Electronic supplementary materials *Mendeleev Commun*., 2025, **35**, 521–523

Synthesis of 3-amino triterpenes involving the $NaBH_3CN/MoCl_5$ reduction of the oxime precursors

Albina A. Shalina, Leysan R. Idrisova, Andrey V. Nemtarev, Timur I. Abdullin and Vladimir F. Mironov

Table of Contents

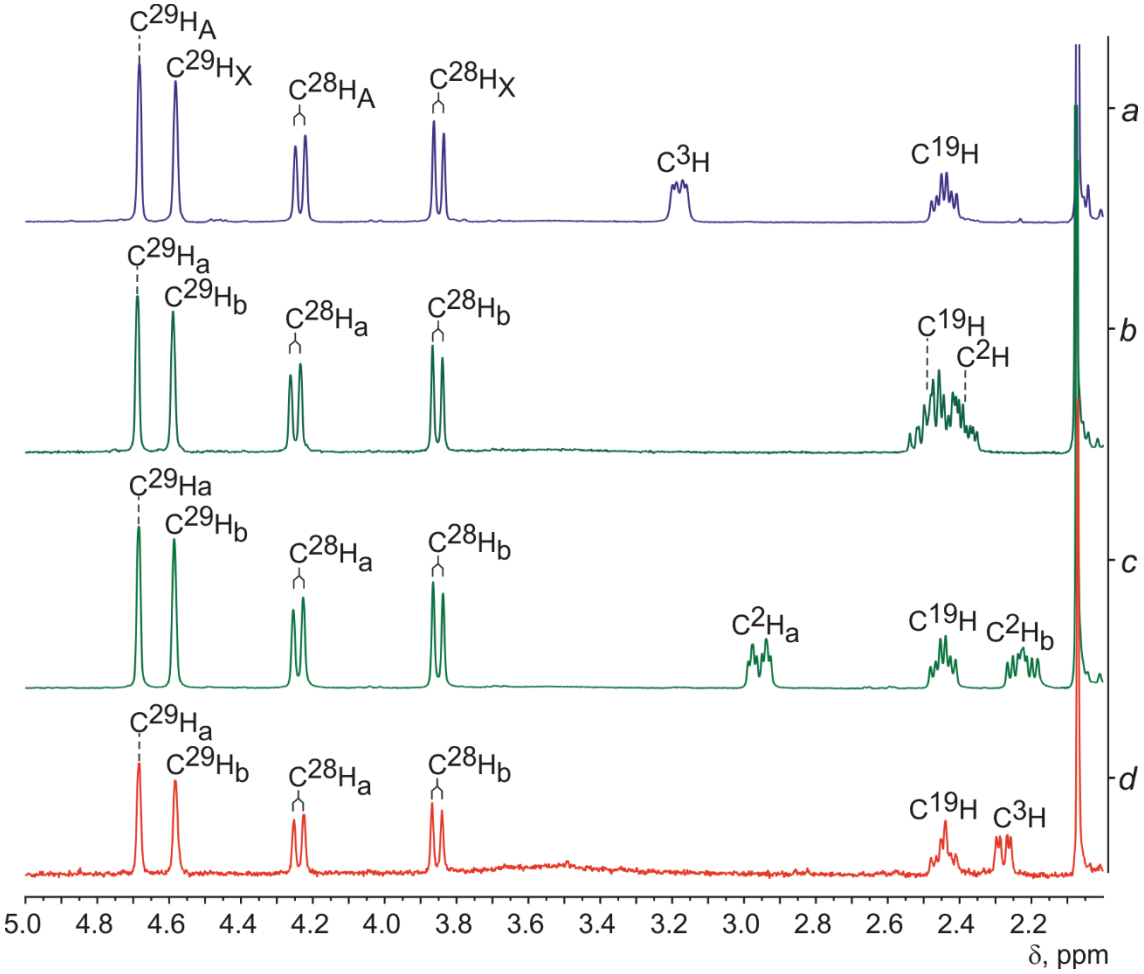
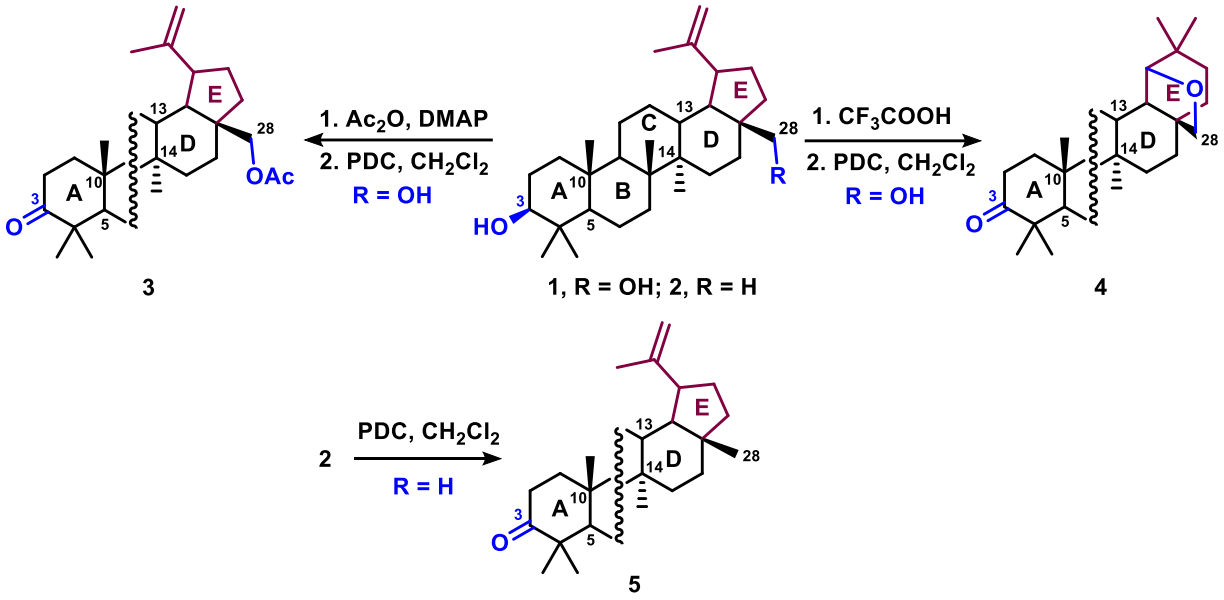


Figure S1 Fragments of the ^{1}H NMR spectra (400 MHz, $CDCl_3$) of 3β-hydroxy-28-acetoxylup-20(29)-ene (*a*), keto derivative **3** (*b*), oxime **6** (*c*), and amine **10** (*d*).

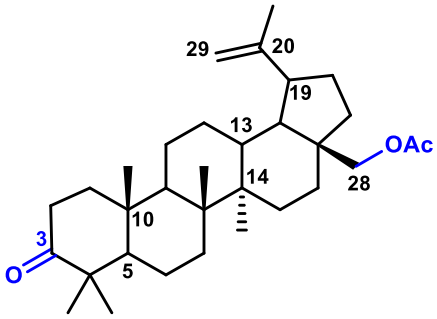
Experimental data

General remarks. The NMR spectra were recorded at 25 °C using a Bruker Avance-400 NMR spectrometer (400.0 MHz, ^{1}H; 100.6 MHz, ^{13}C). Chemical shifts are referenced to the residual solvent peak and reported in ppm (δ scale) and all coupling constant (*J*) values are given in Hz. IR spectra were recorded using a Bruker Vector-22 and a Bruker Tenzor-27 spectrometers for samples in KBr pellets. The ESI MS measurements were performed using an Amazon X ion trap mass spectrometer (Bruker Daltonic GmbH, Bremen, Germany) in positive mode in the mass range of 70–3000. The capillary voltage was − 3500 V, nitrogen drying gas – 10 L·min^{-1}, desolvation temperature – 250 °C. Data processing was performed by Data Analysis 4.0 SP4 software (Bruker Daltonik GmbH, Germany). Elemental analysis was accomplished with an automated EuroVector EA3000 CHNS elemental analyzer (Euro-Vector, Italy). The progress of reactions and the purity of products were monitored by TLC on Sorbfil plates (IMID Ltd., Russian Federation). The TLC plates were visualized by treatment with phosphotungstic acid in ethanol, followed by heating to 120 °C. Solvents were purified and dried by standard protocols.



General procedure for the synthesis of 3-oxo-derivatives 3-5.

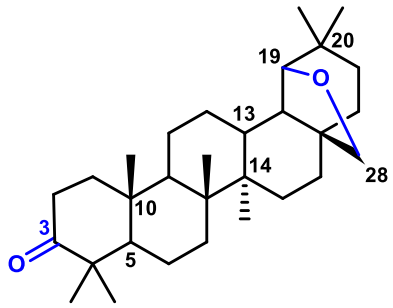
3-Hydroxy triterpene (such as 3*β*-hydroxy-28-acetoxylup-20(29)-ene, 3*β*-hydroxy-19*β*,28-epoxyoleanane (allobetulin) or 3*β*-hydroxylup-20(29)-ene (lupeol)) (1.55 mmol) was dissolved in dry CH_2Cl_2 (30 mL) and stirred at room temperature. Then pyridinium dichromate (1.99 mmol) was added. The reaction was allowed to proceed for a total of 24 h by TLC (Pet : EtOAc = 2 : 1). The mixture was filtered through silica gel and eluted with Et_2O (70 mL). The Et_2O solution was concentrated to dryness to give a white foam solid.



3

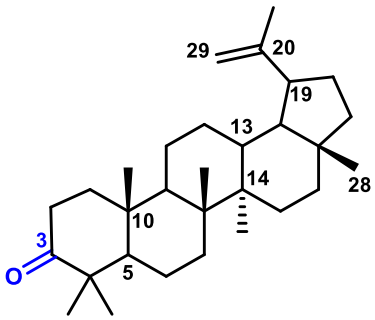
28-Acetoxylup-20(29)-en-3-one 3. Prepared from 0.145 g of 3*β*-hydroxy-28-acetoxylup-20(29)-ene. Yield: 0.141 g (98%), white amorphous substance. ^{1}H and ^{13}C NMR spectroscopic data of **3** were in agreement with published data[S1]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.93, 0.98, 1.02, 1.07, 1.56 (five s, 15*H*, $C^{23\text{-}27}H_3$), 1.68 (s, 3*H*, H^{30}), 1.12 – 2.04 (m, 24*H*), 2.06 (s, 3*H*, OAc), 2.35 – 2.55 (m, 1*H*, H^{19}, $^3J_{HH}$ 12.0, $^3J_{HH}$ 5.9), 3.85 (d, 1*H*, $C^{28}H_A$, $^3J_{HH}$ 10.8), 4.25 (d, 1*H*, $C^{28}H_B$, $^3J_{HH}$ 11.1), 4.59 (br. s, 1*H*, $C^{29}H_A$), 4.69 (d, 1*H*, $C^{29}H_B$, $^3J_{HH}$ 2.4). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 14.8, 15.4, 16.1, 16.2, 18.3, 19.2, 20.9, 21.1, 25.3, 27.1, 27.5, 28.1, 29.6,

29.8, 34.2, 34.6, 37.2, 37.6, 38.7, 38.9, 40.9, 42.8, 46.4, 47.7, 48.8, 50.4, 55.4, 62.8 (C^{28}), 109.9 (C^{29}), 150.2 (C^{20}), 171.7 (C^{31}), 217.57 (C^{3}).



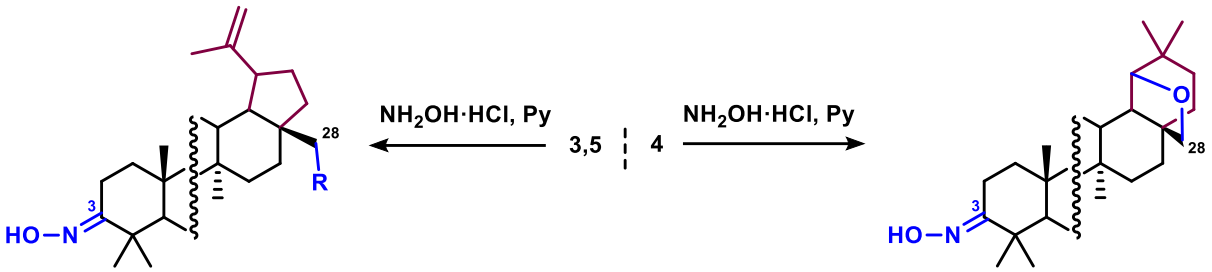
4

19*β*,28-Epoxy-18*α*-oleanan-3-one (allobetulone) 4. Prepared from 0.219 g of allobetulin. Yield: 0.202 g (93%), white amorphous substance. ^{1}H and ^{13}C NMR spectroscopic data of **4** were in agreement with published data[S2]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.79, 0.92, 0.93, 0.94, 1.01, 1.03, 1.08 (seven s, 21*H*, CH_3), 1.05 – 2.56 (m, 24*H*), 3.45 (d, 1*H*, $C^{28}H_A$, $^{3}J_{HH}$ 7.6), 3.53 (s, 1*H*, H^{19}), 3.78 (d, 1*H*, $C^{28}H_B$, $^{3}J_{HH}$ 7.6). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 13.48, 15.37, 16.47, 18.25, 20.96, 24.52, 26.20, 26.42, 27.95, 28.78, 32.15, 32.68, 33.91, 34.10, 35.12, 36.22, 36.68, 37.25, 38.86, 38.93, 40.71, 41.49, 43.29, 46.81, 51.09, 55.50, 71.26 (C^{28}), 87.93 (C^{19}), 217.89 (C^{3}).



5

Lup-20(29)-en-3-one 5. Prepared from 0.663 g of lupeol. Yield: 0.64 g (97%), white amorphous substance. ^{1}H and ^{13}C NMR spectroscopic data of **5** were in agreement with published data[S3]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.76, 0.80, 0.83, 0.97, 0.98, 1.03 (six s, 18*H*, $H^{23\text{-}28}$), 1.05 – 1.97 (m, 24*H*), 1.68 (s, 3*H*, H^{30}), 2.44 (m, 1*H*, H^{19}), 4.59 (s, 1*H*, $C^{29}H_A$), 4.69 (s, 1*H*, $C^{29}H_B$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 14.8, 15.4, 16.1, 16.2, 18.3, 19.2, 20.9, 21.1, 25.3, 27.1, 27.5, 28.1, 29.6, 29.8, 34.2, 34.6, 37.2, 37.6, 38.7, 38.9, 40.9, 42.8, 46.4, 47.7, 48.8, 50.4, 55.4, 109.72 (C^{29}), 150.43 (C^{20}), 218.47 (C^{3}).

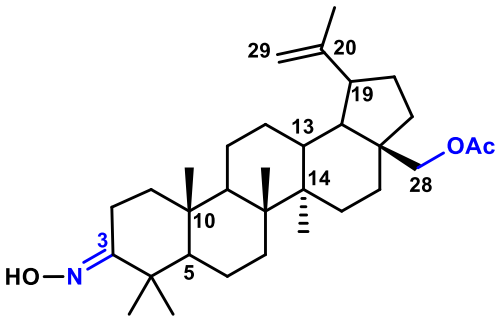


6, R = OAc; 7, R = H

8

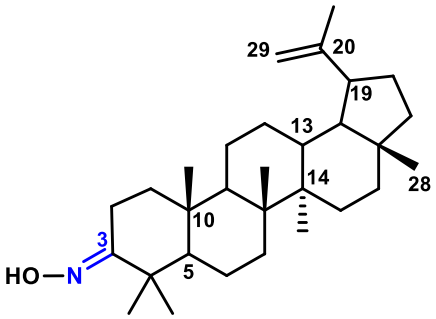
General procedure for the synthesis of oximes 6-8.

To a solution of compounds **3-5** (1 mmol) in pyridine (50 mL), $NH_2OH \cdot HCl$ (4 eq.) was added. The mixture was refluxed for 3 h. The end of the reaction was monitored by TLC (Pet:EtOAc = 9:1). CH_2Cl_2 was added to the reaction mixture, and the organic layer was washed first with a 20% hydrochloric acid solution, and then with an aqueous solution of sodium chloride and chromatographed on SiO_2 (Pet : EtOAc = 9 : 1).



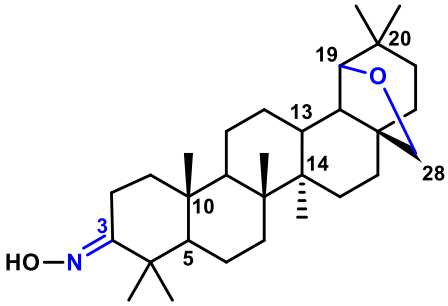
6

28-Acetoxylup-20(29)-en-3-one oxime 6. Prepared from 0.491 g of 28-acetoxylup-20(29)-en-3-one. Yield 0.447 g (88%), white amorphous substance. ^1H and ^{13}C NMR spectroscopic data of **6** were in agreement with published data[S4]. ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.92, 0.95, 1.03, 1.05, 1.12 (five s, 15*H*, $C^{23\text{-}27}H_3$), 1.68 (s, 3*H*, $C^{30}H_3$), 2.07 (s, 3*H*, $\underline{CH_3}C(O)$), 1.01 – 2.28 (m, 22*H*), 2.45 (m, 1*H*, H^{19}, $^3J_{HH}$ 11.0, $^3J_{HH}$ 5.7), 2.96 (m, 1*H*, H^2, $^3J_{HH}$ 15.4, $^3J_{HH}$ 4.9), 3.85 (d, 1*H*, $C^{28}H_A$, $^3J_{HH}$ 10.9), 4.24 (d, 1*H*, $C^{28}H_B$, $^3J_{HH}$ 11.1), 4.59 (br. s, 1*H*, $C^{29}H_A$), 4.68 (d, 1*H*, $C^{29}H_X$, $^3J_{HH}$ 2.2). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 14.8, 15.4, 16.1, 18.3, 19.2, 21.1, 25.3, 27.1, 27.5, 28.1, 29.6, 29.8, 34.2, 34.6, 37.2, 37.6, 38.7, 38.9, 40.9, 42.8, 46.4, 47.7, 48.8, 50.4, 55.5, 62.8, 109.9 (C^{29}), 150.2 (C^{20}), 167.3 (C^3), 171.7 (OAc).



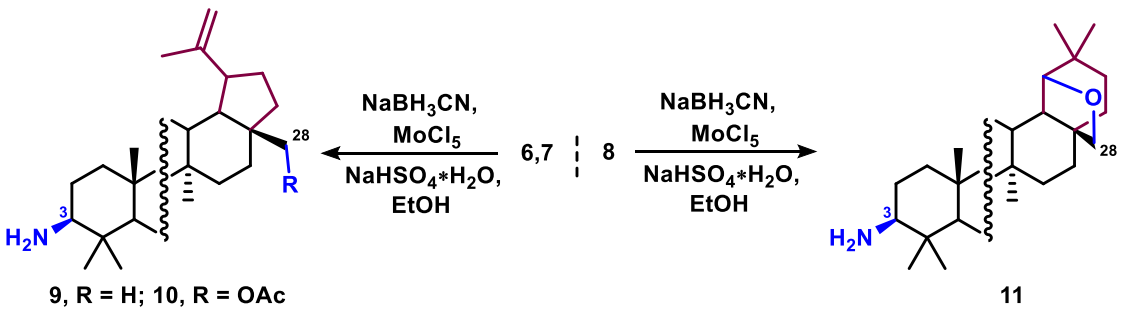
7

Lup-20(29)-en-3-one oxime 7. Prepared from 0.64 g of lup-20(29)-en-3-one. Yield 0.554 g (83%), white amorphous substance. ^{1}H and ^{13}C NMR spectroscopic data of **7** were in agreement with published data[S3]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.76, 0.83, 0.97, 0.98, 1.03 (five s, 15*H*, $C^{23\text{-}27}H_3$), 1.05 – 2.24 (m, CH_2, CH), 1.68 (s, 3*H*, $C^{30}H_3$), 2.37 (m, 1*H*, H^{19}), 2.94 (m, 2*H*, H^2), 4.56 (s, 1*H*, $C^{29}H_A$), 4.68 (s, 1*H*, $C^{29}H_X$). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 14.8, 15.4, 16.1, 16.2, 18.3, 19.2, 20.9, 21.1, 25.3, 27.1, 27.5, 30.0, 34.2, 34.6, 35.8, 37.5, 38.4, 38.9, 40.9, 42.8, 43.6, 47.7, 48.1, 48.8, 50.4, 55.4, 109.9 (C^{29}), 150.4 (C^{20}), 167.62 (C^3).



8

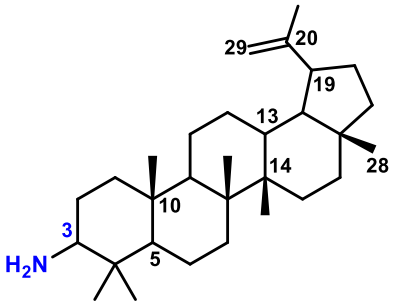
19*β*,28-Epoxy-18*α*-olean-3-one oxime (allobetulone oxime) 8. Prepared from 0.3 g of 19*β*,28-epoxy-18*α*-olean-3-one. Yield 0.23 g (74%), white amorphous substance. ^{1}H and ^{13}C NMR spectroscopic data of **8** were in agreement with published data[S5]. ^{1}H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.79, 0.90, 0.93, 1.00, 1.04, 1.13 (s, 21*H*, CH_3), 1.20 – 2.28 (m, 22*H*, CH, CH_2), 2.95 (m, 2*H*, H^2, $^{3}J_{HH}$ 15.5), 3.44 (d, 1*H*, $C^{28}H_A$, $^{3}J_{HH}$ 7.6), 3.53 (s, 1*H*, H^{19}), 3.78 (d, 1*H*, $C^{28}H_B$, $^{3}J_{HH}$ 7.6). ^{13}C-{^{1}H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 13.48, 15.68, 16.47, 18.25, 20.96, 24.52, 26.20, 26.42, 27.95, 28.78, 32.15, 32.68, 33.91, 34.10, 35.12, 36.22, 36.68, 37.25, 38.86, 38.93, 40.71, 41.49, 43.29, 46.81, 51.09, 55.63, 71.28 (C^{28}), 87.93 (C^{19}), 167.48 (C^3).



9, R = H; 10, R = OAc

11

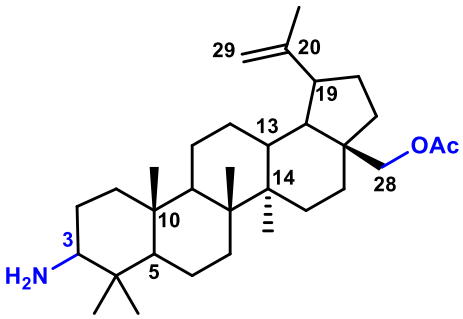
General procedure for the synthesis of 3-*β*-aminotriterpenes. $NaBH_3CN$ (0.03 g, 4 mmol), $MoCl_5$ (0.03 g, 1 mmol) and $NaHSO_4 \cdot H_2O$ (0.04 g, 3 mmol) were successively added to the triterpenoid oxime (1 mmol) in absolute ethanol (5 ml). The mixture was stirred under argon for 4 h at 80 °C. The end of the reaction was monitored by TLC (Pet : EtOAc = 1 : 1). Upon completion of the reaction, 5% $NaHCO_3$ solution (30 ml) was added to the reaction mixture, which was then extracted with CH_2Cl_2 (2 × 40 ml) and dried over Na_2SO_4. Column chromatography in the CH_2Cl_2 : 5N NH_3 (in MeOH) (95 : 5 v/v) system (R_f = 0.3) gave the target compounds.



9

3*β*-Amino-20(29)-lupene 9. Prepared from 0.1 g of lup-20(29)-en-3-one oxime **6**. Yield: 0.045 g (46%), white amorphous substance. $[\alpha]^{20}_D$ –15.217 (*c* 0.1 mg/ml, $CHCl_3$); mp 113-114 °C. R_f 0.3 (CH_2Cl_2 : 5N NH_3 in MeOH). ^1H and ^{13}C NMR spectroscopic data of **9** were in agreement with published data[S6]. ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 0.70, 0.78, 0.80, 0.92, 0.94, 1.02 (six s, 18*H*, $C^{23\text{-}28}H_3$), 0.71 – 1.91 (m, 24*H*), 1.68 (s, 3*H*, $C^{30}H_3$), 2.00 – 1.79 (m, 1*H*, C^2), 2.20 – 1.84 (m, 1*H*, C^3H^{α} $^3J_{HH}$ 8.8, $^3J_{HH}$ 8.1), 2.29 – 2.42 (m, 1*H*, $C^{19}H$, $^3J_{HH}$ 11.4, $^3J_{HH}$ 4.8), 4.56 (d, 1*H*, $C^{28}H_A$, $^3J_{HH}$ 2.5 Hz,), 4.68 (d, 1*H*, $C^{28}H_B$, $^3J_{HH}$ 2.5). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 14.28, 14.65, 16.19, 18.14, 18.48, 19.43, 20.99, 22.84, 24.47, 25.18, 25.92, 27.55, 28.44, 29.64, 29.87, 32.07, 34.27, 35.68, 37.23, 38.12, 38.69, 40.12, 43.14, 48.12, 48.39, 50.46, 55.90, 59.66 (C^3-NH_2), 109.36 (C^{29}), 151.07 (C^{20}). Found, %: C 84.53, H 12.29, N 3.24. $C_{30}H_{51}N$. Calculated, %: C 84.44, H 12.28, N 3.28. IR (KBr, cm^{-1}): 2921, 2851, 1708, 1624, 1543, 1465, 1384, 1037, 721. Mass-spectrum ESI, *m/z*: calc. for $C_{30}H_{52}N^+$ $[M + H]^+$, 426.41; found 426.36.

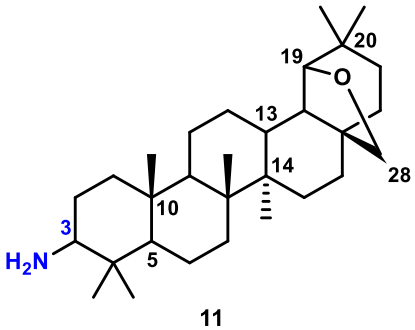
3*α*-Amino-20(29)-lupene. ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 2.54-2.58 (m, 1*H*, C^3H). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 56.63 (C^3-NH_2).



10

3*β*-Amino-28-*O*-acetoxylup-20(29)-ene 10. Prepared from 0.2 g of 28-acetoxylup-20(29)-en-3-one oxime **7**. Yield 0.129 g (67%), white amorphous substance. mp 116-117 °C. $[\alpha]^{20}_{D}$ +9.733 (*c* 0.1 mg/ml, $CHCl_3$). R_f 0.35 (CH_2Cl_2 : 5N NH_3 in MeOH). IRS (KBr) ν_{max}, cm^{-1}: 2946, 2869, 1740, 1642, 1544, 1457, 1388, 1365, 1235, 1033, 981, 884, 755. ^1H and ^{13}C NMR spectroscopic data of **10** were in agreement with published data[S4]. ^1H NMR ($CDCl_3$, 400 MHz, δ, ppm, *J*, Hz): 0.67, 0.79, 0.91, 0.97, 1.02 (five s, 15*H*, H^{23-27}), 0.81-2.0 (m, 24*H*, CH_2 and CH lupane scaffold proton signals), 1.67 (s, 3*H*, $C^{30}H$), 2.07 (s, 3*H*, $OCOCH_3$), 2.27 dd (1*H*, H^3, $^3J_{HH}$ 11.7), 2.40-2.49 td (1*H*, $C^{19}H$, $^3J_{HH}$ 11.0), 3.85 d (1*H*, $C^{28}H_A$, $^3J_{HH}$ 11.0), 4.24 d (1*H*, $C^{28}H_X$, $^3J_{HH}$ 11.1), 4.58 s (1*H*, $C^{29}H_A$, $^2J_{HH}$ 2.4), 4.68 s (1*H*, $C^{29}H_B$, $^2J_{HH}$ 2.3). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 14.79, 15.46, 16.05, 18.68, 19.14, 20.72, 21.10, 25.23, 27.07, 28.30, 28.35, 29.60, 29.71, 29.77, 34.27, 34.58, 37.35, 37.60, 38.32, 39.46, 40.83, 42.71, 46.33, 47.71, 48.80, 50.50, 55.99, 59.67(C^{28}), 62.85 (C^3–NH_2), 109.87 (C^{29}), 150.22 (C^{20}), 171.70 ($CH_3\underline{C}$=O). Found, %: C 79.38, H 10.97, N 2.84. $C_{32}H_{53}NO_2$. Calculated, %: C 79.45, H 11.04, N 2.90. Mass-spectrum ESI, *m/z*: calc. for $C_{32}H_{54}NO_2^+$ $[M + H]^+$, 484.41; found 484.35.

3*α*-Amino-28-O-acetoxylup-20(29)-ene. ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 2.56 – 2.59 (m, 1*H*, C^3H). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 56.56 (C^3-NH_2).

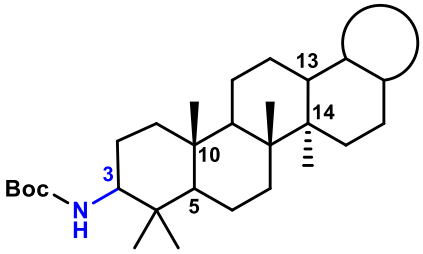


11

3*β*-Amino-19*β*,28-epoxyoleanan 11. Prepared from 0.108 g of 19*β*,28-epoxy-18*α*-olean-3-one oxime **8**. Yield: 0.041 g (39%), white amorphous substance. $[\alpha]^{20}_{D}$ +1.9167 (*c* 0.1 mg/ml, $CHCl_3$); mp >200 °C. R_f 0.65 (CH_2Cl_2 : 5N NH_3 in MeOH). ^1H and ^{13}C NMR spectroscopic data of **11** were in agreement with published data[S5]. ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz) of 3-

β-isomer: 0.70, 0.79, 0.81, 0.85, 0.91, 0.92, 0.96 (seven s, 21*H*, $C^{23\text{-}27,29,30}H_3$), 0.83 – 1.72 (m, 22*H*), 2.29 (m, 1*H*, C^3H), 3.44 (d, 1*H*, $C^{28}H_B$, $^3J_{HH}$ 7.9 Hz), 3.52 (s, 1*H*, $C^{19}H$), 3.77 (d, 1*H*, $C^{28}H_A$, $^3J_{HH}$ 7.9). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm) of 3-*β*-isomer: 13.53, 15.49, 15.72, 16.44, 18.63, 20.89, 24.57, 26.27, 26.44, 28.29, 28.83, 32.71, 33.95, 34.15, 36.28, 36.75, 37.44, 38.32, 39.63, 40.69, 41.49, 46.82, 48.96, 51.18, 56.15, 56.56, 59.64(C^3-NH_2), 71.28 (C^{28}), 87.94 (C^{19}). ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz) of 3-*α*-isomer: 0.70, 0.79, 0.81, 0.85, 0.91, 0.92, 0.96 (seven s, 21*H*, $C^{23\text{-}27,29,30}H_3$), 0.83 – 1.72 (m, 22*H*), 2.29 (m, 1*H*, C^3H), 3.44 (d, 1*H*, $C^{28}H_B$, $^3J_{HH}$ 7.9), 3.52 (m, 1*H*, $C^{19}H$), 3.77 (d, 1*H*, $C^{28}H_A$, $^3J_{HH}$ 7.9). IR (KBr, cm^{-1}): 2926, 2854, 1639, 1534, 1456, 1381, 1165, 1136, 1039, 882. Found, %: C 81.29, H 11.89, N 3.14. $C_{32}H_{53}NO_2$. Calculated, %: C 81.38, H 11.84, N 3.16. Mass-spectrum ESI, *m/z*: calc. for $C_{30}H_{52}NO^+$ $[M + H]^+$, 442.40; found 442.33.

3*α*-Amino-19*β*,28-epoxyoleanane. ^1H NMR (400 MHz, $CDCl_3$, 25°C, δ, ppm, *J*, Hz): 2.58 – 2.61 (m, 1*H*, C^3H). ^{13}C-{^1H} NMR ($CDCl_3$, 100.6 MHz, δ_C, ppm): 56.56 (C^3-NH_2).



General procedure for the synthesis of Boc-derivatives of amines.

To a solution of 3α/*β*-amino triterpenes (1 mmol) in dry DCM (30 mL), Boc_2O (1.6 mmol) was added. The mixture was stirred at room temperature for 20 h. The end of the reaction was monitored by TLC ($CHCl_3$: MeOH = 25 : 1 (v/v)). Column chromatography on Al_2O_3 by gradient elution in the system benzene – $CHCl_3$ – MeOH (R_f= 0.65) gave the target compounds.

3*β*-(*tert*-butoxycarbonylamino)-28-*O*-acetoxylup-20(29)-ene. Prepared from 0.155 g of 3α/*β*-amino-28-*O*-acetoxylup-20(29)-ene. Yield: 0.089 g (57%). R_f 0.65 ($CHCl_3$: MeOH = 25 : 1). ^1H and ^{13}C NMR spectroscopic data were in agreement with published data. The removal of the Boc-functional group was carried out according to the method described in the literature[S7].

References

S1. G. R. Petit, N. Melody, F. Hempenstall, J.-C. Chapuis, T. L. Groy and L. Williams, *J. Nat. Prod.*, 2014, **77**, 863; https://doi.org/10.1021/np400947d.

S2. S. Lavoie, A. Pichette, F.-X. Garneau, M. Girard and D. Gaudet, *Synth. Commun*., 2001, **31**, 1565; https://doi.org/10.1081/scc-100104070.

S3. M. F. Khan, D. P. Mishra, E. Ramakrishna, A. K. Rawat, A. Mishra, A. K. Srivastava and R. Maurya, *Med. Chem. Res.*, 2014, **23**, 4156; https://doi.org/10.1007/s00044-014-0984-2.

S4. G. R. Pettit, N. Melody and J.-C. Chapuis, *J. Nat. Prod.*, 2018, **81**, 458; https://doi.org/10.1021/acs.jnatprod.7b00536.

S5. L. Heller, A. Obernauer and R. Csuk, *Bioorg. Med. Chem.*, 2015, **23**, 3002; https://doi.org/10.1016/j.bmc.2015.05.015.

S6. S. Kumar, N. Misra, K. Raj, K. Srivastava and S. K. Puri, *Nat. Prod. Res.*, 2008, **22**, 305; https://doi.org/10.1080/14786410701766349.

S7. G. V. Giniyatullina, O. B. Flekhter, I. P. Baikova, Z. A. Starikova and G. A. Tolstikov, *Chem. Nat. Compd.*, 2008, **44**, 603; https://doi.org/10.1007/s10600-008-9138-4.

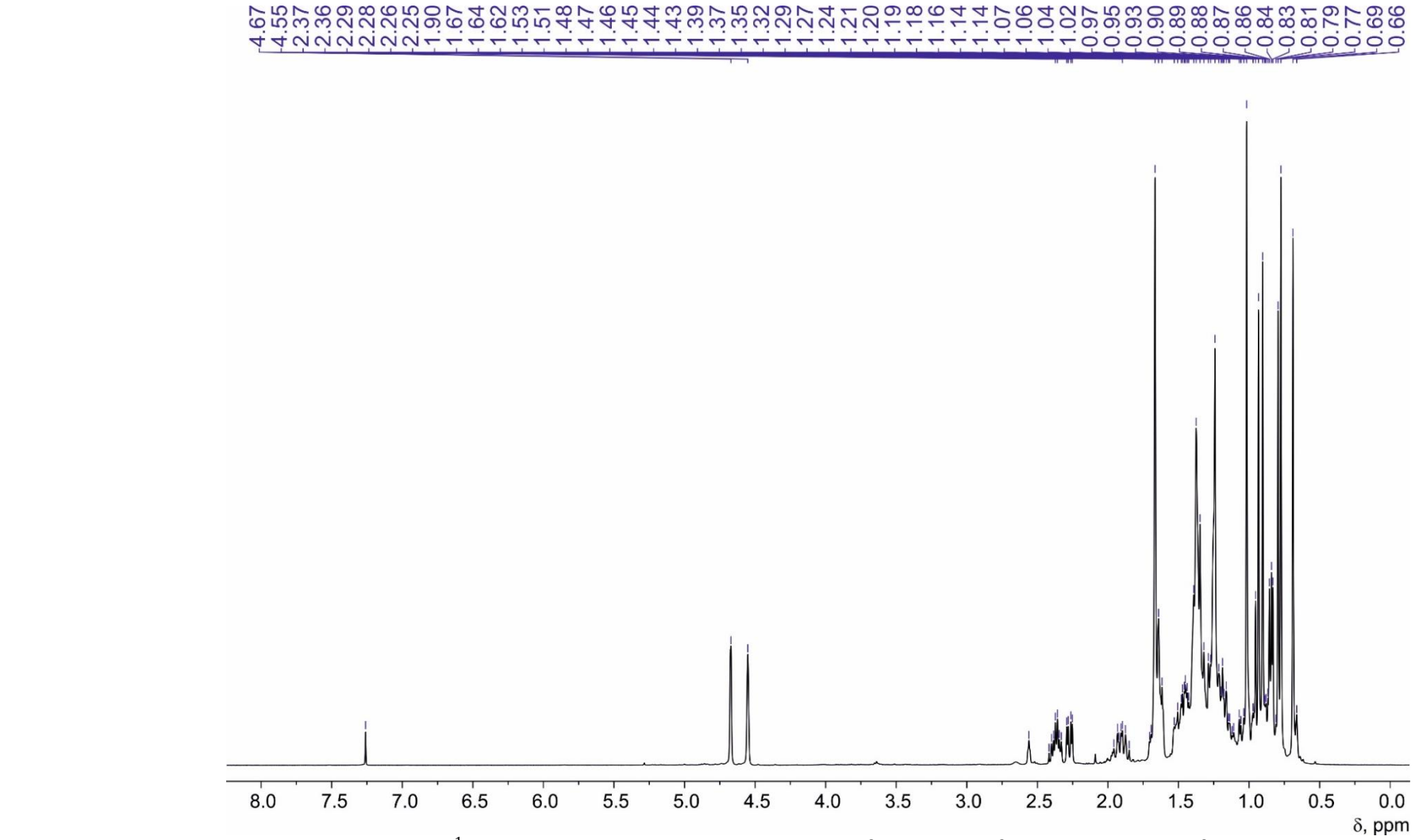


Figure S2. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 3-α- and 3-β-isomers mixture of amine **9**.

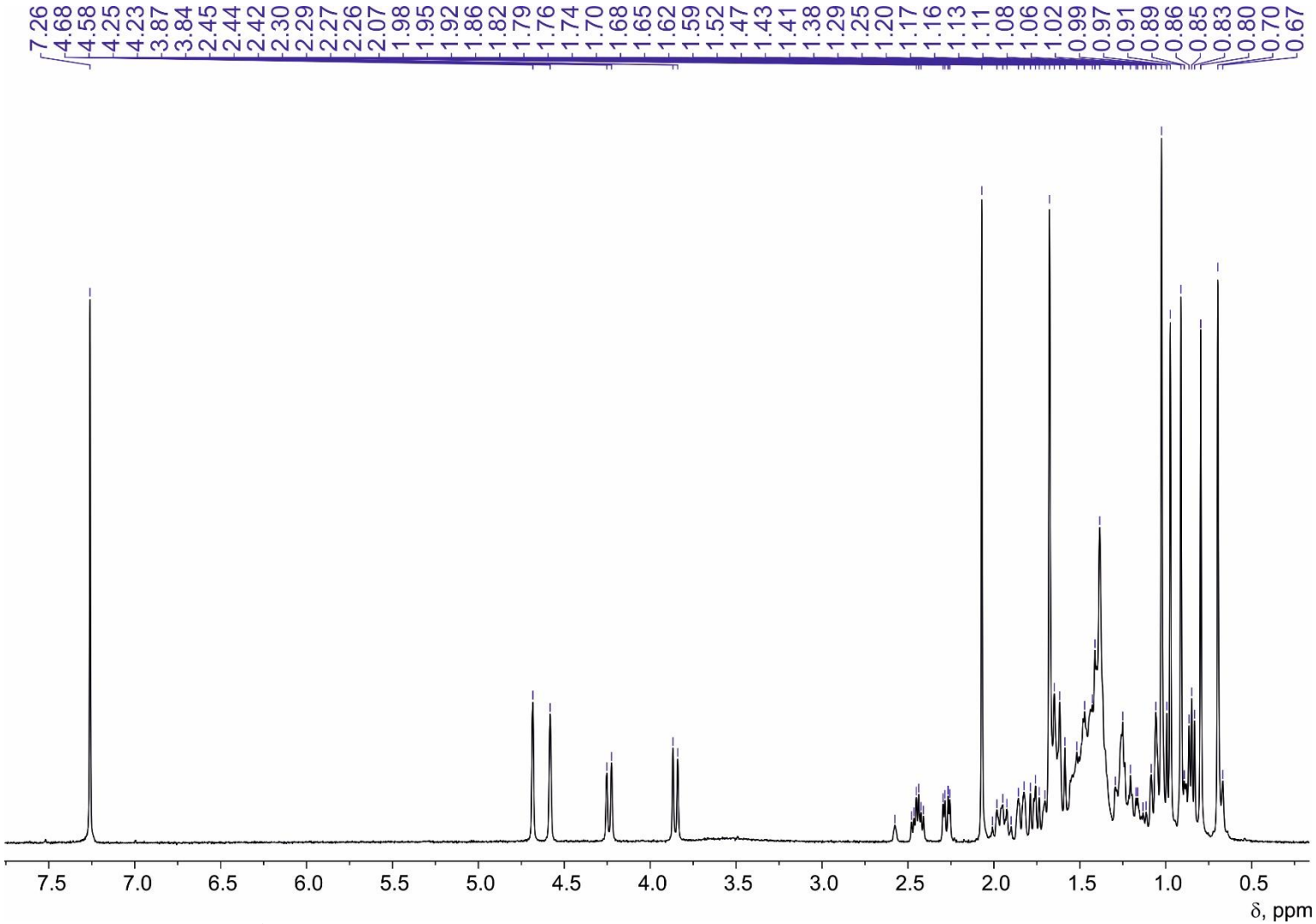


Figure S3. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 3-*α*- and 3-*β*-isomers mixture of amine **10**.

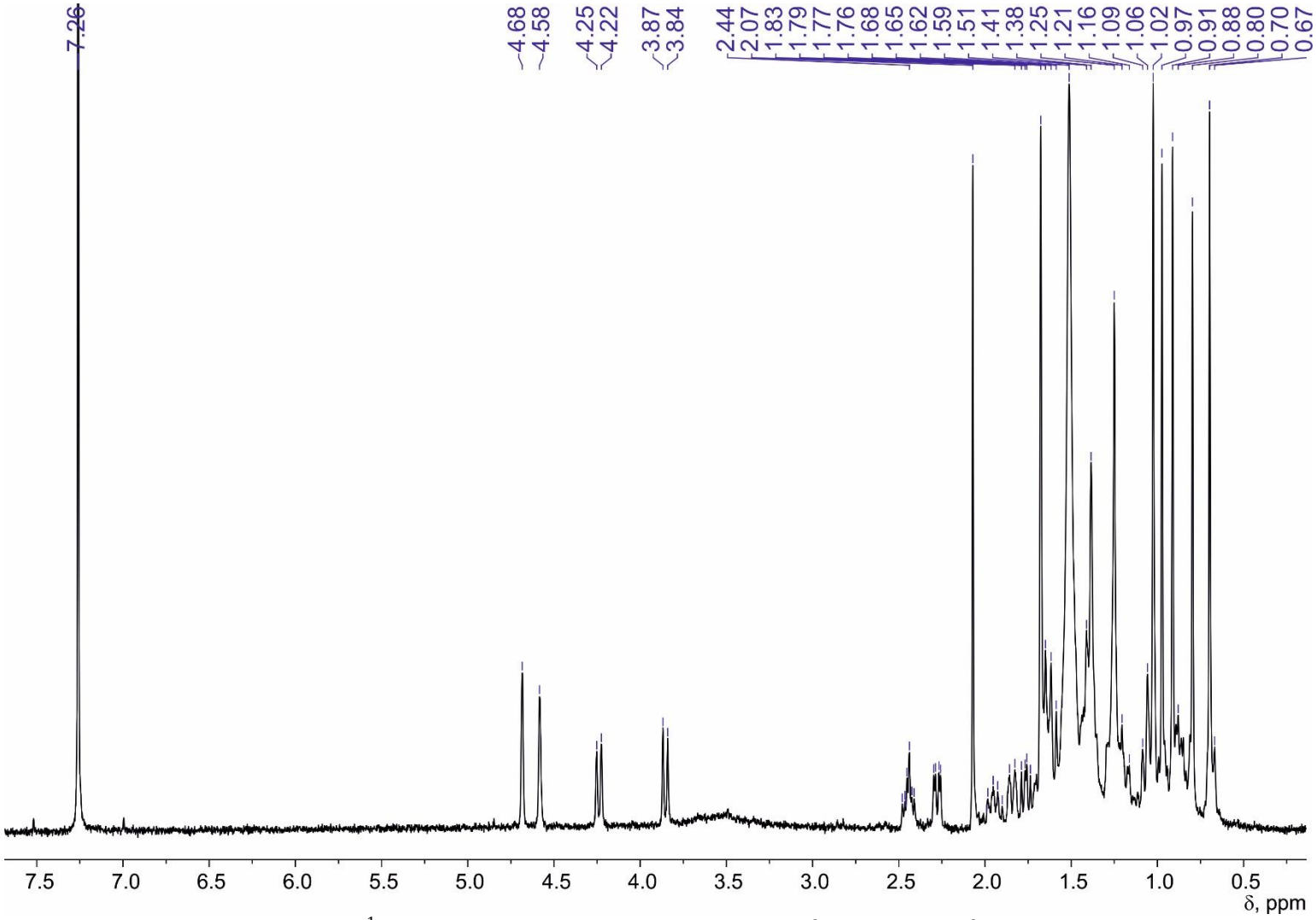


Figure S4. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of amine **10** (3-*β*-isomer).

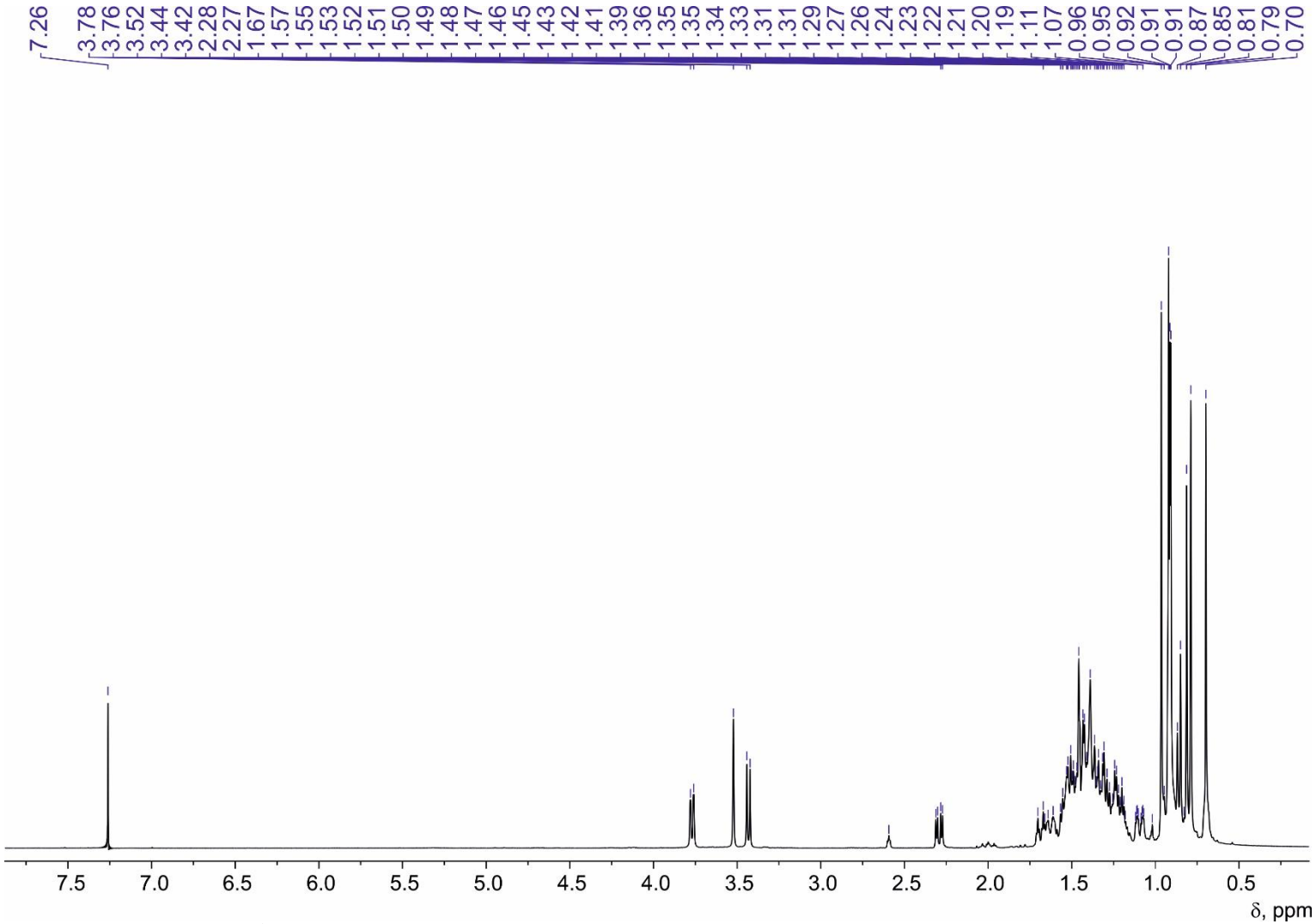


Figure S5. ^{1}H NMR ($CDCl_3$, 400 MHz) spectrum of 3-*α*- and 3-*β*-isomers mixture of amine **11**.

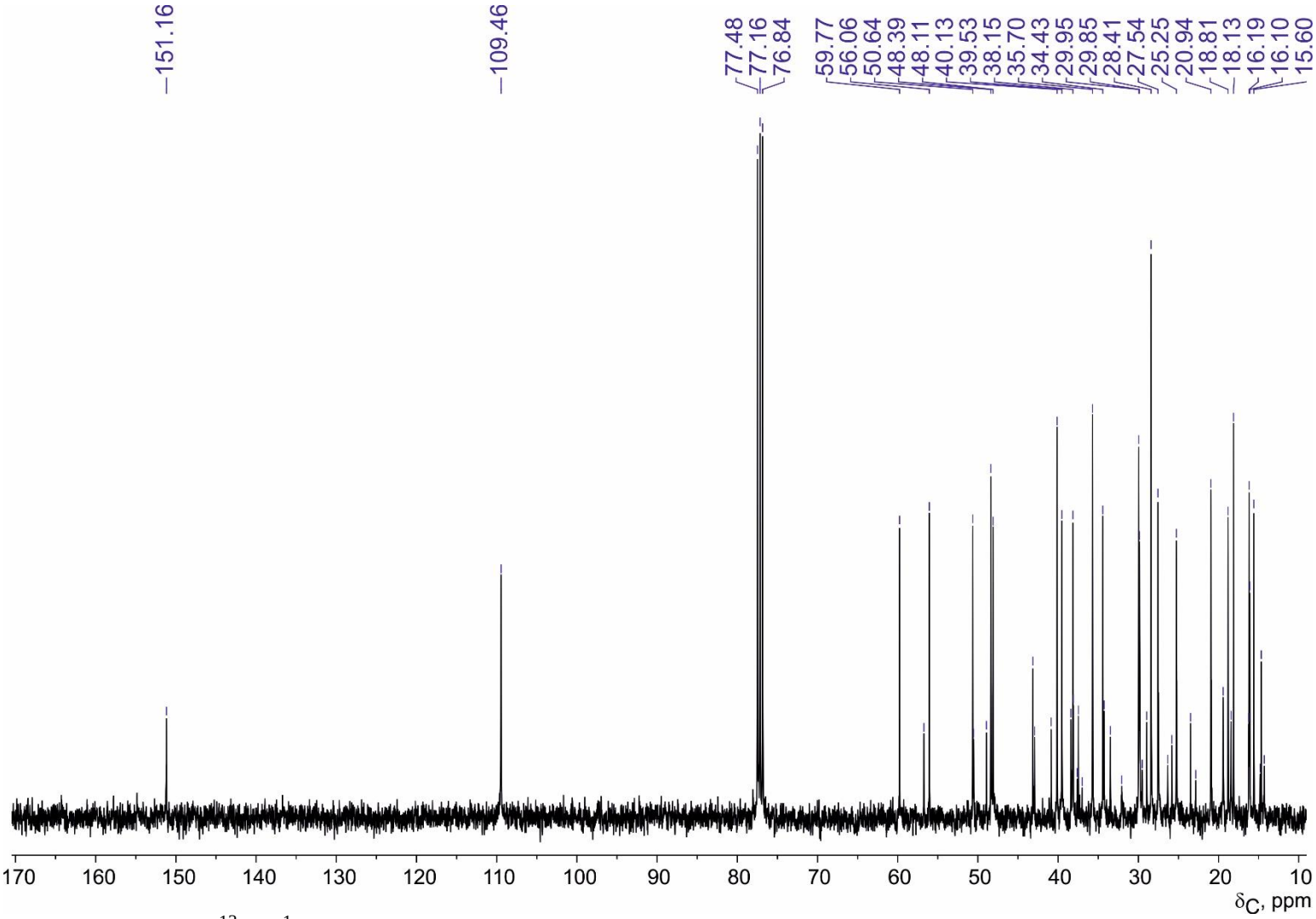


Figure S6. $^{13}C–\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz) spectrum of 3-*α*- and 3-*β*-isomers mixture of amine **9**.

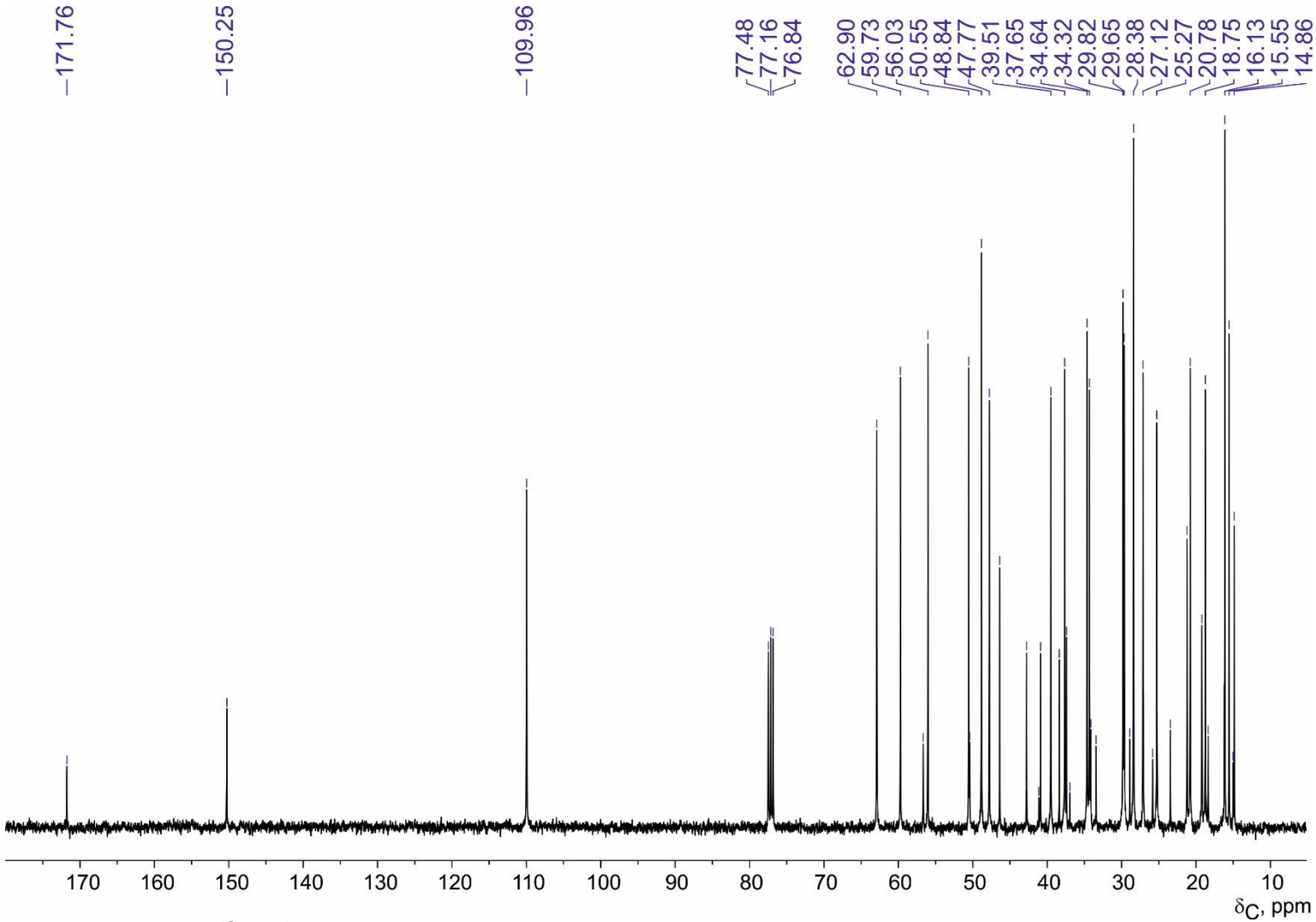


Figure S7. $^{13}C–\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz) spectrum of mixture of α- and β-isomers of amine **10**.

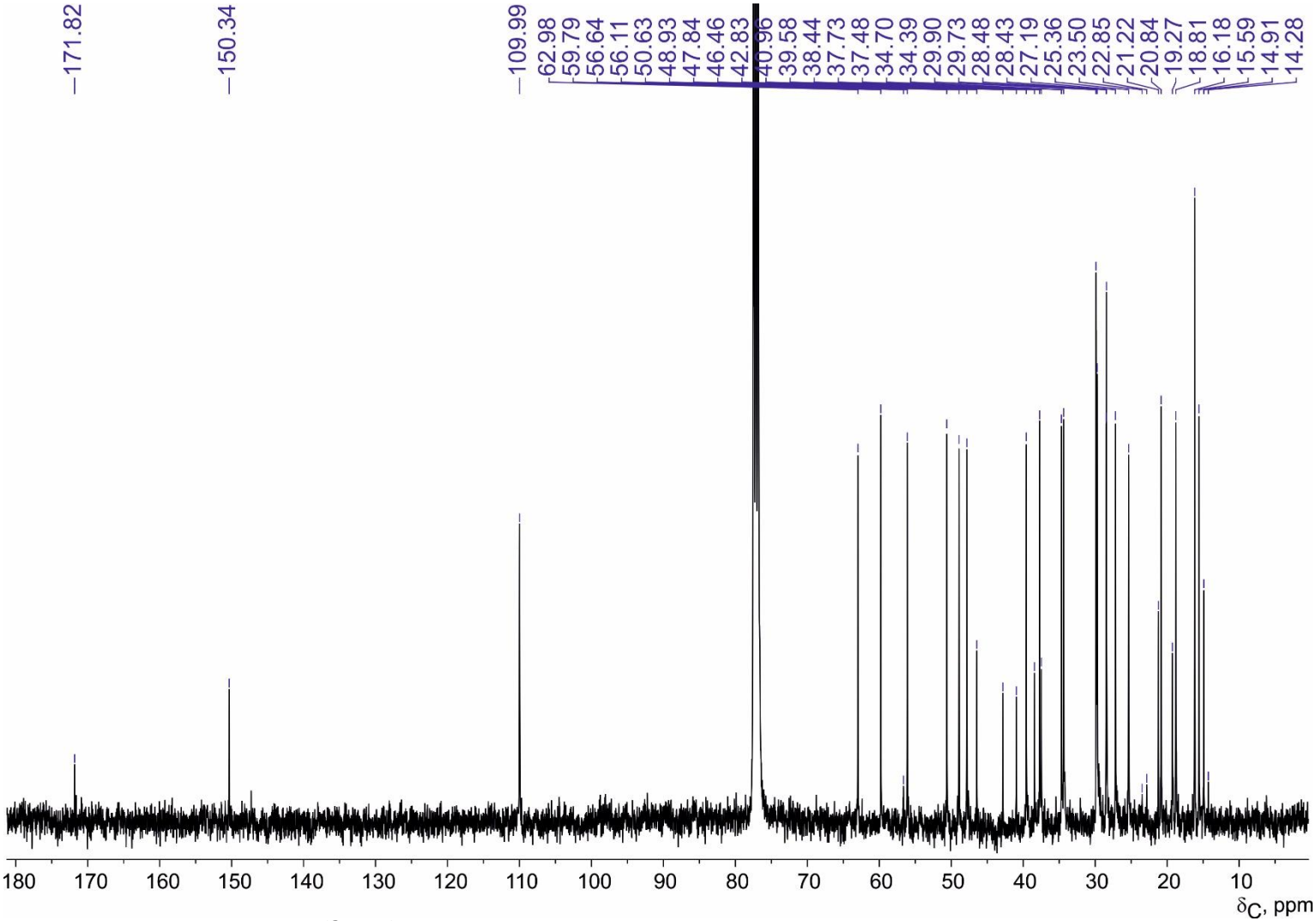


Figure S8. $^{13}C–\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz) spectrum of amine **10** (*β*-isomers).

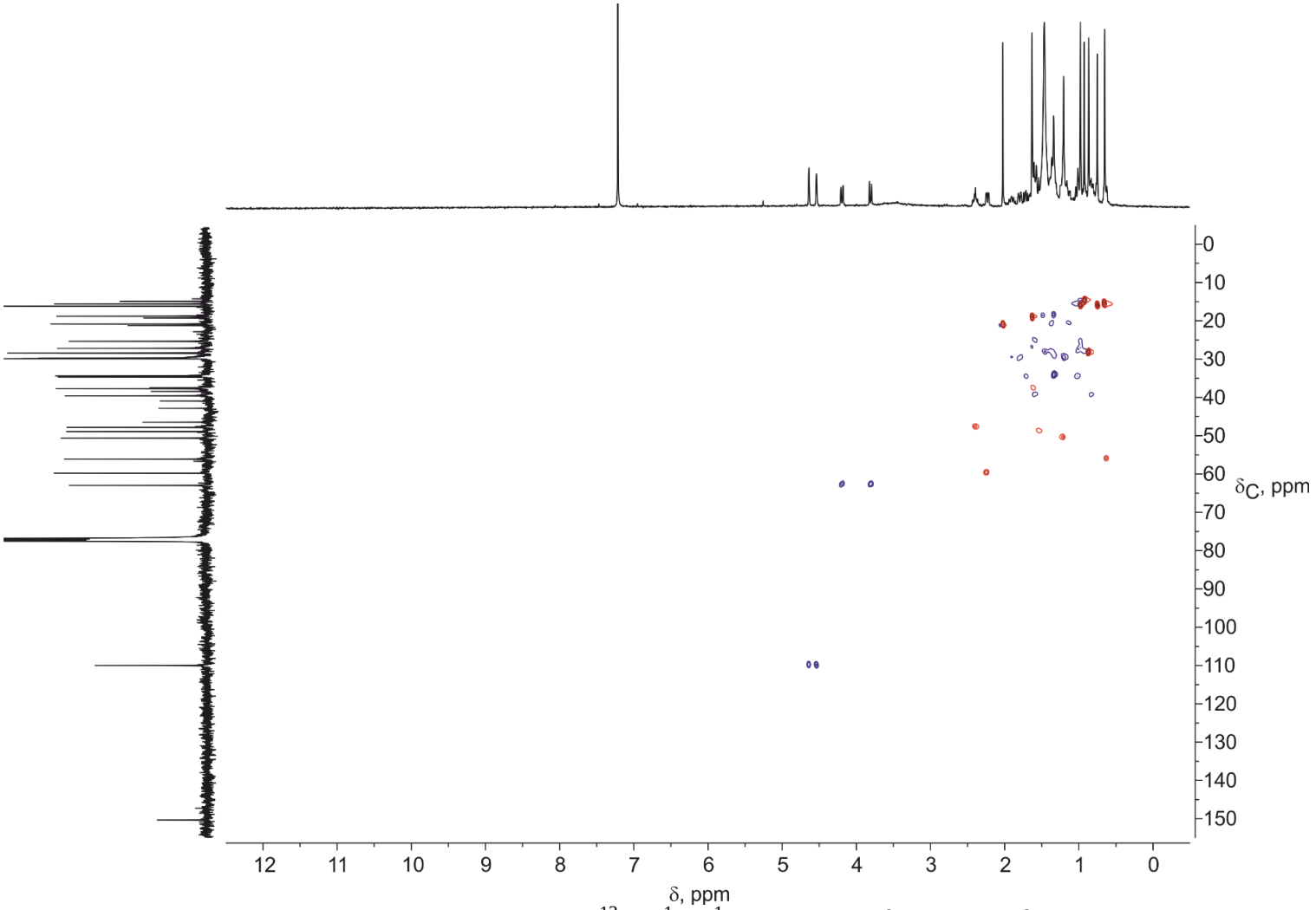


Figure S9. 2D HSQC NMR ($CDCl_3$) (^{13}C–{^1H}/^1H) spectrum of amine **10** (*β*-isomers).

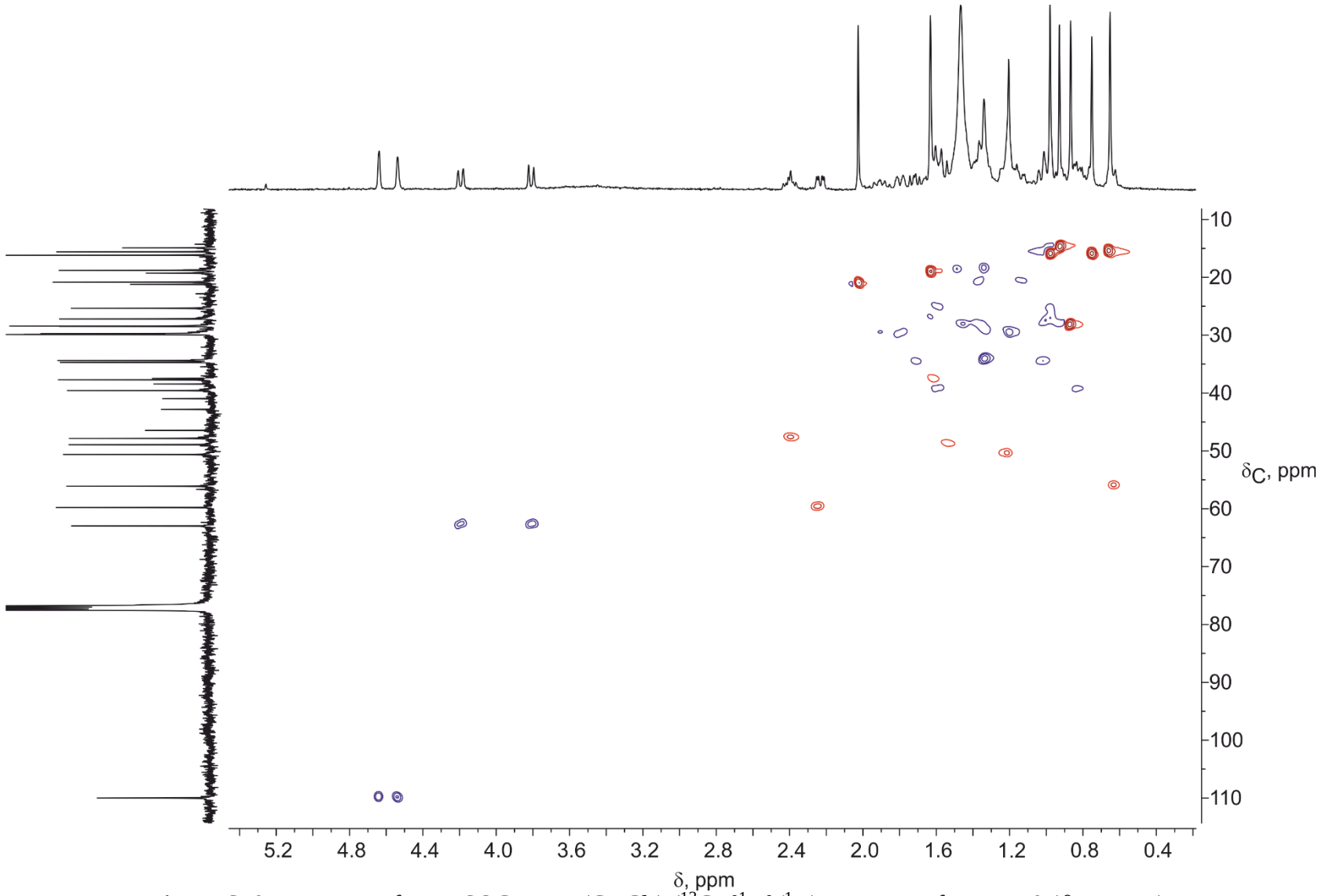


Figure S10. Fragment of 2D HSQC NMR ($CDCl_3$) (^{13}C–{^1H}/^1H) spectrum of amine **10** (*β*-isomers).

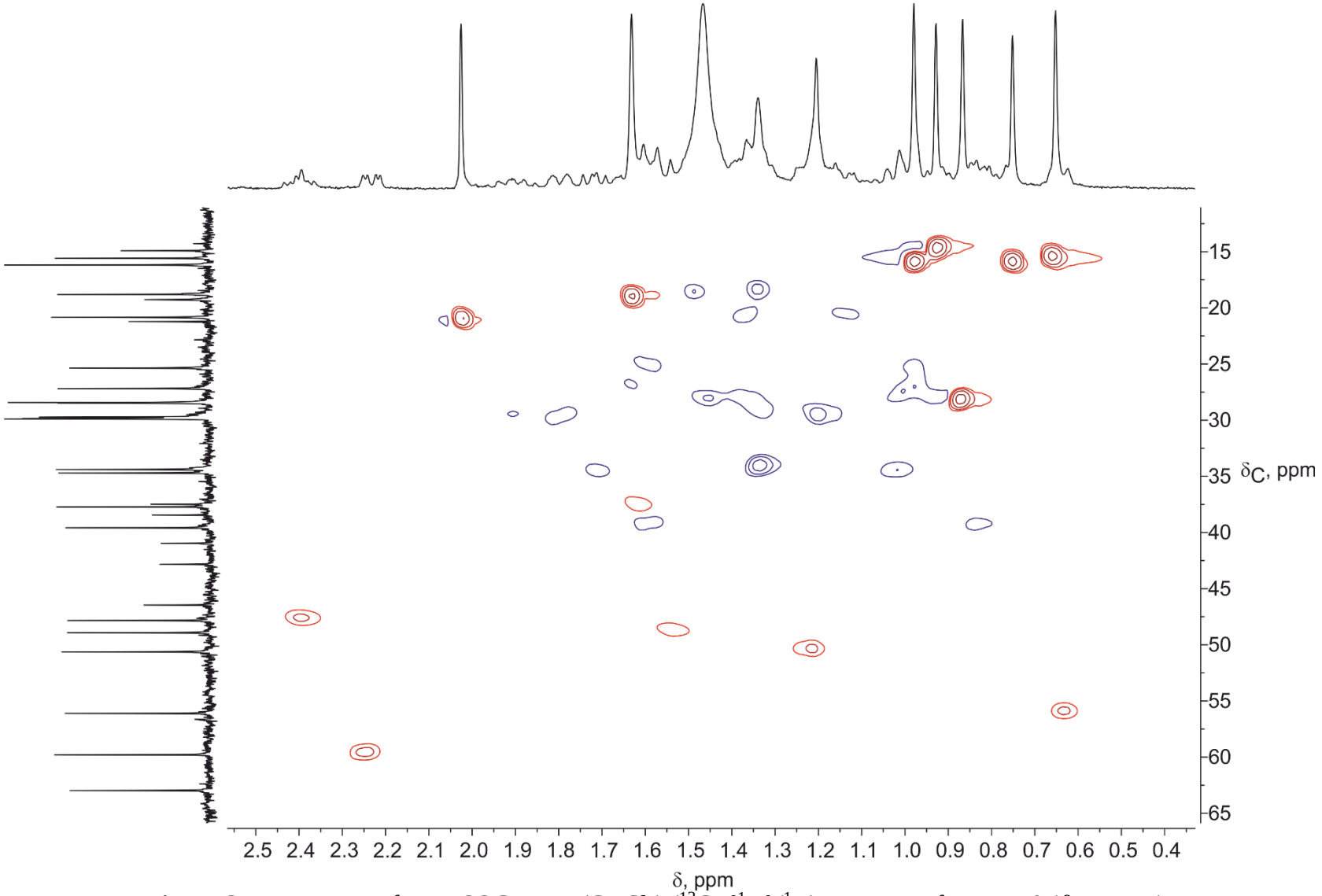


Figure S11. Fragment of 2D HSQC NMR ($CDCl_3$) (^{13}C–{^1H}/^1H) spectrum of amine **10** (*β*-isomers).

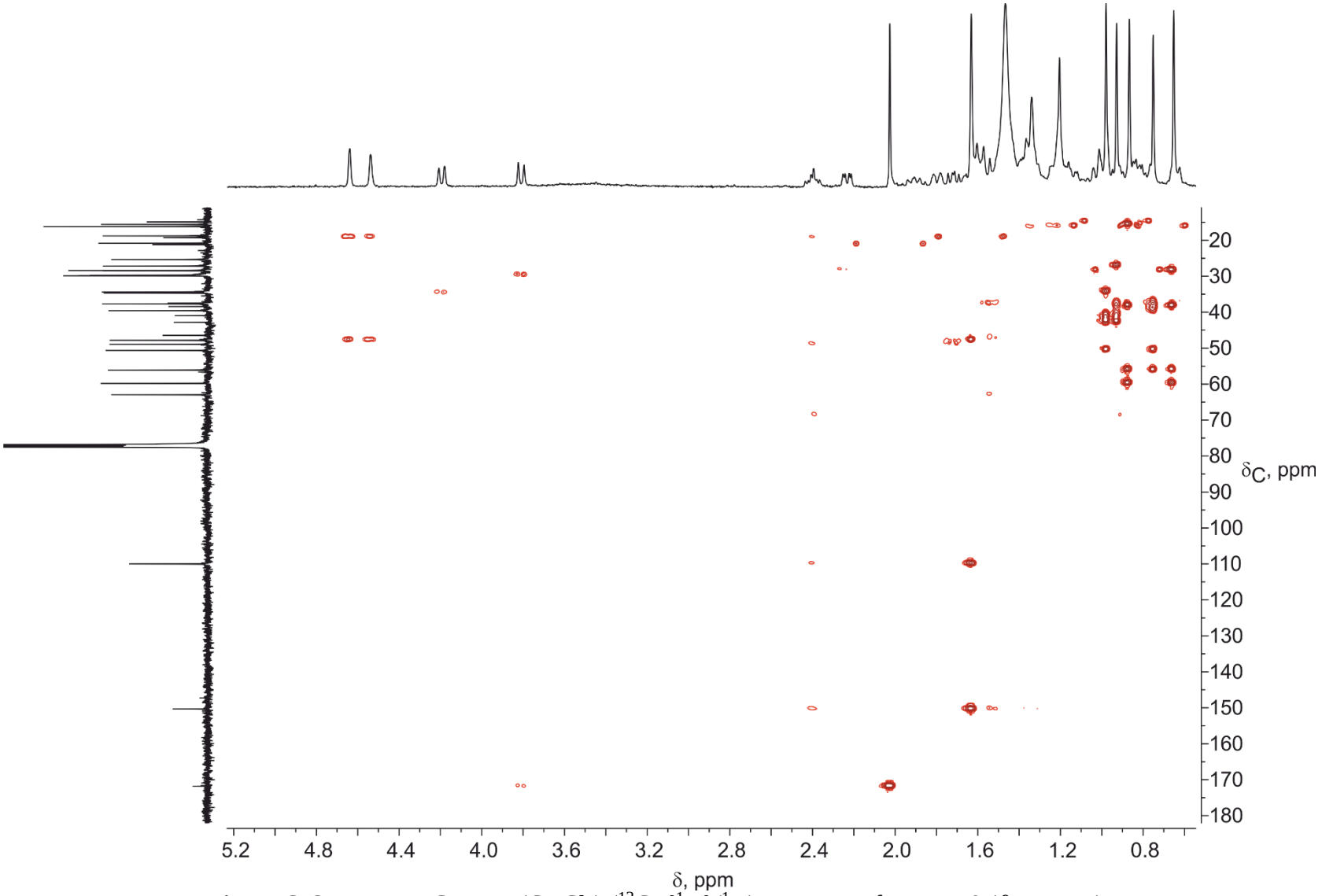


Figure S12. 2D HMBC NMR ($CDCl_3$) (^{13}C–{^1H}/^1H) spectrum of amine **10** (*β*-isomers).

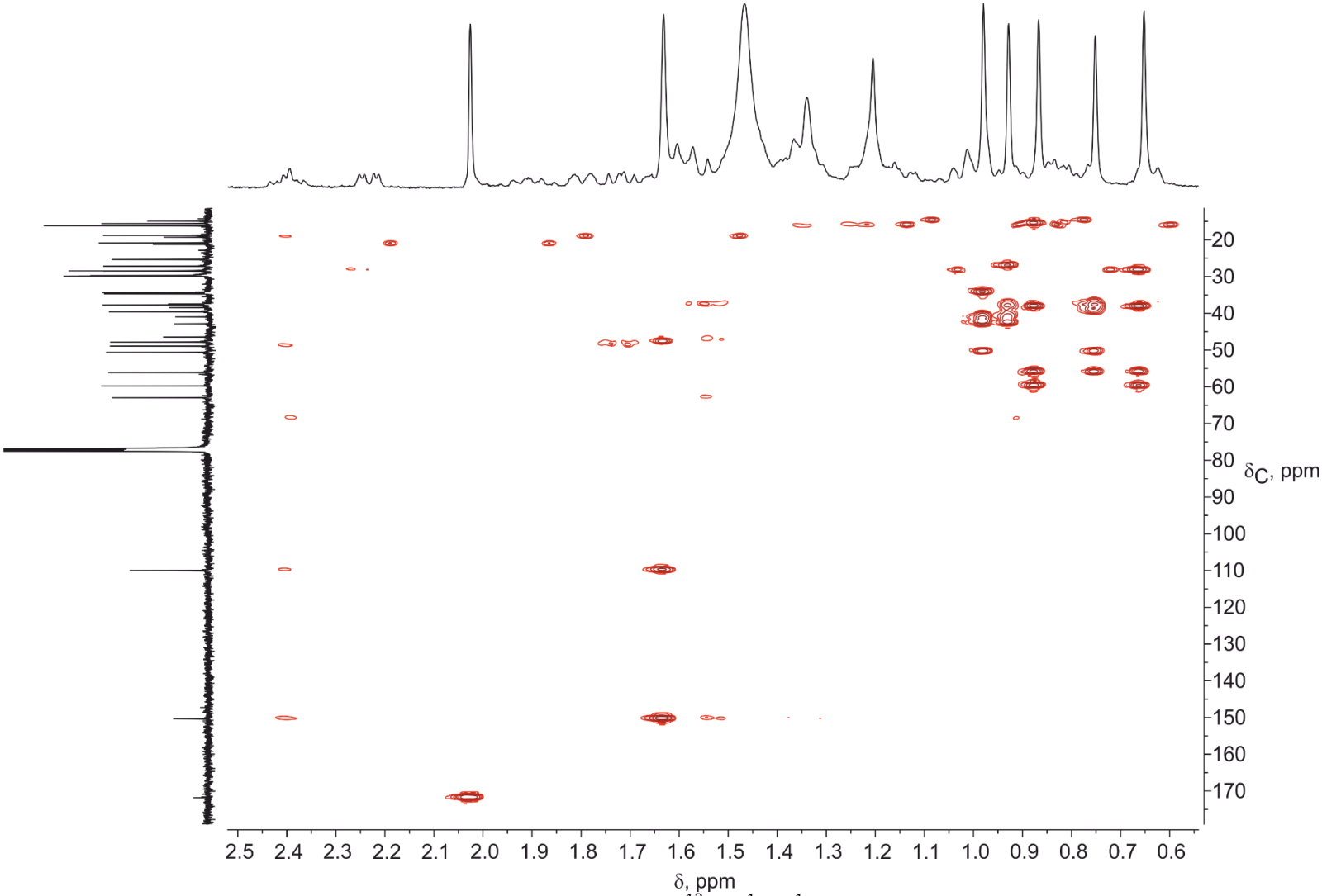


Figure S13. Fragment of 2D HMBC NMR ($CDCl_3$) (^{13}C–{^1H}/^1H) spectrum of amine **10** (β-isomers).

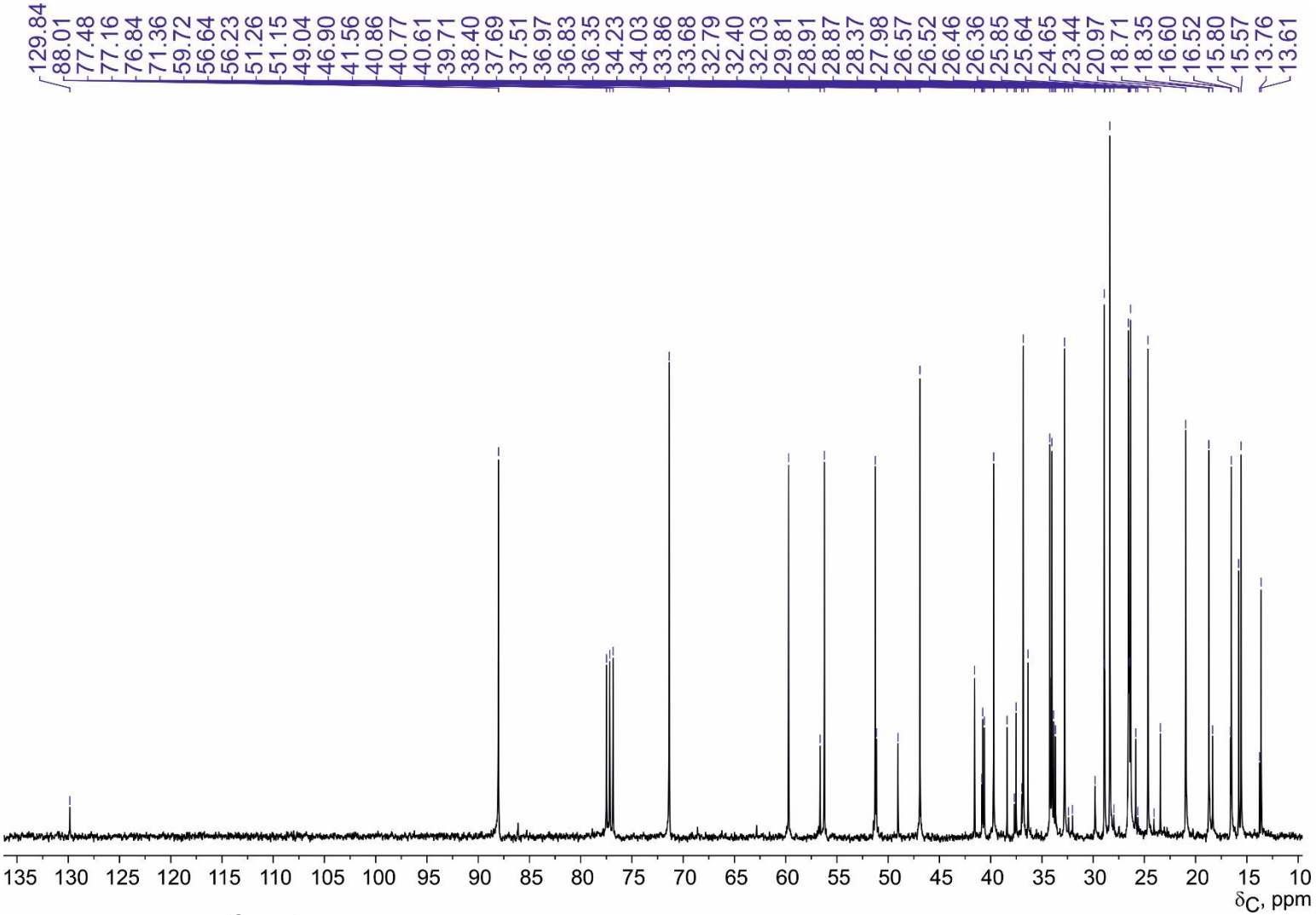


Figure S14. $^{13}C–\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz) spectrum of mixture of α- and β-isomers of amine **11**.

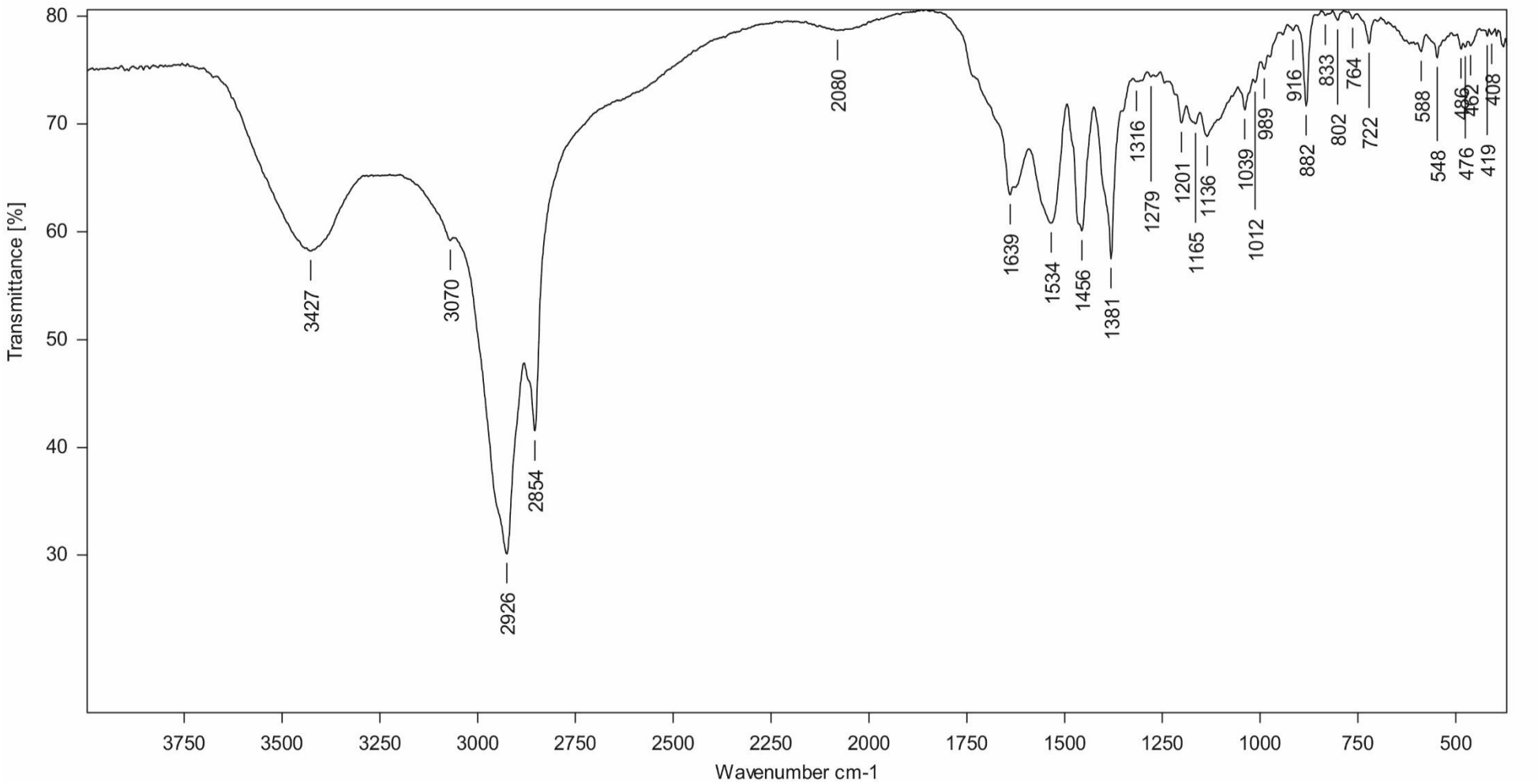


Figure S15. IR (thin film) spectrum of amine **9** (3-*α*/*β*-isomers mixture).

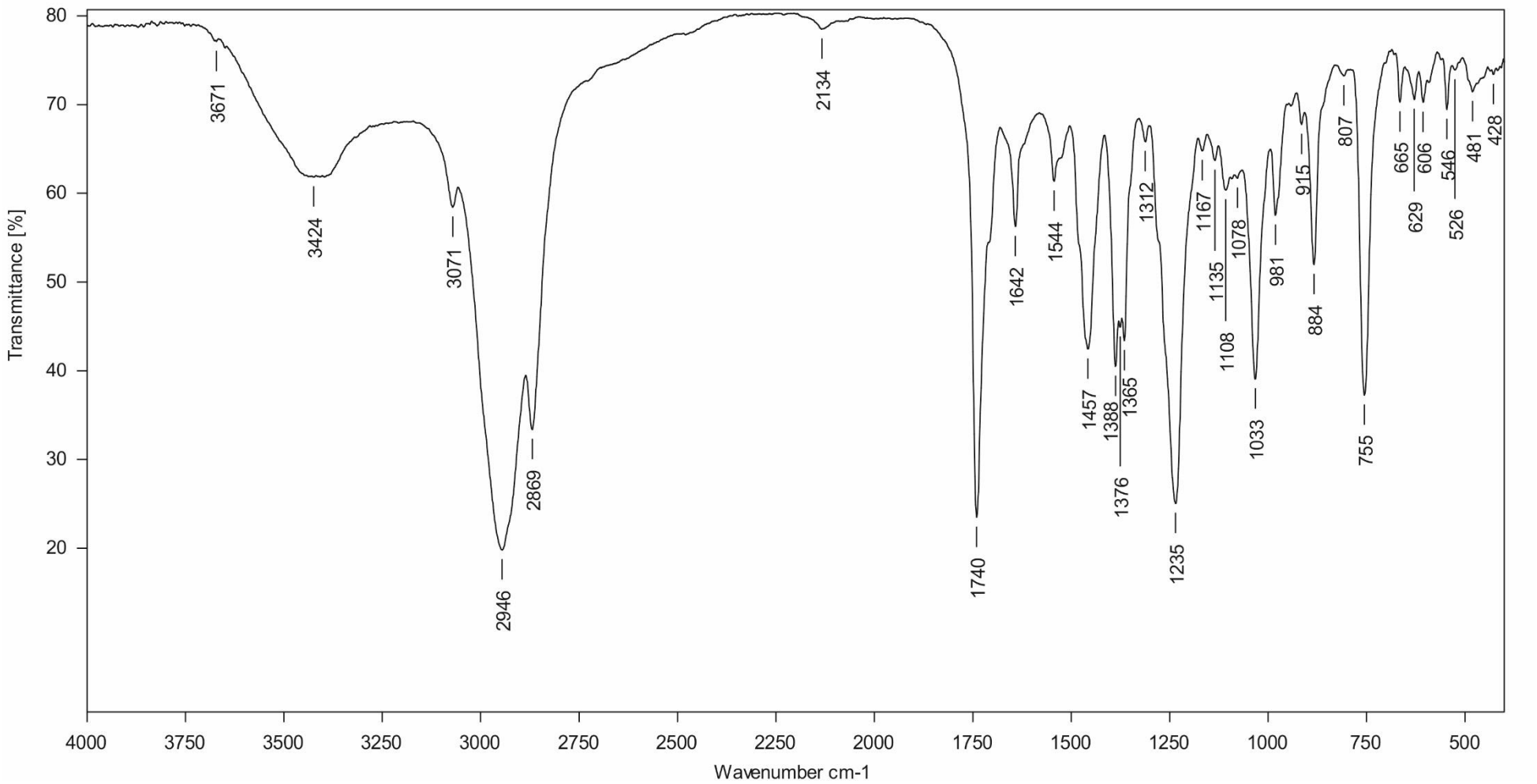


Figure S16. IR (thin film) spectrum of amine **10** (3-*β*-isomer).

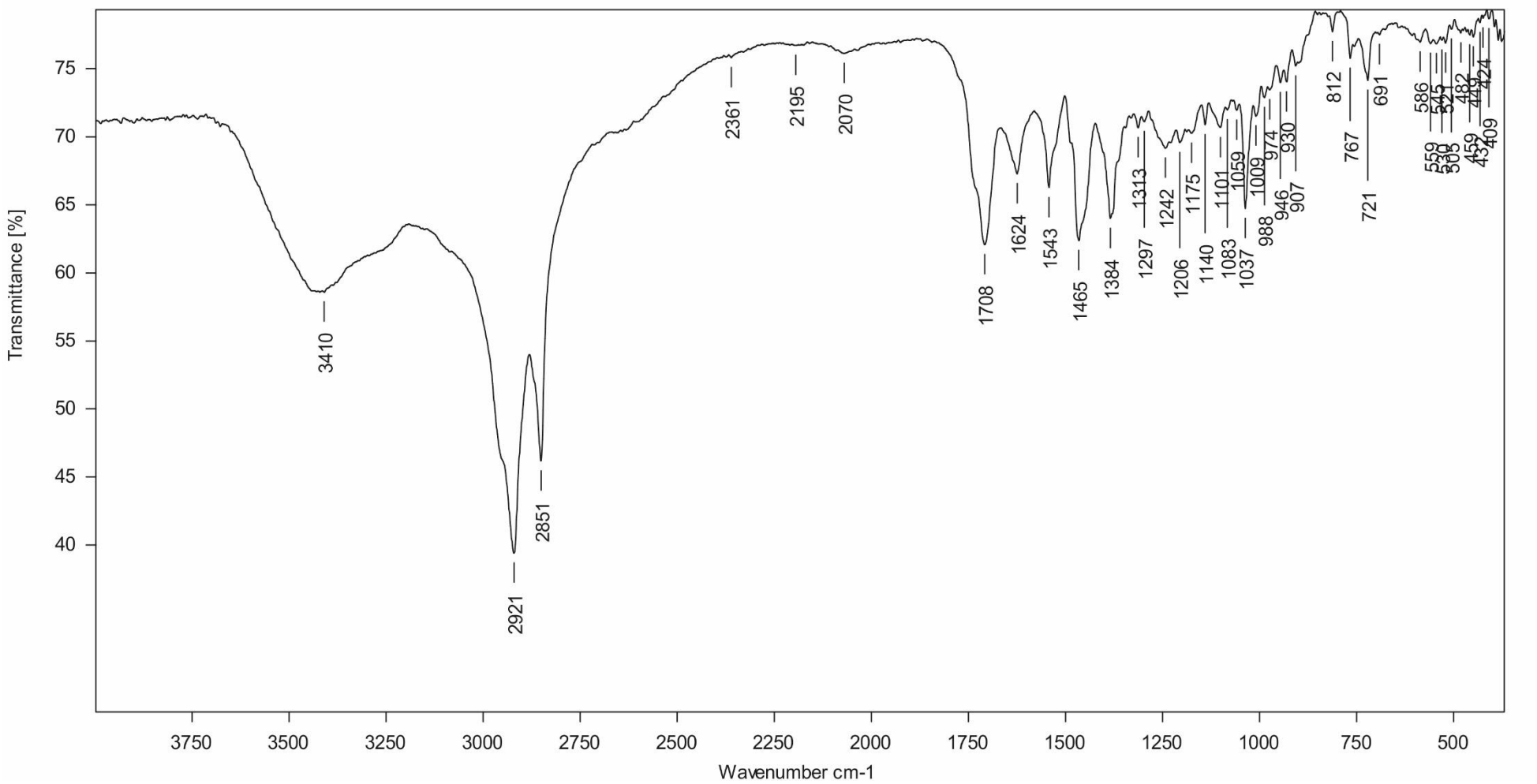


Figure S17. IR (thin film) spectrum of amine **11** (3-α/β-isomers mixture).

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	UltraScan	Scan Begin	50 m/z	Scan End	3000 m/z
Capillary Exit	140.0 V	n/a	n/a	Trap Drive	54.3
Accumulation Time	7786 µs	Averages	5 Spectra	n/a	n/a

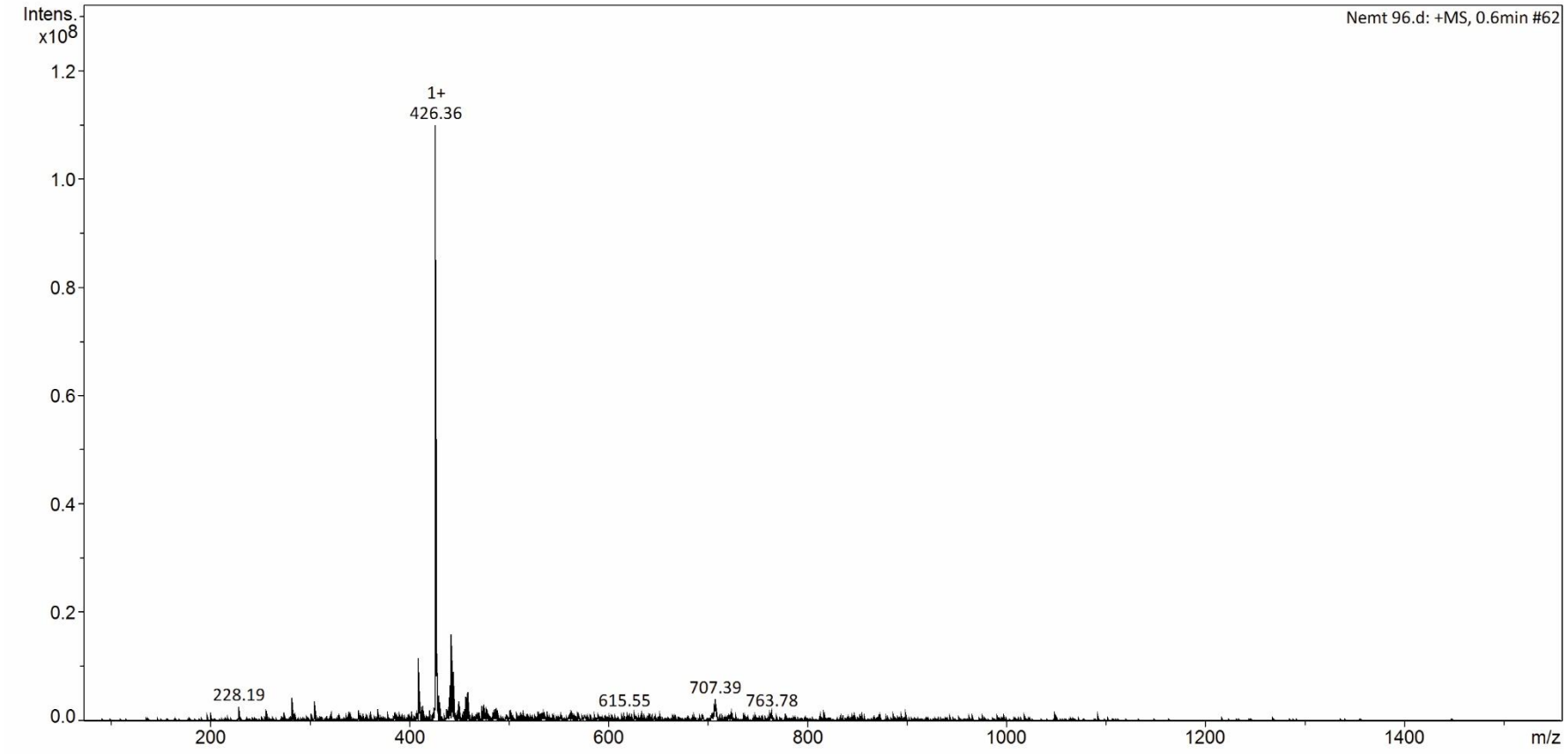


Figure S18. ESI MS spectrum of amine **9** (3-α/β-isomers mixture).

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	UltraScan	Scan Begin	70 m/z	Scan End	3000 m/z
Capillary Exit	140.0 V	n/a	n/a	Trap Drive	54.3
Accumulation Time	1729 µs	Averages	5 Spectra	n/a	n/a

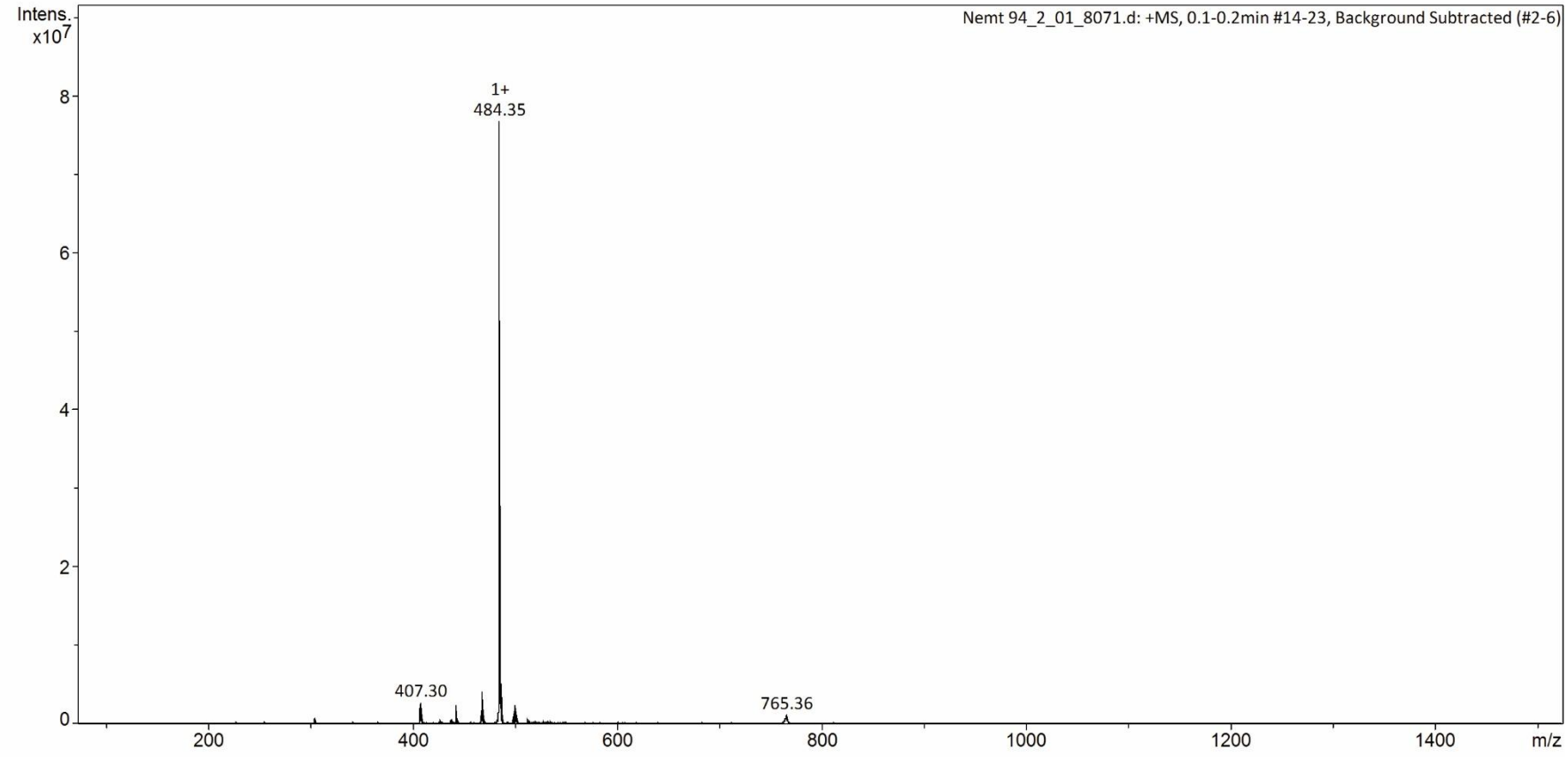


Figure S19. ESI MS spectrum of amine **10** (3-β-isomer).

Acquisition Parameter

Ion Source Type	ESI	Ion Polarity	Positive	Alternating Ion Polarity	off
Mass Range Mode	UltraScan	Scan Begin	70 m/z	Scan End	3000 m/z
Capillary Exit	140.0 V	n/a	n/a	Trap Drive	54.3
Accumulation Time	1769 µs	Averages	5 Spectra	n/a	n/a

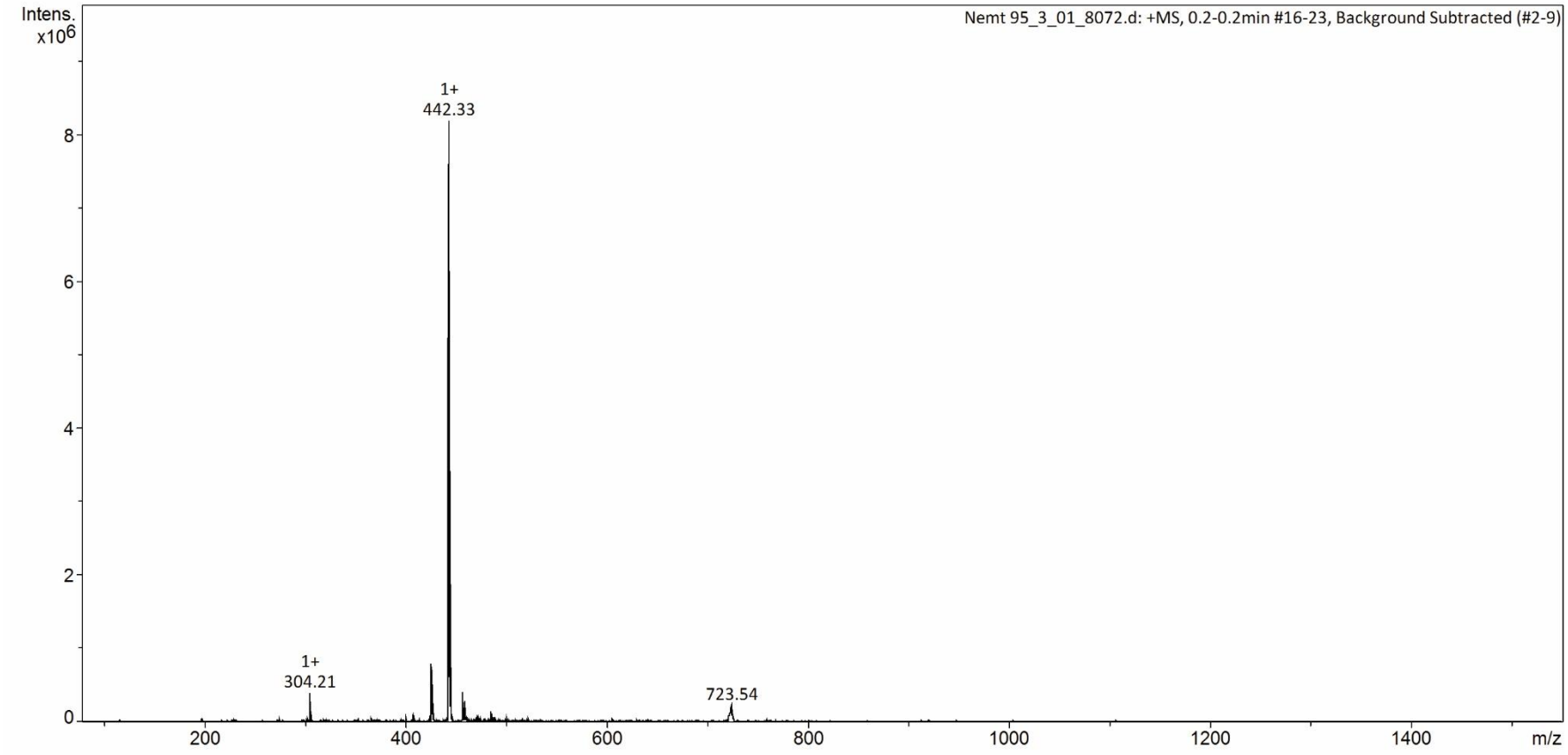


Figure S20. ESI MS spectrum of amine **11** (3-α/β-isomers mixture).