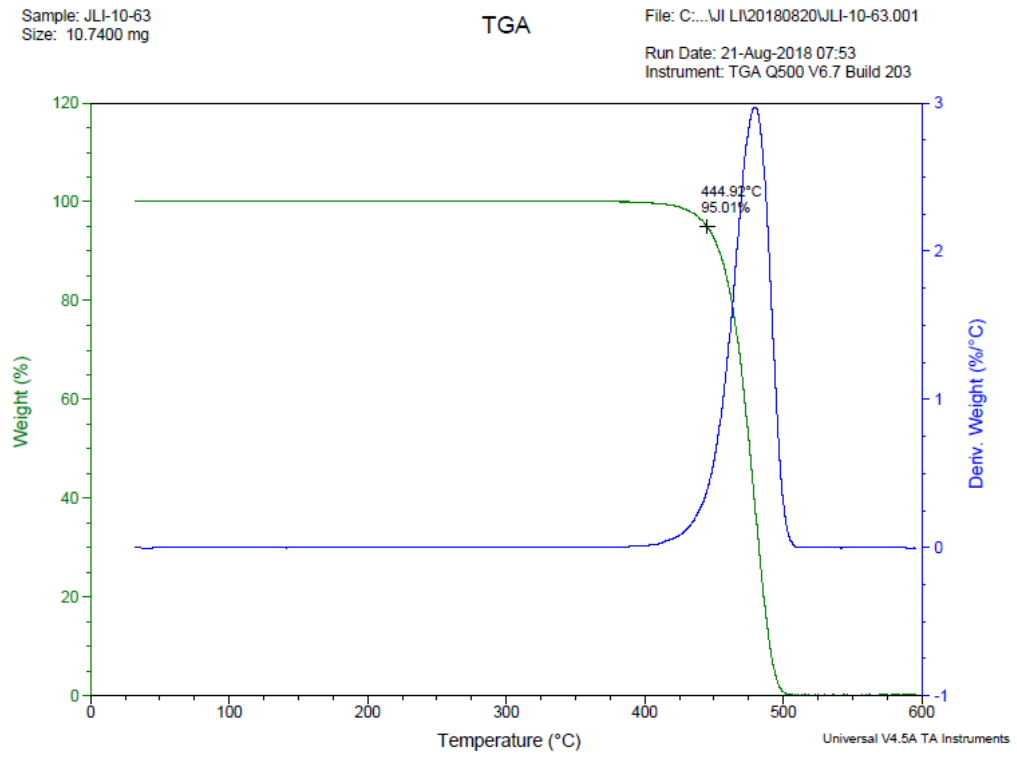


Figure S95. TGA spectrum of the sample from entry 6 in table 2.

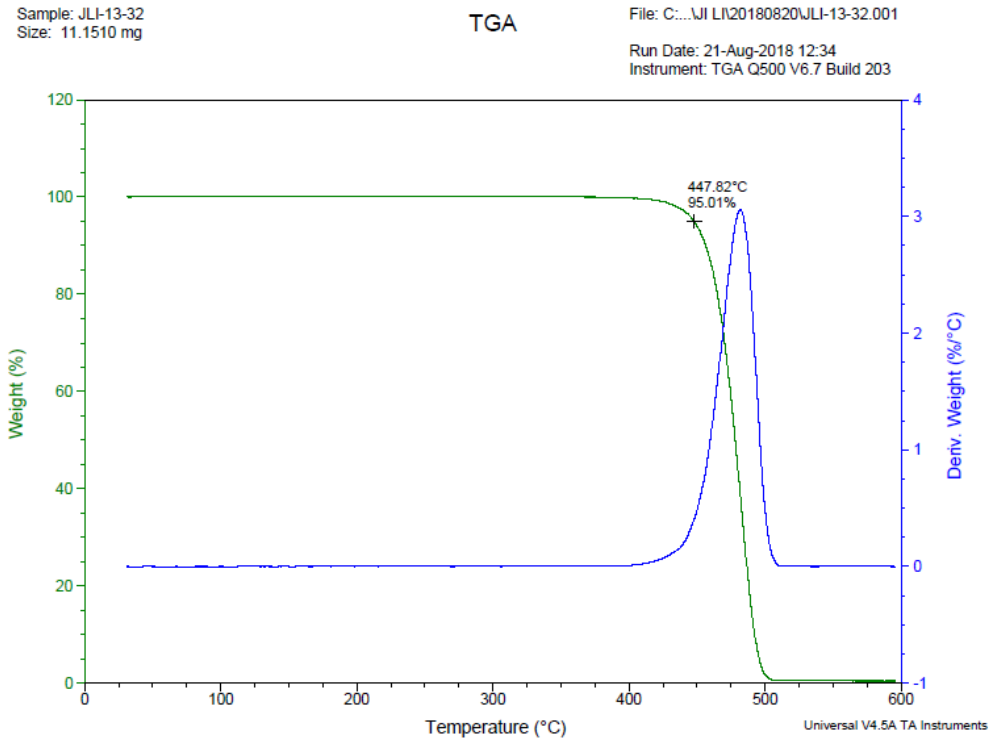


Figure S96. TGA spectrum of the sample from entry 7 in table 2.

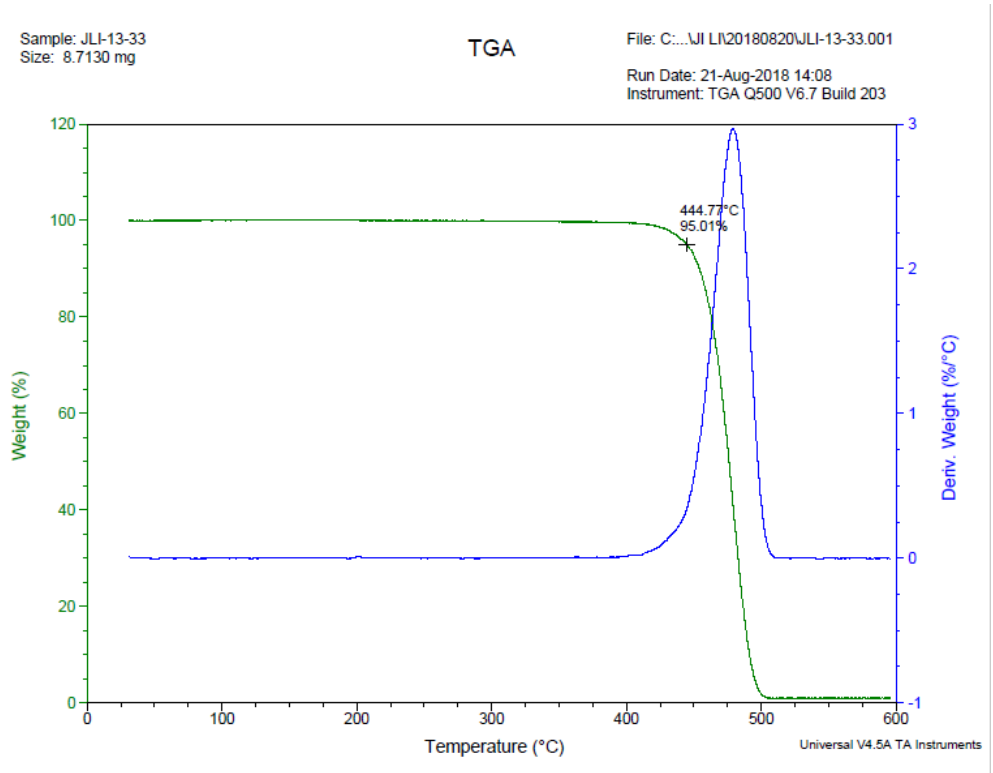


Figure S97. TGA spectrum of the sample from entry 8 in table 2.

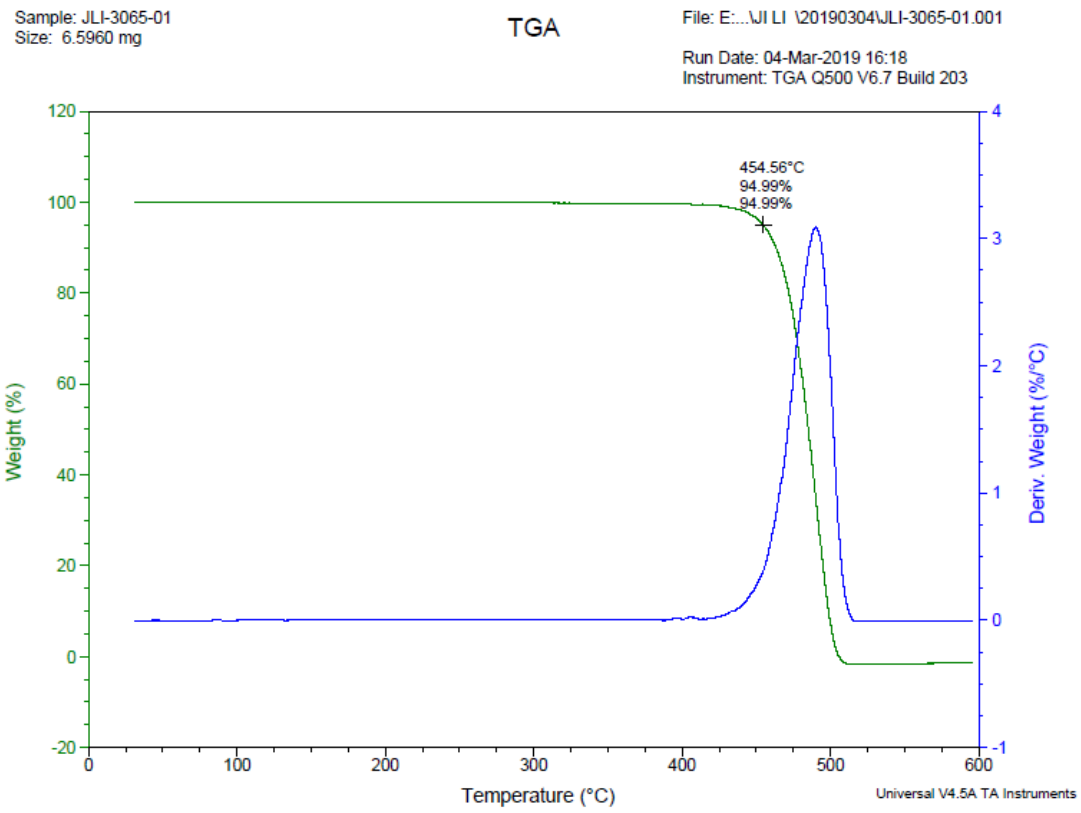


Figure S98. TGA spectrum of the sample from entry 9 in table 2.

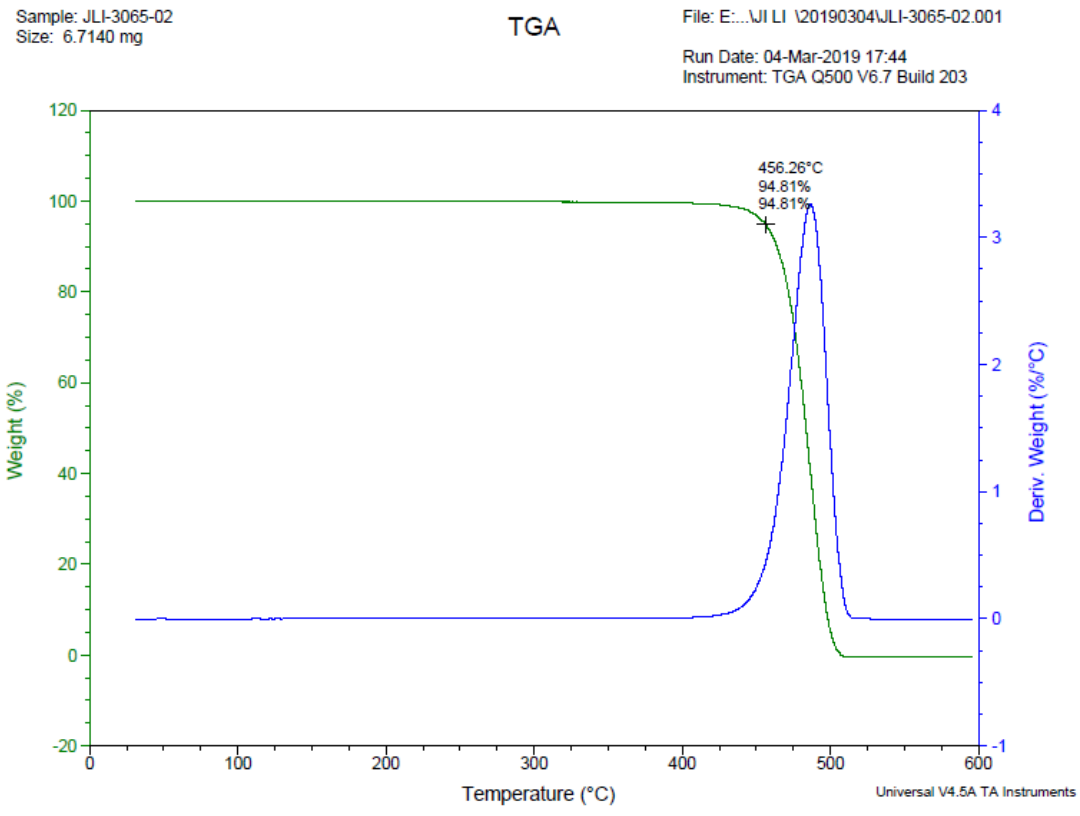
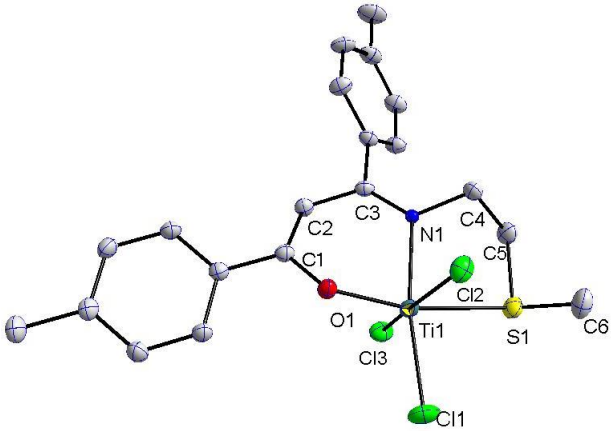
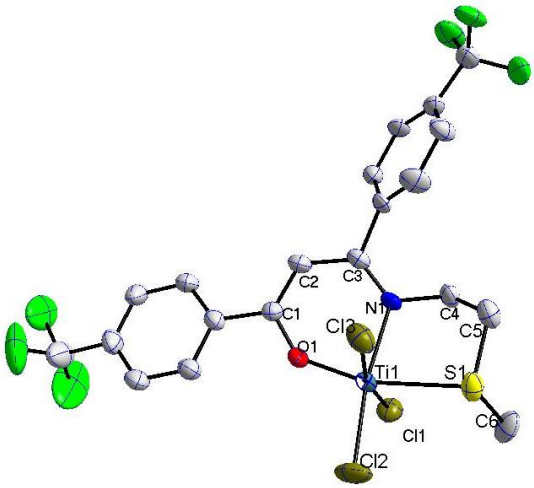


Figure S99. TGA spectrum of the sample from entry 10 in table 2.

7. X-Ray structures of complexes 4c-4d



Molecular structure of complex **4c** (H atoms are omitted for clarity). Selected bond lengths(Å) and angles (deg): Ti(1)-O(1) = 1.819(1), Ti(1)-N(1) = 2.154(2), Ti(1)-Cl(3) = 2.323(1), Ti(1)-Cl(1) = 2.267(1), Ti(1)-Cl(2) = 2.270(1), Ti(1)-S(1) = 2.588(1), O(1)-Ti(1)-N(1) = 84.91(6), O(1)-Ti(1)-Cl(1) = 105.35(5), N(1)-Ti(1)-Cl(1) = 169.66(5), O(1)-Ti(1)-Cl(2) = 97.42(5), N(1)-Ti(1)-Cl(2) = 87.40(5), O(1)-Ti(1)-Cl(3) = 91.99(5), N(1)-Ti(1)-Cl(3) = 84.84(5), Cl(1)-Ti(1)-Cl(2) = 92.41(3), Cl(1)-Ti(1)-Cl(3) = 93.42(3), Cl(2)-Ti(1)-Cl(3) = 167.22(3).



Molecular structure of complex **4d** (H atoms are omitted for clarity). Selected bond lengths(Å) and angles (deg): Ti-O(1) = 1.814(3), Ti(1)-N(1) = 2.143(4), Ti(1)-Cl(1) = 2.307(1), Ti(1)-Cl(2) = 2.258(1), Ti(1)-Cl(3) = 2.342(1), Ti(1)-S(1) = 2.557(1), O(1)-Ti(1)-N(1) = 83.9(1), O(1)-Ti(1)-Cl(1) = 96.0(1), N(1)-Ti(1)-Cl(1) = 87.6(1), O(1)-Ti(1)-Cl(2) = 105.4(1), N(1)-Ti(1)-Cl(2) = 170.3(1), O(1)-Ti(1)-Cl(3) = 92.7(1),

N(1)-Ti(1)-Cl(3) = 83.6(1), Cl(1)-Ti(1)-Cl(2) = 93.97(6), Cl(1)-Ti(1)-Cl(3) = 166.86(5), Cl(2)-Ti(1)-Cl(3) = 93.21(6).

8. References

[1] D. Lim, F. Fang, G. Zhou, D. M. Coltart, *Org. Lett.*, **2007**, *9*, 4139–4142.

[2] (a) X-H. Yang, X-L.Sun, F-B. Han, B-Liu, Y.Tang. Z-Wang, M-L. Gao, Z-W. Xie, and S-Z .Bu. *Organometallics.* **2008**, *27,* 4618–4624. (b) X-H. Yang, Z-Wang, X-L. Sun, and Y. Tang, *Dalton Trans*., **2009**, 8945–8954.

[3] (a) E. Perez, J. P. Laval, M. Bon, I. Rico, A. J. Lattes, *J. Fluorine Chem*. 1988, **39**, 173–196. (b) C. J. Faulkner, R. E. Fischer, G. K. Jennings, *Macromolecules* 2010, **43**, 1203–1209.