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Stereoselective synthesis of functionalized hexene oligomers catalyzed by chiral *ansa*-zirconocene in the presence of Al- and B-containing activators

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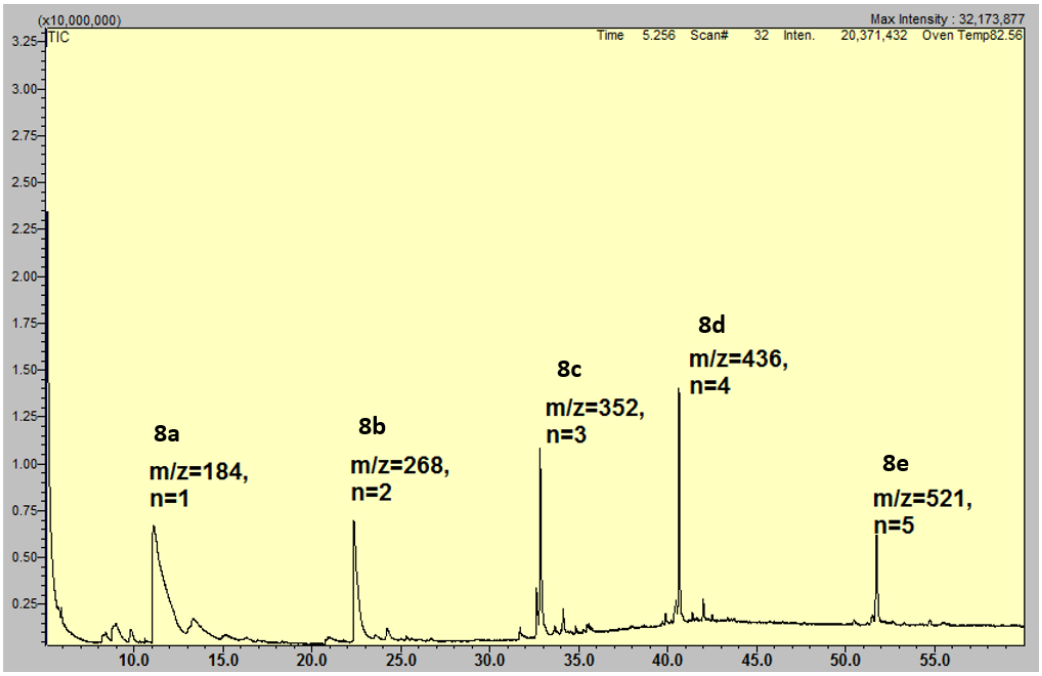
General procedure

All operations for organometallic compounds were performed under argon according to Schlenk technique. The solvents (toluene) were distilled from $Bu^{i}_{2}AlH$ immediately prior to use; THF and diethyl ether were dried and distilled from sodium/benzophenone before use. Dichloromethane was dried over P_2O_5. Commercially available 97% $AlMe_3$ (Aldrich), MMAO-12 (7 wt% Al in toluene, Sigma-Aldrich) and $[Ph_3C][B(C_6F_5)_4]$ (97%, Alfa Aesar) were involved into the reactions. Dichloro[(*R,R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium(IV) (Sigma-Aldrich) and 1-hexene (97%, Acros) were used.

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE-400 spectrometer (400.13 MHz (^{1}H), 100.62 MHz (^{13}C), and 376.44 MHz (^{19}F)). As the solvent and the internal standard, $CDCl_3$ and C_6D_6 were employed. 1D and 2D NMR spectra (COSY HH, HSQC, HMBC) were recorded using standard Bruker pulse sequences. The deuterated products were analyzed using a gas chromatograph mass spectrometer GCMS-QP2010 Ultra (Shimadzu) equipped with the GC-2010 Plus chromatograph, TD-20 thermal desorber, and an ultrafast quadrupole mass-selective detector. The optical rotation $[a]^{D}_{20}$ was measured on a Perkin Elmer-341 polarimeter.

Reaction of 1-alkenes with $AlMe_3$ in the presence of dichloro[(*R,R*)-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]zirconium(IV) and activators (MMAO-12, $[Ph_3C][B(C_6F_5)_4]$) .

A 25 ml glass reactor mounted on a magnetic stirrer and filled with argon was charged with catalyst (***p*-*R*,*p*-*R*-1** or *rac*-**1**) (5 mg, 0.0117 mmol), $C_6H_5CH_3$ (5 ml), 1-hexene (0.37-0.73 ml, 2.93-5.85 mmol), $AlMe_3$ (0.23ml, 2.34 mmol) and MMAO-12 (0.3 ml, 0.585 mmol) or $[Ph_3C][B(C_6F_5)_4]$ (6.5 mg, 0.007 mmol). The reaction was carried out at 20°C with continuous stirring for 72 hours. After completion of the reaction, a part of the reaction mixture was quenched with 10% DCl at 0°C. The products were extracted with benzene and filtered, and the organic layer was dried with Na_2SO_4. The composition of OAC products (**2,3a-f**) was determined by analyzing the hydrolysis and deuterolysis products (**6, 7a-f**) by GC and GC/MS.



GLC of hydrolysis products **7a-f** obtained in the reaction catalyzed by complex **1**.

The remaining reaction mixture was cooled to 0°C and oxidized by bubbling O_2 for 2 h, then kept in an oxygen atmosphere for 24 hours. The products were quenched with HCl and extracted by diethyl ether, and the organic layer was dried with Na_2SO_4, filtered, and concentrated. Functionally substituted oligomers (**5a-f**) were isolated by column chromatography on silica gel (0.060–0.200 mm, 60 A) using a hexane/diethyl ether system 7:1. Fractions were collected in flasks and dried over Na_2SO_4. Each fraction was evaporated and the resulting oily liquid was analyzed by ^{1}H and ^{13}C NMR spectroscopy.

The alcohols (**5a-f**) were involved in the reaction with (*S*)-(+)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride (*S*-MTPA-Cl) [18,19] to give diastereomeric esters **8a-f**, which were then analyzed by ^{1}H, ^{13}C, and ^{19}F NMR. Esters *rac*-**8a-f** were synthesized from racemic *rac*-**5a-f** obtained in the reaction catalyzed with *rac*-**1**

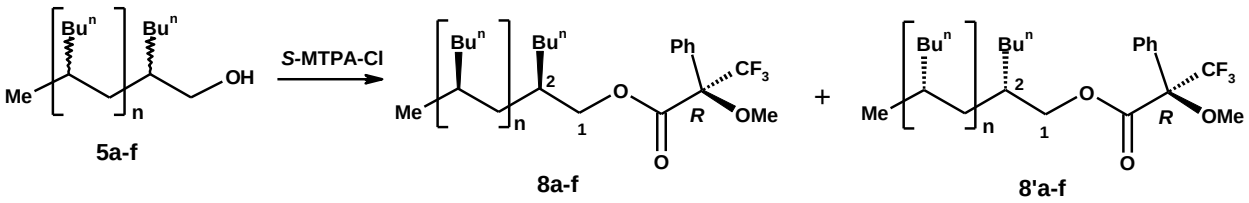


Figure S1. ^{1}H NMR of **5a** (n=1) in $CDCl_3$

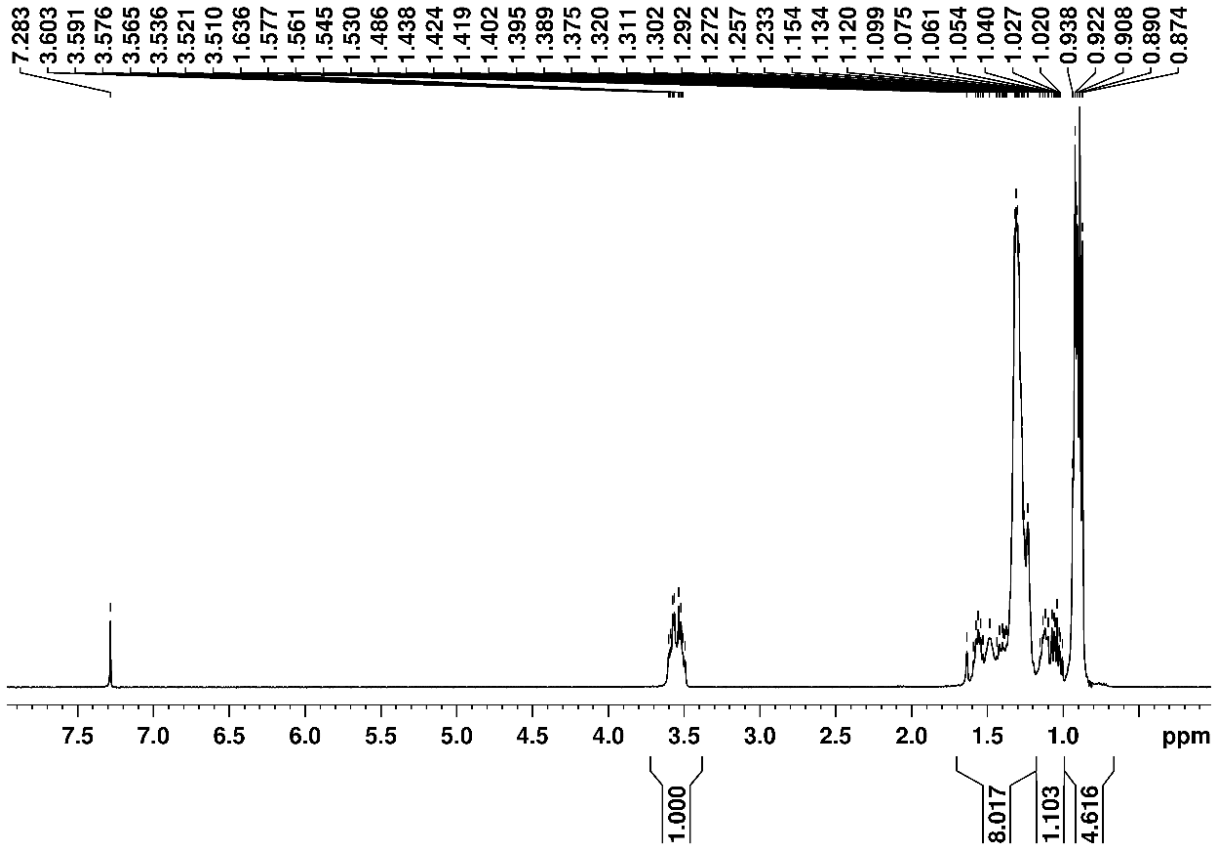


Figure S2. ^{13}C NMR of **5a** (n=1) in $CDCl_3$

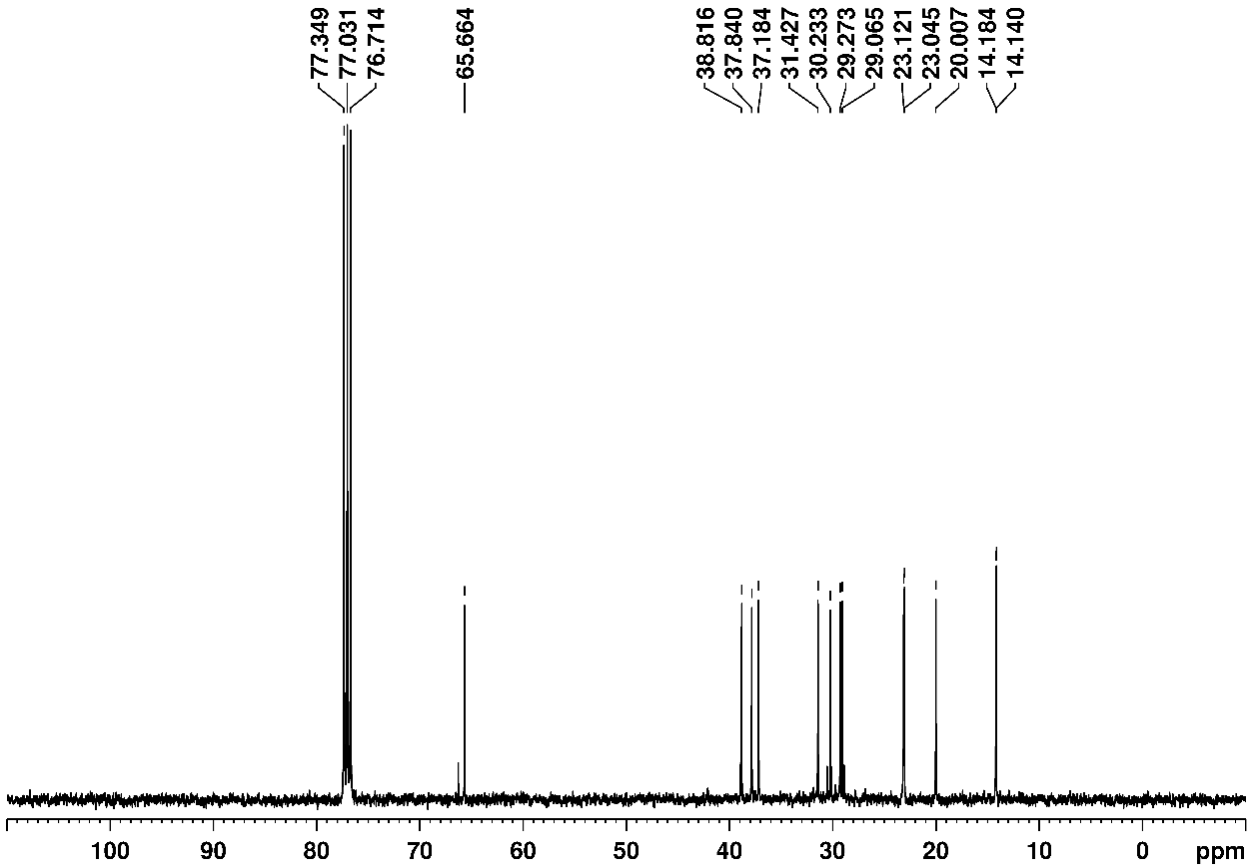


Figure S3. COSY HH of **5a** (n=1) in $CDCl_3$

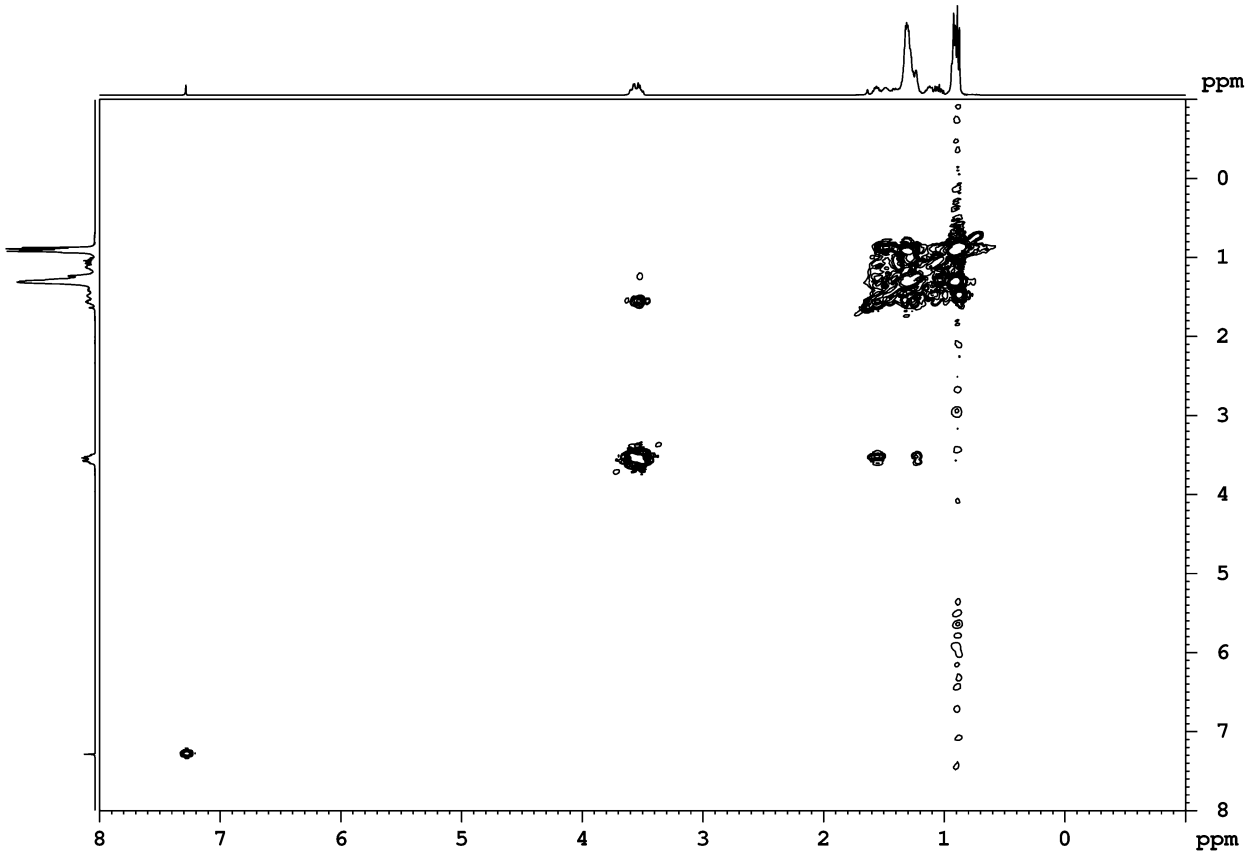


Figure S4. HSQC of **5a** (n=1) in $CDCl_3$

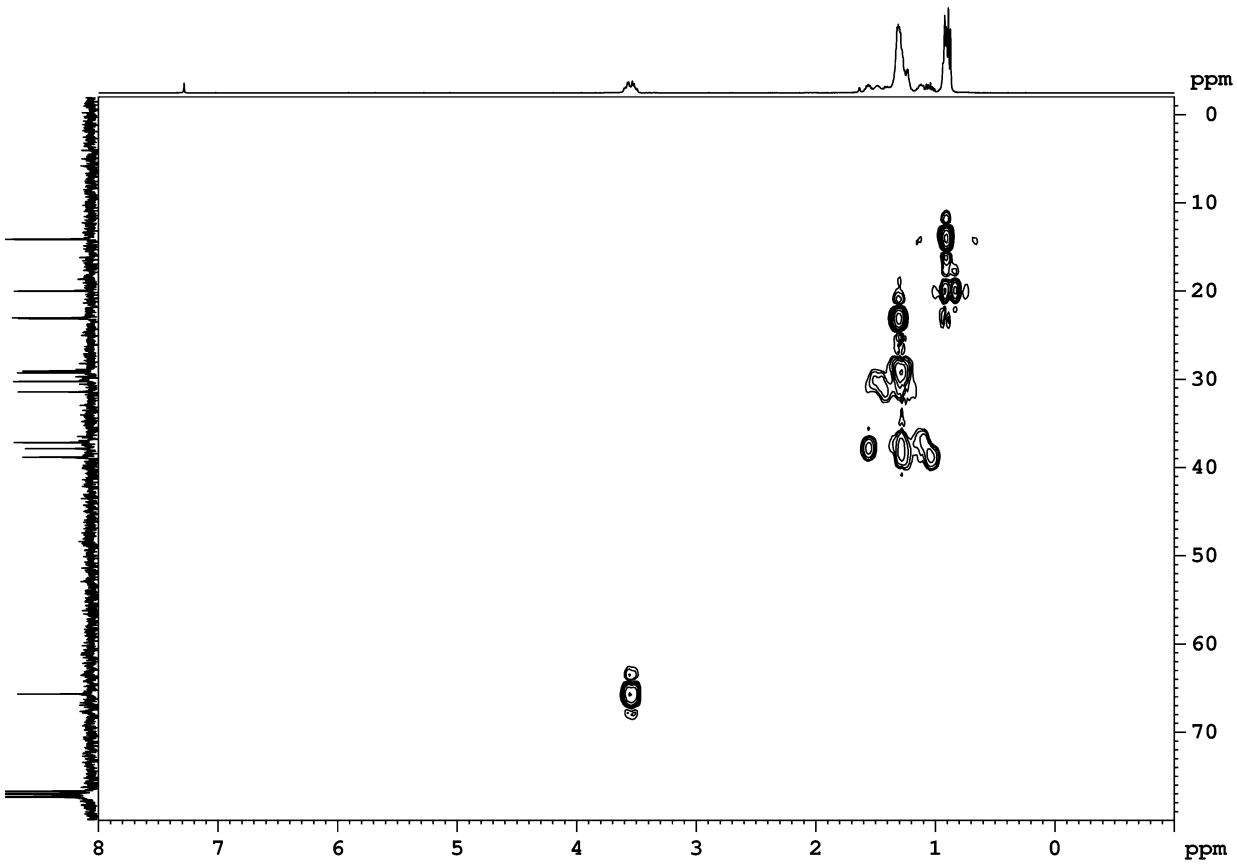


Figure S5. HMBC of **5a** (n=1) in $CDCl_3$

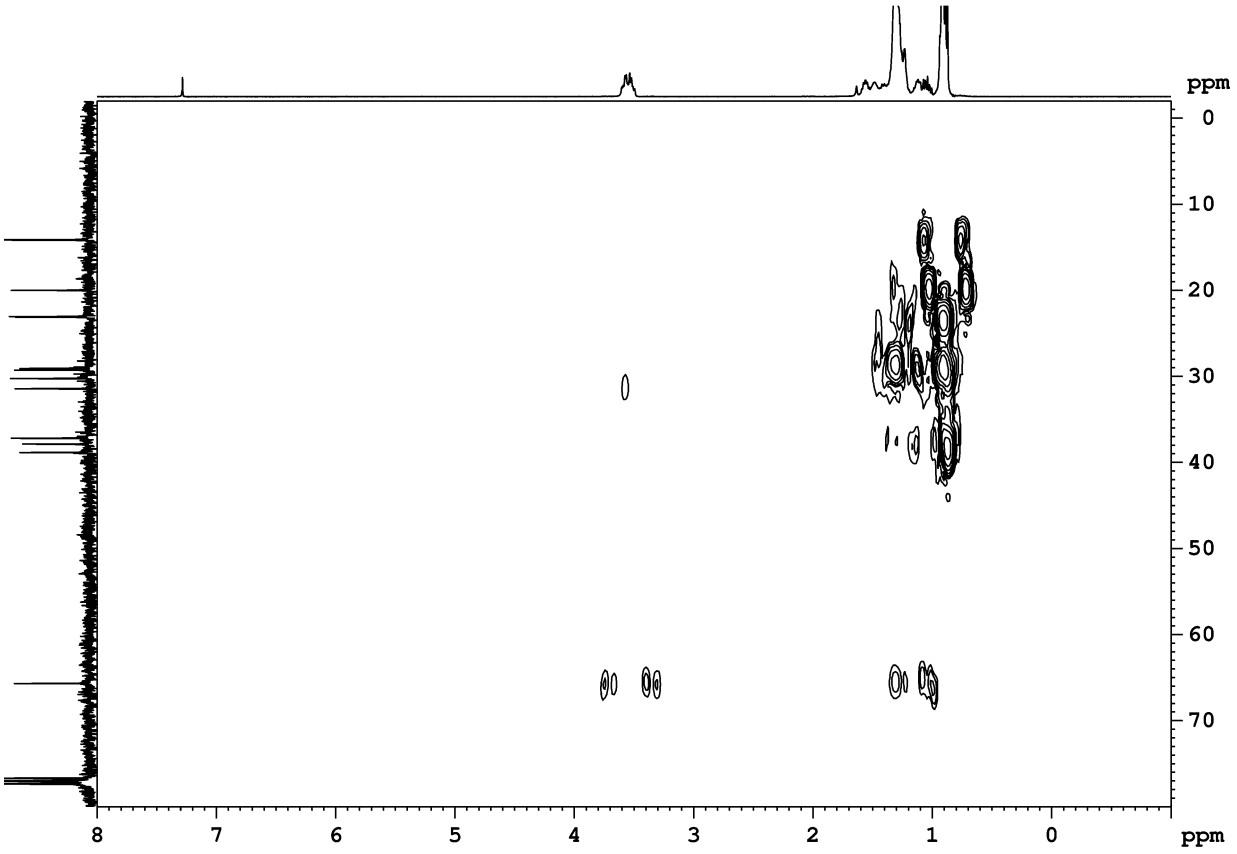


Figure S6. ^1H NMR of **5b-d** (n=2-4) in $CDCl_3$

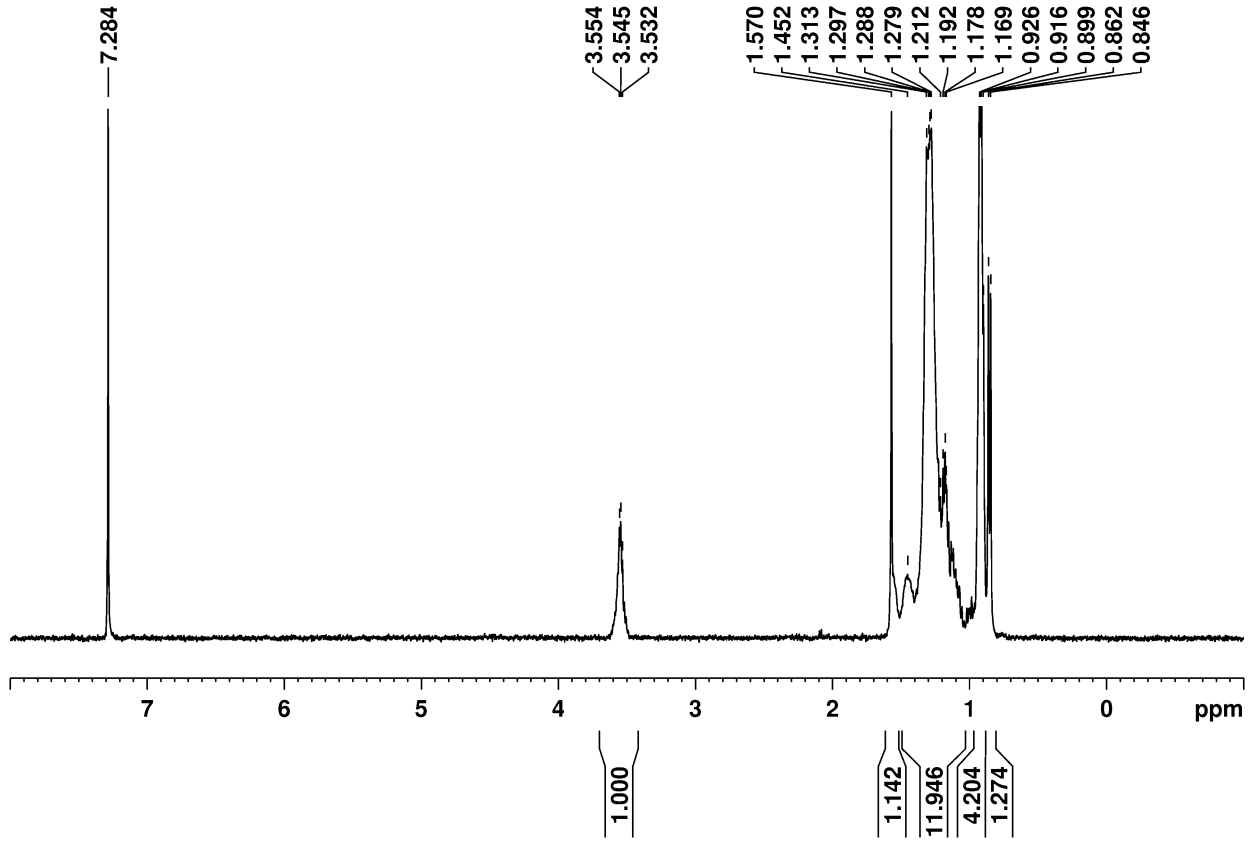


Figure S7. ^{13}C NMR of **5b-d** (n=2-4) in $CDCl_3$

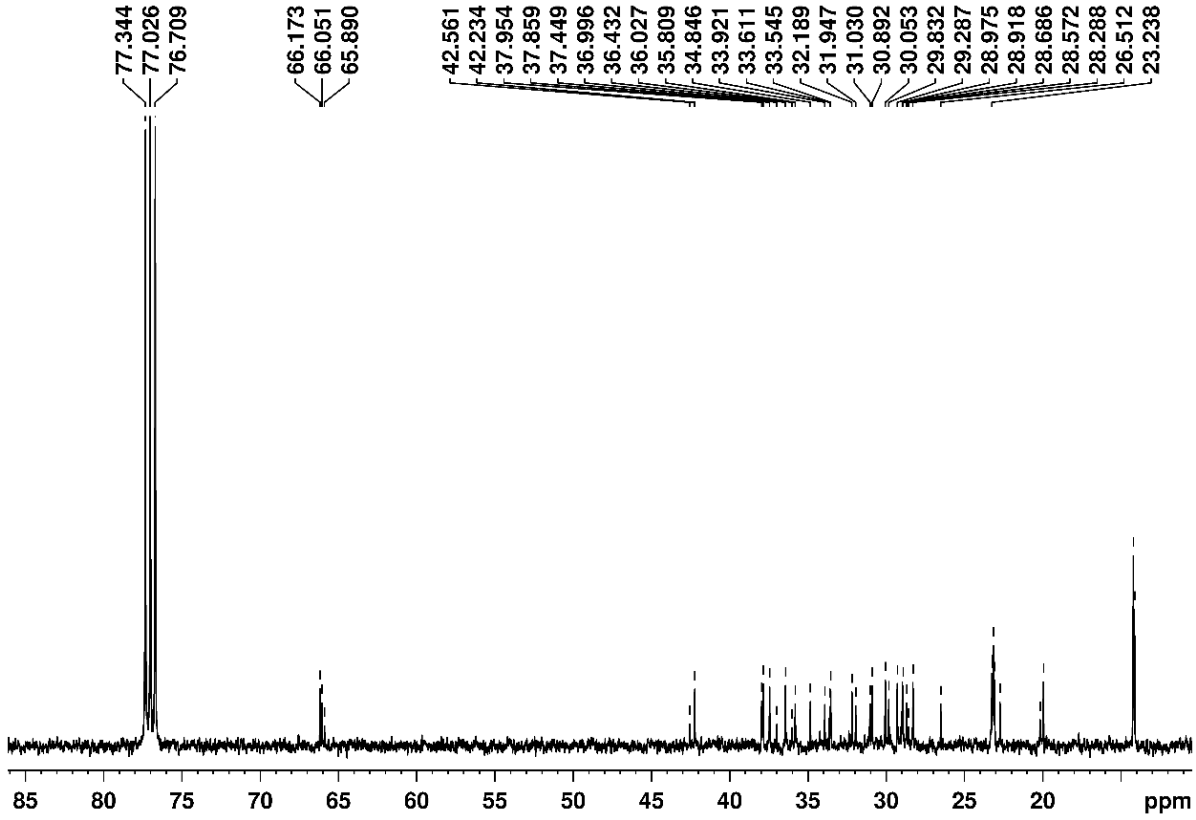


Figure S8. COSY HH of **5b-d** (n=2-4) in $CDCl_3$

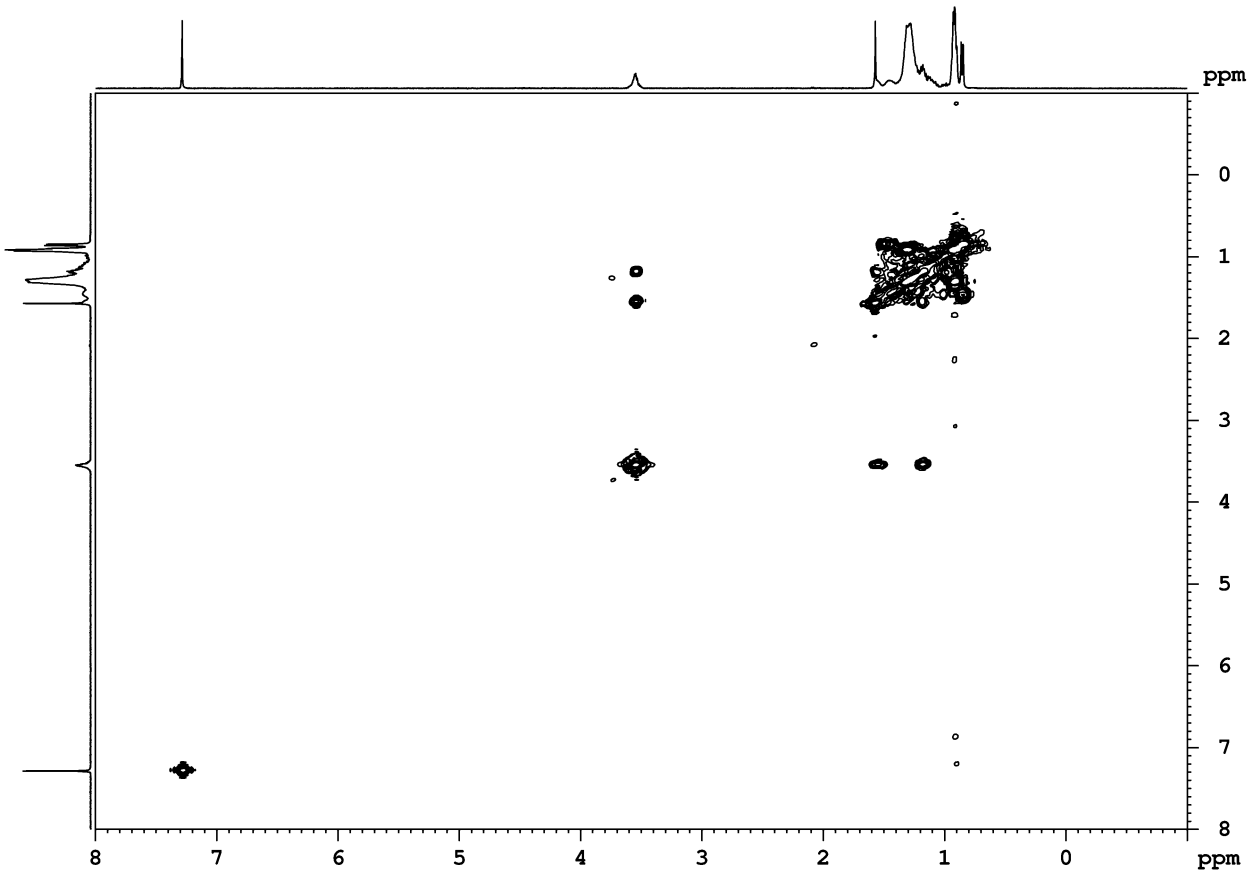


Figure S9. HSQC of **5b-d** (n=2-4) in $CDCl_3$

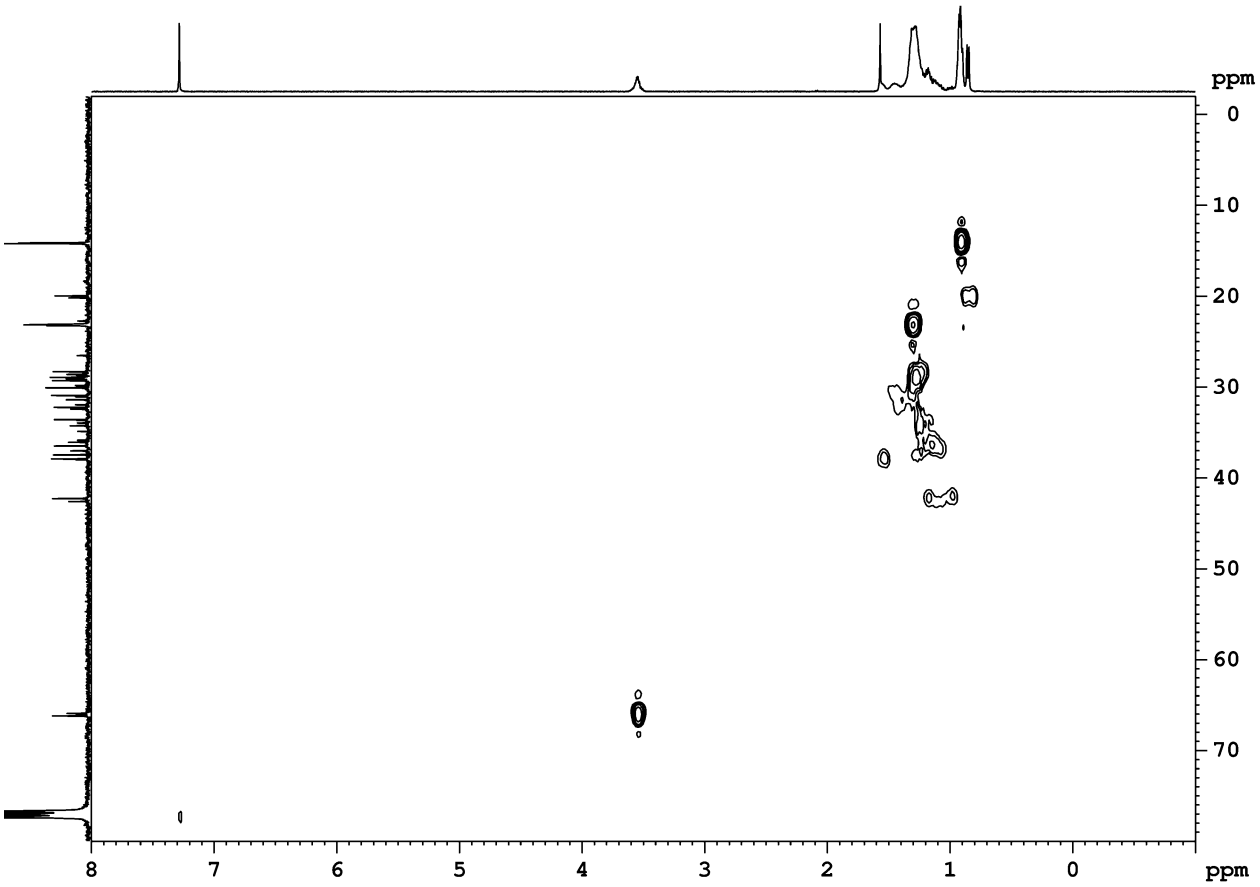


Figure S10. HMBC of **5b-d** (n=2-4) in $CDCl_3$

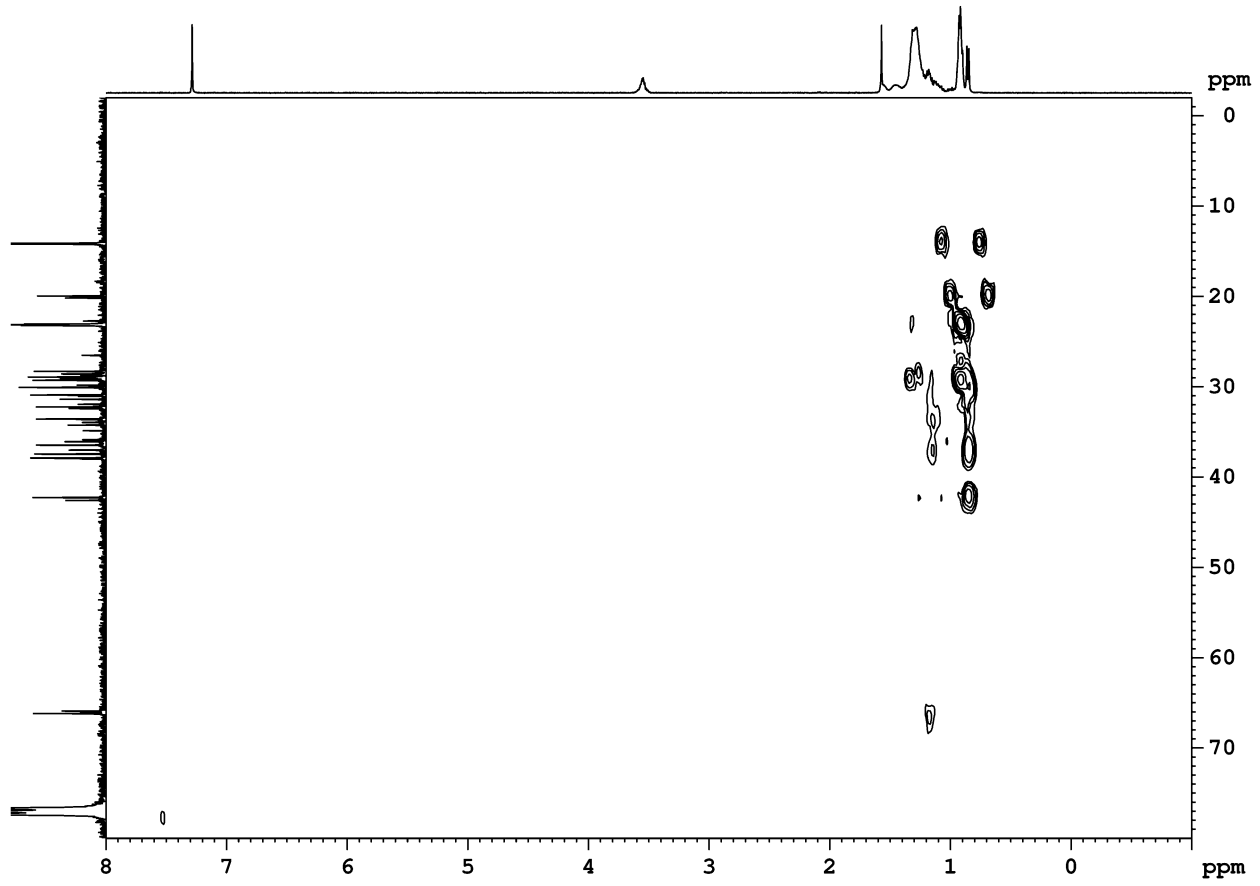


Figure S11. ^{1}H NMR of **5e,f** (n=5,6) in $CDCl_3$

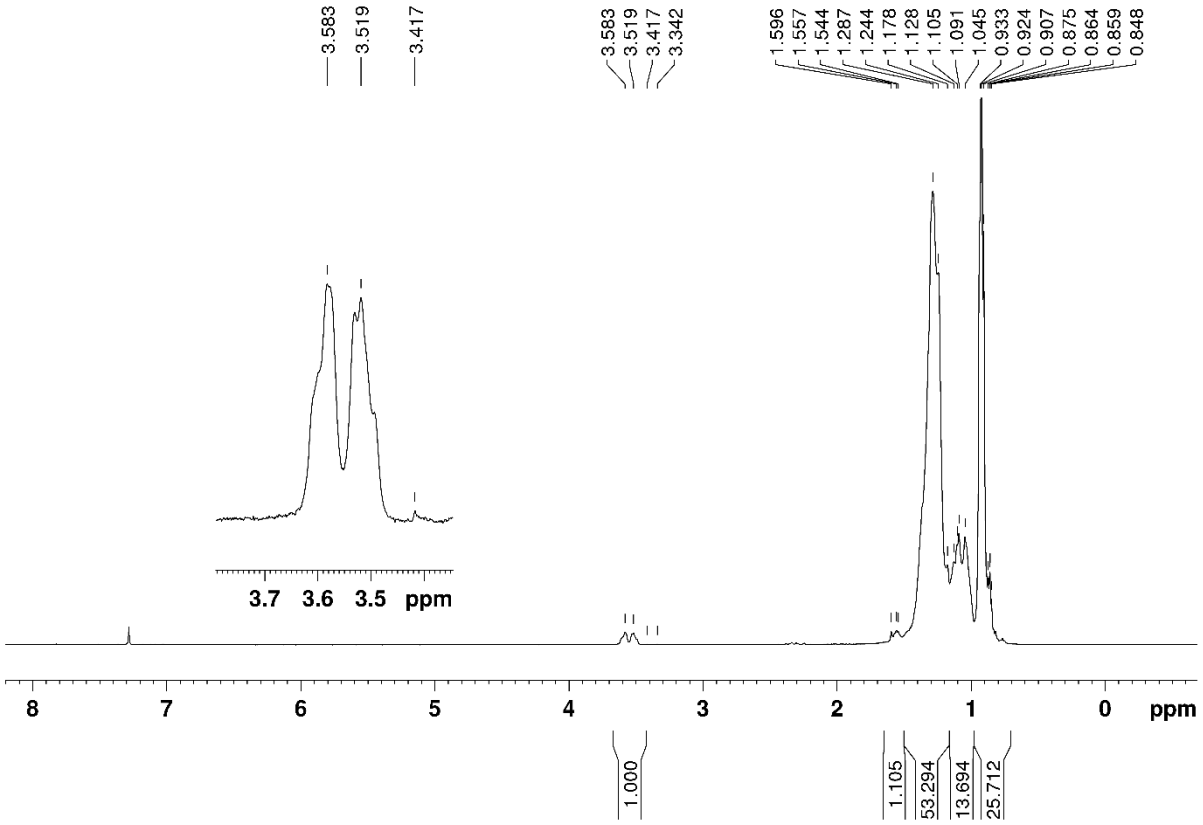


Figure S12. ^{13}C NMR of **5e,f** (n=5,6) in $CDCl_3$

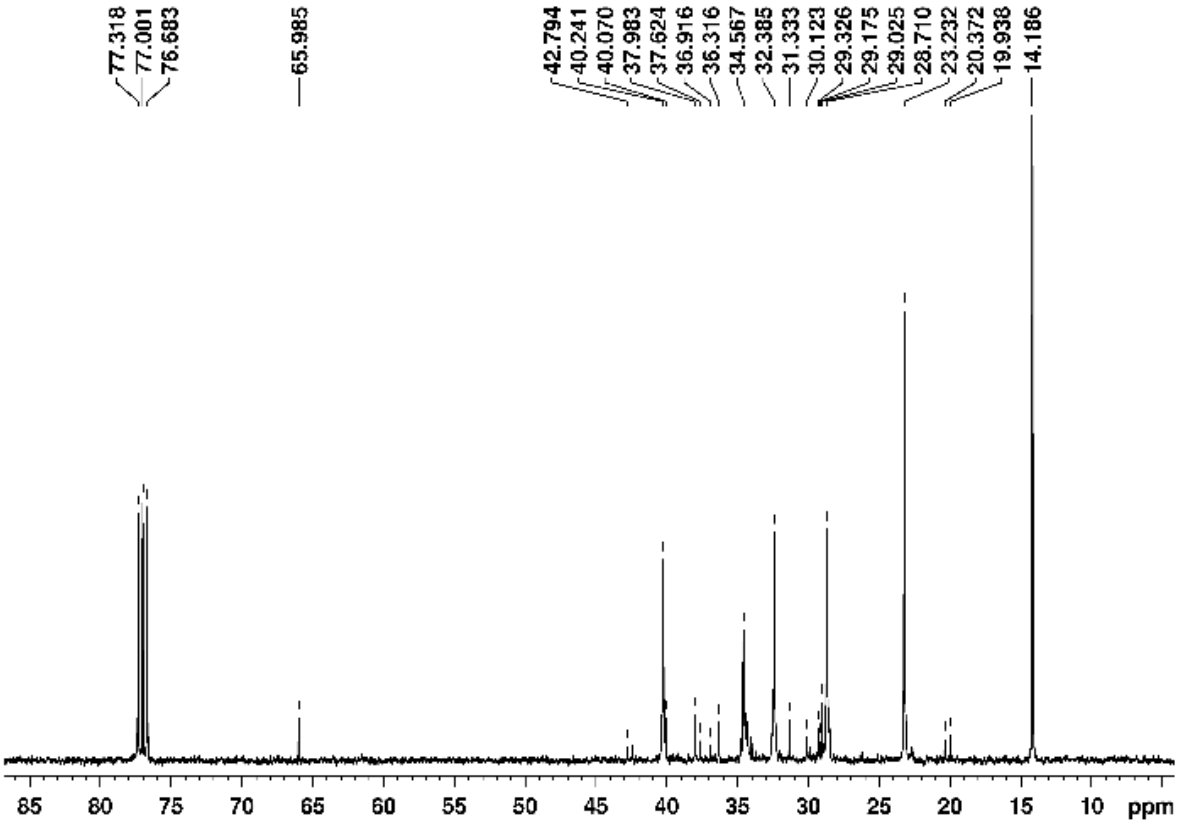


Figure S13. COSY HH of **5e,f** (n=5,6) in $CDCl_3$

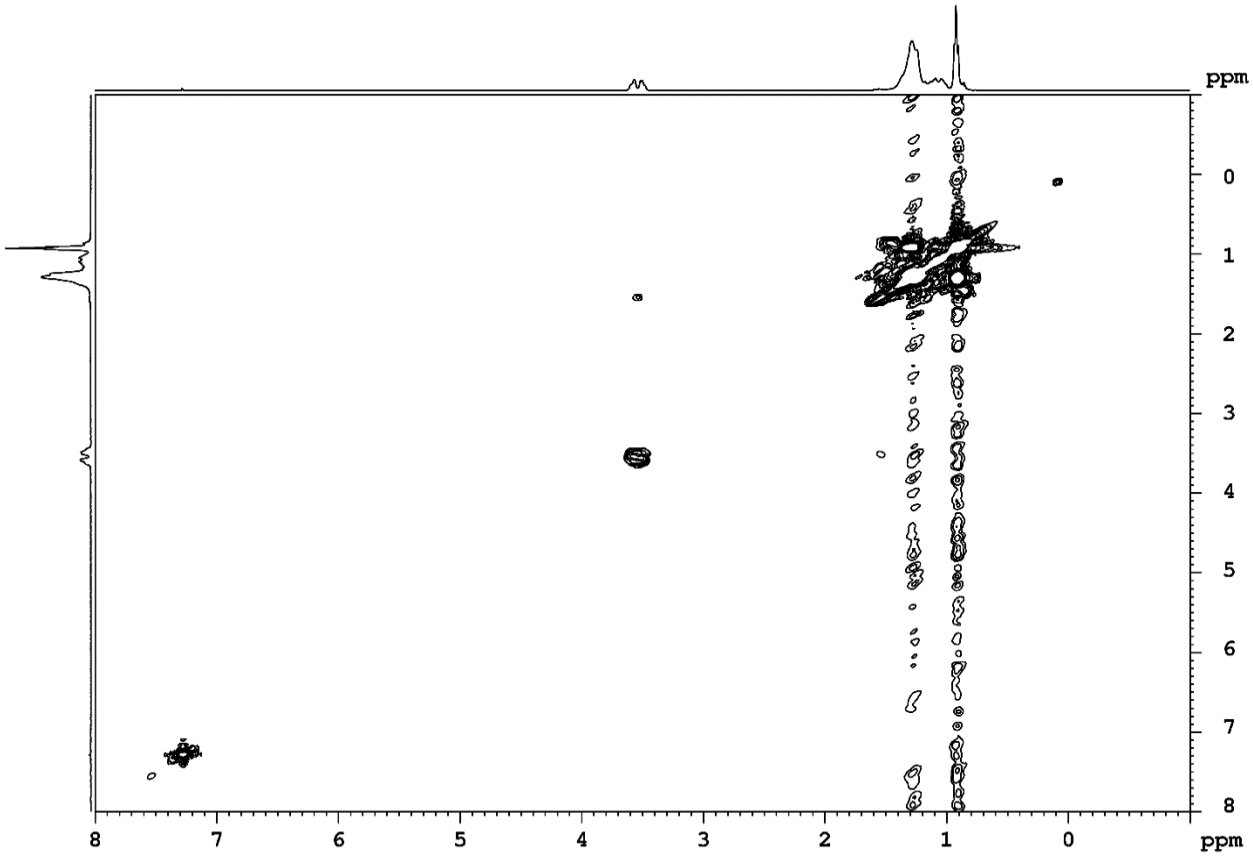


Figure S14. HSQC of **5e,f** (n=5,6) in $CDCl_3$

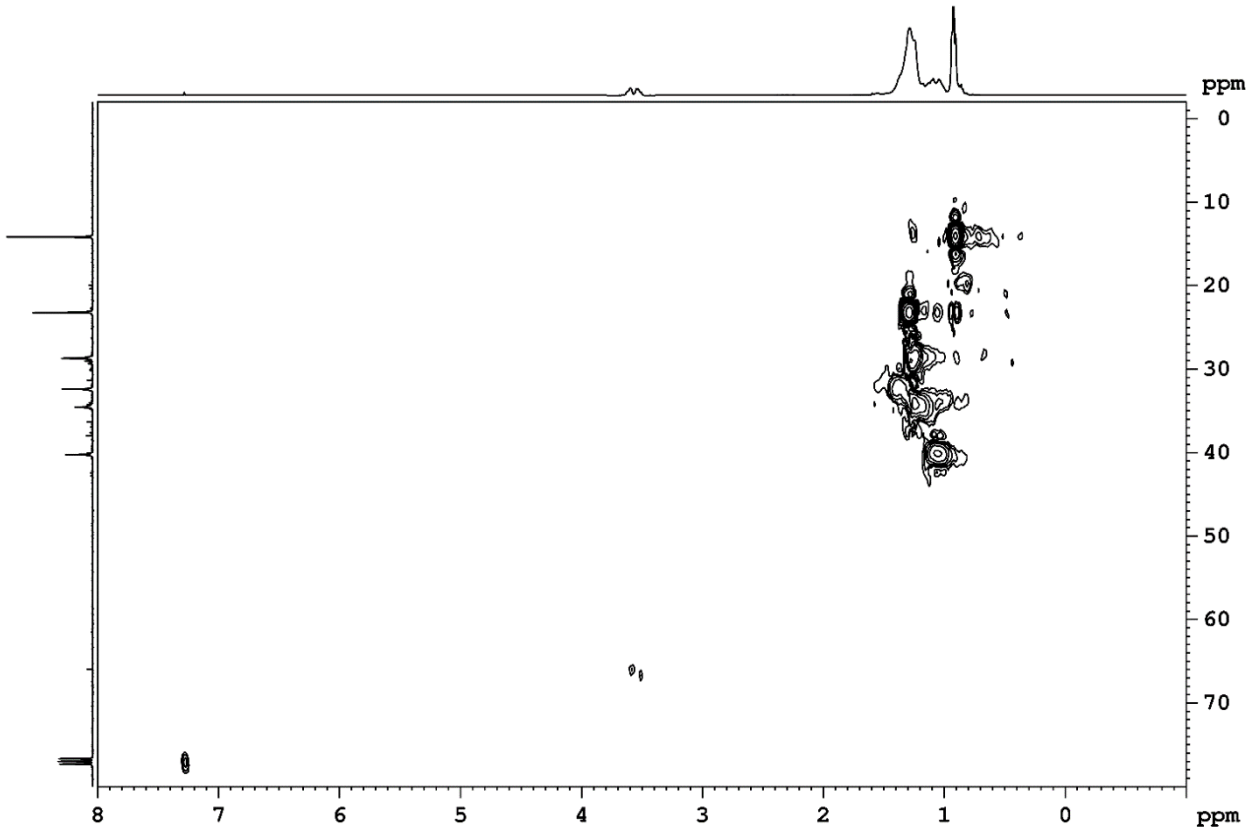


Figure S15. ^{1}H NMR of **8a** (n=1) in C_6D_6

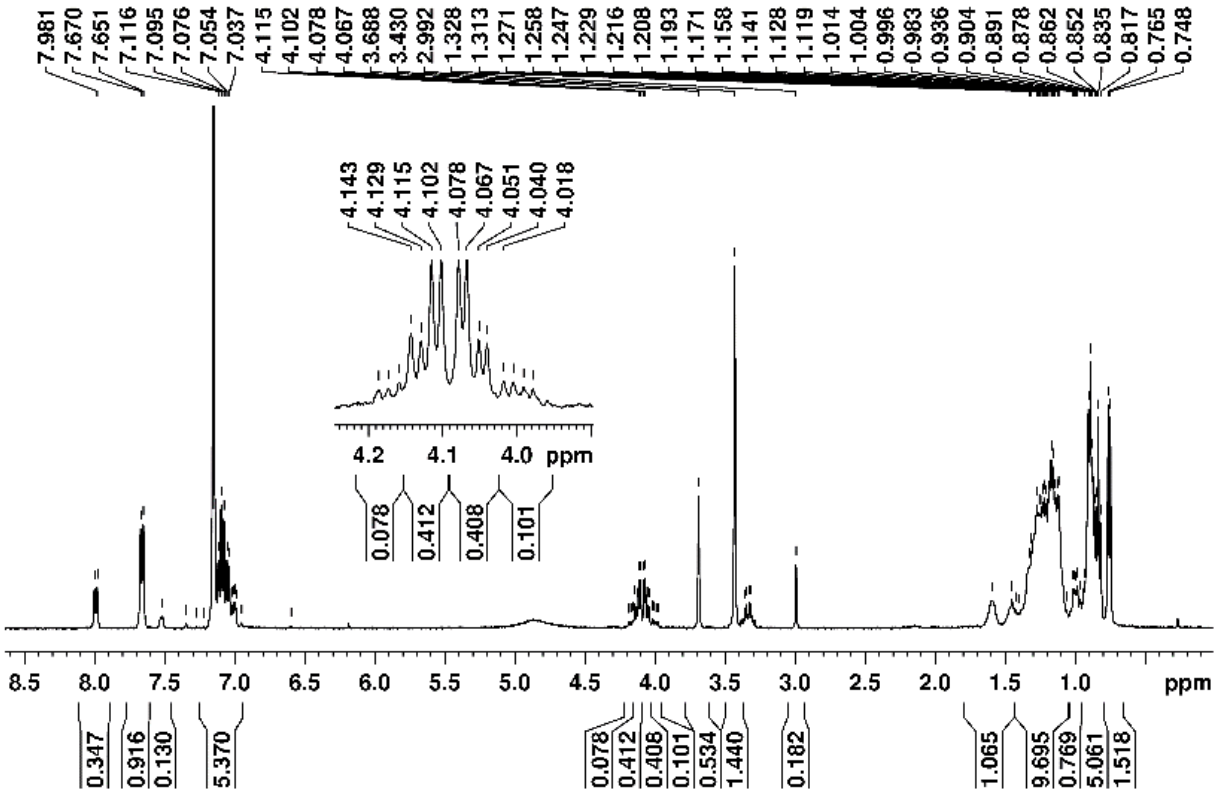


Figure S16. ^{19}F NMR of **8a** (n=1) in C_6D_6

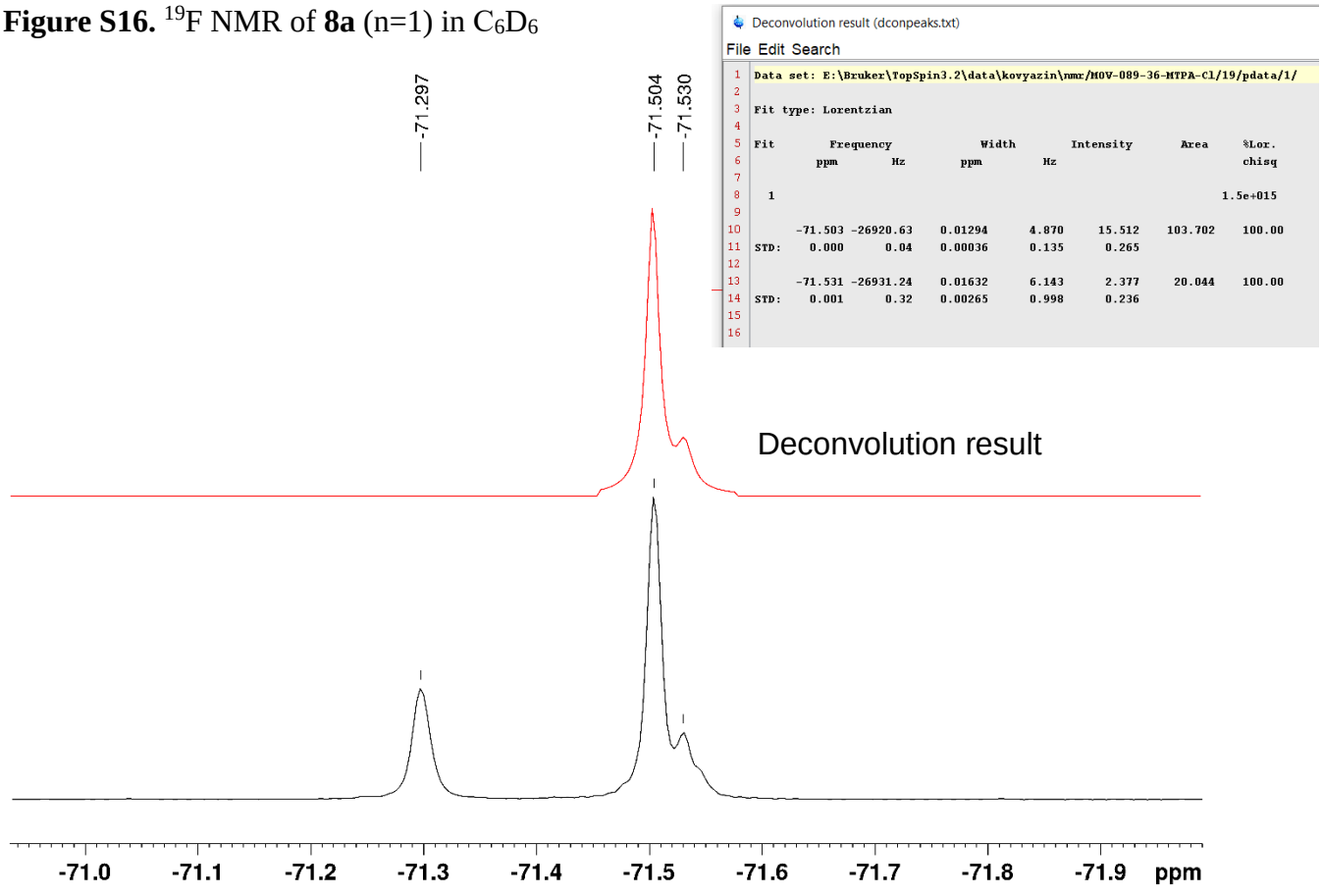


Figure S17. [1]H NMR of *rac*-**8a+8'a** (n=1) synthesized from racemic *rac*-**5a** (n=1) obtained in the reaction catalyzed with *rac*-**1**

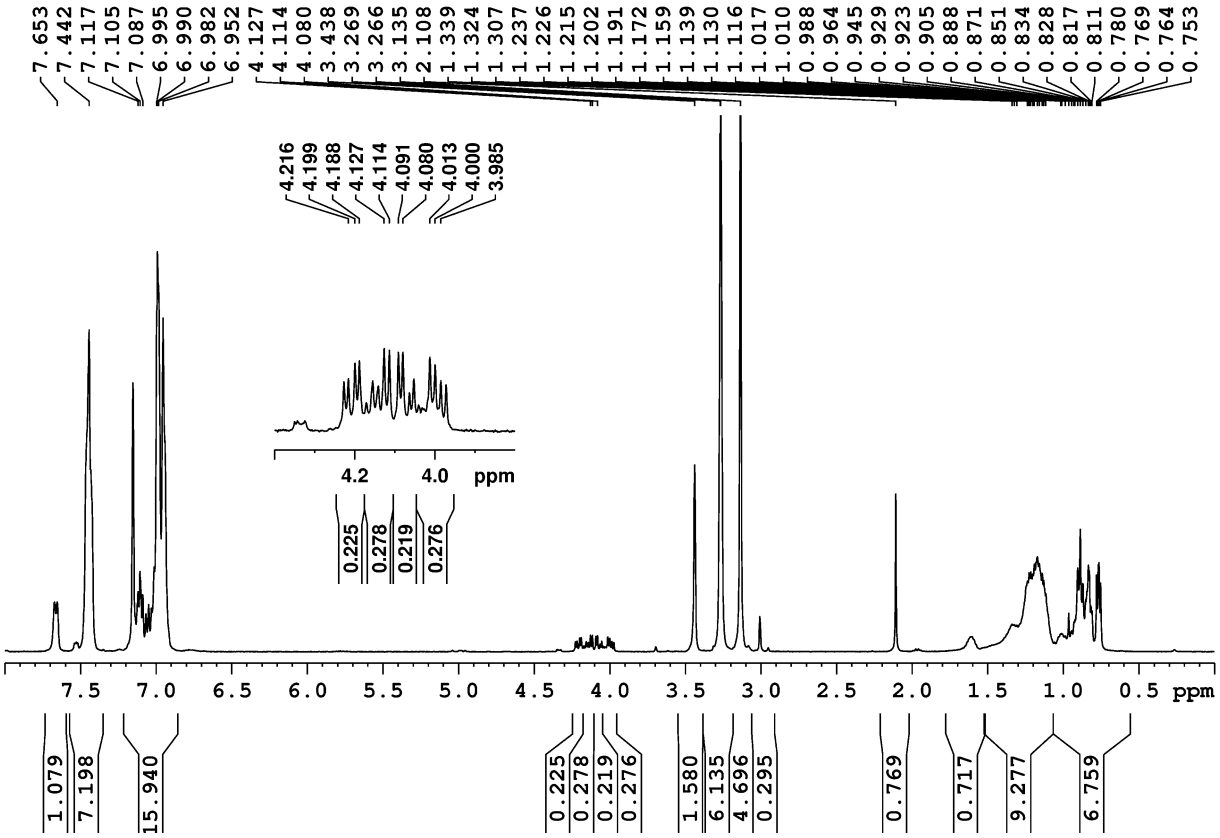


Figure S18. [19]F NMR of *rac*-**8a+8'a** (n=1) synthesized from racemic *rac*-**5a** (n=1)

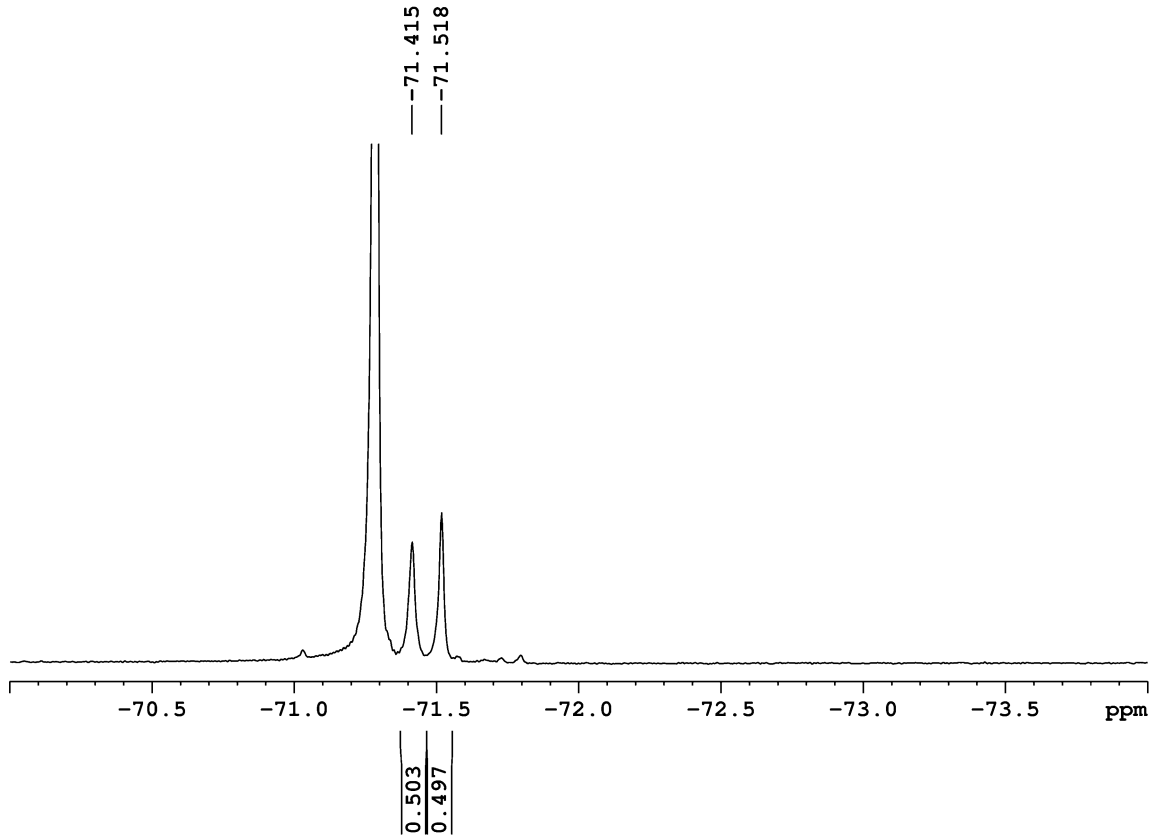


Figure S19. ^{1}H of **8b-d** (n=2-4) in C_6D_6

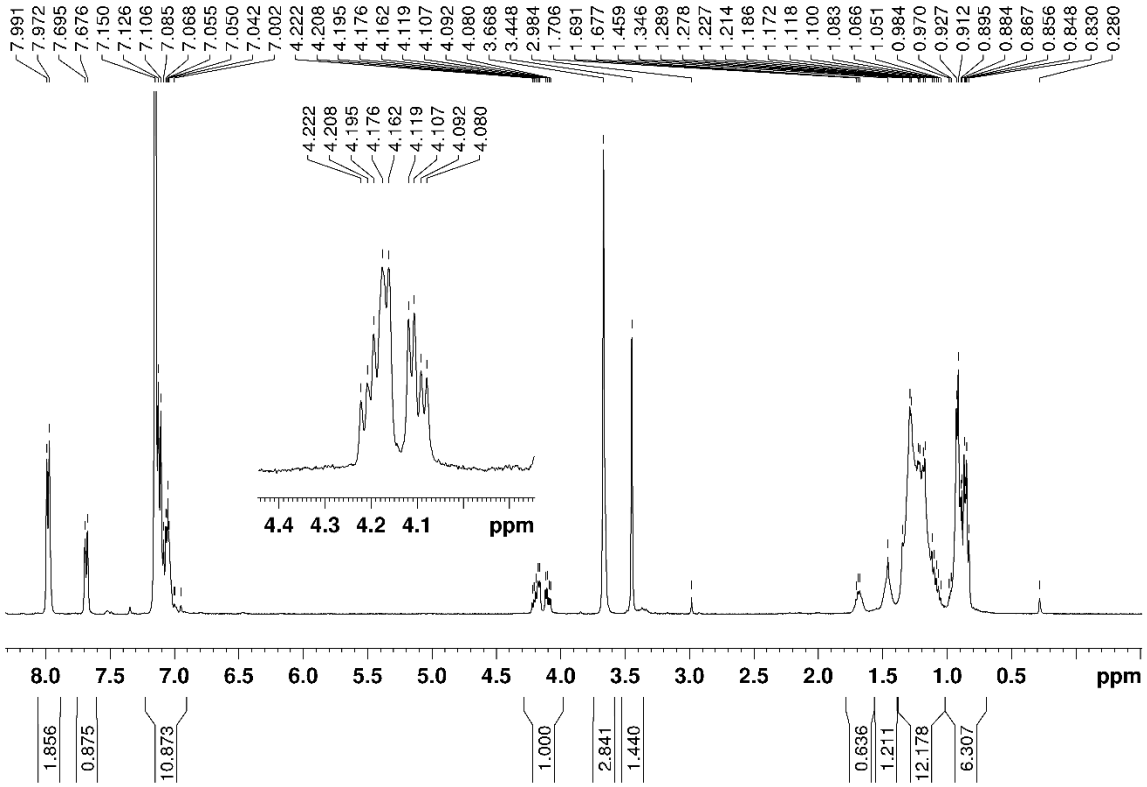


Figure S20. ^{19}F NMR of **8b-d** (n=2-4) in C_6D_6

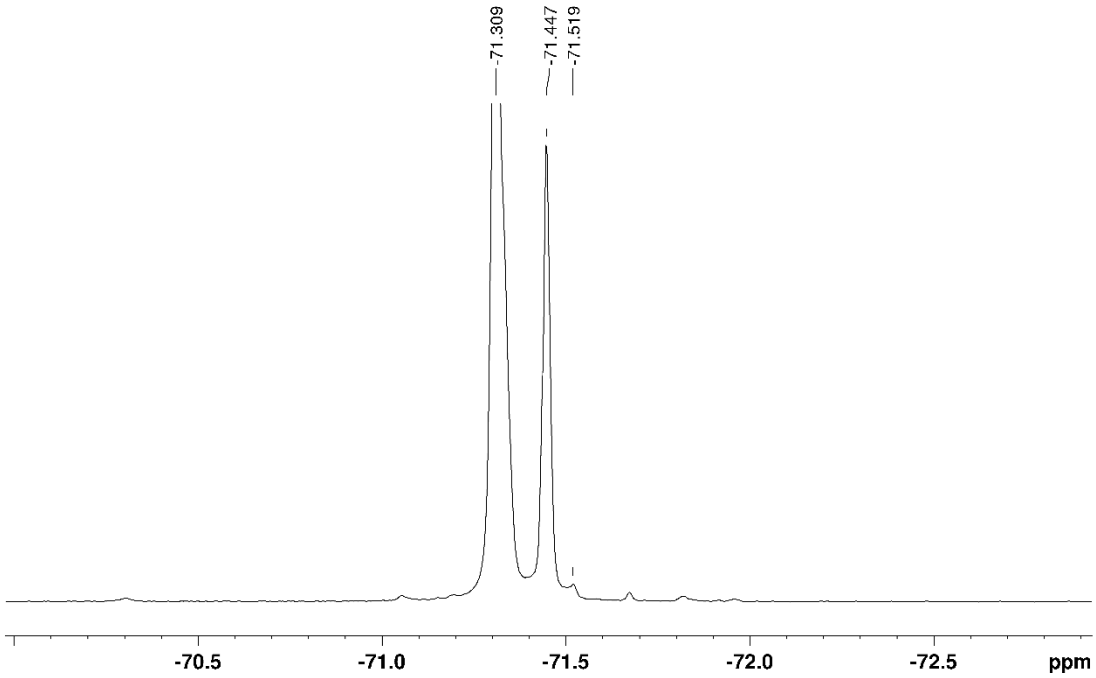


Figure S21. ^{1}H NMR of **8e,f** (n=5,6) in C_6D_6

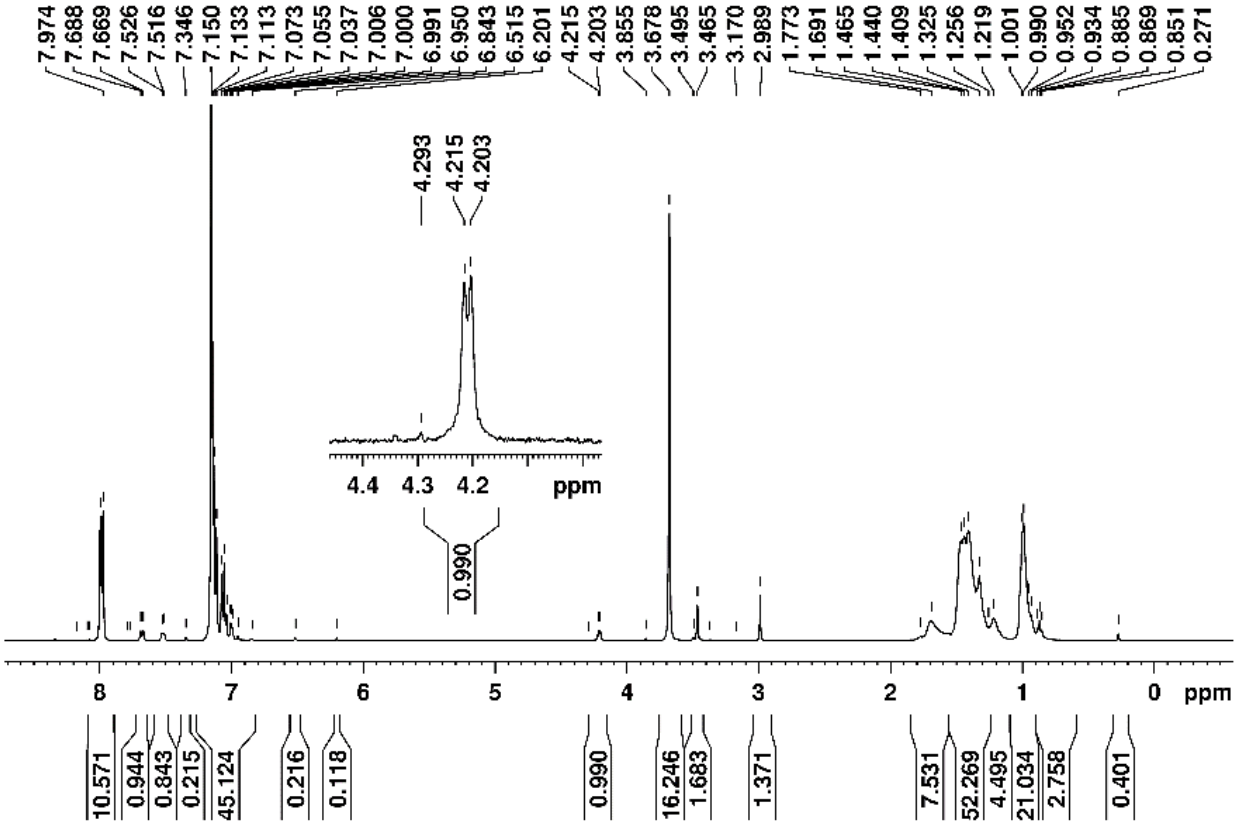


Figure S22. ^{19}F NMR of **8e,f** (n=5,6) in C_6D_6

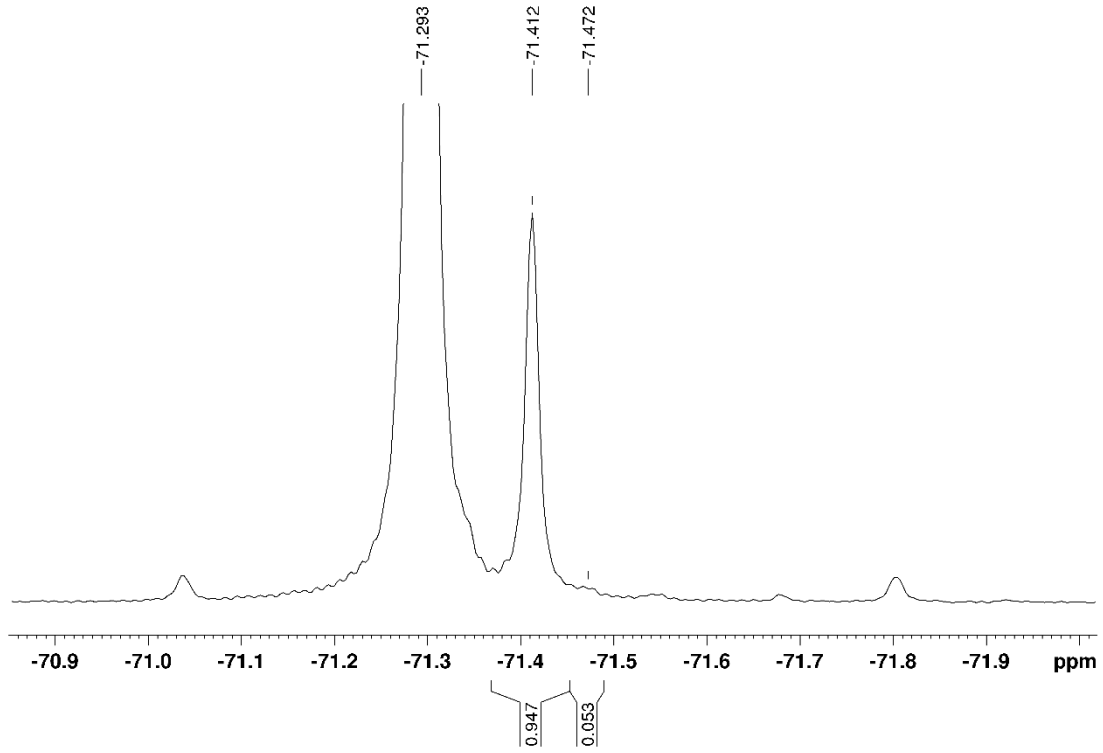


Figure S23. ^{1}H NMR of *rac*-**8e,f+8'e,f** (n=5,6) synthesized from racemic *rac*-**5e,f** (n=5,6)

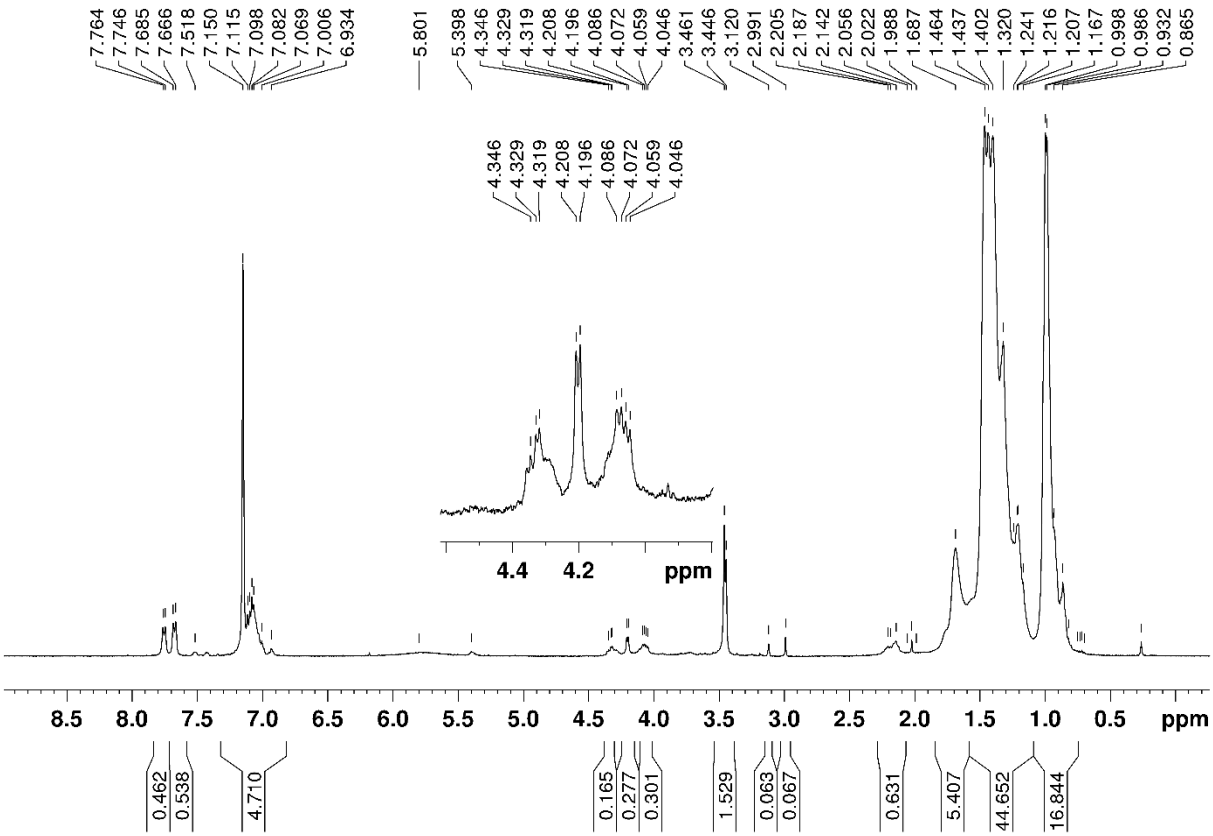


Figure S24. ^{19}F NMR of *rac*-**8e,f+8'e,f** (n=5,6) synthesized from racemic *rac*-**5e,f** (n=5,6)