Amino Acid Appended Cholic acid-Azobenzene Dyad: An Effective & Smart Phase selective Gelator for Aromatic solvents

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General

All the chemicals were purchased from Sigma-Aldrich, Alfa Aesar, and Spectrochem India Pvt. Ltd and used without further purification. The solvents used were purchased from Merck (India) and were distilled and dried before use. Nuclear magnetic resonance spectra were recorded on Bruker 400 spectrometer. The ^{1}H NMR experiments were reported in δ units, parts per million (ppm), and were measured relative to residual chloroform (7.26 ppm) or DMSO (2.5 ppm) in the deuterated solvent. The ^{13}C NMR spectra were reported in ppm relative to deuterochloroform (77.0 ppm) or DMSO-d_6 (39.5 ppm). All coupling constants J were reported in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, m = multiplet and br s = broad singlet. Melting points were determined on a capillary point apparatus equipped with a digital thermometer and are uncorrected. Reactions were monitored by using thin layer chromatography (TLC) on 0.2 mm silica gel F254 plates (Merck). High resolution mass spectrometry (HRMS) was performed with a waters synapt G2 HDMS instrument using time-of-flight (TOF-MS) with ESI/APCI- hybrid quadrupole.

Absorption Study

Electronic absorption spectra were taken using dual beam Thermo Evolution 201 UV/Vis/NIR spectrophotometer. The data were analysed using related Software. The concentration of 9a for UV-vis spectroscopy 2×10^{-6} M (in xylene).

Scanning Electron Microscopy Analysis (SEM)

Morphology of the freeze dried gels were determined using scanning electron microscope (SEM) from Carl Zeiss (Σigma VP). The powder samples were spread over the carbon tape and coated with Au-Pd alloy for 2 min. The gel sample was spread over a silicon wafer and dried completely followed by coating with Au-Pd alloy for 2 min. Gels were dried using a labcon.

Transmission Electron Microscopy Analysis (TEM)

The TEM analysis were performed by placing a small amount of **9a** gel in xylene and toluene at MGC on the copper grid and dried at room temperature for 24hrs. Images were taken on JEOL-2010F TEM operating with electron beam of energy of 200 kV.

FT-IR Analysis

FT-IR was taken on ABB Bomen MB 3000 FTIR for gelator and freeze dried gels, using KBr disk technique.

Polarising Optical Microscopic Study (POM)

A small amount of gel obtained from respective solvents at minimum gel concentration was placed on a glass coverslip slide and placed under polarising optical microscope and was visualized under 100x magnification with yellow light. The images was taken by an Olympus instrument.

Fluorescence Microscopic Study

A small amount of gel obtained from respective solvents at minimum gel concentration was placed on a glass coverslip slide and was kept undisturbed under dust free environment for slow evaporation of the solvent and finally dried under vaccum to obtain xerogel which was placed under the epi-fluorescence microscope (Olympus-BX41, Olympus, Japan) with a red and blue filter using 100X objective lens and 10 X eyepiece lens.

Wide Angle X-ray Diffraction Study

The XRD pattern were made on the gel of **9a** xylene at minimum gel concentration. The experiment was carried out on Powder X-ray diffraction (PXRD) using a Rigaku Mini Flex II diffractometer with Cu-Kα radiation at 25º C with 2θ values ranging from 10–90 and scanning rate of 2º/min.

Procedure for gelation[1]

In a screw cap vial, gelator (8 mg-18 mg) was added in a solvent (1 mL) and heated in an oil bath until all the solid was completely dissolved. In most aromatic solvents, all gelator becomes soluble at room temperature upon gentle swirling and heating was not required.. The vials were left undisturbed for few minutes at room temperature. The gelation (G) was confirmed when no flow was observed after inversion of the vial, if the formed gel was stable at lower temperature (>20˚C) but unstable at room temperature (20˚C) it was confirmed as weak gel (WG), if the gelator was partially soluble at room temperature it was confirmed as partial soluble (PS), if a clear solution (>70mg) was obtained the state was marked as soluble (S). Some formed gels were found to be transparent while others were found to be opaque. The minimum gelation concentration (MGC) was determined by measuring the minimum amount of gelator required for the formation of the gel at room temperature.

Efficiency of water purification [2]

The efficiency of water purification was calculated using the formula given below where A^0 is absorbance of water before purification and A is the absorbance of water after purification.

$E = (A^0-A)/A^0$

1. Synthesis and Characterisation

Compound **3** was synthesized from Ethyl *p*-aminobenzoate and phenol according to reported protocol.[3]

General procedure for the synthesis of Ethyl 4-((4-(alkoxy)phenyl)diazenyl)benzoate (3a-c). To the stirred solution of **1** (7.3 mmol) in acetone K_2CO_3 (18.2 mmol) was added at 0 ^oC, the reaction mixture was stirred for 15 mins. at 0 ^oC after which 1-bromoalkane (**2**) (8.8 mmol) was added and the reaction was refluxed for 16 h. The completion of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was concentrated under reduced pressure and water (50 mL) was added. The formed precipitate was filtered under suction to yield crude product which was recrystallized using ethanol to yield pure product (**3a-c**) as orange solid.

(*E*)-Ethyl 4-((4-(octyloxy)phenyl)diazenyl)benzoate (3a). Orange solid; Yield: 82.3% (2.32 g); mp: 86.5-87 °C (Lit.[1] mp: 87 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.5 Hz, 2H), 7.91 (dd, J = 15.9, 8.7 Hz, 4H), 7.00 (d, J = 9.0 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H, O-$CH_{2\ Ester}$), 4.04 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.87 – 1.77 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.48 (dd, J = 14.6, 7.3 Hz, 2H, $CH_{2\ Alkoxy}$), 1.42 (t, J = 7.1 Hz, 3H, Me_{ester}), 1.38 – 1.22 (m, 8H, $CH_{2\ Alkoxy}$), 0.88 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.12 (C=O), 162.32, 155.33, 146.83, 131.47, 130.55, 125.19, 122.31, 114.79, 68.44 (O-$CH_{2\ Ester}$), 61.21 (O-$CH_{2\ Alkoxy}$), 31.83, 29.37, 29.26, 29.18, 26.03, 22.69, 14.37 ($CH_{3\ Ester}$), 14.14 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 2924, 2854, 1713, 1605, 1257, 1103, 841.

(*E*)-Ethyl 4-((4-(dodecyloxy)phenyl)diazenyl)benzoate (3b). Orange solid; yield: 81.7% (2.65 g); mp: 98.2-98.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.6 Hz, 2H), 7.91 (dd, J = 15.7, 8.8 Hz, 4H), 7.00 (d, J = 9.0 Hz, 2H), 4.40 (q, J = 7.1 Hz, 2H, O-$CH_{2\ Ester}$), 4.04 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.86 – 1.77 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.48 (dd, J = 14.8, 7.3 Hz, 2H,

$CH_{2\ Alkoxy}$), 1.42 (t, J = 7.1 Hz, 3H, Me_{ester}), 1.38 – 1.20 (m, 16H, $CH_{2\ Alkoxy}$), 0.87 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.22 (C=O), 162.34, 155.35, 146.85, 131.48, 130.56, 125.20, 122.32, 114.80, 68.45 (O-$CH_{2\ Ester}$), 61.21(O-$CH_{2\ Alkoxy}$), 31.94, 29.69, 29.66, 29.62, 29.59, 29.40, 29.38, 29.18, 26.02, 22.72, 14.37 ($CH_{3\ Ester}$), 14.16 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 2924, 2854, 1713, 1605, 1281, 1103, 841.

(*E*)-Ethyl 4-((4-(hexadecyloxy)phenyl)diazenyl)benzoate (3c). Orange solid; yield: 84.6% (3.09 g); mp: 96.5-97.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.6 Hz, 2H), 7.99 – 7.90 (m, 4H), 7.03 (d, J = 9.0 Hz, 2H), 4.43 (q, J = 7.1 Hz, 2H, O-$CH_{2\ Ester}$), 4.07 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.87 – 1.81 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.54 – 1.44 (m, 2H, $CH_{2\ Alkoxy}$), 1.45 (t, J = 7.1 Hz, 3H, Me_{ester}), 1.40 – 1.26 (m, 24H, $CH_{2\ Alkoxy}$), 0.90 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.23 (C=O), 162.34, 155.38, 146.85, 131.47, 130.56, 125.21, 122.32, 114.80, 68.45 (O-$CH_{2\ Ester}$), 61.22 (O-$CH_{2\ Alkoxy}$), 33.59, 31.95, 30.54, 29.72, 29.71, 29.69, 29.62, 29.59, 29.45, 29.40, 29.18, 28.57, 26.02, 22.72, 14.37 ($CH_{3\ Ester}$), 14.16 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 2916, 2847, 1713, 1504, 1466, 1295, 841.

General procedure for the synthesis of 4a-c. To a solution of LAH (18.0 mmol), in dry THF (20 mL) at 0 ^{o}C, a solution of **3** (6.0 mmol) in dry THF was added and the reaction mixture was stirred at room temperature for 2 h. The completion of the reaction was monitored by TLC. After completion of the reaction, the reaction was cooled to 0 ^{o}C and quenched by adding 1N NaOH solution (30 mL). Subsequently ethyl acetate (20 mL) was added and the reaction was filtered through celite and extracted using ethyl acetate (20 mL x 2). The organic layer was dried over anhydrous sodium sulphate and concentrated under reduced pressure to give crude product which was recrystallized using ethanol to give pure product (**4a-c**) as orange solid.

(*E*)-(4-((4-(Octyloxy)phenyl)diazenyl)phenyl)methanol (4a). Orange solid; yield: 83.8% (1.71 g); mp: 118.5-119 °C Lit.[1] mp: 117 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 14.5,

8.6 Hz, 4H), 7.48 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 9.0 Hz, 2H), 4.76 (s, 2H, O-$CH_{2\ Alcohol}$), 4.03 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.84 – 1.77 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.50 – 1.43 (m, 2H, $CH_{2Alkoxy}$), 1.37– 1.29 (m, 8H, $CH_{2\ Alkoxy}$), 0.89 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.76, 152.27, 146.82, 143.05, 127.48, 124.77, 122.78, 114.72, 68.40 (O-$CH_{2\ Alcohol}$), 64.99 (O-$CH_{2\ Alkoxy}$), 31.83, 29.37, 29.26, 29.21, 26.04, 22.69, 14.14 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3310, 3217, 2924, 2854, 1605, 1497, 1250, 841.

(*E*)-(4-((4-(Dodecyloxy)phenyl)diazenyl)phenyl)methanol (4b). Orange solid; yield: 82.6% (1.94 g); mp: 115-115.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (dd, J = 14.1, 8.6 Hz, 4H), 7.48 (d, J = 8.2 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 4.77 (s, 2H, O-$CH_{2\ Alcohol}$), 4.03 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.85 – 1.77 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.51 – 1.42 (m, 2H, $CH_{2\ Alkoxy}$),1.37 –1.26 (m, 16H, $CH_{2\ Alkoxy}$), 0.87 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.76, 152.27, 146.82, 143.07, 127.47, 124.77, 122.77, 114.72, 68.39 (O-$CH_{2\ Alcohol}$), 64.97 (O-$CH_{2\ Alkoxy}$), 31.94, 29.69, 29.66, 29.62, 29.60, 29.41, 29.38, 29.21, 26.03, 22.72, 14.16 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3310, 3209, 2916, 2854, 1744, 1497, 1466, 1250, 841.

(*E*)-(4-((4-(Hexadecyloxy)phenyl)diazenyl)phenyl)methanol (4c). Orange solid; Yield: 82.6% (2.26 g); mp: 124.6-125.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 15.9, 8.7 Hz, 4H), 7.49 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 4.77 (s, 2H, O-$CH_{2\ Alcohol}$), 4.04 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.84 – 1.79 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.50 – 1.43 (m, 2H, $CH_{2\ Alkoxy}$), 1.35 – 1.23 (m, 28H, $CH_{2\ Alkoxy}$), 0.87 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.74, 150.27, 146.81, 143.03, 127.46, 124.75, 122.77, 114.70, 68.38 (O-$CH_{2\ Alcohol}$), 65.00 (O-$CH_{2\ Alkoxy}$), 31.94, 29.72, 29.68, 29.61, 29.59, 29.40, 29.38, 29.20, 26.03, 22.71, 14.15 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3055, 2924, 2854, 1713, 1597, 1466, 1281, 1250, 1142, 841.

General Procedure for Compound 6a-f. To the stirred solution of **4** (2.81 mmol) in DCM (20 mL), DMAP (0.23 mmol) was added at 0 ^{o}C and subsequently EDC.HCl (4.22 mmol) and HOBt (2.34 mmol) was added. The reaction mixture was stirred for 15 min. at 0 °C, after which, **5** (2.34 mmol) was added and the reaction was stirred at room temperature for 6-8 h. The completion of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with water and extracted with DCM (2 x 20 mL). The organic layer was separated and dried over anhydrous sodium sulfate and evaporated under reduced pressure to give crude product as orange solid. The crude product was recrystallized from ethanol to yield pure **6a-f** as orange solid.

(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)benzyl (*tert*-butoxycarbonyl)-*L*-alaninate (6a). Yellow solid; yield: 69.3% (0.833 g); mp: 128-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 17.9, 8.7 Hz, 4H), 7.47 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 9.0 Hz, 2H), 5.24 (m, 2H, O-$CH_{2\ Benzylic}$), 5.04 (d, J = 9.1 Hz, 1H, $NH_{Alanine}$), 4.44 – 4.34 (m, 1H, $CH_{Alanine}$), 4.04 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.87 – 1.78 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.55 – 1.42 (m, 11H, 3xMe_{Boc} & $CH_{2\ Alkoxy}$), 1.41 (d, J = 7.2 Hz, 3H, $Me_{Alanine}$), 1.37 – 1.24 (m, 8H, $CH_{2\ Alkoxy}$), 0.89 (t, J = 6.9 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.23 (C=O), 161.89, 155.15 (C=O_{Boc}), 152.65, 146.79, 137.48, 128.75, 124.86, 122.75, 114.73, 79.96, 68.41 (O-$CH_{2\ Benzylic}$), 66.52 (O-$CH_{2\ Alkoxy}$), 49.33 ($CH_{Alanine}$), 31.83, 29.37, 29.26, 29.20, 28.34 ($CH_{3\ Boc}$), 26.03, 22.69, 18.63 ($CH_{3\ Alanine}$), 14.14 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3340, 2932, 2862, 1751, 1690, 1528, 1250, 1157, 841.

(*E*)-4-((4-(Dodecyloxy)phenyl)diazenyl)benzyl (*tert*-butoxycarbonyl)-*L*-alaninate (6b). Yellow solid; yield: 72.8% (0.885 g); mp: 132-133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, J = 17.8, 8.7 Hz, 4H), 7.49 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 9.0 Hz, 2H), 5.26 (dd, J = 32.1, 12.7 Hz, 2H, O-$CH_{2\ Benzylic}$), 5.08 (d, J = 7.1 Hz, 1H, $NH_{Alanine}$), 4.47 – 4.35 (m, 1H, CH

$_{Alanine}$), 4.06 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.87 – 1.81 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.54 – 1.45 (m, 11H, 3xMe_{Boc} & $CH_{2\ Alkoxy}$), 1.43 (d, J = 7.2 Hz, 3H, Me $_{Alanine}$), 1.41– 1.22 (m, 16H, $CH_{2\ Alkoxy}$), 0.90 (t, J = 6.8 Hz, 3H, Me $_{Alkoxy}$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.20 (C=O), 161.88, 155.12 (C=O_{Boc}), 152.64, 146.78, 137.47, 128.73, 124.85, 122.74, 114.72, 79.95, 68.40 (O-$CH_{2\ Benzylic}$), 66.52 (O-$CH_{2\ Alkoxy}$), 49.32 (CH $_{Alanine}$), 31.94, 29.68, 29.66, 29.62, 29.59, 29.40, 29.38, 29.19, 28.33 ($CH_{3\ Boc}$), 26.03, 22.72, 18.63 ($CH_{3\ Alanine}$), 14.16 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3340, 2924, 2854, 1751, 1690, 1528, 1250, 1157, 841.

(*E*)-4-((4-(Hexadecyloxy)phenyl)diazenyl)benzyl (*tert*-butoxycarbonyl)-*L*-alaninate (6c). Yellow solid; yield: 72.8% (1.1 g); mp: 119-120 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (dd, J = 19.2, 8.6 Hz, 4H), 7.46 (d, J = 8.3 Hz, 2H), 6.99 (d, J = 8.9 Hz, 2H), 5.23 (dd, J = 30.3, 12.7 Hz, 2H, O-$CH_{2\ Benzylic}$), 5.04 (d, J = 4.7 Hz, 1H, $NH_{Alanine}$), 4.44 – 4.32 (m, 1H, $CH_{Alanine}$), 4.03 (t, J = 6.5 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.85 – 1.77 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.69 – 1.42 (m, 11H, 3xMe_{Boc} & $CH_{2\ Alkoxy}$), 1.40 (d, J = 7.2 Hz, 3H, $Me_{Alanine}$), 1.38 – 1.18 (m, 24H, $CH_{2\ Alkoxy}$), 0.87 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.22 (C=O), 161.89, 155.15 (C=O_{Boc}), 152.65, 146.79, 137.48, 128.75, 124.86, 122.76, 114.73, 79.96, 68.40 (O-$CH_{2\ Benzylic}$), 66.53 (O-$CH_{2\ Alkoxy}$), 49.31 ($CH_{Alanine}$), 31.95, 29.72, 29.71, 29.69, 29.62, 29.59, 29.41, 29.40, 29.20, 28.34 (CH_{3Boc}), 26.03, 22.72, 18.63 ($CH_{3\ Alanine}$), 14.16 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3364, 2916, 2847, 1744, 1695, 1528, 1250, 1173, 833.

(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)benzyl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (6d). Yellow solid; Yield: 72.5% (1.00 g); mp: 156-157 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 9.0 Hz, 2H), 7.88 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.28 – 7.20 (m, 3H, $Ar_{Phenylalanine}$), 7.13 – 7.06 (m, 2H, $Ar_{Phenylalanine}$), 7.03 (d, J = 9.0 Hz, 2H), 5.21 (m, 2H, O-$CH_{2\ Benzylic}$), 5.02 (d, J = 8.2 Hz, 1H, $NH_{Phenylalanine}$), 4.74 – 4.64 (m, 1H, $CH_{Phenylalanine}$), 4.07 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 3.17 – 3.06 (m, 2H, $CH_{2\ Phenylalanine}$), 1.89 – 1.80 (m, 2H, O-β-CH_2

$_{Alkoxy}$), 1.55 – 1.40 (m, 11H, 3xMe_{Boc} & $CH_{2\ Alkoxy}$), 1.39 – 1.25 (m, 8H, $CH_{2\ Alkoxy}$), 0.92 (t, J = 6.9 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.73 (C=O), 161.86, 155.06 ($C{=}O_{Boc}$), 152.63, 146.76, 137.13, 135.78, 129.30, 129.08, 128.56, 127.02, 124.84, 122.67, 114.70, 79.98, 68.37 (O-$CH_{2\ Benzylic}$), 66.58 (O-$CH_{2\ Alkoxy}$), 54.47 ($CH_{Phenylalanine}$), 38.30, 31.80, 29.33, 29.22, 29.16, 28.28 ($CH_{3\ Boc}$), 26.00, 22.65, 14.11 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3387, 2924, 2854, 1744, 1697, 1466, 1250, 1173, 841.

(*E*)-4-((4-(Dodecyloxy)phenyl)diazenyl)benzyl (*tert*-butoxycarbonyl)-*L*-phenylalaninate (6e). Yellow solid; Yield: 68.5% (0.945 g); mp: 142.3-144.2°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, J = 27.1, 8.6 Hz, 4H), 7.38 (d, J = 8.3 Hz, 2H), 7.23 (m, 3H, $Ar_{Phenylalanine}$), 7.06 (m, 2H, $Ar_{Phenylalanine}$), 7.00 (d, J = 8.9 Hz, 2H), 5.18 (m, 2H, O-$CH_{2\ Benzylic}$), 4.98 (d, J = 7.6 Hz, 1H, $NH_{Phenylalanine}$), 4.70 – 4.58 (m, 1H, $CH_{Phenylalanine}$), 4.04 (t, J = 6.6 Hz, 2H, O-$CH_{2\ Alkoxy}$), 3.09 (d, J = 4.2 Hz, 2H, $CH_{2\ Phenylalanine}$), 1.85 – 1.77 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.53 – 1.35 (m, 11H, 3xMe_{Boc} & $CH_{2\ Alkoxy}$), 1.34 – 1.16 (m, 16H, $CH_{2\ Alkoxy}$), 0.87 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.78 (C=O), 161.77, 155.10 ($C{=}O_{Boc}$), 152.28, 146.83, 143.08, 135.81, 130.30, 129.33, 128.59, 127.47, 124.76, 122.78, 114.72, 80.03, 68.39 (O-$CH_{2\ Benzylic}$), 66.62 (O-$CH_{2\ Alkoxy}$), 54.52 ($CH_{Phenylalanine}$), 38.33, 31.95, 29.73, 29.68, 29.62, 29.59, 29.41, 29.39, 29.20, 28.32 ($CH_{3\ Boc}$), 26.03, 22.72, 14.16 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3286, 2916, 2847, 1697, 1605, 1466, 1250, 841.

(*E*)-4-((4-(Hexadecyloxy)phenyl)diazenyl)benzyl (*tert*-butoxycarbonyl)-*L* phenylalaninate (6f). Yellow solid; yield: 70.2% (1.194 g); mp: 150.8-151.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 8.9 Hz, 2H), 7.88 (d, J = 8.3 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.26 – 7.23 (m, 3H, $Ar_{Phenylalanine}$), 7.15 – 7.07 (d, J = 7.0 Hz, 2H, $Ar_{Phenylalanine}$), 7.03 (d, J = 8.9 Hz, 2H), 5.21 (m, 2H, O-$CH_{2\ Benzylic}$), 5.02 (d, J = 8.1 Hz, 1H, NH $_{Phenylalanine}$), 4.68 (dd, J = 13.9, 6.2 Hz, 1H, CH $_{Phenylalanine}$), 4.07 (t, J = 6.5 Hz, 2H, O-$CH_{2\ Alkoxy}$), 3.17 – 3.06 (m, 2H, $CH_{2\ Phenylalanine}$), 1.90 –

1.78 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.50 – 1.39 (m, 11H, 3xMe_{Boc} & $CH_{2\ Alkoxy}$), 1.39 – 1.16 (m, 24H, $CH_{2\ Alkoxy}$), 0.90 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.99 (C=O), 161.86, 154.84 (C=$O_{\ Boc}$), 152.54, 146.78, 137.28, 136.68, 128.95, 128.54, 128.41, 127.20, 124.83, 122.63, 114.72, 80.24, 68.40 (O-$CH_{2\ Benzylic}$), 68.76 (O-$CH_{2\ Alkoxy}$), 57.79 ($CH_{Phenylalanine}$), 37.61, 31.83, 29.37, 29.26, 29.20, 28.33 ($CH_{3\ Boc}$), 26.03, 22.68, 14.14 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3371, 2916, 2847, 1744, 1697, 1504, 1250, 1165, 841.

General procedure for the synthesis of 7a-f. A solution of dioxane-HCl (5 mL) was added drop-wise to a solutiom of **6a-f** (1 mmol) dissolved in dioxane at 0 °C. The reaction was stirred at room temperature for 2 h and monitored *via* TLC. After the completion, the reaction mixture was concentrated, dried under vacuum, washed with diethyl ether (2 x 10 mL) and filtered off to give **7a-f** in pure form as hydrochloride salt.

(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)benzyl *L*-alaninate hydrochloride (7a). Orange solid; Yield: 98.8 % (0.692 g); mp: 146-147 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.66 (brs, 3H, $NH_3^+{}_{Alanine}$), 7.84 (dd, J = 10.4, 8.7 Hz, 4H), 7.59 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.9 Hz, 2H), 5.30 (s, 2H, O-$CH_{2\ Benzylic}$), 4.18 – 4.11 (m, 1H, $CH_{Alanine}$), 4.04 (t, J = 6.4 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.75 – 1.66 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.45 (d, J = 7.2 Hz, 3H, $CH_{3\ Alanine}$), 1.40 – 1.19 (m, 10H, $CH_{2\ Alkoxy}$), 0.83 (t, J = 6.6 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, DMSO) δ 170.30 (C=O), 162.09 , 152.22 , 146.43 , 138.36 , 129.34 , 125.14 , 122.76, 115.50, 68.47 (O-$CH_{2\ Benzylic}$), 66.87 (O-$CH_{2\ Alkoxy}$), 48.34 ($CH_{Alanine}$), 31.71, 29.20, 29.14, 29.04, 25.93, 22.56, 16.16 ($CH_{3\ Alanine}$), 14.43 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3402, 2924, 2854, 1744, 1605, 1504, 1250, 841.

(*E*)-4-((4-(Dodecyloxy)phenyl)diazenyl)benzyl *L*-alaninate hydrochloride (7b). Orange solid; Yield: 98 % (0.739 g); mp: 173-173.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.61 (brs, 2H, $NH_3^+{}_{Alanine}$), 8.38 (brs, 1H, $NH_3^+{}_{Alanine}$), 8.04 – 7.77 (m, 4H), 7.62 (d, J = 8.3 Hz, 2H), 7.13

(d, J = 8.9 Hz, 2H), 5.33 (s, 2H, O-$CH_{2\ Benzylic}$), 4.25 – 4.15 (m, $CH_{Alanine}$), 4.08 (t, J = 6.4 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.82 – 1.67 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.46 (d, J = 7.2 Hz, 3H, $CH_{3\ Alanine}$), 1.41 – 1.17 (m, 18H, $CH_{2\ Alkoxy}$), 0.85 (t, J = 6.6 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, DMSO) δ 170.32 (C=O), 162.10, 152.24, 146.43, 138.34, 129.37, 125.15, 122.77, 115.52, 68.46 (O-$CH_{2\ Benzylic}$), 66.91(O-$CH_{2\ Alkoxy}$), 48.35 ($CH_{Alanine}$), 31.76, 29.50, 29.48, 29.43, 29.18, 29.00, 25.89, 22.57, 16.17 ($CH_{3\ Alanine}$), 14.44 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3418, 2924, 2847, 1744, 1697, 1504, 1250, 1165, 841.

(*E*)-4-((4-(Hexadecyloxy)phenyl)diazenyl)benzyl *L*-alaninate hydrochloride (7c). Orange solid; Yield: 99 % (0.88 g); mp: 166-167 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.58 – 8.41 (m, 3H, $NH_3^+{}_{Alanine}$), 7.92 – 7.78 (m, 4H), 7.59 (d, J = 8.3 Hz, 2H), 7.10 (d, J = 8.9 Hz, 2H), 5.31 (s, 2H, O-$CH_{2\ Benzylic}$), 4.18 (dd, J = 14.4, 7.5 Hz, 1H, $CH_{Alanine}$), 4.05 (t, J = 6.4 Hz, 2H, O-$CH_{2\ Alkoxy}$), 1.76 – 1.68 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.43 (d, J = 7.2 Hz, 3H, $CH_{3\ Alanine}$), 1.40 – 1.35 (m, 2H, $CH_{2\ Alkoxy}$), 1.34 – 1.06 (m, 24H, $CH_{2\ Alkoxy}$), 0.82 (t, J = 6.6 Hz, 3H, $Me_{\ Alkoxy}$); ^{13}C NMR (100 MHz, DMSO) δ 170.34 (C=O), 162.11, 152.25, 146.41, 138.32, 129.39, 125.15, 122.78, 115.52, 68.45 (O-$CH_{2\ Benzylic}$), 66.95 (O-$CH_{2\ Alkoxy}$), 48.36 ($CH_{Alanine}$), 31.76, 29.50, 29.48, 29.41, 29.18, 29.00, 25.89, 22.57, 16.19 ($CH_{3\ Alanine}$), 14.44 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3405, 2916, 2854, 1744, 1597, 1250, 841.

(*E*)-4-((4-(Octyloxy)phenyl)diazenyl)benzyl *L*-phenylalaninate hydrochloride (7d). Orange solid; Yield: 98 % (0.786 g); mp: 156.8-157.4 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.17 (brs, 3H, $NH_3^+{}_{Phenylalanine}$), 7.89 (d, J = 9.0 Hz, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.5 Hz, 2H), 7.35 – 7.19 (m, 5H, $Ar_{Phenylalanine}$), 7.13 (d, J = 9.1 Hz, 2H), 5.27 – 5.18 (m, 2H, O-$CH_{2\ Benzylic}$), 4.32 (t, J = 6.6 Hz, 1H, $CH_{Phenylalanine}$), 4.08 (t, J = 6.5 Hz, 2H, O-$CH_{2\ Alkoxy}$), 3.17 (dd, J = 14.0, 6.0 Hz, 1H, $CH_{2\ Phenylalanine}$), 3.07 (dd, J = 13.9, 7.5 Hz, 1H, $CH_{2\ Phenylalanine}$), 1.79 – 1.71 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.52 – 1.39 (m, 2H, $CH_{2\ Alkoxy}$), 1.39 – 1.12 (m, 8H, $CH_{2\ Alkoxy}$), 0.87

(t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, DMSO) δ 170.16 (C=O), 162.11, 152.21, 146.43, 138.01, 135.42, 129.87, 129.55, 129.05, 127.65 , 125.16, 122.66, 115.53, 68.49 (O-$CH_{2\ Benzylic}$), 66.81 (O-$CH_{2\ Alkoxy}$), 54.00 ($CH_{Phenylalanine}$), 37.11, 31.71, 29.19, 29.14, 29.04, 25.94, 22.56, 14.45 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3402, 2924, 2854, 1751, 1597, 1504, 1250, 841.

(*E*)-4-((4-(Dodecyloxy)phenyl)diazenyl)benzyl *L*-phenylalaninate hydrochloride (7e). Orange solid; yield: 99 % (0.802 g); mp: 182.7-183 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.69 (brs, 3H, $NH_3^+{}_{Phenylalanine}$), 7.86 (d, J = 8.9 Hz, 2H), 7.78 (d, J = 8.4 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.34 – 7.13 (m, 5H, $Ar_{Phenylalanine}$), 7.10 (d, J = 9.0 Hz, 2H), 5.26 – 5.13 (m, 2H, O-$CH_{2\ Benzylic}$), 4.33 (dd, J = 7.8, 5.8 Hz, 1H, $CH_{Phenylalanine}$), 4.05 (t, J = 6.5 Hz, 2H, O-$CH_{2\ Alkoxy}$), 3.22 (dd, J = 14.0, 5.6 Hz, 1H, $CH_{2\ Phenylalanine}$), 3.08 (dd, J = 14.0, 8.0 Hz, 1H, $CH_{2\ Phenylalanine}$), 1.76 – 1.67 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.42 – 1.35 (m, 2H, $CH_{2\ Alkoxy}$), 1.33 – 1.16 (m, 16H, $CH_{2\ Alkoxy}$), 0.82 (t, J = 6.8 Hz, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, DMSO) δ 169.52 (C=O), 162.11, 152.22, 146.43, 137.89, 135.14, 129.89, 129.57, 129.08, 127.72, 125.16, 122.64, 115.52, 68.47 (O-$CH_{2\ Benzylic}$), 66.93 (O-$CH_{2\ Alkoxy}$), 53.74 ($CH_{Phenylalanine}$), 36.58, 31.77, 29.51, 29.49, 29.44, 29.19, 29.01, 25.90, 22.57, 14.44 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 3394, 2916, 2854, 1751, 1690, 1499, 1196, 841.

(*E*)-4-((4-(Hexadecyloxy)phenyl)diazenyl)benzyl *L*-phenylalaninate hydrochloride (7f). Orange solid; yield: 99 % (0.979 g); mp: 153.6-154.2 °C; ^1H NMR (400 MHz, DMSO-d_6 + $CDCl_3$) δ 8.73 (brs, 3H, $NH_3^+{}_{Phenylalanine}$), 7.86 (d, J = 7.2 Hz, 2H), 7.78 (d, J = 4.5 Hz, 2H), 7.37 (d, J = 7.1 Hz, 2H), 7.31– 7.15 (m, 5H, $Ar_{Phenylalanine}$), 7.02 (d, J = 6.0 Hz, 2H), 5.25 – 5.15 (m, 2H, O-$CH_{2\ Benzylic}$), 4.22 – 4.32 (m, 1H, $CH_{Phenylalanine}$), 4.09 – 3.99 (m, 2H, O-$CH_{2\ Alkoxy}$), 3.29 – 3.24 (m, 1H, $CH_{2\ Phenylalanine}$), 3.12 (dd, J = 13.8, 7.5 Hz, 1H, $CH_{2\ Phenylalanine}$), 1.80 – 1.69 (m, 2H, O-β-$CH_{2\ Alkoxy}$), 1.45 – 1.35 (m, 2H, $CH_{2\ Alkoxy}$), 1.21 (brs, 24H, $CH_{2Alkylchain}$), 0.87 –

0.80 (m, 3H, Me_{Alkoxy}); ^{13}C NMR (100 MHz, DMSO-d_6 + $CDCl_3$) 169.20 (C=O), 162.04, 152.31, 146.44, 139.11, 134.74, 129.78, 129.40, 128.91, 127.59, 125.02, 122.61, 115.13, 68.38 (O-$CH_{2\ Benzylic}$), 66.99 (O-$CH_{2\ Alkoxy}$), 53.86 ($CH_{Phenylalanine}$), 36.44, 31.80, 29.55, 29.53, 29.47, 29.27, 29.23, 29.09, 29,08, 25.94, 22.60, 14.36 ($CH_{3\ Alkoxy}$); IR (KBr, υ, cm^{-1}) 2916, 2847, 1744, 1589, 1474, 1242, 1242, 1142, 833.

General procedure for the synthesis of CA-AA-AZA, 9a-f. To the stirred solution of cholic acid (8) (1.3 mmol) in DCM (20 mL), triethyl amine (3.2 mmol) was added at 0 ^oC and subsequently EDC.HCl (1.7 mmol) and HOBt (1.3 mmol) was added. The reaction mixture was stirred for 15 min. at 0 ^oC, after which, 7a-f (1.4 mmol) was added and the reaction was stirred at room temperature for 6-8 h. The completion of the reaction was monitored by TLC. After the completion of the reaction, the reaction mixture was diluted with water and extracted with DCM (3 x 20 mL). The organic layer was separated, dried over anhydrous sodium sulfate and evaporated under reduced pressure to give crude product as a dark orange solid. The crude product was recrystallized using ethyl acetate/hexane to yield pure 9a-f as orange solids.

4-((*E*)-(4-(Octyloxy)phenyl)diazenyl)benzyl (4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*) 3,7,12-trihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17 yl)pentanoyl)-*L*-alaninate (9a). Orange solid; Yield: 82.6% (0.877 g); mp: 125-126 °C; ^1H NMR (400 MHz, DMSO-d_6) δ 8.21 (d, J = 6.6 Hz, 1H, NH_{Amide}), 7.82 (dd, J = 18.5, 8.6 Hz, 4H), 7.51 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 9.0 Hz, 2H), 5.17 (s, 2H, O-$CH_{2\ Benzylic}$), 4.34 – 4.27 (m, 1H, $CH_{Alanine}$), 4.25 – 4.22 (brs, 1H, OH_{CA}), 4.07 – 4.00 (m, 3H, H-12_{CA} & O-$CH_{2\ Alkoxy}$), 3.91 (brs, 1H, H-7_{CA}), 3.73 (brs, 1H, OH_{CA}), 3.54 (brs, 1H, OH_{CA}), 3.18 – 3.13 (m, 1H, H-3_{CA}), 2.20 – 1.93 (m, 6H), 1.75 – 1.69 (m, 4H), 1.66 – 1.57 (m, 4H), 1.43 – 1.36 (m, 5H), 1.30 – 1.13 (m, 18H), 0.89 (d, J = 6.4 Hz, 3H, $Me_{Alanine}$), 0.88 – 0.78 (m, 6H, Me-21_{CA} & Me_{Alkoxy}), 0.74 (s, 3H, Me-19_{CA}), 0.49 (s, 3H, Me-18_{CA}); ^{13}C NMR (100 MHz, DMSO) δ 173.20 (C=O), 173.15

(C=O), 162.03, 152.00, 146.45, 139.24, 128.88, 125.10, 122.72, 115.46, 71.45 (C-12_{CA}), 70.89 (C-3_{CA}), 68.45 (O-$CH_{2\ Benzylic}$), 66.68 (C-7_{CA}), 65.69 (O-$CH_{2\ Alkoxy}$), 48.12 ($CH_{Alanine}$), 46.70, 46.15, 41.98, 41.77, 35.76, 35.48, 34.82, 32.48, 31.88, 31.72, 30.84, 29.20, 29.15, 29.03, 28.98, 27.71, 26.63, 25.95, 23.24, 23.06, 22.57 (C-19_{CA}), 17.54 ($CH_{3\ Alanine}$), 17.33 (C-21_{CA}), 14.45 ($CH_{3\ Alkoxy}$), 12.75 (C-18_{CA}); HRMS (ESI): *m/z* $[M + H]^+$ calcd for Chemical Formula: $C_{48}H_{72}N_3O_7$: 802.5370 found : 802.5386; IR (KBr, υ, cm^{-1}) 3310. 2924, 2862, 1744, 1651, 1597, 1250, 1142, 841.

4-((*E*)-(4-(Dodecyloxy)phenyl)diazenyl)benzyl (4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trihydroxy-10,13 dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)-*L*-alaninate (CA-Ala-Azo, 9b). Orange solid; Yield: 86.5% (1.03 g); mp: 125.8-126.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, J = 7.0 Hz, 1H, NH_{Amide}), 7.86 (dd, J = 18.4, 8.6 Hz, 4H), 7.54 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 9.0 Hz, 2H), 5.20 (s, 2H, O-$CH_{2\ Benzylic}$), 4.35 (d, J = 2.6 Hz, 1H, $CH_{Alanine}$), 4.34 – 4.28 (brs, 1H, OH_{CA}), 4.10 – 4.05 (m, 3H, H-12_{CA} & O-$CH_{2\ Alkoxy}$), 4.02 – 3.98 (m, 1H, H-7_{CA}), 3.75 (brs, 1H, OH_{CA}), 3.56 (brs, 1H, OH_{CA}), 3.21 – 3.14 (m, 1H, H-3_{CA}), 2.22 – 1.96 (m, 6H), 1.77 – 1.72 (m, 4H), 1.67– 1.56 (m, 4H), 1.43 – 1.30 (m, 13H), 1.22 – 1.09 (m, 17H), 0.91 (d, J = 6.2 Hz, 3H, $Me_{Alanine}$), 0.85 (t, J = 6.7 Hz, 6H, Me-21_{CA} & Me_{Alkoxy}), 0.77 (s, 3H, Me-19_{CA}), 0.50 (s, 3H, Me-18_{CA}); ^{13}C NMR (100 MHz, DMSO) δ 173.20 (C=O), 173.15 (C=O), 162.03, 152.00, 146.44, 139.24, 128.88, 125.10, 122.72, 115.46, 71.45 (C-12_{CA}), 70.89 (C-3_{CA}), 68.43 (O-$CH_{2\ Benzylic}$), 66.68 (C-7_{CA}), 65.69 (O-$CH_{2\ Alkoxy}$), 48.12 ($CH_{Alanine}$), 46.70, 46.15, 41.97, 41.81, 41.77, 35.75, 35.48, 35.32, 34.84, 34.82, 32.47, 31.88, 31.78, 30.85, 29.52, 29.50, 29.45, 29.20, 29.00, 27.71, 26.65, 26.63, 25.91, 23.24, 23.09, 23.06, 22.58 (C-19_{CA}), 17.54 ($CH_{3\ Alanine}$), 17.33 (C-21_{CA}), 14.44 ($CH_{3\ Alkoxy}$), 12.75 (C-18_{CA}); HRMS (ESI): *m/z* $[M + H]^+$ calcd for Chemical Formula: $C_{52}H_{80}N_3O_7$: 858.5996 found : 858.5981; IR (KBr, υ, cm^{-1}) 3371, 2924, 2854, 1744, 1651, 1597, 1250, 1149, 841.

4-((*E*)-(4-(Hexadecyloxy)phenyl)diazenyl)benzyl (4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)-L-alaninate (CA-Ala-Azo, 9c). Orange solid; Yield: 82.8% (1.081 g); mp: 139.5-140.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.24 (d, J = 7.0 Hz, 1H, NH_{Amide}), 7.83 (dd, J = 18.6, 8.7 Hz, 4H), 7.51 (d, J = 8.4 Hz, 2H), 7.08 (d, J = 9.0 Hz, 2H), 5.17 (s, 2H, O-$CH_{2\ Benzylic}$), 4.33 – 4.27 (m, 2H, $CH_{Alanine}$ & OH_{CA}), 4.06 – 4.01 (m, 3H, H-12_{CA} & O-$CH_{2\ Alkoxy}$), 3.94 (brs, 1H, H-7_{CA}), 3.72 (brs, 1H, OH_{CA}), 3.53 (brs, 1H, OH_{CA}), 3.19 – 3.11 (m, 1H, H-3_{CA}), 2.22 – 1.88 (m, 9H), 1.75 – 1.57 (m, 9H), 1.43 – 1.36 (m, 5H), 1.29 – 1.26 (m, 6H), 1.22 – 1.03 (m, 24H), 0.88 (d, J = 6.4 Hz, 3H, $Me_{Alanine}$), 0.82 (t, J = 6.8 Hz, 6H, Me-21_{CA} & Me_{Alkoxy}), 0.74 (s, 3H, Me-19_{CA}), 0.48 (s, 3H, Me-18_{CA}); ^{13}C NMR (100 MHz, DMSO) δ 173.20 (C=O), 173.15 (C=O), 162.02, 151.99, 146.44, 139.24, 128.88, 125.10, 122.71, 115.45, 71.45 (C-12_{CA}), 70.89 (C-3_{CA}), 68.42 (O-$CH_{2\ Benzylic}$), 66.67 (C-7_{CA}), 65.70 (O-$CH_{2\ Alkoxy}$), 48.12 ($CH_{Alanine}$), 46.70, 46.15, 41.98, 41.77, 35.48, 35.31, 34.82, 32.47, 31.77, 30.86, 29.53, 29.51, 29.47, 29.42, 29.19, 29.15, 28.98, 27.70, 26.63, 25.89, 23.25, 23.05, 22.58 (C-19_{CA}), 17.54 ($CH_{3\ Alanine}$), 17.32 (C-21_{CA}), 14.43 ($CH_{3\ Alkoxy}$), 12.75 (C-18_{CA}); HRMS (ESI): m/z $[M + H]^+$ calcd for Chemical Formula: $C_{56}H_{88}N_3O_7$: 914.6622 found : 914.6616; IR (KBr, υ, cm^{-1}) 3364, 3333, 2924, 2854, 1744, 1651, 1605, 1250, 1149, 841.

4-((*E*)-(4-(Octyloxy)phenyl)diazenyl)benzyl (4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)-*L*-phenylalaninate (CA-Phe-Azo, 9d). Orange solid; Yield: 85.6% (0.988 g); mp: 129.8-130.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (d, J = 7.6 Hz, 1H, NH_{Amide}), 7.88 (d, J = 8.9 Hz, 2H), 7.82 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.30 – 7.20 (m, 5H, $Ar_{Phenylalanine}$), 7.12 (d, J = 9.0 Hz, 2H), 5.26 – 5.08 (m, 2H, O-$CH_{2\ Benzylic}$), 4.58 – 4.48 (m, 1H, $CH_{Phenylalanine}$), 4.35 (d, J = 4.2 Hz, 1H, OH_{CA}), 4.13 – 4.05 (m, 3H, H-12_{CA} & O-$CH_{2\ Alkyoxy}$), 4.01 (d, J = 3.1 Hz, 1H, H-7_{CA}), 3.74 (brs, 1H, OH_{CA}), 3.57 (d, J = 5.9 Hz, 1H, OH_{CA}), 3.18 (d,

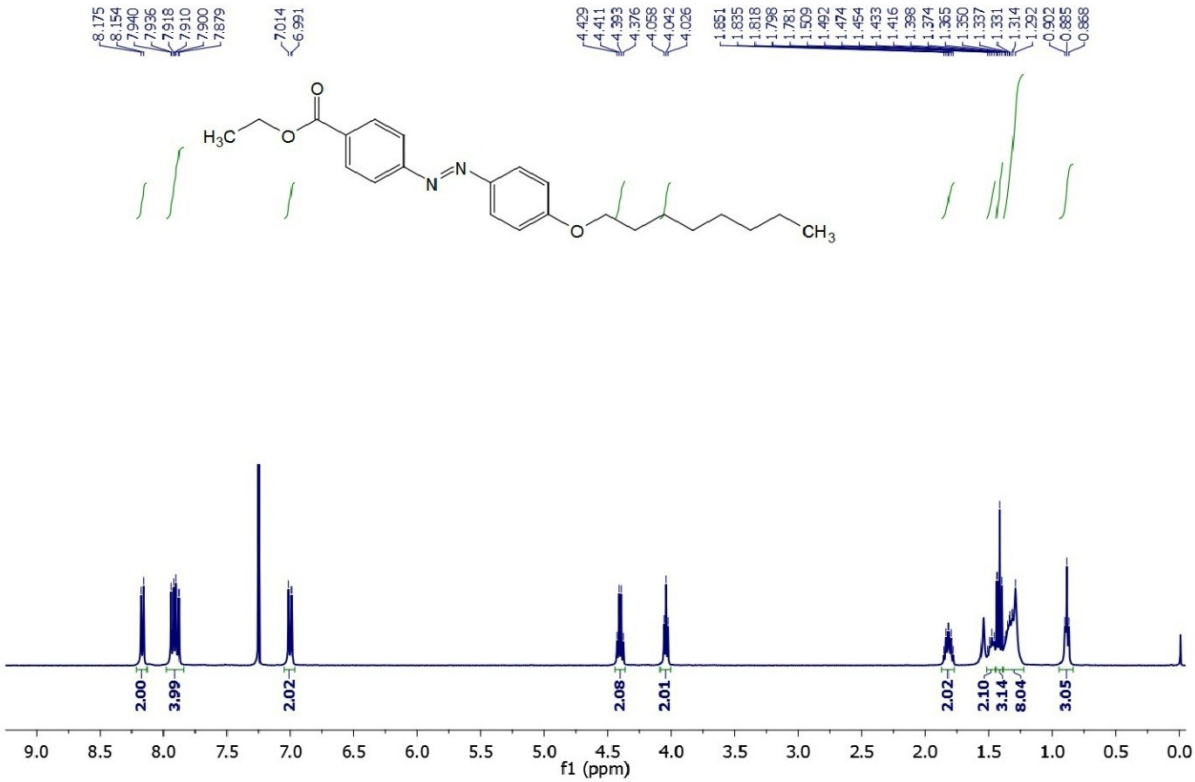
J = 4.1 Hz, 1H, H-3_{CA}), 3.07 (dd, J = 13.6, 5.7 Hz, 1H, $CH_{2\ Phenylalanine}$), 2.94 (dd, J = 13.6, 9.5 Hz, 1H, $CH_{2\ Phenylalanine}$), 2.23 – 1.93 (m, 5H), 1.82 – 1.69 (m, 4H), 1.67 – 1.52 (m, 4H), 1.46 – 1.21 (m, 21H), 1.11 – 1.01 (m, 2H), 0.92 – 0.84 (m, 8H, Me-21_{CA} & Me_{Alkoxy}), 0.77 (s, 3H, Me-19_{CA}), 0.49 (s, 3H, Me-18_{CA}); ^{13}C NMR (100 MHz, DMSO) δ 173.38 (C=O), 172.11 (C=O), 162.03, 152.01, 146.44, 139.01, 137.74, 129.55, 128.97, 128.69, 126.99, 125.11, 122.67, 115.46, 71.45 (C-12_{CA}), 70.89 (C-3_{CA}), 68.45 (O-$CH_{2\ Benzylic}$), 66.68 (C-7_{CA}), 65.80 (O-$CH_{2\ Alkoxy}$), 54.16 ($CH_{Phenylalanine}$), 46.65, 46.13, 41.97, 41.77, 37.07, 35.75, 35.45, 35.31, 34.82, 32.51, 31.89, 31.72, 30.85, 29.20, 29.15, 29.03, 27.66, 26.63, 25.95, 23.24, 23.06, 22.57 (C-19_{CA}), 17.49 (C-21_{CA}), 14.45 ($CH_{3\ Alkoxy}$), 12.76 (C-18_{CA}); HRMS (ESI): *m/z* $[M + H]^+$ calcd for Chemical Formula: $C_{54}H_{76}N_3O_7$: 878.5683 found : 878.5676; IR (KBr, υ, cm^{-1}) 3286, 2924, 2862, 1744, 1651, 1597, 1304, 1142, 841.

4-((*E*)-(4-(Dodecyloxy)phenyl)diazenyl)benzyl (4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)-*L*-phenylalaninate (CA-Phe-Azo, 9e). Orange solid; Yield: 81.2 % (0.972 g); mp: 142.8-143.5 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.36 (d, J = 7.7 Hz, 1H, NH_{Amide}), 7.88 (d, J = 8.9 Hz, 2H), 7.81 (d, J = 8.3 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 7.30 – 7.21 (m, 5H, $Ar_{Phenylalanine}$), 7.12 (d, J = 9.0 Hz, 2H), 5.22 – 5.11 (m, 2H, O-$CH_{2\ Benzylic}$), 4.57 – 4.47 (m, 1H, $CH_{Phenylalanine}$), 4.34 (d, J = 4.3 Hz, 1H, OH_{CA}), 4.09 – 4.04 (m, 3H, H-12_{CA} & O-$CH_{2\ Alkoxy}$), 4.00 (d, J = 3.2 Hz, 1H, H-7_{CA}), 3.74 (brs, 1H OH_{CA}), 3.56 (brs, 1H, OH_{CA}), 3.20 – 3.14 (m, 1H, H-3_{CA}), 3.07 (dd, J = 13.7, 5.8 Hz, 1H, $CH_{2\ Phenylalanine}$), 2.93 (dd, J = 13.6, 9.4 Hz, 1H, $CH_{2\ Phenylalanine}$), 2.28 – 1.88 (m, 6H), 1.76 – 1,69 (m, 4H), 1.65 – 1.53 (m, 3H), 1.47 – 1.32 (m, 9H), 1.29 – 1.23 (m, 18H), 1.09 – 1.00 (m, 2H), 0.88 – 0.80 (m, 8H, Me-21_{CA} & Me_{Alkoxy}), 0.77 (s, 3H, Me-19_{CA}), 0.49 (s, 3H, Me-18_{CA}); ^{13}C NMR (100 MHz, DMSO) δ 173.38 (C=O), 172.11 (C=O), 162.03, 152.00, 146.44, 139.02, 137.75, 129.56, 129.56, 128.98, 128.69, 126.99, 125.11, 122.67, 115.47, 71.45 (C-12_{CA}), 70.89 (C-3_{CA}), 68.43 (O-$CH_{2\ Benzylic}$), 66.68 (C-7_{CA}),

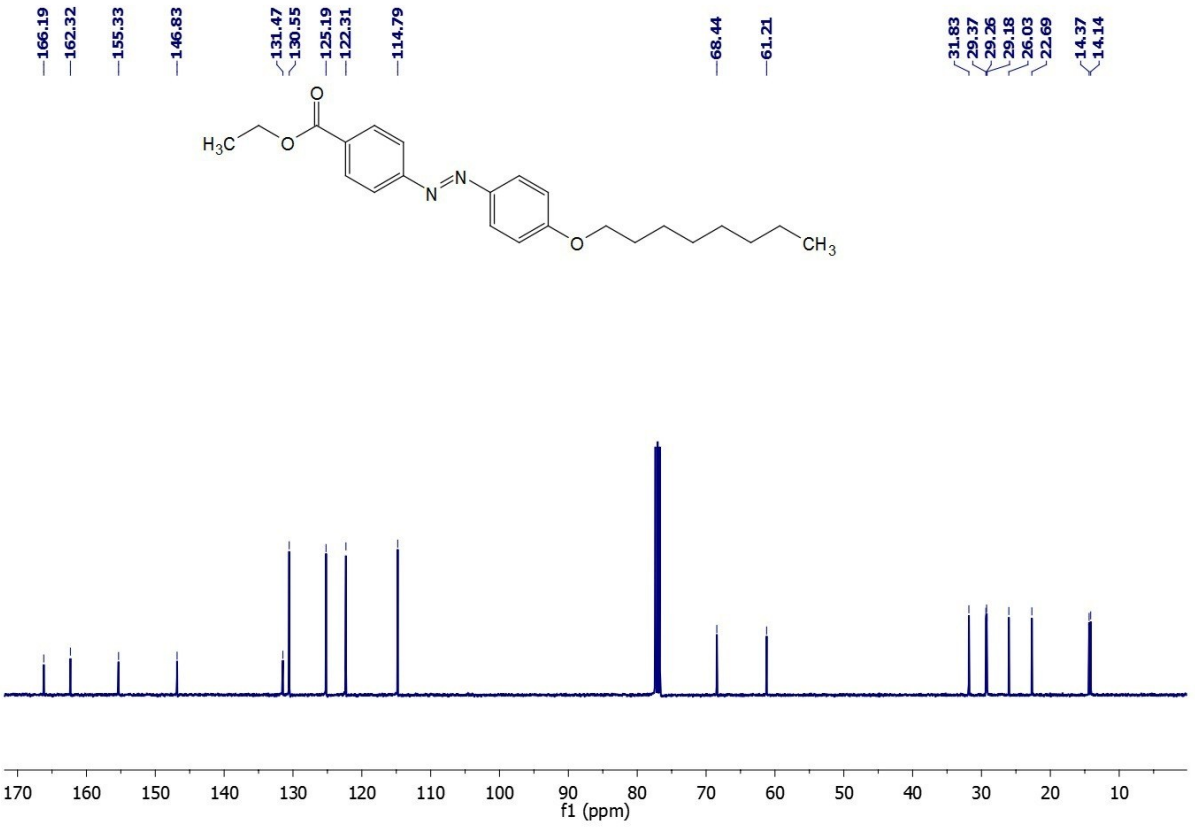
65.81 (O-$CH_{2\ Alkoxy}$), 54.16 ($CH_{Phenylalanine}$), 46.65, 46.13, 41.97, 41.77, 37.06, 35.75, 35.45, 35.31, 34.82, 32.50, 32.34, 31.93, 31.89, 31.77, 30.85, 29.51, 29.49, 29.45, 29.20, 29.00, 27.65, 26.63, 25.91, 23.06, 22.58 (C-19_{CA}), 17.49 (C-21_{CA}), 14.44 ($CH_{3\ Alkoxy}$), 12.76 (C-18_{CA}); HRMS (ESI): *m/z* $[M + H]^+$ calcd for Chemical Formula: $C_{58}H_{84}N_3O_7$: 934.6309 found : 934.6316; IR (KBr, υ, cm^{-1}) 3286, 2924, 2854, 1744, 1659, 1597, 1250, 1142, 841.

4-((*E*)-(4-(Hexadecyloxy)phenyl)diazenyl)benzyl (4-((3*R*,5*S*,7*R*,8*R*,9*S*,10*S*,12*S*,13*R*,14*S*,17*R*)-3,7,12-trihydroxy-10,13-dimethylhexadecahydro-1*H*-cyclopenta[*a*]phenanthren-17-yl)pentanoyl)-*L*-phenylalaninate (CA-Phe-Azo, 9f). Orange solid; Yield: 81.5% (1.14 g); mp: 125.8-126.6 °C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.30 (d, *J* = 7.7 Hz, 1H, NH_{Amide}), 7.85 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.43 (d, J = 8.4 Hz, 2H), 7.31 – 7.14 (m, 5H, $Ar_{Phenylalanine}$), 7.09 (d, *J* = 9.0 Hz, 2H), 5.14 (m, 2H, O-$CH_{2\ Benzylic}$), 4.53 – 4.47 (m, 1H, $CH_{Phenylalanine}$), 4.28 (d, *J* = 4.2 Hz, 1H, OH_{CA}), 4.09 – 4.02 (m, 3H, H-12_{CA} & O-$CH_{2\ Alkoxy}$), 3.94 (d, *J* = 3.3 Hz, 1H, H-7_{CA}), 3.74 – 3.65 (brs, 1H, OH_{CA}), 3.53 (brs, 1H, OH_{CA}), 3.18 – 3.12 (m, 1H, H-3_{CA}), 3.04 (dd, *J* = 13.7, 5.7 Hz, 1H, $CH_{2\ Phenylalanine}$), 2.91 (dd, *J* = 13.7, 9.4 Hz, 1H, $CH_{2\ Phenylalanine}$), 2.30 – 1.81 (m, 8H), 1.81 – 1.47 (m, 10H), 1.47 – 0.89 (m, 32H), 0.89 – 0.76 (m, 8H, Me-21_{CA} & Me_{Alkoxy}), 0.74 (s, 3H, Me-19_{CA}), 0.47 (s, 3H, Me-18_{CA}); ^{13}C NMR (100 MHz, DMSO) *δ* 173.39 (C=O), 172.19 (C=O), 162.05, 152.02, 146.45, 139.03, 137.76, 129.57, 128.99, 128.70, 127.00, 125.12, 122.68, 115.48, 71.45 (C-12_{CA}), 70.90 (C-3_{CA}), 68.44 (O-$CH_{2\ Benzylic}$), 66.67 (C-7_{CA}), 65.80(O-$CH_{2\ Alkoxy}$), 46.14 ($CH_{Phenylalanine}$), 41.98, 41.77, 37.08, 36.10, 35.95, 35.76, 35.46, 34.83, 31.78, 31.41, 30.87, 29.52, 29.50, 29.45, 29.20, 29.00, 27.66, 26.63, 25.91, 23.23, 23.07, 22.58 (C-19_{CA}), 17.49 (C-21_{CA}), 14.44 ($CH_{3\ Alkoxy}$), 12.76 (C-18_{CA}); HRMS (ESI): *m/z* $[M + H]^+$ calcd for Chemical Formula: $C_{62}H_{92}N_3O_7$: 990.6935 found : 990.6918; IR (KBr, υ, cm^{-1}) 3286, 2924, 2854, 1744, 1651, 1597, 1242, 1149, 841.

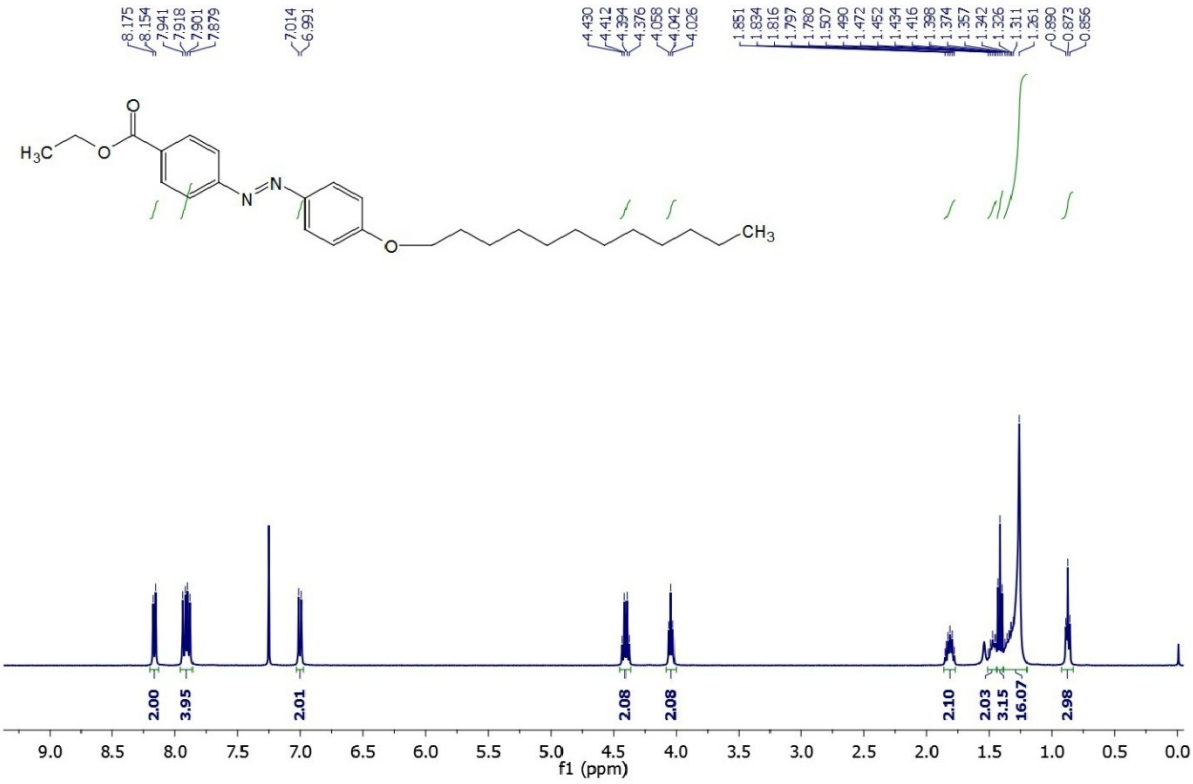
^{1}H NMR of 3a



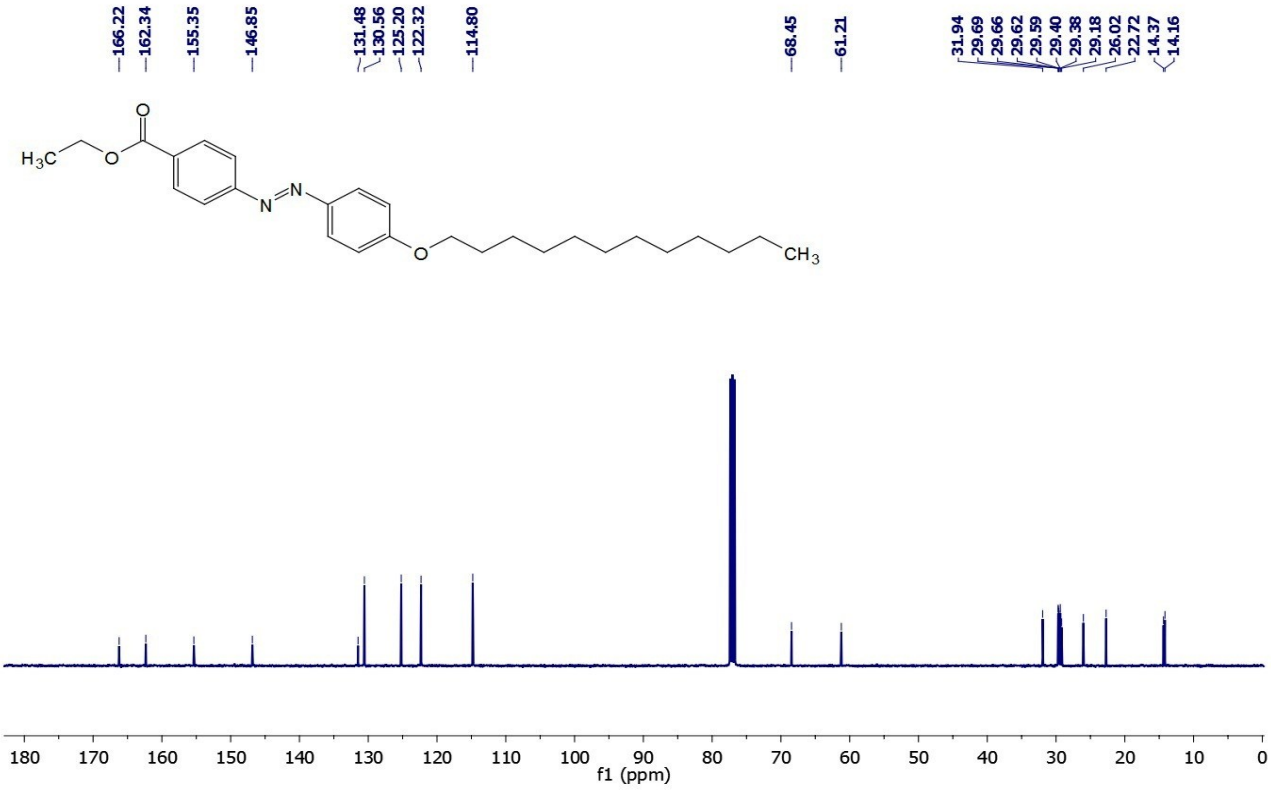
^{13}C NMR of 3a



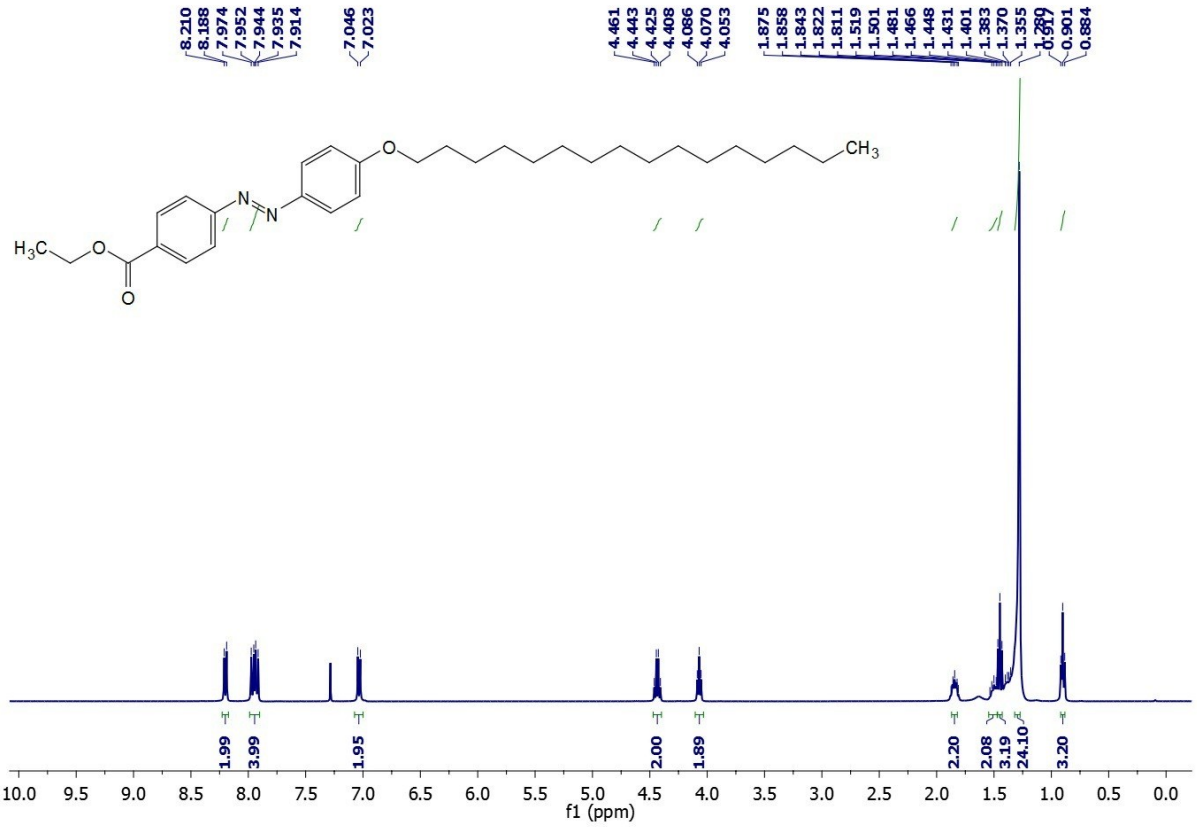
^{1}H NMR of 3b



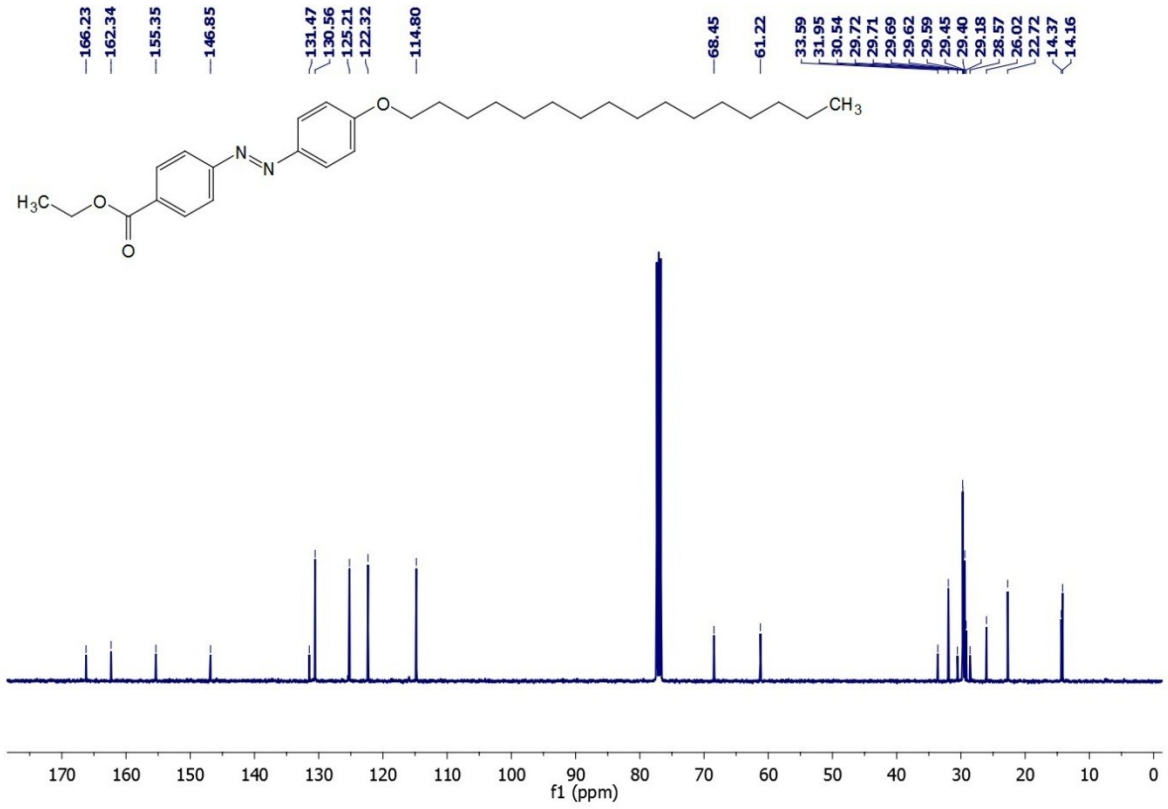
^{13}C NMR of 3b



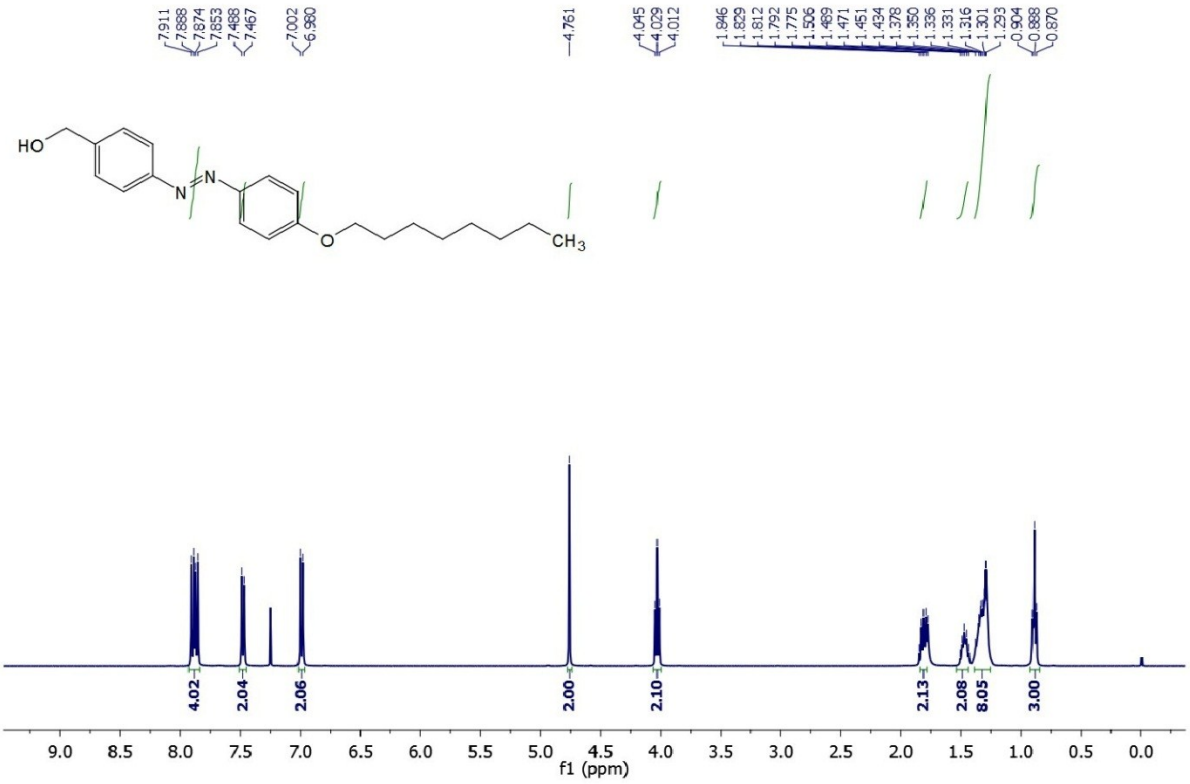
^{1}H NMR of 3c



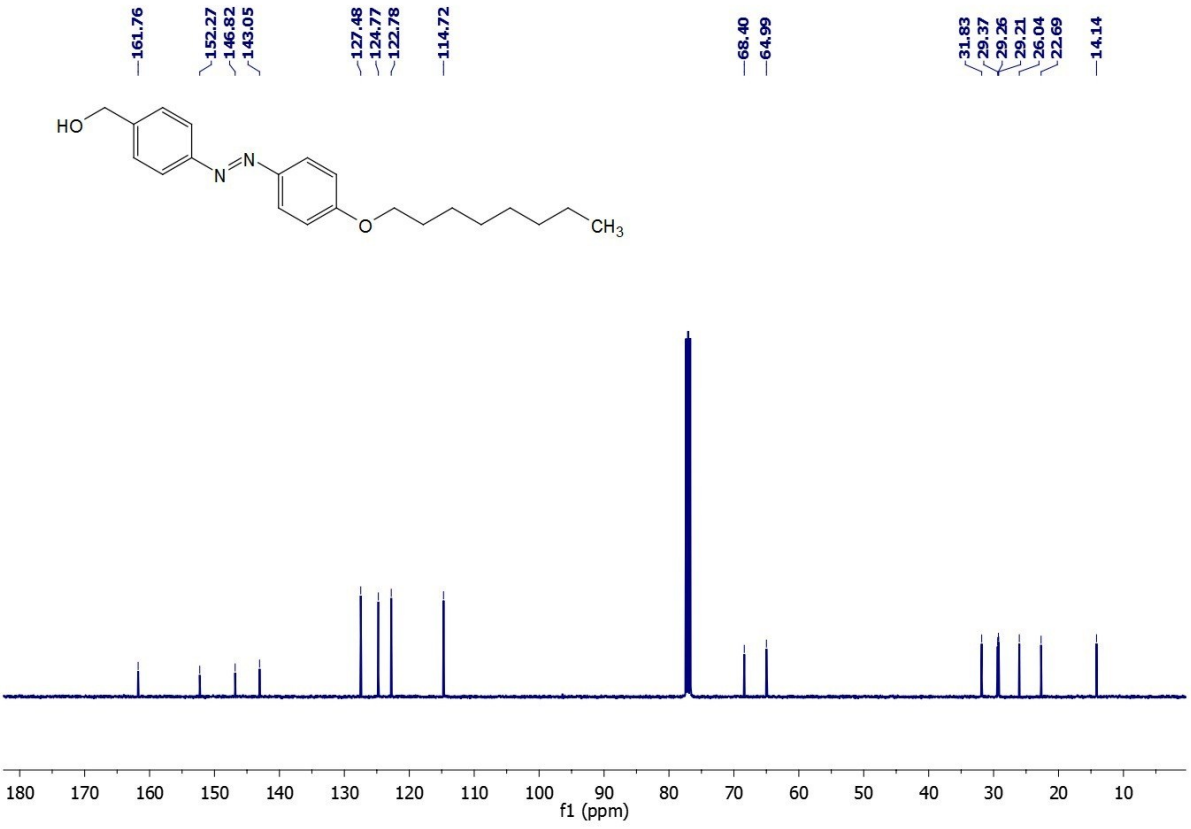
^{13}C NMR of 3c



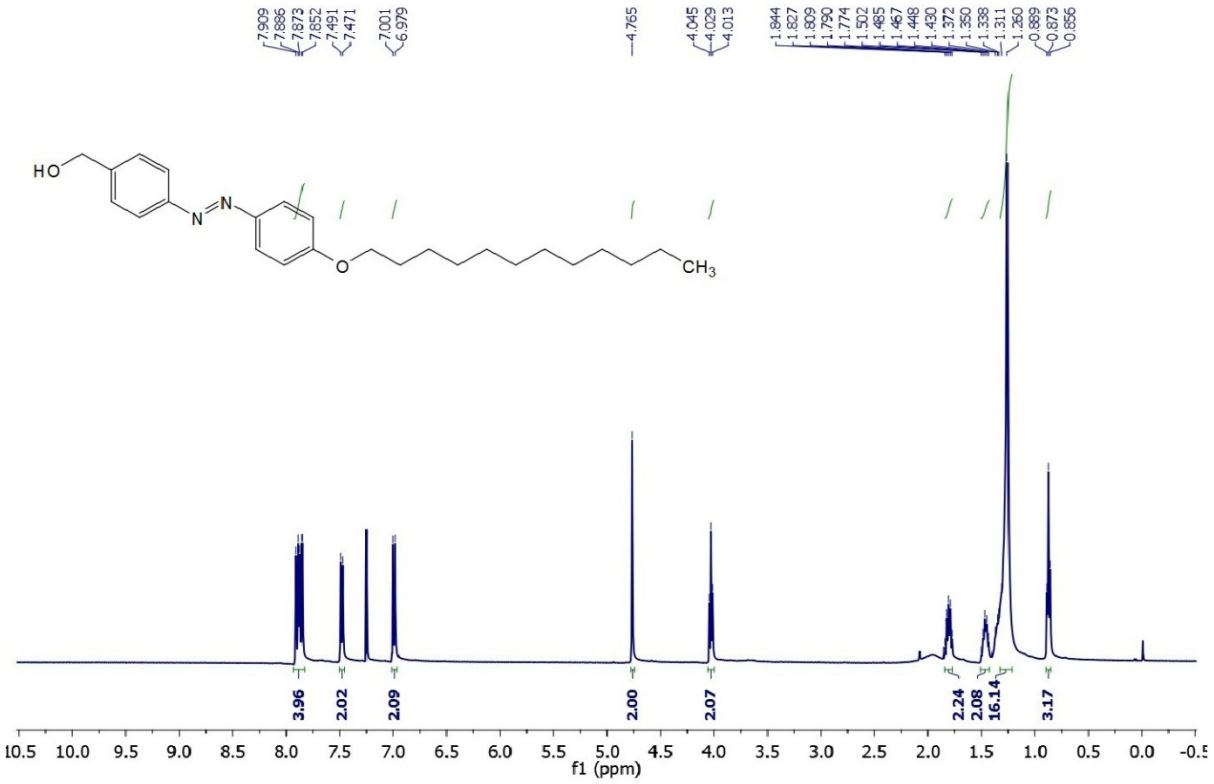
^{1}H NMR of 4a



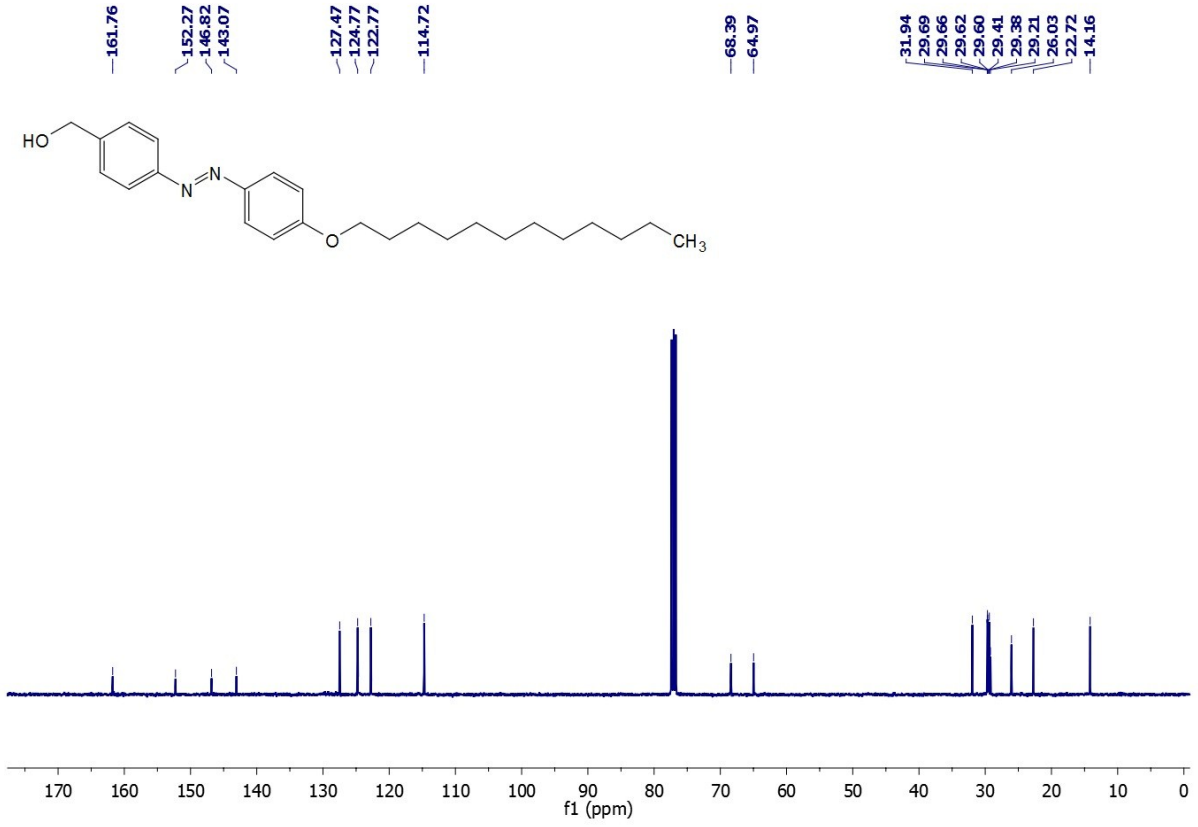
^{13}C NMR of 4a



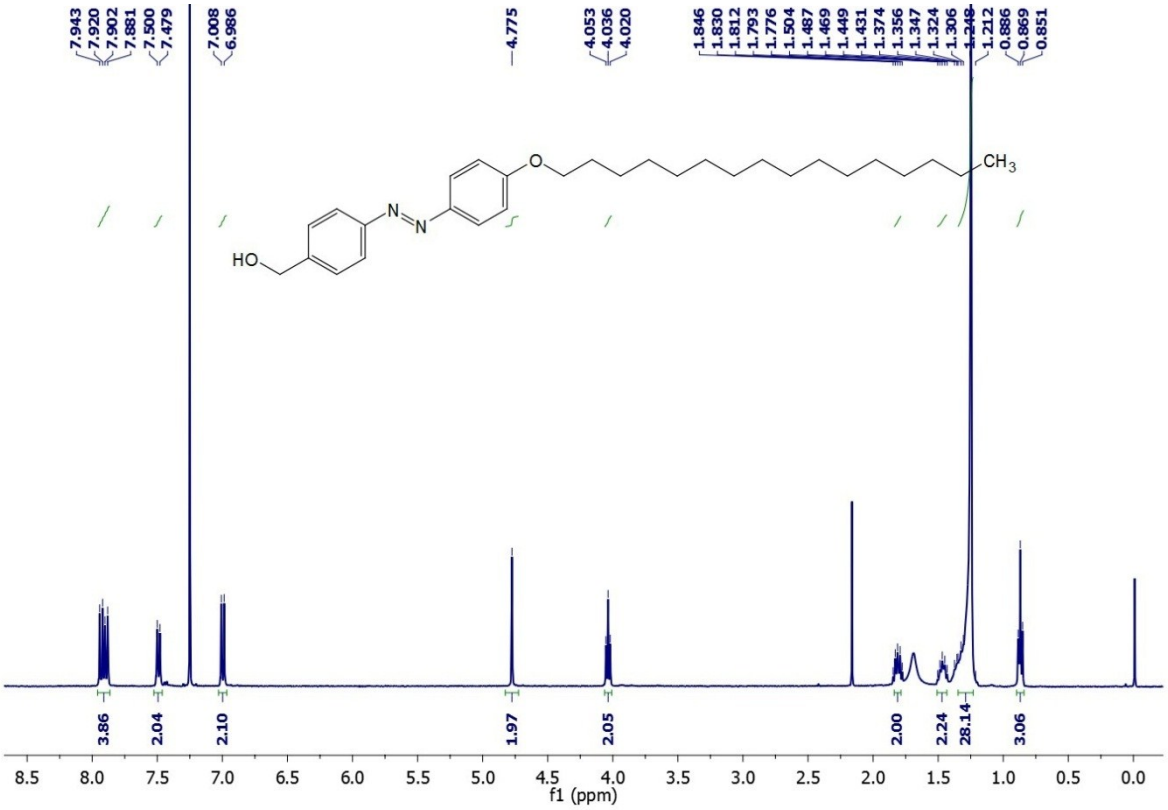
^{1}H NMR of 4b



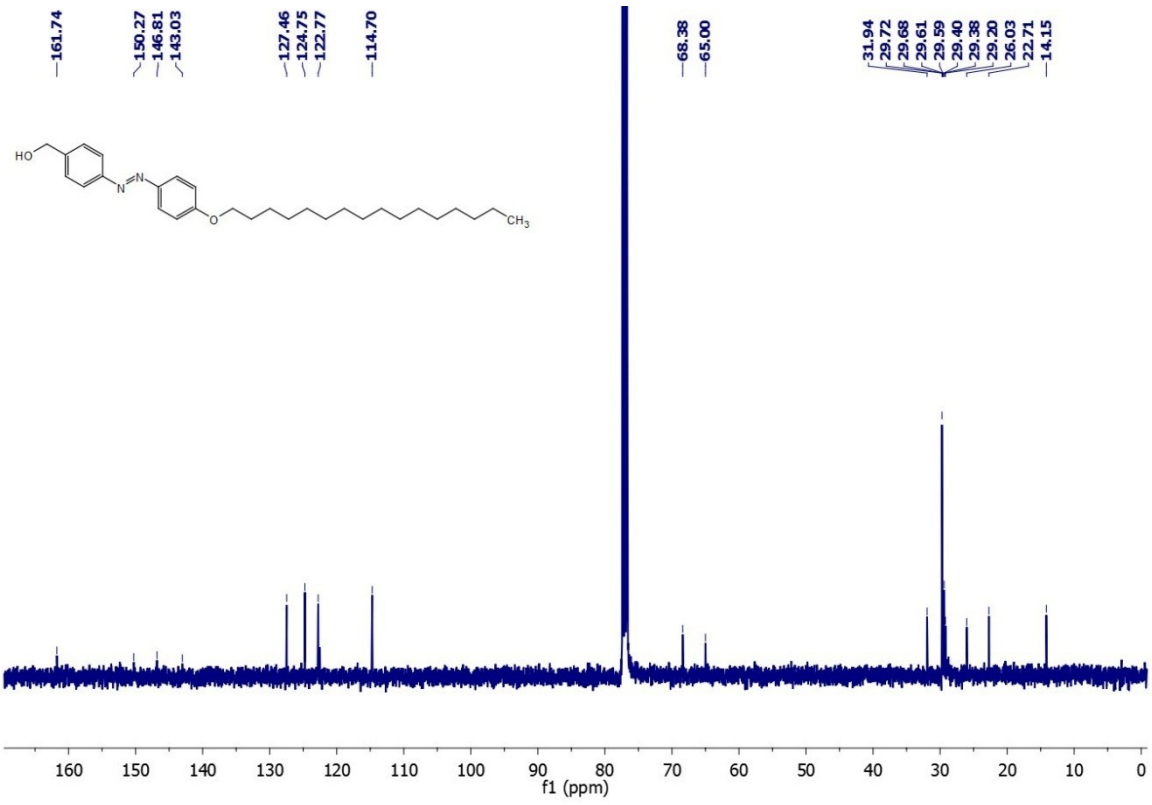
^{13}C NMR of 4b



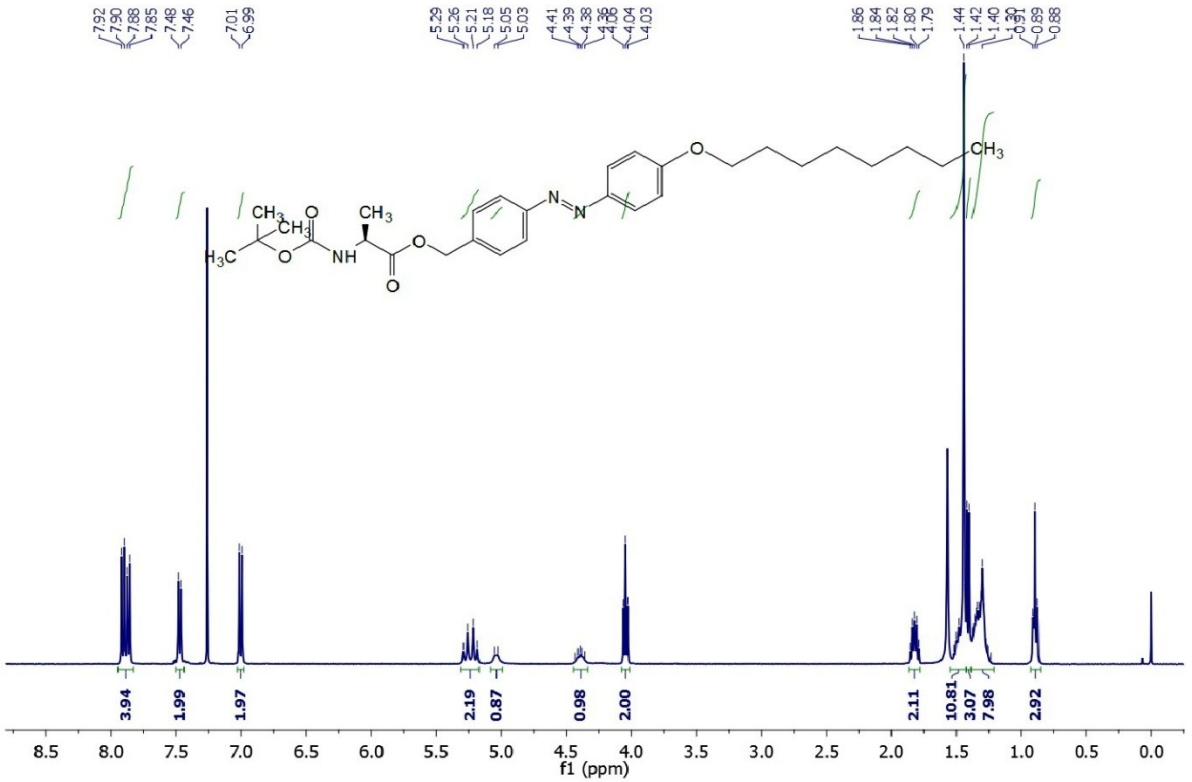
^{1}H NMR of 4c



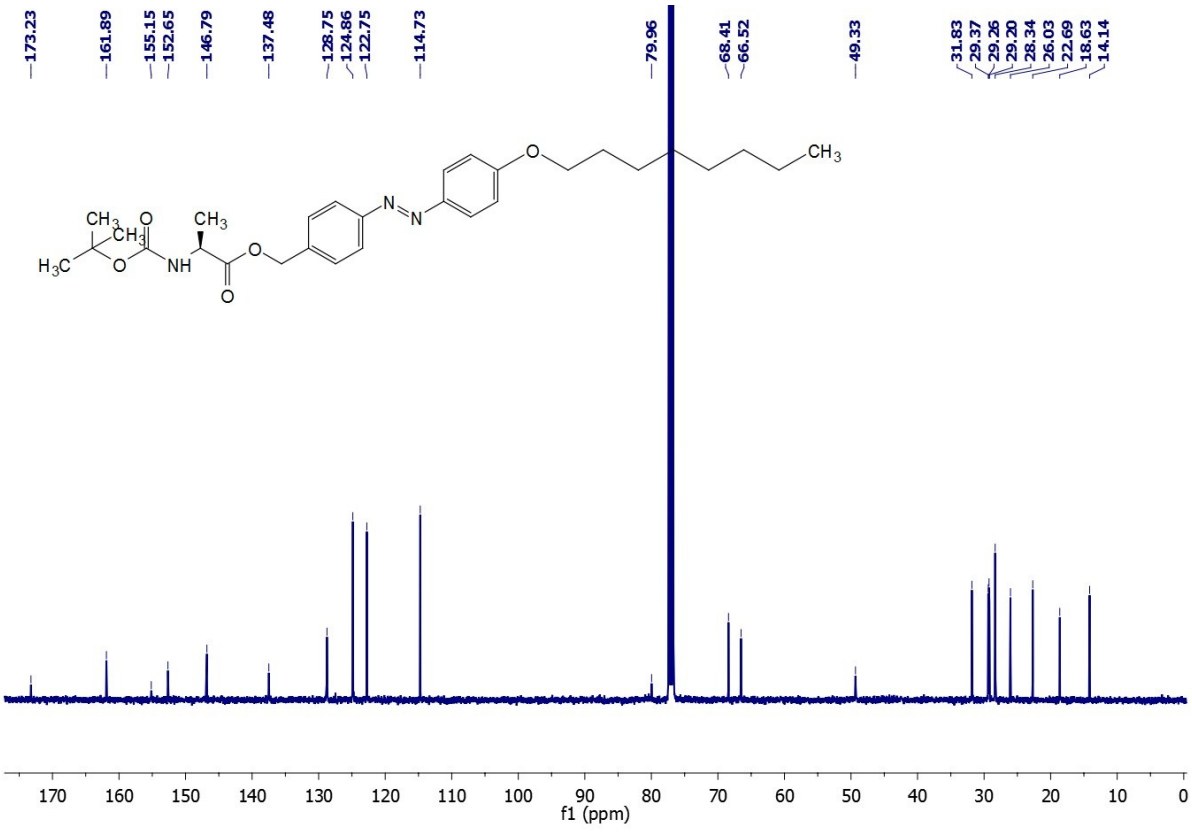
^{13}C NMR of 4c



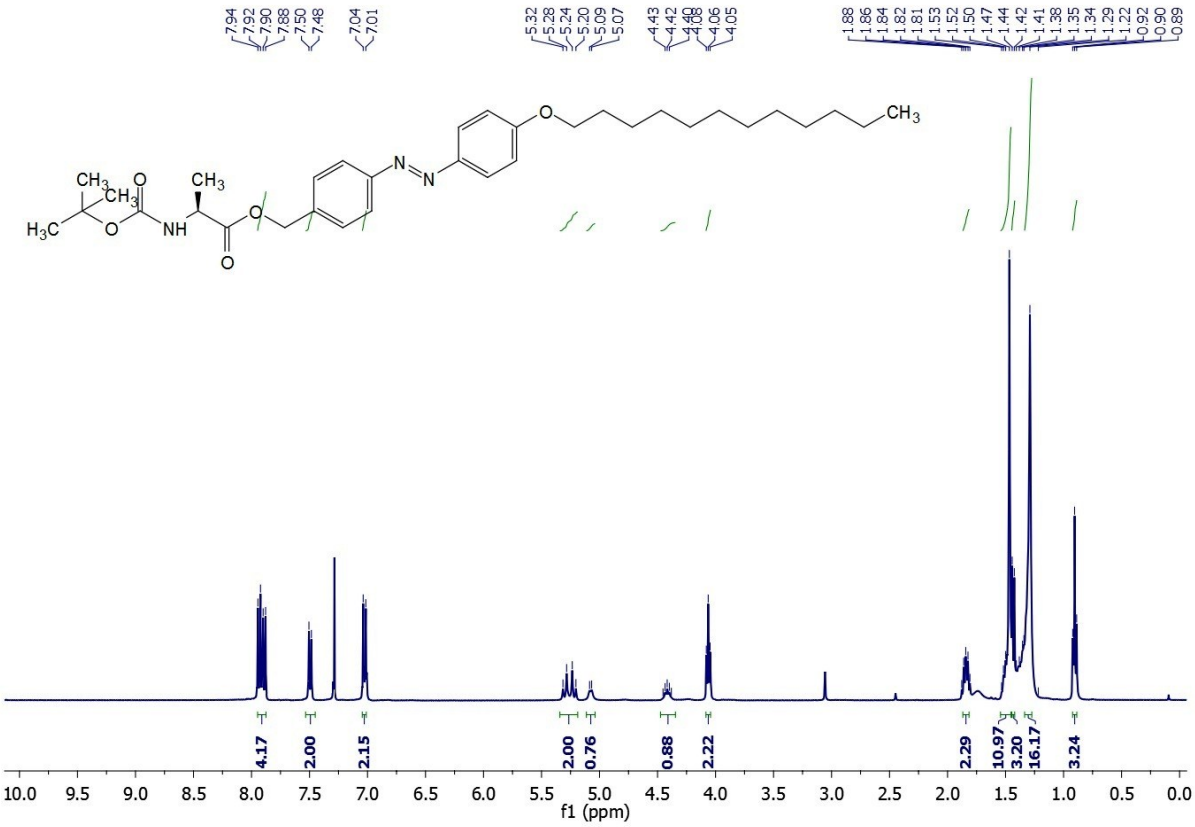
^{1}H NMR of 6a



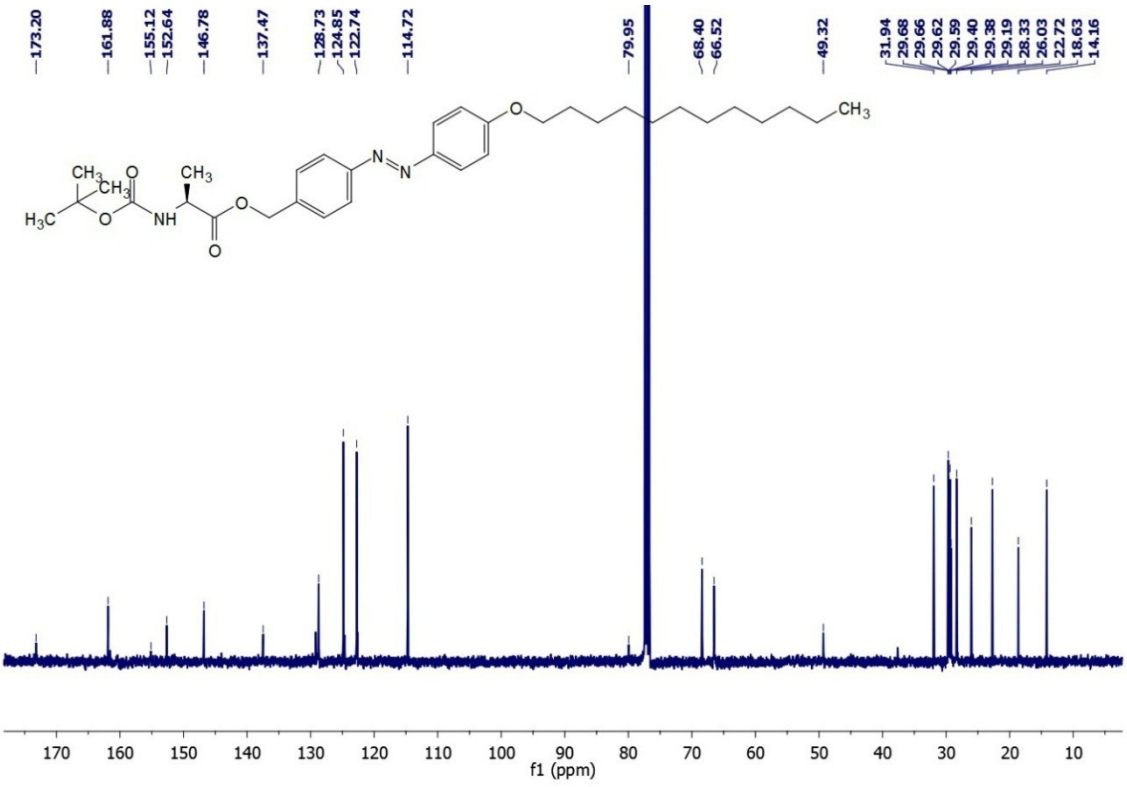
^{13}C NMR of 6a



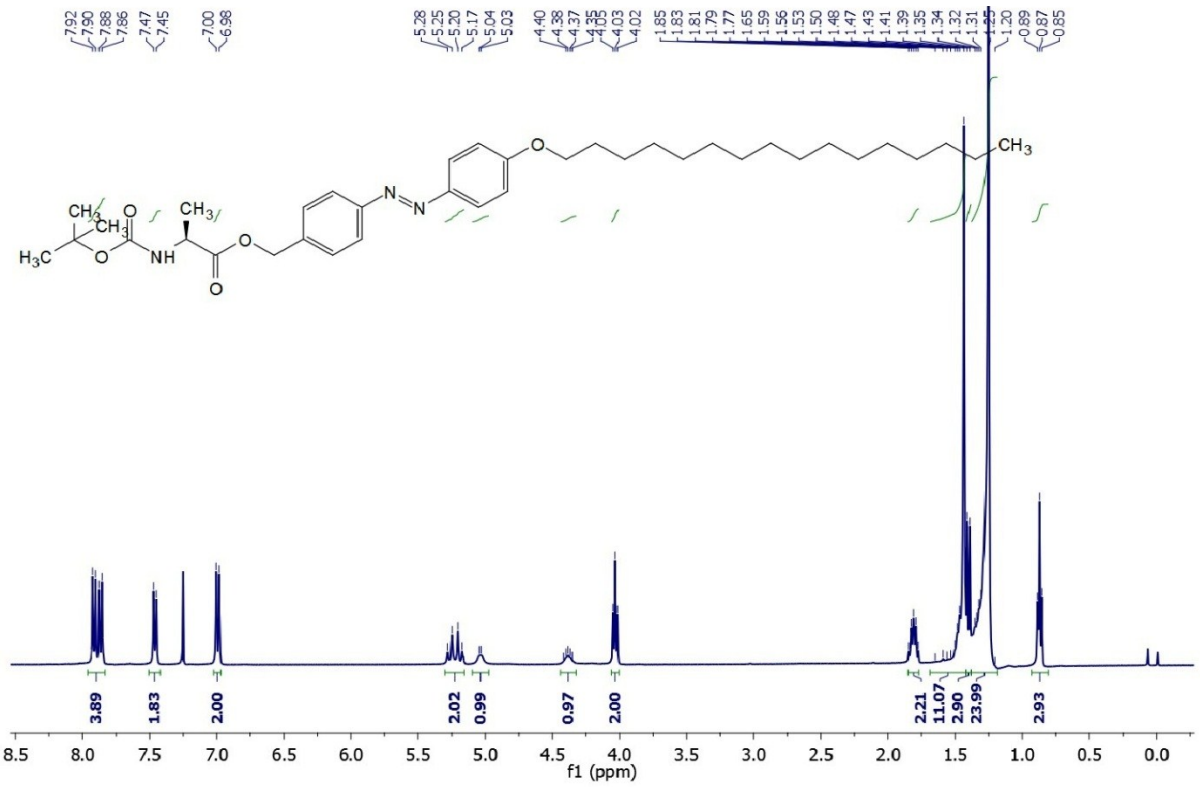
^{1}H NMR of 6b



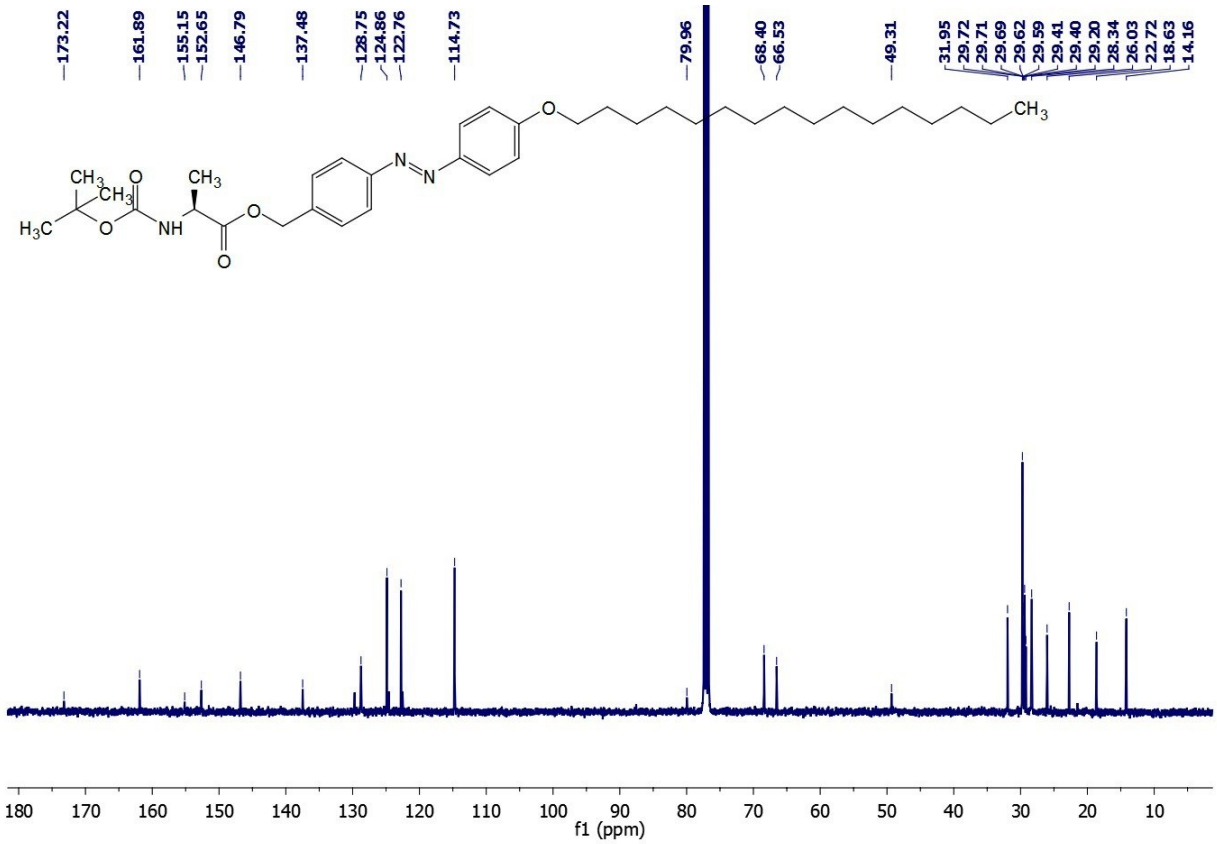
^{13}C NMR of 6b



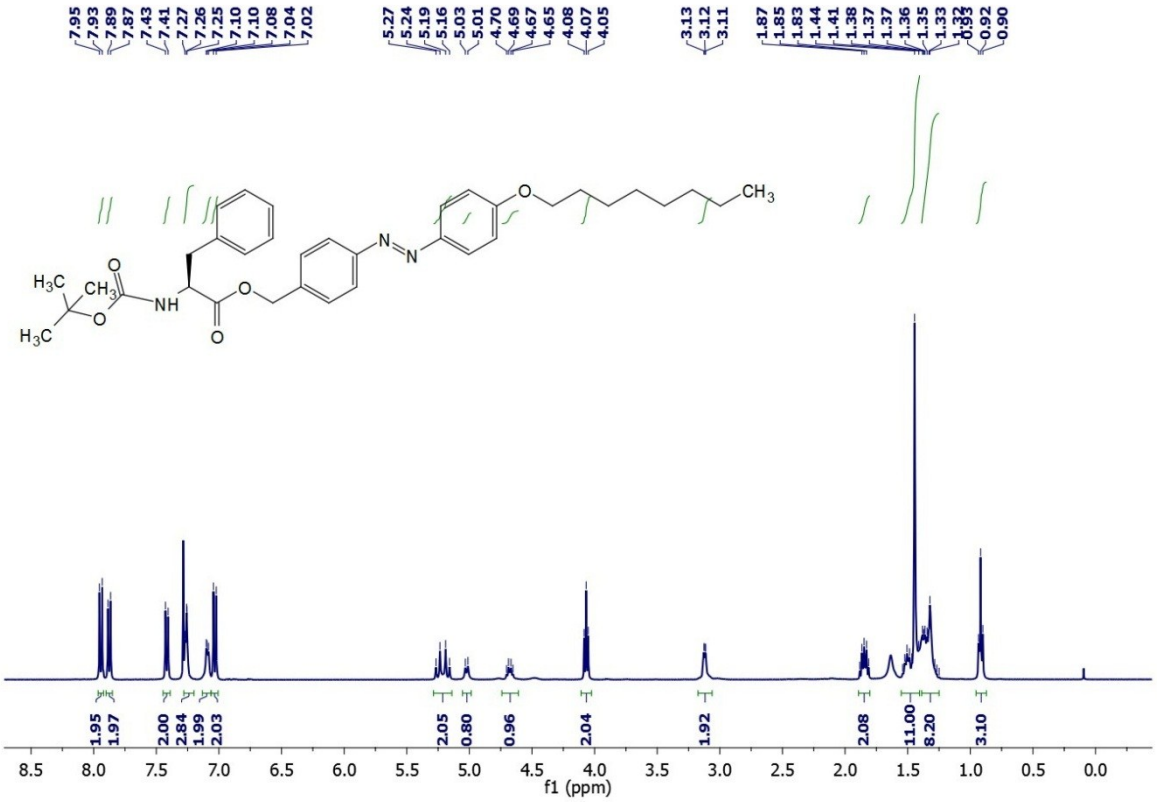
^{1}H NMR of 6c



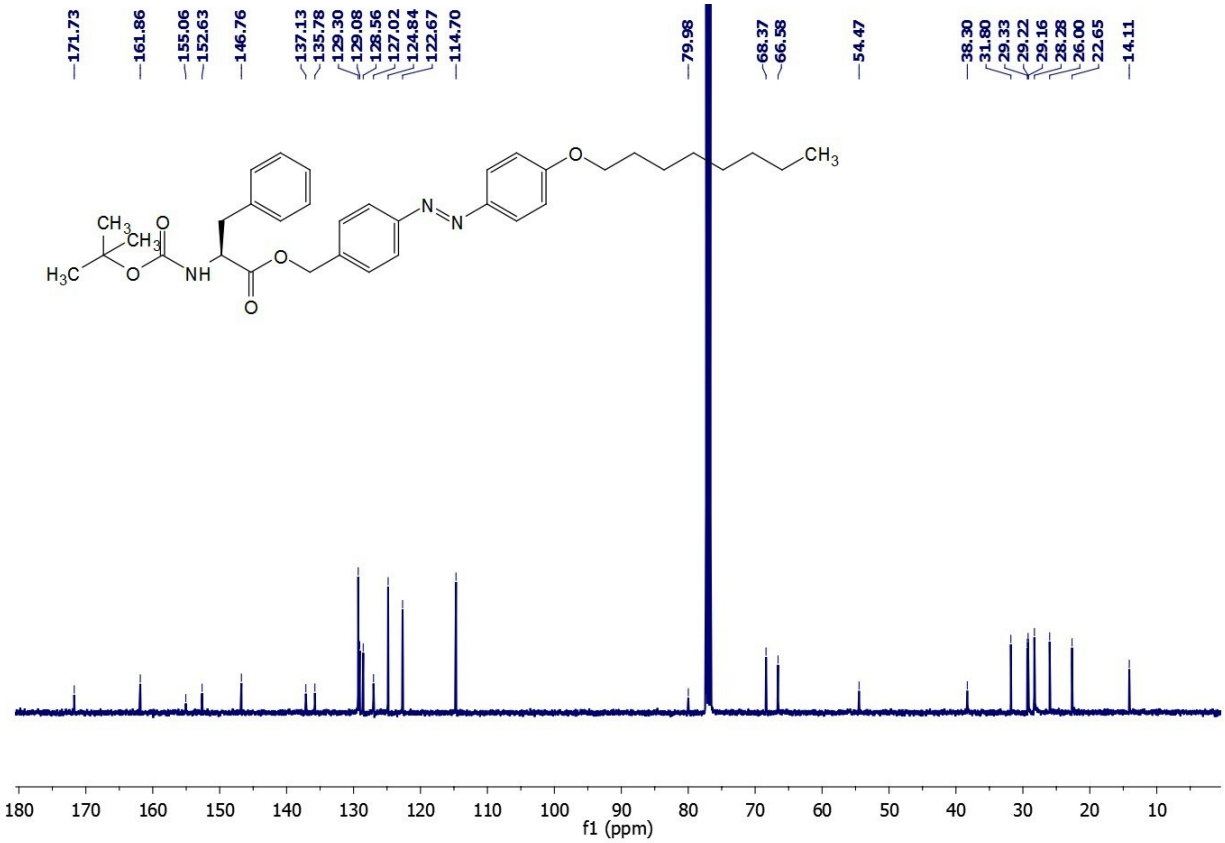
^{13}C NMR of 6c



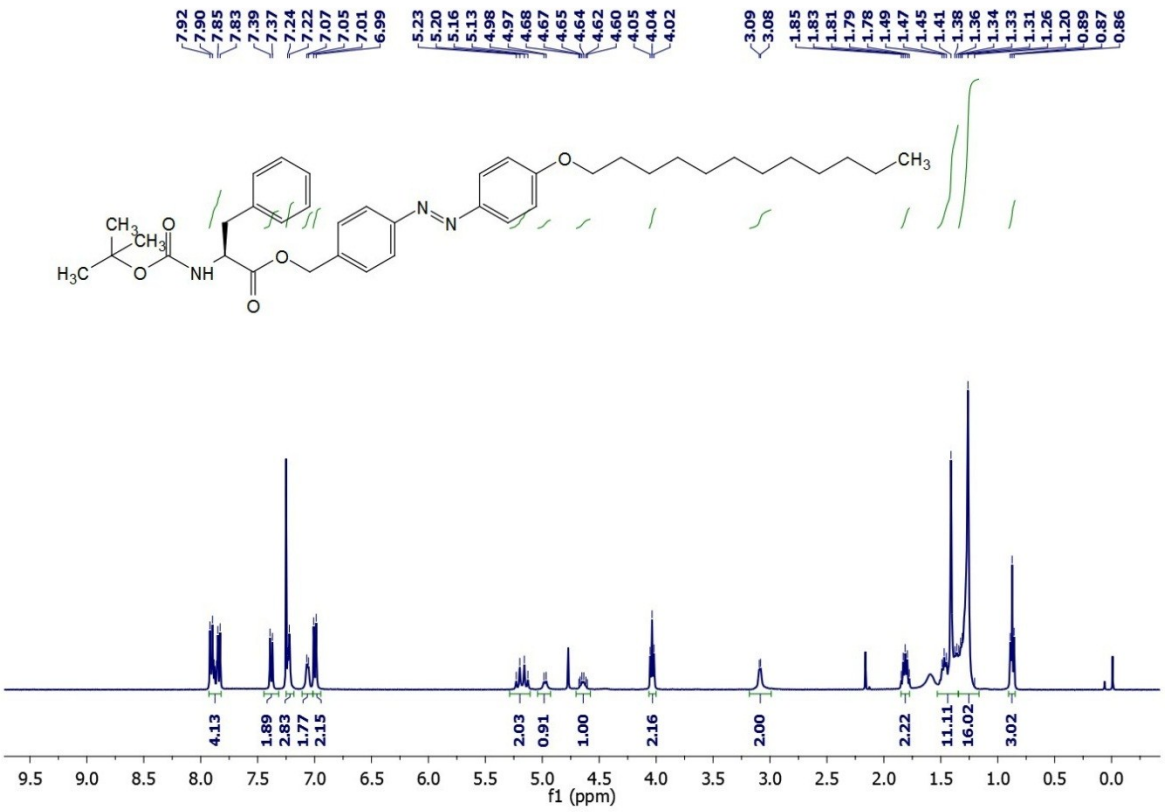
^{1}H NMR of 6d



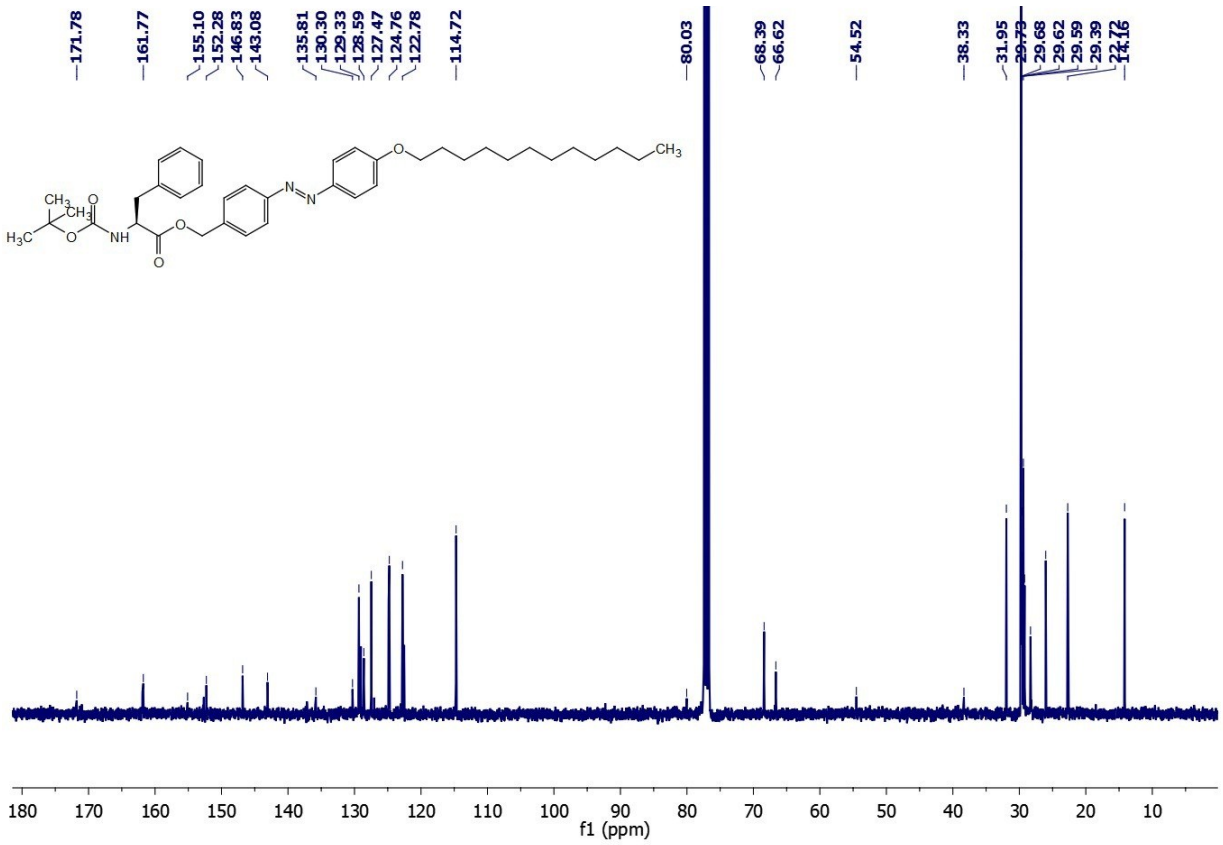
^{13}C NMR of 6d



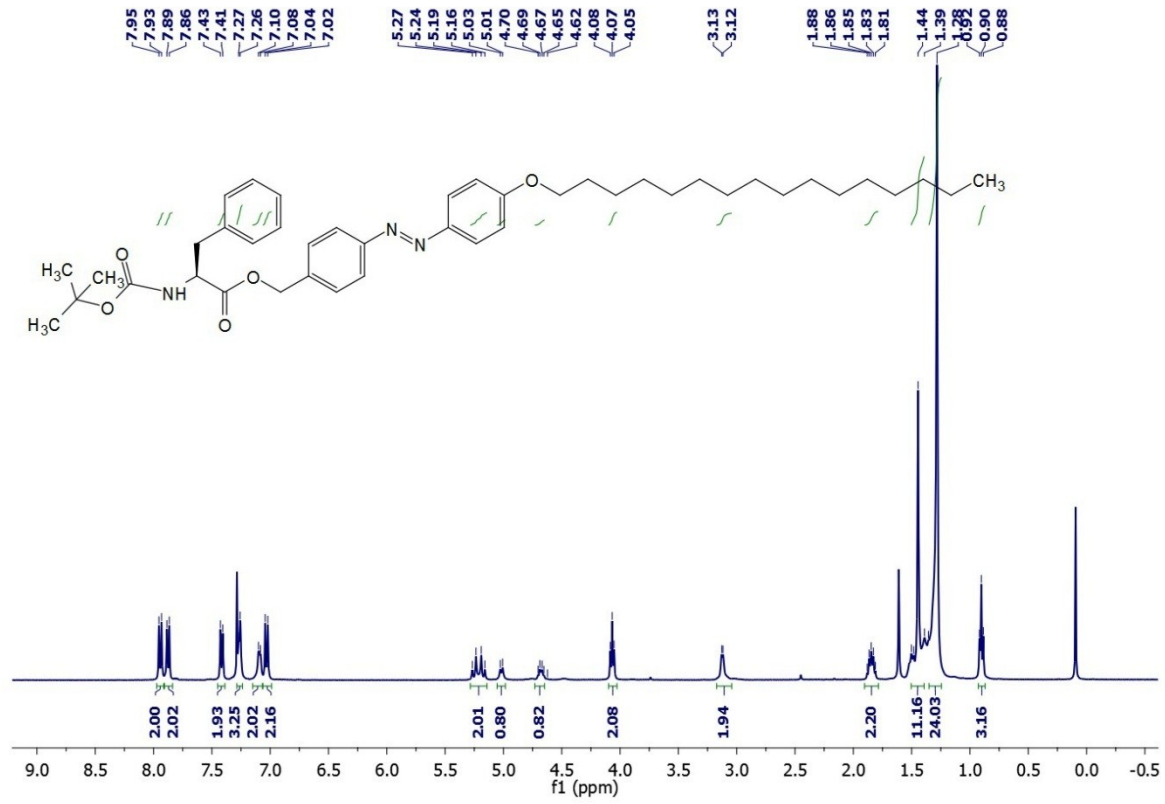
^{1}H NMR of 6e



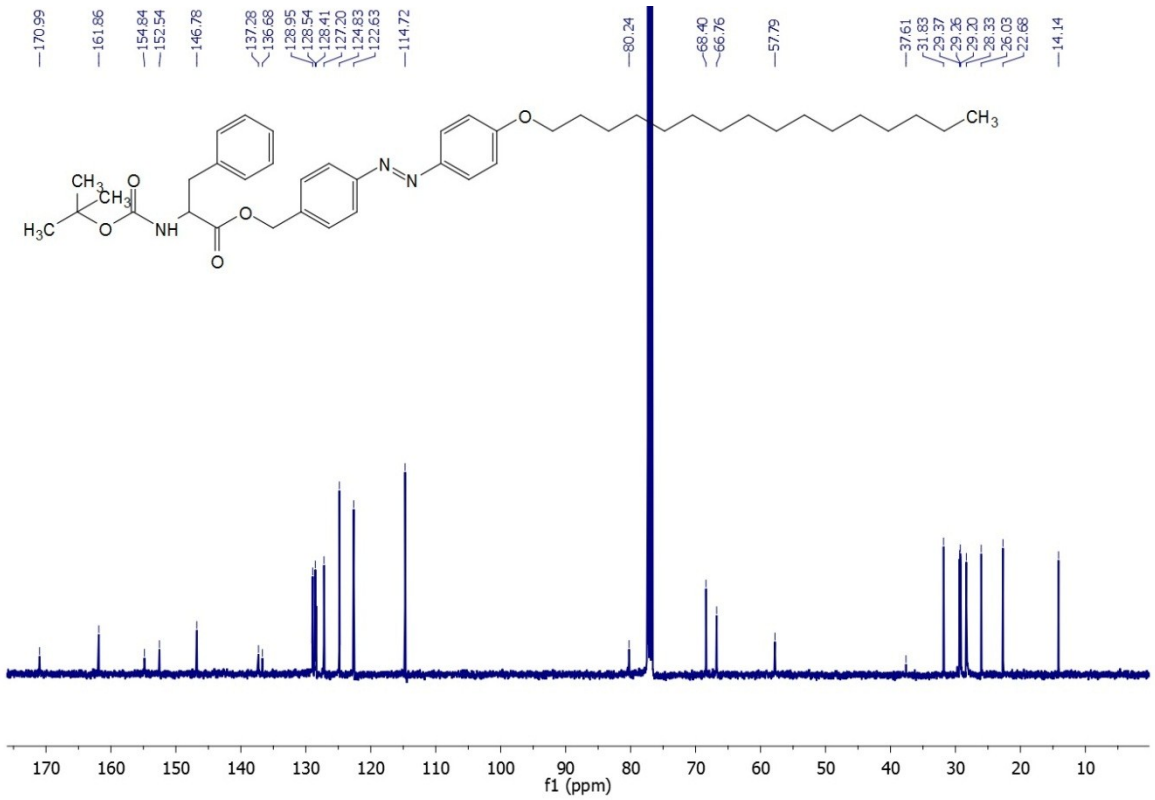
^{13}C NMR of 6e



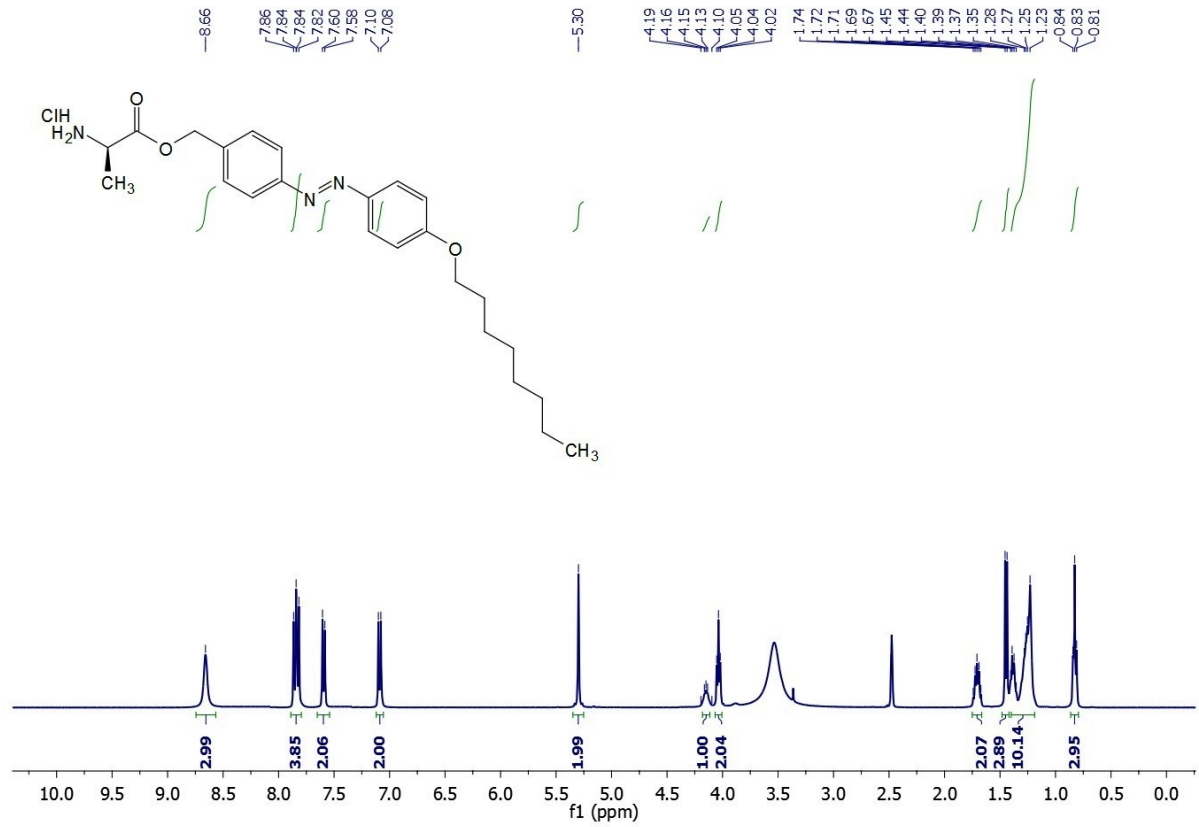
^{1}H NMR of 6f



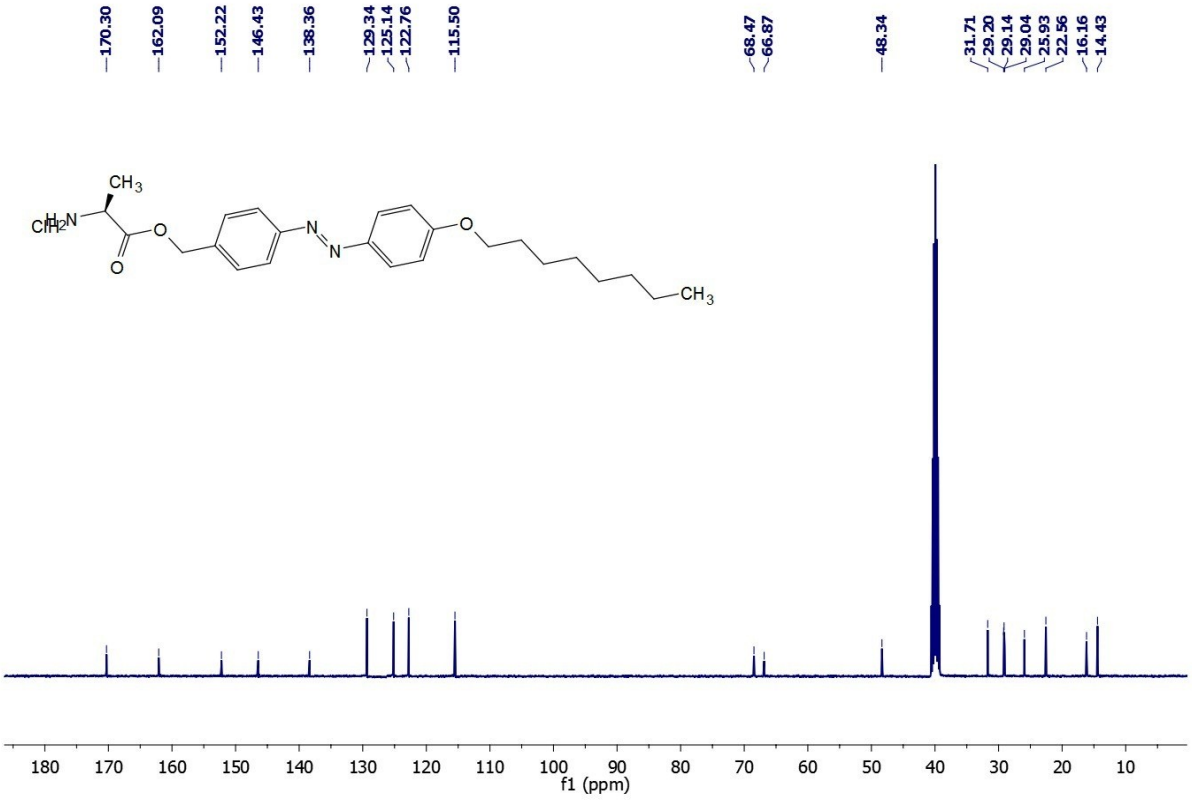
^{13}C NMR of 6f



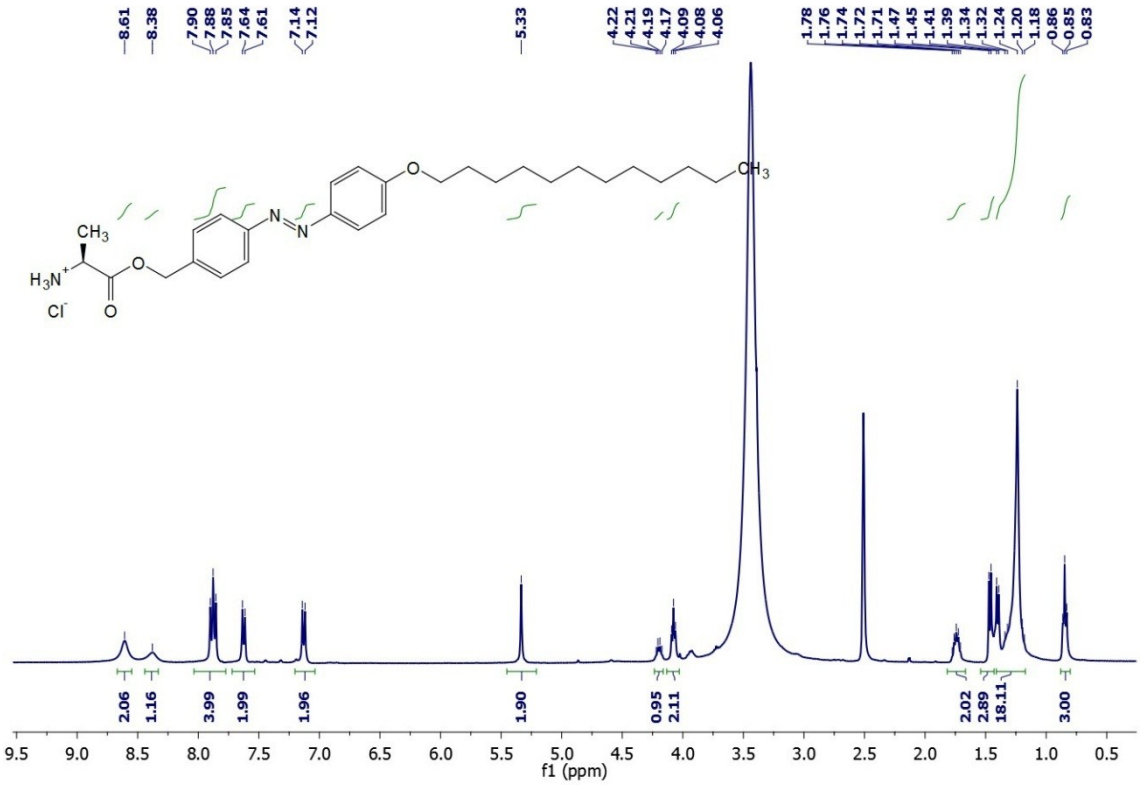
^{1}H NMR of 7a



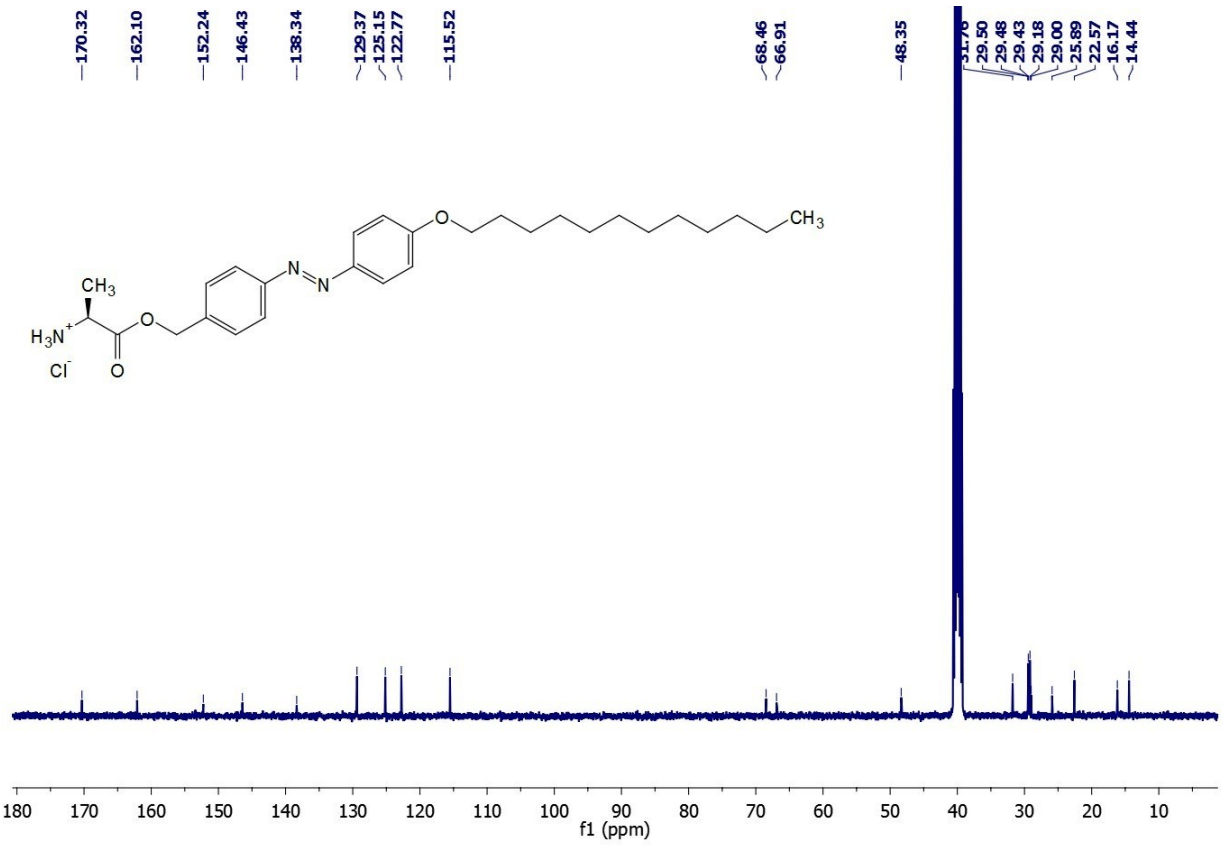
^{3}C NMR of 7a



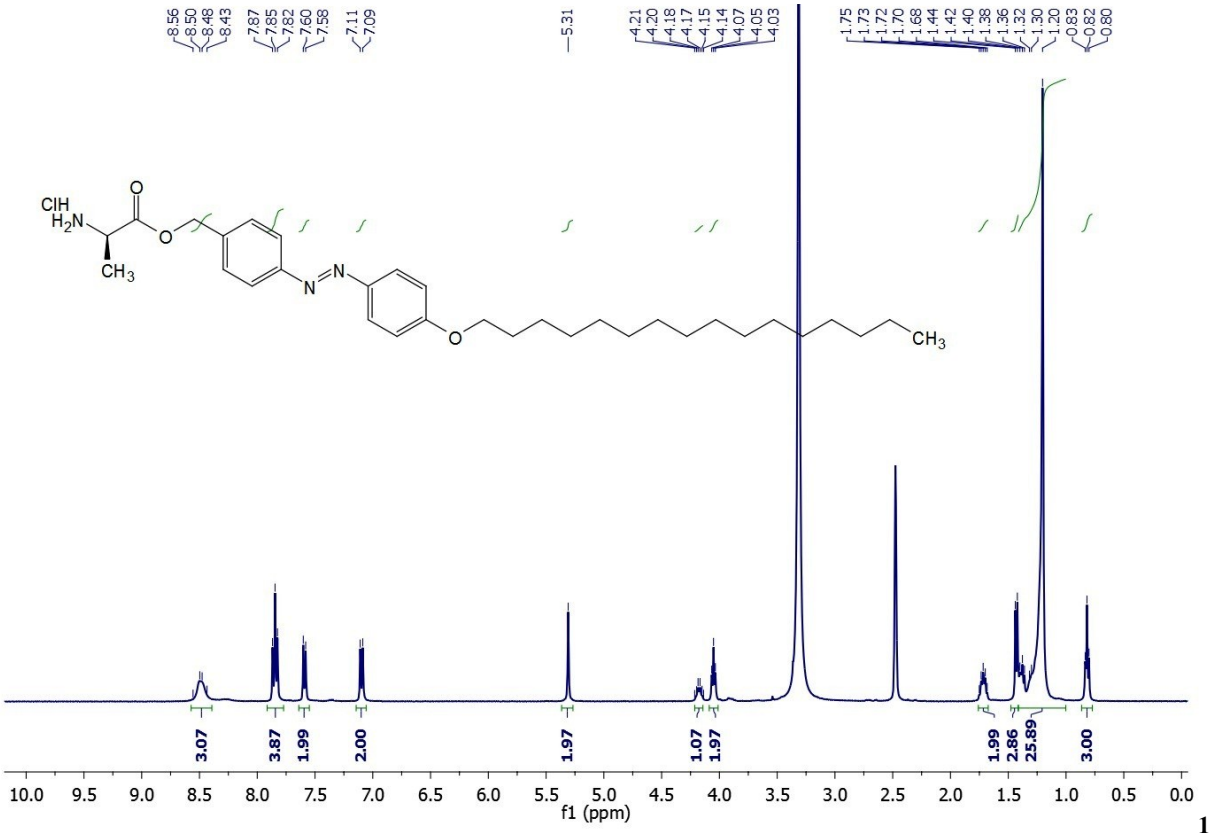
^{1}H NMR of 7b



^{13}C NMR of 7b


170.32
162.10
152.24
146.43
138.34
129.37
125.15
122.77
115.52
68.46
66.91
48.35
31.76
29.50
29.48
29.43
29.18
29.00
25.89
22.57
16.17
14.44
CH3
H3N+
Cl-
O
N
N
O
CH3
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

^{1}H NMR of 7c



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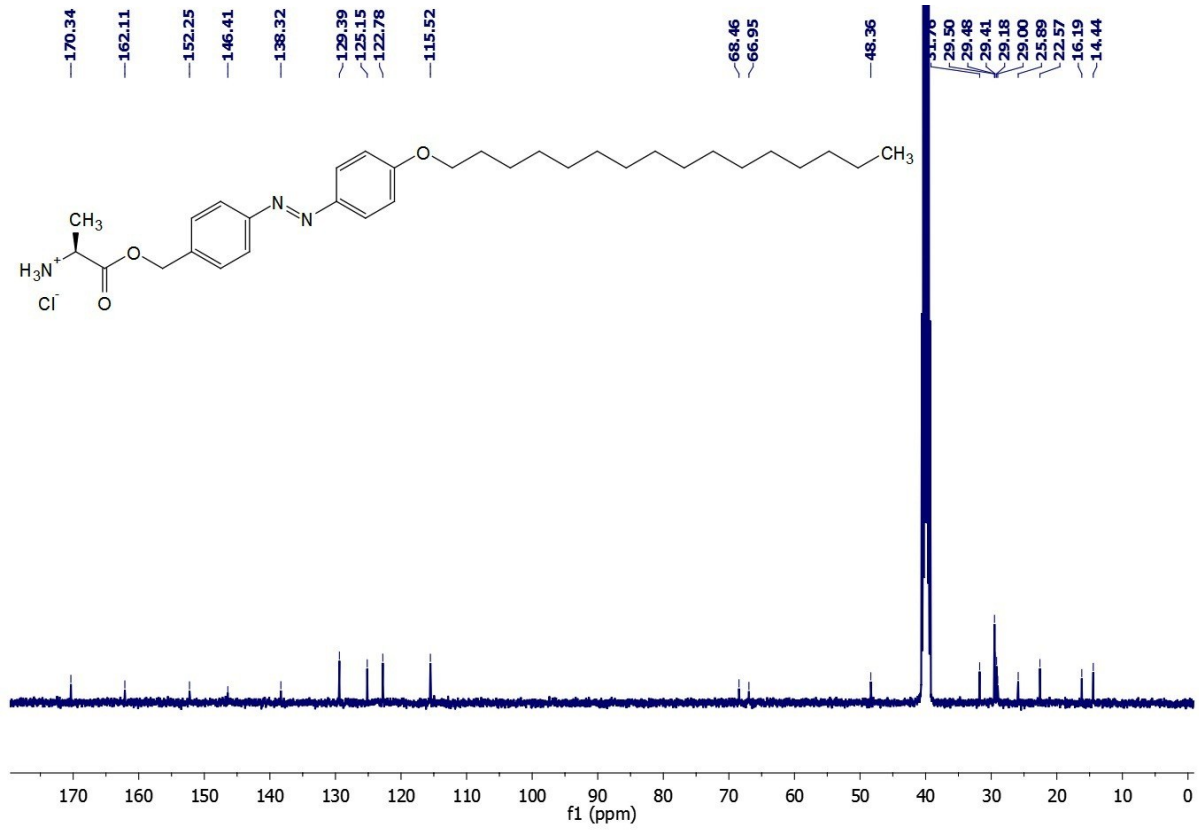
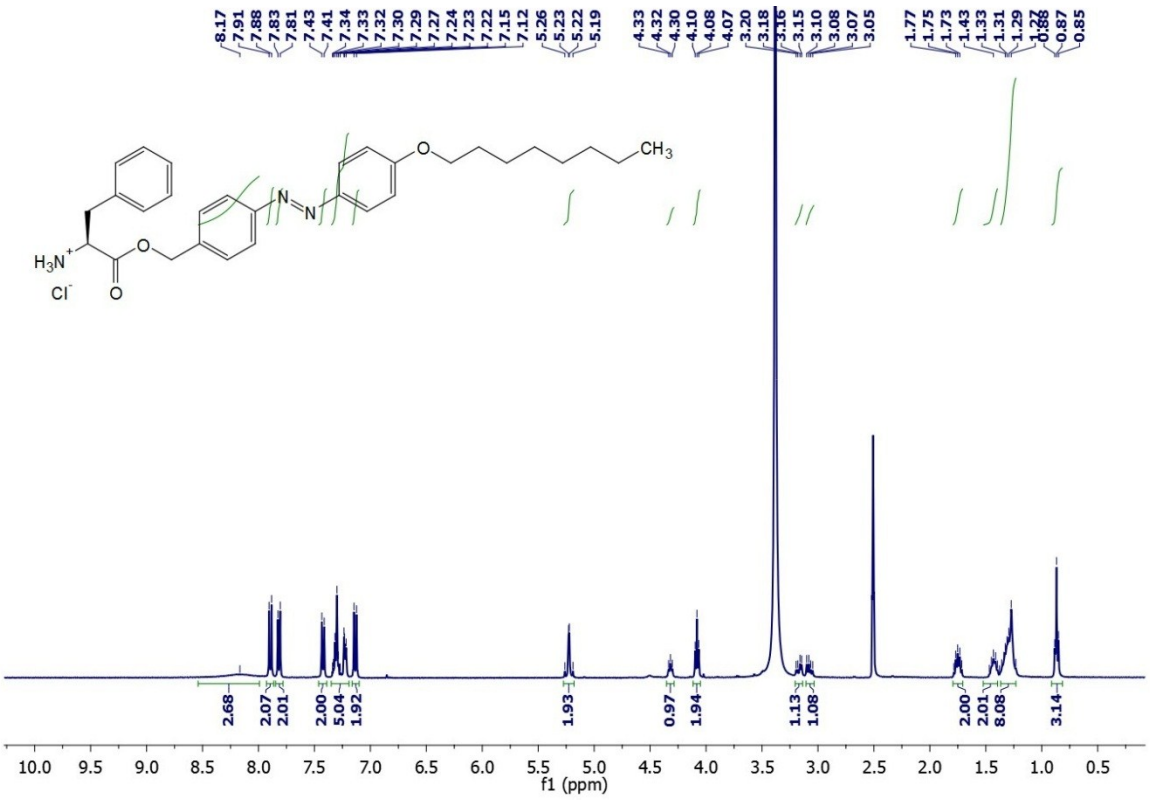
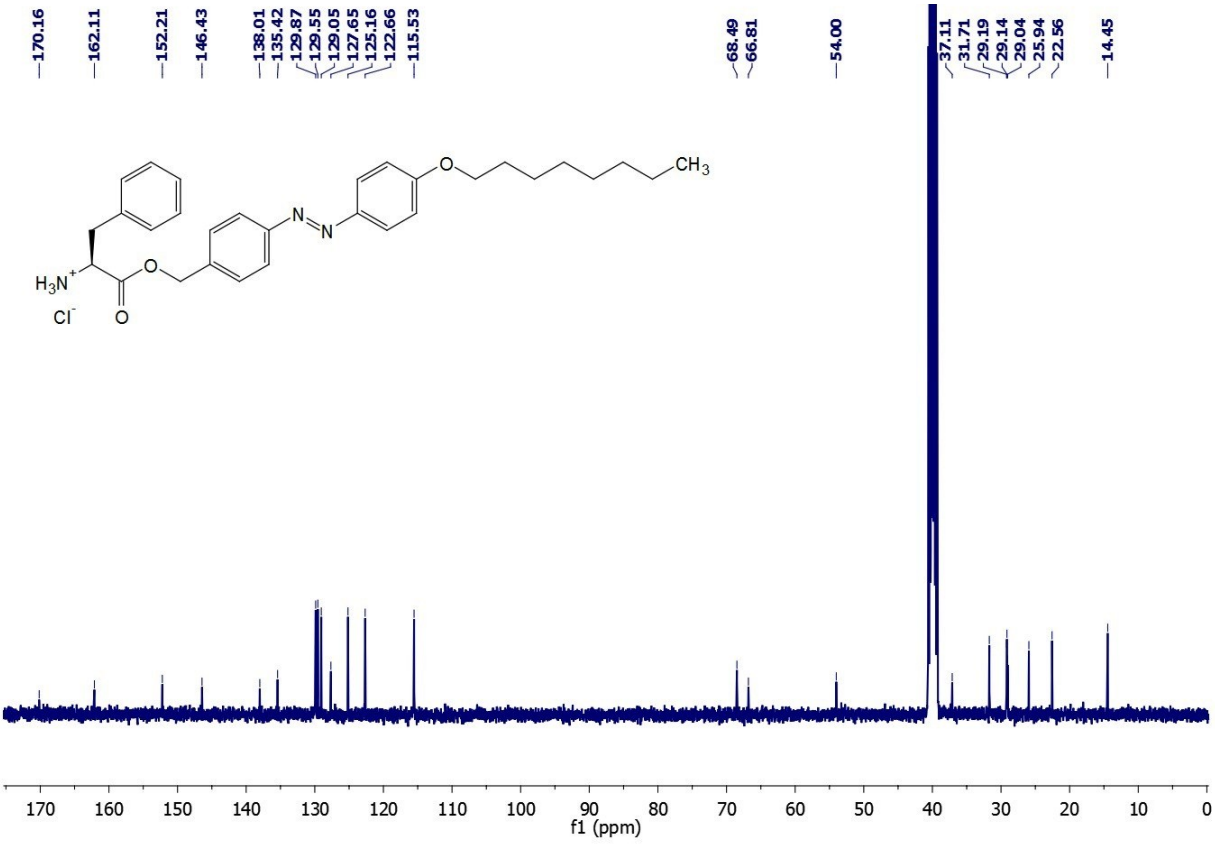
^{3}C NMR of 7c



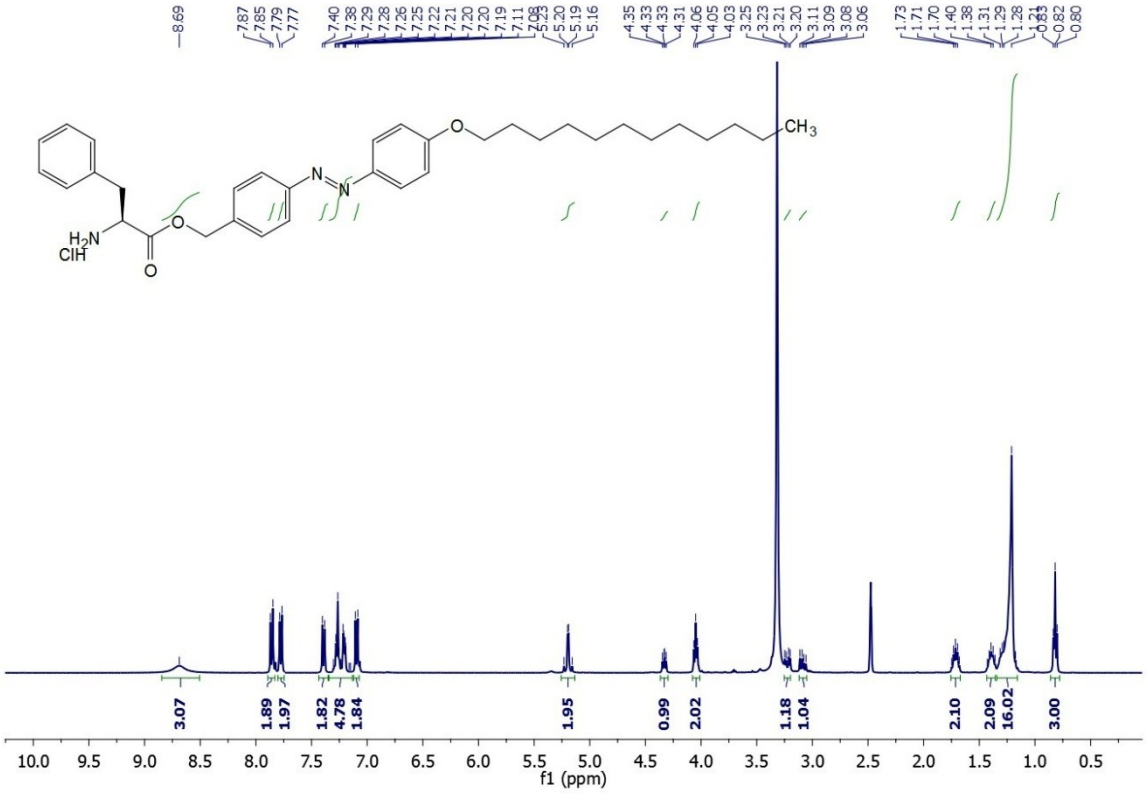
^{1}H NMR of 7d



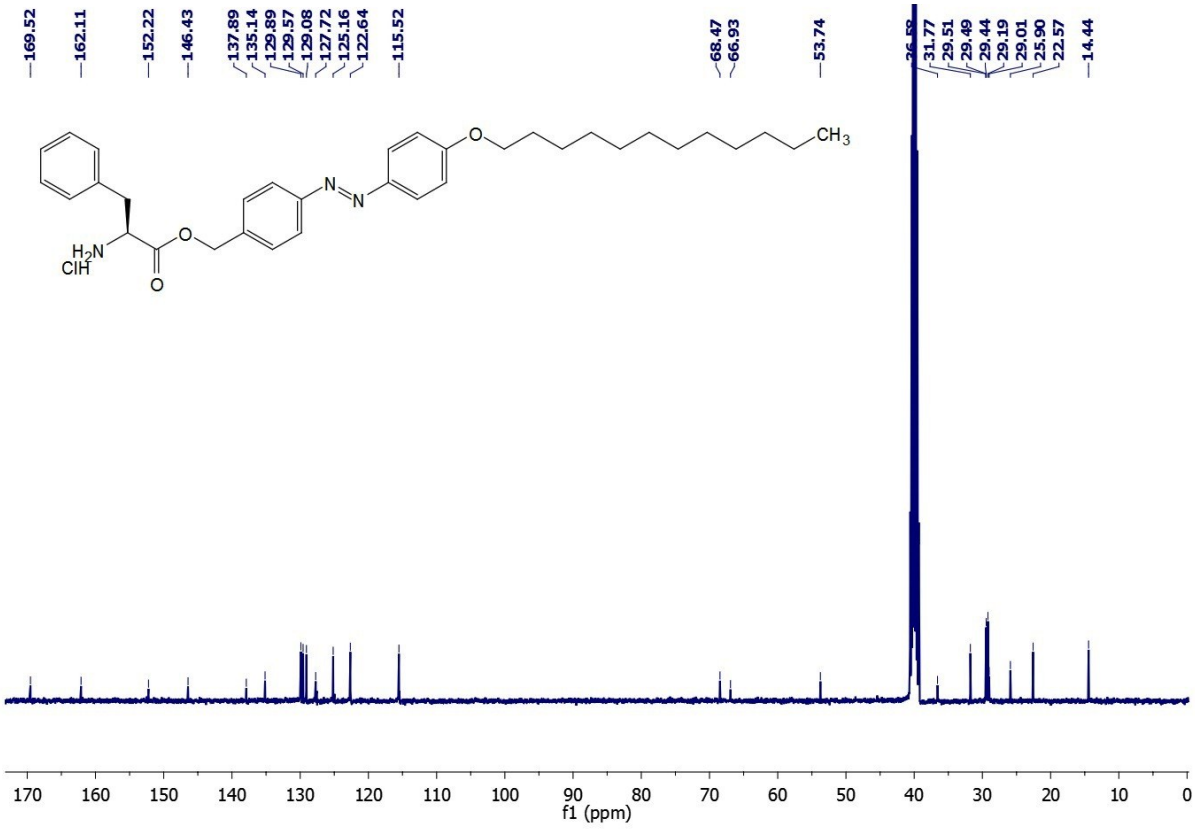
^{13}C NMR of 7d



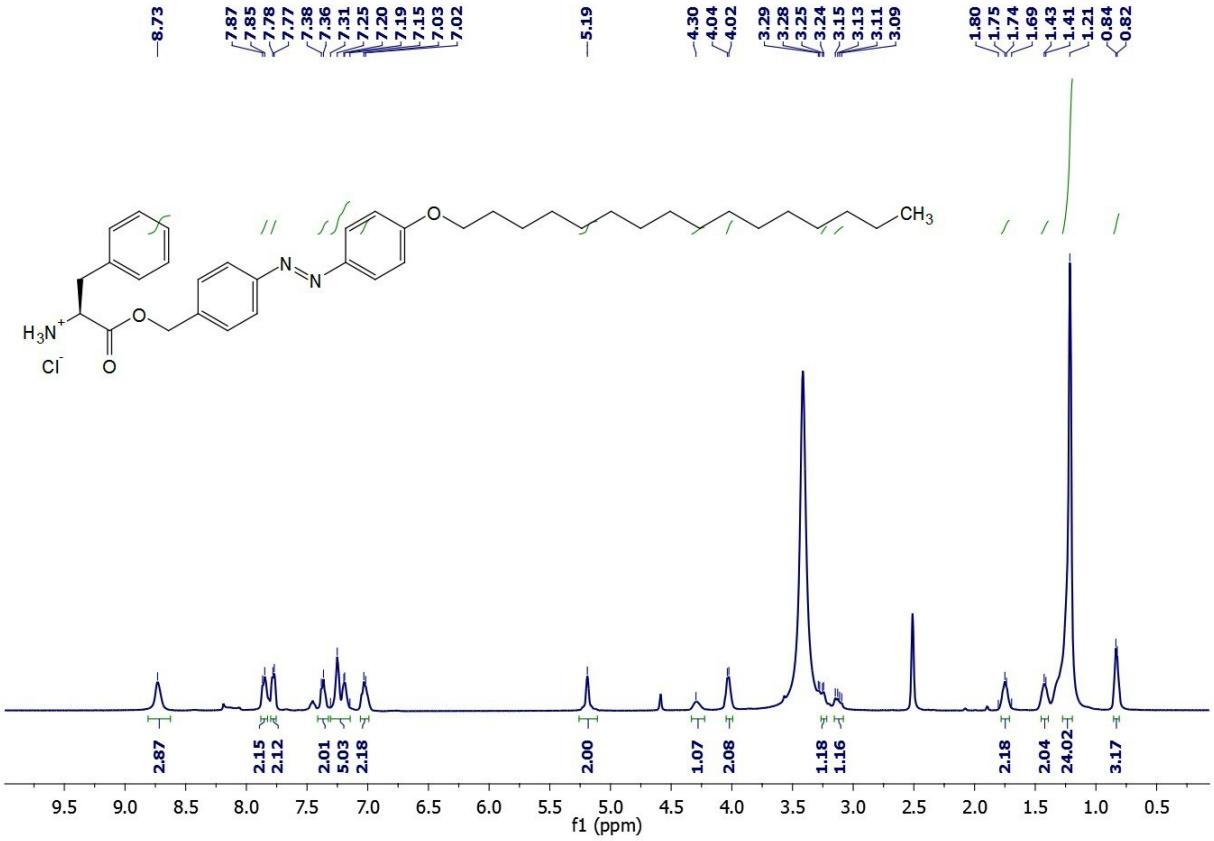
^{1}H NMR of 7e



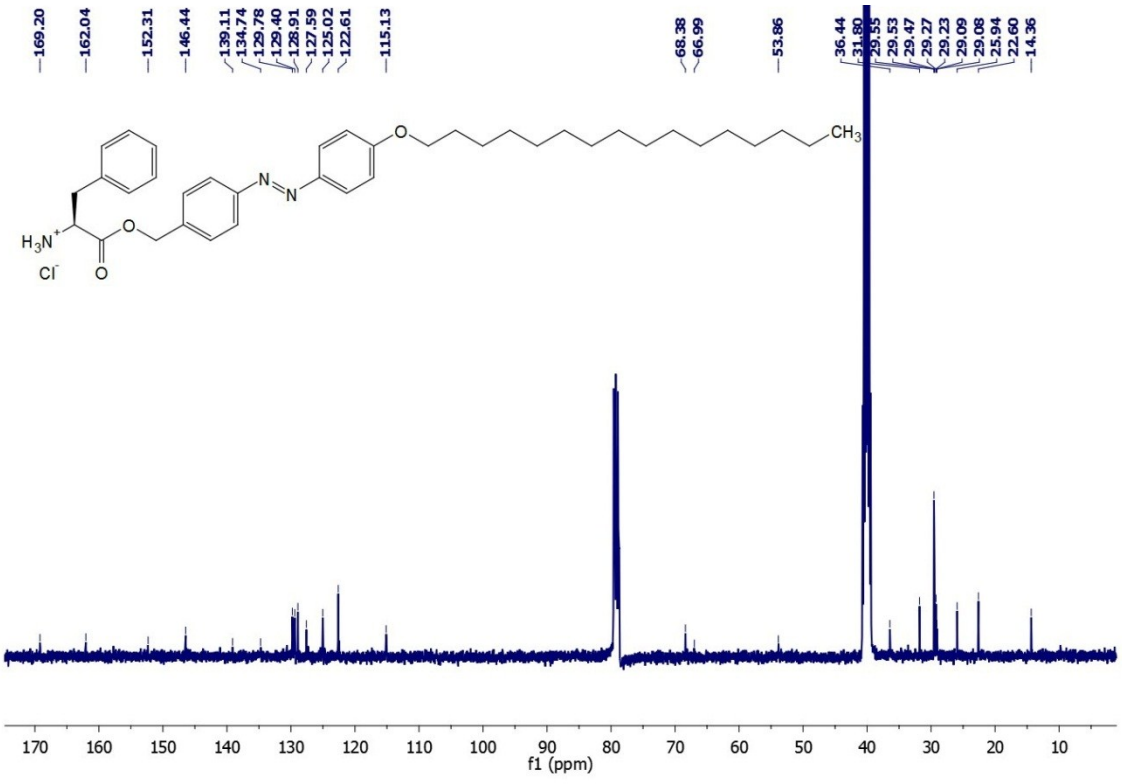
^{13}C NMR of 7e



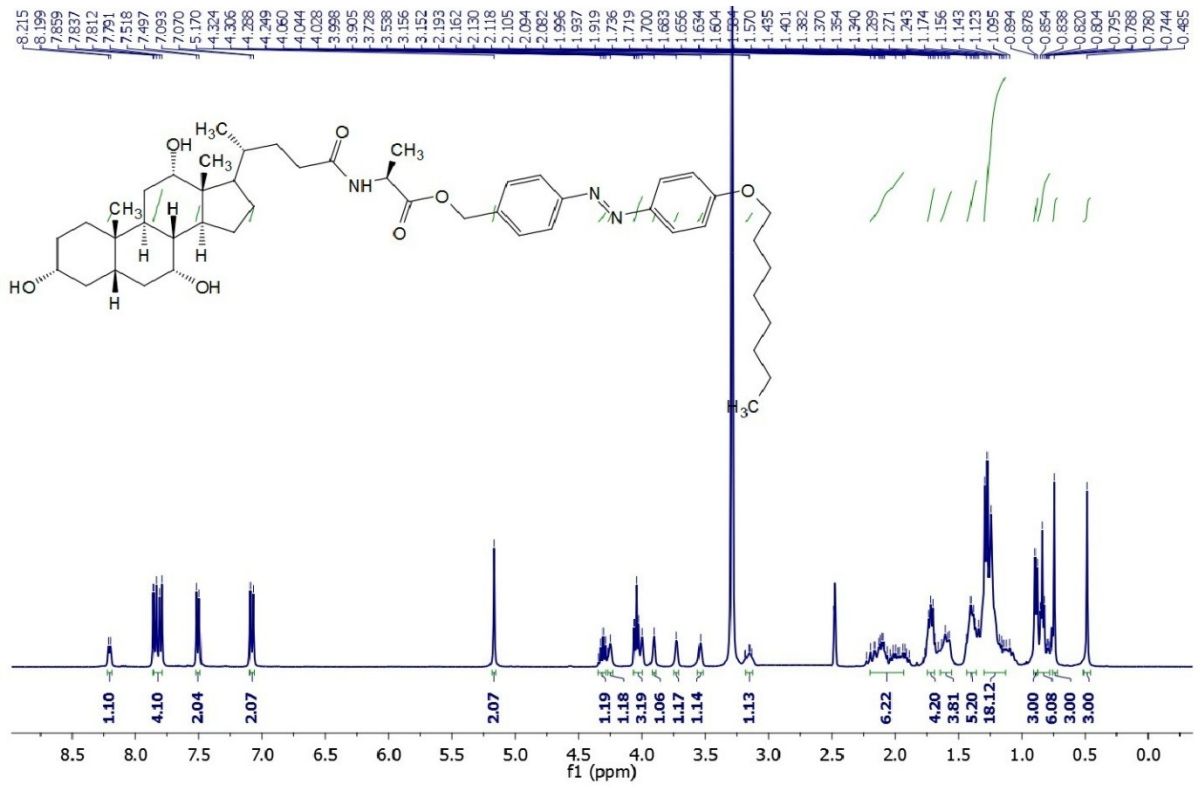
^{1}H NMR of 7f



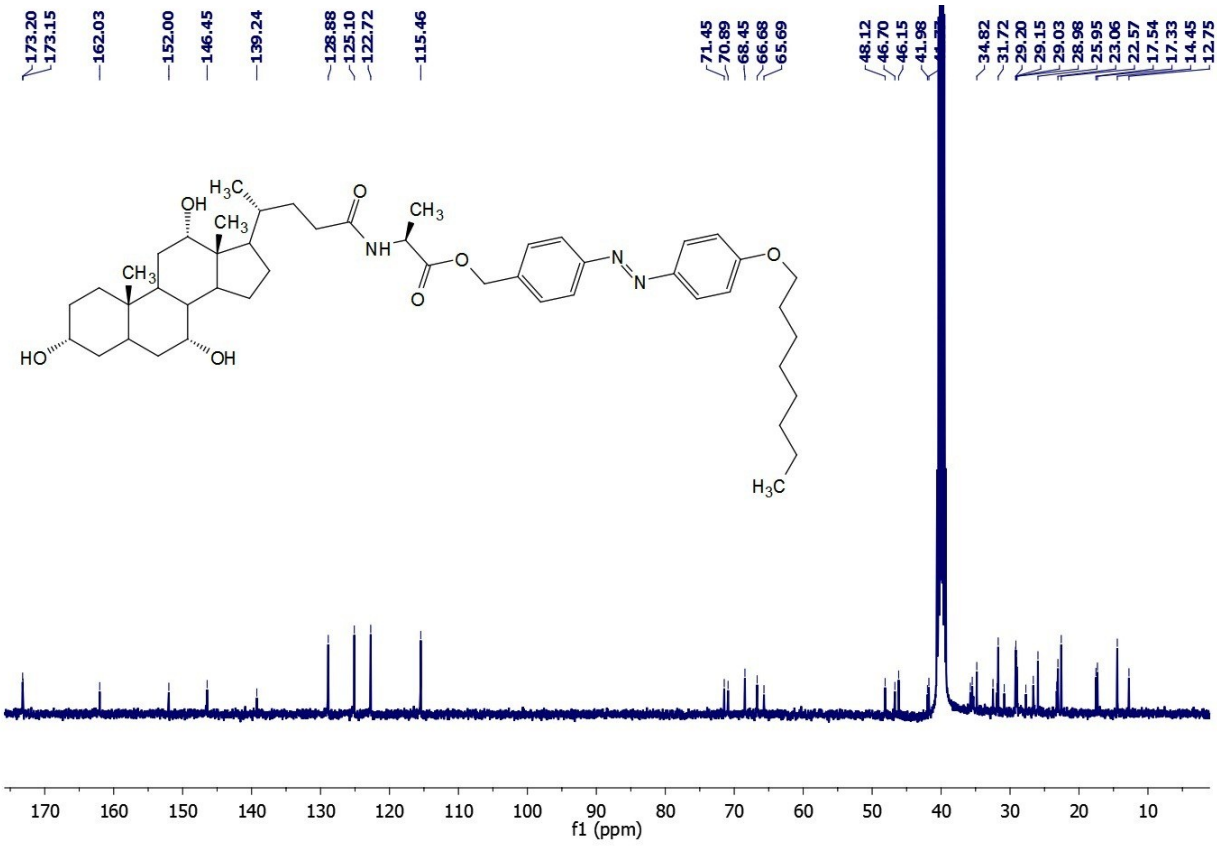
^{13}C NMR of 7f



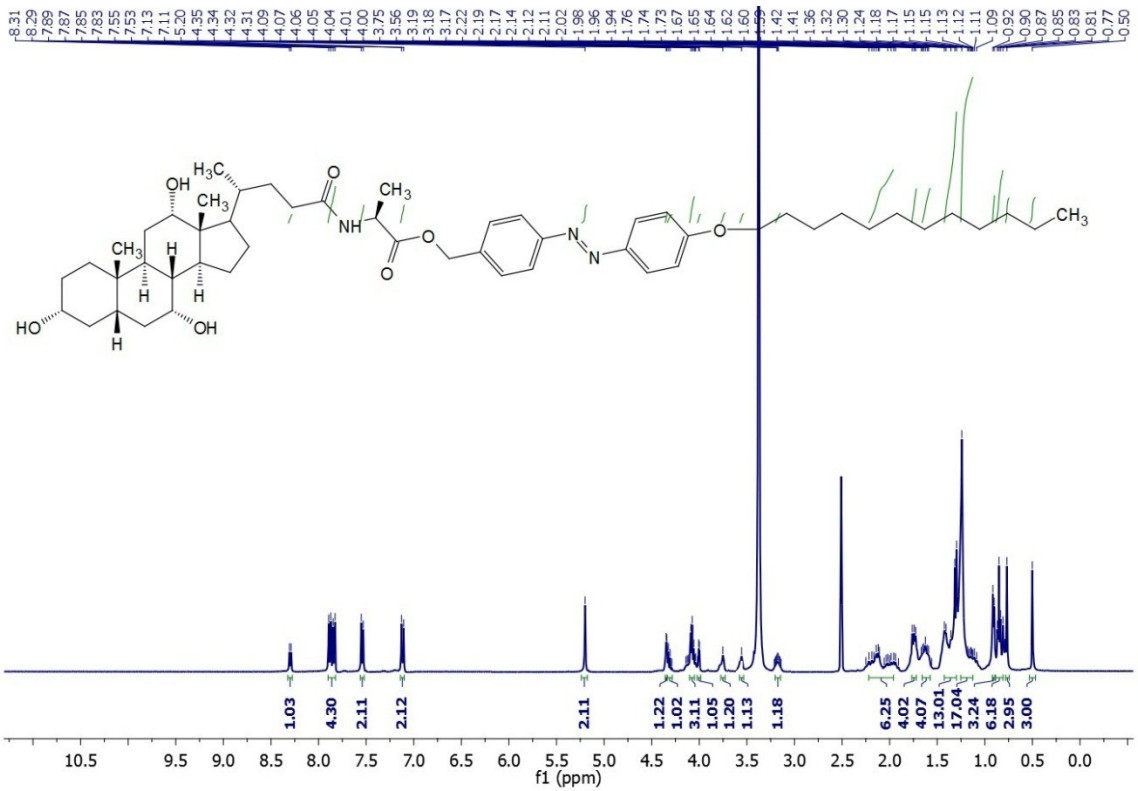
^{1}H NMR of 9a



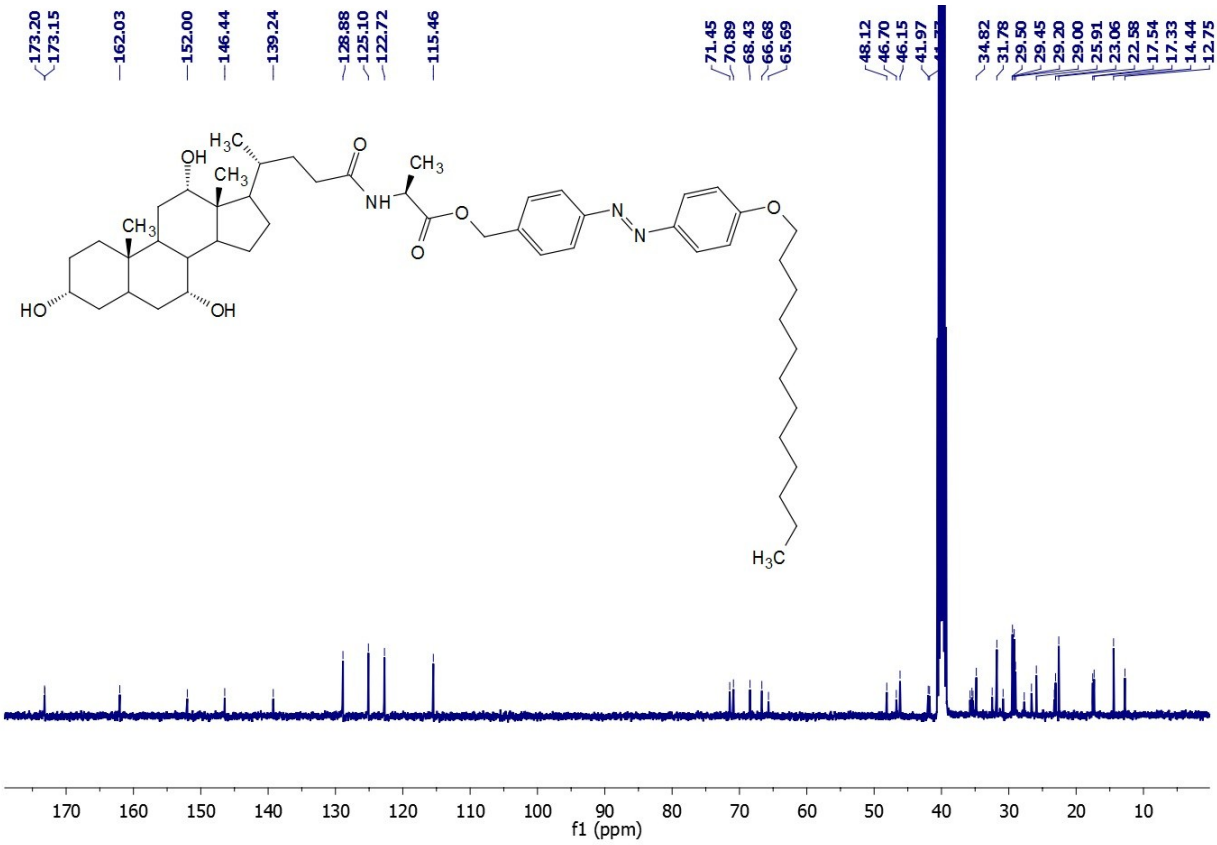
^{13}C NMR of 9a



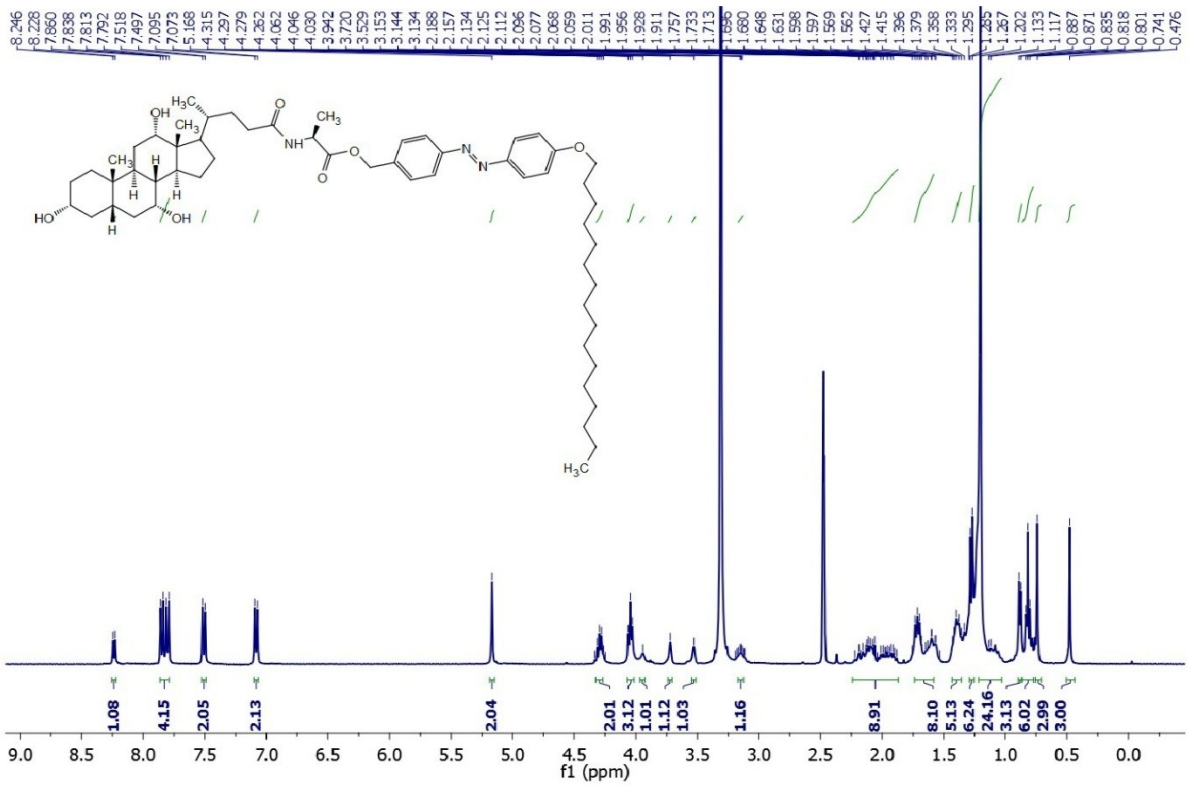
^{1}H NMR of 9b



^{13}C NMR of 9b



^{1}H NMR of 9c



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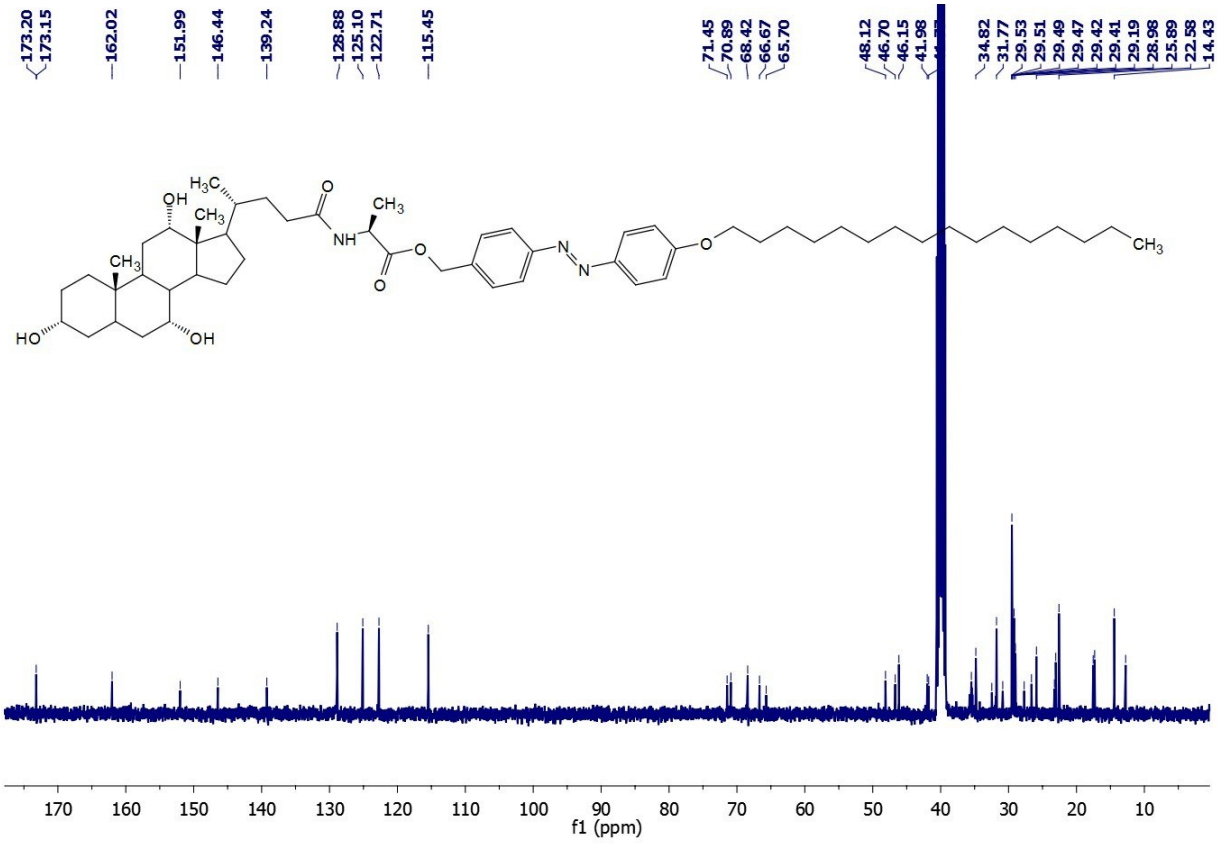
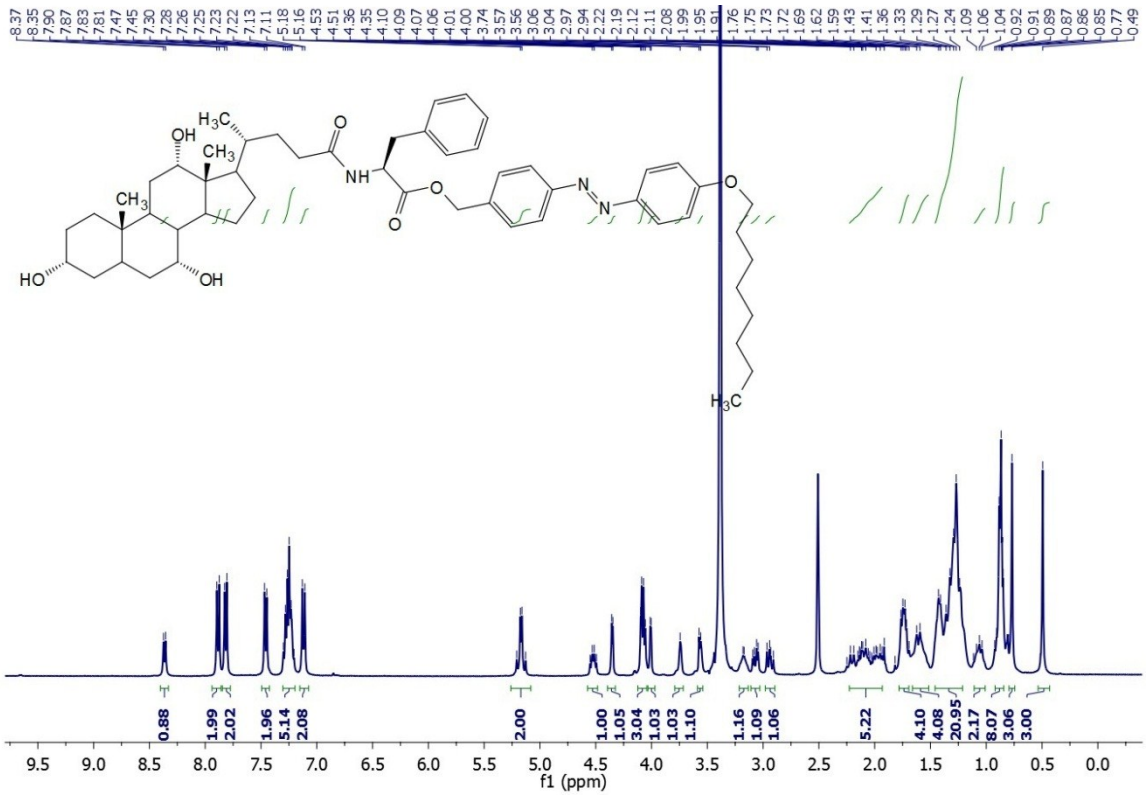
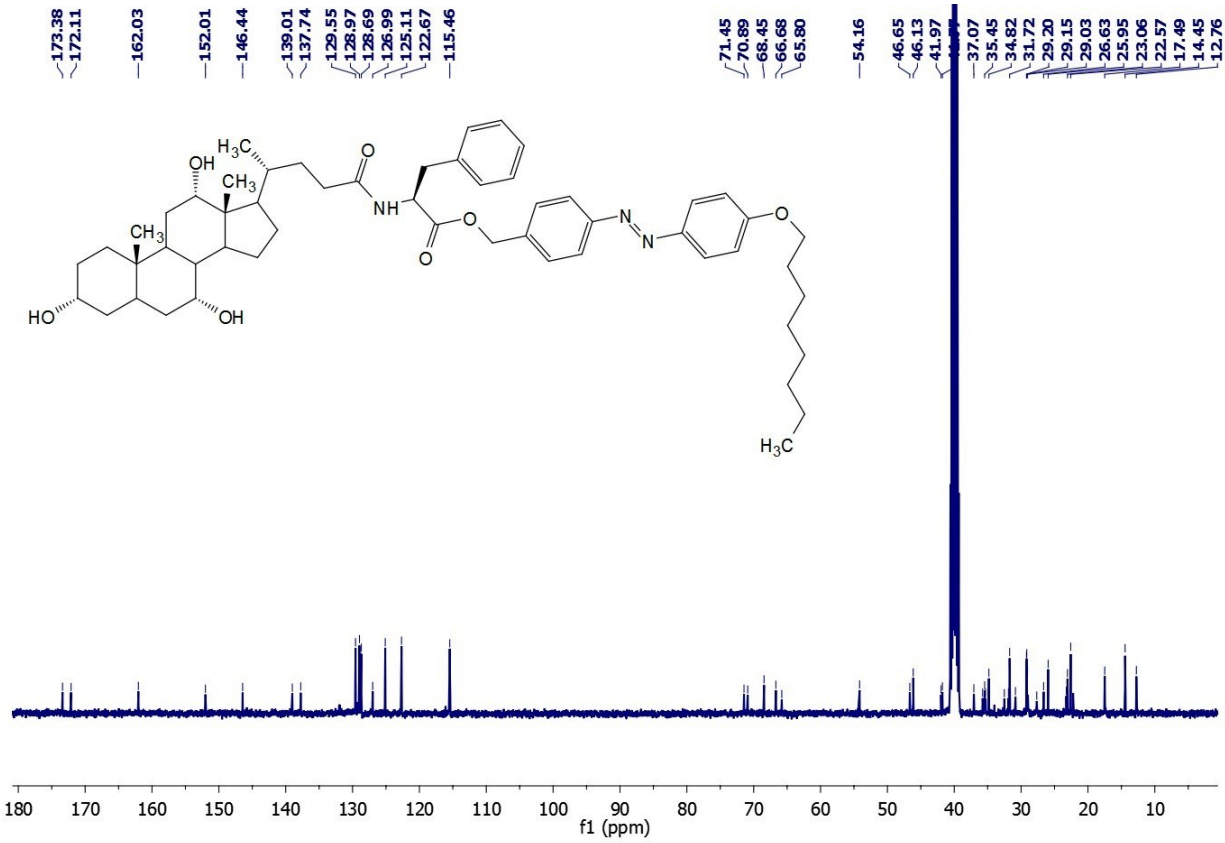
^{3}C NMR of 9c



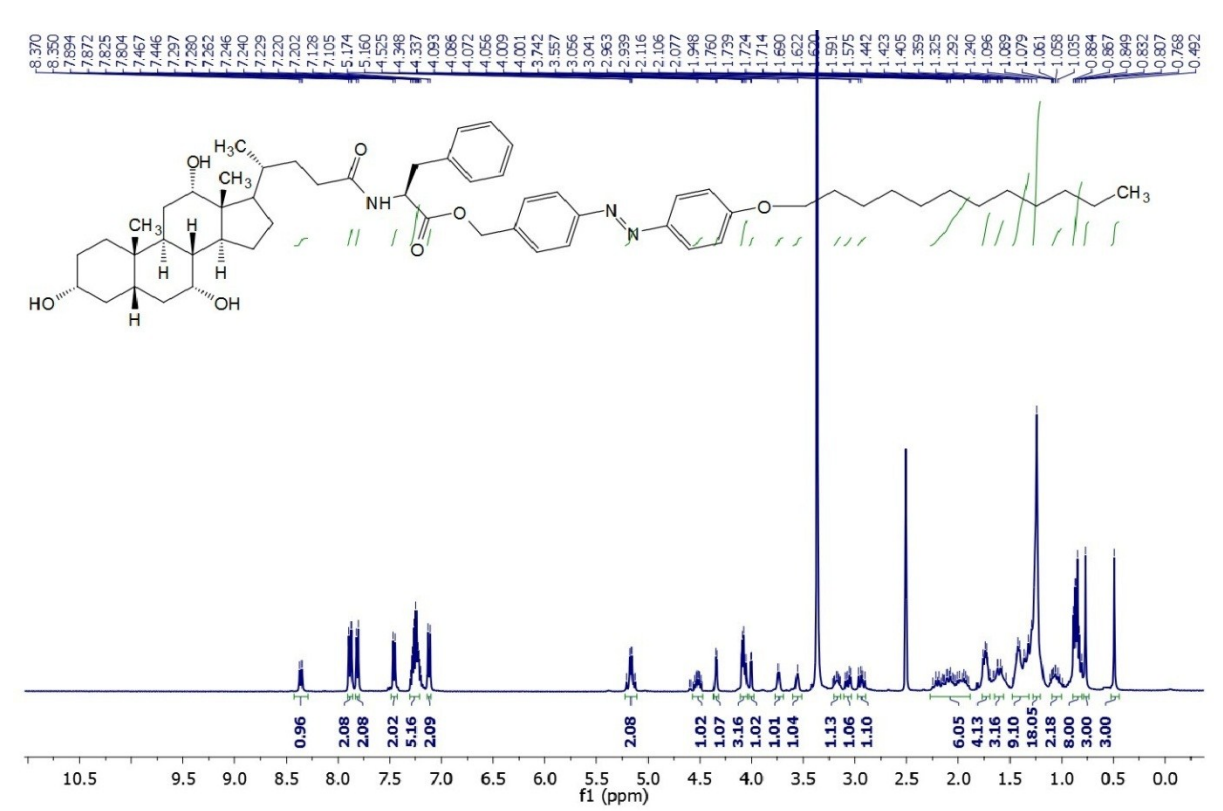
^{1}H NMR of 9d



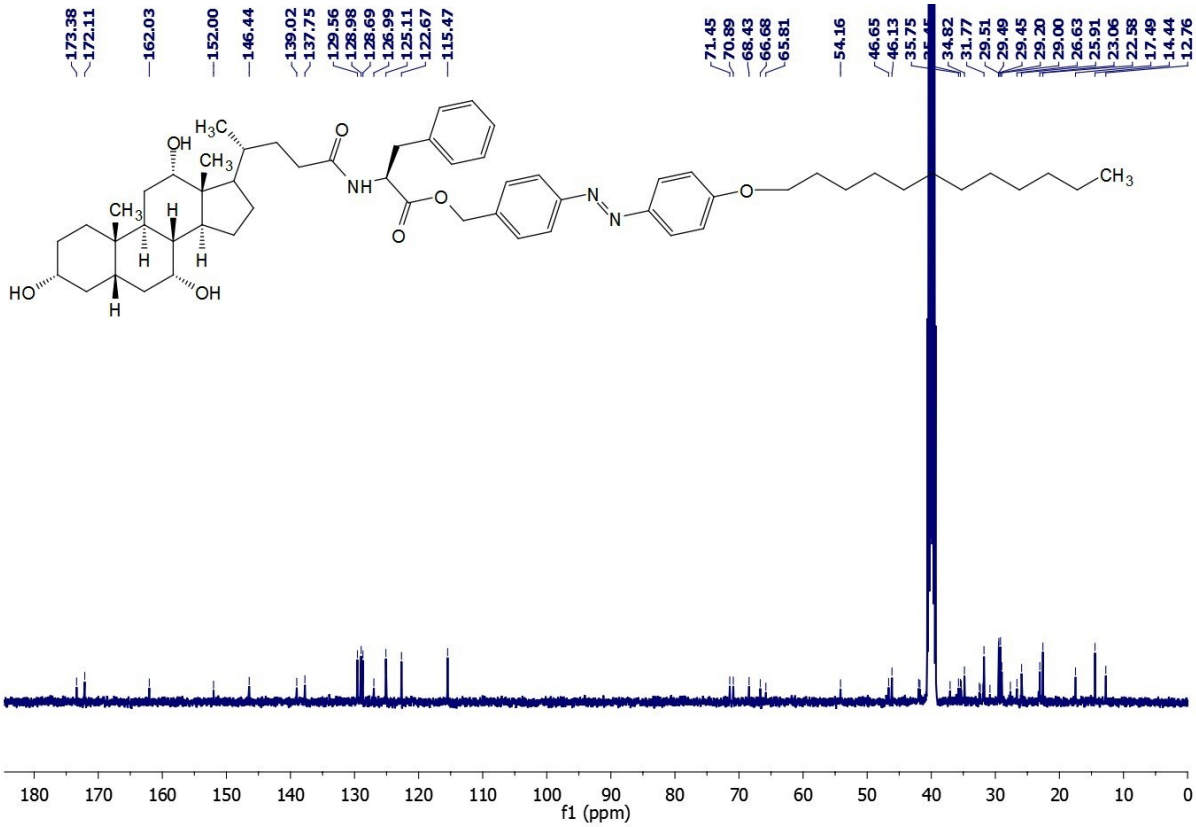
^{13}C NMR of 9d



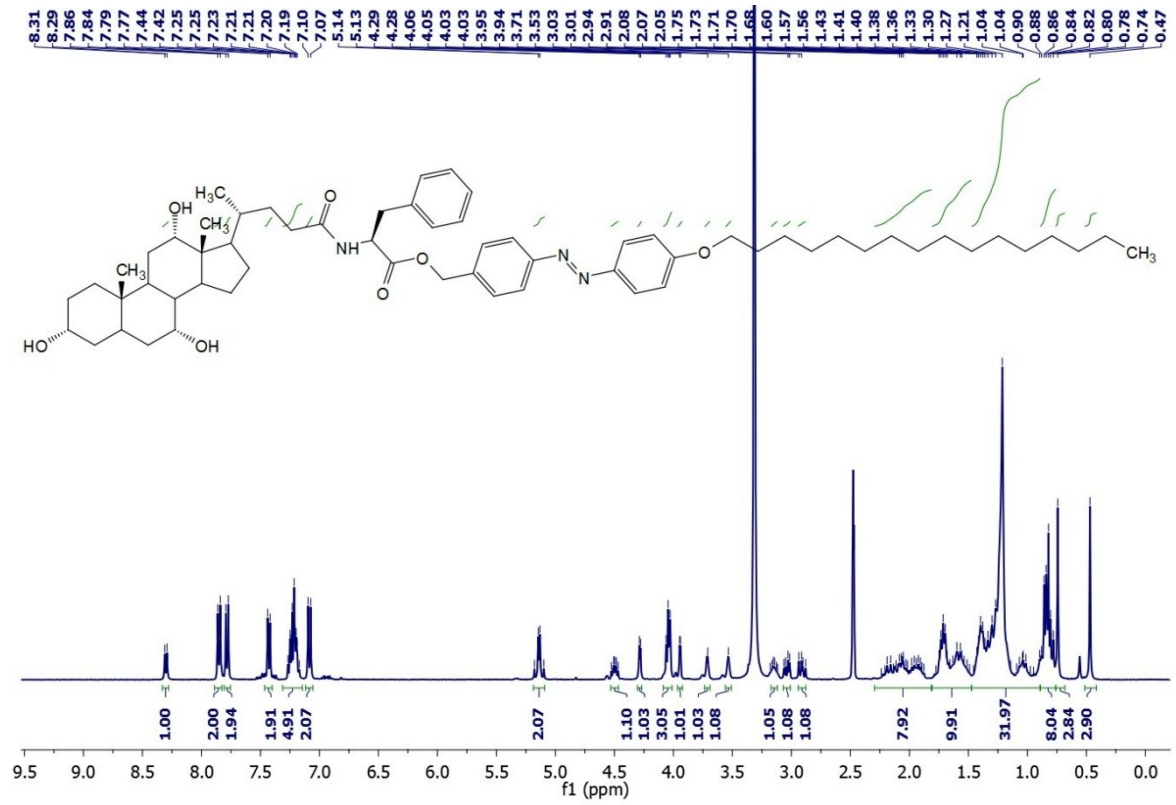
^{1}H NMR of 9e



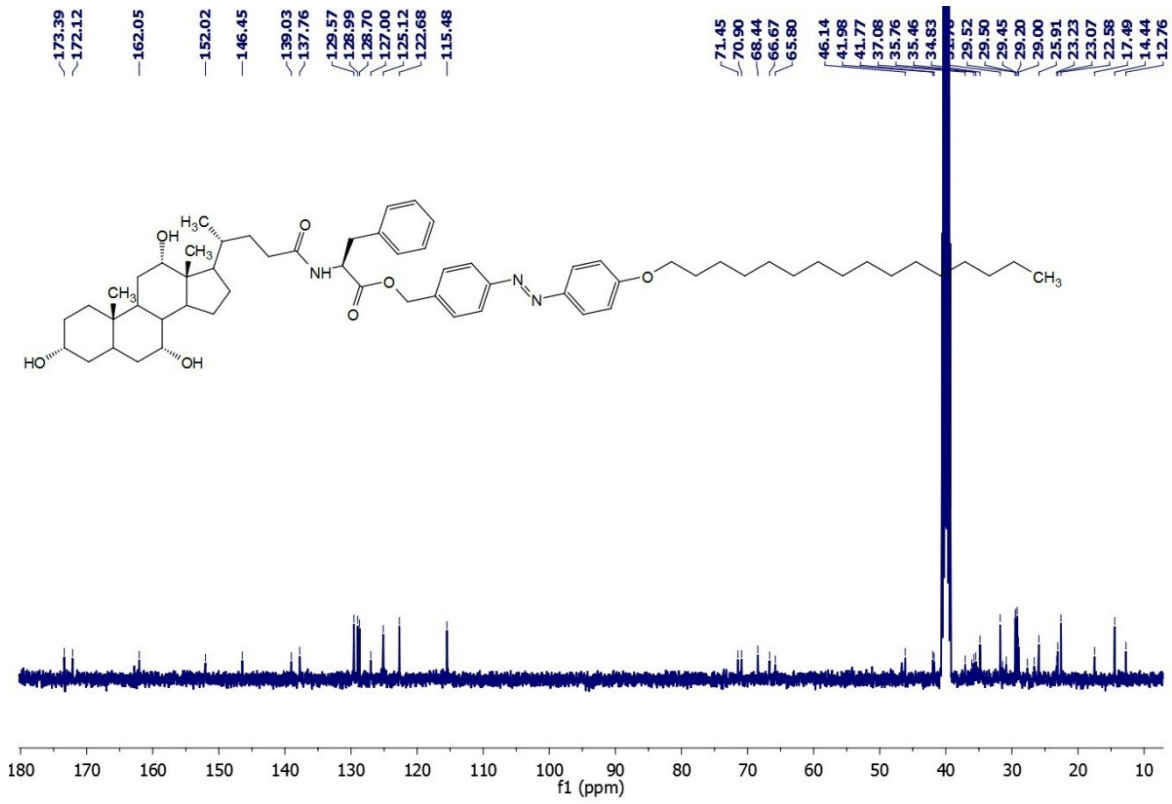
^{13}C NMR of 9e



^{1}H NMR of 9f



^{13}C NMR of 9f



4. SEM images

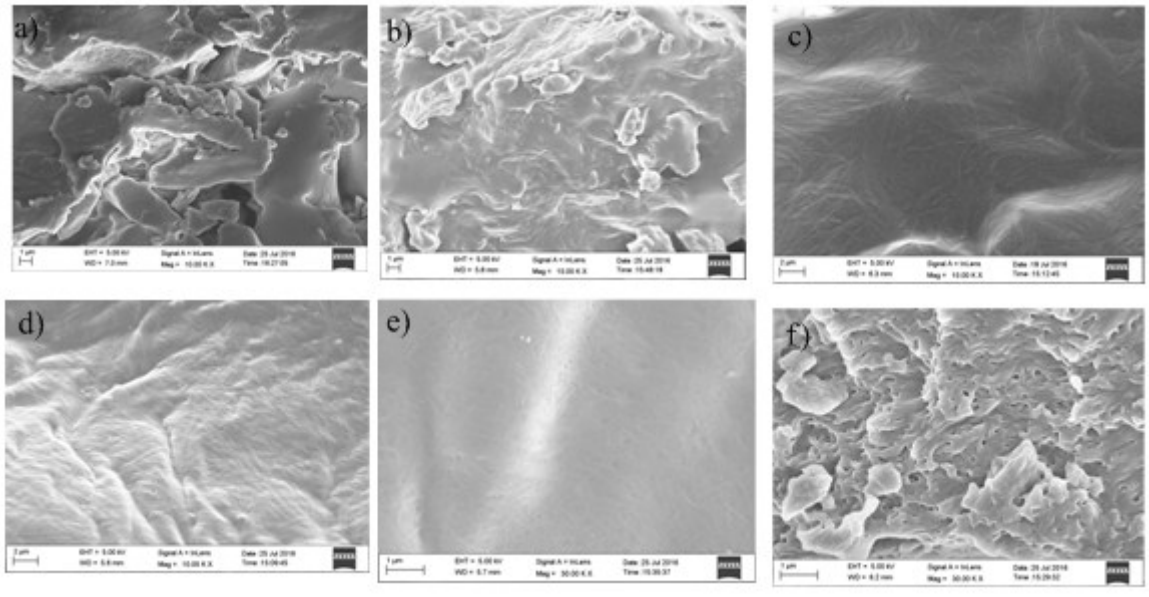


Figure S1 SEM images of the xerogels of **9a** a) Cyclohexane b) Hexane c) Benzene d) *tert*-butyl benzene e) Mesitylene. f) SEM image of gel of **9e** Dodecane

5. References

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