Supporting information

Synthesis of five-membered azaperoxides based on lanthanide-catalyzed recyclization of 5-(tert-butyl)-1,3,5-triazinan-2-one

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-Table of Contents-

A. General Information

General Remarks. All reactions were performed at room temperature in air in round-bottom flasks equipped with a magnetic stir bar. NMR spectra were recorded on a Bruker Avance 500 spectrometer at 500.17 MHz for ^{1}H and 125.78 MHz for ^{13}C according to standard Bruker procedures. $CDCl_3$ was used as a solvent, and tetramethylsilane as an internal standard. Mixing time for the NOESY experiments was 0.3 sec. Mass spectra were recorded on a Bruker Autoflex III MALDI TOF/TOF instrument with α-cyano-4-hydroxycinnamic acid as a matrix. Samples were prepared by the dried droplet method. C, H were quantified by a Carlo Erba 1108

analyzer. Reaction progress was monitored by TLC on Sorbfil (PTSKh-AF-A) plates, with a 5:1 hexane : EtOAc mixture as an eluent and visualization with I_2 vapor. Silica gel MACHEREY-NAGEL (0.063-0.2 mm) was used for column chromatography.

The starting aromatic diamines were from Acros. Tetrahydrofuran, hexane, EtOAc, petroleum ether, Et_2O ("pure" grade) were distilled prior to use. Hydrogen peroxide ("technical" grade) concentration 31.6%. Reagents I_2, $MgSO_4$ ("pure" grade). Synthesis of 5-(tert-butyl)-1,3,5-triazinan-2-one 1 was performed according to the described procedure [1].

Recyclization reaction of 5-(tert-butyl)-1,3,5-triazinan-2-one (1) with hydrogen peroxide in the presence of Sm(NO□)□·6H□O catalyst. Into a Schlenk flask placed on a magnetic stirrer at approx. 20 °C, 10 ml of THF, 1.00 mmol of 5-(tert-butyl)-1,3,5-triazinan-2-one 1, and 0.05 mmol of $Sm(NO_3)_3 \cdot 6H_2O$ were charged. After 30 min, 1.00 mmol of hydrogen peroxide was added. The reaction mixture was stirred for 5 h at ~20 °C, and THF was evaporated. 10 ml of Et_2O were added, and the mixture was washed with H_2O (4 × 5 ml). The ether layer was dried over $MgSO_4$ and purified by column chromatography on silica gel, eluent petroleum ether – Et_2O, 10:1. 4-(Tert-butyl)-1,2,4-dioxazolidine 2, stable during storage at room temperature, was isolated. The reaction progress was monitored by TLC, eluent hexane – EtOAc, 5:1, developed in I_2 vapor.

Recyclization reaction of 4-(tert-butyl)-1,2,4-dioxazolidine (2) with aromatic diamines 3, 5, 6, 9, 10 (o-, m-, p-phenylenediamines, 4,4'-methylenedianiline, 4,4'-oxydianiline) in the presence of $Sm(NO_3)_3 \cdot 6H_2O$ catalyst. Into a Schlenk flask placed on a magnetic stirrer at ~20 °C, 10 ml of THF, 1.00 mmol of 4-(tert-butyl)-1,2,4-dioxazolidine 2, and 0.05 mmol of $Sm(NO_3)_3 \cdot 6H_2O$ were charged. After 30 min, 1.00 mmol of the corresponding aromatic diamine 3, 5, 6, 9, 10 (o-, m-, p-phenylenediamines, 4,4'-methylenedianiline, 4,4'-oxydianiline) was added. The reaction mixture was stirred for 5 h at ~20 °C, and THF was evaporated. 10 ml of Et_2O were added, and the mixture was washed with H_2O (4 × 5 ml). The ether layer was dried over $MgSO_4$ and purified by column chromatography on silica gel, eluent petroleum ether – Et_2O, 10:1. Five-membered azaperoxides 4, 7, 8, 11, 12, stable during storage at room temperature, were isolated. The reaction progress was monitored by TLC, eluent hexane – EtOAc, 5:1, developed in I_2 vapor.

4-(Tert-butyl)-1,2,4-dioxazolidine (2). Yield 0.11 g (90%), colorless oil, Rf 0.74 (PE/Et_2O = 10/1). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 1.20 (s, 9 H, CH_3), 5.12 (s, 4 H, CH_2, conformer A), 5.16 (s, 4 H, CH_2, conformer B). ^{13}C NMR ($CDCl_3$, δ, ppm, J/Hz): 27.0, 27.1, 54.3, 78.1, 80.0. Mass spectrum (MALDI TOF/TOF), m/z: 130 $[M - H]^+$. Found (%): C, 54.94; H, 9.99; N, 10.68; O, 24.39. $C_6H_{13}NO_2$. Calculated (%): C, 54.92; H, 9.98; N, 10.66; O, 24.38.

2H,5H-1,6-(Methanediyloxymethano)benzo[e][1,2,4,7]dioxazocine (4). Yield 0.27 g (90%). Spectral data (^{1}H NMR, ^{13}C NMR) are consistent with those reported in the literature [2].

1,3-Bis(1,2,4-dioxazolidin-4-yl)benzene (7). Yield 0.19 g (85%), colorless oil, Rf 0.81 (PE/Et_2O = 10/1). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.16 (s, 4 H, CH_2, conformer A), 5.18 (s, 4 H, CH_2, conformer B), 6.01 (m, 1 H, CH), 6.28 (m, 2 H, CH), 6.99 (m, 1 H, CH). ^{13}C NMR ($CDCl_3$, δ, ppm, J/Hz): 81.3, 104.8, 122.4, 130.1, 149.7. Mass spectrum (MALDI TOF/TOF), m/z: 223 $[M-H]^+$. Found (%): C, 53.55; H, 5.37; N, 12.46. $C_{10}H_{12}N_2O_4$. Calculated (%): C, 53.57; H, 5.39; N, 12.49.

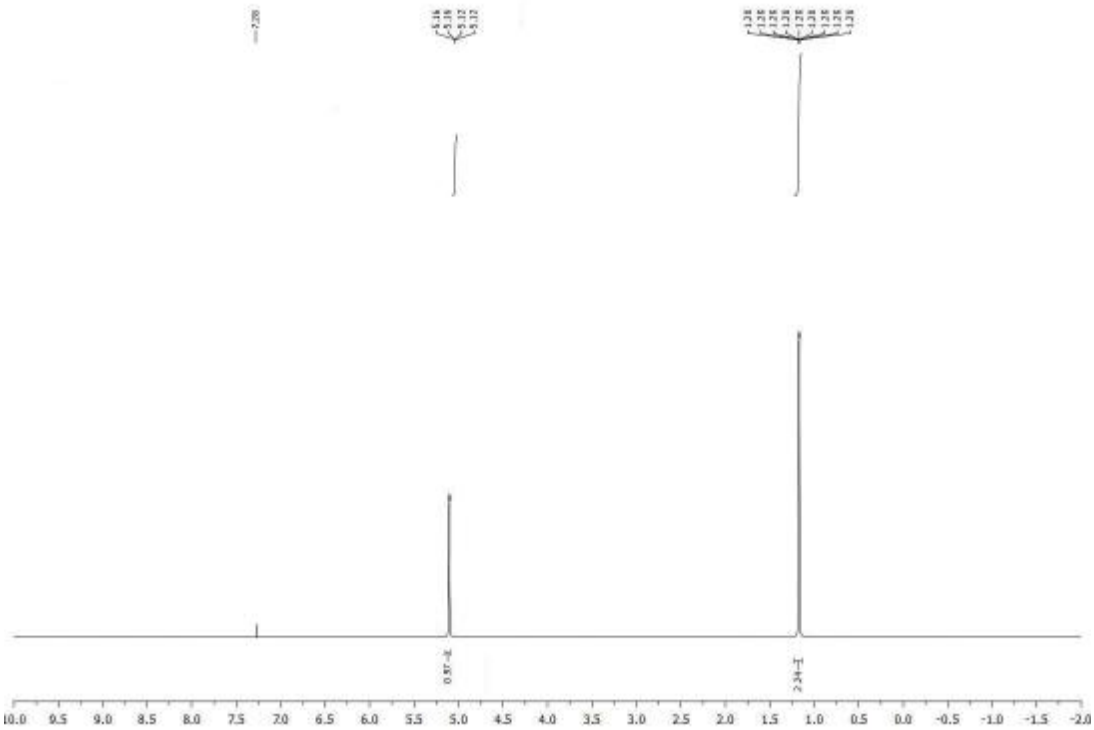
1,4-Bis(1,2,4-dioxazolidin-4-yl)benzene (8). Yield 0.21 g (92%), colorless oil, Rf 0.80 (PE/Et_2O = 10/1). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.15 (s, 4 H, CH_2, conformer A), 5.17 (s, 4 H, CH_2, conformer B), 6.50 (m, 4 H, CH). ^{13}C NMR ($CDCl_3$, δ, ppm, J/Hz): 82.3, 116.9, 139.4. Mass spectrum (MALDI TOF/TOF), m/z: 223 $[M-H]^+$. Found (%): C, 53.56; H, 5.37; N, 12.48. $C_{10}H_{12}N_2O_4$. Calculated (%): C, 53.57; H, 5.39; N, 12.49.

Bis(4-(1,2,4-dioxazolidin-4-yl)phenyl)methane (11). Yield 0.26 g (83%), colorless oil, Rf 0.86 (PE/Et_2O = 10/1). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 3.85 (s, 2 H, CH_2), 5.14 (s, 4 H, CH_2, A), 5.17 (s, 4 H, CH_2, B), 6.65 (m, 2 H, CH), 6.80 (m, 2 H, CH). ^{13}C NMR ($CDCl_3$, δ, ppm, J/Hz): 39.9, 82.0, 112.8, 120.4, 130.1, 145.2. Mass spectrum (MALDI TOF/TOF), m/z: 313 $[M-H]^+$. Found (%): C, 64.94; H, 5.75; N, 8.90. $C_{17}H_{18}N_2O_4$. Calculated (%): C, 64.96; H, 5.77; N, 8.91.

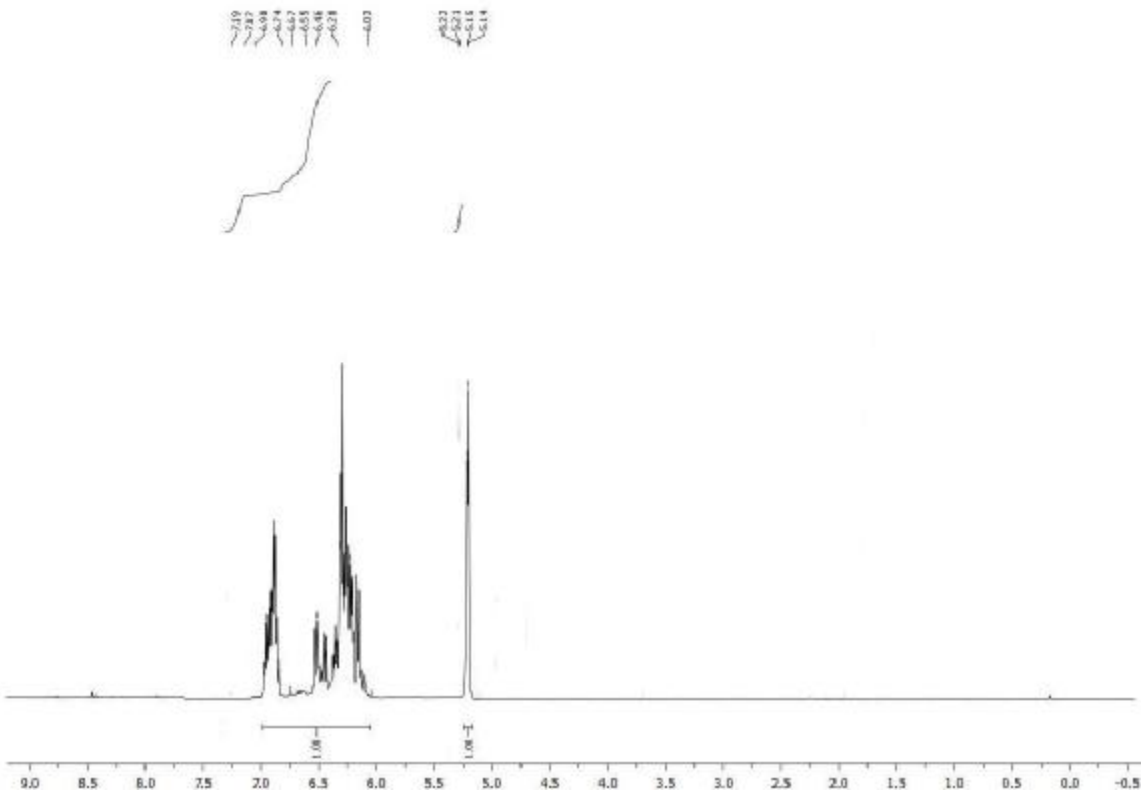
4,4'-(Oxybis(4,1-phenylene))bis(1,2,4-dioxazolidine) (12). Yield 0.25 g (80%), colorless oil, Rf 0.88 (PE/Et_2O = 10/1). ^{1}H NMR ($CDCl_3$, δ, ppm, J/Hz): 5.12 (s, 4 H, CH_2, A), 5.15 (s, 4 H, CH_2, B), 6.70 (m, 2 H, CH), 6.81 (m, 2 H, CH). ^{13}C NMR ($CDCl_3$, δ, ppm, J/Hz): 82.0, 82.3, 115.4, 117.6, 140.3, 142.7. Mass spectrum (MALDI TOF/TOF), m/z: 315 $[M-H]^+$. Found (%): C, 60.75; H, 5.08; N, 8.84. $C_{16}H_{16}N_2O_5$. Calculated (%): C, 60.76; H, 5.10; N, 8.86.

B. Copy of NMR spectra

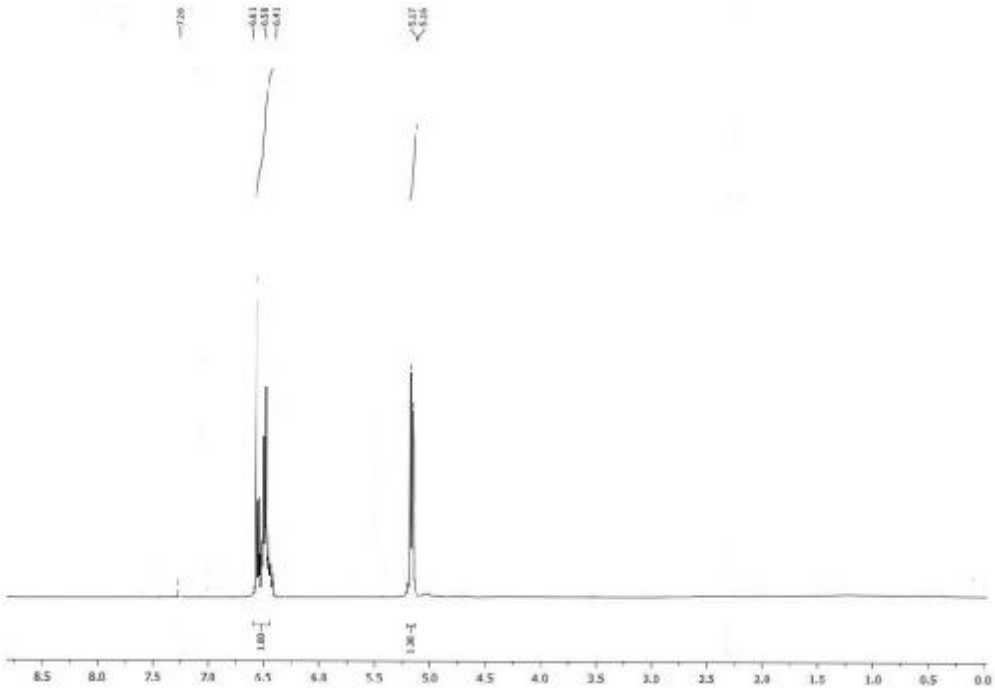
^{1}H-NMR (500 MHz, $CDCl_3$, 25 ^{o}C) spectrum of **2**



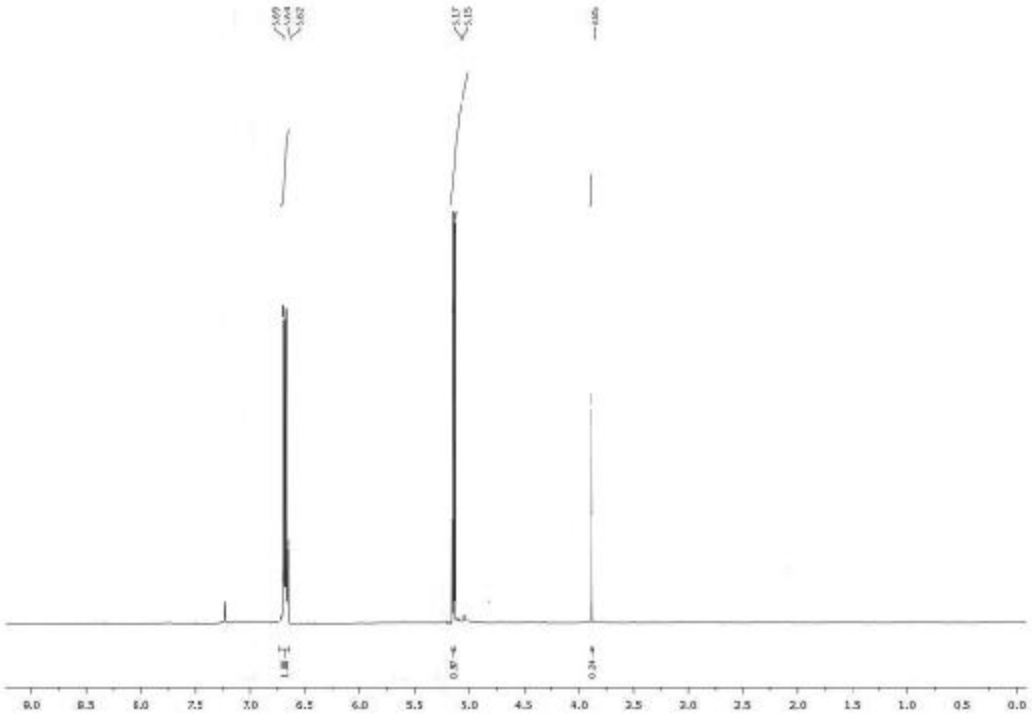
^{1}H-NMR (500 MHz, $CDCl_3$, 25 ^{o}C) spectrum of 7



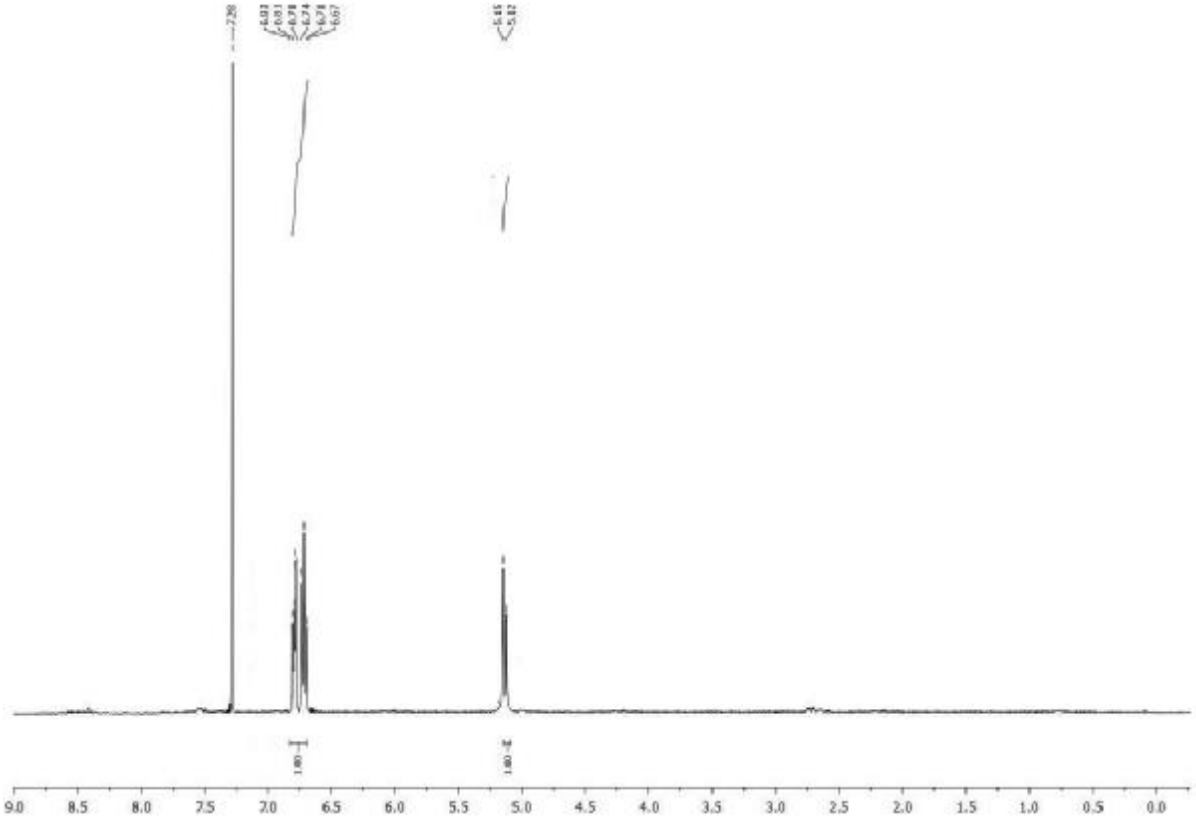
^{1}H-NMR (500 MHz, $CDCl_3$, 25 ^oC) spectrum of 8



^{1}H-NMR (500 MHz, $CDCl_3$, 25 ^oC) spectrum of 11



^{1}H-NMR (500 MHz, $CDCl_3$, 25 ^oC) spectrum of 12



C. References

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