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Molecular structure of gaseous 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, established by electron diffraction and quantum chemical calculations

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Contents

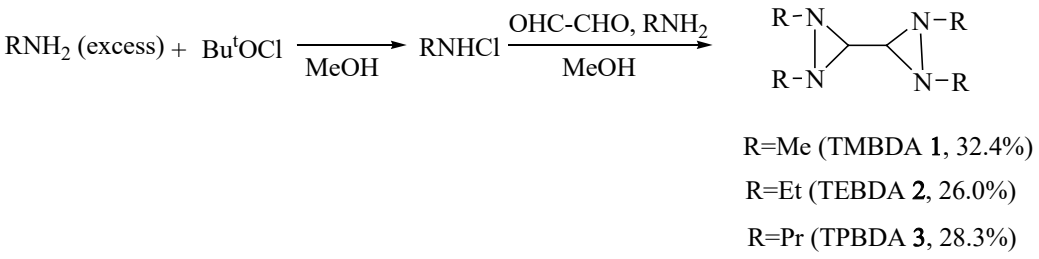
S1. Synthetic procedures

S1.1. General remarks

All starting materials were purchased from commercial sources. NMR spectra were recorded on Bruker Avance 400 and Bruker Avance 600 spectrometers instrument equipped with a Z-gradient broadband observe probe at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$: ^1H δ: 7.26 ppm, ^{13}C δ: 77.0 ppm). A 25-mg portion of the sample was dissolved in 0.6 mL of $CDCl_3$. Splitting patterns are designated as s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Coupling constants (*J*) are given in Hz. The structures of synthesized compounds were elucidated using 1D NMR (^1H, ^{13}C) and 2D NMR spectroscopies: {^1H–^{13}C}HSQC (*Heteronuclear Spectroscopy Quantum Correlation*), {^1H–^{13}C}HMBC (*Heteronuclear Multiple Bond Correlation*), {^1H–^1H}COSY (*Correlation Spectroscopy*), {^1H–^1H}gNOESY (*Nuclear Overhauser Effect Spectroscopy*) and {^1H–^1H}ROESY (*Rotating frame Overhauser Effect Spectroscopy*). The IR spectra were recorded on Bruker "Alpha" spectrometers in the range 400–4000 cm^{-1} (resolution 2 cm^{-1}). High resolution mass spectra were recorded on a Bruker microTOF-QTM spectrometer with electrospray ionization (ESI). All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with *m/z* scan range of 50–3000. External calibration of the mass spectrometer was performed with Electrospray Calibrant Solution (Fluka). A direct syringe injection was used for all analyzed solutions in MeCN (flow rate: 3 μl min^{-1}). Mass spectra were also measured using a TRACE GC ULTRA instrument with mass detector DSQ II. Capillary column TR-5MS was 30 m long with 0.25 mm internal diameter and 0.25 μm active phase thickness. Carrier gas was helium (1.2 ml min^{-1}). Ionization energy was 70 eV. Elemental analyses were performed with CHNS Analyzer Leco TruSpec Micro (LECO, USA). Column chromatography was performed on silica gel 60 (230–400 mesh, Merck or Macherey-Nagel). Analytical thin-layer chromatography (TLC) was carried out using Silufol UV 254. The visualization of the TLC plates was done by spraying of the plates with 5% alcoholic solution of diphenylamine followed by heating of plates.

S1.2. Synthesis of 1,1′,2,2′-tetraalkyl-3,3′-bidiaziridines (general procedure)

1,1′,2,2′-Tetraalkyl-3,3′-bidiaziridines (**1**–**3**) were synthesized at the N. D. Zelinsky Institute of Organic Chemistry, RAS. Substances **2** and **3** were previously unknown. Bu^tOCl (4.4 ml, 40 mmol) was added dropwise to a solution of the amine (200 mmol) in MeOH (100 ml) with vigorous stirring at 0–5 ºC. A 40% aqueous solution of glyoxal (2.90 g, 20 mmol) was added to the resulting mixture. The reaction mixture was stirred at 0–5 ºC for 6 h. Then $CHCl_3$ (150 ml) was added, the resulting mixture was dried with K_2CO_3 and the solvent was evaporated *in vacuo*. The residue was purified by column chromatography on silica gel (SiO_2) using $CHCl_3$–MeOH (25:1) as eluent to afford 1,1′,2,2′-tetraalkyl-3,3′-bidiaziridines (mixture of diastereomers).



Scheme S1.1 Synthesis of substances **1**–**3**.

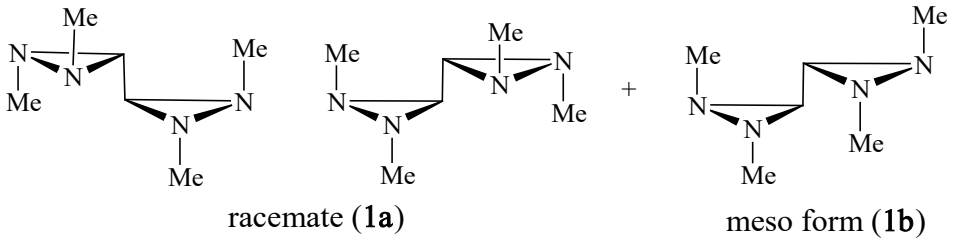
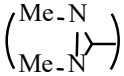
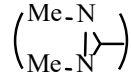
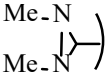


Figure S1.1 Diastereomers of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (TMBDA) **1**.

1,1′,2,2′-Tetramethyl-3,3′-bidiaziridine (TMBDA) **1** was synthesized as a mixture of diastereomers by the general procedure from methylamine (6.2 g, 200 mmol) in MeOH (100 ml). Yield 0.92 g (32.4%). Colorless liquid, bp 68–70 °C (18 Torr). R_f 0.52 ($CHCl_3$–MeOH, 10:1), 0.33 ($CHCl_3$–MeOH, 20:1).

Racemate. ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K) *δ*: 2.42 (s, 6H, 2 N–Me), 2.45 (s, 2H, H–C–C–H), 2.54 (s, 6H, 2 N–Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 298 K) δ: 40.64 (2 N–Me), 46.90 (2 N–Me), 61.83 (H–C–C–H). MS (EI, 70 eV), *m/z* (%): 143 ($[M+H]^+$, 1) 127 ($[M–Me]^+$, 1) 112 ($[M–2Me]^+$, 1) 127 ($[M–3Me+H]^+$, 18), 83 ($[M–4Me+H]^+$, 48), 71 ([M– ]$^+$, 38), 43 ([M–  –Me–(CH)]$^+$, 100).

***Meso* form.** ^{1}H NMR (400.16 MHz, $CDCl_3$, 298 K) δ: 2.39 (s, 2H, H–C–C–H), 2.41 (s, 6H, 2 N–Me), 2.53 (s, 6H, 2 N–Me). ^{13}C NMR (100.62 MHz, $CDCl_3$, 298 K) δ: 40.84 (2 N–Me), 47.35 (2 N–Me), 60.39 (H–C–C–H). MS (EI, 70 eV), *m/z* (%): 143 ($[M+H]^+$, 1), 127 ($[M–Me]^+$, 1), 112 ($[M–2Me]^+$, 1), 127 ($[M–3Me+H]^+$, 18), 83 ($[M–4Me+H]^+$, 48), 71 ([M– ]$^+$, 38), 43 ([M–  –Me–(CH)]$^+$, 100). IR (KBr, *ν*/cm^{-1}): 3010, 2073, 2919, 2866, 2788, 1476, 1453, 1398, 1353, 1314, 1284, 1270, 1190, 1148, 1112, 1077, 942, 779, 710, 558, 499.

Racemate/*meso* form (66.7 : 33.3). IR (thin layer, *ν*/cm^{-1}): 2971, 2925, 2867, 2780, 1664, 1649, 1558, 1537, 1558, 1455, 1401, 1302, 1274, 1190, 1149, 1129, 1102, 1079, 958, 889, 830, 801, 775, 718, 645, 553, 517, 503. HRMS (ESI-TOF), *m/z*: 143.1298 $[M+H]^+$, 165.1108 $[M+Na]^+$ (calc. for $C_6H_{14}N_4$, *m/z*: 143.1291, 165.1111). Found (%): C, 50.57; H, 10.12; N, 39.30. Calc. for $C_6H_{14}N_4$ (%): C, 50.70; H, 9.86; N, 39.44.

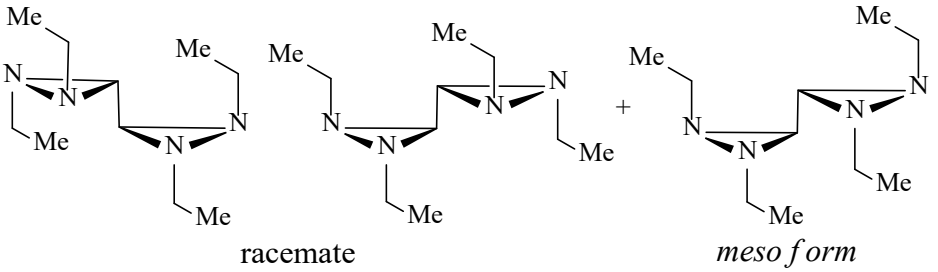


Figure S1.2 Diastereomers of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**.

1,1',2,2'-Tetraethyl-3,3'-bidiaziridine (TEBDA) **2** was synthesized as a mixture of diastereomers by the general procedure from ethylamine, (9.0 g, 200 mmol) in MeOH (100 ml). Yield 1.03 g (26.0%), colorless liquid. R_f 0.52 ($CHCl_3$–MeOH, 20:1).

Racemate. ^{1}H NMR (600.13 MHz, $CDCl_3$, 298 K) δ: 1.15 (t, 6H, 2Me, ^3J 7.2 Hz), 1.21 (t, 6H, 2Me, ^3J 7.2 Hz), 2.18–2.23 (m, 2H, 2 N–CH_a–), 2.52–2.57, (m, 2H, 2 N–CH_a–), 2.58 (s, 2H, H–C–C–H), 2.63–2.69, (m, 2H, 2 N–CH_b–), 2.78–2.83, (m, 2H, 2 N–CH_b–). ^{13}C NMR (150.90 MHz, $CDCl_3$, 298 K) δ: 13.33 (2C, 2Me), 14.21 (2C, 2Me), 47.97 (2C, 2 N–CH_2–),55.12 (2C, N–CH_2–),61.06 (2C, H–C–C–H).

***Meso* form.** ^{1}H NMR (600.13 MHz, $CDCl_3$, 298 K) δ: 1.17 (t, 6H, 2Me, ^3J 7.2 Hz), 1.22 (t, 6H, 2Me, ^3J 7.2 Hz), 2.11–2.18 (m, 2H, 2 N–CH_a–), 2.55 (s, 2H, H–C–C–H), 2.55–2.60, (m, 2H, 2 N–CH_a–), 2.63–2.85, (m, 4H, 4 N–CH_b–). ^{13}C NMR (150.90 MHz, $CDCl_3$, 298 K) δ: 13.36 (2C, 2Me), 13.98 (2C, 2Me), 48.12 (2C, 2 N–CH_2–), 55.39 (2C, 2 N–CH_2–), 59.68 (2C, H–C–C–H).

Racemate/*meso* form (60 : 40). IR (thin layer, ν/cm^{-1}): 2973, 2934, 2871, 1683, 1448, 1379, 1347, 1303, 1285, 1256, 121, 1109, 1081, 1020, 961, 813, 793, 755, 735, 643. HRMS (ESI-TOF), *m/z*: 199.1923 $[M+H]^+$, 221.1742 $[M+Na]^+$ (calc. for $C_{10}H_{22}N_4^+$, *m/z*: 199.1917, 221.1737).

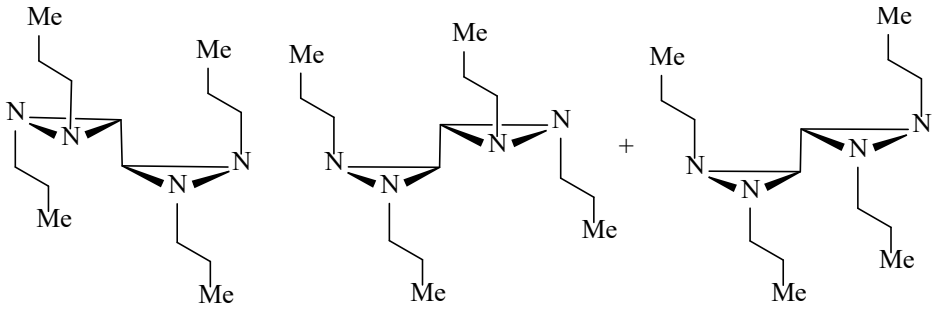
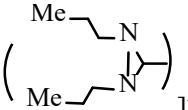
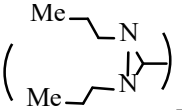
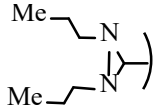
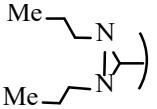
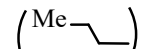


Figure S1.3 Diastereomers of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**.

1,1',2,2'-Tetrapropyl-3,3'-bidiaziridine (TPBDA) **3** was synthesized as a mixture of diastereomers by the general procedure from propylamine (16.4 ml, 200 mmol). Yield 1.44 g (28.3%), colorless liquid. R_f 0.54 ($CHCl_3$–MeOH, 10:1), 0.33 ($CHCl_3$–MeOH, 20:1).

Racemate. ^{1}H NMR (600.13 MHz, $CDCl_3$, 298 K) δ: 0.948 (t, 6H, 2Me, ^3J 7.5 Hz), 0.975 (t, 6H, 2Me, ^3J 7.4 Hz), 1.60–1.70 (m, 8H, 4 –CH_2–Me), 2.32–2.37 (m, 2H, 2 N–CH_a–), 2.46–2.56, (m, 4H, 2 N–CH_a–, 2 N–CH_b–), 2.59 (s, 2H, H–C–C–H), 2.72–2.78, (m, 2H, 2 N–CH_b–). ^{13}C NMR (150.90 MHz, $CDCl_3$, 298 K) δ: 11.68 (2Me), 11.71 (2Me), 21.80 (2 –*C*H_2–Me), 22.75 (2 –*C*H_2–Me), 55.74 (2 N–CH_2–), 61.23 (2C, H–C–C–H), 62.87 (2 N–CH_2–).

***Meso* form.** ^{1}H NMR (600.13 MHz, $CDCl_3$, 298 K) δ: 0.945 (t, 6H, 2Me), 0.978 (t, 6H, 2Me), 2.10–2.16 (m, 2H, 2 N–CH_a–), 2.46–2.56 (m, 2H, 2 N–CH_a–), 2.55 (s, 2H, H–C–C–H), 2.56–2.63 (m, 2H, 2 N–CH_b–), 2.64–2.70 (m, 2H, 2 N–CH_b–). ^{13}C NMR (150.90 MHz, $CDCl_3$, 298 K) δ: 11.70 (4Me), 21.95 (2 –*C*H_2–Me), 22.51 (2 –*C*H_2–Me), 55.82 (2 N–CH_2–), 59.71 (2C, H–C–C–H), 63.07 (2 N–CH_2–). MS (EI, 70 eV), *m/z* (%): 225 ([M–C_2H_5]$^+$, 1), 196 ([M–C_3H_7–Me]$^+$, 1), 197 ([M–C_3H_7–Me+H]$^+$, 3), 168 ([M–2C_3H_7]$^+$, 3), 154 ([M–2C_3H_7–Me+H]$^+$, 11), 141 ([M–2C_3H_7–C_2H_5+2H]$^+$, 100), 139 ([M–2C_3H_7–C_2H_5]$^+$, 18), 127 ([]$^+$, 27), 111 ([ –Me–H]$^+$, 62), 97 ([ –2Me]$^+$, 47), 82 ([ –C_2H_5–Me–H]$^+$, 8), 43 ([]$^+$, 77).

Racemate/*meso* form (~ 80 : 20). IR (thin layer, *v*/cm^{-1}): 2961, 2935, 2875, 2854, 1270, 1681, 1560, 1462, 1382, 1290, 1268, 1113, 1083, 1025, 902, 825, 755, 700, 638, 559. HRMS (ESI-TOF), *m/z*: 255.2540 [M+H]$^+$, 277.2355 [M+Na]$^+$ (calc. for $C_{14}H_{30}N_4$, *m/z*: 255.2543, 277.2363).

S2. Copies of NMR, mass and IR spectra

S2.1. TMBDA 1 after column chromatography (racemate and *meso*-form)

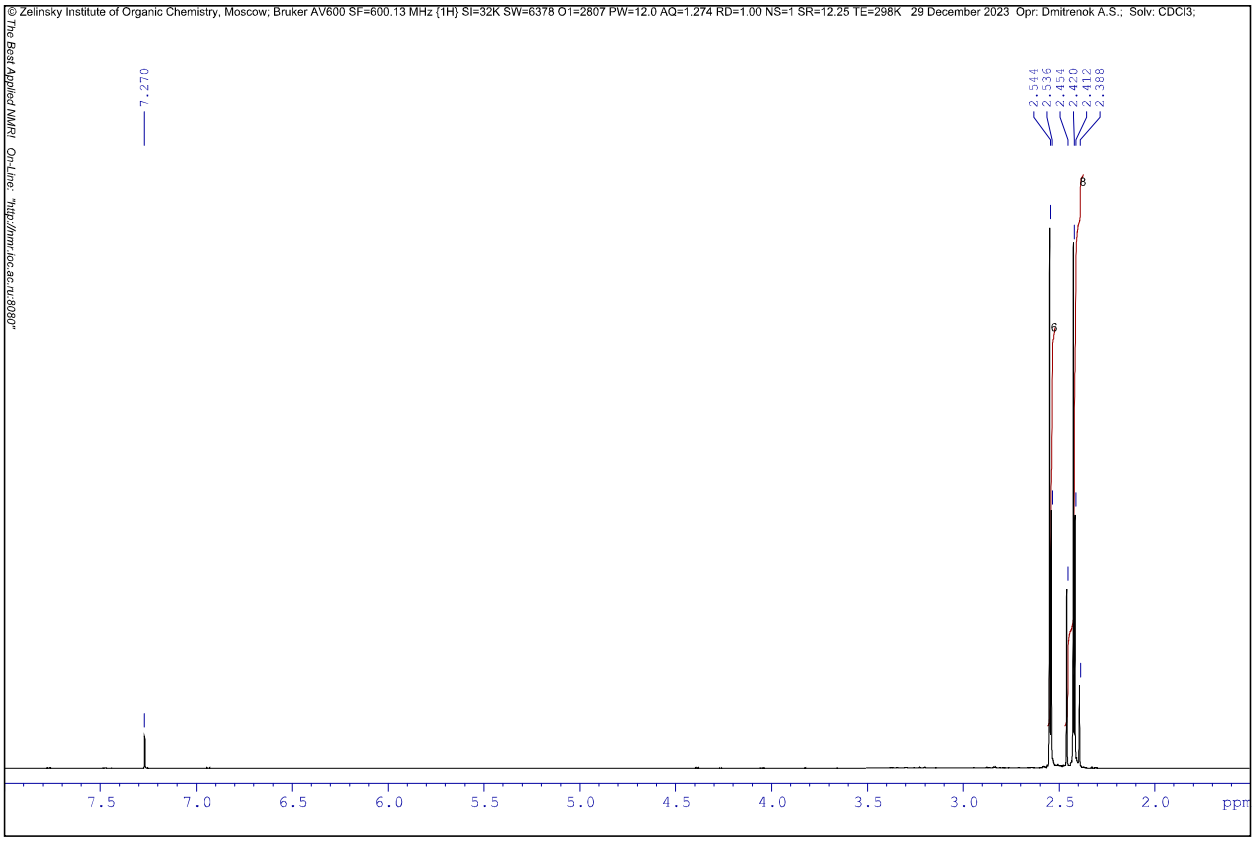


Figure S2.1 ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (TMBDA) **1** at the beginning of column chromatography, with racemate/*meso*-form ≈ 67 : 33.

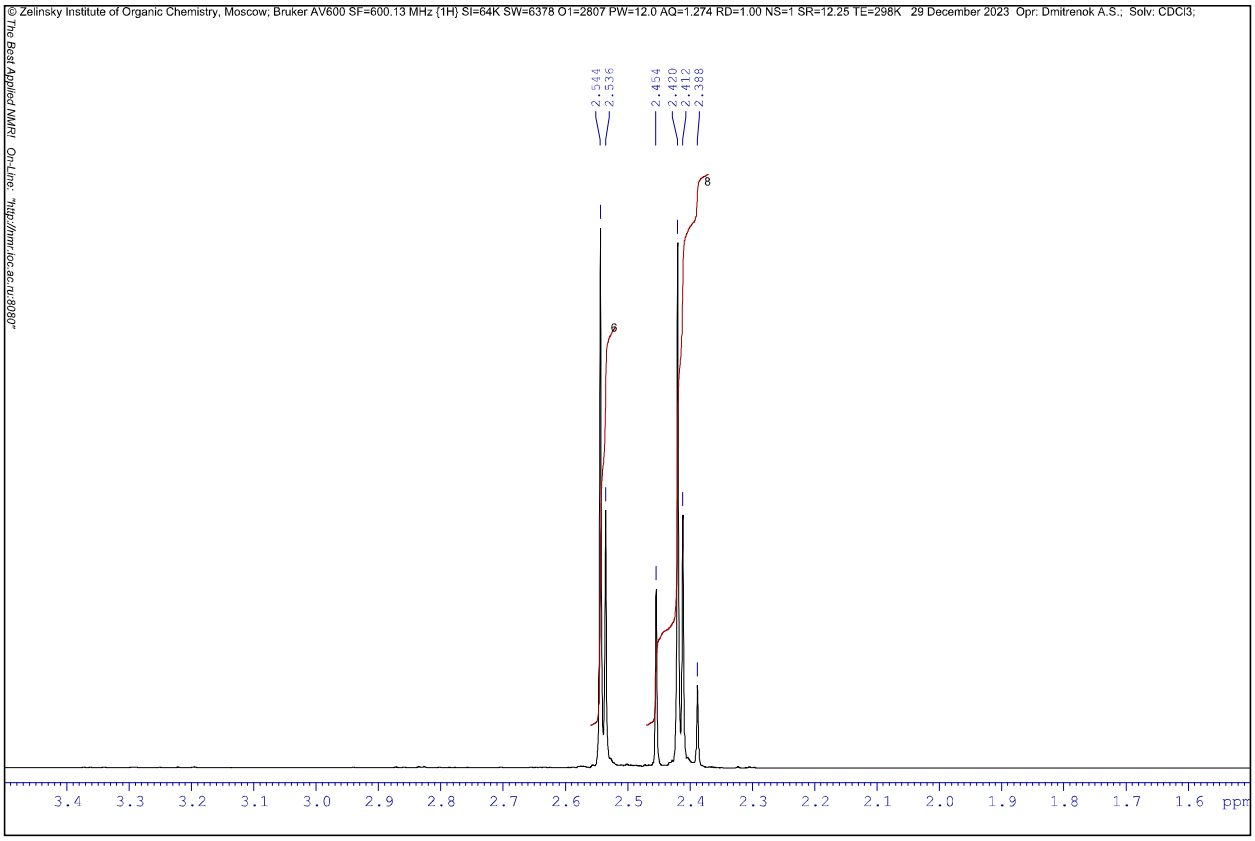


Figure S2.2 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1** at the beginning of column chromatography, with racemate/*meso*-form ≈ 67 : 33.

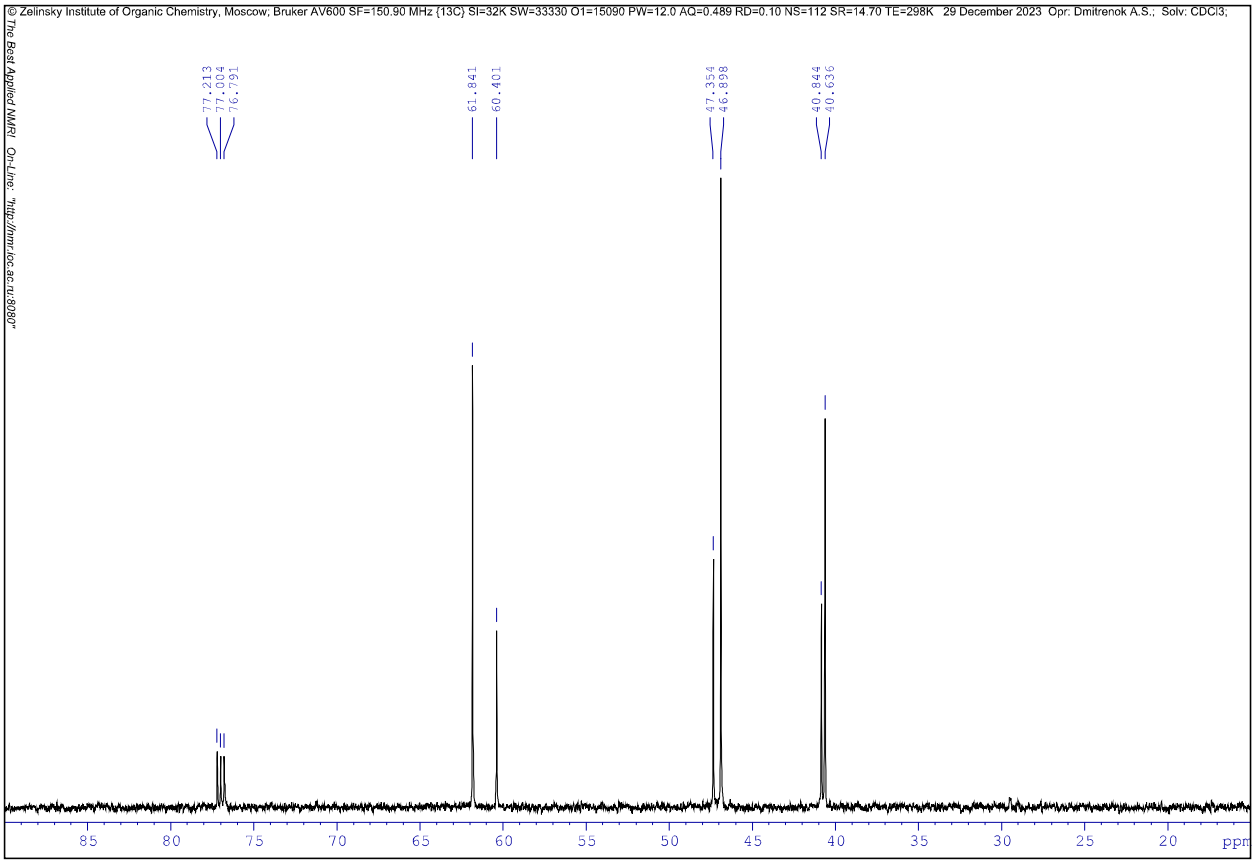


Figure S2.3 ^{13}C NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1** at the beginning of column chromatography.

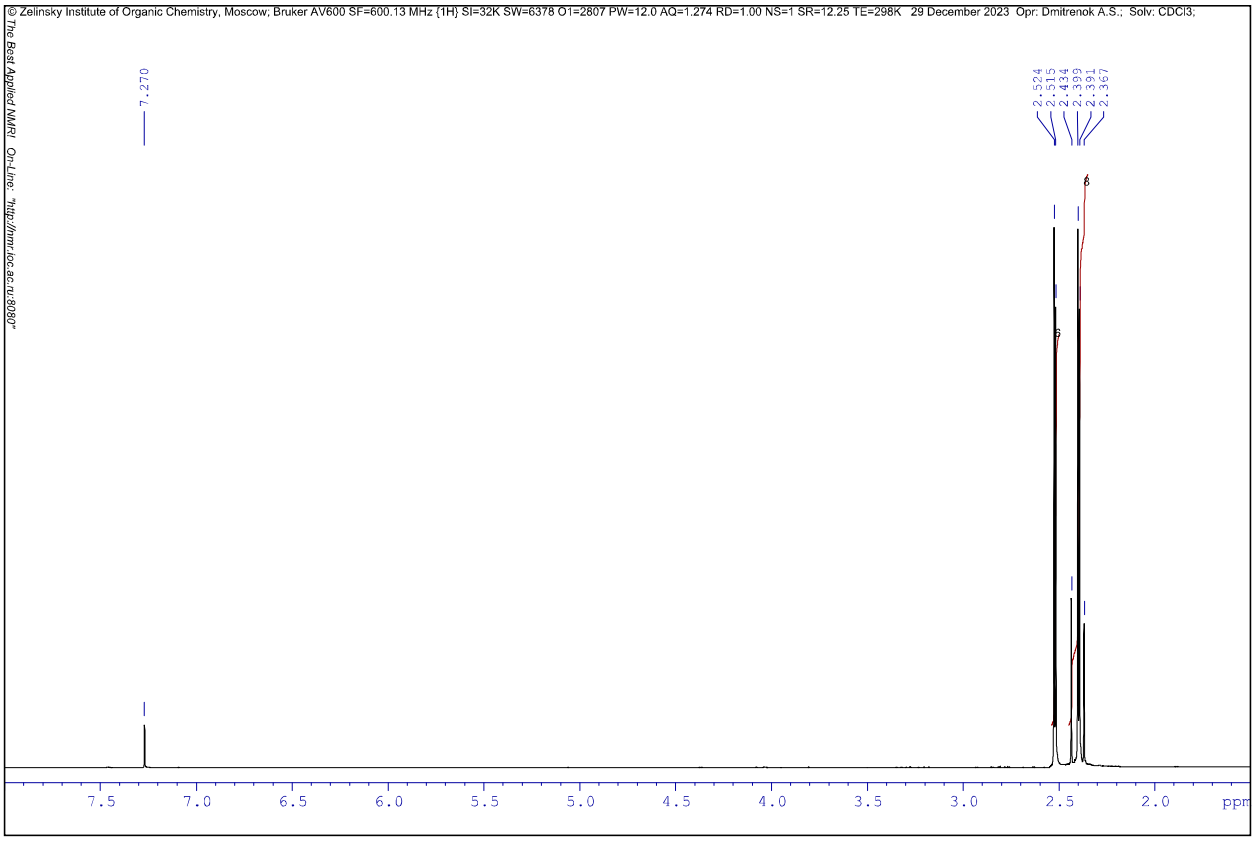


Figure S2.4 ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**, the main product of column chromatography, with racemate/*meso*-form ≈ 53 : 47.

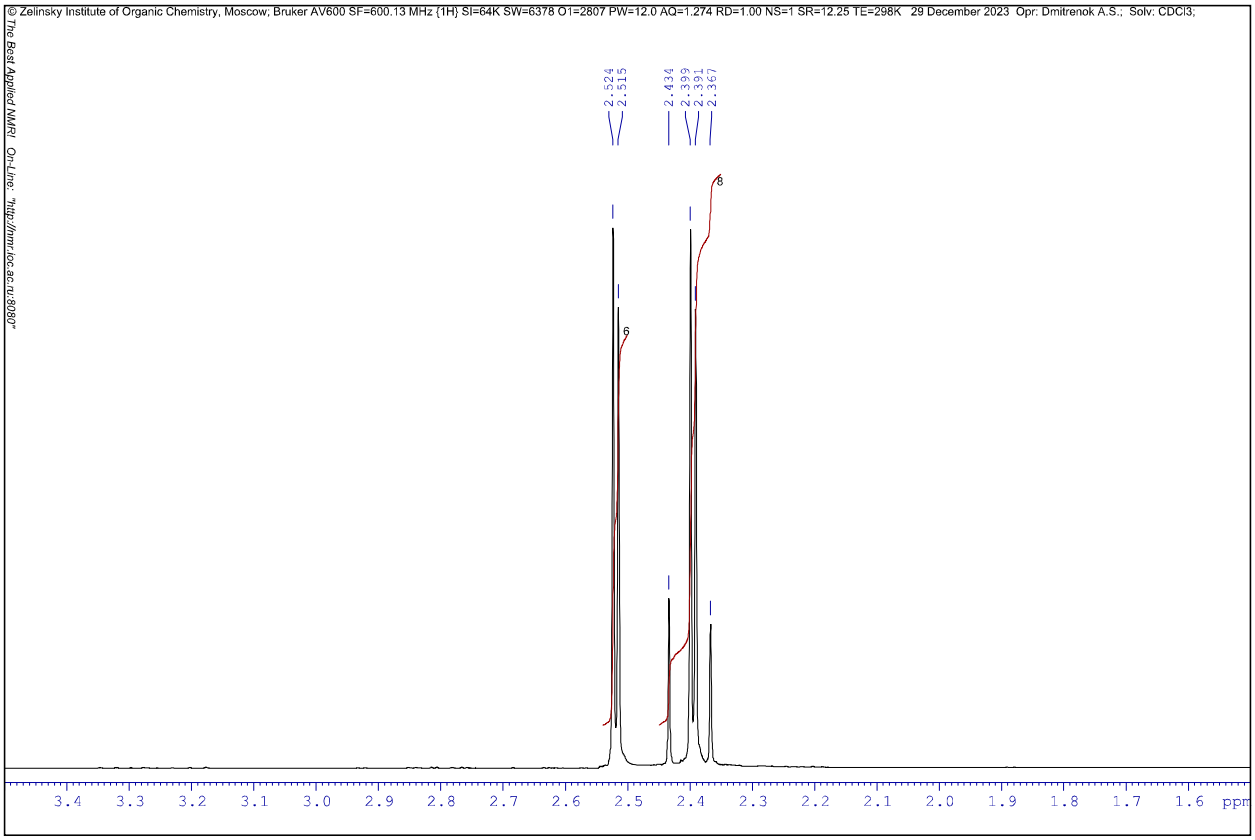


Figure S2.5 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**, the main product of column chromatography, with racemate/*meso*-form ≈ 53 : 47.

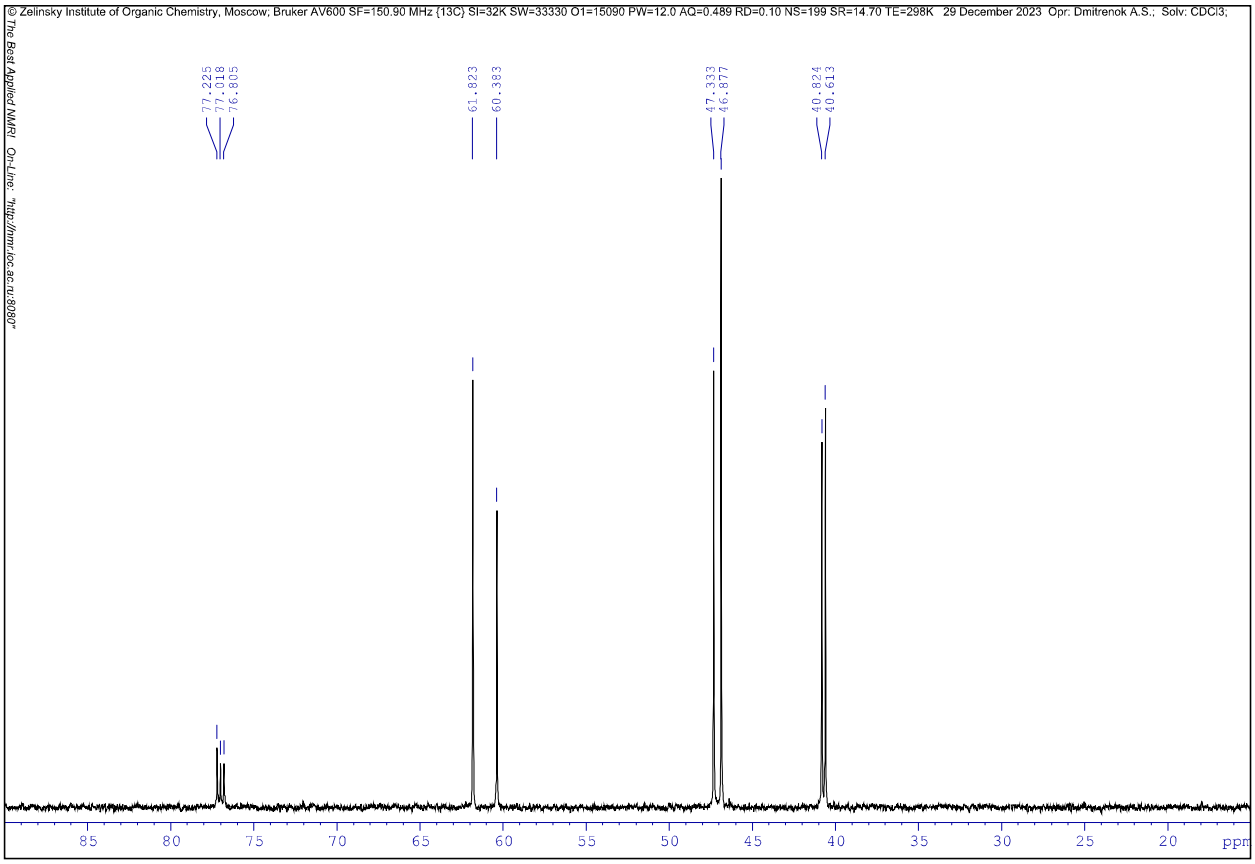


Figure S2.6 ^{13}C NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1**, the main product of column chromatography.

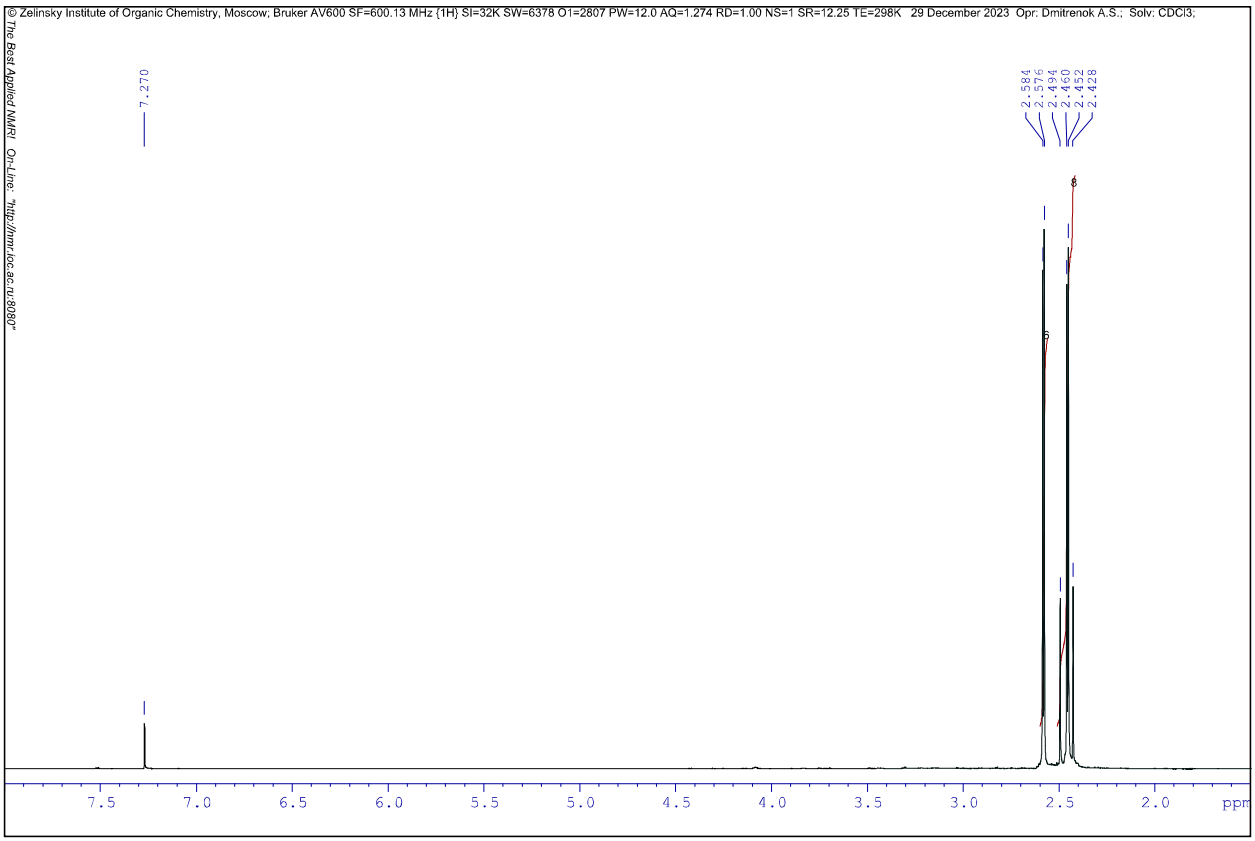


Figure S2.7 ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**, the final product of column chromatography, with racemate/*meso*-form ≈ 48 : 52.

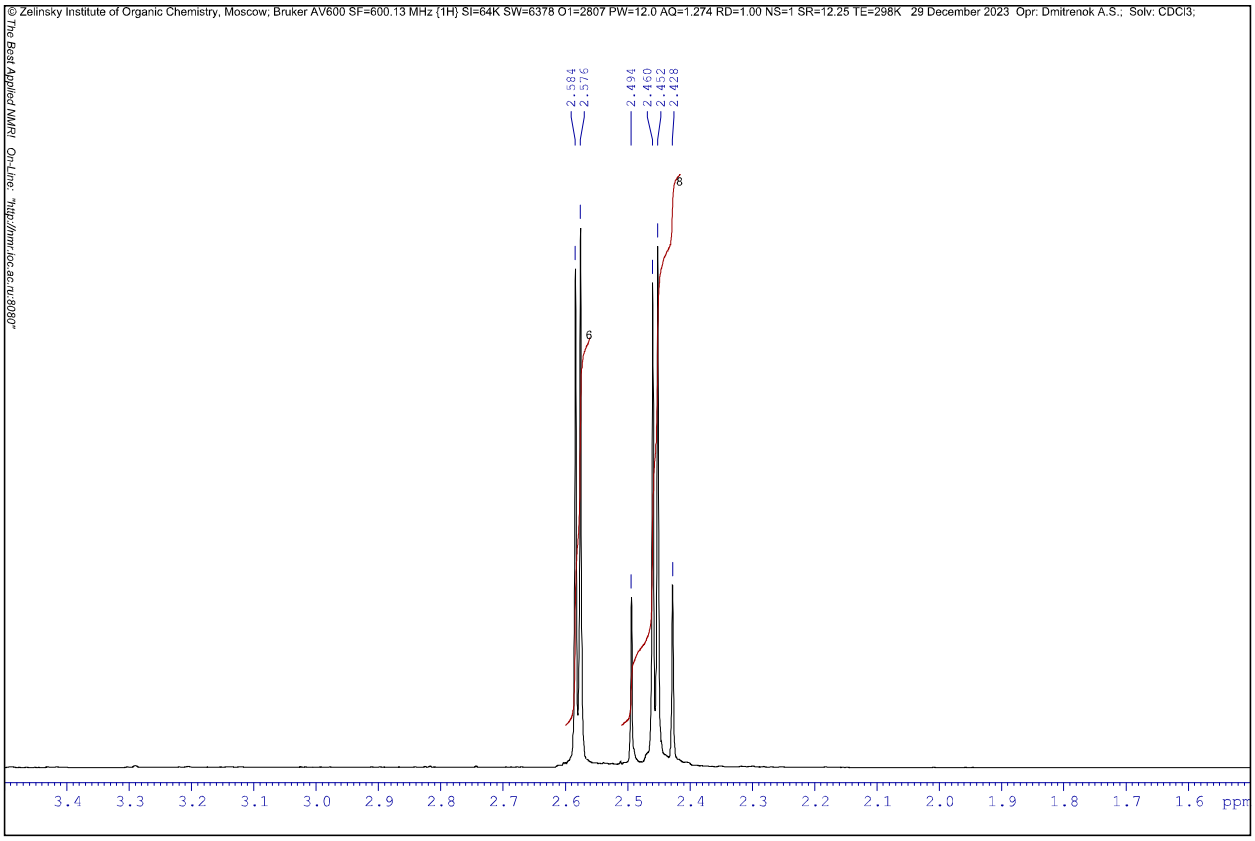


Figure S2.8 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**, the final product of column chromatography, with racemate/*meso*-form ≈ 48 : 52.

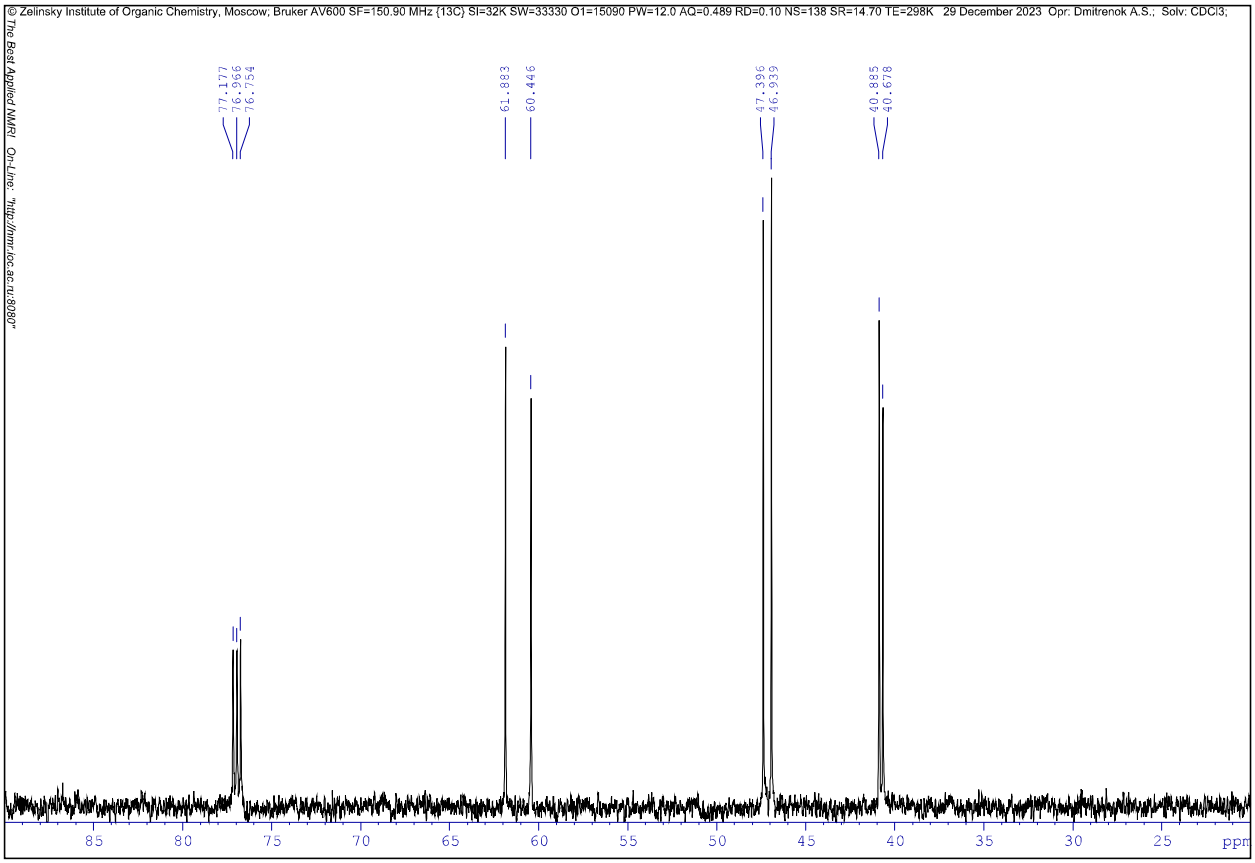


Figure S2.9 ^{13}C NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1**, the final product of column chromatography.

S2.2. TMBDA 1 after vacuum distillation of chromatography products (racemate and *meso*-form). Fraction with bp 68–70 °C (18 Torr).

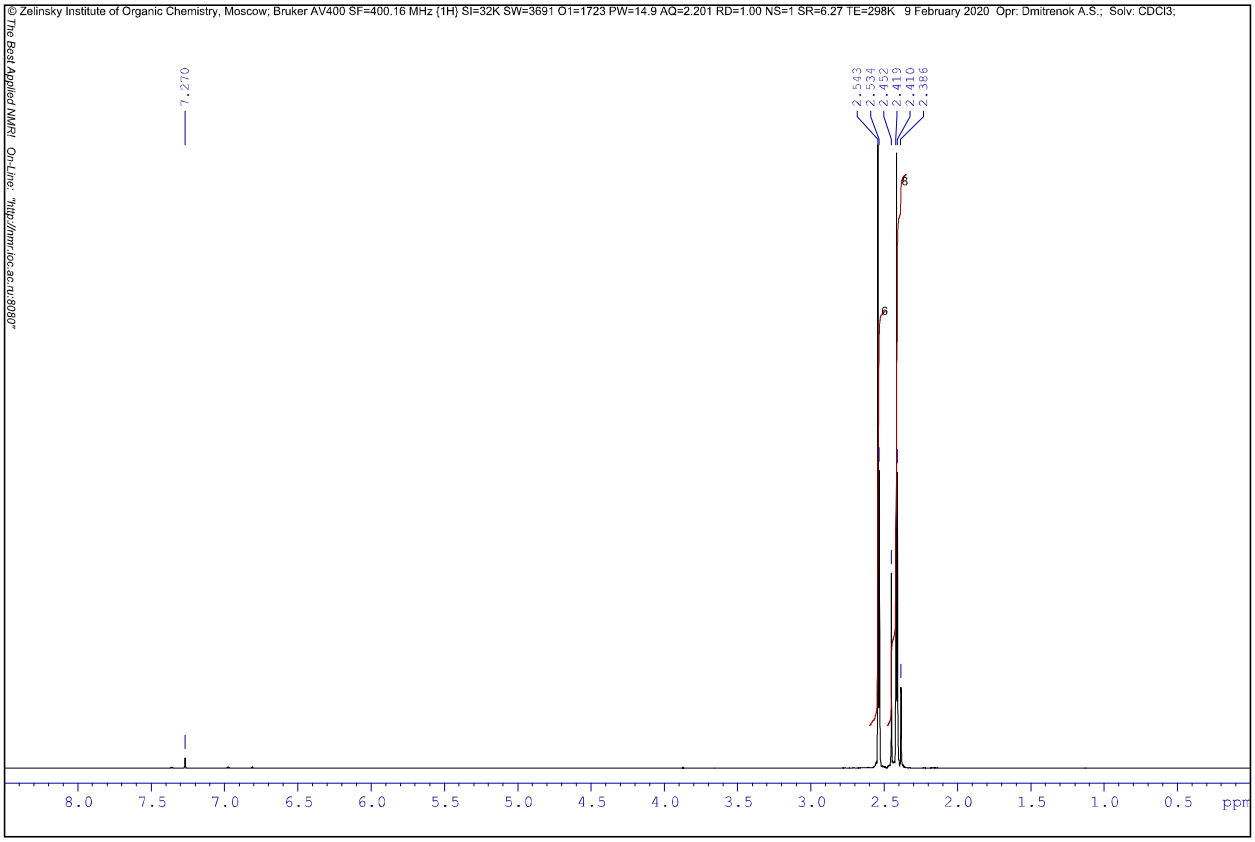


Figure S2.10 ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1** after vacuum distillation, with racemate/*meso*-form ≈ 66 : 34.

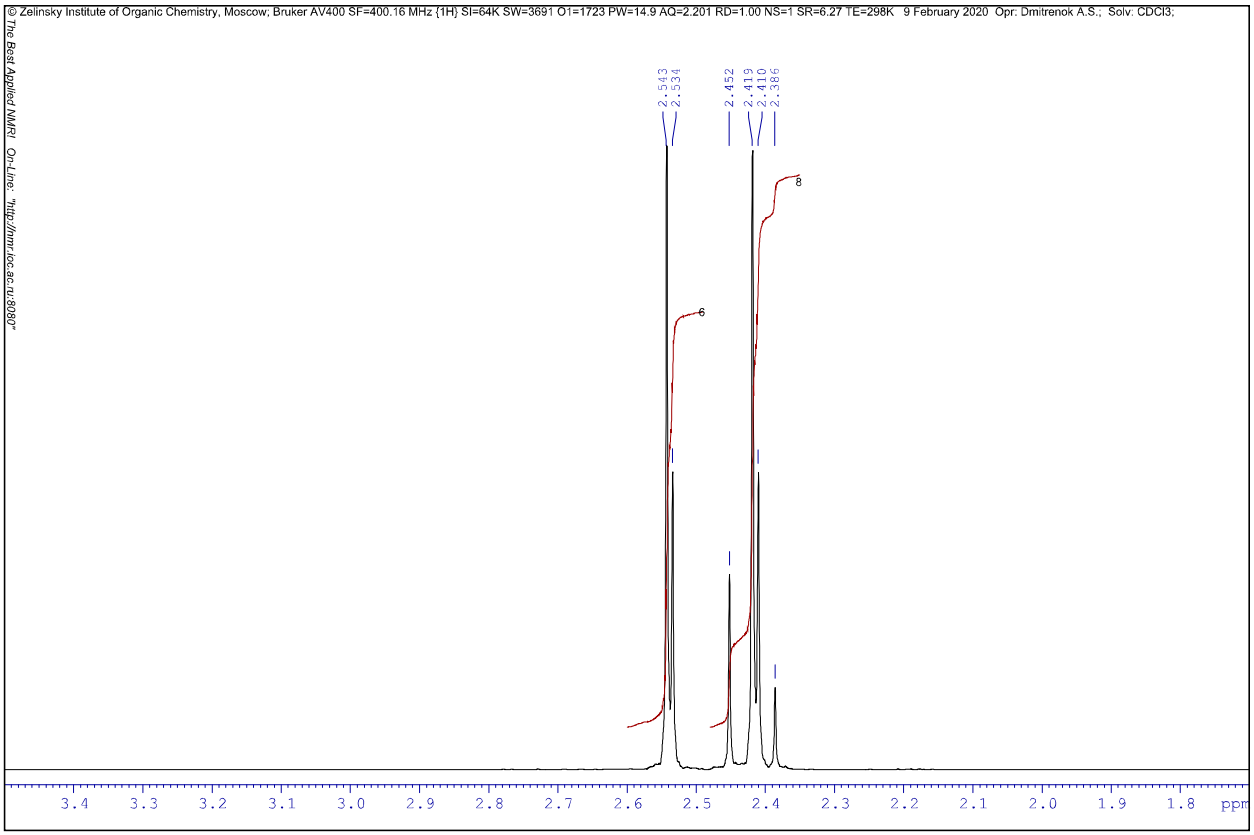


Figure S2.11 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1** after vacuum distillation, with racemate/*meso*-form ≈ 66 : 34.

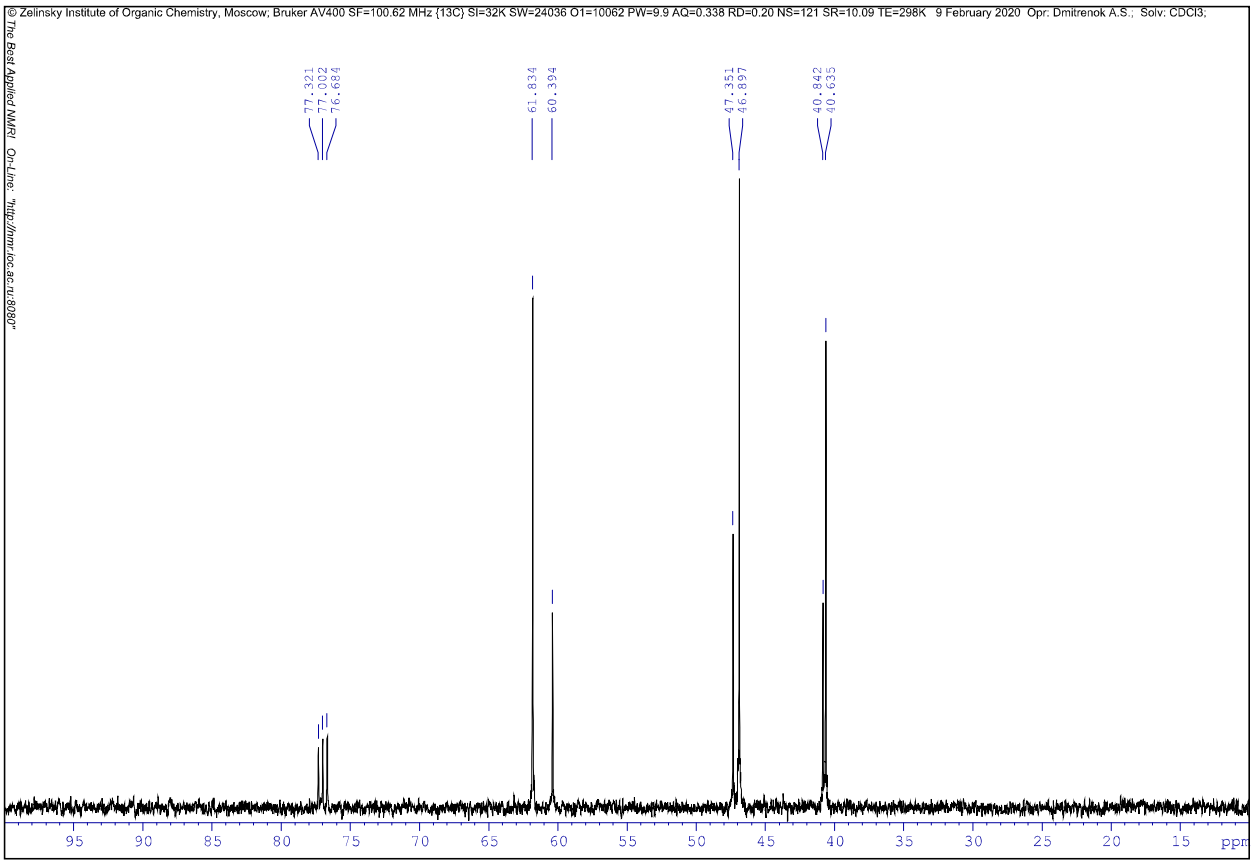


Figure S2.12 ^{13}C NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1**.

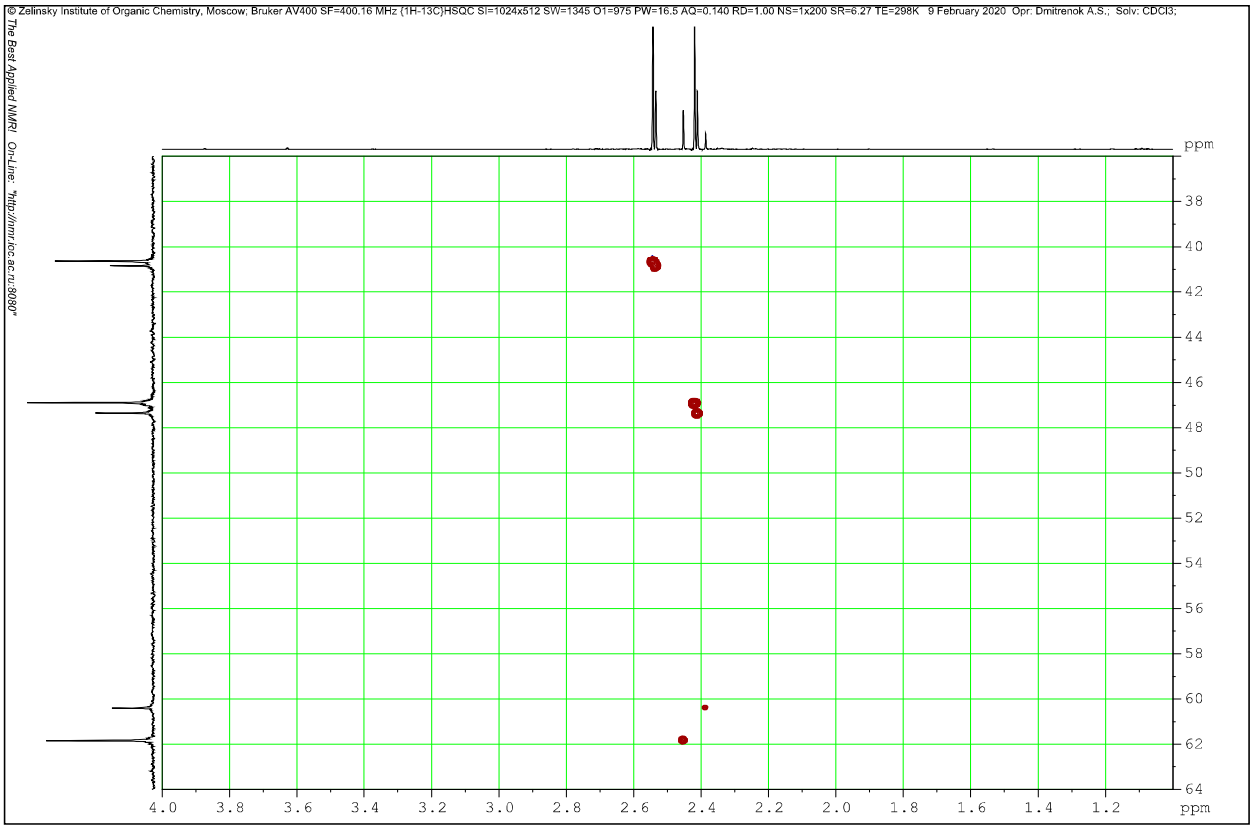


Figure S2.13 {^{1}H–^{13}C} HSQC spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1**.

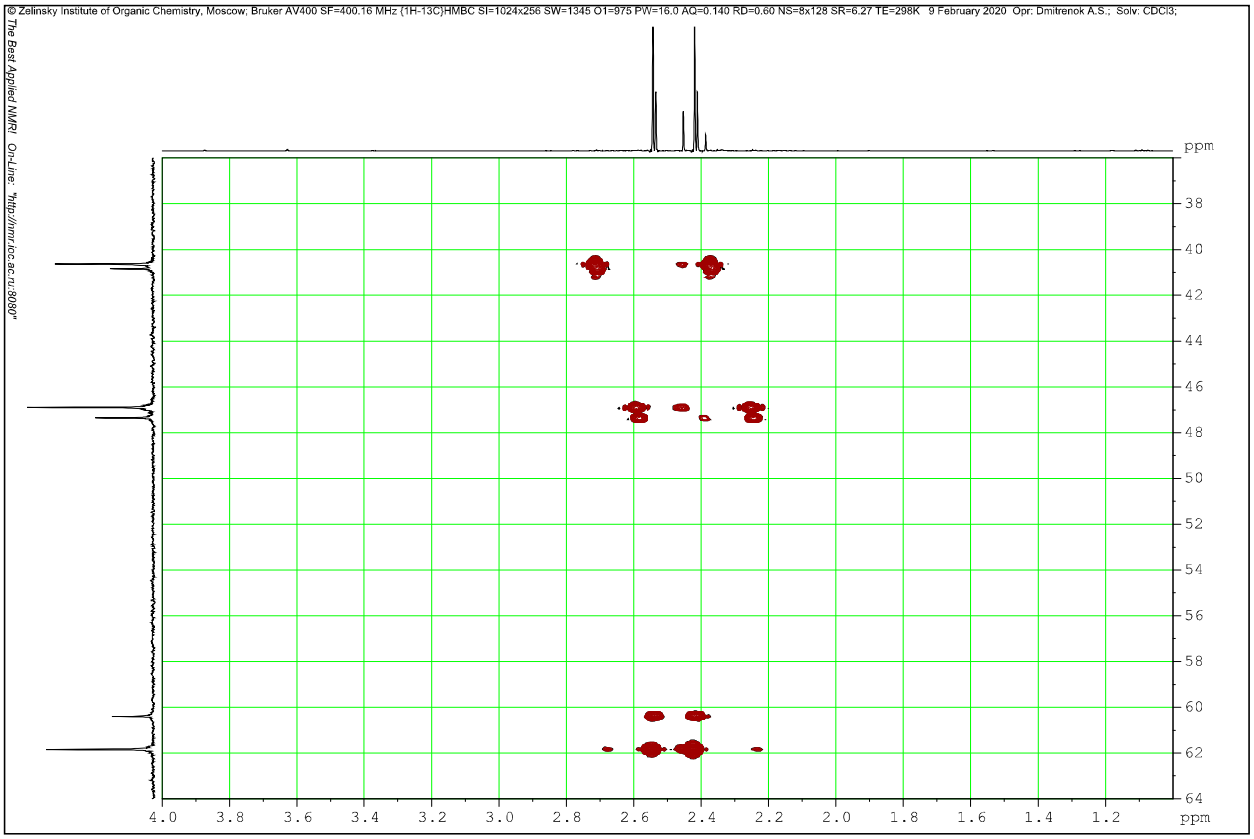


Figure S2.14 {^{1}H–^{13}C} HMBC spectrum ($CDCl_3$) of 1,1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1**.

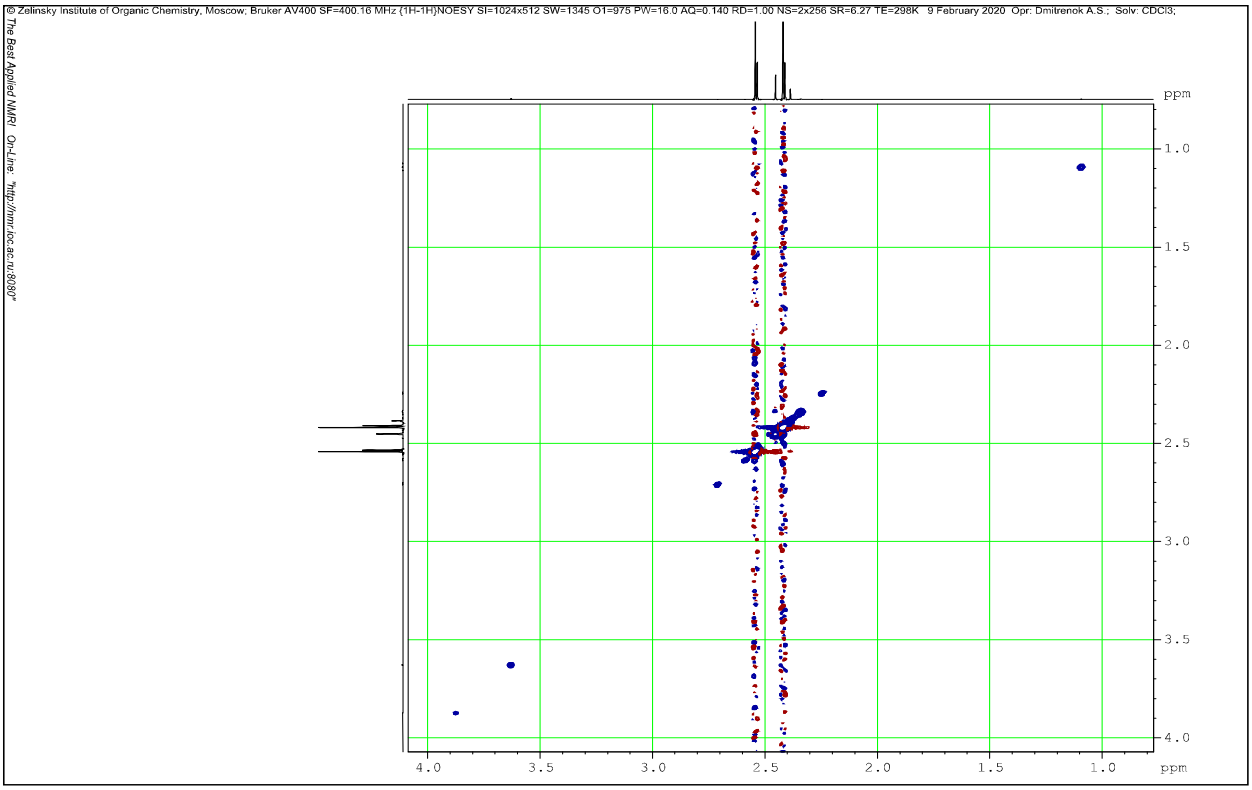


Figure S2.15 {^{1}H–^{1}H} gNOESY spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine (racemate and *meso*-form) **1**.

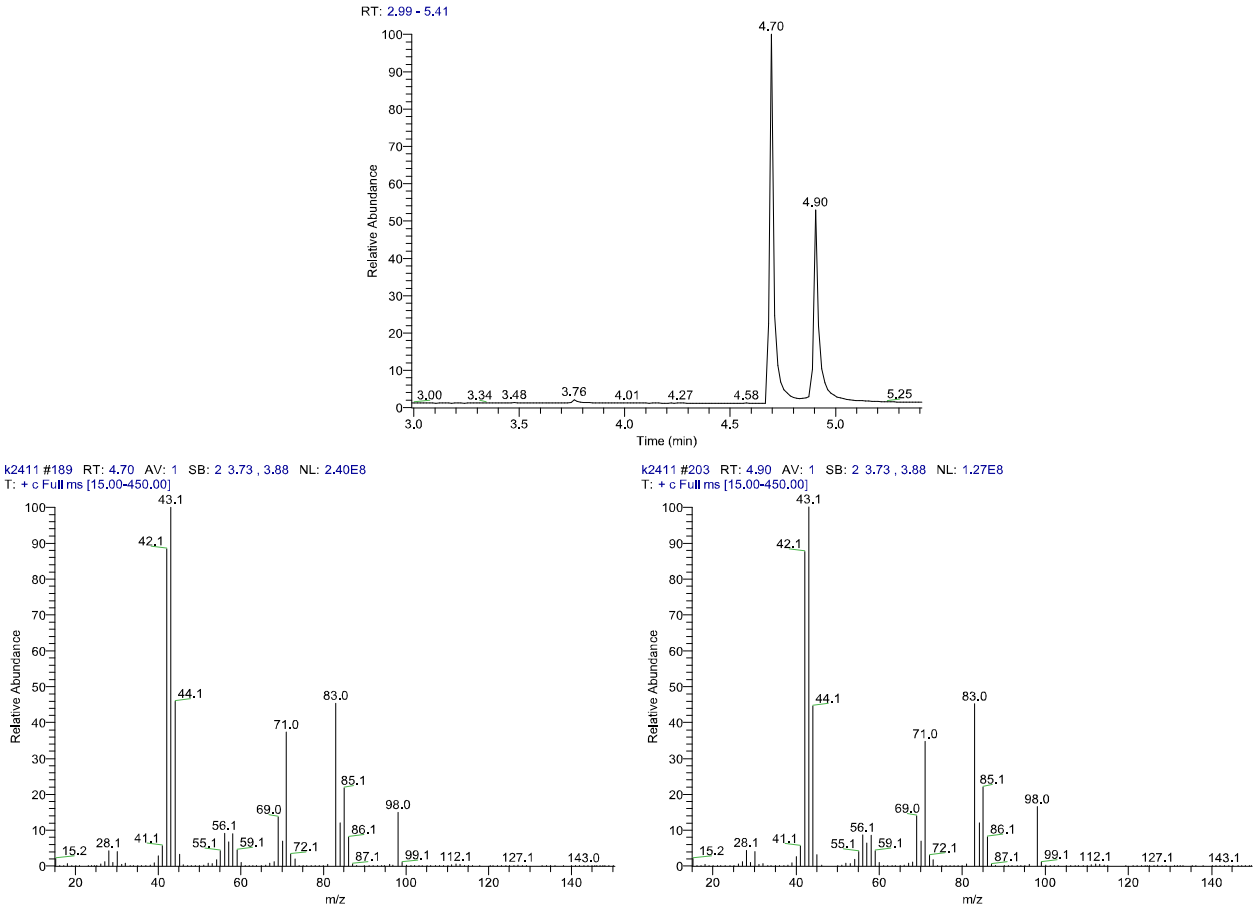


Figure S2.16 Chromato-mass spectrum of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**, with racemate/*meso*-form = 66 : 34.

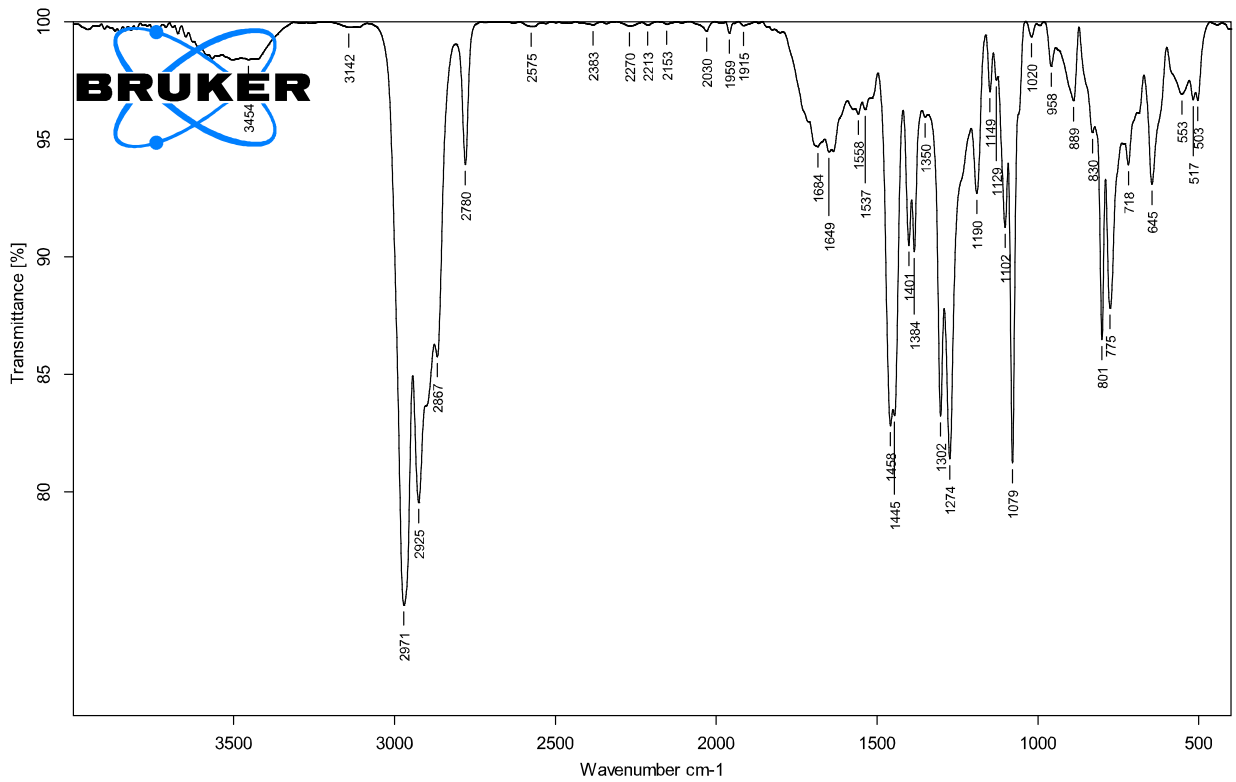


Figure S2.17 IR spectrum (thin layer) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**, with racemate/*meso*-form = 66 : 34.

S2.3. TMBDA 1: *Meso*-form of TMBDA 1b, crystalline product that precipitates when a mixture of diastereomers is cooled

Separation of the *meso*-form **1b** of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine **1**.

Product **1** (1 g) isolated by chromatography was cooled to –20 °C for 3 h, the precipitate that formed was filtered off, washed with a small amount of cold hexane, dried in air for 3 h and placed in a closed vessel (the product is volatile). 0.12 g of *meso*-form **1b** (12%) was obtained, mp 40 °C.

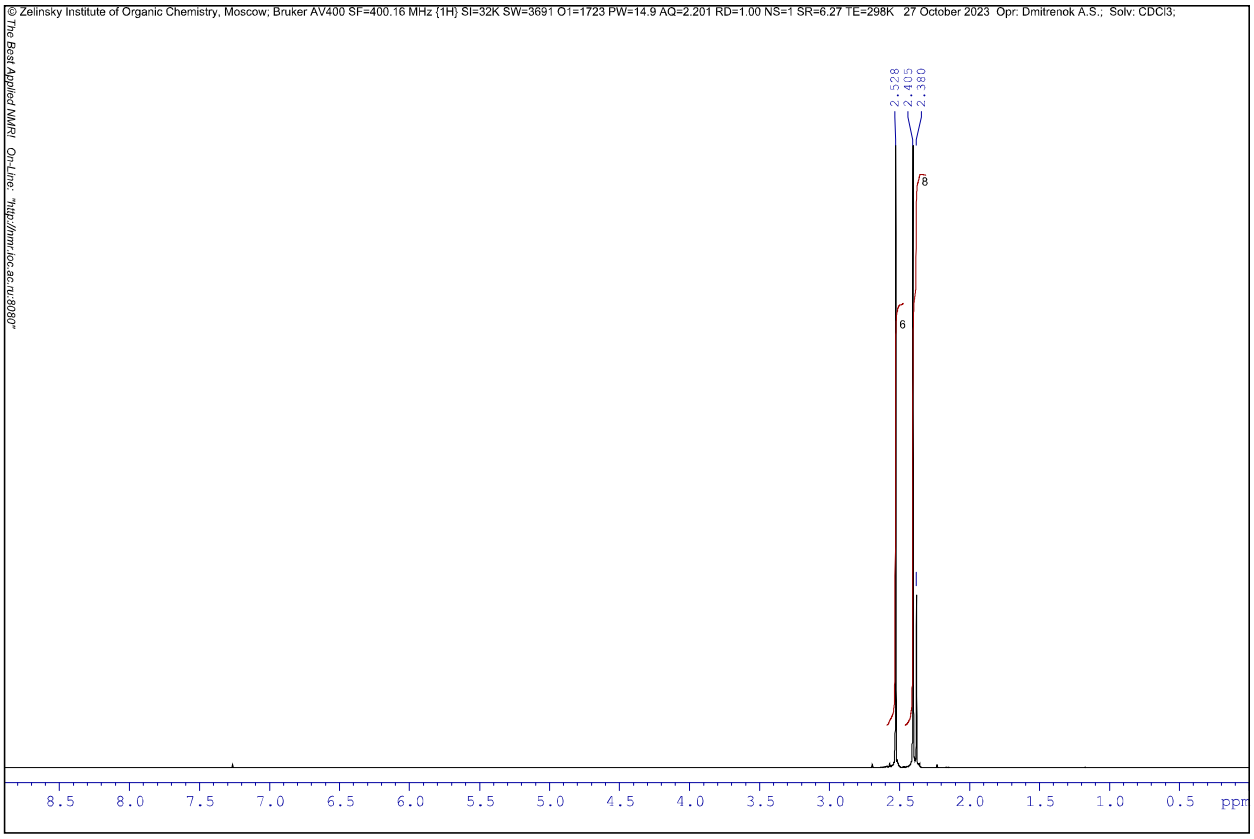


Figure S2.18 ^{1}H NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

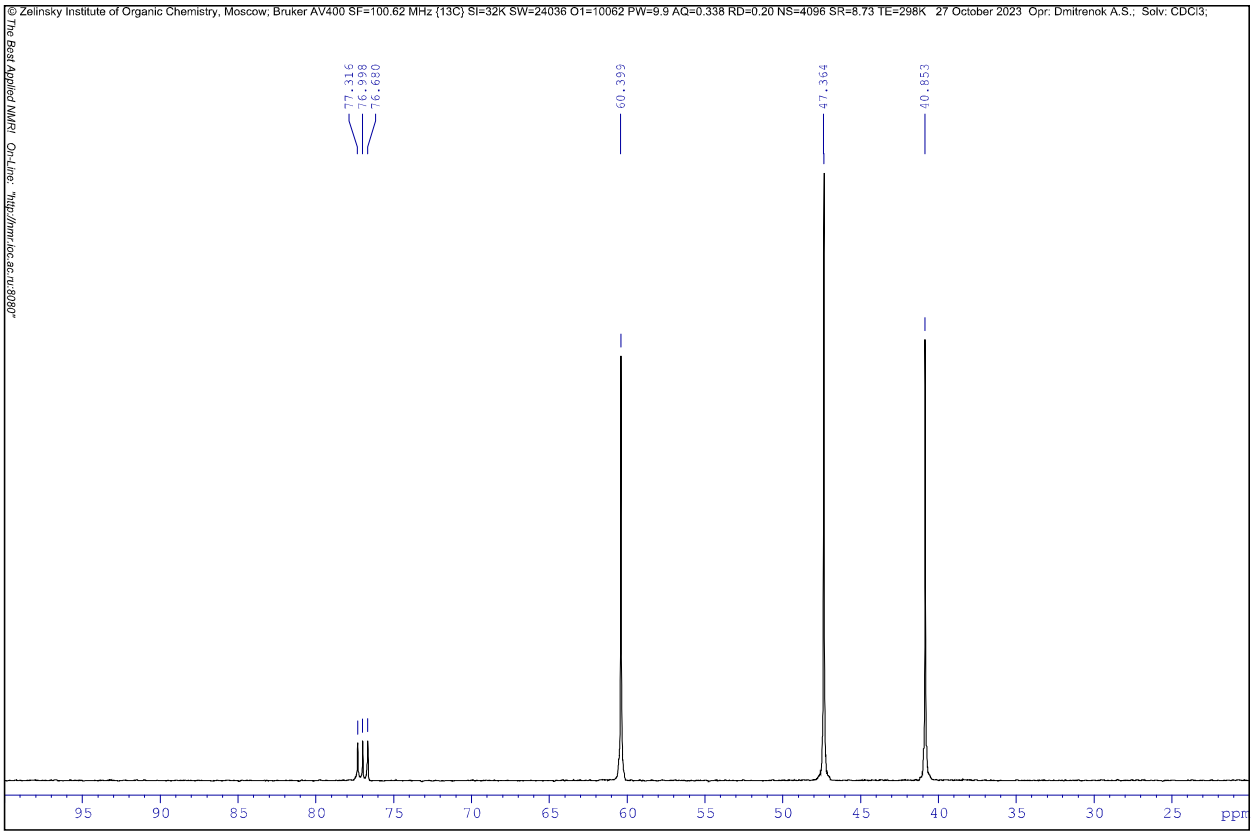


Figure S2.19 ^{13}C NMR spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

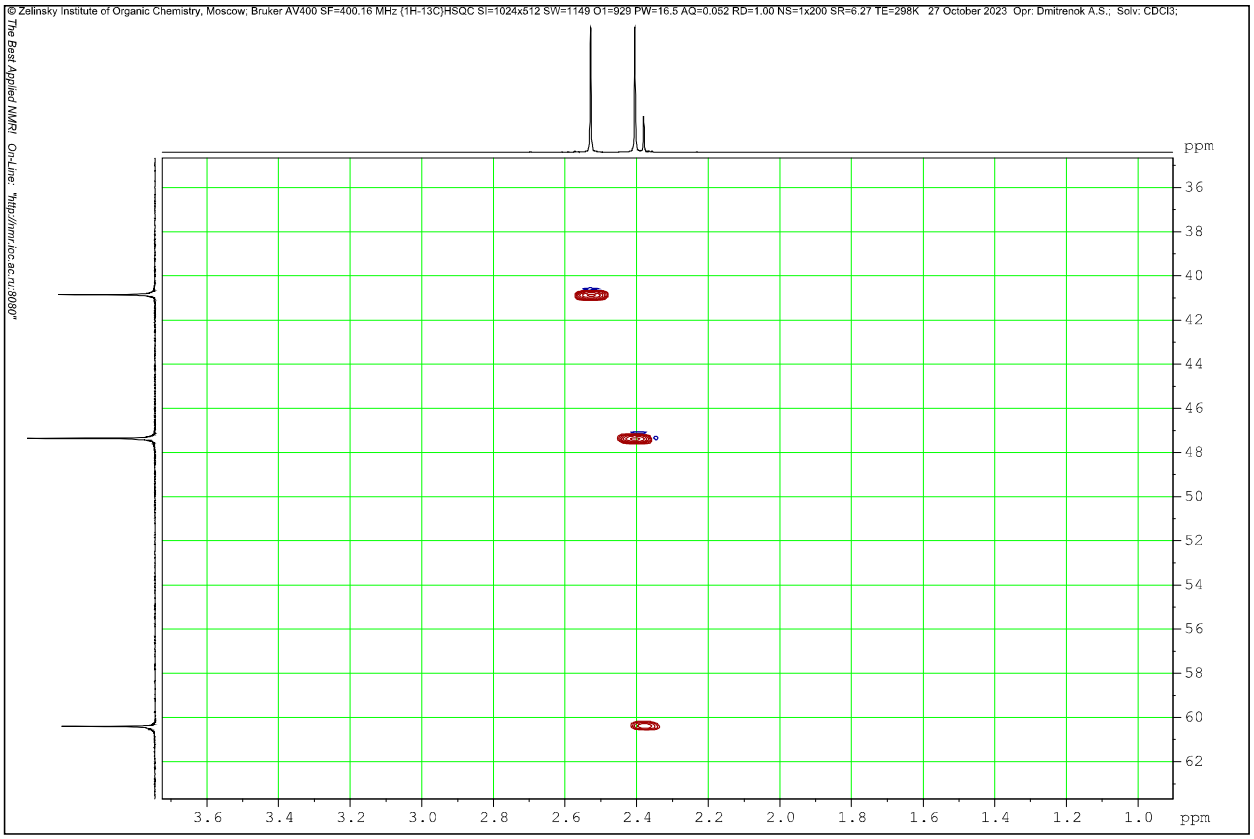


Figure S2.20 {^{1}H–^{13}C} HSQC spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

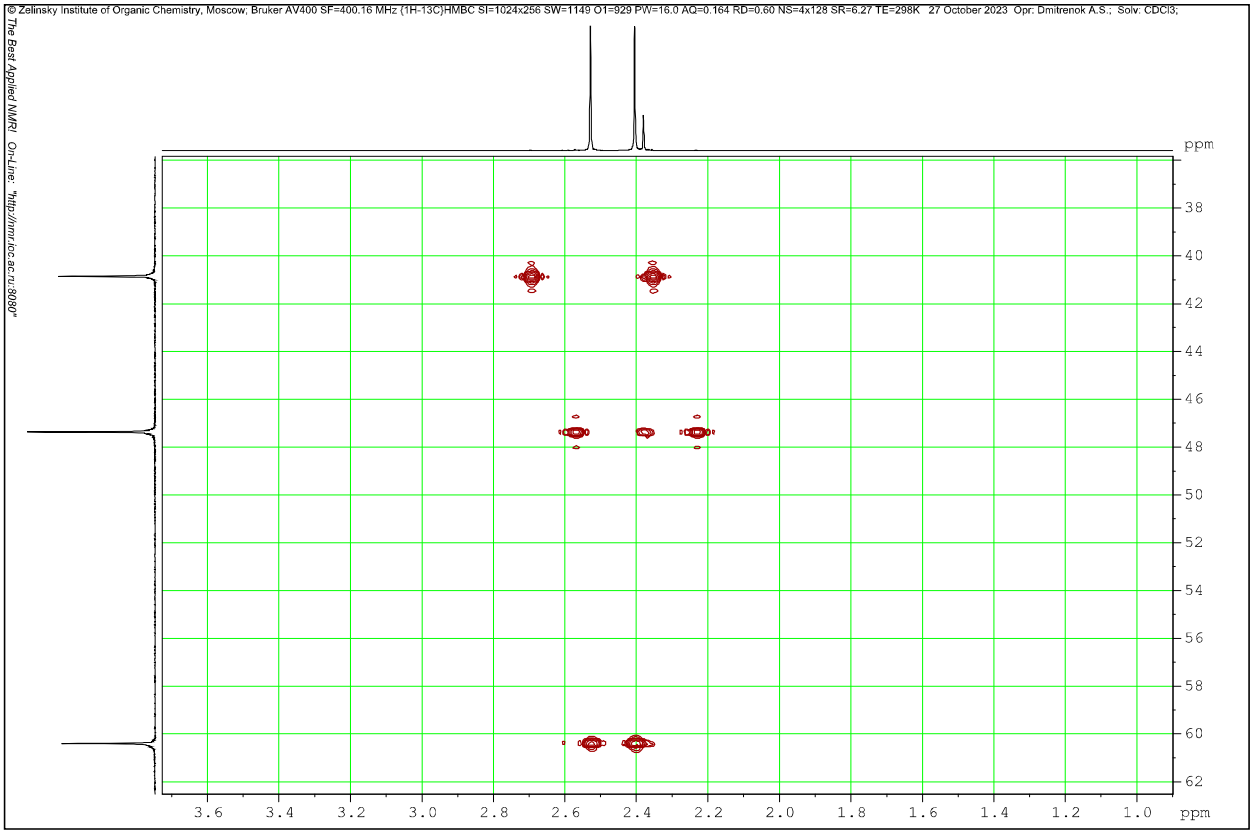


Figure S2.21 {^{1}H–^{13}C} HMBC spectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

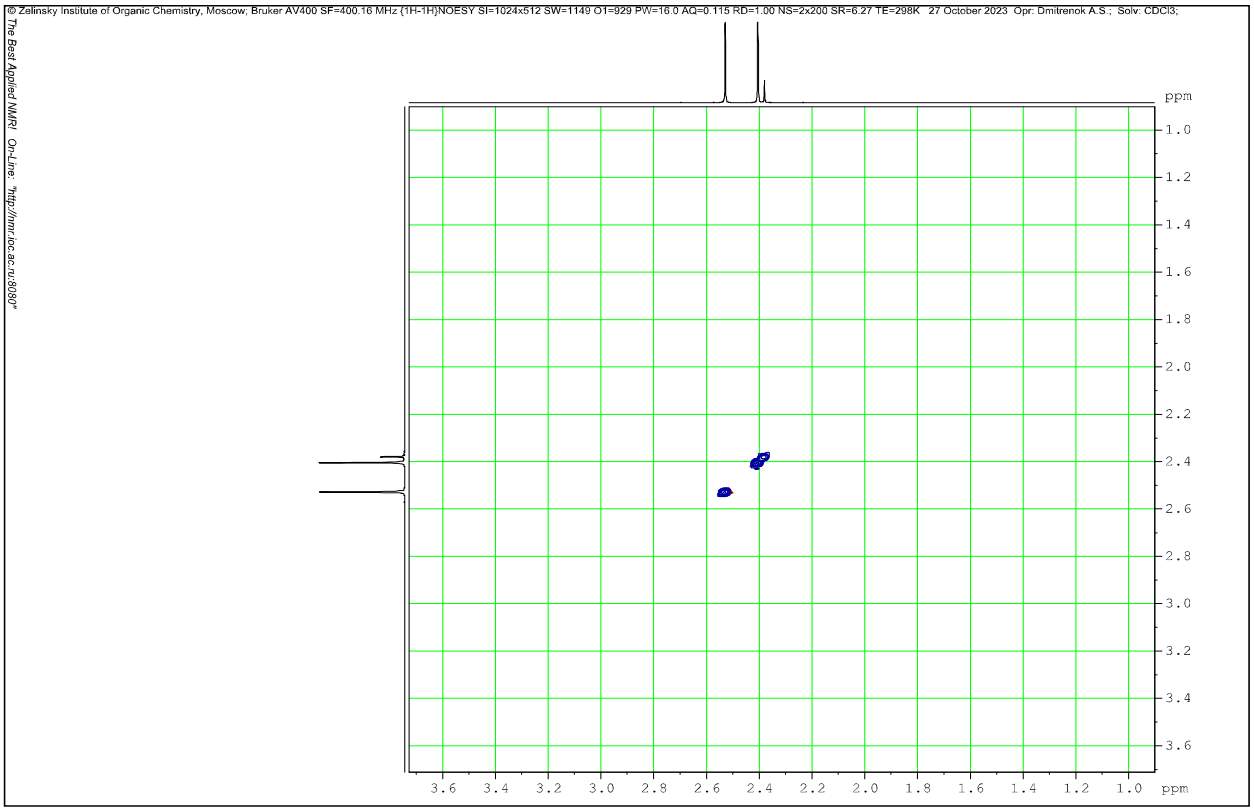


Figure S2.22 {^{1}H–^{1}H} gNOESYspectrum ($CDCl_3$) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

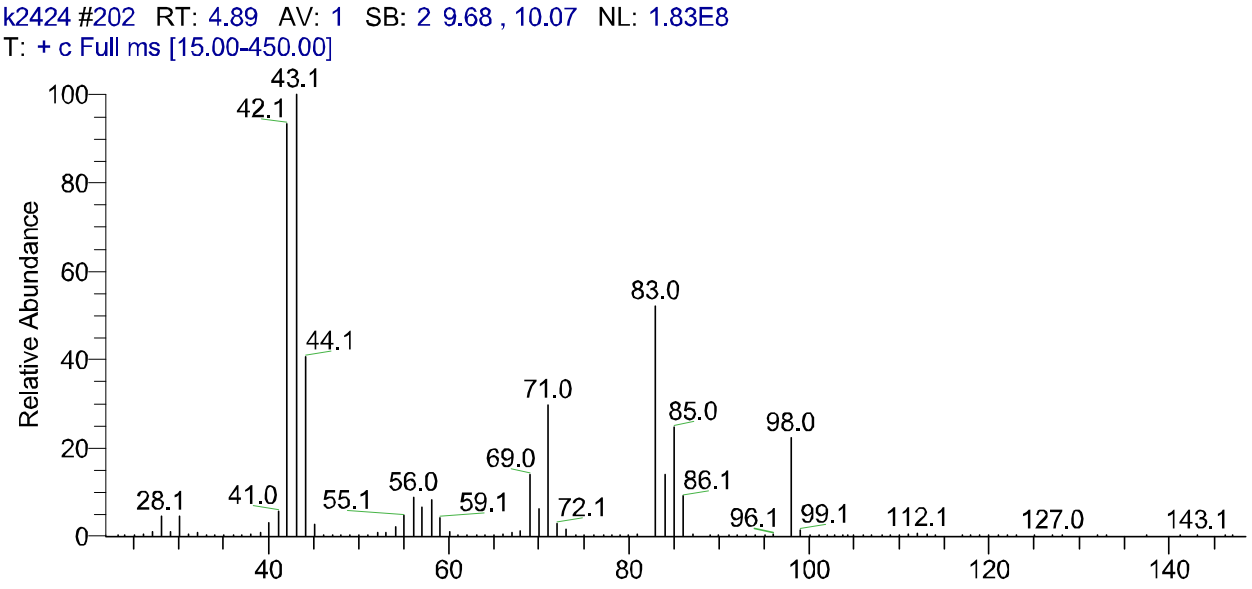


Figure S2.23 Mass spectrum of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

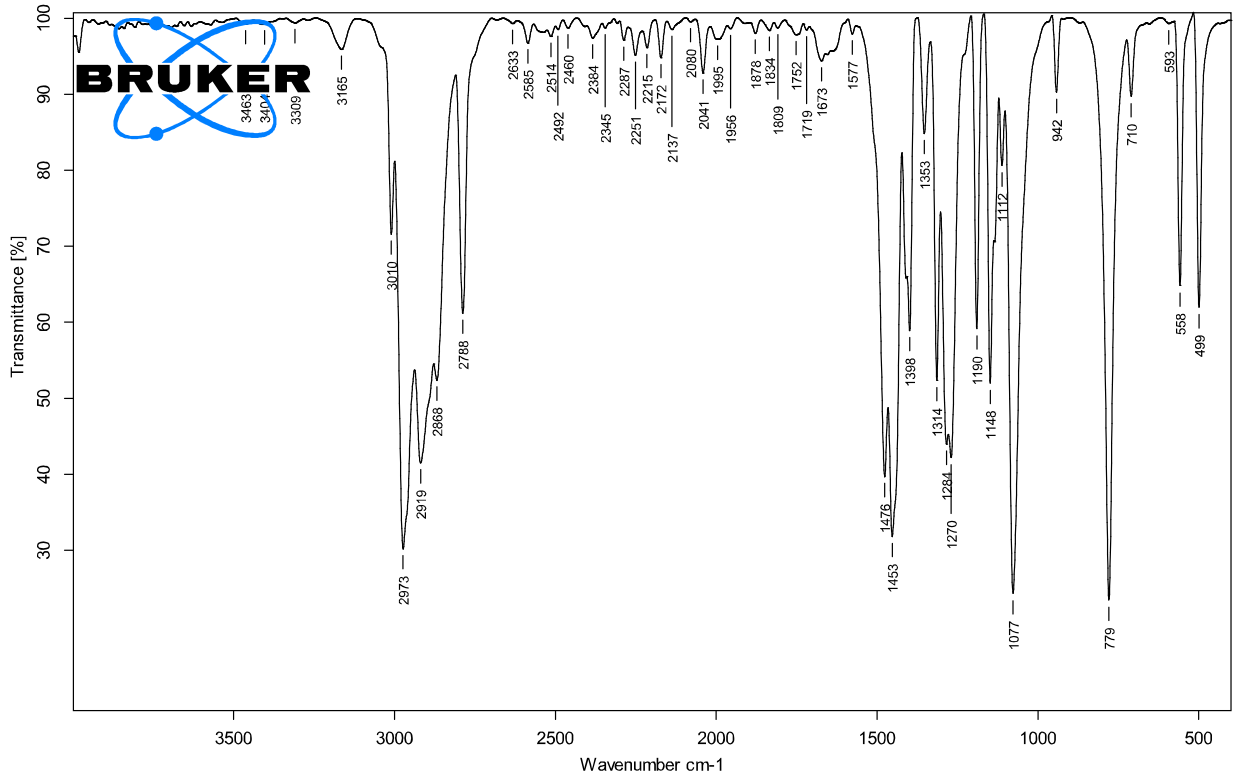


Figure S2.24 IR spectrum (KBr) of 1,1′,2,2′-tetramethyl-3,3′-bidiaziridine, *meso*-form **1b**.

S2.4. TEBDA 2 after column chromatography (racemate and *meso*-form)

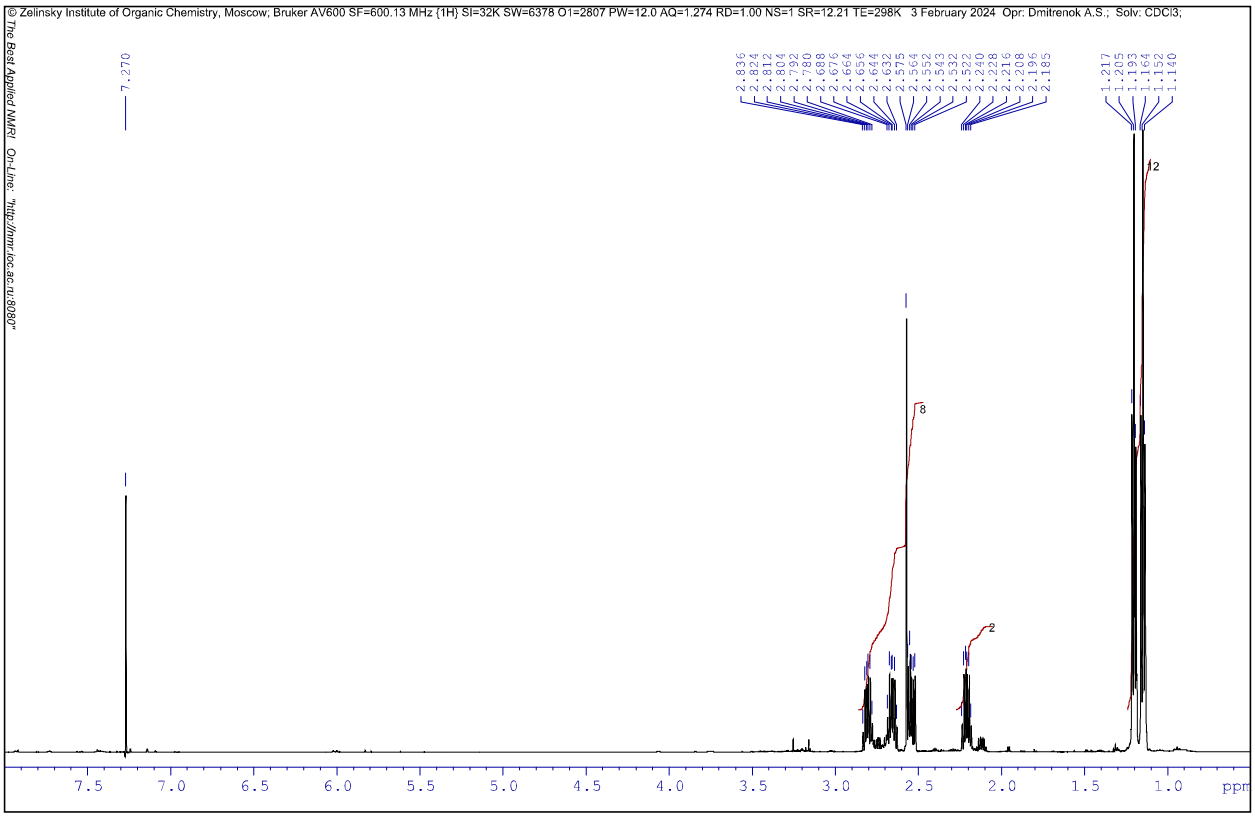


Figure S2.25 ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2** at the beginning of column chromatography, with racemate/*meso*-form ≈ 85 : 15.

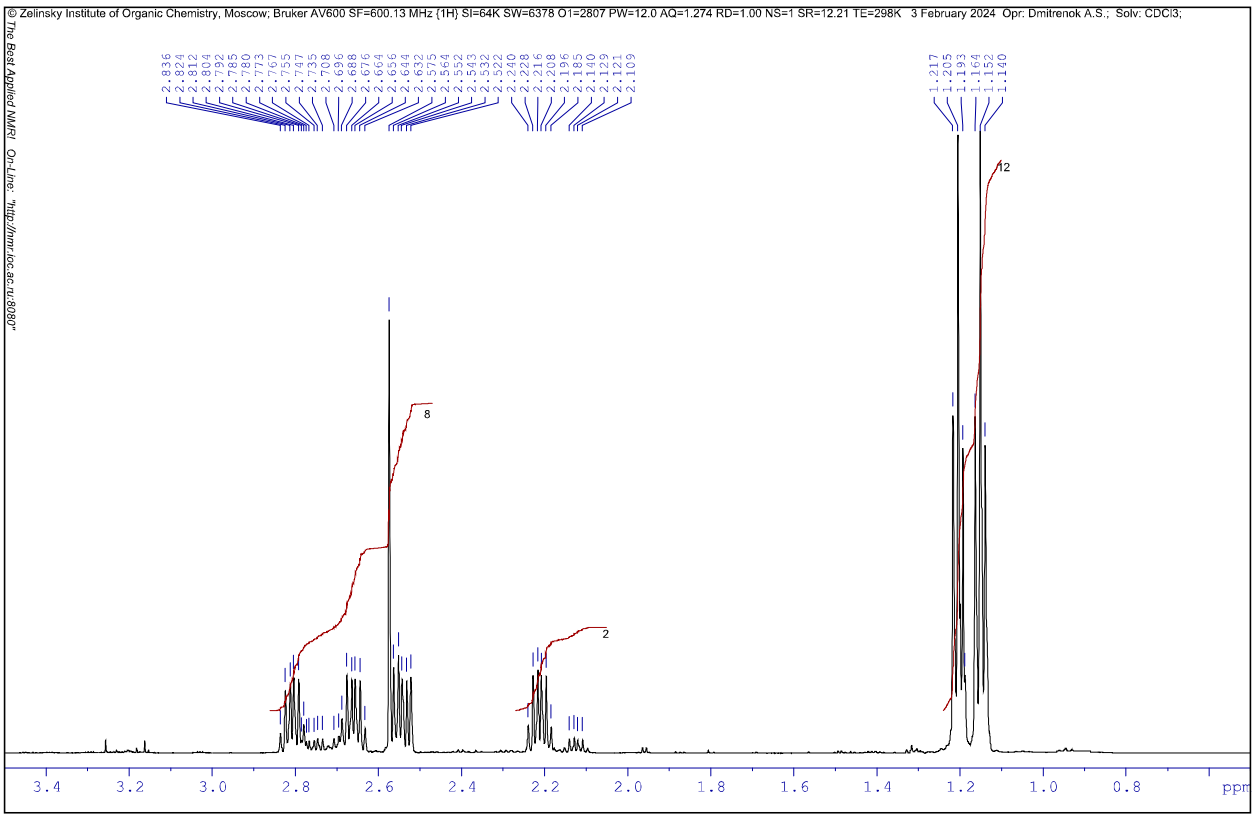


Figure S2.26 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2** at the beginning of column chromatography, with racemate/*meso*-form ≈ 85 : 15.

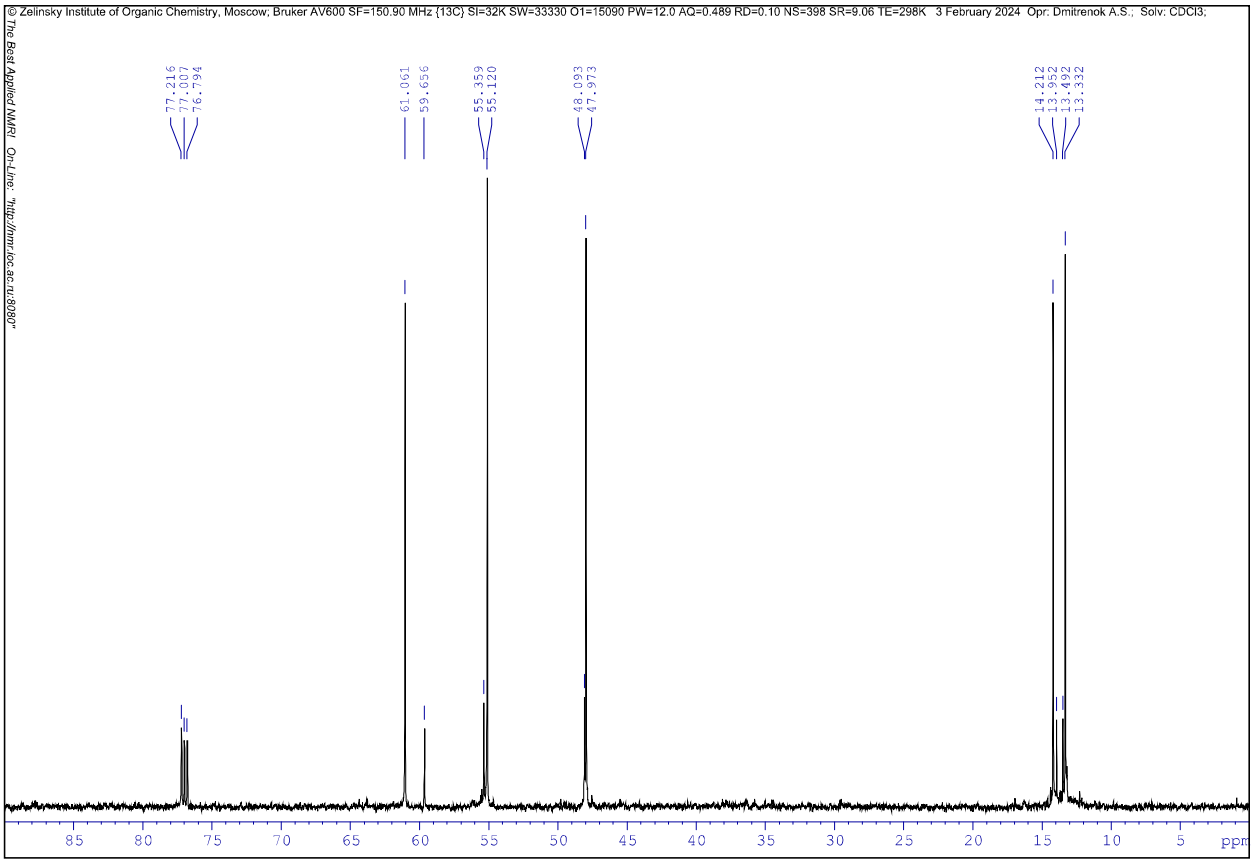


Figure S2.27 ^{13}C NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2** at the beginning of column chromatography, racemate and *meso*-form.

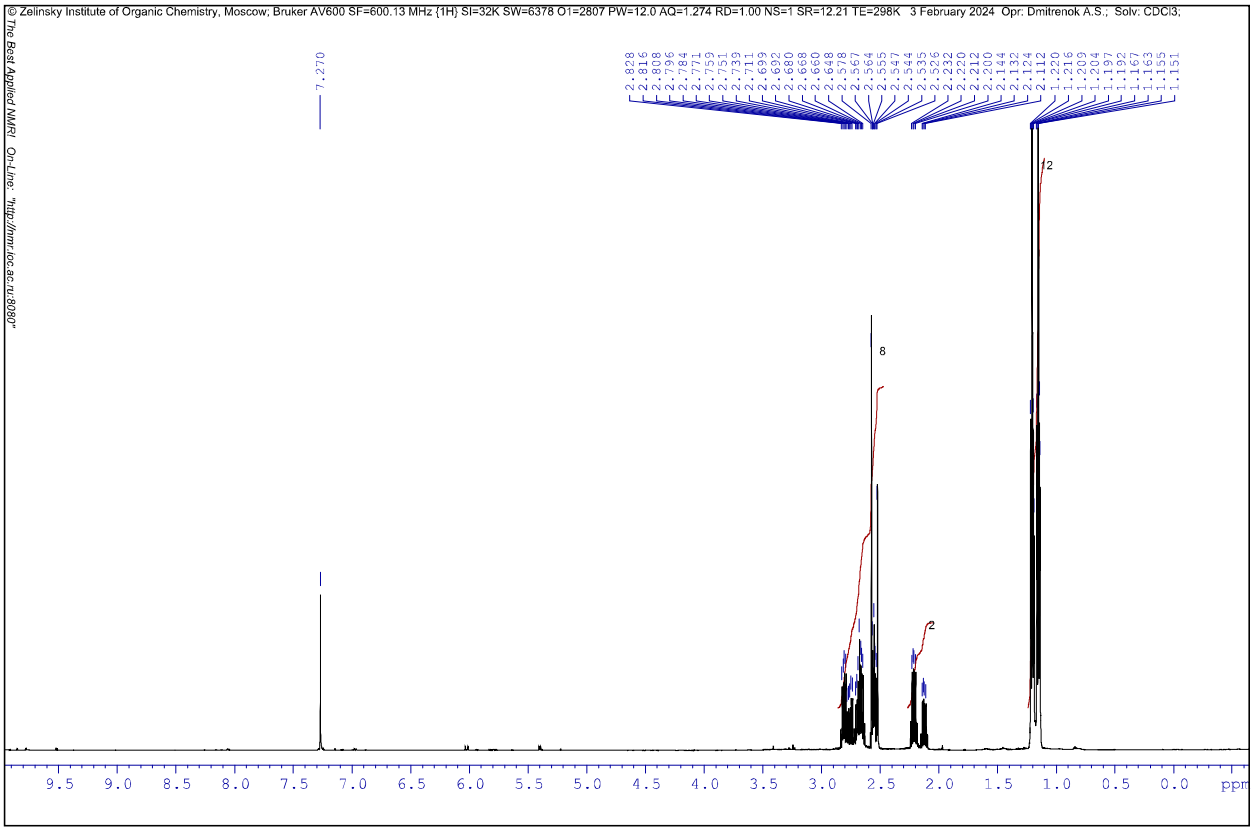


Figure S2.28 ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, the main product of column chromatography, with racemate/*meso*-form ≈ 60 : 40.

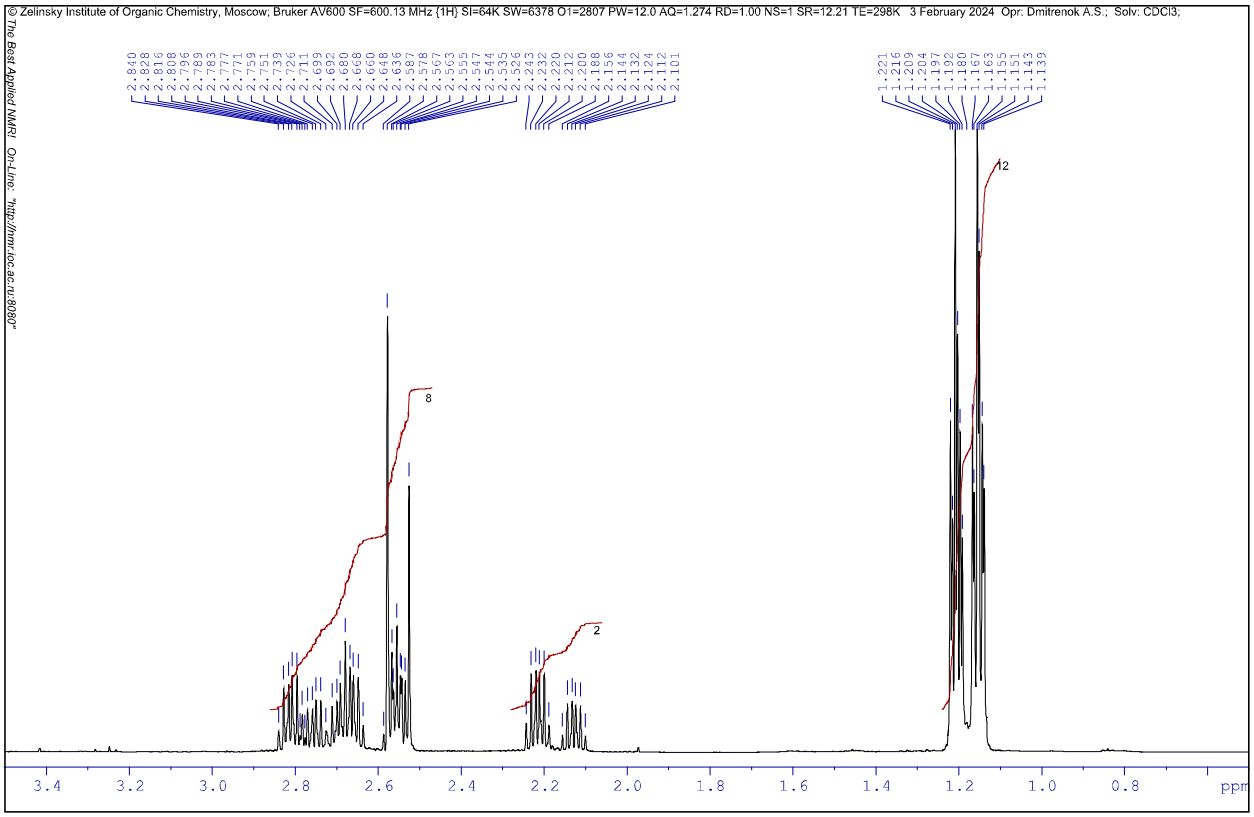


Figure S2.29 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, the main product of column chromatography, with racemate/*meso*-form ≈ 60 : 40.

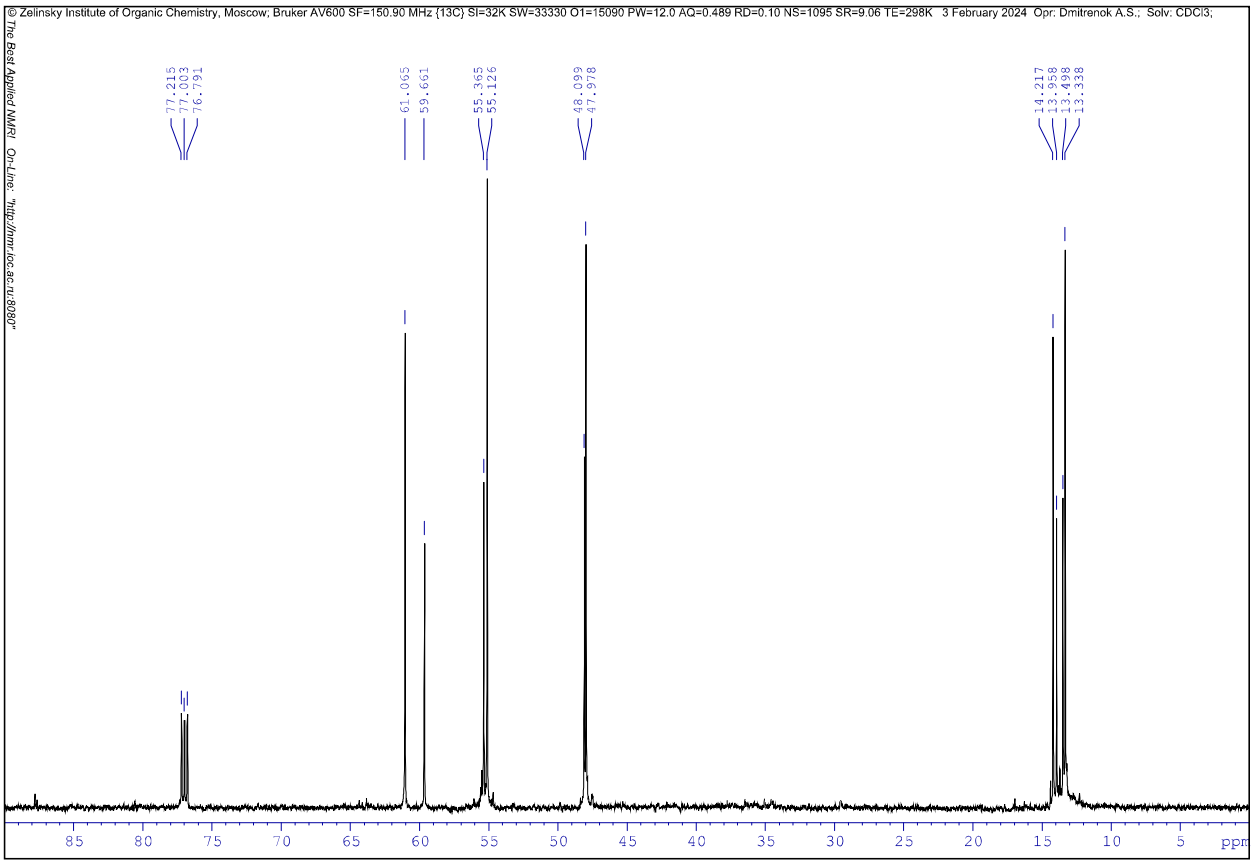


Figure S2.30 ^{13}C NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, the main product of column chromatography, racemate and *meso*-form.

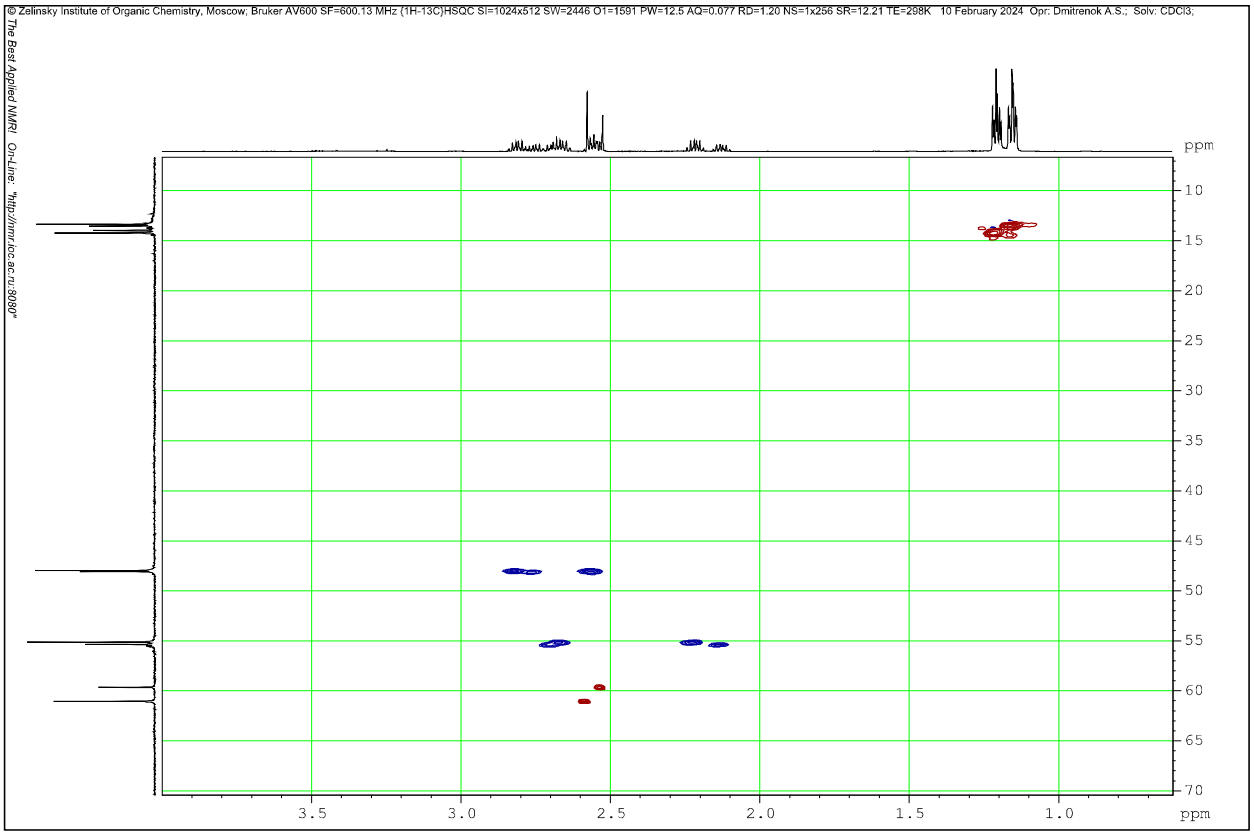


Figure S2.31 {^{1}H–^{13}C} HSQC spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, racemate and *meso*-form.

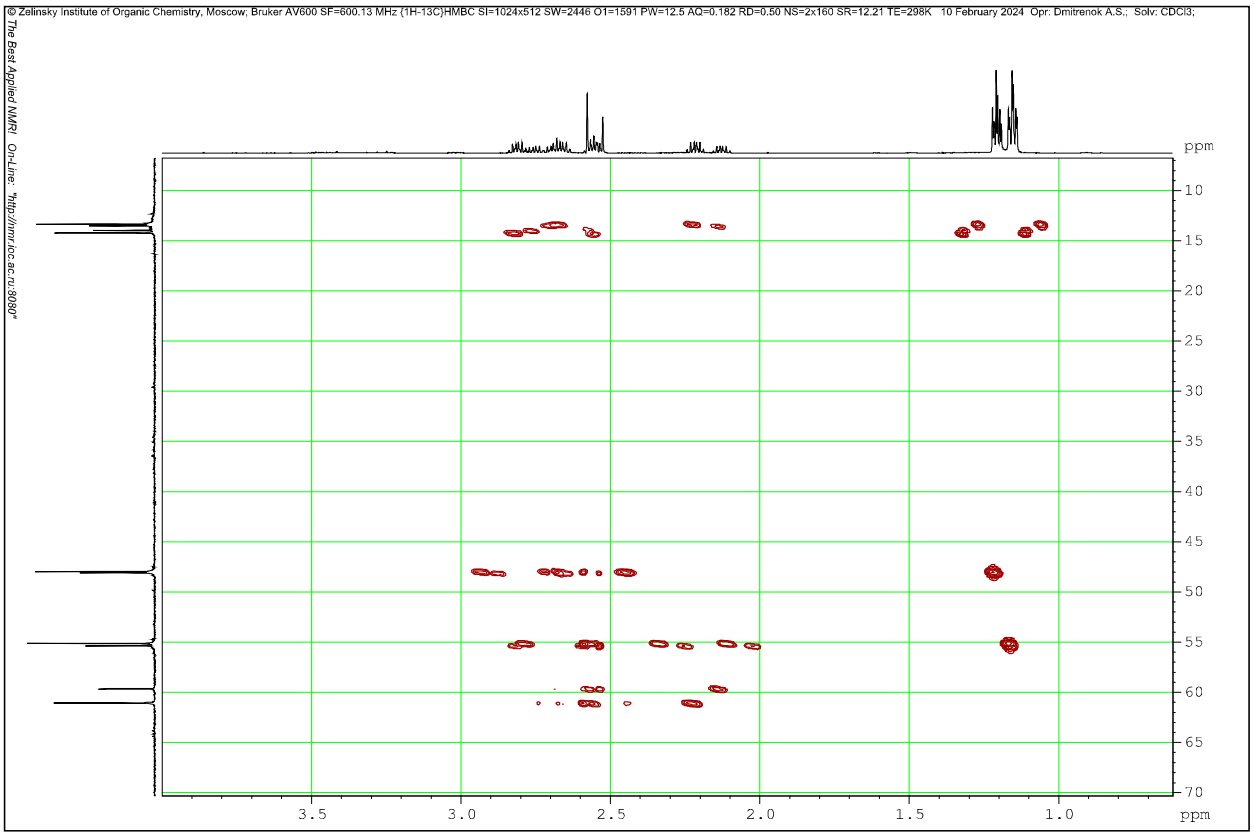


Figure S2.32 {^{1}H–^{13}C} HMBC spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, racemate and *meso*-form.

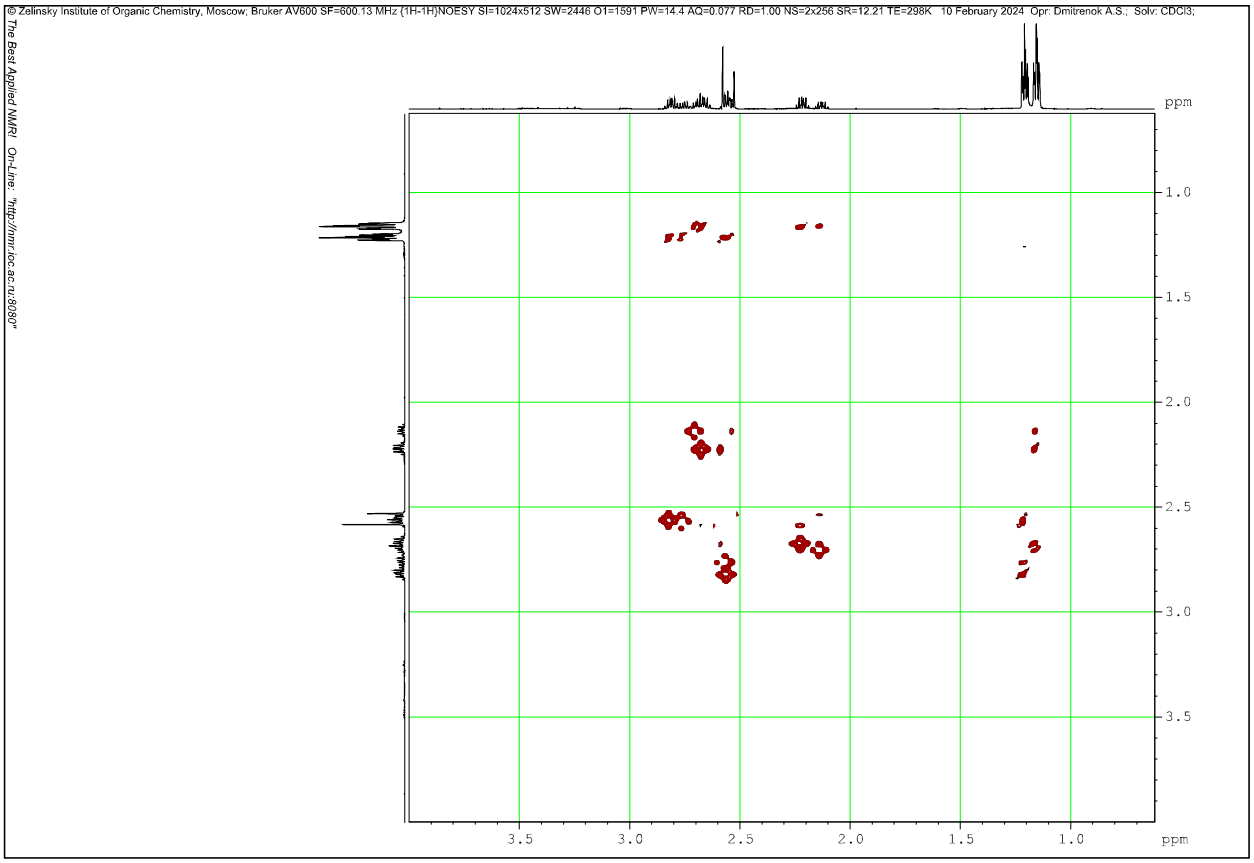


Figure S2.33 {^{1}H–^{1}H} gNOESYspectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, racemate and *meso*-form.

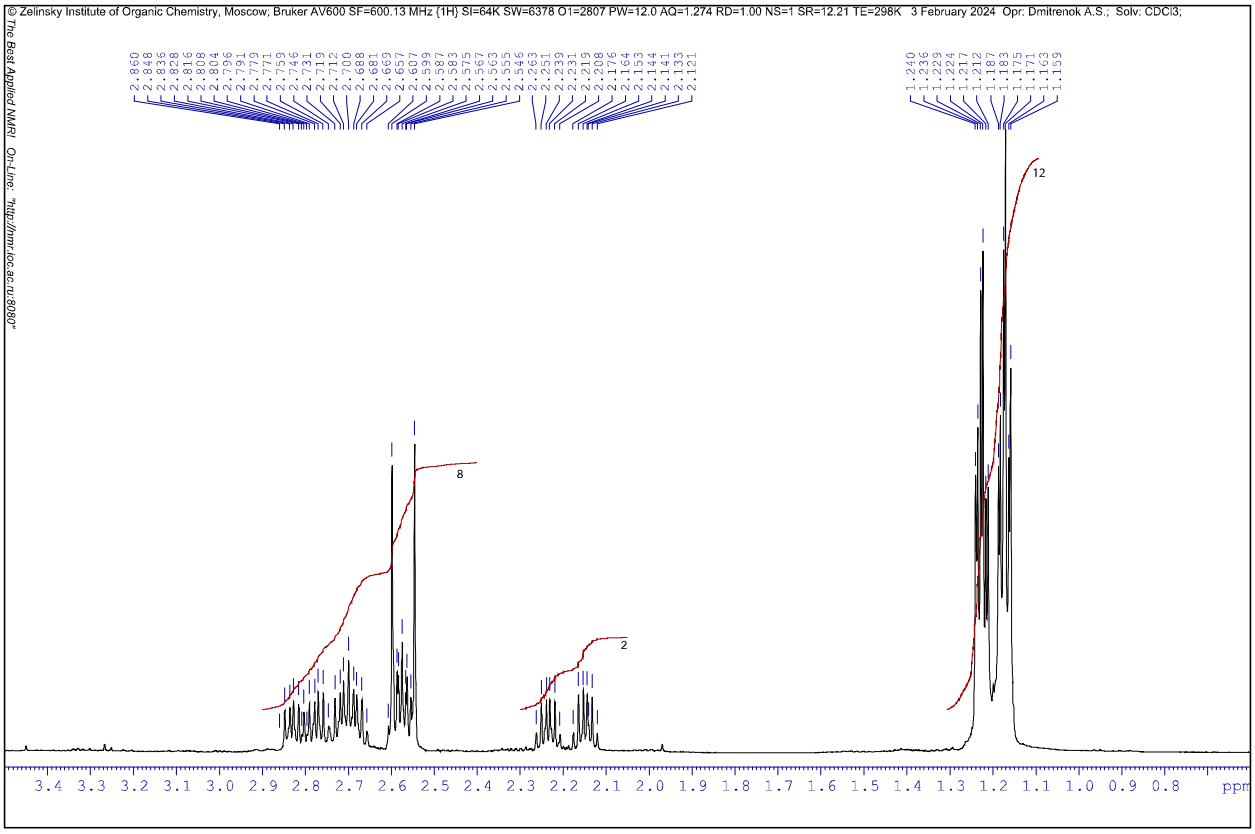


Figure S2.34 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, the final product of column chromatography, with racemate/*meso*-form ≈ 45 : 55.

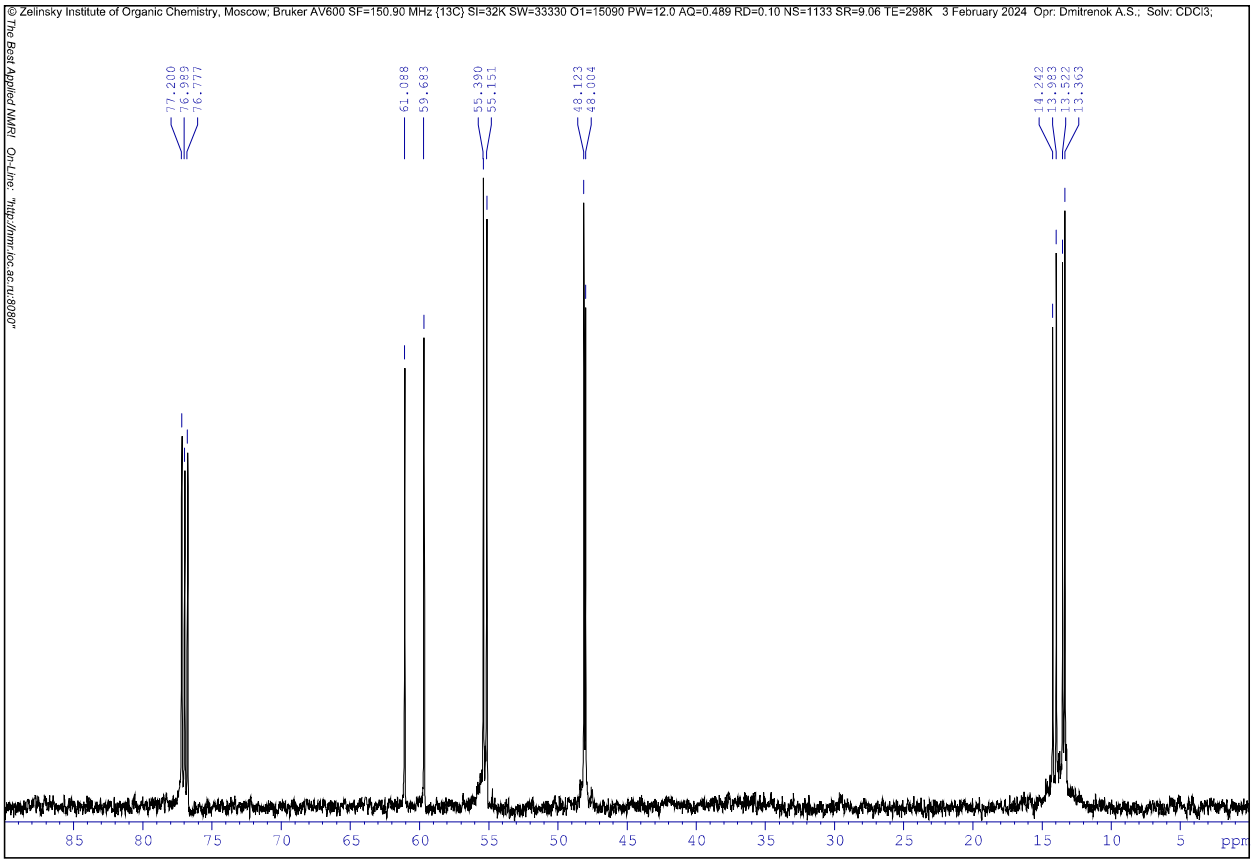


Figure S2.35 ^{13}C NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, the final product of column chromatography, racemate and *meso*-form.

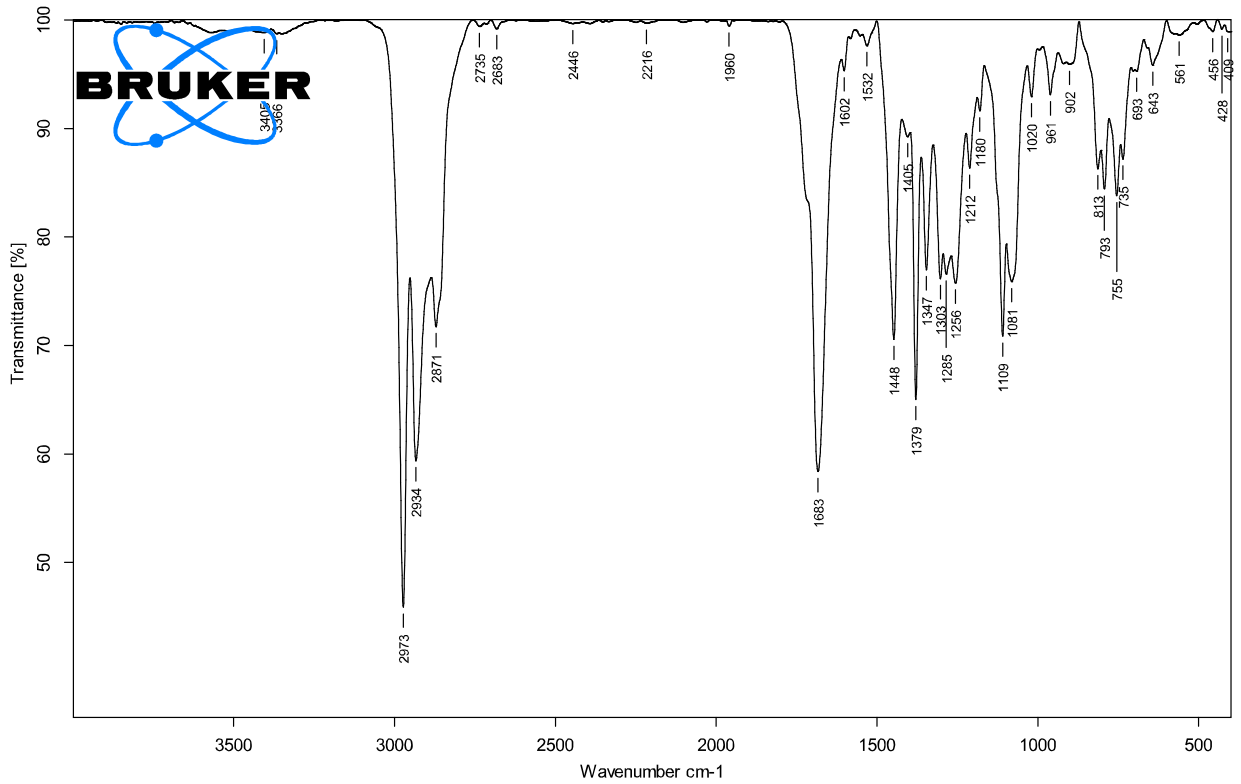


Figure S2.36 IR spectrum (thin layer) of 1,1',2,2'-tetraethyl-3,3′-bidiaziridine (TEBDA) **2**, with racemate/*meso*-form ≈ 60 : 40.

S2.5. TPBDA 3 after column chromatography (racemate and *meso*-form)

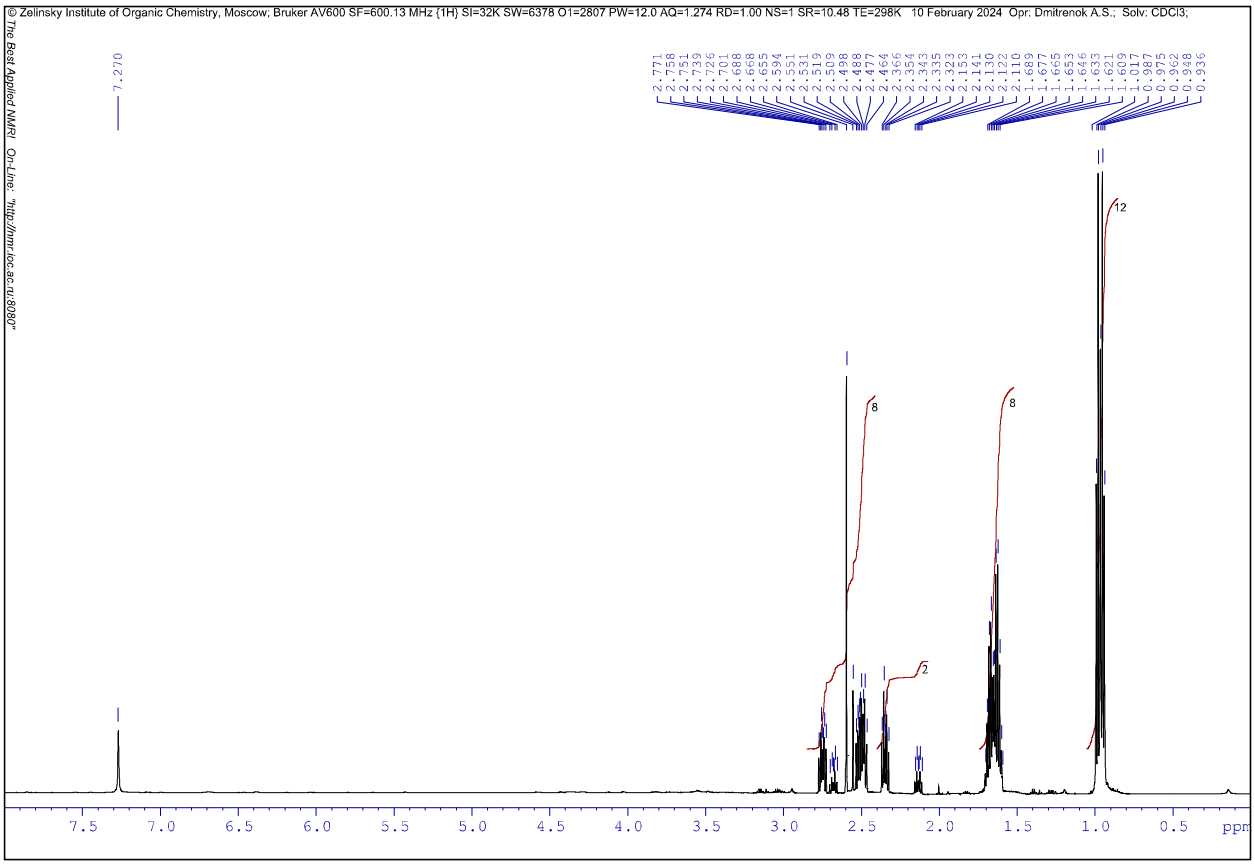


Figure S2.37 ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, the main product of column chromatography, with racemate/*meso*-form ≈ 80 : 20.

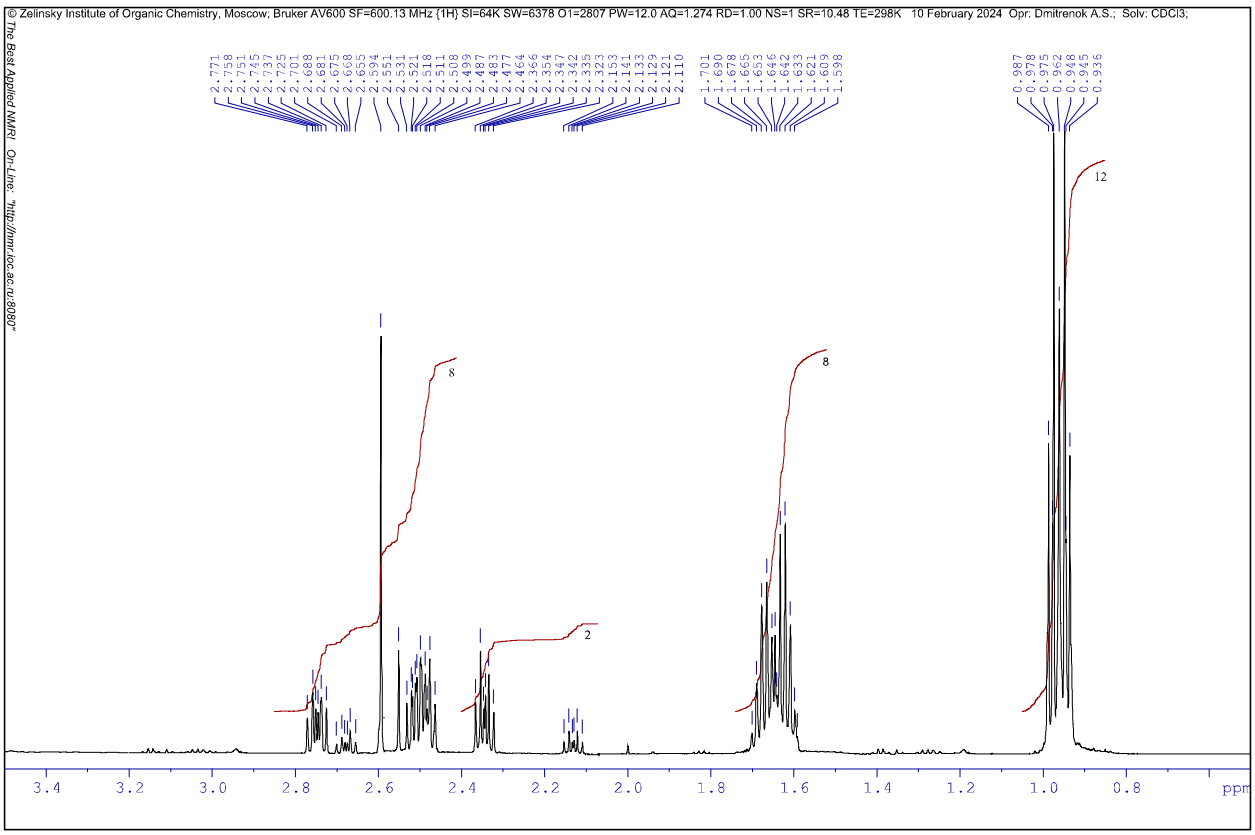


Figure S2.38 Fragment of the ^{1}H NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, the main product of column chromatography, with racemate/*meso*-form ≈ 80 : 20.

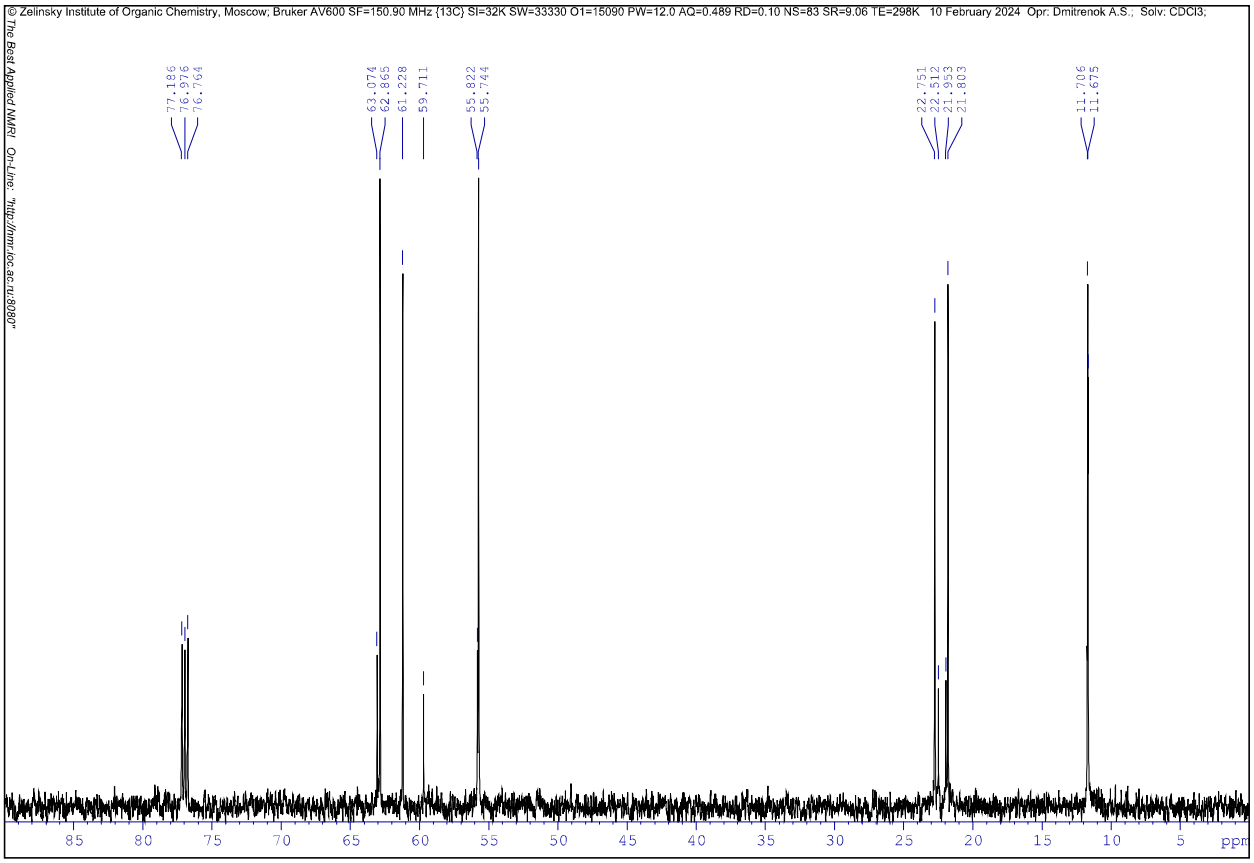


Figure S2.39 ^{13}C NMR spectrum ($CDCl_3$) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, the main product of column chromatography, racemate and *meso*-form.

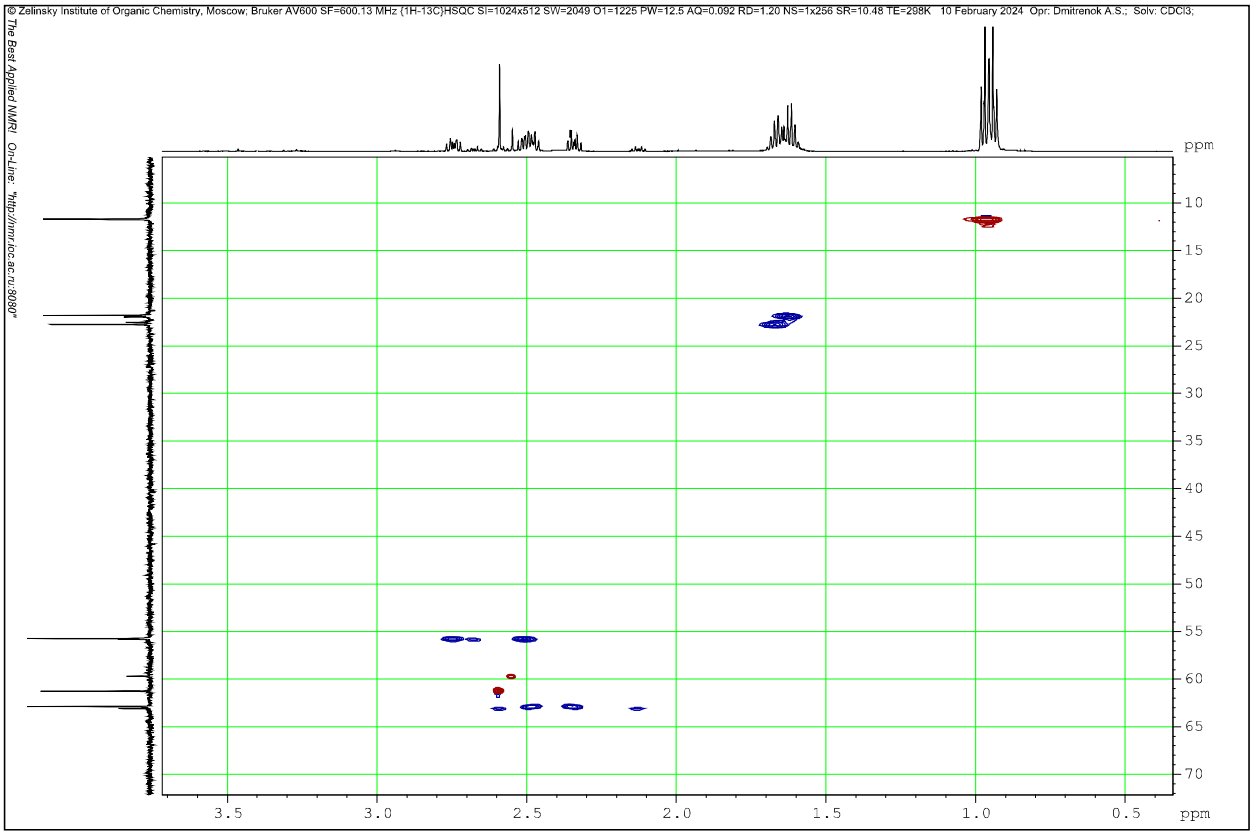


Figure S2.40 {^{1}H–^{13}C} HSQC spectrum ($CDCl_3$) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, racemate and *meso*-form.

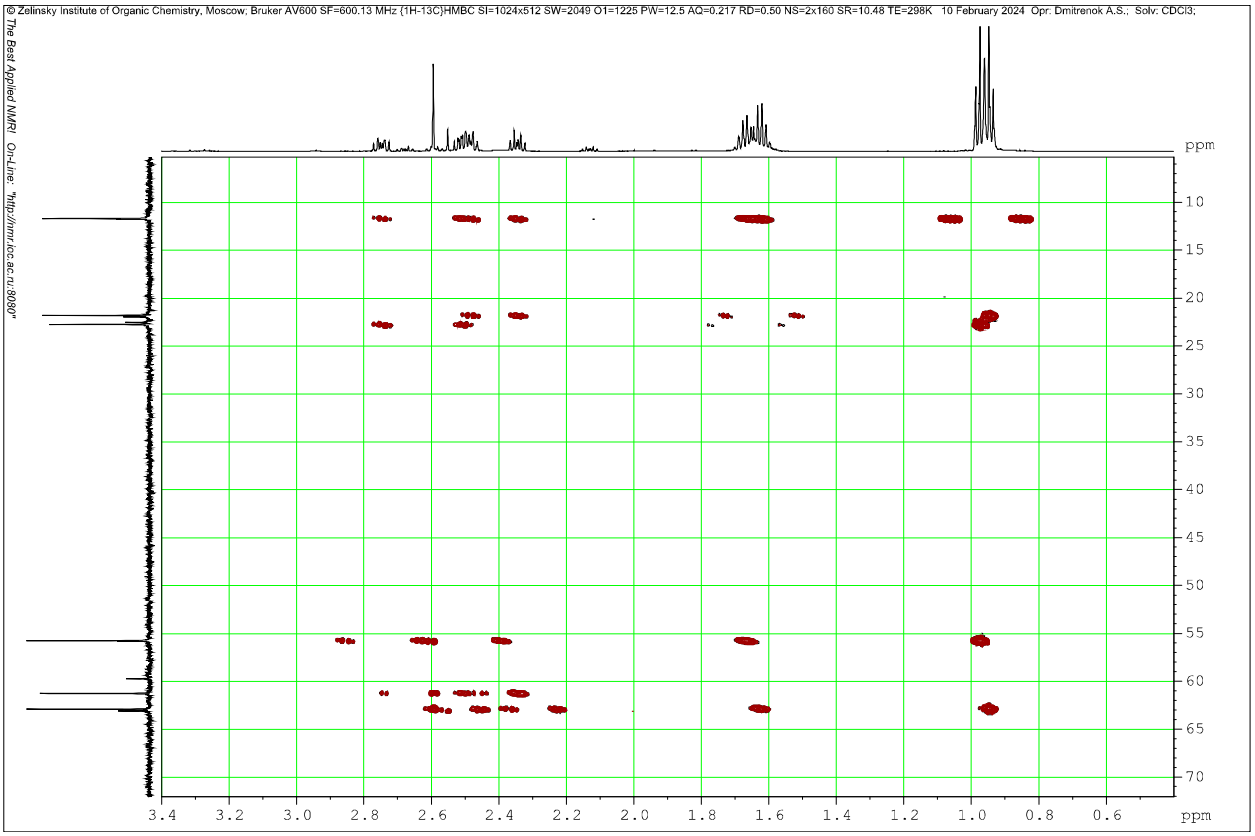


Figure S2.41 {^{1}H–^{13}C} HMBC spectrum ($CDCl_3$) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, racemate and *meso*-form.

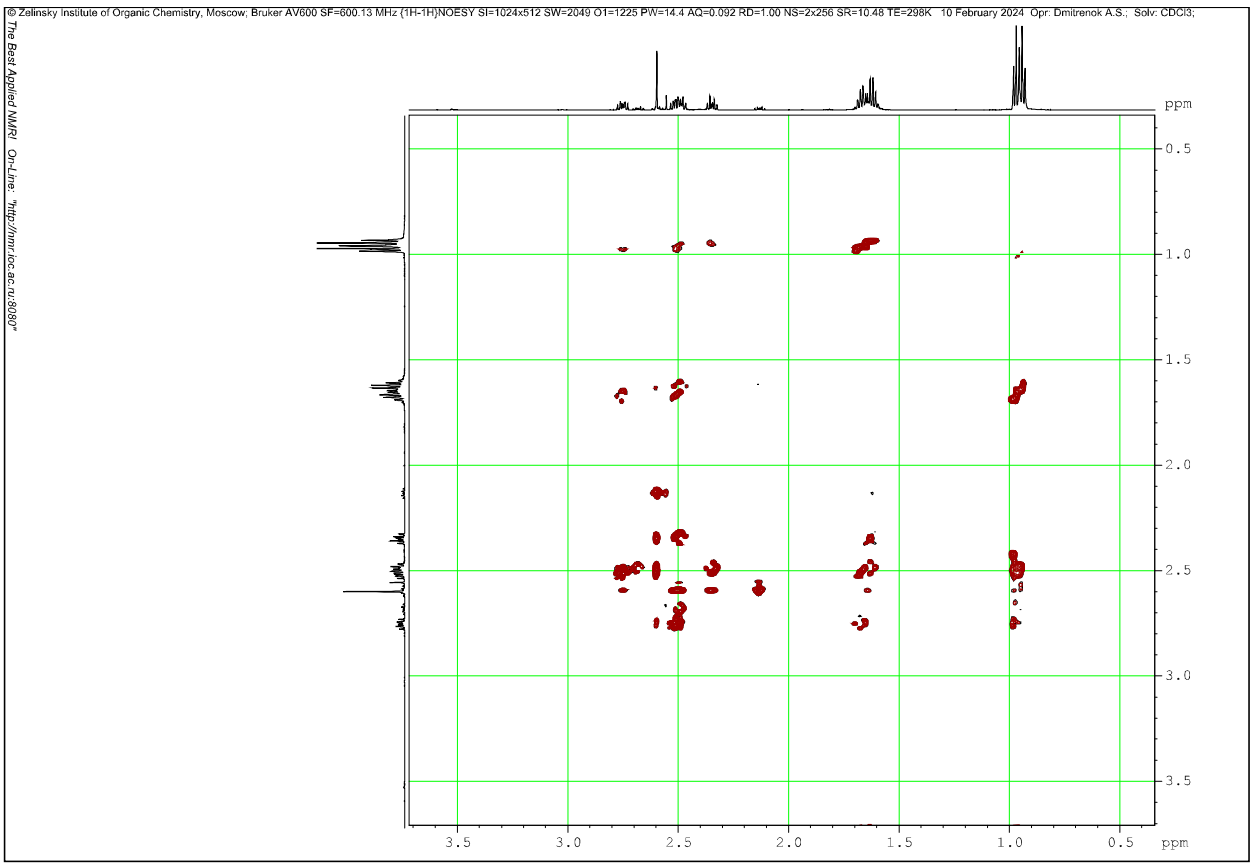


Figure S2.42 {^{1}H–^{1}H} gNOESYspectrum ($CDCl_3$) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, racemate and *meso*-form.

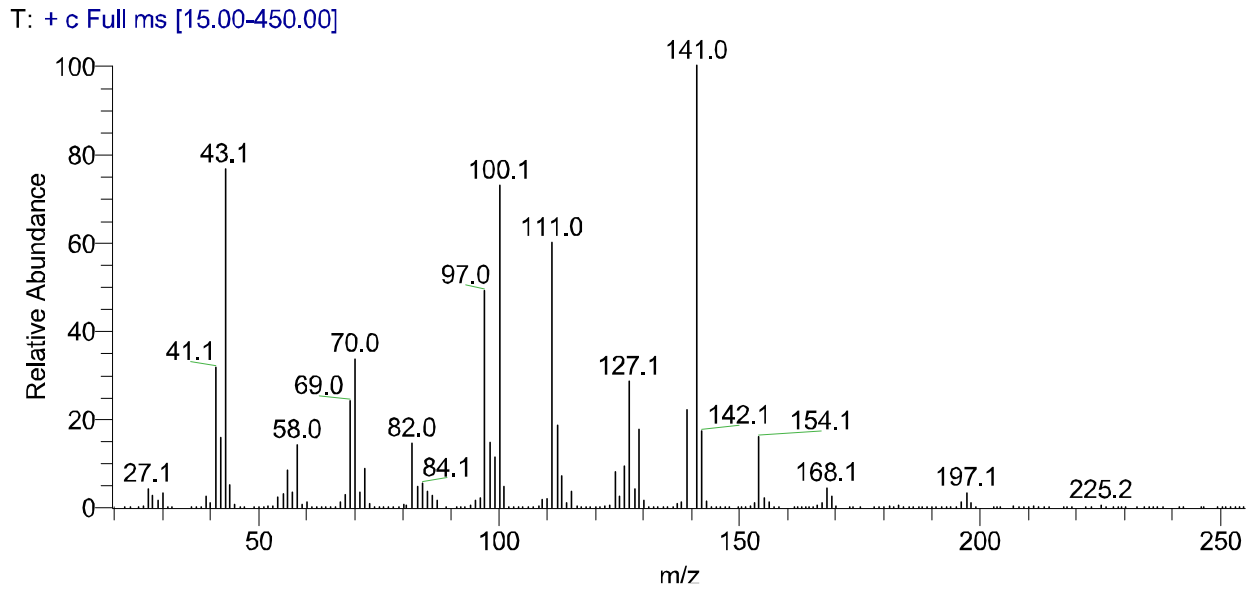


Figure S2.43 Mass spectrum of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**.

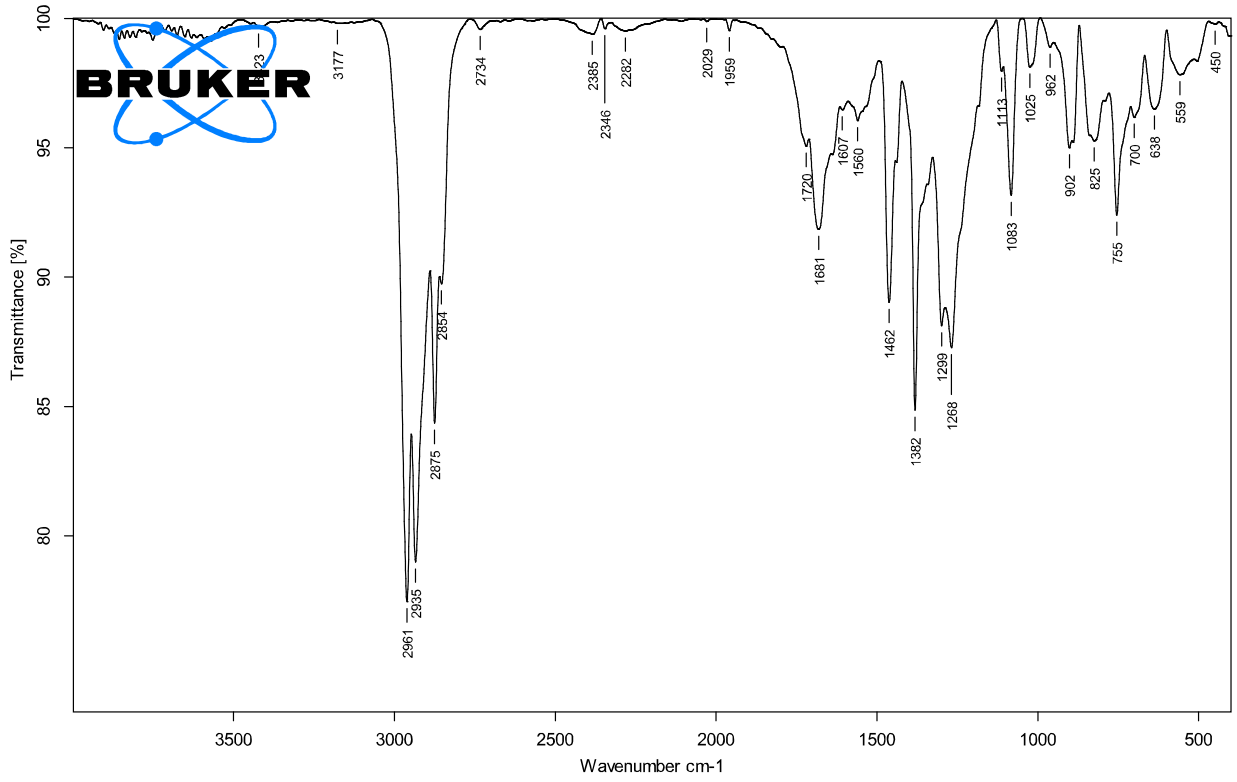


Figure S2.44 IR spectrum (thin layer) of 1,1',2,2'-tetrapropyl-3,3′-bidiaziridine (TPBDA) **3**, with racemate/*meso*-form ≈ 80 : 20.

S3. Gas-electron diffraction experiment

The electron diffraction patterns were recorded in the Moscow State University on the EG-100M apparatus using the R^3 sector made of brass. The electron wavelength was calibrated against gaseous CCl_4. The structural parameters of the CCl_4 molecule were taken from Reference S1. Information about the experimental conditions for all datasets used in the present investigation is given in the Table S3.1.

Photo films (TASMA FT-41P) were scanned with the use of Epson Perfection Photo 4870 commercial scanner in the 16-bit/4800-dpi gray scale scanning mode and with the use of VueScan computer program.[S2] This program enables one to retrieve data directly from the detector without any modifications. The data were processed using a computer program written by A.V.B. as in Reference S3. Preliminarily, the high resolution was reduced by averaging over square regions of pixels as described in Reference S3. With this method, mean transmittances and standard deviations were collected. The latter were used as weights for smoothing the transmittance surface with the use of 2D cubic splines.[S4] The calibration of the scanner was carried out against MD100 microdensitometer with the use of 24-bit gray scale optical wedge of IT8 transmissive target on Kodak Ektachrome Professional E100G film.[S5] Displacements of the scanner were corrected against a special ruler manufactured by LOMO. After refinement of the center of electron diffraction pattern by the least squares method, the data of scanning were transformed into the total intensity curve taking into account 2D background. The atomic scattering factors were taken from Reference S6.

Table S3.1 Experimental conditions of the gas-phase electron diffraction experiment for TMBDA.

	TMBDA	
	LD	SD
Camera distance (mm)	362.3	193.9
Nozzle temperature (K)	293	294
Accelerating voltage (kV)	60	60
Vacuum (Torr)	$2.5 \cdot 10^{-5}$	$2.0 \cdot 10^{-5}$
Electron beam current (μA)	2.4	1.8
Electron wavelength (Å)	0.049512	0.050245
Number of films used	3	3
Range of s value ($Å^{-1}$)[a]	4.2–16.0	13.0–31.2

[a] $s = (4\pi/\lambda)\sin(\theta/2)$, where θ is the scattering angle and λ is the electron wavelength. Experimental intensity curves were digitized with a step of 0.2 $Å^{-1}$.

References

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S3 (*a*) S. Ó. Wallevik, R. Bjornsson, Á. Kvaran, S. Jonsdottir, I. Arnason, A. V. Belyakov, T. Kern and K. Hassler, *Organometallics*, 2013, **32**, 6996; (*b*) A. V. Belyakov, A. A. Baskakov, V. N. Naraev, A. N. Rykov, H. Oberhammer, I. Arnason and S. O. Wallevik, *Russ. J. Phys. Chem. A*, 2012, **86**, 1563.

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S5 P. Karp and A. Kraushaar, *Fogra-Report Nr. 23024*, LaserSoft Imaging AG, 2009, pp. 1–9; http://www.silverfast.com/showdocu/ru.html?docu=1150.

S6 A. W. Ross, M. Fink and R. L. Hilderbrandt, in *International Tables for Crystallography*, Kluwer Acad. Publ., Dodrecht, 1992, vol. C, p. 245.

S4. Quantum chemical calculations and GED data

Table S4.1 Cartesian coordinates of the conformers of TMBDA at the B3LYP/cc-pVTZ level of theory (r_e/Å).

	I (C_2)			II (C_i)		
Atom	x	y	z	x	y	z
C1	-0.748660	-0.092996	0.017159	-0.746909	0.019631	0.007657
C2	0.748660	-0.092996	-0.017159	0.746909	-0.019631	-0.007657
H3	1.212820	0.095341	0.945334	1.204456	-0.049152	0.975259
H4	-1.212820	0.095341	-0.945334	-1.204456	0.049152	-0.975259
N5	1.534160	-0.957972	-0.874733	1.520446	-0.751404	-0.991509
N6	1.376954	0.477909	-1.183375	1.423228	0.720819	-1.045159
C7	0.835992	-1.812999	-1.834076	0.830830	-1.401561	-2.103889
C8	2.614869	1.213412	-0.938888	2.680548	1.354016	-0.657044
N9	-1.534160	-0.957972	0.874733	-1.423228	-0.720819	1.045159
N10	-1.376954	0.477909	1.183375	-1.520446	0.751404	0.991509
C11	-0.835992	-1.812999	1.834076	-2.680548	-1.354016	0.657044
C12	-2.614869	1.213412	0.938888	-0.830830	1.401561	2.103889
H13	-0.065190	-1.367660	-2.258426	0.013481	-0.814614	-2.526215
H14	1.525558	-2.041843	-2.645733	1.562506	-1.585625	-2.889811
H15	0.576550	-2.746928	-1.333873	0.451396	-2.364664	-1.759434
H16	3.189845	0.806329	-0.102033	3.218604	0.789731	0.110524
H17	2.359389	2.254099	-0.734406	2.458986	2.355947	-0.286301
H18	3.228657	1.178331	-1.838256	3.316089	1.445292	-1.537111
H19	0.065190	-1.367660	2.258426	-3.218604	-0.789731	-0.110524
H20	-1.525558	-2.041843	2.645733	-2.458986	-2.355947	0.286301
H21	-0.576550	-2.746928	1.333873	-3.316089	-1.445292	1.537111
H22	-3.189845	0.806329	0.102033	-0.013481	0.814614	2.526215
H23	-2.359389	2.254099	0.734406	-1.562506	1.585625	2.889811
H24	-3.228657	1.178331	1.838256	-0.451396	2.364664	1.759434

Table S4.2 Cartesian coordinates of the conformers of TMBDA at the RI-MP2/cc-pVQZ level of theory (r_e/Å).

	I (C_2)			II (C_i)		
Atom	x	y	z	x	y	z
C1	0.621875	0.408897	-0.240024	-0.190111	-0.338593	-0.631510
C2	-0.621875	-0.408897	-0.240024	0.190111	0.338593	0.631510
H3	-0.485849	-1.451211	-0.503927	0.865681	1.177973	0.523753
H4	0.485849	1.451211	-0.503927	-0.865681	-1.177973	-0.523753
N5	-1.699081	-0.186014	0.706331	-0.737994	0.523510	1.730476
N6	-1.821760	0.242332	-0.706613	0.338392	-0.491774	1.802998
C7	-1.552936	0.974478	1.579352	-2.047029	-0.108107	1.605836
C8	-2.736834	-0.651173	-1.405907	1.381314	-0.036134	2.713364
N9	1.699081	0.186014	0.706331	-0.338392	0.491774	-1.802998
N10	1.821760	-0.242332	-0.706613	0.737994	-0.523510	-1.730476
C11	1.552936	-0.974478	1.579352	-1.381314	0.036134	-2.713364
C12	2.736834	0.651173	-1.405907	2.047029	0.108107	-1.605836
H13	-1.025458	1.805611	1.115759	-1.999751	-1.124917	1.221566
H14	-2.547874	1.304234	1.864740	-2.498469	-0.132473	2.593542
H15	-1.021043	0.659888	2.474803	-2.666185	0.507223	0.955385
H16	-2.681860	-1.671686	-1.024187	1.494836	1.048901	2.692989
H17	-2.481439	-0.637264	-2.463461	2.315879	-0.511837	2.422231
H18	-3.749886	-0.279280	-1.281837	1.126585	-0.348097	3.722218
H19	1.025458	-1.805611	1.115759	-1.494836	-1.048901	-2.692989
H20	2.547874	-1.304234	1.864740	-2.315879	0.511837	-2.422231
H21	1.021043	-0.659888	2.474803	-1.126585	0.348097	-3.722218
H22	2.681860	1.671686	-1.024187	1.999751	1.124917	-1.221566
H23	2.481439	0.637264	-2.463461	2.498469	0.132473	-2.593542
H24	3.749886	0.279280	-1.281837	2.666185	-0.507223	-0.955385

Table S4.3 GED Cartesian coordinates of TMBDA molecule of C_2 symmetry (r_e/Å).

	GED		
Atom	x	y	z
C1	-0.73816	0.00000	0.00000
C2	0.73816	0.00000	0.00000
H3	1.19719	0.26393	0.94573
H4	-1.19719	0.26393	-0.94573
N5	1.50380	-0.92121	-0.79748
N6	1.37141	0.48967	-1.18583
C7	0.72120	-1.76890	-1.67139
C8	2.60051	1.19745	-0.90719
N9	-1.50380	-0.92121	0.79748
N10	-1.37141	0.48967	1.18583
C11	-0.72120	-1.76890	1.67139
C12	-2.60051	1.19745	0.90719
H13	-0.18098	-1.29625	-2.04171
H14	1.34492	-2.04374	-2.51395
H15	0.46140	-2.66817	-1.12524
H16	3.10300	0.80700	-0.02996
H17	2.36087	2.24398	-0.75954
H18	3.25774	1.10335	-1.76372
H19	0.18098	-1.29625	2.04171
H20	-1.34492	-2.04374	2.51395
H21	-0.46140	-2.66817	1.12524
H22	-3.10300	0.80700	0.02996
H23	-2.36087	2.24398	0.75954
H24	-3.25774	1.10335	1.76372

Table S4.4 Total corrections Δ ($r_{ij,e} - r_{ij,a}$) to internuclear distances $r_{ij,a}$, theoretical $u_{ij,h1}$ and experimental $u_{ij,exp}$ rms vibrational amplitudes (Å) for the TMBDA molecule of C_2 symmetry.

Type	At.Num.	$r_{ij,a}$	$r_{ij,e} - r_{ij,a}$ [a]	$u_{ij,h1}$ [b]	$u_{ij,exp}$
C C	1 2	1.4977	-0.0079	0.0501	0.064(2)
C H	1 4	1.0850	-0.0166	0.0763	0.075(6)
N C	1 9	1.4494	-0.0084	0.0500	0.064(2)
N N	5 6	1.4771	-0.0104	0.0536	0.068(2)
N C	1 10	1.4425	-0.0071	0.0493	0.063(2)
N C	5 7	1.4625	-0.0105	0.0498	0.064(2)
N C	6 8	1.4605	-0.0096	0.0496	0.064(2)
N C	1 6	2.5071	-0.0084	0.0700	0.087(6)
N C	1 5	2.5990	-0.0135	0.0685	0.085(6)
N C	5 8	2.4263	-0.0210	0.0703	0.087(6)
N C	6 7	2.4422	-0.0181	0.0707	0.088(6)
C C	1 12	2.4574	-0.0181	0.0688	0.086(6)
C C	1 11	2.5034	-0.0215	0.0678	0.085(6)
C C	7 8	3.6228	-0.0206	0.0807	0.099(6)
C C	1 7	2.9827	-0.0299	0.1100	0.127(6)
C C	1 8	3.6228	-0.0150	0.0796	0.099(23)
N N	6 10	3.6312	0.0488	0.1318	0.150(23)
N N	5 9	3.5320	-0.0600	0.1502	0.168(23)
N N	5 10	3.8435	-0.0166	0.0797	0.099(23)
N C	6 12	4.5804	0.0496	0.1767	0.29(15)
N C	5 11	3.6995	-0.1068	0.2704	0.29(15)
N C	5 12	5.0218	-0.0004	0.0880	0.21(15)
N C	6 11	4.3875	-0.0329	0.1320	0.25(15)
C C	8 12	5.5566	0.0463	0.2107	0.34(15)
C C	7 11	4.0312	-0.1573	0.4471	0.34(15)
C C	7 12	5.3625	-0.0008	0.1494	0.27(15)

[a] Calculated with the DFT-B3LYP/VTZ cubic force constants (see text). [b] Calculated with the DFT-B3LYP/VTZ quadratic force constants (see text).

Table S4.5 Correlation matrix for the TMBDA molecule of C_2 symmetry.

R(1,2)	1	100										
R(C-H)av	2	-14	100									
R(6,1)	3	53	-4	100								
A(7,5,2)	4	50	-10	-33	100							
u(CH)av	5	1	7	0	5	100						
u(1,2)gr	6	-28	14	-14	-9	37	100					
u(6,1)gr	7	-65	12	-26	-31	14	49	100				
u(5,9)gr	8	-32	5	-42	1	10	20	20	100			
u(6,11)gr	9	9	-4	-20	27	-1	-7	-10	15	100		
scale1	10	-3	13	0	1	32	57	30	14	-10	100	
scale2	11	-6	15	-1	1	54	83	38	15	-4	54	100

S5. Simulations of TMBDA crystal packing

S5.1. The structures for calculations.

TMBDA_Meso (point group C_i)

C	-0.65443200	-0.10822200	-0.34795100
H	-0.60493900	-0.77958400	-1.20856100
C	0.65443200	0.10822200	0.34795100
H	0.60493900	0.77958400	1.20856100
N	-1.64542000	0.94378300	-0.51495900
N	-1.84714200	-0.14128300	0.47320800
N	1.64542000	-0.94378300	0.51495900
N	1.84714200	0.14128300	-0.47320800
C	-2.87925600	-1.07917900	0.02367200
H	-2.68677800	-2.04976300	0.50462400
H	-3.86046800	-0.70831000	0.34921400
H	-2.88445600	-1.20125200	-1.07322300
C	2.87925600	1.07917900	-0.02367200
H	3.86046800	0.70831000	-0.34921400
H	2.68677800	2.04976300	-0.50462400
H	2.88445600	1.20125200	1.07322300
C	-1.38862300	2.23826900	0.12666800
H	-0.65996400	2.78710600	-0.48796400
H	-2.33189400	2.80023100	0.14355000
H	-1.01337500	2.14762000	1.15729100
C	1.38862300	-2.23826900	-0.12666800
H	2.33189400	-2.80023100	-0.14355000
H	0.65996400	-2.78710600	0.48796400
H	1.01337500	-2.14762000	-1.15729100

TMBDA_Racemate (point group C_2)

C	0.12830200	0.74087500	-0.25156300
H	-0.74173600	1.34731200	-0.51782800
C	-0.12830200	-0.74087500	-0.25156300
H	0.74173600	-1.34731200	-0.51782800
N	1.43069900	1.18566300	-0.69936700
N	1.01619300	1.37779700	0.71031700
N	-1.01619300	-1.37779700	0.71031700
N	-1.43069900	-1.18566300	-0.69936700
C	1.75356100	0.49229100	1.61974300
H	2.04710600	-0.46348500	1.16067600
H	2.65555800	1.02187800	1.95360700
H	1.11337900	0.29729400	2.49175500
C	-1.43069900	-2.46092200	-1.42179500
H	-2.40661700	-2.94507500	-1.28238900
H	-1.28759700	-2.24433500	-2.49076500
H	-0.63577300	-3.14067400	-1.07001000
C	1.43069900	2.46092200	-1.42179500
H	0.63577300	3.14067400	-1.07001000
H	2.40661700	2.94507500	-1.28238900
H	1.28759700	2.24433500	-2.49076500
C	-1.75356100	-0.49229100	1.61974300
H	-2.65555800	-1.02187800	1.95360700
H	-1.11337900	-0.29729400	2.49175500
H	-2.04710600	0.46348500	1.16067600

TMBDA_Racemate_Naphtene (point group C_i)

C	-0.63602100	-0.15134300	-0.36458800
H	-0.50592700	-0.76365900	-1.25788800
C	0.63602100	0.15134300	0.36458800
H	0.50592700	0.76365900	1.25788800
C	-2.87866400	-1.48268100	-0.04495600
H	-2.58245700	-2.45646800	0.37603200
H	-3.91124900	-1.27011400	0.27451100
H	-2.87545700	-1.57291200	-1.14199300
C	2.87866400	1.48268100	0.04495600
H	3.91124900	1.27011400	-0.27451100
H	2.58245700	2.45646800	-0.37603200
H	2.87545700	1.57291200	1.14199300
C	-1.65204400	2.23249700	0.19966000
H	-1.05617100	2.92052000	-0.42023600
H	-2.64908800	2.67706900	0.34199200
H	-1.17301200	2.16626500	1.18603400
C	1.65204400	-2.23249700	-0.19966000
H	2.64908800	-2.67706900	-0.34199200
H	1.05617100	-2.92052000	0.42023600
H	1.17301200	-2.16626500	-1.18603400
C	-1.76432400	0.86668300	-0.44647400
H	-2.31339000	0.86339900	-1.39213300
C	-1.92992300	-0.38527900	0.38730100
H	-1.86218500	-0.22838000	1.46795300
C	1.76432400	-0.86668300	0.44647400
H	2.31339000	-0.86339900	1.39213300
C	1.92992300	0.38527900	-0.38730100
H	1.86218500	0.22838000	-1.46795300

TMBDA_ Meso_Naphtene (point group C_2)

C	0.08784400	0.74611600	-0.27676200
H	-0.80951500	1.30946000	-0.54055500
C	-0.08784400	-0.74611600	-0.27676200
H	0.80951500	-1.30946000	-0.54055500
C	1.74062900	0.59155800	1.76972700
H	2.03755000	-0.37938400	1.35071100
H	2.64913400	1.10806900	2.11544200
H	1.10190500	0.39703800	2.64496400
C	-1.39398900	-2.62745100	-1.56343900
H	-2.33553100	-3.18653700	-1.44426700
H	-1.26332900	-2.39746500	-2.63254800
H	-0.56790100	-3.28579600	-1.25445000
C	1.39398900	2.62745100	-1.56343900
H	0.56790100	3.28579600	-1.25445000
H	2.33553100	3.18653700	-1.44426700
H	1.26332900	2.39746500	-2.63254800
C	-1.74062900	-0.59155800	1.76972700
H	-2.64913400	-1.10806900	2.11544200
H	-1.10190500	-0.39703800	2.64496400
H	-2.03755000	0.37938400	1.35071100
C	-1.00655800	-1.41840300	0.73540000
H	-0.67195200	-2.39762900	1.08841600
C	-1.39398900	-1.36743400	-0.72463200
H	-2.17974400	-0.64624600	-0.96947900
C	1.00655800	1.41840300	0.73540000
H	0.67195200	2.39762900	1.08841600
C	1.39398900	1.36743400	-0.72463200
H	2.17974400	0.64624600	-0.96947900

S5.2. Lattice energy minimization

The optimal geometry and distributions of electrostatic potentials of the molecules and ions were calculated on the program package Gaussian 09 using DFT method with B3LYP functional and the extended basis aug-cc-pVDZ. Grimme dispersion correction DFT-D2 was used (GD2). The optimized molecular structures were treated as rigid bodies throughout the lattice energy calculations in this study.

The current version of program PMC was used throughout the crystal packing calculations. In calculation of lattice energy the convergence acceleration was applied for both the r^{-1} electrostatic and r^{-6} dispersion terms in the lattice sums with the convergence K_{conv} of 0.175 and the cutoff parameters R_{cut} = 9 Å and R^* = 0.5 Å for direct and reciprocal spaces, respectively. During minimization, the parameters of the unit cell and six parameters of rigid body of the crystallographically independent molecules were varied simultaneously, including three components of the center of mass and three Euler angles, while all the other molecules in the crystal environment perform the dependent motion in accordance with the symmetry group of a crystal. The local energy minimization was performed with the quasi Newton method using the Fortran subroutine VA09 A with analytical first derivatives. Each local minimum was refined in a series of few minimization stages: at each stage (p), lists of pairs of atoms {i, j} and points of the reciprocal space {h, k, l} contributing to the approximate energy function of the lattice F(p) are not updated to ensure continuity and perfect integrity F(p) with smooth motion from the initial X_0(p) to the lower point of X_{min}(p); at which these lists are updated and the next minimization stage, p+1, is carried out starting from X_0(p+1) = X_{min}(p) down to a new minimum approximation X_{min}(p+1), *etc.*, until the self-consistency condition X_{min}(s) = X_{min}(s−1) is finally reached.

The enthalpies (H) and free energies (G) were calculated using G3B3 method. The enthalpies of the gas-phase species M were computed according to the atomization energy method:

$\Delta H_f°$(g, M, 298) = H(Molecule, 298) – Σ$H°$(Atoms, 298) + ΣΔ$H_f°$(Atoms, 298).

Table S5.1 Literature values for atomic $H°$ and $\Delta H_f°$ (kcal mol^{-1}).

	H°(Atoms, 298)	$\Delta H_f°$(Atoms, 298) G3B3
H	52.1	-0.49872823
C	171.3	-37.8259642
N	113	-54.56280323
O	59.6	-75.02973288

Table S5.2 Atom–atom potentials LJ 6–12.

Atom 1[a]	Atom 2[a]	r/Å	E/kcal mol^{-1}
H	H	2.930	-0.0359
H	C	3.315	-0.0474
H	N	3.460	-0.0357
H	O	3.025	-0.0795
H	N'	3.460	-0.0357
H	H*	2.805	-0.0467
C	C	3.700	-0.0722
C	N	3.845	-0.0567
C	O	3.410	-0.1170
C	N'	3.845	-0.0567
C	H*	3.190	-0.0597
N	N	3.990	-0.0450
N	O	3.555	-0.0906
N	N'	3.990	-0.0450
N	H*	3.335	-0.0445
O	O	3.120	-0.2001
O	N'	3.555	-0.0906
O	H*	1.900	-1.1100
N'	N'	3.990	-0.0450
N'	H*	1.960	-0.9000
H*	H*	2.680	-0.0614

[a] N' stands for N(sp^2), and H* stands for H atoms that form hydrogen bonds.

S5.3. Lattice energies and packings

Table S5.3 The lattice energies E_{latt} (kcal mol^{-1}), unit cell lengths *a*, *b*, *c* (Å) and angles α, β, γ (deg), densities at room temperature ρ_{298} (g cm^{-3}) and space groups (SG) with numbers of independent molecules (*Z*') of crystal model packings of five polymorphs of **1b**.

Polymorph	$-E_{latt}$	*a*	*b*	*c*	β	SG	ρ_{298}
1	19.32	9.832	7.31	11.717	98.26	$P2_1/c$ (*Z*'=1)	1.085–1.134
2	19.23	9.804	7.317	12.096	74.52	$P2_1/a$ (*Z*'=1)	1.081–1.13
3	19.16	9.794	7.315	11.829	98.21	$P2_1/n$ (*Z*'=1)	1.078–1.126
		5.914	7.315	9.794	98.21	$P2_1/c$ (*Z*'=1)	1.1–1.15 (163 K)
4	18.91	13.087	8.018	9.358	122.42	$P2_1/n$ (*Z*'=1)	1.091–1.14
5	18.8	7.73	10.124	12.033	116.45	$P2_1/a$ (*Z*'=1)	1.073–1.12
Exp.	–	5.781	7.306	9.674	96.8	$P2_1/c$ (*Z*'=1)	1.164 (163 K)

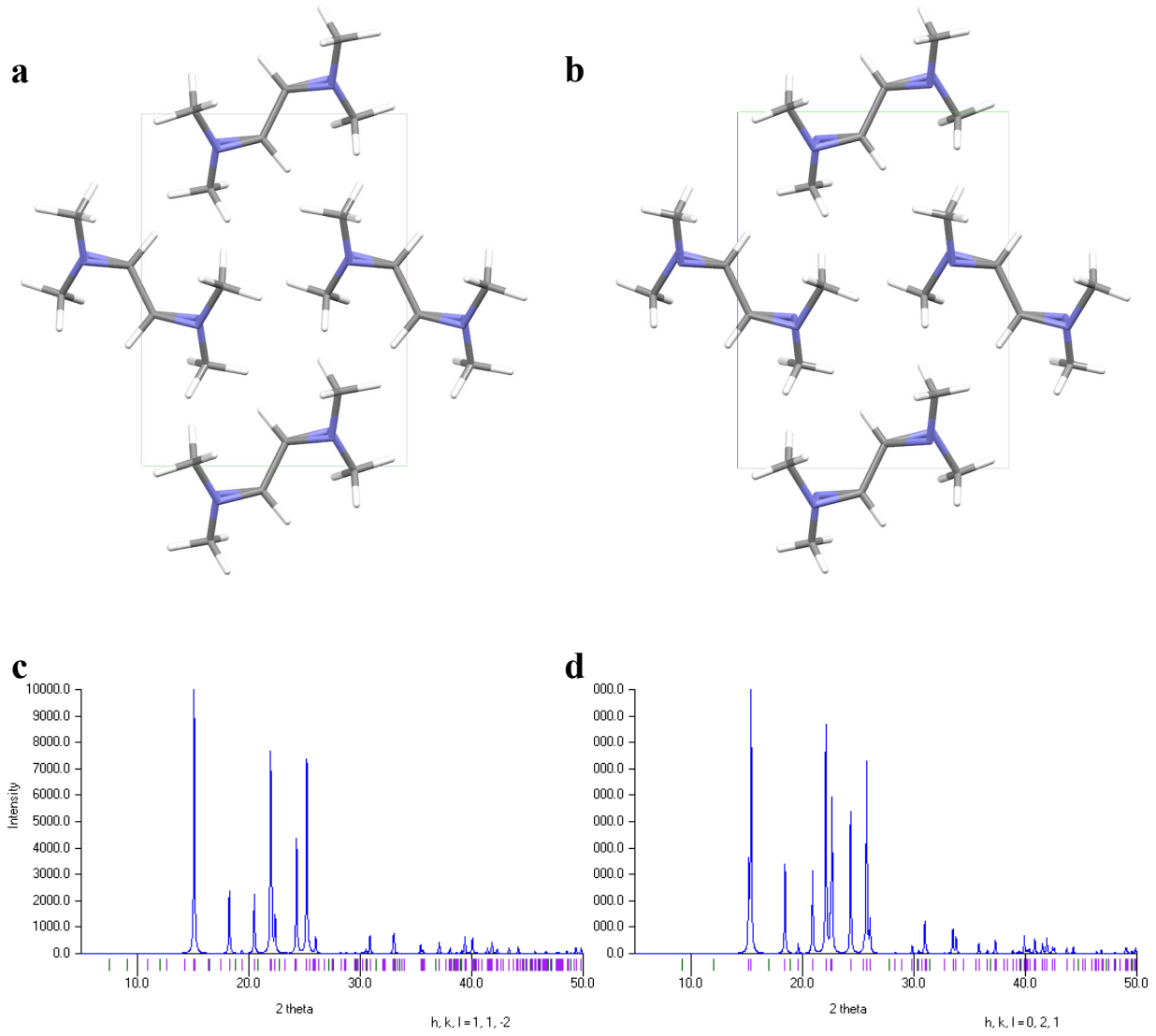

Figure S5.1 Spatial (the same orientation) and powder patterns of model (3-rd polymorph) and experimental (XRD) structures of **1b**: crystal packings of (**a**) **1** (model **#3**) and (**b**) **1b** (experimental); powder patterns of (**c**) **1** (model **#3**) and (**d**) **1b** (experimental).

Table S5.4 The lattice energies E_{latt} (kcal mol^{-1}), unit cell lengths *a*, *b*, *c* (Å) and angles α, β, γ (deg), densities at room temperature ρ_{298} (g cm^{-3}) and space groups (SG) with numbers of independent molecules (*Z*') of crystal model packings of five polymorphs of **1a**.

Polymorph	$-E_{latt}$	*a*	*b*	*c*	α, β, γ	SG	ρ_{298}
1	16.93	6.422	8.281	8.653	100.281 96.478 107.619	$P\bar{1}$ (*Z*'=1)	1.065–1.112
2	16.92	6.417	7.946	9.131	82.76 80.42 71.56	$P\bar{1}$ (*Z*'=1)	1.041–1.088
3	16.81	11.28	7.834	9.969	90 80.57 90	$P2_1/c$ (*Z*'=1)	1.041–1.087
4	16.73	6.39	8.182	17.485	83.01 87.9 72.86	$P\bar{1}$ (*Z*'=2)	1.043–1.09
5	16.72	5.435	6.382	13.048	92.68 96.85 105.71	$P\bar{1}$ (*Z*'=1)	1.049–1.096

S5.4. Optimized crystal structure coordinates for 5 polymorphs of TMBDA_Meso

data_TMBDA_Meso_1

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/c'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
_cell_length_a                   9.832
_cell_length_b                   7.310
_cell_length_c                   11.717
_cell_angle_alpha                90.00
_cell_angle_beta                 98.26
_cell_angle_gamma                90.00
_cell_volume                     833.387
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.31900 0.45446 0.76018
H2 H 0.40599 0.54896 0.77193
C3 C 0.18100 0.54512 0.73968
H4 H 0.09401 0.45062 0.72793
N5 N 0.34957 0.28555 0.70331
N6 N 0.33036 0.28646 0.82641
N7 N 0.15043 0.71403 0.79655
N8 N 0.16964 0.71312 0.67345
C9 C 0.46160 0.26157 0.90156
H10 H 0.45211 0.32308 0.98575
H11 H 0.48147 0.11443 0.91327
H12 H 0.54806 0.32526 0.86574
C13 C 0.03840 0.73801 0.59830
H14 H 0.01853 0.88515 0.58659
H15 H 0.04789 0.67650 0.51411
H16 H -0.04806 0.67432 0.63412
C17 C 0.23641 0.19322 0.63021
H18 H 0.21733 0.26602 0.54730
H19 H 0.26952 0.05305 0.61470
H20 H 0.14109 0.18704 0.66913
C21 C 0.26359 0.80636 0.86965
H22 H 0.23048 0.94653 0.88516
H23 H 0.28267 0.73356 0.95256
H24 H 0.35891 0.81254 0.83073

#END
```

data_TMBDA_Meso_2

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/a'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,-z
3 -x,-y,-z
4 1/2+x,1/2-y,z
_cell_length_a                   9.804
_cell_length_b                   7.317
_cell_length_c                   12.096
_cell_angle_alpha                90.00
_cell_angle_beta                 74.52
_cell_angle_gamma                90.00
_cell_volume                     836.239
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.31135 0.45424 0.75951
H2 H -0.23033 0.54851 0.77203
C3 C -0.43955 0.54502 0.73935
H4 H -0.52057 0.45075 0.72683
N5 N -0.25167 0.28645 0.70196
N6 N -0.33282 0.28533 0.82431
N7 N -0.49923 0.71281 0.79690
N8 N -0.41808 0.71393 0.67455
C9 C -0.23904 0.25934 0.89921
H10 H -0.29104 0.31939 0.98328
H11 H -0.22464 0.11217 0.90996
H12 H -0.13456 0.32362 0.86424
C13 C -0.51186 0.73992 0.59965
H14 H -0.52626 0.88709 0.58890
H15 H -0.45986 0.67987 0.51558
H16 H -0.61634 0.67564 0.63462
C17 C -0.32808 0.19532 0.62839
H18 H -0.30569 0.26940 0.54637
H19 H -0.28674 0.05558 0.61216
H20 H -0.44315 0.18844 0.66679
C21 C -0.42282 0.80394 0.87047
H22 H -0.46416 0.94368 0.88670
H23 H -0.44521 0.72986 0.95249
H24 H -0.30775 0.81082 0.83207

#END
```

data_TMBDA_Meso_3

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/n'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,1/2-z
3 -x,-y,-z
4 1/2+x,1/2-y,1/2+z
_cell_length_a                   9.794
_cell_length_b                   7.315
_cell_length_c                   11.829
_cell_angle_alpha                90.00
_cell_angle_beta                 98.21
_cell_angle_gamma                90.00
_cell_volume                     838.781
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.43076 -0.04553 -0.25984
H2 H 0.34350 0.04889 -0.27326
C3 C 0.56928 0.04511 -0.24006
H4 H 0.65654 -0.04931 -0.22664
N5 N 0.39945 -0.21208 -0.20140
N6 N 0.41986 -0.21571 -0.32309
N7 N 0.60059 0.21166 -0.29850
N8 N 0.58018 0.21529 -0.17681
C9 C 0.28866 -0.24264 -0.39781
H10 H 0.29897 -0.18429 -0.48189
H11 H 0.26872 -0.38998 -0.40746
H12 H 0.20149 -0.17729 -0.36374
C13 C 0.71138 0.24222 -0.10209
H14 H 0.73132 0.38956 -0.09244
H15 H 0.70107 0.18387 -0.01801
H16 H 0.79855 0.17687 -0.13616
C17 C 0.51246 -0.30224 -0.12718
H18 H 0.53092 -0.22660 -0.04607
H19 H 0.47899 -0.44156 -0.11008
H20 H 0.60859 -0.31029 -0.16507
C21 C 0.48758 0.30182 -0.37272
H22 H 0.52105 0.44114 -0.38982
H23 H 0.46912 0.22618 -0.45383
H24 H 0.39145 0.30987 -0.33483

#END
```

data_TMBDA_Meso_4

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/n'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,1/2-z
3 -x,-y,-z
4 1/2+x,1/2-y,1/2+z
_cell_length_a                   13.087
_cell_length_b                   8.018
_cell_length_c                   9.358
_cell_angle_alpha                90.00
_cell_angle_beta                 122.42
_cell_angle_gamma                90.00
_cell_volume                     828.904
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.26098 0.55407 0.42792
H2 H -0.18287 0.62794 0.45298
C3 C -0.23896 0.44575 0.57226
H4 H -0.31707 0.37188 0.54720
N5 N -0.37533 0.63899 0.31656
N6 N -0.34081 0.48990 0.25828
N7 N -0.12461 0.36083 0.68362
N8 N -0.15913 0.50992 0.74190
C9 C -0.30735 0.53561 0.13699
H10 H -0.24595 0.43891 0.14177
H11 H -0.38951 0.53807 0.00933
H12 H -0.26268 0.65857 0.16508
C13 C -0.19259 0.46421 0.86319
H14 H -0.11043 0.46175 0.99085
H15 H -0.25399 0.56091 0.85841
H16 H -0.23726 0.34125 0.83510
C17 C -0.47603 0.60512 0.33912
H18 H -0.46081 0.67685 0.44911
H19 H -0.55970 0.64939 0.22565
H20 H -0.48645 0.47199 0.35720
C21 C -0.02391 0.39470 0.66106
H22 H 0.05976 0.35043 0.77453
H23 H -0.03913 0.32297 0.55107
H24 H -0.01349 0.52783 0.64298

#END
```

data_TMBDA_Meso_5

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/a'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,-z
3 -x,-y,-z
4 1/2+x,1/2-y,z
_cell_length_a                   7.730
_cell_length_b                   10.124
_cell_length_c                   12.033
_cell_angle_alpha                90.00
_cell_angle_beta                 116.45
_cell_angle_gamma                90.00
_cell_volume                     843.112
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.72305 0.07075 0.73281
H2 H 0.83970 0.13232 0.73364
C3 C 0.77721 -0.07075 0.76719
H4 H 0.66056 -0.13232 0.76636
N5 N 0.59360 0.14315 0.76901
N6 N 0.52809 0.09753 0.63952
N7 N 0.90666 -0.14315 0.73099
N8 N 0.97217 -0.09753 0.86048
C9 C 0.51020 0.20842 0.55682
H10 H 0.52691 0.16945 0.47680
H11 H 0.36530 0.25149 0.52384
H12 H 0.61936 0.28576 0.60341
C13 C 0.99006 -0.20842 0.94318
H14 H 1.13496 -0.25149 0.97616
H15 H 0.97335 -0.16945 1.02320
H16 H 0.88090 -0.28576 0.89659
C17 C 0.50036 0.07030 0.83310
H18 H 0.60662 0.05751 0.93062
H19 H 0.38004 0.13057 0.82976
H20 H 0.44373 -0.02661 0.79131
C21 C 0.99990 -0.07030 0.66690
H22 H 1.12022 -0.13057 0.67024
H23 H 0.89364 -0.05751 0.56938
H24 H 1.05653 0.02661 0.70869

#END
```

S5.5. Optimized crystal structure coordinates for 5 polymorphs of TMBDA_Racemate.

```
data_TMBDA_Rac_1
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   10.857
_cell_length_b                   11.343
_cell_length_c                   6.422
_cell_angle_alpha                49.29
_cell_angle_beta                 71.29
_cell_angle_gamma                46.70
_cell_volume                     424.668
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.02881 0.31310 0.52440
H2 H -0.00608 0.42021 0.40180
C3 C 0.13395 0.08867 0.67037
H4 H 0.12581 -0.02151 0.86885
N5 N -0.16850 0.35678 0.67108
N6 N -0.19054 0.40171 0.40500
N7 N 0.24299 0.01113 0.51567
N8 N 0.29818 0.03983 0.65130
C9 C -0.19313 0.25748 0.45474
H10 H -0.11420 0.10217 0.66176
H11 H -0.32863 0.32566 0.43878
H12 H -0.14457 0.24341 0.28701
C13 C 0.43946 -0.16128 0.90269
H14 H 0.56388 -0.21845 0.83829
H15 H 0.43606 -0.13645 1.04458
H16 H 0.42770 -0.27793 1.01388
C17 C -0.27021 0.54958 0.62556
H18 H -0.27772 0.67028 0.41412
H19 H -0.40227 0.60835 0.65023
H20 H -0.20825 0.51244 0.78829
C21 C 0.19576 0.16583 0.20677
H22 H 0.31297 0.10149 0.12760
H23 H 0.09944 0.18993 0.12601
H24 H 0.14198 0.31585 0.13057

#END
```

data_TMBDA_Rac_2

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   7.946
_cell_length_b                   9.131
_cell_length_c                   8.489
_cell_angle_alpha                89.55
_cell_angle_beta                 45.82
_cell_angle_gamma                97.24
_cell_volume                     434.206
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.03073 0.27193 -0.13082
H2 H -0.03373 0.37723 -0.09924
C3 C 0.11020 0.23821 -0.01955
H4 H 0.08390 0.11942 0.02654
N5 N -0.08635 0.14724 -0.14703
N6 N 0.14980 0.23244 -0.34949
N7 N 0.31903 0.32643 -0.08148
N8 N 0.07462 0.34022 0.12729
C9 C 0.34002 0.14557 -0.45062
H10 H 0.30670 0.06594 -0.32991
H11 H 0.35735 0.08444 -0.57090
H12 H 0.50748 0.22433 -0.53935
C13 C 0.01684 0.27065 0.31976
H14 H 0.07886 0.35305 0.37081
H15 H -0.17844 0.23786 0.45526
H16 H 0.10067 0.17213 0.28365
C17 C -0.27483 0.18021 -0.12875
H18 H -0.23874 0.29655 -0.19527
H19 H -0.28934 0.10487 -0.22047
H20 H -0.44397 0.15884 0.04758
C21 C 0.43884 0.45937 -0.24565
H22 H 0.53532 0.53742 -0.22276
H23 H 0.56865 0.42479 -0.41130
H24 H 0.31566 0.51575 -0.23245

#END
```

data_TMBDA_Rac_3

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/c'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
_cell_length_a                   11.280
_cell_length_b                   7.834
_cell_length_c                   9.969
_cell_angle_alpha                90.00
_cell_angle_beta                 80.57
_cell_angle_gamma                90.00
_cell_volume                     869.031
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.78732 0.67380 -0.16873
H2 H 0.82685 0.61663 -0.26587
C3 C 0.75065 0.54683 -0.05646
H4 H 0.75708 0.59468 0.04514
N5 N 0.83503 0.83537 -0.13154
N6 N 0.71884 0.82852 -0.18244
N7 N 0.65311 0.42577 -0.05885
N8 N 0.78022 0.36958 -0.08614
C9 C 0.61704 0.86400 -0.07417
H10 H 0.63228 0.82325 0.02725
H11 H 0.60005 1.00204 -0.07270
H12 H 0.53792 0.79758 -0.09992
C13 C 0.81066 0.27133 0.02864
H14 H 0.78806 0.13670 0.01528
H15 H 0.90810 0.28249 0.02697
H16 H 0.76203 0.31702 0.12720
C17 C 0.92929 0.90834 -0.23422
H18 H 0.91720 0.87495 -0.33867
H19 H 0.92783 1.04785 -0.22320
H20 H 1.01634 0.85975 -0.21464
C21 C 0.59795 0.42213 -0.18236
H22 H 0.55732 0.29577 -0.18943
H23 H 0.52657 0.51907 -0.17122
H24 H 0.66195 0.44680 -0.27609

#END
```

data_TMBDA_Rac_4

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   18.835
_cell_length_b                   6.390
_cell_length_c                   8.182
_cell_angle_alpha                107.14
_cell_angle_beta                 77.70
_cell_angle_gamma                111.92
_cell_volume                     867.071
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.63467 -0.05696 0.16981
H2 H 0.69136 -0.05993 0.17886
C3 C 0.60619 -0.17963 -0.00319
H4 H 0.54354 -0.25830 0.00169
N5 N 0.57786 -0.07326 0.31981
N6 N 0.61938 0.15307 0.27381
N7 N 0.64300 -0.09476 -0.15751
N8 N 0.65297 -0.30063 -0.12976
C9 C 0.56868 0.23046 0.20941
H10 H 0.52257 0.08678 0.14218
H11 H 0.54269 0.33575 0.31961
H12 H 0.60455 0.34030 0.12109
C13 C 0.60949 -0.51415 -0.24418
H14 H 0.64568 -0.54416 -0.36722
H15 H 0.59649 -0.65874 -0.18349
H16 H 0.55543 -0.50493 -0.26843
C17 C 0.60516 -0.08123 0.47203
H18 H 0.66711 0.01740 0.47788
H19 H 0.57210 -0.00848 0.58778
H20 H 0.59424 -0.26437 0.46727
C21 C 0.71406 0.10667 -0.14069
H22 H 0.74752 0.10374 -0.26836
H23 H 0.69770 0.26417 -0.09800
H24 H 0.74990 0.10960 -0.04944
C1 C 0.11883 0.08494 0.87440
H2 H 0.05636 0.00463 0.87522
C3 C 0.14495 0.20524 1.04982
H4 H 0.20137 0.20350 1.06231
N5 N 0.16717 -0.03270 0.75005
N6 N 0.15741 0.17349 0.72233
N7 N 0.12823 0.41311 1.15376
N8 N 0.08644 0.18487 1.19657
C9 C 0.22788 0.37642 0.74415
H10 H 0.26247 0.37859 0.83773
H11 H 0.26285 0.37658 0.61829
```

```
H12 H 0.21091 0.53281 0.78644
C13 C 0.11176 0.17485 1.35068
H14 H 0.07728 0.24475 1.46485
H15 H 0.10107 -0.00853 1.34464
H16 H 0.17337 0.27492 1.36061
C17 C 0.12543 -0.24530 0.63209
H18 H 0.07181 -0.23696 0.60455
H19 H 0.16308 -0.27224 0.51094
H20 H 0.11183 -0.39135 0.69162
C21 C 0.07842 0.49044 1.08642
H22 H 0.05104 0.59316 1.19558
H23 H 0.11521 0.60278 1.00050
H24 H 0.03340 0.34679 1.01581

#END
```

data_TMBDA_Rac_5

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   7.175
_cell_length_b                   13.048
_cell_length_c                   5.435
_cell_angle_alpha                83.15
_cell_angle_beta                 121.11
_cell_angle_gamma                97.58
_cell_volume                     431.05
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.10216 0.76286 0.73009
H2 H -0.09907 0.71913 0.57285
C3 C -0.19017 0.70035 0.90455
H4 H -0.11922 0.72550 1.12250
N5 N 0.07442 0.84142 0.87480
N6 N -0.14227 0.87114 0.63811
N7 N -0.41750 0.65918 0.77722
N8 N -0.24224 0.59055 0.86194
C9 C -0.25739 0.92034 0.74484
H10 H -0.21741 0.89226 0.96441
H11 H -0.21423 1.00420 0.74099
H12 H -0.43371 0.90521 0.59612
C13 C -0.20170 0.52515 1.12076
H14 H -0.31383 0.45468 1.05557
H15 H -0.03265 0.50349 1.22971
H16 H -0.22551 0.56492 1.26945
C17 C 0.23475 0.85641 0.78070
H18 H 0.16075 0.84118 0.55180
H19 H 0.30813 0.93660 0.81411
H20 H 0.36293 0.80348 0.91548
C21 C -0.55524 0.67344 0.46314
H22 H -0.69124 0.61288 0.39087
H23 H -0.62138 0.74941 0.41303
H24 H -0.46758 0.66949 0.34823

#END
```

S5.6. Optimized crystal structure coordinates for 5 polymorphs of TMBDA_Meso_Naphtene.

data_TMBDA_Meso_Napht_1

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   9.760
_cell_length_b                   11.925
_cell_length_c                   4.828
_cell_angle_alpha                66.35
_cell_angle_beta                 64.29
_cell_angle_gamma                86.81
_cell_volume                     458.975
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.25492 0.19285 0.88542
H2 H 0.19485 0.18968 1.13938
C3 C 0.24512 0.30715 0.61450
H4 H 0.30519 0.31032 0.36054
C5 C 0.16316 -0.04678 1.18676
H6 H 0.04175 -0.05708 1.23950
H7 H 0.21035 -0.13054 1.16445
H8 H 0.16704 -0.04185 1.40614
C9 C 0.33688 0.54678 0.31316
H10 H 0.28969 0.63054 0.33547
H11 H 0.45829 0.55708 0.26042
H12 H 0.33300 0.54185 0.09378
C13 C 0.53957 0.18188 0.47744
H14 H 0.60788 0.26056 0.44546
H15 H 0.61383 0.11023 0.44970
H16 H 0.50680 0.21387 0.27018
C17 C -0.03953 0.31812 1.02248
H18 H -0.11379 0.38977 1.05022
H19 H -0.10784 0.23944 1.05446
H20 H -0.00676 0.28613 1.22974
C21 C 0.39921 0.13080 0.81922
H22 H 0.42562 0.09017 1.03449
C23 C 0.25404 0.06859 0.86964
H24 H 0.25585 0.07211 0.63808
C25 C 0.10083 0.36920 0.68070
H26 H 0.07442 0.40983 0.46543
C27 C 0.24600 0.43141 0.63028
H28 H 0.24419 0.42789 0.86184

#END
```

data_TMBDA_Meso_Napht_2

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   7.811
_cell_length_b                   9.067
_cell_length_c                   7.055
_cell_angle_alpha                77.54
_cell_angle_beta                 72.42
_cell_angle_gamma                96.00
_cell_volume                     457.303
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.06167 0.26283 0.13741
H2 H -0.00353 0.35734 -0.00165
C3 C 0.06107 0.23499 0.26339
H4 H 0.00293 0.14048 0.40245
C5 C -0.20928 0.12954 -0.08602
H6 H -0.09873 0.08419 -0.18183
H7 H -0.34043 0.05882 -0.06524
H8 H -0.20672 0.24718 -0.17135
C9 C 0.20868 0.36828 0.48682
H10 H 0.33983 0.43900 0.46604
H11 H 0.09813 0.41363 0.58263
H12 H 0.20612 0.25064 0.57215
C13 C -0.35804 0.19066 0.47002
H14 H -0.34705 0.28763 0.53914
H15 H -0.50394 0.14301 0.51153
H16 H -0.29476 0.10124 0.54044
C17 C 0.35744 0.30716 -0.06922
H18 H 0.50334 0.35481 -0.11073
H19 H 0.34645 0.21019 -0.13834
H20 H 0.29416 0.39658 -0.13964
C21 C -0.26771 0.24094 0.23816
H22 H -0.33331 0.32256 0.15901
C23 C -0.18573 0.13061 0.11893
H24 H -0.18555 0.01815 0.21424
C25 C 0.26711 0.25688 0.16264
H26 H 0.33271 0.17526 0.24179
C27 C 0.18513 0.36721 0.28187
H28 H 0.18495 0.47967 0.18656

#END
```

data_TMBDA_Meso_Napht_3

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   11.372
_cell_length_b                   8.163
_cell_length_c                   5.459
_cell_angle_alpha                69.27
_cell_angle_beta                 82.61
_cell_angle_gamma                99.77
_cell_volume                     457.183
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.25994 -0.07232 -0.04917
H2 H 0.25540 -0.04022 -0.25893
C3 C 0.24004 0.07240 0.04899
H4 H 0.24458 0.04030 0.25875
C5 C 0.43198 -0.23341 -0.14208
H6 H 0.51426 -0.12449 -0.24693
H7 H 0.46100 -0.35747 -0.03728
H8 H 0.38355 -0.25550 -0.29386
C9 C 0.06800 0.23349 0.14190
H10 H 0.03898 0.35755 0.03710
H11 H -0.01428 0.12457 0.24675
H12 H 0.11643 0.25558 0.29368
C13 C 0.14609 -0.33103 0.41709
H14 H 0.04986 -0.32407 0.42551
H15 H 0.14877 -0.47086 0.53391
H16 H 0.18696 -0.24626 0.51605
C17 C 0.35389 0.33111 -0.41727
H18 H 0.35121 0.47094 -0.53409
H19 H 0.45012 0.32415 -0.42569
H20 H 0.31302 0.24634 -0.51623
C21 C 0.21417 -0.27073 0.13103
H22 H 0.18220 -0.35790 0.02877
C23 C 0.34949 -0.18574 0.05005
H24 H 0.39041 -0.16034 0.20773
C25 C 0.28581 0.27081 -0.13121
H26 H 0.31778 0.35798 -0.02895
C27 C 0.15049 0.18582 -0.05023
H28 H 0.10957 0.16042 -0.20791

#END
```

data_TMBDA_Meso_Napht_4

```
_symmetry_cell_setting           triclinic
_symmetry_space_group_name_H-M   'P -1'
_symmetry_Int_Tables_number      2
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,-y,-z
_cell_length_a                   8.773
_cell_length_b                   8.002
_cell_length_c                   7.088
_cell_angle_alpha                83.52
_cell_angle_beta                 93.22
_cell_angle_gamma                67.92
_cell_volume                     455.515
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C -0.20400 -0.06135 0.33974
H2 H -0.13662 -0.00347 0.42852
C3 C -0.29596 0.06135 0.16020
H4 H -0.36334 0.00347 0.07142
C5 C -0.26051 -0.20903 0.66478
H6 H -0.36116 -0.09879 0.71612
H7 H -0.26538 -0.33994 0.72435
H8 H -0.14226 -0.20657 0.72212
C9 C -0.23945 0.20903 -0.16484
H10 H -0.23458 0.33994 -0.22441
H11 H -0.13880 0.09879 -0.21618
H12 H -0.35770 0.20657 -0.22218
C13 C -0.13028 -0.35681 0.17010
H14 H -0.03904 -0.34573 0.07407
H15 H -0.10468 -0.50242 0.21109
H16 H -0.25336 -0.29355 0.08894
C17 C -0.36968 0.35681 0.32984
H18 H -0.39528 0.50242 0.28885
H19 H -0.46091 0.34573 0.42587
H20 H -0.24660 0.29355 0.41100
C21 C -0.12264 -0.26692 0.34547
H22 H -0.00612 -0.33250 0.43822
C23 C -0.27394 -0.18525 0.44877
H24 H -0.38850 -0.18496 0.37897
C25 C -0.37732 0.26692 0.15447
H26 H -0.49384 0.33250 0.06172
C27 C -0.22602 0.18525 0.05117
H28 H -0.11146 0.18496 0.12097

#END
```

data_TMBDA_Meso_Napht_5

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P c'
_symmetry_Int_Tables_number      7
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 x,-y,1/2+z
_cell_length_a                   5.638
_cell_length_b                   10.871
_cell_length_c                   7.748
_cell_angle_alpha                90.00
_cell_angle_beta                 103.55
_cell_angle_gamma                90.00
_cell_volume                     461.662
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.69601 0.31664 0.37640
H2 H 0.70129 0.37406 0.26190
C3 C 0.74777 0.18340 0.35278
H4 H 0.74249 0.12598 0.46728
C5 C 0.33783 0.46101 0.41423
H6 H 0.17647 0.42929 0.31460
H7 H 0.27472 0.50442 0.52393
H8 H 0.42948 0.53197 0.35196
C9 C 1.10595 0.03903 0.31495
H10 H 1.16906 -0.00438 0.20525
H11 H 1.26731 0.07075 0.41458
H12 H 1.01430 -0.03193 0.37722
C13 C 0.92150 0.31158 0.71762
H14 H 1.11543 0.30239 0.71579
H15 H 0.91063 0.36057 0.83989
H16 H 0.84747 0.21873 0.72469
C17 C 0.52228 0.18846 0.01156
H18 H 0.53315 0.13947 -0.11071
H19 H 0.32835 0.19765 0.01339
H20 H 0.59631 0.28131 0.00449
C21 C 0.78055 0.38000 0.55544
H22 H 0.83648 0.47581 0.54819
C23 C 0.51185 0.35598 0.47991
H24 H 0.43564 0.28049 0.54318
C25 C 0.66323 0.12004 0.17374
H26 H 0.60730 0.02423 0.18099
C27 C 0.93193 0.14406 0.24927
H28 H 1.00814 0.21955 0.18600

#END
```

S5.7. Optimized crystal structure coordinates for 5 polymorphs of TMBDA_Racemate_Naphtene

data_TMBDA_Meso_Napht_1

```
_symmetry_cell_setting            monoclinic
_symmetry_space_group_name_H-M    'P 21/a'
_symmetry_Int_Tables_number       14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,-z
3 -x,-y,-z
4 1/2+x,1/2-y,z
_cell_length_a                    9.906
_cell_length_b                    8.726
_cell_length_c                    12.247
_cell_angle_alpha                 90.00
_cell_angle_beta                  116.25
_cell_angle_gamma                 90.00
_cell_volume                      949.454
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.67922 0.63995 0.77745
H2 H 0.55685 0.64580 0.74087
C3 C 0.74857 0.76775 0.73724
H4 H 0.86195 0.79989 0.80347
C5 C 0.88024 0.44493 0.77373
H6 H 0.95736 0.54328 0.79953
H7 H 0.94278 0.34491 0.82679
H8 H 0.84559 0.42099 0.67674
C9 C 0.71090 1.06105 0.68390
H10 H 0.65559 1.13225 0.60163
H11 H 0.69186 1.11457 0.75735
H12 H 0.83273 1.06226 0.71123
C13 C 0.67306 0.53197 0.97542
H14 H 0.56175 0.48625 0.91336
H15 H 0.73243 0.44361 1.04431
H16 H 0.65569 0.63244 1.02216
C17 C 0.61725 0.66800 0.51091
H18 H 0.56649 0.71822 0.41898
H19 H 0.68171 0.56587 0.50951
H20 H 0.52586 0.63000 0.53221
C21 C 0.71718 0.78302 0.60421
H22 H 0.81150 0.82507 0.58907
C23 C 0.65251 0.89813 0.66046
H24 H 0.53198 0.88572 0.63350
C25 C 0.74509 0.47889 0.79669
H26 H 0.66278 0.38599 0.77215
C27 C 0.76002 0.57407 0.90457
H28 H 0.87221 0.62176 0.95906

#END
```

data_TMBDA_Meso_Napht_2

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/c'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
_cell_length_a                   5.240
_cell_length_b                   16.455
_cell_length_c                   13.278
_cell_angle_alpha                90.00
_cell_angle_beta                 55.46
_cell_angle_gamma                90.00
_cell_volume                     943.077
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.86729 0.22191 0.21337
H2 H 1.04283 0.21165 0.23193
C3 C 0.65299 0.15135 0.24382
H4 H 0.41955 0.16822 0.27224
C5 C 0.85541 0.25870 0.02291
H6 H 0.61725 0.23519 0.07723
H7 H 0.85882 0.31416 -0.02419
H8 H 1.00252 0.21285 -0.04686
C9 C 0.38070 0.03325 0.40417
H10 H 0.42580 -0.03122 0.41093
H11 H 0.28310 0.06183 0.49397
H12 H 0.20418 0.03595 0.38393
C13 C 0.85713 0.37224 0.28216
H14 H 1.10148 0.36180 0.24737
H15 H 0.83819 0.43372 0.25418
H16 H 0.72005 0.37043 0.38276
C17 C 1.11411 0.06332 0.06982
H18 H 1.18660 -0.00080 0.05535
H19 H 1.15914 0.08725 -0.01628
H20 H 1.26030 0.09732 0.09012
C21 C 0.77522 0.07186 0.17313
H22 H 0.61564 0.03991 0.15861
C23 C 0.67274 0.07614 0.30478
H24 H 0.86110 0.07698 0.31779
C25 C 0.96726 0.27606 0.10380
H26 H 1.20433 0.29917 0.05545
C27 C 0.74923 0.30834 0.23217
H28 H 0.50712 0.31363 0.26276

#END
```

data_TMBDA_Meso_Napht_3

```
_symmetry_cell_setting           orthorhombic
_symmetry_space_group_name_H-M   'P b c a'
_symmetry_Int_Tables_number      61
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 1/2-x,1/2+y,z
3 x,1/2-y,1/2+z
4 1/2-x,-y,1/2+z
5 -x,-y,-z
6 1/2+x,1/2-y,-z
7 -x,1/2+y,1/2-z
8 1/2+x,y,1/2-z
_cell_length_a                   16.345
_cell_length_b                   11.515
_cell_length_c                   10.124
_cell_angle_alpha                90.00
_cell_angle_beta                 90.00
_cell_angle_gamma                90.00
_cell_volume                     1905.47
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.34922 -0.22468 0.56731
H2 H 0.33032 -0.26724 0.47590
C3 C 0.28007 -0.17735 0.64896
H4 H 0.29128 -0.17732 0.75528
C5 C 0.44327 -0.04888 0.63595
H6 H 0.40973 -0.05039 0.72995
H7 H 0.50845 -0.03437 0.65778
H8 H 0.42071 0.02565 0.57839
C9 C 0.12780 -0.22526 0.71167
H10 H 0.06623 -0.20104 0.67706
H11 H 0.12729 -0.31836 0.73659
H12 H 0.14040 -0.17626 0.80276
C13 C 0.46396 -0.38420 0.57730
H14 H 0.46038 -0.38338 0.46875
H15 H 0.52900 -0.38920 0.60517
H16 H 0.43329 -0.46344 0.61277
C17 C 0.24571 -0.02325 0.46472
H18 H 0.19061 0.01798 0.42337
H19 H 0.29378 0.04332 0.47284
H20 H 0.26702 -0.08928 0.39439
C21 C 0.22782 -0.07744 0.59788
H22 H 0.20681 -0.01633 0.67326
C23 C 0.19209 -0.19814 0.60855
H24 H 0.18475 -0.24384 0.51453
C25 C 0.43099 -0.16143 0.56122
H26 H 0.46230 -0.16563 0.46590
C27 C 0.42414 -0.27610 0.63303
H28 H 0.42434 -0.26986 0.74088

#END
```

data_TMBDA_Meso_Napht_4

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'P 21/c'
_symmetry_Int_Tables_number      14
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 -x,1/2+y,1/2-z
3 -x,-y,-z
4 x,1/2-y,1/2+z
_cell_length_a                   14.049
_cell_length_b                   7.380
_cell_length_c                   9.903
_cell_angle_alpha                90.00
_cell_angle_beta                 112.25
_cell_angle_gamma                90.00
_cell_volume                     950.307
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.26343 0.30512 0.50670
H2 H 0.21591 0.38132 0.55216
C3 C 0.20677 0.16205 0.39804
H4 H 0.23712 0.13653 0.31331
C5 C 0.42877 0.09913 0.60605
H6 H 0.40401 0.04765 0.49389
H7 H 0.51270 0.11821 0.64823
H8 H 0.41132 -0.00563 0.67242
C9 C 0.02555 0.10175 0.19235
H10 H -0.04662 0.03383 0.18239
H11 H 0.00598 0.22686 0.12693
H12 H 0.06718 0.01190 0.14485
C13 C 0.36090 0.61267 0.52082
H14 H 0.33938 0.64314 0.61433
H15 H 0.44083 0.65769 0.54854
H16 H 0.31089 0.69301 0.42708
C17 C 0.17463 -0.02524 0.60337
H18 H 0.11320 -0.11075 0.61267
H19 H 0.24905 -0.08867 0.66731
H20 H 0.17212 0.10677 0.65315
C21 C 0.16162 -0.00241 0.44540
H22 H 0.16409 -0.12874 0.38914
C23 C 0.09141 0.14148 0.35025
H24 H 0.05632 0.23130 0.40629
C25 C 0.37446 0.27507 0.61003
H26 H 0.39496 0.33356 0.71885
C27 C 0.34964 0.41175 0.48781
H28 H 0.36879 0.36898 0.39532

#END
```

data_TMBDA_Meso_Napht_5

```
_symmetry_cell_setting           monoclinic
_symmetry_space_group_name_H-M   'C c'
_symmetry_Int_Tables_number      9
loop_
_symmetry_equiv_pos_site_id
_symmetry_equiv_pos_as_xyz
1 x,y,z
2 x,-y,1/2+z
3 1/2+x,1/2+y,z
4 1/2+x,1/2-y,1/2+z
_cell_length_a                   6.542
_cell_length_b                   13.934
_cell_length_c                   10.877
_cell_angle_alpha                90.00
_cell_angle_beta                 107.49
_cell_angle_gamma                90.00
_cell_volume                     945.668
loop_
_atom_site_label
_atom_site_type_symbol
_atom_site_fract_x
_atom_site_fract_y
_atom_site_fract_z
C1 C 0.50974 0.11589 0.51403
H2 H 0.44007 0.17808 0.45527
C3 C 0.58108 0.13410 0.65679
H4 H 0.57011 0.07191 0.71555
C5 C 0.83417 -0.00200 0.53727
H6 H 0.81756 -0.01962 0.63224
H7 H 0.86445 -0.06906 0.49215
H8 H 0.97572 0.04450 0.55277
C9 C 0.47161 0.23480 0.83127
H10 H 0.51437 0.30438 0.88033
H11 H 0.29745 0.22458 0.80980
H12 H 0.55259 0.17808 0.89882
C13 C 0.22582 0.01521 0.33955
H14 H 0.23932 0.07193 0.27200
H15 H 0.21951 -0.05438 0.29049
H16 H 0.07313 0.02545 0.36102
C17 C 0.88235 0.25195 0.63355
H18 H 0.95776 0.31900 0.67867
H19 H 1.00839 0.20543 0.61806
H20 H 0.77084 0.26957 0.53859
C21 C 0.76585 0.20246 0.71685
H22 H 0.86776 0.18217 0.81280
C23 C 0.53923 0.23005 0.70999
H24 H 0.46514 0.28365 0.63659
C25 C 0.63443 0.04751 0.45397
H26 H 0.64045 0.06779 0.35802
C27 C 0.41466 0.01994 0.46083
H28 H 0.41390 -0.03365 0.53423

#END
```