Electronic Supporting Information for

Switchable Living Nickel(II) Sandwich α-Diimine Catalyst for Ethylene Polymerisation

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I. General Considerations

Air and/or moisture sensitive compounds were manipulated under an atmosphere of nitrogen using standard Schlenk techniques or in an MBraun Unilab glovebox. Column chromatography was performed using silica gel (particle size 40-64 μm, 230-400 mesh).

The ^{1}H NMR, ^{13}C{^{1}H} NMR and ^{19}F{^{13}C} NMR spectra were recorded on a Varian INOVA (400 MHz) and a Bruker AV III HD spectrometer with a broad band Prodigy cryoprobe ((^{1}H, 500MHz), (^{13}C, 126 MHz)) at 22 °C and were referenced to the residual solvent signal [$CDCl_3$: 7.26 ppm (^{1}H), 77.16 ppm (^{13}C)]. All J values are given in Hertz. All polymer samples were dissolved in 1,1,2,2-tetrachloroethane-d_2 in a 5 mm O. D. tube. Spectra were recorded at 130 °C and were referenced to the residual solvent signal [$Cl_2CDCDCl_2$: 6.00 ppm (^{1}H)]. ^{1}H NMR spectra of polymers were recorded on a Varian INOVA (500 MHz) spectrometer equipped with a ^{1}H/BB switchable with Z-pulse field gradient probe. DART-HRMS analyses were performed on a Thermo Scientific Exactive Orbitrap MS system with an Ion Sense DART ion source.

Molecular weights (M_n and M_w) and molecular weight distributions ($Đ$) were determined by gel permeation chromatography (GPC). Analyses were performed using an Agilent PL-220 equipped with a RI detector. The column set (three Agilent PL-Gel Mixed B columns and one PL-Gel Mixed B guard column) was eluted with 1,2,4-trichlorobenzene containing 0.01 wt% of 3,5-di-tert-butyl-4-hydroxytoluene (BHT) at 1.0 mL min^{-1} at 150 °C. Data were measured relative to a polyethylene calibration curve (Varian and Polymer Standards Service). Peak polymer melting temperatures (T_m) were measured by differential scanning calorimetry (DSC) using a Mettler Polymer DSC calorimeter equipped with an autosampler. Analyses were performed in aluminum pans under nitrogen and data were collected from the second heating run at a heating rate of 10 °C min^{-1} from 0 °C to 200 °C and cooled from 200 °C to 0 °C at a cooling rate of 10 °C min^{-1}.

Compression molding was carried out using a 4120 Hydraulic Unit Carver press and stainless-steel die molds. Mylar protective sheets were obtained from Carver. Uniaxial tensile elongation was carried out using a Shimadzu Autograph AGS-X tensile tester. Melt blends were prepared using a vertical conical counter-rotating twin screw batch compounder with a 2.5 mm diameter extrusion die and 5 g capacity mixing chamber. All polymer processing was carried out on pristine materials (i.e. no BHT, other anti-oxidants, or additives were added). Further experimental details are provided in the appropriate sections below.

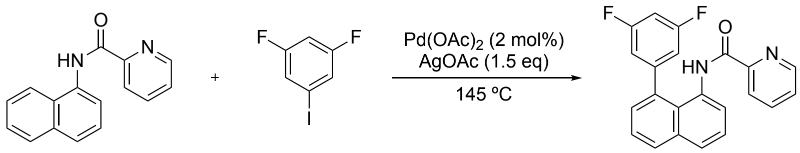
II. Materials

Acenaphthenequinone (Sigma), triphenyl phosphite (Sigma), sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (Sigma), zinc chloride (Strem), nickel bromide dimethoxyethane adduct (Strem), palladium acetate (Oakwood Chemicals), 1-napthylamine (AK Scientific), silver acetate (Oakwood Chemicals), potassium hydroxide (Macron), acetic acid (Macron), 2-picolinic acid (Alfa Aesar), potassium oxalate (Alfa Aesar), 3,5-difluoroiodobenzene (Oakwood Chemical), and pyridine (Fisher Scientific) were purchased and used as received. *N*-(Naphthalen-1-yl)picolinamide was prepared according to known literature procedure and its characterization data matched literature reports.[1]

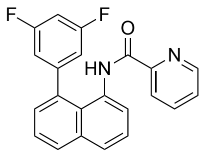
Anhydrous chlorobenzene was purchased from Sigma Aldrich, sparged with nitrogen for 40 minutes and stored over activated 4 Å molecular sieves. Toluene was purified over columns of alumina and copper(II) oxide (Q5) and degassed via three freeze-pump-thaw cycles prior to use. Ethylene (Matheson, ultra high purity 99.95%) was purified over columns of copper(II) oxide (Q5) and 4 Å molecular sieves. NMR solvents were purchased from Cambridge Isotope Laboratories and stored over activated 4 Å molecular sieves.

III. Preparation and Characterization of Aryl Naphthyl Ligand and Precursors

Scheme S1. Synthesis of amide precursor S1



S1

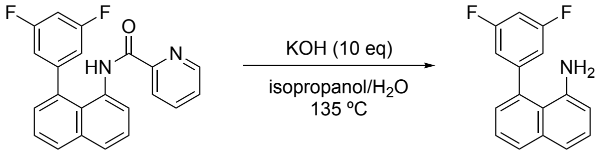


S1

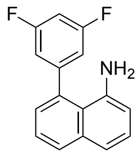
***N*-(8-(3,5-difluorophenyl)naphthalen-1-yl)picolinamide (S1)**

The synthetic procedure was adapted from a reported synthesis of a similar compound.[1] *N*-(Naphthalen-1-yl)picolinamide (1.97 g, 7.93 mmol), $Pd(OAc)_2$ (0.0354 g, 0.158 mmol), AgOAc (1.98 g, 11.9 mmol) and 3,5-difluoroiodobenzene (7.61 g, 31.7 mmol) were combined in a 100 mL pressure vessel. The reaction mixture was stirred at 145 °C for 24 h. After cooling to room temperature, the reaction mixture was diluted with CH_2Cl_2 and filtered through a pad of Celite. The solids were thoroughly washed with CH_2Cl_2 (100 mL). Combined filtrate and washings were concentrated *in vacuo*. The residue was purified by flash column chromatography in EtOAc/hexanes (gradient 1/20 to 1/3) affording product **S1** as a light orange solid (2.25 g, 79%). R_f = 0.24 (1/5 EtOAc/hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 9.50 (s, 1H), 8.33 (d, *J* = 4.2 Hz, 1H), 8.15 (t, *J* = 7.8 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.83 (t, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.41 (ddd, *J* = 7.6, 4.8, 1.1 Hz, 1H), 7.30 (d, *J* = 7.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 2.2 Hz, 2H), 6.39 (tt, *J* = 9.1, 2.3 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 162.75 (dd, *J* = 249.0, 13.0 Hz, 2C), 162.09, 149.64, 147.45, 146.36 (t, *J* = 9.6 Hz), 137.46, 135.56, 135.42, 132.43, 130.17, 129.77, 127.01, 126.41, 126.39, 125.40, 124.98, 123.96, 122.27, 112.49 (dd, *J* = 19.0, 6.0 Hz, 2C), 102.09 (t, *J* = 25.3 Hz). **^{19}F NMR** (400 MHz, $CDCl_3$, ppm) δ –110.60 (m, 2F). **HRMS** (DART-Orbitrap) *m/z* calculated for $C_{22}H_{15}F_2N_2O$ $[M+H]^+$ 361.11470, found 361.11551 (error 2.24 ppm).

Scheme S2. Synthesis of aniline precursor S2



S1 S2

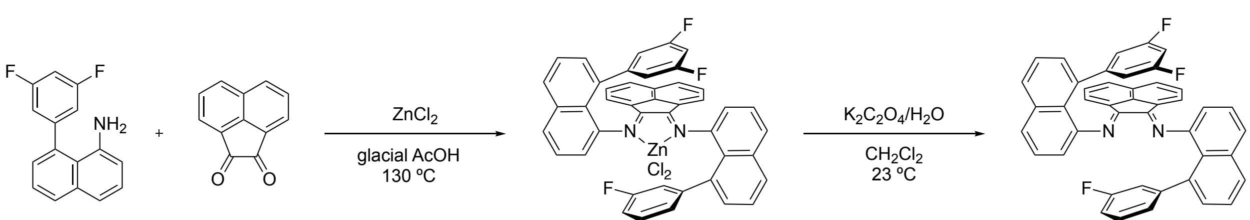


S2

8-(3,5-difluorophenyl)naphthalen-1-amine (S2)

A solution of KOH (3.74 g, 66.6 mmol) in isopropanol/H_2O (10/1 v/v, 36 mL) was added to *N*-(8-(3,5-difluorophenyl)naphthalen-1-yl)picolinamide (2.40 g, 6.66 mmol) in a 100 mL round bottom flask connected to a reflux condenser. The mixture was stirred at 135 °C for 24 h. After cooling to room temperature, the reaction was diluted with H_2O (40 mL) and transferred to a separatory funnel. The aqueous layer was extracted with EtOAc (3x40 mL). The combined organic layers were dried over $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash column chromatography in EtOAc/hexanes (1/10) affording product **S2** as a light red solid (1.26 g, 74%). R_f = 0.29 (1/10 EtOAc/hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.82 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.44 – 7.28 (m, 3H), 7.14 (dd, *J* = 7.0, 1.2 Hz, 1H), 7.00 (d, *J* = 5.6 Hz, 2H), 6.88 (tt, *J* = 9.0, 2.3 Hz, 1H), 6.69 (dd, *J* = 7.3, 1.3 Hz, 1H), 3.69 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 162.40 (dd, *J* = 250.5, 13.0 Hz, 2C), 146.83 (t, *J* = 9.4 Hz), 143.29, 135.97, 135.94, 129.68, 128.24, 126.97, 124.61, 120.34, 119.40, 112.80 (dd, *J* = 18.5, 6.0 Hz, 2C), 111.94, 103.11 (t, *J* = 25.1 Hz). **^{19}F NMR** (400 MHz, $CDCl_3$, ppm) δ –109.58 (m, 2F). **HRMS** (DART-Orbitrap) *m/z* calculated for $C_{16}H_{12}F_2N$ $[M+H]^+$ 256.09323, found 256.09378 (error 2.15 ppm).

Scheme S3. Synthesis of aryl naphthyl α-diimine S3



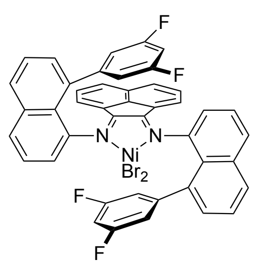
S2 S3

***N,N*-bis(8-(3,5-difluorophenyl)naphthalen-1-yl)acenaphthylene-1,2-diimine (S3)**

In an MBraun Unilab glovebox, a 20 mL scintillation vial was loaded with acenaphthenequinone (0.43 g, 2.4 mmol), 8-(3,5-difluorophenyl)naphthalen-1-amine (1.27 g, 4.98

mmol) and anhydrous $ZnCl_2$ (0.35 g, 2.6 mmol). The vial was removed from the glovebox and glacial AcOH (2 mL) was added. The resulting reaction mixture was stirred at 130 °C for 1 h. A bright red solid precipitated. After cooling to room temperature, the mixture was filtered and the resulting solid was washed with acetic acid (3x5 mL) and Et_2O (8x6 mL) and dried *in vacuo,* affording 1.46 g (78%) of a bright red solid. The zinc dichloride complex (1.46 g, 1.84 mmol) was then dissolved in CH_2Cl_2 (5 mL) and a solution of $K_2C_2O_4$ (0.90 g, 5.4 mmol) in H_2O (1 mL) was added. The resulting biphasic mixture was vigorously stirred at room temperature for 1 h. A white precipitate of $Zn(C_2O_4)$ was formed. The two phases were separated, and the organic layer was washed with H_2O (3x20 mL), dried over Na_2SO_4, filtered and concentrated *in vacuo*, affording product **S3** as a bright orange powder (1.10 g, 91% based on Zn dichloride complex). R_f = 0.41 (1/5 EtOAc/hexanes). **^{1}H NMR** (500 MHz, $CDCl_3$, ppm) δ 7.97 (d, *J* = 8.2 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.2 Hz, 2H), 7.68 (t, *J* = 7.7 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.19 (t, *J* = 7.7 Hz, 2H), 7.03 (dt, *J* = 15.6, 8.0 Hz, 6H), 6.45 (t, *J* = 8.9 Hz, 2H), 6.40 (d, *J* = 7.2 Hz, 2H), 5.47 (d, *J* = 9.0 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$, ppm) δ 161.89 (dd, *J* = 246.4, 12.2 Hz), 160.99 (dd, *J* = 246.4, 12.2 Hz), 160.35, 148.23, 147.29 (t, *J* = 9.9 Hz), 140.68, 136.87, 135.46, 130.95, 129.37, 129.29, 128.99, 128.76, 127.63, 126.68, 125.20, 125.19, 122.81, 121.89, 114.73, 113.93 (d, *J* = 21.3 Hz), 110.95 (d, *J* = 21.5 Hz), 101.61 (t, *J* = 25.0 Hz). **^{19}F NMR** (400 MHz, $CDCl_3$, ppm) δ –110.06 (m, 2F), –113.28 (m, 2F). **HRMS** (DART-Orbitrap) *m/z* calculated for $C_{44}H_{25}F_4N_2$ $[M+H]^+$ 657.19484, found 657.19586 (error 1.55 ppm).

IV. Preparation and Characterization of Complex 1



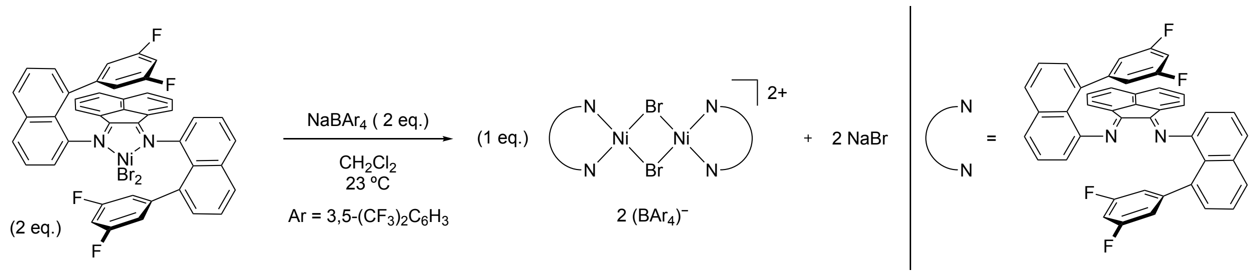
1

Complex 1

To a Schlenk tube containing α-diimine ligand **S3** (467 mg, 0.711 mmol) was added 25 mL of CH_2Cl_2 followed by $NiBr_2(DME)$ (199 mg, 0.645 mmol). Upon stirring for 24 h a red powdery precipitate formed. Volatiles were removed *in vacuo*, the red solid was washed with CH_2Cl_2, and excess solvent was removed via canula filtration. The red powder was dried *in vacuo* to obtain 424 mg of **1** (75%). **HRMS** (DART-Orbitrap) *m/z* calculated for $C_{44}H_{24}BrF_4N_2Ni$ $[M–Br]^+$ 793.04070, found 793.04205 (error 1.71 ppm). Attempts to obtain crystals of the complex suitable for X-ray analysis were unsuccessful.

V. Preparation and X-ray Crystallography Data for Complex 2

Scheme S4. Synthesis of Complex 2



1 **2**

In an MBraun Unilab glovebox, complex **1** (5.0 mg, 5.7 μmol), sodium tetrakis(3,5-bis(trifluoromethyl)phenyl)borate (NaBAr$_4$) (5.1 mg, 5.7 μmol) and CH_2Cl_2 (0.5 mL) were added to a 4 mL scintillation vial. The mixture was stirred vigorously for 5 minutes and filtered. The sample was crystallized by slow diffusion of pentane into the CH_2Cl_2 solution, yielding dark red crystals of **2**.

X-ray Structure Determination of Complex 2

Low-temperature X-ray diffraction data for **2** were collected on a Rigaku XtaLAB Synergy diffractometer coupled to a Rigaku Hypix detector with Cu Kα radiation (λ = 1.54184 Å), from a PhotonJet micro-focus X-ray source at 100 K. The diffraction images were processed and scaled using the CrysAlisPro software.[2] The structures were solved through intrinsic phasing using SHELXT[3] and refined against F^3 on all data by full-matrix least squares with SHELXL[4] following established refinement strategies.[5] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms bound to carbon were included in the model at geometrically calculated positions and refined using a riding model. The isotropic displacement parameters of all hydrogen atoms were fixed to 1.2 times the U(eq) value of the atoms they are linked to (1.5 times for methyl groups). Details of the data quality and a summary of the residual values of the refinements are listed in Tables S1-S5.

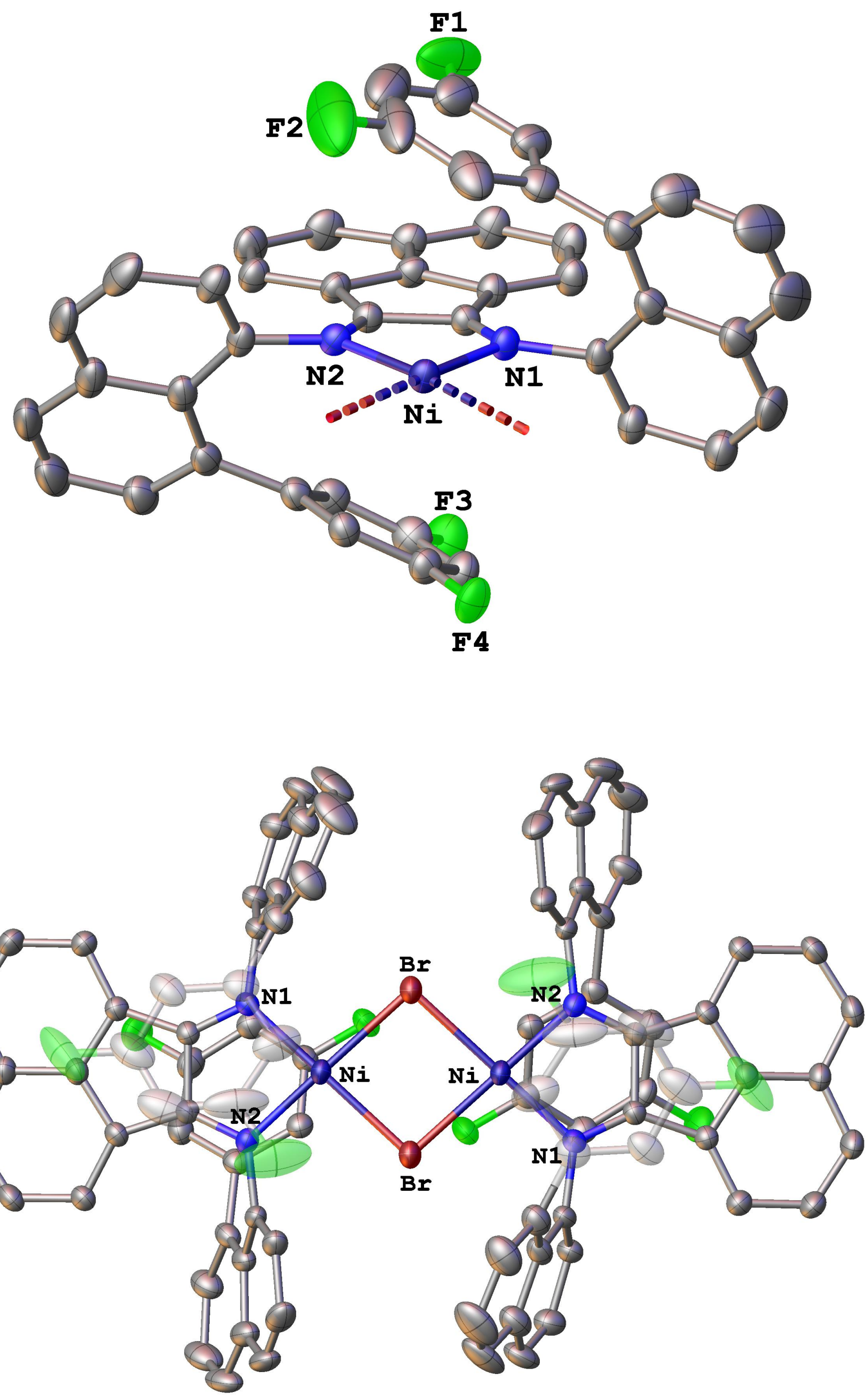


Figure S1. X-ray crystal structure of the dicationic complex **2**. Counterions, solvent and hydrogen atoms have been omitted for clarity. Displacement ellipsoids shown at 50% probability. (top) View of half of the dimer (Br atoms omitted for clarity). (bottom) Top view of the dimer (fluoroarene groups of the ligand have been faded for clarity).

Table S1. Crystal data and structure refinement for **2**.

Identification code	padilla_lnibr_cat	
Empirical formula	C153 H74 B2 Br2 Cl2 F56 N4 Ni2	
Formula weight	3401.92	
Temperature	100.01(10) K	
Wavelength	1.54184 Å	
Crystal system	Orthorhombic	
Space group	P b c n	
Unit cell dimensions	a = 35.5335(4) Å	α = 90°
	b = 18.9692(2) Å	β = 90°
	c = 20.8833(2) Å	γ = 90°
Volume	14076.2(3) $Å^3$	
Z	4	
Density (calculated)	1.605 Mg/m^3	
Absorption coefficient	2.503 mm^{-1}	
F(000)	6776	
Crystal size	0.189 x 0.17 x 0.075 mm^3	
Theta range for data collection	2.487 to 66.600°.	
Index ranges	-33<=h<=42, -18<=k<=22, -24<=l<=14	
Reflections collected	65136	
Independent reflections	12392 [R(int) = 0.0496]	
Completeness to theta = 66.600°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	1.00000 and 0.68671	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	12392 / 482 / 1123	
Goodness-of-fit on F^2	1.098	
Final R indices [I>2sigma(I)]	R1 = 0.0673, wR2 = 0.1829	
R indices (all data)	R1 = 0.0698, wR2 = 0.1855	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.111 and -0.968 e.$Å^{-3}$	

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x10^3) for **2**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br	5386(1)	7642(1)	7140(1)	37(1)
Ni	4770(1)	7582(1)	6784(1)	25(1)
F(1)	4179(1)	9056(2)	4698(2)	88(1)
F(2)	4234(1)	9671(2)	6852(3)	117(2)
F(3)	4485(1)	4951(2)	5063(1)	51(1)
F(4)	5124(1)	5761(1)	6867(1)	39(1)
N(1)	4897(1)	7500(2)	5897(1)	26(1)
N(2)	4258(1)	7441(2)	6497(1)	25(1)
C(1)	4751(1)	8941(2)	5251(2)	44(1)
C(2)	4374(1)	9128(3)	5245(3)	59(1)
C(3)	4192(2)	9360(3)	5764(4)	73(2)
C(4)	4395(2)	9425(3)	6308(4)	78(2)
C(5)	4782(2)	9237(2)	6361(3)	59(1)
C(6)	4960(1)	8989(2)	5814(2)	40(1)
C(7)	5370(1)	8810(2)	5808(2)	38(1)
C(8)	5622(1)	9348(3)	5893(3)	53(1)
C(9)	6009(2)	9246(3)	5816(3)	67(2)
C(10)	6140(1)	8606(3)	5640(3)	63(2)
C(11)	5892(1)	8018(2)	5555(2)	42(1)
C(12)	6033(1)	7347(3)	5376(2)	46(1)
C(13)	5802(1)	6779(2)	5319(2)	39(1)
C(14)	5418(1)	6853(2)	5469(2)	31(1)
C(15)	5275(1)	7489(2)	5641(2)	27(1)
C(16)	5500(1)	8119(2)	5669(2)	33(1)
C(17)	4608(1)	7345(2)	5548(2)	24(1)
C(18)	4538(1)	7219(2)	4870(2)	26(1)
C(19)	4756(1)	7195(2)	4323(2)	31(1)
C(20)	4574(1)	7069(2)	3733(2)	36(1)
C(21)	4190(1)	6956(2)	3692(2)	36(1)
C(22)	3959(1)	6968(2)	4246(2)	30(1)
C(23)	3568(1)	6842(2)	4278(2)	36(1)

C(24)	3382(1)	6875(2)	4852(2)	35(1)
C(25)	3566(1)	7031(2)	5433(2)	29(1)
C(26)	3950(1)	7156(2)	5420(2)	25(1)
C(27)	4142(1)	7111(2)	4826(2)	26(1)
C(28)	4240(1)	7316(2)	5889(2)	24(1)
C(29)	3925(1)	7438(2)	6900(2)	26(1)
C(30)	3848(1)	8064(2)	7192(2)	33(1)
C(31)	3518(1)	8136(3)	7565(2)	45(1)
C(32)	3276(1)	7580(3)	7612(2)	44(1)
C(33)	3352(1)	6932(3)	7314(2)	41(1)
C(34)	3082(1)	6378(3)	7336(2)	50(1)
C(35)	3146(1)	5750(3)	7046(3)	53(1)
C(36)	3491(1)	5626(2)	6751(2)	41(1)
C(37)	3771(1)	6130(2)	6718(2)	30(1)
C(38)	3696(1)	6826(2)	6974(2)	31(1)
C(39)	4137(1)	5896(2)	6450(2)	29(1)
C(40)	4145(1)	5555(2)	5857(2)	34(1)
C(41)	4482(1)	5291(2)	5637(2)	36(1)
C(42)	4816(1)	5356(2)	5955(2)	35(1)
C(43)	4799(1)	5698(2)	6539(2)	31(1)
C(44)	4471(1)	5966(2)	6800(2)	29(1)
B	3076(1)	6668(2)	2287(2)	26(1)
C(45)	2874(1)	6323(2)	1648(2)	27(1)
C(46)	3077(1)	6033(2)	1144(2)	28(1)
C(47)	2906(1)	5771(2)	593(2)	29(1)
C(48)	2520(1)	5795(2)	517(2)	28(1)
C(49)	2312(1)	6088(2)	1008(2)	30(1)
C(50)	2483(1)	6347(2)	1558(2)	29(1)
C(51)	3145(1)	5446(2)	84(2)	36(1)
C(52)	1892(1)	6115(2)	960(2)	36(1)
F(5)	3242(1)	4786(2)	236(1)	72(1)
F(6)	2970(1)	5383(2)	-476(1)	62(1)
F(7)	3465(1)	5770(2)	-5(2)	86(1)
F(8)	1762(1)	5914(2)	390(1)	65(1)
F(9)	1724(1)	5707(2)	1405(1)	51(1)
F(10)	1757(1)	6760(2)	1070(1)	54(1)

C(53)	3475(1)	6249(2)	2430(2)	25(1)
C(54)	3800(1)	6415(2)	2086(2)	26(1)
C(55)	4140(1)	6067(2)	2181(2)	26(1)
C(56)	4172(1)	5532(2)	2627(2)	30(1)
C(57)	3852(1)	5348(2)	2971(2)	32(1)
C(58)	3512(1)	5702(2)	2875(2)	27(1)
C(59)	4478(1)	6313(2)	1818(2)	33(1)
C(60)	3877(1)	4775(3)	3462(2)	47(1)
F(11)	4581(1)	6971(1)	1993(2)	53(1)
F(12)	4783(1)	5912(1)	1907(1)	40(1)
F(13)	4422(1)	6340(2)	1187(1)	50(1)
F(14)	4053(1)	4169(2)	3201(2)	54(1)
F(15)	4080(3)	4906(3)	3936(3)	107(3)
F(16)	3553(2)	4501(5)	3609(5)	80(3)
F(14B)	4221(3)	4571(6)	3590(5)	54(1)
F(15B)	3810(3)	5165(5)	4072(4)	45(2)
F(16B)	3592(5)	4349(11)	3525(9)	57(5)
C(61)	2791(1)	6593(2)	2903(2)	28(1)
C(62)	2719(1)	7136(2)	3334(2)	31(1)
C(63)	2481(1)	7046(2)	3864(2)	33(1)
C(64)	2306(1)	6410(2)	3979(2)	35(1)
C(65)	2365(1)	5862(2)	3547(2)	31(1)
C(66)	2603(1)	5957(2)	3022(2)	28(1)
C(67)	2401(1)	7661(2)	4298(2)	45(1)
C(68)	2158(1)	5182(2)	3619(2)	40(1)
F(17)	2624(3)	8200(4)	4222(5)	91(4)
F(18)	2049(2)	7821(6)	4302(5)	98(5)
F(19)	2465(3)	7473(3)	4915(2)	71(2)
F(17B)	2702(3)	7980(9)	4475(9)	104(6)
F(18B)	2188(6)	7530(6)	4783(7)	106(6)
F(19B)	2225(4)	8181(5)	3983(5)	76(4)
F(20)	2034(1)	5066(2)	4208(1)	67(1)
F(21)	1855(1)	5164(2)	3242(2)	66(1)
F(22)	2364(1)	4624(2)	3453(2)	65(1)
C(69)	3175(1)	7495(2)	2158(2)	35(1)
C(70)	3413(1)	7869(2)	2567(2)	36(1)

C(71)	3504(1)	8574(2)	2489(2)	49(1)
C(72)	3457(4)	8971(6)	1952(5)	35(3)
C(73)	3252(3)	8587(5)	1511(4)	32(2)
C(74)	3123(4)	7899(5)	1604(5)	27(3)
C(75)	3763(1)	8912(2)	2998(3)	55(1)
C(76)	3168(3)	8944(5)	877(5)	54(3)
C(72B)	3287(3)	8910(6)	1994(5)	65(3)
C(73B)	3016(4)	8577(4)	1598(4)	62(2)
C(74B)	2955(3)	7850(5)	1683(5)	46(2)
C(76B)	2799(4)	8978(6)	1080(5)	92(3)
F(23)	3605(1)	8940(2)	3562(1)	62(1)
F(24)	4085(1)	8559(2)	3052(3)	101(2)
F(25)	3853(1)	9575(2)	2826(2)	78(1)
F(26)	3431(3)	9389(4)	703(3)	65(2)
F(27)	3127(3)	8492(4)	405(3)	88(4)
F(28)	2857(3)	9309(7)	907(8)	89(4)
F(26B)	3028(5)	9222(7)	636(5)	151(5)
F(27B)	2638(2)	9539(3)	1325(4)	95(2)
F(28B)	2520(3)	8610(4)	840(4)	139(4)
Cl(1S)	4957(1)	8828(1)	3382(1)	60(1)
Cl(2S)	5658(1)	8485(2)	4006(1)	77(1)
C(1S)	5439(3)	8689(5)	3286(4)	52(2)

Table S3. Bond lengths [Å] and angles [°] for **2**.

Br-Ni	2.3139(7)	C(19)-C(20)	1.412(5)
Br-Ni#1	2.3153(7)	C(20)-C(21)	1.384(6)
Ni-N(1)	1.914(3)	C(21)-C(22)	1.417(5)
Ni-N(2)	1.932(3)	C(22)-C(23)	1.415(5)
F(1)-C(2)	1.342(7)	C(22)-C(27)	1.400(5)
F(2)-C(4)	1.353(7)	C(23)-C(24)	1.368(6)
F(3)-C(41)	1.362(4)	C(24)-C(25)	1.409(5)
F(4)-C(43)	1.348(4)	C(25)-C(26)	1.385(5)
N(1)-C(15)	1.447(5)	C(26)-C(27)	1.417(5)
N(1)-C(17)	1.293(5)	C(26)-C(28)	1.456(5)
N(2)-C(28)	1.293(5)	C(29)-C(30)	1.362(5)
N(2)-C(29)	1.454(5)	C(29)-C(38)	1.426(5)
C(1)-C(2)	1.387(7)	C(30)-C(31)	1.412(6)
C(1)-C(6)	1.395(7)	C(31)-C(32)	1.364(7)
C(2)-C(3)	1.337(9)	C(32)-C(33)	1.404(7)
C(3)-C(4)	1.352(10)	C(33)-C(34)	1.424(7)
C(4)-C(5)	1.427(9)	C(33)-C(38)	1.428(5)
C(5)-C(6)	1.387(7)	C(34)-C(35)	1.354(8)
C(6)-C(7)	1.494(6)	C(35)-C(36)	1.393(7)
C(7)-C(8)	1.371(6)	C(36)-C(37)	1.382(6)
C(7)-C(16)	1.422(6)	C(37)-C(38)	1.449(6)
C(8)-C(9)	1.397(8)	C(37)-C(39)	1.485(5)
C(9)-C(10)	1.351(8)	C(39)-C(40)	1.399(5)
C(10)-C(11)	1.431(7)	C(39)-C(44)	1.399(5)
C(11)-C(12)	1.418(7)	C(40)-C(41)	1.378(6)
C(11)-C(16)	1.423(6)	C(41)-C(42)	1.367(6)
C(12)-C(13)	1.360(6)	C(42)-C(43)	1.382(5)
C(13)-C(14)	1.410(5)	C(43)-C(44)	1.383(5)
C(14)-C(15)	1.357(5)	B-C(45)	1.652(5)
C(15)-C(16)	1.439(5)	B-C(53)	1.652(5)
C(17)-C(18)	1.457(5)	B-C(61)	1.643(5)
C(17)-C(28)	1.488(5)	B-C(69)	1.629(6)
C(18)-C(19)	1.383(5)	C(45)-C(46)	1.391(5)
C(18)-C(27)	1.425(5)	C(45)-C(50)	1.401(5)

C(46)-C(47)	1.393(5)	C(65)-C(68)	1.493(6)
C(47)-C(48)	1.381(5)	C(67)-F(17)	1.302(8)
C(47)-C(51)	1.494(5)	C(67)-F(18)	1.286(6)
C(48)-C(49)	1.382(5)	C(67)-F(19)	1.357(7)
C(49)-C(50)	1.389(5)	C(67)-F(17B)	1.283(10)
C(49)-C(52)	1.495(5)	C(67)-F(18B)	1.290(9)
C(51)-F(5)	1.337(5)	C(67)-F(19B)	1.340(8)
C(51)-F(6)	1.330(4)	C(68)-F(20)	1.325(5)
C(51)-F(7)	1.306(5)	C(68)-F(21)	1.333(5)
C(52)-F(8)	1.331(5)	C(68)-F(22)	1.332(5)
C(52)-F(9)	1.350(5)	C(69)-C(70)	1.397(6)
C(52)-F(10)	1.335(5)	C(69)-C(74)	1.399(10)
C(53)-C(54)	1.398(5)	C(69)-C(74B)	1.431(9)
C(53)-C(58)	1.400(5)	C(70)-C(71)	1.386(6)
C(54)-C(55)	1.391(5)	C(71)-C(72)	1.360(10)
C(55)-C(56)	1.382(5)	C(71)-C(75)	1.545(7)
C(55)-C(59)	1.495(5)	C(71)-C(72B)	1.439(10)
C(56)-C(57)	1.390(5)	C(72)-C(73)	1.381(11)
C(57)-C(58)	1.395(5)	C(73)-C(74)	1.396(10)
C(57)-C(60)	1.496(6)	C(73)-C(76)	1.517(12)
C(59)-F(11)	1.351(5)	C(75)-F(23)	1.306(7)
C(59)-F(12)	1.338(5)	C(75)-F(24)	1.329(6)
C(59)-F(13)	1.333(4)	C(75)-F(25)	1.346(6)
C(60)-F(14)	1.417(6)	C(76)-F(26)	1.311(11)
C(60)-F(15)	1.251(6)	C(76)-F(27)	1.314(10)
C(60)-F(16)	1.299(7)	C(76)-F(28)	1.303(12)
C(60)-F(14B)	1.311(9)	C(72B)-C(73B)	1.417(11)
C(60)-F(15B)	1.494(9)	C(73B)-C(74B)	1.408(10)
C(60)-F(16B)	1.301(12)	C(73B)-C(76B)	1.530(13)
C(61)-C(62)	1.392(5)	C(76B)-F(26B)	1.318(11)
C(61)-C(66)	1.401(5)	C(76B)-F(27B)	1.314(11)
C(62)-C(63)	1.405(5)	C(76B)-F(28B)	1.312(11)
C(63)-C(64)	1.377(6)	Cl(1S)-C(1S)	1.745(12)
C(63)-C(67)	1.503(6)	Cl(2S)-C(1S)	1.736(10)
C(64)-C(65)	1.391(6)		
C(65)-C(66)	1.396(5)		

Ni-Br-Ni#1	94.78(2)	C(15)-C(14)-C(13)	120.6(4)
Br-Ni-Br#1	84.94(2)	C(14)-C(15)-N(1)	117.2(3)
N(1)-Ni-Br#1	178.16(9)	C(14)-C(15)-C(16)	122.8(3)
N(1)-Ni-Br	95.30(9)	C(16)-C(15)-N(1)	119.4(3)
N(1)-Ni-N(2)	84.83(12)	C(7)-C(16)-C(11)	118.5(4)
N(2)-Ni-Br	174.85(9)	C(7)-C(16)-C(15)	126.3(3)
N(2)-Ni-Br#1	94.77(9)	C(11)-C(16)-C(15)	115.2(4)
C(15)-N(1)-Ni	125.3(2)	N(1)-C(17)-C(18)	136.0(3)
C(17)-N(1)-Ni	112.1(2)	N(1)-C(17)-C(28)	115.8(3)
C(17)-N(1)-C(15)	121.8(3)	C(18)-C(17)-C(28)	108.1(3)
C(28)-N(2)-Ni	112.1(2)	C(19)-C(18)-C(17)	135.5(3)
C(28)-N(2)-C(29)	121.8(3)	C(19)-C(18)-C(27)	119.8(3)
C(29)-N(2)-Ni	126.0(2)	C(27)-C(18)-C(17)	104.7(3)
C(2)-C(1)-C(6)	120.4(5)	C(18)-C(19)-C(20)	117.9(3)
F(1)-C(2)-C(1)	118.7(6)	C(21)-C(20)-C(19)	122.2(4)
C(3)-C(2)-F(1)	118.3(5)	C(20)-C(21)-C(22)	121.0(3)
C(3)-C(2)-C(1)	123.0(6)	C(23)-C(22)-C(21)	127.2(3)
C(2)-C(3)-C(4)	117.0(5)	C(27)-C(22)-C(21)	116.3(3)
F(2)-C(4)-C(5)	115.4(7)	C(27)-C(22)-C(23)	116.6(3)
C(3)-C(4)-F(2)	120.8(7)	C(24)-C(23)-C(22)	120.5(3)
C(3)-C(4)-C(5)	123.8(5)	C(23)-C(24)-C(25)	122.7(3)
C(6)-C(5)-C(4)	117.5(6)	C(26)-C(25)-C(24)	118.4(3)
C(1)-C(6)-C(7)	119.8(4)	C(25)-C(26)-C(27)	118.7(3)
C(5)-C(6)-C(1)	118.3(5)	C(25)-C(26)-C(28)	136.1(3)
C(5)-C(6)-C(7)	121.9(5)	C(27)-C(26)-C(28)	105.2(3)
C(8)-C(7)-C(6)	117.9(4)	C(22)-C(27)-C(18)	122.7(3)
C(8)-C(7)-C(16)	119.9(4)	C(22)-C(27)-C(26)	123.1(3)
C(16)-C(7)-C(6)	122.0(3)	C(26)-C(27)-C(18)	114.2(3)
C(7)-C(8)-C(9)	121.7(5)	N(2)-C(28)-C(17)	114.8(3)
C(10)-C(9)-C(8)	119.6(4)	N(2)-C(28)-C(26)	137.3(3)
C(9)-C(10)-C(11)	121.5(4)	C(26)-C(28)-C(17)	107.8(3)
C(12)-C(11)-C(10)	120.9(4)	C(30)-C(29)-N(2)	114.9(3)
C(12)-C(11)-C(16)	120.7(4)	C(30)-C(29)-C(38)	123.1(3)
C(16)-C(11)-C(10)	118.4(4)	C(38)-C(29)-N(2)	122.0(3)
C(13)-C(12)-C(11)	121.4(4)	C(29)-C(30)-C(31)	119.9(4)
C(12)-C(13)-C(14)	119.1(4)	C(32)-C(31)-C(30)	119.1(4)

C(31)-C(32)-C(33)	121.6(4)	C(48)-C(47)-C(46)	121.2(3)
C(32)-C(33)-C(34)	120.3(4)	C(48)-C(47)-C(51)	119.7(3)
C(32)-C(33)-C(38)	120.5(4)	C(47)-C(48)-C(49)	117.3(3)
C(34)-C(33)-C(38)	119.2(4)	C(48)-C(49)-C(50)	121.3(3)
C(35)-C(34)-C(33)	121.6(4)	C(48)-C(49)-C(52)	119.9(3)
C(34)-C(35)-C(36)	119.5(4)	C(50)-C(49)-C(52)	118.8(3)
C(37)-C(36)-C(35)	122.6(4)	C(49)-C(50)-C(45)	122.3(3)
C(36)-C(37)-C(38)	118.7(4)	F(5)-C(51)-C(47)	111.4(3)
C(36)-C(37)-C(39)	116.3(4)	F(6)-C(51)-C(47)	113.5(3)
C(38)-C(37)-C(39)	124.9(3)	F(6)-C(51)-F(5)	104.2(3)
C(29)-C(38)-C(33)	115.3(4)	F(7)-C(51)-C(47)	113.6(3)
C(29)-C(38)-C(37)	126.7(3)	F(7)-C(51)-F(5)	104.5(4)
C(33)-C(38)-C(37)	118.0(4)	F(7)-C(51)-F(6)	108.9(4)
C(40)-C(39)-C(37)	119.2(3)	F(8)-C(52)-C(49)	113.4(3)
C(40)-C(39)-C(44)	119.4(3)	F(8)-C(52)-F(9)	107.3(3)
C(44)-C(39)-C(37)	121.2(3)	F(8)-C(52)-F(10)	106.9(3)
C(41)-C(40)-C(39)	118.6(3)	F(9)-C(52)-C(49)	112.1(3)
F(3)-C(41)-C(40)	118.1(4)	F(10)-C(52)-C(49)	112.2(3)
F(3)-C(41)-C(42)	117.7(4)	F(10)-C(52)-F(9)	104.2(3)
C(42)-C(41)-C(40)	124.2(4)	C(54)-C(53)-B	120.6(3)
C(41)-C(42)-C(43)	115.5(4)	C(54)-C(53)-C(58)	115.4(3)
F(4)-C(43)-C(42)	116.8(3)	C(58)-C(53)-B	124.0(3)
F(4)-C(43)-C(44)	119.2(3)	C(55)-C(54)-C(53)	122.6(3)
C(42)-C(43)-C(44)	124.0(4)	C(54)-C(55)-C(59)	118.5(3)
C(43)-C(44)-C(39)	118.2(3)	C(56)-C(55)-C(54)	121.0(3)
C(53)-B-C(45)	109.1(3)	C(56)-C(55)-C(59)	120.4(3)
C(61)-B-C(45)	109.2(3)	C(55)-C(56)-C(57)	117.8(3)
C(61)-B-C(53)	110.2(3)	C(56)-C(57)-C(58)	120.9(3)
C(69)-B-C(45)	110.0(3)	C(56)-C(57)-C(60)	119.2(3)
C(69)-B-C(53)	108.0(3)	C(58)-C(57)-C(60)	119.9(3)
C(69)-B-C(61)	110.3(3)	C(57)-C(58)-C(53)	122.3(3)
C(46)-C(45)-B	122.9(3)	F(11)-C(59)-C(55)	111.6(3)
C(46)-C(45)-C(50)	115.2(3)	F(12)-C(59)-C(55)	113.7(3)
C(50)-C(45)-B	121.8(3)	F(12)-C(59)-F(11)	105.5(3)
C(45)-C(46)-C(47)	122.6(3)	F(13)-C(59)-C(55)	113.2(3)
C(46)-C(47)-C(51)	119.1(3)	F(13)-C(59)-F(11)	105.9(3)

F(13)-C(59)-F(12)	106.3(3)	F(19B)-C(67)-C(63)	111.4(5)
F(14)-C(60)-C(57)	110.6(3)	F(20)-C(68)-C(65)	113.6(4)
F(15)-C(60)-C(57)	115.7(4)	F(20)-C(68)-F(21)	105.9(4)
F(15)-C(60)-F(14)	102.2(5)	F(20)-C(68)-F(22)	106.9(4)
F(15)-C(60)-F(16)	113.7(7)	F(21)-C(68)-C(65)	111.2(3)
F(16)-C(60)-C(57)	113.6(5)	F(22)-C(68)-C(65)	112.9(3)
F(16)-C(60)-F(14)	99.0(6)	F(22)-C(68)-F(21)	105.7(4)
F(14B)-C(60)-C(57)	114.2(5)	C(70)-C(69)-B	121.2(3)
F(14B)-C(60)-F(15B)	96.9(8)	C(70)-C(69)-C(74)	107.8(6)
F(15B)-C(60)-C(57)	102.5(4)	C(70)-C(69)-C(74B)	121.1(5)
F(16B)-C(60)-C(57)	118.3(10)	C(74)-C(69)-B	129.5(6)
F(16B)-C(60)-F(14B)	121.4(12)	C(74B)-C(69)-B	116.7(5)
F(16B)-C(60)-F(15B)	95.5(10)	C(71)-C(70)-C(69)	124.1(4)
C(62)-C(61)-B	123.7(3)	C(70)-C(71)-C(75)	117.3(4)
C(62)-C(61)-C(66)	115.8(3)	C(70)-C(71)-C(72B)	112.7(6)
C(66)-C(61)-B	120.5(3)	C(72)-C(71)-C(70)	127.0(6)
C(61)-C(62)-C(63)	122.0(4)	C(72)-C(71)-C(75)	114.3(6)
C(62)-C(63)-C(67)	119.5(4)	C(72B)-C(71)-C(75)	129.1(6)
C(64)-C(63)-C(62)	121.0(3)	C(71)-C(72)-C(73)	108.9(8)
C(64)-C(63)-C(67)	119.4(3)	C(72)-C(73)-C(74)	124.8(9)
C(63)-C(64)-C(65)	118.3(3)	C(72)-C(73)-C(76)	116.8(8)
C(64)-C(65)-C(66)	120.3(4)	C(74)-C(73)-C(76)	118.3(8)
C(64)-C(65)-C(68)	120.4(3)	C(73)-C(74)-C(69)	125.8(9)
C(66)-C(65)-C(68)	119.2(3)	F(23)-C(75)-C(71)	112.4(4)
C(65)-C(66)-C(61)	122.6(3)	F(23)-C(75)-F(24)	108.2(5)
F(17)-C(67)-C(63)	115.0(5)	F(23)-C(75)-F(25)	107.7(4)
F(17)-C(67)-F(19)	102.7(6)	F(24)-C(75)-C(71)	111.3(4)
F(18)-C(67)-C(63)	111.8(4)	F(24)-C(75)-F(25)	106.8(4)
F(18)-C(67)-F(17)	113.9(8)	F(25)-C(75)-C(71)	110.2(5)
F(18)-C(67)-F(19)	102.6(7)	F(26)-C(76)-C(73)	112.8(9)
F(19)-C(67)-C(63)	109.6(4)	F(26)-C(76)-F(27)	106.9(9)
F(17B)-C(67)-C(63)	112.5(7)	F(27)-C(76)-C(73)	112.5(8)
F(17B)-C(67)-F(18B)	110.7(12)	F(28)-C(76)-C(73)	111.2(11)
F(17B)-C(67)-F(19B)	100.5(9)	F(28)-C(76)-F(26)	106.0(10)
F(18B)-C(67)-C(63)	115.8(6)	F(28)-C(76)-F(27)	106.9(12)
F(18B)-C(67)-F(19B)	104.7(9)	C(73B)-C(72B)-C(71)	125.9(8)

C(72B)-C(73B)-C(76B)	122.2(8)	F(27B)-C(76B)-F(26B)	105.0(10)
C(74B)-C(73B)-C(72B)	118.0(8)	F(28B)-C(76B)-C(73B)	112.7(9)
C(74B)-C(73B)-C(76B)	119.8(8)	F(28B)-C(76B)-F(26B)	112.6(13)
C(73B)-C(74B)-C(69)	117.6(8)	F(28B)-C(76B)-F(27B)	104.4(10)
F(26B)-C(76B)-C(73B)	111.2(10)	Cl(2S)-C(1S)-Cl(1S)	111.9(5)
F(27B)-C(76B)-C(73B)	110.4(9)		

Symmetry transformations used to generate equivalent atoms:

#1 –x+1, y, –z + 3/2

Table S4. Anisotropic displacement parameters ($Å^2$ x10^3) for **2**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h^2 a^{*2} U^{11} + … + 2 h k a* b* U^{12}]

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br	27(1)	60(1)	22(1)	2(1)	-5(1)	0(1)
Ni	24(1)	34(1)	17(1)	-1(1)	-3(1)	1(1)
F(1)	52(2)	72(2)	141(3)	42(2)	-48(2)	-12(2)
F(2)	128(4)	66(2)	158(4)	-39(3)	89(3)	-11(2)
F(3)	51(2)	64(2)	37(1)	-21(1)	-3(1)	2(1)
F(4)	22(1)	58(1)	36(1)	-7(1)	-6(1)	4(1)
N(1)	20(2)	32(2)	24(1)	1(1)	-1(1)	0(1)
N(2)	25(2)	30(1)	21(1)	0(1)	-1(1)	3(1)
C(1)	35(2)	35(2)	61(3)	9(2)	-4(2)	-4(2)
C(2)	41(3)	42(2)	94(4)	12(3)	-4(3)	-6(2)
C(3)	48(3)	41(3)	130(6)	2(3)	12(4)	-2(2)
C(4)	78(4)	33(2)	124(6)	-14(3)	63(4)	-4(2)
C(5)	75(4)	36(2)	67(3)	-10(2)	24(3)	-11(2)
C(6)	41(2)	28(2)	50(2)	0(2)	4(2)	-5(2)
C(7)	33(2)	42(2)	39(2)	4(2)	-4(2)	-6(2)
C(8)	47(3)	43(2)	69(3)	1(2)	-13(2)	-8(2)
C(9)	43(3)	53(3)	105(5)	10(3)	-18(3)	-22(2)
C(10)	23(2)	69(3)	96(4)	17(3)	-10(2)	-12(2)
C(11)	30(2)	49(2)	48(2)	8(2)	-4(2)	-3(2)
C(12)	19(2)	61(3)	58(3)	6(2)	1(2)	3(2)
C(13)	29(2)	49(2)	40(2)	2(2)	4(2)	3(2)
C(14)	22(2)	43(2)	28(2)	0(2)	1(1)	-1(2)
C(15)	18(2)	40(2)	24(2)	4(1)	0(1)	-1(1)
C(16)	25(2)	42(2)	32(2)	8(2)	-4(2)	-7(2)
C(17)	22(2)	27(2)	23(2)	1(1)	-1(1)	-1(1)
C(18)	23(2)	30(2)	24(2)	-2(1)	-1(1)	-1(1)
C(19)	27(2)	42(2)	25(2)	0(2)	1(1)	2(2)
C(20)	33(2)	52(2)	24(2)	-4(2)	2(2)	4(2)
C(21)	33(2)	51(2)	25(2)	-8(2)	-5(2)	4(2)
C(22)	29(2)	38(2)	23(2)	-4(1)	-4(1)	2(2)
C(23)	30(2)	48(2)	31(2)	-4(2)	-11(2)	0(2)

C(24)	22(2)	48(2)	36(2)	3(2)	-6(2)	-2(2)
C(25)	22(2)	37(2)	28(2)	1(2)	-2(1)	3(1)
C(26)	20(2)	29(2)	26(2)	2(1)	-2(1)	3(1)
C(27)	26(2)	29(2)	24(2)	1(1)	-4(1)	3(1)
C(28)	23(2)	27(2)	22(2)	1(1)	-1(1)	0(1)
C(29)	21(2)	39(2)	18(2)	2(1)	0(1)	4(1)
C(30)	28(2)	46(2)	26(2)	-3(2)	0(1)	9(2)
C(31)	43(2)	64(3)	30(2)	-4(2)	5(2)	24(2)
C(32)	29(2)	72(3)	31(2)	9(2)	12(2)	11(2)
C(33)	29(2)	62(3)	31(2)	12(2)	5(2)	9(2)
C(34)	25(2)	71(3)	55(3)	26(2)	11(2)	3(2)
C(35)	30(2)	63(3)	66(3)	25(2)	3(2)	-9(2)
C(36)	29(2)	46(2)	48(2)	12(2)	-1(2)	-5(2)
C(37)	21(2)	38(2)	32(2)	9(2)	-3(1)	-2(1)
C(38)	23(2)	46(2)	25(2)	8(2)	0(1)	2(2)
C(39)	26(2)	31(2)	30(2)	4(1)	-1(1)	-4(1)
C(40)	32(2)	37(2)	31(2)	0(2)	-5(2)	-3(2)
C(41)	42(2)	37(2)	28(2)	-7(2)	-1(2)	-2(2)
C(42)	32(2)	39(2)	34(2)	-4(2)	4(2)	3(2)
C(43)	25(2)	37(2)	31(2)	3(2)	-3(1)	-1(2)
C(44)	27(2)	33(2)	27(2)	2(1)	1(1)	-3(1)
B	25(2)	35(2)	20(2)	-1(2)	-1(2)	5(2)
C(45)	27(2)	34(2)	20(2)	2(1)	0(1)	5(1)
C(46)	23(2)	38(2)	23(2)	2(1)	0(1)	3(1)
C(47)	26(2)	40(2)	20(2)	0(1)	4(1)	2(2)
C(48)	25(2)	38(2)	21(2)	0(1)	-1(1)	4(1)
C(49)	26(2)	38(2)	25(2)	2(2)	-1(1)	4(2)
C(50)	27(2)	39(2)	20(2)	1(1)	3(1)	8(2)
C(51)	25(2)	58(2)	26(2)	-11(2)	0(2)	5(2)
C(52)	27(2)	52(2)	28(2)	-2(2)	-1(2)	9(2)
F(5)	82(2)	86(2)	47(2)	-16(2)	8(2)	44(2)
F(6)	38(1)	122(3)	26(1)	-21(1)	-3(1)	17(2)
F(7)	47(2)	143(3)	69(2)	-58(2)	38(2)	-40(2)
F(8)	27(1)	125(3)	43(1)	-25(2)	-9(1)	9(1)
F(9)	26(1)	67(2)	60(2)	10(1)	5(1)	2(1)
F(10)	34(1)	62(2)	64(2)	0(1)	-3(1)	23(1)

C(53)	23(2)	32(2)	19(2)	-4(1)	-1(1)	-1(1)
C(54)	27(2)	32(2)	19(2)	-1(1)	-1(1)	1(1)
C(55)	22(2)	37(2)	19(2)	-5(1)	1(1)	-4(1)
C(56)	23(2)	44(2)	22(2)	0(2)	-2(1)	2(2)
C(57)	27(2)	46(2)	22(2)	5(2)	-1(1)	4(2)
C(58)	21(2)	38(2)	21(2)	0(1)	0(1)	1(1)
C(59)	27(2)	41(2)	30(2)	-2(2)	2(2)	1(2)
C(60)	32(2)	74(3)	36(2)	23(2)	1(2)	13(2)
F(11)	42(1)	39(1)	78(2)	-10(1)	24(1)	-11(1)
F(12)	24(1)	50(1)	45(1)	1(1)	7(1)	1(1)
F(13)	38(1)	84(2)	27(1)	12(1)	8(1)	-2(1)
F(14)	57(2)	53(2)	52(2)	21(2)	19(2)	18(2)
F(15)	204(7)	54(3)	63(3)	14(3)	-90(5)	-4(4)
F(16)	56(3)	94(6)	89(5)	65(5)	29(3)	21(3)
F(14B)	57(2)	53(2)	52(2)	21(2)	19(2)	18(2)
F(15B)	63(6)	46(5)	25(4)	29(3)	0(4)	4(4)
F(16B)	87(9)	42(7)	42(7)	6(5)	-34(7)	-20(7)
C(61)	21(2)	40(2)	22(2)	-1(1)	-3(1)	6(1)
C(62)	23(2)	45(2)	24(2)	-7(2)	-5(1)	6(2)
C(63)	25(2)	50(2)	25(2)	-8(2)	-1(1)	8(2)
C(64)	25(2)	58(2)	23(2)	-1(2)	2(1)	7(2)
C(65)	24(2)	47(2)	23(2)	3(2)	-4(1)	2(2)
C(66)	24(2)	42(2)	20(2)	-2(1)	-1(1)	7(2)
C(67)	41(2)	62(3)	34(2)	-14(2)	5(2)	10(2)
C(68)	34(2)	56(3)	29(2)	6(2)	3(2)	2(2)
F(17)	137(8)	51(4)	85(6)	-26(4)	70(6)	-21(5)
F(18)	46(3)	133(9)	116(8)	-77(8)	-18(4)	44(4)
F(19)	106(6)	74(4)	32(2)	-24(2)	-6(3)	24(4)
F(17B)	58(5)	113(11)	141(13)	-98(9)	-34(6)	23(5)
F(18B)	160(15)	86(7)	73(8)	-14(5)	80(10)	29(8)
F(19B)	106(9)	60(5)	61(5)	-26(4)	-18(5)	38(5)
F(20)	80(2)	80(2)	40(1)	13(1)	18(1)	-19(2)
F(21)	50(2)	75(2)	72(2)	23(2)	-27(1)	-23(1)
F(22)	59(2)	46(2)	91(2)	9(2)	19(2)	2(1)
C(69)	42(2)	36(2)	28(2)	-1(2)	7(2)	10(2)
C(70)	27(2)	36(2)	44(2)	1(2)	7(2)	2(2)

C(71)	53(3)	36(2)	57(3)	-2(2)	16(2)	3(2)
C(72)	48(7)	25(5)	30(5)	1(4)	8(5)	-20(5)
C(73)	42(6)	27(4)	26(4)	8(3)	-6(4)	-5(4)
C(74)	38(7)	24(4)	18(5)	0(3)	3(5)	-5(4)
C(75)	37(2)	34(2)	95(4)	-9(2)	5(2)	-7(2)
C(76)	90(7)	30(5)	42(5)	16(4)	-28(5)	-10(4)
C(72B)	82(8)	34(4)	78(7)	1(4)	20(5)	-23(5)
C(73B)	93(7)	37(4)	55(5)	10(3)	-1(5)	0(4)
C(74B)	64(7)	34(4)	40(5)	6(3)	-5(5)	0(4)
C(76B)	153(10)	50(5)	74(7)	22(5)	-22(5)	6(5)
F(23)	68(2)	60(2)	58(2)	-2(1)	-16(2)	-14(1)
F(24)	50(2)	68(2)	184(5)	-28(3)	-15(2)	8(2)
F(25)	74(2)	45(2)	115(3)	-6(2)	28(2)	-20(2)
F(26)	111(6)	44(4)	39(4)	15(3)	-9(4)	-23(4)
F(27)	187(10)	45(4)	31(3)	18(3)	-52(5)	-44(5)
F(28)	76(6)	80(7)	113(10)	60(7)	-33(6)	1(5)
F(26B)	214(12)	148(9)	92(6)	77(6)	34(7)	66(8)
F(27B)	109(6)	61(3)	117(6)	35(3)	-13(4)	14(3)
F(28B)	217(10)	68(4)	133(7)	31(4)	-107(7)	7(5)
Cl(1S)	72(2)	61(1)	48(1)	7(1)	-6(1)	-14(1)
Cl(2S)	62(2)	120(3)	49(1)	13(2)	-11(1)	-27(2)
C(1S)	89(7)	34(4)	32(4)	7(3)	4(4)	-20(4)

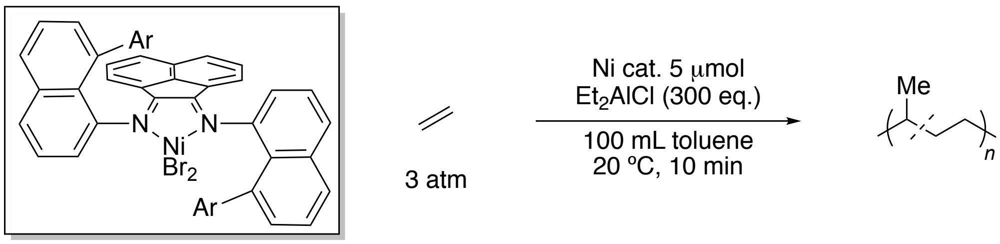
Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$ x10^3) for **2**.

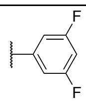
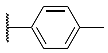
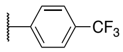
	x	y	z	U(eq)
H(1)	4868	8779	4869	52
H(3)	3931	9473	5751	88
H(5)	4913	9280	6755	71
H(8)	5532	9802	6008	64
H(9)	6179	9624	5886	80
H(10)	6402	8544	5571	75
H(12)	6295	7294	5293	56
H(13)	5899	6338	5179	47
H(14)	5256	6454	5450	37
H(19)	5021	7261	4342	38
H(20)	4720	7061	3352	43
H(21)	4079	6869	3286	44
H(23)	3432	6734	3899	44
H(24)	3119	6790	4859	42
H(25)	3430	7049	5824	34
H(30)	4015	8451	7145	40
H(31)	3466	8566	7780	55
H(32)	3051	7633	7852	53
H(34)	2853	6449	7560	60
H(35)	2956	5398	7043	63
H(36)	3535	5177	6564	49
H(40)	3922	5506	5610	40
H(42)	5046	5177	5787	42
H(44)	4473	6193	7206	35
H(46)	3344	6012	1177	34
H(48)	2403	5616	142	34
H(50)	2330	6546	1884	34
H(54)	3789	6780	1775	31
H(56)	4405	5299	2697	36
H(58)	3299	5566	3121	32
H(62)	2834	7582	3267	37

H(64)	2149	6347	4343	42
H(66)	2639	5575	2734	34
H(70)	3519	7626	2921	43
H(72)	3550	9436	1891	41
H(74)	2989	7687	1262	32
H(72B)	3328	9399	1927	78
H(74B)	2774	7603	1434	55
H(1SA)	5479	8298	2979	62
H(1SB)	5555	9118	3103	62

VI. Ni(II) α-Diimine Catalyst Screen

Table S6. Ethylene Polymerisation Results for Ni(II) α-Diimine Catalysts



entry	Ar	yield (g)	TOF (h^{-1})[a]	$M_n^{theo.}$ (kg mol^{-1})[b]	M_n (kg mol^{-1})[c]	$Đ$[c]	T_m (°C)[d]	ΔH (J g^{-1})[d]	B/1000 C[e]
1		0.82	36,500	164	171	1.09	c[f]	–[f]	112
2[g]		0.59	26,300	118	124	1.07	–[f]	–[f]	116
3[h]		1.13	50,300	226	172	1.31	69	20	55

[a]Turnover frequency (TOF) = mol ethylene (mol Ni•h)$^{-1}$. [b]Theoretical molar mass = mass of polyethylene (mol Ni)$^{-1}$. [c]Determined using gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C vs polyethylene standards. [d] Melting point and heat of fusion determined using differential scanning calorimetry (DSC), melting endotherm of second heat. [e]*Methyl* branches per 1000 backbone carbons determined using ^{1}H NMR spectroscopy. [f]No T_m observed. [g]Complex was synthesized according to literature procedure.[1] [h]Complex was synthesized according to literature procedure.[6]

VII. Ethylene Polymerisation

All polymerisations were set up in an MBraun Unilab glovebox. In a typical reaction, an oven-dried 200 mL Fisher-Porter bottle (Andrew Glass) equipped with a magnetic stir bar was charged with Et_2AlCl (0.19 mL, 1.5 mmol) and toluene (100 mL). The vessel was sealed with a Swagelok reactor head. Complex **1** (4.4 mg, 5.0 μmol) was dissolved in chlorobenzene (2 mL) and drawn into a 3 mL Hamilton Gas-tight syringe equipped with a stainless-steel needle, sealed at the tip using a rubber septum. The reactor and syringe were removed from the glovebox. Ethylene was charged into the reactor and then vented. The cycle was repeated 3 times to exchange the nitrogen environment. The reactor was equilibrated for 10 min at the desired temperature and pressure. While open to ethylene, the catalyst was immediately injected into the reaction vessel. For the polymerisations done at 6 atm, the ethylene feed was stopped after equilibration, the reactor was partially vented to 3 atm, the catalyst was immediately injected, and the ethylene feed was raised to 6 atm. After the desired polymerisation time, the reactor was vented, and the reaction mixture was quenched with methanol (10 mL) under vigorous stirring. The polymer solution was precipitated into acidic methanol (5% HCl v/v, ~500 mL), and stirred for at least 4 hours. The resulting polymers were filtered, washed with methanol and dried under vacuum at 60 °C to constant weight.

VIII. DSC Thermograms and ^{1}H NMR Spectra of Polyethylenes

All DSC second heating cycle thermograms are presented as shown below for entry 1 in Table 1, where measurements were conducted between 0°C and 200 °C at 10 °C min^{-1}.

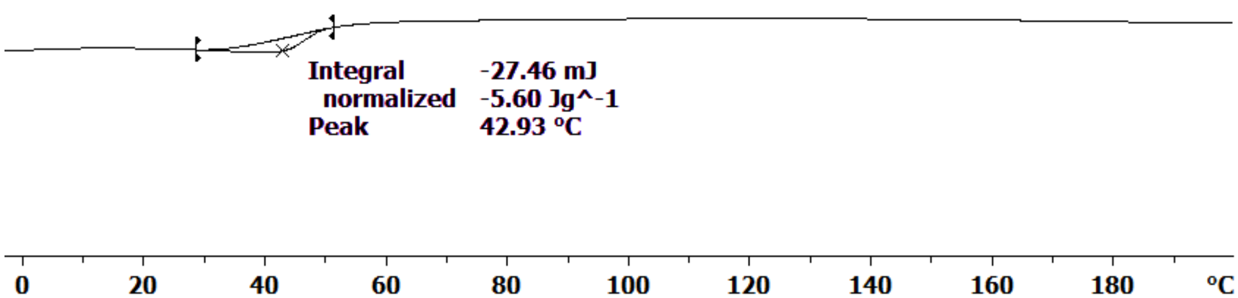


Figure S2. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 1).

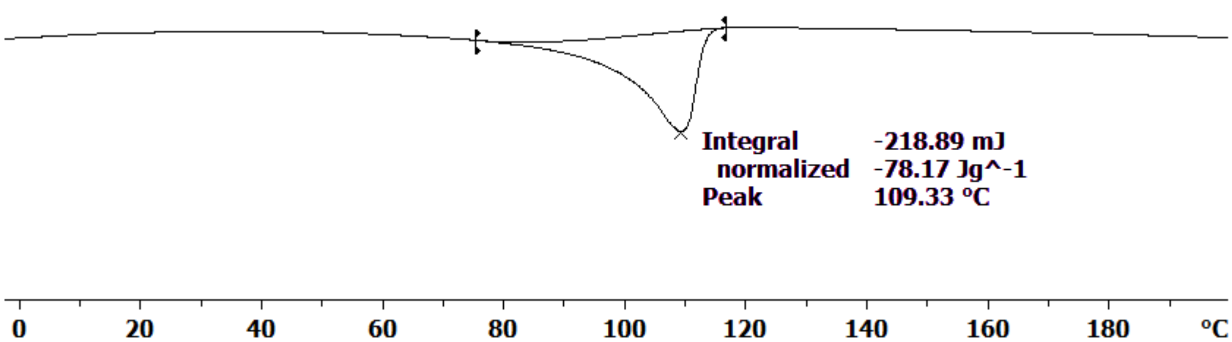


Figure S3. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 2).

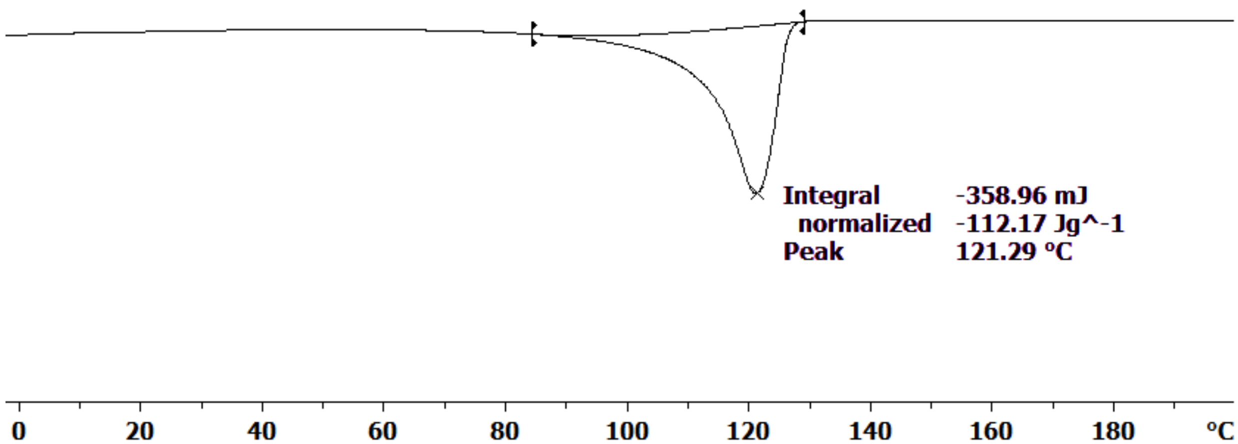


Figure S4. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 3).

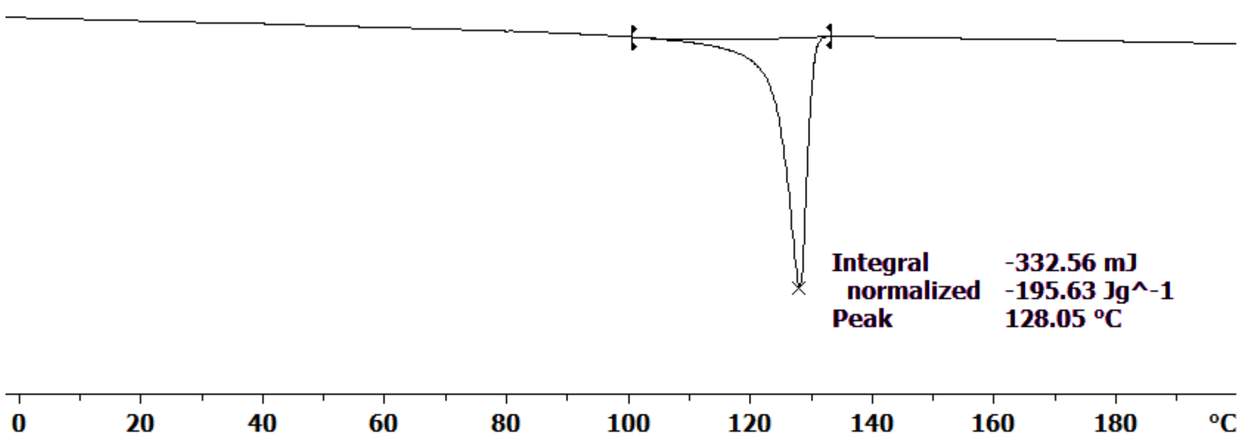


Figure S5. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 4).

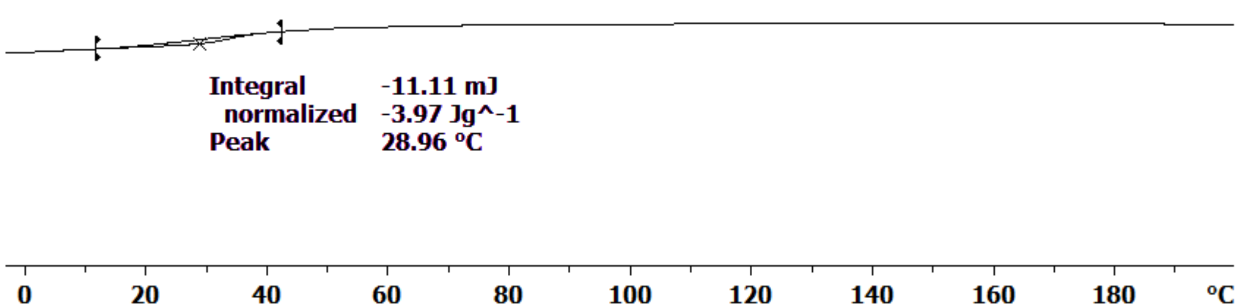


Figure S6. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 5).

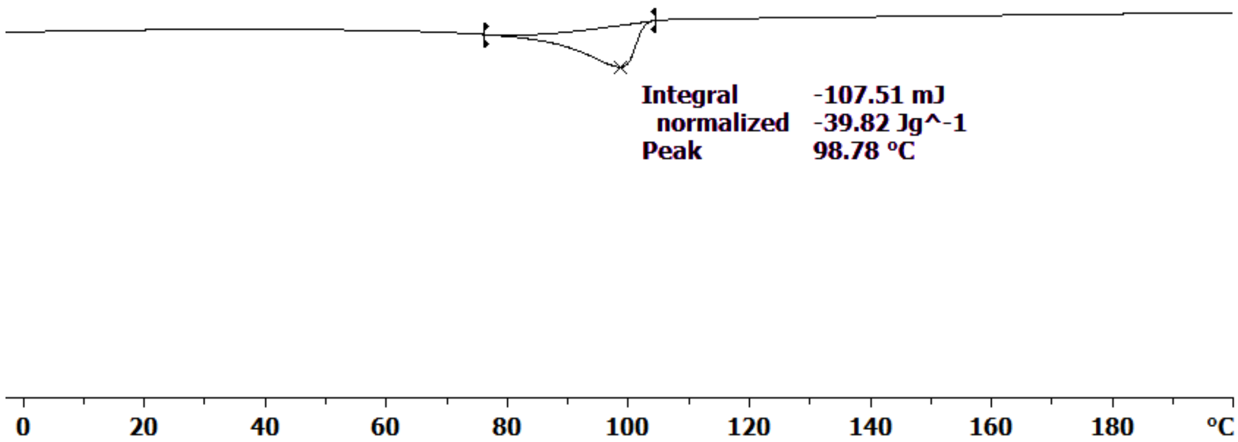


Figure S7. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 6).

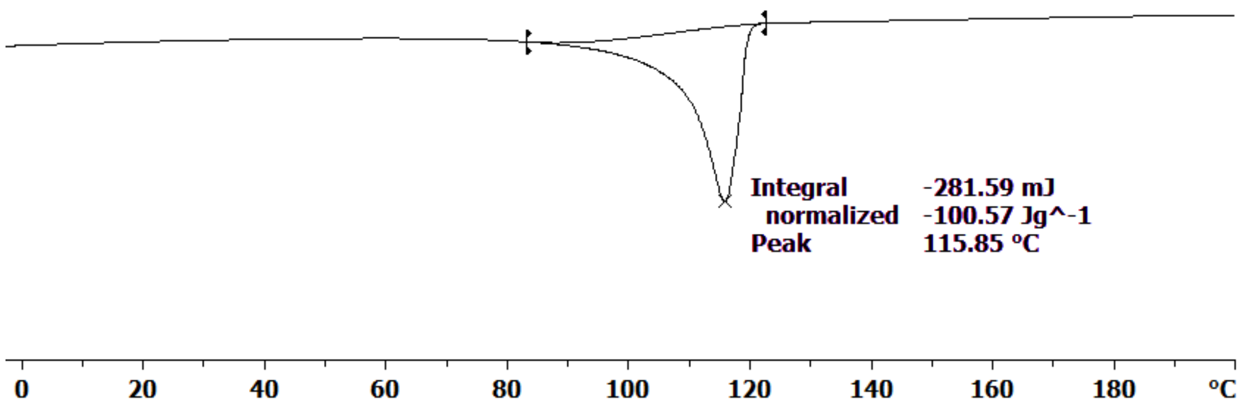


Figure S8. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 7).

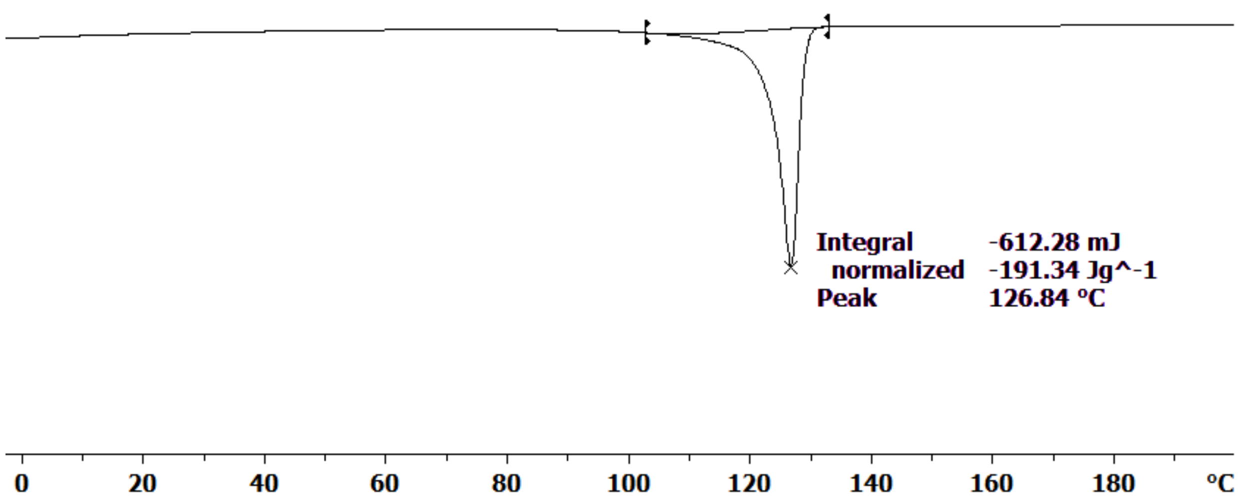


Figure S9. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 8).

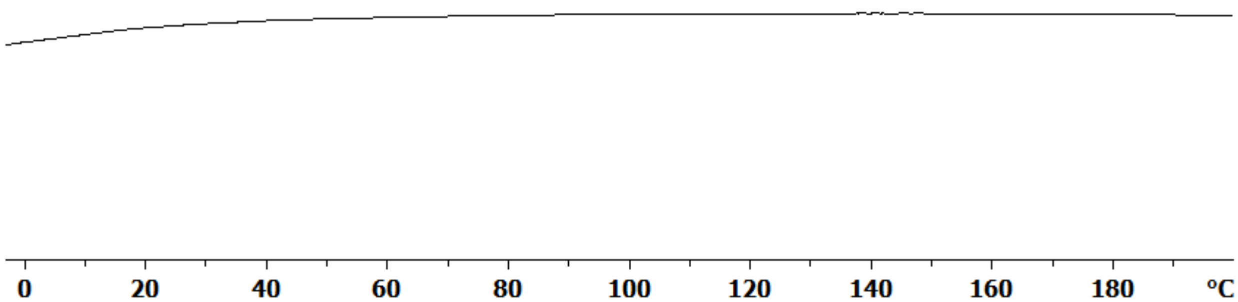


Figure S10. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 9).

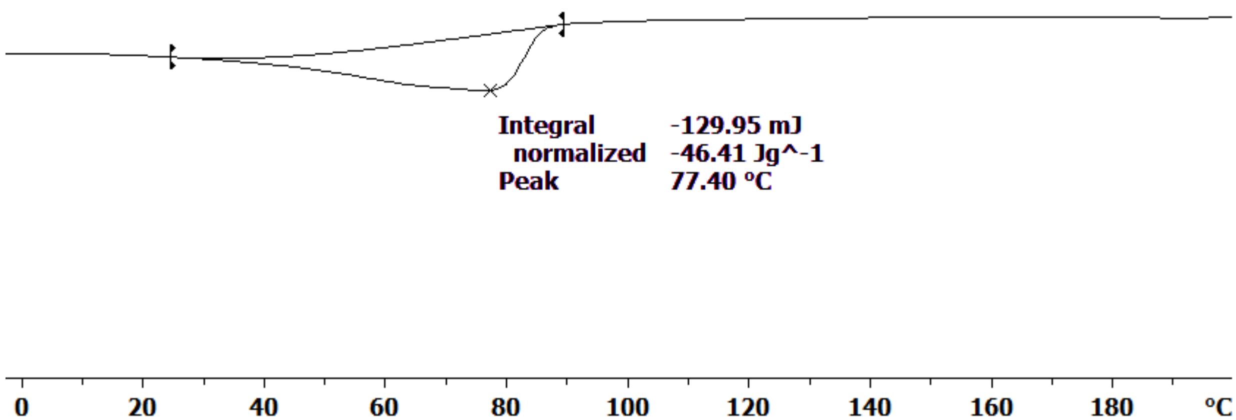


Figure S11. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 10).

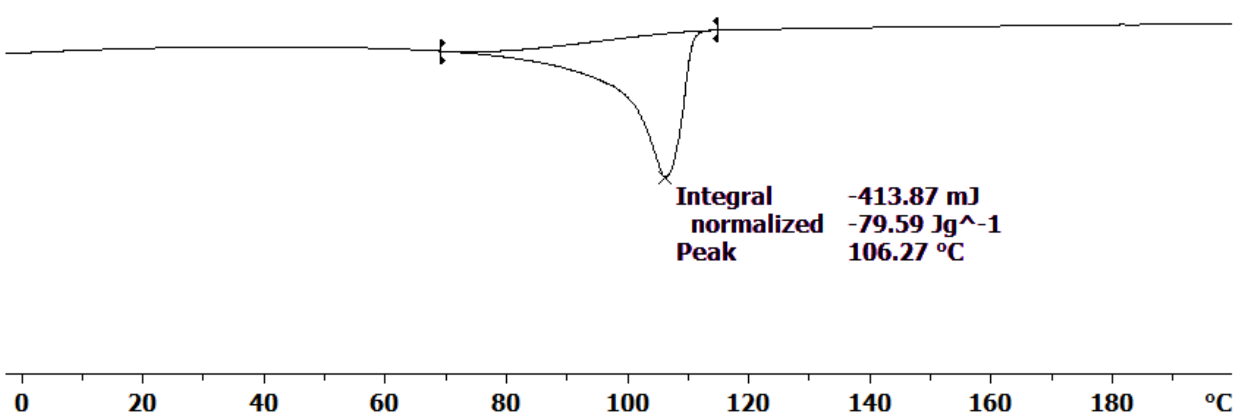


Figure S12. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 11).

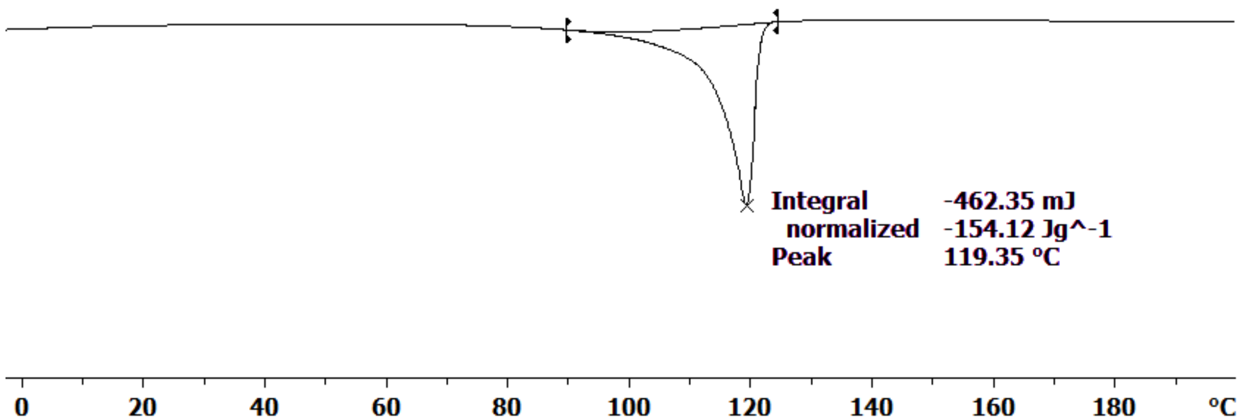


Figure S13. DSC thermogram of polymer obtained from ethylene using **1** (Table 1, entry 12).

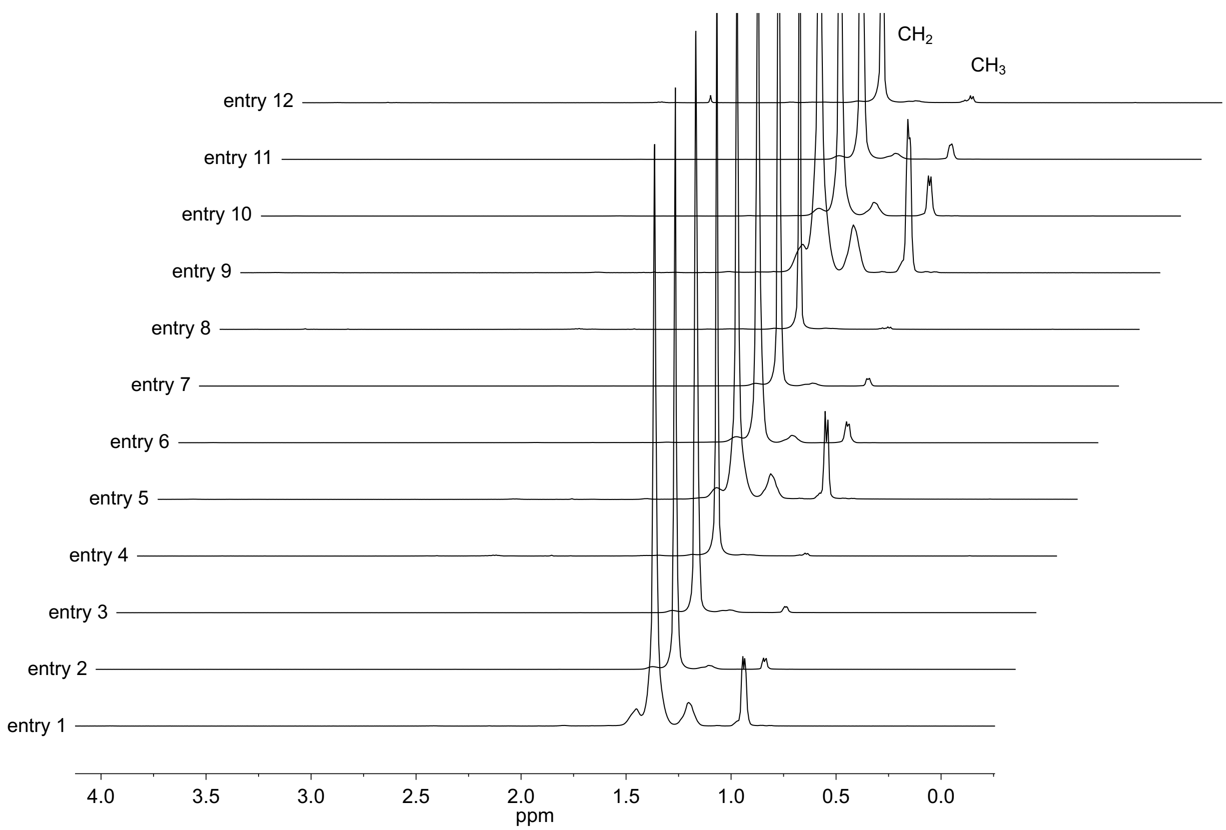


Figure S14. Stacked ^{1}H NMR plot showing the decrease of the *methyl* (CH_3) branch resonance at ~0.9 ppm (entries taken from Table 1). ^{1}H NMR spectra taken in $Cl_2CDCDCl_2$. Branching content calculated according to the method reported by Brookhart and coworkers.[7]

IX. Synthesis of Tetra-Block Copolymer

The polymerisation was set up in an MBraun Unilab glovebox. An oven-dried 200 mL Fisher-Porter bottle (Andrew Glass) equipped with a magnetic stir bar was charged with Et_2AlCl (0.19 mL, 1.5 mmol) and toluene (100 mL). The vessel was sealed with a Swagelok reactor head. Complex **1** (4.4 mg, 5.0 µmol) was dissolved in chlorobenzene (2 mL) and drawn into a 3 mL Hamilton Gas-tight syringe equipped with a stainless-steel needle, sealed at the tip using a rubber septum. The reactor and syringe were removed from the glovebox. The reactor was placed in an ethanol bath at –35 °C for 20 minutes. Ethylene was charged into the reactor and then vented, cycling 3 times to exchange the nitrogen environment, at 6 atm and then was equilibrated for 10 min at –35 °C. The ethylene feed was stopped after equilibration, the reactor was partially vented to 3 atm, the catalyst was immediately injected, and the ethylene feed was raised to 6 atm. After 60 minutes, an aliquot was removed (20 mL) and precipitated into acidic methanol (5% HCl v/v ~100 mL) for future analysis. The ethylene feed was stopped, and vacuum was applied for 10 seconds. The reactor was placed in a 30 °C oil bath for 5 minutes then immediately switched to a 20 °C water bath. Ethylene was reintroduced at 1 atm, and the reaction was allowed to proceed for another 20 minutes. An aliquot was removed (10 mL) and precipitated into acidic methanol for future analysis. The ethylene feed was stopped, and vacuum was applied for 10 seconds. The reactor was placed back in the ethanol bath at –35 °C for 20 minutes. The ethylene (6 atm) was then reintroduced, and the reaction was allowed to proceed for another 70 minutes at –35 °C. An aliquot was removed (10 mL) and precipitated into acidic methanol for future analysis. The ethylene feed was stopped once more, and vacuum was applied for 10 seconds. The reactor was placed in the 30 °C oil bath for 5 minutes then immediately switched to a 20 °C water bath. Ethylene (1 atm) was reintroduced, and the reaction was allowed to proceed for another 20 minutes. The polymerisation was then quenched after the given time by venting the reactor and injecting 10 mL of methanol into the vessel with vigorous stirring. The polymer solution was then precipitated into a solution of acidic methanol (5 % HCl v/v ~500 mL) and stirred for at least 4 hours. All polymers were filtered, washed with methanol and dried under vacuum at 60 °C to constant weight.

X. Tetra-Block Copolymer DSC Data

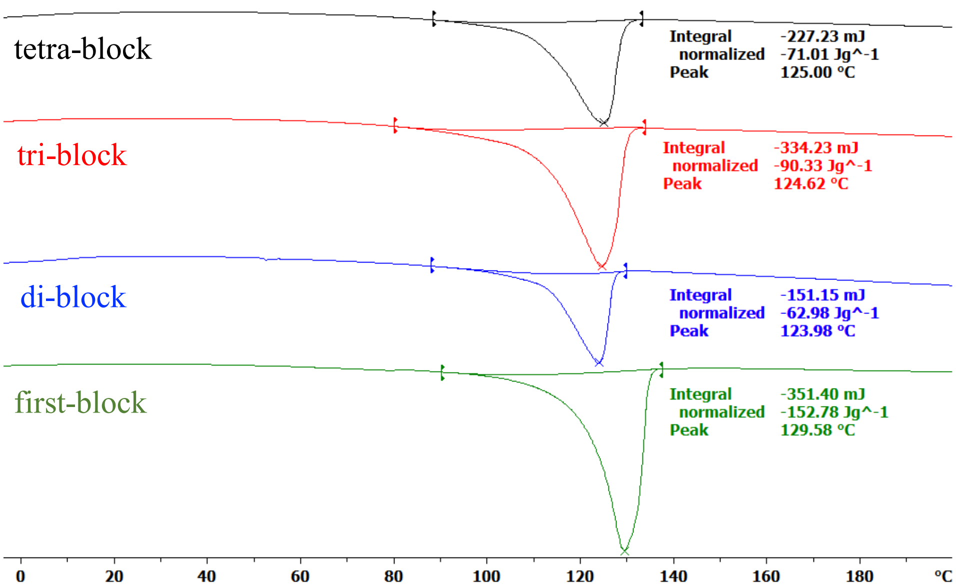


Figure S15. DSC thermogram obtained from tetra-block aliquots and copolymer.

XI. Melt Blend Studies

Blend Preparation

Polymer pellets of Dow LDPE (955I, 3.2 g) and Dow HDPE (DMDA8904, 0.8 g), and block copolymer powder (200 mg) were combined and pressed at 180 °C for 5 minutes with minimal pressure to create a coherent film. The film was fed into a twin screw microcompounder at 190 °C with a steady flow of argon and a residence time of 8 minutes at 130 rpm. The material was then extruded through a 2.5 mm diameter die and air cooled. The resulting blend was then pressed at 180 °C for 5 minutes with minimal pressure to create a coherent film.

Sample Preparation

Blend films were loaded into a stainless-steel dogbone die (gauge length = 10 mm, gauge width = 2.6 mm, gauge thickness = 0.6 mm) and pressed on a Carver press hot plate under ~52 MPa at 180 °C for 5 minutes. Maintaining this pressure, the sample was cooled using water circulation (~10 °C min^{-1}). The samples were removed and trimmed with a razor blade.

Mechanical Testing

Mechanical studies were performed using a Shimadzu Autograph AGS-X tensile tester elongated with a crosshead velocity of 10 mm min^{-1}. Tensile bars were elongated until break, and at least five tensile bars were tested for each composite. Results were analyzed using TrapeziumX v. 1.5.1 software. Representative traces are presented in Figure 4 and compiled individual traces are presented below (Figure S16).

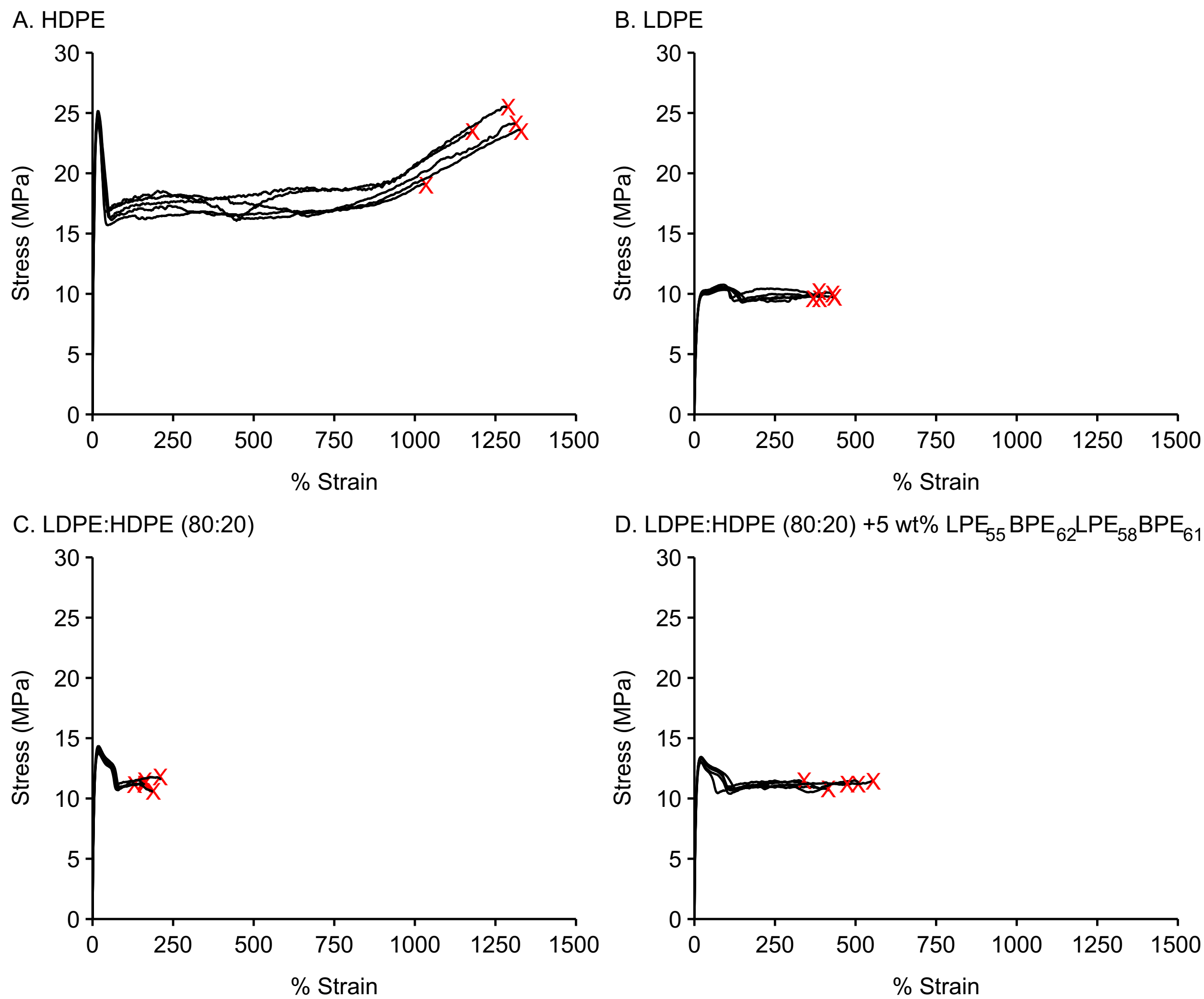
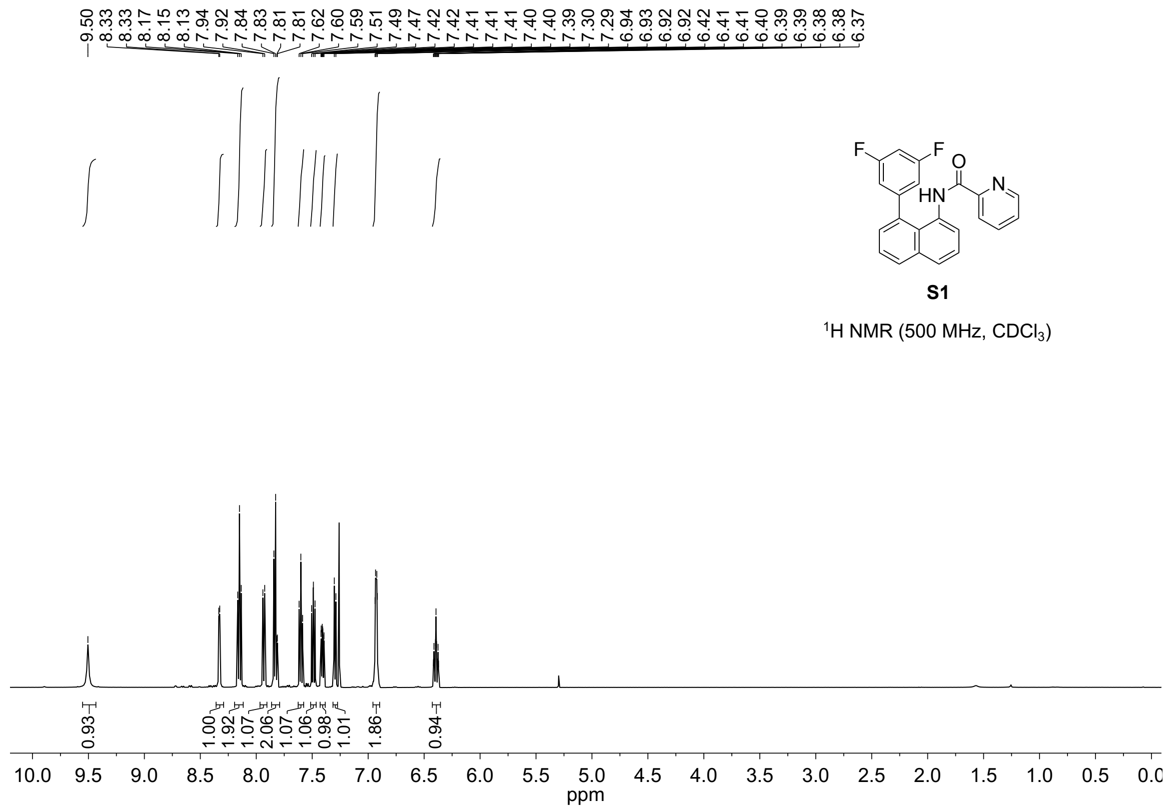
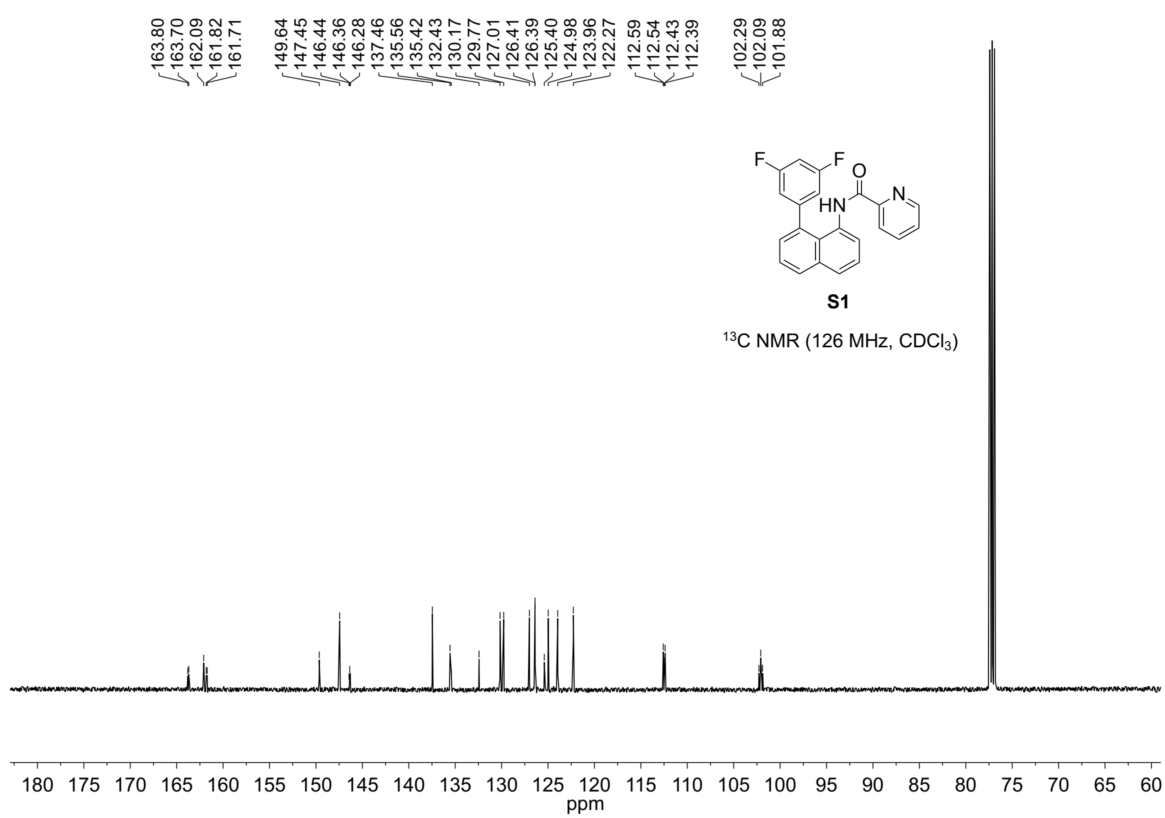
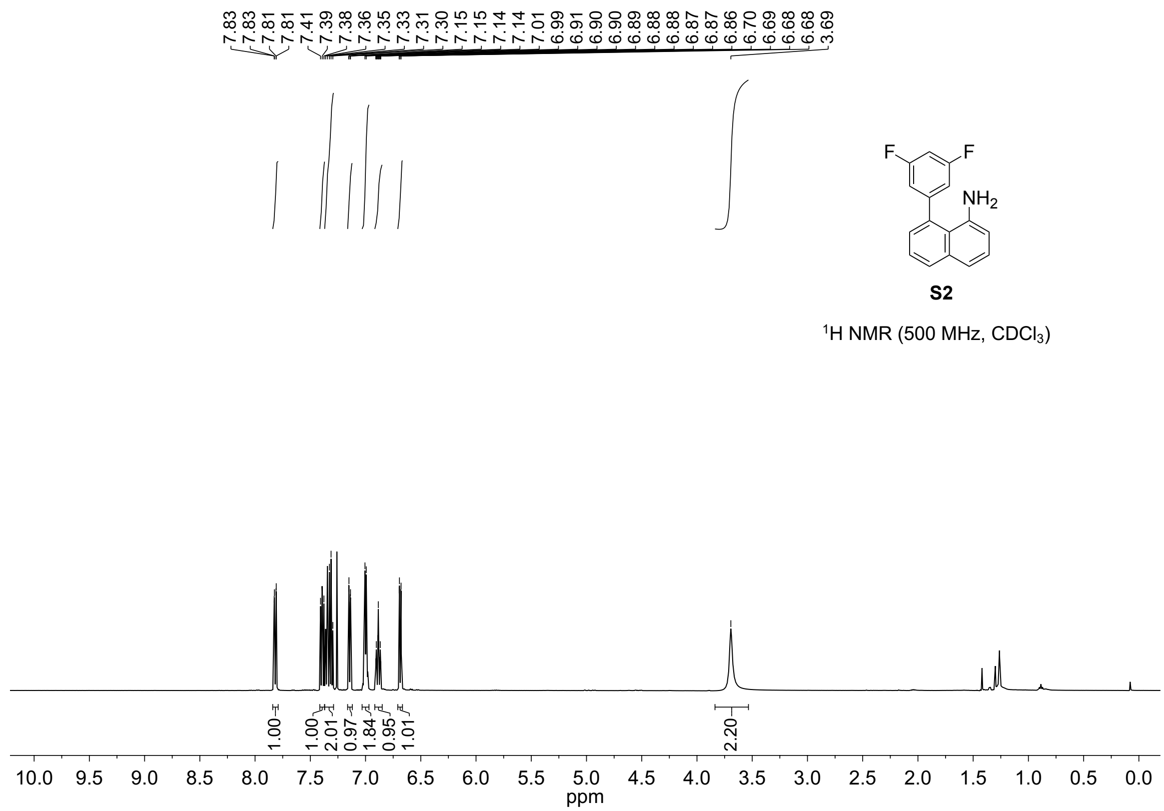


Figure S16. Compiled uniaxial tensile elongation of (A) HDPE, (B) LDPE, and (C) LDPE/HDPE blend (80:20, LDPE:HDPE). (D) Compiled tests of LDPE/HDPE blend (80:20, LDPE:HDPE) with the addition of 5 wt% tetra-block copolymer. The samples were strained at a rate of 100 % min^{-1} at 25 °C.

XII. ^{1}H NMR and ^{13}C NMR Spectra of S1-S3

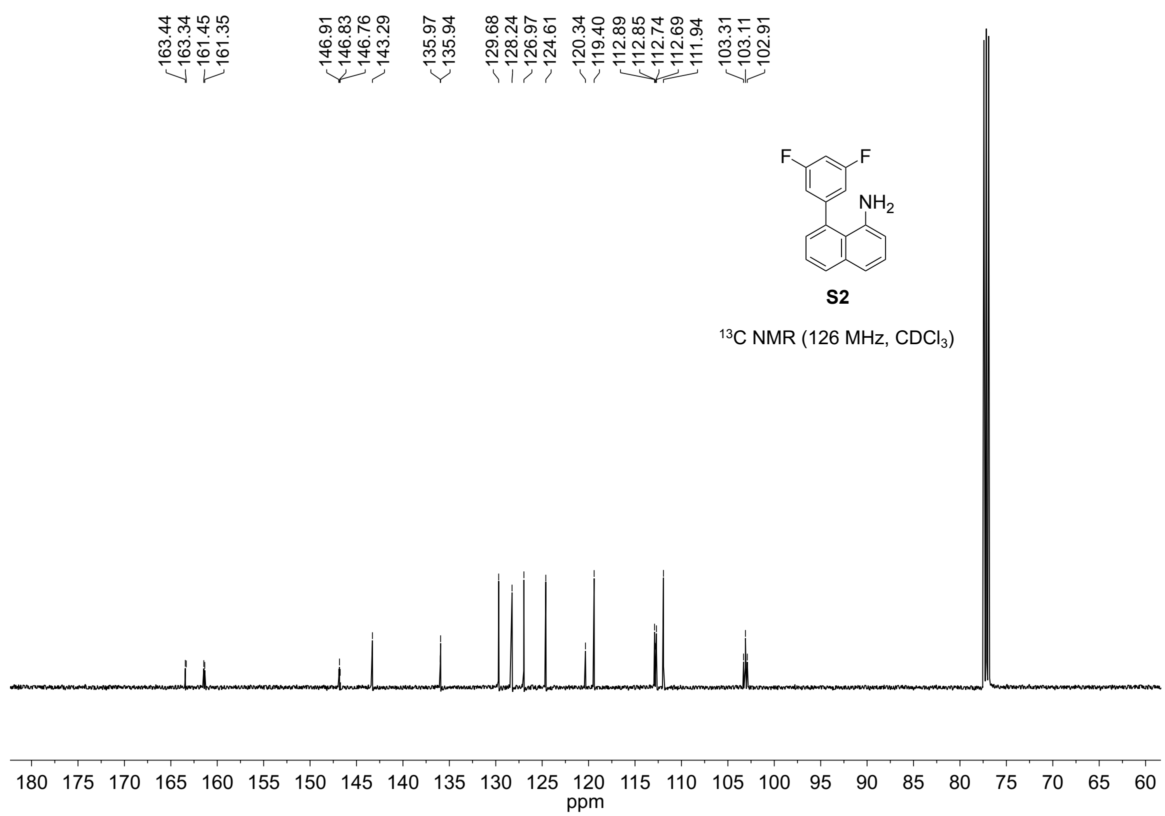






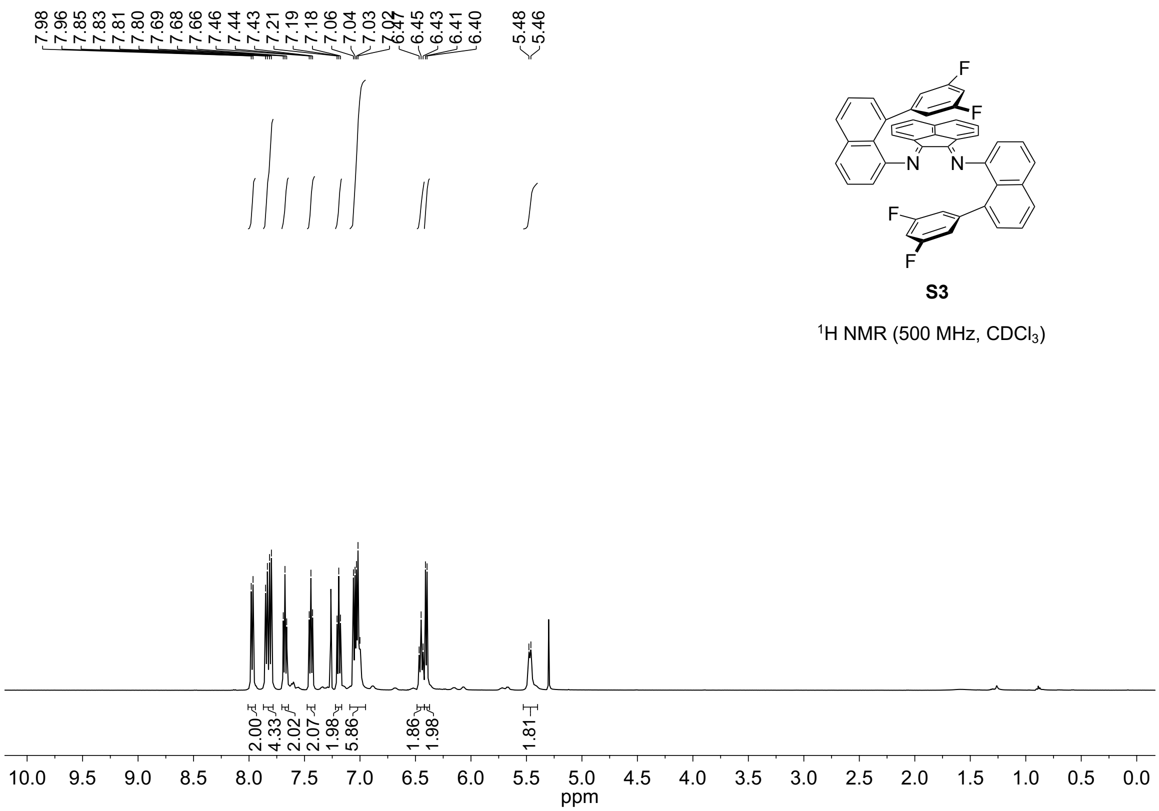
S2

^{1}H NMR (500 MHz, $CDCl_3$)



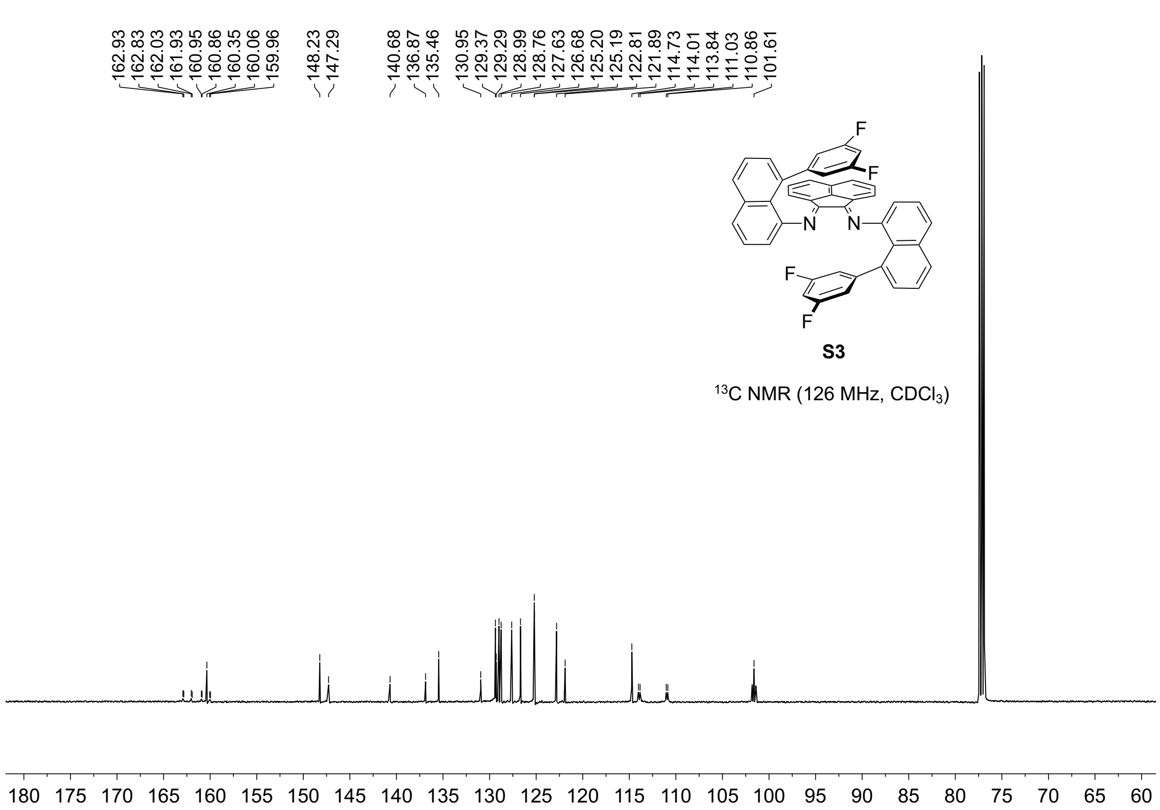
S2

^{13}C NMR (126 MHz, $CDCl_3$)



S3

^1H NMR (500 MHz, $CDCl_3$)



S3

^{13}C NMR (126 MHz, $CDCl_3$)

XIII. References

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