

**Unified Strategy for 1,5,9- and 1,5,7-Triols via Configuration-Encoded
1,5-Polyol Synthesis: Preparation and Coupling of
C15–C25 and C26–C40 Fragments of Tetrafibricin**

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Supporting Information

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2D NMR Spectra

Arrows = DQF ^1H - ^1H COSY

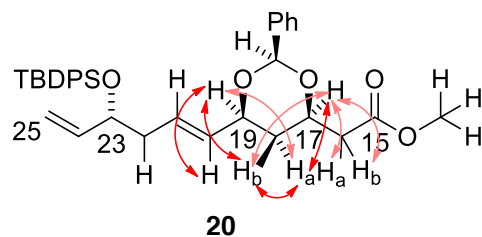
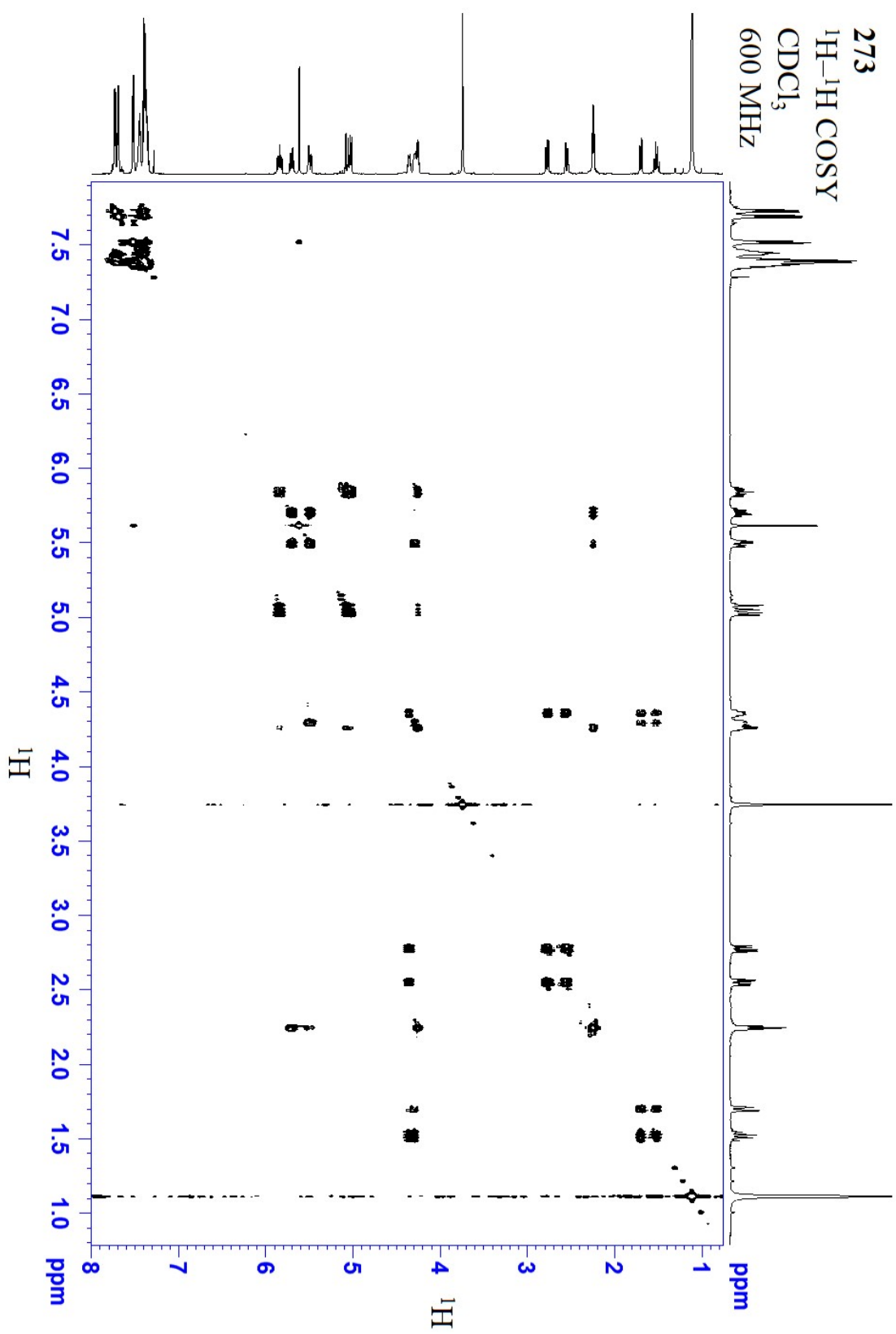
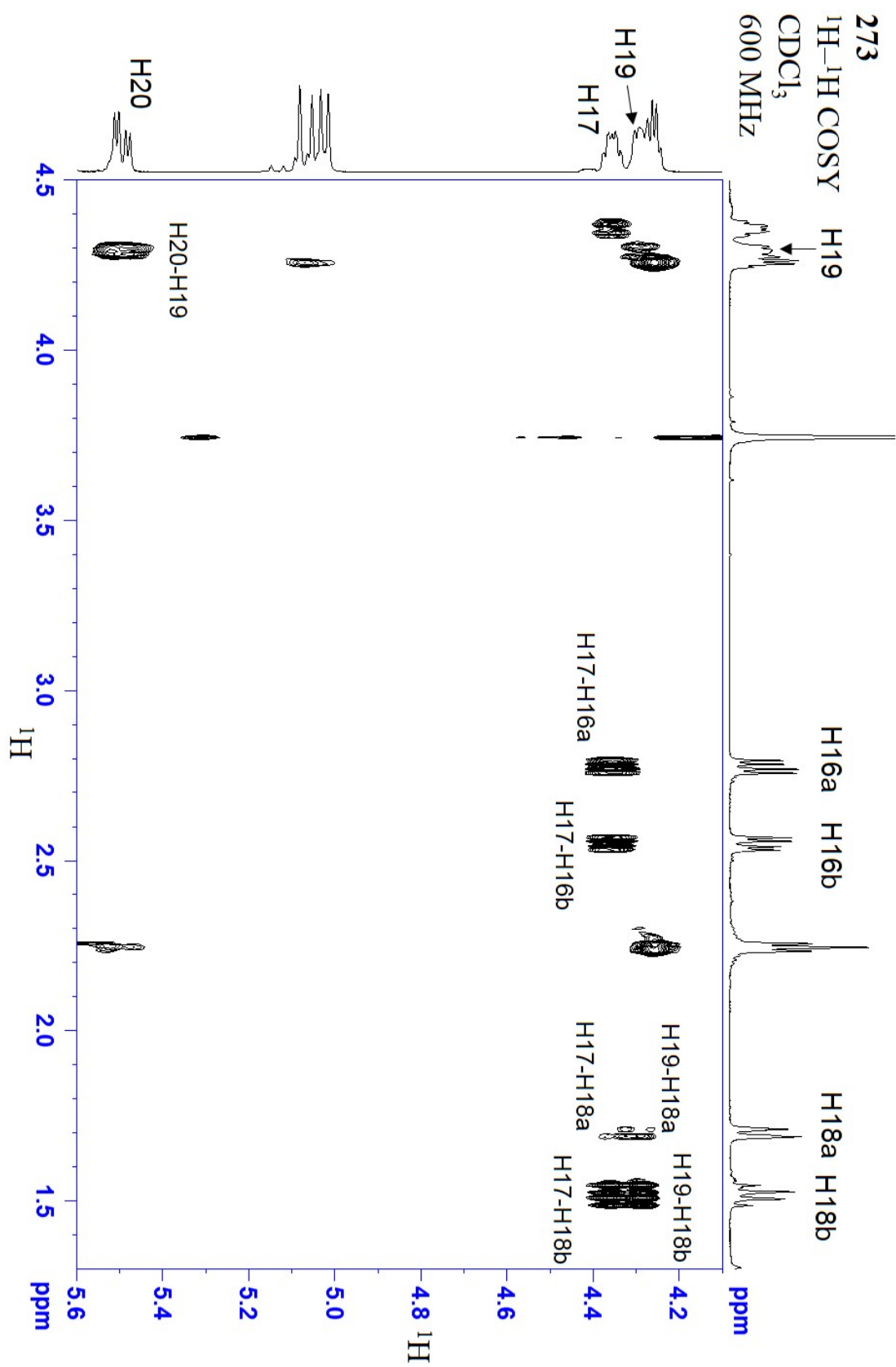


Figure S1: Diagnostic 2D NMR correlations of benzylidene acetal portion of C15–C25 fragment of tetrafibricin

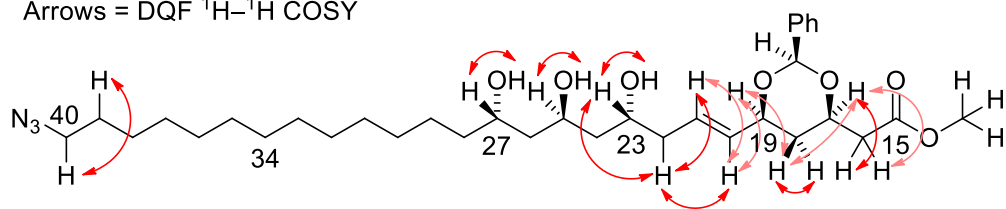


DQF ^1H - ^1H COSY spectrum of **20**



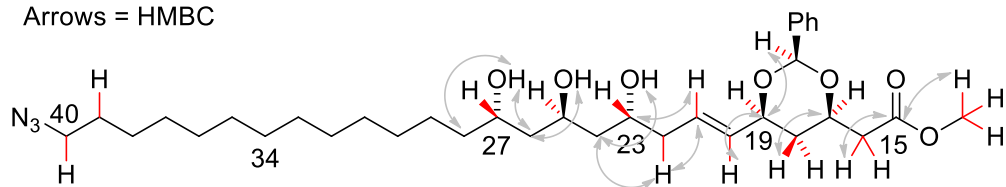
DQF ^1H - ^1H COSY spectrum of **20**

Arrows = DQF ^1H - ^1H COSY



Red Bonds = HSQC

Arrows = HMBC



Arrows = TOCSY

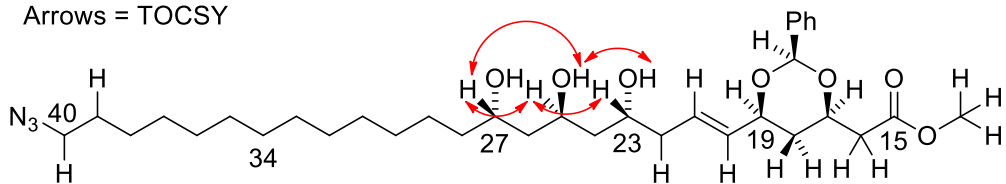
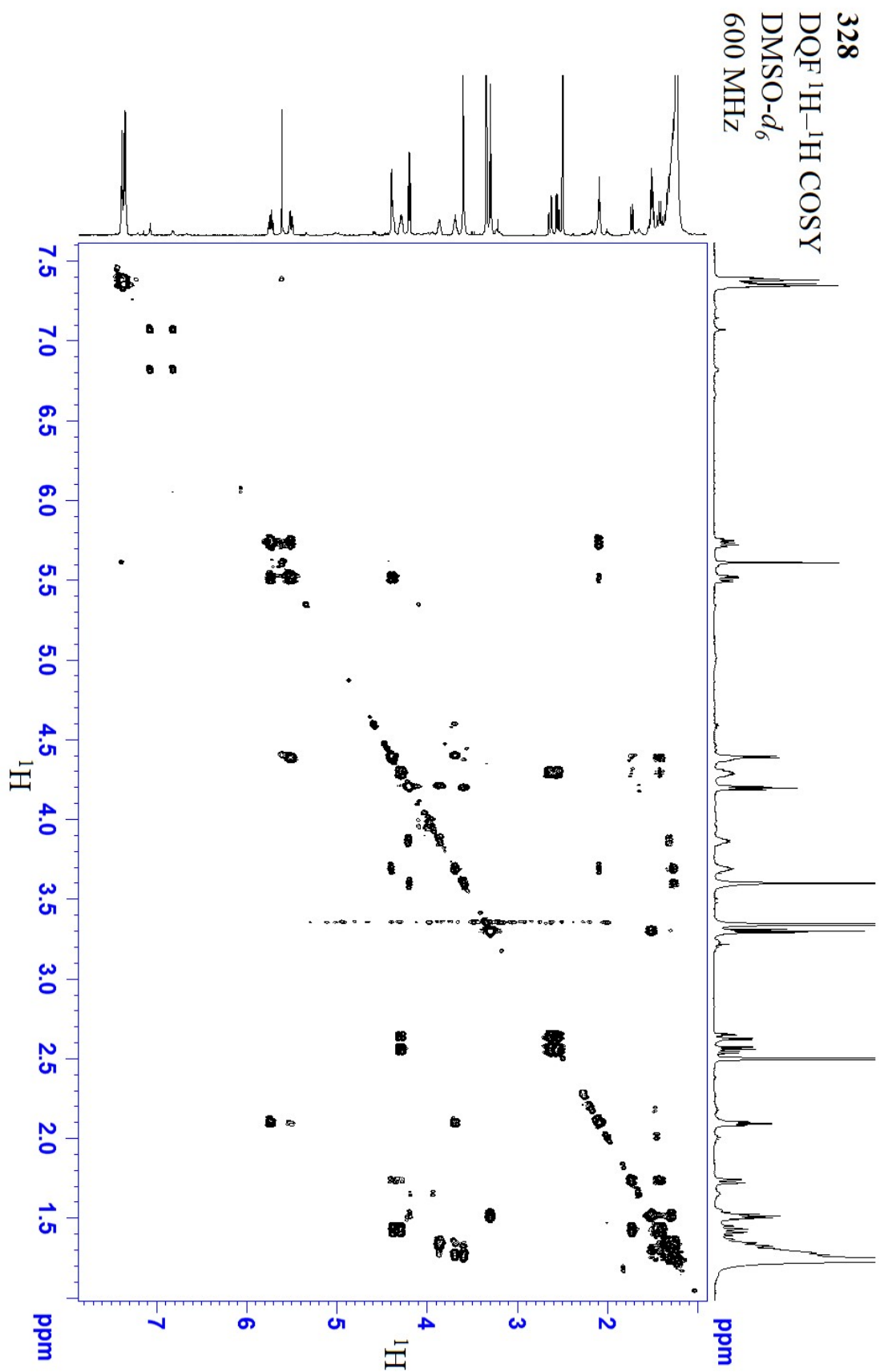
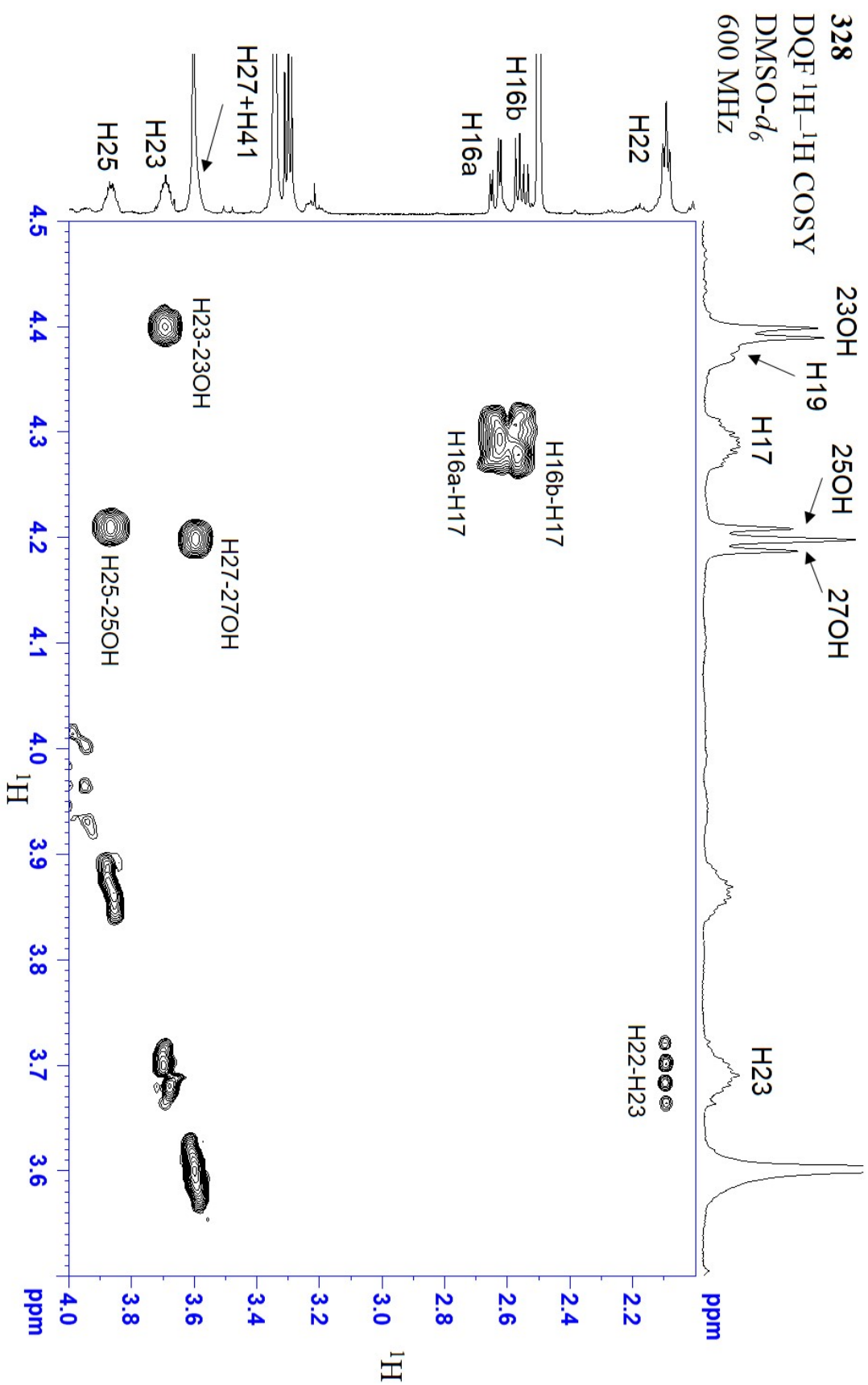


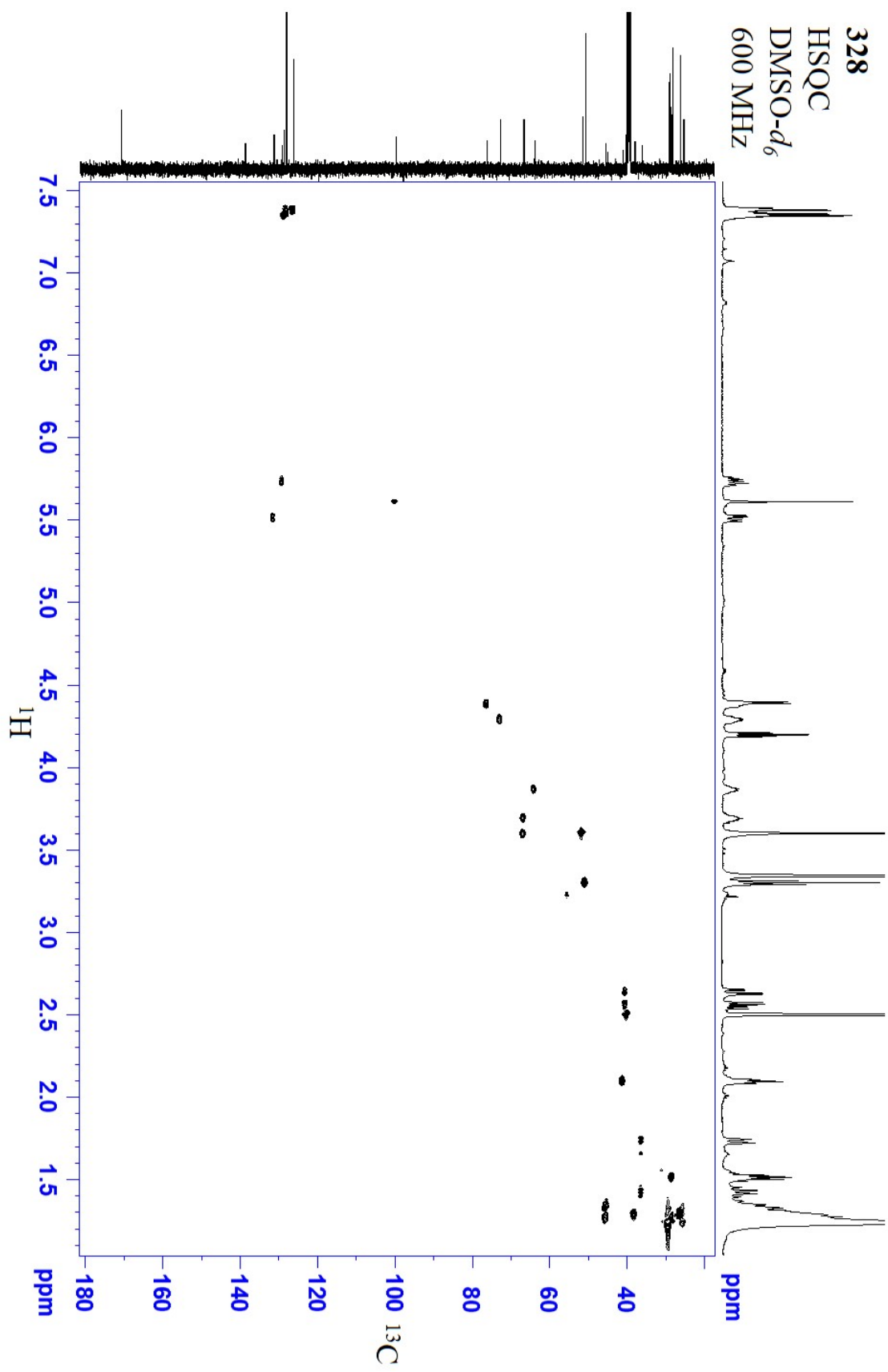
Figure S2: Diagnostic 2D NMR correlations of **28** (model C15–C40 fragment of tetrafibricin)



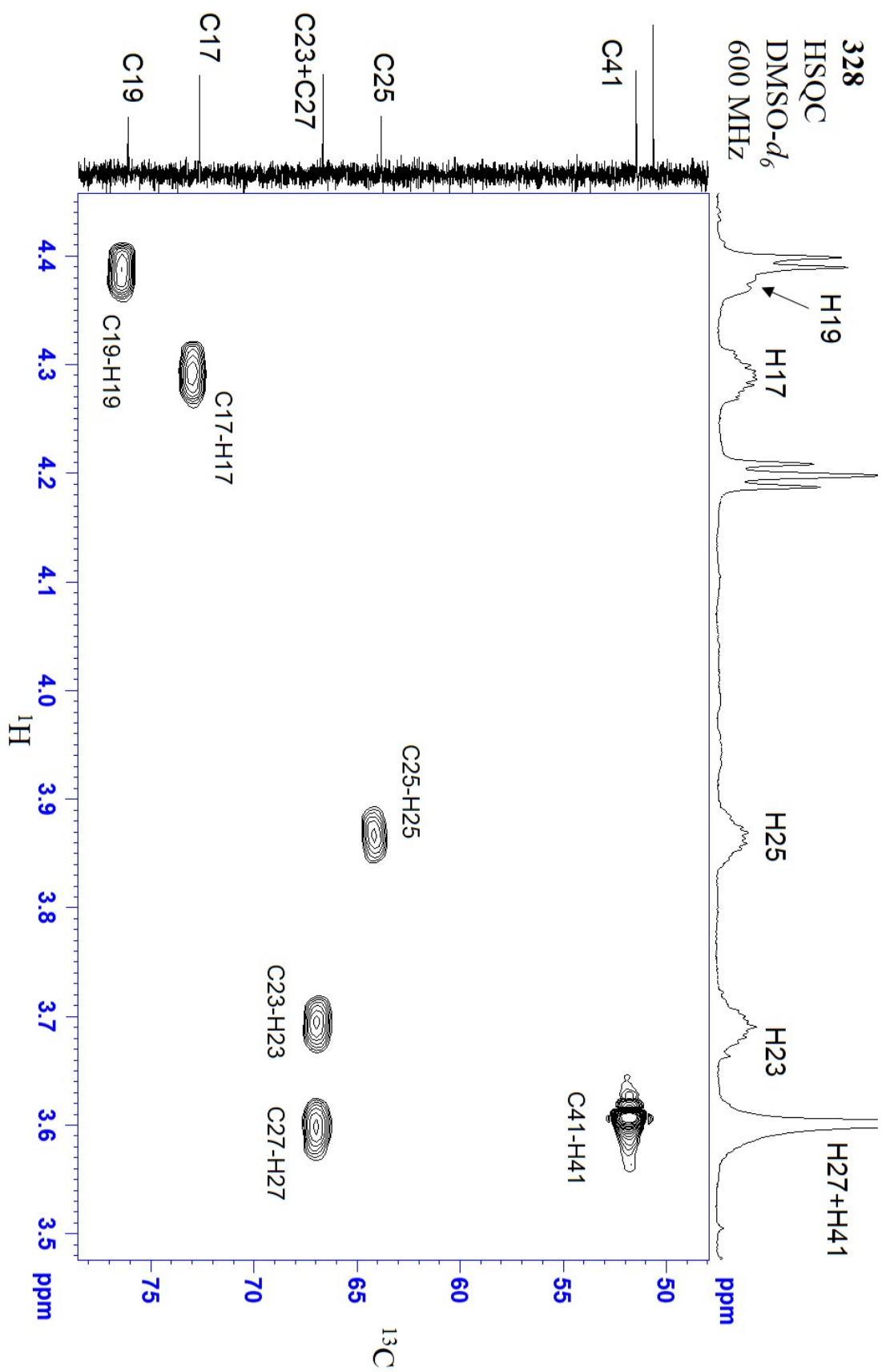
DQF ^1H - ^1H COSY spectrum of **28**



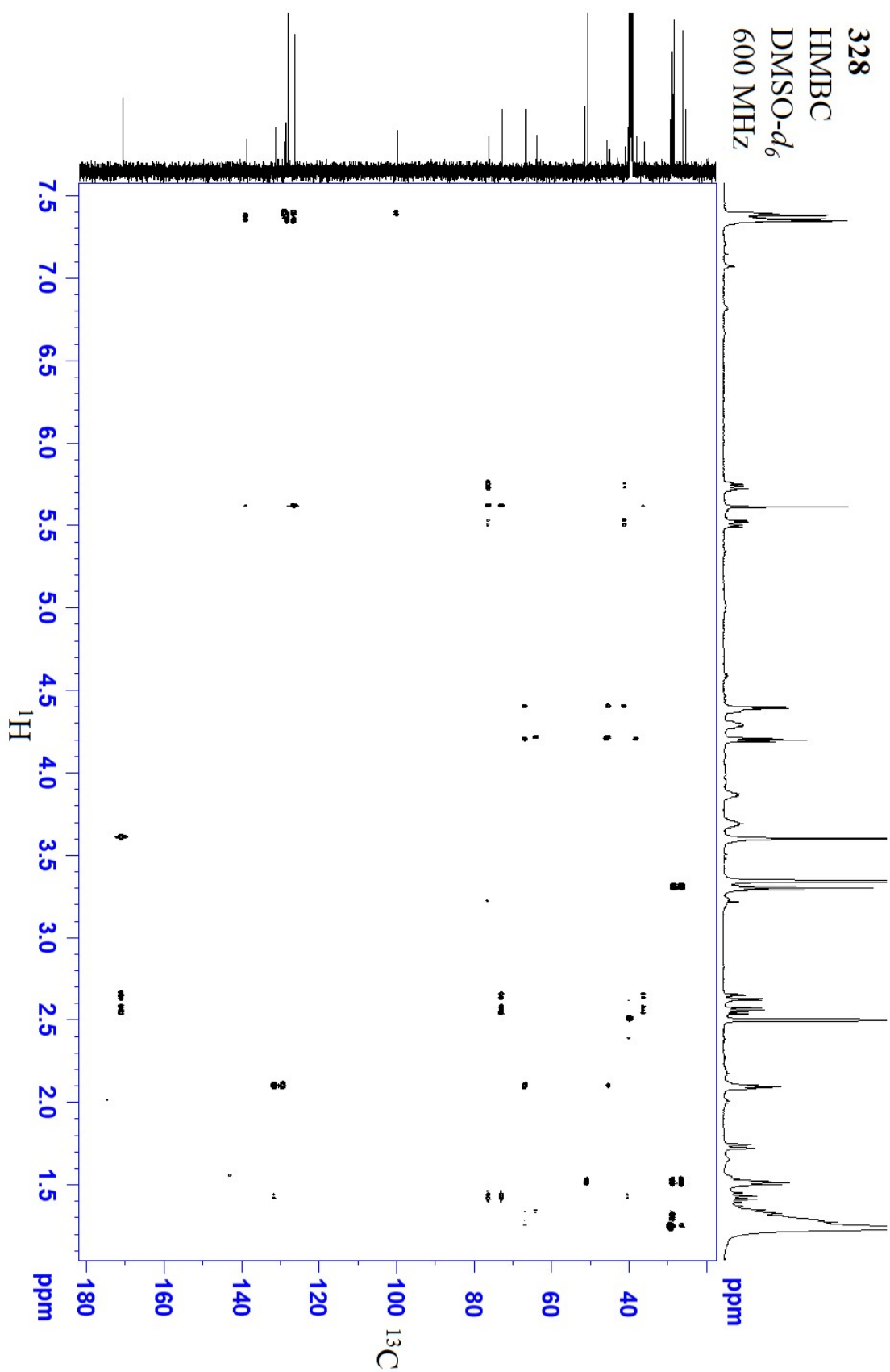
DQF ^1H - ^1H COSY spectrum of **28**



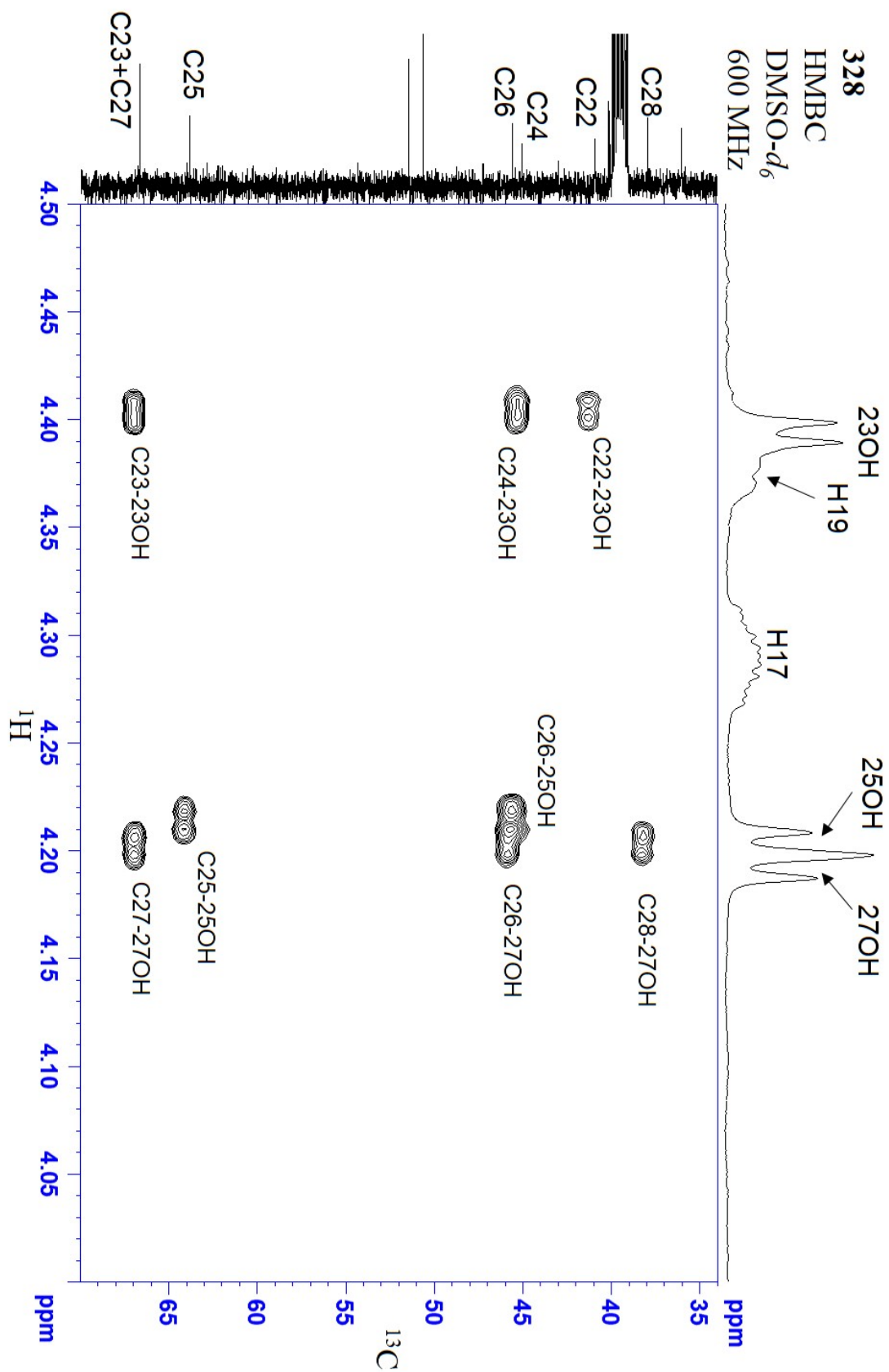
HSQC spectrum of **28**



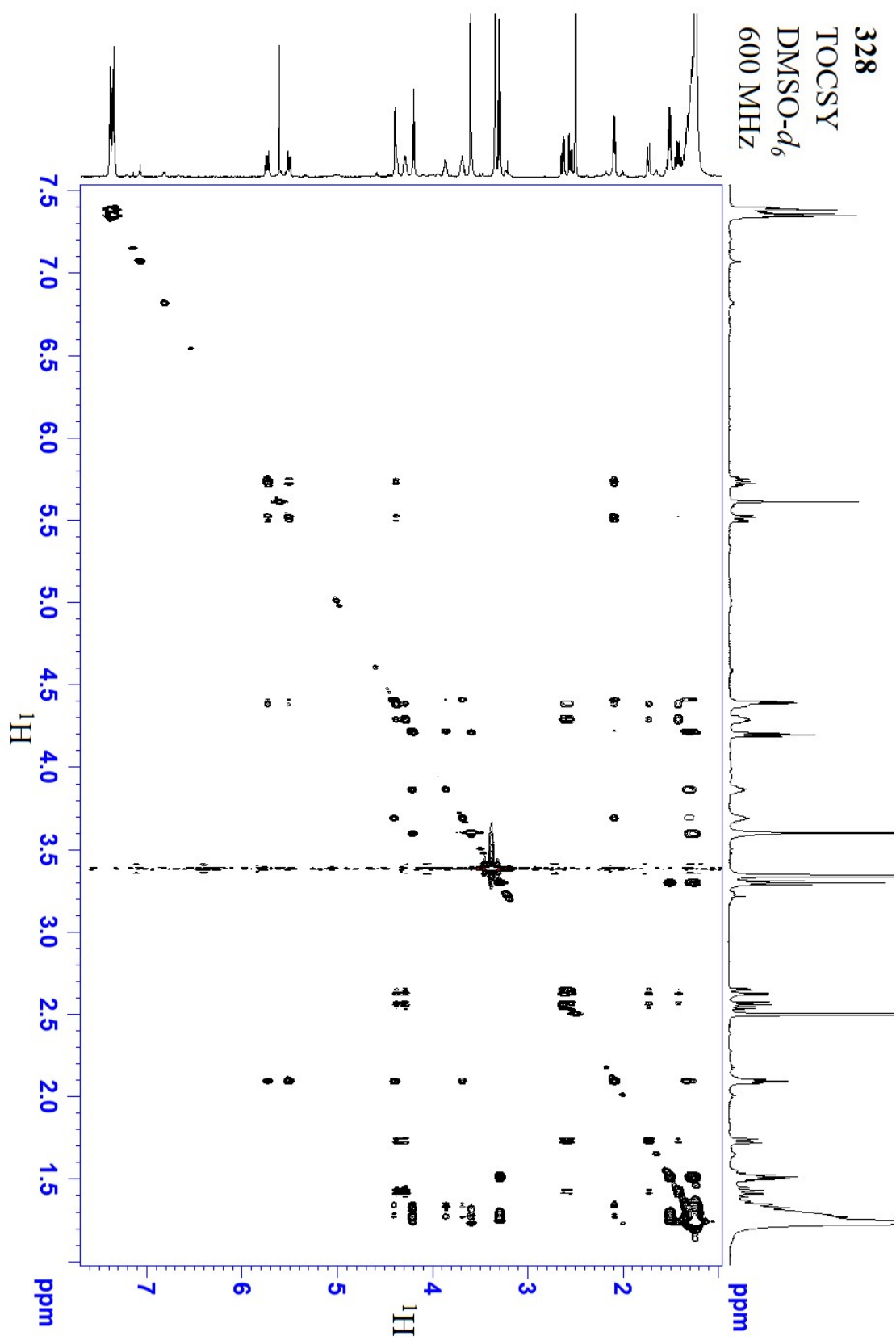
HSQC spectrum of **28**



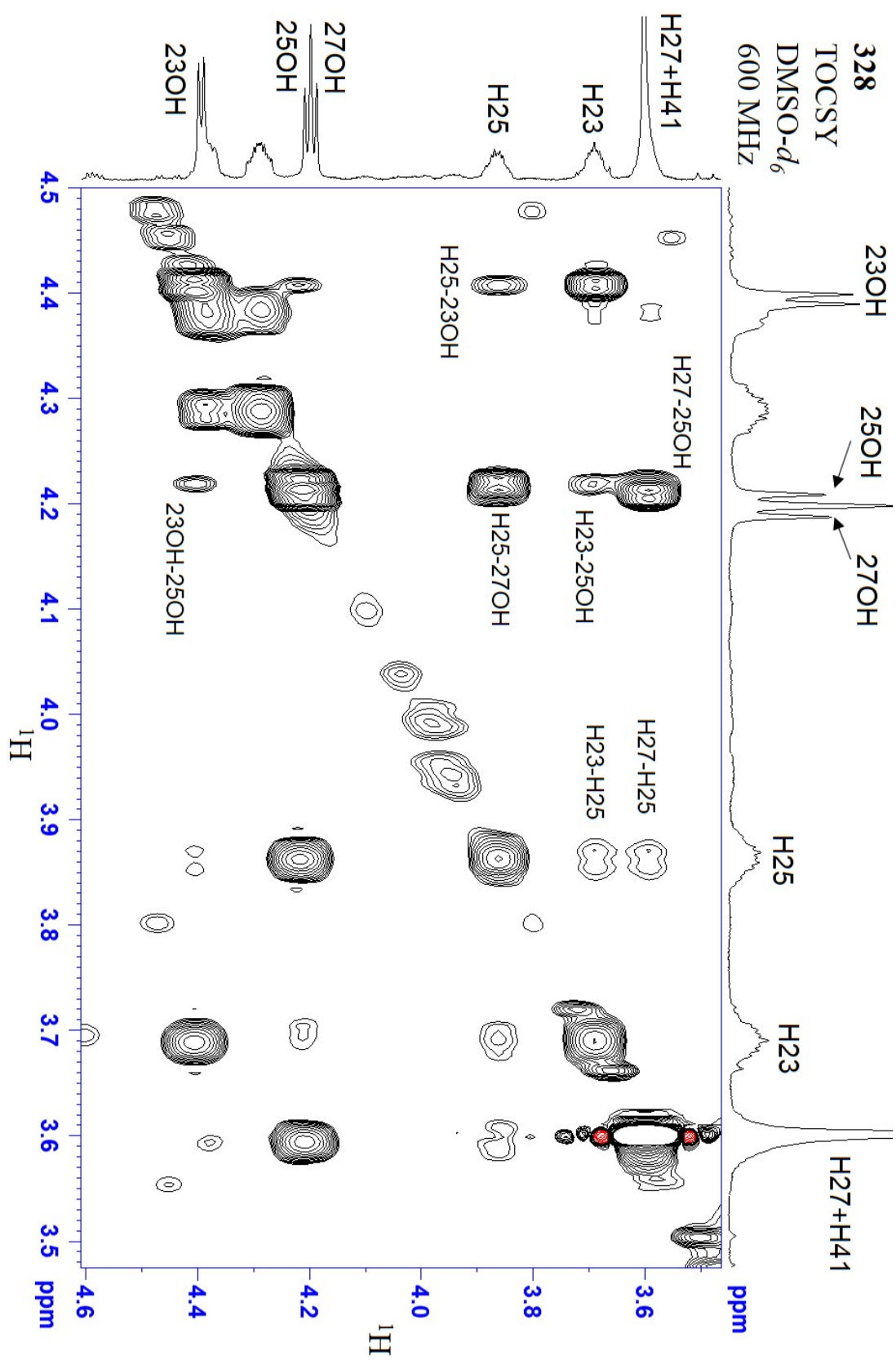
HMBC spectrum of **28**



HMBC spectrum of **28**

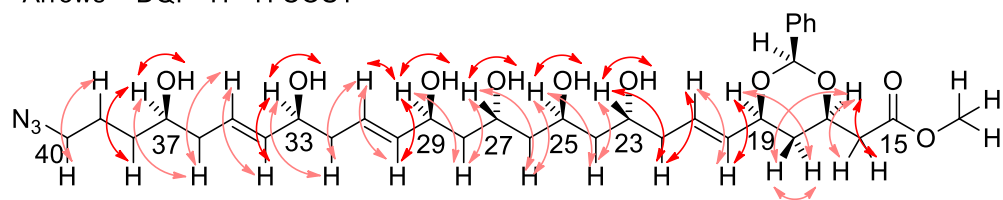


TOCSY spectrum of **28**



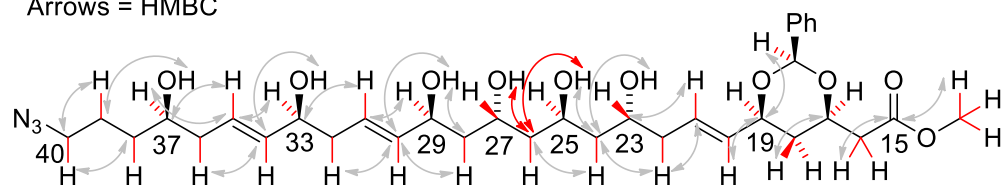
TOCSY spectrum of **28**

Arrows = DQF ^1H - ^1H COSY



Red Bonds = HSQC

Arrows = HMBC



Arrows = TOCSY

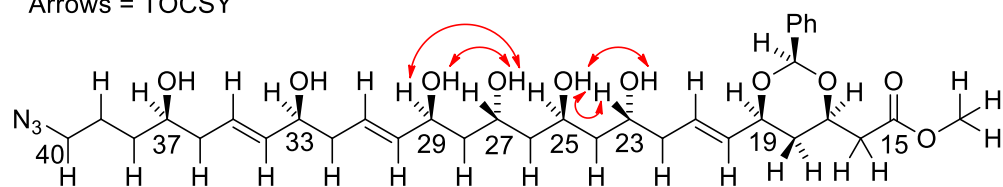
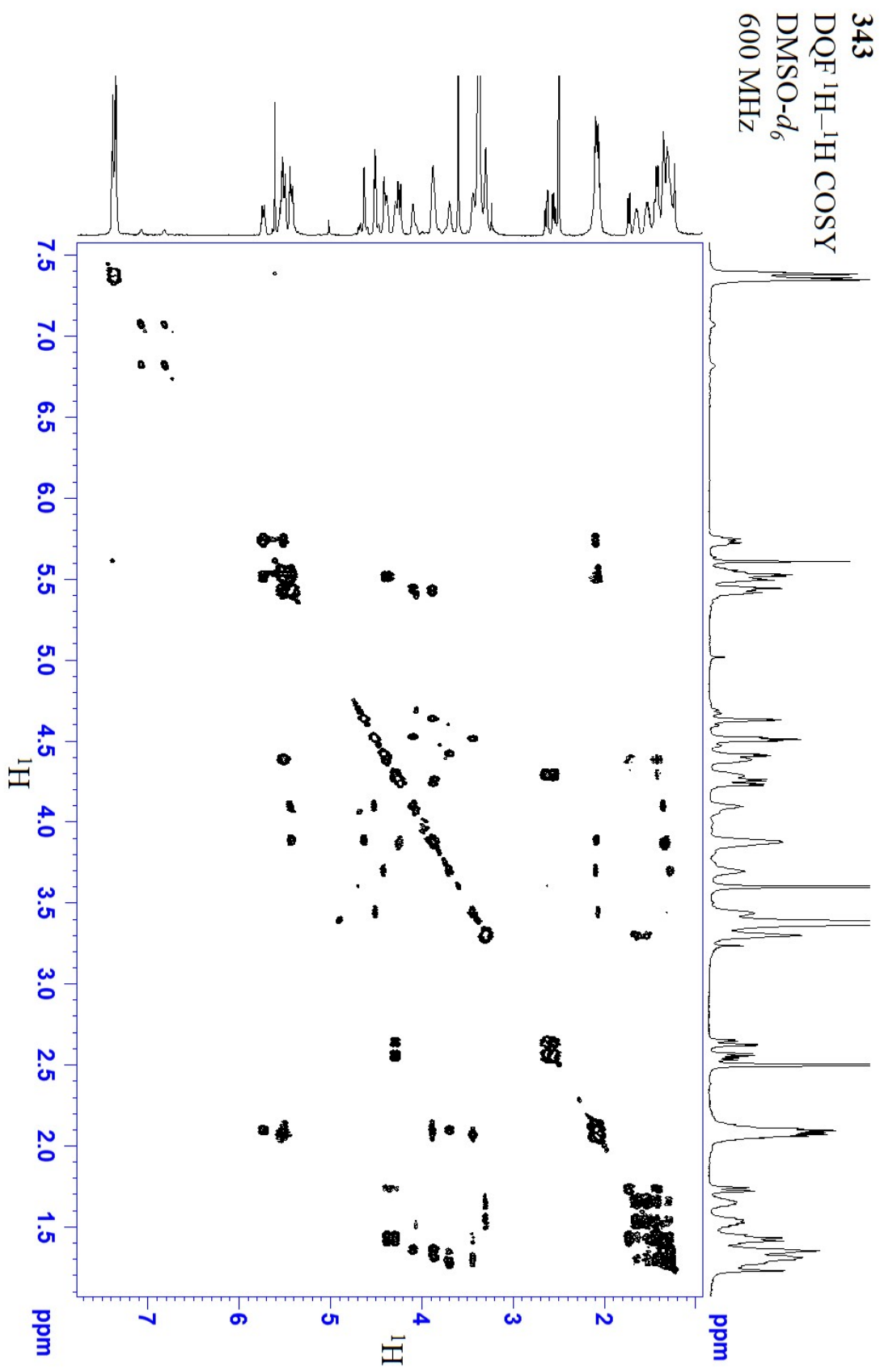
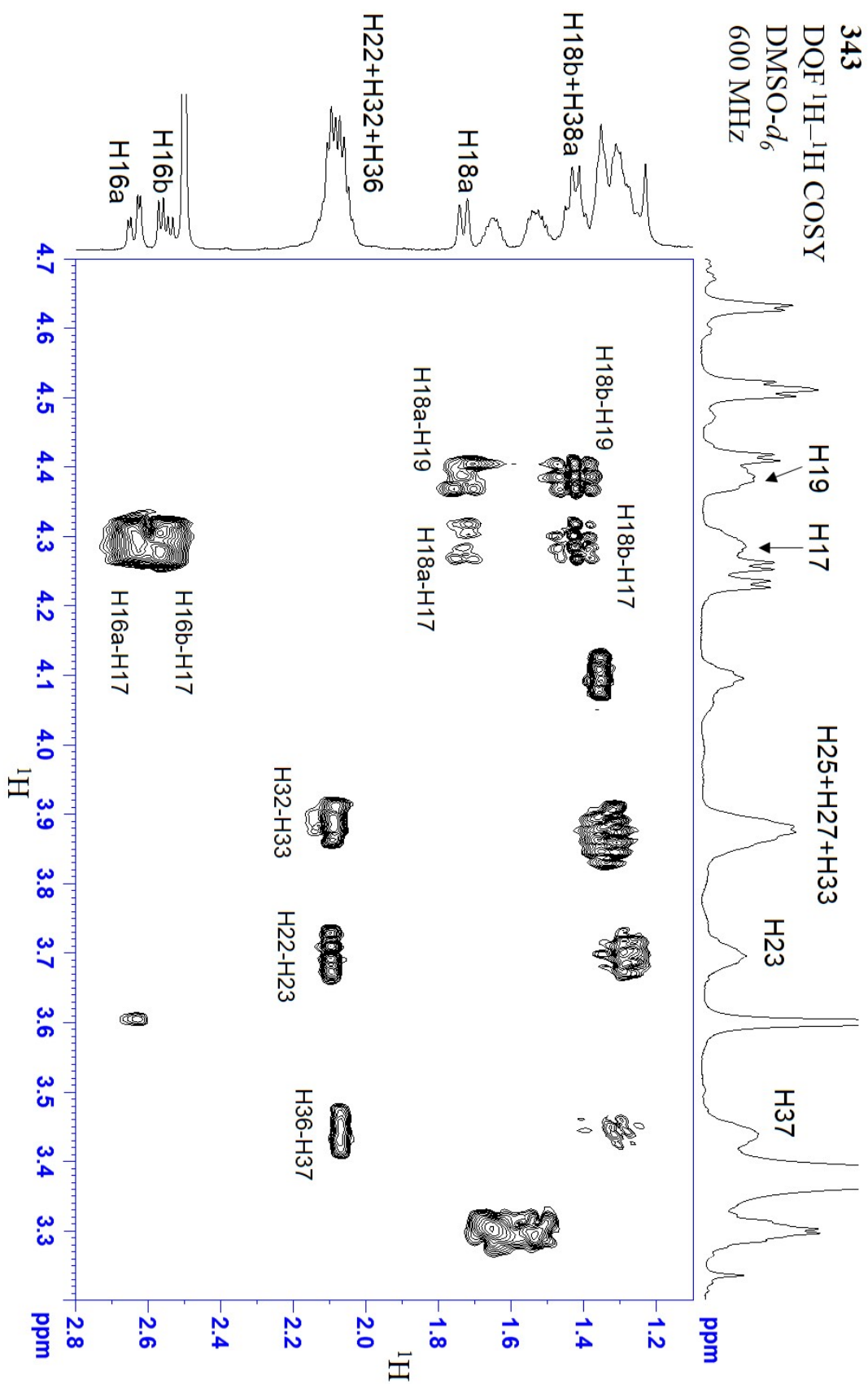
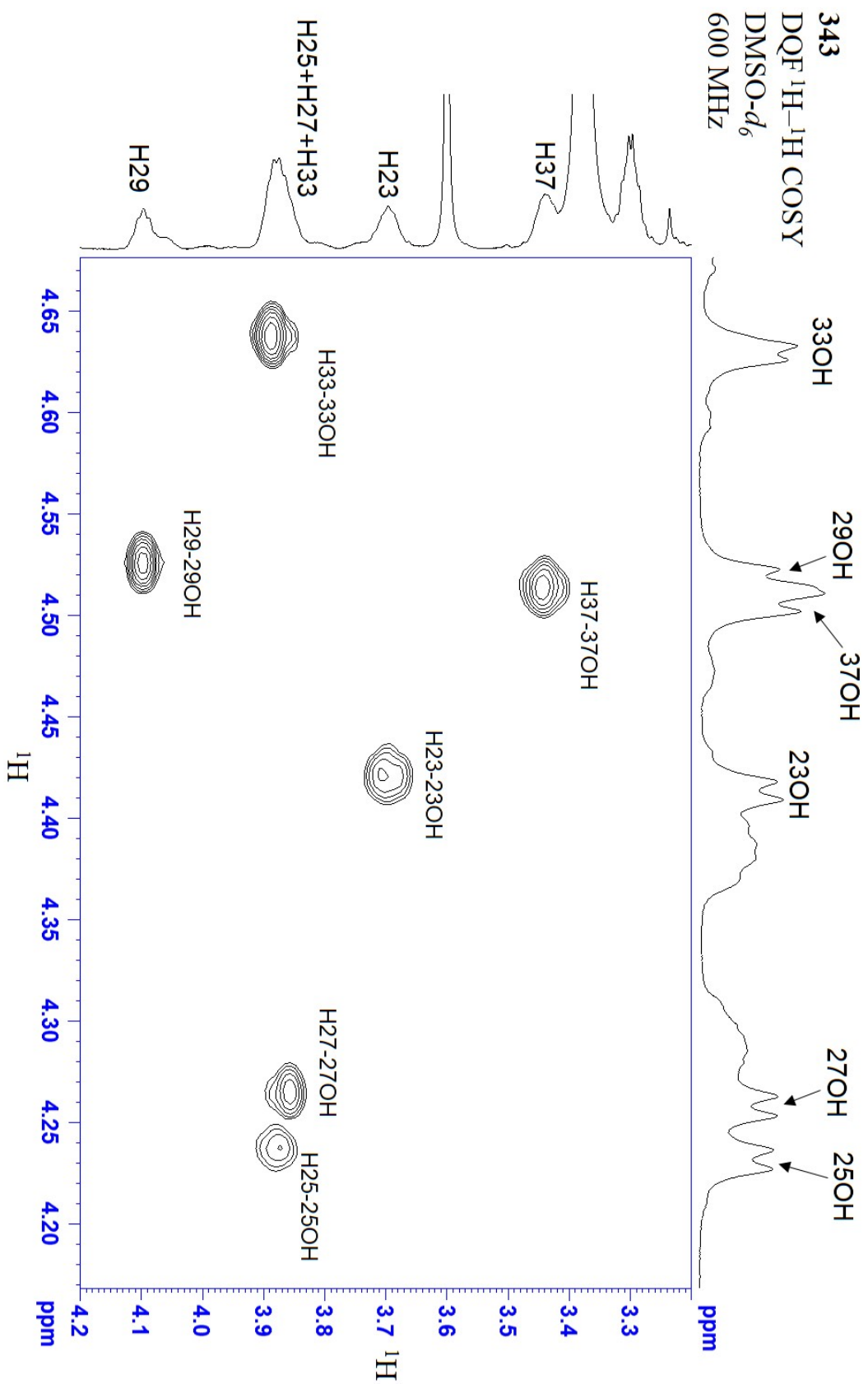


Figure S3: Diagnostic 2D NMR correlations of **35** (C15-C40 fragment of tetrafibricin)

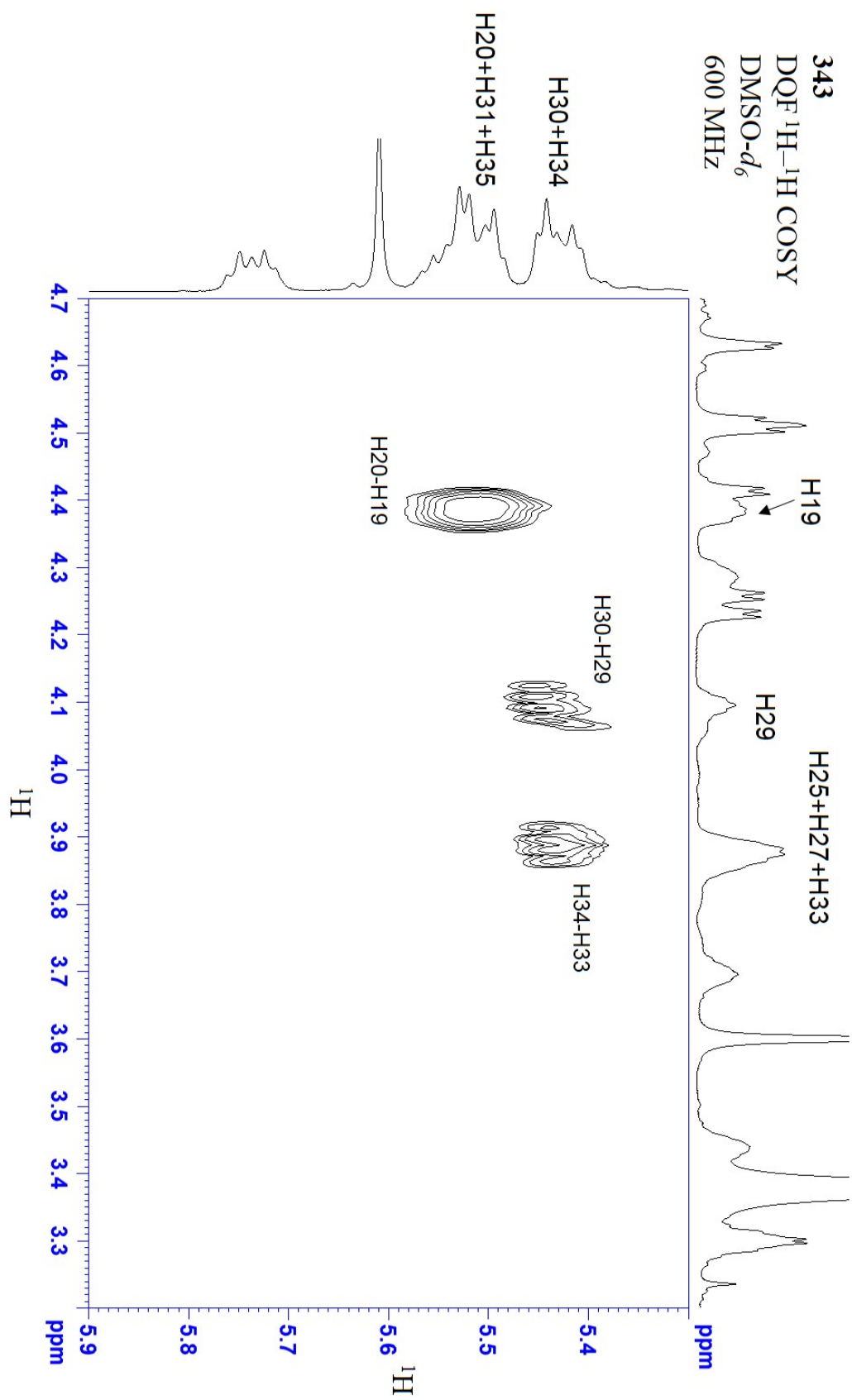


DQF ^1H - ^1H COSY spectrum of **35**

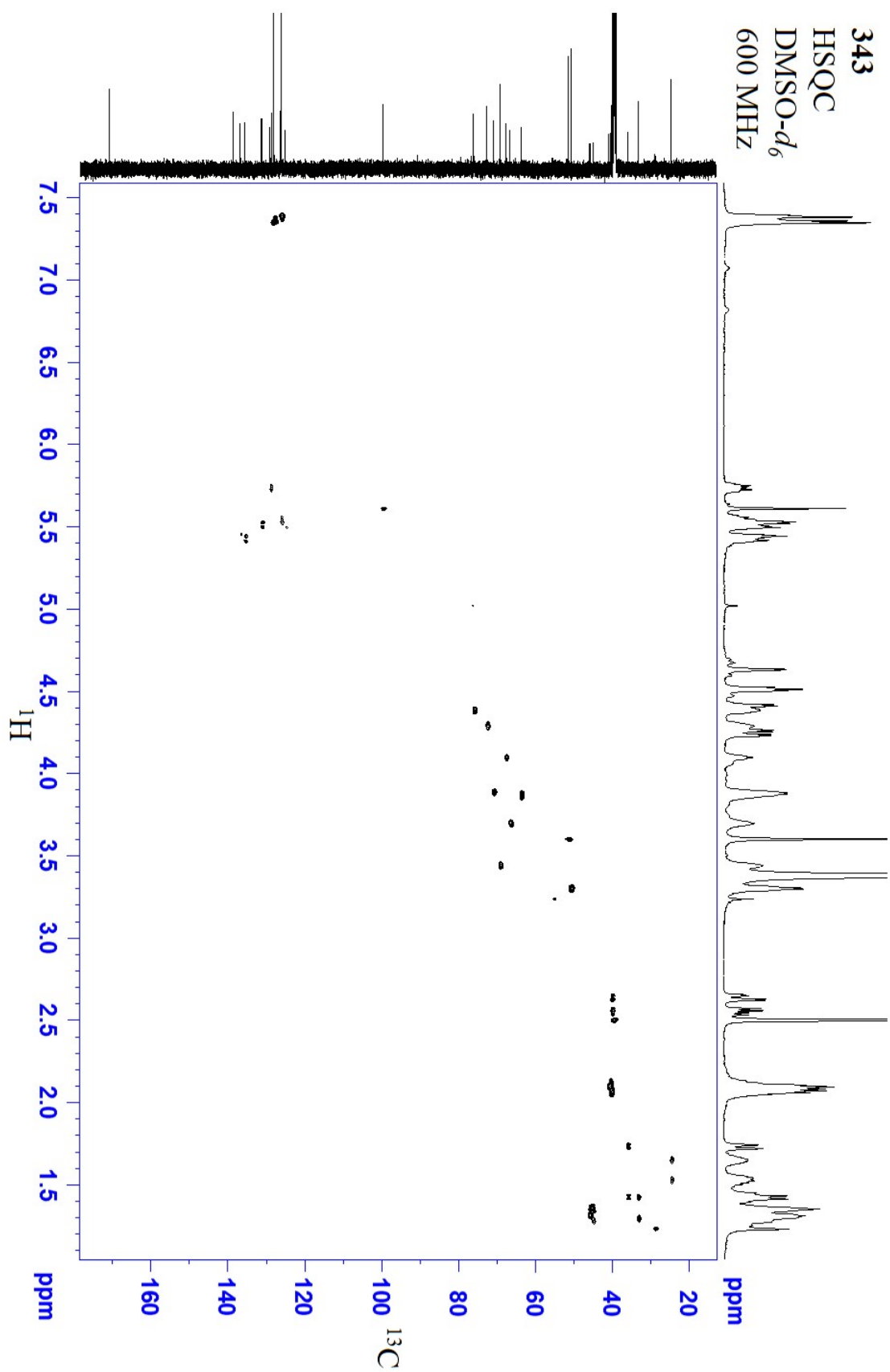
DQF ^1H - ^1H COSY spectrum of **35**



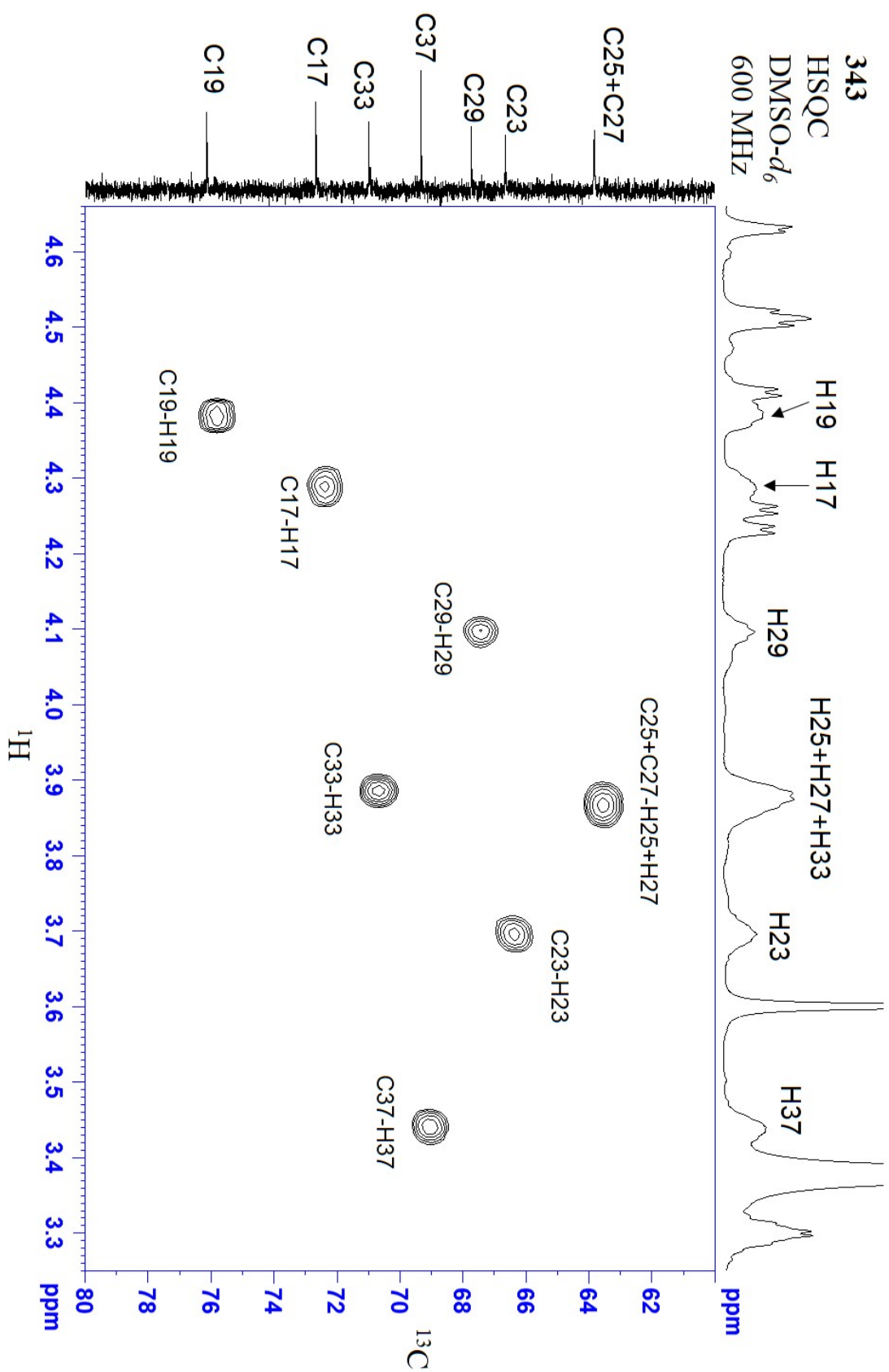
DQF ^1H - ^1H COSY spectrum of **35**



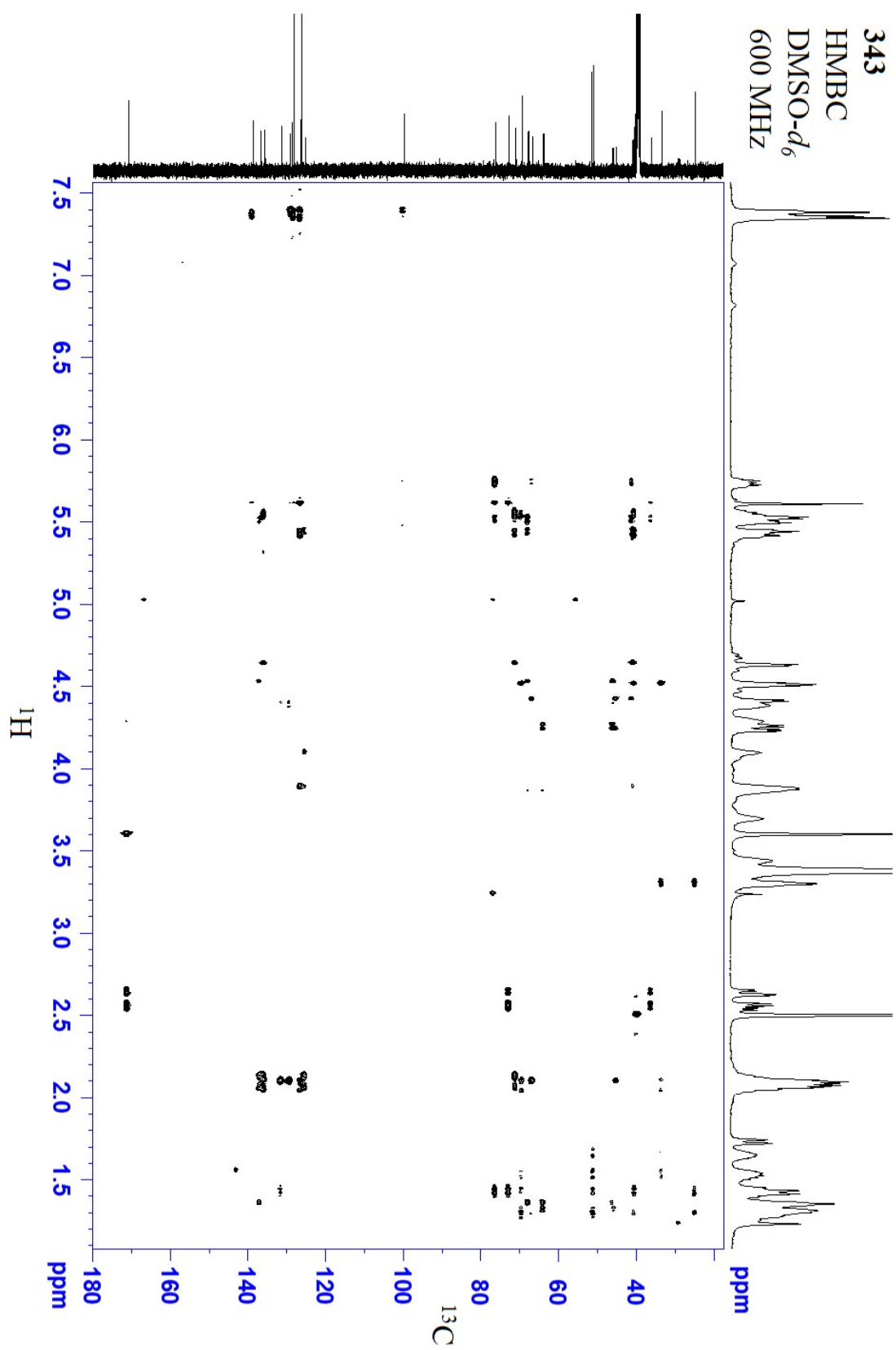
DQF ^1H - ^1H COSY spectrum of **35**



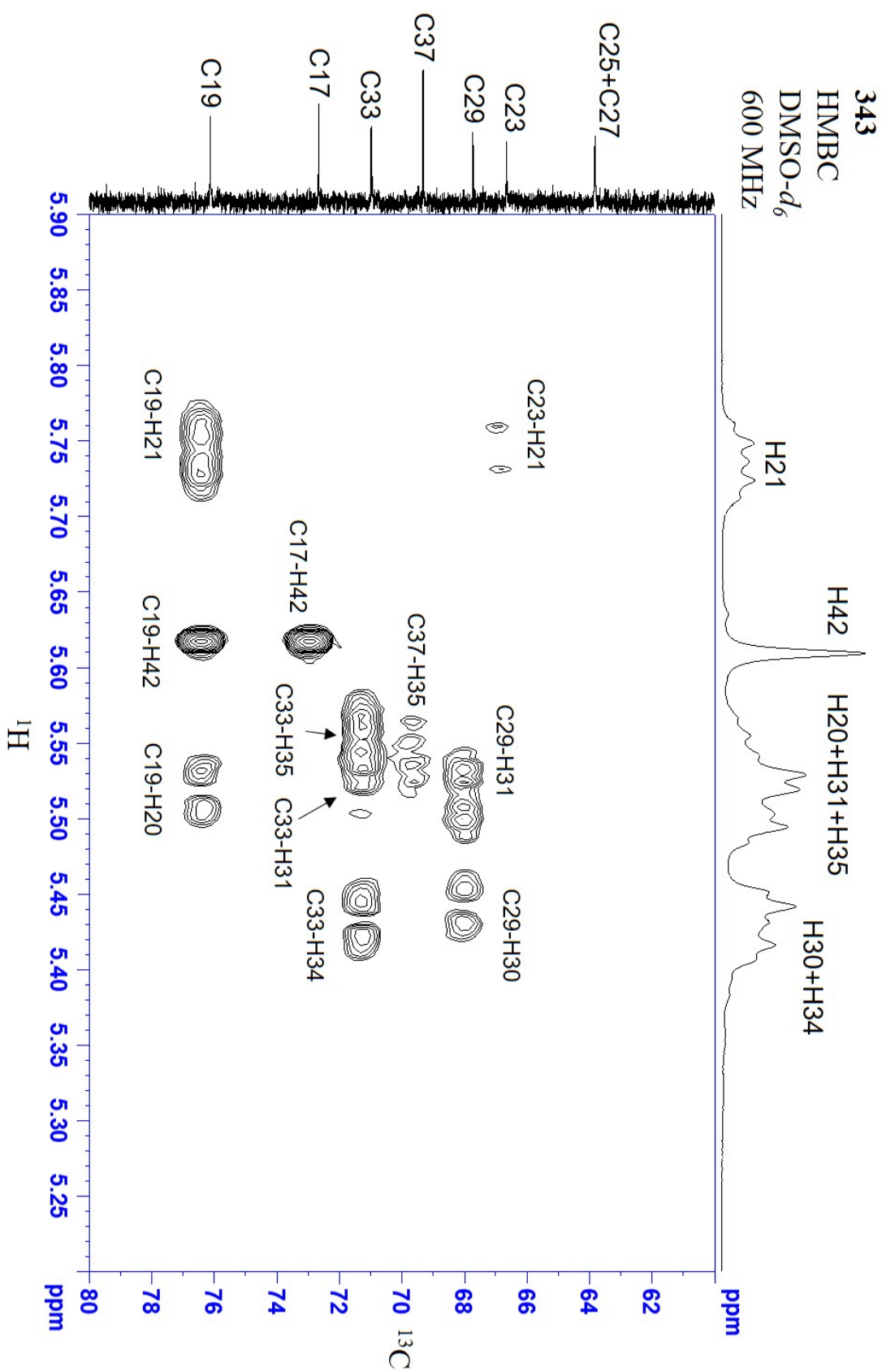
HSQC spectrum of **35**

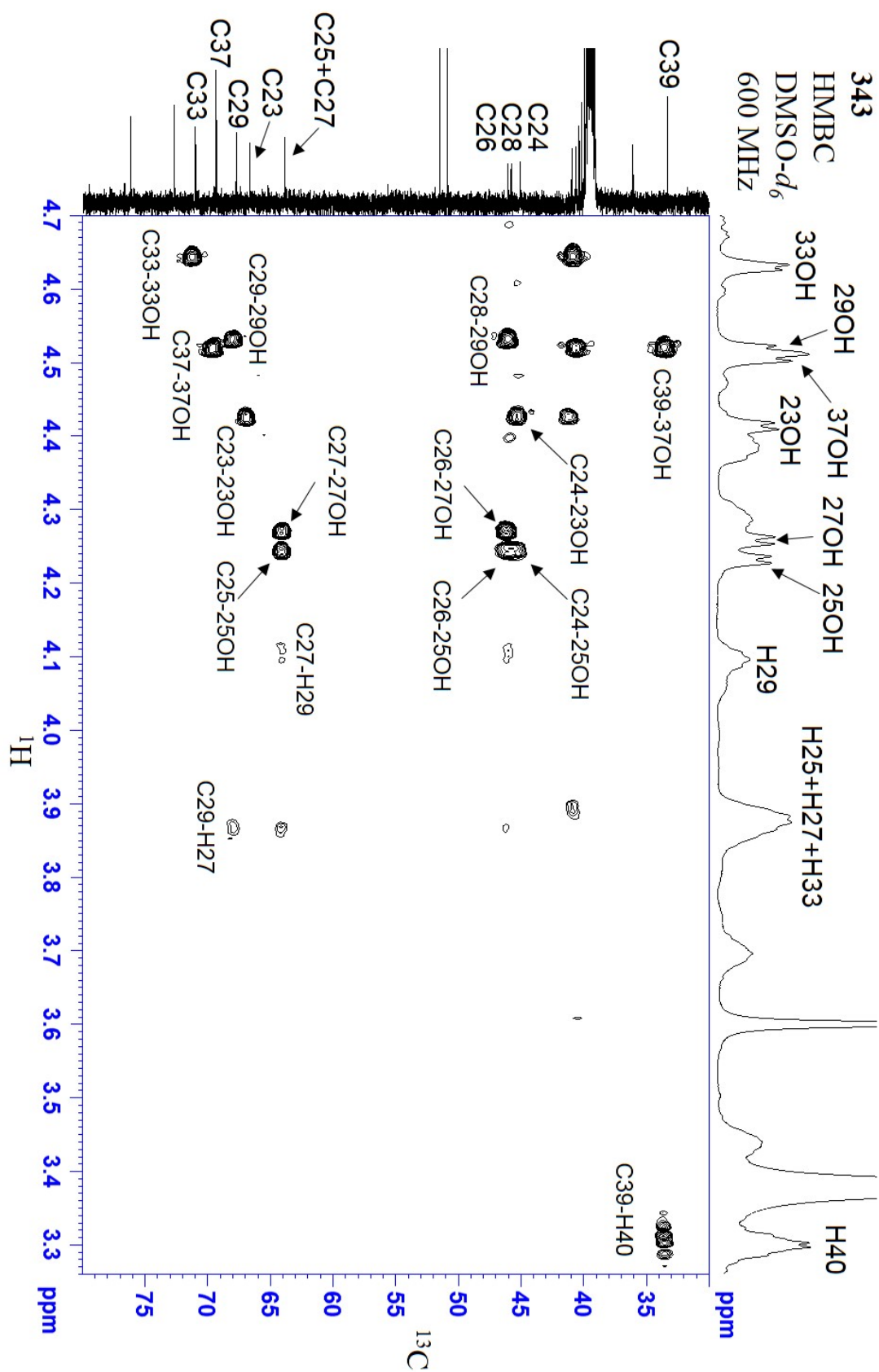


HSQC spectrum of **35**

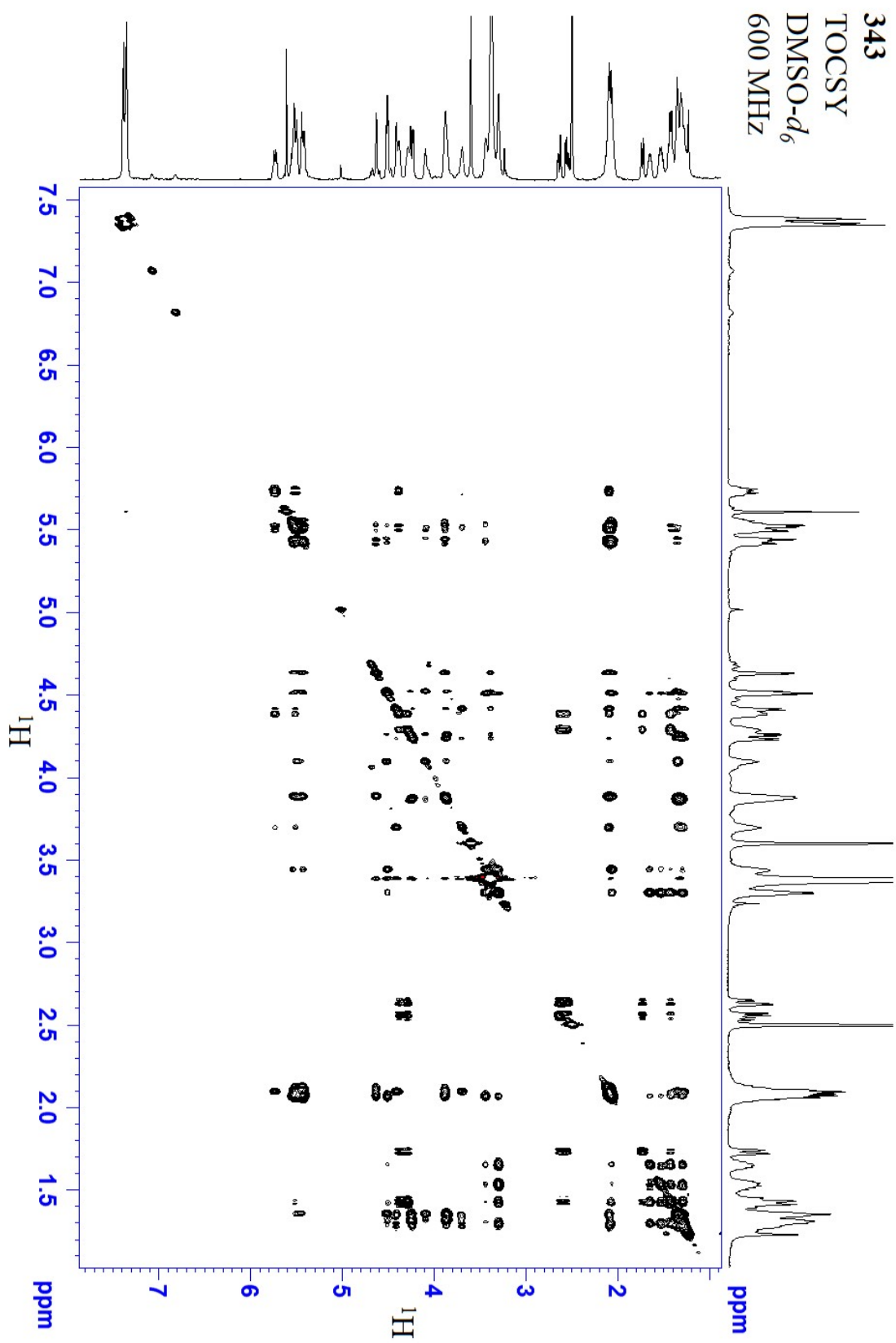


HMBC spectrum of 35

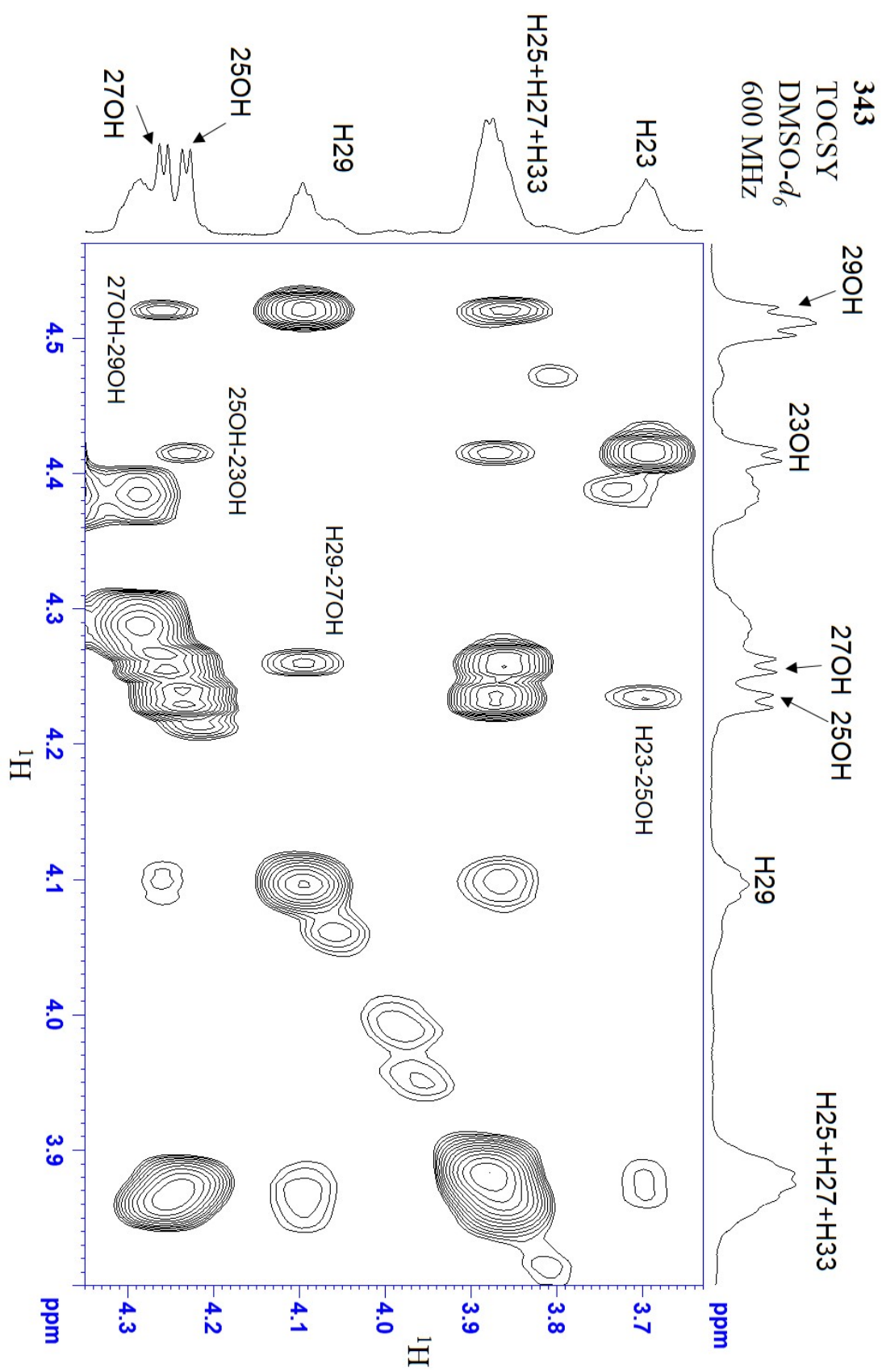
HMBC spectrum of **35**



HMBC spectrum of **35**



TOCSY spectrum of **35**



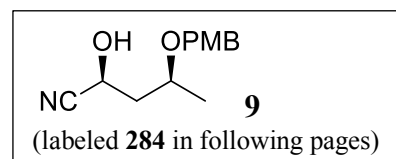
TOCSY spectrum of **35**

Diastereomer Ratios and Configuration Assignments

Compound 9: Diastereoselective Cyanation

¹H NMR spectrum of purified minor diastereomer

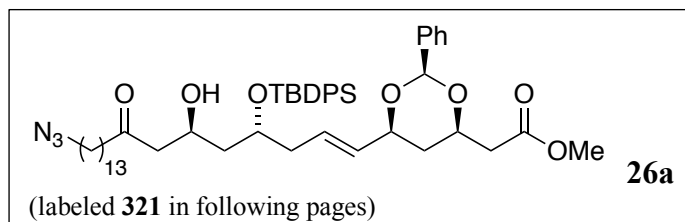
¹H NMR integration: Diastereomer ratios before separation



Compound 26a: Model Mukaiyama Aldol with TBDPS

¹H NMR integration: Ratios of all four products before separation

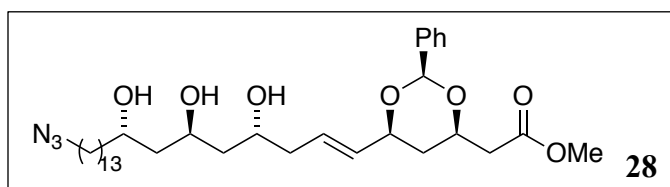
¹H NMR integration: Diastereomer ratios after separation of kinetic and thermodynamic products



Compound 41a and 41b: Acetonide Derivatives of 1,3,5-Triol 28

(labeled **327a** and **327b** in following pages)

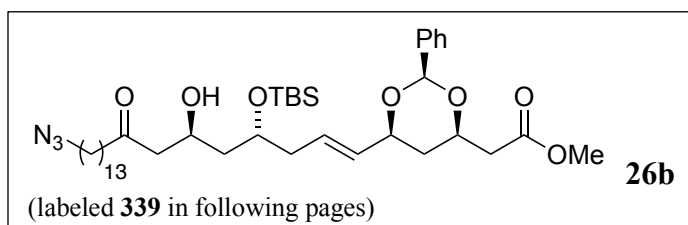
DEPT spectrum showing *anti,anti* configuration (acetonide methyl groups at ca. 25 ppm)



Compound 26b: Model Mukaiyama Aldol with TBS

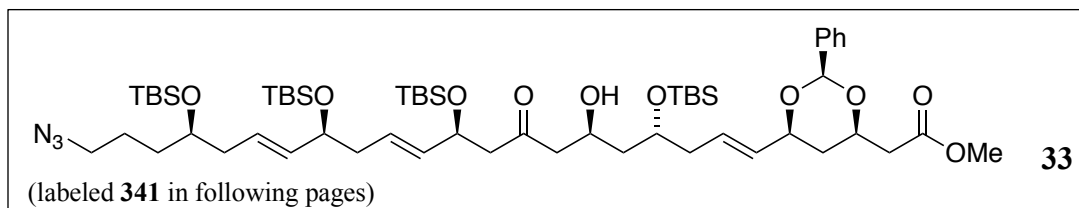
¹H NMR integration: Ratios of all four products before separation

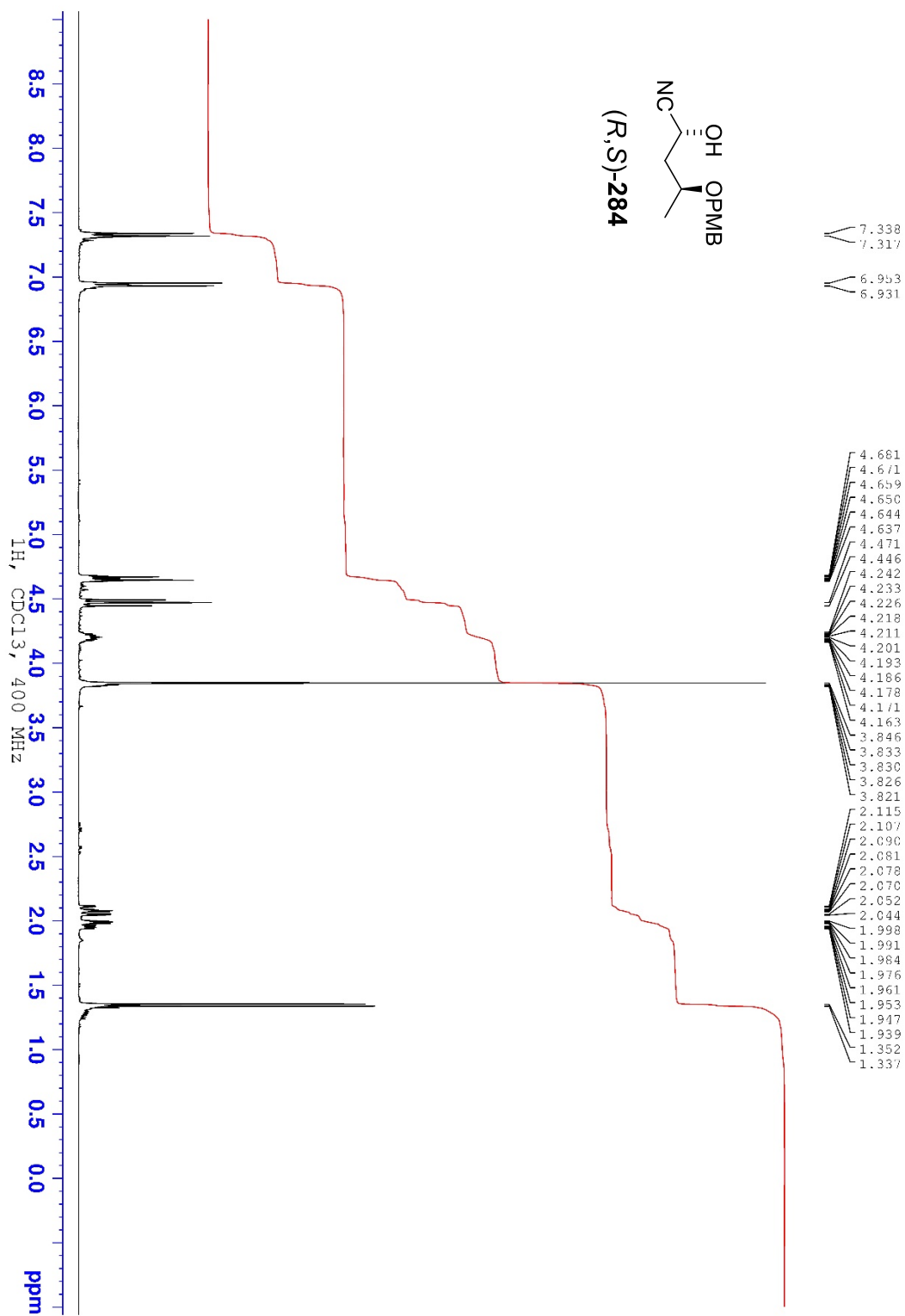
¹H NMR integration: Diastereomer ratios after separation of kinetic and thermodynamic products



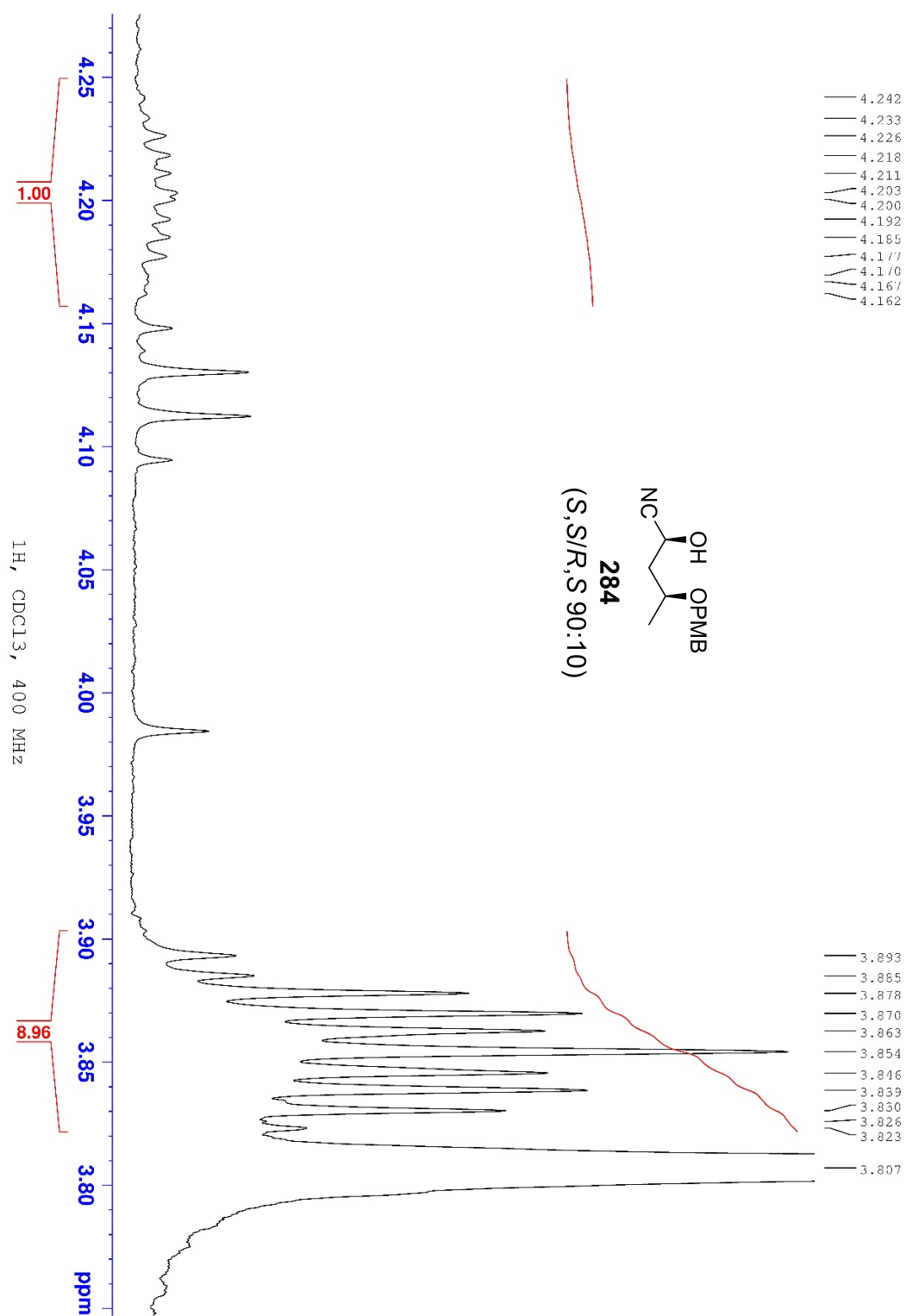
Compound 33: Mukaiyama Aldol (fully functionalized)

¹H NMR integration: Diastereomer ratio

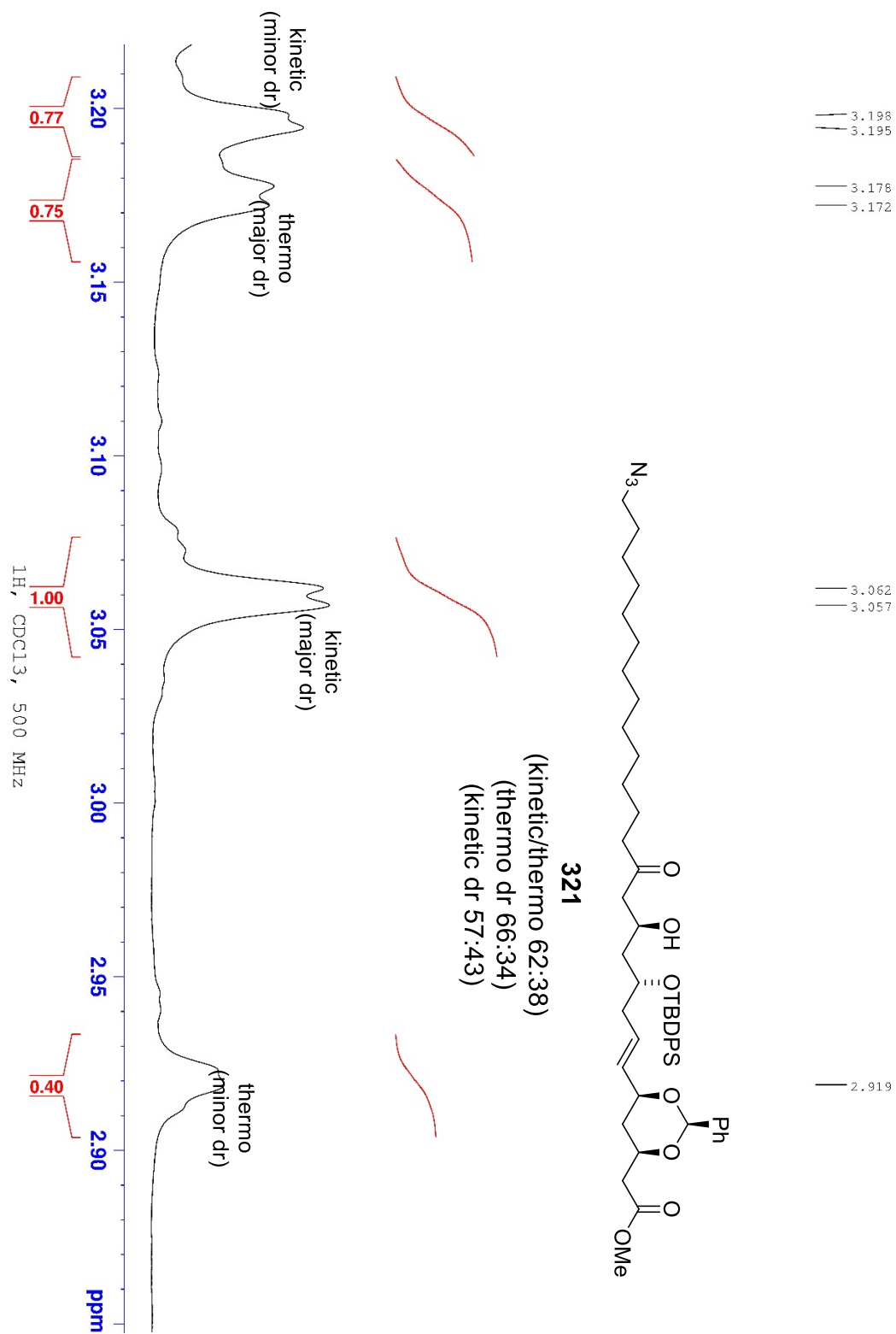




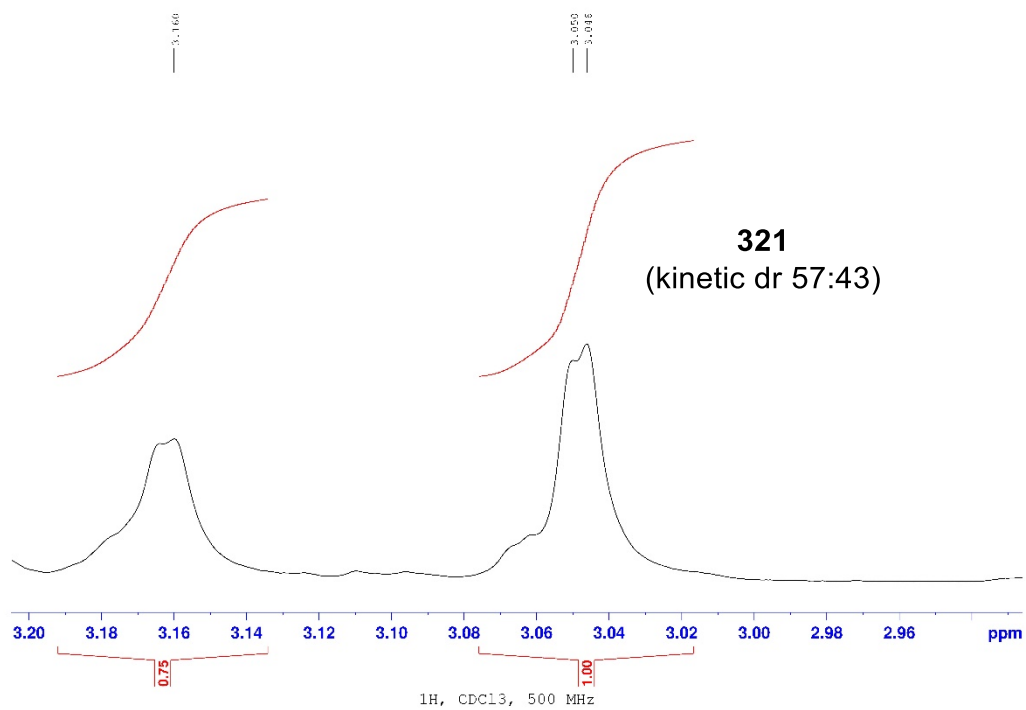
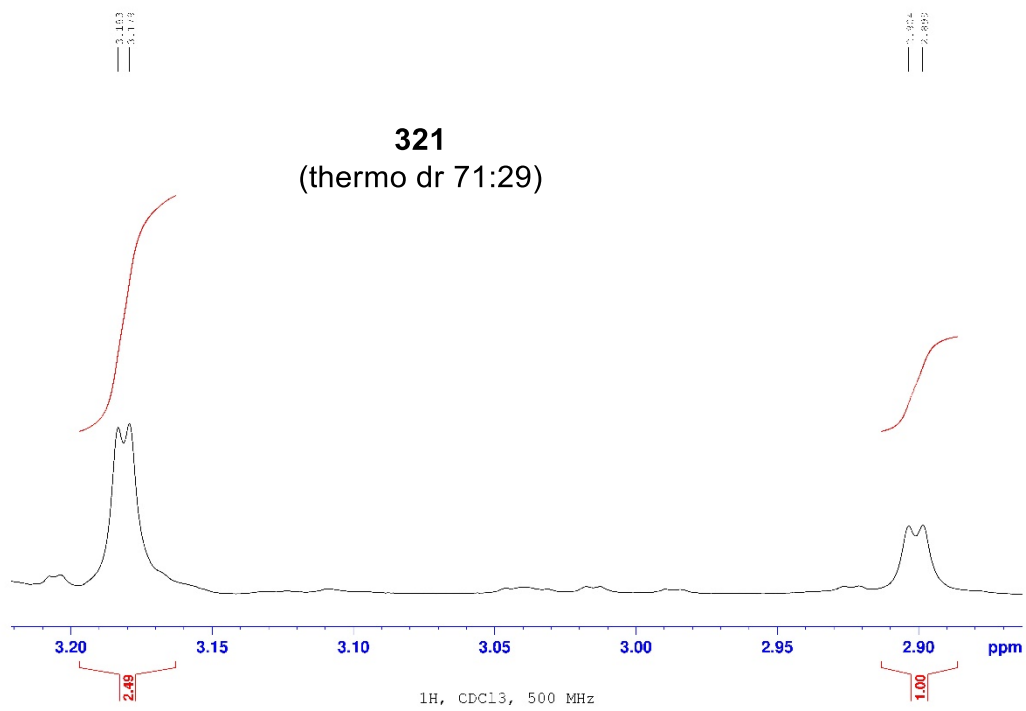
HNMR of the authentic minor diastereomer of **9**



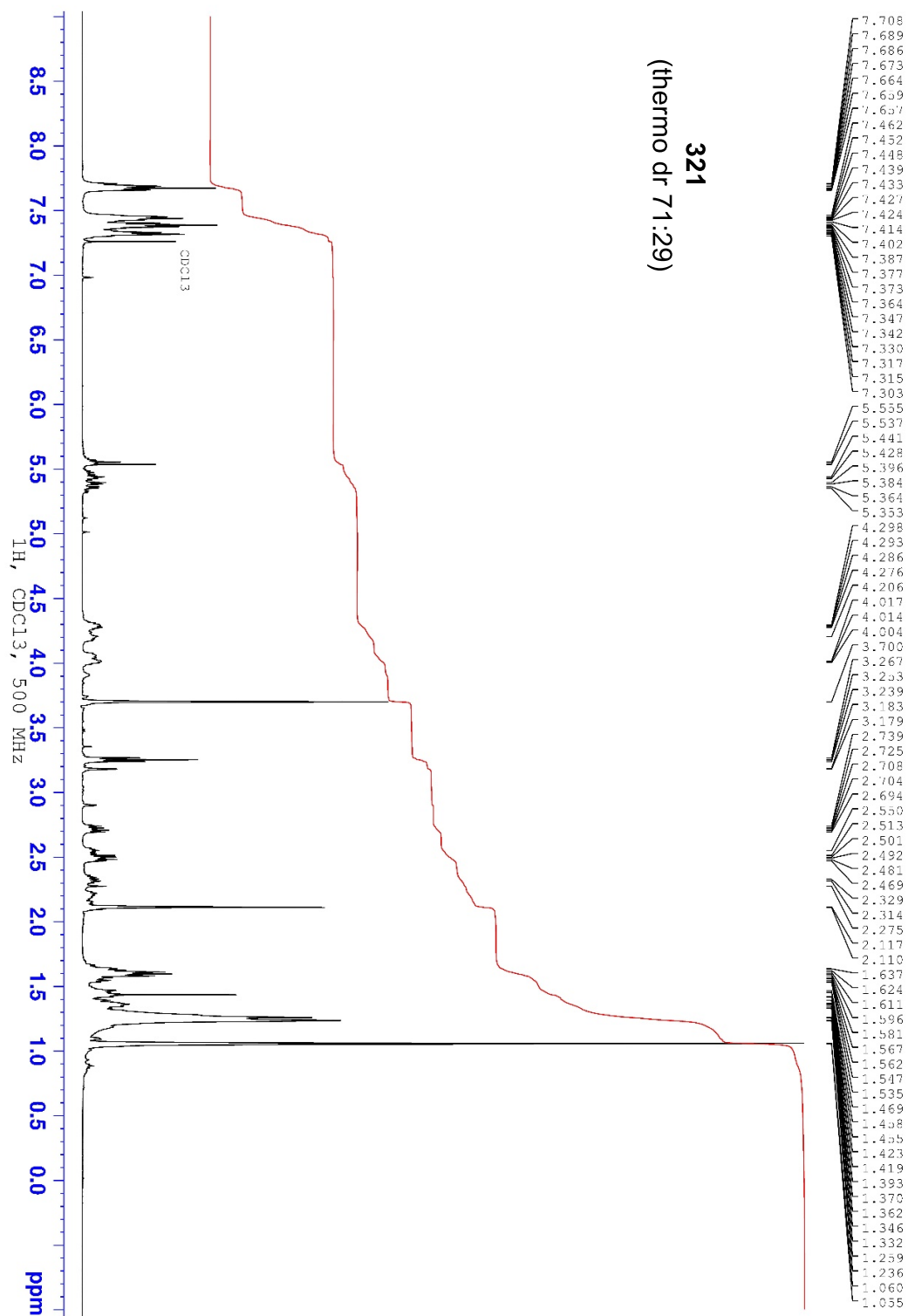
¹H NMR of **9**, integration of 90:10 mixture



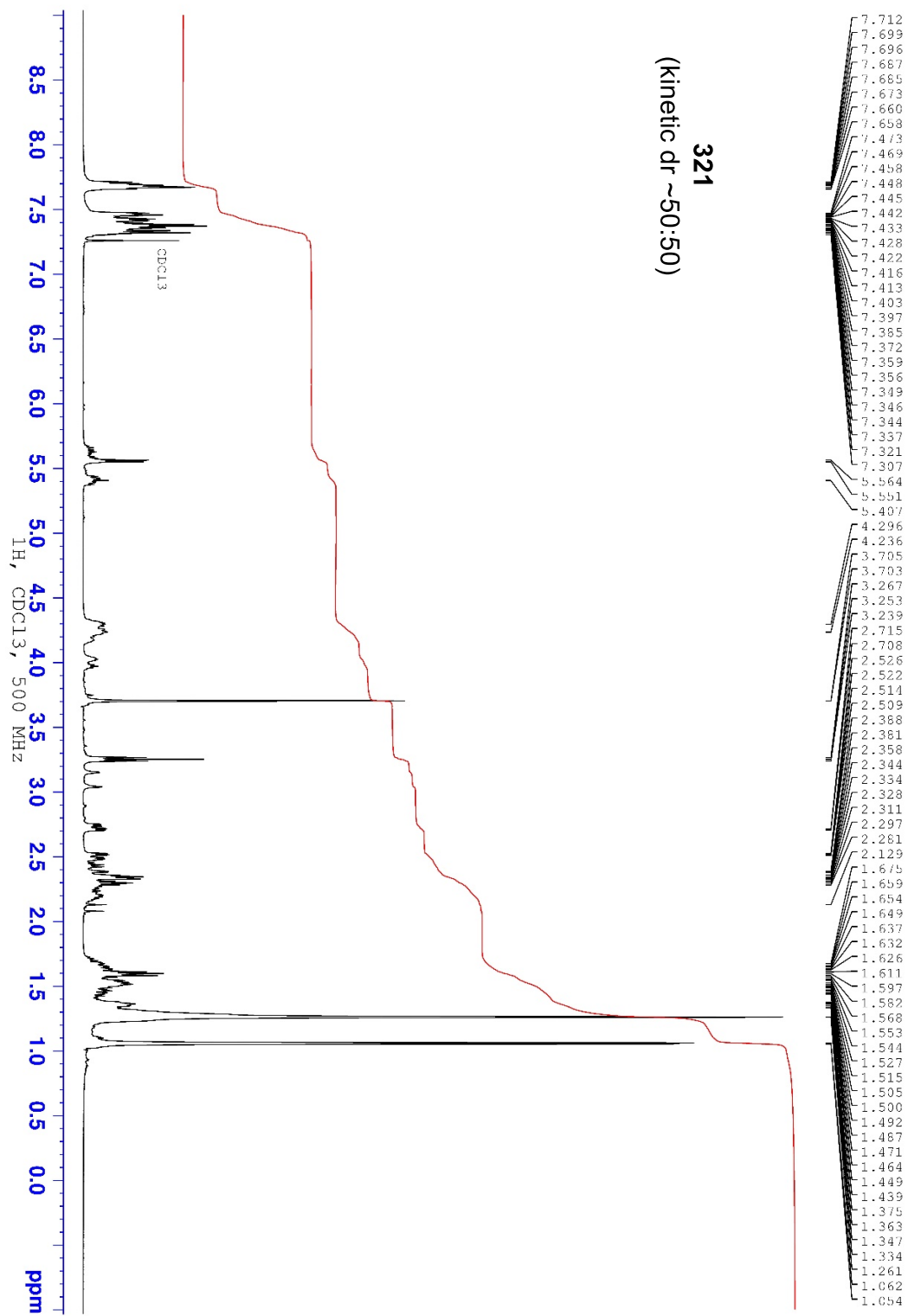
HNMR of **26a** product mixture



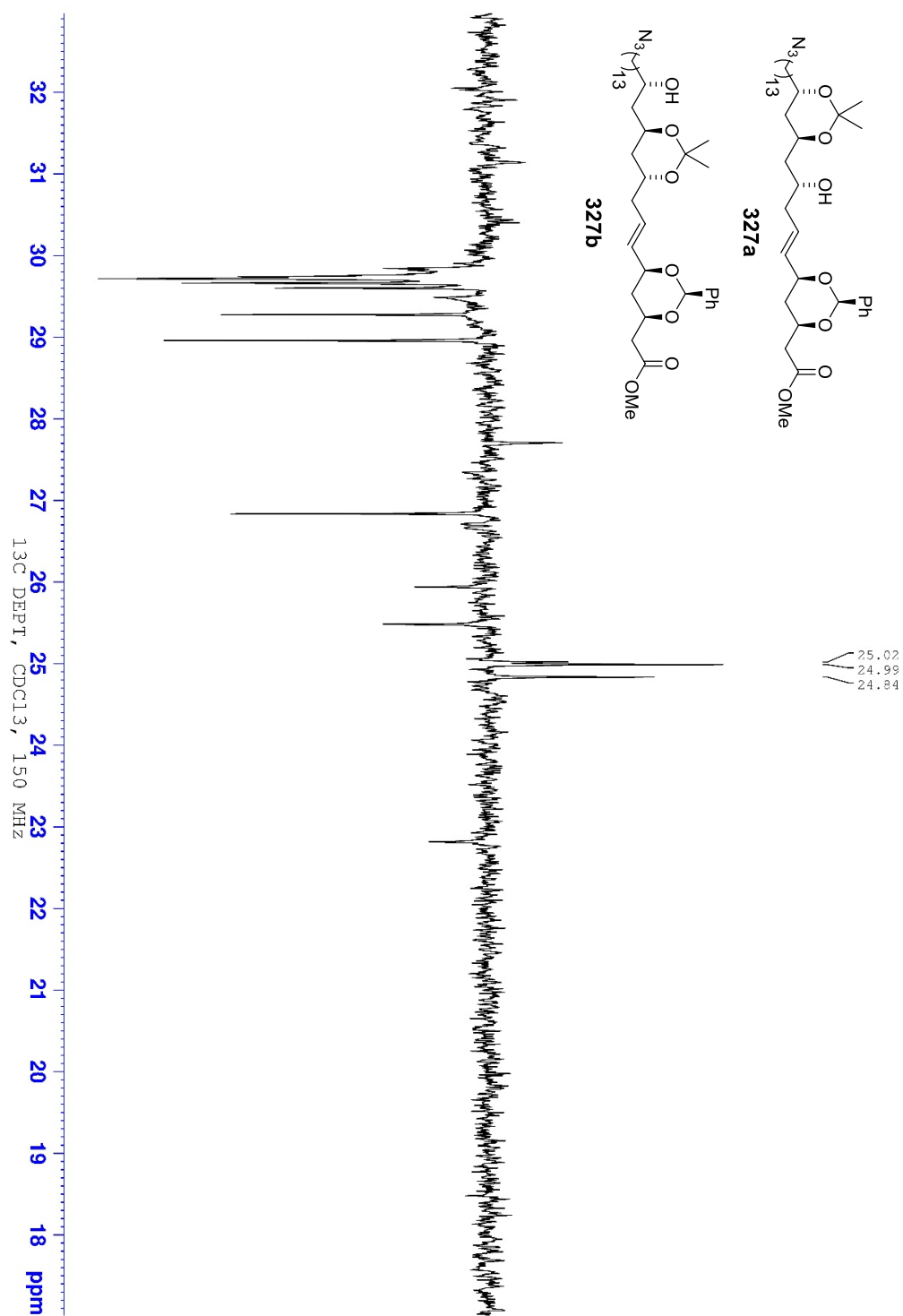
HNMR of **26a** after separation of kinetic and thermodynamic enolate products



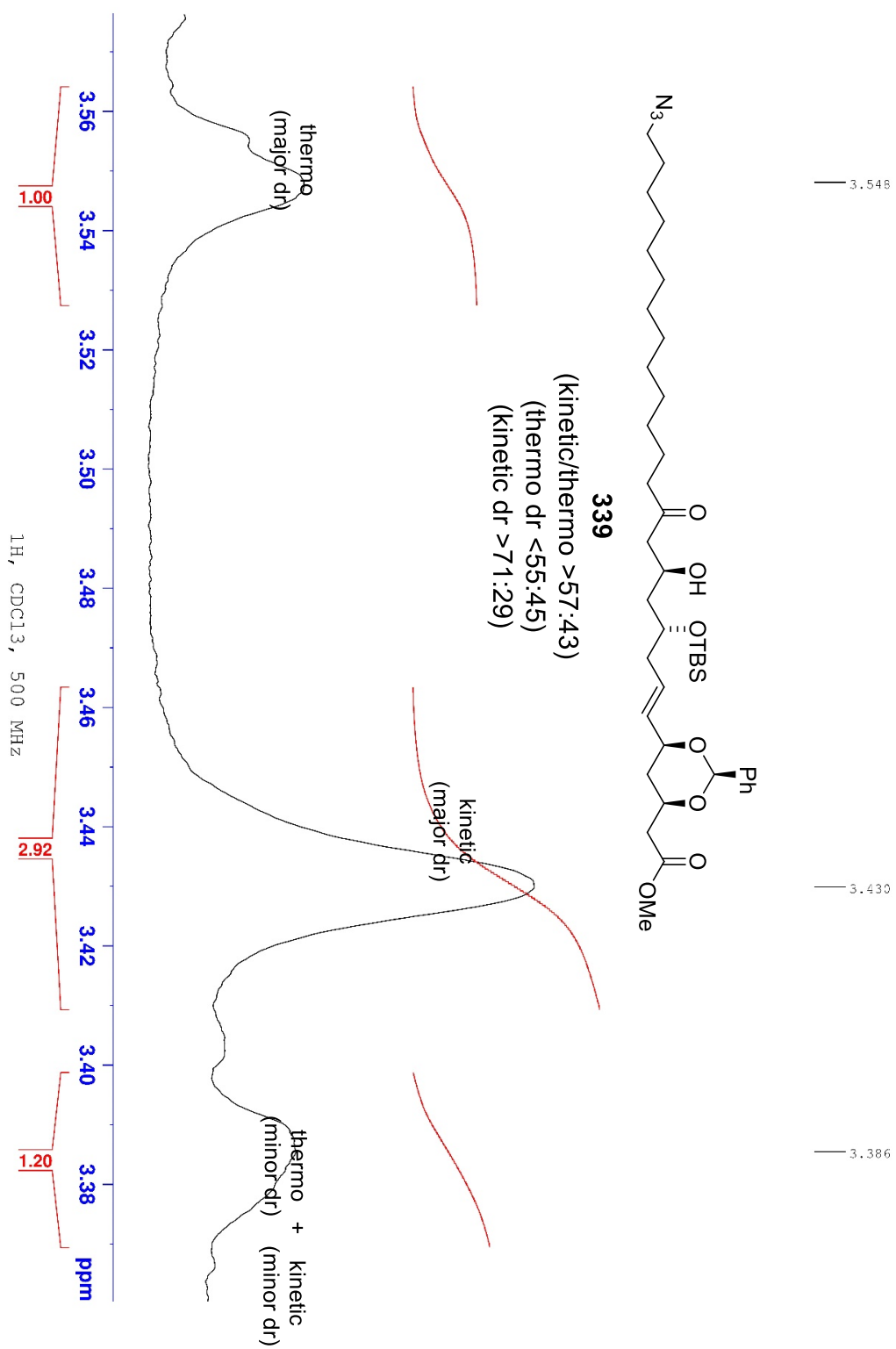
HNMR of **26a**, thermodynamic enolate product



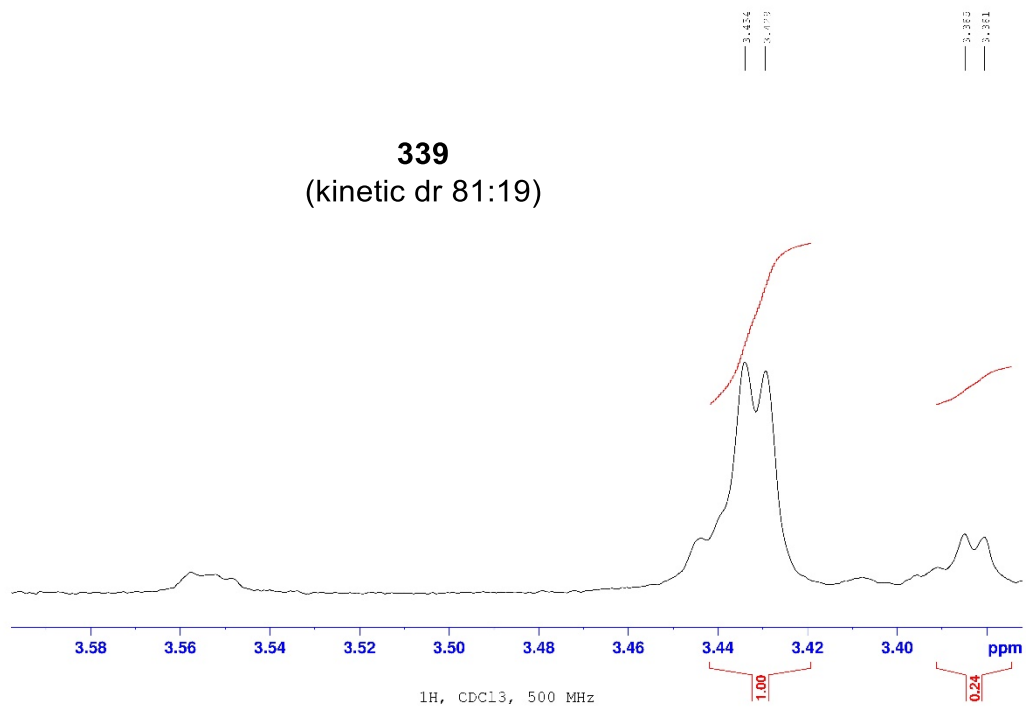
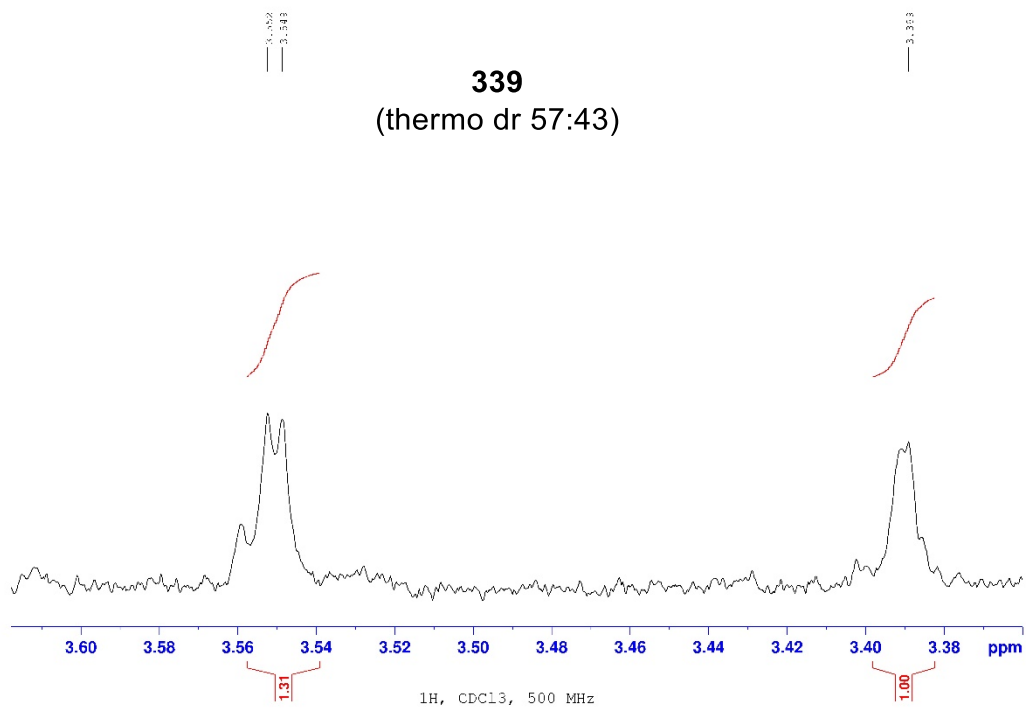
HNMR of **26a**, kinetic enolate product



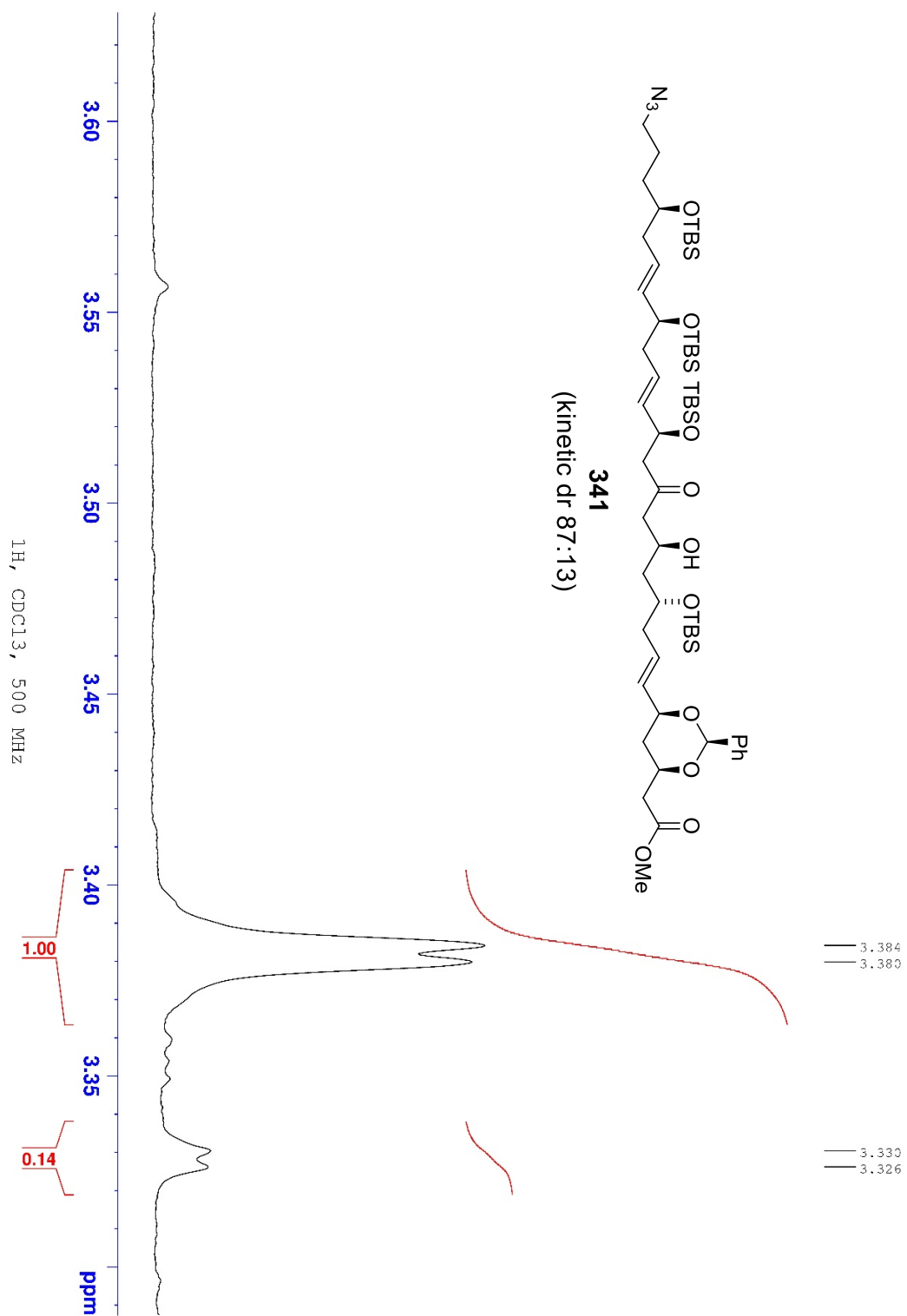
DEPT-135 spectrum of **41a** and **41b**



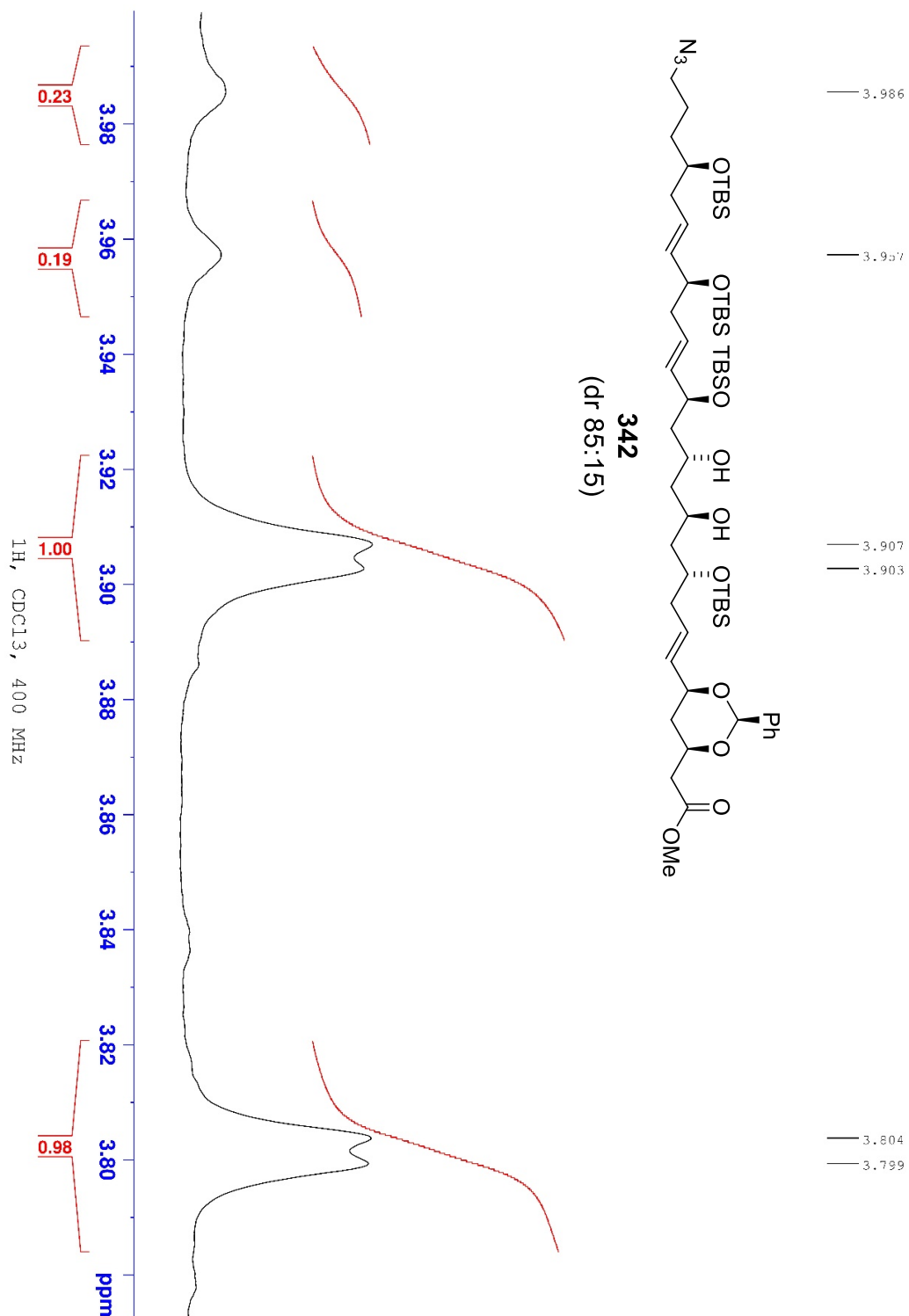
HNMR of **26b** product mixture



HNMR of **26b** after separation of kinetic and thermodynamic enolate products



HNMR of **33** product mixture



HNMR of **34** product mixture