Supporting Information

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Comparison of Current Chemical and Stereochemical Tests for the Identification and Differentiation of *Pelargonium* Essential Oils: Analytical Data for (-)-(1*S*, 4*R*, 5*S*)-Guaia-6,9-diene and (-)-(7*R*,10*S*)-10-epi-γ-Eudesmol.

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S1: General procedures

^{1}H (400 or 500 MHz) and ^{13}C (100 or 126 MHz) NMR spectra were recorded on a American Varian Mercury plus 400 NMR spectrometers (400 MHz) or Bruker AVANCE DRX spectrometer (500 MHz). Chemical shifts in ppm were referenced to the residual solvent signal (C_6H_6: δH = 7.16, δC = 128.06; $CDCl_3$: δH = 7.26, δC = 77.16). Homonuclear ^{1}H connectivities were determined by the COSY experiment. One-bond heteronuclear ^{1}H-^{13}C connectivities were determined with the HSQC experiment. Two- and three-bond ^{1}H-^{13}C connectivities were determined by HMBC experiments optimized for a $^{2,3}J$ = 8 Hz. Through-space ^{1}H connectivities were evidenced using a NOESY experiment with a mixing time of 500 ms. Silica gel 60 (40-63 µm) (Sorbtech, Norcross, GA, USA) was used for gravity column chromatography. Flash chromatography purifications were performed on Biotage Isolera Four (Biotage, Charlotte, North Carolina, USA) using FLASH+ silica gel cartridges. The UV detection of the collected fractions was performed at 254 and 220 nm. Collected fractions were monitored by TLC on Merck 60 F254 (0.25 mm) plates, which were visualized by UV inspection and staining with *p*-anisaldehyde staining mix. *P. graveolens* essential oil originated from China was purchased by Sigma-Aldrich (St. Louis, MO, USA). *P. graveolens* essential oil originated from Egypt was purchased by Now Foods (Bloomingdale, IL, USA).

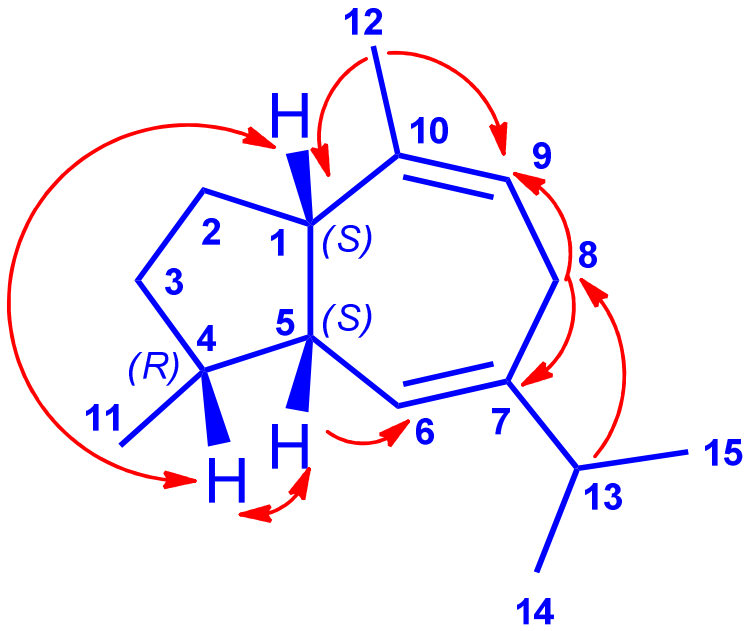
S2: Compounds isolation

(-)-(1*S*,4*R*,5*S*)-Guaia-6,9-diene **(13)**

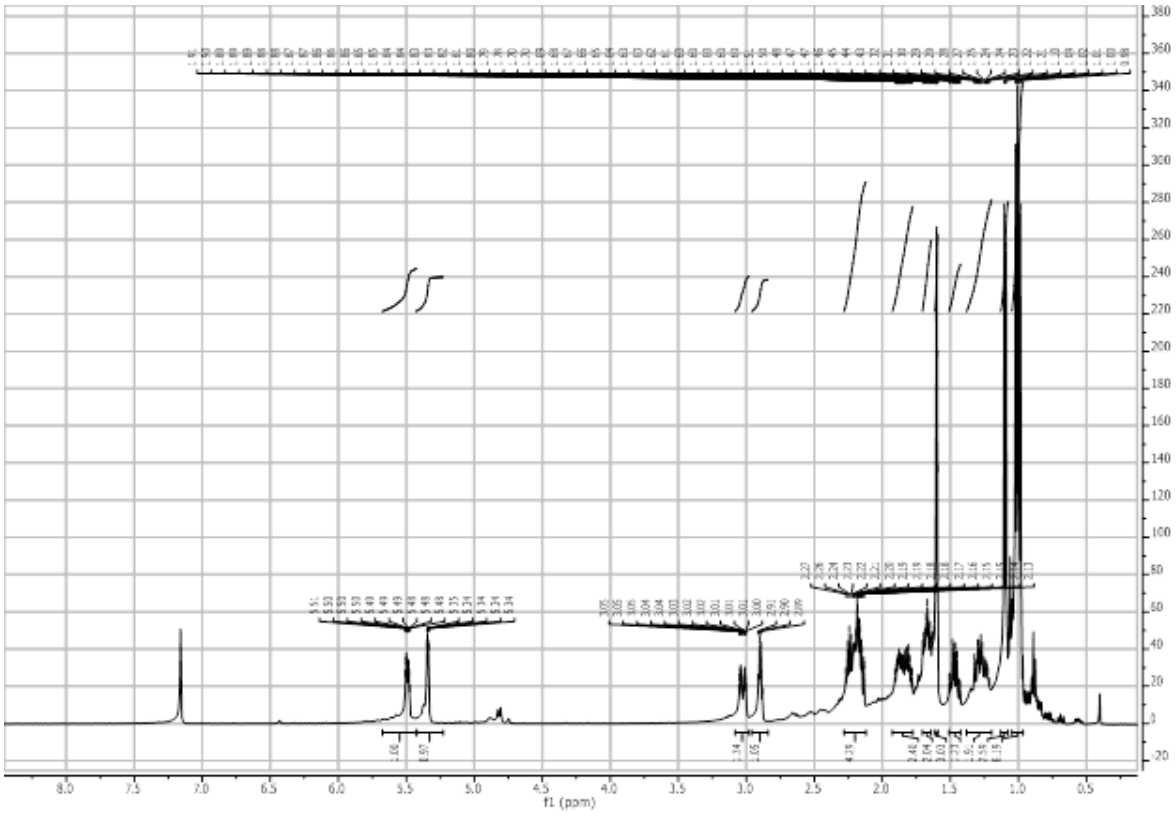
Isolation of (-)-(1*S*,4*R*,5*S*)-guaia-6,9-diene (**13**) was performed on silica gel gravimetric column. Five grams of *P. graveolens* essential oil (originated from China) was directly loaded on the silica gel (180 g, 1:36 w/w, 50x3 cm) and elution was performed using *n*-hexane. Collected fractions were checked on TLC plates and dried under nitrogen flux. (-)-Guaia-6,9-diene (323 mg) was isolated as a colorless oil. Collected fractions were checked for purity by GC/MS and NMR.

(-)-10-epi-γ-Eudesmol **(15)**

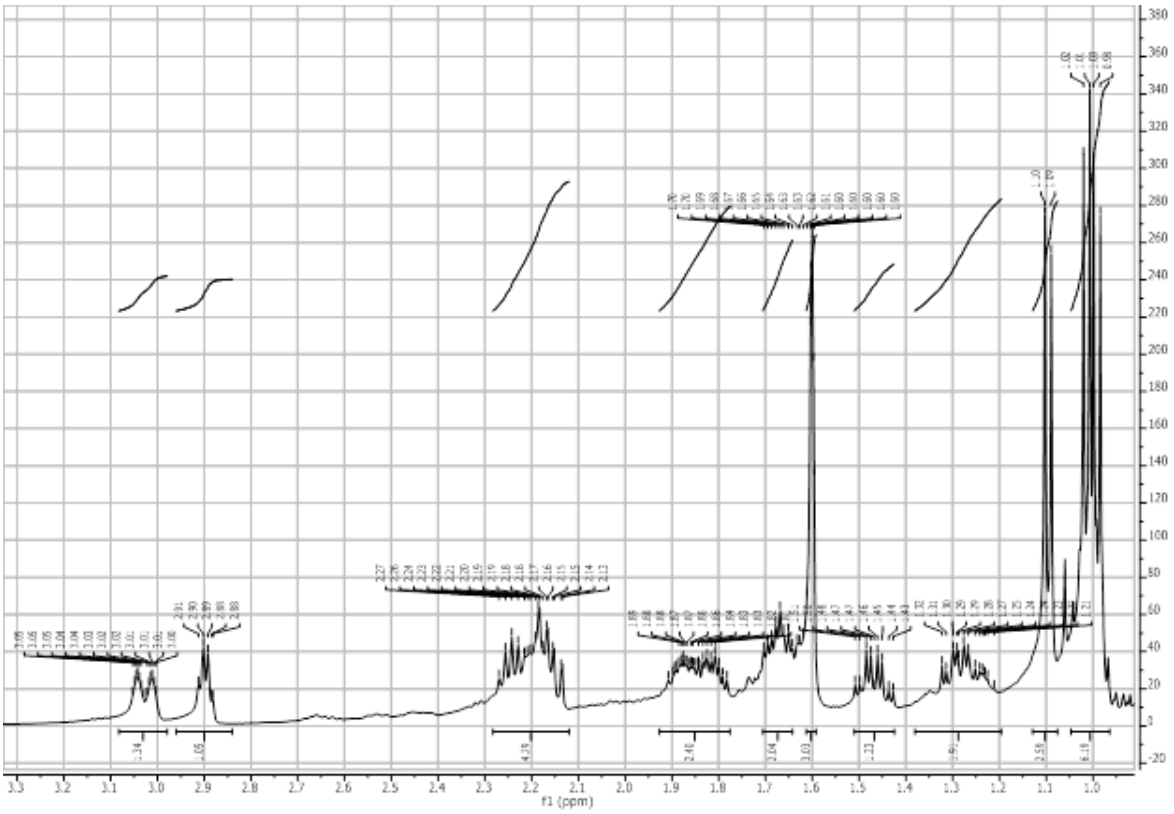
(-)-10-epi-γ-Eudesmol was isolated using a flash chromatography system. The essential oil of *P. graveolens* originated from Egypt (1.7 g) was loaded on a silica gel samplet then purified on a SNAP KP-Sil 50 g cartridge before elution. Isolation was performed using hexane/methylene chloride (50 mL/min flow rate, gradient elution from 3% to 80% methylene chloride in 20 column volumes). Collected fractions were checked on TLC plates then dried under nitrogen flux. Identification and purity of (-)-10-epi-γ-eudesmol (213 mg, colorless oil) was performed by GC/MS and NMR.



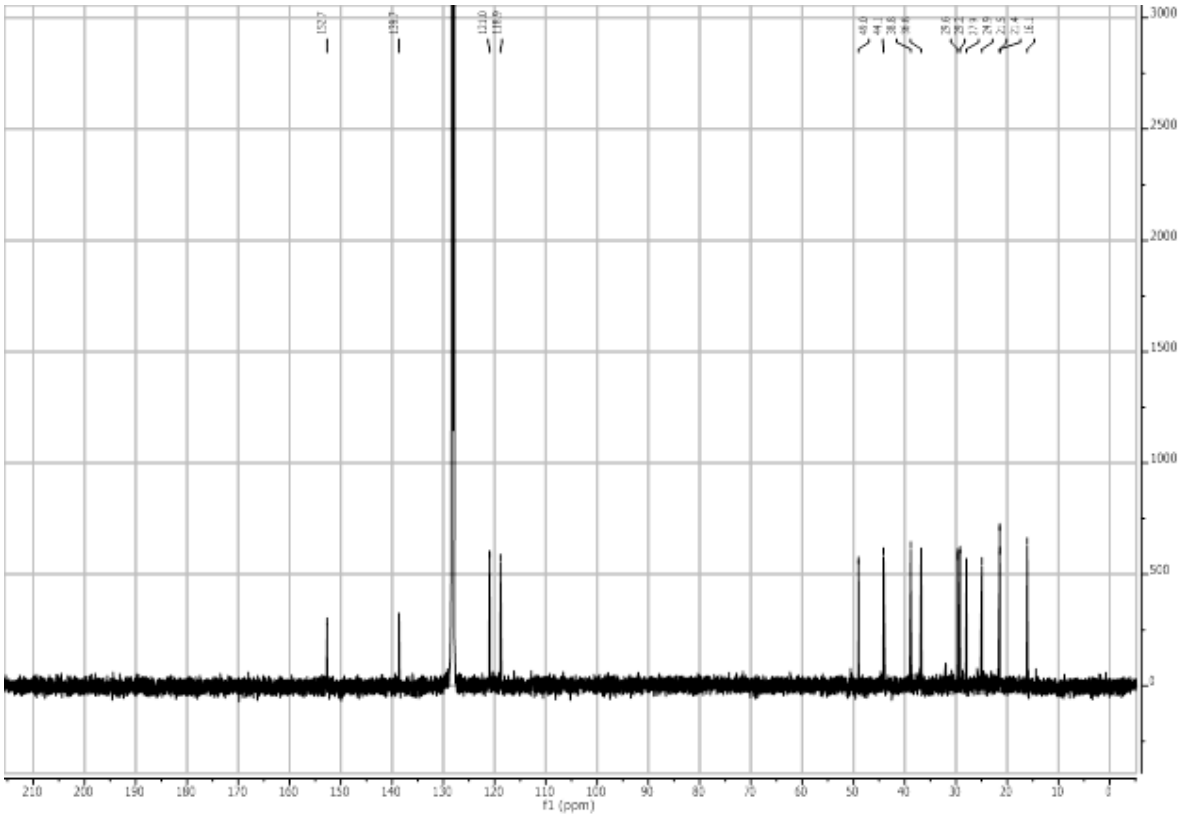
S3: Selected ^{1}H-^{13}C HMBC (→) and NOESY (↔) correlations for (-)-(1*S*,4*R*,5*S*)-guaia-6,9-diene (**13**)



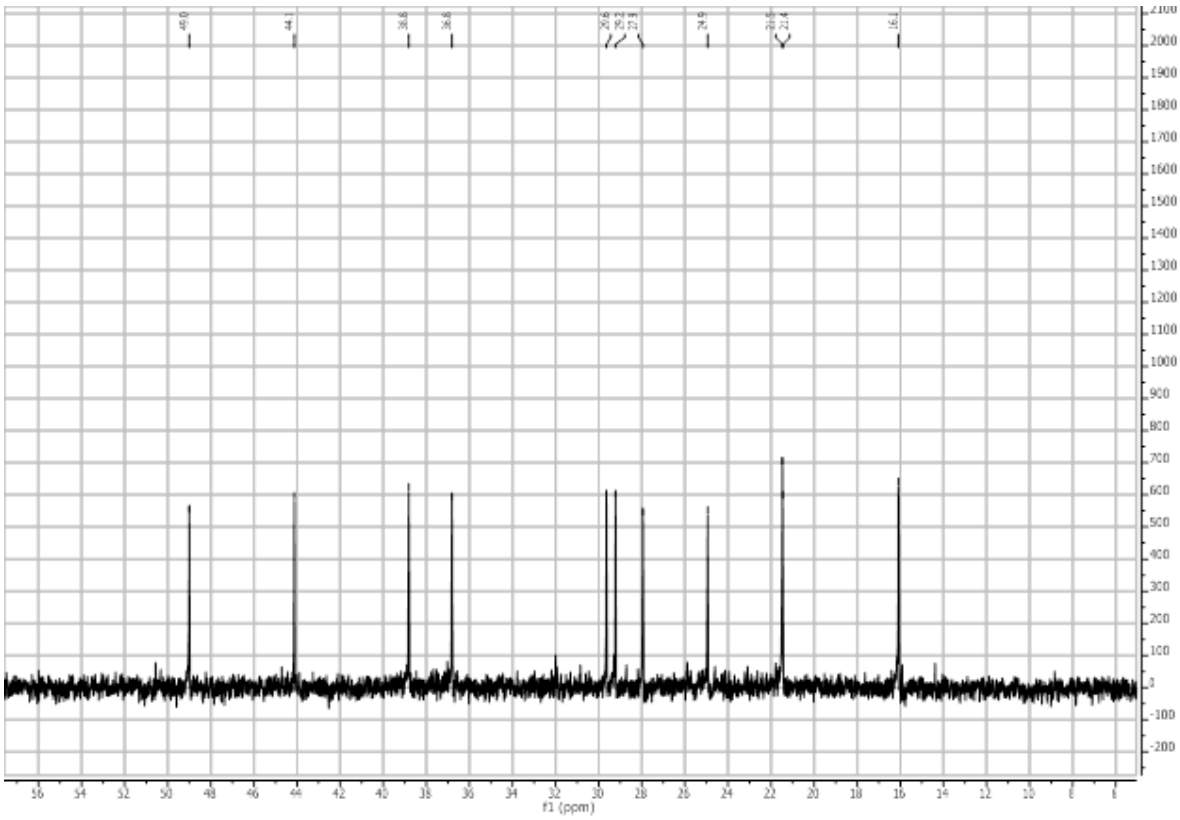
S4a: ^{1}H NMR spectrum (C_6H_6, 500MHz) of compound **13**



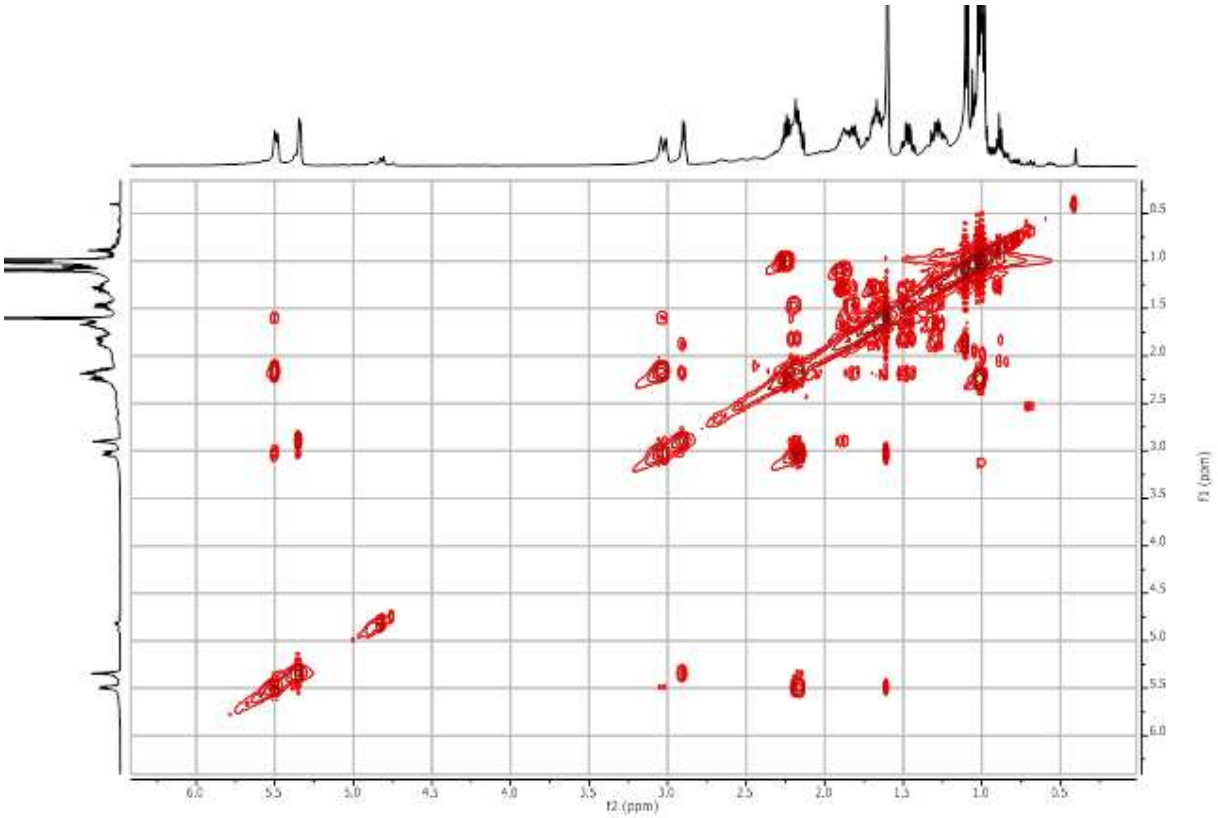
S4b: Expansion of ^{1}H NMR spectrum (C_6H_6, 500 MHz) of compound **13**



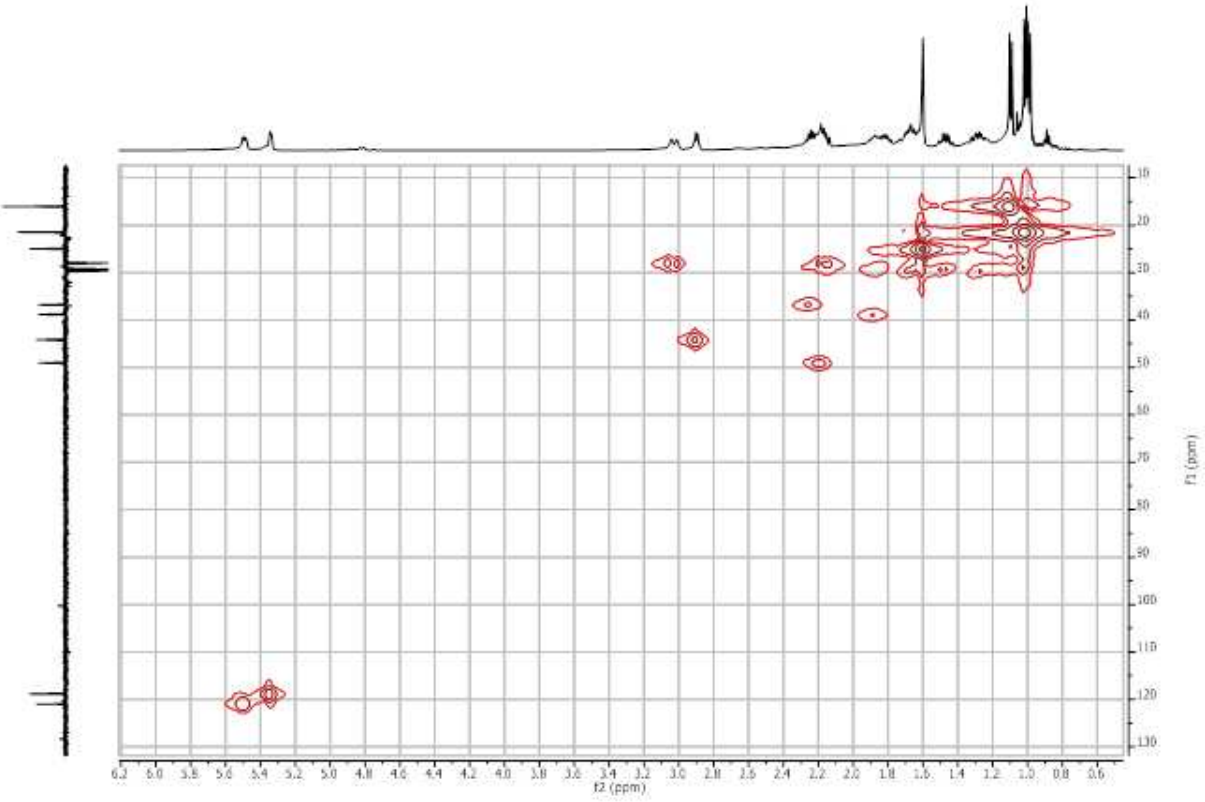
S5a: ^{13}C NMR spectrum (C_6H_6, 126 MHz) of compound **13**



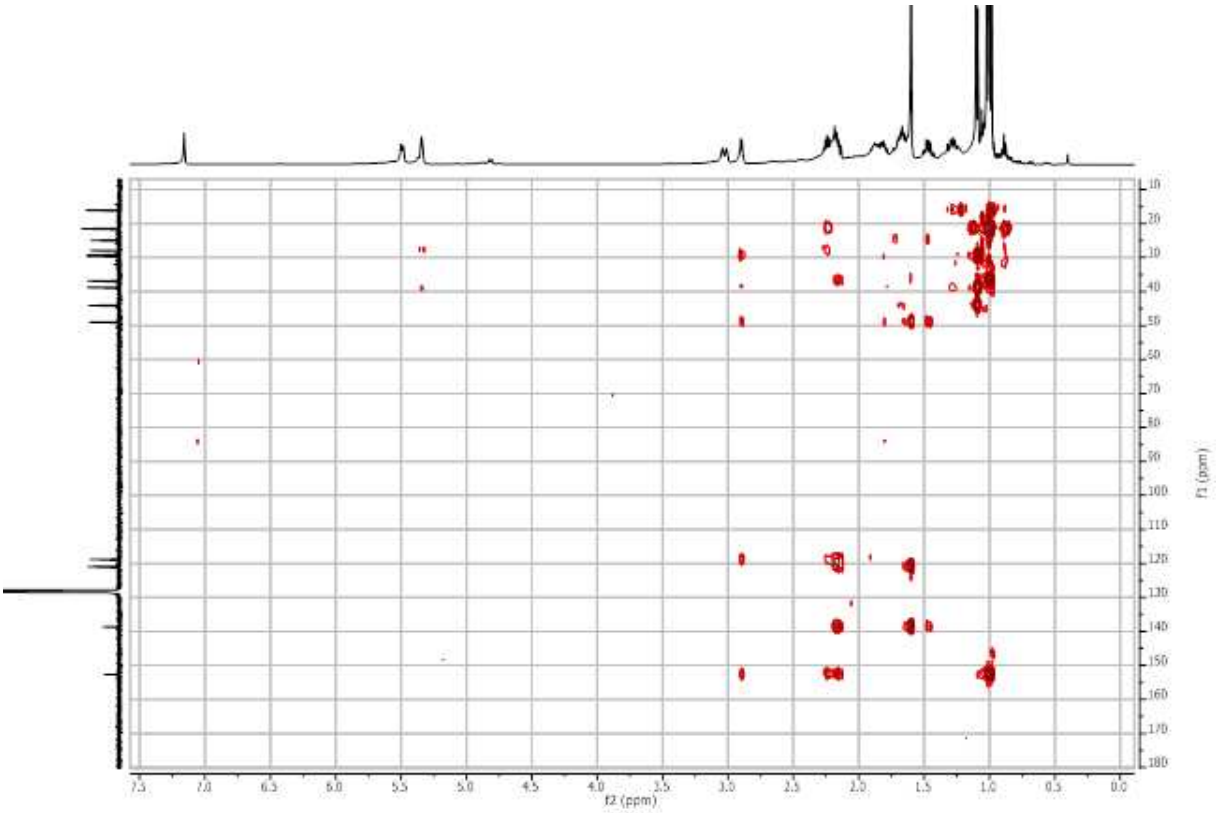
S5b: Expansion of ^{13}C NMR spectrum (C_6H_6, 126 MHz) of compound **13** between δ 58 and 5 ppm



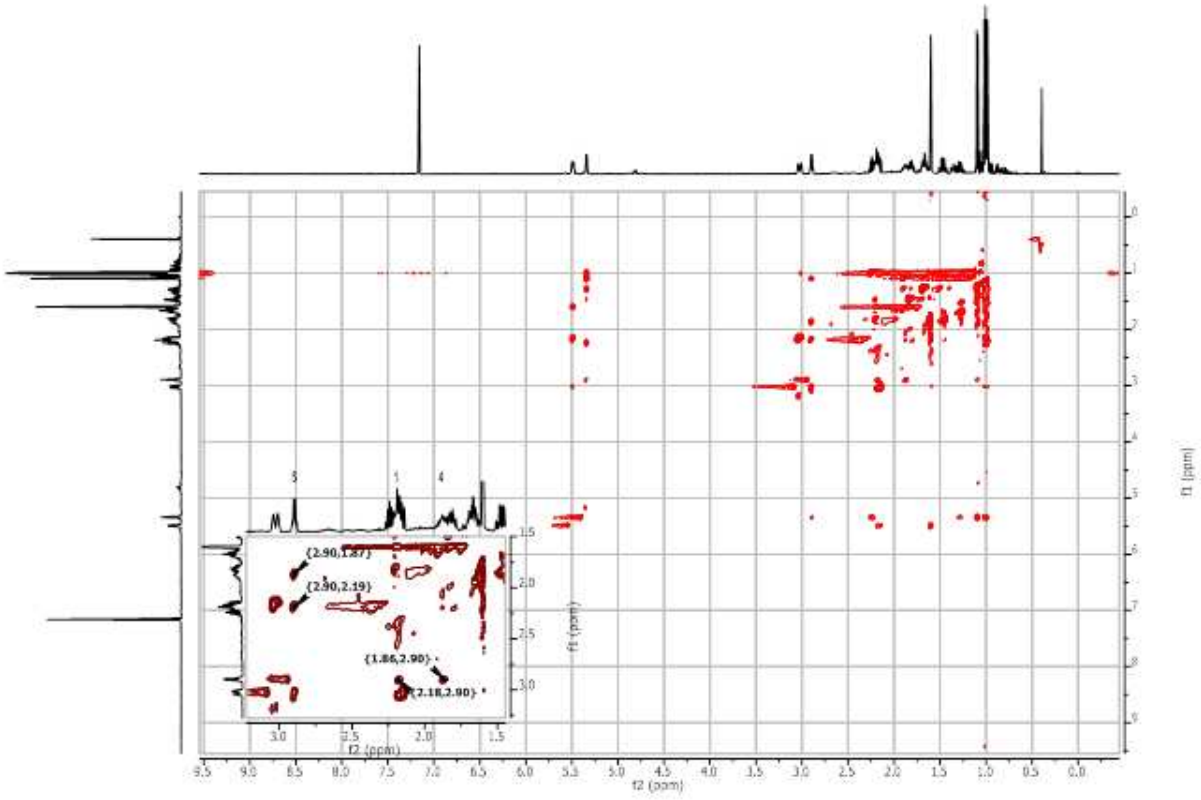
S6: ^{1}H-^{1}H DQFCOSY NMR spectrum (C_6H_6, 500MHz) of compound **13**



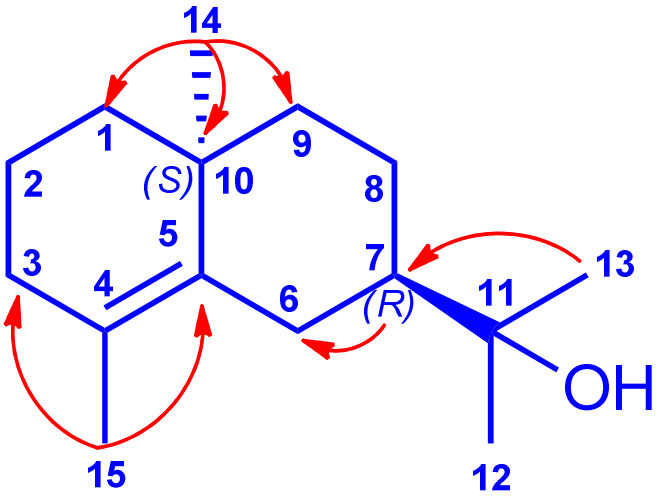
S7: HMQC spectrum of compound **13**



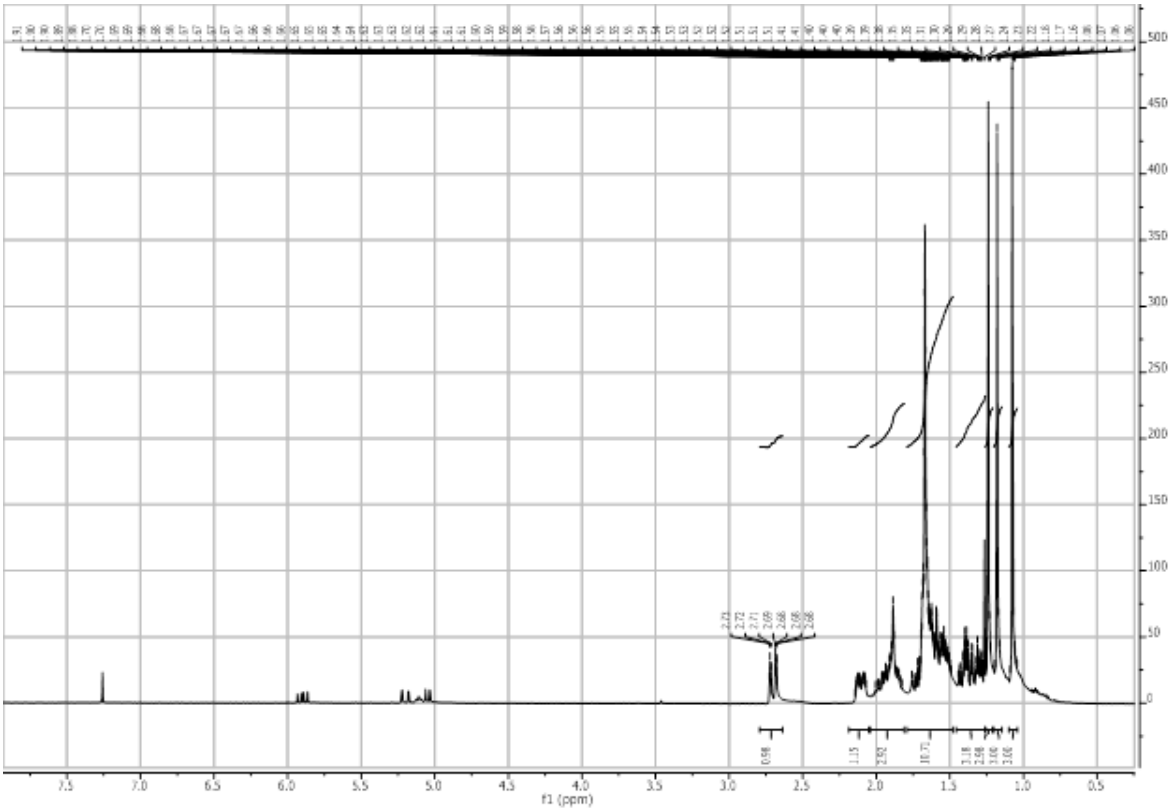
S8: HMBC spectrum of compound **13**



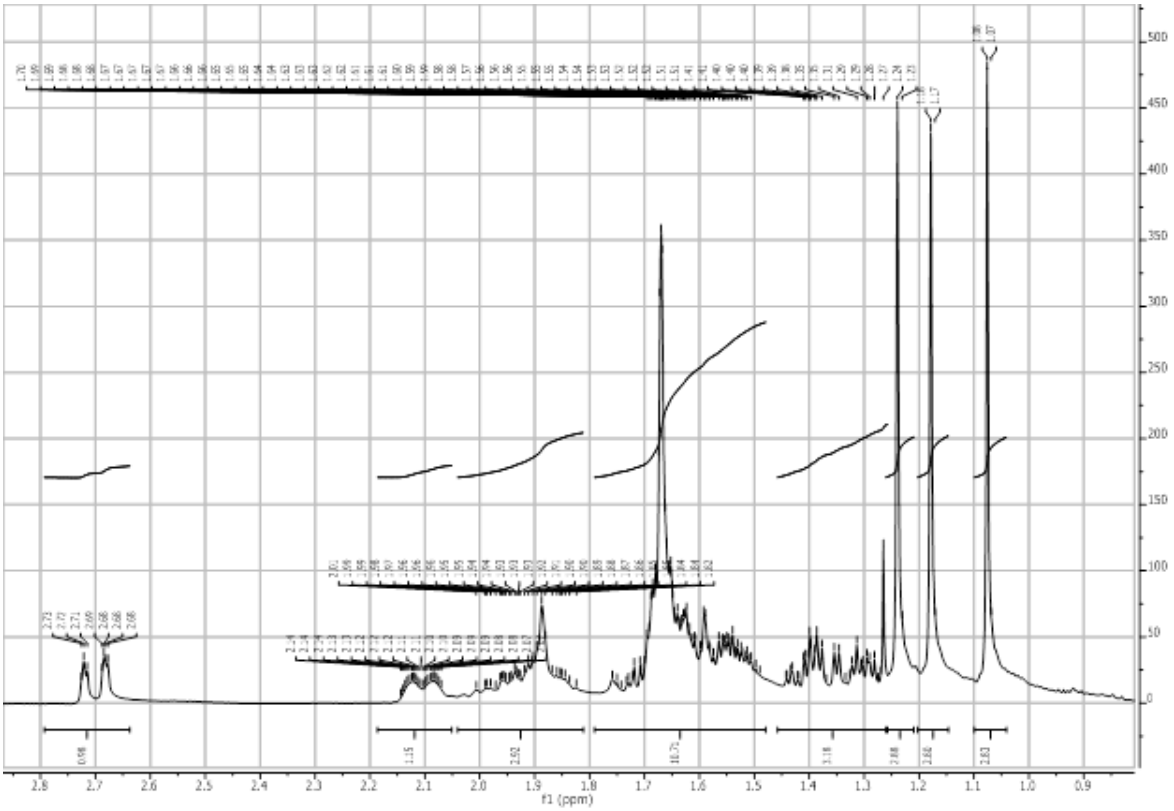
S9: NOESY spectrum (C_6H_6, 500MHz) of compound **13**



S10: Selected ^{1}H-^{13}C HMBC (→) correlations for (-)-10-epi-γ-eudesmol (**15**)

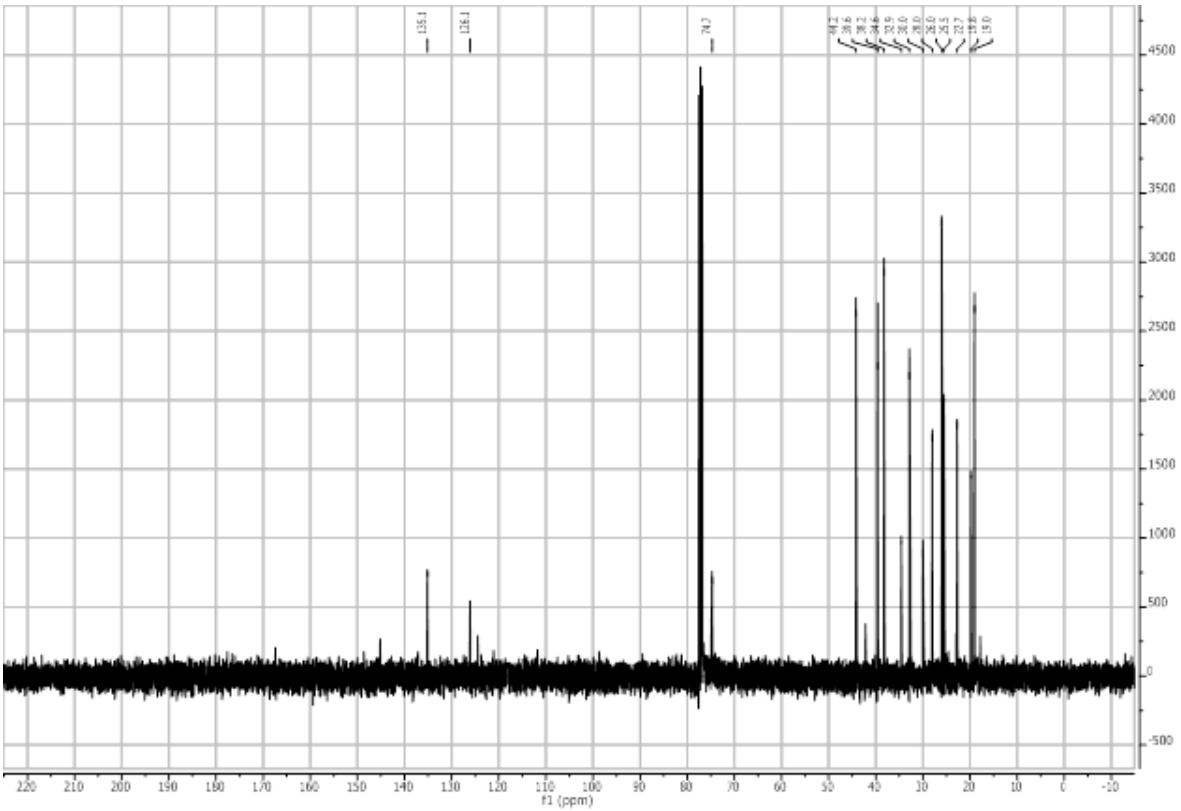


S11a: ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of compound **15**

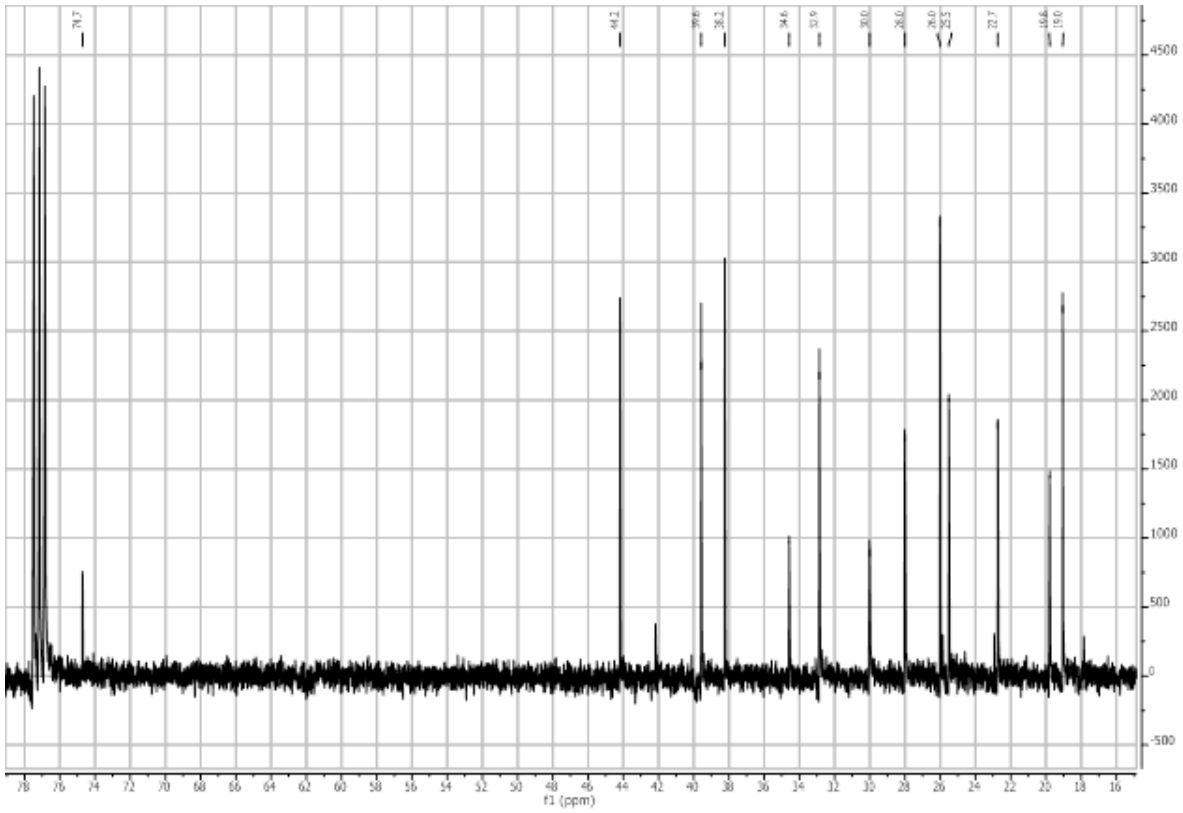


S11b: Expansion of ^{1}H NMR spectrum ($CDCl_3$, 400MHz) of compound **15**

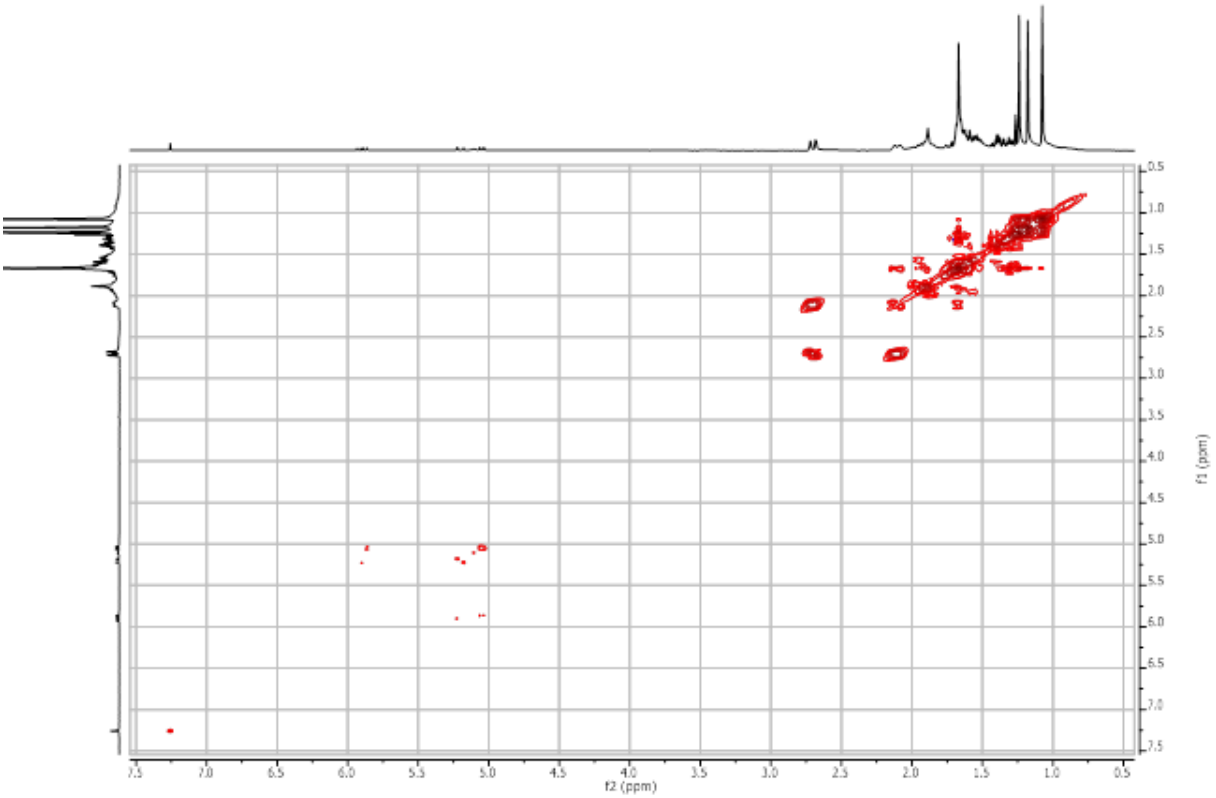
between δ 2.8-0.75 ppm



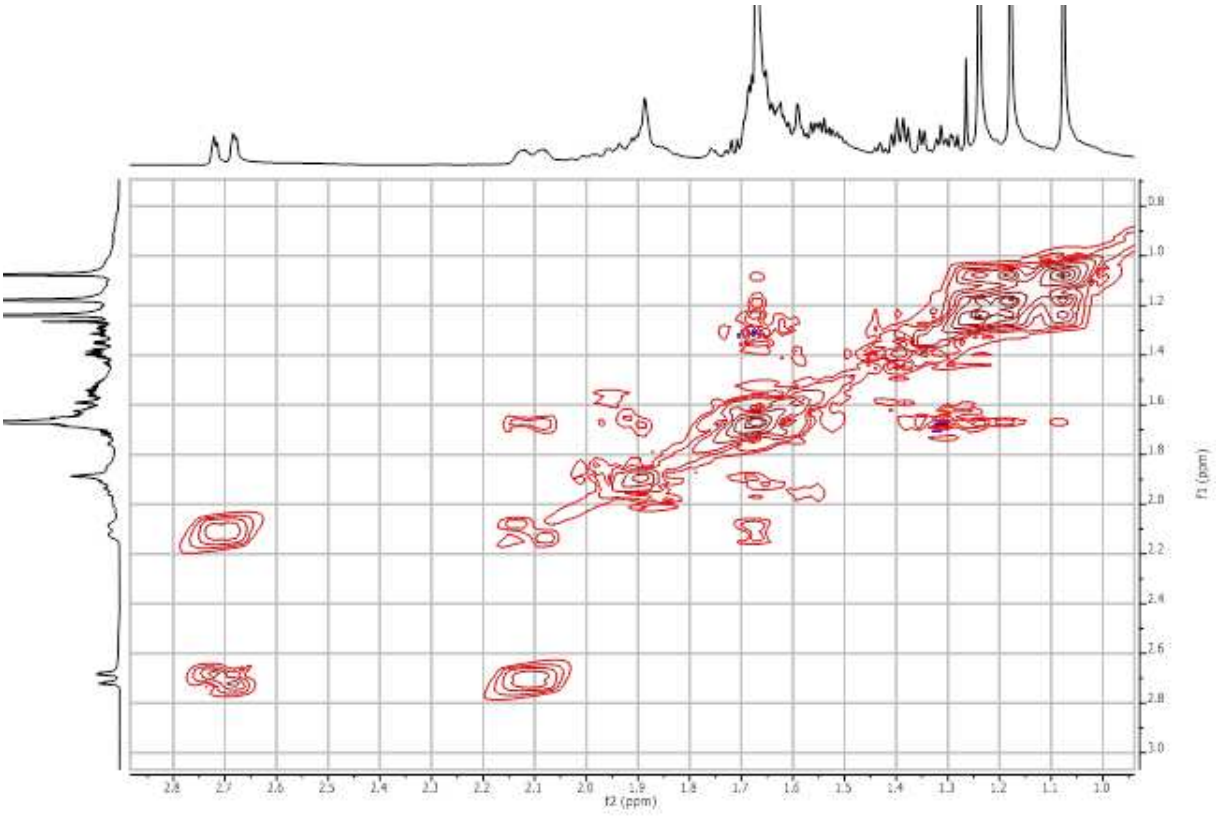
S12a: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **15**



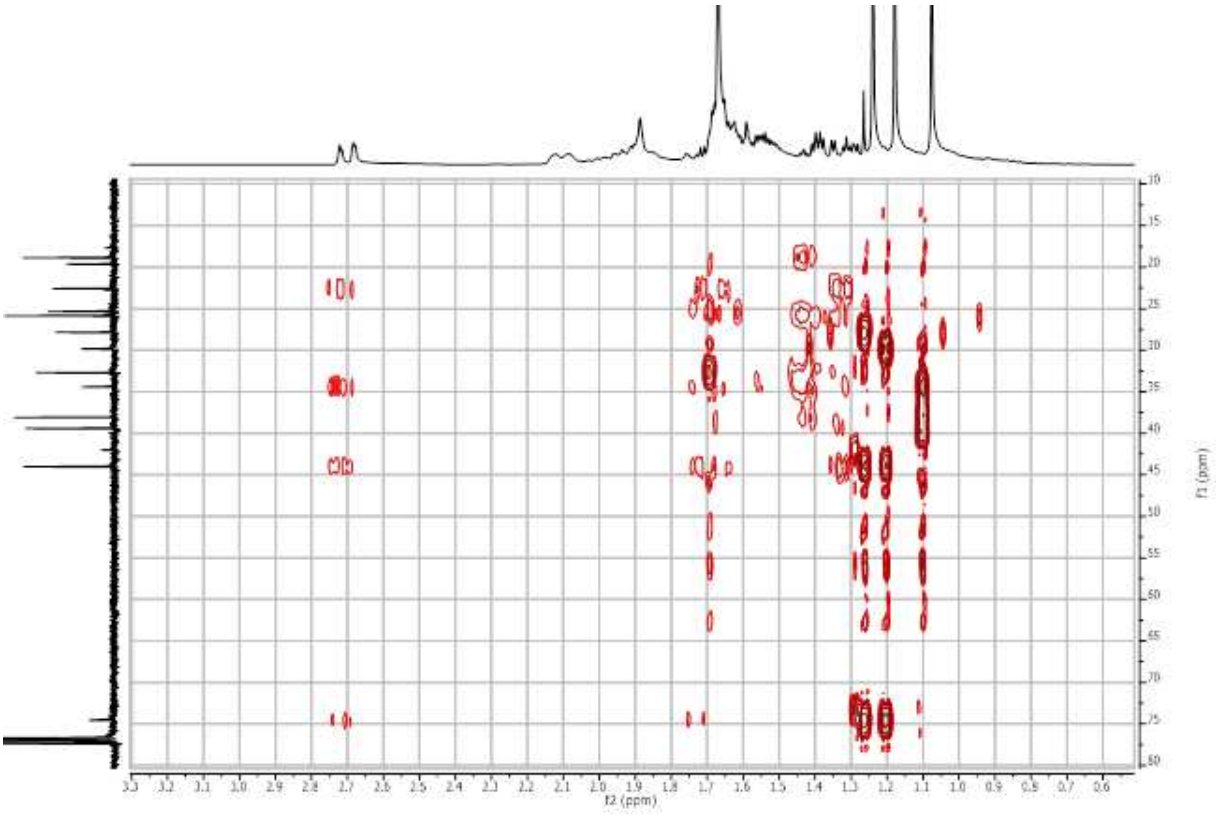
S12b: Expansion of ^{13}C NMR spectrum ($CDCl_3$, 100 MHz) of compound **15** between δ 78 and 15 ppm



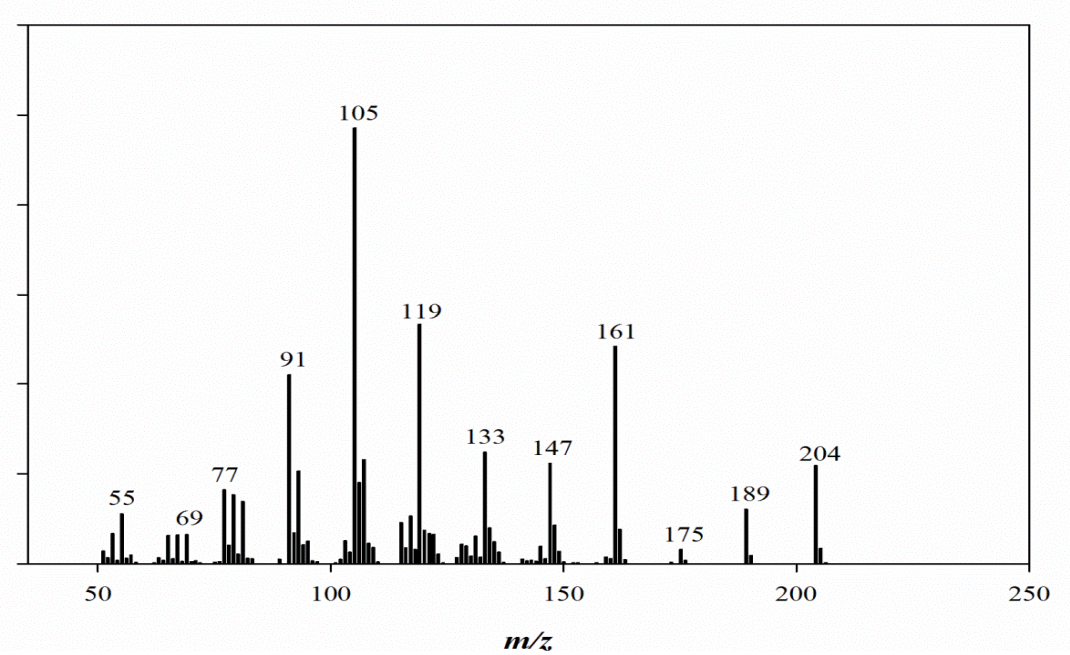
S13a: ^{1}H-^{1}H DQFCOSY NMR spectrum ($CDCl_3$, 400MHz) of compound **15**



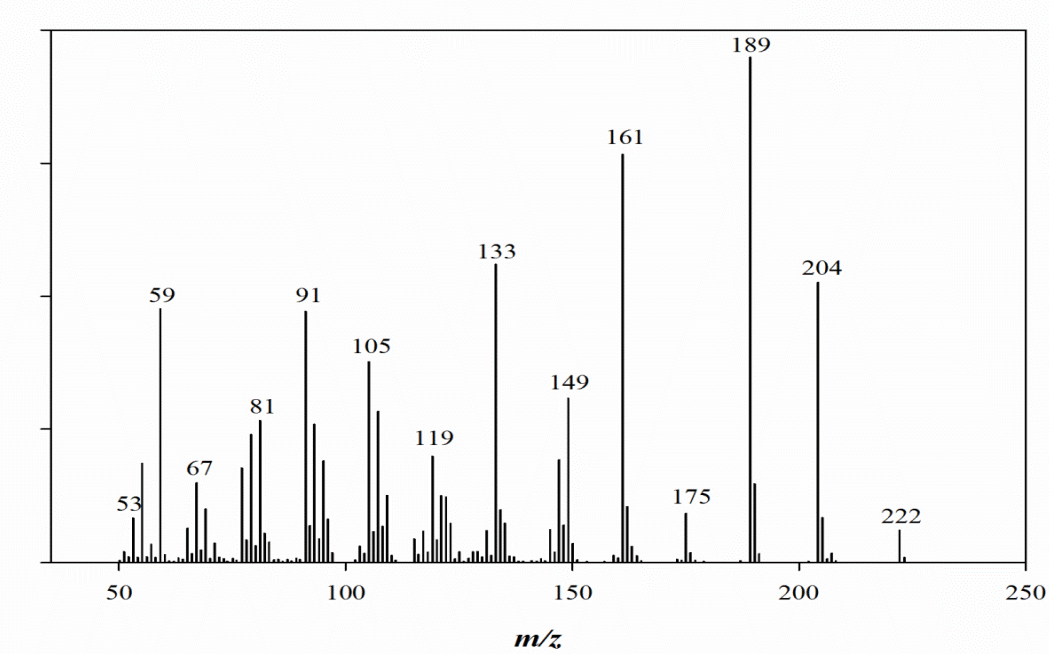
S13b: Expansion of ^{1}H-^{1}H DQFCOSY NMR spectrum ($CDCl_3$, 400MHz) of compound **15** between δ 2.8-0.9 ppm



S14: HMBC spectrum of compound **15**



S15: EI mass spectrum of compound **13**



S16: EI mass spectrum of compound **15**