Electronic supplementary materials *Mendeleev Commun.*, 2021, **31**, 693–695

Stereospecific synthesis of aryltetraline lignan analogues using 1,6-bis(dipropylboryl)hexa-2,4-diene

Mikhail E. Gurskii, Maxim I. Zuev, Artur V. Eshtukov, Dmitry A. Cheshkov, Sergey V. Baranin and Yurii N. Bubnov

Table of Contents

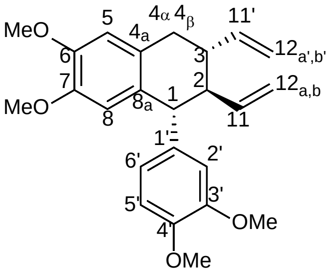
1. INSTUMENTATION

NMR spectra were measured at 303K on a Bruker AVANCE AV 600 spectrometer operating at 600.03 MHz for proton nuclei and 150.9 MHz for carbon nuclei and a Bruker AVANCE III 400 spectrometer operating at 400.16 MHz for proton nuclei and 100.6 MHz for carbon nuclei. Proton chemical shifts are expressed in ppm (δ scale) and are referenced to residual protons in the NMR solvent ($CHCl_3$: δ 7.26, Acetone-d_6: 2.05). ^{1}H NMR spectroscopic data are reported as follows: chemical shift in ppm (multiplicity, spin-spin coupling constants J (Hz), integration intensity, H-position in chemical structure). The multiplicities are abbreviated with s (singlet), d (doublet), t (triplet), broaden (br.), combinations thereof, and m (multiplet). In case of combined multiplicities, the multiplicity with the larger coupling constant is stated first. Except for complex and overlapping multiplets, where a resonance range is given, the chemical shift of all other symmetric signals is reported as the center of the resonance multiplet. ^{13}C NMR spectroscopic data are reported as follows: chemical shift in ppm (C-position in chemical structure). In addition to ^{1}H and ^{13}C NMR measurements, 2D NMR techniques such as homonuclear correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond coherence (HMBC, optimized for $^nJ_{CH} = 8$ Hz) were used to assist the signal assignment. For elucidation of relative stereochemical configuration of structures of the products, nuclear Overhauser effect spectroscopy (NOESY and HSQC-NOESY without ^{13}C decoupling) was conducted with mixing time of 800 ms. Spectra processing were performed using Bruker TopSpin 2.1 and 4.0 software packages.

2. Synthesis of (1*R**,2*R**,3*R**)-1-(3,4-dimethoxyphenyl)-6,7-dimethoxy- (3a) and (1*R**,2*R**,3*R**)-1-(3,4,5-trimethoxyphenyl)-6,7,8-trimethoxy-2,3-divinyl-1,2,3,4-tetrahydronaphthalene (3b) (*general procedure*).

To a solution of diol **2a,b** (0.5 mmol) in Et_2O or CH_2Cl_2 (20 ml), Et_3SiH (0.5 mmol) was added followed by dropwise addition of $BF_3{\cdot}OEt_2$ (1.6 mmol). The mixture was stirred for 9-10 h (1-2 min in case of CH_2Cl_2) at 20 °C. Then, $NaHCO_3$ solution (10% aq., 20 ml) was added, the organic layer was separated and dried over Na_2SO_4. The solvent was removed, the residue was chromatographed on a SiO_2 column (eluent: EtOAc/hexane, 1:1).

2.1. (1*R**,2*R**,3*R**)-1-(3,4-Dimethoxyphenyl)-6,7-dimethoxy-2,3-divinyl-1,2,3,4-tetrahydronaphthalene (3a).



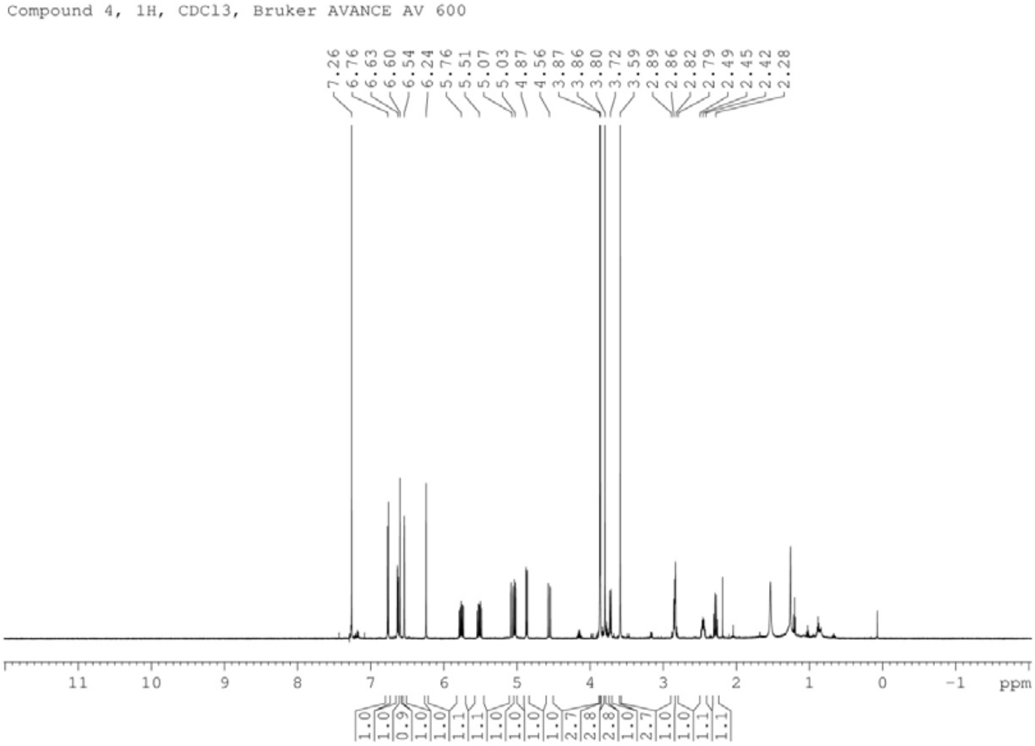
Yield 68% (Et_2O), 87% (CH_2Cl_2), m.p. 93.5 °C. HRMS (ESI): found *m/z* 381.2062 $[M+H]^+$; calculated for $C_{24}H_{29}O_4$ 381.2060.

^{1}H NMR (600.03 MHz, $CDCl_3$) 6.76 (d, $^3J_{H5'-H6'}$ = 8.2 Hz, 1H, H-5′), 6.62 (dd, $^3J_{H6'-H5'}$ = 8.2 Hz, $^4J_{H6'-H2'}$ = 2.0 Hz, 1H, H-6′), 6.60 (s, 1H, H-5), 6.54 (d, $^4J_{H2'-H6'}$ = 2.0 Hz, 1H, H-2′), 6.24 (s, 1H, H-8), 5.76 (ddd, $^3J_{H11'-H12b}$ = 17.2 Hz, $^3J_{H11'-H12a}$ = 10.3 Hz, $^3J_{H11'-H3}$ = 8.0 Hz, 1H, H-11′), 5.51 (ddd, $^3J_{H11-H12b}$ = 17.1 Hz, $^3J_{H11-H12a}$ = 10.2 Hz, $^3J_{H11-H2}$ = 9.2 Hz, 1H, H-11), 5.07 (ddd, $^3J_{H12b'-H11'}$ = 17.2 Hz, $^2J_{H12b'-H12a'}$ = 1.8 Hz, $^4J_{H12b'-H3}$ = 1.0 Hz, 1H, H-12b′), 5.03 (ddd, $^3J_{H12a'-H11'}$ = 10.3 Hz, $^2J_{H12a'-H12b'}$ = 1.8 Hz, $^4J_{H12a'-H3}$ = 0.6 Hz, 1H, H-12a′), 4.87 (br. dd, $^3J_{H12a-H11}$ = 10.2 Hz, $^3J_{H12a-H12b}$ = 1.8 Hz, 1H, H-12a), 4.56 (ddd, $^3J_{H12b-H11}$ = 17.1 Hz, $^3J_{H12b-H12a}$ = 1.8 Hz, $^3J_{H12b-H2}$ = 0.5 Hz, 1H, H-12b), 3.87 (s, 3H, OMe-4′), 3.86 (s, 3H, OMe-6), 3.80 (s, 3H, OMe-3′), 3.72 (br. dd, $^3J_{H1-H2}$ = 10.4 Hz, $^5J_{H1-H4\beta}$ = 1.0 Hz, 1H, H-1), 3.59 (3H, s, OMe-7), 2.89-2.86 (m, 1H, H-4α, overlapping with H-4β), 2.82-2.79 (m, $^5J_{H4\beta-H1}$ = 1.0 Hz, 1H, H-4β, overlapping with H-4α), 2.49-2.42 (m, $^3J_{H3-H2}$ = 10.4 Hz, $^3J_{H3-H11'}$ = 9.0 Hz, 1H, H-3), 2.28 (br. ddd, $^3J_{H2-H1}$ = 10.4 Hz, $^3J_{H2-H3}$ = 10.4 Hz, $^3J_{H2-H11}$ = 9.2 Hz, 1H, H-2).

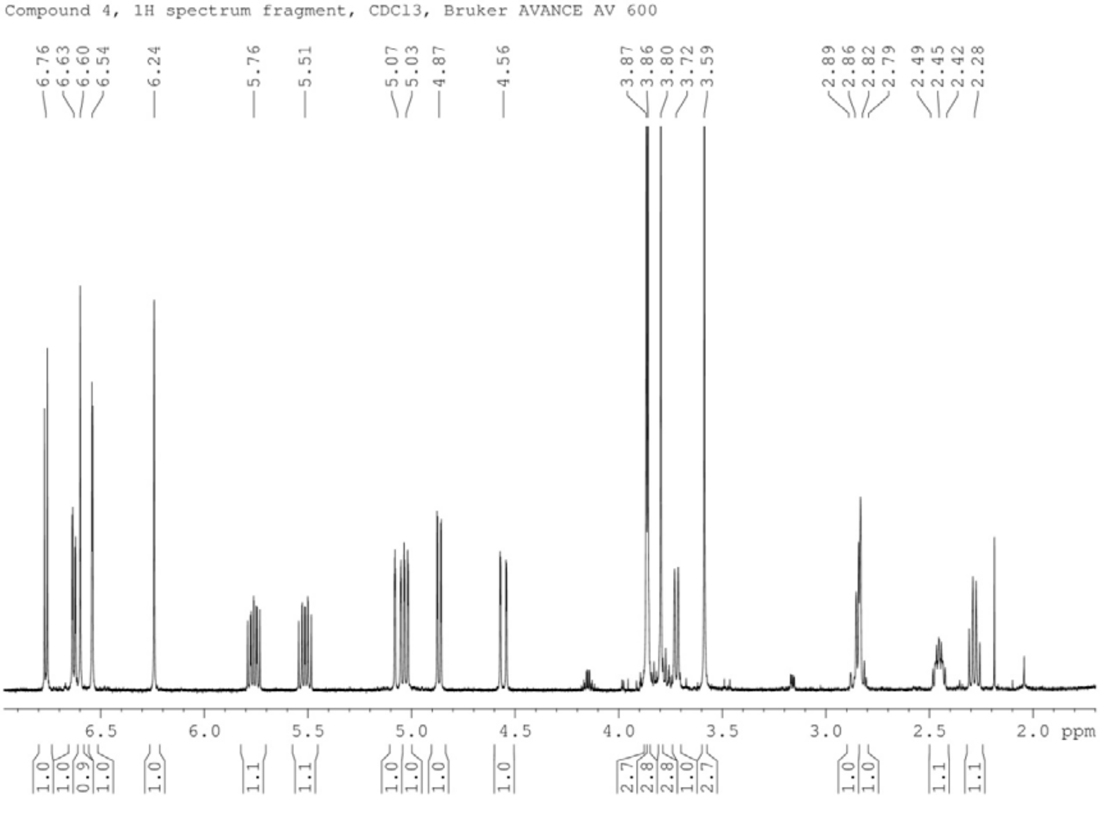
^{13}C NMR (150.9 MHz, $CDCl_3$) 148.7 (C-3′), 147.3 (C-4′), 147.3 (C-6), 147.2 (C-7), 142.3 (C-11′), 140.4 (C-11), 137.9 (C-1′), 131.2 (C-4a), 128.1 (C-8a),122.0 (C-6′), 116.4 (C-12ab), 114.1 (C- 12′ab), 112.9 (C-8), 112.5 (C-2′), 110.8 (C-5), 110.6 (C-5′), 55.9 (OCH_3-3′), 55.9 (OCH_3-7), 55.8 (OCH_3-6), 55.7 (OCH_3-4′), 53.4 (C-2), 51.7 (C-1), 43.9 (C-3), 36.0 (C-4α,β).

2.1.1. Synthesis of (1*R**,2*R**,3*R**)-1-(3,4-dimethoxyphenyl)-6,7-dimethoxy-2,3-divinyl-1,2,3,4-tetrahydronaphthalene (3a) from (2*R**,3*R**,4*R**,5*R**)-2,5-bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran (4).

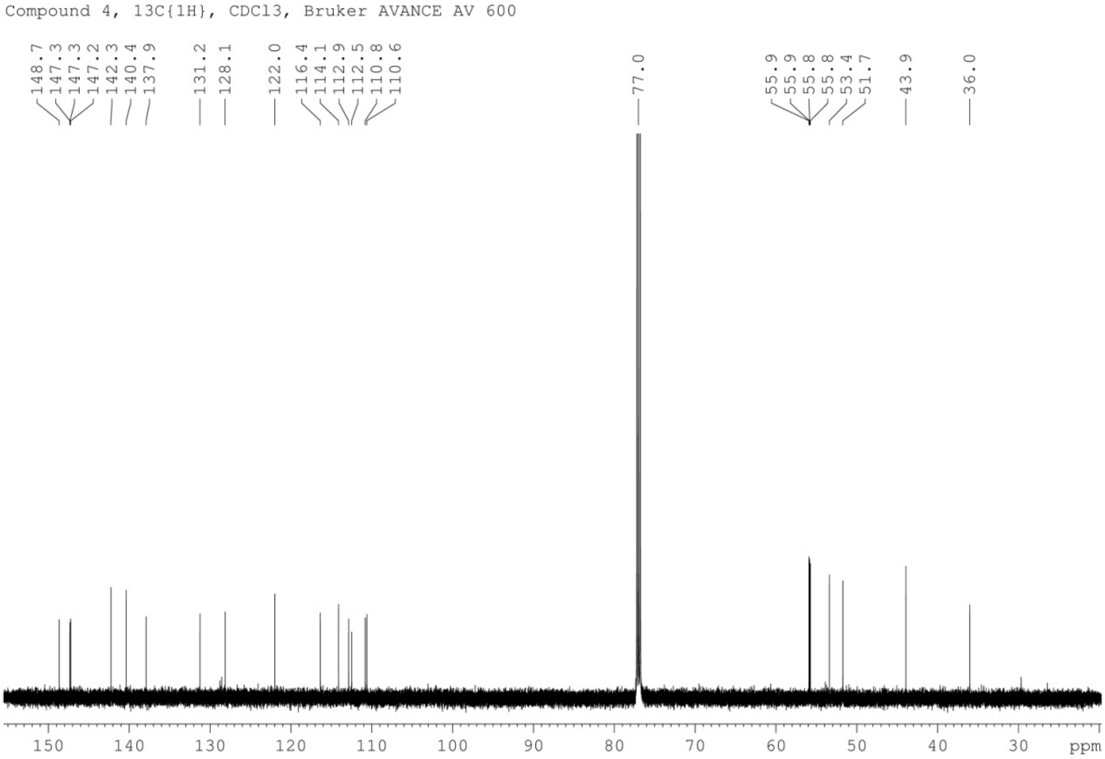
To a solution of tetrahydrofuran **4** (0.5 mmol) in CH_2Cl_2 (20 ml), Et_3SiH (1.1 mmol) was added followed by dropwise addition of $BF_3{\cdot}OEt_2$ (1.1 mmol). The mixture was stirred for 1-2 min. at 20 °C. Then, $NaHCO_3$ solution (10% aq., 20 ml) was added, the organic layer was separated and dried over Na_2SO_4. The solvent was removed, the residue was chromatographed on a SiO_2 column (eluent: EtOAc/hexane, 1:1), and the target product **3a** was obtained. Yield 94%.



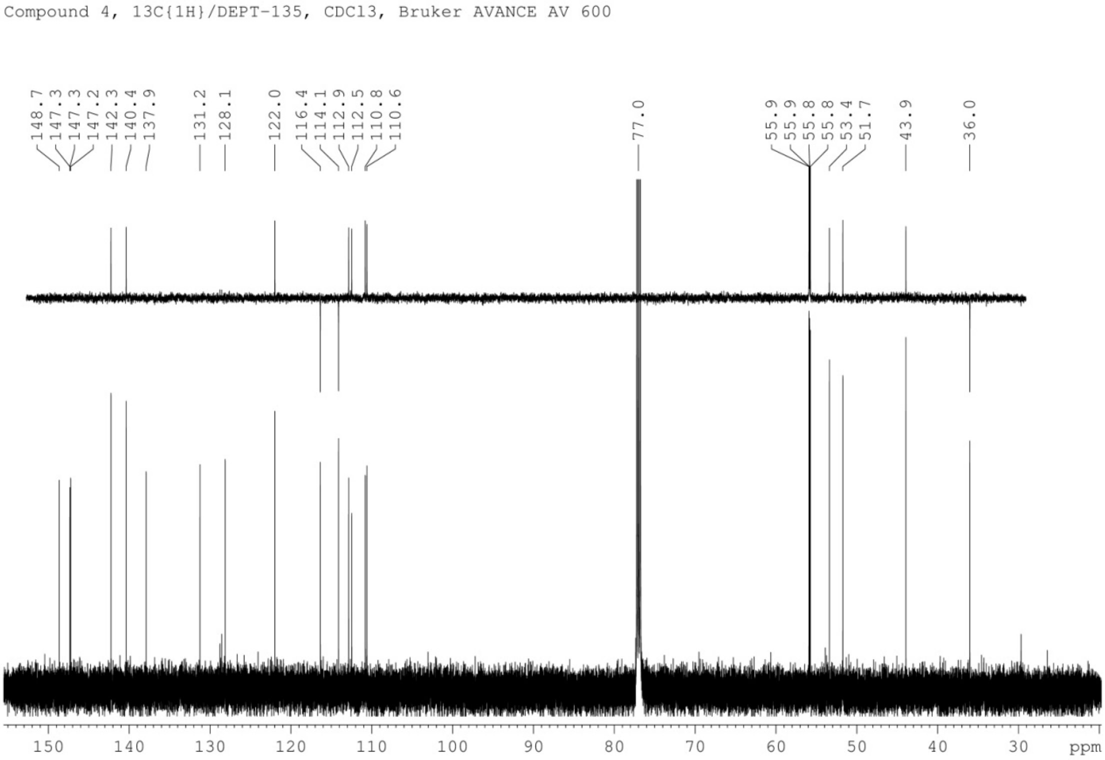
^{1}H NMR spectrum of compound **3a**.



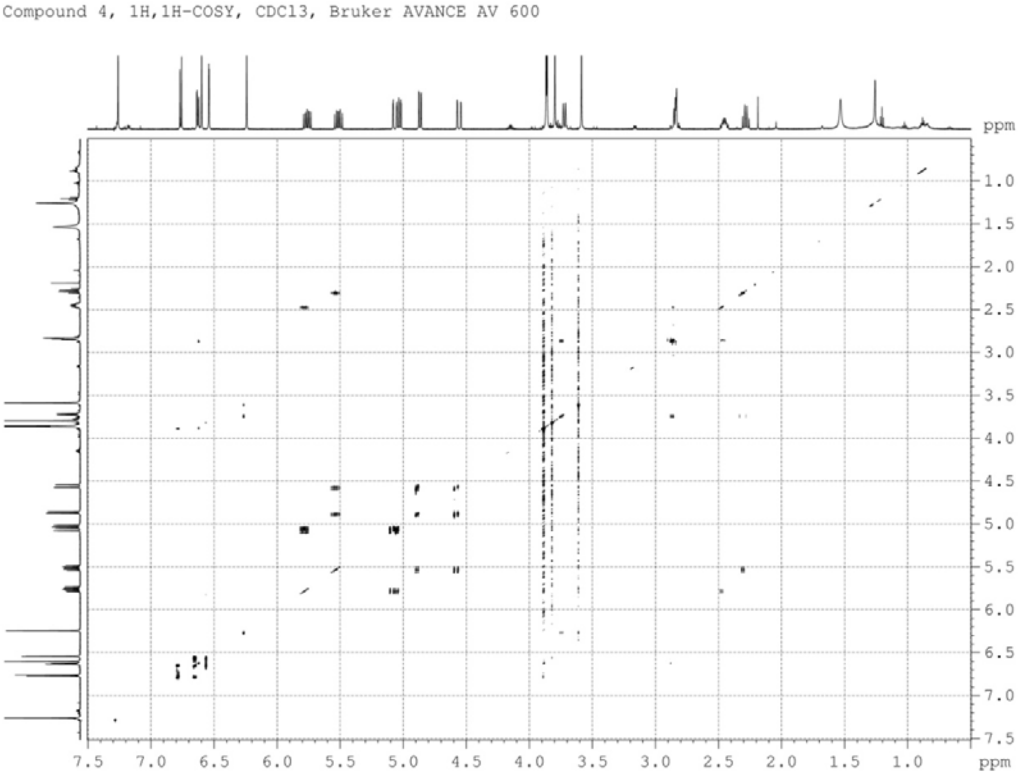
^{1}H NMR spectrum fragment of compound **3a**.



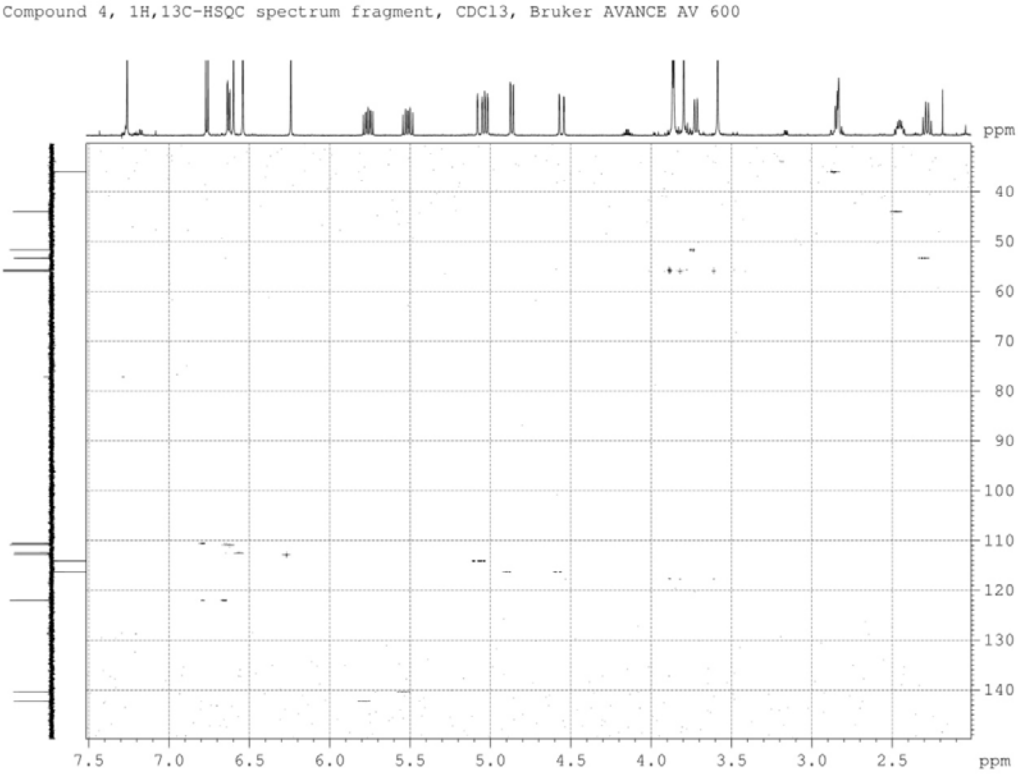
^{13}C NMR spectrum of compound **3a**.



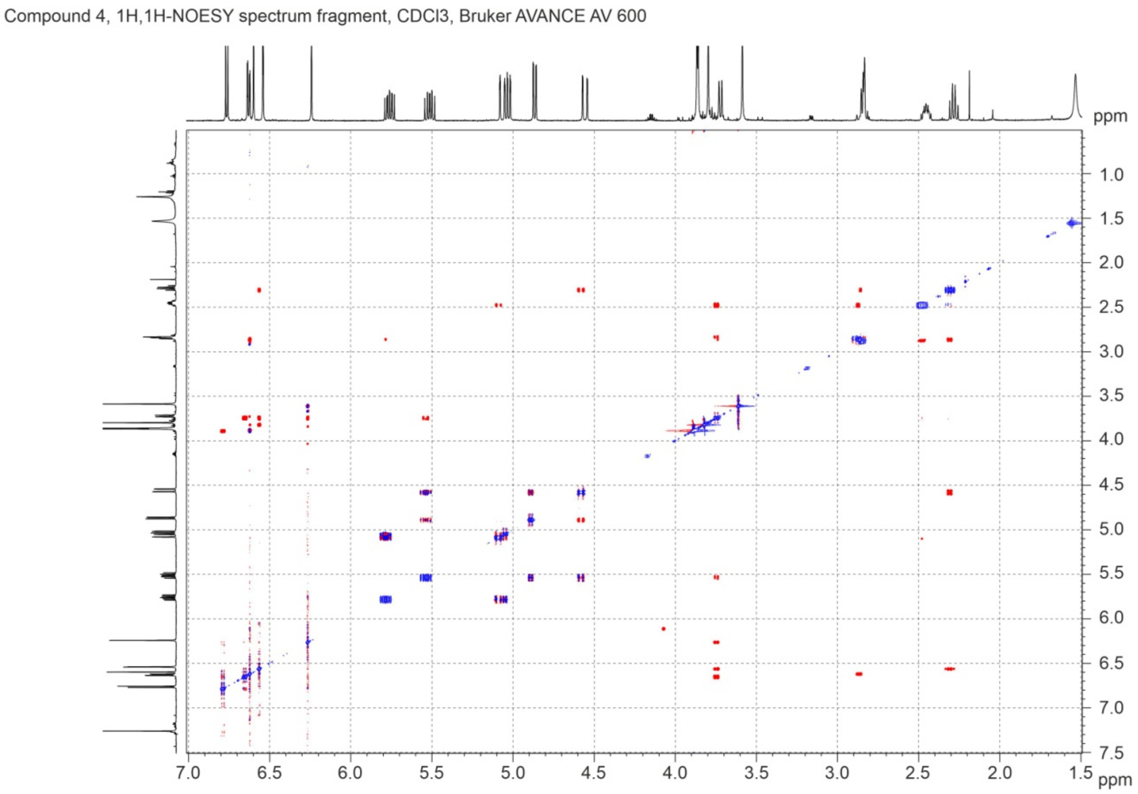
^{13}C NMR spectrum of compound **3a** (^{13}C(^{1}H) / DEPT-135).



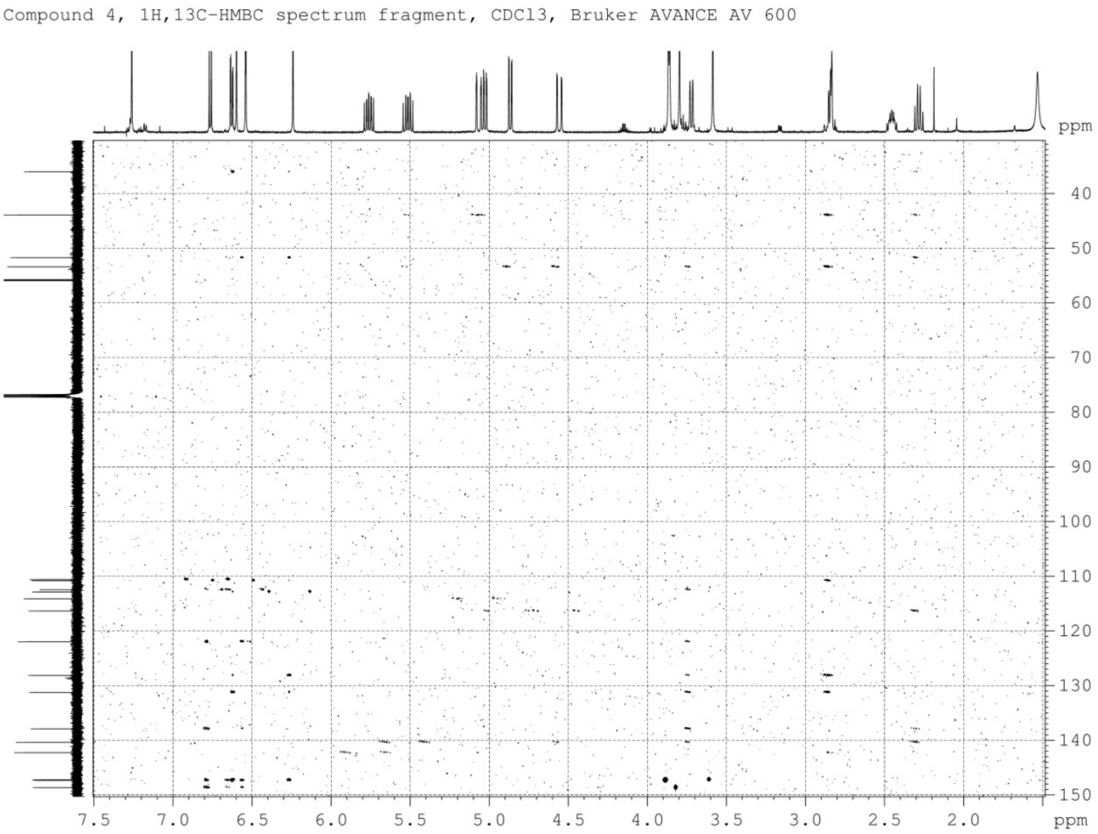
{^{1}H-^{1}H}-COSY spectrum of compound **3a**.



{^{1}H-^{13}C}-HSQC spectrum fragment of compound **3a**.

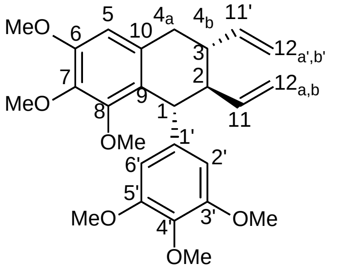


{^{1}H-^{1}H}-NOESY spectrum fragment of compound **3a**.



{^{1}H-^{13}C}-HMBC spectrum fragment of compound **3a**.

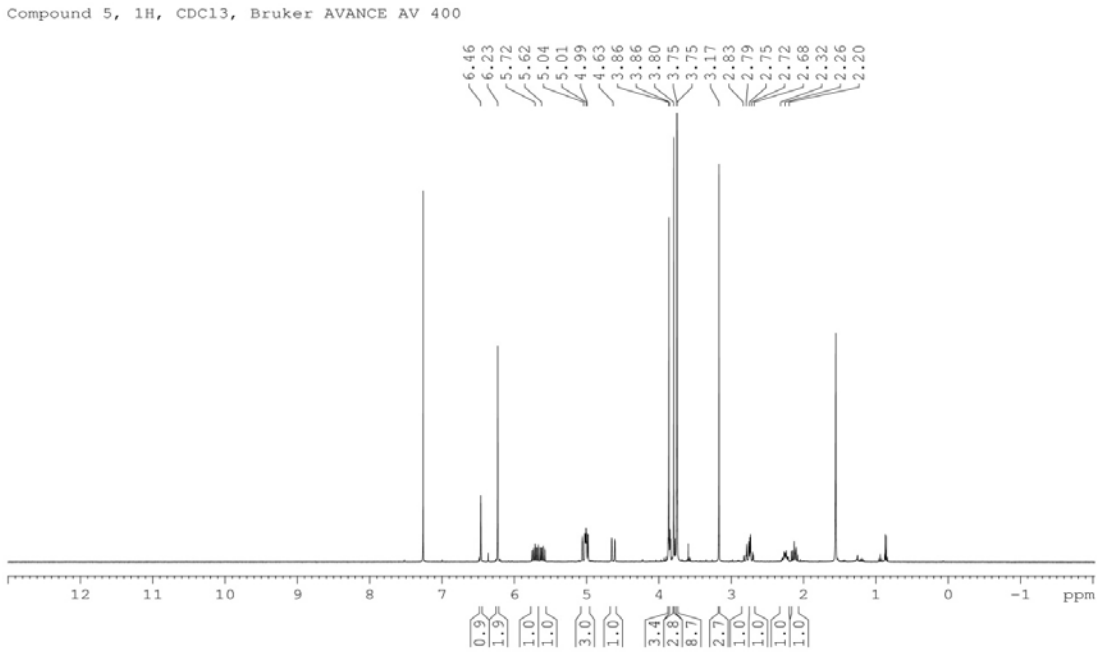
2.2. (1*R**,2*R**,3*R**)-6,7,8-Trimethoxy-1-(3,4,5-trimethoxyphenyl)-2,3-divinyl-1,2,3,4-tetrahydronaphthalene (3b).



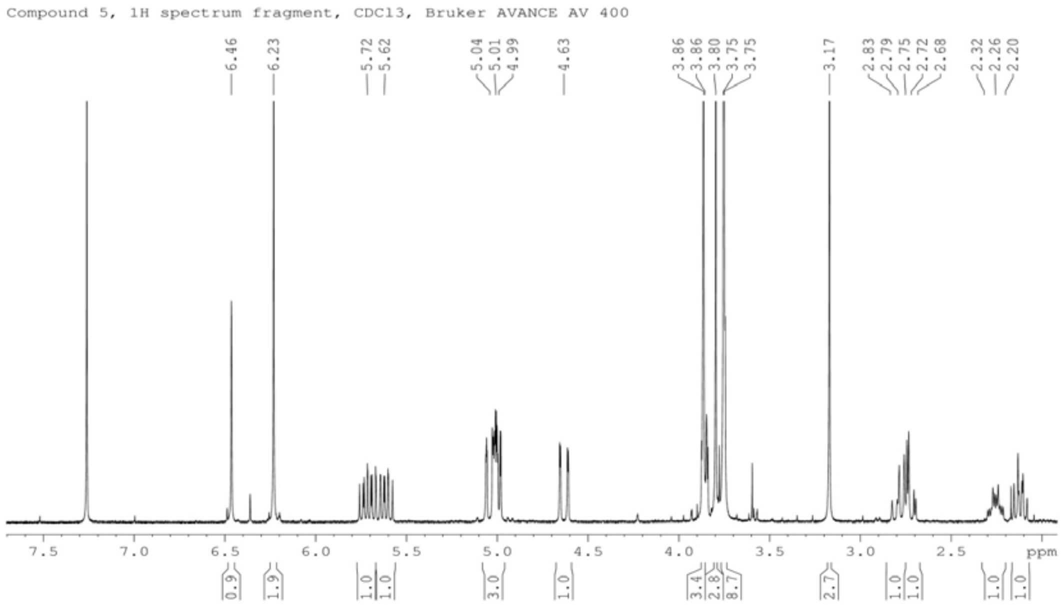
Yield 65%, m.p. 112 °C. HRMS (ESI): found *m/z* 441.2265 [M+H]$^+$; calculated for $C_{26}H_{33}O_6$ 441.2272.

^{1}H NMR (400.16 MHz, CDCl$_3$) 6.46 (s, 1H, H-5), 6.23 (s, 2H, H-2′ and H-6′), 5.71 (ddd, $^3J_{\text{H11′-H12b′}}$ = 17.2 Hz, $^3J_{\text{H11′-H12a′}}$ = 10.4 Hz, $^3J_{\text{H11′-H3}}$ = 7.8 Hz, 1H, H-11′), 5.62 (ddd, $^3J_{\text{H11-H12b}}$ = 17.1 Hz, $^3J_{\text{H11-H12a}}$ = 10.2 Hz, $^3J_{\text{H11-H2}}$ = 9.0 Hz, 1H, H-11), 5.04 (ddd, $^3J_{\text{H12b′-H11′}}$ = 17.2 Hz, $^2J_{\text{H12b′-H12a′}}$ = 1.8 Hz, $^4J_{\text{H12b′-H3}}$ = 1.1 Hz, 1H, H-12b′, overlapping with H-12a′ and H-12a), 5.01 (ddd, $^3J_{\text{H12a′-H11′}}$ = 10.4 Hz, $^2J_{\text{H12a′-H12b′}}$ = 1.8 Hz, $^4J_{\text{H12a′-H3}}$ = 0.7 Hz, 1H, H-12a′, overlapping with H-12b′ and H-12a), 4.99 (dd, $^3J_{\text{H12a-H11}}$ = 10.2 Hz, $^2J_{\text{H12a-H12b}}$ = 1.9 Hz, 1H, H-12a, overlapping with H-12b and H-12a′), 4.63 (ddd, $^3J_{\text{H12b-H11}}$ = 17.1 Hz, $^2J_{\text{H12b-H12a}}$ = 1.9 Hz, $^4J_{\text{H12b-H2}}$ = 0.6 Hz, 1H, H-12b), 3.86 (s, 3H, OMe-6, overlapping with H-1), 3.86 (dd, $^3J_{\text{H1-H2}}$ = 8.6 Hz, $^5J_{\text{H1-H4β}}$ = 1.0 Hz, 1H, H-1), 3.80 (s, 3H, OMe-4′), 3.75 (s, 3H, OMe-7, overlapping with OMe-3′ and OMe-5′), 3.75 (s, 6H, OMe-3′ and OMe-5′, overlapping with OMe-7), 3.17 (3H, s, OMe-8), 2.79 dd, $^2J_{\text{H4α-H4β}}$ = 15.5 Hz, $^3J_{\text{H4α-H3}}$ = 11.2 Hz, 1H, H-4α), 2.72 (ddd, $^2J_{\text{H4β-H4α}}$ = 15.5 Hz, $^3J_{\text{H4β-H3}}$ = 4.1 Hz, $^5J_{\text{H4β-H1}}$ = 1.0 Hz 1H, H-4β), 2.32-2.20 (m, $^3J_{\text{H3-H4α}}$ = 11.2 Hz, $^3J_{\text{H3-H2}}$ = 11.1 Hz, $^3J_{\text{H3-H11′}}$ = 7.8 Hz, $^3J_{\text{H3-H4β}}$ = 4.2 Hz, 1H, H-3), 2.12 (ddd, $^3J_{\text{H2-H3}}$ = 11.1 Hz, $^3J_{\text{H2-H11}}$ = 9.0 Hz, $^3J_{\text{H2-H1}}$ = 8.6 Hz, 1H, H-2).

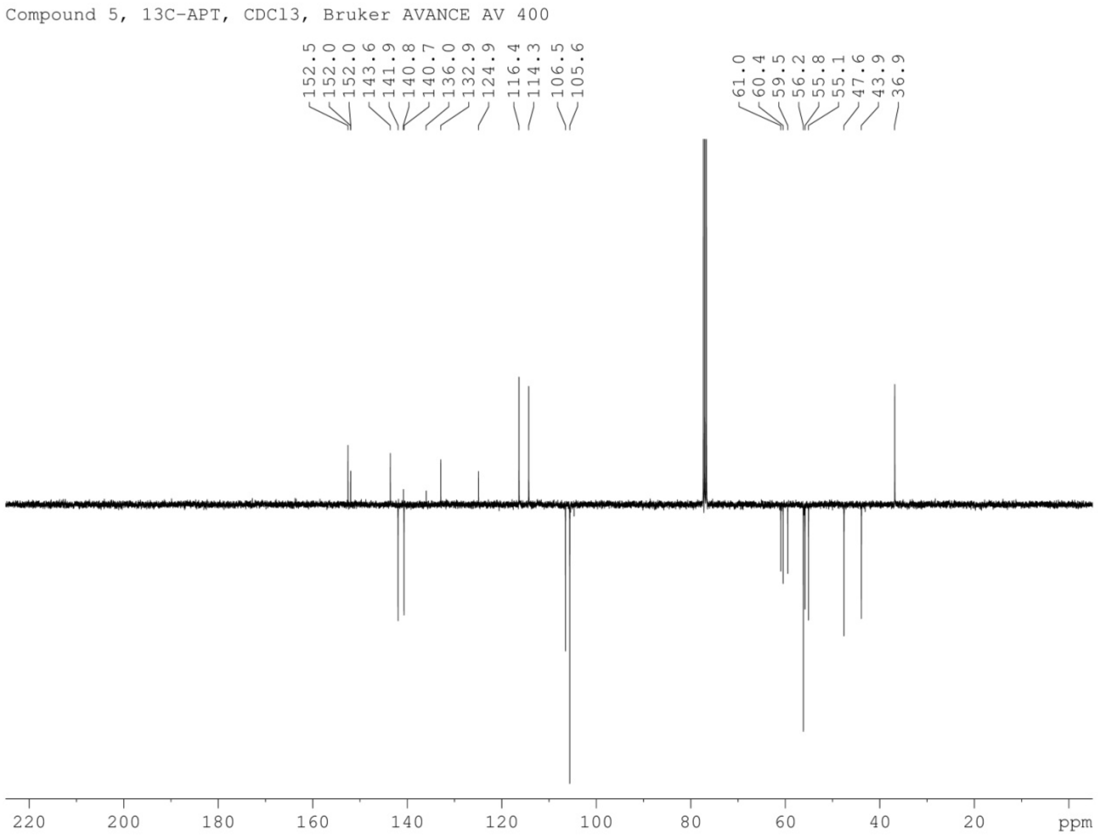
^{13}C NMR (100.6 MHz, CDCl$_3$) 152.5 (C-3′ and C-5′), 152.0 (C-8), 152.0 (C-6), 143.6 (C-1′), 141.9 (C-11′), 140.8 (C-7) 140.7 (C-11), 136.0 (C-4′), 132.9 (C-4a), 124.9 (C-8a), 116.3 (C-12ab), 114.3 (C-12′ab), 106.5 (C-5), 105.6 (C-2′ and C-6′), 61.0 (OCH$_3$-4′), 60.4 (OCH$_3$-4), 59.5 (OCH$_3$-3), 56.2 (OCH$_3$-3′ and OCH$_3$-5′), 55.8 (OCH$_3$-6), 55.1 (C-2), 47.6 (C-1), 43.9 (C-3), 36.9 (C-4αβ).



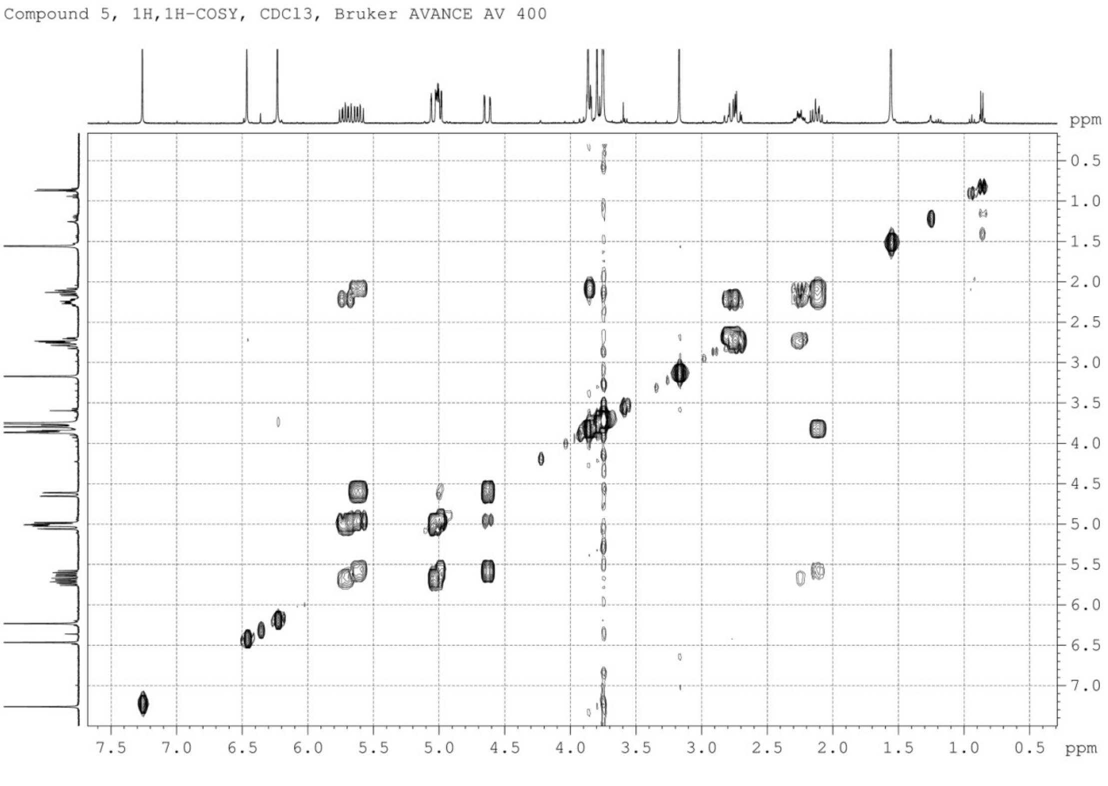
^{1}H NMR spectrum of compound **3b**.



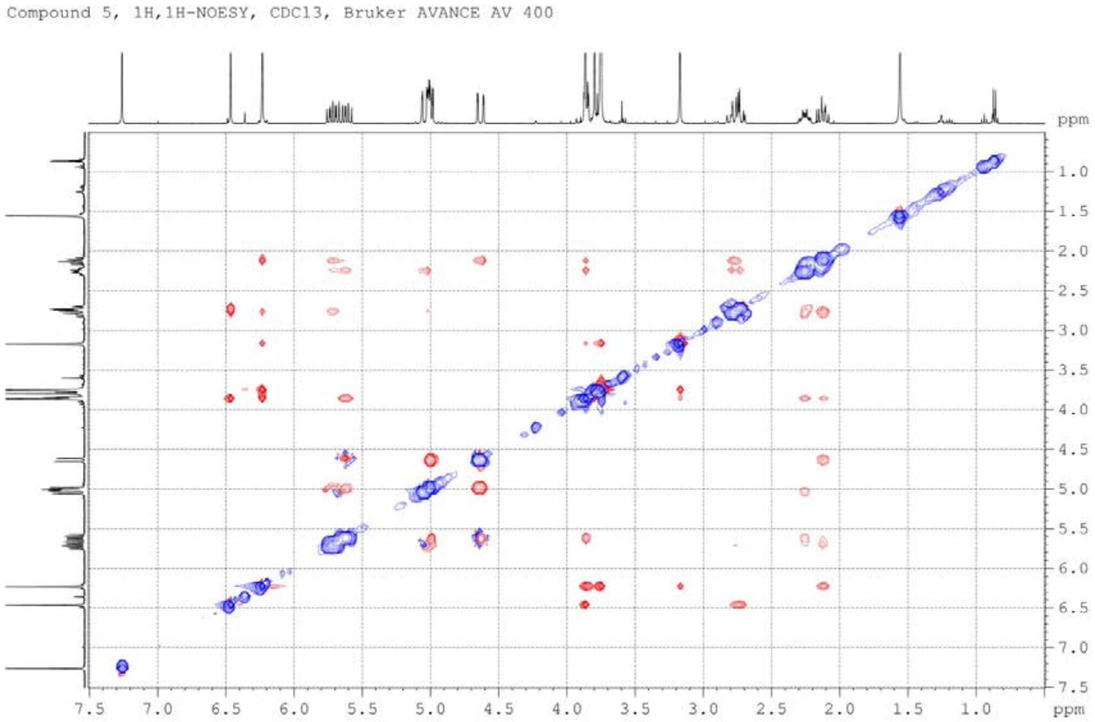
^{1}H NMR spectrum fragment of compound **3b**.



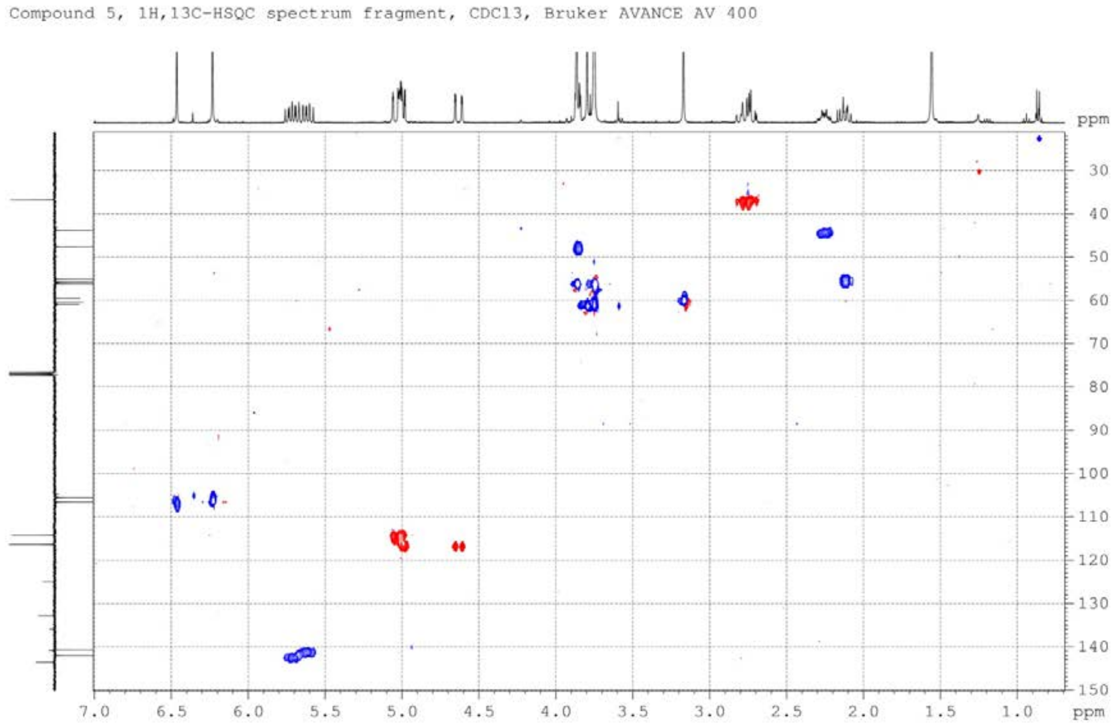
^{13}C NMR spectrum of compound **3b** (^{13}C-APT).



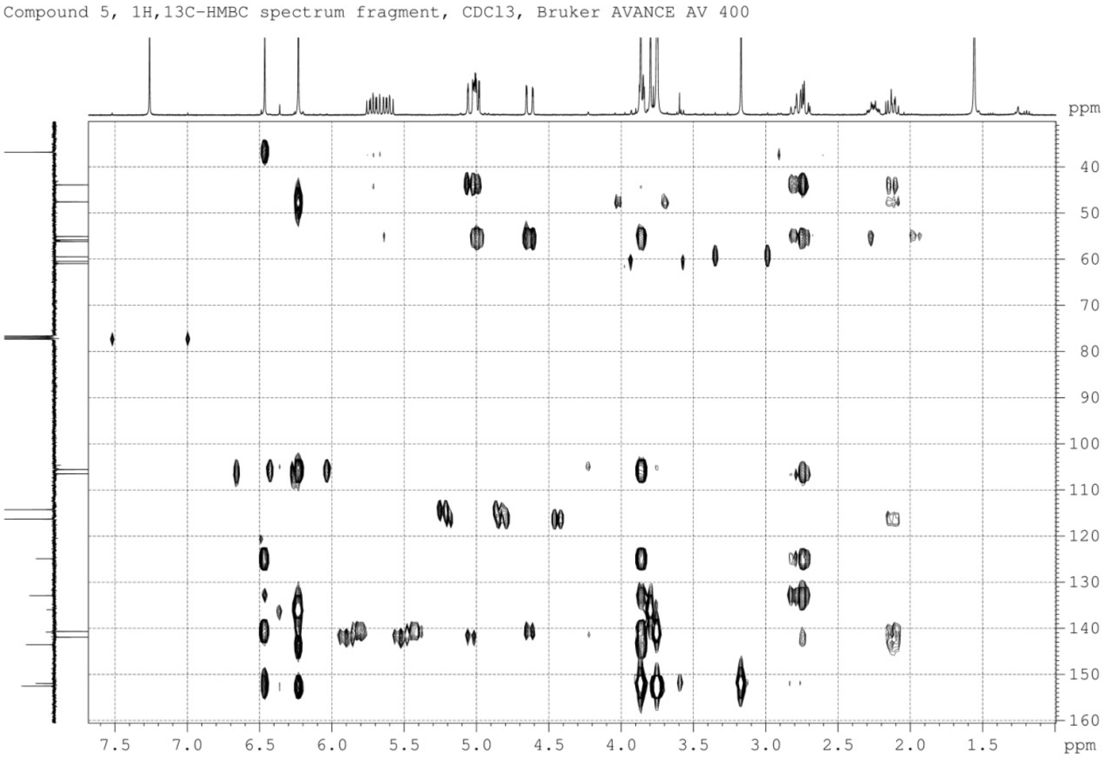
{^{1}H-^{1}H}-COSY spectrum of compound **3b**.



{^{1}H-^{1}H}-NOESY spectrum of compound **3b**.

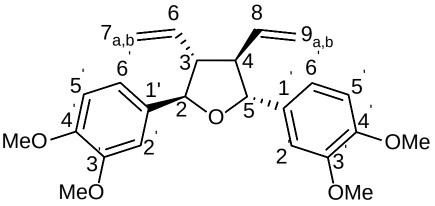


{^{1}H-^{13}C}-HSQC spectrum fragment of compound **3b**.



{^{1}H-^{13}C}-HMBC spectrum fragment of compound **3b**.

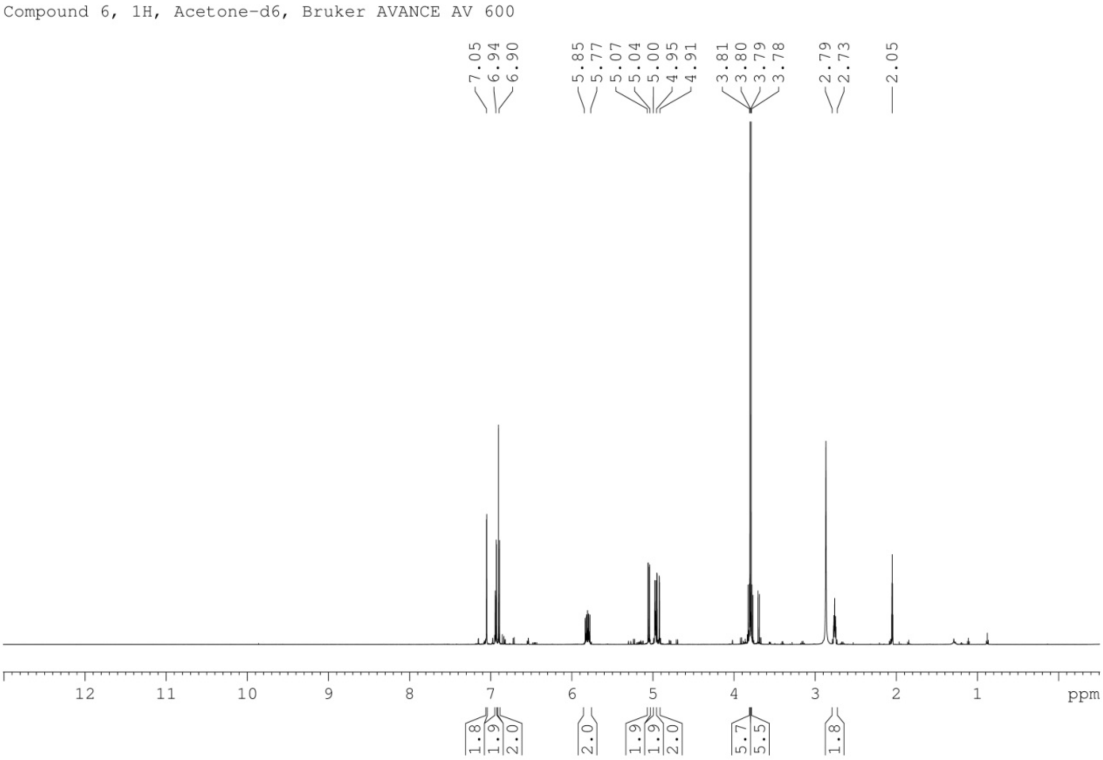
2.3. **(2*R**,3*R**,4*R**,5*R**)-2,5-Bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran (4).**



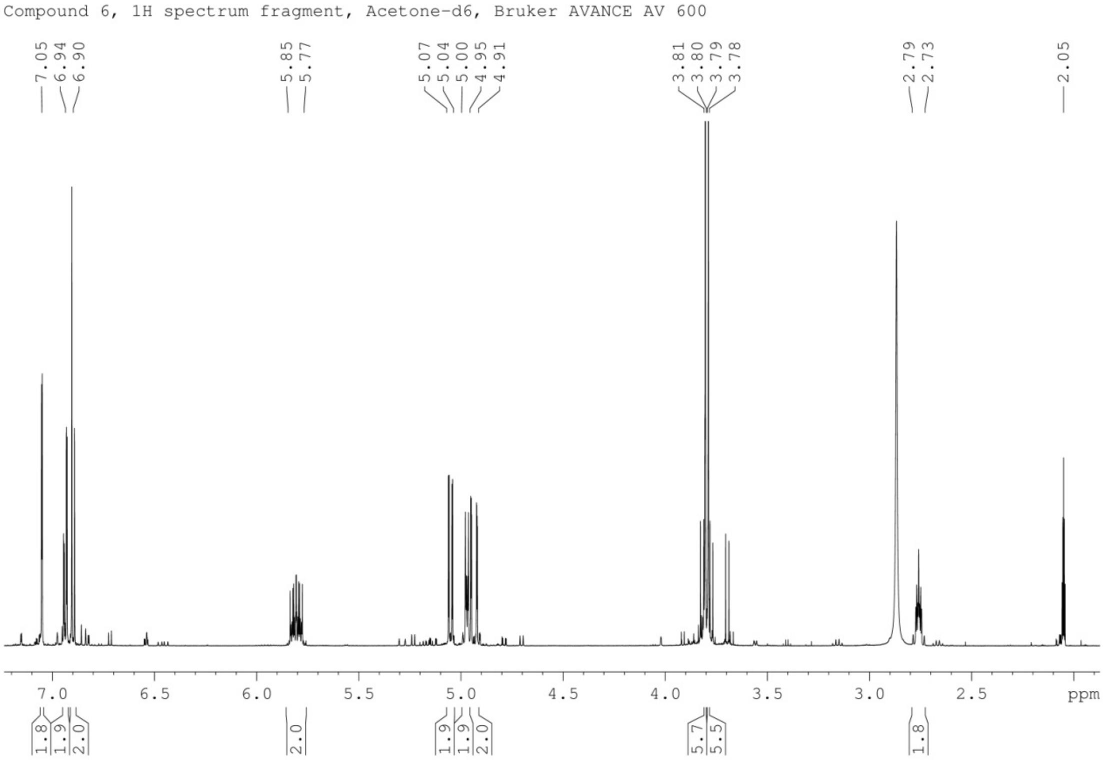
To a solution of diol *ent*-**2a** (0.5 mmol) in CH_2Cl_2 or Et_2O (20 ml), $BF_3{\cdot}OEt_2$ (1.1 mmol) was added dropwise, and the mixture was stirred for 1-2 min. (7-8 h in case of Et_2O) at 20 °C. Then, $NaHCO_3$ solution (10% aq., 20 ml) was added, the organic layer was separated and dried over Na_2SO_4. The solvent was removed, the residue was chromatographed on a SiO_2 column (eluent: EtOAc/hexane, 1:1) to afford product **4**. Yield 94% (85% in case of Et_2O), yellow oil. HRMS (ESI): found *m/z* 396.1944 $[M+H]^+$; calculated for $C_{24}H_9O_6$ 396.1949.

^{1}H NMR (600.03 MHz, acetone-*d₆*) 7.06 (d, $^4J_{H2'-H6'}$ = 2.0 Hz, 2H, H-2′), 6.94 (dd, $^3J_{H6'-H5'}$ = 8.2 Hz, $^4J_{H6'-H2'}$ = 2.0 Hz, 2H, H-6′), 6.89 (d, $^3J_{H5'-H6'}$ = 8.2 Hz, 2H, H-5′), 5.85-5.75 (m, 2H, H-6 and H-8), 5.07-5.04 (m, 2H, H-7b and H-9b), 5.00-4.95 (m, 2H, H-2 and H-5, overlapping with H-7a and H-9a), 4.94-4.91 (m, 2H, H-7a and H-9a, overlapping with H-2 and H-5), 3.80 (s, 6H, OMe-3′), 3.78 (s, 6H, OMe-4′), 2.79-2.73 (m, 2H, H-3 and H-4).

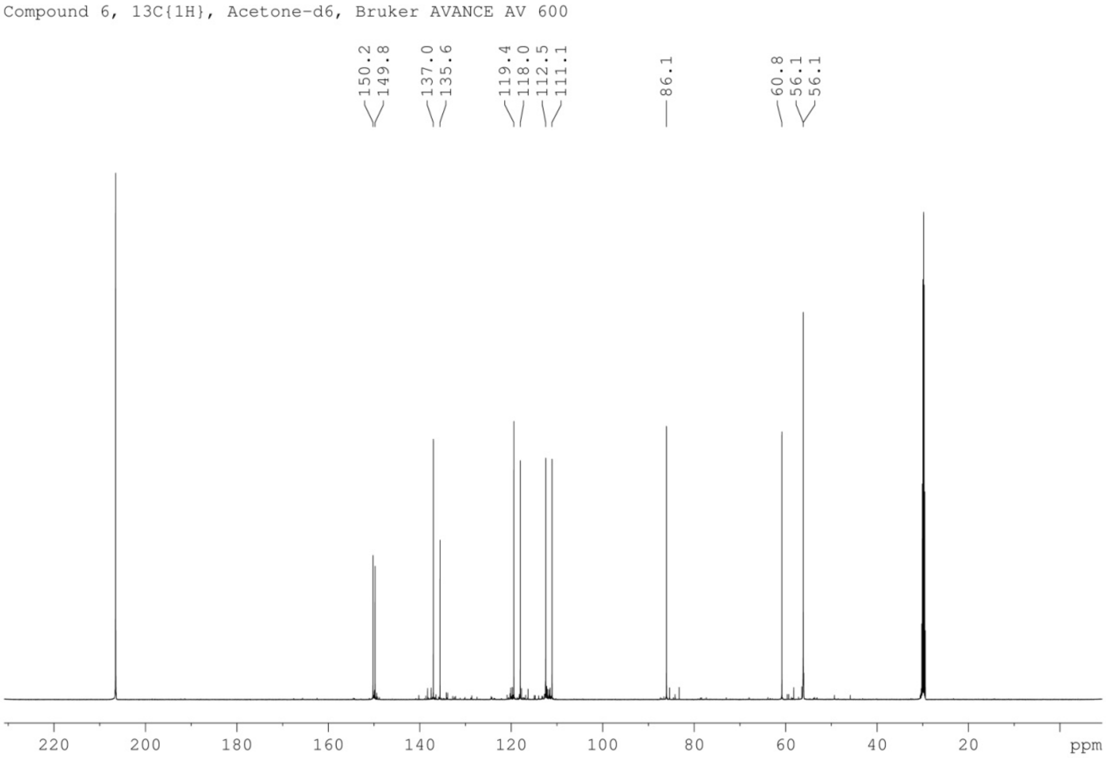
^{13}C NMR (150.9 MHz, $CDCl_3$) 150.2 (2C-3′), 149.8 (2C-4′), 137.0 (C-6 and C-8), 135.6 (2C-1′), 119.4 (2C-6′), 118.0 (C-7a, C-7b and C-9a, C-9b) 112.4 (2C-5′), 111.1 (2C-2′), 86.1 (C-2 and C-5), 60.8 (C-3 and C-4), 56.1 (2OMe-4′), 56.1 (2OMe-3′).



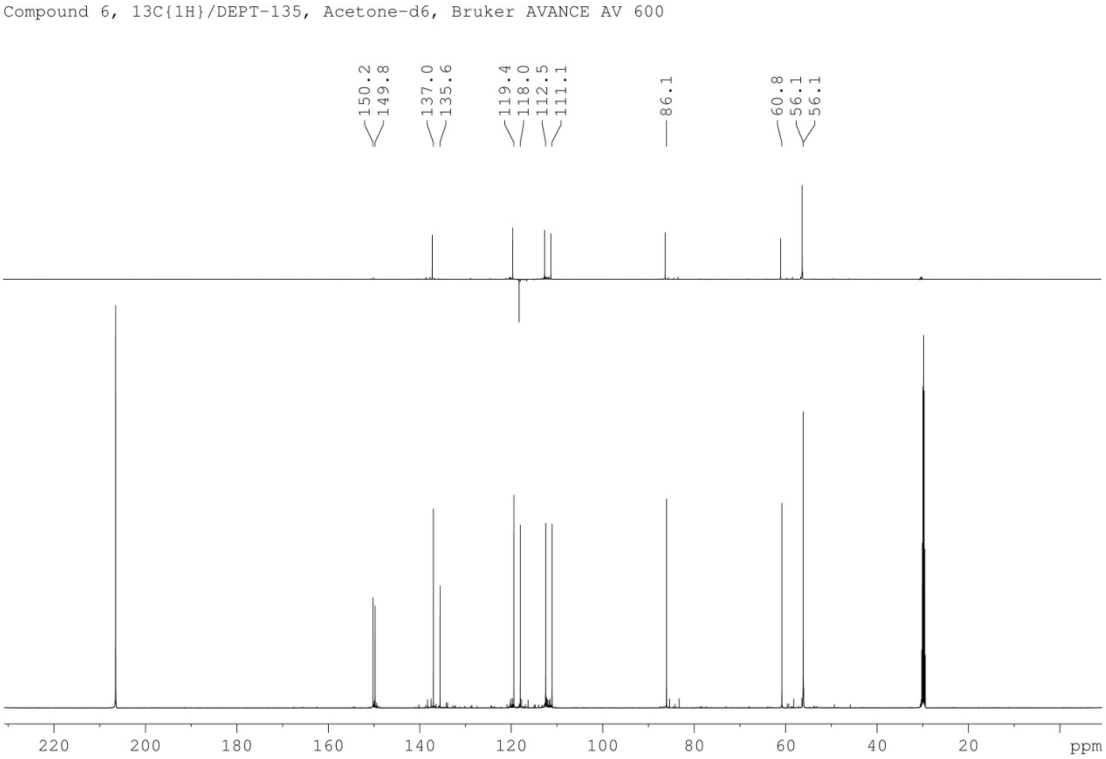
^{1}H NMR spectrum of compound **4**.



^{1}H NMR spectrum fragment of compound **4**.

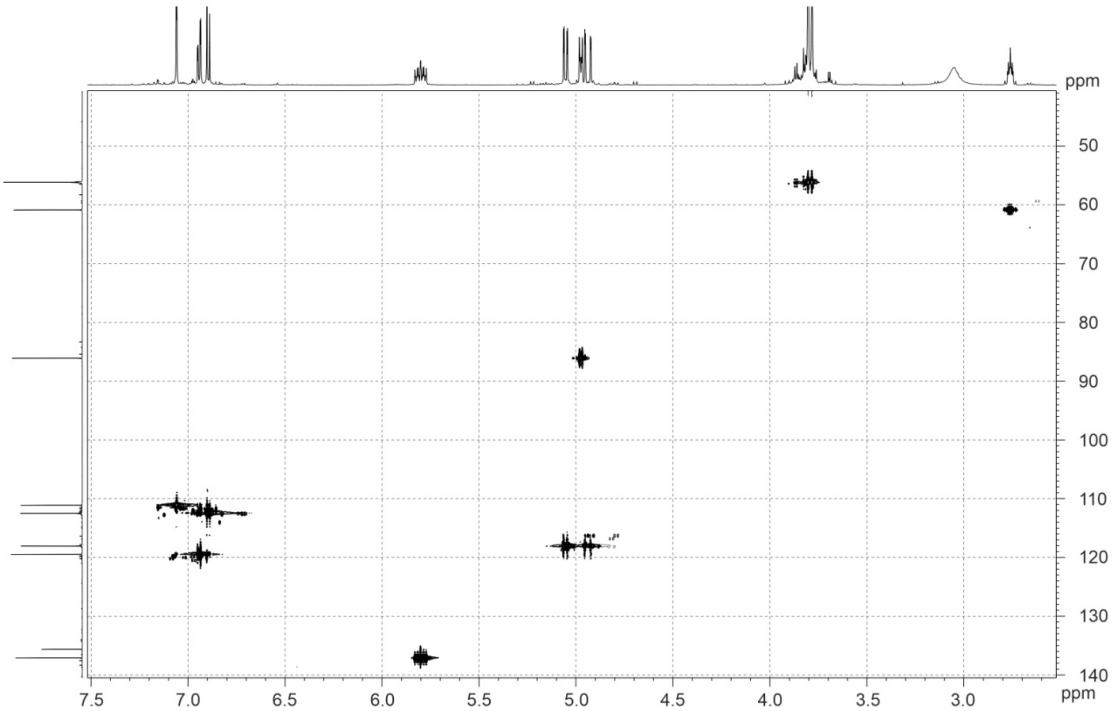


^{13}C NMR spectrum of compound **4**.



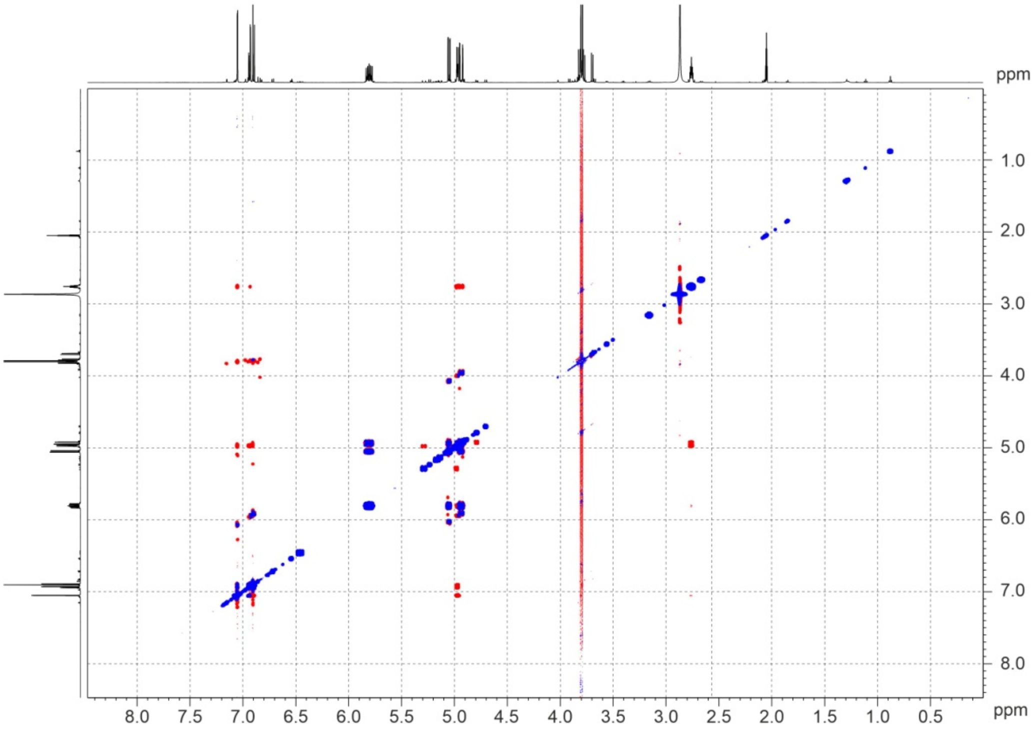
^{13}C NMR spectrum of compound **4** (^{13}C(^{1}H) / DEPT-135).

Compound 6, 1H,13C-HSQC spectrum fragment, Acetone-d6, Bruker AVANCE AV 600

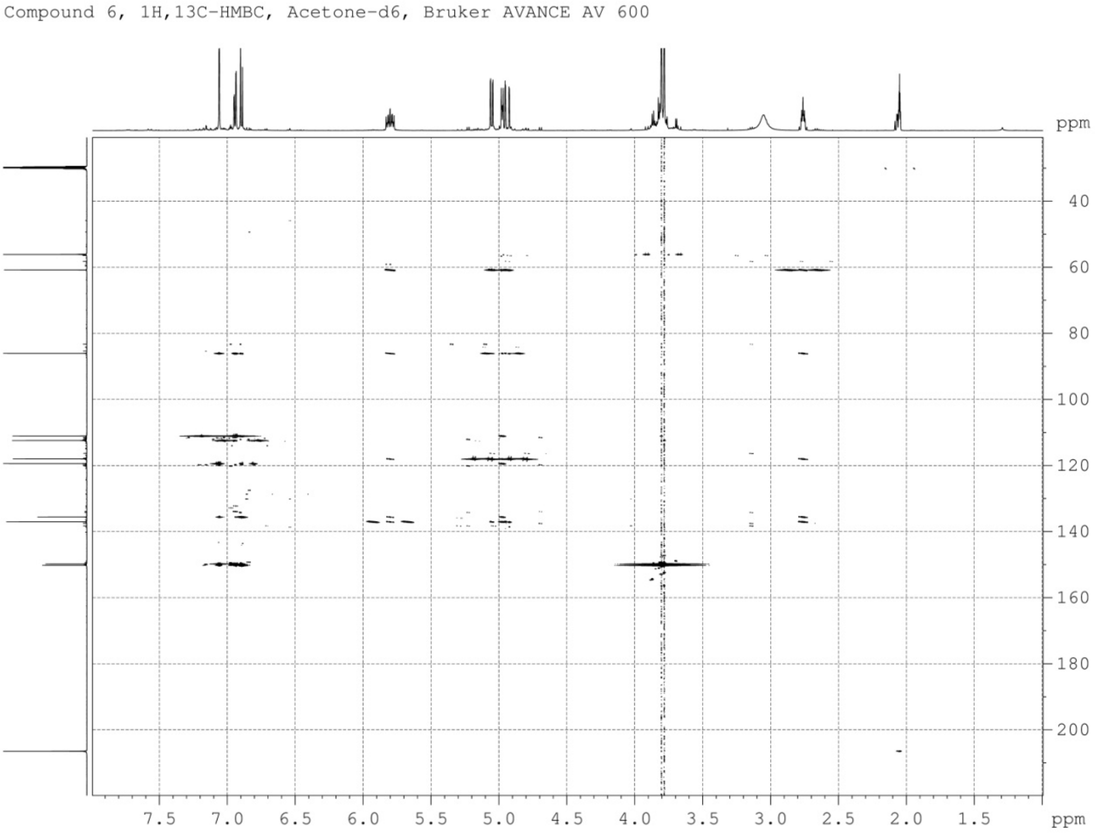


{^{1}H-^{13}C}-HSQC spectrum fragment of compound **4**.

Compound 6, 1H,1H-NOESY, Acetone-d6, Bruker AVANCE AV 600

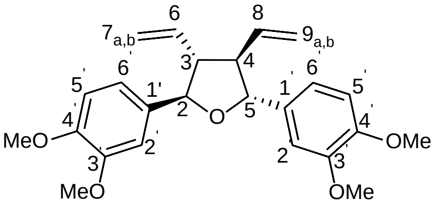


{^{1}H-^{1}H}-NOESY spectrum of compound **4**.



{^{1}H-^{13}C}-HMBC spectrum of compound **4**.

3. Analysis of high-resolution NMR spectra of (2*R**,3*R**,4*R**,5*R**)-2,5-bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran (4).



From ^{1}H NMR spectrum of (2*R**,3*R**,4*R**,5*R**)-2,5-bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran (**4**) it is followed, that protons in pairs H-8, H-8′ and H-9, H-9' are chemically equivalent as well as corresponding protons of substitutes. This indicates the presence of an element of symmetry (axis/plane) in the molecule. At the same time, this chemical equivalence complicates the determination of the stereochemical configuration, since the measurement of coupling constants and NOE contacts between chemically equivalent but magnetically non-equivalent protons needs to be done. Such spins systems lead to non-first order multiplets in NMR spectra, in which the direct measurement of $J_{\mathrm{H\text{-}H}}$-coupling constants is impossible. Therefore, the total lineshape analysis of ^{1}H NMR spectrum was performed using ANATOLIA NMR software [S1]. Spectrum was analyzed within AA′MM′PP′XX′ZZ′ spin system which includes protons of the cycle and the vinyl substituents.

High-resolution ^{1}H NMR of (2*R**,3*R**,4*R**,5*R**)-2,5-bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran in acetone-d_6 spectra were acquired at 14.1 T (^{1}H Larmor frequency of 600.03 MHz). Total lineshape analysis was performed to find the $J_{\mathrm{H\text{-}H}}$-couplings in (2*R**,3*R**,4*R**,5*R**)-2,5-bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran molecule. As usual, analysis was done in several steps by gradual removing of the Lorentzian broadening of the experimental data and consequent refinement of the spin system parameters. Comparison of the experimental and calculated NMR spectra for compound 2*R**,3*R**,4*R**,5*R**)-2,5-bis(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran is shown in Figure S1.

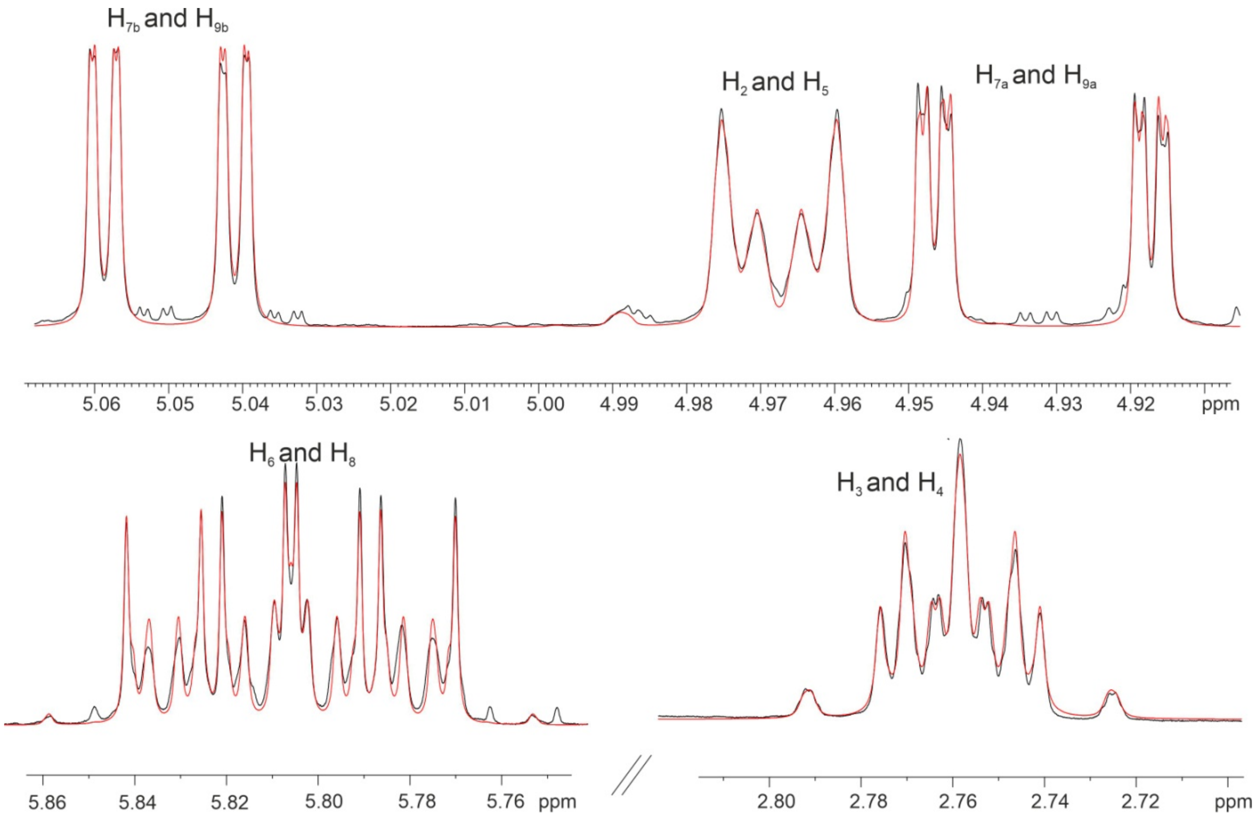


Figure S1. Total lineshape analysis of NMR signals corresponding to the compound **4** (14.1 T, acetone-d_6). The results of calculation (shown in red) are overlapped with the experimental spectra (shown in black).

The results of this analysis are presented in Table S1.

Table S1. Determined spin system parameters of the compound **4**. Standard deviation was not more than 0.05 Hz for each parameter.

δ (ppm)		ν (Hz)		*J* (Hz)	
δ_{H2}	4.97	ν_{H2}	2982.48	$^{4}J_{H2\text{-}H5}$	0.45
δ_{H5}	4.97	ν_{H5}	2982.48	$^{3}J_{H2\text{-}H3} = {}^{3}J_{H5\text{-}H4}$	9.47
δ_{H3}	2.76	ν_{H3}	1655.66	$^{4}J_{H2\text{-}H4} = {}^{4}J_{H5\text{-}H3}$	-0.26
δ_{H4}	2.76	ν_{H4}	1655.66	$^{4}J_{H2\text{-}H6} = {}^{4}J_{H5\text{-}H8}$	0.14
δ_{H6}	5.80	ν_{H6}	3484.02	$^{5}J_{H2\text{-}H8} = {}^{5}J_{H5\text{-}H6}$	0.10
δ_{H8}	5.80	ν_{H8}	3484.02	$^{5}J_{H2\text{-}H7b} = {}^{5}J_{H5\text{-}H9b}$	0.47
δ_{H7b}	5.05	ν_{H7b}	3030.74	$^{7}J_{H2\text{-}H9b} = {}^{7}J_{H5\text{-}H7b}$	0.00
δ_{H9b}	5.05	ν_{H9b}	3030.74	$^{5}J_{H2\text{-}H7a} = {}^{5}J_{H5\text{-}H9a}$	0.70
δ_{H7a}	4.94	ν_{H7a}	2961.62	$^{3}J_{H3\text{-}H4}$	10.86
δ_{H9a}	4.94	ν_{H9a}	2961.62	$^{3}J_{H3\text{-}H6} = {}^{3}J_{H4\text{-}H8}$	8.29
				$^{4}J_{H3\text{-}H8} = {}^{4}J_{H4\text{-}H6}$	-0.22
				$^{4}J_{H3\text{-}H7b} = {}^{4}J_{H4\text{-}H9b}$	0.22
				$^{4}J_{H3\text{-}H7a} = {}^{4}J_{H4\text{-}H9a}$	0.36
				$^{5}J_{H6\text{-}H8}$	-0.01
				$^{3}J_{H7b\text{-}H6} = {}^{3}J_{H9b\text{-}H8}$	10.33
				$^{3}J_{H7a\text{-}H6} = {}^{3}J_{H9a\text{-}H8}$	17.15
				$^{2}J_{H7b\text{-}H7a} = {}^{3}J_{H9b\text{-}H9a}$	1.87

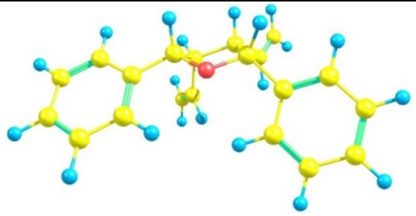
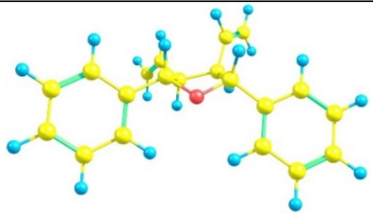
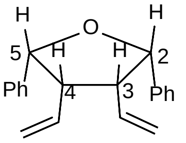
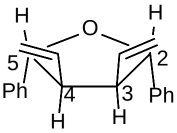
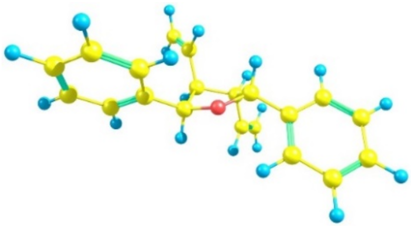
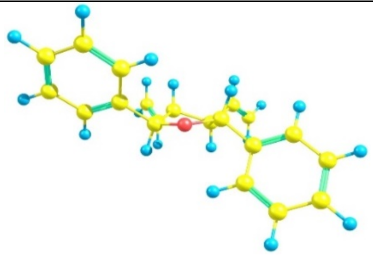
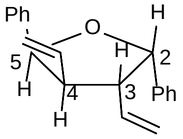
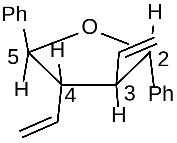
Note: other $J_{H\text{-}H}$-couplings were equated 0.00 Hz.

It was found that $^{3}J_{H2,H3}$ is 9.5 Hz and $^{3}J_{H3,H4}$ is 10.9 Hz.

4. Quantum chemical calculations of geometry and $J_{H\text{-}H}$-coupling constants

Generally, according to the literature data [S2-S4], in five-membered rings ${}^3J_{cis} > {}^3J_{trans}$. As far as the *cis*-orientation of all substituents seemed doubtful, quantum chemical calculations of geometry (B3LYP/6-311++G(2df,2p)) and $J_{H\text{-}H}$-coupling constants (B3LYP/6-311++G(2df,2p) using Mixed scheme) for the four model symmetrically substituted tetrahydrofuran stereoisomers were performed using Gaussian 09 software package [S5]. It was done for the interpretation of large values of spin-spin coupling constants and making the conclusion about orientation of ring substituents. Two of them **A** (2,3-*cis*-3,4-*cis*-4,5-*cis*), **B** (2,3-*trans*-3,4-*cis*-4,5-*trans*) have a plane of symmetry and two other stereoisomers **C** (2,3-*cis*-3,4-*trans*-4,5-*cis*), **D** (2,3-*trans*-3,4-*trans*-4,5-*trans*) have a C_2-axis of symmetry (Table S2).

Table S2 Determined parameters of the model structures **A**, **B**, **C** and **D.**

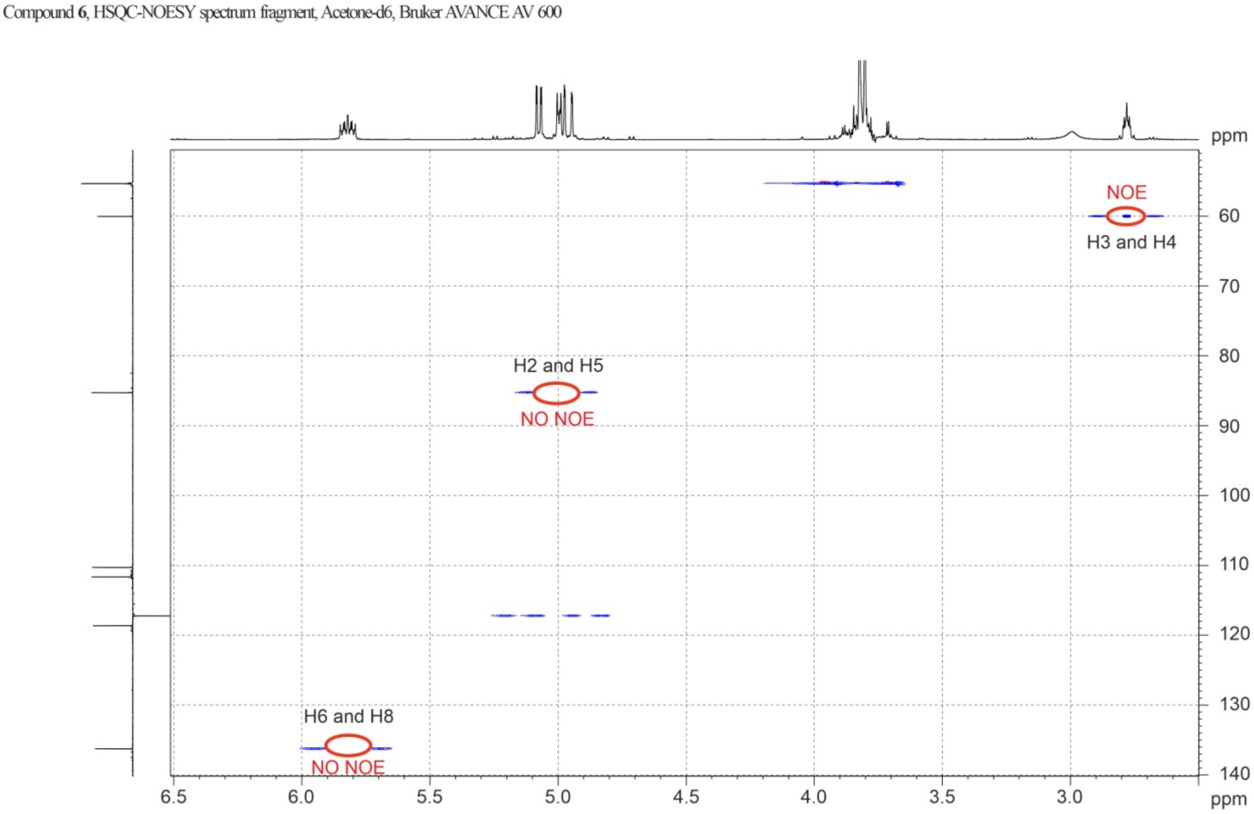
			
	$\varphi_{H2\text{-}H3}$ = 12.3 ° $\varphi_{H3\text{-}H4}$ = 34.0 ° $\varphi_{H4\text{-}H5}$ = 42.1 ° ${}^3J_{H2\text{-}H3}$ = 8.2 Hz ${}^3J_{H3\text{-}H4}$ = 8.0 Hz		$\varphi_{H2\text{-}H3}$ = 152.2 ° $\varphi_{H3\text{-}H4}$ = 2.3 ° $\varphi_{H4\text{-}H5}$ = 155.6 ° ${}^3J_{H2\text{-}H3}$ = 8.9 Hz ${}^3J_{H3\text{-}H4}$ = 13.2 Hz
A (2,3-*cis*-3,4-*cis*-4,5-*cis*)		**B** (2,3-*trans*-3,4-*cis*-4,5-*trans*)	
			
	$\varphi_{H2\text{-}H3}$ = 33.5 ° $\varphi_{H3\text{-}H4}$ = 89.3 ° $\varphi_{H4\text{-}H5}$ = 33.6 ° ${}^3J_{H2\text{-}H3}$ = 6.3 Hz ${}^3J_{H3\text{-}H4}$ = 0.5 Hz		$\varphi_{H7\text{-}H8}$ = 159.8 ° $\varphi_{H8\text{-}H8'}$ = 167.9 ° $\varphi_{H8'\text{-}H7'}$ = 159.8 ° ${}^3J_{H2\text{-}H3}$ = 9.5 Hz ${}^3J_{H3\text{-}H4}$ = 10.9 Hz
C (2,3-*cis*-3,4-*trans*-4,5-*cis*)		**D** (2,3-*trans*-3,4-*trans*-4,5-*trans*)	

Note: ${}^3J_{H2\text{-}H3}$ *were averaged over two conformers.*

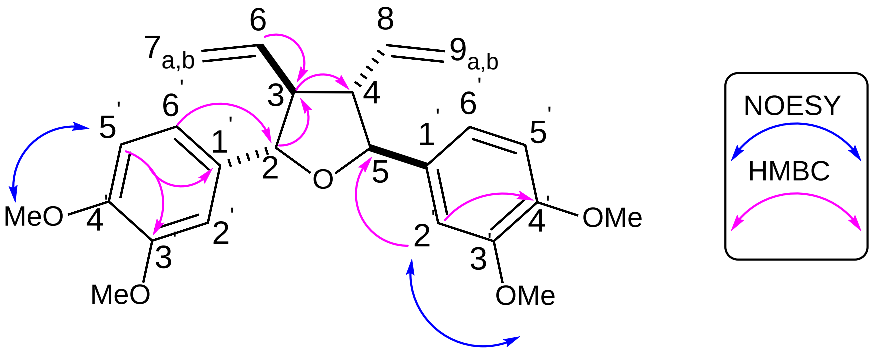
As a result, the stereoisomer **D**, containing all substituents in trans- orientation relative to each other, showed the best correspondence of theoretical and experimental values of ${}^{3}J_{H\text{-}H}$-coupling constants between the ring protons.

5. Key HSQC-NOESY correlations of the (2*R**,3*R**,4*R**,5*R**)-2,5-*bis*(3,4-dimethoxyphenyl)-3,4-divinyltetrahydrofuran (4)

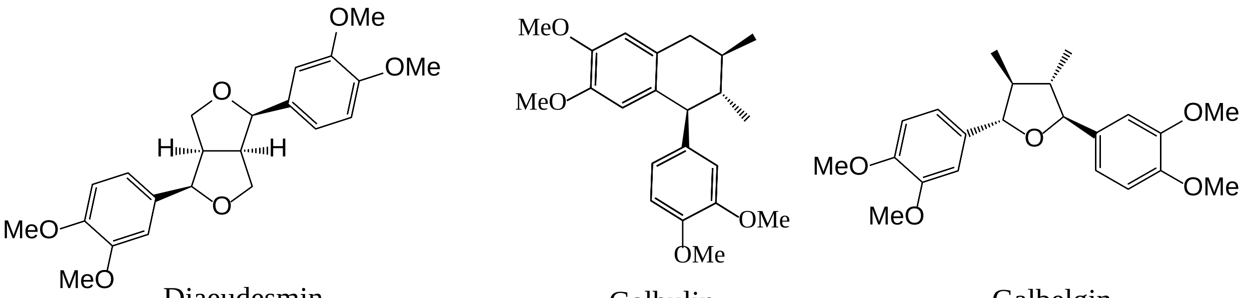
In addition, for the reinforcement of stereochemical assignment, the ^{1}H,^{1}H-NOESY spectrum with the enhanced signal-to-noise ratio and the ^{1}H,^{13}C-HSQC NOESY spectrum without decoupling during signal acquisition were recorded to explore the NOE-effects between ^{1}H-^{13}C satellite and central ^{1}H-^{12}C signals. From these spectra, it follows, that there are no NOE contacts between H-2, H-5 and α-protons of vinyl- substituents, which also indicates the *trans*-orientation of substituents attached to the tetrahydrofurane ring.



HSQC-NOESY spectrum fragment of compound **4.**



Key NOESY and HMBC correlations for determination of the compound **4** structure.



Diaeudesmin

Galbulin

Galbelgin

Figure S2 Some natural lignans structures of furofuran, aryltetrahydronaphthalene and 2,5-diaryltetrahydrofuran series, that can be obtained from diols **2a,b.**

6. References

[S1] D. A. Cheshkov, K. F. Sheberstov, D. O. Sinitsyn, V. A. Chertkov, *Magn. Reson. Chem.* 2018, **56**, 449.

[S2] Y. Y. Samitov, A. A, Musina, R. M, Aminova, M. A, Pudovik, A. I, Khayarov, M. D. Medvedeva, *Org. Magn. Reson.*, 1980, **13**, 163.

[S3] R. J. Abraham, C. J. Medforth, *Magn. Reson. Chem.*, 1990, **28**, 343.

[S4] M. Karplus, Contact electron-spin coupling of nuclear magnetic moments. *J. Chem. Phys.*, 1959, **30**, 11.

[S5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian 09W, Revision A.02*, Gaussian, Inc., Wallingford CT, 2009.