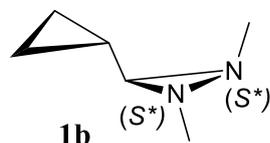


Synthesis of hybrid structures comprising diaziridine and cyclopropane rings in one molecule

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Experimental

General remarks. The IR spectra were recorded on a Bruker “Alpha” spectrometer in the range 400-4000 cm^{-1} (resolution 2 cm^{-1}) as a thin layer. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 (300.13 and 75.47 MHz, respectively) spectrometers. The chemical shifts of the signals of CDCl_3 residual proton (δ 7.27 ppm) and carbon (δ 77.0 ppm) were used as the internal standards. The spectra were measured at 30 °C. 2D-spectra were recorded on Bruker AV-600 (600 and 150 MHz for ^1H and ^{13}C accordingly) or on Bruker Avance III 400 (400.16 and 100.62 MHz, respectively) spectrometers and standard Bruker methods with Z-gradient broadband observe probe. Samples (25 mg) were dissolved in CDCl_3 (0.6 ml). Mass spectra were measured using a Finnigan MAT INCOS-50 instrument. High resolution mass spectra were recorded on a Bruker microTOF spectrometer with electrospray ionization (ESI). All measurements were performed in a positive (+MS) ion mode (interface capillary voltage: 4500 V) with scan range m/z : 50-3000 Analytical thin-layer chromatography (TLC) was carried out on Silufol UV-254 TLC silica gel 60 F₂₅₄ aluminum plates. The visualization of the TLC plates was accomplished in I_2 vapors. Value of pH was measured with handy waterproof Pen-type pH Meter PH-033. All reagents and solvents were purchased (Sigma Aldrich, Merck) and used without further purification.



(1*S**,2*S**)-3-Cyclopropyl-1,2-dimethyldiaziridine **1b**. Colorless liquid, yield 1.9 g (34%), bp 65-66 °C (15 Torr), highly volatile compound. IR (v/cm^{-1}): 756, 1025, 1047, 1267, 1445, 1460, 1648, 2776, 2864, 2931, 2957, 2970, 3007, 3065. ^1H NMR (400 MHz, CDCl_3) δ : 0.25–0.33 (m, 1H, *c*-Pr), 0.40–0.49 (m, 1H, *c*-Pr), 0.54–0.66 (m, 2H, *c*-Pr), 0.70–0.80 (m, 1H, *c*-Pr), 1.89 (d, 1H, N-CH_{ring}-N, 3J 7.1 Hz), 2.37 (s, 3H, Me), 2.49 (s, 3H, Me). ^{13}C NMR (100 MHz, CDCl_3) δ : 2.1, 3.6, 6.7, 39.7, 47.8, 69.9. MS (EI, 70 eV), m/z : 111 $[\text{M} - \text{H}]^+$, 97 $[\text{M} - \text{Me}]^+$, 82 $[\text{M} - 2\text{Me}]^+$, 70 $[\text{M} - \text{c-Pr}]^+$, 56 $[\text{M} - (\text{c-Pr}) - \text{Me}]^+$, 42 $[\text{c-Pr}]^+$. HRMS (ESI): m/z for $\text{C}_6\text{H}_{12}\text{N}_2$ (M+H)⁺: calcd 113.1073, found 113.1078.

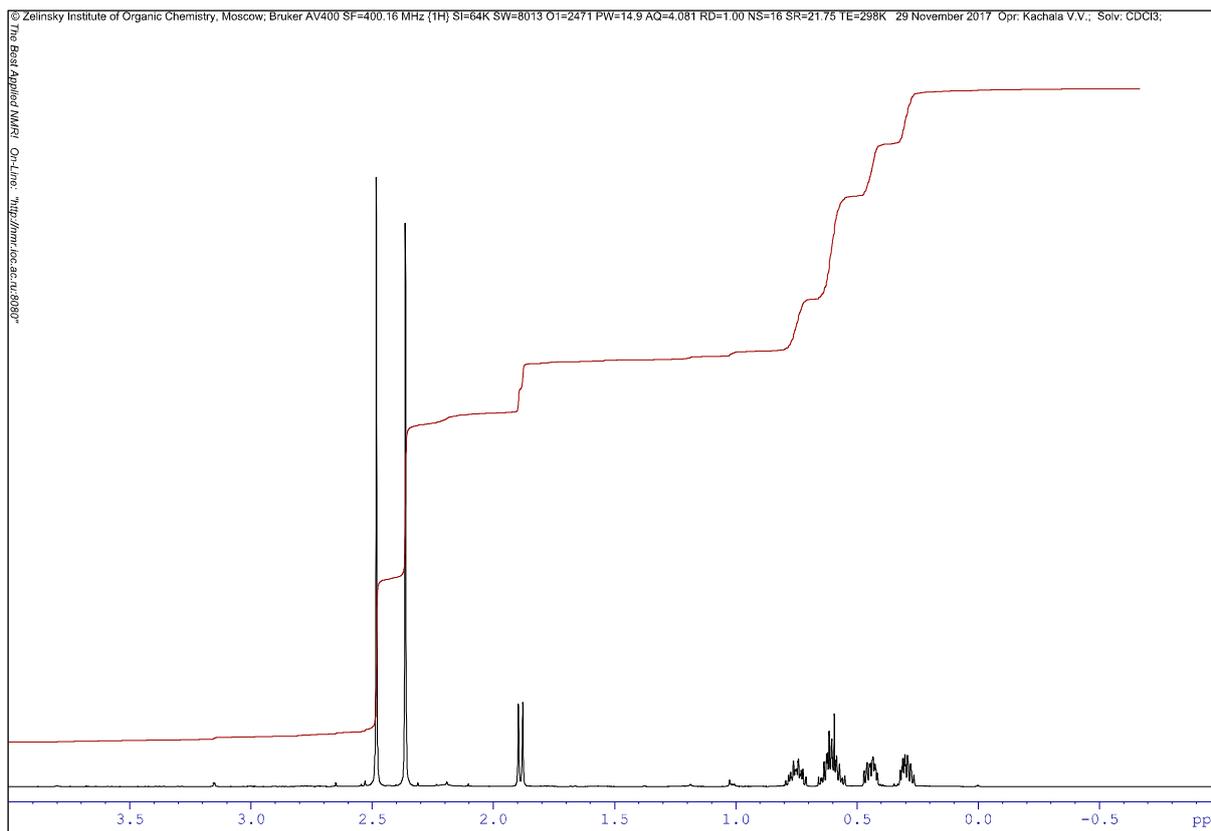


Figure S1. ^1H NMR spectrum of compound **1b** (CDCl_3).

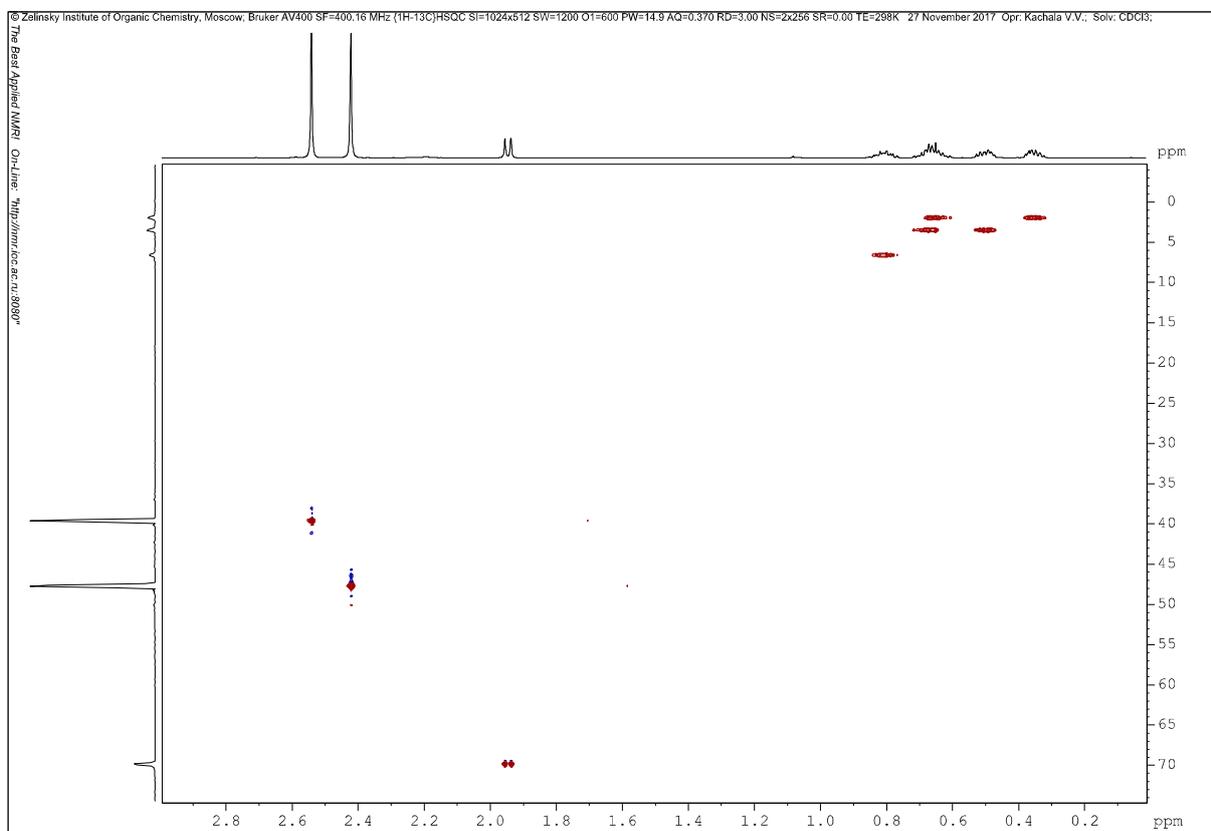
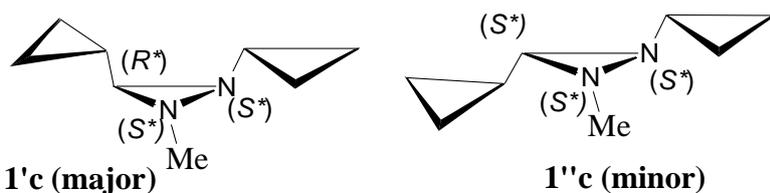


Figure S2. $\{^1\text{H}-^{13}\text{C}\}$ HSQC spectrum of compound **1b** (CDCl_3)



1,3-Dicyclopropyl-2-methyldiaziridine 1c. Colorless liquid, yield 0.91 g (13.1%), b.p. 69 °C (15 Torr), highly volatile compound. The diaziridine **1c** was formed as a mixture of two diastereomers in ~ 2.5:1 ratio (¹H NMR spectra). IR (ν/cm⁻¹): 503, 767, 815, 971, 1017, 1194, 1354, 1394, 1453, 1655, 2359, 2858, 2955, 3009, 3087. *Major diastereomer (1S*,2S*,3R*)-1,3-dicyclopropyl-2-methyldiaziridine 1'c.* ¹H NMR (300 MHz, CDCl₃) δ: 0.49–0.55 (m, 1H, *c*-Pr), 0.55–0.67 (m, 2H, *c*-Pr), 0.67–0.80 (m, 4H, *c*-Pr), 0.81–0.92 (m, 2H, *c*-Pr), 1.59–1.70 (m, 1H, N-CH (*c*-Pr)), 2.07 (d, 1H, N-HC_{ring}-N, ³J 6.9 Hz), 2.42 (s, 3H, Me-N). ¹³C NMR (75 MHz, CDCl₃) δ: 2.4, 3.8, 4.6, 5.1, 7.8, 33.1, 47.9, 70.2. *Minor diastereomer (1S*,2S*,3S*)-1,3-dicyclopropyl-2-methyldiaziridine 1''c.* ¹H NMR (300 MHz, CDCl₃) δ: 0.49–0.55 (m, 1H, *c*-Pr), 0.55–0.67 (m, 2H, *c*-Pr), 0.67–0.80 (m, 4H, *c*-Pr), 0.81–0.92 (m, 2H, *c*-Pr), 1.59–1.69 (m, 1H, N-CH (*c*-Pr)), 1.96 (d, 1H, N-HC_{ring}-N, ³J 6.9 Hz), 2.55 (s, 3H, Me-N). ¹³C NMR (75 MHz, CDCl₃) δ: 2.1, 3.5, 4.0, 4.4, 7.3, 39.9, 40.0, 68.3. MS (EI, 70 eV), *m/z*: 138 [M]⁺, 137 [M – H]⁺, 123 [M – Me]⁺, 97 [M – (*c*-Pr)]⁺, 96 [M – *c*-Pr]⁺, 84 [M – *c*-Pr, – Me]⁺, 83 [M – *c*-Pr, – Me]⁺, 55 [M – *c*-Pr, – *c*-Pr]⁺. HRMS (ESI): *m/z* for C₈H₁₄N₂ (M+H)⁺: calcd 139.1230, found 139.1228.

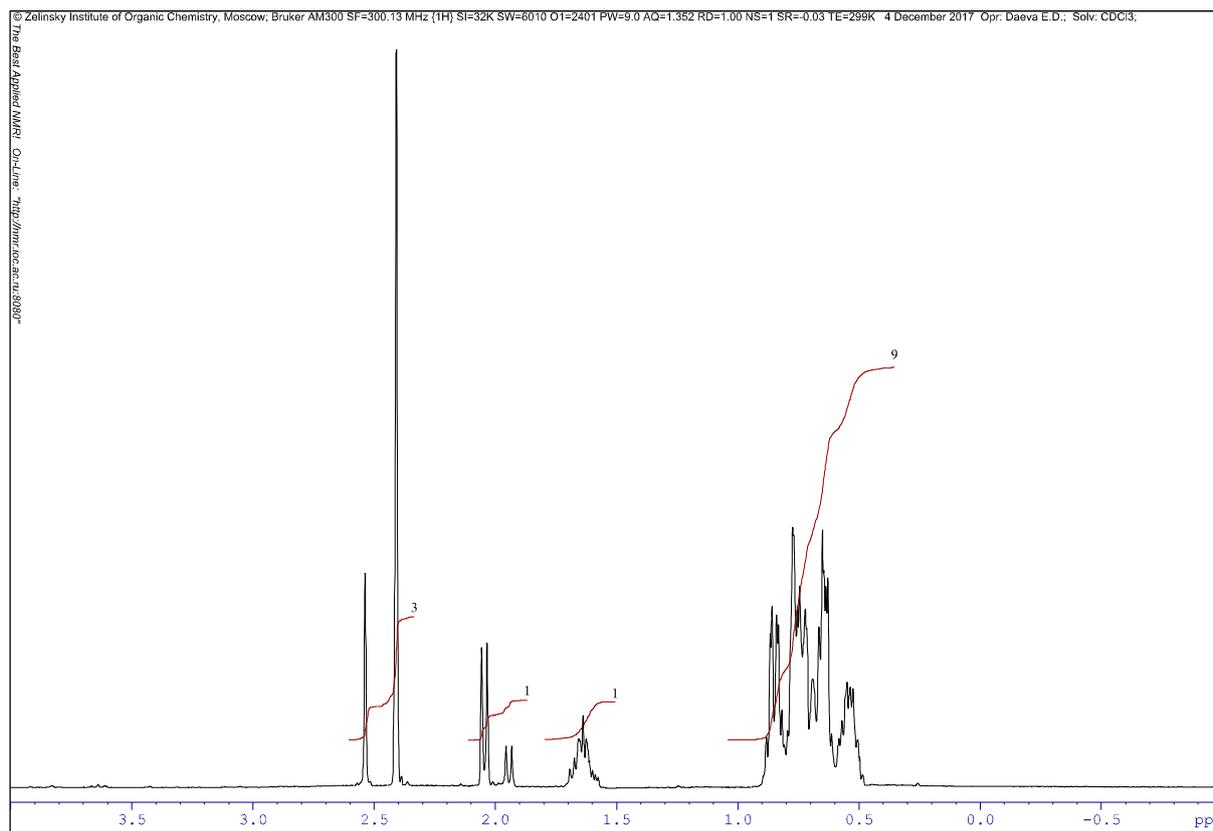


Figure S3. ¹H NMR spectrum of ~ 2.5:1 diastereomer mixture **1'c**+**1''c** (CDCl₃).

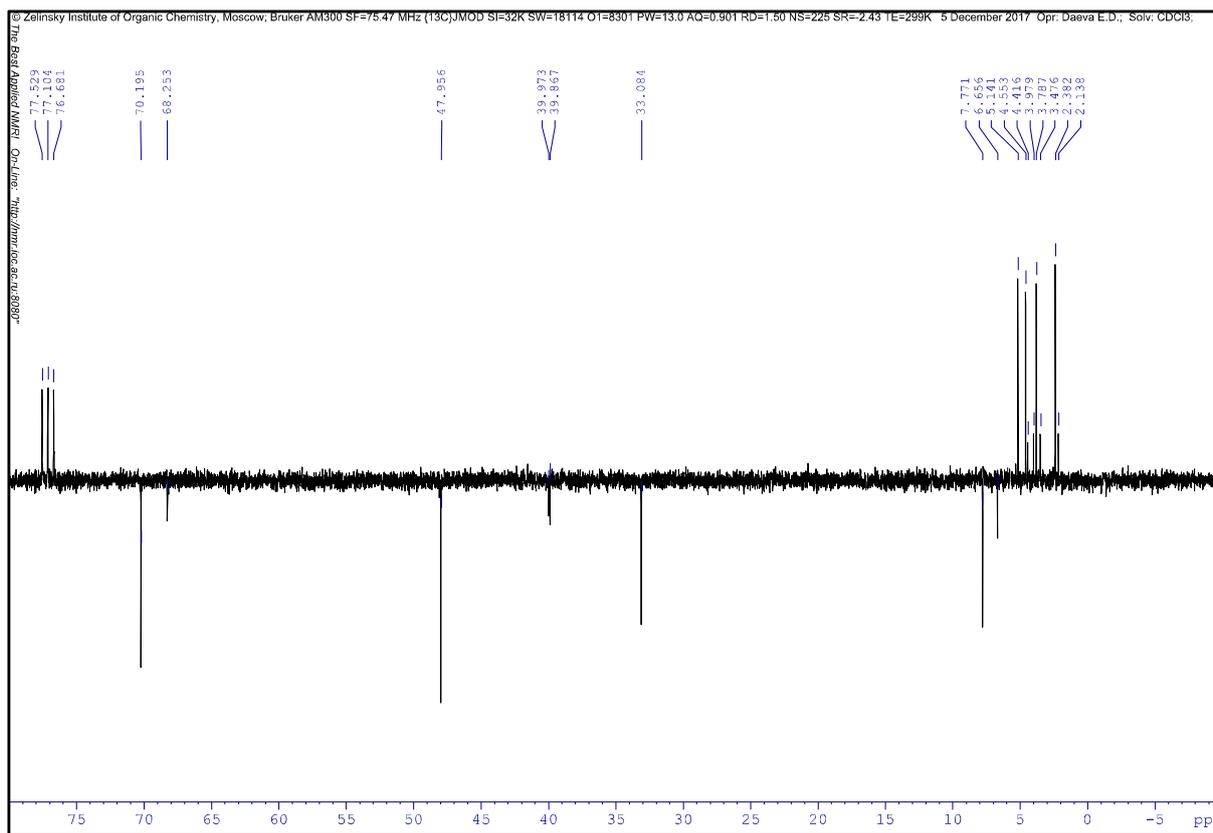


Figure S4. ^{13}C NMR JMOD spectrum of diastereomer mixture **1c+1''c** (CDCl_3).

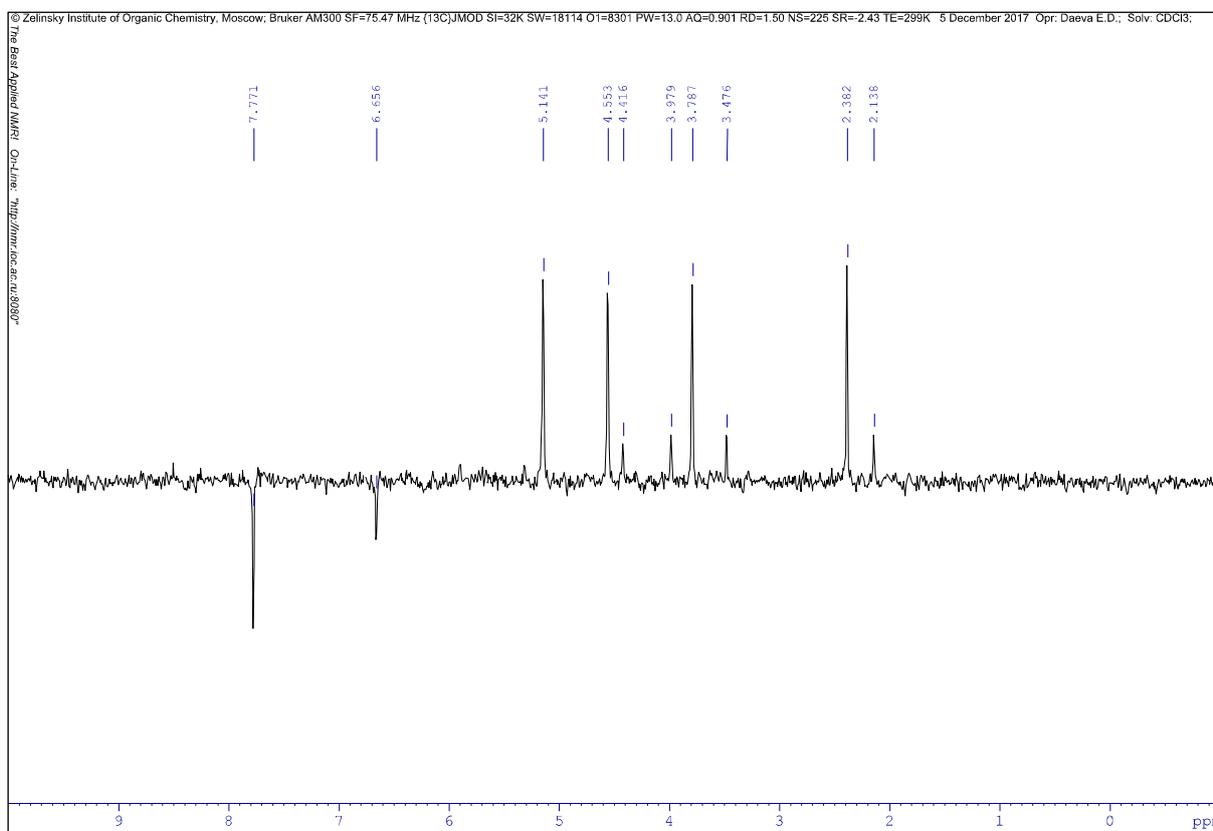
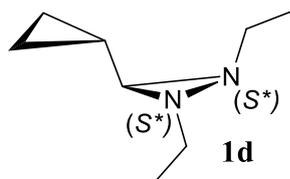


Figure S5. ^{13}C NMR JMOD spectrum (part) of diastereomer mixture **1c+1''c** (CDCl_3).



(1*S**,2*S**)-3-Cyclopropyl-1,2-diethylidiaziridine **1d**. Colorless liquid, yield 2.2 g (31%), bp 75-76 °C (15 Torr), highly volatile compound. IR (ν/cm^{-1}): 583, 677, 759, 825, 880, 951, 1024, 1115, 1259, 1276, 1345, 1376, 1432, 1665, 1752, 2871, 2936, 2972, 3005. ^1H NMR (300 MHz, CDCl_3) δ : 0.34–0.43 (m, 1H, *c*-Pr), 0.43–0.53 (m, 1H, *c*-Pr), 0.61–0.75 (m, 2H, *c*-Pr), 0.81–0.91 (m, 1H, *c*-Pr), 1.14 (t. Me, 3J 7.2 Hz), 1.21 (t. Me, 3J 7.2 Hz), 1.97 (d, 1H, N-CH_{ring}-N, 3J 7.4 Hz), 2.25–2.36 (dq, 1H, CH_aN, $^3J=7.2$, 2J –11.8 Hz), 2.46–2.57 (dq, 1H, CH_bN, 3J 7.2 Hz, 2J –11.8 Hz, ABX₃-спектр, $\Delta\nu$ 63.2 Hz), 2.59–2.67 (dq, 1H, CH_aN, 3J 7.2 Hz, 2J –12.2 Hz), 2.67–2.78 (dq, 1H, 3J 7.2 Hz, 2J –12.2 Hz, CH_bN, ABX₃-спектр, $\Delta\nu$ 30.0 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 2.5, 3.6, 6.9, 13.5, 14.0, 47.4, 55.5, 69.0. MS (EI, 70 eV), m/z : 139 [M – H]⁺, 125 [M – Me]⁺, 111 [M – Et]⁺, 98 [M – *c*-Pr]⁺, 85 [M – *c*-Pr – Me]⁺, 82 [M – 2Et]⁺, 69 [M – *c*-Pr, – Et]⁺, 68 [M – *c*-Pr, – 2Me]⁺, 42 *c*-Pr⁺, 41 [*c*-Pr – H]⁺. HRMS (ESI): m/z for C₈H₁₆N₂ (M+H)⁺: calcd 141.1386, found 141.1389.

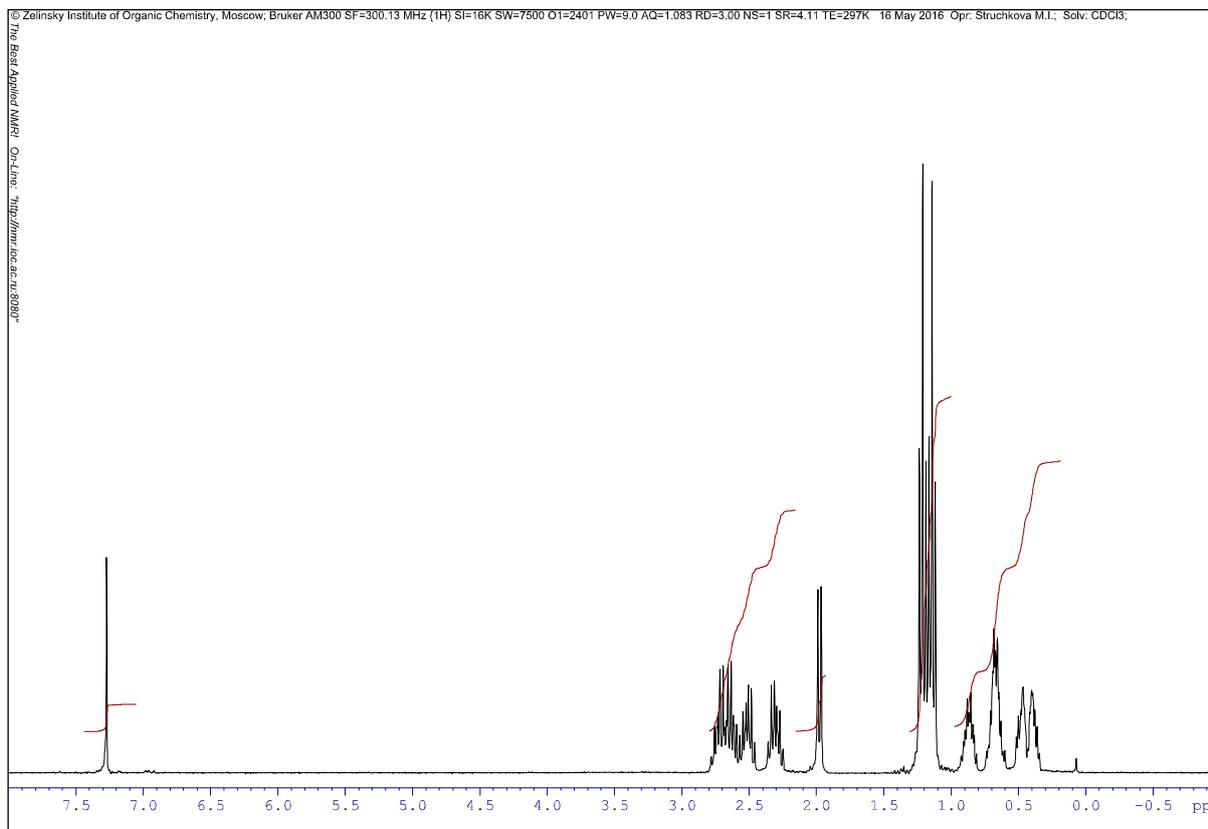


Figure S6. ^1H NMR spectrum of compound **1d** (CDCl_3).

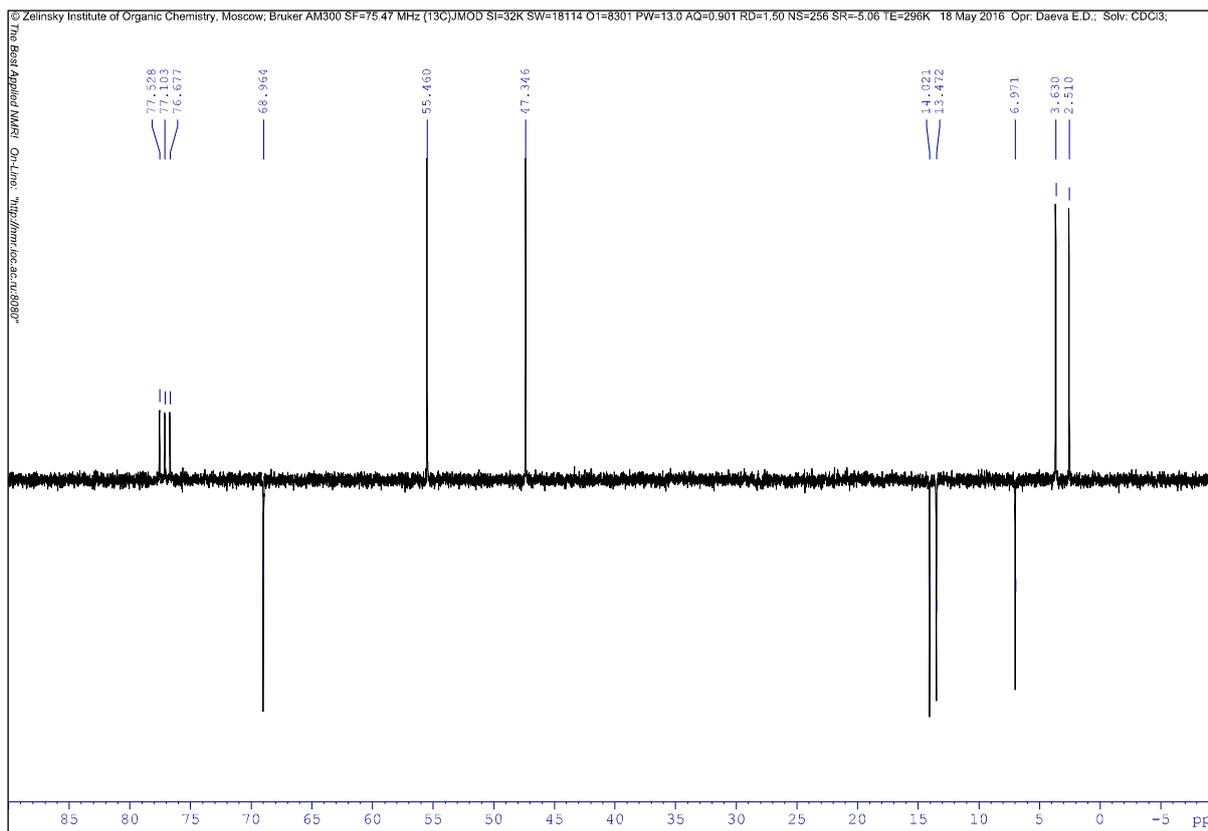
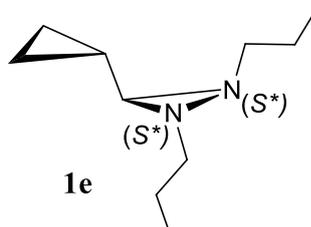


Figure S7. ^{13}C NMR JMOD spectrum of compound **1d** (CDCl_3).



(1S^,2S^*)*-3-Cyclopropyl-1,2-dipropyldiaziridine **1e**. Colorless liquid, yield 2.9 g (35%), bp 92-93 °C (15 Torr), highly volatile compound. IR (v/cm^{-1}): 755, 830, 904, 1024, 1084, 1266, 1379, 1431, 1465, 1642, 1779, 2854, 2875, 2935, 2960, 3006. ^1H NMR (300 MHz, CDCl_3) δ : 0.32–0.42 (m, 1H, *c*-Pr), 0.42–0.51 (m, 1H, *c*-Pr), 0.60–0.76 (m, 2H, *c*-Pr), 0.81–0.89 (m, 1H, *c*-Pr), 0.94 (t, 3H, Me, 3J 7.4 Hz), 0.98 (t, 3H, Me, 3J 7.5 Hz), 1.51–1.71 (m, 4H, 2 CH_2Me), 1.96 (d, 1H, N- CH_{ring} -N, 3J 7.4 Hz), 2.29–2.42 (m, 2H, 2(CH_αN)), 2.44–2.59 (dq, 1H, CH_bN , $^3J_{\text{AX}}$ 7.4 Hz), 2.59–2.71 (dq, 1H, CH_bN , $^3J_{\text{AX}}$ 7.6 Hz, ABX₃-спектр, $\Delta\nu$ 40.5 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 2.4, 3.6, 7.1, 11.8, 12.0, 21.9, 22.6, 55.0, 63.2, 69.1. MS (EI, 70 eV), m/z : 139 [$\text{M} - \text{Et}$]⁺, 126 [$\text{M} - c\text{-Pr}$]⁺, 125 [$\text{M} - \text{Pr}$]⁺, 111 [$\text{M} - c\text{-Pr} - \text{Me}$]⁺, 97 [$\text{M} - c\text{-Pr} - \text{Et}$]⁺, 83 [$\text{M} - c\text{-Pr} - \text{Pr}$]⁺, 82 [$\text{M} - 2\text{Pr}$]⁺, 68 [$\text{M} - c\text{-Pr} - \text{Pr} - \text{Me}$]⁺, 43 [Pr]⁺, 42 [$c\text{-Pr}$]⁺, 41 [$c\text{-Pr} - \text{H}$]⁺. HRMS (ESI): m/z for $\text{C}_{10}\text{H}_{20}\text{N}_2$ ($\text{M}+\text{H}$)⁺: calcd 169.1699, found 169.1702.

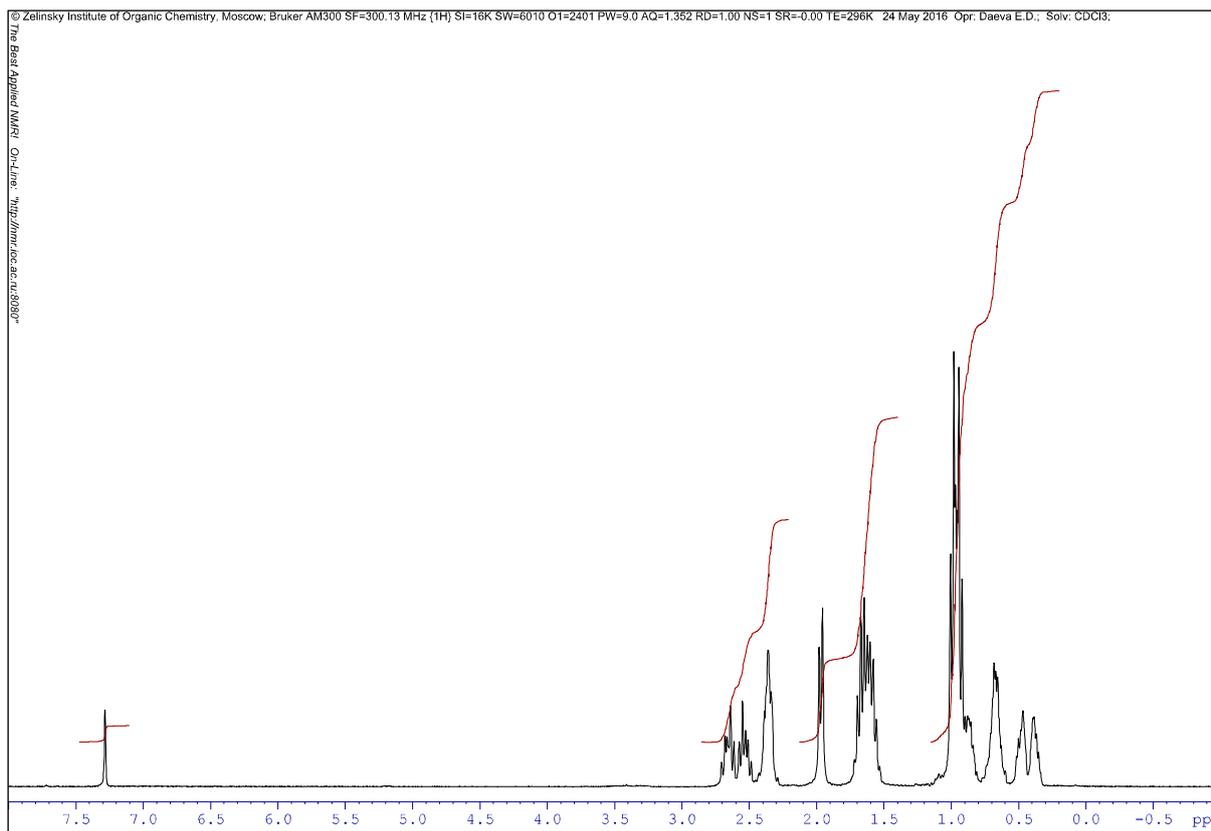


Figure S8. ^1H NMR spectrum of compound **1e** (CDCl_3).

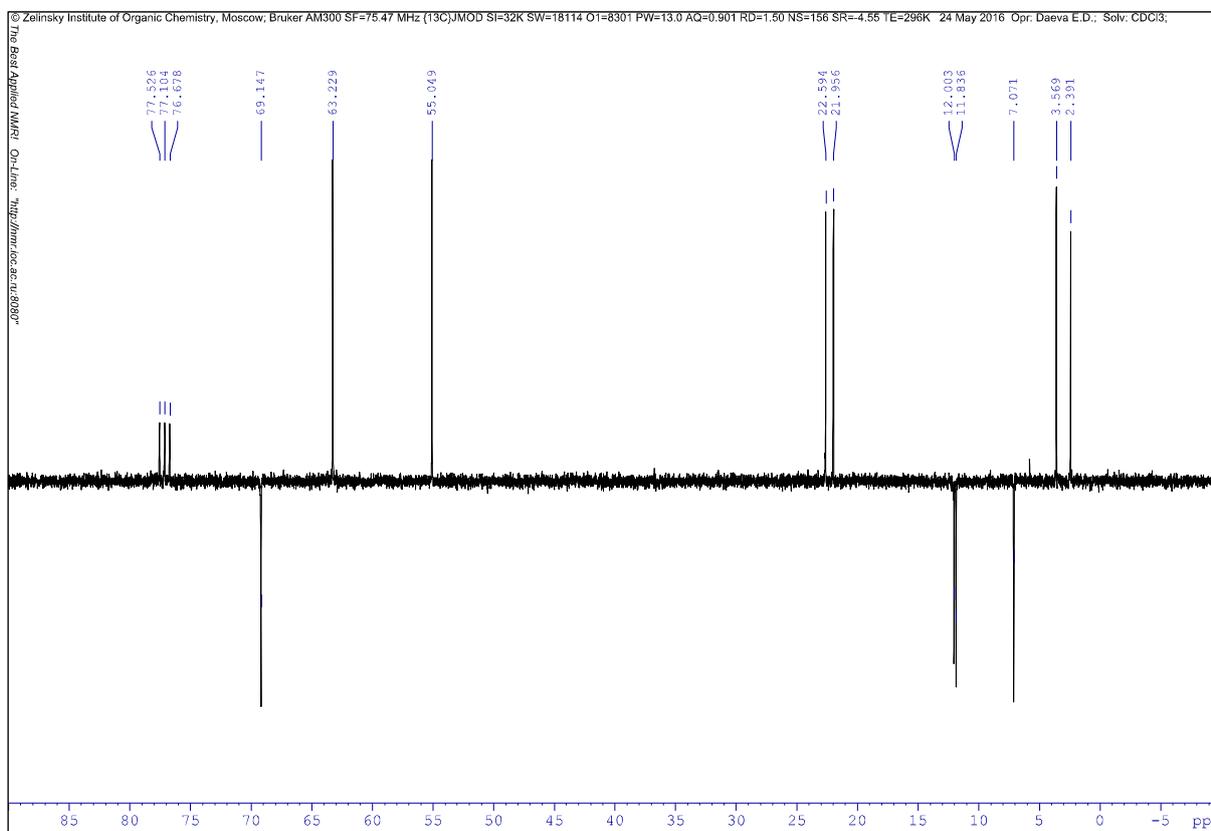
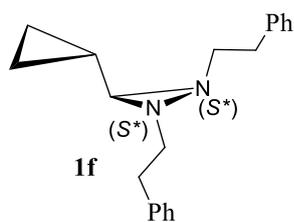


Figure S9. ^{13}C NMR JMOD spectrum of compound **1e** (CDCl_3).



(1*S**,2*S**)-(3-Cyclopropyl-1,2-diphenethyldiaziridine **1f**. Colorless oil, yield 6.0 g (41%). $R_f = 0.19$ (CHCl_3). IR (v/cm^{-1}): 486, 572, 699, 749, 827, 889, 1029, 1083, 1180, 1258, 1357, 1431, 1454, 1496, 1603, 2857, 2941, 3004, 3027, 3062, 3984. ^1H NMR (300 MHz, CDCl_3) δ : 0.29–0.39 (m, 2H, *c*-Pr), 0.58–0.68 (m, 2H, *c*-Pr), 0.79–0.90 (m, 1H, *c*-Pr), 2.04 (d, 1H, N- $\text{CH}_{\text{ring}}\text{-N}$, 3J 7.4 Hz), 2.60–2.80 (m, 2H, 2(CH_aN)), 2.83–2.87 (m, 2H, 2(CH_bN)). 2.87–3.05 (m, 4H, 2 CH_2Ph), 7.20–7.35 (m, 10H, 2Ph). ^{13}C NMR (75 MHz, CDCl_3) δ : 2.4, 3.7, 7.1, 35.3, 36.0, 54.9, 62.7, 69.3, 126.0, 128.4, 128.7, 128.8, 139.8, 140.1. MS (EI, 70 eV), m/z : 291 [$\text{M} - \text{H}$] $^+$, 201 [$\text{M} - \text{CH}_2\text{Ph}$] $^+$, 187 [$\text{M} - (\text{CH}_2)_2\text{Ph}$] $^+$, 146 [$\text{M} - (\text{CH}_2)_2\text{Ph} - (c\text{-Pr})$] $^+$, 105 [$(\text{CH}_2)_2\text{Ph}$] $^+$, 91 [CH_2Ph] $^+$, 77 [Ph] $^+$, 42 [$c\text{-Pr}$] $^+$, 41 [$c\text{-Pr} - \text{H}$] $^+$. 40 [$c\text{-Pr} - 2\text{H}$] $^+$. HRMS (ESI): m/z for $\text{C}_{20}\text{H}_{24}\text{N}_2$ ($\text{M}+\text{H}$) $^+$: calcd 293.2012, found 293.2018; m/z for $\text{C}_{20}\text{H}_{24}\text{N}_2$ [$\text{M}+\text{Na}$] $^+$: calcd 315.1832, found 315.1824.

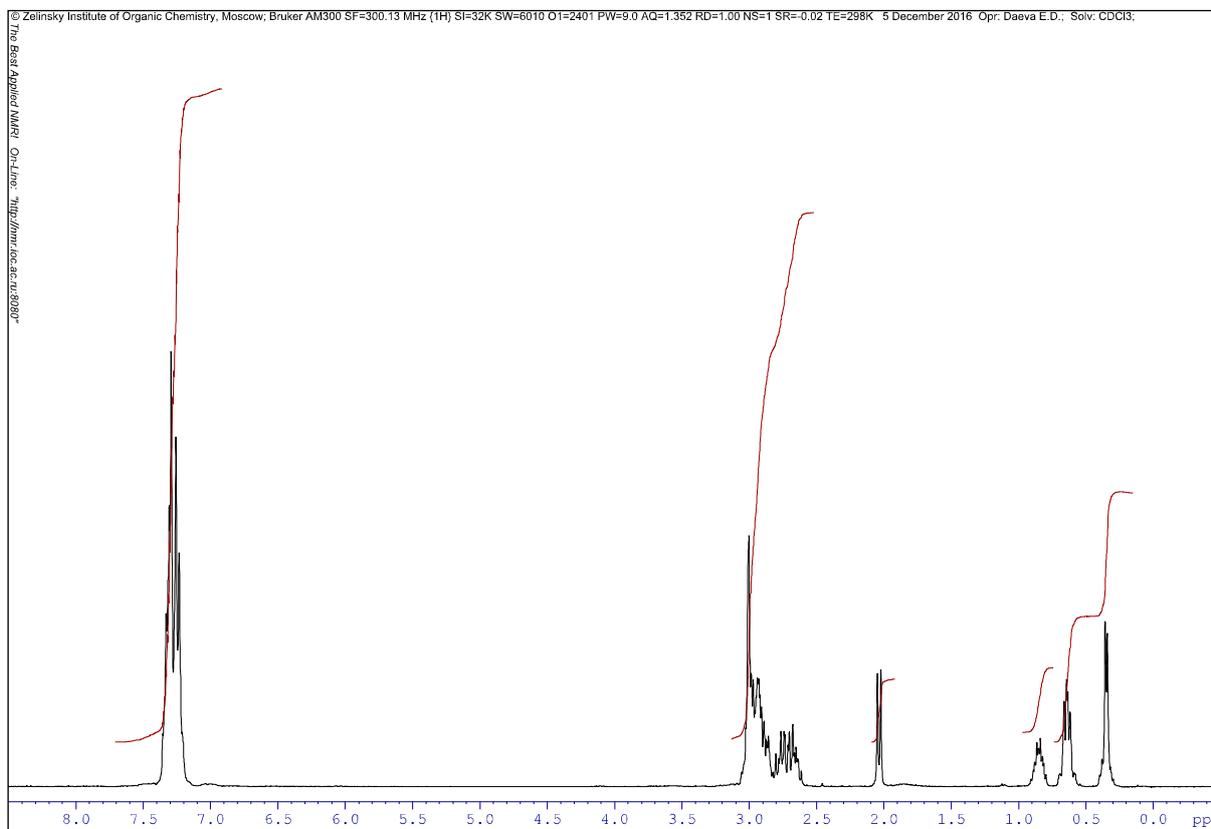


Figure S10. ^1H NMR spectrum of compound **1f** (CDCl_3).

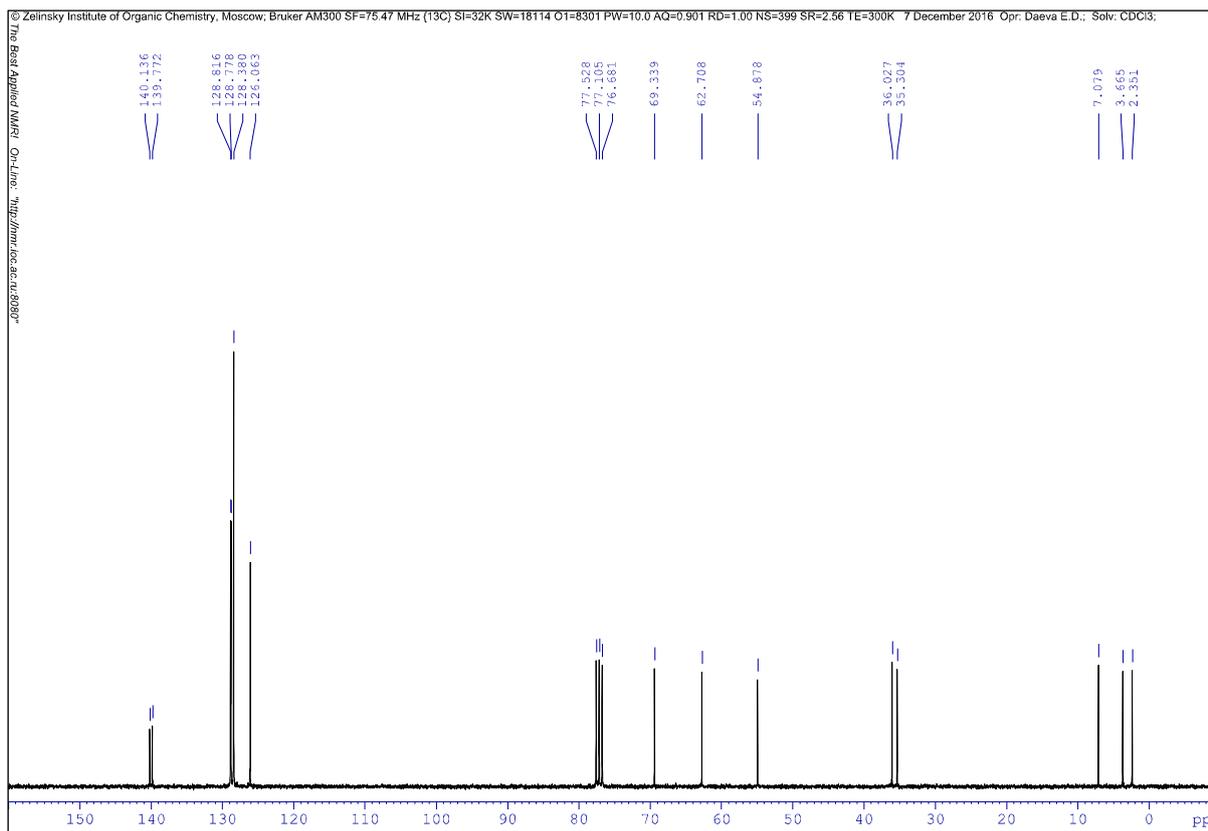
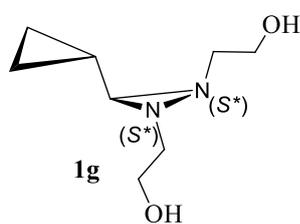


Figure S11. ^{13}C NMR spectrum of compound **1f** (CDCl_3)



(1S^,2S^*)*-(3-Cyclopropyl-1,2-di-(2-hydroxyethyl)diaziridine) **1g**.

Colorless oil, yield 2.6 g (30%), $R_f = 0.38$ ($\text{CHCl}_3:\text{MeOH} = 10:1$). IR (v/cm^{-1}): 601, 669, 687, 761, 830, 887, 853, 1063, 1236, 1265, 1353, 1430, 1661, 2876, 2942, 3006, 3087, 3355. ^1H NMR (300 MHz, CDCl_3) δ : 0.34–0.43 (m, 1H, *c*-Pr), 0.45–0.57 (m, 1H, *c*-Pr), 0.63–0.76 (m, 2H, *c*-Pr), 0.80–0.91 (m, 1H, *c*-Pr), 2.14 (d, 1H, $\text{N-HC}_{\text{ring-N}}$, 3J 7.2 Hz), 2.16–2.23 (dq, 1H, CH_αN , 3J 7.7 Hz), 2.63–2.74 (dq, 1H, CH_αN , 3J 7.8 Hz), 2.94–3.09 (m, 2H, $2\text{CH}_\beta\text{N}$, 3J 7.5 Hz), 3.79–3.99 (m, 4H, $2\text{CH}_2\text{OH}$), 4.00–4.13 (br s, 2H, 2OH). ^{13}C NMR (75 MHz, CDCl_3) δ : 2.2, 3.7, 7.1, 54.7, 61.8, 62.1, 62.4, 66.7. MS (EI, 70 eV), m/z : 141 [$\text{M} - \text{CH}_2\text{OH}$] $^+$, 127 [$\text{M} - (\text{CH}_2)_2\text{OH}$], 113 [$\text{M} - \text{N}(\text{CH}_2)_2\text{OH}$] $^+$, 100 [$\text{M} - \text{CH}_2\text{OH} - (\text{c-Pr}^-)$] $^+$, 82 [$\text{M} - 2(\text{CH}_2)_2\text{OH}$] $^+$, 68 [$\text{M} - \text{N}(\text{CH}_2)_2\text{OH} - (\text{CH}_2)_2\text{OH}$] $^+$, 55 [$\text{M} - \text{CH}_2\text{OH} - (\text{CH}_2)_2\text{OH} - (\text{c-Pr}^-)$] $^+$, 45 [$(\text{CH}_2)_2\text{OH}$] $^+$, 42 [*c*-Pr] $^+$, 41 [*c*-Pr - H] $^+$, 31 [CH_2OH] $^+$. HRMS (ESI): m/z for $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2$ ($\text{M}+\text{H}$) $^+$: calcd 173.1285, found 173.1280; m/z for $\text{C}_8\text{H}_{16}\text{N}_2\text{O}_2$ ($\text{M}+\text{Na}$) $^+$: calcd 195.1104, found 195.1101.

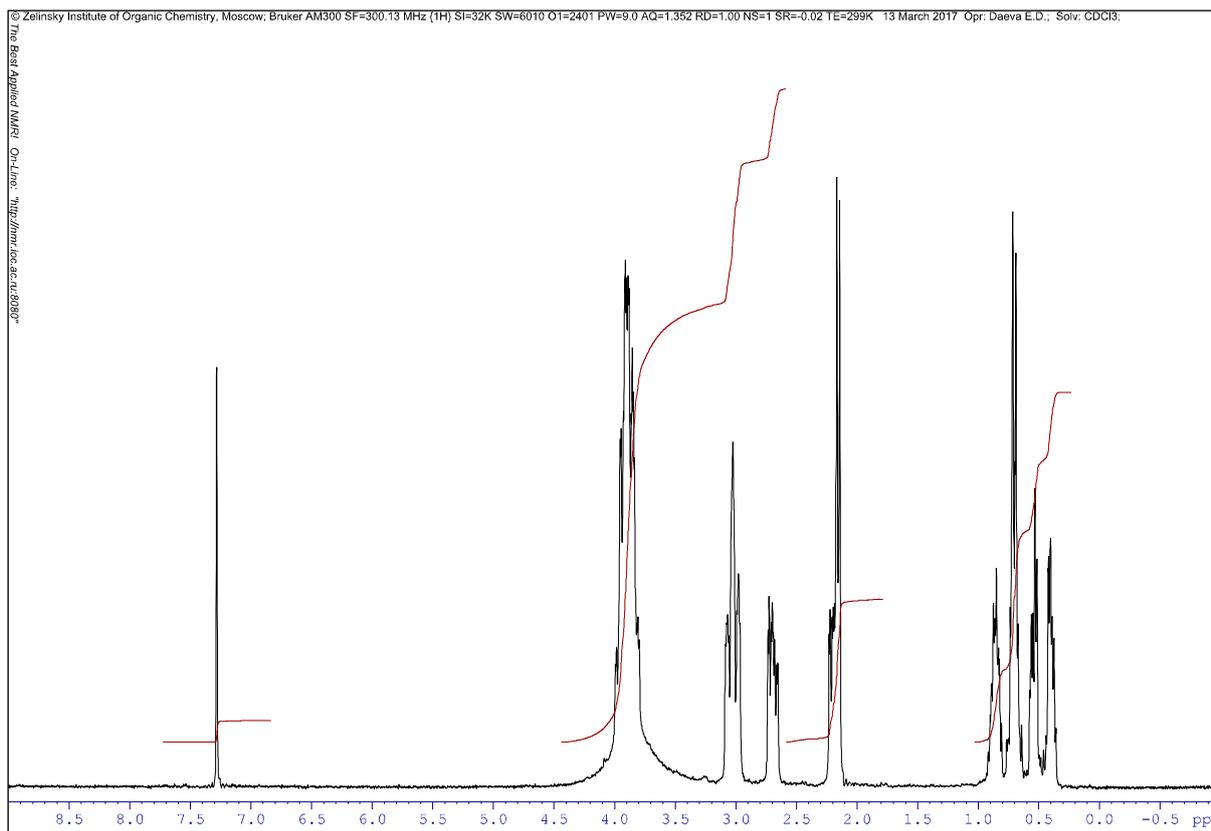


Figure S12. ^1H NMR spectrum of compound **1g** (CDCl_3).

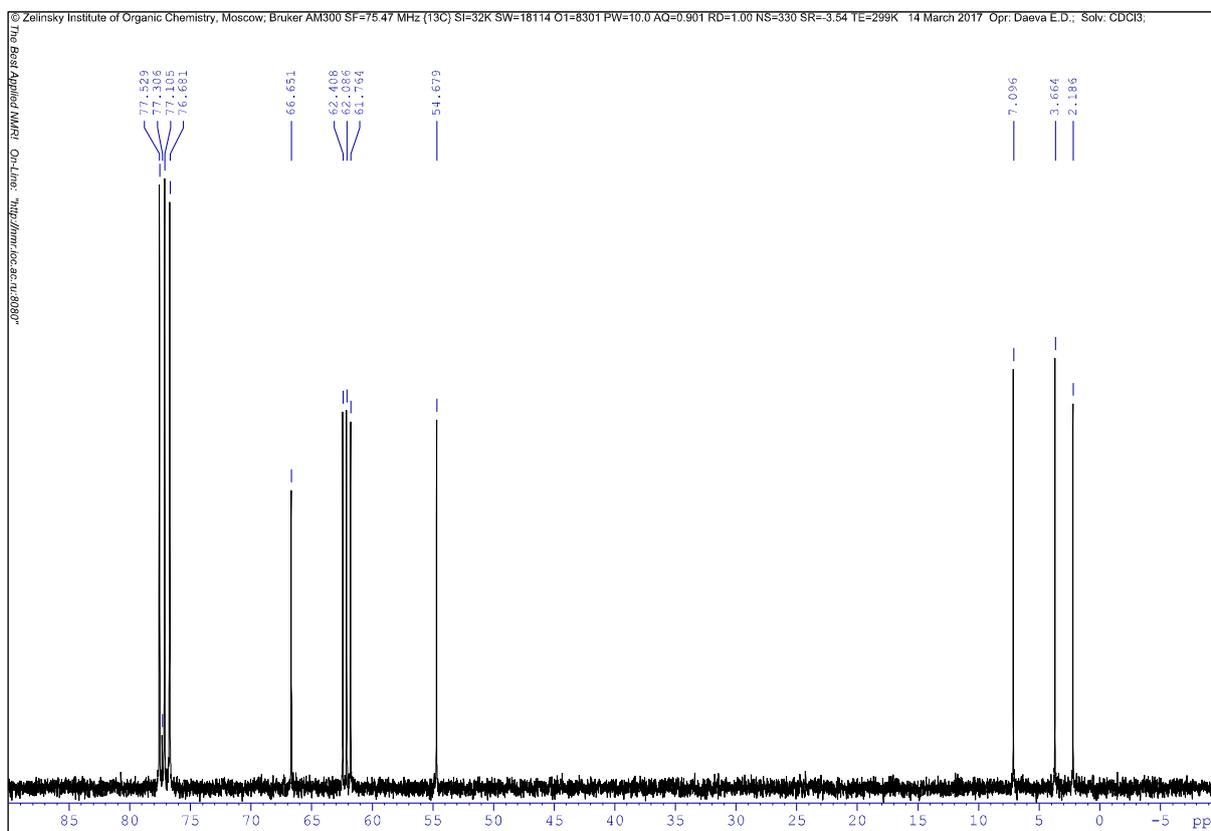
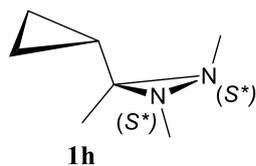


Figure S13. ^{13}C NMR spectrum of compound **1g** (CDCl_3)



(1*S**,2*S**)-3-Cyclopropyl-1,2,3-trimethyldiaziridine. **1h**. Colorless liquid, yield 1.1 g (17%), b.p. 73-74 °C (15 Torr), highly volatile compound. IR (ν/cm^{-1}): 526, 645, 756, 823, 877, 958, 1026, 1094, 1228, 1260, 1331, 1383, 1440, 1662, 1697, 2928, 2966, 3003, 3088, 3307. ^1H NMR (300 MHz, CDCl_3) δ : 0.18–0.28 (m, 1H, *c*-Pr), 0.45–0.54 (m, 1H, *c*-Pr), 0.55–0.65 (m, 1H, *c*-Pr), 0.68–0.76 (m, 1H, *c*-Pr), 0.86–0.95 (m, 1H, *c*-Pr), 1.23 (s, 3H, Me- C_{ring}), 2.40 (s, 3H, Me-N), 2.59 (s, 3H, Me-N). ^{13}C NMR (75 MHz, CDCl_3) δ : 1.7, 3.4, 13.3, 16.7, 39.3, 40.2, 63.9. MS (EI, 70 eV), m/z : 127 $[\text{M} + \text{H}]^+$, 125 $[\text{M} - \text{H}]^+$, 111 $[\text{M} - \text{Me}]^+$, 85 $[\text{M} - (\textit{c}\text{-Pr})]^+$, 69 $[\text{M} - \text{Me} - \textit{c}\text{-Pr}]^+$, 42 $[\textit{c}\text{-Pr}]^+$. HRMS (ESI): m/z for $\text{C}_7\text{H}_{14}\text{N}_2$ (M+H) $^+$: calcd 127.1230, found 127,1226.

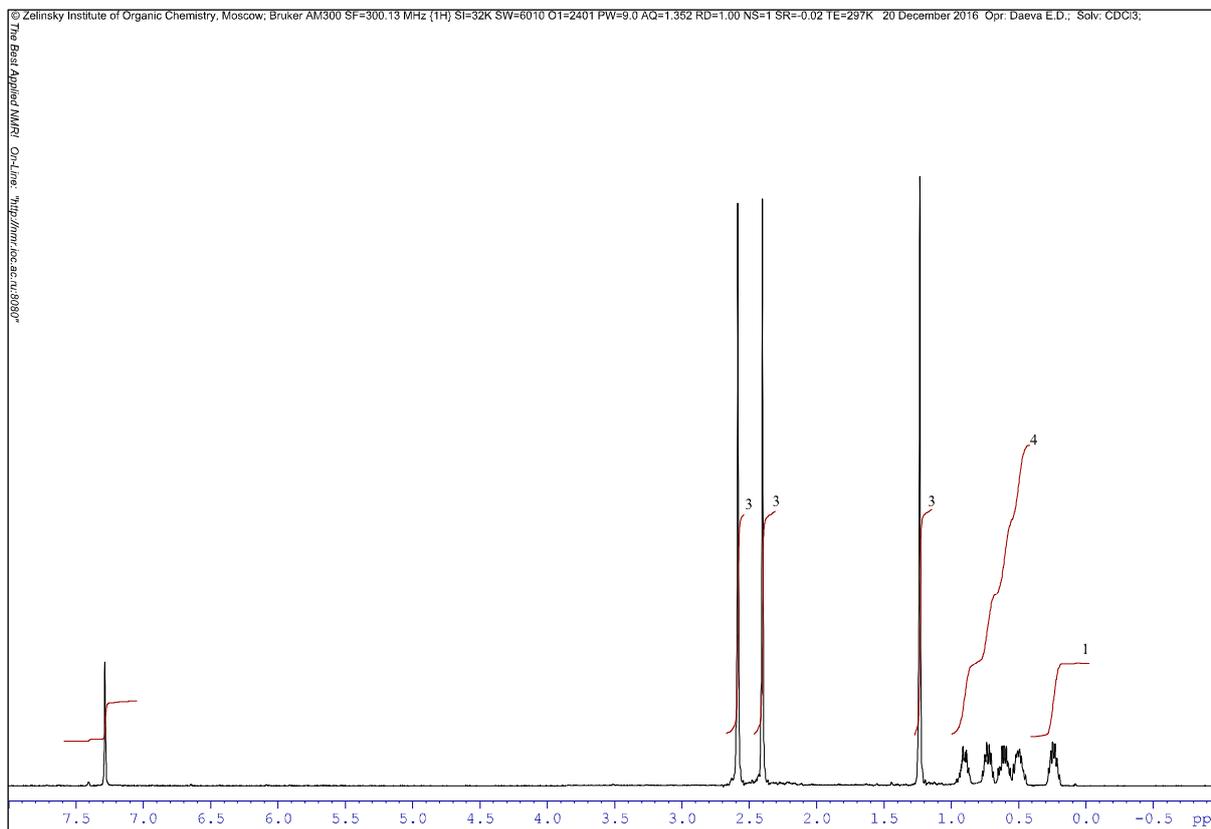


Figure S14. ^1H NMR spectrum of compound **1h** (CDCl_3).

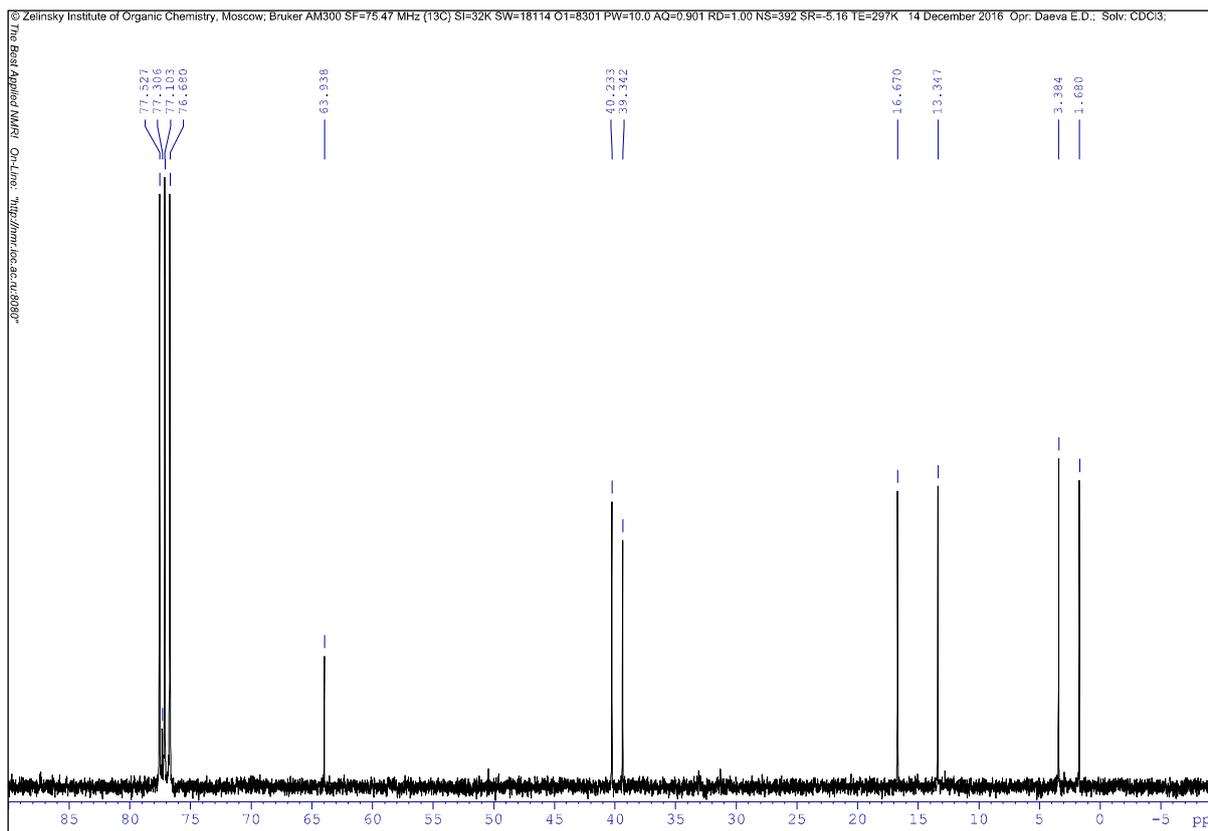
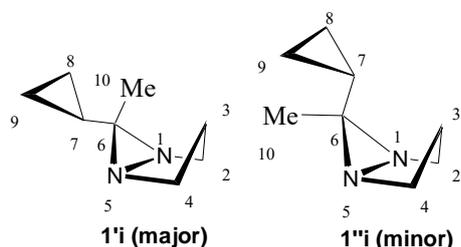


Figure S15. ^{13}C NMR spectrum of compound **1h** (CDCl_3)



6-Cyclopropyl-6-methyl-1,5-diazabicyclo[3.1.0]hexane

1i. Colorless liquid, yield 2.9 g (42%), b.p. 58–59 °C (1 Torr). The diaziridine **1i** was formed as a mixture of two structural isomers in ~ 2.5:1 ratio (NMR spectra). IR (v/cm^{-1}): 462, 527, 586, 621, 752, 774, 825, 866, 897, 911, 955, 978, 1022, 1051, 1096, 1111, 1173, 1240, 1294, 1347, 1385, 1432, 1461, 1482, 1572, 1655, 1695, 2887, 2938, 2869, 3005. *Major isomer 1'i:* ^1H NMR (600 MHz, CDCl_3) δ : 0.31–0.33 (m, 4H, C(8) H_2 , C(9) H_2), 0.98–1.02 (m, 1H, C(7)H), 1.18 (s, 3H C(10) H_3), 1.89–1.91 (m, 1H, C(3) H_a), 2.17–2.19 (m, 1H, C(3) H_e , 2J –9.3 Hz), 2.73–2.78 (m, 2H, C(2) H_e , C(4) H_e), 3.15–3.26 (m 2H, C(2) H_a , C(4) H_a , 2J –12.0 Hz, $^3J_{2a-3e}$ 6.6 Hz, $^3J_{2e-3a}$ 8.0, Hz, $^3J_{2e-3e}$ 5.1 Hz); ^{13}C NMR (75 MHz, CDCl_3) δ : 1.1, 12.6, 18.7, 32.9, 48.1, 62.7. *minor isomer 1''i:* ^1H NMR (600 MHz, CDCl_3) δ : 0.31–0.33 (m, 1H, C(7)H), 0.51–0.52 (m, 2H, C(8) H_e , C(9) H_e), 0.61–0.62 (m, 2H, C(8) H_a , C(9) H_a), 0.88 (c, 3H, C(10) H_3), 1.97–2.02 (m, 1H, C(3) H_e), 2.24–2.28 (m, 1H, C(3) H_a), 3.07–3.11 (m, 2H, C(2) H_e , C(4) H_e), 3.18–3.27 (m 2H, C(2) H_a , C(4) H_a); ^{13}C NMR (75 MHz, CDCl_3) δ : 1.9, 6.4, 21.8, 33.3, 47.5, 63.4 MS (EI, 70 eV), m/z : 138 [M^+], 123 [$\text{M} - \text{Me}^+$], 97 [$\text{M} - (c\text{-Pr})^+$], 70 [$\text{M} - (c\text{-Pr}, -\text{C-Me})^+$], 69 [$\text{M} - c\text{-Pr}, - (\text{C-Me})^+$], 41 [$c\text{-Pr} - \text{H}^+$]. HRMS (ESI): m/z for $\text{C}_8\text{H}_{14}\text{N}_2$ ($\text{M}+\text{H}^+$): calcd 139.1230, found 139.1231.

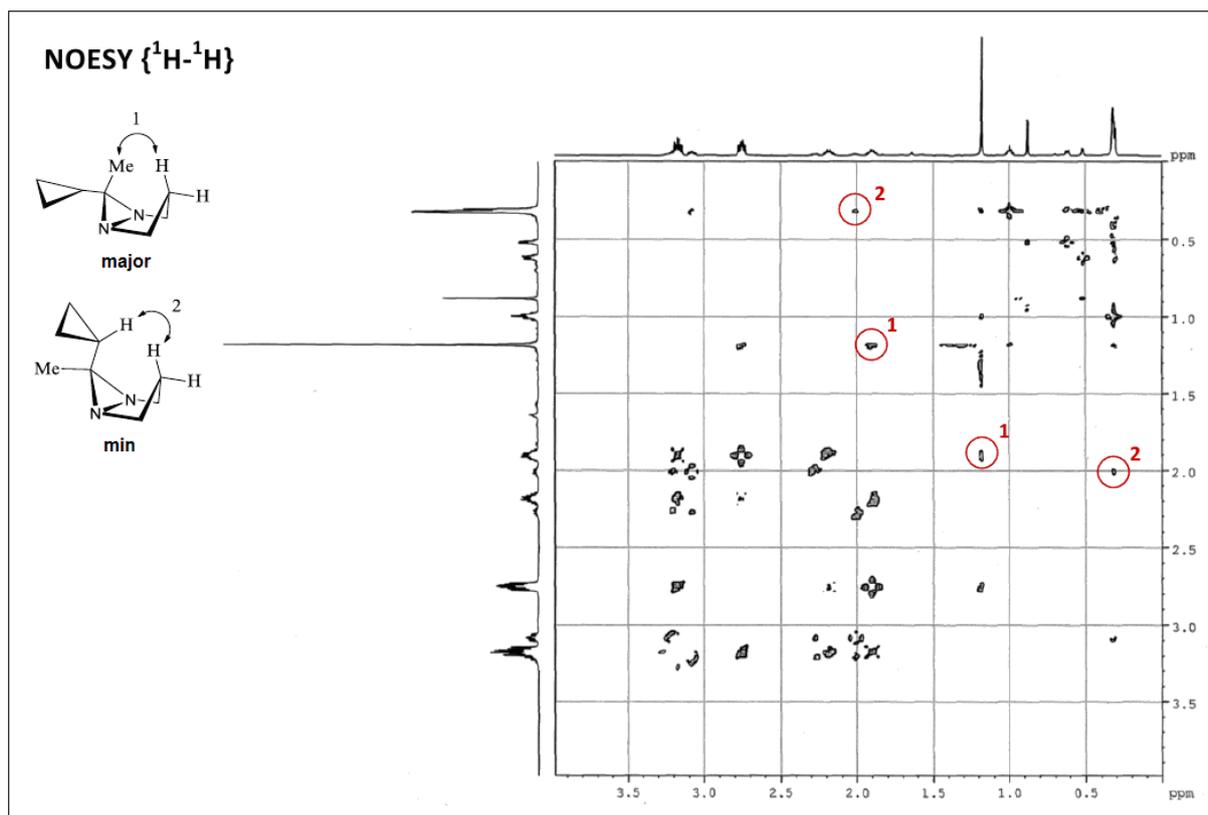


Figure S16. $\{^1\text{H}-^1\text{H}\}$ gNOESY spectrum of compound **1i** (CDCl_3).

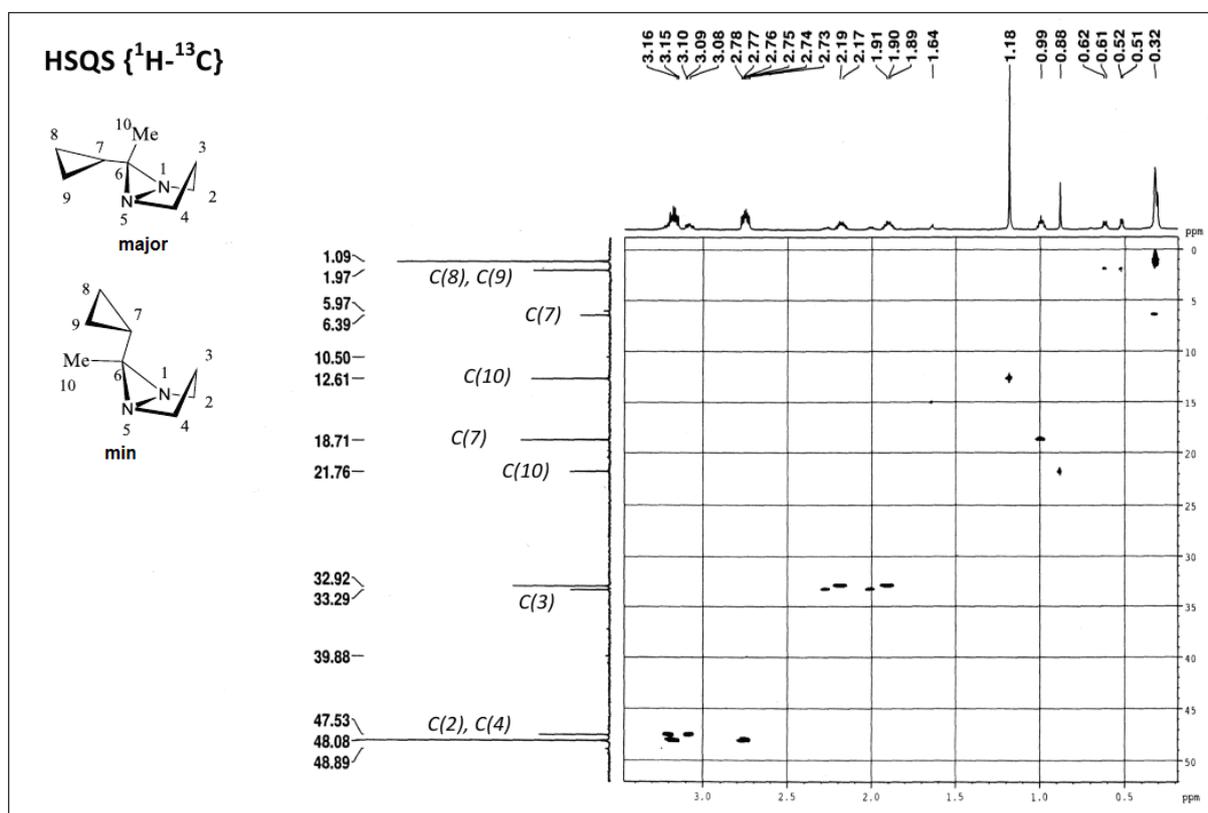
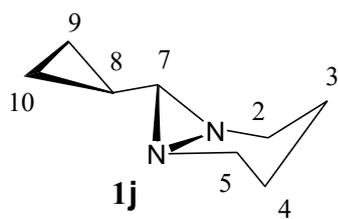


Figure S17. $\{^1\text{H}-^{13}\text{C}\}$ HSQC spectrum of compound **1i** (CDCl_3)



7-Cyclopropyl-1,6-diaza-bicyclo[4.1.0]heptane **1j**.

Colorless liquid, yield 4.1g (59%), bp 58-59 °C (1 Torr). IR (ν/cm^{-1}): 466, 632, 751, 835, 928, 1021, 1054, 1097, 1259, 1345, 1413, 1457, 1486, 1664, 2864, 2939, 3005, 3083. ^1H NMR (300 MHz, CDCl_3) δ : 0.31–0.38 (m, 2H, C(9) H_e , C(10) H_e 3J 6.6 Hz), 0.41–0.52 (m, 2H, C(9) H_a , C(10) H_a , 3J 6.3 Hz), 0.81–0.98 (m, 1H, C(8)H), 1.50–1.65 (m, 2H, C(3) H_e , C(4) H_e), 1.65–1.80 (m, 2H, C(3) H_a , C(4) H_a), 2.51 (d, 1H, C(7)H, 3J 4.8 Hz), 2.58–2.72 (m 2H, C(2) H_e , C(5) H_e), 3.30–3.43 (m 2H, C(2) H_a , C(5) H_a). ^{13}C NMR (75 MHz, CDCl_3) δ : 1.4, 11.8, 17.2, 46.9, 71.1. MS (EI, 70 eV), m/z : 139 $[\text{M} + \text{H}]^+$, 138 $[\text{M}]^+$, 137 $[\text{M} - \text{H}]^+$, 97 $[\text{M} - (c\text{-Pr})]^+$, 96 $[\text{M} - c\text{-Pr}]^+$, 95 $[\text{M} - c\text{-Pr} - \text{H}]^+$, 82 $[\text{M} - c\text{-Pr}, - \text{CH}_2]^+$, 68 $[\text{M} - c\text{-Pr}, - (\text{CH}_2)_2]^+$, 42 $[c\text{-Pr}]^+$, 41 $[c\text{-Pr} - \text{H}]^+$, 28 $[\text{N}_2]^+$. HRMS (ESI): m/z for $\text{C}_8\text{H}_{14}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: calcd 139.1230, found 139.1233.

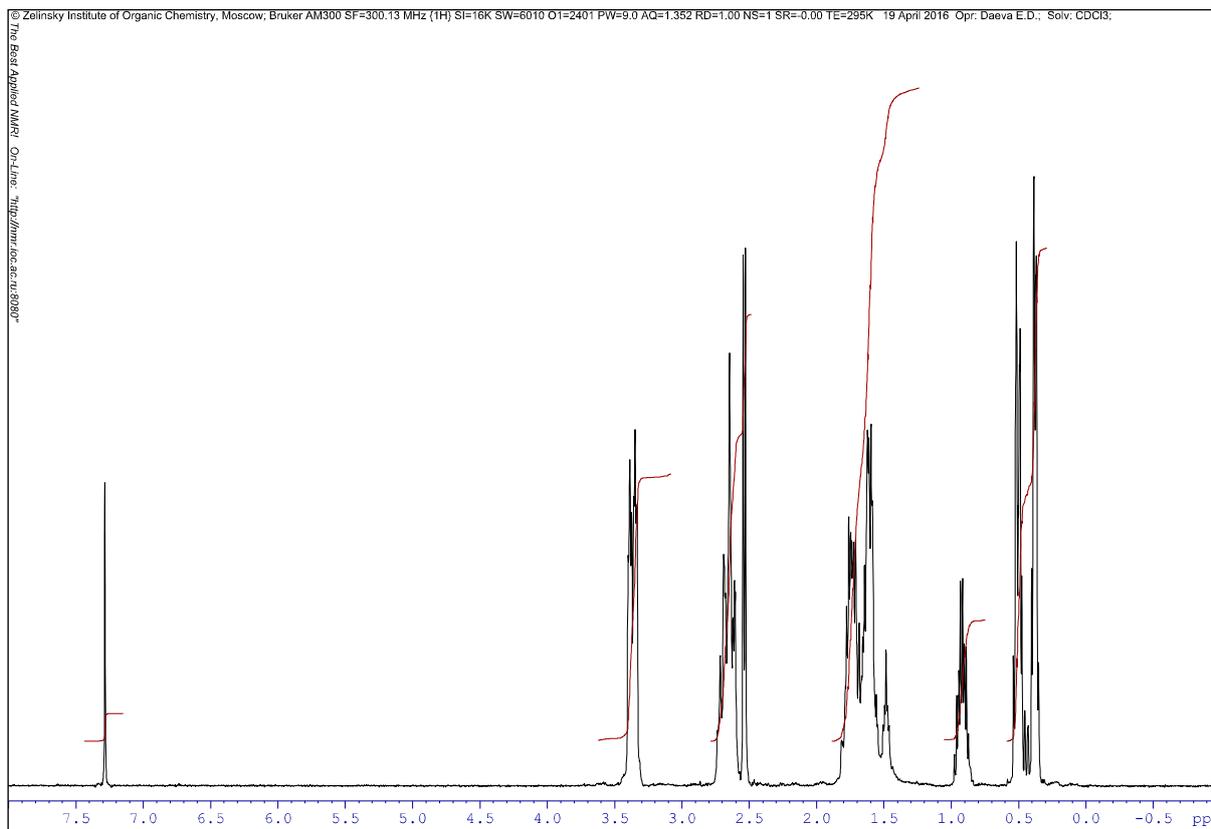


Figure S18. ^1H NMR spectrum of compound **1j** (CDCl_3).

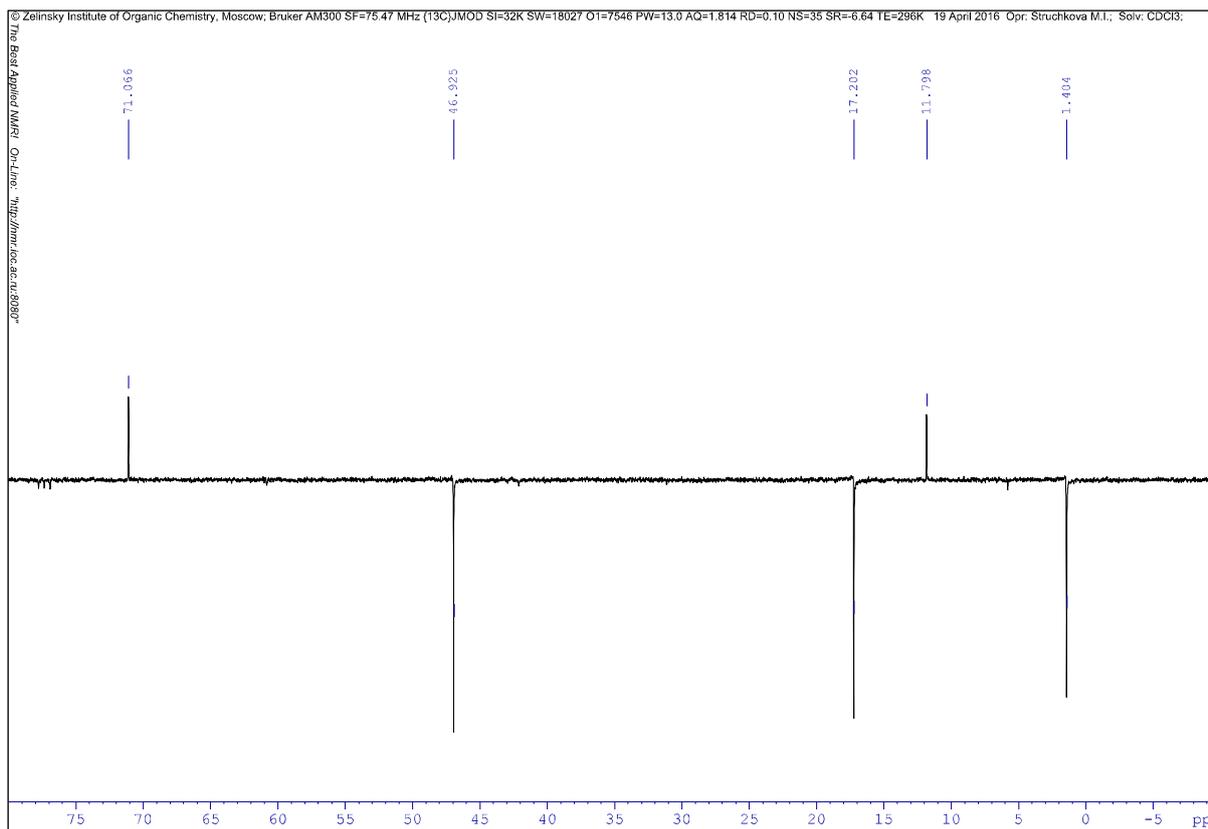


Figure S19. ^{13}C NMR JMOD spectrum of compound **1j** (CDCl_3)

1'k (major) **1''k (minor)** *3-Cyclopropyl-1-methyl-2-phenethyldiaziridine*

1k. Colorless liquid, yield 3.2 g (31%), bp 98–99 °C (1 Torr). The mixture of two diastereomers in ~ 1.7:1 ratio (TLC and ^1H NMR spectra). IR (v/cm^{-1}): 496, 572, 699, 750, 829, 876, 1026, 1082, 1195, 1266, 1359, 1396, 1440, 1454, 1497, 1604, 2859, 2929, 3006, 3027, 3064, 3084. *Major diastereomer: (1S*,2S*,3R*)-3-cyclopropyl-1-methyl-2-phenethyldiaziridine 1'k.* $R_f = 0.37$ ($\text{CHCl}_3:\text{MeOH}=30:1$). ^1H NMR (300 MHz, CDCl_3) δ : 0.29–0.39 (m, 2H, *c*-Pr), 0.60–0.70 (m, 2H, *c*-Pr), 0.75–0.88 (m, 1H, *c*-Pr.), 1.96 (d, 1H, $\text{N-HC}_{\text{ring-N}}$, $^3J = 7.3$ Hz), 2.57 (s, 3H, Me-N), 2.60–2.71 (m, 2H, CH_2N), 2.79–3.04 (m, 2H, CH_2Ph), 7.19–7.31 (m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 2.1, 3.5, 6.8, 35.3, 40.1, 62.6, 69.1, 126.1, 128.4, 128.9, 139.9; *minor diastereomer: (1S*,2S*,3S*)-3-cyclopropyl-1-methyl-2-phenethyldiaziridine 1''k:* $R_f = 0.49$ ($\text{CHCl}_3:\text{MeOH}=30:1$), ^1H NMR (300 MHz, CDCl_3) δ , м.д. J/Hz : 0.29–0.39 (m, 1H, *c*-Pr), 0.47–0.53 (m, 1H, *c*-Pr), 0.60–0.70 (m, 2H, *c*-Pr), 0.75–0.88 (m, 1H, *c*-Pr), 2.02 (d, 1H, $\text{N-HC}_{\text{ring-N}}$, $^3J = 7.3$), 2.45 (s, 3H, Me-N), 2.60–2.71 (m, 1H, CH_aN), 2.79–2.89 (m, 1H, CH_bN), 2.87–3.01 (m, 2H, CH_2Ph), 7.15–7.26 (m, 5H, Ph); ^{13}C NMR (75 MHz, CDCl_3) δ : 2.3, 3.8, 7.0, 36.2, 48.2, 54.9, 70.2, 126.3, 128.4, 128.9, 140.3.; MS (EI, 70 eV), m/z : 202 $[\text{M}]^+$, 201 $[\text{M} - \text{H}]^+$, 161 $[\text{M} - (\text{c-Pr})]^+$, 111 $[\text{M} - \text{CH}_2\text{Ph}]^+$, 105 $[(\text{CH}_2)_2\text{Ph}]^+$, 97 $[\text{M} - (\text{CH}_2)_2\text{Ph}]^+$, 91 $[\text{CH}_2\text{Ph}]^+$, 77 $[\text{Ph}]^+$, 69 $[\text{M} - (\text{CH}_2)_2\text{Ph} - \text{c-Pr}]^+$, 42 $[\text{c-Pr}]^+$, 41 $[\text{c-Pr} - \text{H}]^+$. HRMS (ESI): m/z for $\text{C}_{13}\text{H}_{18}\text{N}_2$ ($\text{M} + \text{H}$) $^+$: calcd 203.1543, found 203.1543.

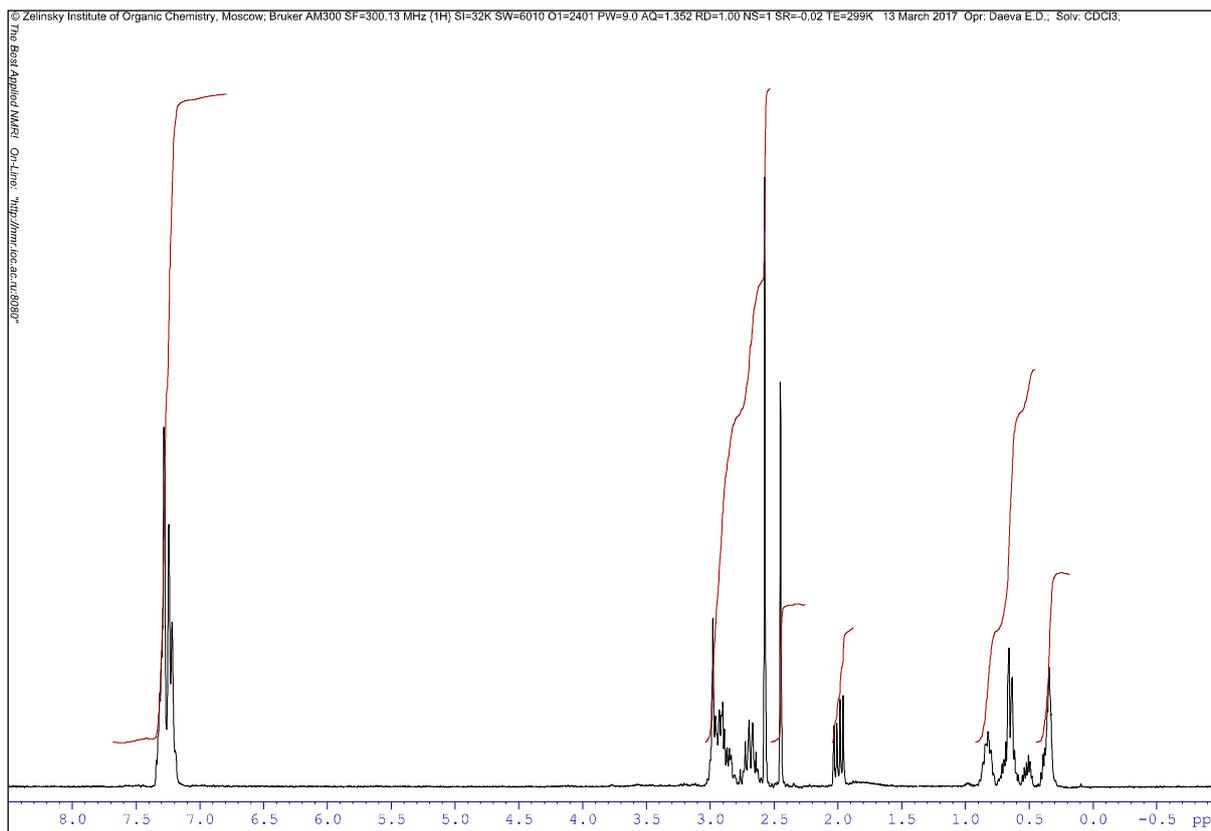


Figure S20. ^1H NMR spectrum of $\sim 1.7:1$ diastereomers $1'\mathbf{k}+1''\mathbf{k}$ (CDCl_3).

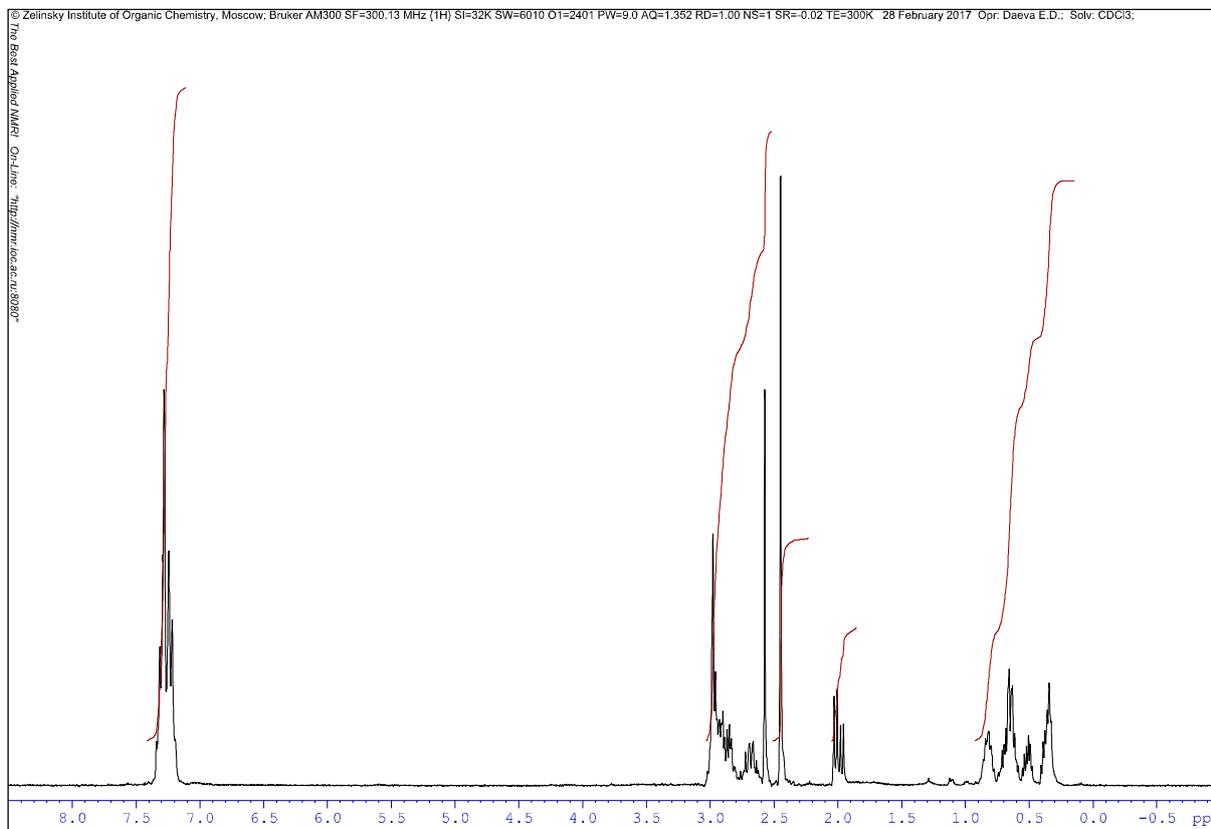


Figure S21. ^1H NMR spectrum of diastereomers $1'\mathbf{k}+1''\mathbf{k}$ (CDCl_3), enriched with $1''\mathbf{k}$.

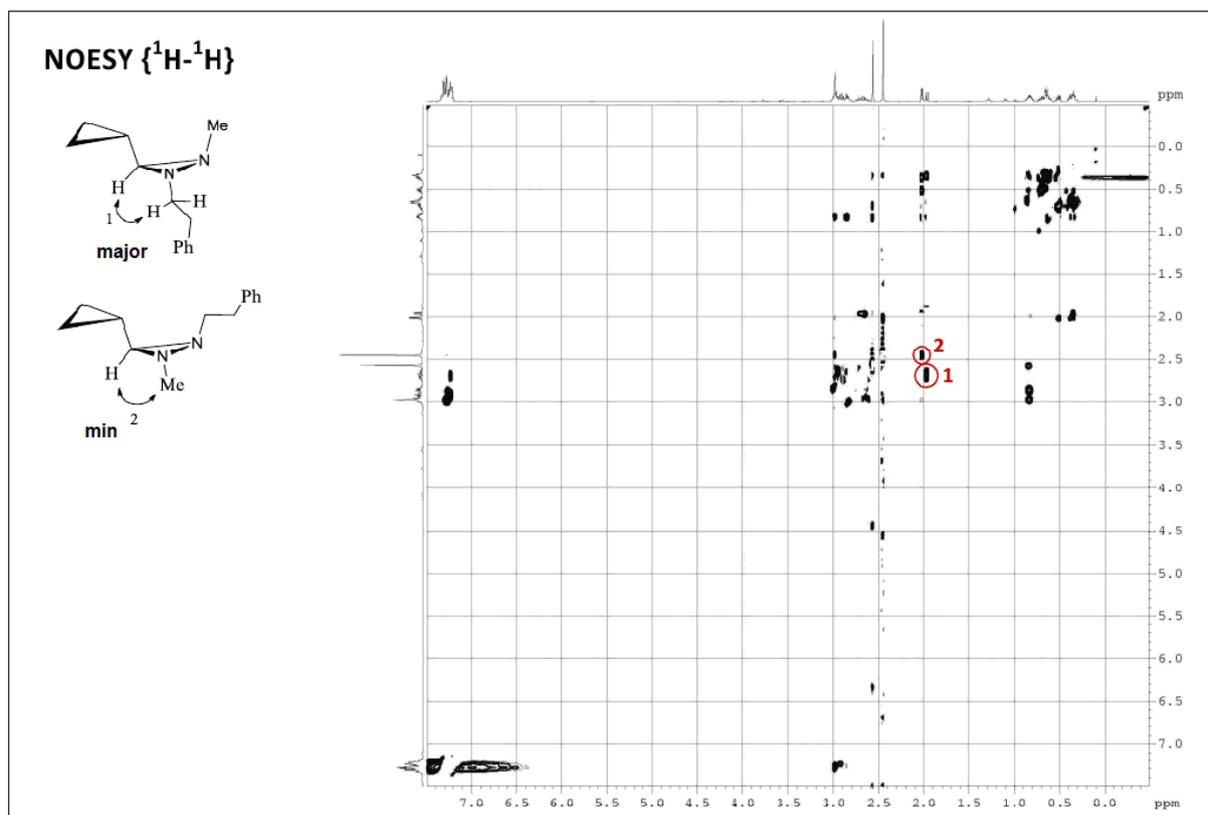


Figure S22. {¹H-¹H}gNOESY spectrum of **1'k+1''k** mixture (CDCl₃), enriched with **1''k**.

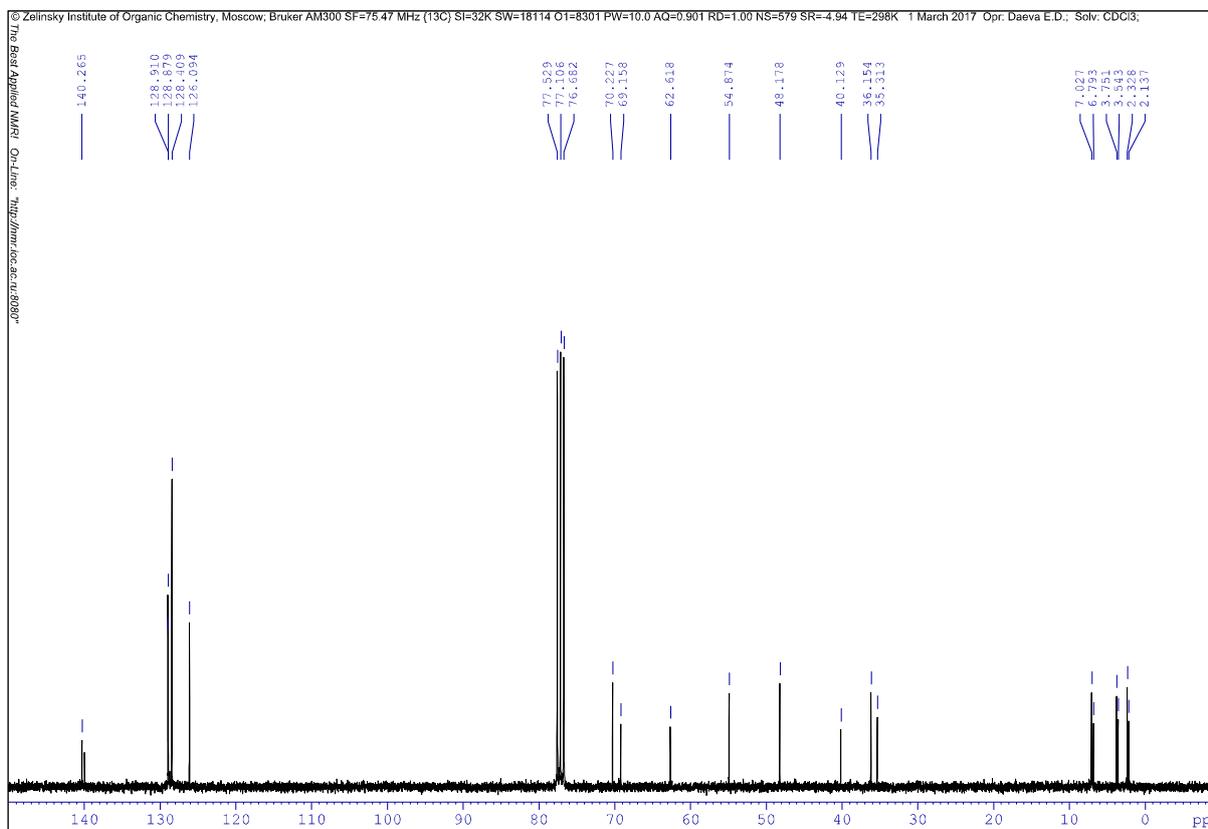
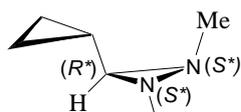


Figure S23. ¹³C NMR spectrum of diastereomers **1'k+1''k** (CDCl₃), enriched with **1''k**.



1'1 (major) OH 2-(3-cyclopropyl-2-methyldiaziridin-1-yl)ethanol **11**. Colorless liquid, yield 2.8 g (39%), b.p. 67-68°C (1 Torr). The diaziridine **11** was formed as a mixture of two diastereomers **1'1** and **1''1** in ~ 2.5:1 ratio, which were separated by column chromatography (eluent Kieselgel 60F₂₅₄ (eluent CHCl₃ + 5% EtOH). IR (ν/cm⁻¹) (for mixture of diastereomers): 523, 595, 767, 831, 877, 893, 919, 948, 1027, 1063, 1177, 1196, 1219, 1268, 1354, 1399, 1442, 1659, 2870, 2948, 3006, 3085, 3357. Major diastereomer: (1*S**,2*S**,3*R**)-2-(3-Cyclopropyl-2-methyldiaziridin-1-yl)ethanol **1'1**: R_f = 0.15 (CHCl₃:MeOH=20:1). ¹H NMR (400 MHz, CDCl₃) δ: 0.31–0.38 (m, 1H, *c*-Pr), 0.47–0.52 (m, 1H, *c*-Pr), 0.60–0.70 (m, 2H, *c*-Pr), 0.75–0.85 (m, 1H, *c*-Pr), 2.11 (d, 1H, N-HC_{ring}-N, ³*J* 7.2 Hz), 2.30–2.36 (m, 1H, CH_aN), 2.55 (s, 3H, Me), 2.77–2.84 (m, 1H, CH_bN), 3.16–3.27 (br s, 1H, OH), 3.72–3.78 (m, 2H, CH₂OH). ¹³C NMR (100 MHz, CDCl₃) δ: 1.8, 3.2, 6.3, 39.6, 61.1, 61.7, 68.2.

IR and mass spectra of diastereomers did not practically differ.

IR (ν/cm⁻¹) (for mixture of diastereomers): 523, 595, 767, 831, 877, 893, 919, 948, 1027, 1063, 1177, 1196, 1219, 1268, 1354, 1399, 1442, 1659, 2870, 2948, 3006, 3085, 3357.

MS (EI, 70 eV), *m/z*: 127 [M – Me]⁺, 111 [M – CH₂OH]⁺, 100 [M – *cyclo*Pr]⁺, 97 [M – (CH₂)₂OH], 82 [M – (CH₂)₂OH – Me], 55 [M – (CH₂)₂OH – *cyclo*Pr]⁺, 45 [(CH₂)₂OH]⁺, 42 [*cyclo*Pr]⁺, 31 [CH₂OH]⁺, 28 [N₂]⁺, 18 [H₂O]⁺. HRMS (ESI): *m/z* for C₇H₁₄N₂O (M+H)⁺: calcd 143.1179, found 143.1178; *m/z* for C₇H₁₄N₂O (M+Na)⁺: calcd 165.0998, found 165.0994.

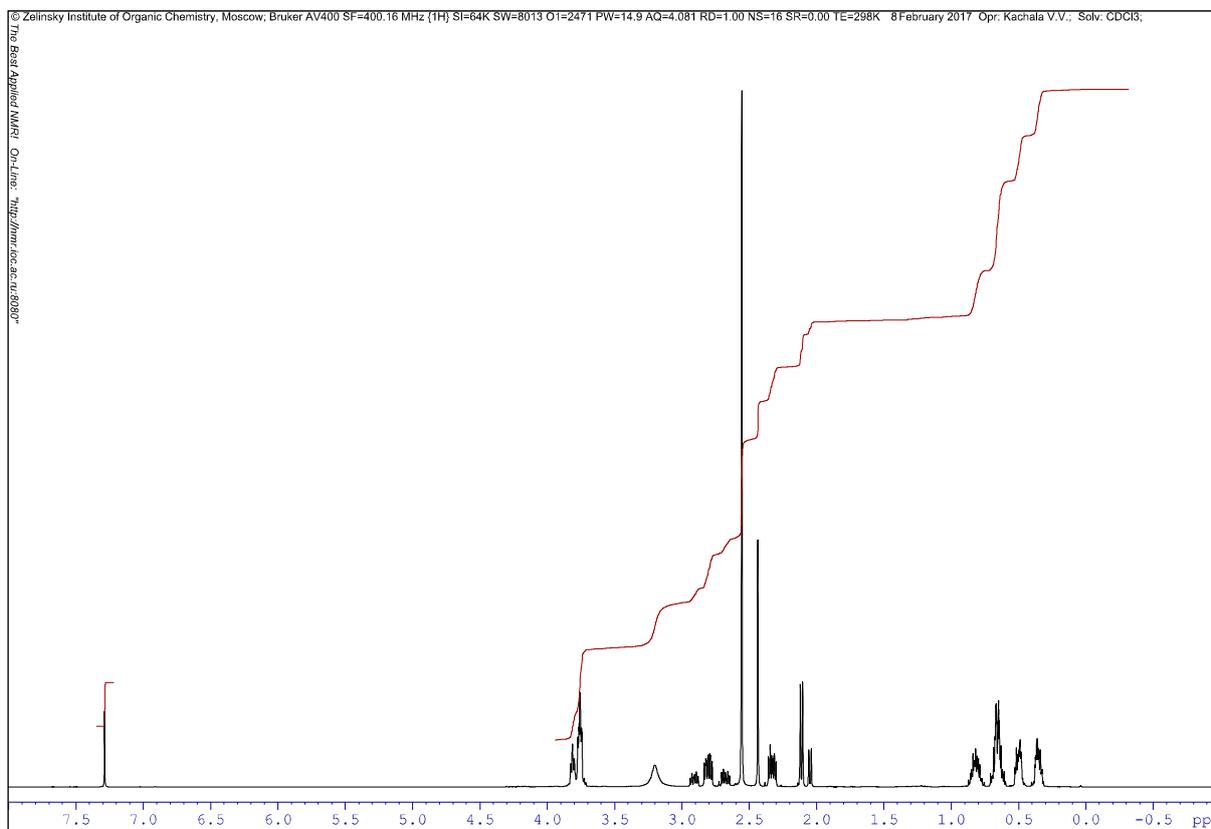


Figure S24. ¹H NMR spectrum of ~ 2.5:1 diastereomer mixture **1'1**+**1''1** (CDCl₃).

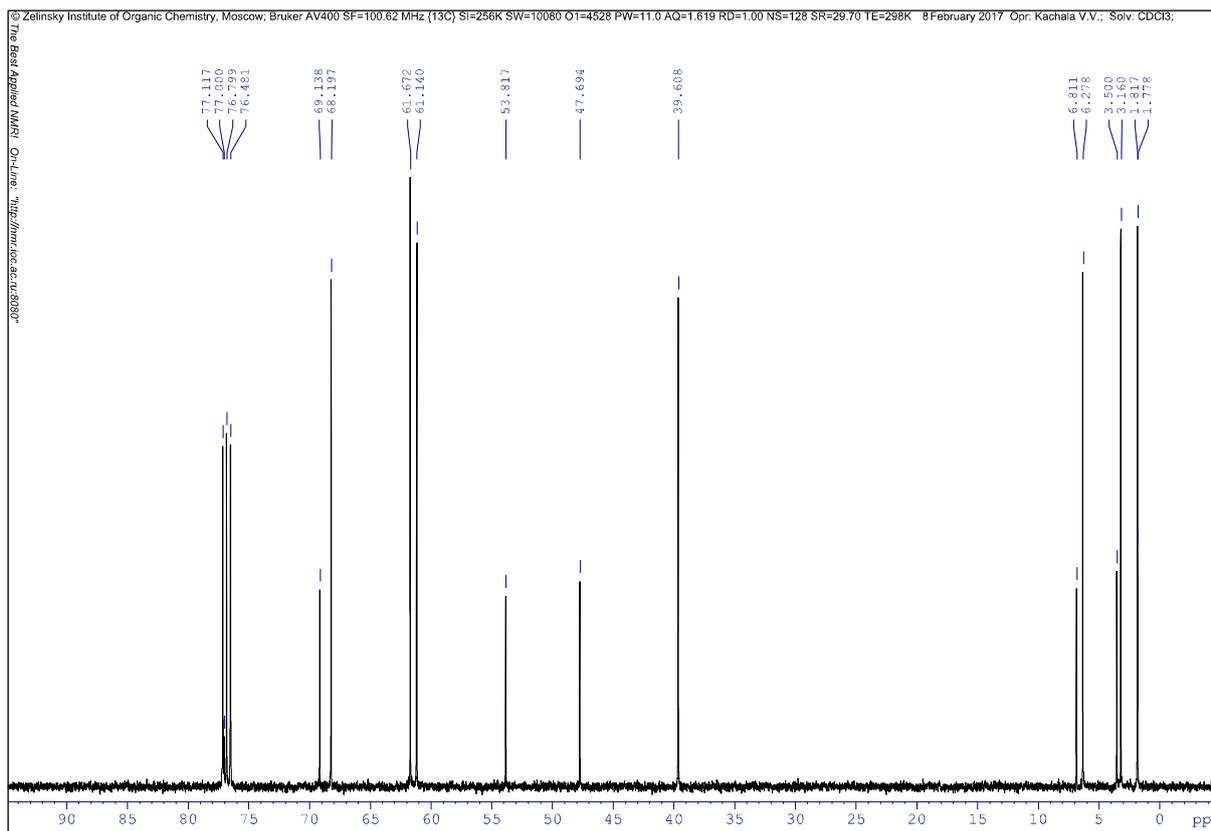


Figure S25. ^{13}C NMR spectrum of the mixture of diastereomers **1'1+1''1** (CDCl_3)

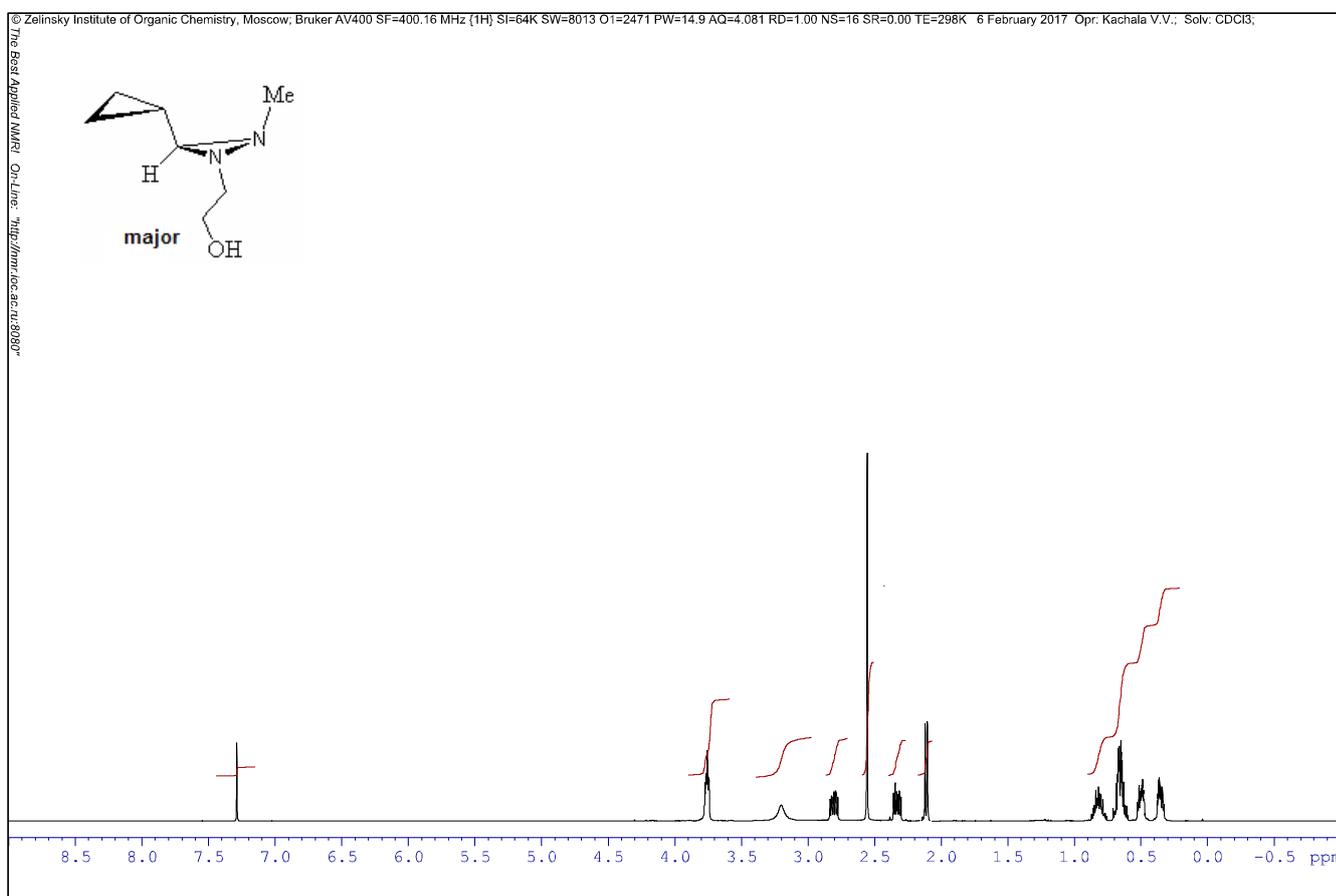


Figure S26. ^1H NMR spectrum of major diastereomer **1'1** (CDCl_3)

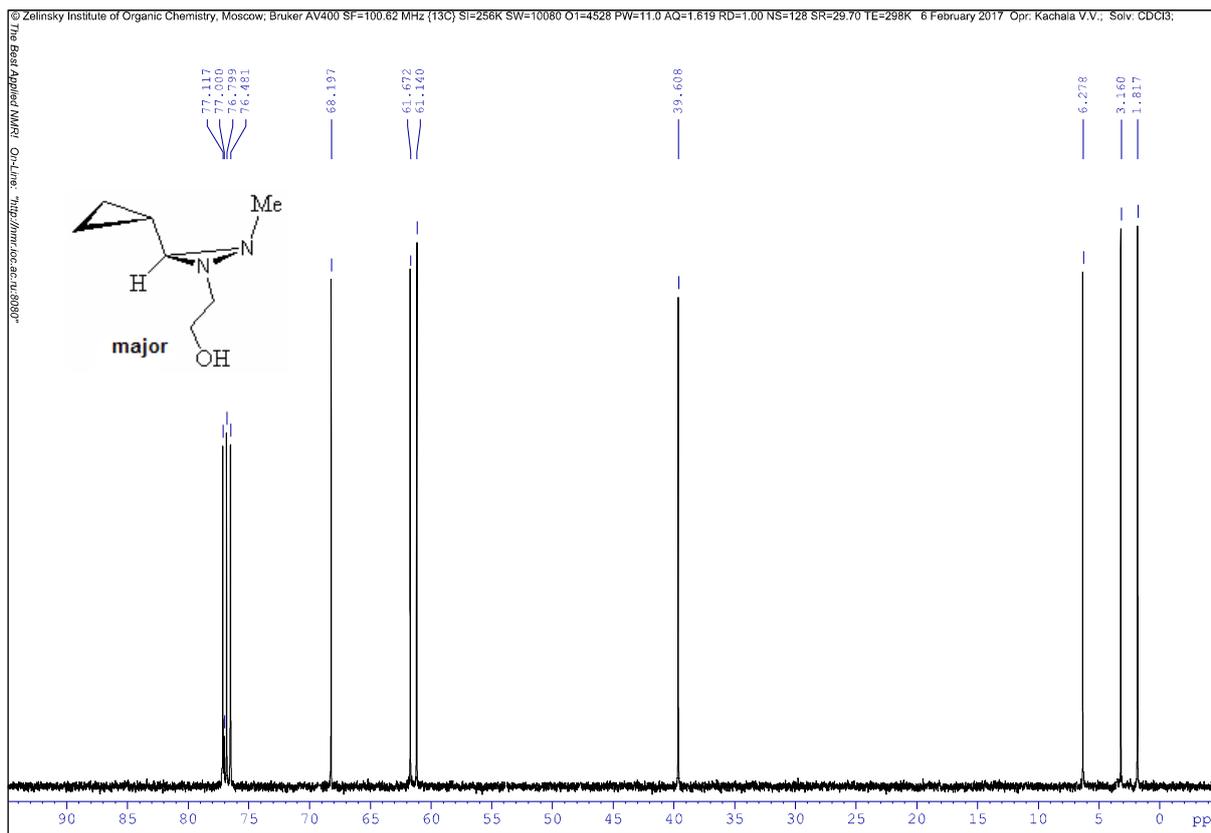


Figure S27. ^{13}C NMR spectrum of major diastereomer **1'1** (CDCl_3)

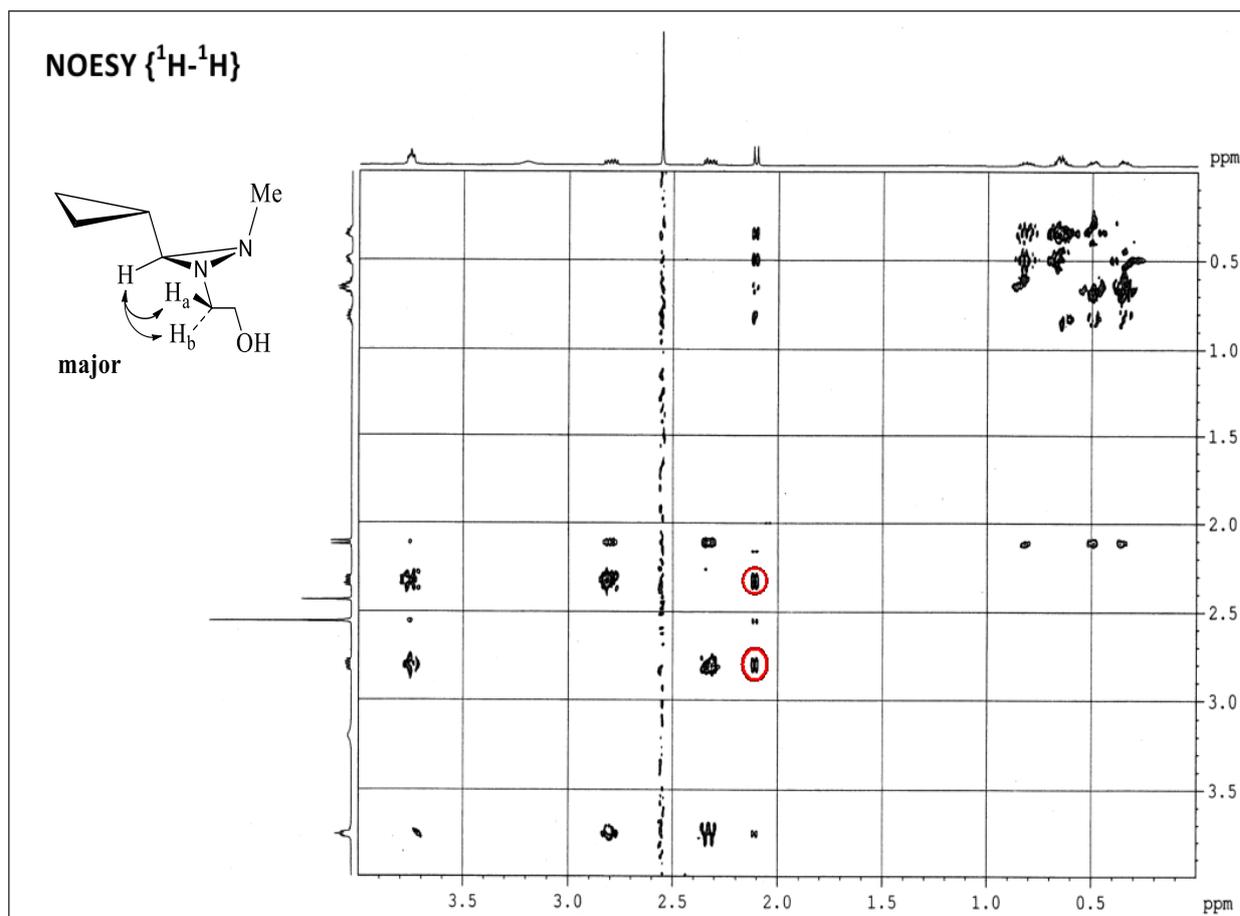
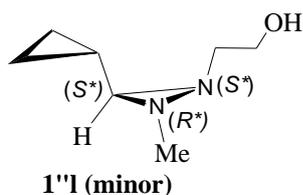
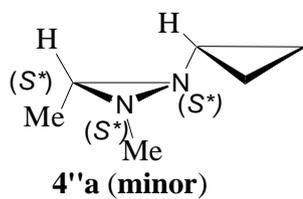
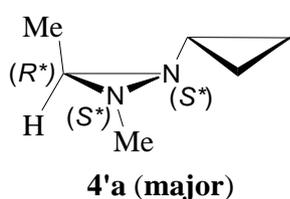


Figure S28. $\{^1\text{H}-^1\text{H}\}$ gNOESY spectrum of major diastereomer **1'1** (CDCl_3)



Minor diastereomer (*1S**,*2S**,*3S**)-2-(3-Cyclopropyl-2-methyldiaziridin-1-yl)ethanol **1''I**. R_f = 0.29 (CHCl₃:MeOH=20:1). ¹H NMR (400 MHz, CDCl₃) δ : 0.31–0.38 (m, 1H, *c*-Pr), 0.47–0.52 (m, 1H, *c*-Pr), 0.60–0.70 (m, 2H, *c*-Pr), 0.78–0.86 (m, 1H, *c*-Pr), 2.05 (d, 1H, N-HC_{ring}-N, ³*J* 7.1 Hz), 2.43 (3H, Me), 2.63–2.71 (m, 1H, CH_aN), 2.87–2.94 (m, 1H, CH_bN), 3.16–3.27 (br s, 1H, OH), 3.79–3.83 (m, 2H, CH₂OH). ¹³C NMR (100 MHz, CDCl₃) δ : 1.8, 3.5, 6.8, 47.7, 53.8, 61.7, 69.1.



1-Cyclopropyl-2,3-dimethyldiaziridine **4a**.

Colorless liquid, yield 1.18g (21%), b.p. 51 °C (15 Torr), highly volatile compound. The diaziridine **4a** was formed as a mixture of two diastereomers in ~ 2.5:1 ratio (observing in ¹H NMR spectra). IR (v/cm⁻¹): 800, 872, 1017, 1260, 1372, 1455, 1660, 2542, 2775, 3848, 2935, 2963, 3367. Major diastereomer (*1S**,*2S**,*3R**)-1-Cyclopropyl-2,3-dimethyldiaziridine **4'a**. ¹H NMR (600 MHz, CDCl₃) δ : 0.43–0.58 (m, 3H, *c*-Pr), 0.67–0.73 (m, 1H, *c*-Pr), 1.43 (dd, 3H, Me-HC_{ring}, ³*J* 5.4 Hz, ⁵*J* 0.6 Hz), 1.83–1.88 (m, 1H, N-CH (*c*-Pr)), 2.43 (d, 3H, Me-N, ⁴*J* 3.5 Hz), 2.55–2.59 (q, 1H, N-HC_{ring}-N, ³*J* 5.4 Hz). ¹³C NMR (150 MHz, CDCl₃) δ : 4.0, 4.9, 12.7, 32.1, 47.7, 62.0. Minor diastereomer (*1S**,*2S**,*3S**)-1-Cyclopropyl-2,3-dimethyldiaziridine **4''a**: ¹H NMR (600 MHz, CDCl₃) δ : 0.43–0.58 (m, 2H, *c*-Pr), 0.58–0.60 (m, 1H, *c*-Pr), 0.61–0.66 (m, 1H, *c*-Pr), 1.31 (dd, 3H, Me-HC_{ring}, ³*J* 5.4 Hz, ⁵*J* 0.6 Hz), 1.67–1.73 (m, 1H, N-CH (*c*-Pr)), 2.40 (d, 3H, Me-N, ⁴*J* 3.7 Hz), 2.83–2.86 (q, 1H, N-HC_{ring}-N, ³*J* 5.6 Hz). ¹³C NMR (150 MHz, CDCl₃) δ : 3.9, 4.1, 11.6, 38.8, 39.8, 60.10. MS (EI, 70 eV), *m/z*: 111 [M – H]⁺, 97 [M – Me]⁺, 97 [M – N-CH₃]⁺, 70 [M – *c*-Pr]⁺, 56 [M – *c*-Pr-N]⁺, 42 [*c*-Pr]⁺. HRMS (ESI): *m/z* for C₆H₁₂N₂ (M+H)⁺: calcd 113.1073, found 113.1060; *m/z* for C₆H₁₂N₂ (M+Na)⁺: calcd 135.0893, found 135.0890.

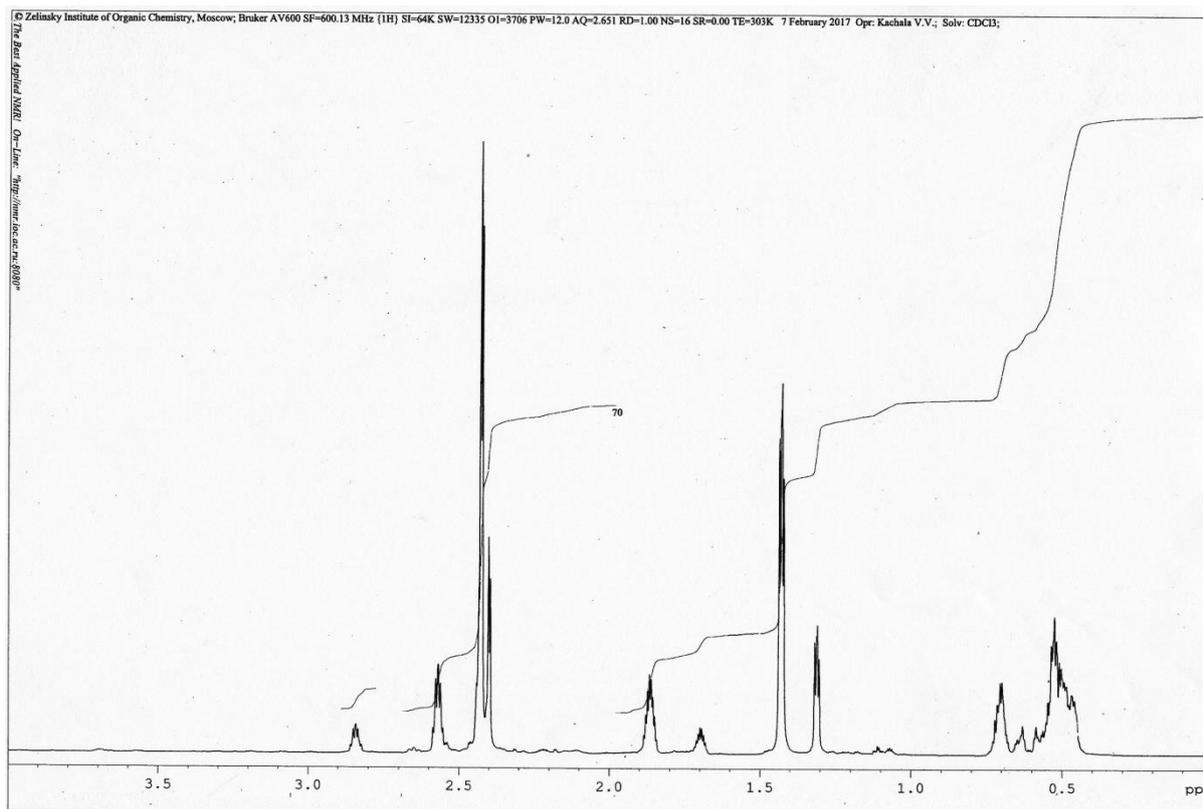


Figure S29. ^1H NMR spectrum of $\sim 2.5:1$ diastereomer mixture **4'a+4''a** in (CDCl_3) .

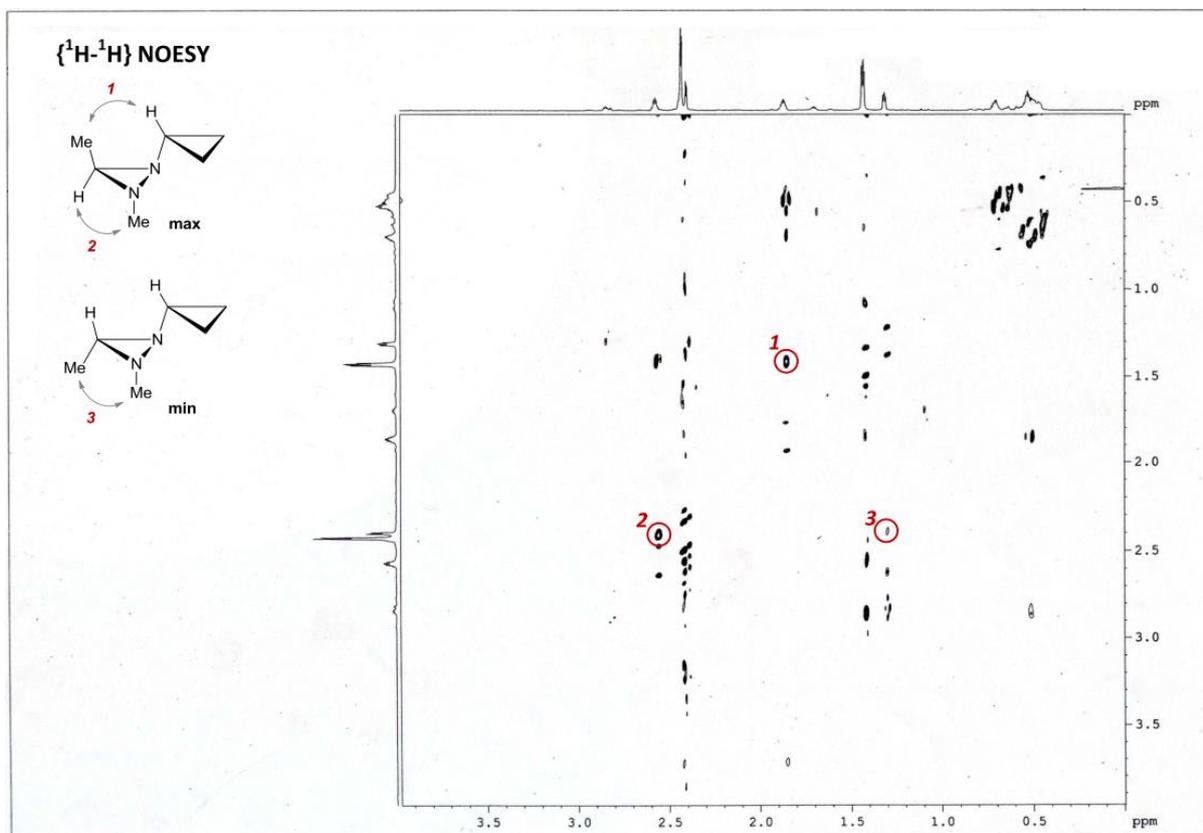


Figure S30. $\{^1\text{H}-^1\text{H}\}$ gNOESY spectrum of diastereomer mixture **4'a+4''a** (CDCl_3).

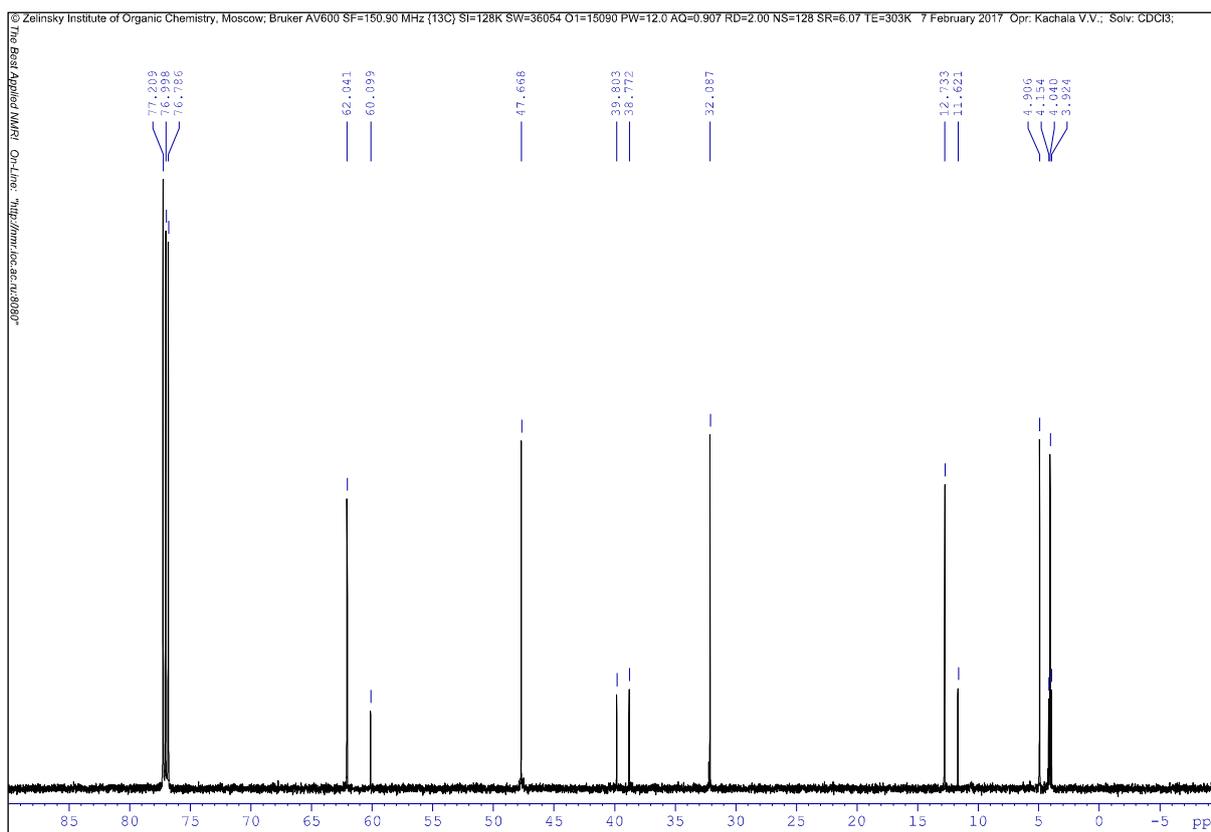
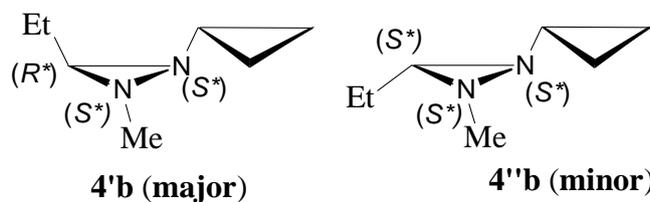


Figure S31. ^{13}C NMR spectrum of diastereomer mixture **4'a+4''a** (CDCl_3).



1-Cyclopropyl-3-ethyl-2-

*methyl*diaziridine **4b**. Colorless liquid, yield 1.45g (23%), b.p. 55 °C (15 Torr), highly volatile compound. The diaziridine **4b** was formed as a mixture of two diastereomers in ~ 2.5:1 ratio (^1H NMR spectra data). IR (ν/cm^{-1}): 669, 744, 821, 871, 936, 1017, 1070, 1139, 1198, 1287, 1354, 1457, 1655, 1729, 2342, 2361, 2879, 2972, 3010. *Major diastereomer (1S*,2S*,3R*)-1-Cyclopropyl-3-ethyl-2-methyldiaziridine 4'b*: ^1H NMR (300 MHz, CDCl_3) δ : 0.43–0.60 (m, 3H, *c*-Pr), 0.63–0.75 (m, 1H, *c*-Pr), 1.12 (t, 3H, Me-CH₂, 3J 7.5 Hz), 1.70–1.80 (m, 2H, Me-CH₂-HC_{ring}, 3J 7.5 Hz), 1.85–1.95 (m, 1H, N-CH *c*-Pr), 2.43 (t, 1H, N-HC_{ring}-N, 3J 6.3 Hz), 2.46 (s, 3H, Me-N). ^{13}C NMR (75 MHz, CDCl_3) δ : 4.3, 5.3, 10.7, 20.7, 32.3, 48.1, 68.3. *Minor diastereomer (1S*,2S*,3S*)-1-Cyclopropyl-3-ethyl-2-methyldiaziridine 4''b*: ^1H NMR (300 MHz, CDCl_3) δ : 0.43–0.60 (m, 3H, *c*-Pr), 0.63–0.75 (m, 1H, *c*-Pr), 1.09 (t, Me-CH₂, 3J 7.5 Hz), 1.56–1.64 (m, 2H, Me-CH₂-C_{ring}, 3J 7.5 Hz), 1.70–1.80 (m, 1H, N-CH (*c*-Pr)), 2.45 (s, 3H, Me-N), 2.68 (t, N-HC_{ring}-N, 3J 7.5 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 3.9, 4.6, 10.6, 19.4, 39.1, 40.1, 66.2. MS (EI, 70 eV), m/z : 125 [$\text{M} - \text{H}$]⁺, 111 [$\text{M} - \text{Me}$]⁺, 97 [$\text{M} - \text{Et}$]⁺, 84 [$\text{M} - c\text{-Pr}$]⁺, 71 [$\text{M} - c\text{-Pr} - \text{N}$]⁺, 42 [*c*-Pr]; HRMS (ESI): m/z for $\text{C}_7\text{H}_{14}\text{N}_2$ ($\text{M} + \text{H}$)⁺: calcd 127.1230, found 127.1235.

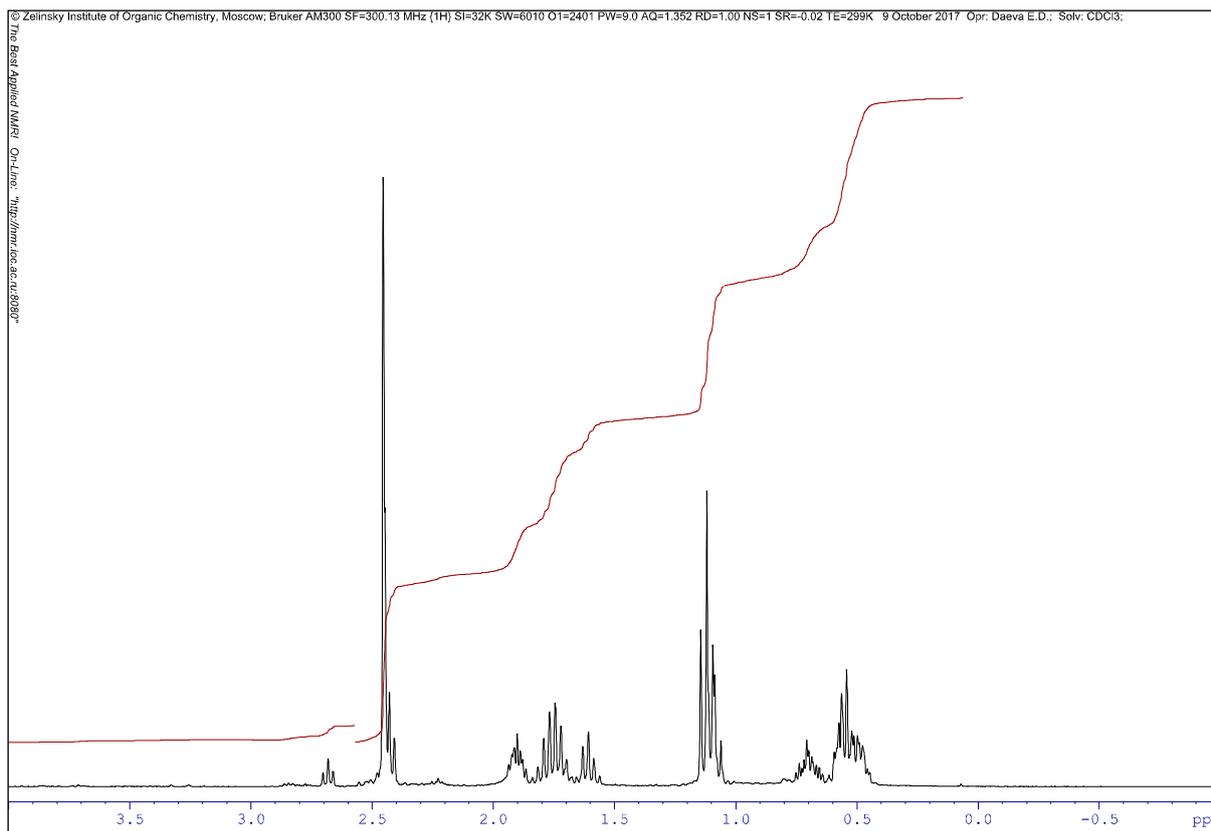


Figure S32. ¹H NMR spectrum of ~ 2.5:1 diastereomer mixture **4'b+4''b** (CDCl₃).

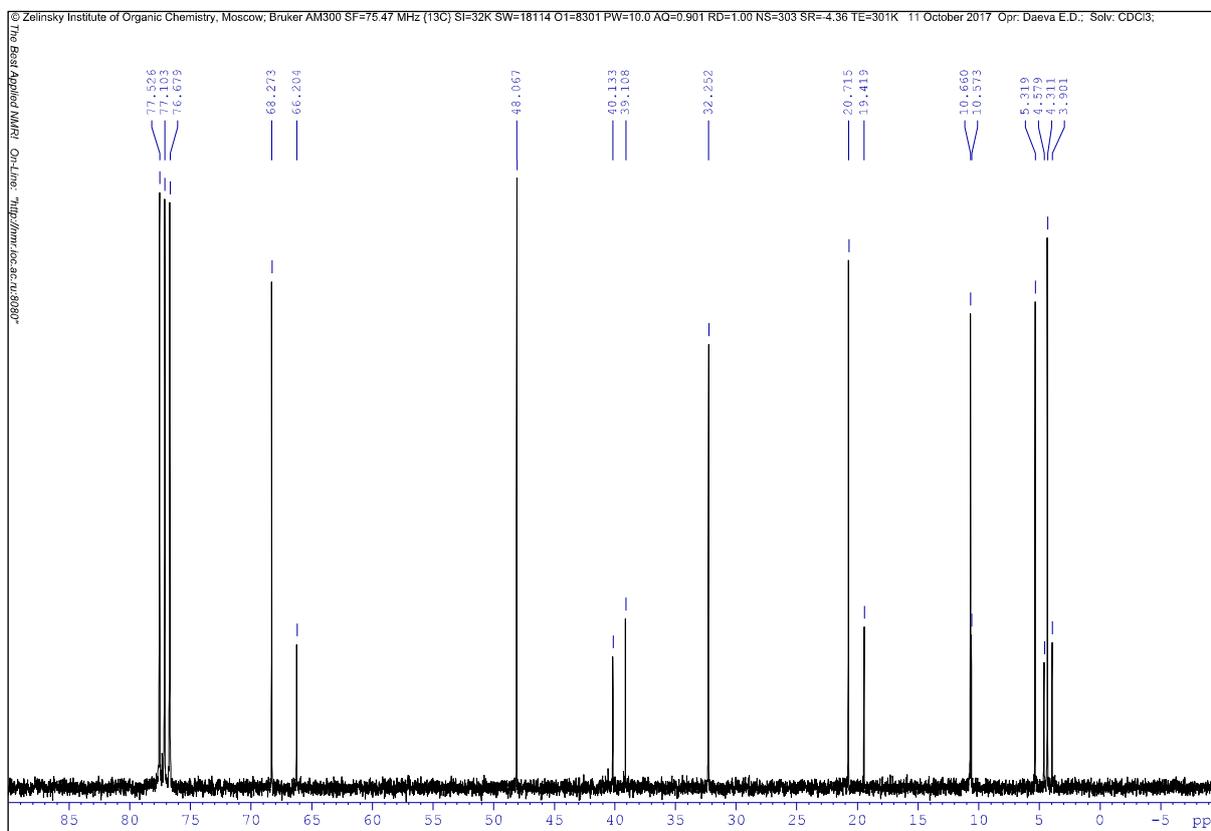


Figure S33. ¹³C NMR spectrum of the mixture of diastereomers **4'b+4''b** (CDCl₃).

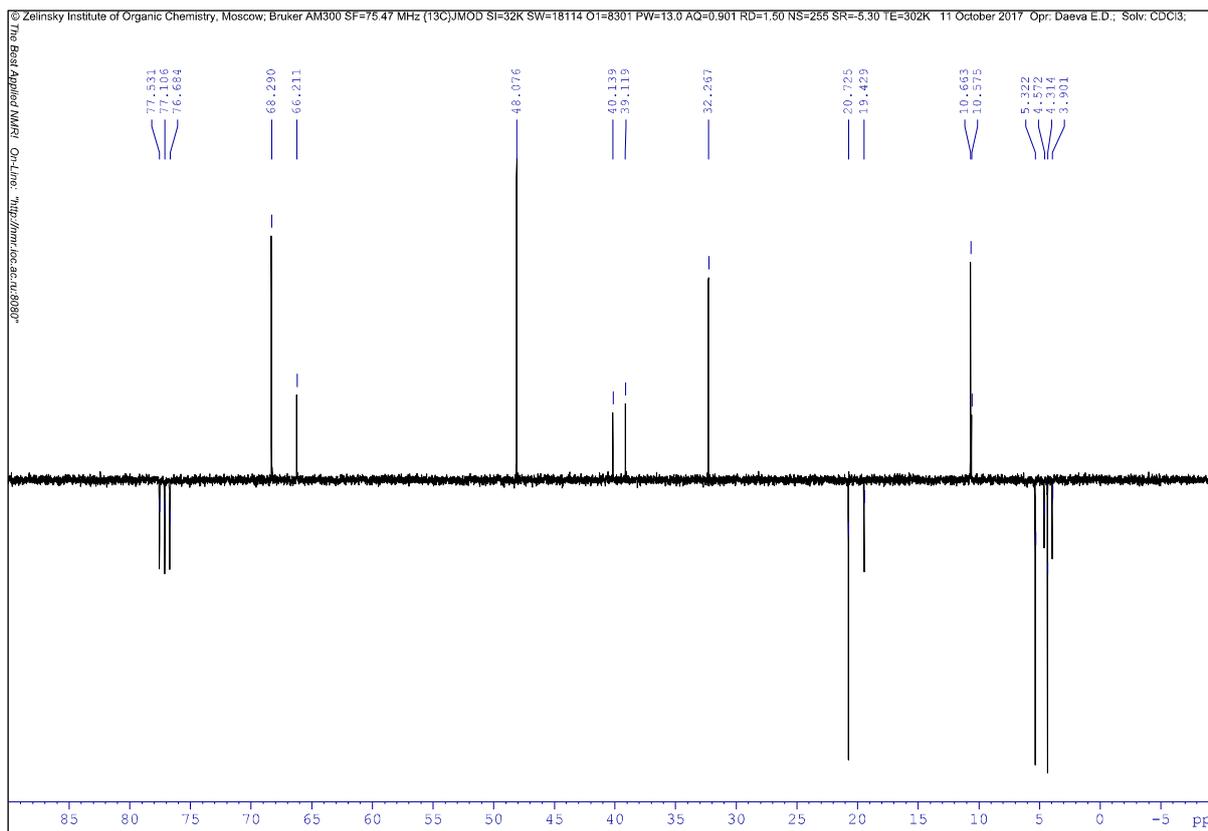


Figure S34. ^{13}C NMR JMOD spectrum of diastereomer mixture **4'b+4''b** (CDCl_3).



Colorless liquid, yield .51g (24.0%), b.p. 66 °C (15 Torr), highly volatile compound. The diaziridine **4c** was formed as a mixture of two stereoisomers in ~ 2:1 ratio (^1H NMR spectra data). IR (v/cm^{-1}): 463, 549, 755, 1016, 1162, 1281, 1348, 1376, 1452, 1731, 1807, 2872, 2933, 2971, 3009, 3089. *Major diastereomer (1S*,2S*,3R*)-1-Cyclopropyl-2-ethyl-3-methyldiaziridine 4'c*: ^1H NMR (300 MHz, CDCl_3) δ : 0.40–0.60 (m, 3H, *c*-Pr), 0.60–0.68 (m, 1H, *c*-Pr), 1.15 (t, $\underline{\text{Me}}\text{-CH}_2$, 3J 7.1 Hz), 1.43 (d, 3H, $\text{Me-C}_{\text{ring}}$, 3J 5.4 Hz), 1.81–1.91 (m, 1H, N-CH (*c*-Pr), 2.09–2.20 (m, 1H, CH_αN), 2.31–2.50 (m, 1H, CH_βN), 2.58 (q, 1H, $\text{N-HC}_{\text{ring-N}}$, 3J 5.4 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 4.7, 5.2, 13.0, 13.5, 32.4, 55.1, 60.8. *Minor diastereomer (1S*,2S*,3S*)-1-Cyclopropyl-2-ethyl-3-methyldiaziridine 4''c*. ^1H NMR (300 MHz, CDCl_3) δ : 0.40–0.60 (m, 3H, *c*-Pr), 0.60–0.68 (m, 1H, *c*-Pr), 1.17 (t, $\underline{\text{Me}}\text{-CH}_2$), 1.30 (d, 3H, $\underline{\text{Me}}\text{-CH}$, 3J 5.4 Hz), 1.61–1.70 (m, 1H, N-CH (*c*-Pr), 2.09–2.20 (m, 1H, CH_αN), 2.31–2.50 (m, 1H, CH_βN), 2.86 (q, 1H, $\text{N-HC}_{\text{ring-N}}$, 3J 5.4 Hz). ^{13}C NMR (75 MHz, CDCl_3) δ : 4.5, 4.6, 11.9, 13.9, 40.2, 45.9, 60.5. MS (EI, 70 eV), m/z : 126 $[\text{M}]^+$, 125 $[\text{M} - \text{H}]^+$, 111 $[\text{M} - \text{Me}]^+$, 83 $[\text{M} - \text{c-Pr} - \text{H}]^+$, 70 $[\text{M} - \text{c-Pr-N}]^+$, 68 $[\text{M} - \text{c-Pr} - \text{Me} - \text{H}]^+$, 56 $[\text{M} - (\text{c-Pr}) - \text{Et}]^+$, 42 $[\text{c-Pr}]^+$, 41 $[\text{c-Pr} - \text{H}]^+$. HRMS (ESI): m/z for $\text{C}_7\text{H}_{14}\text{N}_2$ ($\text{M}+\text{H}$) $^+$: calcd 127.1230, found 127.1230; m/z for $\text{C}_7\text{H}_{14}\text{N}_2$ ($\text{M}+\text{Na}$) $^+$: calcd 149.1049, found 149.1054.

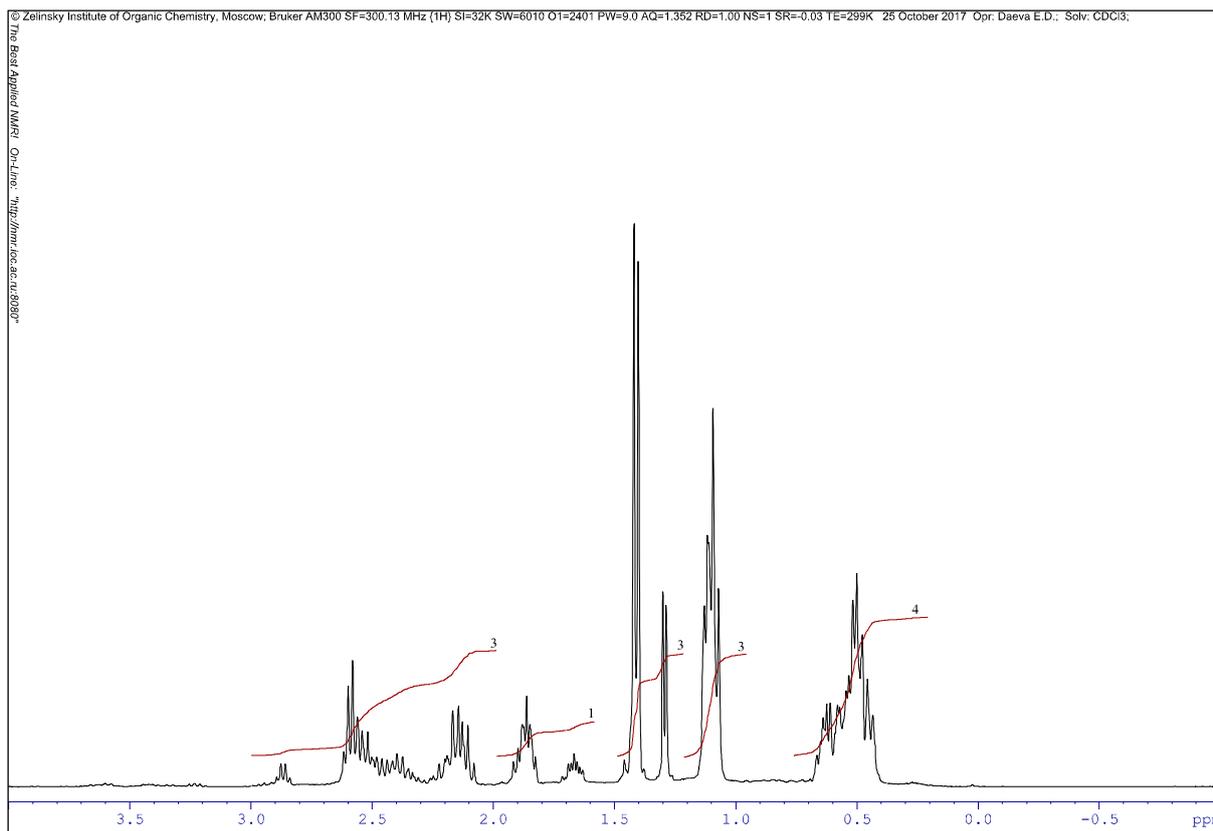


Figure S35. ^1H NMR spectrum of ~ 2:1 diastereomer mixture **4'c**+**4''c** in (CDCl_3).

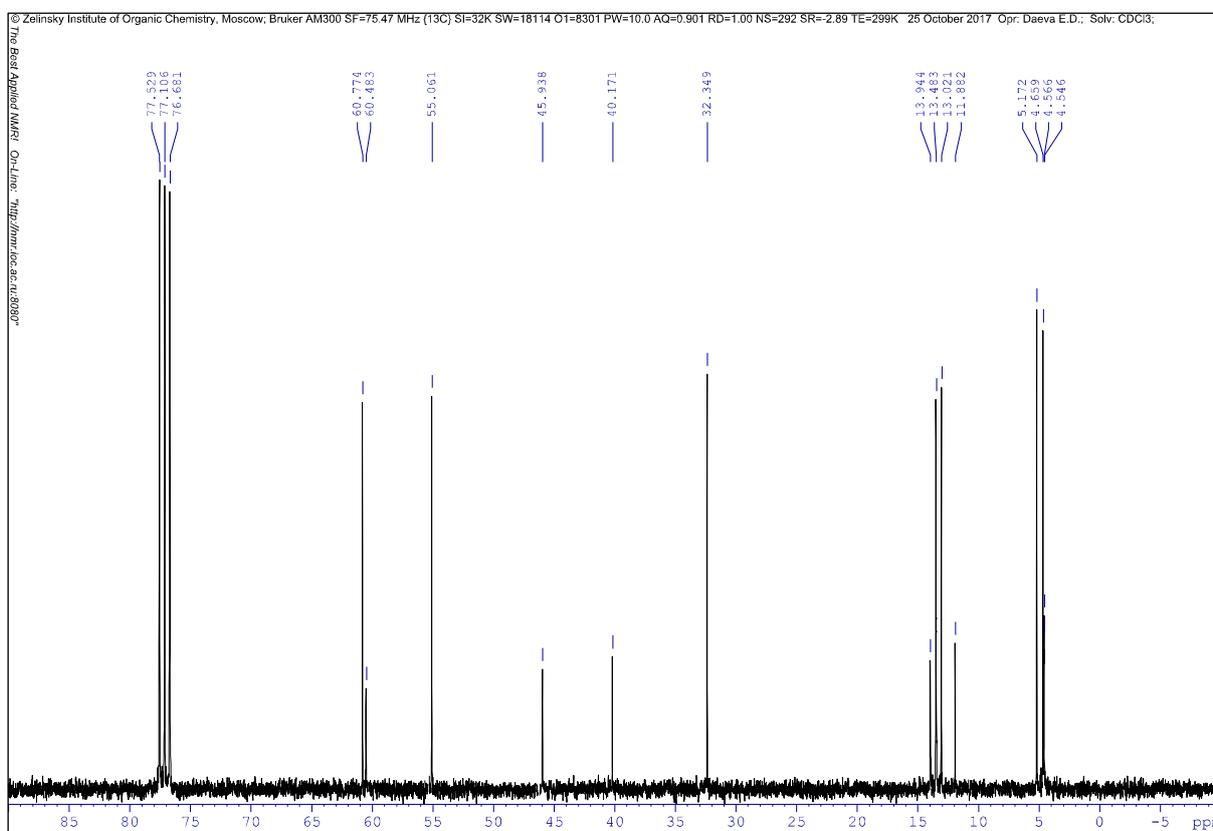


Figure S36. ^{13}C NMR spectrum of diastereomer mixture **4'c**+**4''c** (CDCl_3).