## Supporting Information

# Chlorine-Substituted Germabenzene: Generation and Application as a Precursor for Aryl-Substituted Germabenzenes 

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## 1. Experimental Procedures

## General methods

All manipulations of air- and/or moisture-sensitive compounds were performed in a MIWA-MFG glove box under argon atmosphere. Anhydrous hexane, toluene, $\mathrm{Et}_{2} \mathrm{O}$, THF , and $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ were dried by passage through a GrassContour solvent purification system. Deuterated chloroform $\left(\mathrm{CDCl}_{3}\right)$ was distilled from $\mathrm{CaH}_{2}$ prior to use. Deuterated benzene $\left(\mathrm{C}_{6} \mathrm{D}_{6}\right)$ was distilled from sodium/benzophenone prior to use. Aluminacyclohexadiene 1, ${ }^{\text {S1 }} \mathrm{MesLi}$ (2,4,6-trimethylphenyl), ${ }^{\mathrm{S} 2}$ and Mes*Li (2,4,6-tri(tert-butyl)phenyllithium) ${ }^{53}$ were prepared according to the literature procedures. Other chemicals were used as received.

The nuclear magnetic resonance (NMR) measurements were measured on a JEOL ECS-400 spectrometer ( 399 MHz for ${ }^{1} \mathrm{H}$ and 101 MHz for ${ }^{13} \mathrm{C}$ ). Chemical shifts ( $\delta$ ) are given by definition as dimensionless numbers and relative to ${ }^{1} \mathrm{H}$ or ${ }^{13} \mathrm{C}$ NMR chemical shifts of the residual $\mathrm{CDCl}_{3}$ for ${ }^{1} \mathrm{H}$ ( $\delta=7.26$ ), $\mathrm{CDCl}_{3}$ itself for ${ }^{13} \mathrm{C}(\delta=77.0)$, or the residual $\mathrm{C}_{6} \mathrm{D}_{5} \mathrm{H}$ for ${ }^{1} \mathrm{H}(\delta=7.16), \mathrm{C}_{6} \mathrm{D}_{6}$ itself for ${ }^{13} \mathrm{C}(\delta=128.0)$. The absolute values of the coupling constants are given in Hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet ( t ), quartet ( q ), multiplet ( m ), and broad (br). High-resolution mass spectra were measured on a Bruker micrOTOF II mass spectrometer with an atmospheric pressure chemical ionization (APCI) probe. UV-vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Melting points (m.p.) were determined with a MPA100 OptiMelt (Tokyo Instruments, Inc.) and are uncorrected.

## Synthesis of germacyclohexadiene 5

To a toluene suspension $(5.0 \mathrm{~mL})$ of $\mathrm{GeCl}_{2}$-dioxane $(1.190 \mathrm{~g}, 5.15 \mathrm{mmol})$, toluene solution ( 30.0 $\mathrm{mL})$ of $2(1.226 \mathrm{~g}, 2.06 \mathrm{mmol})$ was added under argon atmosphere. After stirring for 24 h at $100{ }^{\circ} \mathrm{C}$, a reaction mixture was concentrated under vacuum and exposed to air, then quenched with hexane/deionized water. The organic layer was separated, washed with brine, dried over $\mathrm{Na}_{2} \mathrm{SO}_{4}$, then filtered. The resulting solution was concentrated and recrystallized from hexane to give $\mathbf{5}$ as colorless crystals ( $494.5 \mathrm{mg}, 0.947 \mathrm{mmol}, 46 \%$ ).: mp (in a sealed tube) $110-113{ }^{\circ} \mathrm{C}$ (dec.); ${ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 399 \mathrm{MHz}\right) \delta: 1.18(\mathrm{~d}, J=7 \mathrm{~Hz}, 38 \mathrm{H}), 1.36-1.47(\mathrm{~m}, 6 \mathrm{H}), 2.62(\mathrm{t}, J=4 \mathrm{~Hz}, 2 \mathrm{H}), 6.78(\mathrm{t}, J=4$ $\mathrm{Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 100 \mathrm{MHz}\right) \delta: 11.9(\mathrm{CH}), 19.1\left(\mathrm{CH}_{3}\right), 34.7\left(\mathrm{CH}_{2}\right), 137.7\left(4^{\circ}\right), 157.7(\mathrm{CH}$, vinyl); HRMS (APCI, positive) Calc. for $\mathrm{C}_{23} \mathrm{H}_{46} \mathrm{ClGeSi}_{2}$ [ $\left.\mathrm{M}^{+}-\mathrm{Cl}\right]$ : 487.2033. Found: 487.2048. Purity of 5 was confirmed by ${ }^{1} \mathrm{H}$ NMR spectrum shown in Figure S1.

## Generation of chlorogermabenzene 3 using Mes*Li

To a benzene solution $(0.3 \mathrm{~mL})$ of $5(10.0 \mathrm{mg}, 19.1 \mu \mathrm{~mol})$, benzene suspension $(0.3 \mathrm{~mL})$ of Mes*Li ${ }^{\text {S3 }}(6.3 \mathrm{mg}, 25 \mu \mathrm{~mol})$ was added under argon atmosphere. The generation of $\mathbf{3}$ was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy (yield was determined to be $83 \%$ ), and further reaction was performed without any purification: ${ }^{1} \mathrm{H} \mathrm{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 399 \mathrm{MHz}\right) \delta: 1.13(\mathrm{~d}, J=8 \mathrm{~Hz}), 1.45-1.56(\mathrm{~m}), 6.60(\mathrm{t}, J=$ $8 \mathrm{~Hz}), 8.14(\mathrm{~d}, J=8 \mathrm{~Hz})$; HRMS (APCI, positive) Calc. for $\mathrm{C}_{23} \mathrm{H}_{46} \mathrm{ClGeSi}_{2}\left[\mathrm{M}^{+}\right]: 487.2038$. Found: 487.2040.

## Generation of chlorogermabenzene 3 using KHMDS

To a benzene solution ( 0.3 mL ) of $\mathbf{5}(10.0 \mathrm{mg}, 19.1 \mu \mathrm{~mol})$, benzene solution $(0.3 \mathrm{~mL})$ of KHMDS ( $3.8 \mathrm{mg}, 19 \mu \mathrm{~mol}$ ) was added under argon atmosphere. The generation of $\mathbf{3}$ was confirmed by ${ }^{1} \mathrm{H}$ NMR spectroscopy in comparison with 3 generated in the reaction using Mes*Li (yield was determined to be $75 \%$ ), and further reaction was performed without any purification.

## Synthesis of Mes-substituted germabenzene 4-Mes

To a toluene solution ( 3.0 mL ) of $5(200.5 \mathrm{mg}, 0.383 \mathrm{mmol})$, toluene suspension ( 3.0 mL ) of KHMDS $(76.4 \mathrm{mg}, 0.383 \mathrm{mmol})$ was added under argon atmosphere to generate $\mathbf{3}$. After stirred for 5 $\min$, a toluene suspension ( 6.0 mL ) of $\mathrm{MesLi}^{\mathrm{S} 2}(50.0 \mathrm{mg}, 0.396 \mathrm{mmol})$ was add to the reaction mixture. The suspension was stirred for 11 h . After removal of volatiles, the residue was filtered through a pad of Celite ${ }^{\circledR}$ with hexane. The resulting solution was concentrated and recrystallized from hexane to give pure 4-Mes as colorless crystals ( $26.2 \mathrm{mg}, 0.100 \mathrm{mmol}, 26 \%$ ): mp (in a sealed tube) $128-130{ }^{\circ} \mathrm{C}(\mathrm{dec}) ;{ }^{1} \mathrm{H}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 399 \mathrm{MHz}\right) \delta: 1.09(\mathrm{~d}, J=7 \mathrm{~Hz}, 37 \mathrm{H}), 1.19-1.28(\mathrm{~m}, 6 \mathrm{H})$, $2.03(\mathrm{~s}, 3 \mathrm{H}), 2.48(\mathrm{~s}, 6 \mathrm{H}), 6.72(\mathrm{~s}, 2 \mathrm{H}), 6.95(\mathrm{t}, J=9 \mathrm{~Hz}, 1 \mathrm{H}), 8.33(\mathrm{~d}, J=9 \mathrm{~Hz}, 2 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(\mathrm{C}_{6} \mathrm{D}_{6}, 100 \mathrm{MHz}\right) \delta: 12.8(\mathrm{CH}), 19.4\left(\mathrm{CH}_{3}\right), 21.2\left(\mathrm{CH}_{3}\right.$, Mes-4-C), $27.5\left(\mathrm{CH}_{3}\right.$, Mes-2-C), $115.0(\mathrm{CH}$,

3-C of germabenzene ring), 128.0 (CH-Mes) 138.0 ( $4^{\circ}$, Mes), 138.2 ( $4^{\circ}, 2-\mathrm{C}$ of germabenzene ring), $140.2\left(4^{\circ}\right.$, Mes), $142.4\left(4^{\circ}\right.$, Mes), $148.0(\mathrm{CH}, 4-\mathrm{C}$ of germabenzene ring); HRMS (APCI, positive) Calc. for $\mathrm{C}_{32} \mathrm{H}_{56} \mathrm{GeSi}_{2}\left[\mathrm{M}^{+}\right]$: 570.3133. Found: 570.3152. Purity of 4-Mes was confirmed by ${ }^{1} \mathrm{H}$ NMR spectrum shown in Figure S3.

## Estimation of the yield of 4-Mes using KHMDS by ${ }^{1} \mathrm{H}$ NMR spectroscopy

To a toluene solution ( 0.5 mL ) of $\mathbf{5}(20.0 \mathrm{mg}, 38.3 \mu \mathrm{~mol})$, toluene solution $(0.5 \mathrm{~mL})$ of KHMDS ( 7.6 $\mathrm{mg}, 38 \mu \mathrm{~mol}$ ) was added under argon atmosphere to generate 3. After stirred for 5 min , a toluene suspension $(1.0 \mathrm{~mL})$ of $\operatorname{MesLi}(4.8 \mathrm{mg}, 38 \mu \mathrm{~mol})$ was add to the reaction mixture. The suspension was stirred for 6 h . After removal of volatiles, phananthrene $(6.8 \mathrm{mg}, 38 \mu \mathrm{~mol})$ as an internal standard was added. The residue was filtered through a pad of Celite ${ }^{\circledR}$ with hexane. The yield of 4-Mes was estimated by ${ }^{1} \mathrm{H}$ NMR spectroscopy (72\%).

## Synthesis of acridyl-substituted germabenzene 4-Acr using Mes*Li

To a diethyl ether solution ( 2.2 mL ) of $5(100 \mathrm{mg}, 0.191 \mathrm{mmol})$, Mes*Li ( $53.0 \mathrm{mg}, 0.210 \mathrm{mmol}$ ) was added under argon atmosphere to generate 3. To a mixture, diethylether solution of acridyllithium prepared from 9-bromoacridine ( $49.3 \mathrm{mg}, 0.191 \mathrm{mmol}$ ) and ${ }^{n} \mathrm{BuLi} /$ hexane $(74.0 \mu \mathrm{~L}$, $2.76 \mathrm{M}, 0.191 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(2.2 \mathrm{~mL})$ was added at $-35^{\circ} \mathrm{C}$. The reaction mixture was stirred for 10 h at $-35^{\circ} \mathrm{C}$, then removal of volatiles, the residue was filtered through a pad of Celite ${ }^{\circledR}$ with hexane. The resulting solution was concentrated and recrystallized from hexane to give pure 4-Acr as greenish yellow crystals ( $34.9 \mathrm{mg}, 55.6 \mu \mathrm{~mol}, 29 \%$ ): mp (in a sealed tube) $168-170{ }^{\circ} \mathrm{C}(\mathrm{dec}) ;{ }^{1} \mathrm{H}$ NMR ( $\left.\mathrm{C}_{6} \mathrm{D}_{6}, 399 \mathrm{MHz}\right) \delta: 0.50-0.91(\mathrm{~m}, 42 \mathrm{H}), 7.02-7.07(\mathrm{~m}, 3 \mathrm{H}), 7.24$ (ddd, $\left.J=1,7,9 \mathrm{~Hz}, 2 \mathrm{H}\right)$, $8.26(\mathrm{~d}, J=8 \mathrm{~Hz}, 2 \mathrm{H}), 8.39(\mathrm{~d}, J=9 \mathrm{~Hz}, 4 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(\mathrm{C}_{6} \mathrm{D}_{6}, 100 \mathrm{MHz}\right) \delta: 12.5(\mathrm{CH}), 19.1\left(\mathrm{CH}_{3}\right)$, $115.8(\mathrm{CH}, 4-\mathrm{C}$ of germabenzene), $126.0(\mathrm{CH}$, Acr-H), $130.2(\mathrm{CH}$, Acr-H), $131.3(\mathrm{CH}$, Acr-H), 132.0 ( CH, Acr-H), 142.1 ( $4^{\circ}, 2-\mathrm{C}$ of germabenzene ring), $148.4(\mathrm{CH}, 3-\mathrm{C}$ of germabenzene ring), 149.1 ( $4^{\circ}$, Acr) 151.5 ( $4^{\circ}$, Acr) ; HRMS (APCI, positive) Calc. for $\mathrm{C}_{36} \mathrm{H}_{53} \mathrm{GeNSi}_{2}[\mathrm{M}+\mathrm{H}]^{+}: 630.3009$, Found: 630.2993. Purity of 4-Acr was confirmed by ${ }^{1} \mathrm{H}$ NMR spectrum shown in Figure S 4 .

## Estimation of the yield of 4-Acr using Mes*Li by ${ }^{1} \mathrm{H}$ NMR spectroscopy

To a diethyl ether solution $(0.5 \mathrm{~mL})$ of $5(20.0 \mathrm{mg}, 38.3 \mu \mathrm{~mol})$, $\mathrm{Mes} * \mathrm{Li}(10.6 \mathrm{mg}, 42.1 \mu \mathrm{~mol})$ was added under argon atmosphere to generate 3. To a mixture, diethyl ether solution of acridyllithium prepared from 9-bromoacridine $(9.9 \mathrm{mg}, 38.3 \mu \mathrm{~mol})$ and ${ }^{n} \mathrm{BuLi} /$ hexane $(14.0 \mu \mathrm{~L}, 2.76 \mathrm{M}, 38.3$ $\mu \mathrm{mol})$ in $\mathrm{Et}_{2} \mathrm{O}(0.5 \mathrm{~mL})$ was added at $-35^{\circ} \mathrm{C}$. The reaction mixture was stirred for 6 h at $-35^{\circ} \mathrm{C}$, then removal of volatiles, adamantane ( $2.4 \mathrm{mg}, 19 \mu \mathrm{~mol}$ ) as an internal standard was added. The residue was filtered through a pad of Celite ${ }^{\circledR}$ with hexane. The yield of 4-Acr was estimated by ${ }^{1} \mathrm{H}$ NMR spectroscopy (73\%).

## Synthesis of acridyl-substituted germabenzene 4-Acr using KHMDS

To a diethyl ether solution $(3.0 \mathrm{~mL})$ of $5(200 \mathrm{mg}, 0.382 \mathrm{mmol})$, diethyl ether solution ( 3.0 mL ) of KHMDS ( $76.4 \mathrm{mg}, 0.382 \mathrm{mmol}$ ) was added under argon atmosphere to generate 3. To a mixture, diethylether solution of acridyllithium prepared from 9-bromoacridine ( $98.8 \mathrm{mg}, 0.382 \mathrm{mmol}$ ) and ${ }^{n} \mathrm{BuLi} /$ hexane $(140 \mu \mathrm{~L}, 2.76 \mathrm{M}, 0.382 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(6.0 \mathrm{~mL})$ was added at $-35{ }^{\circ} \mathrm{C}$. The reaction mixture was stirred for 10 h at $-35^{\circ} \mathrm{C}$, then removal of volatiles, the residue was filtered through a pad of Celite ${ }^{\circledR}$ with hexane. The resulting solution was concentrated and recrystallized from hexane to give pure 4-Acr as greenish yellow crystals ( $34.6 \mathrm{mg}, 55.0 \mu \mathrm{~mol}, 14 \%$ ).

## Synthesis of Mes-substituted germabenzene 4-Mes by using 2 equiv. of MesLi

To a toluene solution $(0.5 \mathrm{~mL})$ of $5(20.0 \mathrm{mg}, 38.3 \mu \mathrm{~mol})$ and $\mathrm{MesLi}(10.1 \mathrm{mg}, 80.4 \mu \mathrm{~mol})$ was added under argon atmosphere. After stirring for 11 h , a reaction mixture was concentrated under vacuum and phananthrene $(6.8 \mathrm{mg}, 38 \mu \mathrm{~mol})$ as an internal standard was added. The residue was filtered through a pad of Celite ${ }^{\circledR}$ with hexane. The yield of 4-Mes was estimated by ${ }^{1} \mathrm{H}$ NMR spectroscopy (81\%).


Figure S1. ${ }^{1} \mathrm{H}$ (top) and ${ }^{13} \mathrm{C}$ (bottom) NMR spectra of 5 in $\mathrm{C}_{6} \mathrm{D}_{6} \cdot{ }^{\bullet}$ :residual solvent signal.



Figure S2. ${ }^{1} \mathrm{H}$ NMR spectrum of in-situ generated $\mathbf{3}$ in $\mathrm{C}_{6} \mathrm{D}_{6}$ using Mes*Li (top) and KHMDS (bottom). •:residual solvent signal, *: tri(tert-butyl)benzene, ${ }^{\circ}$ : hexamethyldisilazane, x: phenanthrene as an internal standard.


Figure S3. ${ }^{1} \mathrm{H}$ (top) and ${ }^{13} \mathrm{C}$ (bottom) NMR spectra of 4-Mes $\mathrm{inC}_{6} \mathrm{D}_{6}$ ). ${ }^{\bullet}$ :residual solvent signal.


Figure S4. ${ }^{1} \mathrm{H}$ (top) and ${ }^{13} \mathrm{C}$ (bottom) NMR spectra of 4-Acr in $\mathrm{C}_{6} \mathrm{D}_{6} \cdot \bullet$ :residual solvent signal.

## 2. X-ray Crystallographic Analysis

Crystallographic data for 2, 4-Mes, and 4-Acr are summarized in table S1. The crystals were coated with immersion oil and put on a MicroMount ${ }^{\mathrm{TM}}$ (MiTeGen, LLC), and then mounted on diffractometer. Diffraction data were collected on a Rigaku Saturn CCD or a Bruker Photon detectors using MoK $\alpha$ radiation. The Bragg spots were integrated using CrysAlis ${ }^{\text {Pro }}$ program package. ${ }^{\text {S4 }}$ Absorption corrections were applied. All the following procedure for analysis, Yadokari-XG 2009 was used as a graphical interface. ${ }^{\text {S5 }}$ The structure was solved by a direct method with programs of SIR2014 ${ }^{\mathrm{S} 6}$ or SHELEXT ${ }^{\mathrm{S} 7}$ and refined by a full-matrix least squares method with the program of SHELXL-2014 or SHELXL-2018. ${ }^{\text {S7 }}$ Anisotropic temperature factors were applied to all non-hydrogen atoms. The hydrogen atoms were put at calculated positions, and refined applying riding models. The detailed crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition code CCDC 1886739 (2), CCDC 1886740 (4-Mes), and CCDC 1886741 (4-Acr). A copy of the data can be obtained free of charge via http://www.ccdc.cam.ac.uk/products/csd/request.

Table S1. Crystallographic data for 2, 4-Mes, and 4-Acr.

|  | 2 | 4-Mes | 4-Acr |
| :---: | :---: | :---: | :---: |
| Formula | $\mathrm{C}_{23} \mathrm{H}_{46} \mathrm{Cl}_{2} \mathrm{GeSi}_{2}$ | $\mathrm{C}_{32} \mathrm{H}_{56} \mathrm{GeSi}_{2}$ | $\mathrm{C}_{36} \mathrm{H}_{53} \mathrm{GeNSi}_{2}$ |
| M | 522.27 | 569.53 | 628.56 |
| $T / \mathrm{K}$ | 93 | 113 | 123 |
| color | colorless | colorless | yellow |
| size / mm | $0.30 \times 0.14 \times 0.10$ | $0.80 \times 0.02 \times 0.02$ | $0.40 \times 0.38 \times 0.36$ |
| crystal system | Monoclinic | Monoclinic | Monoclinic |
| space group | $P 2{ }_{1} / m$ | $P 2_{1} / n$ | $P 2_{1}$ |
| $a / \AA$ | 7.742(2) | 15.4609(14) | 9.3730 (2) |
| $b / \AA$ | 25.402(6) | 9.2117(9) | $29.3546(9)$ |
| $c / \AA$ | 7.893(2) | 23.847(3) | $12.7365(3)$ |
| $\alpha 1^{\circ}$ | 90 | 90 | 90 |
| $\beta{ }^{\circ}$ | 114.755(3) | 100.048(9) | 93.073(2) |
| $\gamma 1^{\circ}$ | 90 | 90 | 90 |
| $V / \AA^{3}$ | 1409.6(6) | 3344.2(6) | 3499.29(15) |
| Z | 2 | 4 | 4 |
| $D_{x} / \mathrm{g} \mathrm{cm}^{-3}$ | 1.230 | 1.131 | 1.193 |
| $\mu / \mathrm{mm}-1$ | 1.369 | 1.005 | 0.968 |
| $F(000)$ | 556 | 1232 | 1344 |
| $\theta$ range ${ }^{\circ}$ | 3.006 to 27.430 | 2.375 to 25.999 | 1.745 to 25.000 |
| reflections collected | 11373 | 24280 | 25635 |
| unique reflections | 3259 | 6402 | 11482 |
| refined parameters | 140 | 331 | 745 |
| GOF on $F^{2}$ | 1.181 | 1.040 | 1.034 |
| $R 1[I>2 \sigma(I)]^{\text {a }}$ | 0.0405 | 0.0597 | 0.0273 |
| ${ }_{\mathrm{w}} R 2[I>2 \sigma(I)]^{\mathrm{b}}$ | 0.1069 | 0.1223 | 0.0591 |
| $R 1$ (all data) ${ }^{\text {a }}$ | 0.0467 | 0.1116 | 0.0294 |
| $\mathrm{w} R 2$ (all data) ${ }^{\text {b }}$ | 0.1096 | 0.1481 | 0.0615 |
| $\Delta \rho_{\text {min }}, \max / \mathrm{e} \AA^{-3}$ | 0.684, -0.669 | 0.802, -0.882 | 0.545, -0.493 |



Figure S5. Molecular structure of 2 ( $50 \%$ thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 2: Ge1- $\mathrm{C} 1=1.918(3), \mathrm{Ge} 1-\mathrm{Cl} 1=$ $2.1779(12), \mathrm{Ge} 1-\mathrm{Cl} 2=2.1580(12), \mathrm{C} 1-\mathrm{C} 2=1.342(4), \mathrm{C} 1-\mathrm{Sil}=1.890(3), \mathrm{C} 2-\mathrm{C} 3=1.518(4), \mathrm{C} 1-$ $\mathrm{Ge} 1-\mathrm{C} 1 *=109.34(18), \mathrm{Ge} 1-\mathrm{C} 1-\mathrm{C} 2=110.0(2), \mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3=128.5(3), \mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 2 *=118.6(4)$.



Figure S6. A) Molecular structure of 4-Mes (50\% thermal ellipsoid probability). Hydrogen atoms are omitted for clarity. B) Side view of germabenzene ring. Hydrogen atoms and isopropyl groups are omitted for clarity. Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4-Mes: Ge1-C1 $=1.867(4)$, $\mathrm{Ge} 1-\mathrm{C} 5=1.861(4), \mathrm{Ge} 1-\mathrm{C} 6=1.951(4), \mathrm{C} 1-\mathrm{C} 2=1.414(5), \mathrm{C} 1-\mathrm{Si} 1=1.886(4), \mathrm{C} 2-\mathrm{C} 3=1.395(5)$, $\mathrm{C} 3-\mathrm{C} 4=1.387(5), \mathrm{C} 4-\mathrm{C} 5=1.423(5), \mathrm{C} 5-\mathrm{Si} 2=1.880(4), \mathrm{C} 1-\mathrm{Ge} 1-\mathrm{C} 5=111.26(17), \mathrm{Ge} 1-\mathrm{C} 1-\mathrm{C} 2=$ $112.4(3), \mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3=128.6(4), \mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4=126.6(4), \mathrm{C} 3-\mathrm{C} 4-\mathrm{C} 5=128.8(4), \mathrm{C} 4-\mathrm{C} 5-\mathrm{Ge} 1=$ 112.2(3), $\mathrm{C} 1-\mathrm{Ge} 1-\mathrm{C} 6=123.05(16), \mathrm{C} 5-\mathrm{Ge} 1-\mathrm{C} 6=125.54(17)$.


Figure S7. Molecular structure of 4-Acr ( $50 \%$ thermal ellipsoid probability). There are two crystallographically independent molecules in asymmetric unit. Hydrogen atoms are omitted for clarity. Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4-Acr: Ge1-C1 $=1.861(4), \mathrm{Ge} 1-\mathrm{C} 5=$ $1.854(4), \mathrm{Ge} 1-\mathrm{C} 6=1.954(3), \mathrm{C} 1-\mathrm{C} 2=1.406(5), \mathrm{C} 2-\mathrm{C} 3=1.394(5), \mathrm{C} 3-\mathrm{C} 4=1.381(6), \mathrm{C} 4-\mathrm{C} 5=$ $1.405(5), \mathrm{C} 1-\mathrm{Ge} 1-\mathrm{C} 5=111.91(16), \mathrm{Ge} 1-\mathrm{C} 1-\mathrm{C} 2=111.9(3), \mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3=128.2(4), \mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4=$ 127.3(3), C3-C4-C5 = 128.7(3), C4-C5-Ge1 = 111.9(3), C1-Ge1-C6 = 122.13(16), C5-Ge1-C6 = $125.90(16), \mathrm{Ge} 2-\mathrm{C} 37=1.857(4), \mathrm{Ge} 2-\mathrm{C} 41=1.866(4), \mathrm{Ge} 2-\mathrm{C} 42=1.963(3), \mathrm{C} 37-\mathrm{C} 38=1.399(5)$, $\mathrm{C} 38-\mathrm{C} 39=1.397(5), \mathrm{C} 39-\mathrm{C} 40=1.386(6), \mathrm{C} 40-\mathrm{C} 41=1.407(5), \mathrm{C} 37-\mathrm{Ge} 2-\mathrm{C} 41=111.88(16)$, $\mathrm{Ge} 2-\mathrm{C} 37-\mathrm{C} 38=112.2(3), \mathrm{C} 37-\mathrm{C} 38-\mathrm{C} 39=128.6(4), \mathrm{C} 38-\mathrm{C} 39-\mathrm{C} 40=126.7(3), \mathrm{C} 39-\mathrm{C} 40-\mathrm{C} 41=$ 129.3(3), C40-C41-Ge2 = 111.3(3), C37-Ge2-C42 = 120.16(16), C41-Ge2-C42 = 127.74(16).

## 3. UV-vis Absorption Spectra

UV-vis absorption spectra were recorded on a Shimadzu UV-3600 spectrometer using a 10 mm square quartz cell. Dry hexane was used for the sample solution. UV-vis spectra of 4-Mes, 4-Acr and acridine are shown in Figure S8-10.


Figure S8. UV-vis absorption spectra of 4-Mes (yellow line) and 4-Acr (red line) at room temperature in hexane. $\lambda_{\text {max }}$ of 4-Mes ( $\varepsilon$ ): 346 nm (5500), $\lambda_{\text {max }}$ of 4-Acr $(\varepsilon): 386 \mathrm{~nm}(5700), 364 \mathrm{~nm}$ (9900), 346 nm (12000).


Figure S9. Normalized UV-vis absorption spectra of 4-Acr (red line) and acridine (blue line) at room temperature in hexane. $\lambda_{\text {max }}$ of 4-Acr: $386 \mathrm{~nm}, 364 \mathrm{~nm}, 346 \mathrm{~nm}$; $\lambda_{\text {max }}$ of acridine: $371 \mathrm{~nm}, 355$ $\mathrm{nm}, 339 \mathrm{~nm}$.


Figure S10. UV-vis absorption spectra of 4-Acr in hexane (red line) and THF (yellow line) at room temperature in hexane. $\lambda_{\max }$ of 4-Acr in hexane ( $\varepsilon$ ): 386 nm (5700), 364 nm (9900), 346 nm (12000); $\lambda_{\text {max }}$ of 4-Acr in THF ( $\varepsilon$ ): 389 nm (5700), 365 nm (9700), 346 nm (12000).

## 4. Theoretical Calculations

Theoretical calculations were carried out by using Gaussian 16 program package. ${ }^{\mathrm{S} 8}$ The geometry optimizations of 4-Mes, and 4-Acr were performed at the B3LYP/6-31G(d) ${ }^{\text {S9-11 }}$ level of theory. The optimized structures and selected structural parameters of 4-Mes, and 4-Acr are shown in Figures S11 and S12. The HOMO and LUMO of optimized structures of 4-Mes, and 4-Acr are shown in Figures S13 and S14. The calculated excitation energies of 4-Acr at the B3LYP/6-311+G(2d,p) were summarized in Table S2.


Figure S11. Optimized structure of 4-Mes at the B3LYP/6-31G(d) level of theory. Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4-Mes: Ge1-C1 $=1.853$, Ge1-C5 $=1.853, \mathrm{Ge} 1-\mathrm{C} 6=1.943, \mathrm{C} 1-\mathrm{C} 2$ $=1.408, \mathrm{C} 1-\mathrm{Si} 1=1.889, \mathrm{C} 2-\mathrm{C} 3=1.399, \mathrm{C} 3-\mathrm{C} 4=1.399, \mathrm{C} 4-\mathrm{C} 5=1.408, \mathrm{C} 5-\mathrm{Si} 2=1.889, \mathrm{C} 1-$ $\mathrm{Ge} 1-\mathrm{C} 5=110.61, \mathrm{Ge} 1-\mathrm{C} 1-\mathrm{C} 2=113.28, \mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3=128.48, \mathrm{C} 2-\mathrm{C} 3-\mathrm{C} 4=125.82, \mathrm{C} 3-\mathrm{C} 4-\mathrm{C} 5=$ $128.48, \mathrm{C} 4-\mathrm{C} 5-\mathrm{Ge} 1=113.28, \mathrm{C} 1-\mathrm{Ge} 1-\mathrm{C} 6=124.57, \mathrm{C} 5-\mathrm{Ge} 1-\mathrm{C} 6=125.57$.


Figure S12. Optimized structure of 4-Acr at the B3LYP/6-31G(d) level of theory. Selected bond distances $(\AA)$ and angles $\left({ }^{\circ}\right)$ for 4-Acr: Ge1-C1 $=1.848, \mathrm{Ge} 1-\mathrm{C} 4=1.957, \mathrm{C} 1-\mathrm{C} 2=1.406, \mathrm{C} 1-\mathrm{Si} 1$ $=1.894, \mathrm{C} 2-\mathrm{C} 3=1.401, \mathrm{C} 1-\mathrm{Ge} 1-\mathrm{C} 1 *=111.84, \mathrm{Ge} 1-\mathrm{C} 1-\mathrm{C} 2=112.57, \mathrm{C} 1-\mathrm{C} 2-\mathrm{C} 3=128.31, \mathrm{C} 2-$ $\mathrm{C} 3-\mathrm{C} 2 *=126.37, \mathrm{C} 1-\mathrm{Ge} 1-\mathrm{C} 4=124.08$.


Figure S13. Selected MOs of 4-Mes calculated at the B3LYP/6-31G(d) level of theory.
A

B

C

D


F


Figure S14. Selected MOs of 4-Acr calculated at the B3LYP/6-31G(d) level.

Table S2. Calculated electronic transitions of 4-Acr by TD-DFT method (number of states: 8 ) at the B3LYP/6-311+G(2d,p) level (168th orbital and 169th orbitals are the HOMO and LUMO).

| excited state | transition energy / eV | wavelength / nm | oscillator strength | orbital number |
| :---: | :---: | :---: | :---: | :---: |
| 1 | 2.5063 | 494.69 | 0.0002 | 168 -> 169 (0.70612) |
| 2 | 3.0992 | 400.05 | 0.0853 | 167 -> 169 (0.69988) |
| 3 | 3.5852 | 345.82 | 0.0004 | 160 -> 169 (0.57316) |
|  |  |  |  | 161 -> 169 (-0.25907) |
|  |  |  |  | 163 -> 169 (0.26248) |
|  |  |  |  | 164 -> 169 (0.15130) |
| 4 | 3.6539 | 339.32 | 0.0035 | 166 -> 169 (0.69510) |
| 5 | 3.7823 | 327.80 | 0.0019 | 165 -> 169 (0.68991) |
| 6 | 3.7884 | 327.27 | 0.0380 | 163 -> 169 (-0.20203) |
|  |  |  |  | 164 -> 169 (0.53613) |
|  |  |  |  | 167 -> 171 (0.34970) |
|  |  |  |  | 167 -> 172 (0.14192) |
| 7 | 4.0093 | 309.25 | 0.0016 | 160 -> 169 (-0.30640) |
|  |  |  |  | 162 -> 169 (-0.16978) |
|  |  |  |  | 163 -> 169 (0.52957) |
|  |  |  |  | 164 -> 169 (0.26238) |
|  |  |  |  | 168 -> $171(-0.11074)$ |
| 8 | 4.0386 | 307.00 | 0.0712 | 163 -> 169 (0.11310) |
|  |  |  |  | 166 -> 170 (-0.16832) |
|  |  |  |  | 168 -> 171 (0.63838) |
|  |  |  |  | 166 -> 170 (-0.18252) |
|  |  |  |  | 105 -> 110 (-0.17989) |
|  |  |  |  | 106 -> 113 (0.33767) |

## 5.

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