General Comments

NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 500 spectrometers. Chemical shifts (ppm) are given relative to solvent: references for CDCl₃ were 7.26 ppm (¹H-NMR) and 77.0 ppm (¹³C-NMR). ¹³CNMR spectra were acquired on a broad band decoupled mode. High resolution mass spectra (HRMS) were recorded on Agilent 6210. The data are given as mass units per charge (m/z). Multiplets were assigned as s (singlet), d (doublet), t (triplet), dd (doublet of doublet), m (multiplet). All measurements were carried out at room temperature unless otherwise stated. Gas chromatography analysis was performed on an Agilent HP-5890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck).

All reactions were carried out under Ar atmosphere. Except 1a[¹], 2d, 2k, 2m, 2n, 2o, 2q, 2r, 2s these terminal alkynes[²] were synthesized by the relevant literatures, all other reagents were purchased from Sigma-Aldrich or Alfa-Aesar or TCI chemical company.

General procedure

Under an open atmosphere, a 4 mL screwcap vial was charged with Pd(PPh₃)₄ (1 mol %), DABCO (0.3 mmol), alkyne (0.2 mmol), dibutyl(2-iodophenyl)germane (0.2 mmol), toluene (1 mL) and an oven-dried stirring bar. The vial was closed by a Teflon septum and a phenolic cap and connected to the atmosphere through a needle. Then the vial was fixed in an alloy plate and put into Paar 4560 series autoclave (300 mL). At room temperature, the autoclave is flushed with carbon monoxide for three times and 10 bar of carbon monoxide was charged. The autoclave was placed on a heating plate equipped with magnetic stirring and an aluminum block. The reaction was heated at 100°C for 16 hours. Afterwards, the autoclave was cooled to room temperature and the pressure carefully released. After removal of solvent under reduced pressure, pure product was obtained by column chromatography on silica gel (eluent: pentane/ethyl acetate 20:1).

The failed examples for scope:

![Failed examples for scope](image)

References

Characterization of Products

1,1-Dibutyl-2-phenylbenzo[b]germin-4(1H)-one

3aa, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 61 mg, yield 77%.

\(^1\)H NMR (500 MHz, Chloroform-d) δ 8.28 – 8.25 (m, 1H), 7.46 – 7.43 (m, 3H), 7.32 – 7.22 (m, 7H), 1.38 – 1.30 (m, 4H), 1.26 – 1.21 (m, 4H), 1.09 (dq, J = 10.1, 6.5 Hz, 4H), 0.78 (t, J = 7.2 Hz, 6H).

\(^13\)C NMR (126 MHz, CDCl\(_3\)) δ 188.15, 155.88, 145.35, 142.03, 141.77, 140.49, 133.23, 131.09, 130.02, 129.23, 128.68, 127.87, 127.61, 27.38, 26.05, 14.28, 13.64.

HRMS-(EI): calcd. for C\(_{23}\)H\(_{28}\)GeO \([\text{H}]^+\) 391.1461, found 391.1461.

1,1-Dibutyl-2-(m-tolyl)benzo[b]germin-4(1H)-one

3ab, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 48 mg, yield 60%.

\(^1\)H NMR (250 MHz, Chloroform-d) δ 8.25 (ddd, J = 5.8, 3.5, 1.8 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.28 – 7.13 (m, 3H), 7.12 – 7.04 (m, 3H), 2.31 (s, 3H), 1.35 – 1.18 (m, 8H), 1.14 – 1.04 (m, 4H), 0.81 – 0.73 (m, 6H).

\(^13\)C NMR (63 MHz, CDCl\(_3\)) δ 188.06, 156.02, 144.90, 142.07, 141.73, 140.44, 137.34, 133.16, 130.99, 129.95, 129.28, 129.18, 128.33, 127.75, 125.70, 27.34, 26.01, 21.47, 14.25, 13.59.

HRMS-(EI): calcd. for C\(_{24}\)H\(_{30}\)GeO \([\text{H}]^+\) 405.1617, found 405.1616.

1,1-Dibutyl-2-(p-tolyl)benzo[b]germin-4(1H)-one

3ac, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 51 mg, yield 62%.

\(^1\)H NMR (250 MHz, Chloroform-d) δ 8.32 – 8.20 (m, 1H), 7.49 – 7.38 (m, 3H), 7.25 (s, 1H), 7.19 (d, J = 8.2 Hz, 2H), 7.13 – 7.06 (m, 2H), 2.30 (s, 3H), 1.33 – 1.20 (m, 8H), 1.13 – 1.04 (m, 4H), 0.76 (dt, J = 4.7, 2.8 Hz, 6H).

\(^13\)C NMR (63 MHz, CDCl\(_3\)) δ 188.09, 155.73, 144.45, 142.11, 140.44, 138.86, 137.35, 133.14, 130.96, 129.95, 129.16, 128.52, 27.35, 26.01, 21.19, 14.26, 13.59.

HRMS-(EI): calcd. for C\(_{24}\)H\(_{30}\)GeO \([\text{H}]^+\) 405.1617, found 405.1616.
1,1-Dibutyl-2-(3,5-dimethylphenyl)benzo[b]germin-4(1H)-one

![Chemical Structure](image)

**3ad**, eluting with n-heptane and ethyl acetate 30:1 (V/V), yellow oil, 56 mg, yield 67%.

**H NMR** (250 MHz, Chloroform-d) \(\delta\) 8.17 – 8.01 (m, 1H), 7.27 (ddt, \(J = 6.0, 4.8, 2.9\) Hz, 3H), 7.09 – 7.01 (m, 1H), 6.79 – 6.66 (m, 3H), 2.11 (s, 6H), 1.20 – 1.04 (m, 8H), 0.93 (ddddd, \(J = 9.2, 7.6, 4.9, 2.6, 4\) Hz, 4H), 0.65 – 0.56 (m, 6H).

**13C NMR** (63 MHz, CDCl₃) \(\delta\) 190.29, 158.27, 146.63, 144.22, 143.83, 142.51, 139.36, 135.23, 133.04, 132.01, 131.36, 131.25, 128.46, 29.42, 28.10, 23.42, 16.34, 15.68.

**HRMS-(EI):** calcd. for C₂₅H₃₂GeO [M⁺] 419.1774, found 419.1772.

1,1-Dibutyl-2-(4-methoxyphenyl)benzo[b]germin-4(1H)-one

![Chemical Structure](image)

**3ae**, eluting with n-heptane and ethyl acetate 5:1 (V/V), yellow oil, 51 mg, yield 60%.

**H NMR** (250 MHz, Chloroform-d) \(\delta\) 8.30 – 8.19 (m, 1H), 7.48 – 7.40 (m, 3H), 7.28 – 7.21 (m, 3H), 6.83 (d, \(J = 8.8\) Hz, 2H), 3.74 (s, 3H), 1.37 – 1.17 (m, 8H), 1.16 – 1.01 (m, 4H), 0.81 – 0.72 (m, 6H).

**13C NMR** (63 MHz, CDCl₃) \(\delta\) 188.25, 159.19, 155.17, 143.89, 142.16, 140.44, 134.19, 133.13, 130.94, 129.95, 129.85, 129.16, 113.27, 55.31, 27.35, 25.99, 14.26, 13.59.

**HRMS-(EI):** calcd. for C₂₄H₃₀GeO₂ [M⁺] 421.1566, found 421.1566.

1,1-Dibutyl-2-(4-fluorophenyl)benzo[b]germin-4(1H)-one

![Chemical Structure](image)

**3af**, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 62 mg, yield 74%.

**H NMR** (250 MHz, Chloroform-d) \(\delta\) 8.35 – 8.30 (m, 1H), 7.54 – 7.50 (m, 3H), 7.37 – 7.30 (m, 3H), 7.09 – 7.01 (m, 2H), 1.42 – 1.26 (m, 8H), 1.22 – 1.13 (m, 4H), 0.85 (t, \(J = 7.1\) Hz, 6H).

**13C NMR** (63 MHz, CDCl₃) \(\delta\) 187.76, 164.31, 160.40, 154.73, 145.56, 141.79, 140.45, 137.69, 137.63, 133.22, 131.14, 130.43, 130.31, 130.02, 129.25, 114.82, 114.48, 27.34, 25.99, 14.24, 13.58.

**HRMS-(EI):** calcd. for C₂₃H₂₇FGeO [M⁺] 409.1367, found 409.1364.
1,1-Dibutyl-2-(2-fluorophenyl)benzo[b]germin-4(1H)-one

![Structure](image)

3ag, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 57 mg, yield 69%.

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.31 – 8.20 (m, 1H), 7.48 – 7.39 (m, 3H), 7.31 (s, 1H), 7.25 – 7.14 (m, 2H), 7.11 – 6.94 (m, 2H), 1.38 – 1.16 (m, 8H), 1.15 – 1.02 (m, 4H), 0.81 – 0.66 (m, 6H).

$^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 186.65, 161.32, 157.39, 151.30, 147.62, 141.35, 140.39, 133.21, 131.18, 130.82, 130.76, 130.05, 129.42, 129.29, 129.25, 123.85, 123.79, 115.41, 115.05, 27.31, 25.96, 14.24, 13.58.

HRMS-(EI): calcd. for C$_{23}$H$_{27}$FGeO $[\text{M} + \text{H}]^+$ 409.1367, found 409.1364.

1,1-Dibutyl-2-(3-fluorophenyl)benzo[b]germin-4(1H)-one

![Structure](image)

3ah, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 64 mg, yield 78%.

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.40 – 8.28 (m, 1H), 7.56 – 7.48 (m, 3H), 7.40 – 7.35 (m, 1H), 7.35 – 7.25 (m, 1H), 7.16 – 6.96 (m, 3H), 1.47 – 1.25 (m, 8H), 1.22 – 1.05 (m, 4H), 0.85 (t, $J$ = 7.0 Hz, 6H).

$^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 187.46, 164.27, 160.37, 154.64, 154.61, 146.31, 143.79, 143.67, 141.72, 140.36, 133.24, 131.21, 130.03, 129.29, 129.26, 129.13, 124.40, 124.36, 115.98, 115.63, 114.55, 114.22, 27.33, 25.99, 14.24, 13.58.

HRMS-(EI): calcd. for C$_{23}$H$_{27}$FGeO $[\text{M} + \text{H}]^+$ 409.1367, found 409.1367.

1,1-Dibutyl-2-(4-chlorophenyl)benzo[b]germin-4(1H)-one

![Structure](image)

3ai, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 66 mg, yield 78%.

$^1$H NMR (250 MHz, Chloroform-$d$) $\delta$ 8.29 – 8.21 (m, 1H), 7.47 – 7.40 (m, 3H), 7.28 (d, $J$ = 1.1 Hz, 1H), 7.26 – 7.16 (m, 4H), 1.37 – 1.17 (m, 8H), 1.14 – 1.01 (m, 4H), 0.77 (dd, $J$ = 7.5, 6.6 Hz, 6H).

$^{13}$C NMR (63 MHz, CDCl$_3$) $\delta$ 187.56, 154.66, 146.00, 141.71, 140.43, 140.07, 133.52, 133.24, 131.20, 130.05, 130.03, 129.28, 127.96, 27.34, 25.99, 14.25, 13.59.

HRMS-(EI): calcd. for C$_{23}$H$_{27}$ClGeO $[\text{M} + \text{H}]^+$ 425.1071, found 425.1067.
2-(4-Bromophenyl)-1,1-dibutylbenzo[b]germin-4(1H)-one

\[
\begin{align*}
\text{Ge} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} \\
\text{Br} & 
\end{align*}
\]

3aj, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 79 mg, yield 84%.

**H NMR (250 MHz, Chloroform-d)** \(\delta\) 8.28 – 8.21 (m, 1H), 7.50 – 7.41 (m, 4H), 7.40 – 7.38 (m, 1H), 7.28 (s, 1H), 7.19 – 7.12 (m, 2H), 1.36 – 1.17 (m, 8H), 1.14 – 1.01 (m, 4H), 0.82 – 0.72 (m, 6H).

**13C NMR (63 MHz, CDCl3)** \(\delta\) 187.48, 154.70, 146.08, 146.08, 141.69, 140.55, 140.43, 133.26, 131.22, 130.92, 130.39, 130.04, 129.29, 121.74, 27.34, 26.00, 14.25, 13.60.

HRMS-(EI): calcd. for C\(_{23}\)H\(_{27}\)BrGeO \([\text{H}]^+\) 469.0566, found 469.0567.

1,1-Dibutyl-2-(3,4-dichlorophenyl)benzo[b]germin-4(1H)-one

\[
\begin{align*}
\text{Ge} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} \\
\text{Cl} & \quad \text{Cl} 
\end{align*}
\]

3ak, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 68 mg, yield 74%.

**H NMR (250 MHz, Chloroform-d)** \(\delta\) 8.30 – 8.22 (m, 1H), 7.49 – 7.42 (m, 3H), 7.40 – 7.30 (m, 3H), 7.14 – 7.07 (m, 1H), 1.35 – 1.17 (m, 8H), 1.16 – 1.04 (m, 4H), 0.77 (td, \(J = 6.9, 6.4, 0.7\) Hz, 6H).

**13C NMR (63 MHz, CDCl3)** \(\delta\) 187.13, 153.52, 147.07, 141.49, 141.42, 140.36, 133.29, 131.85, 131.63, 131.37, 130.65, 130.08, 129.67, 129.35, 128.16, 27.32, 25.99, 14.24, 13.57.

HRMS-(EI): calcd. for C\(_{23}\)H\(_{26}\)Cl\(_2\)GeO \([\text{H}]^+\) 459.0681, found 459.0682.

1,1-Dibutyl-2-(4-(trifluoromethyl)phenyl)benzo[b]germin-4(1H)-one

\[
\begin{align*}
\text{Ge} & \quad \text{O} \\
\text{Bu} & \quad \text{Bu} \\
\text{CF3} & 
\end{align*}
\]

3al, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 71 mg, yield 76%.

**H NMR (250 MHz, Chloroform-d)** \(\delta\) 8.33 – 8.22 (m, 1H), 7.59 – 7.44 (m, 5H), 7.43 – 7.32 (m, 3H), 1.28 (dtdd, \(J = 15.3, 8.1, 3.9, 1.8\) Hz, 8H), 1.16 – 1.03 (m, 4H), 0.78 (t, \(J = 7.1\) Hz, 6H).

**13C NMR (63 MHz, CDCl3)** \(\delta\) 187.28, 154.68, 147.23, 145.21, 141.49, 140.43, 133.30, 131.35, 130.07, 129.34, 129.31, 129.03, 124.86, 124.80, 124.74, 124.68, 27.33, 25.98, 14.25, 13.57.

HRMS-(EI): calcd. for C\(_{24}\)H\(_{27}\)F\(_3\)GeO \([\text{H}]^+\) 459.1335, found 459.1335.
1,1-Dibutyl-2-(3-nitrophenyl)benzo[b]germin-4(1H)-one

$$\text{Ge} \quad \text{O} \quad \text{Bu} \quad \text{Bu} \quad \text{NO}_2$$

3an, eluting with n-heptane and ethyl acetate 5:1 (V/V), colorless oil, 60 mg, yield 69%.

$^1$H NMR (250 MHz, Chloroform-$d$) δ 8.41 – 8.30 (m, 1H), 8.27 – 8.14 (m, 2H), 7.69 (dt, $J = 7.7, 1.5$ Hz, 1H), 7.59 – 7.45 (m, 5H), 1.49 – 1.27 (m, 8H), 1.27 – 1.13 (m, 4H), 0.86 (t, $J = 7.0$ Hz, 6H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 186.94, 153.53, 148.15, 147.94, 143.09, 141.21, 140.43, 134.95, 133.36, 131.51, 130.15, 129.42, 128.58, 123.77, 122.43, 27.32, 25.99, 14.25, 13.56.

HRMS-(EI): calcd. for C$_{23}$H$_{27}$GeNO$_3$ [H]$^+$ 436.1312, found 436.1312.

3-(1,1-Dibutyl-4-oxo-1,4-dihydrobenzo[b]germin-2-yl)benzonitrile

$$\text{Ge} \quad \text{O} \quad \text{Bu} \quad \text{Bu} \quad \text{CN}$$

3an, eluting with n-heptane and ethyl acetate 10:1 (V/V), colorless oil, 54 mg, yield 65%.

$^1$H NMR (250 MHz, Chloroform-$d$) δ 8.44 – 8.38 (m, 1H), 7.73 (td, $J = 1.7, 0.7$ Hz, 1H), 7.71 – 7.58 (m, 5H), 7.57 – 7.53 (m, 1H), 7.51 – 7.49 (m, 1H), 1.49 – 1.34 (m, 8H), 1.30 – 1.22 (m, 4H), 0.96 – 0.89 (m, 6H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 186.97, 153.71, 147.90, 142.71, 141.25, 140.42, 133.34, 133.21, 132.41, 131.47, 131.03, 130.11, 129.40, 128.54, 118.84, 112.07, 27.32, 25.98, 14.24, 13.56.

HRMS-(EI): calcd. for C$_{24}$H$_{27}$GeNO $[H]^+$ 416.1413, found 416.1415.

1,1-Dibutyl-2-(naphthalen-2-yl)benzo[b]germin-4(1H)-one

$$\text{Ge} \quad \text{O} \quad \text{Bu} \quad \text{Bu}$$

3ao, eluting with n-heptane and ethyl acetate 30:1 (V/V), colorless oil, 58 mg, yield 68%.

$^1$H NMR (250 MHz, Chloroform-$d$) δ 8.26 – 8.17 (m, 1H), 7.71 – 7.65 (m, 4H), 7.40 – 7.30 (m, 7H), 1.35 – 1.15 (m, 8H), 1.10 – 0.99 (m, 4H), 0.71 (t, $J = 7.1$ Hz, 6H).

$^{13}$C NMR (63 MHz, CDCl$_3$) δ 188.10, 155.84, 145.83, 142.01, 140.51, 139.43, 133.22, 132.82, 131.10, 130.00, 129.25, 128.16, 127.56, 127.42, 127.04, 126.98, 125.95, 125.93, 27.38, 26.03, 14.31, 13.61.

HRMS-(EI): calcd. for C$_{27}$H$_{30}$GeO $[H]^+$ 441.1617, found 441.1617.
3ak