

SUPPORTING INFORMATION

Synthesis of cordiaquinones B, C, J and K on the basis of a bio-inspired approach, and the revision of the relative stereochemistry of cordiaquinone C

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Experimental Section

General: Nuclear magnetic resonance spectra were obtained on 300 and 500 MHz instruments. Isomeric purities were determined by ^1H NMR and by GC analysis on a 60 meters HP-5 capillary column. All spectra reported herein were taken in CDCl_3 .

(*Z*)-2,2-Dimethyl-3-(3-methyl-7-methylenenona-3,8-dienyl)oxirane (**21**)

Following a procedure similar to the synthesis of **4**, the (*Z*)-epoxide **21** was prepared as the only regioisomer in 72% yield. ^1H NMR: 6.33 (dd, $J_1=17.5$ Hz, $J_2=11.0$ Hz, 1H), 5.19 (d, $J=17.5$ Hz, 1H), 5.16 (t, $J=6.0$ Hz, 1H), 5.02 (d, $J=10.5$ Hz, 1H), 4.98 (s, 1H), 4.95 (s, 1H), 2.67 (t, $J=6.0$ Hz, 1H), 2.10-2.21 (m, 6H), 1.68 (s, 3H), 1.58 (m, 2H), 1.26 (s, 3H), 1.23 (s, 3H). ^{13}C NMR: 145.9, 138.8, 134.5, 125.4, 115.8, 113.1, 64.0, 58.2, 31.5, 28.5, 27.4, 26.4, 24.9, 23.3, 18.7. MS (EI): 220 (M^+ , 1%), 202 (1%), 187 (3%), 159 (7%), 134 (24%), 93 (100%).

Zeolite NaY-promoted cyclization of epoxide **21**

To a hexane (15 mL) slurry of dry NaY (2 gr) were added 100 mg of epoxide **21**. After 6 minutes, the heterogeneous mixture was filtered and the solid residue was washed with methanol (2 x 15 mL) for 30 minutes each time. The combined solvents were removed under vacuum to afford 79 mg a mixture containing cyclized alcohols **22** (exo) and **23** (endo), bicyclic ether **24** and the non-cyclized allylic alcohol **25**, in a relative ratio (**22+23**)/**24/25** = 70/10/5/15. The desired non-separable mixture of **22** and **23** (48 mg) was isolated from the reaction mixture by column chromatography, using hexane/ethyl acetate = 15/1 as eluant. ^1H NMR of the major **22** (exo): 6.36 (dd, $J_1=17.5$ Hz, $J_2=11.0$ Hz, 1H), 5.18 (d, $J=17.5$ Hz, 1H), 5.04 (d, $J=11.0$ Hz, 1H), 5.01 (s, 1H), 4.99 (s, 1H), 4.84 (br. s, 1H), 4.64 (br. s, 1H), 3.65 (dd, $J_1=10.0$ Hz, $J_2=5.5$ Hz, 1H), 2.15-2.28 (m, 3H), 1.90-1.99 (m, 2H), 1.63-1.81 (m, 2H), 1.47-1.58 (m, 2H), 0.97 (s, 3H), 0.90 (s, 3H). ^{13}C NMR of **22**: 147.8, 147.2, 139.4, 116.0, 113.5, 111.2, 74.3, 54.4, 39.4, 31.9, 30.6, 30.4, 25.4, 24.7, 22.0.

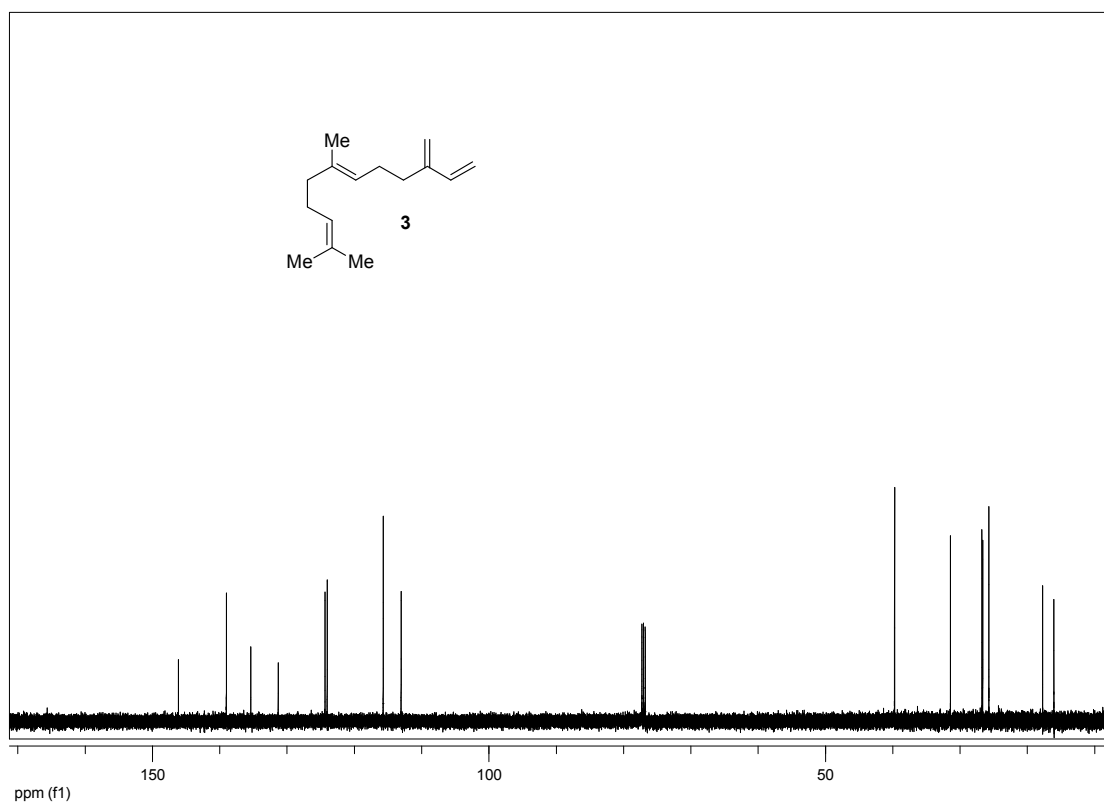
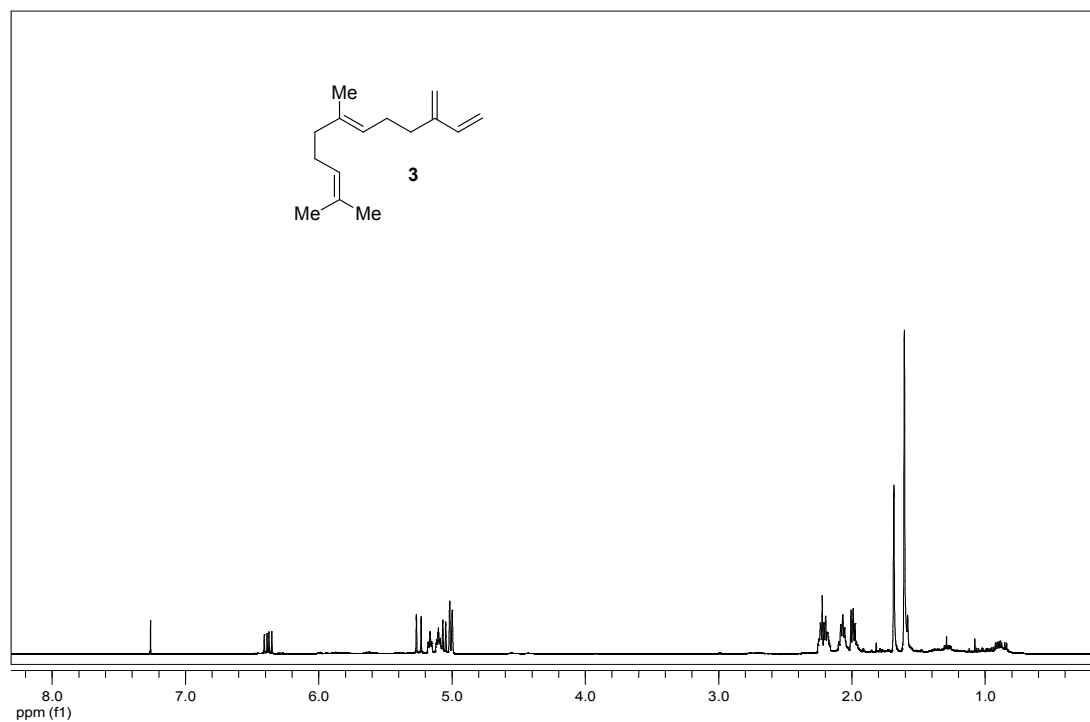
MS (EI): 220 (M^+ , 3%), 205 (6%), 202 ($M^+ - H_2O$, 4%), 187 (32%), 174 (48%), 159 (52%), 91 (82%), 79 (100%), 55 (89%).

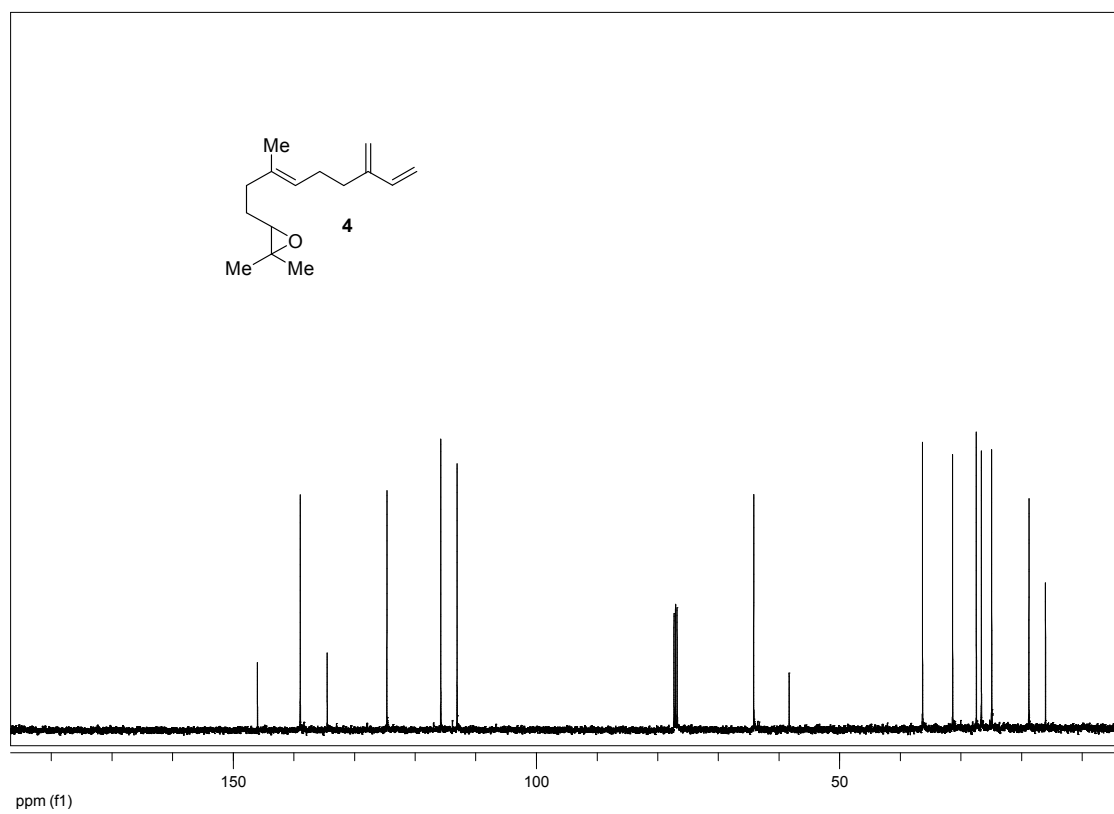
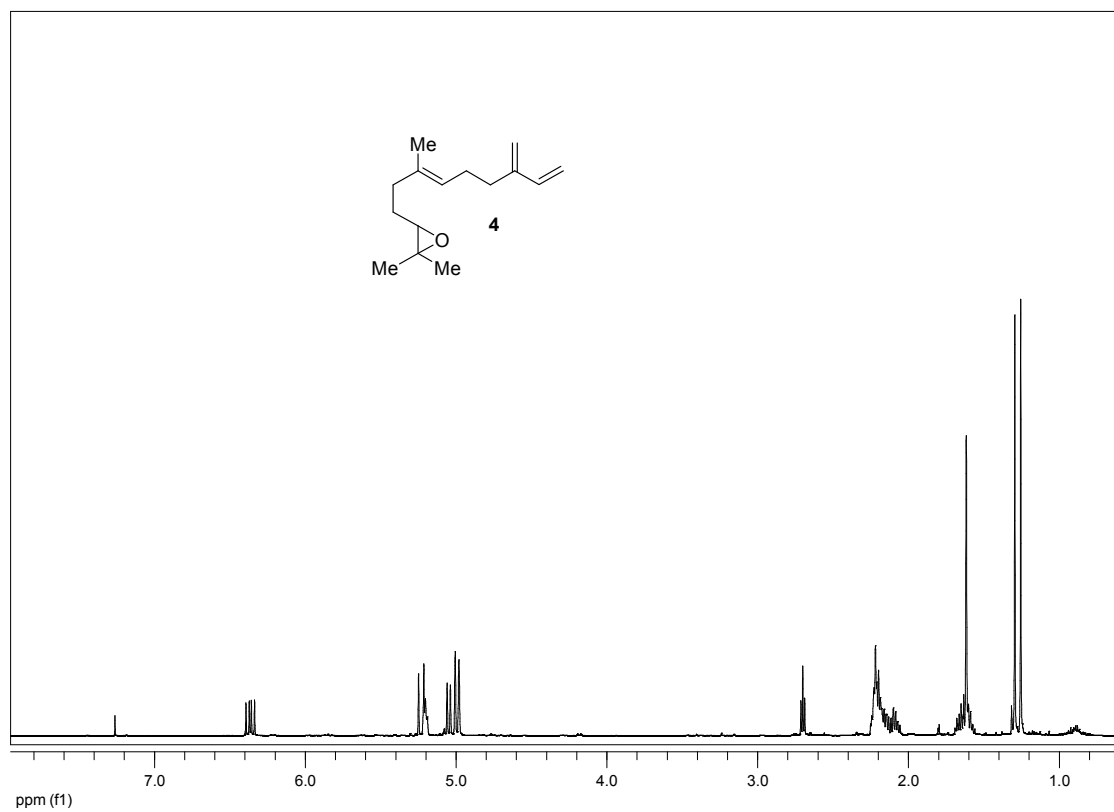
***trans*-2,2-Dimethyl-4-methylene-3-(3-methylenepent-4-enyl)cyclohexyl 3-methylbut-2-enoate (26)**

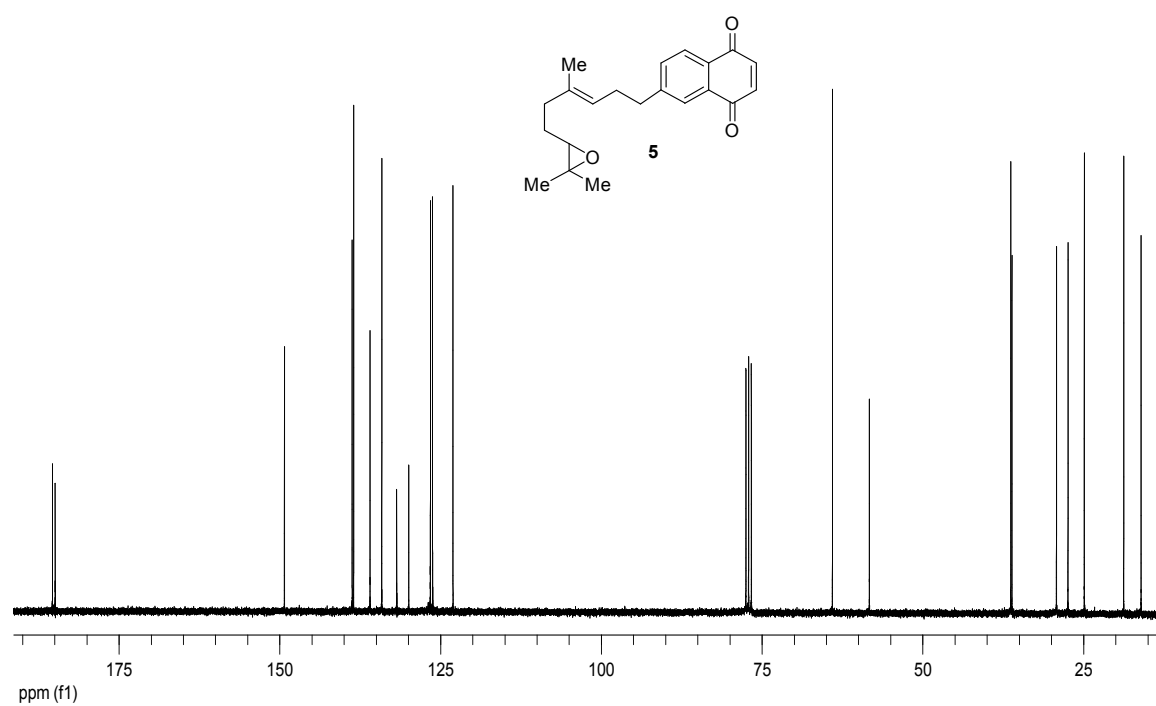
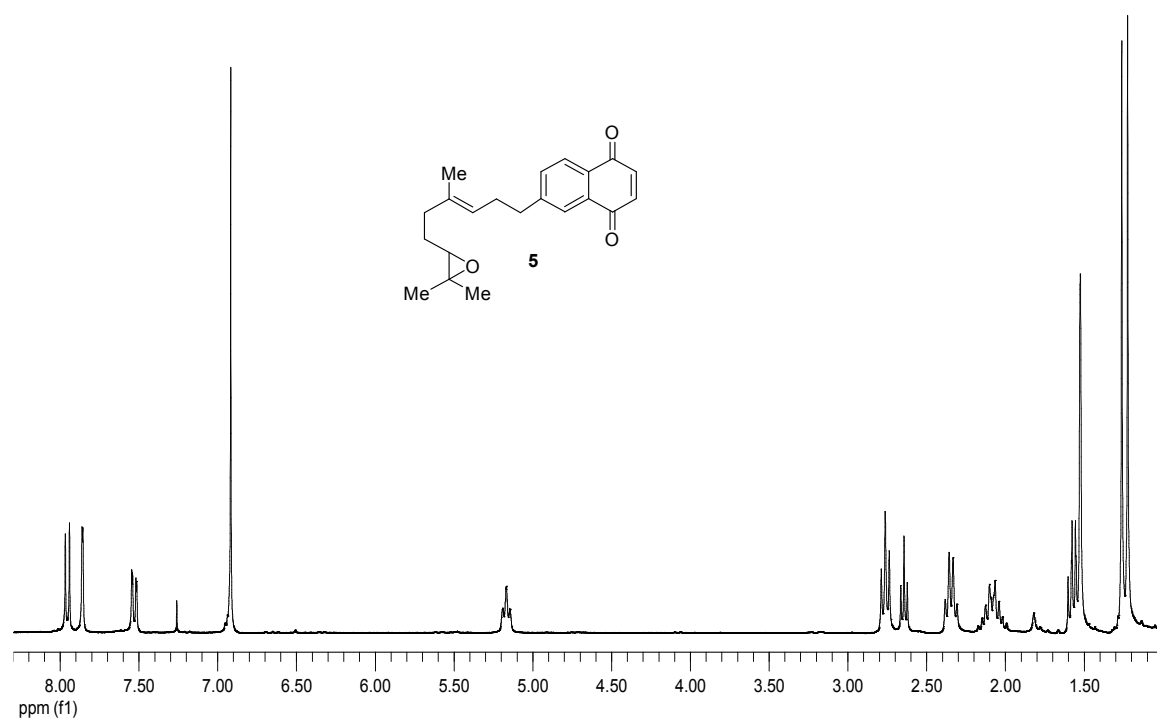
The mixture of regioisomeric alcohols **22/23** reacted with 3,3-dimethylacryloyl chloride, as described in the synthesis of **14/15**, to form the dimethylacryloyl esters **26** (exo) and **27** (endo) in 81% yield. 1H NMR of the major **26** (exo): 6.35 (dd, $J_1=17.5$ Hz, $J_2=10.5$ Hz, 1H), 5.68 (br. s., 1H), 4.98-5.21 (m, 4H), 4.93 (dd, $J_1=10.0$ Hz, $J_2=4.5$ Hz, 1H), 4.85 (s, 1H), 4.65 (s, 1H), 2.14-2.36 (m, 4H), 2.16 (s, 3H), 1.89 (s, 3H), 1.55-2.00 (m, 5H), 0.95 (s, 3H), 0.89 (s, 3H). ^{13}C NMR of **26** (exo): 166.4, 156.2, 147.0, 146.6, 139.0, 116.5, 115.6, 113.2, 110.8, 75.1, 51.0, 38.2, 32.1, 30.0, 28.3, 29.3, 27.4, 24.9, 22.7, 20.2. MS (EI): 302 (M^+ , <1%), 219 (4%), 202 (5%), 187 (4%), 159 (7%), 133 (10%), 83 (100%), 73 (96%).

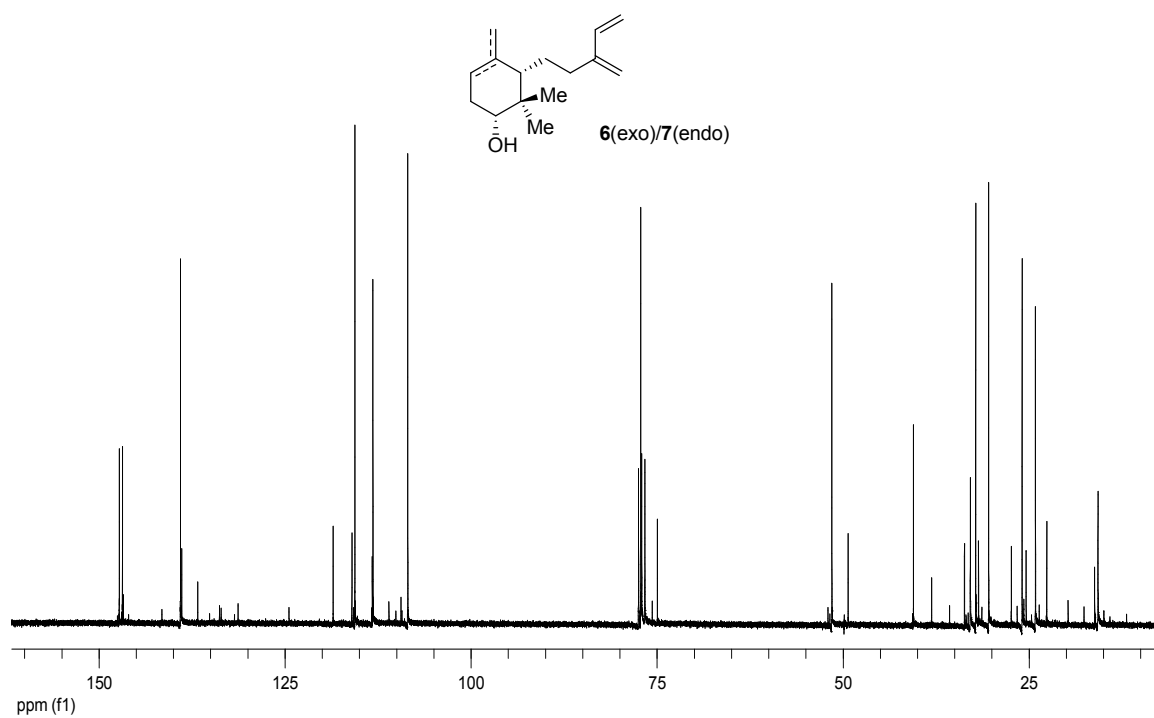
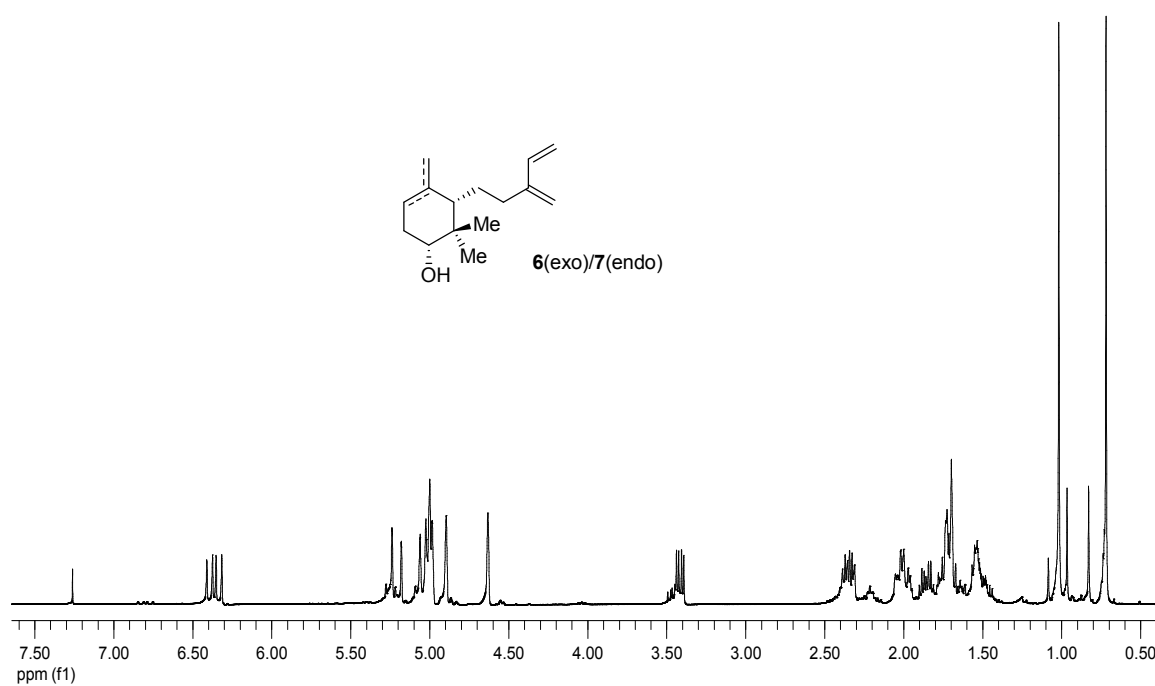
***trans*-3-(2-(5,8-Dioxo-5,8-dihydronaphthalen-2-yl)ethyl)-2,2-dimethyl-4-methylene-cyclohexyl 3-methylbut-2-enoate (28, proposed structure of cordiaquinone C)**

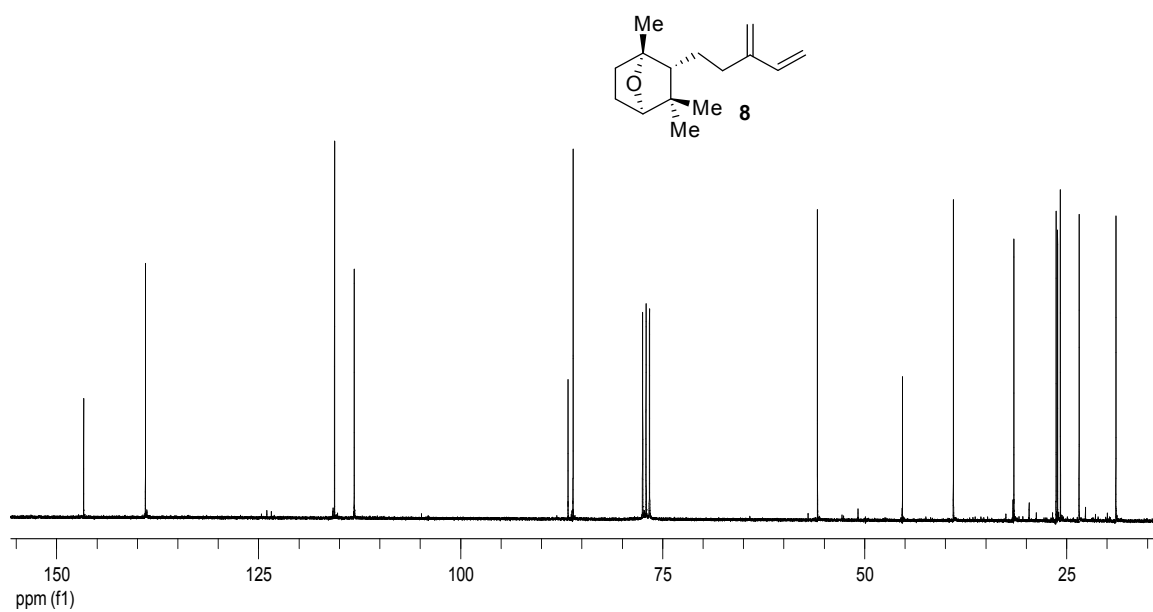
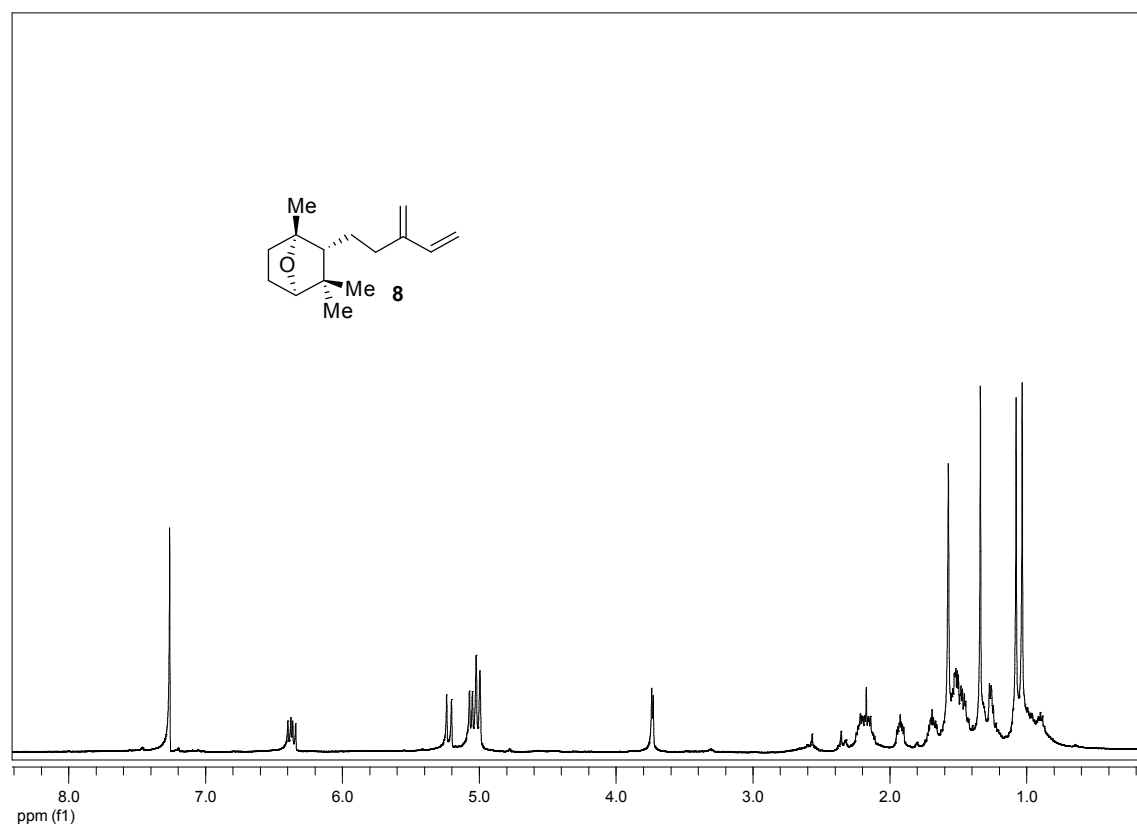
Under identical conditions applied to the synthesis of **16/17**, the regioisomeric naphthoquinones **28** and **29** were isolated in 70% yield and in a relative ratio **28/29** ~ 6/1. 1H NMR of the major **28** (proposed structure of cordiaquinone C): 8.00 (d, $J=8.0$ Hz, 1H), 7.87 (d, $J=3.0$ Hz, 1H), 7.54 (dd, $J_1=8.0$ Hz, $J_2=3.0$ Hz, 1H), 6.95 (s, 2H), 5.66 (br. s, 1H), 4.93 (br. s, 1H), 4.92 (dd, $J_1=9.5$ Hz, $J_2=4.0$ Hz, 1H), 4.68 (br. s, 1H), 2.75 (m, 1H), 2.50 (m, 1H), 2.25 (m, 1H), 2.15 (s, 3H), 2.00 (dd, $J_1=9.0$ Hz, $J_2=2.5$ Hz, 1H), 1.72-1.89 (m, 4H), 1.88 (s, 3H), 1.61 (m, 1H), 0.95 (s, 3H), 0.89 (s, 3H). ^{13}C NMR of the major **28**: 185.4, 185.0, 166.4, 156.5, 149.9, 146.5, 138.8, 138.5, 134.0, 131.9, 129.9, 126.7, 126.2, 116.4, 111.4, 74.8, 53.7, 38.3, 34.7, 29.9, 28.2, 27.7, 27.4, 23.9, 22.7, 20.4. HRMS (EI): calcd for $C_{26}H_{30}O_4$ 406.21441; found 406.21432.

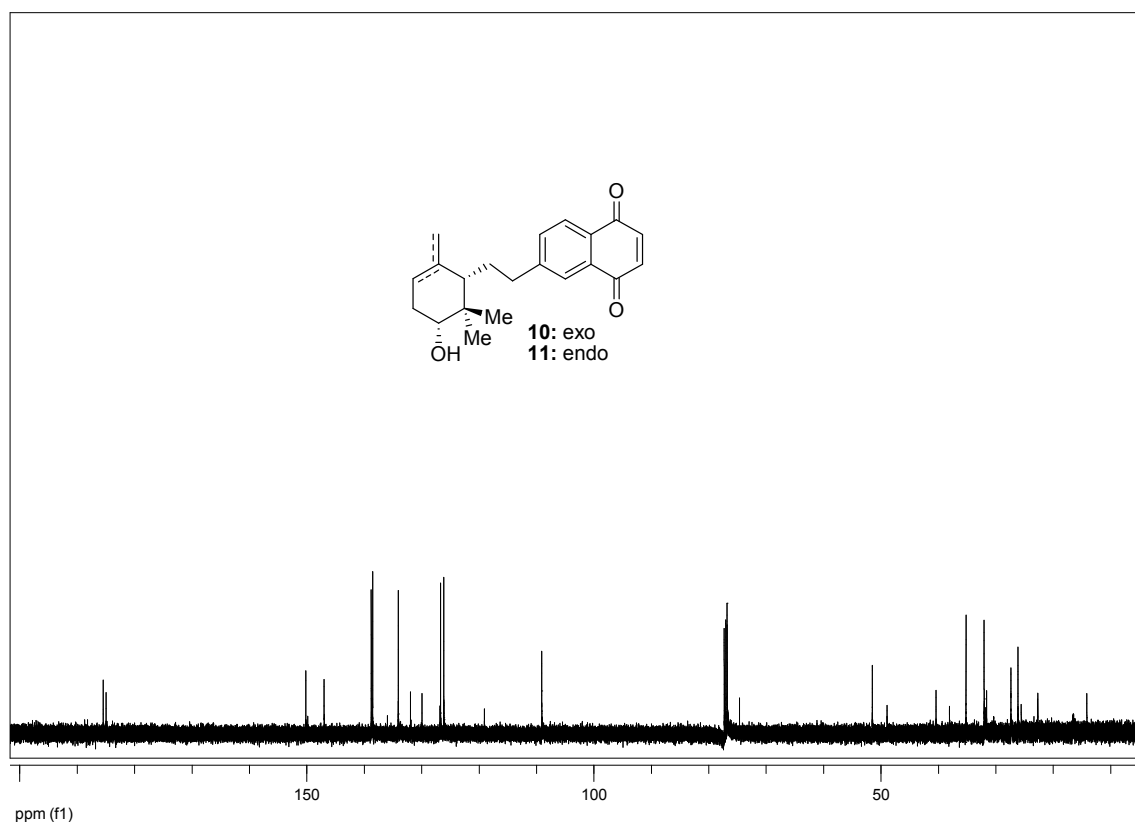
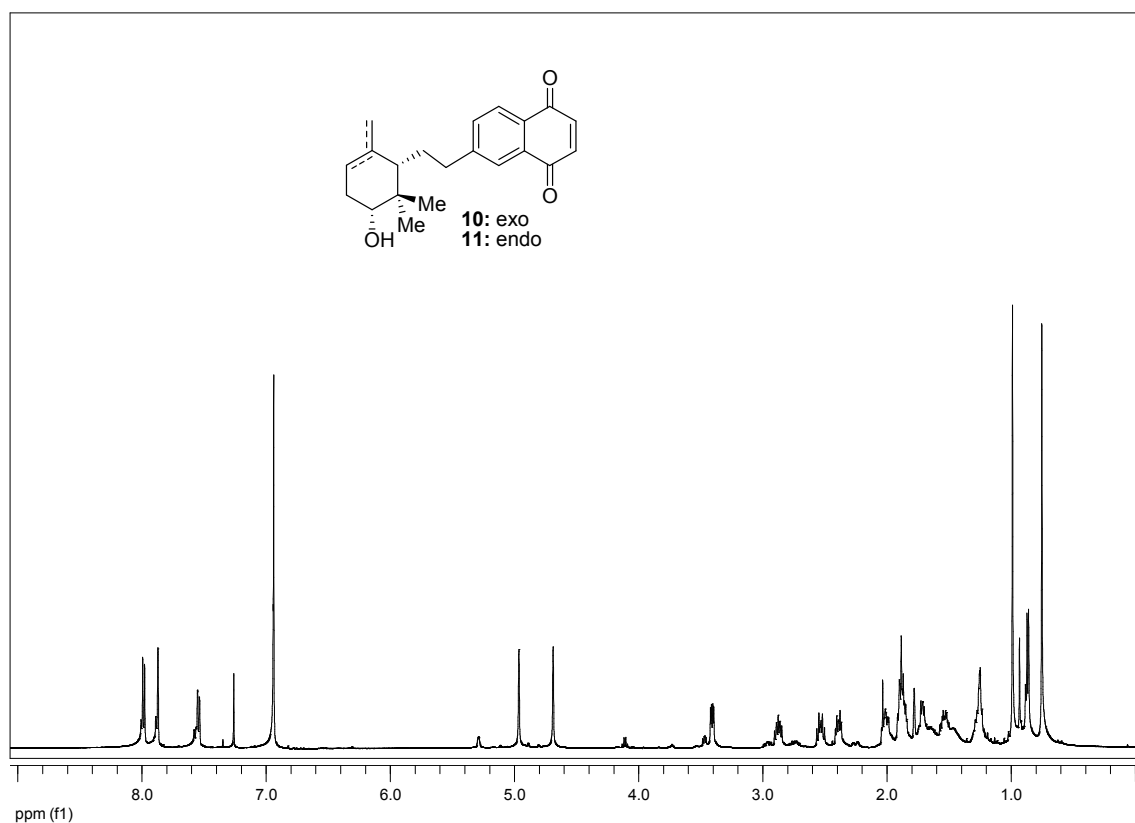
^1H and ^{13}C NMR spectra of (*E*)- β -farnesene (**3**)

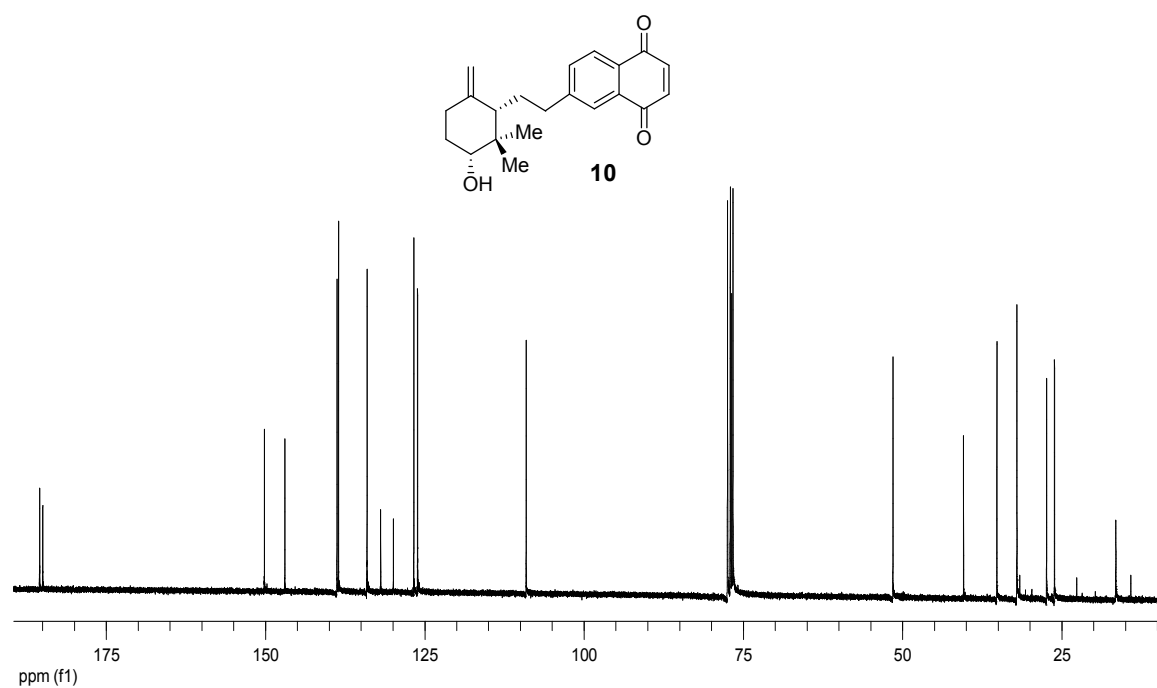
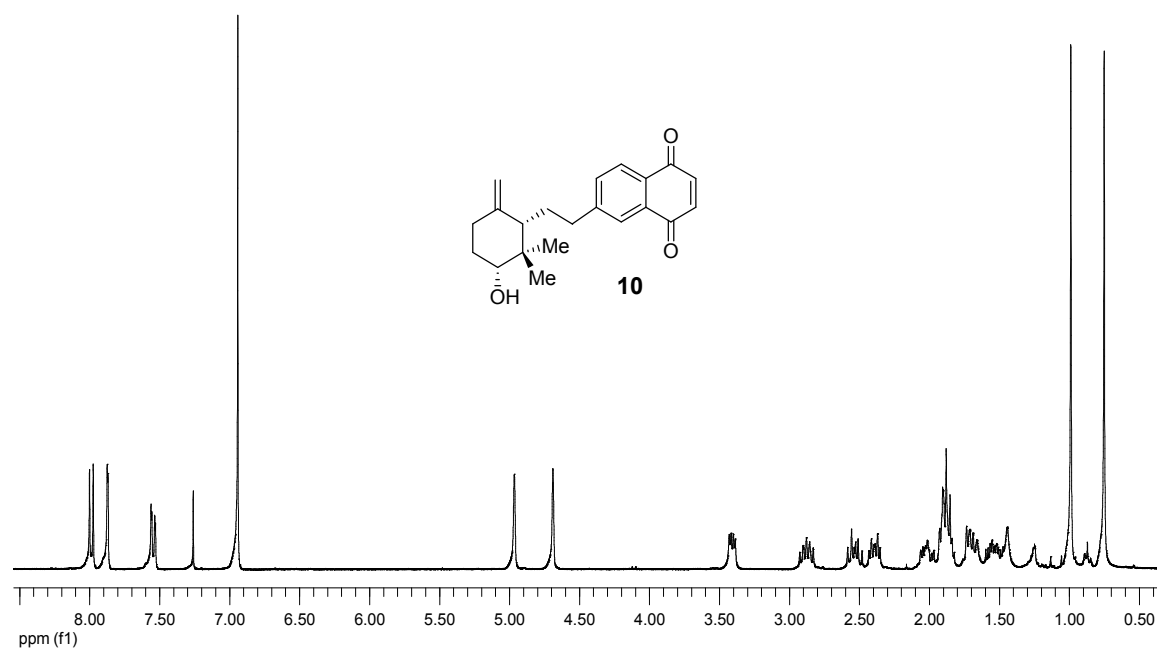
^1H and ^{13}C NMR spectra of epoxy (*E*)- β -farnesene (**4**)

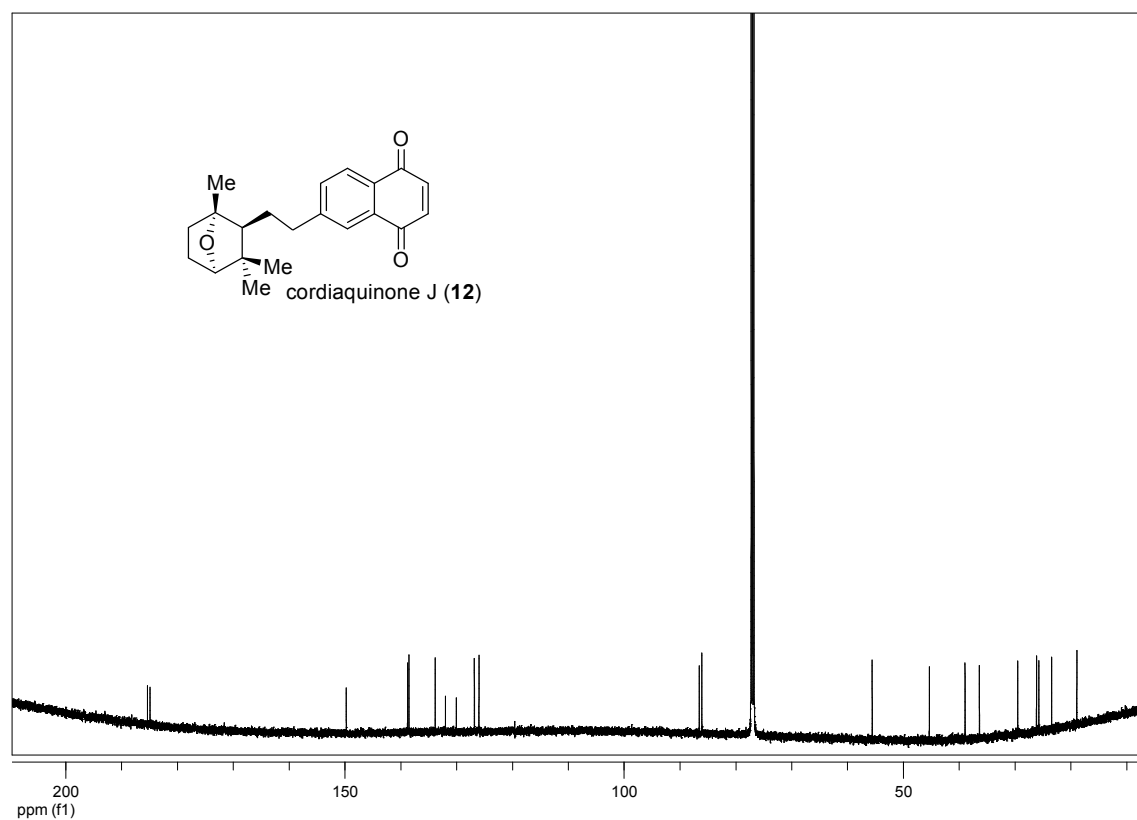
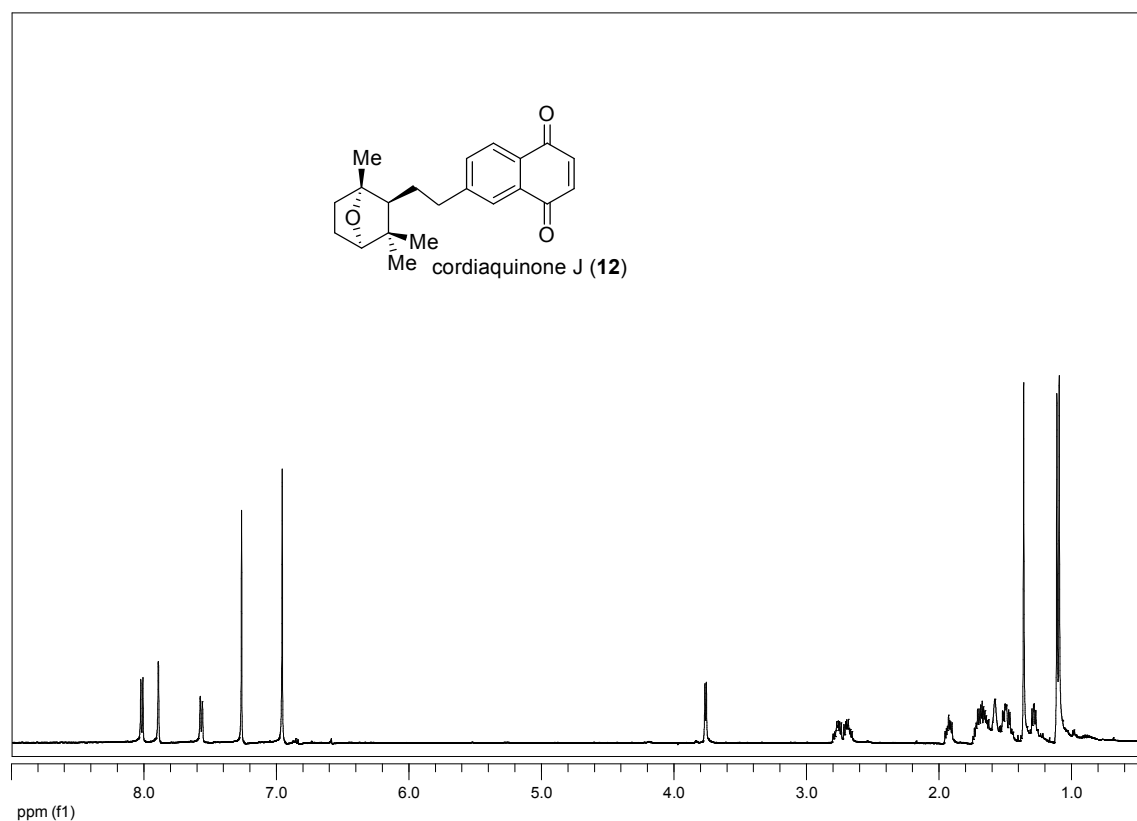
^1H and ^{13}C NMR spectra of epoxide **5**

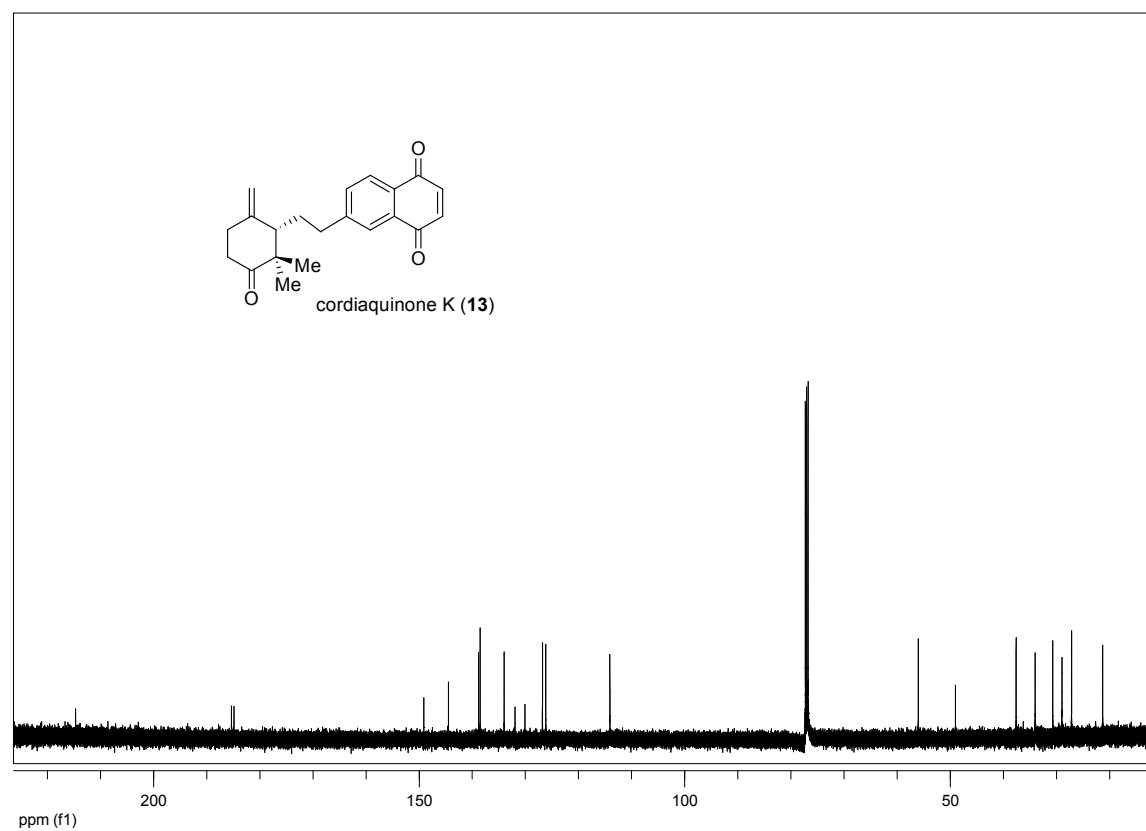
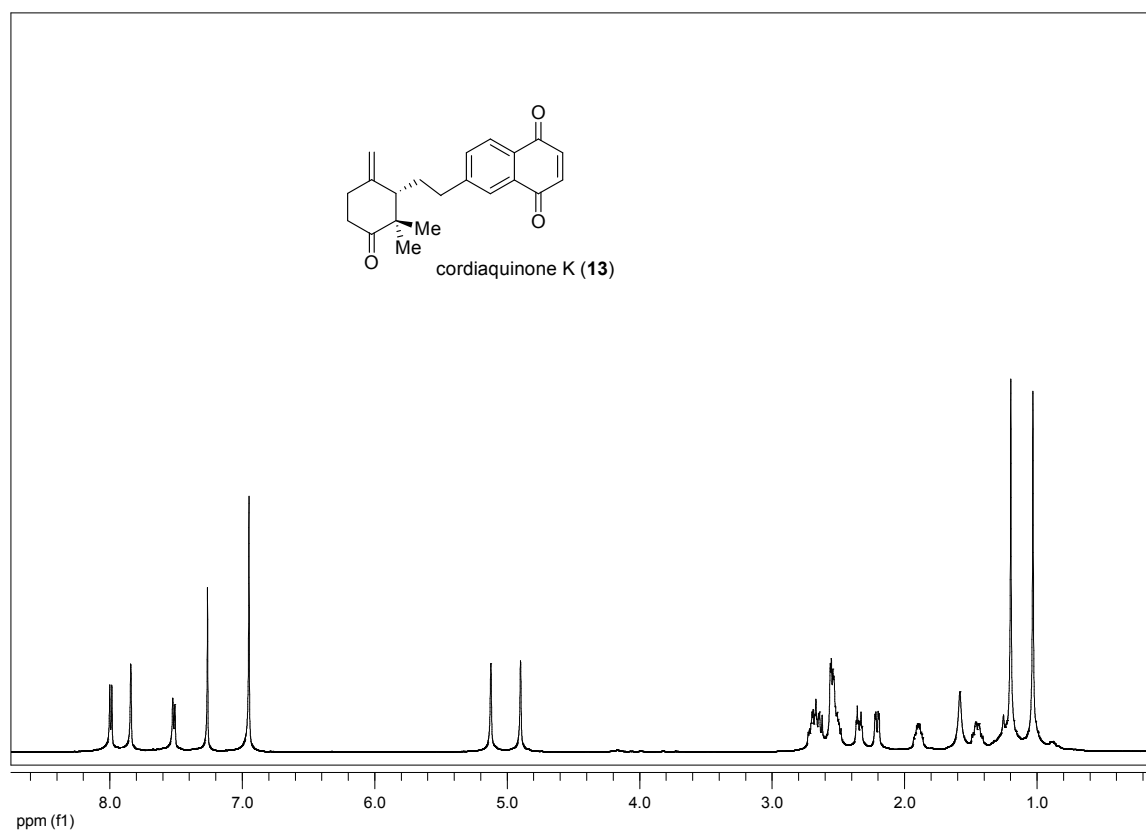
^1H and ^{13}C NMR spectra of the regioisomeric compounds **6/7**

^1H and ^{13}C NMR spectra of bicyclic ether **8**

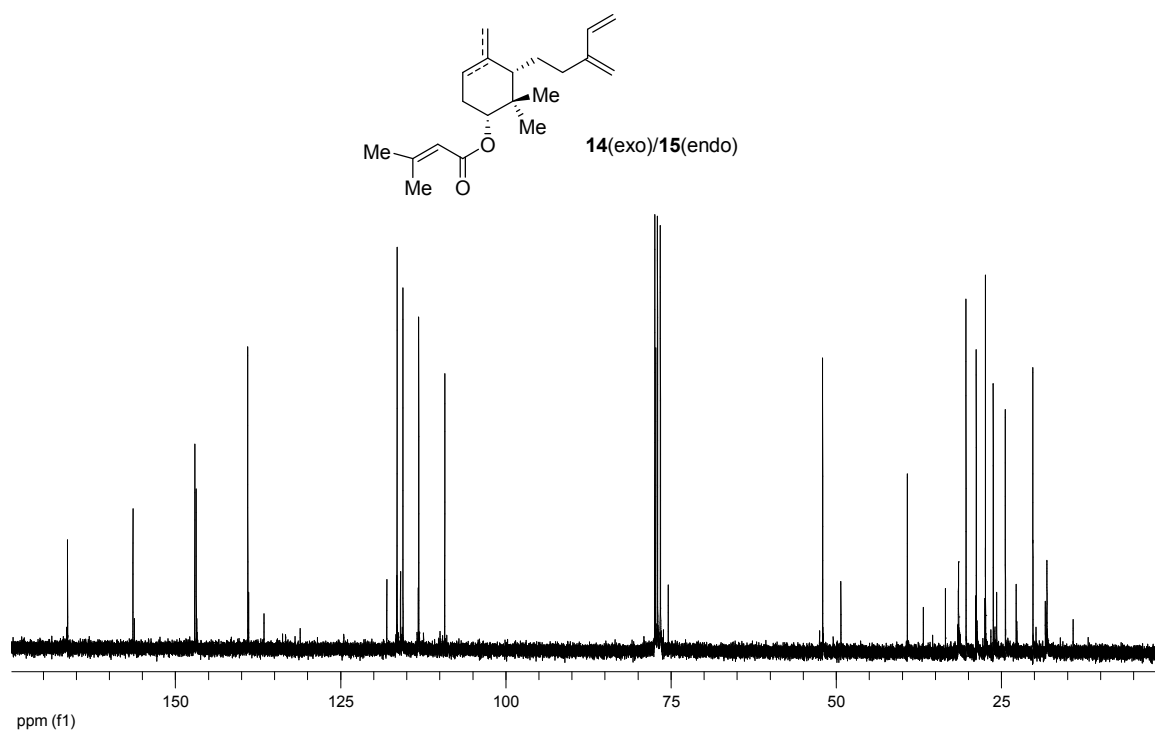
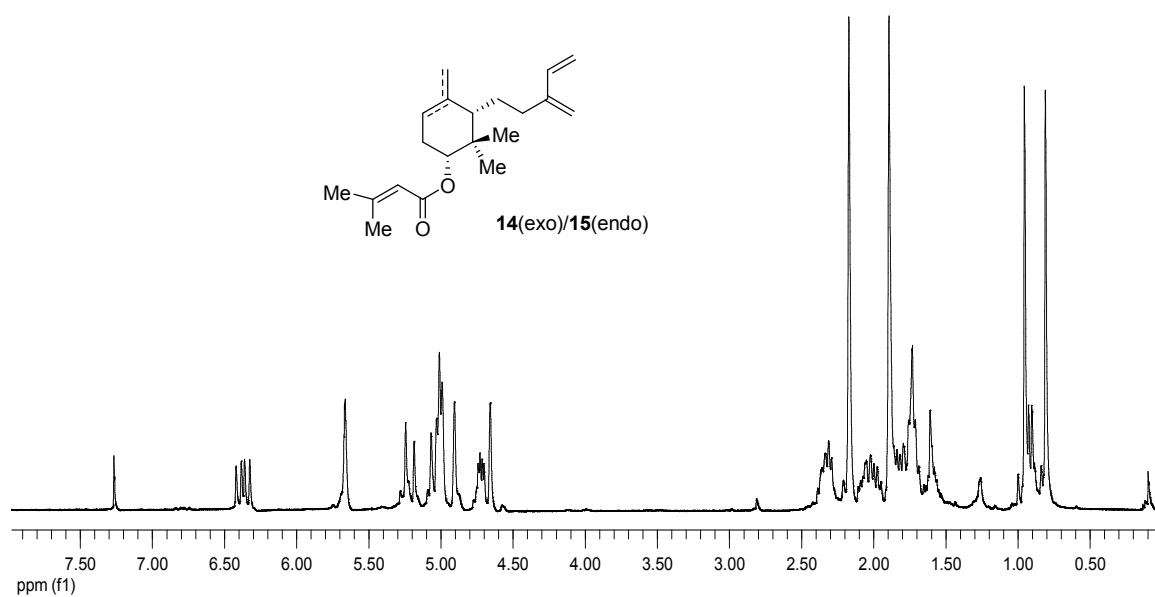
^1H and ^{13}C NMR spectra of the regioisomeric compounds **10** and **11**

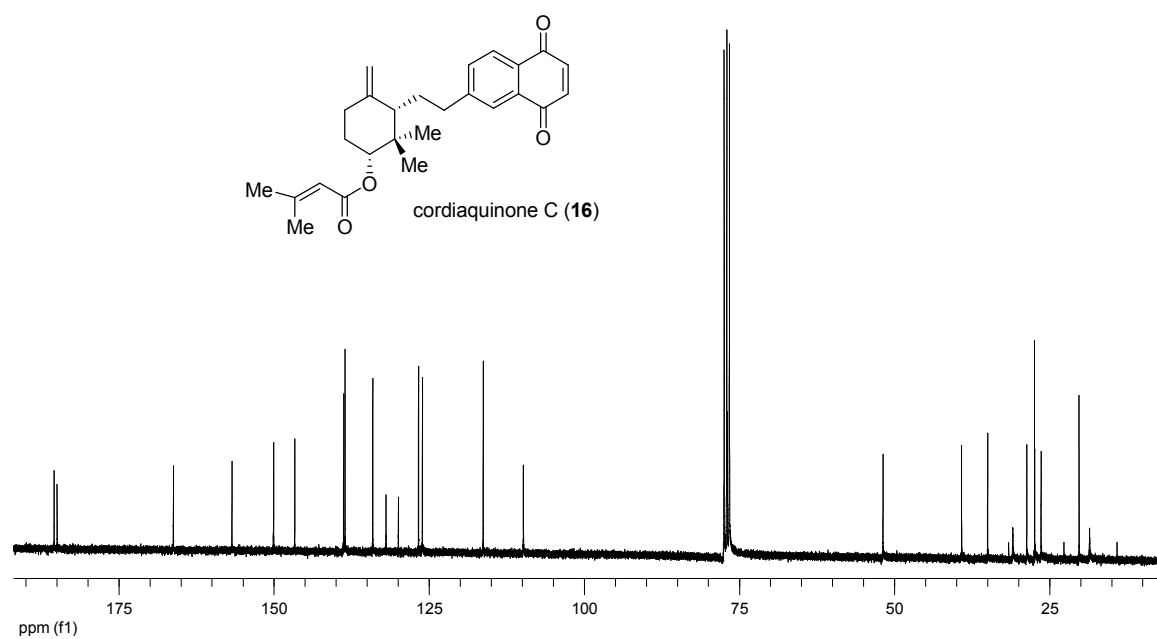
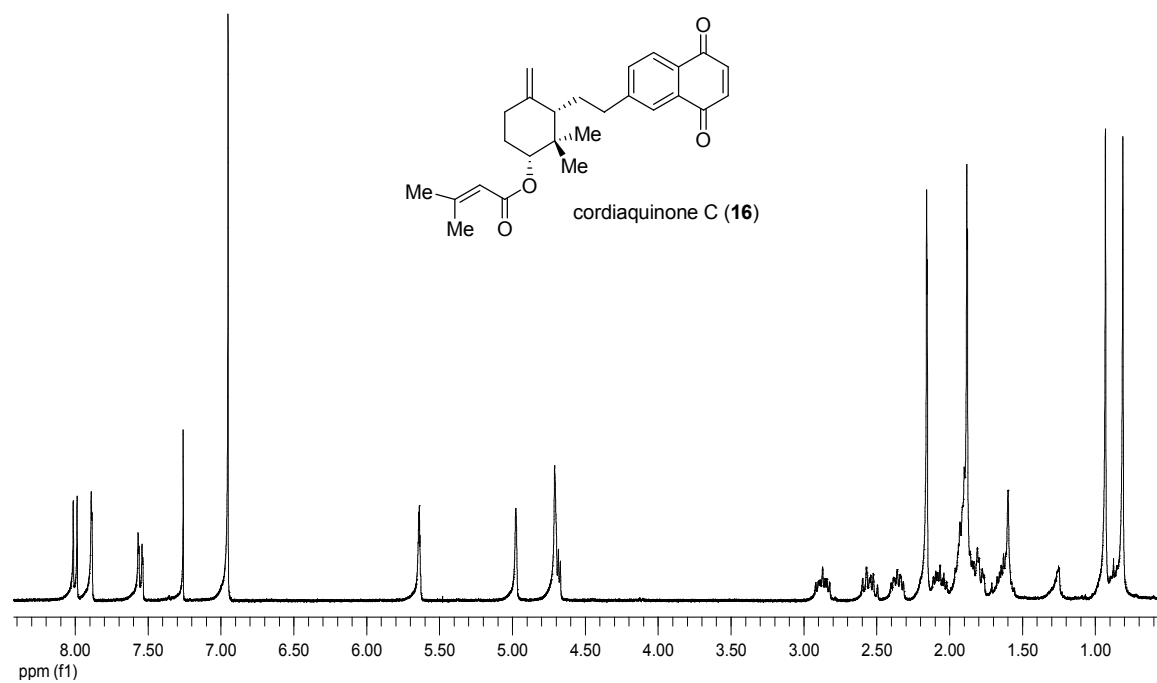
^1H NMR and ^{13}C NMR spectra of compound **10**

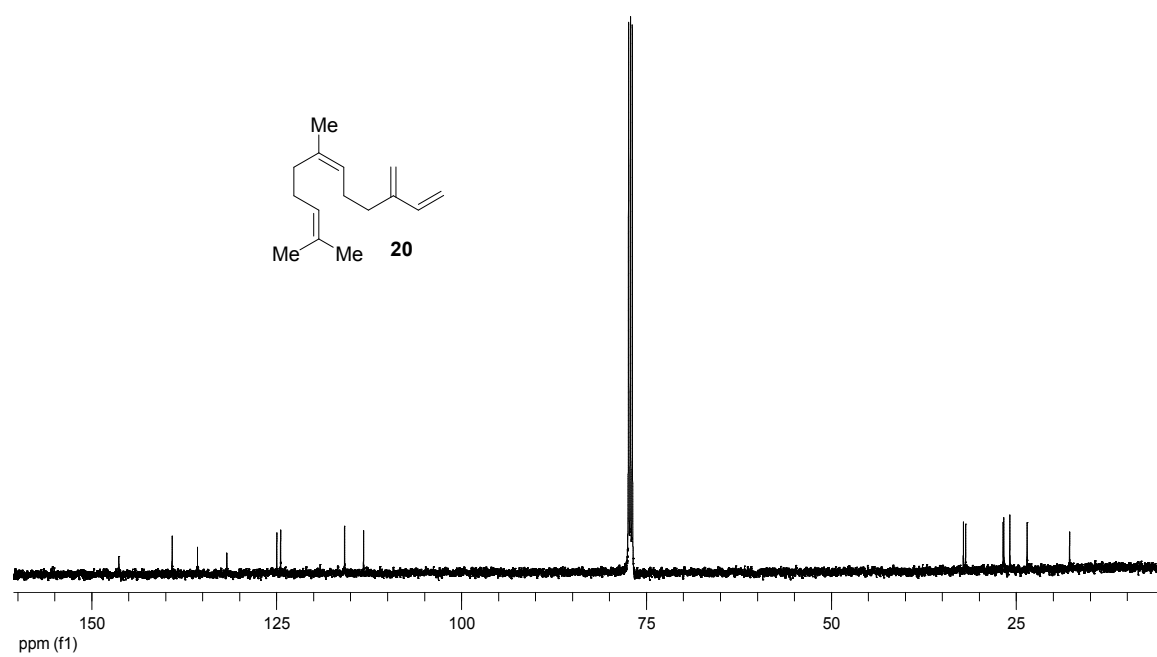
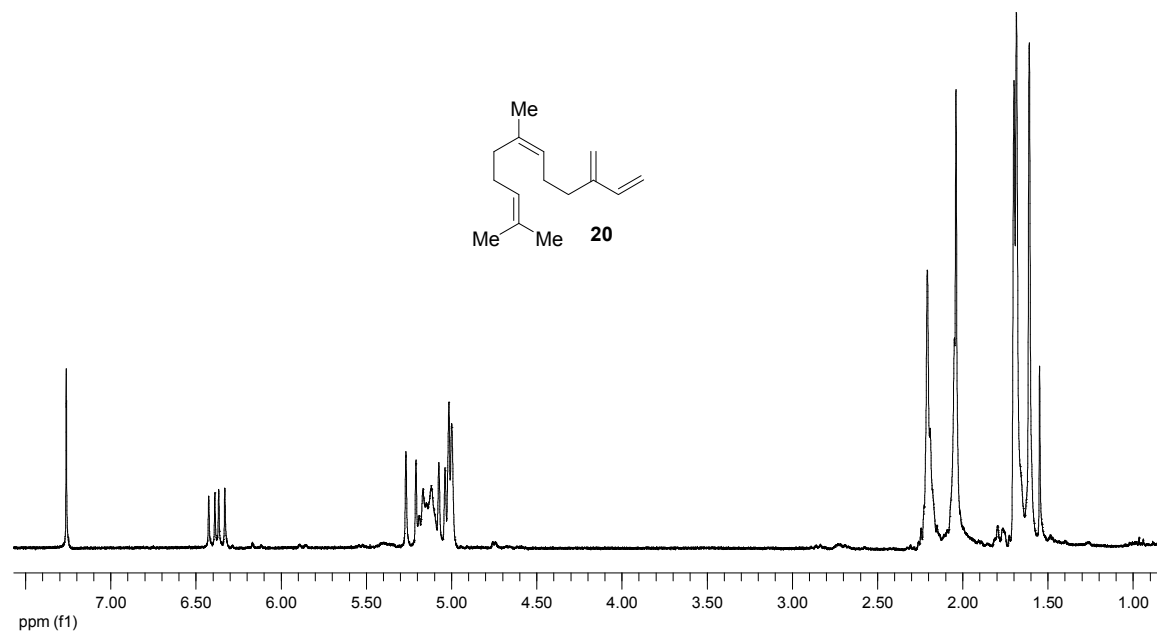
^1H and ^{13}C NMR spectra of cordiaquinone J (**12**)

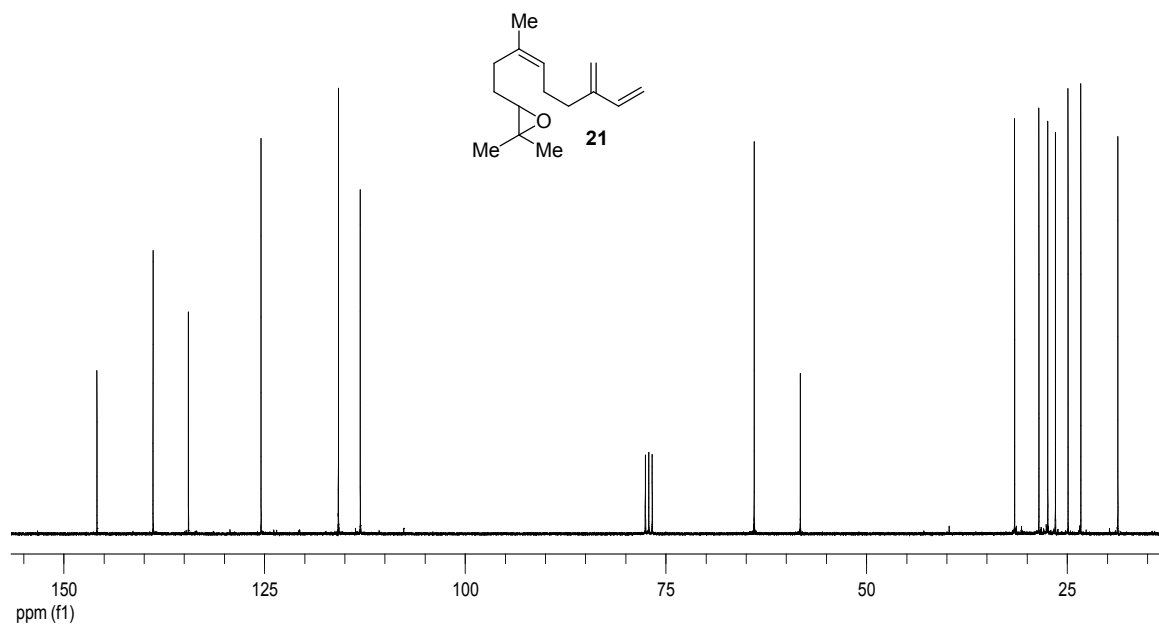
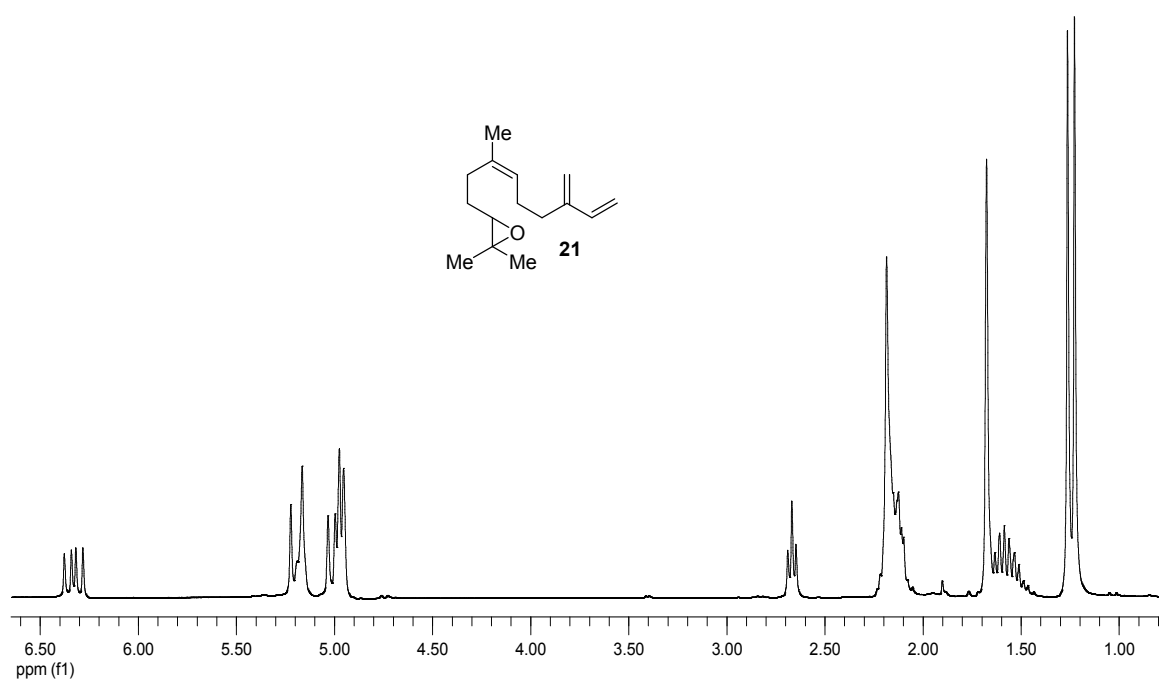
^1H and ^{13}C NMR spectra of cordiaquinone K (**13**)

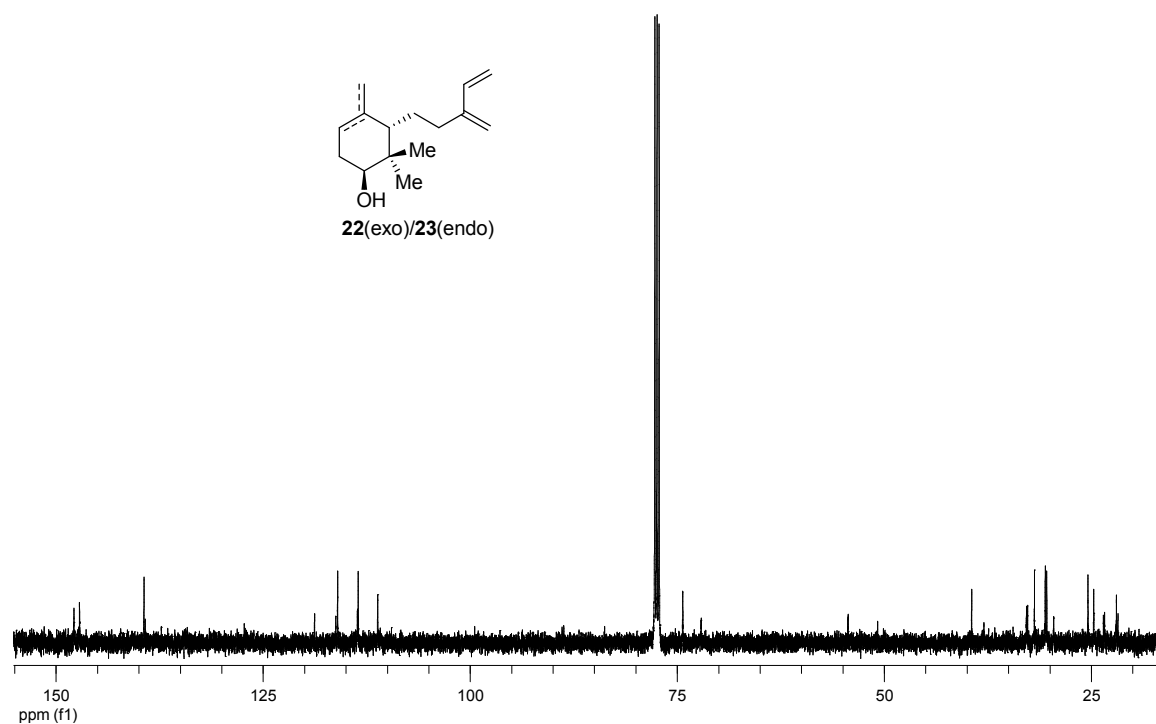
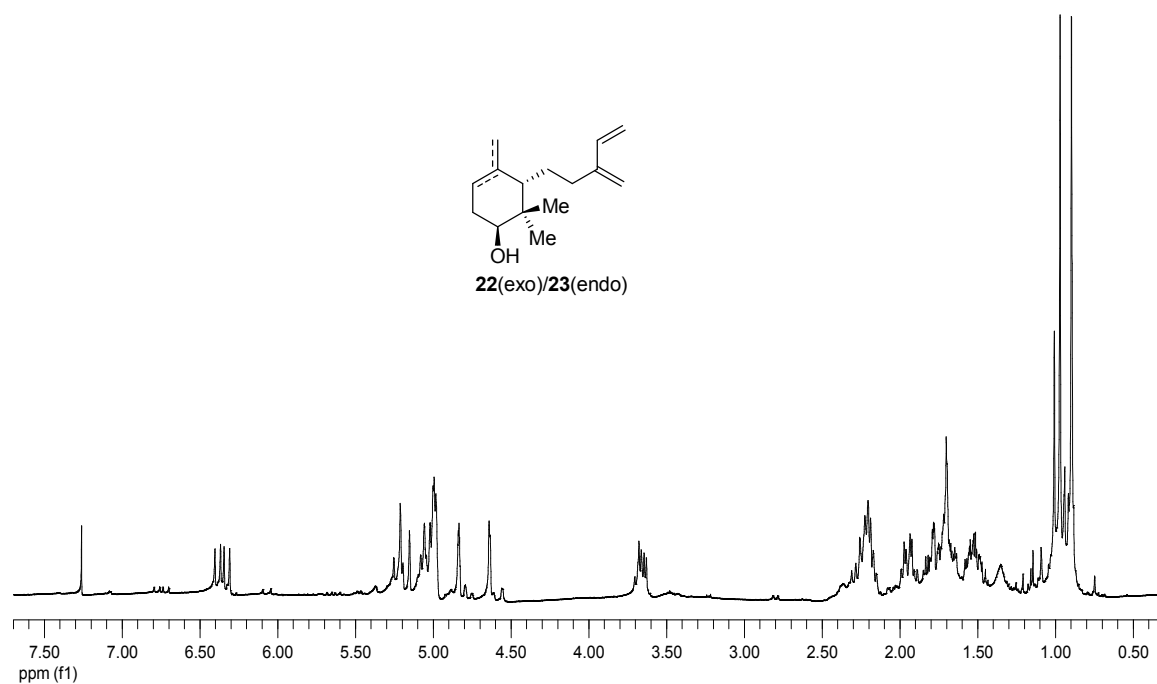
^1H and ^{13}C NMR spectra of the regiosomeric compounds **14/15**.

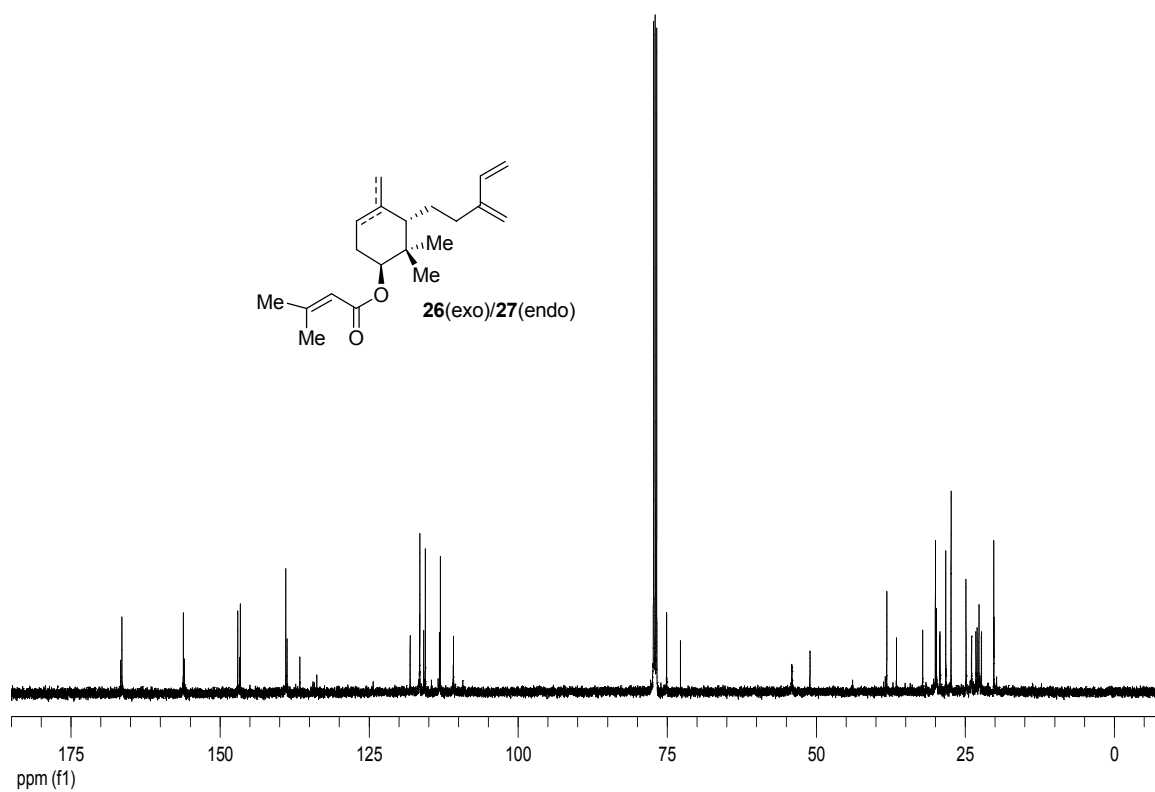
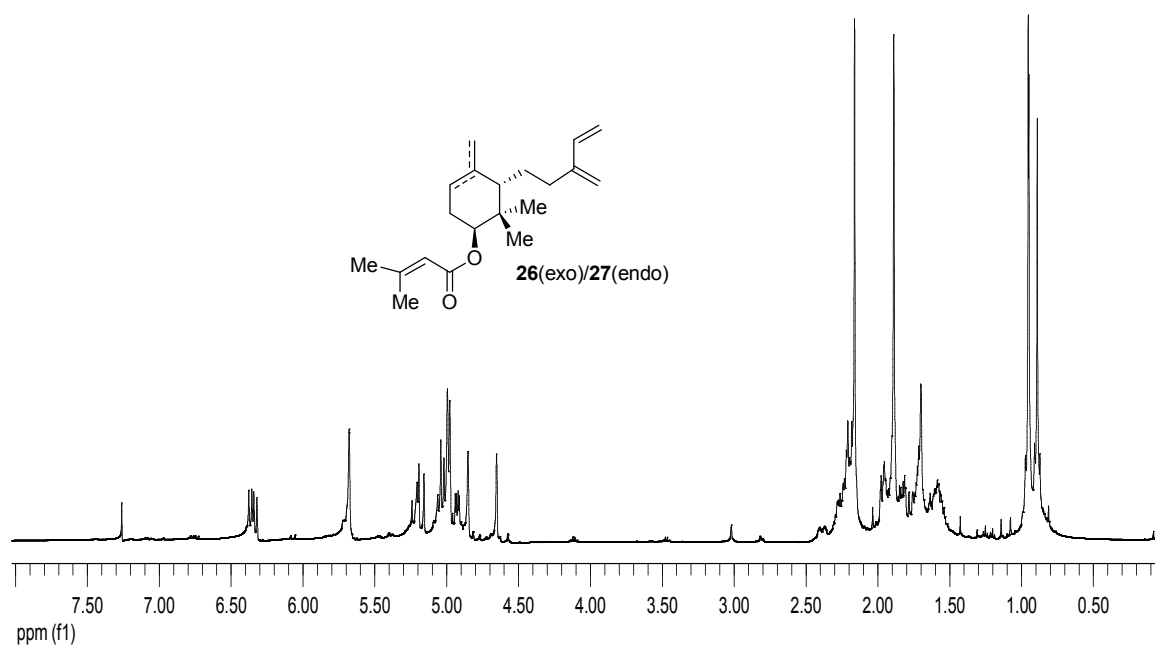


^1H and ^{13}C NMR spectra of cordiaquinone C (revised structure, **16**)

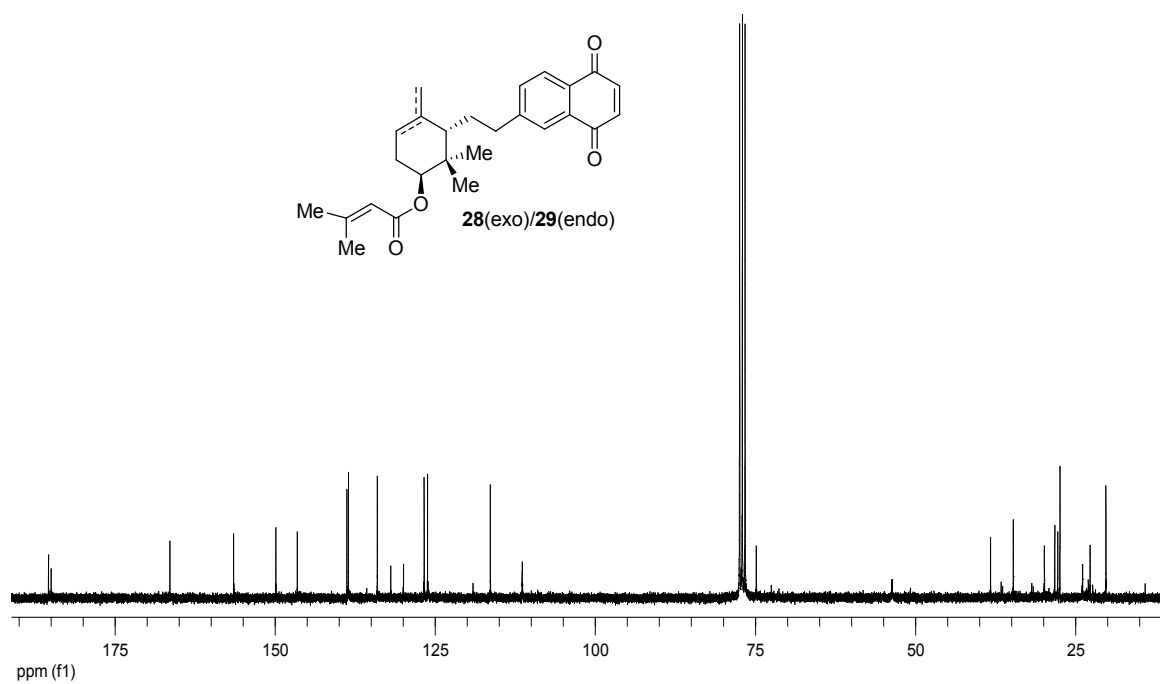
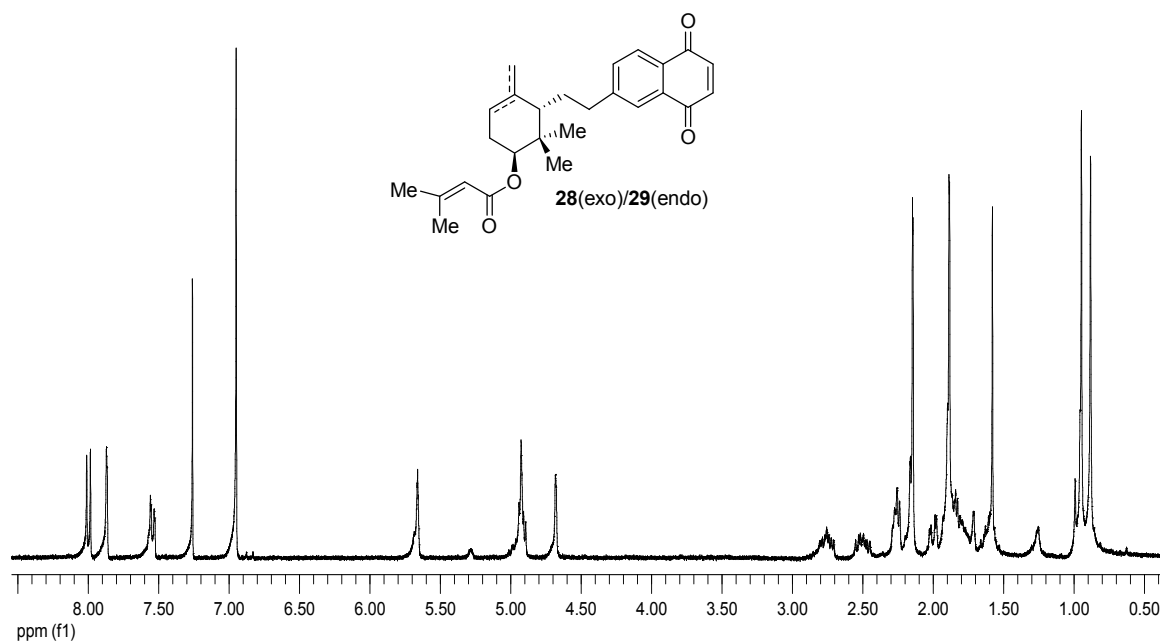
^1H and ^{13}C NMR spectra of (*Z*)- β -farnesene (**20**)

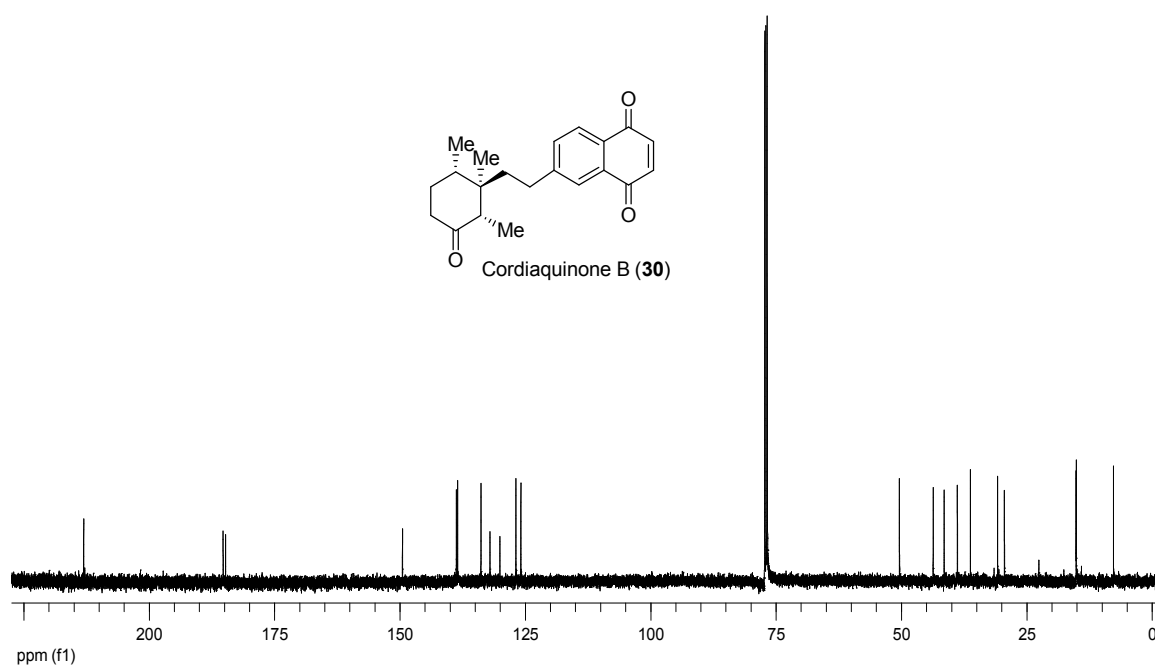
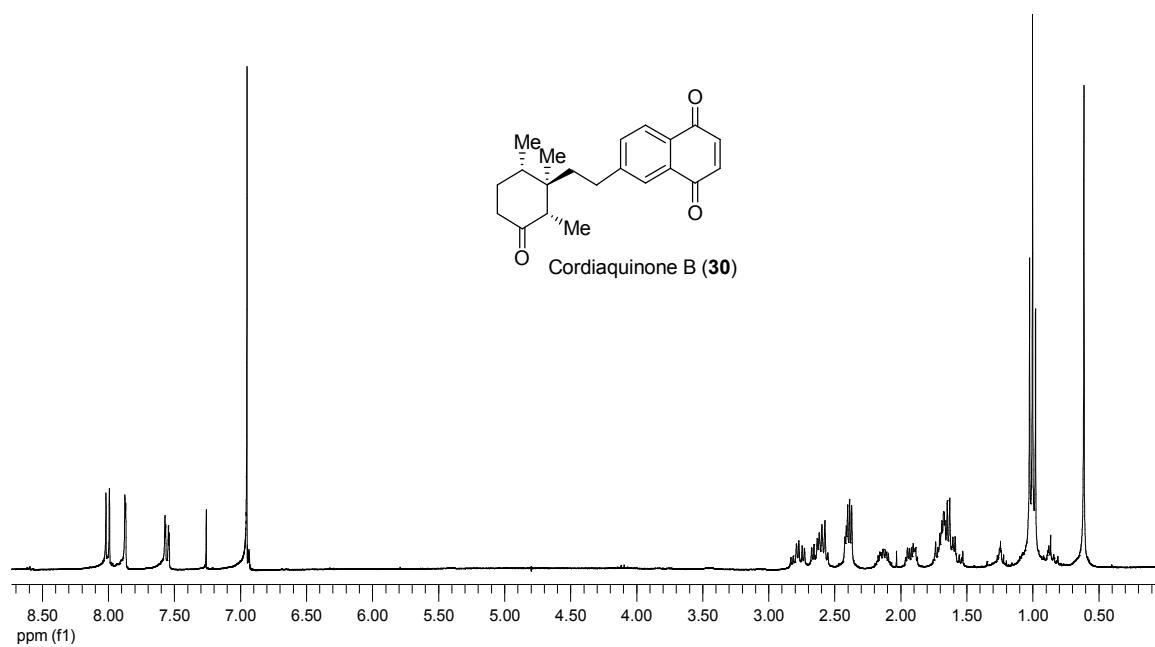
^1H and ^{13}C NMR spectra of epoxy (*Z*)- β -farnesene (**21**)

^1H and ^{13}C NMR spectra of the regioisomeric compounds **22/23**

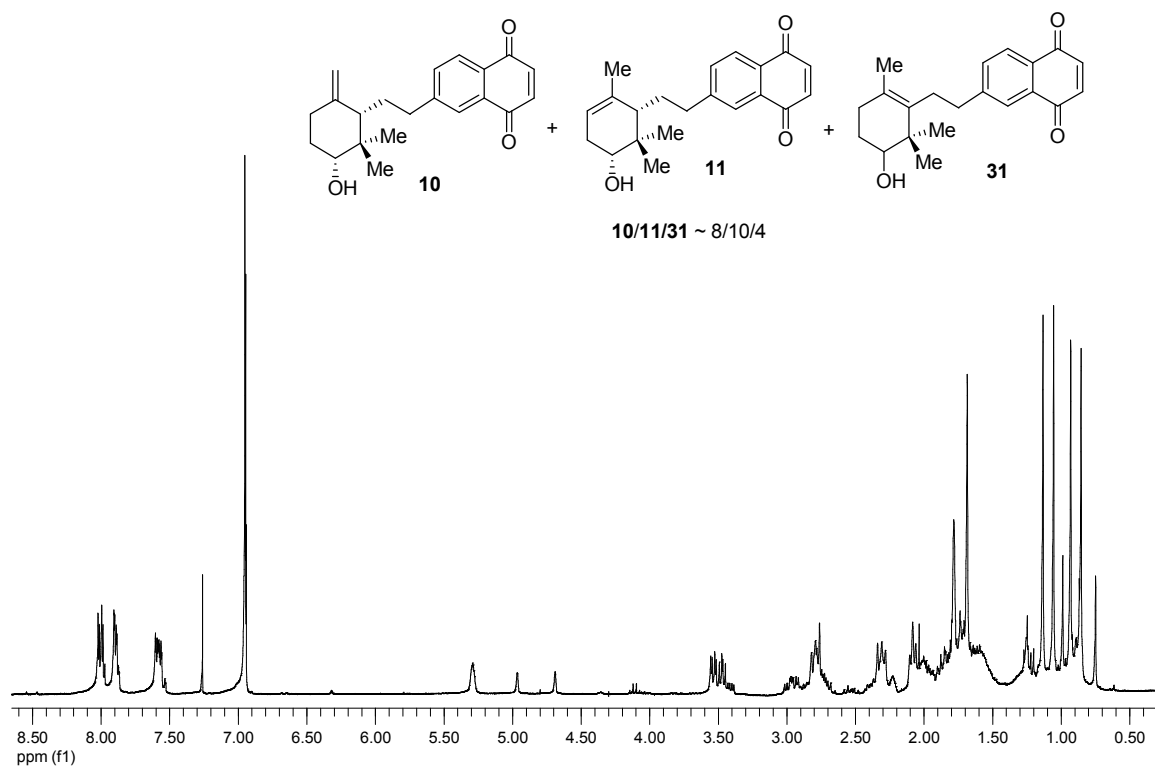
^1H and ^{13}C NMR spectra of the regioisomeric compounds **27/27**

^1H and ^{13}C NMR spectra of **28** (proposed structure of cordiaquinone C), and its minor regioisomer **29**.

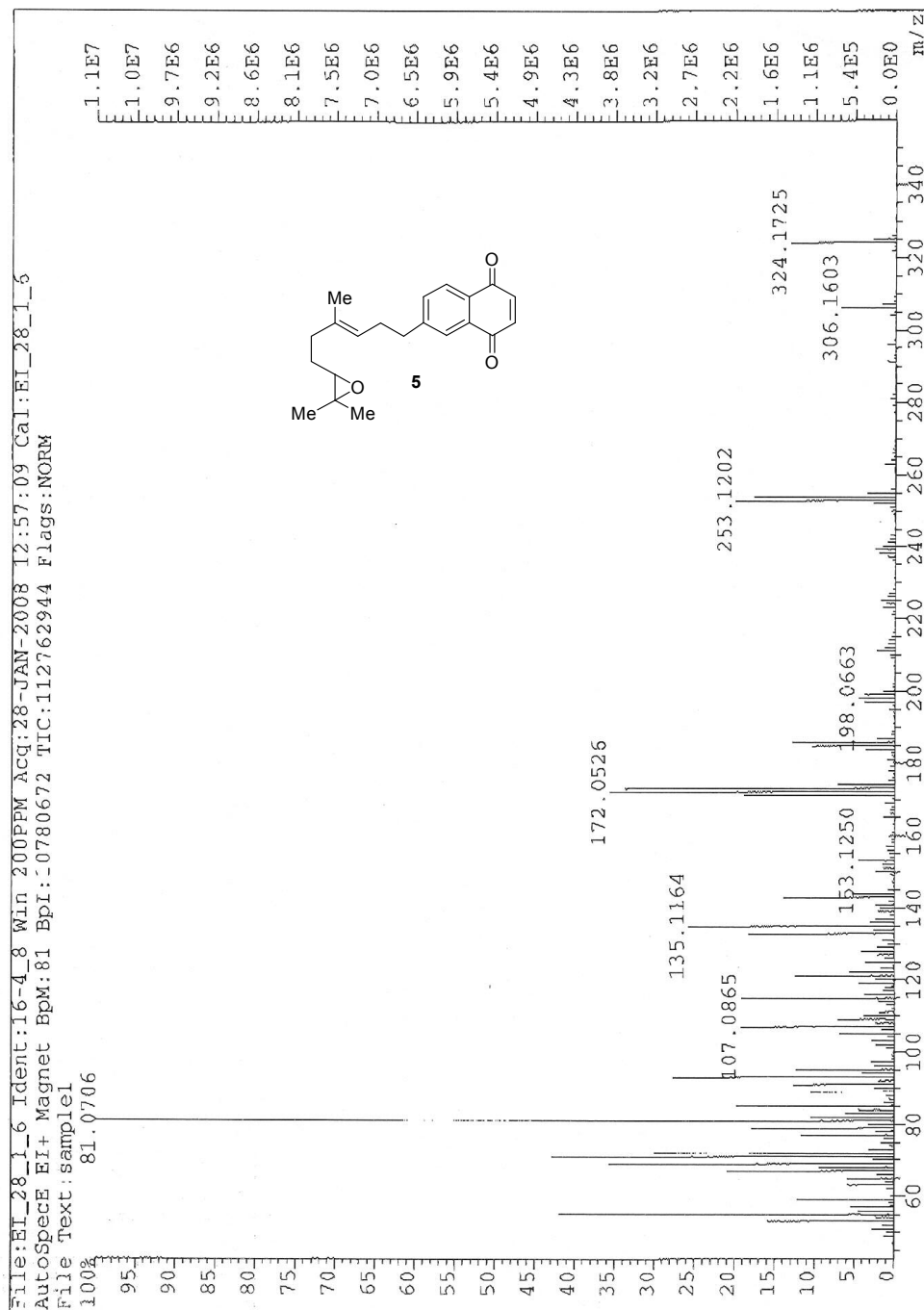


^1H and ^{13}C NMR spectra of cordiaquinone B (**30**)

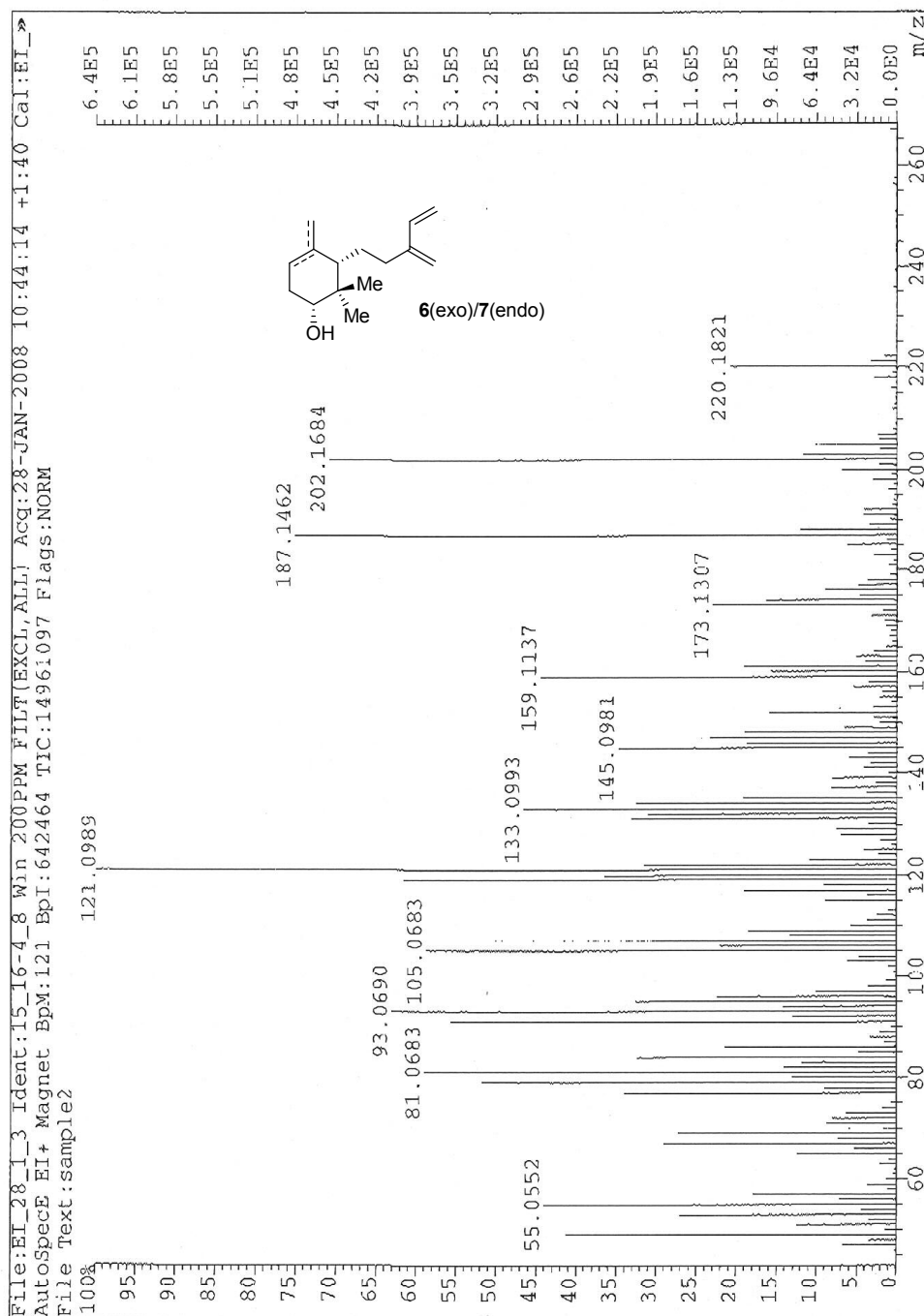
^1H NMR spectra of the mixture **10/11/31**.

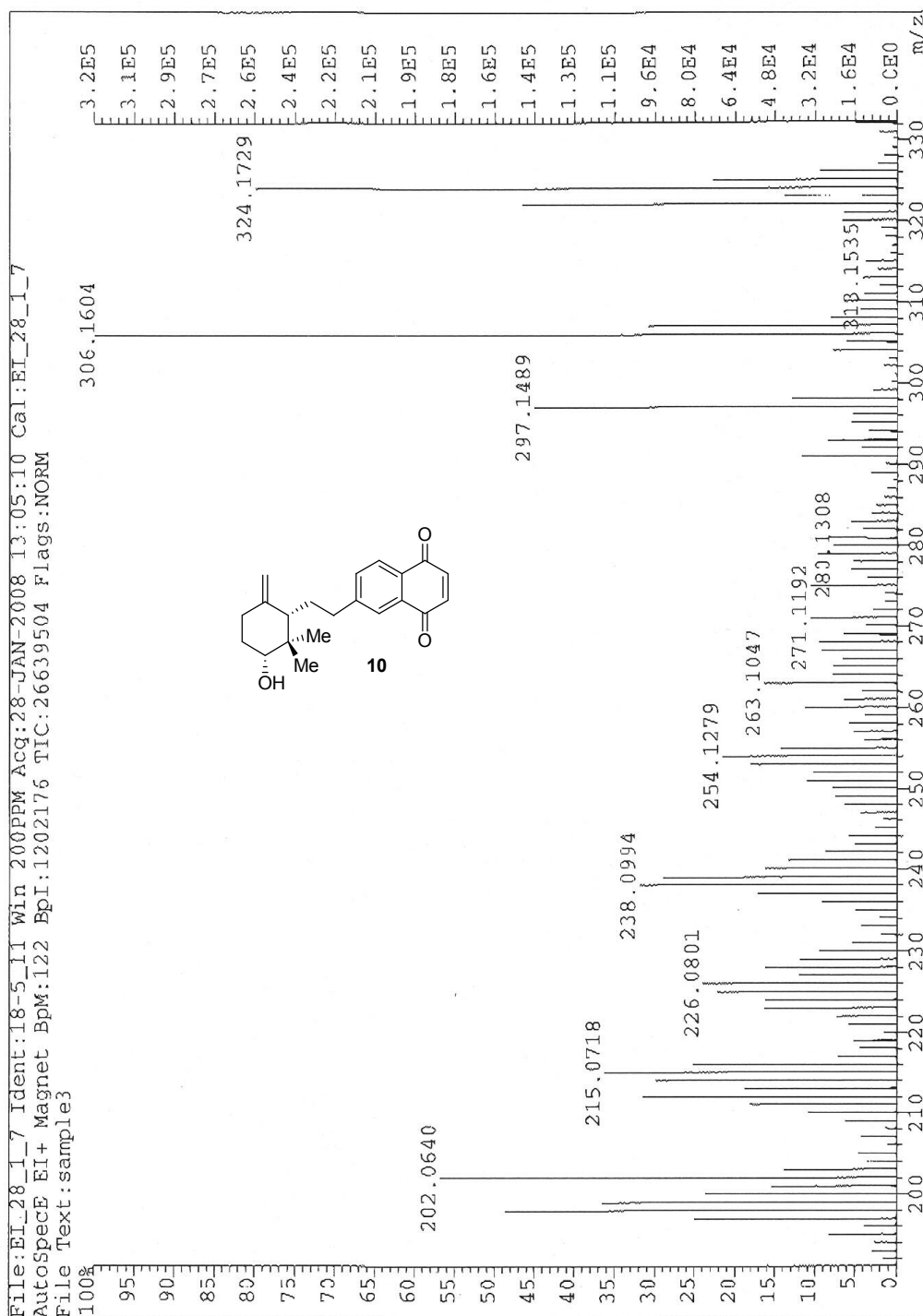


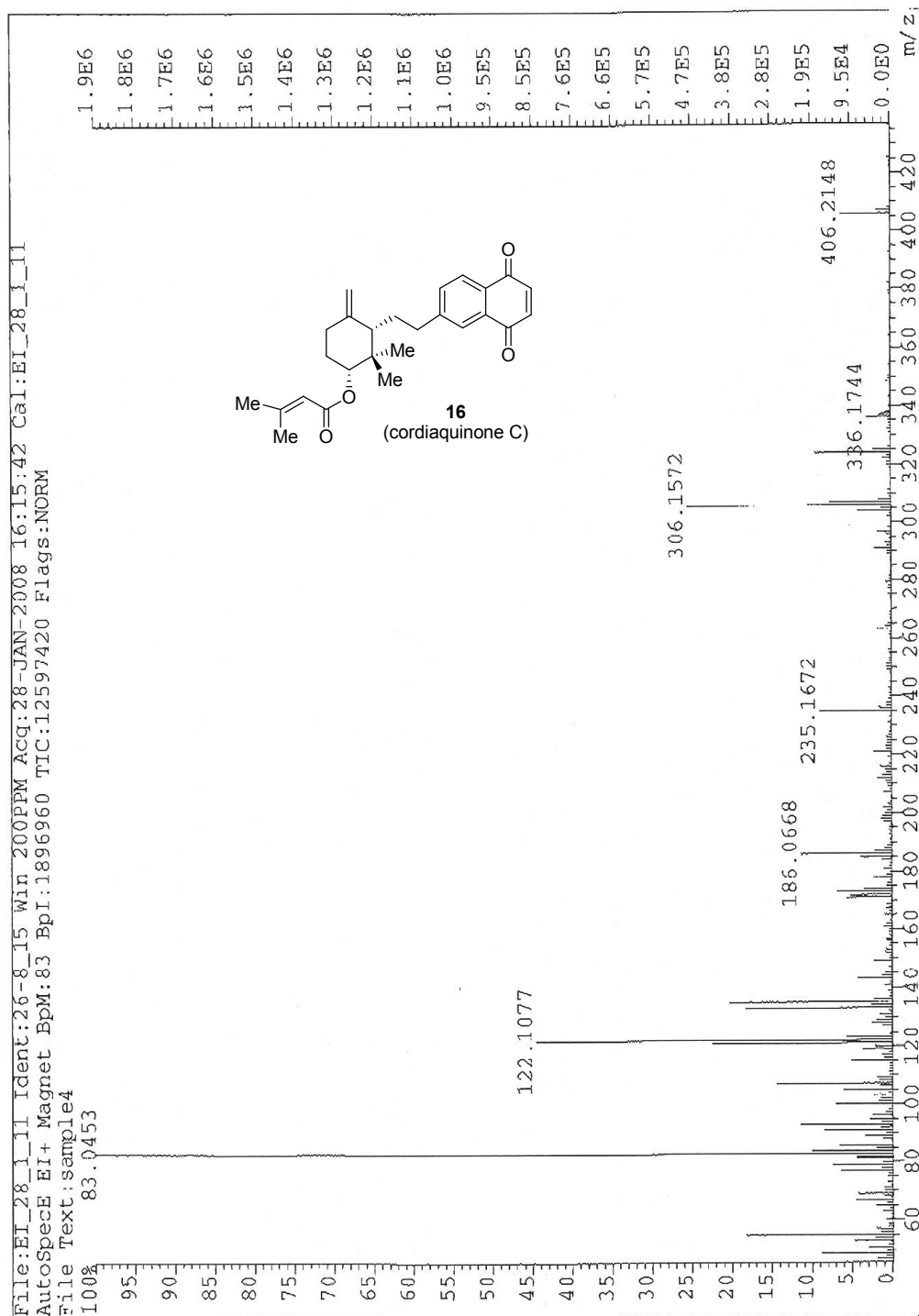
HRMS spectrum of compound 5



HRMS spectrum of compounds 6/7



HRMS spectrum of compound **10**

HRMS spectrum of compound **16**

HRMS spectrum of compounds **28/29**