

Electronic Supplementary Information

β -Silicon-Effect-Promoted Intermolecular Site-Selective C(sp³)-H Amination with Dirhodium Nitrenes

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Contents:

General	S2
List of abbreviation	S2
Optimization of conditions for dirhodium-catalyzed intermolecular C-H amination (Table S1)	S3
Effects of base and solvent on dirhodium-catalyzed intermolecular C-H amination (Table S2)	S4
Effects of aminating agents on dirhodium-catalyzed intermolecular C-H amination (Table S3)	S4
General procedure for dirhodium-catalyzed intermolecular C-H amination	S5
Specific procedures and characterization data of 2,2,2-trichloroethylcarbamate 2 and 6	S5
Synthesis of substrates and characterization data of new compounds	S16
KIE measurements (Scheme S1, S2 and Figure S1, S2)	S21
Computational details (Figure S3, S4 and S5)	S25
References	S44
¹ H, ¹³ C and ¹⁹ F NMR spectra of new compounds	S46

General. ^1H NMR spectra were recorded on BRUKER Ultrashield Plus (400 MHz) and JEOL ECX-400 (400 MHz), and are reported in ppm using solvent resonance as the internal standard (C_6D_6 at 7.16 ppm, CDCl_3 at 7.26 ppm). Chemical shifts are reported in ppm. When peak multiplicities are reported, the following abbreviations are used: s, singlet; d, doublet; t, triplet; quint, quintet; sept, septet; m, multiplet; br, broadened. ^{13}C NMR spectra were recorded on Ultrashield Plus (100 MHz), JEOL ECX-400 (100 MHz), BRUKER Ascend (125 MHz) and JEOL ECA-600 (150 MHz) and are reported in ppm using solvent resonance as the internal standard (CDCl_3 at 77.16 ppm). ^{19}F NMR spectra were recorded on BRUKER Ultrashield Plus (376 MHz), and are reported in ppm using solvent resonance as the internal standard (trifluoroacetic acid at -76.55 ppm). Infrared (IR) spectra were recorded using HORIBA FT-720. High-resolution mass spectra (HRMS) were obtained on WATERS H-class/Xevo G2-XS and Bruker Impact HD mass spectrometers for ESI, and were obtained on JEOL JMS-700 mass spectrometer for EI. Column chromatography was performed on silica gel 60N (spherical, neutral, KANTO). Preparative TLC was performed on precoated plates (0.50 mm, Merck). TrocNHOTs^1 , $\text{Rh}_2(\text{tpa})_4^2$ and $\text{Rh}_2(\text{piv})_4^3$ were prepared according to the literature procedure. $\text{Rh}_2(\text{oct})_4$ was purchased from TCI. $\text{Rh}_2(n\text{-C}_3\text{F}_7\text{CO}_2)_4$, $\text{Rh}_2(\text{esp})_2$, and KOAc were purchased from Sigma-Aldrich. K_2CO_3 , Na_2CO_3 , Cs_2CO_3 and K_3PO_4 were purchased from Wako Chemical. Anhydrous chlorobenzene and trifluoromethylbenzene were purchased from Sigma-Aldrich. Anhydrous dichloromethane, THF, Et_2O and AcOEt were purchased from Kanto Kagaku.

List of abbreviation

Ns	2-nitrobenzenesulfonyl
Py	pyridine
$\text{Rh}_2(\text{esp})_2$	bis[rhodium($\alpha,\alpha,\alpha',\alpha'$ -tetramethyl-1,3-benzenedipropionic acid)]
$\text{Rh}_2(\text{oct})_4$	rhodium(II) octanoate dimer
$\text{Rh}_2(\text{piv})_4$	rhodium(II) pivalate dimer
$\text{Rh}_2(\text{tpa})_4$	rhodium(II) triphenylacetate dimer
THF	tetrahydrofuran
Troc	2,2,2-trichloroethoxycarbonyl
Ts	<i>p</i> -toluenesulfonyl

Table S1. Optimization of conditions for dirhodium-catalyzed intermolecular C-H amination

$\text{1a (X equiv.)} \xrightarrow[\text{solvent (0.1 M), temperature, time}]{\text{TrocNH-OTs (1.0 equiv.)}, \text{Rh cat. (5 mol\%)}, \text{K}_2\text{CO}_3 \text{ (1.5 equiv.)}} \text{2a}$						
entry	catalyst	solvent	equiv of 1a	Temp (°C)	time (h)	yield ^a
1	Rh ₂ (tpa) ₄	PhCl	10	20	12	80% (72% ^b)
2	Rh ₂ (oct) ₄	PhCl	10	20	12	11%
3	Rh ₂ (piv) ₄	PhCl	10	20	12	14%
4	Rh ₂ (<i>n</i> -C ₃ F ₇ CO ₂) ₄	PhCl	10	20	12	0%
5	Rh ₂ (esp) ₂	PhCl	10	20	12	45%
6	Rh ₂ (tpa) ₄	CH ₂ Cl ₂	10	20	12	0%
7	Rh ₂ (oct) ₄	CH ₂ Cl ₂	10	20	12	7%
8	Rh ₂ (piv) ₄	CH ₂ Cl ₂	10	20	12	13%
9	Rh ₂ (<i>n</i> -C ₃ F ₇ CO ₂) ₄	CH ₂ Cl ₂	10	20	12	0%
10	Rh ₂ (esp) ₂	CH ₂ Cl ₂	10	20	12	16%
11	Rh ₂ (tpa) ₄	AcOEt	10	20	12	46%
12	Rh ₂ (oct) ₄	AcOEt	10	20	12	6%
13	Rh ₂ (piv) ₄	AcOEt	10	20	12	15%
14	Rh ₂ (<i>n</i> -C ₃ F ₇ CO ₂) ₄	AcOEt	10	20	12	0%
15	Rh ₂ (esp) ₂	AcOEt	10	20	12	35%
16	Rh ₂ (tpa) ₄	MeOH	10	20	12	0%
17	Rh ₂ (oct) ₄	MeOH	10	20	12	0%
18	Rh ₂ (piv) ₄	MeOH	10	20	12	0%
19	Rh ₂ (<i>n</i> -C ₃ F ₇ CO ₂) ₄	MeOH	10	20	12	0%
20	Rh ₂ (esp) ₂	MeOH	10	20	12	0%
21	Rh ₂ (tpa) ₄	benzene	10	20	12	72%
22	Rh ₂ (tpa) ₄	PhCF ₃	10	20	12	40%
23	Rh ₂ (tpa) ₄	PhCl	1.5	20	12	21%
24	Rh ₂ (tpa) ₄	PhCl	5.0	20	12	64%
25	Rh ₂ (tpa) ₄	PhCl	10	0	24	56%
26	Rh ₂ (tpa) ₄	PhCl	10	40	6	74%

^a Determined by ¹H NMR using 1,3-dinitrobenzene as an internal standard. ^b Isolated yield.

Rh₂(tpa)₄

Rh₂(oct)₄

Rh₂(piv)₄

Rh₂(*n*-C₃F₇CO₂)₄

Rh₂(esp)₂

Table S2. Effects of base and solvent on dirhodium-catalyzed intermolecular C-H amination

entry	base	solvent	yield ^a
1	K ₂ CO ₃	PhCl	80%
2	Cs ₂ CO ₃	PhCl	50%
3	K ₃ PO ₄	PhCl	54%
4	KOAc	PhCl	53%
5	KOAc	AcOEt	46%
6	KOAc	MeOH	0%

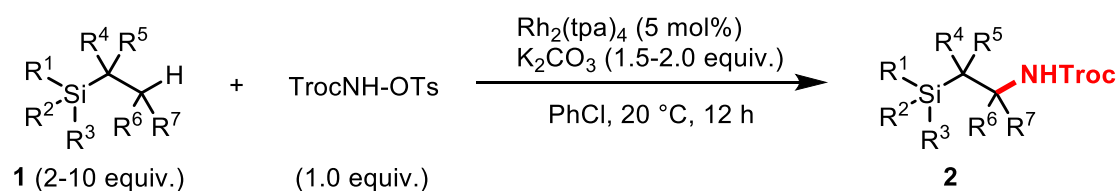
^a Determined by ¹H NMR using 1,3-dinitrobenzene as an internal standard.

Table S3. Effects of aminating agents on dirhodium-catalyzed intermolecular C-H amination

entry	aminating agents	results	entry	aminating agents	results
1	(TrocNH-OTs)	72% yield 2a: R = Troc	5	S9	0% yield S3: R = CO ₂ Et
2	(TrocNH-OMs)	66% yield 2a: R = Troc	6	S10	0% yield S4: R = CO ₂ <i>t</i> -Bu
3	S7	24% yield S1: R = CO ₂ CH ₂ CF ₃	7 ^a	S11	0% yield S5: R = Ts
4	S8	12% yield S2: R = CO ₂ CH ₂ (CF ₃) ₂	8 ^a	S12	0% yield S6: R = Ns

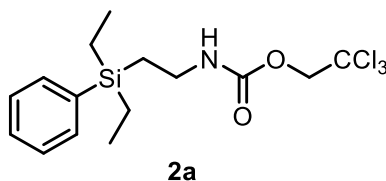
^aRun without K₂CO₃.

General procedure for dirhodium-catalyzed intermolecular C-H amination



To a suspension of silanes **1** (0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.) and K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.) in PhCl (0.5 mL) were added Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) at 20 °C. After being stirred for 12 h, the reaction was quenched by addition of water and extracted with CHCl₃. The organic layer was washed with brine, and dried over Na₂SO₄, filtered, and concentrated. The residue was purified by preparative thin-layer chromatography purification to afford the aminated product **2**.

Specific procedures and characterization data of 2,2,2-trichloroethylcarbamate **2** and **6**



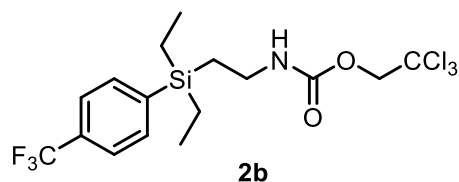
Following the general procedure for intermolecular amination, **1a** (96.2 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2a** (13.7 mg, 72%) as a colorless oil.

Analytical data: ¹H NMR (400 MHz, CDCl₃, 313K) δ: 7.51–7.47 (m, 2H), 7.39–7.34 (m, 3H), 4.85 (br s, 1H), 4.69 (s, 2H), 3.33–3.26 (m, 2H), 1.17–1.13 (m, 2H), 1.03–0.99 (m, 6H), 0.89–0.82 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 154.3, 136.1, 134.2, 129.4, 128.1, 95.8, 74.6, 37.9, 13.8, 7.4, 3.7; IR (neat, cm⁻¹): 3328, 2952, 2360, 1737, 1508, 1365, 1230, 1133, 1014, 721; HRMS-ESI⁺ (*m/z*): Calcd. for C₁₅H₂₂Cl₃NO₂Si [M+Na]⁺ 404.0383; found, 404.0381.

Procedure for C-H amination of **1a** on 1 mmol scale

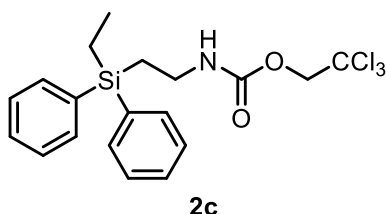
To a suspension of **1a** (1.92 g, 10 mmol, 10 equiv.), TrocNHOTs (363 mg, 1.0 mmol, 1.0 equiv.), K₂CO₃ (207 mg, 1.5 mmol, 1.5 equiv.) in PhCl (10 mL) were added Rh₂(tpa)₄ (67.8 mg, 0.05 mmol, 0.05 equiv.) at 20 °C. After being stirred for 12 h, the reaction was quenched by addition of water

and extracted with CHCl₃. The organic layer was washed with brine, and dried over Na₂SO₄, filtered, and concentrated. The residue was chromatographed on silica gel (CHCl₃/Hexane = 2/1) to afford **2a** (288 mg, 75%) as a colorless oil.



Following the general procedure for intermolecular amination, **1b** (130.2 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2b** (12.9 mg, 57%) as a colorless oil.

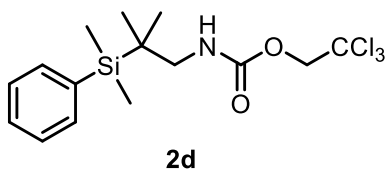
Analytical data: ¹H NMR (400 MHz, CDCl₃, 313K) δ: 7.61 (s, 4H), 4.88 (br s, 1H), 4.69 (s, 2H), 3.42–3.25 (m, 2H), 1.12–1.06 (m, 2H), 1.04–0.98 (m, 6H), 0.92–0.83 (m, 4H); ¹³C NMR (150 MHz, CDCl₃) δ: 154.3, 141.3, 134.4, 131.3 (q, *J* = 31.5 Hz), 124.6, 124.3 (q, *J* = 271.5 Hz), 95.7, 74.6, 37.6, 13.7, 7.3, 3.5; ¹⁹F NMR (376 MHz, CDCl₃) δ: -63.7 (s); IR (neat, cm⁻¹): 3446, 3341, 2957, 1725, 1516, 1326, 1240, 1129, 1061, 726; HRMS-ESI⁺ (*m/z*): Calcd. for C₁₆H₂₁Cl₃F₃NO₂Si [M+Na]⁺ 472.0251; found, 472.0214.



Following the general procedure for intermolecular amination, **1c**⁴ (120 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2c** (9.9 mg, 46%) as a colorless oil.

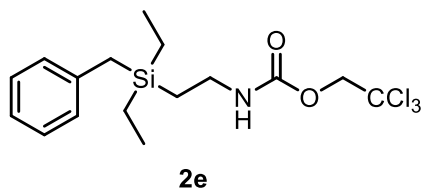
Analytical data: ¹H NMR (400 MHz, CDCl₃, 313K) δ: 7.53–7.51 (m, 4H), 7.43–7.30 (m, 6H), 4.85 (br s, 1H), 4.68 (s, 2H), 3.36–3.31 (m, 2H), 1.47–1.43 (m, 2H), 1.17–1.11 (m, 2H), 1.06–1.02 (m, 3H); ¹³C NMR (100 MHz, CDCl₃) δ: 154.3, 134.9, 129.7, 128.2, 95.8, 74.5, 37.8, 14.2, 7.5, 4.5; IR

(neat, cm^{-1}): 3328, 2952, 1716, 1513, 1232, 1110, 1027, 815, 700; **HRMS-ESI**⁺ (m/z): Calcd. for $\text{C}_{19}\text{H}_{22}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 452.0383; found, 452.0404.



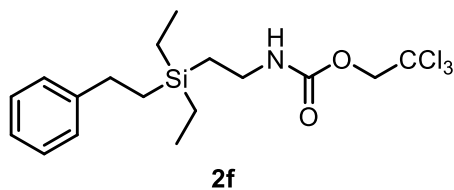
Following the general procedure for intermolecular amination, **1d** (96.2 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K_2CO_3 (10.4 mg, 0.075 mmol, 1.5 equiv.), and $\text{Rh}_2(\text{tpa})_4$ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification ($\text{CHCl}_3/\text{hexane} = 2/1$) to afford **2d** (4.8 mg, 25%) as a colorless oil.

Analytical data: **^1H NMR** (400 MHz, CDCl_3 , 313K) δ : 7.54–7.51 (m, 2H), 7.37–7.34 (m, 3H), 4.85 (br s, 1H), 4.59 (s, 2H), 1.48 (s, 2H), 1.32 (s, 6H), 0.36 (s, 6H); **^{13}C NMR** (100 MHz, CDCl_3) δ : 152.5, 139.3, 133.7, 129.2, 128.1, 96.0, 74.1, 53.8, 30.6, 30.2, -1.1; **IR** (neat, cm^{-1}): 3332, 2969, 2360, 1739, 1506, 1455, 1228, 1110, 835, 715; **HRMS-ESI**⁺ (m/z): Calcd. for $\text{C}_{15}\text{H}_{22}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 404.0383; found, 404.0379.



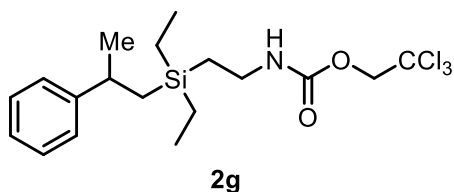
Following the general procedure for intermolecular amination, **1e**⁵ (103 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K_2CO_3 (10.4 mg, 0.075 mmol, 1.5 equiv.), and $\text{Rh}_2(\text{tpa})_4$ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification ($\text{CHCl}_3/\text{hexane} = 2/1$) to afford **2e** (10.5 mg, 53%) as a colorless oil.

Analytical data: **^1H NMR** (400 MHz, CDCl_3 , 313K) δ : 7.23–7.19 (m, 2H), 7.09–7.06 (m, 1H), 7.02 (d, $J = 7.2$ Hz, 2H), 4.80 (br s, 1H), 4.71 (s, 2H), 3.25–3.19 (m, 2H), 2.14 (s, 2H), 0.96 (t, $J = 7.9$ Hz, 6H), 0.89–0.84 (m, 2H), 0.58 (q, $J = 7.9$ Hz, 4H); **^{13}C NMR** (100 MHz, CDCl_3) δ : 154.3, 139.9, 128.5, 128.2, 124.4, 95.8, 74.6, 37.7, 21.9, 13.4, 7.4, 3.5; **IR** (neat, cm^{-1}): 3332, 2950, 2358, 1737, 1515, 1365, 1230, 1133, 1027, 767, 721; **HRMS-ESI**⁺ (m/z): Calcd. for $\text{C}_{16}\text{H}_{24}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 418.0540; found, 418.0533.



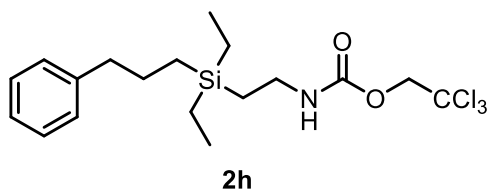
Following the general procedure for intermolecular amination, **1f**⁶ (110 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2f** (12.9 mg, 63%) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.30–7.26 (m, 2H), 7.21–7.15 (m, 3H), 4.86 (br s, 1H), 4.72 (s, 2H), 3.32–3.26 (m, 2H), 2.67–2.62 (m, 2H), 1.00–0.88 (m, 10H), 0.64–0.58 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ: 154.3, 145.0, 128.5, 127.9, 125.8, 95.8, 74.6, 37.9, 30.0, 13.9, 13.7, 7.5, 3.7; **IR** (neat, cm⁻¹): 3328, 2950, 2360, 1735, 1515, 1371, 1228, 1133, 1129, 813, 727; **HRMS-ESI**⁺ (*m/z*): Calcd. for C₁₇H₂₆Cl₃NO₂Si [M+Na]⁺ 432.0696; found, 432.0690.



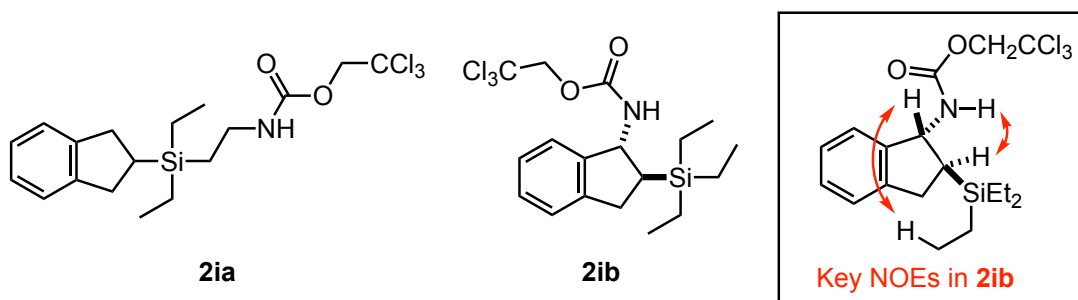
Following the general procedure for intermolecular amination, **1g**⁶ (117 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2g** (14.5 mg, 68%) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.29–7.26 (m, 2H), 7.23–7.15 (m, 3H), 4.71 (br s, 3H), 3.23–3.07 (m, 2H), 2.92–2.84 (m, 1H), 1.30 (d, *J* = 6.8 Hz, 3H), 1.08–1.02 (m, 1H), 0.97–0.91 (m, 1H), 0.89 (t, *J* = 7.9 Hz, 6H), 0.78–0.70 (m, 1H), 0.68–0.60 (m, 1H), 0.54–0.39 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ: 154.2, 149.5, 128.5, 126.8, 126.2, 95.9, 74.5, 37.8, 36.3, 27.0, 22.0, 13.8, 7.5, 4.1, 4.0; **IR** (neat, cm⁻¹): 3325, 2950, 2360, 1739, 1508, 1371, 1228, 1133, 1014, 725; **HRMS-ESI**⁺ (*m/z*): Calcd. for C₁₈H₂₈Cl₃NO₂Si [M+Na]⁺ 446.0853; found, 446.0854.



Following the general procedure for intermolecular amination, **1h**⁶ (117 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2h** (12.4 mg, 58%) as a colorless oil.

Analytical data: ¹H NMR (400 MHz, CDCl₃, 313K) δ: 7.30–7.26 (m, 2H), 7.20–7.16 (m, 3H), 4.85 (br s, 1H), 4.72 (s, 2H), 3.29–3.23 (m, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.67–1.59 (m, 2H), 0.93 (t, *J* = 7.9 Hz, 6H), 0.89–0.85 (m, 2H), 0.63–0.58 (m, 2H), 0.55 (q, *J* = 7.9 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 154.3, 142.5, 128.6, 128.4, 125.9, 95.8, 74.6, 40.2, 38.0, 26.0, 13.7, 11.6, 7.5, 3.7; IR (neat, cm⁻¹): 3325, 2948, 2360, 1739, 1508, 1365, 1228, 1133, 1029, 721; HRMS-ESI⁺ (*m/z*): Calcd. for C₁₈H₂₈Cl₃NO₂Si [M+Na]⁺ 446.0853; found, 446.0850.

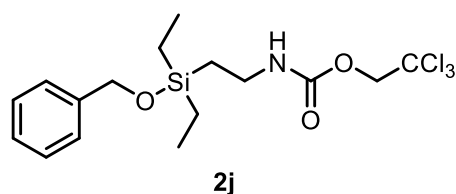


Following the general procedure for intermolecular amination, **1i**⁶ (116 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2ia** (6.8 mg, 34%) and **2ib** (6.5 mg, 31%) as a colorless oil. The relative configuration of **2ib** was assigned from the observed NOEs, shown in the square box.

Analytical data of **2ia**: ¹H NMR (400 MHz, CDCl₃, 313K) δ: 7.23–7.19 (m, 2H), 7.14–7.10 (m, 2H), 4.88 (br s, 1H), 4.72 (s, 2H), 3.35–3.29 (m, 2H), 3.08–3.02 (m, 2H), 2.89–2.83 (m, 2H), 1.79–1.69 (m, 1H), 1.03–0.94 (m, 8H), 0.65 (q, *J* = 7.9 Hz, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 154.3, 144.5, 126.2, 124.3, 95.8, 74.6, 38.0, 35.1, 23.2, 13.2, 7.8, 3.1; IR (neat, cm⁻¹): 3325, 2950, 2360, 1737,

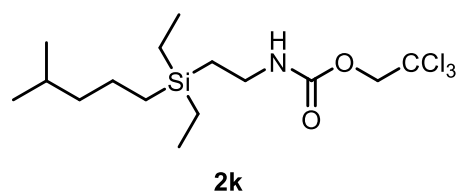
1508, 1373, 1230, 1133, 1016, 725; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₈H₂₆Cl₃NO₂Si [M+Na]⁺ 444.0696; found, 444.0692.

Analytical data of **2ib**: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.31–7.29 (m, 1H), 7.23–7.18 (m, 3H), 5.30 (t, *J* = 9.1 Hz, 1H), 5.07 (br d, *J* = 9.2 Hz, 1H), 4.85–4.78 (m, 2H), 3.13–3.07 (m, 1H), 2.86–2.79 (m, 1H), 1.56–1.49 (m, 1H), 0.98 (t, *J* = 7.9 Hz, 9H), 0.66 (q, *J* = 7.9 Hz, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ: 154.3, 144.3, 143.5, 128.1, 126.9, 124.6, 124.1, 95.9, 74.6, 58.7, 32.9, 32.2, 7.8, 2.7; **IR** (neat, cm⁻¹): 3332, 2950, 2360, 1737, 1508, 1455, 1373, 1228, 1143, 1035, 721; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₈H₂₆Cl₃NO₂Si [M+Na]⁺ 444.0696; found, 444.0693.



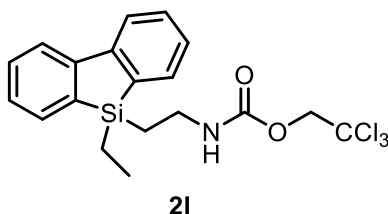
Following the general procedure for intermolecular amination, **1j**⁷ (111 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2j** (9.0 mg, 44%) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.37–7.23 (m, 5H), 5.16 (br s, 1H), 4.75 (s, 2H), 4.71 (s, 2H), 3.41–3.35 (m, 2H), 1.02–0.97 (m, 8H), 0.70 (q, *J* = 7.9 Hz, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ: 154.4, 140.7, 128.5, 127.4, 126.5, 95.9, 74.6, 65.2, 37.3, 14.3, 6.8, 5.2; **IR** (neat, cm⁻¹): 3328, 2954, 2875, 2362, 1716, 1515, 1454, 1236, 1064, 727; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₆H₂₄Cl₃NO₂Si [M+Na]⁺ 434.0489; found, 434.0486.



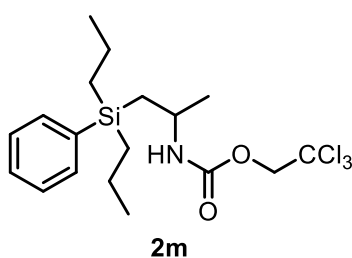
Following the general procedure for intermolecular amination, **1k** (100 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2k** (15.0 mg, 77%) as a colorless oil.

Analytical data: $^1\text{H NMR}$ (400 MHz, CDCl_3 , 313K) δ : 4.87 (br s, 1H), 4.72 (s, 2H), 3.32–3.26 (m, 2H), 1.60–1.50 (m, 1H), 1.35–1.26 (m, 2H), 1.24–1.17 (m, 2H), 1.03–0.86 (m, 14H), 0.62–0.50 (m, 6H); $^{13}\text{C NMR}$ (100 MHz, CDCl_3) δ : 154.3, 95.8, 74.6, 43.4, 38.0, 27.7, 22.7, 21.6, 13.7, 11.9, 7.5, 3.8; **IR** (neat, cm^{-1}): 3328, 2952, 2362, 1735, 1508, 1365, 1230, 1133, 1014, 721; **HRMS-ESI** $^+$ (m/z): Calcd. for $\text{C}_{15}\text{H}_{30}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 412.1009; found, 412.1002.



Following the general procedure for intermolecular amination, **1l**⁸ (119 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K_2CO_3 (10.4 mg, 0.075 mmol, 1.5 equiv.), and $\text{Rh}_2(\text{tpa})_4$ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification ($\text{CHCl}_3/\text{hexane} = 2/1$) to afford **2l** (12.8 mg, 37%) as a colorless oil.

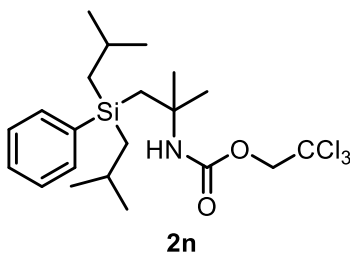
Analytical data: $^1\text{H NMR}$ (400 MHz, CDCl_3 , 323K) δ : 7.83 (d, $J = 7.8$ Hz, 2H), 7.63 (m, $J = 6.9$ Hz, 2H), 7.45 (t, $J = 7.3$ Hz, 2H), 7.28 (t, $J = 7.3$ Hz, 2H), 4.71 (br s, 1H), 4.63 (s, 2H), 3.26–3.21 (m, 2H), 1.34 (t, $J = 8.3$ Hz, 2H), 1.05–0.96 (m, 5H); $^{13}\text{C NMR}$ (150 MHz, CDCl_3 , 323K) δ : 154.1, 148.6, 136.0, 133.3, 130.6, 127.6, 121.1, 95.7, 74.5, 37.6, 13.6, 7.3, 4.3; **IR** (neat, cm^{-1}): 3343, 3064, 2956, 1723, 1515, 1429, 1236, 1131; **HRMS-ESI** $^+$ (m/z): Calcd. for $\text{C}_{19}\text{H}_{20}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{H}]^+$ 428.0402; found, 428.0409.



Following the general procedure for intermolecular amination, **1m** (117 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K_2CO_3 (10.4 mg, 0.075 mmol, 1.5 equiv.), and $\text{Rh}_2(\text{tpa})_4$ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification ($\text{CHCl}_3/\text{hexane} = 2/1$) to afford **2m** (3.8 mg, 18%) as a colorless oil.

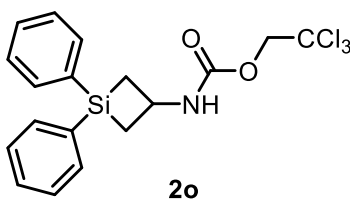
Analytical data: $^1\text{H NMR}$ (400 MHz, CDCl_3 , 313K) δ : 7.50–7.47 (m, 2H), 7.36–7.33 (m, 3H), 4.69–4.61 (m, 3H), 3.93–3.83 (m, 1H), 1.44–1.34 (m, 4H), 1.21–1.15 (m, 4H), 1.09–1.03 (m, 1H), 0.984

(t, $J = 7.2$ Hz, 3H), 0.981 (t, $J = 7.2$ Hz, 3H), 0.89–0.84 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.4, 137.2, 134.1, 129.2, 128.1, 95.9, 74.4, 45.5, 24.7, 22.4, 18.7, 17.5, 15.4, 15.2; **IR** (neat, cm^{-1}): 3328, 2952, 2362, 1739, 1508, 1448, 1371, 1108, 1060, 811, 728; **HRMS-ESI**⁺ (m/z): Calcd. for $\text{C}_{18}\text{H}_{28}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 446.0853; found, 446.0847.



Following the general procedure for intermolecular amination, **1n** (138 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K_2CO_3 (10.4 mg, 0.075 mmol, 1.5 equiv.), and $\text{Rh}_2(\text{tpa})_4$ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification ($\text{CHCl}_3/\text{hexane} = 2/1$) to afford **2n** (2.3 mg, 10%) as a colorless oil.

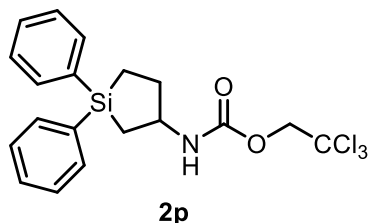
Analytical data: ^1H NMR (400 MHz, CDCl_3 , 313K) δ : 7.56–7.54 (m, 2H), 7.35–7.32 (m, 3H), 4.75 (br s, 1H), 4.56 (s, 2H), 1.86 (sep, $J = 6.6$ Hz, 2H), 1.45 (s, 2H), 1.26 (s, 6H), 0.95 (d, $J = 6.5$ Hz, 6H), 0.89 (d, $J = 6.6$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ : 152.4, 138.2, 134.4, 129.2, 128.0, 96.0, 74.0, 53.9, 30.3, 28.9, 27.0, 26.5, 25.0, 24.1; **IR** (neat, cm^{-1}): 3339, 2952, 2360, 1743, 1500, 1455, 1363, 1226, 1106, 827, 734; **HRMS-ESI**⁺ (m/z): Calcd. for $\text{C}_{21}\text{H}_{34}\text{Cl}_3\text{NO}_2\text{Si}$ $[\text{M}+\text{Na}]^+$ 488.1322; found, 488.1318.



Following the general procedure for intermolecular amination, **1o**⁹ (56.1 mg, 0.25 mmol, 5.0 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K_2CO_3 (10.4 mg, 0.075 mmol, 1.5 equiv.), and $\text{Rh}_2(\text{tpa})_4$ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (hexane/EtOAc = 10/1) to afford **2o** (12.0 mg, 58%) as a colorless oil

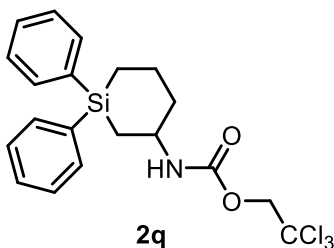
Analytical data: ^1H NMR (400 MHz, C_6D_6 , 343K) δ : 7.49–7.45 (m, 4H), 7.19–7.14 (m, 6H), 4.64 (s, 2H), 4.57 (br s, 1H), 4.27 (m, 1H), 1.90 (ddd, $J = 11.9, 7.8, 2.4$ Hz), 1.27 (ddd, $J = 11.9, 10.1, 2.8$ Hz); ^{13}C NMR (100 MHz, CDCl_3) δ : 153.3, 135.1, 134.8, 134.6, 133.1, 130.4, 128.3, 95.8, 74.5, 45.7, 24.3; **IR** (neat, cm^{-1}): 3407, 3330, 3068, 2978, 1716, 1513, 1428, 1389, 1321, 1240, 1183, 1064,

1027, 941, 840, 734, 700, 585, 496, 468; **HRMS-ESI**⁺ (*m/z*): Calcd. for C₁₈H₁₈Cl₃NO₂Si [M+Na]⁺ 438.0038; found, 437.9991.



Following the general procedure for intermolecular amination, **1p** (23.8 mg, 0.10 mmol, 2.0 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (13.8 mg, 0.10 mmol, 2.0 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.25 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2p** (18.8 mg, 88%) as a colorless oil.

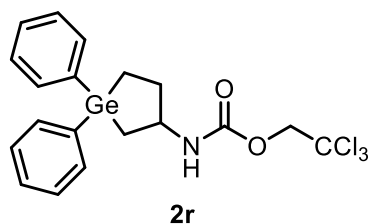
Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.57-7.51 (m, 4H), 7.45-7.34 (m, 6H), 4.96 (br, 1H), 4.73 (s, 2H), 4.11-3.99 (m, 1H), 2.41-2.32 (m, 1H), 1.83-1.74 (m, 1H), 1.69-1.57 (m, 1H), 1.41-1.33 (m, 1H), 1.20-1.10 (m, 1H), 1.09-1.02 (m, 1H); **¹³C NMR** (100 MHz, CDCl₃) δ: 153.9, 135.5, 135.3, 134.8, 129.9, 128.3, 128.2, 95.8, 74.5, 54.1, 33.8, 20.3, 9.7; **IR** (neat, cm⁻¹): 3327, 3052, 2949, 1718, 1519, 1125, 722; **HRMS-ESI**⁺ (*m/z*): Calcd. for C₁₉H₂₀Cl₃NO₂Si [M+Na]⁺ 450.0221; found, 450.0221.



Following the general procedure for intermolecular amination, **1q**¹⁰ (25.2 mg, 0.10 mmol, 2.0 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (13.8 mg, 0.10 mmol, 2.0 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.25 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford a mixture of β-aminated and γ-aminated products (19.8 mg, 89%, β/γ = 25/1). The β-aminated product **2q** was isolated by preparative HPLC (AcOEt/Hexane = 15/85).

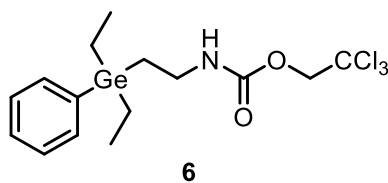
Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.66-7.60 (m, 2H), 7.48-7.30 (m, 8H), 4.92 (br, 1H), 4.71 (s, 2H), 3.89-3.78 (m, 1H), 2.15-2.03 (m, 2H), 1.88 (m, 1H), 1.68-1.56 (m, 1H), 1.41-1.31 (m, 2H), 1.09-0.92 (m, 2H); **¹³C NMR** (150 MHz, CDCl₃) δ: 153.4, 136.3, 134.8, 134.4, 134.1, 129.8, 129.7, 128.4, 128.2, 95.9, 74.5, 50.5, 36.5, 21.7, 20.2, 10.4; **IR** (neat, cm⁻¹): 3335, 3064, 2921,

1718, 1503, 1117, 703; **HRMS-ESI⁺** (*m/z*): Calcd. for C₂₀H₂₂Cl₃NO₂Si [M+Na]⁺ 464.0378; found, 464.0385.



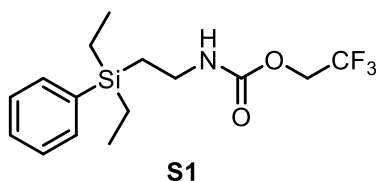
Following the general procedure for intermolecular amination, **1r** (28.8 mg, 0.10 mmol, 2.0 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (13.8 mg, 0.10 mmol, 2.0 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.25 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **2r** (16.7 mg, 71%) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.53–7.48 (m, 4H), 7.42–7.35 (m, 6H), 4.93 (br, 1H), 4.73 (s, 2H), 4.09–4.02 (m, 1H), 2.38–2.32 (m, 1H), 1.87–1.80 (m, 1H), 1.70–1.62 (m, 1H), 1.53–1.47 (m, 1H), 1.33–1.24 (m, 1H) 1.13 (dd, *J* = 8.8, 6.4 Hz); **¹³C NMR** (150 MHz, CDCl₃) δ: 153.9, 137.4, 137.2, 134.2, 129.3, 129.0, 128.6, 128.5, 95.8, 74.5, 54.9, 34.5, 20.5, 11.0; **IR** (neat, cm⁻¹): 3407, 3319, 2917, 1726, 1503, 1225, 1120, 801, 739, 699; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₉H₂₀Cl₃NO₂Ge [M+Na]⁺ 491.9694; found, 491.9645.



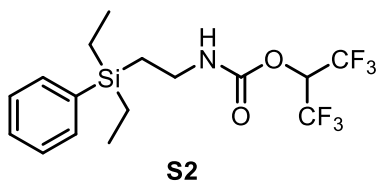
Following the general procedure for intermolecular amination, **5** (118 mg, 0.50 mmol, 10 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **6** (9.8 mg, 46%) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.44–7.42 (m, 2H), 7.38–7.32 (m, 3H), 4.87 (br s, 1H), 4.69 (s, 2H), 3.37–3.32 (m, 2H), 1.30–1.26 (m, 2H), 1.15–1.02 (m, 10H); **¹³C NMR** (100 MHz, CDCl₃) δ: 154.3, 138.6, 133.9, 128.7, 128.3, 95.8, 74.5, 38.8, 13.6, 9.0, 4.7; **IR** (neat, cm⁻¹): 2948, 2360, 1716, 1509, 1234, 1133, 1020, 813, 700; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₅H₂₂Cl₃GeNO₂ [M+Na]⁺ 449.9826; found, 449.9811.



Following the general procedure for intermolecular amination, **1a** (96.2 mg, 0.50 mmol, 10 equiv.), CF₃CH₂OCONHOTs (15.7 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford **S1** (3.0 mg, 24%) as a colorless oil.

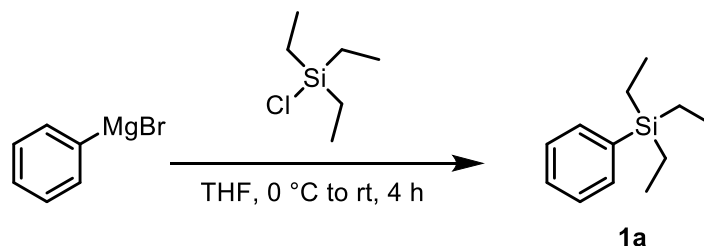
Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.51–7.46 (m, 2H), 7.39–7.33 (m, 3H), 4.77 (br s, 1H), 4.41 (q, *J* = 8.5 Hz, 2H), 3.29–3.24 (m, 2H), 1.16–1.10 (m, 2H), 1.03–0.99 (m, 6H), 0.88–0.82 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ: 154.2, 136.1, 134.1, 129.4, 128.1, 123.3 (q, *J* = 275.8 Hz), 60.8 (q, *J* = 36.3 Hz), 37.9, 13.8, 7.4, 3.7; **IR** (neat, cm⁻¹): 3328, 2954, 2360, 1716, 1508, 1365, 1284, 1232, 1164, 983, 700; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₅H₂₂F₃NO₂Si [M+Na]⁺ 356.1270; found, 356.1263.



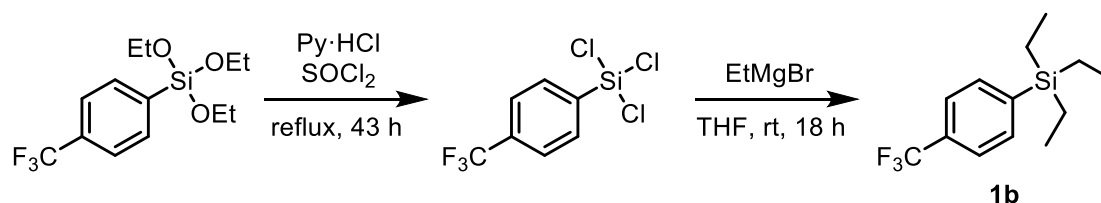
Following the general procedure for intermolecular amination, **1a** (96.2 mg, 0.50 mmol, 10 equiv.), (CF₃)₂CHOCONHOTs (19.1 mg, 0.05 mmol, 1.0 equiv.), K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.), and Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) were stirred at 20 °C in PhCl (0.5 mL) for 12 h. The crude material was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 1/1) to afford **S2** (2.4 mg, 12%) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃, 313K) δ: 7.49–7.47 (m, 2H), 7.40–7.34 (m, 3H), 5.65 (sep, *J* = 6.2 Hz, 2H), 4.92 (br s, 1H), 3.33–3.28 (m, 2H), 1.17–1.13 (m, 2H), 1.03–0.99 (m, 6H), 0.89–0.83 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ: 152.2, 135.9, 134.1, 129.5, 128.2, 120.8 (q, *J* = 279.7 Hz), 67.6 (sep, *J* = 34.2 Hz), 38.4, 13.6, 7.4, 3.6; **IR** (neat, cm⁻¹): 3332, 2969, 2360, 1739, 1508, 1375, 1230, 1190, 1108, 904, 721; **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₆H₂₁F₆NO₂Si [M+Na]⁺ 424.1143; found, 424.1143.

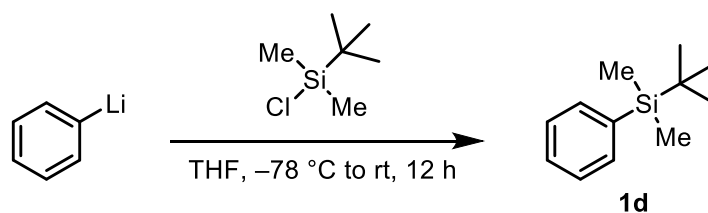
Synthesis of substrates and characterization data of new compounds



Following the literature procedure,¹¹ chlorotriethylsilane (240 mg, 1.59 mmol) and CuI (15 mg, 0.08 mmol) was placed in a 20-mL reaction flask under argon in THF (10 mL). The flask was cooled to 0 °C. Phenylmagnesium bromide (1.0 M THF solution, 3.2 mL, 3.2 mmol) was slowly introduced to the flask. The reaction mixture was stirred for 1 h at 0 °C. After being stirred for 3 h at rt, a saturated aqueous solution of NH₄Cl was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na₂SO₄, filtered and concentrated. The residue was chromatographed on silica gel (Hexane) to afford **1a** (270 mg, 88% yield) as a colorless oil. The spectral data of **1a** were identical to those reported.¹²

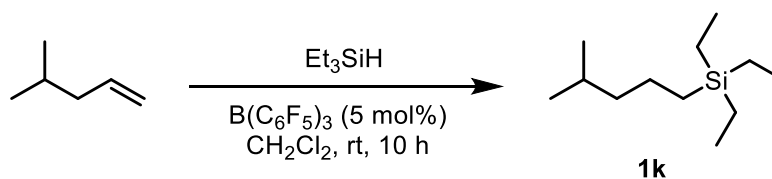


Following the literature procedure,¹³ triethoxy(4-(trifluoromethyl)phenyl)silane (8.12 g, 26.3 mmol) was mixed with thionyl chloride (30 mL) and pyridinium hydrochloride (400 mg, 3.46 mmol), and the mixture was refluxed and stirred for 43 h. The excess thionyl chloride was removed under reduced the pressure, and the residue was dissolved in THF (130 mL) and cooled to 0 °C. Ethylmagnesium bromide (3.0 M in Et₂O) was added slowly to the solution. After being stirred for 18 h at rt, the reaction was quenched by addition of 1N HCl. The resulting mixture was extracted with diethylether, the organic layer was washed with NaHCO₃ aq., brine, and dried over Na₂SO₄, filtered and concentrated. The residue was chromatographed on silica gel (Hexane) to afford **1b** (3.79 g, 55% yield) as a colorless oil. The spectral data of **1b** were identical to those reported.¹⁴ **1b-d₁₅** (1.67 g, 49%) was also synthesized by the same procedure using the deuterated Grignard reagent (C₂D₅MgBr)



Following the literature procedure,¹⁵ solution of phenyllithium in dibutyl ether (1.0 mL of 1.8 M solution, 1.80 mmol) was mixed with dry THF (5 mL) under N₂ and cooled to -78 °C. *tert*-Butyldimethylsilyl chloride (0.29 g, 1.89 mmol) was added slowly to this solution. After being stirred for 12 h at rt, the reaction was quenched by addition of water and extracted with diethylether. The organic layer was washed with water, and brine, and dried over Na₂SO₄, filtered, and concentrated. The residue was chromatographed on silica gel (hexane) to afford **1d** (280 mg, 82% yield) as a colorless oil.

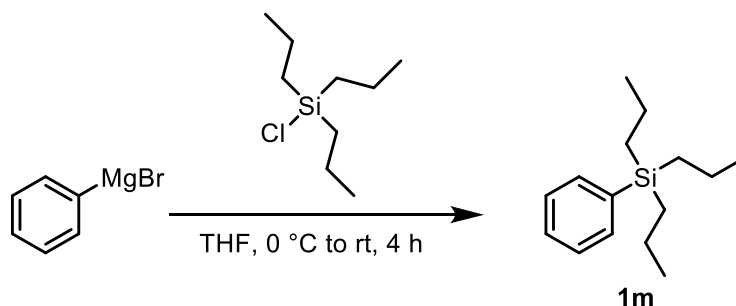
Analytical data: **¹H NMR** (400 MHz, CDCl₃) δ: 7.54–7.50 (m, 2H), 7.38–7.32 (m, 3H), 0.88 (s, 9H), 0.28 (s, 6H); **¹³C NMR** (100 MHz, CDCl₃) δ: 137.9, 134.6, 128.9, 127.6, 26.6, 17.0, -6.0; **IR** (neat, cm⁻¹): 2925, 2854, 2360, 1461, 1247, 1105, 831, 769, 734, 700. **HRMS-EI⁺** (*m/z*): Calcd. for C₁₂H₂₀Si [M⁺] 192.1334; found, 192.1335.



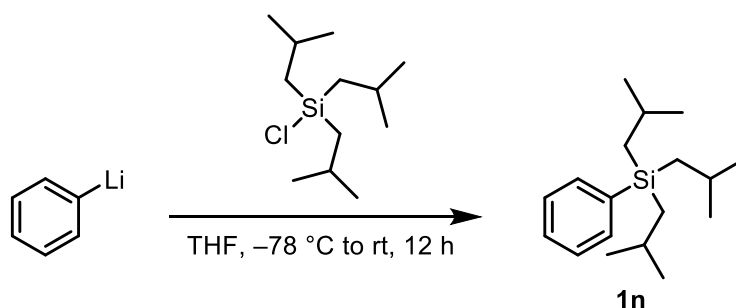
Following the literature procedure,⁶ to a stirred solution of B(C₆F₅)₃ (26 mg, 5 mol%) in anhydrous CH₂Cl₂ (1 mL) was added Et₃SiH (0.19 mL, 1.2 mmol), followed by addition of 4-methyl-1-pentene (0.13 mL, 1.0 mmol). The reaction mixture was stirred at rt for 10 h. The mixture was filtered through a short column (silica gel, CH₂Cl₂) and concentrated. The residue was chromatographed on silica gel (hexane) to afford **1k** (240 mg, 67% yield) as a colorless oil.

Analytical data: **¹H NMR** (400 MHz, CDCl₃) δ: 1.61–1.48 (m, 1H), 1.32–1.24 (m, 2H), 1.22–1.16 (m, 2H), 0.95–0.90 (m, 9H), 0.86 (d, *J* = 6.6 Hz, 6H), 0.55–0.45 (m, 8H); **¹³C NMR** (100 MHz, CDCl₃) δ: 43.6, 27.7, 22.8, 21.7, 11.6, 7.6, 3.5; **IR** (neat, cm⁻¹): 2952, 2873, 1739, 1463, 1417, 1365, 1232, 1016, 906, 730.

HRMS-EI⁺ (*m/z*): Calcd. for C₁₂H₂₈Si [M⁺] 200.1960; found, 200.1961.

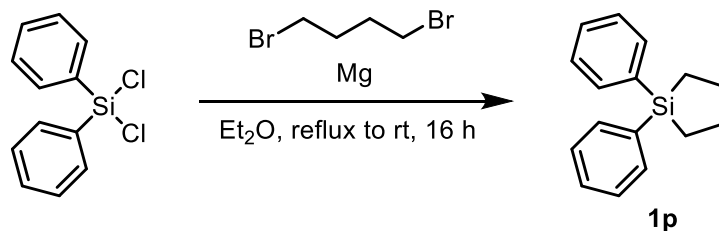


Following the literature procedure,¹¹ chlorotripropylsilane (307 mg, 1.59 mmol) and CuI (15 mg, 0.08 mmol) was placed in a 20-mL reaction flask under argon in THF (10 mL). The flask was cooled to 0 °C. Phenylmagnesium bromide (1.0 M THF solution, 3.2 mL, 3.2 mmol) was slowly introduced to the flask. The reaction mixture was stirred for 1 h at 0 °C. After being stirred for 3 h at rt, a saturated aqueous solution of NH₄Cl was added. The organic compounds were extracted with ethyl acetate three times. The combined organic part was dried over Na₂SO₄, filtered and concentrated. The residue was chromatographed on silica gel (Hexane) to afford **1m** (350 mg, 94% yield) as a colorless oil. The spectral data of **1m** were identical to those reported.¹⁶



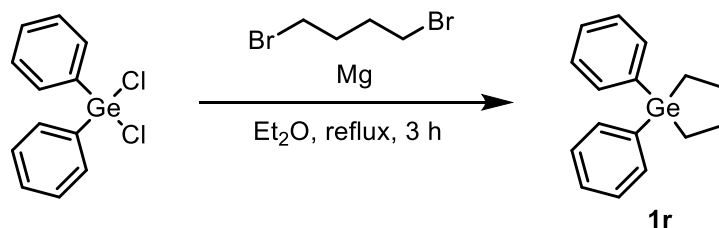
Following the literature procedure,¹⁵ solution of phenyllithium in dibutyl ether (1.0 mL of 1.8 M solution, 1.80 mmol) was mixed with dry THF (5 mL) under N₂ and cooled to -78 °C. Triisobutylsilyl chloride (0.51 mL, 1.89 mmol) was added slowly to this solution. After being stirred for 12 h at rt, the reaction was quenched by addition of water and extracted with diethylether. The organic layer was washed with water, and brine, and dried over Na₂SO₄, filtered, and concentrated. The residue was chromatographed on silica gel (hexane) to afford **1n** (270 mg, 55% yield) as a colorless oil.

Analytical data: ¹H NMR (400 MHz, CDCl₃) δ: 7.54–7.49 (m, 2H), 7.33–7.30 (m, 3H), 1.84–1.71 (m, 3H), 0.88 (d, *J* = 6.6 Hz, 18H), 0.85 (d, *J* = 6.8 Hz, 6H); ¹³C NMR (100 MHz, CDCl₃) δ: 139.4, 134.3, 128.6, 127.6, 26.7, 25.0, 24.3; IR (neat, cm⁻¹): 2952, 2360, 1463, 1326, 1216, 1106, 1037, 906, 829, 732. HRMS-EI⁺ (*m/z*): Calcd. for C₁₈H₃₂Si [M⁺] 276.2273; found, 276.2272.



Following the literature procedure,¹⁷ a portion of 1 mL of a solution of 1,4-dibromobutane (1.54 mL, 13 mmol) in diethyl ether (5 mL) was added to a stirred suspension of magnesium turnings (729 mg, 30 mmol) in diethyl ether (5 mL), and the reaction was started by gentle heating. Subsequently, the remaining 1,4-dibromobutane solution was added within 2 h, causing the mixture to boil under reflux. After the addition was complete, the mixture was heated under reflux for a further 90 min and then cooled to 20 °C within 1 h. The resulting two-phase Grignard reagent was added dropwise within 2 h to a solution of dichlorodiphenylsilane (2.08 mL, 10 mmol) in diethyl ether (5 mL), causing the mixture to boil under reflux. The reaction mixture was stirred at 20 °C for 16 h and acidified with 1N HCl. The resulting mixture was extracted with diethylether, the organic layer was washed with NaHCO₃ aq., brine, and dried over Na₂SO₄, filtered and concentrated. The residue was chromatographed on silica gel (Hexane) to afford **1p** (1.37 g, 57% yield) as a colorless oil.

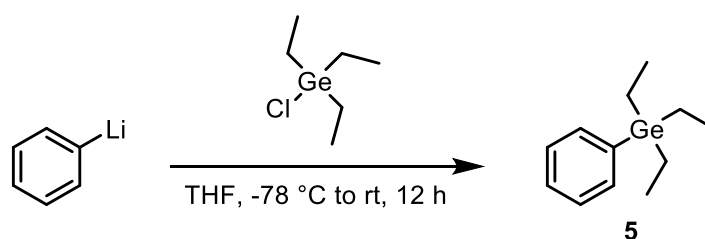
Analytical data: **¹H NMR** (400 MHz, CDCl₃) δ: 7.59-7.55 (m, 4H), 7.42-7.35 (m, 6H), 1.85-1.80 (m, 4H), 1.17-1.11 (m, 4H); **¹³C NMR** (100 MHz, CDCl₃) δ: 137.1, 134.9, 129.3, 128.0, 27.9, 12.3; **IR** (neat, cm⁻¹): 3066, 2933, 1427, 1109, 694. **HRMS-ESI⁺** (*m/z*): Calcd. for C₁₈H₃₂Si [M⁺] 238.1178; found, 238.1175.



Following the literature procedure,¹⁷ a portion of 0.2 mL of a solution of 1,4-dibromobutane (0.23 mL, 1.95 mmol) in diethyl ether (1 mL) was added to a stirred suspension of magnesium turnings (109 mg, 4.5 mmol) in diethyl ether (1 mL), and the reaction was started by gentle heating. Subsequently, the remaining 1,4-dibromobutane solution was added within 2 h, causing the mixture to boil under reflux. After the addition was complete, the mixture was heated under reflux for a further 90 min and then cooled to 20 °C within 1 h. The resulting two-phase Grignard reagent was added dropwise within 2 h to a solution of dichlorodiphenylgermane (0.31 mL, 1.5 mmol) in diethyl ether (1 mL), causing the mixture to boil under reflux. The reaction mixture was stirred under reflux

for 1 h and acidified with 1N HCl. The resulting mixture was extracted with diethylether, the organic layer was washed with NaHCO₃ aq., brine, and dried over Na₂SO₄, filtered and concentrated. The residue was chromatographed on silica gel (Hexane) to afford **1r** (184 mg, 43% yield) as a colorless oil.

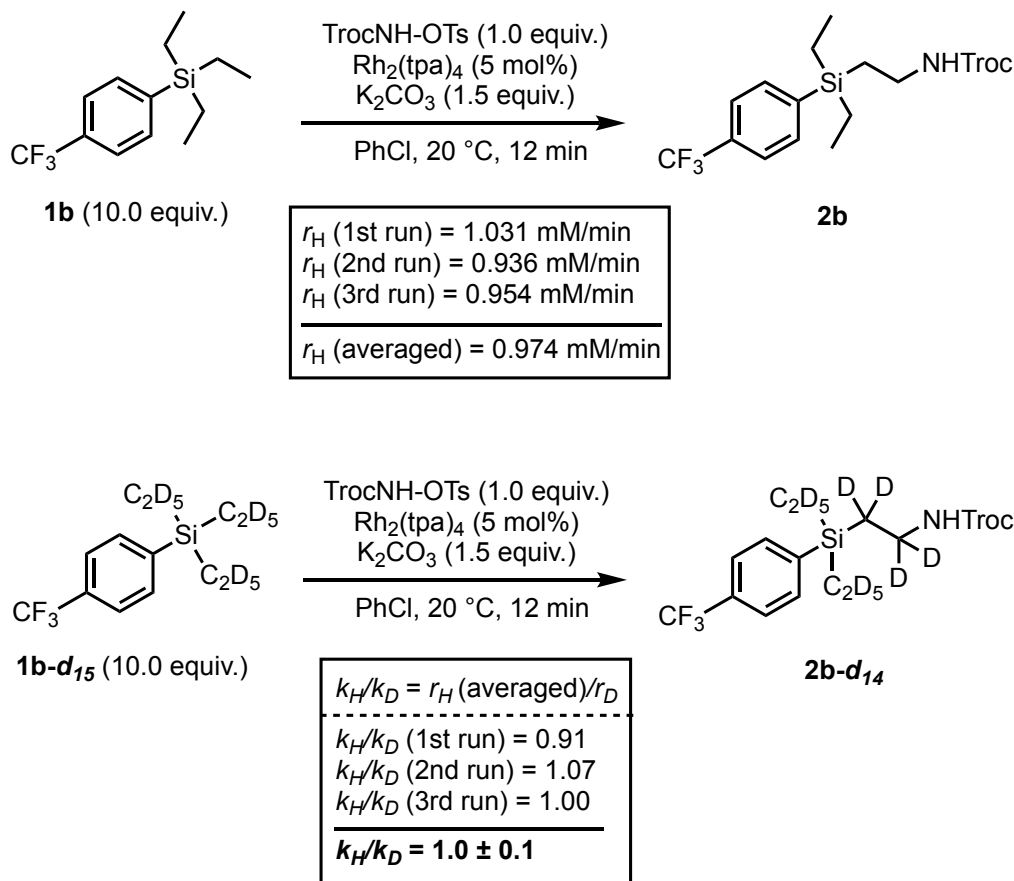
Analytical data: ¹H NMR (400 MHz, CDCl₃) δ: 7.56-7.50 (m, 4H), 7.40-7.33 (m, 6H), 1.88-1.77 (m, 4H), 1.29-1.20 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ: 138.9, 134.4, 128.8, 128.3, 28.8, 13.5; IR (neat, cm⁻¹): 3064, 2924, 2850, 1429, 1092, 776, 697, 583, 461. HRMS-EI⁺ (*m/z*): Calcd. for C₁₈H₃₂Ge [M⁺] 284.0623; found, 284.0619.



A solution of phenyllithium in dibutyl ether (2.0 mL of 1.8 M solution, 3.60 mmol) was mixed with dry THF (10 mL) under N₂ and cooled to -78 °C. Chlorotriethylgermane (0.64 mL, 3.78 mmol) was added slowly to this solution. After being stirred for 12 h at rt, the reaction was quenched by addition of water and extracted with diethylether. The organic layer was washed with water, and brine, and dried over Na₂SO₄, filtered, and concentrated. The residue was chromatographed on silica gel (hexane) to afford **5** (600 mg, 70% yield) as a colorless oil. The spectral data of **5** were identical to those reported.¹⁸

KIE measurement

Parallel KIE



Scheme S1. Determination of intermolecular KIE via initial rate (r_{H} and r_{D}) analysis. (a) Determination of r_{H} (averaged) by three times experiments. See also Figure S1. (b) Determination of $k_{\text{H}}/k_{\text{D}}$ by using r_{D} (1st-3rd run) and r_{H} (averaged). See also Figure S2.

To a suspension of **1b** or **1b-d₁₅** (1.0 mmol, 10.0 equiv.), TrocNHOTs (36.3 mg, 0.10 mmol, 1.0 equiv.) and K_2CO_3 (20.7 mg, 0.15 mmol, 1.5 equiv.) in PhCl (1.0 mL) was added $\text{Rh}_2(\text{tpa})_4$ (6.8 mg, 0.0050 mmol, 0.05 equiv.) at 20 °C. Aliquots (50 μL) were taken every 2 minutes from the reaction flask for 12 minutes, and filtered through a short silica pad with 1 mL of CDCl_3 for ^{19}F NMR analysis. The yield was determined from the comparison of the integrals of the product peaks relative to the 4-bromobenzofluoride internal standard. The experiments were performed three times for each substrate (Figure S1 and S2). The averaged r_{H} was calculated by the three runs shown in Figure S1. The $k_{\text{H}}/k_{\text{D}}$ value ($k_{\text{H}}/k_{\text{D}} = 1.0 \pm 0.1$) was determined by using the averaged r_{H} and r_{D} (1st-3rd runs) shown in Figure S2.

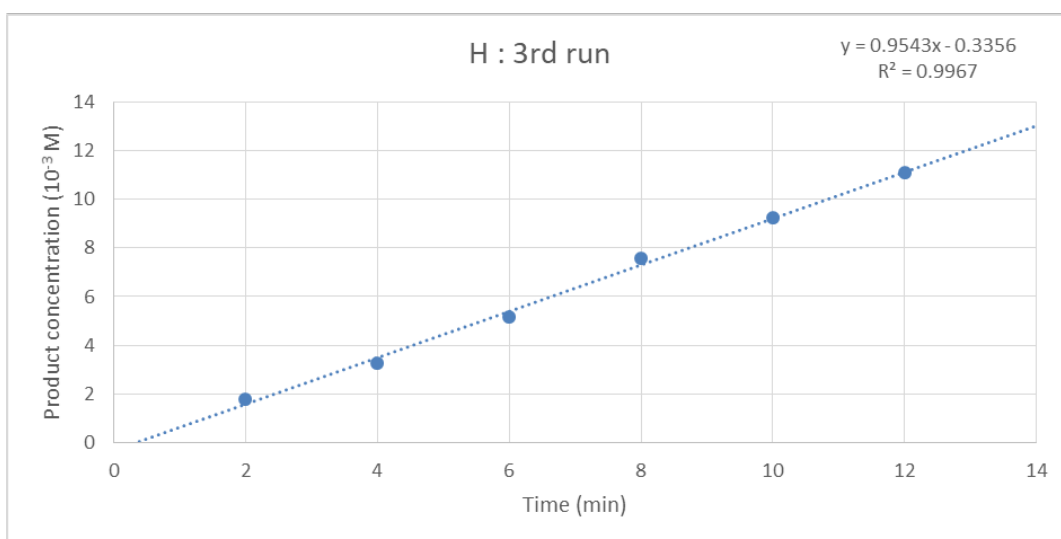
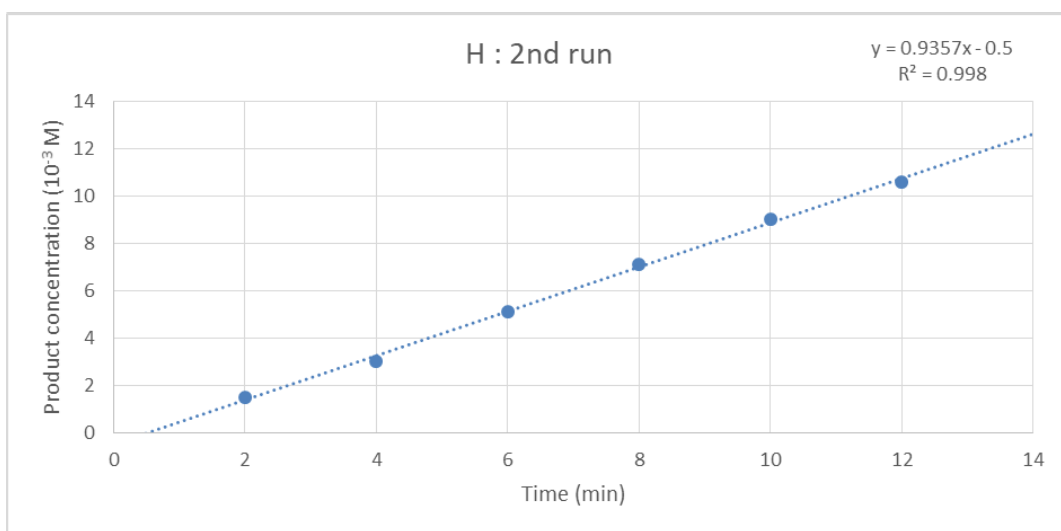
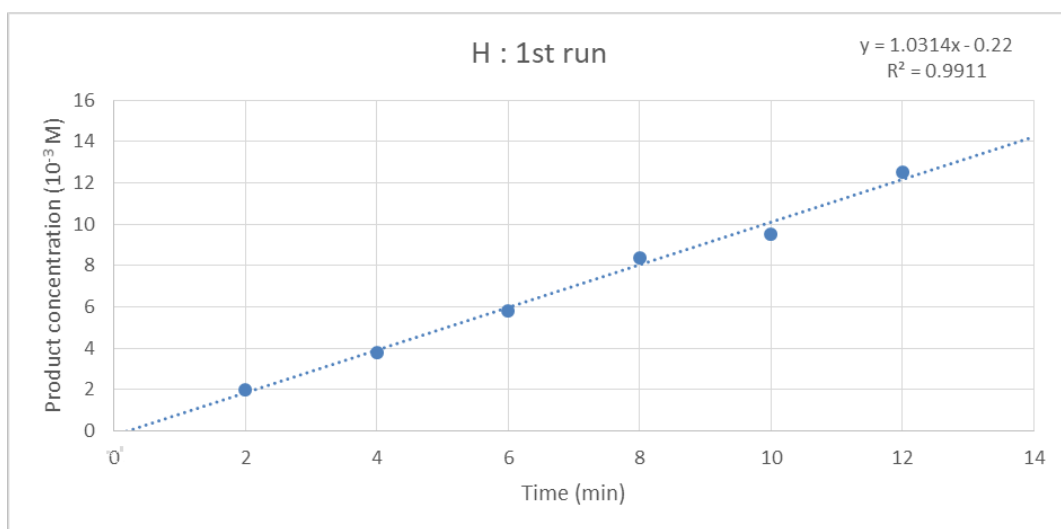


Figure S1. Initial rate analysis for C-H amination of 1b

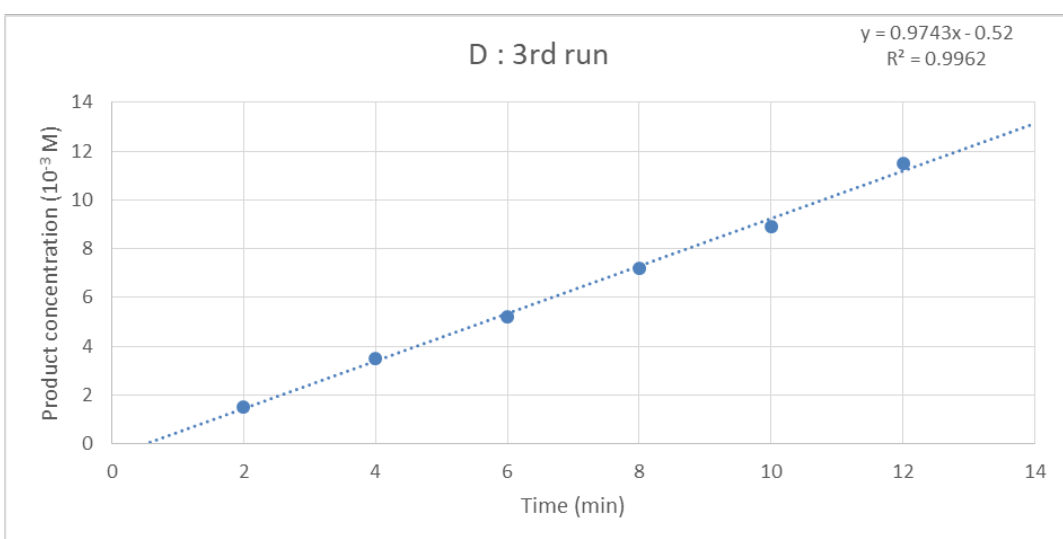
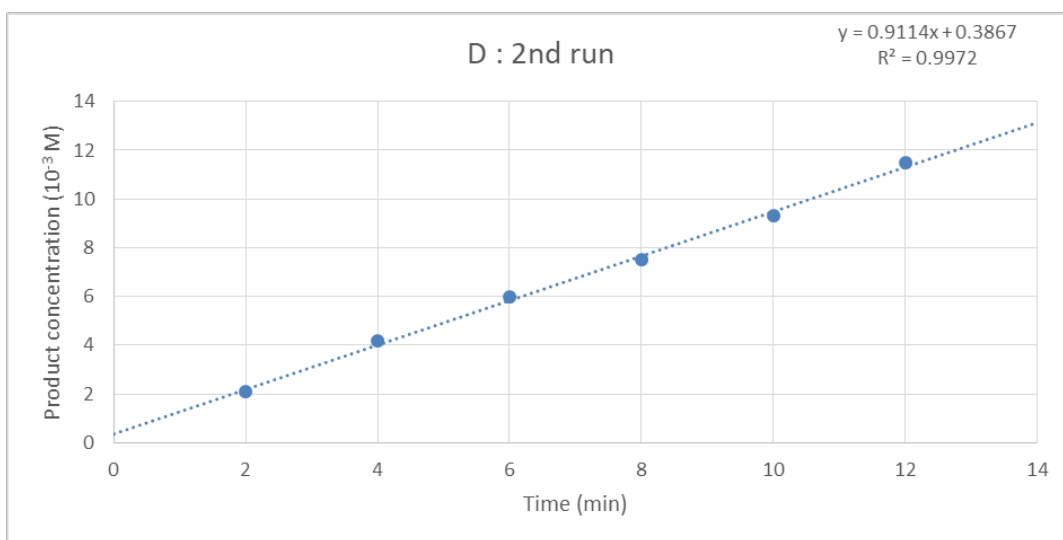
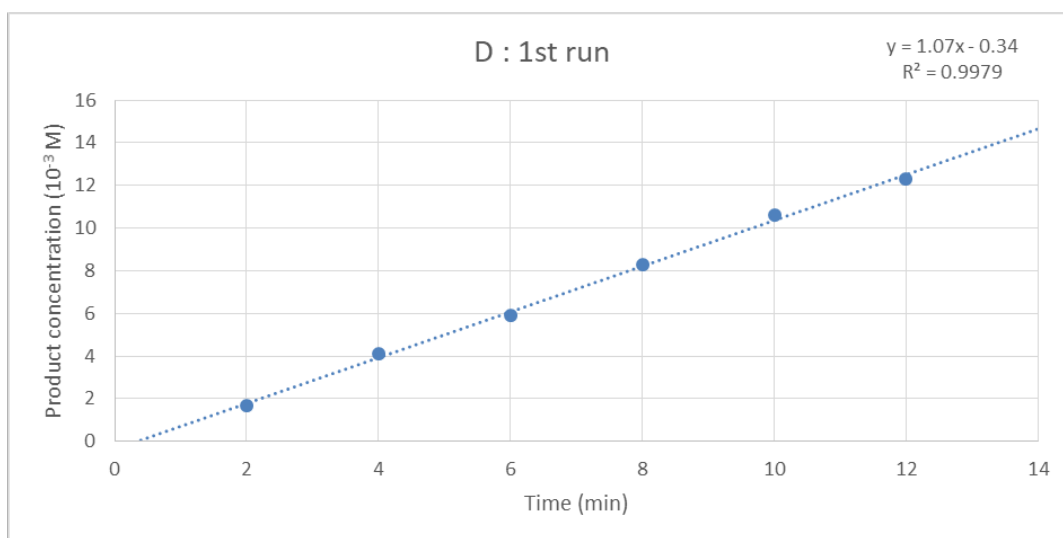
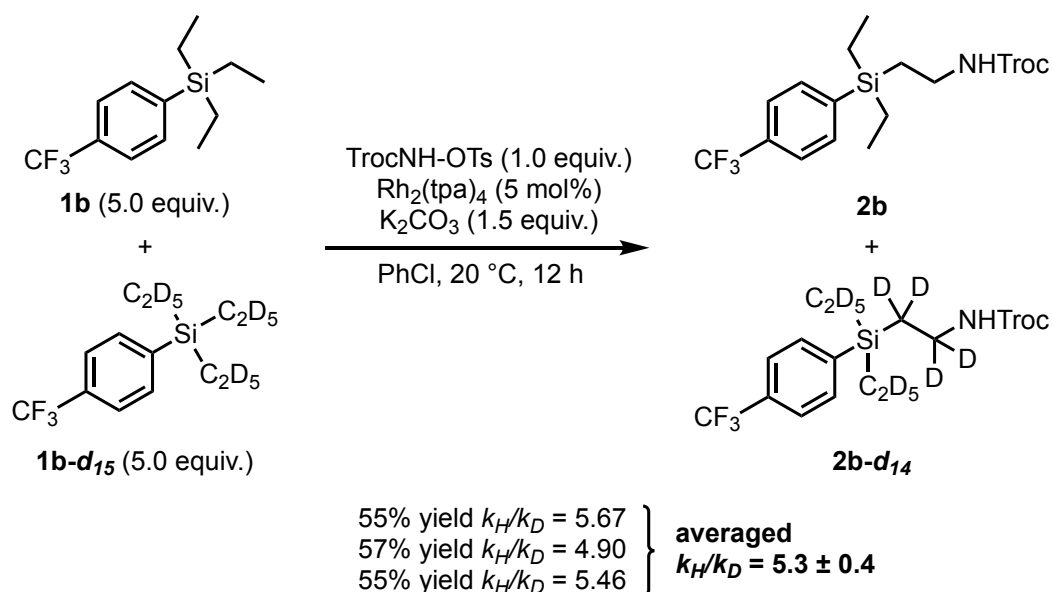


Figure S2. Initial rate analysis for C-H amination of 1b-*d*₁₅

Competitive KIE



Scheme S2. Intermolecular competitive KIE experiments.

To a suspension of **1b** (65.1 mg, 0.25 mmol, 5.0 equiv.), **1b-d₁₅** (68.9 mg, 0.25 mmol, 5.0 equiv.), TrocNHOTs (18.1 mg, 0.05 mmol, 1.0 equiv.) and K₂CO₃ (10.4 mg, 0.075 mmol, 1.5 equiv.) in PhCl (0.5 mL) was added Rh₂(tpa)₄ (3.4 mg, 0.0025 mmol, 0.05 equiv.) at 20 °C. After being stirred for 12 h at 20 °C, the reaction was quenched by addition of water and extracted with CHCl₃. The organic layer was washed with brine, and dried over Na₂SO₄, filtered, and concentrated *in vacuo*. The residue was purified by preparative thin-layer chromatography purification (CHCl₃/hexane = 2/1) to afford a mixture of **2b** and **2b-d₁₄**. KIE was calculated from the comparison of the integrals between a nitrogen α signal (δ 3.42–3.25 ppm, 2H of **2b**) and a trichloroethyl signal (δ 4.69 ppm, 2H of **2b** and **2b-d₁₄**) in ¹H NMR of a solution of **2b** and **2b-d₁₄** (CDCl₃). The experiments were performed three times and the determined KIE was the average of three runs.

Computational details

All calculation reported in the present study were carried out using density functional theory (DFT) with (U)M06¹⁹ or B3PW91 functional, as implemented in the Gaussian 09 (Revision E.01)²⁰. For geometry optimizations, the 6-31G(d,p) basis set was used for the H, C, N, O, Si, Cl elements, and the LANL2DZ²¹ basis set and pseudopotential for Rh. Based on these optimized geometries, single-point energy calculations were performed using the 6-311++G(2d,2p) basis set for the H, C, N, O, Si, Cl elements, and the SDD²² basis set and pseudopotential for Rh with solvents effects simulated by SMD²³ solvent model (chlorobenzene). The stationary points were confirmed as minima (no imaginary frequencies) or transition state (only one imaginary frequency) by analytical frequency calculations as the same theory level as the geometry optimizations. Computational time was generously provided by the Supercomputer Laboratory in the Institute for Chemical Research of Kyoto University.

Highest occupied molecular orbital of diphenylsilacyclopentane **1p**

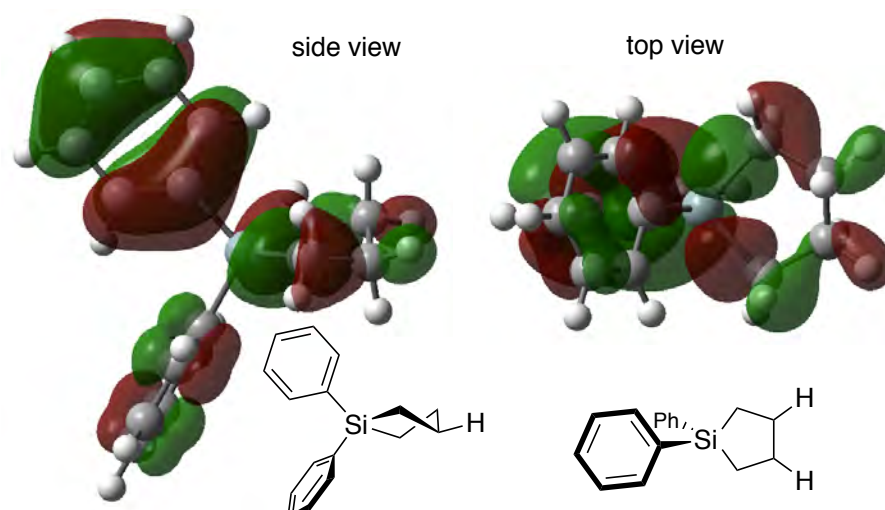
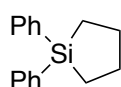


Figure S3. HOMO of **1p** calculated by DFT at the B3PW91/6-31g(d,p) level of theory.

XYZ coordinates and thermochemical data (energies in Hartree)

Temperature = 298.15 K, Pressure = 1.00 atm

Diphenylsilacyclopentane (**1p**)



B3PW91/6-31G(d,p)

Electronic Energy = -909.813987997 Electronic and Zero-Point Energy = -909.518600

Enthalpy = -909.502000 Free Energy = -909.563908

C	-0.19495200	2.02239100	1.40964000
C	0.06125200	3.36645900	0.69740200
C	-0.60263000	3.32219000	-0.68807900
C	-0.17022400	2.02516500	-1.40497500
H	0.49808600	1.85200100	2.23938900
H	-1.20698800	2.00354800	1.83415900
H	1.14259200	3.51017000	0.56805100
H	-0.29945000	4.21909900	1.28587100
H	-1.69410400	3.32451300	-0.56007400
H	-0.35893800	4.21564800	-1.27600100
H	-0.85062500	1.74932000	-2.21608800
H	0.82409000	2.16039200	-1.84935600
Si	-0.06768400	0.74286200	0.00365800
C	-1.50179800	-0.48854900	0.00331500
C	-1.29694500	-1.86863400	-0.15116600
C	-2.82675600	-0.03743200	0.13677500
C	-2.36813700	-2.76133100	-0.17313100
H	-0.28483400	-2.25246600	-0.25297400
C	-3.90087200	-0.92355300	0.11468800
H	-3.02867700	1.02489400	0.26141600
C	-3.67246600	-2.29051400	-0.04055500
H	-2.18310100	-3.82570500	-0.29265600
H	-4.91587300	-0.54925400	0.22011400
H	-4.50841500	-2.98477100	-0.05663300
C	1.56872400	-0.19929100	0.00597900
C	2.28794100	-0.42664500	-1.17874400
C	2.10282400	-0.71361700	1.19981800
C	3.48920500	-1.13420500	-1.17414000
H	1.90735500	-0.04460800	-2.12350200
C	3.30344700	-1.42080900	1.21233800
H	1.57411900	-0.55936300	2.13822600
C	3.99981800	-1.63179400	0.02315000
H	4.02745200	-1.29539400	-2.10450900
H	3.69687400	-1.80592500	2.14943000
H	4.93743400	-2.18113800	0.03003900

Mechanism of C-H amination of dimethylsilacyclopentane mediated by dirhodium nitrene

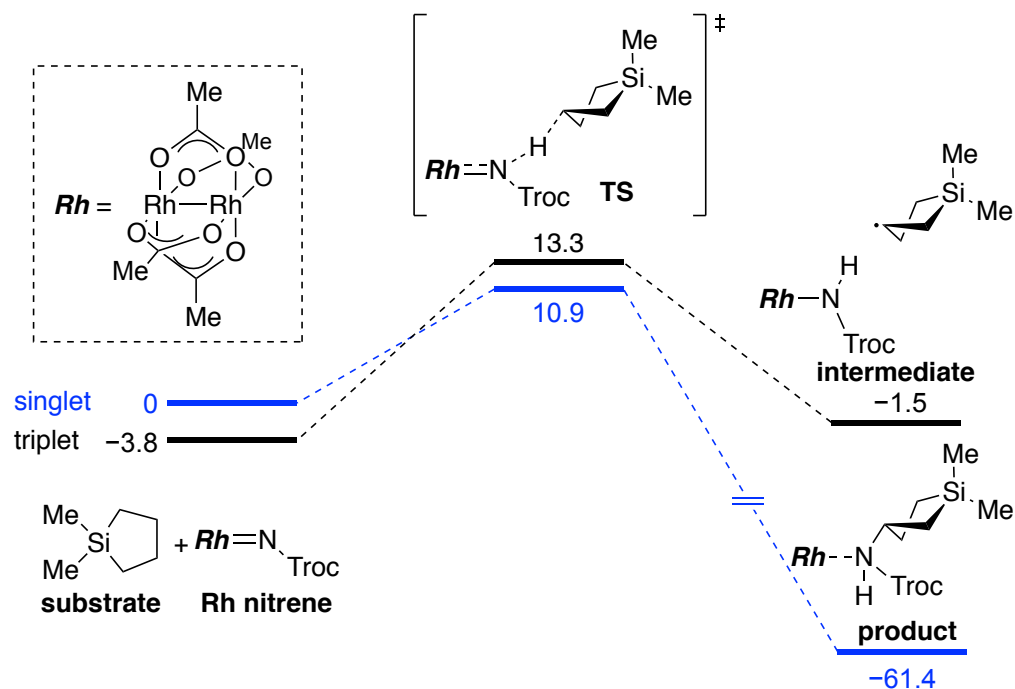


Figure S4. Energy diagram for C-H insertion step of silacyclopentane. (U)M06 functional were used.

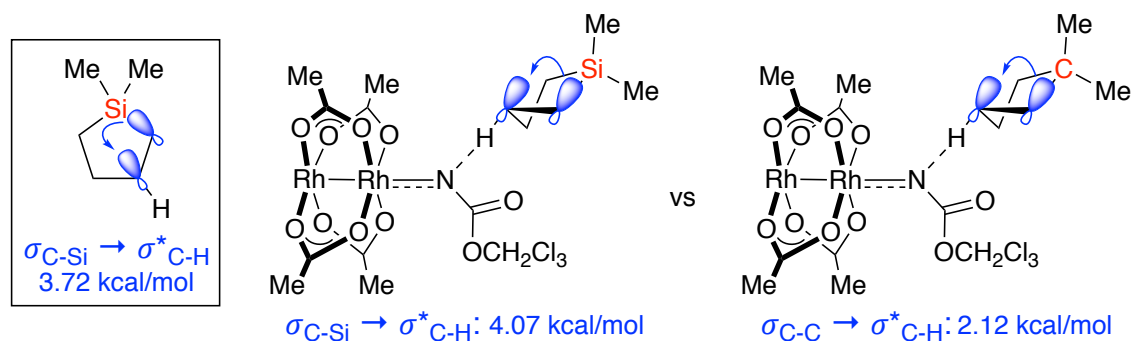
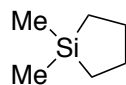


Figure S5. Natural bond orbital (NBO) analysis of the substrate and TS structures.

XYZ coordinates and thermochemical data (energies in Hartree)

Temperature = 298.15 K, Pressure = 1.00 atm

substrate (1,1-dimethylsilacyclopentane)



M06/6-31G(d,p)

Electronic Energy = -526.384354413

Electronic and Zero-Point Energy = -526.1994434

Enthalpy = -526.1887754

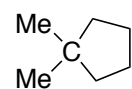
Free Energy = -526.2335804

M06/6-311++G(2d,2p)

Electronic Energy = -526.473103

C	-0.61013200	-0.53690400	-1.29524300
C	-1.91745800	-0.58755600	-0.49029600
C	-1.91743100	0.58755600	0.49040800
C	-0.61005600	0.53690800	1.29527800
H	-0.38487600	-1.48558400	-1.79536000
H	-0.68267900	0.23166900	-2.07876100
H	-1.95549200	-1.52577400	0.08722700
H	-2.80831100	-0.58125000	-1.13243000
H	-1.95550100	1.52577400	-0.08711200
H	-2.80824600	0.58124800	1.13259400
H	-0.38477200	1.48558900	1.79537900
H	-0.68255600	-0.23166300	2.07880300
Si	0.67295100	0.00000000	-0.00001900
C	1.73709800	-1.42865800	0.60467500
H	2.42827400	-1.77921100	-0.17004800
H	2.33211300	-1.14345300	1.47990200
H	1.10296000	-2.27537800	0.89571100
C	1.73706800	1.42865400	-0.60477600
H	2.42828300	1.77921400	0.16991000
H	2.33203800	1.14344400	-1.48003200
H	1.10291400	2.27537100	-0.89578600

substrate (1,1-dimethylcyclopentane)



M06/6-31G(d,p)

Electronic Energy = -274.974048652

Electronic and Zero-Point Energy = -274.777917

Enthalpy = -274.769414

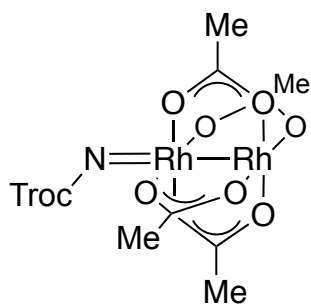
Free Energy = -274.808820

M06/6-311++G(2d,2p)

Electronic Energy = -275.045048687

C	-1.65259300	-0.77409200	-0.00868800
C	-0.22934400	-1.18397500	-0.40942000
C	0.66089800	0.00000100	-0.01004300
C	-0.22934600	1.18397400	-0.40942800
C	-1.65259600	0.77408800	-0.00869500
H	-2.40141400	-1.18992600	-0.69161000
H	-1.90105000	-1.15950100	0.98796900
H	-0.16677300	-1.31644900	-1.50022400
H	0.09733000	-2.12818700	0.04717000
H	0.09732700	2.12818700	0.04716100
H	-0.16677600	1.31645100	-1.50023200
H	-1.90104900	1.15950400	0.98796000
H	-2.40141800	1.18991600	-0.69161900
C	0.90856300	0.00000700	1.49734400
H	1.48168400	-0.88691800	1.79832500
H	1.48166000	0.88694600	1.79832300
H	-0.02706900	-0.00000500	2.06932900
C	1.99226700	-0.00000300	-0.74326000
H	2.58721000	0.88594800	-0.48400100
H	2.58720200	-0.88596300	-0.48400800
H	1.84604400	0.00000000	-1.83139800

Rh nitrene (singlet state)



M06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -2833.52349

Electronic and Zero-Point Energy = -2833.255374

Enthalpy = -2833.227067

Free Energy = -2833.314106

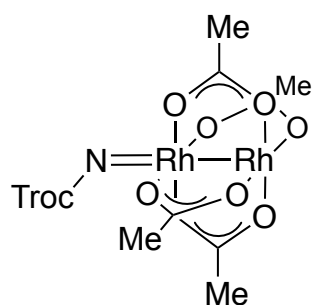
M06/6-311++G(2d,2p)[SDD]

Electronic Energy = -2836.132154

Rh	0.000002686	0.000002787	0.000005616
Rh	-0.000001629	0.000000304	0.000001338
O	0.000001324	-0.000000116	-0.000000784
O	0.000005401	0.000002126	0.000003282
O	-0.000000428	0.000003479	0.000008449
O	-0.000004407	0.000001220	0.000004412
O	0.000001738	-0.000000297	-0.000001301
O	0.000005779	0.000001948	0.000002760
O	-0.000000341	0.000003156	0.000007694
O	-0.000004469	0.000000874	0.000003605
C	0.000004147	0.000000892	0.000000698
C	0.000006266	0.000000462	-0.000000990
H	0.000004421	-0.000000186	-0.000001969
H	0.000007927	-0.000000157	-0.000003078
H	0.000008007	0.000001468	0.000000809
C	-0.000003264	0.000002601	0.000007289
C	-0.000005475	0.000003139	0.000009315
H	-0.000008350	0.000002680	0.000009209
H	-0.000005056	0.000002739	0.000008242
H	-0.000004686	0.000004334	0.000011921
C	-0.000003042	0.000002157	0.000006168
C	-0.000005316	0.000002474	0.000007742
H	-0.000007994	0.000002430	0.000008478
H	-0.000004000	0.000003583	0.000009908
H	-0.000005577	0.000001670	0.000005852
C	0.000004549	0.000000632	-0.000000115
C	0.000006690	0.000000010	-0.000002255
H	0.000005167	-0.000000316	-0.000002454
H	0.000007128	-0.000001001	-0.000004780
H	0.000009294	0.000000826	-0.000001186
N	-0.000004742	-0.000001694	-0.000002345

C	-0.000004070	-0.000002687	-0.000005006
O	-0.000006185	-0.000003063	-0.000005307
O	-0.000001199	-0.000003101	-0.000007007
C	-0.000000222	-0.000004070	-0.000009554
H	-0.000002192	-0.000004304	-0.000009535
H	0.000002459	-0.000003476	-0.000009132
C	-0.000000156	-0.000005420	-0.000012972
Cl	-0.000004464	-0.000006440	-0.000013848
Cl	0.000003061	-0.000005120	-0.000013180
Cl	0.000001220	-0.000006543	-0.000015988

Rh nitrene (triplet state)



UM06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -2833.530333

Electronic and Zero-Point Energy = -2833.262826

Enthalpy = -2833.235075

Free Energy = -2833.321382

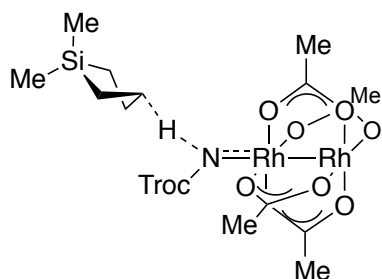
UM06/6-311++G(2d,2p)[SDD]

Electronic Energy = -2836.137797

Rh	-0.000000573	0.000000686	-0.000002045
Rh	0.000000673	0.000001570	-0.000000674
O	-0.000002057	-0.000001884	-0.000001686
O	-0.000003253	-0.000002421	-0.000003412
O	-0.000000934	0.000003107	-0.000005858
O	-0.000000070	0.000003567	-0.000004708
O	0.000001339	-0.000000473	0.000003290
O	-0.000000164	-0.000001712	0.000001854
O	0.000002152	0.000003819	-0.000000625

O	0.000003217	0.000004891	0.000000201
C	-0.000003416	-0.000003032	-0.000002902
C	-0.000005340	-0.000005346	-0.000003813
H	-0.000005726	-0.000004685	-0.000005413
H	-0.000005329	-0.000006680	-0.000002077
H	-0.000006378	-0.000006336	-0.000004619
C	-0.000000697	0.000003951	-0.000006359
C	-0.000001079	0.000005552	-0.000009226
H	0.000000110	0.000007316	-0.000009109
H	-0.000002308	0.000004434	-0.000010256
H	-0.000001381	0.000006003	-0.000010417
C	0.000003434	0.000005267	0.000000136
C	0.000005385	0.000007620	0.000000991
H	0.000005832	0.000009360	-0.000000326
H	0.000005417	0.000007787	0.000000842
H	0.000006378	0.000007518	0.000003106
C	0.000000740	-0.000001709	0.000003653
C	0.000001184	-0.000003283	0.000006529
H	0.000002698	-0.000001942	0.000007854
H	0.000000897	-0.000004372	0.000007353
H	0.000000371	-0.000004574	0.000006581
N	0.000001276	0.000001674	0.000000442
C	0.000000195	-0.000000320	0.000000786
O	-0.000000650	-0.000000403	-0.000000813
O	0.000000193	-0.000002155	0.000003141
C	-0.000000958	-0.000004370	0.000003693
H	-0.000001818	-0.000004358	0.000001929
H	-0.000001833	-0.000006102	0.000004129
C	0.000000298	-0.000004414	0.000006236
Cl	0.000001741	-0.000001691	0.000005620
Cl	0.000001727	-0.000004497	0.000009159
Cl	-0.000001294	-0.000007363	0.000006816

transition state TS for C-H insertion of dimethylsilacyclopentane (singlet state)



M06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -3359.90675919

Electronic and Zero-Point Energy = -3359.455442

Enthalpy = -3359.411894

Free Energy = -3359.536186

M06/6-311++G(2d,2p)[SDD]

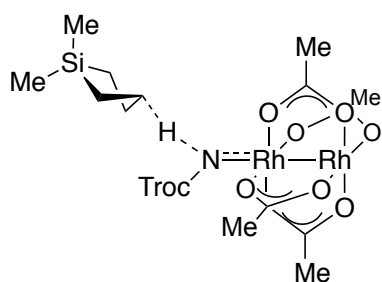
Electronic Energy = -3362.606526

Rh	-2.91839300	-1.74742900	0.06572100
Rh	-0.80023100	-0.56170600	-0.00771300
O	-0.20067200	-1.82790100	-1.51774400
O	-2.10876800	-3.03641200	-1.34754200
O	-3.59179900	-0.51432500	-1.45000000
O	-1.67241900	0.66692800	-1.40166100
O	-0.14430600	-1.93730300	1.38279900
O	-2.16802200	-2.92226900	1.57925200
O	-3.54532200	-0.34971300	1.45634000
O	-1.51218000	0.64543900	1.51498400
C	-0.97022500	-2.79588000	-1.83030800
C	-0.43251200	-3.74155600	-2.86366900
H	0.06793200	-3.18295000	-3.65842600
H	0.31431600	-4.39032200	-2.39409700
H	-1.23528400	-4.35888400	-3.26988800
C	-2.84376500	0.42012400	-1.83781900
C	-3.33802600	1.32764700	-2.92334000
H	-2.99411100	2.35018900	-2.74462200
H	-2.91581400	0.99759700	-3.87834900
H	-4.42679000	1.28777900	-2.98579300
C	-2.72663600	0.51530900	1.87196600
C	-3.20872400	1.50597000	2.89113300

H	-3.08152300	2.51917200	2.49534900
H	-4.25618100	1.32669700	3.13775000
H	-2.59190600	1.43060100	3.79150300
C	-0.95503400	-2.77446400	1.89108200
C	-0.40110000	-3.64303400	2.98059500
H	-0.40010300	-3.07406900	3.91619900
H	0.63300500	-3.91461800	2.75676700
H	-1.02063600	-4.53239400	3.10781900
N	0.87487200	0.44678800	0.00842700
C	1.90490700	0.01685000	-0.80056900
O	2.21554600	0.48537100	-1.87214600
O	2.56313300	-0.98583300	-0.15989500
C	3.77834100	-1.39343600	-0.73767800
H	3.88860300	-0.97798600	-1.74631200
H	3.79377300	-2.48802800	-0.77447100
C	4.95661000	-0.93063200	0.11147000
Cl	4.98468100	0.84794900	0.21241200
Cl	4.85914400	-1.62093100	1.75216100
Cl	6.44377100	-1.51718500	-0.69755500
C	1.49379600	5.08863100	-0.50937600
C	1.68810900	3.56091900	-0.54872500
C	0.34294000	2.94063000	-0.89283300
C	-0.71691800	3.44891000	0.06046300
H	2.29946500	5.59695500	0.03213100
H	1.48946000	5.49265300	-1.53221100
H	1.98340700	3.19780000	0.44950400
H	2.46878000	3.24506600	-1.25160100
H	0.07993300	3.09305600	-1.95147000
H	0.42393900	1.80334700	-0.78752600
H	-1.73752400	3.24423400	-0.28331500
H	-0.59547600	2.94967200	1.03490400
Si	-0.23704400	5.28758500	0.25157800
C	-0.20866100	5.80330700	2.05941000
H	0.13511600	6.83668800	2.18210200
H	-1.20469500	5.72574400	2.51118300
H	0.46691200	5.15346400	2.62899700

C	-1.34538200	6.41844800	-0.76296100
H	-2.37090000	6.43223200	-0.37649100
H	-0.97423900	7.44986600	-0.76325900
H	-1.38385300	6.07827300	-1.80525700

transition state TS for C-H insertion of dimethylsilacyclopentane (triplet state)



UM06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -3359.903298

Electronic and Zero-Point Energy = -3359.45522

Enthalpy = -3359.412421

Free Energy = -3359.533915

UM06/6-311++G(2d,2p)[SDD]

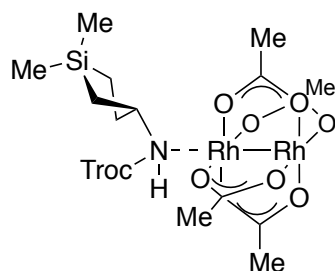
Electronic Energy = -3362.601964

Rh	3.81826300	0.19484600	-0.22856400
Rh	1.46413600	-0.26023200	0.11926800
O	1.50737900	-1.26328400	-1.68542900
O	3.70541700	-0.84319200	-2.00638400
O	4.21777900	-1.57571500	0.74873600
O	2.01996600	-1.98636500	1.08901600
O	1.07400400	1.52468700	-0.86157000
O	3.27064000	1.95089700	-1.18353100
O	3.79902100	1.20274600	1.57394100
O	1.59791400	0.79822400	1.88521500
C	2.59773200	-1.35118300	-2.33299800
C	2.53889800	-2.15034200	-3.60081900

H	1.70294200	-1.80618300	-4.21577700
H	3.47790300	-2.06745300	-4.15000000
H	2.34801600	-3.19862300	-3.35062600
C	3.25553600	-2.26367600	1.19165900
C	3.58911000	-3.51946700	1.94028300
H	3.63081500	-3.28894600	3.01012300
H	2.81082100	-4.26969600	1.78629400
H	4.56509300	-3.89638900	1.62848200
C	2.71984800	1.29678700	2.21922600
C	2.73684100	2.05950900	3.51075600
H	2.47486900	1.38522500	4.33164200
H	3.72162800	2.49493500	3.68615400
H	1.97544400	2.84412600	3.48031300
C	2.04522100	2.22690200	-1.28698600
C	1.66658400	3.49438200	-1.99690000
H	1.32475000	3.24504500	-3.00707500
H	2.52401500	4.16571500	-2.06758200
H	0.83526400	3.97980200	-1.47690800
N	-0.49185500	-0.52694100	0.25208900
C	-1.25473900	-1.58710900	-0.15022600
O	-0.90356500	-2.74428300	-0.17404200
O	-2.50347400	-1.16304300	-0.53880100
C	-3.41312100	-2.15904900	-0.92583300
H	-2.95041000	-3.15197800	-0.86956500
H	-3.74936300	-1.96289200	-1.95144000
C	-4.63581700	-2.13735700	-0.01980800
Cl	-4.16550400	-2.45811700	1.66567200
Cl	-5.46446300	-0.54937000	-0.12203600
Cl	-5.74455300	-3.41371900	-0.60027800
C	-2.43306200	2.12540100	-0.81173100
C	-1.78266200	1.74107000	0.49071500
C	-2.81200800	1.55398000	1.58953800
C	-3.73183600	2.79710900	1.60006900
H	-1.71010400	2.46026300	-1.56338800
H	-3.00103200	1.27574300	-1.22082800
H	-0.94802800	2.40222600	0.77134000

H	-1.17761100	0.65870600	0.34988900
H	-3.40866300	0.66132400	1.35114600
H	-2.33617000	1.37188800	2.56080800
H	-4.74004900	2.55387800	1.95672600
H	-3.33132600	3.56585900	2.27530600
Si	-3.66879800	3.44077400	-0.19185200
C	-5.32034700	3.42421100	-1.09020300
H	-6.01980900	4.13733700	-0.63846100
H	-5.20363600	3.69601200	-2.14541700
H	-5.78441100	2.43176600	-1.05078800
C	-2.88436000	5.15013400	-0.26512500
H	-2.75453900	5.49430100	-1.29765300
H	-3.48832900	5.89679600	0.26356600
H	-1.89460800	5.12864200	0.20936000

Product (singlet state)



M06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -3360.043432

Electronic and Zero-Point Energy = -3359.581922

Enthalpy = -3359.540332

Free Energy = -3359.655018

M06/6-311++G(2d,2p)[SDD]

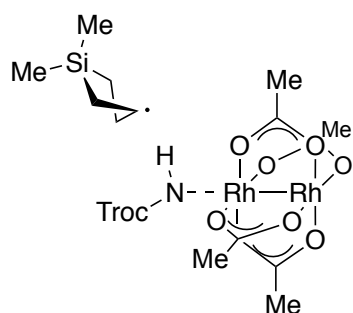
Electronic Energy = -3362.739627

Rh	0.86755300	-2.91013200	0.34853700
Rh	0.50829500	-0.58732400	-0.20455000
O	-0.40590000	-0.37997900	1.64061400
O	-0.07709700	-2.56214900	2.14798100
O	2.67650200	-2.38439300	1.20156900
O	2.31564000	-0.19708000	0.75803500

O	-1.28604200	-1.11466300	-1.06492000
O	-0.95902700	-3.29002300	-0.53488300
O	1.79306200	-3.10385100	-1.49594300
O	1.47979300	-0.92140800	-1.99761500
C	-0.49650500	-1.39410300	2.39548700
C	-1.18638900	-1.19959200	3.71584500
H	-1.32110900	-0.13828700	3.93261200
H	-2.16576300	-1.68901000	3.67888300
H	-0.61157500	-1.68528900	4.50871700
C	2.98760900	-1.16248900	1.23738100
C	4.26788800	-0.79338000	1.93168400
H	4.80630100	-0.04038700	1.34829600
H	4.02948600	-0.34741900	2.90344900
H	4.89065900	-1.67552000	2.08888600
C	1.89344100	-2.09799000	-2.24963600
C	2.55218200	-2.29304400	-3.58463800
H	3.32245000	-1.53088700	-3.73226900
H	2.98661100	-3.29118500	-3.65794800
H	1.80572200	-2.15988300	-4.37421400
C	-1.62512600	-2.34011300	-1.03434200
C	-2.95540400	-2.68537800	-1.63583800
H	-3.12765900	-2.08840600	-2.53475300
H	-3.74501600	-2.44033600	-0.91633300
H	-3.00176100	-3.75203100	-1.86239200
N	0.20314200	1.56278100	-1.03422700
C	-1.16458400	1.84757300	-1.18764800
O	-1.72057400	1.95988500	-2.24758700
O	-1.74832500	1.98593300	0.02052300
C	-3.06224800	2.49038500	0.04760900
H	-3.28329700	3.07202800	-0.85581700
H	-3.12681900	3.12977500	0.93432200
C	-4.13618600	1.41060100	0.18813300
Cl	-4.36244500	0.49201100	-1.31186500
Cl	-3.74043200	0.29981700	1.52140500
Cl	-5.65884500	2.29199900	0.56878700
C	1.65069300	4.80342900	0.44589400

C	0.62301700	3.97834700	-0.34411000
C	1.05790400	2.51092000	-0.25496700
C	2.49581000	2.43618500	-0.76210700
H	1.64365600	5.85820400	0.15112000
H	1.41522600	4.76958700	1.51871500
H	0.62901600	4.27487800	-1.40620900
H	-0.39924200	4.12432800	0.02817400
H	1.01037700	2.18537000	0.79680000
H	0.58059600	1.43368500	-1.97385500
H	2.95185400	1.46114500	-0.56621300
H	2.49999200	2.61678600	-1.84993800
Si	3.30244900	3.90777600	0.12073000
C	4.46972000	4.87615800	-0.98669900
H	4.84189300	5.77791700	-0.48759200
H	5.33821400	4.27368200	-1.27636400
H	3.95888300	5.18938700	-1.90526400
C	4.13087600	3.34580100	1.71084200
H	5.11907400	2.91245200	1.51727900
H	4.25825800	4.16375200	2.42859500
H	3.51340700	2.56977000	2.18221400

Intermediate (triplet state)



UM06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -3359.926392

Electronic and Zero-Point Energy = -3359.472912

Enthalpy = -3359.429006

Free Energy = -3359.552601

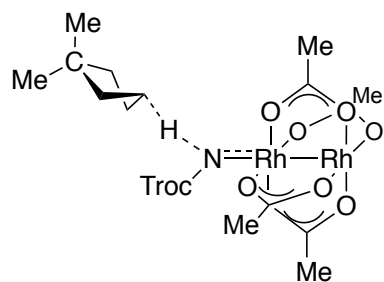
UM06/6-311++G(2d,2p)[SDD]

Electronic Energy = -3362.629534

Rh	3.83302400	0.27093200	0.28627800
Rh	1.49874100	-0.13639100	-0.17211500
O	2.10381000	-1.41947000	-1.65845500
O	4.28911000	-1.07992500	-1.19772100
O	3.76810300	-1.28032000	1.63984600
O	1.58597900	-1.66194700	1.19834000
O	1.56175400	1.46045300	-1.48379200
O	3.76323100	1.79395300	-1.10387200
O	3.23341100	1.60679600	1.74480700
O	1.04913500	1.20513000	1.33046300
C	3.34479500	-1.62328700	-1.83782400
C	3.69686300	-2.60111400	-2.91729100
H	3.28675100	-2.25074700	-3.86903600
H	4.77903500	-2.71582600	-2.99380600
H	3.22725200	-3.56415000	-2.69727700
C	2.68068000	-1.90566400	1.79423300
C	2.65253800	-3.02605100	2.78905000
H	2.25550200	-2.64625600	3.73638300
H	1.98692600	-3.81823900	2.43976800
H	3.66101600	-3.40733000	2.95905500
C	2.00010900	1.78336500	1.94622500
C	1.59072100	2.74272700	3.02328000
H	1.26416900	2.17131100	3.89849700
H	2.42817400	3.38252100	3.30614400
H	0.73972200	3.34077500	2.68566500
C	2.66566500	2.06528000	-1.66459100
C	2.64103800	3.19466100	-2.65043600
H	2.49833700	2.78625100	-3.65590700
H	3.57557500	3.75632800	-2.61351600
H	1.79036400	3.84833800	-2.44004700
N	-0.43256300	-0.37345900	-0.56745600
C	-1.12691600	-1.51223600	-0.80631400
O	-0.71524600	-2.64837200	-0.80370300
O	-2.44864500	-1.18848100	-1.07948500
C	-3.33180200	-2.26350600	-1.22767900

H	-2.78370300	-3.21171800	-1.28628000
H	-3.92691700	-2.11543500	-2.13670000
C	-4.29418100	-2.33495400	-0.04816600
Cl	-3.40161000	-2.57795000	1.47155600
Cl	-5.25635500	-0.82692500	0.06143700
Cl	-5.39429600	-3.71470800	-0.34076800
C	-2.82058300	2.45702300	-1.07681500
C	-1.94238100	2.24823400	0.10638100
C	-2.62788300	1.62104600	1.28264800
C	-4.01099800	2.29987400	1.47913400
H	-2.38785200	3.10658400	-1.84383400
H	-3.09590000	1.49677800	-1.55261400
H	-0.96722400	2.72573600	0.20233200
H	-0.98590900	0.49092500	-0.59516300
H	-2.79956000	0.54737600	1.07600000
H	-2.00682400	1.66000800	2.18552400
H	-4.77771200	1.58324100	1.79779400
H	-3.95142400	3.07001400	2.25991900
Si	-4.36686600	3.14086800	-0.19088100
C	-6.00699000	2.69271700	-0.99650400
H	-6.85297700	2.95602500	-0.35114300
H	-6.13441200	3.22826800	-1.94447300
H	-6.06808400	1.61963100	-1.21134600
C	-4.21573500	5.00879900	-0.01237800
H	-4.32986900	5.52368400	-0.97326500
H	-4.96893600	5.41003100	0.67595200
H	-3.22721600	5.26245700	0.39159000

transition state TS for C-H insertion of dimethylcyclopentane (singlet state)



M06/6-31G(d,p)[LANL2DZ]

Electronic Energy = -3108.49541320

Electronic and Zero-Point Energy = -3108.032977

Enthalpy = -3107.992282

Free Energy = -3108.107547

M06/6-311++G(2d,2p)[SDD]

Electronic Energy = -3111.17669927

Rh	-3.45990600	-0.05040800	0.76138500
Rh	-1.31846700	-0.13049900	-0.36909500
O	-0.92408100	-1.89315100	0.63739100
O	-2.92190800	-1.81600100	1.69911000
O	-4.27258400	-1.11930300	-0.79610000
O	-2.27700500	-1.18814200	-1.85549300
O	-0.53905000	0.91979800	1.22240600
O	-2.53489500	1.02628700	2.27166500
O	-3.82930100	1.70827500	-0.26531800
O	-1.81330500	1.64801200	-1.29521500
C	-1.79930100	-2.33348500	1.45085300
C	-1.42964000	-3.57908600	2.20235500
H	-0.85033400	-3.29696000	3.08828700
H	-2.32876500	-4.10360200	2.53091600
H	-0.80646800	-4.22627900	1.58114700
C	-3.51246200	-1.46248400	-1.74380300
C	-4.09918900	-2.29088100	-2.84737400
H	-3.77838900	-1.89962700	-3.81607300
H	-3.71281300	-3.31183500	-2.76405300
H	-5.18779900	-2.30736100	-2.77618400
C	-2.95660300	2.15586200	-1.05875700
C	-3.29253200	3.39956800	-1.82865500
H	-3.58249400	3.11502500	-2.84557300
H	-4.12379000	3.92674700	-1.35745700
H	-2.41492800	4.04591900	-1.90446100
C	-1.30795900	1.28524100	2.17119900
C	-0.66452100	2.11015300	3.24646600
H	0.24382400	1.61387000	3.60033900
H	-1.35825700	2.27269700	4.07251000

H	-0.36598000	3.07567300	2.82333000
N	0.42612700	-0.12042400	-1.35604100
C	1.21906700	-1.20625700	-1.10709100
O	1.05797200	-2.20494300	-1.77785200
O	2.12791400	-1.06652500	-0.11087300
C	2.93209100	-2.20191200	0.12132300
H	2.72956700	-2.97324500	-0.63090400
H	2.71760400	-2.59711300	1.12133800
C	4.40614100	-1.83444600	0.05704700
Cl	4.79373400	-1.10677000	-1.52368300
Cl	4.83298100	-0.69490600	1.36564200
Cl	5.33025200	-3.34928200	0.27270600
C	2.47138300	2.26895700	0.55161000
C	1.58445200	2.07196100	-0.65338100
C	2.49615600	2.26588800	-1.84114400
C	3.26502400	3.51971900	-1.41697500
H	1.91250600	2.51182300	1.46319000
H	3.02745100	1.34135300	0.74751300
H	0.68738600	2.70785200	-0.67754700
H	1.09119000	1.01521500	-0.67786700
H	3.18040300	1.40544300	-1.91825100
H	1.96840000	2.36016400	-2.79498700
H	4.22197900	3.63421300	-1.94164900
H	2.66290900	4.40975900	-1.65062500
C	4.89141000	3.01947800	0.46102500
H	5.58497000	3.83110800	0.20297000
H	5.00379700	2.80685200	1.53293200
H	5.20160300	2.12144000	-0.09071200
C	3.08807400	4.71105900	0.80917600
H	3.24910300	4.65176900	1.89378600
H	3.69652800	5.54032100	0.42369600
H	2.03219700	4.96284400	0.63684100
C	3.45574100	3.40091700	0.12274000

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