# Electronic Supplementary Information

## Triplet Energy Management Between Two Signaling Units Through Cooperative Rigid Scaffolds

Paula Miro, Ignacio Vayá, Germán Sastre, M. Consuelo Jiménez, M. Luisa Marin and Miguel A. Miranda*

Departamento de Química/Instituto de Tecnología Química UPV-CSIC, Universitat Politècnica de València, Camino de Vera s/n, 46022 Valencia, Spain, E-mail: mmiranda@qim.upv.es

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## 1. Experimental procedures

**Absorption Measurements**. UV spectra were recorded on a Cary 300 (Varian) spectrophotometer.

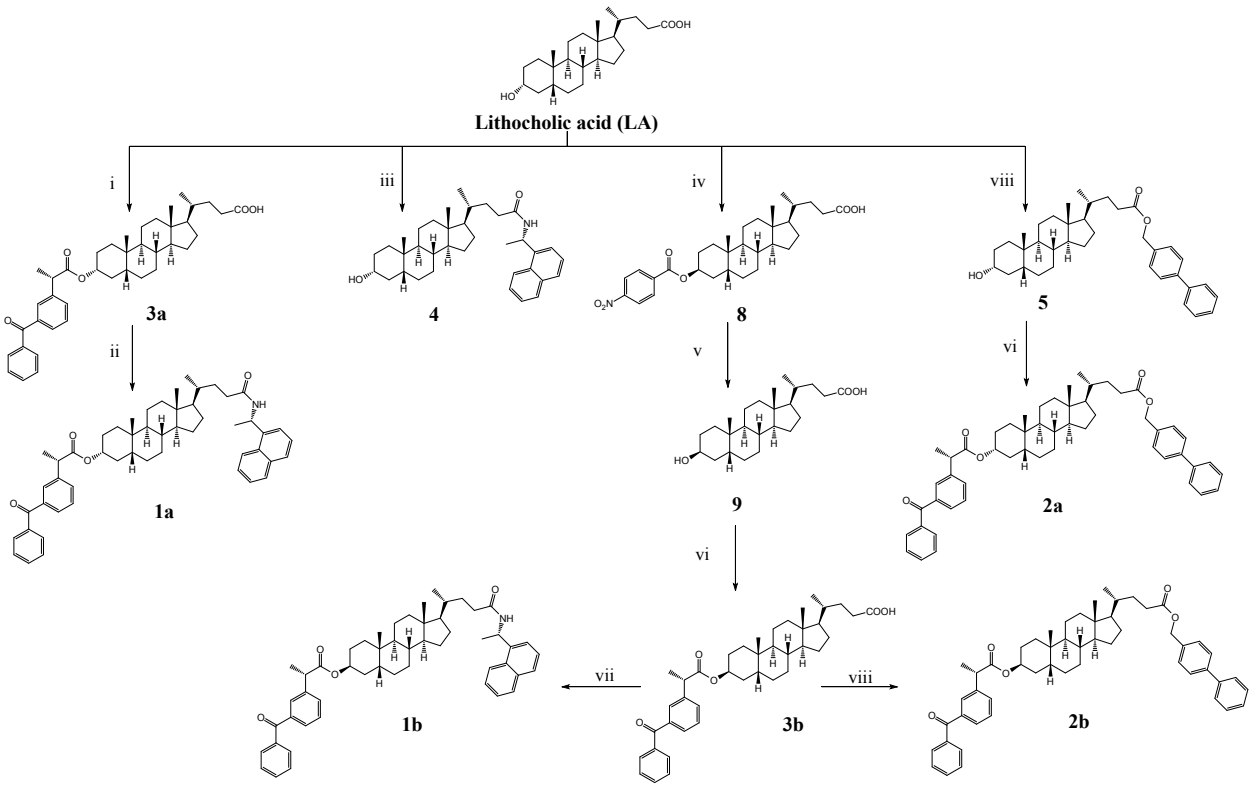
**Laser Flash Photolysis (LFP)**. A pulsed Nd:YAG L52137 V LOTIS TII with an excitation wavelength of 355 nm was employed. The equipment consists of a pulsed laser, a 77250 Oriel monochromator and an oscilloscope DP04054 Tektronixwith connection to a personal computer for the transference of the output signal. The single pulses were *ca*. 10 ns duration, and the energy was maintained at 20 mJ/pulse. Transient spectra were recorded using quartz cells of 1 cm path length containing $N_2$-purged solutions.

**Phosphorescence.** Phosphorescence spectra were performed in a Photon Technology International (PTI, TimeMaster TM-2/2003) spectrophotometer equipped with a pulsed Xe lamp, operating in a time-resolved mode with a delay time of 0.5 ms. The samples were dissolved in ethanol, introduced in a quartz tube of 5 mm of diameter and cooled at 77 K for the measurements.

**Nuclear Magnetic Resonance (NMR).** Both Brucker 400 MHz and a Brucker 300 MHz spectrometers were used for the NMR experiments. The signal of the solvent, chloroform or methanol, was used as a reference for the determination of the chemical shifts (δ) in ppm.

**UPLC-MS-MS.** Chromatography was performed on an ACQUITY UPLC system (Waters Corp.) containing a conditioned autosampler at 4 °C. The separation was carried out on an ACQUITY UPLC BEH C18 column (50 mm × 2.1 mm i.d., 1.7 μm) at the temperature of 40 °C. The analysis was performed with isocratic elution of 70% MeOH and 30% water (containing 0.01% formic acid) as the mobile phase during 12 minutes followed by a gradient to reach 100% of MeOH. The injection volume was 1μL. The Waters ACQUITY™ XevoQToF Spectrometer (Waters Corp.) was connected to the UPLC system via an electrospray ionization (ESI) interface. The ESI source was operated in positive or negative ionization mode depending on the experiment with the capillary voltage at 3.0 kV. The temperature of the source and desolvation was set at 120 °C and 500 °C, respectively. All data collected in Centroid mode were acquired using Masslynx™ software (Waters Corp.). Leucine-enkephalin was used as the lock mass generating an $[M+H]^+$ ion (*m*/*z* 556.2771) at a concentration of 500 pg/mL and flow rate of 20 μL/min to ensure accuracy during the MS analysis.

**2. Synthetic strategy to prepare LA derivatives incorporating BZP at 3-position and NEA or BIP at the lateral chain.**




**Scheme S1.** Reagents and conditions: (i) KP, DCC, 4-DMAP, pyridine; (ii) NEA, EDC, CH2Cl2; (iii) NEA, EDC, toluene; (iv) 4-nitobenzoic acid, Ph3P, DEAD, THF; (v) KOH, THF; (vi) KP, TBTU, DIEA, DMF; (vii) NEA, TBTU, DIEA, DMF; (viii) PBA, TBTU, DIEA, DMF.

### 3. Synthesis of all compounds

LA, KP, NEA, PBA, *N,N*′-Dicyclohexylcarbodiimide (DCC), 4-dimethylaminopyridine (4-DMAP), *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide (EDC), triphenylphosphine ($Ph_3P$), diethyl azodicarboxylate (DEAD), *O*-(Benzotriazol-1-yl)-*N,N,N′,N*′-tetramethyluronium tetrafluoroborate (TBTU), *N,N*-Diisopropylethylamine (DIEA), glacial acetic acid ($CH_3COOH$) dimethylformamide (DMF), methanol (MeOH), dichloromethane synthetic grade ($CH_2Cl_2$), tetrahydrofuran (THF), hexane, ethylacetate (EtOAc), acetonitrile ($CH_3CN$) and KOH were purchased from Sigma–Aldrich. Dichloromethane (HPLC grade) was from Scharlab.

**Synthesis of 3a**

To a solution of KP (0.203 g, 0.8 mmol) in $CH_2Cl_2$ (10 mL), DCC (0.207 g, 0.85 mmol) and 4-DMAP (catalytic amount) were added as solids. The reaction was stirred while **LA** (0.301 g, 0.8 mmol) in $CH_2Cl_2$ was added dropwise. After 24h, the crude product was washed with diluted $NaHCO_3$, HCl 1 M and brine. Final purification by preparative layer chromatography ($SiO_2$ Merck 60 PF254, EtOAc:Hexane, 80:20) followed by recrystallization gave **3a** (0.343 g, 70%). $^1$H NMR (400 MHz, $CD_3OD$): δ (ppm) 0.64 (s, 3H, $CH_3$); 0.65 (s, 3H, $CH_3$); 0.91 (d, $J$ = 6.3 Hz, 3H, $CH_3$); 1.51 (d, $J$ = 7.2 Hz, 3H, KP-$CH_3$); 3.75 (q, $J$ = 7.2 Hz, 1H, KP-CH); 4.72 (m, 1H, 3β-H); 7.40-7.84 (m, 9H, arom). $^{13}$C NMR (100 MHz, $CD_3OD$): δ (ppm) 196.8 (C), 179.3 (C), 173.9 (C), 141.3 (C), 138.0 (C), 137.7 (C), 132.6 (CH), 131.6 (CH), 130.2 (2xCH), 129.4 (CH), 129.0 (CH), 128.7 (CH), 128.4 (2xCH), 74.2 (CH), 56.7 (CH), 56.2 (CH), 45.8 (CH), 42.9 (C), 42.1 (CH), 40.6 (CH), 40.3 ($CH_2$), 36.0 (CH), 35.5 (CH), 35.2 ($CH_2$), 34.7 (C), 32.4 ($CH_2$), 31.9 ($CH_2$), 31.2 ($CH_2$), 31.0 ($CH_2$), 28.3 ($CH_2$), 27.2 ($CH_2$), 26.5 ($CH_2$), 24.3 ($CH_2$), 23.5 ($CH_3$), 21.0 ($CH_2$), 18.8 ($CH_3$), 18.4 ($CH_3$), 12.2 ($CH_3$). m/z found 613.3893, calculated for $C_{40}H_{52}O_5$ ($MH^+$) 613.3896.

**Synthesis of 1a**

To a solution of **3a** (0.140 g, 0.23 mmol) in $CH_2Cl_2$ (10 mL) containing EDC (0.048 g, 0.25 mmol), a solution of NEA (0.058 g, 0.23 mmol) in $CH_2Cl_2$ (2 mL) was added dropwise. The mixture was stirred overnight at rt and then the solvent was evaporated under vacuum; the crude product was dissolved in $CH_2Cl_2$ and washed with diluted $NaHCO_3$, HCl 1 M and brine. Final purification by preparative layer chromatography ($SiO_2$ Merck 60 PF254, $CH_2Cl_2$:EtOAc, 80:20) followed by recrystallization gave **1a** (0.127 g, 72%). $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.59 (s, 3H, $CH_3$); 0.86 (d, $J$ = 6.0 Hz, 3H, 21-$CH_3$); 0.91 (s, 3H, $CH_3$); 1.51 (d, $J$ = 6.8 Hz, 3H, KP-$CH_3$); 1.66 (d, $J$ = 6.8 Hz, 3H, NEA-$CH_3$); 3.74 (q, $J$ = 6.8 Hz, 1H, KP-CH); 4.72 (m, 1H, 3□-H); 5.63 (d, $J$ = 8.0 Hz, 1H, NEA-NH); 5.93 (m, 1H, NEA-CH); 7.39-7.90 (m, 15H, arom); 8.09 (d, $J$ = 8.4 Hz, 1H, arom). $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.7 (C), 173.8 (C), 172.5 (C), 141.3 (C), 138.5 (C), 138.0 (C), 137.7 (C), 134.1 (C), 132.6 (CH), 131.6 (CH), 131.3 (C), 130.2 (2xCH), 129.4 (CH), 129.0 (CH), 128.9 (CH), 128.7 (CH), 128.5 (CH), 128.4 (2xCH), 126.7 (CH), 126.1 (CH), 125.3 (CH), 123.7 (CH), 122.7 (CH), 75.1 (CH), 56.6 (CH), 56.2 (CH), 45.9 (CH), 44.6 (CH), 42.9 (C), 42.1 (CH), 40.6 (CH), 40.2 ($CH_2$), 35.9 (CH), 35.6 (CH), 35.1 ($CH_2$), 34.7 (C), 33.9 ($CH_2$), 32.1 ($CH_2$), 31.9 ($CH_2$), 28.4 ($CH_2$), 27.2 ($CH_2$), 26.6 ($CH_2$), 26.4 ($CH_2$), 24.3 ($CH_2$), 23.5 ($CH_3$),

21.0 ($CH_2$), 20.7 ($CH_3$), 18.8 ($CH_3$), 18.5 ($CH_3$), 12.2 ($CH_3$). m/z found 766.4835, calculated for $C_{40}H_{52}O_5$ ($MH^+$) 766.4799.

**Synthesis of 4**

To a solution of **LA** (0.338 g, 0.9 mmol) in anhydrous toluene (10 mL) containing EDC (0.182 g, 0.95 mmol), a solution of NEA (0.154 g, 0.9 mmol) in anhydrous toluene (5 mL) was added dropwise. The reaction was stirred overnight at rt. Then the solvent was concentrated under vacuum; the crude product was dissolved in EtOAc and washed consecutively with diluted $NaHCO_3$, HCl 1M and brine. Purification by preparative layer chromatography ($SiO_2$ Merck 60 PF254, EtOAc:MeOH, 95:5) followed by recrystallization gave **4** (0.350 g, 74%).$^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 0.60 (s, 3H, $CH_3$); 0.64 (s, 3H, $CH_3$); 0.86 (d, *J* = 6.4 Hz, 3H, 21-$CH_3$); 1.67 (d, *J* = 6.8 Hz, 3H, NEA-$CH_3$); 2.15-2.30 (m, 2H, $CH_2$); 2.33-2.45 (m, 2H, $CH_2$); 3.62 (m, 1H, 3β-H); 5.63 (d, *J* = 8.0 Hz, 1H, NEA-NH); 5.93 (m, 1H, NEA-CH); 7.38-7.57 (m, 4H, arom); 7.75-7.89 (m, 2H, arom); 8.09 (d, *J* = 8.4 Hz, 1H, arom). $^{13}$C NMR (100 MHz, $CD_3OD$): δ (ppm) 172.6 (C), 138.4 (C), 134.1 (C), 131.3 (C), 128.9 (CH), 128.5 (CH), 126.7 (CH), 126.0 (CH), 125.3 (CH), 123.7 (CH), 122.7 (CH), 72.1 (CH), 56.6 (CH), 56.2 (CH), 44.7 (CH), 42.9 (C), 42.2 (CH), 40.6 (CH), 40.3 ($CH_2$), 36.6 ($CH_2$), 36.0 (CH), 35.6 (CH), 35.5 ($CH_2$), 34.7 (C), 33.9 ($CH_2$), 31.9 ($CH_2$), 31.0 ($CH_2$), 30.7 ($CH_2$), 28.4 ($CH_2$), 27.3 ($CH_2$), 26.6 ($CH_2$), 24.4 ($CH_2$), 23.5 ($CH_3$), 21.0 ($CH_2$), 20.7 ($CH_3$), 18.5 ($CH_3$), 12.2 ($CH_3$). m/z found 530.3998, calculated for $C_{36}H_{51}NO_2$ ($MH^+$) 530.3989.

**Synthesis of 8**

To a stirred solution of **LA** (0.500 g, 1.33 mmol), 4-nitrobenzoic acid (0.266 g, 1.59 mmol) and $Ph_3P$ (0.418 g, 1.59 mmol) in anhydrous THF (5 mL) at 0 ºC, DEAD 40% (0.625 mL, 1.59 mmol) was added dropwise, and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into brine and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography ($SiO_2$, EtOAc:Hexane:$CH_3COOH$, 10:90:1) gave **8** as a colorless solid (0.614 g, 87%). $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.67 (s, 3H, $CH_3$); 0.93 (d, *J* = 6.3 Hz, 3H, 21-$CH_3$); 1.02 (s, 3H, $CH_3$); 2.33 (m, 2H, $CH_2$); 5.38 (*br* s, 1H, 3α-H); 8.16-8.33 (m, 4H, arom). $^{13}$C NMR

(75 MHz, $CDCl_3$): δ (ppm) 180.2 (C), 164.2 (C), 150.6 (C), 136.7 (C), 130.7 (2xCH), 123.7 (2xCH), 73.0 (CH), 56.7 (CH), 56.1 (CH), 42.9 (C), 40.3 ($CH_2$), 40.1 (CH), 37.9 (CH), 35.8 (CH), 35.5 (CH), 35.2 (C), 31.2 ($CH_2$), 31.1 ($CH_2$), 30.9 ($CH_2$), 30.8 ($CH_2$), 28.3 ($CH_2$), 26.6 ($CH_2$), 26.3 ($CH_2$), 25.3 ($CH_2$), 24.3 ($CH_2$), 24.2 ($CH_3$), 21.3 ($CH_2$), 18.4 ($CH_3$), 12.2 ($CH_3$). m/z found 524.3012, calculated for $C_{31}H_{42}NO_6$ ($M\text{-}H^+$) 524.3012.

**Synthesis of 9**

A stirred solution of **8** (0.386 g, 0.73 mmol) in THF (4 mL) was treated with 7.3 mL of KOH 1M in MeOH and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into HCl 1M and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (Li Chroprep RP-18, $CH_3CN$:$H_2O$, 90:10) gave **9** as a colorless solid (0.227 g, 82%). $^1$H NMR (300 MHz, $CD_3OD$): δ (ppm) 0.71 (s, 3H, $CH_3$); 0.96 (d, $J$ = 6.6 Hz, 3H, 21-$CH_3$); 0.98 (s, 3H, $CH_3$); 2.27 (m, 2H, $CH_2$); 4.04 (*br* s, 1H, 3α-H). $^{13}$C NMR (75 MHz, $CD_3OD$): δ (ppm) 178.1 (C), 67.8 (CH), 58.0 (CH), 57.5 (CH), 43.9 (C), 41.6 ($CH_2$), 41.1 (CH), 37.8 (CH), 37.1 (CH), 36.7 (CH), 36.2 (C), 34.4 ($CH_2$), 32.3 ($CH_2$), 32.0 ($CH_2$), 31.0 ($CH_2$), 29.2 ($CH_2$), 28.5 ($CH_2$), 27.9 ($CH_2$), 27.5 ($CH_2$), 25.3 ($CH_2$), 24.5 ($CH_3$), 22.2 ($CH_2$), 18.8 ($CH_3$), 12.6 ($CH_3$). m/z found 375.2896, calculated for $C_{24}H_{39}O_3$ ($M\text{-}H^+$) 375.2899.

**Synthesis of 3b**

To a stirred solution of **9** (0.163 g, 0.36 mmol), TBTU (0.174 g, 0.54 mmol) and KP (0.139 g, 0.54 mmol) in DMF (5 mL), DIEA (0.19 mL, 1.08 mmol) was added dropwise and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into brine and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (Li Chroprep RP-18, $CH_3CN$:$H_2O$, 80:20) gave **3b** as a colorless oil (0.057 g, 21%). $^1$H NMR (300 MHz, $CD_3OD$): δ (ppm) 0.65 (s, 3H, $CH_3$); 0.79 (s, 3H, $CH_3$); 0.91 (d, $J$ = 6.3 Hz, 3H, 21-$CH_3$); 1.50 (d, $J$ = 6.9 Hz, 3H, KP-$CH_3$); 2.24 (m, 2H, $CH_2$); 3.85 (q, $J$ = 6.9 Hz, 1H, KP-CH); 5.00 (*br* s, 1H, 3α-H); 7.43-7.85 (m, 9H, arom). $^{13}$C NMR (75 MHz, $CD_3OD$): δ (ppm) 198.0 (C), 178.1 (C), 174.9 (C), 143.0 (C), 139.1 (C), 138.7 (C), 133.9 (CH), 133.0 (CH), 131.0 (2xCH), 130.2 (CH), 129.9 (CH),

129.7 (CH), 129.5 (2xCH), 72.8 (CH), 57.8 (CH), 57.4 (CH), 46.9 (CH), 43.9 (C), 41.4 ($CH_2$), 41.0 (CH), 38.7 (CH), 37.0 (CH), 36.7 (CH), 35.8 (C), 32.3 ($CH_2$), 32.0 ($CH_2$), 31.7 ($CH_2$), 31.3 ($CH_2$), 29.2 ($CH_2$), 27.6 ($CH_2$), 27.2 ($CH_2$), 25.9 ($CH_2$), 25.2 ($CH_2$), 24.4 ($CH_3$), 22.2 ($CH_2$), 18.8 ($CH_3$), 18.2 ($CH_3$), 12.5 ($CH_3$). m/z found 613.3918, calculated for $C_{40}H_{53}O_5$ ($MH^+$) 613.3993.

**Synthesis of 1b**

To a stirred solution of **3b** (0.057 g, 0.093 mmol) and TBTU (0.060 g, 0.186 mmol) in DMF (5 mL), NEA (0.03 mL, 0.186 mmol) and DIEA (0.065 mL, 3.72 mmol) were added dropwise and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into brine and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography (Li Chroprep RP-18, $CH_3CN$:$H_2O$:EtOAc, 70:10:20) gave **1b** as a colorless oil (0.063 g, 88%). $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.58 (s, 3H, $CH_3$); 0.84 (m, 6H, $CH_3$+21-$CH_3$); 1.54 (d, *J* = 7.2 Hz, 3H, KP-$CH_3$); 1.65 (d, *J* = 6.6 Hz, 3H, NEA-$CH_3$); 3.78 (q, *J* = 7.2 Hz, 1H, KP-CH); 5.03 (*br* s, 1H, 3α-H); 5.74 (d, *J* = 8.1 Hz, 1H, NEA-NH); 5.92 (m, 1H, NEA-CH); 7.36-7.91 (m, 15H, arom); 8.08 (d, *J* = 8.4 Hz, 1H, arom). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 196.6 (C), 173.4 (C), 172.5 (C), 141.4 (C), 138.5 (C), 137.9 (C), 137.7 (C), 134.0 (C), 132.6 (CH), 131.7 (CH), 131.3 (C), 130.1 (2xCH), 129.3 (CH), 129.0 (CH), 128.8 (CH), 128.5 (CH), 128.4 (CH), 128.3 (2xCH), 126.6 (CH), 126.0 (CH), 125.2 (CH), 123.7 (CH), 122.6 (CH), 71.5 (CH), 56.6 (CH), 56.2 (CH), 46.0 (CH), 44.6 (CH), 42.8 (C), 40.3 ($CH_2$), 39.9 (CH), 37.4 (CH), 35.7 (CH), 35.5 (CH), 34.8 (C), 33.8 ($CH_2$), 31.9 ($CH_2$), 30.7 ($CH_2$), 30.5 ($CH_2$), 28.3 ($CH_2$), 26.6 ($CH_2$), 26.2 ($CH_2$), 25.0 ($CH_2$), 24.3 ($CH_2$), 23.9 ($CH_3$), 21.2 ($CH_2$), 20.7 ($CH_3$), 18.4 ($CH_3$), 18.1 ($CH_3$), 12.1 ($CH_3$). m/z found 766.4835, calculated for $C_{52}H_{64}NO_4$ ($MH^+$) 766.4860.

**Synthesis of 2b**

To a stirred solution of **3b** (0.148 g, 0.25 mmol), TBTU (0.094 g, 0.29 mmol) and PBA (0.053 g, 0.29 mmol) in DMF (3 mL), DIEA (0.105 mL, 0.6 mmol) was added dropwise, and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into brine and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$

and concentrated under reduced pressure. Purification by column chromatography ($SiO_2$,EtOAc:Hexane, 10:90) gave **2b** as a colorless oil (0.107 g, 57%). $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.61 (s, 3H, $CH_3$); 0.84 (s, 3H, $CH_3$); 0.90 (d, *J* = 6.0 Hz, 3H, 21-$CH_3$); 1.55 (d, *J* = 7.2 Hz, 3H, KP-$CH_3$); 3.80 (q, *J* = 6.9 Hz, 1H, KP-CH); 5.06 (*br* s, 1H, 3α-H); 5.16 (m, 2H, $CH_2$); 7.30-7.88 (m, 18H, arom). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 196.5 (C), 174.2 (C), 173.4 (C), 141.4 (C), 141.2 (C), 140.8 (C), 137.9 (C), 137.7 (C), 135.2 (C), 132.5 (CH), 131.7 (CH), 130.1 (2xCH), 129.3 (CH), 129.0 (CH), 128.9 (2xCH), 128.8 (2xCH), 128.5 (CH), 128.4 (2xCH), 127.5 (CH), 127.4 (2xCH), 127.2 (2xCH), 71.4 (CH), 65.9 ($CH_2$), 56.6 (CH), 56.1 (CH), 46.0 (CH), 42.8 (C), 40.2 ($CH_2$), 39.9 (CH), 37.5 (CH), 35.7 (CH), 35.4 (CH), 34.8 (C), 31.4 ($CH_2$), 31.1 ($CH_2$), 30.7 ($CH_2$), 30.5 ($CH_2$), 28.3 ($CH_2$), 26.6 ($CH_2$), 26.2 ($CH_2$), 25.1($CH_2$), 24.3 ($CH_2$), 23.9 ($CH_3$), 21.2 ($CH_2$), 18.4 ($CH_3$), 18.1 ($CH_3$), 12.1 ($CH_3$). m/z found 801.4520, calculated for $C_{53}H_{62}O_5Na$ ($MNa^+$) 801.4495.

**Synthesis of 5**

To a stirred solution of **LA** (0.200 g, 0.55 mmol) and TBTU (0.212 g, 0.66 mmol) in anhydrous DMF (1 mL), PBA (0.121 g, 0.66 mmol) in DMF (4 mL) followed by DIEA (0.285 mL, 1.65 mmol) were added dropwise, and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into brine and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography ($SiO_2$, EtOAc:Hexane, 10:90) gave **5** as a colorless oil (0.218 g, 76%). $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.62 (s, 3H, $CH_3$); 0.91 (m, 6H, 2x$CH_3$); 2.35 (m, 2H, $CH_2$); 3.63 (m, 1H, 3β-H); 5.15 (m, 2H, $CH_2$); 7.30-7.65 (m, 9H, arom). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 174.3 (C), 141.3 (C), 140.8 (C), 135.3 (C), 128.9 (2xCH), 128.8 (2xCH), 127.6 (CH), 127.5 (2xCH), 127.3 (2xCH), 72.0 (CH), 66.0 ($CH_2$), 56.6 (CH), 56.1 (CH), 42.9 (C), 42.2 (CH), 40.6 (CH), 40.3 ($CH_2$), 36.6 ($CH_2$), 36.0 (CH), 35.5 ($CH_2$+CH), 34.7 (C), 31.5 ($CH_2$), 31.1 ($CH_2$), 30.7 ($CH_2$), 28.3 ($CH_2$), 27.3 ($CH_2$), 26.6 ($CH_2$), 24.4 ($CH_2$), 23.5 ($CH_3$), 21.0 ($CH_2$), 18.4 ($CH_3$), 12.2 ($CH_3$). m/z found 565.3668, calculated for $C_{37}H_{50}O_3Na$ ($MNa^+$) 565.3658.

**Synthesis of 2a**

To a stirred solution of **5** (0.100 g, 0.16 mmol) and TBTU (0.063 g, 0.20 mmol) in anhydrous DMF (1 mL), PBA (0.037 g, 0.20 mmol) in DMF (4 mL) followed by DIEA (0.084 mL, 0.48 mmol) were added dropwise, and then the reaction mixture was allowed to react overnight at rt. Afterwards, it was poured into brine and extracted with $CH_2Cl_2$; the combined organic layers were washed with brine, dried over $MgSO_4$ and concentrated under reduced pressure. Purification by column chromatography ($SiO_2$, EtOAc:Hexane, 10:90) gave **2a** as a colorless oil (0.088 g, 69%). $^1$H NMR (300 MHz, $CDCl_3$): δ (ppm) 0.62 (s, 3H, $CH_3$); 0.91 (m, 6H, 2x$CH_3$); 1.52 (d, *J* = 7.2 Hz, 3H, KP-$CH_3$); 2.35 (m, 2H, $CH_2$); 3.75 (q, *J* = 7.2 Hz, 1H, KP-CH); 4.73 (m, 3H, 3β-H); 5.16 (m, 2H, $CH_2$); 7.32-7.84 (m, 18H, arom). $^{13}$C NMR (75 MHz, $CDCl_3$): δ (ppm) 196.6 (C), 174.2 (C), 173.7 (C), 141.3 (2xC), 140.8 (C), 138.0 (C), 137.7 (C), 135.2 (C), 132.6 (CH), 131.5 (CH), 130.2 (2xCH), 129.3 (CH), 128.9 (5xCH), 128.6 (CH), 128.4 (2xCH), 127.5 (CH), 127.4 (2xCH), 127.2 (2xCH), 75.0 (CH), 66.0 ($CH_2$), 56.5 (CH), 56.1 (CH), 45.8 (CH), 42.8 (C), 42.1 (CH), 40.5 (CH), 40.2 ($CH_2$), 35.9 (CH), 35.4 (CH), 35.1 ($CH_2$), 34.7 (C), 32.3 ($CH_2$), 31.4 ($CH_2$), 31.1 ($CH_2$), 28.3 ($CH_2$), 27.1 ($CH_2$), 26.6 ($CH_2$), 26.4 ($CH_2$), 24.3 ($CH_2$), 23.4 ($CH_3$), 21.0 ($CH_2$), 18.7 ($CH_3$), 18.4 ($CH_3$), 12.2 ($CH_3$). m/z found 779.4693, calculated for $C_{53}H_{63}O_5$ ($MH^+$) 779.4676.

**Synthesis of 6**

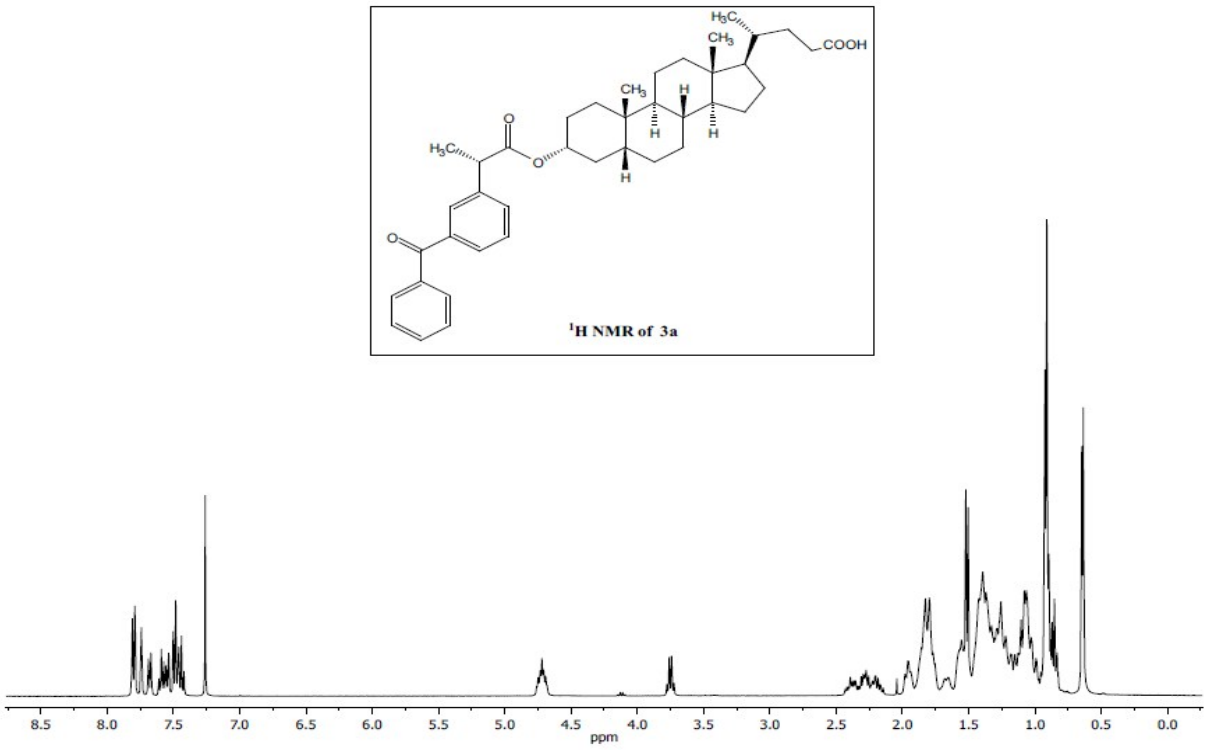
To a solution of KP (0.203 g, 0.8 mmol) in $CH_2Cl_2$ (10 mL), EDC (0.163 g, 0.85 mmol) was added as solid. The mixture was stirred at rt and then a solution of NEA (0.137 g, 0.8 mmol) in $CH_2Cl_2$ was added dropwise. After one day, the crude product was washed with diluted $NaHCO_3$, HCl 1 M and brine. Purification by preparative layer chromatography ($SiO_2$ Merck 60 PF254, EtOAc:Hex, 50:50) followed by recrystallization gave **6** (0.280 g, 82%). $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.54 (d, *J* = 7.2 Hz, 3H, $CH_3$); 1.63 (d, *J* = 6.8 Hz, 3H, $CH_3$); 3.57 (q, *J* = 7.2 Hz, 1H, KP-CH); 5.66 (*br* d, *J* = 7.6 Hz, 1H, NEA-NH); 5.85 (m, 1H, NEA-CH); 7.27-7.86 (m, 16H, arom). $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.6 (C), 172.4 (C), 141.7 (C), 138.1 (2xC), 137.5 (C), 134.0 (C), 132.6 (CH), 131.5 (CH), 131.1 (C), 130.1 (2xCH), 129.2 (CH), 129.1 (CH), 128.8 (2xCH), 128.5 (CH), 128.4 (2xCH), 126.4 (CH), 125.9 (CH), 125.2 (CH), 123.3 (CH), 122.5 (CH), 47.2 (CH), 45.1 (CH), 20.7 ($CH_3$), 18.6 ($CH_3$). m/z found 408.1964, calculated for $C_{28}H_{25}NO_2$ ($MH^+$) 408.1967.

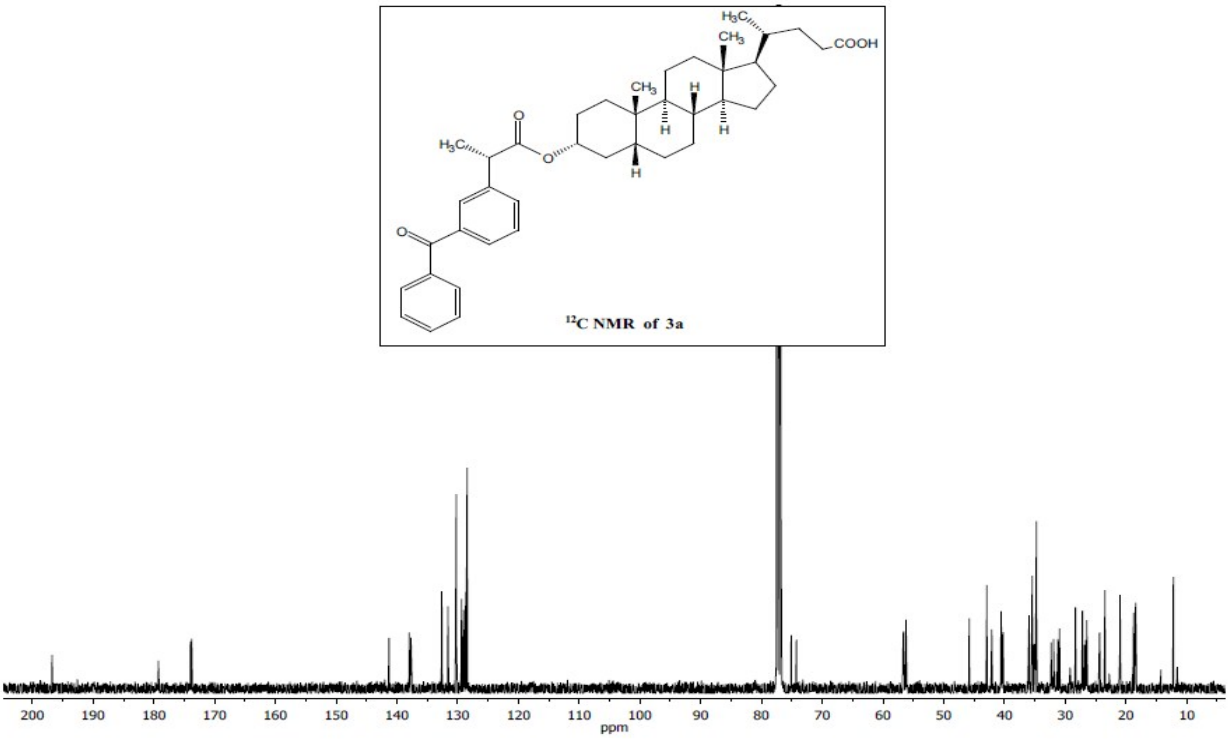
**Synthesis of 7**

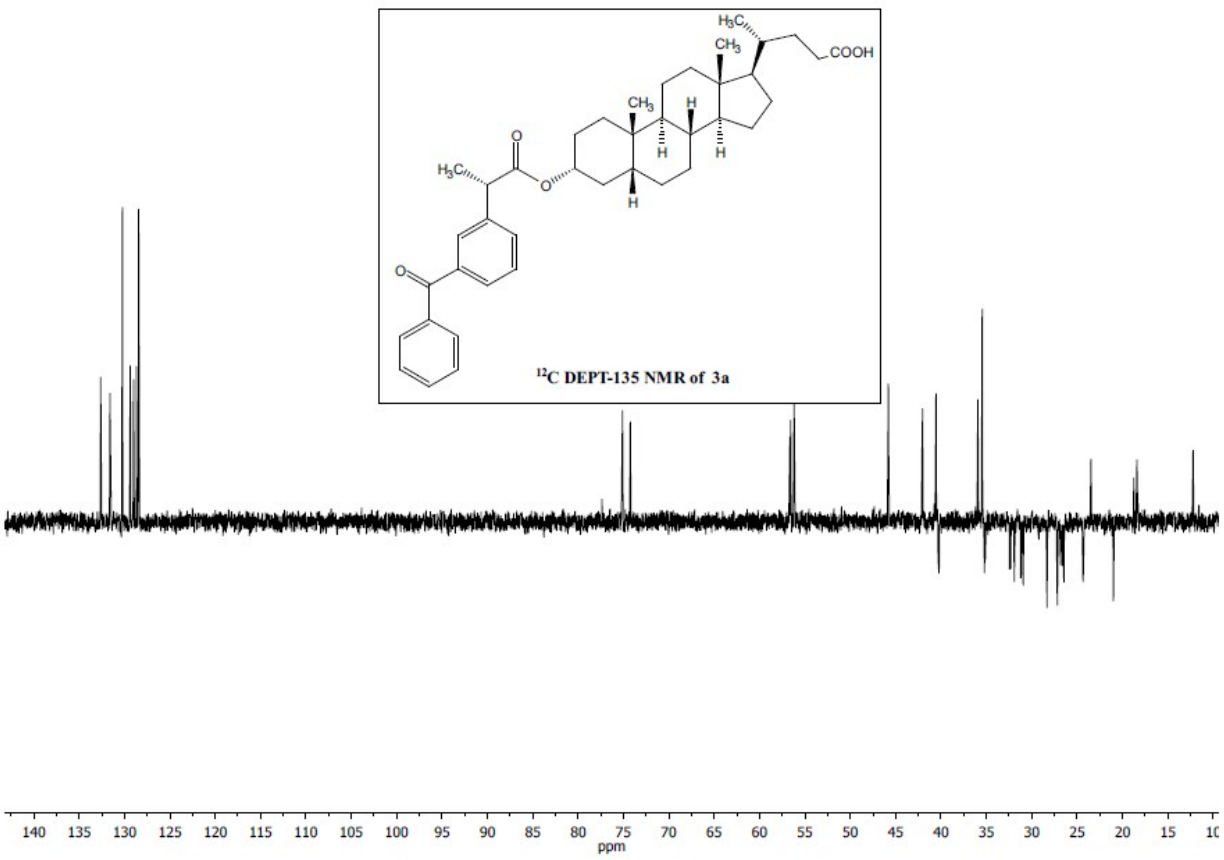
To a solution of KP (0.270 g, 1.1 mmol) in $CH_2Cl_2$ (10 mL), DCC (0.250 g, 1.1mmol) and 4-DMAP (catalytic amount) were added as solids. The mixture was stirred at rt and then a solution of PBA (0.200 g, 1.09 mmol) in $CH_2Cl_2$ was added dropwise. After 2h, the crude product was washed with diluted $NaHCO_3$, HCl 1 M and brine. Purification by preparative layer chromatography ($SiO_2$ Merck 60 PF254, EtOAc:Hex, 20:80) gave **7** (0.416 g, 90%). $^1$H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.61 (d, *J* = 8.0 Hz, 3H, KP-$CH_3$); 3.91 (q, *J* = 8.0 Hz, 1H, KP-CH); 5.19 (m, 2H, $CH_2$); 7.34-7.49 (m, 8H, arom); 7.55-7.59 (m, 6H, arom); 7.71-7.82 (m, 4H, arom). $^{13}$C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.3 (C), 173.7 (C), 141.0 (C), 140.6 (C), 140.5 (C), 137.8 (C), 137.4 (C), 134.2 (C), 132.4 (C), 131.4 (CH), 129.9 (2xCH), 129.2 (CH), 128.9 (CH), 128.7 (2xCH), 128.5 (CH), 128.3 (2xCH), 128.2 (2xCH), 127.3 (CH), 127.1 (2xCH), 127.0 (2xCH), 66.3 ($CH_2$), 45.3 (CH), 18.3 ($CH_3$). m/z found 443.1628, calculated for $C_{29}H_{24}O_3Na$ ($MH^+$) 443.1623.

## 4. Characterization of the synthesized compounds

### 4.1. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 3a

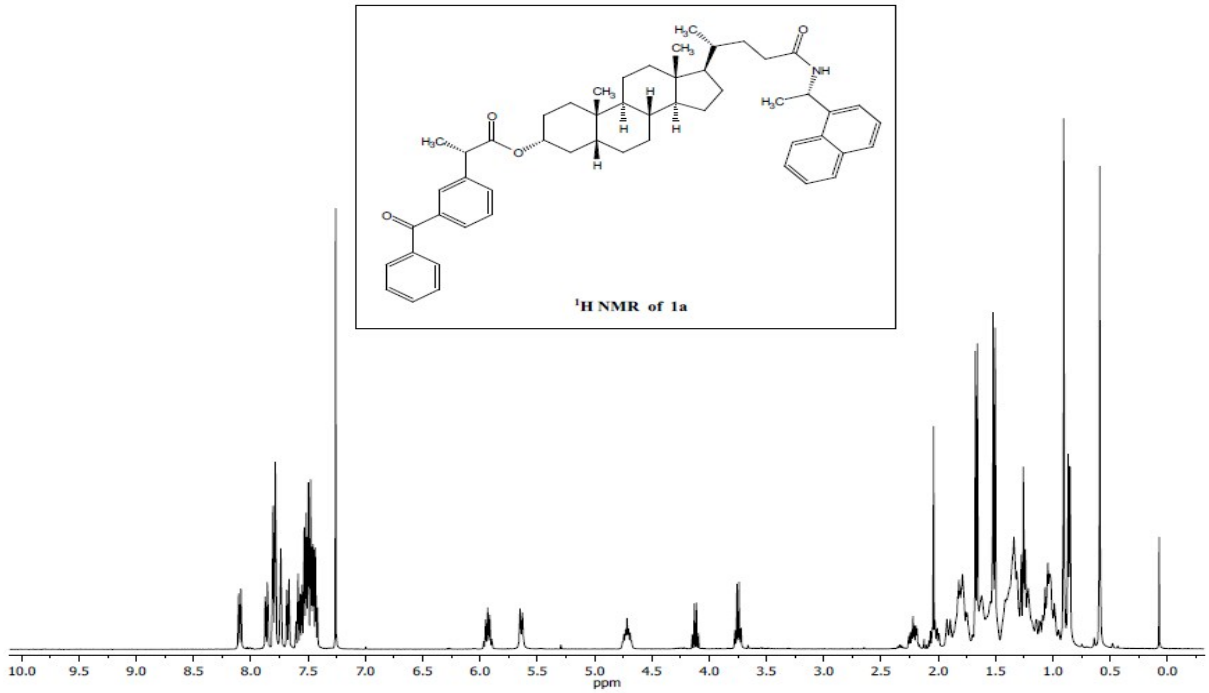


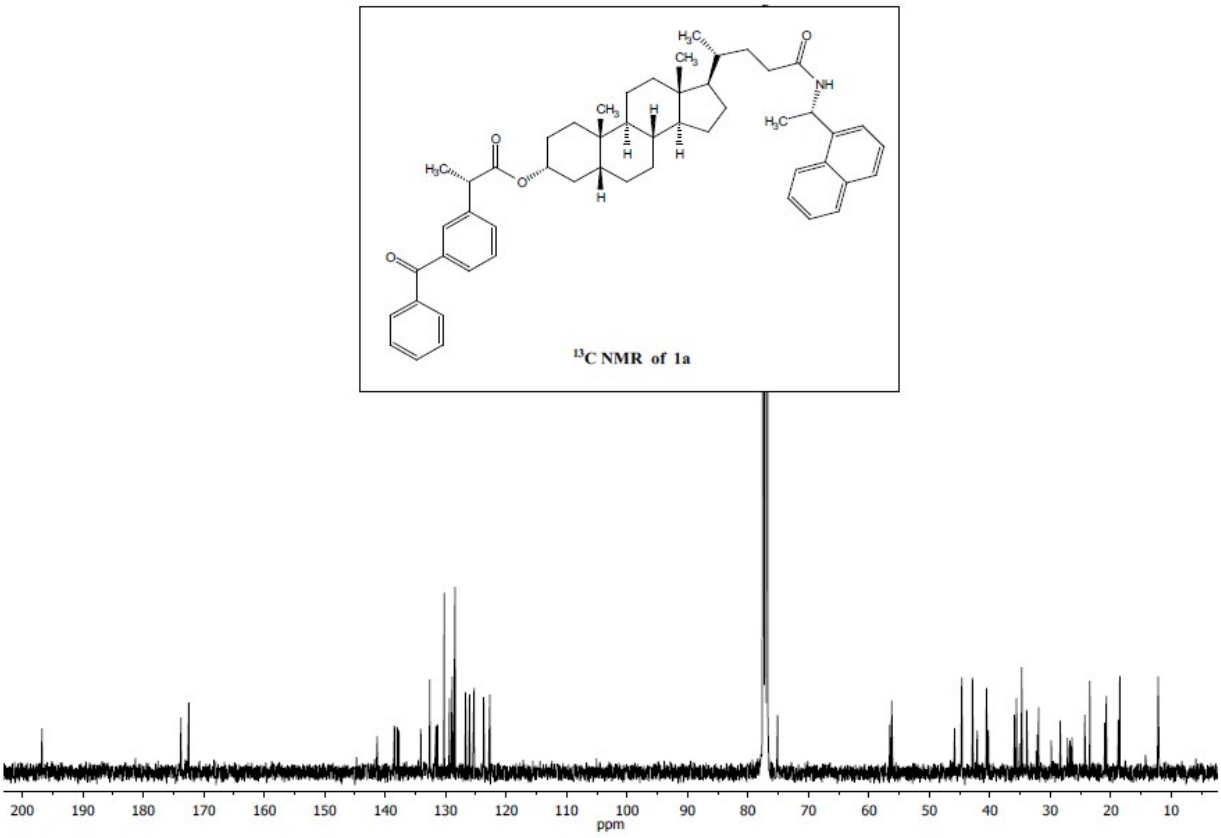



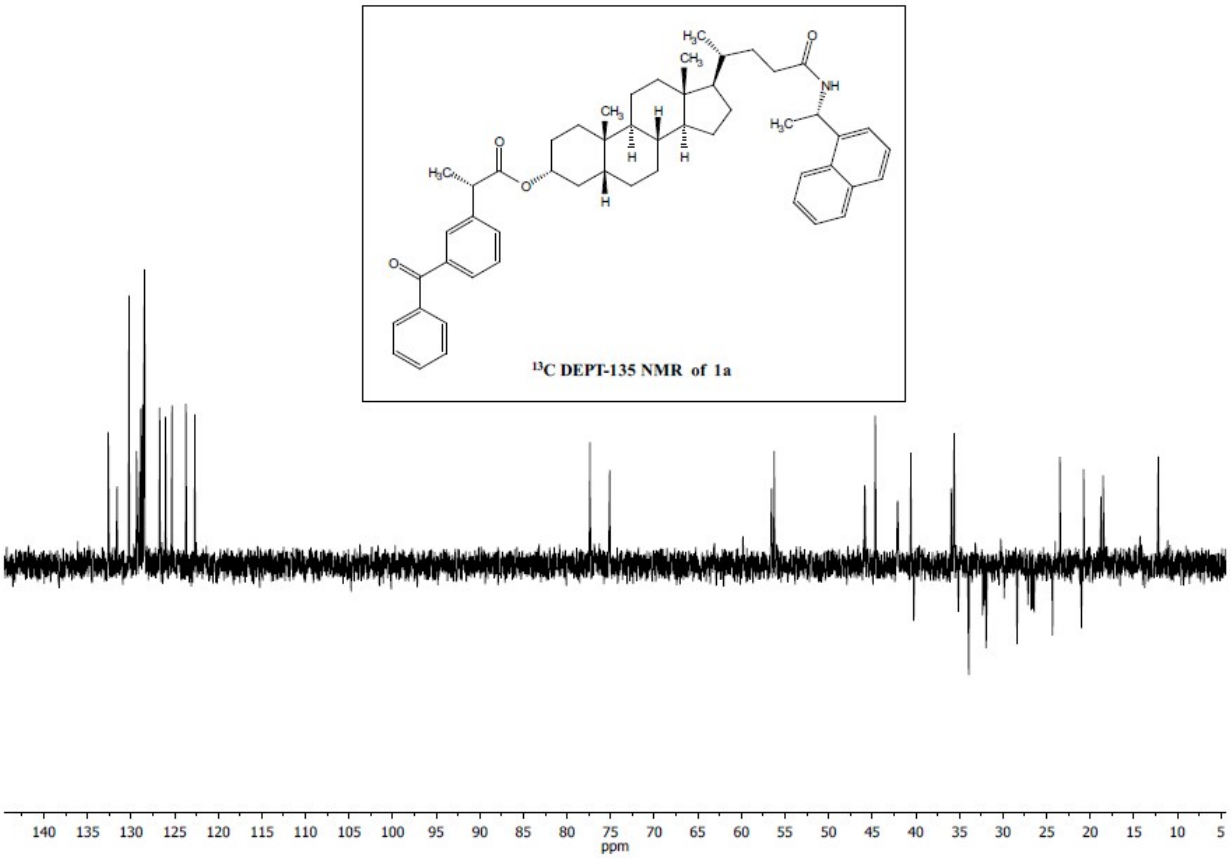



**$^{12}$C DEPT-135 NMR of 3a**

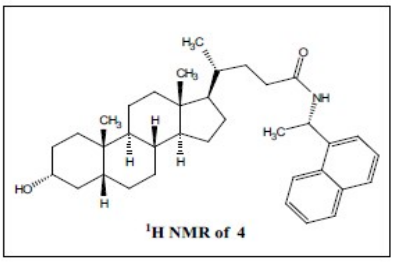
## 4.2. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 1a

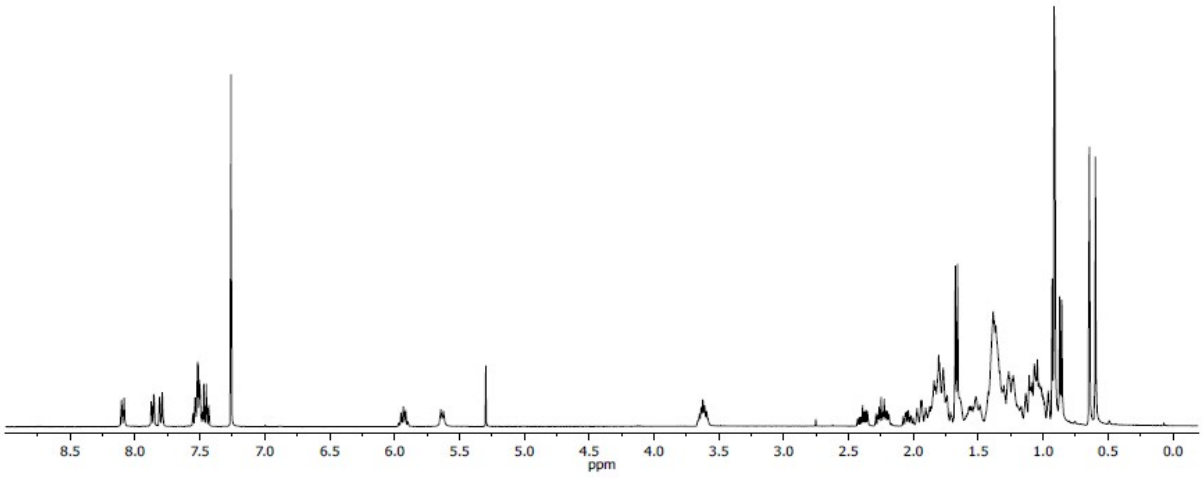


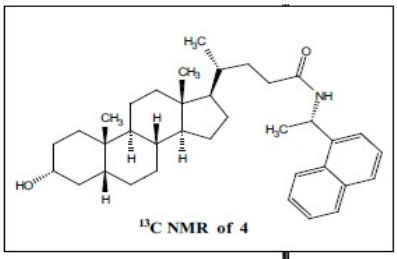



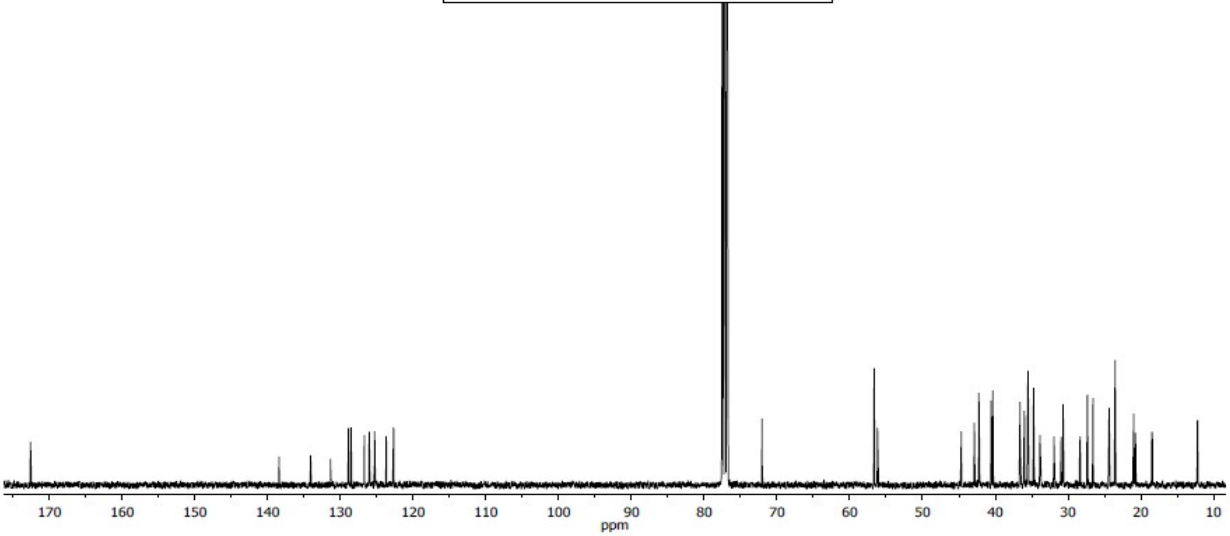

$^{13}$C DEPT-135 NMR of 1a
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
ppm

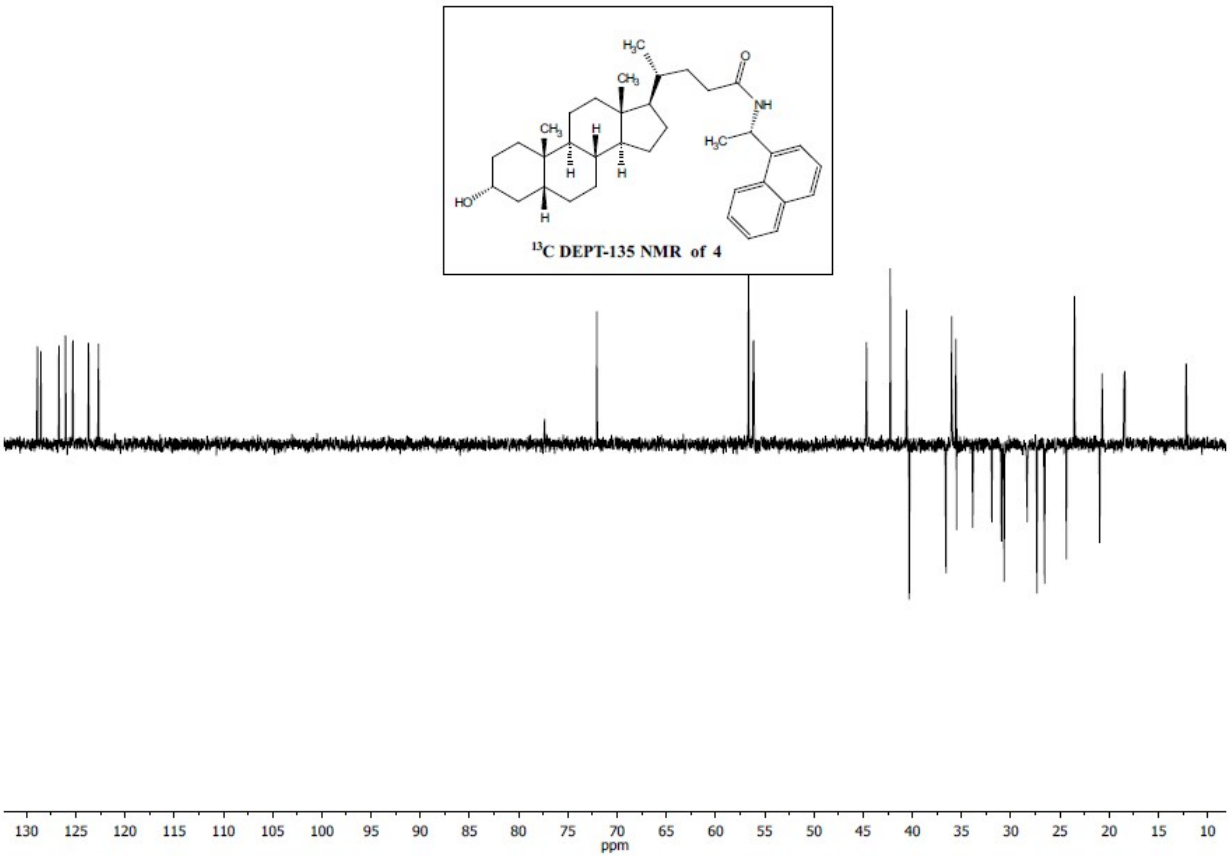
## 4.3. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 4



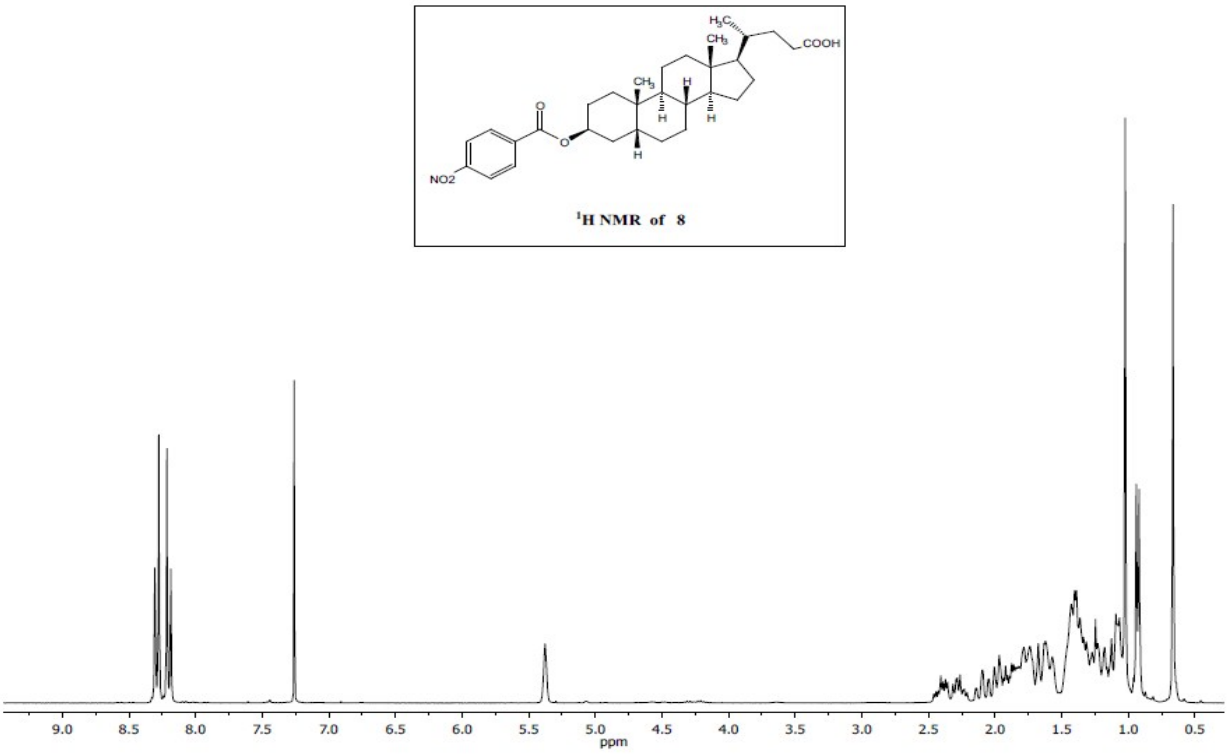



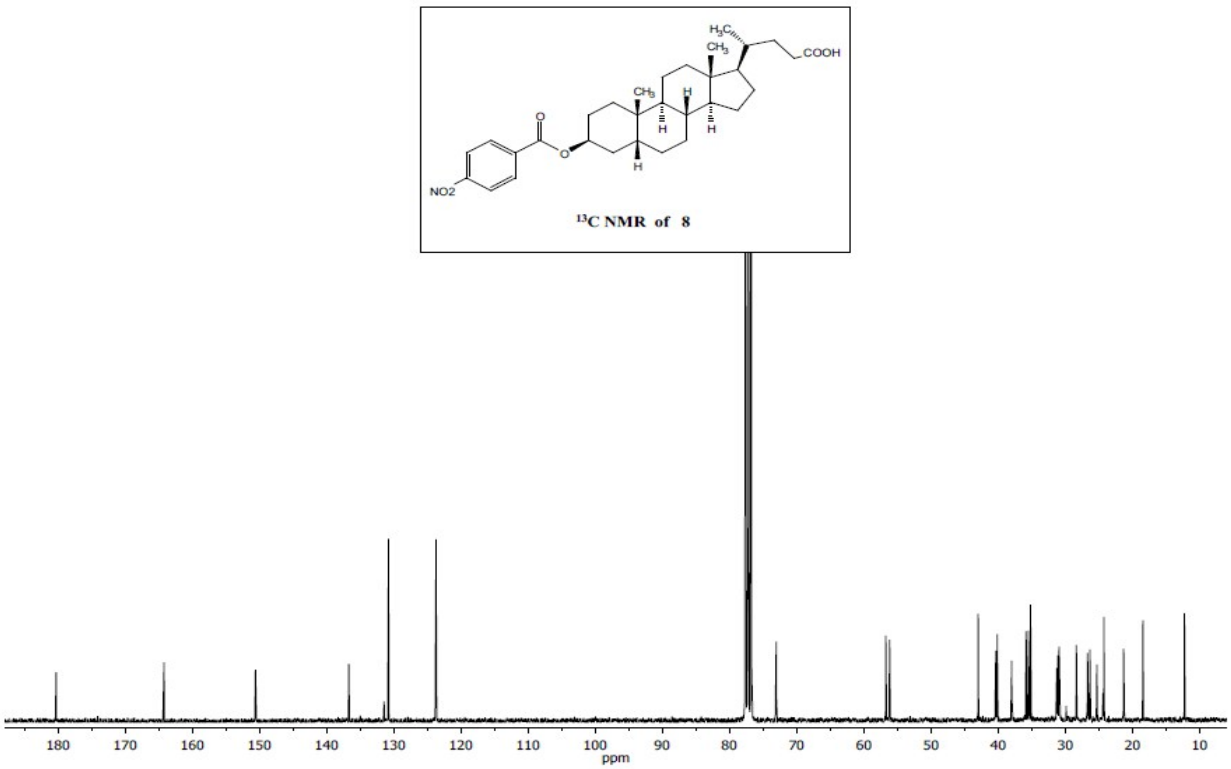



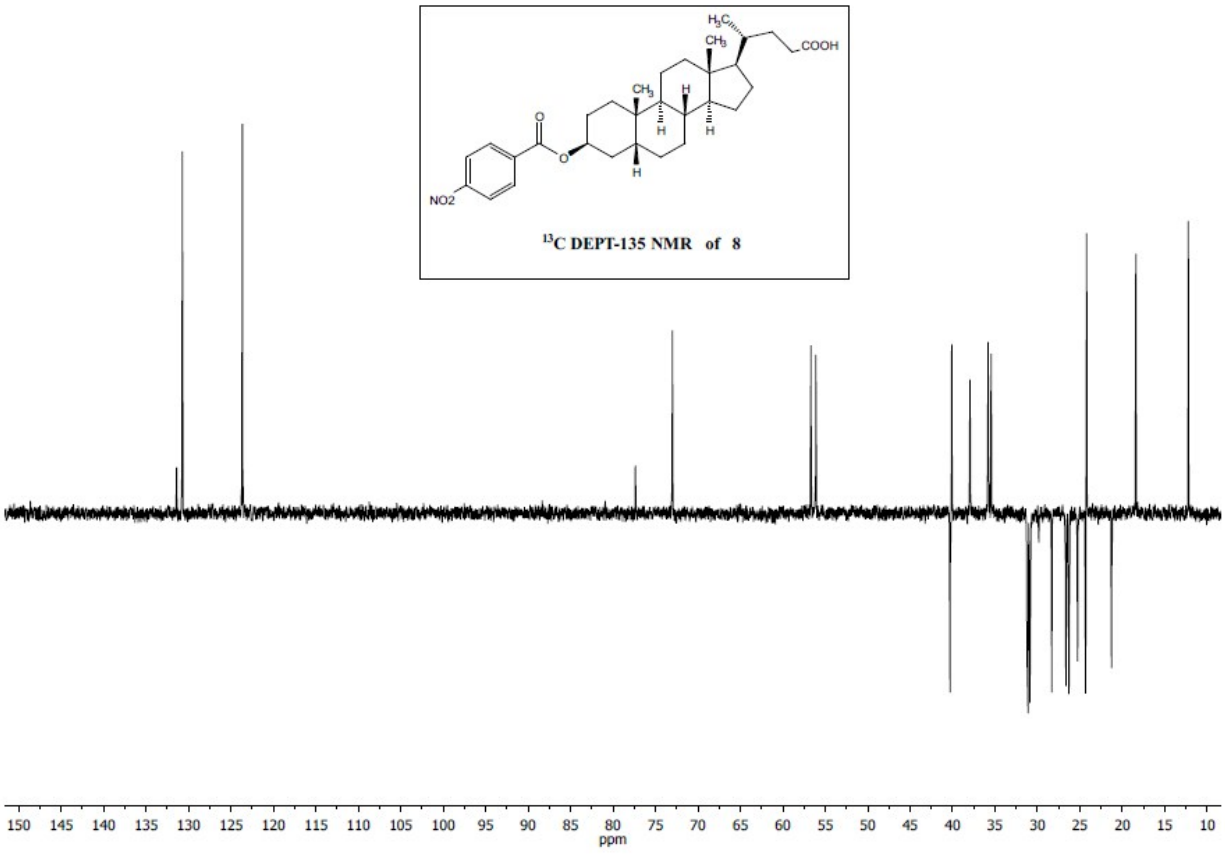




$^{13}$C DEPT-135 NMR of 4
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
ppm

## 4.4. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 8

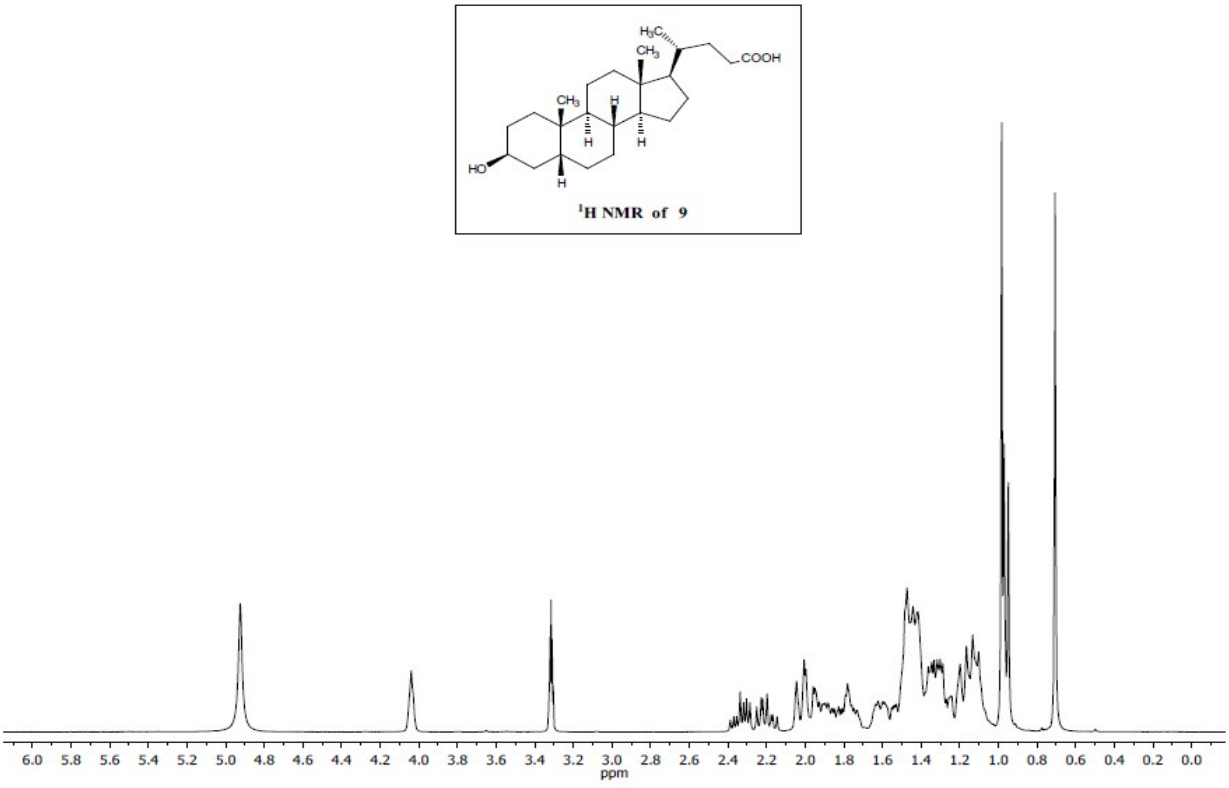


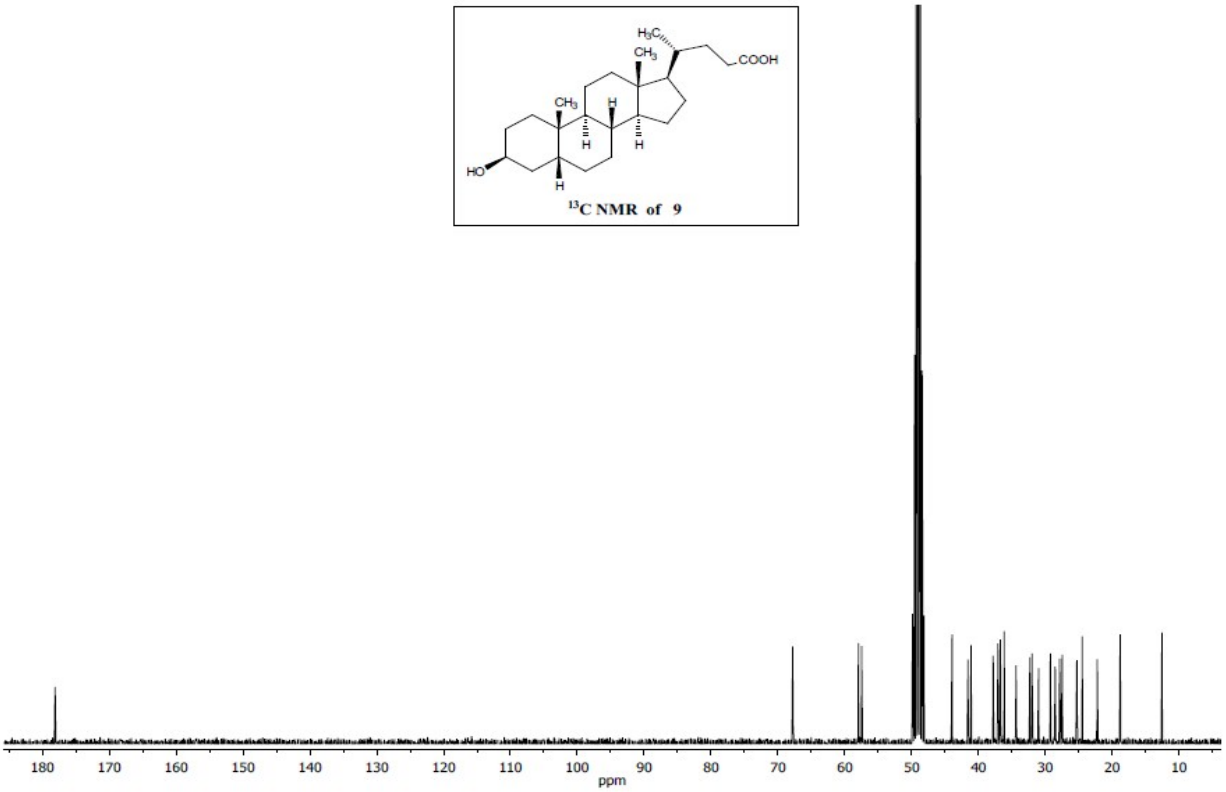



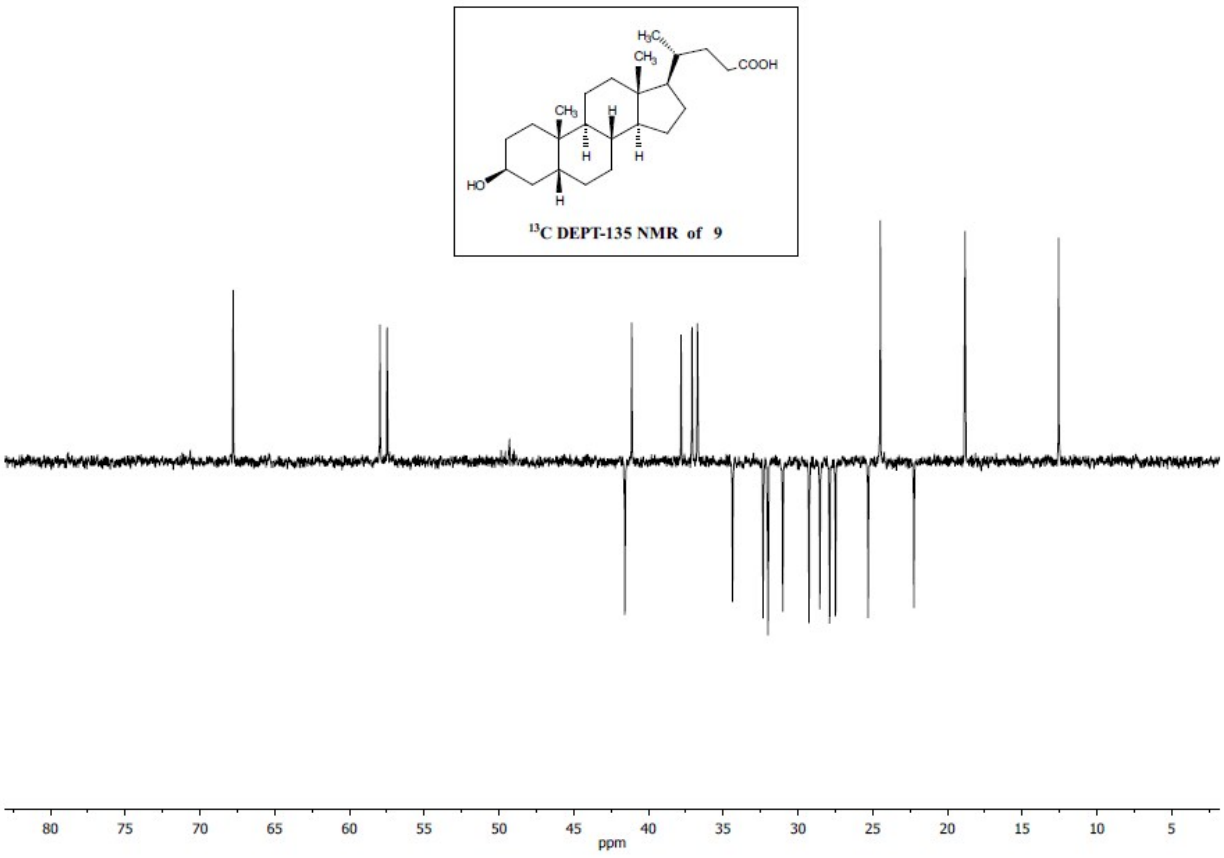



**$^{13}$C DEPT-135 NMR of 8**

## 4.5. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 9

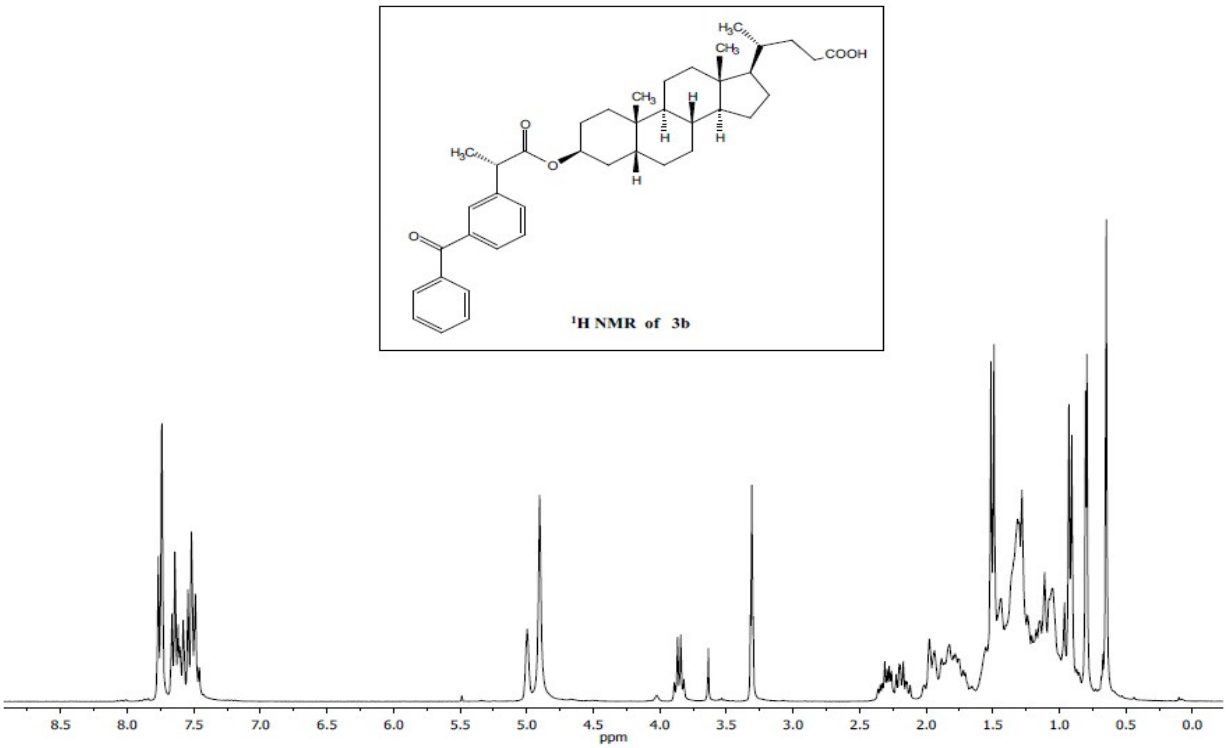


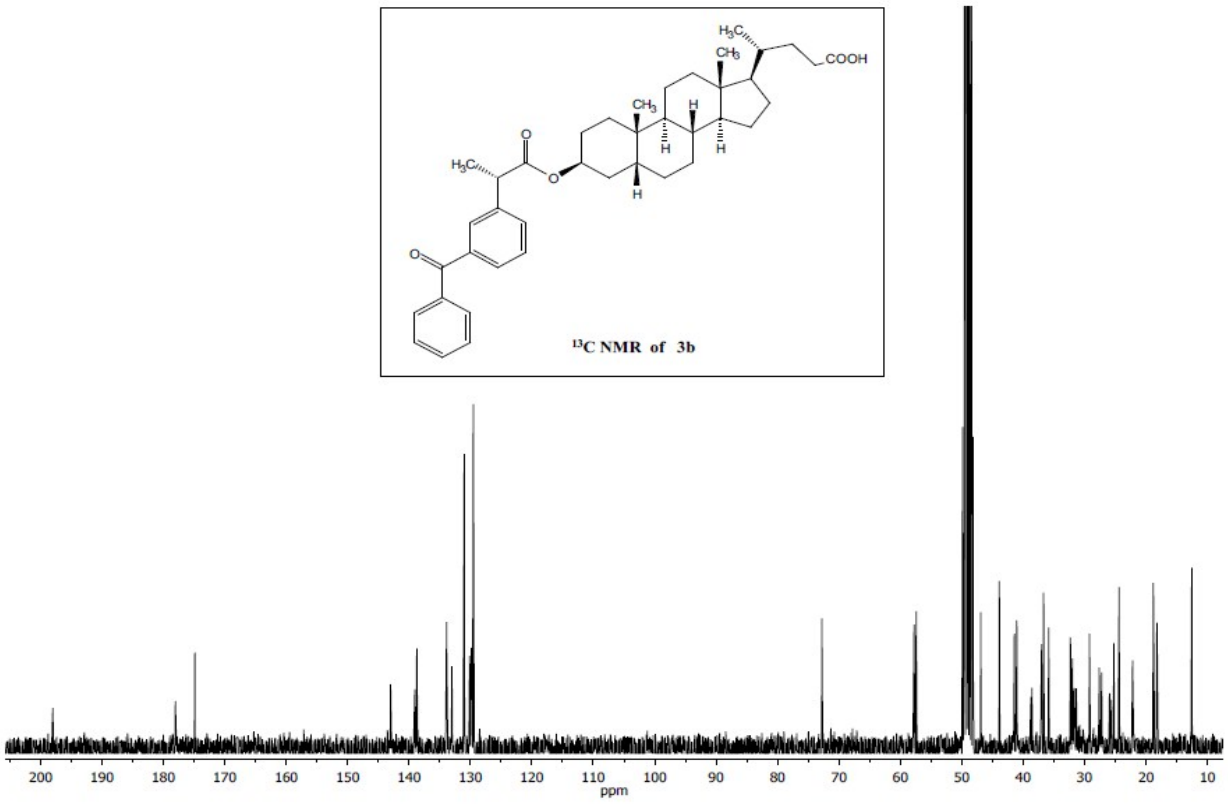



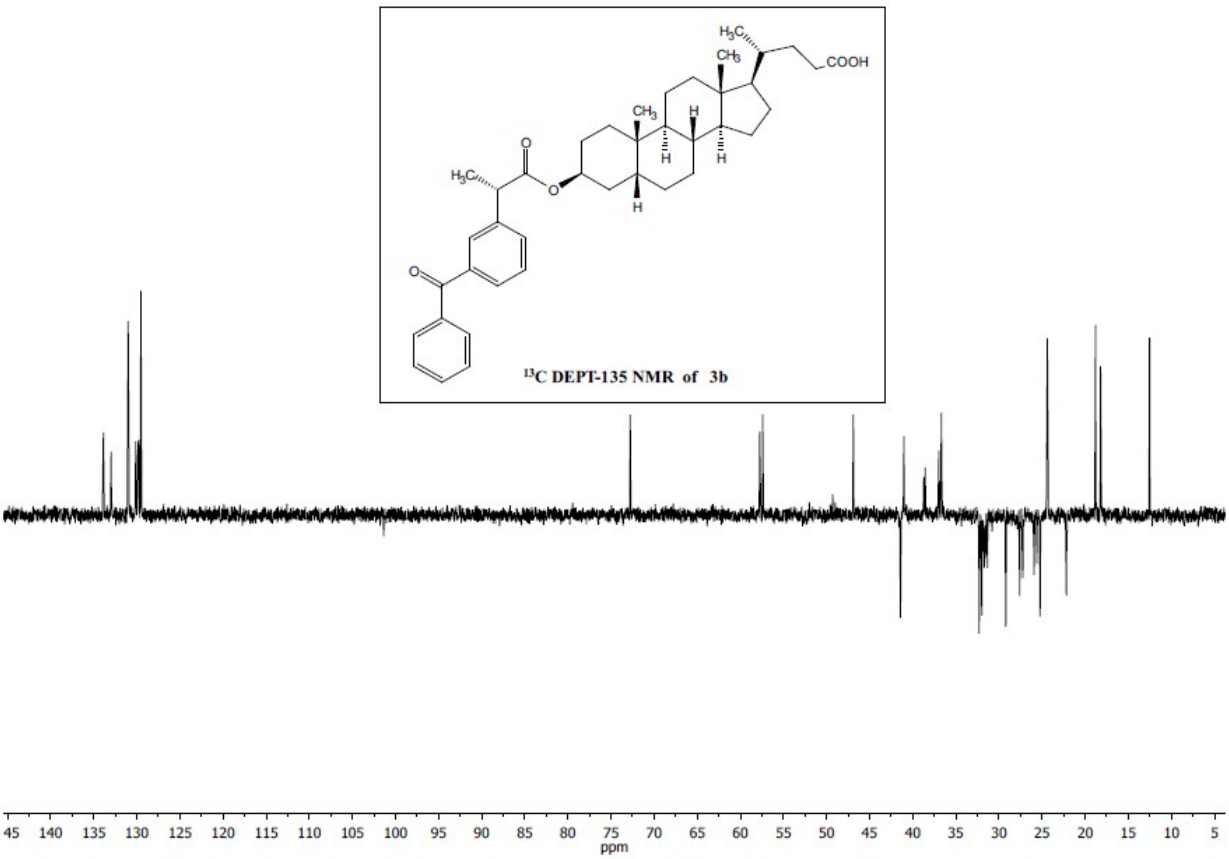



$^{13}$C DEPT-135 NMR of 9

## 4.6. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 3b

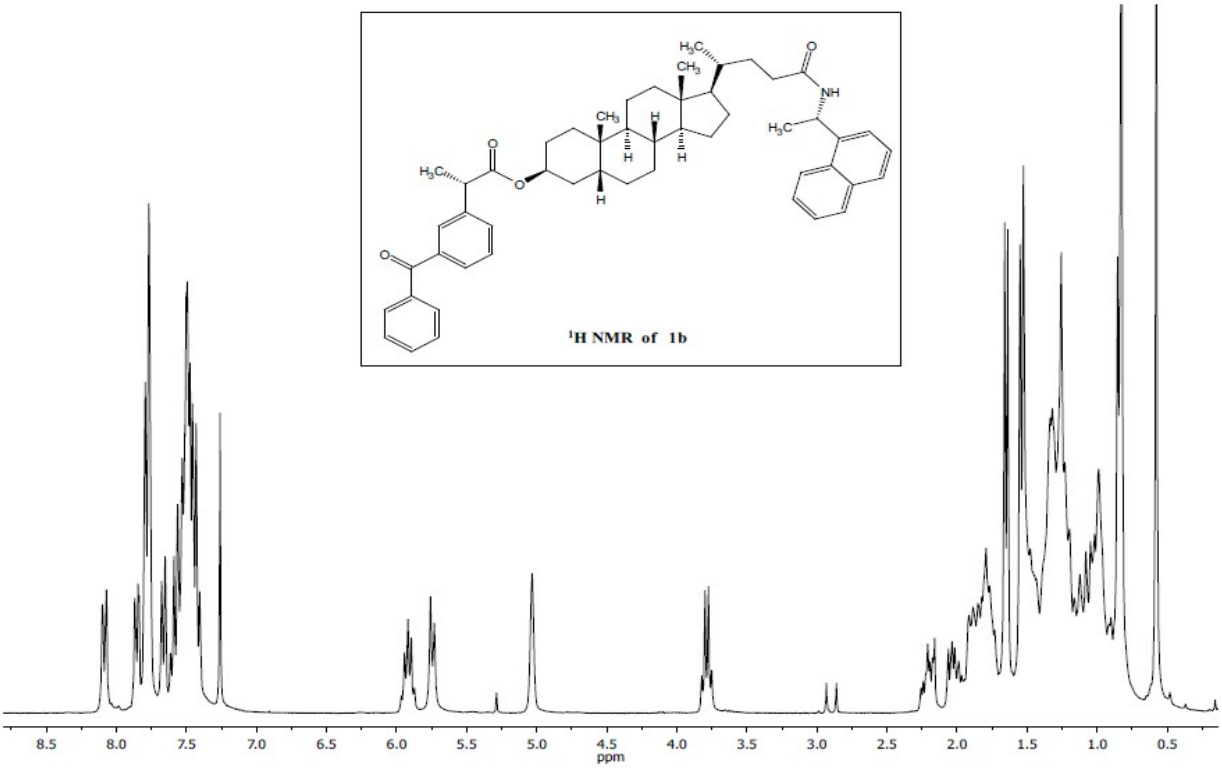


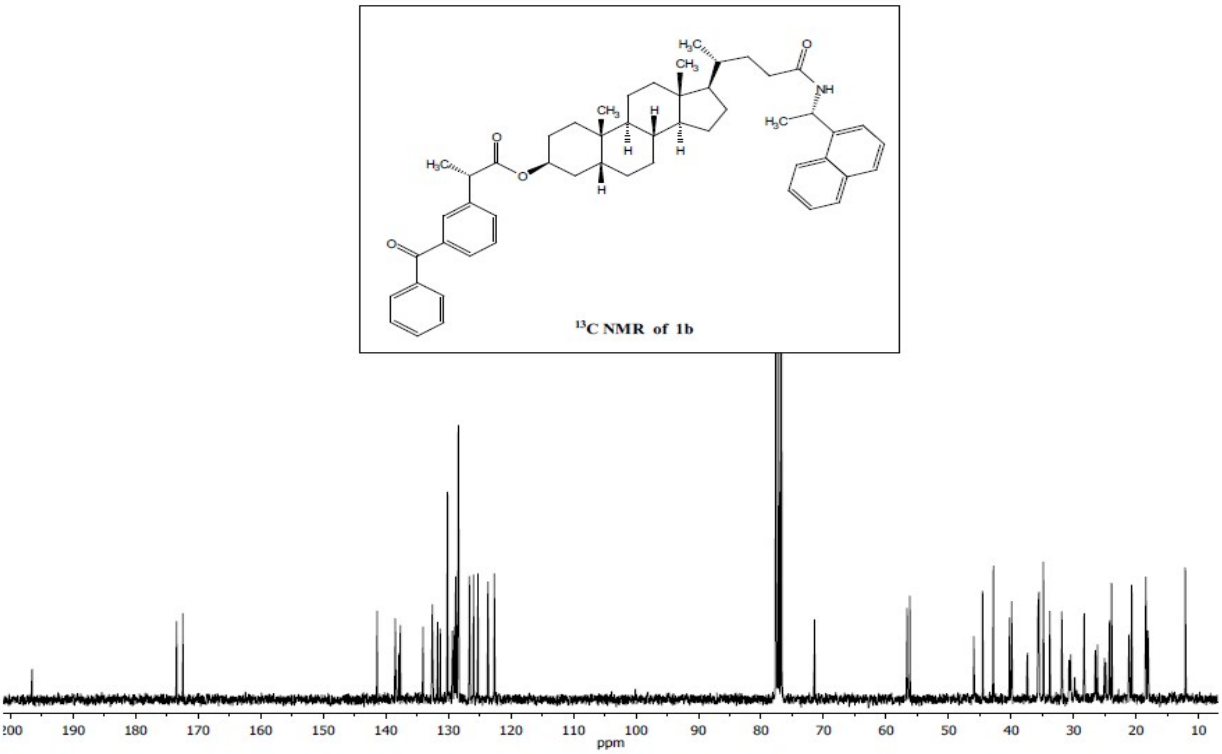



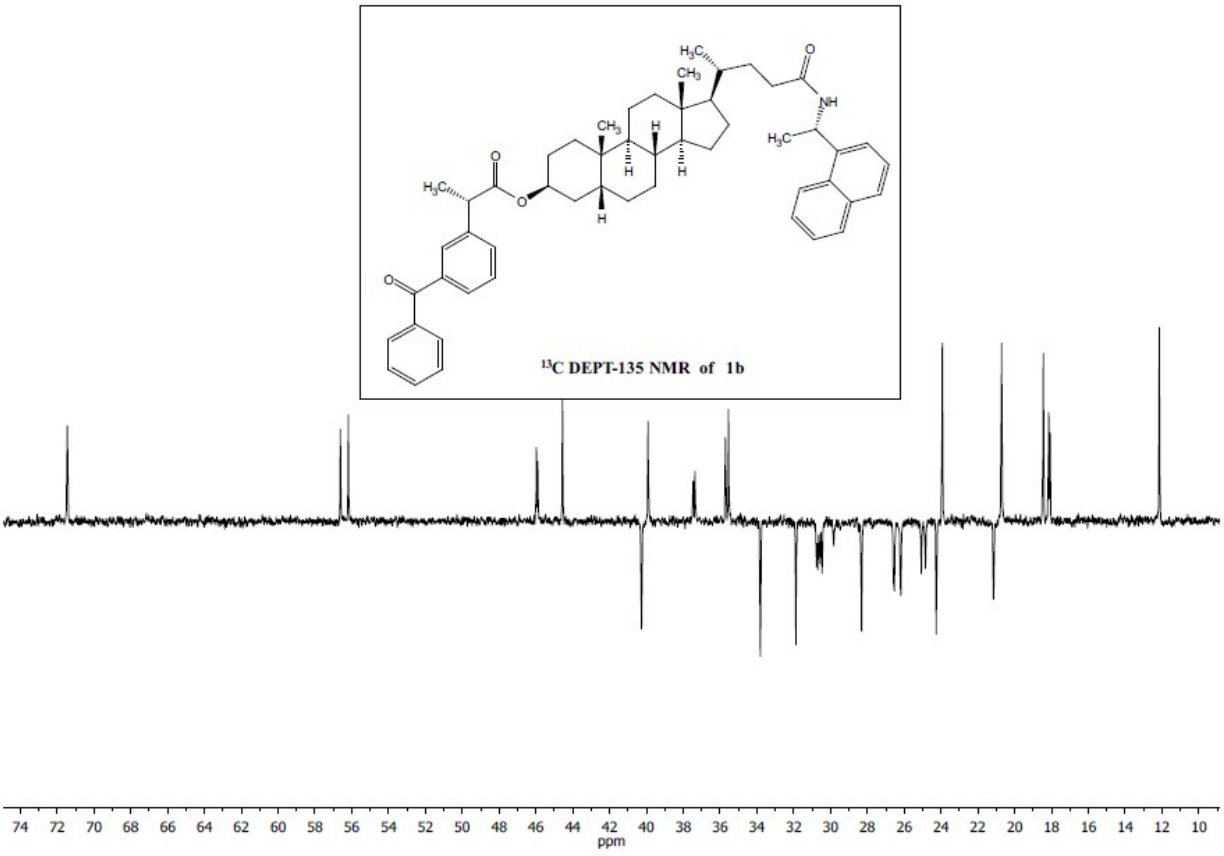



**$^{13}$C DEPT-135 NMR of 3b**

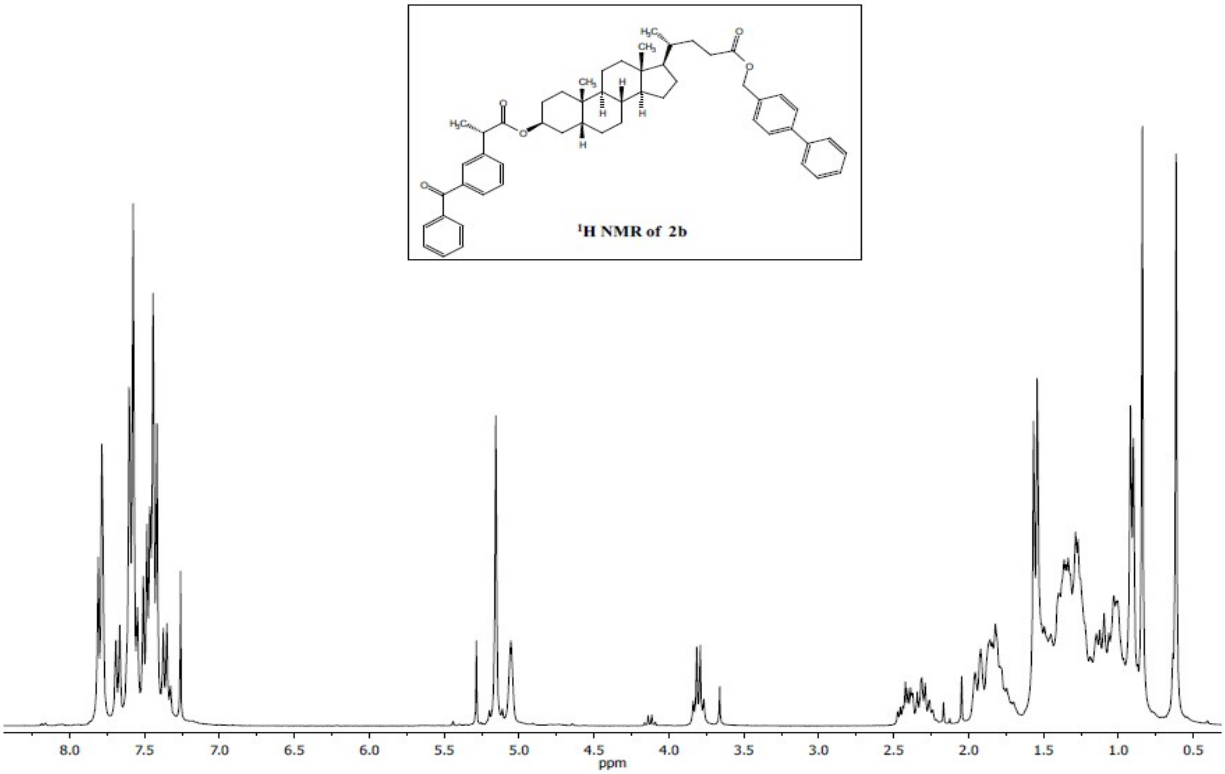
## 4.7. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 1b

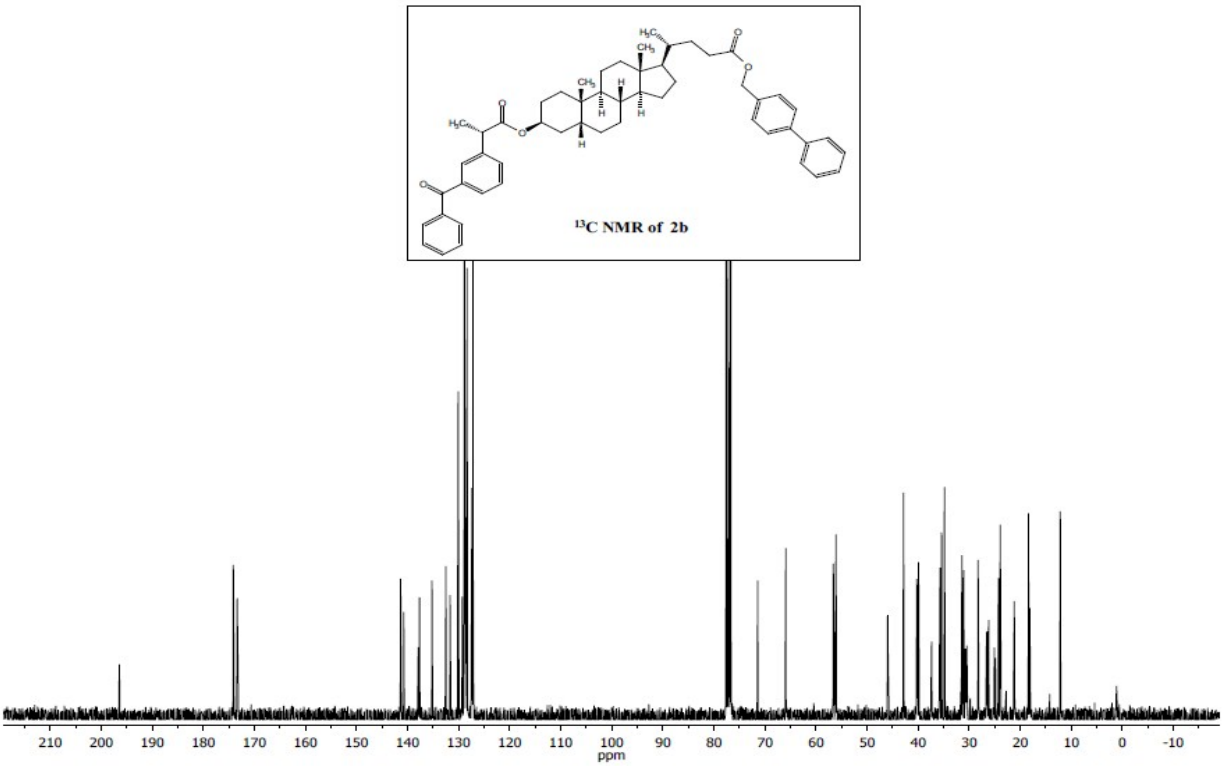


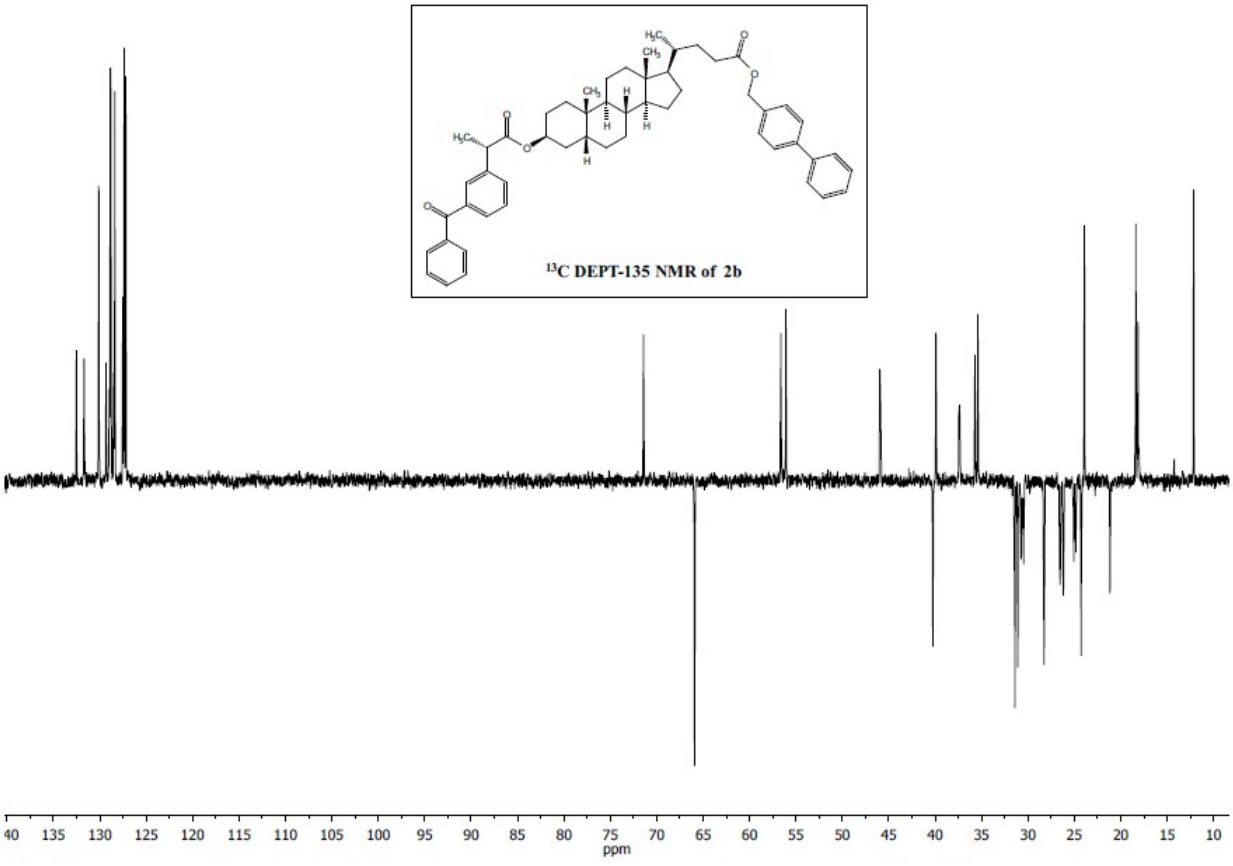




$^{13}$C DEPT-135 NMR of 1b
74 72 70 68 66 64 62 60 58 56 54 52 50 48 46 44 42 40 38 36 34 32 30 28 26 24 22 20 18 16 14 12 10
ppm

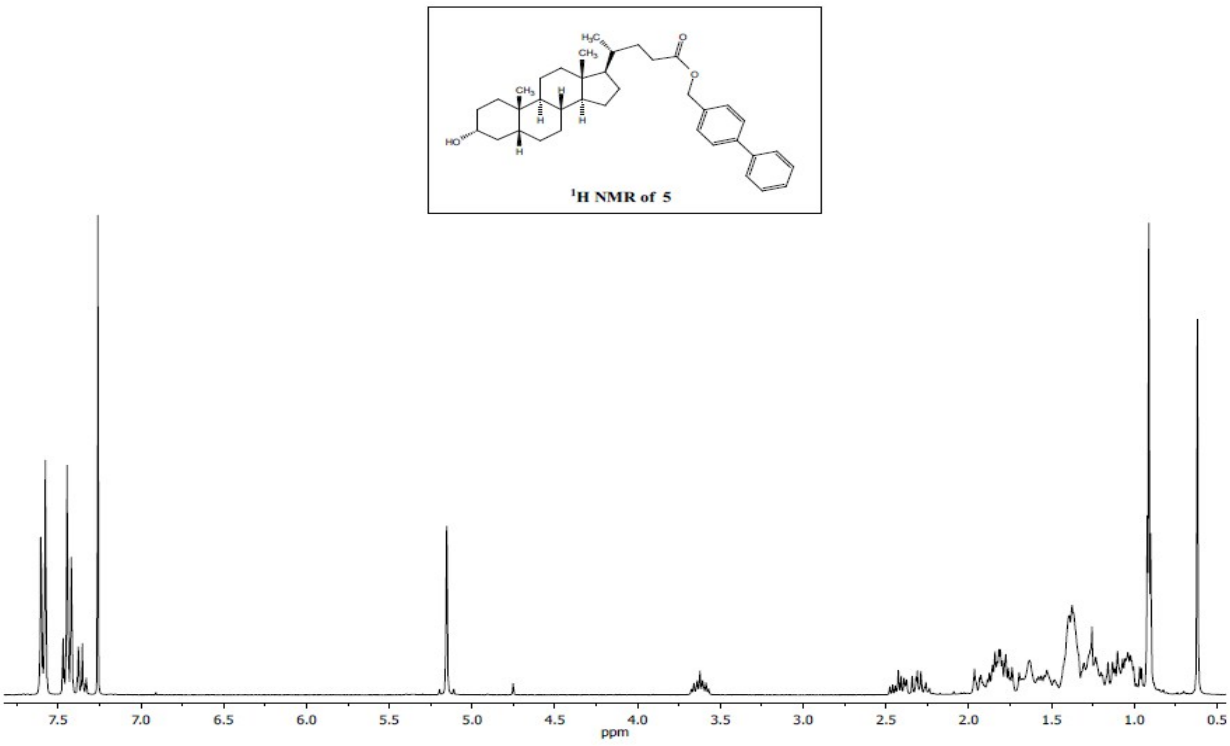
## 4.8. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 2b

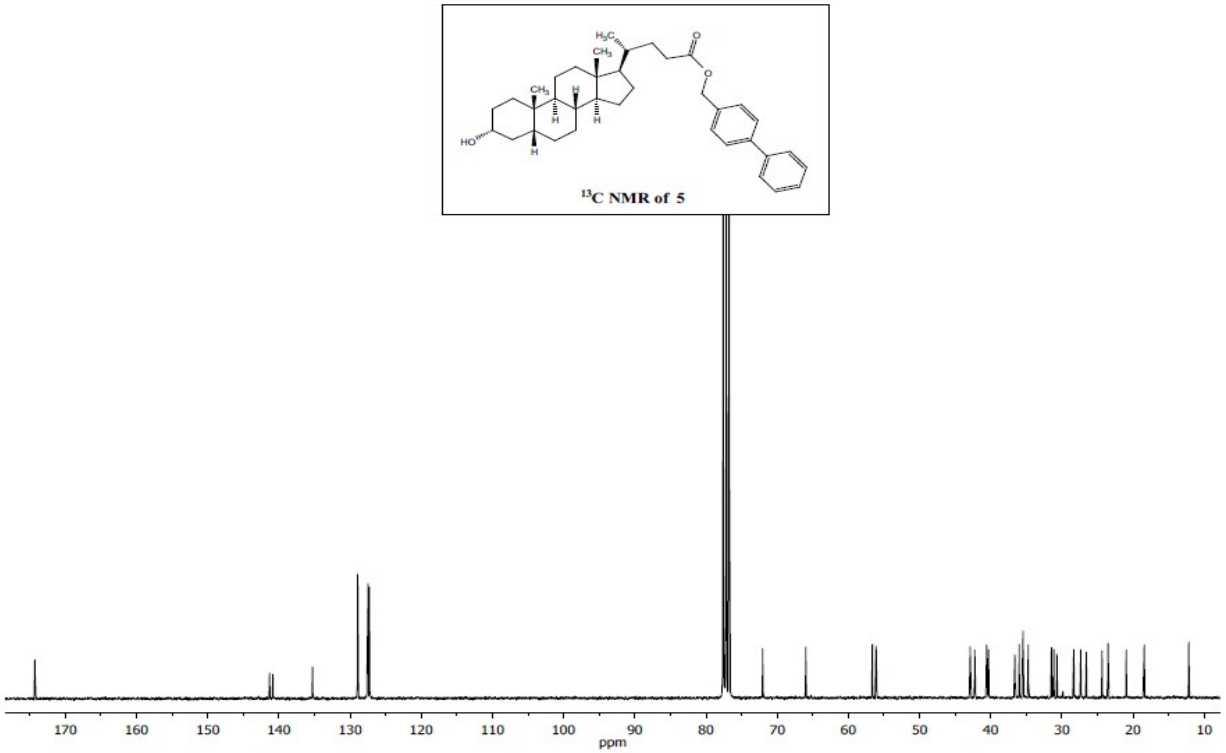


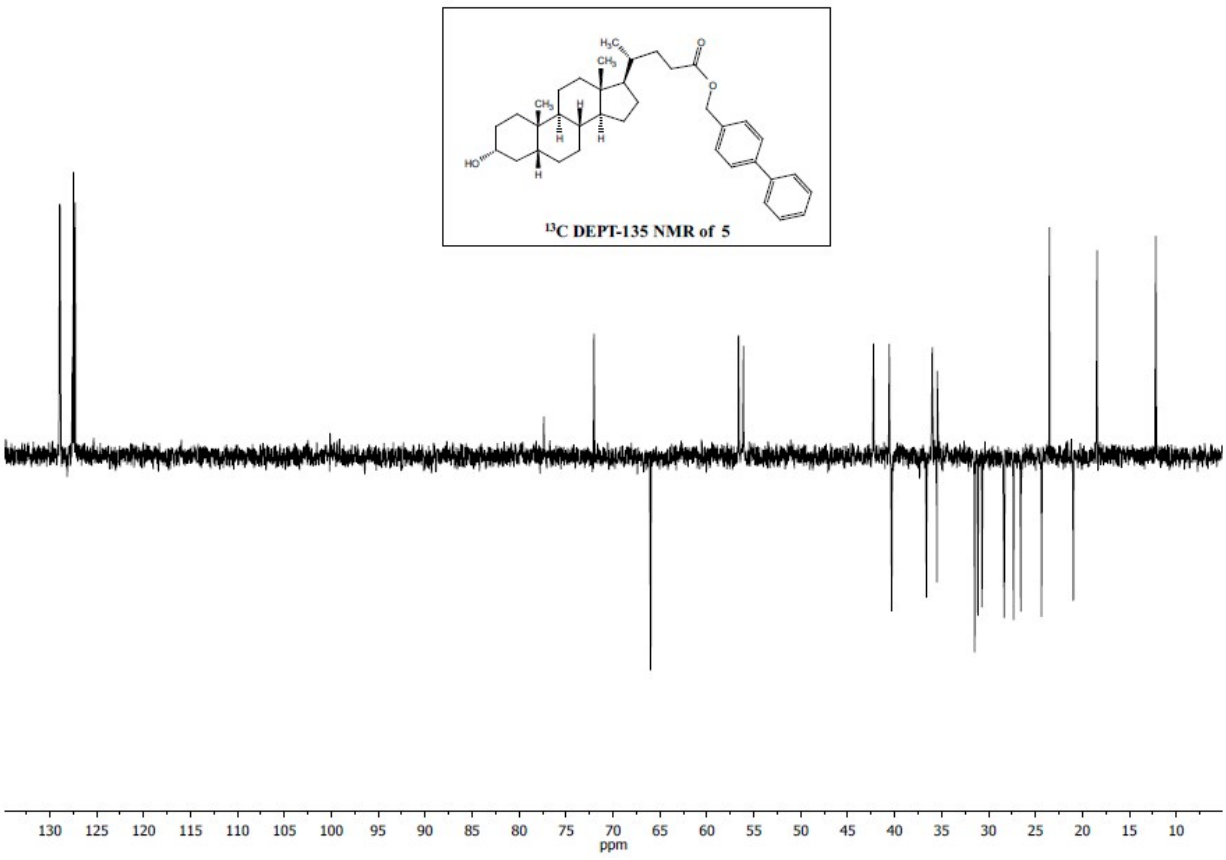




$^{13}$C DEPT-135 NMR of 2b
40 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
ppm

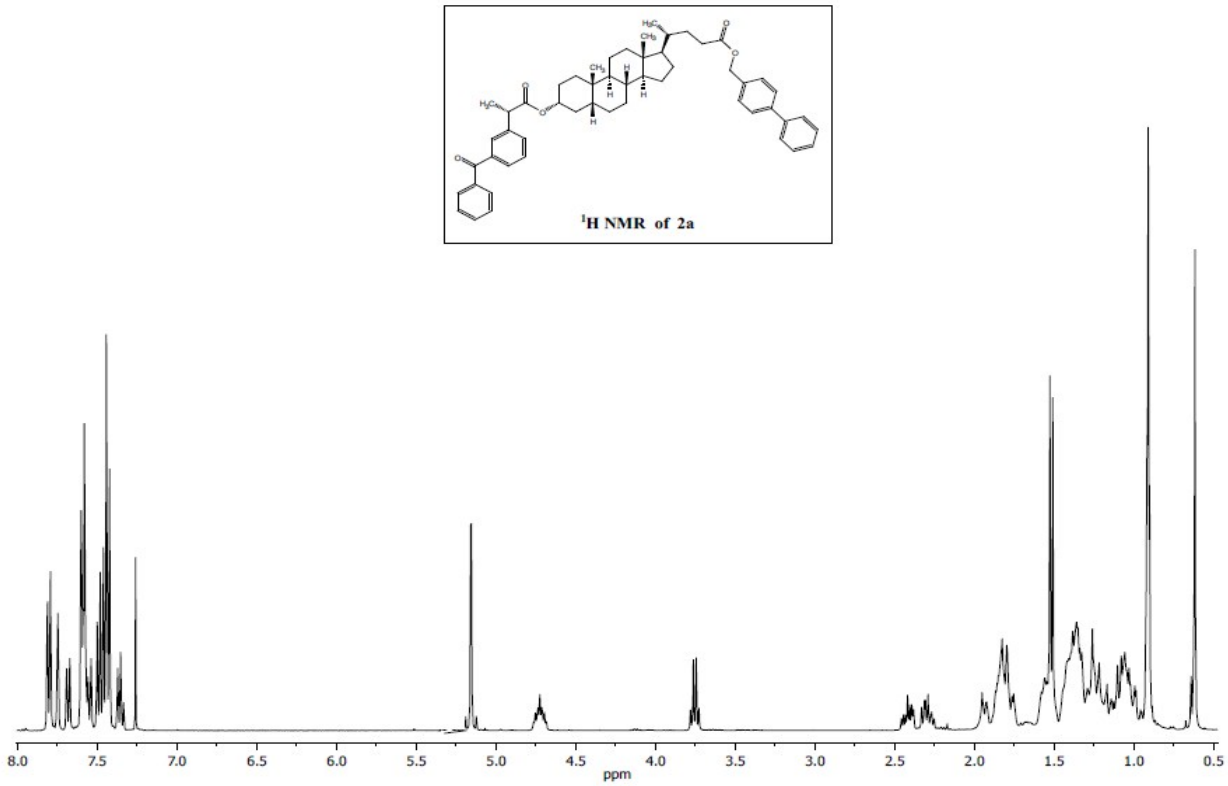
## 4.9. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 5

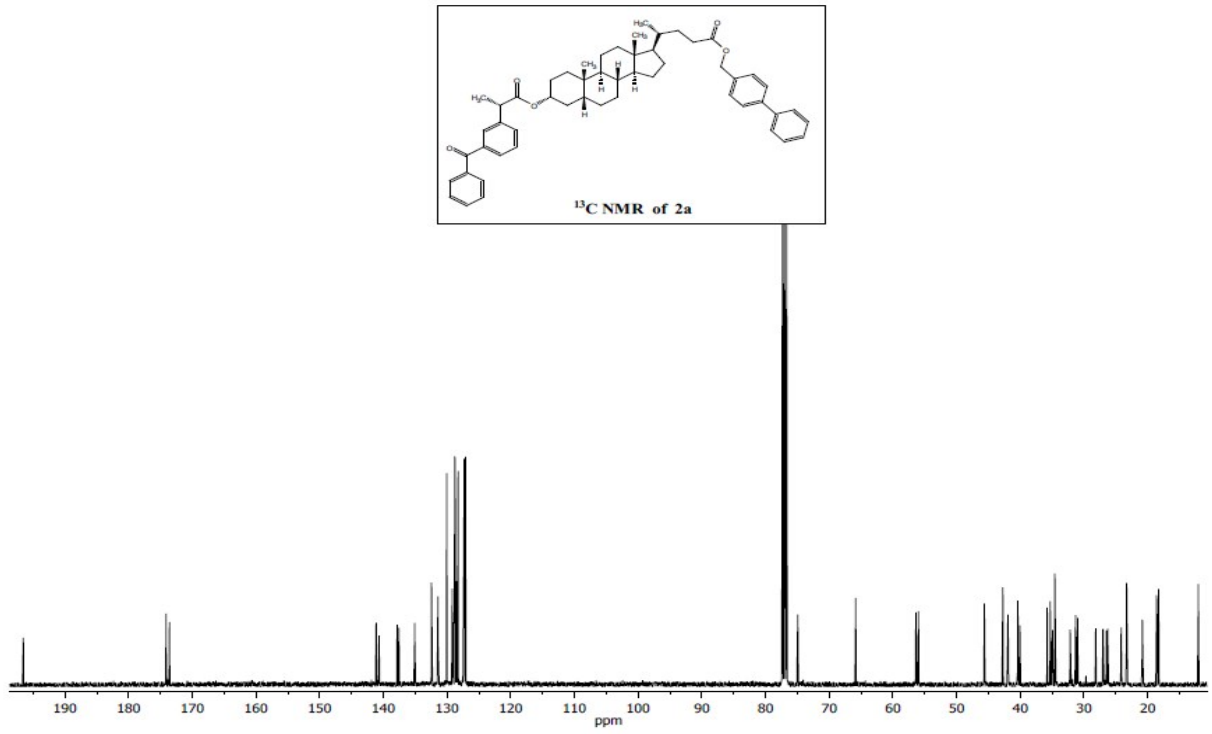


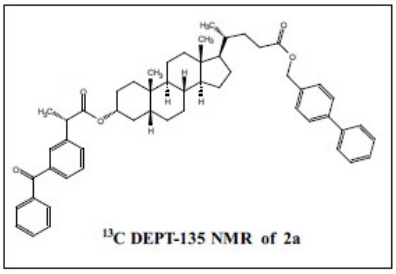




$^{13}$C DEPT-135 NMR of 5
130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
ppm

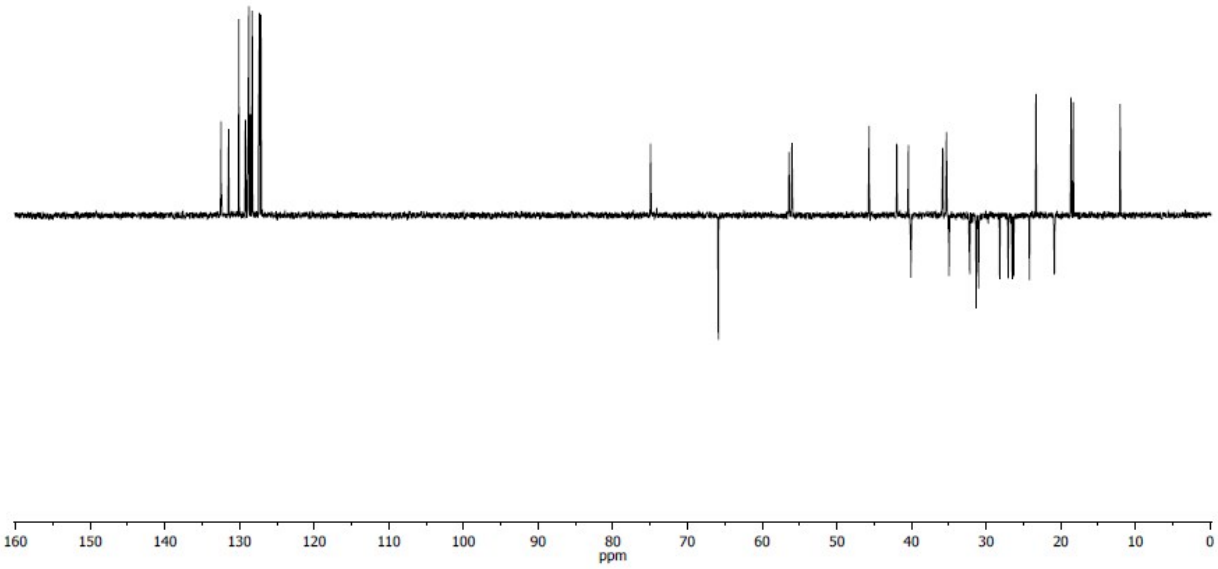
## 4.10. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 2a



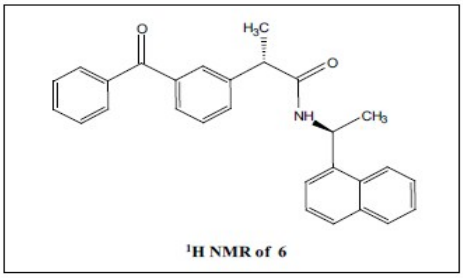





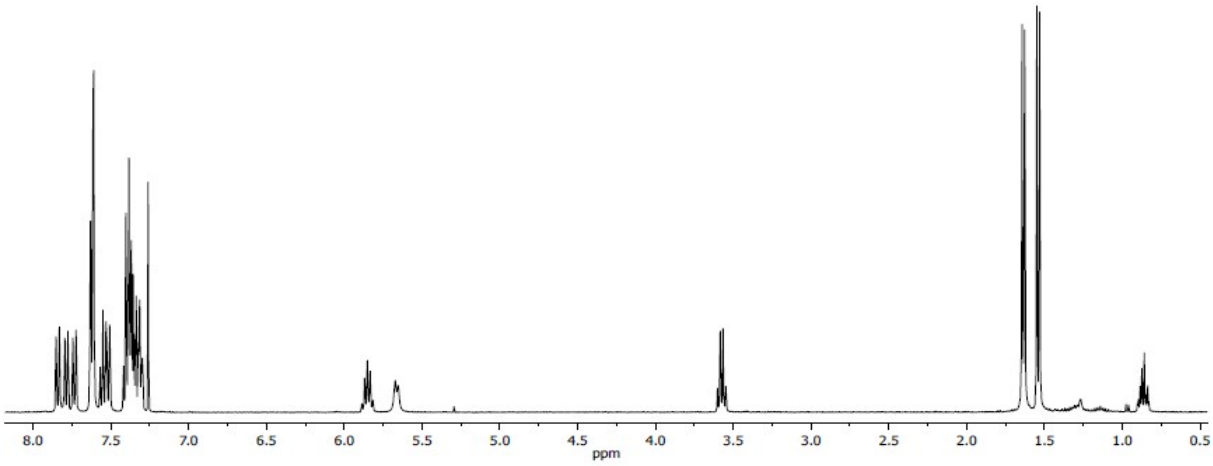
$^{13}$C DEPT-135 NMR of 2a

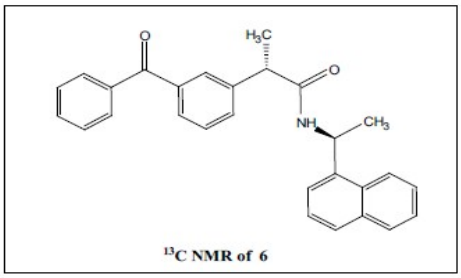


## 4.11. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 6

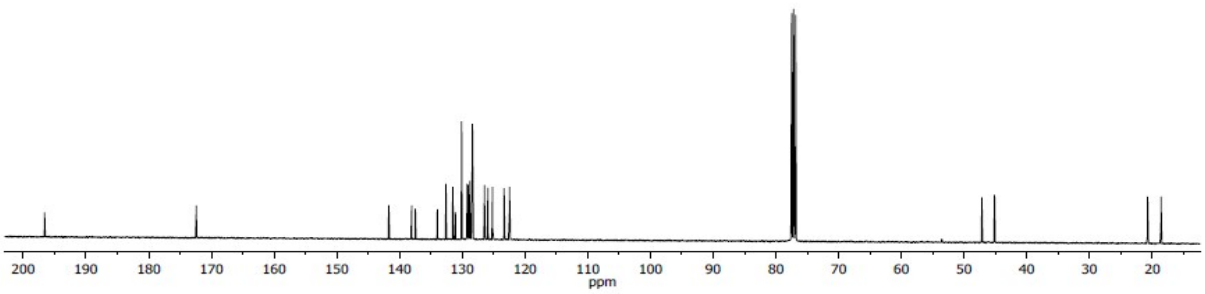


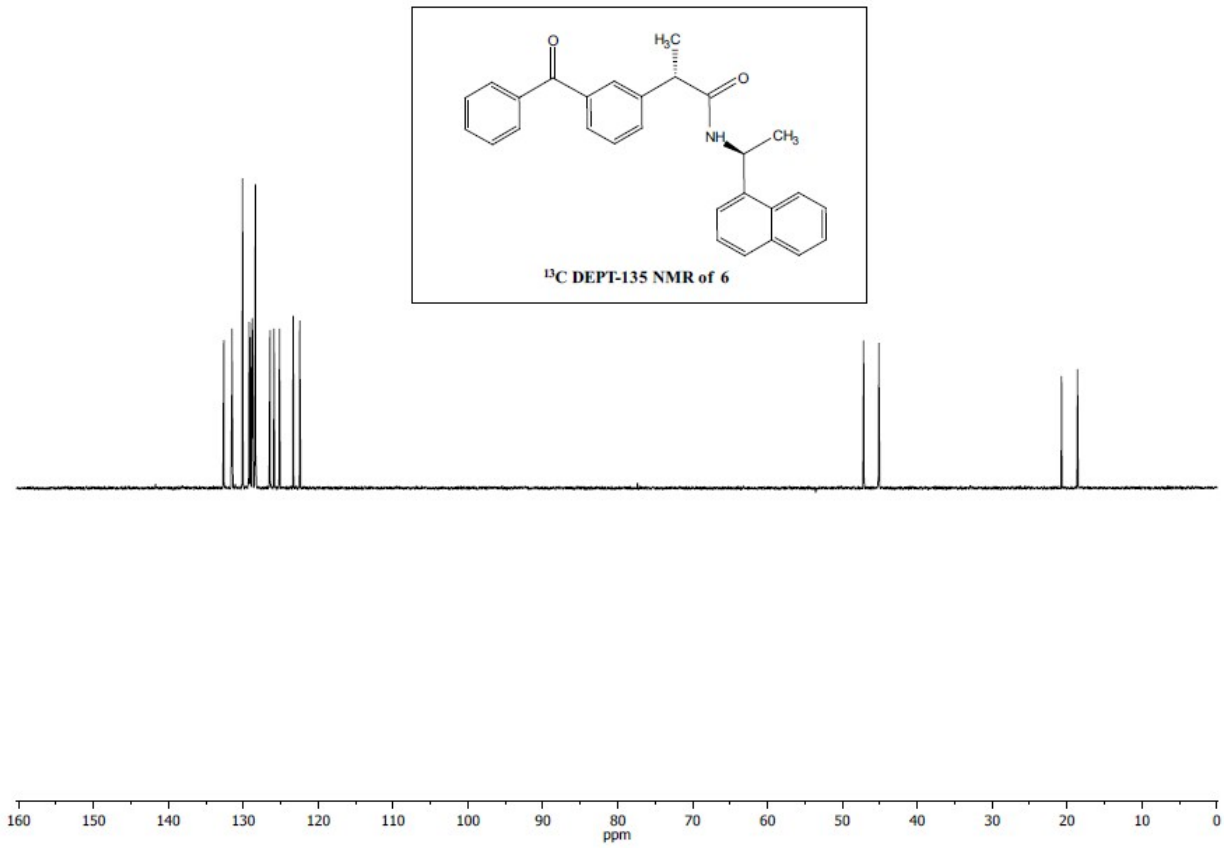

$^{1}H$ NMR of 6



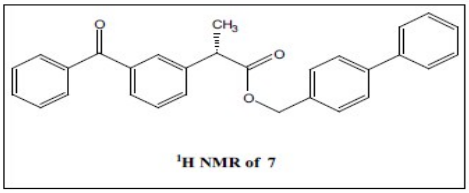

$^{13}C$ NMR of 6



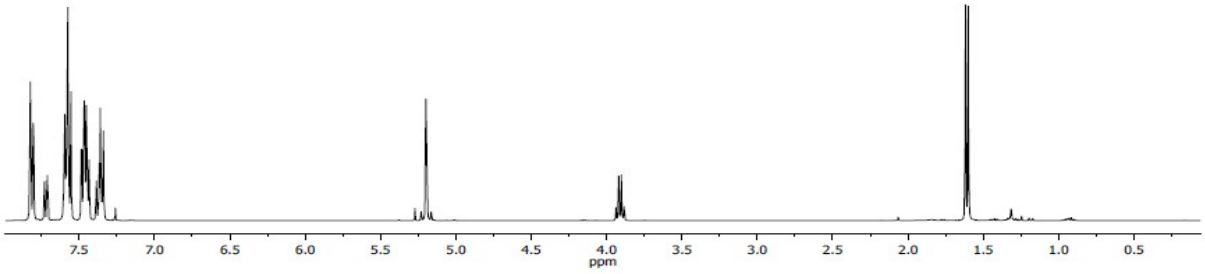


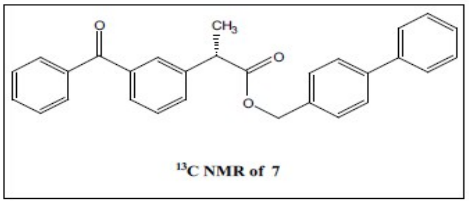

$^{13}$C DEPT-135 NMR of 6

## 4.12. $^{1}H$, $^{13}C$ and $^{13}C$ DEPT-135 NMR of 7

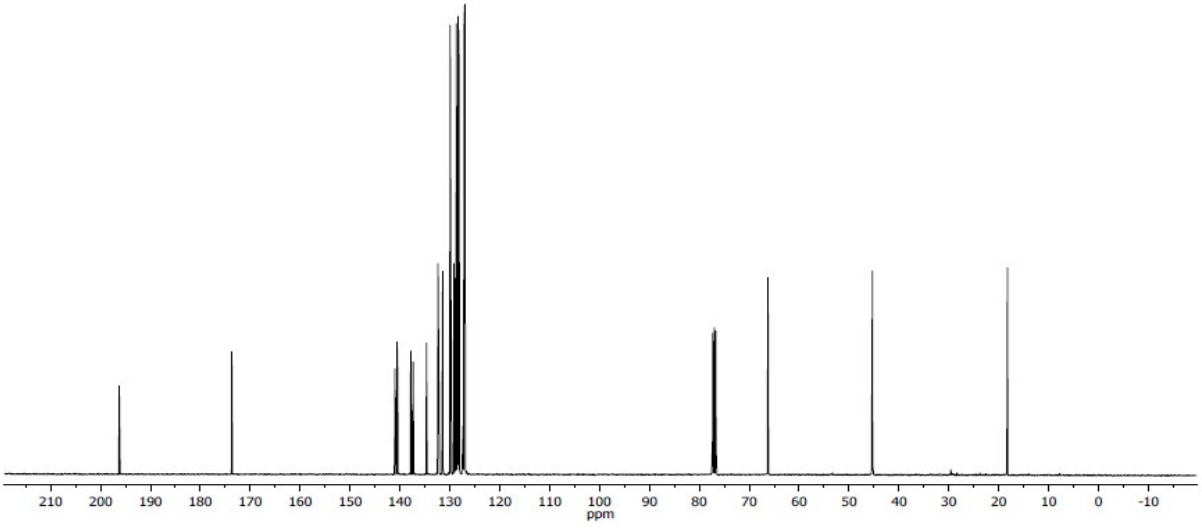


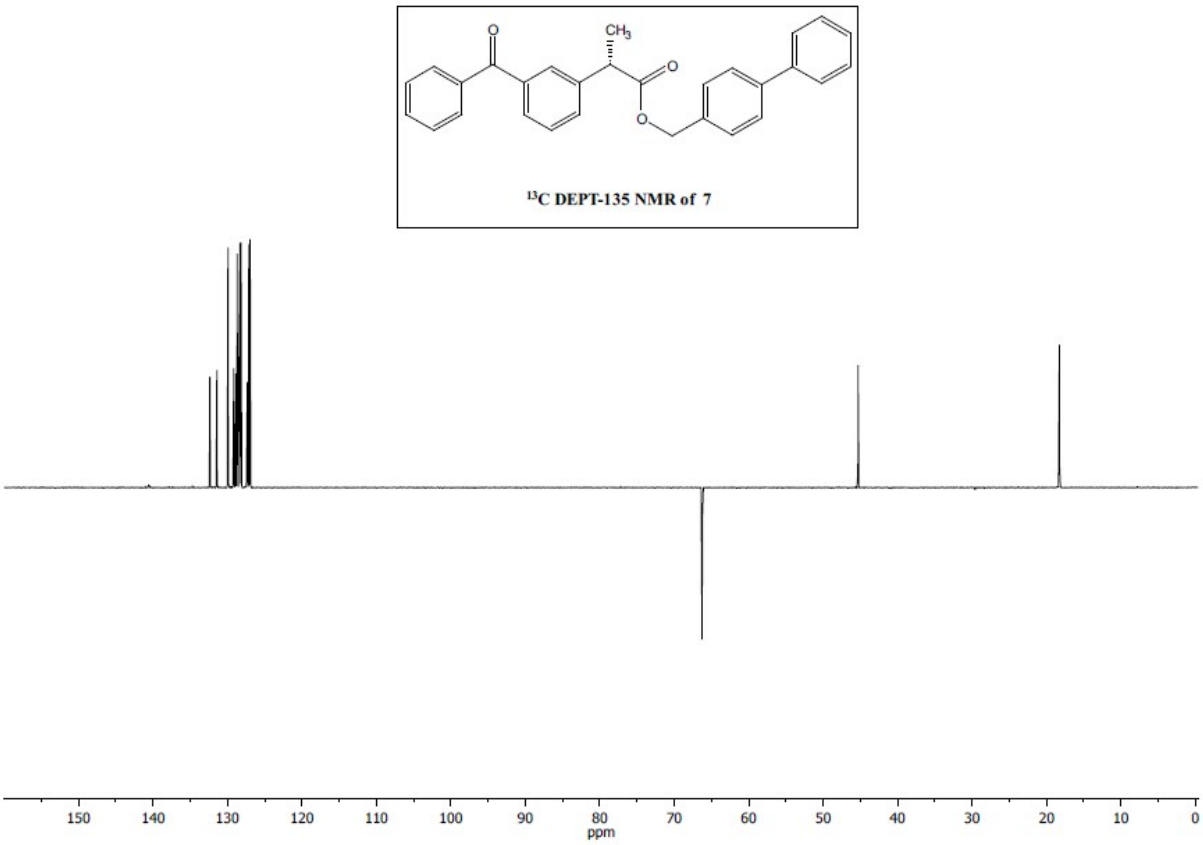

$^{1}H$ NMR of 7




$^{13}C$ NMR of 7






$^{13}$C DEPT-135 NMR of 7

## 5. Control experiments: UV-Vis and transient absorption spectroscopy

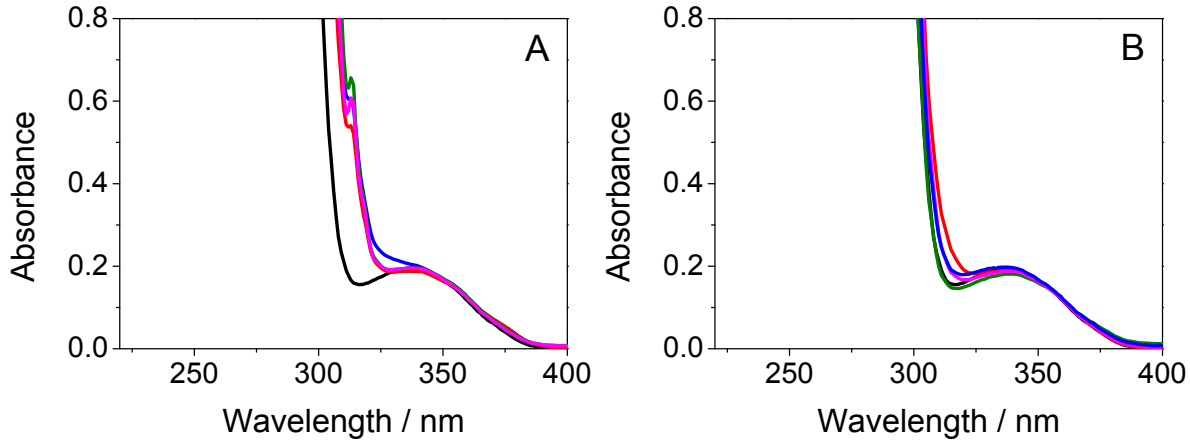



**Figure S1. A**: UV-Vis absorption spectra of **1a** (red), **1b** (magenta), **3a** (black), **3a+4** (blue) and **6** (green). **B**: UV-Vis absorption spectra of **2a** (red), **2b** (magenta), **3a** (black), **3a+5** (blue) and **7** (green).

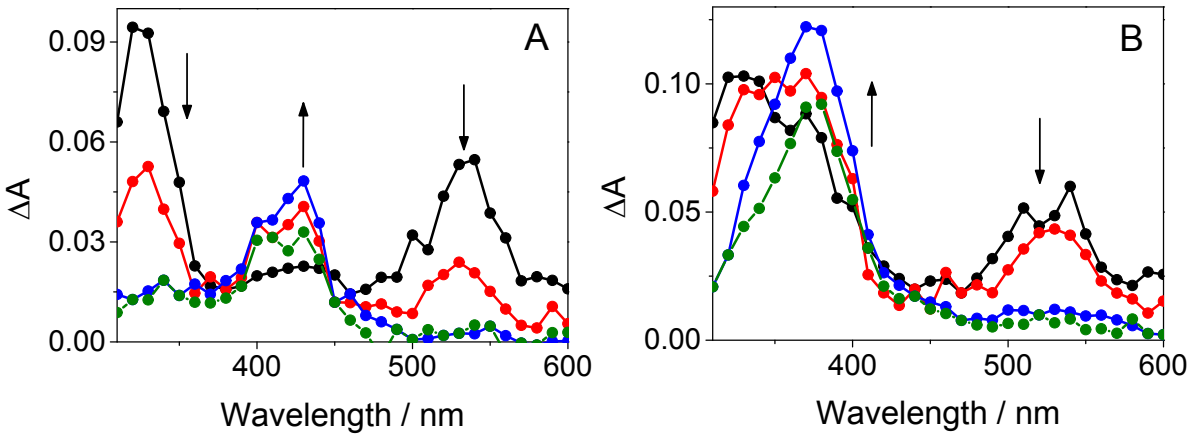



**Figure S2.** LFP transient absorption spectra ($\lambda_{exc}$ = 355 nm, $CH_2Cl_2$, $N_2$, $A_{355}$ = 0.2, 5 × $10^{-4}$ M) of **A**: **1b** obtained 0.02 μs (black), 0.2 μs (red), 1 μs (blue) and 2 μs (green) and **B**: **2b** obtained 0.1 μs (black), 0.2 μs (red), 1.0 μs (blue) and 2.0 μs (green) after the laser pulse.

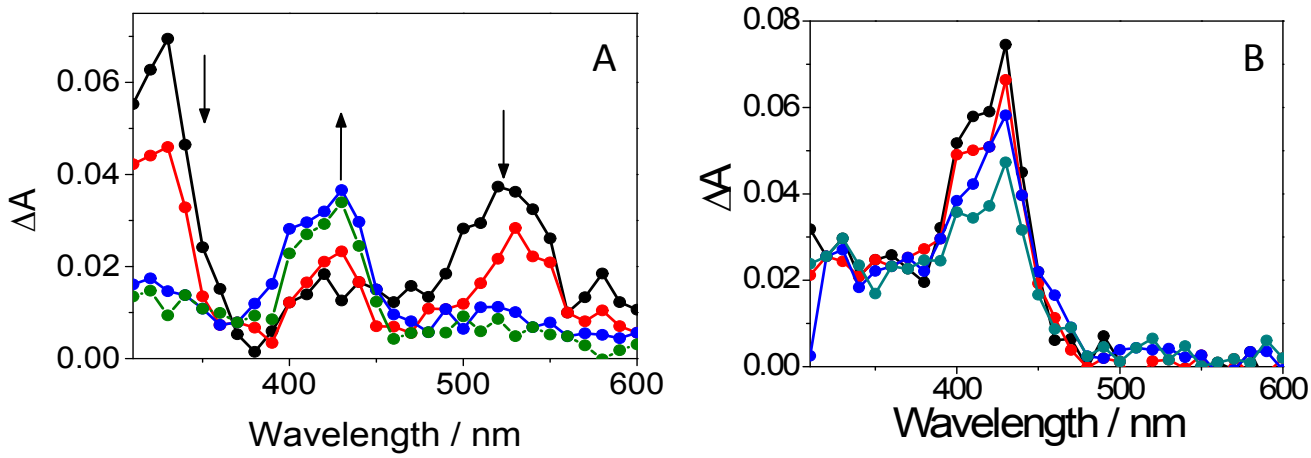



**Figure S3.** LFP transient absorption spectra ($\lambda_{exc}$ = 355 nm, $CH_2Cl_2$, $N_2$, $A_{355}$ = 0.2, 5 × $10^{-4}$ M) of **A**: **3a+4** obtained at 0.02 μs (black), 0.2 μs (red), 1.0 μs (blue) and 2.0 μs (green) and **B**: **6** obtained at 0.02 μs (black), 0.2 μs (red), 1.0 μs (blue) and 2.0 μs (green) after the laser pulse.

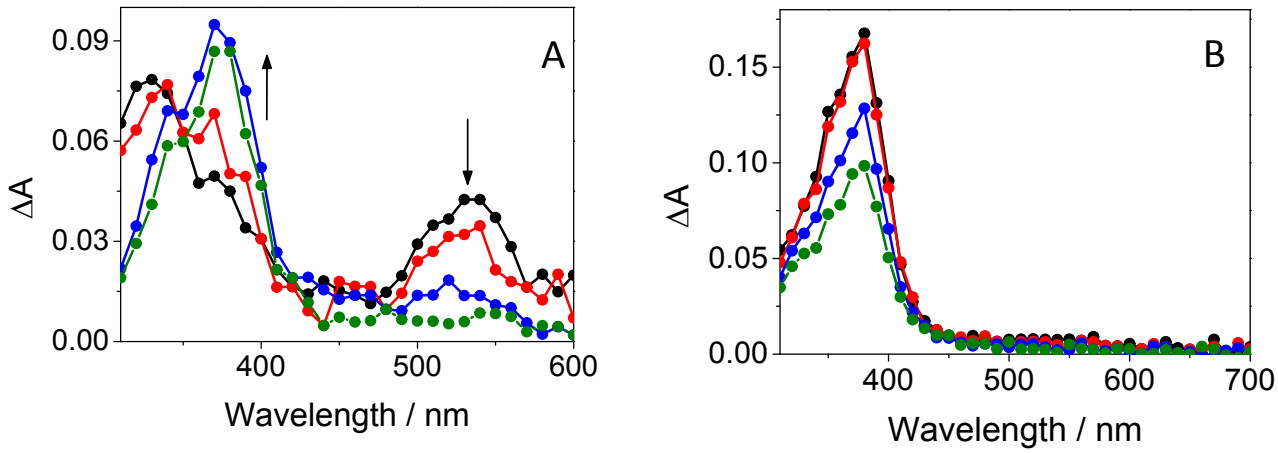



**Figure S4.** LFP transient absorption spectra ($\lambda_{exc}$ = 355 nm, $CH_2Cl_2$, $N_2$, $A_{355}$ = 0.2, 5 × $10^{-4}$ M) of **A**: **3a+5** and **B**: **7** obtained at 0.02 μs (black), 0.2 μs (red), 1.0 μs (blue) and 2.0 μs (green) after the laser pulse.

## 6. Computational methodology

Molecular dynamics were performed using the widely used Universal force field[1] (UFF) as well as a modified version, which we will call modified-UFF. Universal Force Field (UFF) has been used in previous studies with reasonable results for the two- three- and four-body interactions and here a modification has been introduced in the van der Waals interactions. Due to the presence of two chromophores containing aromatic rings at either end of the molecules **2a** and **2b**, the dispersion interactions will play an important role, and hence we have employed a force field (modified-UFF) containing dispersion coefficients taken from recent quantum chemistry results.

In the modified-UFF, the usual 12-6 Lennard-Jones term has been maintained with a slight modification. The repulsive term and the corresponding parameters have been kept, whilst the dispersive-attractive terms have been replaced by that of Grimme-D2,[2] recently introduced in DFT in order to account for dispersive interactions. In this term, a damping function has been introduced, which removes the artifact at short distances without noticeable changes in the region of the minimum.

After making several comparisons with the DFT results it was observed that UFF energetically overfavoured the folded conformations with respect to the unfolded due to the very large dispersive coefficients in the van der Waals term. Therefore, the modified-UFF, which corrected this missbehaviour by using smaller dispersive coefficients, was used throughout.

The GULP[3] software (version 4.3.2) has been used, able to run in parallel for the evaluation of the energy and first derivatives using MPI, based on a replicated data algorithm. This version allows the introduction in the force field of the Grimme-D2 functional to describe the dispersion interactions. The use of an atomistic (rather than quantum) approach allowed us two advantages in the calculations: a) the simulations could be extended to a much longer simulation time which means that a statistically significant number of configurations was sampled, and b) the solvent molecules could be included in the simulations. Solvent molecules were included in a continuum model according to the COSMIC algorithm introduced in GULP since version 4.0. The solvent included was dichloromethane and the temperature selected was 300 K. Molecular dynamics were carried out in the NPT ensemble using a timestep of 1 fs, and with relaxation times for thermostat and barostat set to 1 ps and with explicit flexibility of all the atoms of the system. The simulations comprised one molecule of either **2a** or **2b** and run for 2 ns.

The molecular dynamics runs during 2 ns sample widely all range of possible conformations available at 300 K. Every 50 ps, the resulting conformation obtained from the vibrational/rotational/translational free motions of the system at the given temperature are stored. At the final of the run, 40000 configurations are saved and from them an analysis is made. The results of this methodology include both enthalpic and entropic contributions and free energies are routinely obtained from molecular dynamics. This means that, for instance, conformations of low energy but with a high entropic penalty will become a small fraction of the conformations obtained at the end of the run. In summary, the larger the number of conformations obtained of a given type, the smaller the correspnding free energy and hence the more stable is that conformation. In our case, we estimate that the through-space mechanism requires the necessary (but not sufficient) condition that intramolecular chromophore-chromophore distances should be lower than 10 Å. In fact, another necessary condition would be that for short chromophore-chromophore distances, the aromatic groups should be in a parallel orientation in order to the through-space energy transfer mechanism to operate. In the present work we have only considered the first condition because we already obtain an extremelly low occurency (see Figure S5) of conformations where the chromophore-chromophore distances is lower than 10 Å As said above, one bottleneck for the quality of the molecular dynamics is the quality of the force field employed. We have not only employed one of the better tested and reliable model (Universal Force Field, UFF) but we have also implemented a modified version which takes into account the important dispersion interactions into account and this modified version is the one finally used. An internal comparison

with quantum chemistry DFT calculations has been done showing that both methods identify correctly the most important geometries corresponding to the relative minima. In general we believe the employed approach is of general validity although we do not have estimations about the energetic accuracy in terms of kJ/mol.

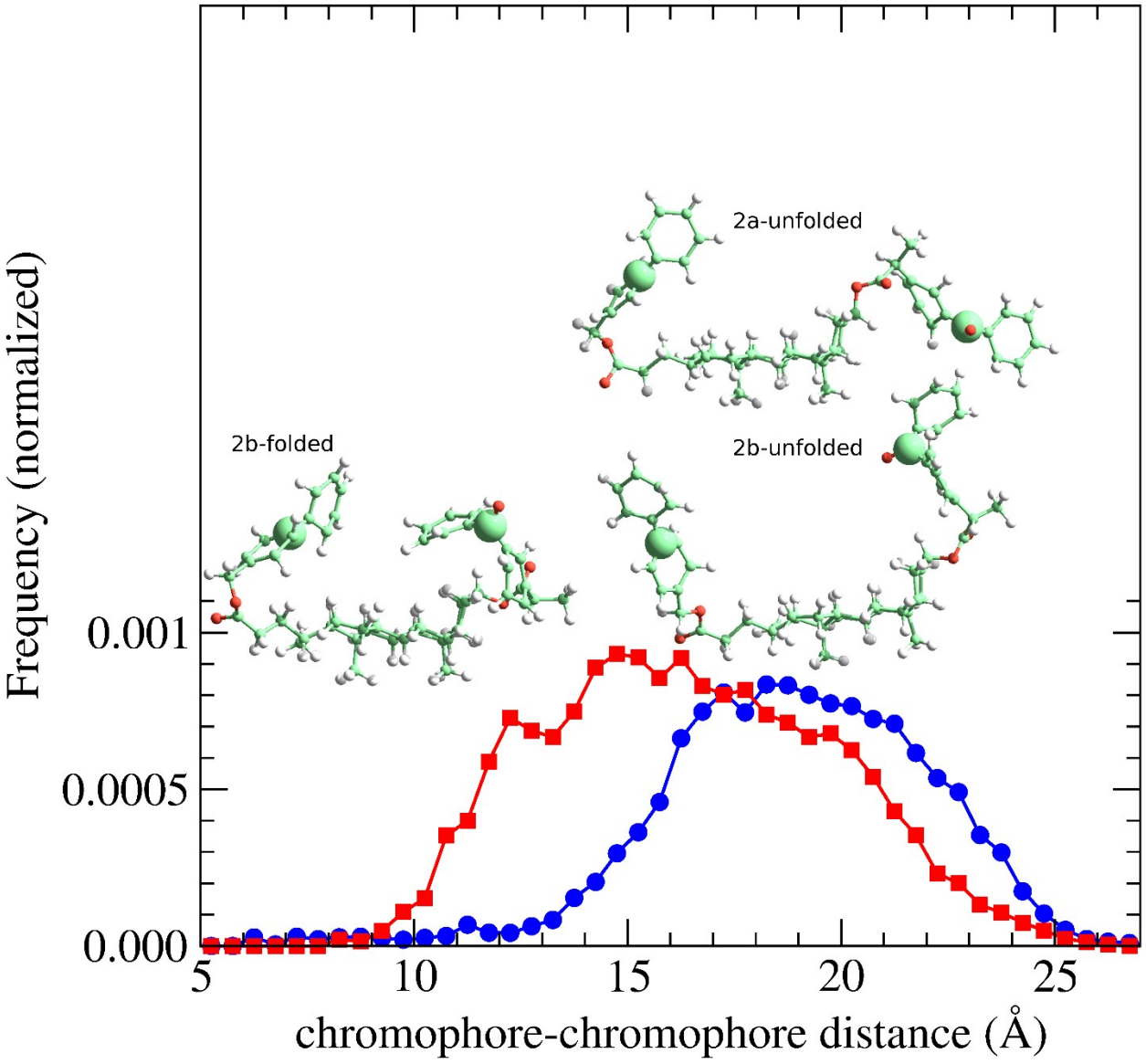



**Figure S5**. Conformational landscape of molecules **2a** and **2b**, based on the intramolecular chromophore-chromophore distance. The definition of the chromophore-chromophore distance is shown by the highlighted atoms. Conformation of one representative example of conformations of **2a** (top), with chromophore-chromophore distance 18 Å; and two conformations of **2b** (bottom), with chromophore-chromophore distances of 11 (folded) and 15 (unfolded) Å. The histograms have been produced from two molecular dynamics calculations of compounds **2a** and **2b** in dichloromethane solvent at 300 K. Conformations with chromophore-chromophore distance in the range [14-19] Å dominate the landscape with frequencies of 45.5 % (**2a**) and 49.3% (**2b**) of the total. A folded conformation of **2b** is also shown corresponding to a chromophore-chromophore distance of 9 Å. These folded conformations (with chromophore-chromophore distance < 10 Å) represent in both cases (**2a** and **2b**) a population of less than 2 %.

## 7. References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2. S. Grimme; *J. Comput. Chem.* 2006, **27**, 1787-1799.
3. (a) J. D. Gale; *J. Chem. Soc. Faraday Trans.* 1997, **93**, 629-637; (b) J. D. Gale and A. L. Rohl; *Mol. Simul.* 2003, **29**, 291-341; (c) J. D. Gale and A.L. Rohl; *Mol. Simul.* 2007, **33**, 1237-1246.