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Massachusetts Institute of Technology

Stereoselective Ring-Opening Metathesis Polymerization (ROMP) of Methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate by Molybdenum and Tungsten Initiators

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Abstract

Ring-opening metathesis polymerization (ROMP) of methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (PhEtNNBE; (*S*) and racemic) was investigated employing six molybdenum and tungsten imido alkylidene initiators and two tungsten oxo alkylidene initiators. Of the six initiators that we proposed should yield *cis,syndiotactic*-poly[(*S*)-PhEtNNBE], two molybdenum OHMT alkylidene initiators, Mo(NR)($CHMe_2Ph$)(pyr)(OHMT) (R = Ad or 2,6-$Me_2C_6H_3$; OHMT = O-2,6-$Mesityl_2C_6H_3$; pyr = pyrrolide) and two tungsten oxo alkylidene initiators, W(O)($CHMe_2Ph$)(2,5-dimethylpyrrolide)(PMe_2Ph)(OR) (OR = OHMT or (*R*)-OBr_2Bitet where (*R*)-Br_2BitetOH = (*R*)-3,3'-Dibromo-2'-(tert-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol) produced essentially pure *cis,syndiotactic*-poly[(*S*)-PhEtNNBE]. Essentially pure *cis*,*isotactic*-poly[(*S*)-PhEtNNBE] was formed when (*S*)-PhEtNNBE was polymerized by Mo(NAr')($CHCMe_2Ph$)($OBiphen_{CF3}$)(thf) or W(NAr')($CHCMe_2Ph$)((S)-$OBiphen_{Me}$) ($OBiphen_{CF3}$ = 3,3'-di-*tert*-butyl-5,5'-bistrifluoromethyl-6,6'-dimethyl-1,1'-biphenyl-2,2'-diolate; (*S*)-$OBiphen_{Me}$ = 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate). The best initiator for ROMP of *rac*-PhEtNNBE was Mo(NAd)($CHMe_2Ph$)(pyr)(OHMT) at 0 °C, which led to a polymer that is biased (~80%) toward a *cis*,*syndiotactic* structure and that contains alternating enantiomers in the chain (*cis*,*syndio*,*alt*-poly[(*rac*)-PhEtNNBE]).

INTRODUCTION

The development of "well-defined" alkylidene complexes of Mo,[1] W,[1] or Ru,[2] in the last two decades has been of great benefit to the field of Ring-Opening Metathesis Polymerization (ROMP),[3] since the nature of the initiator can be altered systematically and fundamental mechanistic issues can be addressed directly. In the last several years we have been developing molybdenum and tungsten catalysts for stereospecific ROMP, *i.e.*, those that yield polymers with all *cis* C=C bonds and that have an *isotactic* or *syndiotactic* relationship between neighboring monomer units (dyads) in the polymer.[4] Stereospecific polymerization of cyclic olefins is an important step toward controlling the bulk properties of a polymer as well as they can be.

Molybdenum and tungsten alkylidene **initiators that** contain a racemic chiral biphenolate ligand (M(NR)(CHR')(Biphen)) produce *cis,isotactic* polymers through enantiomorphic site control, while MonoAlkoxidePyrrolide (MAP) initiators of Mo and W (M(NR)(CHR')(pyrrolide)(aryloxide)) produce *cis,syndiotactic* polymers.[5] In MAP species the configuration of the metal usually inverts with every insertion of monomer, thereby causing the monomer to approach one side of the M=C bond and then the other.[4] This "stereogenic metal control" has also allowed the synthesis of AB copolymers prepared from racemic monomers in which enantiomers are incorporated in an alternating fashion into the polymer chain.[6] So far only Mo MAP catalysts have been successful in forming alternating polymers from *endo*,*exo*-2,3-dicarbomethoxynorbornene, *endo*,*exo*-2,3-dicyanonorbornene, and 1-methyl-2,3-dicarbomethoxy-7-oxanorbornene.[6]

At this stage, the tacticity of a highly tactic polymer prepared through ROMP can only be proven for polymers prepared from enantiomerically pure monomers.[4] In that case the tacticity usually can be assigned readily through proton NMR spectroscopy. For example, stereoregular polymers have been prepared made from 2,3-dicarbomenthoxynorbornadiene (or the pantolactonyl ester analog) or enantiomerically pure 5,6-dicarbomethoxynorbornene. With the aim of expanding the number of proofs of stereoregularity, we turned to examination of methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate (PhEtNNBE),[7] a monomer that

can be prepared in both enantiomerically pure and racemic forms readily. (The (*R*) or (*S*) label refers to the chirality of the phenethyl (CHMePh) group on N, which dictates the chirality in the entire monomer; Figure 1). The four regular structures for poly[(*S*)-PhEtNNBE] are shown in Figure 2. IR spectroscopy usually can establish whether a polymer contains *trans* C=C configurations on the basis of a strong absorption near 980 cm^{-1}. The tacticity can then be assigned readily on the basis of whether the two inequivalent olefinic protons are on one C=C bond (isotactic), and therefore coupled to one another, or two different C=C bonds (syndiotactic). The $^{3}J_{HH}$ coupling between inequivalent protons in an isotactic structure will confirm that the configuration is *cis*.

Polymerization of *rac*-PhEtNNBE was first explored with $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ and $Mo(NAr)(CHCMe_2Ph)(OCMe_3)_2$ (Ar = 2,6-*i*-$Pr_2C_6H_3$) as initiators,[8] but only atactic polymers were obtained. Polymerization of (*R*)-PhEtNNBE with $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ gave a polymer with a structure that is largely *cis,isotactic* through what must be chain end control. In this paper we report the polymerization of *rac*-PhEtNNBE and (*S*)-PhEtNNBE with a selection of molybdenum and tungsten initiators that have been used to prepare *cis,isotactic, cis,syndiotactic,* and *cis,syndiotactic,alt* polymers in the last several years.[4,9]

RESULTS

The Mo and W initiators that were explored as initiators for polymerization of (*S*)-PhEtNNBE are shown in Figure 3. On the basis of past behavior, MAP complexes (**1** and **3**) would be expected to yield *cis,syndiotactic* structures, while **2a** and **2b** should yield *cis,isotactic* structures. Complex **3b** is the only initiator that has not been reported. It was prepared through addition of one equivalent of (*R*)-Br_2BitetOH ((*R*)-3,3'-Dibromo-2'-(tert-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol) to $W(O)(CHCMe_2Ph)(Me_2Pyr)_2(PMe_2Ph)$, which is a standard method of preparing MAP complexes.[10] Two diastereomers of **3b** were observed (through ^{1}H NMR spectroscopy in C_6D_6 at 22 °C) in a ratio of 83:17.

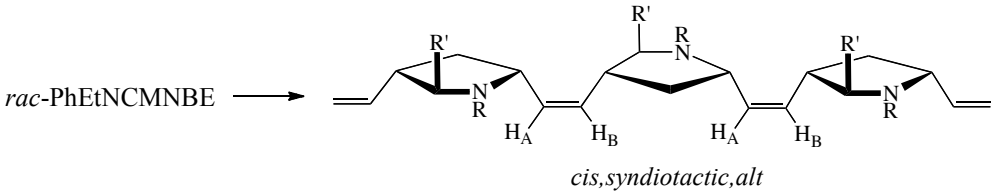
The most successful initiators for preparing *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] (>95%; Table 1) were found to be **1a**, **1b**, **3a**, and **3b**. Addition of 50 equiv of (*S*)-PhEtNNBE to either initiator in toluene led to the complete consumption of monomer within one hour. Polymers were precipitated through addition of the reaction mixture to methanol. The white polymers were found to be relatively soluble in toluene, tetrahydrofuran, dichloromethane, and chloroform.

Proton and carbon NMR spectra in $CDCl_3$ revealed that the olefinic protons in ^{1}H NMR spectra of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] appear as two doublets with second order characteristics (Figures 4a and 5a), typical of a *cis,syndiotactic* polymer prepared from an enantiomerically pure monomer (Figure 2) in which the two olefinic protons are found on different double bonds; no coupling between olefinic protons was confirmed through **^{1}H-^{1}H** COSY NMR experiments**.** An IR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] (see Figure S5 in the Supporting Information) does not contain a strong absorption in the 970 to 980 cm^{-1} characteristic of *trans* internal C=C bonds. Polymerization of (*S*)-PhEtNNBE with **1c** yielded only atactic polymer. The difference between an initiator that contains a hexaisopropylterphenoxide (OHIPT**, 1c**) or a hexamethylterphenoxide (OHMT, **1a**) can be significant and has been noted in other circumstances.[6] The sterically more demanding OHIPT derivative can create an environment that is too crowded for the stereoselective polymerization of sterically demanding monomers. Addition of (*S*)-PhEtNNBE to a toluene solution of **1d** led to consumption of the monomer within one hour, but the resulting polymer is only ~90% *cis,syndiotactic*.

A sample of poly[(*S*)-PhEtNNBE] prepared from 50 equivalents of monomer employing initiator **1a** in toluene was shown by gel permeation chromatography (in THF versus polystyrene) to have a unimodal distribution with a PDI of 1.10 (MW theory =12850; found 13890). A new doublet alkylidene proton resonance was observed in the ^{1}H NMR spectrum for the propagating species at 10.96 ppm ($^3J_{HH}$ = 5.5 Hz). Because this paper focuses on polymer structures, molecular weights and dispersities of all polymers were not determined.

Polymerization of (*S*)-PhEtNNBE by **2a** or **2b** in toluene in one hour led to formation of *cis,isotactic*-poly[(*S*)-PhEtNNBE] (see Figure 2). The off-white polymers were soluble in most organic solvents. The olefinic protons appear in the ^{1}H NMR spectrum as two sets of pseudo triplets with $^{3}J_{HH}$ ~ 9.6 Hz (Figure 4b), consistent with *cis* olefinic protons on a given double bond being magnetically inequivalent and coupled to one another and to the methine protons, as confirmed through ^{1}H-^{1}H COSY NMR studies. The degree of stereoselectivity is estimated to be >95% for both **2a** and **2b**. This *cis,isotactic* content is higher than that in the polymer made through polymerization of (*R*)-PhEtNNBE with Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (~90%),[8] most likely because the polymerization is under enantiomorphic site control for **2a** and **2b** and only end group control for Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$.

Addition of 50 equiv of *rac*-PhEtNNBE to **1a** or **1b** in toluene led to complete consumption of the monomer within one hour. The polymers were precipitated through addition of the reaction mixture to a solution of methanol and found to be insoluble in most non-polar solvents and slightly soluble in halogenated solvents. Proton NMR spectra in $CDCl_3$ revealed that the polymers have a bias (**80**%) toward a *cis,syndiotactic,alt* structure (equation 1).

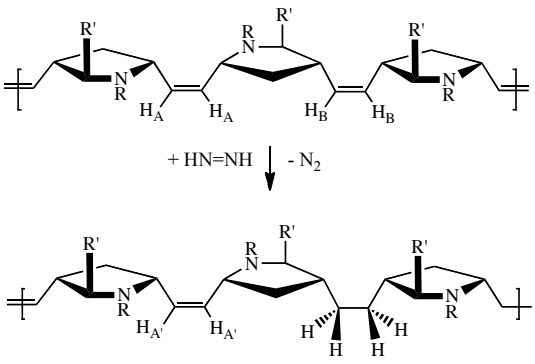


(1)

The $^{3}J_{HH}$ value (10.0 Hz) is consistent with a *cis*-configuration. At 0 °C with **1a** as the initiator, the polymerization was complete within 1 h and the percentage of *cis*,*syndiotactic*,*alt* dyads was ~80% (Figure 4c). Results were similar at temperatures between -78 °C and 20 °C. When initiator **1d** was employed to polymerize *rac*-PhEtNNBE, the resulting polymer had a much lower percentage of *cis*,*syndiotactic*,*alt* dyads than found when **1a** was employed (see Supporting Information).

Tosyl hydrazide has been employed often to hydrogenate polymers obtained through

ROMP reactions in order to eliminate *cis/trans* isomers and focus on tacticity.[3] Attempted hydrogenation of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] yielded a polymer, *cis,syndiotactic*-poly[H-(*S*)-PhEtNNBE], in which only half of the double bonds (the $H_BC{=}CH_B$ bonds in *cis,syndiotactic*-poly[(*S*)-PhEtNNBE]) were hydrogenated (eq 2, Figure 5, and Figure S12 in the SI). One of two aliphatic proton resonances derived from hydrogenation of the $H_BC{=}CH_B$ bonds



(2)

is found at 1.40 ppm, while the second must overlap with the doublet for the phenethyl methyl group at 1.25 ppm, because that resonance is broadened at the base and integrates as four protons (see SI and Figure 5b). The $H_{A'}$ proton resonance in *cis,syndiotactic*-poly[H-(*S*)-PhEtNNBE] is found at 4.8 ppm. These results are supported by ^1H, ^{13}C, and ^1H-^1H COSY NMR spectra. "Half hydrogenation" of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] (Figure 2) is consistent with the $H_AC{=}CH_A$ bonds being relatively well-protected by the NCHMePh groups on each face of that C=C bond and apparently, therefore, being resistant to hydrogenation by HN=NH; the $H_BC{=}CH_B$ bonds are clearly the more accessible. *Cis,isotactic*-poly[(*S*)-PhEtNNBE] could be hydrogenated only very slowly and incompletely, which is consistent with each $H_AC{=}CH_B$ bond (Figure 1) being more resistant to hydrogenation than the $H_BC{=}CH_B$ bonds, but not as resistant as the $H_AC{=}CH_A$ bonds, in *cis,syndiotactic*-poly[(*S*)-PhEtNNBE].

DISCUSSION

Polymerizations of (*S*)-PhEtNNBE to give *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] by Mo MAP initiators are proposed to proceed in a manner analogous to that proposed for most other

norbornenes and norbornadienes, *i.e.*, the monomer adds to the metal *trans* to the pyrrolide ligand and the metal's configuration that is found in the new alkylidene is opposite to that in the previous alkylidene.[11] Most likely the configuration of the metal inverts through Berry-type processes[12] in five-coordinate olefin/alkylidene or metallacyclobutane intermediates when rearrangement is rapid relative to formation of the new alkylidene (ring-opening). Formation of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] requires that each chiral metal center produce the same stereochemical result in terms of the basic structure of the resulting polymer chain (*cis,syndiotactic*) upon reaction with (*S*)-PhEtNNBE. If the configuration at the metal does *not* invert with each propagation step, which is what has been found recently for a polymer made from 7-isopropylidene-2,3-dicarbomenthoxynorbornadiene made with W(O)(CH-*t*-Bu)(OHMT)(Me_2Pyr), a close relative of **3a**,[13] then the resulting structure will be *cis,isotactic*. Therefore, we conclude that both diastereomeric 5-coordinate intermediates (olefin/alkylidene or metallacyclobutane complexes) invert before forming the next alkylidene in the *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] product.

It has been reported that polymerization of (*R*)-PhEtNNBE', a *diastereomer* of (*R*)-PhEtNNBE, with "Umicore M31" ([1,3-bis(2,4,6-trimethylphenyl)-2-imidazolidinylidene]dichloro-(3-phenyl-1*H*-inden-1-ylidene)(pyridyl)ruthenium(II), yields *cis,syndiotactic*-poly[(*R*)-PhEtNNBE'] that has "a high degree of *cis*-TT stereoregularity" (*cis*-TT = *cis* tail-to-tail = *cis,syndiotactic*).[14] The published proton NMR spectrum of the polymer has an extremely broad olefinic resonance extending between 5.20 and 5.86 ppm (in $CDCl_3$), in contrast to the sharp olefinic proton resonances at 5.32 and 4.92 in the proton NMR spectrum in $CDCl_3$ of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] that we have prepared (Figure 4a and 5a). All ^{13}C resonances at 133.3, 132.9, 57.6, 57.2, 40.2, and 39.4 ppm in the ^{13}C NMR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] (see SI) are also much sharper and more intense than those for *cis,syndiotactic*-poly[(*R*)-PhEtNNBE']. Therefore, although *cis,syndiotactic*-poly[(*R*)-PhEtNNBE'] and *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] technically are diastereomers and therefore cannot be compared directly with one another, it seems unlikely to us that the

cis,syndiotactic-poly[(*S*)-PhEtNNBE'] prepared with "Umicore M31" has a structure as regular as we have found here for *cis,syndiotactic*-poly[(*S*)-PhEtNNBE].

We expected that polymerization of (*S*)-PhEtNNBE by **2a** or **2b** would yield a *cis,isotactic* structure, because **2** and similar initiators of this type are known to yield *cis,isotactic* polymers from achiral norbornenes and norbornadienes through enantiomorphic site control.[6,8] In initiators that contain a C_2 symmetric ligand the monomer should approach one of the two CNO faces of the pseudotetrahedral initiator preferentially and repeatedly; chain end control is likely to play a minor role. The biphenolate ligand in **2b** is enantiomerically pure. In contrast, the biphenolate ligand in **2a** is *racemic*. Therefore, the two enantiomers of **2a** both must produce *cis,isotactic*-poly[(*S*)-PhEtNNBE] in spite of the fact that the pathways for their reaction with (*S*)-PhEtNNBE are energetically different. It is not possible that only one enantiomer of **2a** initiates and polymerizes (*S*)-PhEtNNBE, because addition of 10 equiv of (*S*)-PhEtNNBE to **2a** consumes 72% of **2a**.

Rac-PhEtNNBE could be polymerized by **1a** or **1b** to give a *cis,syndio,alt* structure because both enantiomers of the monomer are present (Scheme 2) and the metal can invert its configuration with each insertion.[8] Therefore, a single diastereomeric propagation step is available to yield a *cis,syndio,alt*-poly(*rac*-PhEtNNBE). However, the fact that only 80% of the final structure (at best) is *cis,syndio,alt* suggests that the rates of the "matched" and "mismatched" propagation steps are not different enough in energy at room temperature to yield a purely alternating enantiomer structure. This result is consistent with others here that suggest that the chirality in (*S*)-PhEtNNBE does not strongly influence formation of the basic *cis,syndiotactic* or *cis,isotactic* structures.

CONCLUSION

This study extends the class of enantiomerically pure monomers that can be polymerized by Mo or W catalysts to yield essentially pure *cis,isotactic* structures (from MAP initiators) or *cis,syndiotactic* structures (from biphenolate initiators) in spite of what are technically

"mismatched" propagation steps when the enantiomerically pure monomer is involved. *Cis*,*syndio*,*alt* structures cannot form readily from racemic monomer because a single diastereomeric pathway does not dominate the polymerization process.

Experimental Section

General Details. All air-sensitive manipulations were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. NMR spectra were obtained on Bruker 400 MHz and Varian 500 MHz spectrometers, reported in δ (parts per million), and referenced to residual $^{1}H/^{13}C$ signals of the deuterated solvent ($^{1}H(\delta)$ benzene 7.16, chloroform 7.26, methylene chloride 5.32, toluene 2.08; $^{13}C(\delta)$ benzene 128.06, chloroform 77.16, methylene chloride 53.84, toluene 20.43. Elemental analyses were performed by CENTC Elemental Analysis Facility at the University of Rochester. All reagents were used without further purification unless noted otherwise. Pentane was washed with H_2SO_4, followed by water, and saturated aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets over at least two weeks prior to use in the solvent purification system. HPLC grade diethyl ether, toluene, tetrahydrofuran, pentane, and methylene chloride were sparged with nitrogen and passed through activated alumina. In addition, benzene was passed through a copper catalyst. Organic solvents were then stored over activated 4 Å Linde-type molecular sieves. Deuterated solvents were degassed and stored over activated 4 Å Linde-type molecular sieves. Benzaldehyde was distilled and stored under nitrogen. Mo(NAd)($CHCMe_2Ph$)(pyr)(OHMT)[5a] (**1a**) (HMT = 2,6-(2,4,6-$Me_3C_6H_2)_2C_6H_3$)), Mo(NAr')($CHCMe_2Ph$)(pyr)(OHMT)[15] (**1b**) (Ar' = 2,6-$Me_2C_6H_3$), Mo(NAd)($CHCMe_2Ph$)(pyr)(OHIPT) (**1c**) (HIPT = 2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2C_6H_3$)), W(N-*t*-Bu)($CHCMe_3$)(pyr)(OHMT)[16] (**1d**), Mo(NAr')($CHCMe_2Ph$)($OBiphen_{CF3}$)(thf) ($OBiphen_{CF3}$ = 3,3'-di-*tert*-butyl-5,5'-bistrifluoromethyl-6,6'-dimethyl-1,1'-biphenyl-2,2'-diolate) (**2a**),[17] W(NAr')($CHCMe_2Ph$)((S)-$OBiphen_{Me}$) ((S)-$OBiphen_{Me}$ = 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate) (**2b**),[18] W(O)($CHCMe_2Ph$)(Me_2Pyr)(OHMT)(PMe_2Ph)[19] (**3a**), W(O)($CHCMe_2Ph$)($Me_2Pyr)_2$(PMe_2Ph),[20] (R)-Br_2BitetOH ((R)-3,3'-Dibromo-2'-(tert-

butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol),[21] (*S*)-PhEtNNBE, (*R*)-PhEtNNBE, and *rac*-PhEtNNBE were prepared according to literature procedures.[22] Unless otherwise noted, all other reagents were obtained from commercial sources and used as received.

W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)[(R)-OBr$_2$Bitet](PMe$_2$Ph) (**3b**). A 100 mL Schlenk tube was charged with 390 mg of W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$(PMe$_2$Ph) (0.593 mmol, 1.0 equiv), 336 mg of (R)-Br$_2$BitetOH (0.593 mmol, 1.0 equiv), a stir bar, and 30 mL of benzene. The tube was closed, and the mixture was stirred at 70 °C for 3 h. The volatiles were removed *in vacuo* and the residue was triturated with 5 mL of pentane for 30 min to give a yellow powder, which was collected by filtration; yield 345 mg (0.306 mmol, 52%). The product is a mixture of two diastereomers (83:17): ^{1}H NMR (500 MHz, C$_6$D$_6$, 20 °C) δ 12.21 (s, 1H, C*H*CMe$_2$Ph, minor), 11.22 (s, 1H, C*H*CMe$_2$Ph, $^1J_{CH}$ = 122 Hz, major), 7.25 – 6.79 (m, 12H, aryl), 6.18 (br, 2H, Me$_2$*Pyr*), 2.63 – 0.76 (overlapping signals, 43H, *Me*$_2$Pyr, P*Me*$_2$Ph, CHC*Me*$_2$Ph, and OBr$_2$Bitet ligand), 0.47 (s, 3H), 0.21 (s, 3H), -0.14 (s, 3H), -0.75 (s, 3H); ^{13}C-NMR (125 MHz, CD$_2$Cl$_2$, 20 °C): δ 291.4 (*C*HCMe$_2$Ph), 288.2 (*C*HCMe$_2$Ph), 157.0, 156.8, 150.0, 149.5, 148.6, 148.3, 138.2, 137.8, 137.5, 136.0, 135.2, 134.9, 133.8, 133.4, 133.3, 131.5, 131.4, 131.2, 131.1, 131.0, 130.8, 130.3, 130.1, 129.0, 128.8, 128.7, 128.6, 127.5, 126.5, 126.4, 126.3, 113.4, 112.6, 111.7, 106.8, 106.0, 53.37, 33.28, 29.55, 29.45, 29.40, 29.32, 28.75, 28.64, 28.52, 27.87, 27.38, 27.09, 26.21, 23.65, 23.48, 23.30, 23.13, 22.89, 22.61, 20.33, 18.59, 16.23, 15.50, 15.34, 15.13, 14.24, 13.02, -1.90, -2.54, -2.92, -5.17; ^{31}P NMR (202 MHz, C$_6$D$_6$, 20 °C) δ 8.77 (s, $^1J_{WP}$ = 319 Hz), 2.21 (s), -5.89 (broad s). Anal. Calcd for C$_{50}$H$_{64}$Br$_2$NO$_3$PSiW: C, 53.16; H, 5.71; N, 1.24. Found: C, 53.32; H, 5.76; N, 1.14.

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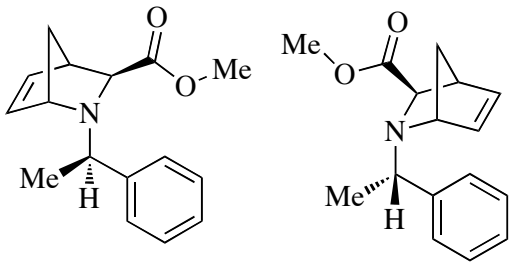
Supporting Information Available. Experimental details for the synthesis of **3b** and various polymers and NMR spectra of all polymers. This material is available free of charge via the Internet at http://pubs.acs.org.



(*R*)-PhEtNNBE **(*S*)-PhEtNNBE**

Figure 1. PhEtNNBE Monomers employed in this study.

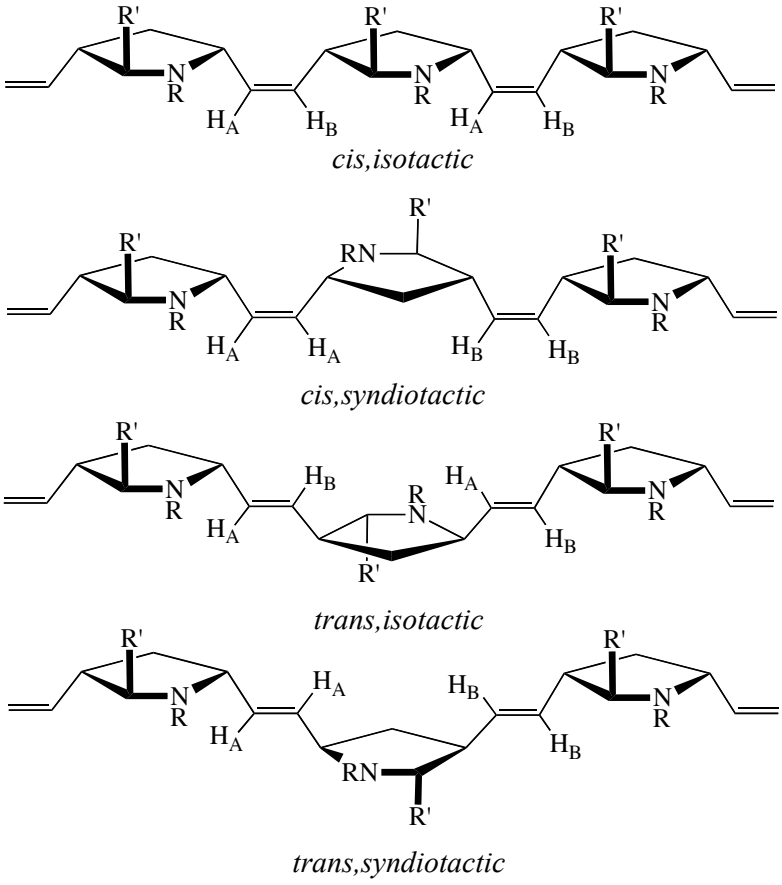


Figure 2. The four possible regular structures for poly[(*S*)-PhEtNNBE] (R = (*S*)-CHMePh, R' = CO_2Me).

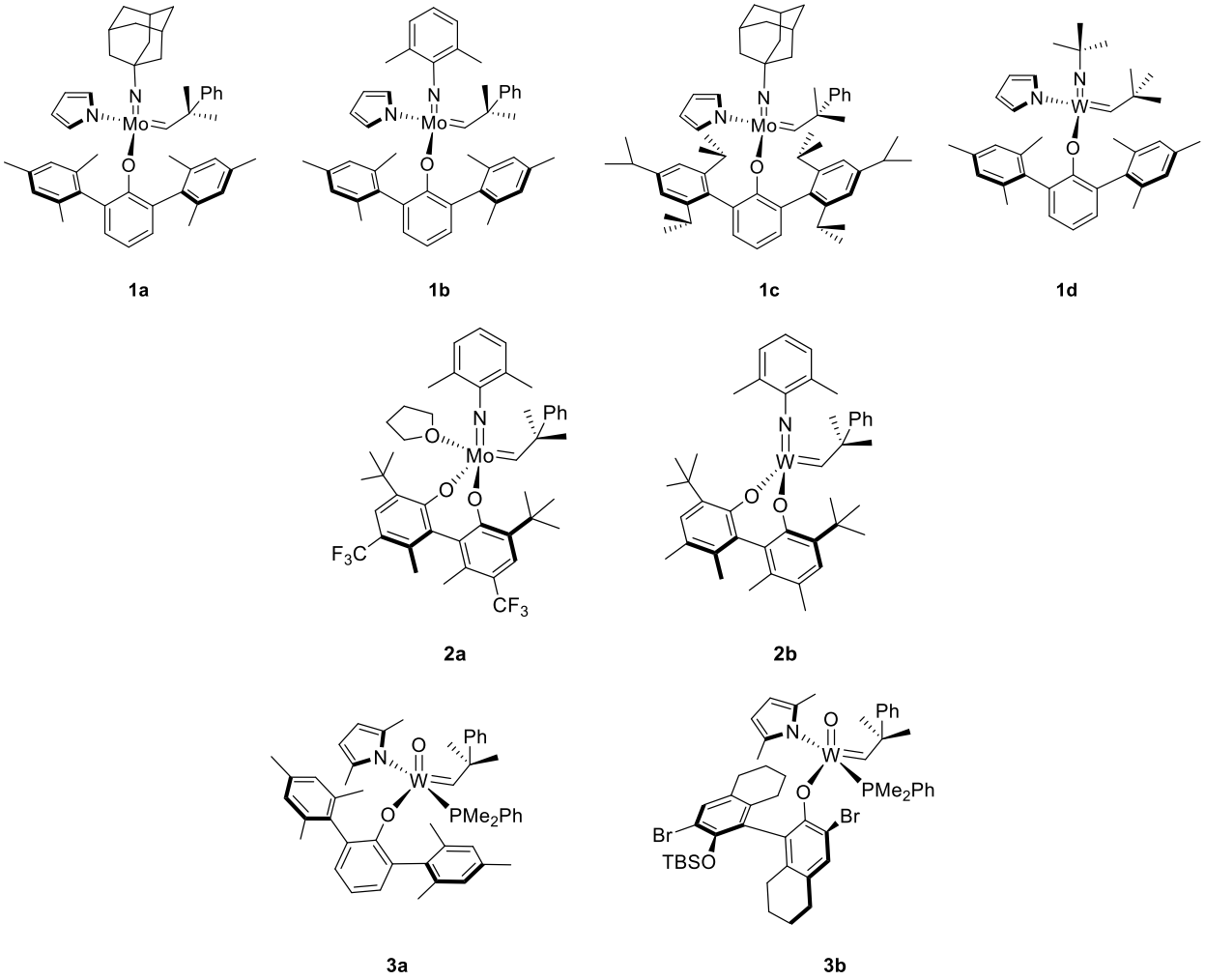


Figure 3. Molybdenum and tungsten catalysts used for the polymerization of PhEtNNBE.

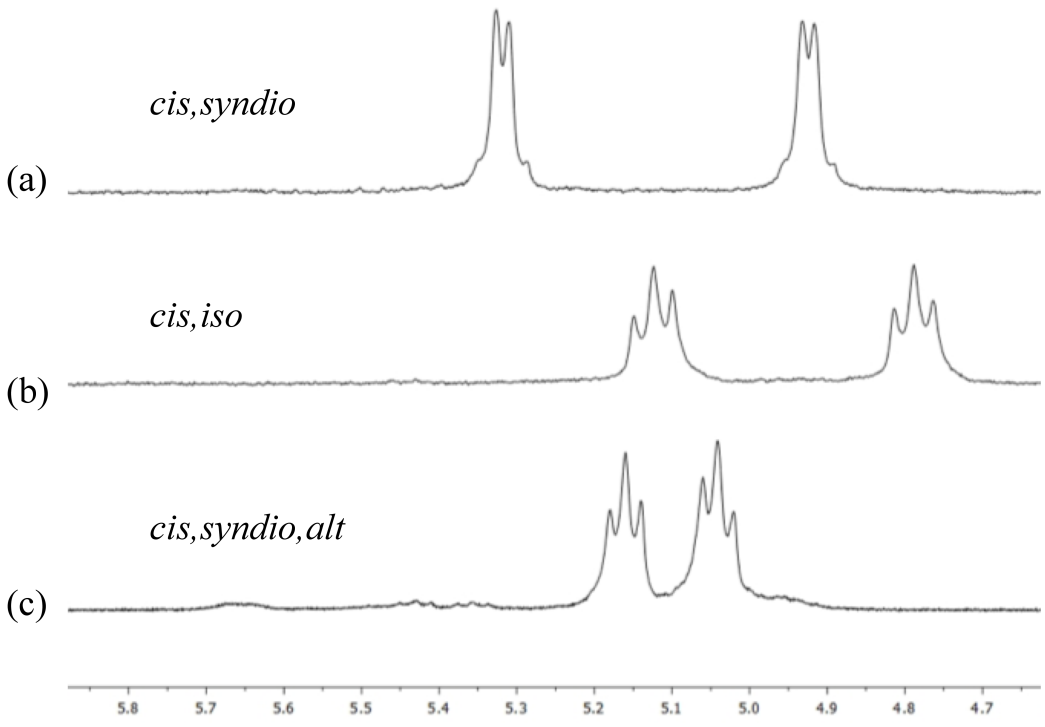


Figure 4. ^{1}H NMR spectra of poly[(*S*)-PhEtNNBE] prepared from (a) **3a** (in $CDCl_3$, 400 MHz) and (b) **2b** (in $CDCl_3$, 400 MHz); (c) ^{1}H NMR spectrum of poly[*rac*-PhEtNNBE] prepared from **1a** at 0 °C (in $CDCl_3$, 500 MHz).

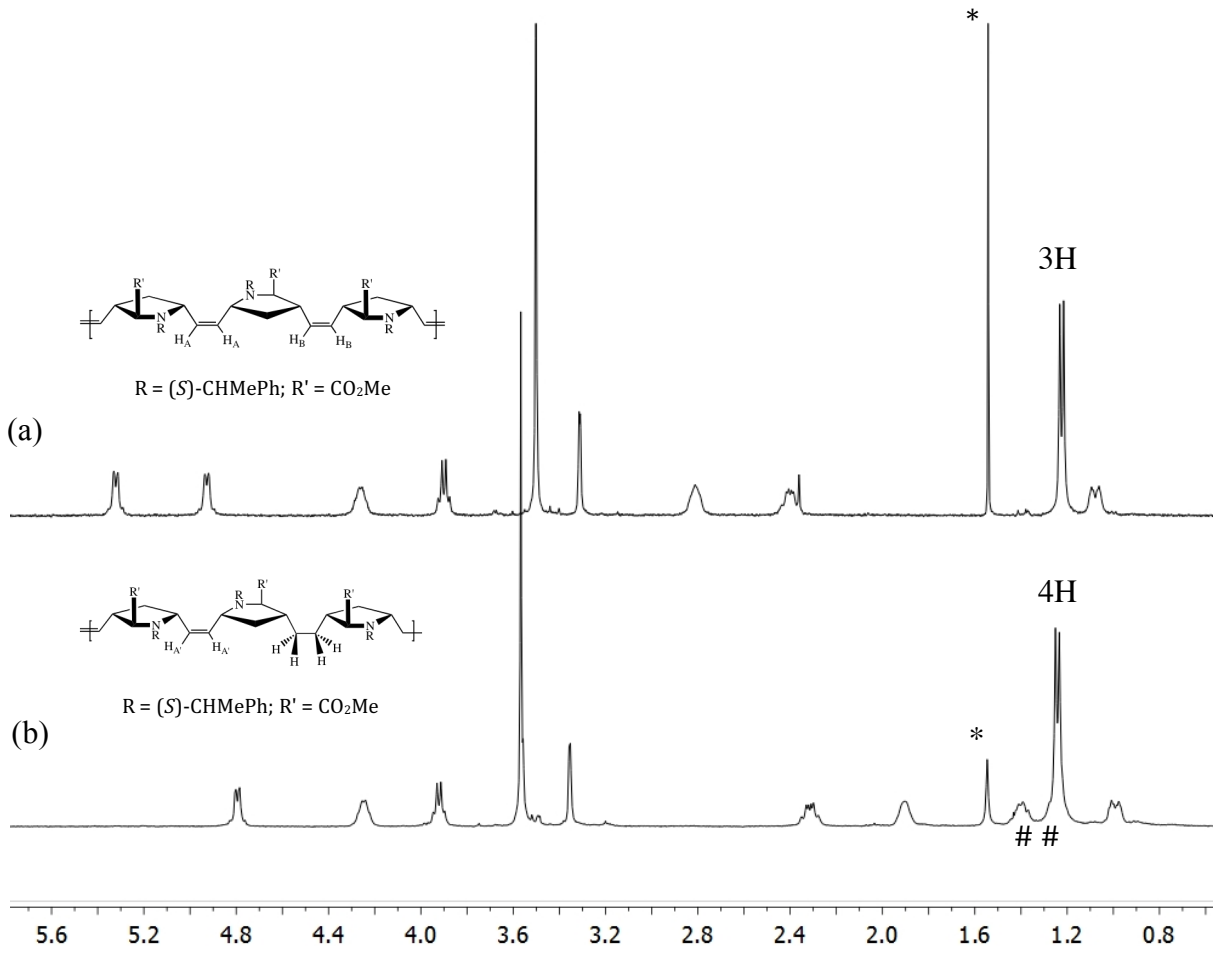


Figure 5. ^{1}H NMR spectra of (a) c*is*,*syndiotactic*-poly[(*S*)-PhEtNNBE] (in $CDCl_3$, 400 MHz) and (b) c*is*,*syndiotactic*-poly[H-(*S*)-PhEtNNBE] (in $CDCl_3$, 400 MHz). (* Residual water resonance in $CDCl_3$; # # new aliphatic proton resonances.)

Table 1. The structures of poly[(*S*)-PhEtNNBE] and poly[(*rac*)-PhEtNNBE] formed with initiators **1-3**.

Initiator	Monomer	Structure
Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHMT) (**1a**)	(*S*)-PhEtNNBE	> 95% *cis*,*syndio*
Mo(NAr')(CHCMe$_2$Ph)(Pyr)(OHMT) (**1b**)	(*S*)-PhEtNNBE	> 95% *cis*,*syndio*
Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT) (**1c**)	(*S*)-PhEtNNBE	mixture; *atactic*
W(N-t-Bu)(CHCMe$_3$)(Pyr)(OHMT) (**1d**)	(*S*)-PhEtNNBE	~ 90% *cis*,*syndio*
W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)(OHMT)(PMe$_2$Ph) (**3a**)	(*S*)-PhEtNNBE	> 95% *cis*,*syndio*
W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)((R)-OBr$_2$Bitet)(PMe$_2$Ph) (**3b**)	(*S*)-PhEtNNBE	> 95% *cis*,*syndio*
Mo(NAr')(CHCMe$_2$Ph)(OBiphen$_{CF3}$)(thf) (**2a**)	(*S*)-PhEtNNBE	> 95% *cis*,*iso*
W(NAr')(CHCMe$_2$Ph)((S)-OBiphen$_{Me}$) (**2b**)	(*S*)-PhEtNNBE	> 95% *cis*,*iso*
Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHMT) (**1a**)	(*rac*)-PhEtNNBE	~ 80% *cis*,*syndio,alt*
W(N-t-Bu)(CHCMe$_3$)(Pyr)(OHMT) (**1d**)	(*rac*)-PhEtNNBE	~ 50% *cis*,*syndio,alt*

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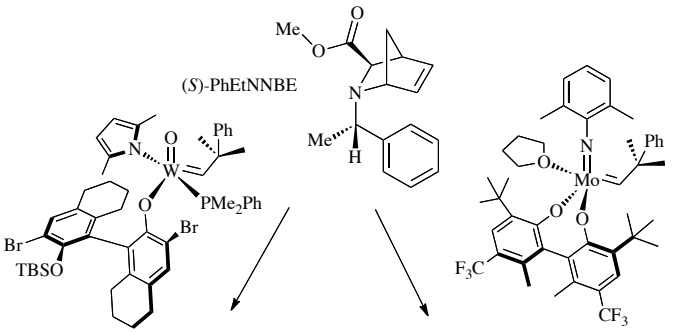

cis,*syndiotactic*-polymer *cis*,*isotactic*-polymer

Supporting Information for

Stereoselective Ring-Opening Metathesis Polymerization (ROMP) of Methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate Initiated by Molybenum and Tungsten Initiators

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Table of Contents

General considerations

All air-sensitive manipulations were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. NMR spectra were obtained on Bruker 400 MHz and Varian 500 MHz spectrometers, reported in δ (parts per million), and referenced to residual $^{1}H/^{13}C$ signals of the deuterated solvent ($^{1}H(\delta)$ benzene 7.16, chloroform 7.26, methylene chloride 5.32, toluene 2.08; $^{13}C(\delta)$ benzene 128.06, chloroform 77.16, methylene chloride 53.84, toluene 20.43. Elemental analyses were performed by CENTC Elemental Analysis Facility at the University of Rochester. All reagents were used without further purification unless noted otherwise. Pentane was washed with H_2SO_4, followed by water, and saturated aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets over at least two weeks prior to use in the solvent purification system. HPLC grade diethyl ether, toluene, tetrahydrofuran, pentane, and methylene chloride were sparged with nitrogen and passed through activated alumina. In addition, benzene was passed through a copper catalyst. Organic solvents were then stored over activated 4 Å Linde-type molecular sieves. Deuterated solvents were degassed and stored over activated 4 Å Linde-type molecular sieves. Benzaldehyde was distilled and stored under nitrogen. Mo(NAd)(CHCMe$_2$Ph)(pyr)(OHMT) [1] (**1a**) (HMT = 2,6-(2,4,6-Me$_3$C$_6$H$_2$)$_2$C$_6$H$_3$)), Mo(NAr')(CHCMe$_2$Ph)(pyr)(OHMT) [2] (**1b**) (Ar' = 2,6-Me$_2$C$_6$H$_3$), Mo(NAd)(CHCMe$_2$Ph)(pyr)(OHIPT)[1] (**1c**) (HIPT = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$)), W(N-t-Bu)(CHCMe$_3$)(pyr)(OHMT)[3] (**1d**), Mo(NAr')(CHCMe$_2$Ph)(OBiphen$_{CF3}$)(thf) (OBiphen$_{CF3}$ = 3,3'-di-*tert*-butyl-5,5'-bistrifluoromethyl-6,6'-dimethyl-1,1'-biphenyl-2,2'-diolate) [4] (**2a**), W(NAr')(CHCMe$_2$Ph)((S)-OBiphen$_{Me}$) ((S)-OBiphen$_{Me}$ = 3,3'-di-*tert*-butyl-5,5',6,6'-tetramethyl-1,1'-biphenyl-2,2'-diolate) [5] (**2b**), W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)(OHMT)(PMe$_2$Ph) [6] (**3a**), W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)$_2$, [7] (R)-Br$_2$BitetOH [8] ((R)-3,3'-Dibromo-2'-(tert-butyldimethylsilyloxy)-5,5',6,6',7,7',8,8'-octahydro-1,1'-binaphthyl-2-ol), (*S*)-PhEtNNBE, [9] (*R*)-PhEtNNBE, and *rac*-PhEtNNBE were prepared according to literature procedures. Unless otherwise noted, all other reagents were obtained commercial sources and used as received.

W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)((R)-OBr$_2$Bitet)(PMe$_2$Ph)

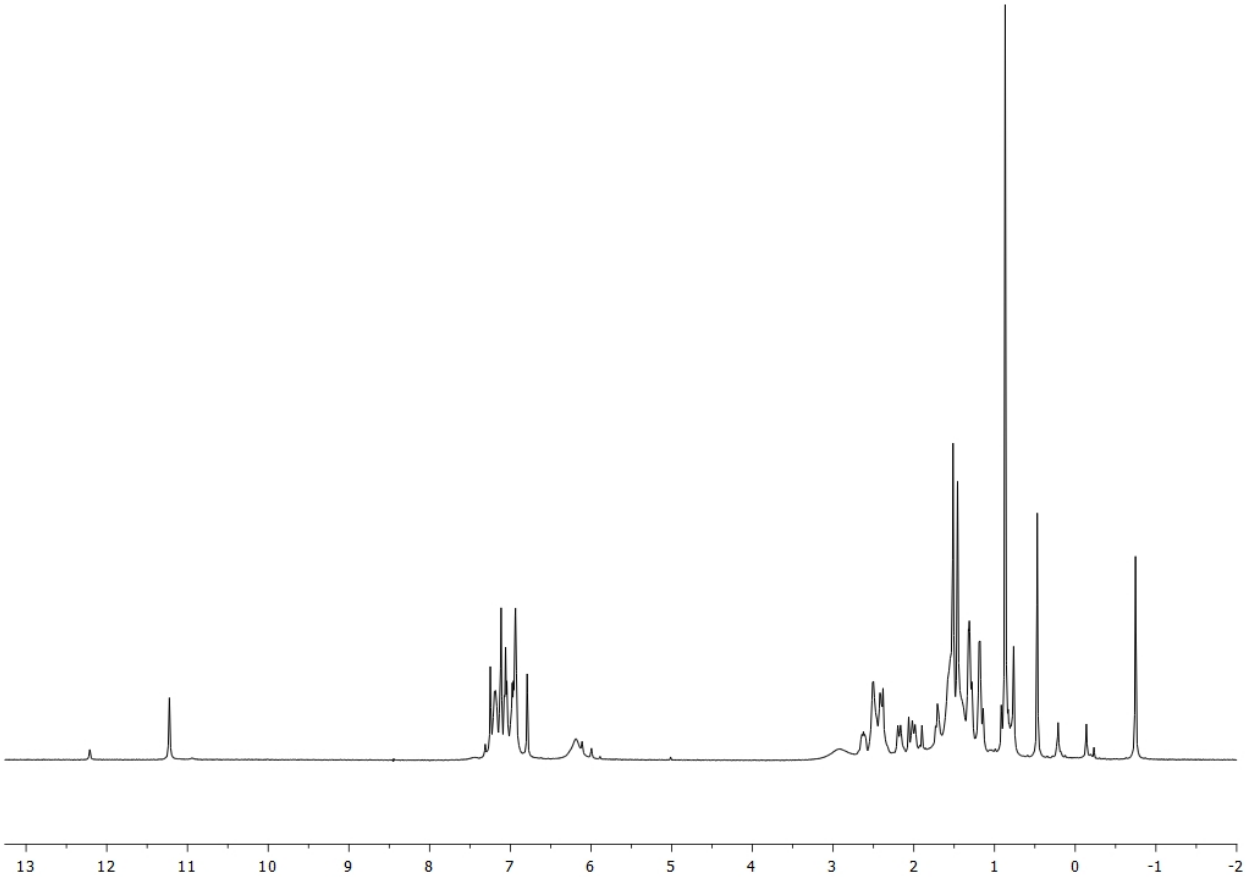

Figure S1. ^{1}H NMR spectrum of W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)[(R)-OBr$_2$Bitet](PMe$_2$Ph) (in C_6D_6, 500 MHz).

General polymerization procedure

Monomer (0.449 mmol (100 eq.) or 0.225 mmol (50 eq.)) was dissolved in 1 mL toluene, and added to a 1 mL toluene solution of initiator (4.49 μmol) under stirring. The progress of the reaction was monitored by diluting aliquots of the reaction mixture with $CDCl_3$ and recording the ^1H NMR spectra. After consumption of the monomer was observed, 1 mL of benzaldehyde was added and the mixture was stirred for at least 1 h. The polymer was precipitated by adding the mixture dropwise to 100 mL of vigorously stirred methanol. The solid was isolated by centrifugation, washed with methanol and dried *in vacuo*.

General hydrogenation procedure

The unsaturated polymer (37 mg, 0.144 mmol), p-tosyl hydrazide (84 mg, 0.451 mmol), tributylamine (0.1 mL, 0.431 mmol) and butylated hydroxytoluene (1 mg) were added in a 20 mL pressurized tube. The mixture was dissolved in dry chloroform (3 mL) and was refluxed for 10 hours at 130 °C and allowed to cool to room temperature. The mixture was poured into 5 mL methanol and centrifuged to precipitate polymer. It was washed and centrifuged again with 5 mL methanol. The hydrogenated polymer was isolated by decantation and dried in vacuum for overnight to yield white solid.

***cis*,*syndiotactic*-poly[(*S*)-PhEtNNBE]**.

White solid in 87% yield with W(O)(CHCMe$_2$Ph)(Me$_2$Pyr)((R)-OBr$_2$Bitet)(PMe$_2$Ph) (**3b**) initiator. ^{1}H-NMR (400 MHz, $CDCl_3$, 20°C): δ 7.11-7.23 (m, 5H, C*H*), 5.32 (d, 1H, $^3J_{HH}$ = 6 Hz, Ha), 4.92 (d, 1H, $^3J_{HH}$ = 6 Hz, Hb), 4.26 (m, 1H, $^3J_{HH}$ = 4 Hz, Hd), 3.89 (q, 1H, $^3J_{HH}$ = 7 Hz, NC*H*CH$_3$ (Hg)), 3.49 (s, 3H, COO*Me*), 3.31 (s, 1H, Hh), 2.81 (s, 1H, Hc), 2.40 (m, 1H, He or Hf), 1.22 (d, 3H, $^3J_{HH}$ = 7 Hz, NCH*CH$_3$*), 1.08 (d, 1H, $^3J_{HH}$ = 13 Hz, He or Hf); ^{13}C NMR (125 MHz, $CDCl_3$, 20°C): δ 175.4, 144.5, 133.3, 132.9, 128.1, 128.0, 127.0, 67.8, 57.6, 57.2, 51.5, 40.2, 39.4, 19.4.

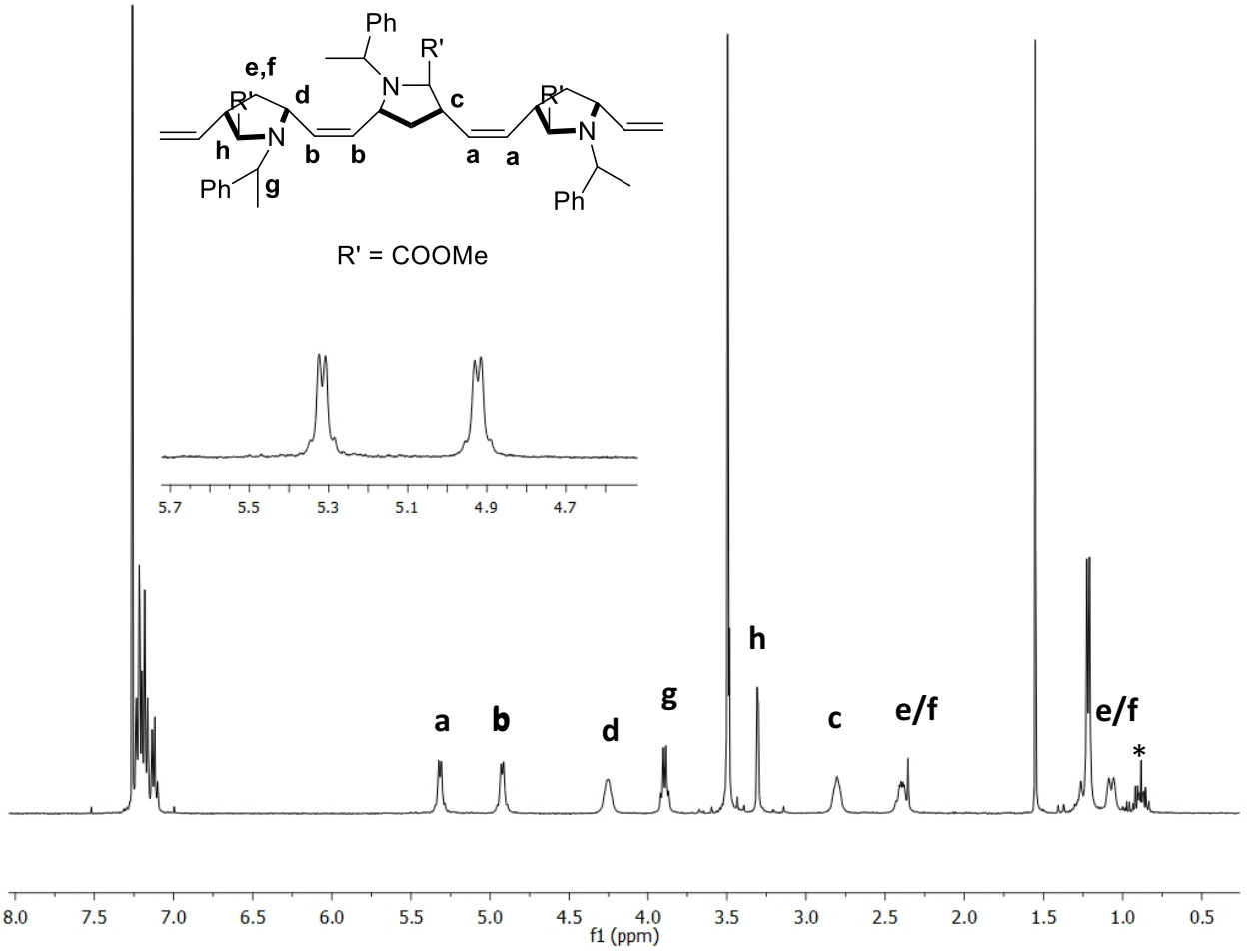

Figure S2. ^{1}H NMR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **3b** (in $CDCl_3$, 400 MHz) (* residual solvent in $CDCl_3$)

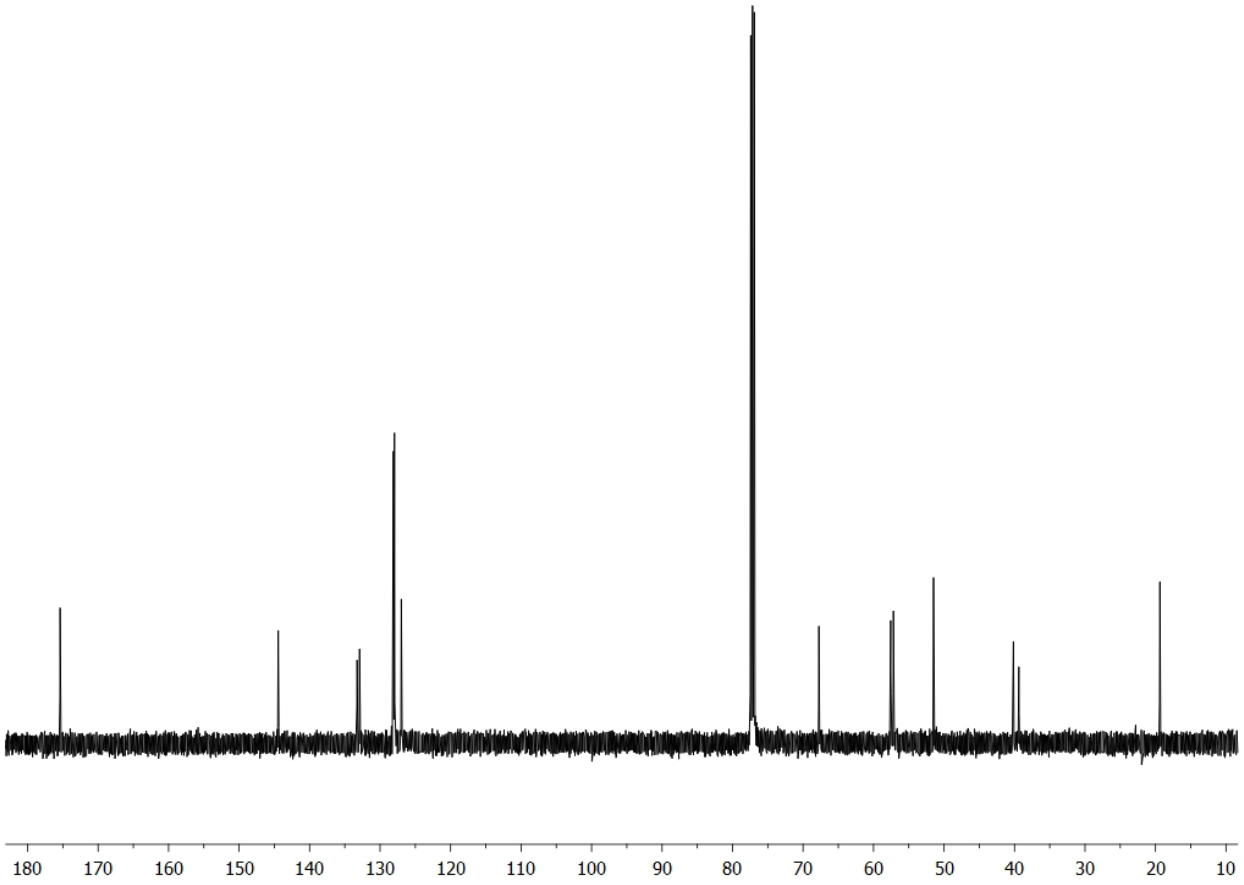

Figure S3. ^{13}C NMR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **3b** (in $CDCl_3$, 125 MHz)

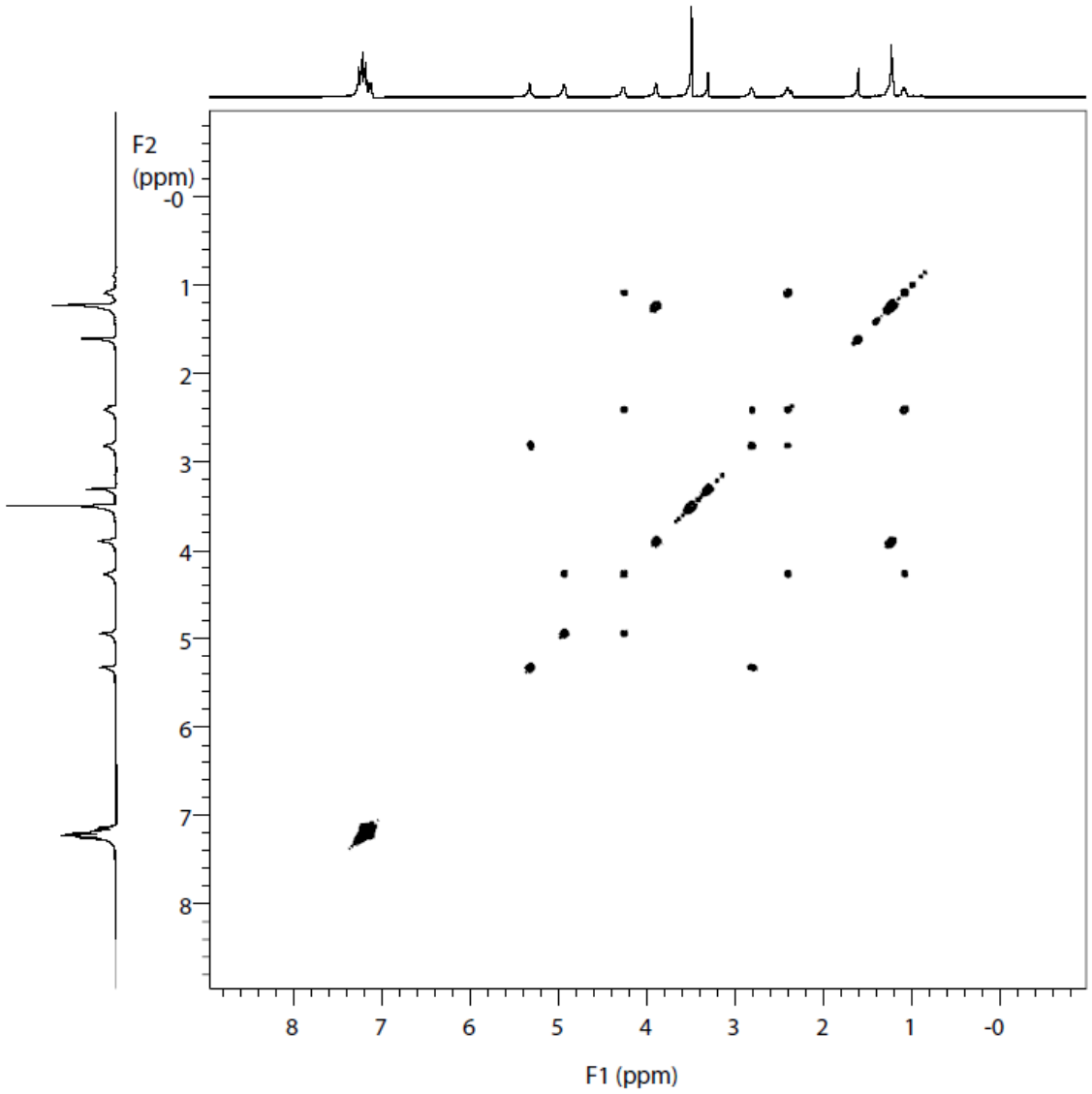

Figure S4. ^{1}H-^{1}H COSY spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **3b** (in $CDCl_3$, 500 MHz).

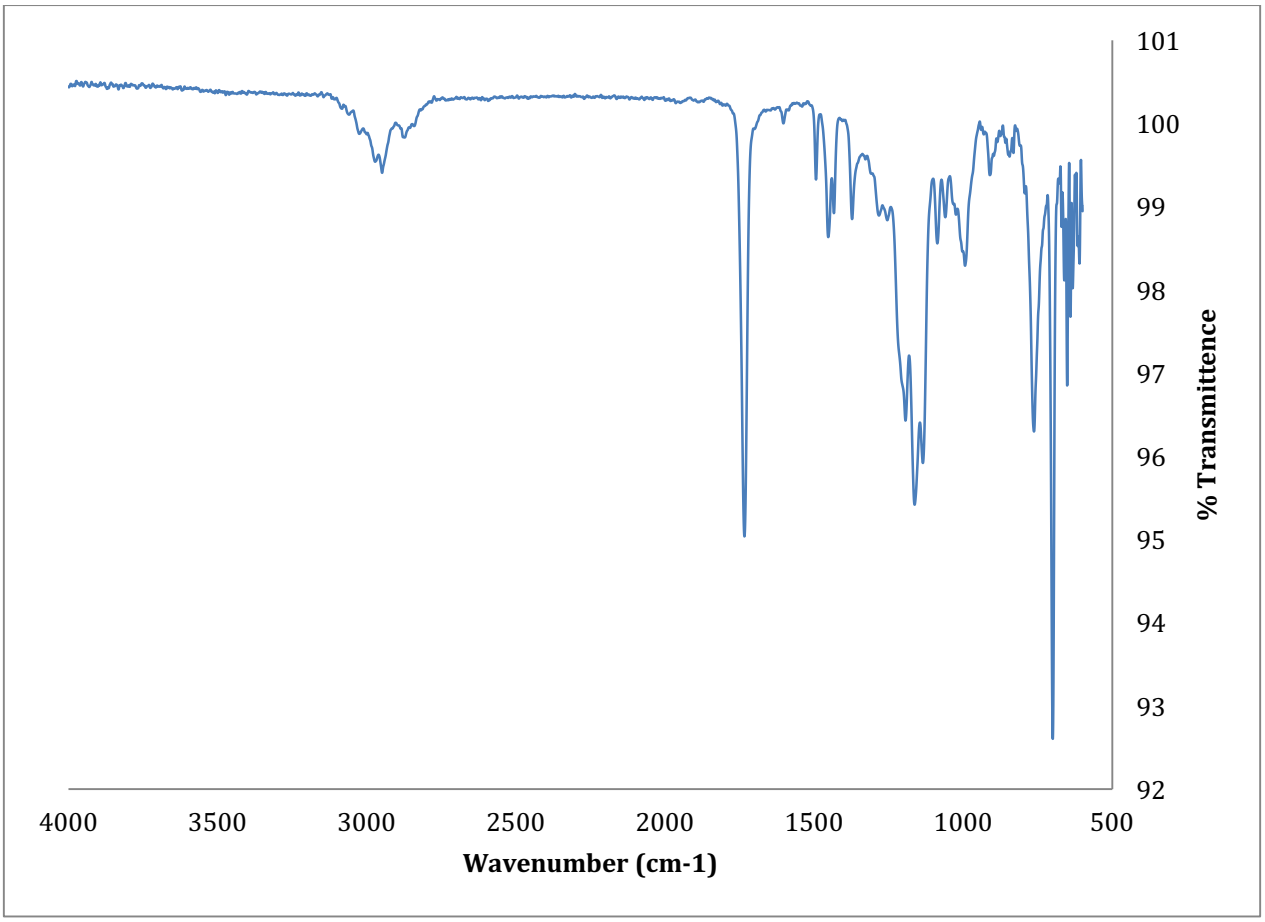

Figure S5. IR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **3b**

***cis,isotactic*-poly[(*S*)-PhEtNNBE]**.

White solid in 98% yield with W(NAr')(CHCMe$_2$Ph)((S)-OBiphen$_{Me}$) (**2b**) initiator. ^{1}H-NMR (400 MHz, $CDCl_3$, 20°C): δ 7.13–7.25 (m, 5H, Ph), 5.12 (t, 1H, $^3J_{HH}$ = 9.6 Hz, Hb), 4.79 (t, 1H, $^3J_{HH}$ = 10 Hz, Ha), 4.14 (m, 1H, Hc), 3.96 (q, 1H, $^3J_{HH}$ = 6.8 Hz, NC*H*CH$_3$ (Hf)), 3.75 (s, 3H, COO*Me*), 3.33 (s, 1H, He), 2.89 (s, 1H, Hd), 2.49 (s, 1H, Hg or Hh), 1.24 (d, 3H, $^3J_{HH}$ = 6.4 Hz, NCH*CH$_3$*), 1.11 (br s, 1H, Hg or Hh); ^{13}C-NMR (125 MHz, $CDCl_3$, 20°C): δ 175.5 (*C*=O), 145.8 (*C-ipso*), 133.5 (*C*=C), 132.2 (C=*C*), 127.9 (*C*-Ph), 127.8 (*C*-Ph), 126.8 (*C-para*), 67.7 (*C*-3), 57.7, 57.6, 51.5 (O*C*H$_3$), 39.7, 39.1, 20.3 (NC*C*H$_3$).

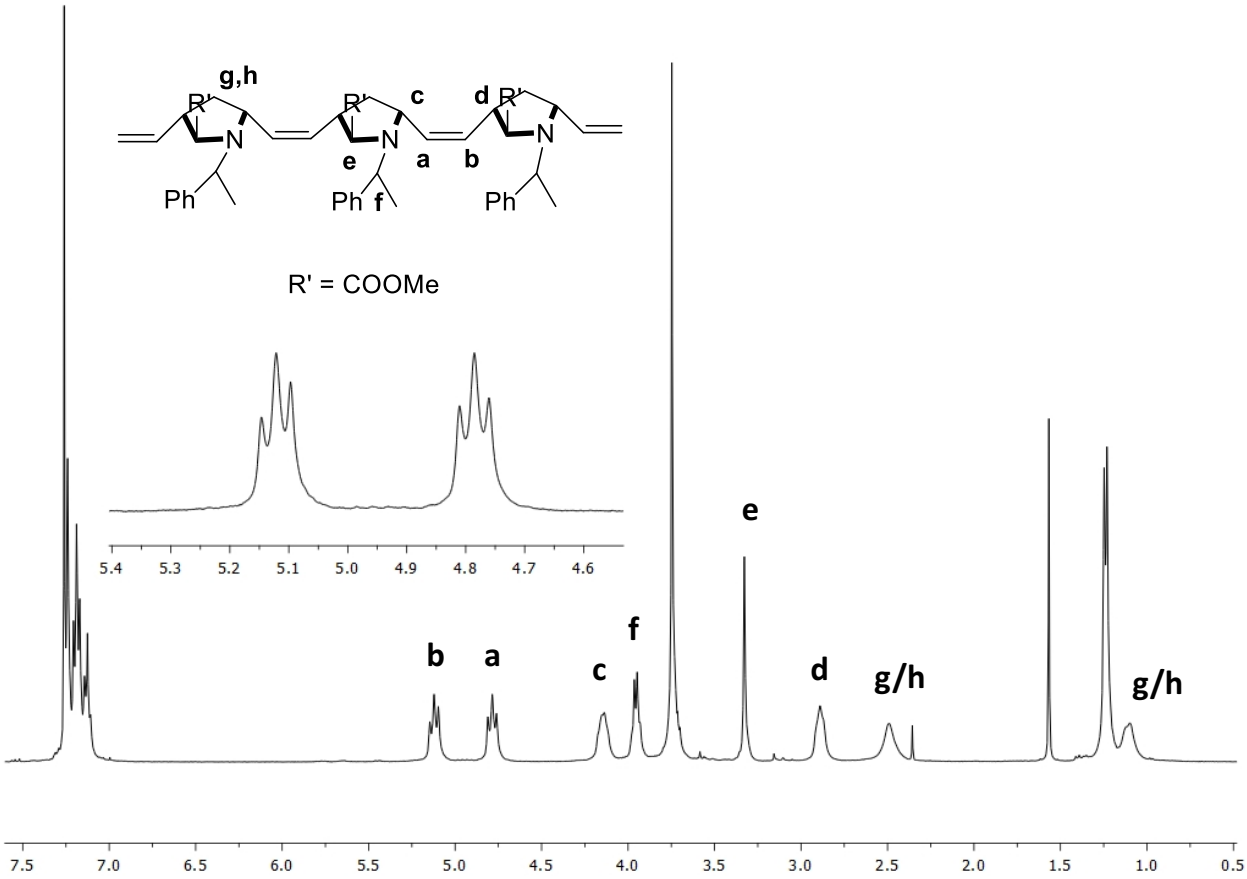

Figure S6. ^{1}H NMR spectrum of *cis,isotactic*-poly[(S)-PhEtNBE] made with **2b** (in $CDCl_3$, 400 MHz)

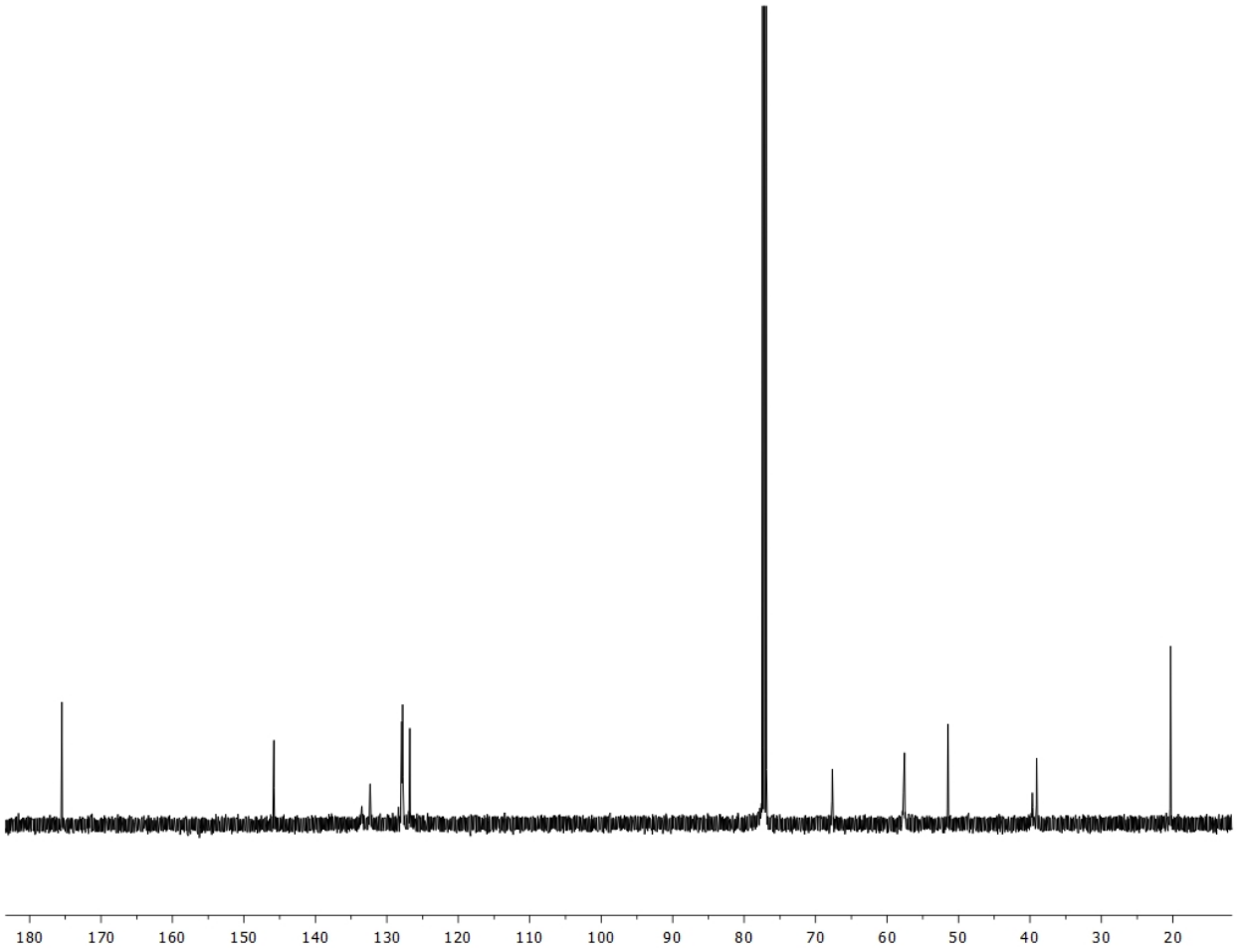

Figure S7. ^{13}C NMR spectrum of *cis,isotactic*-poly[(S)-PhEtNBE] made with **2b** (in $CDCl_3$, 125 MHz)

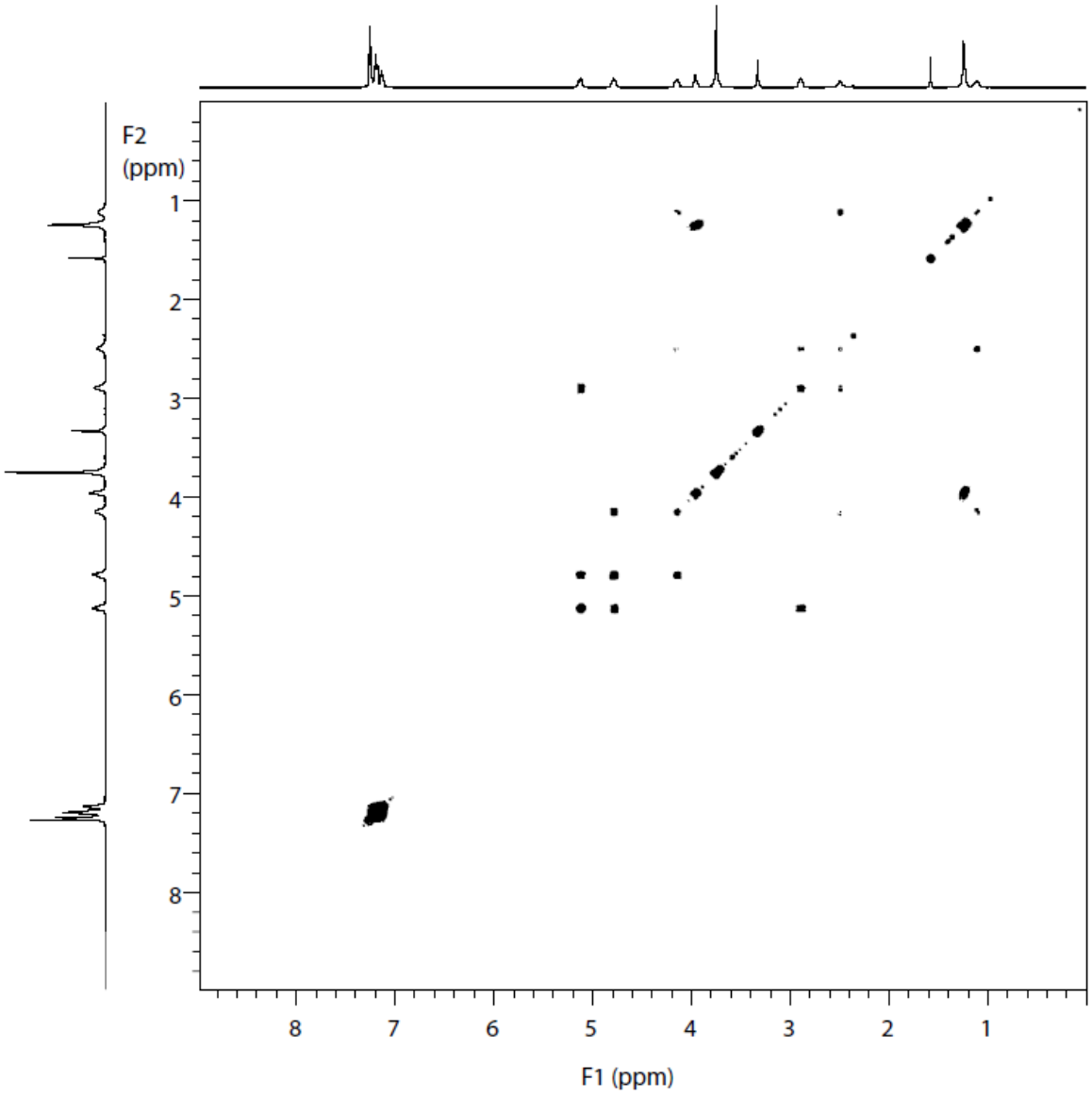

Figure S8. ^{1}H-^{1}H COSY spectrum of *cis,isotactic*-poly[(S)-PhEtNBE] made with **2b** (in $CDCl_3$, 500 MHz).

***cis,syndiotactic,alt*-poly[(*rac*)-PhEtNNBE]**.

Light yellow solid in 83% yield with Mo(NAd)(CHCMe$_2$Ph)(pyr)(OHMT) initiator at 0°C. ^{1}H-NMR (500 MHz, $CDCl_3$, 20°C): δ 7.11–7.22 (m, 5H, Ph), 5.16 (t, 1H, $^3J_{HH}$ = 10 Hz, Ha), 5.04 (t, 1H, $^3J_{HH}$ = 10 Hz, Hb), 4.11 (m, 1H, Hd), 3.84 (q, 1H, $^3J_{HH}$ = 6.5 Hz, NC*H*CH$_3$ (Hf)), 3.74 (s, 3H, COO*Me*), 3.34 (d, 1H, $^3J_{HH}$ = 2.5 Hz, He), 2.89 (s, 1H, Hc), 2.33 (m, 1H, Hg or Hh), 1.22 (d, 3H, $^3J_{HH}$ = 7 Hz, NCH*CH$_3$*), 1.06 (d, 1H, $^3J_{HH}$ = 13.5 Hz, Hg or Hh); ^{13}C-NMR (125 MHz, $CDCl_3$, 20°C): δ 174.8, 144.6, 133.1, 132.1, 128.2, 127.9, 127.1, 68.9, 58.3, 58.1, 51.5, 40.1, 39.3, 20.5.

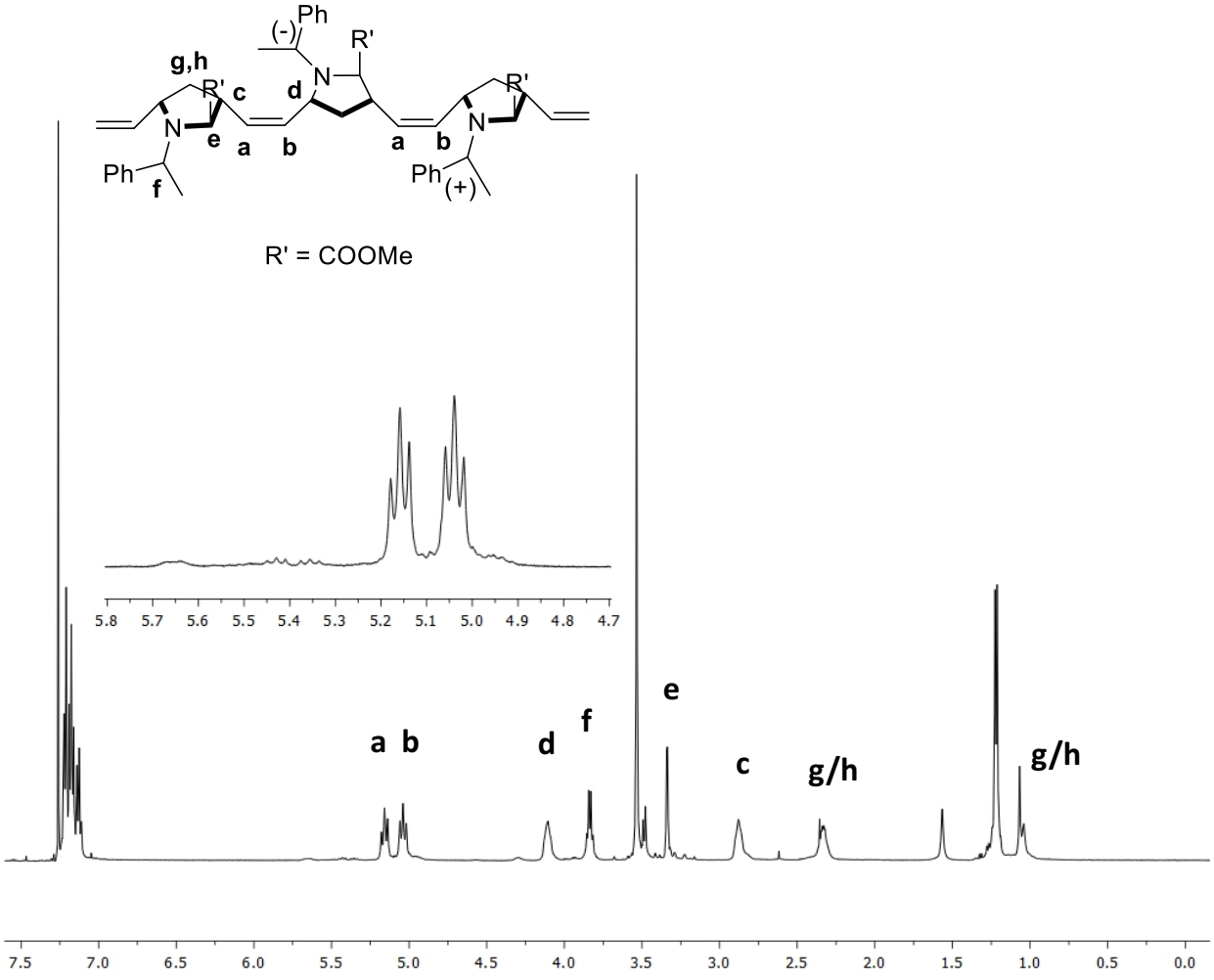

Figure S9. ^{1}H NMR spectrum of *cis,syndiotactic,alt*-[(*rac*)-PhEtNBE] made with **1a** (in $CDCl_3$, 500 MHz)

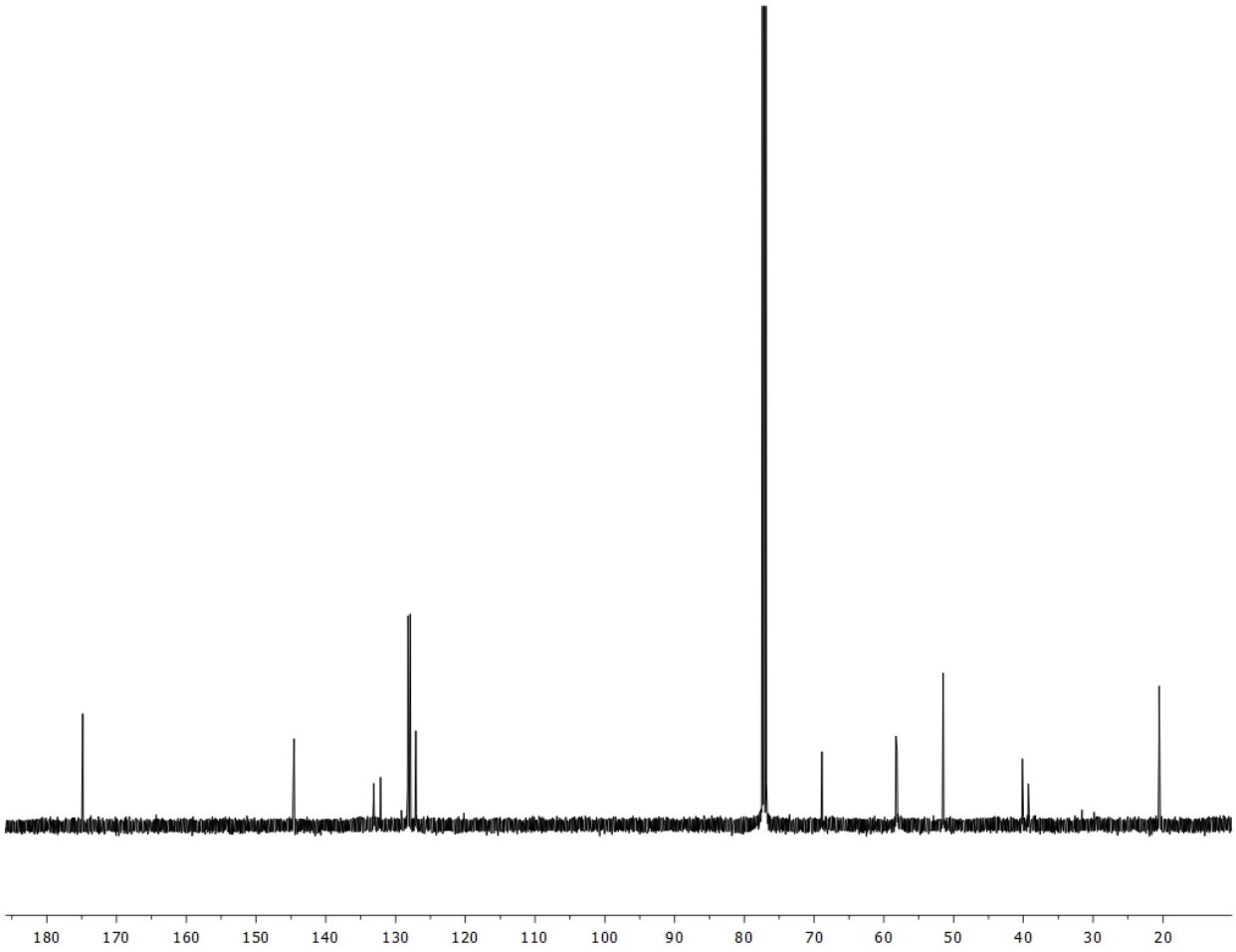

Figure S10. ^{13}C NMR spectrum of *cis,syndiotactic,alt*-[(*rac*)-PhEtNBE] made with **1a** (in $CDCl_3$, 125 MHz)

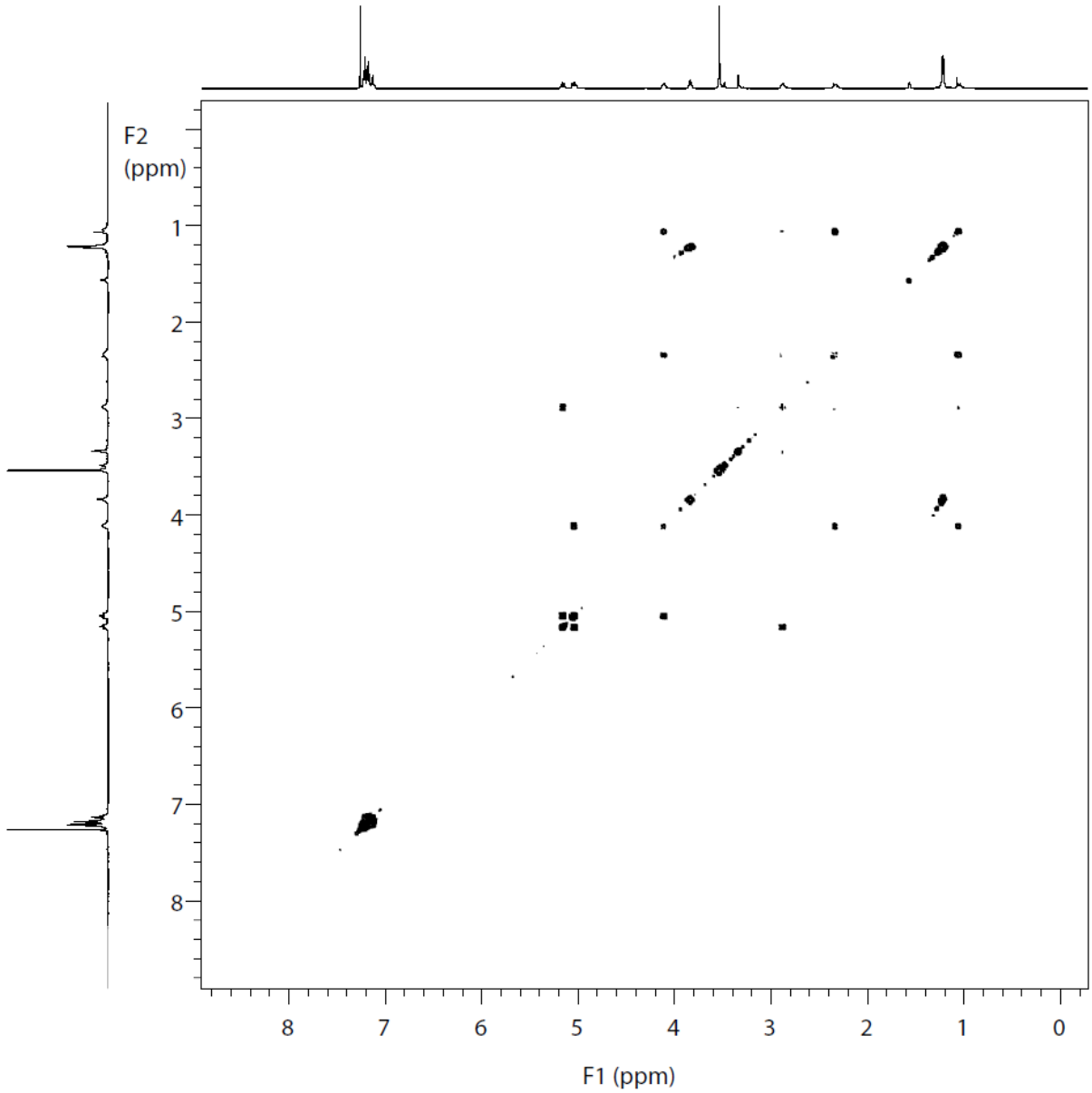

Figure S11. ^{1}H-^{1}H COSY spectrum of *cis,syndiotactic,alt*-[(*rac*)-PhEtNBE] made with **1a**. (in $CDCl_3$, 500 MHz)

***cis,syndiotactic*-poly[H-(*S*)-PhEtNNBE]**.

White solid in 62% yield. ^{1}H-NMR (400 MHz, $CDCl_3$, 20°C): δ 7.10–7.25 (m, 5H, Ph), 4.78 (d, 1H, $^{3}J_{HH}$ = 6.4 Hz, Hb), 4.24 (m, 1H, $^{3}J_{HH}$ = 6 Hz, Hd), 3.90 (q, 1H, $^{3}J_{HH}$ = 7 Hz, NC*H*CH_3 (Hg)), 3.57 (s, 3H, COO*Me*), 3.35 (d, 1H, $^{3}J_{HH}$ = 2.4 Hz, Hh), 2.30 (m, 1H, He or Hf), 1.90 (s, 1H, Hc), 1.40 (m, 1H, Ha), 1.25 (d, 4H, $^{3}J_{HH}$ = 7 Hz, NCH*CH_3* and Ha), 1.01 (d, 1H, $^{3}J_{HH}$ = 13 Hz, He or Hf); ^{13}C-NMR (125 MHz, $CDCl_3$, 20°C): δ 176.3, 145.0, 133.4, 128.1, 127.9, 126.9, 67.2, 57.8, 57.5, 51.4, 42.4, 38.3, 34.9, 20.0.

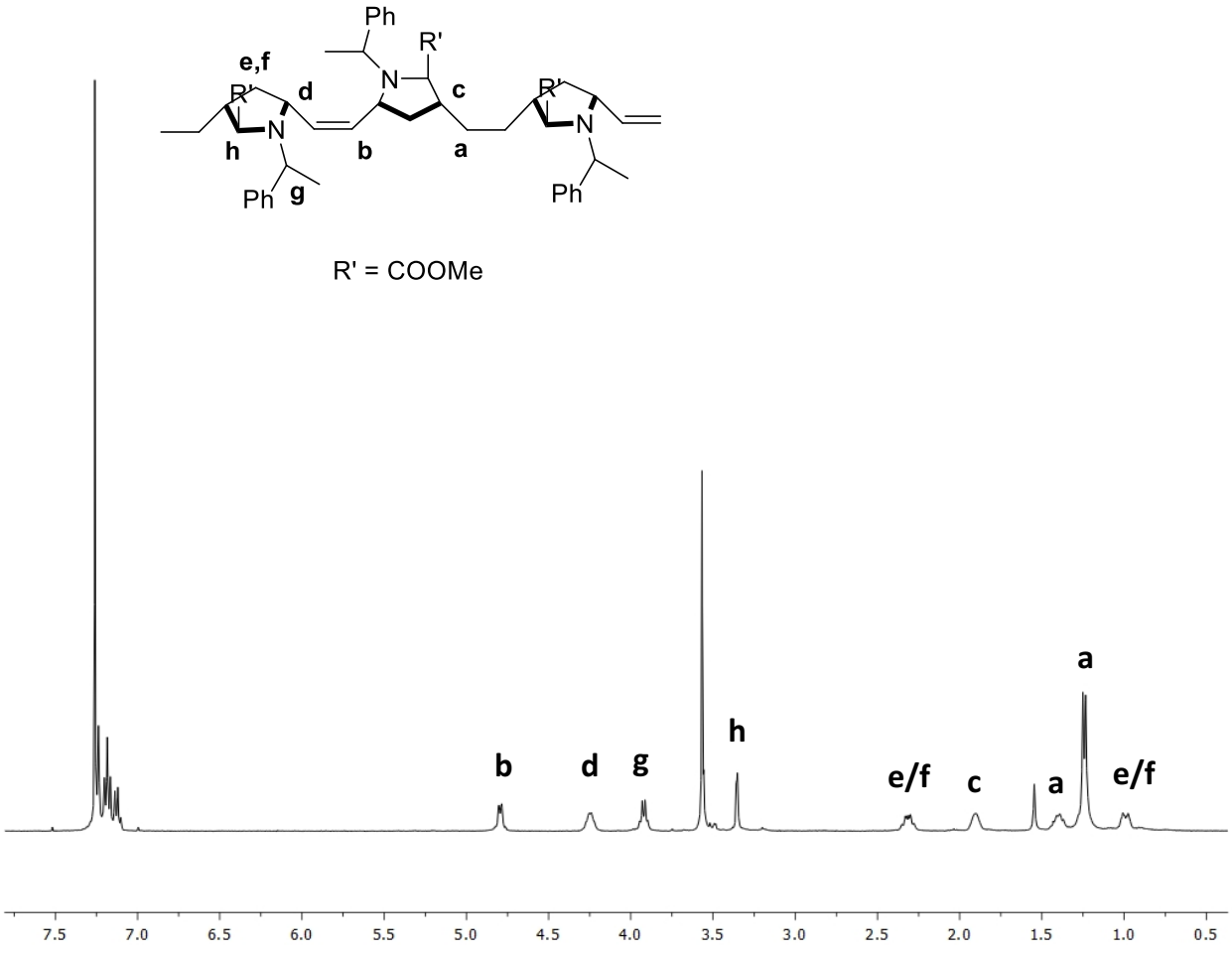

Figure S12. ^{1}H NMR spectrum of c*is*,*syndiotactic*-poly[H-(*S*)-PhEtNNBE] (in $CDCl_3$, 400 MHz)

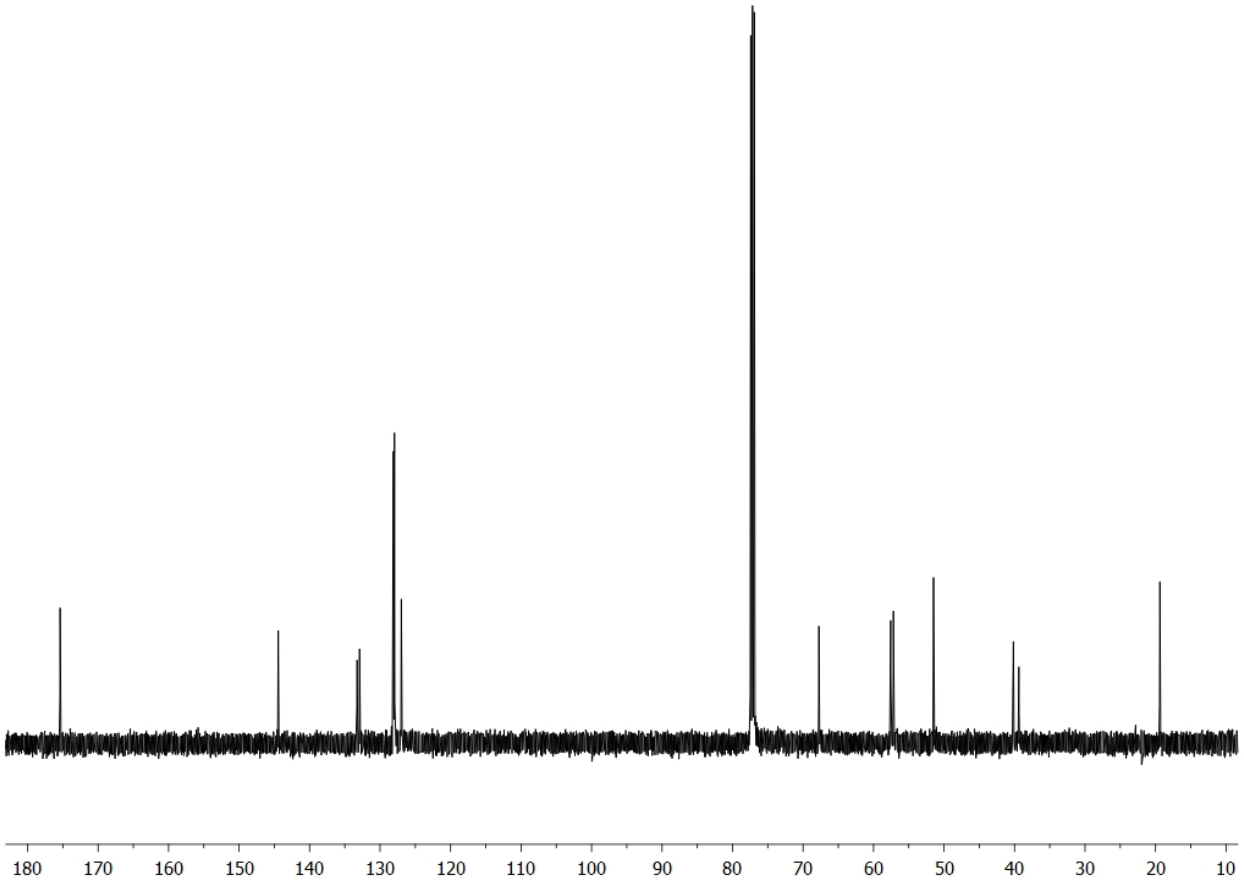

Figure S13. ^{13}C NMR spectrum of *cis,syndiotactic*-poly[H-(*S*)-PhEtNNBE] (in $CDCl_3$, 125 MHz)

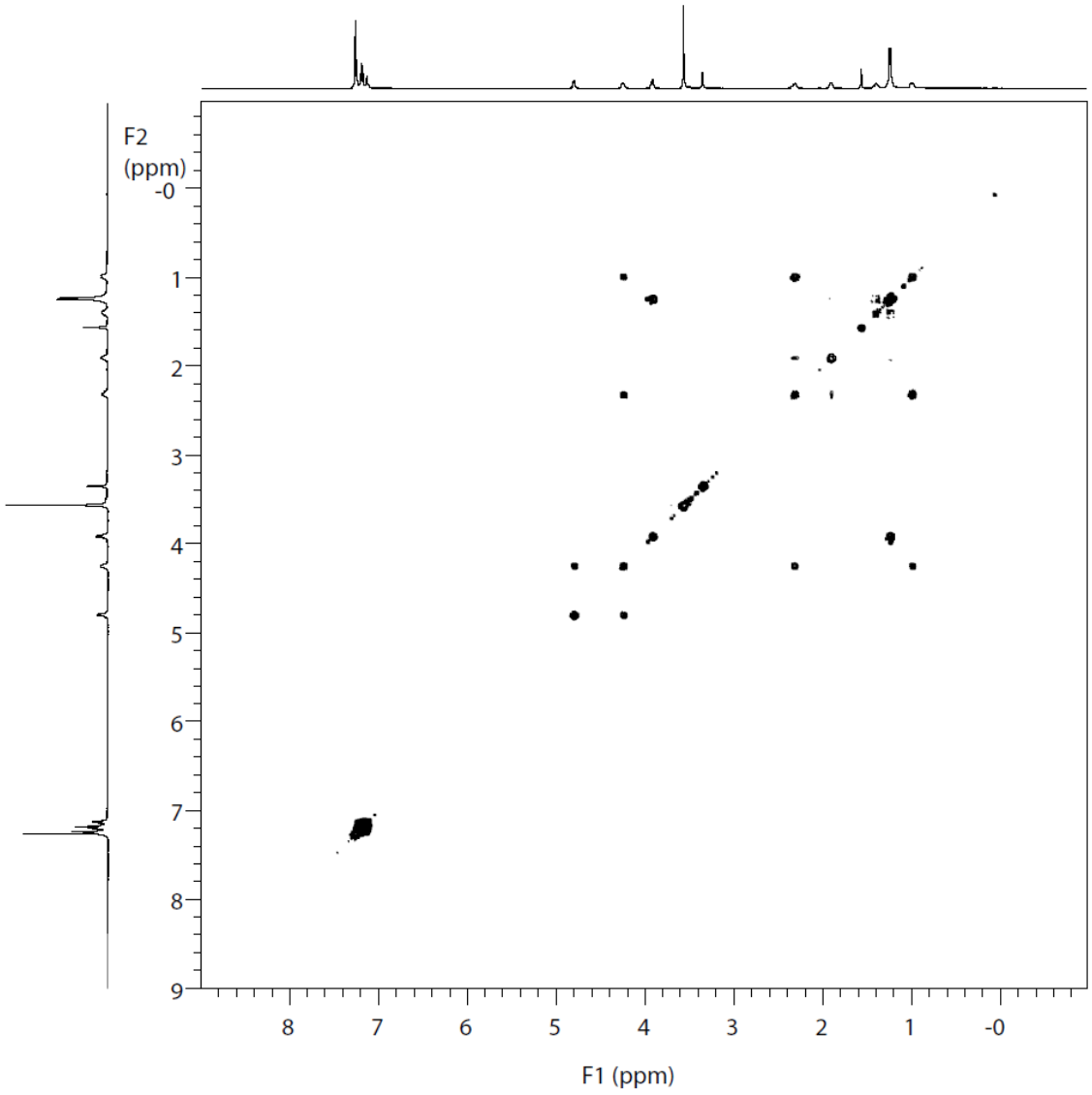

Figure S14. ^{1}H-^{1}H COSY spectrum of *cis*,*syndiotactic*-poly[H-(*S*)-PhEtNNBE] (in $CDCl_3$, 500 MHz)

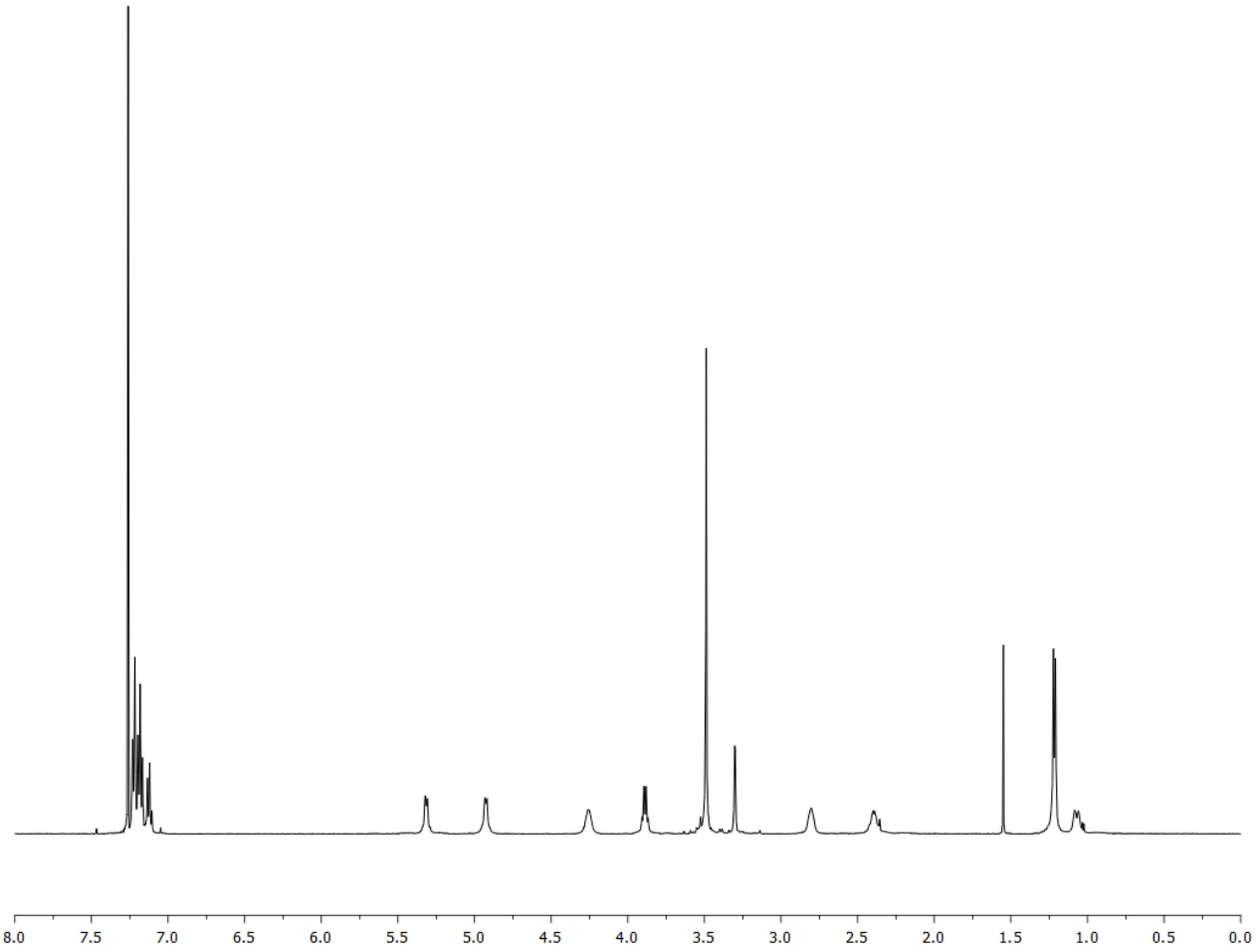

Figure S15. ^{1}H NMR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **1a** (in $CDCl_3$, 500 MHz)

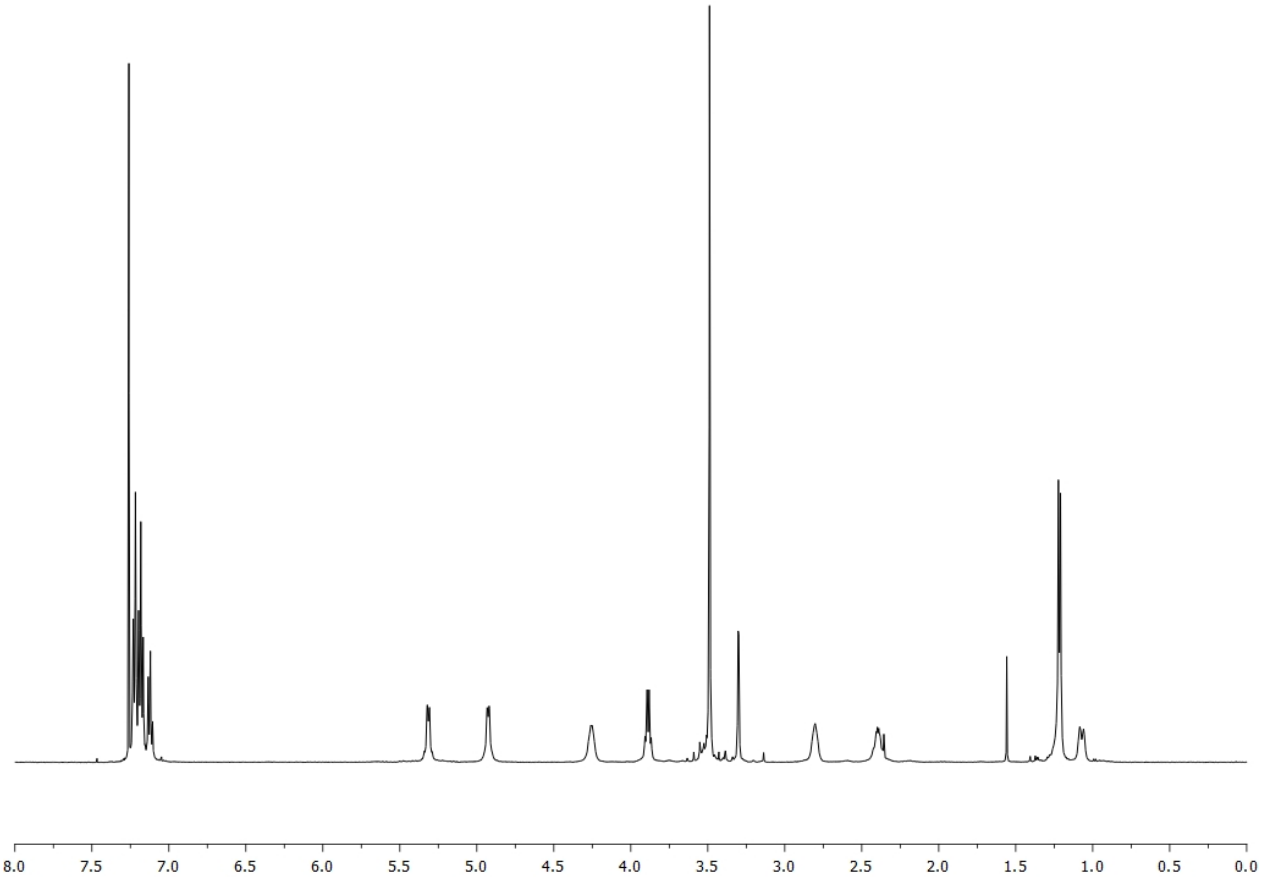

Figure S16. ^{1}H NMR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **1b** (in $CDCl_3$, 500 MHz)

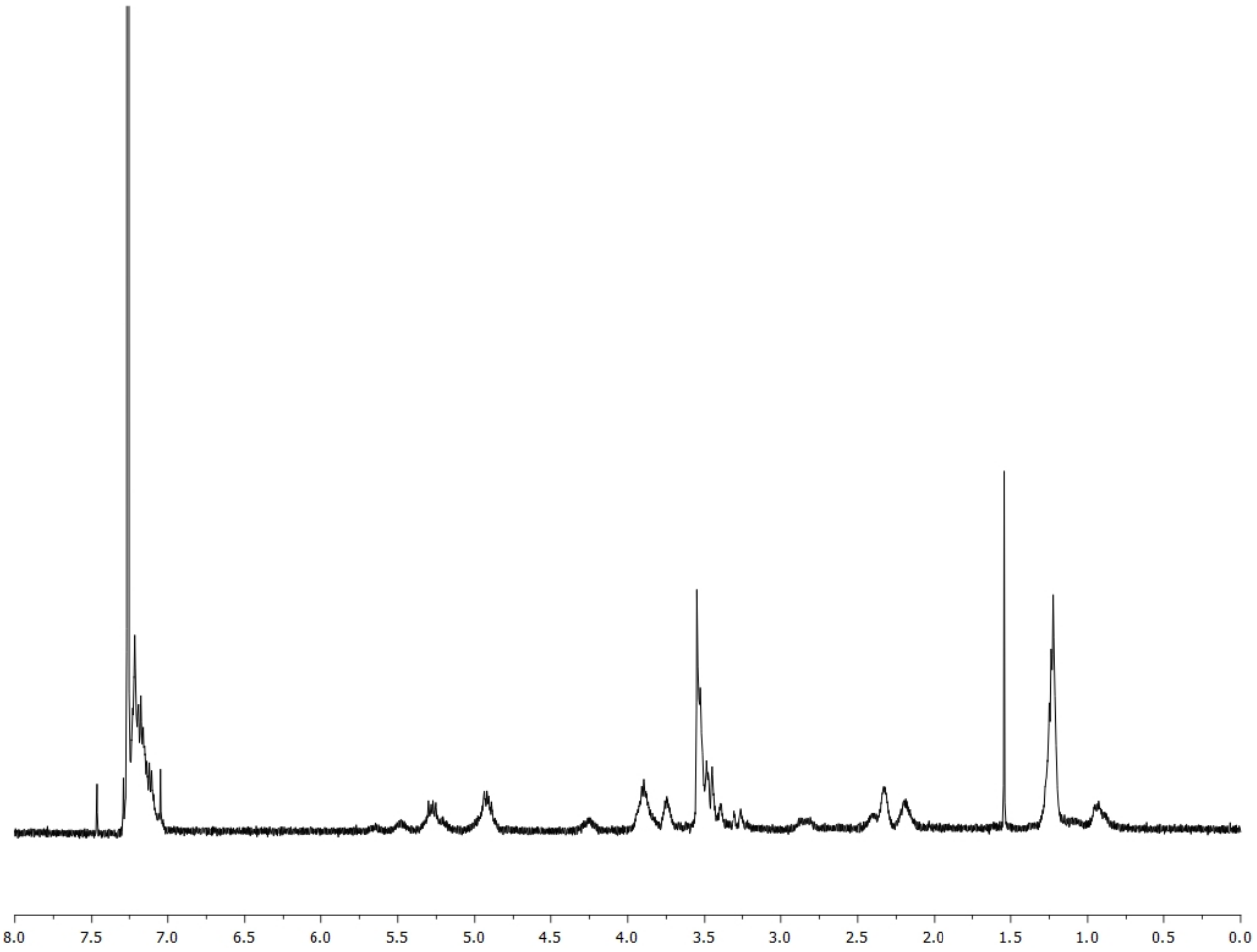

Figure S17. ^{1}H NMR spectrum of atactic-poly[(*S*)-PhEtNNBE] made with **1c** (in $CDCl_3$, 500 MHz)

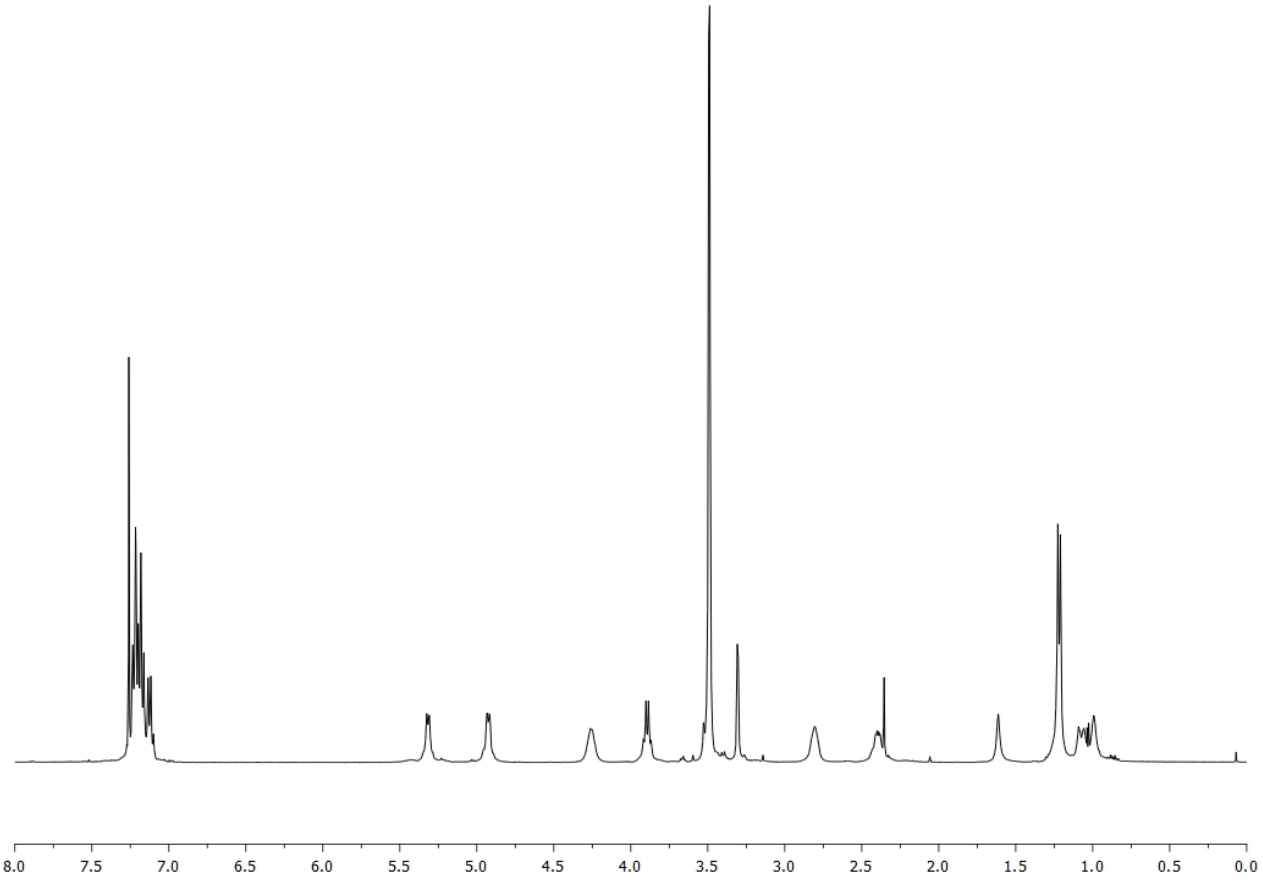

Figure S18. ^{1}H NMR spectrum of *cis,syndiotactic*-poly[(*S*)-PhEtNNBE] made with **1d** (in $CDCl_3$, 400 MHz)

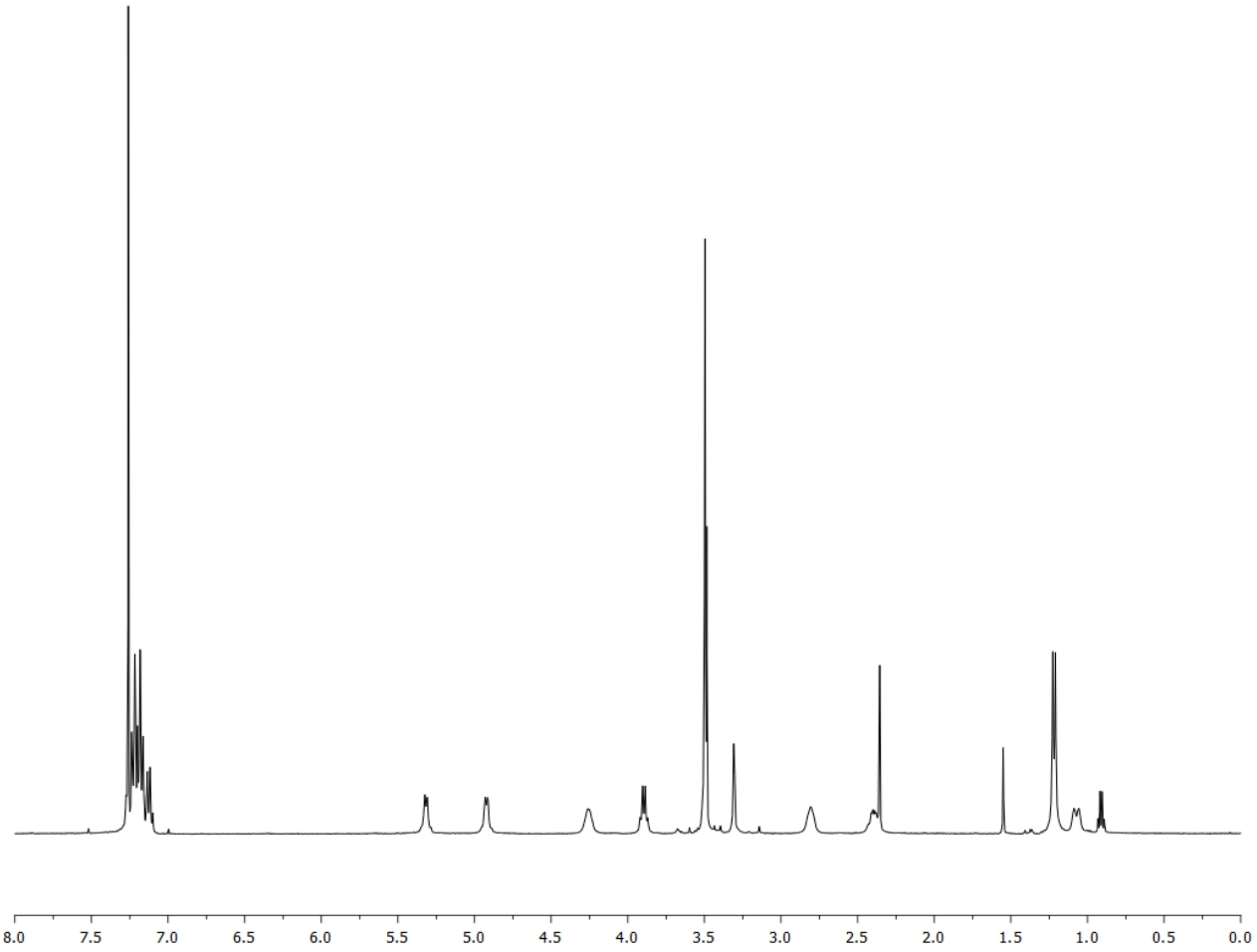

Figure S19. ^{1}H NMR spectrum of *cis*,*syndiotactic*-poly[(*S*)-PhEtNNBE] made with **3a** (in $CDCl_3$, 400 MHz)

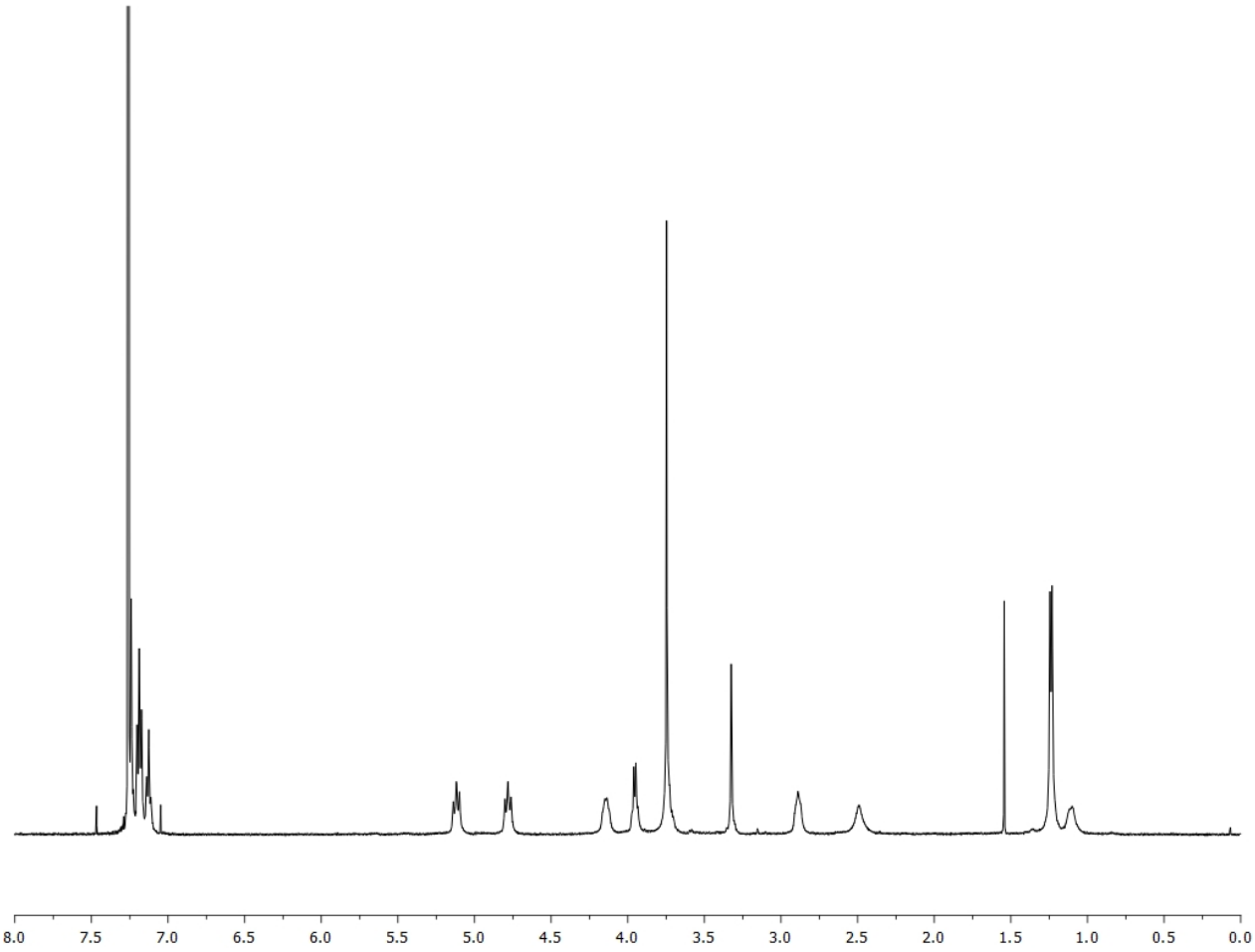

Figure S20. ^{1}H NMR spectrum of *cis*,*isotactic*-poly[(*S*)-PhEtNNBE] made with **2a** (in $CDCl_3$, 500 MHz)

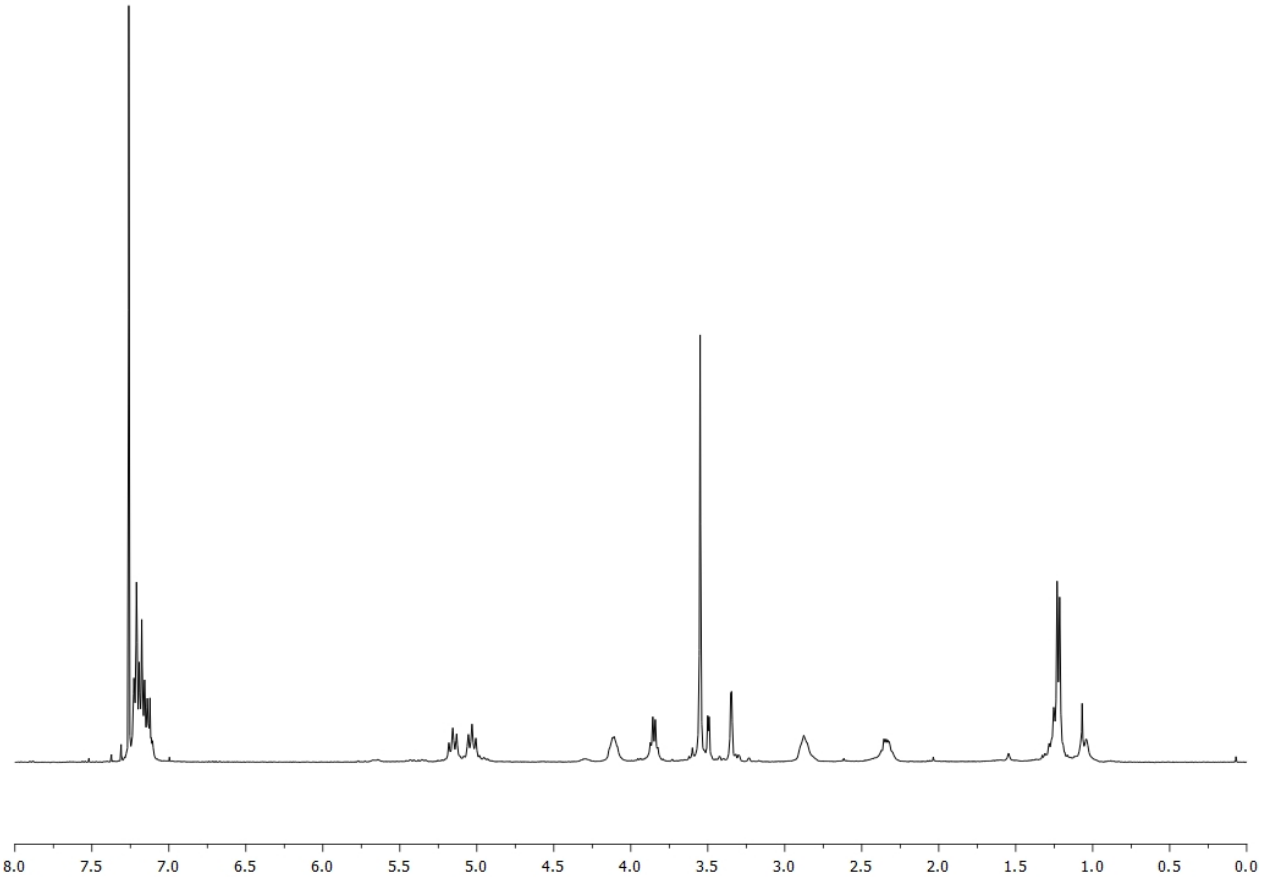

Figure S21. ^{1}H NMR spectrum of *cis,syndiotactic,alt*-poly[(rac)-PhEtNNBE] made with **1a** at -78 °C (in $CDCl_3$, 400 MHz)

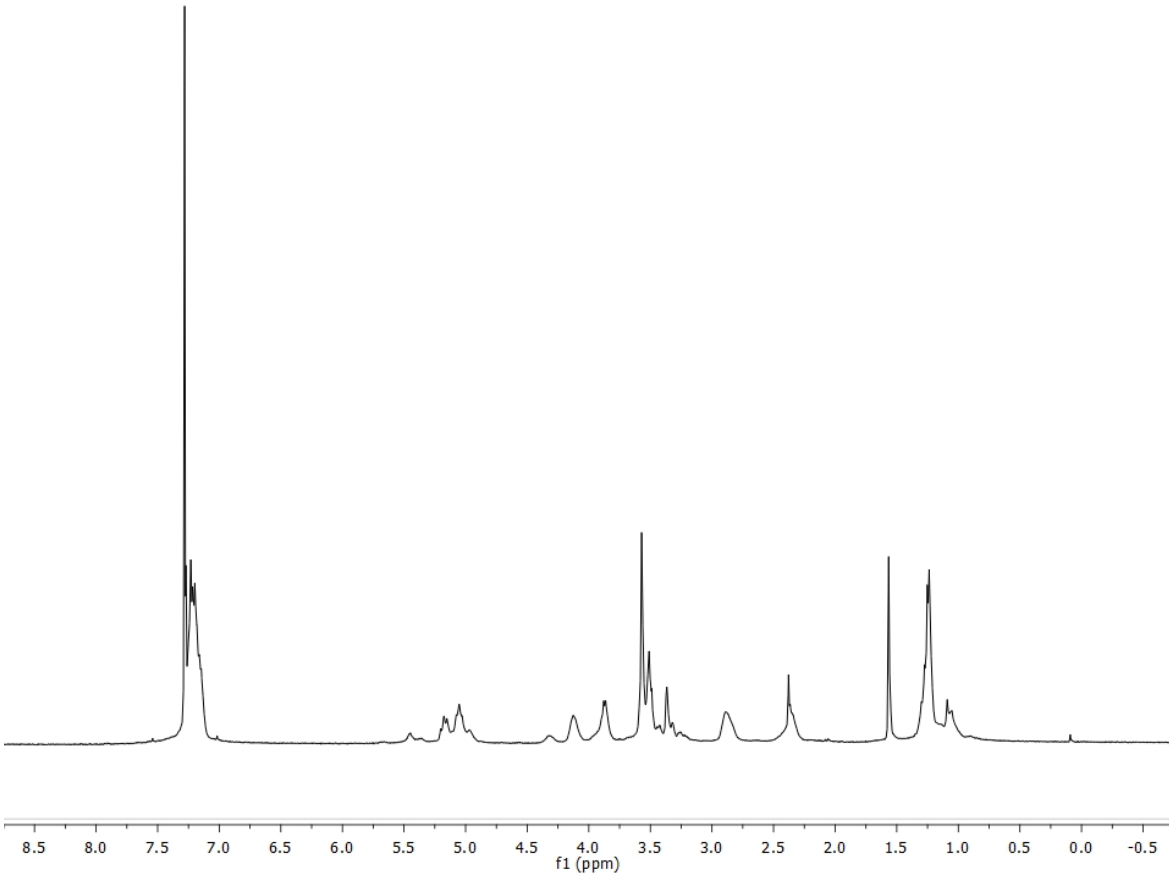

Figure S22. ^{1}H NMR spectrum of *cis,syndiotactic,alt*-poly[(rac)-PhEtNNBE] made with **1d** (in $CDCl_3$, 400 MHz)

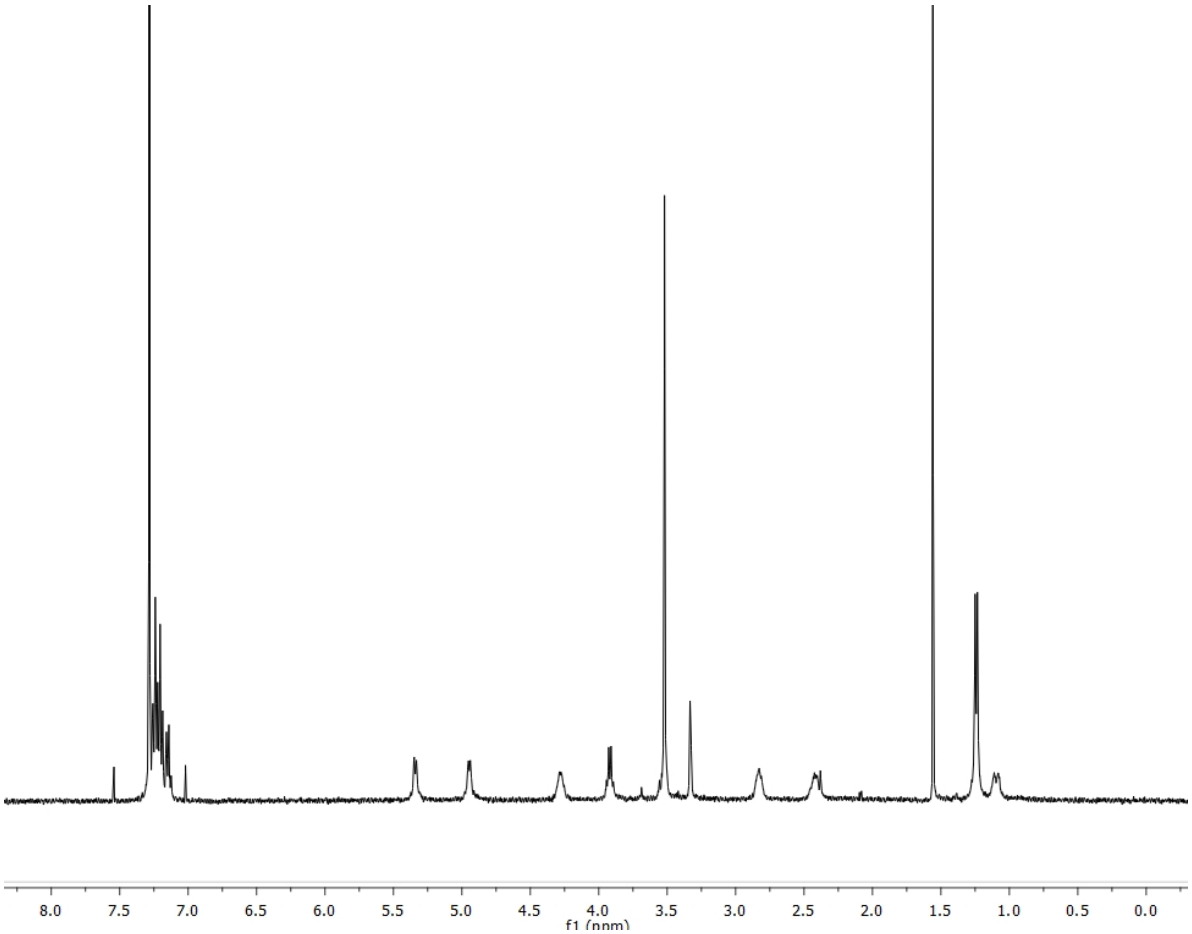

Figure S23. ^{1}H NMR spectrum of *cis,syndiotactic*-poly[(*R*)-PhEtNNBE] made with **3b** (in $CDCl_3$, 400 MHz)

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