^{13}C INEPT Diffusion-Ordered NMR Spectroscopy with Internal References

*Deyu Li, Russell Hopson, Weibin Li, Jia Liu, and Paul G. Williard**

Department of Chemistry, Brown University, Providence, RI 02912 USA

E-mail: pgw@brown.edu

Supporting Information

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Part 1. Experimental Procedures

General. All samples were directly prepared in the NMR tubes. All NMR tubes were sealed with septum and then flame-dried under vacuum and filled with argon before use. Toluene-d_8 was kept with 4 Å molecular sieves under argon. LDA mono-THF was obtained from Aldrich Chemical Co. (1.5 M in cyclohexane). All NMR experiments were recorded on a Bruker DRX 400 spectrometer. Standard ^{1}H and ^{13}C INEPT NMR spectra were recorded at 400.13 and 100.613 MHz respectively. All the data were processed with the Topspin 1.3 pl6 software.

DOSY experiments. DOSY experiments were performed on a Bruker DRX400 spectrometer equipped with an Accustar *z*-axis gradient amplifier and an ATMA BBO probe with a z-axis gradient coil. Maximum gradient strength was 0.214 T/m. Bipolar rectangular gradients with longitudinal eddy current delay (LEDbpgp2s) were used with total durations 0.5 to 3 ms. Gradient recovery delays were 0.5 to 1 ms. Diffusion times were between 500 and 2000 ms. The pulse-field gradients were incremented in 64 steps from 2% to 75% of the maximum gradient strength in a linear ramp. The diffusion coefficient was determined by fitting the peak areas to the Stejskal-Tanner equation. Individual rows of the quasi-2-D diffusion databases were phased and baseline corrected. Different INEPT DOSY experiments were carried out with different concentrations and every experiment was repeated twice. The experiment results are comparable to each other. Diffusion coefficients of each ^{13}C INEPT signal were generated from T1/T2 analysis.

Preparation of the LDA-THF dimer with internal references and ethylbenzene sample. The NMR sample was prepared by mixing 0.60 ml LDA mono-THF 1.5 M in cyclohexane with 0.60 ml toluene-d_8 solution under argon. Then 0.29 ml ODE, 0.17 ml CDDE and 0.03 ml benzene were added to the above sample as internal references for

DOSY experiments. ^{1}H NMR, ^{13}C INEPT NMR, COSY, HSQC, HMBC, and ^{13}C INEPT DOSY spectra were recorded.

Determination of the stereochemistry of CDDE. The olefin configurations of *cis*- and *trans*-CDDE were determined by ^{1}H CW off-resonance ^{13}C NMR spectra. The coupling constants ^{3}J (H, H) of the *cis*- and *trans*-CDDE were calculated as 12.1 and 16.1 Hz respectively (**Figure S20**).

Calculations of volumes of *cis*- and *trans*-CDDE. The calculations of the volume of *cis*- and *trans*-CDDE were performed with Spartan 04, Wavefunction Inc.: 18401 Von Karman Avenue, Suite 370, Irvine, CA 92612. The lowest energy conformers were optimized at the PM3 semi-empirical level. The volumes of the *cis*- and *trans*-CDDE were calculated as 213.02 Å^{3} and 213.00 Å^{3}.

Part 2. NMR Spectra

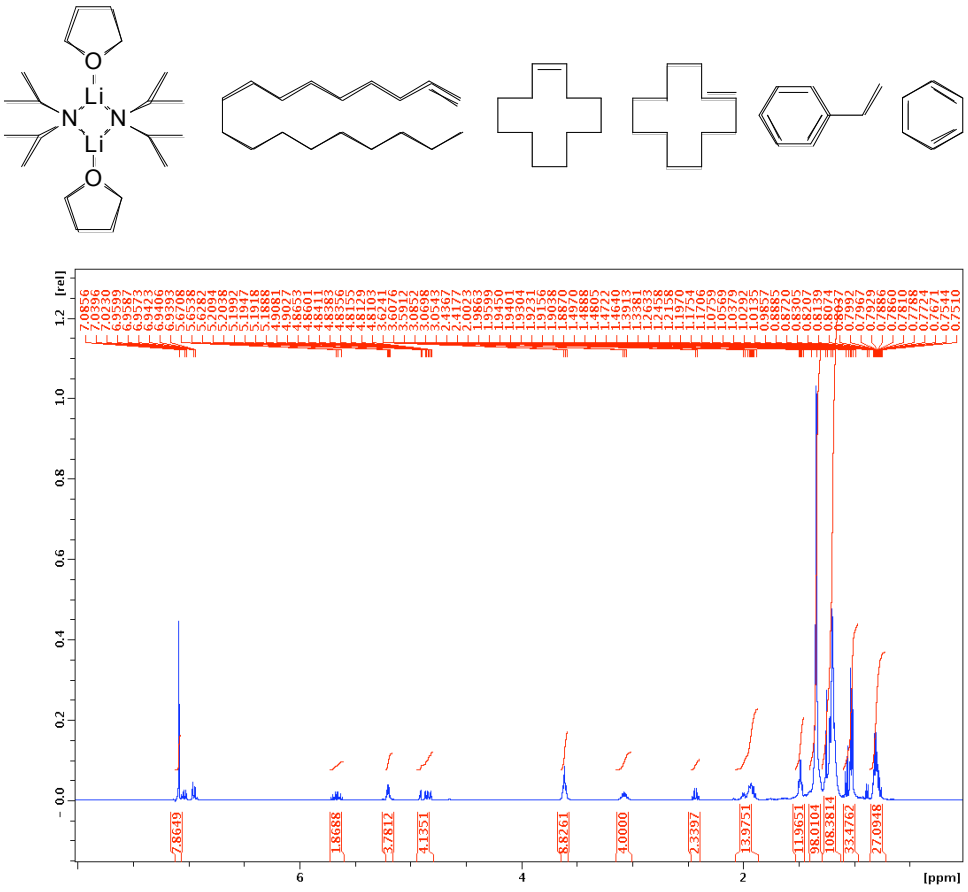


Figure S1. ^{1}H NMR spectrum of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8.

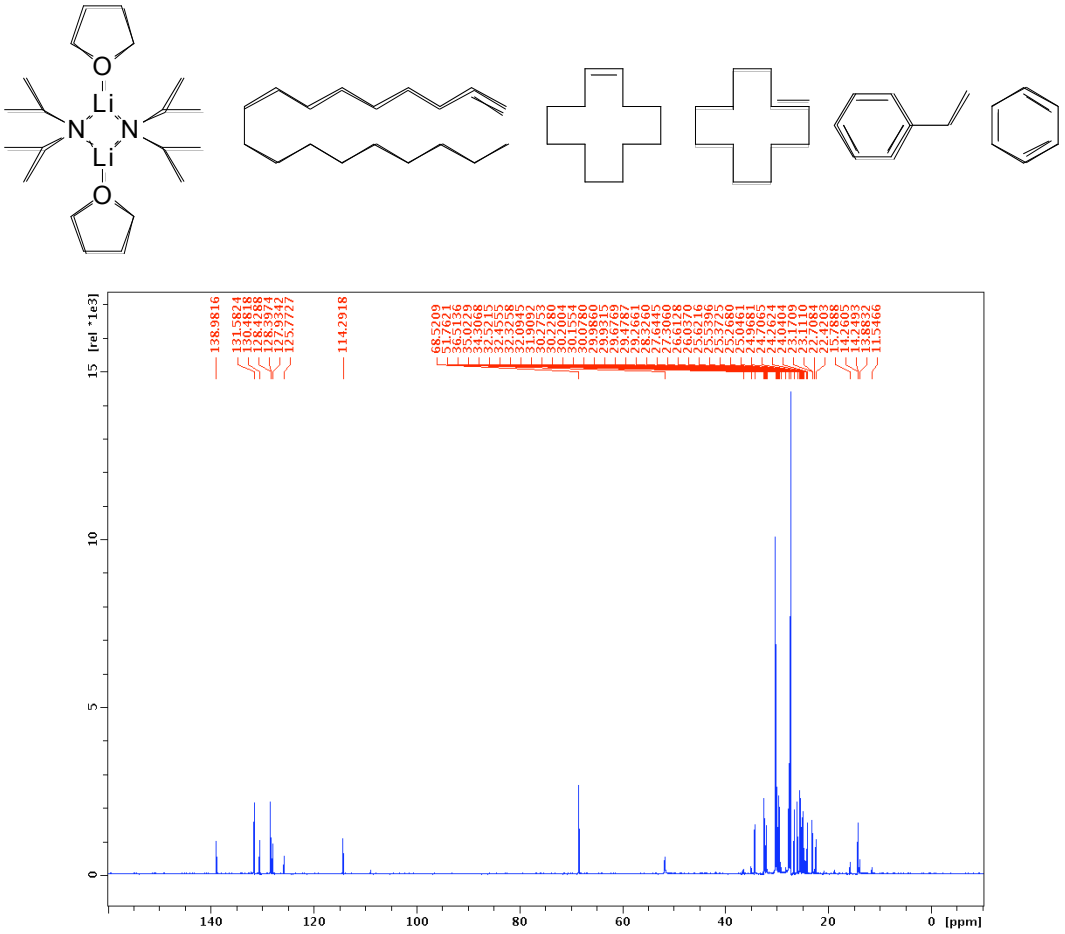


Figure S2. ^{13}C INEPT NMR spectrum of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8.

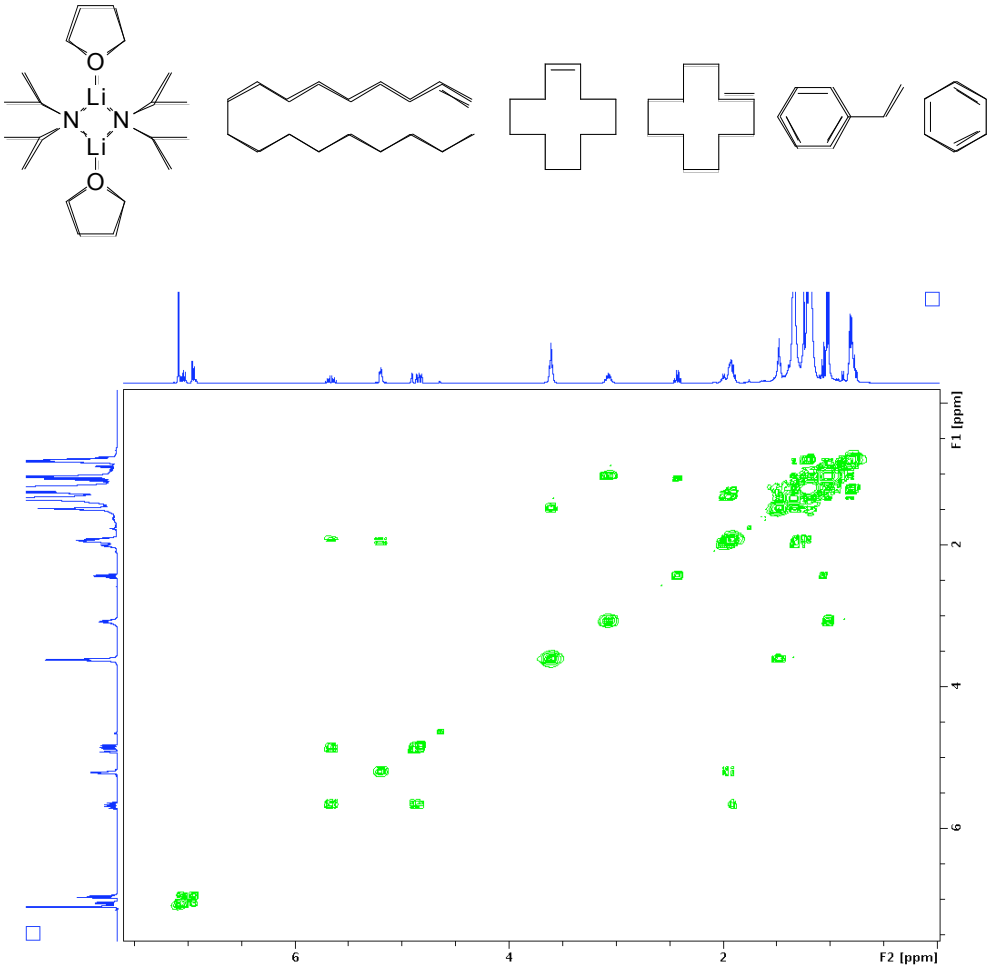


Figure S3. COSY NMR spectrum of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8.

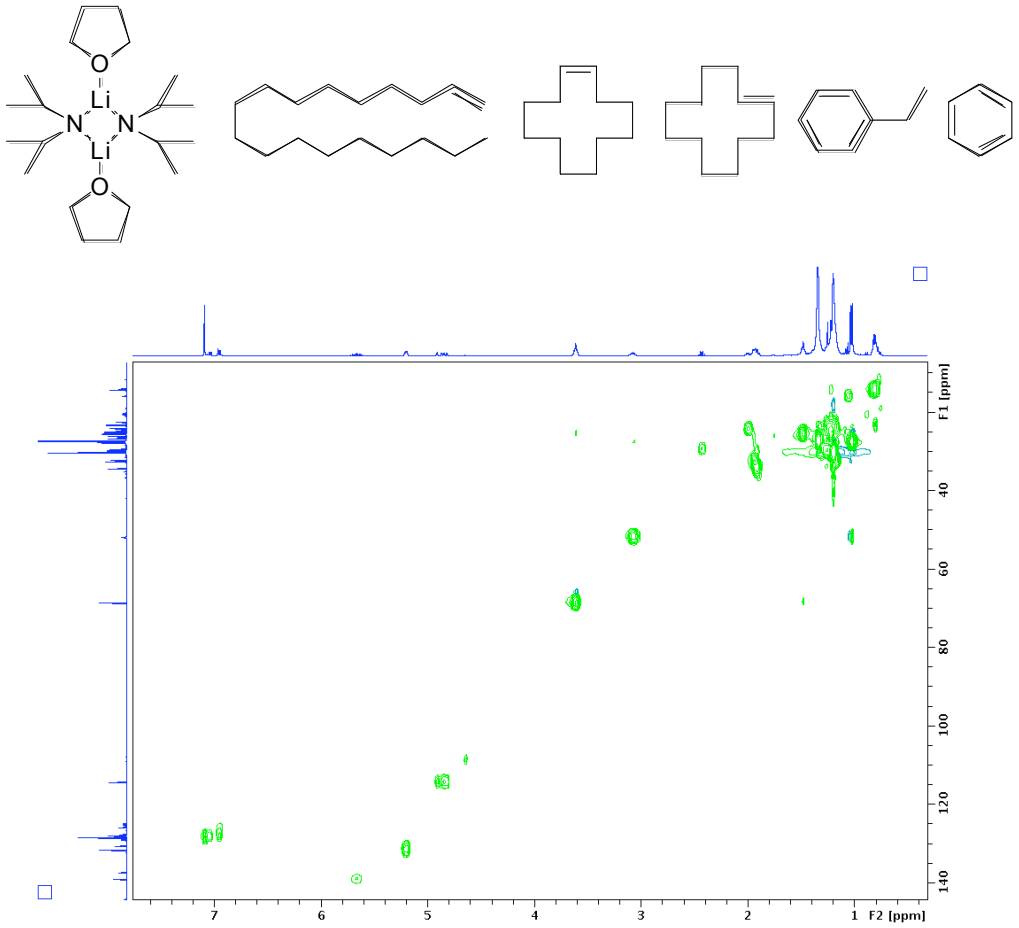


Figure S4. HSQC NMR spectrum of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8.

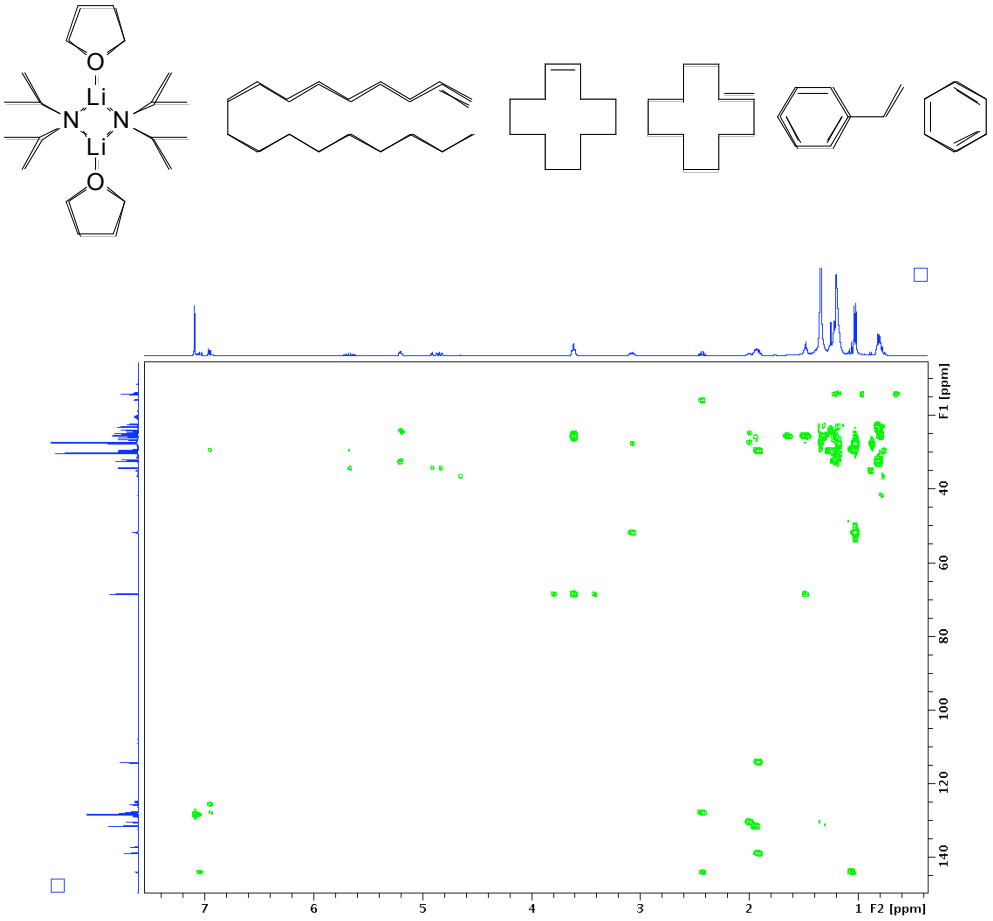


Figure S5. HMBC NMR spectrum of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8.

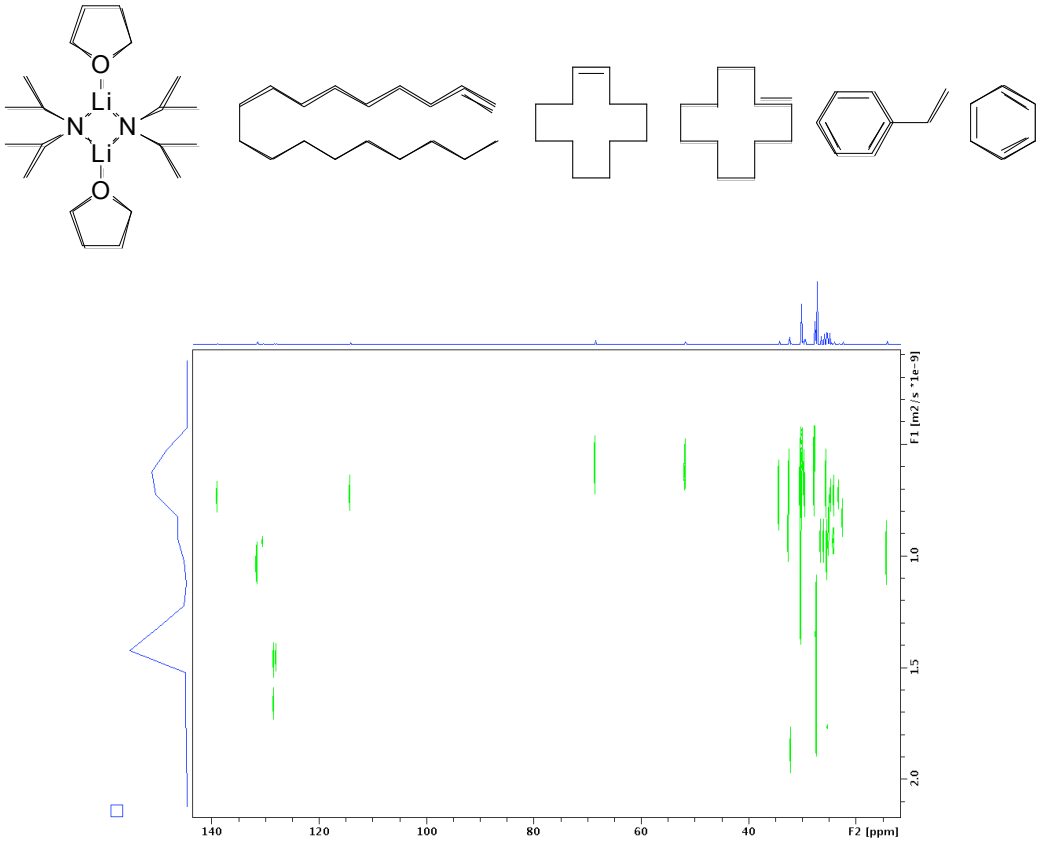


Figure S6. ^{13}C INEPT DOSY NMR spectrum of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8.

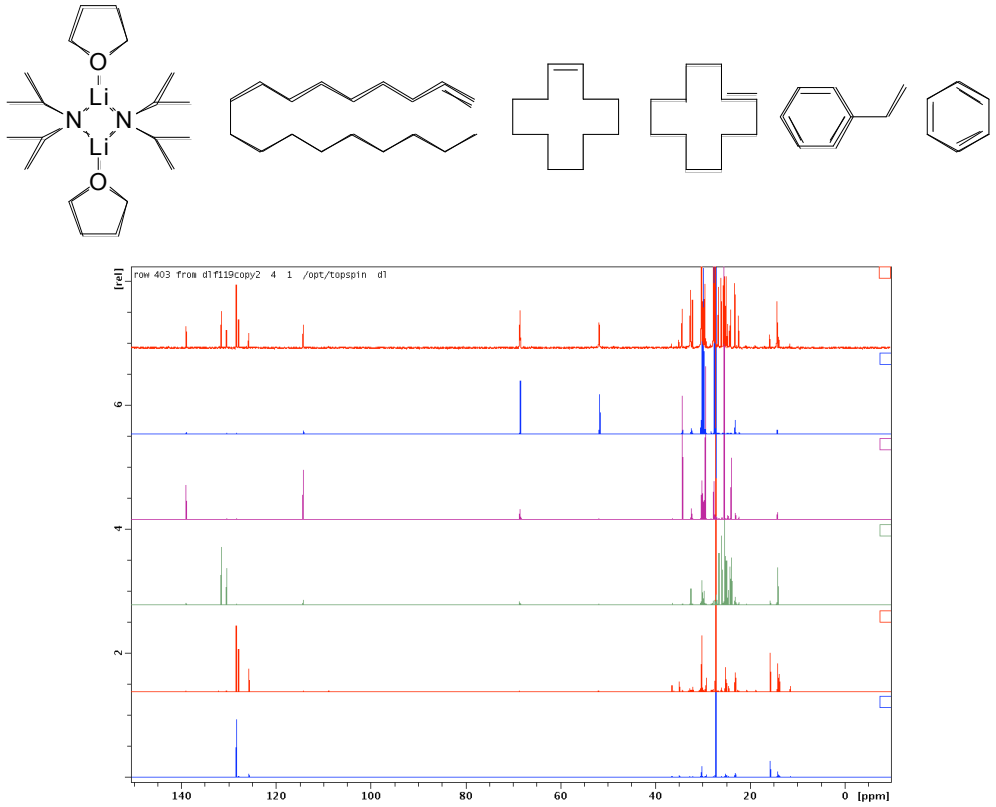


Figure S7. ^{13}C INEPT DOSY slices of LDA-THF dimer with internal references and ethylbenzene in toluene-d_8. From top to bottom, slice is belonging to LDA dimer with internal references and ethylbenzene, LDA-THF dimer, ODE, *cis*- and *trans*-CDDE mixture, ethylbenzene and benzene.

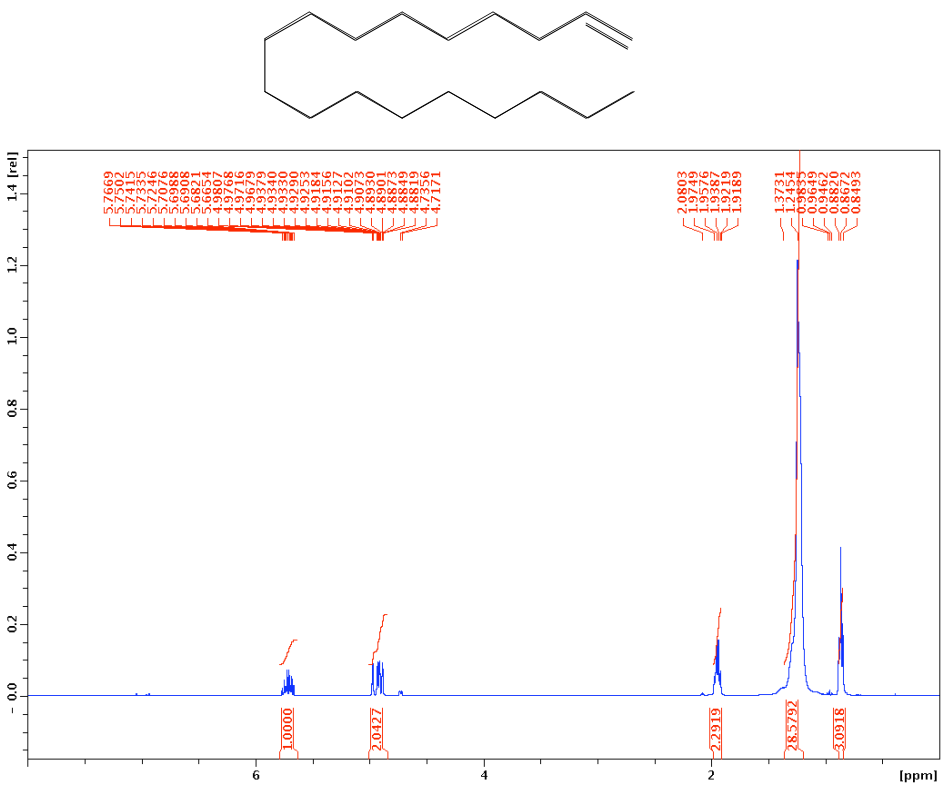


Figure S8. ^{1}H NMR spectrum of ODE in toluene-d_8.

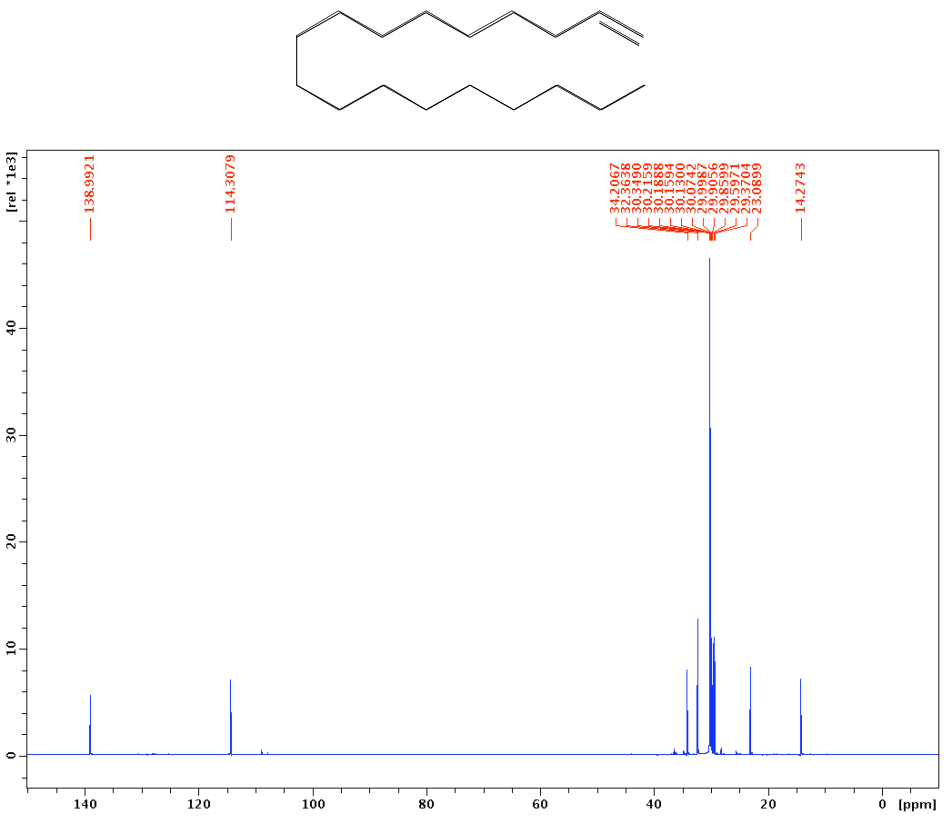


Figure S9. ^{13}C INEPT NMR spectrum of ODE in toluene-d_8.

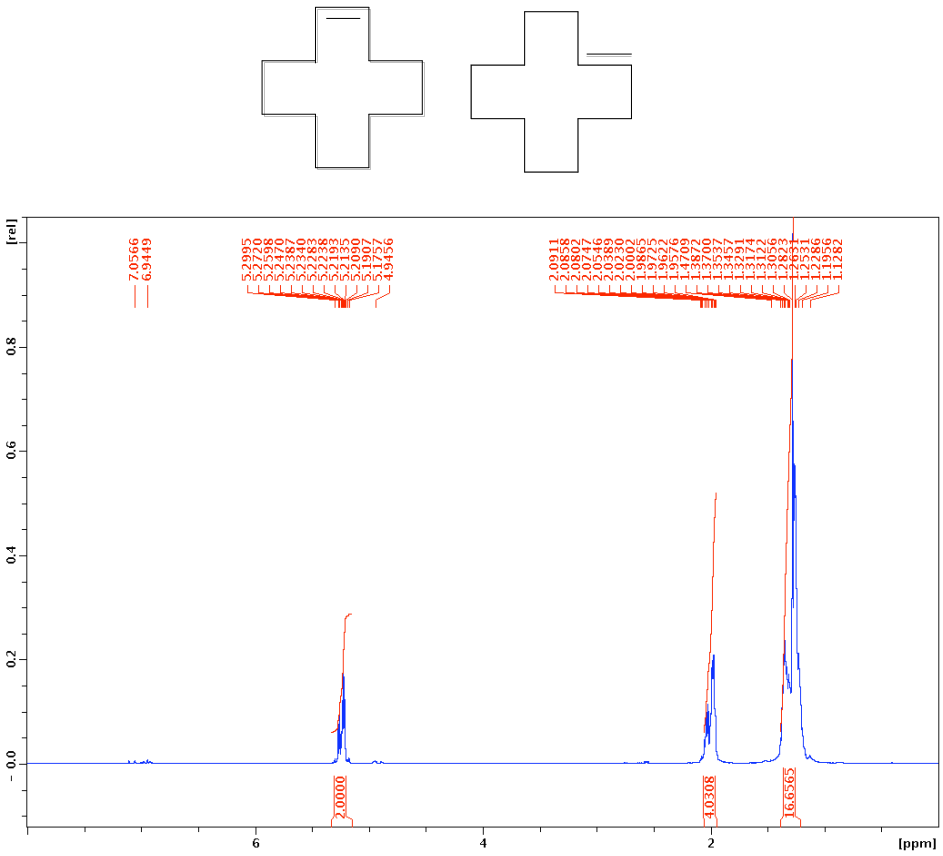


Figure S10. ^{1}H NMR spectrum of *cis*- and *trans*-CDDE in toluene-d_8.

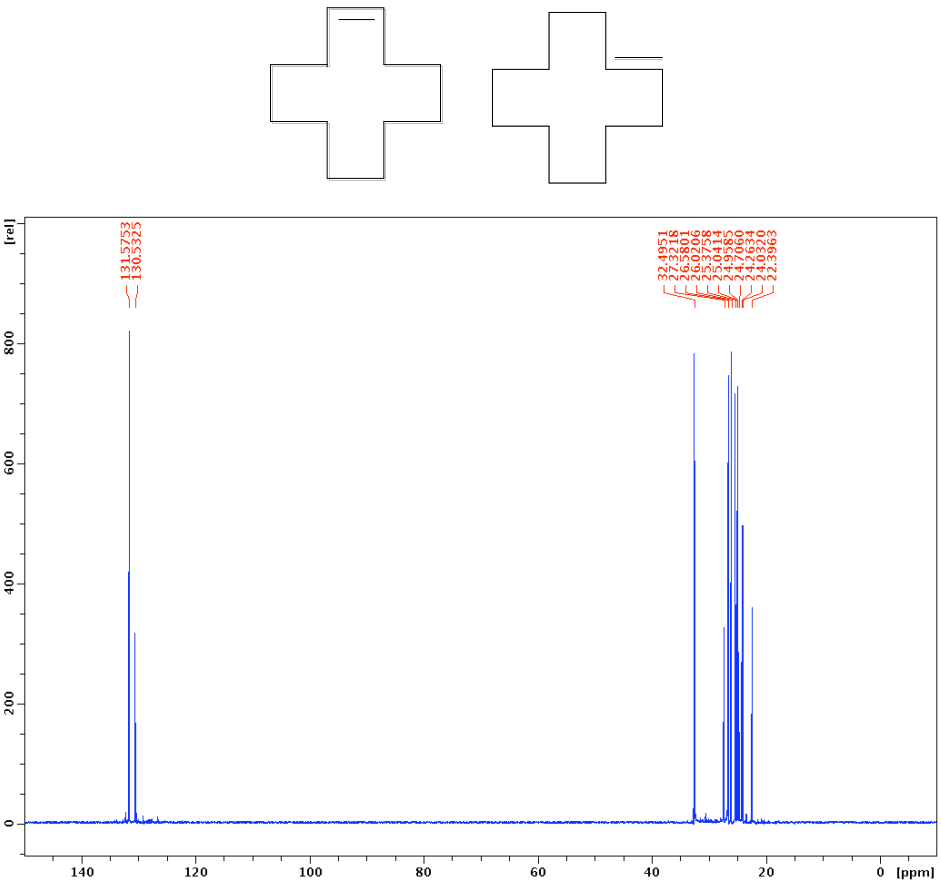


Figure S11. ^{13}C INEPT NMR spectrum of *cis*- and *trans*-CDDE in toluene-d_8.

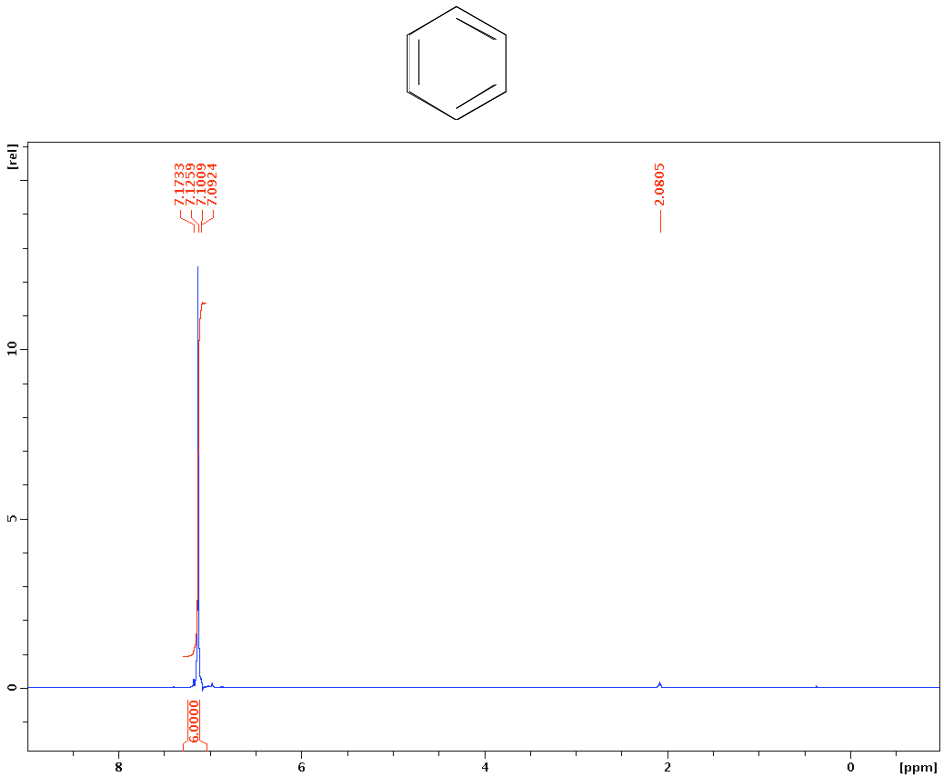


Figure S12. ^{1}H NMR spectrum of benzene in toluene-d_8.

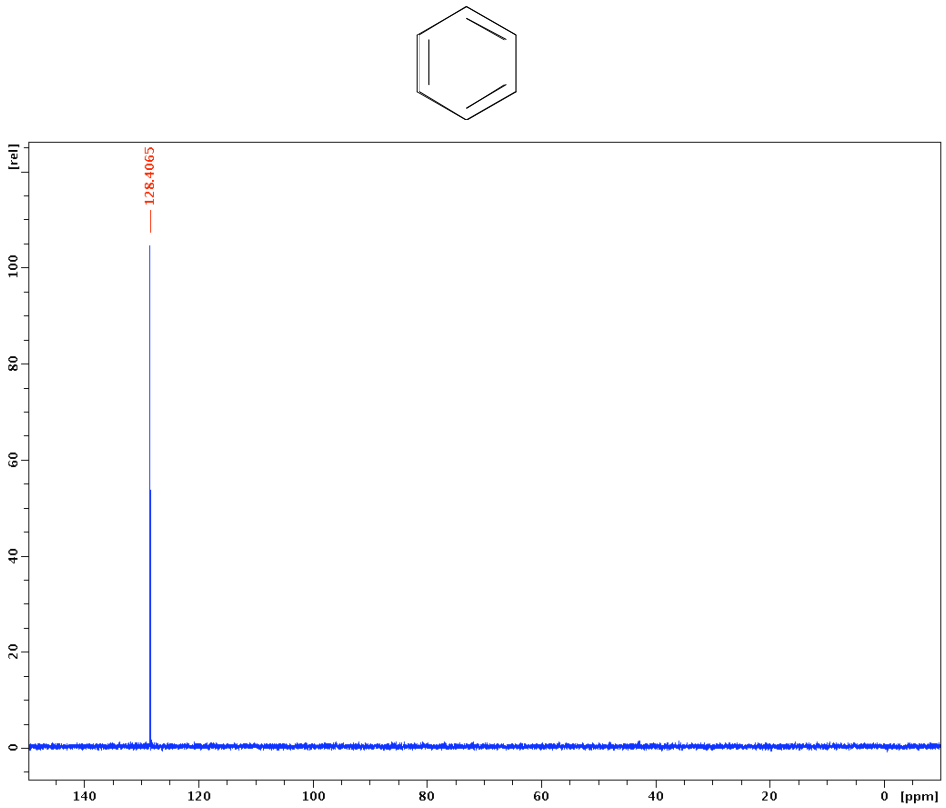


Figure S13. ^{13}C INEPT NMR spectrum of benzene in toluene-d_8.

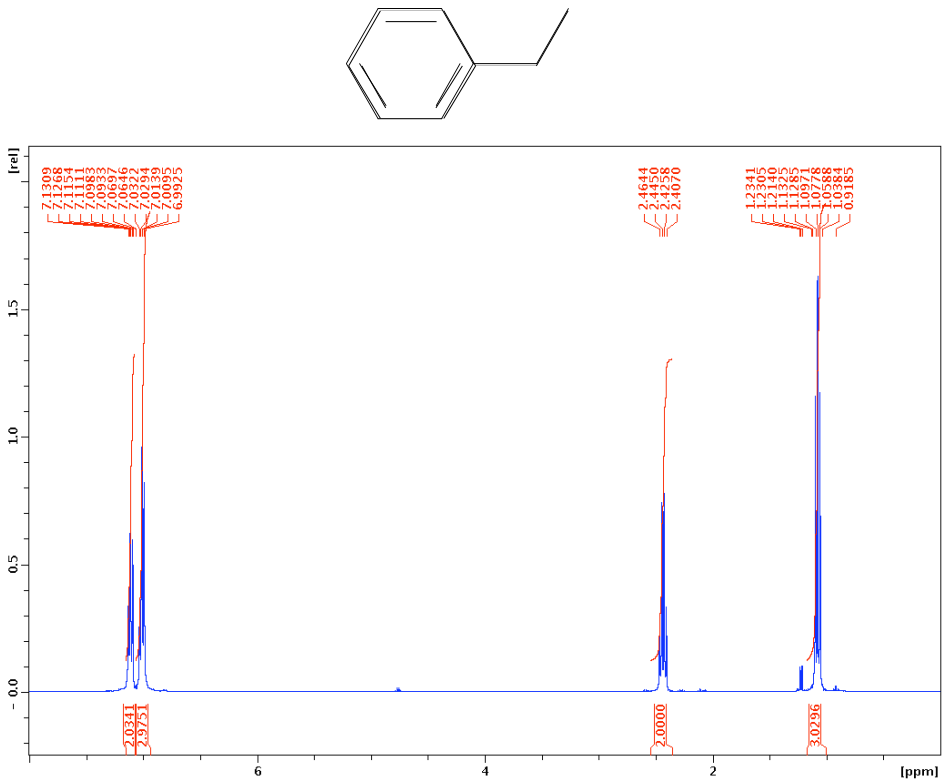


Figure S14. ^{1}H NMR spectrum of ethylbenzene in toluene-d_8.

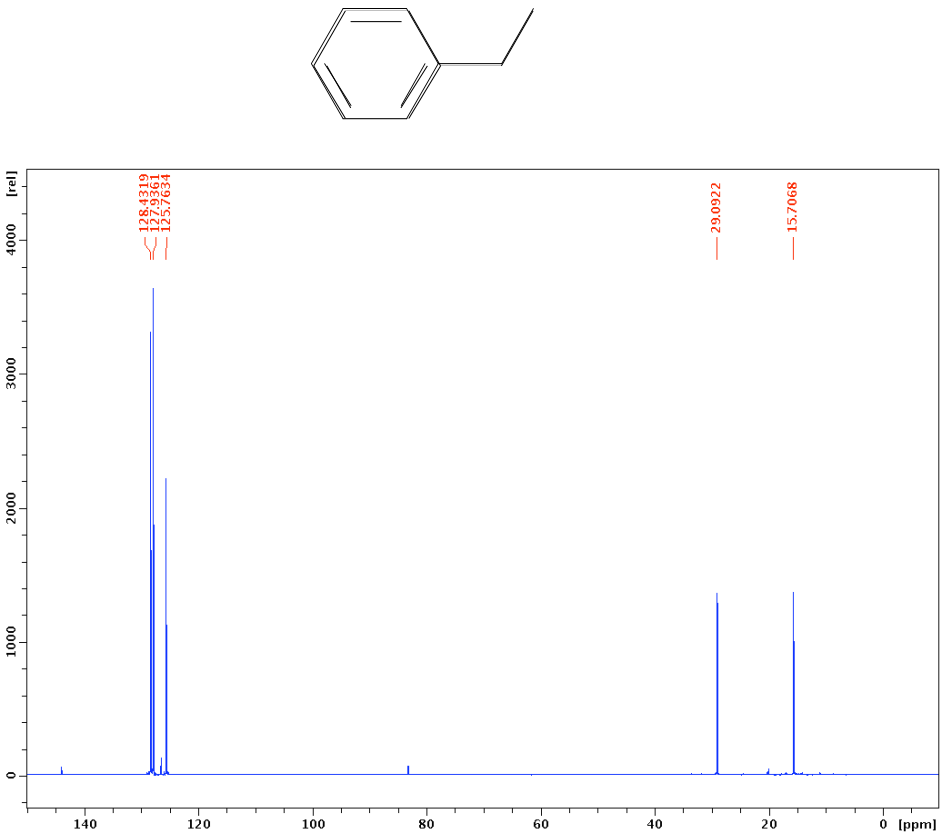
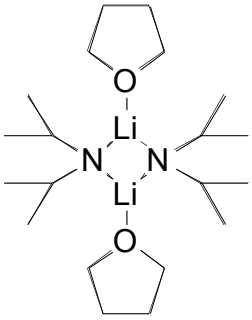


Figure S15. ^{13}C INEPT NMR spectrum of ethylbenzene in toluene-d_8.



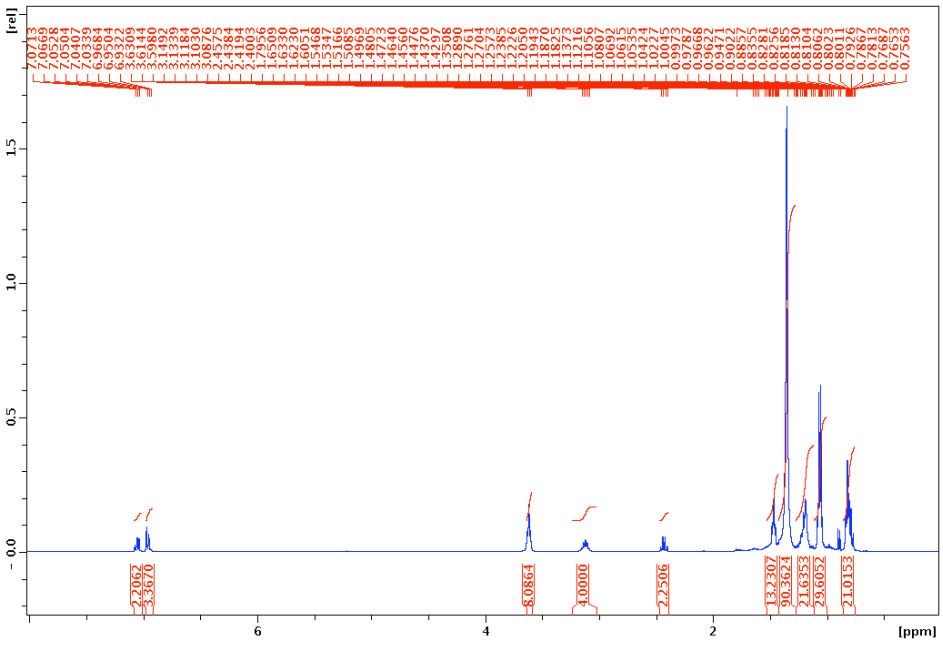
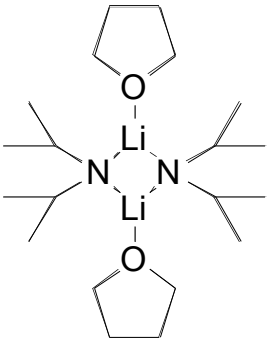


Figure S16. ^{1}H NMR spectrum of LDA-THF dimer in toluene-d_8.



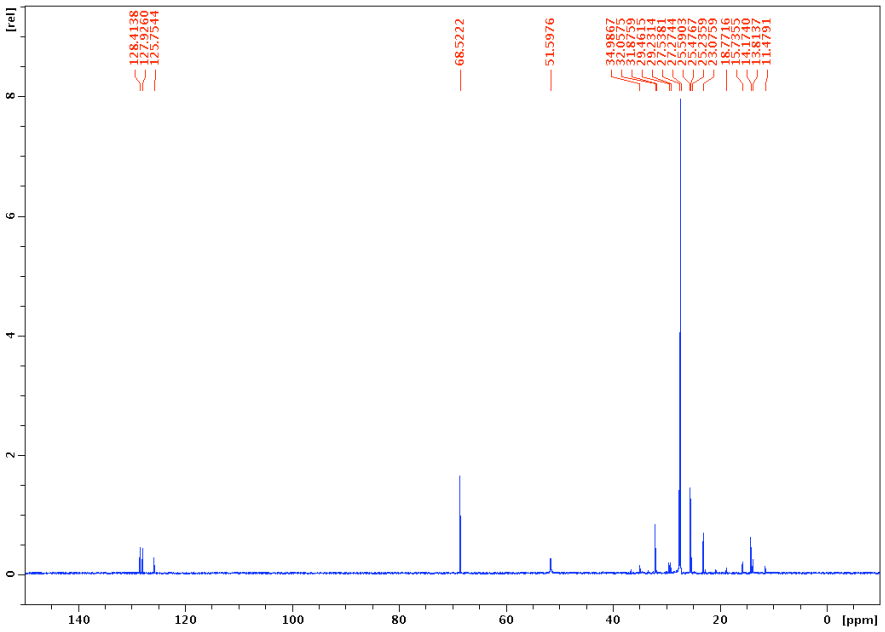


Figure S17. ^{13}C INEPT NMR spectrum of LDA-THF dimer in toluene-d_8.

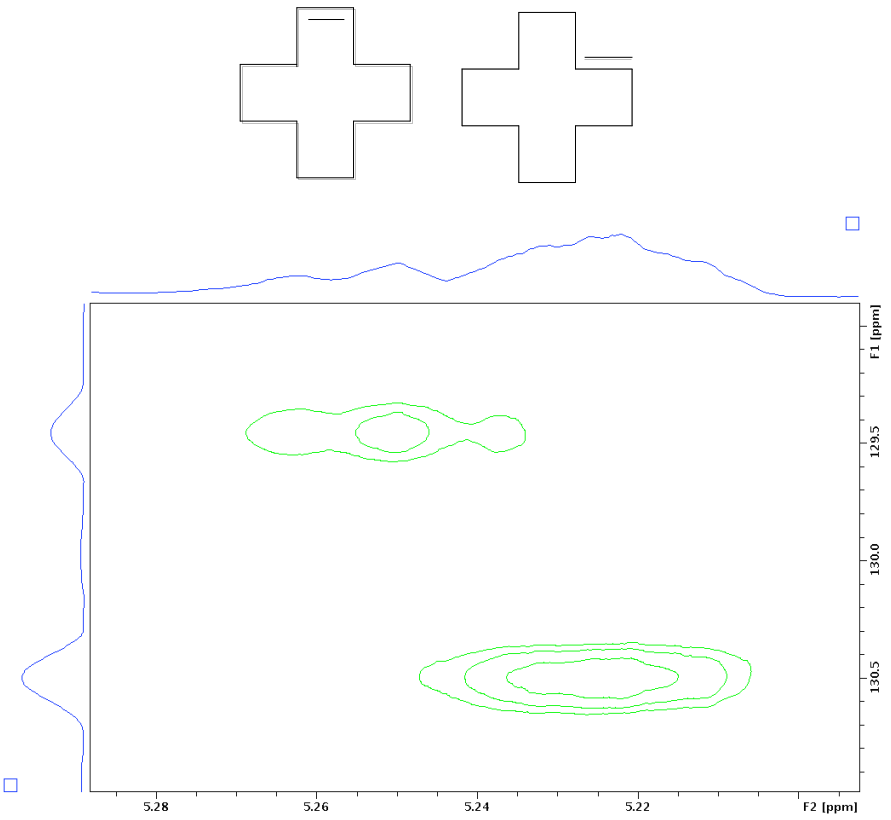


Figure S18. HSQC NMR spectrum of *cis*- and *trans*-CDDE toluene-d_8.

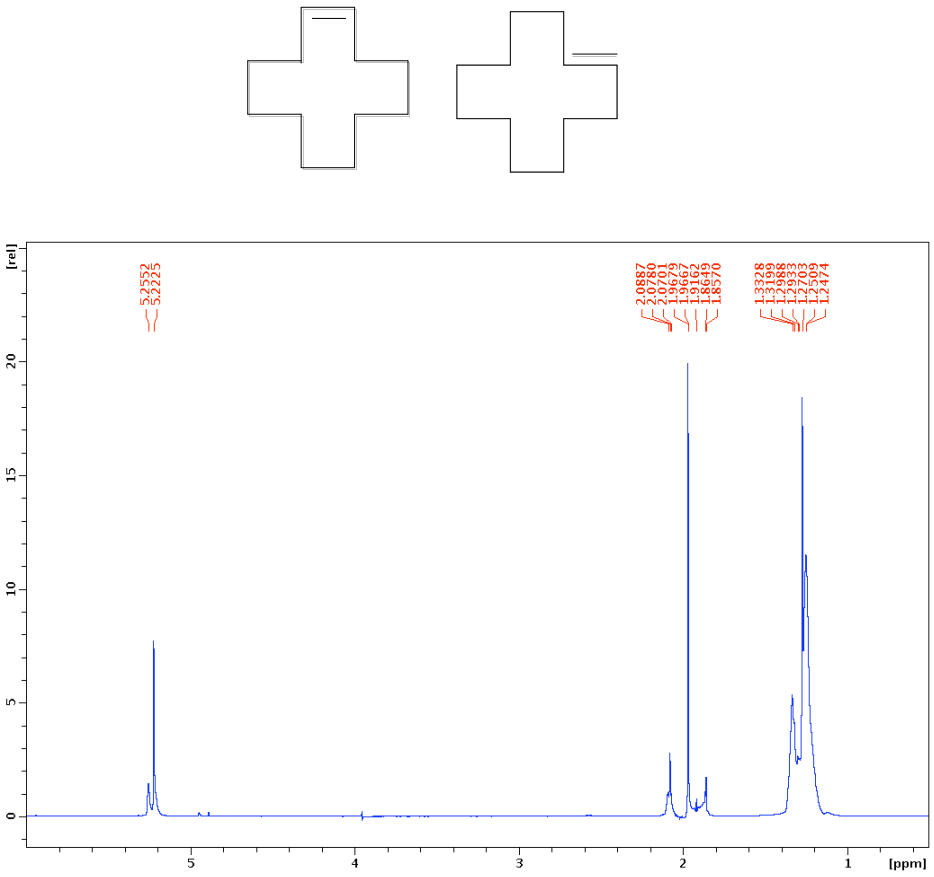


Figure S19. ^{1}H homodecoupling NMR spectrum of *cis*- and *trans*-CDDE toluene-d_8. (Irradiation of the methylene carbons next to the double bond, δ = 2.0ppm)

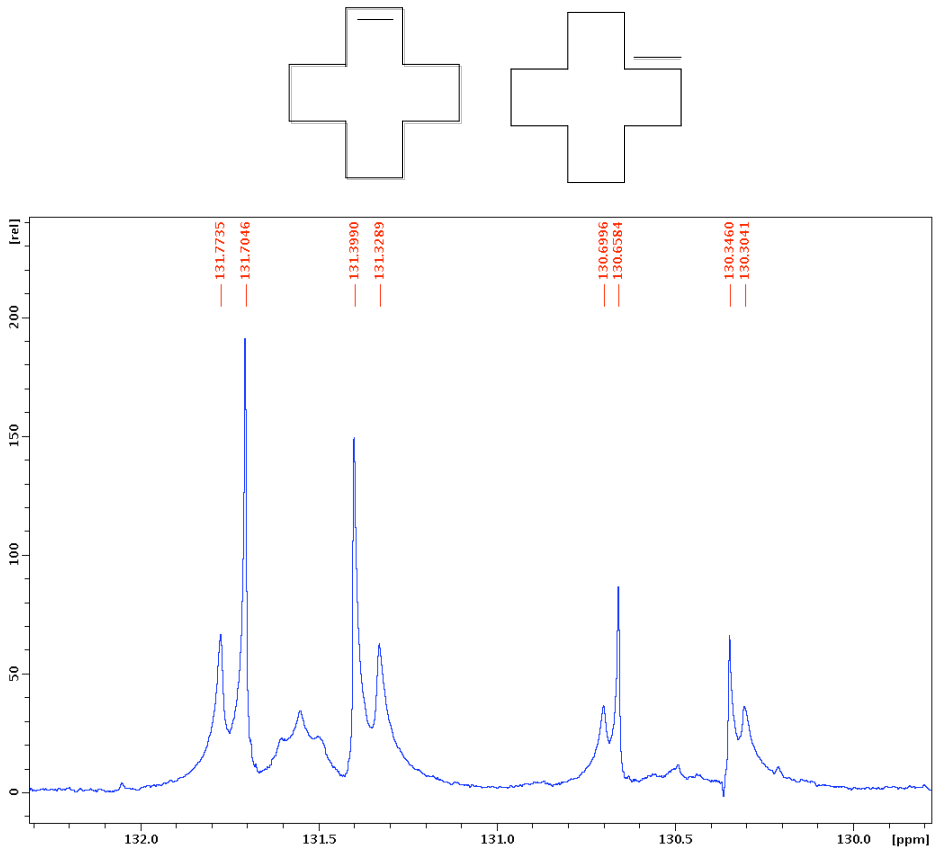


Figure S20. ^{1}H CW off-resonance ^{13}C NMR spectrum of the olefinic carbons of *cis*- and *trans*-CDDE.

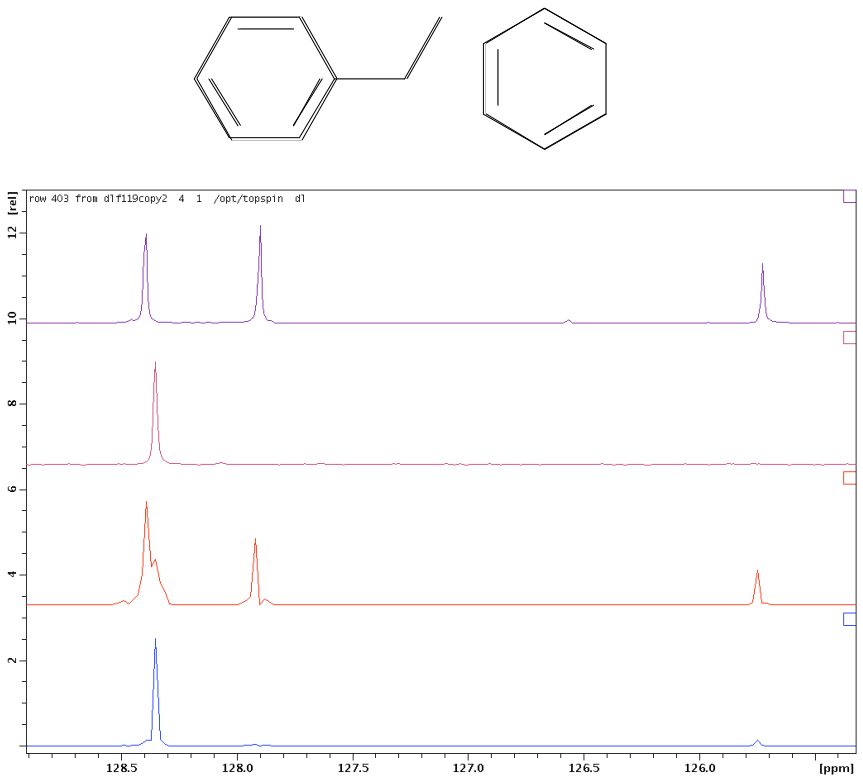


Figure S21. Comparison of the ^{13}C INEPT spectra of ethylbenzene and benzene to the ethylbenzene and benzene slices of ^{13}C INEPT DOSY NMR spectra. From top to bottom, ^{13}C INEPT of ethylbenzene, ^{13}C INEPT of benzene, DOSY slice of ethylbenzene and DOSY slice of benzene.

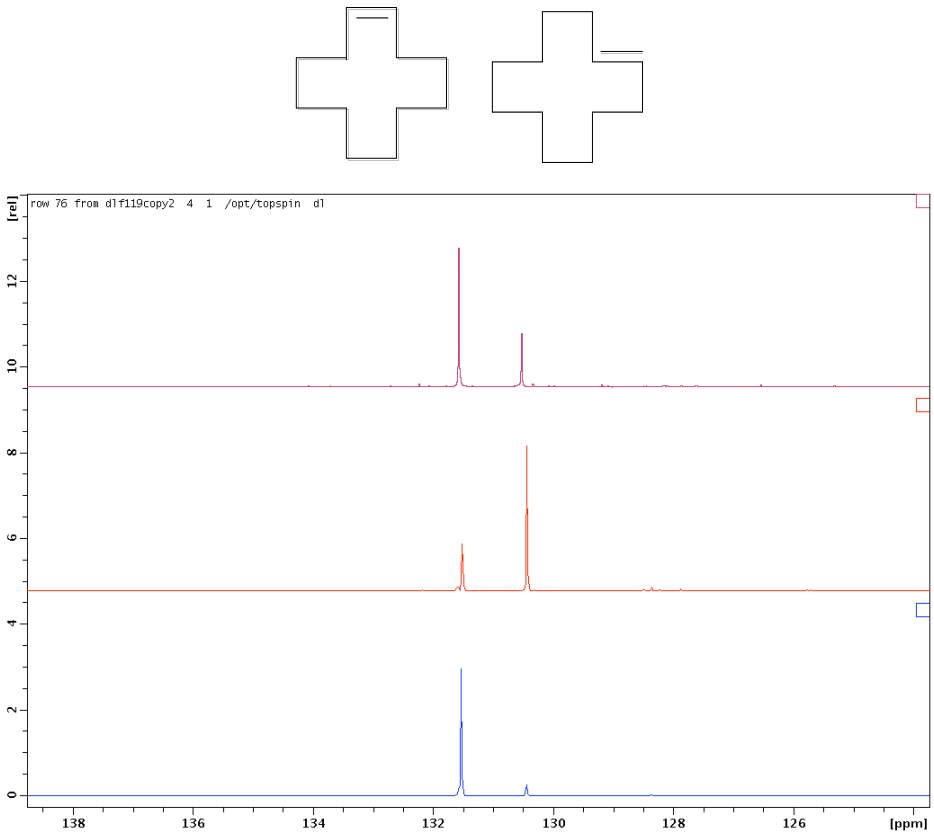


Figure S22. Comparison of the ^{13}C INEPT spectrum of *cis*- and *trans*-CDDE mixture to the *cis*-CDDE and *trans*-CDDE slices of ^{13}C INEPT DOSY NMR spectra. From top to bottom, ^{13}C INEPT of *cis*- and *trans*-CDDE mixture, DOSY slice of *cis*-CDDE and DOSY slice of *trans*-CDDE.

Table S1. Diffusion coefficients and formula weights for the THF solvated LDA dimer, ethylbenzene and three internal references.

	diffusion coefficients ($\times 10^{-10}$ m^2 s^{-1})	Log (D)	theoretical FW (Dalton)	Log (FW)
benzene	18.20	-8.740	78.1	1.89
ethylbenzene	14.72	-8.832	106.2	2.03
trans-CDDE	10.40	-8.947	166.3	2.22
cis-CDDE	10.07	-8.952	166.3	2.22
ODE	7.91	-9.102	252.3	2.40
LDA-dimer	6.14	-9.212	351.5	2.55