Electronic supplementary materials *Mendeleev Commun.*, 2022, **32**, 549–550

Reaction of 2-azabicyclo[2.2.1]heptenes with nitrile oxides

Tatiana A. Solodovnikova, Nikolai V. Zyk and Anna Yu. Gavrilova

Experimental part

General details. The NMR spectra were recorded on spectrometer Bruker Avance 400 (400.1 MHz for ^{1}H NMR and at 100.6 MHz for ^{13}C NMR). HRMS spectra were acquired at TripleTOF 5600+ and Orbitrap Elite instrument using electrospray ionization (ESI).

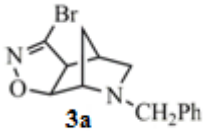
Compound **1a** was synthesized according to the previously described procedure [S1].

Synthesis of compounds 1b-e (general procedure). To a mixture of NH_4Cl (0.083 mol) and formaldehyde (37% aq., 0.117 mol) in methanol (14 ml), freshly distilled cyclopentadiene (0.167 mol) in methanol (10 ml) was added with vigorous stirring. The mixture was stirred for 12 h, then diluted with water and extracted with diethyl ether (2 × 30 ml), the organic extracts were discarded. The aqueous phase was brought to pH ~ 9 with NaOH, the product was extracted with diethyl ether (2 × 30 ml). To a mixture of the isolated product and NaOH solution (10% aq., 17 ml) was added the corresponding acid anhydride (in case of **1c**) or acid chloride (in cases of **1b**,**d**,**e**) (0.033 mol). The mixture was stirred at room temperature for 24 h, the organic layer was separated, dried over Na_2SO_4, the solvent was evaporated. In some cases, additional chromatographic purification was required. The physicochemical characteristics of the compounds coincided with those published earlier: **1c** (81%) [S2], **1e** (81%) [S3].

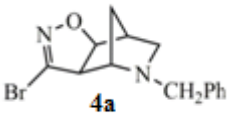
Methyl 2-azabicyclo[2.2.1]hept-5-ene-2-carboxylate 1b. Yield 68%. Colourless oil. ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (two rotamers 1:1): 1.51 (bs, 2H, H_2C^7), 2.56 (d, 0.5H, HC^3_{endo}, J = 8.2), 2.61 (d, 0.5H, HC^3_{endo}, J = 8.6), 3.13 (bs, 1H, HC^4), 3.30 (m, 1H, HC^3_{exo}), 3.59 and 3.61 (both s, 3H, OCH_3), 4.57 (bs, 0.5H, HC^1), 4.69 (bs, 0.5H, HC^1), 6.22 (s, 1.5H, HC^5+HC^6), 6.31 (bs, 0.5H, HC^6). ESI-MS (m/z): calculated for $C_8H_{11}NO_2$, 154.0863 [M+1], found: 154.0861.

2-Tosyl-2-azabicyclo[2.2.1]hept-5-ene 1d. Yield 78%. Crystallizing oil. ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.40 (d, 1H, HC^7, J = 8.5), 1.45 (d, 1H, HC^7, J = 8.5), 2.4 (s, 3H, CH_3), 2.52 (d, 1H, HC^3_{endo}, J = 8.5), 3.12 (bs, 1H, HC^4), 3.33 (dd, 1H, HC^3_{exo}, J_1= 8.5, J_2 = 3), 4.62 (s, 1H, HC^1), 5.97 (d, 1H, HC^5, J = 5.5), 6.08 (m, 1H, HC^6), 7.25 (d, 2H, Ar, J = 8.3), 7.65 (d, 2H, Ar, J = 8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 21.10 (CH_3), 43.31, 46.67, 47.50 (C^3 ,C^4 ,C^7), 63.76 (C^1), 127.25, 129.08 (C^2_{arom}, C^3_{arom}, C^5_{arom}, C^6_{arom}), 133 (C^5 or C^6), 135.63 (C^4_{arom}), 136.35 (C^6 or C^5), 142.80 (C^1_{arom}). ESI-MS (m/z): calculated for $C_{13}H_{15}NSO_2$, 250.0896 [M+1], found: 250.0894.

Synthesis of compounds 3a-c, 4a-c (general procedure). To a mixture of alkene (2.5 mmol) and dibromoformaldoxime (2.5 mmol) in ethyl acetate (25 ml) at 5°C was added sodium bicarbonate (12.5 mmol), and this was stirred for 1 h, then warmed to room temperature and stirred for more 4 h. The mixture was diluted with water, the organic layer was separated, the aqueous one was extracted with CH_2Cl_2, the combined organic extracts were dried over Na_2SO_4, the solvent was evaporated. The residue was chromatographed. The yields of the compounds are shown in Table 1 (see main text). The complete chromatographic separation of isomers **3** and **4** was not possible. The assignment of signals was carried out on the basis of a comprehensive analysis of fractions with different content of isomers.



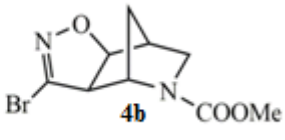
3a



4a

9-Benzyl-5-bromo-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3a) and 8-benzyl-5-bromo-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4a) (mixture). Colourless oil, R_f 0.30 (EtOAc – petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3a** 1.48 (d, 1H, HC^{10}_{syn}, *J*=11.1), 1.68 (dm, 1H, HC^{10}_{anti}, *J*=11.1), 2.52 (d, 1H, HC^{8}_{endo}, *J*=9.5), 2.60 (dd, 1H, HC^{8}_{exo}, *J*=9.5, 3.4), 2.65 (bs, 1H, HC^7), 3.39 (d, 1H, HC^6, *J*=8.4), 3.44 (bs, 1H, HC^1), 3.70 (s, 2H, CH_2Ph), 4.86 (d, 1H, HCO, *J*=8.4); isomer **4a** 1.60 (d, 1H, HC^{10}_{syn}, *J*=11.1), 1.75 (dm, 1H, HC^{10}_{anti}, *J*=11.1), 2.03 (d, 1H, HC^{9}_{endo}, *J*=9.9), 2.73 (bd, 1H, HC^1, *J*=4.2), 2.78 (dd, 1H, HC^{9}_{exo} *J*=9.9, 4.4), 3.48 (bs, 1H, HC^7), 3.65 (s, 2H, CH_2Ph), 3.72 (HC^6, overlaps with CH_2Ph of **3a**), 4.75 (d, 1H, HCO, *J*=8.3); isomers **3a**+**4a** 7.20-7.40 (m, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): isomer **3a** 28.87 (C^{10}), 39.99 (C^7), 56.67 (C^8), 59.12 (CH_2), 60.83 (C^6), 64.22 (C^1), 85.72 (C-O); isomer **4a** 30.16 (C^{10}), 44.39 (C^1), 56.67 (C^6), 58.27 (CH_2), 59.40 (C^9), 62.13 (C^7), 86.45 (C-O); isomers **3a**+**4a** 128.40, 128.42, 128.46 (C_{arom}). ESI-MS (m/z): calculated for $C_{14}H_{16}BrN_2O$ 307.0451 [M+1], found 307.0448, calculated for $C_{14}H_{16}BrN_2O$ 309.0431 [M+3], found 309.0428.

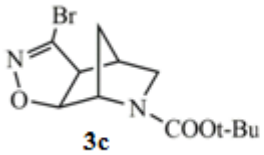
3b



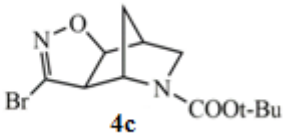
4b

Methyl 5-bromo-3-oxa-4,9-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (3b) and methyl 5-bromo-3-oxa-4,8-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (4b) (mixture). Yellow oil, R_f 0.71 (MeOH – $CHCl_3$, 1:30). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3b** (rotamer major : minor = 54:46) 2.81 (bs, HC^7), 3.00 (d, HC^{8}_{endo} minor, *J*=9.8), 3.05 (d, HC^{8}_{endo} major, *J*=9.9), 3.42 (d, HC^6, *J*=8.3), 4.73 (d, HCO major, *J*=8.0); isomer **4b** (rotamer major : minor = 58:42) 2.91 (HC^{9}_{endo} minor), 2.94 (bs, HC^1), 2.95 (HC^{9}_{endo} major), 3.56 (d, HC^6 minor, *J*=7.8), 3.65 (HC^6 major),); isomer **3b** + isomer **4b** 1.60-1.80 (m, HC^{10}), 3.25-3.39 (m, HC^{8}_{exo} **3b**

and HC^{9}_{exo} **4b**), 3.67, 3.70, 3.72 (three s, OCH_3), 4.39 (bs, HC^1 **3b** major, HC^7 **4b** minor), 4.51 (bs, HC^1 **3b** minor, HC^7 **4b** major), 4.80 (d, HCO **3b** minor +**4b** major, *J*=8.2). ^{13}C NMR ($CDCl_3$, δ ppm): isomer **3b** 30.73 (C^{10} minor), 31.20 (C^{10} major), 38.76 (C^7 major), 39.32 (C^7 minor), 49.44 (C^8), 59.04 (C^1 minor), 59.31 (C^1 major), 60.30 (C^2), 84.27 (C-O minor), 84.42 (C-O major); isomer **4b** 31.00 (C^{10} major), 31.50 (C^{10} minor), 43.19 (C^1 minor), 43.77 (C^1 major), 46.15 (C^9), 56.71 (C^7 major), 56.95 (C^7 minor), 62.31 (C^6 minor), 62.68 (C^6 major), 85.61 (C-O); isomer **3b** + isomer **4b** 52.29, 52.45, 52.52 (OCH_3), 136.50, 136.79, 138.50, 138.70 (C=N), 154.72, 154.95 (C=O). ESI-MS (m/z): calculated for $C_9H_{11}BrN_2O_3$ 275.0026 [M+1], found 275.0024, calculated for $C_9H_{11}BrN_2O_3$ 277.0005 [M+3], found 277.0004,



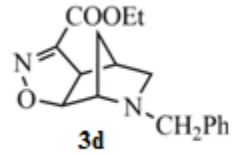
3c



4c

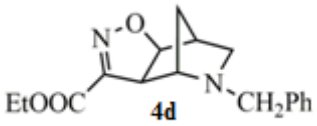
***tert*-Butyl 5-bromo-3-oxa-4,8-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (3c) and *tert*-butyl 5-bromo-3-oxa-4,9-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (4c)** (mixture). Yellow oil, R_f 0.32 (EtOAc – petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3c** (rotamer major : minor = 67:33) 2.80 (bs, HC^7), 2.96 (HC^8_{endo} minor, overlaps with HC^9_{endo} **4c** minor), 3.03 (d, HC^8_{endo} major, *J*=10.3), 3.43 (d, HC^6, *J*=8.2), 4.35 (bs, HC^1 major), 4.73 (d, HCO major, *J*=8.2), 4.81 (d, HCO minor, overlaps with HCO **4c**); isomer **4c** (rotamer major : minor = 53:47) 2.87 (d, HC^9_{endo} major, *J*=9.7), 2.92 (bs, HC^1 minor), 2.93 (HC^9_{endo} minor, overlaps with HC^1), 3.53 (d, HC^6 major, *J*=7.8), 3.66 (d, HC^6 minor, *J*=7.9), 4.31 (bs, HC^7 major), 4.81 (d, HCO, *J*=8.2); isomer **3c +** isomer **4c** 1.45, 1.46, 1.48 (three s, CH_3), 1.6-1.75 (m, HC^{10}_{syn} + HC^{10}_{anti}), 3.23-3.35 (m, HC^8_{exo} **3c**, HC^9_{exo} **4c**), 4.48 (bs, HC^1 **3c** minor, HC^7 **4c** minor). ^{13}C NMR ($CDCl_3$, δ ppm): isomer **3c** 30.71 (C^{10} minor), 31.15 (C^{10} major), 38.85 (C^7 major), 39.36 (C^7 min), 49.03 (C^8 major), 49.64 (C^8 min), 58.51 (C^1 min), 59.45 (C^1 major), 60.33 (C^6); isomer **4c** 30.94 (C^{10} minor), 31.30 (C^{10} major), 43.32 (C^1 major), 43.87 (C^1 minor), 45.81 (C^9 minor), 46.33 (C^9 major), 56.18 (C^7 minor), 57.27 (C^7 major), 62.31 (C^6 major), 62.66 (C^6 minor); isomer **3c** + isomer **4c** 27.99 (CH_3), 79.84, 79.94, 80.07, 80.11 ($O\underline{C}(CH_3)_3$), 84.42, 84.54, 85.69 (C-O), 136.47, 136.61, 138.54, 138.81 (C=N), 153.68 (C=O). ESI-MS (m/z): calculated for $C_{12}H_{17}BrN_2O_3$, 260.9869 [M+1-tBu], found 260.9869, $C_{12}H_{17}BrN_2O_3$, 262.9849 [M+3-tBu], found 262.9848.

Synthesis of compounds 3d-t, 4d-t (general procedure) A solution of *N*-hydroxy imoyl halide (2.25 mmol; 1.5 mmol in case of *N*-hydroxy-4-methoxybenzenecarboximidoyl chloride) in diethyl ether or dichloromethane (10 ml) was added slowly dropwise to a solution of alkene (1.5 mmol) and triethylamine (2.25 mmol; 1.5 mmol in case of *N*-hydroxy-4-methoxybenzene-carboximidoyl chloride) in diethyl ether or dichloromethane (10 ml). The mixture was stirred at room temperature for 0.5-5 h (TLC monitoring). Then water (20 ml) was added, the organic layer was separated, the aqueous layer was extracted with diethyl ether or dichloromethane. The organic phases were combined, dried over sodium sulfate, the solvent was evaporated. The residue was subjected to column chromatography. The yields of the obtained compounds are shown in Table 1 (main text). In those cases when the complete chromatographic separation of isomers **3** and **4** was not possible, the assignment of signals was carried out on the basis of a comprehensive analysis of fractions with different content of isomers. Compounds **3f,j** and **4f,j** were described earlier: **3f** and **4f** [S4], **3j** and **4j** [S5].



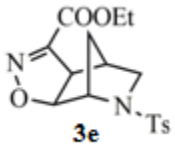
3d

Ethyl 9-benzyl-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene carboxylate (3d). Brown oil: R_f 0.69 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.35 (1H, HC^{10}_{syn}), 1.37 (t, 3H, CH_3, *J*=7.1), 1.66 (dm, 1H, HC^{10}_{anti}, *J*=11.2), 2.58 (s, 2H, HC^8_{endo} + HC^8_{exo}), 2.74 (bs, 1H, HC^7), 3.46 (bs, 1H, HC^1), 3.51 (d, 1H, HC^6, *J*=8.5), 3.71 (s, 2H, CH_2Ph), 4.34 (m, 2H, OCH_2), 4.92 (d, 1H, HCO, *J*=8.5), 7.30-7.38 (m, 5H, CH_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 13.72 (CH_3), 28.47 (C^{10}), 40.34 (C^7), 54.07 (OCH_2), 56.76 (C^8), 59.02 (CH_2Ph), 61.58 (C^6), 63.75 (C^1), 87.71 (C-O), 126.71, 127.95, 127.98 (C_{arom}), 151.85 (C=N), 160.25 (C=O). ESI-MS (m/z): calculated for $C_{17}H_{20}N_2O_3$ 301.1547 [M+1], found 301.1537.



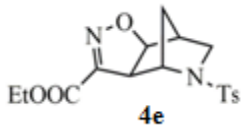
4d

Ethyl 8-benzyl-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene carboxylate (4d). Brown oil: R_f 0.45 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.30 (t, 3H, CH_3, *J*=7.1), 1.48 (d, 1H, HC^{10}_{syn}, *J*=10.8), 1.72 (d, 1H, HC^{10}_{anti}, *J*=10.8), 2.03 (d, 1H, HC^9_{endo}, *J*=10.3), 2.74 (bs, 1H, HC^1), 2.84 (dd, 1H, HC^9_{exo}, *J*=10.3, 4.3), 3.58 (bs, 1H, HC^7), 3.64, 3.71 (two d, 1H, CH_2Ph, *J* = 13.3), 3.85 (d, 1H, HC^6, *J*=8.4), 4.29 (m, 2H, OCH_2), 4.85 (d, 1H, HCO, *J*=8.4) 7.30 (m, 5H, CH_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 13.63 (CH_3), 30.00 (C^{10}), 43.94 (C^1), 51.66 (OCH_2), 52.15 (C^6), 57.53 (CH_2), 61.54 (C^9), 62.16 (C^7), 88.28 (C-O), 159.99 (C=O), 126.83, 127.42, 127.98, 128.18 (C_{arom}), 151.47 (C=N). ESI-MS (m/z): calculated for $C_{17}H_{20}N_2O_3$ 301.1547 [M+1], found 301.1544.



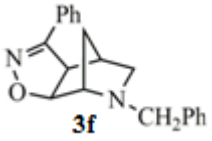
3e

Ethyl 9-[(4-methylphenyl)sulfonyl-3-oxa-4,9-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene-5-carboxylate (3e). Brown oil. R_f 0.60 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.04 (d, 1H, *J*=11.4, HC^{10}_{anti}), 1.35 (t, 3H, $OCH_2C\underline{H}_3$, *J*=7.2), 2.44 (s, 3H, CH_3, Ts), 2.84 (bs, 1H, HC^7), 3.08 (dd, 1H, HC^8_{exo}, *J*=9.3, 3.0), 3.13 (d, 1H, HC^8_{endo}, *J*=9.3), 3.55 (d, 1H, HC^6, *J*=8.4), 4.30 (m, 2H, $OC\underline{H}_2CH_3$), 4.36 (s, 1H, HC^1), 4.99 (dd, 1H, HCO, *J*=8.4, 1.2), 7.34 (d, 2H, H_{arom}, *J*=8.1), 7.71 (d, 2H, H_{arom}, *J*=8.1). The signal of protons HC^7_{syn} overlaps with the signal of $OCH_2C\underline{H}_3$. ^{13}C NMR ($CDCl_3$, δ ppm): 13.66 ($OCH_2\underline{C}H_3$), 21.17 (CH_3), 30.23 (C^{10}), 40.31 (C^7), 51.18 (C^6), 54.16 (C^8), 61.85, 61.91 (C^1, $O\underline{C}H_2CH_3$), 87.25 (C-O), 126.92, 129.59, 134.66, 143.62 (C_{arom}), 151.27 (C=N), 159.77 (C=O). ESI-MS (m/z): calculated for $C_{17}H_{20}N_2O_5S$ 365.1166 [M+1], found 365.1168.



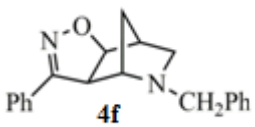
4e

Ethyl 8-[(4-methylphenyl)sulfonyl-3-oxa-4,8-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene-5-carboxylate (4e). Brown oil. R_f 0.68 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.15 (d, 1H, HC^{10}_{anti}, *J*=11.2), 1.39 (t, 3H, $OCH_2C\underline{H}_3$, *J*=7.2), 1.44 (d, 1H, HC^{10}_{syn}, *J*=11.2), 2.43 (s, 3H, CH_3, Ts), 2.89 (bs, 1H, HC^1), 2.96 (d, 1H, HC^9_{endo}, *J*=9.9), 3.16 (dd, 1H, HC^9_{exo} *J*=9.9, 4.1), 3.78 (d, 1H, HC^6, *J*=8.5), 4.30 (m, 2H, $OC\underline{H}_2CH_3$), 4.46 (s, 1H, HC^7), 4.85 (d, 1H, HCO, *J*=8.5), 7.34 (d, 2H, H_{Ar}, *J*=8.2), 7.73 (d, 2H, H_{Ar}, *J*=8.2). ^{13}C NMR ($CDCl_3$, δ ppm): 13.66 ($OCH_2\underline{C}H_3$), 21.14 (CH_3), 30.68 (C^{10}), 44.01 (C^1), 47.14 (C^6), 57.04 (C^9), 60.18 (C^7), 61.85 ($O\underline{C}H_2CH_3$), 87.55 (C-O), 126.97, 129.57, 134.76, 143.57 (C_{arom}), 151.30 (C=N), 159.43 (C=O). ESI-MS (m/z): calculated for $C_{17}H_{20}N_2O_5S$ 365.1166 [M+1], found 365.1166.



3f

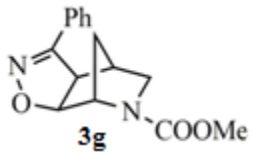
9-Benzyl-5-phenyl-3-oxa-4,9-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene (3f). Colorless oil, R_f 0.61 (EtOAc – petroleum ether, 2:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.49 (d, 1H, HC^{10}_{syn}, *J*=10.9), 1.61 (dt, 1H, HC^{10}_{anti}, *J*=11.1, 1.4), 2.61 (dd, 1H, HC^8_{exo}, *J*=9.2, *J*=3.3), 2.62-2.69 (m, 2H, HC^8_{endo} + HC^7), 3.46 (bs, 1H, HC^1), 3.73 (dd, HC^6, *J*=8.4, *J*=1.1), 3.76 (s, 2H, CH_2Ph), 4.91 (dt, 1H, HCO, *J*=8.4, 1.3), 7.30-7.45 (m, 8H, H_{arom}), 7.70 (m, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 28.96 (C^{10}), 40.70 (C^7), 55.83 (C^6), 57.40 (C^8), 59.54 ($\underline{C}H_2Ph$), 64.50 (C^1), 85.92 (C-O), 126.83, 127.06, 128.37, 128.41, 128.80, 128.99, 129.93, 139.38 (C_{arom}), 156.87 (C=N).



4f

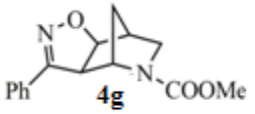
8-Benzyl-5-phenyl-3-oxa-4,8-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene (4f). Crystallizing colorless oil. R_f 0.45 (EtOAc - petroleum ether, 2:1). ^{1}H NMR ($CDCl_3$, δ, ppm, *J*, Hz): 1.59 (d, 1H, HC^{10}_{syn}, *J*=10.6), 1.67 (dt, 1H, HC^{10}_{anti}, *J*=10.6, 1.5), 2.10 (d, 1H, HC^9_{endo}, *J*=9.9), 2.74 (d, 1H, HC^1, *J*=3.7), 2.99 (dd, 1H, HC^9_{exo}, *J*=9.9, 4.3), 3.49 (bs, 1H, HC^7), 3.69, 3.85 (two d, 1H, CH_2Ph, *J*=13.3), 4.02 (d, 1H, *J*=8.4, HC^6), 4.81 (d, 1H, *J*=8.4, HCO), 7.27-7.45 (m, 8H, H_{arom}), 7.53 (m, 2H, H_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): δ

30.49 (C^{10}), 44.55 (C^{1}), 52.38 (C^{9}), 53.42 (C^{6}), 58.05 ($\underline{C}H_2Ph$), 61.93 (C^{7}), 86.35 (C-O), 126.68, 127.23, 128.45, 128.62, 128.70, 128.97, 129.83, 138.90 (C_{arom}), 156.55 (C=N). ESI-MS (m/z) isomers **3f**+**4f**: calculated for $C_{20}H_{21}N_2O$ 305.1648 [M+1], found 305.1654.



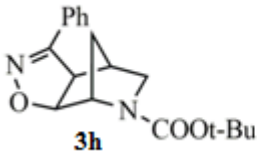
3g

Methyl 5-phenyl-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (3g) (with admixture of **4g**)**.** Yellow oil. ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): (rotamer major : minor = 60:40) 1.57 – 1.68 (m, 2H, HC^{10}_{syn}+ HC^{10}_{anti}), 2.82 (bs, 1H, HC^{7}), 3.12 (d, HC^{8}_{endo} minor, *J*=9.7), 3.18 (d, HC^{8}_{endo} major, *J*=9.8), 3.35 (m, HC^{8}_{exo}), 3.70 (OCH_3 minor), 3.73 (OCH_3, major), 3.76 (d, HC^{6}, *J*=8.3), 4.42 (bs, HC^{1} major), 4.55 (bs, HC^{1} minor), 4.81 (d, HCO major, *J*=8.3), 4.89 (d, HCO minor, *J*=8.3), 7.42 (m, 4H, Ph), 7.71 (m, 1H, Ph). ^{13}C NMR ($CDCl_3$, δ ppm): 30.85 (C^{10} minor), 31.35 (C^{10} major), 39.35 (C^{7} major), 39.93 (C^{7} minor), 50.00 (C^{8} minor), 50.06 (C^{8} major), 52.21 (OCH_3), 55.30 (C^{6} minor), 55.33 (C^{6} major), 59.26 (C^{1} minor), 59.52 (C^{1} major), 84.41 (C-O minor), 84.59 (C-O major), 126.41, 128.51, 129.88 (C_{Ar} major), 126.41, 128.58, 129.88 (C_{Ar} minor), 154.94 (C=N).

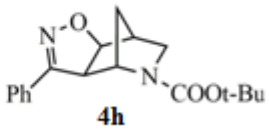


4g

Methyl 5-phenyl-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (4g). Yellow oil, R_f 0.65 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): (rotamer major : minor = 60:40) 1.62 (d, HC^{10}_{syn} minor, *J*=10.3), 1.66 (d, HC^{10}_{syn} major, *J*=9.5), 1.73 (d, HC^{10}_{anti}, *J*=10.5), 2.96 (bs, HC^{1}), 3.00 (d, HC^{9}_{endo} major, *J*=10.2), 3.06 (d, HC^{9}_{endo} minor, *J*=10.5), 3.31 (dd, HC^{9}_{exo} major, *J*=10.2, 3.8), 3.36 (dd, HC^{9}_{exo} minor, *J*=10.5, 3.7), 3.73 (s, OCH_3 major), 3.82 (s, OCH_3 minor), 3.89 (d, HC^{6} minor, *J*=8.2), 3.99 (d, HC^{6} major, *J*=8.2), 4.44 (bs, HC^{7} minor), 4.55 (bs, HC^{7} major), 4.86 (d, HCO, *J*=8.3). 7.43 (m, 4H, Ph), 7.83 (m, 1H, Ph). ^{13}C NMR ($CDCl_3$, δ ppm): 30.88 (C^{10} major), 31.62 (C^{10} minor), 43.27 (C^{1} minor), 43.88 (C^{1} major), 46.13 (C^{9}), 52.08 (OCH_3), 57.58 (C^{6} minor), 57.65 (C^{6} major), 58.14 (C^{7} major), 58.18 (C^{7} minor), 85.31 (C-O major), 85.39 (C-O minor), 126.42, 128.59, 129.88 (C_{Ar}), 154.88 (C=O), 155.08 (C=N, minor), 155.12 (C=N, major). ESI-MS (m/z) isomers **3g** + **4g**: calculated for $C_{15}H_{16}N_2O_3$ 273.1234 [M+1], found 273.1234.

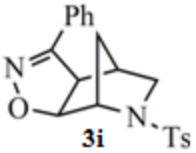


3h

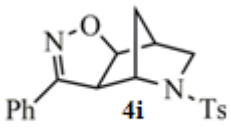


4h

***tert*-Butyl 5-phenyl-3-oxa-4,9-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (3h) and *tert*-butyl 5-phenyl-3-oxa-4,8-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (4h)** (mixture). Yellow oil, R_f 0.32 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3h** (rotamer major : minor = 71:29) 2.80 (bs, HC^7), 3.08 (d, HC^8_{endo} minor, *J*=9.8), 3.14 (d, HC^8_{endo} major, *J*=9.8), 3.77 (d, HC^6, *J*=8.3), 4.38 (s, HC^1 major), 4.50 (HC^1 minor, overlaps with HC^7 **4h** minor), 4.80 (d, HCO major, *J*=8.3), 4.89 (HCO minor, overlaps with HCO **4h**), 7.70 (m, HC_{Ar}); isomer **4h** (rotamer major : minor = 60:40) 2.93 (s, HC^1), 2.95 (HC^9_{endo} minor overlaps with HC^1), 3.02 (HC^9_{endo} major, *J*=10.4), 3.86 (d, HC^6 major, *J*=8.3), 3.98 (d, HC^6 minor, *J*=8.3), 4.39 (bs, HC^7 major), 4.50 (bs, HC^7 minor), 4.86 (d, HCO, *J*=8.3), 7.76 (m, HC_{Ar}), 7.80 (dd, HC_{Ar}, major, *J*=7.8, *J*=2.1), 7.82 (dd, HC_{Ar}, minor, *J*=7.8, *J*=2.3); isomer **3h +** isomer **4h** 1.46, 1.48, 1.57 (three s, CH_3), 1.59 – 1.74 (m, HC^{10}_{syn} + HC^{10}_{anti}), 3.22-3.34 (m, HC^8_{exo} **3h** + HC^9_{exo} **4h**), 7.41 (m, HC_{Ar}). ^{13}C NMR ($CDCl_3$, δ ppm): isomer **3h** 30.21 (C^{10} minor), 30.87 (C^{10} major), 39.44 (C^7 major), 39.95 (C^7 minor), 49.63 (C^8 major), 49.69 (C^8 minor), 59.67 (C^1 minor), 59.96 (C^1 major), 57.05 (C^6 minor), 57.67 (C^6 major); isomer **4h** 31.29 (C^{10}), 43.37 (C^1 major), 43.94 (C^1 minor), 45.92 (C^9 major), 46.43 (C^9 minor), 55.32 (C^6), 58.06 (C^7); isomer **3h** + isomer **4h** 79.41, 79.54, 79.80, 79.82 (O<u>C</u>$(CH_3)_3$), 84.60, 84.68, 85.38, 85.46 (C-O), 126.25, 126.41, 128.02, 128.20, 128.39, 128.48, 128.55, 129.81 (C_{arom}), 153.85, 154.0, 154.67, 154.99 (C=N, C=O). ESI-MS (m/z) isomers **3h** + **4h**: calculated for $C_{18}H_{22}N_2O_3$ 315.1703 [M+1], found 315.1704.



3i

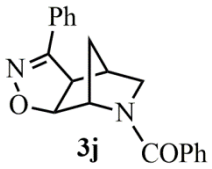


4i

9-[(4-Methylphenyl)sulfonyl]-5-phenyl-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3i) and 8-[(4-methylphenyl)sulfonyl]-5-phenyl-3-oxa-4,8-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4i) (mixture). Colourless oil. R_f 0.70 (MeOH – $CHCl_3$, 1:30). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3i** 1.00 (d, 1H, HC^{10}_{anti}, *J*=11.1), 1.48 (d, 1H, HC^{10}_{syn}, *J*=11.1), 2.44 (s, 3H, CH_3), 2.74 (bs, 1H, HC^7), 3.13 (dd, 1H, HC^8_{exo}, *J*=9.3, 3.3), 3.20 (d, 1H, HC^8_{endo} *J*=9.2,), 3.77 (d, 1H, HC^6, *J*=8.2), 4.37 (s, 1H, HC^1), 4.96 (d, 1H, HCO, *J*=8.2), 7.33 (d, 2H, H_{Ts}, *J*=7.8); isomer **4i**, 1.04 (d, 1H, HC^{10}_{anti}, *J*=11.0), 1.56 (d, 1H, HC^{10}_{syn}, *J*=11.0), 2.43 (s, 3H, CH_3), 2.88 (1H, bs, HC^1), 3.07 (s, 2H, HC^9_{exo} + HC^9_{endo}), 4.13 (d, 1H, HC^6, *J*=8.3), 4.41 (s, 1H, HC^7), 4.86 (d, 1H, HCO, *J*=8.3,), 7.32 (d, 2H, H_{Ts}, *J*=8.0); isomers **3i** + **4i** 7.37-7.46 (m, H_{arom}), 7.65-7.65 (m, H_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): isomer **3i** 21.54 (CH_3), 30.63 (C^{10}), 40.56 (C^7), 51.66 (C^6), 55.78 (C^8), 62.48 (C^1), 85.63 (C-O), 126.75, 127.32, 128.13, 128.89, 129.93, 130.29, 135.27, 143.88 (C_{arom}), 156.32 (C=N); isomer **4i** 21.54 (CH_3), 30.99 (C^{10}), 44.53 (C^1), 47.54 (C^6), 59.10 (C^9), 60.89 (C^7), 85.63 (C-O), 126.75, 127.31,

128.15, 129.08, 129.94, 130.37, 135.31, 143.94 (C_{Ar}), 155.00 (C=N). ESI-MS (m/z) isomers **3i** + **4i**: calculated for $C_{20}H_{20}N_2O_3S$ 369.1267 [M+1], found 369.1263.

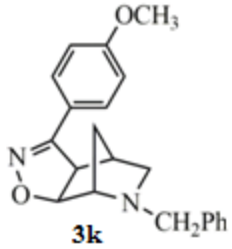
5-Phenyl-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-en-9-yl](phenyl)-methanone (3j) (with admixture of **4j**) Yellow oil. (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 77:23): 1.65-1.90 (m, $HC^{10}{}_{syn}$ + $HC^{10}{}_{anti}$), 2.83 (bs, HC^7 minor), 2.96 (bs, HC^7 major), 3.16 (d, $HC^8{}_{endo}$ minor, *J*=10.0), 3.38 (d, $HC^8{}_{endo}$ major, *J*=11.5), 3.65 (dd, $HC^8{}_{exo}$ major, *J*=11.5, 3.4), 3.79 (d, HC^6 minor, *J*=8.5), 3.91 (d, HC^6 major, *J*=8.1), 4.39 (bs, HC^1 major), 4.96 (d, HCO major, *J*=8.2), 5.08 (d, HCO minor, *J*=8.5), 7.20-8.50 (m, H_{arom}), HC^1 minor overlaps with HCO major, $HC^8{}_{exo}$ minor overlaps with $HC^9{}_{exo}$ major **4j**.



3j

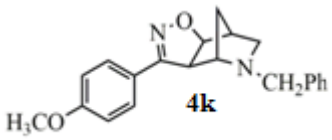
5-Phenyl-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-en-8-yl](phenyl)-methanone (4j). Yellow oil. R_f 0.47 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 55:45): 1.70-1.80 (m, HC^{10}), 1.86 (d, HC^{10} , *J*=10.8), 2.96 (bs, HC^1 minor), 3.01 (dd, $HC^9{}_{endo}$ minor, *J*=10.1, 1.1), 3.08 (bs, HC^1 major), 3.32 (d, $HC^9{}_{endo}$ minor, *J*=11.8), 3.61 (dd, $HC^9{}_{exo}$ minor, *J*=10.0, 3.8), 3.58 (dd, $HC^9{}_{exo}$ major, *J*=11.8, 4.1), 3.85 (d, HC^6 major, *J*=8.4), 4.23 (d, HC^6 minor, *J*=8.3), 4.33 (bs, HC^7 major), 4.82 (d, HCO minor, *J*=8.3), 4.89 (bs, HC^7 minor), 4.96 (d, HCO major, *J*=8.2), 7.17-7.25, 7.32, 7.40-7.62, 7.97 (all m, H_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 30.71 (C^{10} minor), 31.84 (C^{10} major), 43.64, 44.64, 46.30, 50.41, 57.38, 58.08, 59.12, 60.91, 85.22 (C-O minor), 85.72 (C-O major), 126.41, 126.83, 127.04, 127.57, 128.08, 128.48, 128.78, 128.82, 129.04, 130.19, 130.21, 130.34, 130.87, 135.43 (C_{arom}), 154.58 (C=N major), 155.62 (C=N minor). ESI-MS (m/z) isomers **3j**+**4j**: calculated for $C_{20}H_{18}N_2O_2$ 319.1441 [M+1], found 319.1443.

4j



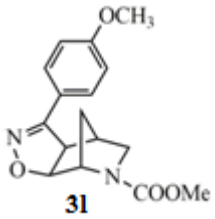
3k

9-Benzyl-5-(4-methoxyphenyl)-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3k). Yellow oil, R_f 0.50 (EtOAc – petroleum ether, 2:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.50 (d, 1H, $HC^{10}{}_{syn}$, *J*=10.8), 1.61 (dt, 1H, $HC^{10}{}_{anti}$, *J*=10.8, 1.4), 2.60 (dd, 1H, $HC^8{}_{exo}$, *J*=9.2, 3.1), 2.62-2.67 (m, 2H, HC^7 + $HC^8{}_{endo}$), 3.46 (bs, 1H, HC^1), 3.70 (d, 1H, HC^6, *J*=8.3), 3.74 (s, 2H, CH_2Ph), 3.84 (s, 3H, OCH_3), 4.88 (d, 1H, HCO, *J*=8.3), 6.93 (d, 2H, HC_{arom}, *J* = 8.8), 7.30-7.40 (m, 5H, Ph), 7.66 (d, 2H, HC_{arom}, *J* = 8.8). ^{13}C NMR ($CDCl_3$, δ ppm): 28.49 (C^{10}), 40.29 (C^7), 54.95(OCH_3), 55.70 (C^6), 56.98 (C^8), 59.13 (CH_2), 64.08 (C^1), 85.19 (C-O), 113.78, 121.06, 126.61, 127.93, 127.99, 139.00 (C_{arom}), 155.98 (C=N), 160.47 (C_{arom}). ESI-MS (m/z): calculated for $C_{21}H_{22}N_2O_2$ 335.1754 [M+1], found 335.1764.



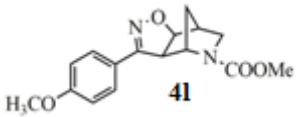
4k

8-Benzyl-5-(4-methoxyphenyl)-3-oxa-4,8-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4k). Yellow oil, R_f 0.40 (EtOAc – petroleum ether, 2:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.57 (d, 1H, HC^{10}_{syn}, *J*=10.7), 1.65 (dt, 1H, HC^{10}_{anti}, *J*=10.9, 1.4), 2.09 (d, 1H, HC^{9}_{endo}, *J*=9.9), 2.74 (bd, 1H, HC^1, *J*=3.1), 2.90 (dd, 1H, HC^{9}_{exo}, *J*=9.8, 4.3), 3.46 (bs, 1H, HC^7), 3.68, 3.83 (two d, 1H, CH_2Ph, *J*=13.5), 3.81 (s, 3H, OCH_3), 3.98 (d, 1H, HC^6, *J*=8.3), 4.55 (d, 1H, HCO, *J*=8.3), 6.80 (d, 2H, CH_{arom}, *J* = 8.8), 7.30-7.46 (m, 7H, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 30.43 (C^{10}), 44.53 (C^1), 52.39 (C^9), 53.69 (C^6), 55.33 (OCH_3), 58.07 (CH_2), 61.93 (C^7), 85.98 (C-O), 114.07, 121.46, 127.20, 128.19, 128.44, 128.6 (C_{arom}), 155.04 (C=N), 160.80 (C_{arom}). ESI-MS (m/z): calculated for $C_{21}H_{22}N_2O_2$ 335.1754 [M+1], found 335.1761.



3l

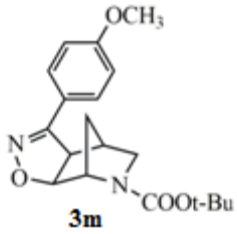
Methyl 5-(4-methoxyphenyl)-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (3l) (with admixture of **4l**). Brown oil, R_f 0.20 (MeOH – $CHCl_3$, 1:25). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): (rotamer major : minor = 54:46) 2.78 (bs, 1H, HC^7), 3.09 (d, HC^{8}_{endo} minor, *J*=9.4), 3.14 (d, HC^{8}_{endo} major, *J*=9.9), 3.25-3.35 (m, 1H, HC^{8}_{exo}), 4.39 (bs, HC^1 major), 4.51 (bs, HC^1 minor), 4.75 (d, HCO major, *J*=8.2), 4.83 (HCO minor, *J*=8.4), 6.90 (m, 2H, HC_{arom}), 7.65 (d, 2H, HC_{arom}, *J*=8.8), the signals HC^1, H_2C^{10}, HC_{arom} overlap with **4l**. ^{13}C NMR ($CDCl_3$, δ ppm): 31.30 (C^{10} major), 30.80 (C^{10} minor), 39.36 (C^7 major), 39.93 (C^7 minor), 49.97 (C^8 minor), 50.04 (C^8 major), 55.40 (C^6), 59.27 (C^1 minor), 59.53 (C^1 major), 84.11 (C-O, minor), 84.28 (C-O, major), 154.61, 154.85, 154.65 (C=O, C=N), C_{arom} overlap with **4l**. ESI-MS (m/z): calculated for $C_{16}H_{18}N_2O_4$ 303.1339 [M+1], found 303.1334.



4l

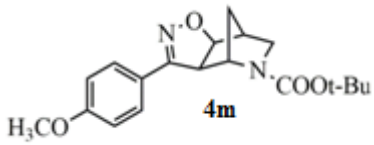
Methyl 5-(4-methoxyphenyl)-3-oxa-4,9-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (4l). Brown oil, R_f 0.27 (MeOH – $CHCl_3$, 1:25). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **4l** (rotamer major : minor = 60:40) 1.55 – 1.65 (m, 1H, HC^{10}_{anti}), 1.71 (d, 1H, HC^{10}_{syn}, *J*=10.8), 2.91 (bs, 1H, HC^1), 2.96 (d, 1H, HC^{9}_{endo} major, *J*=10.2), 3.01 (d, 1H, HC^{9}_{endo} min, *J*=10.4), 3.67 (1H, HC^6 min, overlaps with OCH_3), 3.70, 3.80 (two s, 3H, OCH_3 major), 3.78, 3.82 (two s, 3H, OCH_3 minor), 3.92 (d, 1H, HC^6 major, *J*=8.3), 4.40 (bs, 1H, HC^7 min), 4.49 (bs, 1H, HC^7 major), 4.79 (d, 1H, HCO, *J*=8.3), 6.90 (m, 2H, HC_{arom}), 7.62 (d, HC_{arom} minor, *J*=8.9), 7.65 (d, HC_{arom} major, *J*=8.7), 7.73 (d, HC_{arom} major, *J*=8.7). ^{13}C NMR ($CDCl_3$, δ ppm): 30.82 (C^{10} major), 31.46 (C^{10} minor), 43.24 (C^1 minor), 43.85 (C^1 major), 46.10 (C^9 major), 46.29 (C^9 minor), 52.07 (OCH_3 major), 52.46 (OCH_3 minor), 54.93 (OCH_3 major), 54.95 (OCH_3 minor), 57.39 (C^7 major), 57.74 (C^6 minor), 58.42 (C^7 minor), 85.01 (C-O minor), 84.93 (C-O major), 113.98, 120.40 (C_{arom}), 127.76 (C_{arom} minor), 128.00 (C_{arom} major), 154.15 (C=O minor), 154.40 (C=O major), 154.93

(C=N minor), 155.16 (C=N major). 160.74 (C_{arom}). ESI-MS (m/z): calculated for $C_{16}H_{18}N_2O_4$ 303.1339 [M+1], found 303.1342.



3m

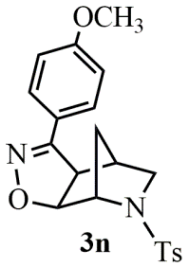
***tert*-Butyl 5-(4-methoxyphenyl)-3-oxa-4,9-diaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-9-carboxylate (3m)** (with admixture of **4m**).Yellow oil, R_f 0.51 (MeOH – $CHCl_3$, 1:25). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 67:33): 1.45 (s, CH_3), 1.6-1.75 (m, HC^{10}_{syn} + HC^{10}_{anti}), 2.78 (bs, HC^7), 3.07 (d, HC^8_{endo} min, *J*=9.6), 3.12 (d, HC^8_{endo} major, *J*=9.6), 3.23-3.33 (m, HC^8_{exo}), 3.74 (d, HC^6, *J*=8.1), 3.80 (s, OCH_3), 4.37 (HC^1 major), 4.49 (s, HC^1 min), 4.78 (d, HCO major, *J*=8.0), 4.86 (d, HCO minor, overlaps with **4m**), 6.93 (d, HC_{arom}, *J*=8.1), 7.65 (d, HC_{arom}, *J*=8.1).



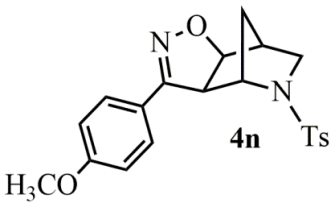
4m

***tert*-Butyl 5-(4-methoxyphenyl)-3-oxa-4,8-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (4m)** Yellow oil, R_f 0.60 (MeOH – $CHCl_3$, 1:25). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 60:40): 1.49 (s, CH_3, major), 1.57 (s, CH_3, minor), 1.65 (d, 1H, HC^{10}_{syn}, *J*=10.1), 1.72 (d, 1H, HC^{10}_{anti}, *J*=10.1), 2.92 (bs, HC^1), 2.94 (HC^9_{endo}, minor, overlaps with HC^1), 3.02 (d, HC^9_{endo}, major, *J*=10.5), 3.27 (dd, HC^9_{exo} minor, *J*=10.3, 3.8), 3.30 (dd, HC^9_{exo} major, *J*=10.5, 3.8), 3.83 (s, minor, OCH_3), 3.85 (s, major, OCH_3), 3.96 (d, HC^6, minor, *J*=8.1), 4.37 (s, HC^7 major), 4.49 (s, HC^7 minor), 4.83 (d, HCO minor, *J*=8.0), 4.84 (d, HCO major, *J*=8.1), 6.93 (m, HC_{Ar}), 7.73 (d, HC_{Ar} major, *J*=8.7), 7.77 (d, HC_{Ar} minor, *J*=8.7), the signal HC^6 major overlaps with the signal of OCH_3. ^{13}C NMR ($CDCl_3$, δ ppm) 28.09 (CH_3 major), 28.19 (CH_3 minor), 30.82 (C^{10} minor), 31.28 (C^{10} major), 43.36 (C^1 major), 43.94 (C^1 minor), 54.95, 55.00 (OCH_3), 57.96, 58.08, 58.36 (C^6, C^7), 79.77 (O<u>C</u>$(CH_3)_3$ major), 80.30 (O<u>C</u>$(CH_3)_3$ minor), 85.04 (C-O minor), 85.11 (C-O major), 154.23 (C=N).

9-[(4-Methylphenyl)sulfonyl]-5-(4-methoxyphenyl)-3-oxa-4,9-diaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3n). Colourless oil. R_f 0.57 (MeOH – $CHCl_3$, 1:30). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.98 (d, 1H, HC^{10}_{anti}, *J*=11.2), 1.48 (d, 1H, HC^{10}_{syn}, *J*=11.2), 2.42 (s, 3H, CH_3), 2.73 (1H, bs, HC^7), 3.12 (dd, 1H, HC^8_{exo}, J_1=9.1, J_2=3.2), 3.18 (d, 1H, *J*=9.1, HC^8_{endo}), 3.73 (d, 1H, HC^6, *J*=8.2), 3.83 (s, 3H, OCH_3), 4.35 (s, 1H, HC^1), 4.92 (d, 1H, HCO, *J*=8.2), 6.90 (d, 2H, H_{Ar}, *J*=8.5), 7.34 (d, 2H, H_{Ar}, *J*=7.6), 7.59 (d, 2H, H_{Ar}, *J*=8.5), 7.73 (d, 2H, H_{Ar}, *J*=7.6). ^{13}C NMR ($CDCl_3$, δ ppm): 21.14 (CH_3), 30.22 (C^{10}), 40.18 (C^7), 51.26 (C^6), 54.97 (OCH_3), 55.68 (C^8), 62.11 (C^1), 84.99 (C-O), 113.91, 120.24, 126.90, 127.95, 129.53, 134.93, 143.46, 160.76 (C_{Ar}), 155.45 (C=N). ESI-MS (m/z) isomers **3m** + **4m**: calculated for $C_{19}H_{24}N_2O_4$ 345.18088 [M+1], found 345.1813.

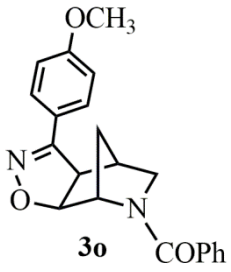


3n

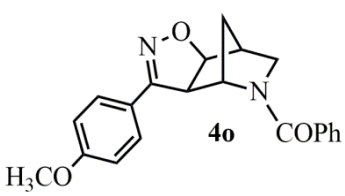


8-[(4-Methylphenyl)sulfonyl]-5-(4-methoxyphenyl)-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4n). Colourless oil. R_f 0.33 (MeOH – $CHCl_3$, 1:30). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.02 (d, 1H, HC^{10}_{anti}, *J*=10.9,), 1.55 (d, 1H, HC^{10}_{syn}, *J*=10.9), 2.42 (s, 3H, CH_3), 2.86 (1H, bs, HC^1), 3.06 (s, 2H, HC^9_{exo} + HC^9_{endo}), 3.86 (s, 3H, OCH_3), 4.10 (d, 1H, HC^6, *J*=8.3), 4.39 (s, 1H, HC^7), 4.82 (d, 1H, HCO, *J*=8.3), 6.96 (d, 2H, H_{arom}, *J*=8.5), 7.31 (d, 2H, H_{arom}, *J*=7.7), 7.68 (d, 2H, H_{arom}, *J*=8.5), 7.71 (d, 2H, H_{arom}, *J*=7.7). ^{13}C NMR ($CDCl_3$, δ ppm): 21.14 (CH_3), 30.56 (C^{10}), 44.14 (C^1), 47.13 (C^6), 55.00 (OCH_3), 59.02 (C^9), 60.56 (C^7), 84.89 (C-O), 114.11, 120.24, 126.90, 127.95, 129.53, 134.98, 143.52, 160.85 (C_{arom}), 154.14 (C=N). ESI-MS (m/z) isomers **3n** + **4n**: calculated for $C_{21}H_{22}N_2O_4S$ 399.1373 [M+1], found 399.1374.

5-Phenyl-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-en-9-yl](phenyl)-methanone (3o). Yellow oil. R_f 0.41 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 77:23): 1.65-1.90 (m, HC^{10}_{syn} + HC^{10}_{anti}), 2.83 (bs, HC^7 minor), 2.94 (bs, HC^7 major), 3.16 (d, HC^8_{endo} minor, *J*=9.9), 3.38 (d, HC^8_{endo} major, *J*=11.3), 3.54 (dd, HC^8_{exo} major, *J*=9.9, 3.5), 3.64 (dd, HC^8_{exo} major, *J*=11.3, 3.5), 3.76 (d, HC^6 minor, *J*=8.0), 3.84 (s, OCH_3 major), 3.86 (s, OCH_3 minor), 3.89 (d, HC^6 major, *J*=8.2), 4.38 (bs, HC^1 major), 4.95 (d, HCO major, *J*=8.2), 4.98 (bs HC^1 minor), 5.05 (d, HCO minor, *J*=8.0), 6.91 (d, H_{arom} minor, *J*=8.8), 6.95 (d, H_{arom} major, *J*=8.9), 7.38-7.57 (m, H_{arom}), 7.61 (d, H_{arom} minor, *J*=8.8), 7.68 (d, H_{arom} major, *J*=8.9).^{13}C NMR ($CDCl_3$, δ ppm): 30.12 (C^{10} minor), 31.85 (C^{10} major), 39.09 (C^7 major), 40.23 (C^7 minor), 54.98 (OCH_3), 49.95, 56.03 (C^6, C^8), 62.42 (C^1 major), 65.13 (C^1 minor), 83.52 (C-O minor), 84.89 (C-O major), 113.97, 120.10, 126.59, 126.84, 128.03, 128.26, 128.40, 130.06, 135.41 (C_{arom}), 155.98 (C=N), 160.85 (C_{arom}), 169.37 (C=O). ESI-MS (m/z): calculated for $C_{21}H_{20}N_2O_3$ 349.1547 [M+1], found 319.1551.

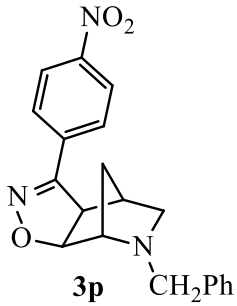


5-Phenyl-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-en-8-yl]-(phenyl)methanone (4o). Yellow oil. R_f 0.50 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 56:44): 1.73 (bs, HC^{10}), 1.77 (d, HC^{10}, *J*=11.2), 1.86 (d, HC^{10}, *J*=11.1), 2.95 (bs, HC^1 minor), 2.99 (d, HC^9_{endo} minor, *J*=10.0), 3.06 (bs, HC^1 major), 3.31 (d, HC^9_{endo} major, *J*=11.9), 3.56 (dd, HC^9_{exo} major, *J*=11.9, 4.1), 3.61 (dd, HC^9_{exo} minor, *J*=10.0, 3.8), 3.80 (s, OCH_3 major), 3.82 (d, HC^6 major, *J*=8.3), 3.86 (s, OCH_3 minor), 4.19 (d, HC^6 minor, *J*=8.3), 4.30 (bs, HC^7 major), 4.79 (d, HCO minor, *J*=8.3), 4.87 (bs, HC^7 minor), 4.92 (d, HCO major, *J*=8.3),



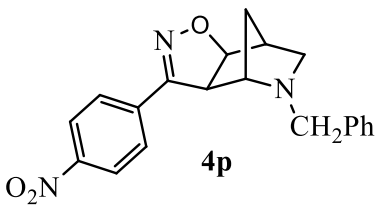
6.70 (d, H_{arom}, *J*=8.8), 6.97 (d, H_{arom}, *J*=8.8), 7.15 (d, H_{arom}, *J*=8.8), 7.40-7.60 (m, H_{arom}), 7.90 (d, H_{arom}, *J*=8.9).^{13}C NMR ($CDCl_3$, δ ppm): 30.16 (C^{10} minor), 31.84 (C^{10} major), 43.14, 45.80 (C^1, C^9 major), 44.16, 49.88 (C^1, C^9 minor), 54.90 (OCH_3), 57.17, 57.65 (C^6, C^7minor), 58.85, 60.47 (C^6, C^7 major), 84.42 (C-O minor), 84.92 (C-O major), 113.71, 113.99, 120.11, 120.42, 126.38, 127.13, 127.53, 128.01, 128.13, 128.35, 129.71, 130.38, 135.01, 136.34 (C_{arom}), 153.68, 154.63 (C=N), 160.57, 160.75 (C_{arom}), 169.45, 170.15 (C=O). ESI-MS (m/z): calculated for $C_{21}H_{20}N_2O_3$ 349.1547 [M+1], found 319.1548.

9-Benzyl-5-(4-nitrophenyl)-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3p) Colourless oil, R_f 0.50 (EtOAc – petroleum ether, 2:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.45 (d, 1H, HC^{10}_{syn}, *J*=11.0), 1.65 (d, 1H, HC^{10}_{anti}, *J*=11.0), 2.60 – 2.70 (m, 2H, HC^8_{endo} + HC^8_{exo}), 3.52 (bs, 1H, HC^1), 3.73 (d, 1H, HC^6, *J*=8.5), 3.76 (s, 2H, CH_2Ph), 5.00 (d, 1H, HCO, *J*=8.3), 7.24-7.40 (m, 5H, Ph), 7.88, 8.27 (two d, 2H, *J*=8.8). ^{13}C NMR ($CDCl_3$, δ ppm): 28.93 (C^{10}), 40.58 (C^7), 55.04 (C^6), 57.26 (C^8), 59.51 (CH_2Ph), 64.29 (C^1), 87.12 (C-O), 155.56 (C=N); isomers **3p**+**4p** (**3p**:**4p** = 3:1): 123.96, 124.04, 127.15, 127.41, 128.38, 128.57, 135.18, 148.26 (C_{arom}).

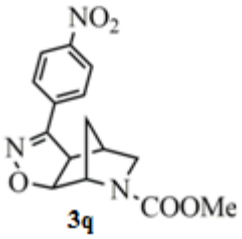


3p

8-Benzyl-5-(4-nitrophenyl)-3-oxa-4,8-diaza-tricyclo[5.2.1.02.6]dec-4-ene (4p) Colourless oil, R_f 0.36 (EtOAc – petroleum ether, 2:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.50 (d, 1H, HC^{10}_{syn}, *J*=10.6), 1.70 (d, 1H, HC^{10}_{anti}, *J*=10.6), 2.15 (d, 1H, HC^9_{endo}, *J*=9.8), 2.81 (bs, 1H, HC^4), 2.98 (dd, 1H, HC^9_{exo}, *J*=9.9, 4.2), 3.44 (bs, 1H, HC^7), 3.65, 3.90 (two d, 1H, CH_2Ph, *J*=13.3), 3.98 (m, 1H, HC^6), 4.90 (d, 1H, HCO, *J*=8.3), 7.60, 8.12 (two d, 2H, *J*=8.8); 7.32-7.45 (m, 5H, Ph). ^{13}C NMR ($CDCl_3$, δ ppm): 30.46 (C^{10}), 44.48 (C^1), 52.32, 58.02 (C^9, CH_2), 52.69 (C^6), 61.44 (C^7), 87.51 (C-O); 155.27 (C=N); 123.96, 127.25, 128.60, 128.66, 135.09, 148.18 (C_{arom}). ESI-MS (m/z): calculated for $C_{20}H_{19}N_3O_3$ 350.1499 [M+1], found 350.1498.



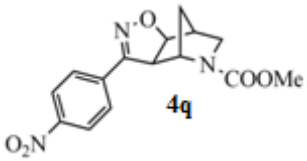
4p



3q

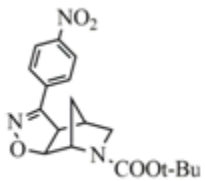
Methyl 5-(4-nitrophenyl)-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (3q). Yellow oil, R_f 0.4 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 63:37): 1.64 (d, 1H, HC^{10}_{syn}, *J*=11.1), 1.71 (d, 1H, HC^{10}_{anti}, *J*=11.3), 2.81 (bs, 1H, HC^7), 3.15 (d, 1H, HC^8_{endo} min, *J*=9.6), 3.20 (d, 1H, HC^8_{endo} major, *J*=9.9), 3.32-3.43 (m, 1H, HC^8_{exo}), 3.71 (s, 3H, OCH_3 min), 3.74 (s, 3H, OCH_3 major), 3.77 (d, 1H, HC^6, *J*=8.5), 4.47 (bs, 1H, HC^1 major), 4.59 (bs, 1H, HC^1 min), 4.92 (d, 1H, HCO major, *J*=8.3), 4.99 (d, HCO min, *J*=8.4), 7.88 (d, HC_{arom}, *J*=8.6), 8.27 (d, HC_{arom}, *J*=8.6). ^{13}C NMR ($CDCl_3$, δ ppm): 30.88 (C^{10} min), 31.39 (C^{10} major), 39.29 (C^7 major), 39.85 (C^7 min), 49.86 (C^8 min), 49.95 (C^8 major),

52.18 (OCH_3 min), 52.30 (OCH_3 major), 54.54 (C^6 min), 54.55 (C^6 major), 59.09 (C^1 min), 59.36 (C^1 major), 85.50 (C-O min), 85.67 (C-O major), 123.75, 127.11, 134.20, 148.09 (C_{arom}), 154.85 (C=N). ^{1}H NMR (DMSO-d_6, δ ppm) δ 1.35 (d, HC^{10}_{syn}, J=11.1), 1.63 (m, HC^{10}_{anti}), 2.75 (bs, HC^7), 3.10-3.25 (m, HC^8_{exo}+ HC^8_{endo}), 3.59 (s, OCH_3, major), 3.61 (s, OCH_3, min), 4.10 (m, HC^6), 4.28 (bs, HC^1), 4.85 (m, HCO), 8.03 (d, HC_{arom}, J=8.6), 8.35 (m, HC_{arom}).



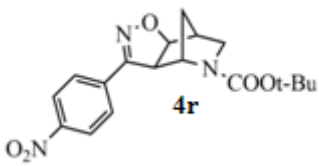
4q

Methyl 5-(4-nitrophenyl)-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (4q). Yellow oil, R_f 0.32 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, J, Hz) (rotamer major : minor = 63:37): 1.54 (s, 2H, H_2C^{10}), 3.01 (bs, 1H, HC^1), 3.03 (HC^9_{endo} minor), 3.07 (d, HC^9_{endo} major, J=10.7), 3.32-3.43 (m, HC^9_{exo}), 3.73 (s, OCH_3 major), 3.82 (s, OCH_3 minor), 3.89 (d, HC^6 minor, J=8.3), 3.98 (d, HC^6 major, J=8.3), 4.42 (bs, HC^7 minor), 4.50 (bs, HC^7 major), 4.97 (d, 1H, HCO, J=8.3), 7.90 (d, HC_{arom} minor, J=8.6), 7.97 (d, HC_{arom} major, J=8.6), 8.26 (d, HC_{arom} major, J=8.6), 8.29 (d, HC_{arom} minor, J=8.6). ^{13}C NMR ($CDCl_3$, δ ppm): 30.82 (C^{10} major), 31.51 (C^{10} minor), 43.22 (C^1 minor), 43.82 (C^1 major), 46.06 (C^9 major), 46.23 (C^9 minor), 52.12 (OCH_3, major), 52.52 (OCH_3, minor), 56.78, 57.38 , 57.50 (C^6,C^7), 86.51 (C-O major), 86.58 (C-O minor), 154.93 (C=N minor), 155.15 (C=N major), 155.42 (C=O minor), 155.63 (C=O major), 123.66, 126.85, 134.20, 147.98 (C_{arom} major), 123.74, 127.04, 134.11, 147.98 (C_{arom} minor). ^{1}H NMR (DMSO-d_6, δ ppm) 1.43 (d, HC^{10}_{syn}, J=10.3), 1.63 (m, HC^{10}_{anti}), 2.88 (bs, HC^1), 2.99 (m, HC^9_{endo}), 3.23 (m, HC^9_{exo}), 3.62 (s, OCH_3, major), 3.70 (s, OCH_3, min), 4.11 (m, HC^6), 4.28 (bs, HC^7, min), 4.31 (bs, HC^7, major), 4.99 (m, HCO), 7.91 (m, HC_{arom}), 8.35 (m, HC_{arom}). ESI-MS (m/z) isomers **3q**+**4q**: calculated for $C_{15}H_{15}N_3O_5$ 318.1084 [M+1], found 318.1074.



3r

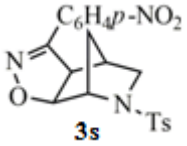
***tert*-Butyl 5-(4-nitrophenyl)-3-oxa-4,9-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-9-carboxylate (3r)**. Yellow oil. R_f 0.47 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, J, Hz) (rotamer major : minor = 73:27): 1.57 (s, CH_3), 1.58-1.74 (m, HC^{10}), 2.79 (s, HC^7), 3.12 (d, HC^8_{endo} min, J=9.2), 3.17 (d, HC^3_{endo}, major, J=10.2), 3.35 (dd, HC^3_{exo}, J=9.9, 3.0), 3.78 (d, HC^6, J=8.4), 4.42 (bs, HC^1 major), 4.56 (bs, HC^1 minor), 4.91 (d, HCO major, J=8.2), 4.99 (d, HCO minor, J=7.7), 7.89 (d, HC_{arom}, J=8.6), 8.28 (d, HC_{arom}, J=8.8). ESI-MS (m/z): calculated for $C_{18}H_{21}N_3O_5$ 360.1554 [M+1], found 360.1551.



4r

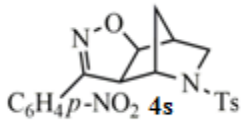
***tert*-Butyl 5-(4-nitrophenyl)-3-oxa-4,8-diazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene-8-carboxylate (4r)**. Yellow oil. R_f 0.54 (MeOH – $CHCl_3$, 1:50). ^{1}H NMR ($CDCl_3$, δ ppm, J, Hz) (rotamer major : minor = 55:45): 1.49 (s, CH_3 major), 1.58 (s, CH_3 minor), 1.62 – 1.78 (m, HC^{10}), 2.99 (s, HC^1), 3.05 (d, HC^9_{endo} major, J=10.5), 3.32 (dd, HC^9_{exo} minor, J_1=10.3, 3.8), 3.35 (dd, HC^9_{exo} major, J_1=10.2, 4.0), 3.87 (d, HC^6 major, J=8.3), 3.98 (d, HC^6 minor, J=8.4), 4.36 (s, HC^7 major),

4.47 (s, HC^7 minor), 4.96 (d, HCO, minor, *J*=7.9), 4.97 (d, HCO, major, *J*=7.9), 7.95 (d, HC_{arom} major, *J*=8.7), 7.99 (d, HC_{arom} minor, *J*=8.7), 8.27 (dd, HC_{arom}, J_1=8.8, 2.9), the signal HC^9 *endo* minor overlaps with HC^1. ^{13}C NMR ($CDCl_3$, δ ppm) 30.86 (C^{10} major), 31.36 (C^{10} minor), 43.34 (C^1 major), 43.93 (C^1 minor), 45.91 (C^9 major), 46.39 (C^9 minor), 56.92 (C^6 minor), 56.87 (C^6 major), 57.31 (C^7 major), 57.88 (C^7 minor), 79.89 ($OC(CH_3)_3$, minor), 80.14 ($OC(CH_3)_3$, major), 86.65 (C-O), 153.44, 153.66 (C=N, C=O). ESI-MS (m/z): calculated for $C_{18}H_{21}N_3O_5$ 360.1554 [M+1], found 360.1552.



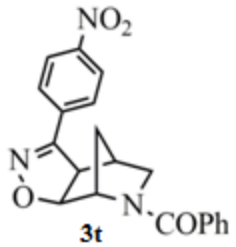
3s

9-[(4-Methylphenyl)sulfonyl]-5-(4-nitrophenyl)-3-oxa-4,9-diaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene (3s). Colourless oil. R_f 0.72 (MeOH – $CHCl_3$, 1:25). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.05 (dm, 1H, HC^{10}_{anti}, *J*=11.2), 1.44 (d, 1H, HC^{10}_{syn}, *J*=11.2), 2.43 (s, 3H, CH_3), 2.73 (bs, 1H, HC^7), 3.16 (dd, 1H, HC^8_{exo}, J_1=9.3, 3.3), 3.23 (d, 1H, HC^8_{endo}, *J*=9.3), 3.79 (d, 1H, HC^6, *J*=8.3), 4.41 (s, 1H, HC^1), 5.07 (d, 1H, HCO, *J*=8.3), 7.35 (d, 2H, H_{arom}, *J*=8.1), 7.74 (d, 2H, H_{arom}, *J*=8.1) 7.84 (d, 2H, H_{arom}, *J*=8.8), 8.26 (d, 2H, H_{arom}, *J*=8.8). ^{13}C NMR ($CDCl_3$, δ ppm): 21.17 (CH_3), 30.30 (C^{10}), 40.11 (C^7), 51.18 (C^6), 54.66 (C^8), 61.91 (C^1), 86.45 (C-O), 123.77, 126.94, 127.07, 129.62, 134.69, 135.50 (C_{arom}), 155.40 (C=N).



4s

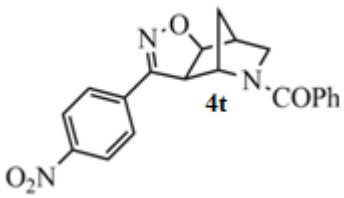
(8-[(4-Methylphenyl)sulfonyl]-5-(4-nitrophenyl)-3-oxa-4,8-diazatricyclo[5.2.1.0^{2,6}]dec-4-ene) (4s). Colourless oil. R_f 0.67 (MeOH – $CHCl_3$, 1:25). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.15 (dm, 1H, HC^{10}_{anti}, *J*=11.4), 1.54 (d, 1H, HC^{10}_{syn}, *J*=11.4), 2.43 (s, 3H, CH_3), 2.95 (bs, 1H, HC^1), 3.11 (m, 2H, HC^9_{exo} + HC^9_{endo}), 4.19 (d, 1H, HC^6, *J*=8.4), 4.37 (s, 1H, HC^7), 4.99 (d, 1H, HCO, *J*=8.4), 7.34 (d, 2H, H_{arom}, *J*=8.0), 7.73 (d, 2H, H_{arom}, *J*=8.0), 7.93 (d, 2H, H_{arom}, *J*=8.8), 8.31 (d, 2H, H_{arom}, *J*=8.8). ^{13}C NMR ($CDCl_3$, δ ppm): 21.17 (CH_3), 30.76 (C^{10}), 44.16 (C^1), 47.01 (C^6), 58.06 (C^9), 60.30 (C^7), 86.43 (C-O), 123.94, 126.86, 127.08, 129.61, 133.90, 134.90, 143.75, 148.17 (C_{arom}), 153.44 (C=N). ESI-MS (m/z) isomers **3s**+**4s**: calculated for $C_{20}H_{19}N_3O_5S$ 414.1111 [M+1], found 414.1118.



3t

5-(4-Nitrophenyl)-3-oxa-4,9-diazatricyclo[5.2.1.0^{2,6}]dec-4-en-9-yl]-(phenyl)methanone (3t) Yellow oil. R_f 0.50 (MeOH – $CHCl_3$, 1:100). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 73:27): 1.65 (d, HC^{10}_{syn} + HC^{10}_{anti} major, *J*=11.2), 1.75 (d, HC^{10}_{syn} + HC^{10}_{anti} minor, *J*=10.7), 2.82 (bs, HC^7 minor), 2.94 (bs, HC^7 major), 3.18 (d, HC^8_{endo} minor, *J*=9.5), 3.42 (d, HC^8_{endo} major, *J*=10.5), 3.57 (d, HC^8_{exo} minor, *J*=9.5), 3.65 (d, HC^8_{exo} major, *J*=10.5), 3.79 (d, HC^6 min, *J*=8.2), 3.92 (d, HC^6 major, *J*=8.2), 4.41 (bs, HC^1 major), 4.97 (bs, HC^1 minor), 5.05 (d, HCO major, *J*=8.2), 5.15 (d, HCO minor, *J*=8.0), 7.40-7.53 (m, Ph), 7.84 (d, HC_{arom}, *J*=8.4), 7.91 (d, HC_{arom} major, *J*=8.4), 8.20-8.30 (m, HC_{arom}). ^{13}C NMR ($CDCl_3$,

δ ppm): 31.94 (C^{10} major), 39.05 (C^{7} major), 49.93, 55.06 (C^{6}, C^{8}), 62.26 (C^{1} major), 86.26 (C-O major), 123/82, 126.56, 127.20, 127.95, 129.14, 132.52 (C_{arom}), 155.01 (C=N), 169.45 (C=O). ESI-MS (m/z): calculated for $C_{20}H_{17}N_3O_4$ 364.1292 [M+1], found 364.1292.



5-(4-Nitrophenyl)-3-oxa-4,8-diazatricyclo[5.2.1.0^{2,6}]dec-4-en-8-yl](phenyl)methanone (4t). Yellow oil. R_f 0.41 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz) (rotamer major : minor = 55:45): 1.67-1.73 (m, HC^{10}_{syn} + HC^{10}_{anti}), 1.77-1.89 (m, HC^{10}_{syn} + HC^{10}_{anti}), 3.02 (bs, HC^1 major), 3.04 (d, HC^9_{endo} major, *J*=9.9), 3.14 (bs, HC^1 minor), 3.36 (d, HC^1 minor, *J*=12.2), 3.58 (dd, HC^9_{exo} minor, *J*=12.2, 4.11), 3.66 (dd, HC^9_{exo} major, *J*=10.0, 3.9), 3.82 (d, HC^6 minor, *J*=8.4), 4.22 (d, HC^6 major, *J*=8.4), 4.30 (bs, HC^7 min), 4.83 (bs, HC^7 major), 4.92 (d, HCO major, *J*=8.5), 5.05 (d, HCO minor, *J*=8.4), 7.32 (d, HC_{aromr}, *J*=8.8), 7.4-7.6 (m, Ph), 8.05 (d, HC_{arom}, *J*=8.8), 8.10 (d, HC_{arom}, *J*=8.8). ^{13}C NMR ($CDCl_3$, δ ppm): 30.14 (C^{10} major), 31.87 (C^{10} minor), 43.10, 45.73 (C^1, C^9 minor), 44.05, 49.85 (C^1, C^9 major), 56.00, 57.42 (C^6, C^7major), 57.76, 60.18 (C^1, C^7 minor), 85.89 (C-O major), 86.41 (C-O minor), 123.46, 123.74, 126.23, 126.55, 127.10, 127.23, 128.03, 128.47, 129.95, 130.61, 133.75, 134.03, 134.52, 136.18, 147.75, 147.98 (C_{arom}), 152.89, 153.89 (C=N), 169.46, 170.40 (C=O). ESI-MS (m/z): calculated for $C_{20}H_{17}N_3O_4$ 364.1292 [M+1], found 364.1294.

References

S1 S.D. Larsen, P.A. Grieco, *J. Am. Chem. Soc.*, 1985, **107**, 1768.
S2 A. Kasyan, C. Wagner, M. E. Maier *Tetrahedron*, 1998, **54**, 8047.
S3 Y. Arakawa, M. Yasuda, M. Ohnishi, S. Yoshifuji, *Chem. Pharm. Bull.*, 1997, **45**, 255.
S4 P. Quadrelli, A. Piccanello, N. V. Martinez, B. Bovio, M. Mella, P. Caramella, *Tetrahedron*, 2006, **62**, 7370.
S5 M.G. Memeo, B. Bovio, P. Quadrelli, *Tetrahedron*, 2011, **67**, 1907.

.

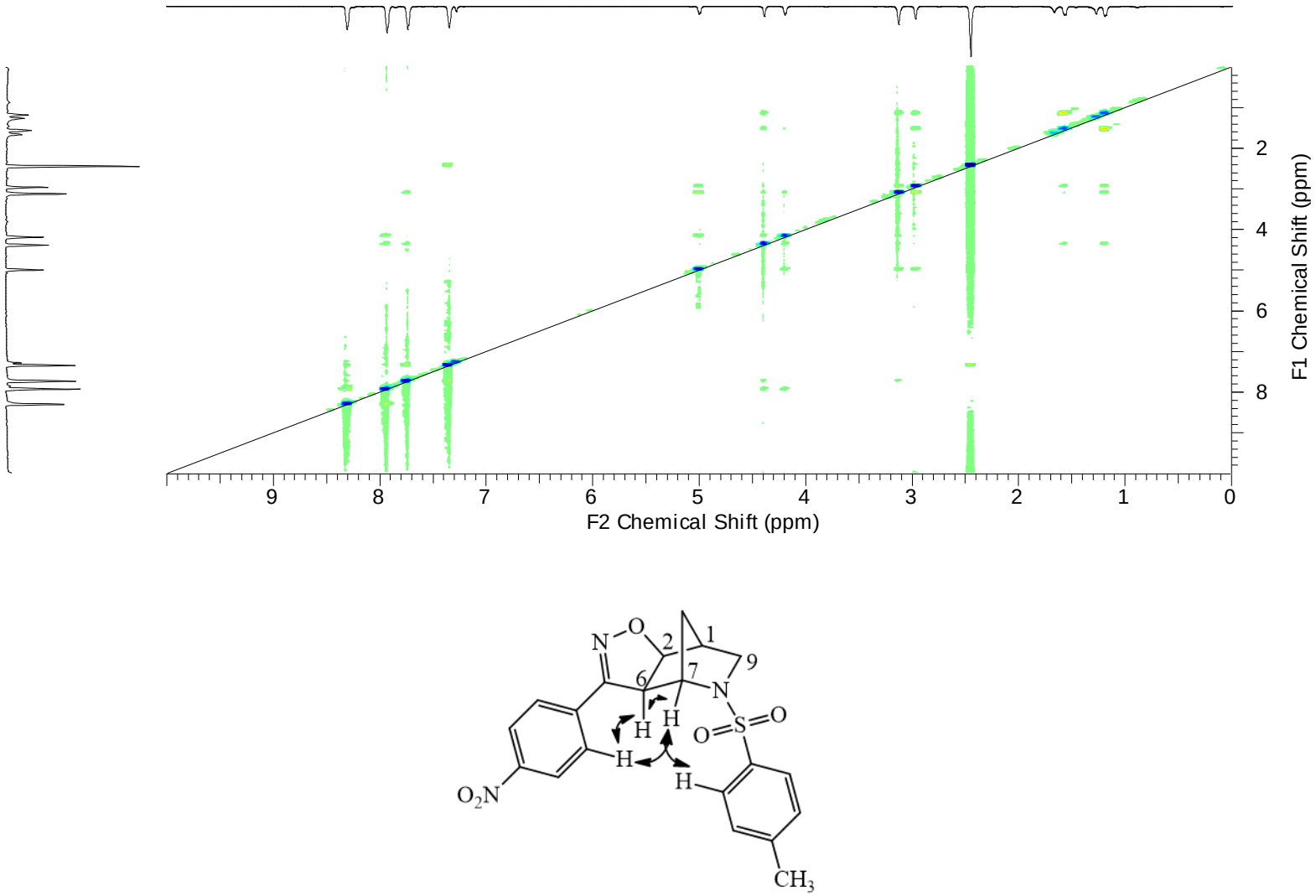


Figure S1. Results of the NOESY experiment for compound **4s**

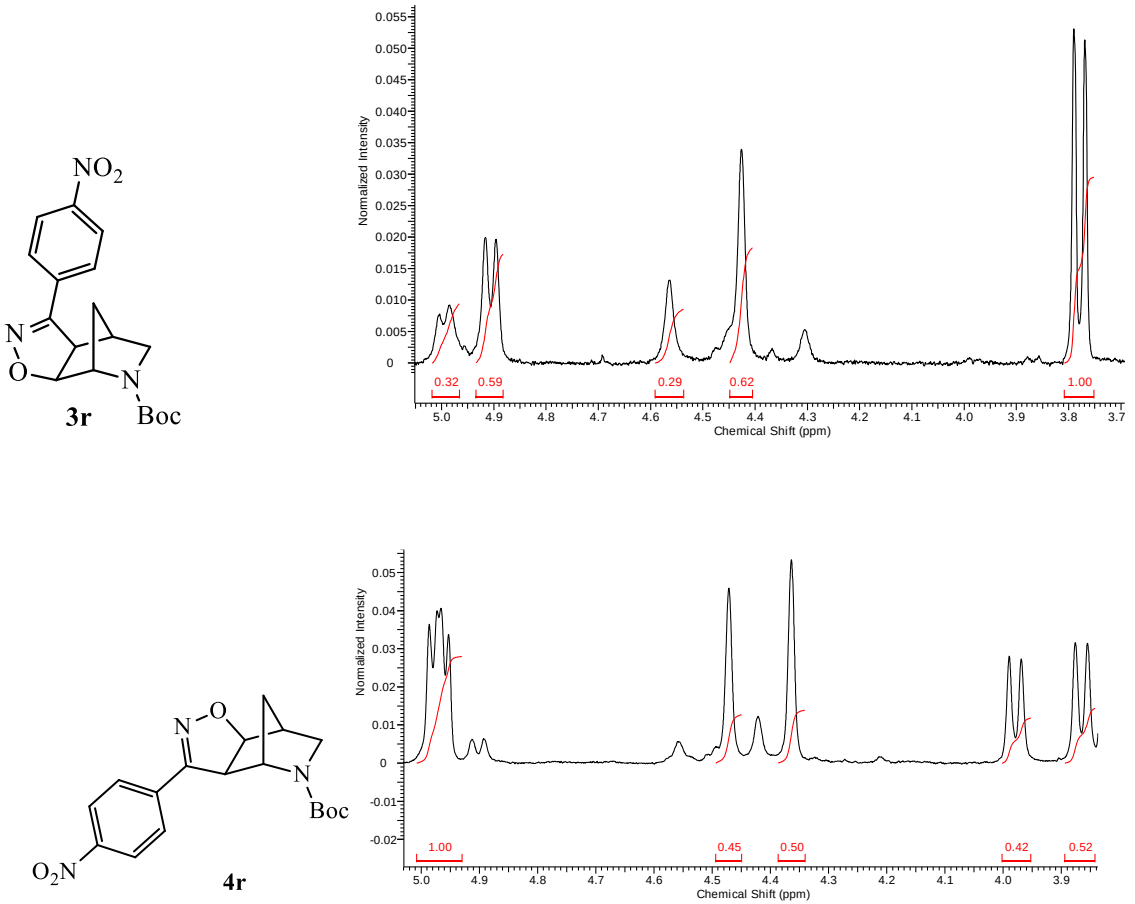
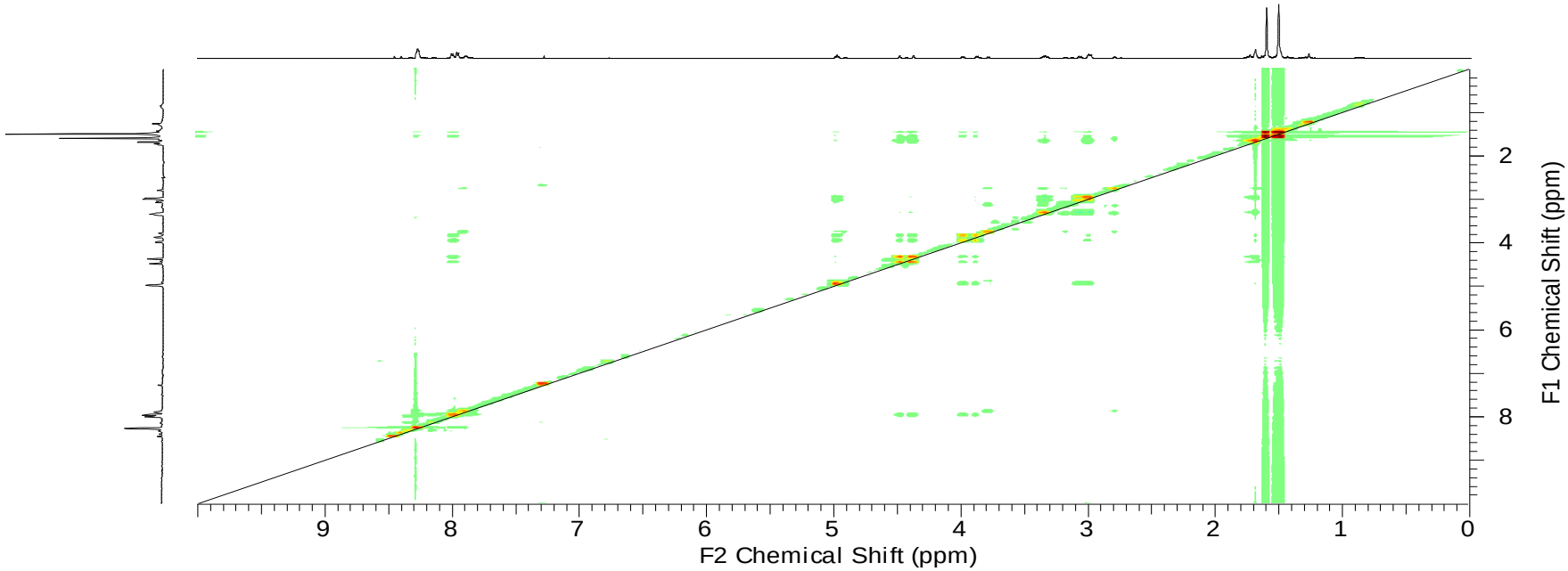
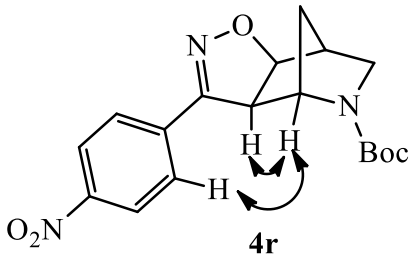


Figure S2. Fragments of ^{1}H NMR spectra of isomers **3r** (upper) and **4r** (lower).





4r

Figure S3. Results of the NOESY experiment for compound **4r**

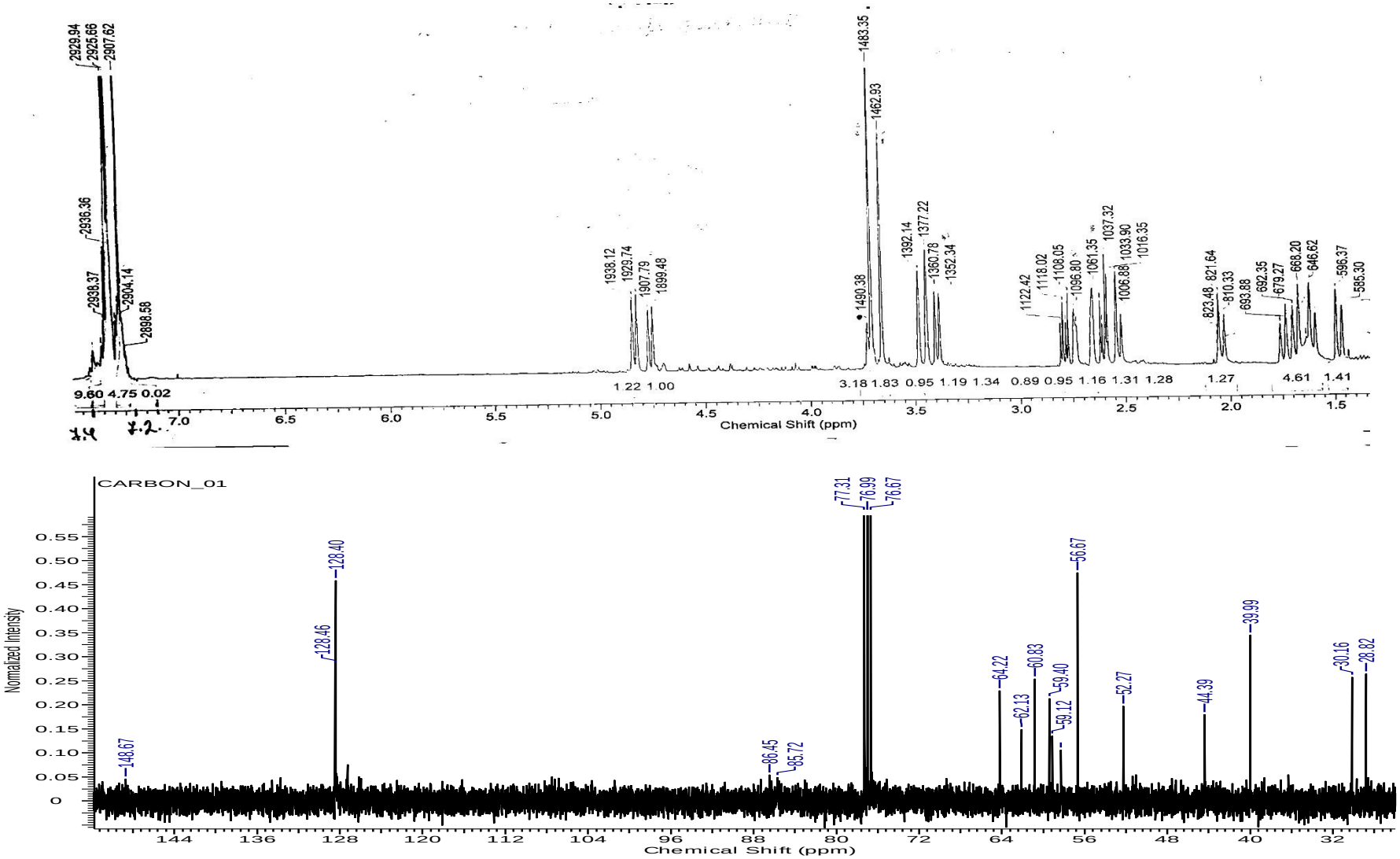


Figure S4. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3a** and **4a**

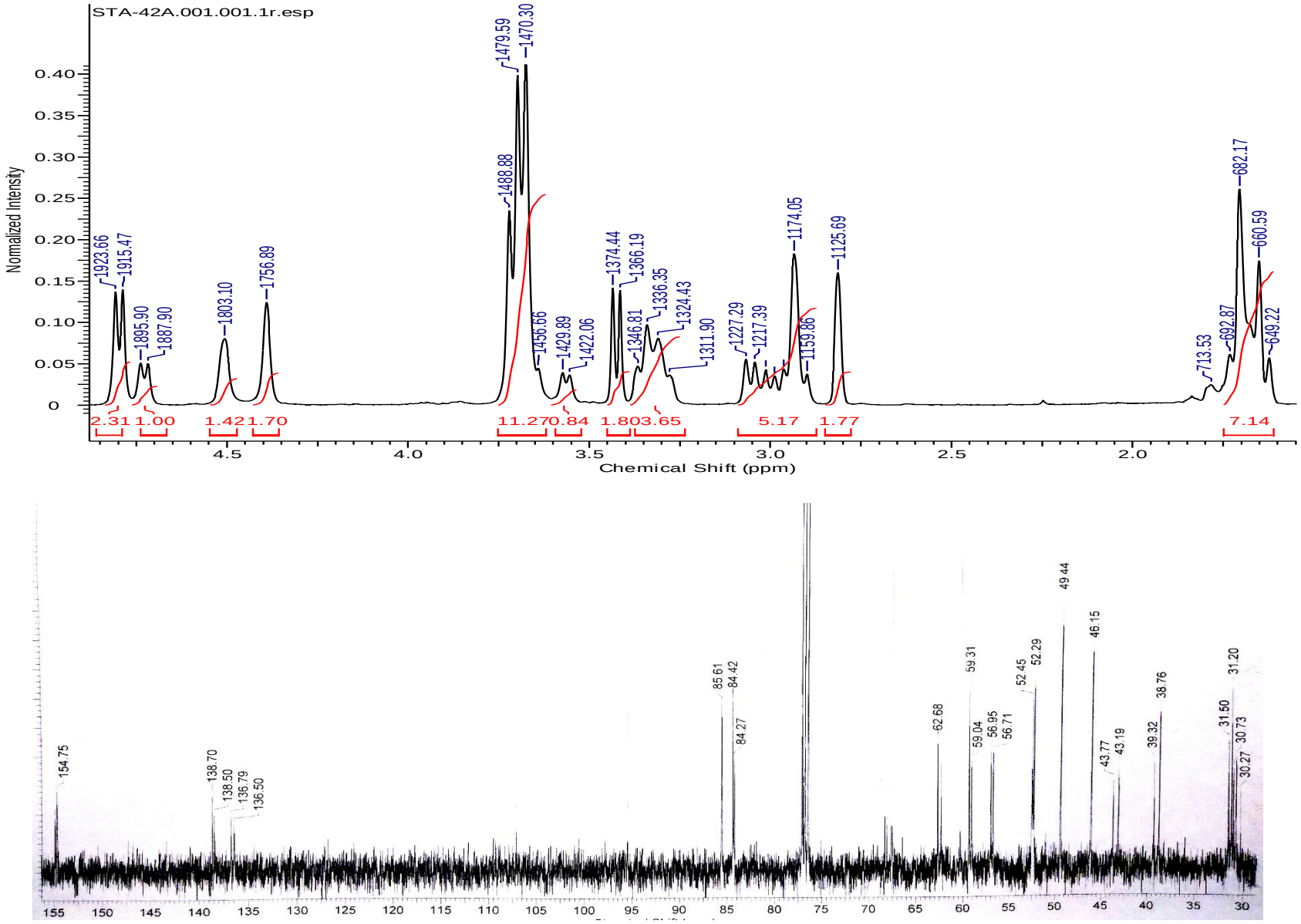


Figure S5. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3b** and **4b**

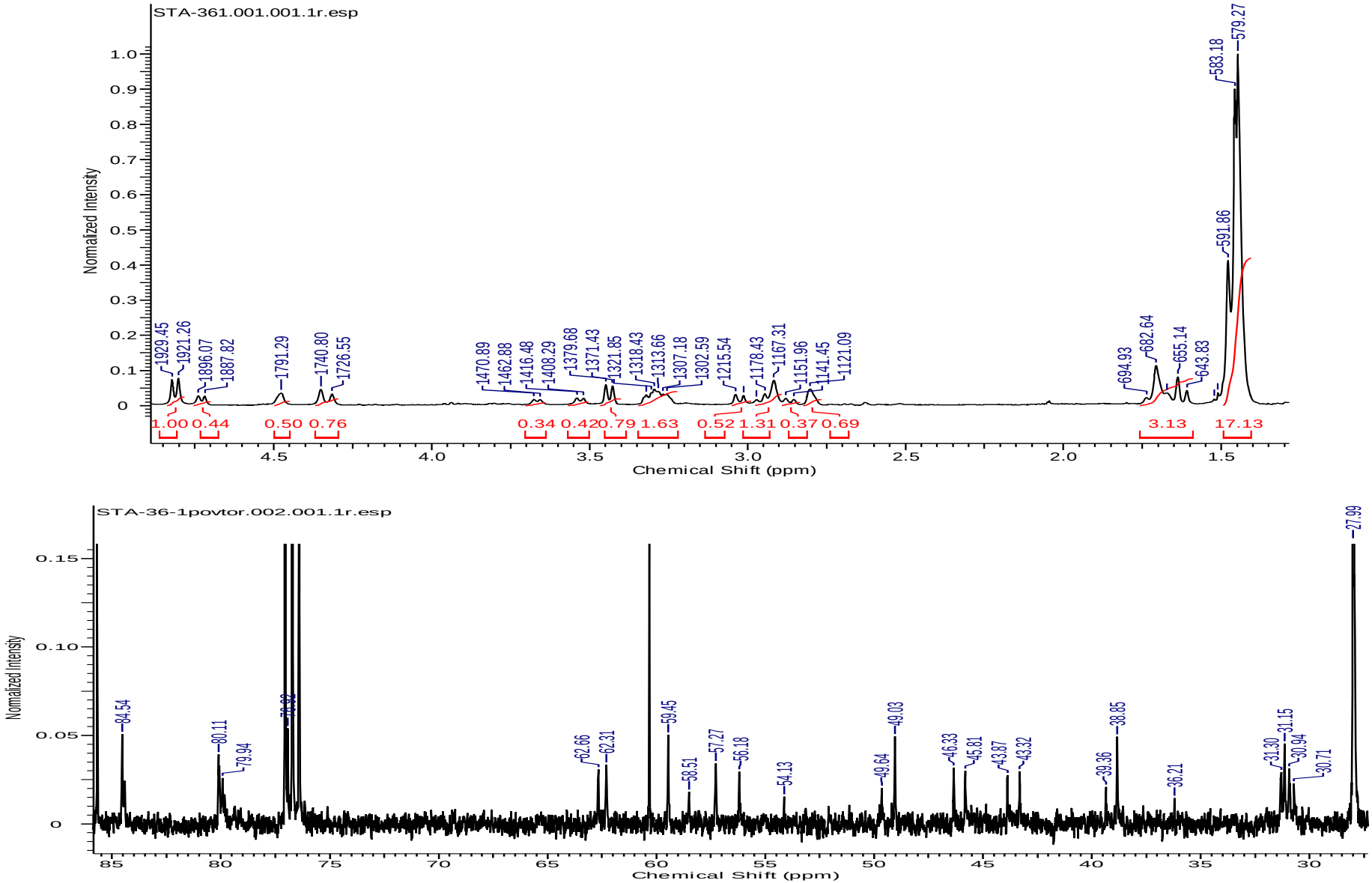


Figure S6. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3c** and **4c**

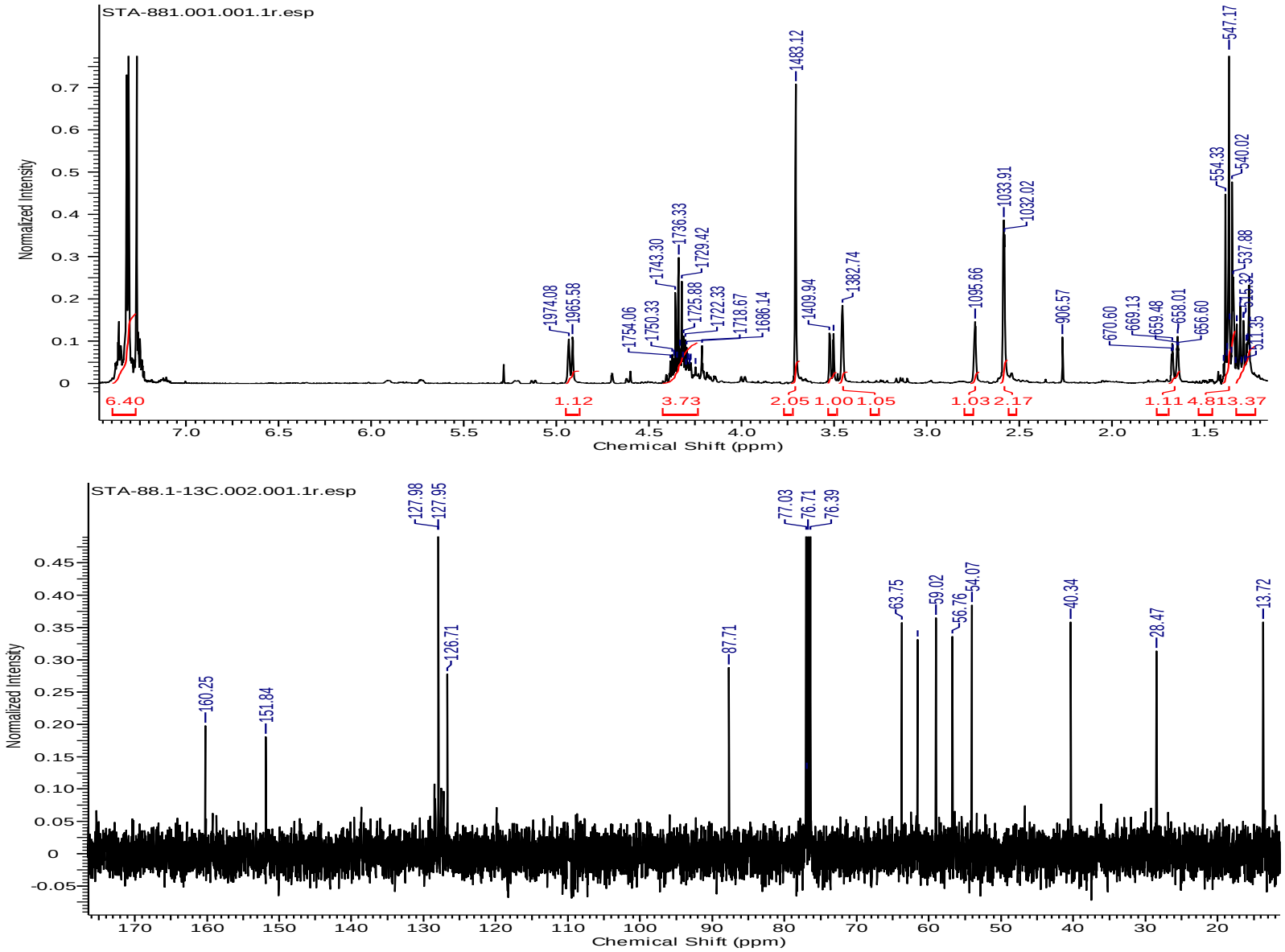


Figure S7. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3d**

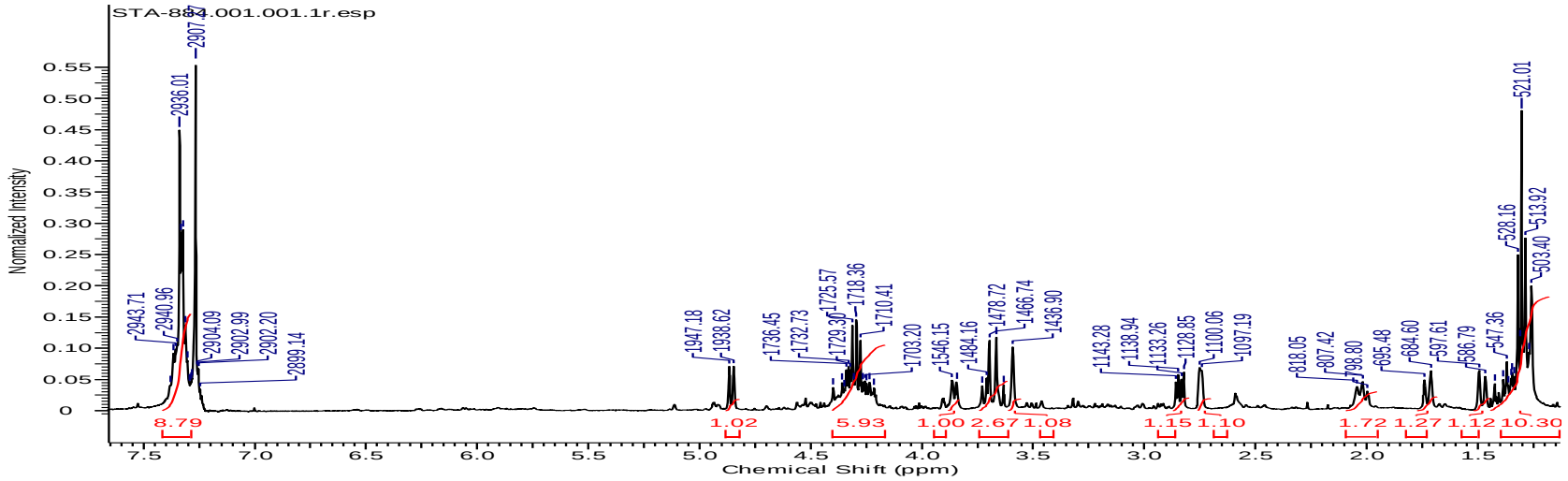


Figure S8. ^{1}H NMR spectrum ($CDCl_3$) of **4d**

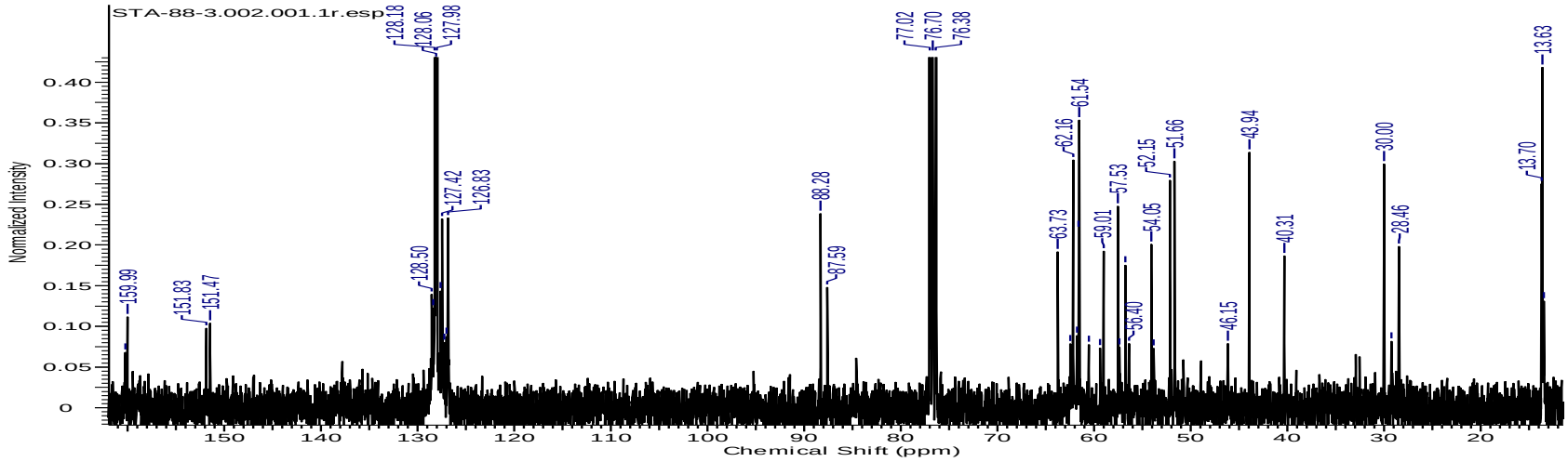


Figure S9. ^{13}C NMR spectrum ($CDCl_3$) of **3d** and **4d**

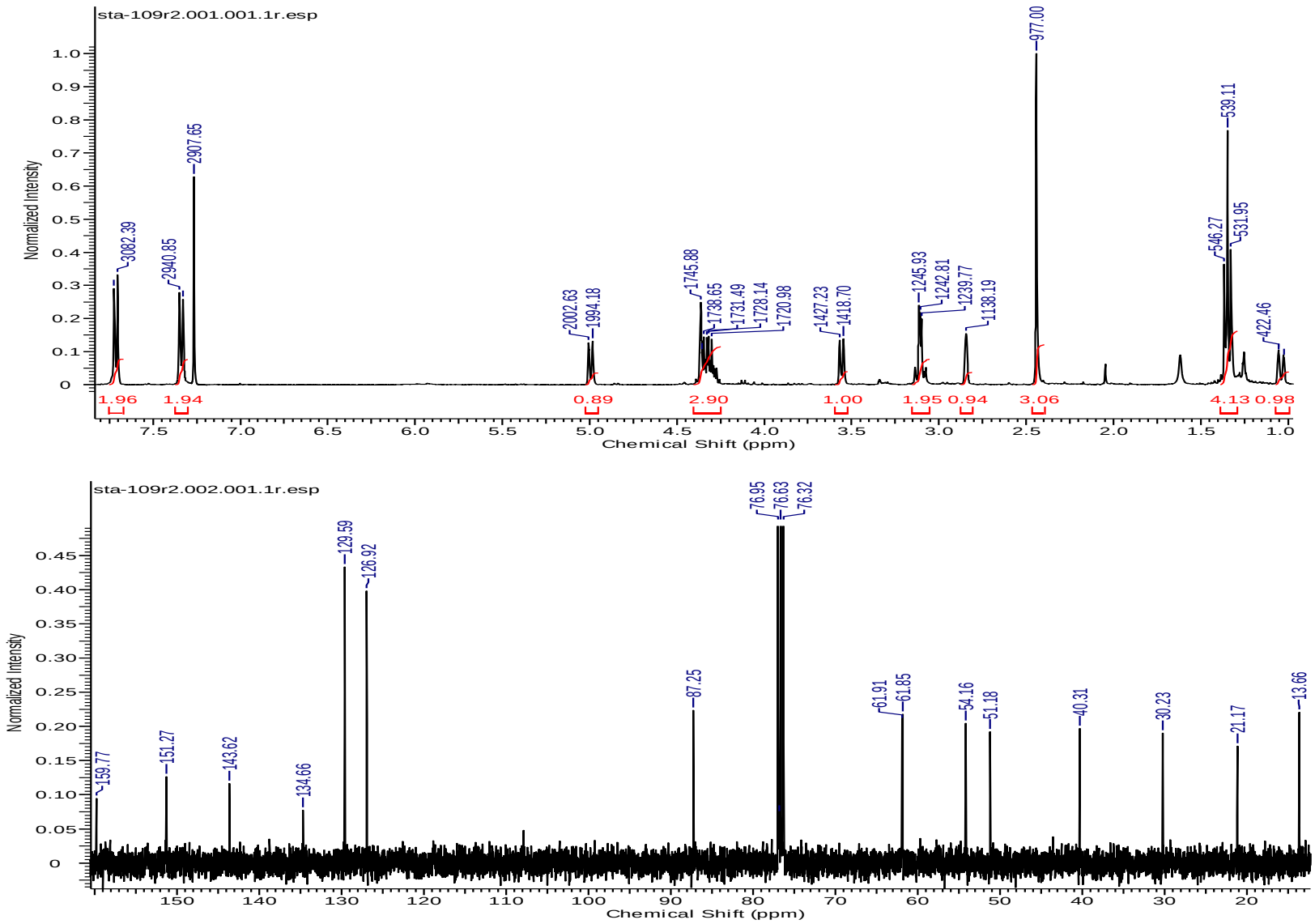


Figure S10. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3e**

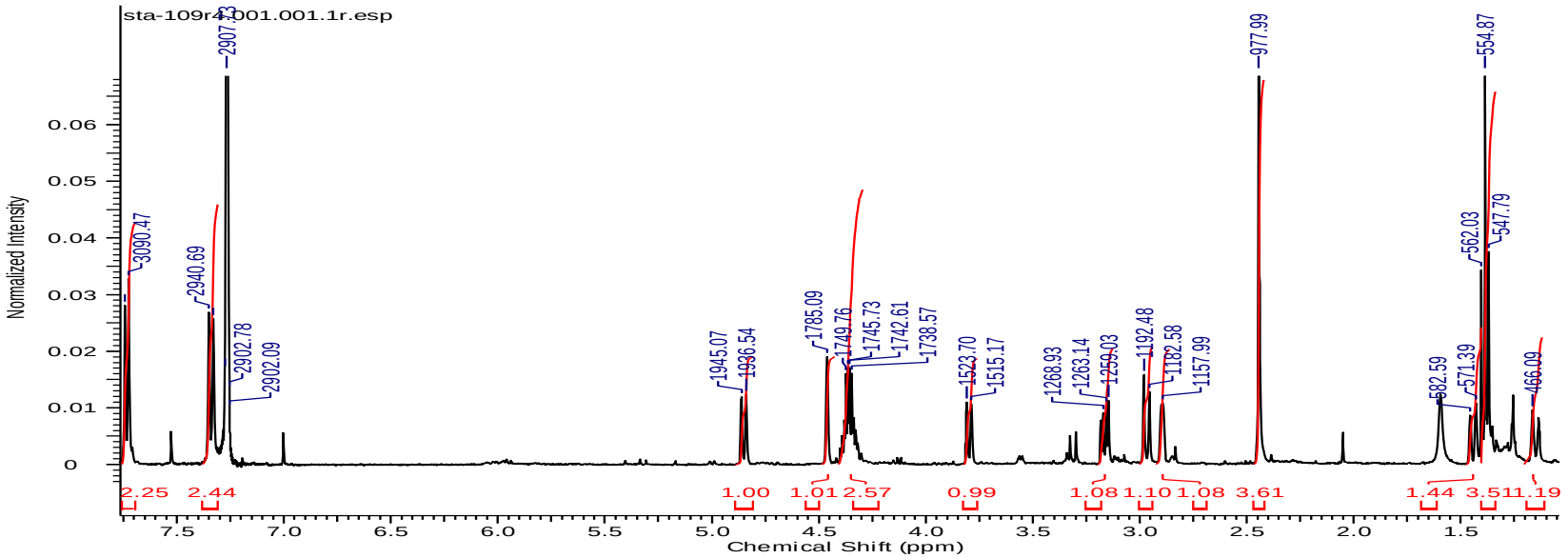


Figure S11. ^{1}H NMR spectrum ($CDCl_3$) of **4e**

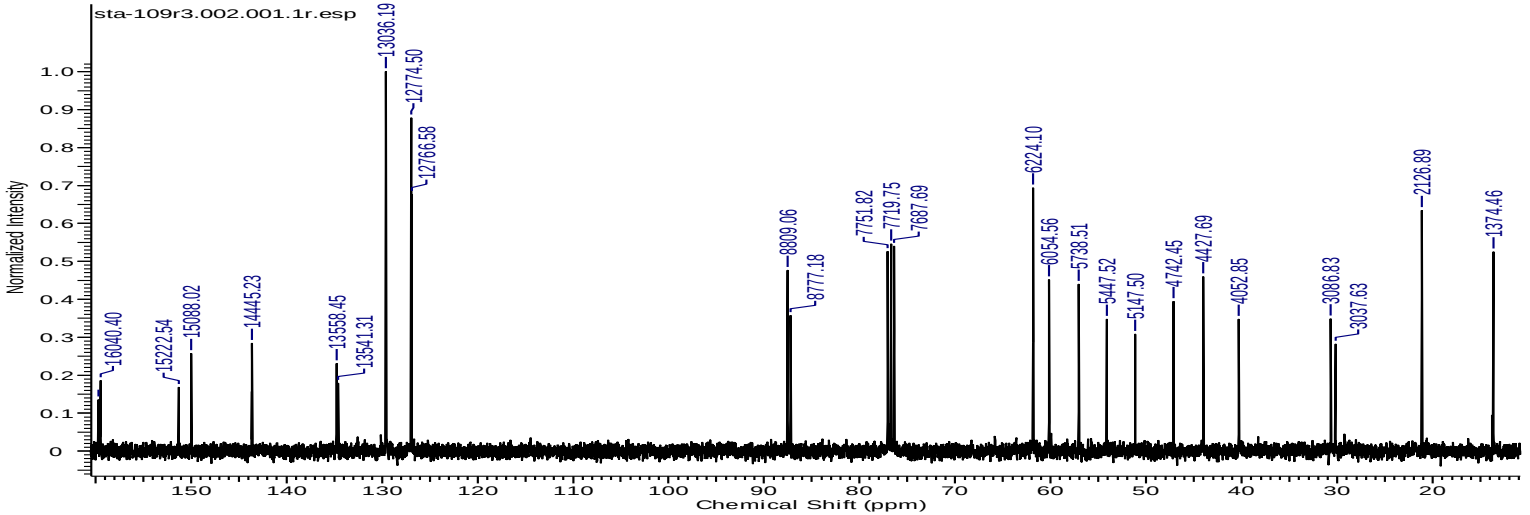


Figure S12. ^{13}C NMR spectrum ($CDCl_3$) of **3e** and **4e**

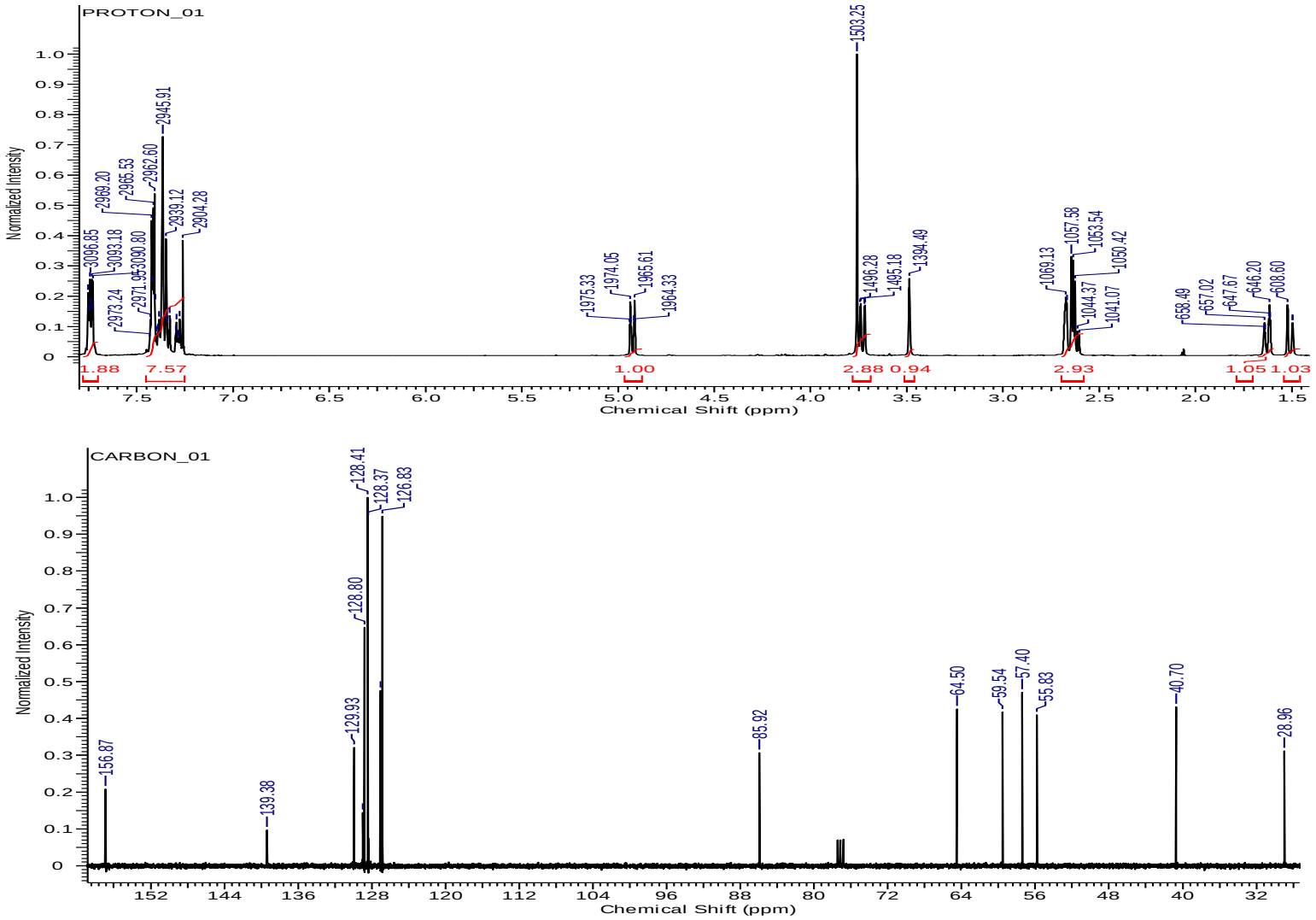


Figure S13. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3f**

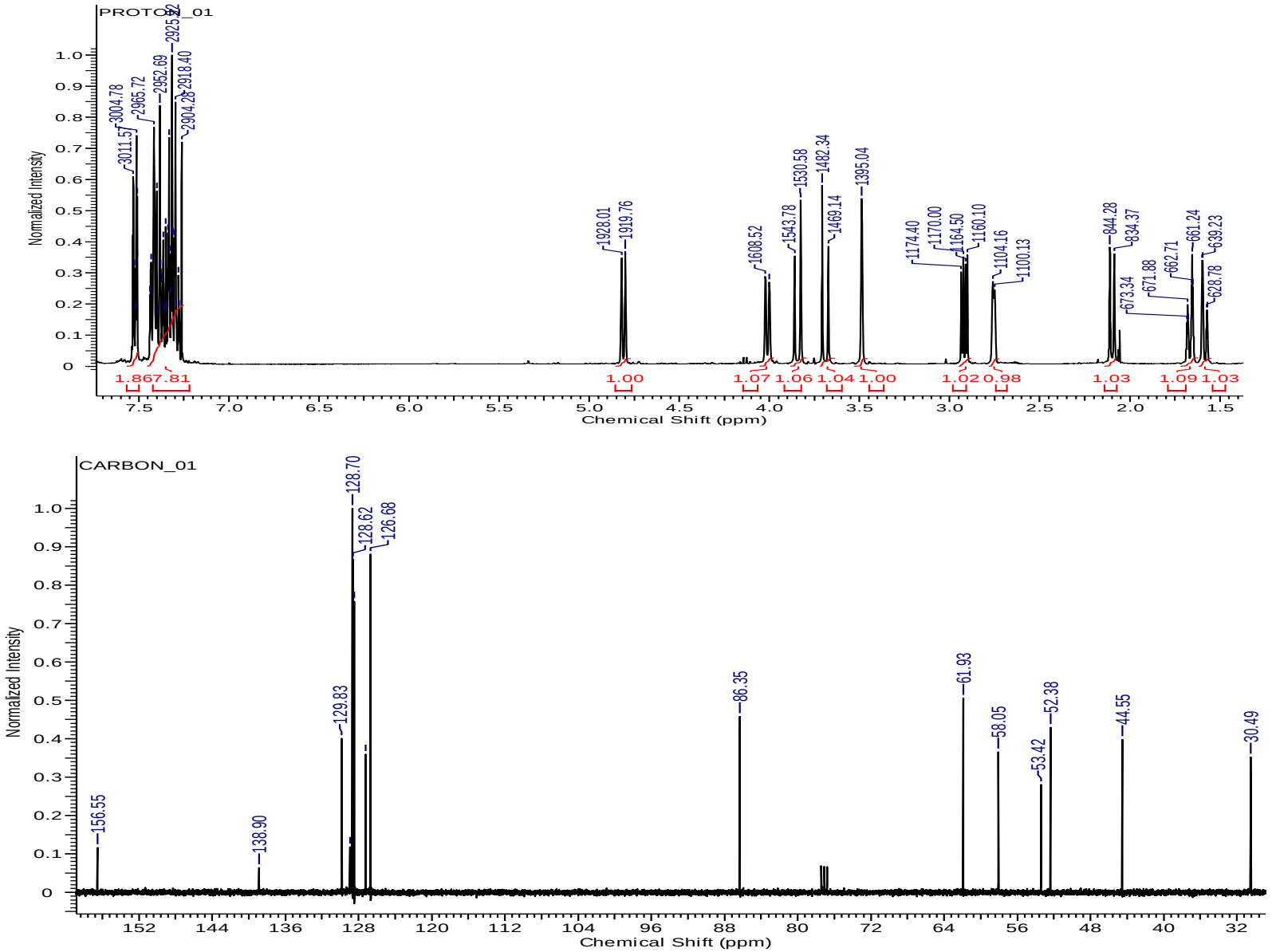


Figure S14. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4f**

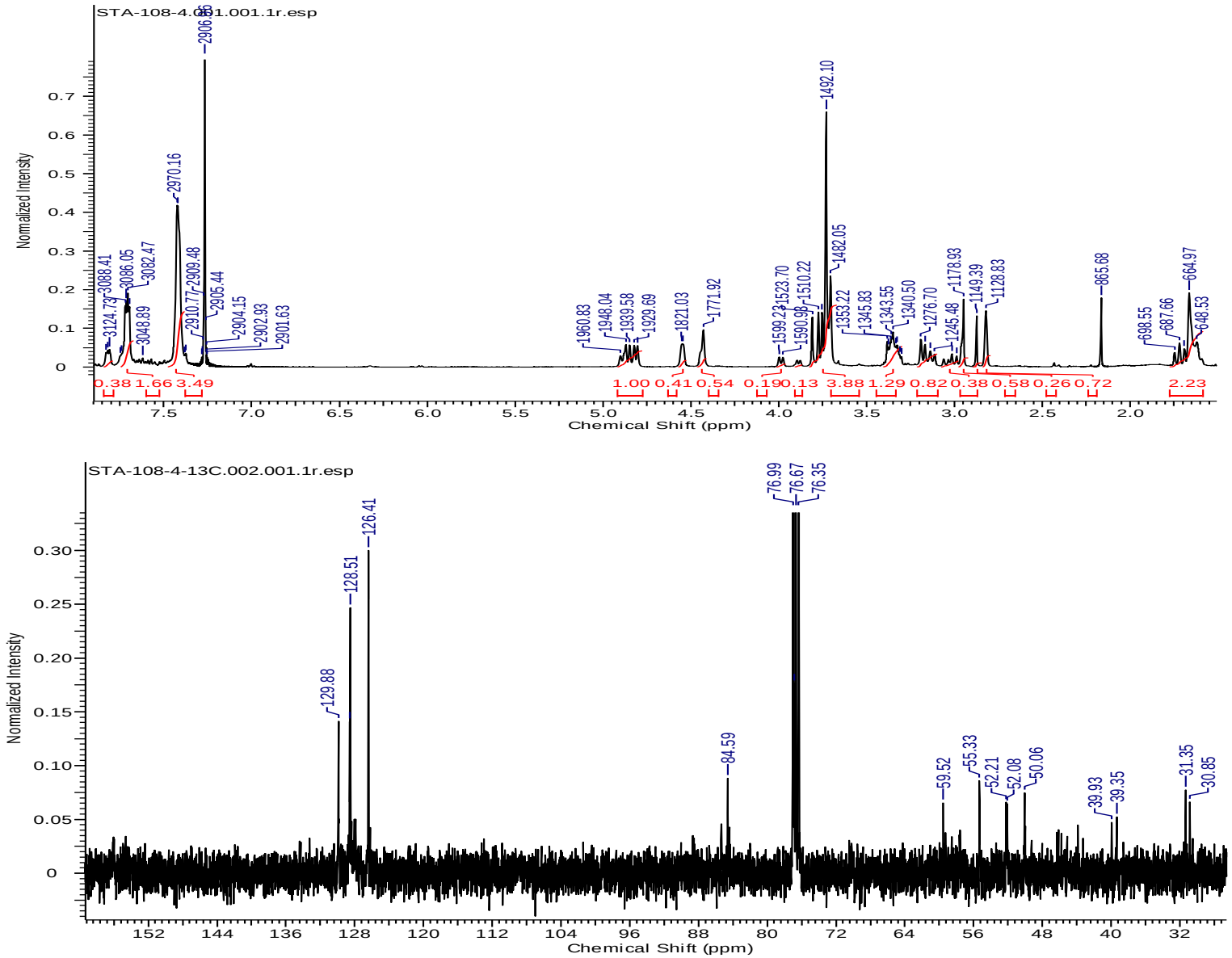


Figure S15. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3g** and **4g** (ratio 65:35)

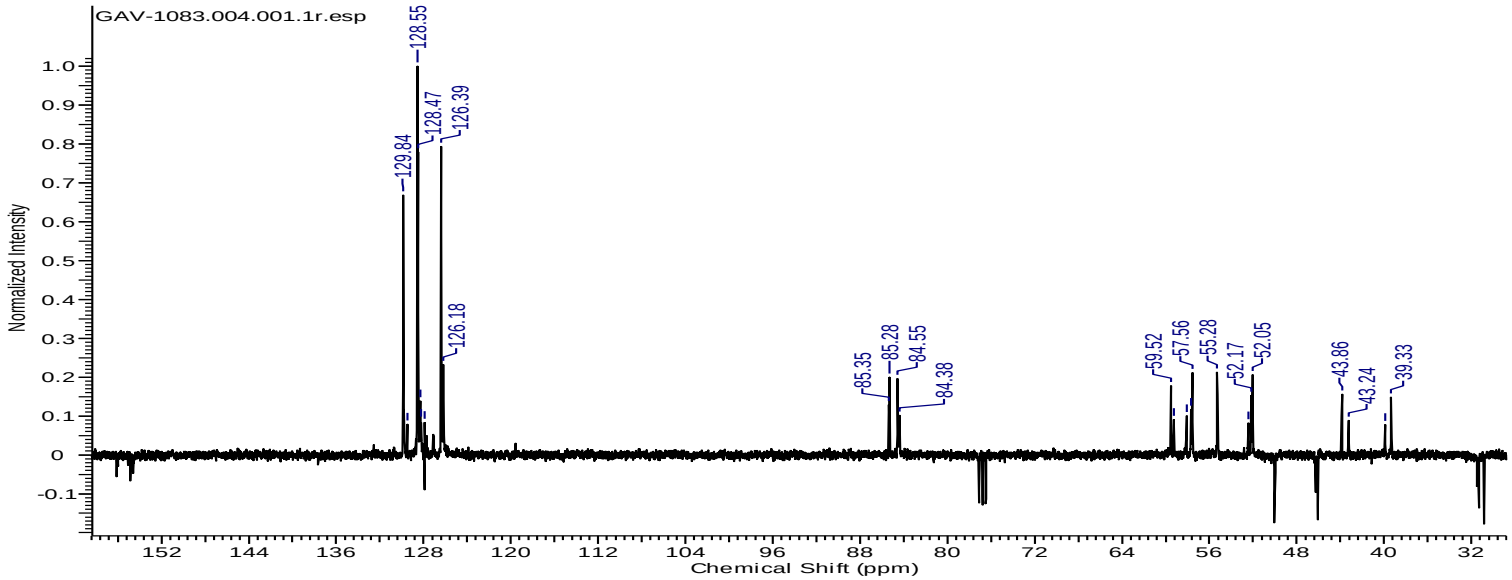


Figure S16. ^{13}C NMR (Apt) spectrum ($CDCl_3$) of **3g** and **4g** (ratio 55:45)

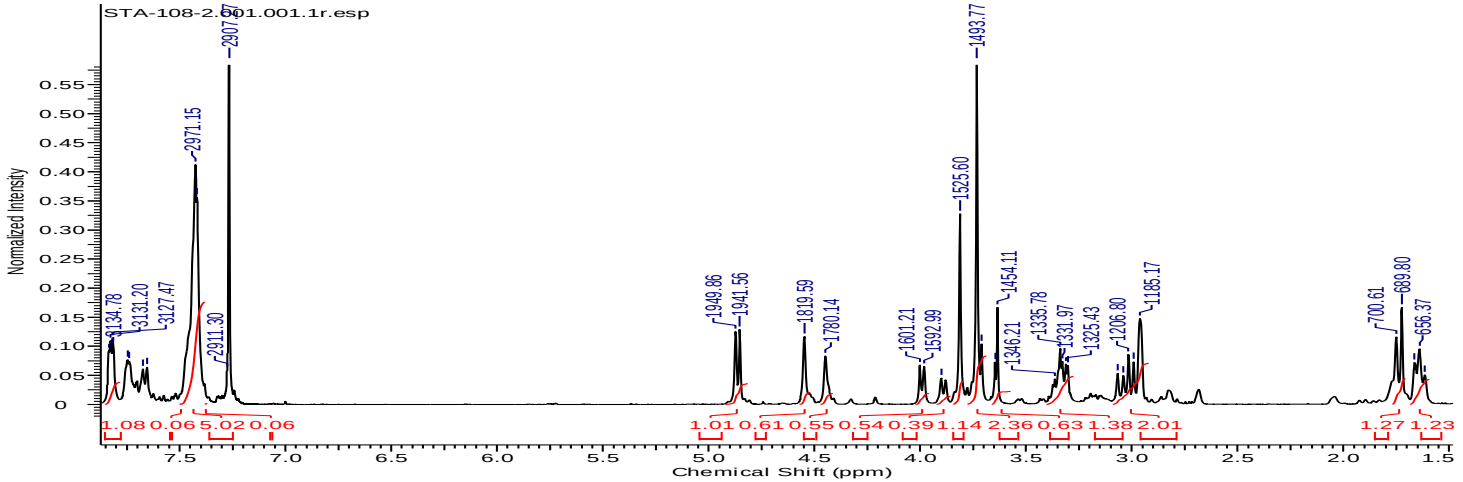


Figure S17. ^{1}H NMR spectrum ($CDCl_3$) of **4g**

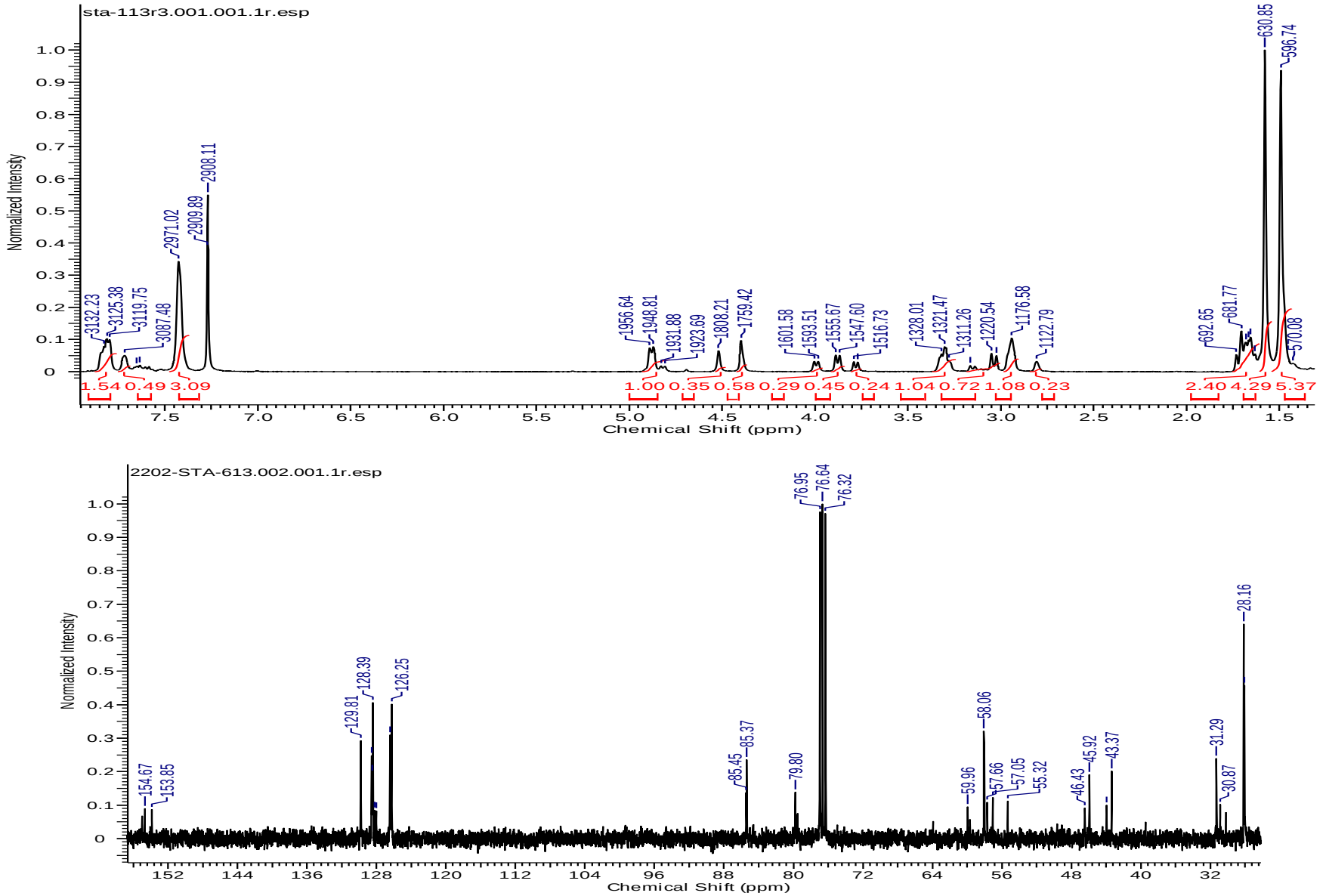


Figure S18. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3h** and **4h** (ratio 25:75)

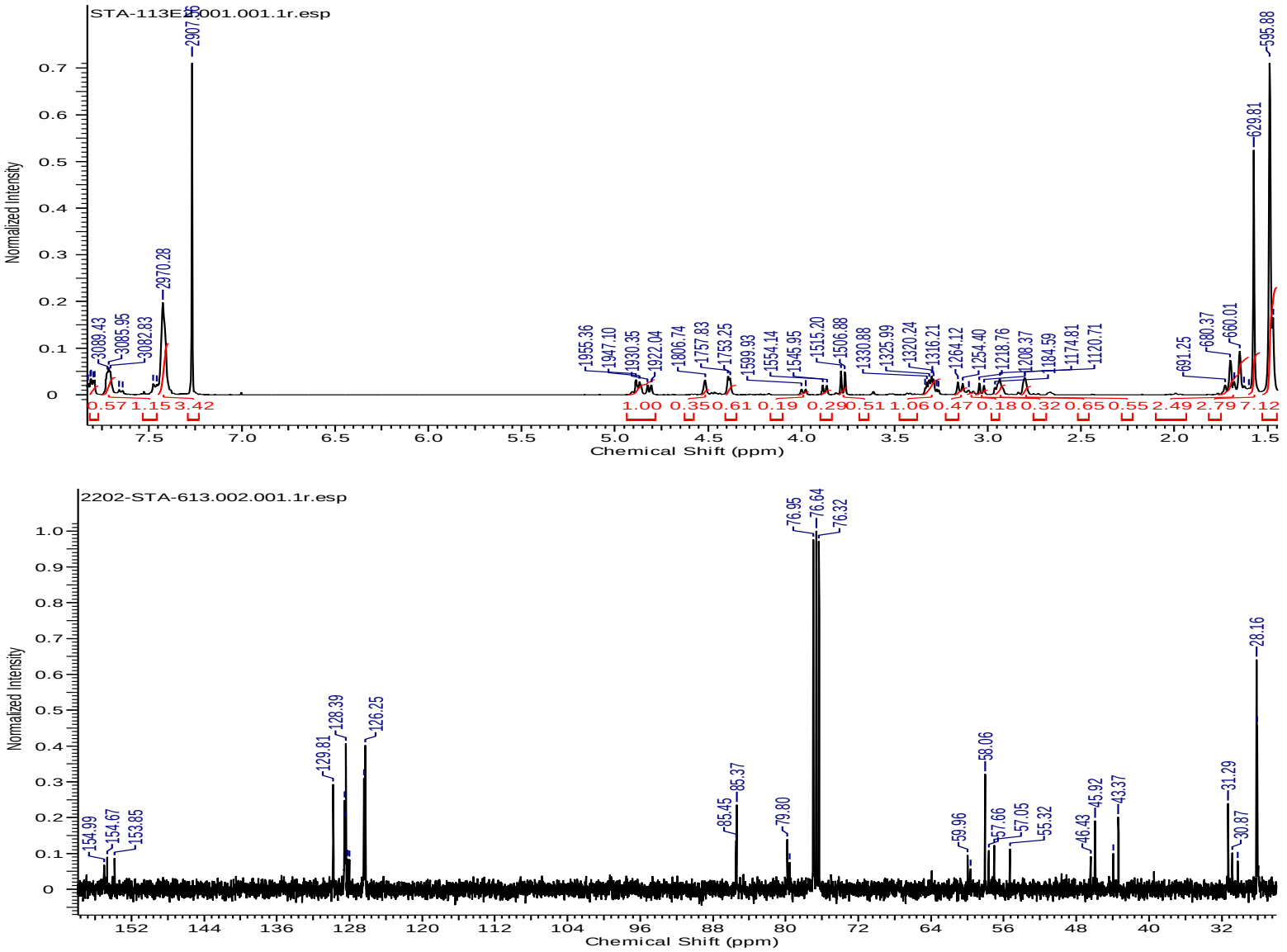


Figure S19. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3h** and **4h** (ratio 52:48)

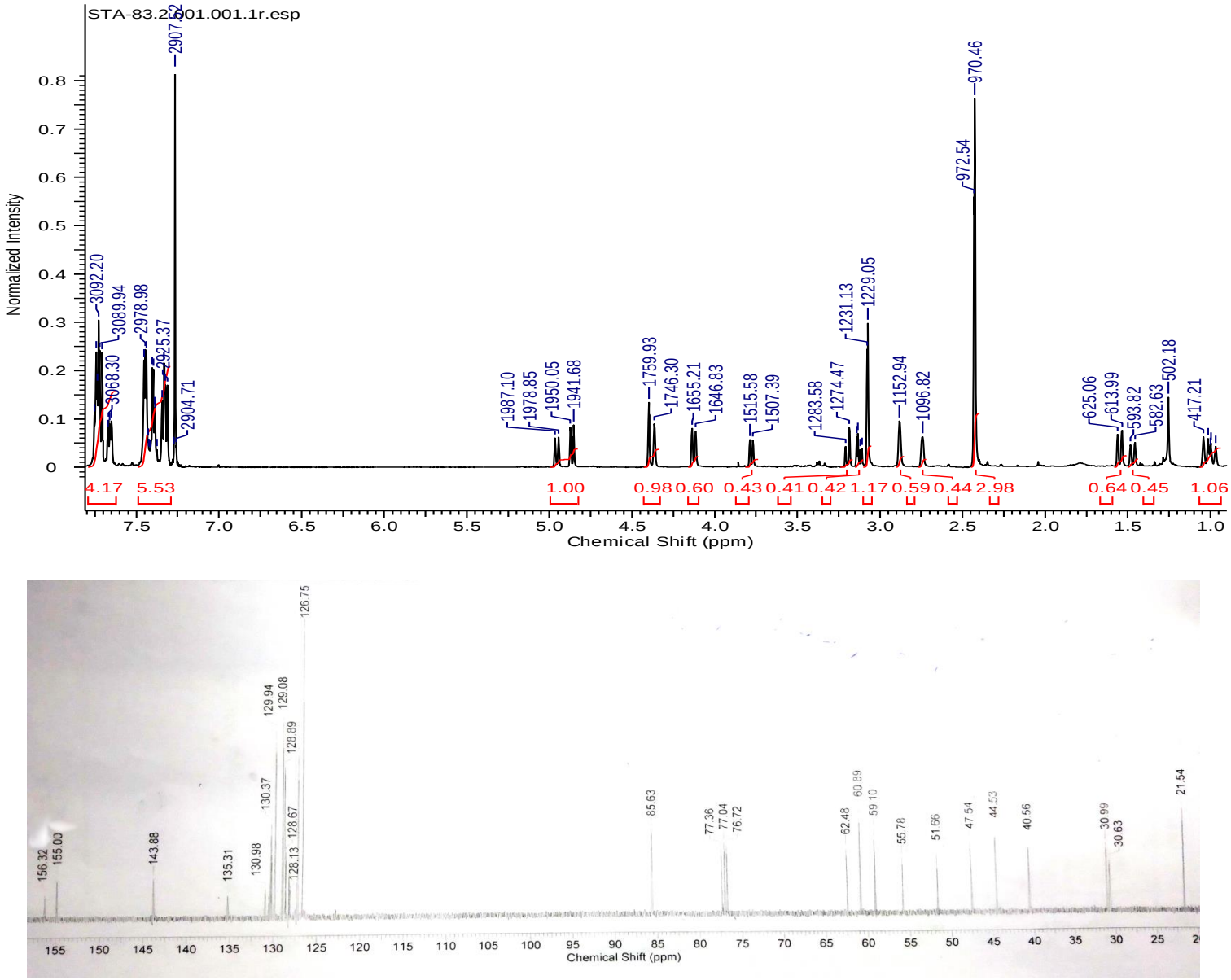


Figure S20. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3i** and **4i**

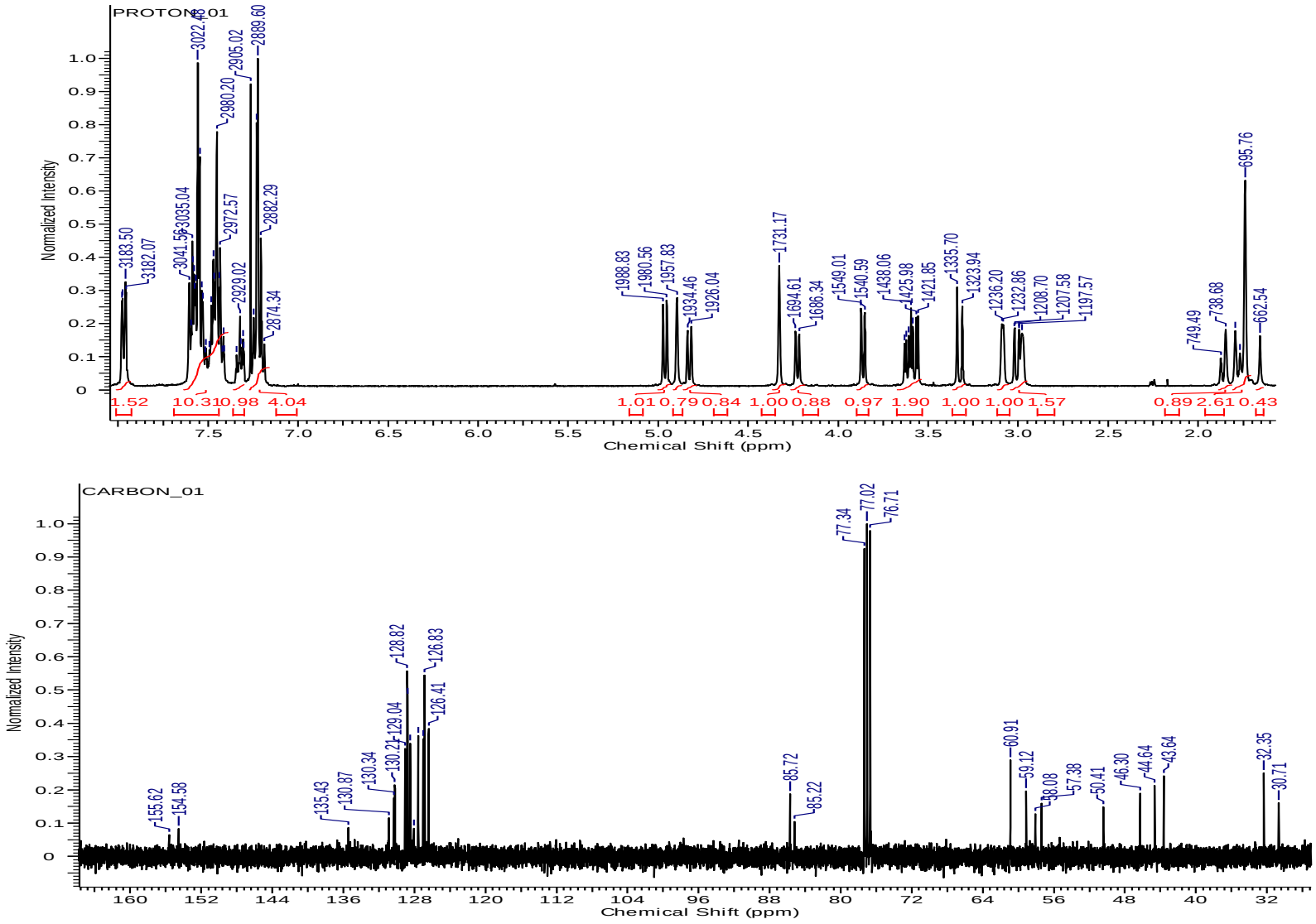


Figure S21. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4j**

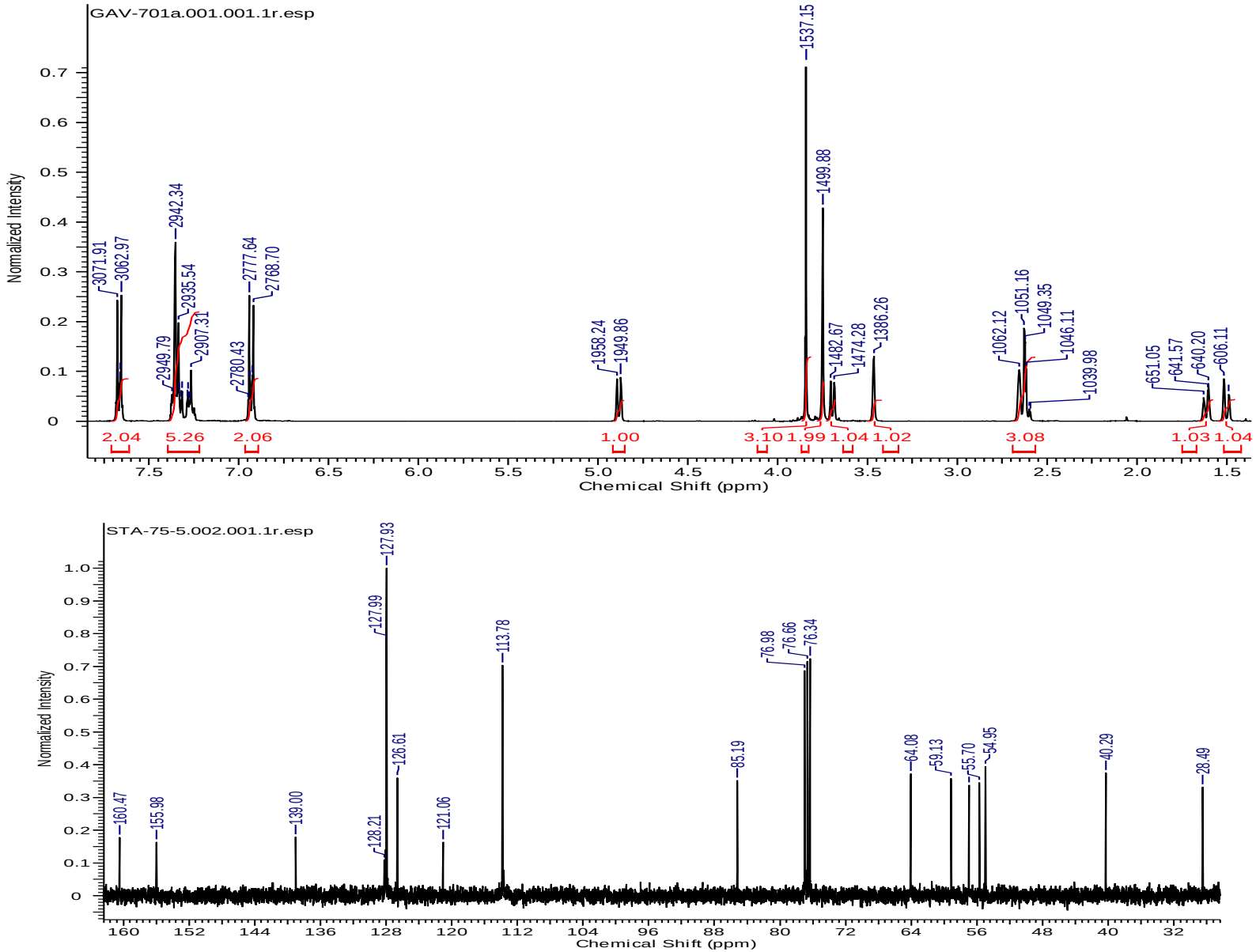


Figure S22. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3k**

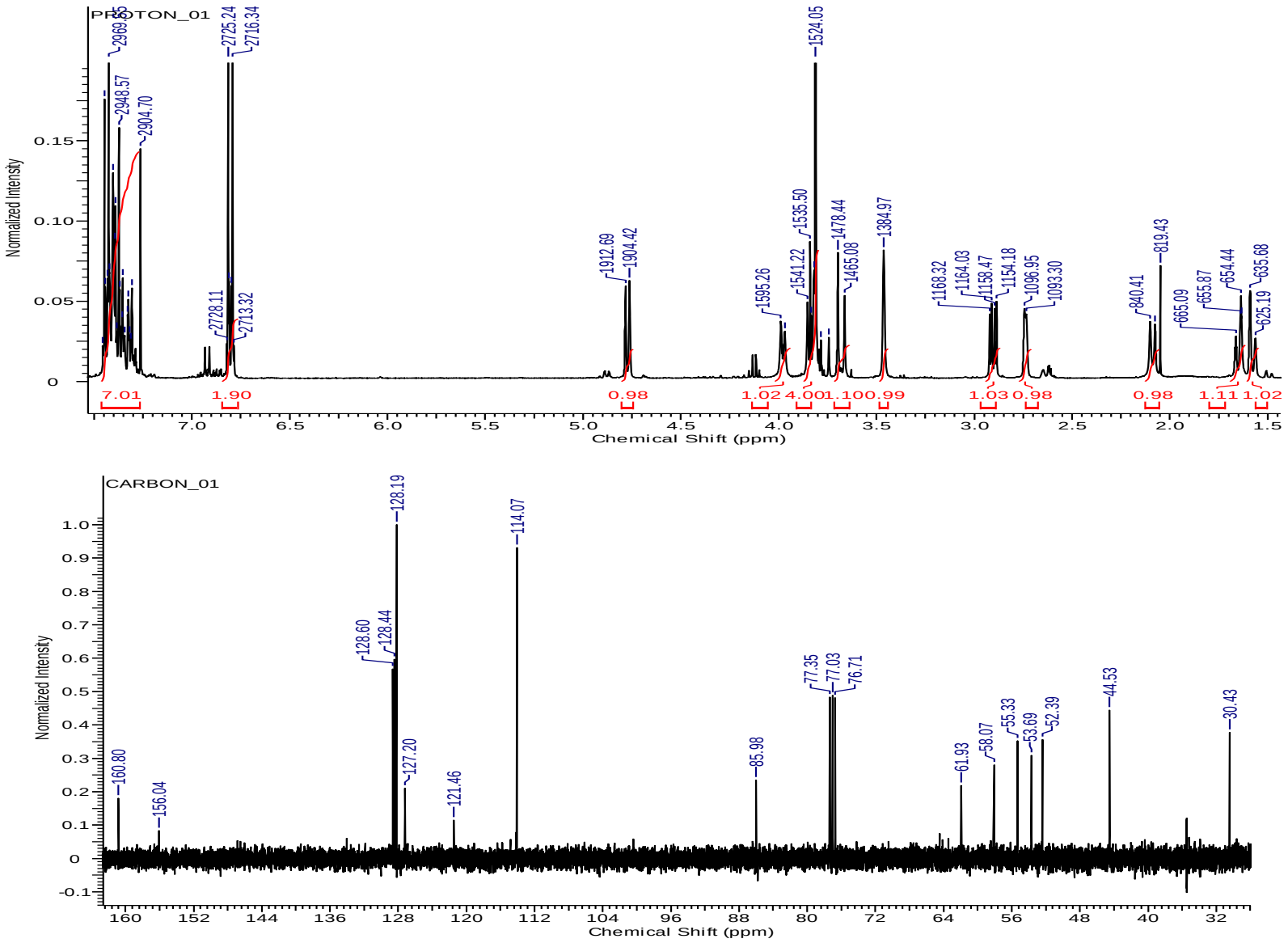


Figure S23. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4k**

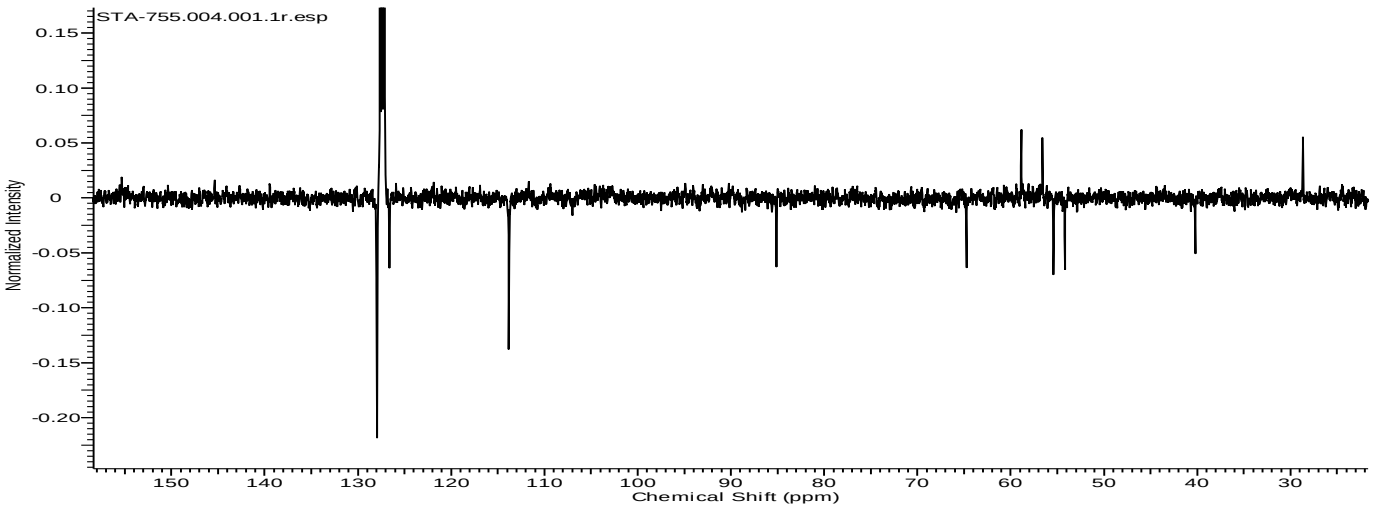


Figure S24. ^{13}C NMR spectrum (Apt) (C_6D_6) of **3k**

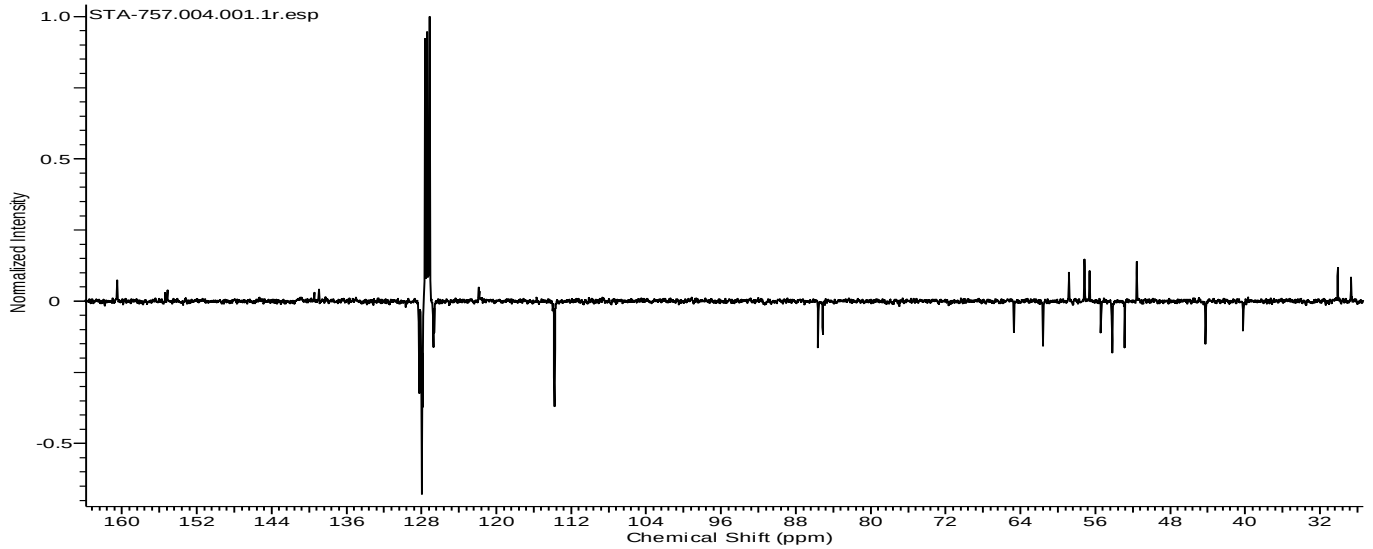


Figure S25. ^{13}C NMR spectrum (Apt) (C_6D_6) of **3k** and **4k**

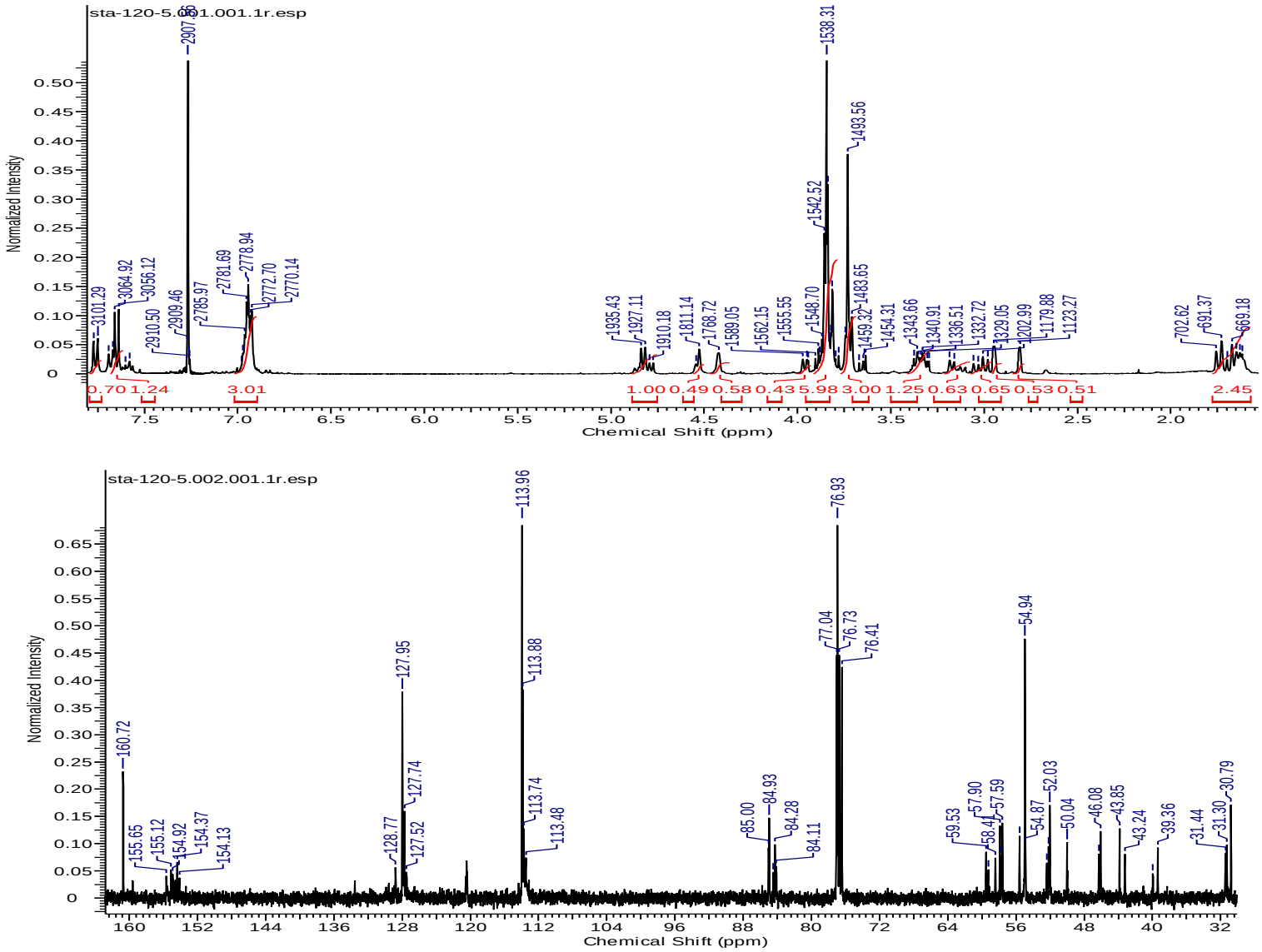


Figure S26. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3l** and **4l**

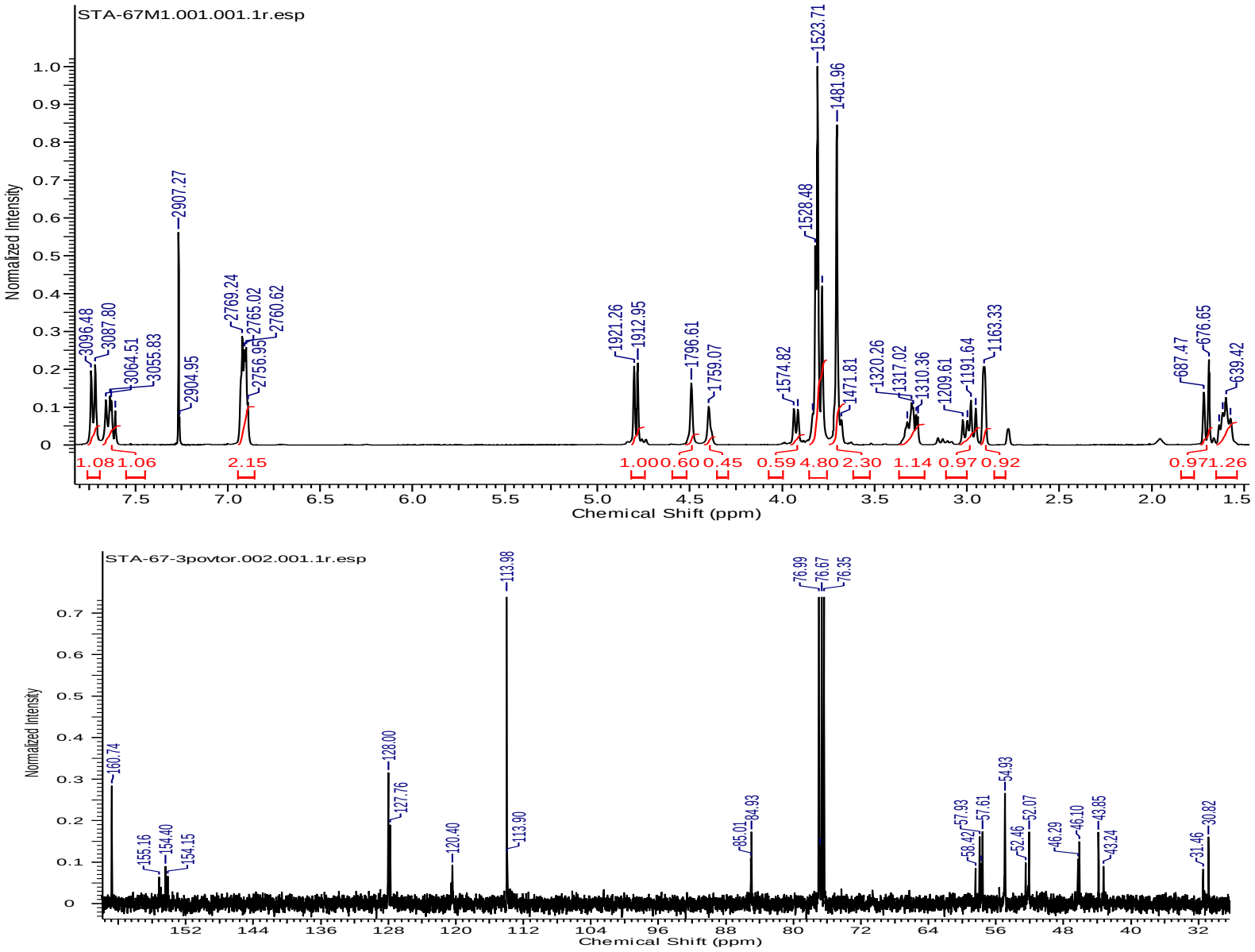


Figure S27. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4l**

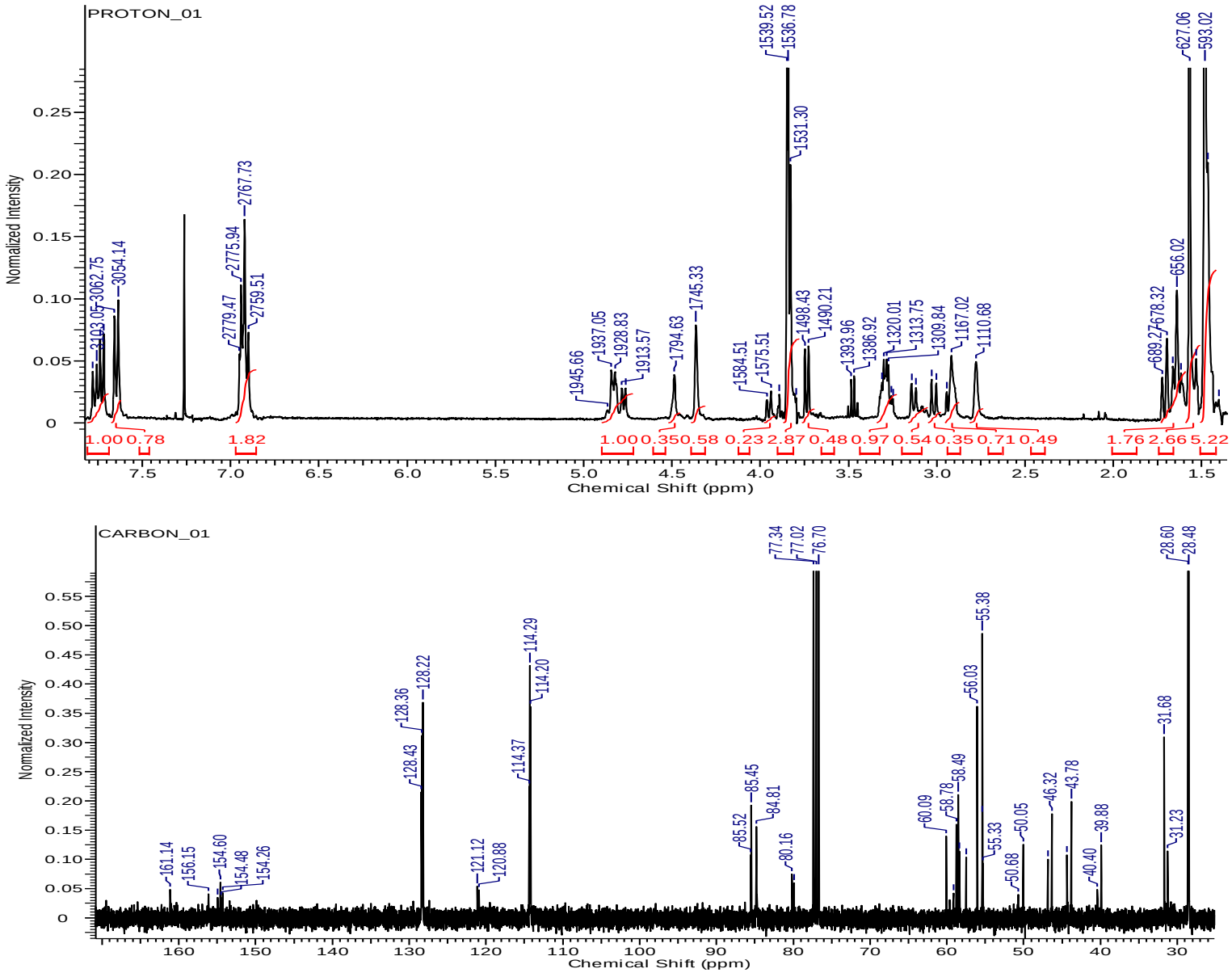


Figure S28. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3m** and **4m**

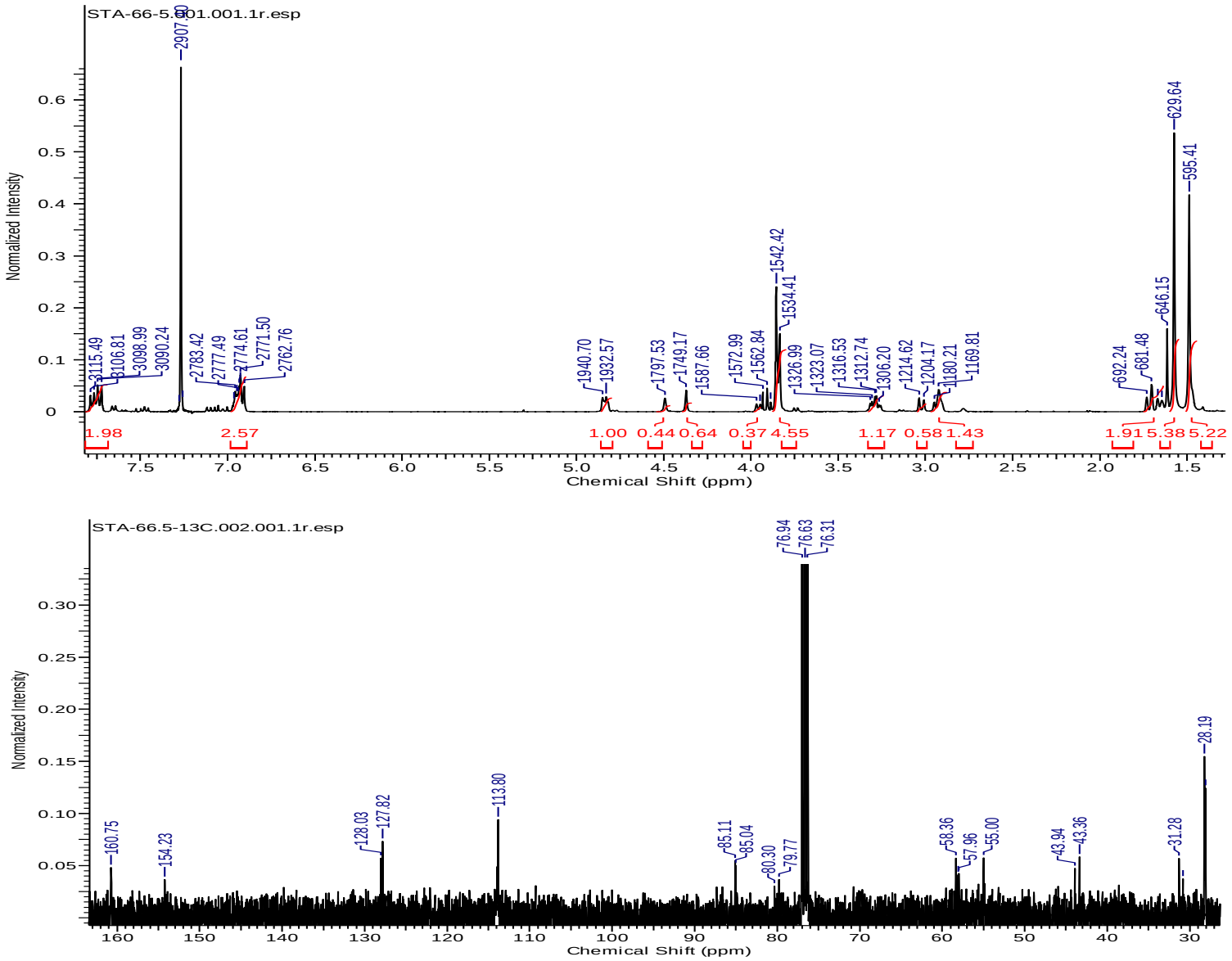


Figure S29. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4m**

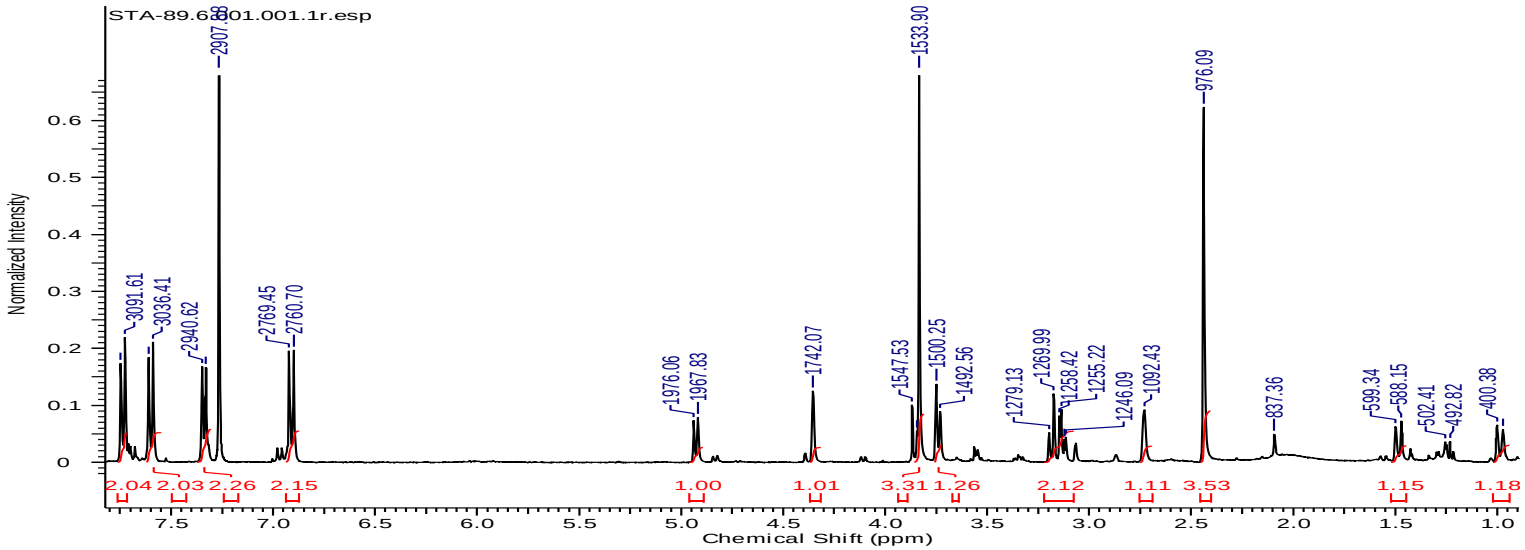


Figure S30. ^{1}H NMR spectrum ($CDCl_3$) of **3n**

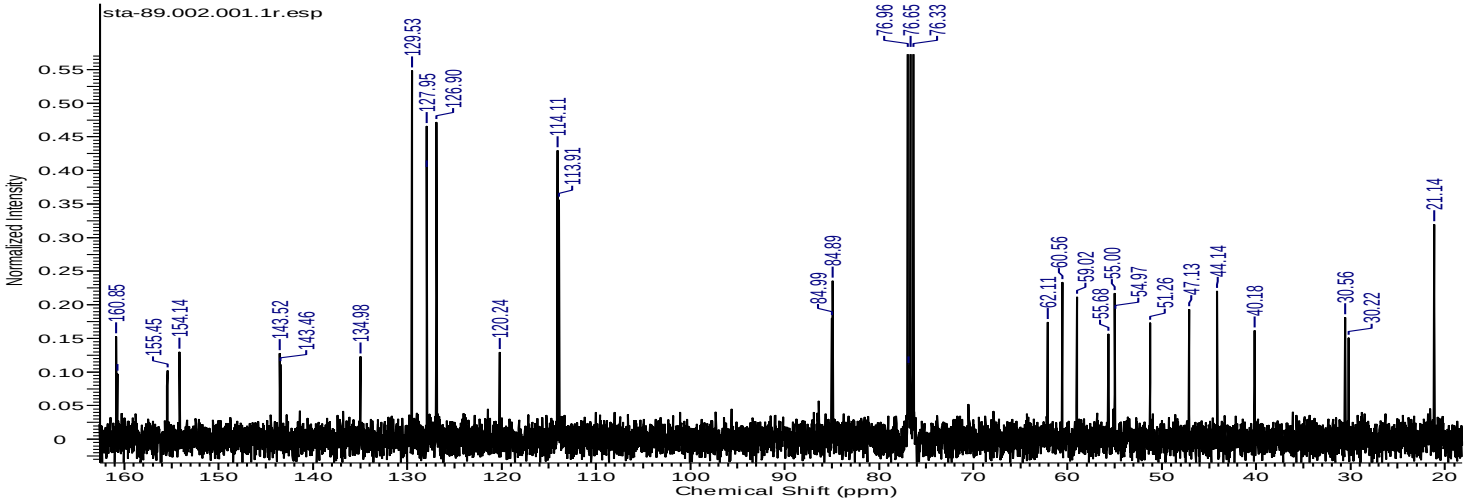


Figure S31. ^{13}C NMR spectrum ($CDCl_3$) of **3n** and **4n** (ratio 45:55)

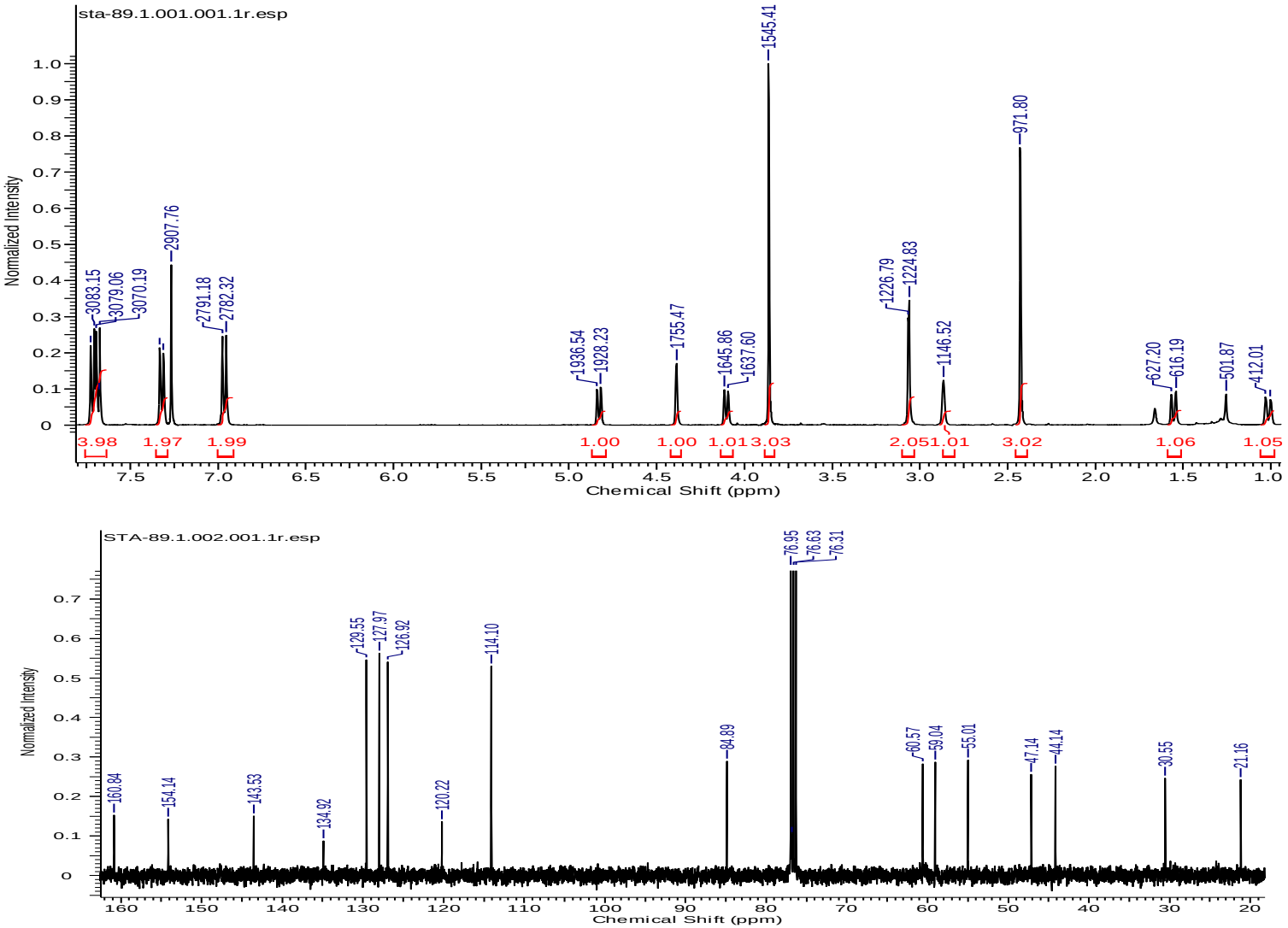


Figure S32. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4n**

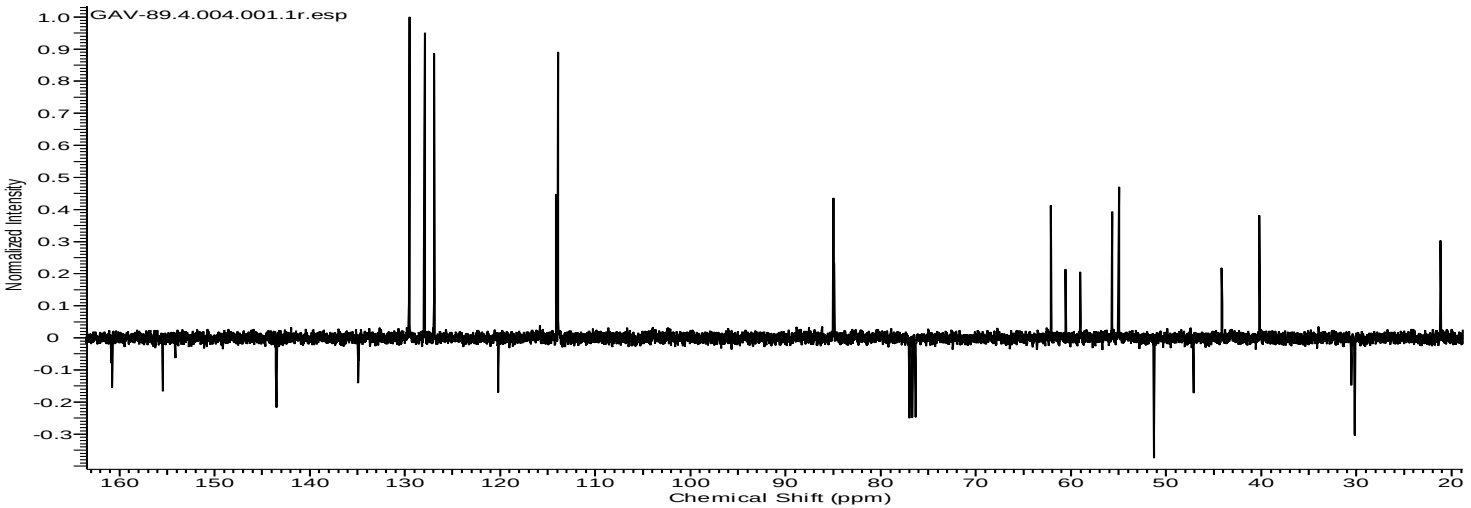


Figure S33. ^{13}C NMR spectrum (Apt) ($CDCl_3$) of **3n** and **4n** (ratio 68:32)

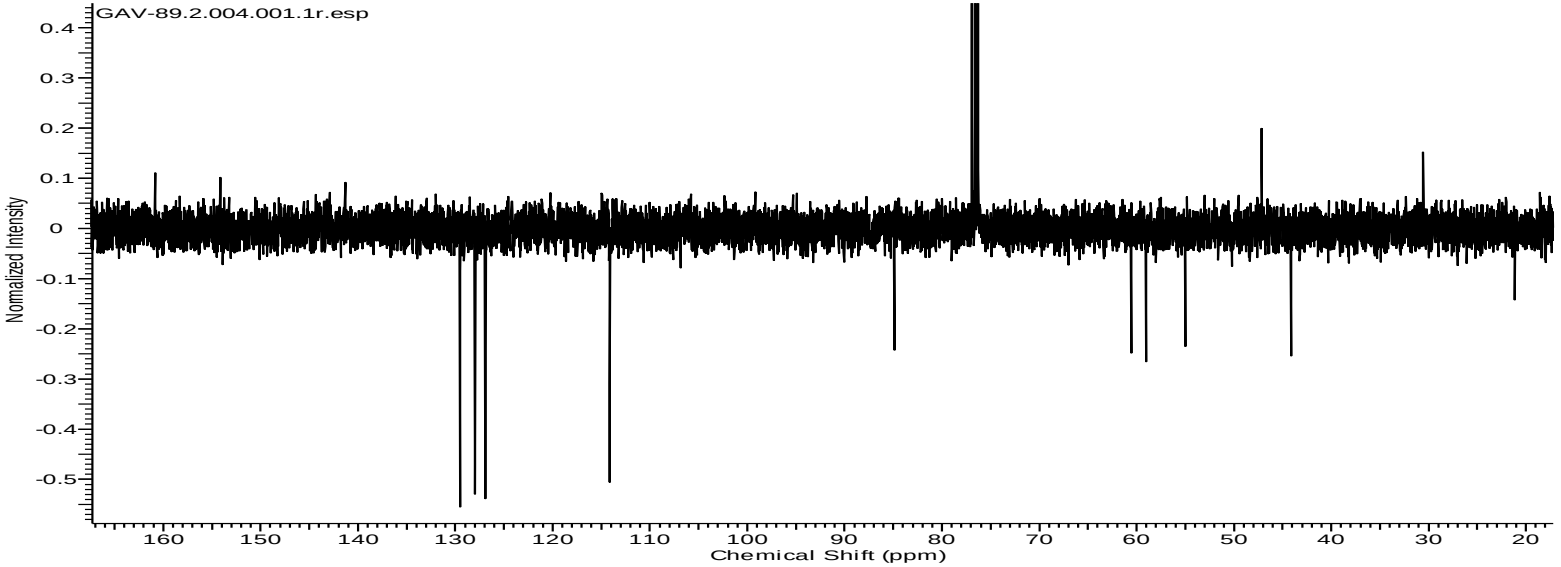


Figure S34. ^{13}C NMR spectrum (Apt) ($CDCl_3$) of **4n**

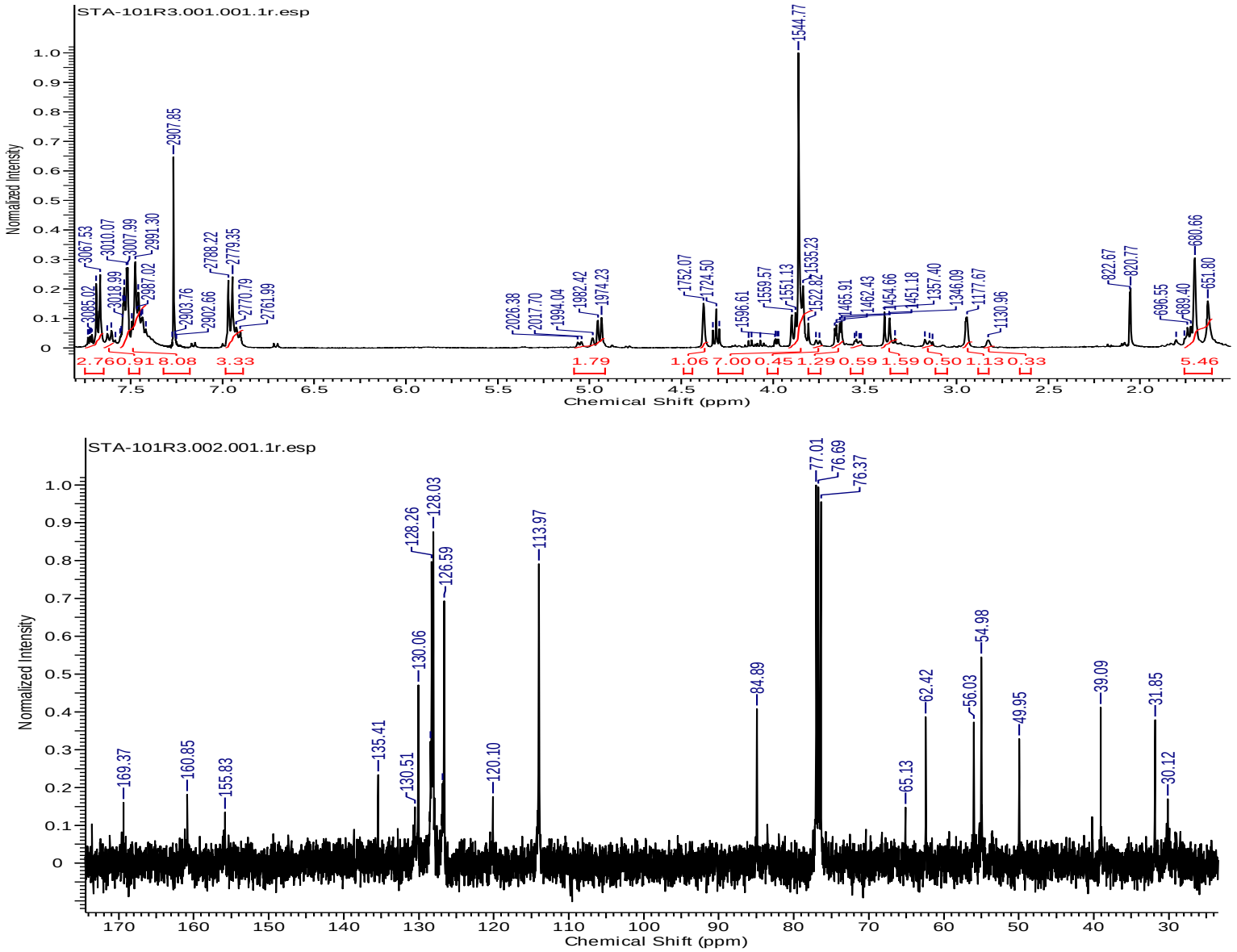


Figure S35. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3o**

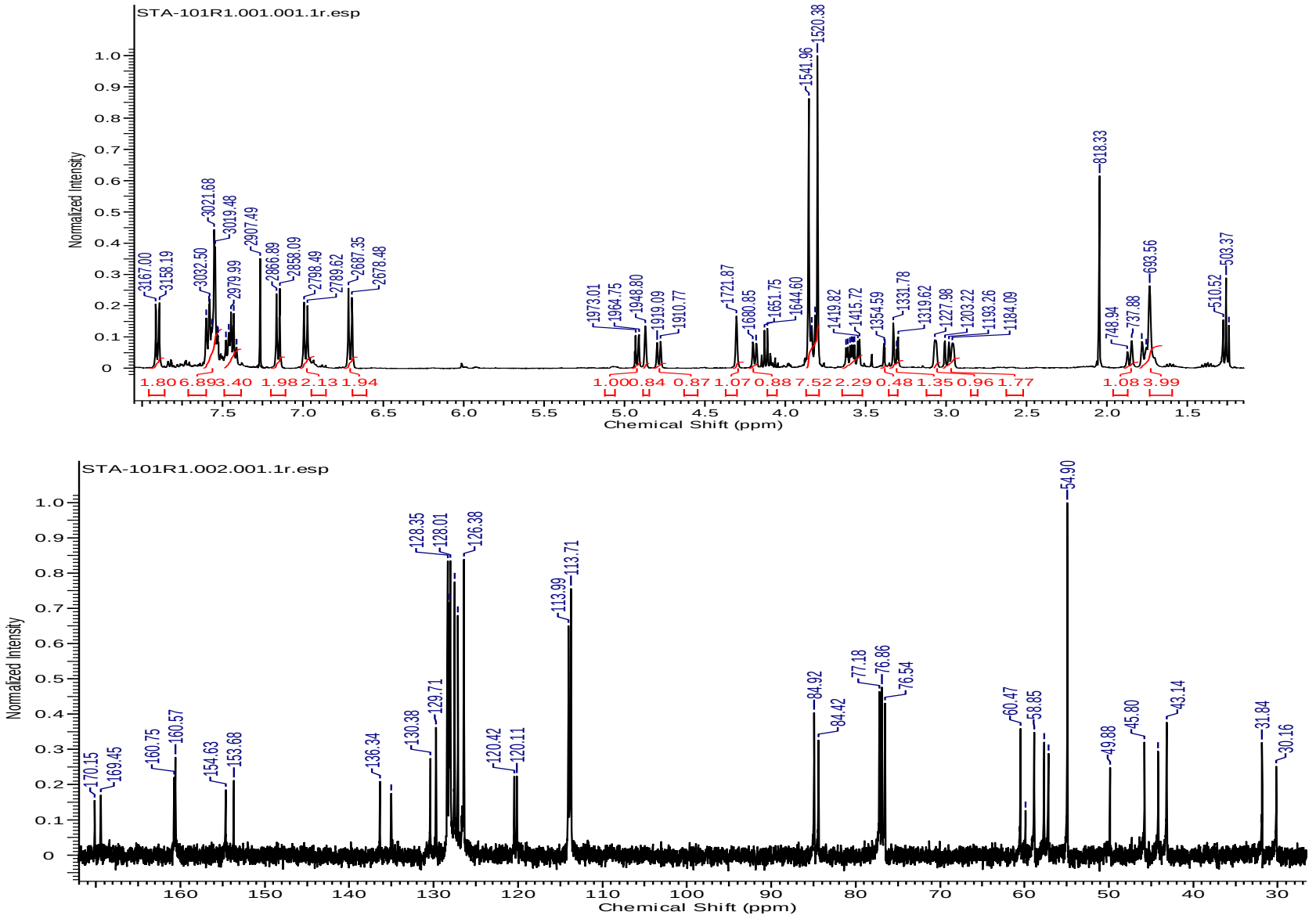


Figure S36. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4o**

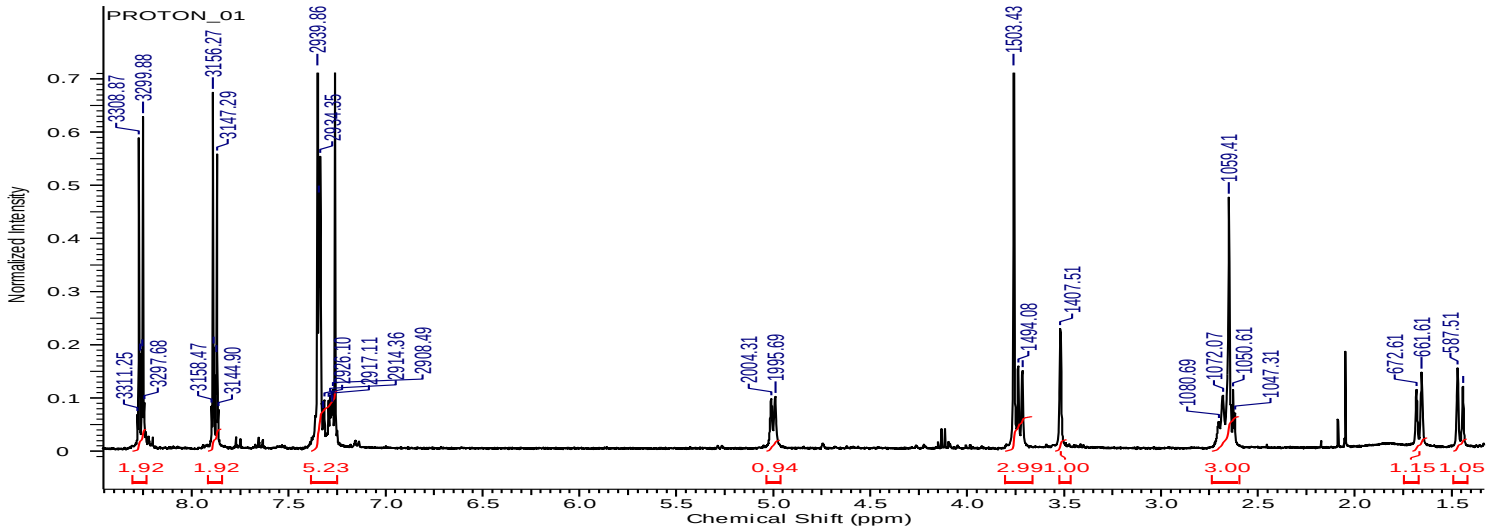


Figure S37. ^{1}H NMR spectrum ($CDCl_3$) of **3p**

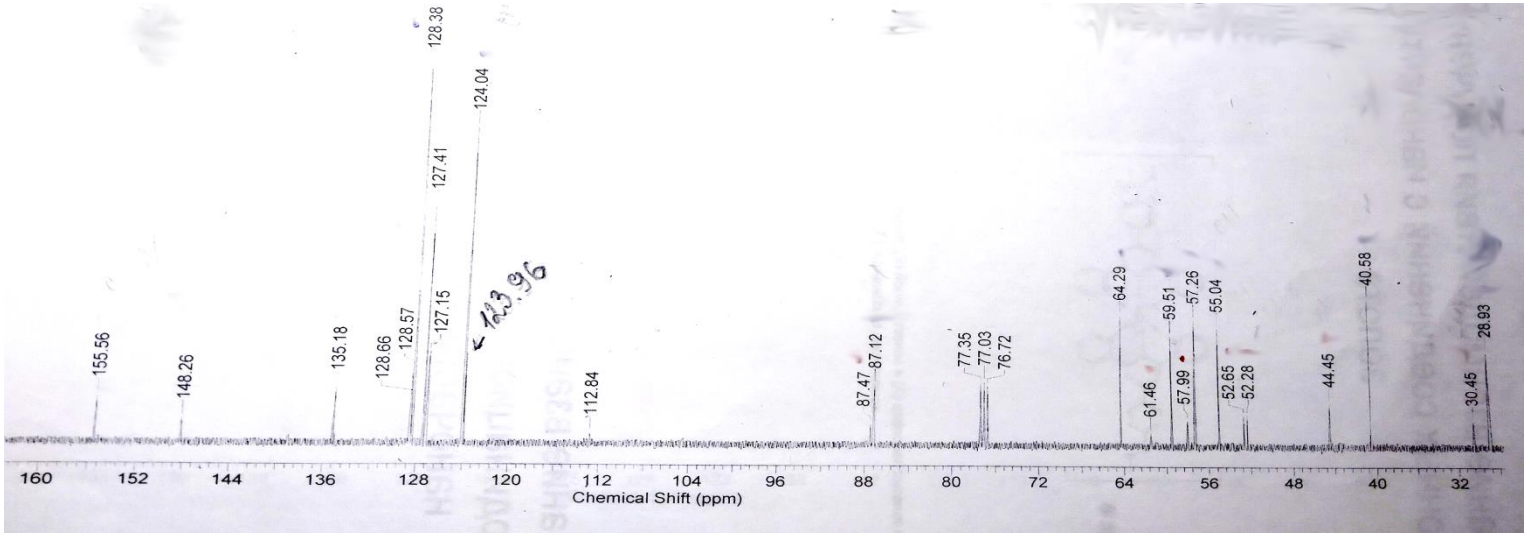


Figure S38. ^{13}C NMR spectrum ($CDCl_3$) of **3p** and **4p** (**3p**:**4p** = 3:1)

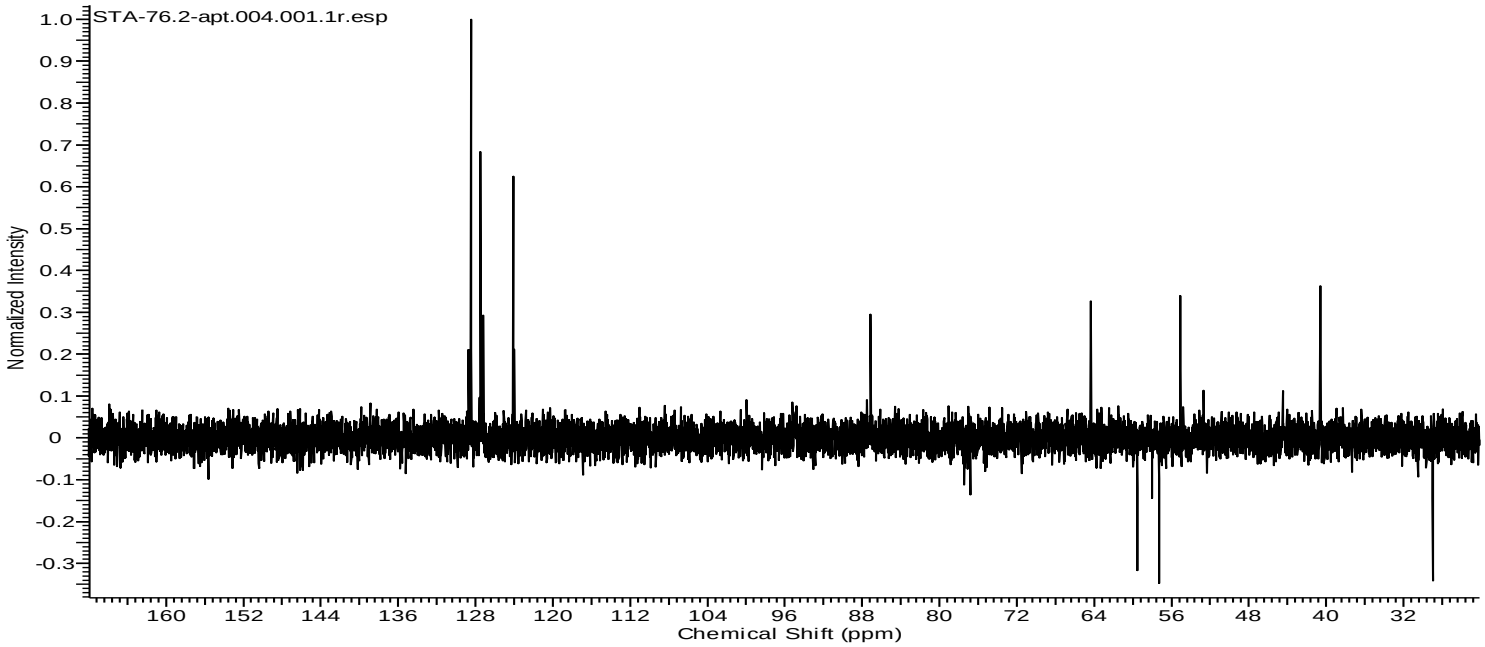


Figure S39. ^{13}C NMR spectrum (Apt) ($CDCl_3$) of **3p** and **4p** (**3p**:**4p** = 3:1)

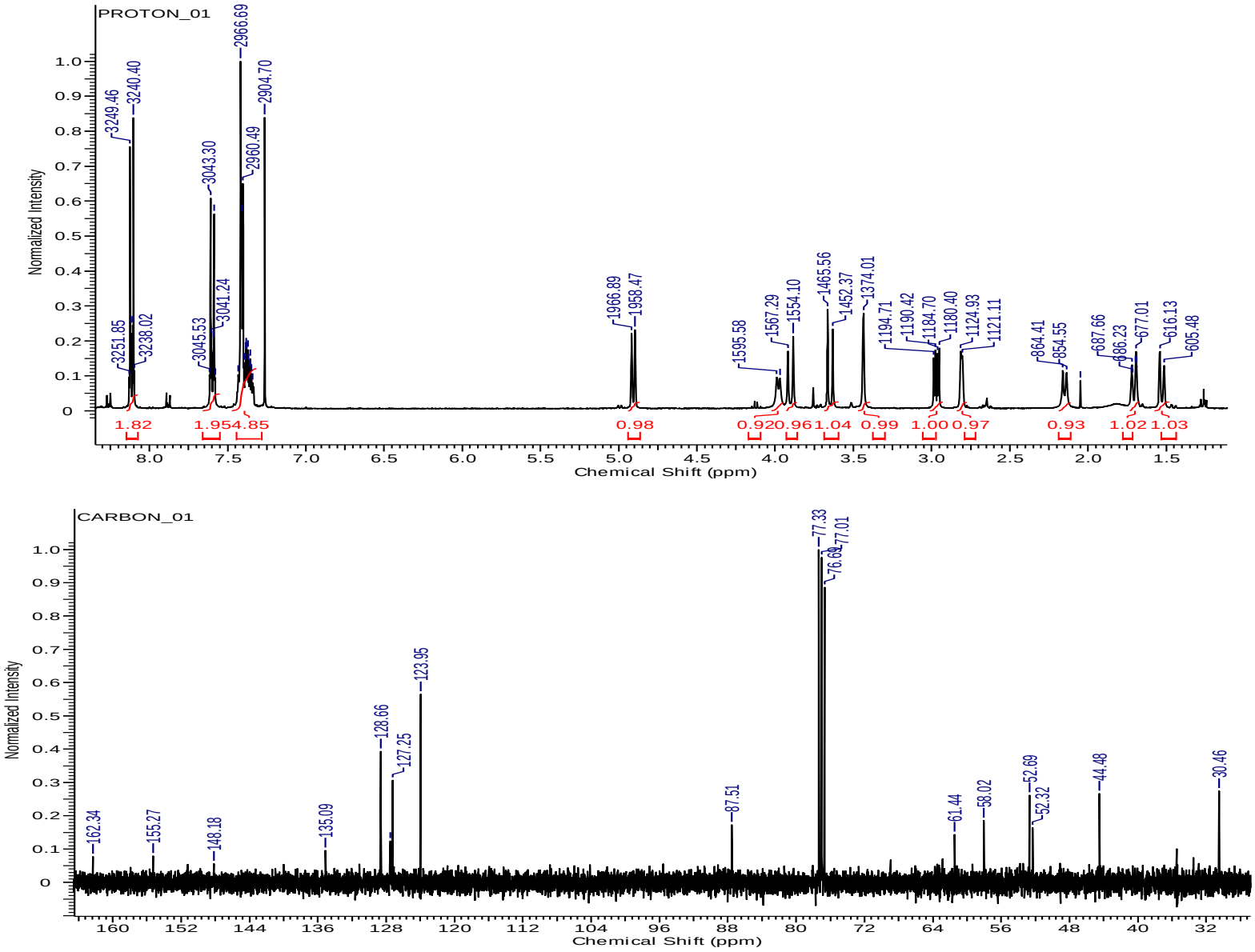


Figure S40. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4p**

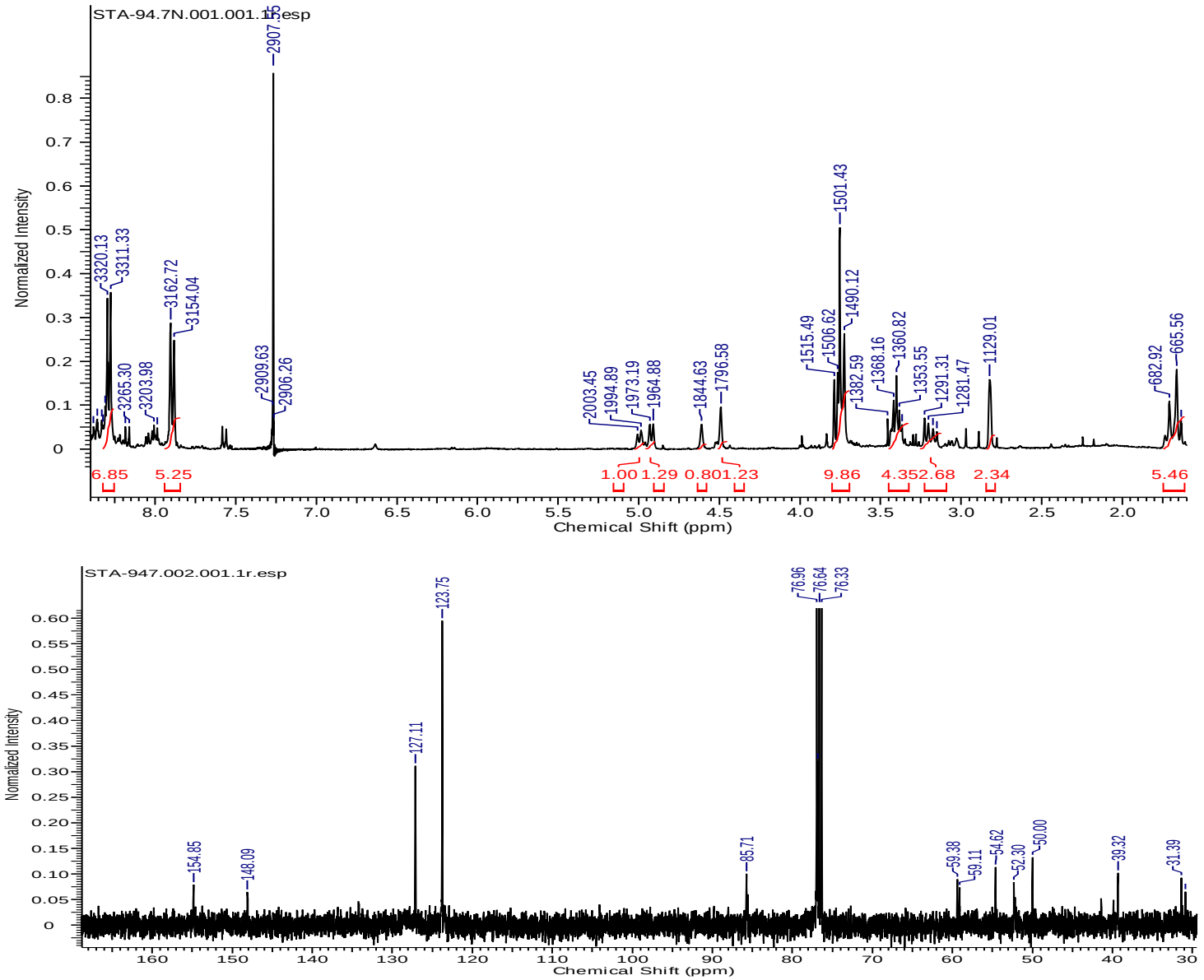


Figure S41. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3q**

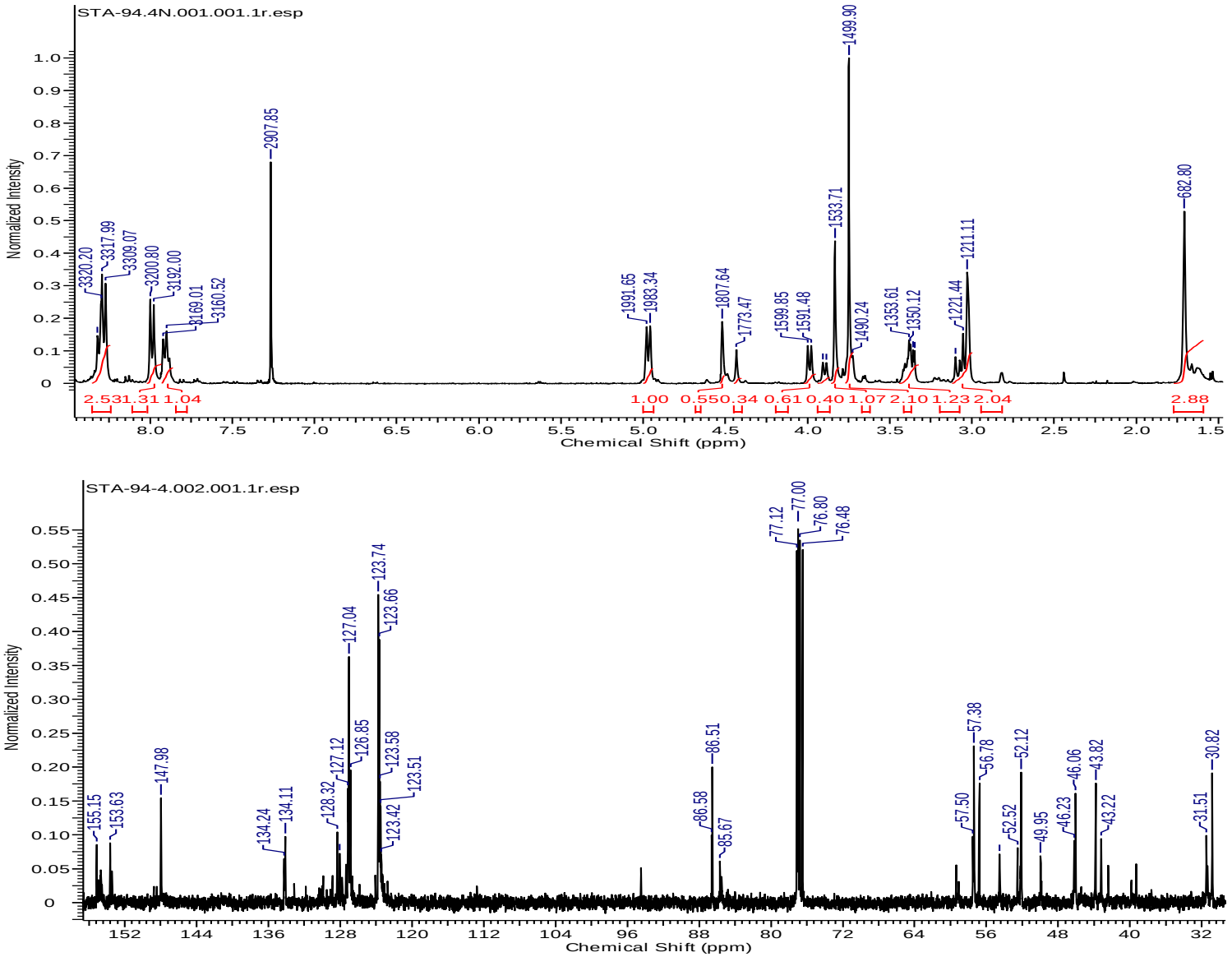


Figure S42. ^{1}H NMR spectrum ($CDCl_3$) of **4q** and ^{13}C NMR spectrum ($CDCl_3$) of **4q** (with admixture of **3q**)

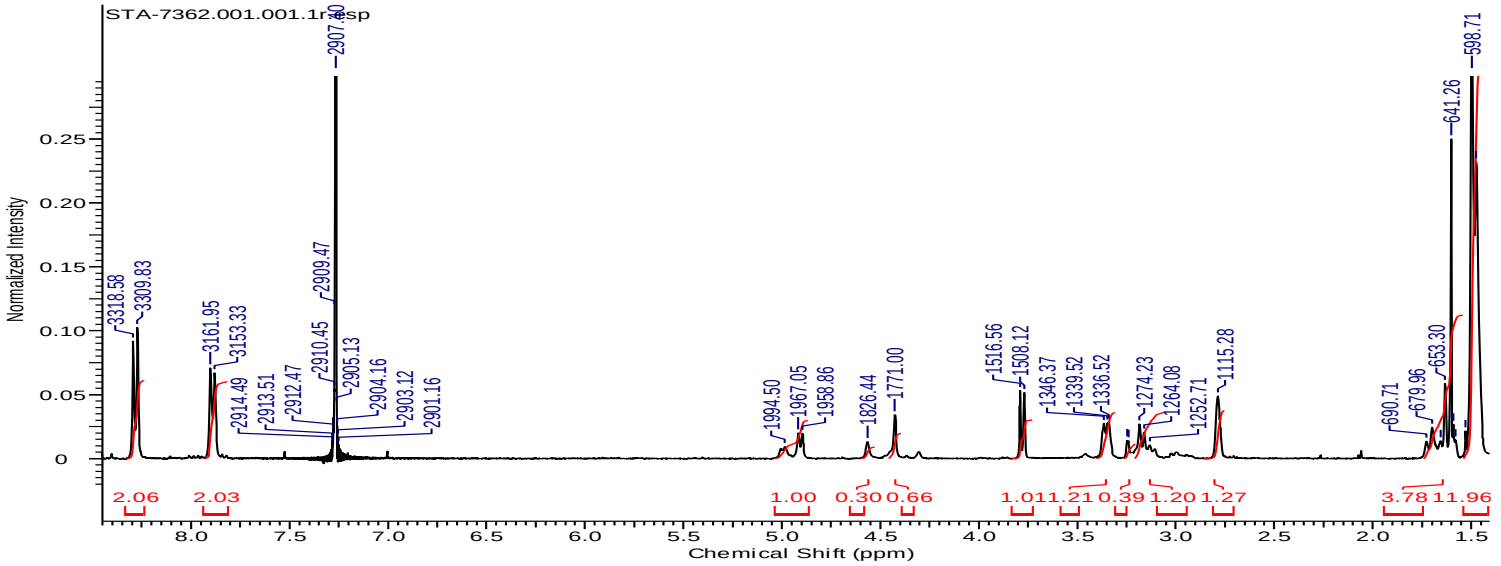


Figure S43. ^{1}H NMR spectrum ($CDCl_3$) of **3r**

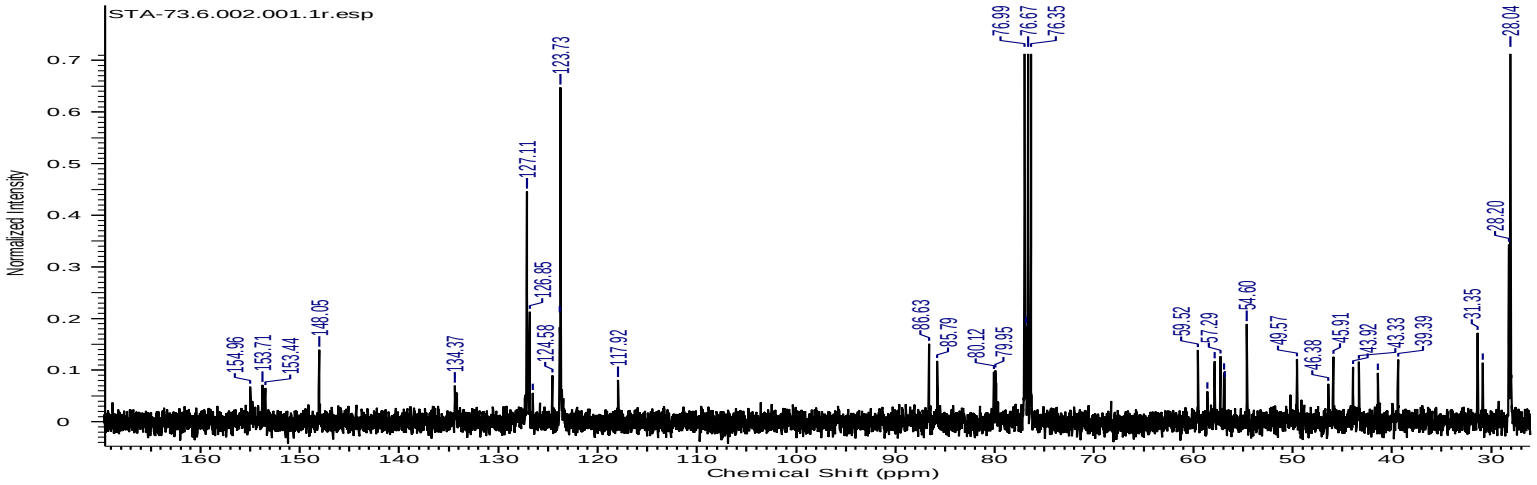


Figure S44. ^{13}C NMR spectrum ($CDCl_3$) of **3r** and **4r** (ratio 55:45)

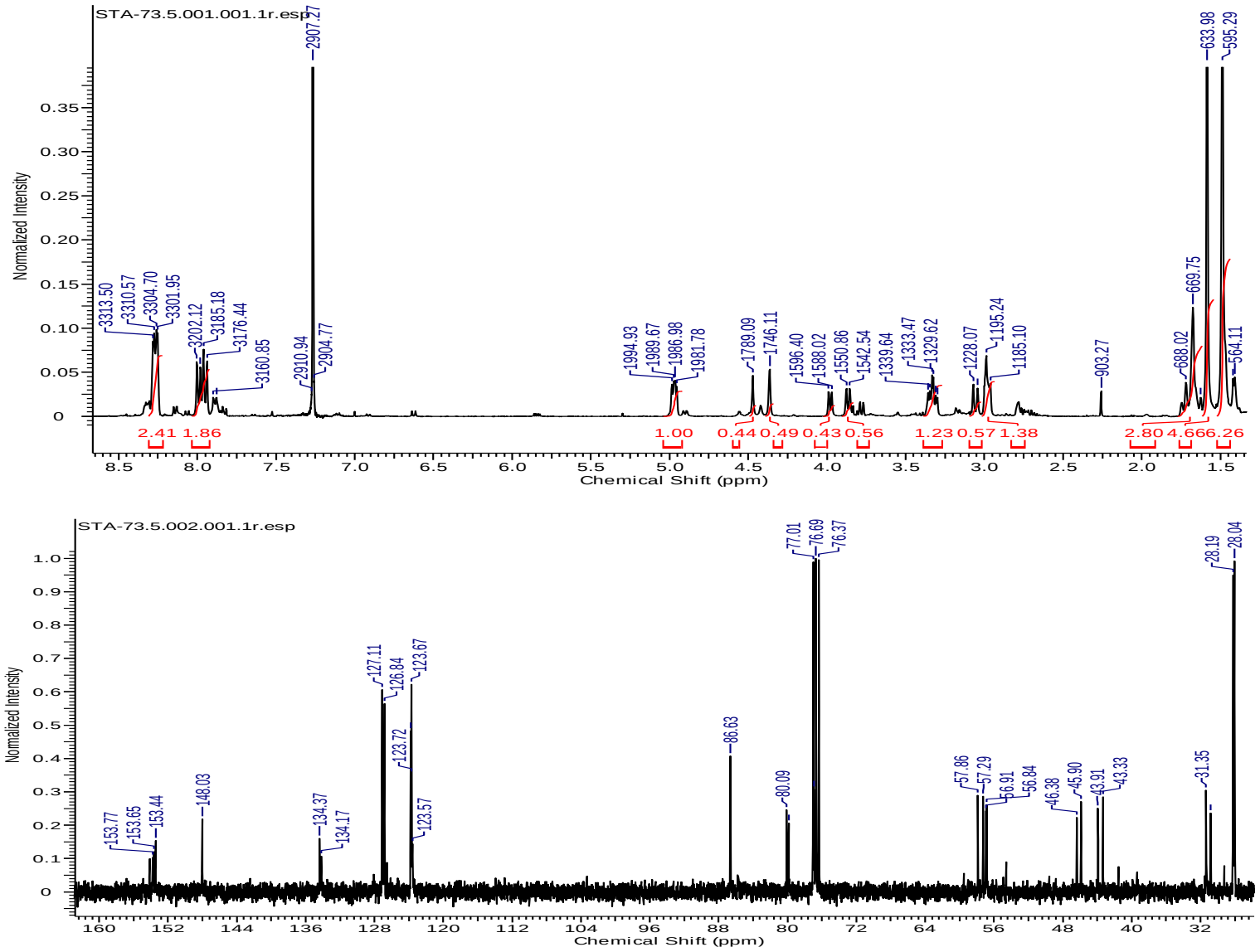


Figure S45. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4r**

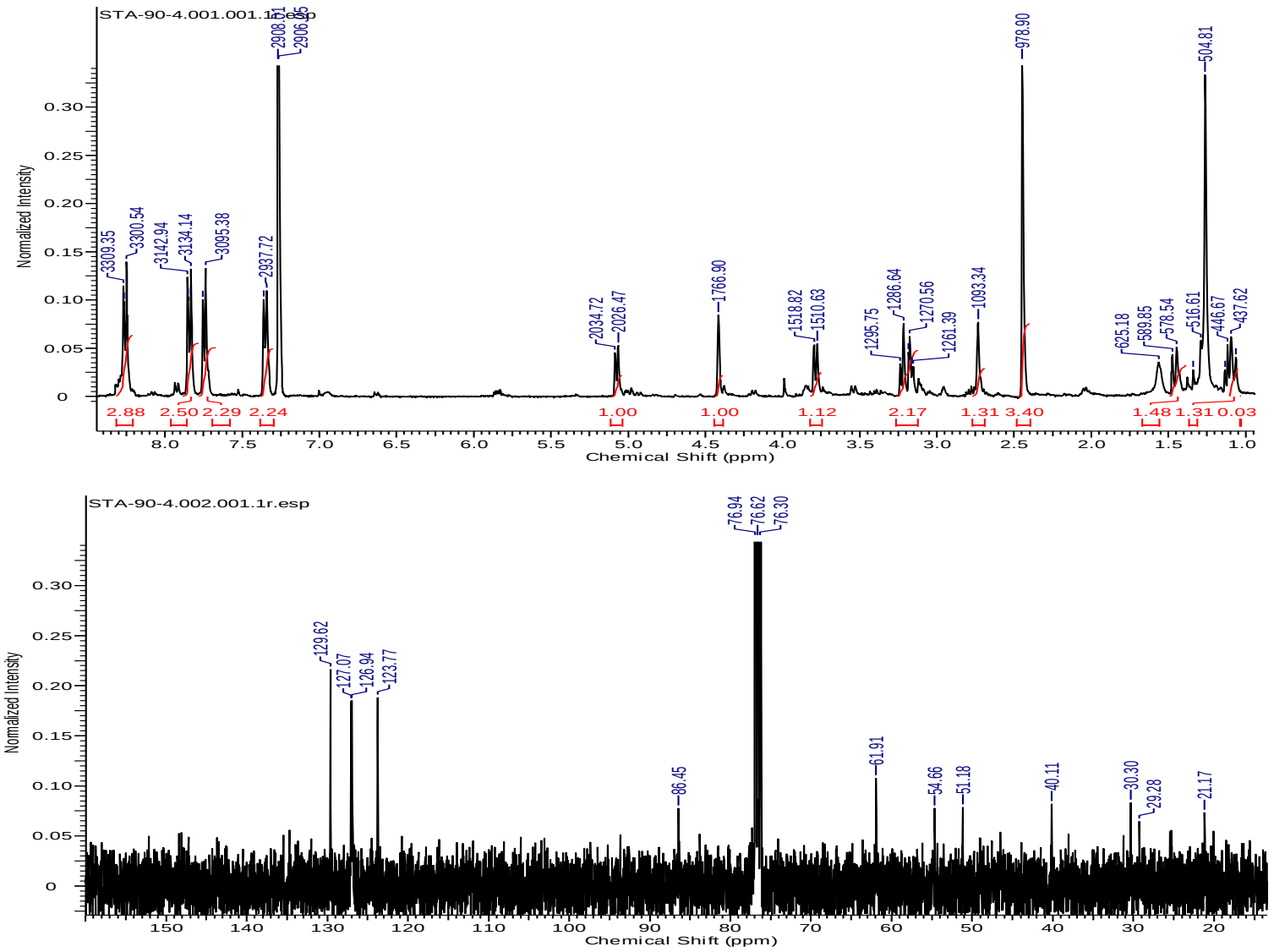


Figure S46. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3s**

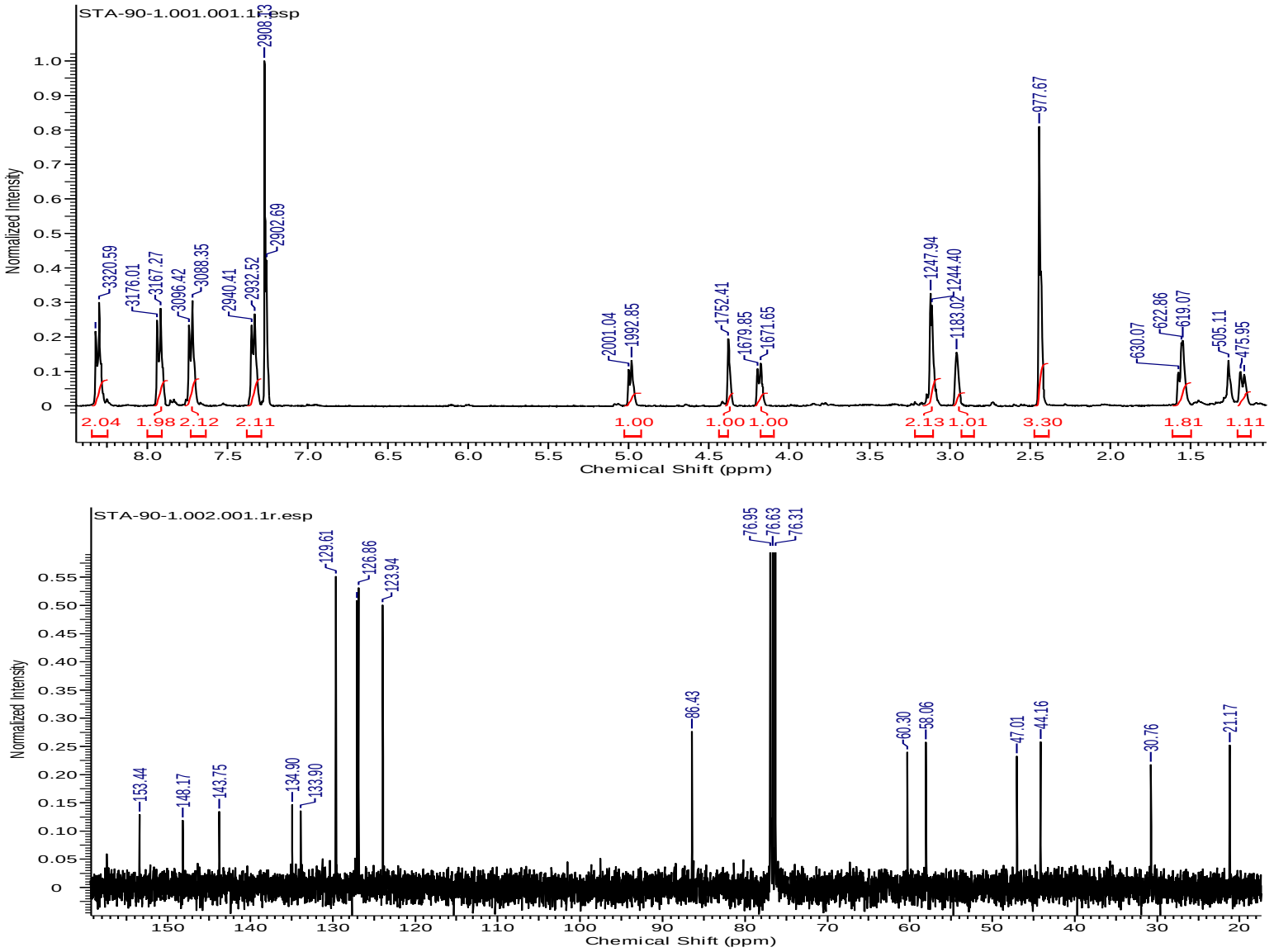


Figure S47. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4s**

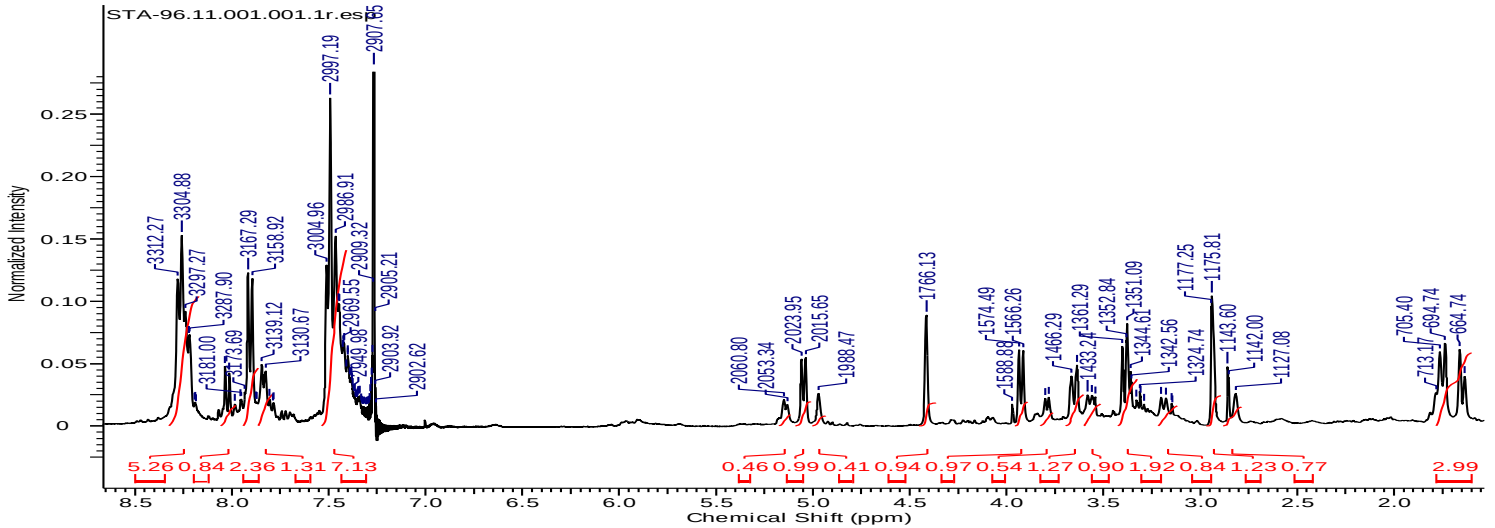


Figure S48. ^{1}H NMR spectrum ($CDCl_3$) of **3t**

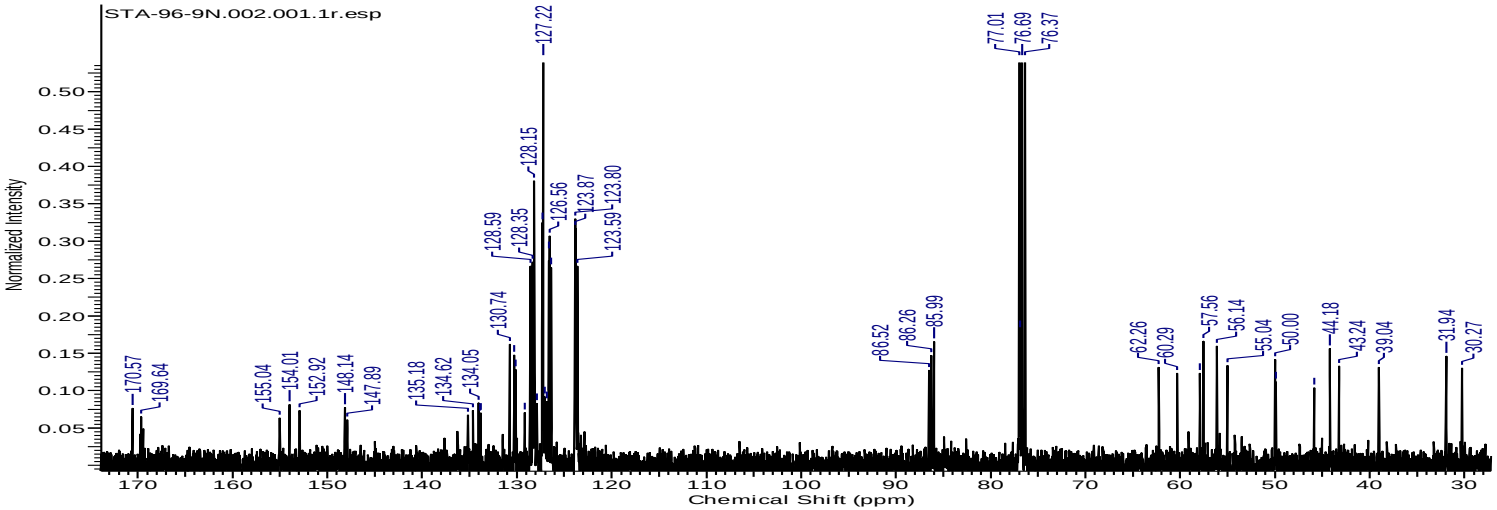


Figure S49. ^{13}C NMR spectrum ($CDCl_3$) of **3t** and **4t** (ratio 43:57)

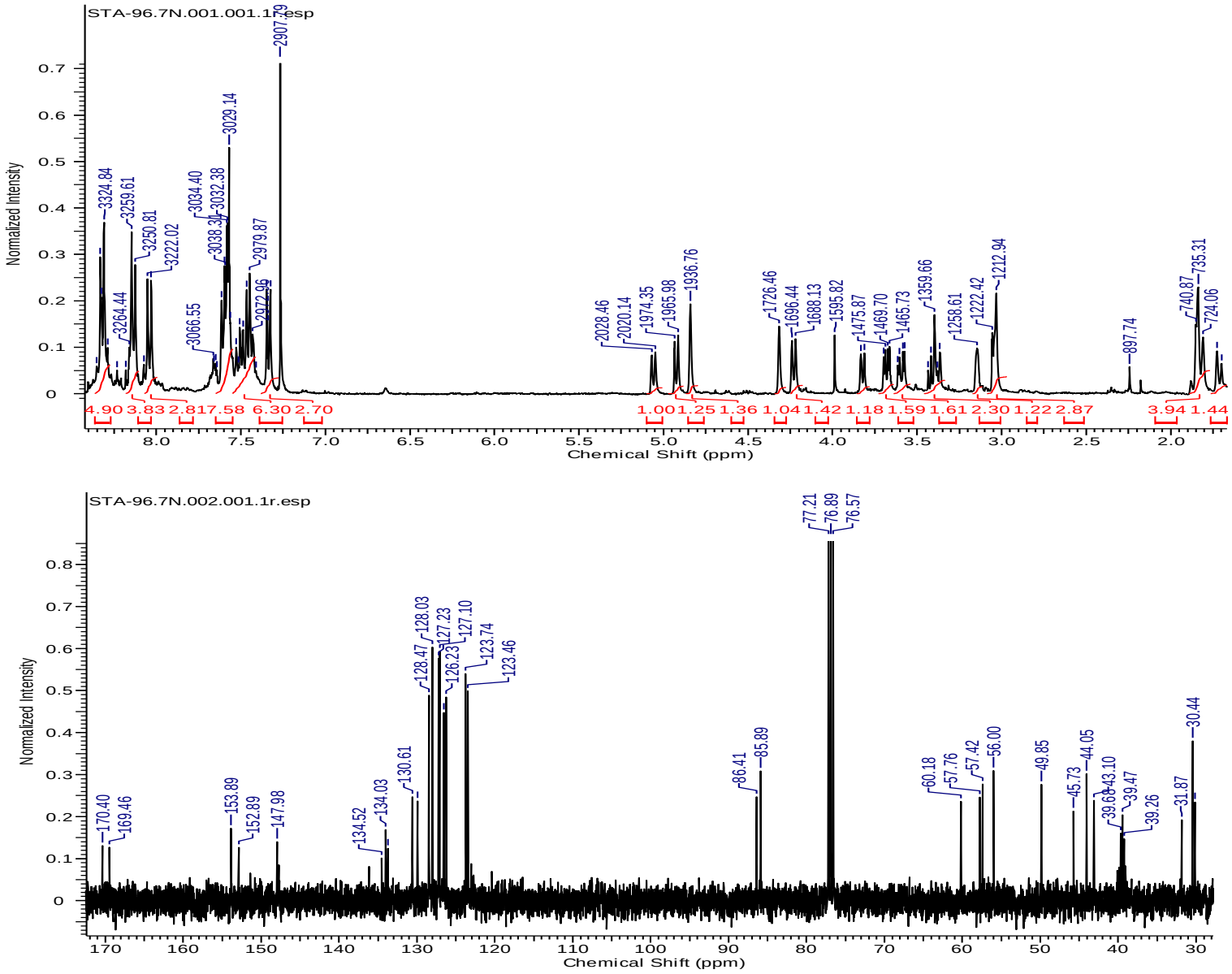


Figure S50. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4t**