Electronic Supplementary Information

Syntheses and Properties of Triborane(5) Possessing Bulky Diamino Substituents on Terminal Boron Atoms

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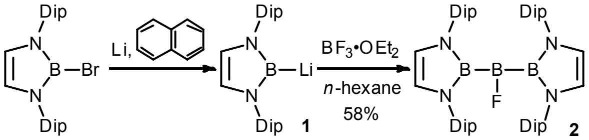
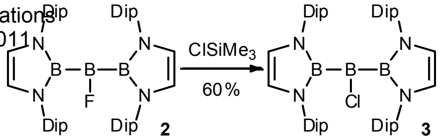
Experimental Section

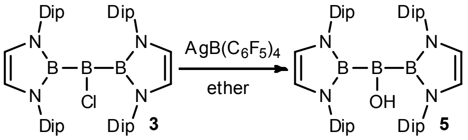
General Procedures. All manipulations involving the air- and moisture-sensitive compounds were carried out by using standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11 or a glovebox. All the solvents used for reactions were distilled under argon after drying over an appropriate drying agent or passed through solvent purification columns. THF was further dried by stirring with Na/K alloy at room temperature in the glovebox prior to use unless otherwise noted. *n*-Hexane was further distilled from *n*-butyllithium under vacuum. Lithium dispersion (purchased from Kanto Chemical Co., Inc., containing 1% sodium) was washed with hexane before the use to make a lithium powder. Most of reagents were used without further purification unless otherwise specified. NMR spectra were recorded on 500 MHz or 400 MHz spectrometers. Chemical shifts are reported in ppm relative to the residual protiated solvent for ^{1}H, $BF_3{\cdot}OEt_2$ for ^{11}B, deuterated solvent for ^{13}C, and $CFCl_3$ for ^{19}F. Data are presented in the following space: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, sept = septet, br = broad, v = virtual), coupling constant in hertz (Hz), and signal area integration in natural numbers. IR spectra were recorded on Shimadzu FTIR-8400. Melting points were measured on MPA100 Optimelt Automated Melting Point System and are uncorrected. Gas chromatograph was recorded on Shimadzu GC-2014 equipped with Sincarbon ST 5MS/Sil capillary column (3 ID, 1 μm df, 4 m). The bromoborane precursor for a preparation of **1**[1] and $Ag[B(C_6F_5)_4]{\cdot}(C_6H_6)_3$[2] were synthesized according to the literature.



Preparation of 2. In a glovebox, a suspension of bromoborane (4.67g, 10.0 mmol), lithium powder (347 mg, 50.0 mmol), and naphthalene (256 mg, 2.00 mmol) in THF (40 mL) was stirred at −35 °C overnight. The reaction mixture was filtered through a pad of Celite to afford a red solution. After solvents were evaporated under reduced pressure in a 250 mL Schlenk flask, *n*-hexane (60 mL) was added to a residue. To the resulting suspension, $BF_3{\cdot}OEt_2$ (1.15 mL, 10.0 mmol) was added at −78 °C and then slowly warmed to ambient temperature over a period of hour. The solvent was removed *in vacuo* and the crude product was recrystallized from *n*-hexane to give yellow crystals of **2** (2.33 g, 58%). mp: 243.8-245.6 °C; ^{1}H NMR (C_6D_6, 500 MHz) δ 7.15 (t, J_{HH} = 8 Hz, 4H), 7.04 (d, J_{HH} = 8 Hz, 8H), 5.88 (s, 4H), 3.08 (sept, J_{HH} = 7 Hz, 8H), 1.09 (d, J_{HH} = 7 Hz, 24H), 1.00 (d, J_{HH} = 7 Hz, 24 H); ^{11}B NMR (C_6D_6, 160 MHz) δ 25 (brs), 83 (brs); ^{19}F NMR (C_6D_6, 470 MHz) δ 66.0 (s); ^{13}C NMR (C_6D_6, 125 MHz) δ 146.1 (4°), 140.7 (4°), 127.6 (CH), 123.6 (CH), 121.9 (CH), 28.6 (CH), 25.6 (CH_3), 23.9 (CH_3). Anal. Calcd. for $C_{52}H_{72}B_3FN_4$: C, 77.62; H, 9.02; N, 6.96. Found: C, 77.38; H, 9.18; N, 6.76.



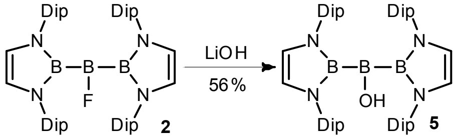
Preparation of 3. To a solution of **2** (505 mg, 0.630 mmol) in THF (10 mL), chlorotrimethylsilane (1.65 mL, 12.5 mmol) was added and the resulting mixture was refluxed for 3 days. After solvents were evaporated under residue pressure, the product was recrystallized from THF/*n*-hexane to give yellow crystals of **3** (306 mg, 60%). Ovelapping signals in ^{13}C NMR spectrum with those of C_6D_6 prevents a complete assignment. Therefore, the ^{13}C NMR spectrum was recorded by using CD_2Cl_2 solution. For comparison, ^{11}B NMR data is also shown here. mp: 165.7-168.2 °C (dec.); ^{1}H NMR (C_6D_6, 500 MHz) δ 7.15 (t, J_{HH} = 8 Hz, 4H, overlapped with C_6D_5H), 7.04 (d, J_{HH} = 8 Hz, 8H), 5.90 (s, 4H), 3.14 (sept, J_{HH} = 7 Hz, 8H), 1.10 (d, J_{HH} = 7 Hz, 24H), 1.01 (d, J_{HH} = 7 Hz, 24 H); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.17 (t, J_{HH} = 8 Hz, 4H), 7.03 (d, J_{HH} = 8 Hz, 8H), 5.95 (s, 4H), 2.88 (sept, J_{HH} = 7 Hz, 8H), 1.00 (d, J_{HH} = 7 Hz, 24H), 0.85 (d, J_{HH} = 7 Hz, 24 H); ^{11}B NMR (C_6D_6, 160 MHz) δ 26 (brs), 103 (brs); ^{11}B NMR (CD_2Cl_2, 160 MHz) δ 26 (brs), 98 (brs); ^{13}C NMR (CD_2Cl_2, 101 MHz) δ 146.1 (4°), 141.1 (4°), 127.5 (CH), 123.8 (CH), 122.8 (CH), 28.7 (CH), 25.8 (CH_3), 23.7 (CH_3). Anal. Calcd. for $C_{52}H_{72}B_3ClN_4$: C, 76.07; H, 8.84; N, 6.82. Found: C, 75.86; H, 8.93; N, 6.72.



Reaction of 3 with silver salt. In a glovebox, to a bright yellow ether (2 mL) solution of **3** (21.3 mg, 0.0260 mmol) and 1,3,5-trimethoxybenzene (2.2 mg, 0.013 mmol, as an internal standard for NMR yield) in a 5 mL vial equipped with a septum, a solution of $Ag[B(C_6F_5)_4]\cdot(C_6H_6)_3$ (29.2 mg, 0.0292 mmol) in ether (0.5 mL) was added at room temperature to give white solid and colorless solution. The reaction mixture was filtered through a pad of Celite and all solvents were evaporated and the crude product dissolved in C_6D_6. The NMR spectrum was compared with the isolated **5** to estimate ^{1}H NMR yield of **5**.

GC analysis for reaction of 3 with silver salt. In a glovebox, **3** (4.1 mg, 5.0 μmol) and $Ag[B(C_6F_5)_4]\cdot(C_6H_6)_3$ (5.6 mg, 5.0 μmol) were placed in a 5 mL vial equipped with a septum. After an addition of ether (0.30 mL) to the mixture, the reaction mixture was stirred for 5 min. Gases in the headspace of the vial were collected up to 15 mL by a gas-tight syringe together with atmospheric argon inside the glovebox (**sample A**). A part (7 mL) of **sample A** was analyzed by GC (Figure S4). On the other hand, ethylene (1 mL) and argon (49 mL) were collected by a gas-tight syringe (**sample B**) from two gas-filled Schlenk flasks (ethylene and argon, respectively). A part (10 mL) of **sample B** was analyzed by GC (Figure S5). Furthermore, a mixture of **sample A** (5 mL) and **sample B** (3.5 mL) was analyzed by GC (Figure S6).

Reaction of 3 with silver salt in CD_2Cl_2. By a replacement of ether in the above experiment with CD_2Cl_2, an NMR sample was prepared to monitor the reaction. The obtained ^{1}H and ^{11}B NMR spectra are illustrated in Figure S3 and S4. Immediate disappearance of **3** and appearance of new species was detected. ^{1}H NMR (CD_2Cl_2) δ 0.76 (d, J = 7 Hz, 12H), 0.94 (d, J = 7 Hz, 6H), 0.95 (d, J = 7 Hz, 6H), 1.03 (d, J = 7 Hz, 6H), 1.14 (d, J = 7 Hz, 12H), 2.59 (sept, J = 7 Hz, 2H), 2.68 (sept, J = 7 Hz, 2H), 2.73 (sept, J = 7 Hz, 2H), 4.78 (s, 2H), 6.07 (s, 2H), 7.14 (d, J = 8 Hz, 4H), 7.19 (d, J = 8 Hz, 2H), 7.25 (d, J = 8 Hz, 2H), 7.30 (t, J = 8 Hz, 2H), 7.42 (s, 1H), 7.48 (t, J = 8 Hz, 1H), 9.02 (s, 1H); ^{11}B NMR (CD_2Cl_2) δ −17.0 (s), 23.7 (br), 38.1 (br), 65.7 (br). Six doublets (2:2:1:1:1:1) and three septets (2:1:1) for methyl and methine protons of Dip substituents would indicate that one diazadihydroborole ring remained but that another ring became unsymmetrical. Further identification was unsuccessful.



Independent synthesis of 5. A solution of **2** (105 mg, 0.130 mmol) and lithium hydroxide (14 mg, 0.58 mmol) in THF (2.5 mL) was refluxed for overnight. After all the volatiles were removed under reduced pressure, the product was recrystallized from ether to give colorless crystals of **5** (58.8 mg, 56%). As a second method to obtain **5**, a solution of **2** was passed through silica-gel column chromatography with *n*-hexane/dichloromethane under air. Recrystallization of the eluting material from THF/*n*-hexane gave white crystals of **5**. Single crystals suitable for X-ray analysis were obtained from CH_2Cl_2 solution of **5**. mp: >300 °C (from 223 °C, co-solvated THF molecules are evaporated); ^{1}H NMR (C_6D_6, 500 MHz) δ 7.15 (t, J_{HH} = 8 Hz, 4H), 7.06 (d, J_{HH} = 8 Hz, 8H), 7.00 (s, 1H, this signal disappeared by a treatment with D_2O), 5.90 (s, 4H), 3.14 (brs, 8H), 1.11 (d, J_{HH} = 7 Hz, 24H), 1.00 (d, J_{HH} = 5 Hz, 24 H); ^{1}H NMR (CD_2Cl_2, 500 MHz) δ 7.17 (t, J_{HH} = 8 Hz, 4H), 7.04 (d, J_{HH} = 8 Hz, 8H), 6.71 (s, 1H), 5.88 (s, 4H), 2.91 (brs, 8H), 0.99 (d, J_{HH} = 7n Hz, 24H), 0.81 (d, J_{HH} = 7 Hz, 24 H); ^{11}B NMR (C_6D_6, 160 MHz) δ 26.0 (brs), 69.5 (brs); ^{11}B NMR (CD_2Cl_2, 160 MHz) δ 25.6 (brs), 68.5 (brs); ^{13}C NMR (CD_2Cl_2, 101 MHz) δ 146.3 (4°), 140.9 (4°), 127.5 (CH), 123.8 (CH), 121.7 (CH), 28.4 (CH), 25.6 (CH_3), 23.7 (CH_3). IR (KBr) ν_{OH} = 3524 cm^{-1}. Anal. Calcd. for $C_{52}H_{73}B_3N_4O{\cdot}Et_2O$: C, 76.72; H, 9.54; N, 6.39. Found: C, 76.55; H, 9.40; N, 6.34.

X-ray Crystallography. A suitable crystal was mounted with mineral oil to the glass fiber and transferred to the goniometer of a diffractmeter (RIGAKU/MSC7-Mercury or MSC10-Saturn CCD) with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) to 2θmax = 50°. The structures were solved by direct methods with SIR-97[3] and refined by full-matrix least-squares techniques against F^2 (SHELXL-97).[4, 5] The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed using AFIX instructions.

Table S1. Crystal data and structure refinement for **3** and **5**.

	3	**5**·1/4(*n*-hexane)
formula	$C_{56}H_{80}B_3ClN_4O$	$C_{107}H_{153}B_6N_8O_2$
fw	893.12	1648.23
T (K)	103(2)	93(2)
λ (Å)	0.71070	0.71070
cryst syst	Triclinic	Monoclinic
space group	*P-1*	$P2_1/c$
a, (Å)	11.478(5)	11.446(3)
b, (Å)	12.946(6)	19.069(4)
c, (Å)	19.381(8)	46.618(11)
α, (°)	103.183(5)	90
β, (°)	98.129(5)	92.284(3)
γ, (°)	103.201(5)	90
V, (Å^3)	2672.6(19)	10167(4)
Z	2	4
D_{calc}, (g / cm^3)	1.110	10.77
μ (mm^{-1})	0.112	0.062
F(000)	968	3588
cryst size (mm)	0.60 × 0.40 × 0.30	0.25 × 0.20 × 0.10
2θ range, (deg)	3.02 to 25.00	3.05 to 25.00
reflns collected	17544	74497
indep reflns/R_{int}	9187 / 0.0360	17856 / 0.0835
params	653	1149
GOF on F^2	1.105	1.190
R_1, wR_2 [I>2σ(I)]	0.0904, 0.2316	0.0833, 0.2006
R_1, wR_2 (all data)	0.1163, 0.2529	0.1081, 0.2261

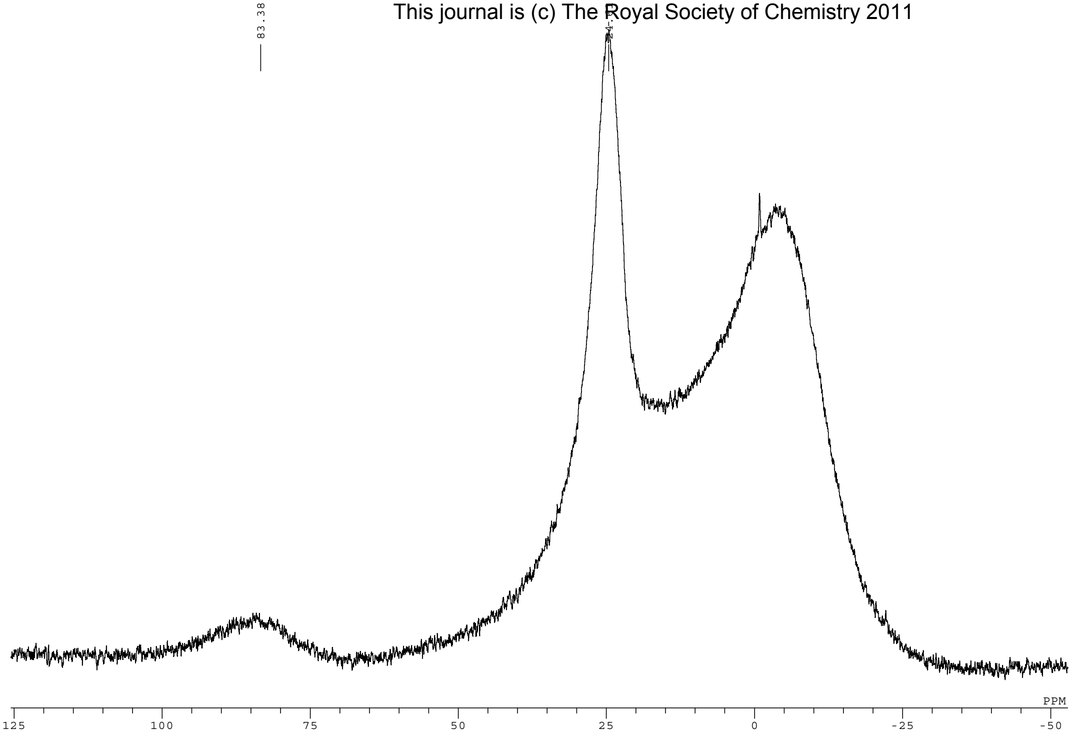


Figure S1. ^{11}B NMR spectrum of **2**.

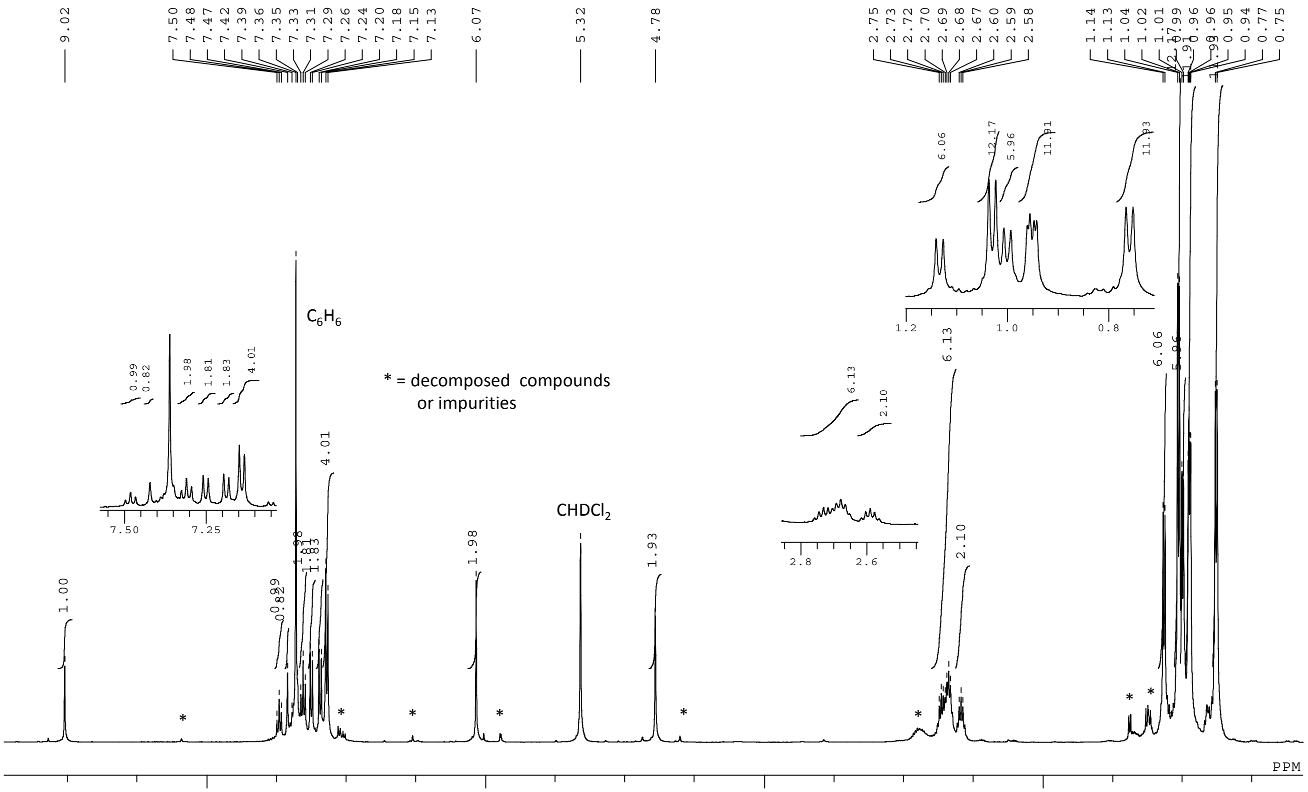


Figure S2. ^{1}H NMR spectrum of crude mixture in the reaction of **3** with Ag[B(C_6F_5)$_4$] in CD_2Cl_2 (rt, 10 min.)

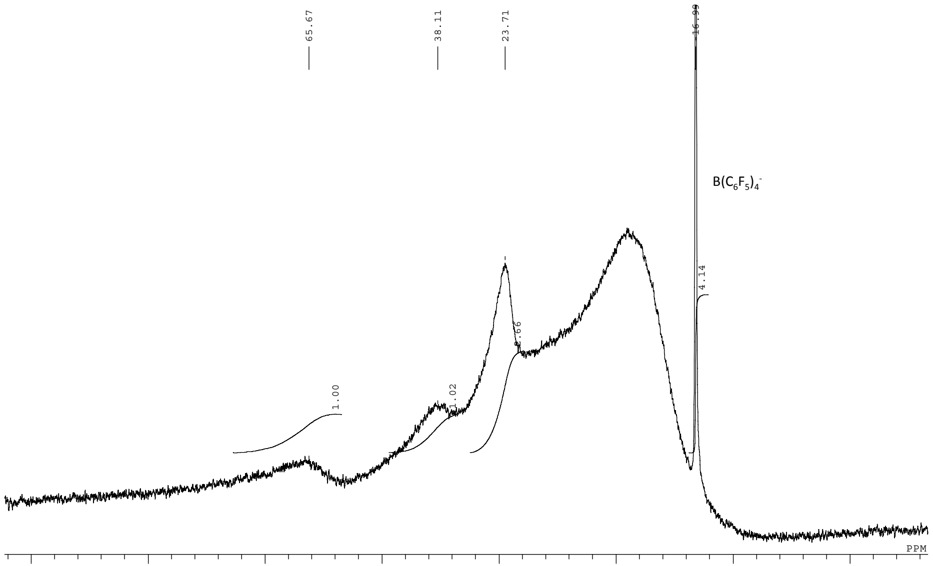


Figure S3. ^{11}B NMR spectrum of crude mixture in the reaction of **3** with Ag[B(C_6F_5)$_4$] in CD_2Cl_2 (rt, 10 min.)

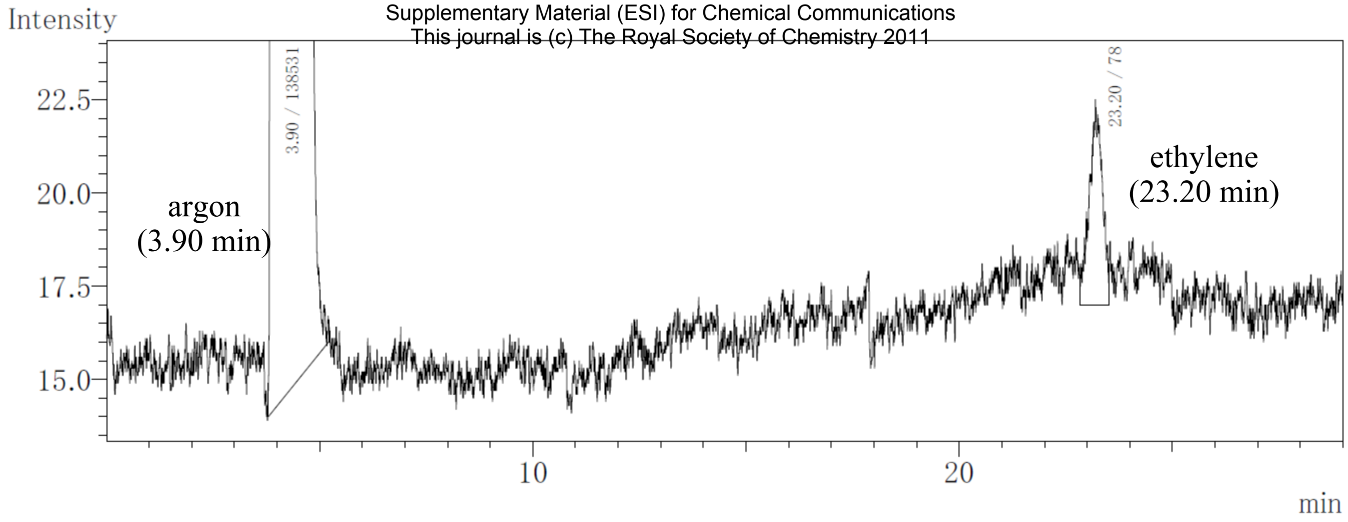


Figure S4. GC chart for the reaction of **3** with silver salt.

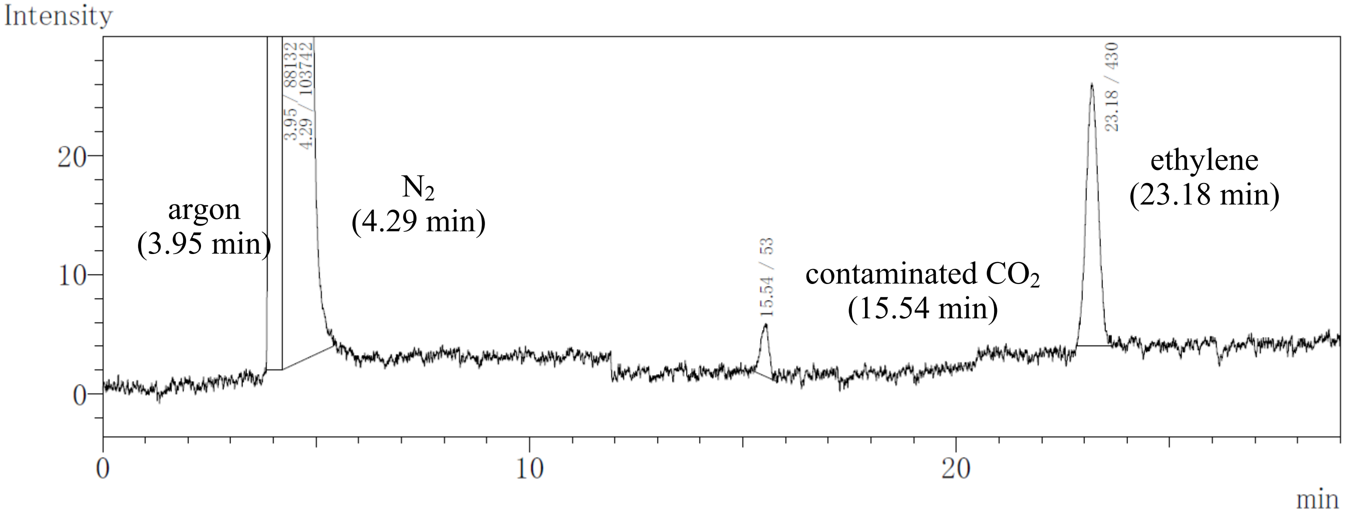


Figure S5. GC chart for the authentic sample.

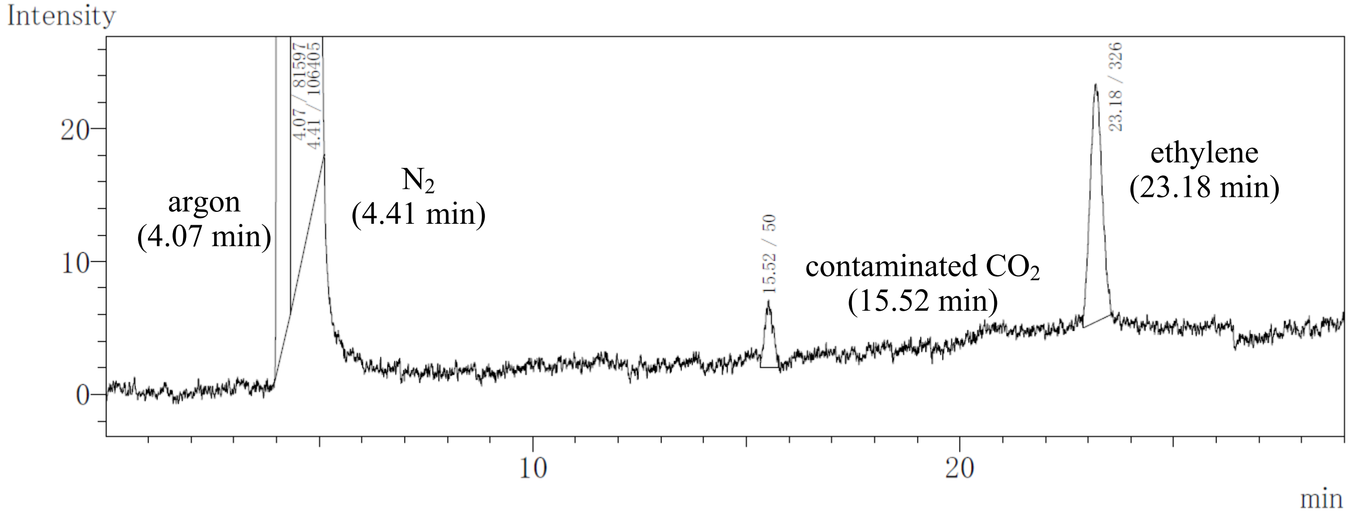


Figure S6. GC chart for a mixture of the reaction of **3** with silver salt and the authentic sample.

References

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