Electronic supplementary materials *Mendeleev Commun.*, 2025, **35**, 467–469

Synthesis of frame pyrazolines based on azabicyclo[2.2.1]heptenes and nitrilimines

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

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).

Alkenes **1a-c**, **5** and **9a,b** were synthesized according to the previously described procedures: **1a** [S1], **1b** [S2], **1c** [S3 (typical procedure), S4 (characterization data)], **5** [S5 (typical procedure), S6 (characterization data)], **9b** [S7].

7*O*-*tert*-Butyl 2*O'*,3*O"*-diethyl 7-azabicyclo[2.2.1]hepta-2,5-diene-2,3,7-tricarboxylate (9a). A mixture of N-Boc pyrrole (2 g, 12 mmol) and diethyl acetylenedicarboxylate (2 g, 12 mmol) in 20 ml of toluene was boiled for three days, then the solvent was evaporated, and the remainder was chromatographed, 0.8 g (20%) of yellow oil was obtained. R_f 0.51 (ethyl acetate-petroleum ether 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.29 (t, 6H, *J*=7.1), 1.38 (s, 9H, $C(CH_3)_3$), 4.23 (q, 4H, CH_2, *J*= 7.1), 5.42 (br.s, 2H, HC^4 + HC^1), 7.11 (br.s, 2H, HC^5 + HC^6).

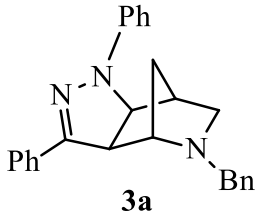
The hydrazonoyl chlorides and the corresponding hydrazides were synthesized according to the previously described procedures: hydrazides [S8], hydrazonoyl chlorides **2a** [S9, S10], **2b,2′a** [S11], **2c** [S12], **2d** [S10].

Reaction of azabicycloalkenes with nitrilimines generated *in situ* (general procedure).

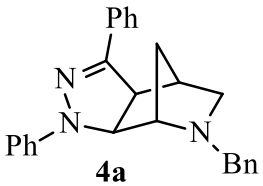
Triethylamine was added to a solution of 0.5 mmol of alkene in 10 ml of dichloromethane at room temperature. Then, slowly, while stirring, a solution of hydrazonoyl chloride in 10 ml of dichloromethane was added dropwise (ratio of alkene:triethylamine:hydrazonoyl chloride for alkenes **1a-c,5** was 1:2:2, for alkenes **9a,b** 1:1:1). The reaction mixture was stirred overnight, the solvent was evaporated, and the residue was chromatographed. The complete chromatographic separation of some 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.

The physicochemical characteristics of the compounds coincided with those published earlier: **7a,7′a** [S13, S14, S15], **7b** [S13, S14], **7c** [S16], **7d** [S13], **12a** [S16, S17, S18], **12c** [S16], **12′a** [S18].

Diethyl 3-(furan-2-yl)-1-phenylpyrazole-4,5-dicarboxylate (12b). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.23, 1.36 (both t, 3H, CH_3, *J* = 7.1), 4.29, 4.37 (both q, 2H, OCH_2, *J* = 7.1), 6.51 (dd, 1H, HC_{furyl}, J_1 = 3.5, J_2 = 1.8), 7.26 (dd, 1H, HC_{furyl}, J_1 = 3.5, J_2 = 0.8), 7.44 – 7.55 (m, 6H, HC_{furyl}, HC_{arom}).

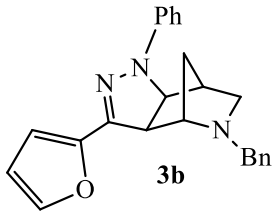


3a

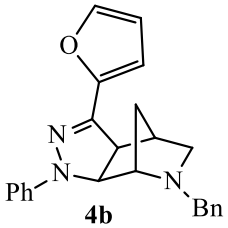


4a

8-Benzyl-3,5-diphenyl-3,4,8-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3a) and **9-benzyl-5-(furan-2-yl)-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4a)**. Oil, R_f 0.51 (MeOH – CH_2Cl_2, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3a**: 1.55 (d, 1H, HC^{10}, *J*=10.4), 1.68 (d, 1H, HC^{10}, *J*=10.4), 2.33 (d, 1H, *endo*-HC^9, *J*=9.5), 2.95 (bs, 1H, HC^1), 3.01 (dd, 1H, *exo*-HC^9, *J*=9.5, 4.0), 3.61 (s, 1H, HC^7), 4.08 (d, 1H, HC^6, *J*=9.5), 4.29 (d, 1H, HC^2, *J*=9.5), 6.90 (t, 1H, HC_{arom}, *J*=7.3); isomer **4a**: 1.48 (d, 1H, HC^{10}, *J*=10.6), 1.62 (d, 1H, HC^{10}, *J*=10.6), 2.73 (d, 1H, *endo*-HC^8, *J*=8.9), 2.78 – 2.87 (m, 2H, HC^7, *exo*-HC^8), 3.66 (s, 1H, HC^1), 4.51 (d, 1H, HC^2, *J*=9.5), 6.83 (t, 1H, HC_{arom}, *J*=7.2), 7.04 (d, 2H, HC_{arom}, *J*=8.3), 7.83 (d, 2H, HC_{arom}, *J*=8.3); isomers **3a**+**4a**: 3.76-3.95 (m, HC^6, CH_2(Bn) **3a**+**4a**), 7.20-7.63 (m, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm) isomer **3a** + isomer **4a**: 29.56, 30.80 (C^{10}), 41.32, 42.63, 51.02, 53.41, 53.62, 57.57, 57.70, 58.88, 62.29, 62.53, 66.21, 66.67 (C^1, C^2, C^6, C^7, C^9, $\underline{C}H_2$(Bn)), 111.91, 112.07, 118.31, 118.45, 125.31, 125.43, 126.80, 126.88, 127.86, 127.91, 128.07, 128.12, 128.14, 128.19, 128.23, 128.37, 128.76, 128.85, 131.85, 131.97, 138.59, 139.08, 143.87, 144.00, 147.87, 148.46 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{26}H_{26}N_3$ 380.2121 [M+1], found 380.2125.



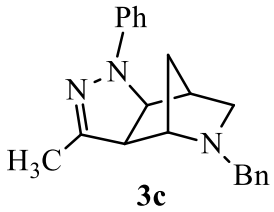
3b



4b

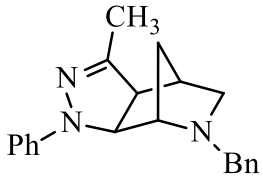
8-Benzyl-5-(furan-2-yl)-3-phenyl-3,4,8-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3b) and **9-benzyl-5-(furan-2-yl)-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4b)** (a mixture). Oil, R_f 0.6 (EtOAc-petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): isomer **3b**: 1.54 (dm, 1H, HC^{10}, *J*=10.6), 1.68 (d, 1H, HC^{10}, *J*=10.6), 2.92 (bs, 1H, HC^1), 2.32 (d, 1H, *endo*-HC^9, *J*=9.6), 2.97 (dd, 1H, *exo*-HC^9, *J*=9.6, 4.1), 3.59 (s, 1H, HC^7), 4.01 (d, 1H, HC^6, *J*=9.5), 4.27 (d, 1H, HC^2, *J*=9.5), 6.31 (d, 1H, HC_{furyl}, *J*=3.3), 6.41 (dd, 1H, HC_{furyl}, *J*=3.3, 1.8), 6.85 (t, 1H, HC_{arom}, *J*=7.2); isomer **4b**: 1.46 (d, 1H, HC^{10}, *J*=10.7), 1.62 (d, 1H, HC^{10}, *J*=10.7), 2.82 (bs, 1H, HC^7), 2.69 (d, 1H, *endo*-HC^8, *J*=9.1), 2.77 (dd, 1H, *exo*-HC^8, *J*=9.1, 3.4), 3.62 (s, 1H, HC^1), 3.69 (d, 1H, HC^6, *J*=9.7), 3.75 (d, 1H, CH_2(Bn), *J*=13.3), 4.45 (d, 1H, HC^2, *J*=9.6), 6.49 (dd, 1H, HC_{furyl}, *J*=3.3, 1.7), 6.63 (d, 1H, HC_{furyl}, *J*=3.4), 6.78 (t, 1H, HC_{arom}, *J*=7.3), 7.50 (d, 1H, HC_{furyl}, *J*=1.7); isomer **3b** + isomer **4b**: 3.78 - 3.88 (m, 2H isomer **3b**, 1H isomer **4b** CH_2(Bn)), 7.25-7.35 (m, HC_{arom}), 7.35-7.47 (m, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm) isomer **3b** + isomer **4b**: 29.43, 30.66 (C^{10}), 41.57, 42.48, 51.54, 53.58, 53.73, 57.38, 57.70, 58.88, 62.37, 62.69, 65.69, 66.11 (C^1, C^2, C^6, C^7, C^9, $\underline{C}H_2$(Bn)), 111.94, 112.10, 118.41, 118.58, 126.82, 126.89, 128.03, 128.06, 128.16, 128.31,

128.65, 128.74, 142. 70, 142.76, 143.50, 143.64, 147.58, 147.85 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{24}H_{24}N_3O$ 370.1914 [M+1], found 370.1917.



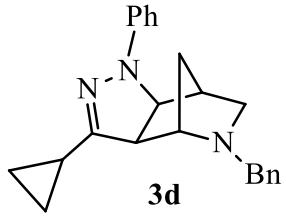
3c

8-Benzyl-5-methyl-3-phenyl-3,4,8-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3c). Oil, R_f 0.40 (EtOAc-petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.47 (d, 1H, HC^{10}, *J*=10.4), 1.68 (d, 1H, HC^{10}, *J*=10.4), 1.96 (d, 3H, CH_3), 2.26 (d, 1H, *endo*-HC^9, *J*=9.4), 2.81 (bs, 1H, HC^1), 2.84 (dd, 1H, *exo*-HC^9, *J*=9.4, 4.2), 3.41 (s, 1H, HC^7), 3.58 (d, 1H, HC^6, *J*=9.2), 3.70, 3.74 (both d, *J*=13.8), 4.04 (d, 1H, HC^2, *J*=9.2), 6.78 (t, 1H, HC_{arom}, *J*=7.3), 7.01 (d, 2H, HC_{arom}, *J*=8.0), 7.26 (dd, 2H, HC_{arom}, *J*=8.4, 7.5), 7.28-7.31 (m, 1H, HC_{arom}), 7.33-7.40 (m, 4H, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 14.63 (CH_3), 30.75 (C^{10}), 43.03, 53.97, 56.07, 58.42, 62.38, 66.61 (C^1, C^2, C^6, C^7, C^9, $\underline{C}H_2$(Bn)), 111.78, 117.99, 127.04, 128.36, 128.45, 129.08, 145.41, 149.33 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{21}H_{24}N_3$ 318.1965 [M+1], found 318.1960.



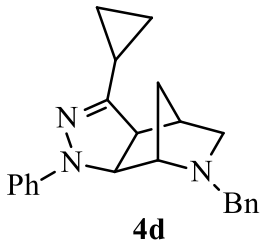
4c

9-Benzyl-5-methyl-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4c). Oil, R_f 0.16 (EtOAc-petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.39 (d, 1H, HC^{10}, *J*=10.7), 1.61 (d, 1H, HC^{10}, *J*=10.7), 2.01 (d, 3H, CH_3, *J*=0.9), 2.57-2.63 (m, 2H, HC^7, *endo*-HC^8), 2.75 (dd, 1H, *exo*-HC^8, *J*=9.3, 3.6), 3.23 (d, 1H, HC^6, *J*=9.2), 3.52 (s, 1H, HC^1), 3.79, 3.83 (both d, *J*=13.4), 4.27 (d, 1H, HC^2, *J*=9.2), 6.72 (tt, 1H, HC_{arom}, *J*=7.3, 0.9), 6.81 (d, 2H, HC_{arom}, *J*=8.7), 7.15 (dd, 2H, HC_{arom}, *J*=8.7, 7.3), 7.30 (tt, 1H, HC_{arom}, *J*=7.1, 1.9), 7.38 (t, 2H, HC_{arom}, *J*=7.4), 7.44 (d, 2H, HC_{arom}, *J*=7.1), ^{13}C NMR ($CDCl_3$, δ ppm): 14.44 (CH_3), 29.65 (C^{10}), 40.49, 57.63, 57.91, 59.29, 63.01, 66.01 (C^1, C^2, C^6, C^7, C^9, $\underline{C}H_2$(Bn)), 111.61, 117.85, 127.16, 128.39, 128.51, 129.04, 145.22, 149.92 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{21}H_{24}N_3$ 318.1965 [M+1], found 318.1959.



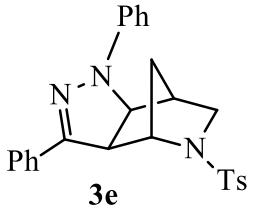
3d

8-Benzyl-5-cyclopropyl-3-phenyl-3,4,8-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3d). Oil, R_f 0.55 (EtOAc-petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.75-0.85 (m, 4H, $C_{cyclopropyl}$), 1.47 (d, 1H, HC^{10}, *J*=10.5), 1.50 (m, 1H, $C_{cyclopropyl}$), 1.69 (d, 1H, HC^{10}, *J*=10.5), 2.25 (d, 1H, *endo*-HC^9, *J*=9.7), 2.80 (bs, 1H, HC^1), 2.87 (dd, 1H, *exo*-HC^9, *J*=9.7, 4.2), 3.46 (s, 1H, HC^7), 3.61 (d, 1H, HC^6, *J*=9.3), 3.70, 3.76 (both d, *J*=13.4), 4.03 (d, 1H, HC^2, *J*=9.3), 6.78 (t, 1H, HC_{arom}, *J*=7.3), 7.00 (dd, 2H, HC_{arom}, *J*=8.7, 1.0), 7.25 (dd, 2H, HC_{arom}, *J*=8.7, 7.3), 7.28-7.32 (m, 1H, HC_{arom}), 7.34-7.42 (m, 4H, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 6.57, 7.13, 9.98 ($C_{cyclopropyl}$), 30.92 (C^{10}), 42.87, 54.09, 54.66, 58.31, 62.95, 66.78 (C^1, C^2, C^6, C^7, C^9, $\underline{C}H_2$(Bn)), 111.76, 117.83, 127.04, 128.39, 128.46, 129.07, 145.42, 154.32 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3$ 344.2121 [M+1], found 344.2125.



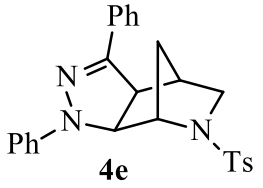
4d

9-Benzyl-5-cyclopropyl-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4d). Oil, R_f 0.43 (EtOAc-petroleum ether, 1:1). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.75-0.92 (m, 4H, $C_{cyclopropyl}$), 1.37 (d, 1H, HC^{10}, *J*=10.6), 1.55 (m, 1H, $C_{cyclopropyl}$), 1.61 (d, 1H, HC^{10}, *J*=10.6), 2.47 (dd, 1H, *exo*-HC^8, *J*=9.1, 3.5), 2.57 (d, 1H, *endo*-HC^8, *J*=9.1), 2.68 (bs, 1H, HC^7), 3.28 (d, 1H, HC^6, *J*=9.3), 3.50 (s, 1H, HC^1), 3.78, 3.83 (both d, *J*=13.4), 4.23 (d, 1H, HC^2, *J*=9.3), 6.70 (t, 1H, HC_{arom}, *J*=7.3), 6.80 (dd, 2H, HC_{arom}, *J*=8.7, 0.9), 7.14 (dd, 2H, HC_{arom}, *J*=8.6, 7.3), 7.30 (t, 1H, HC_{arom}, *J*=7.1), 7.38 (t, 2H, HC_{arom}, *J*=7.2), 7.43 (d, 2H, HC_{arom}, *J*=7.0). ^{13}C NMR ($CDCl_3$, δ ppm): 6.60, 7.30, 9.69 ($C_{cyclopropyl}$), 29.72 (C^{10}), 41.27, 57.76, 57.97, 59.34, 62.85, 66.35 (C^1, C^2, C^6, C^7, C^9, $\underline{C}H_2$(Bn)), 111.63, 117.67, 127.05, 128.34, 128.44, 128.96, 145.31, 154.92 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3$ 344.2121 [M+1], found 344.2125.



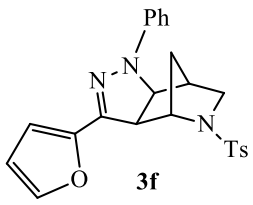
3e

8-[(4-Methylphenyl)sulfonyl]-3,5-diphenyl-3,4,8-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3e). Oil, R_f 0.40 (EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.05 (d, 1H, HC^{10}, *J*=10.9), 1.50 (d, 1H, HC^{10}, *J*=10.9), 2.43 (s, 3H, CH_3), 3.04 (bs, 1H, HC^1), 3.18 (dd, 1H, *exo*-HC^9, *J*=9.5, 3.8), 3.27 (d, 1H, *endo*-HC^9, *J*=9.5), 4.18 (d, 1H, HC^6, *J*=9.5), 4.37 (d, 1H, HC^2, *J*=9.5), 4.51 (s, 1H, HC^7), 6.86 (t, 1H, HC_{arom}, *J*=7.3), 7.13 (d, 2H, HC_{arom}, *J*=7.8), 7.28-7.40 (m, 5H), 7.44 (t, 2H, HC_{arom}, *J*=7.6), 7.76 (d, 2H, HC_{Ts}, *J*=8.2), 7.80 (d, 1H, HC_{arom}, *J*=7.8). ^{13}C NMR ($CDCl_3$, δ ppm): 21.57 (CH_3), 31.76 (C^{10}), 43.16, 48.98, 57.17, 61.68, 66.50 (C^1, C^2, C^6, C^7, C^9), 112.43, 119.39, 125.69, 127.36, 128.74, 128.89, 129.26, 129.93, 131.55, 135.54, 143.84, 143.90,146.37 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{26}H_{26}N_3O_2S$ 444.1740 [M+1], found 444.1742.



4e

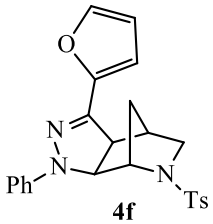
9-[(4-Methylphenyl)sulfonyl]-5-(furan-2-yl)-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4e). Oil, R_f 0.28 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.01 (d, 1H, HC^{10}, *J*=11.1), 1.47 (d, 1H, HC^{10}, *J*=11.1), 2.44 (s, 3H, CH_3), 2.88 (bs, 1H, HC^7), 3.17 (dd, 1H, *exo*-HC^8, *J*=9.0, 3.4), 3.33 (d, 1H, *endo*-HC^8, *J*=9.0), 3.85 (d, 1H, HC^6, *J*=9.5), 4.61 (d, 1H, HC^2, *J*=9.5), 4.55 (s, 1H, HC^1), 6.90 (t, 1H, HC_{arom}, *J*=7.3), 7.21 (d, 2H, HC_{arom}, *J*=8.6), 7.30-7.36 (m, 5H, HC_{arom}), 7.73 (d, 1H, HC_{arom}, *J*=8.6), 7.77 (d, 2H, HC_{Ts}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 21.57 (CH_3), 31.43 (C^{10}), 41.65, 52.22, 53.55, 61.77, 68.11 (C^1, C^2, C^6, C^7, C^9), 112.36, 119.46, 125.70, 127.35, 128.66, 128.68, 129.45, 129.92, 131.60, 135.50, 143.76, 143.82, 147.99 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{26}H_{26}N_3O_2S$ 444.1740 [M+1], found 444.1731.



3f

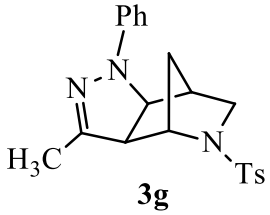
8-[(4-Methylphenyl)sulfonyl]-5-(furan-2-yl)-3-phenyl-3,4,8-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3f). Oil, R_f 0.38 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.10 (dm, 1H, HC^{10}, *J*=11.1), 1.52 (d, 1H, HC^{10}, *J*=11.0), 2.43 (s, 3H, CH_3), 3.03 (bs, 1H, HC^1), 3.18 (dd, 1H, *exo*-HC^9, *J*=9.5, 3.5), 3.22 (d, 1H, *endo*-HC^9, *J*=9.5), 4.04 (d, 1H, HC^6,

J=9.5), 4.31 (d, 1H, HC^2, *J*=9.5), 4.53 (bs, 1H, HC^7), 6.53 (dd, 1H, HC_{furyl}, *J*=3.4, 1.8), 6.71 (d, 1H, HC_{furyl}, *J*=3.4), 6.85 (t, 1H, HC_{arom}, *J*=7.3), 7.09 (d, 2H, HC_{arom}, *J*=8.6), 7.27 (dd, 2H, HC_{arom}, *J*=8.6, 7.3), 7.34 (d, 2H, HC_{Ts}, *J*=8.1), 7.52 (d, 1H, HC_{furyl}, *J*=1.4), 7.76 (d, 2H, HC_{Ts}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 21.57 (CH_3), 31.79 (C^{10}), 43.07, 48.98, 57.22, 61.83, 65.96 (C^1, C^2, C^6, C^7, C^9), 110.00, 111.85, 112.53, 119.52, 127.35, 129.23, 129.95, 135.50, 138.82, 143.63, 143.70, 143.86, 147.34 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{26}H_{26}N_3O_2S$ 434.1533 [M+1], found 434.1527.



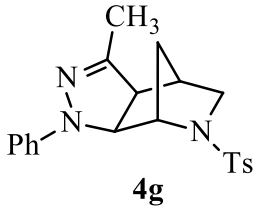
4f

9-[(4-Methylphenyl)sulfonyl]-5-(furan-2-yl)-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4f). Oil, R_f 0.27 ((EtOAc-petroleum ether, 1:3). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.03 (d, 1H, HC^{10}, *J*=11.0), 1.47 (d, 1H, HC^{10}, *J*=11.0), 2.43 (s, 3H, CH_3), 2.92 (bs, 1H, HC^7), 3.17 (dd, 1H, *exo*-HC^8, *J*=9.1, 3.4), 3.30 (d, 1H, *endo*-HC^8, *J*=9.1), 3.75 (d, 1H, HC^6, *J*=9.5), 4.57 (d, 1H, HC^2, *J*=9.5), 4.53 (s, 1H, HC^1), 6.48 (dd, 1H, HC_{furyl}, *J*=3.4, 1.8), 6.65 (d, 1H, HC_{furyl}, *J*=3.4), 6.89 (t, 1H, HC_{arom}, *J*=7.3), 7.16 (d, 2H, HC_{arom}, *J*=7.8), 7.29-7.36 (m, 4H, HC_{arom}), 7.48 (d, 1H, HC_{furyl}, *J*=1.8), 7.76 (d, 2H, HC_{Ts}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 21.56 (CH_3), 31.42 (C^{10}), 41.95, 52.07, 53.96, 61.61, 67.56 (C^1, C^2, C^6, C^7, C^9), 109.23, 111.78, 112.43, 119.57, 127.34, 129.42, 129.92, 135.45, 140.68, 143.30, 143.50, 143.80, 147.64 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{26}H_{26}N_3O_2S$ 434.1533 [M+1], found 434.1527.



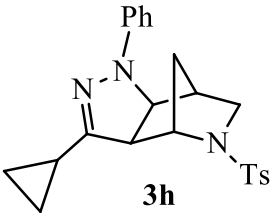
3g

8-[(4-Methylphenyl)sulfonyl]-5-methyl-3-phenyl-3,4,8-triaza-tricyclo[5.2.1.0$^{2.6}$]dec-4-ene (3g). Oil, R_f 0.77 ((EtOAc-petroleum ether, 1:1). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.02 (dm, 1H, HC^{10}, *J*=10.8), 1.41 (d, 1H, HC^{10}, *J*=10.8), 2.01 (d, 3H, CH_3, *J*=1.1), 2.44 (s, 3H, CH_3), 2.89 (bs, 1H, HC^1), 3.10 (dd, 1H, *exo*-HC^9, *J*=9.6, 3.3), 3.14 (d, 1H, *endo*-HC^9, *J*=9.6), 3.59 (d, 1H, HC^6, *J*=9.4), 4.08 (d, 1H, HC^2, *J*=9.4), 4.32 (bs, 1H, HC^7), 6.78 (tt, 1H, HC_{arom}, *J*=7.3, 1.0), 6.94 (d, 2H, HC_{arom}, *J*=8.8), 7.23 (dd, 2H, HC_{arom}, *J*=8.8, 7.3), 7.34 (d, 2H, HC_{Ts}, *J*=8.5), 7.74 (d, 2H, HC_{Ts}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 14.58 (CH_3), 21.51 (CH_3), 31.56 (C^{10}), 43.03, 49.01, 60.74, 60.90, 66.07 (C^1, C^2, C^6, C^7, C^9), 111.90, 118.65, 127.37, 129.16, 129.90, 135.49, 143.77, 144.92, 147.18 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{21}H_{24}N_3O_2S$ 382.1584 [M+1], found 382.1578.



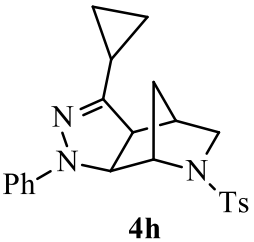
4g

9-[(4-Methylphenyl)sulfonyl]-5-methyl-3-phenyl-3,4,9-triazatricyclo[5.2.1.0$^{2.6}$]dec-4-ene (4g). Oil, R_f 0.58 ((EtOAc-petroleum ether, 1:1). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.02 (dm, 1H, HC^{10}, *J*=11.0), 1.39 (d, 1H, HC^{10}, *J*=11.0), 1.98 (d, 3H, CH_3, *J*=1.0), 2.43 (s, 3H, CH_3), 2.67 (bs, 1H, HC^7), 3.13 (dd, 1H, *exo*-HC^8, *J*=9.1, 3.3), 3.18 (d, 1H, *endo*-HC^8, *J*=9.1), 3.27 (d, 1H, HC^6, *J*=9.4), 4.35 (d, 1H, HC^2, *J*=9.4), 4.42 (bs, 1H, HC^1), 6.82 (tt, 1H, HC_{arom}, *J*=7.4, 1.2), 7.02 (d, 2H, HC_{arom}, *J*=8.7), 7.28 (dd, 2H, HC_{arom}, *J*=8.7, 7.4), 7.33 (d, 2H, HC_{Ts}, *J*=8.5), 7.74 (d, 2H, HC_{Ts}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 14.26 (CH_3), 21.50 (CH_3), 31.22 (C^{10}), 40.49, 52.15, 57.40, 61.77, 67.60 (C^1, C^2, C^6, C^7, C^9), 111.85, 118.70, 127.34, 129.32, 129.84, 135.68, 143.69, 144.77, 148.94 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{21}H_{24}N_3O_2S$ 382.1584 [M+1], found 382.1582.



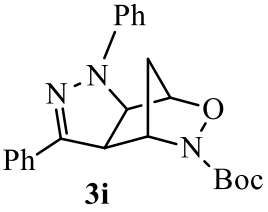
3h

8-[(4-Methylphenyl)sulfonyl]-5-cyclopropyl-3-phenyl-3,4,8-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (3h).Oil, R_f 0.44 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.77 (m, 1H, $C_{cyclopropyl}$), 0.85-0.95 (m, 3H, $C_{cyclopropyl}$), 1.05 (d, 1H, HC^{10}, *J*=10.7), 1.41 (d, 1H, HC^{10}, *J*=10.7), 1.57 (m, 1H, $C_{cyclopropyl}$), 2.45 (s, 3H, CH_3), 2.88 (bs, 1H, HC^1), 3.13 (bs, 2H, *exo*-HC^9, *endo*-HC^9), 3.61 (d, 1H, HC^6, *J*=9.3), 4.06 (d, 1H, HC^2, *J*=9.3), 4.39 (s, 1H, HC^7), 6.78 (t, 1H, HC_{arom}, *J*=7.3), 6.93 (d, 2H, HC_{arom}, *J*=8.6), 7.21 (dd, 2H, HC_{arom}, *J*=8.6, 7.3), 7.35 (d, 2H, HC_{Ts}, *J*=8.1), 7.75 (d, 2H, HC_{Ts}, *J*=8.2). ^{13}C NMR ($CDCl_3$, δ ppm): 6.46, 7.21, 9.33 ($C_{cyclopropyl}$), 21.17 (CH_3), 31.25 (C^{10}), 42.52, 48.68, 59.35, 61.00, 65.79 (C^1, C^2, C^6, C^7, C^9), 111.46, 118.10, 126.95, 128.74, 129.55, 135.05, 143.41, 144.57, 151.98 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3O_2S$ 408.1740 [M+1], found 408.1744.



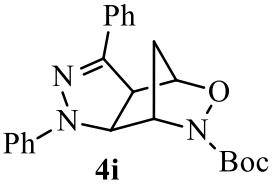
4h

9-[(4-Methylphenyl)sulfonyl]-5-cyclopropyl-3-phenyl-3,4,9-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene (4h). Oil, R_f 0.32 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.76-0.93 (m, 4H, $C_{cyclopropyl}$), 1.01 (d, 1H, HC^{10}, *J*=11.0), 1.37 (d, 1H, HC^{10}, *J*=11.0), 1.48 (m, 1H, $C_{cyclopropyl}$), 2.44 (s, 3H, CH_3), 2.78 (bs, 1H, HC^7), 3.14 (dd, 1H, *exo*-HC^8, *J*=9.0, 3.2), 3.19 (d, 1H, *endo*-HC^8, *J*=9.0), 3.34 (d, 1H, HC^6, *J*=9.3), 4.33 (d, 1H, HC^2, *J*=9.3), 4.41 (s, 1H, HC^1), 6.81 (t, 1H, HC_{arom}, *J*=7.3), 7.00 (d, 2H, HC_{arom}, *J*=8.7), 7.26 (dd, 2H, HC_{arom}, *J*=8.7, 7.3), 7.33 (d, 2H, HC_{Ts}, *J*=8.0), 7.75 (d, 2H, HC_{Ts}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 6.33, 7.20, 9.02 ($C_{cyclopropyl}$), 21.14 (CH_3), 30.82 (C^{10}), 40.75, 51.80, 56.21, 61.27, 67.37 (C^1, C^2, C^6, C^7, C^9), 111.43, 118.14, 126.96, 128.89, 129.47, 135.09, 143.33, 144.42, 153.67 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3O_2S$ 408.1740 [M+1], found 408.1743.



3i

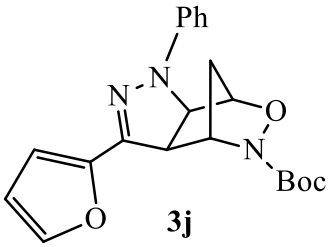
***tert*-Butyl 3,5-diphenyl-9-oxa-3,4,8-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene-8-carboxylate (3i).** Oil, R_f 0.33 ((EtOAc-petroleum ether, 1:5). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.58 (s, 9H, CH_3), 1.95 (bs, 2H, $HC^{10}{}_{syn}$ + $HC^{10}{}_{anti}$), 4.21 (d, 1H, HC^6, *J*=9.7), 4.63 (d, 1H, HC^2, *J*=9.7), 4.87 (s, 1H, HC^7), 5.04 (d, 1H, HC^1, *J*=1.2), 6.90 (t, 1H, HC_{arom}, *J*=7.3), 7.18 (d, 2H, HC_{arom}, *J*=8.6), 7.31 (dd, 2H, HC_{arom}, *J*=8.6, 7.3), 7.37 (t, 1H, HC_{arom}, *J*=7.2), 7.43 (t, 2H, HC_{arom}, *J*=7.1), 7.83 (d, 2H, HC_{arom}, *J*=7.1). ^{13}C NMR ($CDCl_3$, δ ppm): 27.84 (CH_3), 32.92 (C^{10}), 52.94, 60.60, 65.23 (C^2, C^6, C^7), 79.47, 82.60 (C^1, O<u>C</u>$(CH_3)_3$), 112.06, 119.43, 125.29, 128.45, 128.55, 129.0, 130.91, 143.60, 146.07, 156.45 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3O_3$ 392.1969 [M+1], found 392.1971.



4i

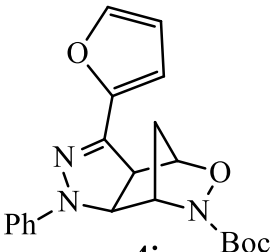
***tert*-Butyl 3,5-diphenyl-8-oxa-3,4,9-triazatricyclo[5.2.1.0^{2,6}]dec-4-ene-9-carboxylate (4i)**. Oil, R_f 0.19 ((EtOAc-petroleum ether, 1:5). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.60 (s, 9H, CH_3), 1.94-2.04 (m, 2H, $HC^{10}{}_{syn}$ + $HC^{10}{}_{anti}$), 4.24 (d, 1H, HC^6, *J*=9.7), 4.66 (d, 1H, HC^2, *J*=9.7), 4.94 (s, 1H, HC^7), 5.00 (s, 1H, HC^1), 6.92 (t, 1H, HC_{arom}, *J*=7.2), 7.25 (d, 2H, HC_{arom}),

7.30-7.38 (m, 3H, HC_{arom}), 7.42 (t, 2H, HC_{arom}, *J*=7.1), 7.77 (d, 2H, HC_{arom}, *J*=7.1). ^{13}C NMR ($CDCl_3$, δ ppm): 27.86 (CH_3), 33.00 (C^{10}), 54.56, 61.00, 64.50 (C^2, C^6, C^7), 79.91, 82.61 (C^1, $O\underline{C}(CH_3)_3$), 112.03, 119.44, 125.25, 128.46, 128.57, 128.98, 131.00, 143.61, 145.64, 155.94 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3O_3$ 392.1969 [M+1], found 392.1972.



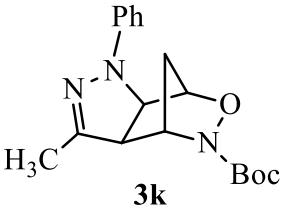
3j

***tert*-Butyl 5-(furan-2-yl)-3-phenyl-9-oxa-3,4,8-triaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-8-carboxylate (3j)**. Oil, R_f 0.59 ((EtOAc-petroleum ether, 1:3). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.56 (s, 9H, CH_3), 1.89-1.98 (m, 2H, HC^{10}_{syn} + HC^{10}_{anti}), 4.10 (d, 1H, HC^6, *J*=9.8), 4.59 (d, 1H, HC^2, *J*=9.8), 4.91 (d, 1H, HC^7, *J*=1.2), 5.02 (s, 1H, HC^1), 6.52 (dd, 1H, HC_{fur}, *J*=3.4, 1.8), 6.74 (d, 1H, HC_{fur}, *J*=3.4), 6.89 (t, 1H, HC_{arom}, *J*=7.4), 7.14 (d, 2H, HC_{arom}, *J*=8.7), 7.30 (dd, 2H, HC_{arom}, *J*=8.7, 7.3), 7.53 (d, 1H, HC_{fur}, *J*=1.8). ^{13}C NMR ($CDCl_3$, δ ppm): 28.20 (CH_3), 33.24 (C^{10}), 53.81, 61.21, 61.25, 65.16 (C^2, C^6, C^7), 79.71, 79.75, 83.01 (C^1, $O\underline{C}(CH_3)_3$), 109.79, 111.88, 111.90, 112.50, 119.93, 129.37, 138.96, 143.71, 147.18, 156.95 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{21}H_{24}N_3O_4$ 382.1761 [M+1], found 382.1765.



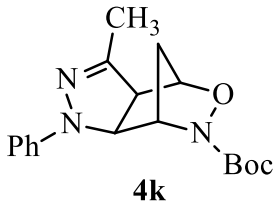
4j

***tert*-Butyl 5-(furan-2-yl)-3-phenyl-8-oxa-3,4,9-triaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-9-carboxylate (4j)**. Oil, R_f 0.52 (EtOAc-petroleum ether, 1:3). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.58 (s, 9H, CH_3), 1.98 (d, 1H, HC^{10}, *J*=11.2), 2.03 (dt, 1H, HC^{10}, *J*=11.2, 1.6), 4.12 (d, 1H, HC^6, *J*=10.0), 4.62 (d, 1H, HC^2, *J*=10.0), 4.93 (s, 1H, HC^7), 5.01 (s, 1H, HC^1), 6.51 (dd, 1H, HC_{furyl}, *J*=3.4, 1.8), 6.68 (d, 1H, HC_{furyl}, *J*=3.4), 6.91 (t, 1H, HC_{arom}, *J*=7.3), 7.22 (d, 2H, HC_{arom}, *J*=8.7), 7.32 (dd, 2H, HC_{arom}, *J*=8.7, 7.3), 7.52 (d, 1H, HC_{furyl}, *J*=1.8).^{13}C NMR ($CDCl_3$, δ ppm): 28.25 (CH_3), 33.40 (C^{10}), 55.21, 61.30, 61.34, 64.35 (C^2, C^6, C^7), 80.42, 80,46, 83.05 (C^1, $O\underline{C}(CH_3)_3$), 109.74, 111.90, 111.92, 112.50, 119.95, 129.36, 138.45, 143.69, 143.71, 143.74, 147.23, 156.28 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{21}H_{24}N_3O_4$ 382.1761 [M+1], found 382.1763.



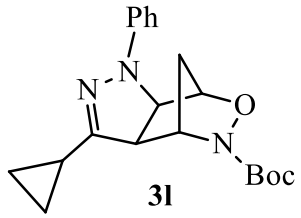
3k

***tert*-Butyl 5-methyl-3-phenyl-9-oxa-3,4,8-triaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-8-carboxylate (3k)**. Oil, R_f 0.46 ((EtOAc-petroleum ether, 1:3). ^1H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.53 (s, 9H, CH_3), 1.80-1.89 (m, 2H, HC^{10}_{syn} + HC^{10}_{anti}), 2.07 (s, 3H, CH_3), 3.65 (d, 1H, HC^6, *J*=9.4), 4.37 (d, 1H, HC^2, *J*=9.4), 4.72 (s, 1H, HC^7), 4.94 (s, 1H, HC^1), 6.84 (t, 1H, HC_{arom}, *J*=7.3), 7.01 (d, 2H, HC_{arom}, *J*=8.6), 7.26 (dd, 2H, HC_{arom}, *J*=8.6, 7.3). ^{13}C NMR ($CDCl_3$, δ ppm): 14.04 (CH_3), 27.76 (CH_3), 32.53 (C^{10}), 56.96, 59.89, 65.05 (C^2, C^6, C^7), 79.48, 82.55 (C^1, $O\underline{C}(CH_3)_3$), 111.54, 118.72, 128.91, 144.59, 147.01, 156.86 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{18}H_{24}N_3O_3$ 330.1812 [M+1], found 330.1815.



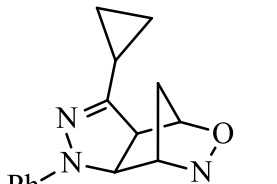
4k

***tert*-Butyl 5-methyl-3-phenyl-8-oxa-3,4,8-triaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-8-carboxylate (4k)**. Oil, R_f 0.30 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.57 (s, 9H, CH_3), 1.91 (d, 1H, HC^{10}, *J*=11.1), 2.00 (dt, 1H, HC^{10}, *J*=11.1, 1.8), 2.03 (d, 3H, CH_3, *J*=0.9), 3.66 (d, 1H, HC^6, *J*=9.3), 4.40 (d, 1H, HC^2, *J*=9.3), 4.81 (bs, 2H, HC^1, HC^7), 6.85 (t, 1H, HC_{arom}, *J*=7.3), 7.08 (d, 2H, HC_{arom}, *J*=8.6), 7.28 (dd, 2H, HC_{arom}, *J*=8.6, 7.3). ^{13}C NMR ($CDCl_3$, δ ppm): 14.27 (CH_3), 27.83 (CH_3), 32.86 (C^{10}), 58.24, 61.03, 64.14 (C^2, C^6, C^7), 79.15, 82.45 (C^1, O<u>C</u>$(CH_3)_3$), 111.54, 118.74, 128.90, 144.65, 146.48, 155.95 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{18}H_{24}N_3O_3$ 330.1812 [M+1], found 330.1813.



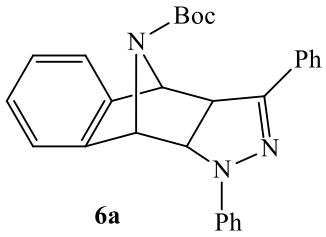
3l

***tert*-Butyl 5-cyclopropyl-3-phenyl-9-oxa-3,4,8-triaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-8-carboxylate (3l)**. Oil, R_f 0.54 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.82-0.97 (m, 4H, $C_{cyclopropyl}$), 1.54 (s, 9H, CH_3), 1.61 (m, 1H, $C_{cyclopropyl}$), 1.82-1.91 (m, 2H, $HC^{10}{}_{syn}$ + $HC^{10}{}_{anti}$), 3.68 (d, 1H, HC^6, *J*=9.4), 4.35 (d, 1H, HC^2, *J*=9.4), 4.76 (s, 1H, HC^7), 4.91 (s, 1H, HC^1), 6.81 (t, 1H, HC_{arom}, *J*=7.4), 6.98 (d, 2H, HC_{arom}, *J*=8.6), 7.24 (dd, 2H, HC_{arom}, *J*=8.6, 7.4). ^{13}C NMR ($CDCl_3$, δ ppm): 6.90, 7.58, 9.65 ($C_{cyclopropyl}$), 28.17 (CH_3), 33.04 (C^{10}), 56.27, 60.86, 60.91, 65.56 (C^2, C^6, C^7), 79.79, 79.84, 82.90 (C^1, O<u>C</u>$(CH_3)_3$), 111.96, 118.99, 129.24, 145.07, 152.51, 157.15 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{20}H_{26}N_3O_3$ 356.1969 [M+1], found 356.1969.



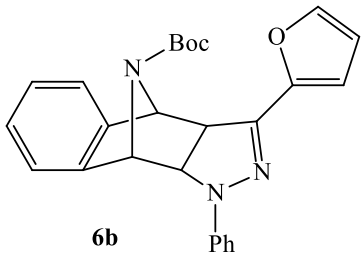
4l

***tert*-Butyl 5-cyclopropyl-3-phenyl-8-oxa-3,4,8-triaza-tricyclo[5.2.1.0^{2,6}]dec-4-ene-8-carboxylate (4l)**. Oil, R_f 0.39 ((EtOAc-petroleum ether, 1:3). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.82 (m, 1H, $C_{cyclopropyl}$), 0.85-0.94 (m, 3H, $C_{cyclopropyl}$), 1.57 (s, 9H, CH_3), 1.58-1.61 (m, 1H, $C_{cyclopropyl}$), 1.90 (d, 1H, HC^{10}, *J*=11.1), 2.01 (dt, 1H, HC^{10}, *J*=11.1, 1.8), 3.68 (d, 1H, HC^6, *J*=9.4), 4.38 (d, 1H, HC^2, *J*=9.4), 4.80 (s, 1H, HC^7), 4.85 (s, 1H, HC^1), 6.84 (t, 1H, HC_{arom}, *J*=7.3), 7.06 (d, 2H, HC_{arom}, *J*=7.8), 7.27 (t, 2H, HC_{arom}, *J*=8.3). ^{13}C NMR ($CDCl_3$, δ ppm): 6.98, 7.44, 9.89 ($C_{cyclopropyl}$), 28.24 (CH_3), 33.30 (C^{10}), 57.50, 61.31, 61.35, 64.67 (C^2, C^6, C^7), 80.14, 80.19, 82.84 (C^1, O<u>C</u>$(CH_3)_3$), 111.96, 119.02, 129.24, 145.12, 152.05, 156.32 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{20}H_{26}N_3O_3$ 356.1969 [M+1], found 356.1969.



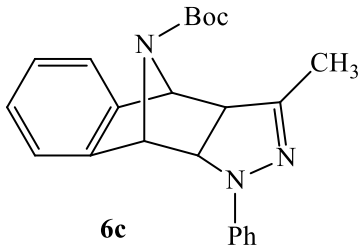
6a

***tert*-Butyl 10,12-diphenyl-10,11,14-triaza-tetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradeca-2,4,6,11-tetraene-14-carboxylate (6a)**. Yellow oil, R_f 0.31 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.08-1.21 (m, 9H, CH_3), 4.00 (m, 1H, HC^{13}), 4.59 (m, 1H, HC^9), 5.52-5.80 (m, 2H, HC^1, HC^8), 6.89 (t, 1H, HC_{arom}, *J*=7.3), 7.19-7.26 (m, 2H, HC_{arom}), 7.27 (m, 2H, HC_{arom}), 7.32-7.40 (m, 3H, HC_{arom}), 7.41-7.50 (m, 4H, HC_{arom}), 7.75-7.90 (m, 2H, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 27.64, 28.62 ($OC(\underline{C}H_3)_3$), 57.59, 63.64, 64.16, 64.38, 69.02, 69.32 (C^1, C^8, C^9, C^{13}), 80.39 ($O\underline{C}(CH_3)_3$), 112.12, 112.52, 118.89, 119.96, 120.21, 120.97, 121.18, 125.58, 127.22, 127.55, 128.70, 129.28, 132.20, 142.14, 143.40, 145.05 (C_{arom}, C=N, C=O). ESI-MS (m/z): calculated for $C_{28}H_{28}N_3O_2$ 438.2176 [M+1], found 438.2179.



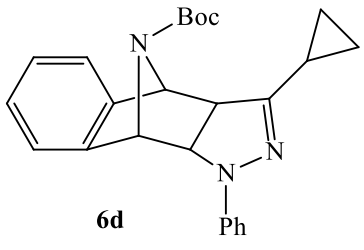
6b

***tert*-Butyl 12-(fur-2-yl)-10-phenyl-10,11,14-triaza-tetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradeca-2,4,6,11-tetraene-14-carboxylate (6b)**. Brown oil, R_f 0.16 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.20 (s, 9H, CH_3), 3.91 (d, 1H, HC^{13}, *J*=9.1), 4.54 (m, 1H, HC^9), 5.54-5.77 (m, 2H, HC^1, HC^8), 6.55 (bs, 1H, HC_{furyl}), 6.77 (d, 1H, HC_{furyl}, *J*=3.3), 6.89 (t, 1H, HC_{arom}, *J*=7.2), 7.19 (bs, 2H, HC_{arom}), 7.26 (m, 2H, HC_{arom}), 7.31-7.38 (m, 2H, HC_{arom}), 7.40 (bs, 1H, HC_{arom}), 7.45 (m, 1H, HC_{arom}), 7.56 (bs, 1H, HC_{furyl}). ^{13}C NMR ($CDCl_3$, δ ppm): 27.69 ($OC(\underline{C}H_3)_3$), 57.80, 63.90, 64.33, 68.54 (C^1, C^8, C^9, C^{13}), 80.49 ($O\underline{C}(CH_3)_3$), 108.36, 108.73, 111.87, 111.89, 112.31, 112.59, 119.01, 119.22, 119.46, 120.24, 120.48, 121.09, 126.52, 127.24, 127.56, 129.26, 129.42, 142.11, 142.89, 143.05, 143.18, 144.91, 145.42, 148.56 (C_{arom}, C=N). ESI-MS (m/z): calculated for $C_{26}H_{26}N_3O_3$ 428.1978 [M+1], found 428.1969.



6c

***tert*-Butyl 12-methyl-10-phenyl-10,11,14-triaza-tetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradeca-2,4,6,11-tetraene-14-carboxylate (6c)**. Yellow oil, R_f 0.68 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 1.21 (s, 6.4H, $C(CH_3)_3$), 1.39 (s, 2.6H, $C(CH_3)_3$), 2.18 (s, 3H, CH_3), 3.46 (d, 1H, HC^{13}, *J*=8.6), 4.32 (d, 1H, HC^9, *J*=8.6), 5.33 (bs, 0.3H) + 5.51 (bs, 0.7H) + 5.54-5.64 (m, 1H) (HC^1 + HC^8), 6.82 (t, 1H, HC_{arom}, *J*=7.3), 7.06 (d, 2H, HC_{arom}, *J*=7.8), 7.23 (m, 2H, HC_{arom}), 7.28-7.35 (m, 3H, HC_{arom}), 7.41 (m, 1H, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 14.80 (CH_3), 27.75, 29.71 ($C(\underline{C}H_3)$), 61.13, 62.29, 64.25, 68.23 (C^1, C^8, C^9, C^{13}), 80.39 ($O\underline{C}(CH_3)_3$), 111.50, 115.41, 117.97, 120.15, 120.79, 125.92, 127.10, 127.39, 142.21, 143.97, 144.74, 153.48 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{23}H_{26}N_3O_2$ 376.2020 [M+1], found 376.2023.



6d

***tert*-Butyl 12-cyclopropyl-10-phenyl-10,11,14-triaza-tetracyclo[6.5.1.0^{2,7}.0^{9,13}]tetradeca-2,4,6,11-tetraene-14-carboxylate (6d)**. Brown oil, R_f 0.43 (MeOH – $CHCl_3$, 1:100). ^{1}H NMR ($CDCl_3$, δ ppm, *J*, Hz): 0.83-1.05 (m, 4H, $C_{cyclopropyl}$), 1.19 (s, 6.5H, $C(CH_3)_3$), 1.39 (s, 2.5H, $C(CH_3)_3$), 1.67 (bs, 1H, $C_{cyclopropyl}$), 3.51 (d, 1H, HC^{13}, *J*=8.5), 4.33 (d, 1H, HC^9, *J*=8.5), 5.40 (bs, 0.3H) + 5.54 (bs, 1H) + 5.59 (m, 0.7H) (HC^1 + HC^8), 6.80 (t, 1H, HC_{arom}, *J*=7.3), 7.04 (d, 2H, HC_{arom},

J=7.7), 7.23 (m, 2H, HC_{arom}), 7.27-7.36 (m, 3H), 7.41 (m, 1H, HC_{arom}). ^{13}C NMR ($CDCl_3$, δ ppm): 6.60, 8.12, 9.79 ($C_{cyclopropyl}$), 27.79, 29.71 ($C(\underline{C}H_3)$), 60.36, 63.08, 64.03, 68.54 (C^1, C^8, C^9, C^{13}), 80.23 ($O\underline{C}(CH_3)_3$), 111.59, 117.89, 118.74, 120.08, 120.83, 125.80, 127.05, 127.38, 129.12, 129.31, 142.33, 144.16, 145.08, 151.12 (C_{arom}, C=O, C=N). ESI-MS (m/z): calculated for $C_{25}H_{28}N_3O_2$ 402.2176 [M+1], found 402.2180.

References

S1. P. A. Grieco and S. D. Larsen, *Org. Synth.,* 1990, **68**, 206; https://doi.org/10.15227/orgsyn.068.0206.

S2. T. A. Solodovnikova, N. V. Zyk and A. Yu. Gavrilova, *Mendeleev Commun*., 2022, **32**, 549; https://doi.org/10.1016/j.mencom.2022.07.038.

S3. M. J. Mulvihill, J. L. Gage and M. J. Miller, *J. Org. Chem.,* 1998, **63**, 3357; https://doi.org/10.1021/jo972265a.

S4. G. W. Kirby, H. McGuigan, J. W. M. Mackinnon, D. McLean and R. P. Sharma, *J. Chem. Soc., Perkin Trans. 1,* 1985, 1437; https://doi.org/10.1039/p19850001437.

S5. M. Lautens, K. Fagnou and V. Zunic, *Org. Lett.,* 2002, **4**, 3465; https://doi.org/10.1021/ol026579i.

S6. Y.-H. Cho, V. Zunic, H. Senboku, M. Olsen and M. Lautens, *J. Am. Chem. Soc.,* 2006, **128**, 6837; https://doi.org/10.1021/ja0577701.

S7. R. C. Bansal, A. W. McCulloch, A. G. McInnes, *Can. J. Chem*., 1969, **47**, 2391; https://doi.org/10.1139/v69-390.

S8. K. Hisler, A. G. J. Commeureuc, S. Zhou and J. A. Murphy, *Tetrahedron Lett.*, 2009, **50**, 3290; https://doi.org/10.1016/j.tetlet.2009.02.060.

S9. H. V. Patel, K. A. Vyas, S. P. Pandey and P. S. Fernandes, *Tetrahedron*, 1996, **52**, 661; https://doi.org/10.1016/0040-4020(95)00916-7.

S10. L. K. B. Garve, M. Petzold, P. G. Jones and D. B. Werz, *Org. Lett.*, 2016, **18**, 564; https://doi.org/10.1021/acs.orglett.5b03598.

S11. G. Wang, X. Liu, T. Huang, Y. Kuang, L. Lin and X. Feng, *Org. Lett.*, 2013, **15**, 76; https://doi.org/10.1021/ol303097j.

S12. B. Joseph and P. Rollin, *J. Carbohydr. Chem*., 1993, **12**, 1127; https://doi:10.1080/07328309308020122.

S13**.** X. Tang, L. Huang, J. Yang, Y. Xu, W. Wu and H. Jiang, *Chem. Commun*., 2014, 14793, https://doi.org/10.1039/C4CC06747A.

S14. L.-M. Chen, C. Zhou, J. Li, J. Li, X.-Q. Guo and T.-R. Kang, *Org. Biomol. Chem*., 2022, **20**, 7011; https://doi.org/10.1039/D2OB01338J.

S15. V. V. Voronin, M. S. Ledovskaya, E. G. Gordeev, K. S. Rodygin and V. P. Ananikov, *J. Org. Chem.,* 2018, **83**, 3819; https://doi.org/10.1021/acs.joc.8b00155.

S16. S. T. Kolla, N. R. Rayala, B. Sridhar and C. R. Bhimapaka, *Org. Biomol. Chem.*, 2022, **20**, 334; https://doi.org/10.1039/D1OB01727F.

S17. E. Kobayashi and H. Togo, *Synthesis*, 2019, **51**, 3723; https://doi.org/10.1055/s-0039-1690102.

S18. C. Ma, Y. Li, P. Wen, R. Yan, Z. Ren and G. Huang, *Synlett*, 2011, 1321; https://doi.org/10.1055/s-0030-1260552.

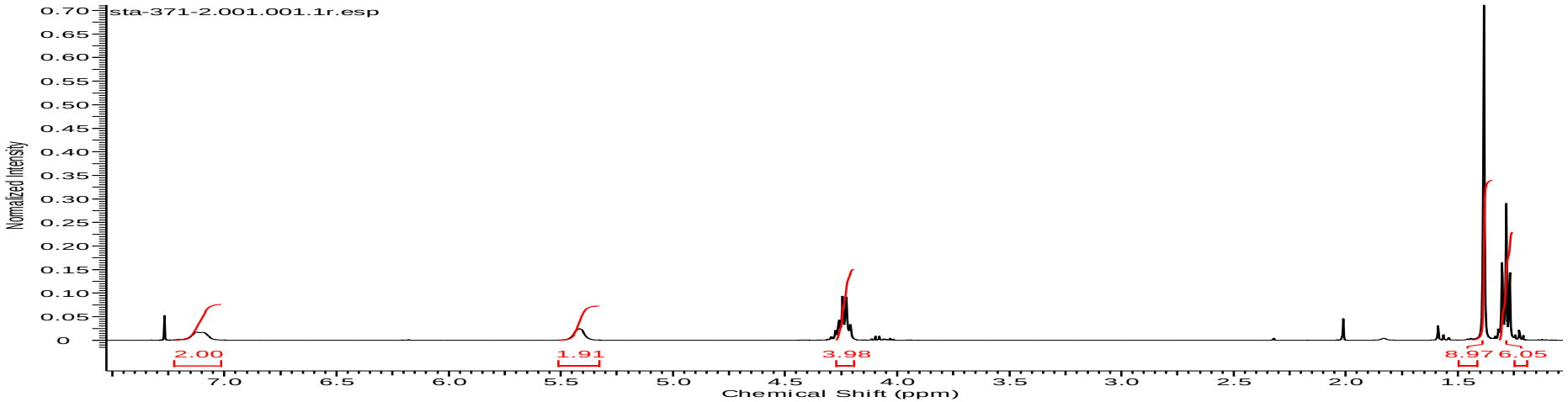


Figure S1. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of alkene **9a**

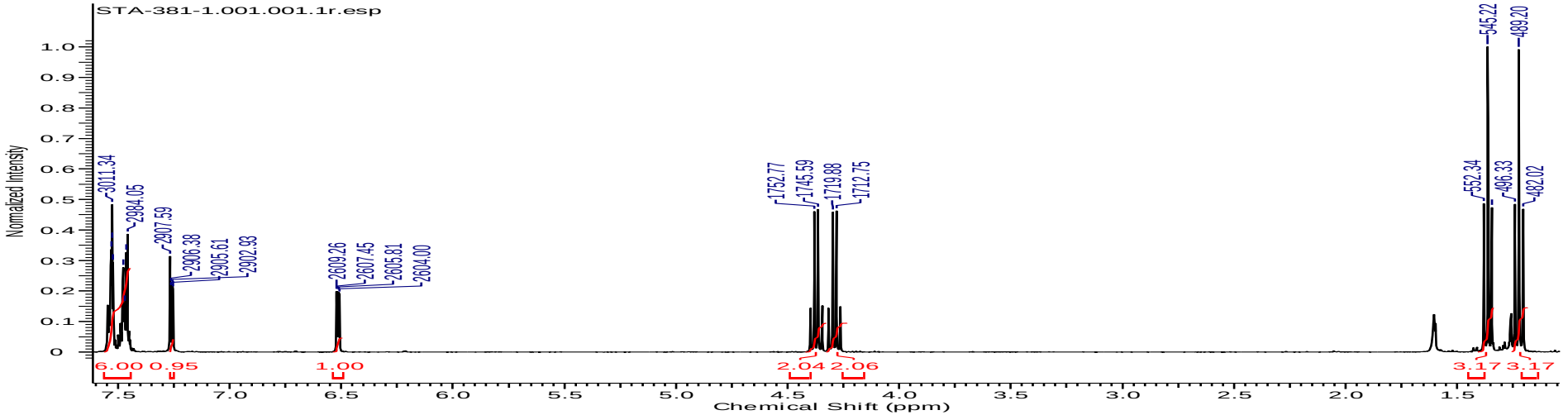


Figure S2. ^{1}H NMR spectrum ($CDCl_3$) of pyrazole **12b**

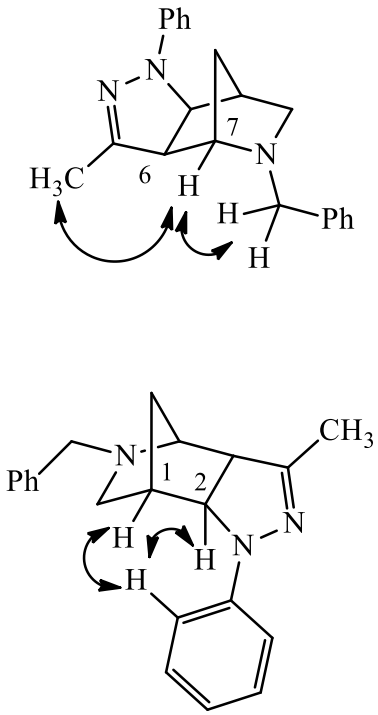
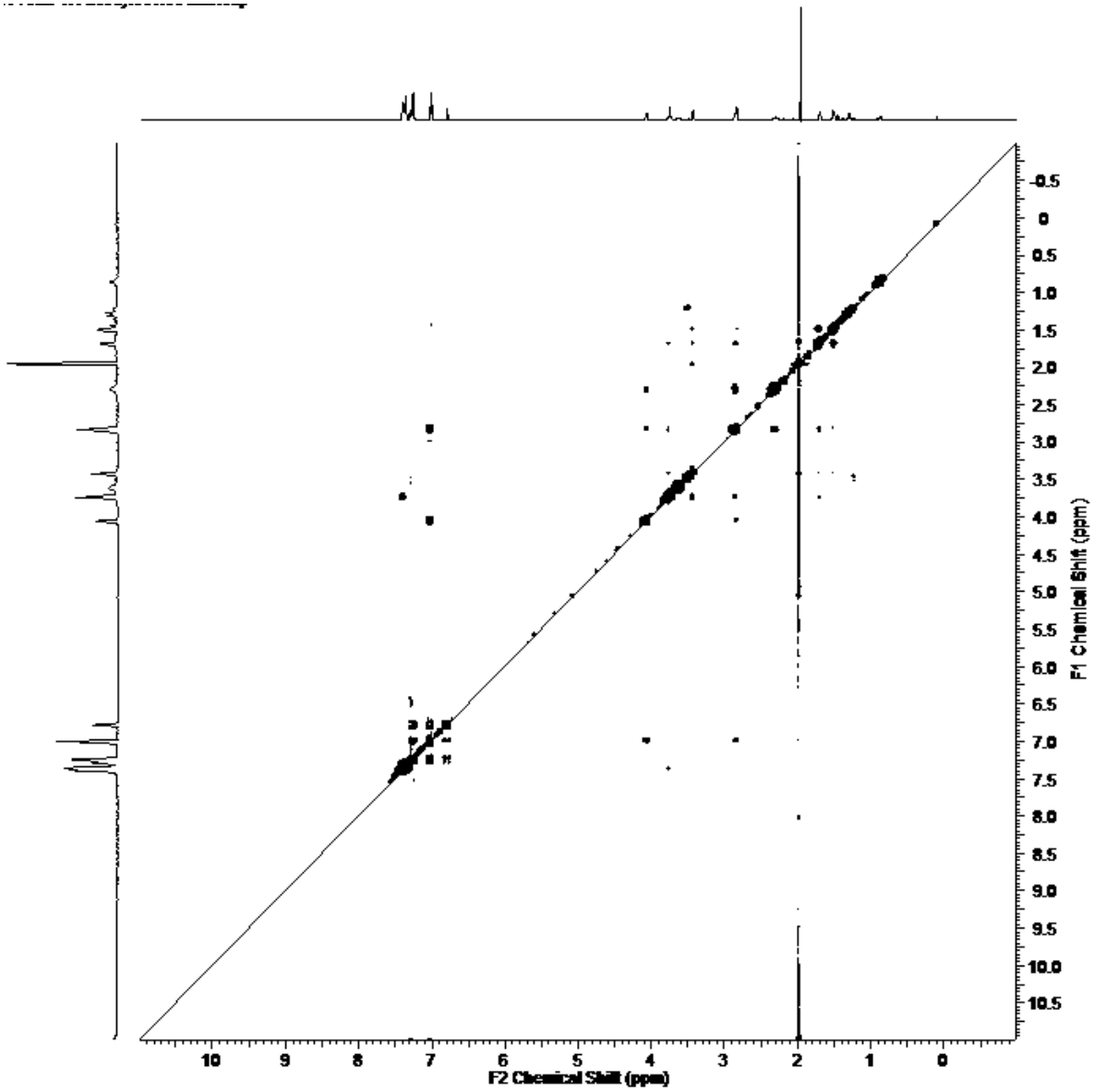


Figure S3. Results of the NOESY experiment for compound **3c**



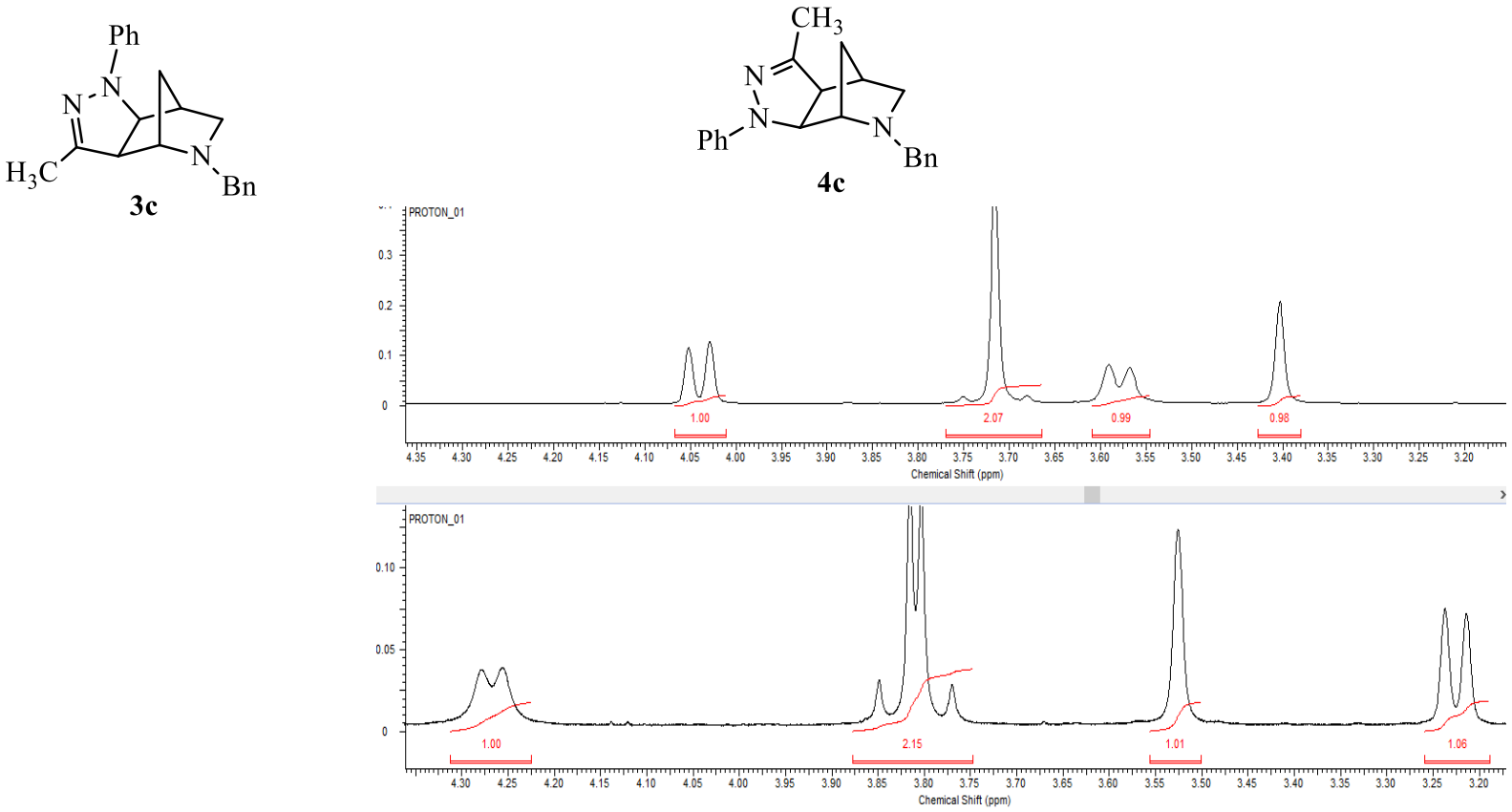


Figure S4. Fragments of the ^{1}H NMR spectra of isomers **3c** (upper) and **4c** (lower).

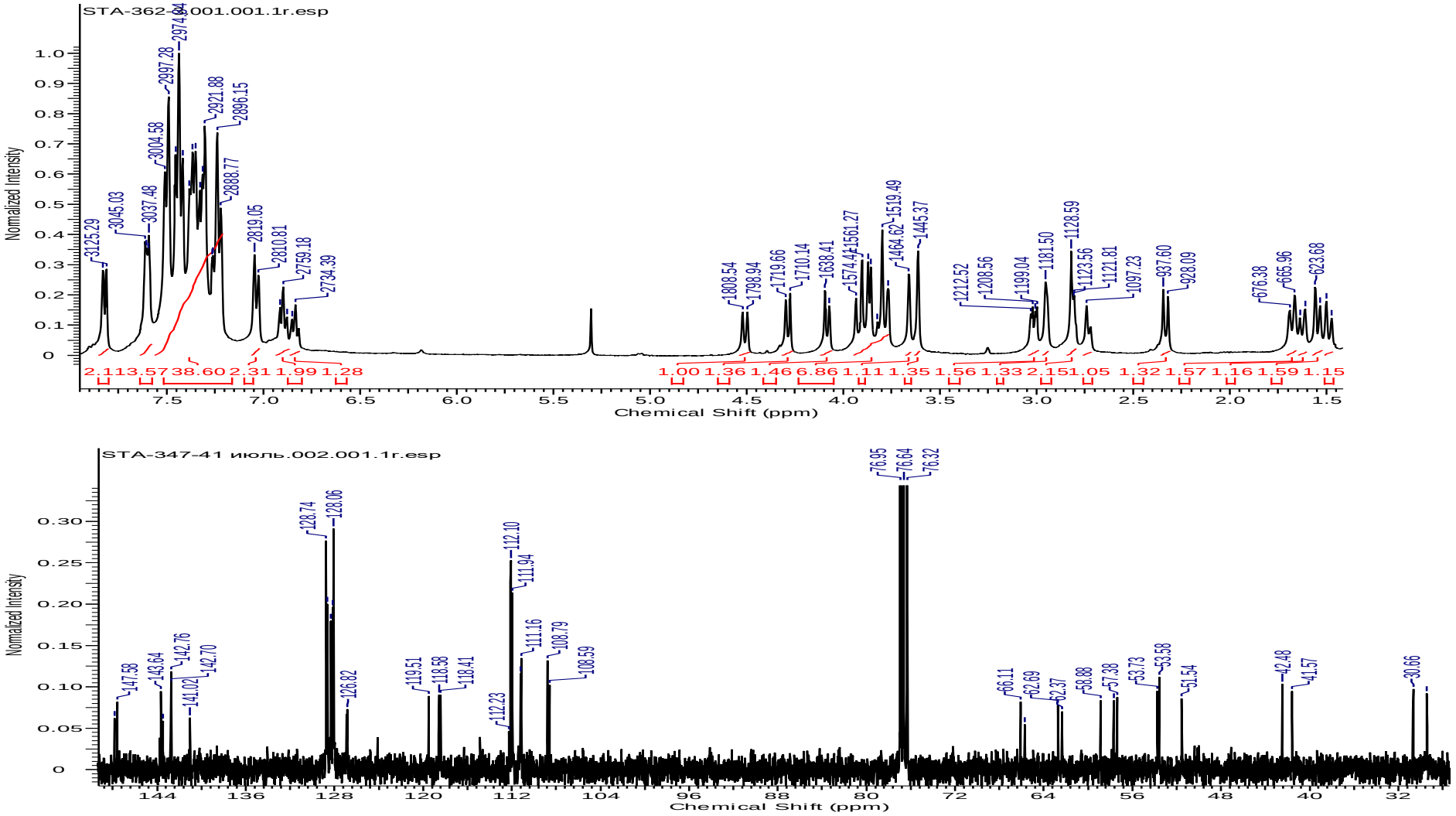


Figure S5. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of mixture **3a+4a**

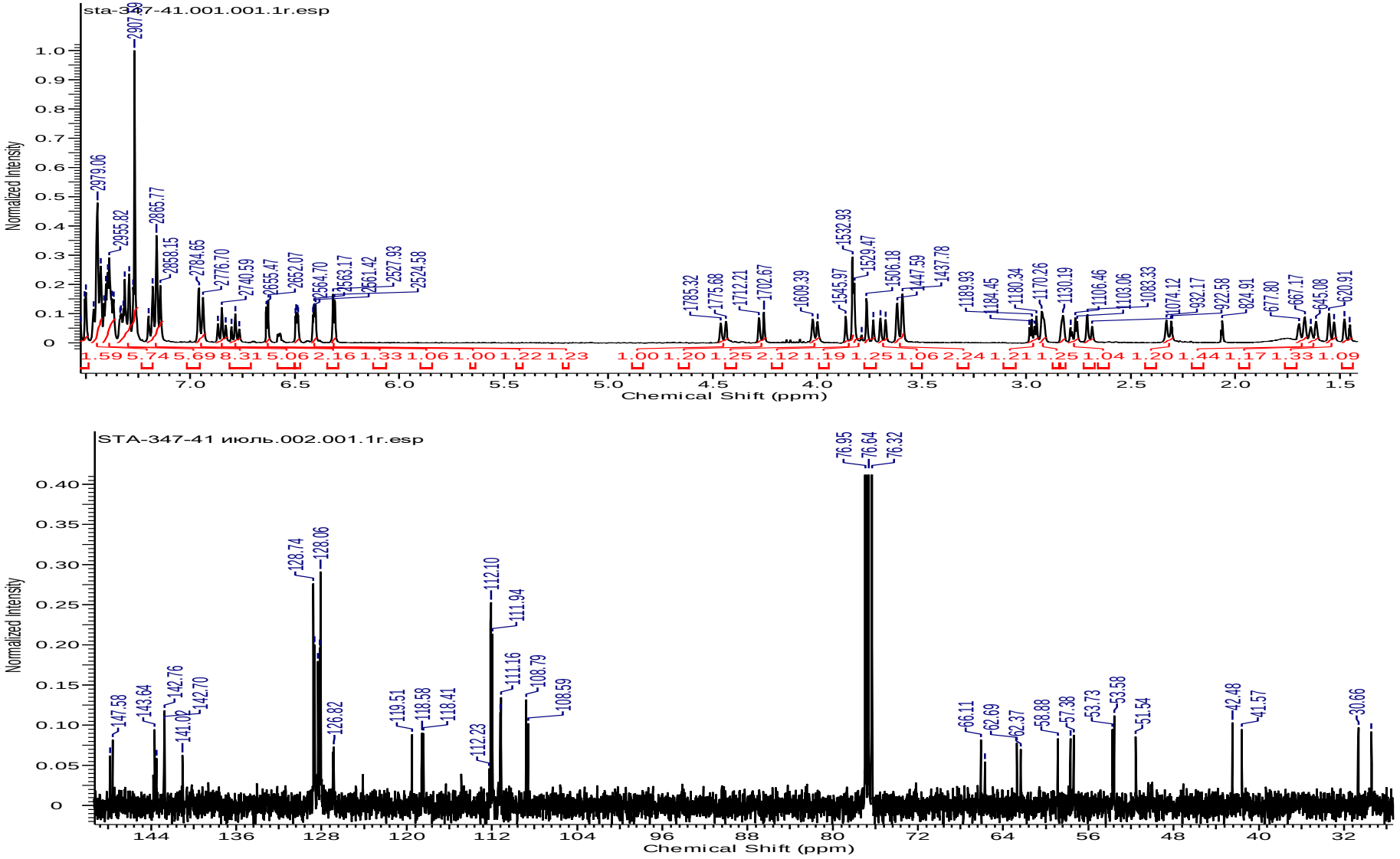


Figure S6. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of mixture **3b+4b**

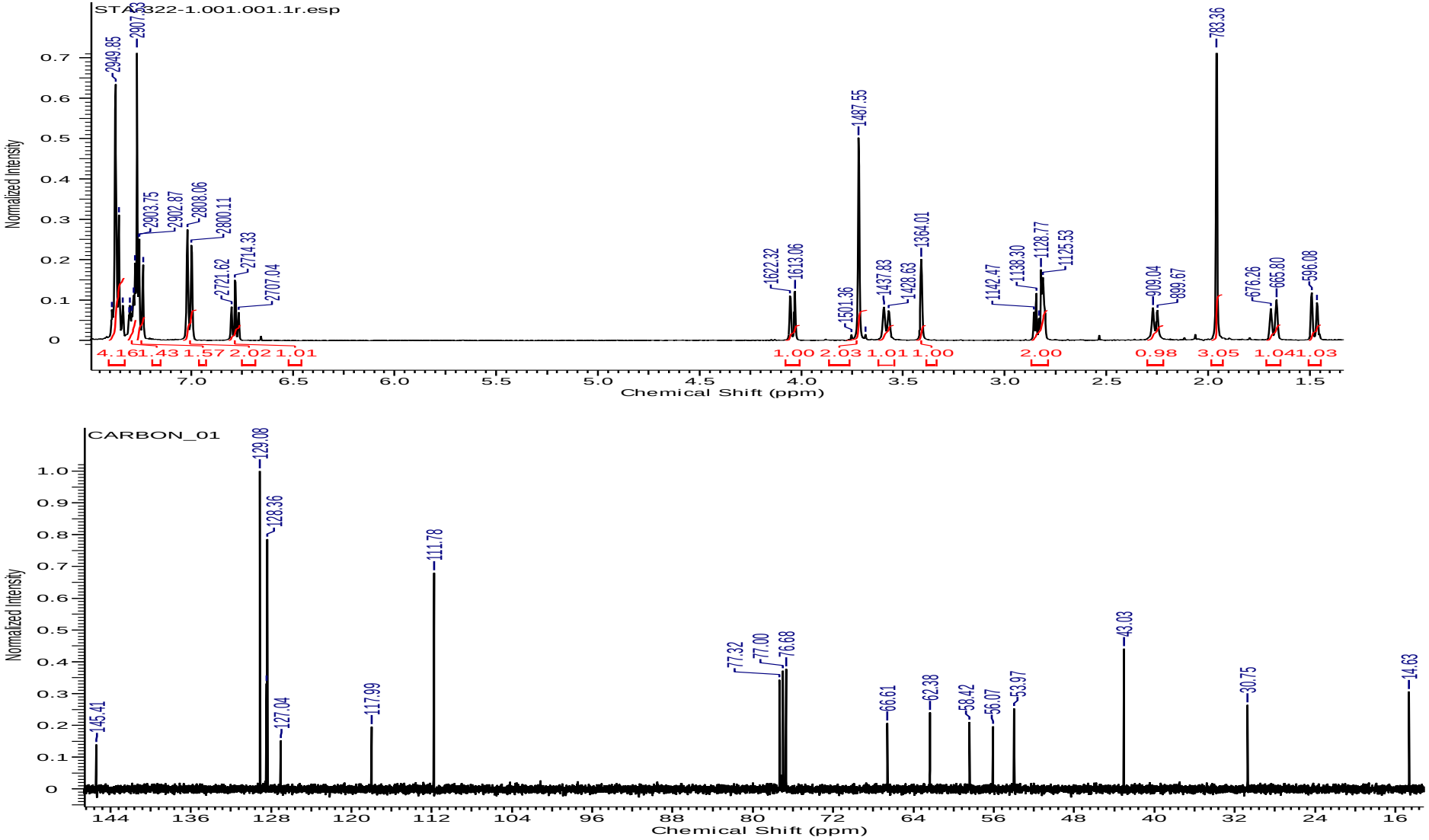


Figure S7. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3c**

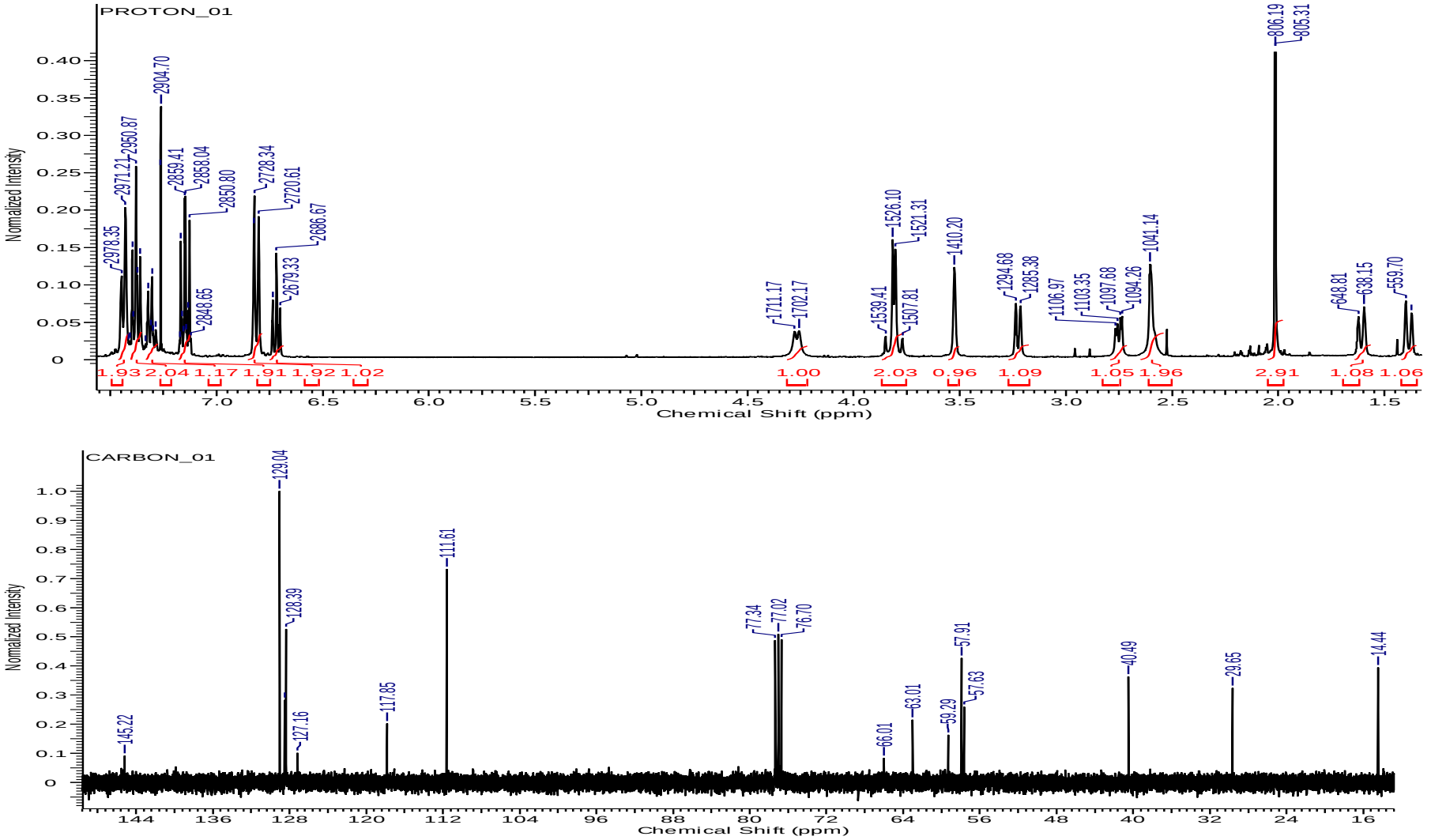


Figure S8. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4c**

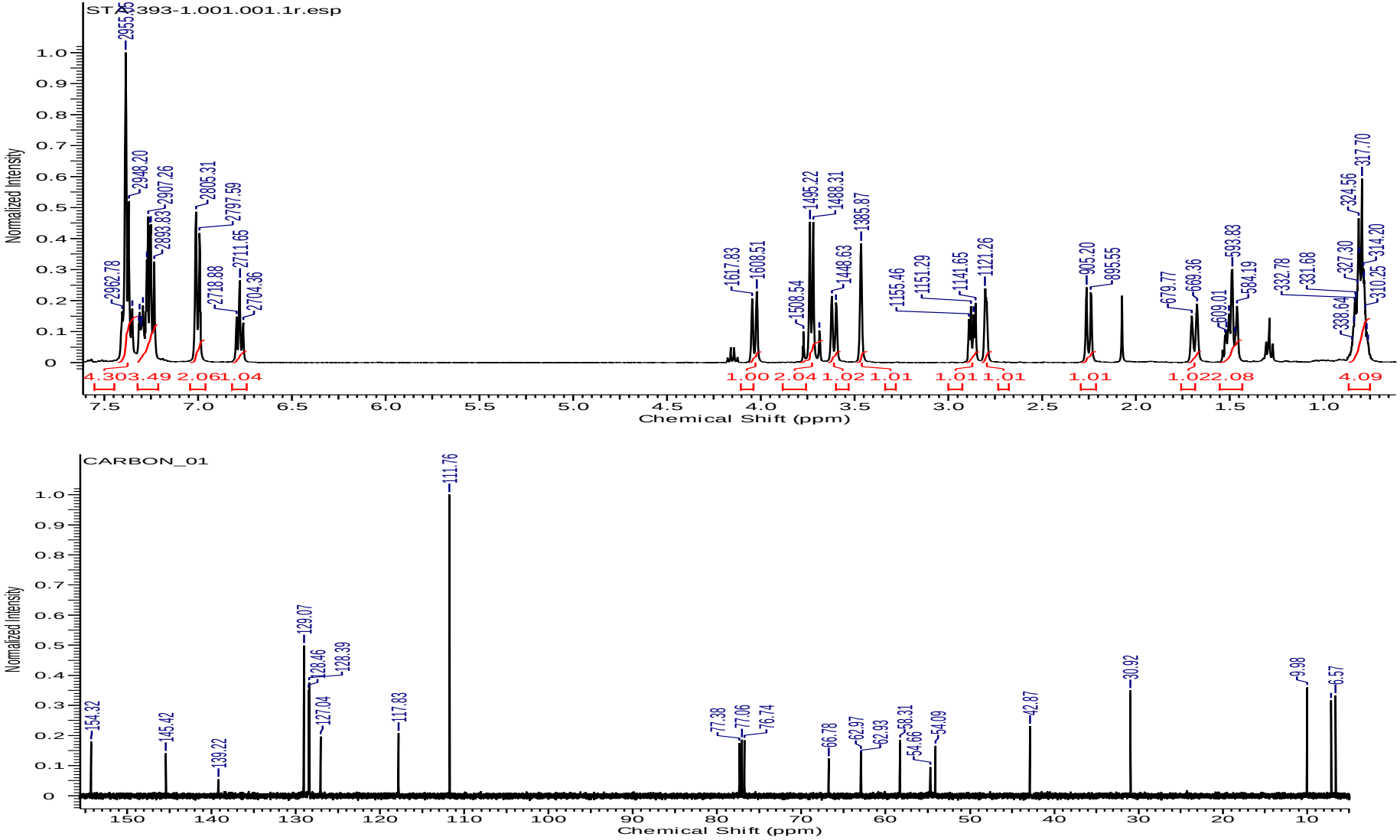


Figure S9. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3d**

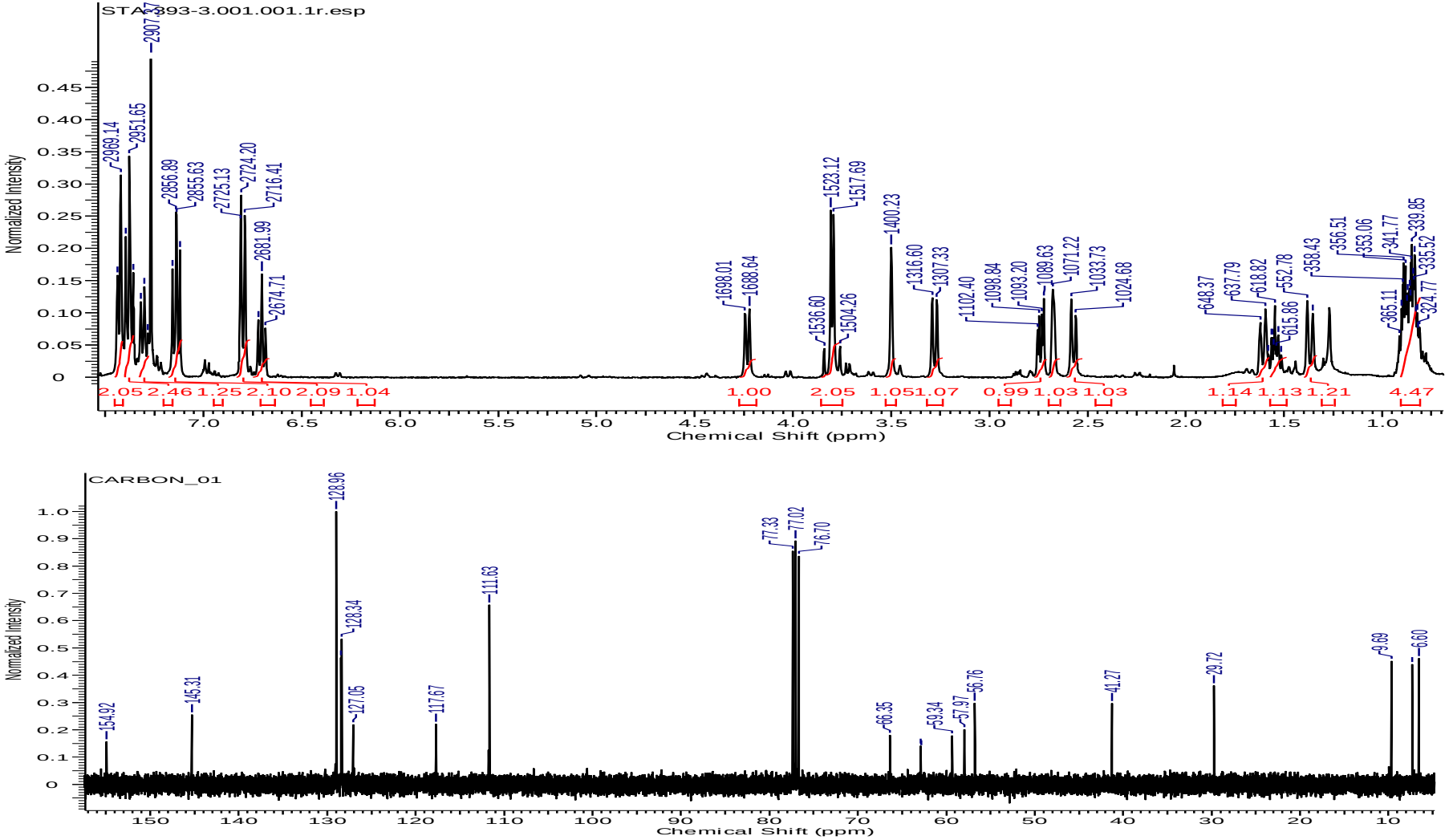


Figure S10. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4d**

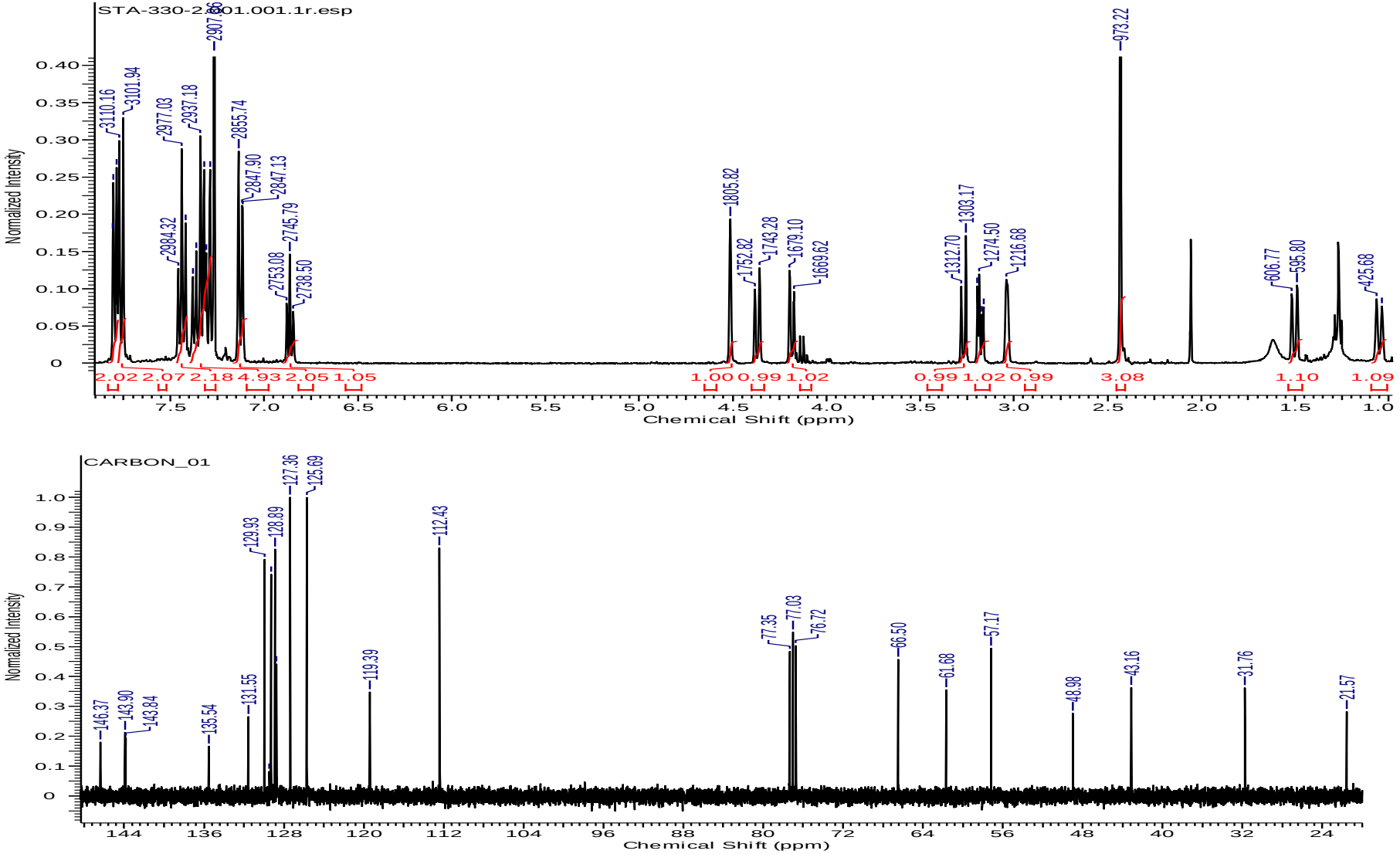


Figure S11. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3e**

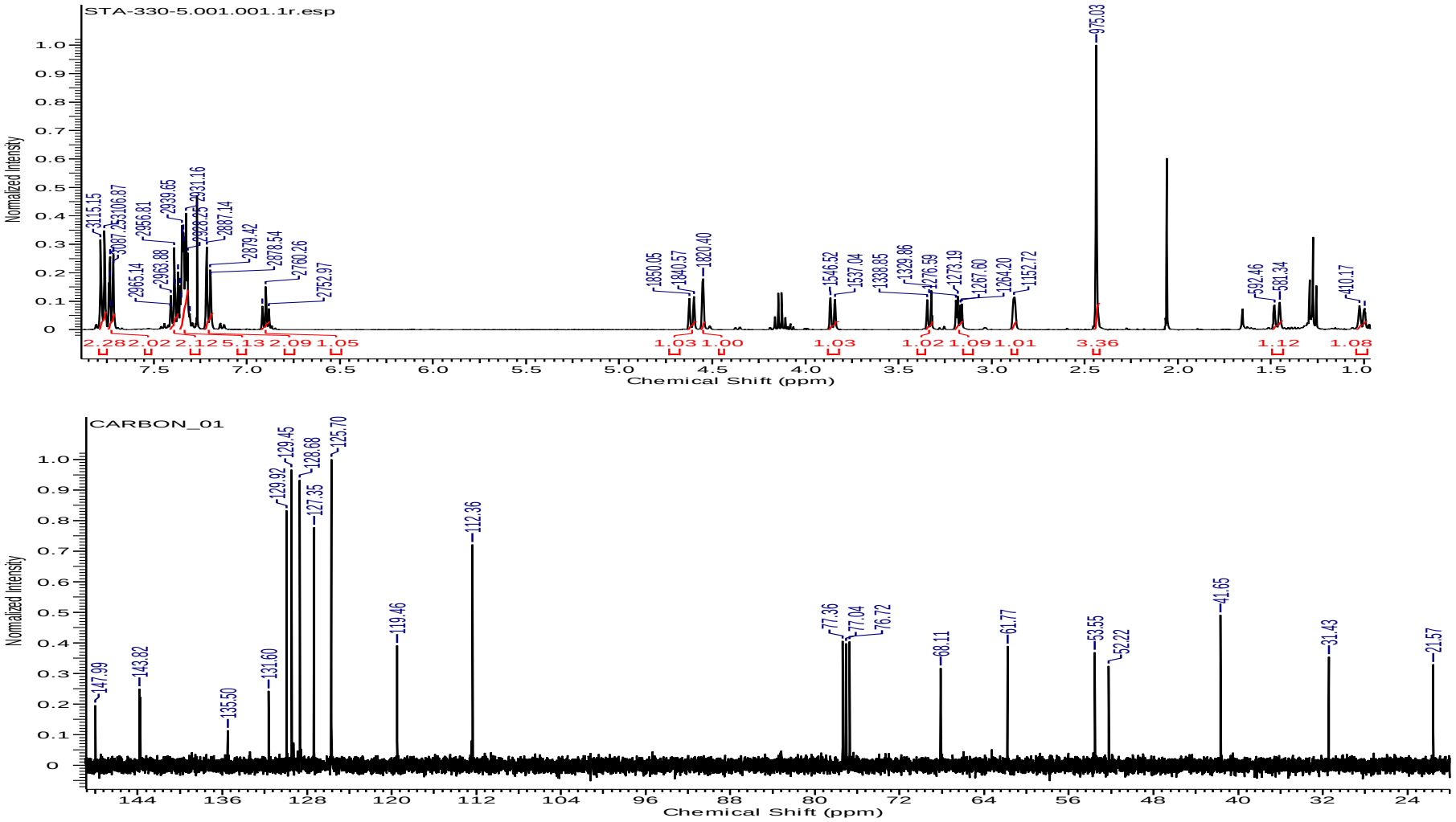


Figure S12. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4e**

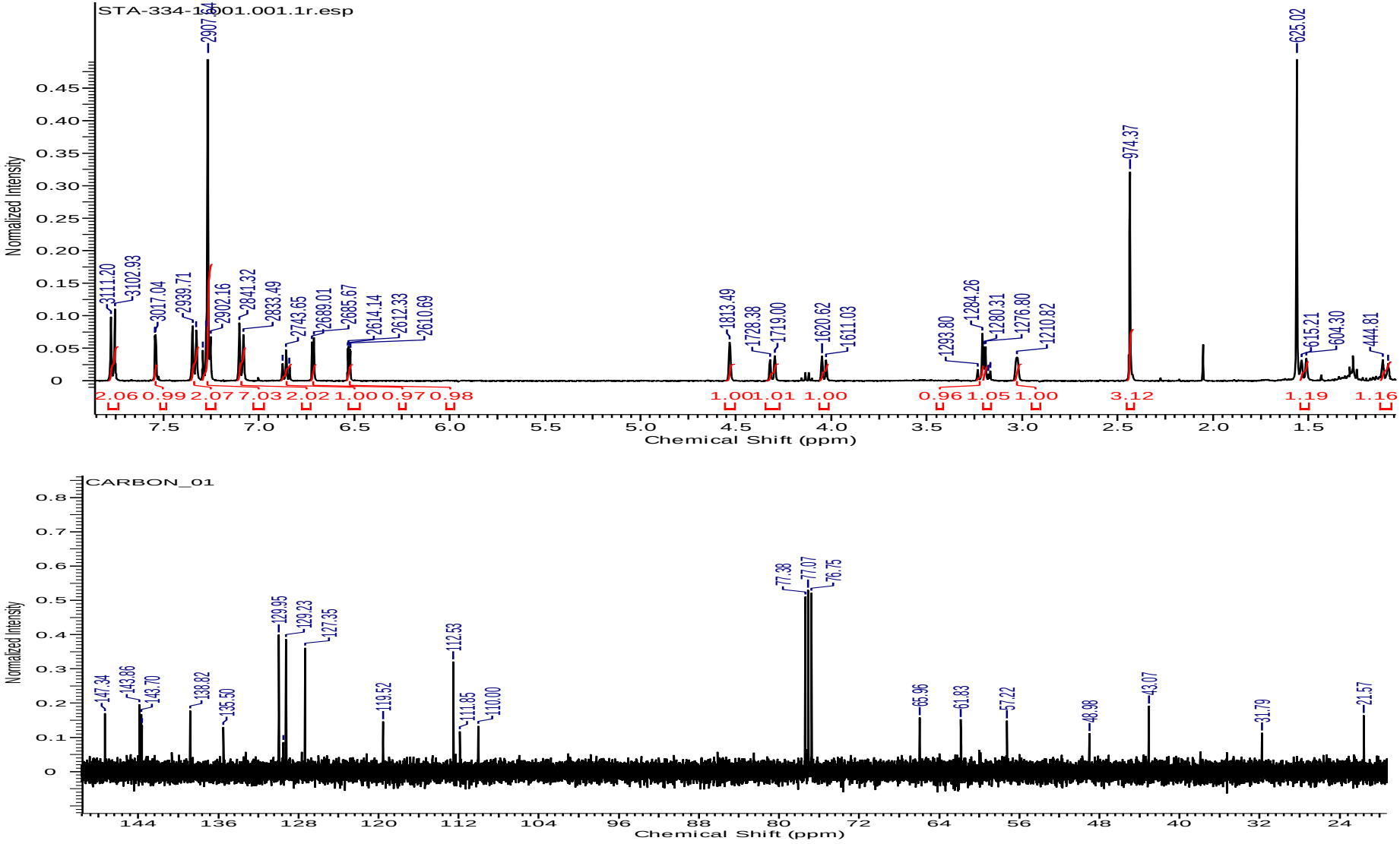


Figure S13. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3f**

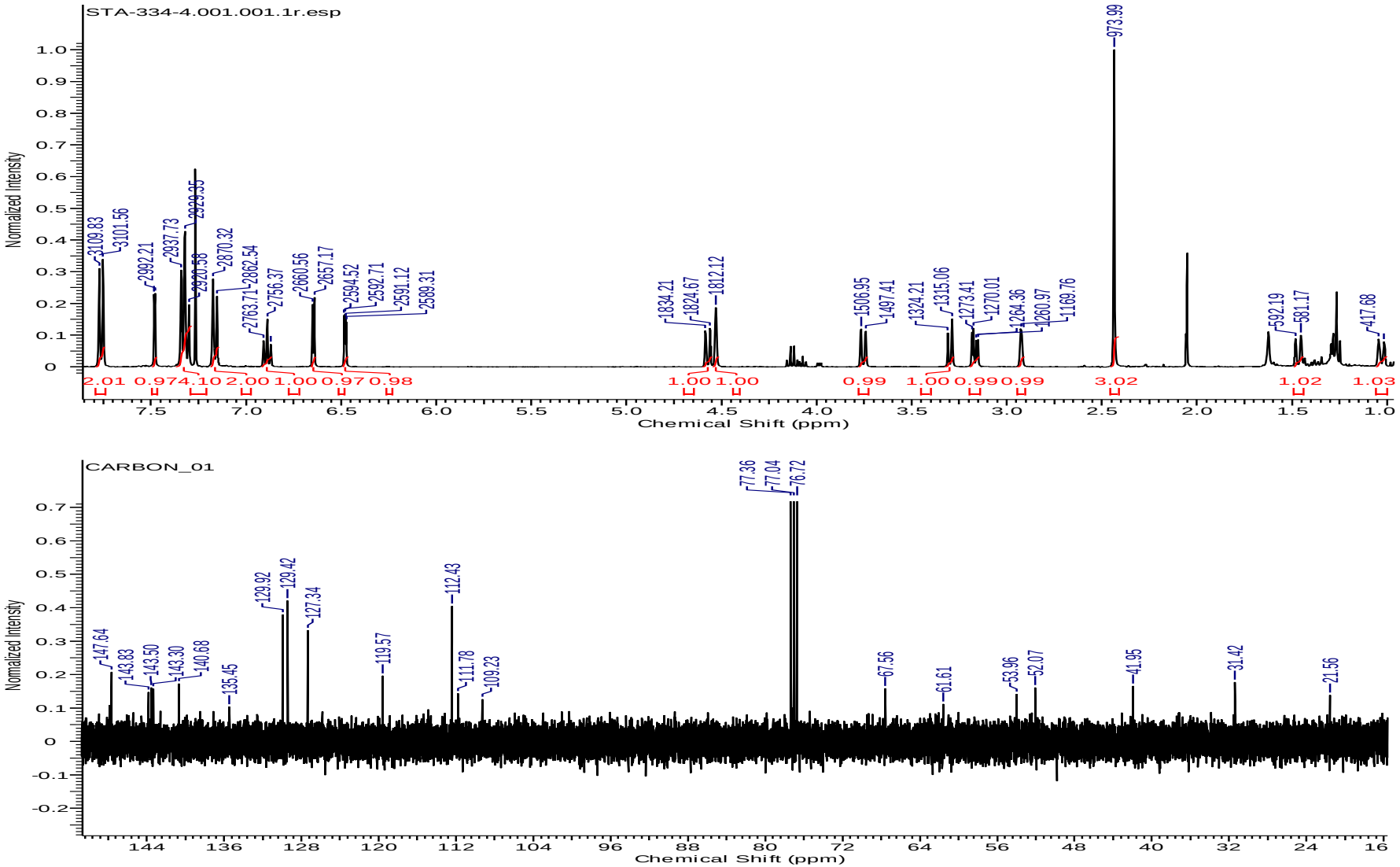


Figure S14. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4f**

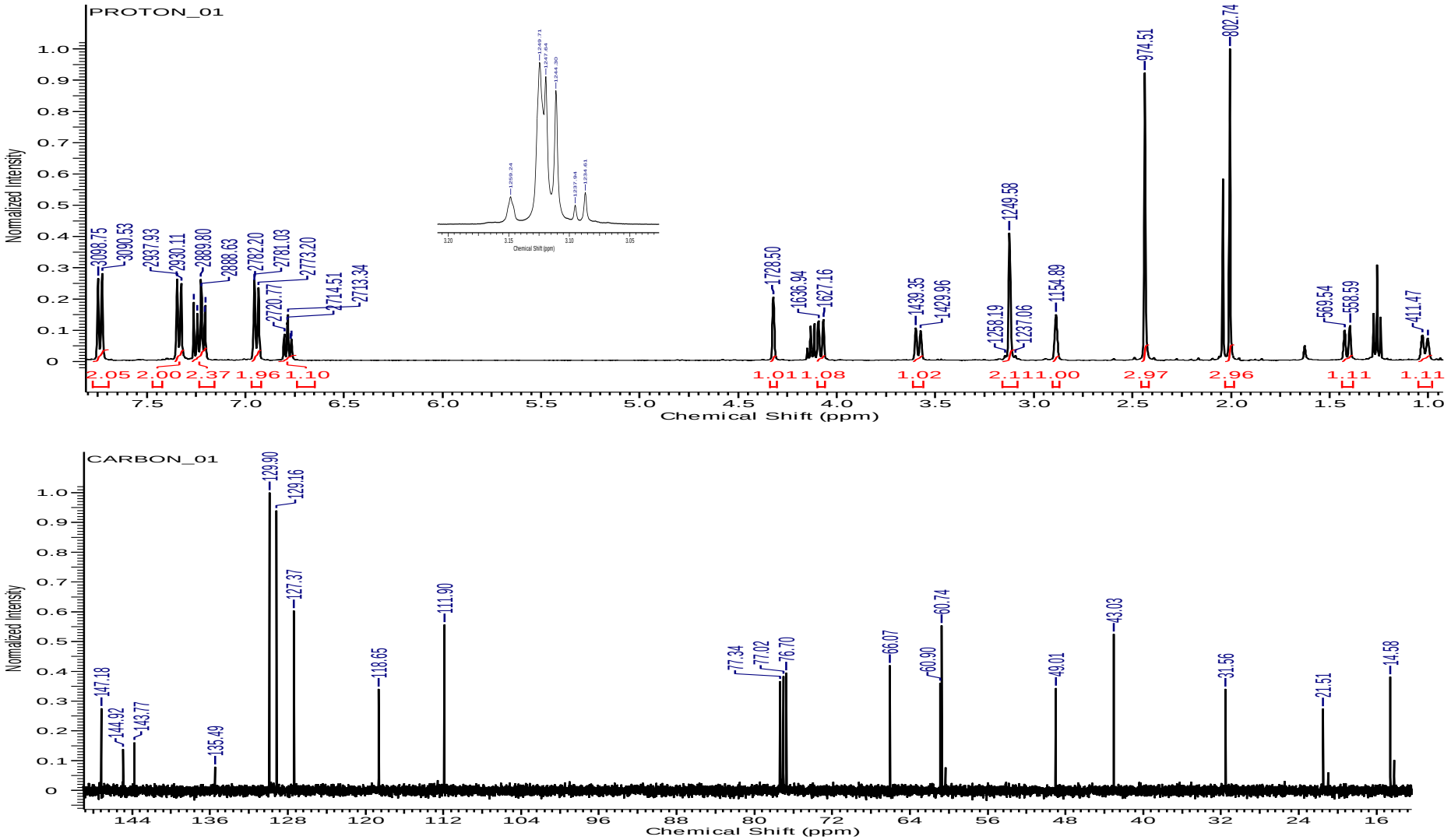


Figure S15. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3g**

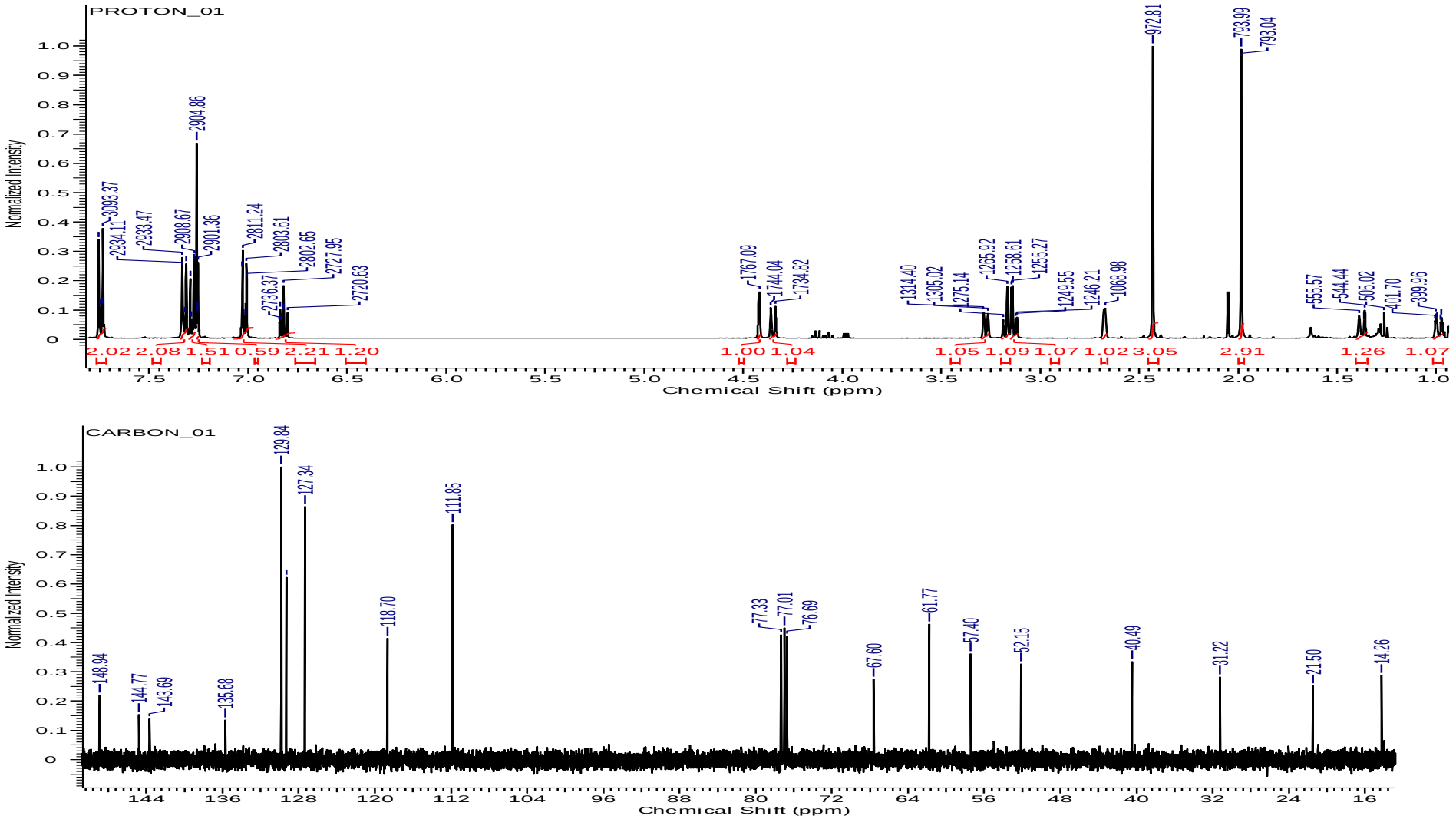


Figure S16. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4g**

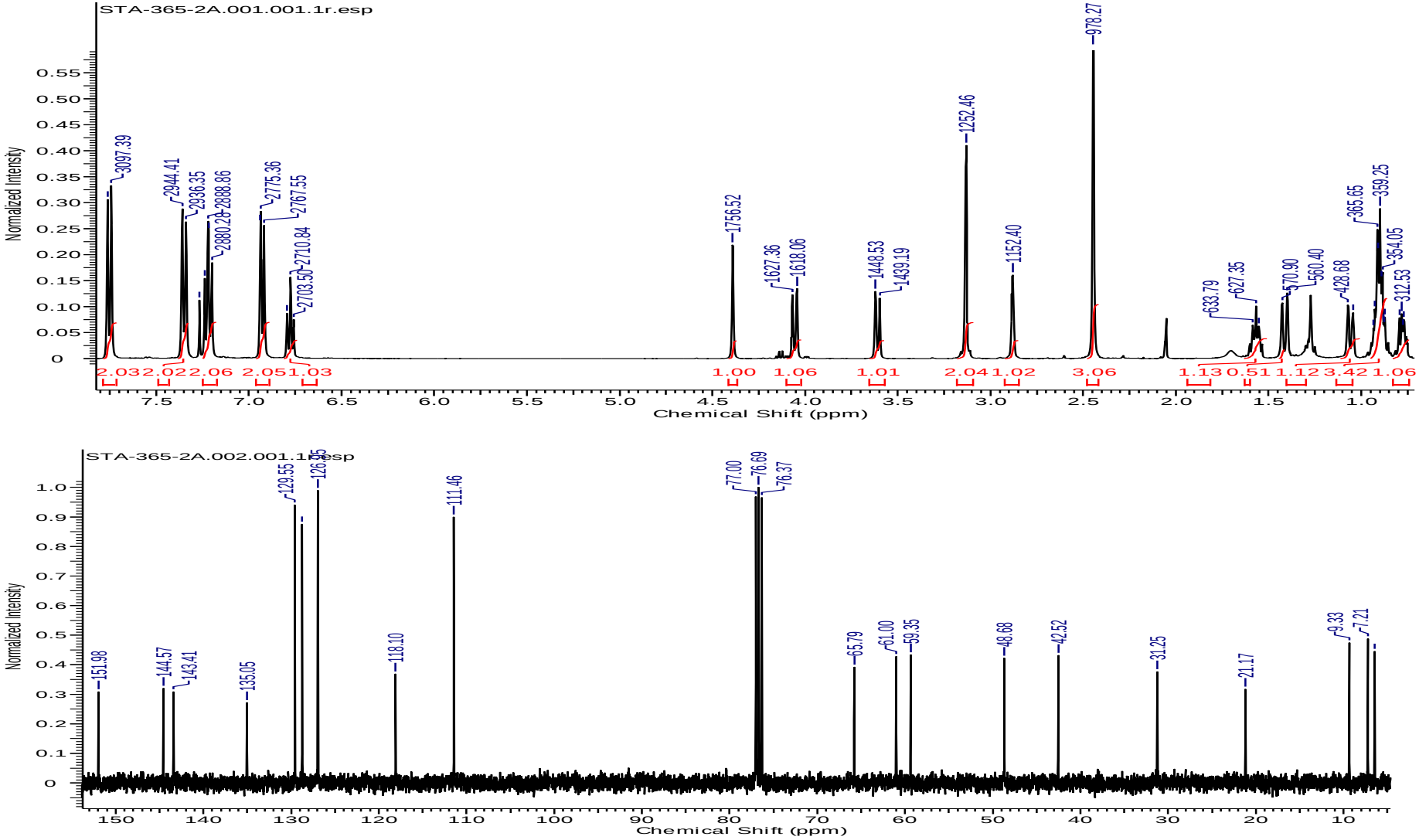


Figure S17. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3h**

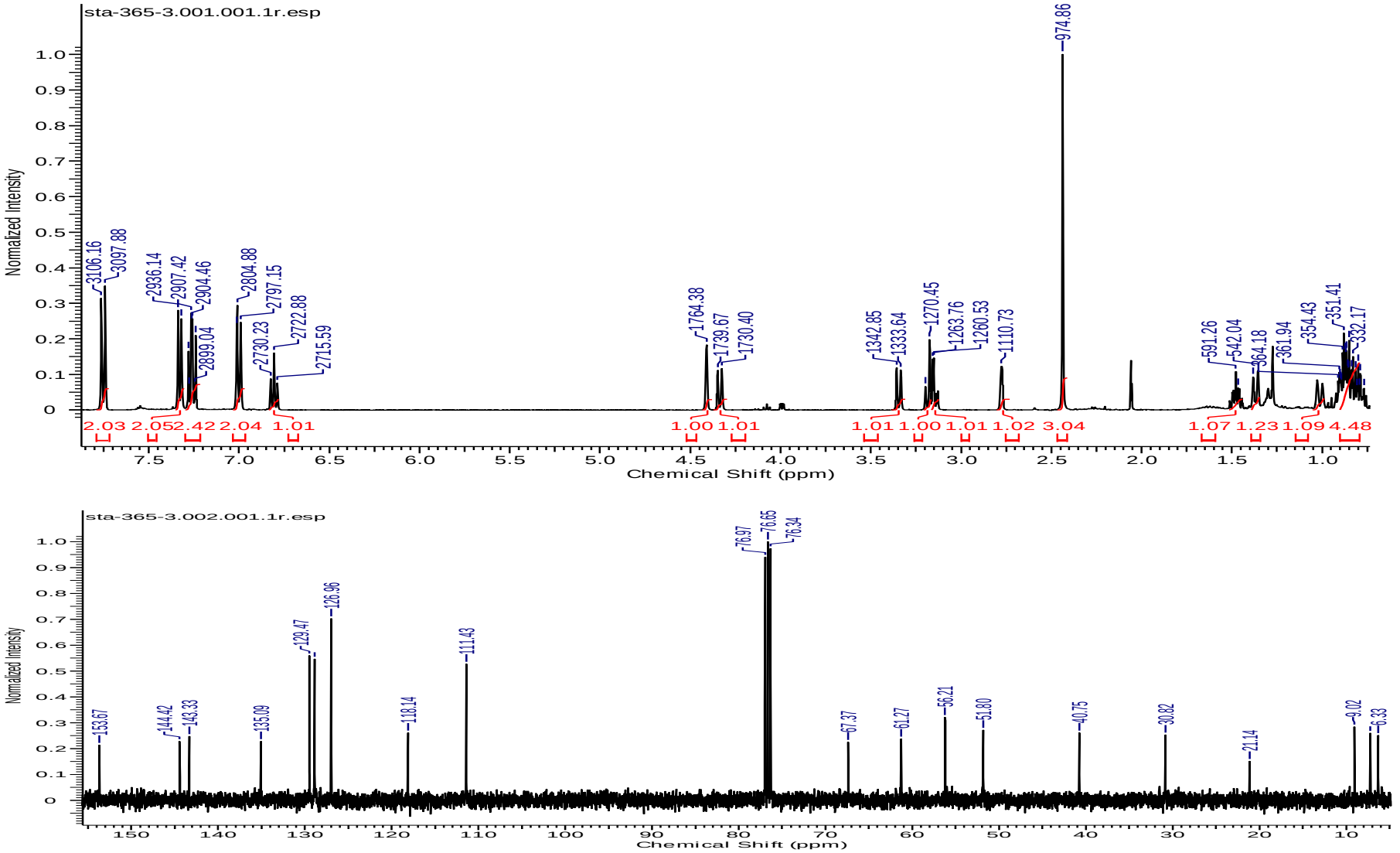


Figure S18. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4h**

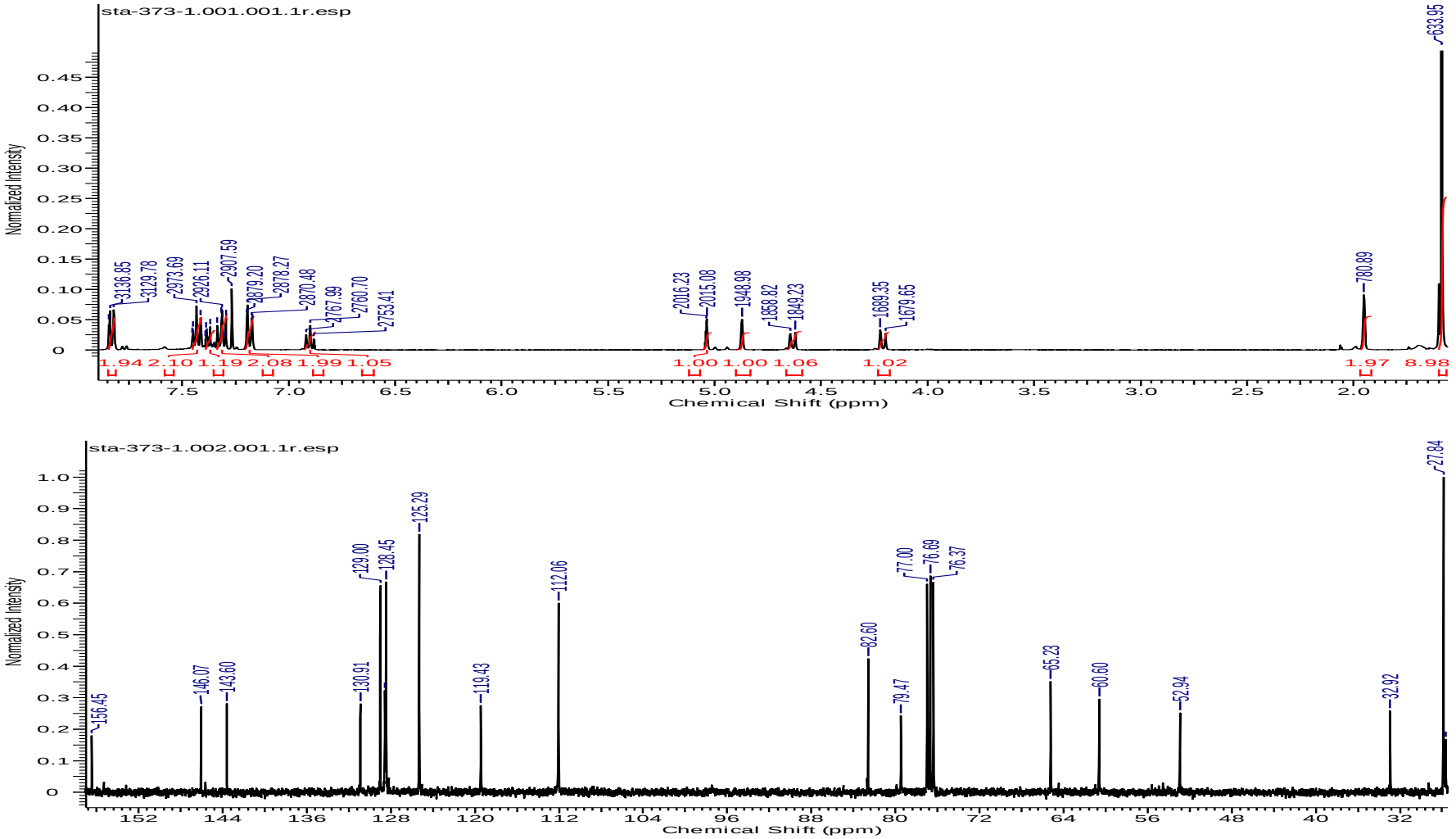


Figure S19. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3i**

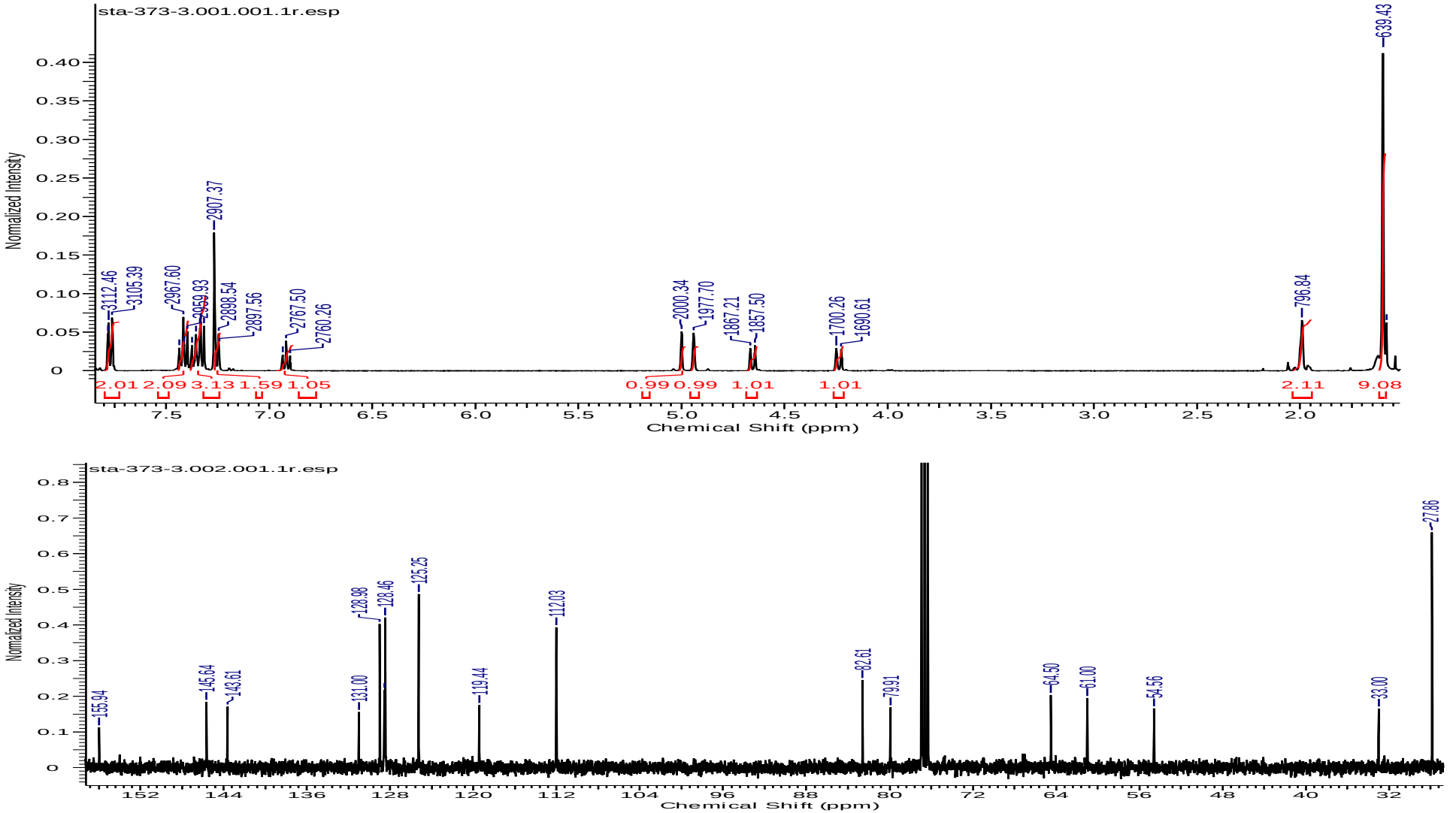


Figure S20. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4i**

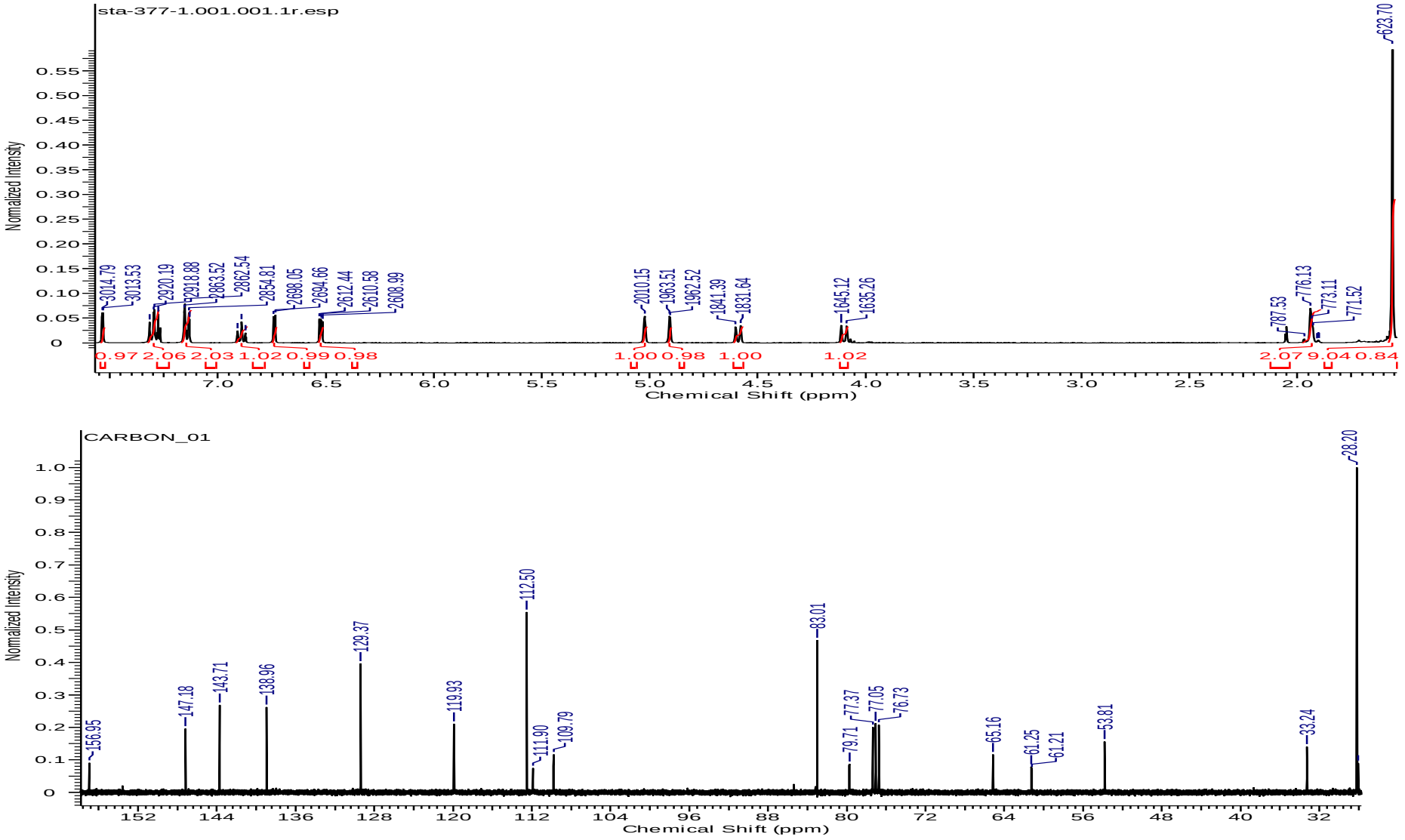


Figure S21. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3j**

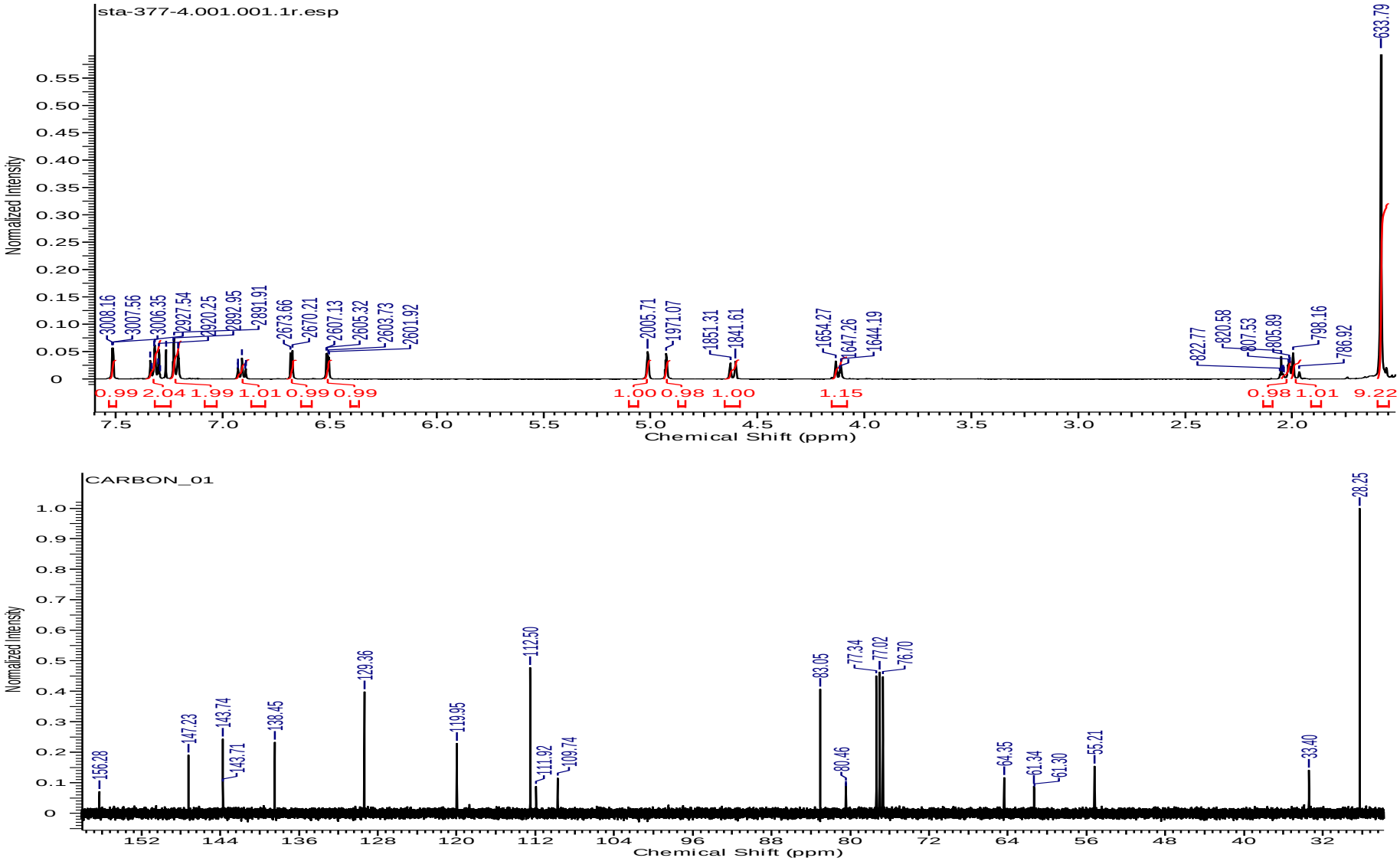


Figure S22. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4j**

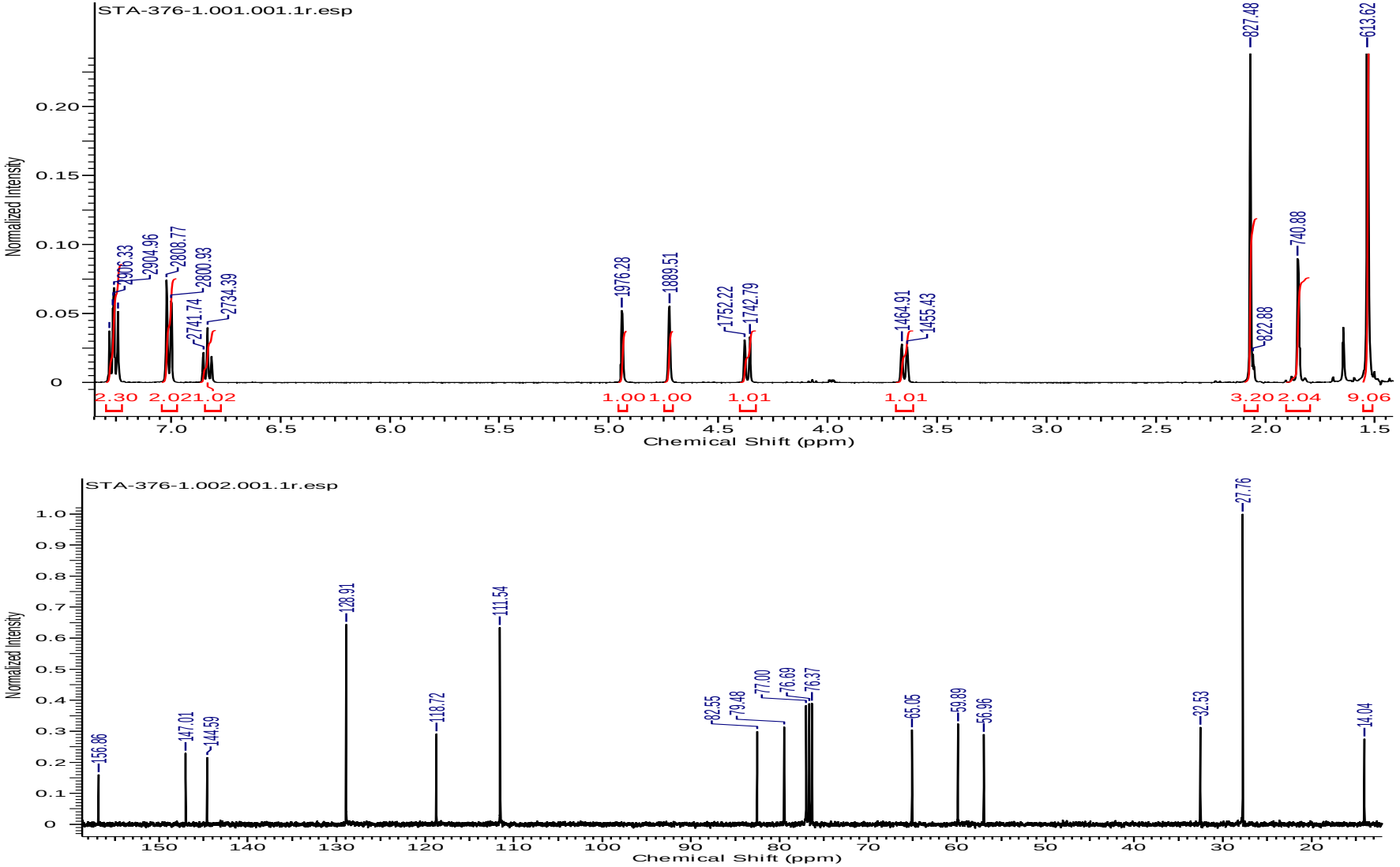


Figure S23. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3k**

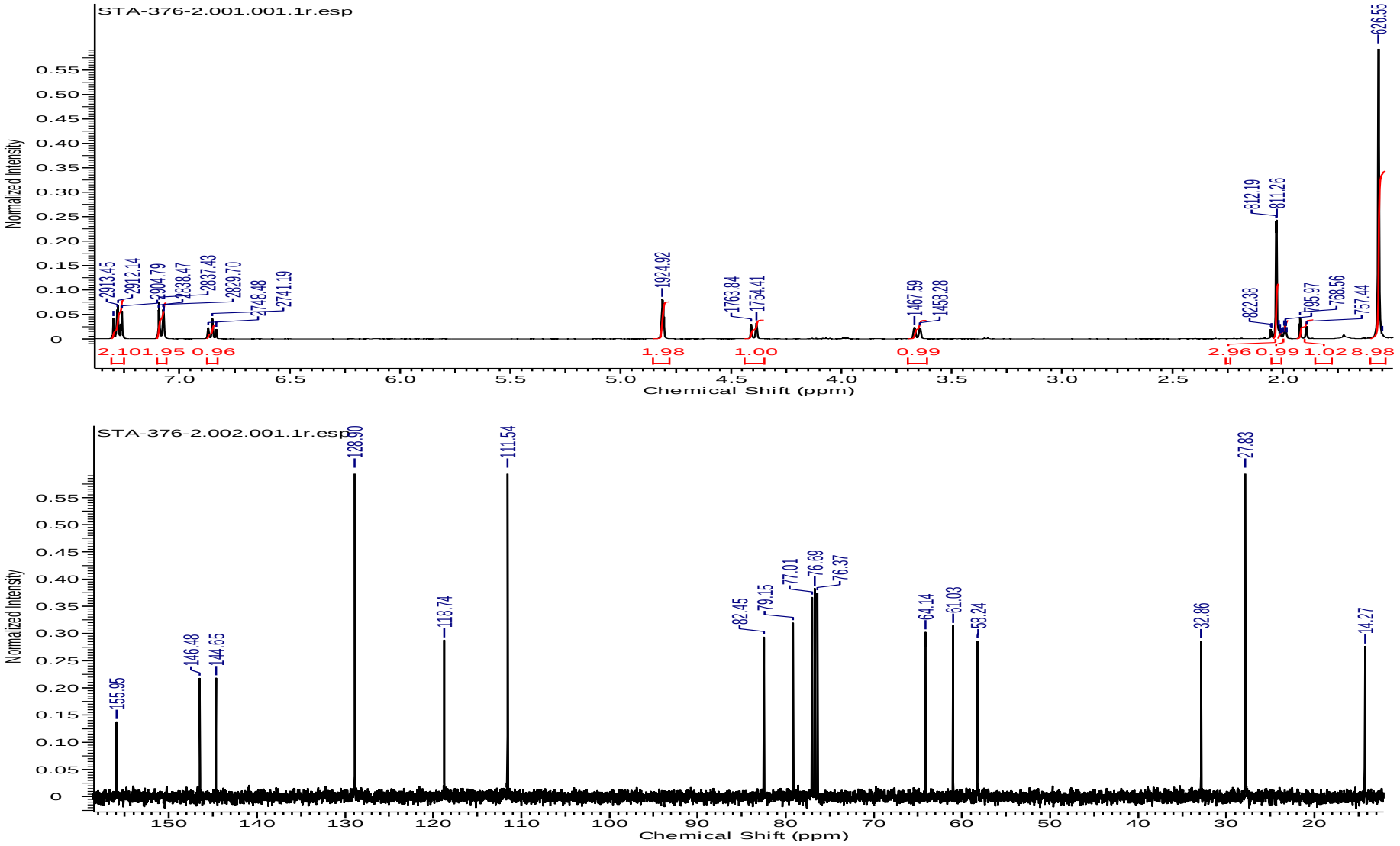


Figure S24. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4k**

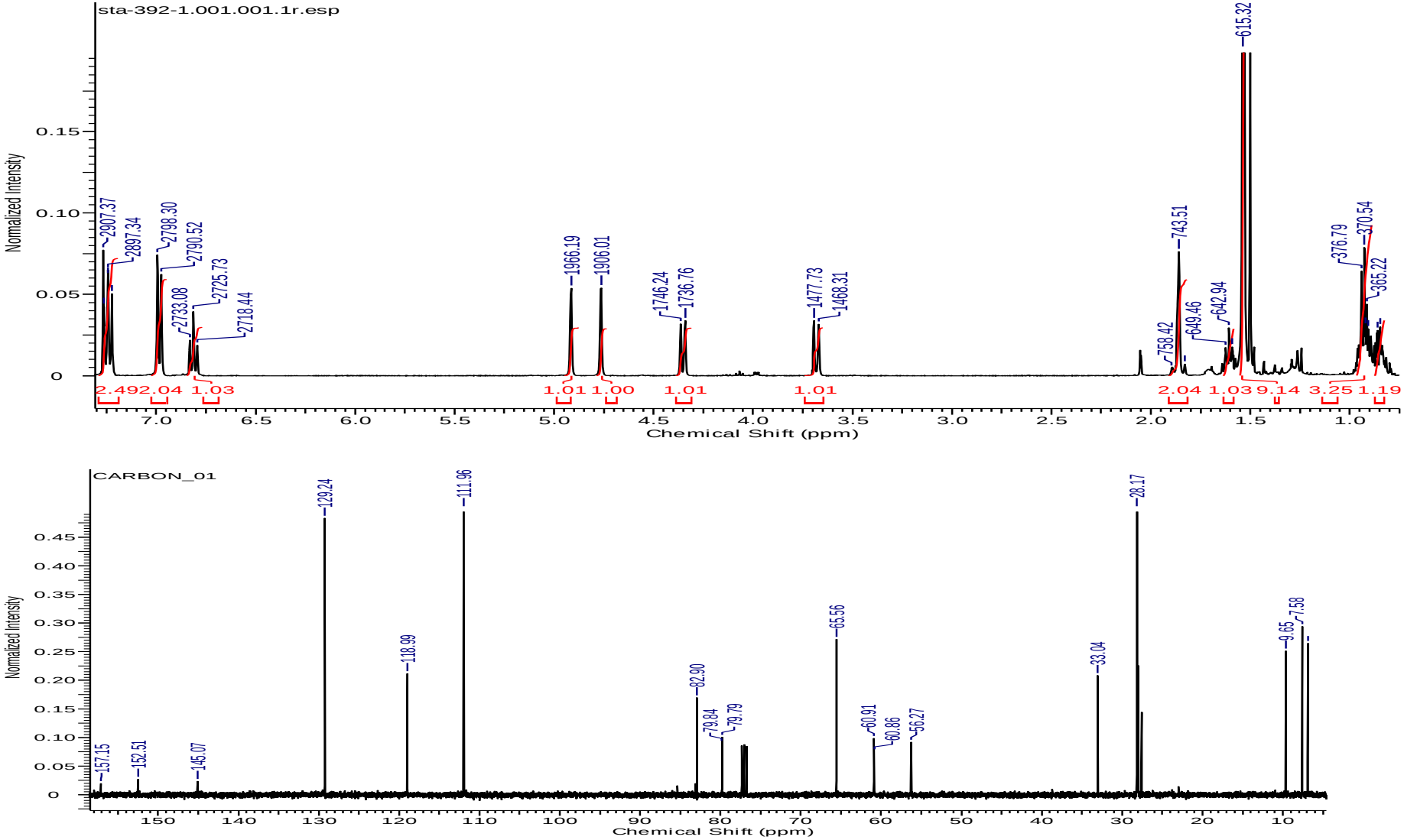


Figure S25. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **3l**

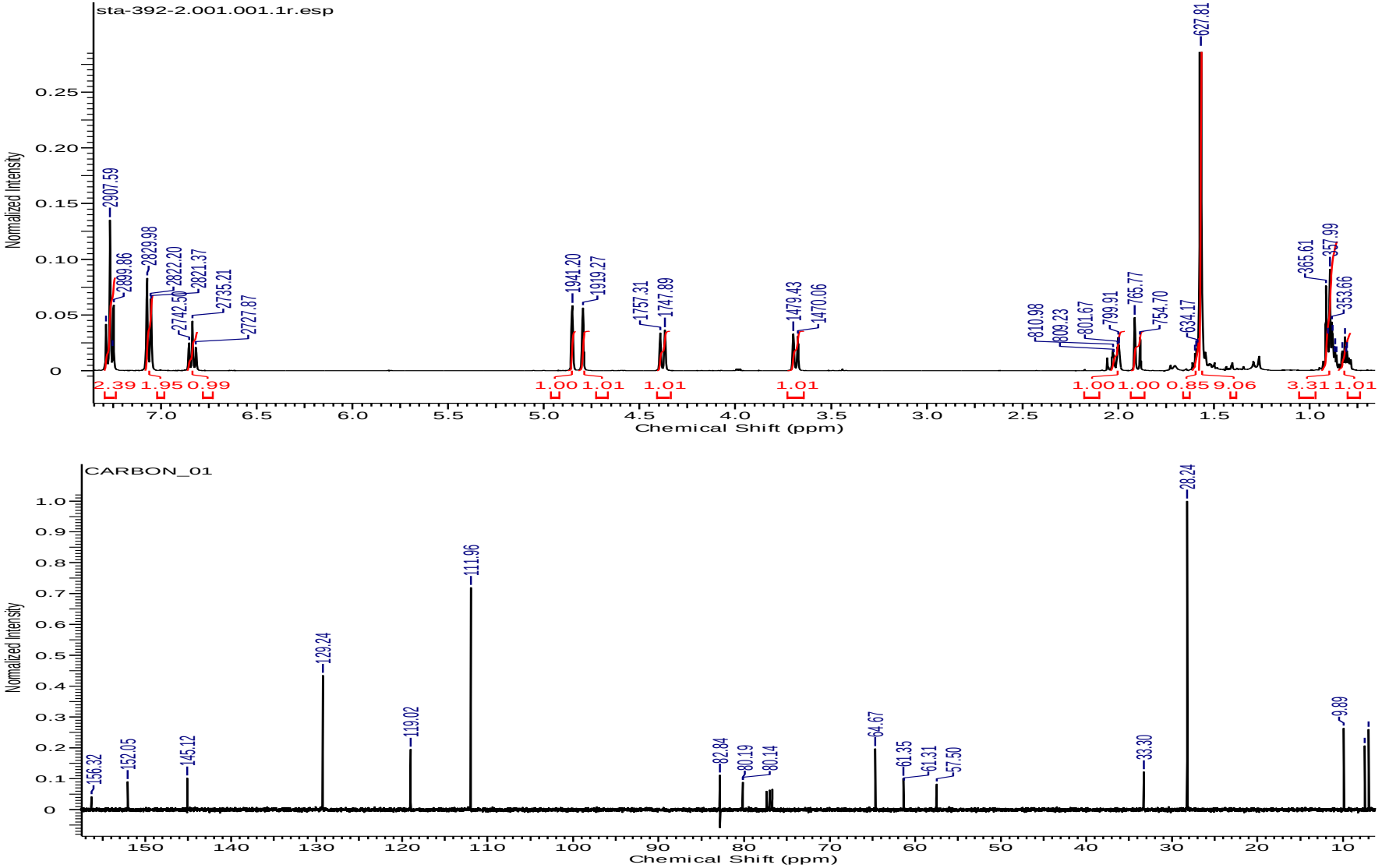


Figure S26. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **4l**

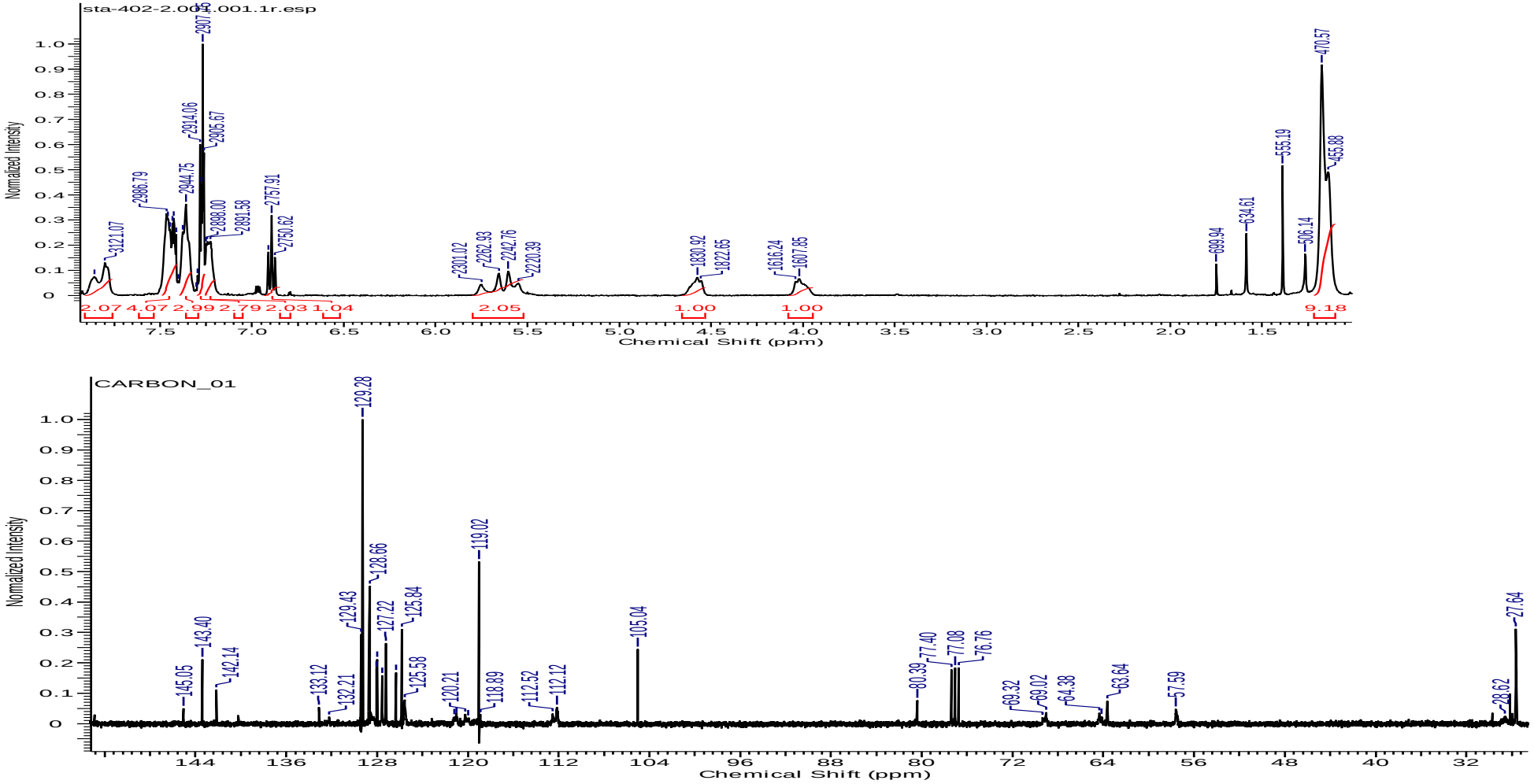


Figure S27. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **6a**

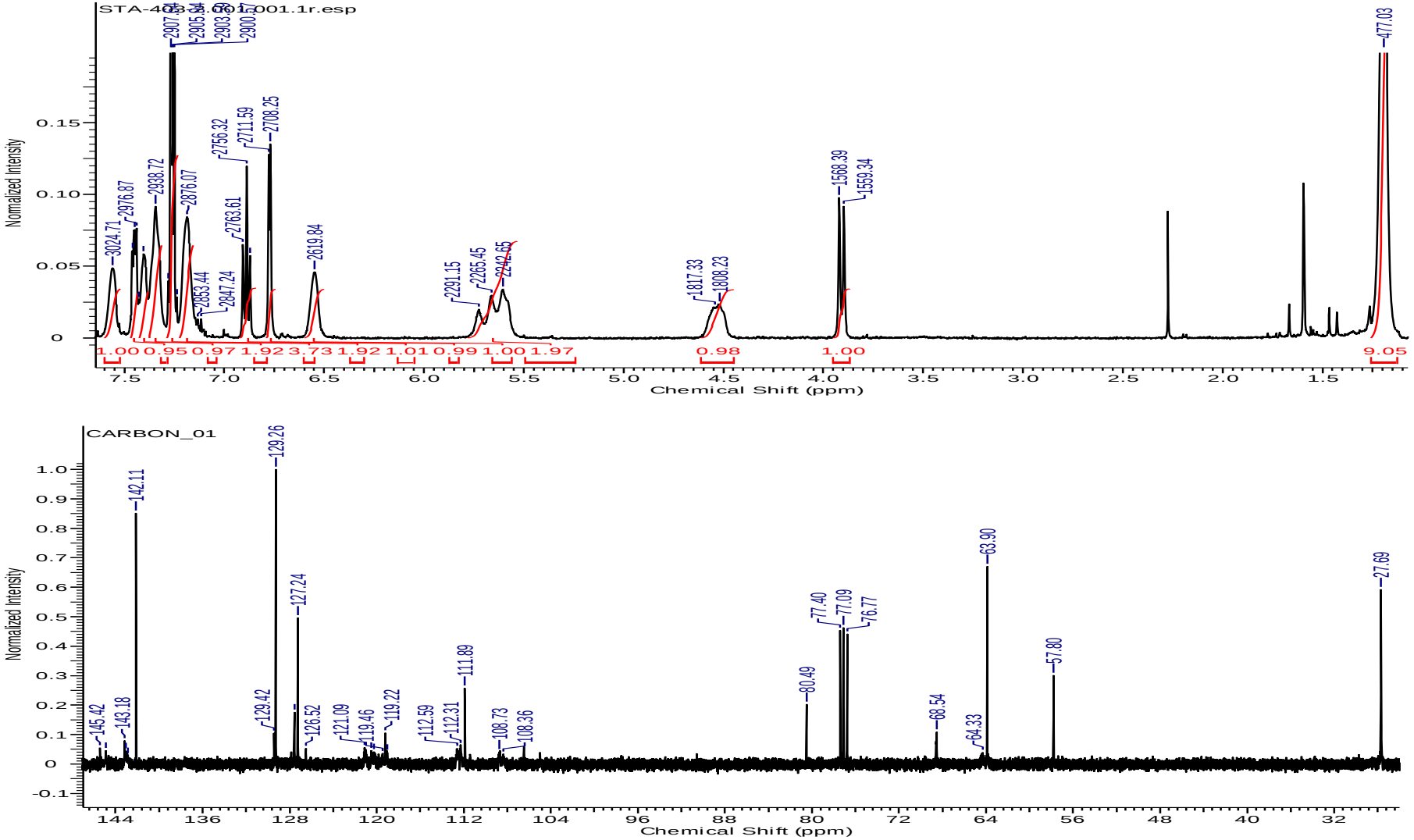


Figure S28. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **6b**

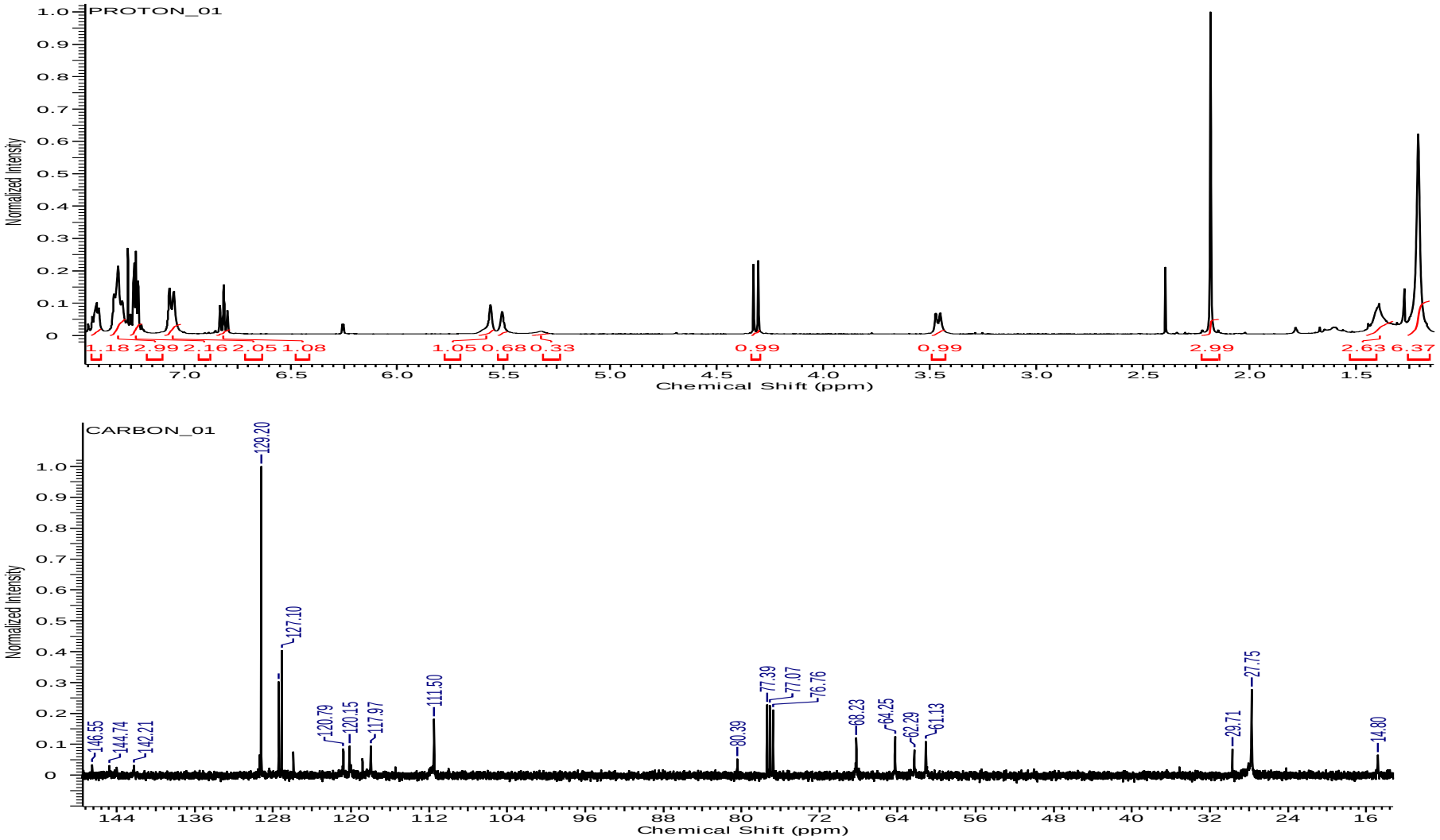


Figure S29. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **6c**

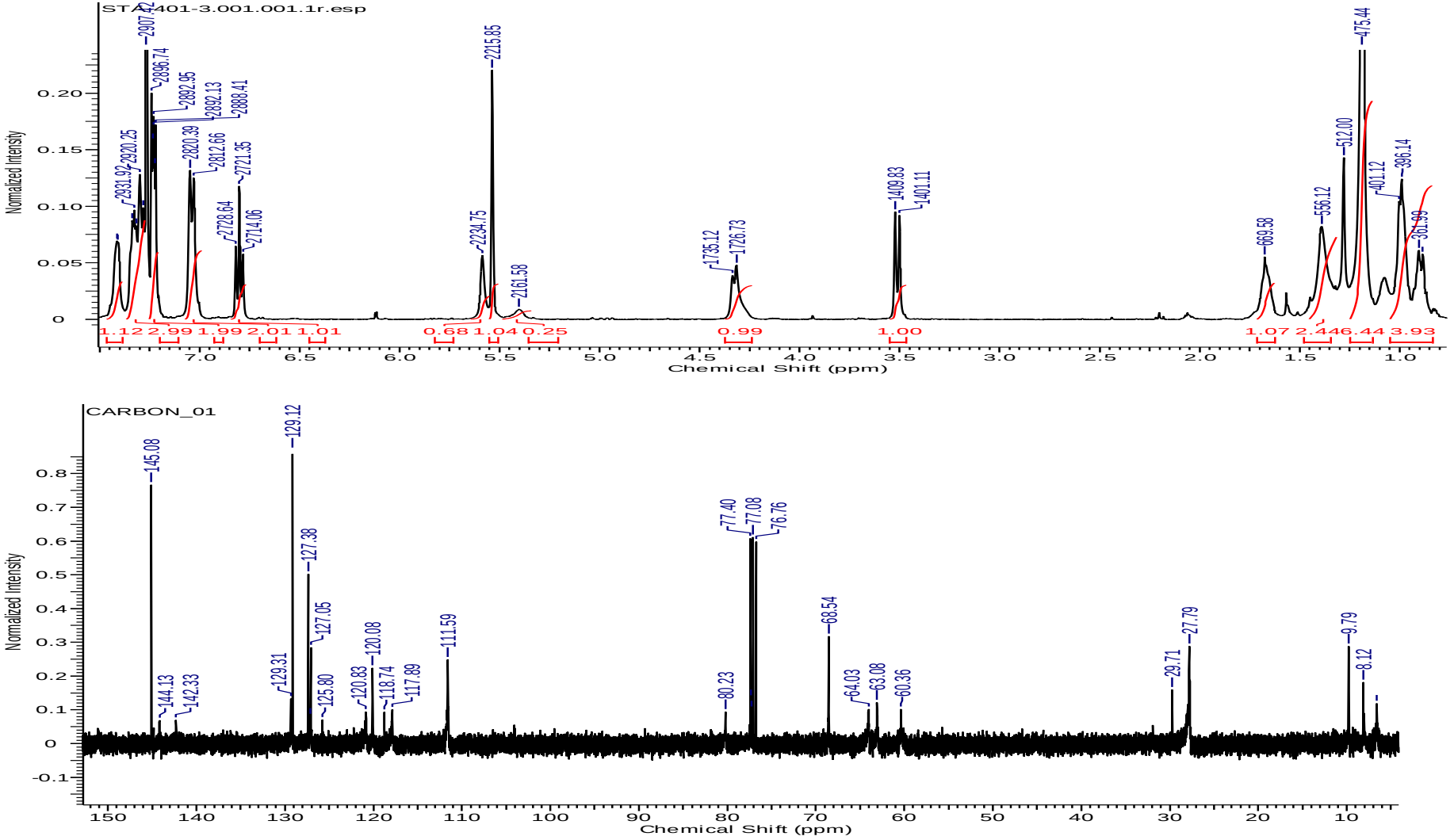


Figure S30. ^{1}H and ^{13}C NMR spectrum ($CDCl_3$) of **6d**