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Supporting Information

Regiodivergent Synthesis of *ortho*- and *para*-Cannabinoquinones

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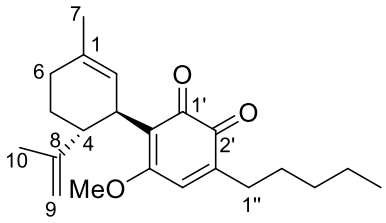
General Experimental Procedures

IR spectra were recorded on an Avatar 370 FT-IR Techno-Nicolet apparatus. ^{1}H (400 MHz) and ^{13}C (100 MHz) NMR spectra were measured on Bruker Avance 400 MHz spectrometer or on a Bruker Avance 500 MHz. Chemical shifts were referenced to the residual solvent signal ($CDCl_3$: δ_H = 7.21, δ_C = 77.0). Homonuclear ^{1}H connectivities were determined by the Correlation spectroscopy (COSY) experiment. One-bond heteronuclear ^{1}H–^{13}C connectivities were determined with the heteronuclear single quantum coherence (HSQC) spectroscopy experiment. Two- and three-bond ^{1}H–^{13}C connectivities were determined by gradient two-dimensional (2D) heteronuclear multiple bond correlation (HMBC) experiments optimized for a $^{2,3}J$ = 9 Hz. Low- and high-resolution electrospray ionization mass spectrometry (ESI-MS) data were determined on an LTQ OrbitrapXL (Thermo Scientific) mass spectrometer.

Reactions were monitored by thin-layer chromatography (TLC) on Merck 60 F254 (0.25 mm) plates, visualized by staining with 5% H_2SO_4 in EtOH and heating. Organic phases were dried with Na_2SO_4 before evaporation. Chemical reagents and solvents were purchased form Sigma-Aldrich and were used without further purification unless stated otherwise. Petroleum ether with boiling point of 40–60 °C was used. Silica gel 60 (70–230 mesh) was used for gravity column chromatography (GCC).

All starting cannabinoids were available from previous studies in the area (see Reff. 9, 13 and 18 in the main text).

SIBX Oxidation of cannabinoids. Reaction with *O*-methyl CBD (1b) as representative: To a cooled (ice bath) solution of *O*-methyl CBD (**1b**, 200 mg, 0.609 mmol, R_f= 0.47 in petroleum ether-EtOAc 95:5 as eluant) in ethyl acetate (10 mL), SIBX (39 wt. %, 1.44 g, 2.010 mmol, 3.33 molar equiv.) was added in small portions. At the end of the addition, the cooling bath was removed, and the suspension was stirred at room temperature. After 18 h, the reaction mixture was filtered over a pad of diatomaceous earth. The filtration cake was washed with EtOAc (10 mL), and the pooled filtrates were washed with saturated $Na_2S_2O_3$ (4 × 15 mL) and next with brine. After drying and evaporation, the residue was purified by GCC on silica gel (10 g, petroleum ether–EtOAc 95:5 as eluant) to obtain a dark red oil identified as *o*-*O*-methyl CBDQ (**10**, 98 mg, 47%, R_f= 0.19 in petroleum ether-EtOAc 95:5). Similar differences in R_f between reactants and reaction products were observed for all other reactions of SIBX oxidation.



10

***ortho*-O-Methylcannabidiolquinone (Me-CBDQ, 10)**: dark red oil, 47% yield, R_f= 0.19 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2955, 2924, 2857, 1643, 1431, 1107, 886 cm^{-1} ^{1}H NMR (400 MHz, $CDCl_3$): δ_H 6.83 (bs, H-4'), 5.06 (bd, *J* = 2.5 Hz, H-2), 4.56 (bs, H-9a), 4.52 (bs, H-9b), 3.87 (s, 5'-OMe), 3.65 (m, H-3), 2.67 (dt, *J* = 9.2, 3.0 Hz, H-4), 2.41 (t, *J* = 7.5 Hz, H-1''), 2.17 (m, H-6a), 2.04 (m, H-6b), 1.95 (m, H-5), 1.64 (bs, H-7), 1.61 (bs, H-10), 1.50 (m, H-2''), 1.32 (overlapped, H-3''), 1.30 (overlapped, H-4''), 0.89 (t, *J* = 6.9 Hz, H-5''). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 180.6 (C-1'), 178.6 (C-2'), 164.4 (C-5'), 148.7 (C-8), 142.6 (C-4'), 133.0 (C-1), 128.0 (C-3'), 124.2 (C-6'), 123.6 (C-2), 110.4 (C-9), 45.1 (C-4), 31.8 (C-1''), 31.5 (C-3''), 30.6 (C-5), 30.4 (C-6), 30.2 (C-2''), 29.3 (C-3), 24.0 (C-7), 22.5 (C-4''), 18.5 (C-10), 14.5 (C-5''). ; HRESI-MS: *m/z* calcd. for $C_{22}H_{31}O3$ $[M+H]^+$ 343.2273, found 343.2279.

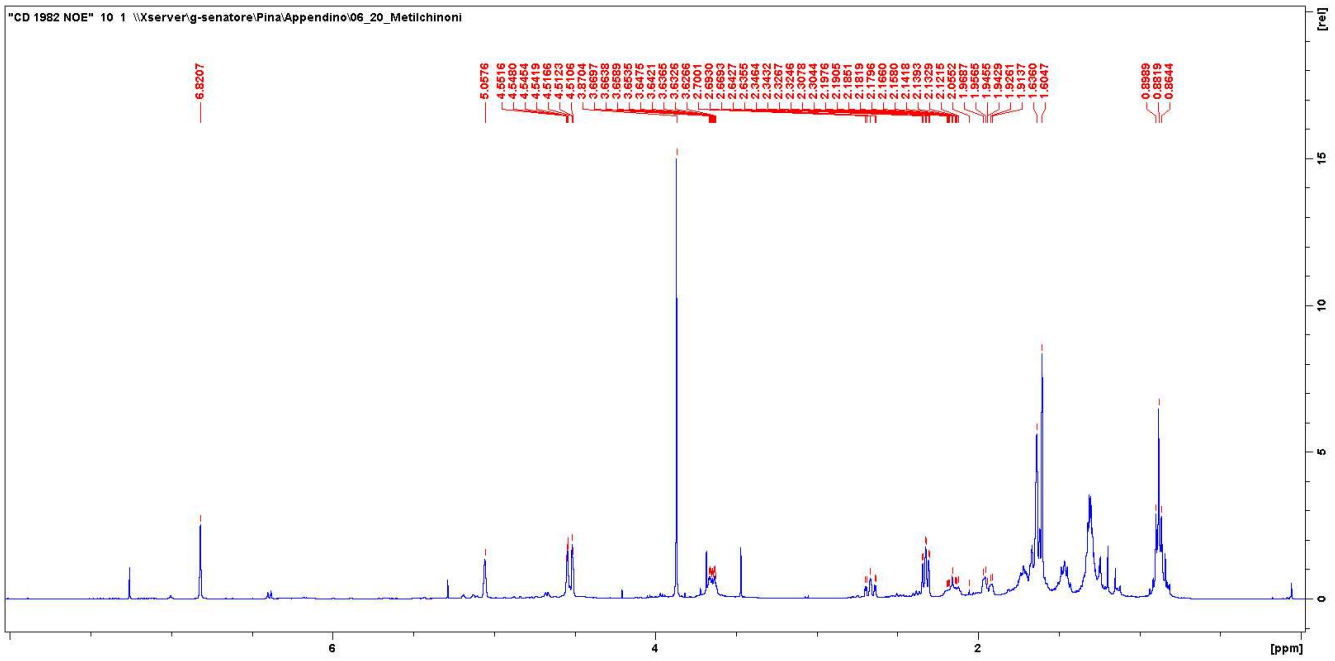


Figure S1. ^{1}H NMR spectrum (400 MHz) of compound **10** in $CDCl_3$

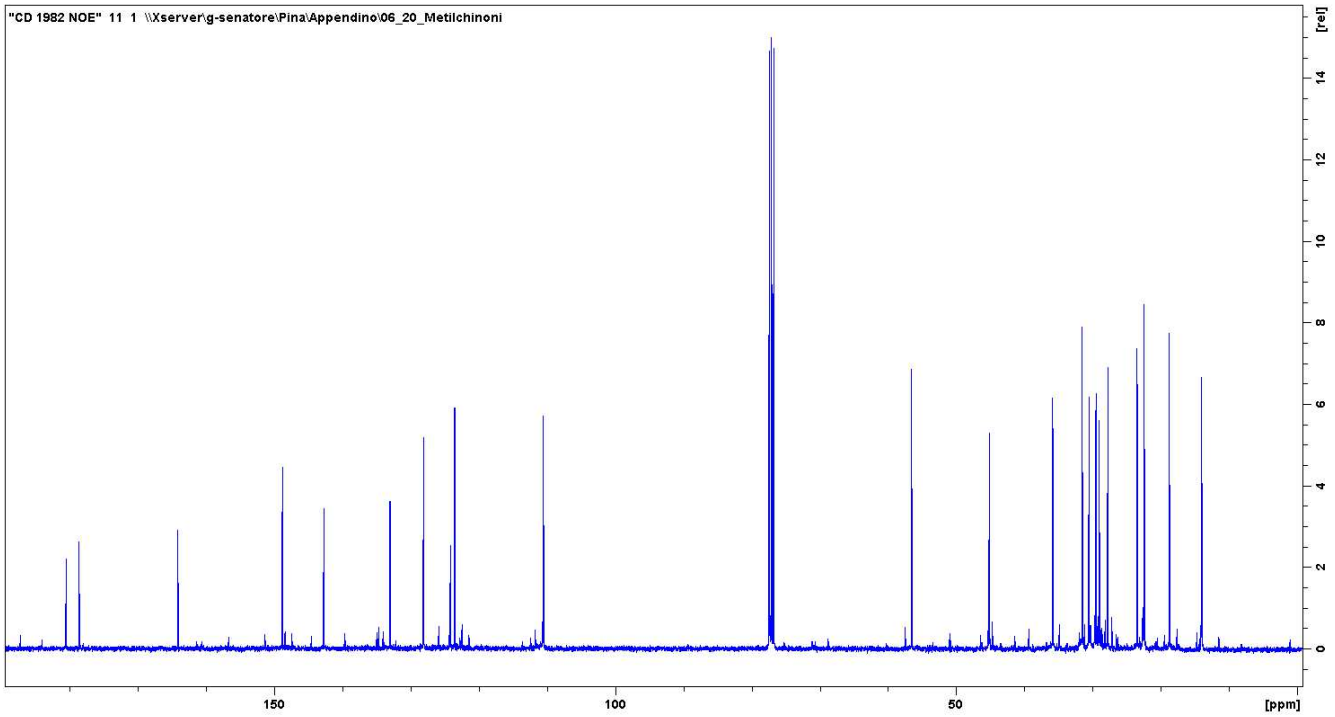


Figure S2. ^{13}C NMR spectrum (100 MHz) of compound **10** in $CDCl_3$

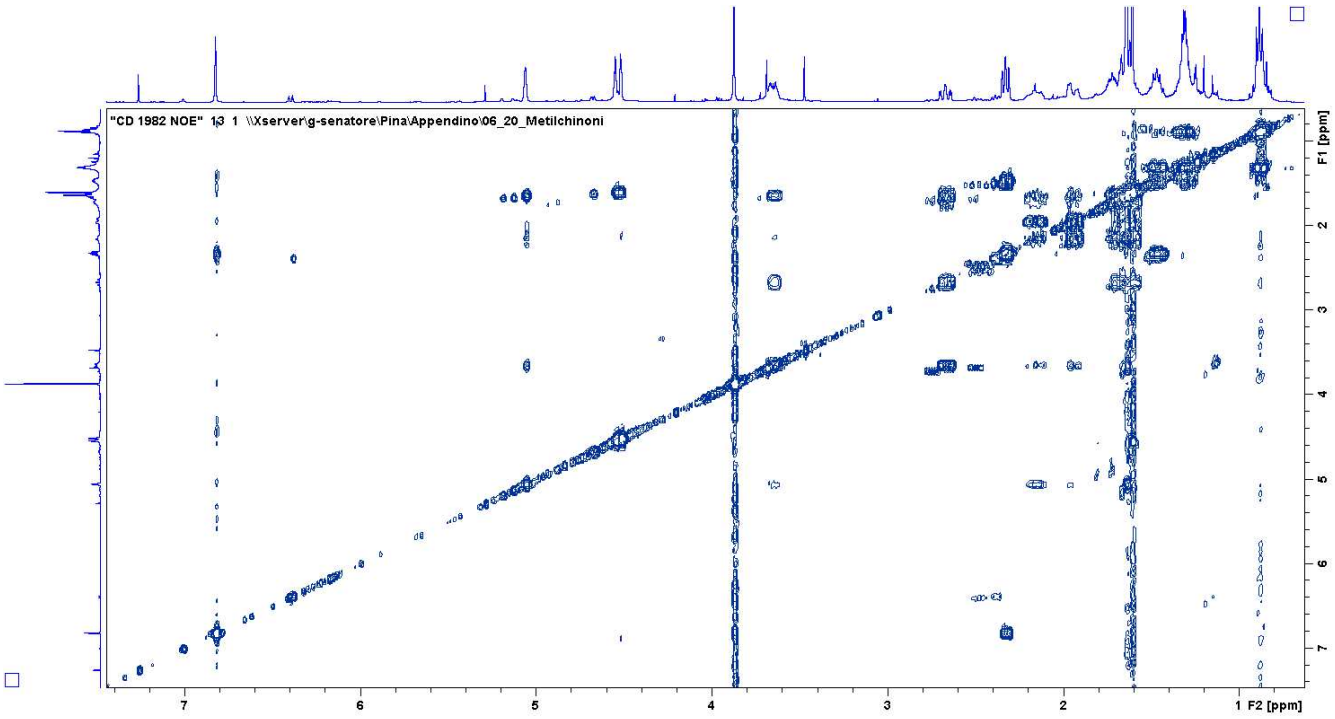


Figure S3. 2D NMR COSY spectrum of compound **10** in $CDCl_3$

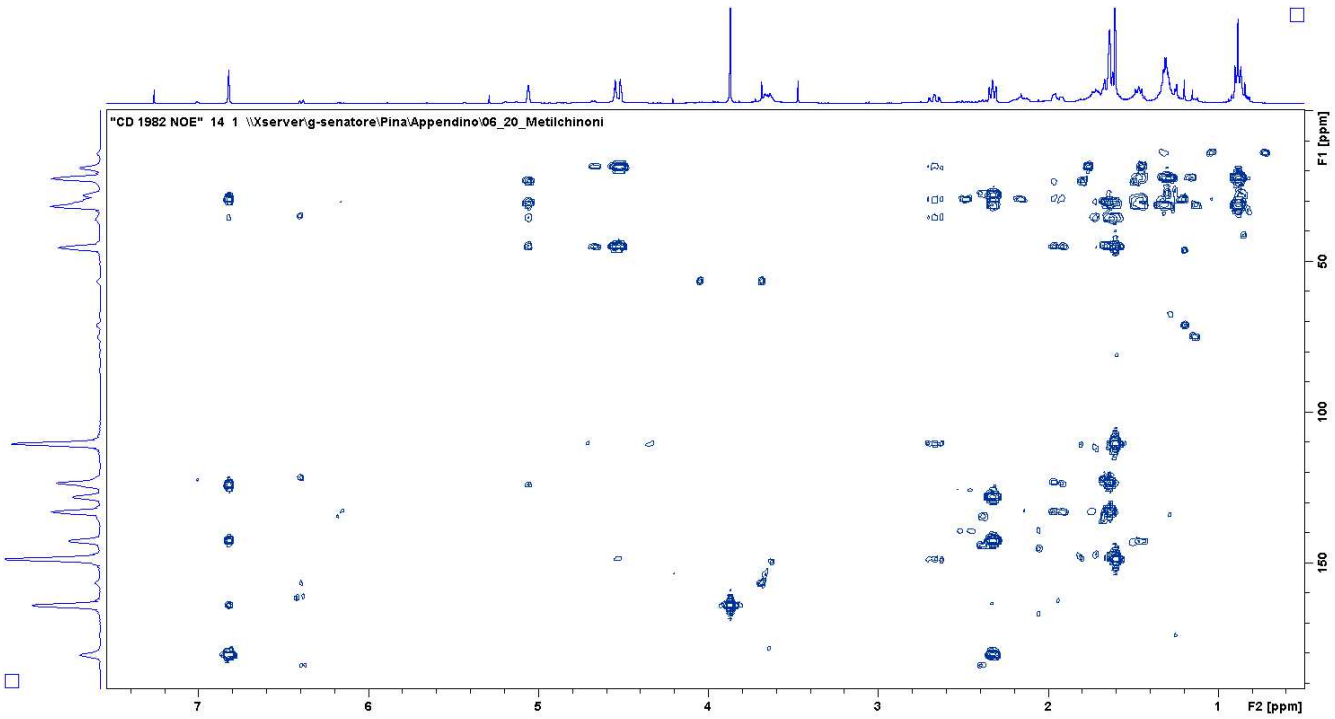


Figure S4. 2D NMR HMBC spectrum of compound **10** in $CDCl_3$

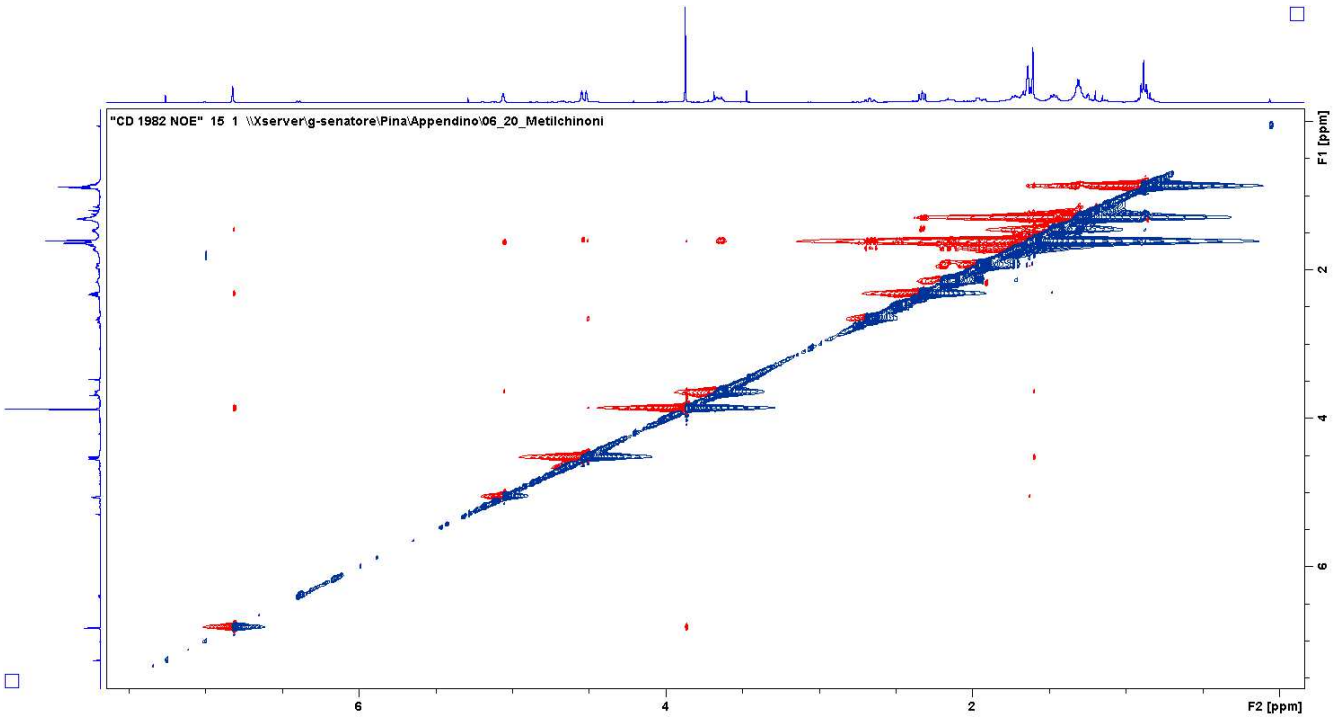
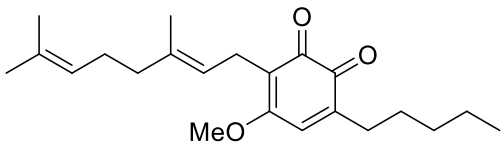


Figure S5. 2D NMR NOESY spectrum of compound **10** in $CDCl_3$



11

***ortho*-O-Methylcannabigeroquinone (CBGQ, 11):** dark red oil, 37% yield R_f= 0.18 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2956, 2925, 2855, 1655, 1638, 1345, 1107 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.89 (bs, 1H), 5.08 (m, 2H), 3.97 (s, 3H), 3.05 (d, *J* = 7.4 Hz, 2H), 2.37 (t, *J* = 7.4 Hz, 2H), 2.04 (m, 2H), 1.98 (m, 2H), 1.72 (bs, 3H), 1.67 (bs, 3H), 1.50 (bs, 3H), 1.49-1.32 (m, 6H), 0.90 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C180.6, 178.9, 163.3, 142.4, 136.1, 134.3, 131.3, 127.7, 124.3, 120.7, 56.6, 39.7, 31.4, 29.7, 27.9, 26.7, 25.7, 22.4, 21.6, 17.7, 16.1, 13.9. . HRESI-MS: *m/z* calcd. for $C_{22}H_{33}O_3$ $[M+H]^+$ 345.2430, found 345.2430.

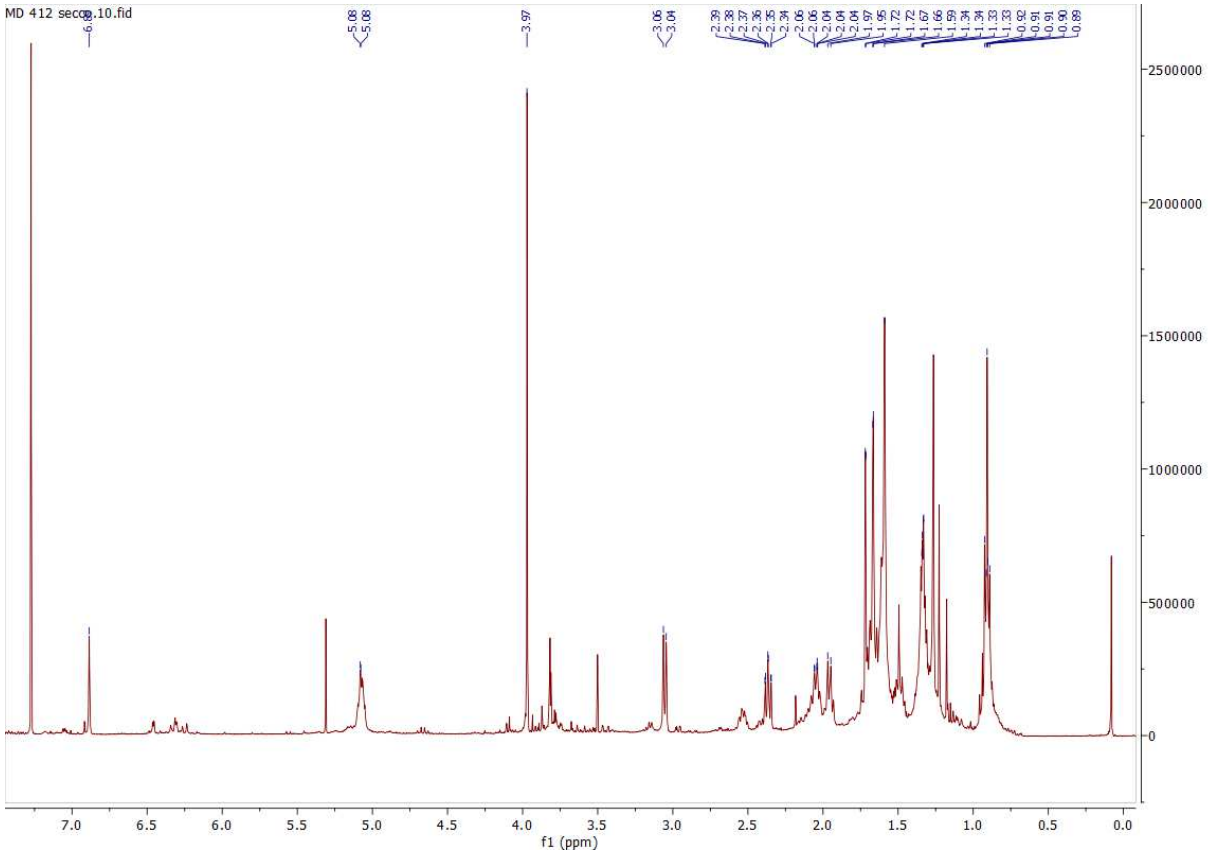


Figure S6. ^1H NMR spectrum (400 MHz) of compound **11** in $CDCl_3$

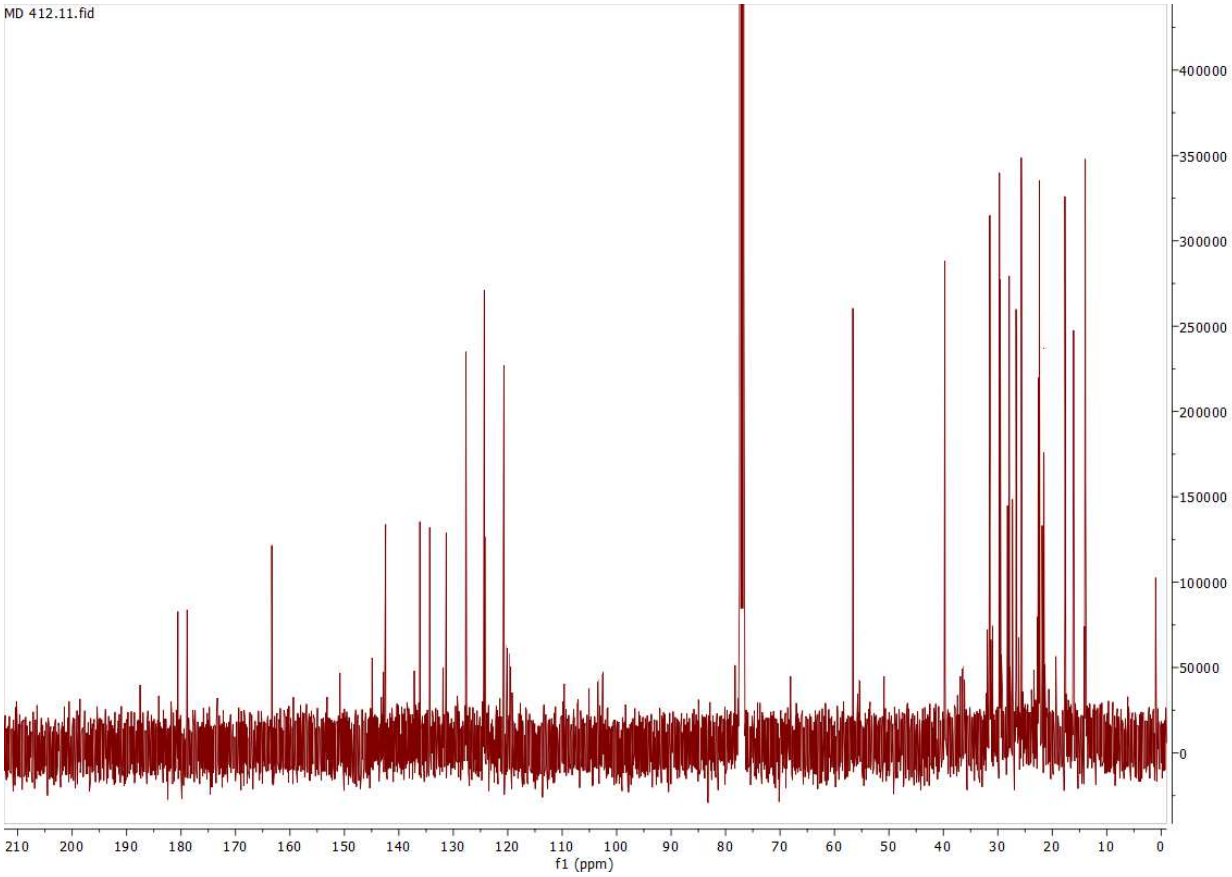
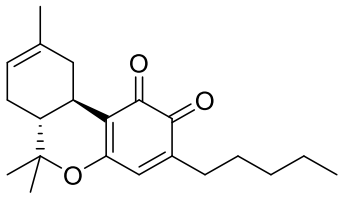


Figure S7. ^{13}C NMR spectrum (100 MHz) of compound **10** in $CDCl_3$



13a

***ortho*-Δ8-Tetrahydrocannabinolquinone (THCQ, 13a):** dark red oil, 51% yield, R_f= 0.46 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2956, 2925, 2852, 1639,1584, 1388, 1184, 1112 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.49 (bs, 1H), 5.30 (bs, 1H), 3.10 (m, 1H), 2.49 (dt, J^1 = 11.0 Hz, J^2 = 4.9 Hz, 1H), 2.35 (t, J = 7.7 Hz, 2H), 2.12 (m, 1H), 1.83 (m, 1H), 1.75-1.20 (overlapped m, 6H), 1.45 (s, 1H), 1.21 (s, 6H), 0.91 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 181.2, 177.7, 162.9, 143.3, 134.4, 118.6, 114.9, 82.1, 43.6, 35.2, 31.4, 29.8, 28.7, 27.4, 27.1, 26.9, 23.3, 22.4, 19.4, 13.9. HRESI-MS: *m/z* calcd. for $C_{21}H_{29}O_3$, $[M+H]^+$ 329.2122, found 329.2122.

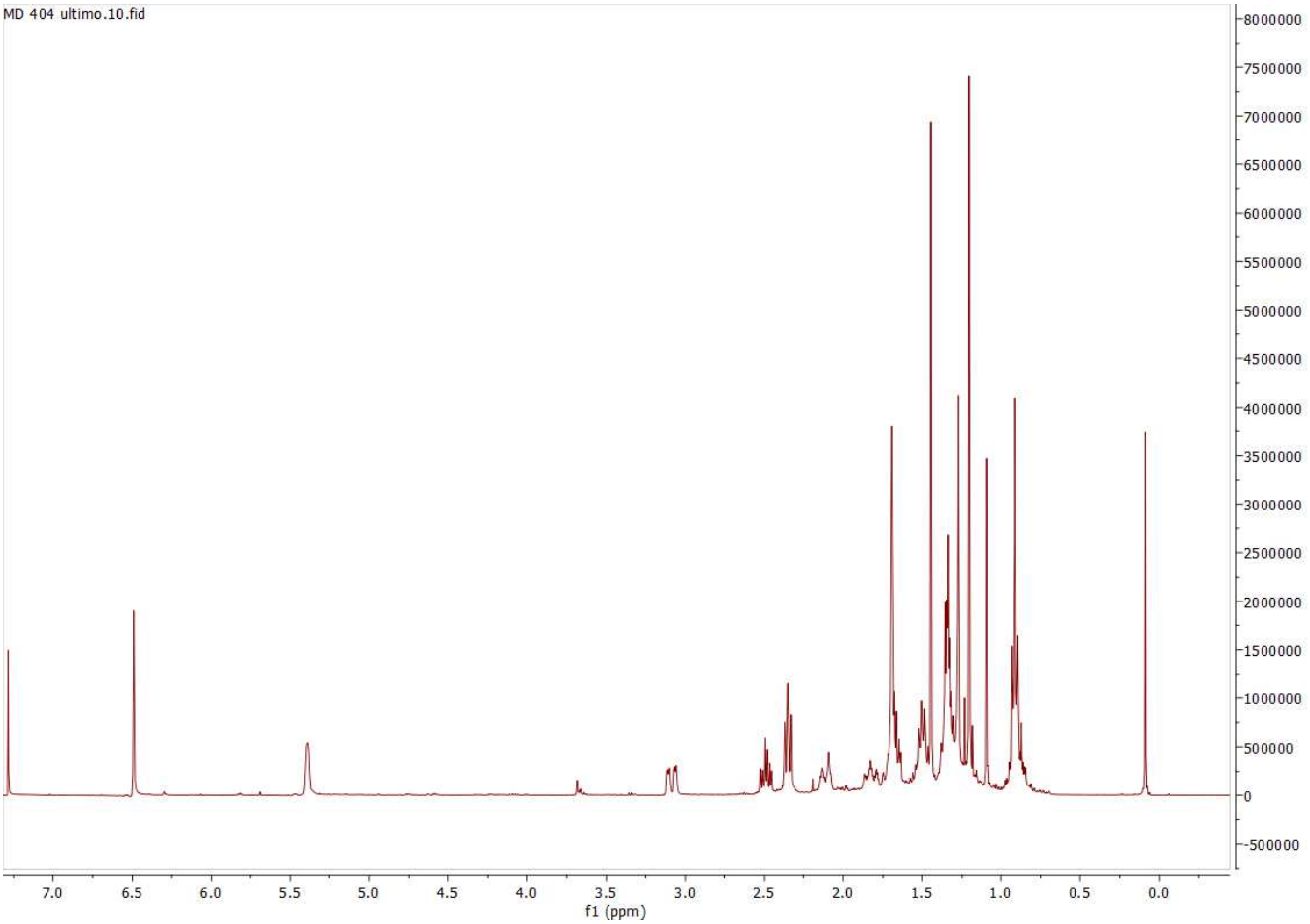


Figure S8. ^1H NMR spectrum (400 MHz) of compound **13a** in $CDCl_3$

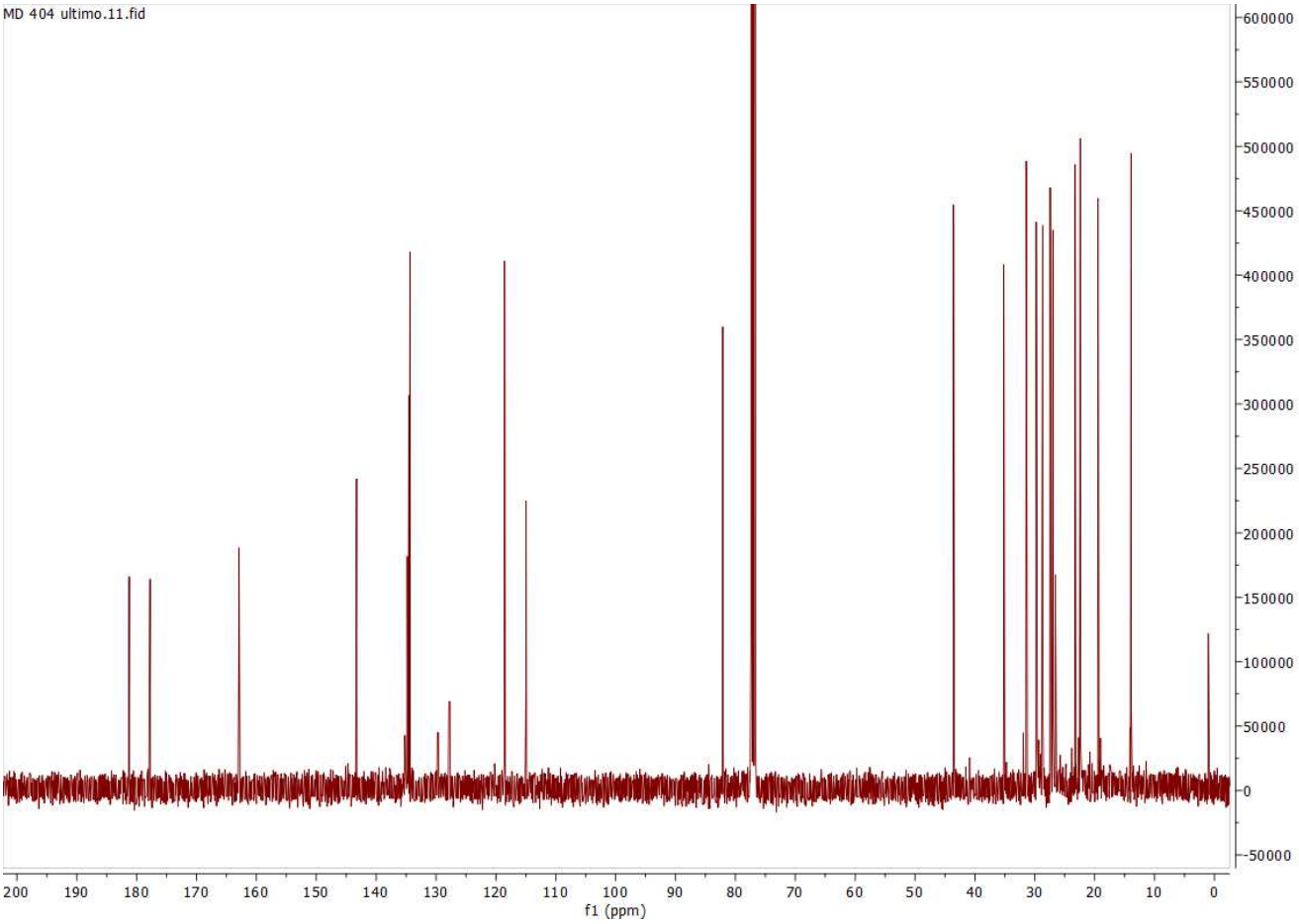
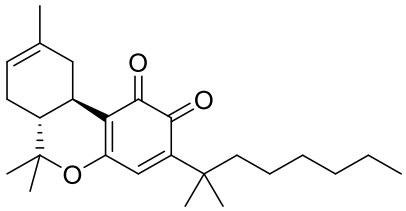


Figure S9. ^{13}C NMR spectrum (100 MHz) of compound **13a** in $CDCl_3$



13b

3'-Depentyl-3'-(α,α-dimethylheptyl)-*ortho*-Δ8-tetrahydrocannabinol quinone (DMH-THCQ, 13b): dark red oil, 54% yield, R_f= 0.30 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2956, 2925, 2856, 1589, 1379, 1112, 919 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.38 (bs, 1H), 5.31 (bs, 1H), 2.98 (m, 1H), 2.39 (dt, J^1 = 11.1 Hz, J^2 = 5.0 Hz, 1H), 2.02 (m, 1H), 1.74 (m, 1H), 1.67-1.49 (overlapped m, 8H), 1.37 (s, 1H), 1.27-0.89(overlapped m, 16H), 0.78 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C (100 MHz, $CDCl_3$) δ 180.7, 177.8, 162.9, 149.8, 134.7, 134.5, 118.6, 114.9, 82.2, 43.5, 40.6, 38.5, 35.1, 31.8, 29.8, 29.7, 27.3, 27.2, 27.1, 27.0, 25.1, 23.3, 22.7, 19.5, 14.1. HRESI-MS: *m/z* calcd. for $C_{25}H_{37}O_3$, $[M+H]^+$ 385.2672, found 385.2677.

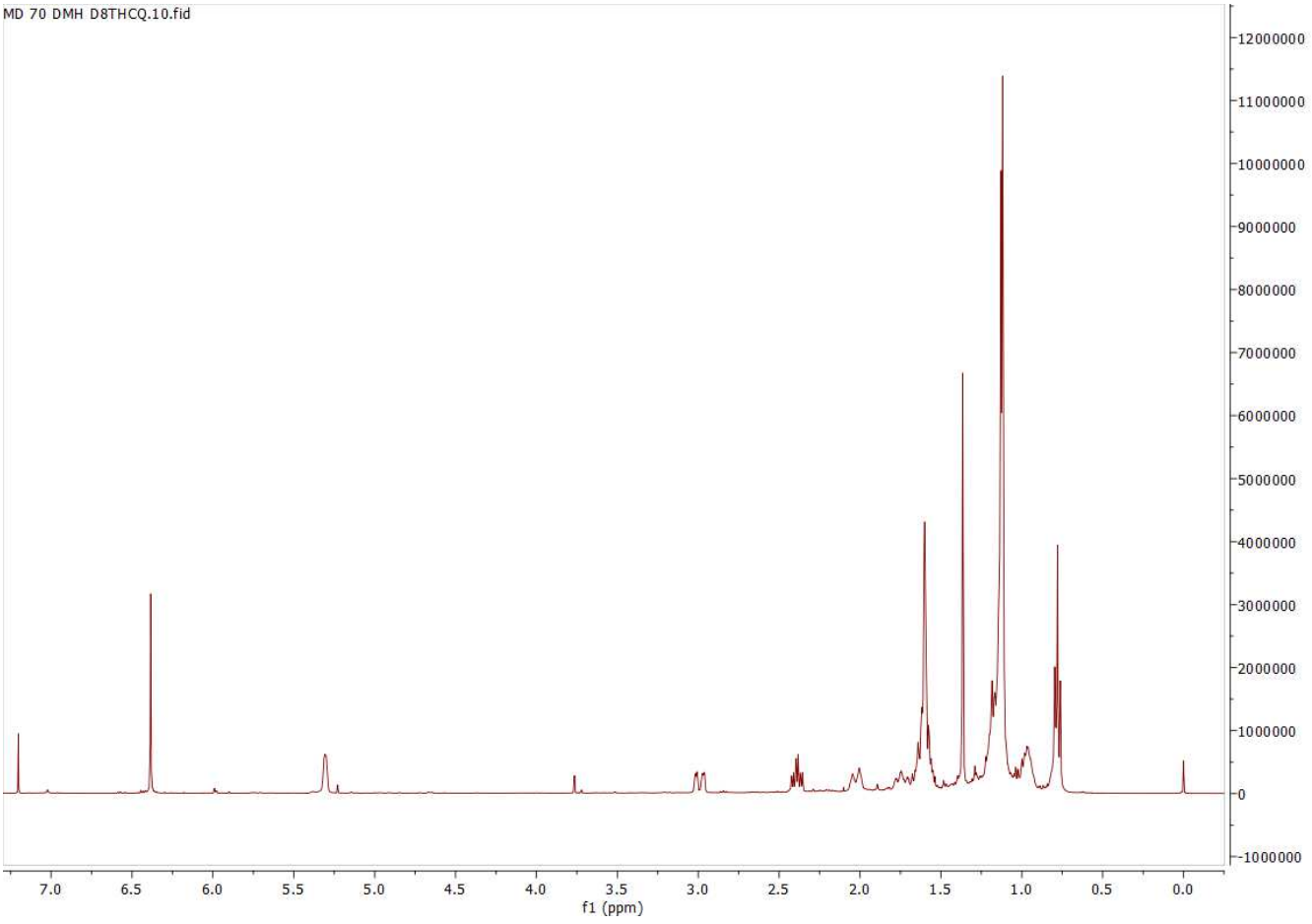


Figure S10. ^1H NMR spectrum (400 MHz) of compound **13b** in $CDCl_3$

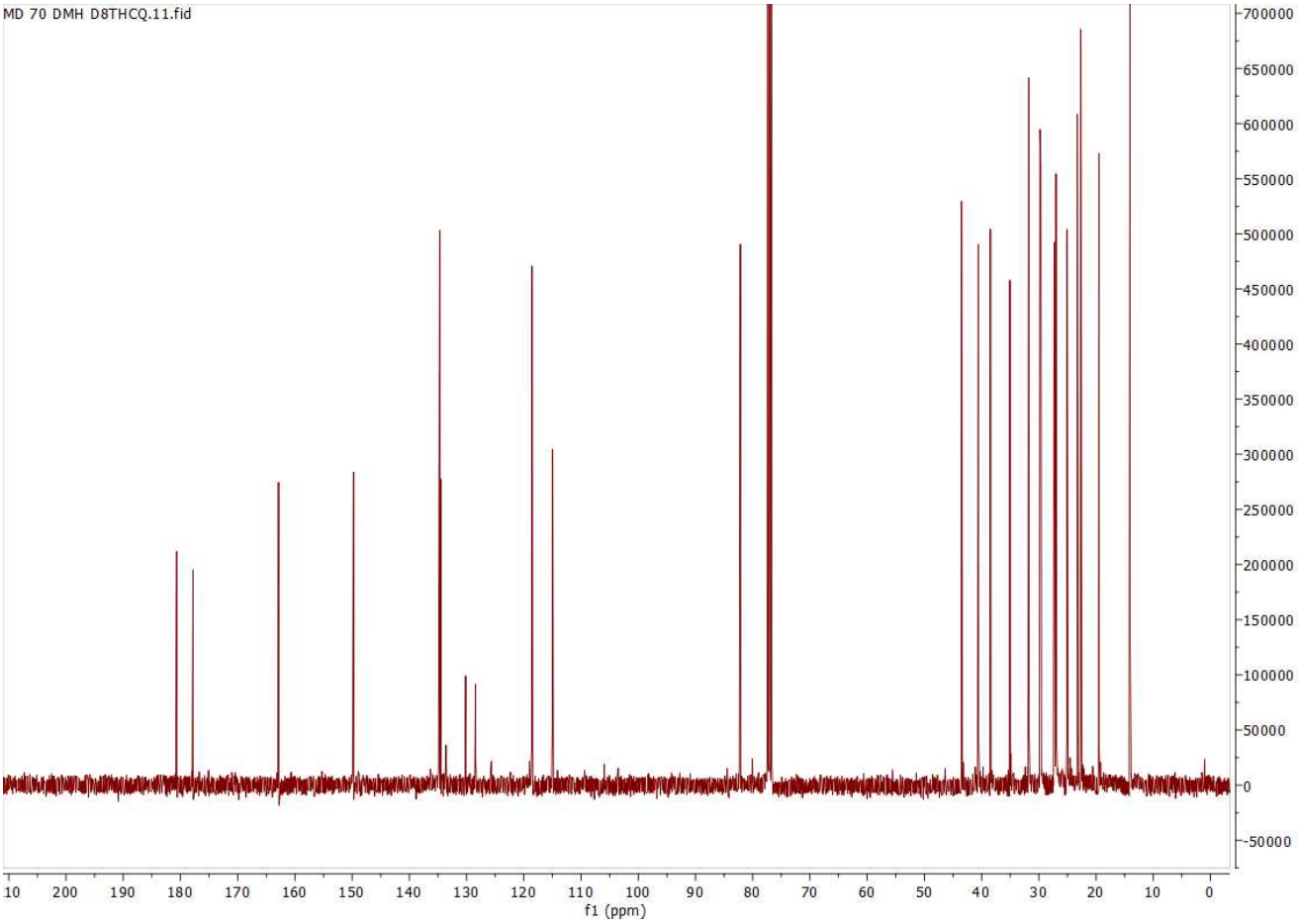
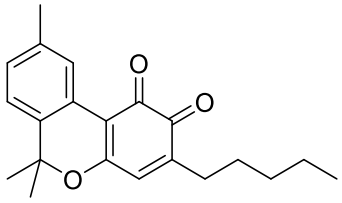


Figure S11. ^{13}C NMR spectrum (100 MHz) of compound **13b** in $CDCl_3$



14a

***ortho*-Cannabinolquinone (CBNQ, 14a)**: purple oil, 58% yield, R_f= 0.31 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2955, 2924, 2855, 1649, 1382, 1145, 1110, 811 cm^{-1} ; ^1H NMR ($CDCl_3$, 400 MHz) δ 8.30 (s, 1H,), 7.09 (d, *J* = 8.9 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.63 (bs, 1H), 2.40 (t, J = 7.7 Hz, 1H), 2.36 (s, 3H), 1.69 (s, 6H), 1.56 (m, 2H), 1.32 (m, 2H), 0.90 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 180.2, 175.3, 163.3, 144.7, 138.1, 133.8, 131.8, 128.9, 125.7, 122.3, 111.0, 82.7, 53.6, 31.6, 29.8, 29.0, 28.3, 27.4, 22.4, 21.4, 13.9; ESI-MS m/z 325 $[M+H]^+$; HR ESI-MS *m/z* 325.1791 $[M+H]^+$, calcd. for $C_{21}H_{25}O_3$, 325.1798.

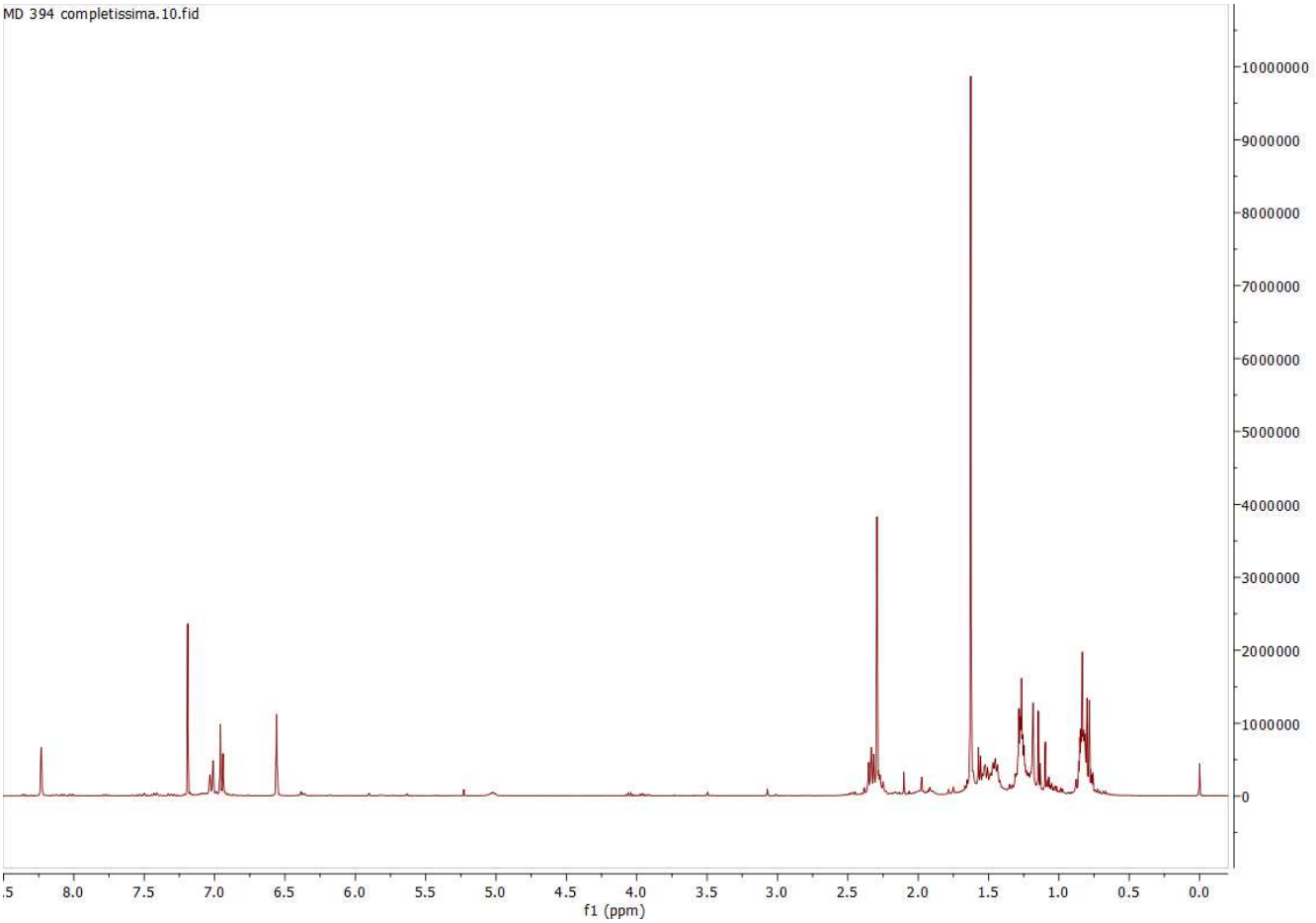


Figure S12. ^1H NMR spectrum (400 MHz) of compound **14a** in $CDCl_3$

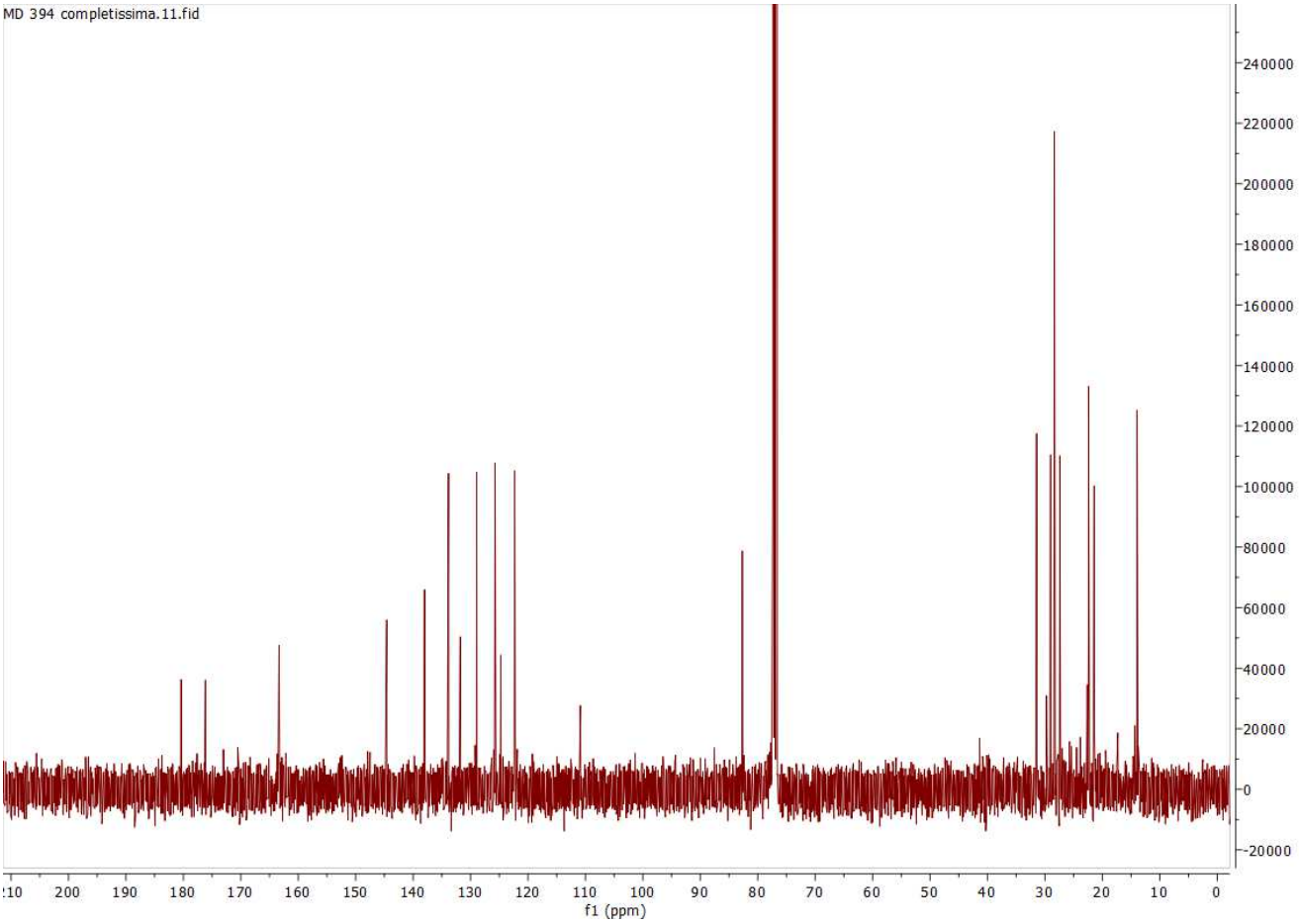
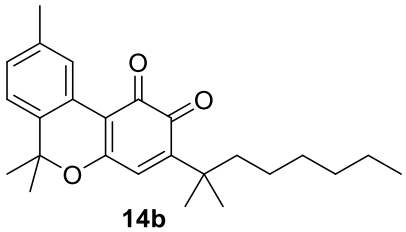


Figure S13. ^{13}C NMR spectrum (100 MHz) of compound **14a** in $CDCl_3$



14b

3'-Depentyl-3'-(α,α-Dimethylhepty)-*ortho*-cannabinolquinone (14b): purple oil, 58% yield R_f= 0.21 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2955, 2924, 2856, 1649, 1376, 1145, 1110, 813 cm^{-}; ^{1}H NMR ($CDCl_3$, 400 MHz) δ_H 8.33 (s, 1H,), 7.12 (d, *J* = 8.9 Hz, 1H), 7.04 (d, *J* = 7.9 Hz, 1H), 6.63 (bs, 1H), 2.39 (s, 3H), 1.73 (s, 6H), 1.70 (overlapped m, 2H) 1.33-0.99 (m, 14H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ_C 179.9, 176.4, 163.1, 151.2, 137.9, 134.1, 131.8, 128.9, 125.7, 124.6, 122.3, 110.8, 82.7, 40.6, 38.8, 31.7, 29.7, 29.7, 28.4, 27.3, 25.1, 22.6, 21.3, 14.0. HRESI-MS: *m/z* calcd. for $C_{25}H_{33}O_3$, $[M+H]^+$ 381.2430, found 381.2437.

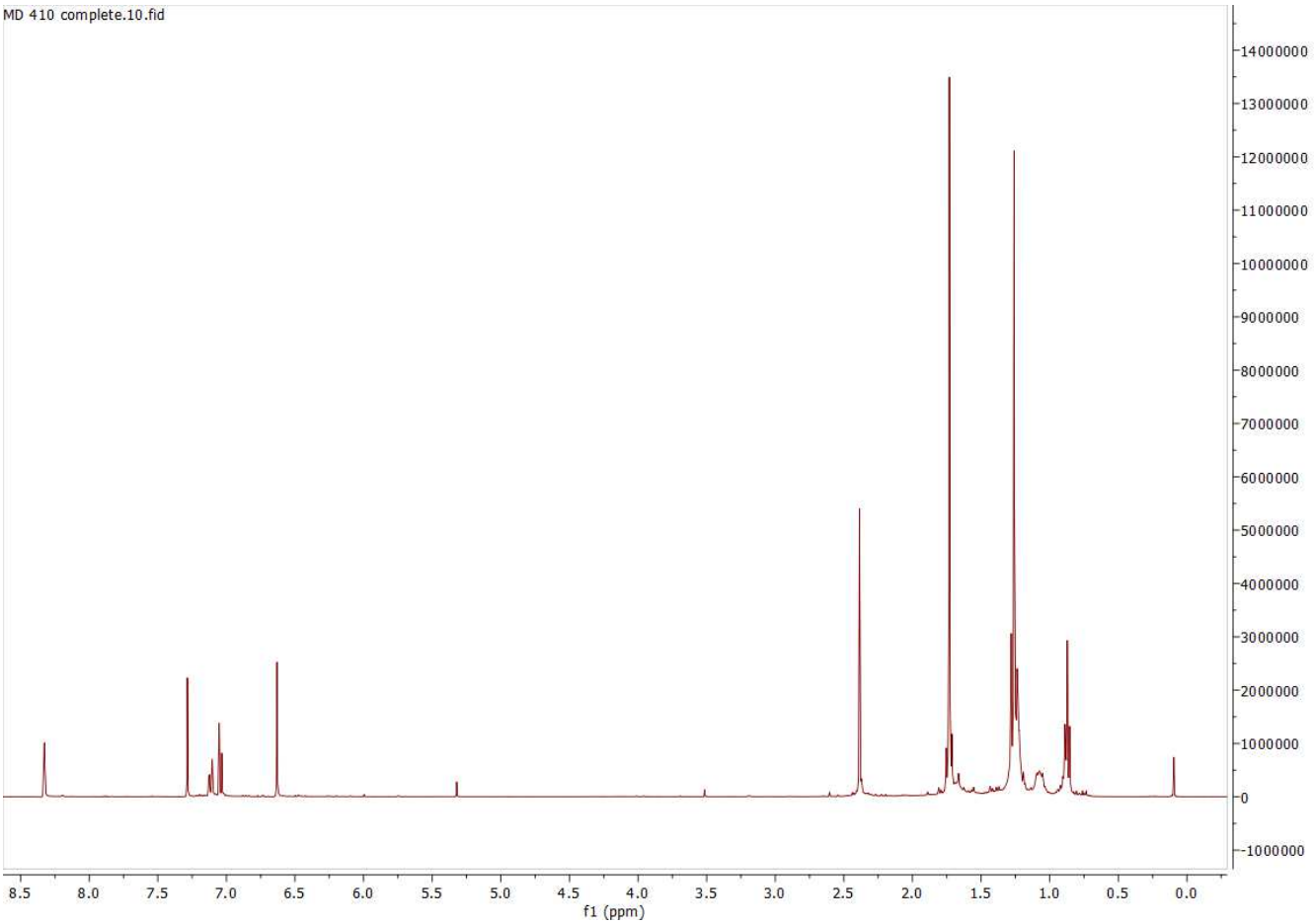


Figure S14. ^{1}H NMR spectrum (400 MHz) of compound **14b** in $CDCl_3$

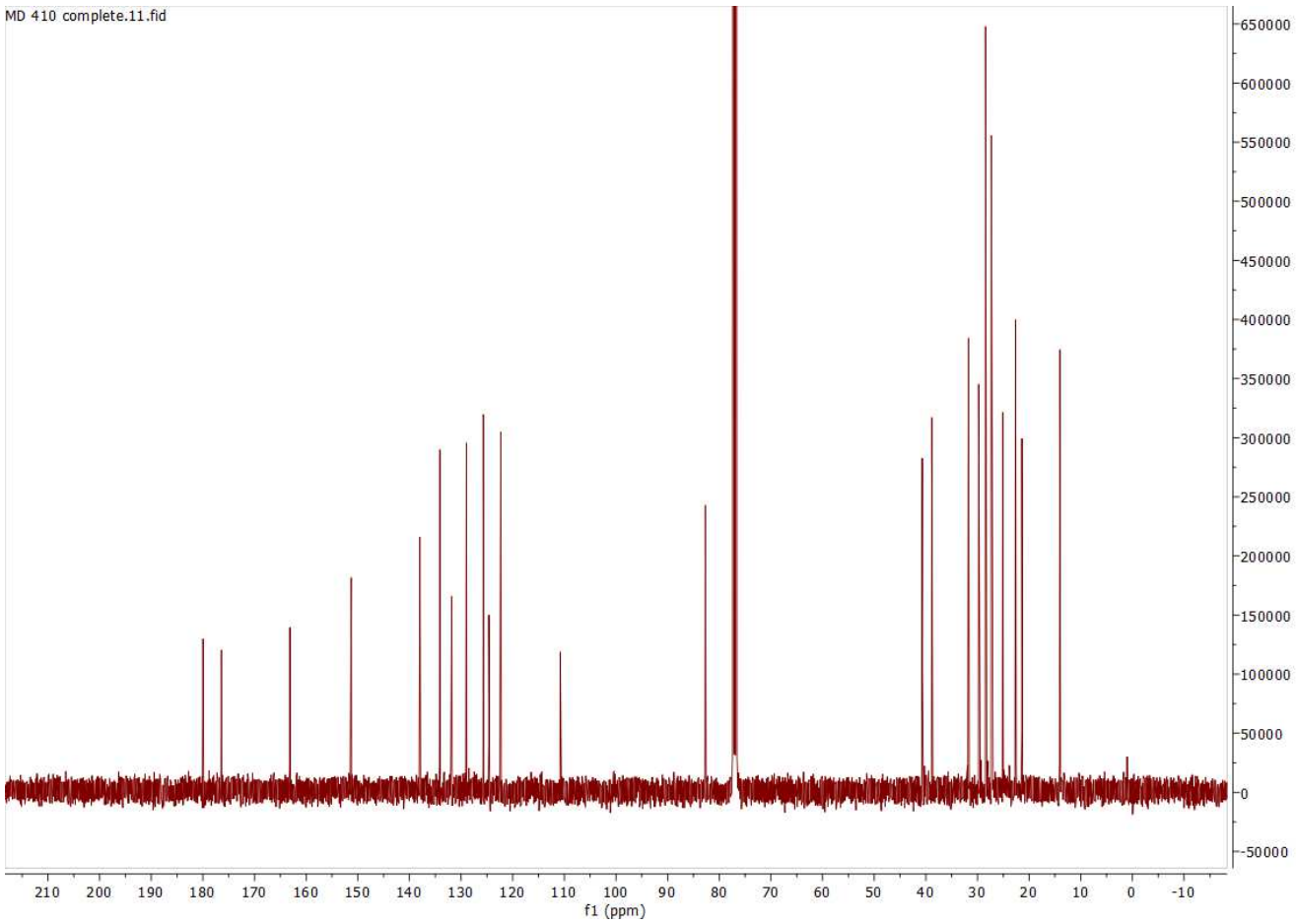
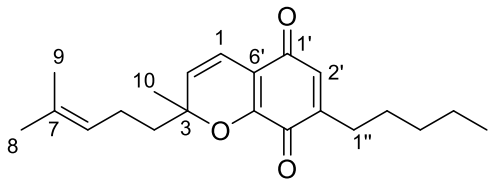


Figure S15. ^{13}C NMR spectrum (100 MHz) of compound **14b** in $CDCl_3$



16a

***para*-Cannabichromenquinone (CBCQ, 16a)**: red oil, 59% yield, R_f= 0.47 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2957, 2926, 2852, 1648, 1580, 1324, 1078, 969, 891 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.48 (d, *J* = 10.2 Hz, H-1), 6.42 (s, H-2'), 5.57 (d, *J* = 10.2 Hz, H-2), 5.09 (bt, *J* = 8.5 Hz, H-6), 2.42 (t, *J* = 8.5 Hz, H-1''), 2.07 (m, H-5), 1.95 (m, H-4a), 1.66 (bs, H-8), 1.63 (overlapped, H-4b), 1.58 (bs, H-9), 1.50 (m, H-2''), 1.48 (s, H-10), 1.32 (overlapped, H-3''), 1.30 (overlapped, H-4''), 0.89 (t, *J* = 6.9 Hz, H-5''). ^{13}C NMR (125 MHz, $CDCl_3$): δ_C 184.6 (C-1'), 181.8 (C-4'), 150.9 (C-5'), 147.8 (C-3'), 132.5 (C-7), 131.1 (C-2'), 128.5 (C-2), 123.3 (C-6), 115.1 (C-1), 114.9 (C-6'), 82.6 (C-3), 41.5 (C-4), 31.5 (C-3''), 30.2 (C-2''), 28.4 (C-1''), 27.2 (C-10), 25.5 (C-8), 22.7 (C-4''), 22.3 (H-5), 17.6 (C-9), 14.2 (C-5''). ESI-MS *m/z* 329 $[M+H]^+$; HR ESI-MS *m/z* 329.2107 $[M+H]^+$, calcd. for $C_{21}H_{25}O_3$, 329.2111.

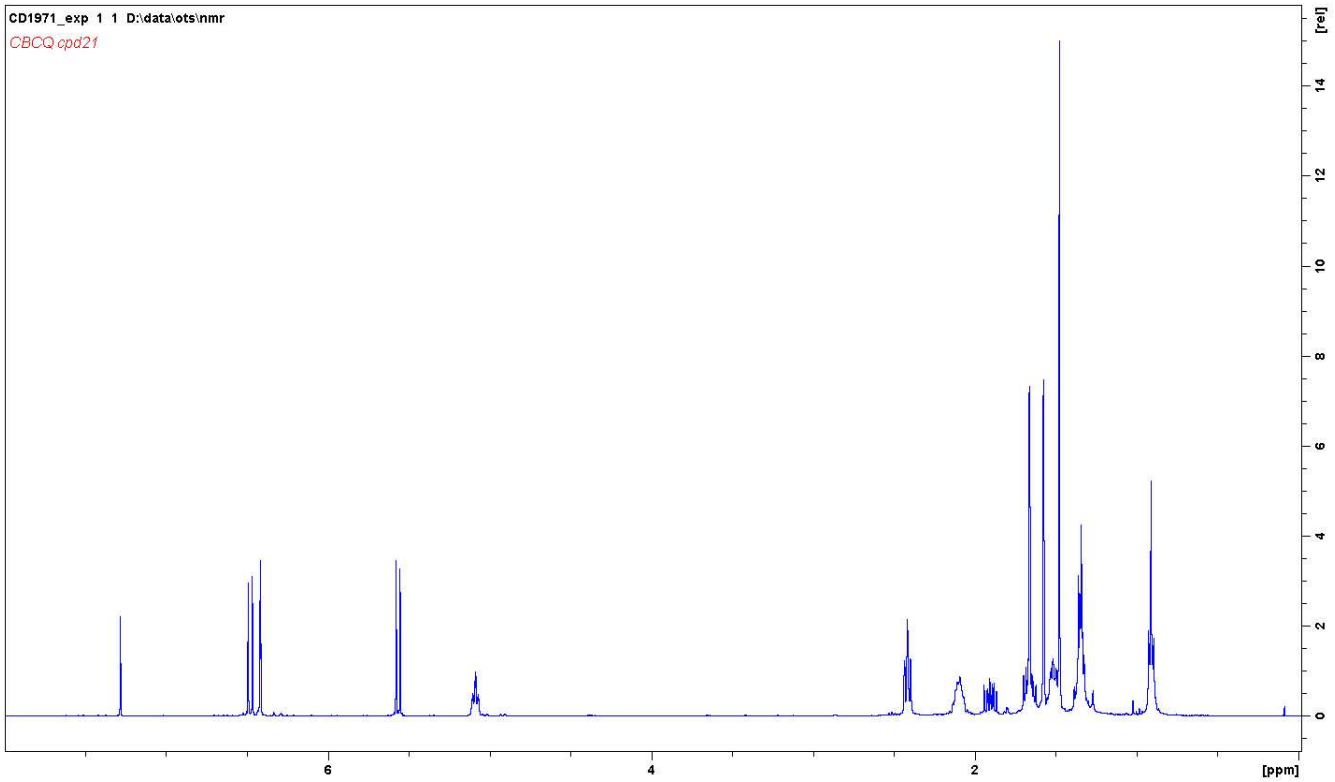


Figure S16. ^1H NMR spectrum (400 MHz) of compound **16a** in $CDCl_3$

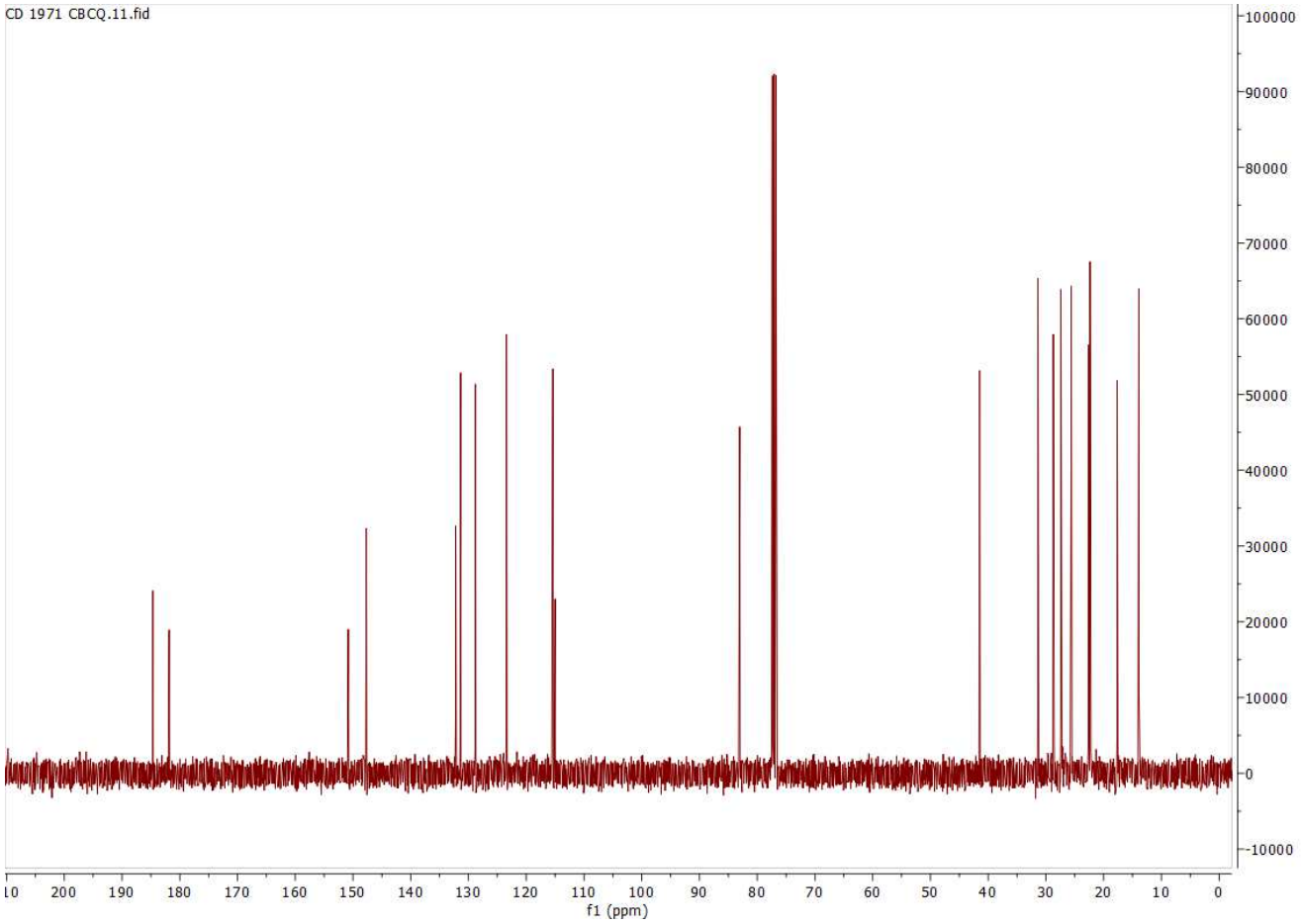


Figure S17. ^{13}C NMR spectrum (100 MHz) of compound **16a** in $CDCl_3$

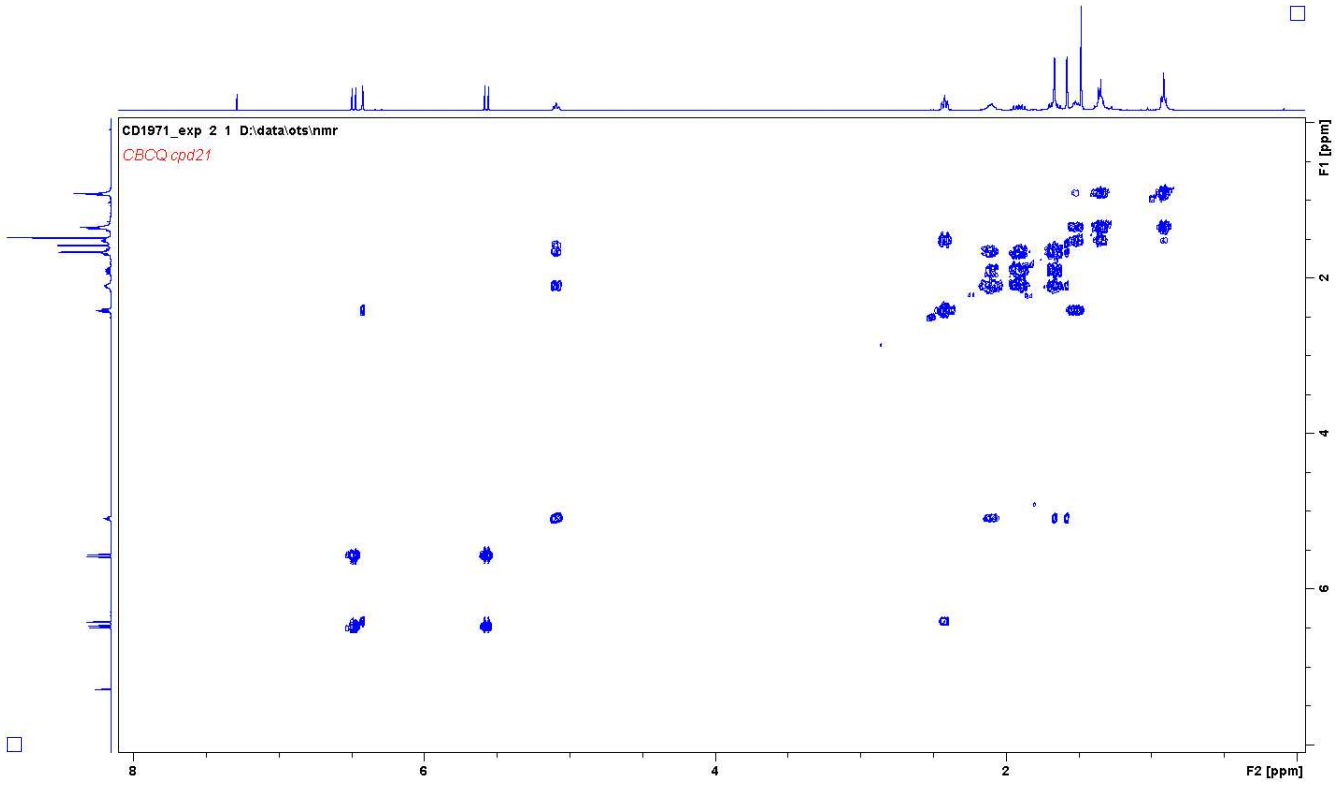


Figure S18. 2D NMR COSY spectrum of compound **16a** in $CDCl_3$

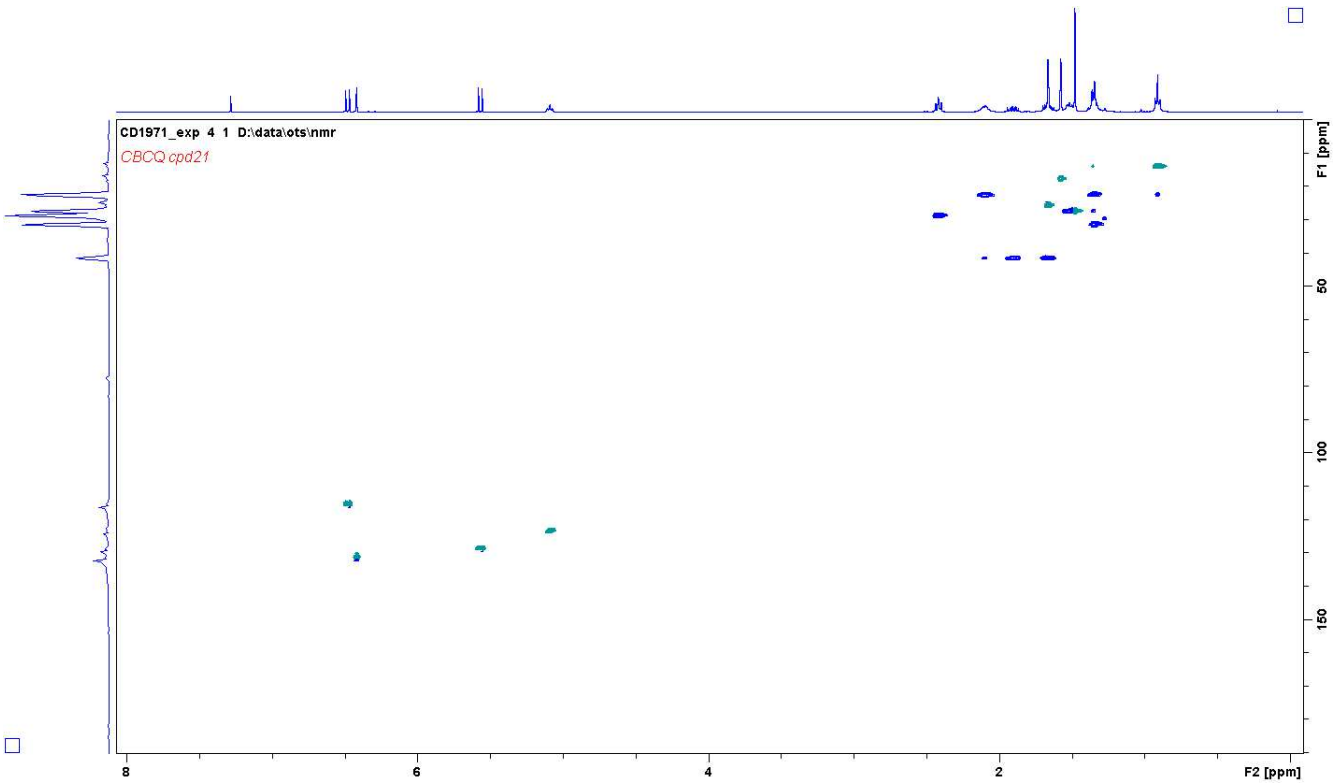


Figure S19. 2D NMR HSQC spectrum of compound **16a** in $CDCl_3$

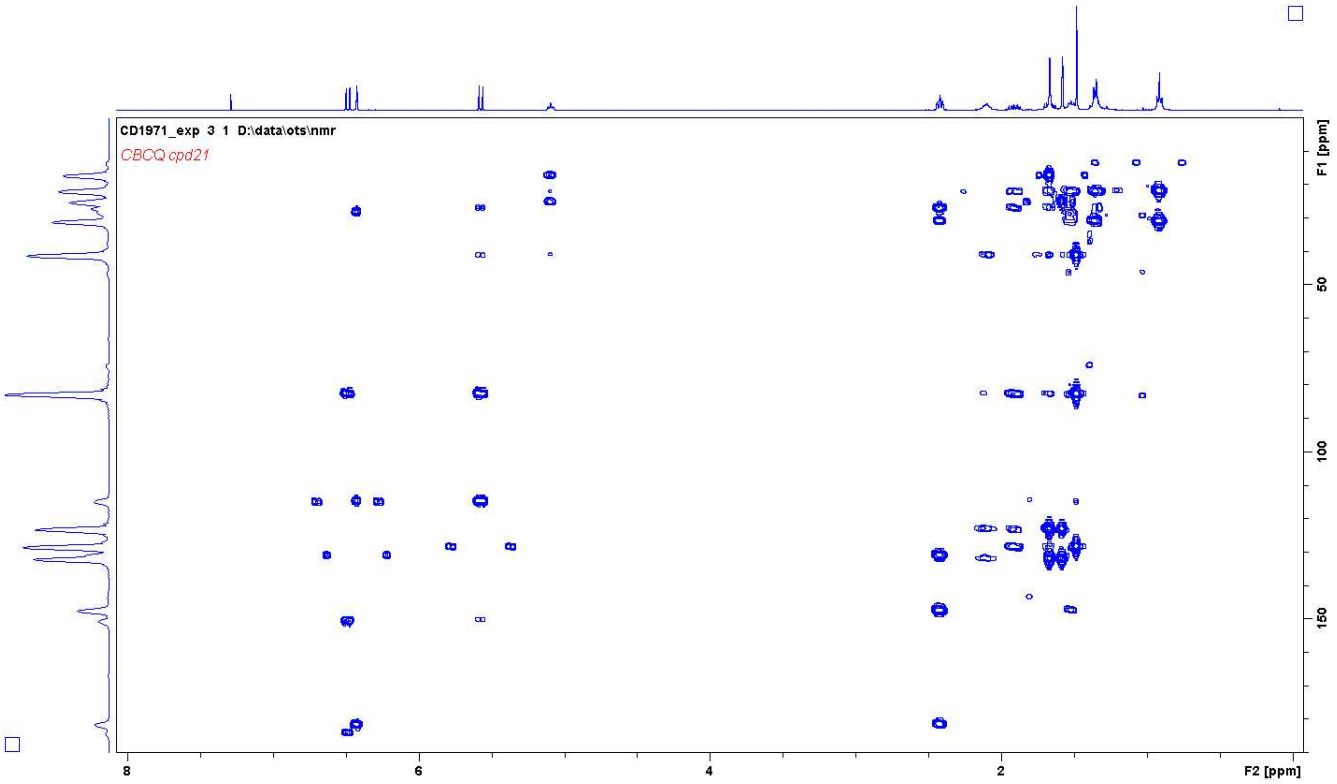
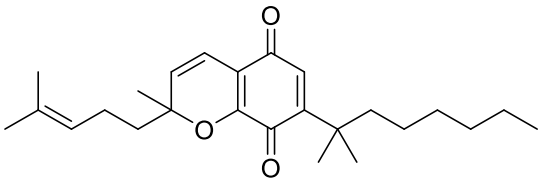


Figure S20. 2D NMR HMBC spectrum of compound **16a** in $CDCl_3$



16b

3'-Depentyl-3'(α,α-dimethylheptyl)cannabichromenquinone (CBCQ, 16b): red oil, 57% yield, R_f= 0.51 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2957,2924, 2856, 1648, 1080 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.47 (d, *J* = 10.0 Hz, 1H), 6.42 (bs, 1H), 5.56 (d, *J* = 10.0 Hz, 1H), 5.09 (bt, *J* = 7.8 Hz, 1H), 2.11 (m, 2H), 1.89 (m, 1H), 1.77-1.52 (m, 4H), 1.67 (bs, 3H), 1.49 (s, 3H), 1.32-0.97 (m, 16H), 0.86 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 184.7, 181.4, 153.2, 151.3, 132.2, 132.1, 128.6, 123.3, 115.2, 114.2, 83.2, 41.5, 40.7, 38.7, 31.7, 29.7, 27.6, 27.3, 25.6, 25.1, 22.6, 22.5, 17.6, 14.0. HRESI-MS: *m/z* calcd. for $C_{25}H_{37}O_3$ $[M+H]^+$ 385.2743, found 385.2739.

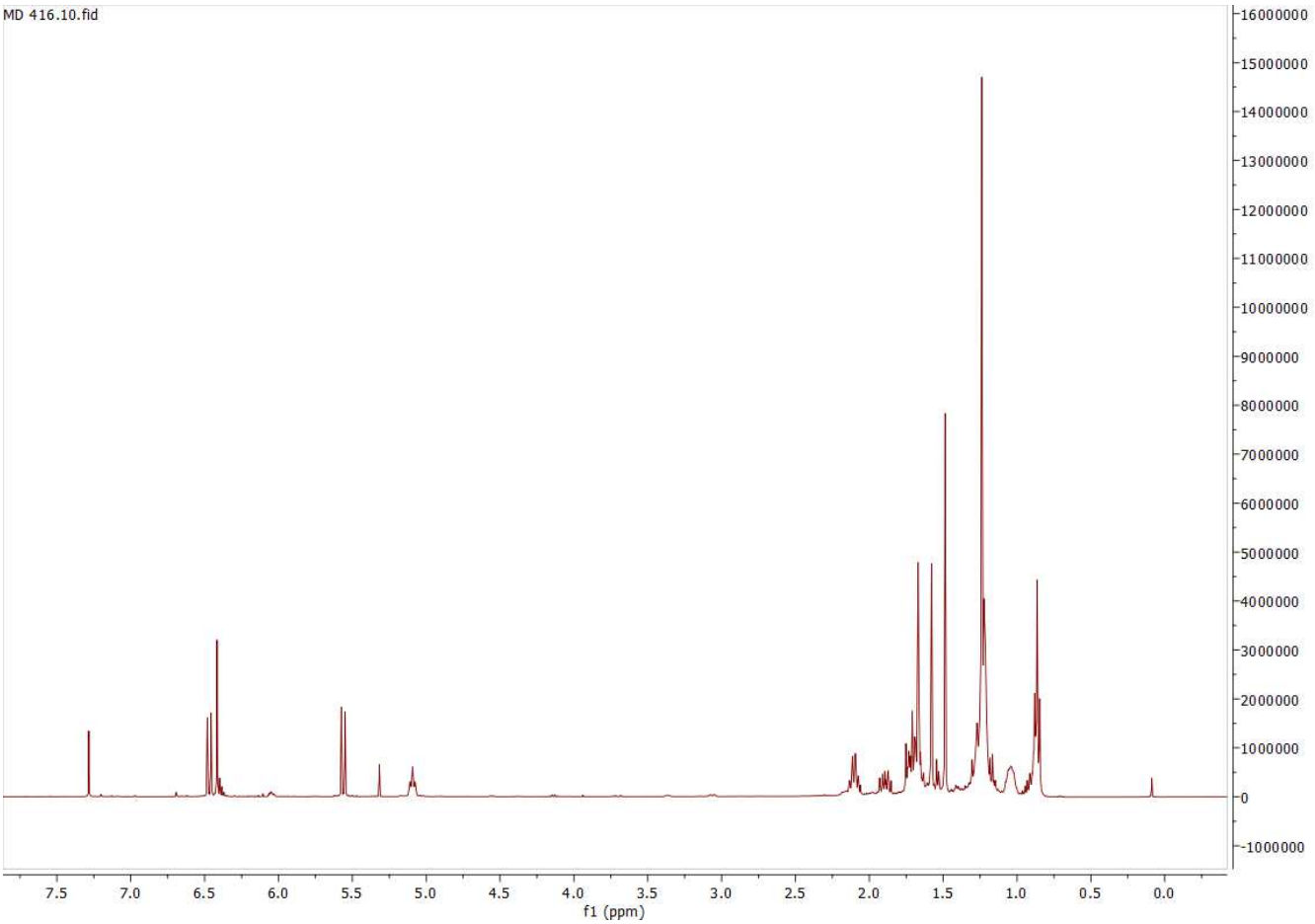


Figure S21. ^1H NMR spectrum (400 MHz) of compound **16b** in $CDCl_3$

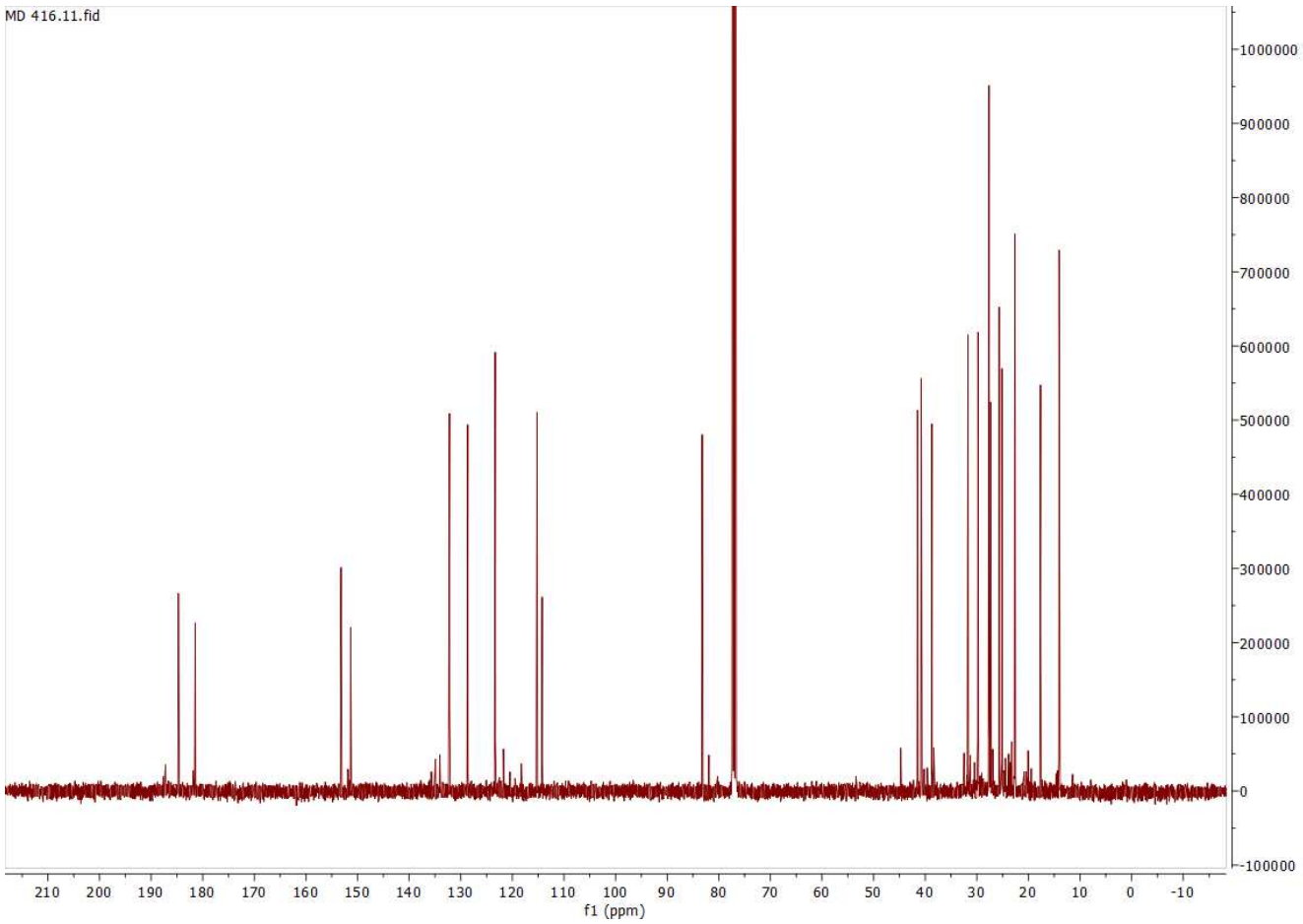
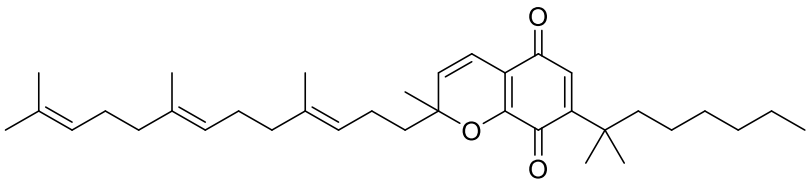


Figure S22. ^{13}C NMR spectrum (100 MHz) of compound **16b** in $CDCl_3$



16c

3'-Depentyl-3'(α,α-dimethylheptyl)geranyl-*para*-cannabichromenquinone (CBCQ, 16c): red oil, 51% yield, R_f= 0.48 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2956,2923, 2855, 1649, 1449, 1181, 1080 cm^{-1} ; ^1H NMR (400 MHz, $CDCl_3$,) δ= 6.47 (d, *J* = 10.0 Hz, 10H), 6,42 (s, 1H), 5.57 (d, *J* = 10.0 Hz, 1H), 5.11 (m, 3H), 2.13-1.96 (m, 10H), 1.74-1.59 (m, 16H), 1.49 (s, 3H), 1.29-1.18 (m, 12 H), 1.05 (m, 2H), 0.87 (t, *J* = 6.9 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ= 184.71, 181.45, 153.22, 151.35, 135.97, 135.05, 132.18, 131.27, 128.67, 124.38, 124.08, 123.14, 115.22, 114.25, 83.21, 41.55, 40.76, 39.72, 39.65, 38.71, 31.71, 29.77, 27.65, 27.63, 27.30, 26.76, 26.54, 25.71, 25.14, 22.62, 22.45, 17.70, 16.01, 14.06.

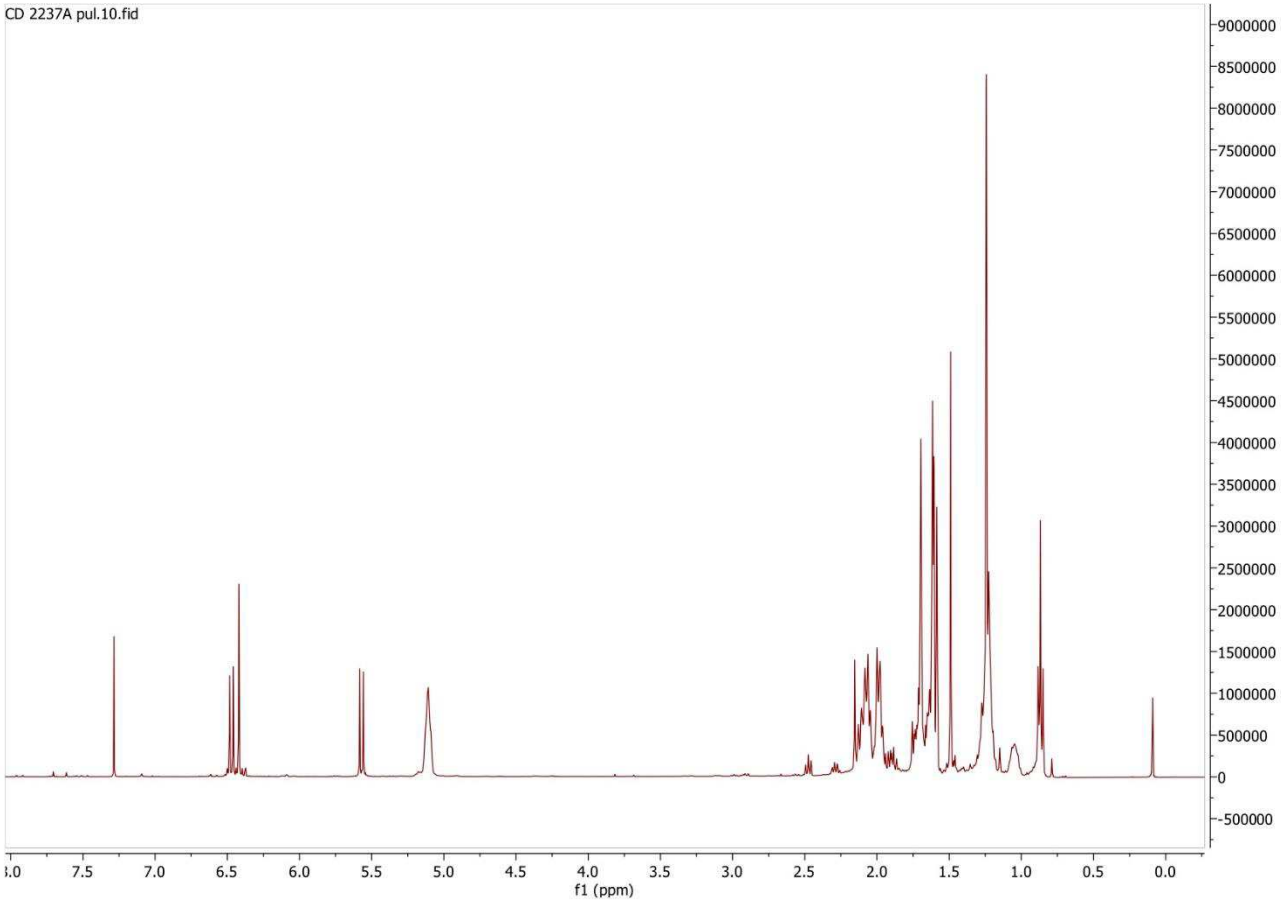


Figure S23. ^1H NMR spectrum (400 MHz) of compound **16c** in $CDCl_3$

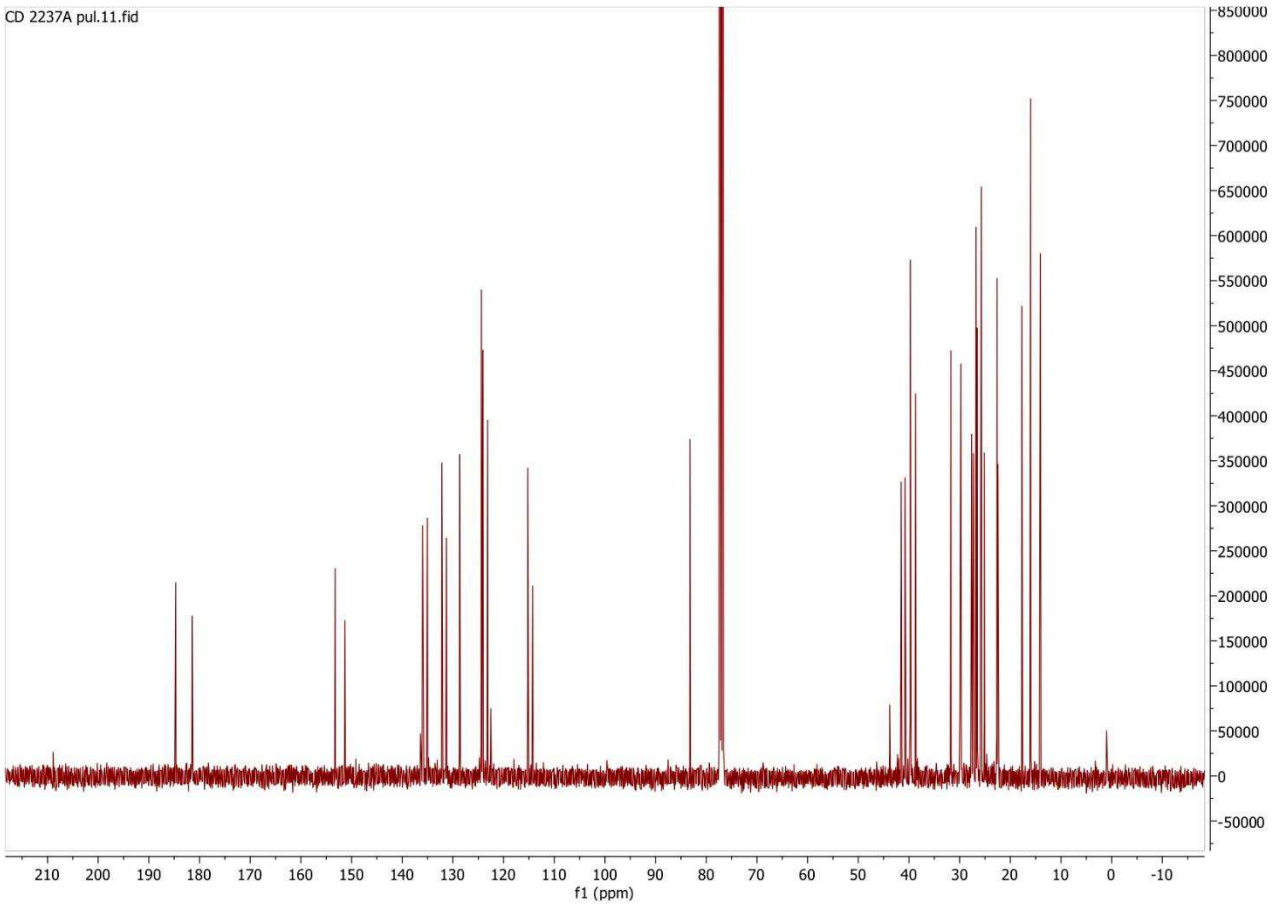


Figure S24. ^{13}C NMR spectrum (100 MHz) of compound **16c** in $CDCl_3$

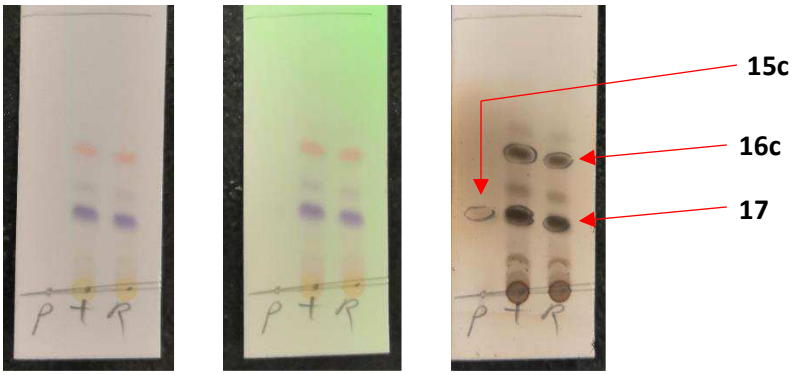
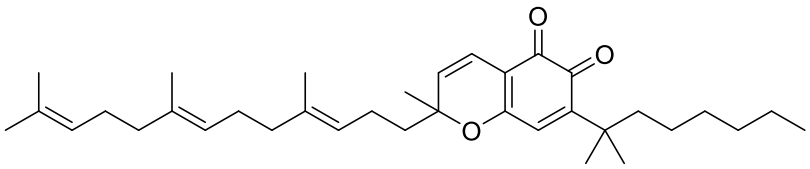


Figure S25. SIBX oxidation of compound **15c** before work-up and purification. Left: TLC in visible light. Centre: TLC under UV lamp (λ= 254 nm). Right: TLC after stain in H_2SO_4 5% in EtOH and heating.



17

3'-Depentyl-3'(α,α-dimethylheptyl)geranyl-*ortho*-cannabichromenquinone (CBCQ, 17): Purple oil (5%), R_f= 0.26 in petroleum ether-EtOAc 95:5. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 6.53 (s, 1H), 6.49 (d, *J* = 10.1 Hz, 1H), 5.34 (d, *J* = 10.1 Hz, 2H), 5.11 (m, 3H), 2.15-1.96 (m, 10H), 1.74-1.54 (m, 16H), 1.49 (s, 3H), 1.3-1.14 (m, 12H), 1.05 (m, 2H), 0.87 (d, *J* = 6.8 Hz, 3H). 13^C NMR (100 MHz, $CDCl_3$) δ = 180.38, 174.72, 163.44, 151.24, 136.06, 135.13, 132.74, 131.31, 124.38, 124.36, 124.01, 123.18, 123.09, 115.71, 109.98, 84.60, 41.88, 40.64, 39.72, 39.68, 39.00, 31.75, 29.78, 27.77, 27.43, 27.40, 26.76, 26.53, 25.71, 25.13, 23.83, 22.65, 22.50, 17.70, 16.03, 14.07. We were not able to collect IR and Mass spectra due to the fast interconversion of **17** in **16c**.

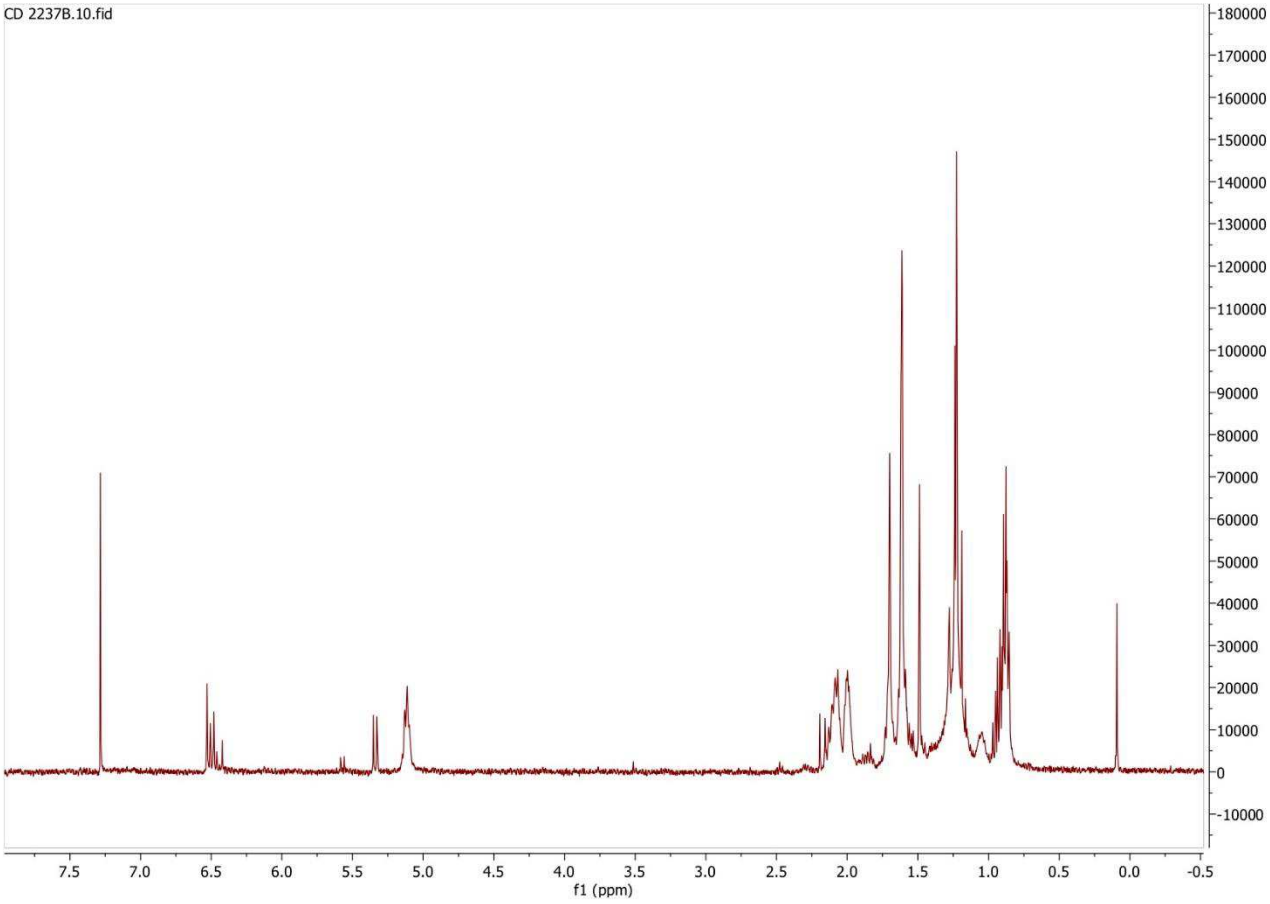


Figure S26. ^{1}H NMR spectrum (400 MHz) of compound **17** in $CDCl_3$

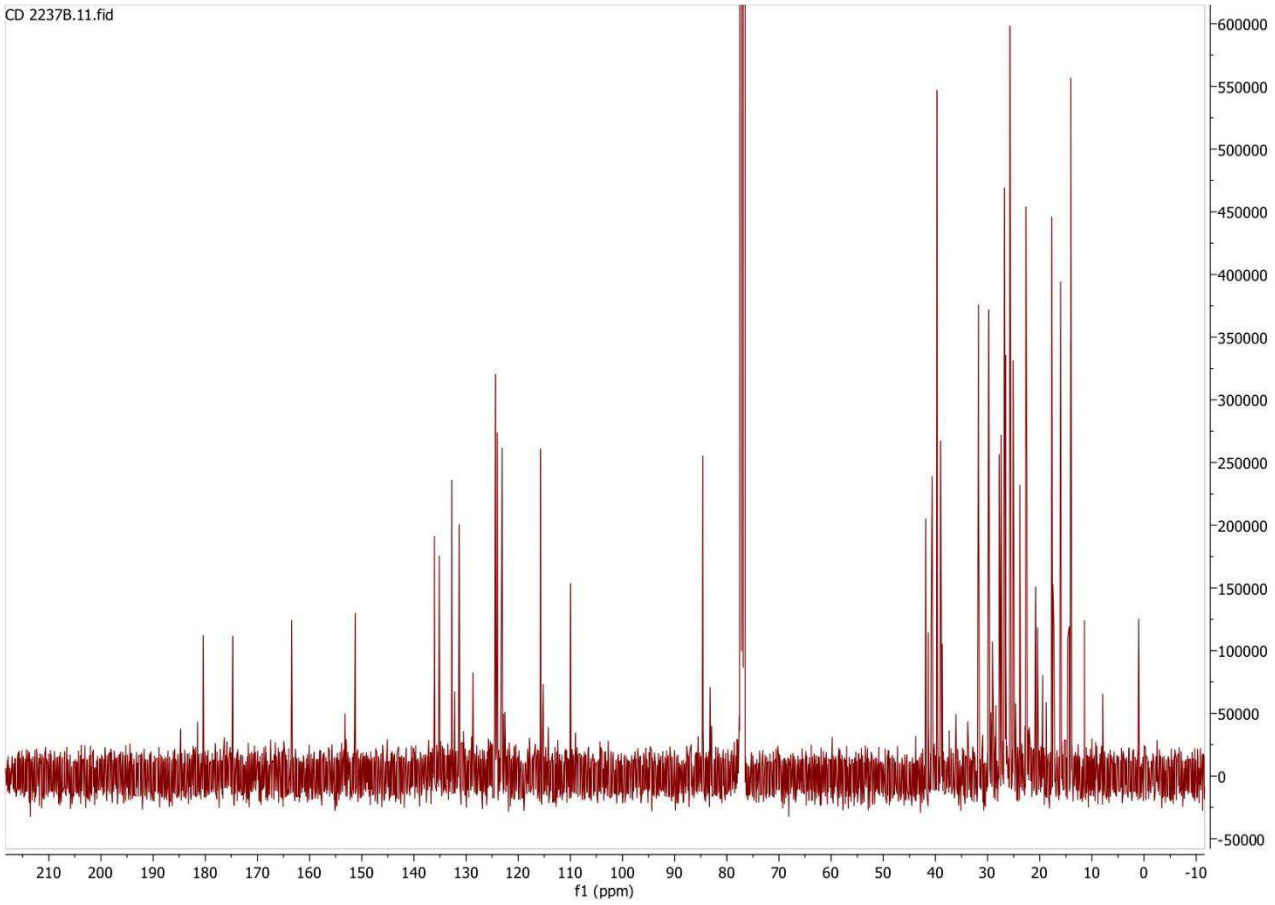
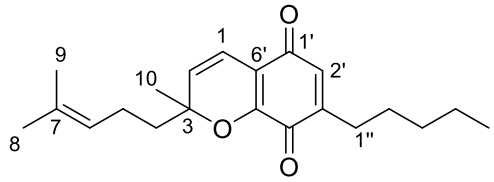


Figure S27. ^{13}C NMR spectrum (100 MHz) of compound **17** in $CDCl_3$

PIFA Oxidation of CBC (15a) to *p*-CBCQ (16a)



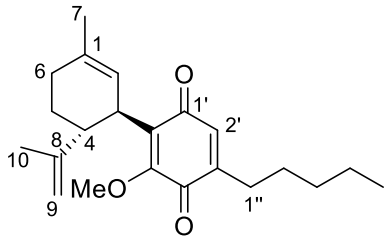
16a

To a stirred solution of CBC (**15a**, 150 mg, 0.478 mmol, R_f= 0.24 in petroleum ether-EtOAc 95:5 as eluant) in MeCN/H_2O 6:1 (2 mL), a solution of bis(trifluoroacetoxy)iodobenzene (PIFA, 641 mg, 1.493 mmol, 3.125 molar equiv.) in MeCN/H_2O 6:1 (2 mL) was added dropwise. The progress of the reaction was monitored by TLC. After completion of the reaction (20 minutes), the mixture was diluted with EtOAc (10 mL) and washed with saturated Na_2CO_3 (4 × 15 mL) and next with brine. After drying and evaporation, the residue was purified by GCC on silica gel (10 g, petroleum ether–EtOAc 95:5 as eluant) to obtain a red oil identified as *p*-CBCQ (**16a**, 86 mg, 55%, R_f= 0.47 in petroleum ether-EtOAc 95:5). Spectroscopic characterizations were in accordance with the previous data reported at page 16.

Methylation of cannabinoquinoids. Reaction with CBDQ (3a) as example

Methylation of cannabinoquinoids. Reaction with CBDQ (3a) as example

To a stirred solution of CBDQ (**3a**, 200 mg, 0.609 mmol, R_f= 0.13, petroleum ether-DCM 95:5) in dry DMF (5 mL), $NaHCO_3$ (102 mg, 1.218 mmol, 2 molar equiv) was added. The resulting solution was stirred at room temperature for 5 minutes, and then methyl Iodide (282 μL, 3,045 mmol, 5 eq) was added dropwise. The solution was stirred at room temperature overnight, then diluted with EtOAc (15 mL). The combined organic phases were washed with NaOH 2M (3x 15 mL) and next with brine. After drying and evaporation, the residue was purified by GCC on silica gel (10 g, petroleum ether as eluant) to obtain **3b** as a dark orange oil (160 mg, 76%, R_f= 0.24, petroleum ether-DCM 95:5).



3b

***para*-O-Methylcannabidiolquinone (Me-CBDQ, 3b)**: dark orange oil, 76% yield, R_f= 0.24 in petroleum ether-DCM 95:5. IR ν_{max} (KBr disc): 2956,2926, 2857, 1649, 1260, 890 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.37 (bs, H-2'), 5.09 (bd, *J* = 2.5 Hz, H-2), 4.54 (bs, H-9a), 4.50 (bs, H-9b), 3.87 (s, 5'-OMe), 3.72 (m, H-3), 2.67 (dt, *J* = 9.2, 2.5 Hz, H-4), 2.36 (t, *J* = 7.5 Hz, H-1''), 2.17 (m, H-6a), 1.97 (overlapped, H-6b), 1.94 (overlapped, H-5), 1.67 (bs, H-7), 1.61 (bs, H-10), 1.50 (m, H-2''), 1.32 (overlapped, H-3''), 1.30 (overlapped, H-4''), 0.89 (t, *J* = 6.9 Hz, H-5''). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 187.9 (C-1'), 184.1 (C-4'), 156.8 (C-5'), 148.2 (C-8), 147.3 (C-3'), 135.5 (C-6'), 133.2 (C-1), 132.5 (C-2'), 122.8 (C-2), 110.9 (C-9), 45.3 (C-4), 31.3 (C-1''), 31.5 (C-3''), 30.6 (C-5), 30.4 (C-6), 30.2 (C-2''), 29.1 (C-3), 24.2 (C-7), 22.5 (C-4''), 18.1 (C-10), 14.5 (C-5''). HRESI-MS: *m/z* calcd. for $C_{22}H_{31}O_3$ $[M+H]^+$ 343.2273, found 343.2279.

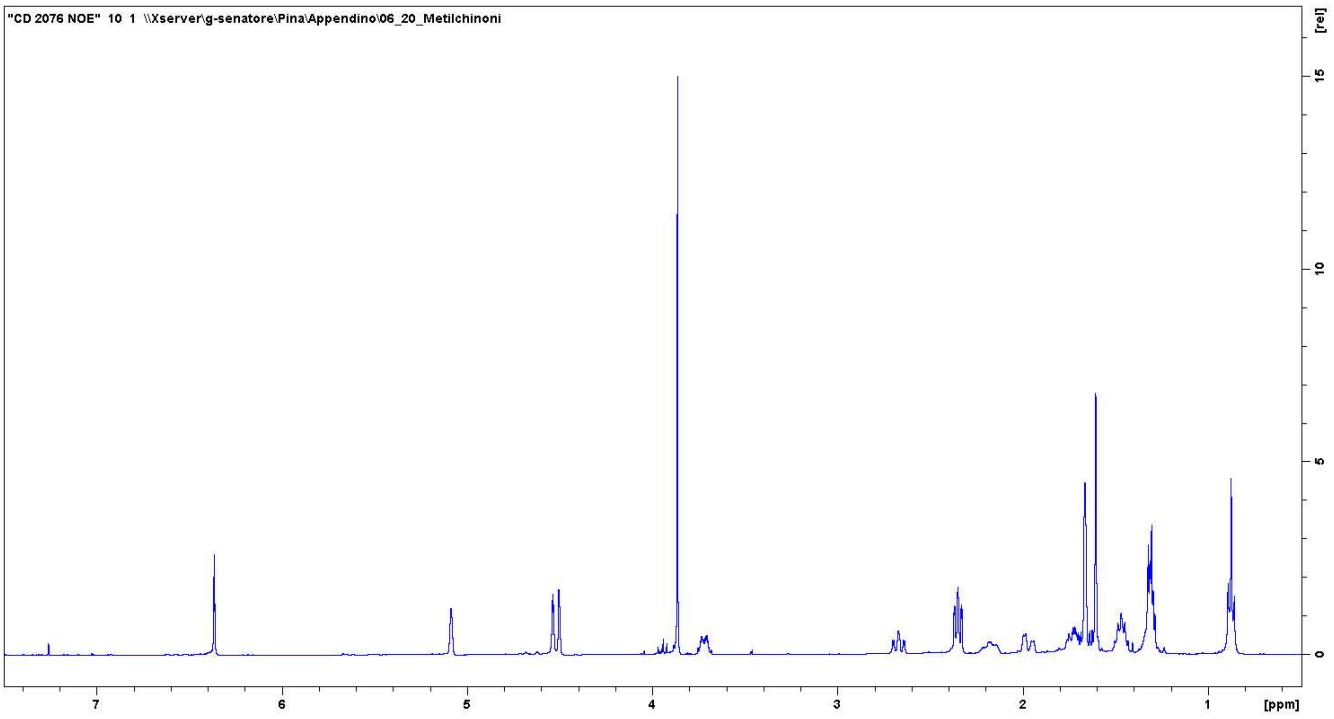


Figure S28. ^{1}H NMR spectrum (500 MHz) of compound **3b** in $CDCl_3$

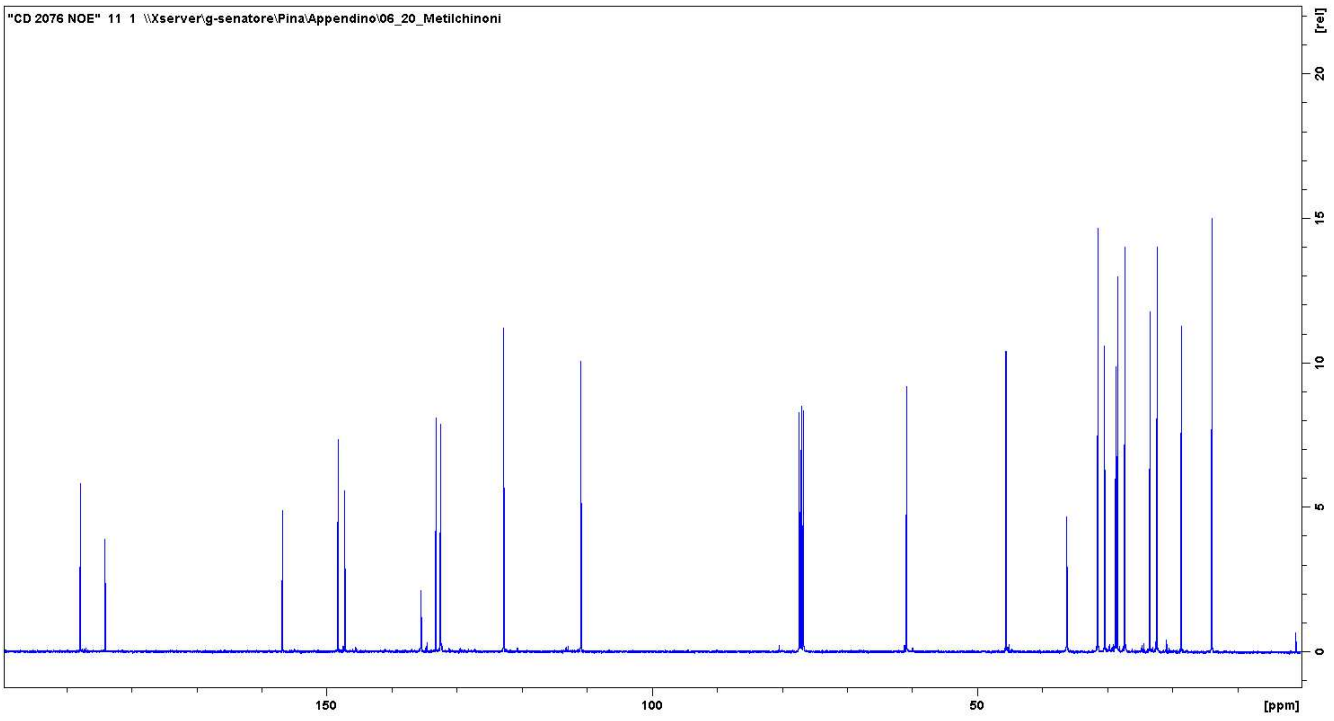


Figure S29. ^{13}C NMR spectrum (125 MHz) of compound **3b** in $CDCl_3$

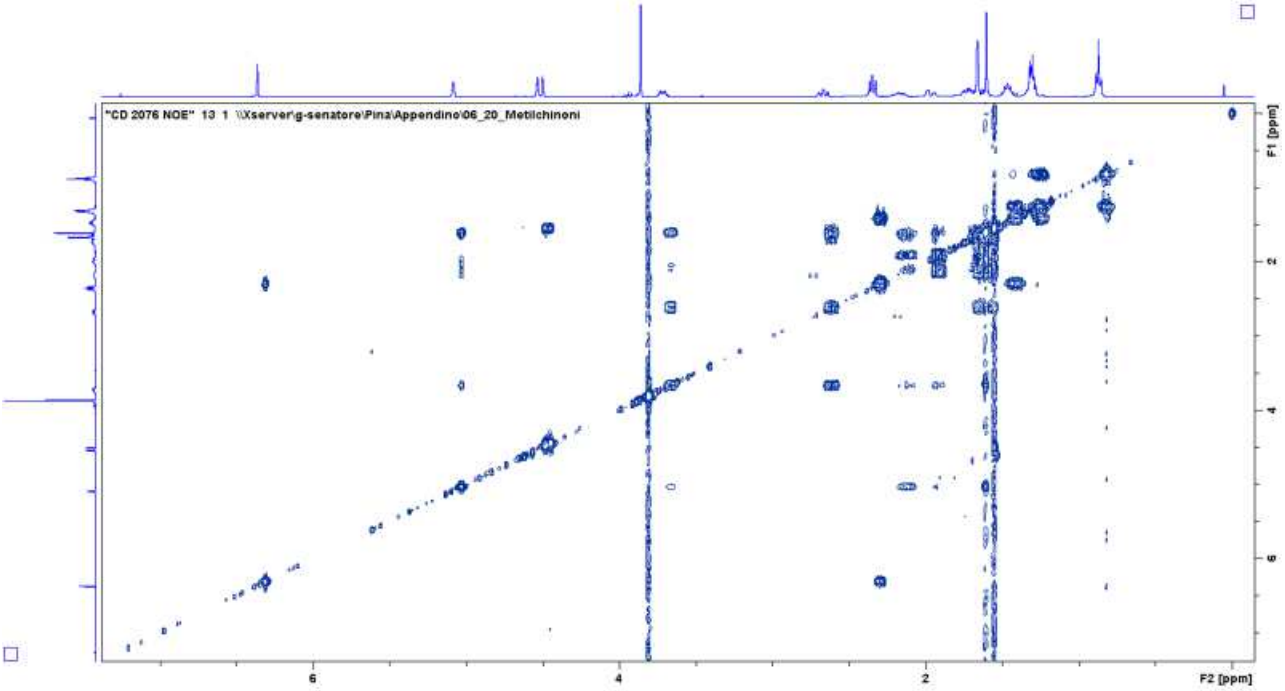


Figure S30. 2D NMR COSY spectrum of compound **3b** in $CDCl_3$

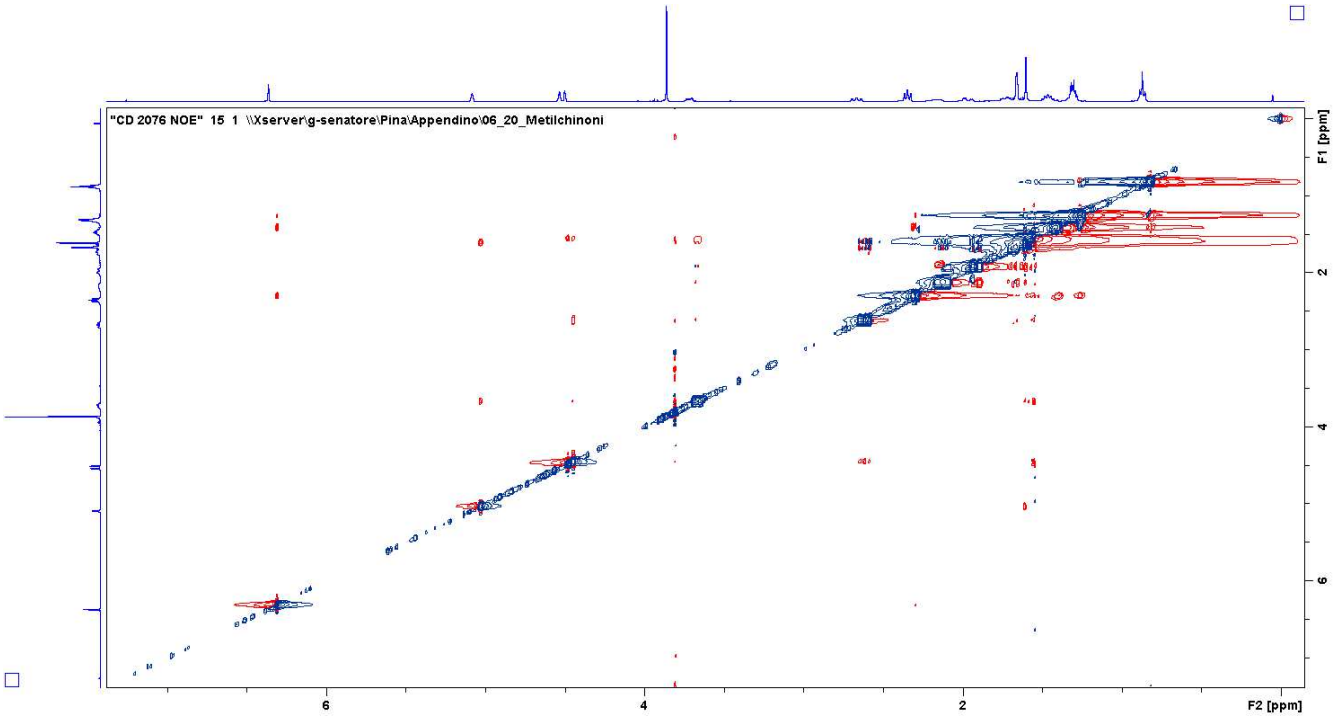
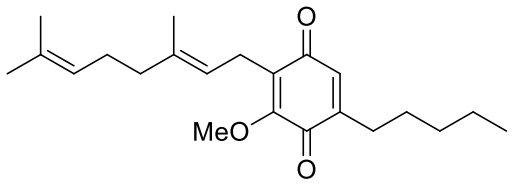


Figure S31. 2D NMR NOESY spectrum of compound **3b** in $CDCl_3$



4b

***para*-O-methylcannabigerolquinone (CBGQ, 4b):** orange oil, 35% yield, R_f= 0.63 in petroleum ether-EtOAc 95:5. IR ν_{max} (KBr disc): 2957, 2926, 2857, 1650, 1445, 1265, 1199, 1107, 894 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ_H 6.89 (bs, 1H), 4.98 (m, 2H), 3.90 (s, 3H), 3.06 (d, J = 7.3 Hz, 2H), 2.31 (td, J^1 = 7.9 Hz, J^2 = 1.4, 2H), 1.97 (m, 2H), 1.89 (m, 2H), 1.66 (bs, 3H), 1.58 (bs, 3H), 1.50 (bs, 3H), 1.42 (m, 2H), 1.26 (m, 4H), 0.83 (t, J = 6.9 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ_C 188.2, 184.1, 155.6, 147.6, 137.1, 132.2, 131.9, 131.4, 124.2, 120.0, 60.9, 39.7, 31.5, 29.7, 28.6, 27.5, 26.6, 25.7, 22.4, 17.7, 16.1, 13.9. HRESI-MS: *m/z* calcd. for $C_{22}H_{33}O_3$ $[M+H]^+$ 345.2430, found 345.2422.

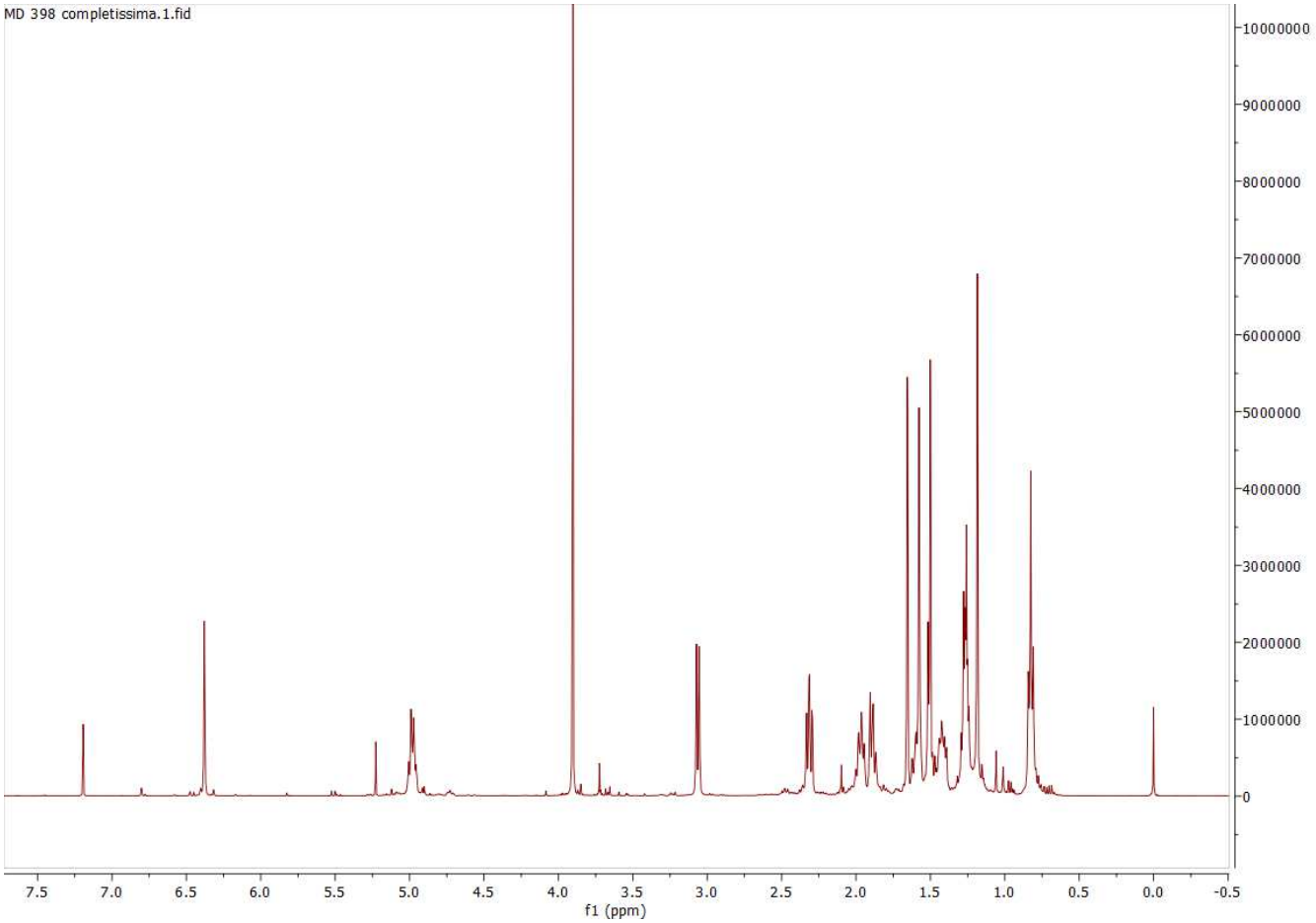


Figure S32. ^1H NMR spectrum (500 MHz) of compound **4b** in $CDCl_3$

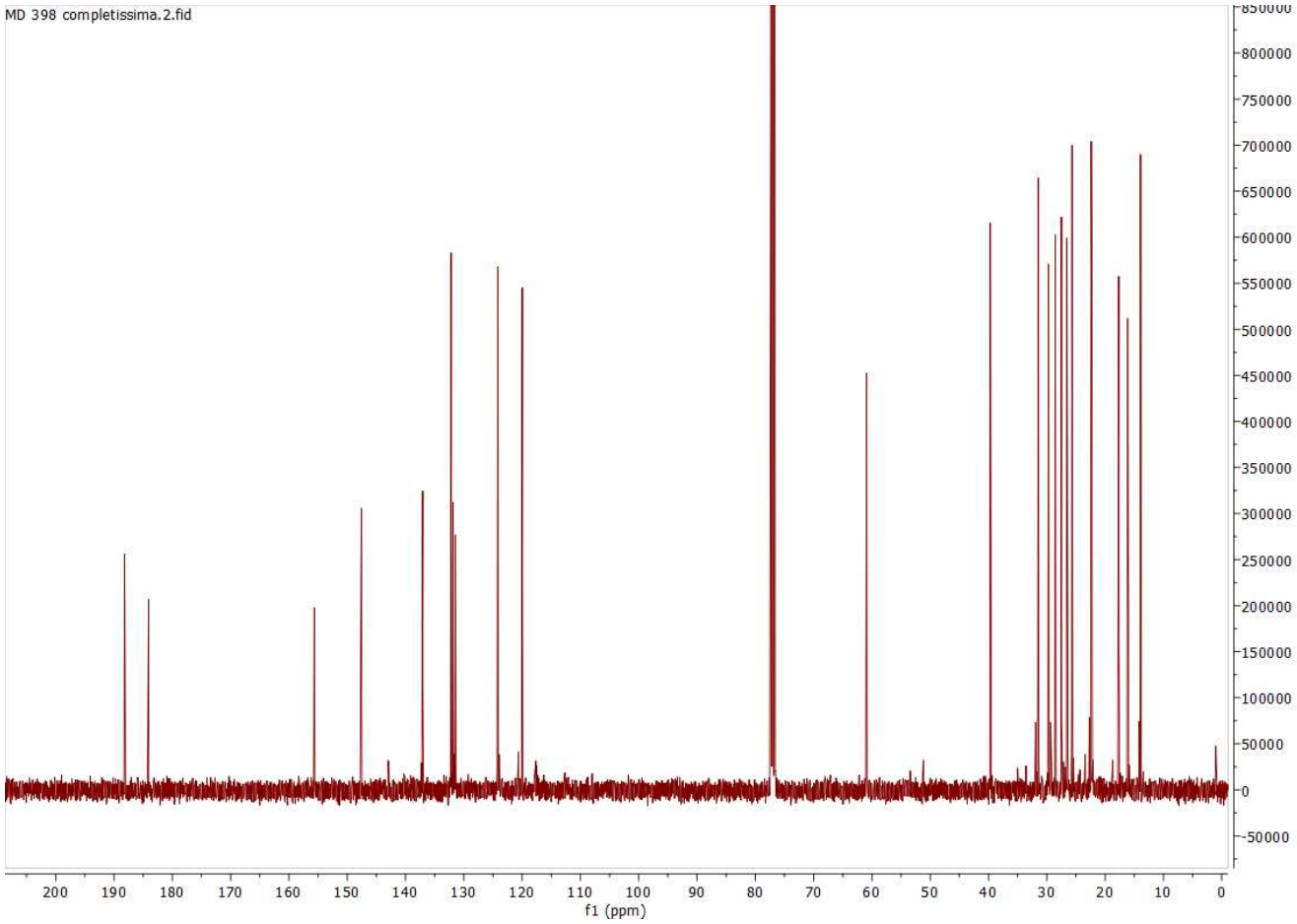


Figure S33. ^{13}C NMR spectrum (125 MHz) of compound 4**b** in $CDCl_3$