Electronic Supplementary Information

A Concise Synthesis of (±)-Antroquinonol with Unusual Scaffold of 4-Hydroxy-2-cyclohexenone

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Synthetic Procedure and Compound Characterization

Reduction of compound 8 and the subsequent hydrolysis

In Table 3, the yield and isomeric ratio of products varied depending on the reducing agent and reaction conditions (base, solvent and temperature).

Entry 1: Reduction of *trans*-**8** with $LiAlH_4$ in THF at –78 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (139 mg, 17%) and **13b** (589 mg, 73%).

Entry 2: Reduction of **8** (*trans*/*cis* = 1:1) with $LiAlH_4$ in THF at –78 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (69 mg, 9%), **1c** (54 mg, 7%), **1d** (145 mg, 18%), **13b** (299 mg, 37%), **13c** (135 mg, 17%) and **13d** (16 mg, 2%).

Entry 3: Reduction of **8** (*trans*/*cis* = 1:1) with *i*-Bu_2AlH in THF at –78 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (101 mg, 12%), **1c** (46 mg, 6%), **1d** (153 mg, 19%), **13b** (274 mg, 34%), **13c** (163 mg, 20%) and **13d** (15 mg, 2%).

Entry 4: Reduction of **8** (*trans*/*cis* = 1:1) with $Li(Ot\text{-}Bu)_3AlH$ in THF at 0 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (38 mg, 5%), **1c** (55 mg, 7%), **1d** (105 mg, 13%), **13a** (145 mg, 18%), **13b** (178 mg, 22%), **13c** (155 mg, 19%) and **13d** (40 mg, 5%).

Entry 5: Reduction of **8** (2.07 mmol, *trans*/*cis* = 1:1) with $NaBH_4$ (4.14 mmol) and $CeCl_3 \bullet 7H_2O$ (4.14 mmol) in MeOH at 0 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (59 mg, 9%), **1c** (38 mg, 5%), **1d** (186 mg, 23%), **13b** (299 mg, 37%), **13c** (69 mg, 9%) and **13d** (70 mg, 9%).

Entry 6: Reduction of **8** (*trans*/*cis* = 1:1) with $LiEt_3BH$ in THF at –78 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (92 mg, 11%), **1c** (85 mg, 10%), 81 mg, 10%), **13b** (283 mg, 35%) and **13c** (178 mg, 22%).

Entry 8: Reduction of **8** (*trans*/*cis* = 1:1) with $Li(siamyl)_3BH$ in THF at –40 ℃ for 5 h, followed by hydrolysis with oxalic acid, gave **1b** (80 mg, 10%), **1c** (147 mg, 18%), **13b** (307 mg, 38%) and **13c** (225 mg, 28%).

5-Benzyl-4-hydroxy-6-methyl-2,3-dimethoxycyclohex-2-en-1-one (15) and 5-benzyl-4-hydroxy-6-methyl-1,2-dimethoxycyclohex-1-en-3-one (16)

According to the representative procedure for alkylation reaction, ketone **12** (0.5 g, 2.17 mmol) was treated with LHMDS (4.34 mmol, 4.3 mL of 1.0 M solution in THF) and benzyl bromide (0.7 g, 4.34 mmol) to give the alkylation product **14** (*trans*/*cis* = 1:1) as shown in the ^1H NMR spectrum. HRMS calcd for $C_{18}H_{25}O_5$: 321.1702, found: *m*/*z* 321.1692 $[M + H]^+$.

According to the representative procedure for reduction, the above-prepared ketone **14** was treated with an appropriate reducing agent ($LiAlH_4$, *i*-Bu_2AlH, $LiAl(Ot\text{-}Bu)_3H$, $NaBH_4/CeCl_3 \bullet 7H_2O$, Superhydride®, L-Selectride® or LS-Selectride®), followed by hydrolysis with oxalic acid, to give isomeric compounds **15b**–**d** and **16a**–**c** in varied ratios depending on the reducing agent and reaction conditions. The diastereomers were separated

by silica gel column chromatography with elution of EtOAc/hexane (10:90). Some diastereomers were recrystallized from EtOAc/hexane for X-ray diffraction analysis.

The (4,5-*cis*-5,6-*cis*)-isomer **15c** (30 mg, 0.11 mmol) was subjected to epimerization by treatment with K_2CO_3 (45 mg, 0.33 mmol) in MeOH (2 mL) at 25 ℃ for 12 h, giving the (4,5-*cis*-5,6-*trans*)-isomer **15a** (27 mg, 90%) after purification on a silica gel column by elution with EtOAc/CH_2Cl_2 (10:90).

(4,5-*Cis*-5,6-*trans*)-isomer **15a**: $C_{16}H_{20}O_4$; IR ν_{max} (neat) 3431, 3026, 2932, 1660, 1619, 1454, 1240, 1015, 942, 751, 703 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.26 (2 H, m), 7.23–7.18 (3 H, m), 3.98 (4 H, br s), 3.64 (3 H, s), 2.90 (1 H, dd, *J* = 13.1, 5.2 Hz), 2.75 (1 H, dd, *J* = 13.1, 11.0 Hz), 2.59 (1 H, qd, *J* = 6.7, 11.0 Hz), 2.03–1.93 (2 H, m), 1.25 (3 H, d, *J* = 6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 196.8, 160.4, 139.2, 135.8, 129.2 (2 ×), 128.6 (2 ×), 126.4, 66.9, 60.7, 59.4, 45.0, 40.3, 34.4, 12.6. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$.

(4,5-*Trans*-5,6-*trans*)-isomer **15b**: $C_{16}H_{20}O_4$; White solid, mp 75.5–77.3 °C; IR ν_{max} (neat) 3427, 3026, 2935, 2880, 1660, 1614, 1454, 1234, 1011, 969, 750, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.33–7.15 (5 H, m), 4.20 (1 H, d, *J* = 7.5 Hz), 4.08 (3 H, s), 3.62 (3 H, s), 3.03 (1 H, dd, *J* = 14.1, 5.0 Hz), 2.84 (1 H, dd, *J*=14.1, 4.5 Hz), 2.65 (1 H, br s), 2.22–2.13 (1 H, m), 2.13–2.00 (1 H, m), 1.35 (3 H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.8, 160.1, 138.0, 134.9, 129.9 (2 ×), 128.4 (2 ×), 126.4, 68.7, 60.7, 60.3, 46.5, 42.2, 34.9, 14.9. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$. A sample of **15b** was recrystallized from EtOAc/hexane. The 4,5-*trans*-5,6-*trans* configuration was unambiguously determined by X-ray crystallography.

(4,5-*Cis*-5,6-*cis*)-isomer **15c**: $C_{16}H_{20}O_4$; White solid, mp 137.8–138.9; IR ν_{max} (neat) 3420, 3025, 2980, 2835, 1665, 1614, 1454, 1204, 1023, 969, 754, 712 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.32–7.15 (5 H, m), 4.23 (1 H, d, *J* = 3.7 Hz), 4.05 (3 H, s), 3.64 (3 H, s), 2.99 (1 H, dd, *J* = 13.4, 8.5 Hz), 2.67 (1 H, dd, *J* = 13.4, 6.1 Hz), 2.49 (1 H, qd, *J*=7.3, 4.3 Hz), 2.41–2.32 (1 H, m), 1.30 (3 H, d, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 199.1, 160.5, 139.6, 135.2, 129.0 (2 ×), 128.6 (2 ×), 126.3, 69.2, 60.6, 59.8, 44.3, 41.5, 33.6, 15.0. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$. A sample of **15c** was recrystallized from EtOAc/hexane. The 4,5-cis-5,6-cis configuration was unambiguously determined by X-ray crystallography.

(4,5-*Trans*-5,6-*cis*)-isomer **15d**: $C_{16}H_{20}O_4$; White solid, mp 168.7–169.5 °C; IR ν_{max} (neat) 3430, 3016, 2970, 2884, 1663, 1620, 1451, 1224, 1013, 959, 757, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.31–7.23 (2 H, m), 7.23–7.15 (1 H, m), 7.11 (2 H, d, *J* = 7.3 Hz), 4.23 (1 H, d, *J* = 5.5 Hz), 4.03 (3 H, s), 3.67 (3 H, s), 2.81 (1 H, qd, *J* = 7.3, 4.3 Hz), 2.77–2.69 (1 H, m), 2.69–2.60 (1 H, m), 2.34–2.25 (1 H, m), 1.17 (3 H, d, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 197.4, 158.9, 139.1, 135.6, 128.8 (2 ×), 128.6 (2 ×), 126.4, 68.9, 60.6, 59.6, 46.0, 40.0, 33.2, 11.8. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$. A

sample of **15d** was recrystallized from EtOAc/hexane. The 4,5-*trans*-5,6-*cis* configuration was unambiguously determined by X-ray crystallography.

(4,5-*Cis*-5,6-*trans*)-isomer **16a**: $C_{16}H_{20}O_4$; IR ν_{max} (neat) 3465, 3025, 2928, 2852, 1667, 1606, 1454, 1260, 1008, 972, 748, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.22 (2 H, m), 7.21–7.16 (1 H, m), 7.08 (2 H, d, *J* = 7.3 Hz), 4.50 (1 H, d, *J* = 5.5 Hz), 3.98 (3 H, s), 3.69 (3 H, s), 3.05 (1 H, dd, *J* = 14.0, 3.1 Hz), 2.49 (1 H, qd, *J* = 7.3, 1.2 Hz), 2.44–2.35 (1 H, m), 2.18–2.05 (1 H, m), 1.21 (3 H, d, *J* = 7.3 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 194.5, 166.7, 139.8, 133.6, 129.1 (2 ×), 128.6 (2 ×), 126.2, 70.7, 60.7, 59.1, 46.5, 33.8, 31.8, 17.7. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$.

(4,5-*Trans*-5,6-*trans*)-isomer **16b**: $C_{16}H_{20}O_4$; Pale yellow solid, mp 59.5–61.2 °C; IR ν_{max} (neat) 3460, 3027, 2937, 2881, 1746, 1602, 1454, 1259, 1040, 977, 753, 702 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.32–7.26 (4 H, m), 7.26–7.17 (1 H, m), 3.98 (3 H, s), 3.83 (1 H, br s), 3.74 (1 H, d, *J* = 12.5 Hz), 3.60 (3 H, s), 3.16 (1 H, dd, *J* = 14.1, 4.5 Hz), 2.92 (1 H, dd, *J* = 14.1, 3.5 Hz), 2.37 (1 H, qd, *J* = 10.2, 6.5 Hz), 1.89–1.76 (1 H, m), 1.31 (3 H, d, *J* = 6.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.8, 166.9, 137.2, 133.3, 130.5 (2 ×), 128.3 (2 ×), 126.4, 71.3, 60.6, 60.5, 46.3, 34.7, 32.7, 15.7. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$. A sample of **16b** was recrystallized from EtOAc/hexane. The 4,5-*trans*-5,6-*trans* configuration was unambiguously determined by X-ray crystallography.

(4,5-*Cis*-5,6-*cis*)-isomer **16c**: $C_{16}H_{20}O_4$; White solid, mp 99.8–101.3 °C; IR ν_{max} (neat) 3440, 2924, 2852, 1755, 1651, 1454, 1226, 1025, 959, 735, 701 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.23–7.10 (5 H, m), 4.12 (1 H, d, *J* = 4.5 Hz), 4.08 (3 H, s), 3.64 (3 H, s), 2.91–2.82 (1 H, m), 2.82–2.71 (1 H, m), 2.59–2.47 (2 H, m), 1.17 (3 H, d, *J* = 7.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.3, 167.2, 141.3, 134.4, 129.0 (2 ×), 128.3 (2 ×), 125.8, 74.9, 60.7, 60.3, 45.9, 37.3, 30.4, 15.3. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$. A sample of **16c** was recrystallized from EtOAc/hexane. The 4,5-*cis*-5,6-*cis* configuration was unambiguously determined by X-ray crystallography.

(4,5-*Trans*-5,6-*cis*)-isomer **16d**: $C_{16}H_{20}O_4$; IR ν_{max} (neat) 3471, 2924, 2853, 1666, 1607, 1454, 1233, 1048, 955, 748, 701 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.26 (2 H, m), 7.22–7.17 (3 H, m), 4.02 (1 H, d, *J* = 12.2 Hz), 3.97 (3 H, s), 3.69 (1 H, s), 3.65 (3 H, s), 3.35 (1 H, dd, *J* = 14.0, 3.7 Hz), 2.57 (1 H, dd, *J* = 14.0, 11.9 Hz), 2.34–2.22 (1 H, m), 1.19 (3 H, d, *J* = 6.7 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.4, 170.2, 138.8, 133.6, 128.9 (2 ×), 128.6 (2 ×), 126.3, 71.3, 60.8, 59.5, 44.7, 33.7, 33.6, 12.1. HRMS calcd for $C_{16}H_{21}O_4$: 277.1440, found: *m*/*z* 277.1439 $[M + H]^+$.

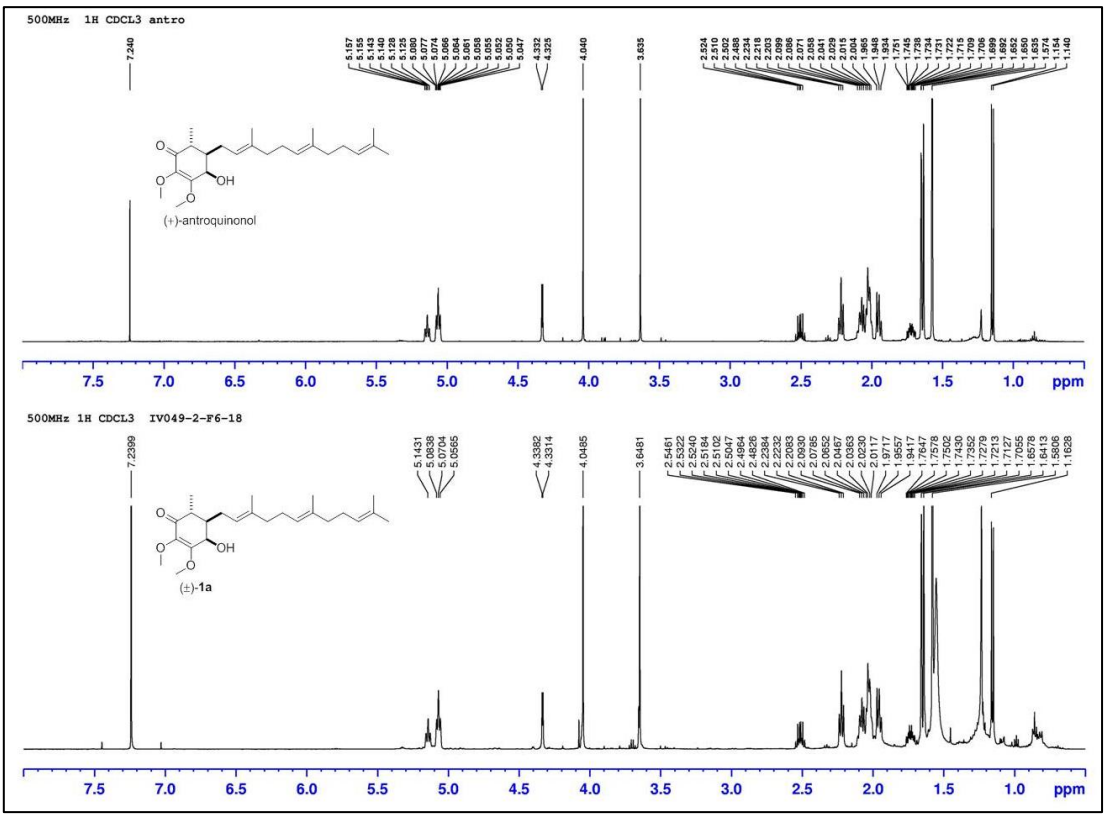

Figure S1. Comparison of the ^{1}H NMR spectra of natural (+)-antroquinonol and the synthetic racemic mixture (±)-**1a** (500 MHz, $CDCl_3$).

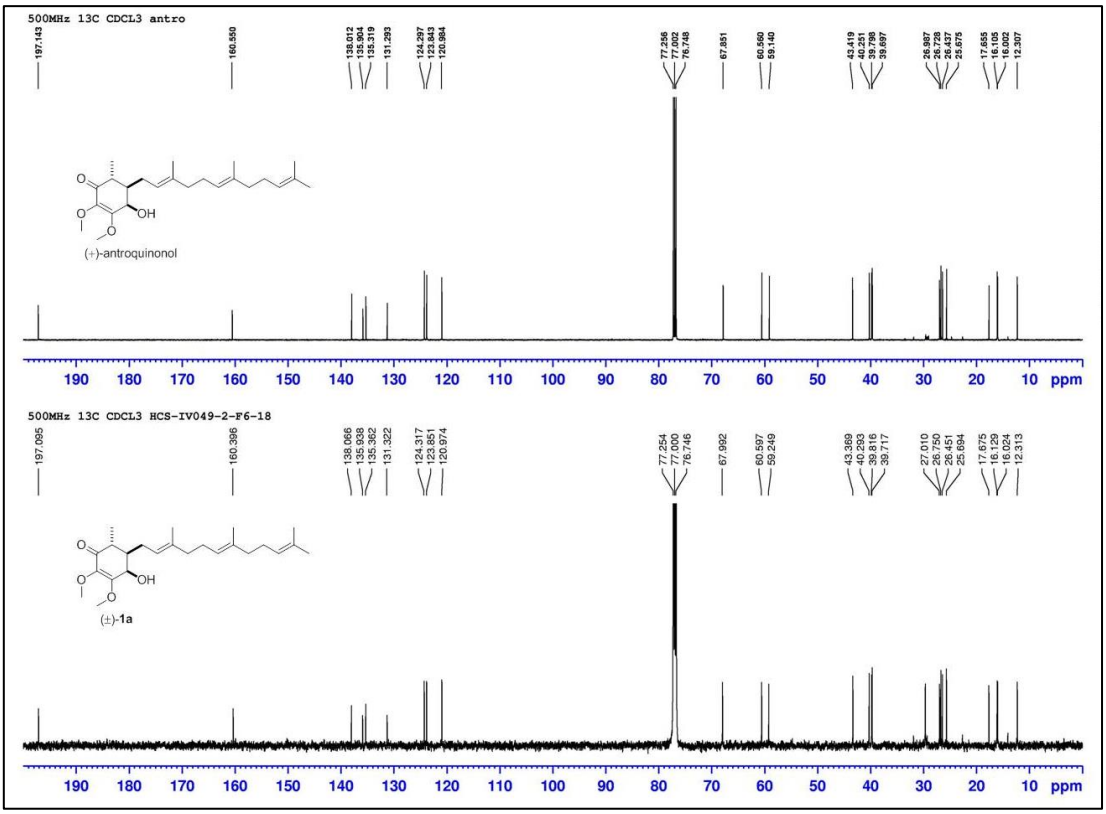

Figure S2. Comparison of the ^{13}C NMR spectra of natural (+)-antroquinonol and the synthetic racemic mixture (±)-**1a** (125 MHz, $CDCl_3$).

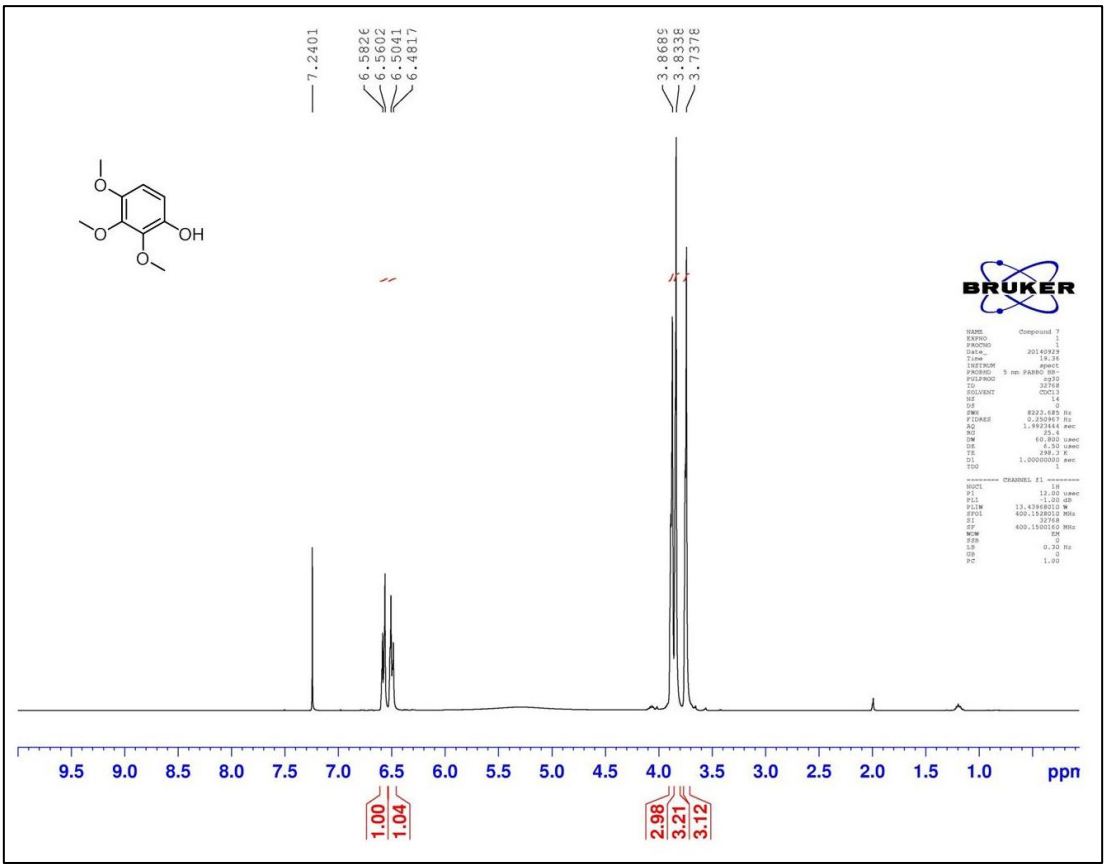

Figure S3. ^{1}H NMR spectrum of compound **10** (400 MHz, $CDCl_3$)

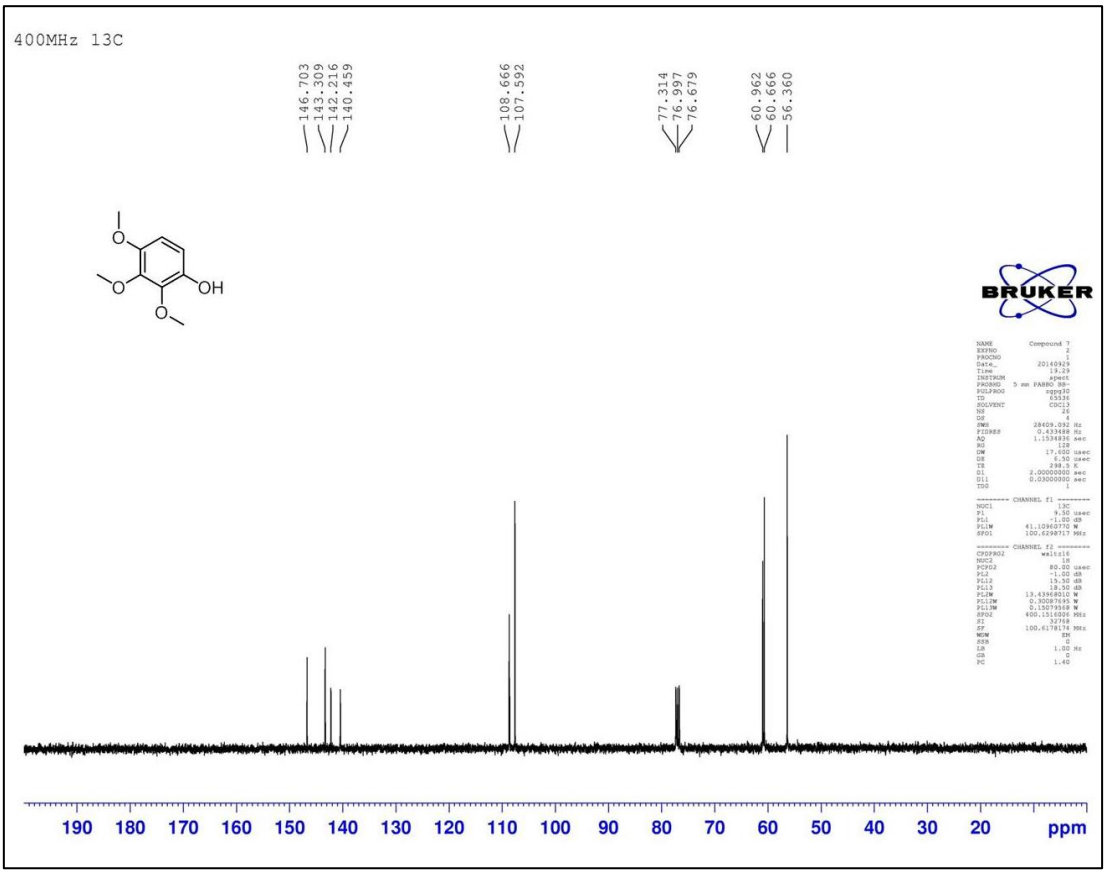

Figure S4. ^{13}C NMR spectrum of compound **10** (100 MHz, $CDCl_3$)

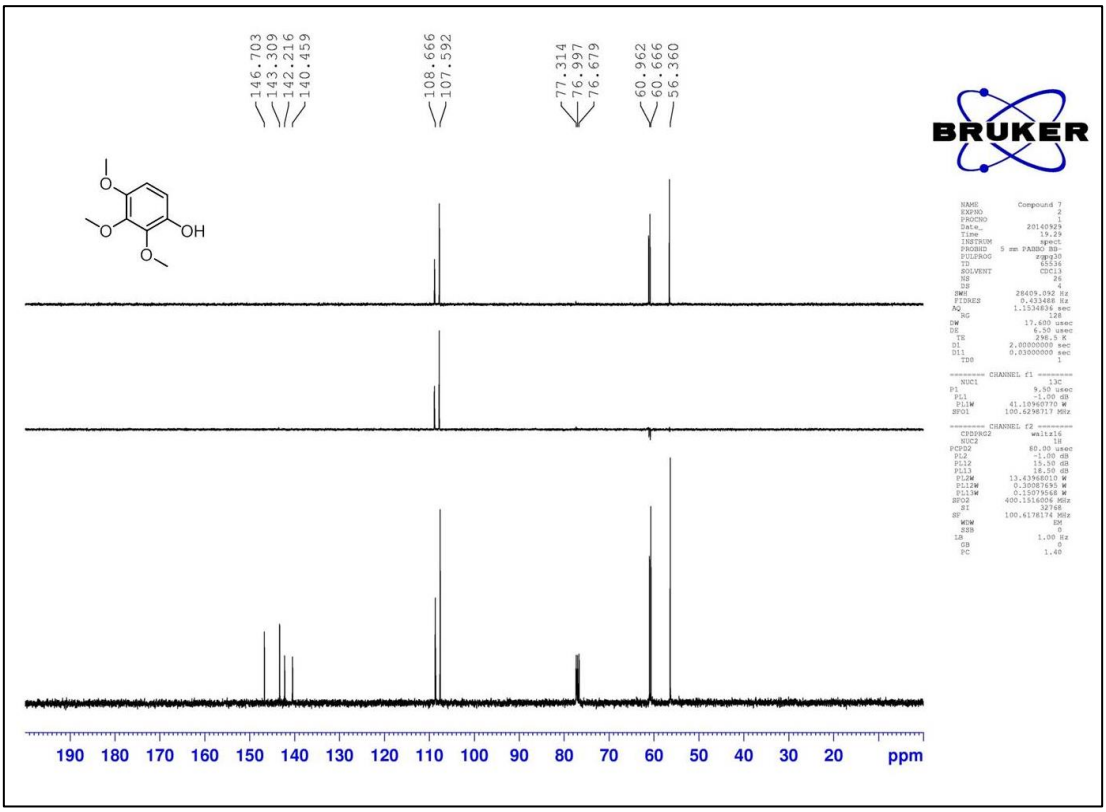

Figure S5. ^{13}C-DEPT NMR spectrum of compound **10** (100 MHz, $CDCl_3$)

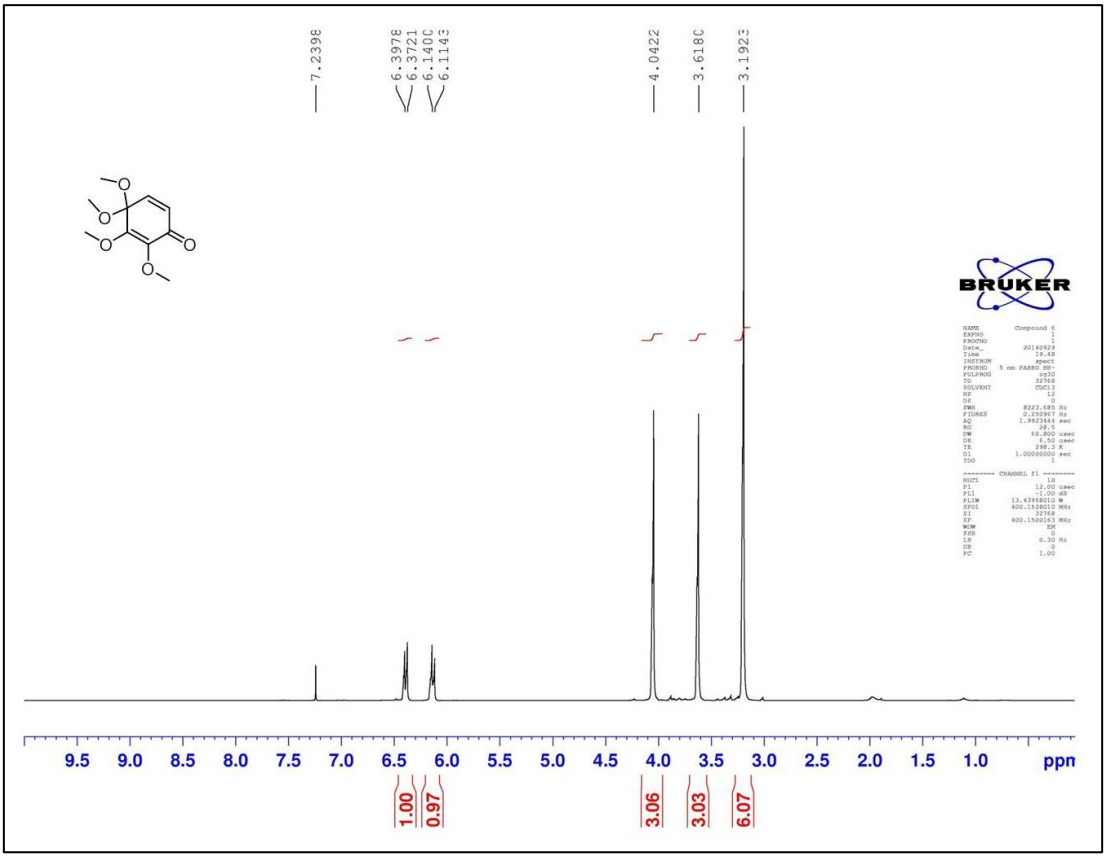

Figure S6. ^{1}H NMR spectrum of compound **9** (400 MHz, $CDCl_3$)

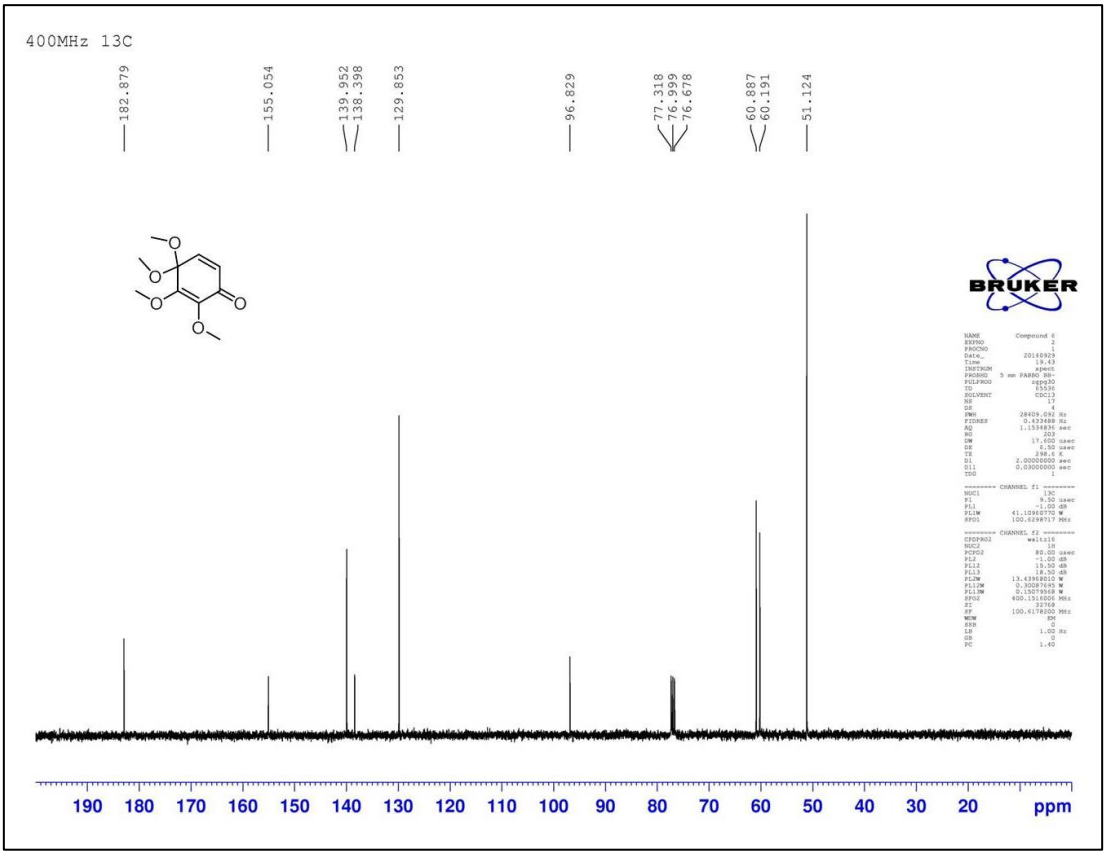

Figure S7. ^{13}C NMR spectrum of compound **9** (100 MHz, $CDCl_3$)

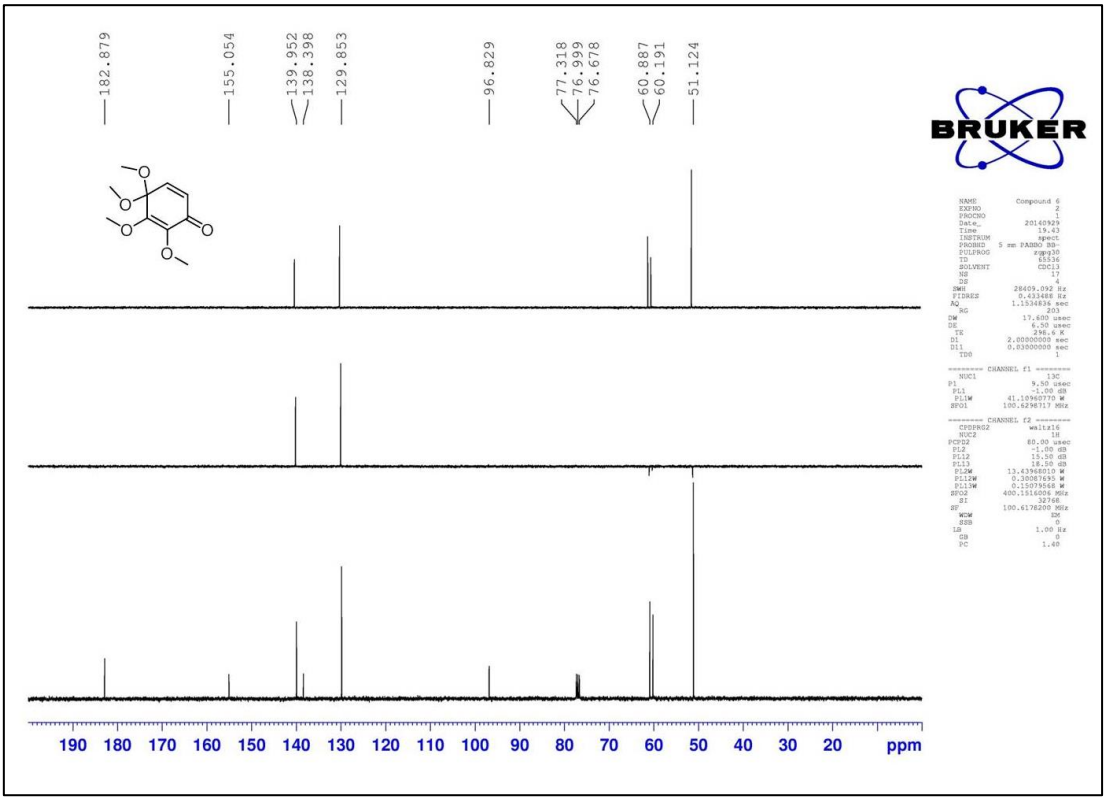

Figure S8. ^{13}C-DEPT NMR spectrum of compound **9** (100 MHz, $CDCl_3$)

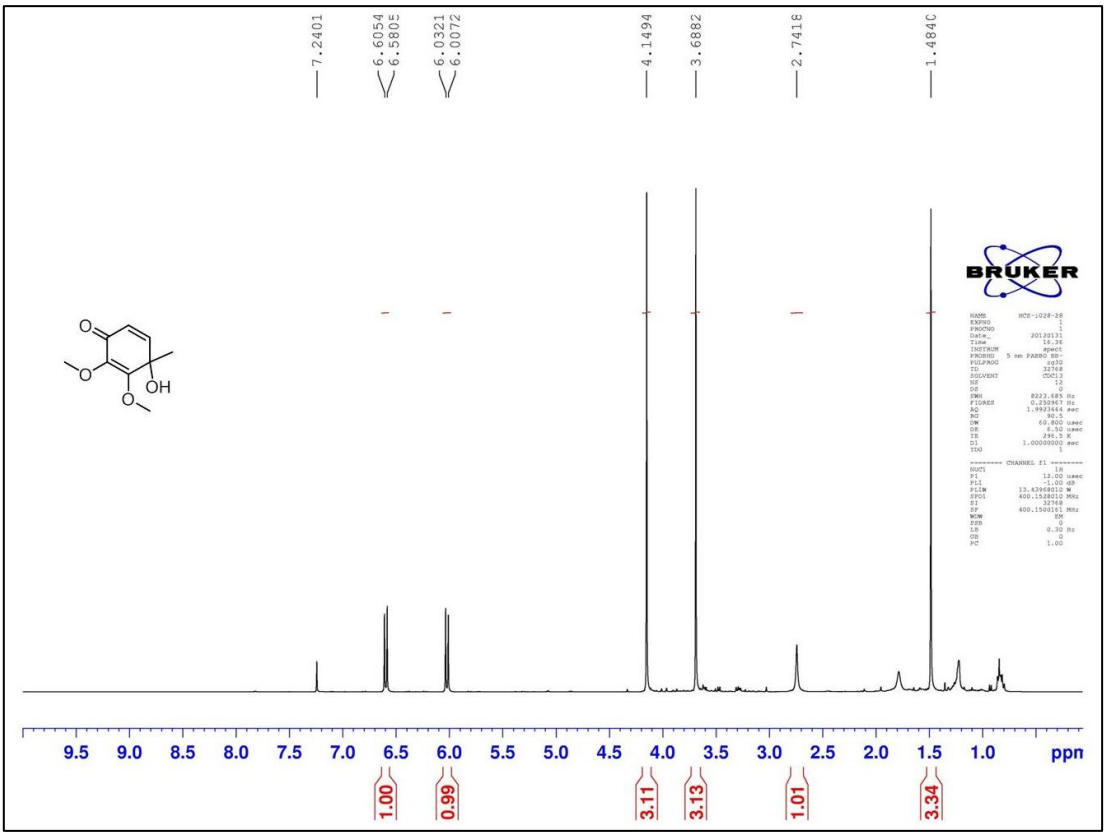

Figure S9. ^{1}H NMR spectrum of compound **11** (400 MHz, $CDCl_3$)

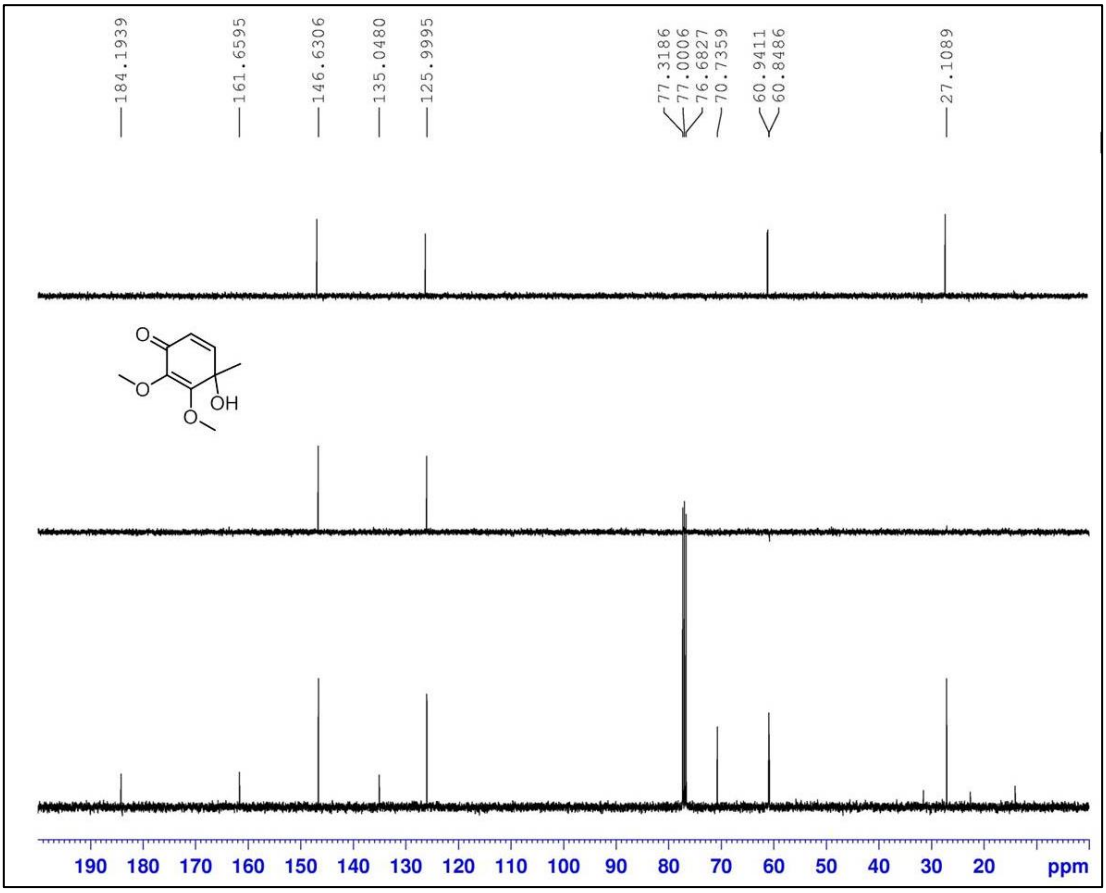

Figure S10. ^{13}C NMR spectrum of compound **11** (100 MHz, $CDCl_3$)

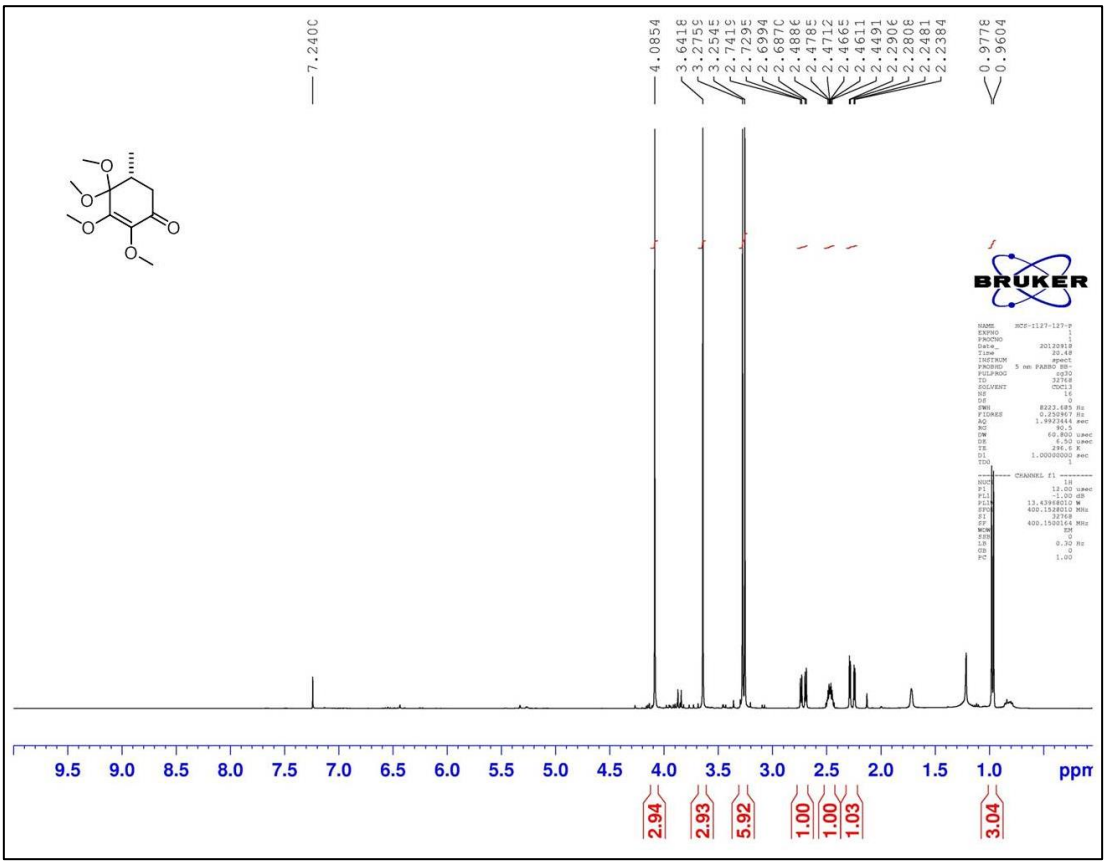

Figure S11. ^{1}H NMR spectrum of compound **12** (400 MHz, $CDCl_3$)

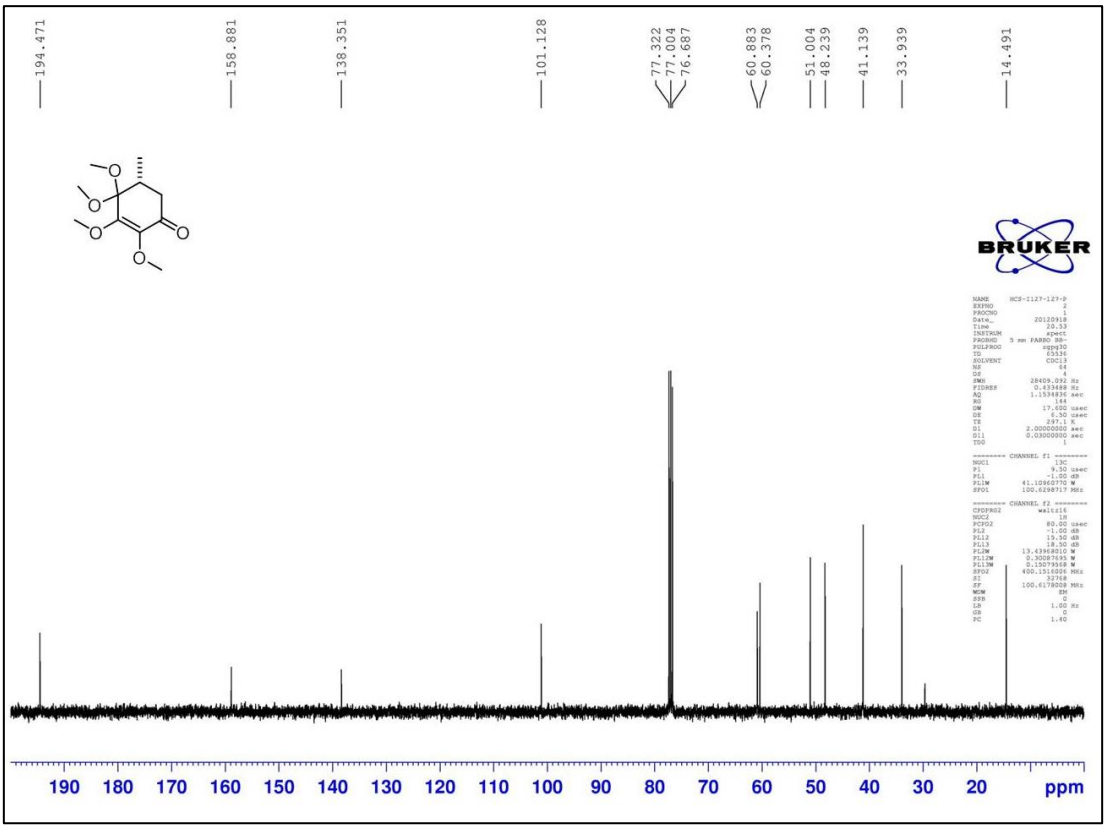

Figure S12. ^{13}C NMR spectrum of compound **12** (100 MHz, $CDCl_3$)

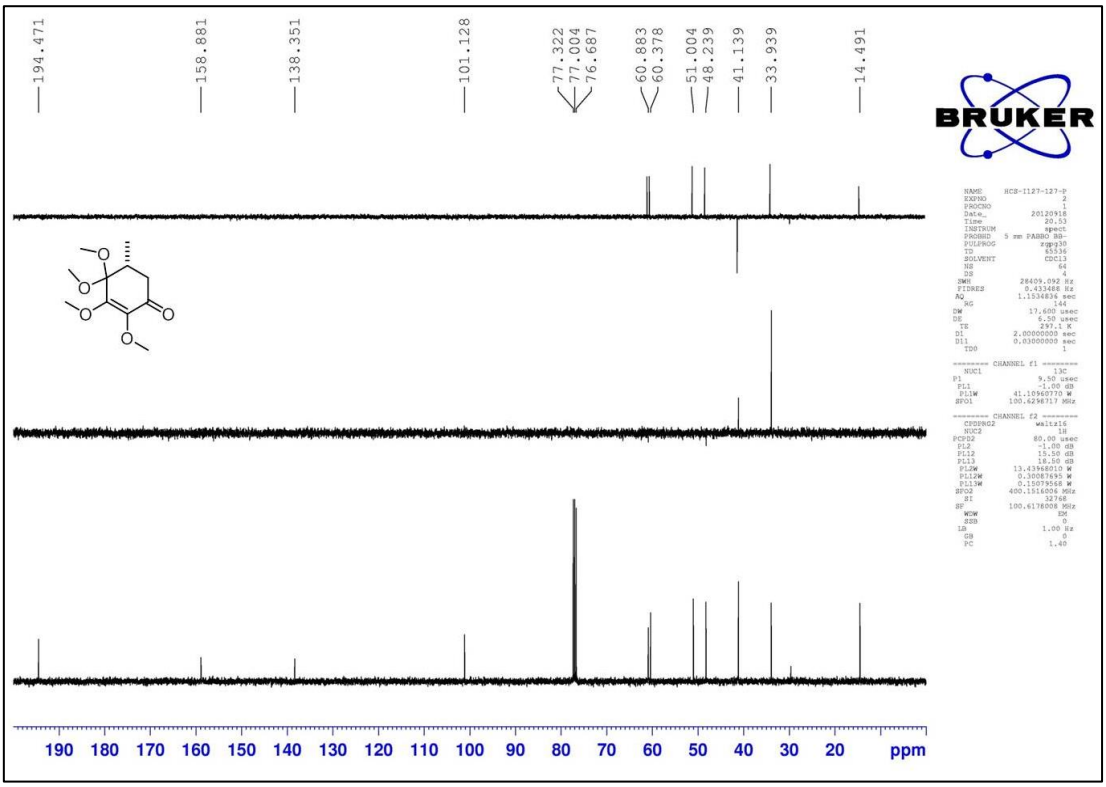

Figure S13. ^{13}C-DEPT NMR spectrum of compound **12** (100 MHz, $CDCl_3$)

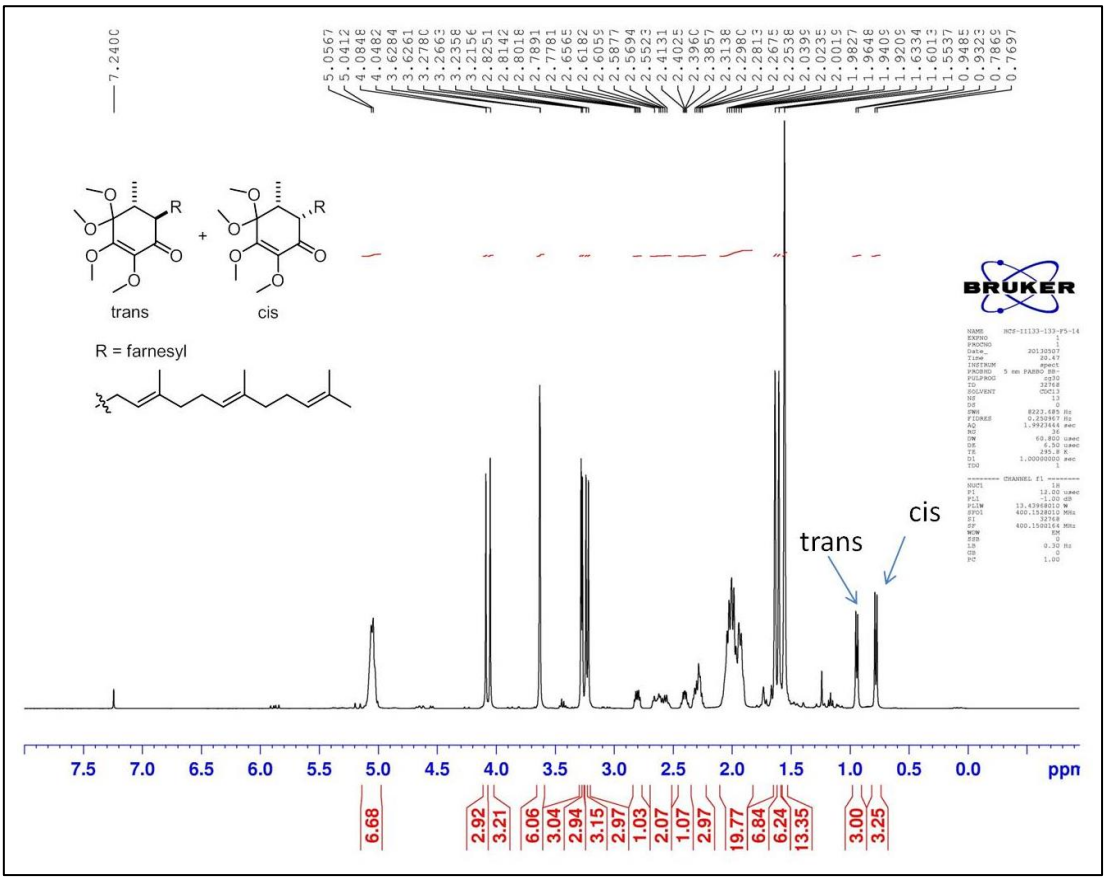

Figure S14. ^{1}H NMR spectrum of *trans*-**8** and *cis*-**8** (400 MHz, $CDCl_3$)

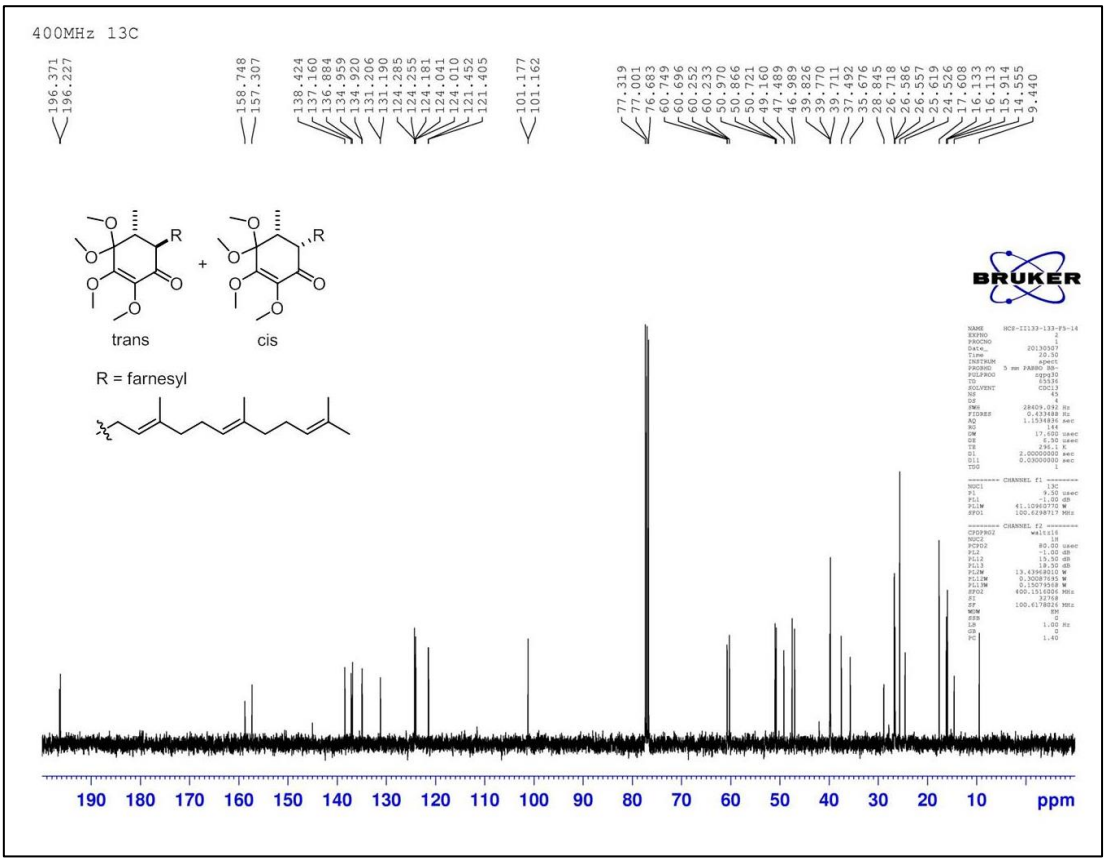

Figure S15. ^{13}C NMR spectrum of *trans*-**8** and *cis*-**8** (100 MHz, $CDCl_3$)

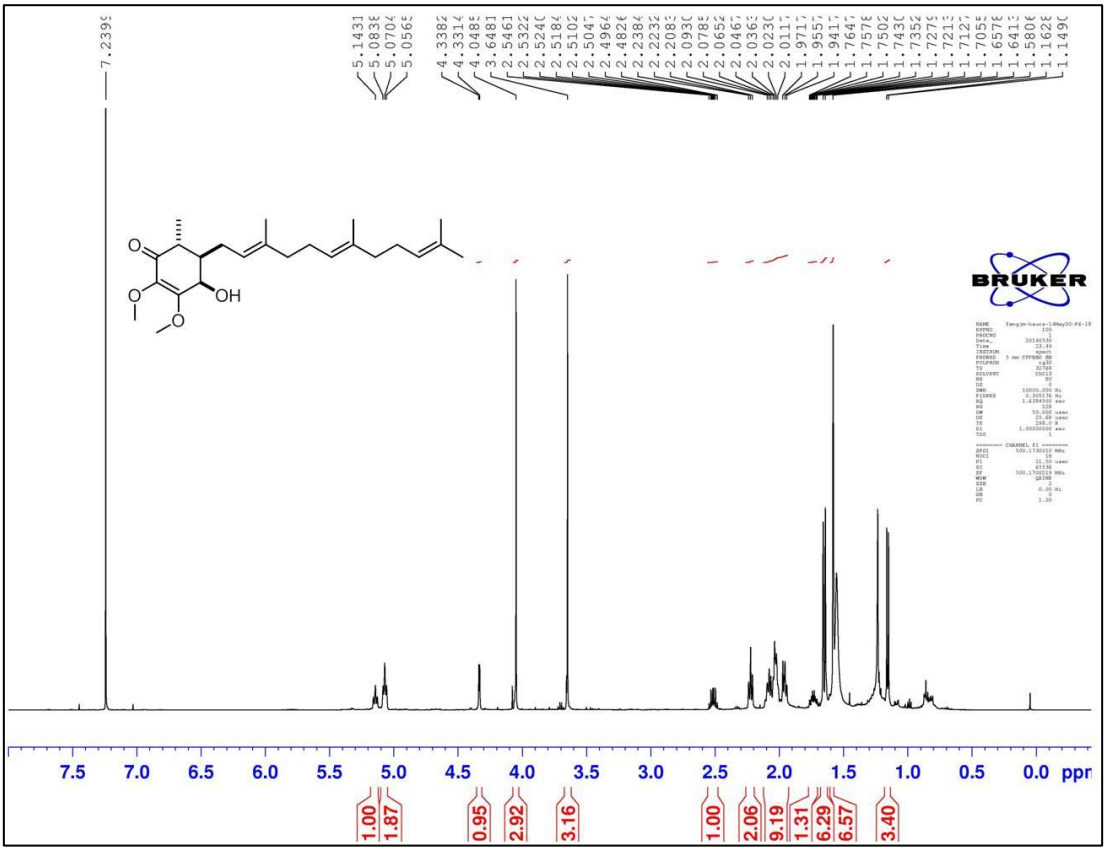

Figure S16. ^{1}H NMR spectrum of compound **1a** (500 MHz, $CDCl_3$)

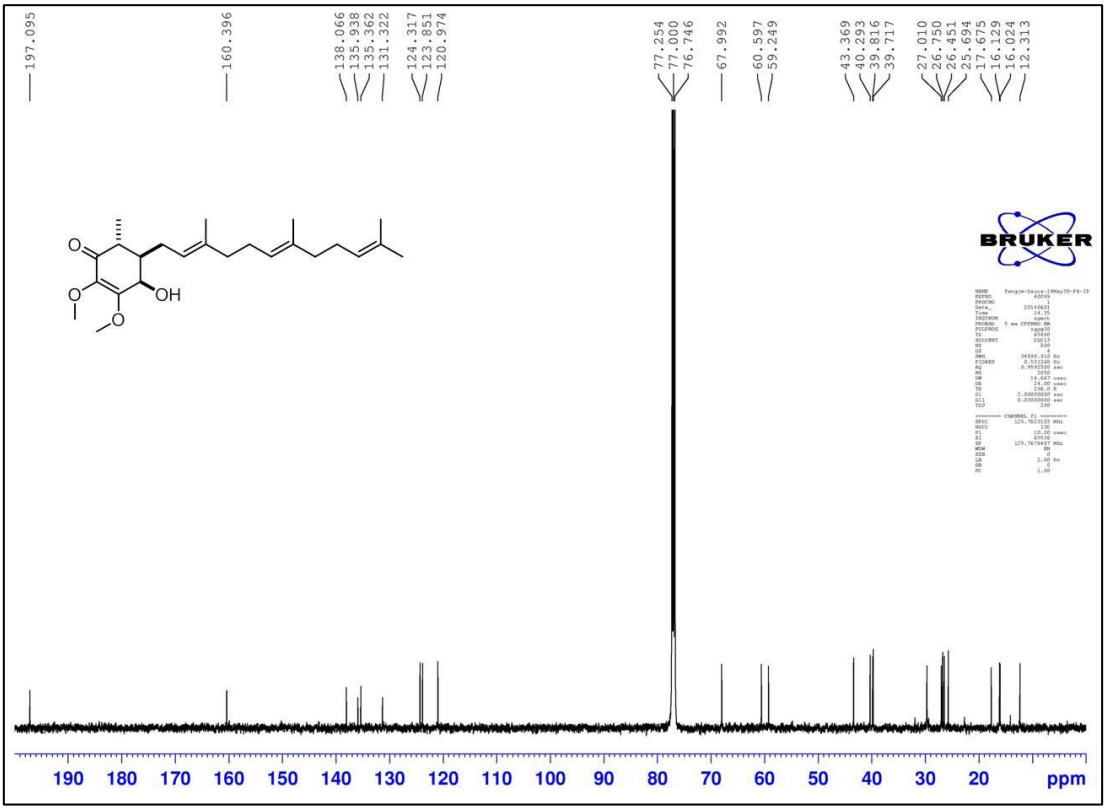

Figure S17. ^{13}C NMR spectrum of compound **1a** (125 MHz, $CDCl_3$)

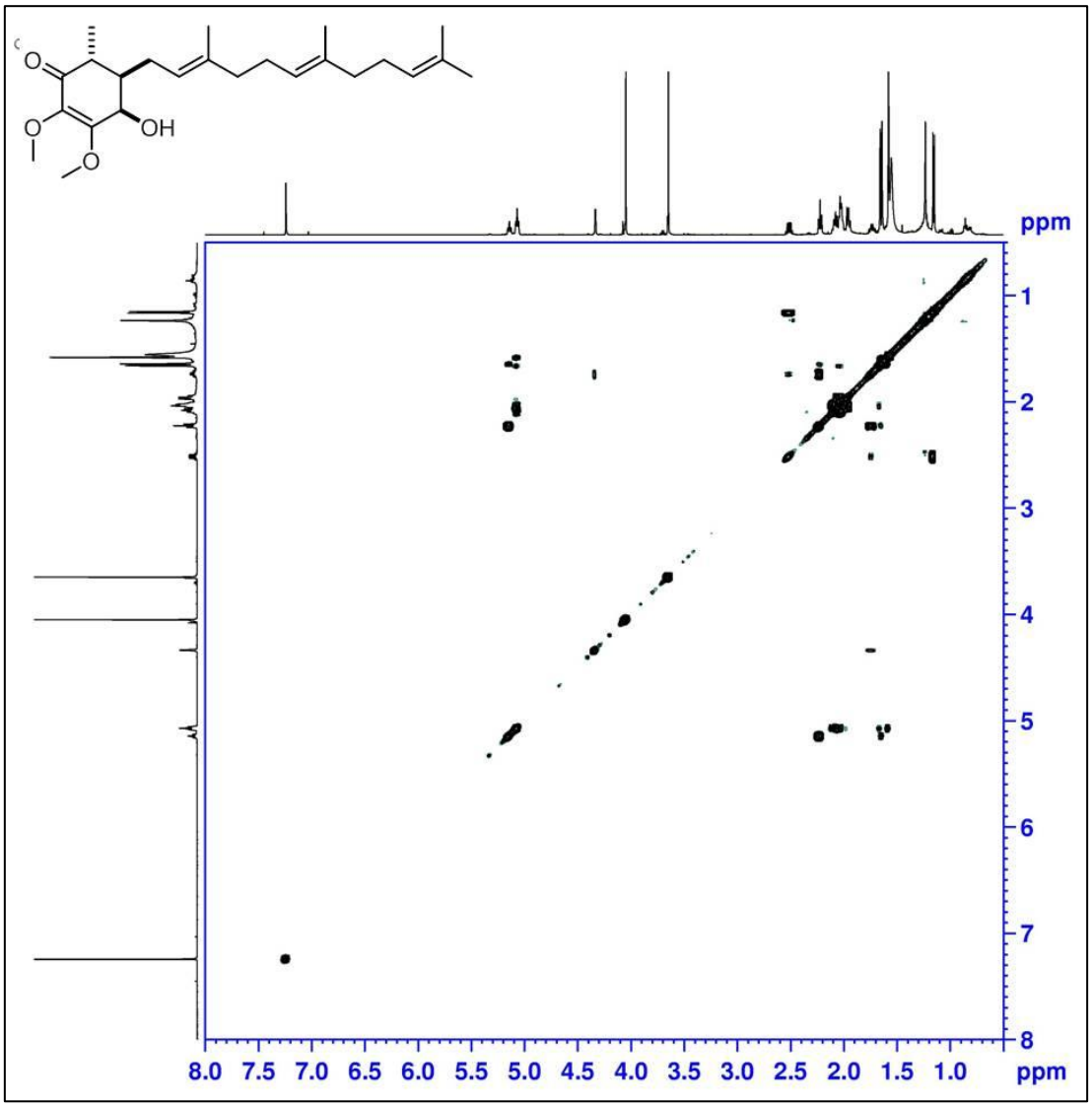

Figure S18. ^{1}H–^{1}H COSY NMR spectrum of compound **1a** (500 MHz, $CDCl_3$)

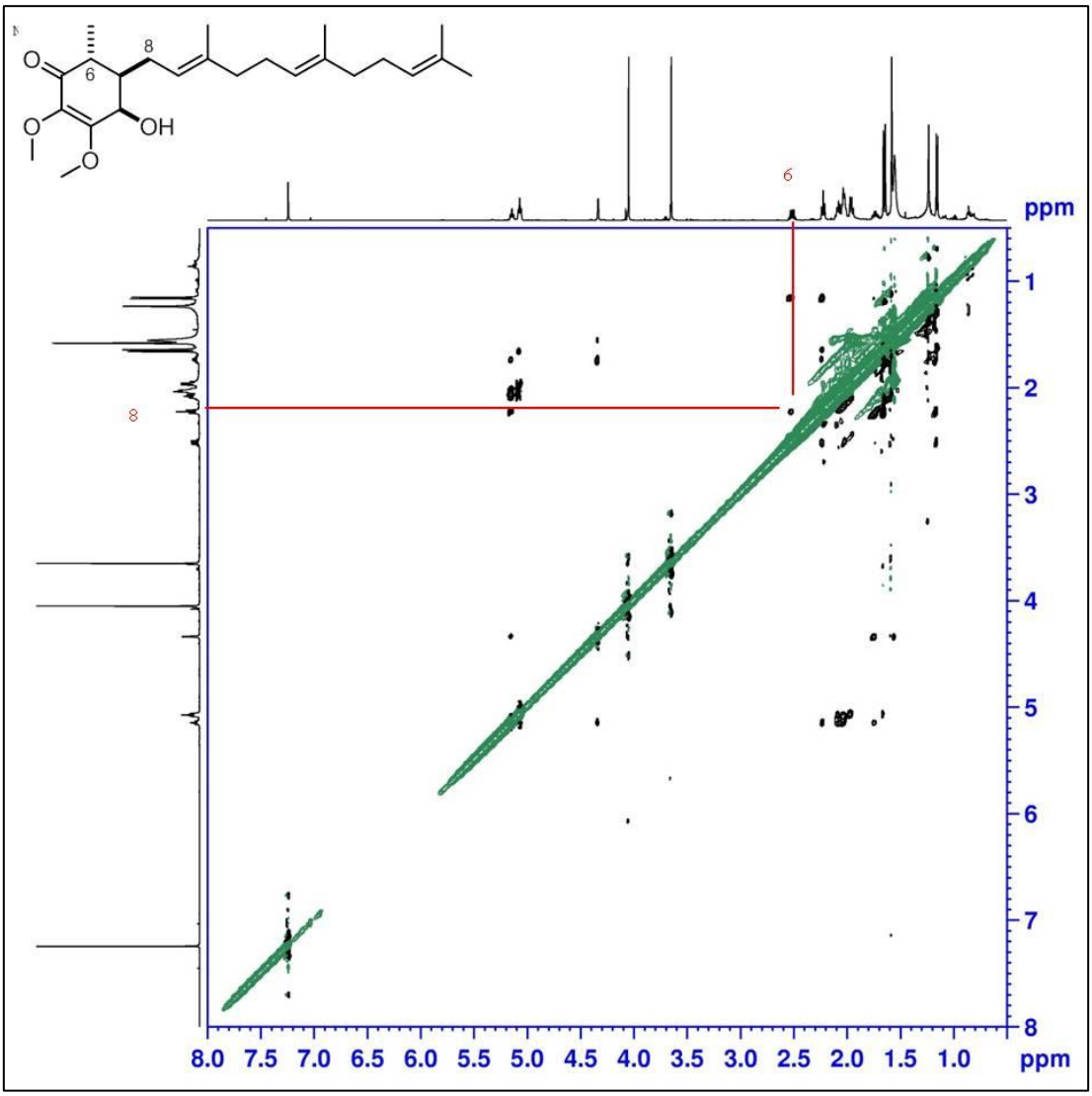

Figure S19. ^{1}H-^{1}H NOESY spectrum of compound **1a** (500 MHz, $CDCl_3$).

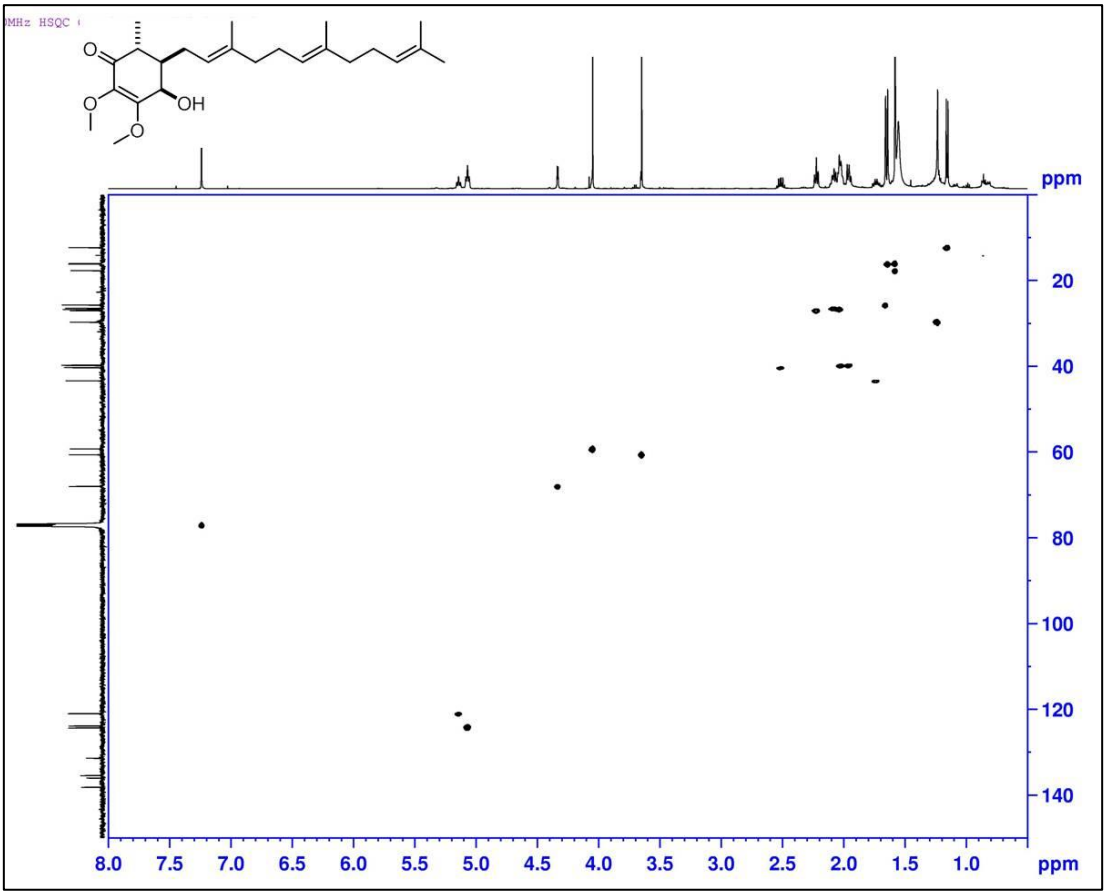

Figure S20. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **1a** (125 MHz, $CDCl_3$)

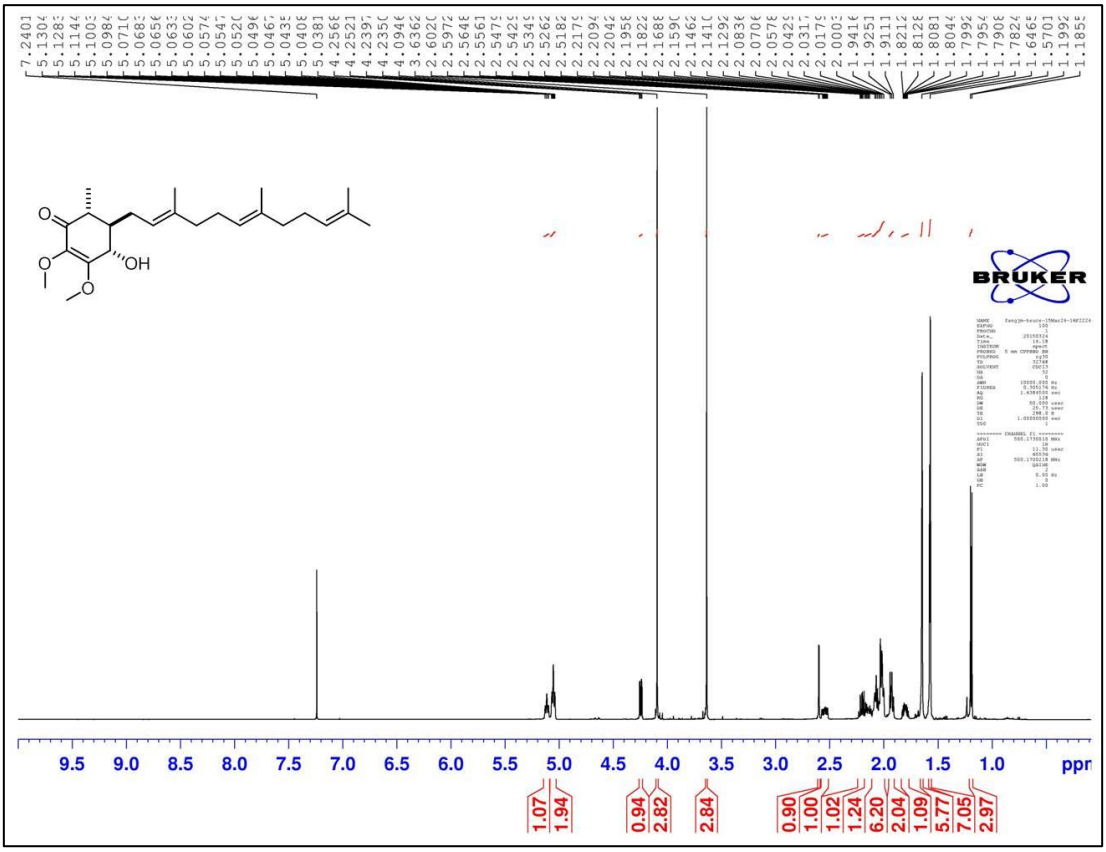

Figure S21. ^{1}H NMR spectrum of compound **1b** (500 MHz, $CDCl_3$)

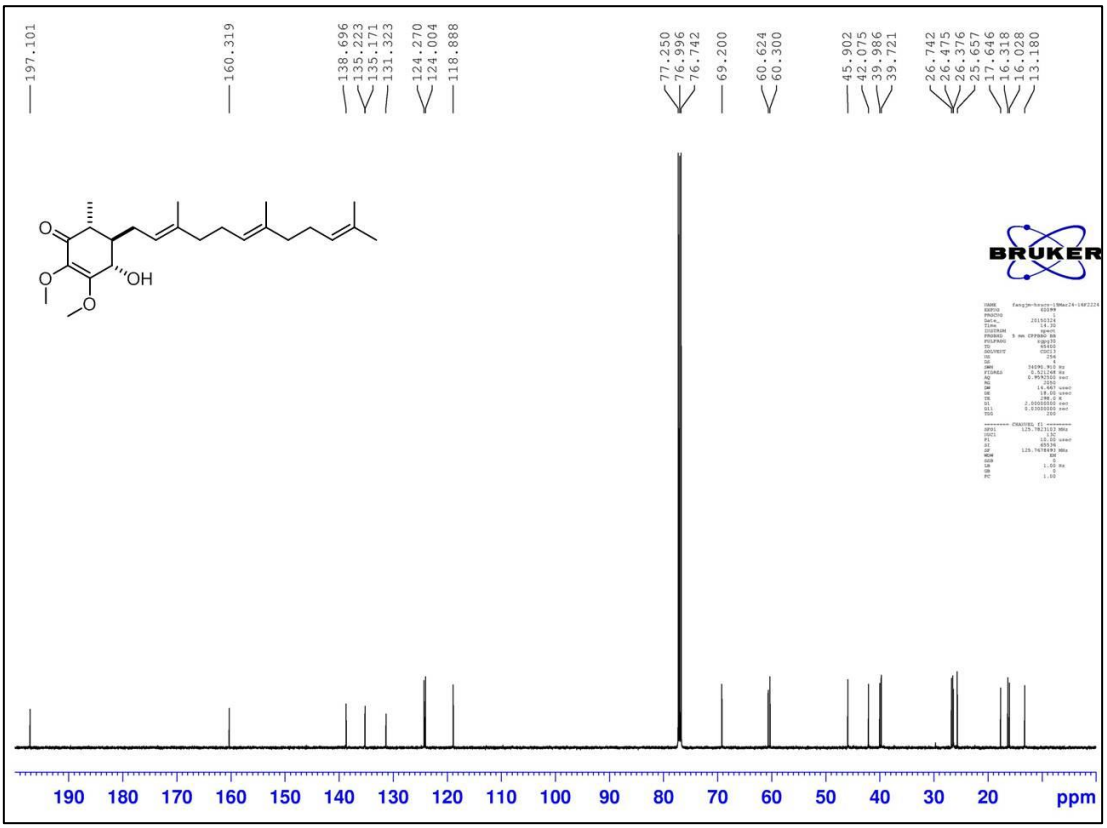

Figure S22. ^{13}C NMR spectrum of compound **1b** (125 MHz, $CDCl_3$)

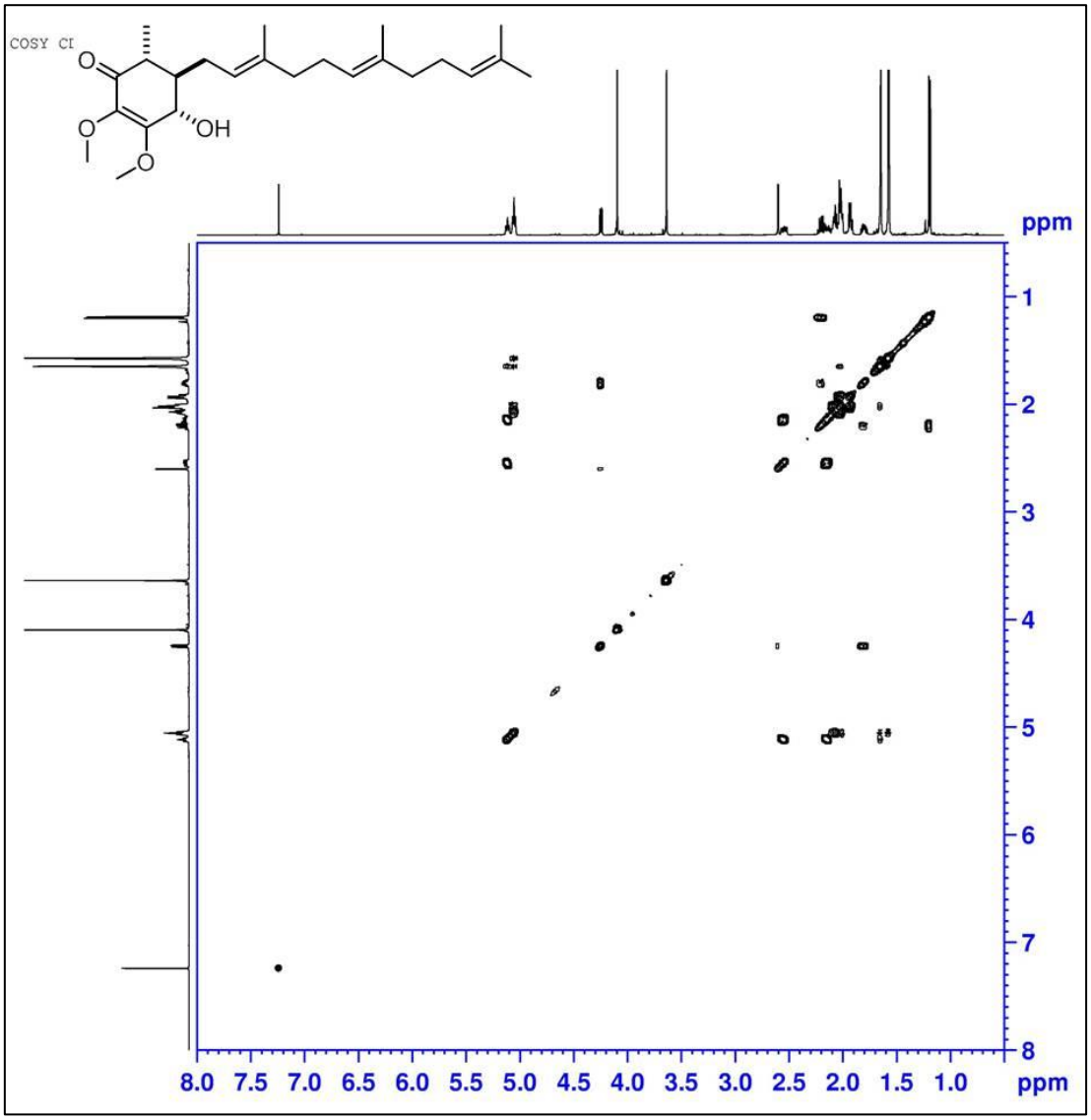

Figure S23. ^{1}H–^{1}H COSY NMR spectrum of compound **1b** (500 MHz, $CDCl_3$)

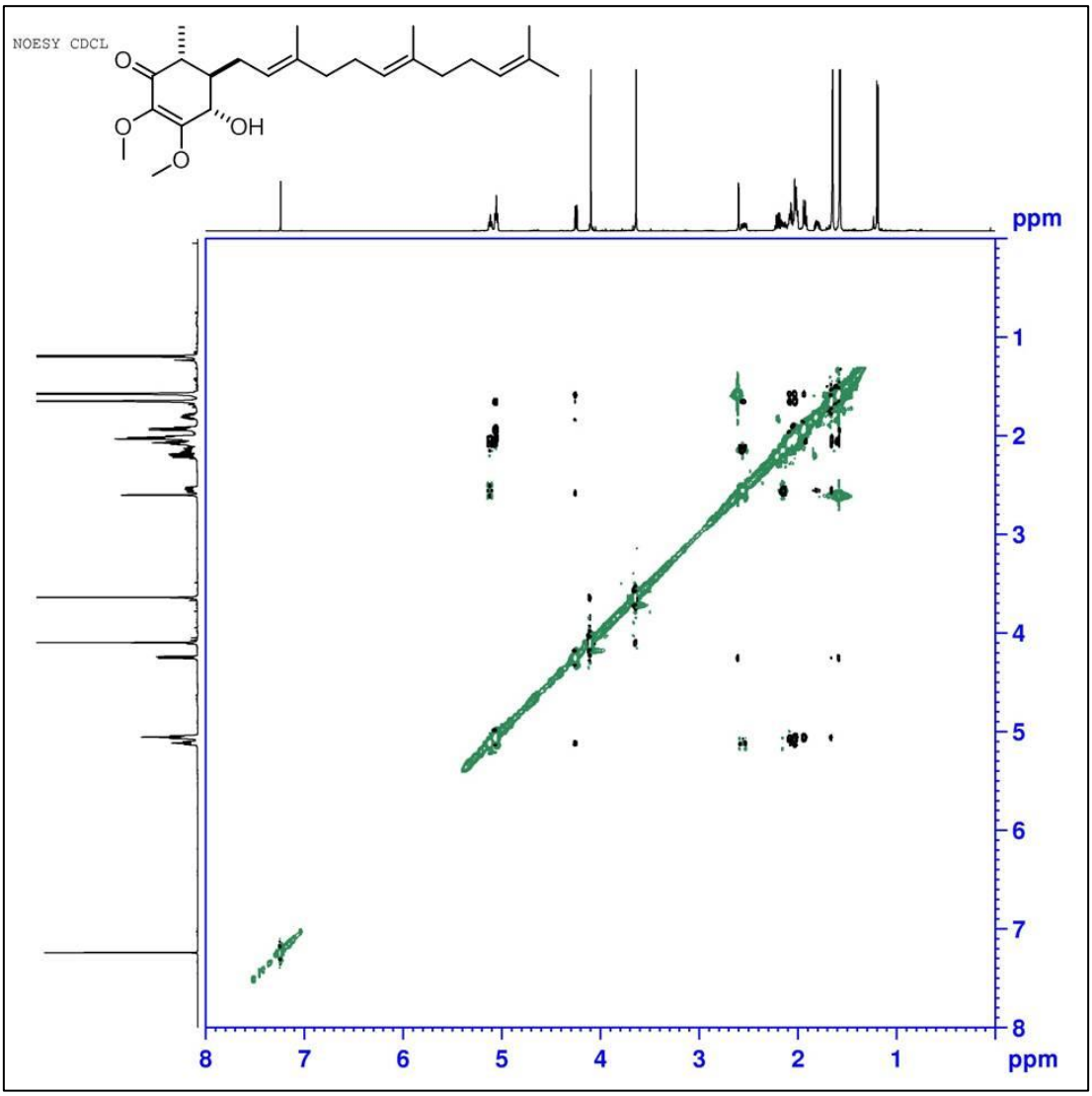

Figure S24. ^{1}H-^{1}H NOESY spectrum of compound **1b** (500 MHz, $CDCl_3$).

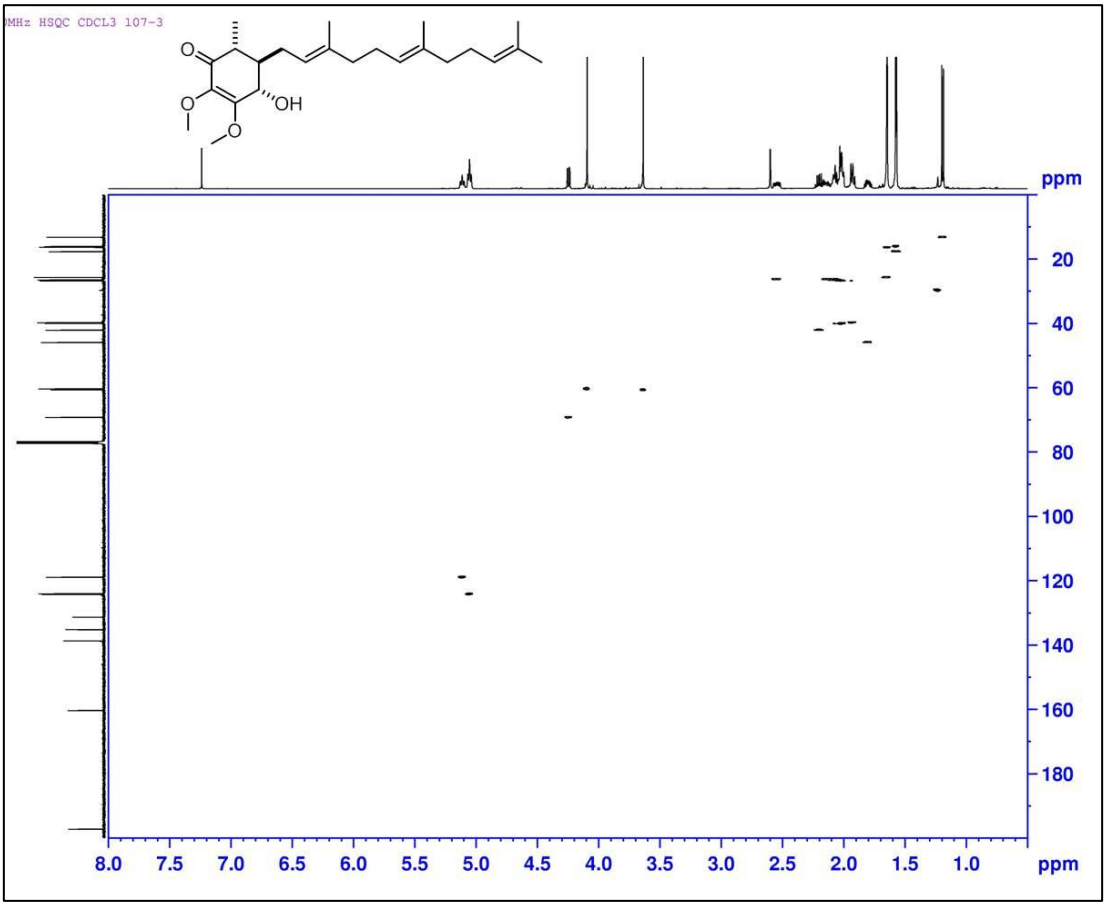

Figure S25. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **1b** (125 MHz, $CDCl_3$)

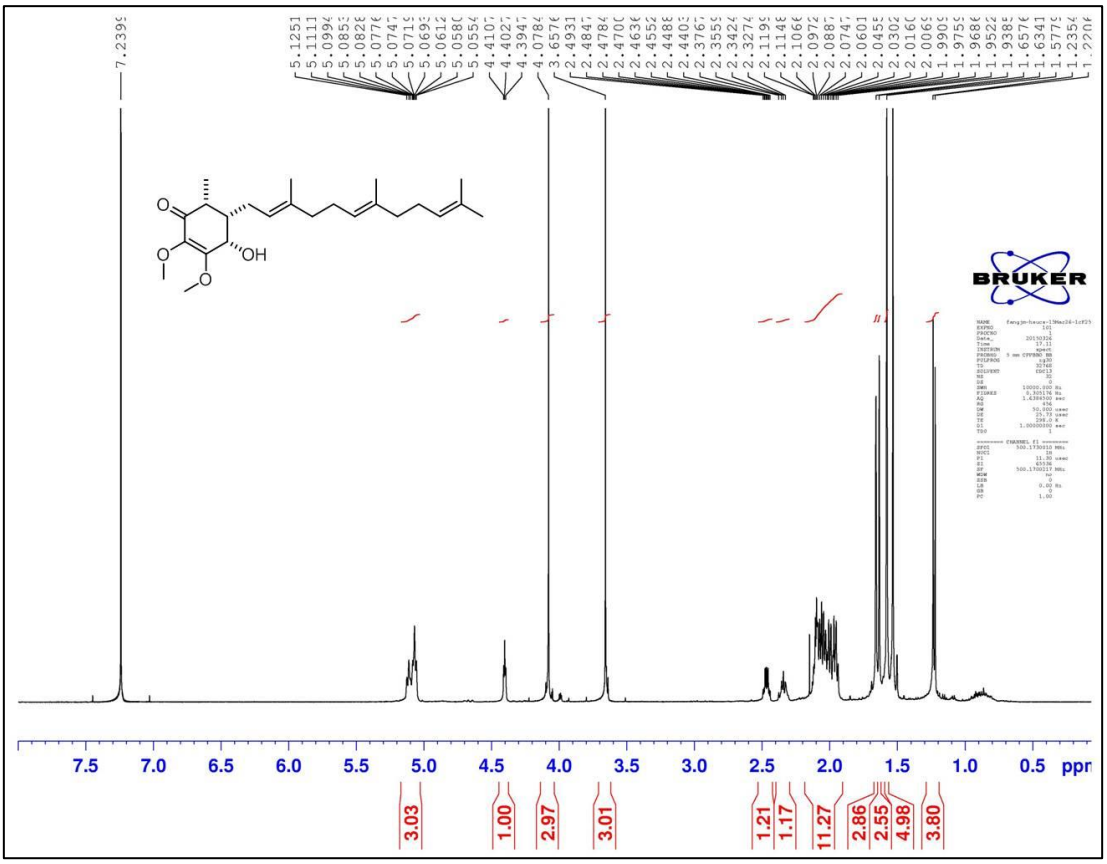

Figure S26. ^{1}H NMR spectrum of compound **1c** (500 MHz, $CDCl_3$)

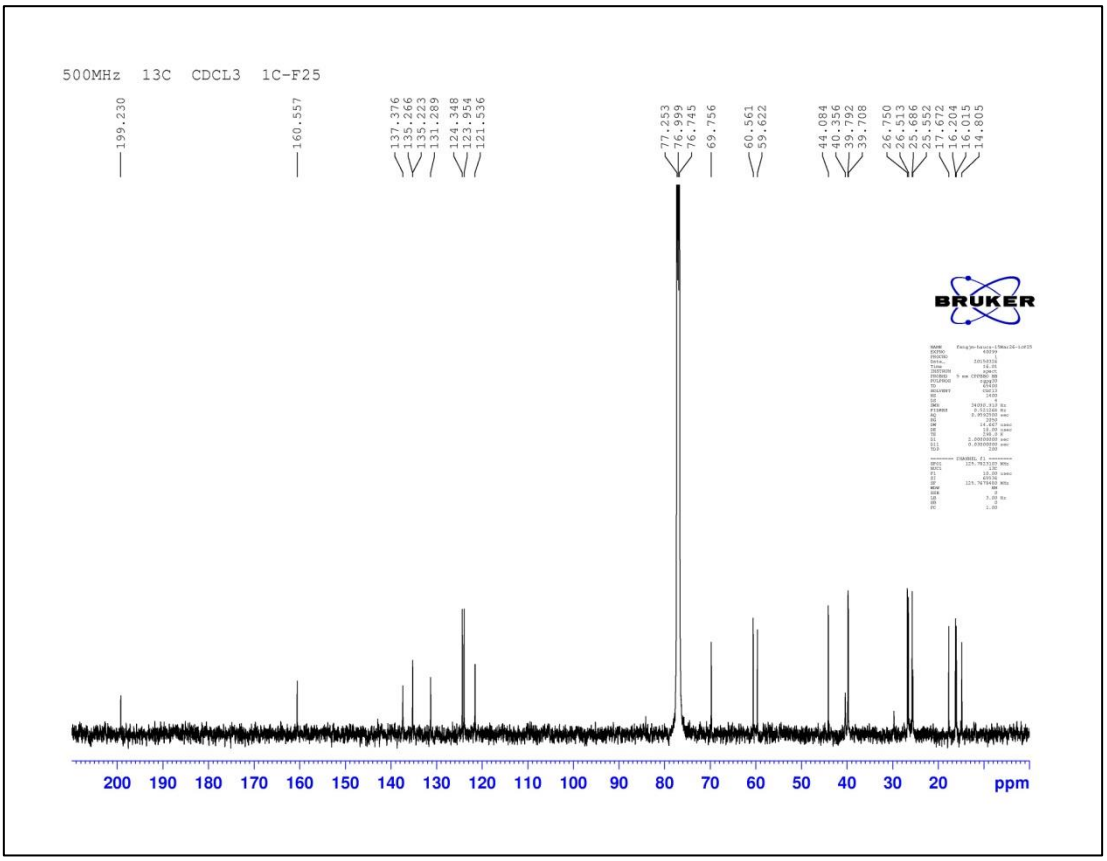

Figure S27. ^{13}C NMR spectrum of compound **1c** (125 MHz, $CDCl_3$)

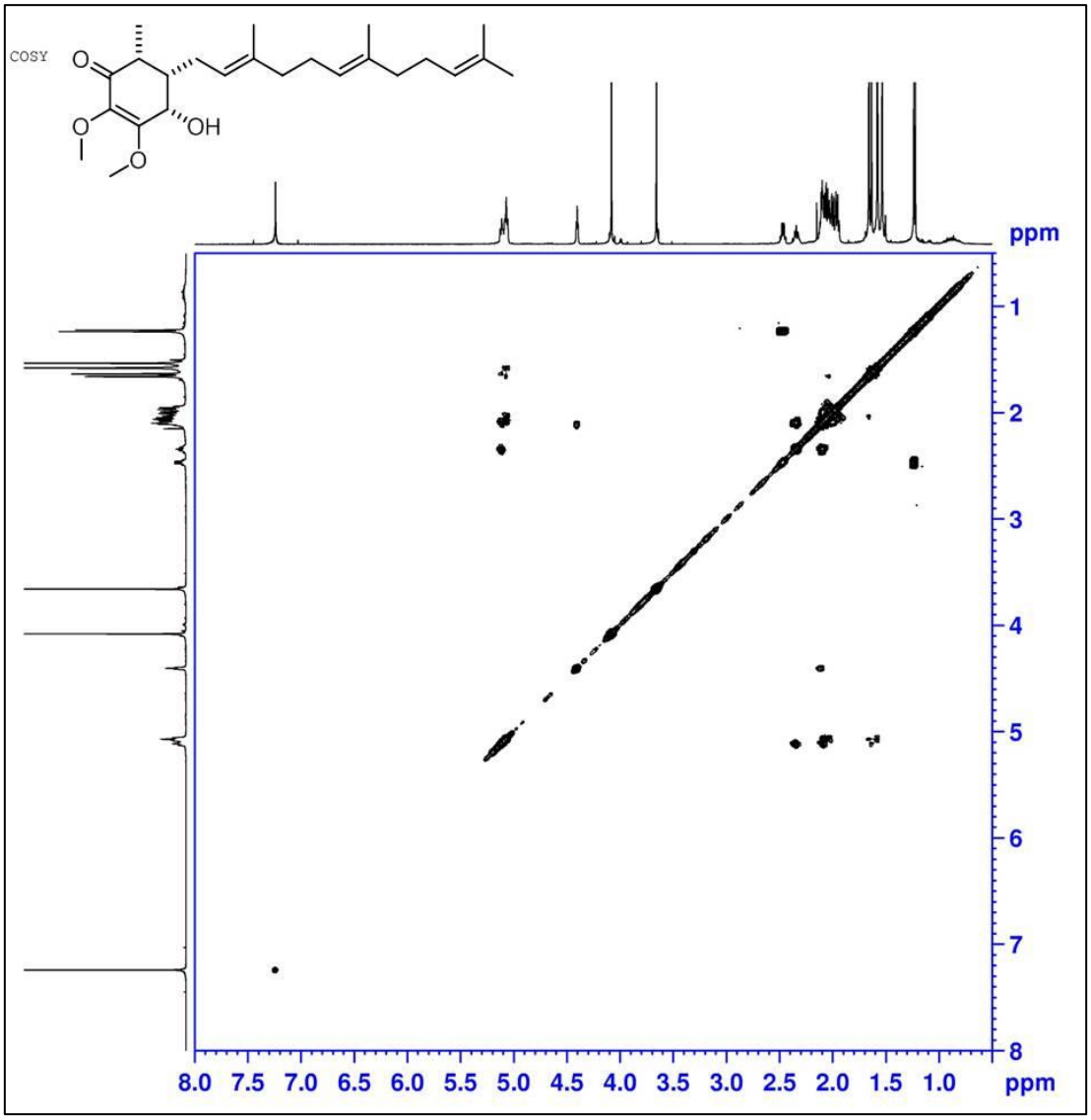

Figure S28. ^{1}H–^{1}H COSY NMR spectrum of compound **1c** (500 MHz, $CDCl_3$)

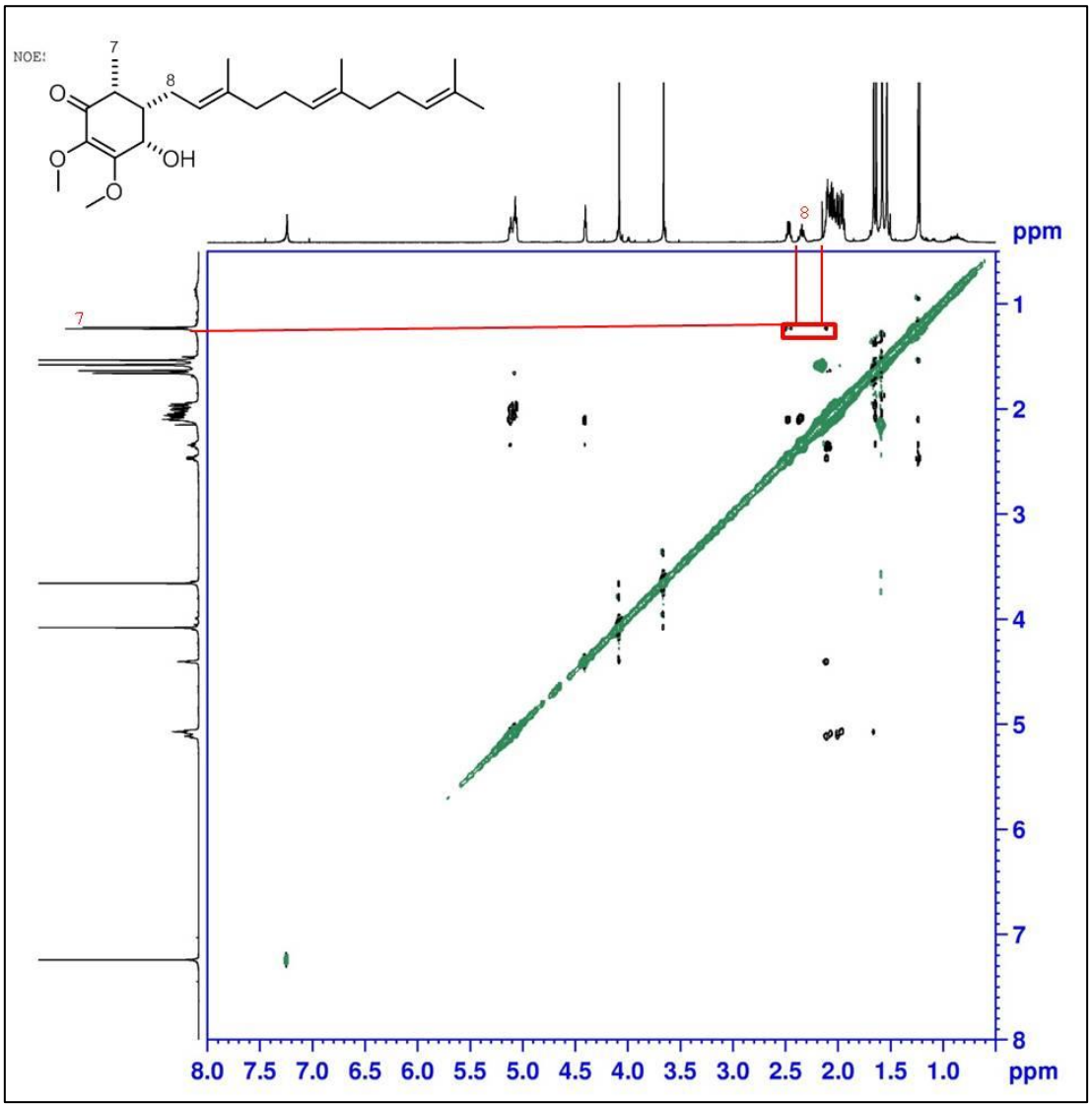

Figure S29. ^{1}H-^{1}H NOESY spectrum of compound **1c** (500 MHz, $CDCl_3$).

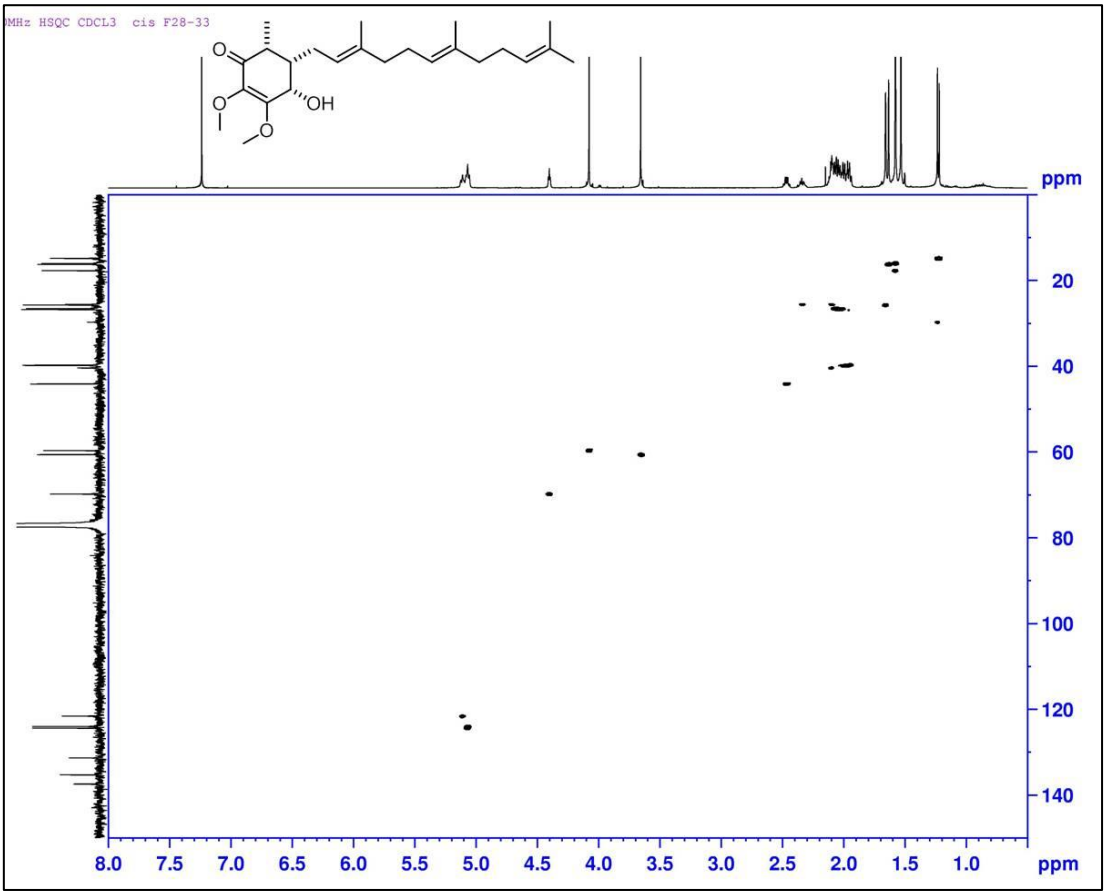

Figure S30. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **1c** (125 MHz, $CDCl_3$)

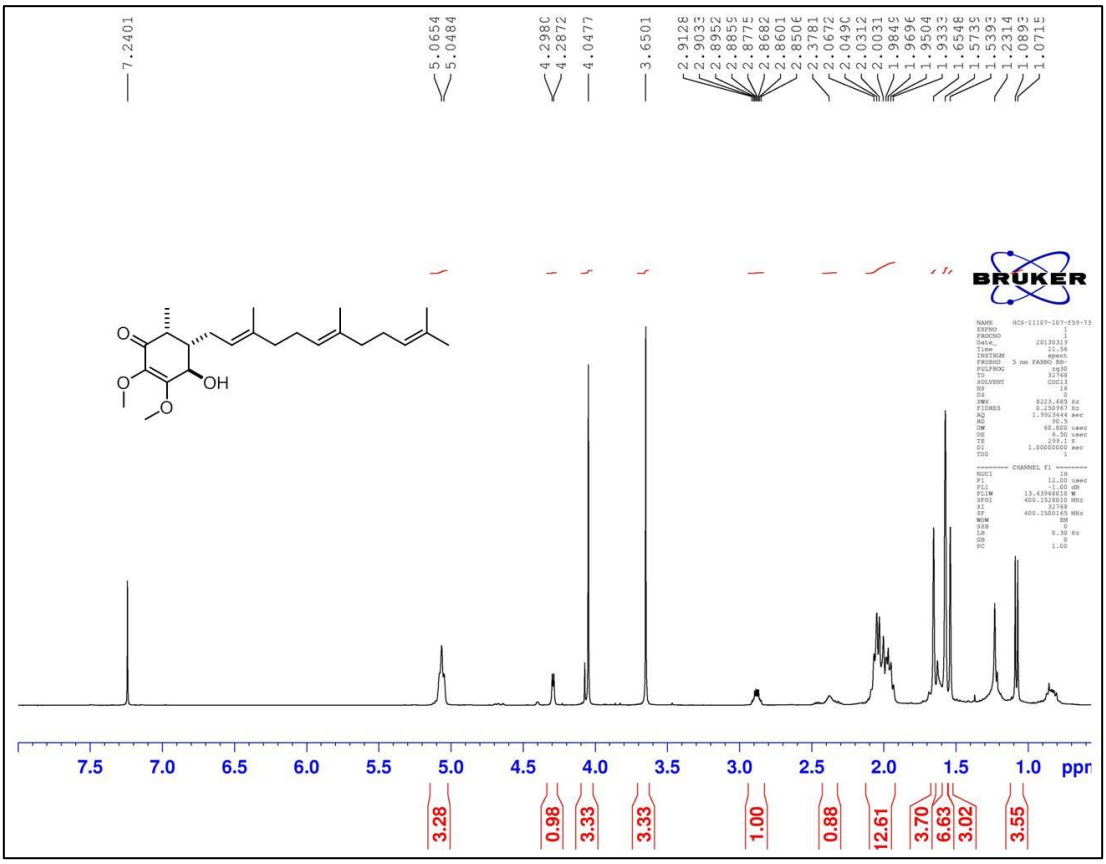

Figure S31. ^{1}H NMR spectrum of compound **1d** (400 MHz, $CDCl_3$)

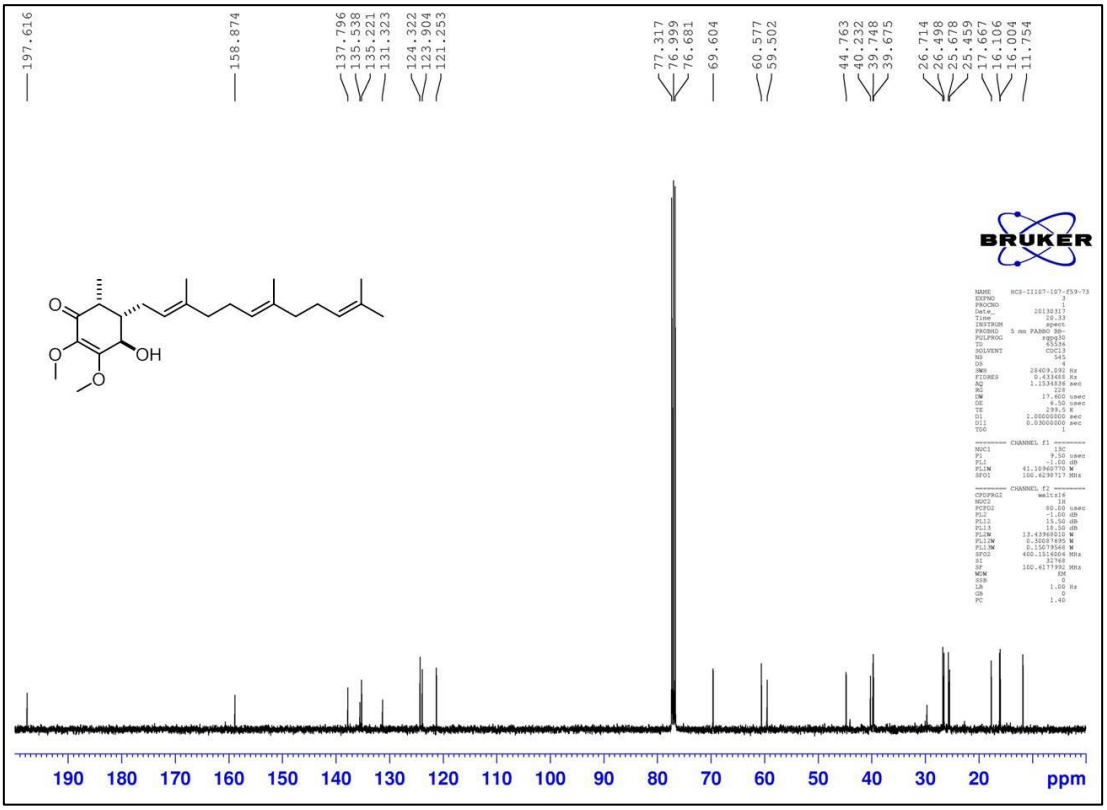

Figure S32. ^{13}C NMR spectrum of compound **1d** (100 MHz, $CDCl_3$)

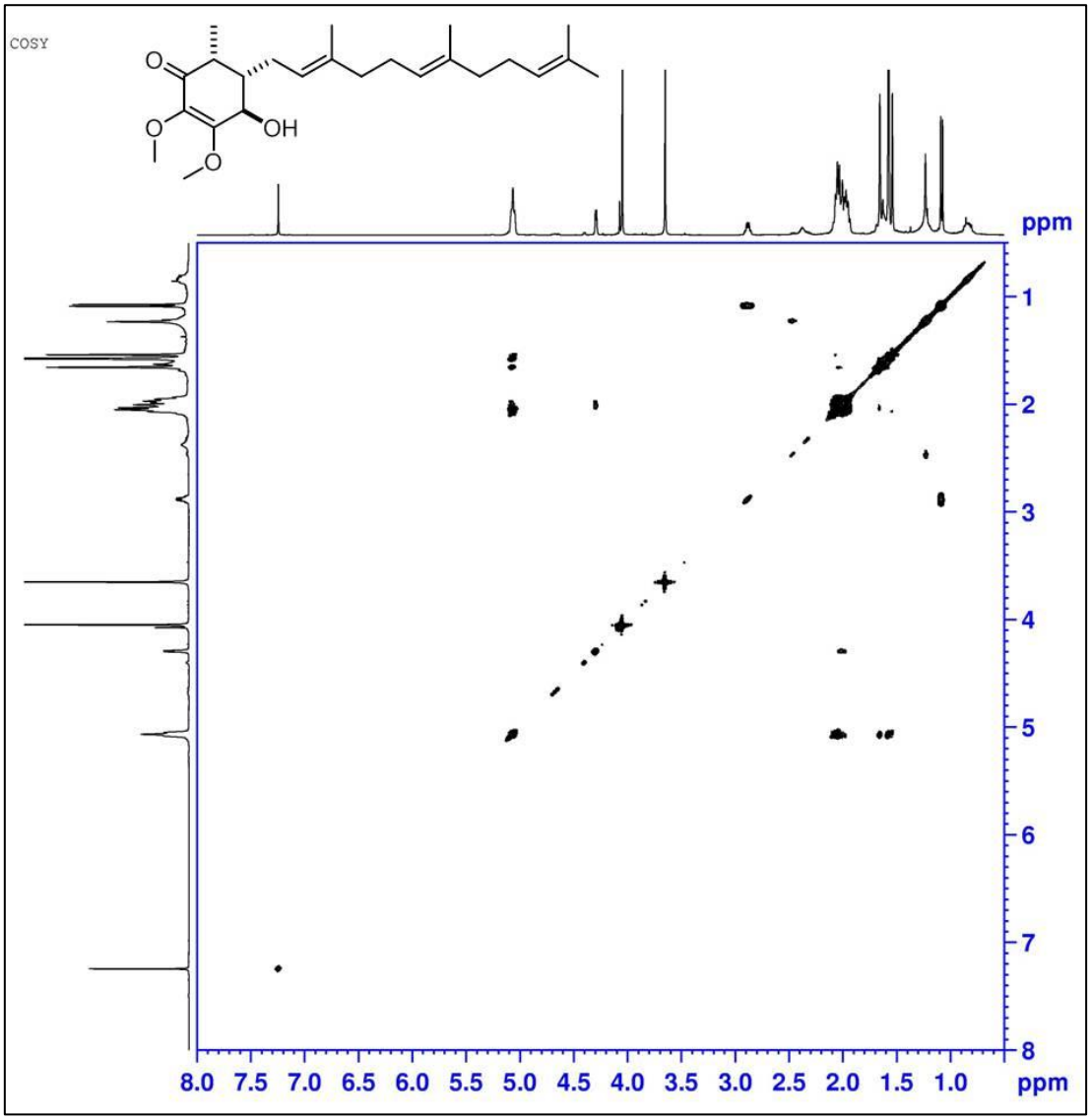

Figure S33. ^{1}H–^{1}H COSY NMR spectrum of compound **1d** (400 MHz, $CDCl_3$)

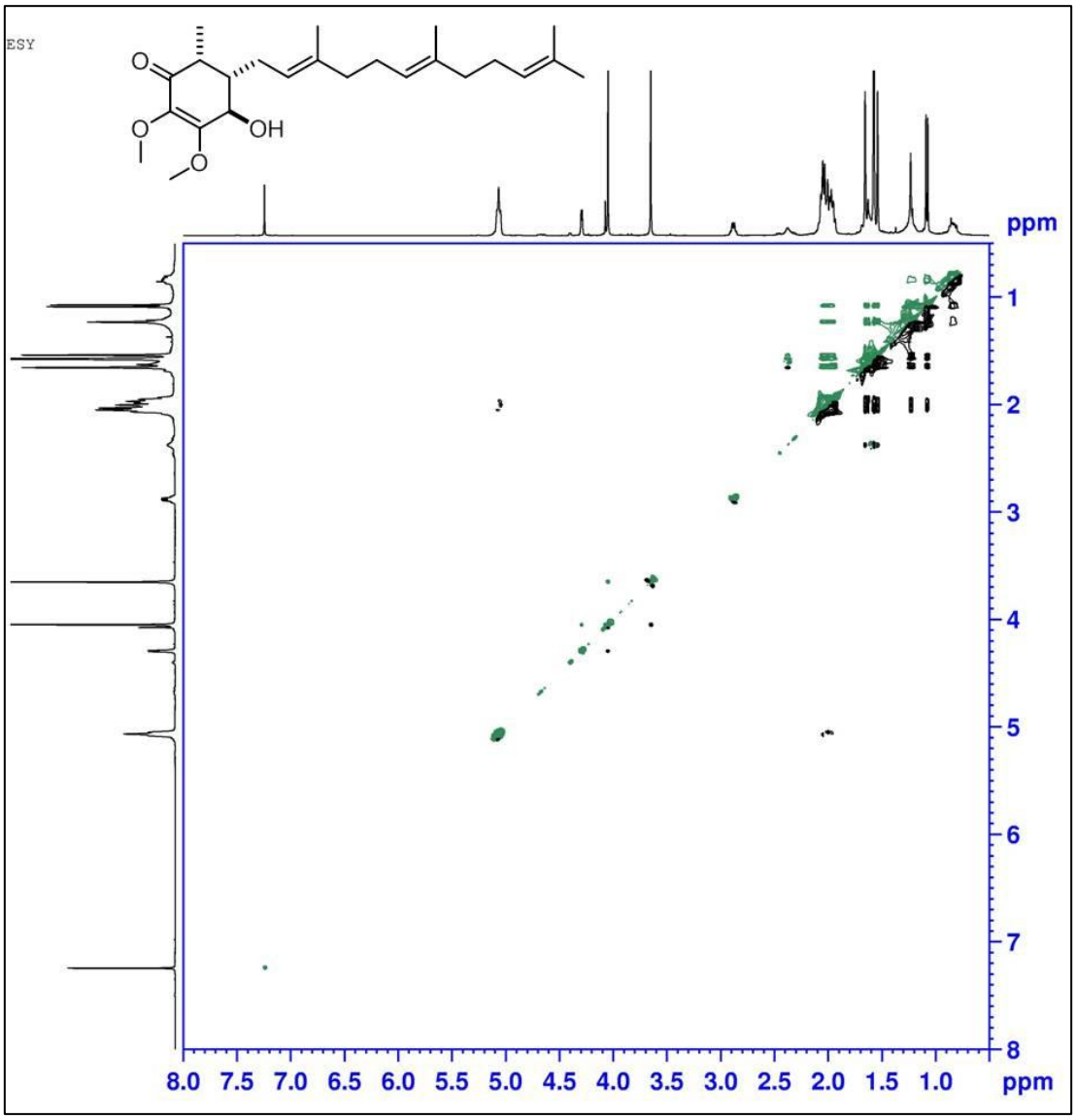

Figure S34. ^{1}H-^{1}H NOESY spectrum of compound **1d** (400 MHz, $CDCl_3$).

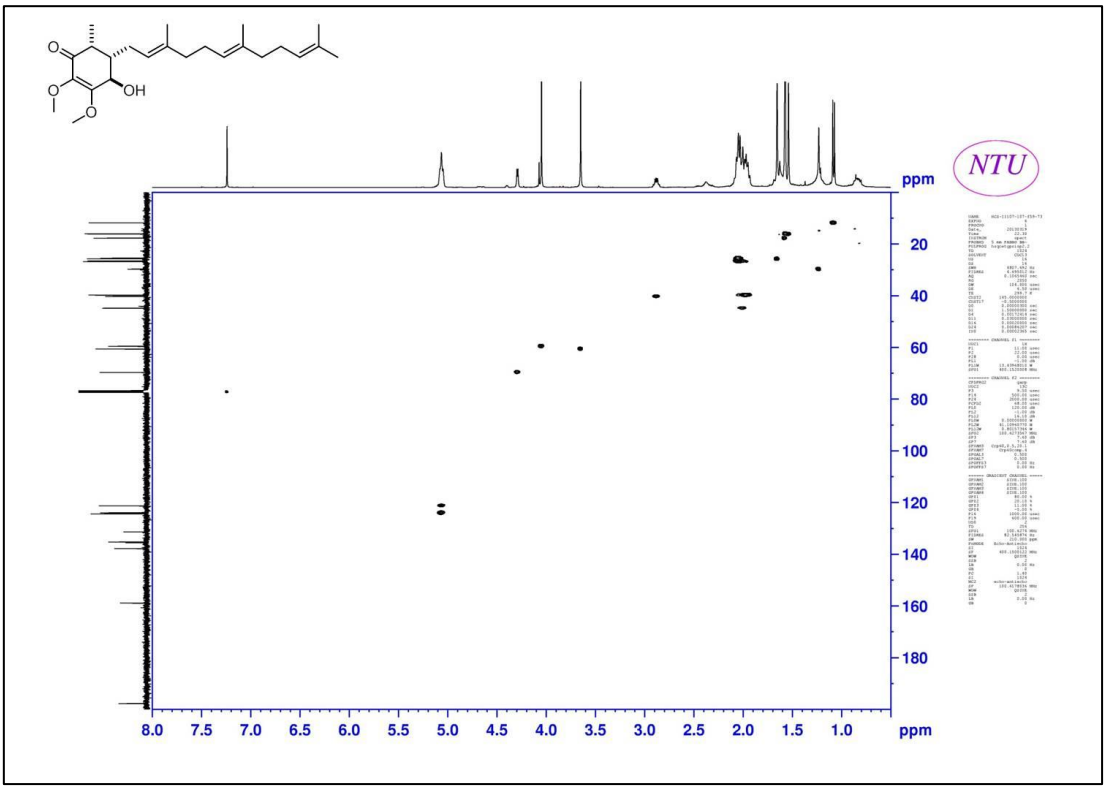

Figure S35. ^{1}H–^{13}C HSQC NMR spectrum of compound **1d** (100 MHz, $CDCl_3$)

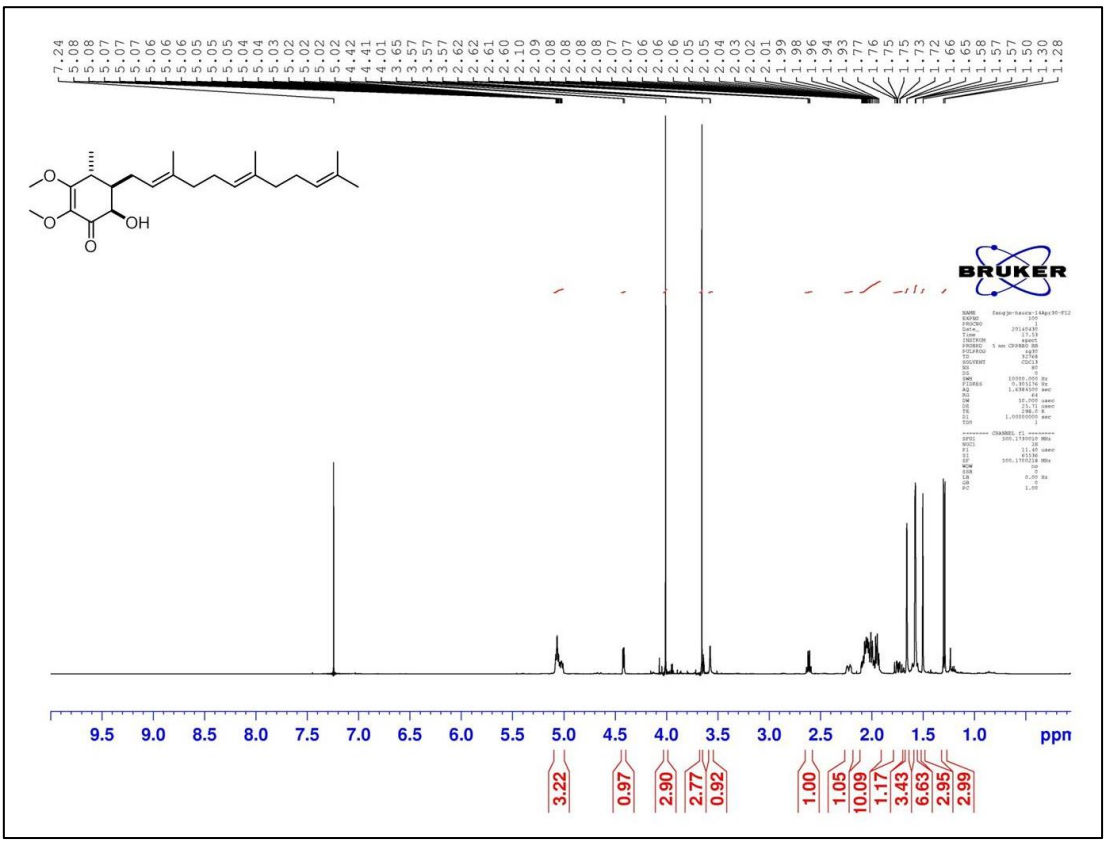

Figure S36. ^{1}H NMR spectrum of compound **13a** (500 MHz, $CDCl_3$)

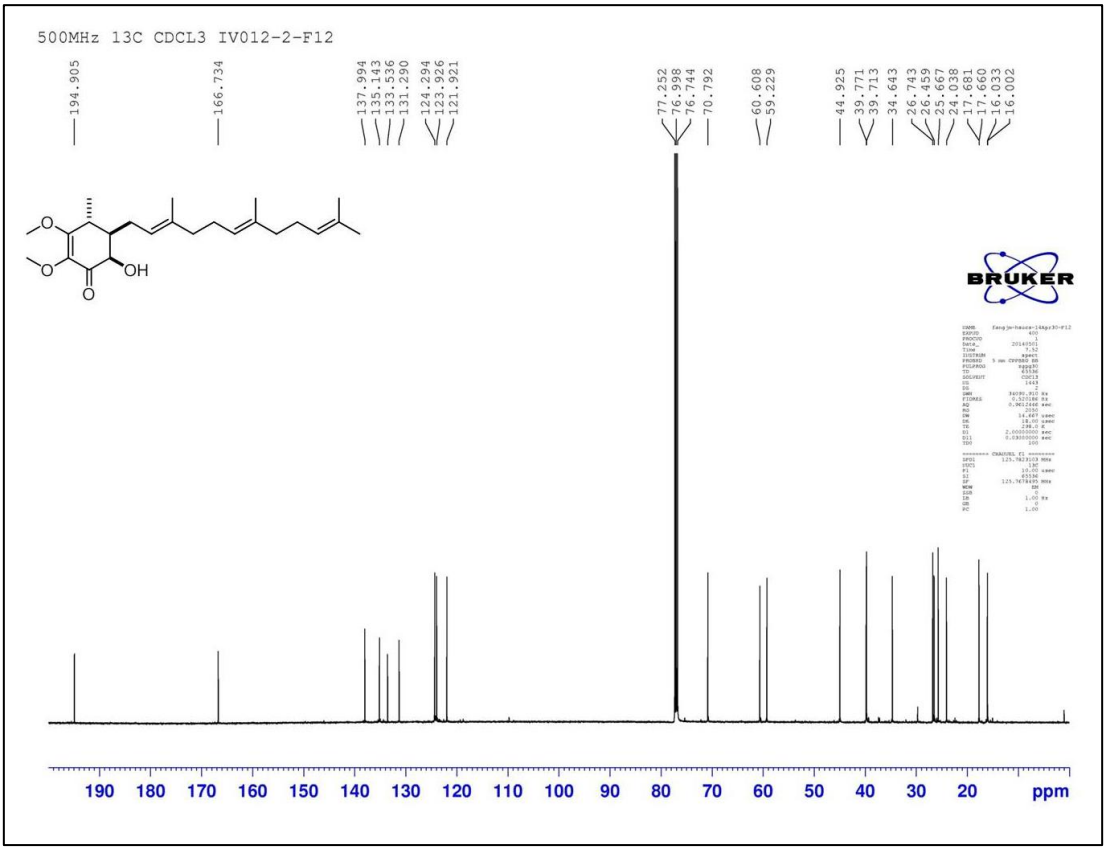

Figure S37. ^{13}C NMR spectrum of compound **13a** (125 MHz, $CDCl_3$)

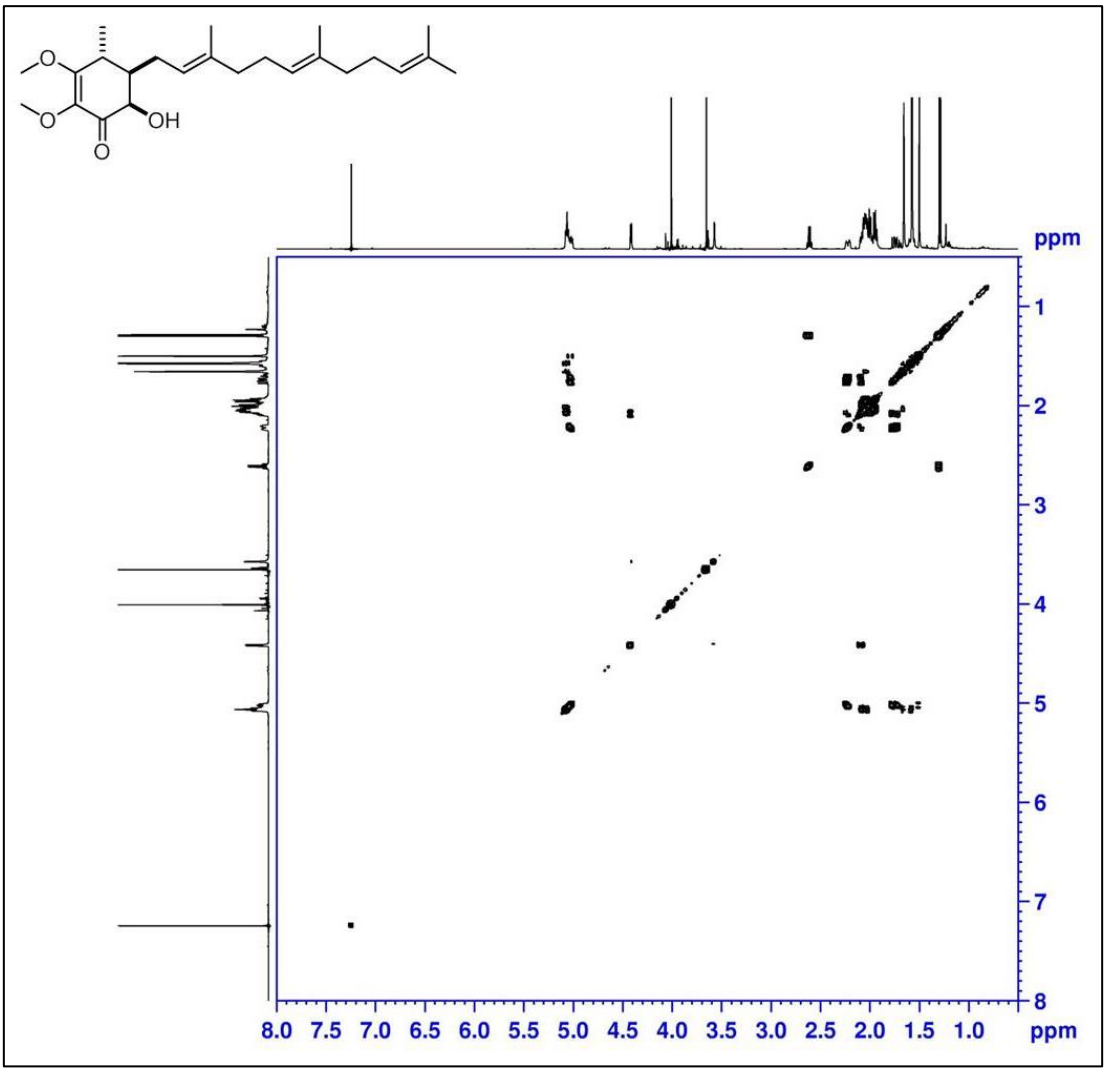

Figure S38. $^{1}H–^{1}H$ COSY NMR spectrum of compound **13a** (500 MHz, $CDCl_3$)

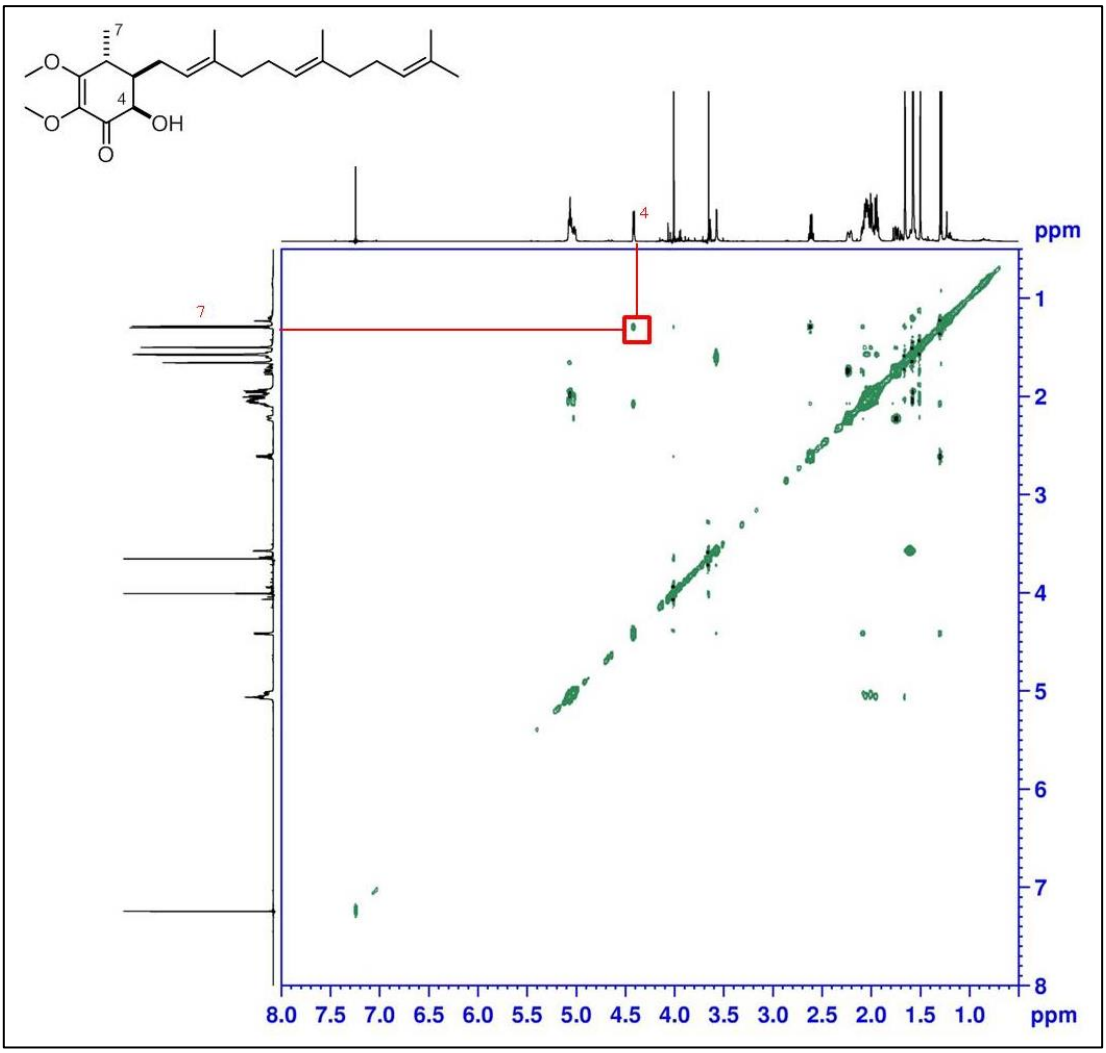

Figure S39. ^{1}H-^{1}H NOESY spectrum of compound **13a** (500 MHz, $CDCl_3$).

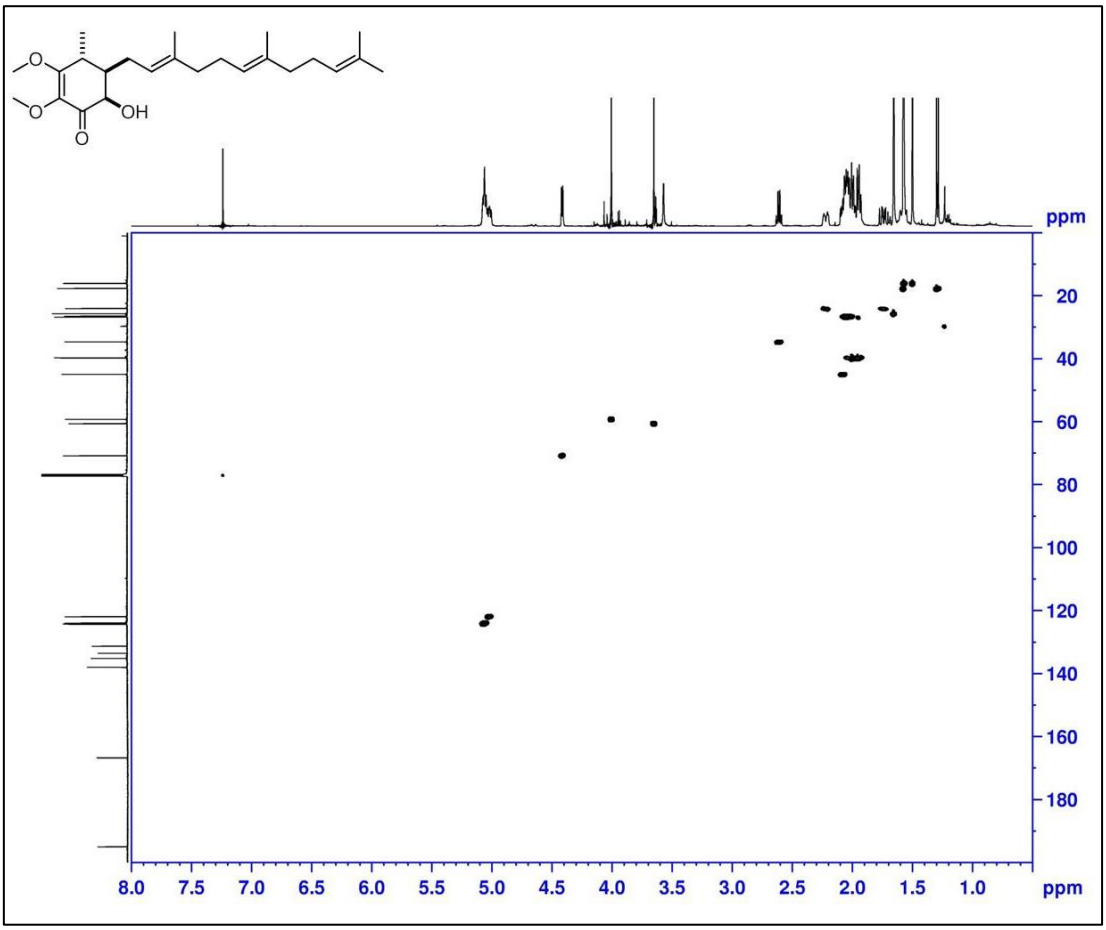

Figure S40. ^{1}H–^{13}C HSQC NMR spectrum of compound **13a** (125 MHz, $CDCl_3$)

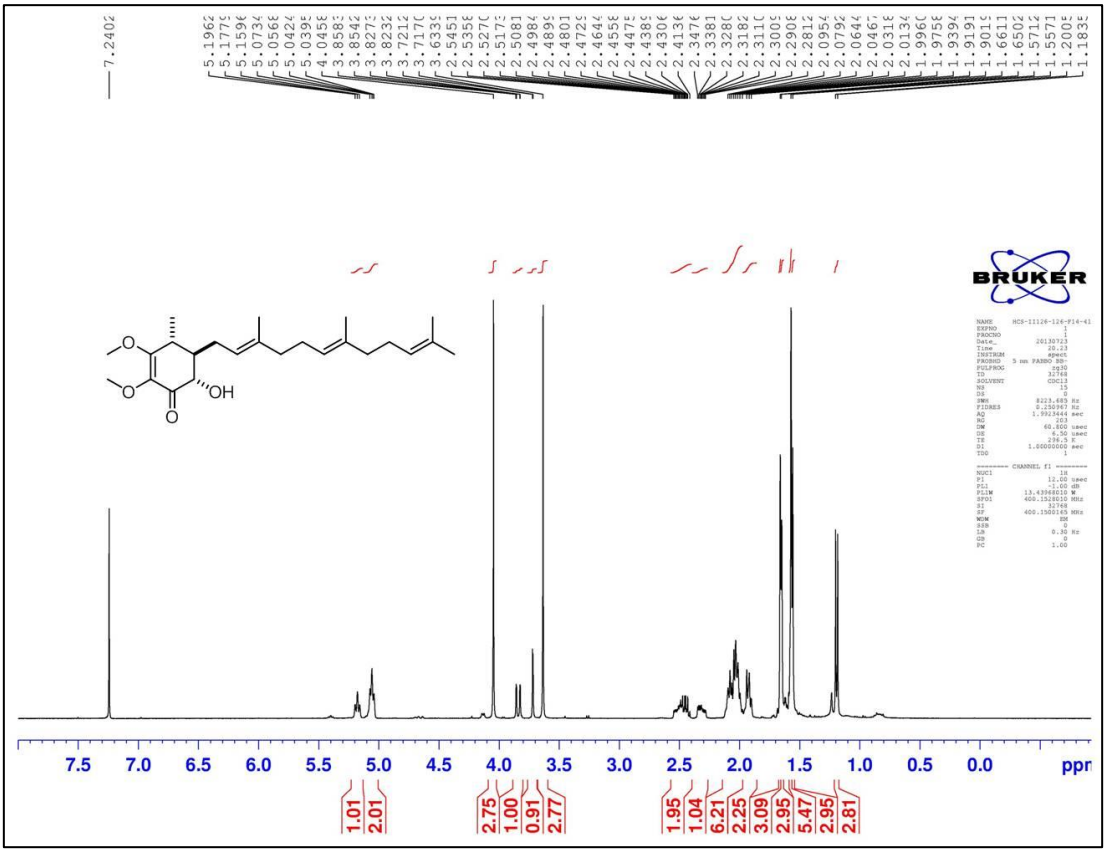

Figure S41. ^{1}H NMR spectrum of compound **13b** (400 MHz, $CDCl_3$)

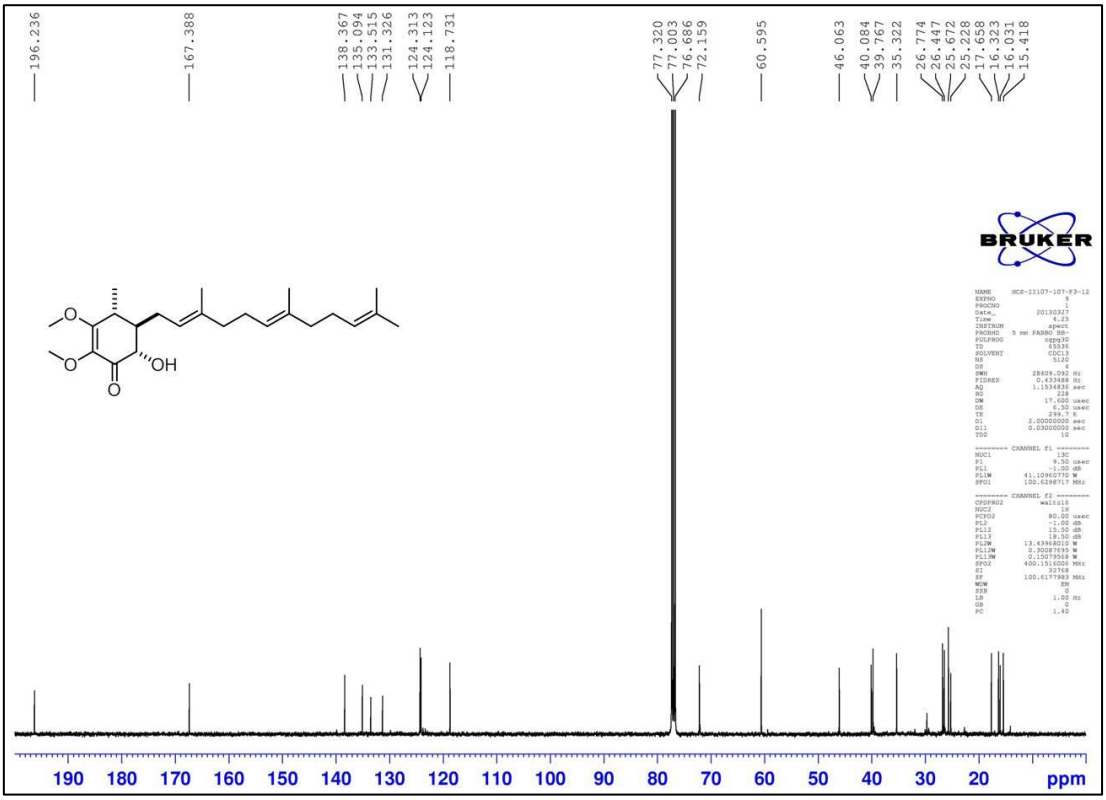

Figure S42. ^{13}C NMR spectrum of compound **13b** (100 MHz, $CDCl_3$)

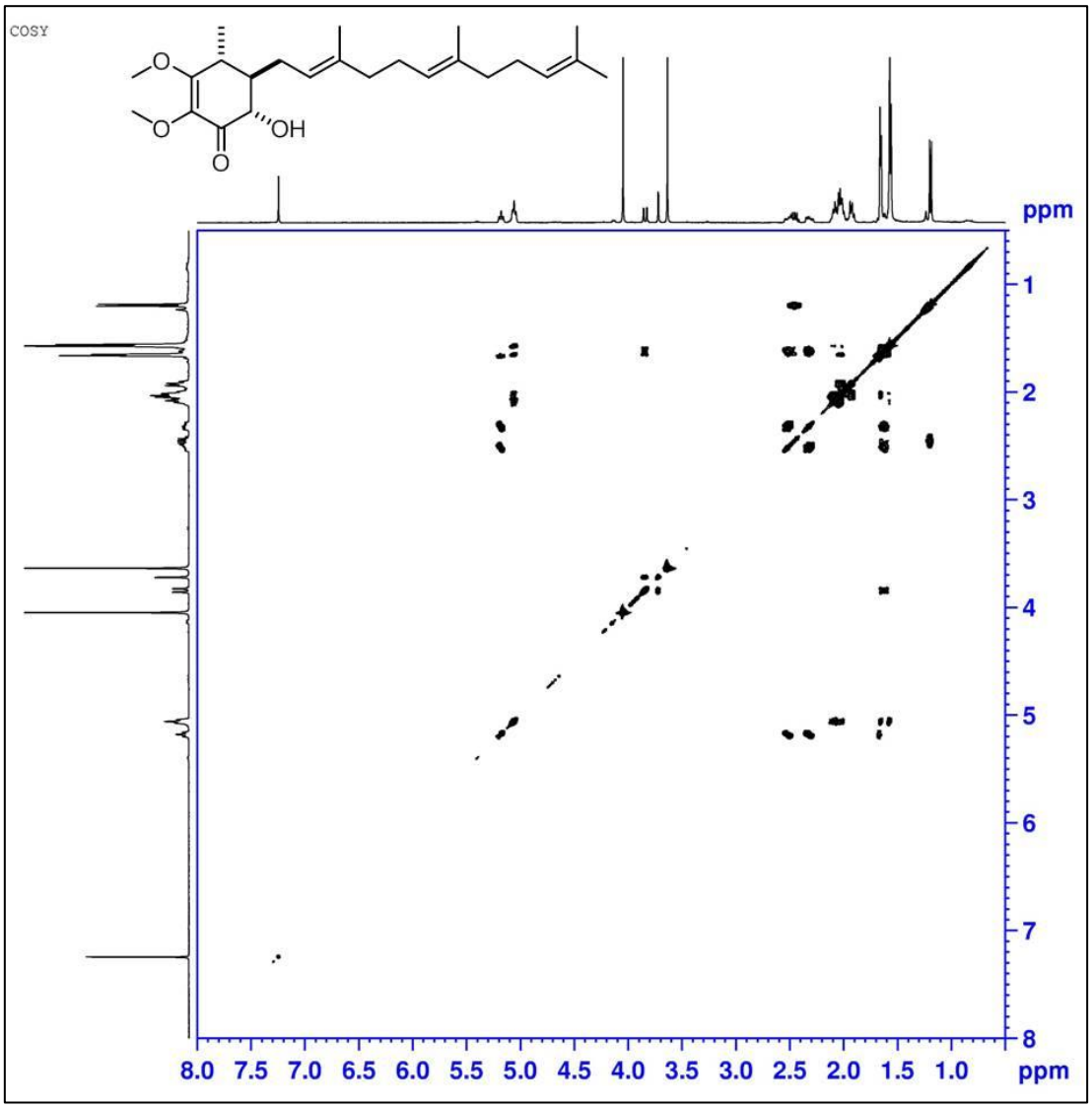

Figure S43. $^{1}H–^{1}H$ COSY NMR spectrum of compound **13b** (400 MHz, $CDCl_3$)

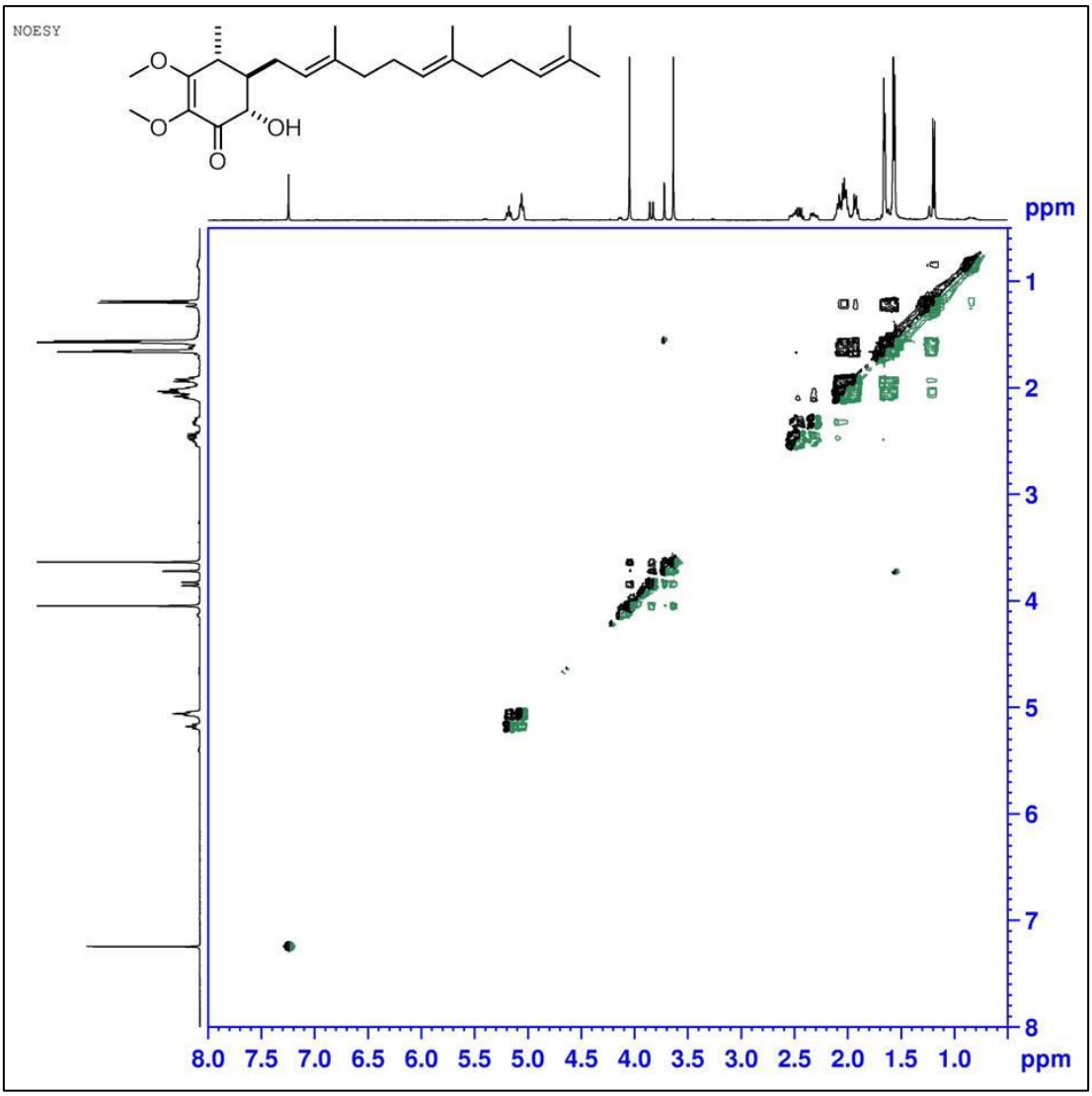

Figure S44. ^{1}H-^{1}H NOESY spectrum of compound **13b** (400 MHz, $CDCl_3$).

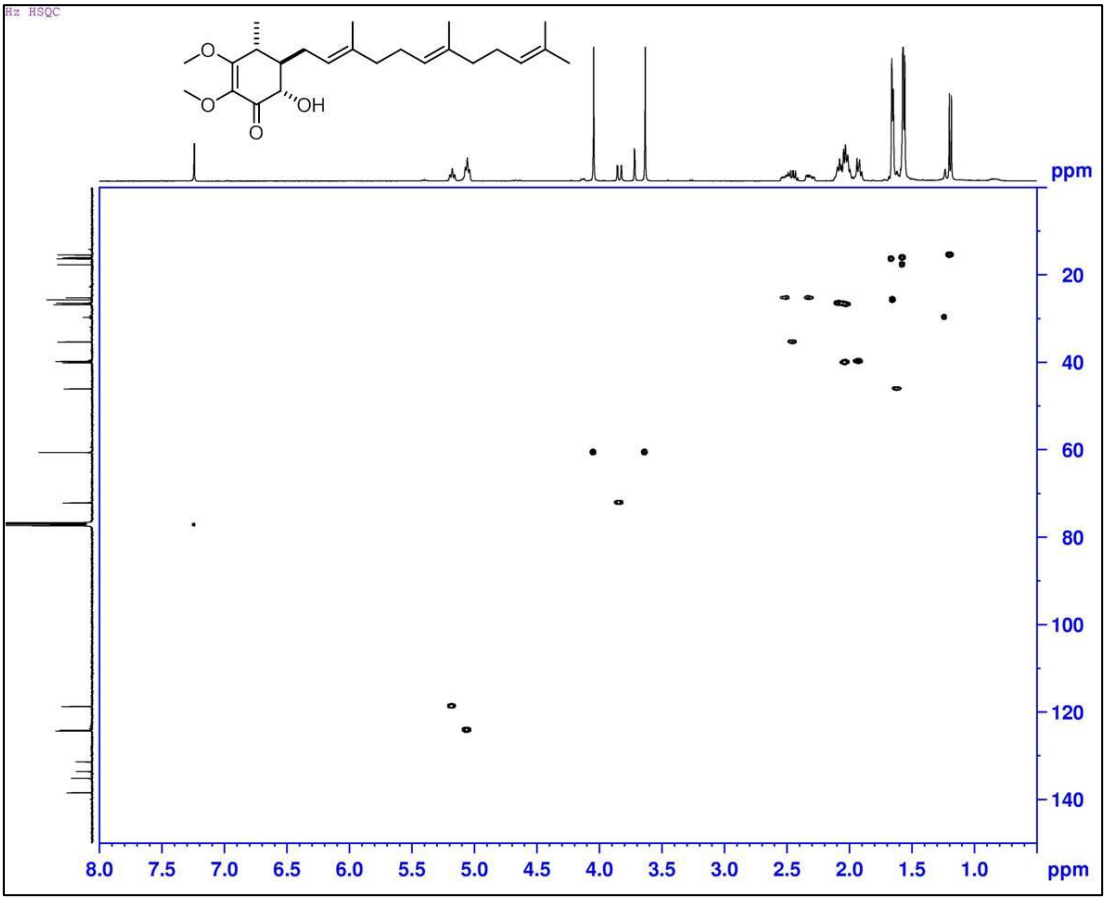

Figure S45. ^{1}H–^{13}C HSQC NMR spectrum of compound **13b** (125 MHz, $CDCl_3$)

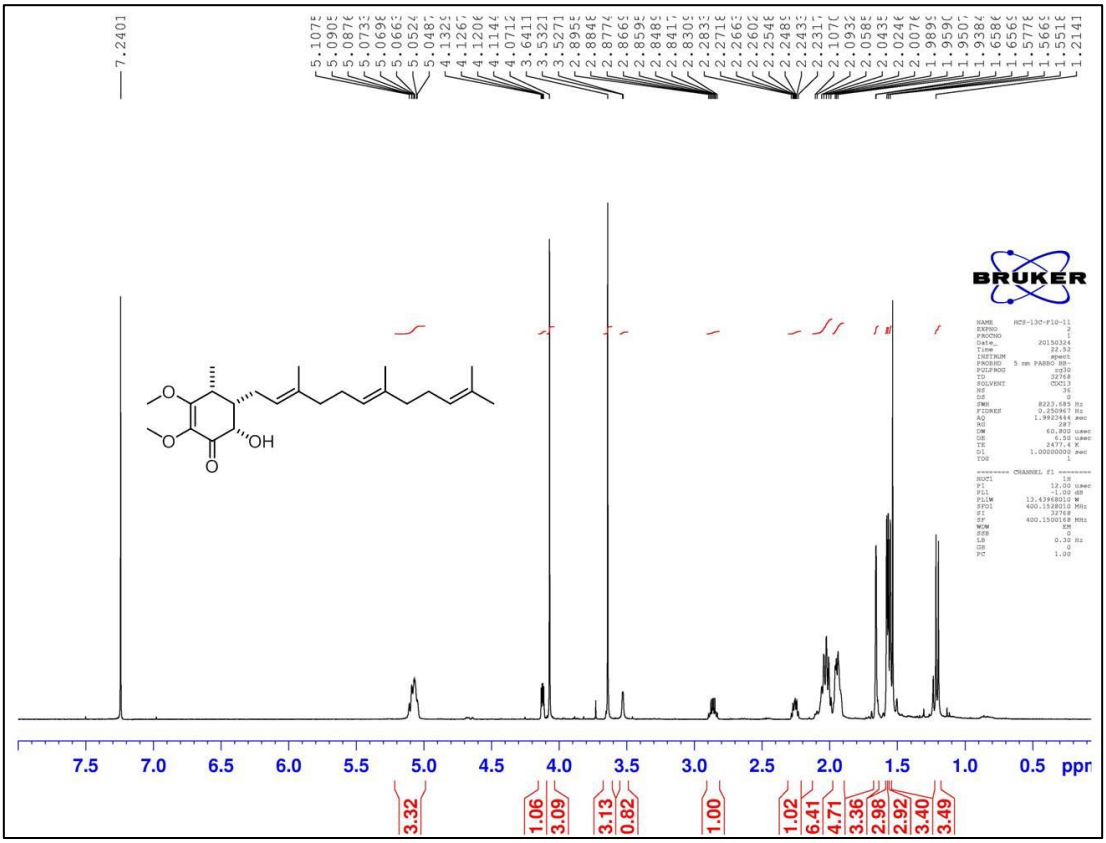

Figure S46. ^{1}H NMR spectrum of compound **13c** (400 MHz, $CDCl_3$)

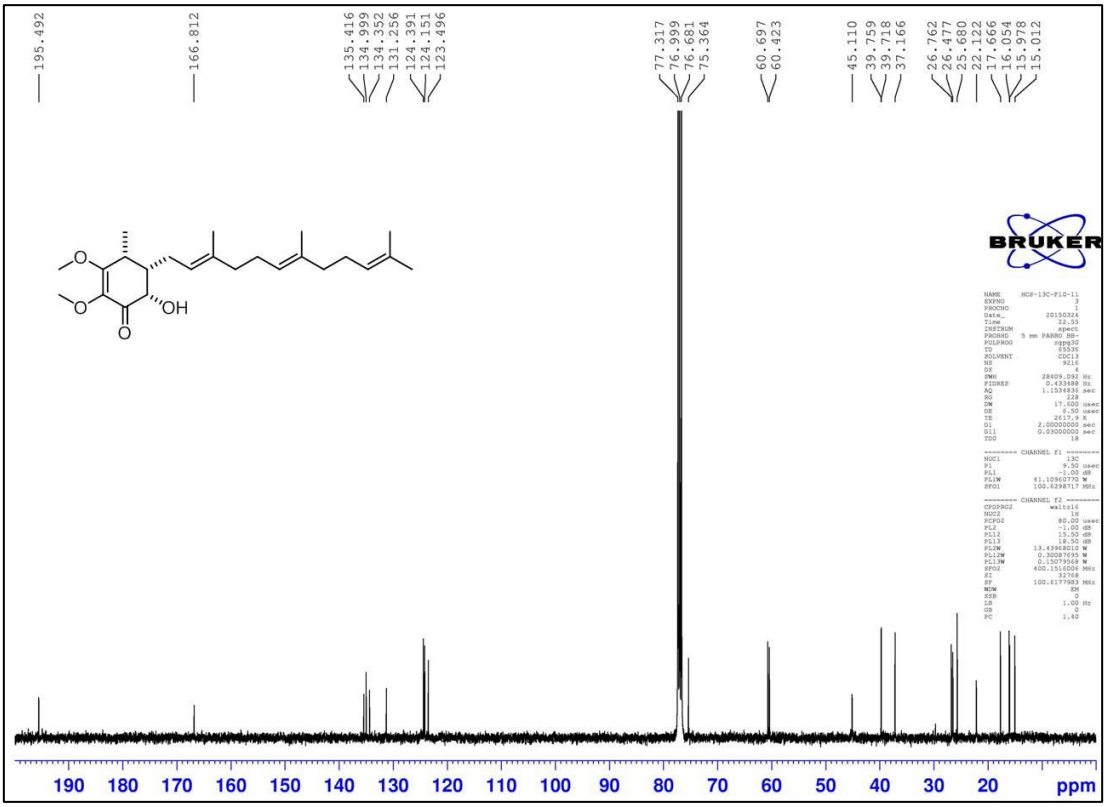

Figure S47. ^{13}C NMR spectrum of compound **13c** (100 MHz, $CDCl_3$)

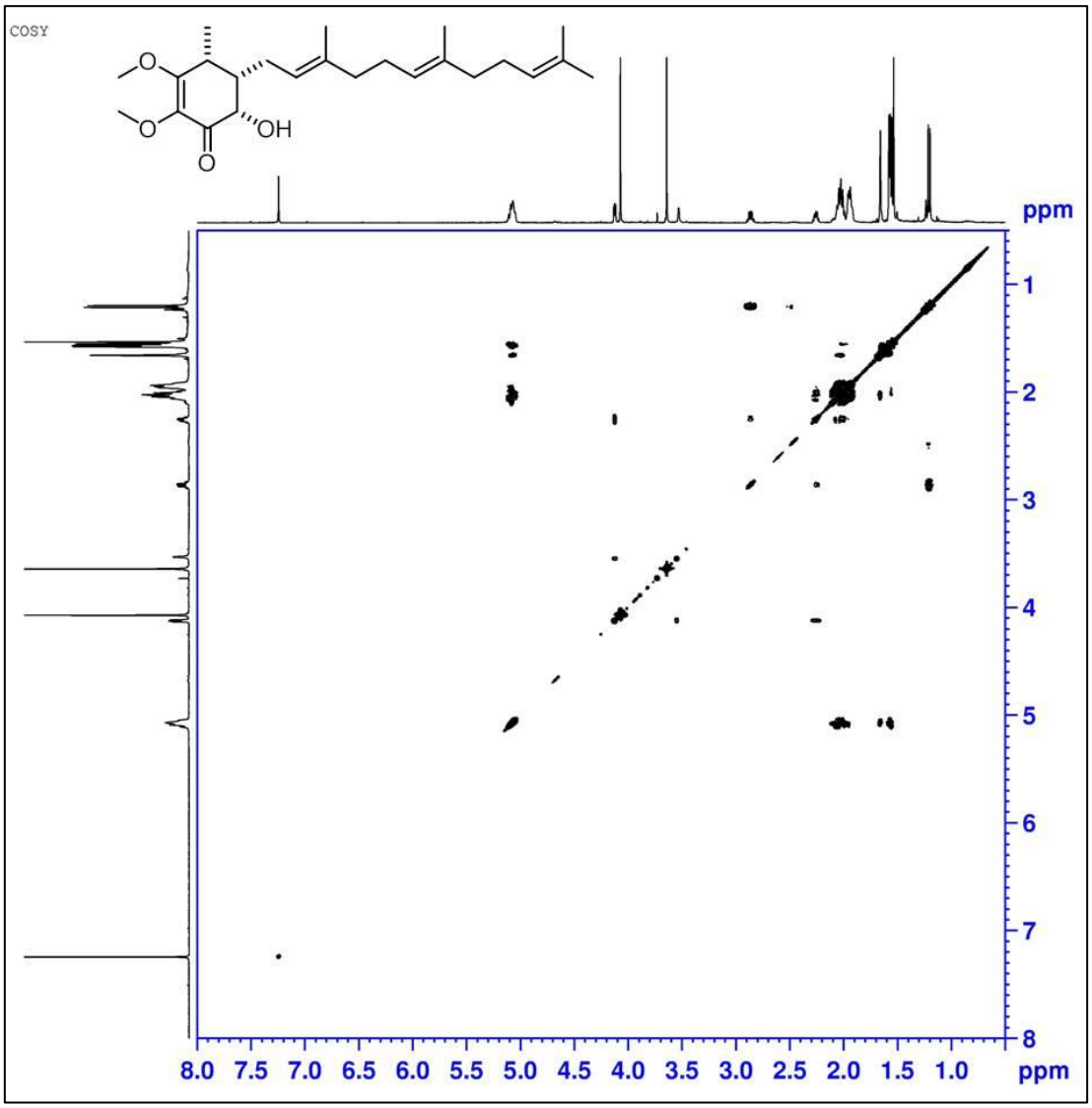

Figure S48. $^{1}H–^{1}H$ COSY NMR spectrum of compound **13c** (400 MHz, $CDCl_3$)

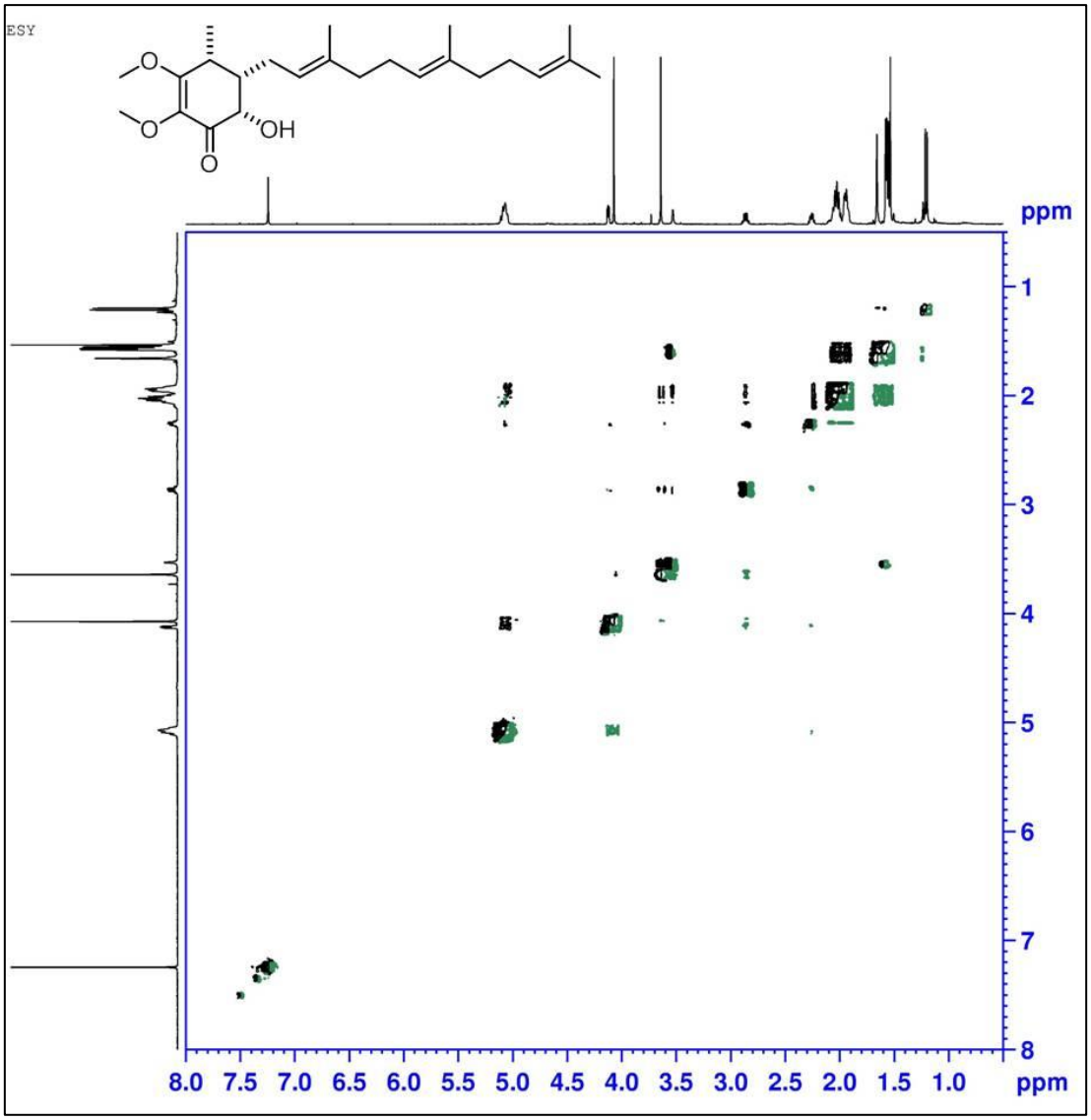

Figure S49. ^{1}H-^{1}H NOESY spectrum of compound **13c** (400 MHz, $CDCl_3$).

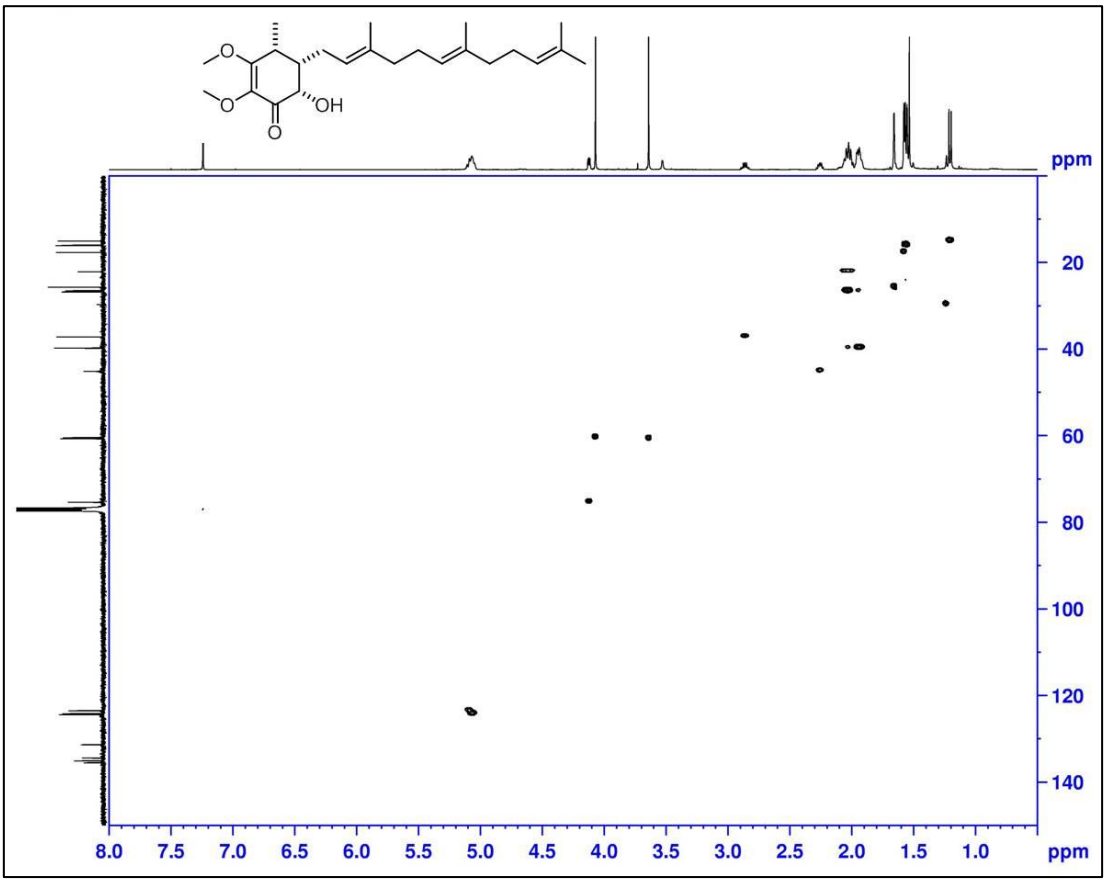

Figure S50. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **13c** (100 MHz, $CDCl_3$)

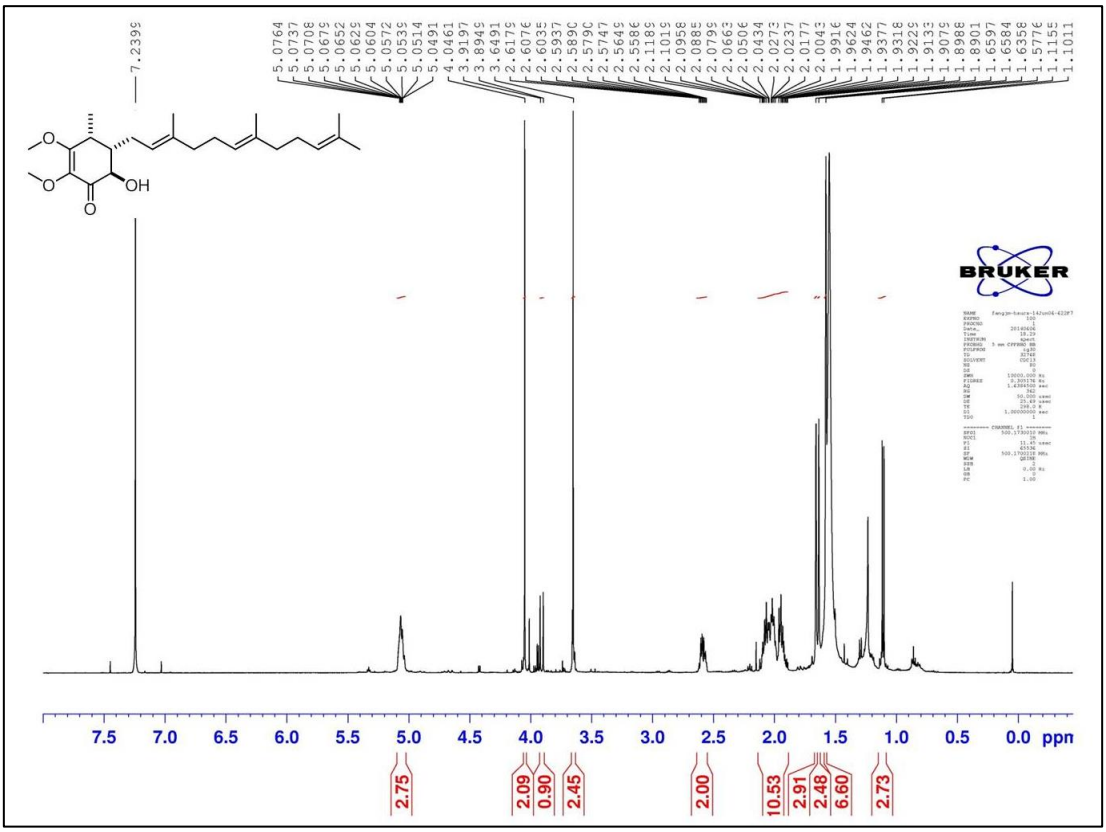

Figure S51. ^{1}H NMR spectrum of compound **13d** (500 MHz, $CDCl_3$)

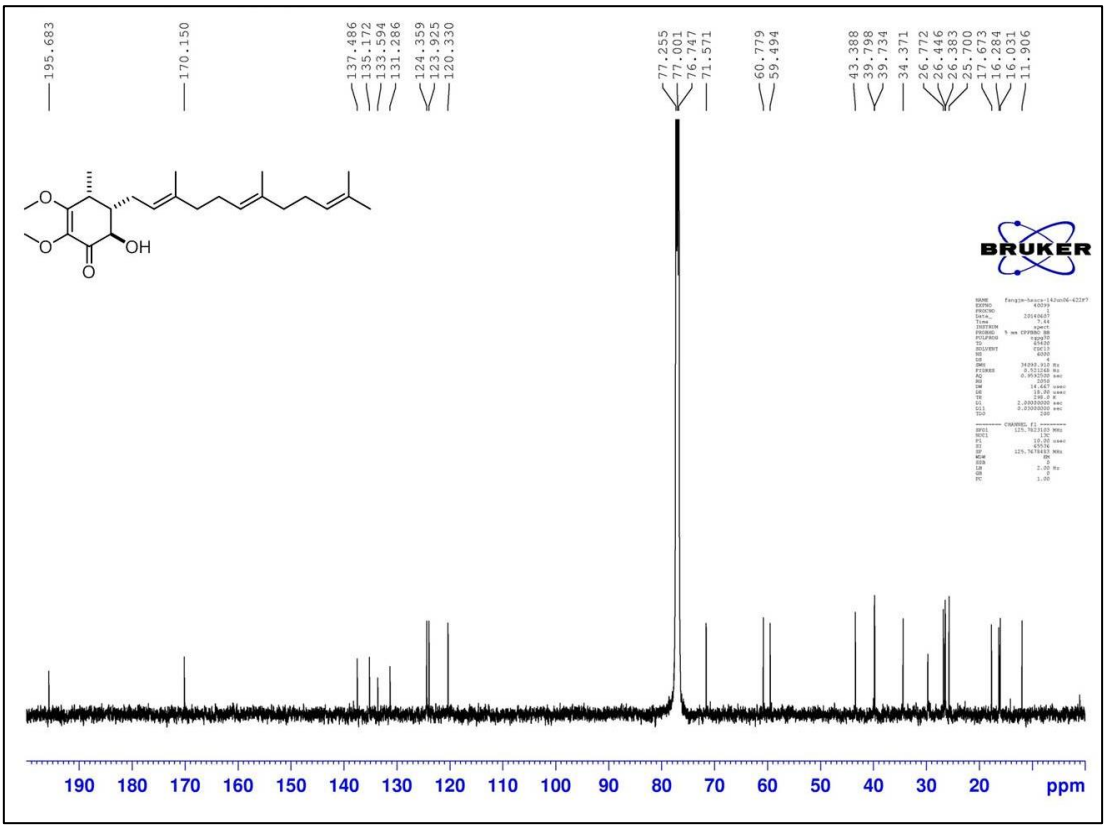

Figure S52. ^{13}C NMR spectrum of compound **13d** (125 MHz, $CDCl_3$)

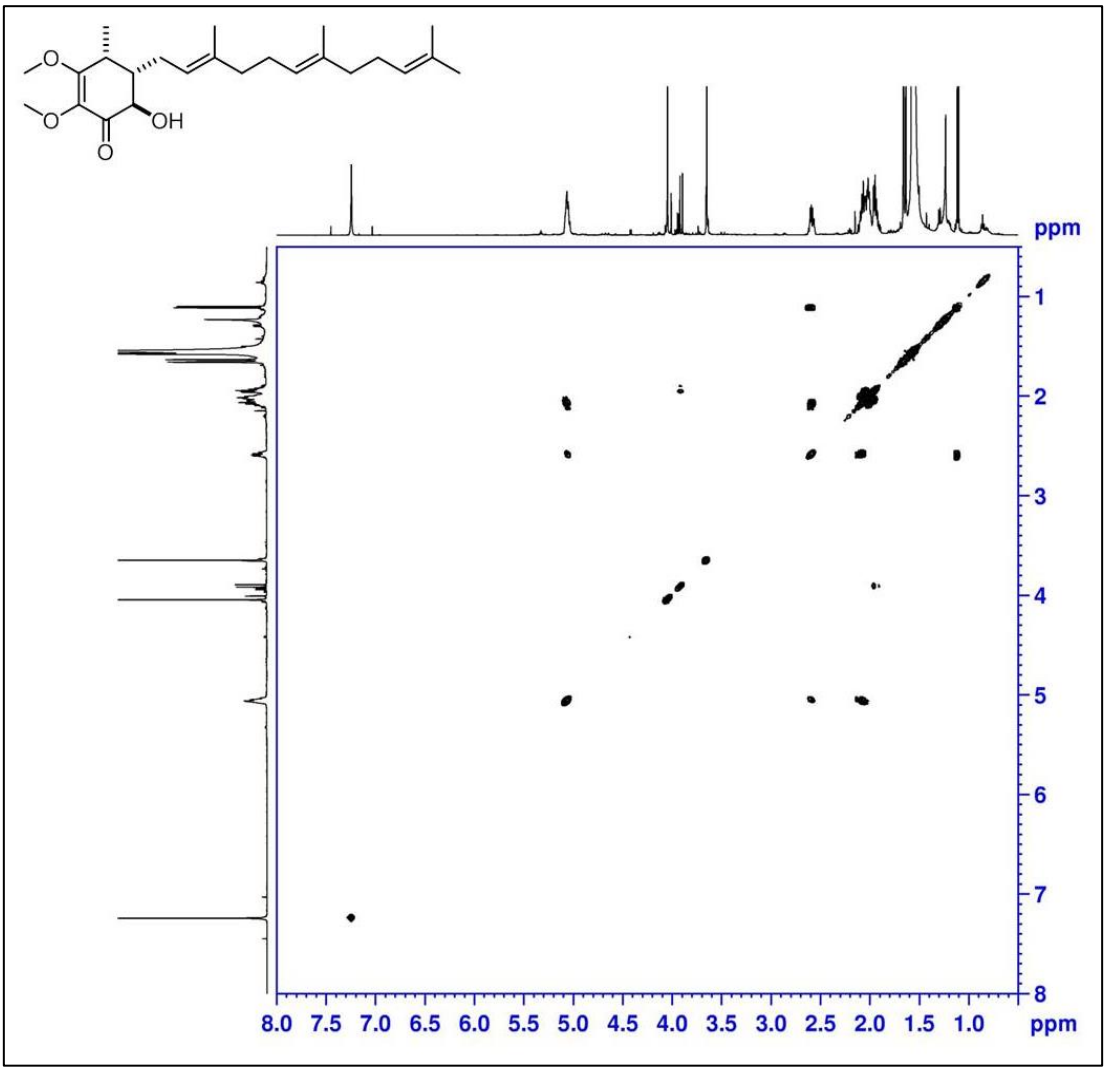

Figure S53. $^{1}H–^{1}H$ COSY NMR spectrum of compound **13d** (500 MHz, $CDCl_3$)

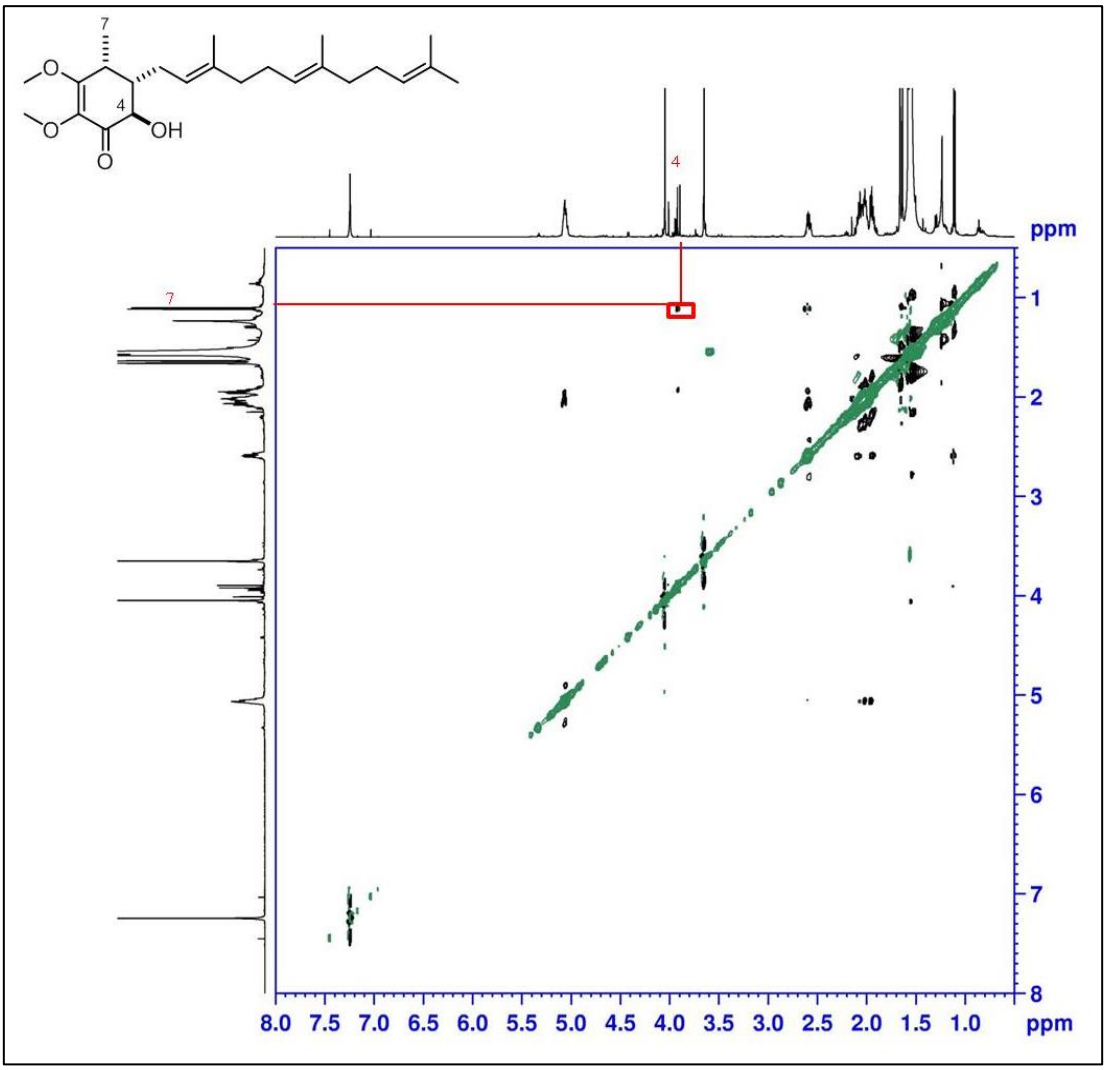

Figure S54. ^{1}H-^{1}H NOESY spectrum of compound **13d** (500 MHz, $CDCl_3$).

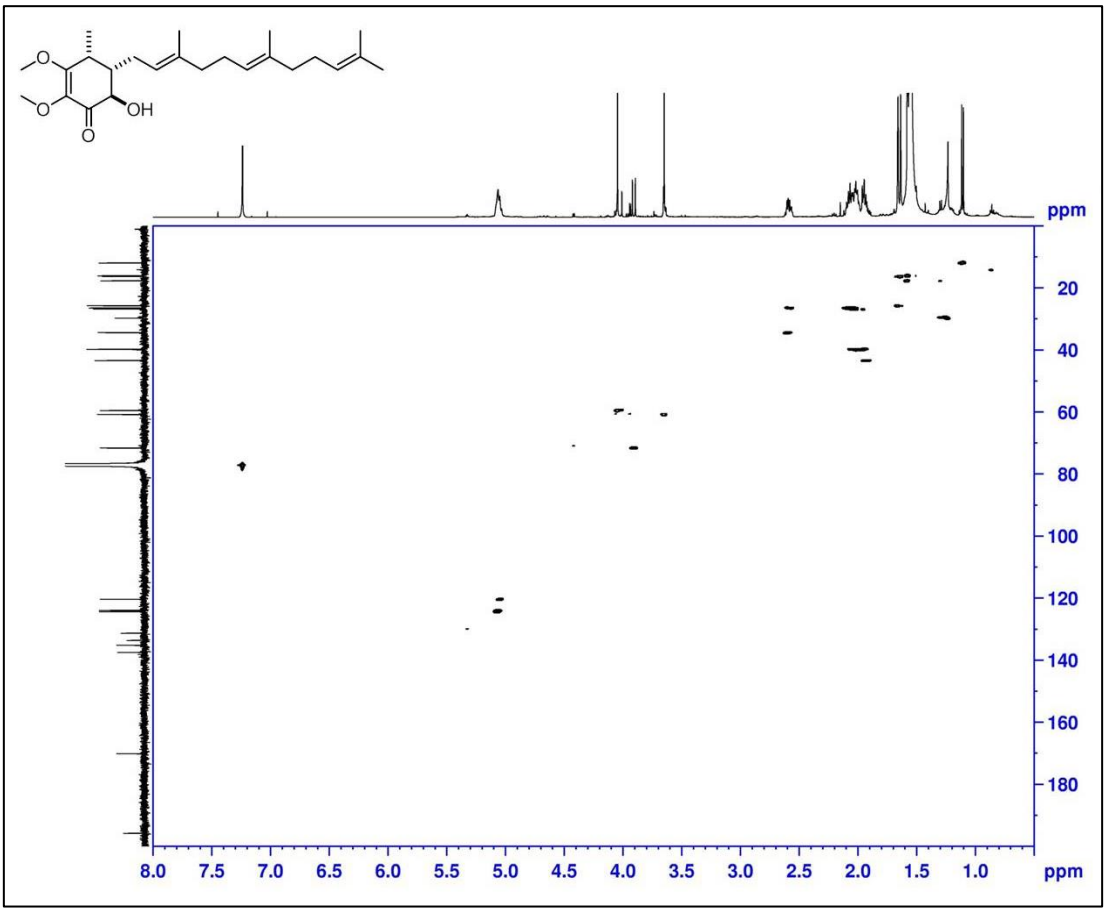

Figure S55. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **13d** (125 MHz, $CDCl_3$)

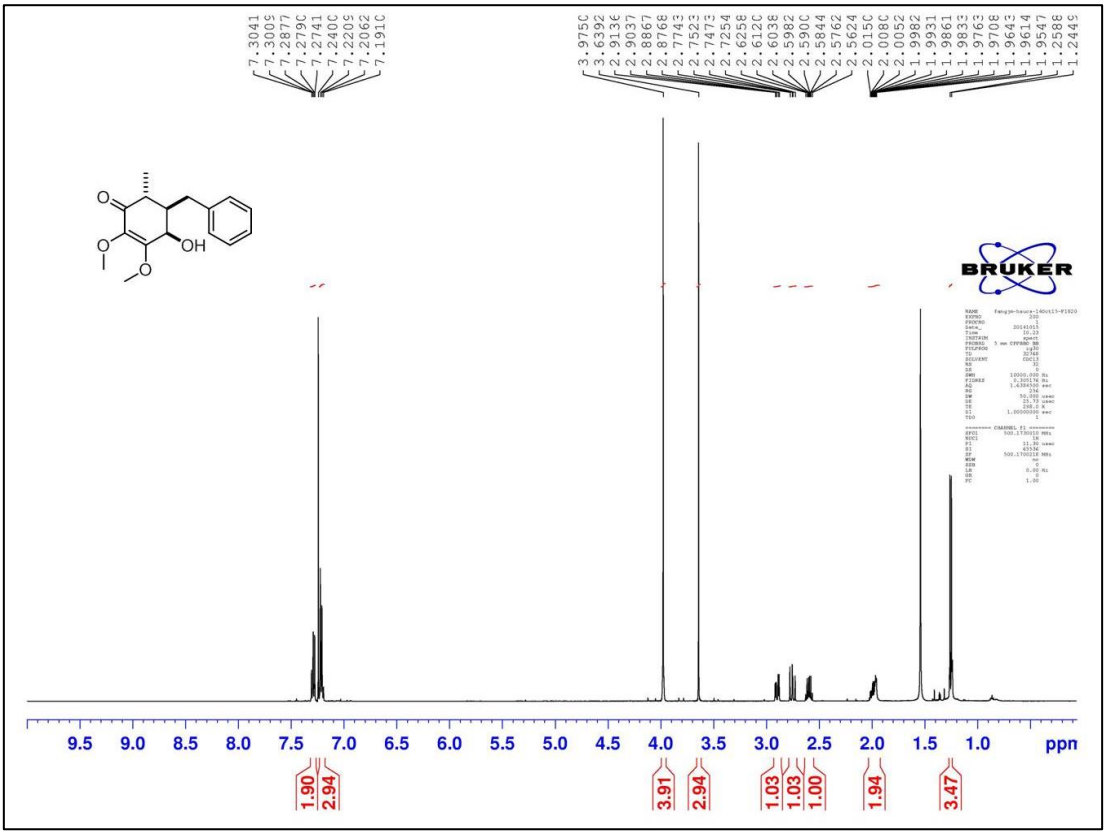

Figure S56. ^{1}H NMR spectrum of compounds **15a** (500 MHz, $CDCl_3$)

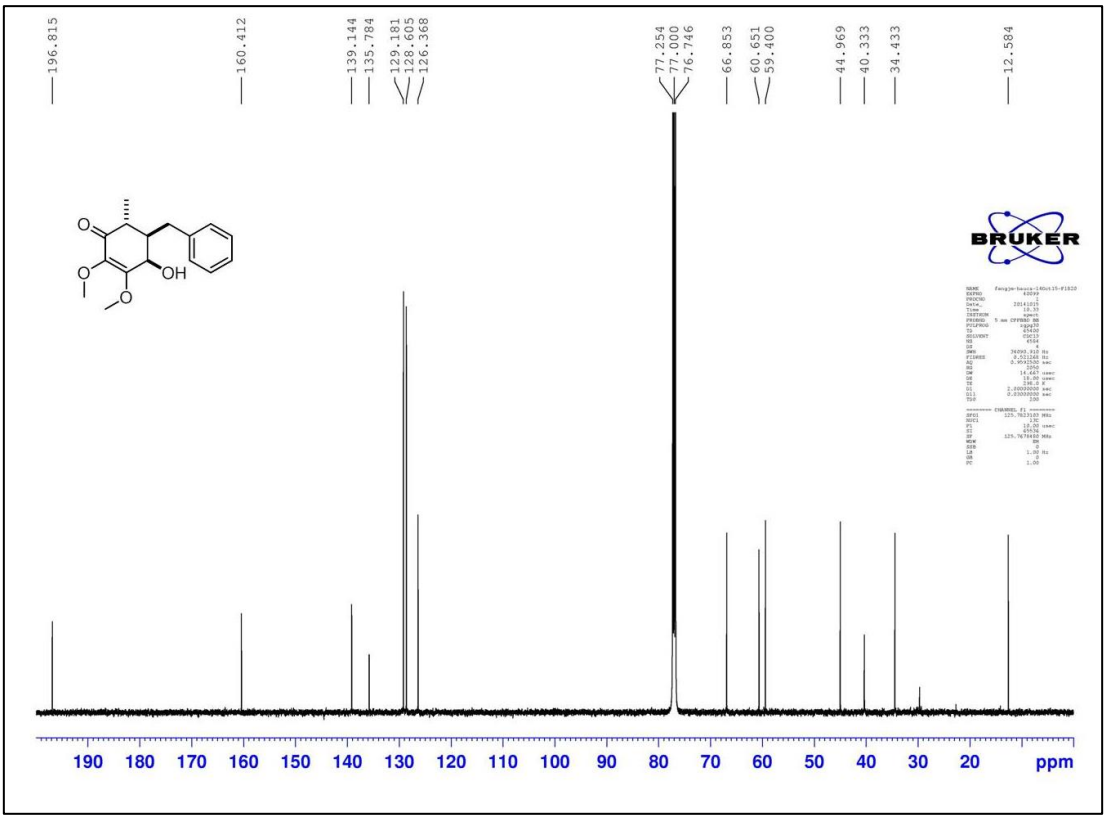

Figure S57. ^{13}C NMR spectrum of compound **15a** (125 MHz, $CDCl_3$)

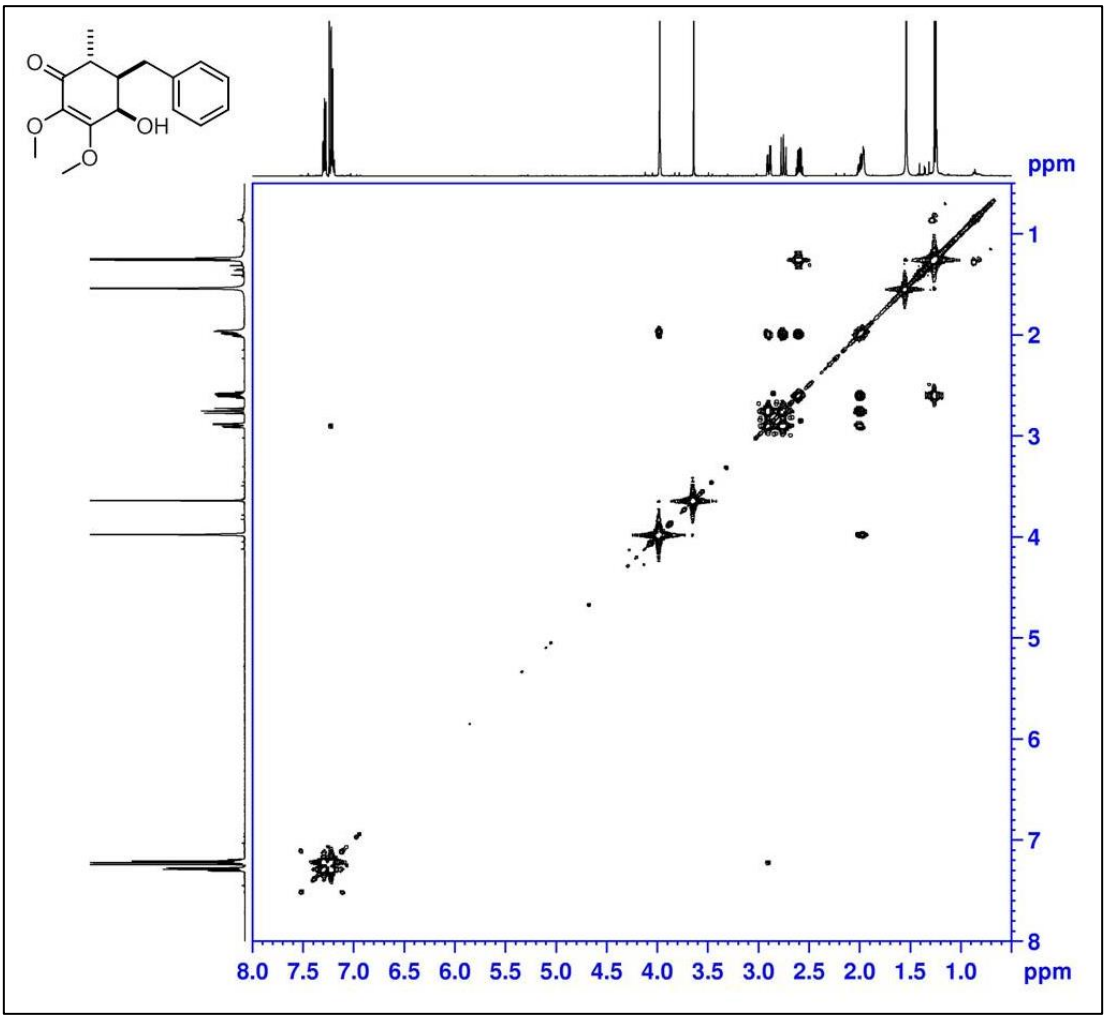

Figure S58. $^{1}H–^{1}H$ COSY NMR spectrum of compound **15a** (500 MHz, $CDCl_3$)

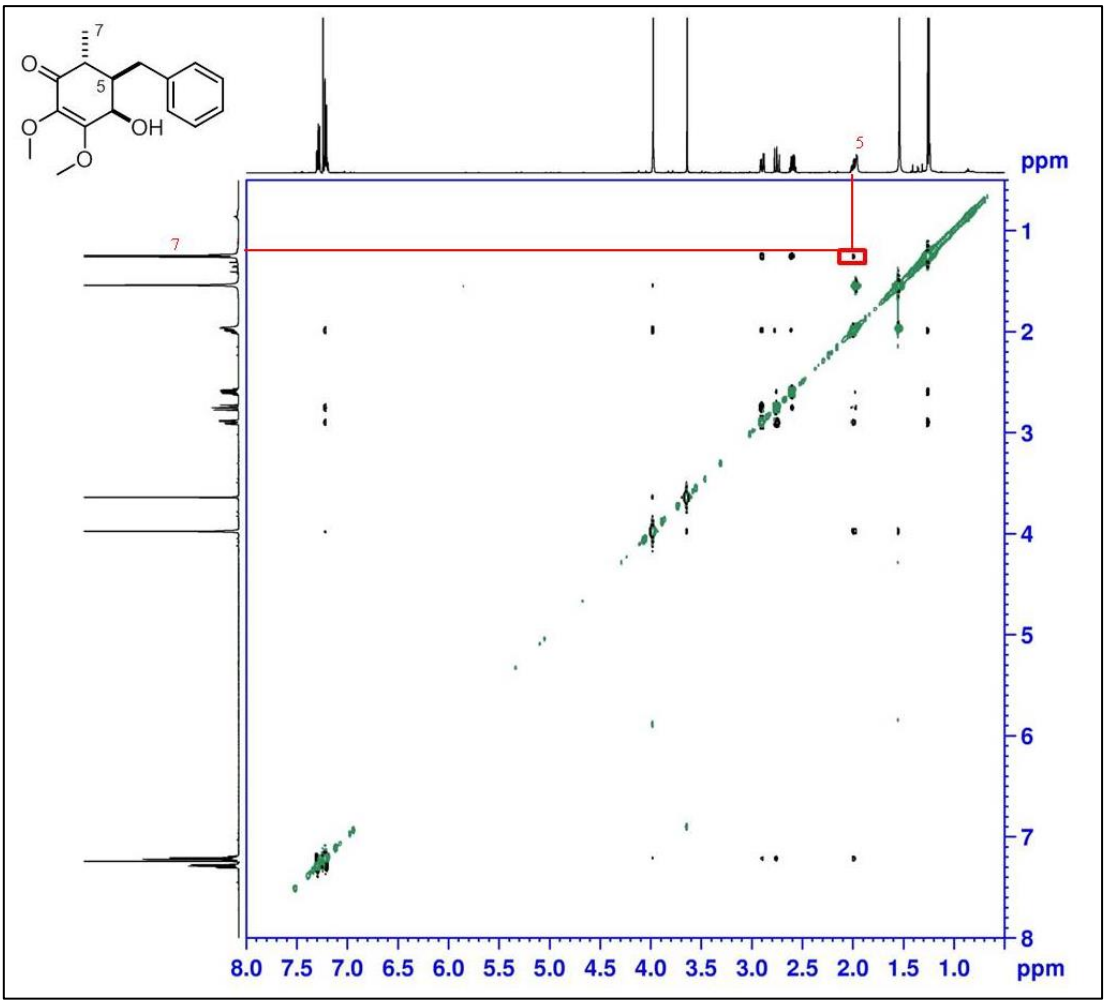

Figure S59. ^{1}H-^{1}H NOESY spectrum of compound **15a** (500 MHz, $CDCl_3$).

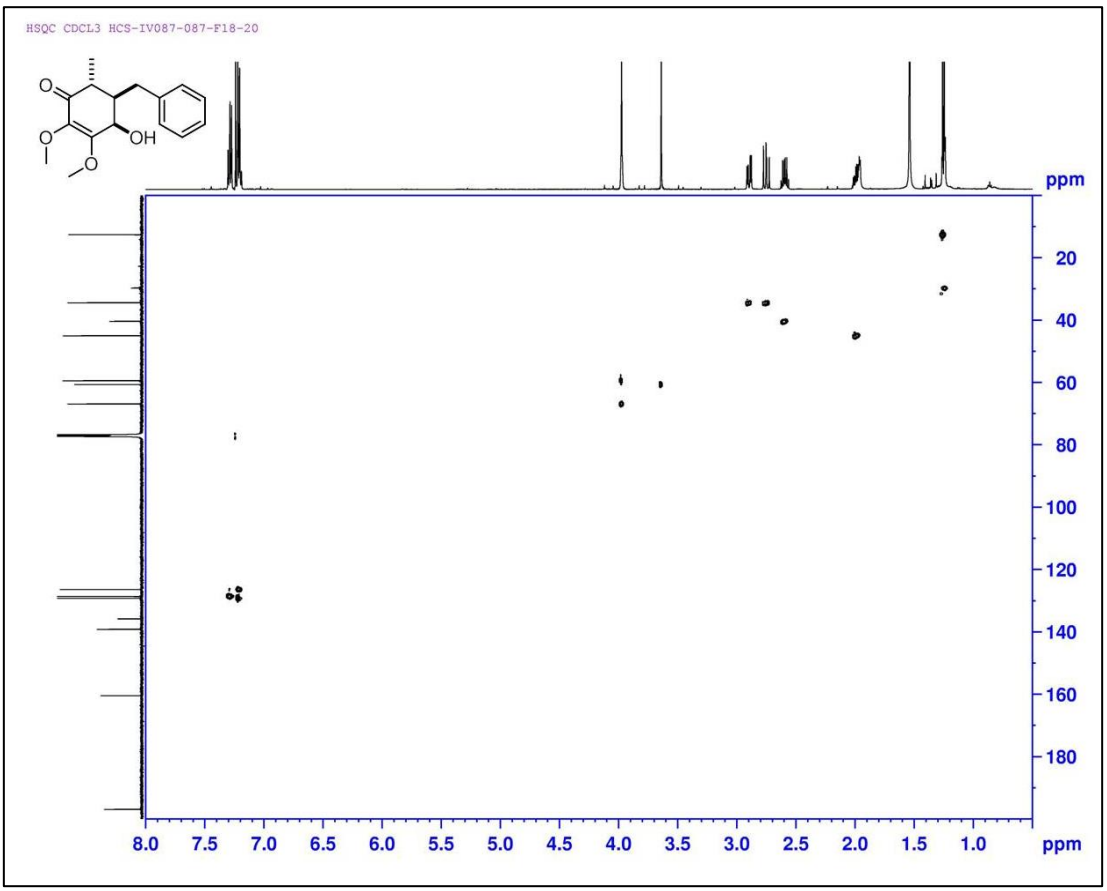

Figure S60. ^{1}H–^{13}C HSQC NMR spectrum of compound **15a** (125 MHz, $CDCl_3$)

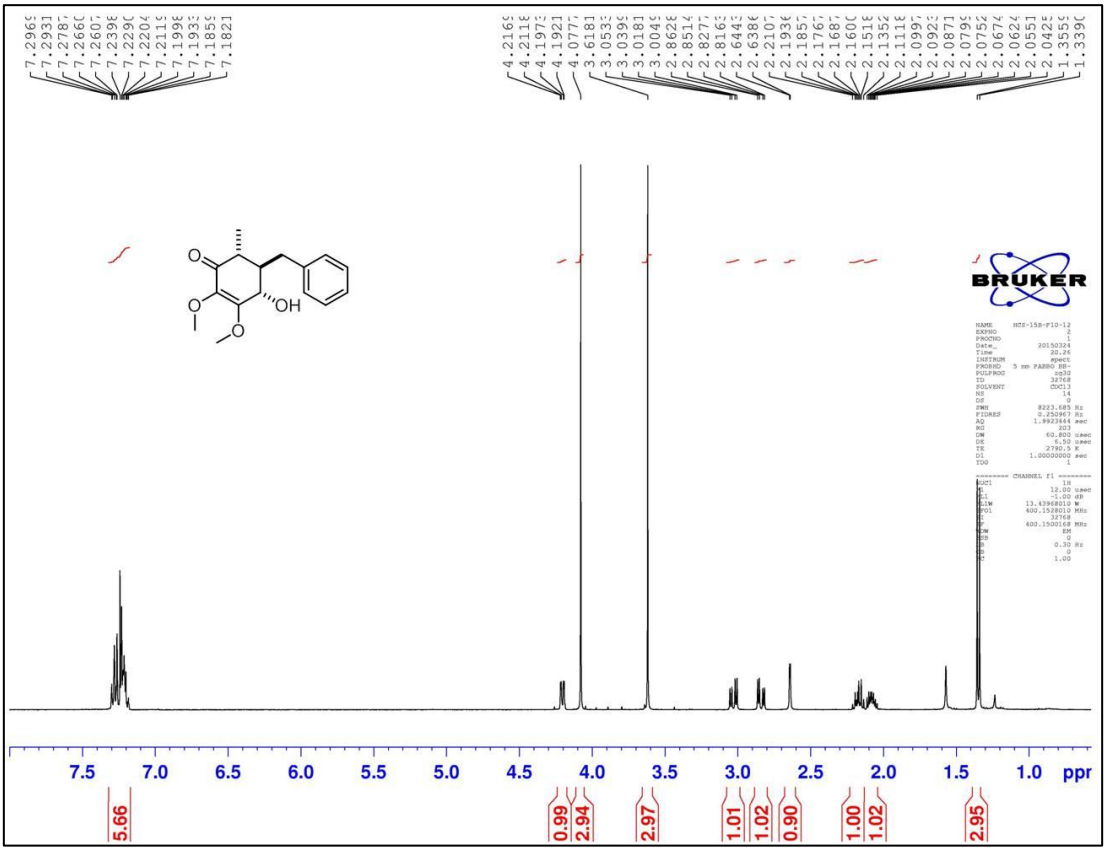

Figure S61. ^{1}H NMR spectrum of compound **15b** (400 MHz, $CDCl_3$)

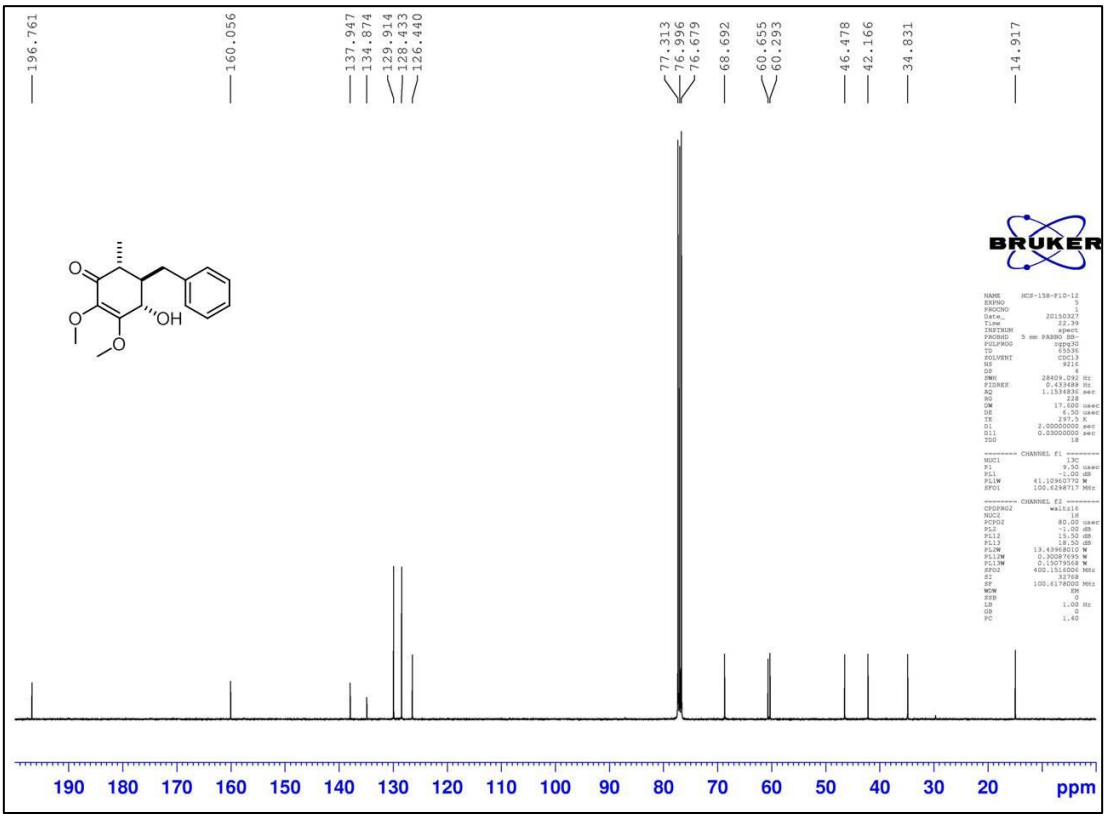

Figure S62. ^{13}C NMR spectrum of compound **15b** (100 MHz, $CDCl_3$)

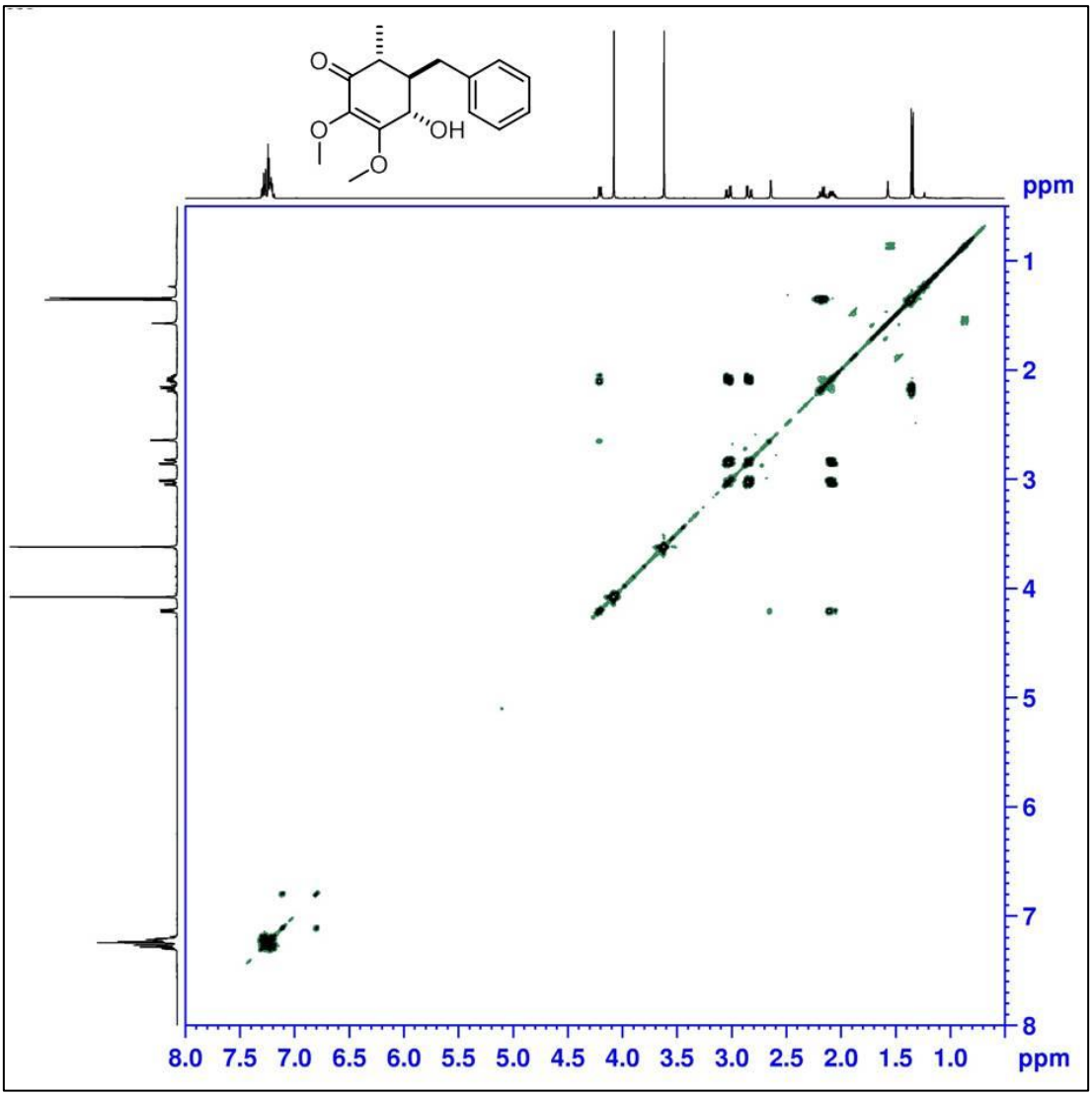

Figure S63. $^{1}H–^{1}H$ COSY NMR spectrum of compound **15b** (400 MHz, $CDCl_3$)

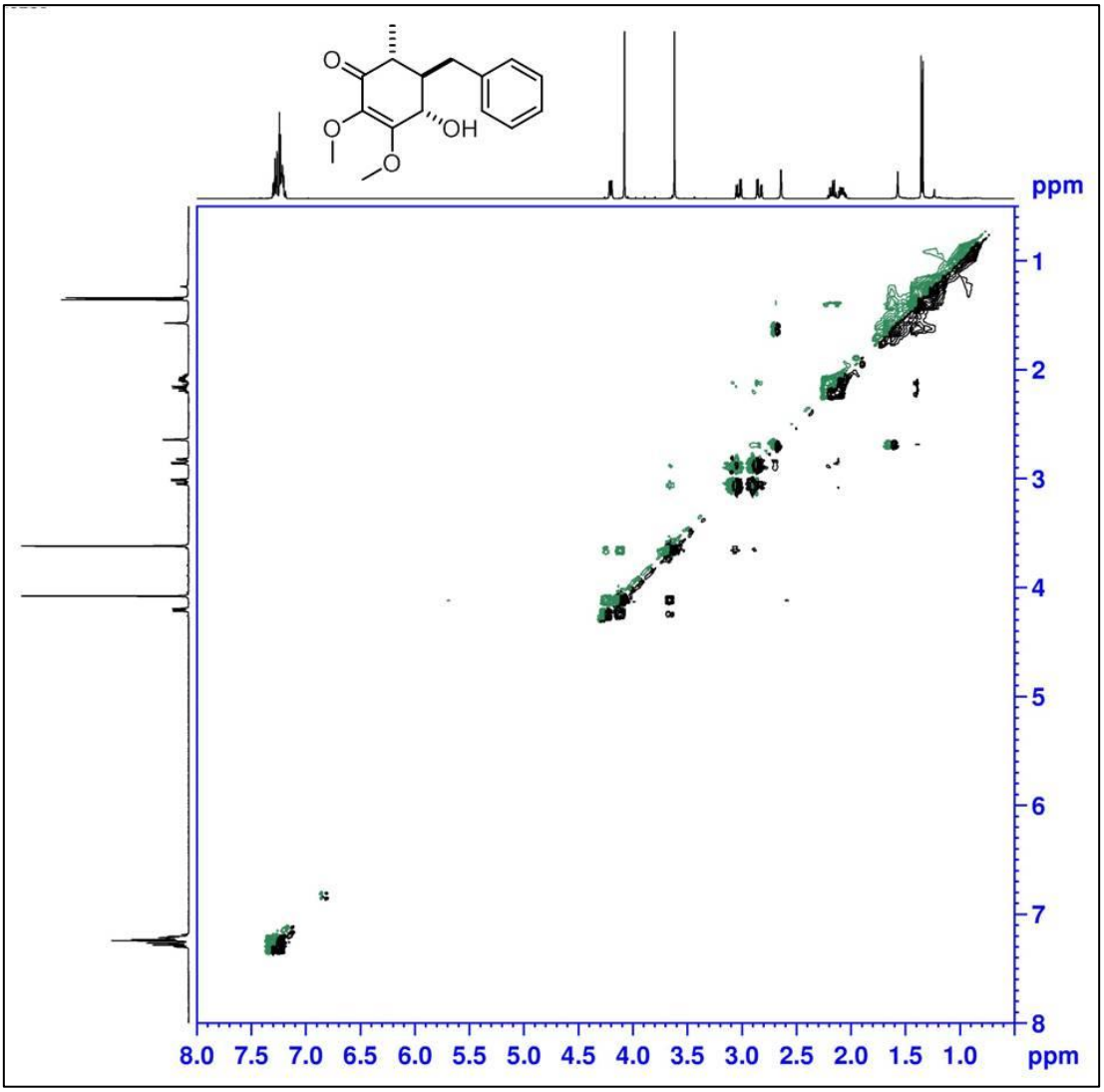

Figure S64. ^{1}H-^{1}H NOESY spectrum of compound **15b** (400 MHz, $CDCl_3$).

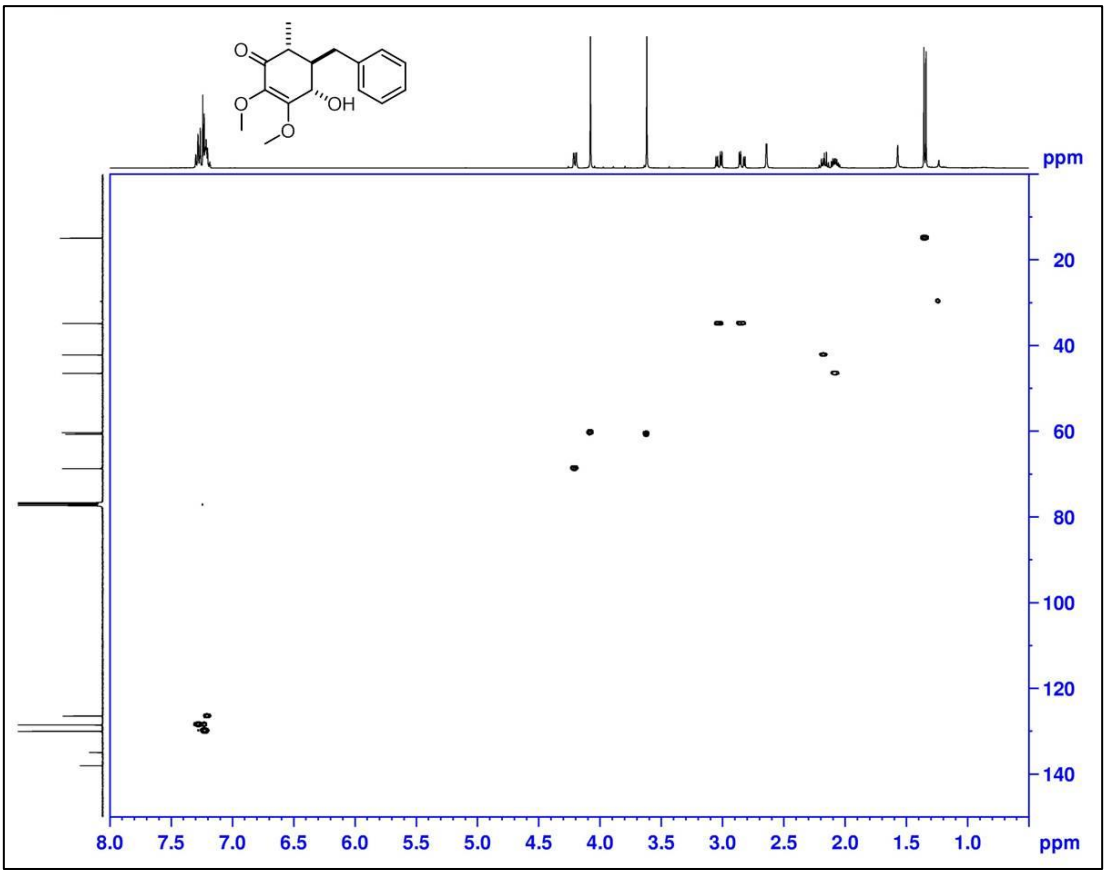

Figure S65. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **15b** (100 MHz, $CDCl_3$)

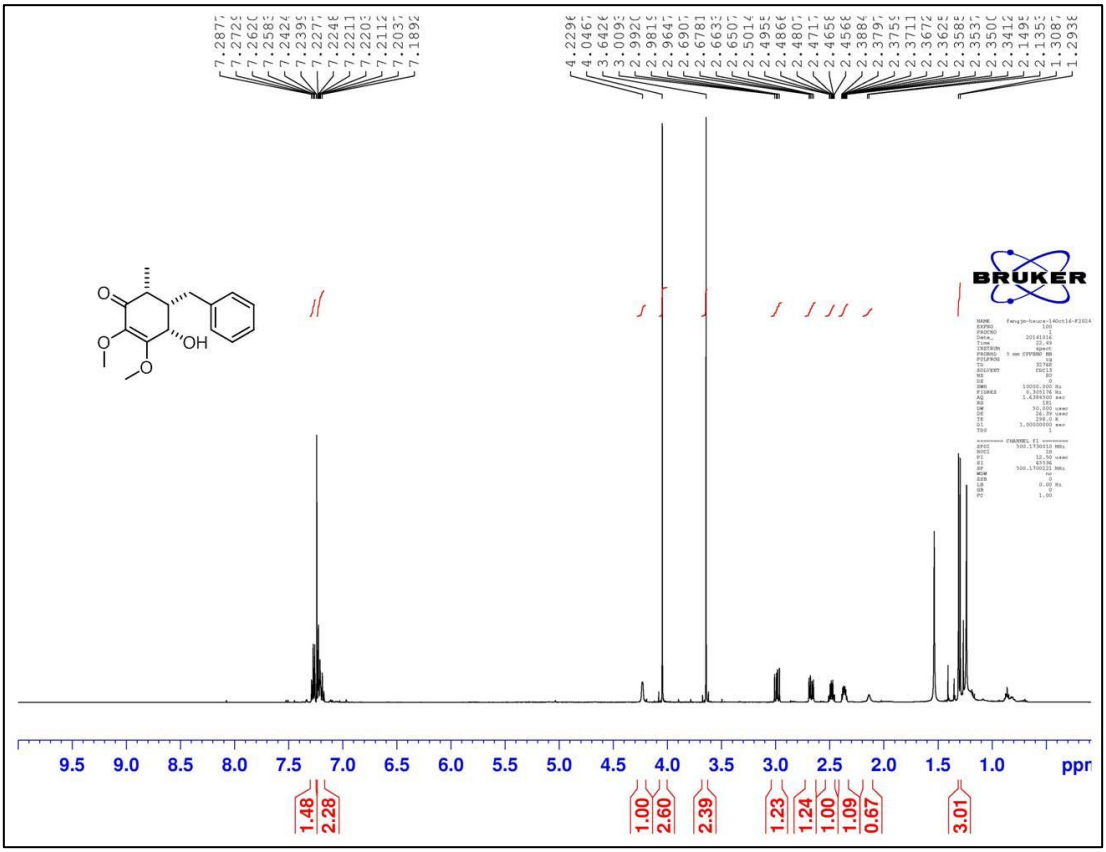

Figure S66. ^{1}H NMR spectrum of compound **15c** (500 MHz, $CDCl_3$)

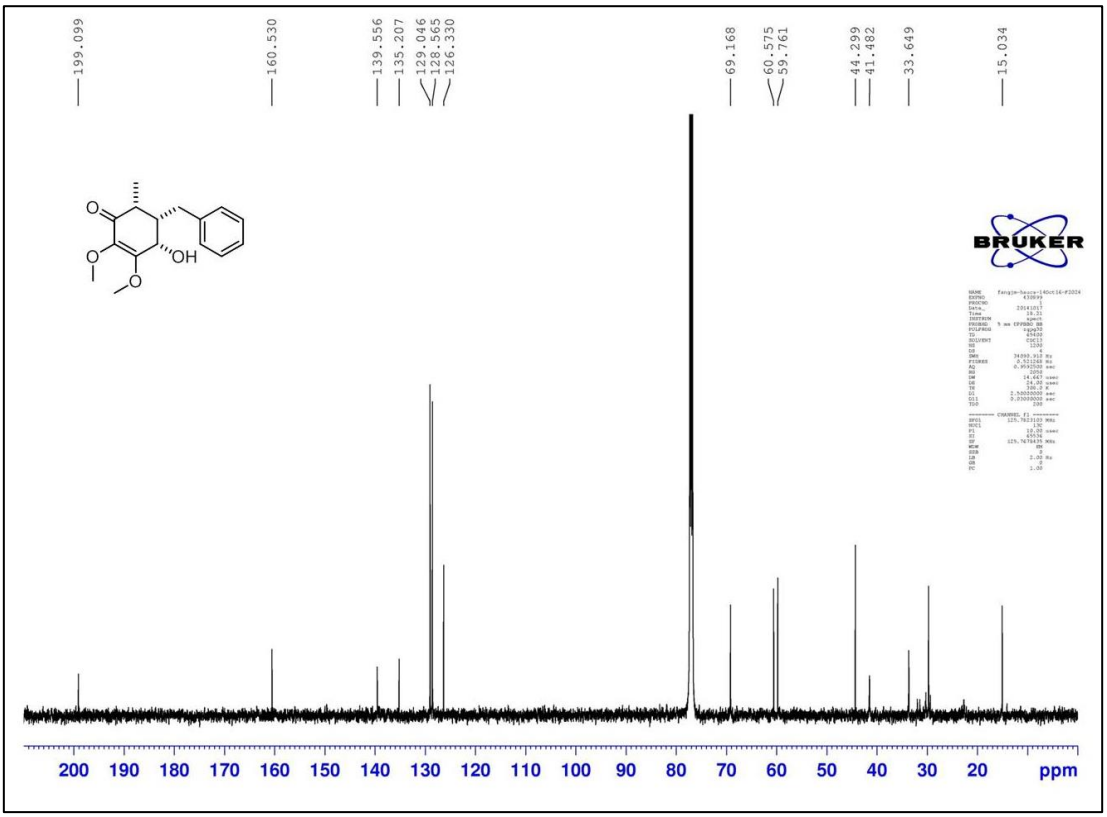

Figure S67. ^{13}C NMR spectrum of compound **15c** (125 MHz, $CDCl_3$)

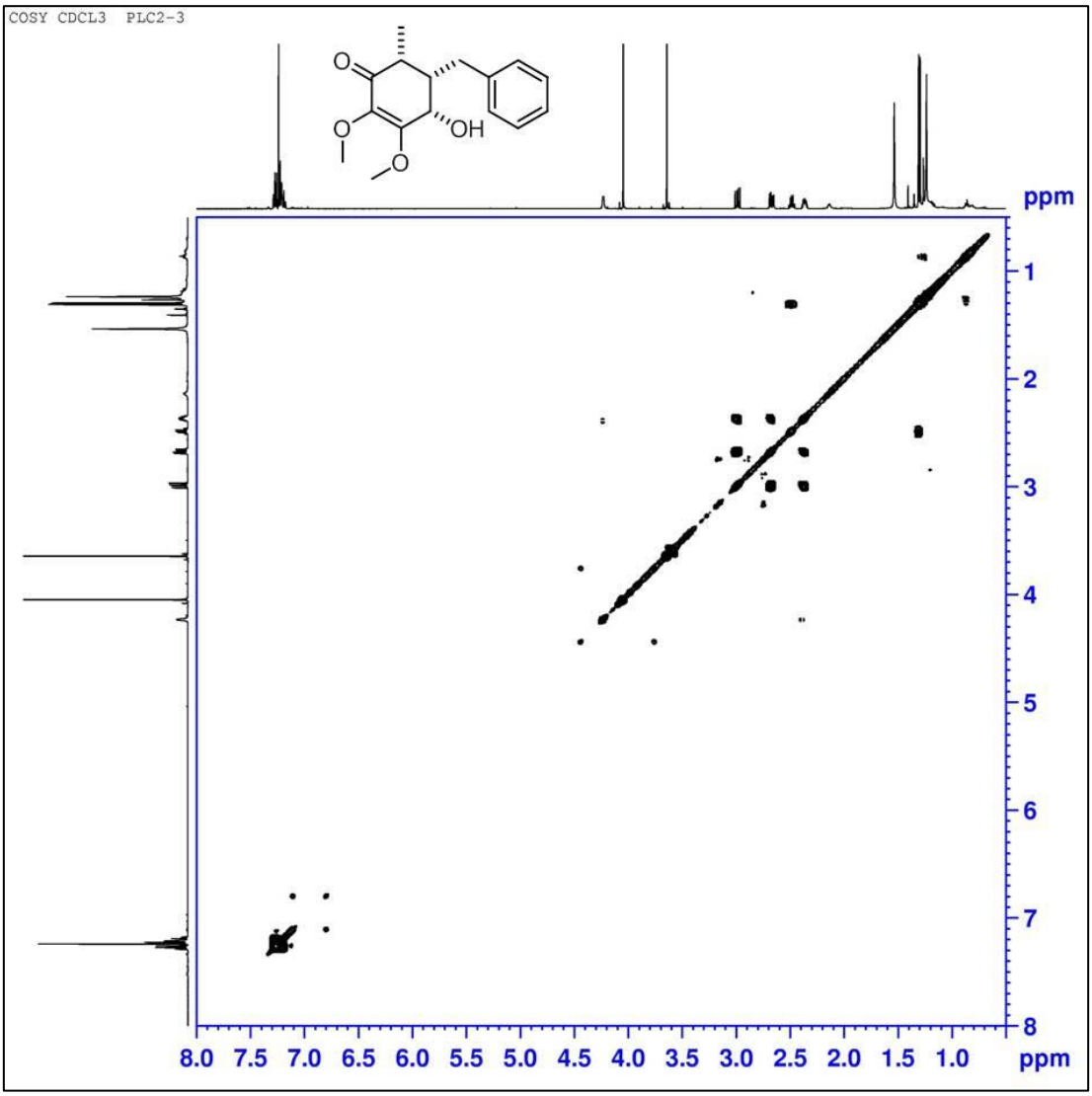

Figure S68. ^{1}H–^{1}H COSY NMR spectrum of compound **15c** (500 MHz, $CDCl_3$)

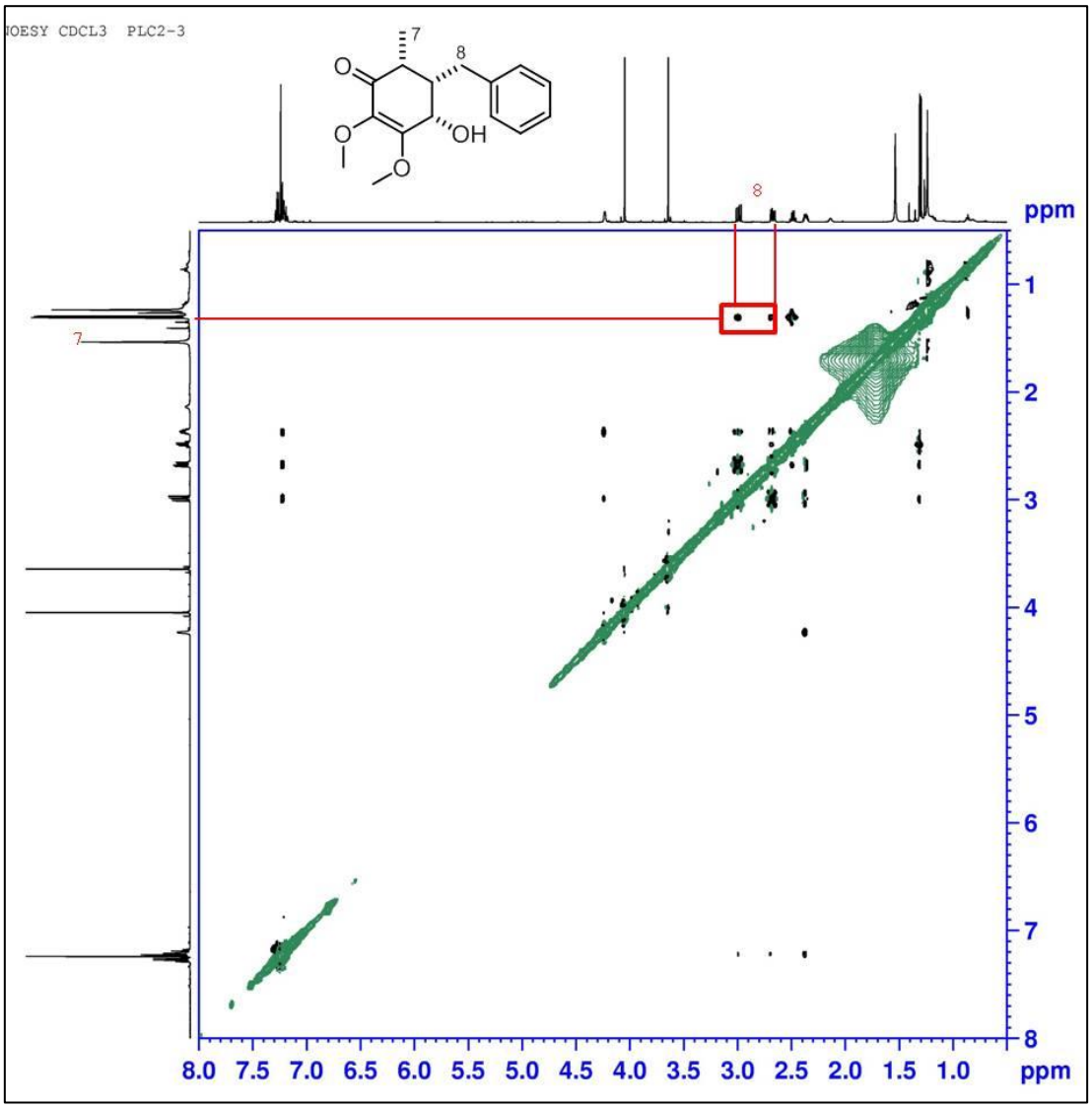

Figure S69. ^{1}H-^{1}H NOESY spectrum of compound **15c** (500 MHz, $CDCl_3$).

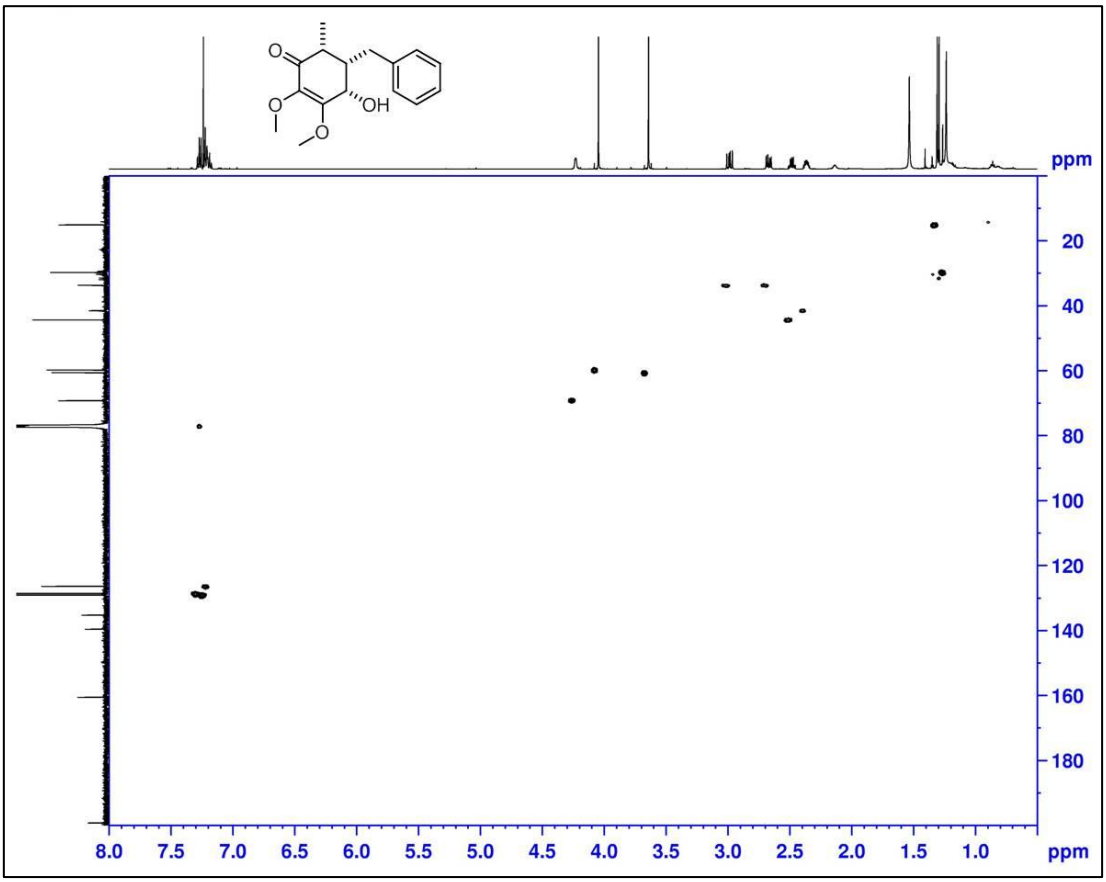

Figure S70. $^{1}H–^{13}C$ HSQC NMR spectrum of compound **15c** (125 MHz, $CDCl_3$)

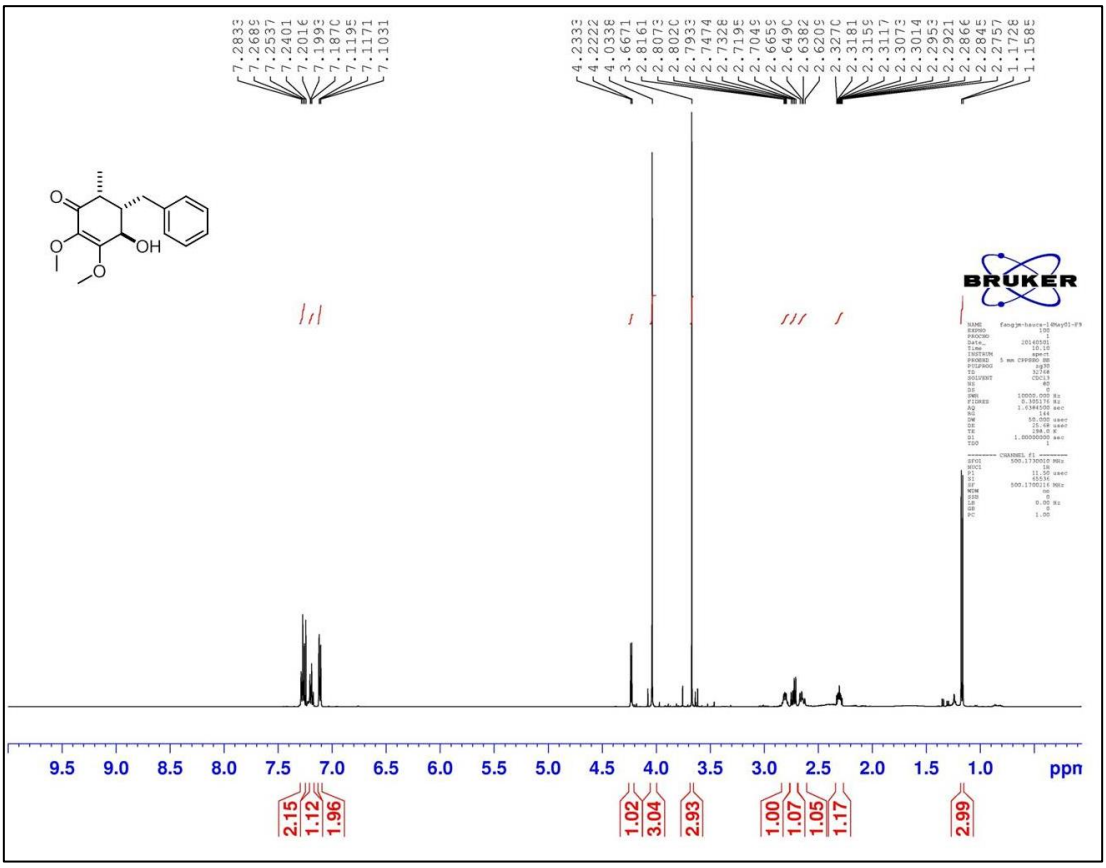

Figure S71. ^{1}H NMR spectrum of compound **15d** (500 MHz, $CDCl_3$)

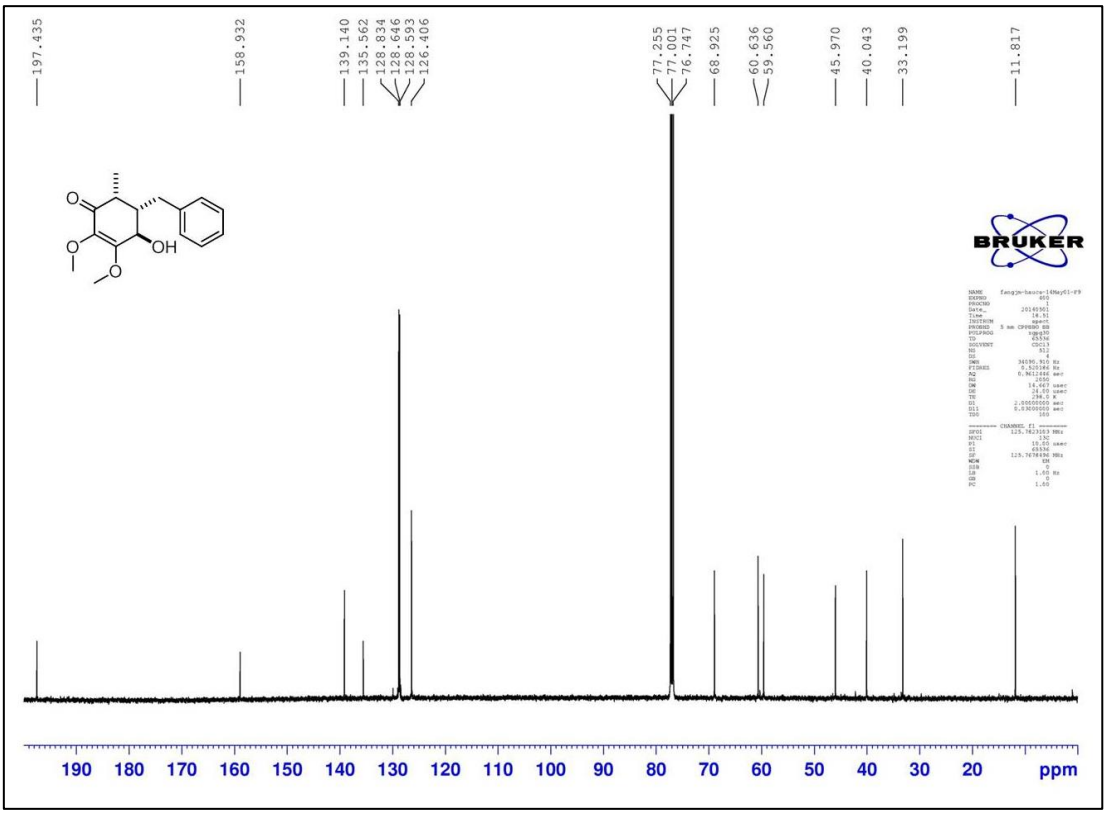

Figure S72. ^{13}C NMR spectrum of compound **15d** (125 MHz, $CDCl_3$)

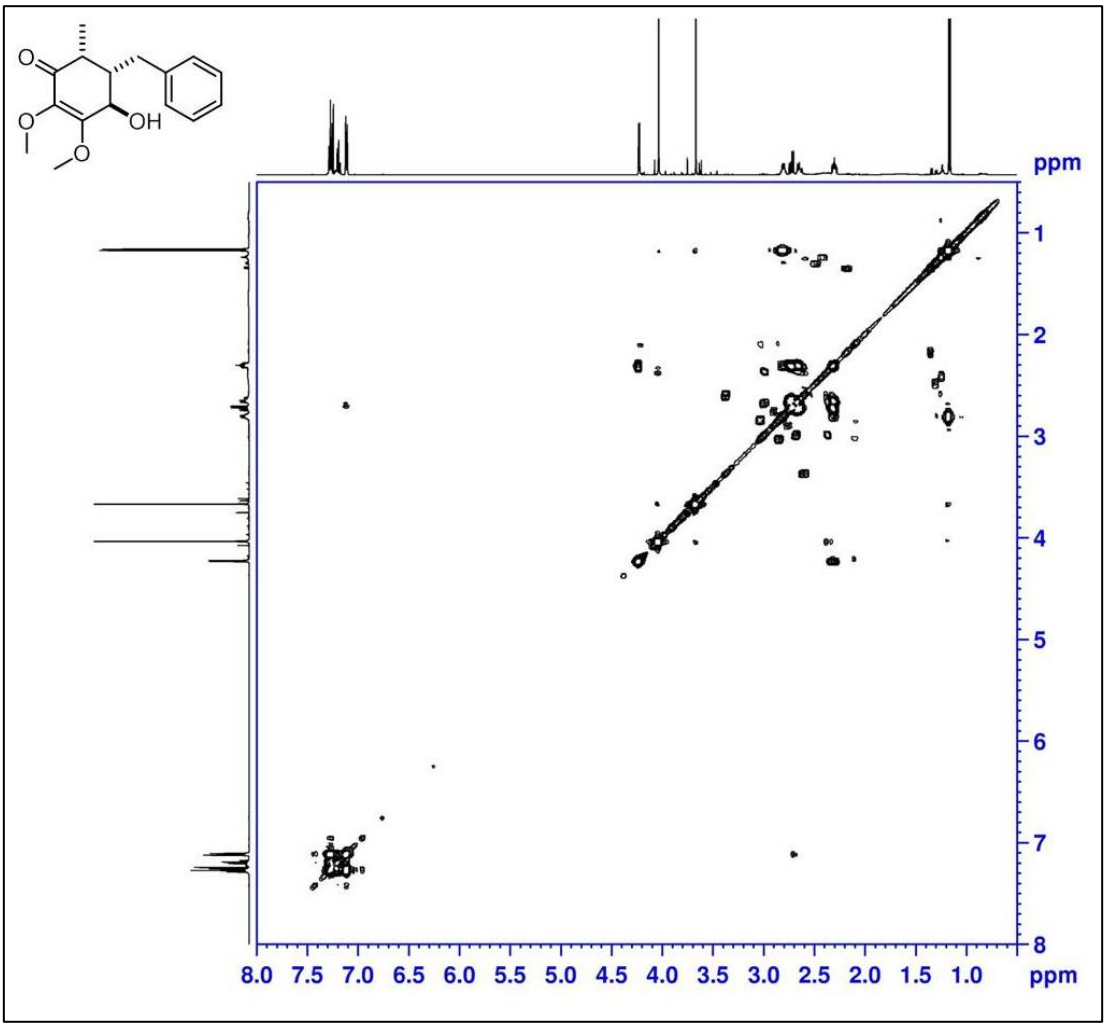

Figure S73. ^{1}H–^{1}H COSY NMR spectrum of compound **15d** (500 MHz, $CDCl_3$)

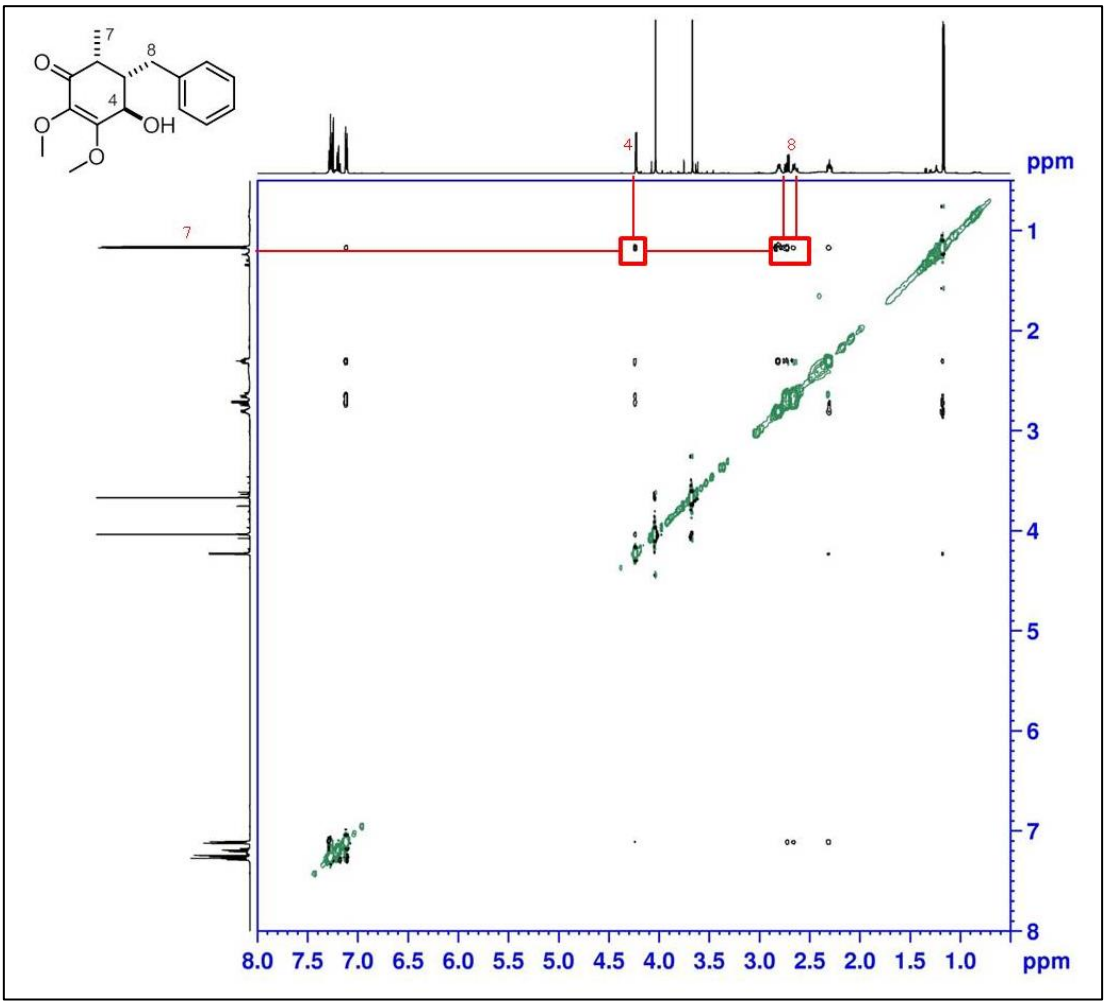

Figure S74. ^{1}H-^{1}H NOESY spectrum of compound **15d** (500 MHz, $CDCl_3$).

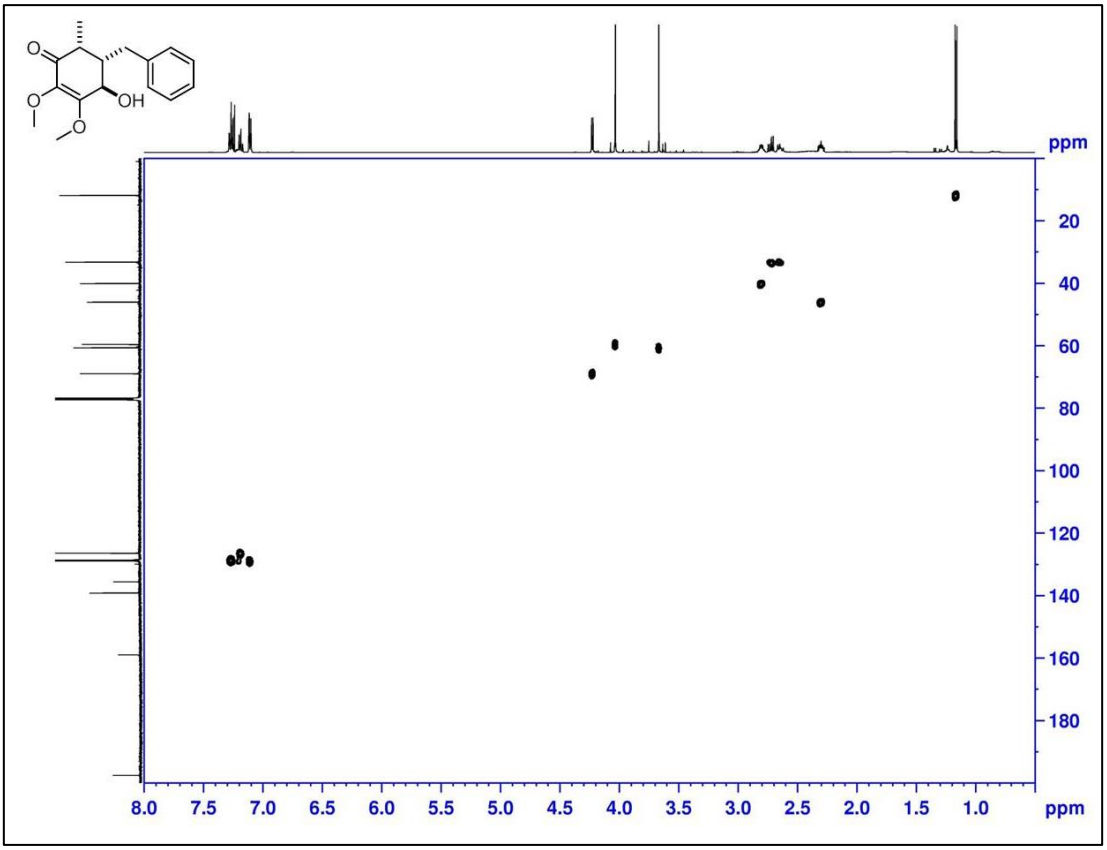

Figure S75. ^{1}H–^{13}C HSQC NMR spectrum of compound **15d** (125 MHz, $CDCl_3$)

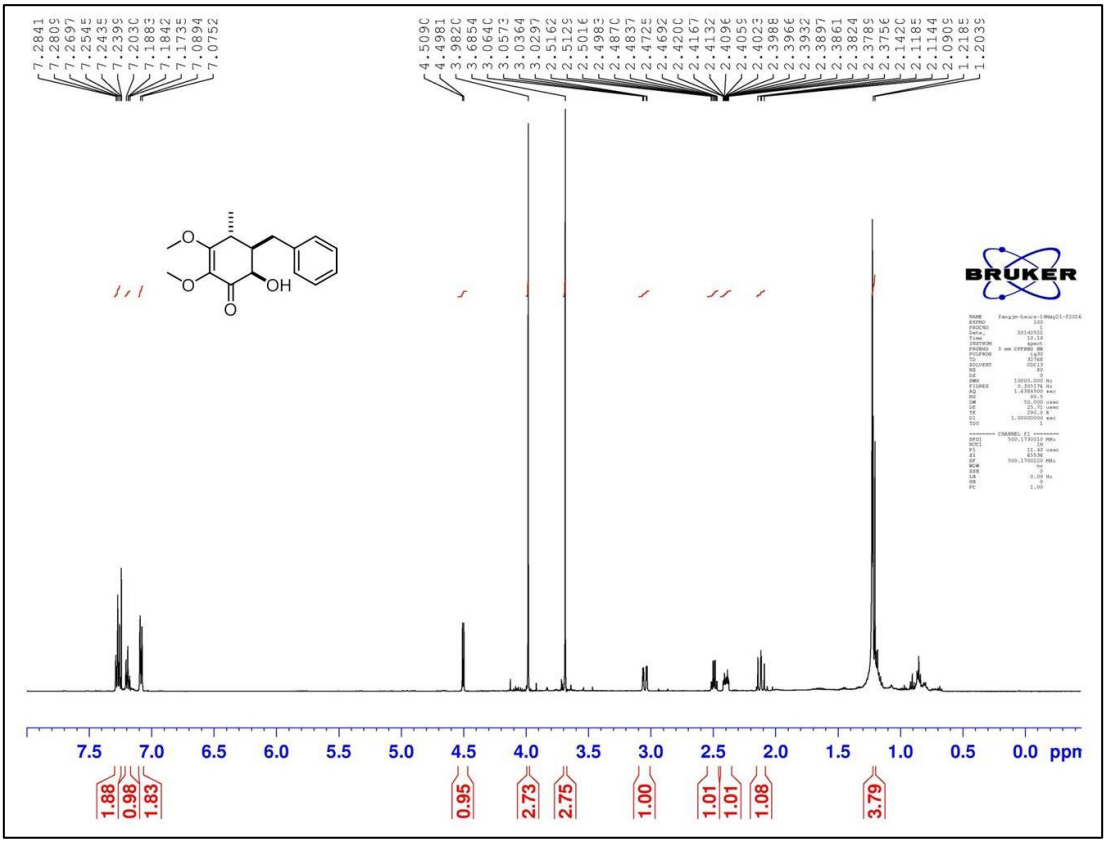

Figure S76. ^{1}H NMR spectrum of compound **16a** (500 MHz, $CDCl_3$)

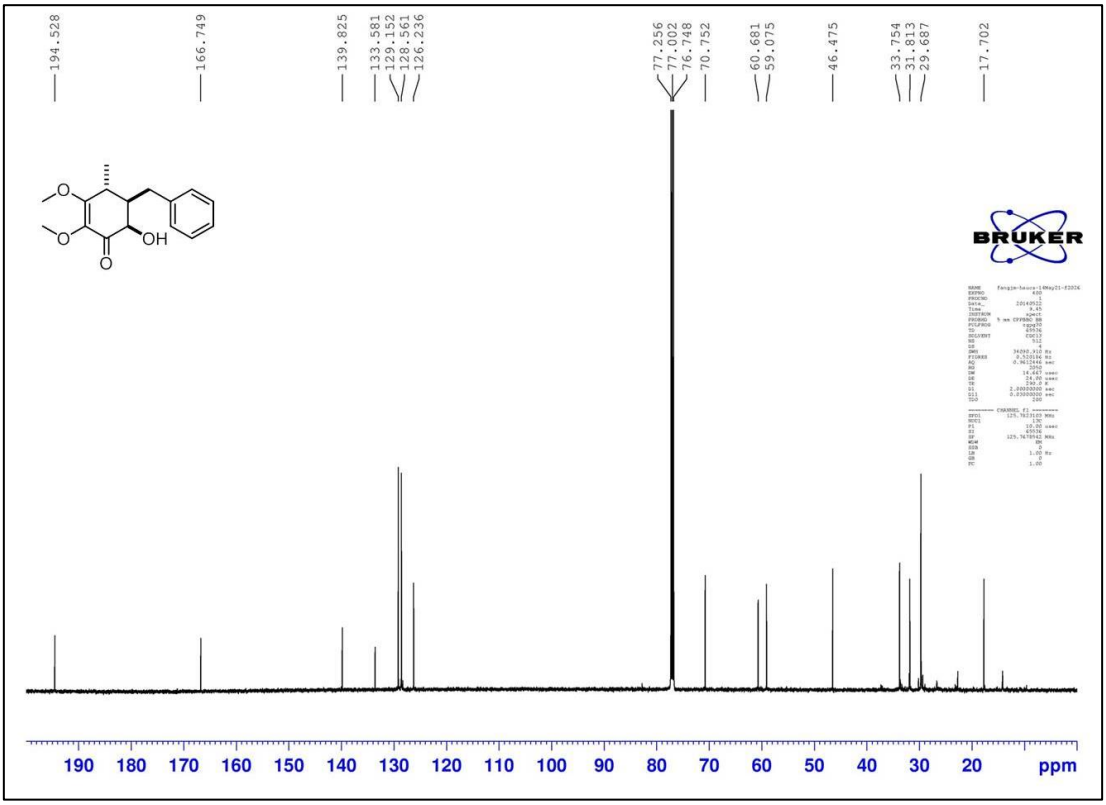

Figure S77. ^{13}C NMR spectrum of compound **16a** (125 MHz, $CDCl_3$)

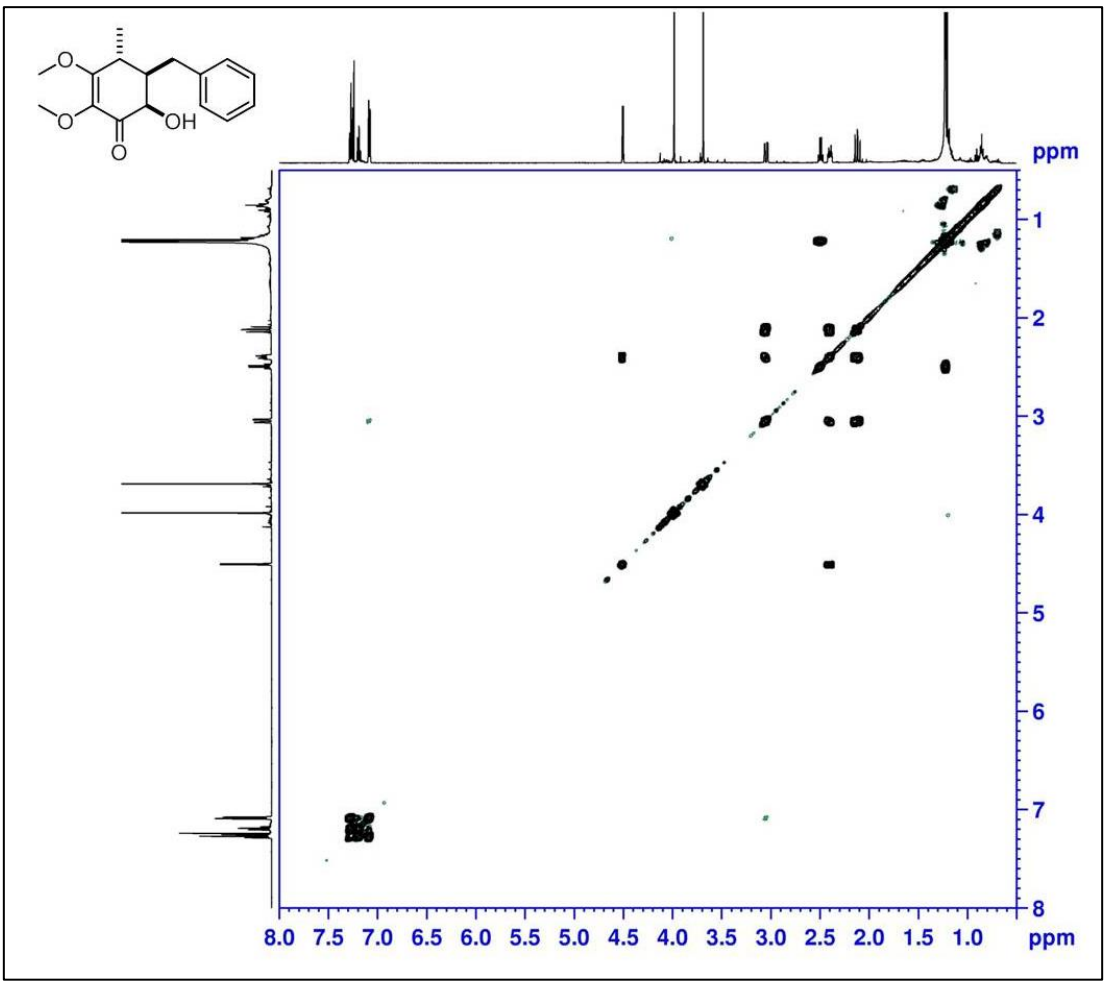

Figure S78. $^{1}H–^{1}H$ COSY NMR spectrum of compound **16a** (500 MHz, $CDCl_3$)

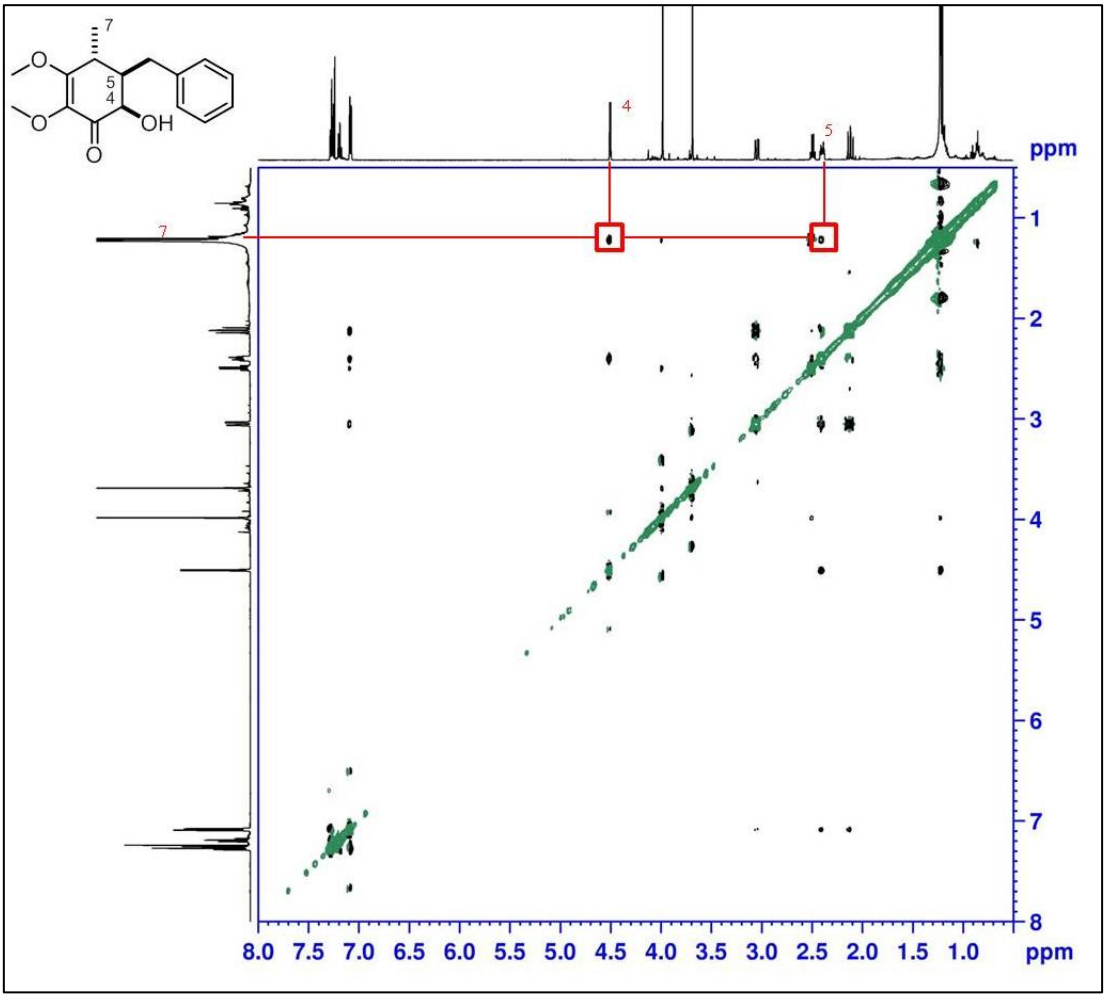

Figure S79. ^{1}H-^{1}H NOESY spectrum of compound **16a** (500 MHz, $CDCl_3$).

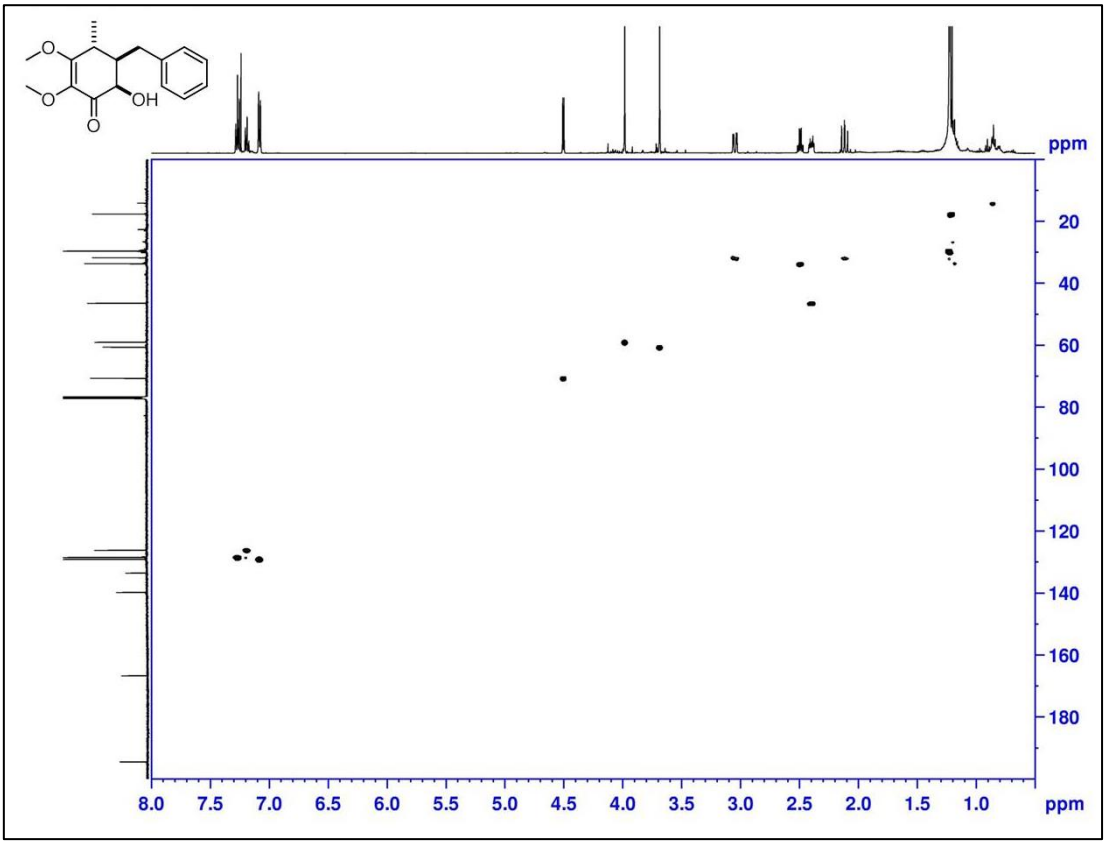

Figure S80. ^{1}H–^{13}C HSQC NMR spectrum of compound **16a** (125 MHz, $CDCl_3$)

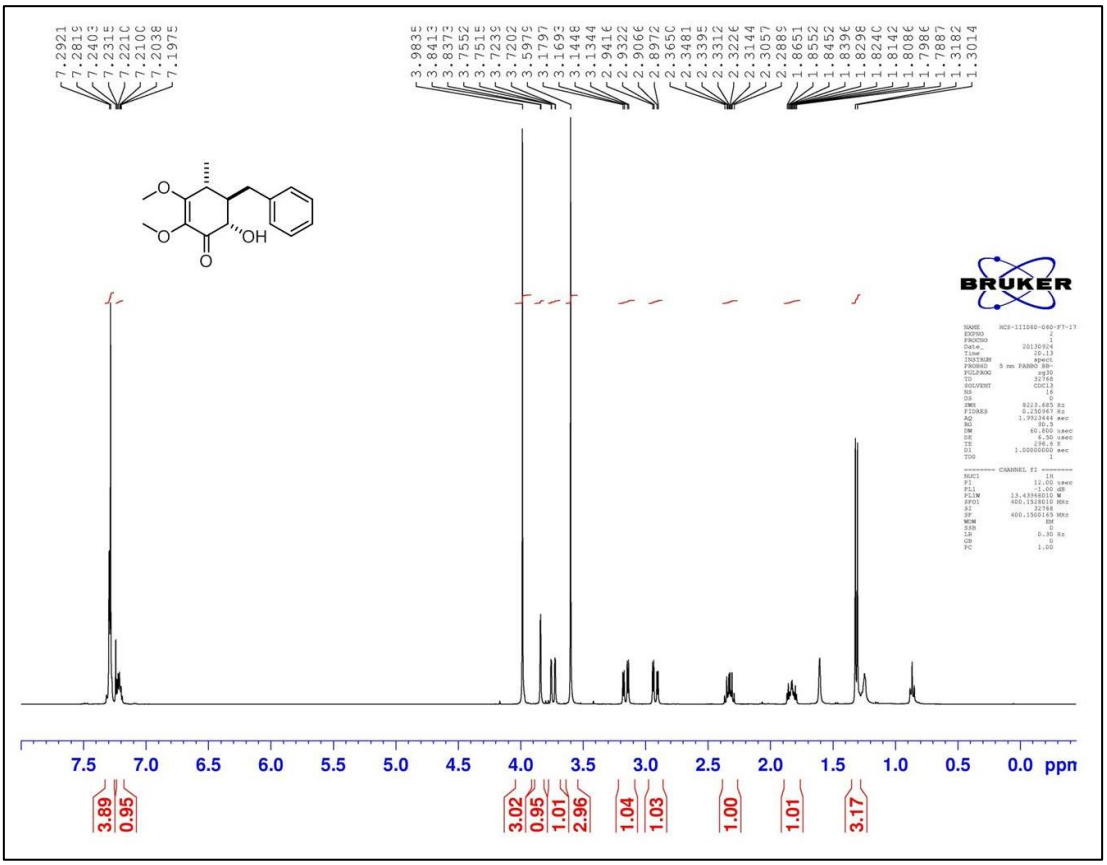

Figure S81. ^{1}H NMR spectrum of compound **16b** (400 MHz, $CDCl_3$)

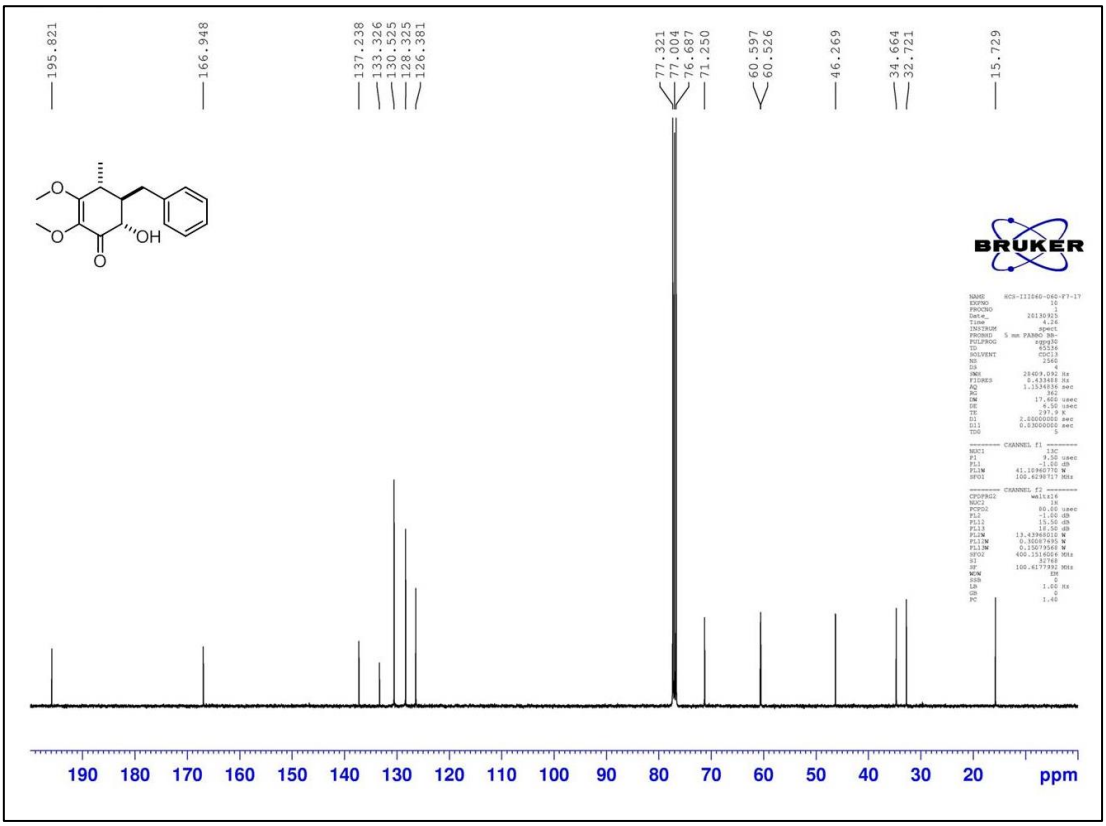

Figure S82. ^{13}C NMR spectrum of compound **16b** (100 MHz, $CDCl_3$)

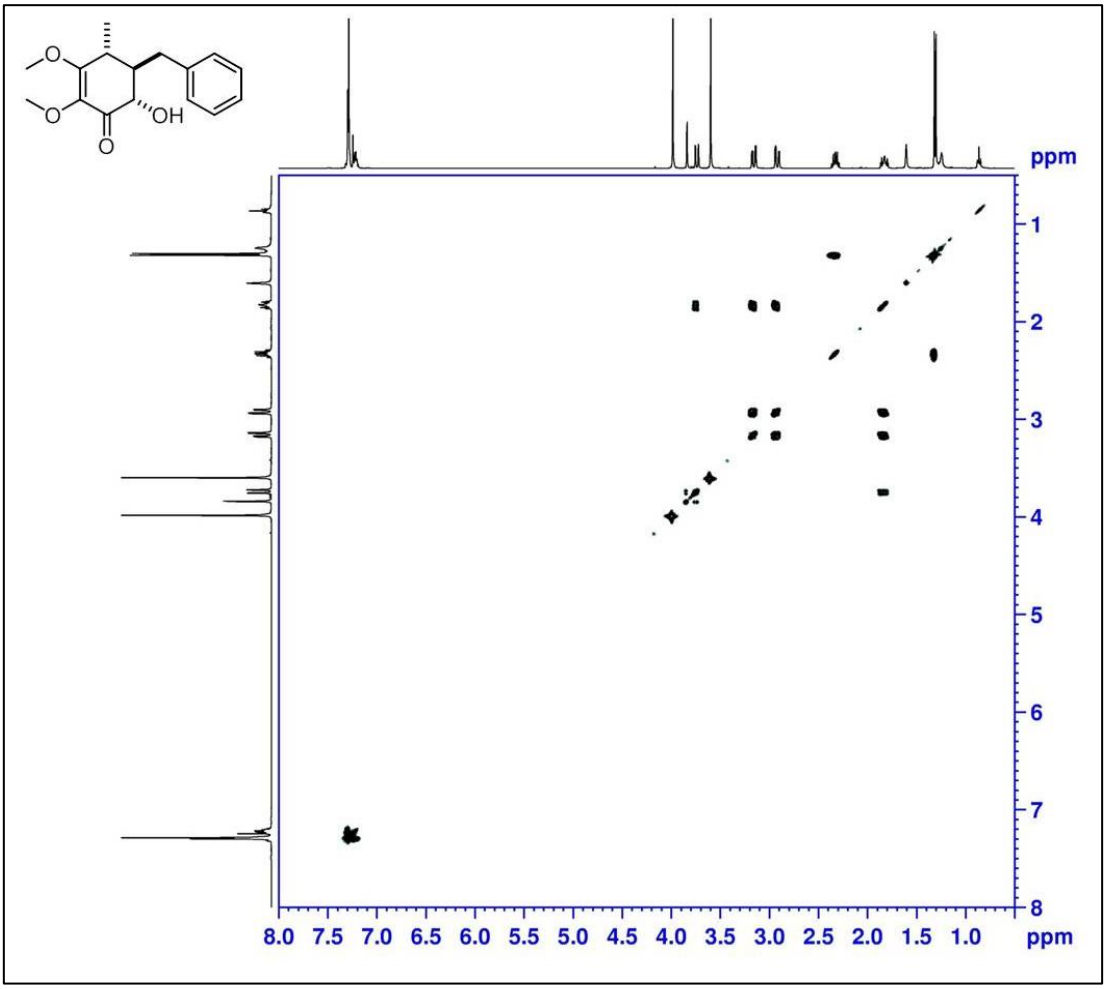

Figure S83. $^{1}H–^{1}H$ COSY NMR spectrum of compound **16b** (400 MHz, $CDCl_3$)

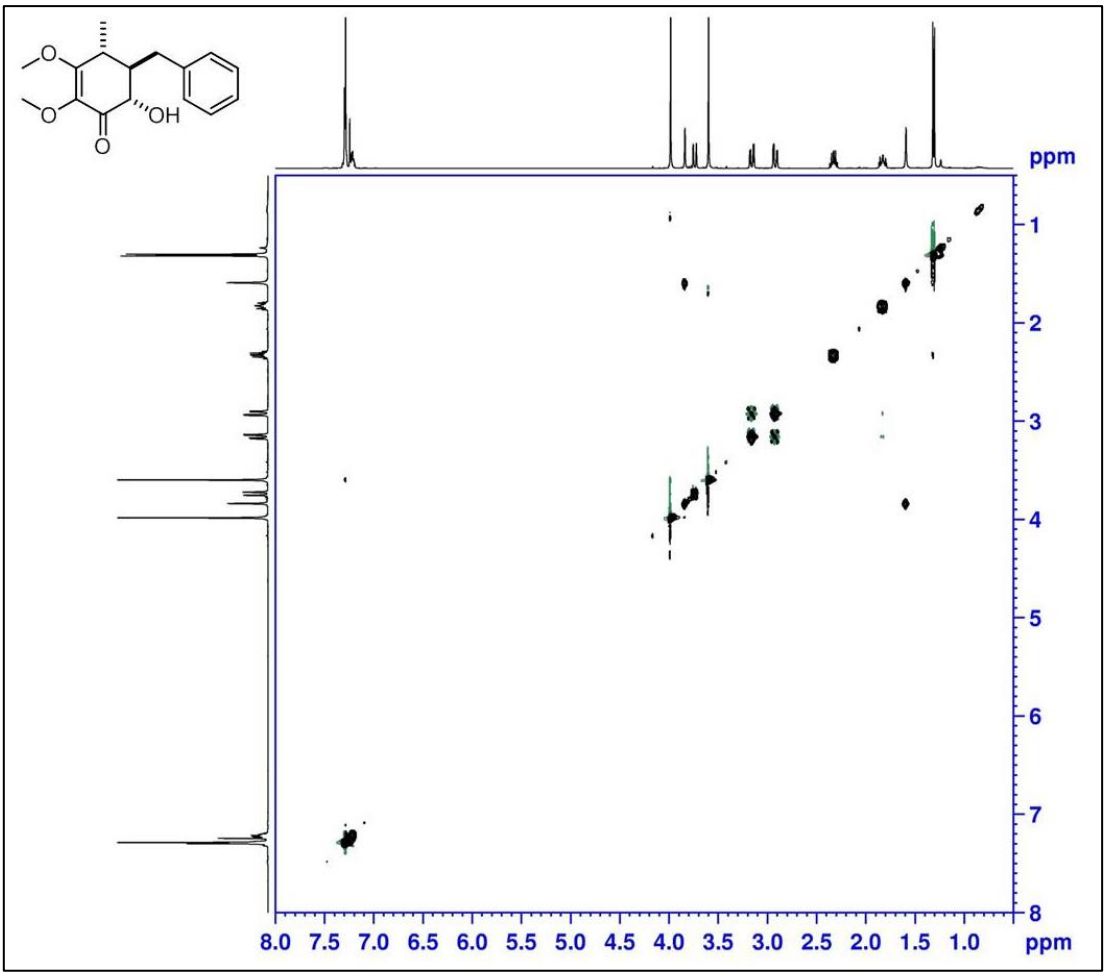

Figure S84. ^{1}H-^{1}H NOESY spectrum of compound **16b** (400 MHz, $CDCl_3$).

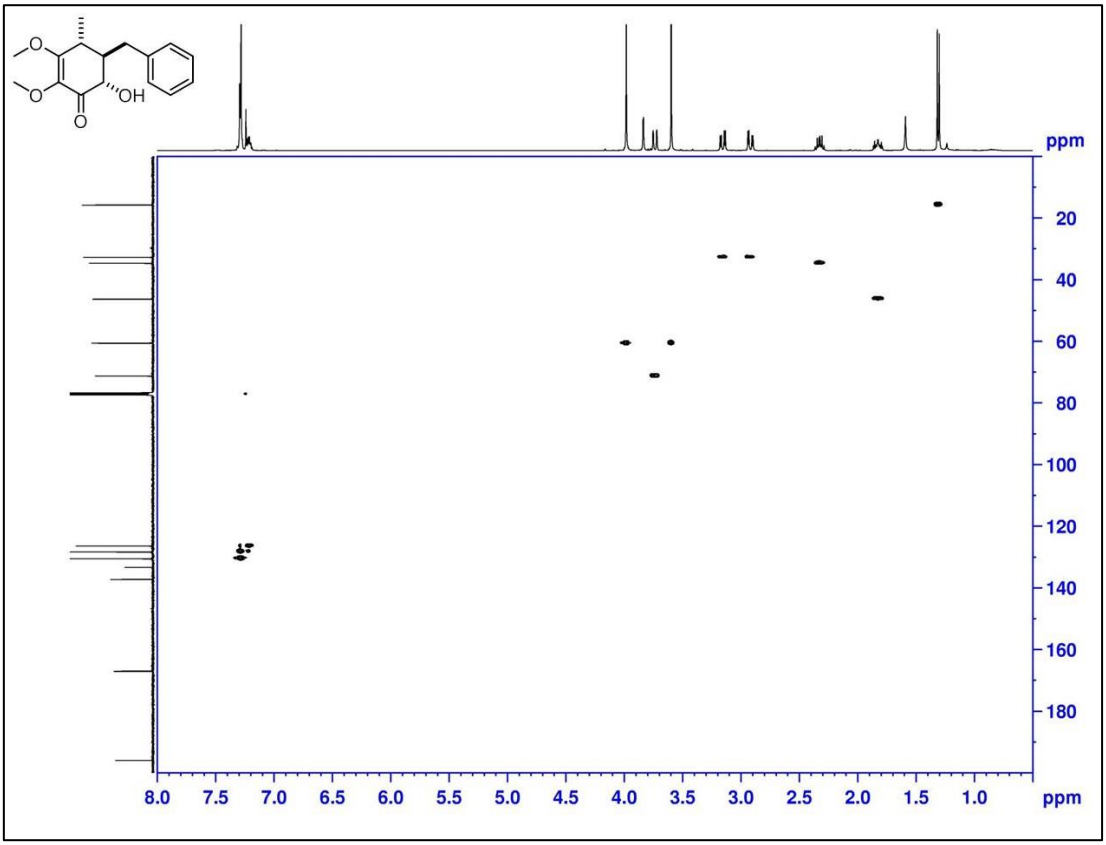

Figure S85. ^{1}H–^{13}C HSQC NMR spectrum of compound **16b** (100 MHz, $CDCl_3$)

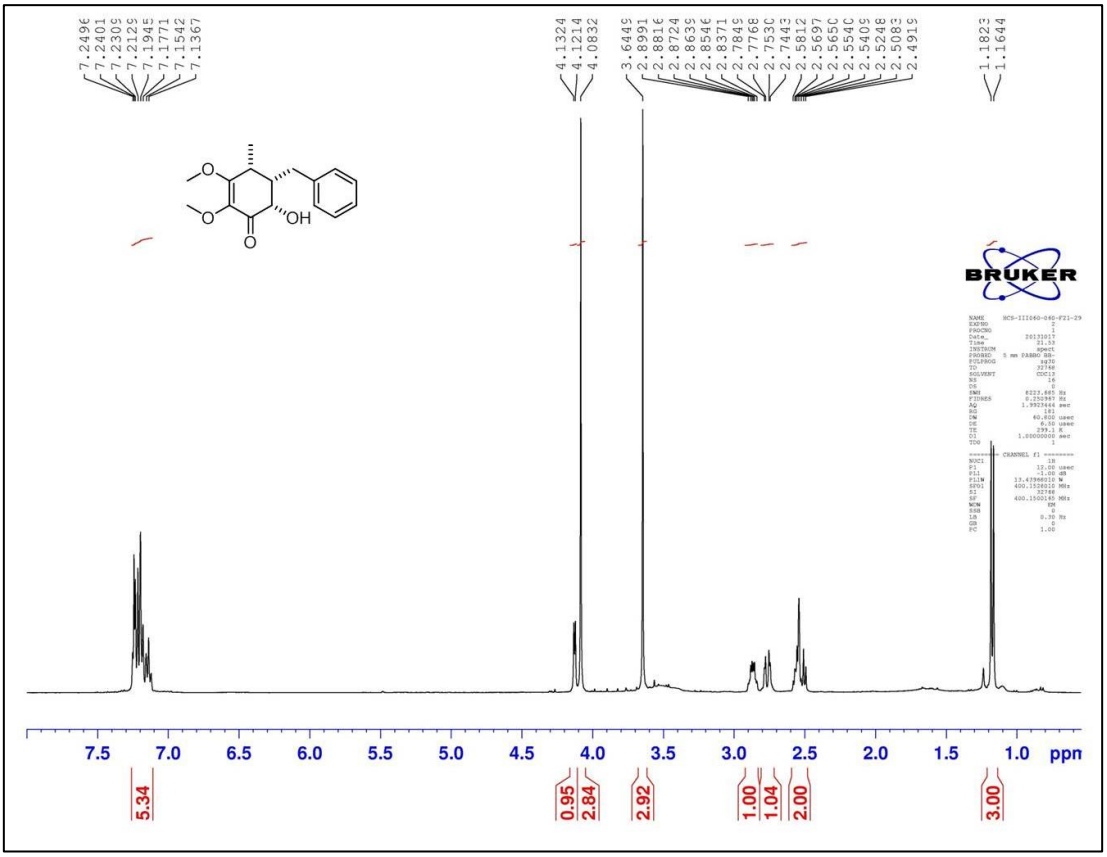

Figure S86. ^{1}H NMR spectrum of compound **16c** (400 MHz, $CDCl_3$)

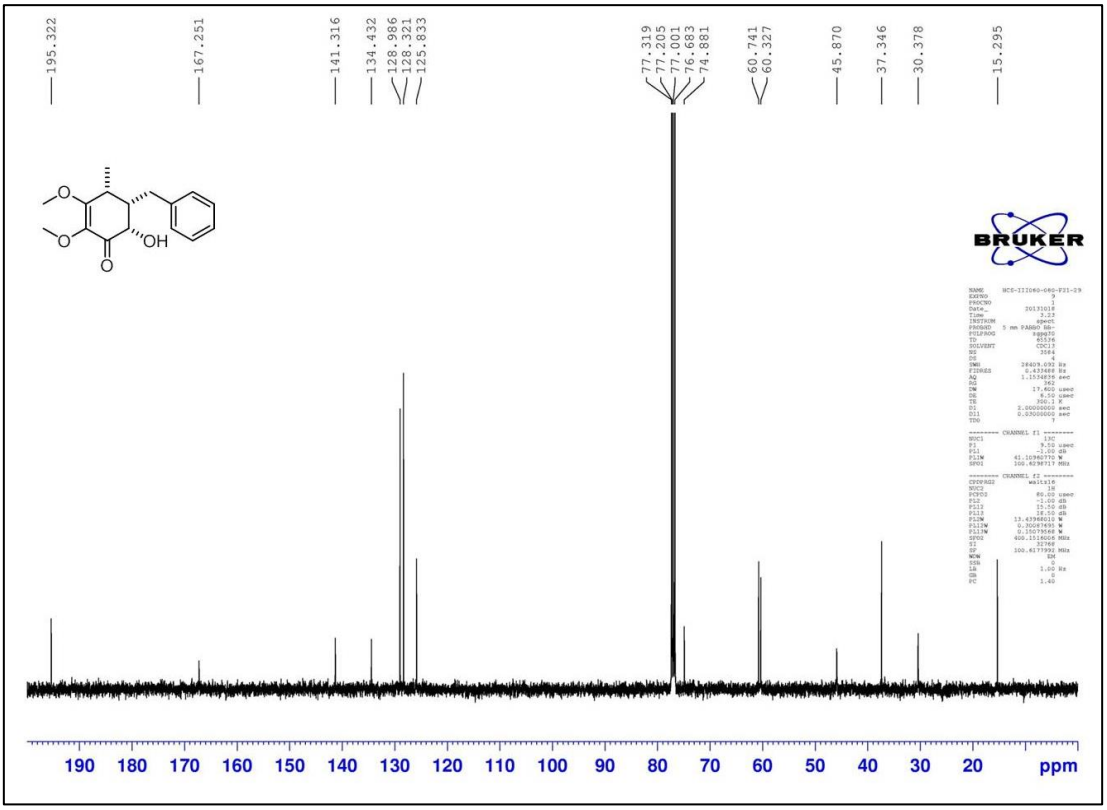

Figure S87. ^{13}C NMR spectrum of compound **16c** (100 MHz, $CDCl_3$)

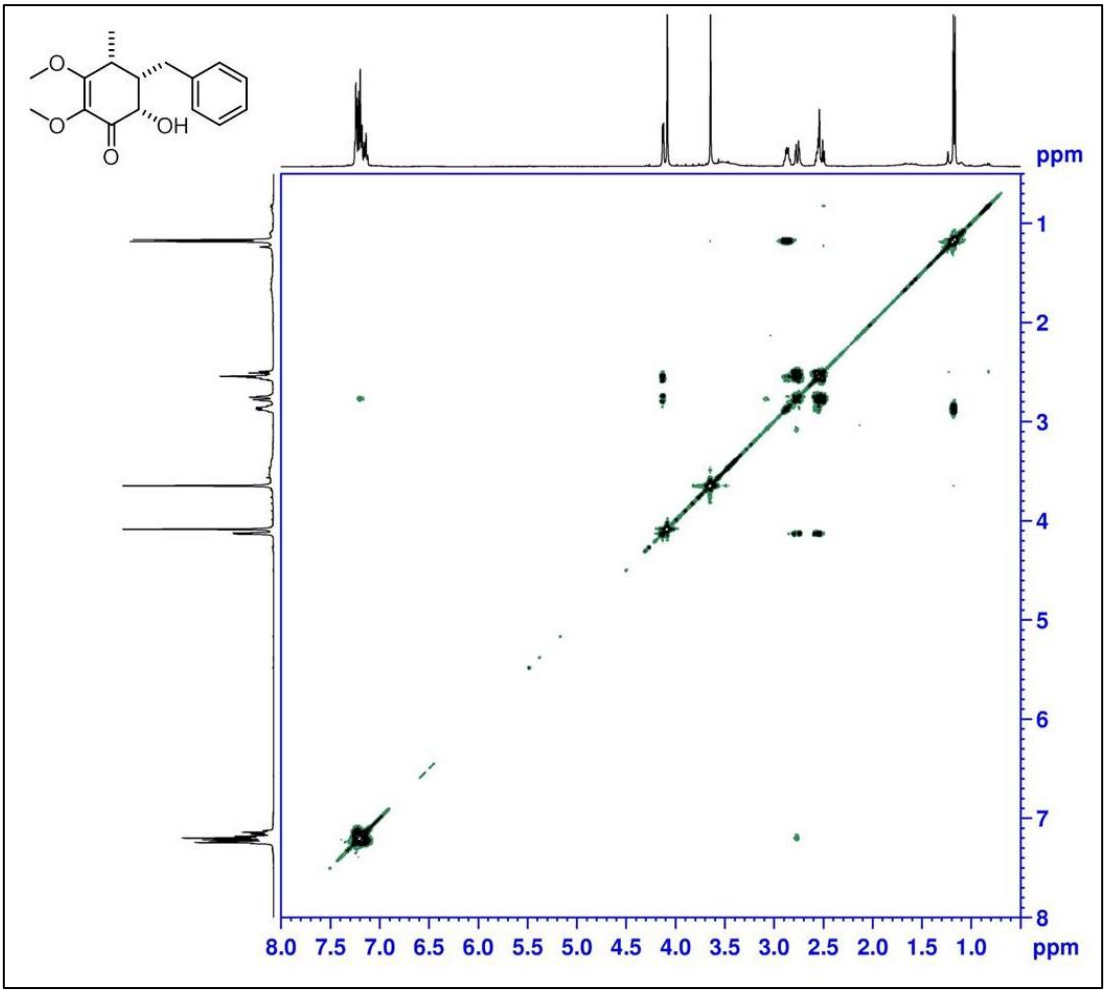

Figure S88. $^{1}H–^{1}H$ COSY NMR spectrum of compound **16c** (400 MHz, $CDCl_3$)

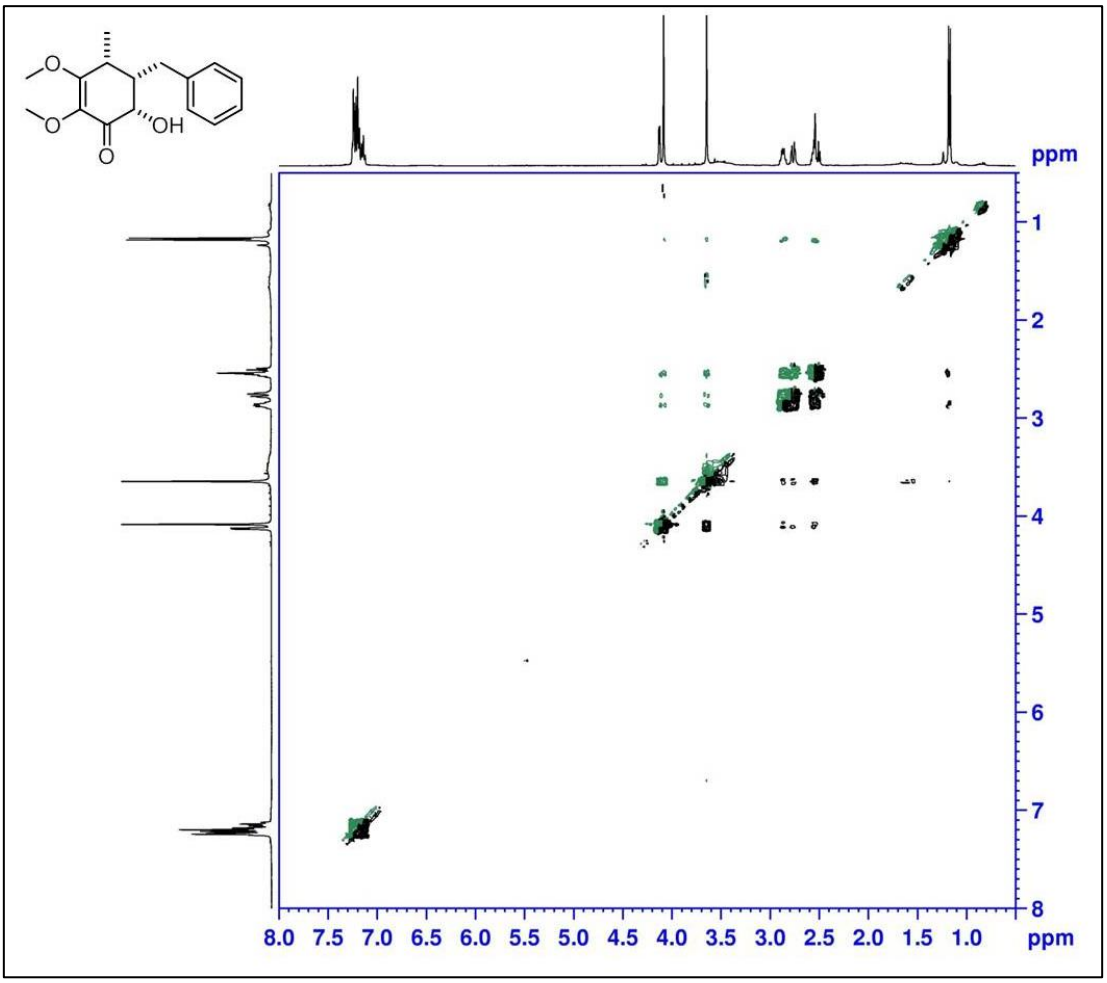

Figure S89. ^{1}H-^{1}H NOESY spectrum of compound **16c** (400 MHz, $CDCl_3$).

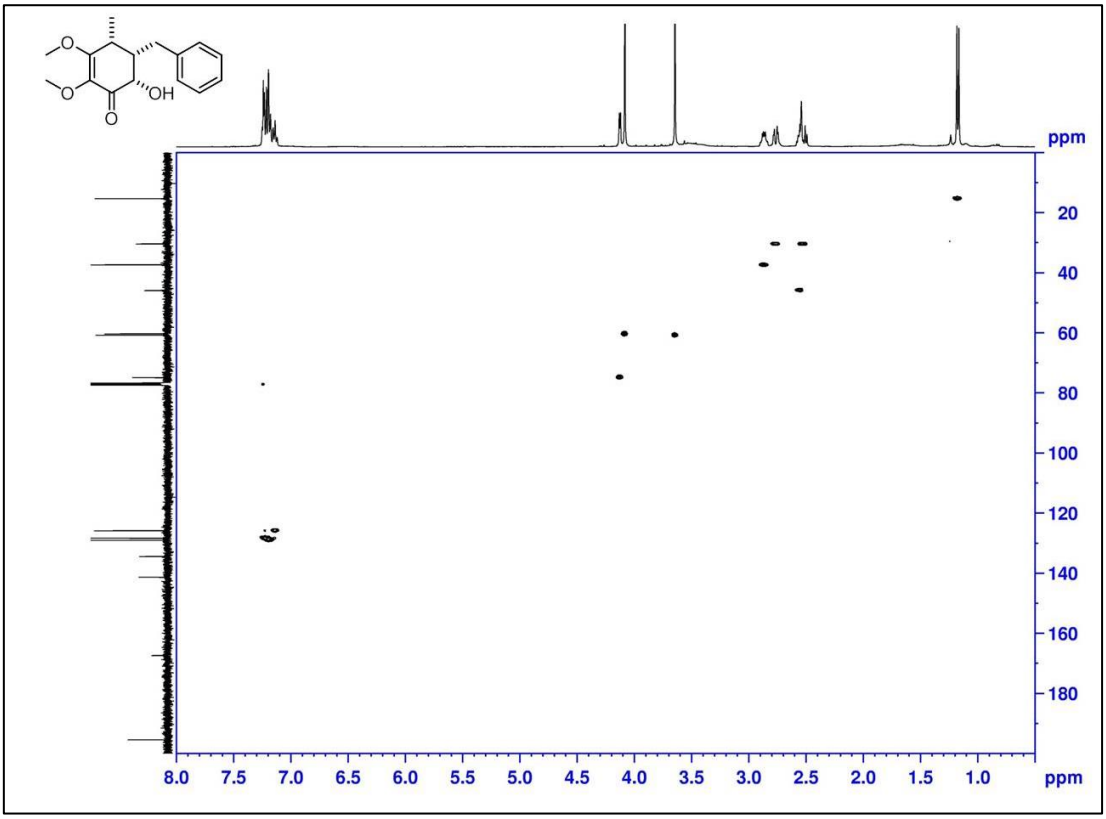

Figure S90. ^{1}H–^{13}C HSQC NMR spectrum of compound **16c** (100 MHz, $CDCl_3$)

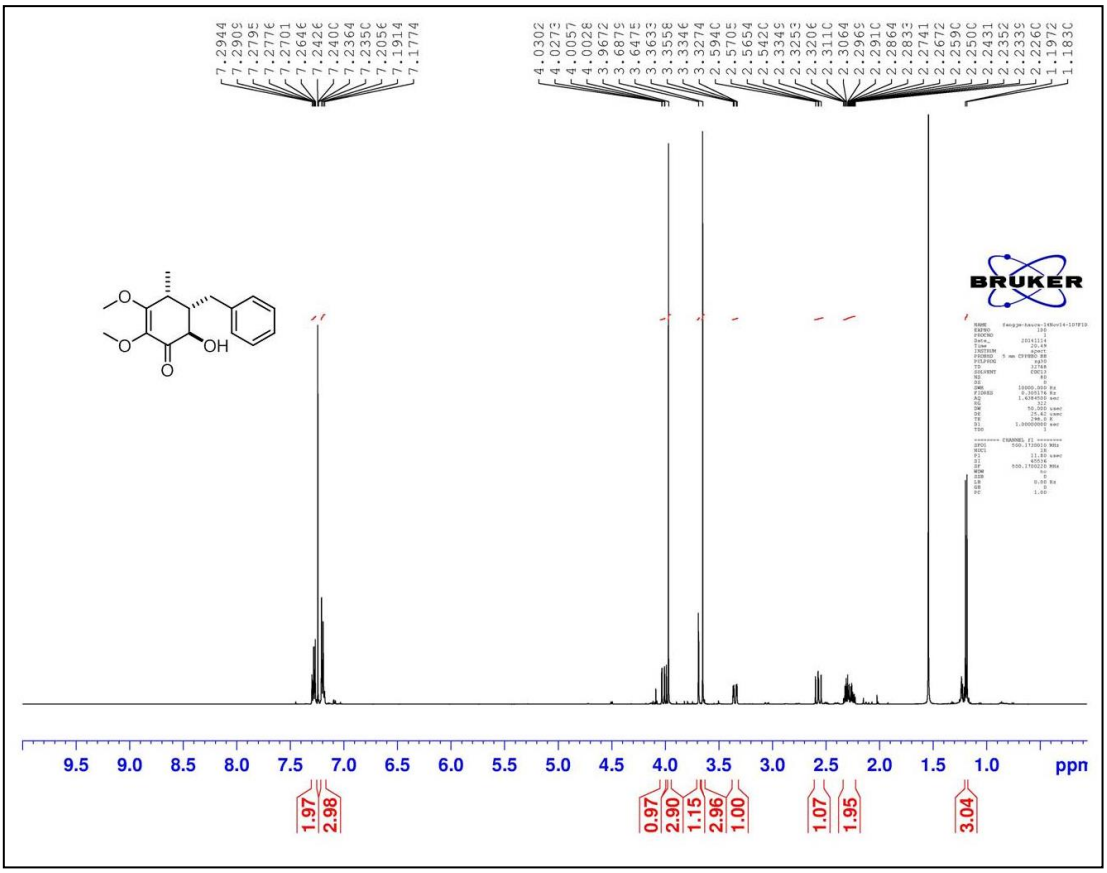

Figure S91. ^{1}H NMR spectrum of compound **16d** (500 MHz, $CDCl_3$)

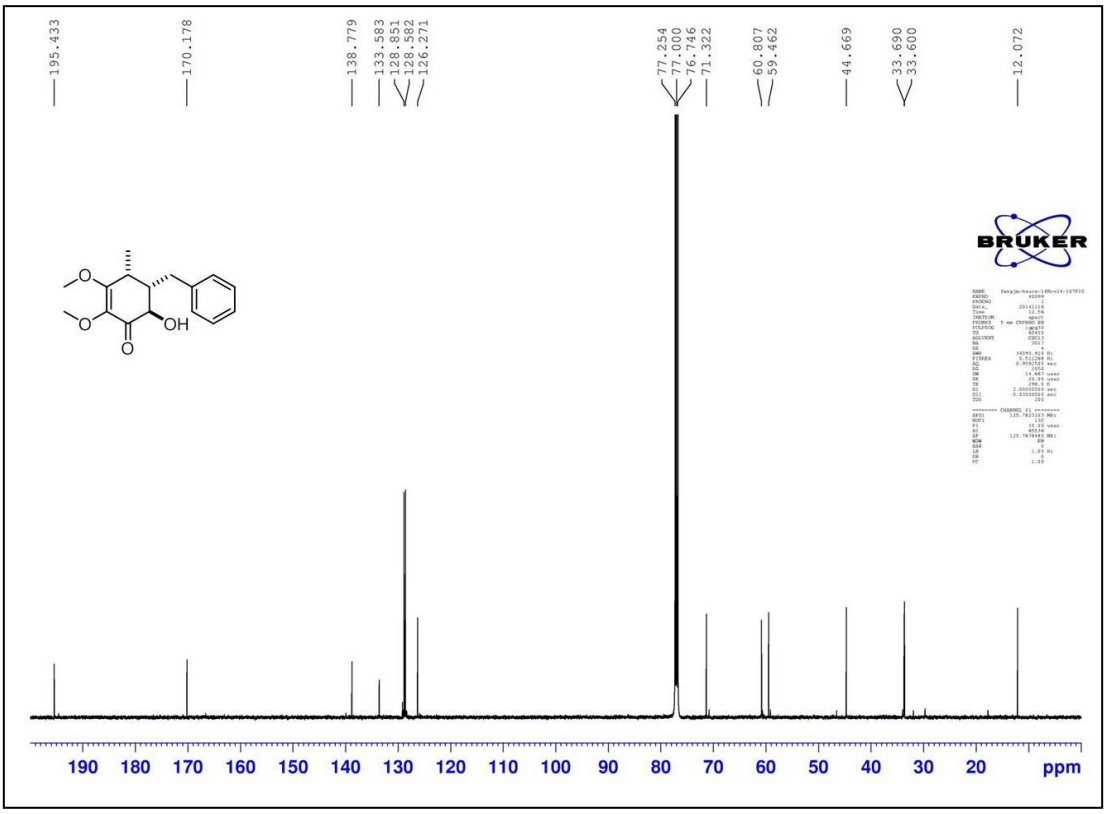

Figure S92. ^{13}C NMR spectrum of compound **16d** (125 MHz, $CDCl_3$)

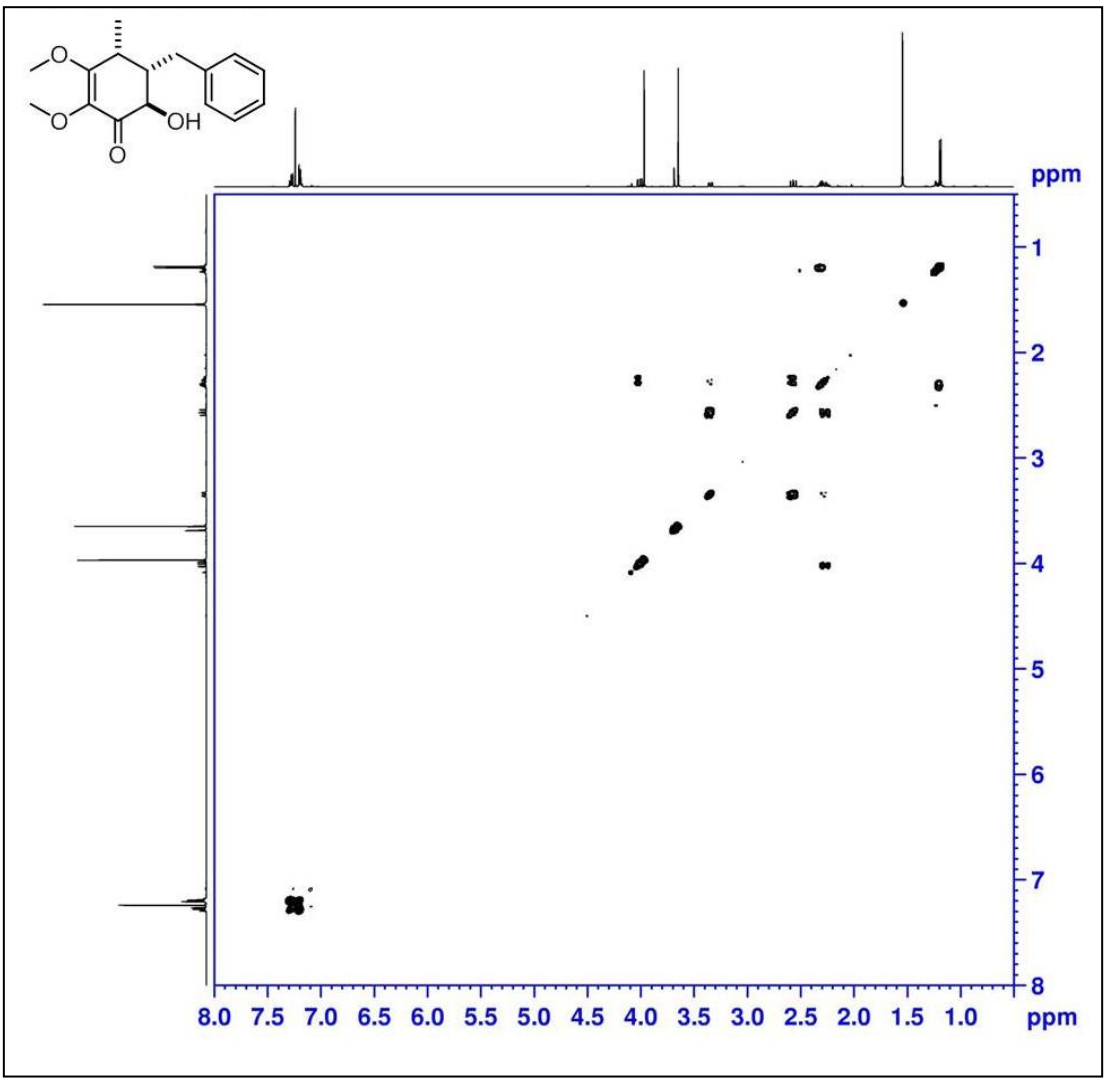

Figure S93. $^{1}H–^{1}H$ COSY NMR spectrum of compound **16d** (500 MHz, $CDCl_3$)

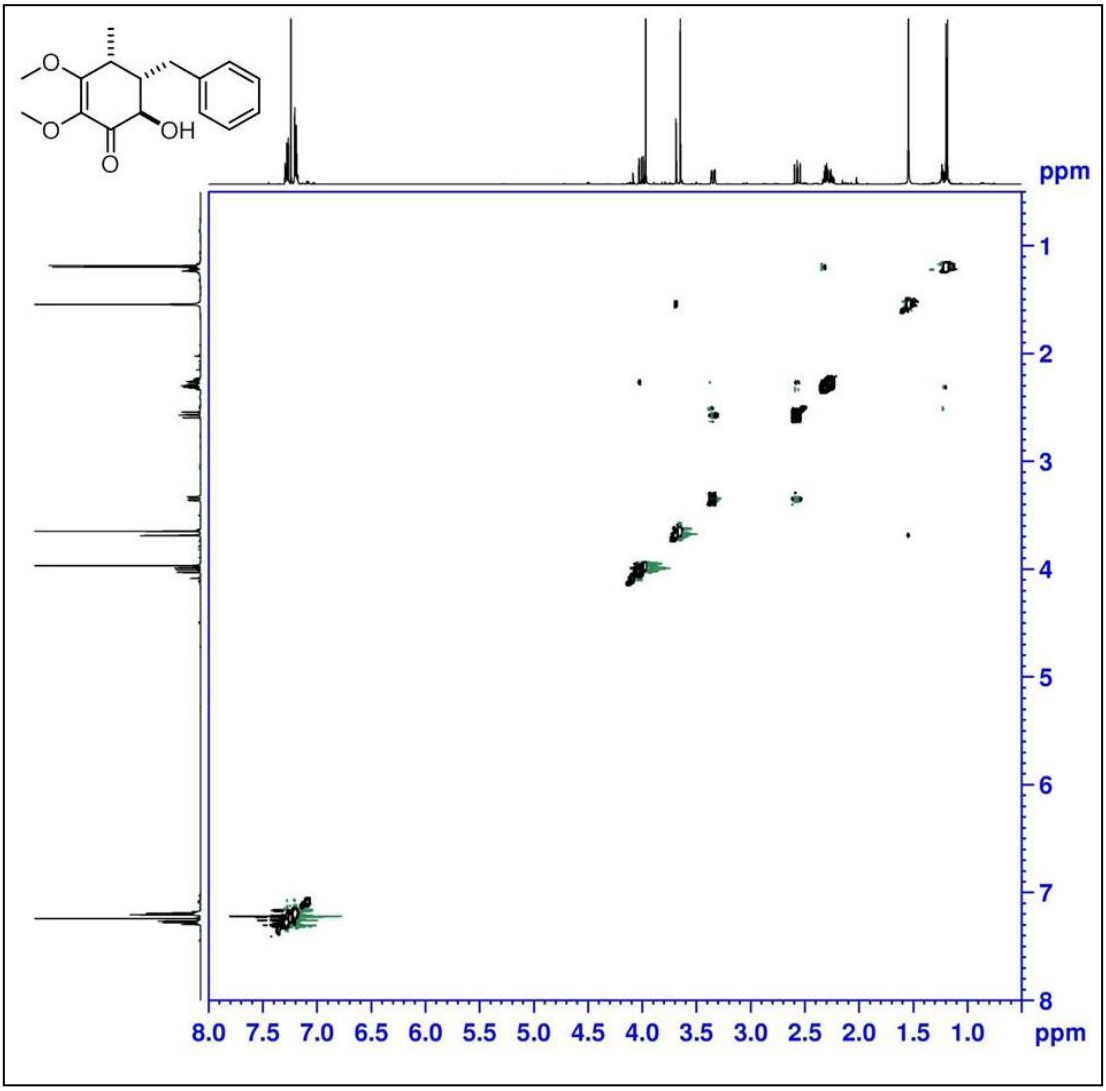

Figure S94. ^{1}H–^{1}H NOESY NMR spectrum of compound **16d** (500 MHz, $CDCl_3$)

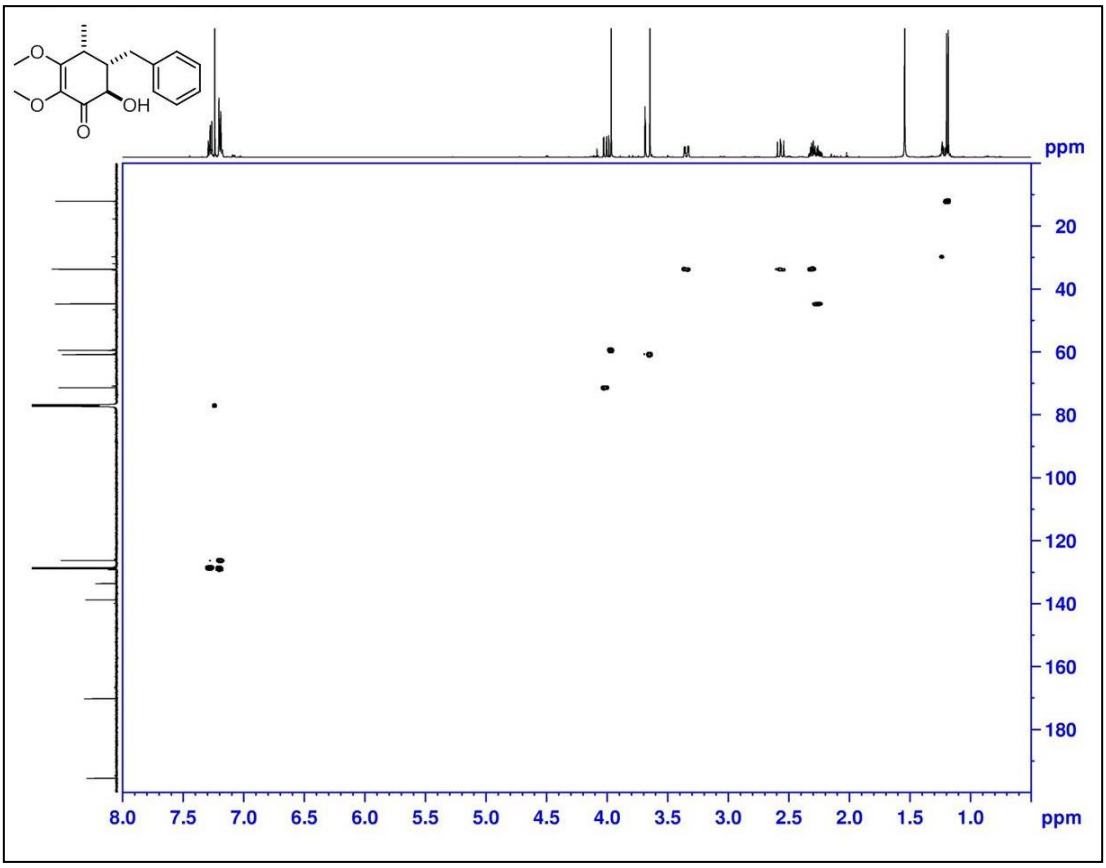

Figure S95. ^{1}H–^{13}C HSQC NMR spectrum of compound **16d** (125 MHz, $CDCl_3$)

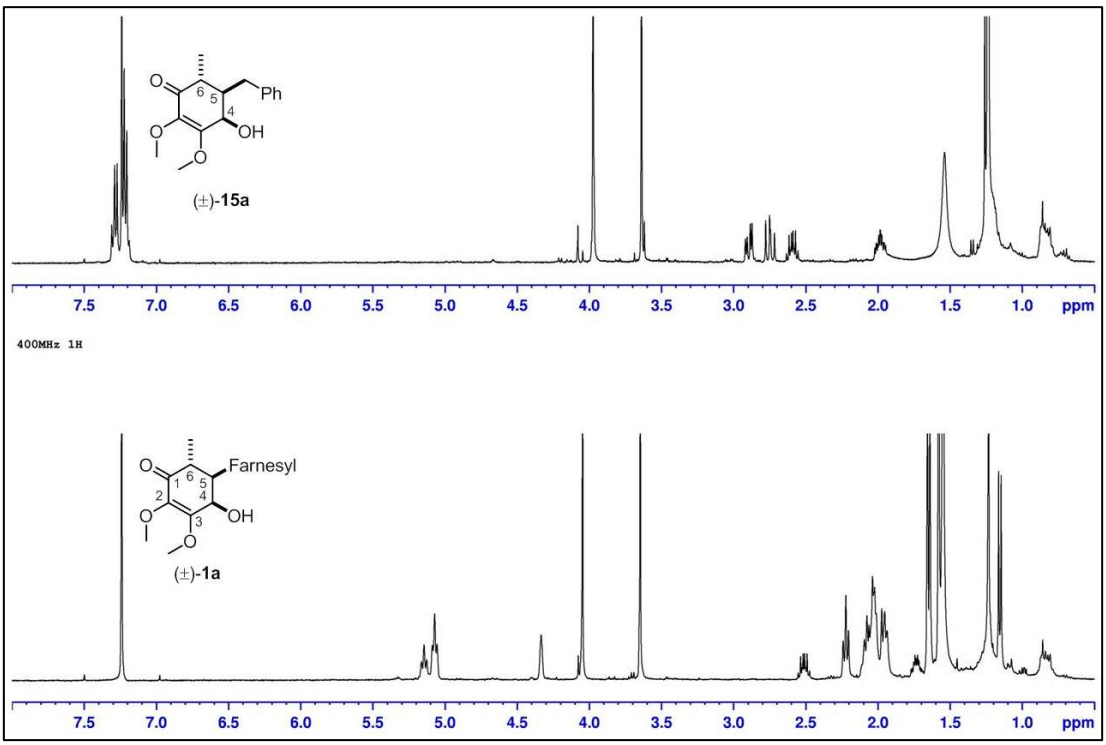

Figure S96. Comparison of the ^{1}H NMR spectra of **1a** and **15a** (400 MHz, $CDCl_3$).

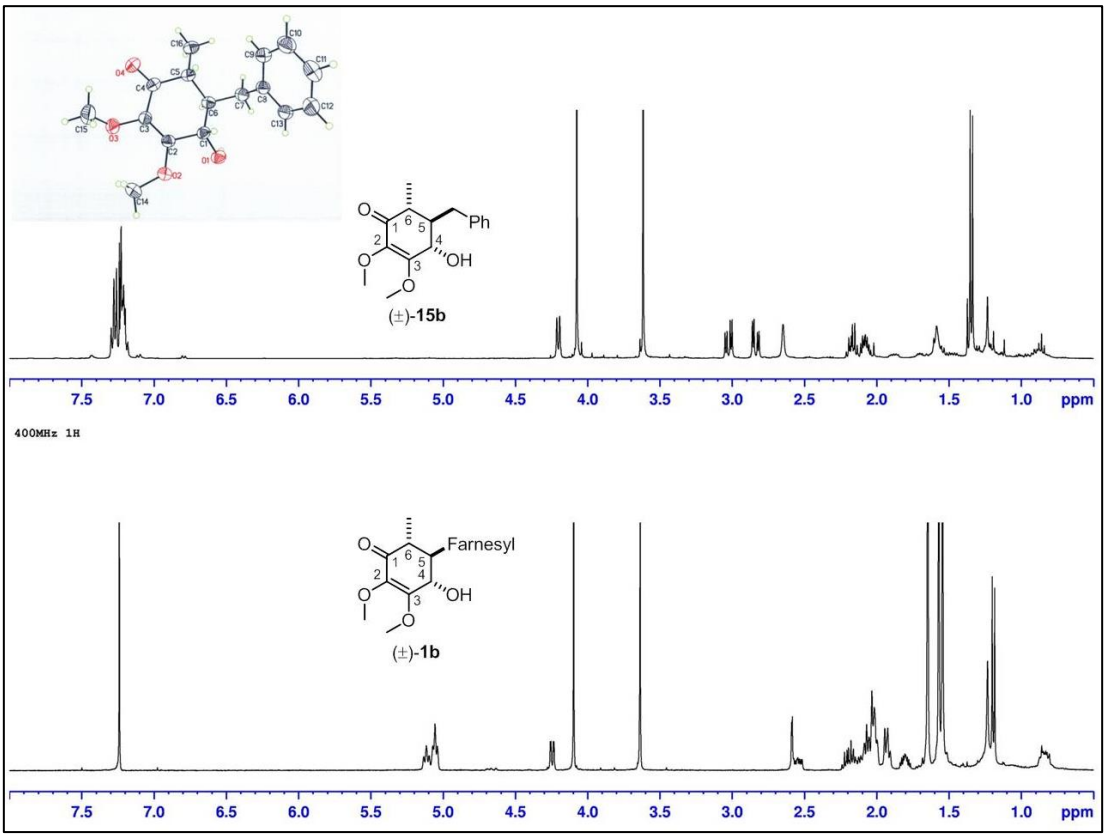

Figure S97. ORTEP drawing of compounds **15b** (IC16470, all-*trans*) and comparison of the ^{1}H NMR spectra of **1b** with **15b** (400 MHz, $CDCl_3$).

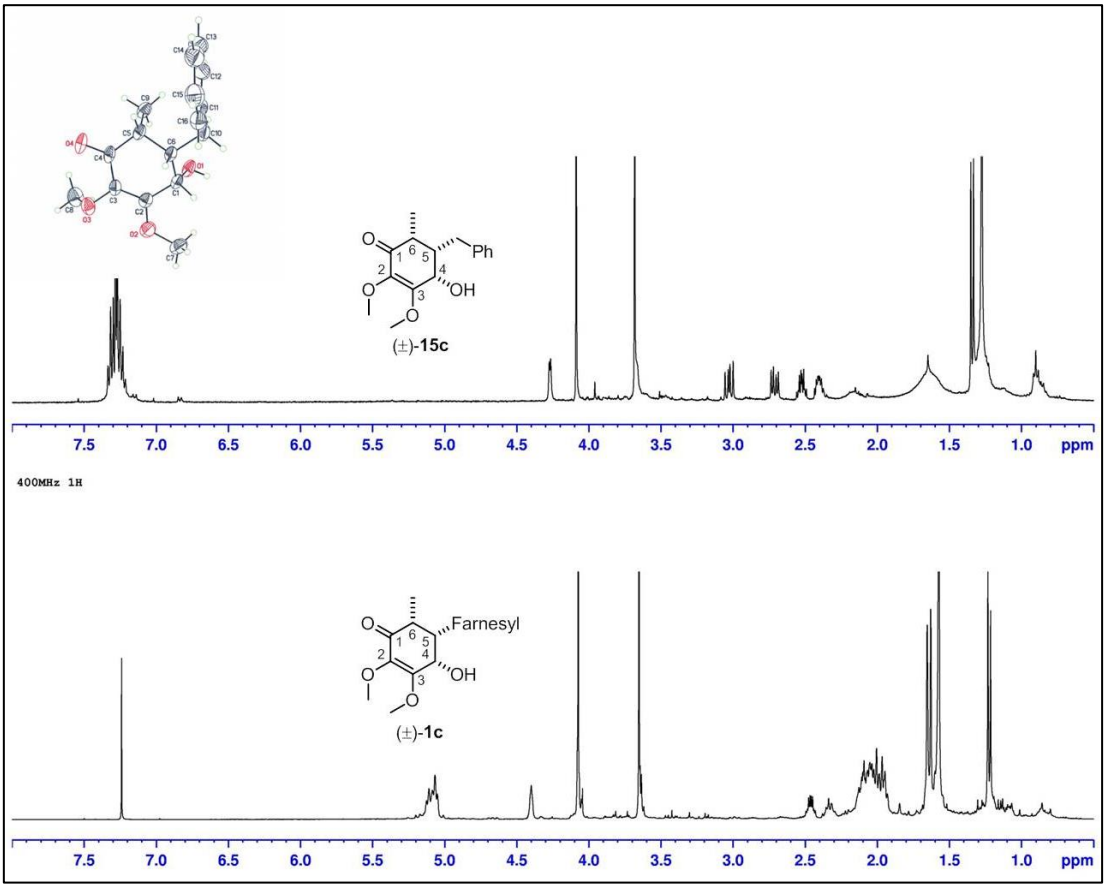

Figure S98. ORTEP drawing (IC16707) of compound **15c** (all-*cis*) and comparison of the ^{1}H NMR spectra of **1c** with **15c** (400 MHz, $CDCl_3$).

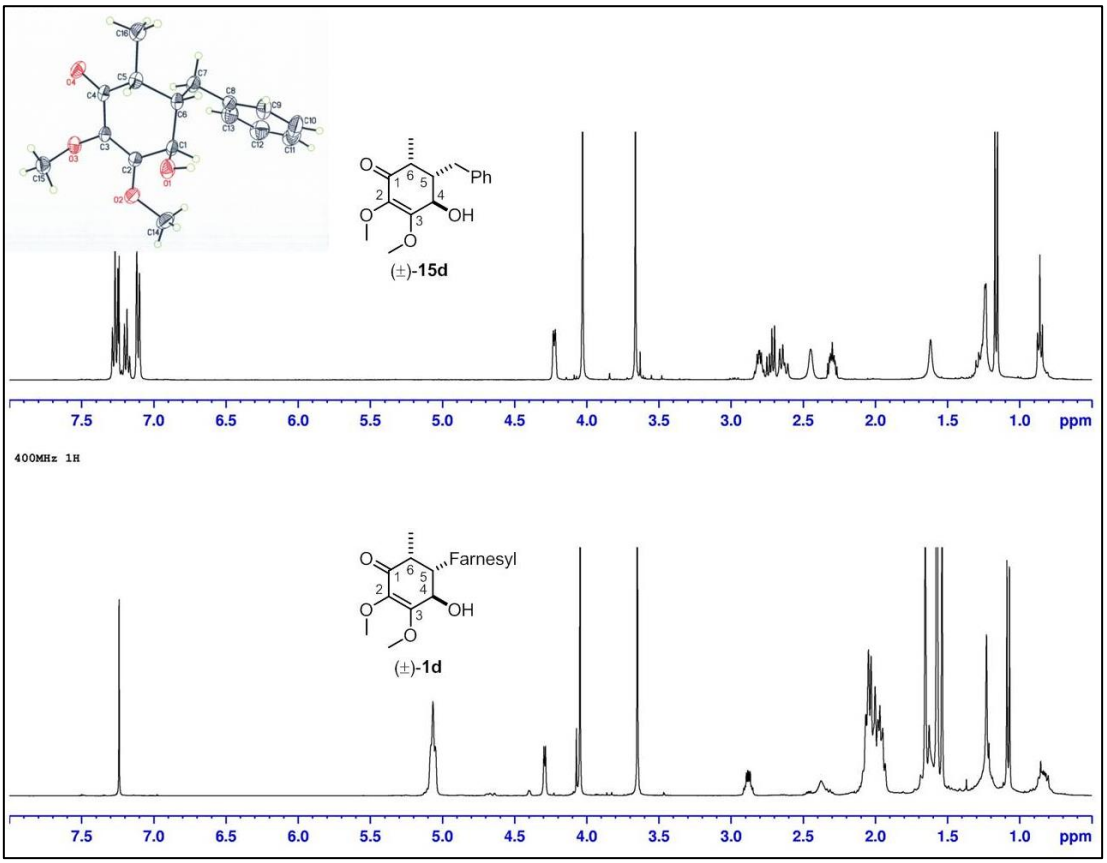

Figure S99. ORTEP drawing (IC16473) of compound **15d** (4,5-*trans*-5,6-*cis*) and comparison of the ^{1}H NMR spectra of **1d** with **15d** (400 MHz, $CDCl_3$).

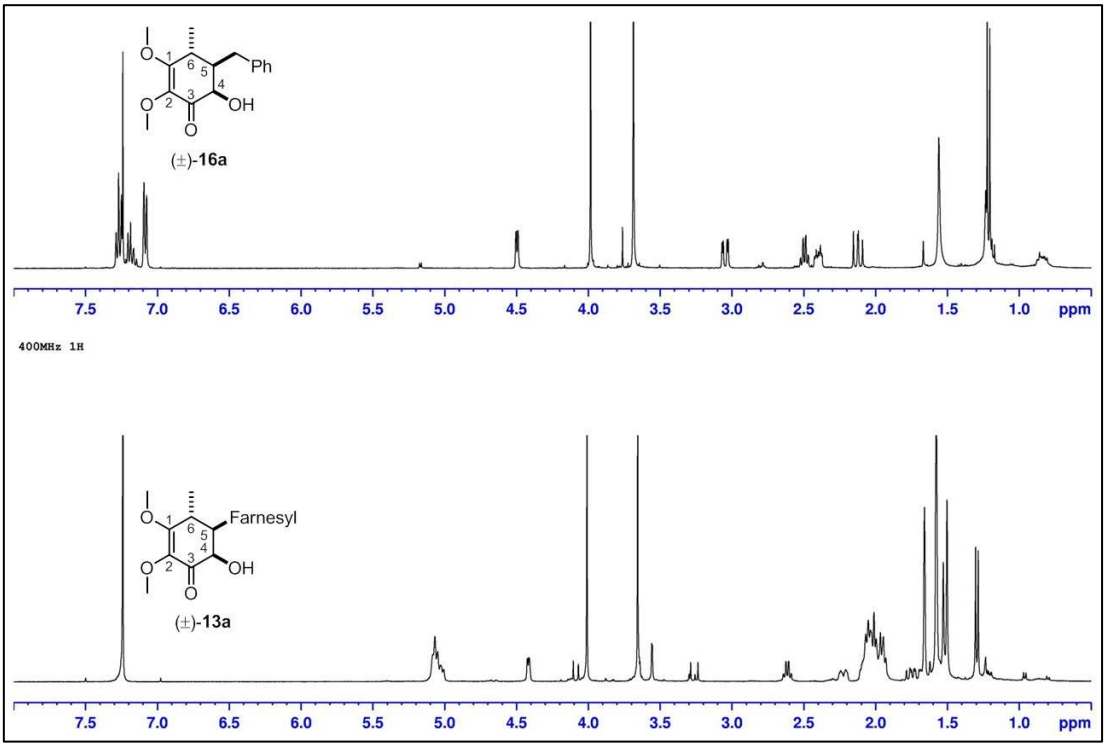

Figure S100. Comparison of the ^{1}H NMR spectra of **13a** and **16a** (400 MHz, $CDCl_3$).

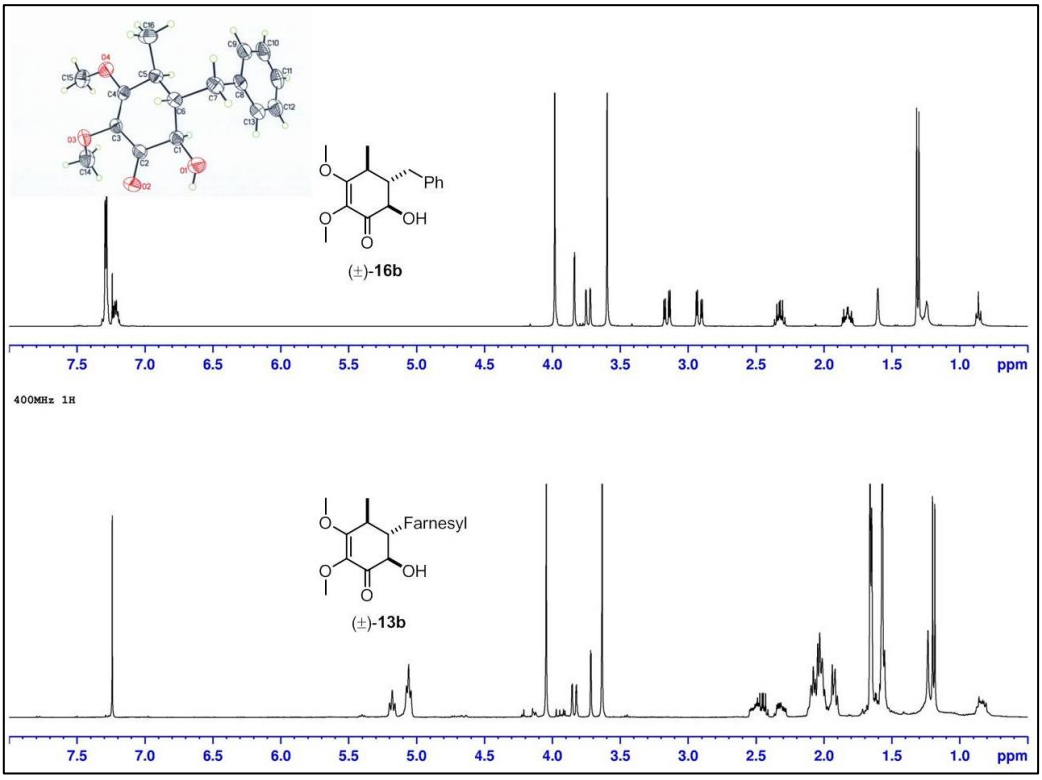

Figure S101. ORTEP drawing (IC16451) of compound **16b** (4,5-*trans*-5,6-*cis*) and comparison of the ^{1}H NMR spectra of **13b** and **16b** (400 MHz, $CDCl_3$).

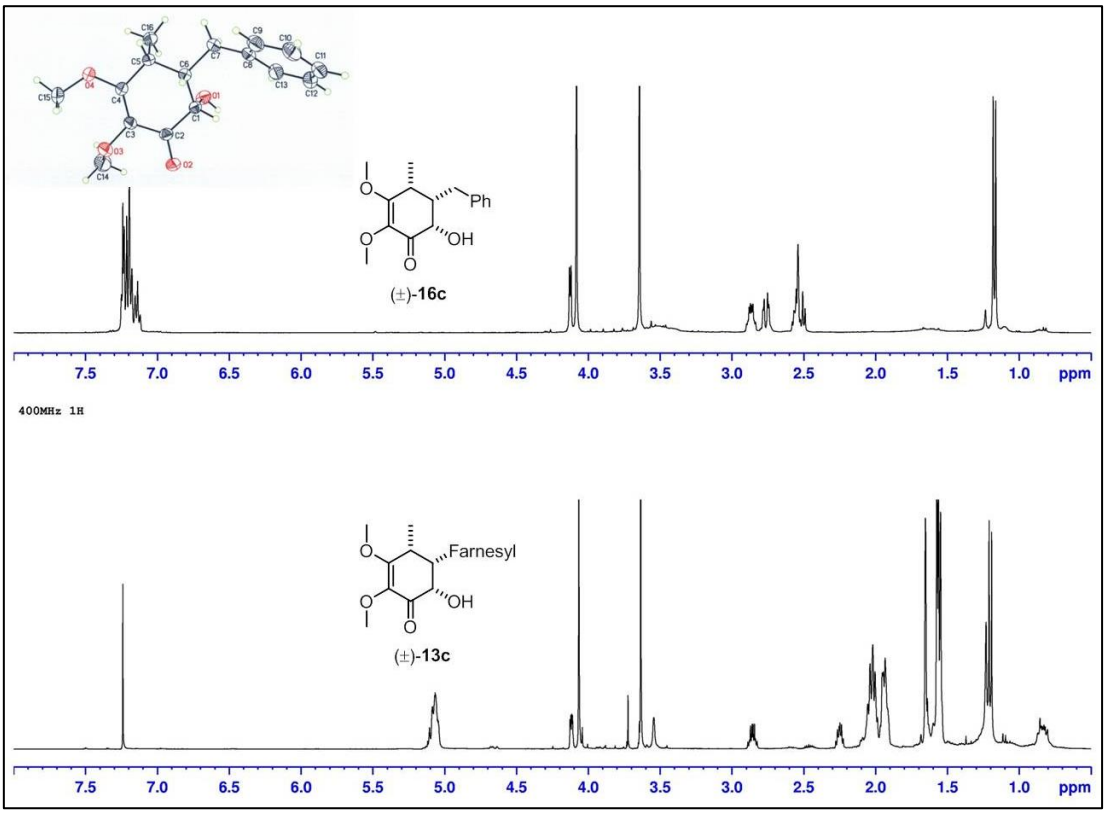

Figure S102. ORTEP drawing (IC16471) of compound **16c** (4,5-*trans*-5,6-*cis*) and comparison of the ^{1}H NMR spectra of **13c** with **11c** (400 MHz, $CDCl_3$).

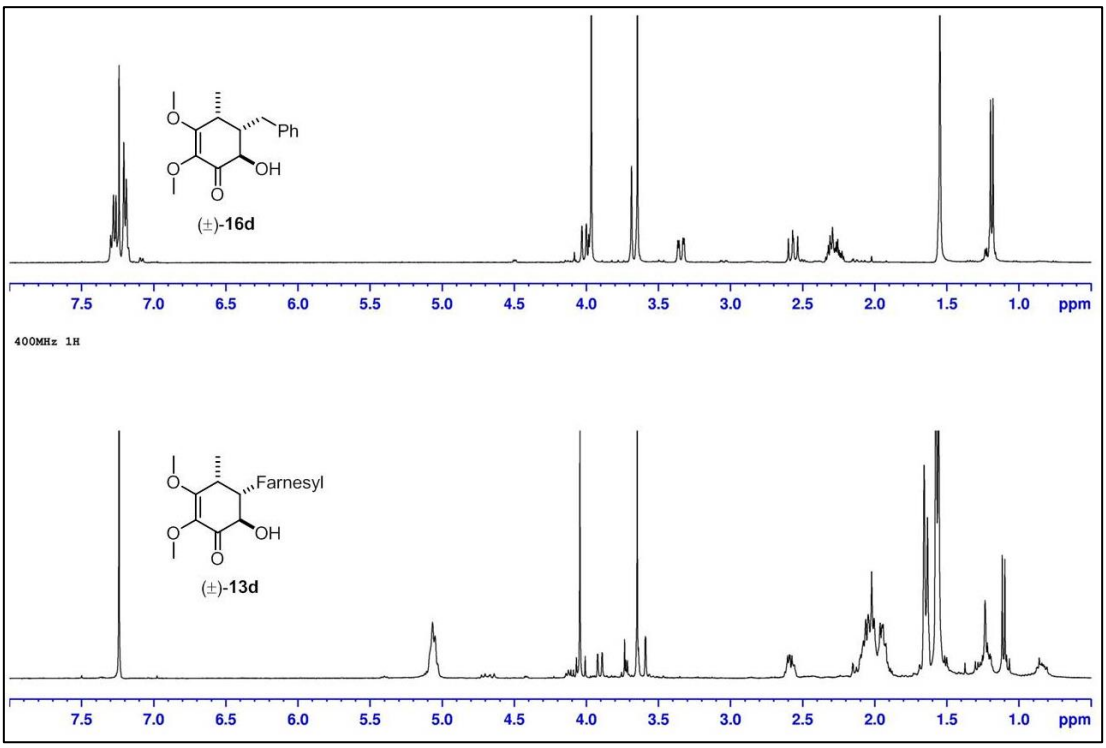

Figure S103. Comparison of the ^{1}H NMR spectra of **13d** and **16d** (400 MHz, $CDCl_3$).

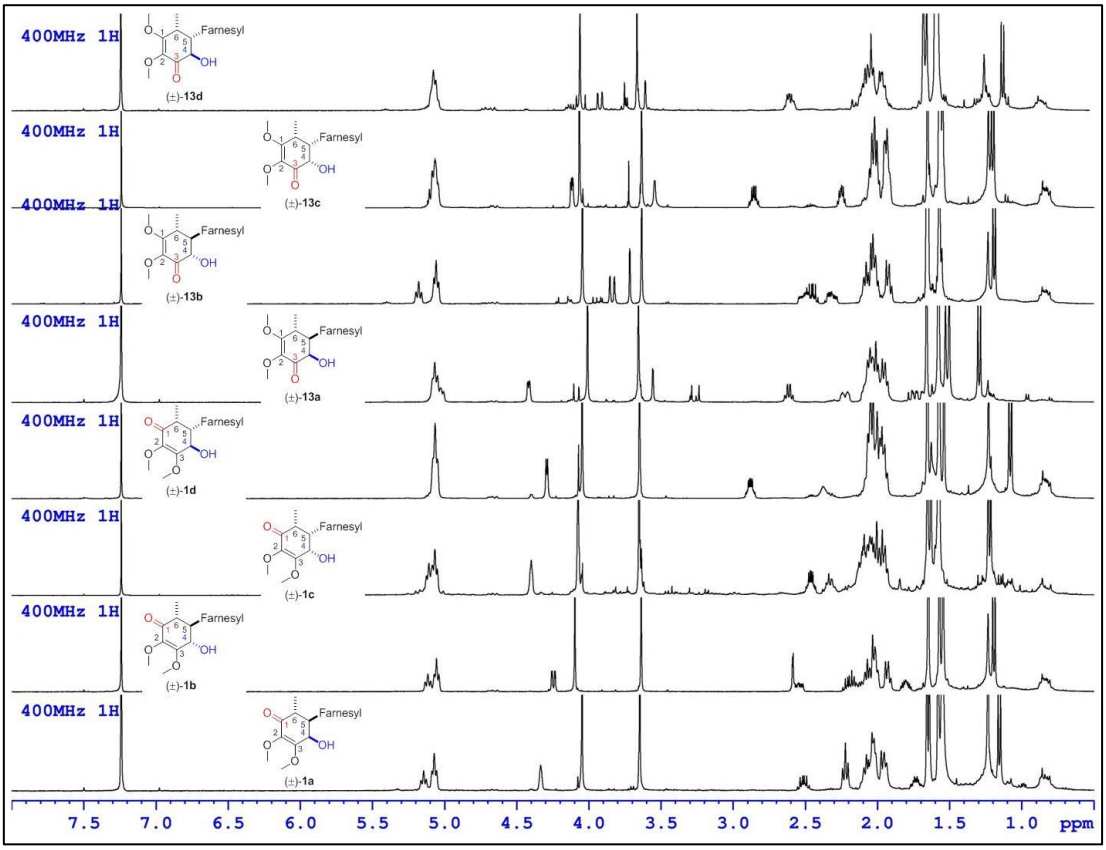

Figure S104. ^{1}H NMR spectra of **1a–d** and **13a–d** (400 MHz, $CDCl_3$).

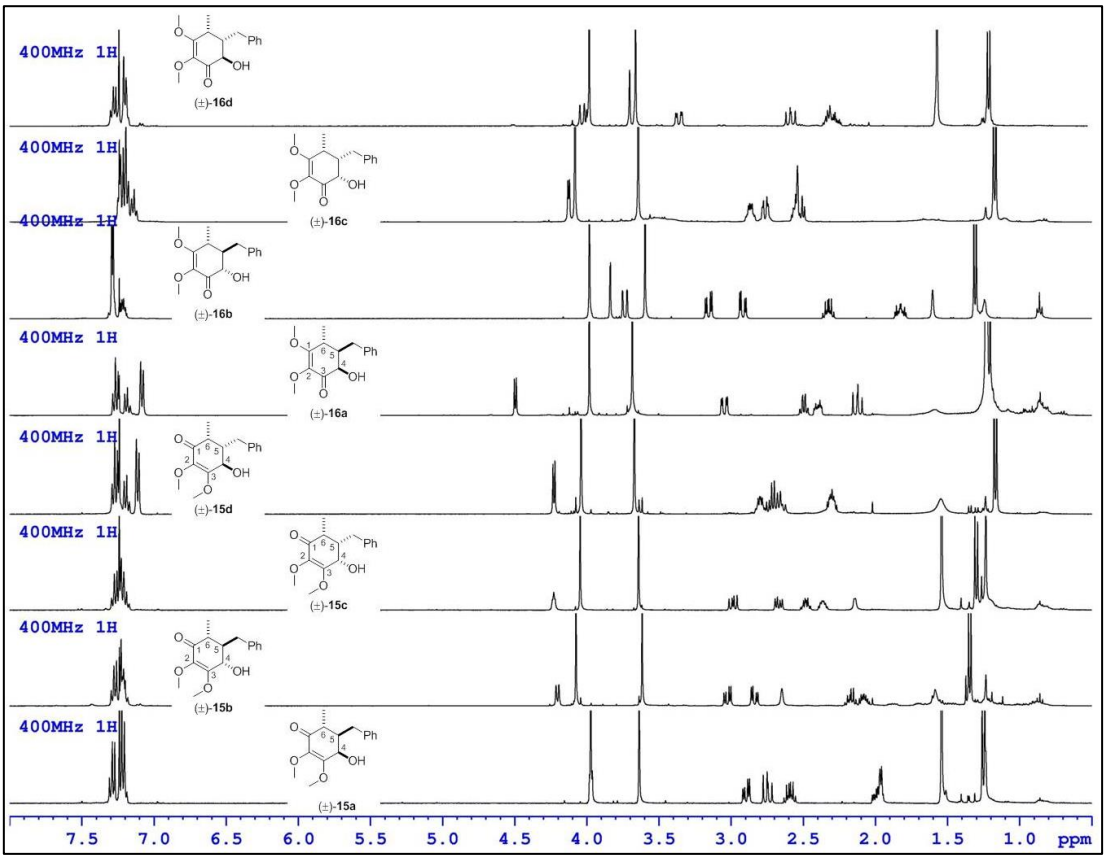

Figure S105. ^{1}H NMR spectra of **15a**–**d** and **16a**–**d** (400 MHz, $CDCl_3$).

Table S1. NMR spectral comparison of **1a–d/15a–d** and **13a–d/16a–d**.[a]

compound	H-4	H-6	Me-6	C-1	C-4	C-6	$\underline{C}H_3$-6
1a	4.34 (d, 3.1)	2.52 (qd, 6.7, 11.0)	1.16 (d, 6.7)	197.1	68.0	40.3	12.3
15a	3.98 (br s)	2.59 (qd, 6.7, 11.0)	1.25 (d, 6.7)	196.8	66.9	40.3	12.6
1b	4.25 (d, 8.5)	2.24–2.17 (m)	1.19 (d, 6.7)	197.1	69.2	42.0	13.1
15b	4.20 (d, 7.5)	2.22–2.13 (m)	1.35 (d, 7.0)	196.8	68.7	42.2	14.9
1c	4.40 (br s)	2.46 (qd, 7.3, 4.3)	1.23 (d, 7.3)	199.2	69.7	44.1	14.8
15c	4.23 (d, 3.7)	2.49 (qd, 7.3, 4.3)	1.30 (d, 7.3)	199.1	69.2	44.3	15.0
1d	4.29 (d, 4.4)	2.88 (qd, 6.8, 3.8)	1.08 (d, 6.8)	197.6	69.6	40.2	11.8
15d	4.23 (d, 5.5)	2.81 (qd, 7.3, 4.3)	1.17 (d, 7.3)	197.4	68.9	40.0	11.8
13a	4.42 (d, 5.5)	2.61 (qd, 7.3, 1.6)	1.29 (d, 7.3)	194.9	70.8	34.6	16.0
16a	4.50 (d, 5.5)	2.49 (qd, 7.3, 1.2)	1.21 (d, 7.3)	194.5	70.7	33.8	17.7
13b	3.84 (d, 12.5)	2.56–2.40 (m)	1.19 (d, 7.0)	196.2	72.2	35.3	15.4
16b	3.74 (d, 12.5)	2.37 (qd, 10.2, 6.5)	1.31 (d, 6.5)	195.8	71.3	34.7	15.7
13c	4.12 (d, 2.0)	2.86 (qd, 7.0, 4.5)	1.20 (d, 7.0)	195.5	75.3	37.1	15.0
16c	4.12 (d, 4.5)	2.91–2.82 (m)	1.17 (d, 7.0)	195.3	74.9	37.3	15.3
13d	3.91 (d, 12.2)	2.62–2.57 (m)	1.11 (d, 7.3)	195.7	71.6	34.4	11.9
16d	4.02 (d, 12.0)	2.34–2.22 (m)	1.19 (d, 6.7)	195.4	71.3	33.6	12.1

[a] Chemical shifts (δ) are given in parts per million (ppm) relative to δ_H 7.24 and δ_C 77.0 (central line of triplet) for $CHCl_3$ and $CDCl_3$, respectively. Data in parenthesis are coupling constants (*J*) given in Hz.

Table S2. Crystal data, atomic coordinates bond lengths and bond angles of compound *cis*-**14** (IC17004, deposit CCDC 1036453)

Table 1. Crystal data and structure refinement for ic17004.

Identification code	ic17004
Empirical formula	$C_{18}H_{24}O_5$
Formula weight	320.37
Temperature	200(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	Pbca
Unit cell dimensions	a = 11.7297(5) Å alpha = 90° b = 8.2689(5) Å beta = 90° c = 34.713(2) Å gamma = 90°
Volume, Z	3366.9(3) $Å^3$, 8
Density (calculated)	1.264 Mg/m^3
Absorption coefficient	0.749 mm^{-1}
F(000)	1376
Crystal size	0.20 x 0.15 x 0.10 mm
Θ range for data collection	4.55 to 68.00°
Limiting indices	$-9 \le h \le 14$, $-9 \le k \le 9$, $-41 \le l \le 40$
Reflections collected	7993
Independent reflections	3052 (R_{int} = 0.0535)
Completeness to Θ = 68.00°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.93119
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3052 / 0 / 208
Goodness-of-fit on F^2	1.022
Final R indices [I>2σ(I)]	R1 = 0.0737, wR2 = 0.1887
R indices (all data)	R1 = 0.1087, wR2 = 0.2200
Largest diff. peak and hole	0.693 and -0.286 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic17004. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	7155(2)	2454(4)	3519(1)	56(1)
O(2)	7151(2)	910(3)	4215(1)	43(1)
O(3)	9284(2)	672(3)	4601(1)	42(1)
O(4)	11066(2)	758(3)	4183(1)	45(1)
O(5)	10572(2)	3473(3)	4212(1)	43(1)
C(1)	8051(3)	2420(5)	3696(1)	45(1)
C(2)	8128(3)	1588(5)	4074(1)	40(1)
C(3)	9126(3)	1372(4)	4250(1)	38(1)
C(4)	10254(3)	1910(4)	4070(1)	37(1)
C(5)	10157(3)	2125(5)	3636(1)	42(1)
C(6)	9123(3)	3285(6)	3558(1)	50(1)
C(7)	8996(3)	3848(6)	3149(1)	54(1)
C(8)	10081(3)	4519(5)	2979(1)	48(1)
C(9)	10675(4)	5800(6)	3138(1)	60(1)
C(10)	11683(4)	6365(6)	2970(1)	64(1)
C(11)	12068(3)	5657(6)	2635(1)	56(1)
C(12)	11465(4)	4403(5)	2472(1)	53(1)
C(13)	10492(3)	3852(5)	2645(1)	51(1)
C(14)	6223(3)	2002(5)	4284(1)	51(1)
C(15)	8427(3)	853(6)	4892(1)	53(1)
C(16)	12215(3)	1097(6)	4061(1)	61(1)
C(17)	10631(4)	3648(6)	4621(1)	58(1)
C(18)	10100(4)	548(6)	3426(1)	63(1)

Table 3. Bond lengths [Å] and angles [°] for ic17004.

O(1)-C(1)	1.218(4)	O(2)-C(2)	1.367(4)
O(2)-C(14)	1.434(5)	O(3)-C(3)	1.359(4)
O(3)-C(15)	1.435(4)	O(4)-C(4)	1.403(4)
O(4)-C(16)	1.441(5)	O(5)-C(17)	1.428(4)
O(5)-C(4)	1.433(4)	C(1)-C(2)	1.484(5)
C(1)-C(6)	1.524(5)	C(2)-C(3)	1.334(5)
C(3)-C(4)	1.528(5)	C(4)-C(5)	1.521(5)
C(5)-C(18)	1.497(6)	C(5)-C(6)	1.570(5)
C(6)-C(7)	1.502(5)	C(7)-C(8)	1.509(5)
C(8)-C(13)	1.369(6)	C(8)-C(9)	1.384(6)
C(9)-C(10)	1.399(6)	C(10)-C(11)	1.377(6)
C(11)-C(12)	1.377(6)	C(12)-C(13)	1.367(6)

C(2)-O(2)-C(14)	115.9(3)	C(3)-O(3)-C(15)	119.4(3)
C(4)-O(4)-C(16)	114.9(3)	C(17)-O(5)-C(4)	116.4(3)
O(1)-C(1)-C(2)	120.6(3)	O(1)-C(1)-C(6)	122.9(3)
C(2)-C(1)-C(6)	116.4(3)	C(3)-C(2)-O(2)	121.1(3)
C(3)-C(2)-C(1)	121.4(3)	O(2)-C(2)-C(1)	117.2(3)
C(2)-C(3)-O(3)	126.0(3)	C(2)-C(3)-C(4)	122.2(3)
O(3)-C(3)-C(4)	111.8(3)	O(4)-C(4)-O(5)	109.9(3)
O(4)-C(4)-C(5)	113.9(3)	O(5)-C(4)-C(5)	104.7(3)
O(4)-C(4)-C(3)	106.0(3)	O(5)-C(4)-C(3)	110.4(3)
C(5)-C(4)-C(3)	112.0(3)	C(18)-C(5)-C(4)	112.7(3)
C(18)-C(5)-C(6)	114.4(3)	C(4)-C(5)-C(6)	107.5(3)
C(7)-C(6)-C(1)	111.1(3)	C(7)-C(6)-C(5)	115.5(3)
C(1)-C(6)-C(5)	107.3(3)	C(6)-C(7)-C(8)	113.6(3)
C(13)-C(8)-C(9)	118.0(4)	C(13)-C(8)-C(7)	118.7(4)
C(9)-C(8)-C(7)	123.3(4)	C(8)-C(9)-C(10)	120.9(4)
C(11)-C(10)-C(9)	119.2(4)	C(10)-C(11)-C(12)	119.9(4)
C(13)-C(12)-C(11)	119.9(4)	C(12)-C(13)-C(8)	122.1(4)

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic17004.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	36(1)	85(2)	48(2)	10(1)	-7(1)	-6(1)
O(2)	39(1)	43(1)	48(1)	1(1)	5(1)	-8(1)
O(3)	46(1)	45(2)	36(1)	10(1)	5(1)	3(1)
O(4)	43(1)	50(2)	41(1)	10(1)	3(1)	14(1)
O(5)	38(1)	40(1)	50(1)	3(1)	1(1)	-5(1)
C(1)	34(2)	58(2)	42(2)	4(2)	-4(2)	-1(2)
C(2)	37(2)	43(2)	40(2)	2(2)	2(2)	-8(2)
C(3)	44(2)	31(2)	37(2)	3(2)	0(2)	-1(2)
C(4)	35(2)	39(2)	36(2)	2(2)	-4(2)	1(2)
C(5)	35(2)	57(2)	34(2)	11(2)	0(2)	-5(2)
C(6)	39(2)	64(3)	46(2)	10(2)	-2(2)	-1(2)
C(7)	46(2)	61(3)	55(2)	10(2)	0(2)	4(2)
C(8)	42(2)	47(2)	54(2)	18(2)	0(2)	7(2)
C(9)	74(3)	62(3)	44(2)	8(2)	10(2)	2(2)
C(10)	70(3)	62(3)	59(3)	12(2)	-7(2)	-18(2)
C(11)	45(2)	67(3)	57(2)	21(2)	6(2)	1(2)
C(12)	57(2)	52(2)	50(2)	9(2)	6(2)	7(2)
C(13)	51(2)	49(2)	52(2)	8(2)	-2(2)	2(2)
C(14)	44(2)	57(3)	53(2)	-5(2)	9(2)	-4(2)
C(15)	57(2)	65(3)	36(2)	6(2)	11(2)	4(2)
C(16)	40(2)	78(3)	66(3)	15(2)	1(2)	20(2)
C(17)	70(3)	59(3)	45(2)	-9(2)	-1(2)	-14(2)
C(18)	65(3)	79(3)	45(2)	-10(2)	10(2)	-9(2)

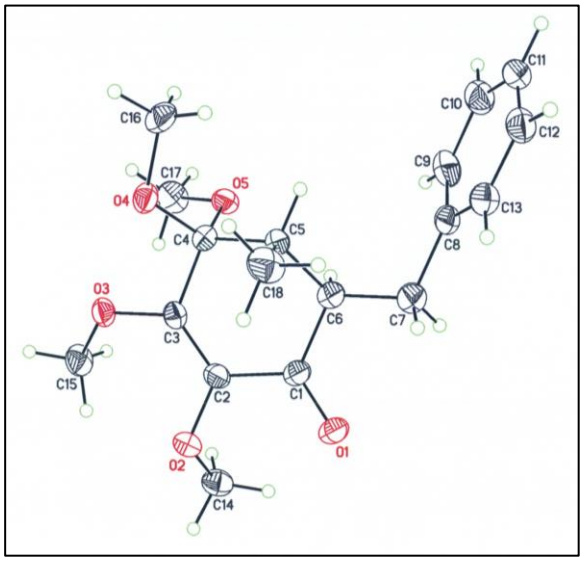

Table S3. Crystal data, atomic coordinates bond lengths and bond angles of compound **15b** (IC16470, deposit CCDC 1036448)

Table 1. Crystal data and structure refinement for ic16470.

Identification code	ic16470
Empirical formula	$C_{16}H_{20}O_4$
Formula weight	276.32
Temperature	295(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	a = 11.0565(7) Å alpha = 90° b = 25.7976(11) Å beta = 103.206(7)° c = 5.1911(3) Å gamma = 90°
Volume, Z	1441.51(14) $Å^3$, 4
Density (calculated)	1.273 Mg/m^3
Absorption coefficient	0.740 mm^{-1}
F(000)	592
Crystal size	0.20 x 0.20 x 0.15 mm
Θ range for data collection	3.43 to 67.96°
Limiting indices	$-11 \le h \le 13$, $-31 \le k \le 27$, $-6 \le l \le 3$
Reflections collected	6579
Independent reflections	2512 (R_{int} = 0.0369)
Completeness to Θ = 67.96°	95.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.89795
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2512 / 0 / 181
Goodness-of-fit on F^2	1.044
Final R indices [I>2σ(I)]	R1 = 0.0584, wR2 = 0.1641
R indices (all data)	R1 = 0.0849, wR2 = 0.1893
Largest diff. peak and hole	0.284 and -0.299 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic16470. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	1345(2)	2771(1)	4621(4)	69(1)
O(2)	3115(2)	3102(1)	2538(5)	76(1)
O(3)	4225(2)	4100(1)	4286(4)	69(1)
O(4)	2724(2)	4763(1)	6131(5)	90(1)
C(1)	1316(2)	3304(1)	3940(5)	50(1)
C(2)	2583(2)	3482(1)	3643(5)	52(1)
C(3)	3031(2)	3957(1)	4378(5)	53(1)
C(4)	2298(3)	4337(1)	5455(5)	58(1)
C(5)	987(3)	4193(1)	5652(5)	53(1)
C(6)	842(3)	3608(1)	6024(5)	52(1)
C(7)	-478(3)	3444(1)	6119(5)	60(1)
C(8)	-1458(3)	3511(1)	3588(6)	55(1)
C(9)	-2008(3)	3986(1)	2845(6)	67(1)
C(10)	-2884(3)	4048(1)	535(7)	79(1)
C(11)	-3265(3)	3634(2)	-1107(7)	80(1)
C(12)	-2754(3)	3153(1)	-390(7)	80(1)
C(13)	-1854(3)	3096(1)	1916(6)	64(1)
C(14)	4181(3)	3173(1)	1487(8)	92(1)
C(15)	4327(4)	4497(1)	2409(8)	95(1)
C(16)	611(3)	4518(1)	7811(6)	70(1)

Table 3. Bond lengths [Å] and angles [°] for ic16470.

O(1)-C(1)	1.419(3)	O(2)-C(2)	1.338(3)
O(2)-C(14)	1.420(4)	O(3)-C(3)	1.382(3)
O(3)-C(15)	1.436(4)	O(4)-C(4)	1.215(3)
C(1)-C(2)	1.514(4)	C(1)-C(6)	1.522(3)
C(2)-C(3)	1.346(3)	C(3)-C(4)	1.461(4)
C(4)-C(5)	1.522(4)	C(5)-C(16)	1.531(4)
C(5)-C(6)	1.535(3)	C(6)-C(7)	1.531(4)
C(7)-C(8)	1.510(4)	C(8)-C(9)	1.385(4)
C(8)-C(13)	1.385(4)	C(9)-C(10)	1.367(4)
C(10)-C(11)	1.370(5)	C(11)-C(12)	1.379(5)
C(12)-C(13)	1.378(4)		

C(2)-O(2)-C(14)	123.7(2)	C(3)-O(3)-C(15)	115.9(2)
O(1)-C(1)-C(2)	110.4(2)	O(1)-C(1)-C(6)	108.2(2)
C(2)-C(1)-C(6)	113.2(2)	O(2)-C(2)-C(3)	128.4(3)
O(2)-C(2)-C(1)	109.3(2)	C(3)-C(2)-C(1)	122.4(2)
C(2)-C(3)-O(3)	121.7(2)	C(2)-C(3)-C(4)	121.3(2)
O(3)-C(3)-C(4)	116.9(2)	O(4)-C(4)-C(3)	120.3(3)
O(4)-C(4)-C(5)	120.9(2)	C(3)-C(4)-C(5)	118.8(2)
C(4)-C(5)-C(16)	109.7(2)	C(4)-C(5)-C(6)	112.1(2)
C(16)-C(5)-C(6)	113.1(2)	C(1)-C(6)-C(7)	111.5(2)
C(1)-C(6)-C(5)	110.7(2)	C(7)-C(6)-C(5)	113.7(2)
C(8)-C(7)-C(6)	116.1(2)	C(9)-C(8)-C(13)	117.0(3)
C(9)-C(8)-C(7)	121.7(3)	C(13)-C(8)-C(7)	121.3(2)
C(10)-C(9)-C(8)	121.6(3)	C(9)-C(10)-C(11)	120.8(3)
C(10)-C(11)-C(12)	118.9(3)	C(13)-C(12)-C(11)	120.0(3)
C(12)-C(13)-C(8)	121.6(3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic16470.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	88(1)	44(1)	83(1)	9(1)	37(1)	2(1)
O(2)	69(1)	58(1)	112(2)	-17(1)	43(1)	-1(1)
O(3)	50(1)	65(1)	91(1)	2(1)	11(1)	-4(1)
O(4)	86(2)	56(1)	133(2)	-26(1)	34(2)	-16(1)
C(1)	57(2)	41(1)	54(1)	4(1)	15(1)	0(1)
C(2)	53(2)	46(1)	58(1)	2(1)	14(1)	7(1)
C(3)	49(1)	50(1)	58(1)	6(1)	7(1)	1(1)
C(4)	65(2)	47(1)	60(2)	1(1)	12(1)	0(1)
C(5)	62(2)	45(1)	52(1)	2(1)	15(1)	6(1)
C(6)	62(2)	49(1)	48(1)	8(1)	17(1)	8(1)
C(7)	66(2)	54(2)	66(2)	11(1)	29(1)	5(1)
C(8)	55(2)	48(1)	70(2)	6(1)	29(1)	2(1)
C(9)	63(2)	54(2)	85(2)	3(1)	17(2)	5(1)
C(10)	67(2)	70(2)	100(2)	19(2)	19(2)	13(2)
C(11)	54(2)	107(3)	79(2)	5(2)	15(2)	10(2)
C(12)	64(2)	87(2)	91(2)	-18(2)	20(2)	-3(2)
C(13)	59(2)	53(2)	86(2)	0(1)	26(2)	2(1)
C(14)	77(2)	88(2)	127(3)	-27(2)	56(2)	-2(2)
C(15)	83(2)	79(2)	129(3)	17(2)	38(2)	-15(2)
C(16)	85(2)	59(2)	68(2)	-10(1)	22(2)	6(1)

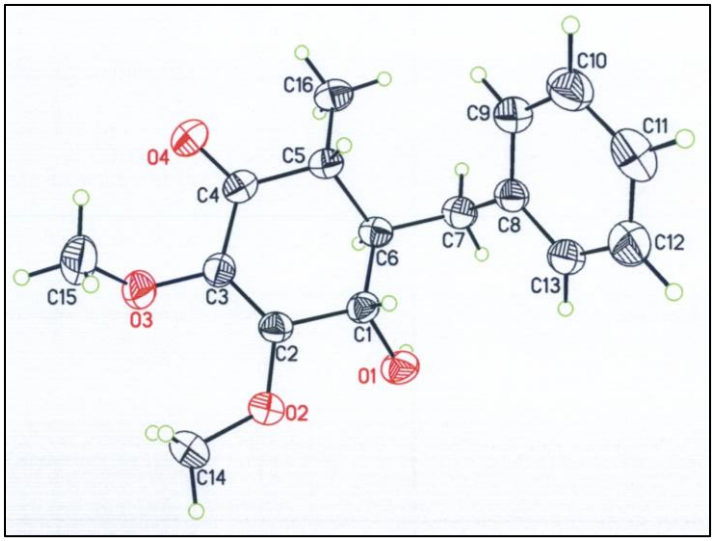

Table S4. Crystal data, atomic coordinates bond lengths and bond angles of compound **15c** (IC16707, deposit CCDC 1036452)

Table 1. Crystal data and structure refinement for ic16707.

Identification code	ic16707
Empirical formula	$C_{16}H_{20}O_4$
Formula weight	276.32
Temperature	295(2) K
Wavelength	1.54178 Å
Crystal system	Orthorhombic
Space group	$Pca2_1$
Unit cell dimensions	a = 7.4859(4) Å alpha = 90° b = 21.3424(16) Å beta = 90° c = 9.3008(5) Å gamma = 90°
Volume, Z	1485.96(16) $Å^3$, 4
Density (calculated)	1.235 Mg/m^3
Absorption coefficient	0.718 mm^{-1}
F(000)	592
Crystal size	0.25 x 0.20 x 0.15 mm
Θ range for data collection	4.14 to 68.00°
Limiting indices	$-7 \le h \le 9$, $-25 \le k \le 18$, $-7 \le l \le 11$
Reflections collected	3281
Independent reflections	1934 (R_{int} = 0.0254)
Completeness to Θ = 68.00°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.89313
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	1934 / 1 / 181
Goodness-of-fit on F^2	1.022
Final R indices [I>2σ(I)]	R1 = 0.0437, wR2 = 0.1080
R indices (all data)	R1 = 0.0526, wR2 = 0.1160
Absolute structure parameter	-0.3(3)
Largest diff. peak and hole	0.114 and -0.159 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic16707. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	7540(2)	2980(1)	3579(2)	65(1)
O(2)	6218(3)	4201(1)	2292(3)	77(1)
O(3)	2704(3)	4157(1)	2734(2)	70(1)
O(4)	1134(2)	3019(1)	3091(3)	84(1)
C(1)	6577(3)	3051(1)	2264(3)	51(1)
C(2)	5463(4)	3631(1)	2394(3)	55(1)
C(3)	3687(3)	3612(1)	2676(3)	56(1)
C(4)	2736(3)	3025(1)	2866(3)	56(1)
C(5)	3789(3)	2422(1)	2877(3)	52(1)
C(6)	5442(3)	2480(1)	1906(3)	50(1)
C(7)	8023(5)	4259(2)	1768(5)	87(1)
C(8)	2335(6)	4364(2)	4147(4)	89(1)
C(9)	4182(4)	2245(2)	4453(3)	65(1)
C(10)	6563(3)	1882(1)	1822(4)	62(1)
C(11)	5575(3)	1338(1)	1189(4)	62(1)
C(12)	5154(5)	813(2)	1993(5)	81(1)
C(13)	4185(6)	322(2)	1403(6)	96(1)
C(14)	3626(6)	346(2)	12(6)	98(1)
C(15)	4057(5)	863(2)	-815(5)	90(1)
C(16)	5008(4)	1349(2)	-236(4)	71(1)

Table 3. Bond lengths [Å] and angles [°] for ic16707.

O(1)-C(1)	1.428(3)	O(2)-C(2)	1.346(4)
O(2)-C(7)	1.441(4)	O(3)-C(3)	1.378(3)
O(3)-C(8)	1.413(4)	O(4)-C(4)	1.218(3)
C(1)-C(2)	1.497(4)	C(1)-C(6)	1.523(4)
C(2)-C(3)	1.356(4)	C(3)-C(4)	1.451(4)
C(4)-C(5)	1.509(4)	C(5)-C(6)	1.537(3)
C(5)-C(9)	1.542(4)	C(6)-C(10)	1.529(4)
C(10)-C(11)	1.497(4)	C(11)-C(12)	1.383(5)
C(11)-C(16)	1.392(5)	C(12)-C(13)	1.388(6)
C(13)-C(14)	1.360(8)	C(14)-C(15)	1.383(7)
C(15)-C(16)	1.368(5)		

C(2)-O(2)-C(7)	119.6(3)	C(3)-O(3)-C(8)	113.8(2)
O(1)-C(1)-C(2)	107.5(2)	O(1)-C(1)-C(6)	112.6(2)
C(2)-C(1)-C(6)	111.60(19)	O(2)-C(2)-C(3)	116.9(3)
O(2)-C(2)-C(1)	120.5(2)	C(3)-C(2)-C(1)	122.6(3)
C(2)-C(3)-O(3)	120.5(3)	C(2)-C(3)-C(4)	121.9(3)
O(3)-C(3)-C(4)	117.5(2)	O(4)-C(4)-C(3)	120.9(3)
O(4)-C(4)-C(5)	120.3(3)	C(3)-C(4)-C(5)	118.7(2)
C(4)-C(5)-C(6)	110.4(2)	C(4)-C(5)-C(9)	108.4(2)
C(6)-C(5)-C(9)	115.1(2)	C(1)-C(6)-C(10)	111.91(19)
C(1)-C(6)-C(5)	112.6(2)	C(10)-C(6)-C(5)	113.9(2)
C(11)-C(10)-C(6)	113.4(2)	C(12)-C(11)-C(16)	117.3(3)
C(12)-C(11)-C(10)	121.9(3)	C(16)-C(11)-C(10)	120.8(3)
C(11)-C(12)-C(13)	121.1(4)	C(14)-C(13)-C(12)	120.6(4)
C(13)-C(14)-C(15)	119.1(4)	C(16)-C(15)-C(14)	120.5(4)
C(15)-C(16)-C(11)	121.4(4)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic16707.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	34(1)	108(2)	52(1)	4(1)	-4(1)	-6(1)
O(2)	71(1)	73(1)	87(2)	0(1)	14(1)	-5(1)
O(3)	68(1)	87(1)	56(1)	-1(1)	5(1)	25(1)
O(4)	34(1)	117(2)	101(2)	-8(2)	10(1)	7(1)
C(1)	34(1)	77(2)	42(1)	4(1)	6(1)	-1(1)
C(2)	52(1)	74(1)	39(1)	1(1)	0(1)	-1(1)
C(3)	47(1)	79(2)	41(1)	1(1)	1(1)	11(1)
C(4)	36(1)	90(2)	42(1)	-2(1)	-3(1)	5(1)
C(5)	32(1)	78(2)	46(1)	2(1)	-2(1)	-5(1)
C(6)	36(1)	73(1)	40(1)	5(1)	1(1)	4(1)
C(7)	76(2)	86(2)	100(3)	9(2)	17(2)	-19(2)
C(8)	96(2)	103(3)	68(2)	-17(2)	8(2)	23(2)
C(9)	49(1)	96(2)	48(1)	11(1)	3(1)	-6(1)
C(10)	40(1)	81(2)	67(2)	6(2)	3(1)	7(1)
C(11)	47(1)	70(2)	68(2)	2(1)	13(1)	12(1)
C(12)	89(2)	72(2)	83(2)	10(2)	16(2)	15(2)
C(13)	106(3)	64(2)	116(4)	-2(2)	30(3)	4(2)
C(14)	87(2)	81(2)	128(4)	-30(2)	10(3)	-2(2)
C(15)	88(2)	95(3)	85(2)	-17(2)	0(2)	10(2)
C(16)	64(2)	80(2)	69(2)	-2(2)	5(2)	8(2)

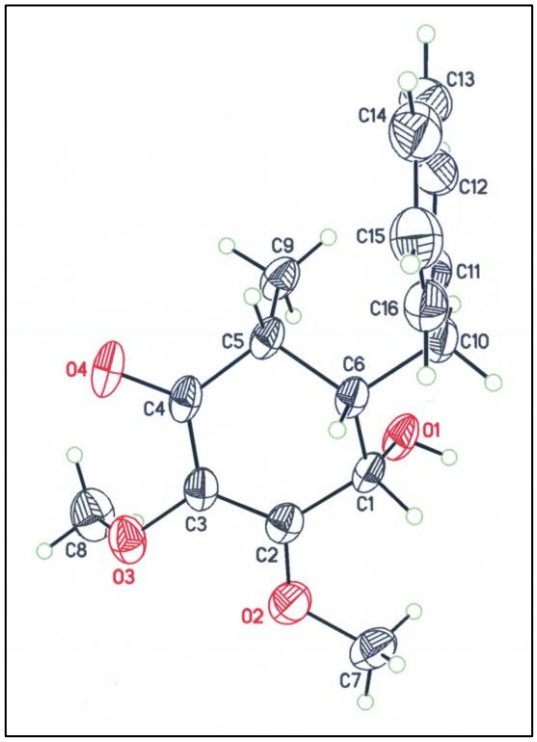

Table S5. Crystal data, atomic coordinates bond lengths and bond angles of compound **15d** (IC16473, deposit CCDC 1036450)

Table 1. Crystal data and structure refinement for ic16473.

Identification code	ic16473
Empirical formula	$C_{16}H_{20}O_4$
Formula weight	276.32
Temperature	295(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 6.9852(5) Å alpha = 73.977(7)° b = 8.4612(7) Å beta = 81.811(6)° c = 13.1167(9) Å gamma = 78.873(7)°
Volume, Z	727.84(9) $Å^3$, 2
Density (calculated)	1.261 Mg/m^3
Absorption coefficient	0.733 mm^{-1}
F(000)	296
Crystal size	0.25 x 0.20 x 0.15 mm
Θ range for data collection	3.52 to 68.00°
Limiting indices	$-7 \le h \le 8$, $-9 \le k \le 10$, $-15 \le l \le 15$
Reflections collected	4603
Independent reflections	2643 (R_{int} = 0.0228)
Completeness to Θ = 68.00°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.92347
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2643 / 0 / 181
Goodness-of-fit on F^2	1.024
Final R indices [I>2σ(I)]	R1 = 0.0455, wR2 = 0.1217
R indices (all data)	R1 = 0.0614, wR2 = 0.1361
Largest diff. peak and hole	0.210 and -0.214 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic16473. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-2600(2)	1455(2)	9053(1)	52(1)
O(2)	-696(2)	4497(2)	8266(1)	56(1)
O(3)	3069(2)	3273(2)	8584(1)	48(1)
O(4)	4439(2)	61(2)	8530(1)	52(1)
C(1)	-1417(2)	1847(2)	8068(1)	40(1)
C(2)	-36(3)	2900(2)	8237(1)	39(1)
C(3)	1837(2)	2282(2)	8430(1)	39(1)
C(4)	2681(2)	548(2)	8470(1)	39(1)
C(5)	1275(3)	-615(2)	8480(2)	42(1)
C(6)	-347(2)	282(2)	7745(1)	40(1)
C(7)	438(3)	641(3)	6560(2)	48(1)
C(8)	-1058(3)	1581(3)	5790(2)	46(1)
C(9)	-2848(3)	1092(4)	5836(2)	67(1)
C(10)	-4200(4)	2002(5)	5122(2)	84(1)
C(11)	-3772(4)	3386(4)	4356(2)	84(1)
C(12)	-2003(5)	3855(4)	4290(2)	87(1)
C(13)	-662(4)	2963(3)	5003(2)	68(1)
C(14)	-2523(3)	5338(3)	7874(2)	68(1)
C(15)	2938(3)	3327(3)	9671(2)	54(1)
C(16)	2341(3)	-2268(3)	8292(2)	64(1)

Table 3. Bond lengths [Å] and angles [°] for ic16473.

O(1)-C(1)	1.424(2)	O(2)-C(2)	1.350(2)
O(2)-C(14)	1.426(2)	O(3)-C(3)	1.380(2)
O(3)-C(15)	1.429(2)	O(4)-C(4)	1.224(2)
C(1)-C(2)	1.508(2)	C(1)-C(6)	1.527(3)
C(2)-C(3)	1.344(2)	C(3)-C(4)	1.461(3)
C(4)-C(5)	1.515(2)	C(5)-C(16)	1.520(3)
C(5)-C(6)	1.538(2)	C(6)-C(7)	1.539(3)
C(7)-C(8)	1.511(3)	C(8)-C(13)	1.373(3)
C(8)-C(9)	1.379(3)	C(9)-C(10)	1.391(3)
C(10)-C(11)	1.368(4)	C(11)-C(12)	1.354(4)
C(12)-C(13)	1.381(4)		

C(2)-O(2)-C(14)	120.49(16)	C(3)-O(3)-C(15)	112.18(14)
O(1)-C(1)-C(2)	105.17(13)	O(1)-C(1)-C(6)	111.84(15)
C(2)-C(1)-C(6)	112.78(14)	C(3)-C(2)-O(2)	117.33(16)
C(3)-C(2)-C(1)	122.39(16)	O(2)-C(2)-C(1)	120.14(15)
C(2)-C(3)-O(3)	121.20(17)	C(2)-C(3)-C(4)	122.10(16)
O(3)-C(3)-C(4)	116.70(15)	O(4)-C(4)-C(3)	120.84(16)
O(4)-C(4)-C(5)	122.12(17)	C(3)-C(4)-C(5)	117.00(15)
C(4)-C(5)-C(16)	112.04(16)	C(4)-C(5)-C(6)	110.68(15)
C(16)-C(5)-C(6)	115.16(16)	C(1)-C(6)-C(5)	110.28(14)
C(1)-C(6)-C(7)	112.62(16)	C(5)-C(6)-C(7)	112.12(15)
C(8)-C(7)-C(6)	115.17(15)	C(13)-C(8)-C(9)	117.4(2)
C(13)-C(8)-C(7)	120.45(19)	C(9)-C(8)-C(7)	122.1(2)
C(8)-C(9)-C(10)	120.5(3)	C(11)-C(10)-C(9)	120.6(3)
C(12)-C(11)-C(10)	119.3(2)	C(11)-C(12)-C(13)	120.3(3)
C(8)-C(13)-C(12)	121.9(3)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic16473.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	33(1)	82(1)	47(1)	-22(1)	0(1)	-19(1)
O(2)	46(1)	49(1)	78(1)	-21(1)	-20(1)	1(1)
O(3)	40(1)	54(1)	55(1)	-13(1)	-9(1)	-20(1)
O(4)	30(1)	58(1)	68(1)	-12(1)	-13(1)	-4(1)
C(1)	28(1)	53(1)	39(1)	-12(1)	-10(1)	-6(1)
C(2)	36(1)	44(1)	38(1)	-10(1)	-5(1)	-6(1)
C(3)	32(1)	45(1)	41(1)	-9(1)	-6(1)	-12(1)
C(4)	30(1)	50(1)	37(1)	-6(1)	-9(1)	-6(1)
C(5)	36(1)	46(1)	44(1)	-8(1)	-9(1)	-8(1)
C(6)	33(1)	49(1)	43(1)	-11(1)	-9(1)	-12(1)
C(7)	37(1)	64(1)	45(1)	-16(1)	-6(1)	-4(1)
C(8)	45(1)	58(1)	39(1)	-20(1)	-4(1)	-3(1)
C(9)	55(1)	96(2)	53(1)	-17(1)	-12(1)	-19(1)
C(10)	49(1)	140(3)	71(2)	-40(2)	-17(1)	-8(2)
C(11)	77(2)	109(2)	59(2)	-25(2)	-28(1)	21(2)
C(12)	100(2)	80(2)	67(2)	1(1)	-22(2)	1(2)
C(13)	69(2)	71(2)	60(1)	-8(1)	-10(1)	-14(1)
C(14)	50(1)	57(1)	94(2)	-19(1)	-20(1)	9(1)
C(15)	54(1)	57(1)	59(1)	-18(1)	-16(1)	-12(1)
C(16)	64(1)	49(1)	83(2)	-16(1)	-29(1)	-3(1)

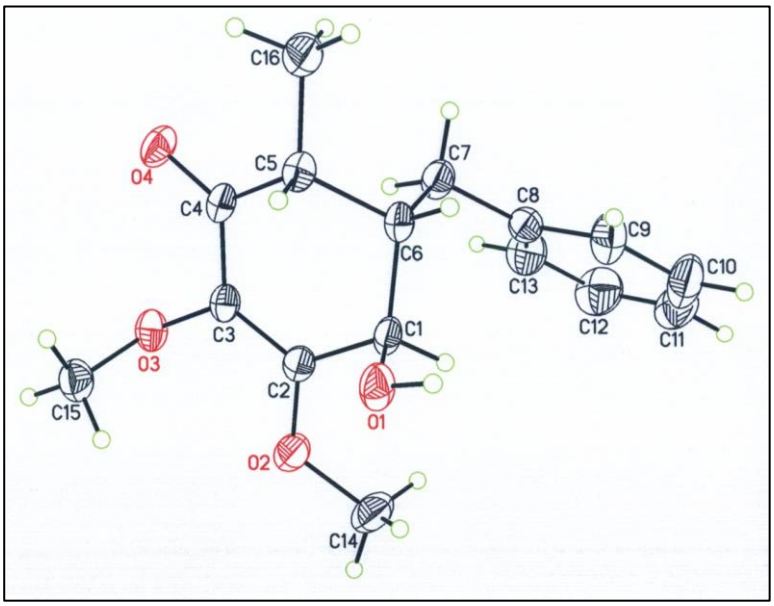

Table S6. Crystal data, atomic coordinates bond lengths and bond angles of compound **16b** (IC16451, deposit CCDC 1036447)

Table 1. Crystal data and structure refinement for ic16451.

Identification code	ic16451
Empirical formula	$C_{16}H_{20}O_4$
Formula weight	276.32
Temperature	295(2) K
Wavelength	1.54178 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	a = 9.8399(6) Å alpha = 90° b = 5.2999(3) Å beta = 98.305(6)° c = 28.5110(16) Å gamma = 90°
Volume, Z	1471.27(15) $Å^3$, 4
Density (calculated)	1.247 Mg/m^3
Absorption coefficient	0.725 mm^{-1}
F(000)	592
Crystal size	0.20 x 0.15 x 0.10 mm
Θ range for data collection	3.13 to 67.96°
Limiting indices	$-9 \le h \le 11$, $-4 \le k \le 6$, $-29 \le l \le 34$
Reflections collected	4894
Independent reflections	2684 (R_{int} = 0.0214)
Completeness to Θ = 67.96°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.97043
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2684 / 0 / 181
Goodness-of-fit on F^2	1.034
Final R indices [I>2σ(I)]	R1 = 0.0483, wR2 = 0.1458
R indices (all data)	R1 = 0.0672, wR2 = 0.1651
Largest diff. peak and hole	0.226 and -0.199 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic16451. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	4968(2)	9650(3)	788(1)	72(1)
O(2)	6365(2)	8151(4)	102(1)	81(1)
O(3)	8579(1)	4964(3)	229(1)	63(1)
O(4)	8967(2)	2317(3)	1119(1)	67(1)
C(1)	5684(2)	7338(4)	854(1)	50(1)
C(2)	6595(2)	6976(4)	475(1)	54(1)
C(3)	7720(2)	5225(4)	571(1)	50(1)
C(4)	8001(2)	4099(4)	994(1)	49(1)
C(5)	7272(2)	4738(4)	1413(1)	52(1)
C(6)	6532(2)	7276(4)	1344(1)	48(1)
C(7)	5664(2)	7985(4)	1734(1)	56(1)
C(8)	4496(2)	6229(4)	1795(1)	52(1)
C(9)	4631(3)	4387(5)	2141(1)	68(1)
C(10)	3541(3)	2770(5)	2193(1)	81(1)
C(11)	2321(3)	3023(5)	1902(1)	81(1)
C(12)	2159(3)	4864(6)	1561(1)	78(1)
C(13)	3237(2)	6460(5)	1509(1)	63(1)
C(14)	7972(3)	3882(6)	-212(1)	84(1)
C(15)	9613(3)	939(5)	777(1)	79(1)
C(16)	8277(3)	4674(7)	1876(1)	94(1)

Table 3. Bond lengths [Å] and angles [°] for ic16451.

O(1)-C(1)	1.413(2)	O(2)-C(2)	1.225(3)
O(3)-C(3)	1.386(2)	O(3)-C(14)	1.431(3)
O(4)-C(4)	1.351(2)	O(4)-C(15)	1.439(3)
C(1)-C(2)	1.514(3)	C(1)-C(6)	1.520(3)
C(2)-C(3)	1.440(3)	C(3)-C(4)	1.337(3)
C(4)-C(5)	1.519(3)	C(5)-C(6)	1.528(3)
C(5)-C(16)	1.530(3)	C(6)-C(7)	1.541(3)
C(7)-C(8)	1.508(3)	C(8)-C(13)	1.387(3)
C(8)-C(9)	1.381(3)	C(9)-C(10)	1.398(4)
C(10)-C(11)	1.365(4)	C(11)-C(12)	1.370(4)
C(12)-C(13)	1.381(3)		

C(3)-O(3)-C(14)	116.00(16)	C(4)-O(4)-C(15)	122.54(19)
O(1)-C(1)-C(2)	110.45(16)	O(1)-C(1)-C(6)	109.80(17)
C(2)-C(1)-C(6)	110.59(15)	O(2)-C(2)-C(3)	122.26(19)
O(2)-C(2)-C(1)	120.15(19)	C(3)-C(2)-C(1)	117.58(17)
C(4)-C(3)-O(3)	121.45(18)	C(4)-C(3)-C(2)	120.85(18)
O(3)-C(3)-C(2)	117.36(18)	C(3)-C(4)-O(4)	126.62(19)
C(3)-C(4)-C(5)	123.39(18)	O(4)-C(4)-C(5)	109.97(17)
C(4)-C(5)-C(6)	111.44(16)	C(4)-C(5)-C(16)	110.68(17)
C(6)-C(5)-C(16)	111.5(2)	C(1)-C(6)-C(7)	111.66(15)
C(1)-C(6)-C(5)	108.94(16)	C(7)-C(6)-C(5)	115.15(17)
C(8)-C(7)-C(6)	116.32(16)	C(13)-C(8)-C(9)	117.9(2)
C(13)-C(8)-C(7)	120.57(19)	C(9)-C(8)-C(7)	121.5(2)
C(8)-C(9)-C(10)	121.0(3)	C(11)-C(10)-C(9)	119.7(2)
C(10)-C(11)-C(12)	120.3(2)	C(13)-C(12)-C(11)	120.0(3)
C(12)-C(13)-C(8)	121.1(2)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2 \times 10^3$] for ic16451.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	85(1)	70(1)	62(1)	14(1)	14(1)	26(1)
O(2)	86(1)	102(1)	58(1)	29(1)	19(1)	21(1)
O(3)	57(1)	75(1)	59(1)	-6(1)	20(1)	-10(1)
O(4)	62(1)	65(1)	75(1)	8(1)	11(1)	14(1)
C(1)	51(1)	48(1)	50(1)	2(1)	10(1)	0(1)
C(2)	56(1)	58(1)	48(1)	5(1)	10(1)	-3(1)
C(3)	50(1)	51(1)	50(1)	-3(1)	12(1)	-8(1)
C(4)	43(1)	44(1)	59(1)	0(1)	7(1)	-5(1)
C(5)	53(1)	55(1)	49(1)	6(1)	7(1)	-1(1)
C(6)	51(1)	43(1)	48(1)	-2(1)	8(1)	-7(1)
C(7)	70(1)	51(1)	49(1)	-8(1)	11(1)	-6(1)
C(8)	66(1)	49(1)	43(1)	-8(1)	21(1)	0(1)
C(9)	79(2)	68(2)	61(1)	6(1)	26(1)	9(1)
C(10)	109(2)	62(2)	84(2)	14(1)	54(2)	7(2)
C(11)	86(2)	74(2)	95(2)	-14(2)	50(2)	-17(1)
C(12)	68(2)	96(2)	73(2)	-11(2)	24(1)	-16(1)
C(13)	68(1)	69(2)	55(1)	2(1)	19(1)	-3(1)
C(14)	85(2)	110(2)	59(2)	-19(2)	21(1)	-10(2)
C(15)	74(2)	64(2)	101(2)	-11(1)	22(1)	13(1)
C(16)	86(2)	140(3)	53(1)	9(2)	-2(1)	34(2)

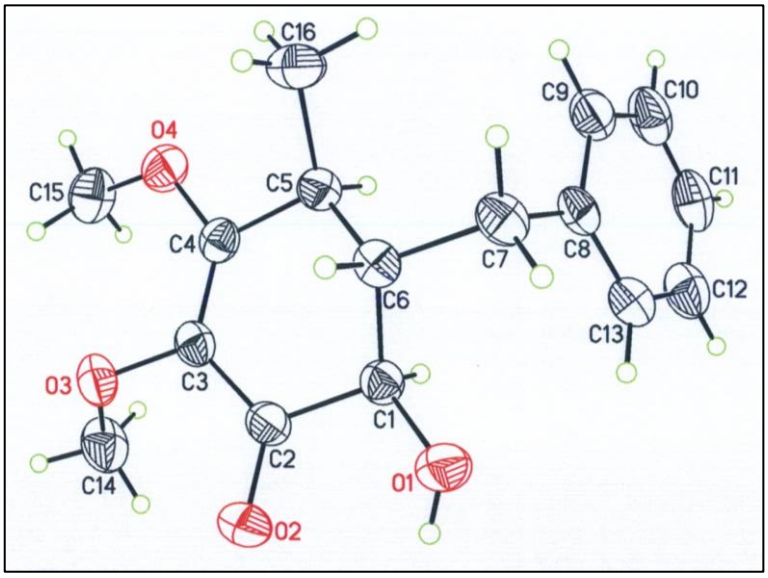

Table S7. Crystal data, atomic coordinates bond lengths and bond angles of compound **16c** (IC16471, deposit CCDC 1036449)

Table 1. Crystal data and structure refinement for ic16471.

Identification code	ic16471
Empirical formula	$C_{16}H_{20}O_4$
Formula weight	276.32
Temperature	295(2) K
Wavelength	1.54178 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 5.8502(3) Å alpha = 88.055(6)° b = 10.6878(8) Å beta = 85.254(5)° c = 11.8197(8) Å gamma = 81.792(5)°
Volume, Z	728.77(8) $Å^3$, 2
Density (calculated)	1.259 Mg/m^3
Absorption coefficient	0.732 mm^{-1}
F(000)	296
Crystal size	0.25 x 0.20 x 0.15 mm
Θ range for data collection	3.75 to 67.98°
Limiting indices	$-4 \le h \le 6$, $-12 \le k \le 12$, $-14 \le l \le 11$
Reflections collected	4363
Independent reflections	2644 (R_{int} = 0.0190)
Completeness to Θ = 67.98°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.00000 and 0.90623
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2644 / 0 / 181
Goodness-of-fit on F^2	1.040
Final R indices [I>2σ(I)]	R1 = 0.0568, wR2 = 0.1625
R indices (all data)	R1 = 0.0687, wR2 = 0.1770
Largest diff. peak and hole	0.714 and -0.185 $eÅ^{-3}$

Table 2. Atomic coordinates [x 10^4] and equivalent isotropic displacement parameters [$Å^2$ x 10^3] for ic16471. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
O(1)	-76(3)	4018(2)	11714(1)	57(1)
O(2)	2954(3)	4339(2)	9565(1)	59(1)
O(3)	6539(3)	2471(2)	9695(1)	65(1)
O(4)	7329(3)	1482(2)	11989(1)	60(1)
C(1)	2017(3)	4557(2)	11554(2)	42(1)
C(2)	3413(4)	3958(2)	10519(2)	44(1)
C(3)	5235(4)	2909(2)	10676(2)	48(1)
C(4)	5725(4)	2457(2)	11720(2)	45(1)
C(5)	4463(4)	2992(2)	12800(2)	44(1)
C(6)	3344(4)	4368(2)	12614(2)	42(1)
C(7)	1867(4)	4879(2)	13684(2)	54(1)
C(8)	1286(4)	6298(2)	13697(2)	48(1)
C(9)	2734(4)	7032(3)	14164(2)	62(1)
C(10)	2188(5)	8334(3)	14205(2)	67(1)
C(11)	211(5)	8927(2)	13781(2)	64(1)
C(12)	-1236(5)	8224(3)	13308(2)	65(1)
C(13)	-716(4)	6918(2)	13268(2)	57(1)
C(14)	5374(7)	1809(3)	8972(3)	93(1)
C(15)	8997(5)	884(3)	11163(2)	72(1)
C(16)	2804(5)	2095(2)	13318(2)	62(1)

Table 3. Bond lengths [Å] and angles [°] for ic16471.

O(1)-C(1)	1.422(3)	O(2)-C(2)	1.223(3)
O(3)-C(3)	1.391(3)	O(3)-C(14)	1.403(4)
O(4)-C(4)	1.347(3)	O(4)-C(15)	1.422(3)
C(1)-C(6)	1.521(3)	C(1)-C(2)	1.521(3)
C(2)-C(3)	1.451(3)	C(3)-C(4)	1.347(3)
C(4)-C(5)	1.508(3)	C(5)-C(16)	1.538(3)
C(5)-C(6)	1.538(3)	C(6)-C(7)	1.541(3)
C(7)-C(8)	1.507(3)	C(8)-C(13)	1.386(3)
C(8)-C(9)	1.391(4)	C(9)-C(10)	1.384(4)
C(10)-C(11)	1.362(4)	C(11)-C(12)	1.372(4)
C(12)-C(13)	1.388(4)		

C(3)-O(3)-C(14)	115.0(2)	C(4)-O(4)-C(15)	122.13(19)
O(1)-C(1)-C(6)	110.74(17)	O(1)-C(1)-C(2)	107.82(18)
C(6)-C(1)-C(2)	112.29(16)	O(2)-C(2)-C(3)	120.7(2)
O(2)-C(2)-C(1)	120.01(19)	C(3)-C(2)-C(1)	119.27(18)
C(4)-C(3)-O(3)	122.5(2)	C(4)-C(3)-C(2)	121.46(19)
O(3)-C(3)-C(2)	115.82(18)	O(4)-C(4)-C(3)	127.7(2)
O(4)-C(4)-C(5)	108.81(17)	C(3)-C(4)-C(5)	123.44(19)
C(4)-C(5)-C(16)	110.23(19)	C(4)-C(5)-C(6)	111.19(16)
C(16)-C(5)-C(6)	115.04(18)	C(1)-C(6)-C(5)	113.09(17)
C(1)-C(6)-C(7)	112.43(17)	C(5)-C(6)-C(7)	111.42(17)
C(8)-C(7)-C(6)	114.35(18)	C(13)-C(8)-C(9)	117.6(2)
C(13)-C(8)-C(7)	121.6(2)	C(9)-C(8)-C(7)	120.7(2)
C(10)-C(9)-C(8)	121.2(2)	C(11)-C(10)-C(9)	120.4(3)
C(10)-C(11)-C(12)	119.5(3)	C(11)-C(12)-C(13)	120.7(3)
C(8)-C(13)-C(12)	120.6(2)		

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters [$Å^2$ x 10^3] for ic16471.

The anisotropic displacement factor exponent takes the form:

$-2\pi^2 [(ha^*)^2 U_{11} + ... + 2hka^* b^* U_{12}]$

	U11	U22	U33	U23	U13	U12
O(1)	38(1)	71(1)	62(1)	18(1)	-7(1)	-8(1)
O(2)	58(1)	74(1)	41(1)	7(1)	-10(1)	6(1)
O(3)	63(1)	80(1)	47(1)	-5(1)	0(1)	6(1)
O(4)	65(1)	60(1)	48(1)	2(1)	-4(1)	19(1)
C(1)	39(1)	44(1)	42(1)	5(1)	-1(1)	-2(1)
C(2)	41(1)	53(1)	38(1)	5(1)	-6(1)	-6(1)
C(3)	48(1)	57(1)	37(1)	-6(1)	-2(1)	2(1)
C(4)	45(1)	45(1)	44(1)	0(1)	-6(1)	1(1)
C(5)	45(1)	50(1)	35(1)	3(1)	-4(1)	1(1)
C(6)	43(1)	45(1)	38(1)	1(1)	0(1)	-3(1)
C(7)	59(1)	57(1)	40(1)	1(1)	6(1)	2(1)
C(8)	51(1)	57(1)	34(1)	-5(1)	4(1)	1(1)
C(9)	54(1)	80(2)	49(1)	-12(1)	-6(1)	-1(1)
C(10)	77(2)	70(2)	58(2)	-21(1)	-2(1)	-18(1)
C(11)	83(2)	55(1)	51(1)	-11(1)	7(1)	-3(1)
C(12)	66(2)	63(2)	60(2)	-7(1)	-6(1)	10(1)
C(13)	53(1)	59(1)	58(1)	-9(1)	-7(1)	-4(1)
C(14)	117(3)	96(2)	60(2)	-30(2)	-21(2)	16(2)
C(15)	73(2)	71(2)	62(2)	-6(1)	-2(1)	26(1)
C(16)	70(2)	54(1)	59(1)	14(1)	7(1)	-3(1)