Electronic Supplementary Information

Catalytic asymmetric aminolactonization of 1,2-disubstitued alkenoic acid esters: Efficient construction of aminolactones with all carbons quaternary stereo-centre

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Experimental Section

A) General:

All reactions were conducted using oven-dried glassware under an atmosphere of Argon (Ar). Commercial grade reagents were used without further purification. Solvents were dried and distilled following usual protocols. Flash chromatography was carried out using silica gel (230-400 mesh). TLC was performed on aluminium-backed plates coated with silica gel 60 with F_{254} indicator.

The ^{1}H NMR spectra were recorded with a 200 and a 400 MHz and ^{13}C NMR spectra were recorded with a 50 and a 100 MHz using $CDCl_3$, d_6-DMSO and CD_3OD. ^{1}H NMR chemical shifts are expressed in parts per million (δ) relative to $CHCl_3$ (d = 7.26), d_6-DMSO (δ = 2.48) and CD_3OD (δ = 3.34); ^{13}C NMR chemical shifts are expressed in parts per million (δ) relative to the CDCl3 resonance (δ = 77.0), d_6-DMSO (δ = 40.1) and CD_3OD (δ = 49.2). Highresolution mass spectra (HRMS) were obtained under positive electron spray ionization (m/z values are given). HPLC analyses were done by Chiralpak IA column and IC column (4.6 mm × 250 mm and particle size 5µm and 3µm). Specific optical rotation values were measured on a Jasco-P1200 polarimeter. NOE experiment was done in 500 MHz NMR.

B) General procedure for the preparation of 4-arylbut-3-enoic acid:

(2-carboxyethyl)triphenylphosphonium bromide (1.2 eq) was suspended in dry THF. Aryl aldehyde (1 eq) was added. The mixture was cooled to – 78 ^{0}C, then a solution of $^{t}BuOK$ (2.5 eq) in dry THF was added continuously over 2 h. The reaction was stirred for 12-18 h during which it was allowed to warm to RT. The reaction was monitored by TLC analysis and after completion of the reaction THF was evaporated. 100 mL H_2O and 100 mL DCM was added. Aqueous layer was separated and acidified with 1(N) HCl up to pH=1. 100 ml Et_2O was added. The layers were separated and the aqueous layer was extracted with Et_2O (2 x100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuum (40 ^{0}C). After flash chromatography on silica gel with hexane/EtOAc (3:1) 4-arylbut-3-enoic acids were obtained as a yellow solid (yield 50-65%).

C) General procedure for the preparation of tert-butyl 4-arylbut-3-enoate[1]:

In a two-necked flask equipped with a magnetic stirring bar, anhydrous $MgCl_2$ (0.10 eq), BOC_2O (1.3 eq) and 4-arylbut-3-enoic acid (1.0 eq) were dissolved in ^tBuOH (2.0eq). The mixture was stirred at 40 ^0C and for 2-3 days and monitored by TLC analysis. The crude reaction mixture was diluted with H_2O (10 mL) and extracted with EtOAc (3 x 10 mL). The organic layer was separated, dried ($MgSO_4$) and filtered, and the solvent was removed by rotary evaporation. The crude mixture was then subjected for column chromatography on silica gel with light petroleum ether/Et_2O (9:1). The *tert*-butyl 4-arylbut-3-enoate esters **1a-g** were obtained as light yellow oil (yield 85-95%).

D) General procedure for the preparation of (*E*)-*tert*-butyl 5-arylpent-4-enoate[2]:

To a heat-dried two-necked round-bottomed flask were added freshly distilled diisopropylamine (1.05 eq) and dry THF under argon. This solution was cooled to -78 °C, and n-BuLi (2.5 M in hexane, 1.05 eq) was then added via syringe. The mixture was stirred for 45 min, followed by addition of tert-butyl acetate (1 eq). The reaction mixture was stirred for 1 h. The resulting ester enolate-solution was was slowly added at -78 °C to the solution of bromide (1 eq) in THF via syringe. After stirring for 4 h at -78 °C the reaction mixture was quenched by addition of saturated NH_4Cl solution and allowed to warm up to room temperature. Then THF was evaporated and the aqueous layer was extracted with EtOAc. The combined extractes were dried over anhydrous $MgSO_4$, and concentrated under reduced

pressure. Flash chromatography on silica gel eluting with light petroleum ether/Et_2O (9:1) furnished (*E*)-tert-butyl 5-arylpent-4-enoate esters **5a-b** light yellow oil (yield 70-75%).

Aziridine reagents $PhINSO_2(4\text{-}NO_2\text{-}C_6H_4)$ [PhINNs] were prepared by literature procedure.[3]

C2-symmetric bis-oxazoline ligands **4a-g** were synthesized by following literature procedure.[4]

E) General Procedure for one-pot enantioselective Synthesis of *N*-nosyl-4-amino-5-arylbutyrolactones and *N*-nosyl-5-amino-6-arylvalerolactones [5] (3a-g, 10, 7a-b):

A 10 mL two-necked round bottom flask was charged with bis-oxazoline ligand **4g** (0.010g, 0.0279 mmol, 0.12 equiv), $Cu(OTf)_2$ (0.009 g, 0.0248 mmol, 0.10 equiv) and 0.2 g of powdered molecular sieves (4Å). Anhydrous chloroform (1.2 mL) was injected and the resulting mixture was stirred for 30 min at rt. Then the reaction mixture was placed at 40° C and to this solution, substrate **1** (0.389 g, 1.23 mmol, 5.0 equiv) in 1.2 mL chloroform, PhINNs (0.100 g, 0.247 mmol, 1.0 equiv) were added and the reaction mixture was allowed to stir at 40 °C under an argon atmosphere. As soon as all the nitrenoid reagent dissolved in the reaction medium, an additional amount of $Cu(OTf)_2$ (0.005 g, 0.0138 mmol) or ~ 0.2 g of silica gel (60-120 mesh) was added. On completion, the reaction was quenched by diluting with ethyl acetate (10 mL) and filtering through a short plug of silica gel. The silica gel was washed with additional 10 mL of ethyl acetate. The filtrate was concentrated by rotary evaporation under reduced pressure. The crude mass was subjected to purification by flash column chromatography using EtOAc/hexane as an eluent, which provided pure arylbutyrolactones and arylvalerolactones.

F) Spectral Data of *N*-nosyl-4-amino-5-arylbutyrolactones and *N*-nosyl-5-amino-6-arylvalerolactones (3a-i, 10, 7a-d and 13a-d):

4-nitro-*N*-((2*S*, 3*R*)-5-oxo-2-phenyltetrahydrofuran-3-yl)benzenesulfonamide(3a): White solid (0.072 g; 80%). M.p. 158-160 °C. **FTIR** (KBr, cm^{-1}): 3369, 2949, 2838, 1652, 1453, 1415, 1113, 1021. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 8.22 (d, *J* = 8.8 Hz, 2H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.41-7.30 (m, 3H), 7.20-7.16 (m, 2H), 5.58 (d, *J* = 8.2 Hz, 1H), 5.27 (d, *J* = 4.8 Hz, 1H), 4.16-4.12 (m, 1H), 3.04-2.92 (dd, *J* = 7.4, 17.4 Hz, 1H), 2.56-2.44 (dd, *J* = 6, 17.8 Hz,

1H). **^{13}C NMR** ($CDCl_3$, 50 MHz): δ 173.0 (C=O), 150.7, 147.2, 140.1, 128.5(2C), 128.1(2C), 127.3(2C), 125.2(2C), 123.6, 84.4, 59.6, 30.9. $[\alpha]_D^{32}$ = −5.42 (c 0.1, Me_2CO) for 87% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 15.06 min and minor 10.71 min). HRMS (ESI) calcd for $C_{16}H_{14}N_2O_6NaS$ 385.0470, m/z $[M+Na]^+$, found 385.0484.

***N*-((2*S*, 3*R*)-2-(4-fluorophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3b):** White solid (0.059 g; 63%). M.p. 134-136 °C. **FTIR** (KBr, cm^{-1}): 3400, 2950, 2840, 1651, 1453, 1412, 1113, 1021. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.94 (d, *J* = 7.2 Hz, 1H), 8.29 (d, *J* = 8.6 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 2H), 7.49-7.40 (m, 2H), 7.29-7.23 (m, 2H), 5.29 (d, *J* = 4.4 Hz, 1H), 4.32-4.29 (m, 1H), 2.99-2.84 (dd, *J* = 6.8, 17.4 Hz, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 175.7 (C=O), 162.2 (d, $^1J_{C,F}$ = 242.9 Hz), 150.0, 146.8, 134.5, 128.7 (d, $^3J_{C,F}$ = 8.3 Hz), 128.2 (2C), 125.1 (2C), 116.1 (d, $^2J_{C,F}$ = 21.4 Hz), 87.4, 56.9, 37.5. $[\alpha]_D^{32}$ = −11.36 (c 0.1, Me_2CO) for 90% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 18.88 min and minor 12.92 min). HRMS (ESI) calcd for $C_{16}H_{13}FN_2O_6NaS$ 403.0376, m/z $[M+Na]^+$, found 403.0389.

***N*-((2*S*, 3*R*)-2-(4-chlorophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3c):** White solid (0.067 g; 68%). M.p. 146-148 °C. **FTIR** (KBr, cm^{-1}): 3391, 2952, 2839, 1648, 1453, 1411, 1111, 1051, 1015. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.92 (d, *J* = 6.8 Hz, NH), 8.21 (d, *J* = 8.6 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.45-7.26 (m, 4H), 5.10 (d, *J* = 7.2 Hz, 1H), 4.26-4.14 (m, 1H), 2.81-2.69 (dd, *J* = 7.2, 17 Hz, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 173.5 (C=O), 149.9, 146.5, 137.2, 134.1(2C), 129.4 (2C), 128.9, 128.4 (2C), 125.0 (2C), 83.4, 56.9, 37.2. $[\alpha]_D^{32}$ = −8.79 (c 0.09, Me_2CO) for 86% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 17.68 min and minor 10.23 min). HRMS (ESI) calcd for $C_{16}H_{12}ClN_2O_6S$ 395.0105, m/z $[M-H]^-$, found 395.0109.

***N*-((2*S*, 3*R*)-2-(2-chlorophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3d):** White solid (0.056 g; 57%). M.p. 122-124 °C. **FTIR** (KBr, cm^{-1}): 3437, 2952, 2841, 1647, 1452, 1410, 1151, 1112, 1017. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.96 (d, *J* = 8.6 Hz, 1H), 8.25 (d, *J* = 8 Hz, 2H), 7.86 (d, *J* = 8 Hz, 2H), 7.55-7.38 (m, 4H), 5.50 (d, *J* = 6.6 Hz, 1H), 4.59-4.54 (m, 1H), 2.93-2.80 (dd, J = 7, 17.4 Hz, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 173.7 (C=O), 149.9, 146.4, 135.1, 133.9, 132.9, 131.1, 129.3, 128.1 (2C), 127.1, 124.9

(2C), 85.7, 56.3, 36.8. $[\alpha]_D^{32}$ = −9.92 (c 0.1, Me_2CO) for 94% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 9.90 min and minor 10.61 min). HRMS (ESI) calcd for $C_{16}H_{12}ClN_2O_6S$ 395.0105, m/z $[M-H]^-$, found 395.0097.

***N*-((2*S*, 3*R*)-2-(2-bromophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3e):** White solid (0.061 g; 56%). M.p. 130-132 °C. **FTIR** (KBr, cm^{-1}): 3411, 2951, 2842, 1649, 1529, 1454, 1409, 1159, 1109, 1020. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.20 (d, *J* = 8.8 Hz, 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 7.39-7.16 (m, 4H), 5.50 (d, *J* = 4.8 Hz, 1H), 4.56 (d, *J* = 5.6 Hz, 1H), 4.09-4.08 (m, 1H), 2.89-2.83 (dd, *J* = 7.6, 17.6 Hz, 1H), 2.78-2.72 (dd, *J* = 6, 17.6 Hz, 1H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 173.8 (C=O), 150.1, 146.6, 135.6, 133.6, 131.6, 131.0, 129.7, 128.8 (2C), 127.5, 125.2 (2C), 83.4, 55.9, 35.8. $[\alpha]_D^{32}$ = −6.65 (c 0.09, Me_2CO) for 80% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 9.72 min and minor 10.74 min). HRMS (ESI) calcd for $C_{16}H_{12}BrN_2O_6S$ 438.9599, m/z $[M-H]^-$, found 438.9608.

***N*-((2*S*, 3*R*)-2-(3-bromophenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3f):** White solid (0.068 g; 62%). M.p. 168-170 °C. **FTIR** (KBr, cm^{-1}): 3400, 2950, 2842, 1653, 1454, 1412, 1114, 1020. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.98 (s, NH), 8.28 (d, *J* = 7.2 Hz, 2H), 7.88 (d, *J* = 7.4 Hz, 2H), 7.54-7.37 (m, 3H), 7.31-7.24 (m, 1H), 5.50 (d, *J* = 6.2 Hz, 1H), 4.40 (m, 1H), 2.91-2.79 (dd, *J* = 8, 17.6 Hz, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 173.7 (C=O), 149.9, 146.4, 135.4, 133.4, 131.4, 129.6, 128.7, 128.3 (2C), 125.0 (2C), 123.4, 83.3, 55.7, 35.6. $[\alpha]_D^{32}$ = −4.94 (c 0.1, Me_2CO) for 82% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 9.78 min and minor 10.47 min). HRMS (ESI) calcd for $C_{16}H_{13}BrN_2O_6NaS$ 462.9575, m/z $[M+Na]^+$, found 462.9575.

***N*-((2*S*, 3*R*)-2-(4-methoxyphenyl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzenesulfonamide (3g):** White solid (0.084 g; 87%). M.p. 164-166 °C. **FTIR** (KBr, cm^{-1}): 3427, 2948, 2845, 1646, 1530, 1451, 1410, 1277, 1113, 1049, 1018. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.86 (s, NH), 8.21 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.6 Hz, 2H), 7.17 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 6.8 Hz, 2H), 5.04 (d, *J* = 7.8 Hz, 1H), 4.25-4.21 (m, 1H), 3.73 (s, 3H), 2.88-2.75 (dd, J = 8.2, 17.6 Hz, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 173.8 (C=O), 160.3, 149.9, 146.7,

129.3 (2C), 128.4 (4C), 125.0 (2C), 114.4, 84.4, 56.9, 55.7, 36.5. $[\alpha]_D^{32}$ = −7.15 (c 0.09, Me_2CO) for 77% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 65/35, 0.8 ml/min, 254 nm, major 27.06 min and minor 17.56 min). HRMS (ESI) calcd for $C_{17}H_{16}N_2O_7NaS$ 415.0576, m/z $[M+Na]^+$, found 415.0585.

4-nitro-*N*-((2*S*,3*R*)-5-oxo-2-(*p*-tolyl)tetrahydrofuran-3-yl)benzenesulfonamide (3h): White solid (0.077 g; 83%). M.p. 126-128 °C. **FTIR** (KBr, cm^{-1}): 3390, 2953, 2843, 1652, 1534, 1454, 1412, 1353, 1169, 1053. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.66 (d, *J* = 8.6 Hz, NH), 8.26 (d, *J* = 8.6 Hz, 2H), 7.83 (d, *J* = 8.6 Hz, 2H), 7.00-6.87 (m, 4H), 5.47 (d, *J* = 8.8 Hz, 1H), 4.03-3.97 (m, 1H), 2.81-2.69 (dd, *J* = 7.0, 17.0 Hz, 2H), 2.19 (s, 3H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 171.8 (C=O), 149.8, 145.6, 139.0, 135.6, 129.4, 127.9, 127.9, 127.7, 124.3, 124.0, 84.4, 56.2, 36.2, 21.3. $[\alpha]_D^{32}$ = −7.33 (c 0.1, Me_2CO) for 88% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 13.04 min and minor 9.77 min). HRMS (ESI) calcd for $C_{17}H_{16}N_2O_6NaS$ 399.0627, m/z $[M+Na]^+$, found 399.0638.

***N*-((2*S*,3*R*)-2-(benzo[*d*][1,3]dioxol-5-yl)-5-oxotetrahydrofuran-3-yl)-4-nitrobenzene sulfonamide (3i):** Light yellow solid (0.082 g; 82%). M.p. 194-196 °C. **FTIR** (KBr, cm^{-1}): 3416, 2952, 2843, 1646, 1527, 1453, 1452, 1406, 1286, 1109, 1054, 1017. **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.84 (bs, NH), 8.23 (d, *J* = 8.8 Hz, 2H), 7.78 (d, *J* = 8.6 Hz, 2H), 6.73 (d, *J* = 8.0 Hz, 3H), 5.93 (s, 2H), 4.96 (d, *J* = 8.2 Hz, 1H), 4.22 (m, 1H), 2.84-2.71 (dd, *J* = 7.8, 16.8 Hz, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 173.6 (C=O), 149.9, 148.3, 147.8, 146.8, 130.3, 128.5, 124.9, 122.3, 108.6, 107.8, 101.9, 84.4, 56.8, 36.5. $[\alpha]_D^{32}$ = −9.81 (c 0.1, Me_2CO) for 85% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 17.69 min and minor 10.12 min). LCMS (ESI) m/z : 405.0 $[M-H]^+$, 424.4 $[M+NH_4]^+$.

4-nitro-*N*-((2*S*, 3*R*)-6-oxo-2-phenyltetrahydro-2*H*-pyran-3-yl)benzenesulfonamide (7a): White solid (0.078 g; 84%). M.p. 138-140 °C. **FTIR** (KBr, cm^{-1}): 3227, 2926, 2831, 1654, 1526, 1457, 1383, 1349, 1158, 1092, 1041. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.23-7.04 (m, 5H), 5.03 (d, *J* = 7.8 Hz, 2H), 3.74-3.54 (m, 1H), 2.78-2.68 (m, 2H), 2.38-2.29 (m, 1H), 2.03-1.93 (m, 1H). **^{1}H NMR** (d_6-DMSO, 200 MHz): δ 8.48 (s, NH), 8.11 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 8.6 Hz, 2H), 7.23-7.04 (m, 5H), 5.04 (d, *J* = 9.2 Hz, 1H), 3.78-3.66 (m, 1H), 2.62 (t, *J* = 5.4, 8.8 Hz, 2H), 1.92-1.76 (m, 2H).

^{13}C NMR (d_6-DMSO, 100 MHz): δ 170.4 (C=O), 149.8, 147.2, 137.8, 128.7 (2C), 128.3 (2C), 128.1 (2C), 126.8, 125.1(2C), 82.9, 52.8, 30.2, 28.5. $[\alpha]_D^{32}$ = −18.20 (c 0.6, Me_2CO) for 89% ee (**HPLC:** Daicel Chiralpak IA(particle size 5µm), hexane/EtOAc = 60/40, 1.0 ml/min, 254 nm, major 9.43 min and minor 10.52 min). HRMS (ESI) calcd for $C_{17}H_{16}N_2O_6NaS$ 399.0627, m/z $[M+Na]^+$, found 399.0628.

***N*-((2*S*, 3*R*)-2-(4-fluorophenyl)-6-oxotetrahydro-2*H*-pyran-3-yl)-4-nitrobenzenesulfon amide (7b):** White solid (0.077 g; 79%). M.p. 102-104 °C. **FTIR** (KBr, cm^{-1}): 3413, 2967, 2844, 1646, 1534, 1455, 1412, 1168, 1113, 1016. **^{1}H NMR** (d_6-DMSO, 200 MHz):): δ 8.54 (d, *J* = 8.6 Hz, NH), 8.18 (d, *J* = 7.4 Hz, 2H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.6, 5.6 Hz, 2H), 6.92 (t, *J* = 8.6, 8 Hz, 2H), 5.06 (d, *J* = 9.6 Hz, 1H), 3.85-3.68 (m, 1H), 2.63 (t, *J* = 6, 5.6 Hz, 2H), 1.97-1.89 (m, 2H). **^{13}C NMR** (d_6-DMSO, 50 MHz): δ 170.8 (C=O), 162.4 (d, $^1J_{C,F}$ = 241.5 Hz), 149.4, 146.9, 135.3, 129.5 (d, $^3J_{C,F}$ = 8 Hz), 127.9 (2C), 124.7 (2C), 115.4 (d, $^2J_{C,F}$ = 20.5 Hz), 84.2, 52.7, 28.5, 26.6. $[\alpha]_D^{32}$ = −34.82 (c 0.5, Me_2CO) for 92% ee (**HPLC:** Daicel Chiralpak IC(particle size 5µm), hexane/EtOAc = 60/40, 1.0 ml/min, 254 nm, major 13.66 min and minor 11.95 min). HRMS (ESI) calcd for $C_{17}H_{15}FN_2O_6NaS$ 417.0533, m/z $[M+Na]^+$, found 417.0546.

***N*-((2*S*, 3*R*)-2-(4-chlorophenyl)-6-oxotetrahydro-2*H*-pyran-3-yl)-4-nitrobenzenesulfon amide (7c):** White solid (0.078 g; 77%). M.p. 131-133 °C. **FTIR** (KBr, cm^{-1}): 3388, 2950, 2838, 1654, 1534, 1451, 1412, 1169, 1112, 1020. **^{1}H NMR** (d_6-DMSO, 200 MHz):): δ 8.62 (d, *J* = 8.8 Hz, NH), 8.21 (d, *J* = 8.8 Hz, 2H), 7.67 (d, *J* = 8.8 Hz, 2H), 7.25-7.13 (m, 4H), 5.09 (d, *J* = 9.8 Hz, 1H), 3.87-3.65 (m, 1H), 2.71 (t, *J* = 7.2, 6.6 Hz, 2H), 2.03-1.93 (m, 2H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 170.4 (C=O), 149.5, 147.1, 136.9, 134.1, 129.8, 128.5, 128.1, 124.8, 81.7, 55.4, 28.7, 27.7. $[\alpha]_D^{32}$ = −22.73 (c 0.5, Me_2CO) for 84% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 14.05 min and minor 19.95 min). HRMS (ESI) calcd for $C_{17}H_{15}ClN_2O_6NS$ 410.0339, m/z $[M]^+$, found 410.0317.

***N*-((2*S*, 3*R*)-2-(2-bromophenyl)-6-oxotetrahydro-2*H*-pyran-3-yl)-4-nitrobenzenesulfon amide (7d):** White solid (0.082 g; 73%). M.p. 162-164 °C. **FTIR** (KBr, cm^{-1}): 3408, 2950, 2842, 1647, 1531, 1452, 1413, 1162, 1019. **^{1}H NMR** (d_6-DMSO, 400 MHz):): δ 8.61 (d, *J* = 8.8 Hz, NH), 8.22 (d, *J* = 8.8 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 2H), 7.46-7.37 (m, 2H), 7.29-7.26 (m, 1H), 7.17-7.13 (m, 1H), 5.43 (d, *J* = 9.2 Hz, 1H), 4.00-3.92 (m, 1H), 2.66 (t, *J* = 6.8, 7.2

Hz, 2H), 1.97-1.89 (m, 1H), 1.87-1.78 (m, 1H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ 169.8 (C=O), 149.8, 147.0, 136.4, 133.3, 130.9, 130.6, 128.3, 128.2, 124.9, 123.3, 81.9, 51.5, 28.3, 26.0. $[\alpha]_D^{32}$ = −21.80 (c 0.5, Me_2CO) for 88% ee (**HPLC:** Daicel Chiralpak IA(particle size 3μm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 11.29 min and minor 12.00 min). LCMS (ESI) m/z : 454.9 $[M+H]^+$, 472.4 $[M+NH_4]^+$.

4-nitro-*N*-((*R*)-1-((S)-3-oxo-1, 3-dihydroisobenzofuran-1-yl)propyl)benzenesulfonamide (10): Light Yellow solid (0.070 g; 75%). M.p. 228-230 °C. **FTIR** (KBr, cm^{-1}): 3385, 2951, 2835, 1654, 1455, 1420, 1113, 1023. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.32 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 8.4 Hz, 2H), 8.00-7.97 (m, 1H), 7.69-7.65 (m, 1H), 7.59-7.46 (m, 2H), 5.40 (d, *J* = 4.8 Hz, 1H), 4.64-4.61 (m, 1H), 3.89-3.84 (m, 1H), 1.69-1.46 (m, 2H), 0.94 (t, *J* = 7.2,7.6 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.7 (C=O), 163.7, 149.9, 146.9, 136.2, 134.5, 130.4, 129.7, 128.8, 128.4(2C), 124.3 (2C), 83.8, 52.6, 29.6, 25.7. $[\alpha]_D^{32}$ = −22.65 (c 0.2, Me_2CO) for 79% ee (**HPLC:** Daicel Chiralpak IA(particle size 5μm), hexane/EtOAc = 65/35, 1.0 ml/min, 254 nm, major 15.02 min and minor 11.17 min). HRMS (ESI) calcd for $C_{17}H_{16}N_2O_6NaS$ 399.0627, m/z $[M+Na]^+$, found 399.0624.

(3*R*,5*R*,6*S*)-*tert*-butyl 3-methyl-5-(4-nitrophenylsulfonamido)-2-oxo-6-phenyltetrahydro-2*H*-pyran-3-carboxylate (13a): White solid (0.103 g; 85%). M.p. 160-162 °C. **FTIR** (KBr, cm^{-1}): 3434, 2952, 2842, 1647, 1532, 1452, 1406, 1163, 1113, 1052, 1017. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.99 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.08 (s, 5H), 4.91-4.86 (m, 1H & NH), 3.91-3.88 (m, 1H), 2.71 (d, *J* = 12.8 Hz, 1H), 1.97 (t, *J* = 13.0, 13.8 Hz, 1H), 1.58 (s, 9H), 1.54 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.6 (C=O), 169.1 (C=O), 149.9, 145.2, 136.2, 129.6, 128.9, 127.9, 127.4, 124.3, 84.9, 84.2, 52.3, 51.7, 40.5, 28.0, 23.1. $[\alpha]_D^{32}$ = −61.32 (c 0.5, Me_2CO) for 90% ee (**HPLC:** Daicel Chiralpak IA(particle size 3μm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 7.74 min and minor 8.53 min). HRMS (ESI) calcd for $C_{23}H_{26}N_2O_8NaS$ 513.1308, m/z $[M+Na]^+$, found 513.1320.

(3*R*,5*R*,6*S*)-*tert*-butyl 3-methyl-5-(4-nitrophenylsulfonamido)-2-oxo-6-(*p*-tolyl)tetra hydro-2*H*-pyran-3-carboxylate (13b): White solid (0.109 g; 87%). M.p. 132-134 °C. **FTIR** (KBr, cm^{-1}): 3392, 2948, 2836, 1653, 1453, 1413, 1114, 1032. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.49 (d, *J* = 9.0 Hz, 2H), 6.99-6.88 (m, 4H), 4.85 (d, *J* = 10.4 Hz, 1H), 4.69 (d, *J* = 7.2 Hz, 1H), 3.87 (m, 1H), 2.81-2.72 (dd, *J* = 4.8, 14.4 Hz, 1H), 2.28 (s, 3H), 1.974 (t, *J* = 13, 14.4,1H), 1.59 (s, 9H), 1.56 (s, 3H). **^{13}C NMR** (d_6-DMSO, 100 MHz): δ

171.2 (C=O), 161.1 (C=O), 149.8, 146.9, 138.8, 134.6, 129.3, 127.9, 127.8, 127.6, 125.1, 124.9, 83.8, 83.4, 51.0, 51.6, 28.1, 22.9, 21.1. $[\alpha]_D^{32}$ = −34.54 (c 0.3, Me_2CO) for 96% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 8.59 min and minor 10.23 min). HRMS (ESI) calcd for $C_{24}H_{28}N_2O_8NaS$ 527.1464, m/z $[M+Na]^+$, found 527.1472.

(3*R*,5*R*,6*S*)-*tert*-butyl 6-(4-fluorophenyl)-3-methyl-5-(4-nitrophenylsulfonamido)-2-oxo tetrahydro-2*H*-pyran-3-carboxylate (13c): White solid (0.102 g; 81%). M.p. 146-148 °C. **FTIR** (KBr, cm^{-1}): 3435, 2953, 2844, 1641, 1532, 1455, 1349, 1162, 1119, 1053, 1016. **^{1}H NMR** ($CDCl_3$, 200 MHz):): δ 8.09 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.12-7.05 (m, 2H), 6.78 (t, *J* = 8.4, 8.6 Hz, 2H), 5.11 (d, *J* = 8.6 Hz, 1H), 4.91 (d, *J* = 10.4, 1H), 3.89-3.85 (m, 1H), 2.65-2.56 (dd, *J* = 3.4, 13.6, 1H),1.96 (t, *J* = 12.8, 13.0 Hz, 1H), 1.58 (s, 9H), 1.51 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.4 (C=O), 168.9 (C=O), 163.4 (d, $^1J_{C,F}$ = 266.4 Hz), 150.0, 145.6, 132.3, 129.3 (d, $^3J_{C,F}$ = 8.4 Hz), 128.0 (2C), 124.3 (2C), 115.9 (d, $^2J_{C,F}$ = 21.7 Hz), 84.3, 52.5, 51.8, 40.4, 28.1, 23.0. $[\alpha]_D^{32}$ = −66.32 (c 0.1, Me_2CO) for 98% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 7.56 min and minor 8.28 min). LCMS (ESI) m/z : 526.0 $[M+NH_4]^+$.

(3*R*,5*R*,6*S*)-*tert*-butyl 6-(2-bromophenyl)-3-methyl-5-(4-nitrophenylsulfonamido)-2-oxo tetrahydro-2*H*-pyran-3-carboxylate (13d): White solid (0.111 g; 79%). M.p. 126-128 °C. **FTIR** (KBr, cm^{-1}): 3426, 2950, 2841, 1651, 1531, 1454, 1350, 1163, 1111, 1018. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.98 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.11 (t, *J* = 6.8, 7.6 Hz, 1H), 7.00 (t, *J* = 7.2, 7.6 Hz, 1H), 5.52 (d, *J* = 8.0 Hz, 1H), 5.09 (d, *J* = 4.4 Hz, 1H), 3.98 (bs, 1H), 2.70 (d, *J* = 11.2 Hz, 1H, 1H), 2.09 (m, 1H), 1.59 (s, 9H), 1.57 (s, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 170.1 (C=O), 168.3 (C=O), 149.8, 145.1, 136.2, 132.5, 130.6, 128.8, 128.3, 127.5, 124.1, 123.1, 84.1, 81.7, 53.4, 51.6, 41.1, 27.9, 22.9. $[\alpha]_D^{32}$ = −94.19 (c 0.7, Me_2CO) for 94% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/EtOAc = 50/50, 0.5 ml/min, 254 nm, major 7.58 min and minor 9.17 min). HRMS (ESI) calcd for $C_{23}H_{25}BrN_2O_8NaS$ 591.0413, m/z $[M+Na]^+$, found 591.0421.

G) Spectral Data of alkenoic acid esters (1a-i, 8, 5a-d, 11a-d and 1a′):

(*E*)-*tert*-butyl 4-phenylbut-3-enoate (1a): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.34-7.16 (m, 5H), 6.37 (d, *J* = 15.6 Hz, 1H), 6.25-6.10 (m, 1H), 3.05 (d, *J* = 6.8 Hz, 2H), 1.37 (s, 9H).

(*E*)-*tert*-butyl 4-(4-chlorophenyl)but-3-enoate (1c): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.41-7.23 (m, 4H), 6.42 (d, *J* = 16.4 Hz, 1H), 6.33-6.18 (m, 1H), 3.15 (d, *J* = 6.6 Hz, 2H), 1.46 (s, 9H).

(*E*)-*tert*-butyl 4-(4-fluorophenyl)but-3-enoate (1b): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.38-7.25 (m, 2H), 7.12-7.09 (m, 2H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.26-6.12 (m, 1H), 3.14 (d, *J* = 7 Hz, 2H), 1.47 (s, 9H).

(*E*)-*tert*-butyl 4-(2-chlorophenyl)but-3-enoate (1d): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.39-7.15 (m, 4H), 6.85 (d, *J* = 16 Hz, 1H), 6.40-6.21 (m, 1H), 3.21 (d, *J* = 7 Hz, 2H), 1.48 (s, 9H).

(*E*)-*tert*-butyl 4-(2-bromophenyl)but-3-enoate (1e): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.40-7.23 (m, 3H), 7.15-6.97 (m, 1H), 6.83 (d, *J* = 15.6 Hz, 1H), 6.34-6.24 (m, 1H), 3.24-3.22 (dd, *J* = 1.6, 7.2 Hz, 2H), 1.49 (s, 9H).

(*E*)-*tert*-butyl 4-(3-bromophenyl)but-3-enoate (1f): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.39-7.12 (m, 4H), 6.44-6.21 (m, 2H), 3.15 (d, *J* = 5.6 Hz, 2H), 1.47 (s, 9H).

(*E*)-*tert*-butyl 4-(4-methoxyphenyl)but-3-enoate (1g): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.30 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 6.41 (d, *J* = 15.8 Hz, 1H), 3.80 (s, 3H), 3.12 (d, *J* = 6.8 Hz, 2H), 1.46 (s, 9H).

(*E*)-*tert*-butyl 4-(*p*-tolyl)but-3-enoate (1h): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.30-7.10 (m, 4H), 6.45 (d, *J* = 15.8 Hz, 1H),6.32-6.17 (m, 1H), 3.16 (d, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.48 (s, 9H).

(*E*)-*tert*-butyl 4-(benzo[*d*][1,3]dioxol-5-yl)but-3-enoate (1i): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 6.93 (s, 1H), 6.88-6.72 (m, 2H), 6.38 (d, *J* = 16.0 Hz, 1H), 6.18-6.07 (m, 1H), 5.92 (s, 2H), 3.13 (d, *J* = 7.0 Hz, 2H), 1.47 (s, 9H).

***tert*-butyl 2-(but-1-en-1-yl)benzoate (8):** *E* :*Z* = 82 : 18. Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.84 (d, *J* = 7.4 Hz, 0.22H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.52-7.19 (m, 3.66H), 7.05 (d, *J* = 15.6 Hz, 1H), 6.77 (d, *J* = 11.6 Hz, 0.22H), 6.21-6.07 (m, 1H), 5.75-5.39 (m, 0.22H), 2.30-2.09 (m, 2.44H), 1.59 (s, 9H), 1.14 (t, *J* = 7.4, 7.4 Hz, 3H), 1.03 (t, *J* = 7.4, 7.4 Hz, 0.66H).

(*E*)-*tert*-butyl 5-phenylpent-4-enoate (5a): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.35-7.16 (m, 5H), 6.42 (d, *J* = 15.8 Hz, 1H), 6.27-6.16 (m, 1H), 2.51-2.34 (m, 4H), 1.45 (s, 9H).

(*E*)-*tert*-butyl 5-(4-fluorophenyl)pent-4-enoate (5b): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.33-7.24 (m, 2H), 7.08-6.92 (m, 2H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.17-6.03 (m, 1H), 2.50-2.33 (m, 4H), 1.44 (s, 9H).

(*E*)-*tert*-butyl 5-(4-chlorophenyl)pent-4-enoate (5c): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.39-7.25 (m, 4H), 6.38 (d, *J* = 15.8 Hz, 1H), 6.25-6.14 (m, 1H), 2.55-2.35 (m, 4H), 1.45 (s, 9H).

(*E*)-*tert*-butyl 5-(2-bromophenyl)pent-4-enoate (5d): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.55-7.46 (m, 2H), 7.28-7.21 (m, 1H), 7.11-7.03 (m, 1H), 6.76 (d, *J* = 15.6 Hz, 1H), 6.24-6.09 (m, 1H), 2.56-2.43 (m, 4H), 1.47 (s, 9H).

di-*tert*-butyl 2-cinnamyl-2-methylmalonate (11a): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.32-7.23 (m, 5H), 6.45 (d, *J* = 15.8 Hz, 1H), 6.19-6.05 (m, 1H), 2.69 (d, *J* = 7.4 Hz, 2H), 1.46 (s, 9H), 1.37 (s, 3H).

(*E*)-di-*tert*-butyl 2-(3-(2-bromophenyl)allyl)-2-methylmalonate (11d): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.50 (t, *J* = 7.8, 11 Hz, 2H), 7.24-7.21 (m, 1H), 7.11-7.04 (m, 1H), 6.79 (d, *J* = 15.6 Hz, 1H), 6.16-6.00 (m, 1H), 2.74 (d, *J* = 7.6 Hz, 2H), 1.46 (s, 9H), 1.38 (s, 3H).

(*E*)-di-*tert*-butyl 2-methyl-2-(3-(*p*-tolyl)allyl)malonate (11c): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.30-7.15 (m, 4H), 6.44 (d, *J* = 15.8 Hz, 1H), 6.16-6.01 (m, 1H), 2.70 (d, *J* = 7.4 Hz, 2H), 2.36 (s, 3H), 1.49 (s, 9H), 1.39 (s, 3H).

(*E*)-di-*tert*-butyl 2-(3-(4-fluorophenyl)allyl)-2-methylmalonate (11b): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.35-7.28 (m, 2H), 7.01 (t, *J* = 8.8, 8.6 Hz, 2H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.14-5.99 (m, 1H), 2.70 (d, *J* = 7.0 Hz, 2H), 1.49 (s, 9H), 1.39 (s, 3H).

(*E*)-methyl 4-phenylbut-3-enoate (1a′): Light yellow oil. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.49-7.24 (m, 5H), 6.51 (d, *J* = 15.8 Hz, 1H), 6.38-6.23 (m, 1H), 3.73 (s, 3H), 3.29 (d, *J* = 6.8 Hz, 2H).

H) Synthesis and Spectral Data of compounds 14-16 and 2a′:

(4*R*, 5*S*)-4-amino-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one (14):To a well stirred solution of **3g** (0.16 g, 0.408 mmol) taken in 3 mL CH_3CN:DMSO (49:1) at rt, 1.1 equiv 4-methoxythiophenol (0.055mL, 0.449 mmol) and 1.1 equiv of K_2CO_3 (0.62 g, 0.449 mmol) were added and the reaction mixture was allowed to stir for 4 h. Upon completion of the reaction the reaction mixture was filtered using MeOH as an eluent. Solvent was evaporated under reduced pressure and the crude yellow oil was immediately used in the next step.

***tert*-butyl ((2*S*, 3*R*)-2-(4-methoxyphenyl)-5-oxotetrahydrofuran-3-yl)carbamate (15):** The crude yellow oil was taken in 10 mL dry THF. 3.3 equiv of BOC_2O (0.309 mL, 1.346 mmol) was added and the reaction mixture was allowed to stir for overnight. Solvent was evaporated under reduced pressure and 20 mL of EtOAc was added. The organic layer washed with H_2O (2 X 15 mL) and the dried over Na_2SO_4. Concentration and column chromatography (20% EtOAc in hexane) gave titled compound **15** as white solid (0.102 g, yield 82% in overall two steps). M.p. 112-114 °C. **^{1}H NMR** ($CDCl_3$, 200 MHz): δ 7.35-7.27 (m, 2H), 6.95-6.90 (m, 2H), 5.41 (bs, NH), 4.91 (d, J = 5.6 Hz, 1H), 4.27 (m, 1H), 3.83 (s, 3H), 3.03-2.86 (dd, *J* = 7.8, 25.6 Hz, 1H), 2.55-2.44 (dd, *J* = 4.8, 17.8 Hz, 1H), 1.45 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 173.5 (C=O), 159.9, 128.9 (2C), 126.8 (2C), 114.4, 86.1, 78.5, 56.6, 55.5, 34.4, 28.4.

(*S*)-3-((*tert*-butoxycarbonyl)amino)-4-(4-methoxyphenyl)butanoic acid (16): Compound **15** (0.1 g, 0.16 mmol) was taken in 4 mL MeOH. After addition of 10% Pd-C (0.1 equiv), the reaction mixture was purged with H_2 and the reaction mixture was stirred under the H_2 atmosphere for 1.5 h. On completion, the mixture was passed through a celite pad, washed with MeOH (3 x 20 mL), on solvent evaporation pure compound **16** was obtained as a colourless solid (0.097 g, yield 96%). M.p. 102-104 °C. **^{1}H NMR** (CD_3OD, 200 MHz): δ 7.12 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8 Hz, 2H), 4.11-4.04 (m, 1H), 3.76 (s, 3H), 2.71(m, 2H), 2.48 (m, 2H), 1.37 (s, 9H). **^{13}C NMR** (CD_3OD, 50 MHz): δ 173.9 (C=O), 158.6, 156.6, 130.4, 130.2, 113.6, 78.8, 54.4, 41.6, 39.7, 27.8.[6] $[\alpha]_D^{26}$ = −17.4 (*c* 1.1, EtOH), [Lit[7]. $[\alpha]_D^{20}$ = −18.7 (*c* 1, EtOH)].

methyl 2-((2*R*,3*R*)-1-((4-nitrophenyl)sulfnyl)-3-phenylazirdin-2-yl)acetate (2a′): White solid (0.054 g, 61% yield). M.p. 138-140 °C. **^{1}H NMR** ($CDCl_3$, 200 MHz):): δ 8.26 (d, *J* = 8.6 Hz, 2H), 8.07 (d, *J* = 8.8 Hz, 2H), 7.22-7.02 (m, 5H), 4.09 (d, *J* = 3.8 Hz, 1H), 3.71 (s, 3H), 3.22-3.03 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz): δ 171.9 (C=O), 151.0, 147.1, 141.3, 135.5, 128.6, 128.4, 127.6, 126.3, 54.7, 52.2, 50.9, 38.3. $[\alpha]_D^{32}$ = −12.11 (c 0.18, Me_2CO) for 72% ee (**HPLC:** Daicel Chiralpak IA(particle size 3µm), hexane/^{i}PrOH = 85/15, 1.0 ml/min, 254 nm, major 13.56 min and minor 9.58 min).

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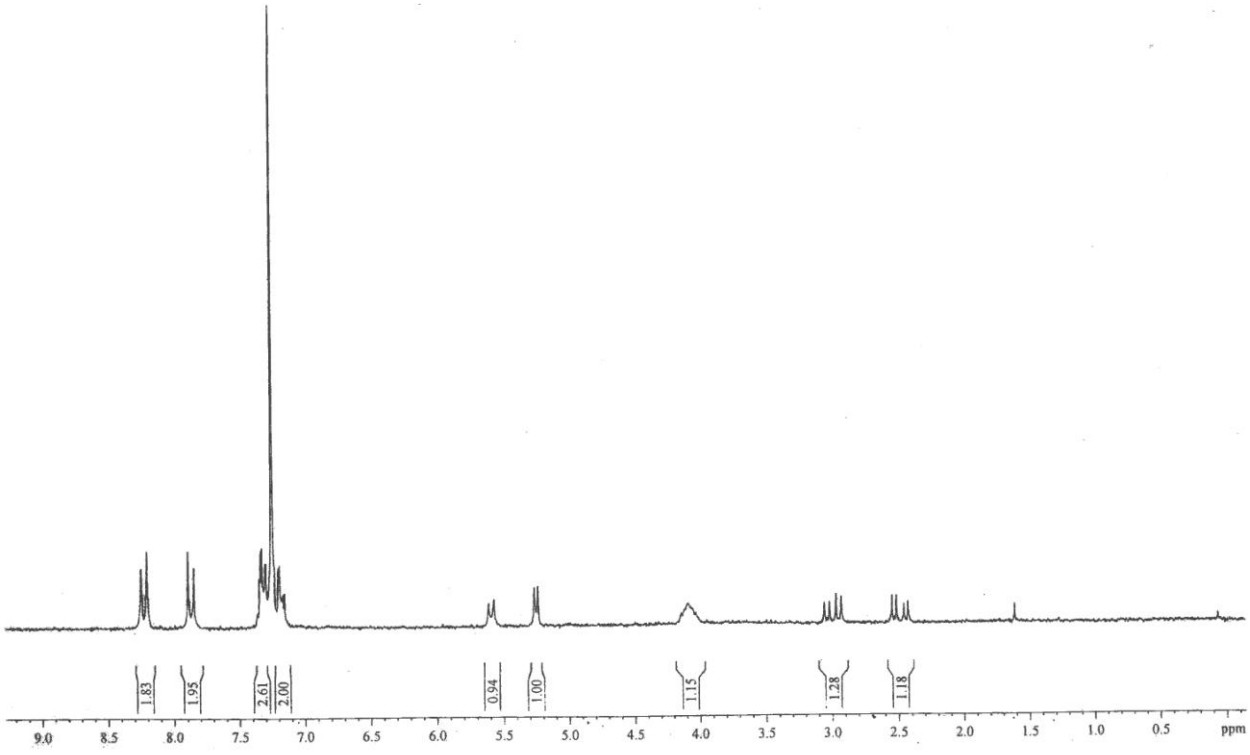
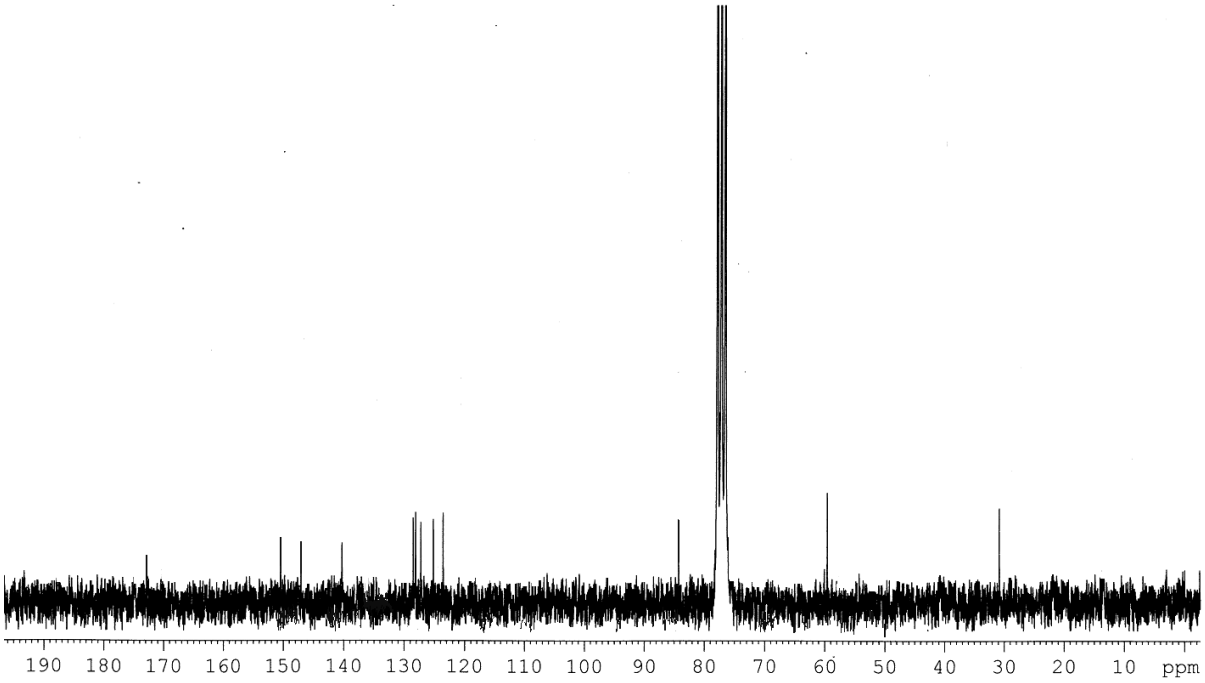
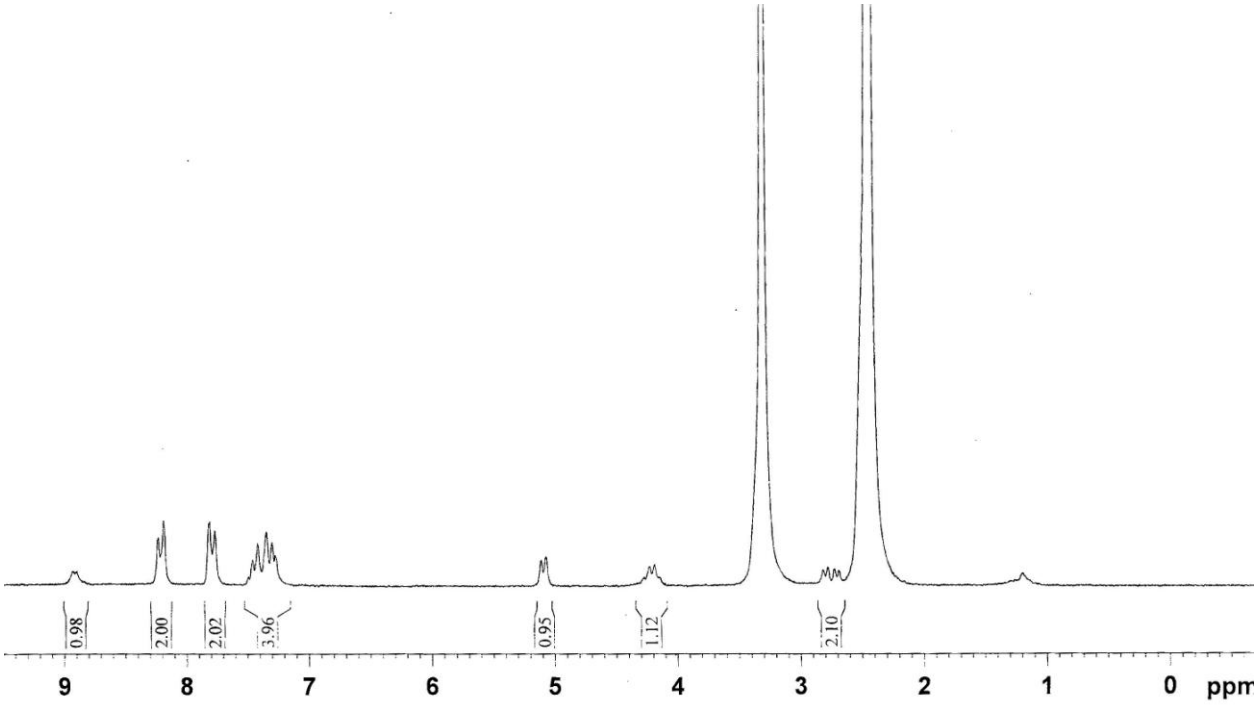
J) NMR Spectra:



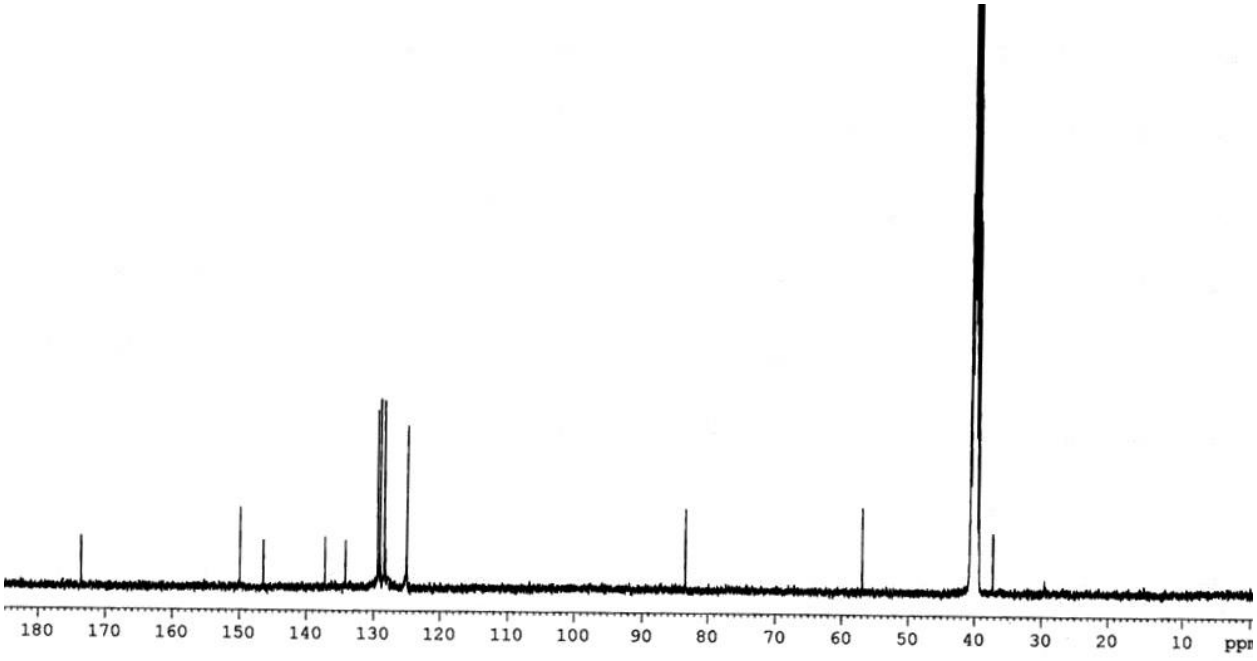
^{1}H NMR of compound **3a** (200 MHz, $CDCl_3$)



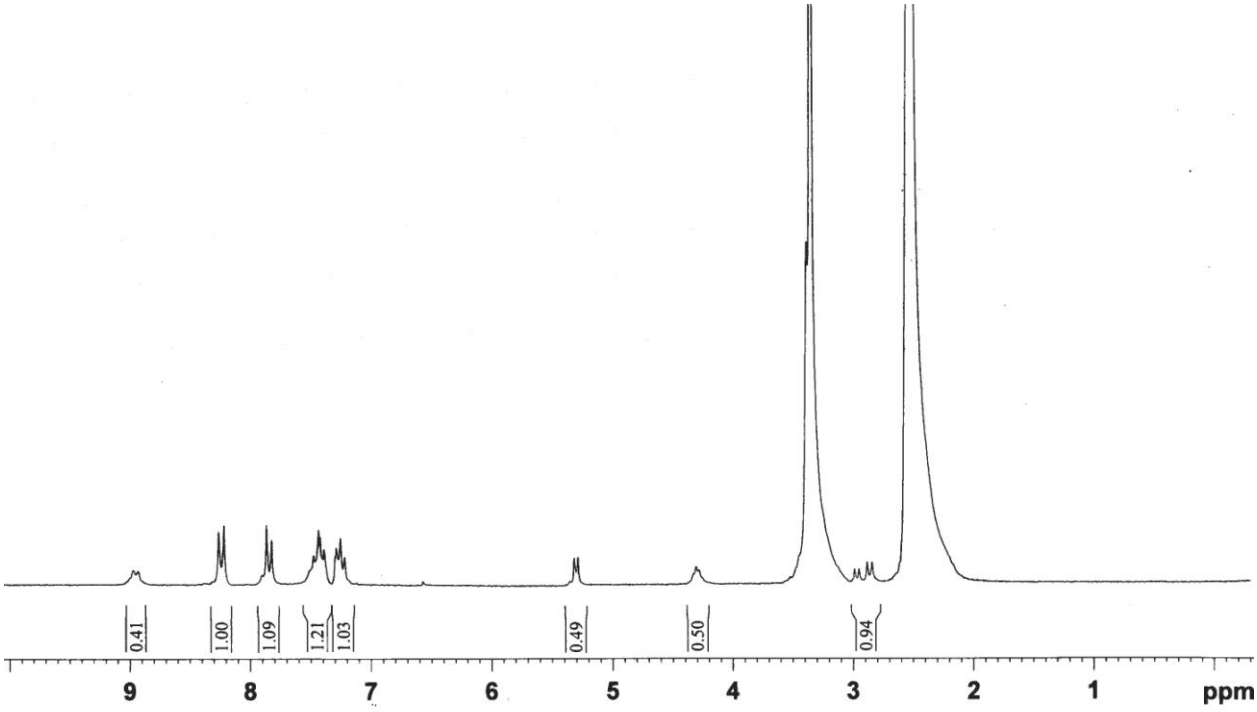
^{13}C NMR of compound **3a** (50 MHz, $CDCl_3$)



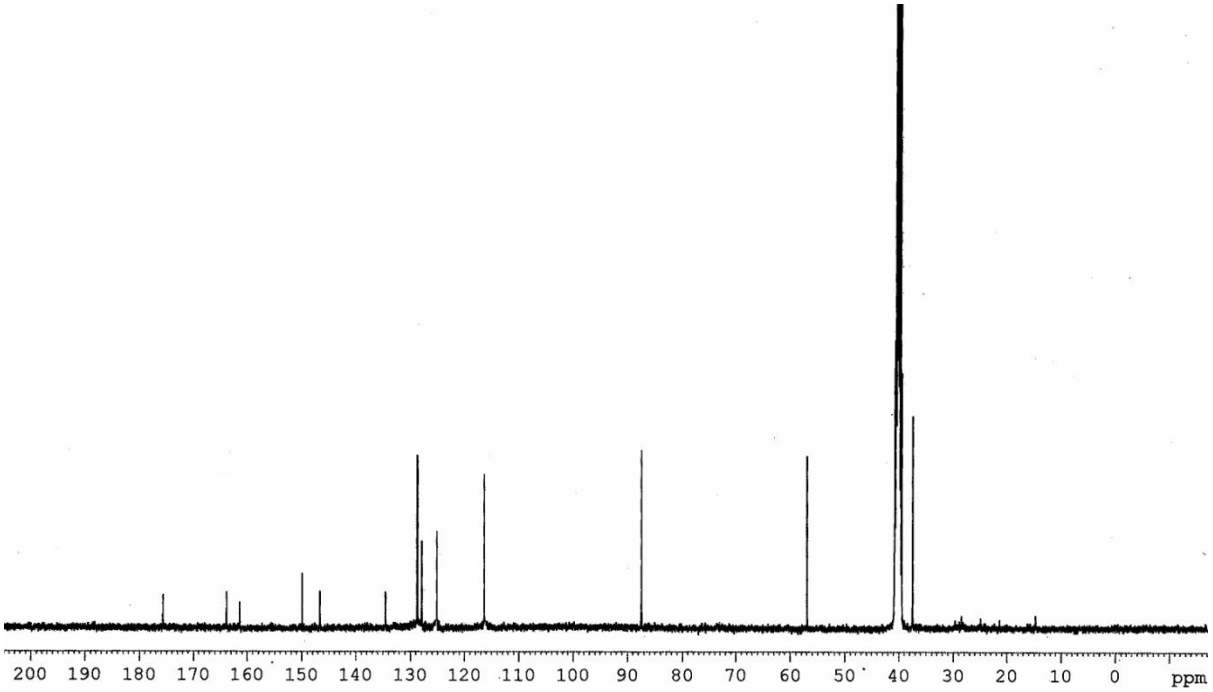
^{1}H NMR of compound **3c** (200 MHz, d_6-DMSO)



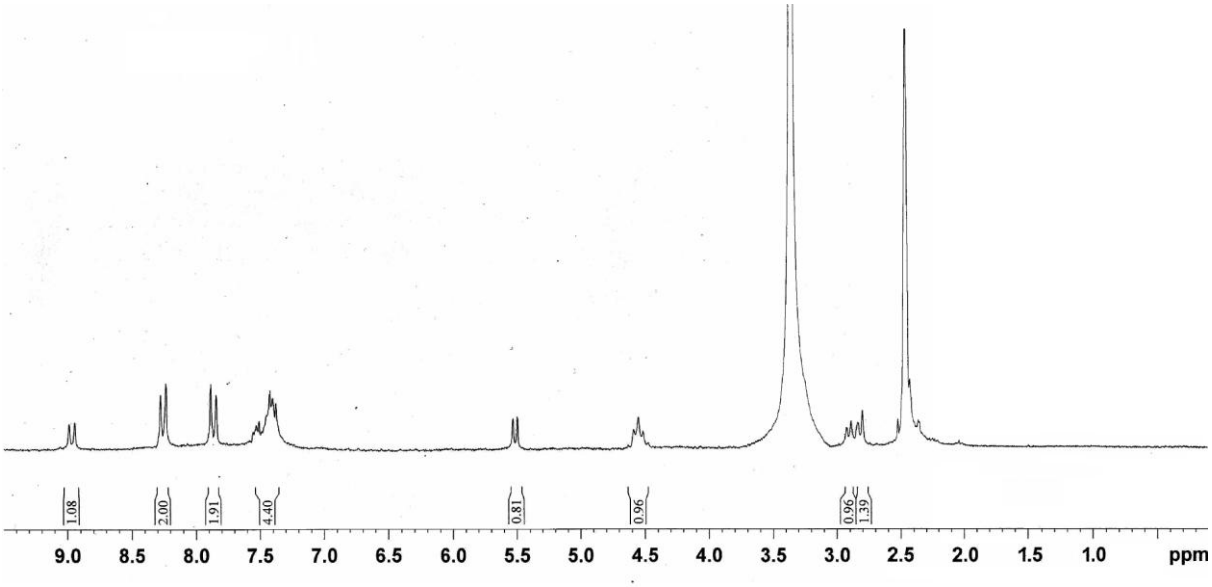
^{13}C NMR of compound **3c** (100 MHz, d_6-DMSO)



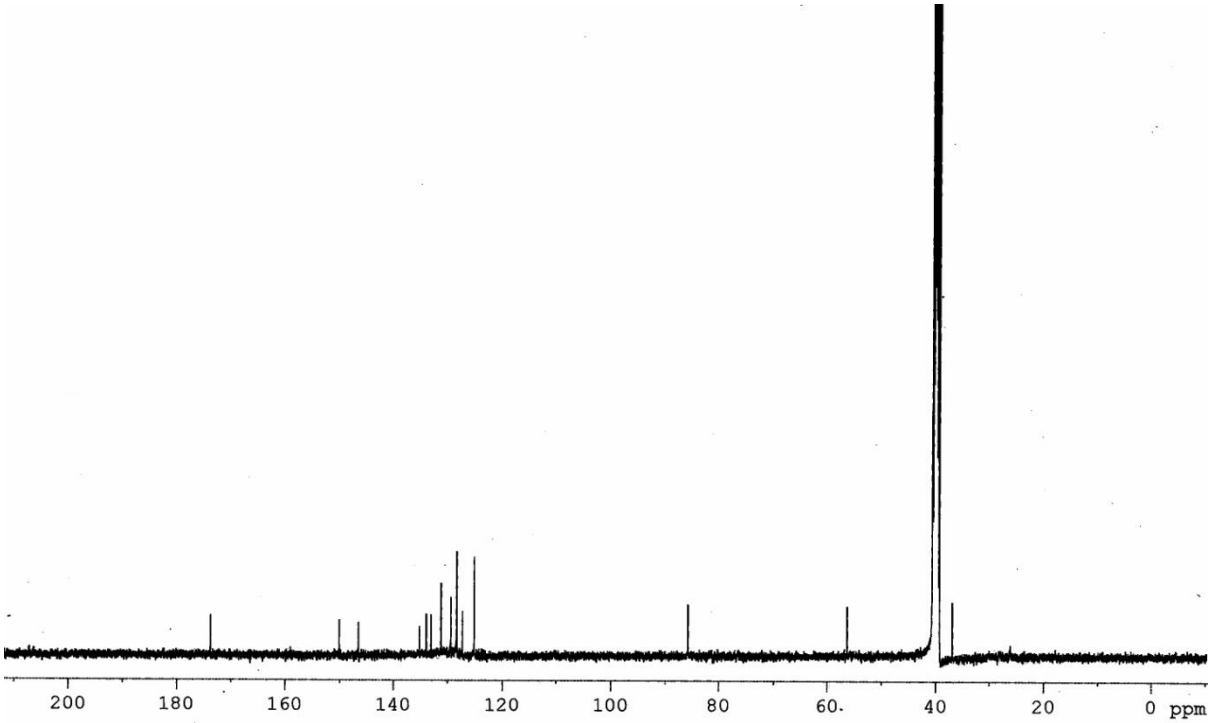
^{1}H NMR of compound **3b** (200 MHz, $CDCl_3$)



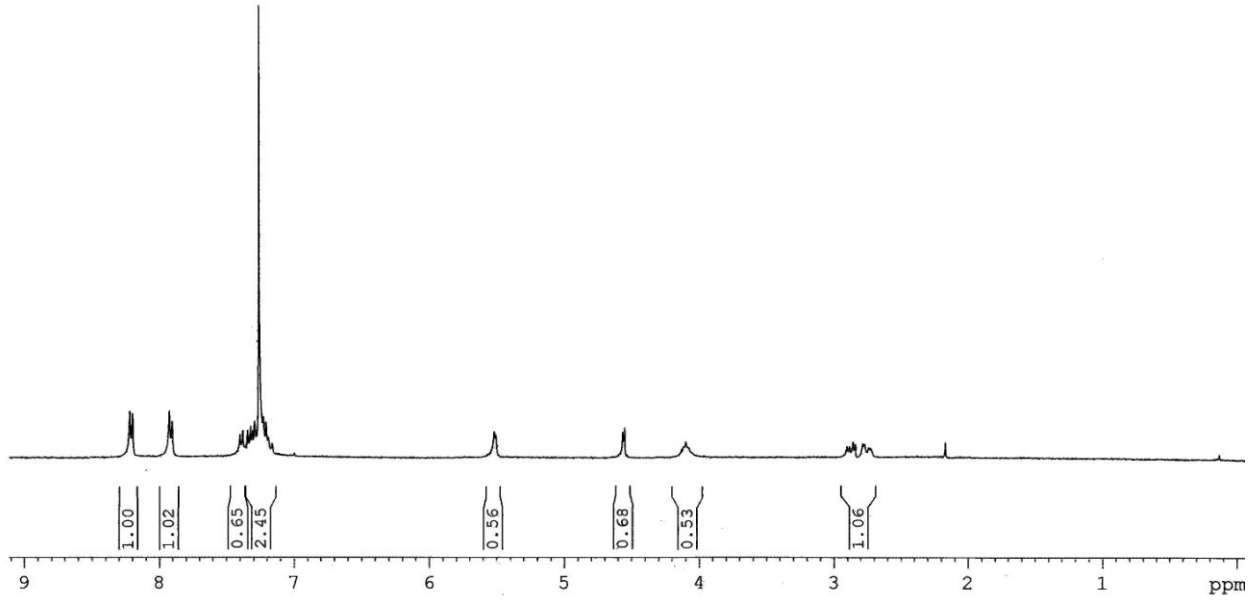
^{13}C NMR of compound **3b** (100 MHz, d_6-DMSO)



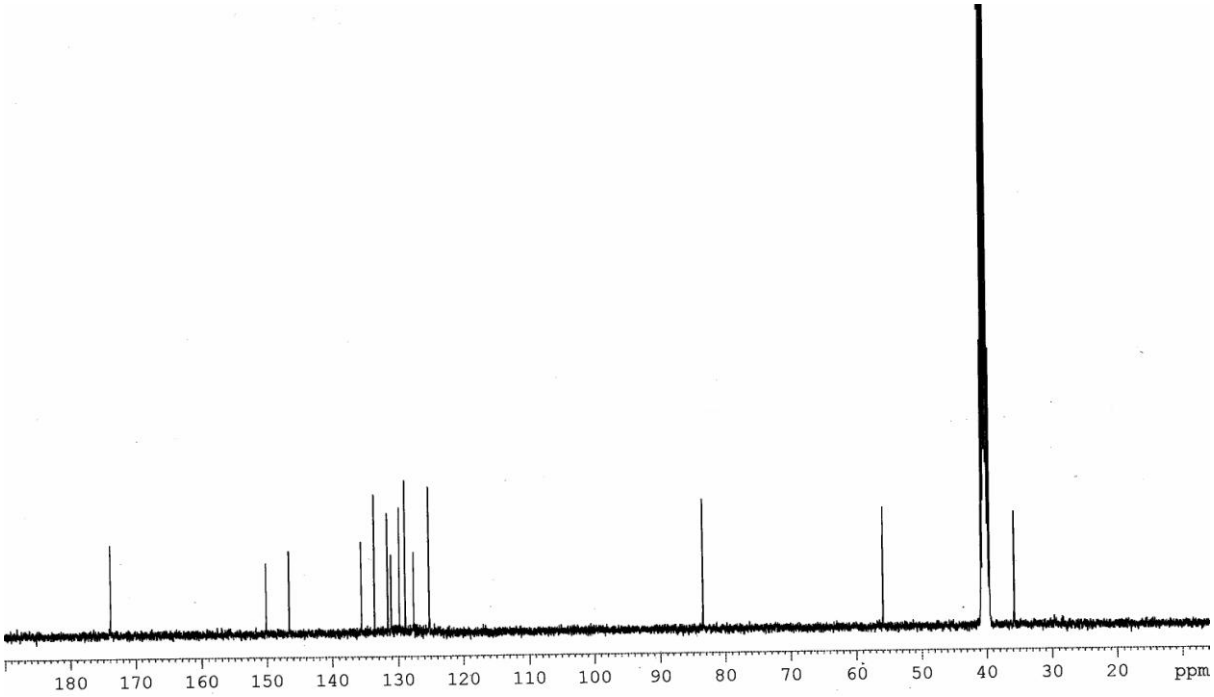
^{1}H NMR of compound **3d** (200 MHz, d_6-DMSO)



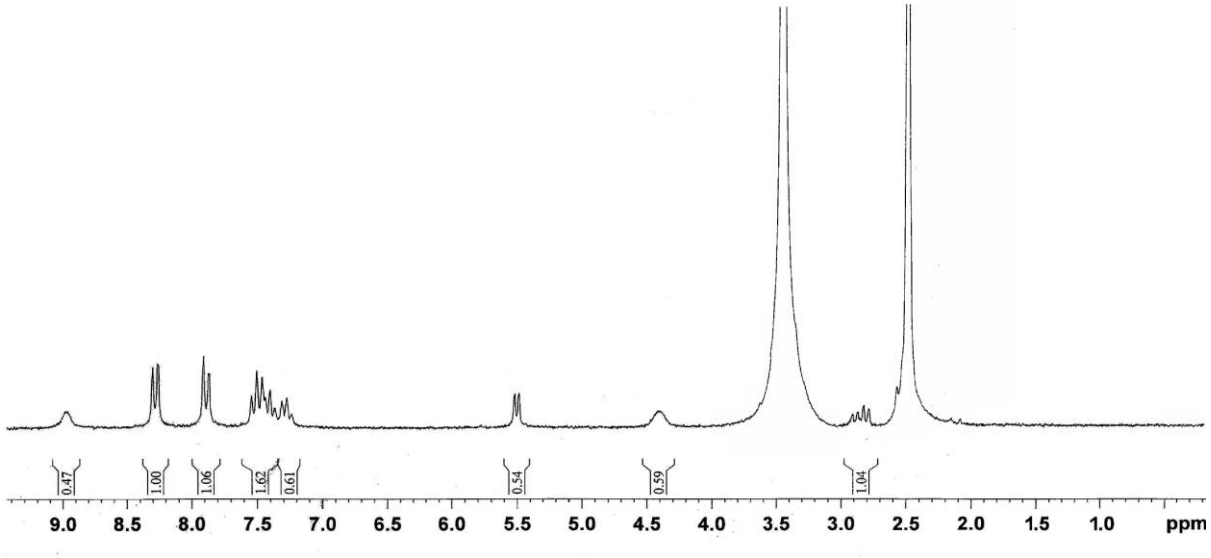
^{13}C NMR of compound **3d** (100 MHz, d_6-DMSO)



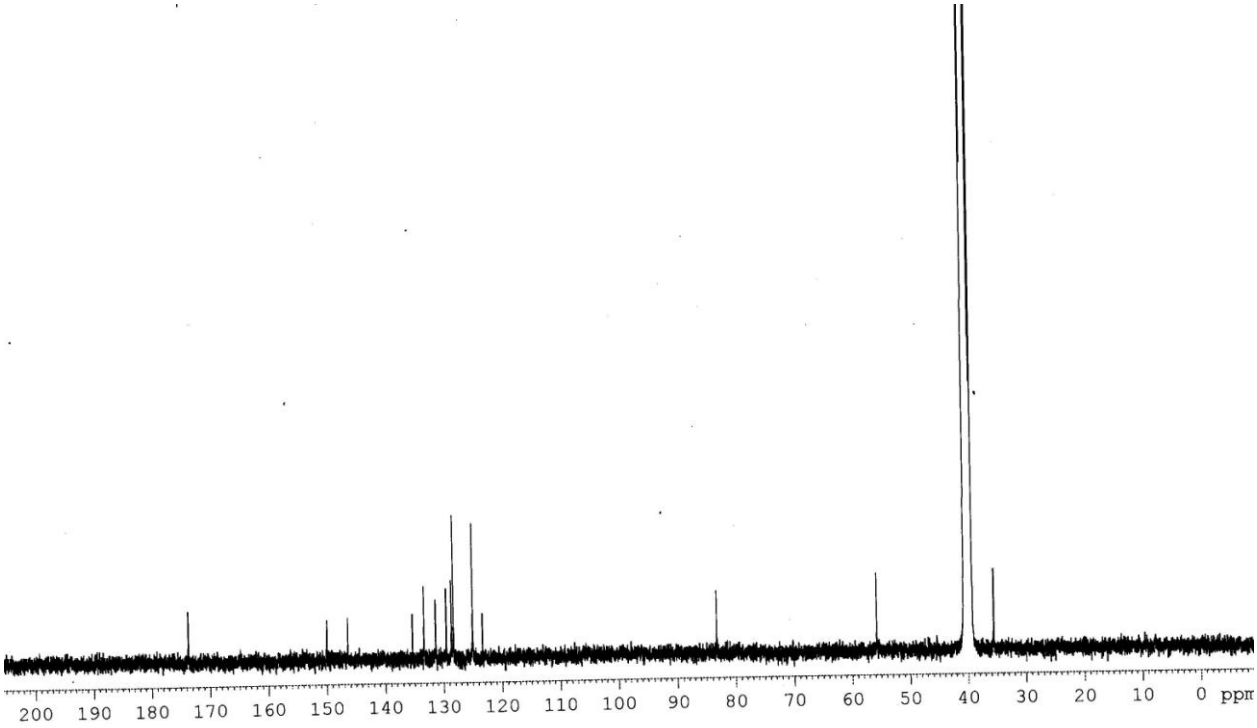
^{1}H NMR of compound **3e** (400 MHz, $CDCl_3$)



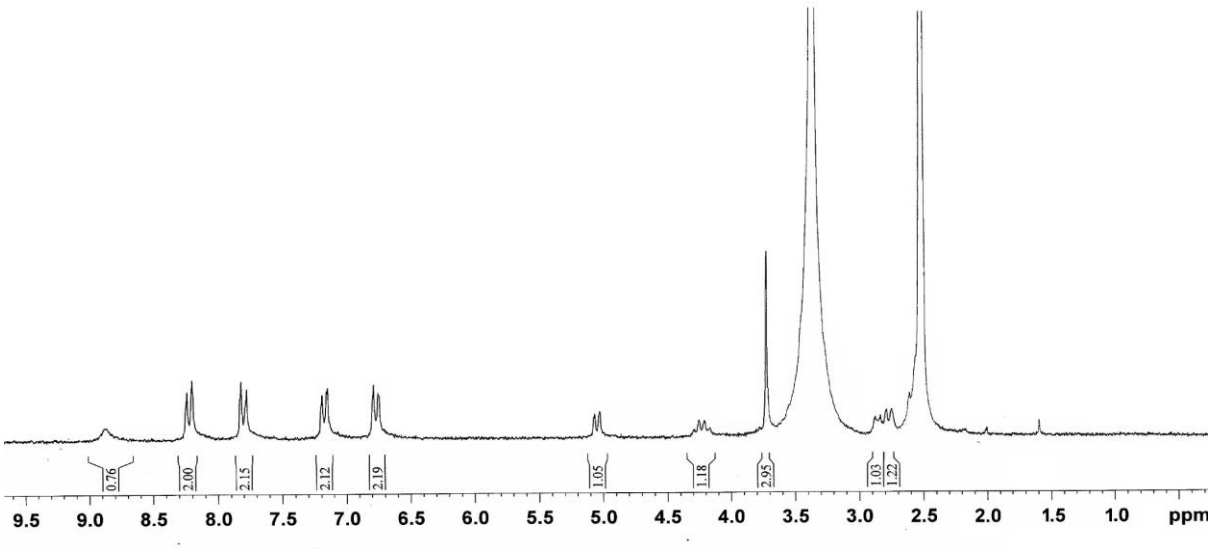
^{13}C NMR of compound **3e** (100 MHz, d_6-DMSO)



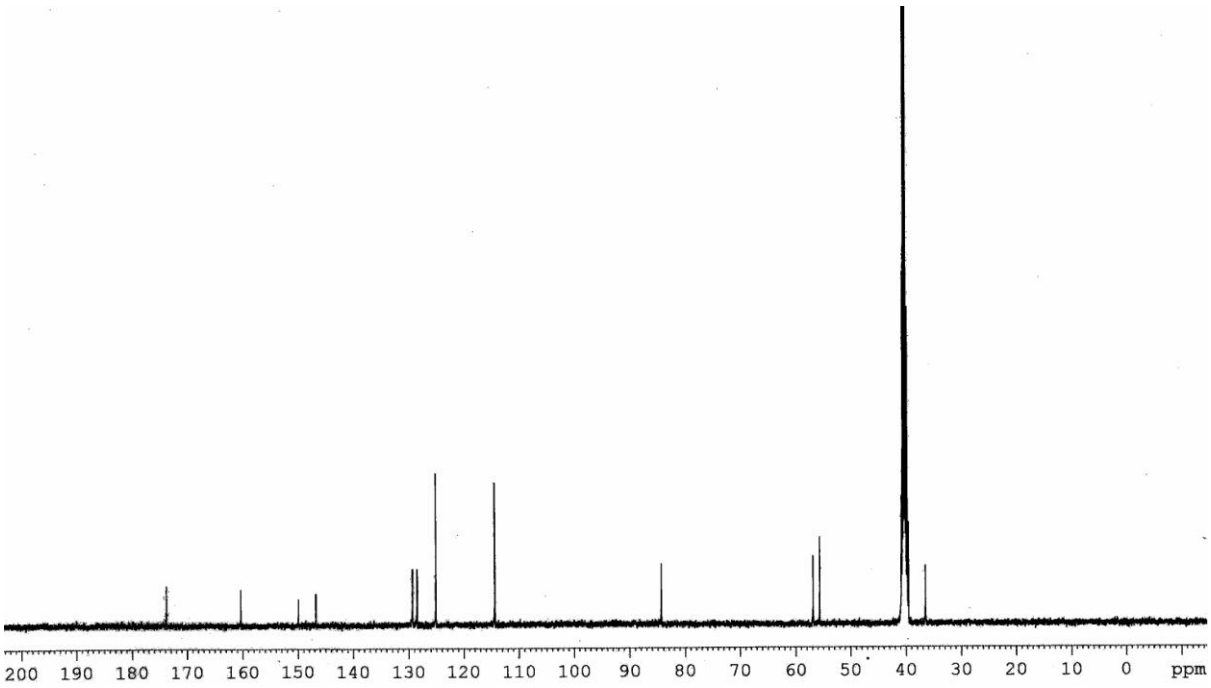
^{1}H NMR of compound **3f** (200 MHz, d_6-DMSO)



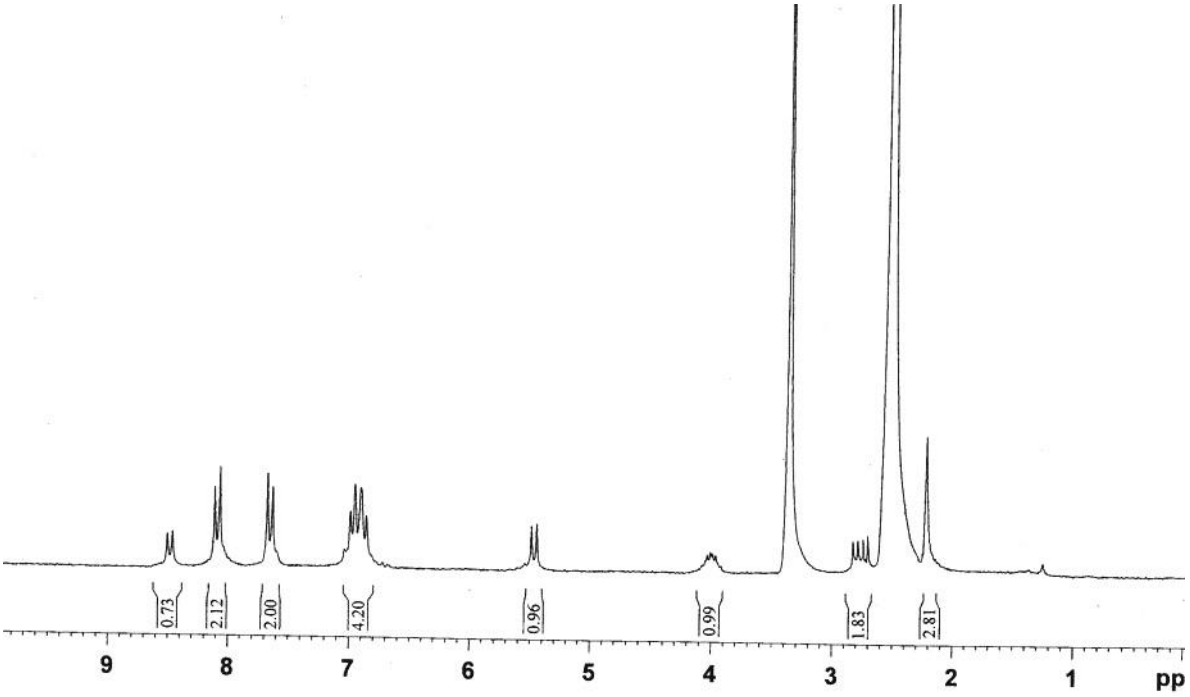
^{13}C NMR of compound **3f** (100 MHz, d_6-DMSO)



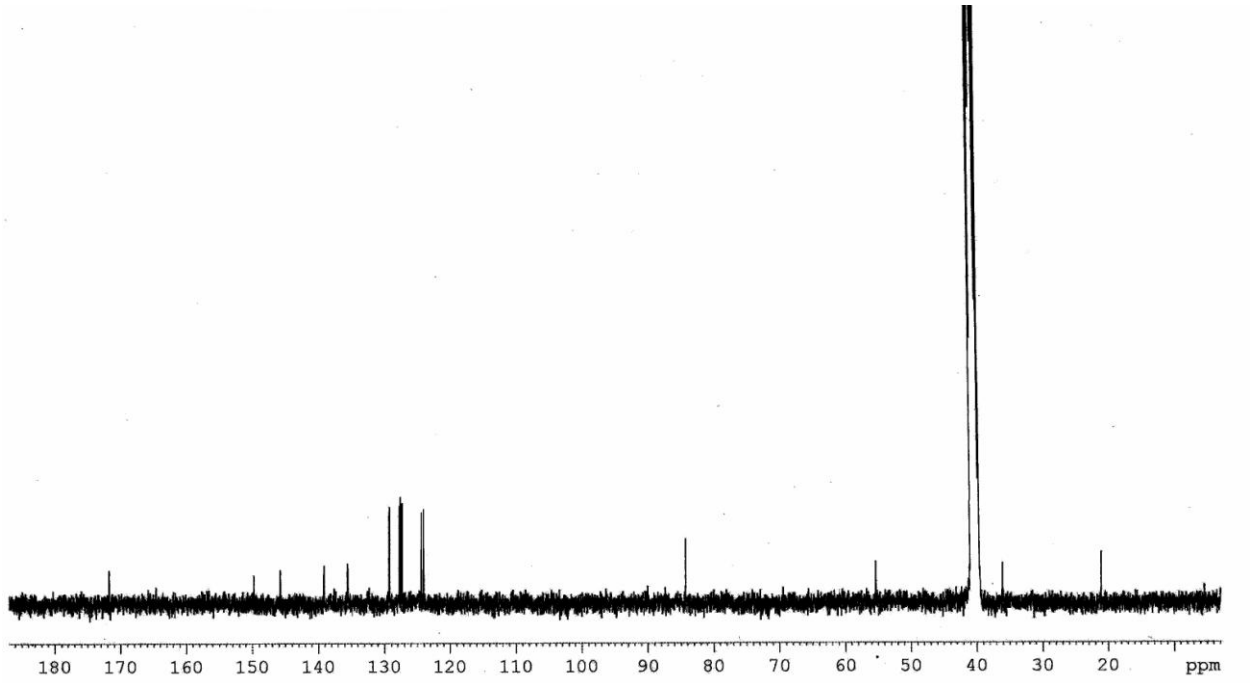
^{1}H NMR of compound **3g** (200 MHz, d_6-DMSO)



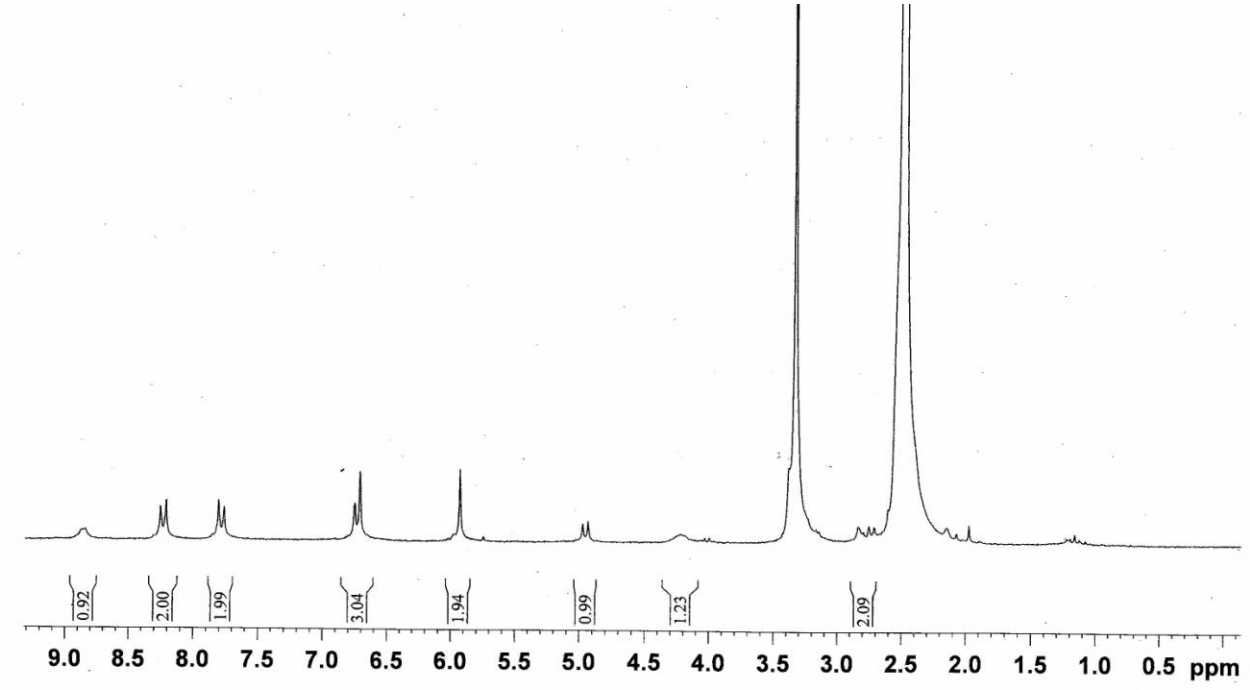
^{13}C NMR of compound **3g** (100 MHz, d_6-DMSO)



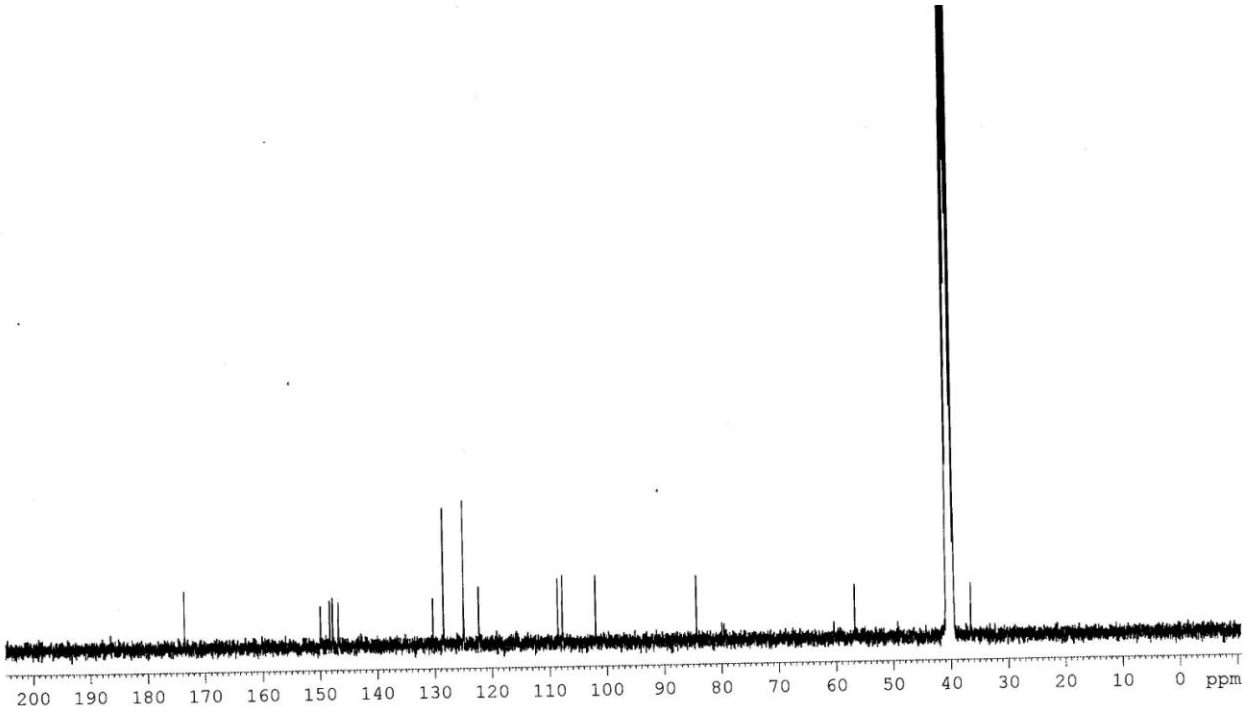
^{1}H NMR of compound **3h** (200 MHz, d_6-DMSO)



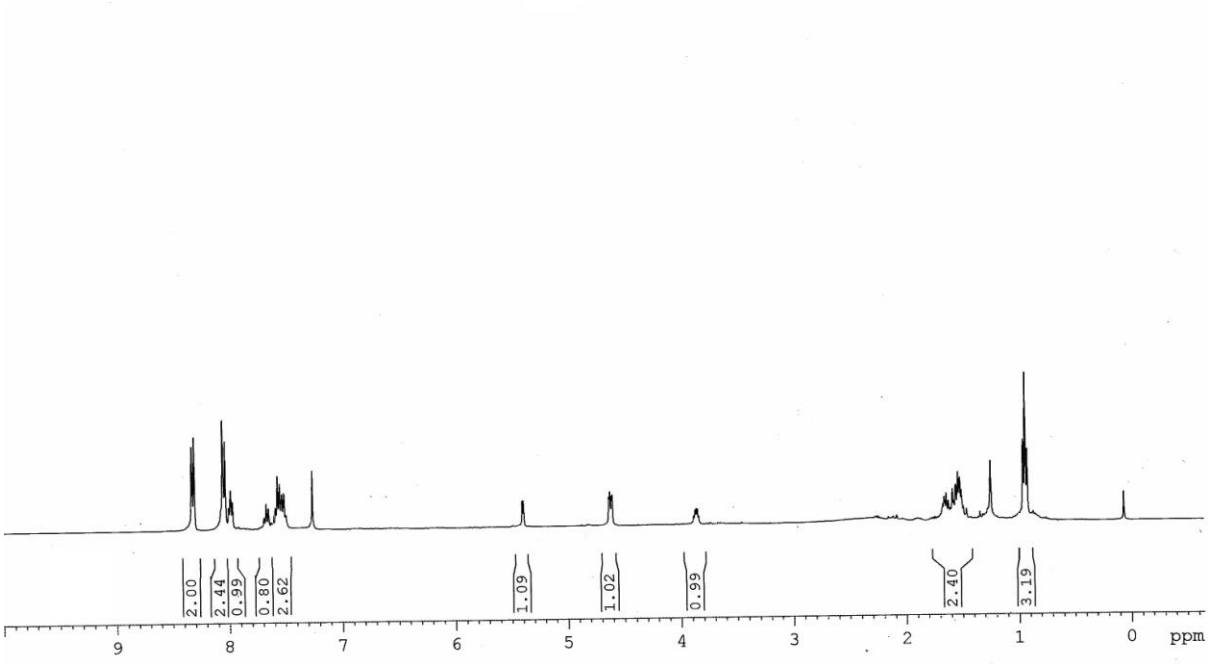
^{13}C NMR of compound **3h** (100 MHz, d_6-DMSO)



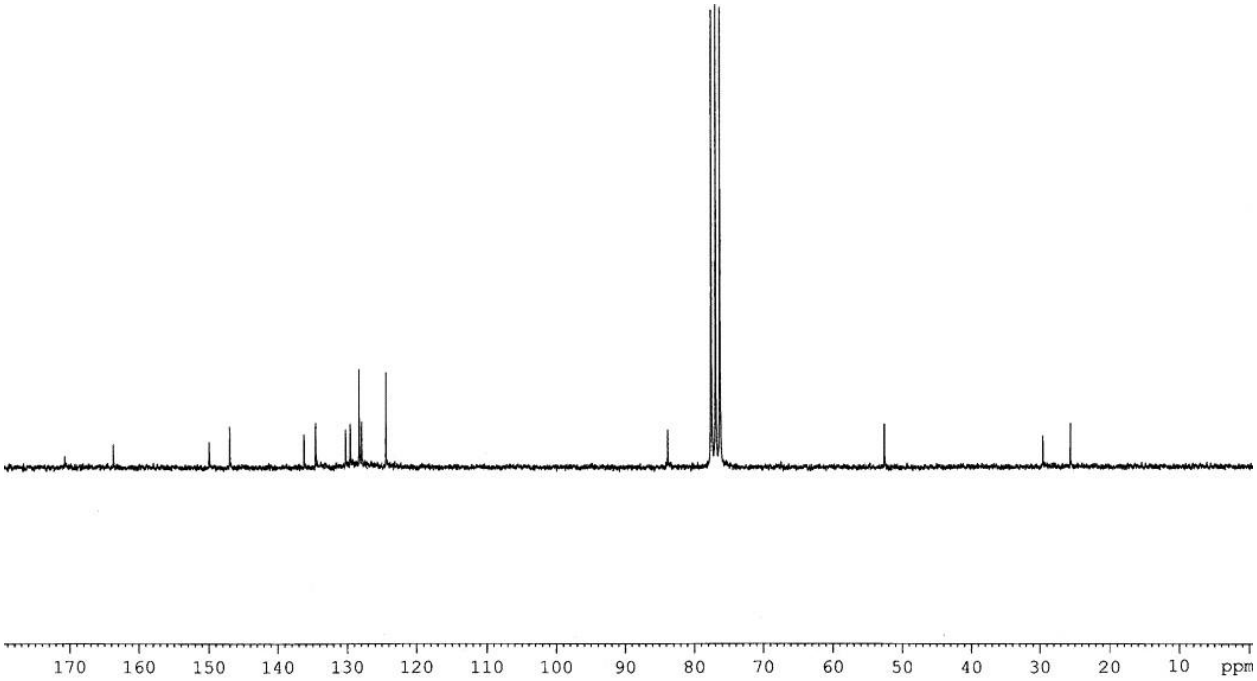
^{1}H NMR of compound **3i** (200 MHz, d_6-DMSO)



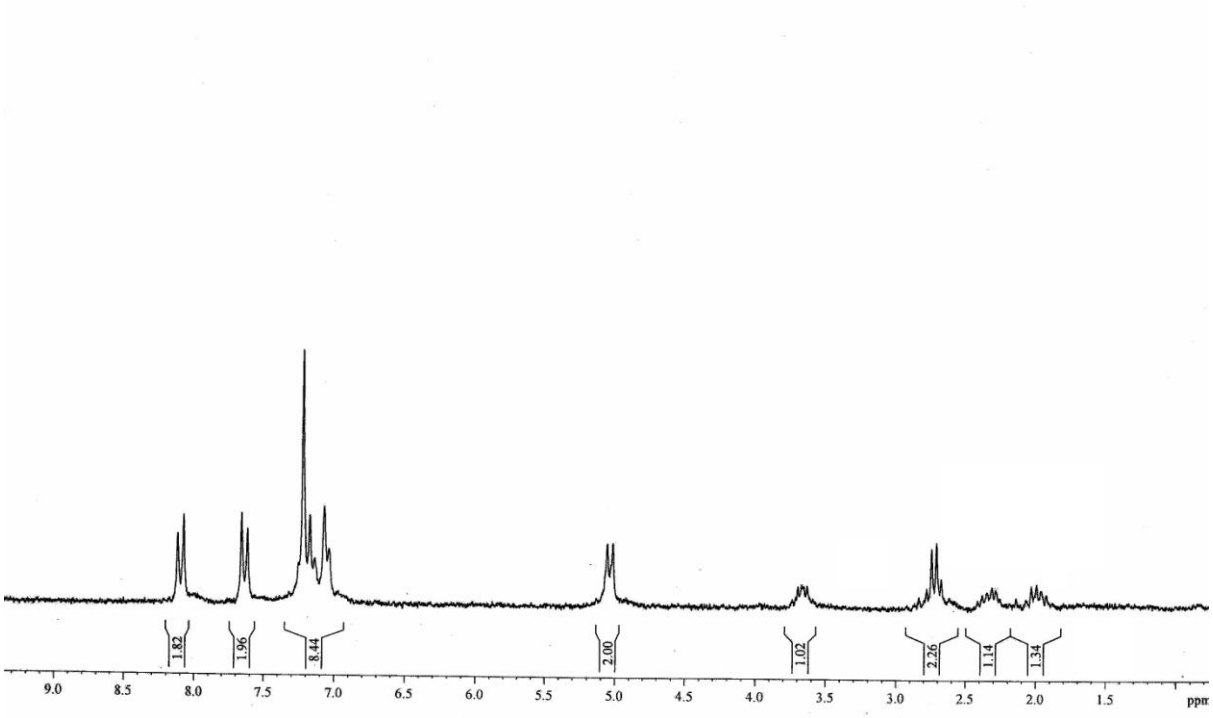
^{13}C NMR of compound **3i** (100 MHz, d_6-DMSO)



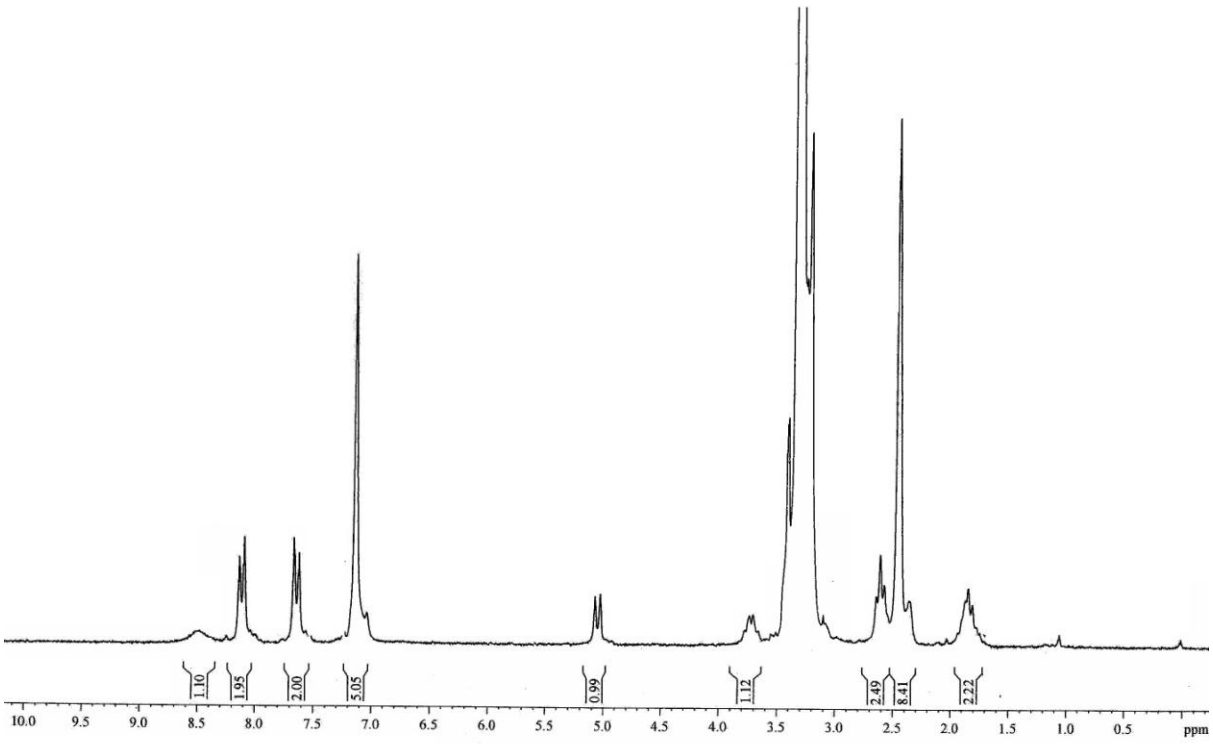
^{1}H NMR of compound **10** (400 MHz, $CDCl_3$)



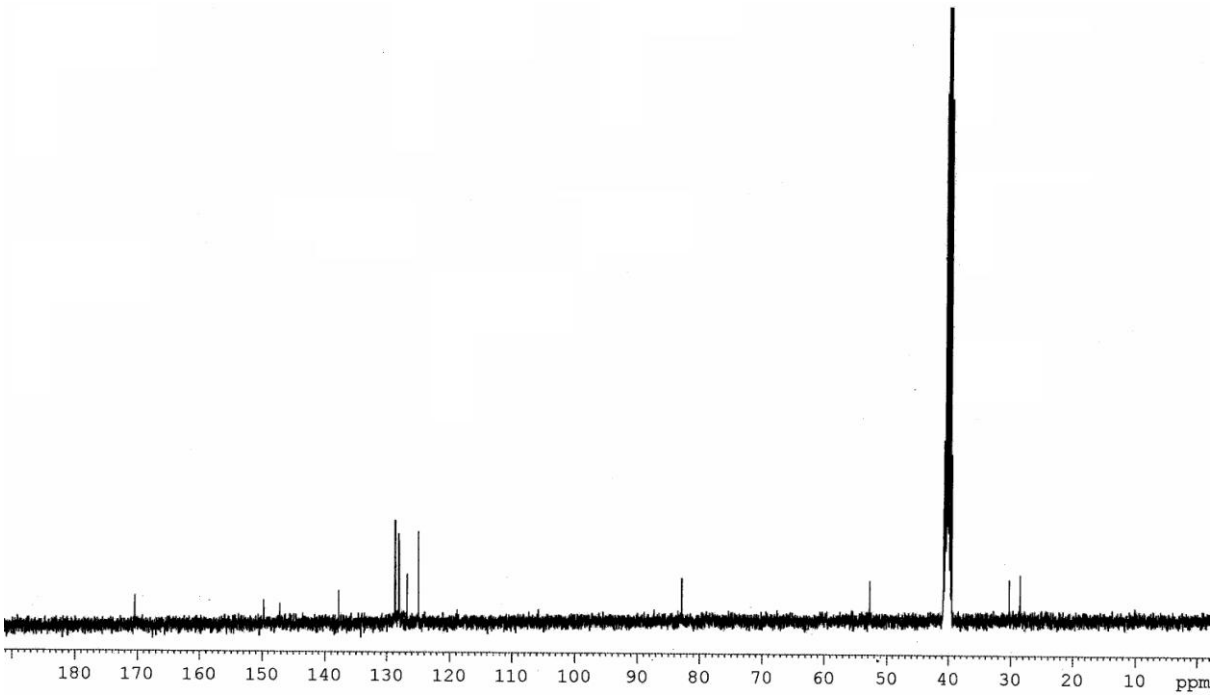
^{13}C NMR of compound **10** (100 MHz, $CDCl_3$)



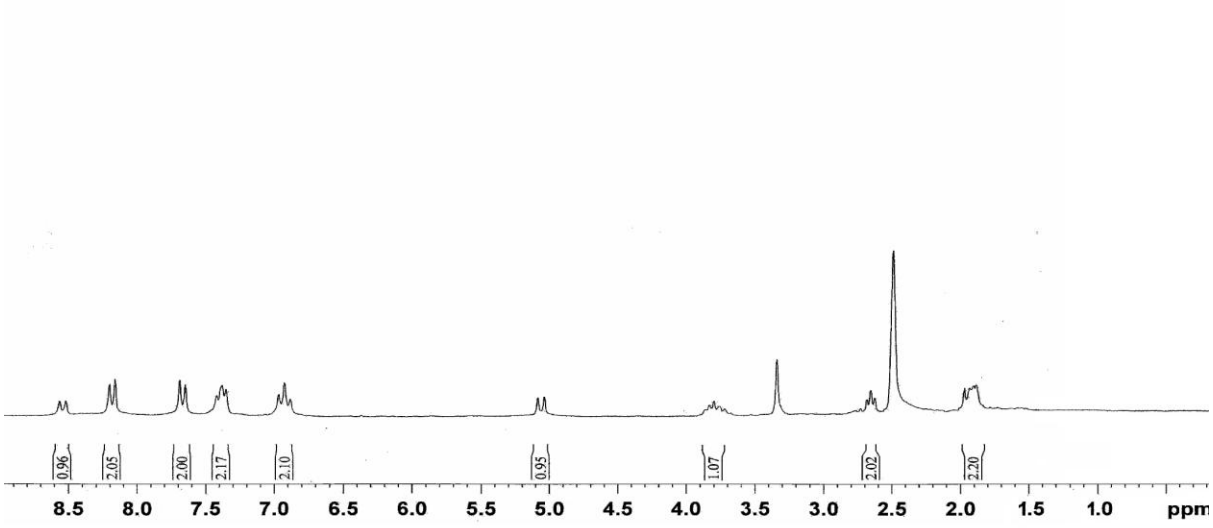
^{1}H NMR of compound **7a** (200 MHz, $CDCl_3$)



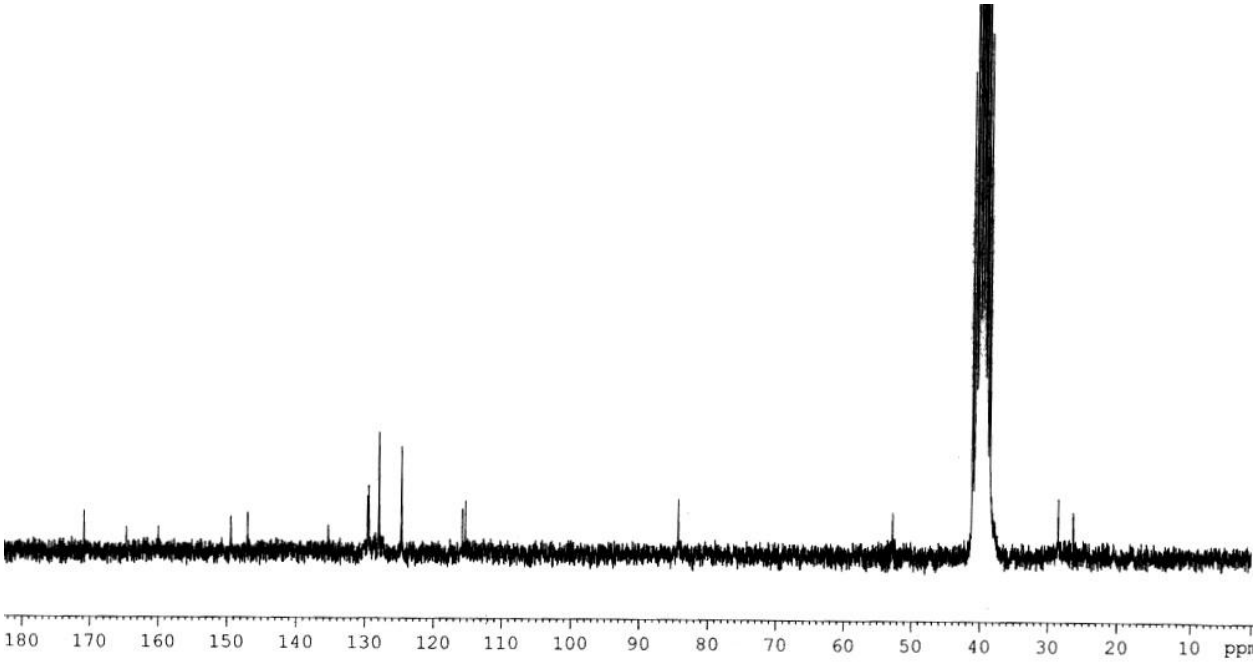
^{1}H NMR of compound **7a** (200 MHz, d_6-DMSO)



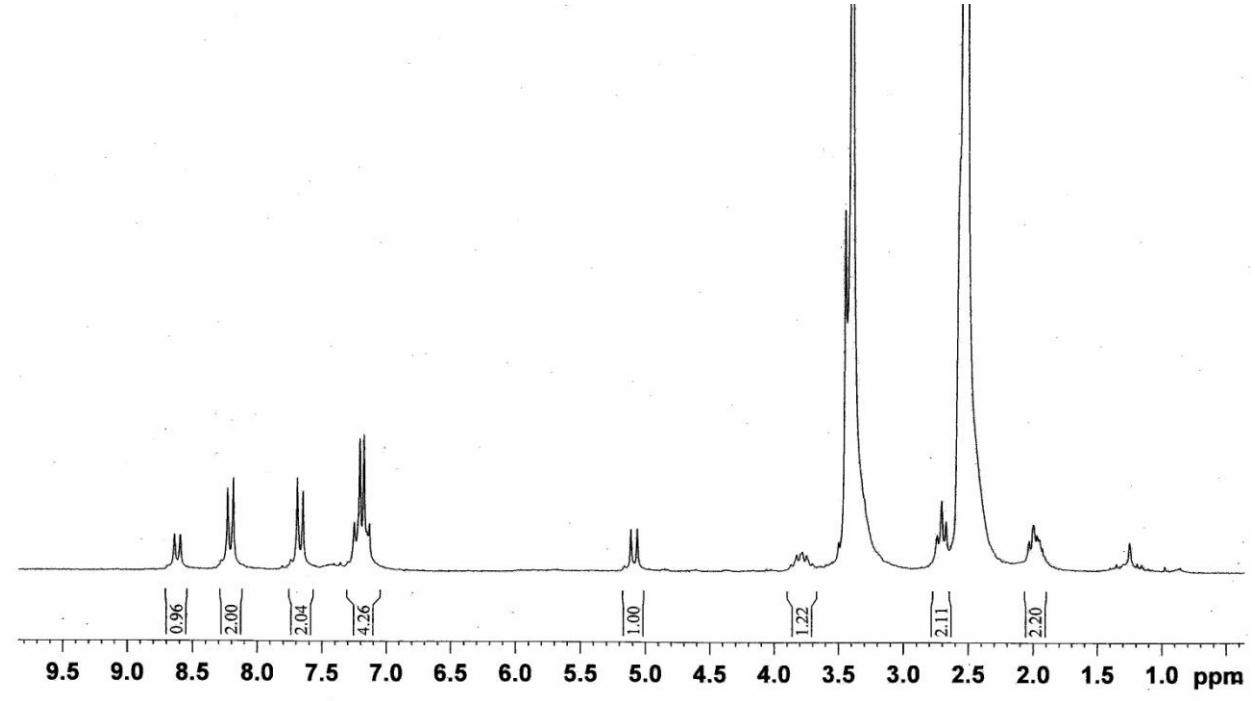
^{13}C NMR of compound **7a** (100 MHz, d_6-DMSO)



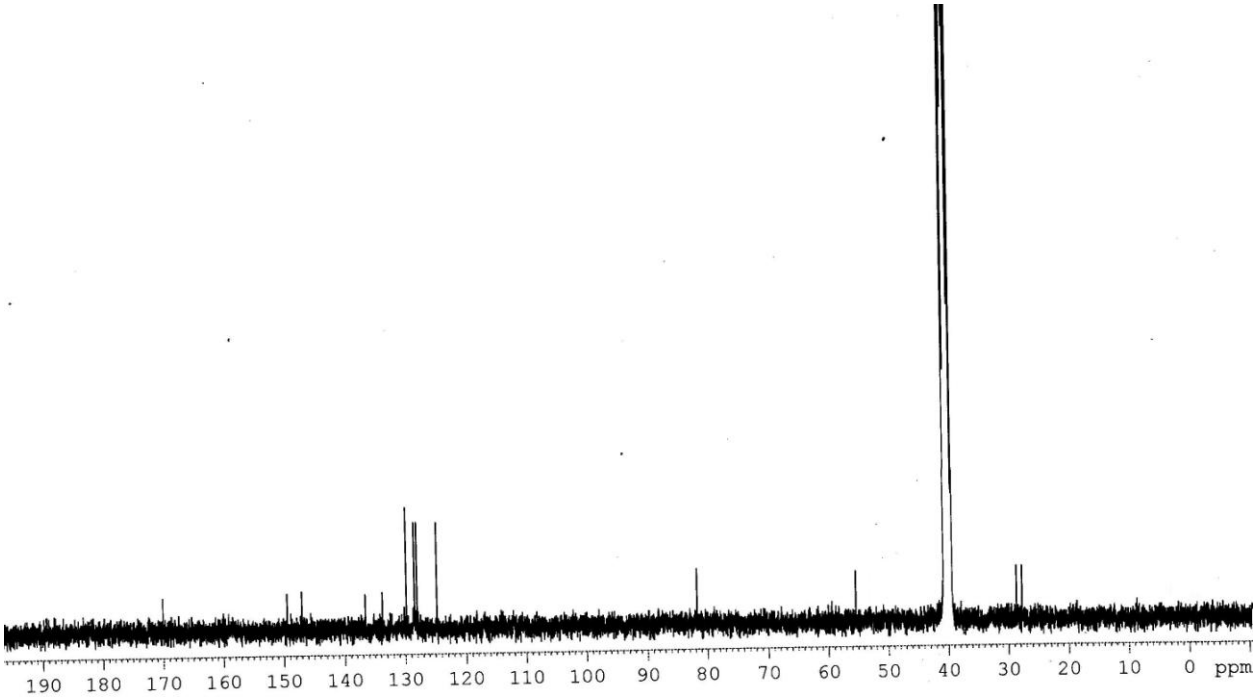
^{1}H NMR of compound **7b** (200 MHz, d_6-DMSO)



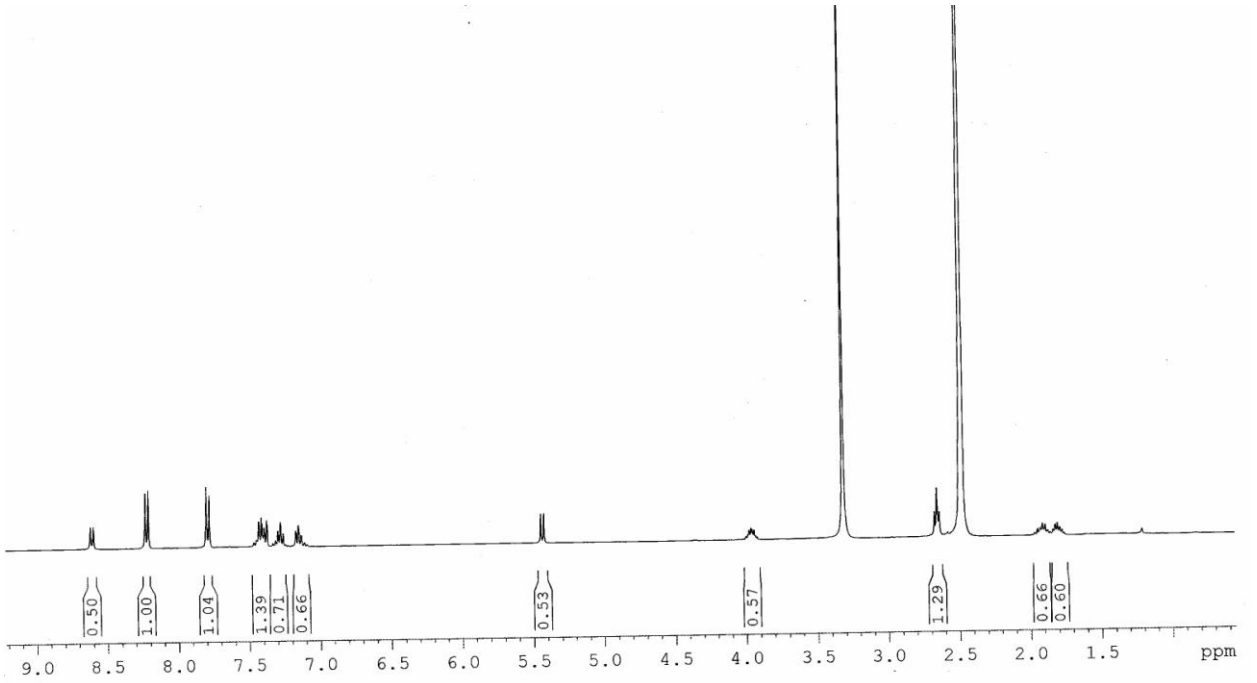
^{13}C NMR of compound **7b** (50 MHz, d_6-DMSO)



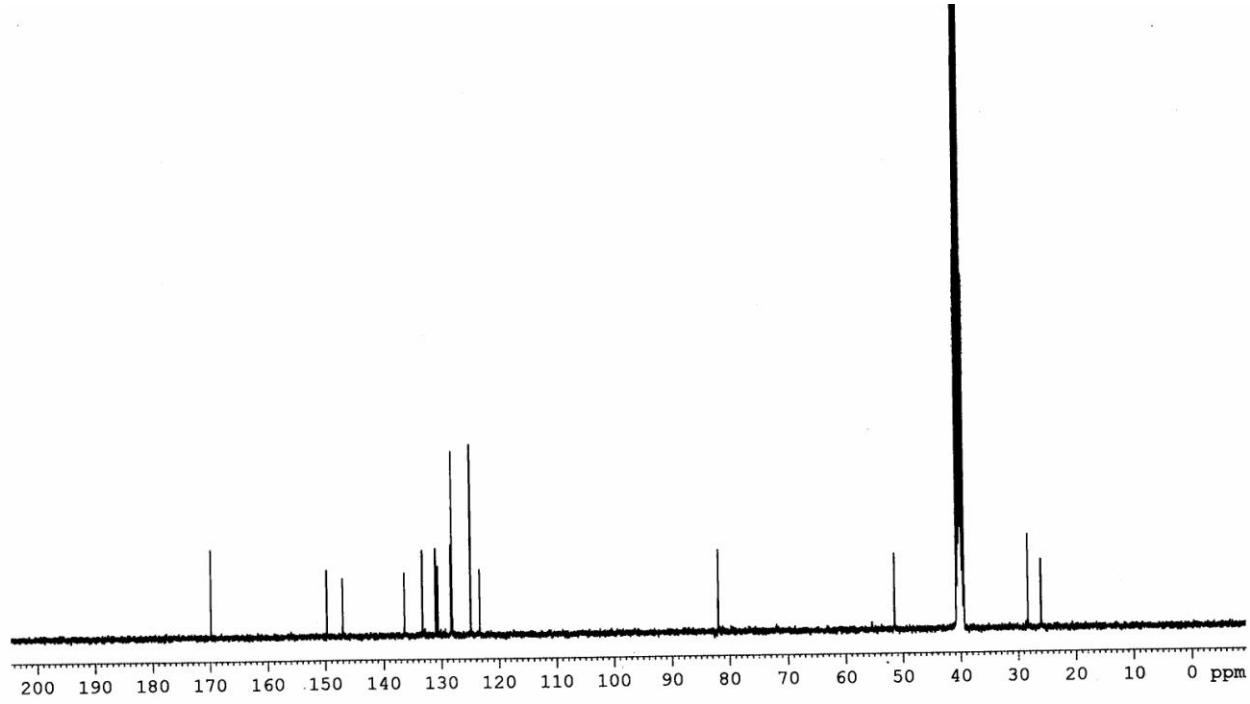
^{1}H NMR of compound **7c** (200 MHz, d_6-DMSO)



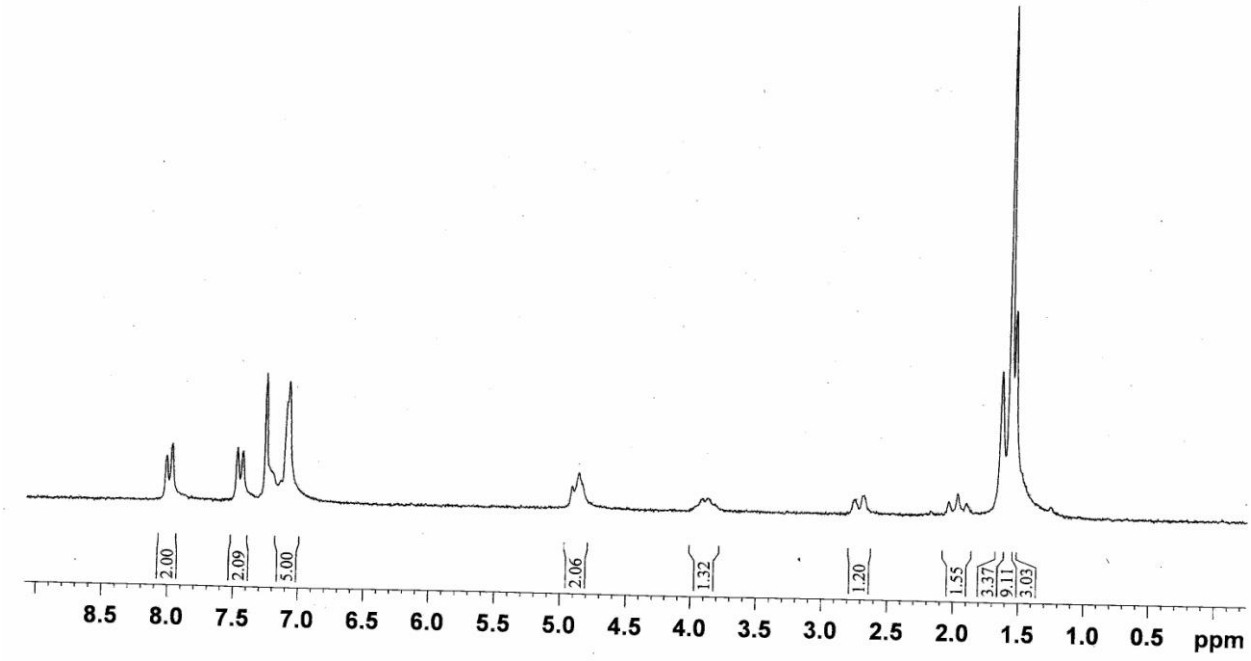
^{13}C NMR of compound **7c** (100 MHz, d_6-DMSO)



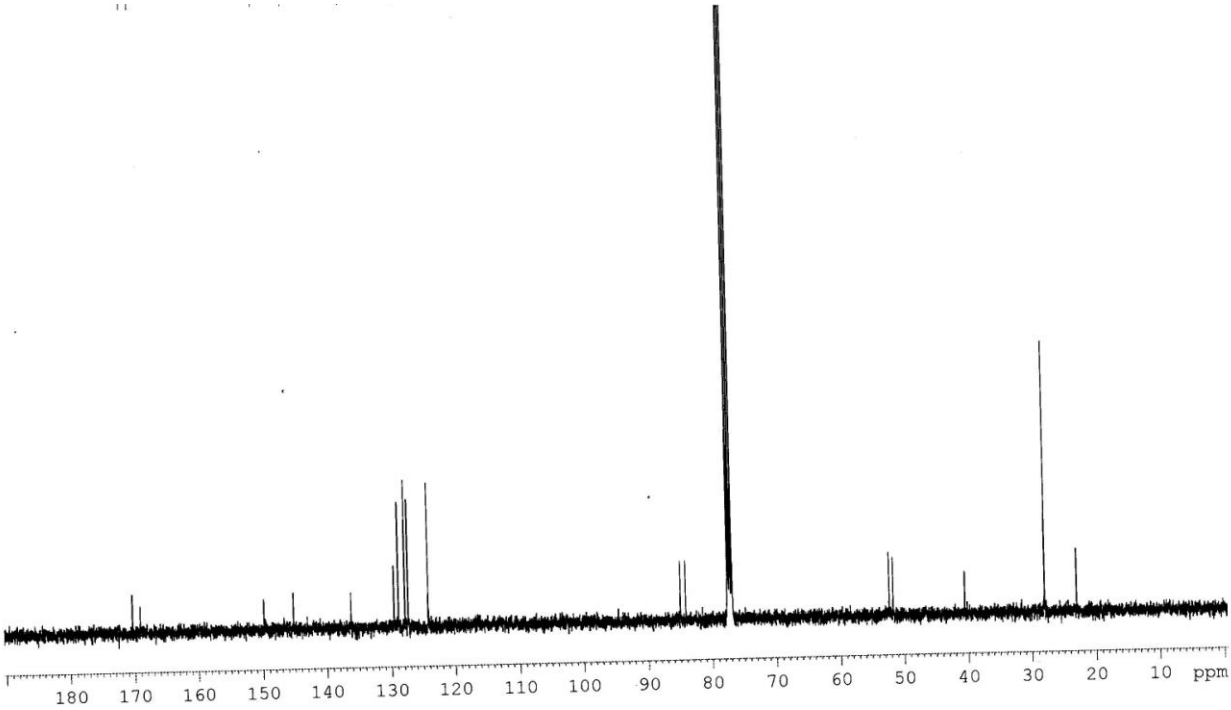
^{1}H NMR of compound **7d** (400 MHz, d_6-DMSO)



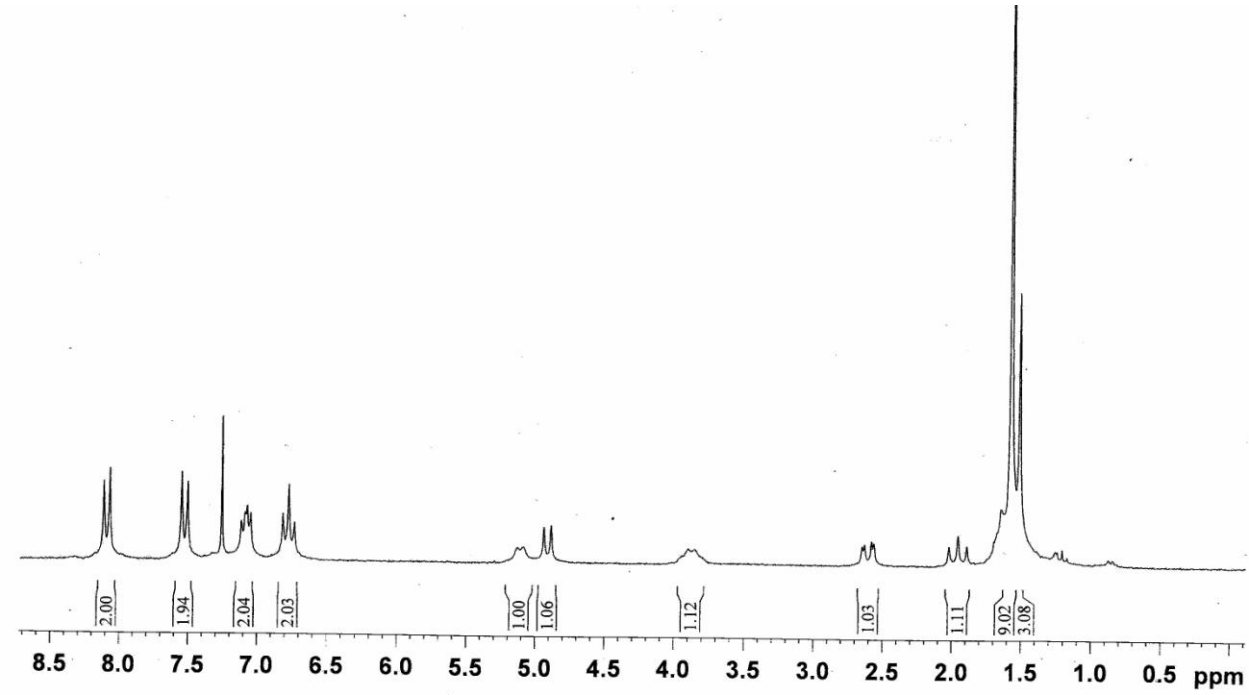
^{13}C NMR of compound **7d** (100 MHz, d_6-DMSO)



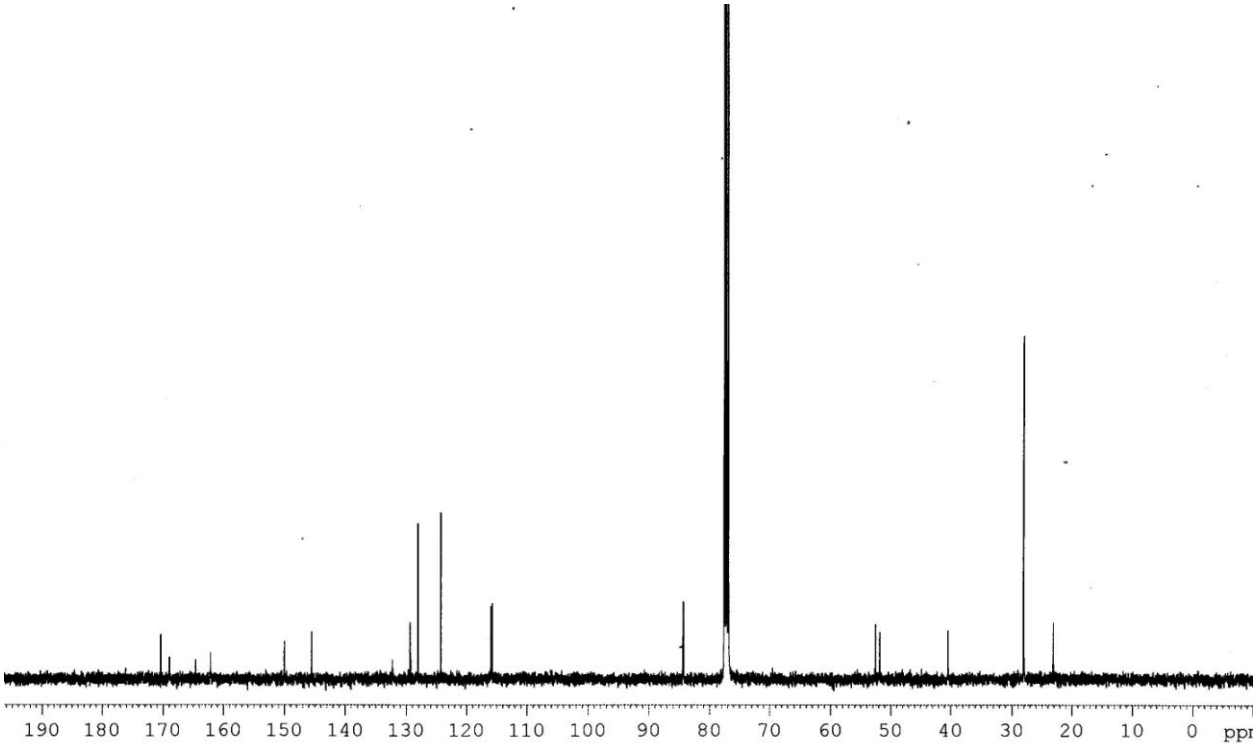
^{1}H NMR of compound **13a** (200 MHz, $CDCl_3$)



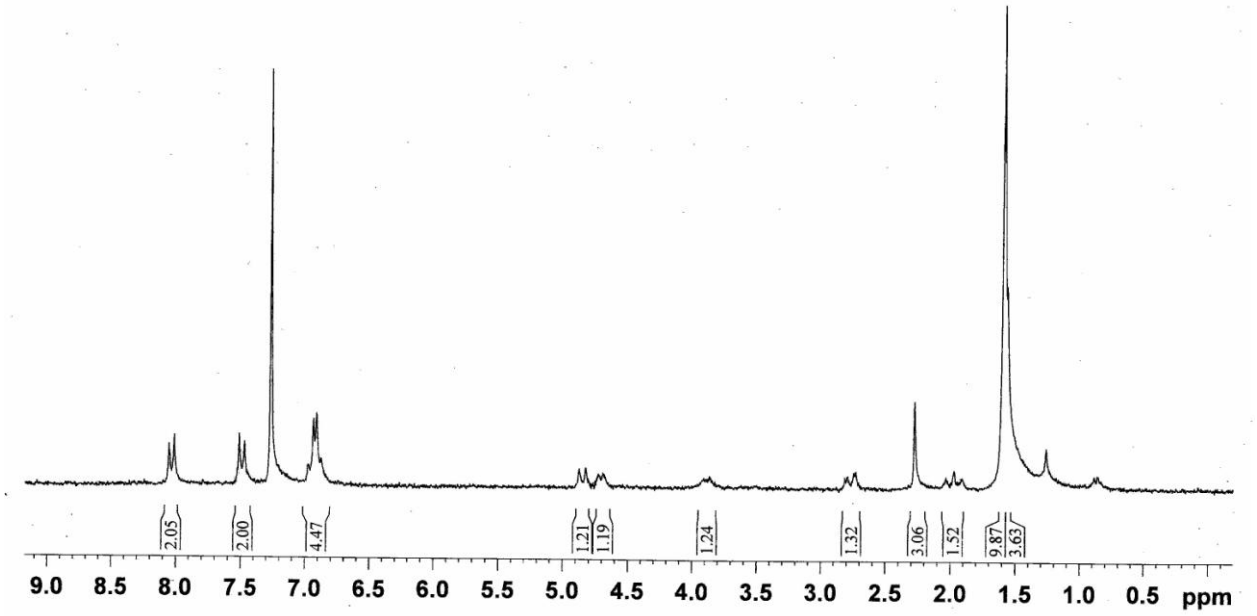
^{13}C NMR of compound **13a** (100 MHz, $CDCl_3$)



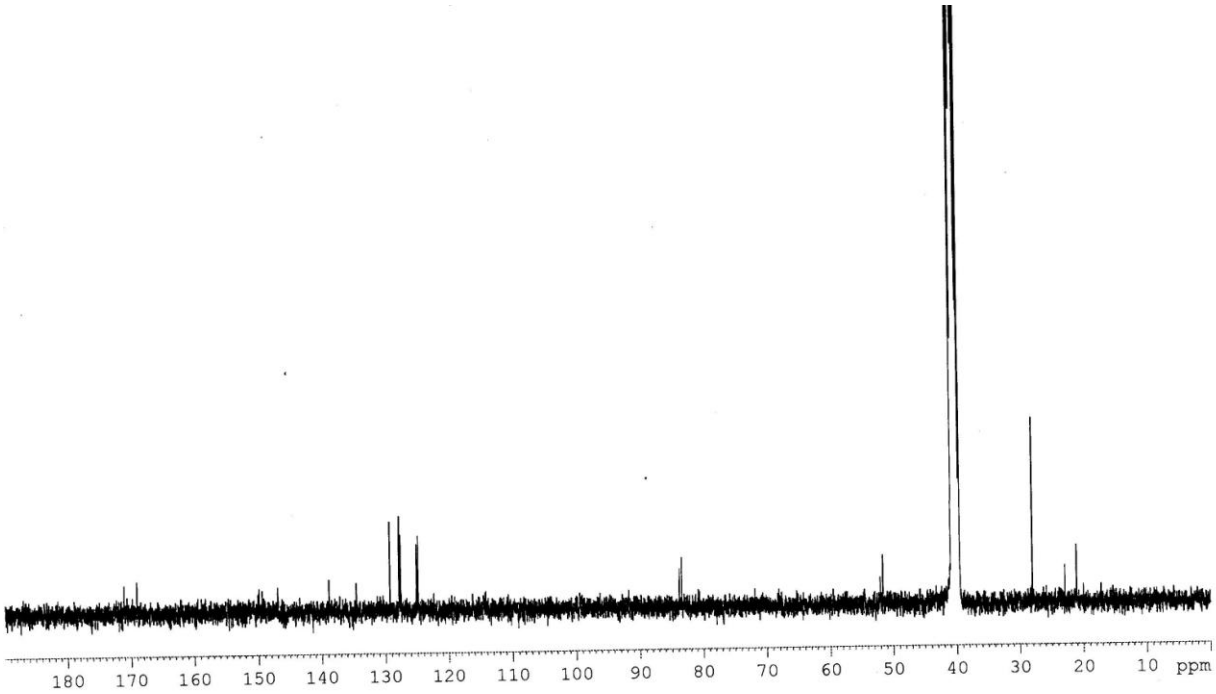
^{1}H NMR of compound **13c** (200 MHz, $CDCl_3$)



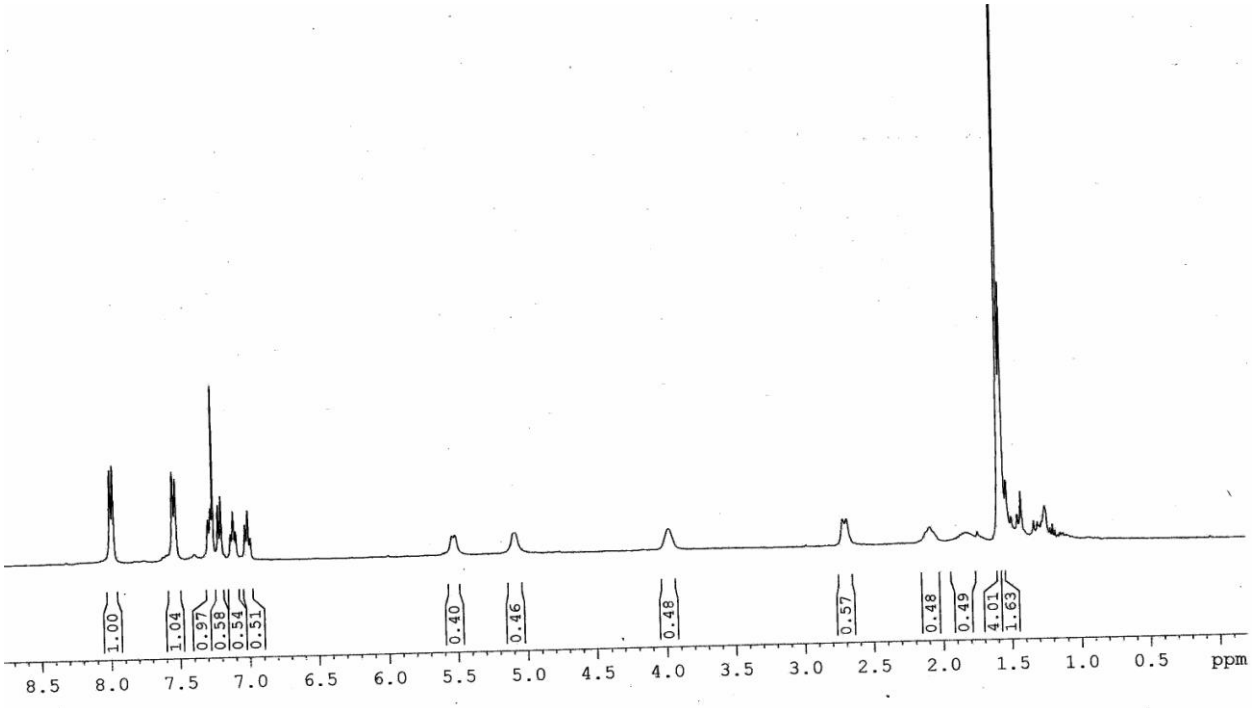
^{13}C NMR of compound **13c** (100 MHz, $CDCl_3$)



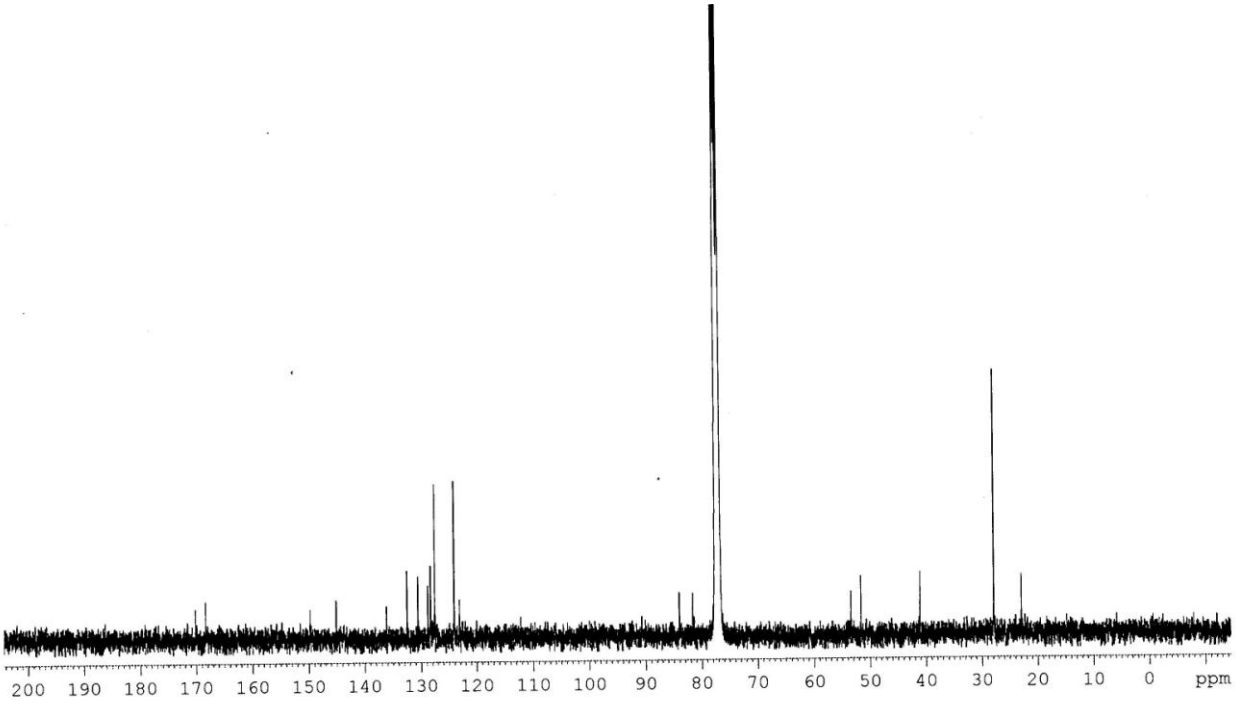
^{1}H NMR of compound **13b** (200 MHz, $CDCl_3$)



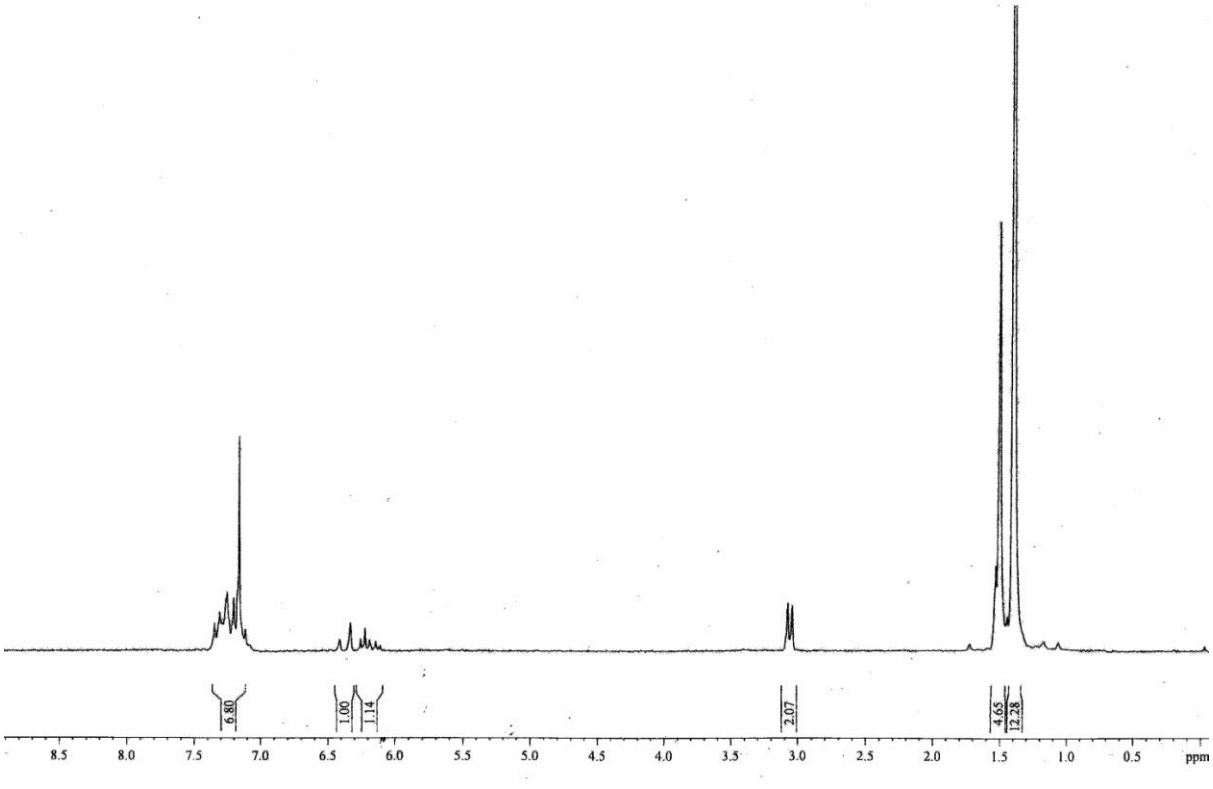
^{13}C NMR of compound **13b** (100 MHz, d_6-DMSO)



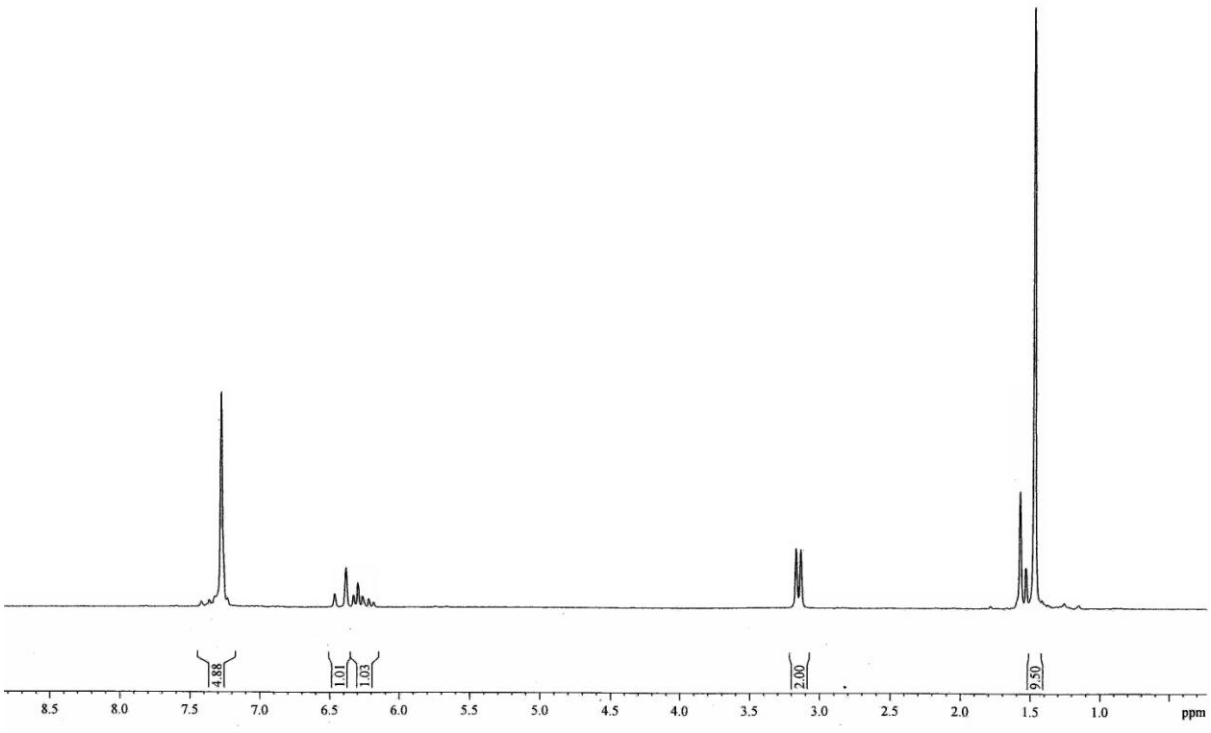
^{1}H NMR of compound **13d** (400 MHz, $CDCl_3$)



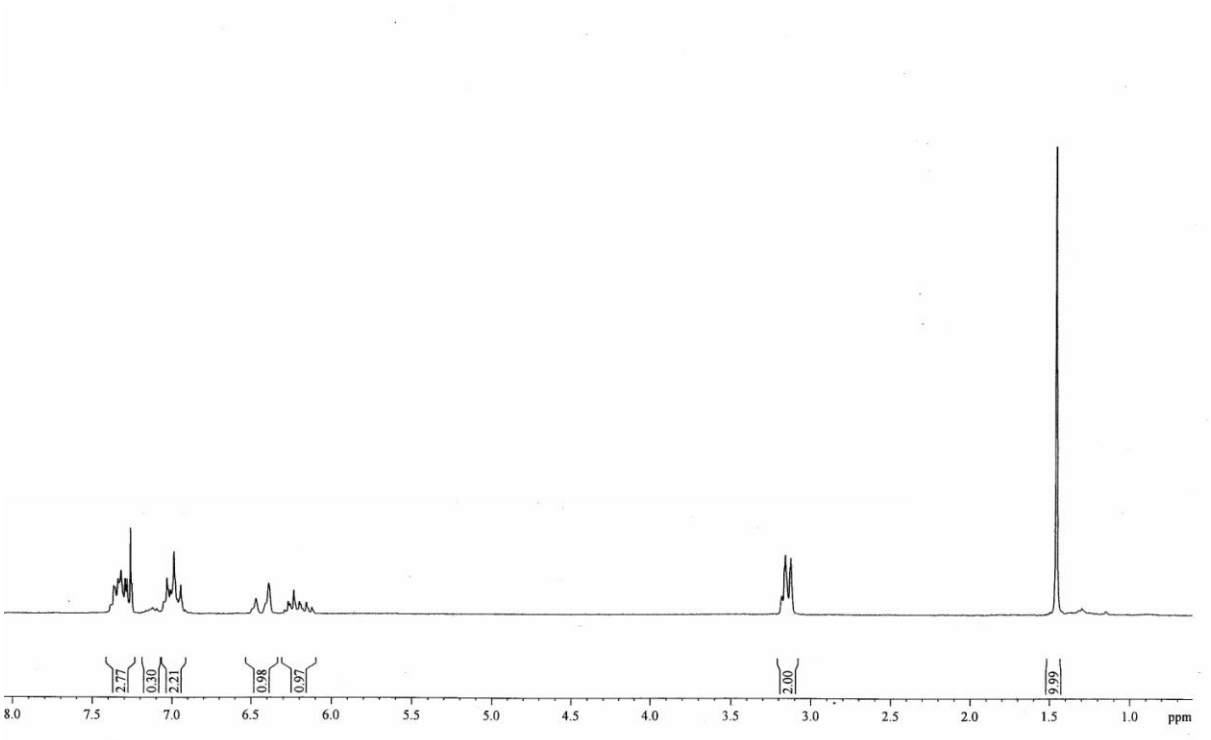
^{13}C NMR of compound **13d** (100 MHz, $CDCl_3$)



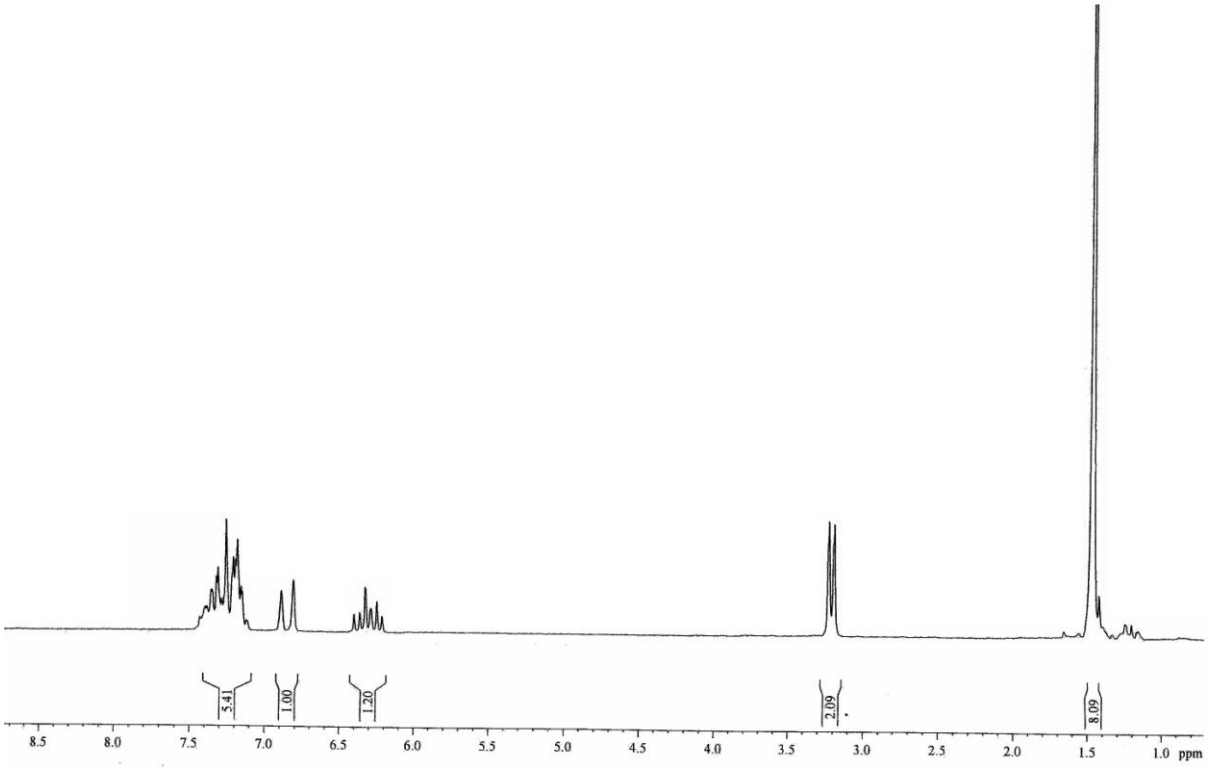
^{1}H NMR of compound **1a** (200 MHz, $CDCl_3$)



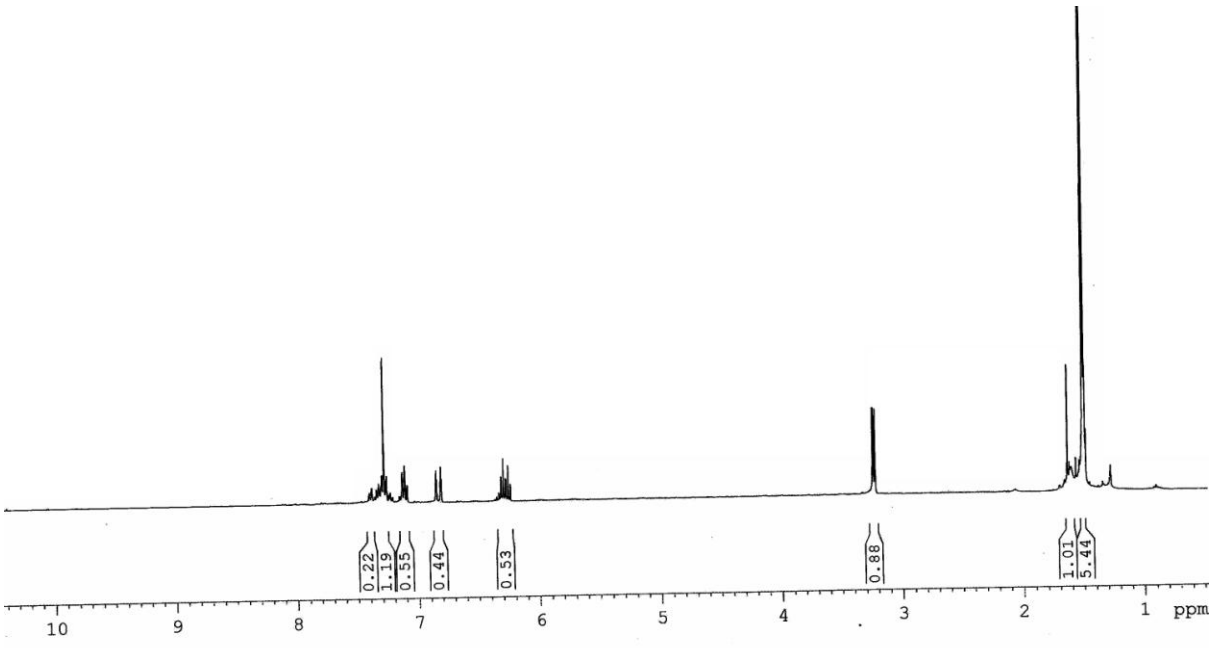
^{1}H NMR of compound **1c** (200 MHz, $CDCl_3$)



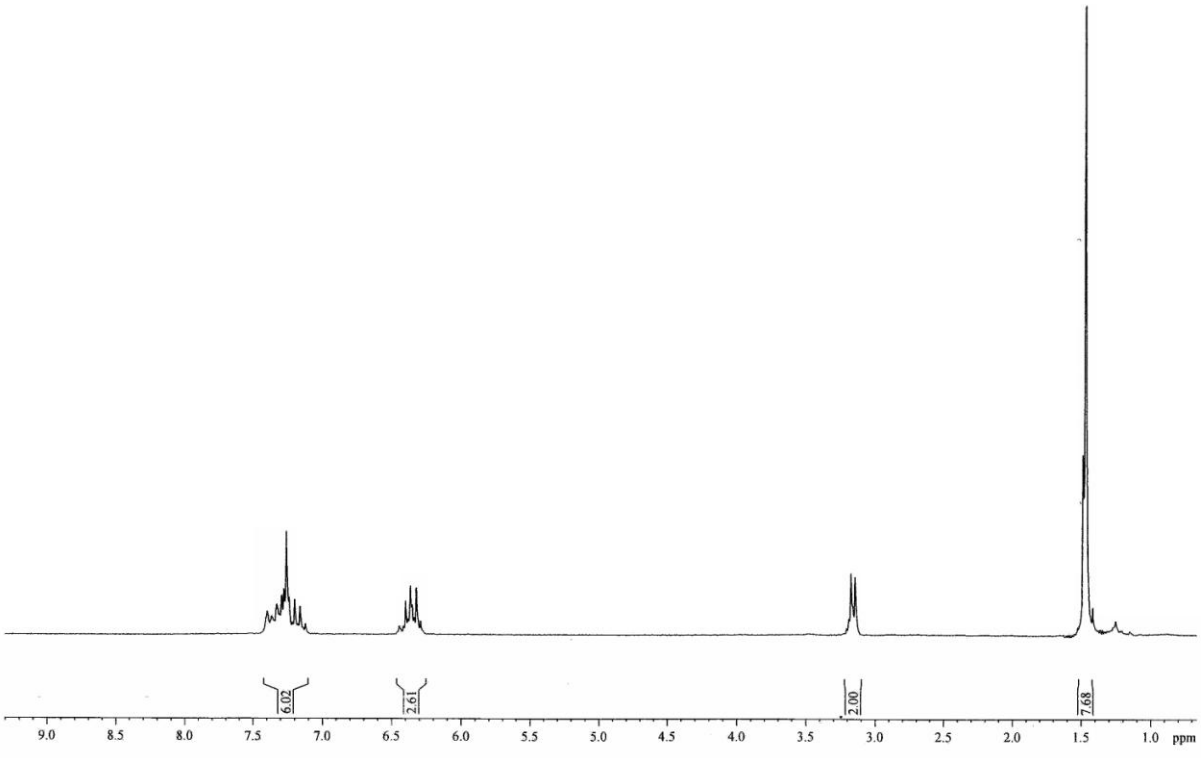
^{1}H NMR of compound **1b** (200 MHz, $CDCl_3$)



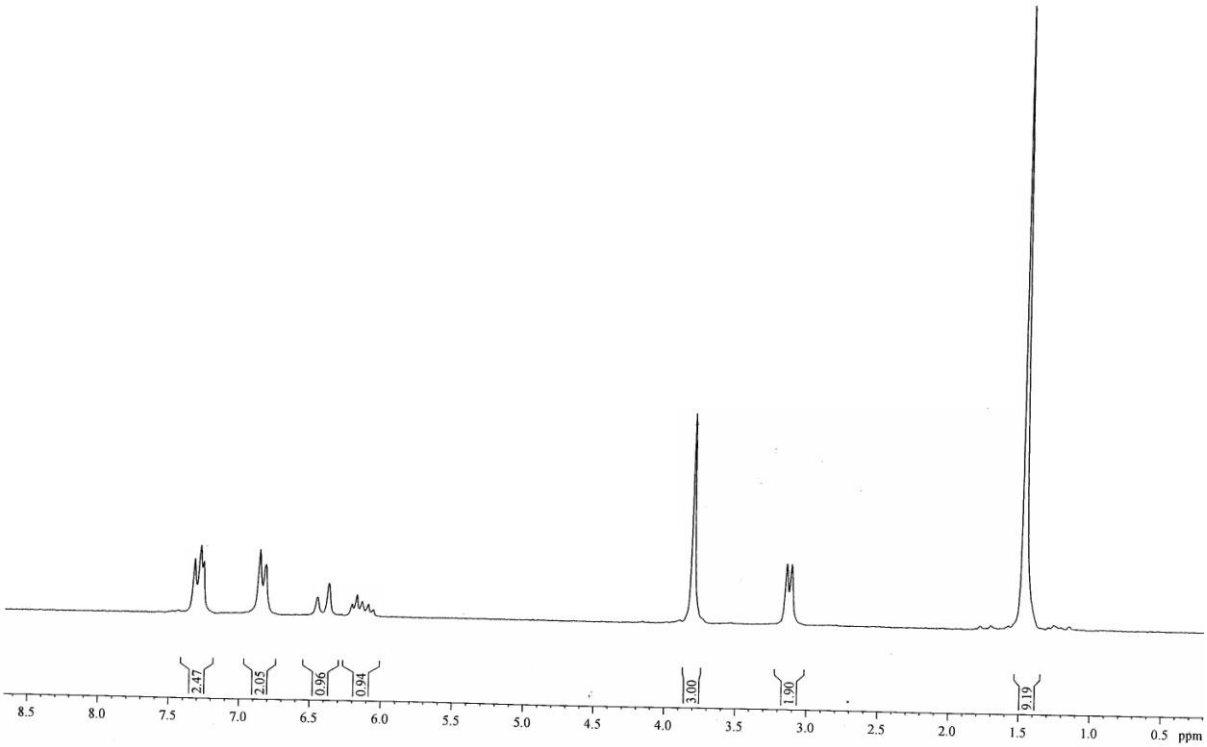
^{1}H NMR of compound **1d** (200 MHz, $CDCl_3$)



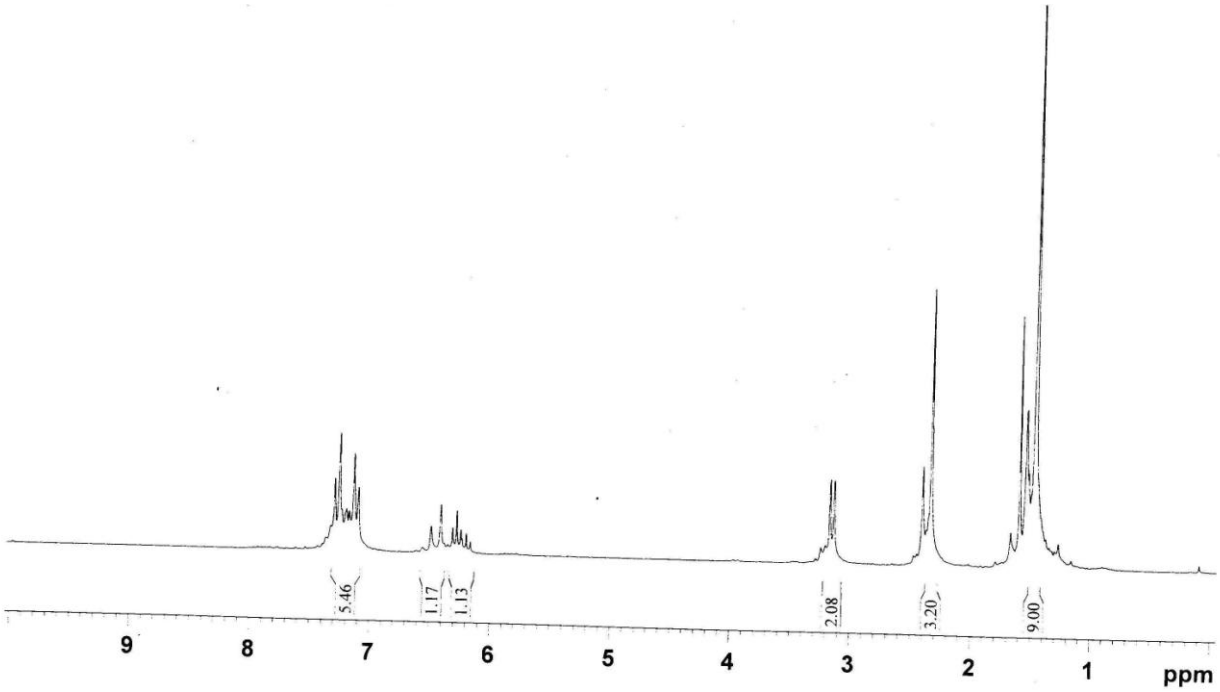
^{1}H NMR of compound **1e** (400 MHz, $CDCl_3$)



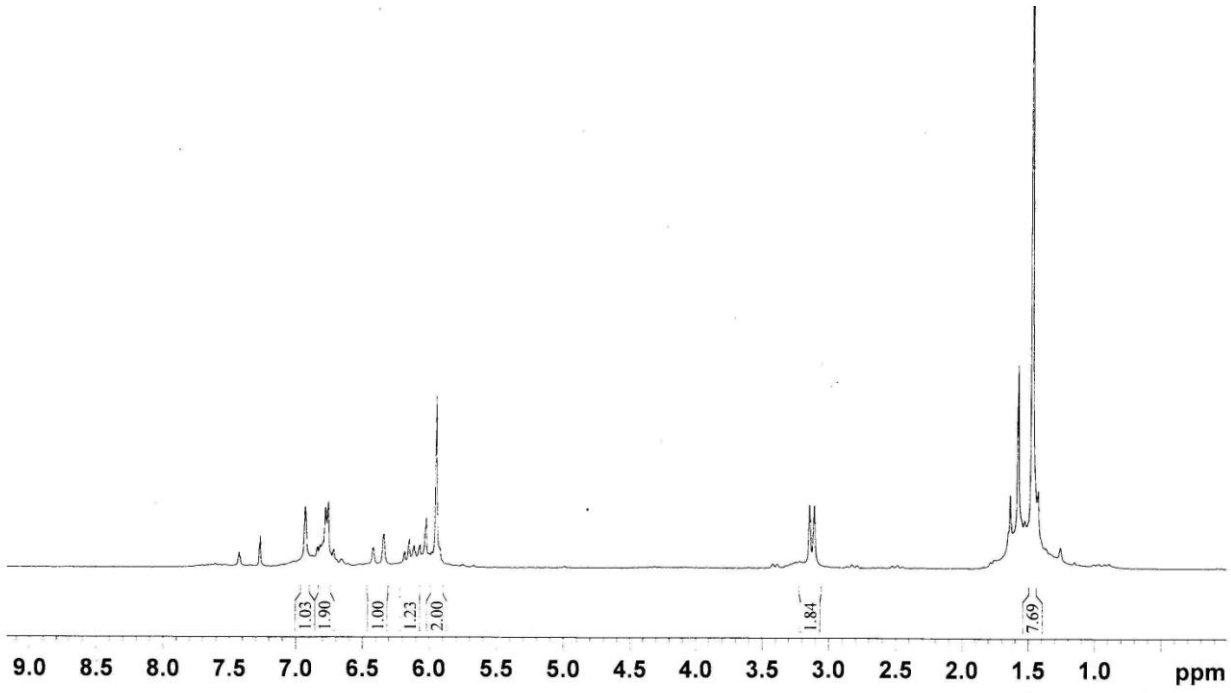
^{1}H NMR of compound **1f** (200 MHz, $CDCl_3$)



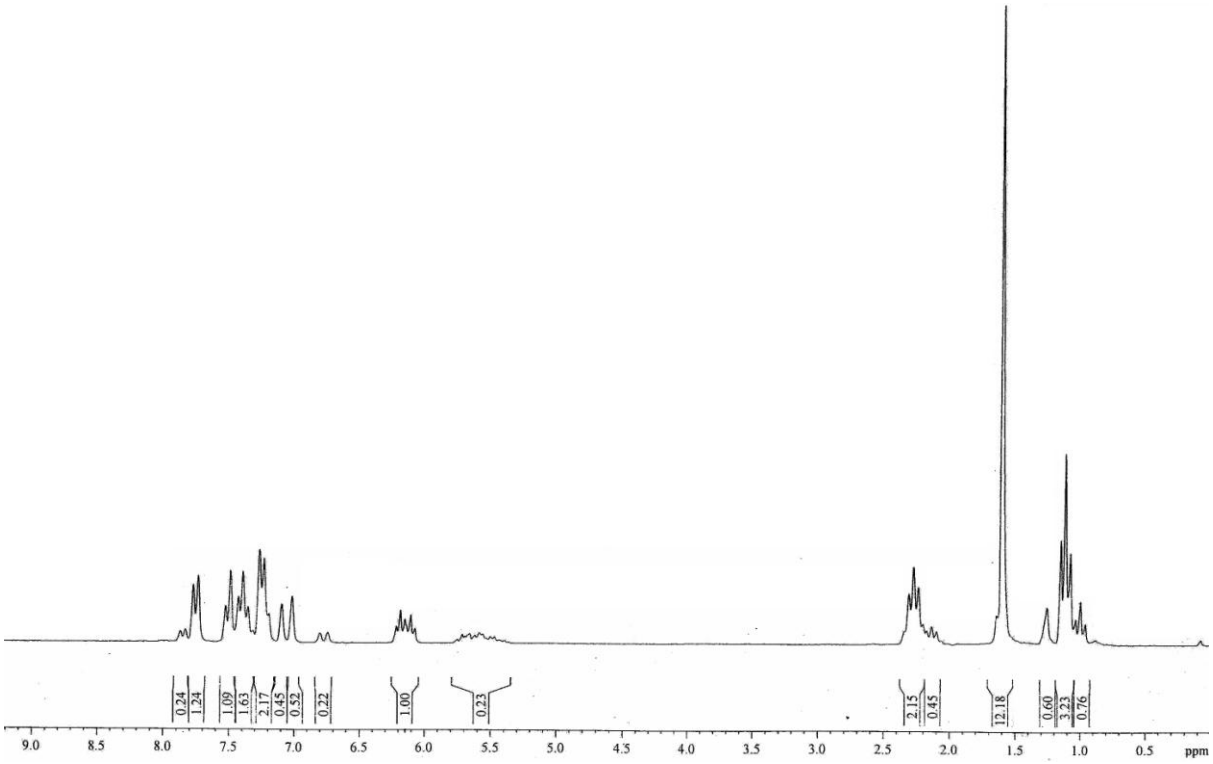
^{1}H NMR of compound **1g** (200 MHz, $CDCl_3$)



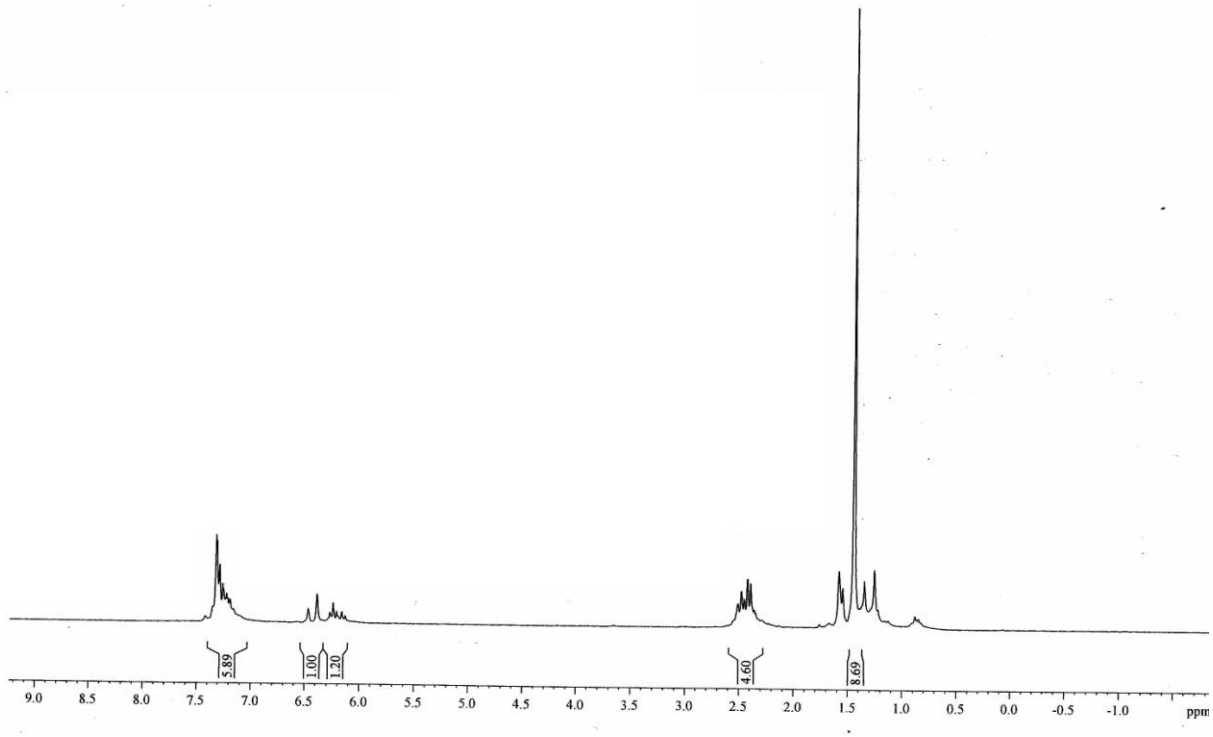
^{1}H NMR of compound **1h** (200 MHz, $CDCl_3$)



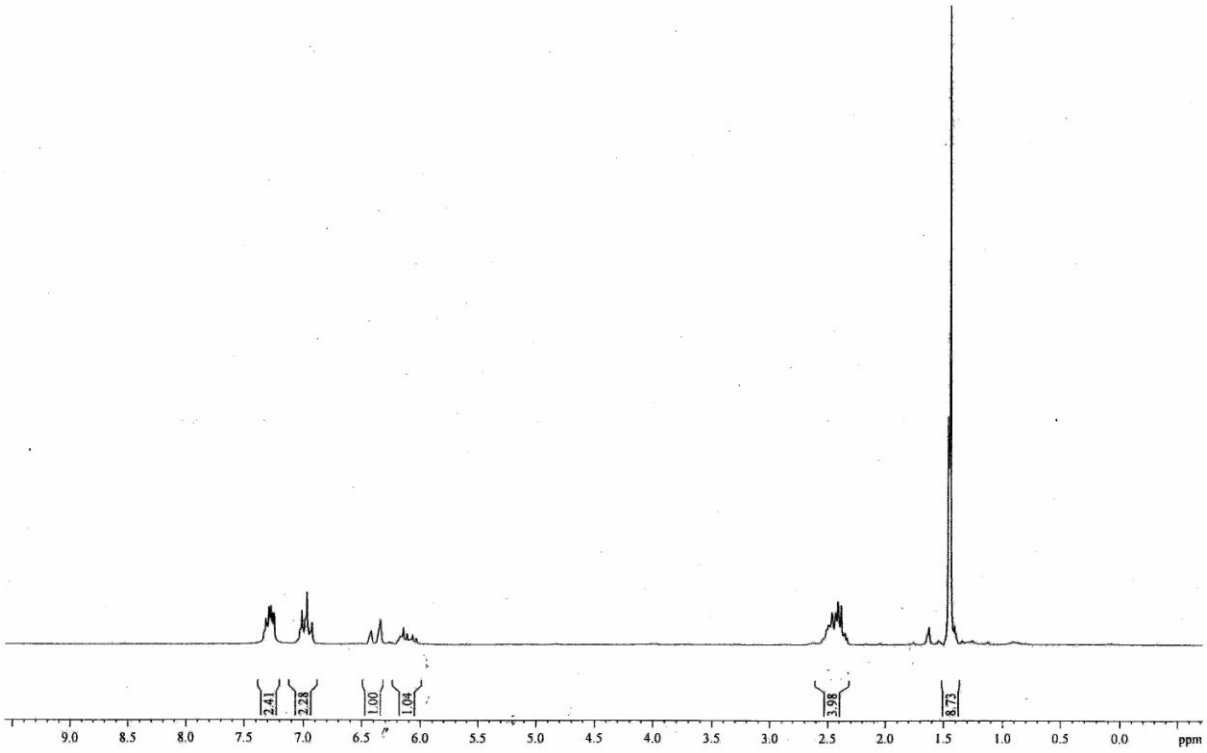
^{1}H NMR of compound **1i** (200 MHz, $CDCl_3$)



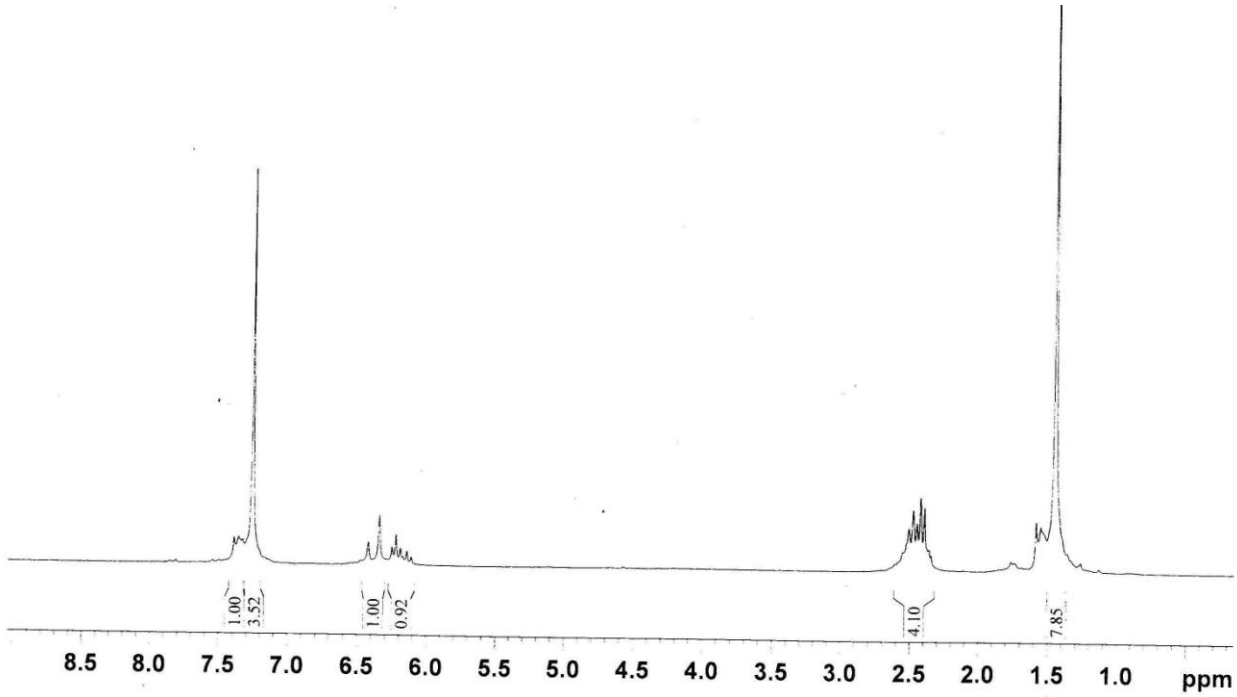
^{1}H NMR of compound **8** (200 MHz, $CDCl_3$)



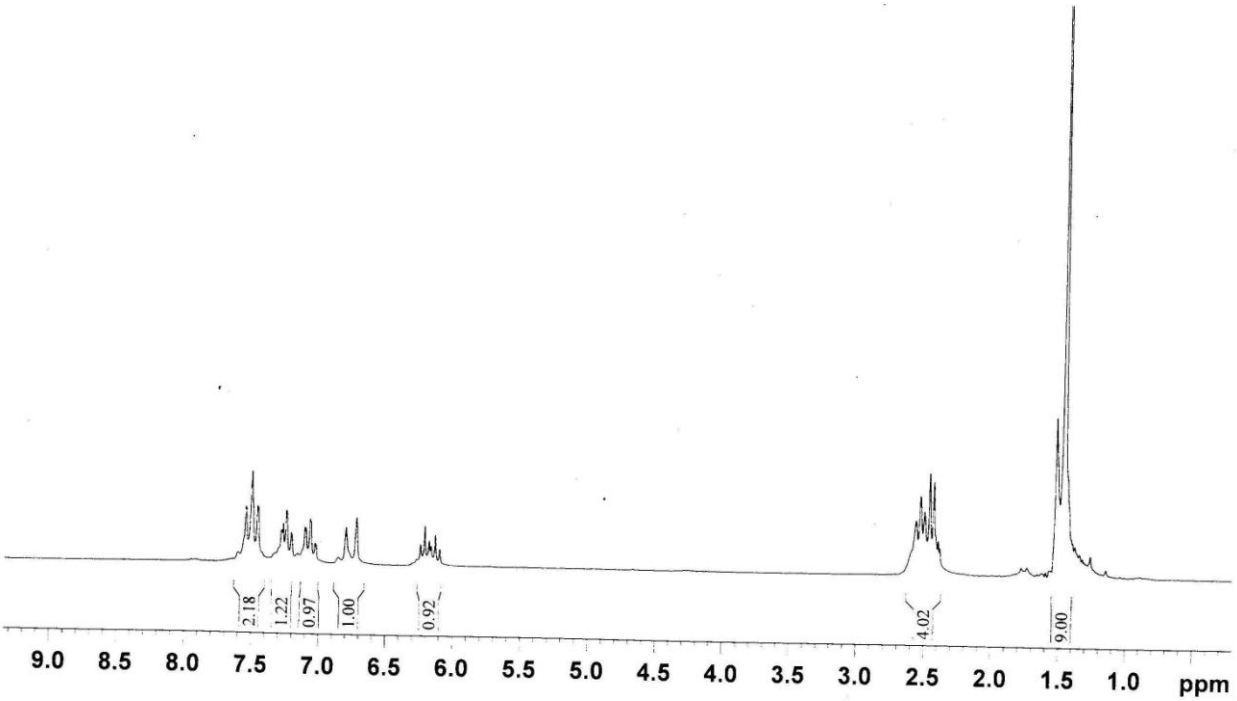
^{1}H NMR of compound **5a** (200 MHz, $CDCl_3$)



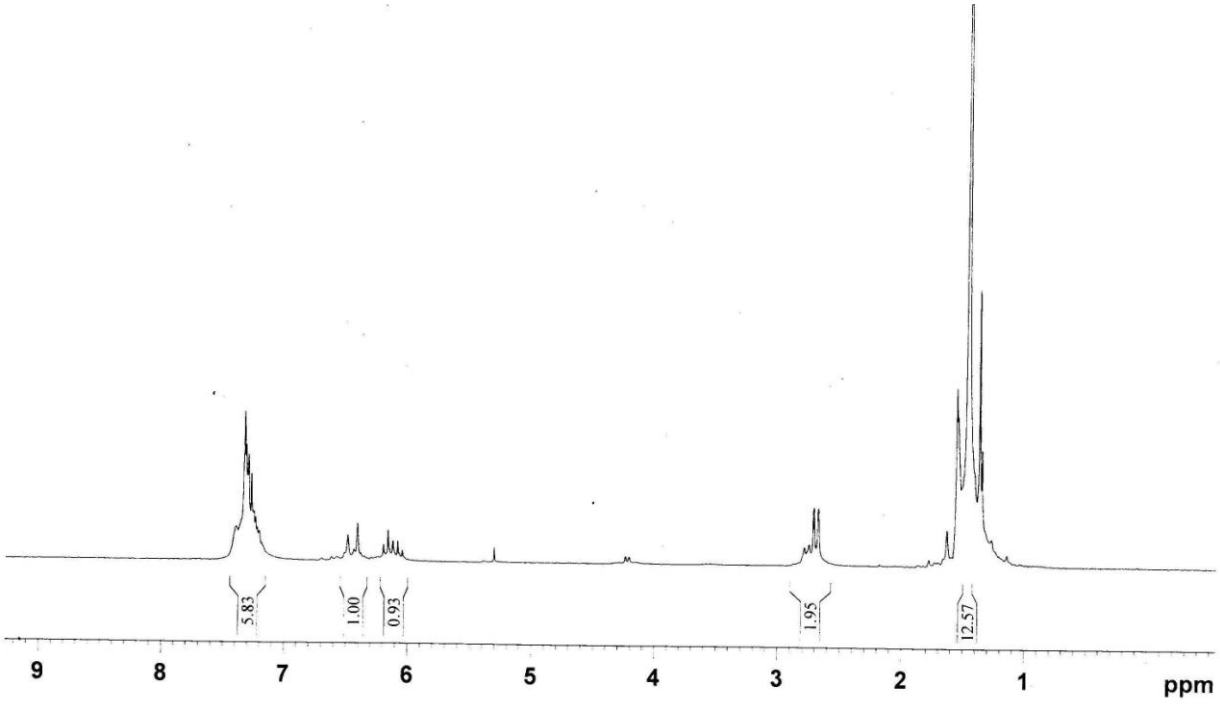
^{1}H NMR of compound **5b** (200 MHz, $CDCl_3$)



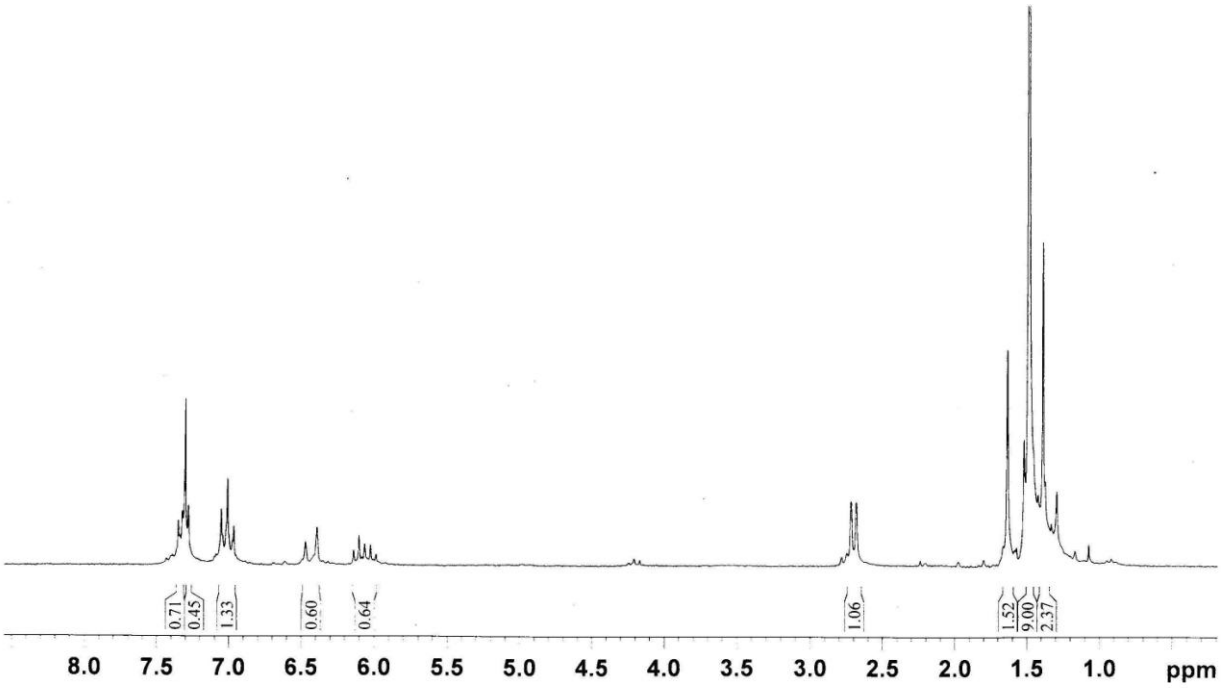
^{1}H NMR of compound **5c** (200 MHz, $CDCl_3$)



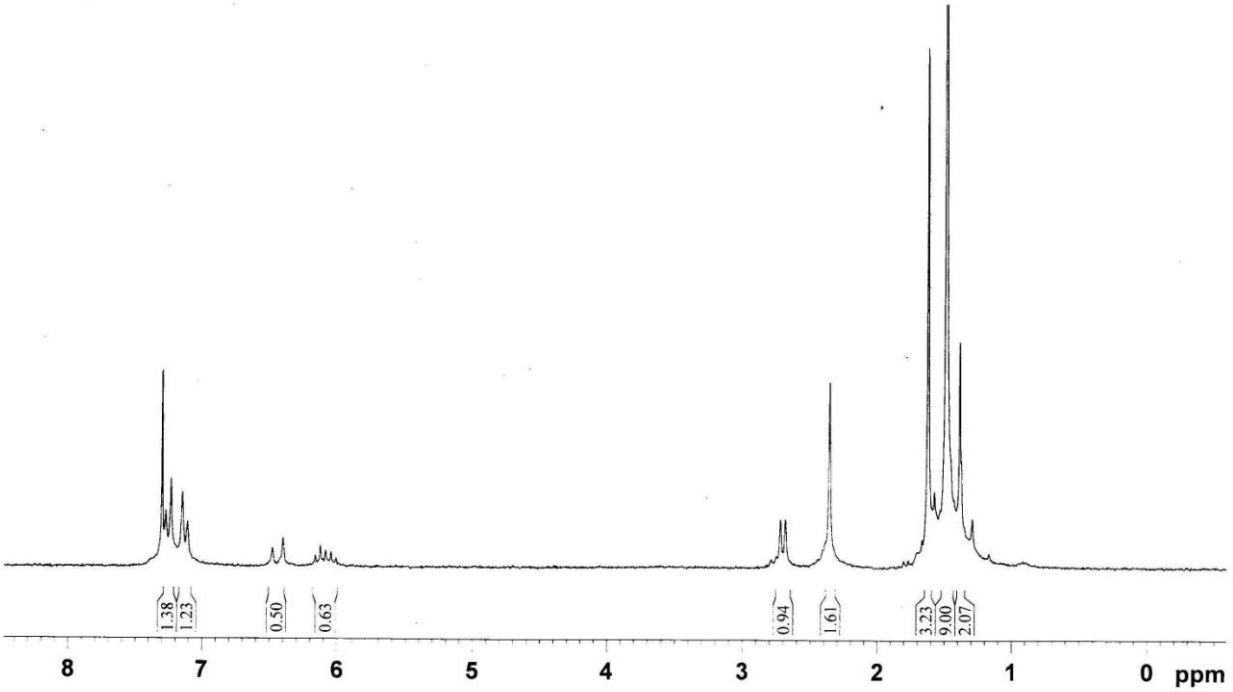
^{1}H NMR of compound **5d** (200 MHz, $CDCl_3$)



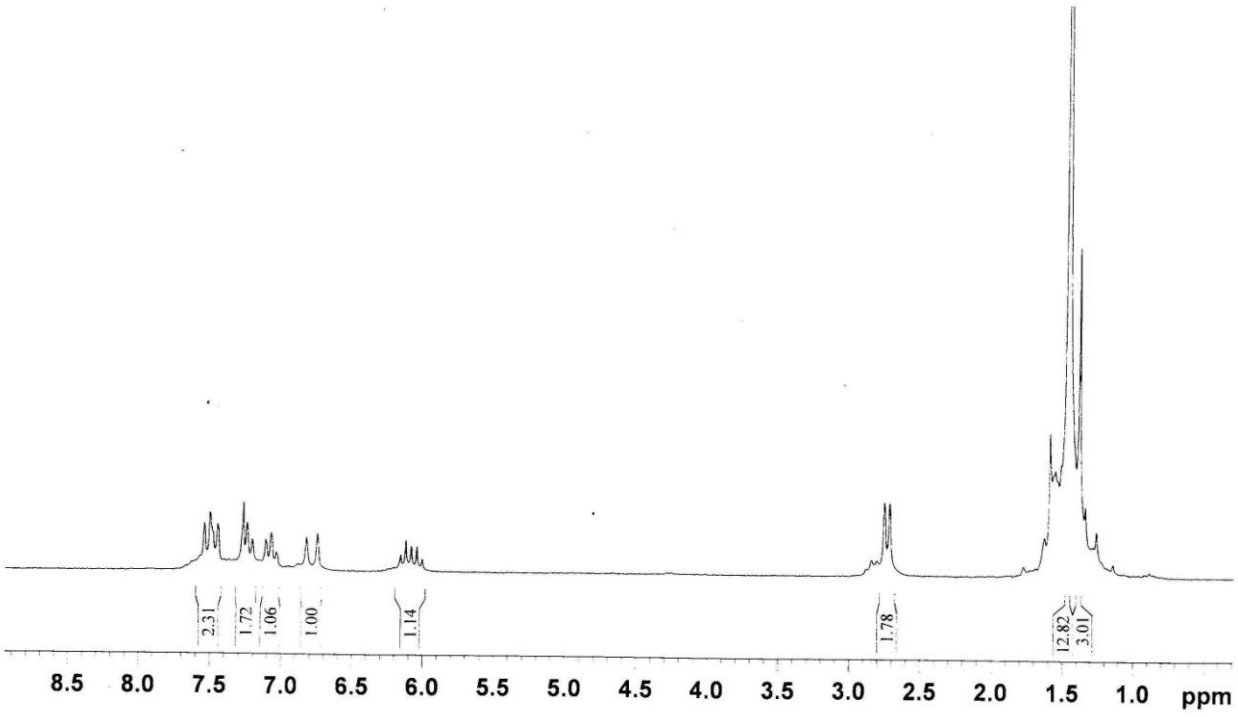
^{1}H NMR of compound **11a** (200 MHz, $CDCl_3$)



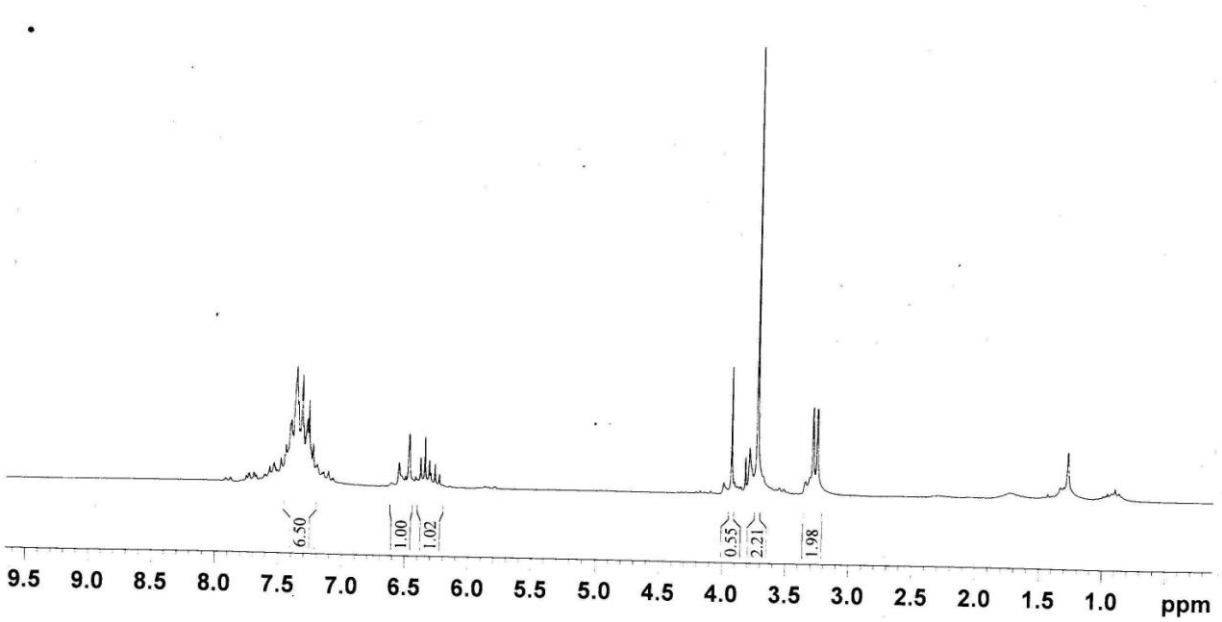
^{1}H NMR of compound **11b** (200 MHz, $CDCl_3$)



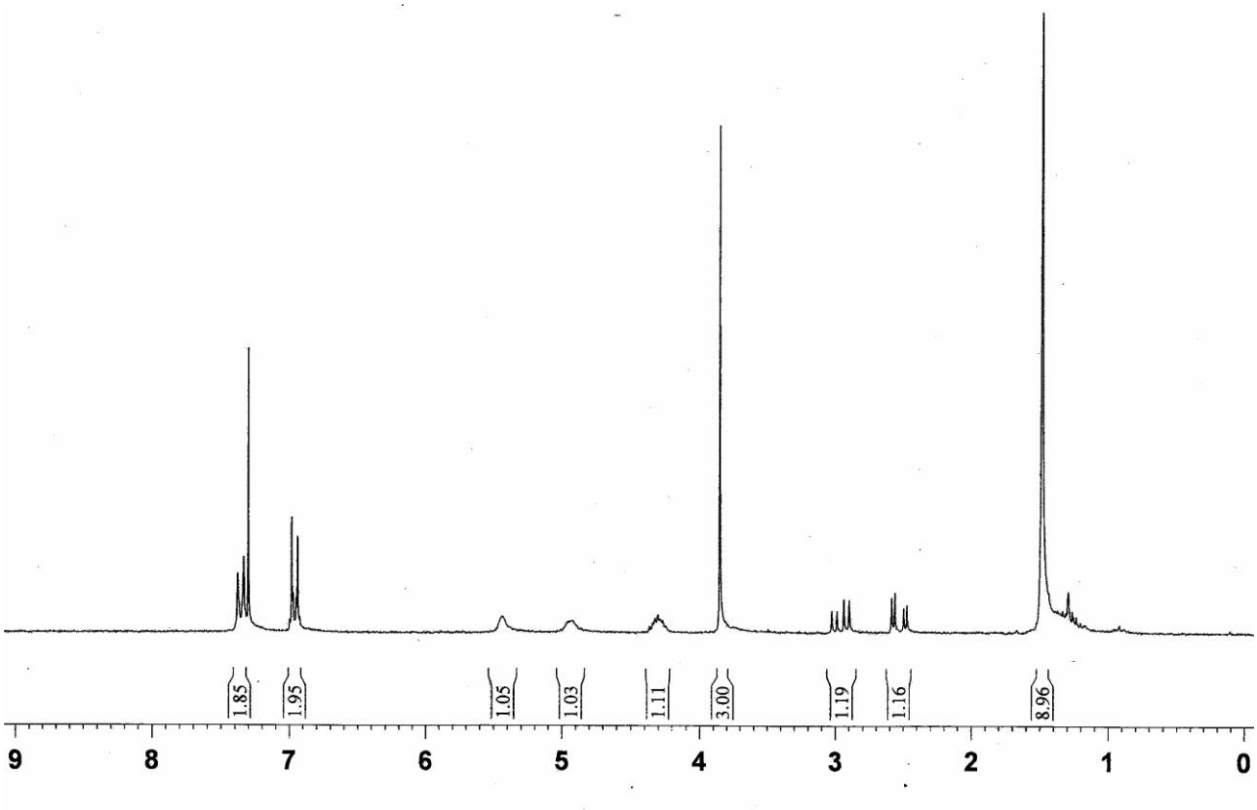
^{1}H NMR of compound **11c** (200 MHz, $CDCl_3$)



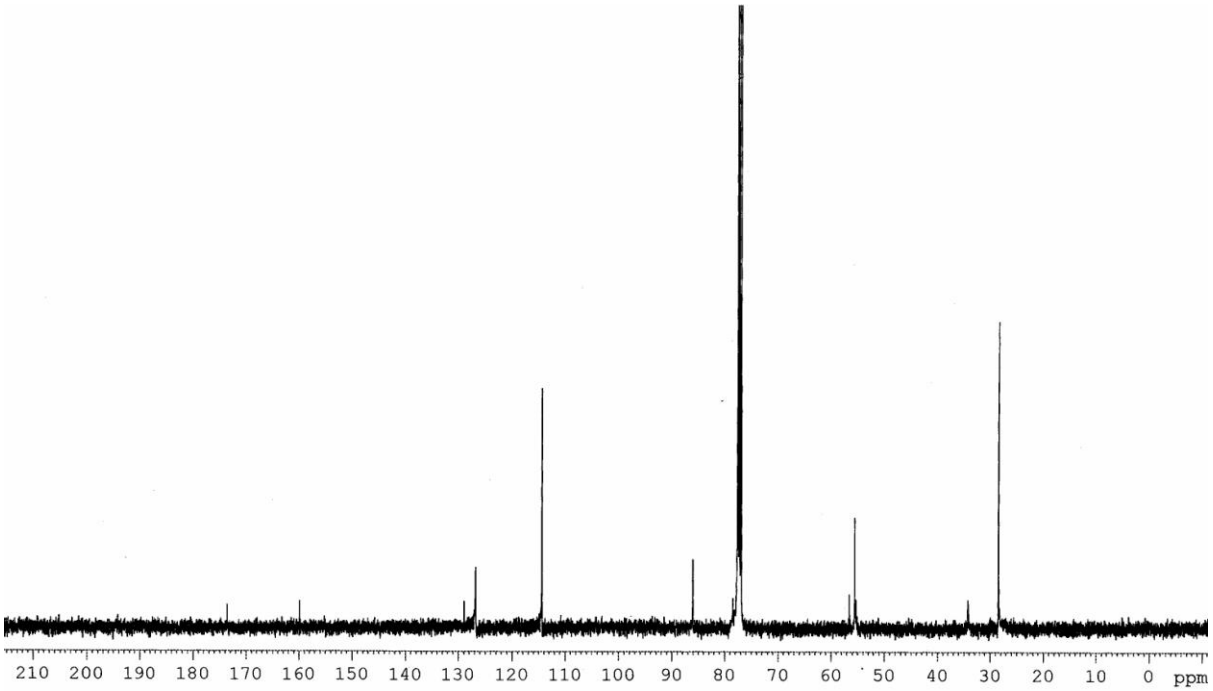
^{1}H NMR of compound **11d** (200 MHz, $CDCl_3$)



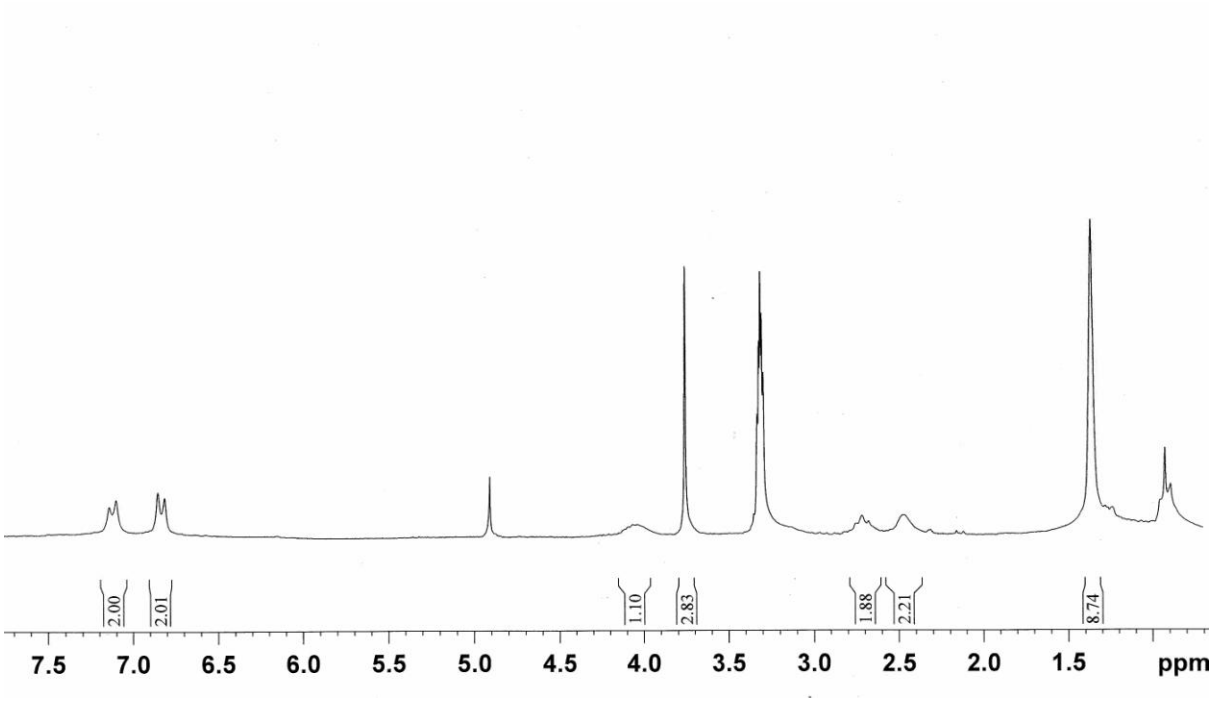
^{1}H NMR of compound **1a′** (200 MHz, $CDCl_3$)



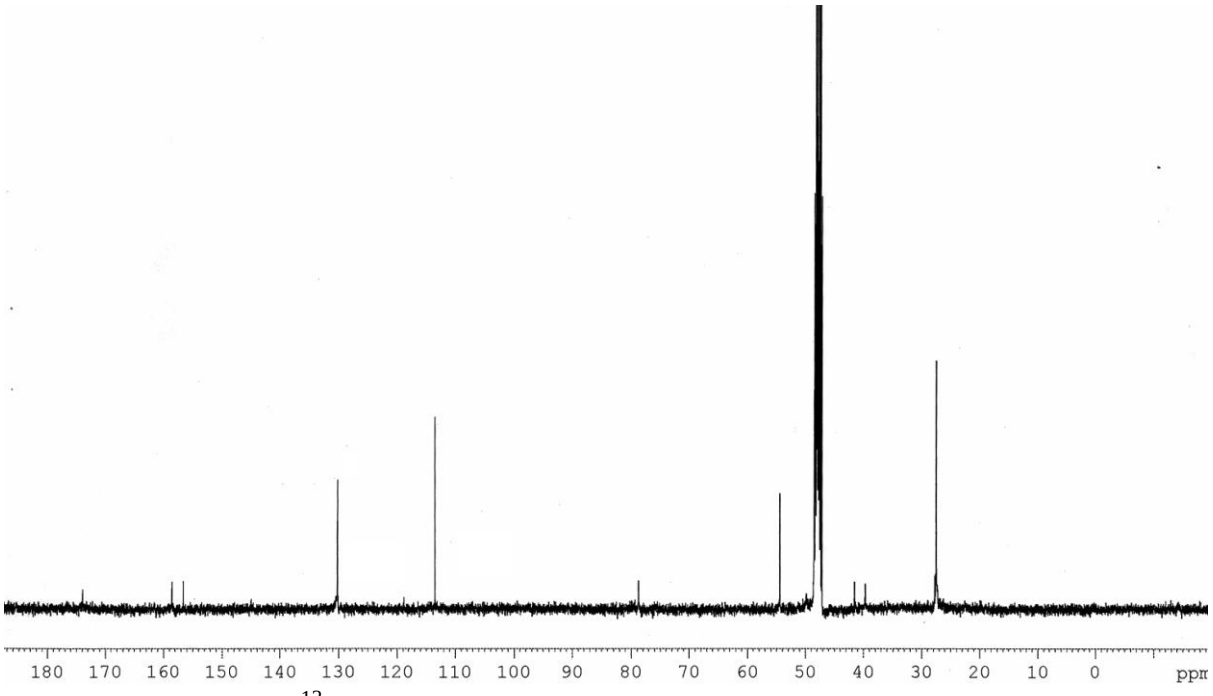
^{1}H NMR of compound **15** (200 MHz, $CDCl_3$)



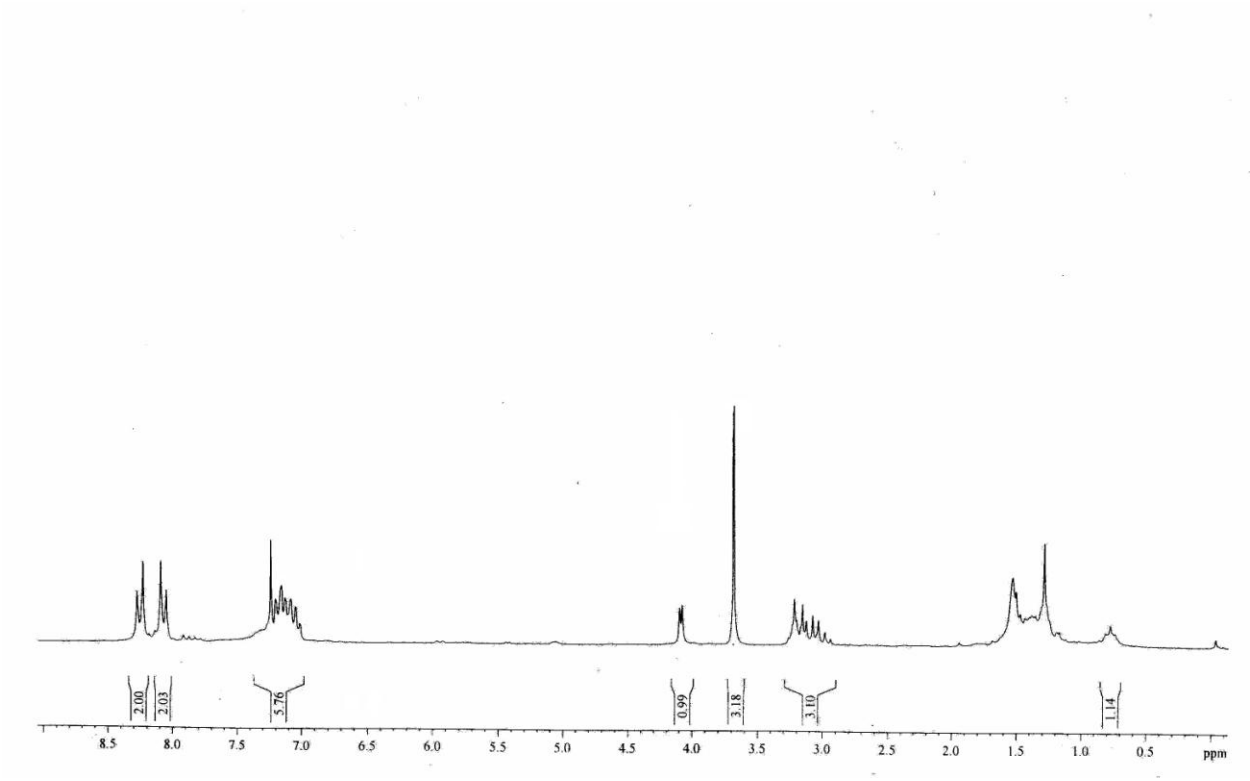
^{13}C NMR of compound **15** (100 MHz, $CDCl_3$)



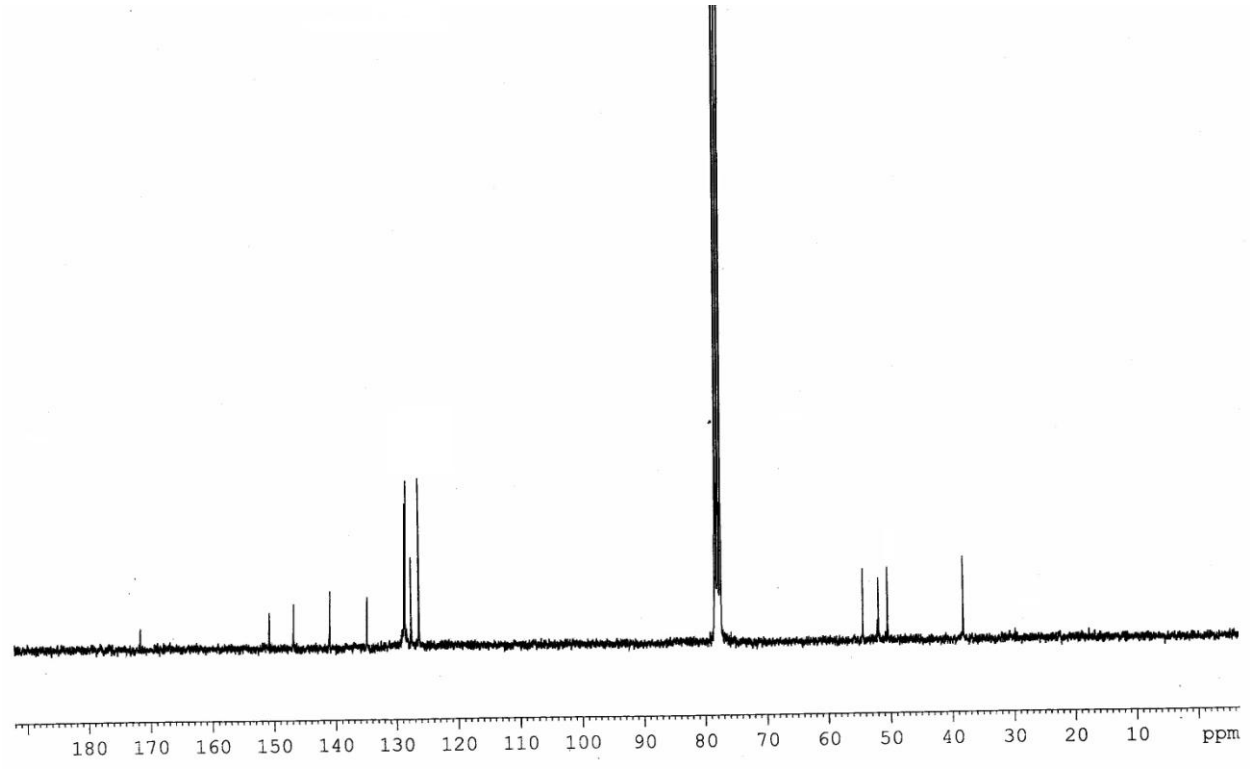
^{1}H NMR of compound **16** (200 MHz, CD_3OD)



^{13}C NMR of compound **16** (100 MHz, CD_3OD)

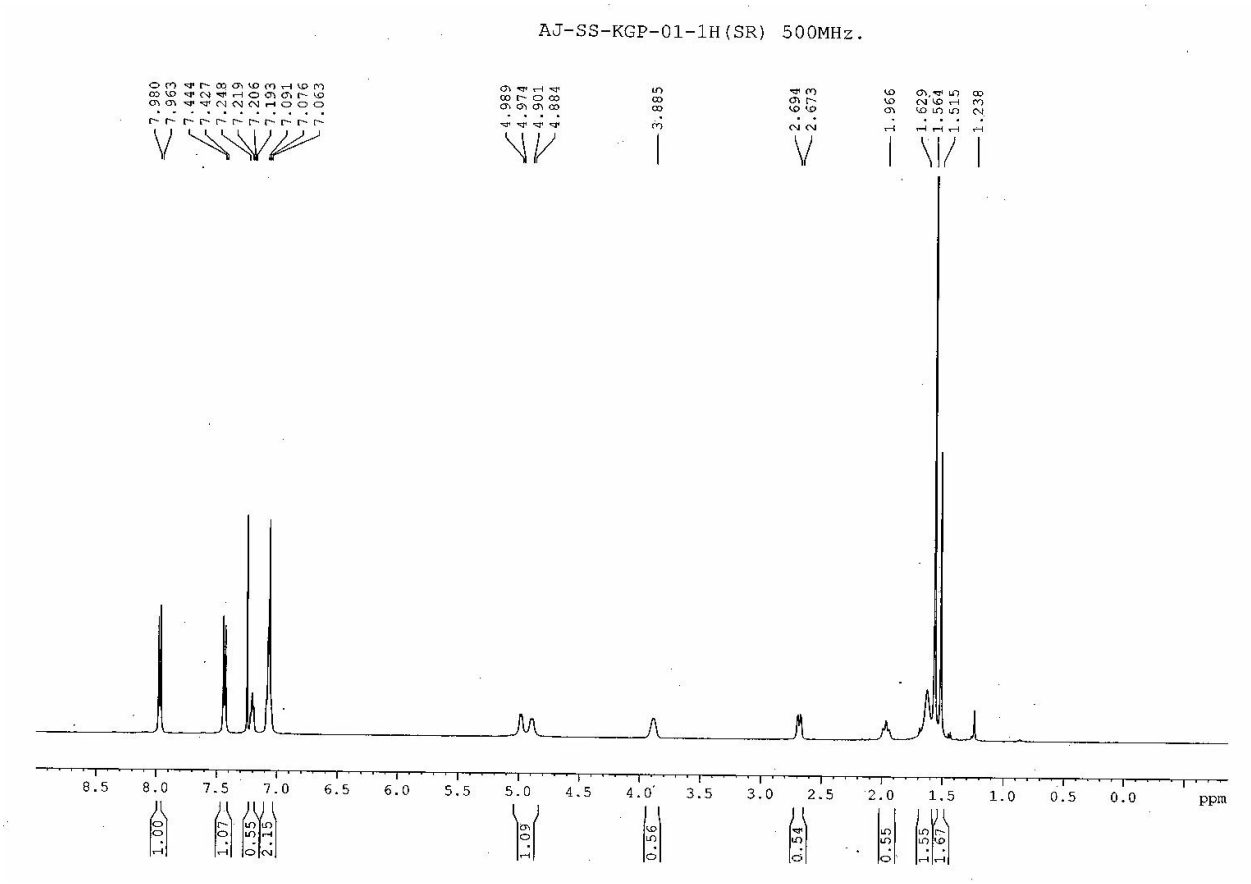


^{1}H NMR of compound **2a′** (200 MHz, $CDCl_3$)

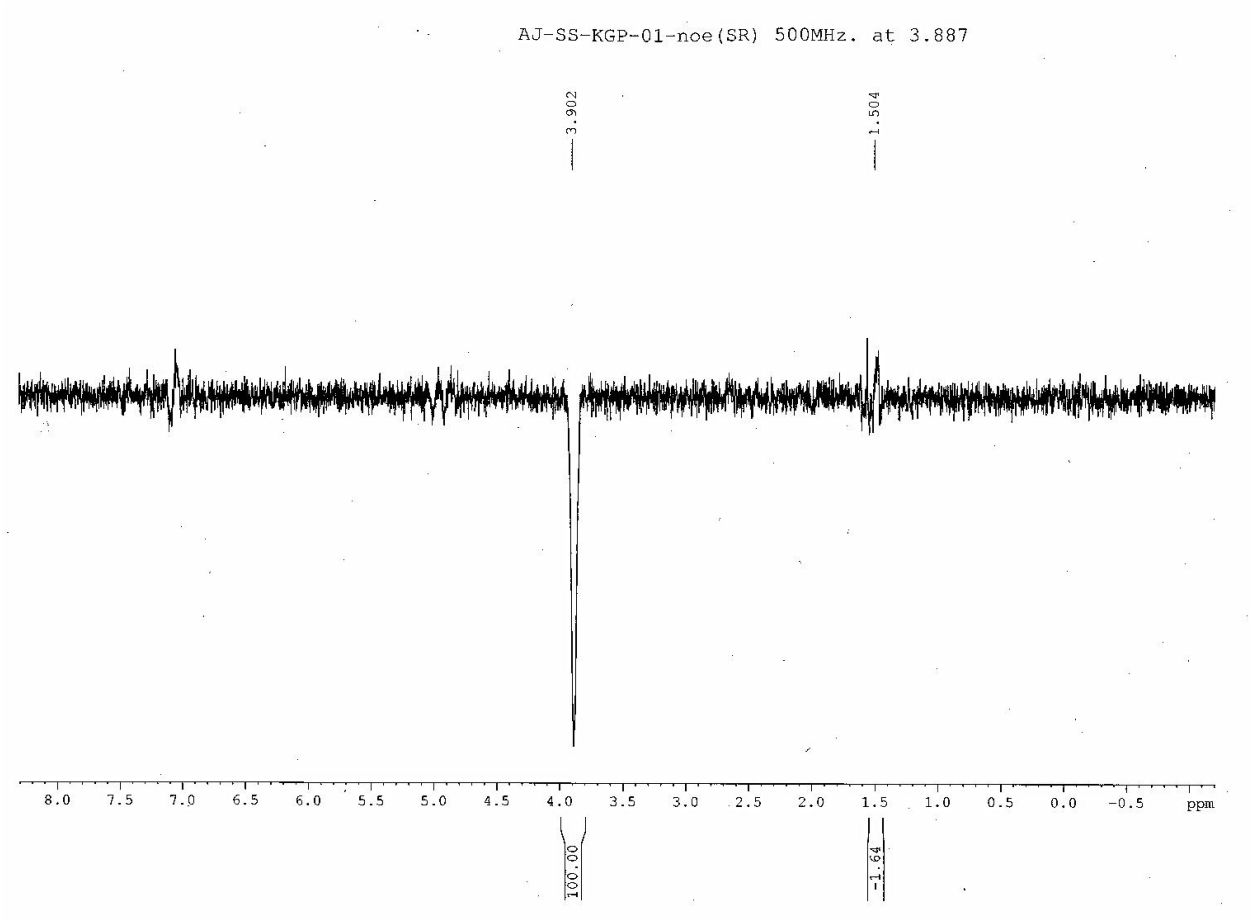


^{13}C NMR of compound **2a′** (50 MHz, $CDCl_3$)

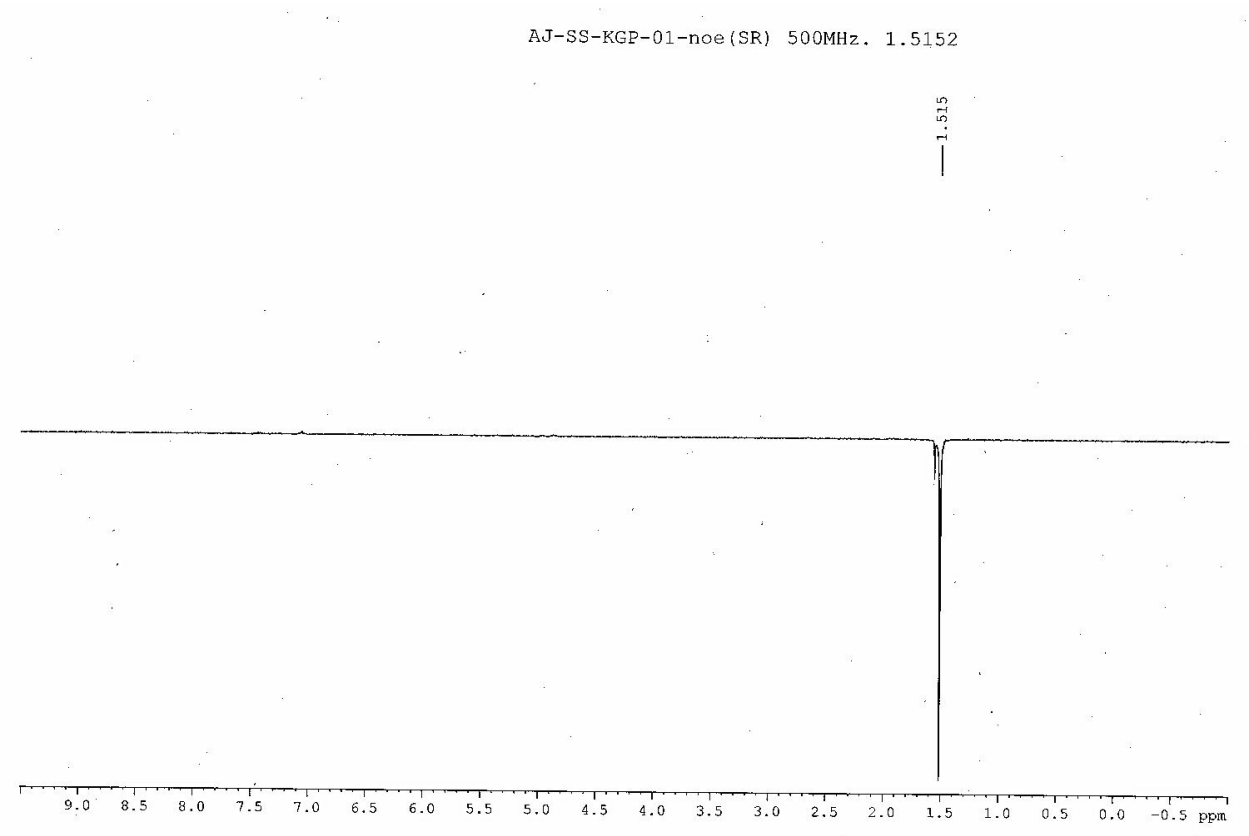
K) 1D-nOe Spectra of compound 13a:



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

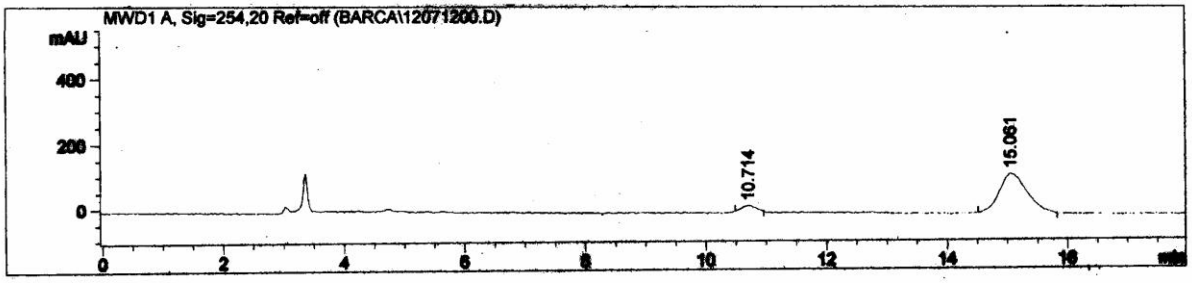


1D-nOe spectrum of compound **13a** (SR at 3.887ppm, 500 MHz, $CDCl_3$)



1D-nOe spectrum of compound **13a** (SR at 1.515ppm, 500 MHz, $CDCl_3$)

L) HPLC Chromatograms:



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

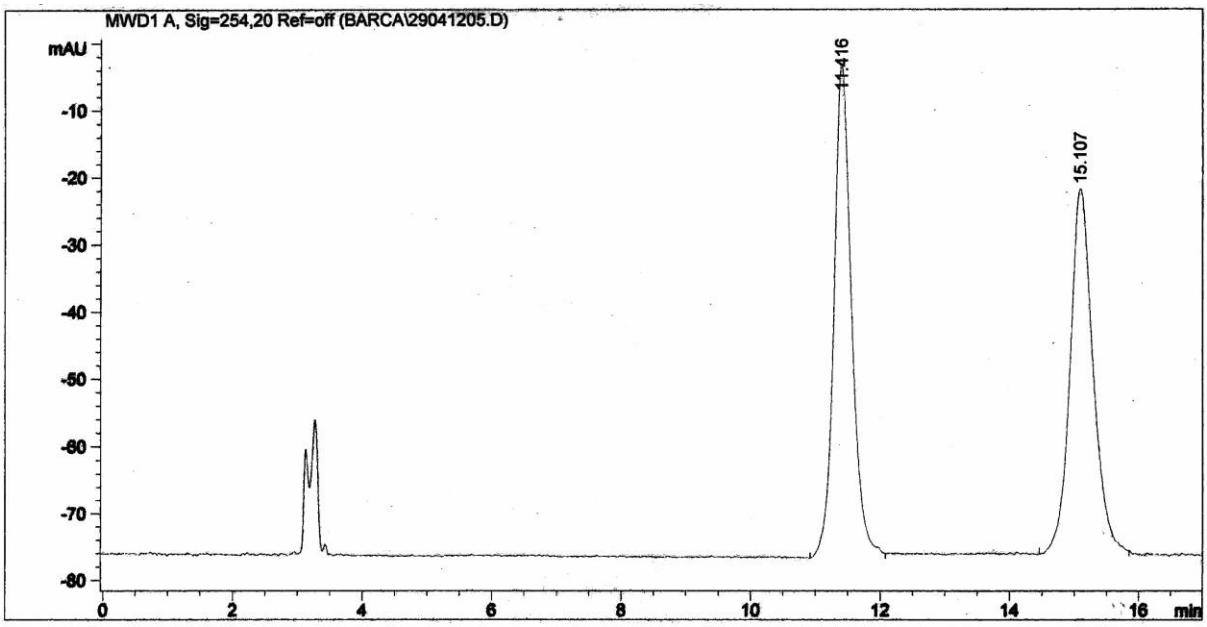
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.714	1	MM	282.09979	18.41279	6.4074
2	15.061	1	VV	4120.58789	125.41027	93.5926
Totals :				4402.68768	143.82306	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3a**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

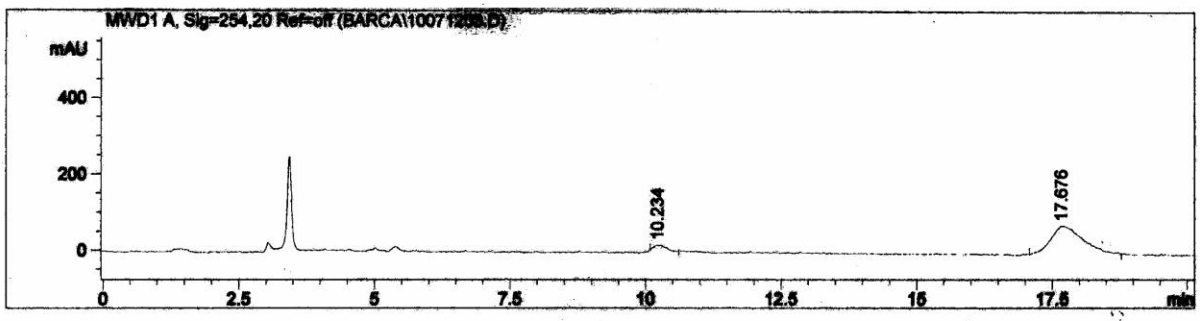
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	11.416	1	VV	1442.76062	74.44961	49.8391
2	15.107	1	VV	1452.07544	55.48281	50.1609
Totals :				2894.83606	129.93242	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3a**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

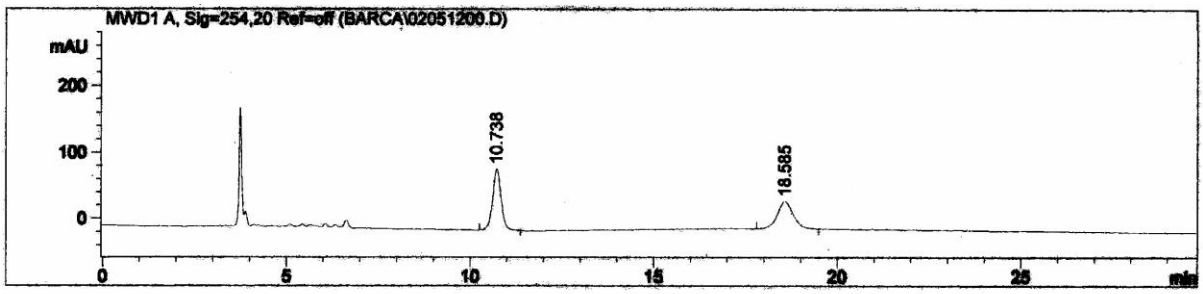
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.234	1	MM	242.78564	14.62041	7.0300
2	17.676	1	MM	3210.79883	75.66816	92.9700
Totals :				3453.58447	90.28857	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3c**



Area.Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

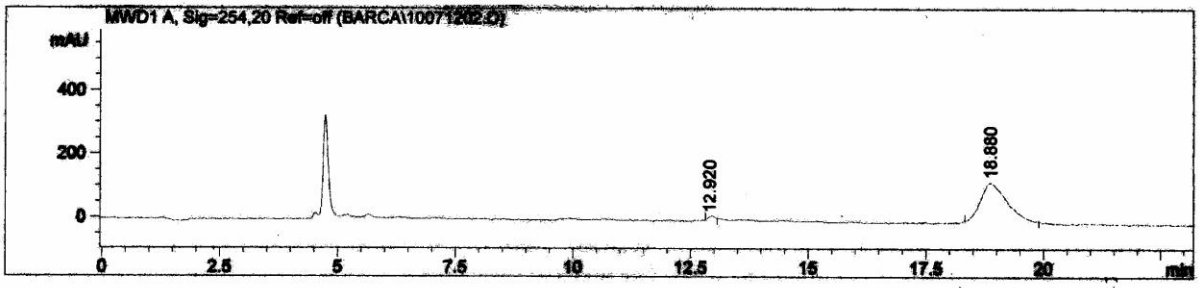
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.738	1	VV	1498.30383	92.93662	47.4891
2	18.585	1	VV	1656.74182	45.53334	52.5109
Totals :				3155.04565	138.46996	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3c**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

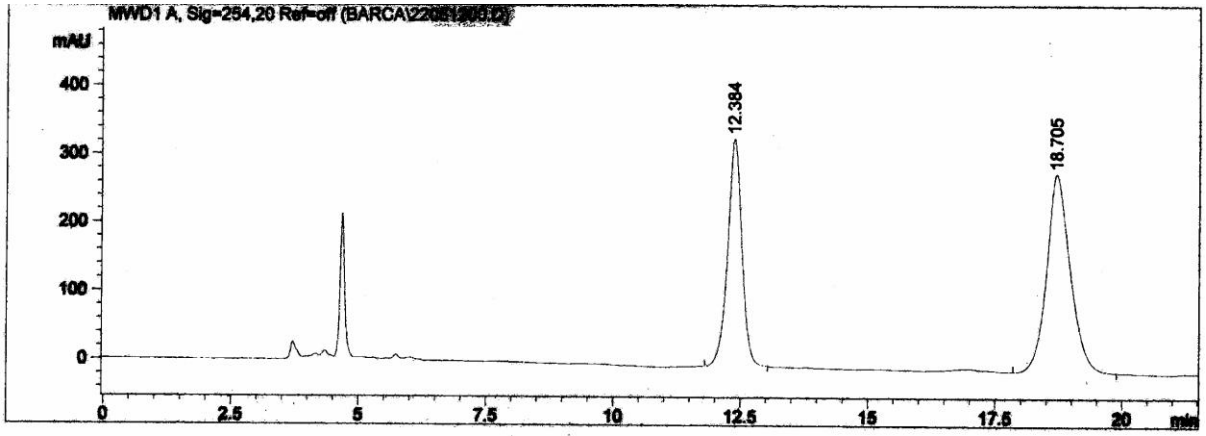
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.920	1	VV	240.31197	18.04769	4.7548
2	18.880	1	MM	4813.76807	122.32579	95.2452
Totals :				5054.08003	140.37348	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3b**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

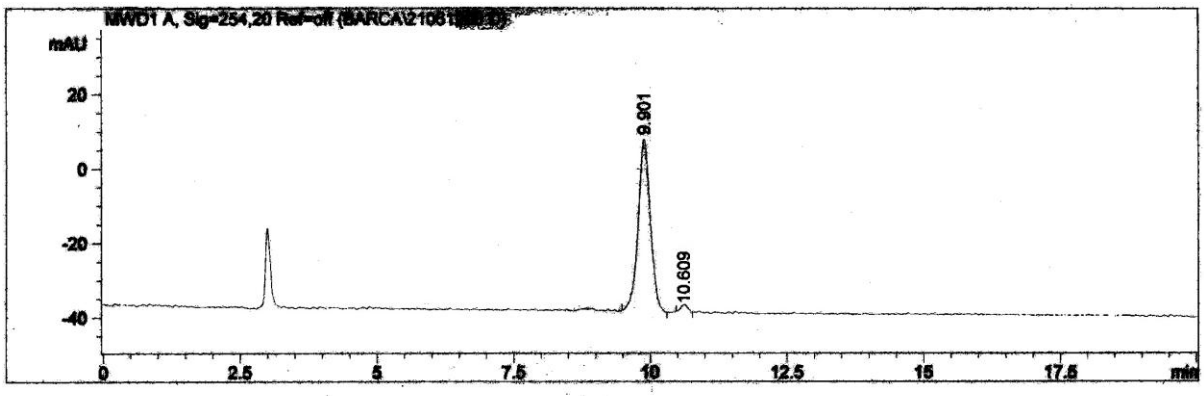
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.384	1	VV	6660.51611	334.51300	41.2288
2	18.705	1	VV	9494.48145	290.41406	58.7712
Totals :				1.61550e4	624.92706	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3b**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

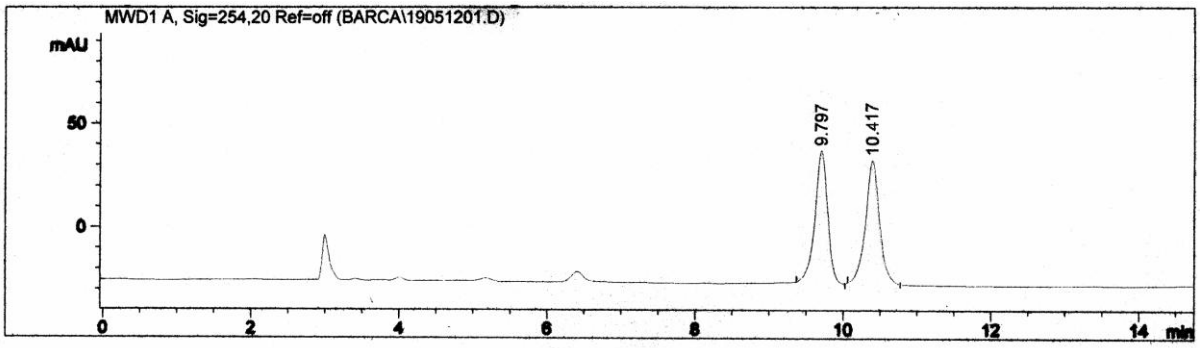
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.901	1	MM	720.01398	46.09703	96.7516
2	10.609	1	MM	24.17415	2.05257	3.2484
Totals :				744.18813	48.14960	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3d**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

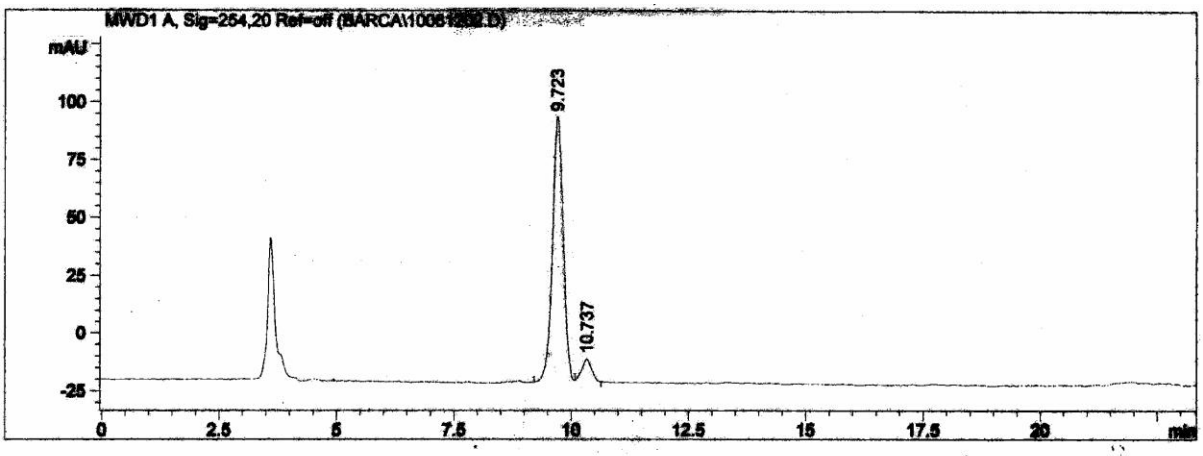
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.797	1	VV	824.98761	64.97095	50.9241
2	10.417	1	VV	795.04614	60.24365	49.0759
Totals :				1620.03375	125.21460	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3d**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

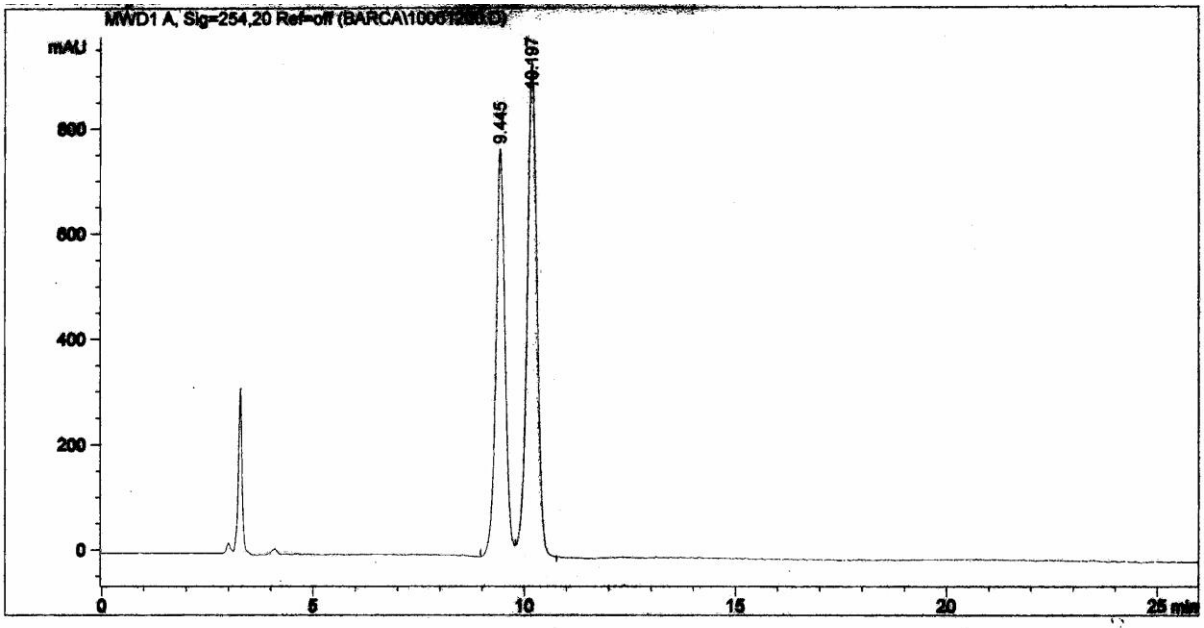
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.723	1	VV	1983.58276	116.76035	90.1504
2	10.737	1	VV	216.72014	12.00198	9.8496
Totals :				2200.30290	128.76232	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3e**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

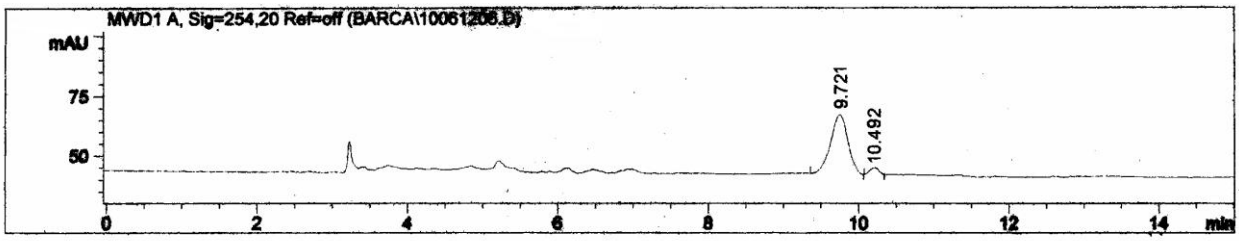
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.445	1	VV	1.19668e4	779.79865	43.1531
2	10.197	1	VV	1.57642e4	944.80670	56.8469
Totals :				2.77309e4	1724.60535	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3e**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

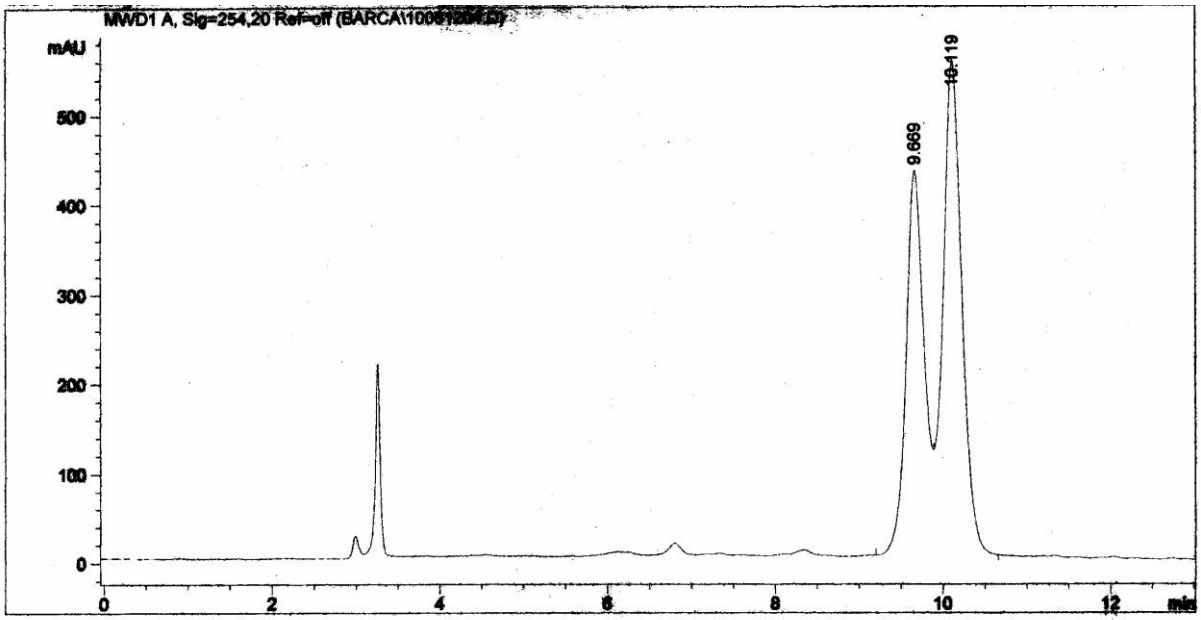
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.721	1	MM	191.72936	22.90052	90.9924
2	10.492	1	MM	18.97967	2.65805	9.0075
Totals :				210.70903	25.58857	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3f**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

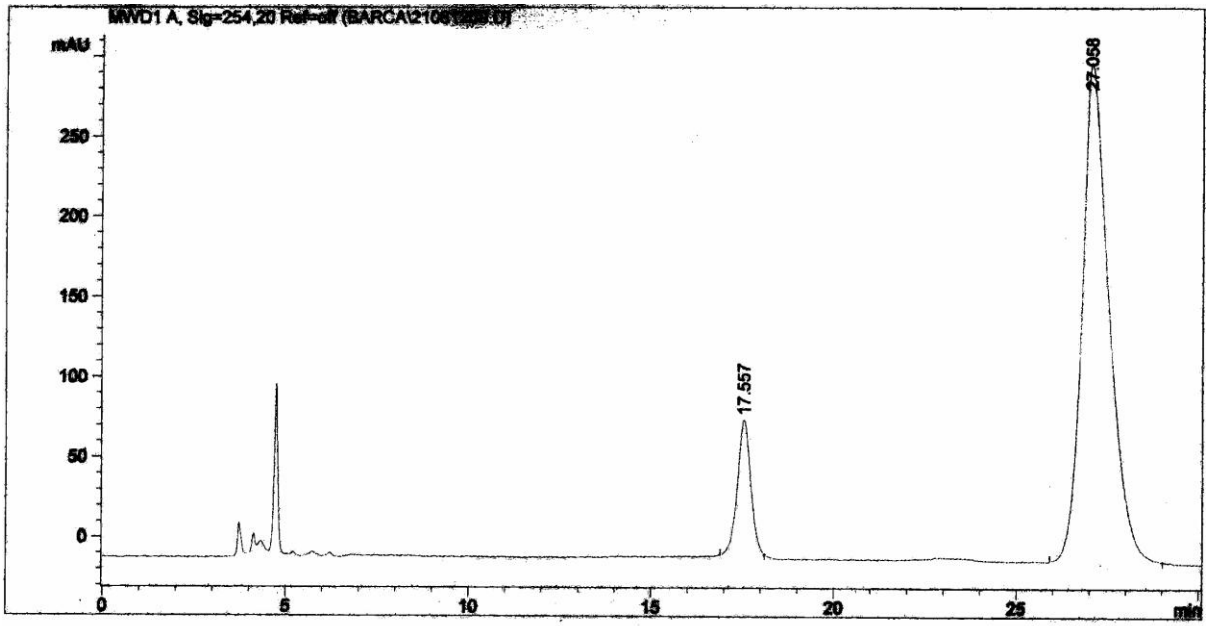
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.669	1	VV	6619.65039	433.60724	42.6584
2	10.119	1	VV	8898.15332	556.32684	57.3416
Totals :				1.55178e4	989.93408	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3f**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

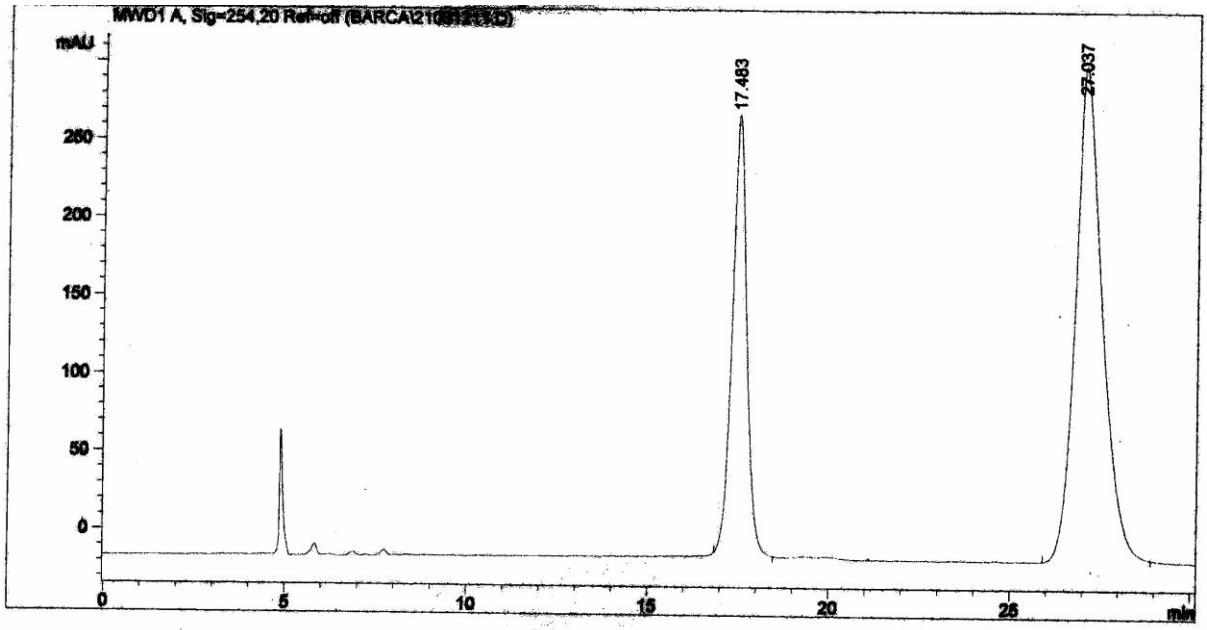
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	17.557	1	MM	2116.89868	83.06984	11.6862
2	27.058	1	MM	1.59977e4	311.09402	88.3138
Totals :				1.81146e4	394.16386	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **3g**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

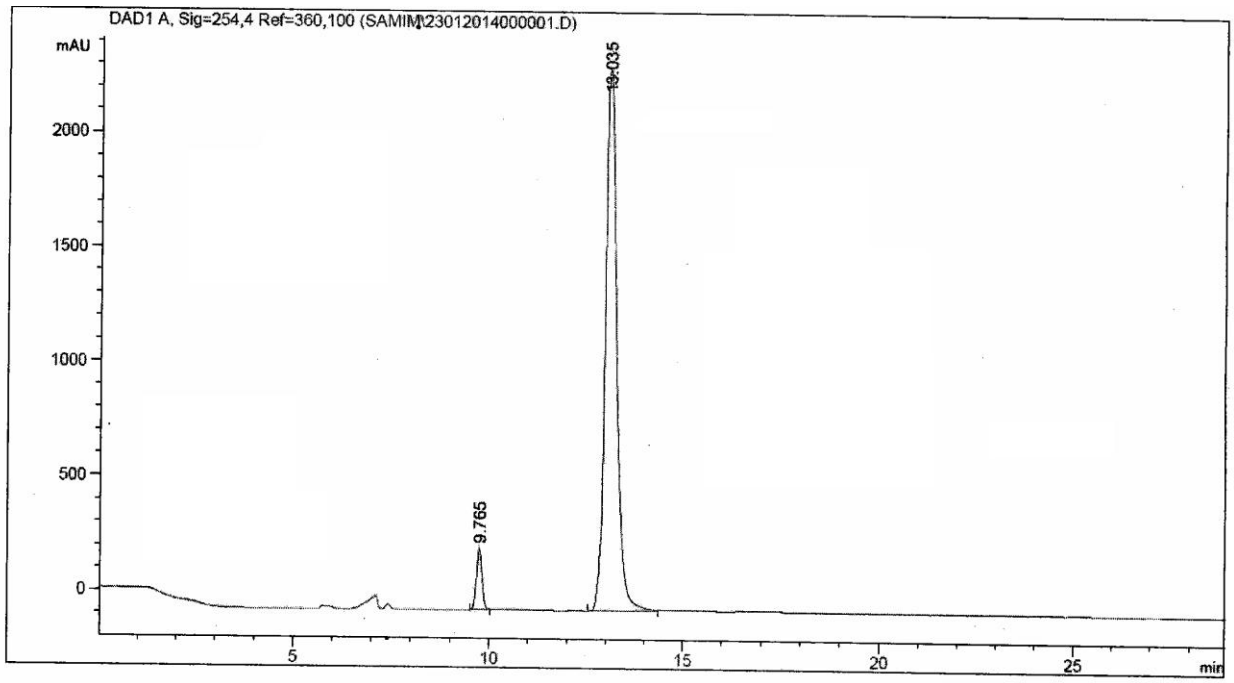
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	17,483	1	VV	8570.39160	286.79462	33.5899
2	27.037	1	VV	1.69444e4	319.12619	66.4101
Totals :				2.55148e4	605.92081	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**3g**

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=====================================================================
                        Area Percent Report
=====================================================================

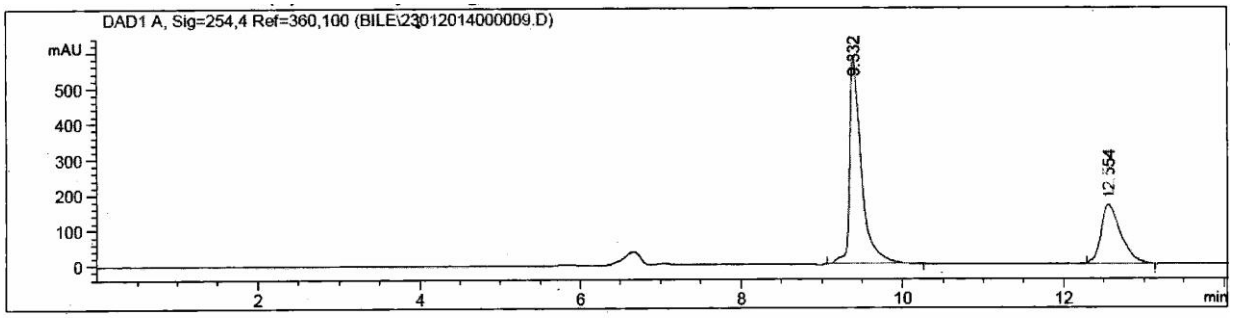
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.765 BV    0.1682 3046.68896  281.54407   6.0274
   2  13.035 VB    0.3041 4.75003e4  2367.10376  93.9726

Totals :                  5.05470e4  2648.64783
```

HPLC Chromatogram of compound **3h**



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Area Percent Report

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Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.332	BV	0.1083	4347.11523	574.42169	59.6755
2	12.554	VV	0.2438	2937.47778	166.49480	40.3245
Totals :				7284.59302	740.91649	

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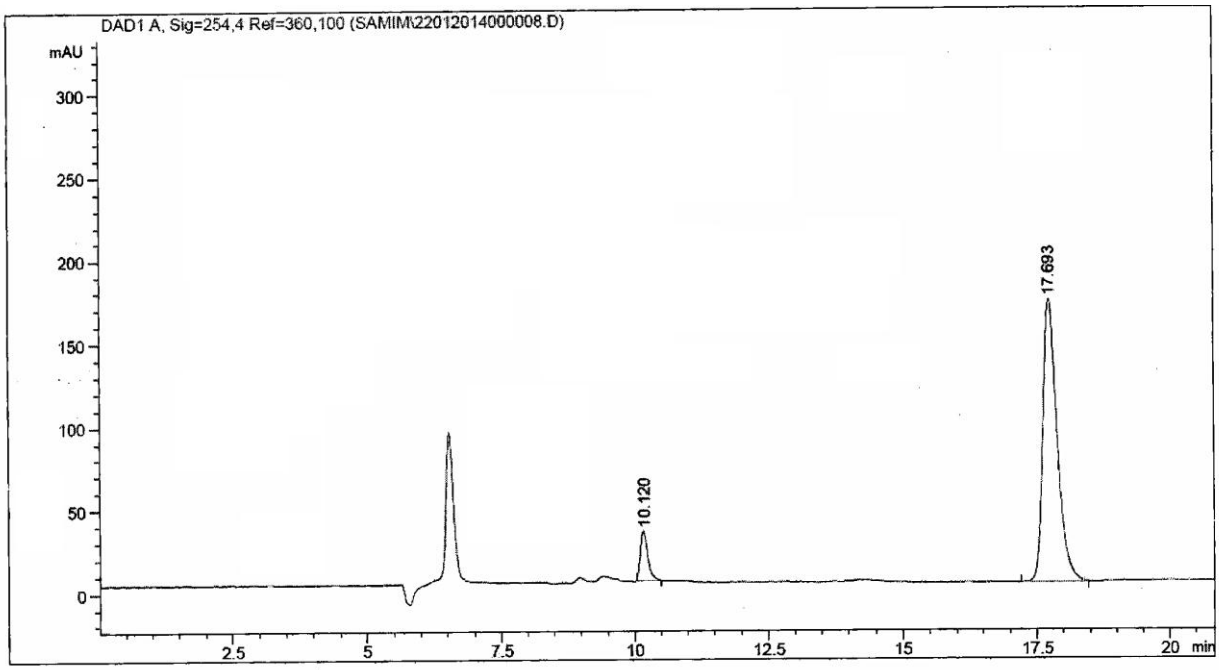
*** End of Report ***

HPLC Chromatogram of compound (±)**3h**



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Area Percent Report

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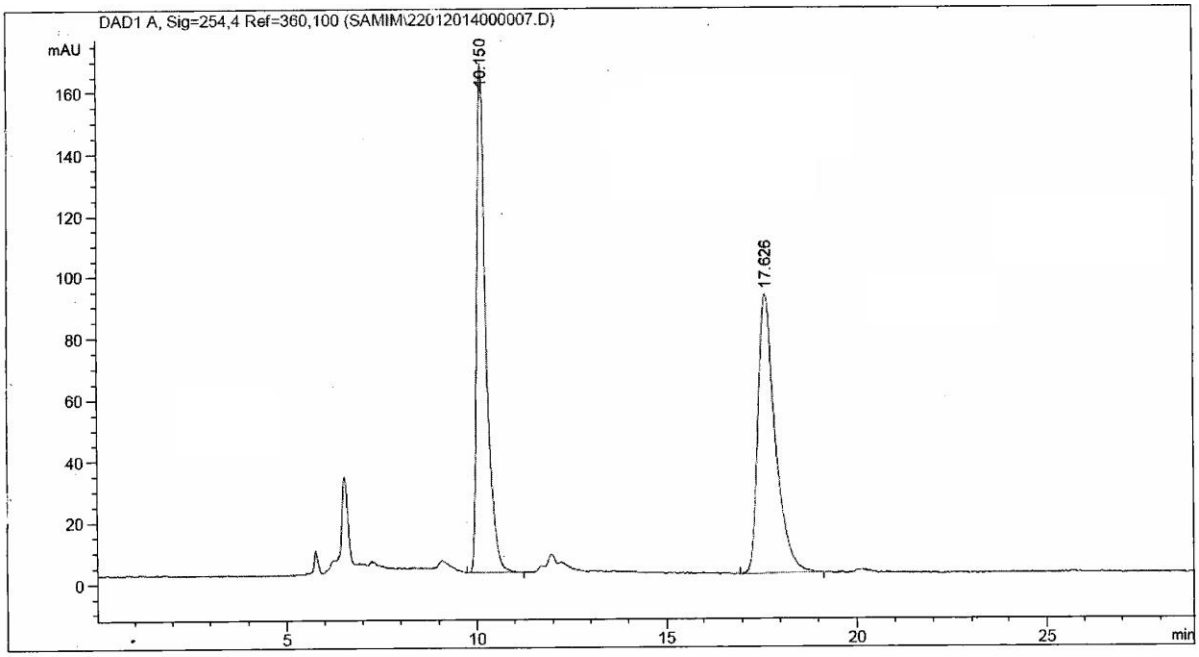
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.120	BB	0.1358	229.20276	28.13960	7.4924
2	17.693	VB	0.2547	2829.93335	169.59680	92.5076
Totals :				3059.13611	197.73640	

HPLC Chromatogram of compound **3i**



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Area Percent Report

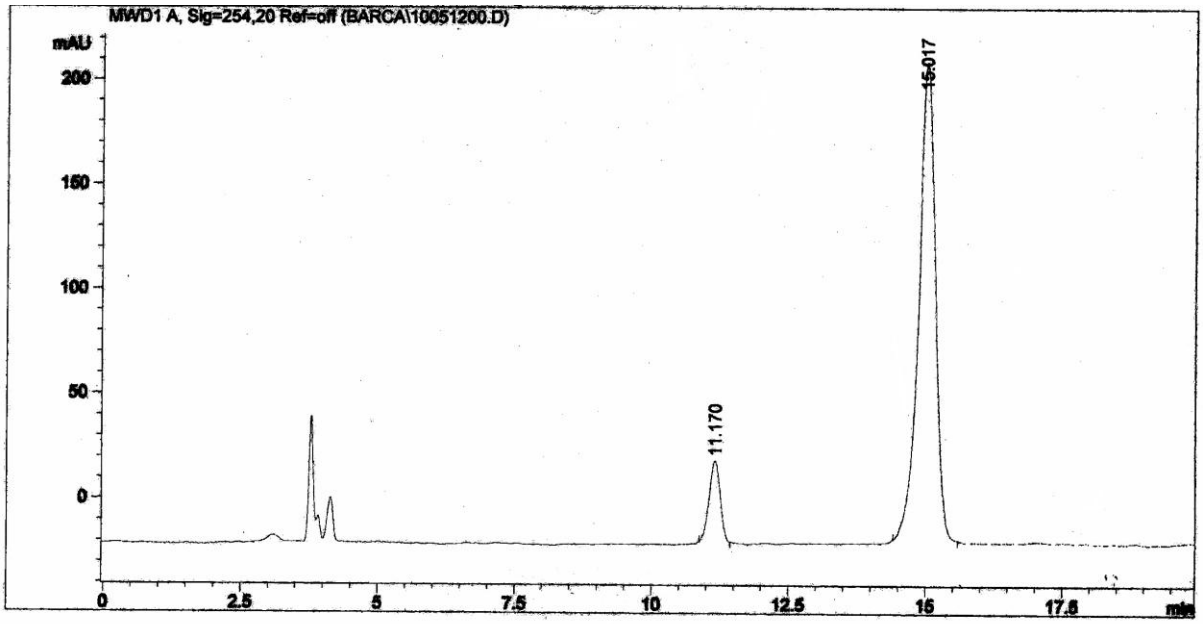
==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.150	BB	0.1810	2027.92419	165.44620	49.6382
2	17.626	BB	0.3341	2057.48682	90.88344	50.3618
Totals :				4085.41101	256.32964	

HPLC Chromatogram of compound (±)**3i**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

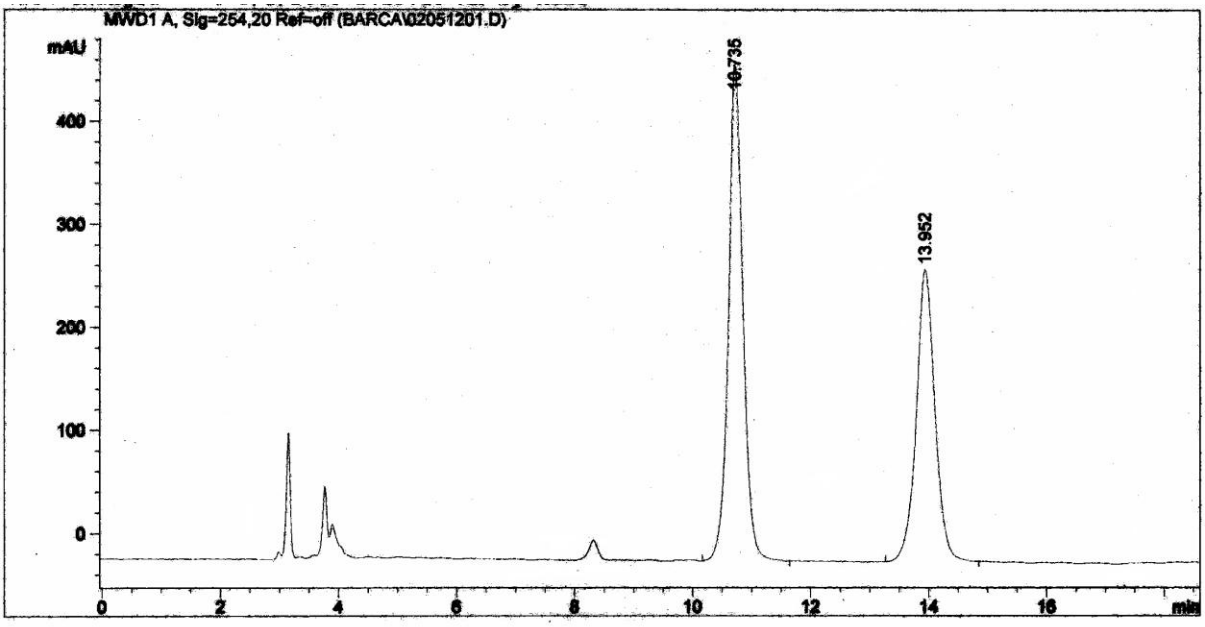
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	11.170	1	MM	543.48041	38.81512	10.5462
2	15.017	1	MM	4609.83594	217.10495	89.4538
Totals :				5153.31635	255.92007	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **10**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

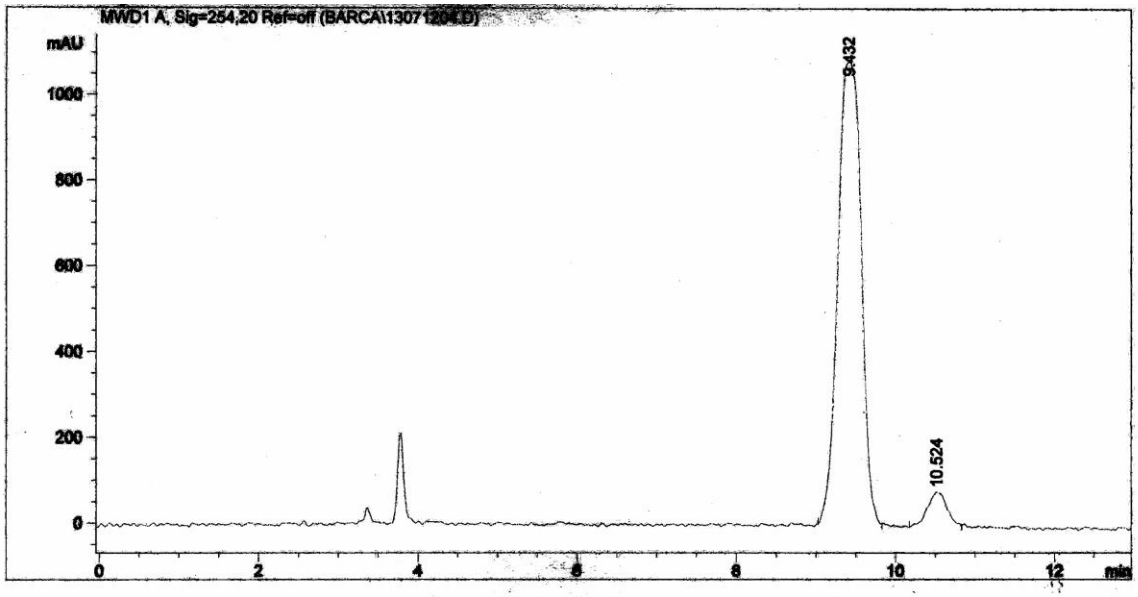
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	10.735	1	VV	8307.18359	484.42422	56.5664
2	13.952	1	VV	6378.54688	285.07300	43.4336
Totals :				1.46857e4	769.49722	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**10**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

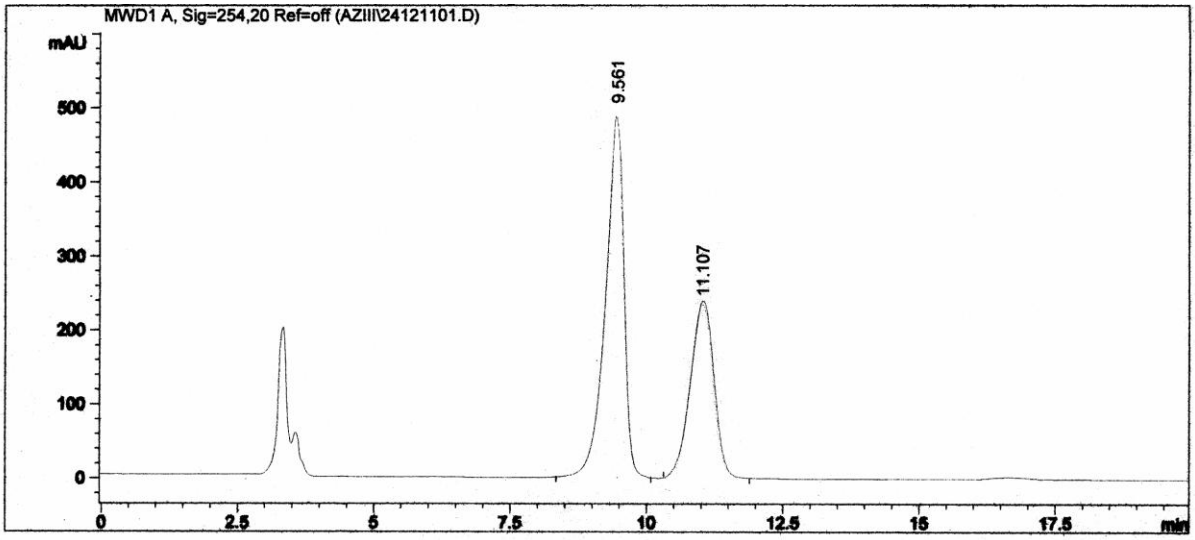
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.432	1	VV	2.26739e4	1098.60828	94.5226
2	10.524	1	MM	1313.91406	78.54959	5.4774
Totals :				2.39879e4	1177.15787	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **7a**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

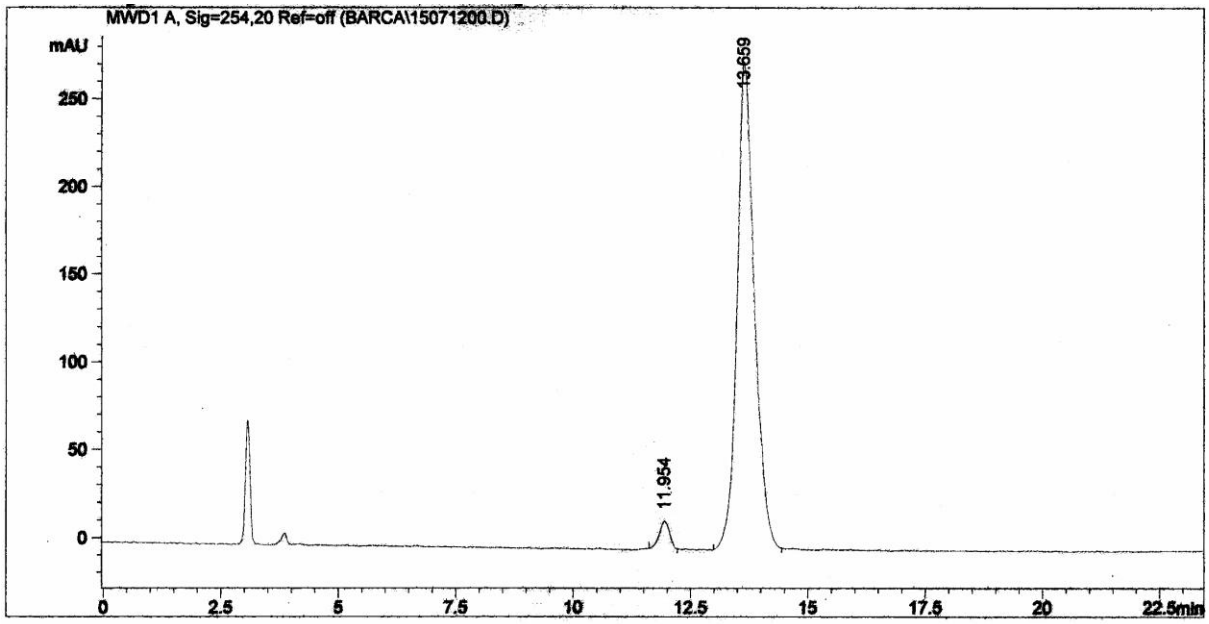
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	9.561	1	VB	8020.86475	502.02359	52.4920
2	11,107	1	BB	7259.31006	239.78349	47.5080
Totals :				1.52802e4	741.80708	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**7a**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

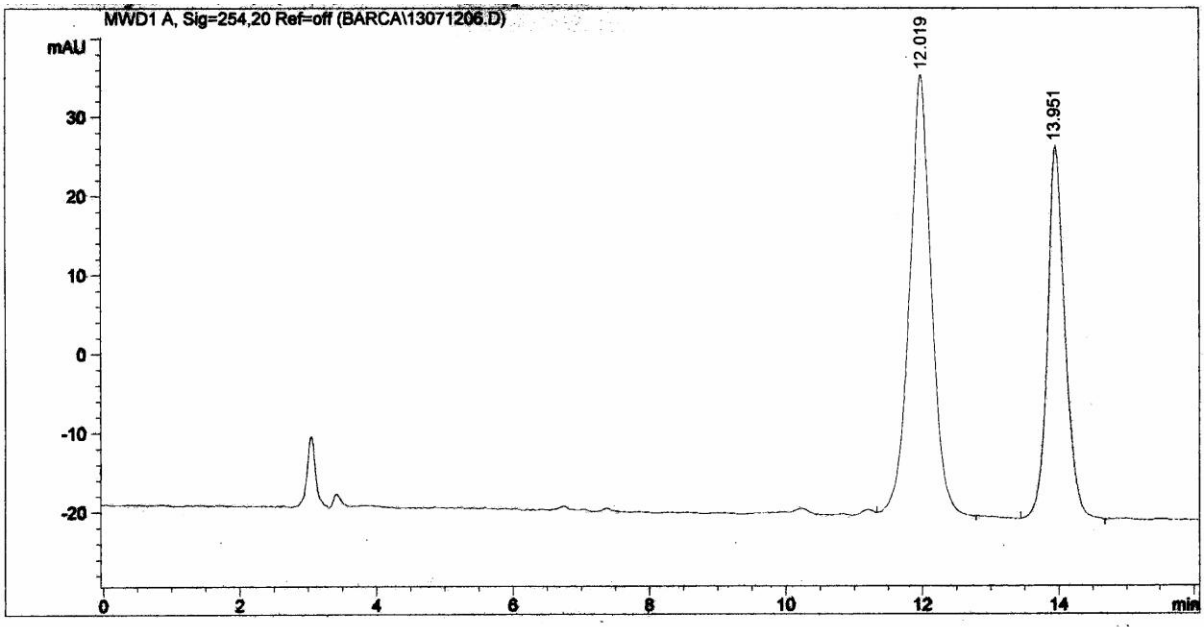
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	11.954	1	MM	283.34760	17.60246	3.8428
2	13.659	1	MM	7090.10010	277.23441	96.1572
Totals :				7373.44769	294.83687	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound **7b**



Area Percent Report

Sorted By : Retention Time
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

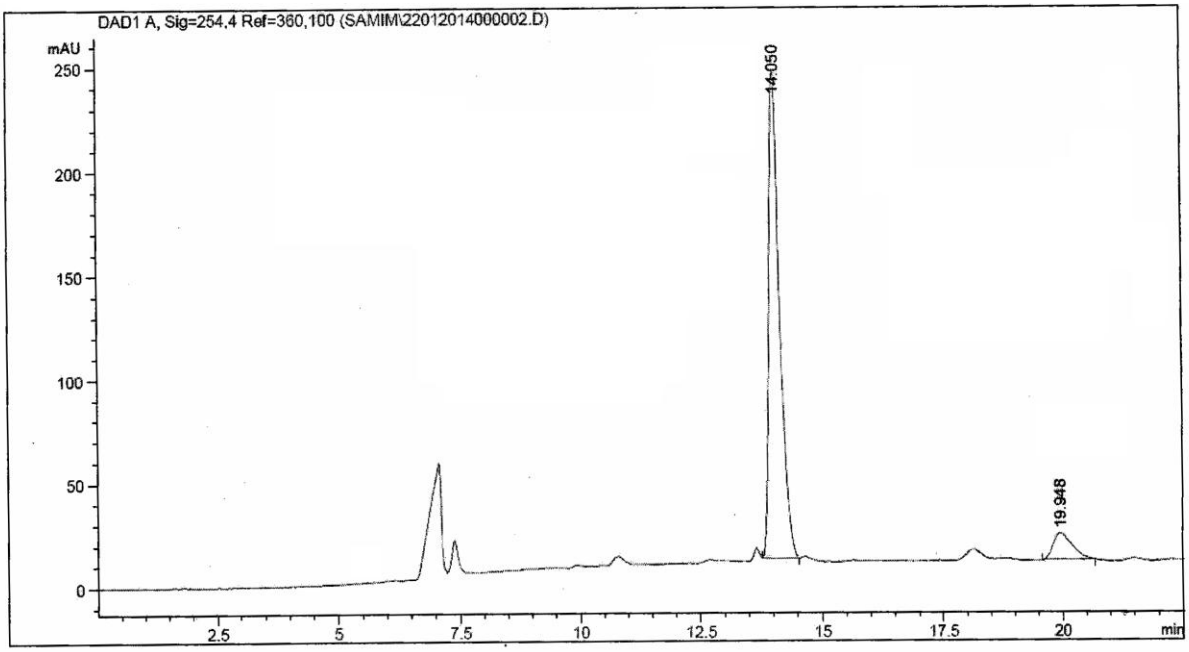
Signal 1: MWD1 A, Sig=254,20 Ref=off

Peak #	RetTime [min]	Sig	Type	Area [mAU*s]	Height [mAU]	Area %
1	12.019	1	MM	1301.30493	57.30381	54.2451
2	13.951	1	MM	1097.62903	46.19674	45.7549
Totals :				2398.93396	103.50055	

Results obtained with enhanced integrator!

*** End of Report ***

HPLC Chromatogram of compound (±)**7b**



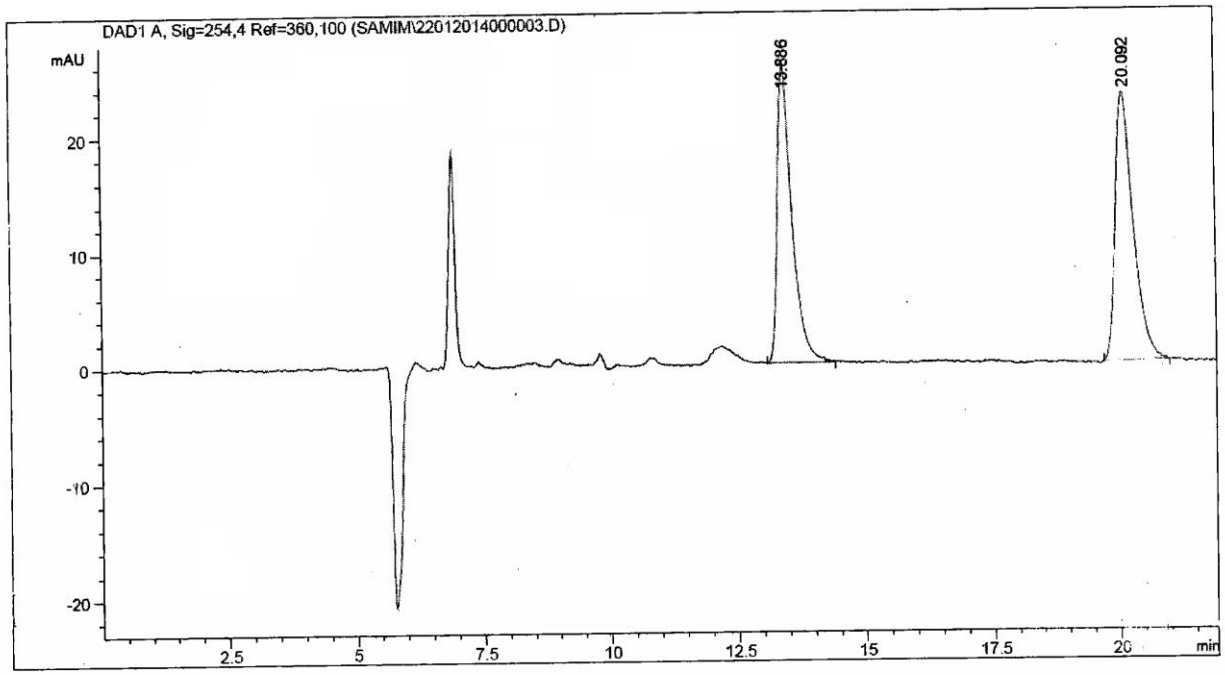
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.050	VV	0.2400	3876.58936	240.51472	91.6754
2	19.948	MM	0.4565	352.01532	12.85077	8.3246
Totals :				4228.60468	253.36550	

HPLC Chromatogram of compound **7c**

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=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  13.886 BB    0.2947  507.66916   25.67156  47.0563
   2  20.092 BB    0.3593  571.18518   23.19553  52.9437

Totals :                  1078.85434   48.86709
```
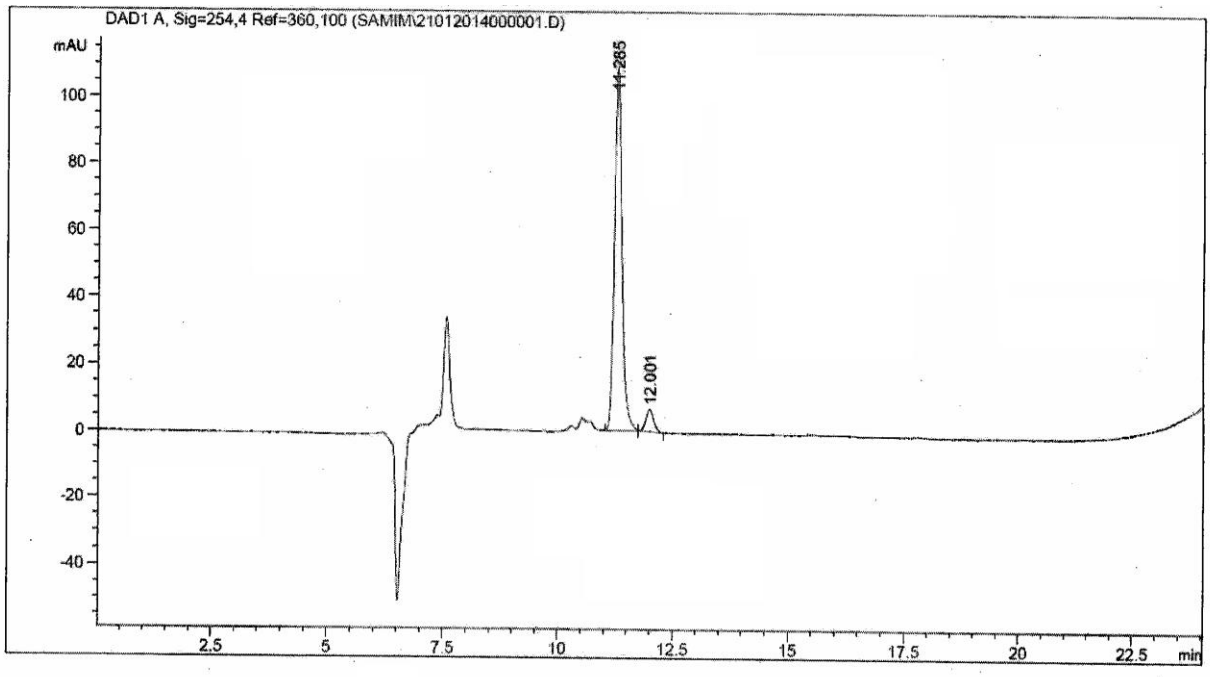

HPLC Chromatogram of compound (±)**7c**



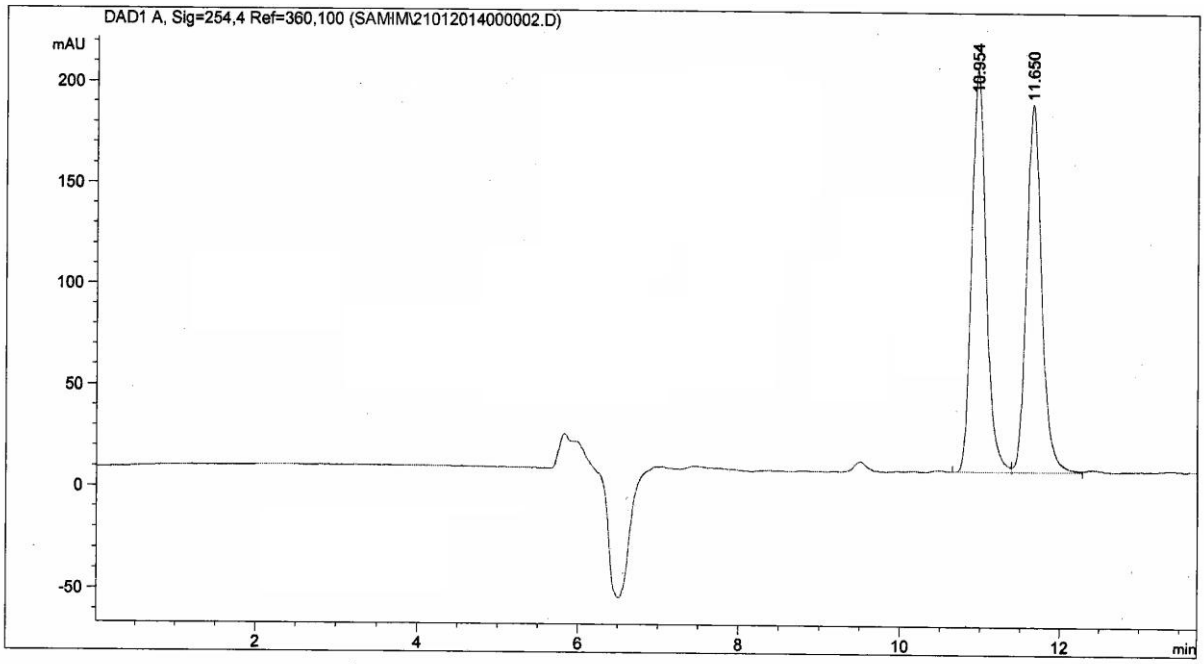
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.285	BB	0.1727	1234.79846	108.57613	94.1664
2	12.001	BB	0.1808	76.49517	6.62057	5.8336
Totals :				1311.29363	115.19670	

HPLC Chromatogram of compound **7d**



Area Percent Report

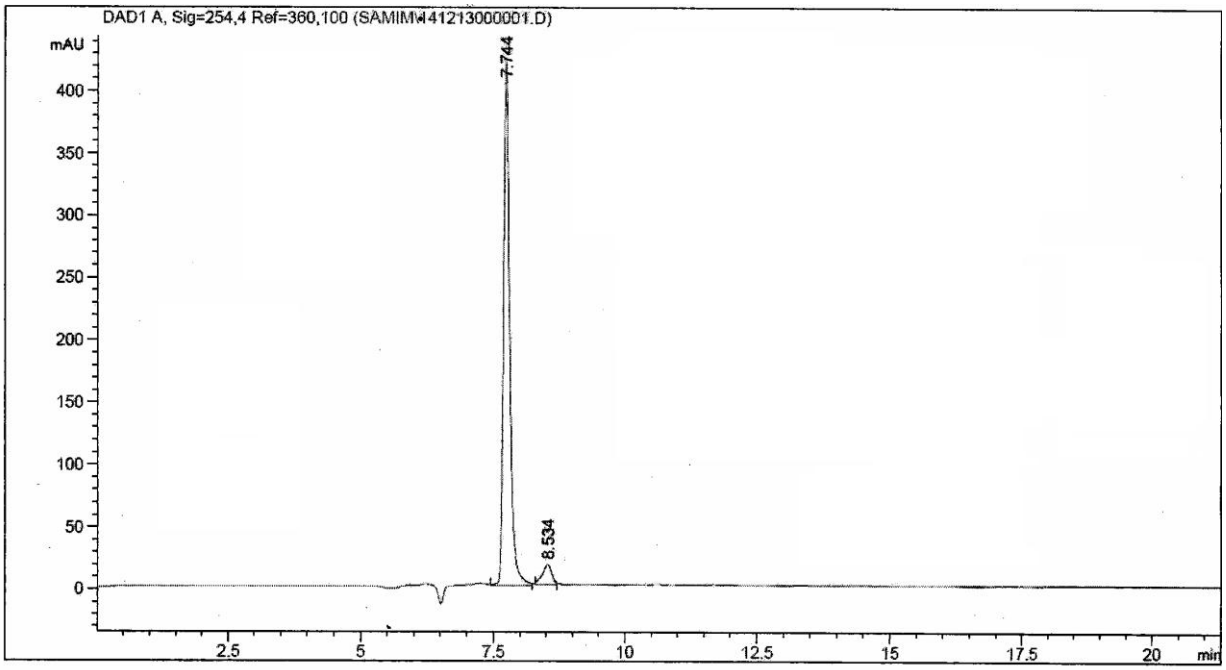
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.954	BV	0.1924	2503.32202	199.42719	50.7857
2	11.650	VV	0.2036	2425.86621	181.90038	49.2143
Totals :				4929.18823	381.32756	

*** End of Report ***

HPLC Chromatogram of compound (±)**7d**

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=====================================================================
                    Area Percent Report
=====================================================================

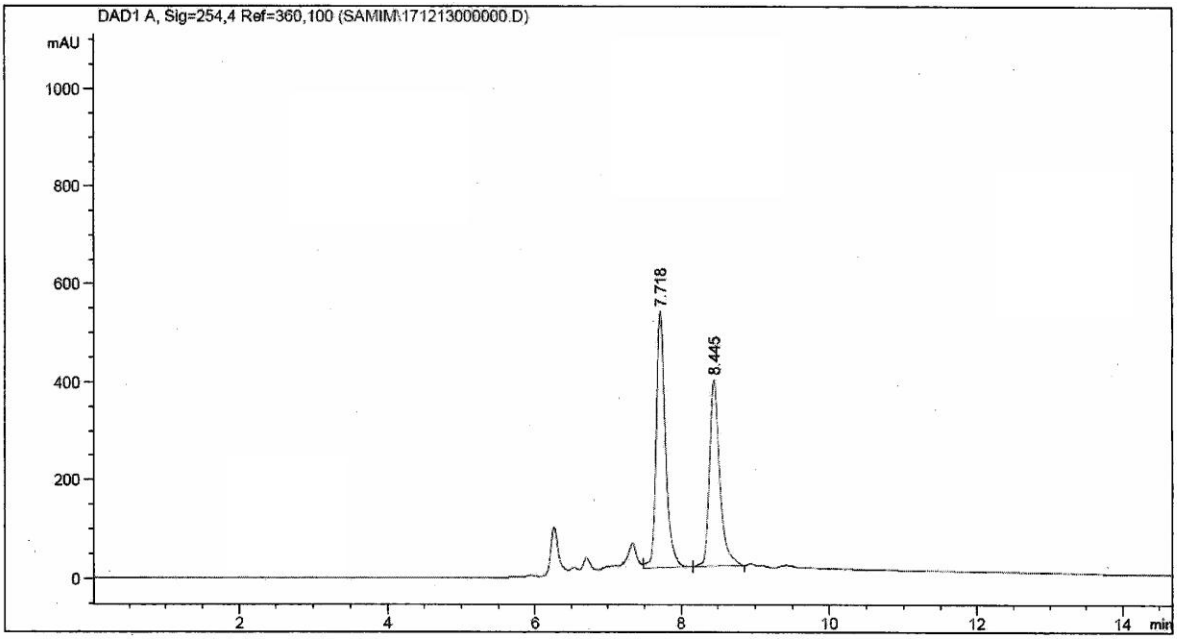
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.744 MM    0.1363 3438.10742  420.31680  94.7960
   2   8.534 MM    0.1986  188.74185   15.83874   5.2040

Totals :                  3626.84927  436.15555
```

HPLC Chromatogram of compound **13a**



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Area Percent Report

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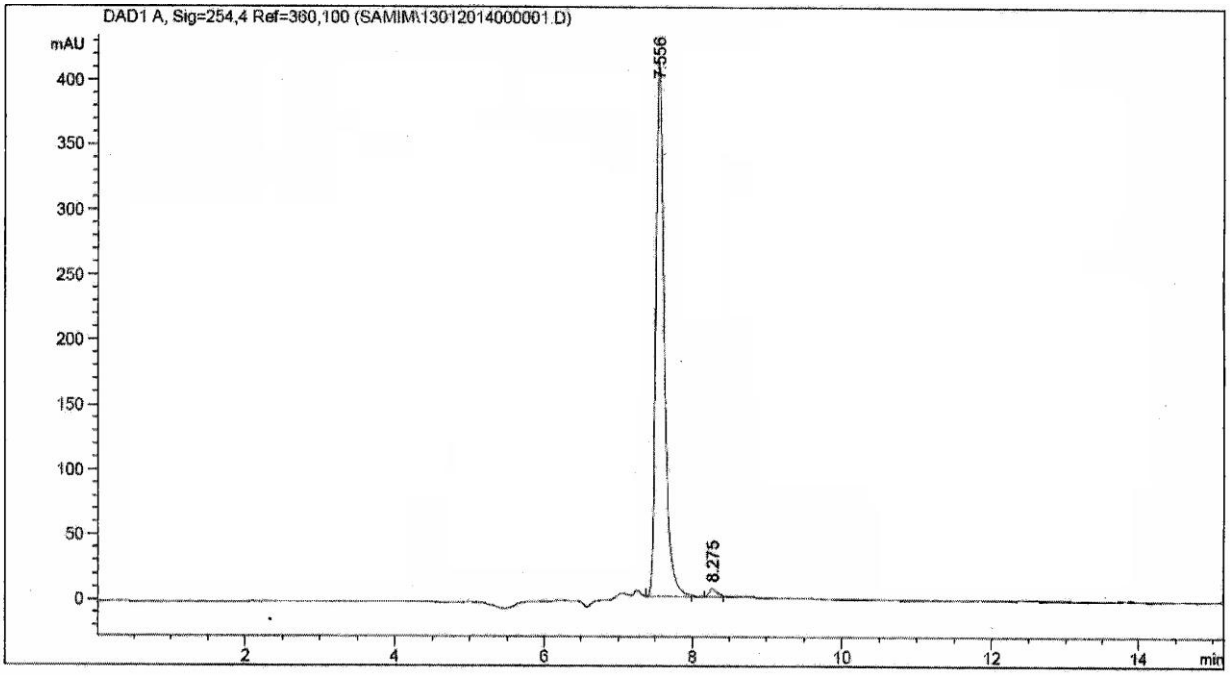
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.718	VB	0.1313	4539.03760	522.71881	55.4352
2	8.445	BB	0.1441	3648.97461	379.72943	44.5648
Totals :				8188.01221	902.44824	

HPLC Chromatogram of compound (±)**13a**



Area Percent Report

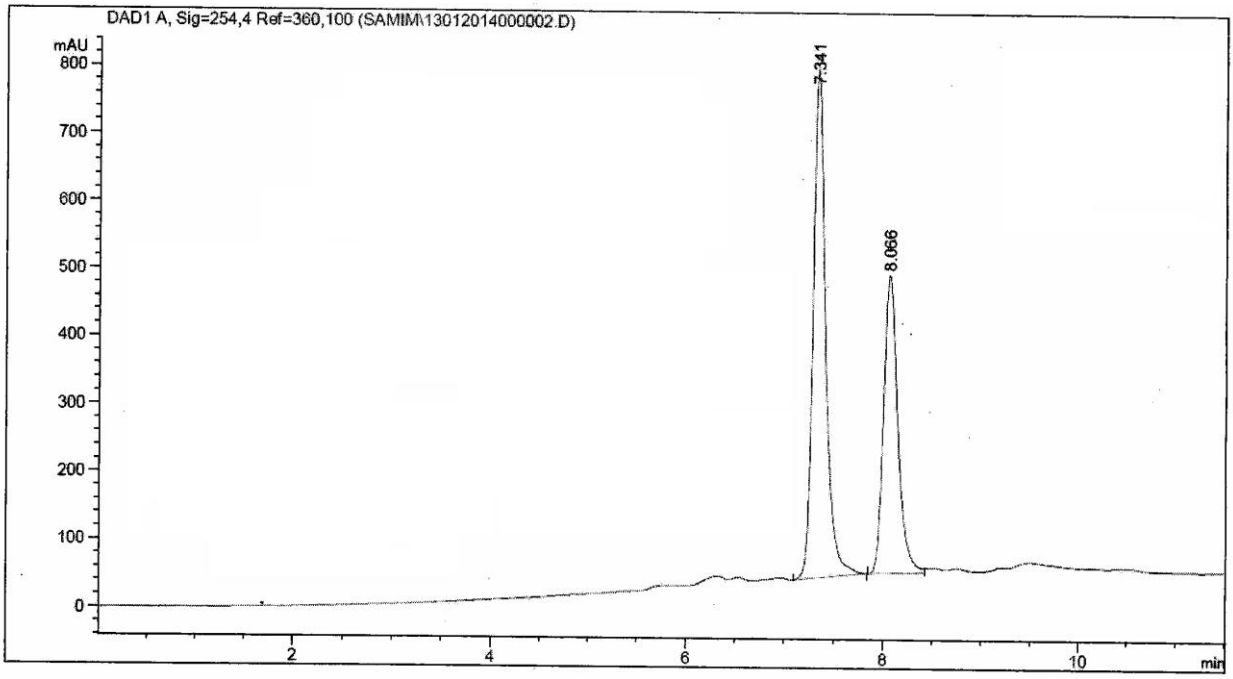
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.556	MM	0.1316	3242.59375	410.75418	98.6723
2	8.275	MM	0.1210	43.63268	6.00773	1.3277
Totals :				3286.22643	416.76191	

*** End of Report ***

HPLC Chromatogram of compound **13c**



Area Percent Report

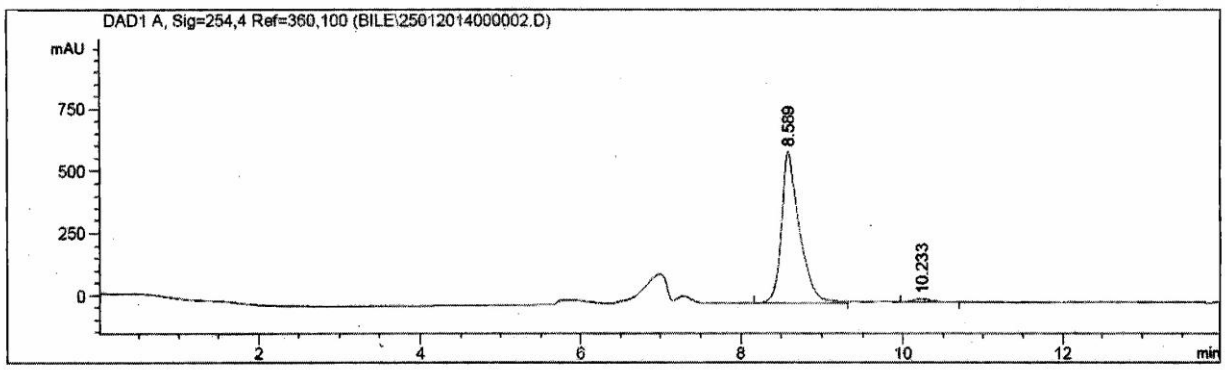
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.341	BB	0.1325	6606.39648	751.66797	60.0601
2	8.066	BV	0.1524	4393.25537	440.16150	39.9399
Totals :				1.09997e4	1191.82947	

*** End of Report ***

HPLC Chromatogram of compound (±)**13c**



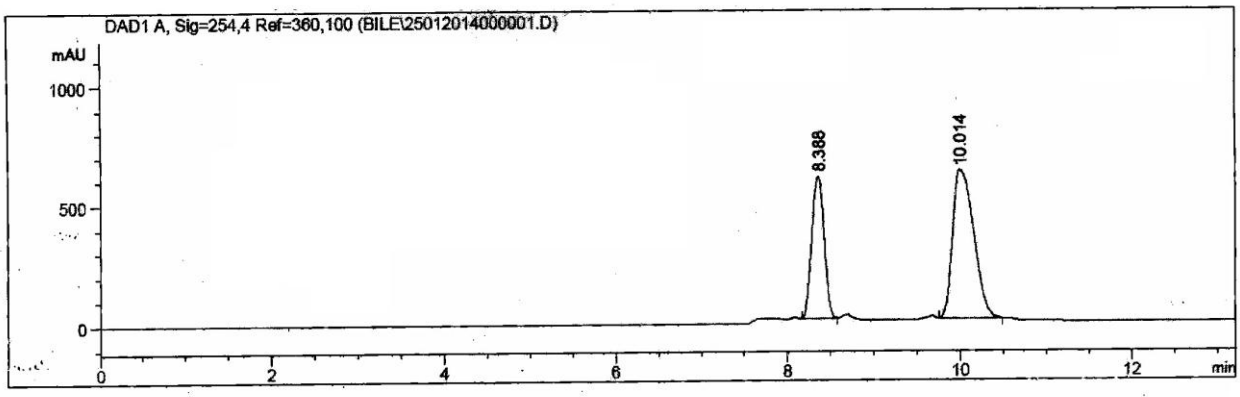
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.589	BV	0.2166	9292.20215	607.05902	97.6260
2	10.233	MM	0.2669	225.96506	14.11243	2.3740
Totals :				9518.16721	621.17145	

HPLC Chromatogram of compound **13b**



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Area Percent Report

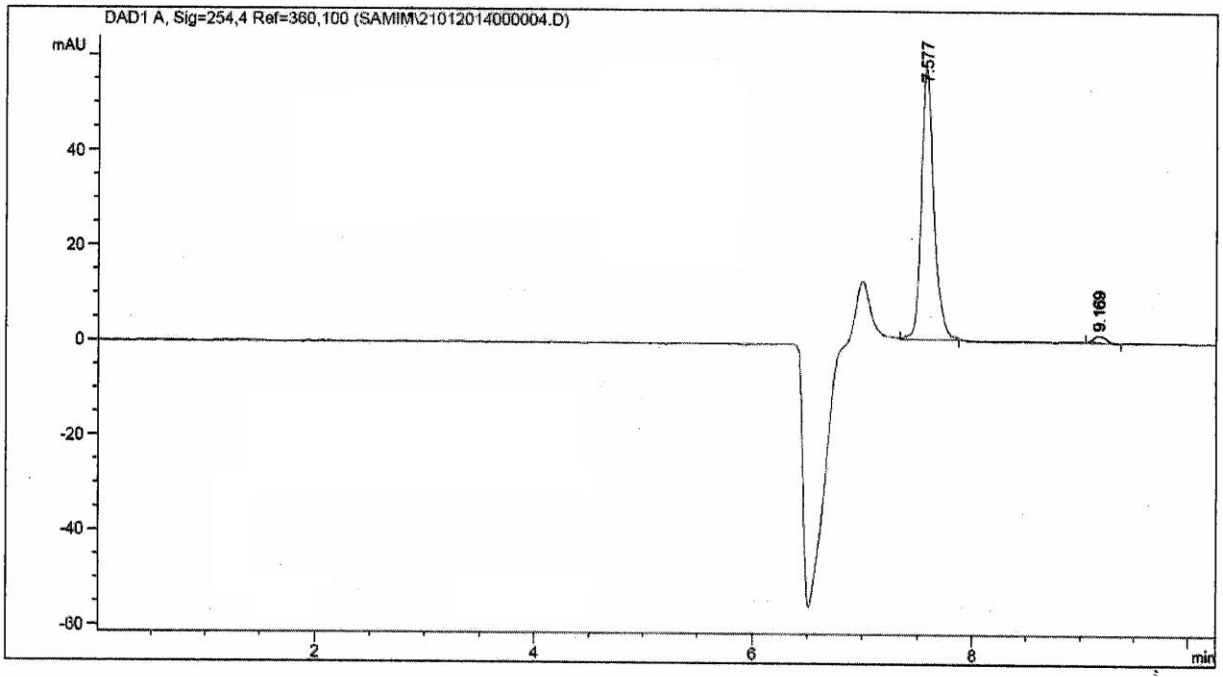
==========

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.388	BV	0.1047	3471.89844	618.80661	39.5818
2	10.014	VB	0.1875	5299.55859	630.96927	60.4182
Totals :				8771.45703	1249.77588	

HPLC Chromatogram of compound (±)**13b**

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=====================================================================
                    Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.577 MM    0.1364  468.41809   57.22437  97.4516
   2   9.169 BB    0.1379   12.24937    1.46005   2.5484

Totals :                   480.66747   58.68441
```
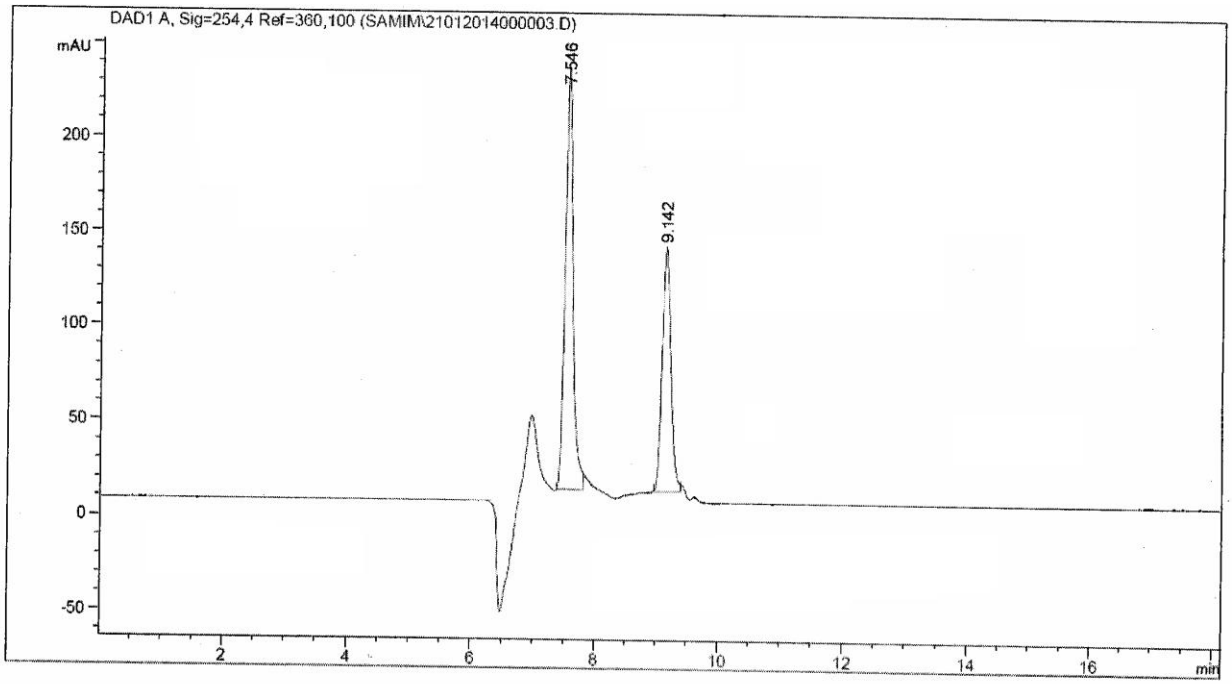

HPLC Chromatogram of compound **13d**



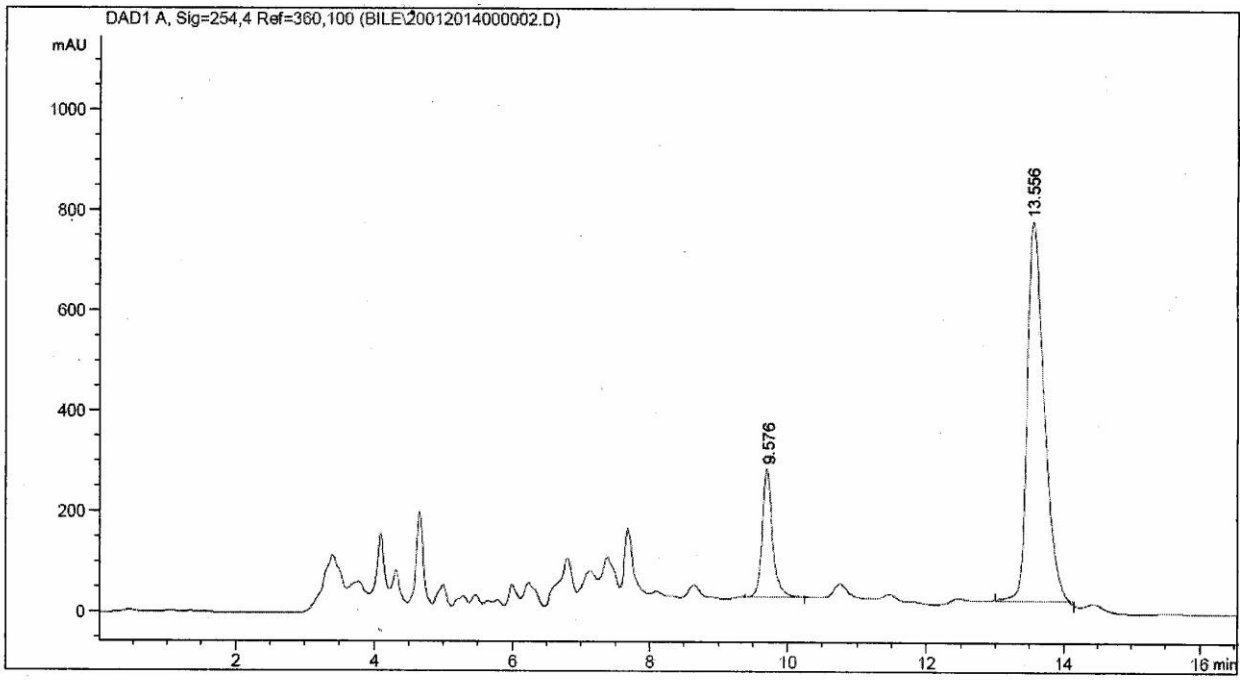
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

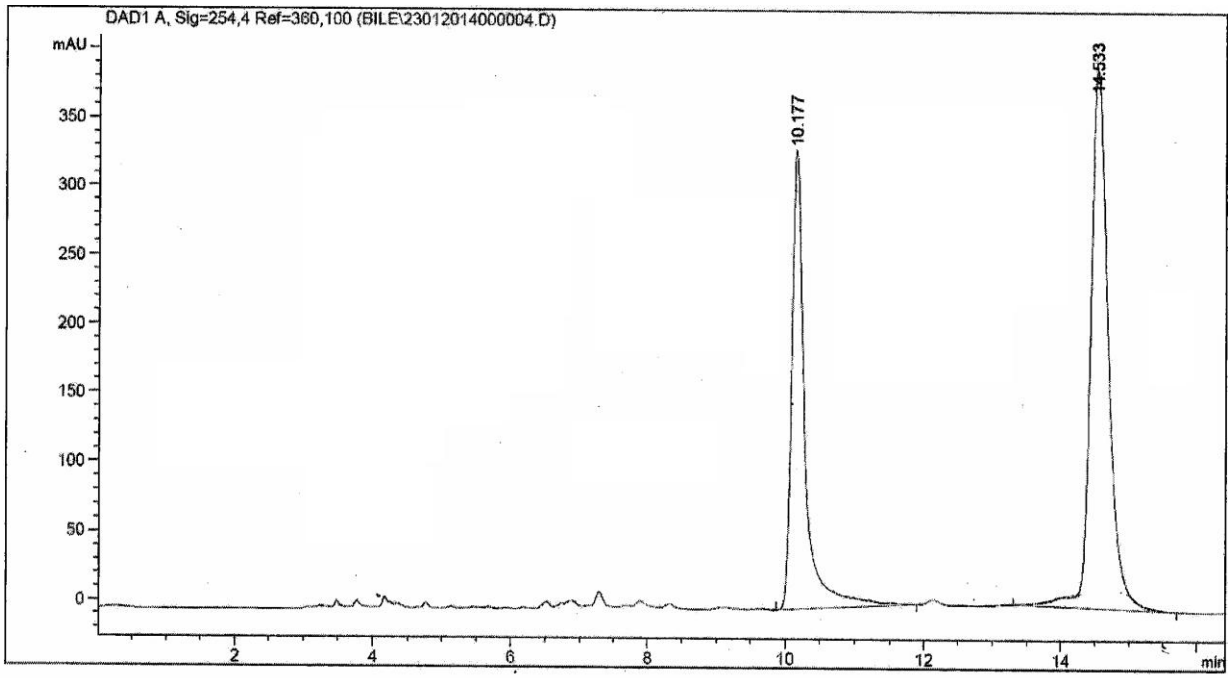
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.546	MM	0.1483	1980.97546	222.58321	60.9675
2	9.142	MM	0.1635	1268.25403	129.26903	39.0325
Totals :				3249.22949	351.85223	

HPLC Chromatogram of compound (±)**13d**




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   9.576 MM    0.1583 2161.94385  227.62804  14.1873
   2  13.556 MM    0.2884 1.30767e4   755.71600  85.8127

Totals :                  1.52386e4   983.34404
```

HPLC Chromatogram of compound **2a′**




```
================================================================================
                          Area Percent Report
================================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1  10.177 BB    0.1946 4409.58984  332.84210  38.2256
   2  14.533 BB    0.2723 7126.11621  391.59109  61.7744

Totals :                  1.15357e4   724.43320
```

HPLC Chromatogram of compound (±) **2a′**