Supplementary Materials for

Stereoselective Helix-Sense-Selective Cationic Polymerization of *N*-vinylcarbazole Using Chiral Lewis Acid Catalysis

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1. Materials and Methods

1.1. General Considerations

Prior to use, *N*-vinylcarbazole was recrystallized twice from hexanes, dried under vacuum overnight, and stored in a N_2-filled glovebox freezer. *1*-isobutoxyethyl acetate was dried over CaH_2, distilled under vacuum, and stored over 3 Å molecular sieves for 48 hours prior to storage in a N_2-filled glovebox freezer before further use. Scandium(III) trifluoromethanesulfonate 99.995% trace metal purity was purchased and used from MilliporeSigma (St. Louis, MO). Unless otherwise noted, solvents were dried and degassed using a Pure Process Technology solvent purification system and then subsequently stored over molecular sieves (3Å) in a N_2-filled glovebox. Other reagents whose syntheses are not described in Section 2 were purchased from commercial sources (Alfa Aesar (Ward Hill, MA), MilliporeSigma (St. Louis, MO), Oakwood Products (West Columbia, SC), Acros Organics (Geel, Belgium), and TCI America (Portland, OR)) and used without further purification. All syntheses were performed under inert atmosphere (N_2 or Ar) using flame-dried or oven-dried glassware unless specified otherwise. Qualitative TLC analysis was performed on 250 mm thick, 60 Å, glass backed, F254 silica (SiliCycle, Quebec City, Canada). Visualization was accomplished with UV light, exposure to *p*-anisaldehyde solution followed by heating, or exposure to $KMnO_4$ solution followed by heating. Flash chromatography was performed using SiliCycle silica gel (230-400 mesh).

NMR spectra were recorded using a Bruker DRX 400 MHz, Bruker AVANCE III 500 MHz, or Bruker AVANCE III 600 MHz CryoProbe spectrometer. Chemical shifts δ (ppm) are referenced to tetramethylsilane (TMS) using the residual solvent as an internal standard (^{1}H and ^{13}C). For ^{1}H NMR: $CDCl_3$, 7.26 ppm and $C_2D_2Cl_4$, 6.04 ppm. For ^{13}C NMR: $CDCl_3$, 77.16 ppm. Coupling constants (J) are expressed in hertz (Hz). High temperature NMR (HT NMR) for poly(NVC) tacticity characterization was recorded on a Bruker 500 MHz spectrometer at 100 °C with solvent resonance as the internal standard (1H NMR: C2D2Cl4 at 6.00 ppm; 13C NMR: C2D2Cl4 at 73.78 ppm). In all experiments, an ethylene glycol standard confirmed the temperature of the NMR and the delay time was set to 5 sec (d1 = 5). 1H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, ddd = doublet of doublet of doublets, td = triplet of doublets, tdd = triplet of doublet of doublets, qd = quartet of doublets, m = multiplet, bs = broad singlet), coupling constants (Hz), and integration.

Circular dichroism (CD) measurements were collected on a Chirascan Plus instrument with a wavelength range of 250-350 nm in 1.0 nm steps with 4.000 sec scans per point. Samples were observed in a 1 mm quartz cuvette at 0.1 mg/mL in HPLC grade, filtered THF. The sample temperature was controlled using a Quantum Northwester TC125 unit with Julabo AWC100 water bath. A Savitzky-Golay smoothing filter with window size < 8 was applied to the chromatogram. Optical rotations were collected using a Jasco P-1010 polarimeter at 25 ºC, using a 2 mL cell with 1 dm path length. All HPLC samples were prepared in HPLC grade methanol. HPLC data was collected using a Perkin Elmer Flexar HPLC system equipped with a Perkin Elmer PDA detector and Daicel CHIRALPAK IA column. Samples **3a** and **3c** degraded significantly on the IA column. Sample **3b** was more stable but hydrolysis did occur—derivatization of **3a** led to similar decomposition via carbazole elimination. Yield refers to isolated yield of pure material unless otherwise noted. Infrared (IR) spectra were obtained using PerkinElmer Frontier FT-IR spectrometer. High-resolution mass spectrometry (HRMS) was performed with a ThermoScientific Q Exactive HF-X mass spectrometer using electrospray ionization at the University of North Carolina Mass Spectrometry Core Laboratory.

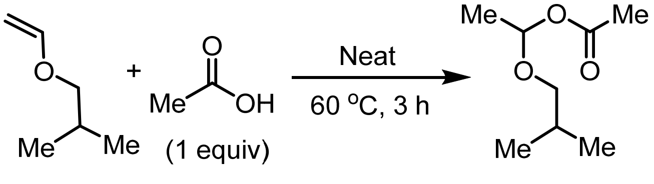
1.2. Macromolecular Characterization

Gel permeation chromatography (GPC) was performed on a Tosoh EcoSEC Elite GPC system equipped with a TSKgel Super HM-M (17392) column maintained at 40 °C with an RI detector and a Tosoh LENS^{TM} 3 multi-angle light scattering detector (MALS) Tetrahydrofuran was used as the mobile phase at a flow rate of 0.5 mL/min. Molecular weight and dispersity data are reported relative to polystyrene standards. For highly isotactic samples, high temperature gel permeation chromatography (HT GPC) spectra were obtained using a Tosoh EcoSEC-HT GPC using TSKgel GMHHR-M columns. 1,2,4-trichlorobenzene (TCB) was prepared with 200 ppm dibutylhydroxytoluene (BHT) by stirring overnight and was the mobile phase. The flow rate was set to 1 mL/min and samples were prepared at concentrations of 2 mg/mL in TCB with 200 ppm BHT. The instrument was calibrated using 17 polystyrene standards in the range of 580 to 5,480,000 Da. A calibration curve was created using refractive index detection against 2 mg/mL polystyrene standards in TCB with 200 ppm BHT at 140 °C. A tandem multi-angle light scattering (MALS) detector could also be employed on the HT GPC via a Wyatt DAWN 8 heated flow cell instrument.

2. Experimental Section

2.1. Ligand and Initiator Synthesis

1-isobutoxyethyl acetate (1a):

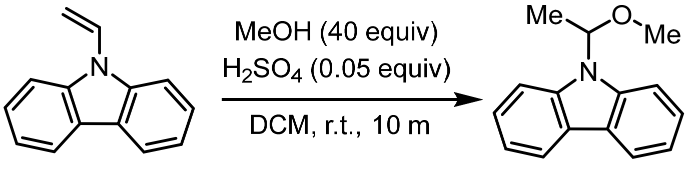


(1a)

1a was prepared according to previously reported literature.[1]

To a 100-mL round bottom flask equipped with a magnetic stir bar was added 2-methyl-1-(vinyloxy)propane (20.0 g, 0.2 mol) and glacial acetic acid (8 g, 7.6-mL, 0.13 mol) at room temperature. The reaction mixture was heated to 60 °C for 3 hours. Afterwards, excess 2-methyl-1-(vinyloxy)propane and acetic acid was removed under reduced pressure. The crude product was distilled twice over calcium hydride under reduced pressure (61 °C, 20 Torr) to give a sweet smelling colorless oil (87%). **^{1}H NMR** (400 MHz, Chloroform-d) δ 5.92 (q, J = 5.2 Hz, 1H), 3.45 (dd, J = 9.2, 6.6 Hz, 1H), 3.25 (dd, J = 9.2, 6.9 Hz, 1H), 2.1 (s, 3H), 1.86 (dp, J = 13.3, 6.7 Hz, 1H), 1.42 (d, J = 5.3 Hz, 3H), 0.92 (dd, J = 6.7, 2.0 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl3) δ 170.86, 96.60, 75.95, 28.39, 21.29, 20.69, 20.64, 19.22, 19.17.

9-(1-methoxyethyl)-9H-carbazole (2a):

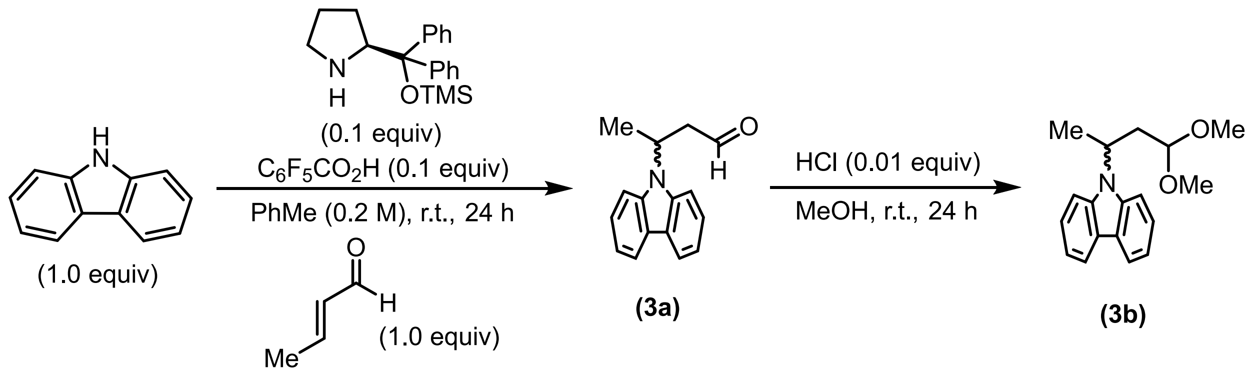


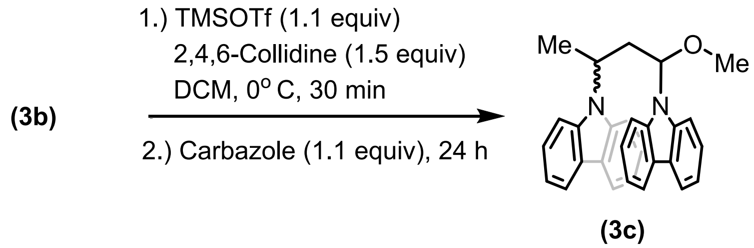
(2a)

(2a) has been previously prepared and characterized.[2] We developed a modified synthetic procedure to access larger quantities of material.

To a 100 mL round bottom flask equipped with a magnetic stir bar was added 9-vinyl-9H-carbazole (5.00 g, 1 equiv, 25.9 mmol) which was suspended in a dry methanol (33.2 g, 41.9 mL, 40 equiv, 1.03 mol) and DCM (5 mL) mixture. After stirring for 5 minutes, concentrated sulfuric acid (127 mg, 0.05 equiv, 1.29 mmol) was added. The suspension turned clear in under 5 minutes, then a white solid precipitates over the course of 10 minutes. The reaction is put on ice and the precipitate is filtered, washed with cold MeOH, and dried under vacuum overnight to yield pure product (85%). **^{1}H NMR** (400 MHz, CDCl3) δ 8.13 (td, J = 7.8, 1.0 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.47 (td, J = 8.3, 7.1, 1.3 Hz, 2H), 7.32 – 7.24 (, 3H), 5.92 (q, J = 6.1 Hz, 1H), 3.25 (s, 3H), 1.82 (d, J = 6.1 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl3) δ 139.15, 125.75, 123.62, 120.34, 119.46, 110.50, 83.99, 55.79, 20.08.

Synthesis route to enantioenriched 3-(9H-carbazol-9-yl)butanal (3a), 9-(4,4-dimethoxybutan-2-yl)-9H-carbazole (3b), and 9,9'-(1-methoxybutane-1,3-diyl)bis(9H-carbazole) (3c):





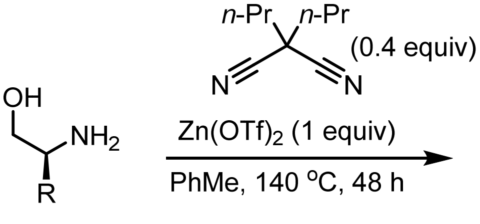
Carbazole to 3a. To a 5-dram scintillation vial equipped with a stir bar were added (S)-2(S)-2-(diphenyl((trimethylsilyl)oxy)methyl)pyrrolidine (19.5 mg, 0.10 Eq, 59.8 µmol), (E)-but-2-enal (62.9 mg, 74.3 µL, 1.5 Eq, 897 µmol), PhMe (5 mL), and 2,3,4,5,6-pentafluorobenzoic acid (12.7 mg, 0.10 Eq, 59.8 µmol) and stirred for 5 minutes until the solution turned yellow before adding 9H-carbazole (100 mg, 1.0 Eq, 598 µmol), capping the vial, and stirring overnight at 23 °C. The reaction was quenched with 10-mL of sat. aq. $NaHCO_3$ and extracted with DCM (5x25-mL) and dried over $NaSO_4$. The organic phase was concentrated at low pressure and purified with flash column chromatography eluted with a gradient of EtOAc:Hexanes from 0% to 10%. Rf: 0.13 (20% EtOAc:Hexanes) to yield pure product **3a** (60%). After isolation of **3a** or used crude, it was used immediately for the synthesis of **3b**. **^{1}H NMR** (400 MHz, CDCl3) δ 9.75 (t, J = 1.3 Hz, 1H), 8.13 (d, J = 7.8, 1.0 Hz, 2H), 7.56 (t, J = 8.3, 0.9 Hz, 2H), 7.49 (td, J = 8.3, 7.0, 1.2 Hz, 2H), 7.26 (m, 2H), 5.48 (sext, J = 7.0 Hz, 1H), δ 3.33 (ABq, J = 17.6, 7.1, 1.3 Hz, 2H), 1.76 (d, J = 7.1 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 199.39, 139.46 (br), 125.66, 123.55 (br), 120.48, 119.11, 109.92 (br) 48.72, 45.08, 19.36. **Specific rotation** $[\alpha]^{20}_{D}$: +3.9 (c=1.0, $CHCl_3$); **IR** (THF) 3076, 2981, 2878, 2713, 1726, 1626, 1596, 1483, 1452, 1332, 1313, 1242, 1229, 1225, 1159, 1067, 1025, 897 cm^{-1}.

NOTE: The racemic initiator was synthesized using piperidine as the amine catalyst instead and gave comparable isolated yields. Isolation of product is not necessary, used for the purpose of characterization. Unable to fly under tested HR-MS conditions, elimination rapidly occurs in polar solvent (MeCN).

3a to 3b. To a 5-dram scintillation vial equipped with a stir bar were added dry 3-(9H-carbazol-9-yl)butanal (50 mg, 1.00 Eq, 0.21 mmol) **(3a)** and methanol (3.16 g, 4.00 mL, 98.8 mmol). A solution of methanol and aq. hydrogen chloride (77 µg, 0.35 µL, 6 molar, 0.01 Eq, 2.1 µmol) were added and the reaction was stirred under N_2 for 4 hours. After the reaction was complete, the crude mixture was poured into 5 mL of saturated aqueous $NaHCO_3$. The aqueous phase was extracted with EtOAc (3 x 10 mL) and the combined organic phases were collected and washed with sat. brine solution, dried over $NaSO_4$, filtered through glass wool, and concentrated under reduced vacuum. The crude mixture was purified with flash chromatography eluted with a gradient of EtOAc:Hexanes from 5-20% to yield **(3b)** a clear white-solid (78%, 69% ee) . RF : 0.28 in 10% EtOAc: Hexanes. **^{1}H NMR** (600 MHz, CDCl3) δ 8.19 – 8.10 (m, 3H), 7.46 – 7.40 (m, 2H), 7.32 – 7.21 (m, 3H), 5.04 (dqd, J = 10.2, 7.1, 4.7 Hz, 1H), 3.96 (dd, J = 8.3, 3.4 Hz, 1H), 3.20 (d, J = 9.8 Hz, 6H), 2.66 (ddd, J = 14.0, 10.4, 3.4 Hz, 1H), 2.25 (ddd, J = 14.0, 8.3, 4.6 Hz, 1H), 1.73 (d, J = 7.2 Hz, 3H); **^{13}C NMR** (151 MHz, CDCl3) δ 139.48, 125.85, 125.51 (br), 123.34, 120.36, 120.28 (br), 119.44, 118.79, 111.43, 102.31, 54.03, 52.63, 47.37, 37.54, 19.42; **Specific rotation** $[\alpha]^{20}_D$: +17.8 (c=1.0, $CHCl_3$); **HPLC** (95:5 hexanes:MeOH, Daicel CHIRALPAK IA): 84.2:15.8, t_R (major) = 4.7 min, t_R (minor) = 6.2 min; **HRMS** (ESI-) ($[C_{17}H_{18}NO]^+$([M-OMe]) 252.13883, Found: 252.13780; **IR** (THF) 3068, 2956, 2942, 2825, 1627, 1593, 1483, 1453, 1408, 1376, 1333, 1316, 1267, 1237, 1222, 1195, 1157, 1124, 1098, 1052, 996, 964, 922, 904, 892 cm^{-1}.

3b to 3c. To a 10-mL vial 9-(4,4-dimethoxybutan-2-yl)-9H-carbazole (250.00 mg, 1.00 Eq, 882 µmol) and 2,4,6-trimethylpyridine (160 mg, 175 µL, 1.50 Eq, 1.32 mmol) were mixed in 4 mL of DCM and cooled to 0 °C. Then a solution of trimethylsilyl trifluoromethanesulfonate (215 mg, 175 µL, 1.00 Eq, 970 µmol) in 1 mL of DCM was added and the solution turned a light pink and faded to a pale green. After stirring for 30 minutes, 9H-carbazole (161 mg, 1.1 Eq, 970 µmol) dissolved in 9-mL of DCM (*tendency to crystallize in syringe*) was added dropwise over 10 minutes. The reaction was allowed to stir overnight and was quenched with 5-mL of sat. aq. $NaHCO_3$, extracted with DCM (3x20-mL), and dried over $NaSO_4$. The organic phase was reduced under reduced pressure and redissolved in minimal dried pentanes, filtered to remove excess carbazole/salts, then dried under reduced pressure. The crude mixture was purified with two separate flash chromatography columns eluted first with EtOAc:hexanes from 5 to 25%, then 20% DCM in hexanes to yield **3c** as a white solid (53%). The major diastereomer was isolated running a 0 to 5% gradient of THF in pentanes. **^{1}H NMR** (400 MHz, CDCl3) δ 8.35 – 6.80 (m, 16H), 5.56 (dd, J = 8.6, 5.2 Hz, 1H), 4.65 – 4.52 (m, 1H), 3.40 (ddd, J = 15.0, 10.0, 5.2 Hz, 1H), 3.13 (ddd, J = 14.5, 8.6, 5.5 Hz, 1H), 3.01 (s, 3H), 1.56 (d, J = 6.9 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 125.73, 125.68, 125.50, 120.13, 119.71, 119.44, 119.16, 118.86, *84.91*, 84.56, *55.94*, 55.67, *47.84*, 47.33, *38.37*, 37.99, 34.18, 22.41, *19.34*, 19.12, 14.14. (diastereomeric minor peaks italicized). **Specific rotation** $[\alpha]^{20}_D$: +2.1 (c=1.0, $CHCl_3$); **HRMS (**ESI-) ($[C_{29}H_{26}N_2O^{*+}]$): 418.20451, Found: 418.20219. **IR** (neat) 3065, 3039, 2981, 2941, 2859, 2847, 1626, 1594, 1482, 1448, 1408, 1321, 1229, 1224, 1194, 1159, 1125, 1102, 1089, 1056, 1049, 1002, 922 cm^{-1}.

Synthesis route to Di-*n*-Pr substituted BOX ligands (L1-L11) (10-50 mmol scale):



Using a reported procedure: [3]

Di-n-propylmalononitrile (2.0 mmol, 1.0 equiv) was dissolved in PhMe (30 mL) and to the solution was added the desired amino alcohol (5.0 mmol, 2.5 equiv), and $Zn(OTf)_2$ (5.0 mmol, 2.5 equiv). The reaction mixture was sealed and heated at 145 ºC for 48 h. The reaction mixture was cooled to ambient temperature and quenched with sat. Na_2CO_3 (30 mL). After extraction with CH_2Cl_2 (100 mL x 1, 50 mL x 3), the combined organic layer was dried over Na_2SO_4, concentrated, and loaded onto silica gel and purified (hexane/ethyl acetate = 9:1) to afford the ligand (**L1-L11**) in 31-87% yield.

(L1) 2,2'-(heptane-4,4-diyl)bis(4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (600 MHz, CDCl3) δ 7.35 – 7.31 (m, 4H), 7.29 – 7.24 (m, 6H), 5.24 (dd, J = 10.1, 8.1 Hz, 2H), 4.66 (dd, J = 10.2, 8.4 Hz, 2H), 4.11 (t, J = 8.2 Hz, 2H), 2.16 – 2.02 (m, 4H), 1.41 – 1.30 (m, 4H), 0.97 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 169.30, 142.56, 128.82, 127.67, 126.90, 75.16, 69.76, 46.45, 35.26, 17.57, 14.58. The characterization data for this compound match the literature data. [3]

(L2) 2,2'-(heptane-4,4-diyl)bis(4,5-dihydrooxazole): Using the procedure outlined above. **1H NMR** (600 MHz, CDCl3) δ 4.26 (t, J = 9.5 Hz, 2H), 3.89 (t, J = 9.5 Hz, 2H), 1.94 – 1.86 (m, 4H), 1.22 (dddd, J = 13.5, 11.1, 6.1, 3.9 Hz, 4H), 0.94 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 67.51, 61.04, 54.19, 34.83, 17.37, 14.43, 14.19.

(L3) (4S,4'S)-2,2'-(heptane-4,4-diyl)bis(4-benzyl-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (600 MHz, CDCl3) δ 7.43 – 7.18 (m, 10H), 4.42 (tdd, J = 9.3, 7.0, 4.6 Hz, 2H), 4.16 (dd, J = 8.0, 6.3 Hz, 2H), 3.99 (dd, J = 8.5, 7.0 Hz, 2H), 3.19 (dd, J = 13.7, 4.6 Hz, 2H), 2.62 (dd, J = 13.7, 9.2 Hz, 2H), 1.95 (ddd, J = 10.5, 5.7, 4.0 Hz, 4H), 1.25 – 1.11 (m, 4H), 0.95 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 168.19, 137.88, 129.36, 128.54, 126.48, 71.67, 67.26, 45.87, 41.60, 34.86, 17.20, 14.48.

(L4) (4S,4'S)-2,2'-(heptane-4,4-diyl)bis(4-phenethyl-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.18 (dd, *J* = 9.3, 7.8 Hz, 1H), 4.05 – 3.89 (m, 2H), 2.03 – 1.87 (m, 2H), 1.87 – 1.80 (m, 1H), 1.80 – 1.72 (m, 2H), 1.72 – 1.63 (m, 2H), 1.63 – 1.56 (m, 1H), 1.48 (tdt, *J* = 12.0, 6.4, 3.3 Hz, 1H), 1.31 – 1.11 (m, 5H), 0.99 (ddq, *J* = 17.5, 8.8, 4.3 Hz, 2H), 0.94 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (151 MHz, CDCl3) δ 168.19, 129.36, 128.54, 126.48, 71.67, 67.26, 45.87, 41.60, 34.86, 17.21, 14.48.

(L5) (4S,4'S)-2,2'-(heptane-4,4-diyl)bis(4-(naphthalen-2-ylmethyl)-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (400 MHz, CDCl3) δ 7.81 (tdd, J = 8.4, 3.1, 2.1

Hz, 6H), 7.69 – 7.61 (m, 2H), 7.54 – 7.42 (m, 4H), 7.35 (dd, J = 8.4, 1.8 Hz, 2H), 4.52 (tdd, J = 9.2, 7.1, 4.5 Hz, 2H), 4.14 – 4.09 (m, 2H), 3.99 (dd, J = 8.6, 7.1 Hz, 2H), 3.32 (dd, J = 13.7, 4.4 Hz, 2H), 2.80 (dd, J = 13.7, 9.0 Hz, 2H), 1.96 (tt, J = 8.5, 7.4 Hz, 4H), 1.25 – 1.04 (m, 4H), 0.91 (t, J = 7.3 Hz, 7H). **^{13}C NMR** (151 MHz, CDCl3) δ 168.25, 135.29, 133.49, 132.24, 129.07, 128.25, 128.13, 127.86, 127.82, 127.63, 127.53, 126.07, 125.50, 125.32, 71.56, 67.08, 45.90, 41.61, 34.89, 17.22, 14.42.

(L6) (4S,4'S)-2,2'-(heptane-4,4-diyl)bis(4-isopropyl-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (400 MHz, CDCl3) δ 4.26 – 4.13 (m, 2H), 4.06 – 3.90 (m, 4H), 2.10 – 1.77 (m, 6H), 1.33 – 1.16 (m, 4H), 0.94 (t, J = 7.1 Hz, 13H), 0.88 (d, J = 6.8 Hz, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 167.49, 71.67, 69.42, 45.90, 34.66, 32.29, 18.87, 17.56, 17.25, 14.46.

(L7) (4S,4'S)-2,2'-(octane-4,4-diyl)bis(4-(tert-butyl)-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (600 MHz, CDCl3) δ 4.13 (dd, J = 10.1, 8.6 Hz, 2H), 4.04 (dd, J = 8.7, 7.3 Hz, 2H), 3.87 (dd, J = 10.1, 7.3 Hz, 2H), 2.02 (ddd, J = 13.9, 12.0, 5.0 Hz, 2H), 1.88 (ddd, J = 13.9, 12.0, 4.9 Hz, 2H), 1.35 – 1.18 (m, 4H), 0.94 (t, J = 7.3 Hz, 6H), 0.90 (s, 18H). **^{13}C NMR** (151 MHz, CDCl3) δ 167.40, 75.48, 68.42, 46.05, 34.94, 33.90, 25.83, 17.40, 14.46.

(L8) (4S,4'S)-2,2'-(heptane-4,4-diyl)bis(4-cyclohexyl-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (600 MHz, CDCl3) δ 4.18 (dd, J = 9.2, 7.8 Hz, 2H), 4.02 – 3.86 (m, 4H), 2.02 – 1.87 (m, 4H), 1.87 – 1.66 (m, 9H), 1.48 (tdt, J = 12.0, 6.4, 3.3 Hz, 2H), 1.34 – 1.09 (m, 11H), 1.00 (dddd, J = 16.4, 12.5, 8.0, 3.8 Hz, 5H), 0.94 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 167.33, 71.03, 69.79, 45.94, 42.40, 34.65, 29.50, 28.27, 26.57, 26.23, 26.07, 17.26, 14.47.

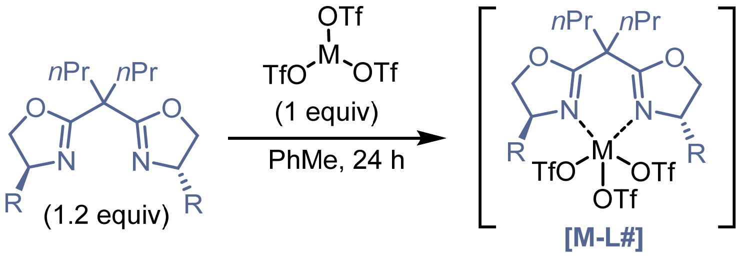
(L9) (4S,4'S,5R,5'R)-2,2'-(octane-4,4-diyl)bis(4,5-diphenyl-4,5-dihydrooxazole): Using the procedure outlined above. **^{1}H NMR** (600 MHz, CDCl3) δ 7.09 – 6.91 (m, 20H), 5.97 (d, J = 10.1 Hz, 2H), 5.60 (d, J = 10.1 Hz, 2H), 2.46 – 2.38 (m, 2H), 2.26 (ddd, J = 14.0, 12.4, 4.7 Hz, 2H), 1.61 – 1.47 (m, 8H), 1.09 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (151 MHz, CDCl3) δ 169.24, 137.40, 136.01, 127.90, 127.62, 127.40, 126.95, 126.65, 86.15, 73.66, 46.87, 35.32, 17.65, 14.54.

(L10) (3aR,3a'R,8aS,8a'S)-2,2'-(heptane-4,4-diyl)bis(3a,8a-dihydro-8H-indeno[1,2-d]oxazole): Using the procedure outlined above. **1H NMR** (600 MHz, Chloroform-d) δ 7.53 (s, 2H), 7.36 – 7.19 (m, 6H), 5.55 (d, J = 7.7 Hz, 2H), 5.23 (d, 2H), 3.28 (dd, J = 17.8, 6.9 Hz, 2H), 2.87 (d, J = 17.8 Hz, 2H), 1.89 (dtd, J = 40.7, 13.8, 4.8 Hz, 4H), 1.11 – 0.87 (m, 4H), 0.80 (t, J = 7.3 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl3) δ 168.01, 141.95, 139.59, 128.31, 127.40, 125.59, 125.01, 82.76, 76.30, 45.62, 39.57, 33.75, 16.76, 14.29. **Specific rotation** $[\alpha]^{20}_{D}$: +307 (c=1.0, $CHCl_3$). **HR-MS** (ESI-) ($[C_{27}H_{31}N_2O_2^+]$[M+H]) Expected = 415.23855, Found = 415.23705; **IR** (neat) 3052, 2966, 2943, 2875, 1647, 1597, 1456, 1453, 1321, 1223, 1135, 1120, 1058, 1003, 910, 859 cm^{-1}.

The enantiomer was synthesized by the same protocol.

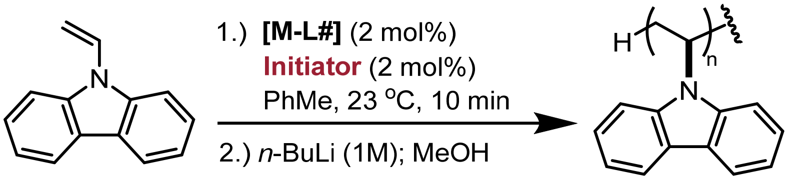
(L11) (3aS,3a'S,8aR,8a'R)-2,2'-(heptane-4,4-diyl)bis(3a,8a-dihydro-8H-indeno[1,2-d]oxazole): Specific rotation $[\alpha]^{20}_{D}$: -301 (c=1.0, $CHCl_3$)

2.2. General Procedure for the In-situ Synthesis of Lewis Acid-BOX Complexes



To a 5-mL vial equipped with a magnetic stir bar in a glove box under inert atmosphere (N_2) was added the designated Lewis acid (5.18 µmol, 1 equiv.) and ligand **(L1-L11)** (6.21 µmol, 1.2 equiv.) and 0.5 mL of toluene to create a 0.0518 M solution relative to Sc. The suspension was stirred overnight at room temperature vigorously to yield a clear solution which was used the same day. No appreciable change in reactivity was noticed for up to a month, but with depreciating % mm values after 2 days. A significantly lower resulting isotacticity was observed when using lower purity metal triflates (e.g. 98% vs. 99.995%)

2.3. General Procedure for the Lewis Acid Catalyzed Polymerization of NVC

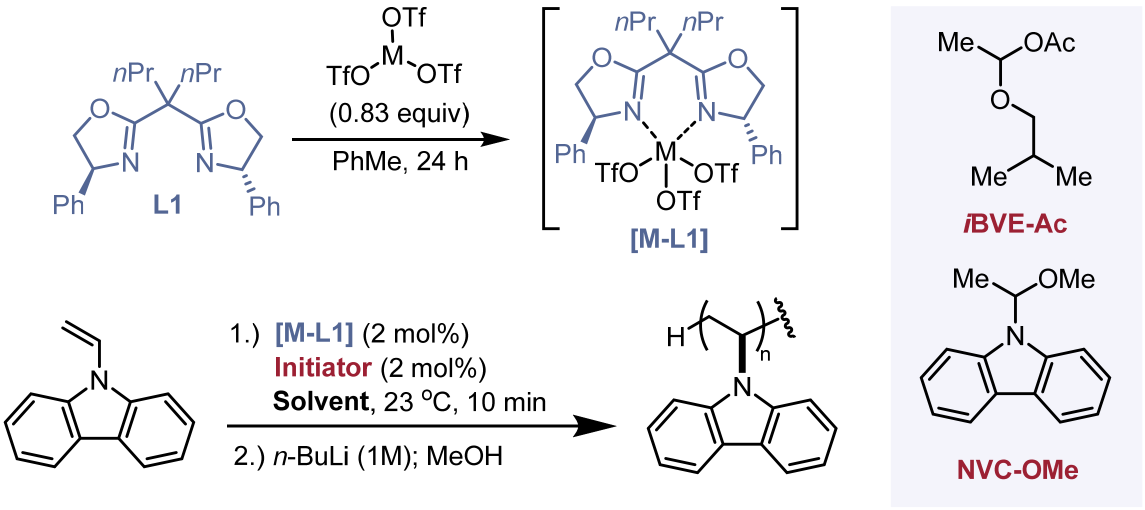


To a 5-mL vial equipped with a magnetic stir bar in a glove box under inert atmosphere (N_2) was added 9-(1-methoxyethyl)-9H-carbazole (1.17 mg, 5.18 µmol, 51.8 mM in PhMe, 100 µL), toluene (1.4 mL), and ligated Lewis acid-BOX complex (5.18 µmol, 51.8 mM in PhMe, 100 µL) and was allowed to stir vigorously for 5 minutes after which a solution of *N*-vinyl carbazole (50 mg, 258 µmol) in 0.5 mL of toluene was added. The reaction was quenched after 10 minutes with a stock solution of 1.0 M *n*-BuLi in hexanes (50 µL), allowed to stir briefly, and protonated with an addition of dry MeOH (1 mL). The solvent was removed under reduced pressure to yield crude polymer. The crude polymer was twice dissolved in 2 mL of dichloromethane and precipitated into MeOH to yield pure polymer. Pure poly(NVC) was analyzed by GPC and $^{1}H/^{13}C$-NMR for molecular weight, dispersity, and tacticity.

2.4. Other Reaction Conditions (Table S1, Figure S1-2)

All reactions entries below (Table S1, 1-18) were ran using the general procedures outlined in 2.2 and 2.3 for Lewis acid ligation and polymerization.

Table S1: Other reaction conditions of polymerization of *N*-vinylcarbazole



Entry	Lewis Acid	Initiator	Ligand	T (°C)	Conc. (M)	Solvent	% Conv.[b]	M_n (kDa)[c]	Đ[c]	%mm[d]
1	$Cu(OTf)_2$	*i* BVE-Ac	L1	23	0.24	PhMe	0	--	--	--
2	$Ca(OTf)_2$	*i* BVE-Ac	L1	23	0.24	PhMe	0	--	--	--
3	$Hf(OTf)_4$	*i* BVE-Ac	L1	23	0.24	PhMe	90	n.d.	n.d.	65
4	$Eu(OTf)_3$	*i* BVE-Ac	L1	23	0.24	PhMe	84	n.d.	n.d.	68
5	$Sc(OTf)_3$	*i* BVE-Ac	L10	23	0.12	PhMe	>99	26	2.6	88
6	$Sc(OTf)_3$	*i* BVE-Ac	L10	0	0.12	PhMe	>99	82	2.8	90
7	$Sc(OTf)_3$	*i* BVE-Ac	L10	-20	0.12	PhMe	>99	94	3.3	92
8	$Sc(OTf)_3$	NVC-OMe	L1	-41	0.12	PhMe	>99	138	3.5	85
9	$Sc(OTf)_3$	NVC-OMe	L1	-78	0.12	PhMe	0	--	--	--
10	$Sc(OTf)_3$	NVC-OMe	L1	23	0.12	CH_2Cl_2	>99	33	3.7	83
11	$Sc(OTf)_3$	NVC-OMe	L1	23	0.12	$PhCF_3$	>99	13	3.8	87
12	$Sc(OTf)_3$	NVC-OMe	L1	23	0.12	C_6H_6	>99	17	3.6	84
13	$Sc(OTf)_3$	NVC-OMe	L11	23	0.12	PhMe	>99	23	4.3	91
14	$Sc(OTf)_3$	NVC-OMe	L11	0	0.12	PhMe	>99	72	4.2	92
15	$Sc(OTf)_3$	NVC-OMe	L11	-20	0.12	PhMe	>99	143	4.0	92
16	$Sc(OTf)_3$	NVC-OMe	L11	-20	0.09	PhMe	>99	123	3.8	93
17	$Sc(OTf)_3$	NVC-OMe	L11	-20	0.06	PhMe	>99	Insoluble in $C_6Cl_3H_3$		94
18	$Sc(OTf)_3$	NVC-OMe	L11:L10 1:1	23	0.12	PhMe	>99	28	3.7	91

[a] All polymerizations were ran with 0.26 mmol of NVC and targeted a M_n of 9.7 kDa. [b] Conversion into poly(NVC) was determine from crude ^{1}H-NMR. [c] Molecular weight distributions were determined by a GPC RI detector in THF at 1 mg/mL. [d] Tacticity was determined by integrating the separated mm and mr/rr peaks by -NMR at 100 °C in $C_2D_2Cl_4$. [e] -20 °C, GPC RI detector in 1,3,5-trichlorobenzene at 140 °C, 1 mg/mL, and a PS standard.

Using the general polymer procedure outlined in section 2.3, but at [0.06] NVC concentration to slow down the observed rate, the reaction conversion was determined over time. [Sc-**L11**] was used in combination with NVC-OMe to initiate polymerization at room temperature. Each time point is a separate reaction to reduce error involved with taking rapid aliquots and quenching with ^{n}BuLi solution.

Conversion was determined by ^{1}H-NMR of the crude sample after solvent was removed and plotted against Mn determined at 140 ºC in 1,3,5-trichlorobenzene by GPC. These data display rapid chain-growth kinetics and highlight the difficulty for achieving oligomeric species for analysis

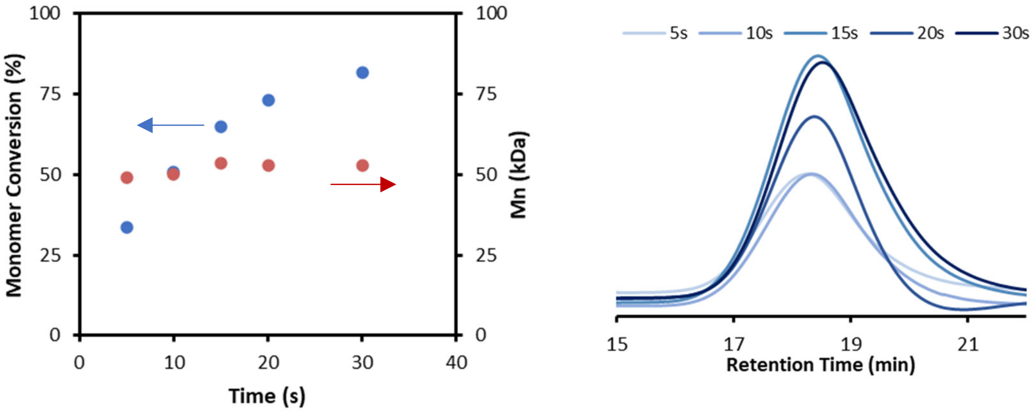


Figure S1: Chain-growth kinetics of polymerization (23 ºC) at [0.06] monomer concentration and the accompany GPC traces measure at 140 ºC in 1,3,5-trichlorobenzene.

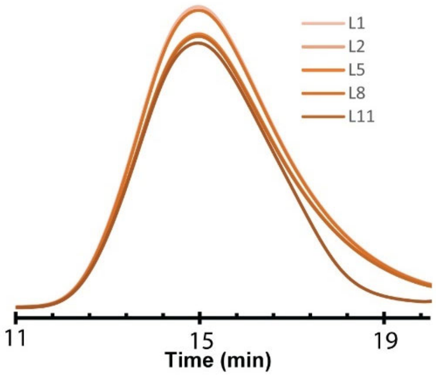


Figure S2: Representative GPC traces measured in THF of samples shown in Figure 3.

2.5.BOX Ligand Bridge Position Substitution (Figure S3)

All reactions entries below (Figure S1) were ran using the general procedures outlined in 2.2 and 2.3 for Lewis acid ligation and polymerization, but at [NVC] = 0.24 M.

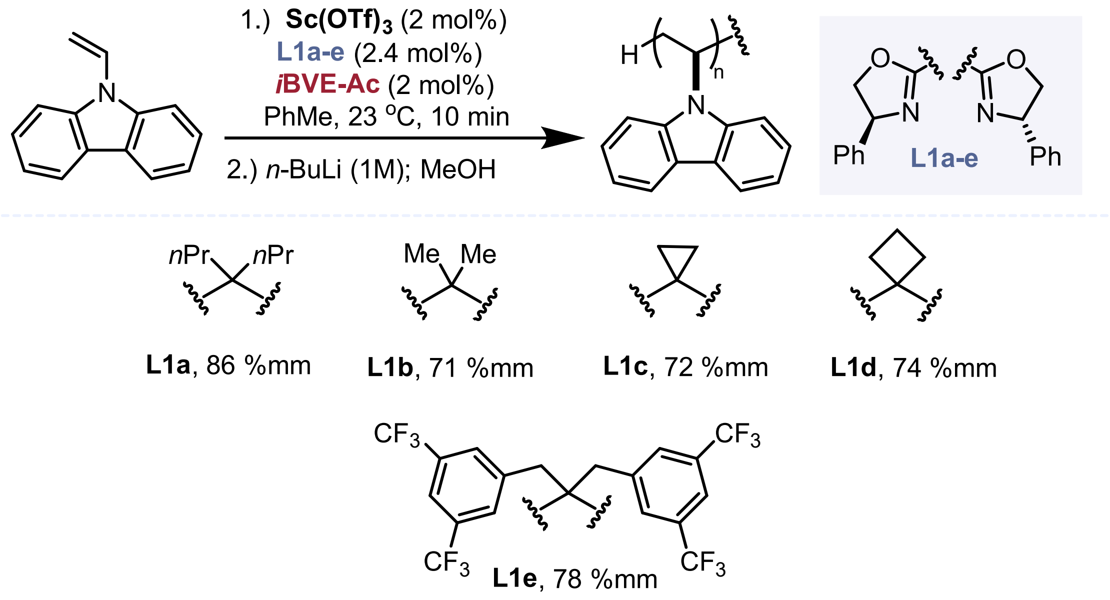


Figure S3: Effect of substitution at bridge position of BOX ligand on tacticity.

2.6. CD Response of Polymers Prepared (Figure S4-S8, Table S2-S4)

Circular dichroism data for the polymers prepared with [Sc-L3] shown in Figure 3 using conditions outlined in 1.1. General Considerations. A 0.1 mg/mL concentration of poly(NVC) in tetrahydrofuran was required as higher concentrations led to absorbances greater than 1.0 abs, non-linear responses, and incomplete solubility. Whereas lower concentrations approached responses similar to the level of detection of the instrument under the designated parameters.

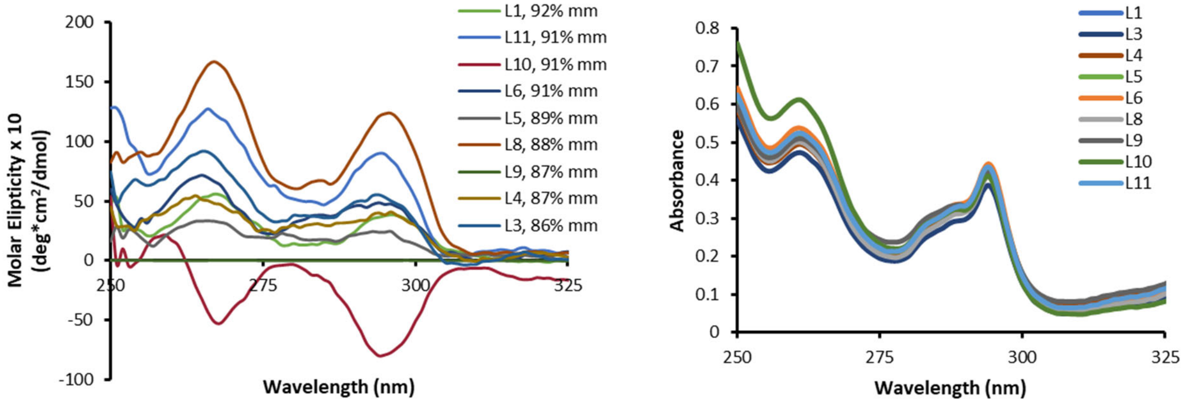


Figure S4: Circular dichroism and absorbance of poly(NVC) prepared using different ligands outlined in Figure 3.

Full spectra values at 296 nm are tabulated below to show the lack of relationship between absolute CD response and *mm* % values

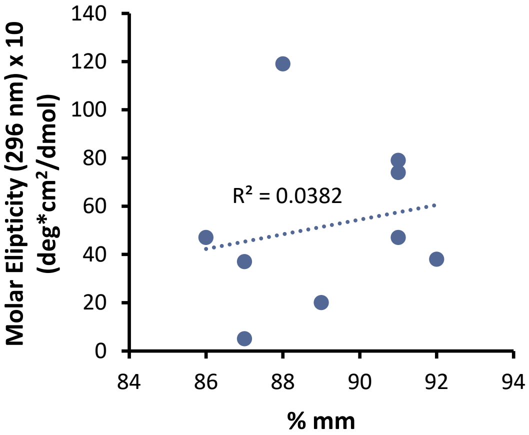


Figure S5: Tabulated molar ellipticity of Figure S2 samples at 296 nm peak.

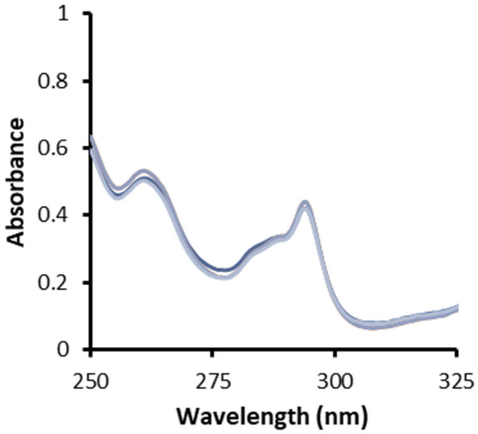


Figure S6: Absorbance spectra of CD data shown in Figure 5B.

(+)-dCz with different ee% were prepared via mixing with racemic initiator synthesized from achiral amine catalyst piperidine to yield the results displayed in Figure 5B. The polymers used in Figure 5 are outlined below.

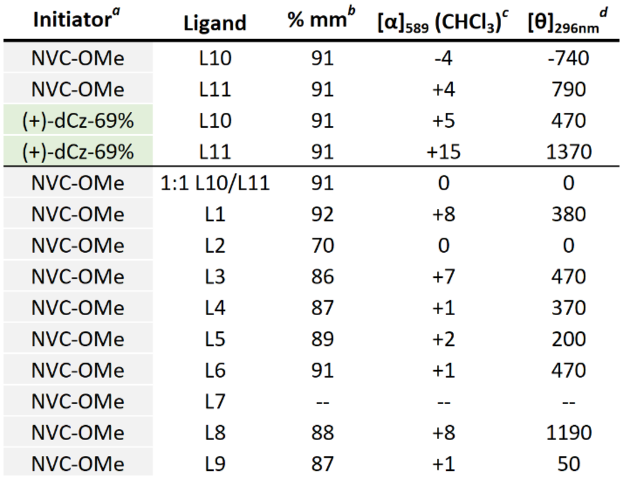
Table S2: Reaction conditions and analysis of samples used in Figure 5

Initiator[a]	ee%	Ligand	Conversion[b]	% mm[c]	Mn (kDa)[d]	Đ, RI[d]	$[\theta]_{296nm}$[e]	$[\theta]_{265nm}$[e]
NVC-OMe	0	L10	>99	91	22.8	4.3	-740	-470
NVC-OMe	0	L11	>99	91	24.5	4.4	790	1190
(+)-dCz	69	L10	>99	91	22.0	4.8	470	820
(+)-dCz	69	L11	>99	91	21.7	4.6	1370	1960
(+)-dCz	50	L11	>99	91	22.9	4.9	1070	1520
(+)-dCz	25	L11	>99	91	20.2	4.7	590	850
(+)-dCz	0	L11	>99	91	21.4	4.8	210	310

[a]All polymerizations were ran with 0.26 mmol of NVC and targeted a M_n of 9.7 kDa. [b]Conversion into poly(NVC) was determine from crude ^{1}H-NMR. [c]Tacticity was determined by integrating the separated mm and mr/rr peaks by ^{1}H-NMR at 100 °C in $C_2D_2Cl_4$. [d]Molecular weight distributions were determined by a GPC RI detector in THF at 1 mg/mL.[e]Molar ellipticity values are in (deg*cm^2*dmol^{-1}).

Polymers shown in Figure 3 and 5 have their specific rotations tabulated below

Table S3: Polarimetry results of polymer samples from Figures 3 & 5:

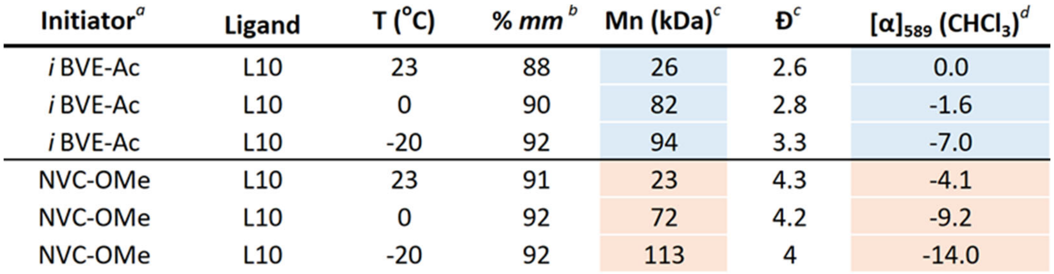


Initiator[a]	Ligand	% mm[b]	[α]$_{589}$ (CHCl$_3$)[c]	[θ]$_{296nm}$[d]
NVC-OMe	L10	91	-4	-740
NVC-OMe	L11	91	+4	790
(+)-dCz-69%	L10	91	+5	470
(+)-dCz-69%	L11	91	+15	1370
NVC-OMe	1:1 L10/L11	91	0	0
NVC-OMe	L1	92	+8	380
NVC-OMe	L2	70	0	0
NVC-OMe	L3	86	+7	470
NVC-OMe	L4	87	+1	370
NVC-OMe	L5	89	+2	200
NVC-OMe	L6	91	+1	470
NVC-OMe	L7	--	--	--
NVC-OMe	L8	88	+8	1190
NVC-OMe	L9	87	+1	50

[a]All polymerizations were ran with 0.26 mmol of NVC and targeted a M_n of 9.7 kDa. [b]Tacticity was determined by integrating the separated mm and mr/rr peaks by ^{1}H-NMR at 100 °C in $C_2D_2Cl_4$.[c]Specific optical rotations were measured in $CHCl_3$ at c = 0.1.[d]Molar ellipticity values are in (deg*cm^2*dmol^{-1}).

Reaction conditions for the synthesis of variable molecular weight polymer samples and their resulting specific optical rotations to investigate the effect of "diluting" the optical activity from the polymer enantioenriched alpha chain-end. Reaction temperature was changed to increase molecular weight, while attempting to reduce the change in % *mm*.

Table S4: Specific optical rotation dependence on average number molecular weight



Initiator[a]	Ligand	T (°C)	% *mm* [b]	Mn (kDa)[c]	Đ[c]	[α]$_{589}$ (CHCl$_3$)[d]
i BVE-Ac	L10	23	88	26	2.6	0.0
i BVE-Ac	L10	0	90	82	2.8	-1.6
i BVE-Ac	L10	-20	92	94	3.3	-7.0
NVC-OMe	L10	23	91	23	4.3	-4.1
NVC-OMe	L10	0	92	72	4.2	-9.2
NVC-OMe	L10	-20	92	113	4	-14.0

[a]All polymerizations were ran with 0.26 mmol of NVC and targeted a M_n of 9.7 kDa. [b]Tacticity was determined by integrating the separated mm and mr/rr peaks by ^{1}H-NMR at 100 °C in $C_2D_2Cl_4$. [c]Molecular weight distributions were determined by a GPC RI detector in THF at 1 mg/mL.[d]Specific optical roations were collected at c=0.1 in chloroform at room temperature.

Circular dichroism spectroscopy of solutions containing the effective concentration of the enantioenriched alpha-chain-end were done to investigate the contribution to optical activity of the chain-ends—rather than from helicity. For this experiment we assumed 100% initiator enchainment which would constitute 4.1 wt% of the total polymer and a 0.0041 mg/mL solution in THF. We observed no response indicating it does not contribute to the measure CD response.

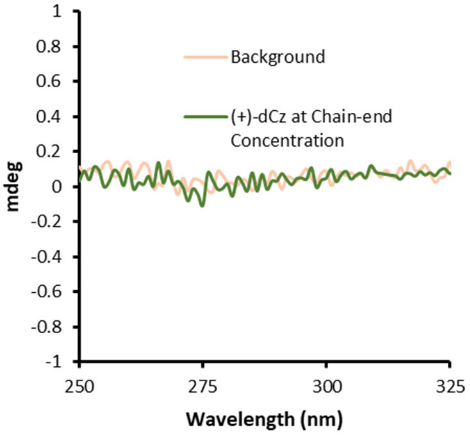


Figure S7: Circular dichroism of (+)-dCz at effective chain-end concentration

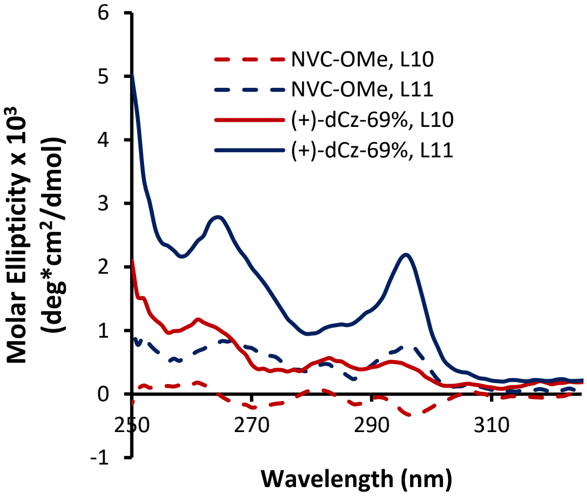


Figure S8: Circular dichroism of optically active samples in Figure 5A in $CHCl_3$

2.7. Isotactic poly(NVC) Solution Stability (Figure S9,S10)

To investigate the stability of isotactic poly(NVC) helices to inversion a sample prepared with a M_n of 22.9 kDa and 91% mm using [Sc-**L11**] was dissolved in HPLC grade THF at 1 mg/mL, capped, and left on the bench top where it was exposed to ambient temperature and sunlight for 3 weeks. Shown below are the CD and absorbance of traces of the sample on day 1 and after 3 weeks, where little to no change in CD response is seen—indicating samples are solution stable for up to that time. Samples storred in a similar manner in chloroform begin to gain a light orange color and eventually lost solubility.

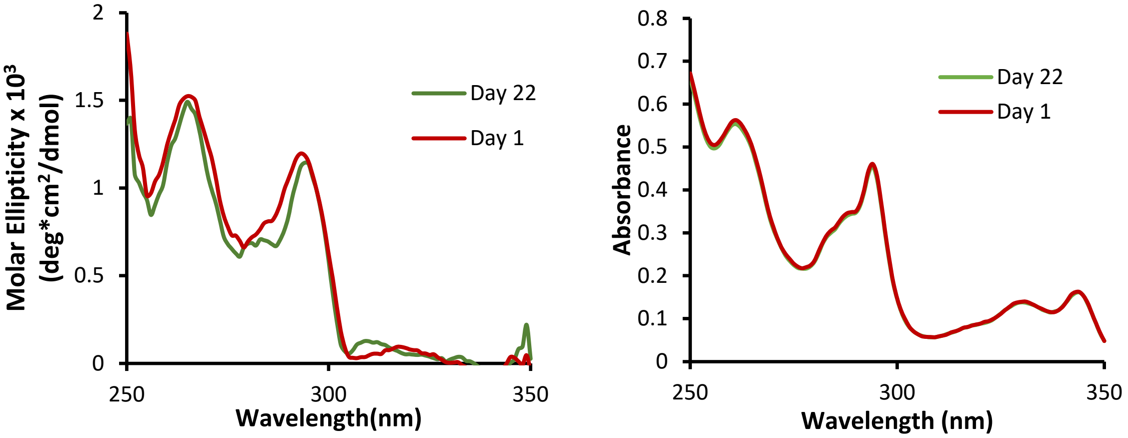


Figure S9: Circular dichroism response and absorbance measurements of poly(NVC) helical stability over 22 days in THF solution.

To probe the stability of the formed helices we subjected a sample of poly(NVC) at 91% *mm* to heated conditions in THF and toluene. The sample at 23 ºC in THF is the initial spectra. Heating in the CD spectrometer to 50 ºC for up to an hour shows no notable degradation of CD response. However, samples of the sample polymer were heated in anhydrous toluene for 1 or 16 hours, the solvent removed under high-vacuum, and redissolved in THF for analysis using the standard conditions outlined above. We observe a decrease in CD response in both the 265 and 296 nm regions indicating racemization of the polymer helix. No change in absorbance accompanied the change in CD response which suggests no chemical degradation of the polymer.

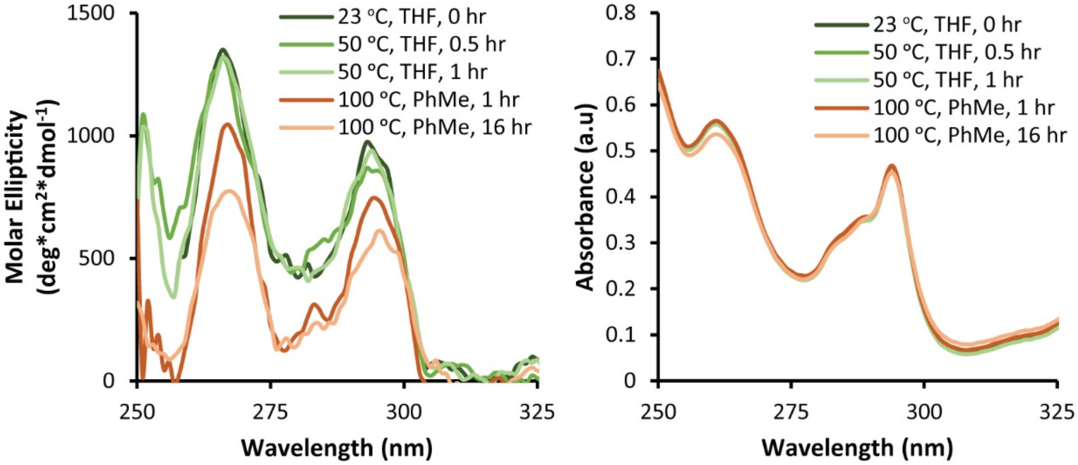


Figure S10: Circular dichroism of poly(NVC) stability in THF at 50 ºC and toluene at 100 ºC.

3. Characterizing poly(NVC) Tacticity

Highly isotactic poly(*N*-vinylcarbazole)'s triad splitting was previously characterized by Watanabe *et* al.[4] They used a combination of ^{1}H-NMR in $CDCl_3$ for moderate isotactic samples and ^{1}H-NMR in $C_2D_2Cl_4$ at 100 ºC. Below are representative spectra for moderately (85% mm) and highly (91%, 94% mm) isotactic poly(NVC) in which tacticity is determined using variable temperature NMR in $C_2D_2Cl_4$ at 100 ºC. Samples were allowed to equilibrate to temperature for 5 minutes before data collection. ns = 32, d1 = 5 seconds. Note: We observed concentration dependent peak shape for the %mm which appears as a shouldering on the lower ppm region.

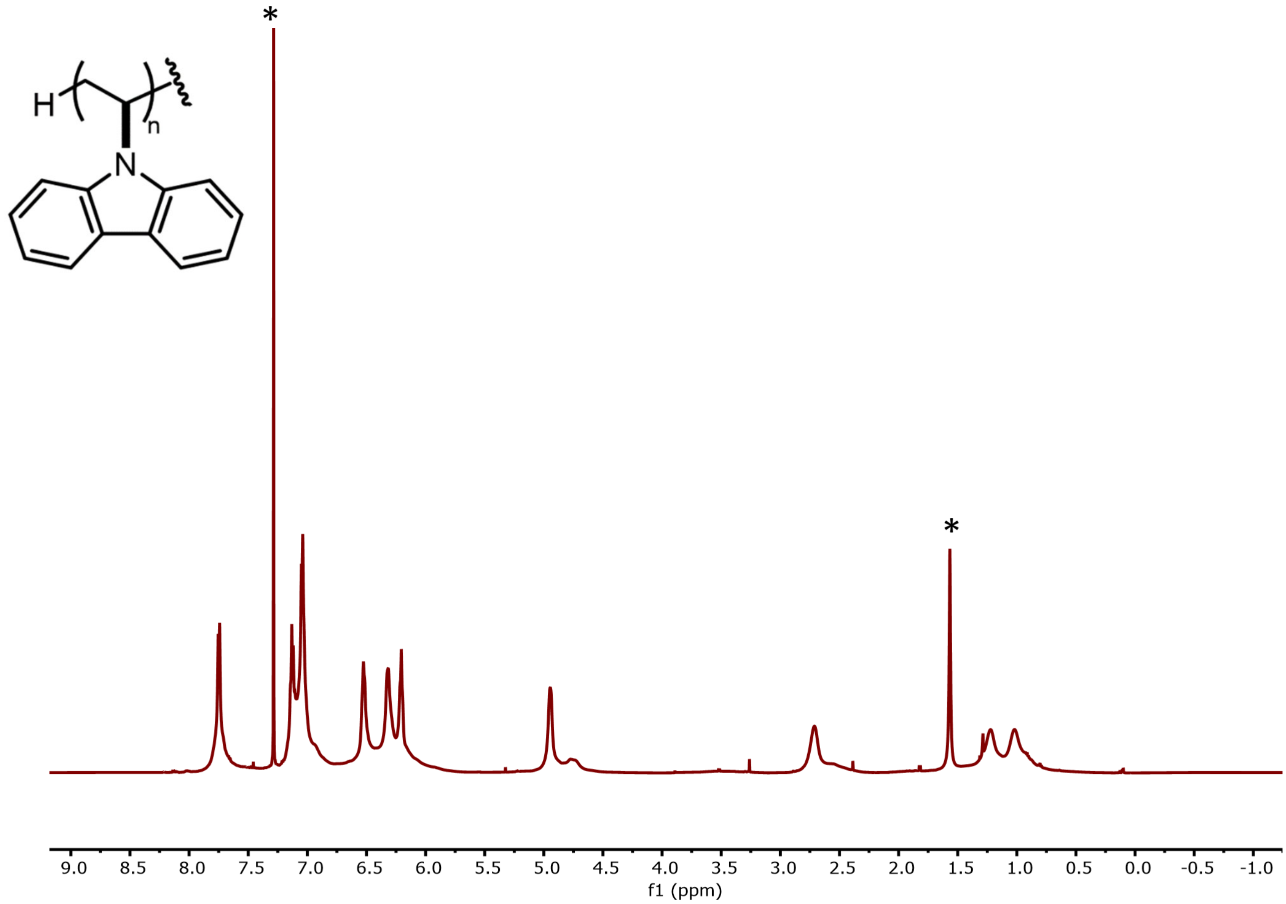


Figure S11: ^{1}H NMR spectrum of highly isotactic PVK (91% mm) in $CDCl_3$.

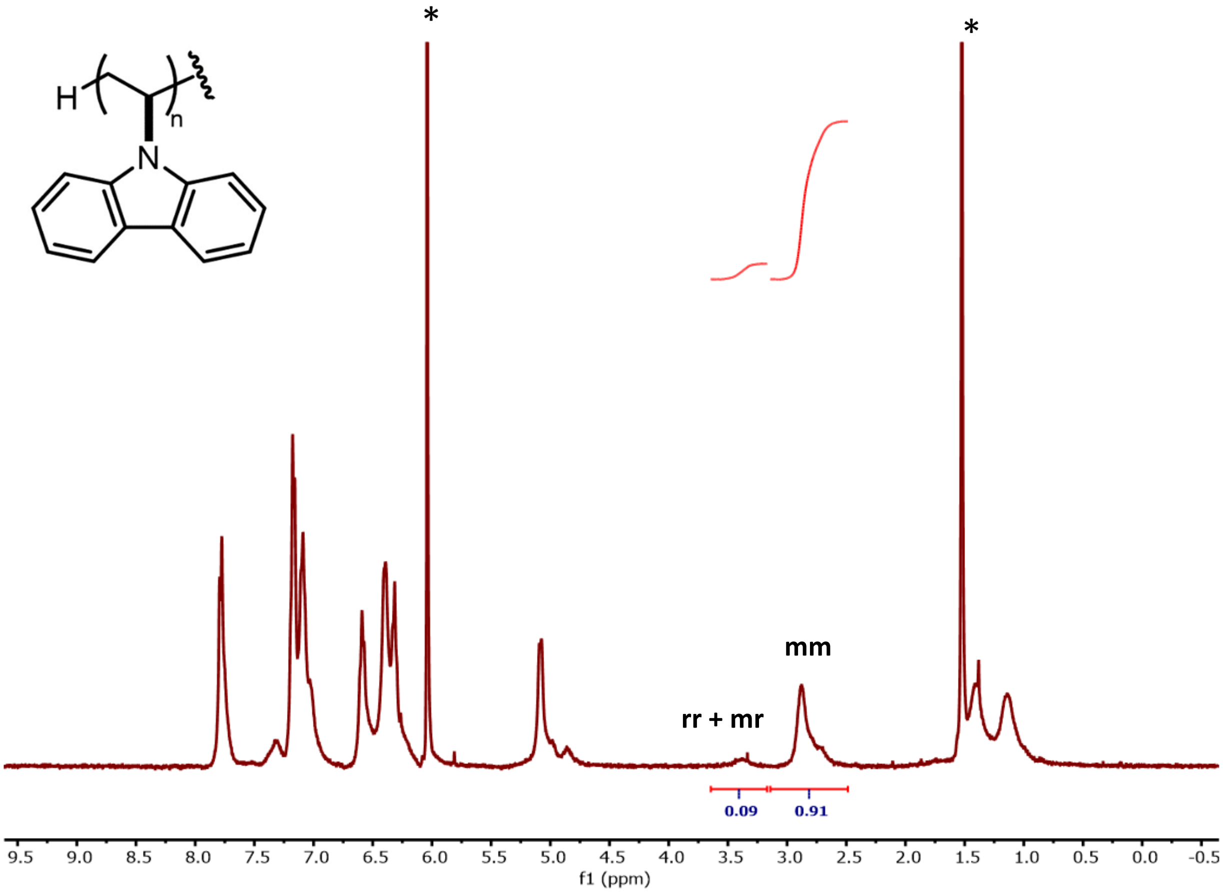


Figure S12: ^{1}H NMR spectrum of highly isotactic poly(NVC) (91% *mm*) in $C_2D_2Cl_4$ at 100 ºC

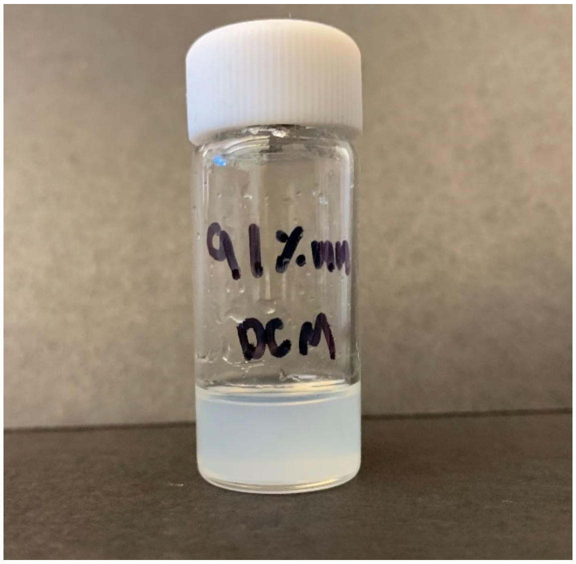


Figure S13: Photograph of a sample of 91% *mm* poly(*N*-vinylcarbazole), 22 kDa, in CH_2Cl_2 at 1mg/ml at room temperature

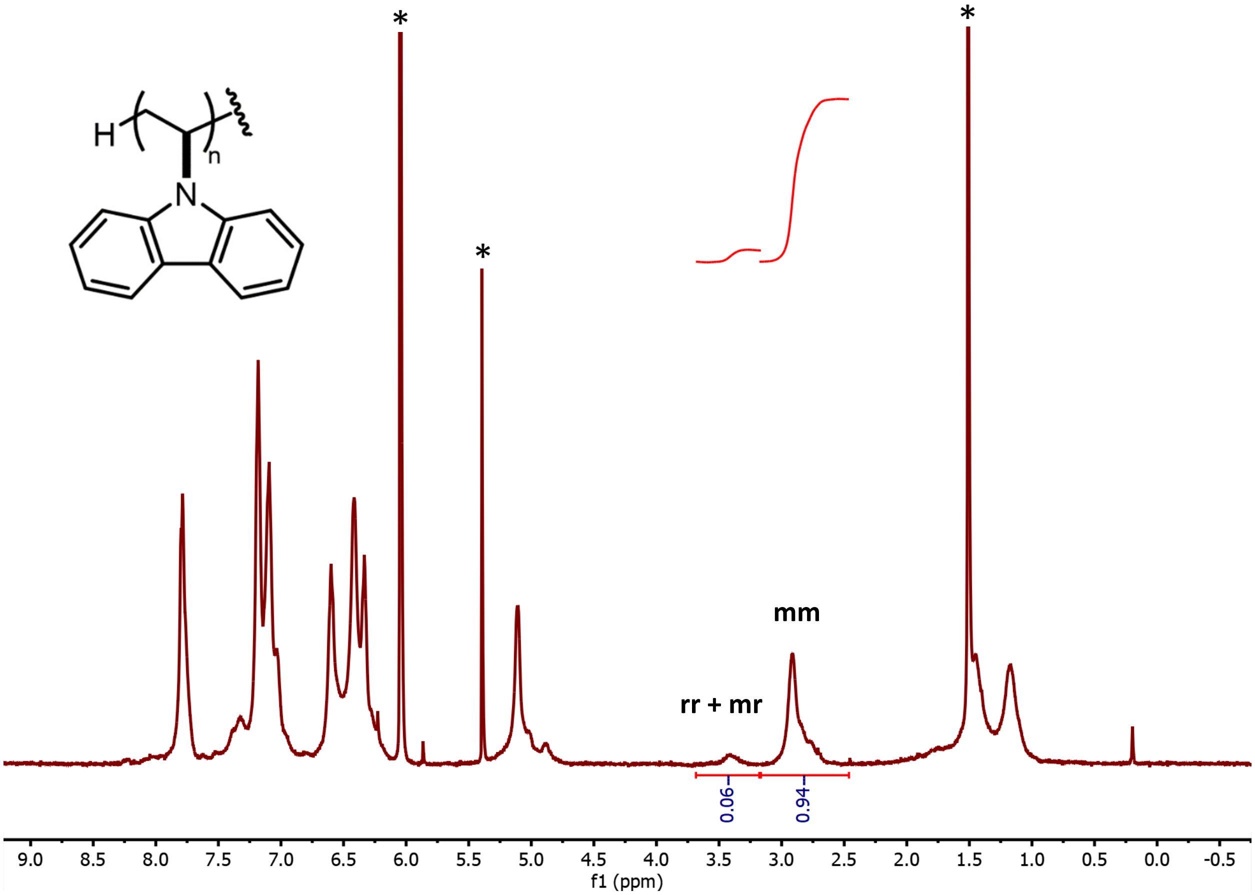


Figure S14: ^{1}H NMR spectrum of highly isotactic poly(NVC) (94% *mm*) in $C_2D_2Cl_4$ at 100 °C.

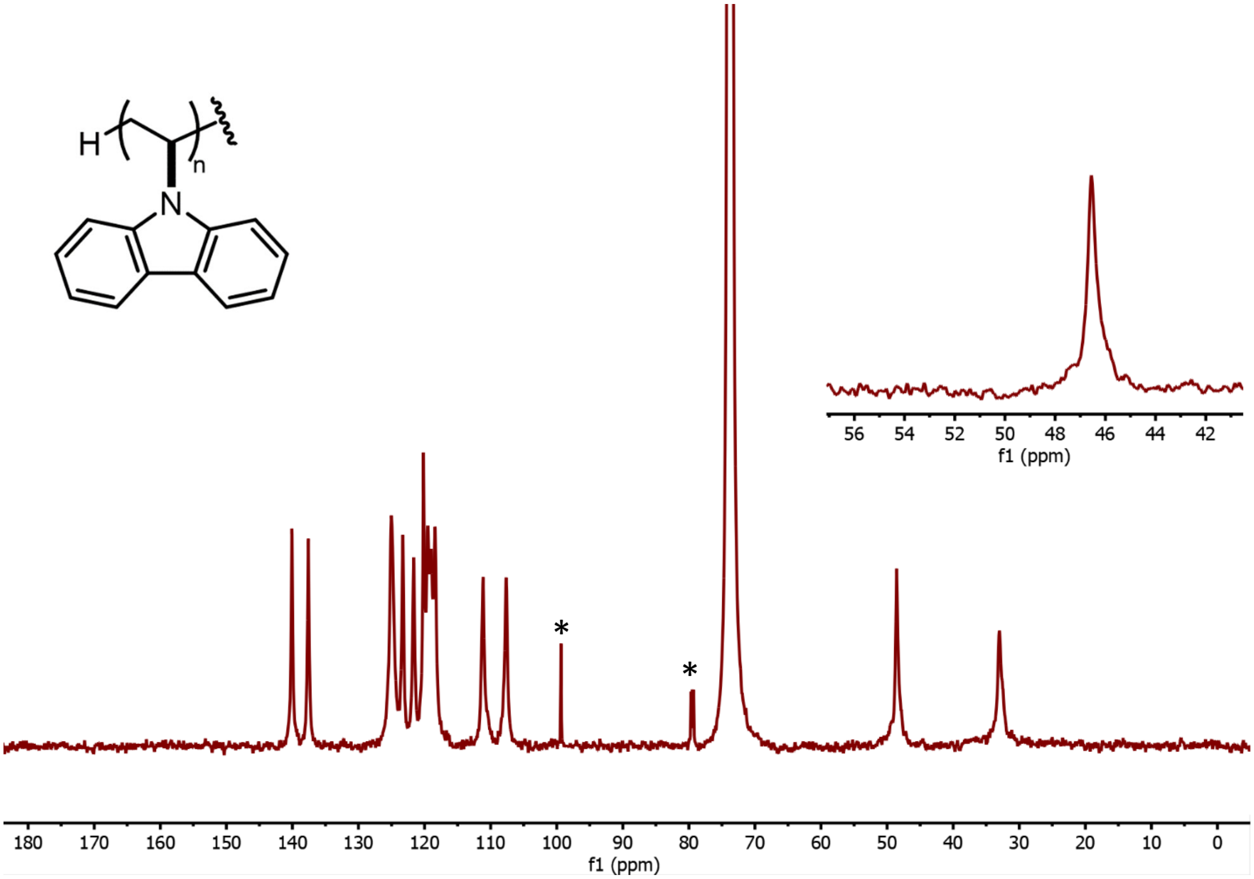


Figure S15: 4096 scan ^{13}C NMR spectrum of soluble portions of highly isotactic poly(NVC) (94% *mm*) in C_2D_2Cl. *CCl_4 and $CDCl_3$ impurities found in d-solvent.

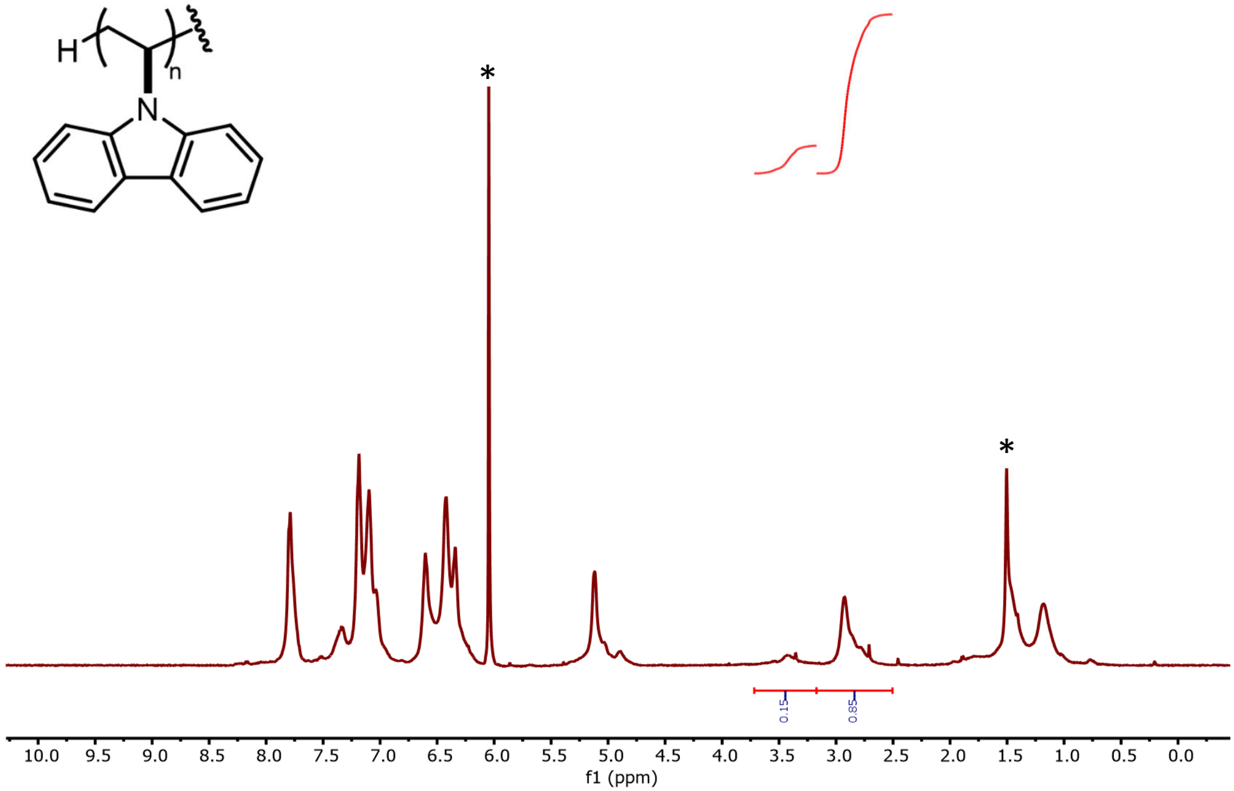


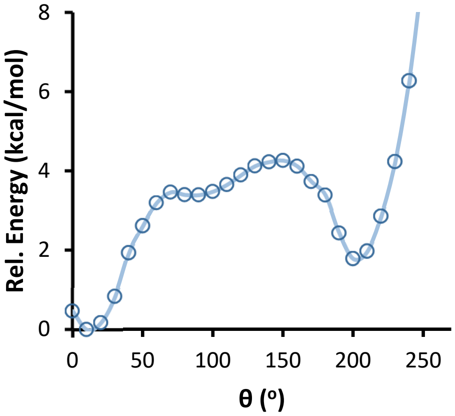
Figure S16: ^{1}H NMR spectrum of moderately isotactic poly(NVC) (85% *mm*) in $C_2D_2Cl_4$ at 100 °C

4. DFT Calculations & Renderings (Figure S17, Table S5,6)

The calculations shown in this work were performed using the Gaussian 16 package.[5] All ground state structures were optimized using the B3LYP[6] approximate exchange-correlation energy density functionals with the basis set def2-SVP[7] and cpcm(toluene)[8] solvent model unless otherwise noted. Grimme's D3 correction was used.[9] All optimizations used the default ultrafine grid size. Vibrational analyses were performed to ensure intermediates had no imaginary frequencies. Grimme-type quasi-harmonic (150 cm-1) Gibb's free energies were estimated at 298 K using the Autoqchem and GoodVibes packages.[10]

We performed relaxed dihedral scans on the *N*-vinylcarbazole iminium dimer (Figure 4 B, (i)) to probe the conformational energies between the *pro-meso* and *pro-racemo* structures. We used a step size of 10° and 36 steps, cpcm(Toluene)/B3LYP-d3/def2-tzvp with a superfine grid size. Rotation in the negative direction or past 250°, in which the larger carbazole ring passes orthogonal to the other carbazole ring produces energies >20 kcal/mol, thus we did not investigate them further.

Figure S17: Dihedral scan of carbazole iminium dimer



We used the semi-optimized geometries from this relaxed dihedral scan for our starting structures for Figure 4D with no anion. For entries with the achiral and chiral BOX-[Sc] complexes, the chiral anion was optimized first, to determine the optimized Sc-OMe (Sc-O) bond length. The Sc-O bond length was frozen for the other thermodynamic optimization and frequency calculations to prevent the charged separated intermediate from collapsing to their more stable, covalent forms.

Table S5: Tabulated Thermodynamic Data for Figure 3E

Grouping	Entry	E	ZPE	H	T.S	T.qh-S	G(T)	qh-G(T) (150 nm)
Chiral BOX-[Sc]	S3-ProMeso	-6097.245678	0.977392	-6096.19111	0.193793	0.172876	-6096.384902	-6096.363986
	S3-ProRacemo	-6097.238904	0.977441	-6096.18453	0.193444	0.172484	-6096.377971	-6096.35701
Achiral BOX-[Sc]	S2-ProMeso	-5559.251632	0.801593	-5558.38243	0.175319	0.156444	-5558.557744	-5558.538869
	S2-ProRacemo	-5559.256676	0.805362	-5558.38528	0.167452	0.151759	-5558.552733	-5558.53704
No Anion	S1-ProMeso	-1189.389314	0.437962	-1188.92784	0.074683	0.070883	-1189.00252	-1188.99872
	S1-ProRacemo	-1189.387283	0.437956	-1188.92578	0.075297	0.071147	-1189.001081	-1188.996931

Table S6: Computational Details: Geometries

Scan Iminium Dimer Initial Geometry

C	-1.01405616	0.38152610	0.00000000
C	-0.99501716	0.34585710	1.52986600
N	0.31817484	0.33267610	2.11953400
C	1.36688384	-0.55439090	1.86114500
C	2.40623284	-0.31200390	2.79109100
C	1.96304884	0.75530510	3.65577400
C	0.67438484	1.12784410	3.21595100
C	-0.04692016	2.13107710	3.85895000
C	0.53867184	2.74939810	4.95712100
C	1.81414984	2.38764910	5.40365700
C	2.53346584	1.39444410	4.75436600
C	3.56603884	-1.08031990	2.75874800
C	3.68207384	-2.08732190	1.81120100
C	2.64602784	-2.32798290	0.90408000
C	1.48010184	-1.57144490	0.91468000
C	-1.89509916	-0.86771490	2.04015200
C	-2.15255416	-0.68321190	3.47266000
N	-1.39053816	-0.99449290	4.47957200
C	-1.49242516	-0.32992790	5.76406500
C	-0.38350616	-0.68440890	6.53277500
C	0.38640884	-1.66561590	5.78165900
C	-0.25516416	-1.87865890	4.55367000
C	0.16380784	-2.85979990	3.67073700
C	1.29520784	-3.59266190	4.01461800
C	1.97529784	-3.35174990	5.20584300
C	1.51877784	-2.39425390	6.10697600
C	-0.20163216	-0.10511590	7.77977100
C	-1.14775016	0.81029510	8.23067500
C	-2.25429716	1.14376710	7.44985200
C	-2.43963416	0.58007210	6.18969400
H	-0.30301816	1.12726810	-0.35394000
H	-2.01031416	0.66159210	-0.34103300
H	-0.76495316	-0.57644790	-0.44882700

H	-1.47098116	1.26278210	1.86994100
H	-1.03161316	2.43514910	3.53138200
H	-0.00767516	3.52611910	5.47572400
H	2.24099284	2.88986910	6.26152100
H	3.52062884	1.11370610	5.09853100
H	4.36128784	-0.89785790	3.46995800
H	4.57740584	-2.69344590	1.77359200
H	2.74967584	-3.11985890	0.17369500
H	0.69876184	-1.78652990	0.20337600
H	-1.38977716	-1.79031390	1.78018800
H	-2.84013316	-0.82121190	1.50209300
H	-2.97364816	-0.02476290	3.72542300
H	-0.34883816	-3.07937390	2.75070800
H	1.65296284	-4.35155190	3.33385200
H	2.85994384	-3.92851390	5.43968800
H	2.02658184	-2.23126890	7.04768200
H	0.65836684	-0.35645490	8.38512800
H	-1.02466416	1.27160810	9.20132800
H	-2.98036916	1.85347910	7.82170400
H	-3.29748216	0.85825910	5.59409700

S1-ProMeso

1 1

C	0.00000000	0.00000000	0.00000000
C	0.00000000	0.00000000	1.53123871
N	1.30663771	0.00000000	2.15095079
C	2.36198926	-0.89942607	1.93464962
C	3.31274637	-0.75174572	2.98392778
C	2.79793966	0.25939354	3.88515483
C	1.56172343	0.69698860	3.34112715
C	0.78296984	1.66237854	3.99315161
C	1.25737349	2.17651276	5.20379148
C	2.47999144	1.75060909	5.75162731
C	3.25811410	0.79608177	5.09373154
C	4.46597089	-1.54392026	3.00806081
C	4.66447554	-2.48364621	1.99597693
C	3.71608526	-2.63229192	0.96984464
C	2.55905930	-1.84921279	0.92265923
C	-0.89035077	-1.20487442	2.07259292
C	-1.10023367	-1.04656517	3.52016906
N	-0.39046320	-1.53015097	4.50584028
C	-0.46453484	-0.97679781	5.84541059
C	0.61745563	-1.46640507	6.59250415
C	1.34487802	-2.41398967	5.75219876
C	0.69737454	-2.47896406	4.50015047
C	1.10192260	-3.37979288	3.51628693
C	2.21326688	-4.18402773	3.78934842
C	2.89363406	-4.09161593	5.00957902
C	2.45689239	-3.21296038	6.00756512
C	0.81433317	-1.01736801	7.89781491
C	-0.09139507	-0.09144527	8.42893736
C	-1.17348557	0.37695416	7.67013696
C	-1.37373517	-0.05804930	6.35379460
H	0.73607865	0.72768044	-0.37036425
H	-0.99513617	0.29322938	-0.36393928
H	0.23193262	-0.98355302	-0.42733769
H	-0.48639488	0.93198239	1.84562264
H	-0.16298510	2.01969709	3.58316145
H	0.66205986	2.92489399	5.73147945
H	2.82151941	2.17204329	6.69934423
H	4.20764358	0.46201936	5.51810934
H	5.19344076	-1.42993527	3.81480661
H	5.55889945	-3.11028237	2.00094267
H	3.88297229	-3.37422046	0.18536409
H	1.84776739	-1.98990249	0.11215025
H	-1.86569994	-1.13474344	1.57001274
H	-0.41271446	-2.14247830	1.77935379
H	-1.85804061	-0.32015096	3.82355282
H	0.59229019	-3.48833189	2.56437375
H	2.55626651	-4.88374594	3.02626147
H	3.76664234	-4.72253912	5.18830666
H	2.96837634	-3.15911793	6.97018068
H	1.65737364	-1.37832415	8.48946121
H	0.04470325	0.27093420	9.45004216
H	-1.87236207	1.09364120	8.10559489
H	-2.21756520	0.32120487	5.77604139

S1-ProRacemo

1 1

C	1.51032500	-0.04276700	-1.36649600
C	1.85083500	-0.59376200	0.02041600
N	1.59004900	0.30033400	1.12587700
C	2.00944200	1.63319100	1.25862100
C	1.84374200	2.03418200	2.61506200
C	1.30490900	0.89511700	3.33014900
C	1.17284800	-0.15499900	2.38528600
C	0.71722800	-1.42238300	2.76778500
C	0.38932800	-1.61962800	4.11213700
C	0.50897800	-0.58334300	5.05608500
C	0.96536900	0.67790200	4.67078500
C	2.21667000	3.32074400	3.02047300
C	2.76161200	4.19865700	2.08196400
C	2.92178700	3.79742000	0.74566600
C	2.54484500	2.52186500	0.31377200
C	3.32720500	-1.20718400	0.08838500
C	4.35857900	-0.16530100	0.19904500
N	4.87916600	0.33857700	1.28826100
C	5.65642700	1.56232700	1.26294900
C	5.82061900	2.01906400	2.57877100
C	5.20683000	1.03782700	3.46870500
C	4.66871400	-0.00079900	2.67844100
C	4.07643900	-1.12083100	3.26176200
C	3.99602500	-1.16456100	4.65790200
C	4.49261200	-0.12088400	5.44719100
C	5.11140300	0.98713100	4.85723000
C	6.47350200	3.22823300	2.81483600
C	6.95785700	3.95008000	1.71753600
C	6.79374800	3.47167000	0.40967500
C	6.13099000	2.26304100	0.16119800
H	0.54778500	0.48720600	-1.33543200
H	1.42238600	-0.87980100	-2.07398300
H	2.26928800	0.64244600	-1.76455800
H	1.20605600	-1.46737200	0.17902500
H	0.61269900	-2.24124400	2.05371300
H	0.02920600	-2.60024300	4.43207900
H	0.24232200	-0.77085200	6.09844800
H	1.06667100	1.48234700	5.40265300
H	2.09113300	3.62493500	4.06212700

H	3.06407300	5.20314100	2.38511500
H	3.34850000	4.49394000	0.02066700
H	2.66828700	2.25406500	-0.73238200
H	3.48586400	-1.75639100	-0.85081200
H	3.35928900	-1.92434400	0.91042700
H	4.67463500	0.32895600	-0.72188100
H	3.67882300	-1.95307200	2.69172500
H	3.52064700	-2.02593900	5.12879100
H	4.40295300	-0.17644100	6.53395100
H	5.51748500	1.79451800	5.46909100
H	6.59959000	3.60362700	3.83183000
H	7.47295900	4.89896100	1.88115200
H	7.18472700	4.04658200	-0.43192400
H	6.00837600	1.90949200	-0.86331400

S2-ProMeso

0 1

Sc	-0.03627800	0.00412300	-0.00492800
S	-0.03926100	0.46672500	3.49020800
O	1.29194600	0.17985500	4.04874800
O	-0.87935000	1.47183700	4.13485600
C	-0.96236200	-1.16065200	3.65258700
F	-0.99339500	-1.52889800	4.92866000
F	-0.32341600	-2.10887700	2.94917100
F	-2.20442600	-1.04987300	3.19633400
S	2.25026600	1.75886300	-1.80618500
O	3.39560400	0.83626600	-1.81244500
O	1.56616500	1.98913400	-3.08405600
C	2.95443600	3.41862000	-1.31640000
F	3.82562100	3.82536300	-2.23213600
F	3.58229100	3.31448000	-0.13829400
F	1.97904200	4.31557100	-1.20532700
S	-2.63577600	-1.96545500	-0.67404300
O	-3.61418400	-0.96253000	-1.11990400
O	-2.07209400	-2.87271600	-1.68227500
C	-3.56575400	-3.05100300	0.52931500
F	-4.51793600	-3.72233300	-0.11439500
F	-4.12978900	-2.29944700	1.47564300
F	-2.73426100	-3.91837100	1.10379500
O	0.01213900	0.63567700	1.97881300
O	1.30182200	1.52755900	-0.63964200
O	-1.58264200	-1.40856700	0.27692300
C	-3.38372900	1.40815800	-3.56216600
C	-2.13447600	1.66548800	-2.68363800
C	-1.11325500	0.58969800	-2.99406100
N	-0.44752600	-0.16709700	-2.19586800
C	0.39901400	-1.05923000	-3.01402100
C	0.23438300	-0.49416400	-4.43430100
O	-0.87234300	0.43738800	-4.29306400
C	-1.49867600	3.04416300	-3.01950000
C	-2.54232800	1.70255200	-1.22611300
N	-1.85538900	1.36323700	-0.19823900
C	-2.72116400	1.51377600	0.98825600
C	-3.94655800	2.26280300	0.43760100
O	-3.75170300	2.21605700	-1.00023500
H	-3.09342700	1.39123200	-4.61974800
H	-4.11726200	2.20810600	-3.40406000
H	-3.84374700	0.44744400	-3.29119100
H	0.01761200	-2.08488000	-2.90448900
H	-1.23885200	3.07852000	-4.08615900
H	-0.58259200	3.20437100	-2.43690200
H	-2.22458800	3.83978100	-2.79862000
H	-2.19588800	2.04474800	1.79242800
H	-3.98542100	3.32115900	0.73649200
H	-0.04515500	-1.24023700	-5.18884800
C	1.13394800	-2.78504900	-0.13590200
H	0.22007800	-3.02920500	-0.70026400
H	1.09240900	-3.35248300	0.80923900
H	2.01276400	-3.12652500	-0.71036000
O	1.20583300	-1.40016800	0.11392700
H	-4.90523700	1.77861400	0.66385200
H	-2.97127800	0.50767800	1.35500500
H	1.43840700	-1.02616100	-2.65941700
H	1.10669300	0.08570700	-4.76357900
C	4.22105800	2.10744500	2.85916500
C	4.17219600	0.58891300	2.66267800
N	5.48214600	-0.02932500	2.53799800
C	6.41655000	0.19765300	1.52661800
C	7.48989900	-0.72657700	1.67402600
C	7.17693800	-1.55261500	2.82132300
C	5.92906000	-1.09314200	3.32439900
C	5.32293800	-1.70574000	4.42994900
C	5.97848500	-2.78876200	5.01759900
C	7.21384600	-3.25462500	4.52782400
C	7.81888200	-2.63862000	3.43242900
C	8.54865000	-0.72300000	0.75729400
C	8.52923900	0.18830000	-0.29870700
C	7.45792800	1.08933600	-0.44198600
C	6.39301500	1.10954500	0.46087300
C	3.24155000	0.19914400	1.46416600
C	2.82168600	-1.20382900	1.67834400
N	3.55972800	-2.27583700	1.46012200
C	3.49025700	-3.45648600	2.28099800
C	4.55490900	-4.30626700	1.93130200
C	5.25839800	-3.69387300	0.80911000
C	4.61632000	-2.47392600	0.51141000
C	4.95927200	-1.70529100	-0.59730200
C	6.03391000	-2.15107300	-1.37428500
C	6.72358400	-3.33107900	-1.05967500
C	6.33222700	-4.12109900	0.02529300
C	4.75534300	-5.48968100	2.64667400
C	3.87924300	-5.79833000	3.69095200
C	2.82044900	-4.93744300	4.02072800
C	2.61383600	-3.74225600	3.32200300
H	4.90690200	2.34883200	3.68451100
H	3.21593500	2.46746600	3.12296700
H	4.55182000	2.64205700	1.96124100
H	3.71700300	0.17923100	3.57221300
H	4.36191000	-1.36770000	4.82052100
H	5.51401500	-3.28904200	5.87052500
H	7.69726800	-4.10774000	5.00949300
H	8.77480000	-3.00031600	3.04561500
H	9.36981000	-1.43586700	0.86451300
H	9.34534100	0.19918700	-1.02496300
H	7.44958000	1.78868000	-1.28171600
H	5.57027400	1.80551600	0.31119300
H	3.72834700	0.38896200	0.50663700

H	2.35450400	0.83275900	1.52483600
H	2.04814000	-1.33775500	2.43184600
H	4.41958000	-0.80520700	-0.87910100
H	6.33896400	-1.55605300	-2.23675800
H	7.56573600	-3.64445600	-1.68072700
H	6.84494000	-5.05796800	0.25213400
H	5.58491200	-6.15378000	2.39644500
H	4.02030200	-6.71944800	4.26078900
H	2.14493500	-5.19710900	4.83853800
H	1.79413300	-3.07857600	3.59523400

S2-ProRacemo

0 1

Sc	0.51657400	0.27692600	0.05093000
S	1.12198000	1.46688500	3.31306000
O	2.36365700	1.10075400	4.00272700
O	0.58461100	2.81593400	3.46141500
C	-0.16258700	0.31122400	4.05594500
F	-0.08631700	0.38009500	5.38019700
F	0.07336900	-0.94583200	3.67319200
F	-1.38675100	0.66625400	3.67478400
S	2.06501900	2.22477900	-2.14633300
O	2.19812400	1.44887800	-3.38513900
O	1.04459600	3.27378400	-2.08206500
C	3.70047400	3.11187200	-1.94867300
F	3.83586200	3.97458700	-2.95141800
F	4.70319000	2.23600700	-1.99201900
F	3.73302800	3.77080000	-0.79678000
S	-2.58314700	-0.87211700	0.69720400
O	-3.46795200	0.28156500	0.87802200
O	-2.69275800	-1.64950800	-0.54768800
C	-3.00214800	-2.09101500	2.05558300
F	-4.21066500	-2.59538400	1.82926100
F	-2.98899000	-1.50212500	3.24529600
F	-2.10880300	-3.08449500	2.05098300
O	1.15173800	1.01389400	1.84872200
O	2.06494700	1.32352800	-0.89735100
O	-1.12796100	-0.57469400	1.05257200
C	-3.32617600	0.84396700	-2.79214500
C	-1.94156800	1.53271800	-2.61574000
C	-0.88751900	0.48406900	-2.89094400
N	-0.12774800	-0.16192900	-2.07140000
C	0.65708000	-1.13530200	-2.86660100
C	0.29157800	-0.79939900	-4.31977300
O	-0.79025300	0.15919400	-4.17384200
C	-1.79019400	2.69679000	-3.63130600
C	-1.86645800	2.10938500	-1.22252600
N	-1.02464200	1.86466000	-0.28540200
C	-1.39510600	2.68147400	0.88864100
C	-2.68401500	3.39154300	0.43790400
O	-2.82113000	2.99447100	-0.95455000
H	-3.40258600	0.44381400	-3.81227100
H	-4.11981800	1.58623300	-2.63647100
H	-3.45033900	0.02525100	-2.07190500
H	0.36399300	-2.15611900	-2.58442100
H	-1.92101200	2.31337700	-4.65094300
H	-0.79913100	3.15939400	-3.53943300
H	-2.56201800	3.45096500	-3.43036400
H	-0.57126200	3.36418200	1.13809000
H	-2.62989300	4.48752900	0.47206200
H	-0.08704600	-1.65077000	-4.89961400
C	0.55213000	-2.64918100	0.07631700
H	-0.40596700	-2.42229500	-0.39944400
H	0.36833700	-3.00746300	1.09558000
H	1.09931100	-3.38452800	-0.52078300
O	1.32827300	-1.41518300	0.13401200
H	-3.57629300	3.03449100	0.96867200
H	-1.56304300	2.02553700	1.74934500
H	1.72773700	-1.00416800	-2.67136300
H	1.10619400	-0.29538800	-4.85477300
C	4.50419900	-1.74592900	3.98498100
C	4.36401000	-2.08944200	2.49862700
N	5.40357100	-1.47211100	1.67676000
C	5.58210500	-0.11138300	1.42268800
C	6.70264700	0.05647600	0.56050900
C	7.22192100	-1.26659700	0.28870000
C	6.39953400	-2.18189500	1.00374700
C	6.64569900	-3.56071900	0.95639600
C	7.71014400	-4.01041500	0.17360700
C	8.52304100	-3.11567400	-0.54824600
C	8.28418300	-1.74238300	-0.49224600
C	7.08316300	1.34222000	0.15198100
C	6.34981500	2.44007800	0.59935300
C	5.23775200	2.25889200	1.44216300
C	4.83692500	0.99058000	1.86534700
C	2.92816900	-1.78530300	2.00230800
C	2.81991500	-1.60512000	0.49384500
N	3.42016900	-2.56391000	-0.34522300
C	4.11789100	-2.19896500	-1.51840000
C	4.68985200	-3.35390500	-2.09654000
C	4.33257700	-4.47220900	-1.24604000
C	3.55141800	-3.96102700	-0.17631400
C	3.05575100	-4.81294100	0.81819000
C	3.37998500	-6.17078000	0.74615400
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F	-1.35243100	6.25791200	3.05359800
F	-2.24267900	4.61429100	4.14887000
F	-3.49347400	6.21477400	3.38892500
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C	-7.13087600	-1.47977600	6.77715100

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C	-8.19284900	3.73972800	-0.87015700
C	-7.85183300	4.89705000	0.04217800
C	-6.77390200	4.57822300	0.87914300
C	-6.30082900	5.48854500	1.82327200
C	-6.91246400	6.74210600	1.91287800
C	-7.98002900	7.07428800	1.06674100
C	-8.45809800	6.15279300	0.12681100
O	-8.24633700	1.85494200	0.70916200
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H	-2.89629200	-3.26953100	3.97719700
H	-4.25472300	-4.95070300	5.20935500
H	-6.25077100	-4.23854500	6.52554800
H	-6.98097400	-1.48302200	7.86993600
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H	-6.55969300	7.45847400	2.65809200
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H	-9.30037100	6.40880000	-0.52166600
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C	-2.79244300	1.94666200	5.68374900
H	-3.54977700	2.61198900	6.13247800
H	-1.83893000	2.50182500	5.68781700
H	-2.67546100	1.05987300	6.33394800
O	-3.15907300	1.57388300	4.38413400

HOMO-LUMO overlap with phasing of carbazole dimer species **S1-ProMeso** shown via contour slice normal to iminium ring and through each nitrogen atom (Figure S12A). Additional renderings of HOMO (MO = 102) and LUMO (MO = 103) separately with an isoval = 0.02 and density = 0.0004 (Figure S12B,C).

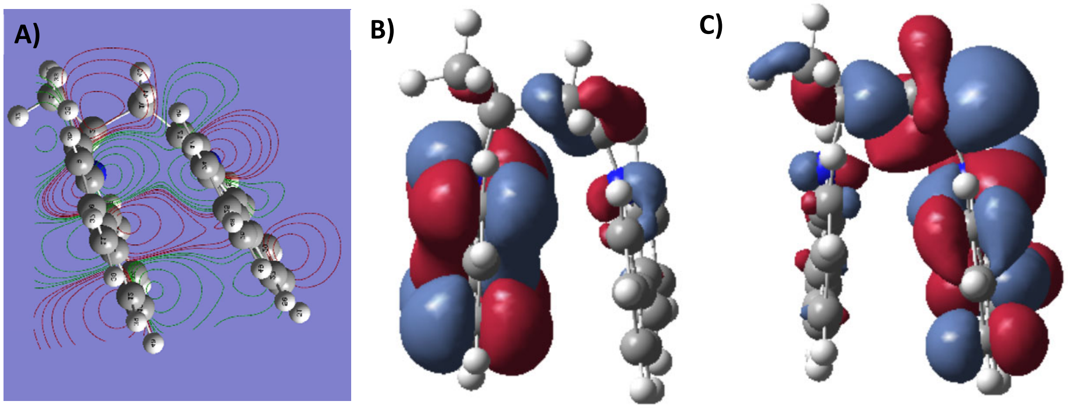


Figure S18: A) contour slice of **S1-ProMeso** with phasing shown in red or green, B) its HOMO, and C) LUMO renderings.

Additionally, when using a functional without electron correlation (HF) we see structure (ii) (Figure S13) in which $A^{1,3}$, $A^{1,2}$, and gauche interactions dominate. These data, the carbazole rings being within their VDW radius, and data from Figure S12, suggests the presence of pi-pi stacking being the operative interaction for the favoring of conformers (i) and (ii).

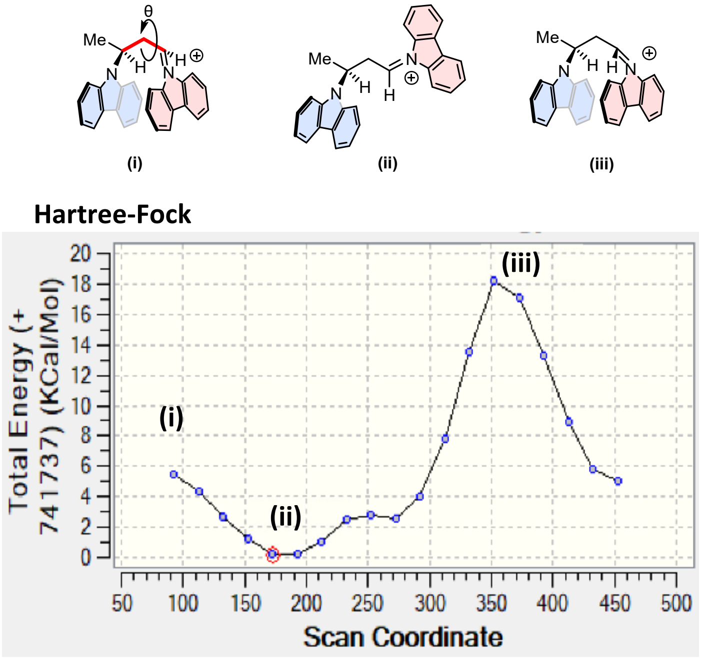


Figure S19: Dihedral scan of iminium carbazole dimer using HF/def2svp method.

5. Spectra

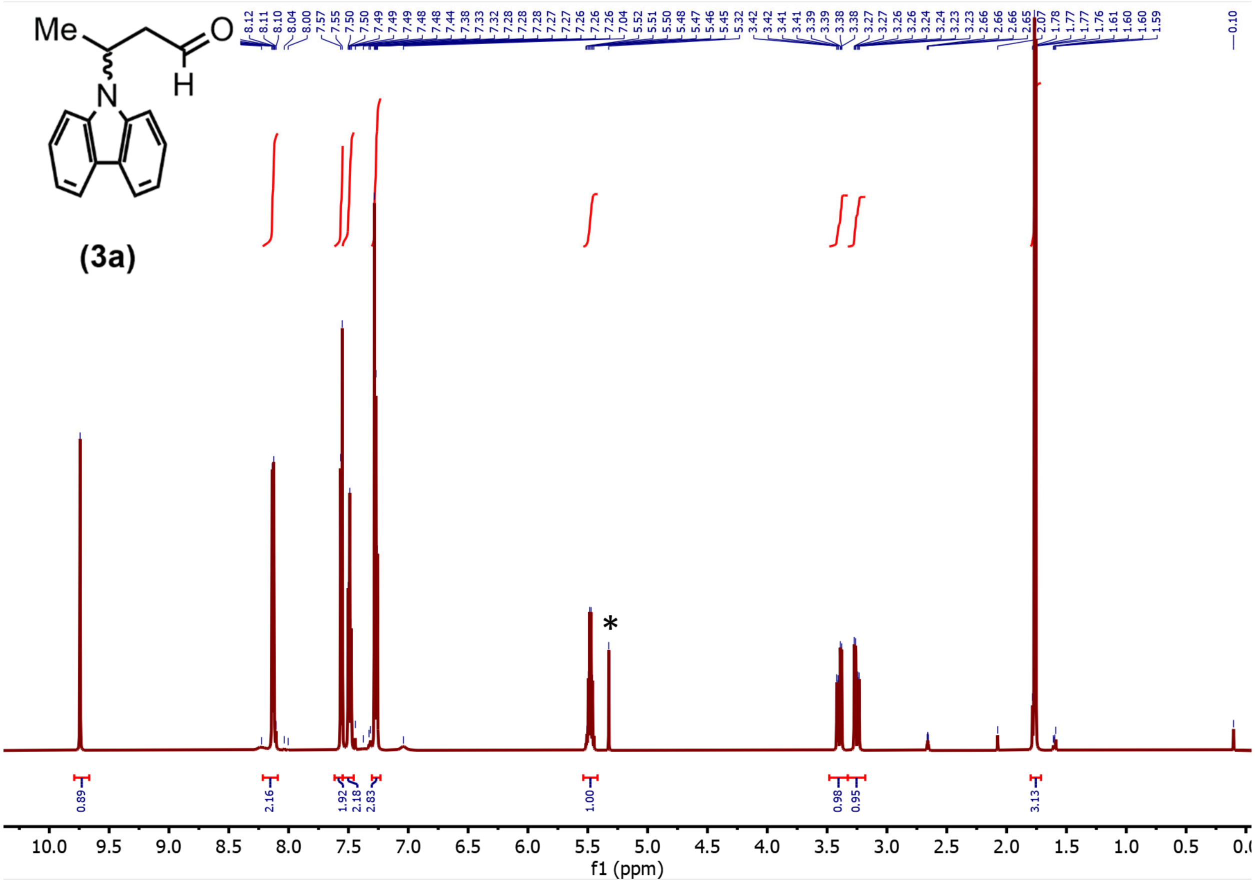


Figure S20. ^{1}H NMR spectrum of (**3a**) in $CDCl_3$. *DCM.

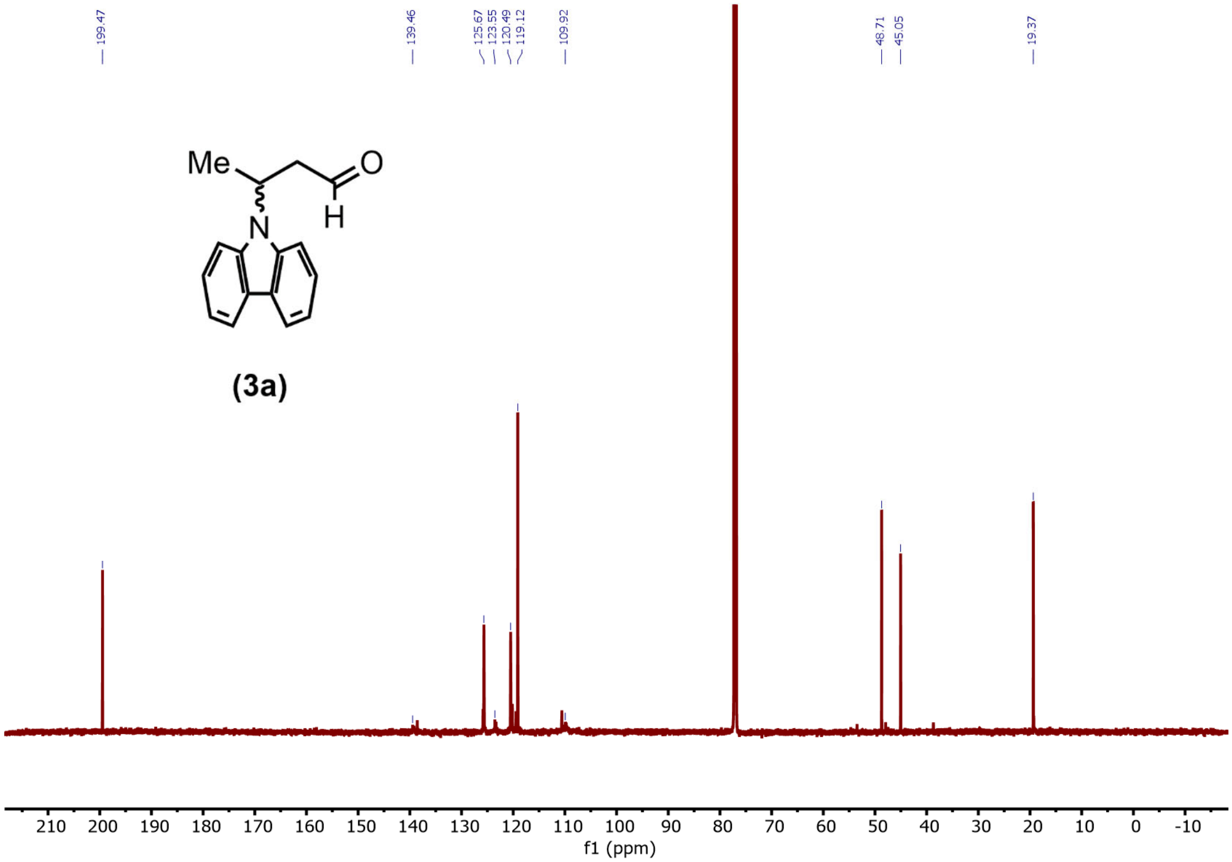


Figure S21. ^{13}C NMR spectrum of (**3a**) in $CDCl_3$

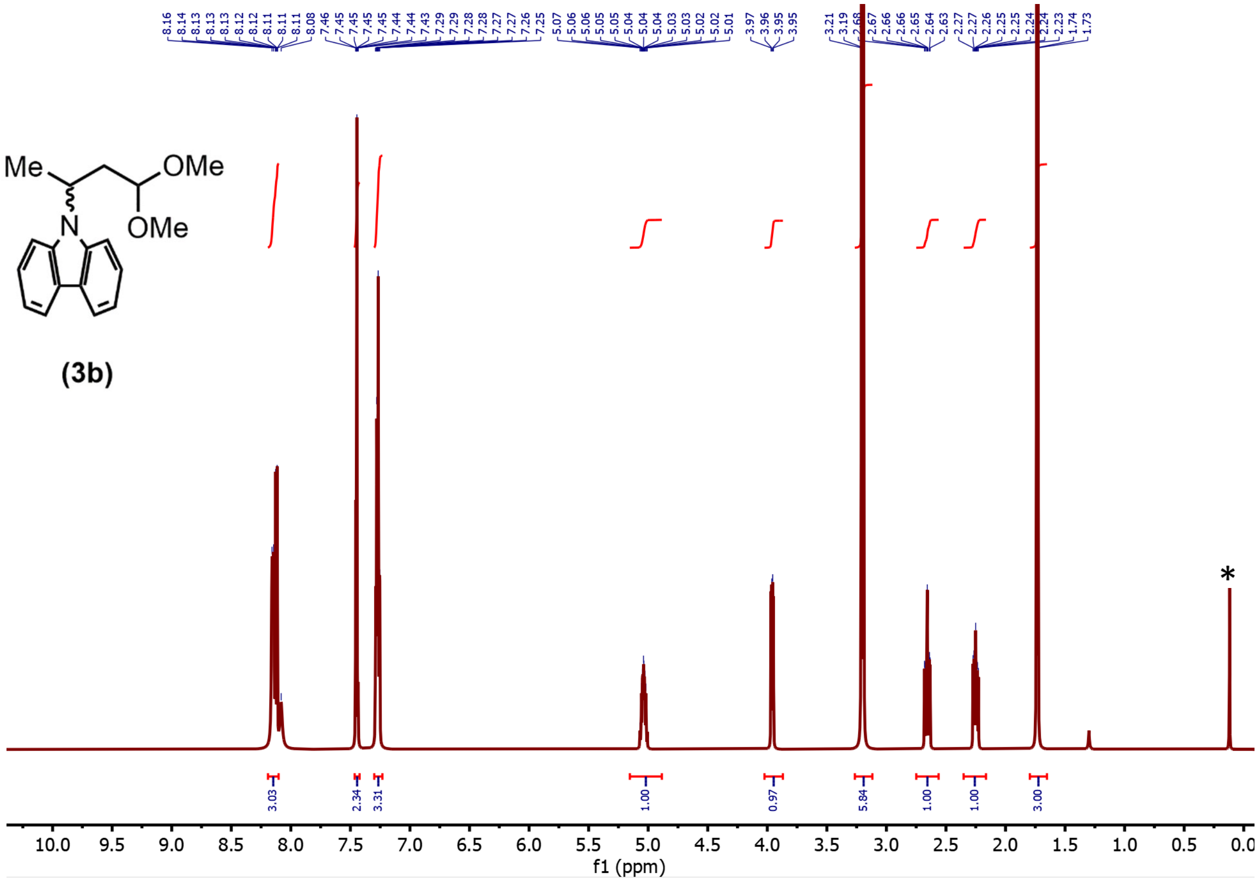


Figure S22. ^{1}H NMR spectrum of (**3b**) in $CDCl_3$

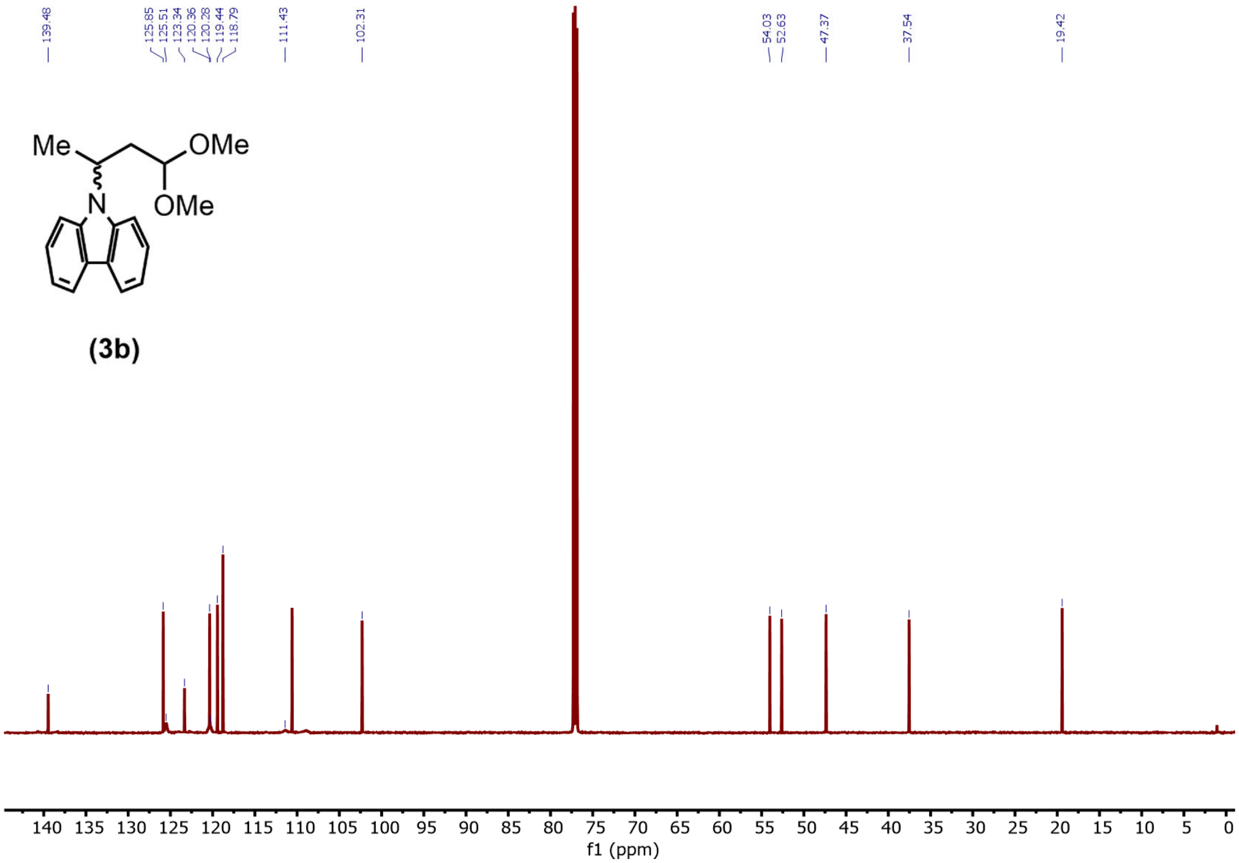
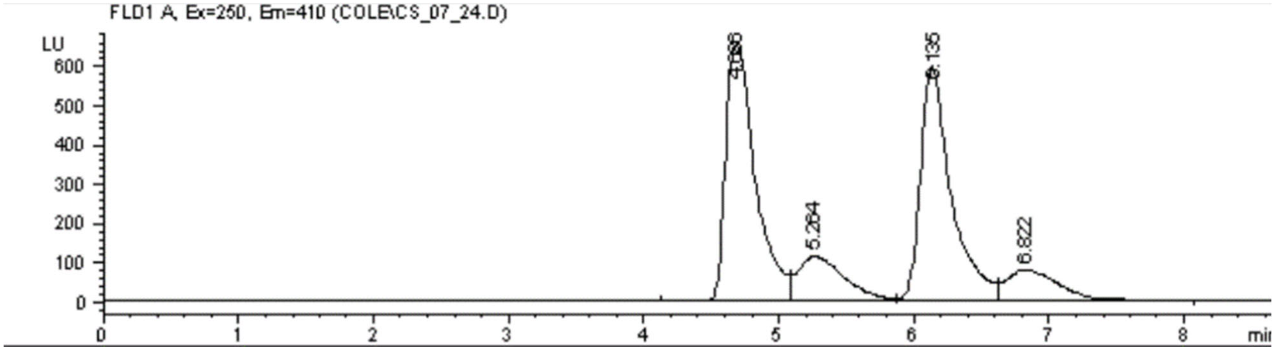


Figure S23. ^{13}C NMR spectrum of (**3b**) in CDCl$_3$



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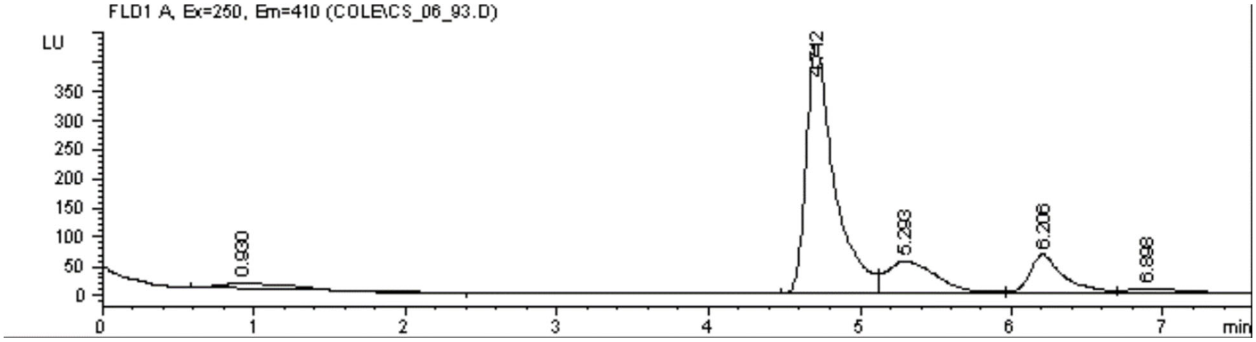
   2   5.264 VV    0.3568 2694.70605  112.64616  11.1344
   3   6.135 VV    0.2324 9440.34473  595.72784  39.0072
   4   6.822 VB    0.4196 2136.34717   78.89744   8.8273

Totals :                  2.42015e4  1437.16262
```

Figure S24. Chiral HPLC trace of (**3b**) in 95:5 Hexanes:Methanol, racemic.

*Note: Degradation occurs with **3a, 3b,** and **3c** in all column conditions attempted. Ratio of paired peaks (e.g. above, the first two peaks at 4.686 and 5.264 have the same relative integration as 6.135 and 6.822) is consistent for racemic and enantioenriched product.*



```
Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]  LU    *s   [LU    ]     %
----|-------|----|-------|----------|----------|--------|
   1   0.930 BP    0.5102  281.56781   10.05823   3.3876
   2   4.712 BV    0.1872 5511.12939  427.31863  66.3052
   3   5.293 VV    0.3602 1275.96033   54.80581  15.3513
   4   6.206 VV    0.2296 1033.13171   65.41988  12.4298
   5   6.898 VB    0.3953  209.96544    8.33895   2.5261

Totals :                  8311.75468  565.94150
```

Figure S25. Chiral HPLC trace of (**3b**) in 95:5 Hexanes:Methanol, 69% ee.

Note: Peak # 2,3 is the major enantiomer + its degradation product; 4,5 is the minor + its degradation product. Ratio of 2:3 is same as 4:5 in all % ee achieved.

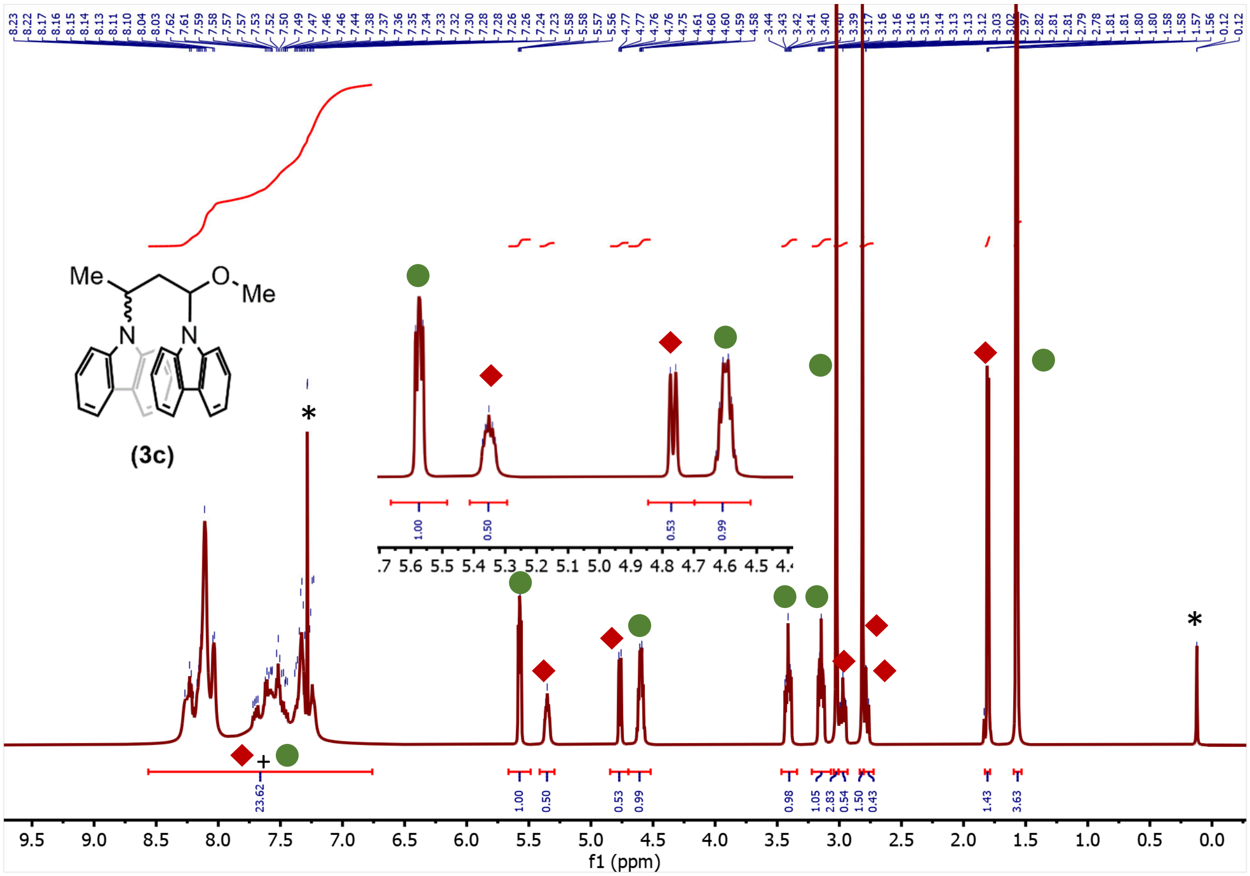


Figure S26. ^{1}H NMR spectrum of diastereomeric mixture of (+)-dCz (**3c**) in $CDCl_3$. *Note: Green circles designate peaks for major diastereomer and red squares for the minor. Hydrolysis of the hemiaminal occurs readily in* $CDCl_3$ *and impurities >5% arose within an hour. Aromatic region normalizes to 16 H when diastereomers are treated as 1 H.*

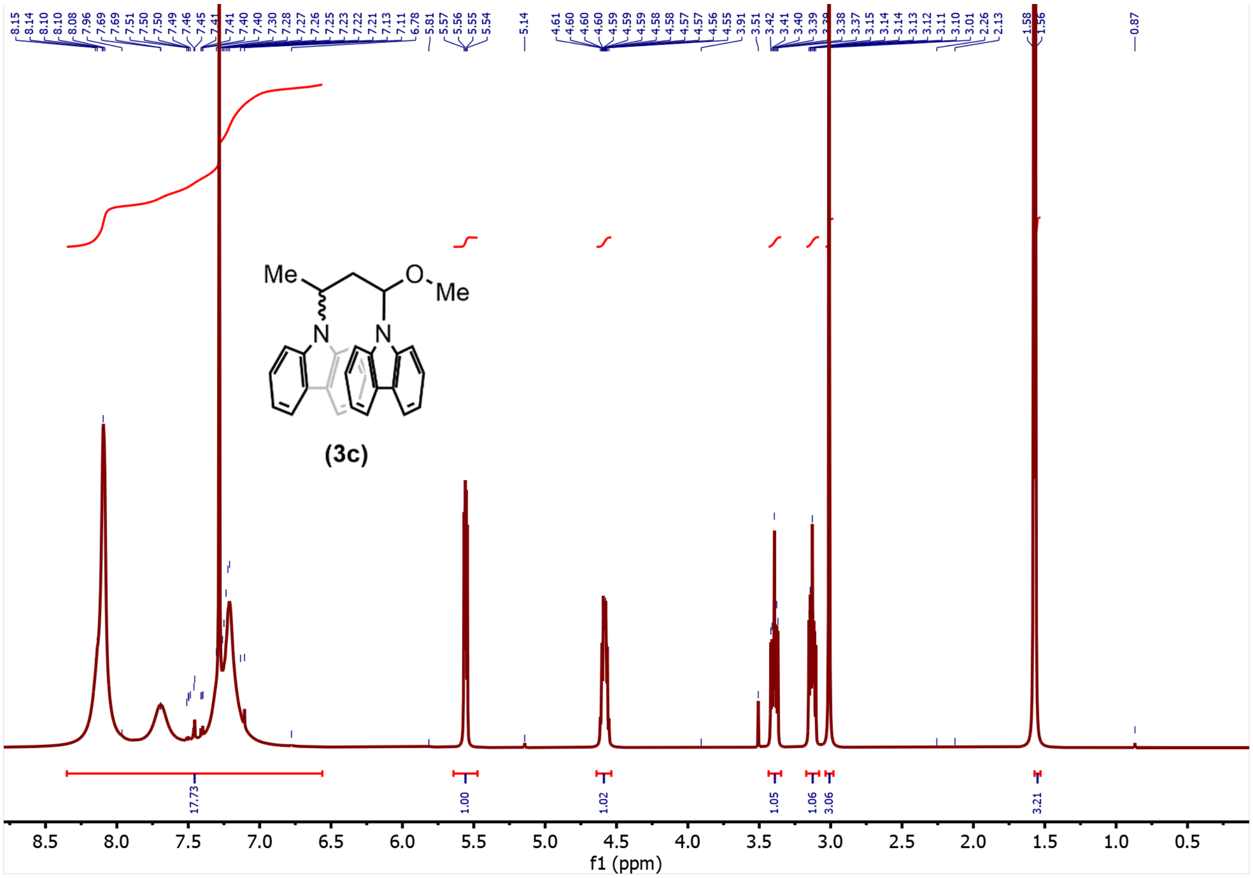


Figure S27. ^{1}H NMR spectrum of (+)-dCz (**3c**) major diastereomer in $CDCl_3$.

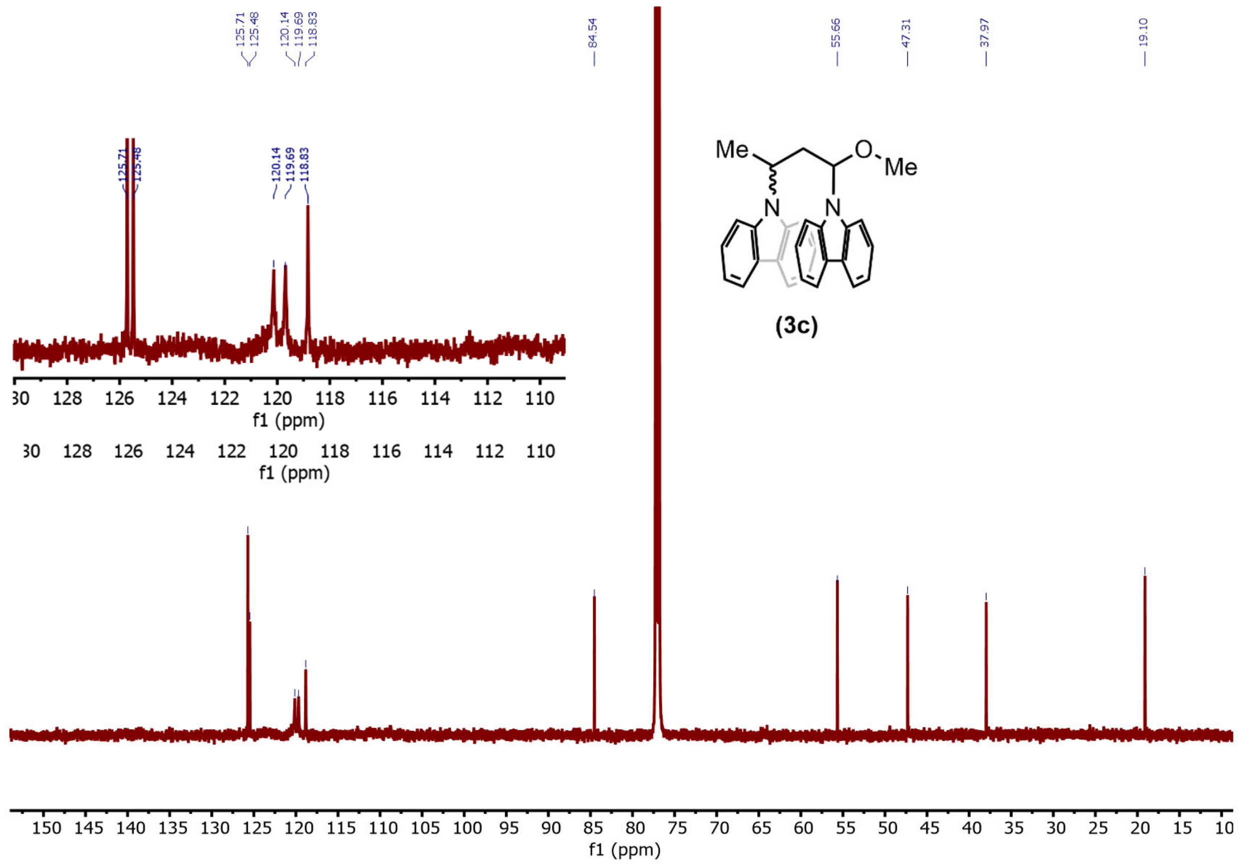


Figure S28. ^{13}C NMR spectrum of (+)-dCz (**3c**) major diastereomer in $CDCl_3$. The internal carbazole ring carbons 8a, 9a, 4a, and 4b of each ring are missing.

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