Supporting Information

Bent-core mesogens with thiophene units

*Karina Geese, Marko Prehm, Carsten Tschierske**

Institute of Chemistry, Organic Chemistry, Martin-Luther-University Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle, Germany; Fax: +49 345 552 7346; Tel: +49 345 552 5664; E-mail: carsten.tschierske@chemie.uni-halle.de

1. Additional Data

1.1 Compound T-Bip-8

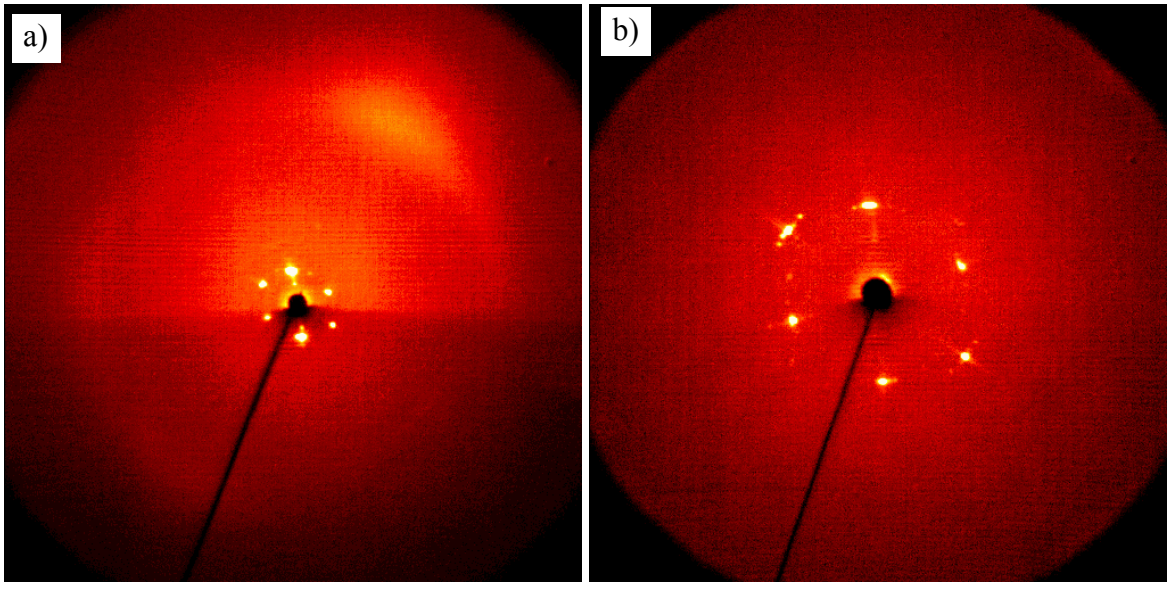


Figure S1. XRD pattern of the Col_{rec} phase of compound **T-Bip-8** at T = 100 °C, (a) wide angle region, (b) small angle region.

Table S1. Numerical XRD data of compound **T-Bip-8** at T = 100 °C.

2 θ	θ	d/nm	hk
3.22	1.63	2.74	11
3.96	1.98	2.23	02
19.18	9.59	0.46	

Col_{rec}: a = 3.48 nm, b = 4.46 nm.

1.1 Compound T-Bip-12

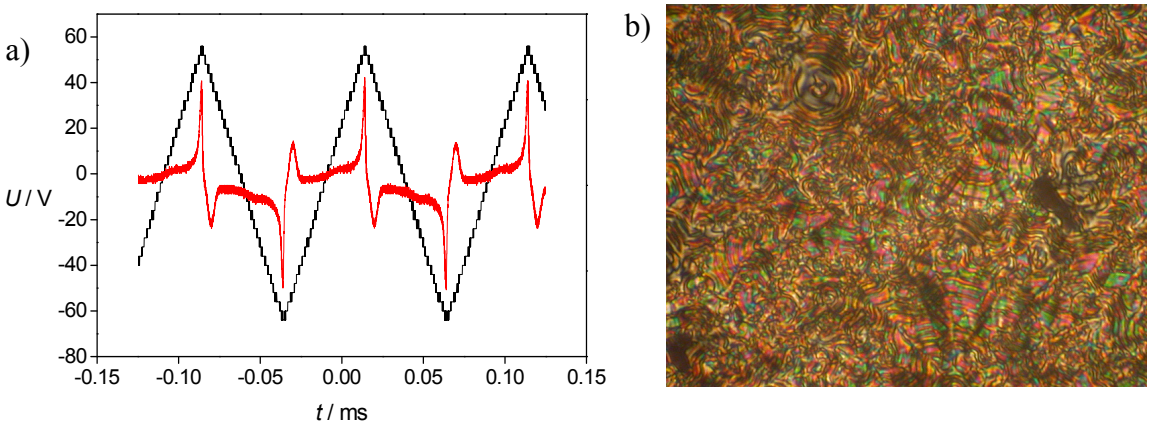
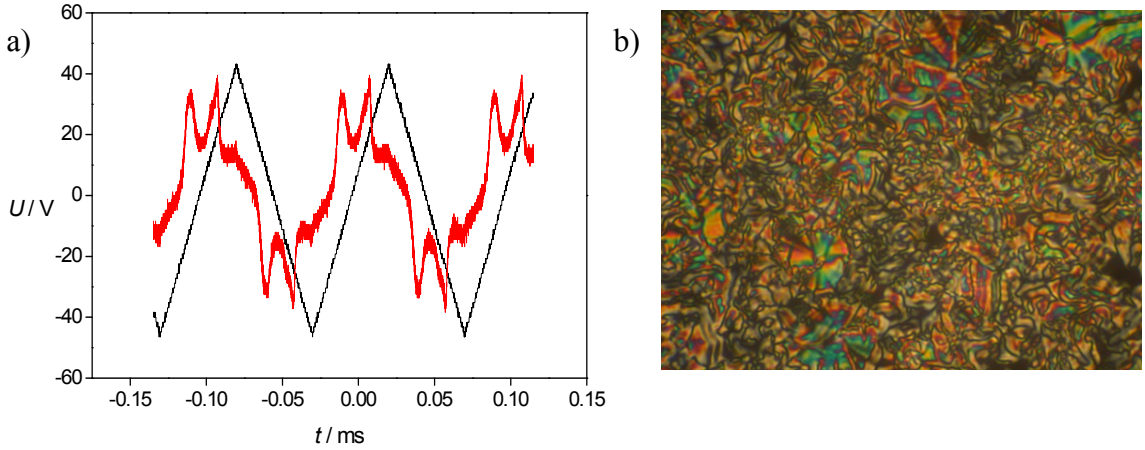


Figure S2. (a) Switching current response curve of **T-Bip-12** at T = 88 °C (120 Vpp, 10 Hz, 5kΩ, 10 µm ITO cell) P_S = 460 nC/cm^2 and (b) texture as observed in the absence of an electric field at T = 108°C.

1.2 Compound T-Bip-en



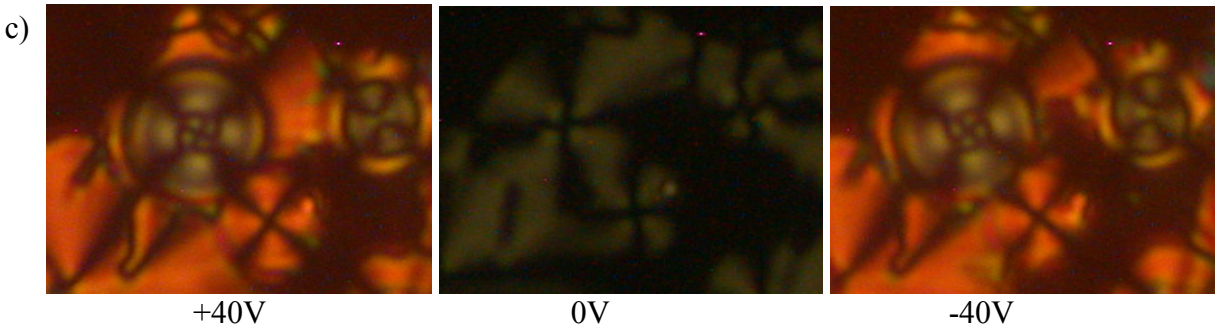


Figure S3. Investigation of compound **T-Bip-en**: (a) Switching current response curve at T = 90 °C (90 Vpp, 10 Hz, 5 kΩ, 10 µm ITO cell), Ps = 500 nC/cm^2 and (b) texture as observed in the absence of an electric field at T = 108 °C; (c) circular domains grown at 98 °C under a DC field of 40 V (left), after switching off the field (middle) and upon application of a DC field with opposite direction (right), indicating an antiferroelectric switching on a cone.

1.3 Compound TT-Res-12

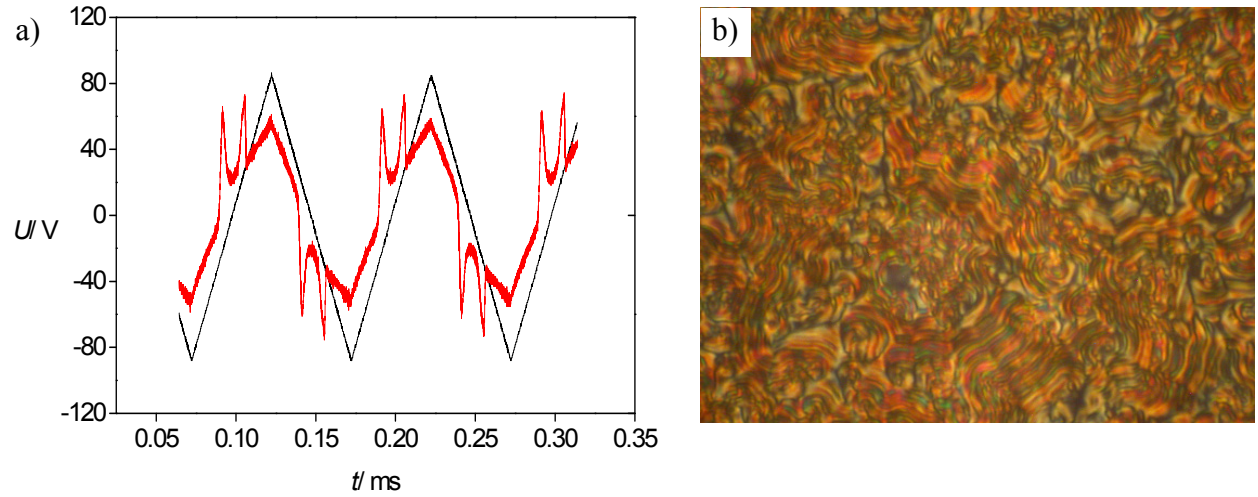


Figure S4. (a) Switching current response curve of **TT-Res-12** at T = 130 °C (170 Vpp, 10 Hz, 7 kΩ, 10µm PI-coated ITO cell, P_S = 700 nC/cm^2 and (b) texture as observed in the absence of an electric field at T = 120 °C.

Table S2. Numerical XRD data of compound **TT-Res-12** at T = 135 °C.

2 θ	θ	d/nm	n	d_{calc}	d_{obs}-d_{calc}
2.08	1.04	4.25	1	4.25	0.00
4.18	2.09	2.11	2	2.13	0.02
6.25	3.13	1.41	3	1.42	0.01
18.89	9.45	0.47	*diff.*		

SmC_sP_A: d = 4.25 nm.

1.4 Compound T-Bip-Si

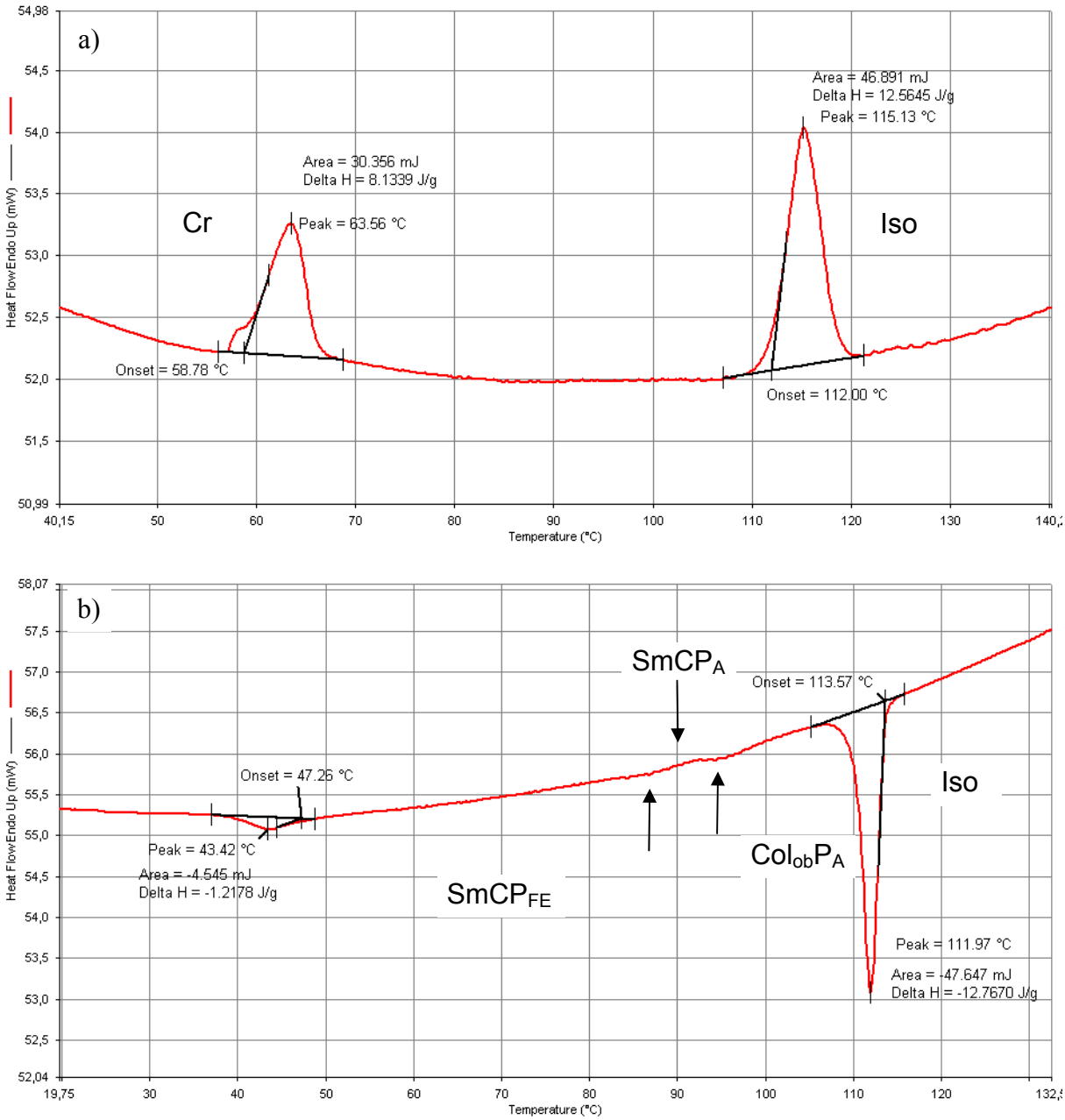


Figure S5. DSC (a) heating and (b) cooling curves (10 K min^{-1}) of compound **T-Bip-Si**.

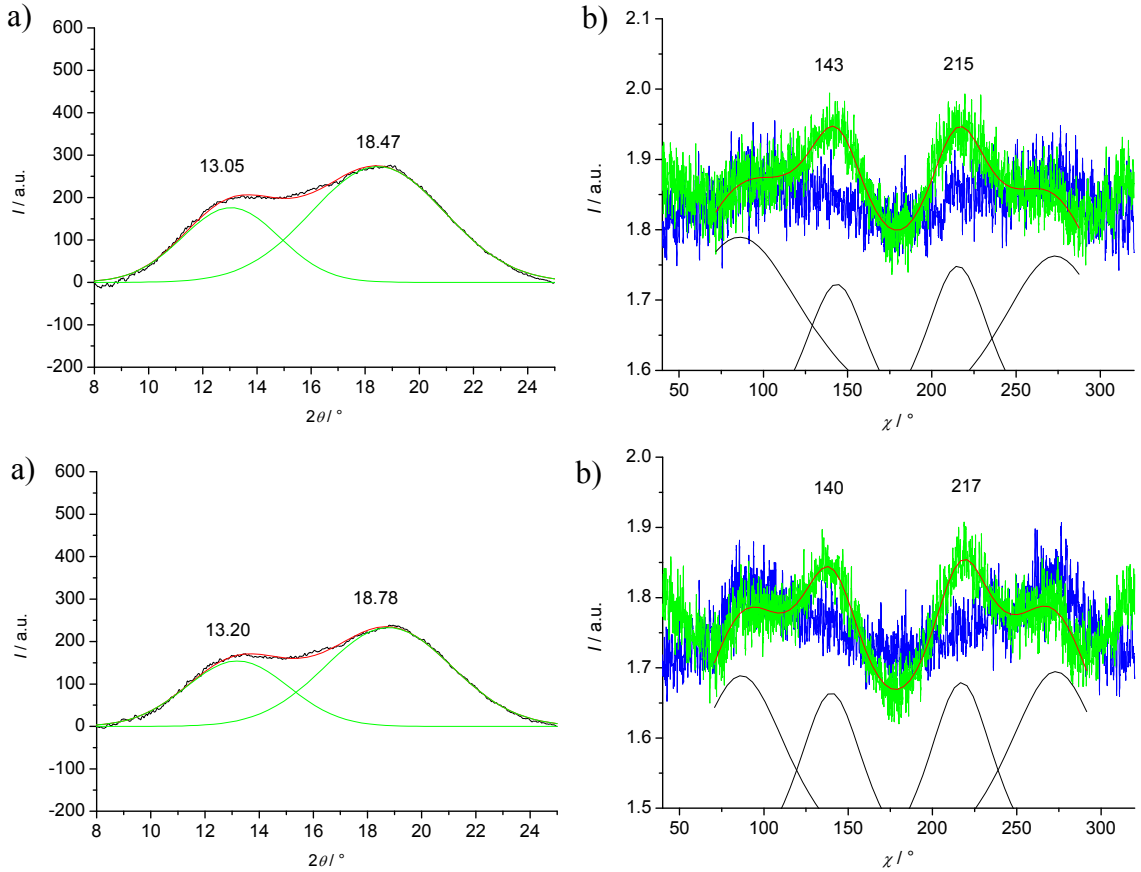


Figure S6. Analysis of the XRD pattern of compound **T-Bip-Si** (Fig. 4): (a) θ-scan over the diffuse wide angle scatterings at T = 104 °C; (b) χ-scan over the wide angle scatterings (blue line: 2θ = 10-15°, green line: 2θ = 15-23°, T = 104 °C); (c) θ-scan over the diffuse wide angle scatterings at T = 80 °C; (d) χ-scan over the wide angle scatterings (blue line: 2θ = 10-15°, green line: 2θ = 17-21°, T = 80 °C).

Table S3. Numerical XRD data of compound **T-Bip-Si.**

T = 104 °C

2 θ	θ	d/nm	n	d_{calc}	d_{obs}-d_{dcalc}
1.95	0.98	4.53	1	4.55	-0.02
3.82	1.91	2.31	2	2.28	0.03
13.05	6.52	0.68	*diff.*		
18.47	9.24	0.48	*diff.*		

d = 4.55 nm.

T = 80 °C

2 θ	θ	d/nm	n	d_{calc}	d_{obs}-d_{dcalc}
1.86	0.93	4.75	1	4.80	-0.05
3.67	1.84	2.41	2	2.40	0.01
7.34	3.67	1.20	4	1.20	0.00
13.20	6.60	0.67	*diff.*		
18.78	9.39	0.47	*diff.*		

d = 4.80 nm.

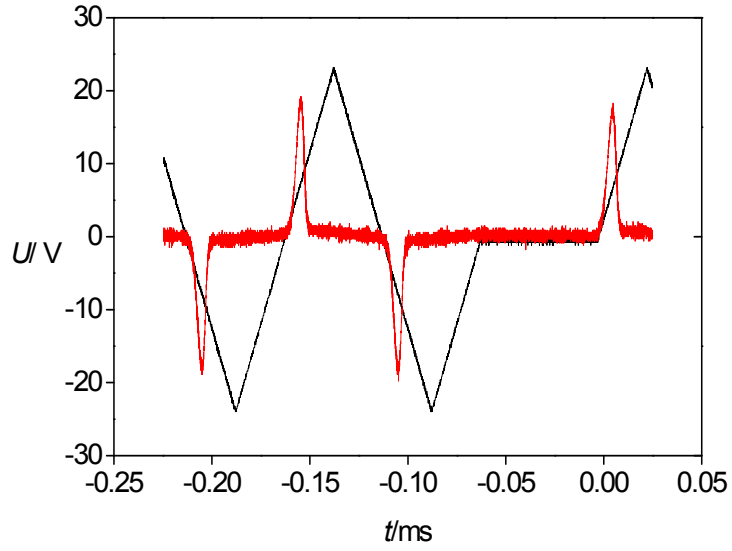


Figure S7. Switching current response curve of **T-Bip-Si** (with delay at 0V) at T = 71 °C (46 Vpp, 10 Hz, 10µm Non-coated ITO cell, 5kΩ)

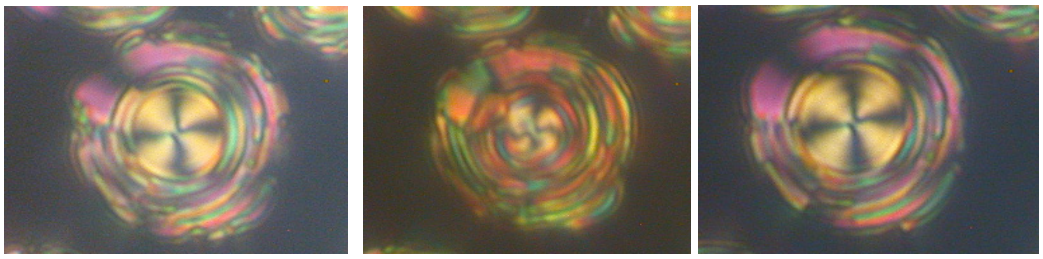


Figure S8. (a) Circular domains grown in the $Col_{ob}P_A$ hase of compound **T-Bip-Si** at 105 °C under a DC field of 100 V (left), after switching off the field (middle) and upon application of a DC field with opposite direction (right).

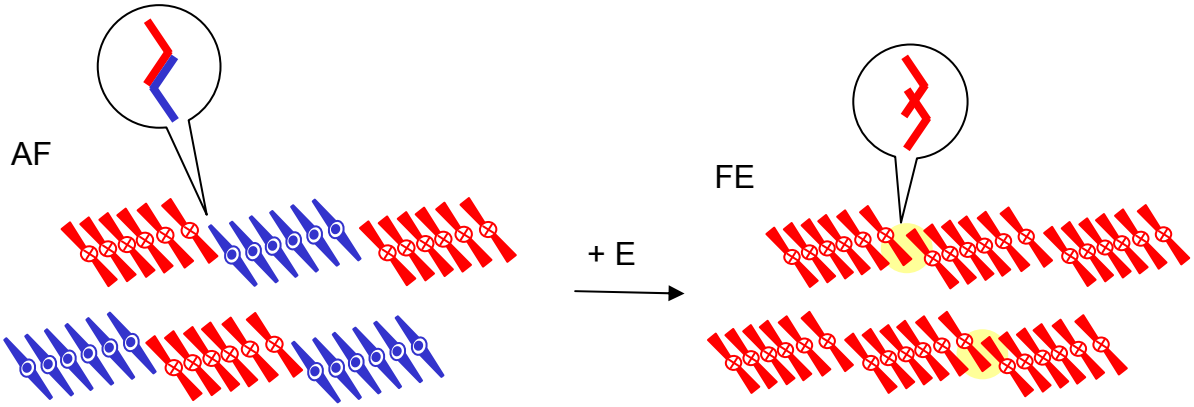
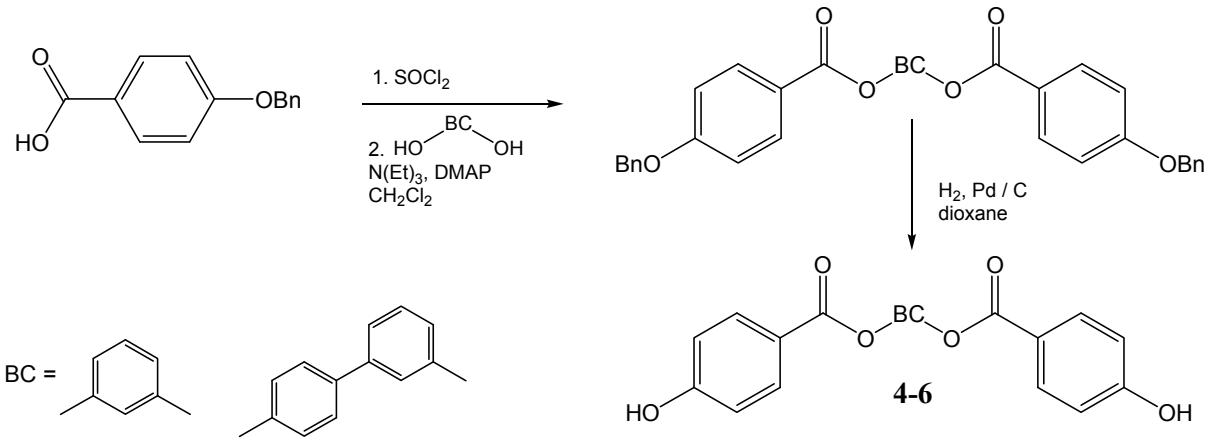


Figure S9. In the AF organization with alternation of polar direction along the modulated layers the rod-like wings of the bent-core mesogens are arranged parallel to each other; however in the FE state unfavorable inter-ribbon interfaces occur due to the non-parallel alignment of the rod-like wings within the modulated layers leads; though this could be reduced by splay is makes the FE order less favorable; the insets show the organization of the aromatic cores at the inter-ribbon interfaces in a side-view

2. Synthesis and Analytical Data

2.1 Synthesis of the bent diphenols 4-6



1,3-Phenylene bis(4-benzyloxybenzoate):[S1] 4-Benzyloxybenzoic acid[S2] (5 g, 22 mmol) was heated under reflux in an excess of thionyl chloride (50 ml) for 2 h. Excess thionyl chloride was removed by distillation under reduced pressure. The resulting acid chloride was dissolved in dry dichloromethane, and resorcinol (1.2 g, 11 mmol) was added. To this clear solution 4-(*N,N*-dimethylamino)pyridine (DMAP) (10 mg, 0.08mmol) and triethylamine (3.9 ml, 28 mmol) were added, and the reaction mixture was refluxed for 4 h at room temperature under a argon atmosphere. The reaction mixture was washed with 1M HCl solution and saturated $NaHCO_3$ solution and dried over Na_2SO_4. After evaporation of the solvent the crude product was purified by column chromatography using chloroform as an eluent and crystallized from ethyl acetate. Yield: 2.37 g (40.6 %), colorless solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.15 (m, 4H, Ar-H), 7.46-7.30 (m, 11H, Ar-H), 7.17 (m, 2H, Ar--H), 7.14 (m, 1H, Ar-H), 7.04 (m, 4H, Ar-H), 5.26 (s, 4H, -CH_2-).

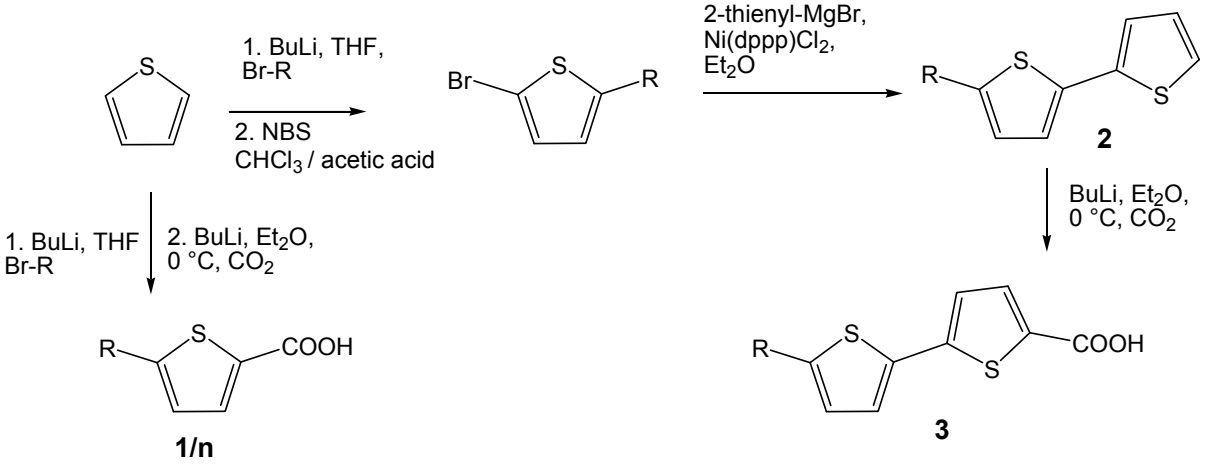
1,3-Phenylene bis(4-hydroxybenzoate) (4):[S1] 1,3-Phenylene bis(4-benzyloxybenzoate) (2.37 g, 4.5 mmol) was dissolved in 1,4-dioxane (50 ml) and 10% Pd–C catalyst (0.05 g) was added. The mixture was stirred at hydrogen pressure of 2.7 bar at 40 °C. The resultant mixture was filtered and the solvent removed under reduced pressure. The residue was passed through a column of silica gel and eluted with a mixture of 5 % methanol in chloroform and after removal of the solvent crystallized from methanol. Yield: 0.87 g (55.2 %), colorless solid, mp.: 235 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.24 (m, 4H, Ar-H), 7.47 (m, 1H, Ar-H), 7.17 (m, 2H, Ar-H), 7.14 (s, 1H, Ar-H), 6.90 (m, 4H, Ar-H).

2,7-Naphthalene bis(4-hydroxybenzoate) (5): Synthesized as described for **4** from 4-benzyloxybenzoic acid and naphthalene-2,7-diol. Colorless solid, mp.: 318 °C; ^{1}H-NMR (DMSO-d_6, *J*/Hz, 400 MHz): δ = 8.03 (m, 6H, Ar-H), 7.79 (m, 2H, Ar-H), 7.42 (m, 2H, Ar-H), 6.95 (m, 4H, Ar-H).

3,4'-Biphenyl bis(4-hydroxybenzoate) (6):[S3] Synthesized as described for **4** from 4-benzyloxybenzoic acid and 3,4'-dihydroxybiphenyl.[S4] Colorless solid, mp.: 190 °C; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400MHz): δ = 7.97 (m, 4H, Ar-H), 7.74 (d, ^3J (H,H) = 8.6, 2H, Ar-H), 7.59 (d,

^3J (H,H) = 8.3, 2H, Ar-H), 7.52 (m, 1H, Ar-H), 7.30 (d, ^3J H,H) = 8.3, 2H, Ar-H), 7.21 (d, ^3J (H,H) = 8.1, 1H, Ar-H), 6.90 (dd, ^3J (H,H) = 8.7, 4H, Ar-H).

2.2 Thiophene-2-carboxylic acids 1/*n*



General procedure for 2-alkylthiophenes:[S5] Under an argon atmosphere thiophene (1 equ.) was solved in anhydrous THF. A solution of *n*-butyl lithium in hexane (0.85 equ.) (1.6 M solution) was added dropwise under cooling with ice. Then the cooling bath was removed and the temperature was allowed to rise to 20 °C. The appropriate alkylbromide was added in one portion without external cooling. The reaction mixture was refluxed for 4 h and afterwards ice water was added. After separation of the layers, the aqueous layer was extracted twice with Et_2O. The organic solutions were combined and dried over sodium sulfate. After evaporation of the solvent the product was purified by fractionated distillation in vacuum.

2-Octylthiophene:[S6] Synthesized from thiophene (8.08 g, 0.096 mol), BuLi in hexane (1.6 M, 50 ml, 0.08 mol), octylbromide (20.1 g, 0.104 mol) in anhydrous THF (60 ml). Yield: 13.3 g (84.6 %), colorless liquid, bp.: 68 °C (3.2x10^{-2} mbar), ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.10 (dd, ^3J (H,H) = 5.1, 1H, Ar-H), 6.92 (m, 1H, Ar-H), 6.78 (m, 1H, Ar-H), 2.83 (t, ^3J (H,H) = 7.6,2H, -Th-CH_2-), 1.70 (quin, ^3J (H,H) = 7.5, 2H, -Th-CH_2-CH_2-), 1.31 (m, 10H, Alk-H), 0.91 (t, ^3J (H,H) = 6.8, 3H, -CH_3).

2-Dodecylthiophene:[S7] Synthesized from thiophene (8.08 g, 0.096 mol), BuLi in hexane (1.6 M, 50 ml, 0.08 mol), dodecyl bromide (23.0 g, 0.1 mol) in anhydrous THF (60 ml). Yield: 14.02 g (69.4 %), colorless liquid, bp.: 115 °C (1.8x10^{-2} mbar), ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.09 (d, ^3J (H,H) = 5.2, 1H, Ar-H), 6.90 (t, ^3J (H,H) = 3.7, 1H, Ar-H), 6.76 (d, ^3J (H,H) = 3.1, 1H, Ar-H), 2.81 (t, ^3J (H,H) = 7.7, 2H,-ThCH_2-), 1.67 (quin, ^3J (H,H) = 7.0, 2H, -Th-CH_2-CH_2-), 1.26 (m, 18H, Alk-H), 0.88 (t, ^3J (H,H) = 6.0, 3H, -CH_3).

2-Hexadecylthiophene:[S8] Synthesized from thiophene (4.04 g, 0.048 mol), BuLi in hexane (1.6 M, 25 ml, 0.04 mol), hexadecylbromide (15.9 g, 0.052 mol) in anhydrous THF (50 ml). The excess hexadecyl bromide was removed by destillation in vacuum. The residue was purified by flash-chromatography using chloroform as eluent. Yield: 14.5 g (97.5 %), brown oil, ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.08 (dd, ^3J (H,H) = 5.2, 1H, Ar-H), 6.89 (m, 1H, Ar-H), 6.76 (d, ^3J (H,H) = 2.3, 1H, Ar-H), 2.81 (t, ^3J (H,H) = 7.4, 2H, -Th-CH_2-), 1.66 (q, ^3J (H,H) = 7.4, 2H, -Th-CH_2-CH_2-), 1.25 (m, 26H, Alk-H), 0.88 (t, ^3J (H,H) = 6.8, 3H, -CH_3).

2-(Undec-10-en-1-yl)thiophene:[S9] Synthesised from thiophene (4.04 g, 0.048 mol), BuLi in hexane (1.6 M, 25 ml, 0.04 mol), 11-bromoundec-1-ene (12.12 g, 0.052 mol) in anhydrous THF (50 ml). Yield: 6.95 g (73.5 %), colorless liquid, bp.: 100 °C ($1.4x10^{-2}$ mbar), ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.09 (dd, ^3J (H,H) = 5.1, 1H, Ar-H), 6.90 (dd, ^3J (H,H) = 5.1, 1H, Ar-H), 6.76 (d, ^3J (H,H) = 3.5, 1H, Ar-H), 5.81 (m, 1H, -C*H*=CH_2), 4.96 (m, 2H, -CH=CH_2), 2.81 (t, ^3J (H,H) = 7.7, 2H, -Th-CH_2-), 2.04 (q, ^3J (H,H) = 4.7, 2H, CH_2-CH=CH_2), 1.67 (quin, ^3J (H,H) = 7.4, 2H, -Th-CH_2-CH_2-), 1.28 (m, 12H, Alk-H).

General procedure for thiophenecarboxylic acids 1/*n* and 3:[S10] The appropriate thiophene (1 equ.) was solved in dry diethyl ether under an argon atmosphere. To this mixture was added dropwise *n*-butyl lithium in hexane (1.6 M) under external ice cooling. After refluxing the reaction mixture for one hour the mixture was cooled down to room temperature and solid CO_2 (at least 10 fold excess) was carefully added. To complete the reaction the mixture was allowed rise to room temperature over night by stirring. The precipitated lithum salts were solved by adding water. The mixture was acidified with HCl and cooled with ice water. The precipitate was filtered and washed with water and crystallized from petroleum ether.

5-Octylthiophene-2-carboxylic acid (1/8):[S10] Synthesized from 2-octylthiophene (4 g, 20.3 mmol), BuLi in hexane (1.6 M, 12.7 ml, 20.3 mmol), dry Et_2O (70 ml) and CO_2 (approx. 10 g, 0.23 mol). Yield: 1.16 g (23.8 %), pale yellow solid, mp.: 72-73 °C, ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.60 (d, ^3J (H,H) = 3.5, 1H, Ar-H), 6.90 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 2.87 (t, ^3J (H,H) = 7.7, 2H, -Th-CH_2-), 1.70 (quin, ^3J (H,H) = 7.5, 2H, -Th-CH_2-CH_2-), 1.28 (m, 10H, Alk-H), 0.87 (t, ^3J (H,H) = 6.9, 3H, -CH_3).

5-Dodecylthiophene-2-carboxylic acid (1/12): Synthesized from 2-dodecylthiophene (1.99 g, 7.8 mmol), BuLi in hexane (1.6 M, 5 ml, 7.8 mmol), dry Et_2O (50 ml) and CO_2 (approx. 10 g, 0.23 mol). Yield: 1.54 g (66.6 %), colorless solid, mp.: 88 °C, ^{1}H-NMR (acetone-d_6, *J*/Hz, 400 MHz): δ = 7.59 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 6.90 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 2.86 (t, ^3J (H,H) = 7.6, 2H, -Th-CH_2-), 1.69 (m, 2H, -Th-CH_2-CH_2-), 1.27 (m, 18H, Alk-H), 0.86 (t, ^3J (H,H) = 6.85, 3H, -CH_3).

5-Hexadecylthiophene-2-carboxylic acid (1/16): Synthesized from 2-hexadecylthiophene (4 g, 12.9 mmol), BuLi in hexane (1.6 M, 8.1 ml, 12.9 mmol), dry Et_2O (70 ml) and CO_2 (approx. 10 g, 0.23 mol). Yield: 1.49 g (32.7 %), colorless solid, mp.: 96 °C, ^{1}H-NMR (acetone-d_6, *J*/Hz, 400 MHz): δ = 7.69 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 6.79 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 2.83 (t, ^3J (H,H) = 7.6, 2H, -Th-CH_2-), 1.68 (m, 2H, -Th-CH_2-CH_2-), 1.24 (m, 26H, Alk-H), 0.86 (t, ^3J (H,H) = 6.7, 3H, -CH_3).

5-(Undec-10-en-1-yl)thiophene-2-carboxylic acid (1/en): Synthesized from 2-(undec-10-en-1-yl)thiophene (2 g, 8.4 mmol), BuLi in hexane (1.6 M, 5.3 ml, 8.4 mmol), dry Et_2O (50 ml) and CO_2 (approx. 10 g, 0.23 mol). Yield: 1.69 g (71.3 %), pale yellow solid, mp.: 61 °C, ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.69 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 6.79 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 5.79 (m, 1H, C*H*=CH_2), 4.94 (m, 2H, CH=CH_2), 2.82 (t, ^3J (H,H) = 7.6, -Th-CH_2-), 2.01 (m, 2H, CH_2-CH=CH_2), 1.68 (qin, ^3J (H,H) = 7.4, 2H, -Th-CH_2-CH_2-), 1.6 (m, 12H, Alk-H).

2.3 5'-Dodecyl-2,2'-bithiopen-5-carboxylic acid 3

2-Bromo-5-dodecylthiophene 2:[S7] To a solution of 2-dodecylthiophene (2 g, 7.92 mmol) in chloroform (50 ml) and acetic acid (50 ml) was added *N*-bromosuccinimide (NBS) (1.4 g,

7.92 mmol) and stirred for 24 h at room temperature. Then the reaction mixture was washed to times with a 50 ml with water and aqueous $NaHCO_3$ and dried over sodium sulfate. After evaporation of the solvent the product was used without further purifications. Yield: 2,6 g (100 %)**,** brown oil, ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 6.82 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 6.51 (d, ^3J (H,H) = 3.7, 1H, Ar-H), 2.71 (t, ^3J (H,H) = 7.6, 2H, -ThCH_2-), 1.61 (quin, ^3J (H,H) = 7.3, 2H, -Th-CH_2-CH_2-), 1.24 (m, 18H, Alk-H), 0.87 (t, ^3J (H,H) = 6.7, 3H, CH_3).

5-Dodecyl-2,2'-bithiophene 3:[S7] In order to prepared the Grignard reagent 2-bromthiophene (4.56 g, 27.9 mmol) solved in anhydrous Et_2O (30 ml) was dropped within 3 h to a suspension of Mg turnings (0.72 g, 29.7 mg-atom) in refluxing dry Et_2O (100 ml). Under an argon atmosphere the Grignard reagent was cooled down and then added dropwise to a suspension of 2-bromo-5-dodecylthiophene (5.8 g,17.5 mmol) and Ni(dppp)Cl_2 (94 mg, 0.17 mmol) in anhydrous Et_2O. The reaction mixture was refluxed for 6 h. After cooling to room temperature the solution was hydrolyzed with 2 M HCl and extracted with Et_2O (3 x 100 ml). The organic phases were combined and washed successively with aqueous $NaHCO_3$, water and brine, and dried with sodium sulfate. After evaporation of the solvent the crude product was purified by centrifugal thin layer chromatography (eluent: petroleum ether) and crystallized from MeOH/Et_2O. Yield: 620 mg (10.2 %), pale yellow solid, mp.: 34 °C, ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.14 (dd, ^3J (H,H) = 5.0, 1H, Ar-H), 7.07 (dd, ^3J (H,H) = 3.5, 1H, Ar-H), 6.95 (m, 2H, Ar-H), 6.65 (d, ^3J (H,H) = 3.5, 1H, Ar-H), 2.76 (t, ^3J (H,H) = 7.6, 2H, -Th-CH_2-), 1.65 (m, 2H, -Th-CH_2-CH_2-), 1.24 (m, 18H, Alk-H), 0.86 (t, ^3J (H,H) = 6.8, 3H, -CH_3).

5'-Dodecyl-2,2'-bithiophene-5-carboxylic acid (3): Synthesized from 5-dodecyl-2,2'-thiophene (620 mg, 1.85 mmol), BuLi in hexane (1.6 M, 1.16 ml, 1.85 mmol) in anhydrous Et_2O (40 ml) and CO_2 (approx. 5 g, 0.115 mol). The crude product precipitate with HCl was purified by flash chromatography using chloroform as eluent and crystallized from petroleum ether. Yield: 250 mg (35.7 %), pale greenis solid, Cr 109 SmC 135 N 149 Iso (°C), ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 7.73 (d, ^3J (H,H) = 3.9, 1H, Ar-H), 7.10 (d, ^3J (H,H) = 3.5, 1H, Ar-H), 7.07 (d, ^3J (H,H) = 3.9, 1H, Ar-H), 6.70 (d, ^3J (H,H) = 3.5, 1H, Ar-H), 2, 78 (t, ^3J (H,H) = 7.6, 2H, -Th-CH_2-), 1.67 (quin, ^3J (H,H) = 7.3, 2H, -Th-CH_2-CH_2-), 1.24 (m, 18H, Alk-H), 0.86 (t, ^3J (H,H) = 6.7, 3H, -CH_3).

2.4 Compounds T-Bip-*n*, T-Rec-12, T-Nap-12 and T-Bip-en

General procedure of the esterification using DCC/CMC:[S11] The appropriate diphenol **4-6** (1 equ.), **1/*n*** or **3** (2.1 equ.) and a catalytic amount of 4-(*N,N*-dimethylamino)pyridine (DMAP) were dissolved in dry dichloromethane and stirred for 10 minutes. To this mixture, *N,N'*-dicyclohexylcarbodiimide (DCC) or *N*-cyclohexyl-*N*'-(2-morpholinoethyl)-carbodiimide methyl-p-toluenesulfonate (CMC) (2.6 equ.) was added and stirring was continued for 24 hours at room temperature. The reaction mixture was washed with water and dried over sodium sulfate and filtered. After evaporation of the solvent the crude product was purified by column chromatography using chloroform as an eluent and crystallized from ethyl acetate.

General procedure of the esterification via the acyl chlorides: 1/n (1 equ.) was heated under reflux in an large excess of thionyl chloride for 2 h. Excess thionyl chloride was removed by distillation at first under normal pressure, then under vacuum (bath temperature < 150 °C). The resulting acid chloride was dissolved in dry dichloromethane, and the appropriate diphenol **4-6** (0.5 equi.) was added. To this clear solution a catalytic amount of 4-

(*N,N*-dimethylamino)pyridine (DMAP) and triethylamine (1.3 equ.) were added, and the reaction mixture was refluxed for 4 h at room temperature under a argon atmosphere. The reaction mixture was washed with a 1M HCl solution and a saturated $NaHCO_3$ solution and dried over Na_2SO_4. After evaporation of the solvent the product was purified by column chromatography using chloroform as an eluent and crystallized from ethyl acetate.

T-Bip-8: The acid chloride was prepared from **1/8** (1.34 g, 5.57 mmol) and thionylchloride (20 ml) and then used for esterification with **6** (1.19 g, 2.79 mmol), triethylamine (1.01 ml, 7.24 mmol), DMAP (10 mg, 0.08 mmol) in dichloromethane (50 ml). Yield: 500 mg (23.8 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.27 (dd, ^3J (H,H) = 8.7, 4H, Ar-H), 7.83 (d, ^3J (H,H) = 3.7, 2H, Ar-H, 7.65 (d, ^3J (H,H) = 8.5, 2H, Ar-H), 7.50 (d, ^3J (H,H) = 5.2, 2H, Ar-H), 7.44 (s, 1H, Ar-H), 7.37 (dd, ^3J (H,H) = 8.6, 4H, Ar-H), 7.29 (d, ^3J (H,H) = 8.7, 2H, Ar-H), 7.21 (m, 1H, Ar-H), 6.87 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 2.87 (t, ^3J (H,H) = 7.6, 4H, -Th-CH_2-), 1.72 (quin, ^3J (H,H) = 7.4, 4H, -Th-CH_2-CH_2-), 1.27 (m, 20H, Alk-H), 0.87 (m, 6H, -CH_3); ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 164.30, 159.85, 156.19, 154.98, 151.36, 150.67, 142.06, 138.01, 135.41, 131.78, 129.80, 129.18, 128.27, 127.02, 125.63, 124.64, 122.02, 121.92, 120.57, 120.41, 31.85, 31.44, 30.64, 29.27, 29.18, 29.05, 22.66, 14.08; anal. calcd. for $C_{52}H_{54}O_8S_2$ C 71.69, H 6.25, S 7.36 found: C 71.59, H 6.22, S 7.35 %.

T-Bip-12: Synthesized from **1/12** (0.77 g, 2.59 mmol) and **6** (0.5 g, 1.18 mmol) with CMC (1.31 g, 3.1 mmol) and DMAP (10 mg, 0.08 mmol) in CH_2Cl_2 (50 ml). Yield: 320 mg (27.6 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.27 (dd, ^3J (H,H) = 8.7, 4H, Ar-H), 7.83 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 7.65 (d, ^3J (H,H) = 8.7, 2H, Ar-H), 7.49 (d, ^3J (H,H) = 5.0, 2H, Ar-H), 7.43 (s, 1H, Ar-H), 7.37 (dd, ^3J (H,H) = 8.9, 4H, Ar-H), 7.29 (d, ^3J (H,H) = 8.7, 2H, Ar-H), 7.20 (m, 1H, Ar-H), 6.86 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 2.87 (t, ^3J (H,H) = 7.6, 4H, -Th-CH_2-), 1.72 (quin, ^3J (H,H) = 7.3, 4H, -Th-CH_2-CH_2-), 1.25 (m, 36H, Alk-H), 0.86 (t, ^3J (H,H) = 6.7, 6H, -CH_3) ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 164.40, 159.92, 156.25, 154.95, 151.31, 150.62, 142.06, 138.02, 135.46, 131.82, 129.84, 129.10, 128.30, 126.96, 126.92, 125.65, 124.68, 122.04, 122.95, 120.58, 120.42, 31.88, 31.39, 30.58, 29.62, 29.60, 29.58, 29.47, 29.31, 29.26, 28.99, 22.65, 14.07; anal.calcd. for $C_{60}H_{70}O_8S_2$: C 73.28, H 7.18, S 6.52 found: C 73.56; H 7.43, S 6.56 %.

T-Bip-16: The acid chloride was prepared from **1/16** and thionylchloride (20 ml), (1.49 g, 4.22 mmol) and then used for esterification with **6** (0.9 g, 2.11 mmol), triethylamine (0.58 ml, 5.48 mmol), DMAP (10 mg, 0.08 mmol) in CH_2Cl_2 (50 ml). Yield: 1.27 g (54.9 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.27 (dd, ^3J (H,H) = 8.7, 4H, Ar-H), 7.83 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 7.65 (d, ^3J (H,H) = 8.5, 2H, Ar-H), 7.49 (d, ^3J (H,H) = 5.0, 2H, Ar-H), 7.43 (s, 1H, Ar-H), 7.36 (dd, ^3J (H,H) = 8.7, 4H, Ar-H), 7.29 (d, ^3J (H,H) = 8.7, 2H, Ar-H), 7.20 (m, 1H, Ar-H), 6.86 (d, ^3J (H,H) = 4.0, 2H Ar-H), 2.87 (t, ^3J (H,H) = 7.6, 4H, -Th-CH_2-), 1.72 (quin, ^3J (H,H) = 7.4, 4H, -Th-CH_2-CH_2-), 1.24 (m, 26H, Alk-H), 0.86 (t, ^3J (H,H) = 6.8, 6H, -CH_3; ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 164.38, 159.84, 156.19, 154.99, 151.36, 150.68, 142.07, 138.02, 135.40, 131.79, 129.81, 29.19, 128.28, 126.99, 125.62, 124.64, 122.02, 121.92, 120.57, 120.41, 31.95, 31.44, 30.65, 29.71, 29.70, 29.68, 29.64, 29.53, 29.37, 29.32, 29.06, 22.71, 14.11; anal. calcd. for $C_{68}H_{86}O_8S_2$: C 74.55, H 7.91, S 5.85 found: C 74.32, H 7.85, S 5.79 %.

T-Bip-en: Synthesized from **1/en** (1.37 g, 4.88 mmol) and **6** (0.94 g, 2.22 mmol) with CMC (2.4 g, 5.7 mmol) and DMAP (10 mg, 0.08mmol) in CH_2Cl_2 (50 ml). Yield: 200 mg (9.5 %), white solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.28 (m, 4H, Ar-H), 7.83 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 7.65 (d, ^3J (H,H) = 8.7, 2H, Ar-H), 7.50 (d, ^3J (H,H) = 5.2, 2H, Ar-H), 7.44 (s,

1H, Ar.H), 7.36 (m, 4H, Ar-H), 7.29 (d, ^{3}J (H,H) = 8.7, 2H, Ar-H), 7.20 (m, 1H, Ar-H), 6.87 (d, ^{3}J (H,H) = 3.7, 2H, Ar-H), 5.80 (m, 2H, -C*H*=CH_2), 4.95 (m, 4H, -CH=C*H*$_2$), 2.87 (t, ^{3}J (H,H) = 7.6, 4H, -Th-C*H*$_2$-), 2.03 (q, ^{3}J (H,H) = 1, 4H, -CH_2-CH=CH_2), 1.70 (quin, ^{3}J (H,H) = 7.4, 2H, -Th-CH_2-C*H*$_2$-), 1.28 (m, 24H, Alk-H); ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 164.31, 159.85, 156.17, 154.97, 151.35, 150.66, 142.06, 139.12, 138.01, 135.41, 131.79, 129.81, 129.18, 128.28, 127.01, 125.63, 124.65, 122.03, 121.93, 120.57, 120.41, 114.10, 33.80, 31.43, 30.64, 29.45, 29.28, 29.12, 29.03, 28.96; anal. calcd. for $C_{58}H_{62}O_8S_2$: C 73.23, H 6.57, S 6.74 found: C 73.08, H 6.31, S 6.84 %.

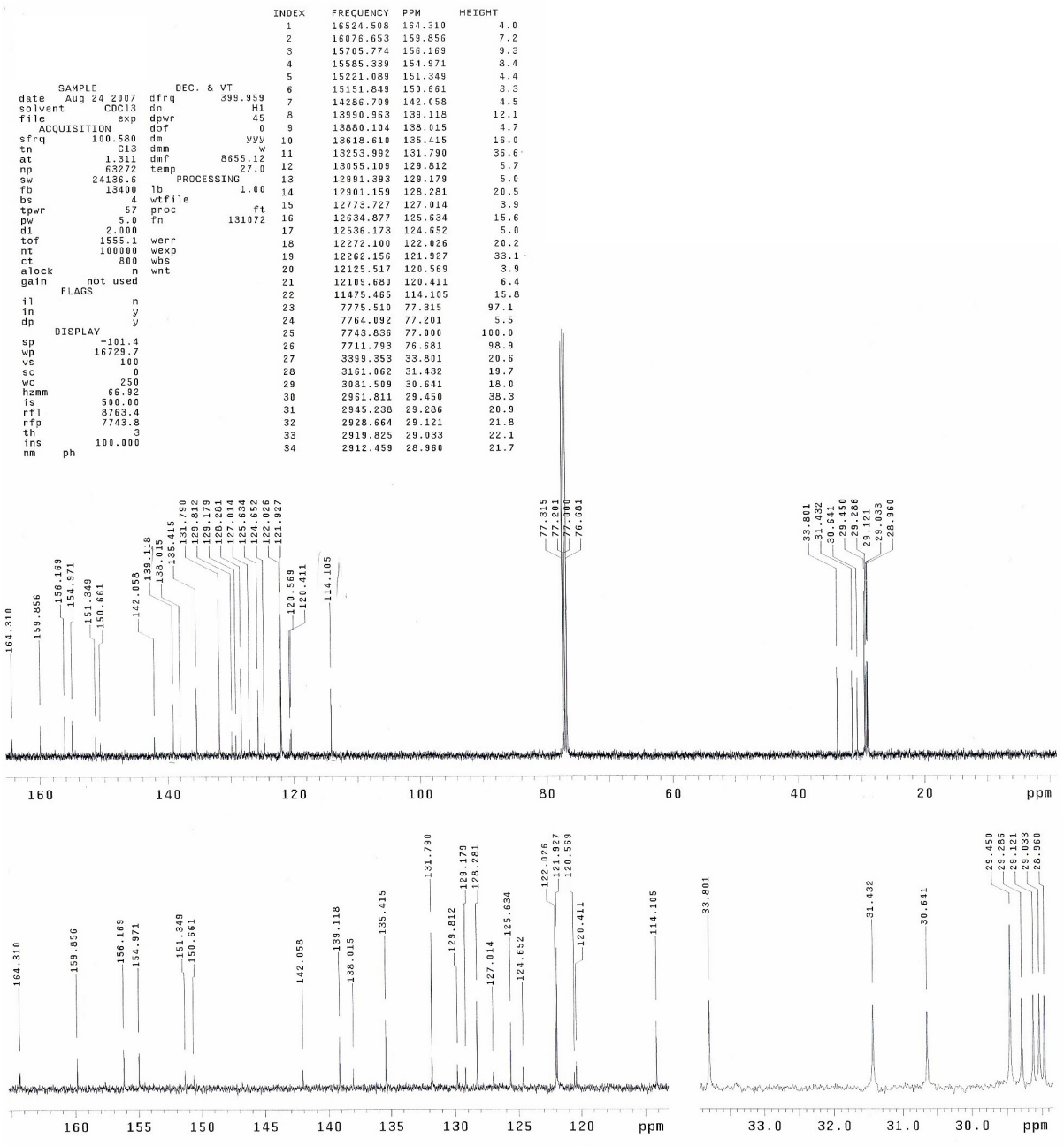


Figure S10. ^{13}C-NMR Spectrum ($CDCl_3$,100 MHz) of compound **T-Bip-en**.

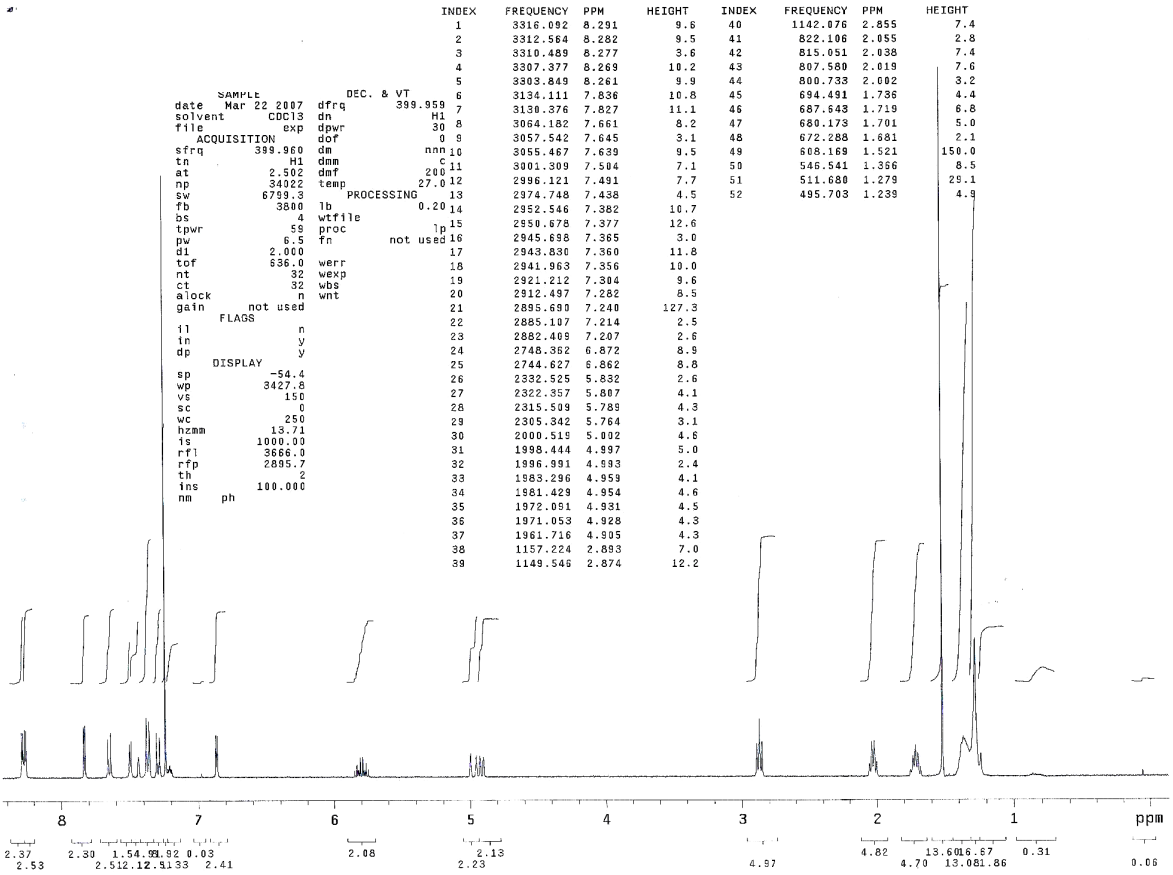


Figure S11. ^{1}H-NMR Spectrum ($CDCl_3$,400 MHz) of compound **T-Bip-en**.

T-Nap-12: Synthesized from **1/12** (0.77 g, 2.59 mmol) and **5** (0.47 g, 1.18 mmol) with DCC (0.6 g, 3.1 mmol) and DMAP (10 mg, 0.08 mmol) in CH_2Cl_2 (40 ml). Yield: 220 mg (19.4 %), colourless solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.30 (d, ^{3}J (H,H) = 8.7, 4H, Ar-H), 7.92 (d, ^{3}J (H,H) = 9.1, 2H, Ar-H), 7.83 (d, ^{3}J H,H) = 3.9, 2H, Ar-H), 7.67 (d, ^{3}J (H,H) = 7.1, 2H, Ar-H), 7.38 (d, ^{3}J (H,H) = 8.9, 4H, Ar-H), 7.35 (d, ^{3}J (H,H) = 2.3, 2H, Ar-H), 6.87 (d, ^{3}J (H,H) = 3.7, 2H, Ar-H), 2.87 (t,^{3}J (H,H) = 7.7, 4H, -Th-CH_2-), 1.72 (quin., ^{3}J (H,H) = 7.3, 4H, -Th-CH_2-CH_2-), 1.25 (m, 36H, Alk-H), 0.86 (t, ^{3}J (H,H) = 6.8, 6H, -CH_3); ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz):δ = 164.36, 159.84, 156.19, 154.99, 149.29, 135.41, 134.39, 131.81, 129.59, 129.36, 129.15, 126.94, 125.62, 121.93, 121.15,118.54, 31.93, 31.43, 30.63, 29.66, 29.64, 29.63, 29.52, 29.35, 29.31, 29.04, 22.70, 14.11; anal. calcd. for $C_{58}H_{68}O_8S_2$: C 72.77, H 7.16, S 6.70 found: C 72.48, H 7.37, S 6.68 %.

T-Res-12: Synthesized from **1/12** (0.77 g, 2.59 mmol) and **4** (0.41 g, 1.18 mmol) with CMC (1.31 g, 3.1 mmol) and DMAP (10 mg, 0.08 mmol) in CH_2Cl_2 (50 ml). Yield: 210 mg (19.6 %), colorless solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.25 (d, ^{3}J (H,H) = 8.7, 4H, Ar-H), 7.82 (d, ^{3}J (H,H) = 3.7, 2H, Ar-H), 7.47 (t, ^{3}J (H,H) = 5.5, 1H, Ar-H), 7,36 (d, ^{3}J (H,H) = 8.7, 4H, Ar-H), 7.17 (s, 2H, Ar-H), 7.15 (s, 1H, Ar-H), 6.86 (d, ^{3}J (H,H) = 3.7, 2H, Ar-H), 2.87 (t, ^{3}J (H,H) = 7.6, 4H, -Th-CH_2-), 1.72 (quin., ^{3}J (H,H) = 7.1, 4H, -Th-CH_2-CH_2-), 1.25 (m, 36H, Alk-H), 0.86 (t, ^{3}J (H,H) = 6.7, 6H, -CH_3); ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 163.95, 159.83, 156.20, 155.02, 151.42, 135.42, 131.80, 129.82, 129.14, 126.75, 125.63, 121.94, 119.22, 115.75, 31.94, 31.43, 30.64, 29.67, 29.65, 29.63, 29.53, 29.36, 29.31, 29.05, 22.71, 14.12; anal. calcd. for $C_{54}H_{66}O_8S_2$: C 71.49, H 7.33, S 7.07 found: C 71.37, H 7.39, S 7.05 %.

2.5 Compound TT-Res-12

TT-Res-12: The acid chloride was prepared from **3** (0.24 g, 0.65 mmol) and thionylchloride (20 ml) and then used for esterification with **4** (0.11 g, 0.32 mmol), triethylamine (0.115 ml, 8.27 mmol), DMAP (10 mg, 0.08mmol) in CH_2Cl_2 (30 ml). Yield: 220 mg (64.6 %), yellowish solid; ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.26 (d, ^3J(H,H) = 8.7, 4H, Ar-H), 7.86 d, ^3J (H,H) = 3.9, 2H, Ar-H), 7.48 (t, ^3J (H,H) = 8.0, 1H, Ar-H), 7.38 (d, ^3J (H,H) = 8.7, 4H, Ar-H), 7.18 (m, 2H, Ar-H), 7.14 (m, 5H, Ar-H), 6.73 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 2.81 (t, ^3J (H,H) = 7.6, 4H, -Th-CH_2-), 1.68 (quin., ^3J (H,H) = 1, 4H, -Th-CH_2- CH_2-), 1.25 (m, 36H, Alk-H), 0.87 (t, ^3J(H,H) = 6.7, 6H, -CH_3); ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 163.83, 159.60, 154.87, 151.35, 148.05, 146.68, 135.90, 133.30, 131.77, 129.77, 128.88, 126.81, 125.49, 125.24, 123.32, 121.85, 119.18, 115.70, 31.99, 31.60, 30.33, 29.73, 29.71, 29.60, 29.42, 29.41, 29.14, 22.77, 14.19; anal. calcd. for $C_{62}H_{70}O_8S_4$: C 69.50, H 6.58, S 11.97 found: C 69.51, H 6.55, S 11.97 %.

2.6 Compound T-Bip-Si

T-Bip-Si: T-Bip-en (200 mg, 0.21 mmol) was dissolved in anhydrous toluene (5 ml) under an argon atmosphere. To this solution, was added 1,1,3,3,5,5,5-heptamethyltrisiloxane (0.140 g, 0.63 mmol) and a drop of Karstedt's catalyst (platinum-divinyltetramethyl-siloxane complex in xylene, 2% Pt).[S12] The resultant reaction mixture was stirred continuously at room temperature under argon till completion of the reaction, which was determined by TLC. The solvent was evaporated and the crude product was purified by chromatography on silica gel using $CHCl_3$ as an eluent Yield: 190 mg (64,8 %), colorless solid, ^{1}H-NMR ($CDCl_3$, *J*/Hz, 400 MHz): δ = 8.27 (dd, ^3J (H,H) = 8.7, 4H, Ar-H), 7.83 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 7.65 (d, ^3J (H,H) = 8.5, 2H, Ar-H), 7.49 (d, ^3J (H,H) = 5.0, 2H, Ar-H), 7.43 (s, 1H, Ar-H), 7.37 (dd, ^3J (H,H) = 8.6, 4H, Ar-H), 7.29 (d, ^3J (H,H) = 8.5, 2H, Ar-H), 7.21 (m, 1H, Ar-H), 6.86 (d, ^3J (H,H) = 3.7, 2H, Ar-H), 2.87 (t, ^3J (H,H) = 7.6, 4H, -Th-CH_2-), 1.72 (quin, ^3J (H,H) = 7.3, 4H, -Th-CH_2-CH_2-), 1.25 (m, 32H, Alk-H), 0.51 (t, ^3J (H,H) = 7.6, 4H, -Si-CH_2-), 0.07 (s, 18H, -Si(CH_3)$_3$), 0.04 (s, 12H,-O-Si(CH_3)$_2$-O-Si(CH_3)$_3$), 0.00 (s, 12H,-CH_2-Si(CH_3)$_2$-O-); ^{13}C-NMR ($CDCl_3$, *J*/Hz, 100 MHz): δ = 164.23, 159.76, 156.11, 154.92, 151.30, 150.62, 142.01, 137.97, 135.34, 131.73, 129.75, 129.15, 128.23, 126.96, 125.57, 124.60, 121.91, 120.53, 120.37, 33.50, 31.51, 30.71, 29.74, 29.65, 29.60, 29.47, 29.39, 29.14, 23.33, 18.44, 1.94, 1.39, 0.35 ^{29}Si-NMR ($CHCl_3$, *J*/Hz, 100MHz): δ = 7.48, 7.04, -21.06.

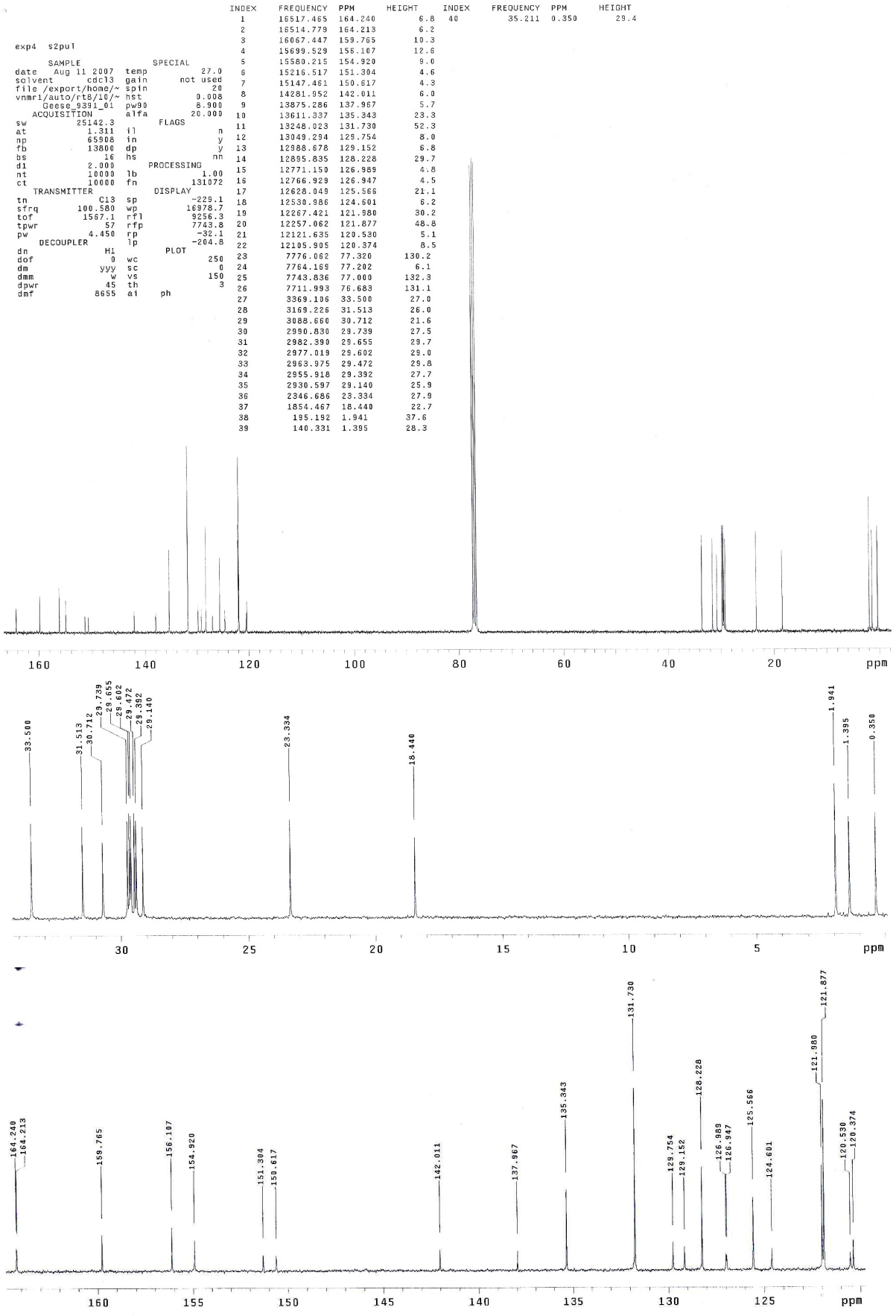
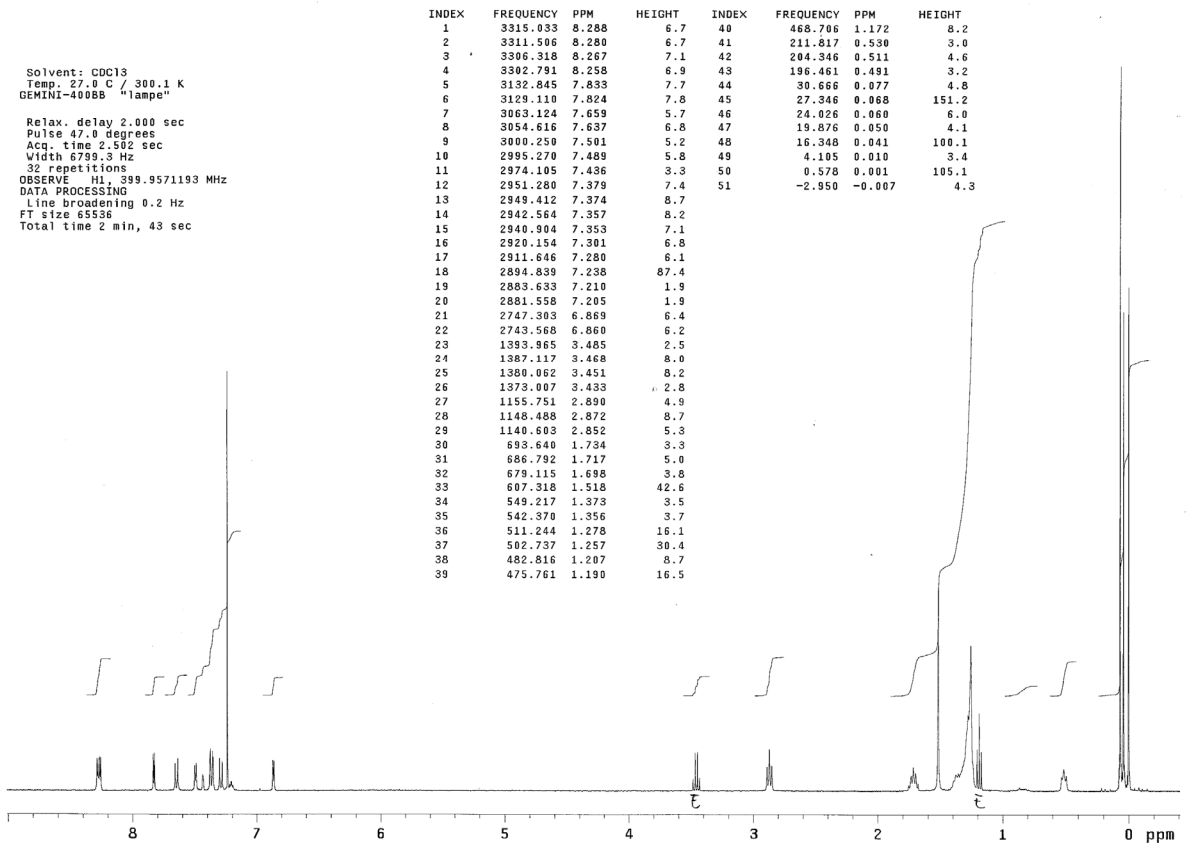


Figure S12. ^{13}C-NMR Spectrum ($CDCl_3$,100 MHz) of compound **T-Bip-Si**.



INDEX	FREQUENCY	PPM	HEIGHT	INDEX	FREQUENCY	PPM	HEIGHT
1	3315.033	8.288	6.7	40	468.706	1.172	8.2
2	3311.506	8.280	6.7	41	211.817	0.530	3.0
3	3306.318	8.267	7.1	42	204.346	0.511	4.6
4	3302.791	8.258	6.9	43	196.461	0.491	3.2
5	3132.845	7.833	7.7	44	30.666	0.077	4.8
6	3129.110	7.824	7.8	45	27.346	0.068	151.2
7	3063.124	7.659	5.7	46	24.026	0.060	6.0
8	3054.616	7.637	6.8	47	19.876	0.050	4.1
9	3000.250	7.501	5.2	48	16.348	0.041	100.1
10	2995.270	7.489	5.8	49	4.105	0.010	3.4
11	2974.105	7.436	3.3	50	0.578	0.001	105.1
12	2951.280	7.379	7.4	51	-2.950	-0.007	4.3
13	2949.412	7.374	8.7				
14	2942.564	7.357	8.2				
15	2940.904	7.353	7.1				
16	2920.154	7.301	6.8				
17	2911.646	7.280	6.1				
18	2894.839	7.238	87.4				
19	2883.633	7.210	1.9				
20	2881.558	7.205	1.9				
21	2747.303	6.869	6.4				
22	2743.568	6.860	6.2				
23	1393.965	3.485	2.5				
24	1387.117	3.468	8.0				
25	1380.062	3.451	8.2				
26	1373.007	3.433	2.8				
27	1155.751	2.890	4.9				
28	1148.488	2.872	8.7				
29	1140.603	2.852	5.3				
30	693.640	1.734	3.3				
31	686.792	1.717	5.0				
32	679.115	1.698	3.8				
33	607.318	1.518	42.6				
34	549.217	1.373	3.5				
35	542.370	1.356	3.7				
36	511.244	1.278	16.1				
37	502.737	1.257	30.4				
38	482.816	1.207	8.7				
39	475.761	1.190	16.5				

Figure S13. ^{1}H-NMR Spectrum ($CDCl_3$,400 MHz) of compound **T-Bip-SI**.

3. References

S1 R. A. Reddy and B. K. Sadashiva, *J. Mater. Chem.,* 2002*,* **12**, 2627-2632.

S2 M. C. Venuti, B. E. Loe, G. H. Jones and J. M. Young, *J. Med. Chem.,*1988*,* **31**, 2132-2136. J. W. Y. Lam, Y. Dong, K. K. L. Cheuk and B. Z. Tang, *Macromolecules,* 2003*,* **36**, 7927-7938.

S3 J. Barbera, N. Gimeno, L. Monreal, R. Pinol, M. B. Ros and J. L. Serrano, *J. Am. Chem. Soc.,* 2004, **126**, 7190-7191.

S4 D. Shen, A. Pegenau, S. Diele, I. Wirth and C. Tschierske, *J. Am. Chem. Soc.,* 2000*,* **122**, 1593-1601.

S5 V. Ramanathan and R. Levine, *J. Org. Chem.,* 1962, **27**, 1667-1670; S. Ponomarenko and S. Kirchmeyer, *J. Mater. Chem.,* 2003, **13**, 197-202.

S6 S. Kotha, D. Kashinath, K. Lahiri and R. Sunoj, *Eur. J. Org. Chem*., **2004**, 4003-4013.

S7 P. Bäuerle, F. Würthner, G. Götz and F. Effenberger, *Synthesis,* 1993, **11**, 1099-1103.

S8 K. E. Miller, C. Haymaker and H. Gilman, *J.Org. Chem.,* 1959, **24**, 622-624.

S9 A. Kreyes, S. Ellinger, K. Landfester, M. Defaux, D. A. Ivanov, A. Elschner, T. Meyer-Friedrichsen and U. Ziener, *Chem. Mater.,* 2010, **22**, 2079-2092.

S10 G. Koßmehl and D. Budwill, *Z. Naturforsch*., **38b**, 1983, 1669-1677.

S11 C. Tschierske and H. Zaschke, *J. Prakt. Chem.,* 1989, **331**, 365-366.

S12 C. Keith, R. Amaranatha Reddy, U. Baumeister and C. Tschierske, *J. Am. Chem. Soc.,* 2004, **126**, 14312-14313; G. Mehl and J.W. Goodby*, Chem. Ber.* 1996, **129**, 521-525.