NHC–Cu-Catalyzed Addition of Propargylboron Reagents to Phosphinoylimines. Enantioselective Synthesis of Trimethylsilyl-Substituted Homoallenylamides and Application to Synthesis of *S*-(–)-Cyclooroidin

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SUPPORTING INFORMATION

Subject Index

General Information: Infrared (IR) spectra were recorded on a Bruker alpha spectrophotometer, λ_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), and weak (w). ^{1}H NMR spectra were recorded on a Varian Unity INOVA 400 (400 MHz) or Varian Unity INOVA 500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm or CD_3OD: δ 3.31 ppm). Data are reported as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet, app = apparent) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Varian Unity INOVA 400 (100 MHz) or a Varian Unity INOVA 500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16 ppm or CD_3OD: δ 49.00 ppm). High-resolution mass spectrometry was performed on a JEOL AccuTOF-DART (positive mode) at the Mass Spectrometry Facility, Boston College. Enantiomeric ratios (er) values were determined by GLC analysis (Alltech Associated Chiraldex B-DM (30 m x 0.25 mm)) or HPLC analysis (Chiral Technologies

Chiralcel, Chiral Technologies Chiralcel OD-H (4.6 x 250 mm), Chiral Technologies Chiralcel OJ-H (4.6 x 250 mm), Chiral Technologies Chiralpak OZ-H (4.6 x 250 mm)). Specific rotations were measured on an ATAGO® AP–300 Automatic Polarimeter or a Rudolph Research Analytical Autopol IV Polarimeter. Melting points were measured on a Thomas Hoover capillary melting point apparatus and are uncorrected. MPLC was carried out using a Teledyne Isco Combiflash RF instrument. X-ray structures were obtained with a Microfocus sealed Cu tube from Incote. It is well established that the aforementioned detector allows for determination of absolute configuration of molecules that do not have a heavy atom.

Unless otherwise noted, all reactions were carried out with distilled and degassed solvents under an atmosphere of dry N_2 in oven- (135 °C) or flame-dried glassware with standard dry box or vacuum-line techniques. Tetrahydrofuran (Aldrich) was purified by distillation from sodium benzophenone ketyl immediately prior to use unless otherwise specified. All work-up and purification procedures were carried out with reagent grade solvents (purchased from Fisher) in air. Aryl-, heteroaryl-, and alkene- *N*-diphenylphosphinoyl imines were synthesized through the use of a condensation promoted by $TiCl_4$ between *P*,*P*-diphenylphosphinic amide and the corresponding aldehyde.[i] Alkyl-substituted aldimines as well as **11** were synthesized via the corresponding sulfinyl adducts according to formerly disclosed methods.[ii] Unless otherwise noted, characterization data for the aldimine substrates have been reported previously.

Reagents:

Acetic acid (glacial): purchased from Fisher and used as received.

Acetonitrile: purchased from Acros and used as received.

Acetyl chloride: purchased from Aldrich and used as received.

Allylamine: purchased from Aldrich and used as received.

1,3-Bis(1-adamantyl)imidazolium tetrafluoroborate (1a): purchased from Aldrich and used as received.

1,3-Bis(*tert*-butoxycarbonyl)guanidine: purchased from Aldrich and used as received.

1,3-Bis(2,4,6-trimethylphenyl)imidazolium chloride (1b): purchased from Aldrich and used as received.

Bromine: purchased from Acros and used as received.

4-Bromo-1-butene: purchased from TCI and used as received.

***n*-Butyllithium:** purchased as a 1.6 M solution in hexanes from Strem and titrated prior to use.

***tert*-Butyl methyl ether:** purchased from Aldrich (anhydrous 99.8%) and used as received.

Copper (I) chloride: purchased from Strem and used as received.

Diethyl oxalate: purchased from Acros and distilled (neat) prior to use.

Dimethyl sulfide: purchased from Aldrich and used as received.

***P*,*P*-Diphenylphosphinic amide:** prepared according to a previously reported procedure.[iii]

Ethynylmagnesium bromide: purchased as a 0.5 M solution in thf from Aldrich and used as received.

Fluorenylmethyloxycarbonyl chloride: purchased from Advanced ChemTech and used as received.

Heptane: purchased from Aldrich and used as received.

Imidazolinium salt (1c): prepared according to a previously reported procedure.[iv]

2-(Iodomethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: purchased from Frontier Scientific and used as received.

2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane: purchased from Aldrich and used as received.

Magnesium (0): purchased from Strem and used as received.

Magnesium (II) chloride: purchased from Strem and used as received.

Methanol: purchased from Fisher and used as received.

Methylene chloride: purchased from Fisher and used as received.

Ozone: generated by passing O_2 (Airgas) through a Pacific Instrument ozonolysis machine.

Peracetic acid: purchased as a 32 wt % solution in dilute acetic acid from Aldrich and used as received.

Potassium bromide: purchased from Strem and used as received.

Potassium carbonate: purchased from Aldrich and used as received.

2-Propanol: purchased from Strem and distilled from Mg prior to use.

1-(Trimethylsilyl)-1-propyne: purchased from TCI and used as received.

Silver acetate: purchased from Aldrich and used as received.

Sodium acetate: purchased from Aldrich and used as received.

Sodium *tert*-butoxide: purchased from Strem and used as received.

Tetrabutylammonium fluoride (TBAF): purchased as a 1.0 M solution in thf from Fisher and used as received.

4,4,5,5-Tetramethyl-2-(prop-2-yn-1-yl)-1,3,2-dioxaborolane (3b): prepared according to a previously reported procedure.[v]

Titanium (IV) chloride: purchased from Fluka and used as received.

Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-yn-1-yl)silane (3a): prepared according to a previously reported procedure.[vi]

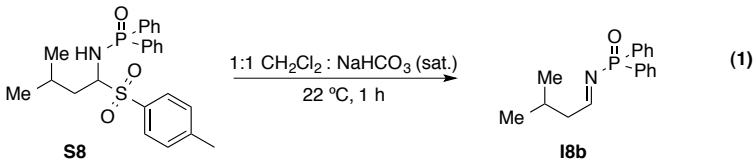
Trifluoroacetic acid: purchased from Fisher and used as received.

Toluene: purchased from Fisher and used as received.

Procedure for Synthesis of Trimethyl(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)prop-1-yn-1-yl)silane (3a). To a flame-dried round bottom flask was added 1-(trimethylsilyl)-1-

propyne (3.75 g, 33.4 mmol) and thf (30 mL) and cooled to –25 ºC (dry ice/acetone) under N_2. *n*-BuLi (1.63 M in hexanes, 19.5 mL, 31.8 mmol) was added drop-wise and the resulting yellow solution was allowed to stir for 1 h at –25 ºC. To a separate flame-dried flask containing magnesium chloride (2.95 g, 31.0 mmol) thf (30 mL) and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.3 mL, 31.0 mmol) was added. The mixture was allowed to cool to –25 ºC, after which it was charged, in a drop-wise fashion, with the solution containing the lithiopropyne. The resulting suspension was allowed to stir between –25 ºC and –20 ºC for 2 h. At this point, a solution of acetyl chloride (2.45 mL, 34.3 mmol) in methyl *t*-butyl ether (mtbe) (2.45 mL) was added to the suspension at –20 ºC and the resulting mixture was allowed to stir for 1 h at –20 ºC, was then allowed to warm to 22 ºC over 1 h and concentrated in vacuo. To the resulting light yellow gummy solid residue was added 60 mL of hexanes, the suspension was filtered, and the yellow solid was washed further with hexanes (2x30 mL); then the volatiles were removed in vacuo, leaving behind a yellow oil that was purified by vacuum distillation to afford **3a** as colorless oil (3.70 g, 15.6 mmol, 50% yield).

Procedure for NHC–Cu-Catalyzed Enantioselective Allenylsilane Additions to Aryl-, Alkenyl- and Heteroaryl-Substituted *N*-Diphenylphosphinoylimines. An oven-dried vial was charged with imidazolinium salt **1c** (10.5 mg, 16.5 μmol), NaO*t*-Bu (2.9 mg, 30.0 μmol), and CuCl (1.9 mg, 15.0 μmol) in a N_2-filled glove box. A separate oven-dried vial was charged with aldimine **2a** (91.6 mg, 0.3 mmol). The vials were sealed with a septum and electrical tape, and removed from the glove box. To the vial containing imidazolinium salt was added thf (1.50 mL) and the resulting solution was allowed to stir for 20 min under N_2 at 22 °C. In a separate vial, aldimine **2a** was dissolved in thf (1.50 mL) and the resulting solution was allowed to cool to –30 ºC (dry ice/acetone; temperature monitored by an external thermometer). The NHC–Cu complex solution was then transferred into the vial containing the aldimine at –30 ºC through a syringe. Propargyl boron reagent **3a** (120 μL, 0.45 mmol) was then added followed by 2-propanol (46.0 μL, 0.6 mmol) and the mixture was allowed to stir for 10 min at –30 ºC. At this point, the reaction was quenched by filtration of the solution through a short silica gel plug eluted with EtOAc. The volatiles were removed in vacuo and the resulting yellow oil was purified by silica gel chromatography (hexanes→50% EtOAc:hexanes) to afford **4a** as colorless oil (100 mg, 0.240 mmol, 80% yield). For homoallenylamides **4e** and **4h**, to hydrolyze any unreacted aldimine, the unpurified mixture was allowed to stir in 6 mL of 1:1 Et_2O:3.0 M HCl for 30 min and then washed with Et_2O (3x2 mL) prior to purification.



S8 **I8b** **(1)**

Procedure for NHC–Cu-Catalyzed Enantioselective Allenylsilane Additions to Alkyl-Substituted *N*-Diphenylphosphinoylimines (eq S1):

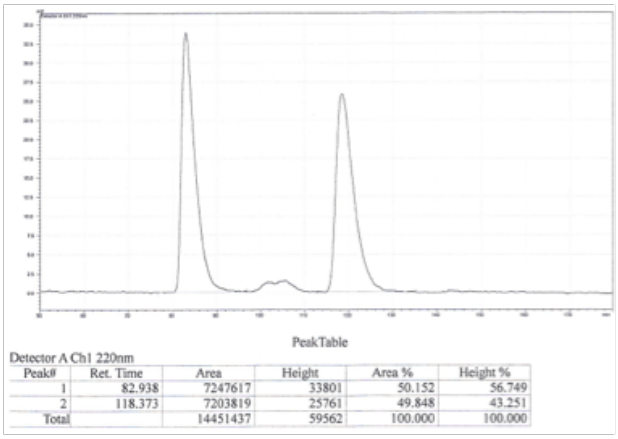
Preparation of the alkyl-substituted aldimine: To a vial charged with sulfinyl adduct **S8** (0.30

mmol) was added CH_2Cl_2 (6.0 mL) and a saturated solution of aqueous $NaHCO_3$ (6.0 mL), respectively. The biphasic mixture was allowed to stir vigorously for 1 h at 22 °C. The organic layer was separated and the aqueous phase was washed with CH_2Cl_2 (2 x 3 mL). The combined organic layers were dried over $MgSO_4$. The volatiles were removed in vacuo and the unpurified imine was used without further purification in the NHC–Cu-catalyzed allenylsilane addition, according to the procedure detailed below.

An oven-dried vial was charged with imidazolinium salt **1c** (9.1 mg, 14.4 μmol), NaO*t*-Bu (2.9 mg, 30 μmol), and CuCl (1.3 mg, 13 μmol) in a N_2-filled glove box. A separate oven-dried vial was charged with aldimine **I8b** (74.5 mg, 0.261 mmol). Each vial was sealed with a septum and electrical tape and removed from the glove box. Tetrahydrofuran (1.50 mL) was added to the solution containing imidazolinium salt and the resulting mixture was allowed to stir for 20 min under N_2 at 22 °C. To the vial containing aldimine was added thf (1.50 mL) and, once dissolved, cooled to –30 ºC (dry ice/acetone bath; monitored by an external thermometer). The solution of NHC–Cu complex was then transferred into the vessel containing the aldimine at –30 ºC by a syringe. Next, propargyl boron reagent **3a** (104 μL, 0.392 mmol) was added, followed by 2-propanol (40.0 μL, 0.522 mmol) and the solution was allowed to stir for 10 min at –30 ºC. The reaction was quenched by filtering the solution through a short silica gel plug with EtOAc as eluent. The volatiles were removed in vacuo and the resulting yellow oil was purified by silica gel chromatography (hexanes→50% EtOAc:hexanes) to afford **8b** as colorless oil (98.0 mg, 0.246 mmol, 94% yield). For products **8c** and **10**, in order to hydrolyze unreacted aldimine, the unpurified mixture was allowed to stir in 6 mL of 1:1 Et_2O:3.0 M HCl for 30 min and washed with Et_2O (3 x 2 mL) prior to purification.

Procedure for Synthesis of (*S*)-*P*,*P*-Diphenyl-*N*-(1-phenylbuta-2,3-dien-1-yl)phosphinic amide (4b). To a vial containing allene **4a** (38.0 mg, 0.091 mmol) was added thf (0.7 mL). The solution was allowed to cool to –78 ºC (dry ice/acetone bath) and a solution of (n-Bu)$_4$NF in thf (1.0 M, 0.182 mmol) was added in one portion while stirring. The resulting yellow solution was allowed to warm to 22 ºC and then allowed to stir for 5 min at 22 ºC. The volatiles were removed in vacuo and the resulting orange oil was purified by silica gel chromatography (hexanes→75% EtOAc:hexanes) to afford **4b** as white solid (28.8 mg, 0.083 mmol, 92% yield). Melting point: 110–111 °C. IR (neat): 3183 (w, br), 3058 (w), 1950 (m), 1436 (m), 1178 (s), 1123 (m), 1107 (m), 1087 (m), 905 (w), 749 (w), 721 (m), 693 (s), 534 (s) cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90–7.84 (2H, m), 7.81–7.75 (2H, m), 7.48–7.37 (4H, m), 7.34–7.28 (2H, m), 7.25–7.16 (4H, m), 5.46–5.41 (1H, m), 4.91–4.77 (3H, m), 3.38 (1H, dd, J = 9.2, 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.4, 142.6 (d, J = 4.9 Hz), 132.8 (d, J = 128.1 Hz), 132.5 (d, J = 9.6 Hz), 132.5 (d, J = 129.4 Hz), 132.3 (d, J = 9.6 Hz), 132.0 (d, J = 2.9 Hz), 131.9 (d, J = 2.5 Hz), 128.7, 128.6 (d, J = 11.7 Hz, only the peak at 128.5 is visible, the other is overlapping), 128.5 (d, J = 12.6 Hz), 127.6, 127.0, 95.5 (d, J = 5.2 Hz), 79.1, 53.5; HRMS Calcd for $C_{22}H_{22}NOP$ $[M + H]^+$: 346.1361; Found: 346.1361. $[\alpha]^{20}_D$ = –40.7 (c = 1.35, $CHCl_3$) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.8 mL/min, 220 nm): t_R of **4b**: 85 min (minor)

and 116 min (major). A crystal suitable for X–ray diffraction was obtained by vapor diffusion of hexanes into a saturated solution of **4b** in CH_2Cl_2 at 22 ºC.



PeakTable

Detector A Ch1 220nm

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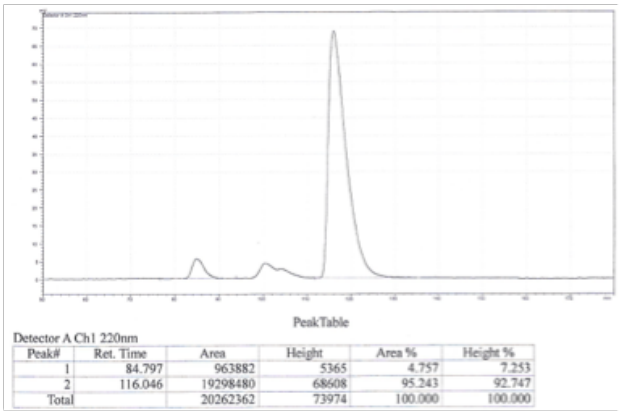
Total		14451437	59562	100.000	100.000



PeakTable

Detector A Ch1 220nm

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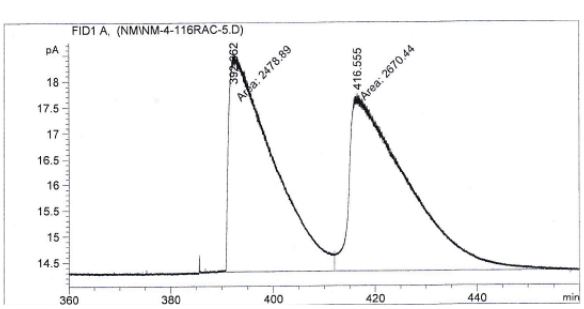
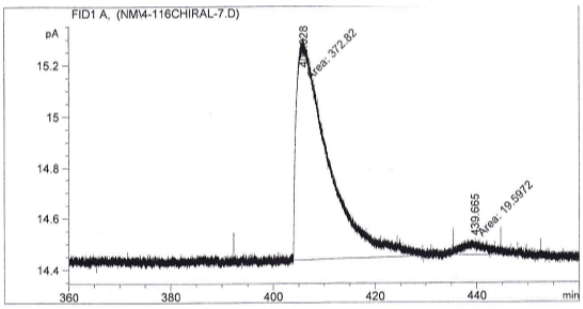
2	116.046	19298480	68608	95.243	92.747
Total		20262362	73974	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
82.938	7247617	50.152	84.797	963882	4.757
118.373	7203819	49.848	116.046	19298480	95.243

Procedure for Synthesis of (*R*)-1-Phenyl-2-(trimethylsilyl)buta-2,3-dien-1-amine (6). Homoallenylamide **4a** (103.0 mg, 0.247 mmol) was first dissolved in MeOH (3.0 mL) in a vial. An aqueous solution of 3.0 M HCl was then introduced (1.0 mL) and the resulting mixture was allowed to stir at 22 ºC for 12 h, after which it was washed with toluene (3x1.0 mL) and the organic layer was separated. The collected organic phase was washed with 3.0 M HCl. Then the combined aqueous fractions were basified with solid NaOH until the pH reached >12. The aqueous layer was then washed with EtOAc (3x1.0 mL) and the combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to afford **6** as light yellow oil (49.8 mg, 0.229 mmol, 93% yield). IR (neat): 2955 (w), 1923 (m), 1601 (w), 1492 (w), 1247 (m), 834 (s), 754 (s), 697 (s), 625 (m), 473 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31–7.29 (4H, m), 7.27–7.21 (1H, m), 4.69 (1H, dd, J = 10.8, 3.2 Hz), 4.64 (1H, dd, J = 10.8, 2.8 Hz), 4.44 (1H, t, J = 3.2 Hz), –0.07 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 145.1, 128.6, 127.5, 127.4, 101.7, 72.9, 55.4, –1.1; HRMS Calcd for $C_{13}H_{20}NSi$ $[M + H]^+$: 218.1365; Found: 218.1372. $[\alpha]^{20}_D$ = –43.4 (c = 0.45, $CHCl_3$) for a 95:5 er sample. The enantiomeric purity of this compound was determined by GLC analysis in comparison with authentic racemic material (CDB-DM column, 70 ºC, 20 psi): t_R of **6**: 406 min (major) and 440 min (minor).



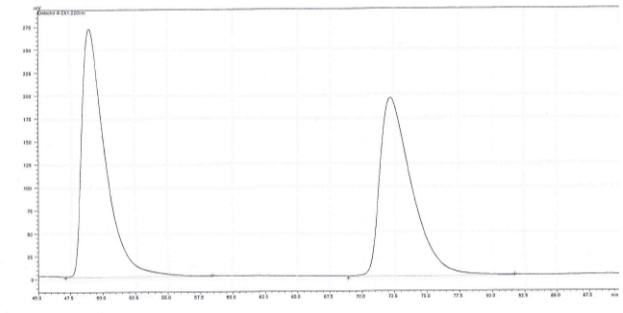


Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	392.362	MF	9.7984	2478.89063	4.21648	48.14002
2	416.555	FM	12.9496	2670.44409	3.43698	51.85998

Peak #	RetTime [min]	Type	Width [min]	Area [pA*s]	Height [pA]	Area %
1	406.028	MM	7.1322	372.81964	8.71210e-1	95.00603
2	439.665	MM	5.2070	19.59717	6.27270e-2	4.99397

Retention Time	Area	Area %	Retention Time	Area	Area %
392.362	2478.89063	48.14002	406.028	372.81964	95.00603
416.555	2670.44409	51.85998	439.665	19.59717	4.99397

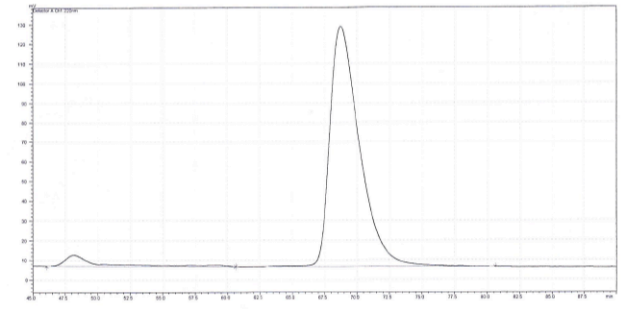
Procedure for synthesis of (*R*)-*N*-(4-Bromo-1-phenylbut-2-yn-1-yl)-*P*,*P*-diphenylphosphinic amide (7). Acetic acid (1.0 mL) was added to a vial containing allene **3a** (53.0 mg, 0.127 mmol), potassium bromide (16.6 mg, 0.140 mmol) and sodium acetate (125.0 mg, 1.52 mmol). A peracetic acid solution was then introduced in a drop-wise fashion (640 μL, 3.04 mmol) and the resulting pale yellow solution was allowed to stir at 22 ºC for 10 min. A saturated solution of sodium thiosulfate was then added until the solution became colorless. The aqueous layer was diluted with water (1.0 mL) and washed with EtOAc (3x1.0 mL). The combined organic layers were dried over $MgSO_4$, concentrated in vacuo and dried through azeotrope with heptane. The resulting yellow oil was purified by silica gel chromatography (hexanes →75% EtOAc:hexanes) affording **7** as white solid (36.2 mg, 0.085 mmol, 67 % yield). Melting point = 157–160 ºC (d). IR (neat): 3148 (m, br), 2862 (w), 1438 (m), 1188 (s), 1146 (m), 1124 (m), 1110 (m), 1062 (w), 724 (m), 696 (s), 545 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.06–8.01 (2H, m), 7.87–7.82 (2H, m), 7.59–7.47 (6H, m), 7.44–7.39 (2H, m), 7.38–7.33 (2H, m), 7.32–7.27 (1H, m), 5.22 (1H, tt, J = 10.0, 2.0 Hz), 3.94 (2H, dd, J = 2.0, 1.2 Hz), 3.44 (1H, dd, J = 9.6, 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.8 (d, J = 4.6 Hz), 132.8 (d, J = 9.7 Hz), 132.3 (d, J = 127.5 Hz), 132.3 (d, J = 2.9 Hz), 132.3 (d, J = 3.0 Hz), 132.0 (d, J = 9.7 Hz), 131.8 (d, J = 129.4 Hz), 128.9, 128.8 (d, J = 12.7 Hz), 128.7 (d, J = 12.6 Hz), 128.3, 127.3, 86.6 (d, J = 5.9 Hz), 80.8, 46.8, 14.6; HRMS Calcd for $C_{22}H_{20}BrNOP$ $[M + H]^+$: 424.0466; Found: 424.0470. $[\alpha]^{20}_D$ = –28.5 (c = 0.70, $CHCl_3$) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 97:3 hexanes:*i*-PrOH, 0.7 mL/min, 220 nm): t_R of **7**: 48 min (minor) and 69 min (major). A crystal suitable for X–ray diffraction was obtained by vapor diffusion of hexanes into a saturated solution of **7** in CH_2Cl_2 at 22 ºC.



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.928	33896894	270550	50.416	58.208
2	72.173	33336876	194251	49.584	41.792
Total		67233770	464801	100.000	100.000



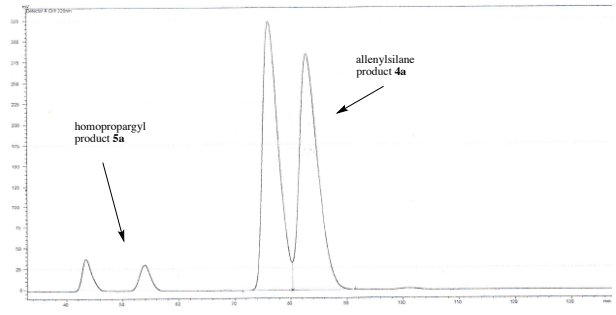
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	48.191	937220	5610	4.600	4.383
2	68.723	19439311	122389	95.400	95.617
Total		20376531	127998	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
48.928	33896894	50.416	48.191	937220	4.600
72.173	33336876	49.584	68.723	19439311	95.400

(*R*)-*P*,*P*-Diphenyl-*N*-(1-phenyl-2-(trimethylsilyl)buta-2,3-dien-1-yl)phosphinic amide (**4a**): IR (neat): 3181 (w, br), 2956 (w), 1929 (m), 1453 (m), 1196 (m), 1123 (m), 839 (s), 697 (s), 536 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.84 (2H, m), 7.78–7.72 (2H, m), 7.52–7.47 (1H, m), 7.45–7.39 (3H, m), 7.33–7.29 (2H, m), 7.24–7.15 (5H, m), 4.86 (1H, dd, J = 12.0, 4.0 Hz), 4.76–4.69 (2H, m), 3.74 (1H, app t, J = 8.4 Hz), –0.18 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 143.1 (d, J = 3.5 Hz), 133.1 (d, J = 128.1 Hz), 132.7 (d, J = 129.0 Hz), 132.4 (d, J = 9.7 Hz), 132.2 (d, J = 9.4 Hz), 131.8 (d, J = 2.8 Hz), 131.7 (d, J = 2.8 Hz), 128.5 (d, J = 12.3 Hz), 128.4, 128.3 (d, J = 12.4 Hz), 127.9, 127.5, 101.0 (d, J = 5.2 Hz), 74.0, 53.8, –1.4; HRMS Calcd for $C_{25}H_{29}NOPSi$ $[M + H]^+$: 418.1756; Found: 418.1760. $[\alpha]^{20}_D$ = –70.1 (c = 1.14, $CHCl_3$) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OZ-H, 97:3 hexanes:*i*-PrOH, 0.6 mL/min, 220 nm): t_R of **4a**: 78 min (minor) and 84 min (major).



PeakTable

Detector A Ch1 220nm

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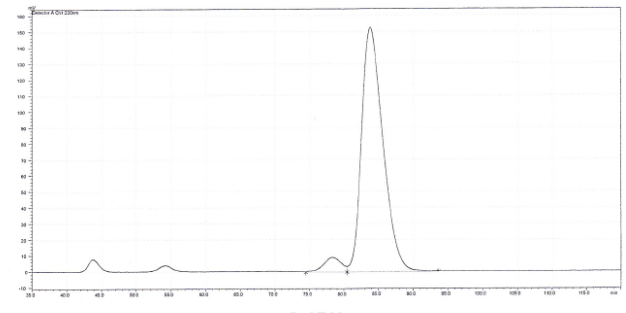
1	75.982	63619046	324819	49.475	53.244
2	82.731	64967990	285240	50.525	46.756
Total		128587036	610059	100.000	100.000



PeakTable

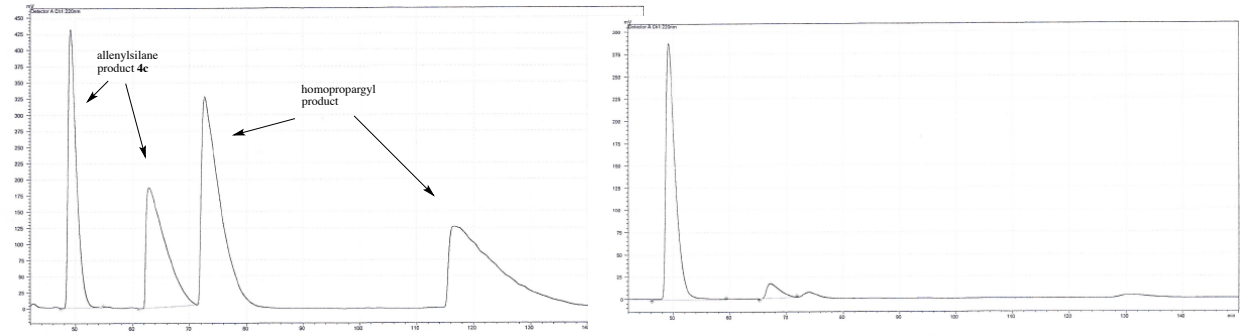
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	78.323	1665801	9144	4.836	5.651
2	83.843	32781014	152661	95.164	94.349
Total		34446815	161805	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
75.982	63619046	49.475	78.323	1665801	4.836
82.731	64967990	50.525	83.843	32781014	95.164

(*R*)-*N*-(1-(2-Fluorophenyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic

amide (4c): IR (neat): 3992 (w, br), 3059 (w), 2958 (w), 1929 (m), 1589 (w), 1489 (w), 1455 (w), 1438 (m), 1249 (m), 1196 (m), 1123 (m), 1108 (m), 841 (s), 753 (s), 724 (m), 696 (m), 550 (m), 529 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.86-7.81 (2H, m), 7.77–7.71 (2H, m), 7.50–7.46 (1H, m), 7.44–7.38 (3H, m), 7.32–7.27 (2H, m), 7.19–7.10 (2H, m), 7.01–6.97 (1H, m), 6.89 (1H, ddd, J = 10.8, 8.4, 1.2 Hz), 4.93 (1H, app tt, J = 9.6, 2.8 Hz), 4.84 (1H, dd, J = 11.2, 3.6 Hz), 4.71 (1H, dd, J = 10.8, 2.8 Hz), 3.93 (1H, br dd, J = 9.6, 8.4 Hz), –0.15 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 160.5 (d, J_{C-F} = 246.3 Hz), 133.0 (d, J = 128.1 Hz), 132.3 (d, J = 129.5 Hz, only the peak at 133.0 is visible, the other is overlapping), 132.5 (d, J = 9.7 Hz), 132.1 (d, J = 9.8 Hz), 131.9 (d, J = 2.9 Hz), 131.7 (d, J = 2.7 Hz), 130.4 (dd, J = 12.4, 3.1 Hz), 129.3 (d, J = 4.5 Hz), 129.2 (d, J = 8.3 Hz), 128.5 (d, J = 12.7 Hz), 128.3 (d, J = 12.3 Hz), 124.1 (d, J = 3.7 Hz), 115.8 (d, J = 21.9 Hz), 100.3 (dd, J = 5.3, 1.1 Hz), 74.4, 48.7 (d, J = 2.1 Hz), –1.5; HRMS Calcd for $C_{25}H_{28}FNOPSi$ $[M + H]^+$: 436.1662; Found: 436.1671. $[\alpha]^{20}_D$ = –53.8 (c = 1.30, $CHCl_3$) for a 92:8 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **4c**: 49 min (major) and 67 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.083	43518232	430784	50.148	69.813
2	62.878	43260977	186271	49.852	30.187
Total		86779209	617055	100.000	100.000

PeakTable

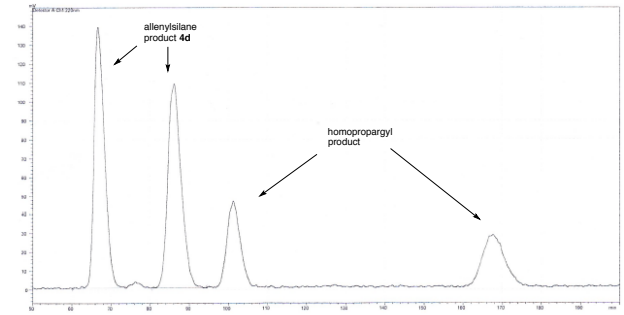
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	49.166	33551018	288066	92.503	94.524
2	67.125	2719029	16687	7.497	5.476
Total		36270047	304753	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
49.083	43518232	50.148	49.166	33551018	92.503
62.878	43260977	49.852	67.125	2719029	7.497

(*R*)-*N*-(1-(2-Chlorophenyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide (**4d**)**:** IR (neat): 3183 (w, br), 2958 (w), 1928 (m), 1438 (m), 1248 (m), 1191 (m), 1123 (m), 1109 (m), 838 (s), 747 (s), 723 (m), 694 (s), 541 (m), 521 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.88–7.83 (2H, m) 7.77–7.72 (2H, m), 7.52–7.46 (1H, m), 7.45–7.38 (3H, m), 7.32–7.27 (2H, m), 7.24–7.19 (2H, m), 7.13 (2H, dquintet, J = 7.2, 2.0 Hz), 5.14 (1H, app tt, J = 10.0, 3.4 Hz), 4.82 (1H, dd, J = 11.2, 3.6 Hz), 4.70 (1H, dd, J = 11.2, 3.2 Hz), 3.95 (1H, dd, J = 9.2, 8.0 Hz), –0.14 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.2, 140.3 (d, J = 3.2 Hz), 133.2, 133.0 (d, J = 127.9 Hz), 132.6 (d, J = 9.6 Hz), 132.3 (d, J = 127.6 Hz, only the peak at 132.9 is visible, the other is overlapping), 132.1 (d, J = 9.8 Hz), 131. 9 (d, J = 2.5 Hz), 131.7 (d, J = 2.7 Hz), 130.0, 130.0, 128.7, 128.5 (d, J = 12.5 Hz), 128.2 (d, J = 12.7 Hz), 126.9, 100.5 (d, J = 5.4 Hz), 74.3, 51.4, –1.33; HRMS Calcd for $C_{25}H_{28}ClNOPSi$ $[M + H]^+$: 452.1366; Found: 452.1350.

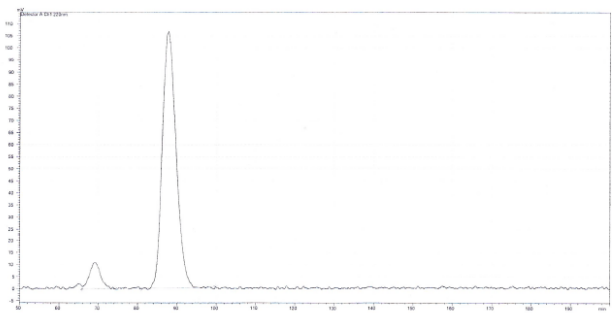
$[\alpha]^{20}_D$ = –26.5 (*c* = 2.07, $CHCl_3$) for a 92:8 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OZ–H, 97:3 hexanes:*i*-PrOH, 0.8 mL/min, 220 nm): t_R of **4d**: 69 min (minor) and 88 min (major).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	66.711	25708448	138434	50.116	56.092
2	86.172	25589249	108365	49.884	43.908
Total		51297697	246799	100.000	100.000



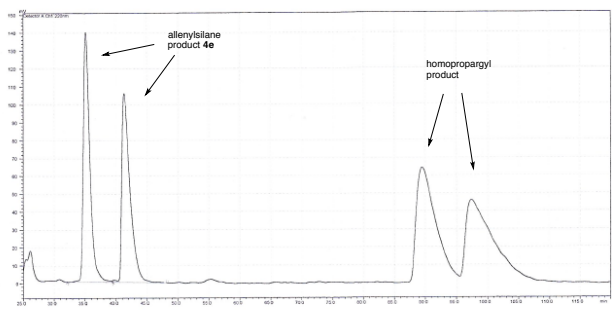
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	69.147	2178605	10846	7.826	9.251
2	87.745	25660821	106400	92.174	90.749
Total		27839426	117246	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
66.711	25708448	50.116	69.147	2178605	7.826
86.172	25589249	49.884	87.745	25660821	92.174

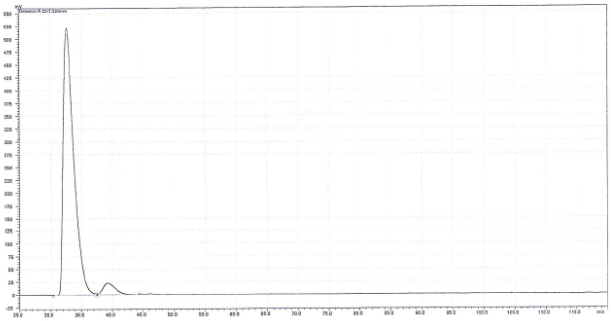
(*R*)- *P*,*P*-Diphenyl-*N*-(1-(*o*-tolyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)phosphinic amide (4e): IR (neat): 3211 (w, br), 3192 (w, br), 3053 (w), 2955 (w), 1928 (m), 1438 (m), 1248 (m), 1201 (m), 1122 (m), 1109 (m), 1073 (m), 840 (s), 752 (m), 723 (m), 697 (m), 550 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.91–7.85 (2H, m), 7.80–7.74 (2H, m), 7.51–7.50 (1H, m), 7.45–7.38 (3H, m), 7.32–7.27 (2H, m), 7.21–7.18 (1H, m), 7.11–7.05 (2H, m), 7.01–6.98 (1H, m), 4.96 (1H, ddt, *J* = 10.4, 9.6, 3.2 Hz), 4.82 (1H, dd, *J* = 10.8, 3.2 Hz), 4.74 (1H, dd, *J* = 11.2, 3.2 Hz), 3.65 (1H, app t, *J* = 8.0 Hz), 2.22 (3H, s), –0.20 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 140.8 (d, *J* = 2.9 Hz), 135.6, 133.1 (d, *J* = 127.1 Hz), 132.7 (d, *J* = 129.6 Hz), 132.5 (d, *J* = 9.4 Hz), 132.2 (d, *J* = 9.4 Hz), 131.8 (d, *J* = 2.7 Hz), 131.7 (d, *J* = 2.9 Hz), 130.9, 128.5 (d, *J* = 12.3 Hz), 128.2 (d, *J* = 12.5 Hz), 128.0, 127.5, 126.0, 101.4 (d, *J* = 5.2 Hz), 73.9, 50.5, 19.3, –1.4; HRMS Calcd for $C_{26}H_{31}NOPSi$ $[M + H]^+$: 432.1913; Found: 432.1894. $[\alpha]^{20}_D$ = –43.2 (*c* = 1.62, $CHCl_3$) for a 95:5 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **4e**: 33 min (major) and 39 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.114	10070636	139609	50.355	56.916
2	41.285	9928449	105682	49.645	43.084
Total		19999085	245291	100.000	100.000



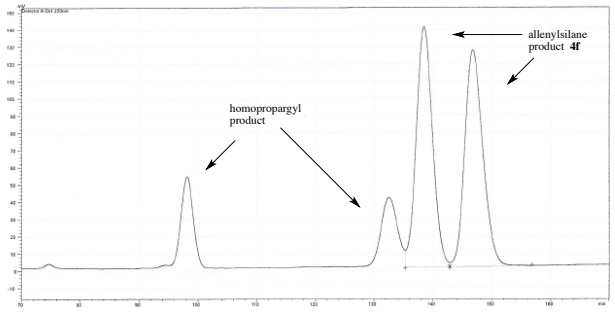
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.695	61994415	521371	95.032	95.811
2	39.312	3241120	22795	4.968	4.189
Total		65235535	544166	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
35.114	10070636	50.355	32.695	61994415	95.032
41.285	9928449	49.645	39.312	3241120	4.968

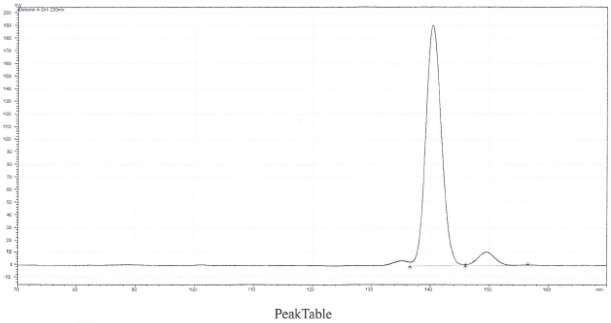
(*R*)-*N*-(1-(3-Bromophenyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide (**4f**): Melting point: 95–97 °C. IR (neat): 3192 (w, br), 2955 (w), 1929 (m), 1592 (w), 1571 (w), 1437 (m), 1248 (m), 1192 (m), 1123 (m), 1072 (m), 837 (s), 724 (s), 695 (s), 545 (m), 522 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–7.82 (2H, m), 7.74–7.70 (2H, m), 7.52–7.48 (1H, m), 7.45–7.40 (3H, m), 7.34–7.27 (4H, m), 7.14–7.12 (1H, m), 7.08–7.04 (1H, m), 4.87 (1H, dd, J = 10.8, 3.2 Hz), 4.77 (1H, dd, J = 11.2, 2.8 Hz) 4.70 (1H, tt, J = 9.6, 2.8 Hz), 3.75 (1H, t, J = 8.4 Hz), –0.15 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 145.4 (d, J = 3.0 Hz), 132.9 (d, J = 127.5 Hz), 132.3 (d, J = 128.9 Hz), 132.4 (d, J = 9.4 Hz), 132.1 (d, J = 9.7 Hz), 132.0 (d, J = 2.5 Hz), 131.9 (d, J = 2.5 Hz), 130.9, 130.6, 130.1, 128.6 (d, J = 12.4 Hz), 128.3 (d, J = 12.8 Hz), 126.8, 122.4, 100.6 (d, J = 5.2 Hz), 74.5, 53.3, –1.3; HRMS Calcd for $C_{25}H_{28}BrNOPSi$ $[M + H]^+$: 496.0861; Found: 496.0878. $[\alpha]^{20}_D$ = –71.4 (c = 1.26, $CHCl_3$) for a 94:6 er sample. The enantiomeric purity is determined by HPLC analysis in comparison with authentic racemic material (Chiracel AZ–H, 97:3 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **4f**: 140 min (major) and 149 min (minor). A crystal suitable for X–ray diffraction was obtained by slow evaporation of a saturated solution of **4f** in hexanes at 4 ºC; see below for a complete set of data.



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	138.474	26751901	139193	50.065	52.639
2	146.704	26682964	125236	49.935	47.361
Total		53434865	264429	100.000	100.000



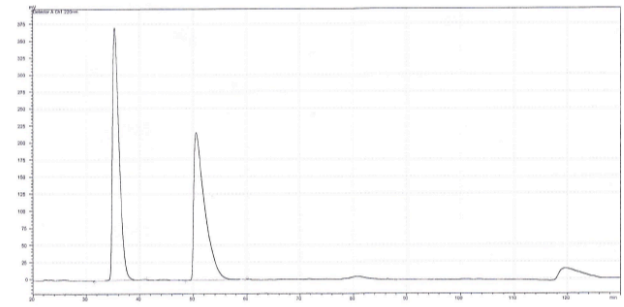
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	140.413	35337940	190941	94.066	94.669
2	149.494	2229203	10753	5.934	5.331
Total		37567144	201694	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
138.474	26565513	50.198	140.413	35337940	94.066
146.704	26356216	49.802	149.494	2229203	5.934

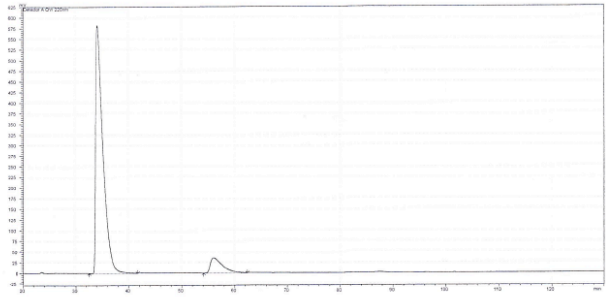
(*R*)-*N*-(1-(4-Chlorophenyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide (4g): IR (neat): 3182 (w, br), 3057 (w), 2955 (w), 1928 (m), 1592 (w), 1489 (w), 1438 (m), 1407 (w), 1248 (m), 1191 (m), 1123 (m), 1108 (m), 1086 (m), 904 (w), 839 (s), 750 (m), 723 (m), 695 (s), 538 (s), 521 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.83 (2H, m), 7.75–7.69 (2H, m), 7.52–7.48 (1H, m), 7.46–7.41 (3H, m), 7.34–7.30 (2H, m), 7.18–7.12 (4H, m), 4.87 (1H, dd, J = 11.2, 3.2 Hz), 4.77–4.69 (2H, m), 3.73 (1H, br t, J = 8.4 Hz), –0.16 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.6, 141.7 (d, J = 2.8 Hz), 133.3, 132.9 (d, J = 127.7 Hz), 132.6 (d, J = 128.6 Hz), 132.3 (d, J = 9.7 Hz), 132.2 (d, J = 9.7 Hz), 132.0 (d, J = 2.8 Hz), 131.8 (d, J = 2.7 Hz), 129.4, 128.6, 128.6 (d, J = 12.3 Hz), 128.4 (d, J = 12.6 Hz), 100.7 (d, J = 5.3 Hz), 74.3, 53.2, –1.3; HRMS Calcd for $C_{25}H_{28}ClNOPSi$ $[M + H]^+$: 452.1366; Found: 452.1369. $[\alpha]^{20}_D$ = –78.2 (c = 1.15, $CHCl_3$) for a 91:9 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **4g**: 34 min (major) and 56 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	35.305	31390399	370847	50.402	63.183
2	50.483	30889225	216090	49.598	36.817
Total		62279624	586937	100.000	100.000



PeakTable

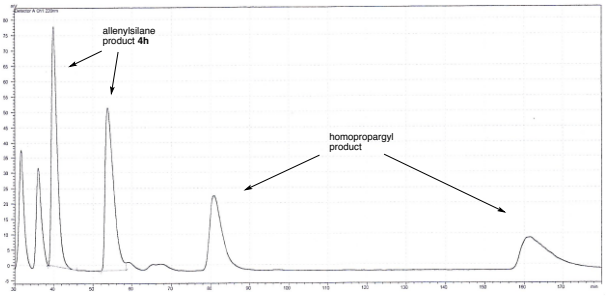
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	34.081	56322561	582962	90.619	94.220
2	55.993	5830845	35765	9.381	5.780
Total		62153406	618727	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
35.305	31390399	50.402	34.081	56322561	90.619
50.483	30889225	49.598	55.993	5830845	9.381

(*R*)-*N*-(1-(4-Methoxyphenyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide (4h): IR (neat): 3363 (w, br), 3202 (w, br), 3056 (w), 2955 (w), 2897 (w), 2836 (w), 1929 (m), 1610 (w), 1511 (m), 1439 (m), 1250 (s), 1198 (m), 1123 (m), 1110 (m), 1074 (m), 1035 (w), 841 (s), 752 (m), 724 (m), 697 (m), 540 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.84 (2H, m), 7.79–7.73 (2H, m); 7.51–7.46 (1H, m); 7.44–7.39 (3H, m), 7.34–7.29 (2H, m), 7.14–7.10 (2H, m), 6.76–6.72 (2H, m), 4.85 (1H, dd, J = 10.8, 3.2 Hz), 4.75–4.66 (2H, m), 3.76 (3H, s), 3.70 (1H, br t, J = 8.4 Hz), –0.18 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 159.0, 135.3 (d, J = 3.5 Hz), 133.2 (d, J = 128.2 Hz), 132.9 (d, J = 128.2 Hz, only the peak at 133.5 is visible, the other is overlapping), 132.4 (d, J = 9.3 Hz), 132.3 (d, J = 9.6 Hz), 131.8 (d, J = 2.7 Hz), 131.6 (d, J = 2.9 Hz), 129.1, 128.5 (d, J = 12.6 Hz), 128.3 (d, J = 12.6 Hz), 113.8, 101.2 (d, J = 5.2 Hz),

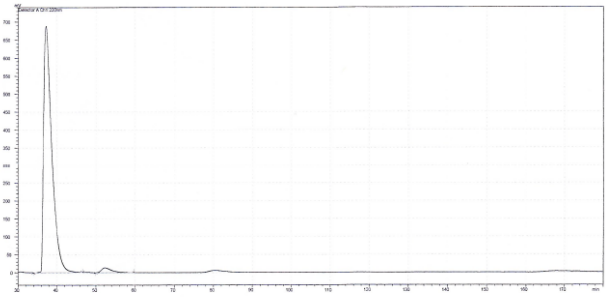
73.9, 55.4, 53.3, –1.3; HRMS Calcd for $C_{26}H_{31}NO_2PSi$ $[M + H]^+$: 448.1862; Found: 448.1847. $[\alpha]^{20}_D$ = –93.5 (*c* = 2.35, $CHCl_3$) for a 98:2 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 98.5:1.5 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **4h**: 37 min (major) and 52 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	39.917	8044689	78067	50.567	59.543
2	53.755	7864242	53043	49.433	40.457
Total		15908931	131110	100.000	100.000



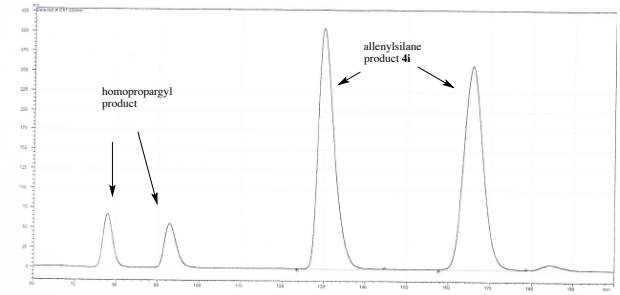
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	37.189	98930392	688289	97.808	98.203
2	52.247	2217581	12593	2.192	1.797
Total		101147973	700882	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
39.917	8044689	50.567	37.189	98930392	97.808
53.755	7864242	49.433	52.247	2217581	2.192

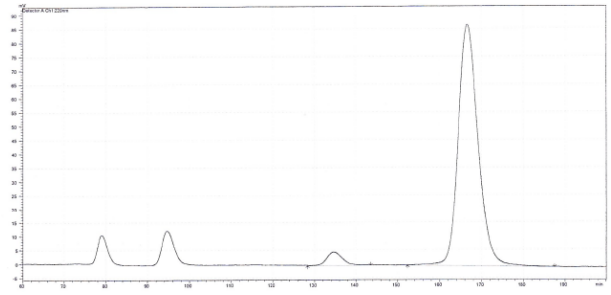
(*R*)-*P*,*P*-Diphenyl-*N*-(1-(pyridin-3-yl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)phosphinic amide (4i): IR (neat): 3059 (w), 2958 (w), 2224 (w), 1928 (m), 1591 (w), 1578 (w), 1438 (m), 1426 (m), 1250 (m), 1193 (m), 1123 (m), 1109 (m), 1081 (m), 906 (s), 839 (s), 723 (s), 695 (s), 536 (m), 520 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.61–8.31 (1H, br s), 7.87–7.82 (2H, m), 7.73–7.68 (2H, m), 7.57 (1H, br d, *J* = 7.2 Hz), 7.53–7.29 (7H, m), 7.26–7.14 (1H, br s), 4.88 (1H, dd, *J* = 10.8, 2.4 Hz), 4.77–4.74 (2H, m), 3.83 (1H, br t, *J* = 8.4 Hz), –0.14 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 149.1, 148.7, 135.6, 132.5 (d, *J* = 130.4 Hz), 132.4, 132.3 (d, *J* = 9.6 Hz) 132.2 (d, *J* = 128.8 Hz), 132.1 (d, *J* = 2.9 Hz), 132.1 (d, *J* = 9.7 Hz), 131.9 (d, *J* = 2.9 Hz), 128.8, 128.7 (d, *J* = 12.4 Hz), 128.4 (d, *J* = 12.4 Hz), 100.3 (d, *J* = 4.9 Hz), 74.6, 51.7, –1.3; HRMS Calcd for $C_{24}H_{28}N_2OPSi$ $[M + H]^+$: 419.1709; Found: 419.1699. $[\alpha]^{20}_D$ = –35.2 (*c* = 1.42, $CHCl_3$) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel AZ–H, 92:8 hexanes:*i*-PrOH, 0.7 mL/min, 220 nm): t_R of **4i**: 135 min (minor) and 167 min (major).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	129.716	82050686	305793	49.534	54.168
2	165.586	83596048	258733	50.466	45.832
Total		165646734	564526	100.000	100.000



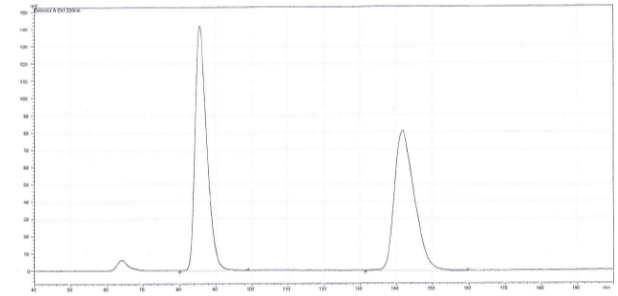
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	134.690	1355425	4942	4.495	5.363
2	166.550	28798403	87215	95.505	94.637
Total		30153828	92157	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
129.716	81602009	49.593	134.690	1355425	4.495
165.586	82940126	50.407	166.550	28798403	95.505

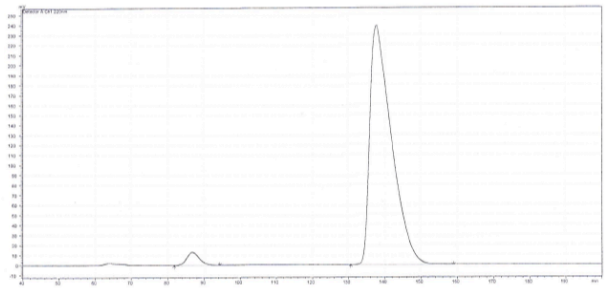
(*R*)-*N*-(1-(Furan-2-yl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide (4j): IR (neat): 3374 (w), 3182 (w, br), 3057 (w), 2956 (w), 1929 (m), 1438 (m), 1248 (m), 1194 (m), 1148 (w), 1123 (m), 1109 (m), 1071 (m), 1011 (m), 838 (s), 748 (m), 723 (s), 694 (s), 549 (m), 525 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–7.78 (4H, m), 7.51–7.34 (6H, m), 7.28 (1H, dd, *J* = 1.6, 0.8 Hz), 6.17 (1H, dd, *J* = 3.2, 1.6 Hz), 6.02–6.01 (1H, m), 4.87–4.81 (2H, m), 4.73–4.69 (1H, m), 3.77 (1H, t, *J* = 8.8 Hz), –0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 154.5 (d, *J* = 4.2 Hz), 142.0, 132.7 (d, *J* = 129.6 Hz, only the peak at 133.3 is visible, the other is overlapping), 132.4 (d, *J* = 9.8 Hz), 132.3 (d, *J* = 129.8 Hz), 132.1 (d, *J* = 9.8 Hz), 132.0 (d, *J* = 2.4 Hz, only the peak at 132.0 is visible, the other is overlapping), 131.8 (d, *J* = 2.9 Hz), 128.6 (d, *J* = 12.7 Hz), 128.4 (d, *J* = 12.8 Hz), 110.3, 107.5, 99.0 (d, *J* = 4.7 Hz), 74.4, 47.4, –1.6; HRMS Calcd for $C_{23}H_{27}NO_2PSi$ $[M + H]^+$: 408.1549; Found: 408.1532. $[\alpha]^{20}_D$ = –46.9 (*c* = 2.13, $CHCl_3$) for a 97:3 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OZ–H, 97:3 hexanes:*i*-PrOH, 0.7 mL/min, 220 nm): t_R of **4j**: 87 min (minor) and 138 min (major).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	85.566	32003456	141991	50.782	63.632
2	141.721	31018009	81154	49.218	36.368
Total		63021465	223145	100.000	100.000



PeakTable

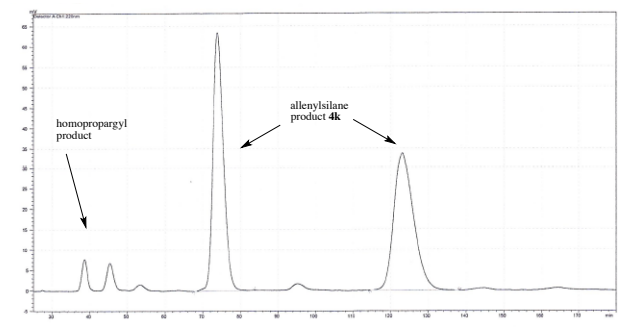
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	86.704	3334652	13182	3.263	5.227
2	137.811	98853376	239003	96.737	94.773
Total		102188028	252185	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
85.566	31629862	50.903	86.704	3334652	3.263
141.721	30508057	49.097	137.811	98853376	96.737

(*R*)-*P*,*P*-Diphenyl-*N*-(1-(thiophen-3-yl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)phosphinic amide (4k): IR (neat): 3192 (w, br), 3057 (w), 2956 (w), 1929 (m), 1438 (m), 1414 (w), 1248 (m), 1195 (m), 1123 (m), 1110 (m), 1080 (m), 840 (s), 751 (m), 725 (m), 696 (s), 546 (m), 526 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.84 (2H, m), 7.80–7.75 (2H, m), 7.51–7.41 (4H, m), 7.37–7.33 (2H, m), 7.19 (1H, dd, *J* = 4.8, 2.8 Hz), 7.07 (1H, dd, *J* = 5.2, 1.2 Hz), 6.94 (1H, br d, 1.6 Hz), 4.85–4.79 (2H, m), 4.71–4.68 (1H, m), 3.73–3.67 (1H, m), –0.13 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.7, 144.4 (d, *J* = 3.6 Hz), 132.9 (d, *J* = 129.0 Hz, only the peak at 133.5 is visible, the other is overlapping), 132.7 (d, *J* = 128.6 Hz), 132.3 (d, *J* = 9.7 Hz), 132.3 (d, *J* = 9.3 Hz), 131.9 (d, *J* = 2.7 Hz), 131.8 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 12.5 Hz), 128.4 (d, *J* = 12.4

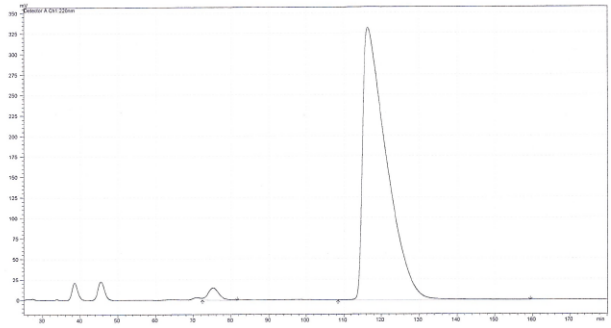
Hz), 127.5, 126.1, 122.5, 100.8 (d, J = 5.1 Hz), 74.0, 49.2, –1.4; HRMS Calcd for $C_{23}H_{27}NOPSSi$ $[M + H]^+$: 424.1320; Found: 424.1306. $[\alpha]^{20}_D$ = +136.2 (c = 1.10, $CHCl_3$) for a 98:2 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OZ–H, 97:3 hexanes:*i*-PrOH, 0.7 mL/min, 220 nm): t_R of **4k**: 75 min (minor) and 116 min (major).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	73.891	12295948	63470	50.119	65.208
2	123.215	12237800	33865	49.881	34.792
Total		24533749	97335	100.000	100.000



PeakTable

Detector A Ch1 220nm

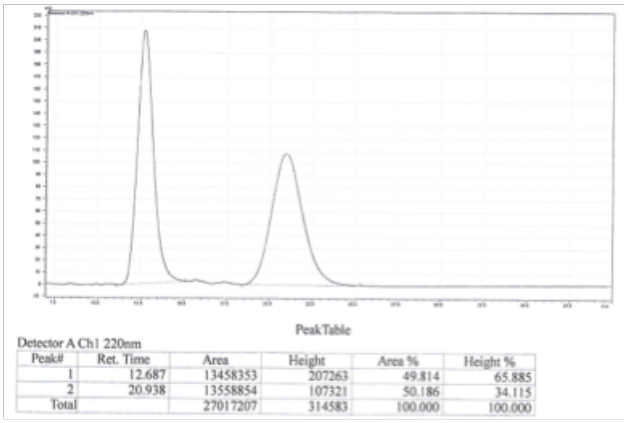
Peak#	Ret. Time	Area	Height	Area %	Height %
1	75.234	3162883	15095	2.123	4.342
2	116.389	145807151	332536	97.877	95.658
Total		148970034	347632	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
73.891	12295948	50.119	75.234	3162883	2.123
123.215	12237800	49.881	116.389	145807151	97.877

***P*,*P*-Diphenyl-*N*-(1-phenyl-4-(trimethylsilyl)but-3-yn-1-yl)phosphinic amide (5a):** IR (neat): 3158 (w, br), 2958 (w), 2175 (m), 1438 (m), 1249 (m), 1184 (m), 1122 (m), 1110 (m), 838 (s), 754 (m), 723 (s), 693 (s), 539 (m), 518 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.89–7.84 (2H, m), 7.83–7.78 (2H, m), 7.50–7.39 (4H, m), 7.36–7.31 (2H, m), 7.27–7.18 (5H, m), 4.41 (1H, dtd, J = 15.2, 6.4, 4.8 Hz), 3.76 (1H, dd, J = 10.4, 6.8 Hz), 2.88 (1H, dd, J = 16.8, 6.4 Hz), 2.72 (1H, dd, J = 16.8, 4.4 Hz), 0.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2 (d, J = 5.3 Hz), 132.9 (d, J = 126.8 Hz), 132.5 (d, J = 9.4 Hz), 132.3 (d, J = 130.5 Hz), 132.0 (d, J = 2.9 Hz), 132.0 (d, J = 9.7 Hz), 132.0 (d, J = 2.7 Hz, only the peak at 132.0 is visible, the other is overlapping), 128.7 (d, J = 13.5 Hz), 128.5 (d, J = 13.1 Hz), 128.4, 127.5, 126.6, 102.8, 89.0, 53.0, 31.0 (d, J = 4.4 Hz), –0.1; HRMS Calcd for $C_{25}H_{29}NOPSi$ $[M + H]^+$: 418.1756; Found: 418.1776.

(*S*)-*P*,*P*-Diphenyl-*N*-(1-phenylbut-3-yn-1-yl)phosphinic amide (**5b**): IR (neat): 3132 (w, br), 1456 (m), 1185 (s), 1122 (m), 1070 (m), 754 (m), 725 (m), 697 (s), 540 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.87–7.82 (2H, m), 7.80–7.75 (2H, m), 7.48–7.37 (4H, m), 7.34–7.20 (7H, m), 4.40 (1H, dddd, J = 10.4, 10.4, 6.4, 4.0 Hz), 3.64 (1H, dd, J = 10.8, 6.8 Hz), 2.88 (1H, ddd, J = 16.8, 6.4, 2.8 Hz), 2.71 (1H, ddd, J = 16.8, 4.4, 2.8 Hz), 1.92 (1H, t, J = 2.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0 (d, J = 6.1 Hz), 132.9 (d, J = 126.9 Hz), 132.6 (d, J = 9.8 Hz), 132.1 (d, J = 2.6 Hz), 132.1 (d, J = 3.3 Hz, only peak at 132.1 visible, the other is overlapping), 132.0 (d, J = 130.4 Hz), 130.0 (d, J = 9.9 Hz), 128.7 (d, J = 12.7 Hz), 128.6 (d, J = 12.7 Hz), 128.6, 127.6, 126.6, 80.1, 72.1, 52.9, 29.4 (d, J = 3.5 Hz); HRMS Calcd for $C_{22}H_{21}NOP$ $[M + H]^+$: 346.1361; Found: 346.1365. $[\alpha]^{20}_D$ = –44.2 (c = 1.13, $CHCl_3$) for a 92:8 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic

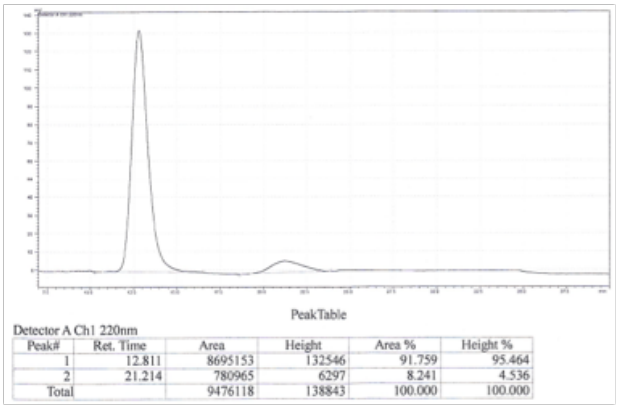
racemic material (Chiracel OJ-H, 92:8 hexanes:*i*-PrOH, 0.8 mL/min, 220 nm): t_R of **5b**: 13 min (major) and 21 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.687	13458353	207263	49.814	65.885
2	20.938	13558854	107321	50.186	34.115
Total		27017207	314583	100.000	100.000



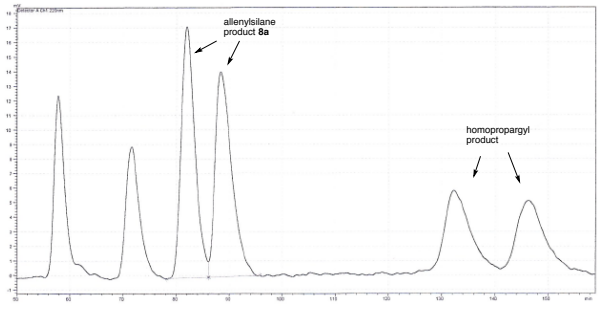
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.811	8695153	132546	91.759	95.464
2	21.214	780965	6297	8.241	4.536
Total		9476118	138843	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
12.687	13458353	49.814	12.811	8695153	91.759
20.938	13558854	50.186	21.214	780965	8.241

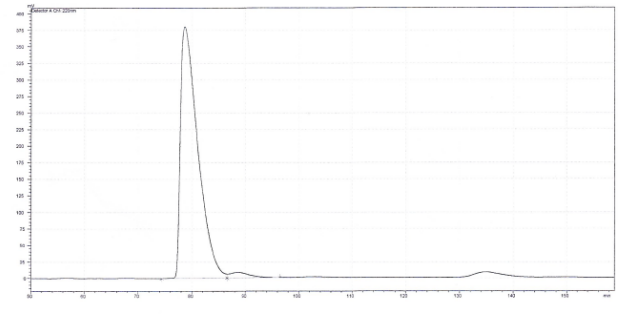
(*R*)-P,P-Diphenyl-N-(1-phenyl-4-(trimethylsilyl)hexa-4,5-dien-3-yl)phosphinic amide (8a): IR (neat): 3190 (w, br), 3025 (w), 2953 (w), 2858 (w), 1924 (m), 1438 (m), 1248 (m), 1191 (m), 1121 (m), 1109 (m), 1070 (m), 836 (s), 749 (m), 722 (s), 694 (s), 552 (s), 524 (s) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.93–7.85 (4H, m), 7.52–7.40 (6H, m), 7.25–7.22 (2H, m), 7.19–7.12 (3H, m), 4.72 (1H, dd, J = 11.0, 2.5 Hz), 4.58 (1H, dd, J = 11.0, 2.0 Hz), 3.70–3.63 (1H, m), 3.31 (1H, t, J = 9.5 Hz), 2.80–2.69 (2H, m), 2.05–1.98 (1H, m), 1.79 (1H, ddt, J = 14.0, 10.0, 6.5 Hz), –0.02 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.2, 142.1, 133.6 (d, J = 128.7 Hz), 132.7 (d, J = 128.7 Hz), 132.6 (d, J = 9.7 Hz), 132.0 (d, J = 9.3 Hz), 131.9 (d, J = 2.9 Hz), 131.8 (d, J = 2.7 Hz) 128.7, 128.6 (d, J = 12.6 Hz), 128.5 (d, J = 13.0 Hz), 128.4, 125.8, 100.7 (d, J = 5.2 Hz), 73.1, 50.3, 40.8, 31.6, –1.1; HRMS Calcd for $C_{27}H_{33}NOPSi$ $[M + H]^+$: 446.2069; Found: 446.2060. $[\alpha]^{20}_D$ = +17.8 (c = 1.12, $CHCl_3$) for a 97:3 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **8a**: 79 min (major) and 89 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	81.996	3124135	17259	50.597	55.058
2	88.368	3050407	14088	49.403	44.942
Total		6174541	31347	100.000	100.000



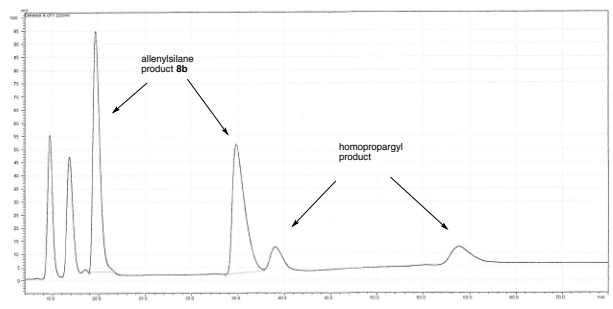
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	78.700	85574583	380288	97.554	97.863
2	88.596	2145757	8305	2.446	2.137
Total		87720339	388593	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
81.996	3124135	50.597	78.700	85574583	97.554
88.368	3050407	49.403	88.596	2145757	2.446

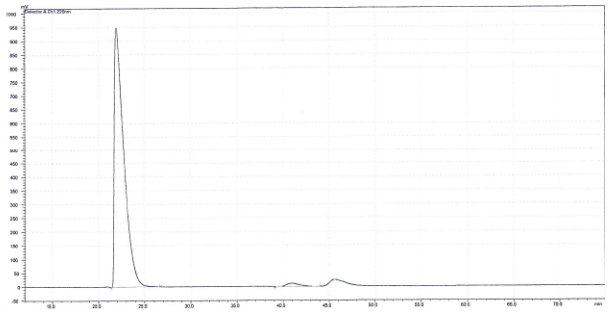
(*R*)-*N*-(6-Methyl-3-(trimethylsilyl)hepta-1,2-dien-4-yl)-*P*,*P*-diphenylphosphinic amide (8b): IR (neat): 3193 (w, br), 3058 (w), 2954 (m), 1925 (m), 1438 (m), 1248 (m), 1193 (m), 1122 (m), 1109 (m), 836 (s), 748 (s), 722 (s), 694 (s), 558 (s), 524 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94–7.86 (4H, m), 7.48–7.39 (6H, m), 4.66 (1H, dd, *J* = 10.8, 2.0 Hz), 4.51 (1H, dd, *J* = 10.8, 1.2 Hz), 3.57–3.49 (1H, m), 3.08 (1H, dd, *J* = 10.4, 8.8 Hz), 1.94 (1H, dq, *J* = 13.6, 6.8 Hz), 1.40 (2H, t, *J* = 7.2 Hz), 0.83 (6H, dd, *J* = 6.8, 2.4 Hz), –0.01 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.4, 133.6 (d, *J* = 127.8 Hz), 132.8 (d, *J* = 128.8 Hz), 132.7 (d, *J* = 9.4 Hz), 132.1 (d, *J* = 9.2 Hz), 131.8 (d, *J* = 2.8 Hz), 131.7 (d, *J* = 2.5 Hz), 128.5 (d, *J* = 12.1 Hz), 128.4 (d, *J* = 12.1 Hz), 101.5 (d, *J* = 4.6 Hz), 72.8, 49.3, 24.8, 23.5, 22.1, –1.0; HRMS Calcd for $C_{23}H_{33}NOPSi$ $[M + H]^+$: 398.2069; Found: 398.2075. $[\alpha]^{20}_D$ = +60.8 (*c* = 1.48, $CHCl_3$) for a 98:2 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.6 mL/min, 220 nm): t_R of **8b**: 21 min (major) and 41 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.637	4741801	91631	50.997	65.091
2	34.790	4556349	49142	49.003	34.909
Total		9298150	140774	100.000	100.000



PeakTable

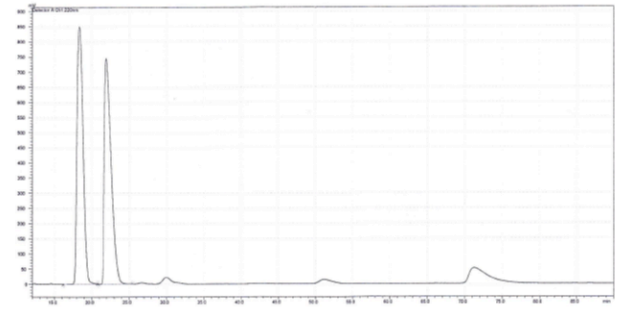
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.935	66882050	947740	98.507	98.861
2	40.945	1013880	10916	1.493	1.139
Total		67895930	958656	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
19.637	4741801	50.997	21.935	66882050	98.507
34.790	4556349	49.003	40.945	1013880	1.493

(*R*)-*N*-(1-Cyclohexyl-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide (8c): IR (neat): 2924 (m), 2851 (m), 1926 (m), 1438 (m), 1248 (m), 1202 (m), 1121 (m), 839 (s), 697 (s), 529 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94–7.84 (4H, m), 7.50–7.38 (6H, m), 4.70 (1H, dd, *J* = 11.2, 2.4 Hz), 4.51 (1H, dd, *J* = 10.8, 2.0 Hz), 3.44–3.37 (1H, m), 3.26 (1H, t, *J* = 10.4 Hz), 1.80–1.72 (3H, m), 1.63–1.46 (3H, m), 1.37–1.29 (1H, m), 1.21–1.11 (3H, m), 0.98–0.87 (1H, m), –0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.6, 133.7 (d, *J* = 128.2 Hz), 132.8 (d, *J* = 9.7 Hz), 132.7 (d, *J* = 127.4 Hz, only peak at 133.3 is visible, the other is overlapping), 132.1 (d, *J* = 9.3 Hz), 131.8 (d, *J* = 2.5 Hz), 131.7 (d, *J* = 2.9 Hz), 128.5 (d, *J* = 12.2 Hz), 128.3 (d, *J* = 12.4 Hz), 99.9 (d, *J* = 4.0 Hz), 72.6, 55.5, 44.2 (d, *J* = 3.3 Hz), 31.1, 26.7, 26.5, 26.4, 26.3, –1.0; HRMS Calcd for $C_{25}H_{35}NOPSi$ $[M + H]^+$: 424.2226; Found: 424.2228.

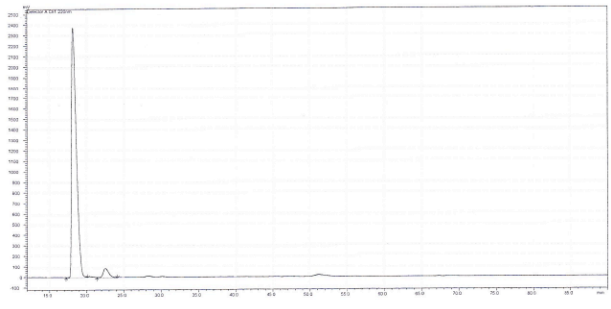
$[\alpha]^{20}_{D}$ = +33.1 (*c* = 1.51, $CHCl_3$) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99:1 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **8c**: 18 min (major) and 23 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.377	47401164	849912	50.180	53.335
2	21.954	47060820	743618	49.820	46.665
Total		94461983	1593530	100.000	100.000



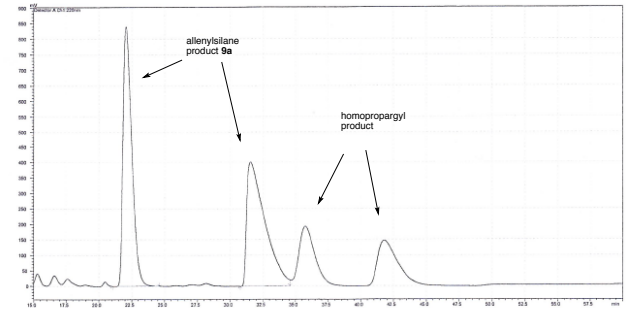
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.195	103247734	2375554	95.660	96.476
2	22.514	4684492	86771	4.340	3.524
Total		107932225	2462325	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
18.377	47401164	50.180	18.195	103247734	95.660
21.954	47060820	49.820	22.514	4684492	4.340

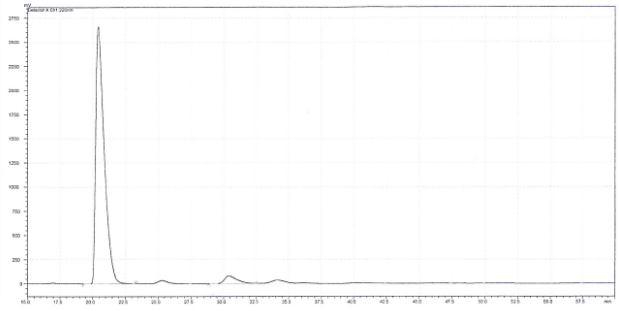
(*R*,*E*)-*P*,*P*-Diphenyl-*N*-(1-phenyl-4-(trimethylsilyl)hexa-1,4,5-trien-3-yl)phosphinic amide (9a): IR (neat): 3184 (w, br), 3056 (w), 2956 (w), 1927 (m), 1493 (m), 1248 (m), 1193 (m), 1123 (m), 1110 (m), 839 (s), 752 (m), 724 (m), 694 (m), 541 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95–7.88 (4H, m), 7.52–7.37 (6H, m), 7.32–7.19 (5H, m), 6.29 (1H, d, *J* = 16.0, Hz), 6.11 (1H, dd, *J* = 15.6, 7.2 Hz), 4.79 (1H, dd, *J* = 11.2, 2.8 Hz), 4.66 (1H, dd, *J* = 10.8, 2.0 Hz), 4.38–4.31 (1H, m), 3.52 (1H, t, *J* = 8.0 Hz), –0.06 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.0, 136.7, 133.1 (d, *J* = 129.4 Hz, only the peak at 133.7 is visible, the other is overlapping), 132.4 (d, *J* = 128.0 Hz, only the peak at 133.5 is visible, the other is overlapping), 132.4 (d, *J* = 9.2 Hz), 132.3 (d, *J* = 9.6 Hz), 131.9 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 2.6 Hz), 131.6 (d, *J* = 3.5 Hz), 130.6, 128.6 (d, *J* = 12.4 Hz), 128.5, 128.4 (d, *J* = 12.0 Hz, only the peak at 128.4 is visible, the other is overlapping), 127.7, 126.7, 99.8 (d, *J* = 5.9 Hz), 73.8, 52.2, –1.0; HRMS Calcd for $C_{27}H_{31}NOPSi$ $[M + H]^+$: 444.1913; Found: 444.1900. $[\alpha]^{20}_{D}$ = –129.9 (*c* = 1.00, $CHCl_3$) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 98:2 hexanes:*i*-PrOH, 0.6 mL/min, 220 nm): t_R of **9a**: 20 min (major) and 30 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	22.072	38952953	839824	50.127	67.730
2	31.551	38755475	400138	49.873	32.270
Total		77708428	1239962	100.000	100.000



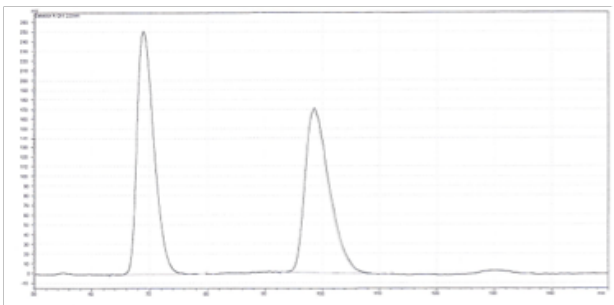
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.421	121121330	2662169	95.749	97.053
2	30.414	5377738	80828	4.251	2.947
Total		126499068	2742996	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
22.072	38952953	50.127	20.421	121121330	95.749
31.551	38755475	49.873	30.414	5377738	4.251

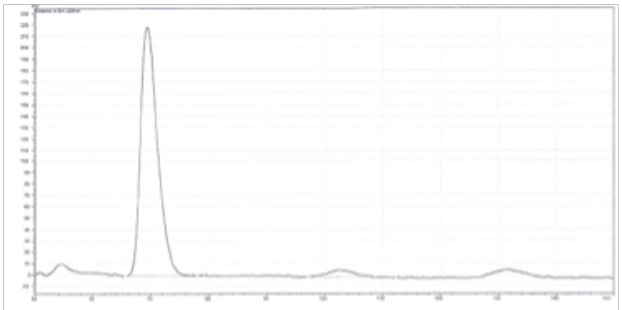
(*R*,*E*)-*N*-(1-(4-Methoxyphenyl)-4-(trimethylsilyl)hexa-1,4,5-trien-3-yl)-*P*,*P*-diphenylphosphinic amide (9b): IR (neat): 3178 (w, br), 2955 (w), 1926 (m), 1607 (m), 1510 (s), 1438 (m), 1248 (s), 1194 (s), 1122 (m), 1035 (m), 839 (s), 724 (s), 696 (s), 527 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94–7.86 (4H, m), 7.51–7.36 (6H, m), 7.17 (2H, d, J = 8.8 Hz), 6.80 (2H, d, J = 8.8 Hz), 6.22 (1H, d, J = 15.6 Hz), 5.95 (1H, dd, J = 15.6, 7.2 Hz), 4.77 (1H, dd, J = 11.2, 2.8 Hz), 4.64 (1H, dd, J = 10.8, 2.4 Hz), 4.35–4.28 (1H, m), 3.80 (3H, s), 3.49 (1H, t, J = 8.4 Hz), –0.03 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.9, 159.3, 133.3 (d, J = 129.5 Hz), 133.0 (d, J = 129.5 Hz), 132.4 (d, J = 9.2 Hz), 132.3 (d, J = 9.6 Hz), 131.8 (d, J = 2.9 Hz), 131.8 (d, J = 2.8 Hz), 130.2, 129.6, 129.5, 128.5 (d, J = 12.2 Hz), 128.4 (d, J = 12.5 Hz), 127.9, 114.0, 100.0 (d, J = 5.8 Hz), 73.7, 55.4, 52.4, –1.0; HRMS Calcd for $C_{28}H_{33}NO_2PSi$ $[M + H]^+$: 474.2018; Found: 474.1996. $[\alpha]^{20}_D$ = –149.9 (c = 1.00, $CHCl_3$) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OZ–H, 97:3 hexanes:*i*-PrOH, 0.8 mL/min, 220 nm): t_R of **9b**: 69 min (major) and 102 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	68.912	51417967	251693	50.686	59.588
2	98.616	50026172	170699	49.314	40.412
Total		101444138	422392	100.000	100.000



PeakTable

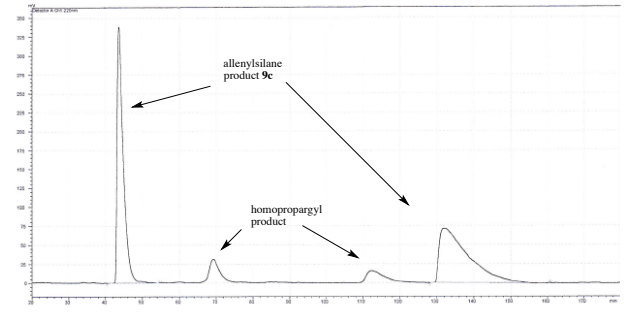
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	69.336	44551661	218824	95.900	97.277
2	102.282	1904654	6125	4.100	2.723
Total		46456314	224948	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
68.912	51417967	50.686	69.336	44551661	95.900

98.616	50026172	49.314	102.282	1904654	4.100

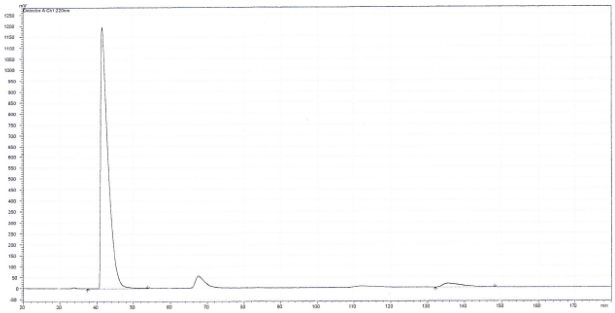
(*R*,*E*)-N-(1-(2-Nitrophenyl)-4-(trimethylsilyl)hexa-1,4,5-trien-3-yl)-P,P-diphenylphosphinic amide (9c): IR (neat): 3170 (w, br), 3060 (w), 2957 (w), 1927 (m), 1523 (s), 1438 (m), 1346 (m), 1249 (m), 1192 (m), 1123 (m), 1110 (m), 839 (s), 751 (m), 725 (m), 697 (m), 555 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.96–7.87 (5H, m), 7.53–7.40 (8H, m), 7.39–7.35 (1H, m), 6.80 (1H, dd, *J* = 15.6 Hz), 6.17 (1H, dd, *J* = 15.6, 7.2 Hz), 4.78 (1H, dd, *J* = 11.2, 2.4 Hz), 4.67 (1H, dd, *J* = 11.2, 2.0 Hz), 4.35–4.28 (1H, m), 3.54 (1H, dd, *J* = 9.2, 7.2 Hz), –0.08 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.2, 147.7, 137.3 (d, *J* = 3.5 Hz), 133.3, 133.1 (d, *J* = 128.5 Hz), 132.7, 132.5 (d, *J* = 127.9 Hz), 132.4 (d, *J* = 9.7 Hz), 132.3 (d, *J* = 9.5 Hz), 132.1 (d, *J* = 2.6 Hz), 132.0 (d, *J* = 2.8 Hz), 129.4, 128.7 (d, *J* = 12.6 Hz), 128.6 (d, *J* = 12.4 Hz), 125.7, 124.6, 99.2 (d, *J* = 5.9 Hz), 74.0, 52.3, –1.1; HRMS Calcd for $C_{27}H_{30}N_2O_3PSi$ $[M + H]^+$: 489.1763; Found: 489.1760. $[\alpha]^{20}_D$ = –90.8 (*c* = 1.10, $CHCl_3$) for a 96:4 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 98:2 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **9c**: 42 min (major) and 136 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.564	39525023	338303	50.592	82.554
2	132.143	38600722	71491	49.408	17.446
Total		78125746	409794	100.000	100.000



PeakTable

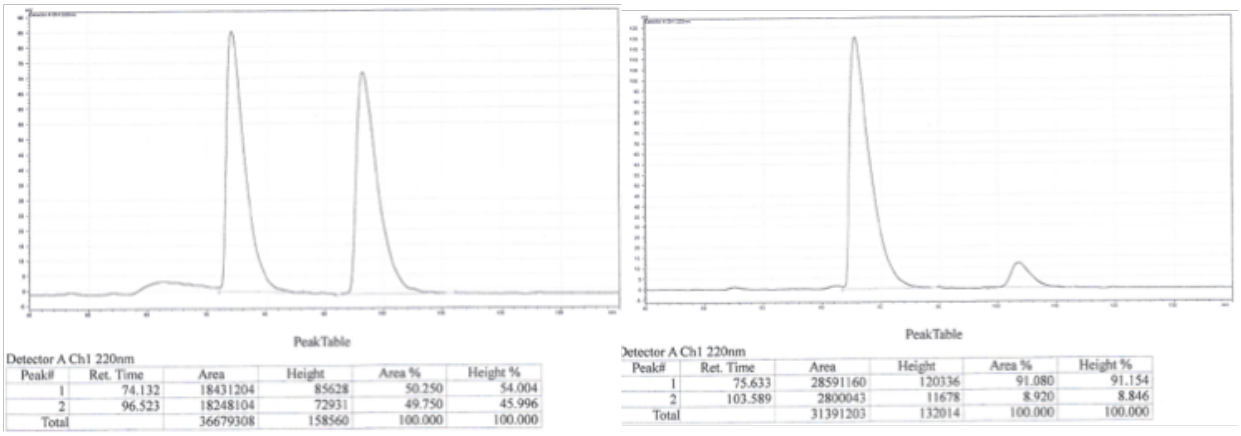
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	41.502	163147249	1195911	95.709	98.534
2	135.528	7314265	17799	4.291	1.466
Total		170461514	1213710	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
43.564	39525023	50.592	41.502	163147249	95.709
132.143	38600722	49.408	135.528	7314265	4.291

(*R*,*E*)-*N*-(2-methyl-1-phenyl-4-(trimethylsilyl)hexa-1,4,5-trien-3-yl)-*P*,*P*-diphenylphosphinic amide (10): IR (neat): 3346 (w), 3204 (w, br), 3024 (w), 2956 (w), 1927 (m), 1438 (m), 1248 (m), 1199 (m), 1123 (m), 1110 (m), 1076 (m), 840 (s), 752 (m), 724 (m), 697 (s), 541 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.94–7.85 (4H, m), 7.52–7.37 (7H, m), 7.29–7.27 (1H, m), 7.20–7.16 (1H, m), 7.07–7.05 (2H, m), 6.09 (1H, s), 4.82 (1H, dd, *J* = 10.8, 3.2 Hz), 4.68 (1H, dd, *J* = 11.2, 2.8 Hz), 4.31 (1H, tt, *J* = 8.8, 2.8 Hz), 3.71 (1H, t, *J* = 8.0 Hz), 1.78 (3H, d, *J* = 1.2 Hz), –0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 207.5, 138.2 (d, *J* = 3.1 Hz), 137.5, 133.0 (d, *J* = 126.9 Hz), 132.5 (d, *J* = 9.7 Hz), 132.1 (d, *J* = 9.8 Hz), 131.9 (d, *J* = 2.5 Hz), 131.8 (d, *J* = 2.4 Hz), 129.0, 128.6 (d, *J* = 12.7 Hz), 128.4 (d, *J* = 12.3 Hz), 128.1, 127.9, 126.6, 99.2 (d, *J* = 5.3 Hz), 74.2, 57.7, 13.2, –1.2; HRMS Calcd for $C_{28}H_{33}NOPSi$ $[M + H]^+$: 458.2069; Found: 458.2064. $[\alpha]^{20}_D$ = –74.9 (*c* = 1.60, $CHCl_3$) for a 91:9 er sample. The enantiomeric purity of this

compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 99.5:0.5 hexanes:*i*-PrOH, 0.5 mL/min, 220 nm): t_R of **10**: 76 min (major) and 104 min (minor).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	74.132	18431204	85628	50.250	54.004
2	96.523	18248104	72931	49.750	45.996
Total		36679308	158560	100.000	100.000

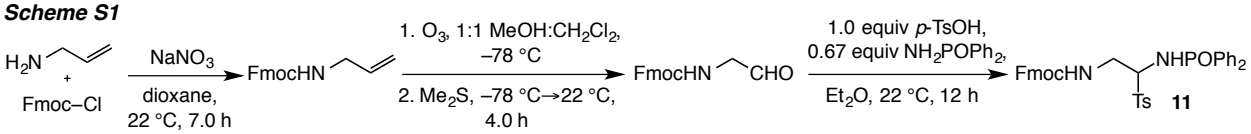
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	75.633	28591160	120336	91.080	91.154
2	103.589	2800043	11678	8.920	8.846
Total		31391203	132014	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
74.132	18431204	50.250	76.633	28591160	91.080
96.523	18248104	49.750	103.589	2800043	8.920

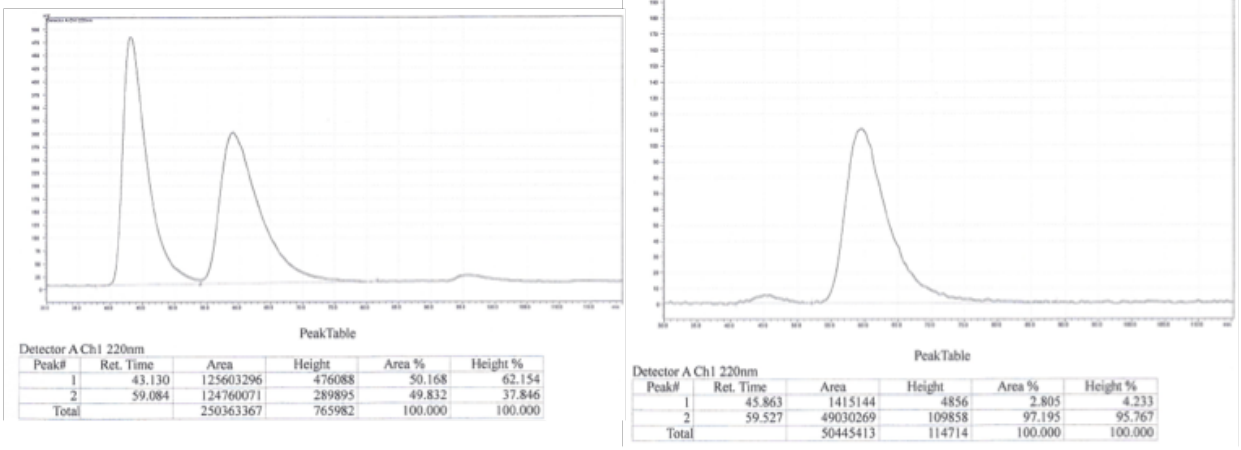
Scheme S1



Procedure for Synthesis of (9*H*-Fluoren-9-yl)methyl (2-((diphenylphosphoryl)amino)-2-tosylethyl)carbamate (11; cf. Scheme S1). To a solution of allylamine (0.65 g, 11.4 mmol) in dioxane (70 mL), placed in a vessel, was added $NaHCO_3$ (1.92 g, 22.8 mmol) and Fmoc–Cl (1.97 g, 7.61 mmol) at 0 ºC. The mixture was allowed to stir at 22 ºC for 7 h until TLC analysis indicated the complete disappearance of Fmoc–Cl. At this point, the resulting solution was diluted by addition of a saturated solution of $NaHCO_3$ (50 mL) and washed with EtOAc (50 mL). The organic layer was subsequently washed with a saturated solution of $NaHCO_3$, brine, and water, respectively; the organic layer was dried over $MgSO_4$ and the volatiles were removed in vacuo. The resulting yellow solid residue was purified by crystallization from hot ethanol to afford Fmoc–protected allylamine **A** as white solid (1.85 g, 6.62 mmol, 87 % yield). The latter compound (**A**; 0.8 g, 2.86 mmol) was dissolved in CH_2Cl_2 (5.0 mL) and MeOH (60 mL) and cooled to –78 ºC in a round bottom flask. At –78 °C, ozone was introduced into the mixture until the solution turned blue (~ 5 min), at which time it was purged with N_2 (~ 10 min); Me_2S (420 µL, 5.72 mmol) was then added in a single portion (at –78 ºC). The solution was subsequently allowed to warm to 22 ºC (over the course of ~ 1 h) and stir for 4 h at 22 ºC. The volatiles were removed in vacuo and the resulting faint yellow solid was purified by silica gel chromatography (CH_2Cl_2→20% EtOAc:CH_2Cl_2) to afford aldehyde **B** as pale yellow solid (640 mg, 2.28 mmol, 80% yield). Aldehyde **B** (260 mg, 0.93 mmol) was placed in a round bottom flask containing *p*-

toluenesulfinic acid (145 mg, 0.93 mmol) and *P*,*P*-diphenylphosphinic amide (134 mg, 0.62 mmol); Et_2O was introduced (25 mL) and the solution was allowed to stir for 12 h at 22 ºC. The resulting white precipitate was filtered, washed with Et_2O and dried under reduced pressure to afford **11** as white solid (290 mg, 0.46 mmol, 74% yield). Melting point: 117–120 ºC. IR (neat): 3325 (w, br), 3061 (w, br), 1704 (s), 1548 (m), 1477 (w), 1435 (m), 1291 (m), 1263 (s), 1189 (s), 1126 (s), 1083 (m), 1023 (m), 907 (w), 808 (w), 724 (s), 539 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.86–7.81 (2H, m), 7.78–7.76 (4H, m), 7.70–7.65 (2H, m), 7.56–7.43 (7H, m), 7.41–7.38 (4H, m), 7.33–7.29 (2H, m), 7.24–7.22 (1H, m), 6.76–6.73 (1H, m), 4.31–4.14 (5H, m), 3.83–3.78 (1H, m), 3.54–3.47 (1H, m), 2.50 (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.9, 145.8, 144.1, 144.0, 141.4, 133.5, 132.8 (d, J = 2.1 Hz), 132.5 (d, J = 3.0 Hz), 132.4 (d, J = 9.9 Hz), 132.0 (d, J = 9.9 Hz), 130.2, 129.6, 128.9 (d, J = 12.9 Hz), 128.7 (d, J = 13.0 Hz), 127.8, 127.2, 125.6, 125.5, 120.0, 71.9, 67.6, 47.2, 41.6, 22.0; HRMS Calcd for $C_{36}H_{33}N_2O_5PS$ $[M]^+$: 636.1848; Found: 636.1835.

Procedure for Synthesis of (9*H*-Fluoren-9-yl)methyl (*R*)-(2-((diphenylphosphoryl)amino)-3-(trimethylsilyl)penta-3,4-dien-1-yl)carbamate (12). To a vial was added sulfinic adduct **11** (200 mg, 0.337 mmol), CH_2Cl_2 (6 mL) and saturated $NaHCO_3$ (6 mL). The biphasic mixture was allowed to stir vigorously for 1 h. The layers were separated and the organic layer was filtered through $MgSO_4$ and the volatiles were removed in vacuo. The unpurified imine was then subjected to the aforementioned conditions for NHC–Cu-catalyzed allenylsilane addition. The resulting yellow oil was purified by silica gel chromatography (hexanes→50% EtOAc:hexanes) to afford homoallenylamide **12** as colorless oil (125 mg, 0.21 mmol, 62.0 % yield). IR (neat): 3259 (m, br), 3056 (m), 2951 (m), 1927 (m), 1718 (s), 1544 (m), 1439 (m), 1249 (s), 1187 (m), 1122 (s), 1110 (m), 757 (s), 741 (s), 726 (s), 697 (s), 668 (m), 555 (m), 525 (m) cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.93 (4H, dt, J = 13.5, 7.0 Hz), 7.76 (2H, d, J = 7.5 Hz), 7.73 (2H, t, J = 8.5 Hz), 7.54–7.42 (6H, m), 7.39 (2H, t, J = 7.5 Hz), 7.33–7.29 (2H, m), 4.79 (1H, dd, J = 11.5, 2.5 Hz), 4.64 (1H, dd, J = 11.0, 1.0 Hz), 4.34 (1H, dd, J = 9.5, 7.0 Hz), 4.28 (1H, t, J = 7.5 Hz), 4.20 (1H, dd, J = 9.5, 7.5 Hz), 3.64 (1H, ddd, J = 13.5, 8.0, 2.0 Hz), 3.53 (1H, q, J = 10.5 Hz), 3.42 (1H, t, J = 10.5 Hz), 2.92 (1H, ddd, J = 12.5, 9.0, 2.5 Hz), –0.09 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 208.1, 157.0, 144.4, 144.3, 141.4, 141.4, 132.9 (d, J = 9.7 Hz), 132.8 (d, J = 9.3 Hz), 132.8 (d, J = 128.6 Hz), 132.3 (d, J = 2.9 Hz), 132.3 (d, J = 2.7 Hz), 131.1 (d, J = 128.4 Hz, only the peak at 130.5 is visible, the other is overlapping), 128.8 (d, J = 12.7 Hz), 128.8 (d, J = 12.7 Hz), 127.7, 127.2, 125.8, 125.7, 120.0, 120.0, 98.3 (d, J = 7.1 Hz), 73.9, 67.2, 57.8, 48.8, 47.4, –1.2; HRMS Calcd for $C_{35}H_{38}N_2O_3PSi$ $[M + H]^+$: 593.2389; Found: 593.2377. $[\alpha]^{20}_D$ = +39.6 (c = 1.26, $CHCl_3$) for a 97:3 er sample. The enantiomeric purity of this compound was determined by HPLC analysis in comparison with authentic racemic material (Chiracel OD–H, 96:4 hexanes:*i*-PrOH, 0.8 mL/min, 220 nm): t_R of **12**: 46 min (minor) and 60 min (major).



PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	43.130	125603296	476088	50.168	62.154
2	59.084	124760071	289895	49.832	37.846
Total		250363367	765982	100.000	100.000

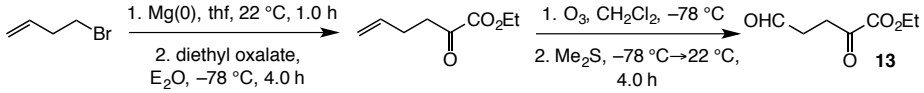
PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	45.863	1415144	4856	2.805	4.233
2	59.527	49030269	109858	97.195	95.767
Total		50445413	114714	100.000	100.000

Retention Time	Area	Area %	Retention Time	Area	Area %
43.130	125603296	50.168	45.863	1415144	2.805
59.084	124760071	49.832	59.527	49030269	97.195

Scheme S2



Procedure for Synthesis of ethyl 2,5-dioxopentanoate (13; cf. Scheme S2). To a flame-dried 100 mL round bottom flask equipped with a reflux condenser was added magnesium turnings (1.25 g, 51.6 mmol) and thf (35 mL) under N_2 atm. 4-Bromo-1-butene (2.25 mL, 22.1 mmol) was added (CAUTION: EXOTHERM!) and the resulting brown heterogeneous solution was allowed to stir for 1 h (leading to the formation of the Grignard reagent). To a separate 250 mL round bottom flask with a stir bar was added diethyl oxalate (2.5 mL, 18.5 mmol), thf (20 mL) and Et_2O (40 mL) and the mixture was allowed to cool to –78 ºC. The solution of the Grignard reagent was added drop-wise to the flask containing diethyl oxalate and the mixture was allowed to stir for 4 h at –78 ºC. The reaction was quenched by the addition of a saturated solution of NH_4Cl (20 mL) and the mixture was diluted by the addition of water (50 mL). The organic layer was separated, washed with water, dried over $MgSO_4$ and the volatiles were removed in vacuo, affording a yellow oil which was purified by silica gel chromatography (hexanes→10% Et_2O:hexanes) to afford ethyl 2-oxohex-5-enoate as yellow oil (1.85 g, 11.9 mmol, 64% yield). The ^1H NMR spectrum matched that reported previously.[vii] ^1H NMR (400 MHz, $CDCl_3$): δ 5.82 (1H, ddt, J = 16.8, 10.0, 6.4 Hz), 5.10–5.00 (2H, m), 4.32 (2H, q, J = 6.8 Hz), 2.95 (2H, t, J = 7.2 Hz), 2.42–2.36 (2H, m), 1.37 (3H, t, J = 7.2 Hz). A sample of ethyl 2-oxohex-5-enoate thus prepared (0.95 g, 6.0 mmol) was added to a 100 mL round bottom flask containing CH_2Cl_2 (50 mL) and the resulting solution was allowed to cool to –78 ºC. Ozone was introduced into the mixture until the solution turned blue (~ 5 min). N_2 was next introduced until the blue color disappeared (~ 10 min) after which the mixture was charged with Me_2S (670 μL, 9.1 mmol) in a single portion at –78 ºC. The solution was allowed to warm slowly to 22 ºC (over the course of ~ 1 h) and stir for 12 h at 22 ºC. The volatiles were removed in vacuo, affording orange oil,

Kugelrohr distillation of which delivered 2,5-dioxopentanoate **13** as light yellow oil (340 mg, 2.15 mmol, 36 % yield). IR (neat): 2985 (w), 2912 (w), 2845 (w), 1721 (s), 1391 (m), 1255 (m), 1087 (m), 1042 (s), 1016 (m), 644 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.79 (1H, s), 4.32 (2H, q, J = 7.2 Hz), 3.13 (2H, t, J = 6.4 Hz), 2.85 (2H, t, J = 6.8 Hz), 1.36 (3H, t, J = 7.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 199.4, 192.5, 160.6, 62.8, 37.2, 31.7, 14.1; HRMS Calcd for $C_7H_{11}O_4$ $[M + H]^+$: 159.0657; Found: 159.0650.

Procedure for Synthesis of Ethyl (*R*)-1-(1-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-3-(trimethylsilyl)penta-3,4-dien-2-yl)-1*H*-pyrrole-2-carboxylate (14). To a vial containing **12** (52 mg, 0.088 mmol) was added MeOH (3 mL), a 3.0 M aqueous solution of HCl (1.0 mL), and the solution was allowed to stir at 22 °C for 24 h. The solvent was then removed in vacuo and the resulting yellow oil was purified by silica gel chromatography (CH_2Cl_2→10% MeOH:CH_2Cl_2) to provide the desired amine as pale yellow solid. To the amine was added 2,5-dioxopentanoate (**13**; 42 mg, 0.263 mmol) followed by toluene (0.9 mL) and a 3.0 M solution of HCl (0.1 mL). The resulting biphasic solution was allowed to stir vigorously at 90 ºC for 1 h. The red solution was subsequently diluted by addition of water (1.0 mL) and then Et_2O (2.0 mL). The layers were separated and the aqueous layer was washed with Et_2O (2x1 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed to give brown oil, which was purified by medium pressure liquid chromatography (MPLC) (hexanes→20% Et_2O:hexanes) to afford pyrrole **14** as colorless oil (23 mg, 0.045 mmol, 51% yield). IR (neat): 3347 (w, br), 2955 (w), 1928 (m), 1700 (s), 1526 (m), 1450 (m), 1417 (m), 1368 (m), 1249 (m), 1227 (s), 1103 (s), 1073 (m), 842 (s), 758 (m), 739 (s) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (2H, d, J = 7.6 Hz), 7.51 (2H, d, J = 7.2 Hz), 7.39 (2H, t, J = 7.6 Hz), 7.31–7.27 (2H, m), 7.05 (1H, t, J = 2.4 Hz), 6.96 (1H, dd, J = 4.0, 1.6 Hz), 6.17 (1H, t, J = 3.6 Hz), 6.08–6.04 (1H, m), 5.14 (1H, t, J = 6.0 Hz), 4.73–4.67 (2H, m), 4.29–4.13 (5H, m), 3.74–3.67 (2H, m), 1.30 (3H, t, J = 7.2 Hz), –0.05 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 209.3, 160.1, 156.2, 144.2, 144.2, 141.4, 127.7, 127.1, 126.5, 125.4, 125.3, 122.8, 120.0, 118.6, 109.1, 95.4, 72.5, 67.0, 60.2, 53.7, 47.3, 46.8, 14.5, –1.8; HRMS Calcd for $C_{30}H_{35}N_2O_4Si$ $[M + H]^+$: 515.2366; Found: 515.2349. $[\alpha]^{20}_D$ = +73.8 (c = 1.49, $CHCl_3$) for a 97:3 er sample.

Procedure for Synthesis of Ethyl (*S*)-1-(1-((((9*H*-fluoren-9-yl)methoxy)carbonyl)amino)-5-bromopent-3-yn-2-yl)-4,5-dibromo-1*H*-pyrrole-2-carboxylate (15). To a vial containing pyrrole **14** (17 mg, 0.033 mmol) was added acetic acid (1.0 mL). Bromine (5.1 μL, 0.1 mmol) was the introduced in a drop-wise manner and the resulting yellowish orange solution was allowed to stir for 1 h at 22 ºC. A saturated solution of sodium thiosulfate was subsequently introduced in a drop-wise manner until the solution turned colorless. The mixture was diluted with water (1.0 mL) and washed with Et_2O (3x1.0 mL). After separation from the aqueous phase, the organic layer was dried over $MgSO_4$, concentrated in vacuo and excess acetic acid was removed through azeotropic removal with heptane in vacuo. The resulting yellow oil was purified by silica gel chromatography (hexanes→25 % EtOAc:hexanes) followed by trituration with hexanes to afford dibromopyrrole **15** as white solid (14.1 mg, 0.021 mmol, 63 % yield). Melting point = 138–140 ºC. IR (neat): 3324 (w, br), 2954 (w), 2926 (m), 1707 (s), 1522 (m),

1449 (m), 1410 (m), 1330 (m), 1255 (m), 1211 (s), 1094 (m), 758 (m), 741 (m) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.76 (2H, d, *J* = 7.6 Hz), 7.59–7.51 (2H, m), 7.40 (2H, t, *J* = 7.2 Hz), 7.33–7.28 (2H, m), 7.06 (1H, s), 5.04 (1H, t, *J* = 6.8 Hz), 4.41–4.17 (6H, m), 4.06–3.98 (1H, m), 3.94–3.92 (2H, m), 3.89–3.82 (1H, m), 1.27 (3H, br t, *J* = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 156.2, 144.0, 143.9, 141.4, 127.8, 127.2, 125.2, 125.2, 124.6, 120.8, 120.1, 112.2, 101.9, 82.5, 81.0, 67.2, 61.1, 47.3, 45.4, 44.5, 14.3, 13.9; HRMS Calcd for $C_{27}H_{24}Br_3N_2O_4$ $[M + H]^+$: 676.9286; Found: 676.9306. $[\alpha]^{20}_D$ = +2.8 (*c* = 1.65, $CHCl_3$) for a 97:3 er sample.

Procedure for Synthesis of *bis*-Boc-2-(3-(6,7-dibromo-1-oxo-1,2,3,4-tetrahydropyrrolo[1,2-*a*]pyrazin-4-yl)prop-2-yn-1-yl)guanidine (17). To a vial containing dibromopyrrole **15** (13.0 mg, 0.019 mmol) were added K_2CO_3 (10.5 mg, 0.076 mmol) and *bis*-Boc-guanidine **16** (14.9 mg, 0.057 mmol). Dimethylformamide (0.5 mL) was then added and the resulting yellow solution was allowed to stir for 8 h at 22 ºC. At this point, the mixture was diluted with water (1.0 mL) and washed with Et_2O (3x1 mL). The combined organic layers were dried over $MgSO_4$ and the volatiles were removed in vacuo, affording yellow oil which was purified by MPLC (hexanes→50% EtOAc:hexanes) to afford protected guanidine **17** as white solid (7 mg, 0.012 mmol, 62% yield). Melting point = 78–81 ºC. IR (neat): 3379 (w), 2980 (w), 2926 (w), 1721 (m), 1672 (m), 1611 (m), 1550 (w), 1509 (w), 1466 (w), 1384 (m), 1368 (m), 1290 (s), 1242 (s), 1143 (s), 1089 (m), 749 (w) cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 9.39–9.31 (1H, br s), 9.21–9.13 (1H, br s), 7.02 (1H, s), 5.07 (1H, app d, *J* = 2.0 Hz), 4.81 (1H, d, *J* = 17.2 Hz), 4.66 (1H, d, *J* = 17.2 Hz), 3.96 (1H, dd, *J* = 12.8, 4.0 Hz), 3.68 (1H, ddd, *J* = 11.6, 4.4, 0.8 Hz), 1.50 (9H, s), 1.39 (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.8, 158.2, 154.1, 125.2, 116.9, 107.3, 101.7, 85.1, 82.5, 79.4, 46.0, 45.6, 34.4, 29.9, 28.5, 28.0; HRMS Calcd for $C_{21}H_{28}{}^{79}Br_1{}^{81}Br_1N_5O_5$ $[M + H]^+$: 590.0437; Found: 590.0458. $[\alpha]^{20}_D$ = +18.6 (*c* = 0.48, $CHCl_3$) for a 97:3 er sample.

Procedure for Synthesis of *S*-(–)-Cyclooroidin: To a vial containing protected guanidine **17** (9.0 mg, 0.015 mmol) was added AgOAc (0.3 mg, 0.002 mmol) followed by acetonitrile (1.0 mL). The resulting heterogeneous mixture was allowed to stir for 1 h at 22 ºC, after which it was filtered through a bed of celite. The volatiles were removed in vacuo to furnish colorless oil to which was added a solution of trifluoroacetic acid (1.0 mL) in CH_2Cl_2 (1.0 mL). The mixture was allowed to stir for 1 h at 22 ºC. Removal of the volatiles afforded orange oil, which was purified by silica gel chromatography (80:15:5 CH_2Cl_2:MeOH:NH_4OH) to afford the target molecule as pale yellow oil (5.4 mg, 0.014 mmol, 90% yield). Spectroscopic data for the synthetic material were in agreement with those reported previously.[viii] IR (neat): 3218 (br, m), 2923 (br, w) 1649 (s), 1571 (w), 1550 (m), 1465 (m), 1428 (m), 1337 (m), 1202 (w), 1121 (w), 749 (w) cm^{-1}; ^1H NMR (400 MHz, CD_3OD): δ 6.94 (1H, s), 6.30 (1H, s), 4.62–4.57 (1H, m), 3.78 (1H, dd, *J* = 13.6, 4.4 Hz), 3.55 (1H, dd, *J* = 13.6, 1.2 Hz), 2.81 (2H, d, *J* = 7.6 Hz); ^{13}C NMR (100 MHz, CD_3OD): δ 161.0, 151.1, 129.7, 125.8, 116.5, 112.4, 108.7, 101.2, 55.4, 43.3, 30.9; HRMS Calcd for $C_{11}H_{12}Br_2N_5O$ $[M + H]^+$: 387.9403; Found: 387.9409. $[\alpha]^{20}_D$ = –11.6 (*c* = 0.25, CH_3OH) for a 97:3 er sample. Previously reported optical rotation values for *S*-(–)-Cyclooroidin[8b]: $[\alpha]^{25}_D$ = –12.5 (*c* = 0.02, CH_3OH), $[\alpha]^{25}_D$ = –33.0 (*c* = 1, CH_3OH). Previously reported optical rotation

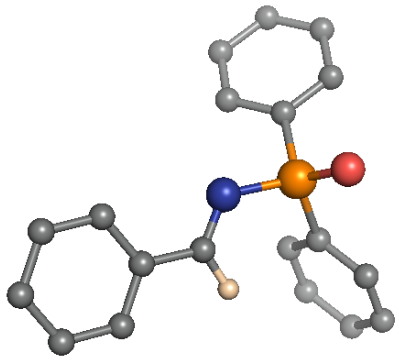
value for *R*-(+)-Cyclooroidin[8a]: $[\alpha]_D = +10.6$ (*c* = 0.02, CH_3OH).

Computational Details

Geometries of the imine substrate, NHC–Cu compounds **1-6, A-C**, and transition states leading to imine addition **7-14** were optimized using the B3LYP/LANL2DZ method. Frequency calculations were carried out at the same level of theory. The computed frequencies of all geometries are real-valued, except for the transition state geometries, which are all real-valued but one, which is imaginary. The reported Gibbs free energies were computed at 298K and 1 atm. using the computed unscaled normal mode frequencies. **1-6** were also computed without solvent corrections as in a previous study.[ix] The calculations were carried out with the

Gaussian09 program.[x] Tetrahydrofuran solvation effects using the PCM method were included in calculations for structures **A-C** and **7-14**. Computed free energies (in kcal/mol) are presented in Tables **S1** through **S4**. The relative Gibbs free energies of the reaction are also depicted in Figure **S1** through **S3**.

The optimized structure for benzaldehyde-derived phosphinoylimine substrate



Cartesian coordinates (Angstroms):

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C	3.903	2.711	-3.882
H	4.880	-0.025	-5.707
C	4.583	0.569	-4.846
C	3.807	2.117	-2.615
C	4.488	-0.029	-3.577
H	3.507	2.694	-1.745
C	4.100	0.740	-2.454
H	4.710	-1.088	-3.455
C	4.008	0.083	-1.138
H	5.375	2.198	1.206
N	3.687	0.730	-0.056
H	4.238	-0.993	-1.139
H	6.341	3.807	2.847
C	5.100	2.136	2.254
C	5.637	3.049	3.182
P	3.460	-0.084	1.518
C	4.186	1.157	2.690
C	5.258	2.987	4.537
C	4.519	-1.623	1.557
H	6.439	-0.594	1.527
C	5.928	-1.554	1.546
C	3.868	-2.872	1.595
C	3.798	1.095	4.044

```
C     4.336     2.011     4.967
C     6.685    -2.740     1.574
C     4.629    -4.057     1.624
H     7.771    -2.689     1.569
H     3.079     0.349     4.374
H     4.036     1.966     6.011
O     1.917    -0.441     1.825
H     6.623    -4.906     1.636
C     6.036    -3.992     1.612
H     4.128    -5.021     1.656
H     2.782    -2.909     1.612
H     5.672     3.695     5.251
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                     1                     2                     3
                     A                     A                     A
 Frequencies --    14.1037               25.4733               31.8527
 Red. masses --     3.8016                3.8025                4.3370
 Zero-point correction=                           0.301270 (Hartree/Particle)
 Thermal correction to Energy=                    0.320215
 Thermal correction to Enthalpy=                  0.321160
 Thermal correction to Gibbs Free Energy=         0.249979
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 Sum of electronic and thermal Energies=         -869.655163
 Sum of electronic and thermal Enthalpies=       -869.654219
 Sum of electronic and thermal Free Energies=    -869.725400

         Item               Value     Threshold  Converged?
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 RMS     Force            0.000000     0.000300     YES

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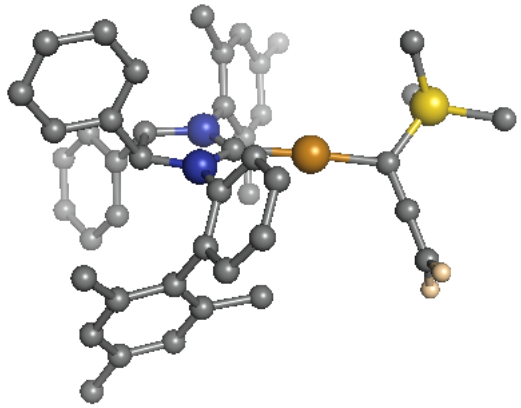
Optimized structure for NHC–Cu–silylallene complex **1** without solvent correction



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Cartesian coordinates (Angstroms):
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C     0.397    -0.052     0.389
N    -0.806    -0.599     0.737
C    -1.982    -2.687     0.027
C    -2.152    -4.079     0.209
C    -1.030    -2.023     0.843
C    -1.389    -4.802     1.141
C    -0.258    -2.749     1.773
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C	-0.427	-4.134	1.920
C	1.532	2.616	2.699
C	1.957	2.890	1.267
C	2.997	3.809	1.021
C	1.361	2.227	0.165
C	3.465	4.070	-0.281
C	4.604	5.043	-0.526
C	1.823	2.453	-1.157
C	2.866	3.377	-1.352
C	1.262	1.699	-2.346
C	-4.879	-2.081	0.369
C	-4.845	-1.116	-1.967
C	-4.138	-1.720	-0.909
C	-5.016	-0.181	-4.330
C	-4.225	-0.810	-3.196
C	-2.754	-2.005	-1.069
C	-2.863	-1.132	-3.347
C	-2.115	-1.732	-2.310
C	-0.667	-2.115	-2.560
C	-2.433	4.962	-0.876
C	-1.835	4.081	0.044
C	-1.764	2.698	-0.222
C	-2.972	4.464	-2.077
C	-2.905	3.084	-2.350
C	-2.304	2.207	-1.431
C	-4.260	0.581	4.056
C	-3.756	0.580	2.742
C	-2.391	0.327	2.495
C	-3.402	0.318	5.141
C	-2.038	0.060	4.901
C	-1.537	0.067	3.588
H	-1.017	2.333	1.740
H	-2.697	0.315	0.375
H	-2.873	-4.598	-0.418
H	-1.532	-5.874	1.246
H	0.479	-2.223	2.372
H	0.186	-4.681	2.631
H	2.315	2.932	3.397
H	1.343	1.549	2.864
H	0.616	3.158	2.974
H	3.460	4.316	1.866
H	4.816	5.646	0.364
H	4.374	5.726	-1.353
H	5.525	4.507	-0.793
H	3.226	3.552	-2.365
H	1.644	0.668	-2.364
H	1.559	2.180	-3.284
H	0.170	1.644	-2.319
H	-4.315	-1.814	1.269
H	-5.064	-3.162	0.425
H	-5.852	-1.578	0.411
H	-5.902	-0.889	-1.833
H	-4.356	0.171	-5.131
H	-5.612	0.672	-3.979
H	-5.716	-0.904	-4.772
H	-2.370	-0.928	-4.296
H	-0.491	-3.181	-2.370
H	0.030	-1.572	-1.910
H	-0.380	-1.908	-3.597
H	-2.480	6.025	-0.656
H	-1.420	4.471	0.971
H	-3.438	5.142	-2.789
H	-3.318	2.690	-3.275
H	-2.263	1.146	-1.666
H	-5.314	0.781	4.232

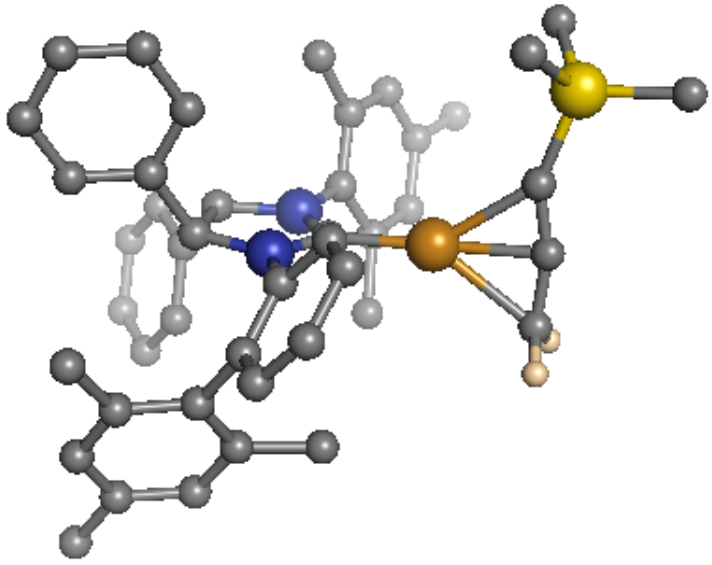
```
H    -4.424     0.786     1.908
H    -3.790     0.312     6.156
H    -1.370    -0.150     5.733
H    -0.482    -0.135     3.415
Cu    2.001    -1.040    -0.104
Si    5.259    -1.619     0.003
C     3.559    -2.043    -0.682
C     3.348    -3.003    -1.556
C     3.119    -3.975    -2.452
H     3.166    -3.783    -3.523
H     2.888    -4.992    -2.141
C     6.572    -2.923    -0.445
C     5.148    -1.483     1.902
C     5.815     0.073    -0.676
H     4.801    -2.429     2.341
H     4.437    -0.697     2.192
H     6.124    -1.239     2.346
H     6.328    -3.896     0.003
H     7.570    -2.625    -0.091
H     6.623    -3.067    -1.532
H     5.929     0.034    -1.768
H     6.778     0.380    -0.242
H     5.073     0.850    -0.446
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --    11.0232               13.7876               17.2469
 Red. masses --     3.2903                4.6453                4.1172
 Zero-point correction=                           0.819088 (Hartree/Particle)
 Thermal correction to Energy=                    0.870946
 Thermal correction to Enthalpy=                  0.871890
 Thermal correction to Gibbs Free Energy=         0.725721
 Sum of electronic and zero-point Energies=       -2052.769835
 Sum of electronic and thermal Energies=          -2052.717977
 Sum of electronic and thermal Enthalpies=        -2052.717033
 Sum of electronic and thermal Free Energies=     -2052.863201

         Item               Value     Threshold  Converged?
 Maximum Force            0.000323     0.000450     YES
 RMS     Force            0.000053     0.000300     YES

 SCF= -2053.58892270 Hartree
```

Transition state for isomerization of NHC–Cu–silylallene to NHC–Cu–silylpropargyl complex **2** without solvent correction



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----------------------------------------
Cartesian coordinates (Angstroms):
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H      6.369      0.473      0.348
H      2.910      0.026     -3.930
H      7.333     -1.763     -1.650
C      5.978     -0.311      1.009
H      6.760     -0.566      1.737
H      5.123      0.110      1.555
C      2.759     -0.899     -3.377
C      6.951     -2.513     -0.946
C      3.590     -1.198     -2.297
Si     5.445     -1.838      0.007
H      7.768     -2.788     -0.263
C      4.066     -1.362     -1.119
H      2.262     -1.707     -3.912
H      6.678     -3.405     -1.525
C      4.831     -3.181      1.209
H      5.631     -3.494      1.894
H      3.992     -2.809      1.813
H      4.486     -4.069      0.662
C     -0.944      1.401      1.187
N      0.285      1.252      0.323
C     -1.546     -0.051      1.157
C      0.462     -0.008     -0.168
N     -0.597     -0.777      0.246
C     -1.892     -2.696     -0.704
C     -1.939     -4.084     -0.969
C     -0.728     -2.178     -0.077
C     -0.866     -4.935     -0.660
C      0.353     -3.032      0.228
C      0.294     -4.402     -0.068
C      2.123      1.849      2.520
C      2.112      2.647      1.229
C      3.018      3.715      1.068
C      1.240      2.328      0.159
C      3.090      4.452     -0.129
C      4.095      5.577     -0.296
C      1.302      3.038     -1.068
C      2.228      4.093     -1.184
C      0.430      2.669     -2.252
```

C	-4.515	-2.768	0.711
C	-5.360	-1.100	-0.989
C	-4.291	-1.880	-0.502
C	-6.388	0.552	-2.631
C	-5.229	-0.296	-2.139
C	-3.037	-1.841	-1.173
C	-3.993	-0.303	-2.813
C	-2.895	-1.064	-2.356
C	-1.610	-1.078	-3.165
C	-2.758	4.778	1.100
C	-1.907	3.722	1.475
C	-1.888	2.514	0.747
C	-3.609	4.634	-0.012
C	-3.599	3.429	-0.742
C	-2.744	2.379	-0.368
C	-2.992	-1.108	4.549
C	-2.885	-0.636	3.227
C	-1.647	-0.656	2.554
C	-1.858	-1.617	5.209
C	-0.618	-1.646	4.540
C	-0.514	-1.166	3.224
H	-0.614	1.631	2.206
H	-2.543	-0.035	0.709
H	-2.823	-4.487	-1.457
H	-0.928	-5.996	-0.891
H	1.242	-2.613	0.687
H	1.141	-5.041	0.166
H	3.037	2.050	3.089
H	2.080	0.772	2.318
H	1.273	2.095	3.173
H	3.692	3.960	1.887
H	4.450	5.946	0.673
H	3.663	6.423	-0.845
H	4.975	5.237	-0.862
H	2.278	4.642	-2.123
H	0.728	1.694	-2.663
H	0.523	3.416	-3.047
H	-0.625	2.597	-1.969
H	-3.686	-2.716	1.425
H	-4.611	-3.823	0.418
H	-5.437	-2.488	1.236
H	-6.314	-1.129	-0.465
H	-6.222	0.902	-3.657
H	-6.529	1.438	-1.995
H	-7.331	-0.010	-2.615
H	-3.880	0.282	-3.725
H	-1.343	-2.100	-3.465
H	-0.752	-0.687	-2.605
H	-1.716	-0.476	-4.074
H	-2.759	5.703	1.672
H	-1.253	3.840	2.337
H	-4.271	5.446	-0.304
H	-4.253	3.308	-1.603
H	-2.754	1.459	-0.948
H	-3.953	-1.085	5.056
H	-3.766	-0.246	2.720
H	-1.939	-1.989	6.228
H	0.261	-2.043	5.042
H	0.447	-1.195	2.716
Cu	1.970	-0.583	-1.194

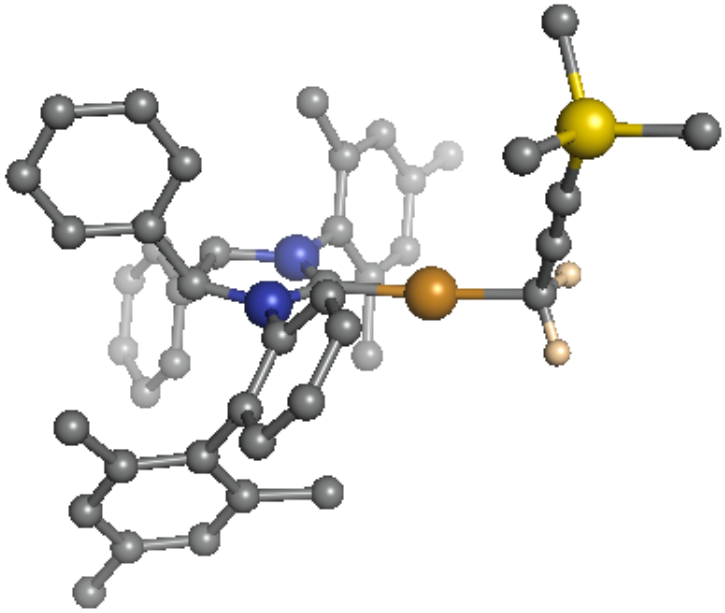
	1	2	3
	A	A	A
Frequencies --	-89.7420	14.0023	14.3967
Red. masses --	13.0684	4.8359	4.7105

```
Zero-point correction=                           0.818202 (Hartree/Particle)
Thermal correction to Energy=                    0.869595
Thermal correction to Enthalpy=                  0.870540
Thermal correction to Gibbs Free Energy=         0.725993
Sum of electronic and zero-point Energies=       -2052.752262
Sum of electronic and thermal Energies=          -2052.700868
Sum of electronic and thermal Enthalpies=        -2052.699924
Sum of electronic and thermal Free Energies=     -2052.844470

         Item               Value     Threshold  Converged?
Maximum Force            0.000004     0.000450     YES
RMS     Force            0.000000     0.000300     YES

SCF= -2053.57046384 Hartree
```

Optimized structure for NHC–Cu–silylpropargyl complex **3** without solvent correction



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Cartesian coordinates (Angstroms):
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H      6.245    -3.099    -0.426
H      5.511    -2.570     1.105
H      7.250    -2.927     1.030
C      6.407    -2.492     0.474
Si     6.755    -0.677     0.009
H      8.267    -1.195    -1.929
H      6.095     0.280     2.238
H      9.213    -1.014    -0.432
H      7.844    -0.044     2.190
C      8.365    -0.611    -1.004
C      6.991     0.332     1.606
H      8.604     0.422    -1.288
H      7.176     1.389     1.376
C     -1.663     0.988     1.232
N     -0.607     1.508     0.282
C     -1.419    -0.564     1.175
C      0.151     0.530    -0.279
N     -0.302    -0.678     0.173
C     -0.466    -2.975    -0.799
C      0.195    -4.183    -1.119
```

C	0.298	-1.939	-0.203
C	1.571	-4.356	-0.896
C	1.682	-2.107	0.012
C	2.322	-3.304	-0.341
C	0.735	3.029	2.400
C	0.237	3.676	1.121
C	0.422	5.061	0.931
C	-0.381	2.926	0.089
C	0.025	5.708	-0.254
C	0.248	7.196	-0.449
C	-0.773	3.545	-1.126
C	-0.564	4.929	-1.271
C	-1.364	2.751	-2.275
C	-2.617	-4.389	0.711
C	-4.272	-3.374	-0.907
C	-2.935	-3.503	-0.482
C	-6.073	-2.496	-2.478
C	-4.624	-2.609	-2.038
C	-1.909	-2.822	-1.195
C	-3.591	-1.972	-2.751
C	-2.239	-2.069	-2.356
C	-1.164	-1.417	-3.209
C	-4.969	2.926	1.385
C	-3.667	2.470	1.666
C	-3.077	1.446	0.897
C	-5.699	2.356	0.326
C	-5.118	1.330	-0.446
C	-3.817	0.879	-0.164
C	-1.835	-2.259	4.590
C	-2.092	-1.787	3.289
C	-1.082	-1.145	2.544
C	-0.556	-2.102	5.157
C	0.460	-1.466	4.416
C	0.197	-0.989	3.121
H	-1.422	1.354	2.235
H	-2.307	-1.069	0.786
H	-0.382	-4.981	-1.582
H	2.053	-5.292	-1.168
H	2.259	-1.295	0.444
H	3.392	-3.406	-0.185
H	1.479	3.667	2.887
H	1.202	2.057	2.203
H	-0.075	2.863	3.126
H	0.902	5.638	1.718
H	0.587	7.677	0.475
H	-0.672	7.699	-0.774
H	1.009	7.383	-1.220
H	-0.863	5.408	-2.202
H	-0.593	2.132	-2.755
H	-1.778	3.422	-3.036
H	-2.160	2.080	-1.938
H	-1.879	-3.936	1.382
H	-2.196	-5.351	0.387
H	-3.522	-4.604	1.290
H	-5.053	-3.891	-0.350
H	-6.175	-1.857	-3.363
H	-6.701	-2.073	-1.682
H	-6.490	-3.481	-2.729
H	-3.836	-1.399	-3.644
H	-0.445	-2.162	-3.576
H	-0.583	-0.673	-2.651
H	-1.606	-0.918	-4.079
H	-5.408	3.717	1.987
H	-3.108	2.916	2.487
H	-6.706	2.703	0.106

```
H    -5.675     0.882    -1.265
H    -3.392     0.085    -0.773
H    -2.624    -2.750     5.154
H    -3.083    -1.913     2.856
H    -0.352    -2.471     6.159
H     1.452    -1.347     4.844
H     0.990    -0.504     2.557
Cu    1.705     0.810    -1.427
C     5.353    -0.002    -0.954
C     4.456     0.481    -1.664
C     3.371     1.037    -2.452
H     3.520     2.111    -2.643
H     3.267     0.519    -3.418
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --     8.4146                12.2918                15.8782
 Red. masses --     5.1686                 5.1226                 4.8557
 Zero-point correction=                           0.819068 (Hartree/Particle)
 Thermal correction to Energy=                    0.871127
 Thermal correction to Enthalpy=                  0.872071
 Thermal correction to Gibbs Free Energy=         0.723812
 Sum of electronic and zero-point Energies=      -2052.769310
 Sum of electronic and thermal Energies=         -2052.717251
 Sum of electronic and thermal Enthalpies=       -2052.716307
 Sum of electronic and thermal Free Energies=    -2052.864566

         Item               Value     Threshold  Converged?
 Maximum Force            0.000088     0.000450     YES
 RMS     Force            0.000013     0.000300     YES

 SCF= -2053.58837802 Hartree
```

Table S1. Relative and Gibbs free energies (298 K, 1 atm) in kcal/mol for the NHC–Cu-allenyl to NHC–Cu-propargyl isomerization without solvent correction

structure	**1**	**2**	**3**
ΔG	0.9	12.6	0.0

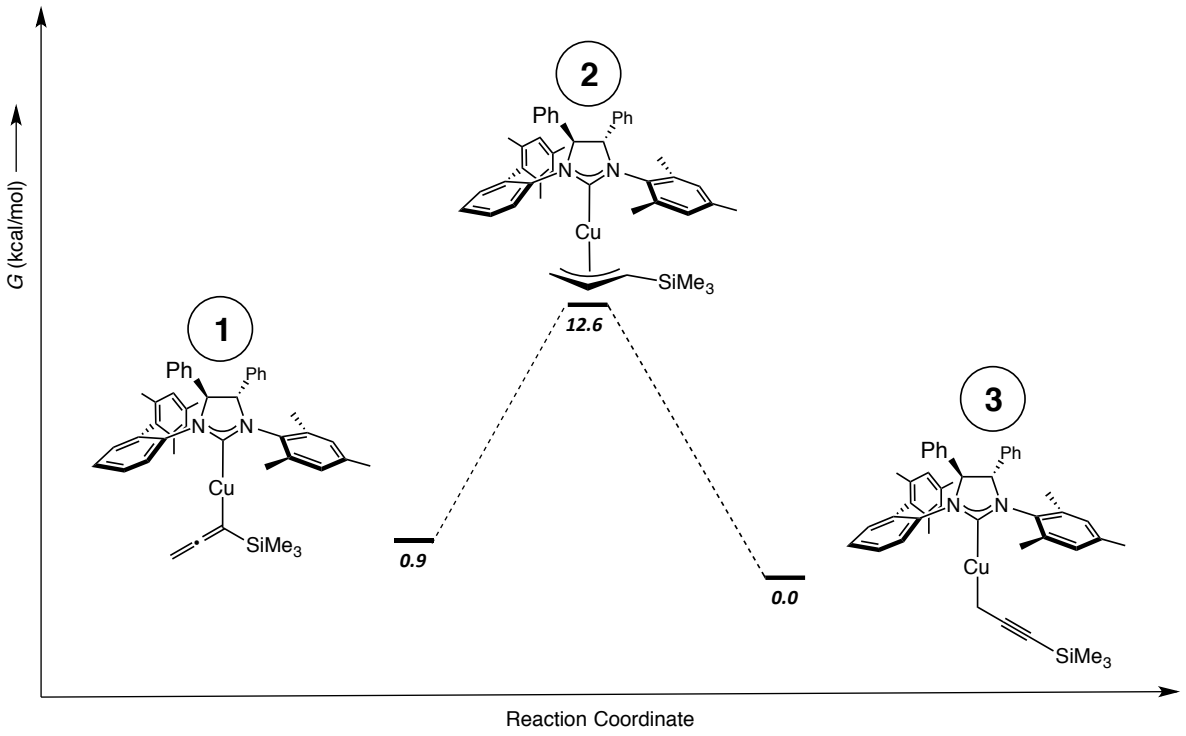
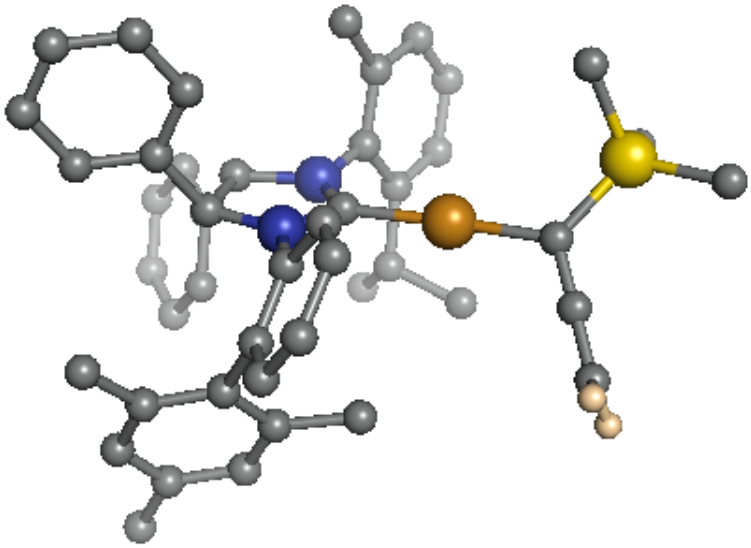


Figure S1. Relative Gibbs Free Energies (kcal/mol) Computed at 298 K and 1.0 atm without solvent correction.

Optimized structure for NHC–Cu–silylallene complex **4** without solvent correction



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----------------------------------------
Cartesian coordinates (Angstroms):
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C    -1.830    -0.028     1.198
N    -0.658    -0.814     0.675
C    -1.270     1.442     1.208
C     0.451    -0.052     0.438
N     0.143     1.246     0.701
C     1.758     2.620     1.951
```

C	2.686	3.678	1.991
C	1.116	2.323	0.716
C	2.985	4.414	0.832
C	1.422	3.038	-0.469
C	2.367	4.087	-0.382
C	0.192	-3.034	1.266
C	0.211	-4.430	1.133
C	-0.690	-2.248	0.496
C	-0.673	-5.053	0.234
C	-1.566	-2.859	-0.438
C	-1.547	-4.269	-0.537
C	-4.175	-0.797	4.133
C	-3.698	-0.464	2.851
C	-2.316	-0.476	2.571
C	-3.270	-1.155	5.150
C	-1.888	-1.175	4.876
C	-1.416	-0.834	3.597
C	-3.139	4.664	0.297
C	-2.356	3.716	0.982
C	-2.100	2.448	0.419
C	-3.680	4.349	-0.963
C	-3.427	3.085	-1.533
C	-2.641	2.143	-0.849
H	-2.659	-0.107	0.490
H	-1.208	1.801	2.241
H	3.187	3.910	2.928
H	3.708	5.225	0.874
C	0.825	2.687	-1.834
H	2.623	4.646	-1.278
H	-2.208	-4.746	-1.256
H	-5.243	-0.780	4.335
H	-4.402	-0.186	2.069
H	-3.636	-1.419	6.139
H	-1.184	-1.457	5.655
H	-0.348	-0.856	3.396
H	-3.328	5.636	0.745
H	-1.944	3.963	1.959
H	-4.291	5.076	-1.493
H	-3.838	2.834	-2.507
H	-2.455	1.177	-1.312
H	-0.671	-6.135	0.123
H	0.867	-2.543	1.960
C	1.513	1.794	3.201
H	2.162	2.131	4.015
H	1.727	0.733	3.019
H	0.477	1.861	3.558
C	0.157	3.912	-2.508
H	0.050	1.928	-1.683
C	1.908	2.074	-2.762
H	-0.611	4.356	-1.864
H	-0.320	3.609	-3.449
H	0.894	4.690	-2.748
H	2.711	2.796	-2.961
H	1.464	1.790	-3.726
H	2.363	1.181	-2.318
C	-5.008	0.013	-4.228
C	-4.661	-1.340	-2.100
C	-4.115	-0.709	-3.235
C	-3.854	-2.037	-1.178
C	-2.723	-0.794	-3.435
C	-2.447	-2.084	-1.379
C	-1.877	-1.476	-2.532
C	-4.512	-2.748	-0.005
H	-5.541	-2.398	0.136
H	-3.966	-2.600	0.932

```
H    -4.553    -3.833    -0.175
C    -0.394    -1.582    -2.837
H    -0.166    -1.163    -3.823
H    -0.050    -2.623    -2.826
H     0.223    -1.050    -2.102
H    -5.722     0.674    -3.719
H    -5.596    -0.701    -4.823
H    -4.422     0.620    -4.928
H    -2.283    -0.336    -4.318
H    -5.736    -1.300    -1.933
H     0.908    -5.020     1.723
H     6.253    -0.790     2.353
C     5.318    -1.069     1.847
H     4.522    -0.407     2.215
H     5.065    -2.097     2.141
H     7.888    -1.680    -0.204
H     6.799     1.218     0.017
C     6.931    -2.033    -0.615
C     5.880     0.879    -0.483
Si    5.483    -0.934    -0.048
H     6.785    -3.073    -0.290
H     5.061     1.545    -0.178
H     7.010    -2.039    -1.710
H     6.019     0.995    -1.566
C     3.852    -1.431    -0.842
Cu    2.172    -0.714    -0.182
C     3.761    -2.273    -1.848
C     3.649    -3.129    -2.875
H     3.521    -4.198    -2.712
H     3.690    -2.787    -3.908
```

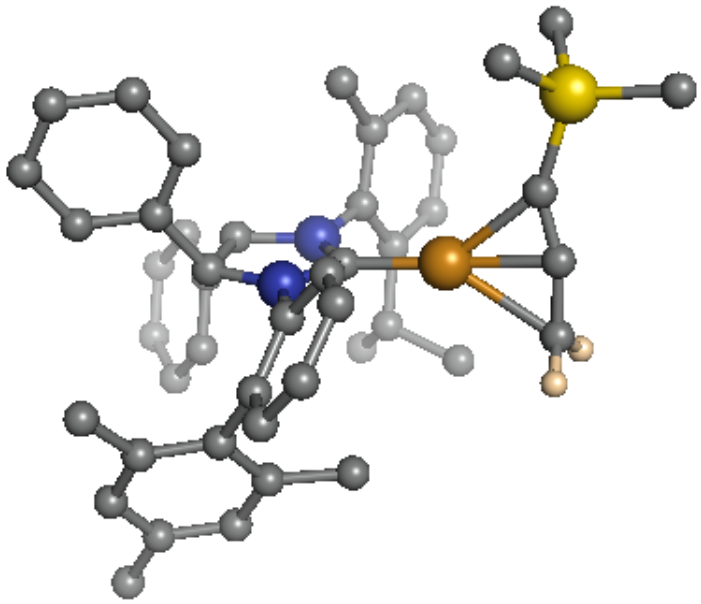
	1	2	3
	A	A	A
Frequencies --	13.2705	13.9216	17.6429
Red. masses --	3.9413	4.9363	4.9970

```
Zero-point correction=                           0.848919 (Hartree/Particle)
Thermal correction to Energy=                    0.901351
Thermal correction to Enthalpy=                  0.902295
Thermal correction to Gibbs Free Energy=         0.756878
Sum of electronic and zero-point Energies=       -2092.039485
Sum of electronic and thermal Energies=          -2091.987053
Sum of electronic and thermal Enthalpies=        -2091.986109
Sum of electronic and thermal Free Energies=     -2092.131526
```

Item	Value	Threshold	Converged?
Maximum Force	0.000309	0.000450	YES
RMS Force	0.000027	0.000300	YES

```
SCF= -2092.88840401 Hartree
```

Transition state for isomerization of NHC–Cu–silylallene to NHC–Cu–silylpropargyl complex **5** without solvent correction



```
----------------------------------------
Cartesian coordinates (Angstroms):
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H      6.316      1.407      0.519
H      6.947      0.293      1.754
C      6.092      0.500      1.095
H      5.218      0.714      1.725
H      7.571     -0.451     -1.710
H      2.982      0.827     -3.859
H      8.167     -1.563     -0.457
C      7.307     -1.323     -1.097
Si     5.747     -0.970     -0.061
C      2.957     -0.145     -3.370
C      3.804     -0.396     -2.293
C      4.286     -0.580     -1.118
H      7.141     -2.169     -1.777
H      2.578     -0.975     -3.962
C      5.354     -2.506      0.994
H      6.206     -2.772      1.635
H      4.486     -2.325      1.642
H      5.127     -3.372      0.357
C     -1.397     -0.495      1.219
N     -0.364     -0.904      0.209
C     -1.050      1.019      1.464
C      0.524      0.094     -0.106
N      0.134      1.226      0.549
C      1.894      2.575      1.621
C      2.642      3.764      1.695
C      0.919      2.445      0.592
C      2.446      4.795      0.760
C      0.721      3.465     -0.372
C      1.504      4.637     -0.265
C      0.934     -2.952     -0.132
C      1.085     -4.256     -0.624
C     -0.272     -2.244     -0.320
C      0.016     -4.875     -1.296
C     -1.348     -2.841     -1.028
```

C	-1.182	-4.166	-1.491
C	-2.556	-2.238	4.432
C	-2.564	-1.571	3.193
C	-1.359	-1.305	2.511
C	-1.338	-2.656	5.000
C	-0.131	-2.399	4.321
C	-0.141	-1.725	3.088
C	-3.460	3.942	2.046
C	-2.393	3.036	2.184
C	-2.207	1.990	1.256
C	-4.361	3.809	0.973
C	-4.181	2.769	0.040
C	-3.112	1.867	0.179
H	-2.393	-0.583	0.778
H	-0.699	1.147	2.494
H	3.393	3.871	2.475
H	3.036	5.706	0.823
C	-0.257	3.327	-1.541
H	1.375	5.431	-0.996
H	-1.998	-4.629	-2.040
H	-3.494	-2.434	4.947
H	-3.509	-1.252	2.757
H	-1.329	-3.177	5.955
H	0.814	-2.725	4.751
H	0.796	-1.535	2.572
H	-3.590	4.742	2.772
H	-1.703	3.141	3.019
H	-5.190	4.504	0.865
H	-4.869	2.660	-0.794
H	-2.994	1.075	-0.556
H	0.117	-5.888	-1.676
H	1.754	-2.469	0.391
C	2.183	1.444	2.592
H	2.983	1.729	3.283
H	2.508	0.547	2.048
H	1.309	1.166	3.195
C	-1.237	4.525	-1.625
H	-0.852	2.422	-1.382
C	0.511	3.149	-2.878
H	-1.784	4.661	-0.686
H	-1.970	4.355	-2.425
H	-0.710	5.461	-1.854
H	1.146	4.021	-3.089
H	-0.197	3.039	-3.711
H	1.148	2.258	-2.852
C	-6.310	-0.088	-2.540
C	-5.020	-1.763	-1.120
C	-5.026	-0.795	-2.146
C	-3.842	-2.434	-0.738
C	-3.809	-0.518	-2.799
C	-2.616	-2.113	-1.384
C	-2.604	-1.162	-2.442
C	-3.916	-3.505	0.339
H	-4.867	-3.448	0.881
H	-3.101	-3.421	1.067
H	-3.843	-4.511	-0.097
C	-1.340	-0.866	-3.228
H	-1.547	-0.179	-4.056
H	-0.912	-1.784	-3.651
H	-0.552	-0.416	-2.612
H	-6.711	0.506	-1.707
H	-7.089	-0.807	-2.827
H	-6.151	0.588	-3.388
H	-3.796	0.202	-3.615
H	-5.954	-2.008	-0.615

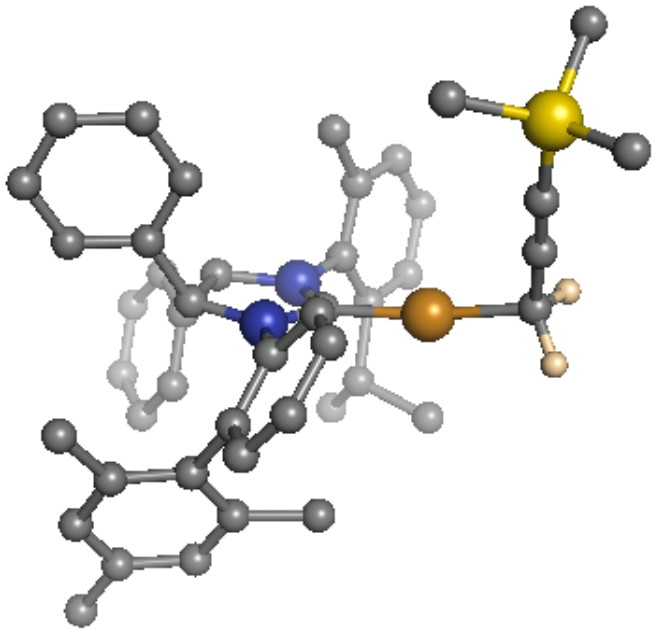
```
H      2.026    -4.782    -0.478
Cu     2.100    -0.099    -1.177

                     1                      2                      3
                     A                      A                      A
 Frequencies --   -90.5143               14.6226                15.0848
 Red. masses --    12.6843                4.5055                 4.6202
 Zero-point correction=                          0.847907 (Hartree/Particle)
 Thermal correction to Energy=                   0.899930
 Thermal correction to Enthalpy=                 0.900874
 Thermal correction to Gibbs Free Energy=        0.756739
 Sum of electronic and zero-point Energies=      -2092.021880
 Sum of electronic and thermal Energies=         -2091.969857
 Sum of electronic and thermal Enthalpies=       -2091.968913
 Sum of electronic and thermal Free Energies=    -2092.113048

         Item               Value     Threshold  Converged?
 Maximum Force            0.000001     0.000450     YES
 RMS     Force            0.000000     0.000300     YES

 SCF= -2092.86978678 Hartree
```

Optimized structure for NHC–Cu–silylpropargyl complex **6** without solvent correction



```
---------------------------------------
Cartesian coordinates (Angstroms):
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H      4.138     1.649    -2.317
H      3.642     0.194    -3.232
C      3.760     0.620    -2.224
C      4.633    -0.196    -1.400
H      8.182    -2.384    -1.423
H      6.963    -3.669    -1.369
C      7.575    -3.001    -0.748
C      5.341    -0.902    -0.661
H      8.254    -3.621    -0.146
Si     6.480    -1.908     0.359
H      8.183    -0.107     0.759
H      4.838    -3.717     0.973
C      7.587    -0.767     1.403
```

C	5.493	-3.039	1.536
H	8.278	-1.350	2.028
H	6.982	-0.131	2.064
H	6.164	-3.654	2.153
H	4.861	-2.445	2.210
C	-1.356	-0.321	1.132
N	-0.299	-0.542	0.083
C	-1.294	1.235	1.350
C	0.381	0.595	-0.253
N	-0.171	1.639	0.418
C	1.281	3.344	1.442
C	1.781	4.660	1.471
C	0.365	2.987	0.413
C	1.400	5.594	0.492
C	-0.008	3.907	-0.600
C	0.528	5.213	-0.536
C	1.349	-2.321	-0.285
C	1.724	-3.577	-0.784
C	0.030	-1.847	-0.445
C	0.770	-4.381	-1.433
C	-0.934	-2.629	-1.132
C	-0.541	-3.904	-1.600
C	-2.034	-2.243	4.381
C	-2.217	-1.594	3.146
C	-1.113	-1.096	2.423
C	-0.738	-2.409	4.904
C	0.370	-1.920	4.185
C	0.184	-1.266	2.956
C	-4.187	3.701	1.853
C	-2.977	3.001	2.019
C	-2.605	1.979	1.122
C	-5.043	3.380	0.783
C	-4.677	2.360	-0.118
C	-3.467	1.668	0.048
H	-2.331	-0.605	0.730
H	-0.969	1.445	2.375
H	2.485	4.943	2.250
H	1.798	6.606	0.523
C	-0.900	3.522	-1.783
H	0.261	5.936	-1.302
H	-1.273	-4.508	-2.131
H	-2.895	-2.620	4.927
H	-3.222	-1.470	2.745
H	-0.592	-2.916	5.855
H	1.375	-2.053	4.578
H	1.047	-0.899	2.408
H	-4.460	4.486	2.554
H	-2.322	3.251	2.852
H	-5.982	3.914	0.654
H	-5.331	2.106	-0.948
H	-3.205	0.888	-0.663
H	1.046	-5.360	-1.818
H	2.086	-1.702	0.219
C	1.780	2.332	2.457
H	2.515	2.793	3.125
H	2.268	1.487	1.956
H	0.977	1.922	3.083
C	-2.072	4.514	-1.988
H	-1.334	2.538	-1.579
C	-0.050	3.397	-3.077
H	-2.680	4.606	-1.081
H	-2.722	4.164	-2.800
H	-1.713	5.514	-2.262
H	0.406	4.360	-3.345
H	-0.678	3.074	-3.917

```
H     0.759     2.667    -2.950
C    -6.332    -0.850    -2.606
C    -4.741    -2.226    -1.172
C    -4.935    -1.294    -2.212
C    -3.456    -2.667    -0.799
C    -3.797    -0.808    -2.884
C    -2.316    -2.141    -1.468
C    -2.491    -1.218    -2.536
C    -3.318    -3.714     0.295
H    -4.245    -3.800     0.874
H    -2.500    -3.487     0.987
H    -3.102    -4.704    -0.131
C    -1.310    -0.702    -3.340
H    -1.646    -0.044    -4.148
H    -0.745    -1.530    -3.790
H    -0.599    -0.141    -2.721
H    -6.893    -0.476    -1.739
H    -6.910    -1.684    -3.028
H    -6.302    -0.054    -3.359
H    -3.924    -0.107    -3.708
H    -5.607    -2.625    -0.646
H     2.750    -3.915    -0.666
Cu    2.001     0.668    -1.339
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --     7.5356                12.0153                16.9275
 Red. masses --     5.1648                 5.2731                 4.8423
 Zero-point correction=                          0.848860 (Hartree/Particle)
 Thermal correction to Energy=                   0.901489
 Thermal correction to Enthalpy=                 0.902433
 Thermal correction to Gibbs Free Energy=        0.755301
 Sum of electronic and zero-point Energies=      -2092.039251
 Sum of electronic and thermal Energies=         -2091.986621
 Sum of electronic and thermal Enthalpies=       -2091.985677
 Sum of electronic and thermal Free Energies=    -2092.132809

         Item               Value     Threshold  Converged?
 Maximum Force            0.000006     0.000450     YES
 RMS     Force            0.000001     0.000300     YES

 SCF= -2092.88811027 Hartree
```

Table S2. Relative and Gibbs free energies (298 K, 1 atm) in kcal/mol for the NHC–Cu-allenyl to NHC–Cu-propargyl isomerization without solvent correction

structure	**4**	**5**	**6**
ΔG	0.8	12.4	0.0

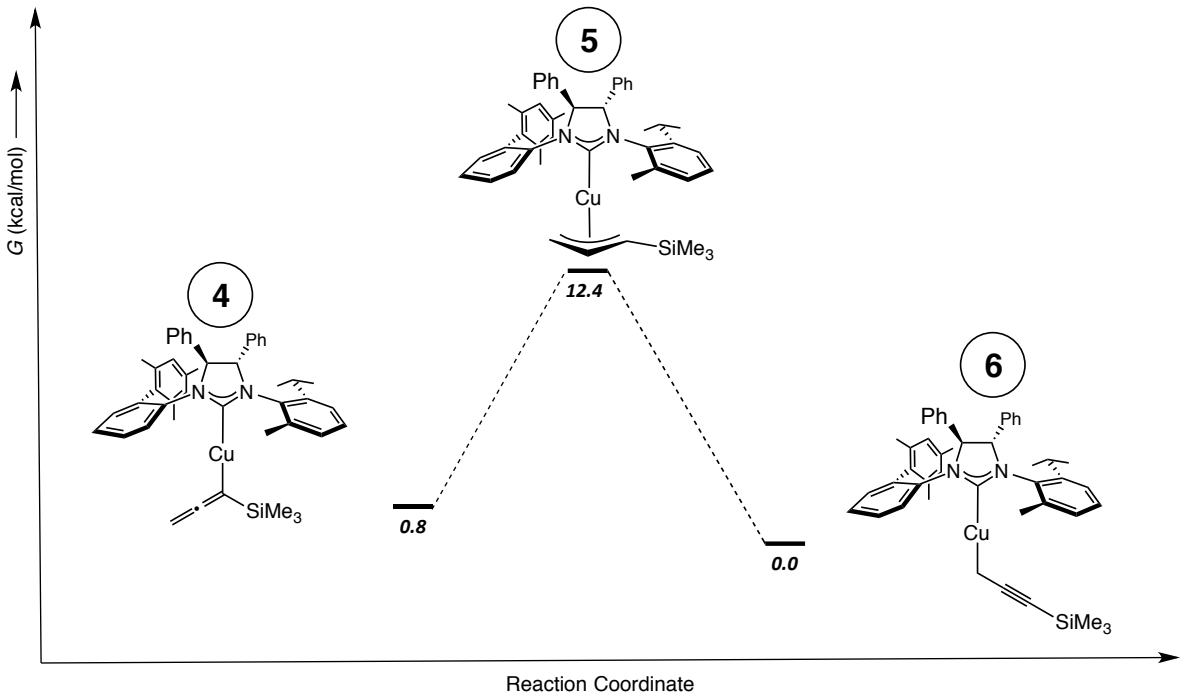
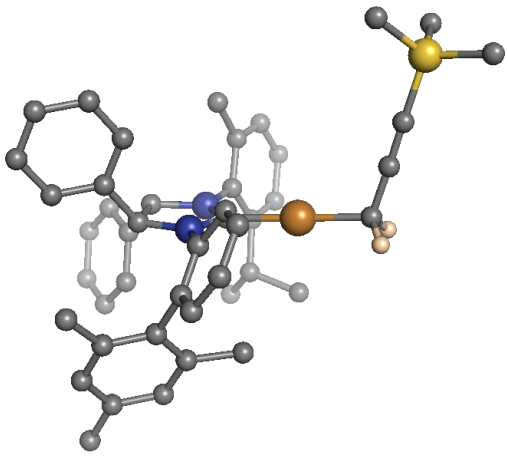


Figure S2. Relative Gibbs Free Energies (kcal/mol) Computed at 298 K and 1.0 atm without solvent correction.

Optimized structure for NHC–Cu–silylpropargyl complex **A**



```
----------------------------------------
Cartesian coordinates (Angstroms):
----------------------------------------
H      3.462      0.935     -3.034
H      3.231     -0.830     -3.207
C      3.409     -0.018     -2.483
C      4.618     -0.249     -1.714
H      8.775     -0.846     -1.936
H      8.195     -2.464     -1.492
C      8.519     -1.495     -1.088
```

C	5.636	-0.442	-1.025
H	9.430	-1.660	-0.497
Si	7.153	-0.710	-0.021
H	8.004	1.650	-0.174
H	6.406	-2.842	1.082
C	7.765	0.962	0.647
C	6.769	-1.869	1.438
H	8.671	0.830	1.256
H	7.000	1.439	1.274
H	7.668	-2.043	2.047
H	5.996	-1.437	2.088
C	-1.590	-0.583	1.224
N	-0.533	-0.924	0.207
C	-1.304	0.937	1.509
C	0.270	0.131	-0.120
N	-0.159	1.227	0.559
C	1.473	2.750	1.604
C	2.134	3.993	1.634
C	0.535	2.502	0.563
C	1.886	4.964	0.647
C	0.283	3.462	-0.452
C	0.978	4.692	-0.387
C	0.862	-2.909	-0.114
C	1.093	-4.194	-0.629
C	-0.364	-2.249	-0.344
C	0.083	-4.836	-1.370
C	-1.383	-2.873	-1.109
C	-1.136	-4.176	-1.600
C	-2.724	-2.535	4.324
C	-2.739	-1.824	3.109
C	-1.534	-1.432	2.490
C	-1.498	-2.870	4.930
C	-0.289	-2.488	4.313
C	-0.308	-1.771	3.103
C	-3.839	3.713	2.257
C	-2.730	2.849	2.343
C	-2.505	1.860	1.362
C	-4.743	3.591	1.185
C	-4.526	2.605	0.201
C	-3.415	1.748	0.287
H	-2.575	-0.700	0.767
H	-0.921	1.047	2.529
H	2.856	4.193	2.423
H	2.407	5.917	0.678
C	-0.664	3.206	-1.628
H	0.808	5.441	-1.155
H	-1.907	-4.663	-2.191
H	-3.661	-2.828	4.791
H	-3.690	-1.569	2.646
H	-1.483	-3.423	5.866
H	0.661	-2.747	4.772
H	0.632	-1.484	2.639
H	-3.998	4.468	3.022
H	-2.039	2.944	3.179
H	-5.604	4.251	1.117
H	-5.220	2.505	-0.630
H	-3.268	0.999	-0.487
H	0.245	-5.834	-1.769
H	1.628	-2.412	0.474
C	1.808	1.704	2.653
H	2.680	2.016	3.236
H	2.040	0.736	2.193
H	0.984	1.543	3.361
C	-1.726	4.325	-1.778
H	-1.196	2.268	-1.444

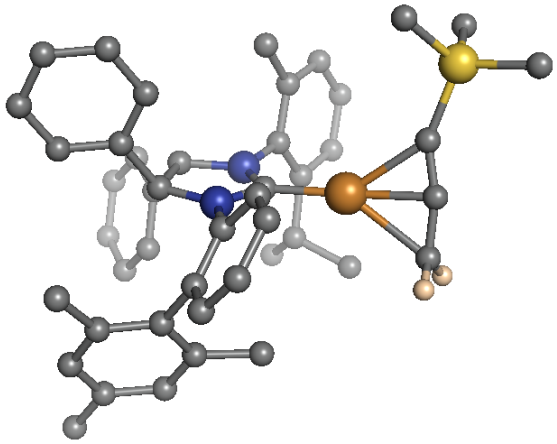
```
C     0.136     3.037    -2.949
H    -2.306     4.450    -0.857
H    -2.422     4.072    -2.589
H    -1.263     5.289    -2.027
H     0.692     3.952    -3.193
H    -0.548     2.823    -3.781
H     0.855     2.212    -2.874
C    -6.440    -0.307    -2.643
C    -5.099    -1.961    -1.241
C    -5.133    -0.960    -2.233
C    -3.896    -2.595    -0.862
C    -3.918    -0.604    -2.854
C    -2.677    -2.197    -1.476
C    -2.693    -1.210    -2.501
C    -3.941    -3.704     0.177
H    -4.896    -3.696     0.714
H    -3.134    -3.617     0.912
H    -3.834    -4.690    -0.294
C    -1.432    -0.830    -3.259
H    -1.657    -0.105    -4.048
H    -0.972    -1.710    -3.728
H    -0.671    -0.388    -2.604
H    -7.158    -0.292    -1.814
H    -6.910    -0.854    -3.473
H    -6.284     0.725    -2.980
H    -3.923     0.150    -3.639
H    -6.026    -2.259    -0.755
H     2.045    -4.687    -0.448
Cu    1.821     0.067    -1.306
```

```
                     1                     2                     3
                     A                     A                     A
 Frequencies --     4.3589               10.6029               14.2626
 Red. masses --     4.5959                5.1509                4.9321
 Zero-point correction=                           0.847933 (Hartree/Particle)
 Thermal correction to Energy=                    0.900639
 Thermal correction to Enthalpy=                  0.901583
 Thermal correction to Gibbs Free Energy=         0.753102
 Sum of electronic and zero-point Energies=      -2092.058218
 Sum of electronic and thermal Energies=         -2092.005512
 Sum of electronic and thermal Enthalpies=       -2092.004568
 Sum of electronic and thermal Free Energies=    -2092.153048

         Item               Value     Threshold  Converged?
 Maximum Force            0.000158     0.000450     YES
 RMS     Force            0.000033     0.000300     YES

 SCF= -2092.90615056 Hartree
```

Transition state for isomerization of NHC–Cu–silylallene to NHC–Cu–silylpropargyl complex **B**



Cartesian coordinates (Angstroms):

H	6.667	1.600	-0.214
H	7.267	0.850	1.283
C	6.407	0.912	0.602
H	5.564	1.349	1.153
H	7.704	-0.846	-1.884
H	2.965	0.378	-3.962
H	8.325	-1.602	-0.398
C	7.441	-1.505	-1.046
Si	5.958	-0.807	-0.074
C	3.030	-0.541	-3.381
C	3.914	-0.619	-2.303
C	4.456	-0.649	-1.143
H	7.211	-2.498	-1.455
H	2.691	-1.452	-3.870
C	5.574	-1.973	1.377
H	6.451	-2.087	2.029
H	4.746	-1.580	1.984
H	5.286	-2.970	1.018
C	-1.299	-0.684	1.220
N	-0.265	-1.100	0.211
C	-0.909	0.812	1.507
C	0.646	-0.117	-0.076
N	0.290	1.007	0.606
C	2.051	2.304	1.741
C	2.831	3.472	1.841
C	1.107	2.203	0.679
C	2.694	4.511	0.903
C	0.966	3.234	-0.285
C	1.778	4.384	-0.150
C	0.999	-3.161	-0.159
C	1.141	-4.456	-0.679
C	-0.195	-2.431	-0.344
C	0.069	-5.043	-1.379
C	-1.276	-3.001	-1.067
C	-1.119	-4.317	-1.563

C	-2.570	-2.482	4.360
C	-2.534	-1.781	3.140
C	-1.307	-1.529	2.491
C	-1.375	-2.950	4.941
C	-0.146	-2.708	4.293
C	-0.113	-2.000	3.079
C	-3.241	3.788	2.140
C	-2.204	2.845	2.268
C	-2.032	1.824	1.310
C	-4.126	3.716	1.047
C	-3.960	2.699	0.084
C	-2.920	1.762	0.213
H	-2.290	-0.731	0.763
H	-0.563	0.903	2.542
H	3.556	3.559	2.647
H	3.306	5.406	0.988
C	0.016	3.131	-1.481
H	1.693	5.184	-0.881
H	-1.938	-4.760	-2.123
H	-3.522	-2.666	4.851
H	-3.462	-1.426	2.695
H	-1.400	-3.496	5.880
H	0.780	-3.071	4.732
H	0.841	-1.821	2.591
H	-3.361	4.567	2.889
H	-1.530	2.901	3.121
H	-4.932	4.438	0.946
H	-4.637	2.639	-0.764
H	-2.813	0.989	-0.544
H	0.161	-6.049	-1.782
H	1.813	-2.708	0.399
C	2.266	1.177	2.735
H	3.115	1.403	3.388
H	2.478	0.232	2.220
H	1.393	1.013	3.379
C	-0.937	4.349	-1.574
H	-0.600	2.235	-1.351
C	0.815	2.963	-2.801
H	-1.516	4.474	-0.652
H	-1.643	4.210	-2.404
H	-0.385	5.279	-1.762
H	1.450	3.838	-2.992
H	0.127	2.851	-3.649
H	1.458	2.075	-2.762
C	-6.254	-0.193	-2.429
C	-4.953	-1.932	-1.096
C	-4.972	-0.931	-2.087
C	-3.766	-2.611	-0.745
C	-3.762	-0.631	-2.747
C	-2.548	-2.264	-1.392
C	-2.553	-1.281	-2.421
C	-3.830	-3.717	0.297
H	-4.775	-3.676	0.850
H	-3.009	-3.654	1.019
H	-3.763	-4.707	-0.173
C	-1.299	-0.959	-3.215
H	-1.510	-0.210	-3.987
H	-0.905	-1.855	-3.713
H	-0.491	-0.573	-2.583
H	-6.410	0.661	-1.754
H	-7.130	-0.846	-2.332
H	-6.231	0.198	-3.453
H	-3.760	0.114	-3.541
H	-5.880	-2.198	-0.590
H	2.069	-5.001	-0.532

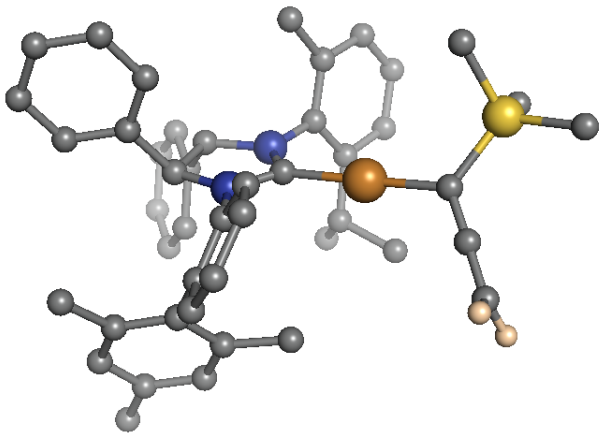
```
Cu    2.211    -0.320    -1.177

                     1                      2                      3
                     A                      A                      A
 Frequencies --   -98.6607               13.4481                14.4412
 Red. masses --    13.0194                4.4487                 4.9649
 Zero-point correction=                          0.846787 (Hartree/Particle)
 Thermal correction to Energy=                   0.898951
 Thermal correction to Enthalpy=                 0.899896
 Thermal correction to Gibbs Free Energy=        0.755460
 Sum of electronic and zero-point Energies=      -2092.038214
 Sum of electronic and thermal Energies=         -2091.986049
 Sum of electronic and thermal Enthalpies=       -2091.985105
 Sum of electronic and thermal Free Energies=    -2092.129540

         Item               Value     Threshold  Converged?
 Maximum Force            0.000001     0.000450     YES
 RMS     Force            0.000000     0.000300     YES

SCF= -2092.88500039 Hartree
```

Optimized structure for NHC–Cu–silylallene complex **C**



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---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
C    -1.800    -0.043     1.156
N    -0.644    -0.841     0.612
C    -1.211     1.414     1.198
C     0.466    -0.089     0.355
N     0.180     1.211     0.631
C     1.815     2.627     1.813
C     2.748     3.682     1.799
C     1.157     2.283     0.598
C     3.032     4.375     0.608
C     1.444     2.958    -0.617
C     2.393     4.006    -0.583
```

C	0.188	-3.074	1.174
C	0.188	-4.470	1.033
C	-0.698	-2.273	0.423
C	-0.720	-5.077	0.145
C	-1.603	-2.867	-0.494
C	-1.601	-4.277	-0.602
C	-4.156	-0.869	4.068
C	-3.675	-0.514	2.793
C	-2.291	-0.514	2.521
C	-3.254	-1.239	5.084
C	-1.870	-1.247	4.817
C	-1.393	-0.884	3.546
C	-3.048	4.704	0.498
C	-2.264	3.710	1.114
C	-2.045	2.467	0.482
C	-3.627	4.462	-0.763
C	-3.412	3.223	-1.400
C	-2.626	2.234	-0.784
H	-2.630	-0.092	0.449
H	-1.100	1.730	2.241
H	3.261	3.951	2.720
H	3.757	5.185	0.611
C	0.813	2.571	-1.957
H	2.634	4.535	-1.501
H	-2.286	-4.745	-1.305
H	-5.225	-0.862	4.264
H	-4.378	-0.230	2.013
H	-3.623	-1.519	6.068
H	-1.168	-1.535	5.595
H	-0.323	-0.894	3.354
H	-3.208	5.656	0.998
H	-1.828	3.900	2.093
H	-4.237	5.225	-1.241
H	-3.854	3.030	-2.375
H	-2.472	1.288	-1.298
H	-0.736	-6.158	0.030
H	0.871	-2.596	1.869
C	1.569	1.870	3.106
H	2.328	2.132	3.851
H	1.608	0.785	2.951
H	0.590	2.105	3.545
C	0.149	3.782	-2.660
H	0.032	1.828	-1.768
C	1.869	1.916	-2.889
H	-0.603	4.252	-2.018
H	-0.347	3.452	-3.583
H	0.890	4.542	-2.937
H	2.678	2.621	-3.123
H	1.403	1.610	-3.835
H	2.318	1.029	-2.424
C	-5.143	0.129	-4.099
C	-4.743	-1.313	-2.038
C	-4.227	-0.641	-3.166
C	-3.912	-2.038	-1.159
C	-2.841	-0.722	-3.406
C	-2.509	-2.075	-1.397
C	-1.973	-1.431	-2.546
C	-4.543	-2.787	0.004
H	-5.562	-2.431	0.191
H	-3.967	-2.679	0.929
H	-4.602	-3.864	-0.206
C	-0.499	-1.534	-2.898
H	-0.301	-1.088	-3.879
H	-0.167	-2.579	-2.927
H	0.139	-1.024	-2.166

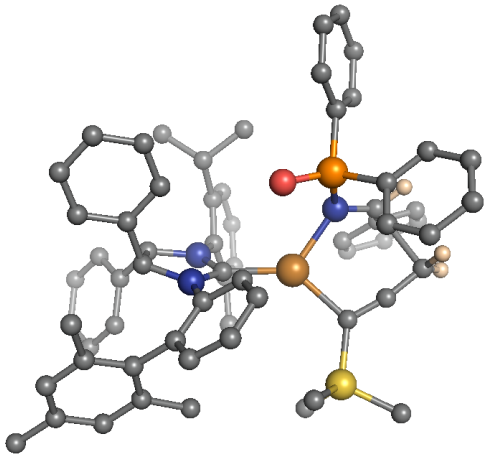
```
H    -5.683     0.922    -3.563
H    -5.901    -0.529    -4.546
H    -4.582     0.596    -4.916
H    -2.424    -0.236    -4.286
H    -5.813    -1.280    -1.843
H     0.881    -5.073     1.613
H     6.070    -0.708     2.559
C     5.201    -1.072     1.993
H     4.319    -0.506     2.322
H     5.042    -2.128     2.254
H     7.916    -1.453     0.160
H     6.615     1.367     0.289
C     7.037    -1.829    -0.383
C     5.741     0.980    -0.255
Si    5.470    -0.868     0.118
H     6.932    -2.899    -0.159
H     4.865     1.574     0.040
H     7.235    -1.730    -1.459
H     5.909     1.141    -1.329
C     3.929    -1.468    -0.793
Cu    2.194    -0.767    -0.244
C     3.962    -2.338    -1.777
C     3.981    -3.225    -2.789
H     3.888    -4.296    -2.610
H     4.083    -2.905    -3.825
```

```
                     1                      2                      3
                     A                      A                      A
 Frequencies --    13.8520                16.8380                18.1505
 Red. masses --     5.1900                 4.9552                 5.0507
 Zero-point correction=                           0.847975 (Hartree/Particle)
 Thermal correction to Energy=                    0.900488
 Thermal correction to Enthalpy=                  0.901432
 Thermal correction to Gibbs Free Energy=         0.756541
 Sum of electronic and zero-point Energies=      -2092.058446
 Sum of electronic and thermal Energies=         -2092.005933
 Sum of electronic and thermal Enthalpies=       -2092.004989
 Sum of electronic and thermal Free Energies=    -2092.149880

         Item               Value     Threshold  Converged?
 Maximum Force            0.000010     0.000450     YES
 RMS     Force            0.000001     0.000300     YES

 SCF= -2092.90642099 Hartree
```

The transition state (7) leading to minor (propargyl) isomer: Dissymmetric N-Aryl methyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from front side of the complex and the terminal allene carbon side pointing to the back.



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----------------------------------------
Cartesian coordinates (Angstroms):
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H     -1.096     -3.891     -0.993
C     -0.726     -2.567     -4.136
C     -0.531     -4.512     -1.695
C      1.568     -2.237     -2.062
Si     0.444     -3.473     -2.946
H     -1.236     -5.175     -2.216
C      2.850     -2.252     -2.083
H      0.152     -5.141     -1.108
C      1.513     -4.657     -3.987
H      0.886     -5.399     -4.501
H      2.081     -4.106     -4.750
H      2.231     -5.196     -3.355
C     -2.748      0.641      1.183
N     -1.804     -0.374      0.592
C     -2.434      1.925      0.352
C     -0.847      0.186     -0.231
N     -1.195      1.497     -0.411
C      0.106      3.589     -0.668
C      0.556      4.629     -1.513
C     -0.557      2.482     -1.261
C      0.366      4.573     -2.900
C     -0.727      2.393     -2.671
C     -0.259      3.452     -3.473
C     -3.014     -2.531      1.059
C     -2.927     -3.854      1.557
C     -1.823     -1.746      1.050
C     -1.726     -4.400      2.035
C     -0.618     -2.290      1.546
C     -0.565     -3.606      2.030
C      0.394      3.682      0.834
C     -3.452      1.577      4.833
C     -3.625      1.260      3.473
C     -2.526      0.869      2.678
```

C	-2.172	1.498	5.417
C	-1.074	1.099	4.629
C	-1.244	0.788	3.267
C	-4.827	4.373	-1.387
C	-3.793	3.845	-0.590
C	-3.562	2.454	-0.528
C	-5.650	3.509	-2.134
C	-5.430	2.118	-2.075
C	-4.394	1.597	-1.281
H	-3.780	0.329	1.018
H	-2.144	2.730	1.031
H	1.063	5.487	-1.078
H	0.711	5.388	-3.532
C	-1.375	1.192	-3.329
H	-0.398	3.400	-4.551
H	-3.829	-4.461	1.558
H	0.370	-3.998	2.423
H	-4.308	1.877	5.433
H	-4.618	1.318	3.030
H	-2.034	1.738	6.468
H	-0.083	1.028	5.072
H	-0.378	0.473	2.688
H	-4.990	5.447	-1.421
H	-3.168	4.522	-0.011
H	-6.452	3.911	-2.748
H	-6.065	1.441	-2.642
H	-4.251	0.523	-1.240
H	-2.324	0.928	-2.853
H	-0.724	0.313	-3.261
H	-1.566	1.389	-4.390
C	1.922	3.678	1.087
H	-0.005	2.788	1.325
C	-0.258	4.927	1.490
H	2.387	2.804	0.622
H	2.129	3.644	2.165
H	2.398	4.580	0.680
H	0.145	5.856	1.065
H	-0.053	4.935	2.568
H	-1.347	4.944	1.354
H	-5.980	-1.512	3.596
H	-5.147	-3.054	3.341
C	-5.176	-2.000	3.032
H	-7.497	-1.375	1.818
H	-4.225	-1.554	3.338
H	-8.694	-1.628	-1.671
C	-6.713	-1.551	1.083
C	-5.416	-1.874	1.536
C	-8.420	-1.090	-0.755
C	-7.025	-1.463	-0.288
C	-4.377	-2.092	0.586
H	-8.488	-0.015	-0.975
H	-9.173	-1.315	0.011
C	-5.993	-1.717	-1.215
C	-4.681	-2.028	-0.802
H	-6.213	-1.676	-2.280
C	-3.627	-2.321	-1.852
H	-3.317	-3.373	-1.821
H	-2.723	-1.721	-1.697
H	-4.007	-2.114	-2.859
H	0.262	-1.656	1.612
H	-1.700	-5.420	2.410
C	4.207	-2.075	-1.977
H	4.413	2.795	-5.617
H	2.185	2.534	-4.519
C	4.324	2.241	-4.686

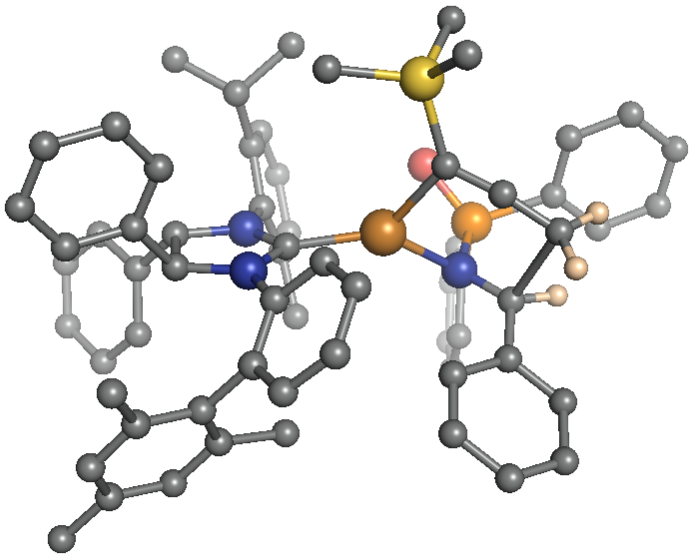
```
C     3.067     2.091    -4.068
H     6.444     1.795    -4.545
C     5.468     1.676    -4.082
C     2.944     1.382    -2.859
C     5.344     0.957    -2.884
H     1.977     1.295    -2.373
C     4.080     0.791    -2.260
H     6.227     0.512    -2.428
C     4.009     0.025    -0.993
H     4.968     1.924     0.500
N     2.906     0.054    -0.197
H     4.986    -0.219    -0.570
H     6.329     3.600     1.704
C     4.979     1.914     1.585
C     5.748     2.876     2.269
P     3.168    -0.350     1.507
C     4.219     0.975     2.308
C     5.755     2.907     3.676
C     4.166    -1.930     1.638
H     6.084    -0.979     2.012
C     5.554    -1.918     1.882
C     3.488    -3.159     1.488
C     4.221     1.011     3.720
C     4.987     1.974     4.402
C     6.263    -3.133     1.973
C     4.196    -4.369     1.582
H     7.333    -3.120     2.162
H     3.623     0.299     4.283
H     4.982     1.997     5.488
O     1.750    -0.500     2.266
Cu    0.928    -0.608    -0.834
H     6.133    -5.295     1.895
C     5.586    -4.359     1.823
H     3.671    -5.313     1.466
H     2.419    -3.170     1.297
H     6.348     3.651     4.202
H    -1.339    -3.293    -4.690
H    -0.153    -1.981    -4.867
H    -1.403    -1.886    -3.612
H     4.765    -2.641    -1.232
H     4.775    -1.718    -2.833
```

```
                     1                     2                     3
                     A                     A                     A
 Frequencies --  -231.5865              12.1531               14.7664
 Red. masses --     8.3145               5.0229                5.1538
 Zero-point correction=                          1.151782 (Hartree/Particle)
 Thermal correction to Energy=                   1.223358
 Thermal correction to Enthalpy=                 1.224302
 Thermal correction to Gibbs Free Energy=        1.038652
 Sum of electronic and zero-point Energies=      -2961.710458
 Sum of electronic and thermal Energies=         -2961.638882
 Sum of electronic and thermal Enthalpies=       -2961.637938
 Sum of electronic and thermal Free Energies=    -2961.823588

         Item               Value     Threshold  Converged?
 Maximum Force            0.000334     0.000450     YES
 RMS     Force            0.000024     0.000300     YES

SCF= -2962.86224001 Hartree
```

The transition state (8) leading to minor (propargyl) isomer: Dissymmetric N-Aryl *iso*-propyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from front side of the complex and the terminal allene carbon side pointing to the back.



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----------------------------------------
Cartesian coordinates (Angstroms):
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H     -0.927    -2.970    -2.866
C     -0.401    -0.334    -4.970
C     -0.282    -3.183    -3.724
C      1.739    -0.984    -2.800
Si     0.735    -1.673    -4.248
H     -0.917    -3.520    -4.556
C      3.021    -0.977    -2.744
H      0.377    -4.015    -3.443
C      1.927    -2.224    -5.628
H      1.370    -2.634    -6.483
H      2.532    -1.381    -5.989
H      2.615    -3.000    -5.265
C     -2.646    -0.254     1.454
N     -1.690    -0.758     0.404
C     -2.274     1.261     1.553
C     -0.778     0.183    -0.018
N     -1.134     1.372     0.561
C     -0.678     3.507    -0.638
C     -0.019     4.757    -0.653
C     -0.427     2.632     0.453
C      0.848     5.138     0.381
C      0.451     3.003     1.511
C      1.081     4.263     1.454
C     -2.875    -2.788    -0.471
C     -2.794    -4.167    -0.779
```

C	-1.698	-2.150	0.015
C	-1.609	-4.902	-0.619
C	-0.507	-2.888	0.185
C	-0.458	-4.254	-0.134
C	-1.613	3.149	-1.796
C	-3.573	-1.698	4.882
C	-3.666	-1.139	3.594
C	-2.512	-0.960	2.801
C	-2.319	-2.096	5.387
C	-1.165	-1.925	4.595
C	-1.255	-1.357	3.311
C	-4.599	4.270	2.041
C	-3.538	3.357	2.186
C	-3.423	2.237	1.334
C	-5.568	4.070	1.038
C	-5.461	2.954	0.184
C	-4.396	2.048	0.328
H	-3.671	-0.370	1.097
H	-1.861	1.461	2.546
H	-0.194	5.441	-1.480
H	1.342	6.106	0.349
C	0.727	2.093	2.693
H	1.759	4.551	2.254
H	-3.683	-4.663	-1.161
H	0.464	-4.811	0.013
H	-4.470	-1.828	5.483
H	-4.638	-0.839	3.206
H	-2.243	-2.533	6.380
H	-0.194	-2.234	4.976
H	-0.349	-1.238	2.719
H	-4.672	5.126	2.707
H	-2.801	3.512	2.971
H	-6.393	4.769	0.926
H	-6.205	2.791	-0.592
H	-4.338	1.194	-0.341
H	0.806	1.043	2.397
H	-0.063	2.168	3.454
H	1.665	2.378	3.179
C	-2.685	4.242	-2.038
H	-2.134	2.221	-1.540
C	-0.810	2.896	-3.099
H	-3.260	4.449	-1.129
H	-3.386	3.912	-2.817
H	-2.232	5.182	-2.380
H	-0.273	3.802	-3.409
H	-1.489	2.613	-3.914
H	-0.080	2.089	-2.970
H	-6.018	-3.371	1.985
H	-5.191	-4.501	0.904
C	-5.183	-3.470	1.283
H	-7.408	-2.147	0.557
H	-4.250	-3.344	1.842
H	-8.236	0.612	-0.818
C	-6.575	-1.880	-0.091
C	-5.313	-2.465	0.149
C	-8.147	-0.335	-1.371
C	-6.788	-0.971	-1.146
C	-4.209	-2.116	-0.681
H	-8.958	-0.988	-1.027
H	-8.315	-0.110	-2.431
C	-5.692	-0.661	-1.977
C	-4.412	-1.215	-1.764
H	-5.836	0.019	-2.815
C	-3.293	-0.868	-2.727
H	-2.929	-1.762	-3.250

H	-2.431	-0.430	-2.213
H	-3.638	-0.155	-3.484
H	0.356	-2.389	0.621
H	-1.586	-5.960	-0.868
C	4.363	-0.864	-2.481
H	4.364	5.139	-3.586
H	2.137	4.347	-2.780
C	4.287	4.225	-3.002
C	3.031	3.775	-2.551
H	6.423	3.833	-3.015
C	5.447	3.487	-2.681
C	2.925	2.597	-1.789
C	5.341	2.306	-1.932
H	1.960	2.273	-1.416
C	4.078	1.839	-1.484
H	6.237	1.735	-1.693
C	4.020	0.591	-0.687
H	4.173	1.969	1.586
N	2.895	0.217	-0.026
H	4.999	0.233	-0.357
H	5.277	3.189	3.444
C	4.364	1.457	2.524
C	4.983	2.152	3.582
P	3.122	-0.865	1.352
C	3.982	0.113	2.694
C	5.211	1.510	4.814
C	4.292	-2.258	0.911
H	6.116	-1.263	1.554
C	5.684	-2.156	1.109
C	3.745	-3.433	0.354
C	4.204	-0.529	3.932
C	4.817	0.167	4.989
C	6.527	-3.225	0.745
C	4.586	-4.500	-0.005
H	7.600	-3.143	0.899
H	3.899	-1.563	4.076
H	4.986	-0.332	5.940
O	1.699	-1.454	1.840
Cu	0.982	-0.144	-0.987
H	6.630	-5.222	-0.090
C	5.980	-4.397	0.188
H	4.161	-5.405	-0.431
H	2.671	-3.512	0.211
H	5.686	2.048	5.629
H	-0.967	-0.741	-5.820
H	0.186	0.521	-5.331
H	-1.116	0.038	-4.231
H	4.893	-1.701	-2.027
H	4.970	-0.159	-3.042

	1	2	3
	A	A	A
Frequencies --	-227.5184	12.7426	12.9178
Red. masses --	8.2141	5.0738	5.2489

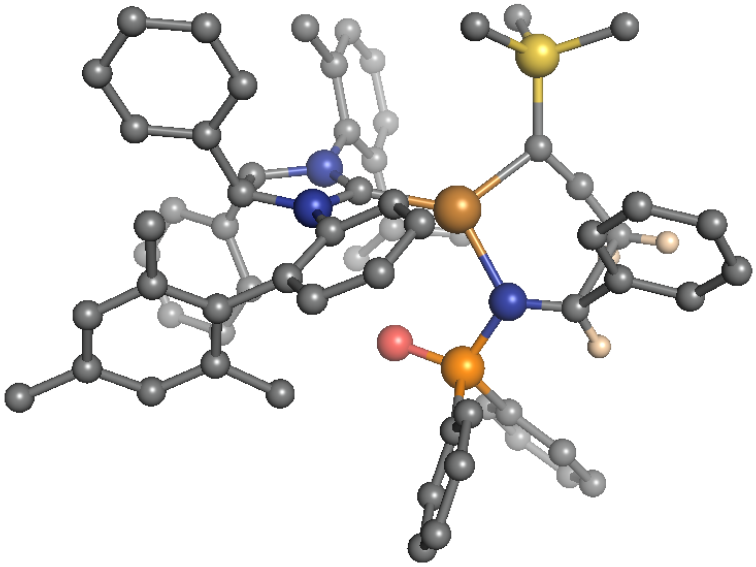
Zero-point correction=	1.151769 (Hartree/Particle)
Thermal correction to Energy=	1.223123
Thermal correction to Enthalpy=	1.224067
Thermal correction to Gibbs Free Energy=	1.039527
Sum of electronic and zero-point Energies=	-2961.713836
Sum of electronic and thermal Energies=	-2961.642482
Sum of electronic and thermal Enthalpies=	-2961.641538
Sum of electronic and thermal Free Energies=	-2961.826079

Item	Value	Threshold	Converged?
Maximum Force	0.000003	0.000450	YES

```
 RMS     Force            0.000000     0.000300     YES

SCF= -2962.86560557 Hartree
```

The transition state (9) leading to minor (propargyl) isomer: Dissymmetric N-Aryl *iso*-propyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from back side of the complex and the terminal allene carbon side pointing to the front.



```
---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
H     -1.163      2.553     -3.904
C     -4.080      3.824     -3.367
C     -1.036      3.399     -3.215
C     -2.921      2.176     -1.070
Si    -2.603      3.659     -2.177
H     -0.813      4.292     -3.815
C     -3.979      1.778     -0.466
H     -0.169      3.190     -2.577
C     -2.459      5.260     -1.166
H     -2.278      6.119     -1.828
H     -3.389      5.447     -0.612
H     -1.637      5.210     -0.442
C      2.993      0.647     -0.295
N      1.620      0.244     -0.754
C      2.671      1.724      0.796
C      0.615      1.072     -0.274
N      1.208      1.991      0.550
C     -0.153      3.371      2.175
C     -0.478      4.666      2.647
C      0.678      3.265      1.027
C     -0.005      5.824      2.020
```

C	1.137	4.441	0.356
C	0.789	5.706	0.869
C	2.207	-1.975	-1.835
C	1.882	-2.902	-2.858
C	1.413	-0.792	-1.738
C	0.840	-2.695	-3.773
C	0.388	-0.572	-2.692
C	0.093	-1.507	-3.691
C	-0.743	2.176	2.925
C	6.166	1.808	-2.093
C	5.285	1.267	-1.141
C	3.899	1.182	-1.404
C	5.674	2.265	-3.332
C	4.296	2.174	-3.606
C	3.415	1.638	-2.647
C	4.406	1.453	4.204
C	4.034	1.897	2.920
C	2.984	1.269	2.217
C	3.727	0.370	4.796
C	2.669	-0.251	4.100
C	2.294	0.194	2.821
H	3.484	-0.201	0.182
H	3.240	2.634	0.595
H	-1.110	4.760	3.526
H	-0.263	6.805	2.411
C	1.990	4.400	-0.899
H	1.138	6.598	0.353
H	2.474	-3.811	-2.921
H	-0.697	-1.300	-4.409
H	7.230	1.866	-1.874
H	5.676	0.901	-0.193
H	6.354	2.680	-4.073
H	3.905	2.518	-4.561
H	2.357	1.567	-2.878
H	5.216	1.946	4.736
H	4.564	2.732	2.466
H	4.011	0.022	5.786
H	2.130	-1.077	4.559
H	1.452	-0.277	2.320
H	1.783	3.523	-1.514
H	3.064	4.387	-0.665
H	1.806	5.292	-1.507
C	-0.254	2.136	4.397
H	-0.438	1.247	2.439
C	-2.293	2.237	2.880
H	0.840	2.106	4.456
H	-0.642	1.238	4.897
H	-0.606	3.011	4.961
H	-2.675	3.124	3.403
H	-2.722	1.354	3.365
H	-2.654	2.269	1.846
H	6.027	-1.652	-3.104
H	4.691	-2.667	-3.667
C	4.965	-1.874	-2.957
H	6.799	-2.655	-1.154
H	4.389	-0.985	-3.233
H	7.676	-3.878	0.823
C	5.798	-2.705	-0.729
C	4.702	-2.306	-1.523
C	6.830	-3.557	1.442
C	5.634	-3.168	0.591
C	3.389	-2.351	-0.973
H	6.582	-4.373	2.132
H	7.174	-2.709	2.052
C	4.322	-3.257	1.099

C	3.200	-2.869	0.338
H	4.164	-3.646	2.103
C	1.811	-3.069	0.907
H	1.222	-3.739	0.269
H	1.241	-2.139	0.994
H	1.860	-3.516	1.907
H	-0.158	0.365	-2.656
H	0.627	-3.436	-4.539
C	-4.994	1.113	0.177
H	-5.672	-1.167	-5.445
H	-3.289	-0.584	-4.989
C	-5.306	-1.126	-4.422
C	-3.961	-0.798	-4.161
H	-7.212	-1.678	-3.539
C	-6.175	-1.413	-3.345
C	-3.484	-0.752	-2.839
C	-5.701	-1.357	-2.026
H	-2.445	-0.526	-2.633
C	-4.350	-1.020	-1.753
H	-6.375	-1.577	-1.199
C	-3.877	-1.015	-0.355
H	-1.778	-2.954	-1.344
N	-2.567	-0.896	-0.035
H	-4.585	-1.433	0.363
H	-1.306	-5.259	-2.162
C	-1.621	-3.761	-0.635
C	-1.351	-5.064	-1.094
P	-1.994	-1.773	1.394
C	-1.682	-3.501	0.748
C	-1.135	-6.109	-0.175
C	-3.319	-2.014	2.703
H	-4.523	-3.446	1.588
C	-4.420	-2.877	2.508
C	-3.168	-1.336	3.929
C	-1.458	-4.547	1.670
C	-1.188	-5.848	1.210
C	-5.377	-3.036	3.528
C	-4.121	-1.504	4.950
H	-6.224	-3.700	3.373
H	-1.497	-4.354	2.740
H	-1.020	-6.650	1.924
O	-0.699	-1.058	2.045
Cu	-1.376	0.805	-0.514
H	-5.970	-2.475	5.536
C	-5.232	-2.347	4.748
H	-3.996	-0.984	5.897
H	-2.294	-0.711	4.085
H	-0.927	-7.115	-0.532
H	-3.931	4.661	-4.064
H	-5.009	4.003	-2.810
H	-4.214	2.908	-3.958
H	-5.860	0.771	-0.381
H	-5.119	1.209	1.256

	1	2	3
	A	A	A
Frequencies --	-205.6019	16.9471	20.7896
Red. masses --	5.8882	5.0465	5.1847

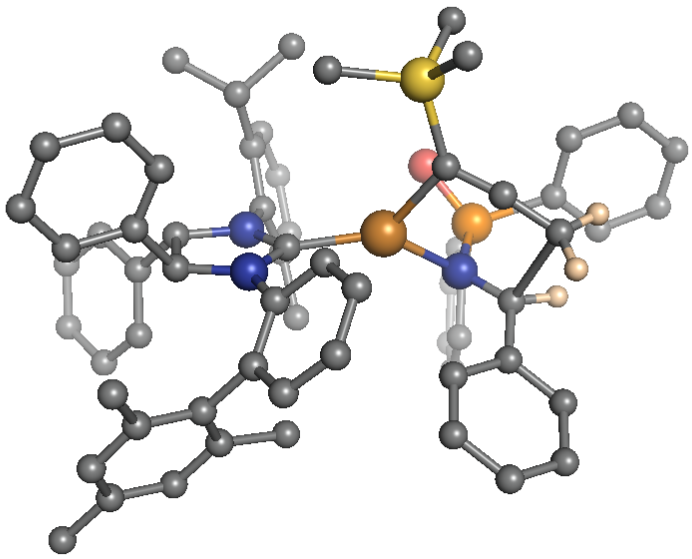
Zero-point correction=	1.151393 (Hartree/Particle)
Thermal correction to Energy=	1.222784
Thermal correction to Enthalpy=	1.223728
Thermal correction to Gibbs Free Energy=	1.040384
Sum of electronic and zero-point Energies=	-2961.696294
Sum of electronic and thermal Energies=	-2961.624903
Sum of electronic and thermal Enthalpies=	-2961.623959

```
 Sum of electronic and thermal Free Energies=     -2961.807302

         Item               Value     Threshold  Converged?
 Maximum Force            0.000062     0.000450     YES
 RMS     Force            0.000008     0.000300     YES

SCF= -2962.84768686 Hartree
```

The transition state (10) leading to minor (propargyl) isomer: Dissymmetric N-Aryl methyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from back side of the complex and the terminal allene carbon side pointing to the front.



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---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
H      3.145      0.748      4.037
C      0.074     -0.701      4.372
C      3.133     -0.188      4.606
C      2.066     -1.635      2.122
Si     1.797     -1.382      3.969
H      2.963      0.056      5.664
C      2.899     -2.426      1.552
H      4.127     -0.650      4.521
C      1.990     -3.045      4.876
H      1.871     -2.916      5.962
H      1.238     -3.770      4.537
H      2.982     -3.477      4.690
C     -3.237      0.292      0.594
N     -1.991     -0.548      0.485
C     -2.664      1.744      0.643
C     -0.820      0.186      0.448
N     -1.174      1.505      0.467
C     -0.063      3.499      1.448
```

C	0.632	4.710	1.235
C	-0.309	2.662	0.329
C	1.087	5.072	-0.040
C	0.174	2.998	-0.966
C	0.872	4.210	-1.129
C	-2.927	-2.681	-0.477
C	-2.904	-4.098	-0.448
C	-2.054	-1.989	0.413
C	-2.056	-4.822	0.405
C	-1.211	-2.721	1.276
C	-1.197	-4.123	1.272
C	-0.436	3.107	2.881
C	-6.332	-0.041	2.829
C	-5.505	0.143	1.705
C	-4.107	-0.018	1.807
C	-5.768	-0.400	4.069
C	-4.372	-0.569	4.175
C	-3.549	-0.376	3.052
C	-4.208	4.952	-0.794
C	-3.620	4.022	0.085
C	-3.288	2.721	-0.349
C	-4.477	4.588	-2.127
C	-4.156	3.289	-2.568
C	-3.569	2.365	-1.686
H	-3.839	0.157	-0.306
H	-2.806	2.157	1.647
H	0.830	5.367	2.079
H	1.618	6.010	-0.184
C	-0.012	2.082	-2.159
H	1.247	4.476	-2.114
H	-3.562	-4.634	-1.127
H	-0.528	-4.657	1.941
H	-7.407	0.088	2.737
H	-5.949	0.410	0.748
H	-6.405	-0.547	4.938
H	-3.929	-0.850	5.128
H	-2.475	-0.505	3.145
H	-4.456	5.949	-0.439
H	-3.426	4.313	1.114
H	-4.932	5.302	-2.809
H	-4.366	2.995	-3.593
H	-3.347	1.366	-2.050
H	-1.062	1.809	-2.305
H	0.553	1.152	-2.029
H	0.345	2.568	-3.073
C	0.852	2.907	3.723
H	-0.957	2.143	2.854
C	-1.369	4.136	3.570
H	1.530	2.197	3.237
H	0.601	2.527	4.722
H	1.391	3.855	3.848
H	-0.887	5.119	3.648
H	-1.614	3.802	4.586
H	-2.311	4.269	3.022
H	-6.913	-2.622	0.090
H	-5.846	-3.998	-0.224
C	-5.868	-2.911	-0.067
H	-7.241	-1.710	-2.039
H	-5.316	-2.710	0.857
H	-6.254	-0.286	-5.357
C	-6.169	-1.616	-2.206
C	-5.282	-2.171	-1.260
C	-6.684	-0.335	-4.350
C	-5.711	-0.951	-3.361
C	-3.877	-2.041	-1.457

H	-6.947	0.691	-4.055
H	-7.617	-0.908	-4.403
C	-4.318	-0.864	-3.558
C	-3.396	-1.397	-2.632
H	-3.938	-0.378	-4.456
C	-1.913	-1.312	-2.949
H	-1.497	-2.306	-3.153
H	-1.332	-0.889	-2.124
H	-1.740	-0.693	-3.836
H	-0.553	-2.180	1.943
H	-2.063	-5.908	0.388
C	3.770	-3.095	0.727
H	0.812	-5.812	-3.787
H	-0.518	-4.290	-2.321
C	1.299	-4.991	-3.266
C	0.548	-4.125	-2.446
H	3.277	-5.443	-4.038
C	2.688	-4.785	-3.404
C	1.170	-3.061	-1.769
C	3.312	-3.731	-2.716
H	0.585	-2.404	-1.134
C	2.564	-2.856	-1.886
H	4.386	-3.584	-2.815
C	3.294	-1.782	-1.176
H	3.018	0.133	-3.263
N	2.715	-0.631	-0.753
H	4.371	-1.799	-1.359
H	3.277	1.408	-5.386
C	3.483	1.114	-3.251
C	3.625	1.840	-4.450
P	3.787	0.746	-0.419
C	3.933	1.667	-2.037
C	4.210	3.121	-4.436
C	5.516	0.148	-0.015
H	6.292	0.210	-2.045
C	6.510	-0.009	-1.003
C	5.816	-0.120	1.337
C	4.514	2.953	-2.021
C	4.653	3.678	-3.219
C	7.801	-0.440	-0.638
C	7.106	-0.546	1.699
H	8.566	-0.560	-1.401
H	4.850	3.389	-1.083
H	5.100	4.668	-3.203
O	3.213	1.664	0.778
Cu	1.084	-0.497	0.501
H	9.098	-1.036	0.993
C	8.100	-0.708	0.712
H	7.336	-0.749	2.742
H	5.048	0.009	2.095
H	4.318	3.681	-5.362
H	0.037	-0.365	5.418
H	-0.693	-1.476	4.247
H	-0.183	0.151	3.734
H	4.830	-2.845	0.762
H	3.525	-4.087	0.353

	1	2	3
	A	A	A
Frequencies --	-197.3564	12.9980	21.0781
Red. masses --	8.7551	5.2331	5.2458

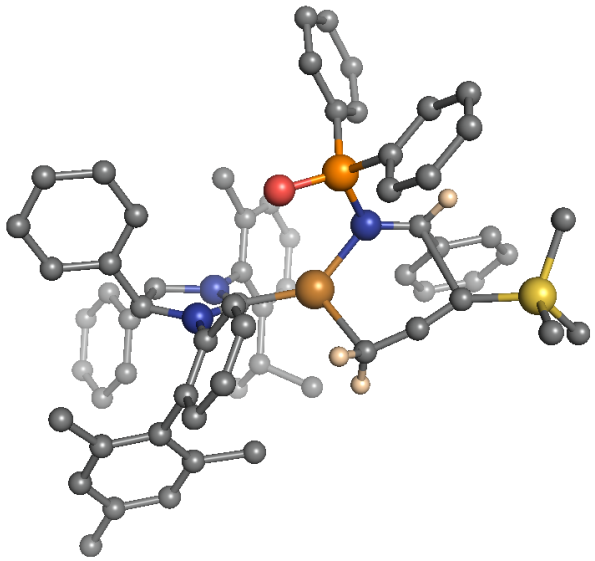
Zero-point correction= 1.152391 (Hartree/Particle)
Thermal correction to Energy= 1.223383
Thermal correction to Enthalpy= 1.224327

```
 Thermal correction to Gibbs Free Energy=         1.042022
 Sum of electronic and zero-point Energies=       -2961.709427
 Sum of electronic and thermal Energies=          -2961.638435
 Sum of electronic and thermal Enthalpies=        -2961.637491
 Sum of electronic and thermal Free Energies=     -2961.819796

         Item               Value     Threshold  Converged?
 Maximum Force            0.000006     0.000450     YES
 RMS     Force            0.000001     0.000300     YES


SCF= -2962.86181801 Hartree
```

The transition state (11) leading to major (silylallene) isomer: Dissymmetric N-Aryl *iso*-propyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from front side of the complex and the propargyl group pointing to the back.



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---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
H      4.723    -2.390    -4.949
C      5.798     0.724    -4.562
C      5.503    -2.341    -4.179
C      1.191    -0.718    -2.520
Si     5.480    -0.656    -3.294
H      6.475    -2.513    -4.664
C      2.569    -0.611    -2.625
H      5.329    -3.159    -3.467
C      6.872    -0.650    -2.000
H      7.832    -0.880    -2.483
H      6.976     0.324    -1.505
H      6.694    -1.406    -1.224
C     -3.206    -0.852     1.077
N     -2.040    -1.022     0.141
C     -3.099     0.661     1.480
C     -1.232     0.081     0.063
N     -1.843     1.090     0.749
```

C	-1.459	3.401	-0.082
C	-0.906	4.683	0.142
C	-1.288	2.415	0.926
C	-0.223	4.984	1.329
C	-0.591	2.702	2.133
C	-0.068	3.997	2.318
C	-2.703	-2.810	-1.469
C	-2.409	-4.067	-2.048
C	-1.788	-2.287	-0.516
C	-1.244	-4.780	-1.718
C	-0.619	-3.000	-0.179
C	-0.342	-4.237	-0.784
C	-2.200	3.130	-1.395
C	-4.338	-3.099	3.973
C	-4.347	-2.305	2.810
C	-3.147	-1.780	2.288
C	-3.120	-3.382	4.622
C	-1.917	-2.867	4.098
C	-1.926	-2.069	2.940
C	-5.928	3.204	1.964
C	-4.777	2.421	2.175
C	-4.335	1.505	1.196
C	-6.656	3.076	0.766
C	-6.221	2.163	-0.217
C	-5.069	1.386	-0.005
H	-4.138	-1.032	0.537
H	-2.892	0.732	2.552
H	-1.018	5.452	-0.617
H	0.193	5.977	1.482
C	-0.381	1.651	3.208
H	0.473	4.224	3.234
H	-3.100	-4.474	-2.783
H	0.563	-4.777	-0.516
H	-5.271	-3.496	4.366
H	-5.292	-2.089	2.315
H	-3.108	-3.999	5.517
H	-0.972	-3.088	4.588
H	-0.984	-1.692	2.548
H	-6.255	3.903	2.730
H	-4.225	2.517	3.108
H	-7.548	3.675	0.600
H	-6.776	2.059	-1.146
H	-4.752	0.692	-0.779
H	-0.102	0.684	2.779
H	-1.286	1.499	3.812
H	0.417	1.960	3.891
C	-3.325	4.167	-1.646
H	-2.669	2.144	-1.324
C	-1.223	3.098	-2.600
H	-4.029	4.202	-0.806
H	-3.888	3.899	-2.550
H	-2.918	5.175	-1.796
H	-0.727	4.068	-2.732
H	-1.771	2.872	-3.525
H	-0.448	2.334	-2.467
H	-6.418	-3.736	-0.183
H	-5.229	-4.669	-1.105
C	-5.402	-3.714	-0.592
H	-7.356	-2.244	-1.739
H	-4.695	-3.676	0.245
H	-8.142	0.257	-2.722
C	-6.374	-1.900	-2.059
C	-5.228	-2.541	-1.544
C	-7.532	-0.173	-3.529
C	-6.281	-0.837	-2.981

C	-3.938	-2.092	-1.944
H	-8.166	-0.896	-4.059
H	-7.284	0.632	-4.229
C	-4.997	-0.422	-3.384
C	-3.824	-1.032	-2.885
H	-4.900	0.385	-4.108
C	-2.471	-0.572	-3.396
H	-1.912	-1.402	-3.847
H	-1.846	-0.174	-2.589
H	-2.586	0.211	-4.154
H	0.069	-2.579	0.552
H	-1.043	-5.740	-2.187
C	3.816	-0.412	-2.501
H	0.764	-1.709	-2.344
H	0.581	-0.077	-3.161
H	3.731	5.761	-2.570
H	1.551	4.756	-1.879
C	3.701	4.764	-2.138
C	2.472	4.194	-1.752
H	5.850	4.472	-2.222
C	4.894	4.035	-1.943
C	2.427	2.908	-1.186
C	4.849	2.748	-1.387
H	1.479	2.493	-0.857
C	3.614	2.157	-1.012
H	5.773	2.195	-1.237
C	3.617	0.817	-0.392
H	3.406	2.077	2.024
N	2.520	0.327	0.236
H	4.604	0.411	-0.161
H	4.033	3.335	4.072
C	3.494	1.553	2.971
C	3.841	2.267	4.134
P	2.747	-0.832	1.550
C	3.245	0.169	3.044
C	3.932	1.602	5.372
C	4.160	-2.004	1.199
H	5.665	-0.935	2.348
C	5.451	-1.802	1.728
C	3.895	-3.137	0.401
C	3.328	-0.497	4.287
C	3.672	0.219	5.448
C	6.473	-2.735	1.465
C	4.916	-4.066	0.138
H	7.466	-2.579	1.877
H	3.123	-1.563	4.352
H	3.735	-0.298	6.402
O	1.378	-1.655	1.811
Cu	0.665	0.085	-0.554
H	6.995	-4.590	0.472
C	6.207	-3.868	0.672
H	4.708	-4.939	-0.475
H	2.898	-3.297	-0.002
H	4.199	2.156	6.269
H	6.794	0.612	-5.013
H	5.743	1.713	-4.092
H	5.053	0.692	-5.369

	1	2	3
	A	A	A
Frequencies --	-135.8461	13.2334	15.8561
Red. masses --	8.2687	5.5720	4.9003

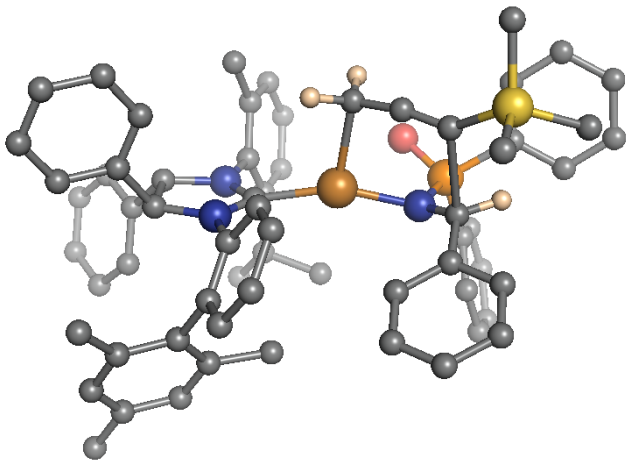
Zero-point correction= 1.150757 (Hartree/Particle)
Thermal correction to Energy= 1.222537
Thermal correction to Enthalpy= 1.223481

```
 Thermal correction to Gibbs Free Energy=         1.037034
 Sum of electronic and zero-point Energies=       -2961.721658
 Sum of electronic and thermal Energies=          -2961.649878
 Sum of electronic and thermal Enthalpies=        -2961.648934
 Sum of electronic and thermal Free Energies=     -2961.835380

         Item               Value     Threshold  Converged?
 Maximum Force            0.000001     0.000450     YES
 RMS     Force            0.000000     0.000300     YES

 SCF= -2962.87241495 Hartree
```

The transition state (12) leading to major (silylallene) isomer: Dissymmetric N-Aryl *iso*-propyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from back side of the complex and the propargyl group pointing to the front.



```
---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
H    -4.680    -4.039    -3.647
C    -4.678    -4.888    -0.444
C    -5.547    -3.608    -3.127
C    -1.645    -0.882    -2.341
Si   -5.138    -3.255    -1.301
H    -6.382    -4.318    -3.210
C    -2.728    -1.595    -1.857
H    -5.832    -2.686    -3.652
C    -6.685    -2.520    -0.480
H    -7.542    -3.192    -0.630
H    -6.556    -2.385     0.601
H    -6.941    -1.544    -0.913
C     3.475    -0.746    -1.045
N     2.093    -0.998    -0.497
C     3.348     0.698    -1.626
C     1.223     0.054    -0.669
N     1.929     1.072    -1.246
C     1.331     3.438    -0.768
```

C	0.880	4.683	-1.259
C	1.401	2.351	-1.679
C	0.523	4.852	-2.604
C	1.028	2.500	-3.044
C	0.594	3.763	-3.490
C	2.464	-2.686	1.312
C	2.155	-3.970	1.820
C	1.782	-2.258	0.138
C	1.206	-4.806	1.209
C	0.826	-3.097	-0.471
C	0.530	-4.362	0.059
C	1.678	3.298	0.717
C	5.747	-3.039	-3.119
C	5.273	-2.179	-2.109
C	3.929	-1.753	-2.098
C	4.874	-3.492	-4.126
C	3.527	-3.074	-4.118
C	3.061	-2.208	-3.114
C	6.018	3.446	-1.755
C	5.006	2.540	-2.125
C	4.421	1.679	-1.172
C	6.463	3.497	-0.420
C	5.884	2.640	0.538
C	4.870	1.741	0.166
H	4.191	-0.760	-0.220
H	3.387	0.650	-2.719
H	0.806	5.529	-0.580
H	0.180	5.821	-2.960
C	1.064	1.341	-4.024
H	0.296	3.886	-4.528
H	2.666	-4.307	2.719
H	-0.214	-4.990	-0.424
H	6.787	-3.355	-3.116
H	5.955	-1.831	-1.336
H	5.235	-4.160	-4.904
H	2.846	-3.421	-4.891
H	2.022	-1.890	-3.125
H	6.458	4.102	-2.503
H	4.674	2.501	-3.161
H	7.248	4.191	-0.131
H	6.219	2.676	1.571
H	4.437	1.095	0.925
H	0.677	0.421	-3.576
H	2.083	1.133	-4.381
H	0.455	1.570	-4.905
C	2.595	4.439	1.226
H	2.218	2.356	0.853
C	0.386	3.224	1.572
H	3.506	4.521	0.623
H	2.890	4.242	2.265
H	2.082	5.409	1.210
H	-0.215	4.135	1.459
H	0.641	3.111	2.635
H	-0.234	2.371	1.277
H	6.413	-3.477	1.150
H	5.095	-4.419	1.859
C	5.327	-3.504	1.298
H	6.846	-1.824	2.749
H	4.851	-3.606	0.317
H	7.247	0.817	3.629
C	5.802	-1.514	2.769
C	4.855	-2.267	2.046
C	6.477	0.409	4.298
C	5.436	-0.380	3.524
C	3.488	-1.863	2.049

H	6.993	-0.227	5.030
H	6.023	1.246	4.840
C	4.076	-0.015	3.542
C	3.096	-0.736	2.825
H	3.764	0.843	4.136
C	1.642	-0.318	2.952
H	1.030	-1.135	3.353
H	1.205	-0.034	1.988
H	1.542	0.537	3.628
H	0.324	-2.757	-1.369
H	0.993	-5.785	1.630
C	-3.698	-2.081	-1.195
H	-1.841	0.014	-2.933
H	-0.745	-1.426	-2.629
H	-2.153	-4.361	4.596
H	-0.322	-3.178	3.381
C	-2.390	-3.641	3.816
C	-1.359	-2.969	3.131
H	-4.541	-3.871	4.009
C	-3.734	-3.368	3.482
C	-1.656	-2.037	2.122
C	-4.031	-2.437	2.474
H	-0.852	-1.522	1.606
C	-2.999	-1.759	1.773
H	-5.069	-2.219	2.236
C	-3.386	-0.731	0.784
H	-2.946	1.197	2.850
N	-2.553	0.275	0.408
H	-4.462	-0.581	0.700
H	-3.046	2.626	4.887
C	-3.144	2.261	2.756
C	-3.193	3.072	3.906
P	-3.293	1.815	-0.079
C	-3.334	2.834	1.484
C	-3.426	4.456	3.786
C	-5.086	1.589	-0.573
H	-5.923	1.778	1.424
C	-6.136	1.638	0.367
C	-5.375	1.428	-1.944
C	-3.560	4.222	1.361
C	-3.606	5.031	2.512
C	-7.472	1.527	-0.064
C	-6.710	1.319	-2.373
H	-8.279	1.568	0.663
H	-3.691	4.669	0.379
H	-3.780	6.100	2.415
O	-2.476	2.540	-1.266
Cu	-0.764	0.039	-0.465
H	-8.792	1.289	-1.767
C	-7.760	1.369	-1.434
H	-6.930	1.201	-3.431
H	-4.564	1.407	-2.667
H	-3.461	5.081	4.675
H	-5.527	-5.586	-0.461
H	-4.393	-4.720	0.602
H	-3.832	-5.370	-0.951

	1	2	3
	A	A	A
Frequencies --	-158.1630	8.9485	13.0116
Red. masses --	8.7582	5.3646	5.4891

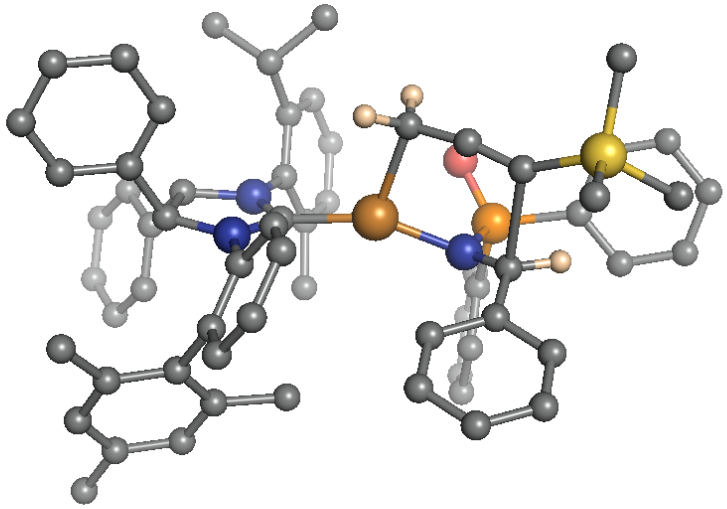
Zero-point correction= 1.151285 (Hartree/Particle)
Thermal correction to Energy= 1.222794
Thermal correction to Enthalpy= 1.223739
Thermal correction to Gibbs Free Energy= 1.038002

```
 Sum of electronic and zero-point Energies=       -2961.713074
 Sum of electronic and thermal Energies=          -2961.641564
 Sum of electronic and thermal Enthalpies=        -2961.640620
 Sum of electronic and thermal Free Energies=     -2961.826357

         Item               Value     Threshold  Converged?
 Maximum Force            0.000005     0.000450     YES
 RMS     Force            0.000000     0.000300     YES

 SCF= -2962.86435875 Hartree
```

The transition state (13) leading to major (silylallene) isomer: Dissymmetric N-Aryl methyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from back side of the complex and the propargyl group pointing to the front.



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---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
H     5.060     2.505    -4.731
C     5.222     4.306    -1.953
C     5.872     2.148    -4.083
C     1.596     0.447    -2.541
Si    5.455     2.442    -2.249
H     6.792     2.679    -4.365
C     2.803     1.079    -2.292
H     6.020     1.079    -4.285
C     6.910     1.816    -1.199
H     7.845     2.279    -1.545
H     6.788     2.067    -0.138
H     7.021     0.727    -1.280
C    -3.547     0.522    -0.849
N    -2.135     0.939    -0.524
C    -3.424    -1.033    -0.954
C    -1.232    -0.099    -0.522
N    -1.939    -1.249    -0.728
```

C	-1.288	-3.263	-2.027
C	-0.894	-4.620	-2.024
C	-1.410	-2.599	-0.778
C	-0.616	-5.293	-0.826
C	-1.103	-3.257	0.444
C	-0.711	-4.609	0.398
C	-2.379	3.073	0.756
C	-2.085	4.455	0.830
C	-1.819	2.334	-0.322
C	-1.258	5.093	-0.109
C	-0.987	2.976	-1.263
C	-0.697	4.344	-1.160
C	-1.531	-2.569	-3.372
C	-5.992	2.075	-3.367
C	-5.437	1.570	-2.175
C	-4.093	1.147	-2.130
C	-5.201	2.170	-4.529
C	-3.855	1.752	-4.490
C	-3.308	1.242	-3.300
C	-5.858	-3.725	0.294
C	-4.998	-2.970	-0.525
C	-4.337	-1.828	-0.025
C	-6.071	-3.343	1.632
C	-5.418	-2.202	2.139
C	-4.558	-1.451	1.319
H	-4.201	0.797	-0.020
H	-3.645	-1.345	-1.979
H	-0.793	-5.148	-2.968
H	-0.316	-6.338	-0.844
C	-1.146	-2.539	1.779
H	-0.476	-5.122	1.327
H	-2.509	5.031	1.650
H	-0.052	4.817	-1.895
H	-7.031	2.395	-3.388
H	-6.056	1.496	-1.284
H	-5.626	2.564	-5.449
H	-3.238	1.825	-5.382
H	-2.269	0.923	-3.285
H	-6.359	-4.602	-0.110
H	-4.845	-3.271	-1.559
H	-6.736	-3.922	2.268
H	-5.577	-1.897	3.171
H	-4.069	-0.575	1.736
H	-2.067	-1.964	1.906
H	-0.308	-1.837	1.869
H	-1.070	-3.256	2.603
C	-0.268	-2.637	-4.273
H	-1.735	-1.509	-3.184
C	-2.747	-3.168	-4.129
H	0.615	-2.261	-3.747
H	-0.418	-2.034	-5.179
H	-0.058	-3.667	-4.587
H	-2.576	-4.226	-4.368
H	-2.910	-2.631	-5.072
H	-3.671	-3.105	-3.540
H	-6.370	3.607	0.834
H	-5.071	4.785	1.071
C	-5.281	3.731	0.843
H	-6.505	2.541	2.926
H	-4.906	3.549	-0.169
H	-6.708	0.483	4.645
C	-5.445	2.294	2.909
C	-4.642	2.812	1.873
C	-5.795	0.946	5.042
C	-4.913	1.475	3.926

C	-3.257	2.480	1.827
H	-6.111	1.755	5.715
H	-5.270	0.198	5.648
C	-3.536	1.181	3.881
C	-2.698	1.672	2.855
H	-3.098	0.565	4.664
C	-1.213	1.362	2.908
H	-0.618	2.283	2.960
H	-0.873	0.814	2.022
H	-0.974	0.757	3.789
H	-0.583	2.397	-2.085
H	-1.051	6.156	-0.019
C	3.879	1.556	-1.814
H	1.634	-0.575	-2.920
H	0.764	1.041	-2.919
H	2.652	5.603	2.869
H	0.713	4.335	1.934
C	2.810	4.649	2.372
C	1.717	3.930	1.848
H	4.963	4.657	2.655
C	4.111	4.117	2.247
C	1.914	2.695	1.206
C	4.308	2.886	1.602
H	1.063	2.153	0.806
C	3.214	2.155	1.067
H	5.312	2.477	1.522
C	3.490	0.841	0.452
H	2.557	-0.649	2.968
N	2.560	-0.144	0.373
H	4.545	0.568	0.441
H	2.092	-1.692	5.185
C	2.514	-1.731	3.062
C	2.244	-2.321	4.312
P	3.131	-1.826	0.261
C	2.712	-2.545	1.930
C	2.167	-3.724	4.429
C	5.001	-1.897	0.138
H	5.421	-1.556	2.245
C	5.841	-1.749	1.261
C	5.557	-2.173	-1.128
C	2.628	-3.948	2.043
C	2.356	-4.536	3.292
C	7.236	-1.874	1.115
C	6.951	-2.302	-1.270
H	7.881	-1.762	1.983
H	2.764	-4.571	1.162
H	2.291	-5.618	3.379
O	2.478	-2.663	-0.954
Cu	0.757	0.000	-0.503
H	8.869	-2.254	-0.260
C	7.792	-2.152	-0.150
H	7.377	-2.522	-2.246
H	4.900	-2.304	-1.984
H	1.959	-4.178	5.394
H	6.151	4.852	-2.166
H	4.936	4.507	-0.913
H	4.434	4.709	-2.604

	1	2	3
	A	A	A
Frequencies --	-163.5904	14.5621	15.8533
Red. masses --	9.1172	5.4607	5.4756

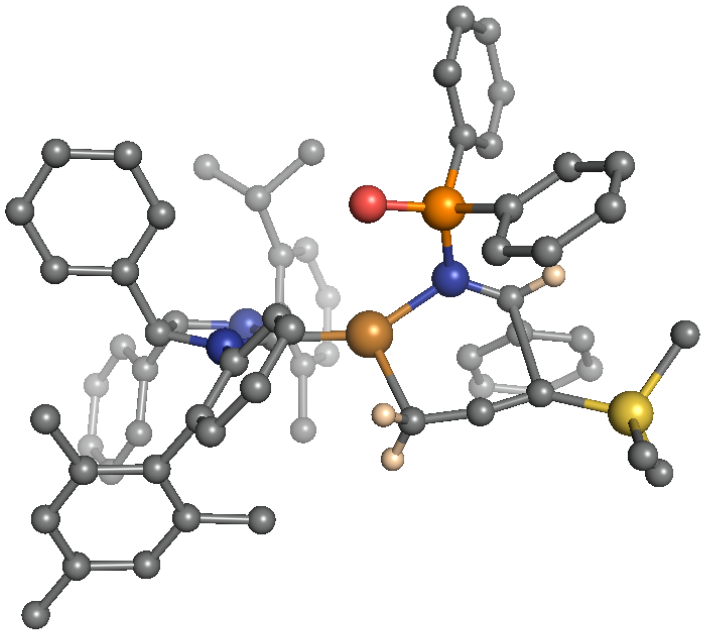
Zero-point correction= 1.151537 (Hartree/Particle)
Thermal correction to Energy= 1.222982

```
 Thermal correction to Enthalpy=                  1.223926
 Thermal correction to Gibbs Free Energy=         1.039777
 Sum of electronic and zero-point Energies=       -2961.714951
 Sum of electronic and thermal Energies=          -2961.643506
 Sum of electronic and thermal Enthalpies=        -2961.642562
 Sum of electronic and thermal Free Energies=     -2961.826711

         Item               Value     Threshold  Converged?
 Maximum Force            0.000000     0.000450     YES
 RMS     Force            0.000000     0.000300     YES

 SCF= -2962.86648802 Hartree
```

The transition state (14) leading to major (silylallene) isomer: Dissymmetric N-Aryl methyl is oriented syn to biaryl mesityl group (both pointing to the rear) with the phosphinoylimine approaching from front side of the complex and the propargyl group pointing to the back.



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---------------------------------------
Cartesian coordinates (Angstroms):
---------------------------------------
H      4.401    -5.284    -2.092
C      5.487    -2.797    -3.999
C      5.239    -4.763    -1.611
C      1.057    -2.202    -1.268
Si     5.275    -2.927    -2.114
H      6.170    -5.267    -1.907
C      2.422    -2.282    -1.493
H      5.125    -4.869    -0.524
C      6.762    -2.108    -1.259
H      7.683    -2.655    -1.508
H      6.901    -1.067    -1.576
H      6.648    -2.118    -0.168
C     -3.441     0.159     0.973
N     -2.153    -0.551     0.654
```

C	-3.326	1.471	0.125
C	-1.268	0.213	-0.069
N	-1.914	1.364	-0.416
C	-0.993	3.663	-0.540
C	-0.562	4.746	-1.339
C	-1.360	2.455	-1.192
C	-0.490	4.637	-2.734
C	-1.269	2.318	-2.604
C	-0.833	3.425	-3.359
C	-2.703	-2.974	0.975
C	-2.348	-4.205	1.578
C	-1.858	-1.854	1.209
C	-1.197	-4.343	2.370
C	-0.705	-1.987	2.011
C	-0.369	-3.225	2.581
C	-1.015	3.825	0.983
C	-5.125	0.830	4.355
C	-4.917	0.473	3.009
C	-3.616	0.455	2.462
C	-4.028	1.163	5.174
C	-2.726	1.139	4.635
C	-2.520	0.790	3.288
C	-5.945	3.190	-2.091
C	-4.951	2.961	-1.121
C	-4.400	1.674	-0.939
C	-6.406	2.128	-2.892
C	-5.864	0.838	-2.714
C	-4.870	0.615	-1.746
H	-4.286	-0.440	0.629
H	-3.358	2.337	0.793
H	-0.278	5.681	-0.861
H	-0.163	5.484	-3.333
C	-1.603	1.017	-3.310
H	-0.776	3.338	-4.442
H	-2.984	-5.069	1.399
H	0.521	-3.307	3.200
H	-6.133	0.841	4.762
H	-5.768	0.214	2.383
H	-4.185	1.434	6.215
H	-1.873	1.388	5.261
H	-1.509	0.770	2.892
H	-6.358	4.188	-2.218
H	-4.606	3.787	-0.503
H	-7.176	2.300	-3.640
H	-6.216	0.010	-3.325
H	-4.473	-0.389	-1.624
H	-2.586	0.638	-3.016
H	-0.871	0.236	-3.070
H	-1.601	1.158	-4.396
C	0.412	4.083	1.532
H	-1.356	2.886	1.431
C	-1.980	4.952	1.437
H	1.095	3.277	1.245
H	0.390	4.138	2.628
H	0.821	5.029	1.155
H	-1.654	5.929	1.056
H	-2.003	5.010	2.533
H	-3.005	4.782	1.084
H	-6.464	-2.930	2.452
H	-5.154	-4.113	2.590
C	-5.418	-3.125	2.189
H	-7.341	-3.227	0.300
H	-4.791	-2.395	2.712
H	-7.928	-2.241	-2.568
C	-6.355	-3.158	-0.156

C	-5.223	-3.075	0.682
C	-7.478	-3.237	-2.441
C	-6.244	-3.168	-1.561
C	-3.928	-2.972	0.098
H	-8.247	-3.885	-2.004
H	-7.237	-3.618	-3.441
C	-4.952	-3.100	-2.120
C	-3.795	-3.000	-1.318
H	-4.839	-3.131	-3.203
C	-2.432	-2.956	-1.984
H	-1.766	-3.733	-1.589
H	-1.932	-1.996	-1.811
H	-2.522	-3.101	-3.066
H	-0.061	-1.127	2.186
H	-0.951	-5.306	2.811
C	3.675	-2.128	-1.611
H	0.639	-2.770	-0.434
H	0.403	-2.141	-2.141
H	3.549	2.226	-5.931
H	1.426	2.067	-4.623
C	3.557	1.824	-4.921
C	2.360	1.727	-4.184
H	5.702	1.491	-4.882
C	4.769	1.405	-4.330
C	2.365	1.213	-2.876
C	4.773	0.880	-3.030
H	1.444	1.179	-2.302
C	3.570	0.760	-2.285
H	5.711	0.560	-2.582
C	3.623	0.227	-0.911
H	4.032	2.651	0.046
N	2.578	0.357	-0.058
H	4.624	0.034	-0.522
H	5.036	4.821	0.704
C	4.129	2.897	1.099
C	4.692	4.133	1.472
P	2.908	0.352	1.679
C	3.679	2.002	2.089
C	4.800	4.480	2.833
C	4.176	-0.948	2.124
H	5.860	0.408	2.341
C	5.517	-0.621	2.406
C	3.743	-2.288	2.216
C	3.778	2.353	3.453
C	4.338	3.589	3.823
C	6.423	-1.631	2.786
C	4.647	-3.295	2.596
H	7.456	-1.375	3.007
H	3.414	1.674	4.220
H	4.412	3.856	4.875
O	1.531	0.113	2.492
Cu	0.659	-0.213	-0.383
H	6.687	-3.746	3.181
C	5.989	-2.967	2.884
H	4.310	-4.325	2.667
H	2.708	-2.541	1.999
H	5.233	5.435	3.119
H	6.443	-3.237	-4.314
H	5.466	-1.750	-4.327
H	4.679	-3.328	-4.520

	1	2	3
	A	A	A
Frequencies --	-130.2405	13.3517	15.0847

```
Red. masses --     8.2953                 5.2883                 5.1982
Zero-point correction=                           1.151081 (Hartree/Particle)
Thermal correction to Energy=                    1.222769
Thermal correction to Enthalpy=                  1.223713
Thermal correction to Gibbs Free Energy=         1.037607
Sum of electronic and zero-point Energies=       -2961.719465
Sum of electronic and thermal Energies=          -2961.647777
Sum of electronic and thermal Enthalpies=        -2961.646833
Sum of electronic and thermal Free Energies=     -2961.832940

        Item               Value     Threshold  Converged?
Maximum Force            0.000003     0.000450     YES
RMS     Force            0.000000     0.000300     YES

SCF= -2962.87054641 Hartree
```

Table S3. Relative and Gibbs free energies (298 K, 1 atm) in kcal/mol for the NHC–Cu-allenyl to NHC–Cu-propargyl isomerization followed by addition to phosphinoylimine

structure	**A**	**B**	**C**	**8**	**11**
ΔG	0.0	14.8	2.0	32.9	27.0
ΔE	0.0	13.3	-0.2	10.0	5.7

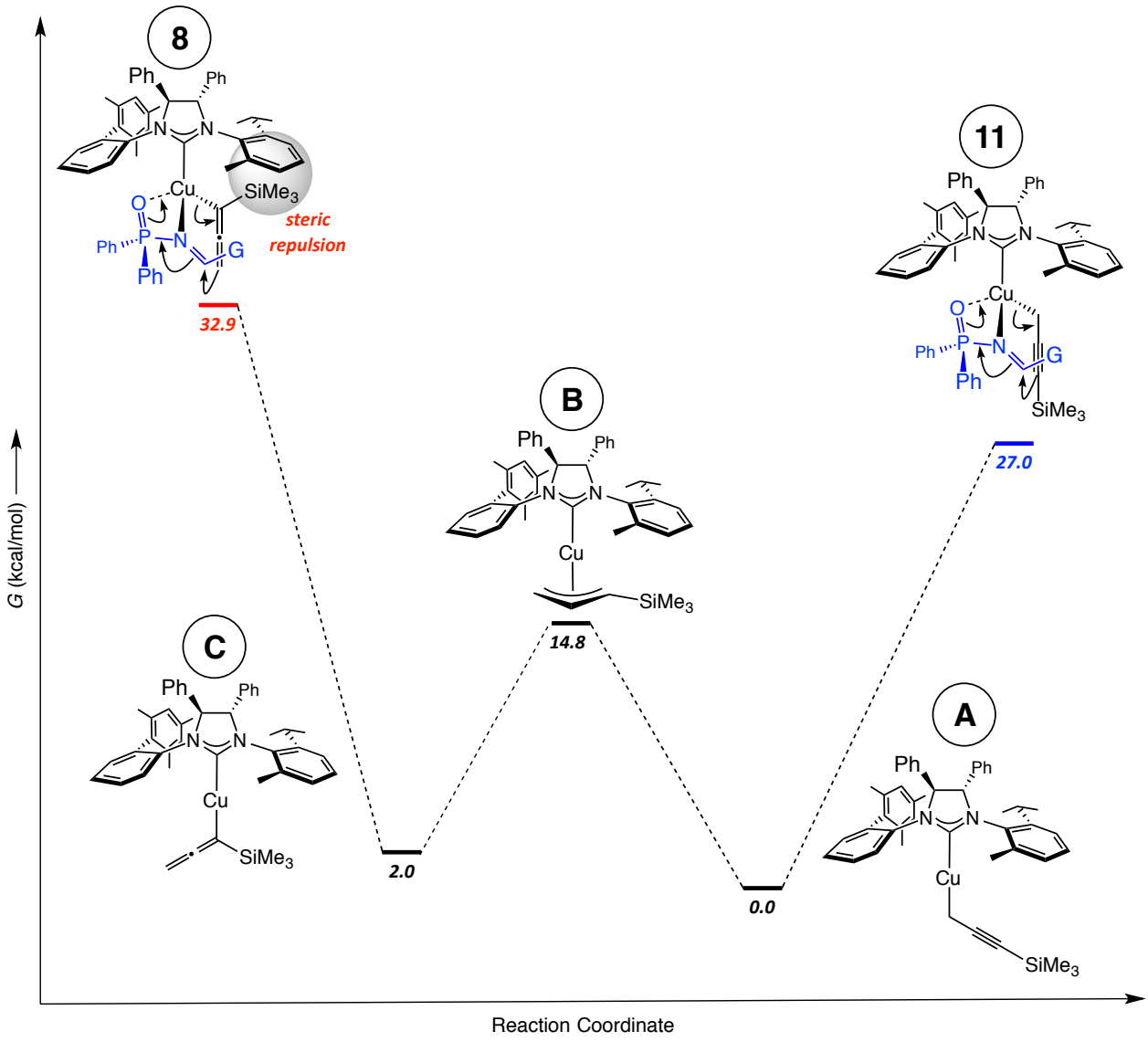

Figure S3. Relative Gibbs Free Energies (kcal/mol) Computed at 298 K and 1.0 atm.

Table S4. Relative and Gibbs free energies (298 K, 1 atm) in kcal/mol of the C–C bond forming transition states governing the Cu-allenyl and Cu-propargyl followed by addition to phosphinoylimine

structure	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
ΔG	7.4	5.8	17.6	9.3	0.0	5.7	5.4	1.5
ΔE	6.4	4.3	15.5	6.7	0.0	5.1	3.7	1.2

X-Ray Crystal Structure of Homoallenylamide 4b

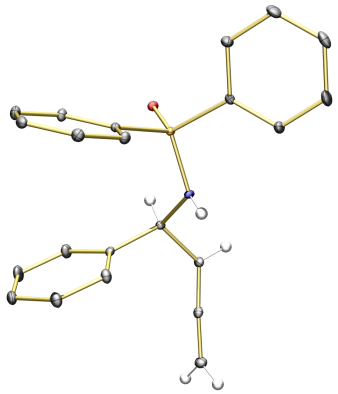

Table S5. Crystal data and structure refinement for (*S*)-*P*,*P*-diphenyl-*N*-(1-phenylbuta-2,3-dien-1-yl)phosphinic amide

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Identification code	C22H20NOP	
Empirical formula	C22H20NOP	
Formula weight	345.36	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2(1)	
Unit cell dimensions	a = 5.3586(5) Å	a= 90°.
	b = 15.5598(15) Å	b= 94.462(5)°.
	c = 21.571(2) Å	g = 90°.
Volume	1793.1(3) Å ^{3}	
Z	4	
Density (calculated)	1.279 Mg/m^3	
Absorption coefficient	0.162 mm^{-1}	
F(000)	728	
Crystal size	0.18 x 0.10 x 0.06 mm^3	
Theta range for data collection	1.62 to 30.00°.	
Index ranges	-7<=h<=7, -21<=k<=21, -30<=l<=30	
Reflections collected	55440	
Independent reflections	10477 [R(int) = 0.0213]	
Completeness to theta = 30.00°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.9903 and 0.9714	

Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10477 / 39 / 616
Goodness-of-fit on F^2	1.066
Final R indices [I>2sigma(I)]	R1 = 0.0297, wR2 = 0.0785
R indices (all data)	R1 = 0.0305, wR2 = 0.0791
Absolute structure parameter	-0.02(4)
Extinction coefficient	na
Largest diff. peak and hole	0.543 and -0.192 e.$Å^{-3}$

Table S6. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $C_{22}H_{20}NOP$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
P(1)	-313(1)	3275(1)	-87(1)	12(1)
O(1)	-2909(1)	2999(1)	16(1)	17(1)
N(1)	1788(2)	2574(1)	202(1)	14(1)
C(1)	294(2)	4332(1)	244(1)	14(1)
C(2)	2349(2)	4818(1)	91(1)	18(1)
C(3)	2801(2)	5626(1)	356(1)	21(1)
C(4)	1226(2)	5948(1)	782(1)	20(1)
C(5)	-802(2)	5468(1)	944(1)	22(1)
C(6)	-1282(2)	4664(1)	671(1)	19(1)
C(7)	302(2)	3373(1)	-893(1)	15(1)
C(8)	-1334(3)	3886(1)	-1267(1)	24(1)
C(9)	-1015(3)	3973(1)	-1898(1)	31(1)
C(10)	934(3)	3558(1)	-2158(1)	27(1)
C(11)	2575(3)	3053(1)	-1789(1)	28(1)
C(12)	2270(2)	2956(1)	-1156(1)	23(1)
C(13)	1370(2)	2120(1)	784(1)	14(1)
C(14)	2587(2)	1241(1)	755(1)	17(1)
C(15)	4492(2)	954(1)	1109(1)	18(1)
C(16)	6380(3)	613(1)	1435(1)	24(1)
C(17)	2183(2)	2629(1)	1366(1)	15(1)
C(18)	4360(2)	3120(1)	1401(1)	22(1)
C(19)	5032(3)	3614(1)	1926(1)	25(1)
C(20)	3543(3)	3620(1)	2421(1)	26(1)
C(21)	1403(3)	3125(1)	2395(1)	32(1)
C(22)	723(2)	2630(1)	1869(1)	26(1)
P(2)	8265(1)	9080(1)	4015(1)	23(1)
O(2)	10736(2)	8762(1)	3843(1)	26(1)
N(2)	5988(2)	8413(1)	3796(1)	26(1)
C(23)	7135(6)	10012(2)	3540(2)	20(1)
C(24)	9009(5)	10561(2)	3365(1)	27(1)
C(25)	8421(6)	11306(2)	3019(1)	33(1)

C(26)	5957(6)	11487(2)	2844(2)	35(1)
C(27)	4066(8)	10935(2)	2990(2)	37(1)
C(28)	4660(7)	10201(2)	3337(1)	31(1)
C(23X)	7531(6)	10141(2)	3765(2)	21(1)
C(24X)	8601(6)	10865(2)	4058(2)	33(1)
C(25X)	8064(7)	11686(2)	3822(2)	43(1)
C(26X)	6456(7)	11778(2)	3287(2)	41(1)
C(27X)	5399(9)	11073(3)	2992(2)	37(1)
C(28X)	5950(8)	10241(2)	3227(2)	31(1)
C(29)	8540(20)	9220(10)	4860(3)	24(1)
C(30)	10756(13)	8982(4)	5257(3)	33(1)
C(31)	10900(14)	9106(3)	5895(2)	40(1)
C(32)	8980(20)	9496(7)	6180(3)	41(2)
C(33)	6855(10)	9754(5)	5833(3)	40(1)
C(34)	6611(7)	9595(4)	5198(3)	34(1)
C(29X)	8270(20)	9344(10)	4820(3)	31(2)
C(30X)	9987(13)	8913(5)	5190(2)	40(1)
C(31X)	10002(13)	9089(6)	5825(3)	68(2)
C(32X)	8387(16)	9657(7)	6053(4)	43(2)
C(33X)	6683(10)	10068(4)	5651(3)	51(1)
C(34X)	6600(8)	9903(4)	5024(3)	39(1)
C(35)	6320(3)	7497(1)	3930(1)	31(1)
C(36)	4433(8)	7344(3)	4473(2)	27(1)
C(37)	5111(6)	7264(2)	5068(1)	32(1)
C(38)	5720(8)	7234(3)	5646(2)	45(1)
C(36X)	5291(9)	7124(3)	4480(2)	32(1)
C(37X)	6619(6)	6859(2)	4940(1)	34(1)
C(38X)	8149(10)	6534(3)	5381(2)	61(1)
C(39)	5608(2)	6944(1)	3363(1)	25(1)
C(40)	7140(3)	6272(1)	3208(1)	31(1)
C(41)	6484(3)	5754(1)	2701(1)	34(1)
C(42)	4270(3)	5898(1)	2341(1)	29(1)
C(43)	2731(3)	6573(1)	2492(1)	28(1)
C(44)	3392(3)	7097(1)	3002(1)	27(1)

Table S7. Bond lengths [Å] and angles [°] for $C_{22}H_{20}NOP$

P(1)-O(1)	1.4887(8)
P(1)-N(1)	1.6541(9)
P(1)-C(7)	1.8005(10)
P(1)-C(1)	1.8133(11)
N(1)-C(13)	1.4743(13)
N(1)-H(1N)	0.871(13)
C(1)-C(6)	1.3951(15)
C(1)-C(2)	1.3961(15)
C(2)-C(3)	1.3944(16)
C(2)-H(2)	0.9500
C(3)-C(4)	1.3889(17)
C(3)-H(3)	0.9500
C(4)-C(5)	1.3857(18)
C(4)-H(4)	0.9500
C(5)-C(6)	1.3968(16)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(7)-C(8)	1.3949(15)
C(7)-C(12)	1.3958(15)
C(8)-C(9)	1.3914(17)
C(8)-H(8)	0.9500
C(9)-C(10)	1.384(2)
C(9)-H(9)	0.9500
C(10)-C(11)	1.383(2)
C(10)-H(10)	0.9500
C(11)-C(12)	1.3962(16)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.5184(15)
C(13)-C(17)	1.5194(15)
C(13)-H(13)	1.0000
C(14)-C(15)	1.3048(16)
C(14)-H(14)	0.9500
C(15)-C(16)	1.3003(16)

C(16)-H(16A)	0.931(14)
C(16)-H(16B)	0.932(14)
C(17)-C(22)	1.3859(16)
C(17)-C(18)	1.3916(16)
C(18)-C(19)	1.3927(16)
C(18)-H(18)	0.9500
C(19)-C(20)	1.3829(18)
C(19)-H(19)	0.9500
C(20)-C(21)	1.379(2)
C(20)-H(20)	0.9500
C(21)-C(22)	1.3960(18)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
P(2)-O(2)	1.4878(9)
P(2)-N(2)	1.6421(12)
P(2)-C(29)	1.830(5)
P(2)-C(23)	1.850(3)
N(2)-C(35)	1.4630(18)
N(2)-H(2N)	0.904(14)
C(23)-C(24)	1.393(4)
C(23)-C(28)	1.396(5)
C(24)-C(25)	1.401(4)
C(24)-H(24)	0.9500
C(25)-C(26)	1.374(5)
C(25)-H(25)	0.9500
C(26)-C(27)	1.384(5)
C(26)-H(26)	0.9500
C(27)-C(28)	1.388(4)
C(27)-H(27)	0.9500
C(28)-H(28)	0.9500
C(29)-C(34)	1.434(8)
C(29)-C(30)	1.458(9)
C(30)-C(31)	1.386(7)
C(30)-H(30)	0.9500
C(31)-C(32)	1.380(10)
C(31)-H(31)	0.9500

C(32)-C(33)	1.373(8)
C(32)-H(32)	0.9500
C(33)-C(34)	1.389(6)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-C(39)	1.520(2)
C(35)-C(36)	1.623(4)
C(35)-H(35)	0.88(2)
C(36)-C(37)	1.313(4)
C(36)-H(36)	0.9500
C(37)-C(38)	1.263(5)
C(38)-H(38A)	0.95(2)
C(38)-H(38B)	0.96(2)
C(39)-C(40)	1.386(2)
C(39)-C(44)	1.3883(18)
C(40)-C(41)	1.383(2)
C(40)-H(40)	0.9500
C(41)-C(42)	1.385(2)
C(41)-H(41)	0.9500
C(42)-C(43)	1.390(2)
C(42)-H(42)	0.9500
C(43)-C(44)	1.393(2)
C(43)-H(43)	0.9500
C(44)-H(44)	0.9500

O(1)-P(1)-N(1)	111.70(5)
O(1)-P(1)-C(7)	114.31(5)
N(1)-P(1)-C(7)	104.42(5)
O(1)-P(1)-C(1)	110.15(5)
N(1)-P(1)-C(1)	110.70(5)
C(7)-P(1)-C(1)	105.27(5)
C(13)-N(1)-P(1)	119.56(7)
C(13)-N(1)-H(1N)	113.9(10)
P(1)-N(1)-H(1N)	117.5(11)
C(6)-C(1)-C(2)	119.04(10)
C(6)-C(1)-P(1)	119.77(8)

C(2)-C(1)-P(1)	121.18(8)
C(3)-C(2)-C(1)	120.35(10)
C(3)-C(2)-H(2)	119.8
C(1)-C(2)-H(2)	119.8
C(4)-C(3)-C(2)	120.13(11)
C(4)-C(3)-H(3)	119.9
C(2)-C(3)-H(3)	119.9
C(5)-C(4)-C(3)	120.01(11)
C(5)-C(4)-H(4)	120.0
C(3)-C(4)-H(4)	120.0
C(4)-C(5)-C(6)	119.96(11)
C(4)-C(5)-H(5)	120.0
C(6)-C(5)-H(5)	120.0
C(1)-C(6)-C(5)	120.50(11)
C(1)-C(6)-H(6)	119.7
C(5)-C(6)-H(6)	119.7
C(8)-C(7)-C(12)	119.46(10)
C(8)-C(7)-P(1)	116.89(9)
C(12)-C(7)-P(1)	123.64(8)
C(9)-C(8)-C(7)	120.11(12)
C(9)-C(8)-H(8)	119.9
C(7)-C(8)-H(8)	119.9
C(10)-C(9)-C(8)	120.33(12)
C(10)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(9)	119.90(11)
C(11)-C(10)-H(10)	120.0
C(9)-C(10)-H(10)	120.0
C(10)-C(11)-C(12)	120.40(12)
C(10)-C(11)-H(11)	119.8
C(12)-C(11)-H(11)	119.8
C(7)-C(12)-C(11)	119.80(11)
C(7)-C(12)-H(12)	120.1
C(11)-C(12)-H(12)	120.1
N(1)-C(13)-C(14)	107.65(9)
N(1)-C(13)-C(17)	113.66(8)

C(14)-C(13)-C(17)	114.01(9)
N(1)-C(13)-H(13)	107.0
C(14)-C(13)-H(13)	107.0
C(17)-C(13)-H(13)	107.0
C(15)-C(14)-C(13)	127.09(10)
C(15)-C(14)-H(14)	116.5
C(13)-C(14)-H(14)	116.5
C(16)-C(15)-C(14)	175.48(12)
C(15)-C(16)-H(16A)	123.3(12)
C(15)-C(16)-H(16B)	119.3(12)
H(16A)-C(16)-H(16B)	117.4(16)
C(22)-C(17)-C(18)	118.65(10)
C(22)-C(17)-C(13)	120.28(10)
C(18)-C(17)-C(13)	121.04(9)
C(17)-C(18)-C(19)	120.60(11)
C(17)-C(18)-H(18)	119.7
C(19)-C(18)-H(18)	119.7
C(20)-C(19)-C(18)	120.27(12)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(21)-C(20)-C(19)	119.49(11)
C(21)-C(20)-H(20)	120.3
C(19)-C(20)-H(20)	120.3
C(20)-C(21)-C(22)	120.36(12)
C(20)-C(21)-H(21)	119.8
C(22)-C(21)-H(21)	119.8
C(17)-C(22)-C(21)	120.60(12)
C(17)-C(22)-H(22)	119.7
C(21)-C(22)-H(22)	119.7
O(2)-P(2)-N(2)	111.96(6)
O(2)-P(2)-C(29)	106.6(3)
N(2)-P(2)-C(29)	111.2(6)
O(2)-P(2)-C(23)	112.41(11)
N(2)-P(2)-C(23)	97.59(12)
C(29)-P(2)-C(23)	117.0(5)
C(35)-N(2)-P(2)	118.83(9)

C(35)-N(2)-H(2N)	115.8(12)
P(2)-N(2)-H(2N)	115.8(12)
C(24)-C(23)-C(28)	118.2(3)
C(24)-C(23)-P(2)	114.8(2)
C(28)-C(23)-P(2)	127.0(2)
C(23)-C(24)-C(25)	121.0(3)
C(23)-C(24)-H(24)	119.5
C(25)-C(24)-H(24)	119.5
C(26)-C(25)-C(24)	119.2(3)
C(26)-C(25)-H(25)	120.4
C(24)-C(25)-H(25)	120.4
C(25)-C(26)-C(27)	121.0(3)
C(25)-C(26)-H(26)	119.5
C(27)-C(26)-H(26)	119.5
C(26)-C(27)-C(28)	119.5(4)
C(26)-C(27)-H(27)	120.2
C(28)-C(27)-H(27)	120.2
C(27)-C(28)-C(23)	121.0(4)
C(27)-C(28)-H(28)	119.5
C(23)-C(28)-H(28)	119.5
C(34)-C(29)-C(30)	113.0(5)
C(34)-C(29)-P(2)	123.4(6)
C(30)-C(29)-P(2)	123.6(6)
C(31)-C(30)-C(29)	121.9(5)
C(31)-C(30)-H(30)	119.1
C(29)-C(30)-H(30)	119.1
C(32)-C(31)-C(30)	121.2(5)
C(32)-C(31)-H(31)	119.4
C(30)-C(31)-H(31)	119.4
C(33)-C(32)-C(31)	120.1(6)
C(33)-C(32)-H(32)	120.0
C(31)-C(32)-H(32)	120.0
C(32)-C(33)-C(34)	119.8(5)
C(32)-C(33)-H(33)	120.1
C(34)-C(33)-H(33)	120.1
C(33)-C(34)-C(29)	123.9(5)

C(33)-C(34)-H(34)	118.1
C(29)-C(34)-H(34)	118.1
N(2)-C(35)-C(39)	111.90(11)
N(2)-C(35)-C(36)	102.27(19)
C(39)-C(35)-C(36)	111.49(17)
N(2)-C(35)-H(35)	111.0(14)
C(39)-C(35)-H(35)	97.7(14)
C(36)-C(35)-H(35)	122.8(14)
C(37)-C(36)-C(35)	125.4(3)
C(37)-C(36)-H(36)	117.3
C(35)-C(36)-H(36)	117.3
C(38)-C(37)-C(36)	176.5(4)
C(37)-C(38)-H(38A)	114(3)
C(37)-C(38)-H(38B)	126(3)
H(38A)-C(38)-H(38B)	120(4)
C(37)-C(38)-H(38D)	105.7(16)
H(38A)-C(38)-H(38D)	67(4)
H(38B)-C(38)-H(38D)	102(3)
C(40)-C(39)-C(44)	119.41(13)
C(40)-C(39)-C(35)	120.26(12)
C(44)-C(39)-C(35)	120.31(13)
C(41)-C(40)-C(39)	120.77(13)
C(41)-C(40)-H(40)	119.6
C(39)-C(40)-H(40)	119.6
C(40)-C(41)-C(42)	120.24(14)
C(40)-C(41)-H(41)	119.9
C(42)-C(41)-H(41)	119.9
C(41)-C(42)-C(43)	119.21(14)
C(41)-C(42)-H(42)	120.4
C(43)-C(42)-H(42)	120.4
C(42)-C(43)-C(44)	120.62(13)
C(42)-C(43)-H(43)	119.7
C(44)-C(43)-H(43)	119.7
C(39)-C(44)-C(43)	119.74(13)
C(39)-C(44)-H(44)	120.1
C(43)-C(44)-H(44)	120.1

Symmetry transformations used to generate equivalent atoms:

Table S8. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{22}H_{20}NOP$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	11(1)	13(1)	12(1)	2(1)	2(1)	0(1)
O(1)	12(1)	20(1)	18(1)	2(1)	3(1)	-1(1)
N(1)	11(1)	15(1)	15(1)	4(1)	3(1)	2(1)
C(1)	15(1)	13(1)	13(1)	1(1)	2(1)	1(1)
C(2)	15(1)	20(1)	20(1)	-1(1)	4(1)	-1(1)
C(3)	20(1)	20(1)	23(1)	-1(1)	2(1)	-3(1)
C(4)	24(1)	16(1)	20(1)	-2(1)	-2(1)	1(1)
C(5)	27(1)	20(1)	21(1)	-4(1)	8(1)	2(1)
C(6)	21(1)	18(1)	19(1)	0(1)	7(1)	0(1)
C(7)	16(1)	15(1)	13(1)	0(1)	1(1)	-3(1)
C(8)	29(1)	24(1)	18(1)	3(1)	0(1)	5(1)
C(9)	44(1)	30(1)	18(1)	7(1)	-4(1)	2(1)
C(10)	40(1)	28(1)	13(1)	0(1)	4(1)	-14(1)
C(11)	28(1)	40(1)	18(1)	-5(1)	9(1)	-4(1)
C(12)	21(1)	33(1)	16(1)	-1(1)	4(1)	4(1)
C(13)	14(1)	13(1)	15(1)	2(1)	2(1)	0(1)
C(14)	21(1)	12(1)	18(1)	0(1)	0(1)	0(1)
C(15)	22(1)	12(1)	19(1)	0(1)	4(1)	0(1)
C(16)	25(1)	20(1)	26(1)	1(1)	-1(1)	3(1)
C(17)	17(1)	14(1)	16(1)	1(1)	3(1)	3(1)
C(18)	27(1)	21(1)	19(1)	-2(1)	6(1)	-6(1)
C(19)	30(1)	22(1)	22(1)	-4(1)	4(1)	-7(1)
C(20)	33(1)	26(1)	20(1)	-7(1)	3(1)	2(1)
C(21)	30(1)	46(1)	22(1)	-10(1)	12(1)	-3(1)
C(22)	21(1)	35(1)	22(1)	-5(1)	8(1)	-4(1)
P(2)	21(1)	17(1)	34(1)	0(1)	13(1)	0(1)
O(2)	20(1)	25(1)	33(1)	-5(1)	10(1)	0(1)
N(2)	18(1)	29(1)	31(1)	4(1)	4(1)	0(1)
C(23)	23(1)	18(1)	18(1)	-3(1)	4(1)	-2(1)
C(24)	31(1)	25(1)	25(1)	1(1)	1(1)	-6(1)
C(25)	46(2)	28(1)	26(1)	6(1)	3(1)	-10(1)

C(26)	47(2)	29(2)	29(1)	7(1)	9(1)	3(1)
C(27)	36(2)	42(2)	32(2)	5(1)	5(1)	4(2)
C(28)	30(2)	34(1)	28(1)	6(1)	6(1)	4(1)
C(23X)	22(1)	22(2)	20(2)	1(1)	1(1)	1(1)
C(24X)	34(2)	23(1)	42(2)	7(1)	-1(1)	-4(1)
C(25X)	46(2)	25(1)	59(2)	13(1)	4(2)	-3(1)
C(26X)	38(2)	34(2)	53(2)	22(2)	10(1)	7(1)
C(27X)	39(2)	42(2)	30(2)	18(2)	4(2)	8(2)
C(28X)	29(2)	41(2)	25(1)	4(1)	5(1)	8(1)
C(29)	25(3)	11(3)	37(2)	-7(2)	20(2)	-3(2)
C(30)	28(3)	38(2)	32(2)	2(1)	-9(2)	-4(2)
C(31)	43(3)	52(2)	22(2)	4(1)	-8(2)	-6(2)
C(32)	61(5)	43(3)	18(2)	-6(2)	6(2)	-29(3)
C(33)	55(3)	40(3)	26(2)	-4(2)	20(2)	-1(2)
C(34)	37(2)	37(2)	29(2)	8(2)	11(1)	9(2)
C(29X)	30(3)	21(5)	43(3)	-15(2)	13(2)	-8(2)
C(30X)	29(3)	69(3)	22(2)	-3(2)	4(2)	15(3)
C(31X)	31(3)	141(6)	30(2)	7(3)	-4(2)	14(3)
C(32X)	52(4)	54(4)	23(3)	-13(3)	13(3)	-27(3)
C(33X)	97(3)	27(2)	33(2)	2(2)	36(2)	12(2)
C(34X)	58(2)	34(2)	26(2)	-3(2)	17(2)	17(2)
C(35)	32(1)	26(1)	32(1)	9(1)	-11(1)	-8(1)
C(36)	39(2)	19(2)	22(1)	8(1)	-4(1)	-2(1)
C(37)	38(2)	22(1)	35(2)	4(1)	1(1)	-2(1)
C(38)	53(2)	42(2)	40(2)	2(1)	10(2)	0(2)
C(36X)	39(2)	25(2)	30(2)	7(1)	-4(1)	3(1)
C(37X)	39(2)	42(2)	21(1)	4(1)	0(1)	-5(1)
C(38X)	76(3)	64(3)	41(2)	18(2)	-11(2)	13(2)
C(39)	24(1)	27(1)	24(1)	8(1)	-1(1)	-5(1)
C(40)	22(1)	31(1)	39(1)	12(1)	-4(1)	1(1)
C(41)	31(1)	30(1)	42(1)	8(1)	4(1)	7(1)
C(42)	32(1)	30(1)	27(1)	4(1)	2(1)	1(1)
C(43)	25(1)	36(1)	24(1)	2(1)	-1(1)	2(1)
C(44)	24(1)	34(1)	24(1)	1(1)	1(1)	4(1)

Table S9. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for $C_{22}H_{20}NOP$

	x	y	z	U(eq)
H(1N)	3360(20)	2684(10)	154(7)	16
H(2)	3446	4596	-195	22
H(3)	4188	5956	245	25
H(4)	1540	6498	963	24
H(5)	-1865	5684	1239	27
H(6)	-2692	4341	777	23
H(8)	-2669	4176	-1090	29
H(9)	-2141	4320	-2151	37
H(10)	1145	3619	-2589	32
H(11)	3918	2771	-1968	34
H(12)	3397	2607	-905	28
H(13)	-474	2023	787	17
H(14)	1884	858	446	21
H(16A)	8040(30)	686(13)	1343(8)	29
H(16B)	6090(30)	284(11)	1784(7)	29
H(18)	5396	3118	1063	26
H(19)	6519	3948	1944	30
H(20)	3992	3962	2777	31
H(21)	386	3121	2737	39
H(22)	-755	2291	1856	31
H(2N)	4420(30)	8619(12)	3817(8)	31
H(24)	10712	10428	3481	33
H(25)	9710	11682	2908	40
H(26)	5545	11999	2619	42
H(27)	2375	11056	2854	44
H(28)	3362	9822	3437	37
H(24X)	9707	10800	4421	40
H(25X)	8789	12178	4025	52
H(26X)	6088	12336	3125	49
H(27X)	4297	11142	2628	45
H(28X)	5242	9751	3018	38

H(30)	12143	8736	5073	40
H(31)	12346	8918	6140	47
H(32)	9129	9587	6617	49
H(33)	5556	10039	6027	47
H(34)	5075	9744	4974	41
H(30X)	11113	8514	5029	48
H(31X)	11179	8802	6105	81
H(32X)	8437	9768	6487	51
H(33X)	5551	10471	5805	61
H(34X)	5397	10174	4742	46
H(35)	7920(40)	7361(14)	3975(10)	37
H(36)	2695	7309	4350	32
H(38A)	5930(90)	6664(17)	5800(20)	54
H(38B)	5740(90)	7710(20)	5927(19)	54
H(36X)	3524	7084	4486	38
H(38C)	9030(90)	5990(20)	5370(30)	74
H(38D)	8560(100)	6940(30)	5710(20)	74
H(40)	8658	6167	3454	37
H(41)	7557	5298	2599	41
H(42)	3808	5539	1994	35
H(43)	1214	6677	2246	34
H(44)	2330	7557	3103	33

Table S10. Torsion angles [°] for $C_{22}H_{20}NOP$

O(1)-P(1)-N(1)-C(13)	-36.01(9)
C(7)-P(1)-N(1)-C(13)	-160.05(8)
C(1)-P(1)-N(1)-C(13)	87.13(9)
O(1)-P(1)-C(1)-C(6)	16.16(10)
N(1)-P(1)-C(1)-C(6)	-107.88(9)
C(7)-P(1)-C(1)-C(6)	139.85(9)
O(1)-P(1)-C(1)-C(2)	-165.21(8)
N(1)-P(1)-C(1)-C(2)	70.76(10)
C(7)-P(1)-C(1)-C(2)	-41.52(10)
C(6)-C(1)-C(2)-C(3)	-0.66(16)
P(1)-C(1)-C(2)-C(3)	-179.31(9)
C(1)-C(2)-C(3)-C(4)	0.95(17)
C(2)-C(3)-C(4)-C(5)	-0.16(18)
C(3)-C(4)-C(5)-C(6)	-0.90(18)
C(2)-C(1)-C(6)-C(5)	-0.41(16)
P(1)-C(1)-C(6)-C(5)	178.26(9)
C(4)-C(5)-C(6)-C(1)	1.19(18)
O(1)-P(1)-C(7)-C(8)	53.15(11)
N(1)-P(1)-C(7)-C(8)	175.50(9)
C(1)-P(1)-C(7)-C(8)	-67.85(10)
O(1)-P(1)-C(7)-C(12)	-125.63(10)
N(1)-P(1)-C(7)-C(12)	-3.28(11)
C(1)-P(1)-C(7)-C(12)	113.37(10)
C(12)-C(7)-C(8)-C(9)	0.55(18)
P(1)-C(7)-C(8)-C(9)	-178.29(10)
C(7)-C(8)-C(9)-C(10)	-0.5(2)
C(8)-C(9)-C(10)-C(11)	0.0(2)
C(9)-C(10)-C(11)-C(12)	0.3(2)
C(8)-C(7)-C(12)-C(11)	-0.20(18)
P(1)-C(7)-C(12)-C(11)	178.55(10)
C(10)-C(11)-C(12)-C(7)	-0.2(2)
P(1)-N(1)-C(13)-C(14)	149.02(8)
P(1)-N(1)-C(13)-C(17)	-83.71(10)
N(1)-C(13)-C(14)-C(15)	114.57(13)

C(17)-C(13)-C(14)-C(15)	-12.49(17)
N(1)-C(13)-C(17)-C(22)	138.94(11)
C(14)-C(13)-C(17)-C(22)	-97.18(13)
N(1)-C(13)-C(17)-C(18)	-39.29(14)
C(14)-C(13)-C(17)-C(18)	84.59(13)
C(22)-C(17)-C(18)-C(19)	-1.08(18)
C(13)-C(17)-C(18)-C(19)	177.18(11)
C(17)-C(18)-C(19)-C(20)	0.2(2)
C(18)-C(19)-C(20)-C(21)	0.7(2)
C(19)-C(20)-C(21)-C(22)	-0.8(2)
C(18)-C(17)-C(22)-C(21)	1.00(19)
C(13)-C(17)-C(22)-C(21)	-177.27(12)
C(20)-C(21)-C(22)-C(17)	-0.1(2)
O(2)-P(2)-N(2)-C(35)	47.22(13)
C(29)-P(2)-N(2)-C(35)	-71.9(4)
C(23)-P(2)-N(2)-C(35)	165.15(14)
O(2)-P(2)-C(23)-C(24)	-33.6(3)
N(2)-P(2)-C(23)-C(24)	-151.2(2)
C(23X)-P(2)-C(23)-C(24)	66.9(6)
C(29X)-P(2)-C(23)-C(24)	92.4(6)
C(29)-P(2)-C(23)-C(24)	90.2(6)
O(2)-P(2)-C(23)-C(28)	144.9(3)
N(2)-P(2)-C(23)-C(28)	27.3(3)
C(29)-P(2)-C(23)-C(28)	-91.2(6)
C(28)-C(23)-C(24)-C(25)	3.1(5)
P(2)-C(23)-C(24)-C(25)	-178.2(2)
C(23)-C(24)-C(25)-C(26)	-1.1(4)
C(24)-C(25)-C(26)-C(27)	-1.6(5)
C(25)-C(26)-C(27)-C(28)	2.2(5)
C(26)-C(27)-C(28)-C(23)	0.0(5)
C(24)-C(23)-C(28)-C(27)	-2.6(5)
P(2)-C(23)-C(28)-C(27)	178.9(3)
O(2)-P(2)-C(29)-C(34)	174.0(11)
N(2)-P(2)-C(29)-C(34)	-63.7(14)
C(23)-P(2)-C(29)-C(34)	47.2(15)
O(2)-P(2)-C(29)-C(30)	-4.5(14)

N(2)-P(2)-C(29)-C(30)	117.8(12)
C(23)-P(2)-C(29)-C(30)	-131.3(11)
C(34)-C(29)-C(30)-C(31)	0.8(17)
P(2)-C(29)-C(30)-C(31)	179.5(8)
C(29)-C(30)-C(31)-C(32)	-2.9(13)
C(30)-C(31)-C(32)-C(33)	1.4(12)
C(31)-C(32)-C(33)-C(34)	2.1(12)
C(32)-C(33)-C(34)-C(29)	-4.3(12)
C(30)-C(29)-C(34)-C(33)	2.7(17)
P(2)-C(29)-C(34)-C(33)	-175.9(7)
P(2)-N(2)-C(35)-C(39)	-131.93(11)
P(2)-N(2)-C(35)-C(36)	108.63(17)
N(2)-C(35)-C(36)-C(37)	-103.3(4)
C(39)-C(35)-C(36)-C(37)	137.0(3)
N(2)-C(35)-C(39)-C(40)	134.84(14)
C(36)-C(35)-C(39)-C(40)	-111.3(2)
N(2)-C(35)-C(39)-C(44)	-46.53(18)
C(36)-C(35)-C(39)-C(44)	67.3(2)
C(44)-C(39)-C(40)-C(41)	0.0(2)
C(35)-C(39)-C(40)-C(41)	178.60(13)
C(39)-C(40)-C(41)-C(42)	-0.4(2)
C(40)-C(41)-C(42)-C(43)	0.6(2)
C(41)-C(42)-C(43)-C(44)	-0.4(2)
C(40)-C(39)-C(44)-C(43)	0.2(2)
C(35)-C(39)-C(44)-C(43)	-178.42(13)
C(42)-C(43)-C(44)-C(39)	0.0(2)

Symmetry transformations used to generate equivalent atoms:

Table S11. Hydrogen bonds for $C_{22}H_{20}NOP$ [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.871(13)	2.104(13)	2.9751(12)	177.4(16)
N(2)-H(2N)...O(2)#2	0.904(14)	1.992(15)	2.8755(14)	165.6(18)

Symmetry transformations used to generate equivalent atoms:

#1 x+1,y,z #2 x-1,y,z

X-Ray Crystal Structure of Homoallenylamide 7

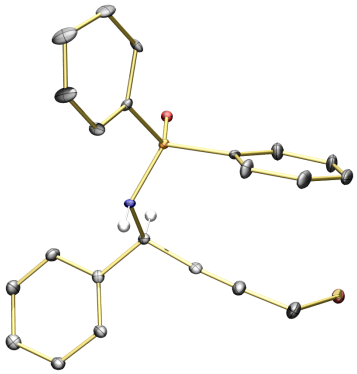


Table S12. Crystal data and structure refinement for (*R*)-*N*-(4-bromo-1-phenylbut-2-yn-1-yl)-*P*,*P*-diphenylphosphinic amide

Identification code	C22H19BrNOP	
Empirical formula	C22H19BrNOP	
Formula weight	424.26	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	I 4	
Unit cell dimensions	a = 27.1750(9) Å	a= 90º.
	b = 27.1750(9) Å	b= 90º.
	c = 5.2579(2) Å	g = 90º.
Volume	3882.9(2) Å ^{3}	
Z	8	
Density (calculated)	1.452 Mg/m^3	

Absorption coefficient	2.210 mm^{-1}
F(000)	1728
Crystal size	0.20 x 0.05 x 0.03 mm^3
Theta range for data collection	1.50 to 28.34º.
Index ranges	-36<=h<=36, -36<=k<=34, -7<=l<=6
Reflections collected	29844
Independent reflections	4780 [R(int) = 0.1011]
Completeness to theta = 28.34°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9367 and 0.6662
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4780 / 287 / 282
Goodness-of-fit on F^2	1.058
Final R indices [I>2sigma(I)]	R1 = 0.0770, wR2 = 0.1752
R indices (all data)	R1 = 0.1098, wR2 = 0.1901
Absolute structure parameter	0.03(2)
Extinction coefficient	na
Largest diff. peak and hole	0.874 and -0.686 e.$Å^{-3}$

Table S13. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $C_{22}H_{19}BrNOP$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
P(1)	7081(1)	10089(1)	1788(3)	15(1)
O(1)	7071(1)	9889(1)	-839(8)	20(1)
N(1)	7154(2)	9648(2)	3927(9)	15(1)
C(1)	6525(2)	10393(2)	2745(10)	18(1)
C(4)	5653(3)	10861(3)	4041(13)	47(2)
C(2)	6173(4)	10125(4)	4130(20)	29(3)
C(3)	5722(4)	10379(4)	4820(30)	36(3)
C(5)	6016(4)	11127(4)	3120(30)	36(2)
C(6)	6453(4)	10889(3)	2450(20)	24(2)
C(2X)	6366(4)	10425(5)	5204(18)	23(3)
C(3X)	5931(5)	10663(7)	5850(20)	41(4)
C(5X)	5859(5)	10928(5)	1640(20)	36(2)
C(6X)	6303(4)	10668(4)	790(20)	21(3)
C(7)	7564(2)	10547(2)	2031(13)	21(1)
C(8)	7587(2)	10867(2)	4014(15)	34(2)
C(9)	7972(2)	11205(2)	4222(16)	36(2)
C(10)	8343(2)	11205(2)	2460(16)	40(2)
C(11)	8322(3)	10878(3)	498(15)	39(2)
C(12)	7934(3)	10551(3)	215(15)	37(2)
C(13)	7538(2)	9273(2)	3438(11)	19(1)
C(14)	8032(2)	9474(2)	3999(12)	22(1)
C(15)	8417(2)	9667(2)	4342(15)	33(2)
C(16)	8877(2)	9928(3)	4727(19)	47(2)
Br(1)	9296(1)	9864(1)	1969(3)	36(1)
Br(1X)	9213(1)	9780(1)	7655(3)	45(1)
C(17)	7433(2)	8802(2)	4900(12)	20(1)
C(18)	7706(2)	8657(2)	6948(14)	26(1)
C(19)	7600(2)	8224(2)	8196(13)	28(1)
C(20)	7219(2)	7917(2)	7419(12)	30(1)
C(21)	6951(3)	8070(3)	5327(13)	35(2)
C(22)	7041(2)	8501(2)	4079(13)	30(1)

Table S14. Bond lengths [Å] and angles [°] for $C_{22}H_{19}BrNOP$

P(1)-O(1)	1.485(4)
P(1)-N(1)	1.657(5)
P(1)-C(1)	1.793(5)
P(1)-C(7)	1.812(5)
N(1)-C(13)	1.480(7)
N(1)-H(1N)	0.91(2)
C(1)-C(2X)	1.367(9)
C(1)-C(6)	1.371(8)
C(1)-C(6X)	1.405(8)
C(1)-C(2)	1.407(8)
C(4)-C(5)	1.315(10)
C(4)-C(3X)	1.331(10)
C(4)-C(3)	1.386(10)
C(4)-C(5X)	1.393(10)
C(4)-H(4)	0.9500
C(2)-C(3)	1.451(13)
C(2)-H(2)	0.9500
C(3)-H(3)	0.9500
C(5)-C(6)	1.397(13)
C(5)-H(5)	0.9500
C(6)-H(6)	0.9500
C(2X)-C(3X)	1.389(14)
C(2X)-H(2X)	0.9500
C(3X)-H(3X)	0.9500
C(5X)-C(6X)	1.469(14)
C(5X)-H(5X)	0.9500
C(6X)-H(6X)	0.9500
C(7)-C(8)	1.359(9)
C(7)-C(12)	1.386(9)
C(8)-C(9)	1.398(8)
C(8)-H(8)	0.9500
C(9)-C(10)	1.368(11)
C(9)-H(9)	0.9500
C(10)-C(11)	1.362(11)

C(10)-H(10)	0.9500
C(11)-C(12)	1.386(9)
C(11)-H(11)	0.9500
C(12)-H(12)	0.9500
C(13)-C(14)	1.479(8)
C(13)-C(17)	1.520(8)
C(13)-H(13)	1.00(2)
C(14)-C(15)	1.186(9)
C(15)-C(16)	1.451(9)
C(16)-Br(1)	1.851(9)
C(16)-H(16A)	0.9900
C(16)-H(16B)	0.9900
Br(1)-Br(1)#1	2.7566(16)
Br(1)-Br(1)#2	2.7567(16)
C(17)-C(18)	1.366(9)
C(17)-C(22)	1.412(8)
C(18)-C(19)	1.378(8)
C(18)-H(18)	0.9500
C(19)-C(20)	1.390(9)
C(19)-H(19)	0.9500
C(20)-C(21)	1.384(10)
C(20)-H(20)	0.9500
C(21)-C(22)	1.364(9)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500

O(1)-P(1)-N(1)	111.6(2)
O(1)-P(1)-C(1)	114.5(2)
N(1)-P(1)-C(1)	104.1(2)
O(1)-P(1)-C(7)	109.3(3)
N(1)-P(1)-C(7)	111.3(3)
C(1)-P(1)-C(7)	106.0(2)
C(13)-N(1)-P(1)	117.6(4)
C(13)-N(1)-H(1N)	108(4)
P(1)-N(1)-H(1N)	121(4)
C(2X)-C(1)-C(6)	89.9(8)

C(2X)-C(1)-C(6X)	121.3(8)
C(6)-C(1)-C(6X)	48.2(7)
C(2X)-C(1)-C(2)	47.7(7)
C(6)-C(1)-C(2)	118.0(7)
C(6X)-C(1)-C(2)	111.2(8)
C(2X)-C(1)-P(1)	124.2(6)
C(6)-C(1)-P(1)	122.8(5)
C(6X)-C(1)-P(1)	113.7(6)
C(2)-C(1)-P(1)	118.7(5)
C(5)-C(4)-C(3X)	93.4(11)
C(5)-C(4)-C(3)	121.8(8)
C(3X)-C(4)-C(3)	47.9(9)
C(5)-C(4)-C(5X)	45.0(8)
C(3X)-C(4)-C(5X)	118.4(9)
C(3)-C(4)-C(5X)	109.7(9)
C(5)-C(4)-H(4)	119.1
C(3X)-C(4)-H(4)	128.9
C(3)-C(4)-H(4)	119.1
C(5X)-C(4)-H(4)	112.3
C(1)-C(2)-C(3)	117.2(8)
C(1)-C(2)-H(2)	121.4
C(3)-C(2)-H(2)	121.4
C(4)-C(3)-C(2)	119.4(9)
C(4)-C(3)-H(3)	120.3
C(2)-C(3)-H(3)	120.3
C(4)-C(5)-C(6)	118.4(9)
C(4)-C(5)-H(5)	120.8
C(6)-C(5)-H(5)	120.8
C(1)-C(6)-C(5)	123.3(9)
C(1)-C(6)-H(6)	118.4
C(5)-C(6)-H(6)	118.4
C(1)-C(2X)-C(3X)	122.2(10)
C(1)-C(2X)-H(2X)	118.9
C(3X)-C(2X)-H(2X)	118.9
C(4)-C(3X)-C(2X)	119.6(11)
C(4)-C(3X)-H(3X)	120.2

C(2X)-C(3X)-H(3X)	120.2
C(4)-C(5X)-C(6X)	122.8(9)
C(4)-C(5X)-H(5X)	118.6
C(6X)-C(5X)-H(5X)	118.6
C(1)-C(6X)-C(5X)	112.8(9)
C(1)-C(6X)-H(6X)	123.6
C(5X)-C(6X)-H(6X)	123.6
C(8)-C(7)-C(12)	119.3(5)
C(8)-C(7)-P(1)	121.8(5)
C(12)-C(7)-P(1)	118.9(5)
C(7)-C(8)-C(9)	121.1(7)
C(7)-C(8)-H(8)	119.5
C(9)-C(8)-H(8)	119.5
C(10)-C(9)-C(8)	119.8(7)
C(10)-C(9)-H(9)	120.1
C(8)-C(9)-H(9)	120.1
C(11)-C(10)-C(9)	118.9(6)
C(11)-C(10)-H(10)	120.6
C(9)-C(10)-H(10)	120.6
C(10)-C(11)-C(12)	122.0(7)
C(10)-C(11)-H(11)	119.0
C(12)-C(11)-H(11)	119.0
C(11)-C(12)-C(7)	118.9(7)
C(11)-C(12)-H(12)	120.6
C(7)-C(12)-H(12)	120.6
C(14)-C(13)-N(1)	110.6(4)
C(14)-C(13)-C(17)	112.3(5)
N(1)-C(13)-C(17)	111.1(4)
C(14)-C(13)-H(13)	106(3)
N(1)-C(13)-H(13)	109(4)
C(17)-C(13)-H(13)	108(4)
C(15)-C(14)-C(13)	174.8(6)
C(14)-C(15)-C(16)	177.0(7)
C(15)-C(16)-Br(1)	111.9(6)
C(15)-C(16)-H(16A)	109.2
Br(1)-C(16)-H(16A)	109.2

C(15)-C(16)-H(16B)	109.2
Br(1)-C(16)-H(16B)	109.2
H(16A)-C(16)-H(16B)	107.9
C(16)-Br(1)-Br(1)#1	105.4(3)
C(16)-Br(1)-Br(1)#2	124.2(3)
Br(1)#1-Br(1)-Br(1)#2	89.998(1)
C(18)-C(17)-C(22)	118.9(5)
C(18)-C(17)-C(13)	122.8(5)
C(22)-C(17)-C(13)	118.3(5)
C(17)-C(18)-C(19)	120.6(6)
C(17)-C(18)-H(18)	119.7
C(19)-C(18)-H(18)	119.7
C(18)-C(19)-C(20)	121.8(6)
C(18)-C(19)-H(19)	119.1
C(20)-C(19)-H(19)	119.1
C(21)-C(20)-C(19)	116.5(6)
C(21)-C(20)-H(20)	121.8
C(19)-C(20)-H(20)	121.8
C(22)-C(21)-C(20)	123.1(6)
C(22)-C(21)-H(21)	118.4
C(20)-C(21)-H(21)	118.4
C(21)-C(22)-C(17)	119.0(6)
C(21)-C(22)-H(22)	120.5
C(17)-C(22)-H(22)	120.5

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+2,z #2 -y+2,x,z

Table S15. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for $C_{22}H_{19}BrNOP$. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ...\ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
P(1)	15(1)	17(1)	12(1)	-3(1)	-1(1)	0(1)
O(1)	20(2)	21(2)	17(2)	-1(2)	1(2)	1(2)
N(1)	16(2)	16(2)	12(2)	0(2)	-2(2)	4(2)
C(1)	14(2)	23(2)	19(3)	-7(2)	-2(2)	0(2)
C(4)	38(4)	59(4)	44(4)	-23(3)	-8(3)	29(3)
C(2)	36(6)	35(6)	16(6)	7(5)	10(5)	10(4)
C(3)	23(5)	65(7)	20(6)	7(6)	5(5)	11(5)
C(5)	31(4)	26(4)	50(5)	-2(4)	-10(4)	16(3)
C(6)	32(5)	15(4)	26(6)	-3(4)	-4(4)	3(4)
C(2X)	27(6)	24(6)	19(6)	-2(5)	7(5)	13(5)
C(3X)	34(8)	65(10)	22(6)	-8(7)	5(5)	26(7)
C(5X)	31(4)	26(4)	50(5)	-2(4)	-10(4)	16(3)
C(6X)	33(6)	16(6)	15(5)	3(5)	9(5)	2(5)
C(7)	22(2)	20(2)	22(3)	6(2)	-11(2)	-5(2)
C(8)	27(3)	27(3)	49(4)	-13(3)	0(3)	-8(2)
C(9)	32(3)	24(3)	53(5)	-10(3)	-11(3)	-9(2)
C(10)	29(3)	30(3)	60(5)	10(3)	-15(3)	-13(2)
C(11)	28(3)	49(4)	40(4)	4(3)	1(3)	-18(3)
C(12)	36(4)	39(4)	37(4)	2(3)	1(3)	-15(3)
C(13)	19(2)	21(3)	17(3)	-2(2)	2(2)	4(2)
C(14)	22(3)	17(2)	26(3)	0(2)	3(2)	9(2)
C(15)	24(3)	31(3)	44(4)	4(3)	0(3)	2(2)
C(16)	26(3)	54(4)	60(5)	9(4)	-6(3)	-9(3)
Br(1)	24(1)	41(1)	43(1)	12(1)	3(1)	-2(1)
Br(1X)	38(1)	55(1)	42(1)	-8(1)	-6(1)	2(1)
C(17)	22(3)	15(2)	24(3)	-6(2)	5(2)	4(2)
C(18)	25(3)	26(3)	28(3)	3(3)	5(3)	7(2)
C(19)	28(3)	28(3)	30(4)	3(2)	1(2)	6(2)
C(20)	38(3)	24(3)	29(4)	-8(2)	6(3)	5(2)
C(21)	36(4)	32(3)	36(4)	-4(3)	-4(3)	-7(3)
C(22)	29(3)	28(3)	34(4)	-3(3)	-9(3)	-2(2)

Table S16. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for $C_{22}H_{19}BrNOP$

	x	y	z	U(eq)
H(1N)	7160(20)	9720(20)	5620(50)	18
H(4)	5335	11004	4177	56
H(2)	6227	9792	4597	35
H(3)	5477	10216	5793	43
H(5)	5982	11472	2911	43
H(6)	6713	11080	1760	29
H(2X)	6558	10280	6512	28
H(3X)	5833	10684	7586	49
H(5X)	5705	11151	499	43
H(6X)	6428	10684	-892	26
H(8)	7338	10860	5279	41
H(9)	7977	11435	5582	44
H(10)	8610	11428	2604	47
H(11)	8581	10874	-714	47
H(12)	7922	10334	-1199	45
H(13)	7540(20)	9190(20)	1580(50)	23
H(16A)	9042	9799	6268	56
H(16B)	8807	10281	5013	56
H(18)	7972	8856	7516	32
H(19)	7793	8132	9628	34
H(20)	7147	7618	8279	36
H(21)	6692	7866	4732	42
H(22)	6842	8597	2677	37

Table S17. Torsion angles [°] for $C_{22}H_{19}BrNOP$

O(1)-P(1)-N(1)-C(13)	46.0(4)
C(1)-P(1)-N(1)-C(13)	170.0(4)
C(7)-P(1)-N(1)-C(13)	-76.3(5)
O(1)-P(1)-C(1)-C(2X)	152.1(8)
N(1)-P(1)-C(1)-C(2X)	30.0(8)
C(7)-P(1)-C(1)-C(2X)	-87.4(8)
O(1)-P(1)-C(1)-C(6)	-92.2(7)
N(1)-P(1)-C(1)-C(6)	145.7(7)
C(7)-P(1)-C(1)-C(6)	28.3(7)
O(1)-P(1)-C(1)-C(6X)	-37.9(7)
N(1)-P(1)-C(1)-C(6X)	-160.0(6)
C(7)-P(1)-C(1)-C(6X)	82.6(7)
O(1)-P(1)-C(1)-C(2)	95.8(7)
N(1)-P(1)-C(1)-C(2)	-26.3(7)
C(7)-P(1)-C(1)-C(2)	-143.7(7)
C(2X)-C(1)-C(2)-C(3)	69.9(12)
C(6)-C(1)-C(2)-C(3)	9.1(14)
C(6X)-C(1)-C(2)-C(3)	-43.8(13)
P(1)-C(1)-C(2)-C(3)	-178.5(8)
C(5)-C(4)-C(3)-C(2)	-13.0(18)
C(3X)-C(4)-C(3)-C(2)	-75.3(13)
C(5X)-C(4)-C(3)-C(2)	35.6(15)
C(1)-C(2)-C(3)-C(4)	1.7(17)
C(3X)-C(4)-C(5)-C(6)	53.8(14)
C(3)-C(4)-C(5)-C(6)	12.7(18)
C(5X)-C(4)-C(5)-C(6)	-74.0(13)
C(2X)-C(1)-C(6)-C(5)	-50.1(13)
C(6X)-C(1)-C(6)-C(5)	84.3(13)
C(2)-C(1)-C(6)-C(5)	-9.9(15)
P(1)-C(1)-C(6)-C(5)	178.0(9)
C(4)-C(5)-C(6)-C(1)	-1.0(18)
C(6)-C(1)-C(2X)-C(3X)	49.4(15)
C(6X)-C(1)-C(2X)-C(3X)	10.9(19)
C(2)-C(1)-C(2X)-C(3X)	-80.2(15)

P(1)-C(1)-C(2X)-C(3X)	-179.8(12)
C(5)-C(4)-C(3X)-C(2X)	-54.6(17)
C(3)-C(4)-C(3X)-C(2X)	76.5(16)
C(5X)-C(4)-C(3X)-C(2X)	-15(2)
C(1)-C(2X)-C(3X)-C(4)	1(2)
C(5)-C(4)-C(5X)-C(6X)	82.0(15)
C(3X)-C(4)-C(5X)-C(6X)	18.3(19)
C(3)-C(4)-C(5X)-C(6X)	-33.6(16)
C(2X)-C(1)-C(6X)-C(5X)	-7.6(15)
C(6)-C(1)-C(6X)-C(5X)	-64.3(11)
C(2)-C(1)-C(6X)-C(5X)	44.9(13)
P(1)-C(1)-C(6X)-C(5X)	-178.0(9)
C(4)-C(5X)-C(6X)-C(1)	-6.7(18)
O(1)-P(1)-C(7)-C(8)	165.0(5)
N(1)-P(1)-C(7)-C(8)	-71.3(5)
C(1)-P(1)-C(7)-C(8)	41.2(6)
O(1)-P(1)-C(7)-C(12)	-18.5(6)
N(1)-P(1)-C(7)-C(12)	105.1(5)
C(1)-P(1)-C(7)-C(12)	-142.4(5)
C(12)-C(7)-C(8)-C(9)	1.2(10)
P(1)-C(7)-C(8)-C(9)	177.7(5)
C(7)-C(8)-C(9)-C(10)	-2.5(11)
C(8)-C(9)-C(10)-C(11)	1.5(11)
C(9)-C(10)-C(11)-C(12)	0.8(12)
C(10)-C(11)-C(12)-C(7)	-2.1(12)
C(8)-C(7)-C(12)-C(11)	1.0(10)
P(1)-C(7)-C(12)-C(11)	-175.5(6)
P(1)-N(1)-C(13)-C(14)	77.0(5)
P(1)-N(1)-C(13)-C(17)	-157.7(4)
N(1)-C(13)-C(14)-C(15)	-47(7)
C(17)-C(13)-C(14)-C(15)	-172(7)
C(13)-C(14)-C(15)-C(16)	19(21)
C(14)-C(15)-C(16)-Br(1)	-101(15)
C(15)-C(16)-Br(1)-Br(1)#1	151.8(5)
C(15)-C(16)-Br(1)-Br(1)#2	-107.4(5)
C(14)-C(13)-C(17)-C(18)	15.8(8)

N(1)-C(13)-C(17)-C(18)	-108.6(6)
C(14)-C(13)-C(17)-C(22)	-163.4(5)
N(1)-C(13)-C(17)-C(22)	72.2(7)
C(22)-C(17)-C(18)-C(19)	-0.2(9)
C(13)-C(17)-C(18)-C(19)	-179.3(5)
C(17)-C(18)-C(19)-C(20)	0.8(9)
C(18)-C(19)-C(20)-C(21)	-0.1(9)
C(19)-C(20)-C(21)-C(22)	-1.1(10)
C(20)-C(21)-C(22)-C(17)	1.7(10)
C(18)-C(17)-C(22)-C(21)	-1.0(9)
C(13)-C(17)-C(22)-C(21)	178.2(6)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+2,z #2 -y+2,x,z

Table S18. Hydrogen bonds for $C_{22}H_{19}BrNOP$ [Å and º]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#3	0.91(2)	1.93(2)	2.838(6)	171(6)

Symmetry transformations used to generate equivalent atoms:

#1 y,-x+2,z #2 -y+2,x,z #3 x,y,z+1

X–Ray Crystal Structure of Homoallenylamide 4f

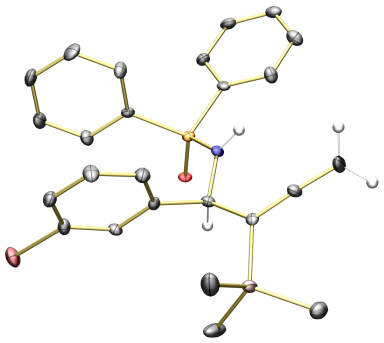


Table S19. Crystal data and structure refinement for (*R*)-*N*-(1-(3-bromophenyl)-2-(trimethylsilyl)buta-2,3-dien-1-yl)-*P*,*P*-diphenylphosphinic amide

Identification code	C25H27BrNOPSi	
Empirical formula	C25H27BrNOPSi	
Formula weight	496.44	
Temperature	100(2) K	
Wavelength	1.54178 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 19.8739(8) Å	a= 90°.
	b = 10.2459(5) Å	b= 96.599(3) °.
	c = 24.6435(9) Å	g = 90°.
Volume	4984.8(4) Å ^{3}	
Z	8	
Density (calculated)	1.323 Mg/m^3	
Absorption coefficient	3.433 mm^{-1}	
F(000)	2048	

Crystal size	0.140 x 0.100 x 0.060 mm^3
Theta range for data collection	1.805 to 68.225°.
Index ranges	-23<=h<=18, -11<=k<=9, -29<=l<=28
Reflections collected	49707
Independent reflections	14390 [R(int) = 0.0895]
Completeness to theta = 67.679°	96.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7532 and 0.6241
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14390 / 314 / 1104
Goodness-of-fit on F^2	1.013
Final R indices [I>2sigma(I)]	R1 = 0.0626, wR2 = 0.1530
R indices (all data)	R1 = 0.0999, wR2 = 0.1717
Absolute structure parameter	0.011(13)
Extinction coefficient	na
Largest diff. peak and hole	1.293 and -0.863 e.$Å^{-3}$

Table S20. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for $C_{25}H_{27}BrNOPSi$. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor

	x	y	z	U(eq)
Br(1)	1609(1)	7553(2)	7202(1)	56(1)
P(1)	224(1)	6992(3)	4987(1)	25(1)
Si(1)	-1764(1)	6958(3)	6428(1)	30(1)
O(1)	181(3)	8430(7)	5037(2)	32(2)
N(1)	-386(3)	6236(8)	5265(3)	25(2)
C(1)	934(5)	6426(12)	6885(3)	36(2)
C(2)	913(5)	5125(13)	7030(4)	43(3)
C(3)	409(6)	4345(12)	6793(4)	41(3)
C(4)	-97(5)	4804(11)	6411(4)	35(2)
C(5)	-82(4)	6110(10)	6250(3)	28(2)
C(6)	427(5)	6923(12)	6503(4)	36(2)
C(7)	-571(4)	6646(9)	5800(3)	25(2)
C(8)	-1314(5)	6316(10)	5852(4)	28(2)
C(9)	-1685(5)	5673(11)	5476(4)	31(2)
C(10)	-2114(6)	5041(15)	5114(5)	50(4)
C(11)	117(5)	6384(10)	4297(3)	29(2)
C(12)	-531(5)	6050(11)	4043(4)	34(2)
C(13)	-612(5)	5636(11)	3509(4)	37(3)
C(14)	-58(5)	5550(13)	3213(4)	45(3)
C(15)	577(6)	5877(14)	3462(4)	52(3)
C(16)	654(5)	6297(12)	4007(4)	46(3)
C(17)	1042(4)	6428(10)	5288(3)	27(2)
C(18)	1201(5)	5106(11)	5315(4)	37(2)
C(19)	1826(6)	4708(13)	5575(5)	51(3)
C(20)	2293(6)	5623(14)	5803(4)	50(3)
C(21)	2129(5)	6938(13)	5783(4)	46(3)
C(22)	1507(4)	7331(11)	5529(3)	32(2)
C(23)	-1184(5)	7465(14)	7024(4)	60(4)
C(24)	-2252(6)	8383(13)	6136(4)	56(3)
C(25)	-2362(6)	5708(13)	6641(4)	55(3)
Br(2)	8730(1)	3219(2)	7582(1)	44(1)

Br(2X)	8377(6)	2806(19)	7845(6)	92(5)
P(2)	9730(1)	2246(3)	10001(1)	23(1)
Si(2)	11750(1)	1944(4)	8580(1)	37(1)
O(2)	9721(3)	3676(7)	9901(2)	28(2)
N(2)	10381(3)	1531(8)	9766(3)	21(2)
C(26)	9230(5)	1967(11)	8035(3)	31(2)
C(27)	9729(4)	2397(11)	8443(3)	33(2)
C(28)	10083(4)	1480(10)	8769(3)	23(2)
C(29)	9957(5)	156(11)	8681(4)	37(2)
C(30)	9473(5)	-243(11)	8272(4)	35(2)
C(31)	9092(5)	655(11)	7950(4)	32(2)
C(32)	10597(4)	1937(10)	9244(3)	27(2)
C(33)	11311(4)	1442(10)	9185(4)	25(2)
C(34)	11647(4)	724(11)	9561(4)	31(2)
C(35)	12005(5)	13(12)	9931(5)	45(3)
C(36)	9816(4)	1770(10)	10709(3)	26(2)
C(37)	10442(5)	1361(11)	10971(3)	32(2)
C(38)	10505(6)	1065(11)	11526(4)	37(3)
C(39)	9952(5)	1197(11)	11815(4)	39(3)
C(40)	9346(6)	1611(12)	11557(4)	47(3)
C(41)	9277(5)	1898(12)	11003(4)	41(3)
C(42)	8956(4)	1514(10)	9692(3)	25(2)
C(43)	8824(5)	194(10)	9764(4)	33(2)
C(44)	8252(5)	-379(11)	9500(4)	41(3)
C(45)	7792(5)	367(13)	9160(4)	46(3)
C(46)	7915(5)	1689(13)	9080(4)	44(3)
C(47)	8492(4)	2255(11)	9339(3)	31(2)
C(48)	11393(6)	1100(18)	7947(4)	80(5)
C(49)	11636(6)	3704(14)	8483(6)	70(4)
C(50)	12665(5)	1561(14)	8722(4)	51(3)
Br(3)	3291(1)	2829(1)	309(1)	47(1)
P(3)	4577(1)	2149(3)	2531(1)	26(1)
Si(3)	6606(1)	1941(3)	1108(1)	36(1)
O(3)	4560(3)	3578(7)	2435(3)	33(2)
N(3)	5220(4)	1446(8)	2290(3)	27(2)
C(51)	3957(5)	1709(11)	642(3)	31(2)

C(52)	3951(5)	420(11)	501(4)	33(2)
C(53)	4451(5)	-408(11)	746(4)	35(2)
C(54)	4942(5)	59(11)	1138(4)	34(2)
C(55)	4944(4)	1367(10)	1296(3)	23(2)
C(56)	4458(4)	2206(11)	1038(3)	32(2)
C(57)	5431(4)	1856(10)	1764(3)	25(2)
C(58)	6157(5)	1491(10)	1717(4)	27(2)
C(59)	6527(5)	818(12)	2092(4)	40(3)
C(60)	6945(5)	135(15)	2440(5)	68(5)
C(61)	4677(5)	1708(10)	3250(3)	28(2)
C(62)	5280(5)	1149(11)	3504(4)	37(2)
C(63)	5353(6)	935(11)	4060(4)	38(2)
C(64)	4835(6)	1242(11)	4364(4)	43(3)
C(65)	4235(6)	1797(12)	4114(4)	45(3)
C(66)	4159(5)	2007(11)	3556(4)	39(2)
C(67)	3796(5)	1410(10)	2244(3)	28(2)
C(68)	3688(5)	60(10)	2271(4)	33(2)
C(69)	3093(5)	-486(12)	2031(4)	42(3)
C(70)	2598(5)	289(13)	1762(4)	44(3)
C(71)	2692(5)	1629(13)	1727(4)	46(3)
C(72)	3289(5)	2184(11)	1969(4)	34(2)
C(73)	6122(5)	3209(15)	705(5)	61(4)
C(74)	6688(7)	499(17)	676(5)	83(5)
C(75)	7445(5)	2538(15)	1363(4)	64(4)
Br(4)	6619(1)	7922(1)	4572(1)	52(1)
P(4)	5181(1)	7125(2)	2385(1)	24(1)
Si(4)	3362(1)	6947(3)	3973(1)	35(1)
O(4)	5214(3)	8556(6)	2478(2)	25(2)
N(4)	4557(3)	6434(8)	2662(3)	24(2)
C(76)	5943(5)	6767(11)	4267(4)	35(2)
C(77)	5997(5)	5458(11)	4392(4)	37(2)
C(78)	5501(6)	4623(11)	4145(5)	42(3)
C(79)	4994(5)	5064(11)	3779(4)	40(2)
C(80)	4942(4)	6393(10)	3648(3)	25(2)
C(81)	5414(4)	7262(10)	3898(3)	28(2)
C(82)	4401(4)	6871(10)	3201(3)	27(2)

C(83)	3682(4)	6513(9)	3305(4)	25(2)
C(84)	3265(5)	5952(11)	2930(4)	31(2)
C(85)	2819(5)	5425(14)	2560(4)	50(3)
C(86)	5018(5)	6648(9)	1676(4)	28(2)
C(87)	4395(5)	6185(11)	1440(4)	37(3)
C(88)	4306(6)	5887(12)	894(4)	44(3)
C(89)	4819(6)	6041(11)	558(4)	40(3)
C(90)	5428(5)	6495(12)	802(4)	43(3)
C(91)	5537(5)	6797(11)	1352(4)	38(3)
C(92)	5974(4)	6378(10)	2643(3)	26(2)
C(93)	6082(5)	5051(11)	2579(4)	39(2)
C(94)	6684(6)	4483(12)	2792(5)	50(3)
C(95)	7193(5)	5229(13)	3082(4)	45(3)
C(96)	7078(5)	6549(13)	3160(4)	46(3)
C(97)	6477(5)	7125(12)	2950(4)	38(2)
C(98)	3750(6)	8492(15)	4217(6)	79(5)
C(99)	3613(6)	5693(15)	4498(4)	63(4)
C(100)	2439(5)	7068(12)	3871(5)	50(3)

Table S21. Bond lengths [Å] and angles [°] for $C_{25}H_{27}BrNOPSi$

Br(1)-C(1)	1.871(11)
P(1)-O(1)	1.482(7)
P(1)-N(1)	1.653(7)
P(1)-C(11)	1.800(9)
P(1)-C(17)	1.803(10)
Si(1)-C(23)	1.836(11)
Si(1)-C(24)	1.851(12)
Si(1)-C(25)	1.864(12)
Si(1)-C(8)	1.882(9)
N(1)-C(7)	1.470(10)
N(1)-H(1N)	0.8800
C(1)-C(2)	1.383(16)
C(1)-C(6)	1.393(13)
C(2)-C(3)	1.360(16)
C(2)-H(2)	0.9500
C(3)-C(4)	1.379(14)
C(3)-H(3)	0.9500
C(4)-C(5)	1.396(15)
C(4)-H(4)	0.9500
C(5)-C(6)	1.401(14)
C(5)-C(7)	1.494(12)
C(6)-H(6)	0.9500
C(7)-C(8)	1.534(12)
C(7)-H(7)	1.0000
C(8)-C(9)	1.296(13)
C(9)-C(10)	1.330(15)
C(10)-H(10A)	0.93(11)
C(10)-H(10B)	0.83(12)
C(11)-C(16)	1.354(13)
C(11)-C(12)	1.408(13)
C(12)-C(13)	1.375(13)
C(12)-H(12)	0.9500
C(13)-C(14)	1.392(14)
C(13)-H(13)	0.9500

C(14)-C(15)	1.380(15)
C(14)-H(14)	0.9500
C(15)-C(16)	1.402(14)
C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
C(17)-C(18)	1.391(14)
C(17)-C(22)	1.392(13)
C(18)-C(19)	1.391(15)
C(18)-H(18)	0.9500
C(19)-C(20)	1.392(17)
C(19)-H(19)	0.9500
C(20)-C(21)	1.386(18)
C(20)-H(20)	0.9500
C(21)-C(22)	1.379(14)
C(21)-H(21)	0.9500
C(22)-H(22)	0.9500
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(25)-H(25A)	0.9800
C(25)-H(25B)	0.9800
C(25)-H(25C)	0.9800
Br(2)-Br(2X)	1.095(17)
Br(2)-C(26)	1.903(10)
Br(2X)-C(26)	1.911(15)
P(2)-O(2)	1.486(7)
P(2)-N(2)	1.649(7)
P(2)-C(42)	1.799(9)
P(2)-C(36)	1.801(9)
Si(2)-C(49)	1.829(14)
Si(2)-C(48)	1.853(12)
Si(2)-C(50)	1.853(10)
Si(2)-C(33)	1.883(9)

N(2)-C(32)	1.464(10)
N(2)-H(2N)	0.8800
C(26)-C(31)	1.383(14)
C(26)-C(27)	1.400(12)
C(27)-C(28)	1.376(13)
C(27)-H(27)	0.9500
C(28)-C(29)	1.392(14)
C(28)-C(32)	1.536(12)
C(29)-C(30)	1.372(14)
C(29)-H(29)	0.9500
C(30)-C(31)	1.383(14)
C(30)-H(30)	0.9500
C(31)-H(31)	0.9500
C(32)-C(33)	1.529(12)
C(32)-H(32)	1.0000
C(33)-C(34)	1.304(13)
C(34)-C(35)	1.312(14)
C(35)-H(35A)	0.9500
C(35)-H(35B)	0.9500
C(36)-C(41)	1.367(12)
C(36)-C(37)	1.399(13)
C(37)-C(38)	1.391(12)
C(37)-H(37)	0.9500
C(38)-C(39)	1.384(14)
C(38)-H(38)	0.9500
C(39)-C(40)	1.364(15)
C(39)-H(39)	0.9500
C(40)-C(41)	1.387(13)
C(40)-H(40)	0.9500
C(41)-H(41)	0.9500
C(42)-C(43)	1.393(14)
C(42)-C(47)	1.415(12)
C(43)-C(44)	1.375(14)
C(43)-H(43)	0.9500
C(44)-C(45)	1.394(15)
C(44)-H(44)	0.9500

C(45)-C(46)	1.394(17)
C(45)-H(45)	0.9500
C(46)-C(47)	1.374(14)
C(46)-H(46)	0.9500
C(47)-H(47)	0.9500
C(48)-H(48A)	0.9800
C(48)-H(48B)	0.9800
C(48)-H(48C)	0.9800
C(49)-H(49A)	0.9800
C(49)-H(49B)	0.9800
C(49)-H(49C)	0.9800
C(50)-H(50A)	0.9800
C(50)-H(50B)	0.9800
C(50)-H(50C)	0.9800
Br(3)-C(51)	1.869(10)
P(3)-O(3)	1.483(7)
P(3)-N(3)	1.638(8)
P(3)-C(67)	1.797(10)
P(3)-C(61)	1.818(9)
Si(3)-C(75)	1.820(11)
Si(3)-C(73)	1.837(12)
Si(3)-C(74)	1.840(14)
Si(3)-C(58)	1.890(9)
N(3)-C(57)	1.467(10)
N(3)-H(3N)	0.8800
C(51)-C(52)	1.365(14)
C(51)-C(56)	1.409(13)
C(52)-C(53)	1.390(14)
C(52)-H(52)	0.9500
C(53)-C(54)	1.377(13)
C(53)-H(53)	0.9500
C(54)-C(55)	1.396(14)
C(54)-H(54)	0.9500
C(55)-C(56)	1.391(13)
C(55)-C(57)	1.504(12)
C(56)-H(56)	0.9500

C(57)-C(58)	1.508(12)
C(57)-H(57)	1.0000
C(58)-C(59)	1.308(13)
C(59)-C(60)	1.324(14)
C(60)-H(60A)	0.9500
C(60)-H(60B)	0.9500
C(61)-C(66)	1.378(13)
C(61)-C(62)	1.409(14)
C(62)-C(63)	1.379(13)
C(62)-H(62)	0.9500
C(63)-C(64)	1.378(15)
C(63)-H(63)	0.9500
C(64)-C(65)	1.399(15)
C(64)-H(64)	0.9500
C(65)-C(66)	1.383(13)
C(65)-H(65)	0.9500
C(66)-H(66)	0.9500
C(67)-C(72)	1.395(13)
C(67)-C(68)	1.402(14)
C(68)-C(69)	1.378(14)
C(68)-H(68)	0.9500
C(69)-C(70)	1.375(16)
C(69)-H(69)	0.9500
C(70)-C(71)	1.389(16)
C(70)-H(70)	0.9500
C(71)-C(72)	1.387(14)
C(71)-H(71)	0.9500
C(72)-H(72)	0.9500
C(73)-H(73A)	0.9800
C(73)-H(73B)	0.9800
C(73)-H(73C)	0.9800
C(74)-H(74A)	0.9800
C(74)-H(74B)	0.9800
C(74)-H(74C)	0.9800
C(75)-H(75A)	0.9800
C(75)-H(75B)	0.9800

C(75)-H(75C)	0.9800
Br(4)-C(76)	1.879(10)
P(4)-O(4)	1.484(7)
P(4)-N(4)	1.642(7)
P(4)-C(92)	1.801(10)
P(4)-C(86)	1.808(9)
Si(4)-C(100)	1.826(10)
Si(4)-C(98)	1.833(13)
Si(4)-C(99)	1.851(13)
Si(4)-C(83)	1.886(9)
N(4)-C(82)	1.468(10)
N(4)-H(4N)	0.8800
C(76)-C(77)	1.377(15)
C(76)-C(81)	1.405(13)
C(77)-C(78)	1.391(15)
C(77)-H(77)	0.9500
C(78)-C(79)	1.351(15)
C(78)-H(78)	0.9500
C(79)-C(80)	1.401(14)
C(79)-H(79)	0.9500
C(80)-C(81)	1.386(12)
C(80)-C(82)	1.528(12)
C(81)-H(81)	0.9500
C(82)-C(83)	1.524(12)
C(82)-H(82)	1.0000
C(83)-C(84)	1.302(12)
C(84)-C(85)	1.312(13)
C(85)-H(85A)	0.9500
C(85)-H(85B)	0.9500
C(86)-C(91)	1.383(13)
C(86)-C(87)	1.389(13)
C(87)-C(88)	1.370(14)
C(87)-H(87)	0.9500
C(88)-C(89)	1.396(15)
C(88)-H(88)	0.9500
C(89)-C(90)	1.369(15)

C(89)-H(89)	0.9500
C(90)-C(91)	1.383(13)
C(90)-H(90)	0.9500
C(91)-H(91)	0.9500
C(92)-C(93)	1.389(14)
C(92)-C(97)	1.408(13)
C(93)-C(94)	1.378(14)
C(93)-H(93)	0.9500
C(94)-C(95)	1.396(16)
C(94)-H(94)	0.9500
C(95)-C(96)	1.389(16)
C(95)-H(95)	0.9500
C(96)-C(97)	1.378(14)
C(96)-H(96)	0.9500
C(97)-H(97)	0.9500
C(98)-H(98A)	0.9800
C(98)-H(98B)	0.9800
C(98)-H(98C)	0.9800
C(99)-H(99A)	0.9800
C(99)-H(99B)	0.9800
C(99)-H(99C)	0.9800
C(100)-H(10C)	0.9800
C(100)-H(10D)	0.9800
C(100)-H(10E)	0.9800

O(1)-P(1)-N(1)	112.3(4)
O(1)-P(1)-C(11)	114.9(4)
N(1)-P(1)-C(11)	102.5(4)
O(1)-P(1)-C(17)	110.0(4)
N(1)-P(1)-C(17)	110.4(4)
C(11)-P(1)-C(17)	106.3(4)
C(23)-Si(1)-C(24)	109.9(6)
C(23)-Si(1)-C(25)	109.3(6)
C(24)-Si(1)-C(25)	109.2(6)
C(23)-Si(1)-C(8)	113.2(5)
C(24)-Si(1)-C(8)	104.8(5)

C(25)-Si(1)-C(8)	110.3(5)
C(7)-N(1)-P(1)	120.6(6)
C(7)-N(1)-H(1N)	119.7
P(1)-N(1)-H(1N)	119.7
C(2)-C(1)-C(6)	119.2(10)
C(2)-C(1)-Br(1)	121.9(8)
C(6)-C(1)-Br(1)	119.0(9)
C(3)-C(2)-C(1)	119.8(10)
C(3)-C(2)-H(2)	120.1
C(1)-C(2)-H(2)	120.1
C(2)-C(3)-C(4)	122.4(11)
C(2)-C(3)-H(3)	118.8
C(4)-C(3)-H(3)	118.8
C(3)-C(4)-C(5)	118.9(10)
C(3)-C(4)-H(4)	120.6
C(5)-C(4)-H(4)	120.6
C(4)-C(5)-C(6)	118.8(9)
C(4)-C(5)-C(7)	122.0(9)
C(6)-C(5)-C(7)	119.1(10)
C(1)-C(6)-C(5)	120.8(11)
C(1)-C(6)-H(6)	119.6
C(5)-C(6)-H(6)	119.6
N(1)-C(7)-C(5)	110.6(7)
N(1)-C(7)-C(8)	110.8(7)
C(5)-C(7)-C(8)	114.1(7)
N(1)-C(7)-H(7)	107.0
C(5)-C(7)-H(7)	107.0
C(8)-C(7)-H(7)	107.0
C(9)-C(8)-C(7)	121.8(8)
C(9)-C(8)-Si(1)	115.8(7)
C(7)-C(8)-Si(1)	122.1(7)
C(8)-C(9)-C(10)	174.9(10)
C(9)-C(10)-H(10A)	116(8)
C(9)-C(10)-H(10B)	103(9)
H(10A)-C(10)-H(10B)	89(10)
C(16)-C(11)-C(12)	119.1(9)

C(16)-C(11)-P(1)	120.4(8)
C(12)-C(11)-P(1)	120.4(7)
C(13)-C(12)-C(11)	120.0(9)
C(13)-C(12)-H(12)	120.0
C(11)-C(12)-H(12)	120.0
C(12)-C(13)-C(14)	120.7(10)
C(12)-C(13)-H(13)	119.7
C(14)-C(13)-H(13)	119.7
C(15)-C(14)-C(13)	119.3(10)
C(15)-C(14)-H(14)	120.4
C(13)-C(14)-H(14)	120.4
C(14)-C(15)-C(16)	119.6(10)
C(14)-C(15)-H(15)	120.2
C(16)-C(15)-H(15)	120.2
C(11)-C(16)-C(15)	121.3(10)
C(11)-C(16)-H(16)	119.3
C(15)-C(16)-H(16)	119.3
C(18)-C(17)-C(22)	119.4(9)
C(18)-C(17)-P(1)	121.4(8)
C(22)-C(17)-P(1)	119.1(8)
C(17)-C(18)-C(19)	119.6(11)
C(17)-C(18)-H(18)	120.2
C(19)-C(18)-H(18)	120.2
C(18)-C(19)-C(20)	120.5(12)
C(18)-C(19)-H(19)	119.8
C(20)-C(19)-H(19)	119.8
C(21)-C(20)-C(19)	119.8(11)
C(21)-C(20)-H(20)	120.1
C(19)-C(20)-H(20)	120.1
C(22)-C(21)-C(20)	119.7(11)
C(22)-C(21)-H(21)	120.2
C(20)-C(21)-H(21)	120.2
C(21)-C(22)-C(17)	121.1(11)
C(21)-C(22)-H(22)	119.5
C(17)-C(22)-H(22)	119.5
Si(1)-C(23)-H(23A)	109.5

Si(1)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
Si(1)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
Si(1)-C(24)-H(24A)	109.5
Si(1)-C(24)-H(24B)	109.5
H(24A)-C(24)-H(24B)	109.5
Si(1)-C(24)-H(24C)	109.5
H(24A)-C(24)-H(24C)	109.5
H(24B)-C(24)-H(24C)	109.5
Si(1)-C(25)-H(25A)	109.5
Si(1)-C(25)-H(25B)	109.5
H(25A)-C(25)-H(25B)	109.5
Si(1)-C(25)-H(25C)	109.5
H(25A)-C(25)-H(25C)	109.5
H(25B)-C(25)-H(25C)	109.5
Br(2X)-Br(2)-C(26)	73.7(8)
Br(2)-Br(2X)-C(26)	72.9(7)
O(2)-P(2)-N(2)	112.0(4)
O(2)-P(2)-C(42)	110.4(4)
N(2)-P(2)-C(42)	109.5(4)
O(2)-P(2)-C(36)	115.1(4)
N(2)-P(2)-C(36)	103.2(4)
C(42)-P(2)-C(36)	106.2(4)
C(49)-Si(2)-C(48)	108.7(7)
C(49)-Si(2)-C(50)	109.7(6)
C(48)-Si(2)-C(50)	109.4(6)
C(49)-Si(2)-C(33)	108.2(5)
C(48)-Si(2)-C(33)	111.8(6)
C(50)-Si(2)-C(33)	109.1(4)
C(32)-N(2)-P(2)	120.3(6)
C(32)-N(2)-H(2N)	119.9
P(2)-N(2)-H(2N)	119.9
C(31)-C(26)-C(27)	121.7(10)
C(31)-C(26)-Br(2)	119.1(7)

C(27)-C(26)-Br(2)	119.2(8)
C(31)-C(26)-Br(2X)	104.2(9)
C(27)-C(26)-Br(2X)	124.7(9)
Br(2)-C(26)-Br(2X)	33.4(6)
C(28)-C(27)-C(26)	118.5(10)
C(28)-C(27)-H(27)	120.7
C(26)-C(27)-H(27)	120.7
C(27)-C(28)-C(29)	120.2(9)
C(27)-C(28)-C(32)	119.2(9)
C(29)-C(28)-C(32)	120.6(9)
C(30)-C(29)-C(28)	120.2(10)
C(30)-C(29)-H(29)	119.9
C(28)-C(29)-H(29)	119.9
C(29)-C(30)-C(31)	121.0(10)
C(29)-C(30)-H(30)	119.5
C(31)-C(30)-H(30)	119.5
C(26)-C(31)-C(30)	118.3(9)
C(26)-C(31)-H(31)	120.8
C(30)-C(31)-H(31)	120.8
N(2)-C(32)-C(33)	111.0(7)
N(2)-C(32)-C(28)	110.2(7)
C(33)-C(32)-C(28)	111.7(7)
N(2)-C(32)-H(32)	107.9
C(33)-C(32)-H(32)	107.9
C(28)-C(32)-H(32)	107.9
C(34)-C(33)-C(32)	121.7(8)
C(34)-C(33)-Si(2)	118.1(7)
C(32)-C(33)-Si(2)	120.2(7)
C(33)-C(34)-C(35)	177.9(10)
C(34)-C(35)-H(35A)	120.0
C(34)-C(35)-H(35B)	120.0
H(35A)-C(35)-H(35B)	120.0
C(41)-C(36)-C(37)	119.5(8)
C(41)-C(36)-P(2)	119.6(7)
C(37)-C(36)-P(2)	120.7(6)
C(38)-C(37)-C(36)	119.6(9)

C(38)-C(37)-H(37)	120.2
C(36)-C(37)-H(37)	120.2
C(39)-C(38)-C(37)	119.9(10)
C(39)-C(38)-H(38)	120.1
C(37)-C(38)-H(38)	120.1
C(40)-C(39)-C(38)	120.1(9)
C(40)-C(39)-H(39)	120.0
C(38)-C(39)-H(39)	120.0
C(39)-C(40)-C(41)	120.4(9)
C(39)-C(40)-H(40)	119.8
C(41)-C(40)-H(40)	119.8
C(36)-C(41)-C(40)	120.5(10)
C(36)-C(41)-H(41)	119.8
C(40)-C(41)-H(41)	119.8
C(43)-C(42)-C(47)	118.7(9)
C(43)-C(42)-P(2)	121.0(7)
C(47)-C(42)-P(2)	120.1(8)
C(44)-C(43)-C(42)	120.8(10)
C(44)-C(43)-H(43)	119.6
C(42)-C(43)-H(43)	119.6
C(43)-C(44)-C(45)	119.9(11)
C(43)-C(44)-H(44)	120.0
C(45)-C(44)-H(44)	120.0
C(44)-C(45)-C(46)	120.3(10)
C(44)-C(45)-H(45)	119.9
C(46)-C(45)-H(45)	119.9
C(47)-C(46)-C(45)	119.6(10)
C(47)-C(46)-H(46)	120.2
C(45)-C(46)-H(46)	120.2
C(46)-C(47)-C(42)	120.6(10)
C(46)-C(47)-H(47)	119.7
C(42)-C(47)-H(47)	119.7
Si(2)-C(48)-H(48A)	109.5
Si(2)-C(48)-H(48B)	109.5
H(48A)-C(48)-H(48B)	109.5
Si(2)-C(48)-H(48C)	109.5

H(48A)-C(48)-H(48C)	109.5
H(48B)-C(48)-H(48C)	109.5
Si(2)-C(49)-H(49A)	109.5
Si(2)-C(49)-H(49B)	109.5
H(49A)-C(49)-H(49B)	109.5
Si(2)-C(49)-H(49C)	109.5
H(49A)-C(49)-H(49C)	109.5
H(49B)-C(49)-H(49C)	109.5
Si(2)-C(50)-H(50A)	109.5
Si(2)-C(50)-H(50B)	109.5
H(50A)-C(50)-H(50B)	109.5
Si(2)-C(50)-H(50C)	109.5
H(50A)-C(50)-H(50C)	109.5
H(50B)-C(50)-H(50C)	109.5
O(3)-P(3)-N(3)	112.3(4)
O(3)-P(3)-C(67)	110.5(5)
N(3)-P(3)-C(67)	110.3(4)
O(3)-P(3)-C(61)	113.5(4)
N(3)-P(3)-C(61)	104.0(4)
C(67)-P(3)-C(61)	105.8(4)
C(75)-Si(3)-C(73)	110.5(6)
C(75)-Si(3)-C(74)	109.3(6)
C(73)-Si(3)-C(74)	109.3(7)
C(75)-Si(3)-C(58)	107.8(4)
C(73)-Si(3)-C(58)	109.7(5)
C(74)-Si(3)-C(58)	110.2(6)
C(57)-N(3)-P(3)	120.6(6)
C(57)-N(3)-H(3N)	119.7
P(3)-N(3)-H(3N)	119.7
C(52)-C(51)-C(56)	120.7(10)
C(52)-C(51)-Br(3)	119.9(7)
C(56)-C(51)-Br(3)	119.4(8)
C(51)-C(52)-C(53)	119.7(9)
C(51)-C(52)-H(52)	120.2
C(53)-C(52)-H(52)	120.2
C(54)-C(53)-C(52)	120.5(10)

C(54)-C(53)-H(53)	119.8
C(52)-C(53)-H(53)	119.8
C(53)-C(54)-C(55)	120.5(10)
C(53)-C(54)-H(54)	119.7
C(55)-C(54)-H(54)	119.7
C(56)-C(55)-C(54)	119.1(8)
C(56)-C(55)-C(57)	119.7(9)
C(54)-C(55)-C(57)	121.0(8)
C(55)-C(56)-C(51)	119.4(10)
C(55)-C(56)-H(56)	120.3
C(51)-C(56)-H(56)	120.3
N(3)-C(57)-C(55)	111.0(7)
N(3)-C(57)-C(58)	111.7(7)
C(55)-C(57)-C(58)	113.3(7)
N(3)-C(57)-H(57)	106.8
C(55)-C(57)-H(57)	106.8
C(58)-C(57)-H(57)	106.8
C(59)-C(58)-C(57)	122.8(8)
C(59)-C(58)-Si(3)	114.3(7)
C(57)-C(58)-Si(3)	122.9(6)
C(58)-C(59)-C(60)	174.8(11)
C(59)-C(60)-H(60A)	120.0
C(59)-C(60)-H(60B)	120.0
H(60A)-C(60)-H(60B)	120.0
C(66)-C(61)-C(62)	119.9(8)
C(66)-C(61)-P(3)	118.3(8)
C(62)-C(61)-P(3)	121.8(7)
C(63)-C(62)-C(61)	119.6(10)
C(63)-C(62)-H(62)	120.2
C(61)-C(62)-H(62)	120.2
C(64)-C(63)-C(62)	120.2(11)
C(64)-C(63)-H(63)	119.9
C(62)-C(63)-H(63)	119.9
C(63)-C(64)-C(65)	120.4(10)
C(63)-C(64)-H(64)	119.8
C(65)-C(64)-H(64)	119.8

C(66)-C(65)-C(64)	119.4(10)
C(66)-C(65)-H(65)	120.3
C(64)-C(65)-H(65)	120.3
C(61)-C(66)-C(65)	120.4(10)
C(61)-C(66)-H(66)	119.8
C(65)-C(66)-H(66)	119.8
C(72)-C(67)-C(68)	118.5(9)
C(72)-C(67)-P(3)	119.6(8)
C(68)-C(67)-P(3)	121.8(8)
C(69)-C(68)-C(67)	120.6(10)
C(69)-C(68)-H(68)	119.7
C(67)-C(68)-H(68)	119.7
C(70)-C(69)-C(68)	120.2(11)
C(70)-C(69)-H(69)	119.9
C(68)-C(69)-H(69)	119.9
C(69)-C(70)-C(71)	120.4(11)
C(69)-C(70)-H(70)	119.8
C(71)-C(70)-H(70)	119.8
C(72)-C(71)-C(70)	119.5(10)
C(72)-C(71)-H(71)	120.2
C(70)-C(71)-H(71)	120.2
C(71)-C(72)-C(67)	120.7(10)
C(71)-C(72)-H(72)	119.7
C(67)-C(72)-H(72)	119.7
Si(3)-C(73)-H(73A)	109.5
Si(3)-C(73)-H(73B)	109.5
H(73A)-C(73)-H(73B)	109.5
Si(3)-C(73)-H(73C)	109.5
H(73A)-C(73)-H(73C)	109.5
H(73B)-C(73)-H(73C)	109.5
Si(3)-C(74)-H(74A)	109.5
Si(3)-C(74)-H(74B)	109.5
H(74A)-C(74)-H(74B)	109.5
Si(3)-C(74)-H(74C)	109.5
H(74A)-C(74)-H(74C)	109.5
H(74B)-C(74)-H(74C)	109.5

Si(3)-C(75)-H(75A)	109.5
Si(3)-C(75)-H(75B)	109.5
H(75A)-C(75)-H(75B)	109.5
Si(3)-C(75)-H(75C)	109.5
H(75A)-C(75)-H(75C)	109.5
H(75B)-C(75)-H(75C)	109.5
O(4)-P(4)-N(4)	112.6(4)
O(4)-P(4)-C(92)	110.1(4)
N(4)-P(4)-C(92)	109.9(4)
O(4)-P(4)-C(86)	114.6(4)
N(4)-P(4)-C(86)	103.0(4)
C(92)-P(4)-C(86)	106.2(4)
C(100)-Si(4)-C(98)	111.4(6)
C(100)-Si(4)-C(99)	109.2(5)
C(98)-Si(4)-C(99)	107.5(7)
C(100)-Si(4)-C(83)	109.3(5)
C(98)-Si(4)-C(83)	108.5(5)
C(99)-Si(4)-C(83)	110.9(5)
C(82)-N(4)-P(4)	119.6(6)
C(82)-N(4)-H(4N)	120.2
P(4)-N(4)-H(4N)	120.2
C(77)-C(76)-C(81)	121.9(10)
C(77)-C(76)-Br(4)	119.4(7)
C(81)-C(76)-Br(4)	118.6(8)
C(76)-C(77)-C(78)	118.0(10)
C(76)-C(77)-H(77)	121.0
C(78)-C(77)-H(77)	121.0
C(79)-C(78)-C(77)	121.5(11)
C(79)-C(78)-H(78)	119.2
C(77)-C(78)-H(78)	119.2
C(78)-C(79)-C(80)	120.7(10)
C(78)-C(79)-H(79)	119.7
C(80)-C(79)-H(79)	119.7
C(81)-C(80)-C(79)	119.5(9)
C(81)-C(80)-C(82)	120.0(9)
C(79)-C(80)-C(82)	120.4(9)

C(80)-C(81)-C(76)	118.4(10)
C(80)-C(81)-H(81)	120.8
C(76)-C(81)-H(81)	120.8
N(4)-C(82)-C(83)	112.3(7)
N(4)-C(82)-C(80)	110.5(7)
C(83)-C(82)-C(80)	113.4(7)
N(4)-C(82)-H(82)	106.8
C(83)-C(82)-H(82)	106.8
C(80)-C(82)-H(82)	106.8
C(84)-C(83)-C(82)	121.3(8)
C(84)-C(83)-Si(4)	118.1(7)
C(82)-C(83)-Si(4)	120.5(6)
C(83)-C(84)-C(85)	177.0(11)
C(84)-C(85)-H(85A)	120.0
C(84)-C(85)-H(85B)	120.0
H(85A)-C(85)-H(85B)	120.0
C(91)-C(86)-C(87)	118.9(9)
C(91)-C(86)-P(4)	117.7(7)
C(87)-C(86)-P(4)	123.3(7)
C(88)-C(87)-C(86)	119.7(9)
C(88)-C(87)-H(87)	120.1
C(86)-C(87)-H(87)	120.1
C(87)-C(88)-C(89)	122.4(11)
C(87)-C(88)-H(88)	118.8
C(89)-C(88)-H(88)	118.8
C(90)-C(89)-C(88)	116.7(10)
C(90)-C(89)-H(89)	121.7
C(88)-C(89)-H(89)	121.7
C(89)-C(90)-C(91)	122.4(10)
C(89)-C(90)-H(90)	118.8
C(91)-C(90)-H(90)	118.8
C(86)-C(91)-C(90)	119.9(10)
C(86)-C(91)-H(91)	120.1
C(90)-C(91)-H(91)	120.1
C(93)-C(92)-C(97)	118.9(9)
C(93)-C(92)-P(4)	121.1(8)

C(97)-C(92)-P(4)	119.8(8)
C(94)-C(93)-C(92)	120.6(10)
C(94)-C(93)-H(93)	119.7
C(92)-C(93)-H(93)	119.7
C(93)-C(94)-C(95)	120.6(11)
C(93)-C(94)-H(94)	119.7
C(95)-C(94)-H(94)	119.7
C(96)-C(95)-C(94)	118.9(10)
C(96)-C(95)-H(95)	120.6
C(94)-C(95)-H(95)	120.6
C(97)-C(96)-C(95)	120.9(10)
C(97)-C(96)-H(96)	119.5
C(95)-C(96)-H(96)	119.5
C(96)-C(97)-C(92)	120.0(11)
C(96)-C(97)-H(97)	120.0
C(92)-C(97)-H(97)	120.0
Si(4)-C(98)-H(98A)	109.5
Si(4)-C(98)-H(98B)	109.5
H(98A)-C(98)-H(98B)	109.5
Si(4)-C(98)-H(98C)	109.5
H(98A)-C(98)-H(98C)	109.5
H(98B)-C(98)-H(98C)	109.5
Si(4)-C(99)-H(99A)	109.5
Si(4)-C(99)-H(99B)	109.5
H(99A)-C(99)-H(99B)	109.5
Si(4)-C(99)-H(99C)	109.5
H(99A)-C(99)-H(99C)	109.5
H(99B)-C(99)-H(99C)	109.5
Si(4)-C(100)-H(10C)	109.5
Si(4)-C(100)-H(10D)	109.5
H(10C)-C(100)-H(10D)	109.5
Si(4)-C(100)-H(10E)	109.5
H(10C)-C(100)-H(10E)	109.5
H(10D)-C(100)-H(10E)	109.5

Symmetry transformations used to generate equivalent atoms:

Table S22. Anisotropic displacement parameters ($Å^2x10^3$) for $C_{25}H_{27}BrNOPSi$. The anisotropic displacement factor exponent takes the form: $-2p^2[h^2 a^{*2}U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	41(1)	89(1)	36(1)	4(1)	-6(1)	-18(1)
P(1)	25(1)	23(2)	27(1)	0(1)	4(1)	1(1)
Si(1)	30(1)	33(2)	28(1)	-5(1)	6(1)	3(1)
O(1)	39(4)	23(4)	34(3)	4(3)	8(3)	1(3)
N(1)	22(4)	35(5)	20(3)	-5(3)	6(3)	-1(3)
C(1)	28(5)	62(7)	20(4)	0(5)	6(3)	-1(5)
C(2)	42(6)	60(7)	27(5)	1(5)	-2(4)	13(5)
C(3)	58(7)	34(7)	33(5)	3(5)	9(5)	5(5)
C(4)	46(6)	31(6)	27(5)	0(4)	4(4)	1(5)
C(5)	27(5)	35(6)	23(4)	-6(4)	7(3)	7(4)
C(6)	32(5)	41(6)	35(5)	-2(5)	8(4)	1(4)
C(7)	34(5)	19(6)	24(4)	-2(4)	10(3)	1(4)
C(8)	28(5)	25(6)	32(4)	0(4)	3(3)	3(4)
C(9)	27(5)	39(7)	29(5)	-13(4)	8(4)	3(4)
C(10)	36(7)	77(11)	37(6)	-24(6)	8(5)	-5(6)
C(11)	34(5)	28(6)	26(4)	3(4)	4(3)	3(4)
C(12)	35(5)	35(7)	33(5)	8(4)	6(4)	0(5)
C(13)	32(5)	46(8)	31(5)	3(5)	-2(4)	-1(5)
C(14)	38(6)	65(9)	33(5)	-8(6)	3(4)	6(6)
C(15)	39(6)	82(11)	35(5)	-10(6)	8(5)	-8(6)
C(16)	42(6)	69(9)	28(5)	0(5)	10(4)	-9(6)
C(17)	27(4)	28(5)	28(4)	1(4)	9(3)	-3(4)
C(18)	34(5)	32(6)	46(6)	7(5)	5(4)	-1(4)
C(19)	43(7)	46(7)	62(7)	5(6)	2(5)	13(5)
C(20)	34(6)	67(8)	49(7)	11(6)	-1(5)	7(5)
C(21)	24(5)	64(7)	51(6)	5(6)	4(4)	-8(5)
C(22)	28(5)	32(6)	35(5)	-5(4)	2(4)	-8(4)
C(23)	49(7)	93(12)	39(5)	-20(6)	12(4)	2(6)
C(24)	75(8)	43(7)	51(6)	-6(6)	15(6)	22(6)
C(25)	60(8)	70(9)	40(6)	-8(6)	23(5)	-3(6)
Br(2)	53(1)	35(1)	37(1)	-3(1)	-21(1)	14(1)

P(2)	22(1)	22(2)	25(1)	-1(1)	4(1)	-1(1)
Si(2)	26(2)	59(2)	26(1)	3(1)	6(1)	0(1)
O(2)	30(4)	24(4)	31(3)	-4(3)	2(3)	-1(3)
N(2)	18(4)	24(5)	22(3)	5(3)	3(3)	0(3)
C(26)	35(5)	32(5)	25(4)	-3(4)	-4(3)	5(5)
C(27)	37(5)	33(6)	29(4)	-4(4)	3(3)	0(4)
C(28)	15(4)	33(5)	22(4)	1(4)	5(3)	1(4)
C(29)	39(6)	33(6)	37(5)	2(5)	-6(4)	3(5)
C(30)	47(6)	19(6)	36(5)	1(4)	-3(4)	-6(5)
C(31)	27(5)	37(6)	31(5)	-8(4)	1(4)	-7(4)
C(32)	26(5)	27(6)	29(4)	-1(4)	5(3)	3(4)
C(33)	15(4)	29(6)	32(4)	-1(4)	3(3)	-2(4)
C(34)	19(5)	43(7)	32(5)	1(4)	6(4)	3(4)
C(35)	24(6)	56(9)	57(7)	25(6)	12(5)	6(5)
C(36)	31(5)	22(6)	25(4)	-5(4)	5(3)	-2(4)
C(37)	29(5)	39(7)	27(4)	-2(4)	5(4)	-1(5)
C(38)	46(6)	38(7)	26(5)	1(5)	0(4)	-8(5)
C(39)	54(6)	37(7)	27(5)	3(5)	3(4)	-16(5)
C(40)	50(6)	60(9)	33(5)	-10(5)	16(4)	-10(6)
C(41)	33(5)	58(8)	32(4)	-4(5)	5(4)	-2(5)
C(42)	22(4)	29(5)	23(4)	2(4)	2(3)	-2(4)
C(43)	27(5)	27(6)	45(6)	0(5)	-1(4)	1(4)
C(44)	39(6)	28(6)	54(6)	-4(5)	-1(5)	-11(5)
C(45)	25(6)	61(8)	49(6)	-1(6)	-4(4)	-3(5)
C(46)	26(5)	58(7)	46(6)	7(6)	-6(4)	5(5)
C(47)	32(5)	29(6)	32(5)	0(4)	1(4)	6(4)
C(48)	43(7)	155(15)	42(6)	-32(8)	2(5)	8(8)
C(49)	56(8)	78(8)	80(9)	44(7)	29(7)	5(7)
C(50)	33(5)	77(10)	44(6)	2(6)	5(4)	-4(6)
Br(3)	49(1)	42(1)	45(1)	-9(1)	-15(1)	13(1)
P(3)	32(1)	22(2)	24(1)	0(1)	3(1)	-1(1)
Si(3)	35(2)	45(2)	28(1)	5(1)	5(1)	9(1)
O(3)	43(4)	23(4)	32(3)	0(3)	5(3)	-1(3)
N(3)	37(4)	25(5)	18(3)	0(3)	1(3)	-2(4)
C(51)	30(5)	37(6)	26(4)	-7(4)	6(3)	3(4)
C(52)	38(6)	31(6)	31(5)	-5(4)	1(4)	-1(4)

C(53)	42(6)	26(6)	35(5)	-10(5)	-4(4)	1(5)
C(54)	35(6)	30(6)	35(5)	-5(5)	-4(4)	-2(5)
C(55)	24(5)	31(5)	14(4)	-2(4)	3(3)	1(4)
C(56)	33(5)	33(6)	30(4)	-8(4)	7(3)	2(4)
C(57)	32(5)	20(5)	23(4)	1(4)	4(3)	-4(4)
C(58)	31(5)	18(5)	31(4)	3(4)	-1(3)	-1(4)
C(59)	32(6)	42(8)	45(6)	14(5)	1(4)	-2(5)
C(60)	25(6)	100(12)	82(9)	69(9)	22(6)	19(7)
C(61)	39(5)	18(6)	28(4)	-2(4)	4(3)	-9(4)
C(62)	54(6)	31(7)	26(4)	-2(4)	5(4)	0(5)
C(63)	68(7)	18(6)	25(5)	6(4)	-2(4)	-4(5)
C(64)	62(7)	29(7)	37(5)	5(5)	4(4)	-11(5)
C(65)	65(7)	43(8)	29(5)	-2(5)	17(5)	-8(6)
C(66)	42(6)	41(7)	34(4)	-2(5)	4(4)	-9(5)
C(67)	45(5)	22(5)	18(4)	-5(4)	6(3)	0(4)
C(68)	38(5)	19(5)	44(6)	1(5)	8(4)	0(4)
C(69)	42(6)	40(7)	44(6)	-5(5)	5(5)	-13(5)
C(70)	28(6)	61(7)	44(6)	-16(6)	8(4)	-6(5)
C(71)	36(6)	58(7)	41(6)	3(6)	-2(4)	8(5)
C(72)	35(5)	27(6)	40(5)	0(5)	3(4)	2(4)
C(73)	48(6)	73(9)	64(7)	39(7)	13(5)	-2(7)
C(74)	80(10)	103(12)	68(9)	-26(8)	19(7)	21(9)
C(75)	39(6)	97(12)	57(7)	29(7)	10(5)	-11(6)
Br(4)	49(1)	52(1)	50(1)	0(1)	-12(1)	-16(1)
P(4)	27(1)	16(1)	31(1)	0(1)	7(1)	-1(1)
Si(4)	30(2)	39(2)	39(1)	-14(1)	12(1)	-7(1)
O(4)	34(4)	13(4)	30(3)	-1(3)	9(3)	-3(3)
N(4)	26(4)	20(4)	26(3)	-3(3)	6(3)	-7(3)
C(76)	26(5)	44(6)	34(5)	5(5)	1(4)	-4(4)
C(77)	30(6)	36(6)	44(6)	2(5)	-1(4)	4(4)
C(78)	48(7)	17(6)	57(7)	1(5)	-7(5)	-3(5)
C(79)	40(6)	29(6)	49(6)	-6(5)	0(4)	-1(5)
C(80)	19(4)	33(6)	26(4)	2(4)	7(3)	-2(4)
C(81)	36(5)	21(5)	28(4)	-3(4)	4(3)	-5(4)
C(82)	34(5)	23(6)	23(4)	-2(4)	6(3)	-2(4)
C(83)	28(4)	13(5)	33(4)	2(4)	1(3)	2(4)

C(84)	36(6)	30(6)	28(5)	-5(4)	8(4)	-7(4)
C(85)	24(6)	83(11)	44(6)	-21(6)	7(4)	-13(6)
C(86)	36(5)	16(6)	31(4)	-5(4)	4(3)	3(4)
C(87)	37(6)	39(7)	35(5)	8(5)	3(4)	-11(5)
C(88)	59(7)	39(8)	32(5)	3(5)	3(5)	-10(6)
C(89)	55(7)	31(7)	34(5)	0(5)	8(4)	11(5)
C(90)	49(6)	46(8)	35(5)	-4(5)	15(5)	15(5)
C(91)	32(5)	45(7)	39(5)	-5(5)	7(4)	6(5)
C(92)	29(4)	24(5)	29(4)	-3(4)	10(3)	0(4)
C(93)	29(5)	25(6)	60(7)	4(5)	-4(5)	-7(4)
C(94)	45(7)	27(6)	77(8)	9(6)	4(6)	14(5)
C(95)	24(5)	61(8)	48(6)	7(6)	2(4)	7(5)
C(96)	24(5)	64(8)	51(6)	-10(6)	4(4)	-9(5)
C(97)	33(5)	38(7)	42(5)	-2(5)	0(4)	-9(4)
C(98)	53(8)	71(9)	118(11)	-61(8)	34(8)	-18(7)
C(99)	47(7)	107(11)	37(6)	14(7)	9(5)	-8(7)
C(100)	41(5)	48(8)	62(7)	-5(6)	15(5)	-5(5)

Table S23. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for $C_{25}H_{27}BrNOPSi$

	x	y	z	U(eq)
H(1N)	-602	5582	5091	30
H(2)	1251	4776	7295	52
H(3)	405	3451	6895	50
H(4)	-449	4242	6259	41
H(6)	427	7825	6413	43
H(7)	-529	7618	5816	30
H(10A)	-2310(60)	5530(130)	4820(50)	60
H(10B)	-1860(60)	4690(130)	4910(50)	60
H(12)	-913	6111	4241	41
H(13)	-1050	5407	3340	44
H(14)	-116	5269	2843	55
H(15)	960	5817	3266	62
H(16)	1092	6526	4176	55
H(18)	885	4479	5157	44
H(19)	1934	3805	5597	61
H(20)	2723	5348	5972	61
H(21)	2443	7566	5943	56
H(22)	1395	8232	5518	38
H(23A)	-809	7965	6903	90
H(23B)	-1005	6690	7225	90
H(23C)	-1429	8009	7264	90
H(24A)	-2445	8852	6428	83
H(24B)	-2618	8084	5864	83
H(24C)	-1951	8967	5962	83
H(25A)	-2105	4971	6813	83
H(25B)	-2656	5400	6320	83
H(25C)	-2640	6095	6903	83
H(2N)	10599	902	9955	25
H(27)	9821	3301	8494	40
H(29)	10207	-474	8904	45
H(30)	9398	-1150	8210	42

H(31)	8745	378	7677	38
H(32)	10609	2913	9237	32
H(35A)	12481	-65	9927	54
H(35B)	11789	-424	10204	54
H(37)	10822	1286	10772	38
H(38)	10927	772	11705	44
H(39)	9994	999	12194	47
H(40)	8968	1704	11757	56
H(41)	8853	2186	10827	49
H(43)	9133	-316	9999	40
H(44)	8169	-1282	9550	49
H(45)	7394	-27	8983	55
H(46)	7602	2196	8848	53
H(47)	8580	3152	9280	38
H(48A)	10952	1480	7816	120
H(48B)	11338	170	8023	120
H(48C)	11701	1203	7667	120
H(49A)	11976	4036	8260	105
H(49B)	11689	4140	8839	105
H(49C)	11181	3877	8298	105
H(50A)	12890	1761	8398	77
H(50B)	12722	633	8811	77
H(50C)	12866	2087	9031	77
H(3N)	5441	817	2477	32
H(52)	3608	91	236	40
H(53)	4453	-1301	644	42
H(54)	5283	-515	1301	41
H(56)	4464	3107	1130	38
H(57)	5407	2831	1755	30
H(60A)	7379	-106	2347	82
H(60B)	6811	-114	2784	82
H(62)	5634	921	3293	44
H(63)	5763	573	4234	45
H(64)	4886	1076	4746	51
H(65)	3883	2028	4326	54
H(66)	3747	2360	3382	47

H(68)	4028	-482	2456	40
H(69)	3025	-1401	2052	51
H(70)	2188	-94	1599	53
H(71)	2350	2161	1538	55
H(72)	3353	3100	1948	41
H(73A)	6135	4021	916	92
H(73B)	5651	2924	619	92
H(73C)	6323	3357	365	92
H(74A)	6914	747	358	125
H(74B)	6237	150	552	125
H(74C)	6957	-169	886	125
H(75A)	7688	2790	1054	96
H(75B)	7698	1848	1573	96
H(75C)	7403	3297	1598	96
H(4N)	4319	5807	2489	28
H(77)	6362	5136	4638	45
H(78)	5520	3722	4237	50
H(79)	4671	4466	3609	48
H(81)	5381	8170	3821	34
H(82)	4426	7845	3201	32
H(85A)	2362	5717	2522	60
H(85B)	2953	4752	2330	60
H(87)	4033	6075	1656	44
H(88)	3878	5564	739	52
H(89)	4750	5841	180	47
H(90)	5790	6606	585	52
H(91)	5967	7106	1507	46
H(93)	5739	4529	2387	46
H(94)	6753	3576	2741	60
H(95)	7610	4840	3223	53
H(96)	7418	7062	3360	56
H(97)	6402	8025	3012	45
H(98A)	3693	9140	3923	119
H(98B)	4234	8356	4330	119
H(98C)	3532	8807	4529	119
H(99A)	4108	5657	4568	95

H(99B)	3439	4841	4368	95
H(99C)	3425	5919	4837	95
H(10C)	2270	7272	4220	74
H(10D)	2247	6236	3732	74
H(10E)	2305	7762	3607	74

Table S24. Torsion angles [º] for $C_{25}H_{27}BrNOPSi$

O(1)-P(1)-N(1)-C(7)	-43.8(8)
C(11)-P(1)-N(1)-C(7)	-167.6(7)
C(17)-P(1)-N(1)-C(7)	79.4(8)
C(6)-C(1)-C(2)-C(3)	1.2(14)
Br(1)-C(1)-C(2)-C(3)	179.3(7)
C(1)-C(2)-C(3)-C(4)	-0.7(16)
C(2)-C(3)-C(4)-C(5)	1.6(15)
C(3)-C(4)-C(5)-C(6)	-3.1(13)
C(3)-C(4)-C(5)-C(7)	173.9(8)
C(2)-C(1)-C(6)-C(5)	-2.8(13)
Br(1)-C(1)-C(6)-C(5)	179.1(6)
C(4)-C(5)-C(6)-C(1)	3.7(13)
C(7)-C(5)-C(6)-C(1)	-173.4(8)
P(1)-N(1)-C(7)-C(5)	-79.6(9)
P(1)-N(1)-C(7)-C(8)	152.8(7)
C(4)-C(5)-C(7)-N(1)	-76.1(10)
C(6)-C(5)-C(7)-N(1)	100.9(9)
C(4)-C(5)-C(7)-C(8)	49.5(11)
C(6)-C(5)-C(7)-C(8)	-133.4(9)
N(1)-C(7)-C(8)-C(9)	4.8(13)
C(5)-C(7)-C(8)-C(9)	-120.8(11)
N(1)-C(7)-C(8)-Si(1)	-169.1(6)
C(5)-C(7)-C(8)-Si(1)	65.3(11)
C(23)-Si(1)-C(8)-C(9)	164.7(9)
C(24)-Si(1)-C(8)-C(9)	-75.5(10)
C(25)-Si(1)-C(8)-C(9)	41.9(10)
C(23)-Si(1)-C(8)-C(7)	-21.0(10)
C(24)-Si(1)-C(8)-C(7)	98.7(8)
C(25)-Si(1)-C(8)-C(7)	-143.8(8)
O(1)-P(1)-C(11)-C(16)	86.5(10)
N(1)-P(1)-C(11)-C(16)	-151.4(9)
C(17)-P(1)-C(11)-C(16)	-35.5(11)
O(1)-P(1)-C(11)-C(12)	-90.4(9)
N(1)-P(1)-C(11)-C(12)	31.6(9)

C(17)-P(1)-C(11)-C(12)	147.5(8)
C(16)-C(11)-C(12)-C(13)	0.4(16)
P(1)-C(11)-C(12)-C(13)	177.4(8)
C(11)-C(12)-C(13)-C(14)	-0.4(17)
C(12)-C(13)-C(14)-C(15)	0.4(19)
C(13)-C(14)-C(15)-C(16)	0(2)
C(12)-C(11)-C(16)-C(15)	-0.4(18)
P(1)-C(11)-C(16)-C(15)	-177.4(10)
C(14)-C(15)-C(16)-C(11)	0(2)
O(1)-P(1)-C(17)-C(18)	177.2(7)
N(1)-P(1)-C(17)-C(18)	52.7(9)
C(11)-P(1)-C(17)-C(18)	-57.7(9)
O(1)-P(1)-C(17)-C(22)	1.3(8)
N(1)-P(1)-C(17)-C(22)	-123.2(7)
C(11)-P(1)-C(17)-C(22)	126.3(7)
C(22)-C(17)-C(18)-C(19)	-0.9(14)
P(1)-C(17)-C(18)-C(19)	-176.8(8)
C(17)-C(18)-C(19)-C(20)	-0.6(16)
C(18)-C(19)-C(20)-C(21)	1.6(17)
C(19)-C(20)-C(21)-C(22)	-1.1(16)
C(20)-C(21)-C(22)-C(17)	-0.4(15)
C(18)-C(17)-C(22)-C(21)	1.4(13)
P(1)-C(17)-C(22)-C(21)	177.5(7)
O(2)-P(2)-N(2)-C(32)	-39.7(8)
C(42)-P(2)-N(2)-C(32)	83.1(7)
C(36)-P(2)-N(2)-C(32)	-164.1(7)
C(31)-C(26)-C(27)-C(28)	-0.6(13)
Br(2)-C(26)-C(27)-C(28)	179.7(6)
Br(2X)-C(26)-C(27)-C(28)	140.6(10)
C(26)-C(27)-C(28)-C(29)	1.8(13)
C(26)-C(27)-C(28)-C(32)	-175.8(7)
C(27)-C(28)-C(29)-C(30)	-0.8(14)
C(32)-C(28)-C(29)-C(30)	176.8(8)
C(28)-C(29)-C(30)-C(31)	-1.4(16)
C(27)-C(26)-C(31)-C(30)	-1.5(14)
Br(2)-C(26)-C(31)-C(30)	178.2(7)

Br(2X)-C(26)-C(31)-C(30)	-149.4(9)
C(29)-C(30)-C(31)-C(26)	2.5(15)
P(2)-N(2)-C(32)-C(33)	163.8(6)
P(2)-N(2)-C(32)-C(28)	-71.9(9)
C(27)-C(28)-C(32)-N(2)	115.8(9)
C(29)-C(28)-C(32)-N(2)	-61.8(11)
C(27)-C(28)-C(32)-C(33)	-120.4(9)
C(29)-C(28)-C(32)-C(33)	62.1(11)
N(2)-C(32)-C(33)-C(34)	1.7(14)
C(28)-C(32)-C(33)-C(34)	-121.7(10)
N(2)-C(32)-C(33)-Si(2)	-174.6(6)
C(28)-C(32)-C(33)-Si(2)	62.0(10)
C(49)-Si(2)-C(33)-C(34)	-130.8(9)
C(48)-Si(2)-C(33)-C(34)	109.6(10)
C(50)-Si(2)-C(33)-C(34)	-11.5(10)
C(49)-Si(2)-C(33)-C(32)	45.7(9)
C(48)-Si(2)-C(33)-C(32)	-73.9(10)
C(50)-Si(2)-C(33)-C(32)	165.0(8)
O(2)-P(2)-C(36)-C(41)	74.4(10)
N(2)-P(2)-C(36)-C(41)	-163.3(9)
C(42)-P(2)-C(36)-C(41)	-48.1(10)
O(2)-P(2)-C(36)-C(37)	-100.9(9)
N(2)-P(2)-C(36)-C(37)	21.4(9)
C(42)-P(2)-C(36)-C(37)	136.6(8)
C(41)-C(36)-C(37)-C(38)	1.3(16)
P(2)-C(36)-C(37)-C(38)	176.6(8)
C(36)-C(37)-C(38)-C(39)	-1.1(17)
C(37)-C(38)-C(39)-C(40)	0.3(18)
C(38)-C(39)-C(40)-C(41)	0.2(18)
C(37)-C(36)-C(41)-C(40)	-0.8(17)
P(2)-C(36)-C(41)-C(40)	-176.1(9)
C(39)-C(40)-C(41)-C(36)	0.0(19)
O(2)-P(2)-C(42)-C(43)	-175.2(7)
N(2)-P(2)-C(42)-C(43)	61.0(8)
C(36)-P(2)-C(42)-C(43)	-49.7(9)
O(2)-P(2)-C(42)-C(47)	9.3(8)

N(2)-P(2)-C(42)-C(47)	-114.5(7)
C(36)-P(2)-C(42)-C(47)	134.8(7)
C(47)-C(42)-C(43)-C(44)	-0.4(14)
P(2)-C(42)-C(43)-C(44)	-176.0(8)
C(42)-C(43)-C(44)-C(45)	-0.7(16)
C(43)-C(44)-C(45)-C(46)	0.9(16)
C(44)-C(45)-C(46)-C(47)	-0.1(16)
C(45)-C(46)-C(47)-C(42)	-1.0(15)
C(43)-C(42)-C(47)-C(46)	1.2(13)
P(2)-C(42)-C(47)-C(46)	176.8(7)
O(3)-P(3)-N(3)-C(57)	-39.6(8)
C(67)-P(3)-N(3)-C(57)	84.2(7)
C(61)-P(3)-N(3)-C(57)	-162.8(7)
C(56)-C(51)-C(52)-C(53)	-0.7(14)
Br(3)-C(51)-C(52)-C(53)	179.6(7)
C(51)-C(52)-C(53)-C(54)	1.2(15)
C(52)-C(53)-C(54)-C(55)	0.4(15)
C(53)-C(54)-C(55)-C(56)	-2.3(14)
C(53)-C(54)-C(55)-C(57)	173.3(9)
C(54)-C(55)-C(56)-C(51)	2.8(12)
C(57)-C(55)-C(56)-C(51)	-172.9(7)
C(52)-C(51)-C(56)-C(55)	-1.2(13)
Br(3)-C(51)-C(56)-C(55)	178.5(6)
P(3)-N(3)-C(57)-C(55)	-74.3(9)
P(3)-N(3)-C(57)-C(58)	158.2(7)
C(56)-C(55)-C(57)-N(3)	100.5(10)
C(54)-C(55)-C(57)-N(3)	-75.1(10)
C(56)-C(55)-C(57)-C(58)	-132.9(9)
C(54)-C(55)-C(57)-C(58)	51.5(11)
N(3)-C(57)-C(58)-C(59)	4.0(14)
C(55)-C(57)-C(58)-C(59)	-122.2(11)
N(3)-C(57)-C(58)-Si(3)	-177.1(6)
C(55)-C(57)-C(58)-Si(3)	56.7(11)
C(75)-Si(3)-C(58)-C(59)	-45.3(10)
C(73)-Si(3)-C(58)-C(59)	-165.7(9)
C(74)-Si(3)-C(58)-C(59)	73.9(10)

C(75)-Si(3)-C(58)-C(57)	135.7(9)
C(73)-Si(3)-C(58)-C(57)	15.3(10)
C(74)-Si(3)-C(58)-C(57)	-105.1(9)
O(3)-P(3)-C(61)-C(66)	66.3(9)
N(3)-P(3)-C(61)-C(66)	-171.4(8)
C(67)-P(3)-C(61)-C(66)	-55.1(9)
O(3)-P(3)-C(61)-C(62)	-109.8(9)
N(3)-P(3)-C(61)-C(62)	12.6(9)
C(67)-P(3)-C(61)-C(62)	128.8(8)
C(66)-C(61)-C(62)-C(63)	-1.5(16)
P(3)-C(61)-C(62)-C(63)	174.5(8)
C(61)-C(62)-C(63)-C(64)	1.2(16)
C(62)-C(63)-C(64)-C(65)	-1.2(17)
C(63)-C(64)-C(65)-C(66)	1.5(17)
C(62)-C(61)-C(66)-C(65)	1.9(16)
P(3)-C(61)-C(66)-C(65)	-174.3(9)
C(64)-C(65)-C(66)-C(61)	-1.9(17)
O(3)-P(3)-C(67)-C(72)	1.0(8)
N(3)-P(3)-C(67)-C(72)	-123.8(7)
C(61)-P(3)-C(67)-C(72)	124.3(7)
O(3)-P(3)-C(67)-C(68)	178.8(7)
N(3)-P(3)-C(67)-C(68)	54.0(8)
C(61)-P(3)-C(67)-C(68)	-57.9(9)
C(72)-C(67)-C(68)-C(69)	0.0(14)
P(3)-C(67)-C(68)-C(69)	-177.8(7)
C(67)-C(68)-C(69)-C(70)	0.0(15)
C(68)-C(69)-C(70)-C(71)	0.2(16)
C(69)-C(70)-C(71)-C(72)	-0.5(16)
C(70)-C(71)-C(72)-C(67)	0.5(15)
C(68)-C(67)-C(72)-C(71)	-0.3(13)
P(3)-C(67)-C(72)-C(71)	177.6(7)
O(4)-P(4)-N(4)-C(82)	-39.5(8)
C(92)-P(4)-N(4)-C(82)	83.6(7)
C(86)-P(4)-N(4)-C(82)	-163.5(7)
C(81)-C(76)-C(77)-C(78)	-1.0(15)
Br(4)-C(76)-C(77)-C(78)	-177.9(8)

C(76)-C(77)-C(78)-C(79)	2.5(17)
C(77)-C(78)-C(79)-C(80)	-1.9(17)
C(78)-C(79)-C(80)-C(81)	-0.1(15)
C(78)-C(79)-C(80)-C(82)	175.2(9)
C(79)-C(80)-C(81)-C(76)	1.6(12)
C(82)-C(80)-C(81)-C(76)	-173.8(7)
C(77)-C(76)-C(81)-C(80)	-1.0(13)
Br(4)-C(76)-C(81)-C(80)	175.9(6)
P(4)-N(4)-C(82)-C(83)	159.2(6)
P(4)-N(4)-C(82)-C(80)	-73.1(9)
C(81)-C(80)-C(82)-N(4)	105.7(9)
C(79)-C(80)-C(82)-N(4)	-69.6(10)
C(81)-C(80)-C(82)-C(83)	-127.3(9)
C(79)-C(80)-C(82)-C(83)	57.4(11)
N(4)-C(82)-C(83)-C(84)	-3.6(13)
C(80)-C(82)-C(83)-C(84)	-129.7(10)
N(4)-C(82)-C(83)-Si(4)	179.2(6)
C(80)-C(82)-C(83)-Si(4)	53.1(11)
C(100)-Si(4)-C(83)-C(84)	-22.1(10)
C(98)-Si(4)-C(83)-C(84)	-143.8(9)
C(99)-Si(4)-C(83)-C(84)	98.4(9)
C(100)-Si(4)-C(83)-C(82)	155.2(8)
C(98)-Si(4)-C(83)-C(82)	33.5(9)
C(99)-Si(4)-C(83)-C(82)	-84.4(9)
O(4)-P(4)-C(86)-C(91)	72.9(9)
N(4)-P(4)-C(86)-C(91)	-164.5(8)
C(92)-P(4)-C(86)-C(91)	-48.9(9)
O(4)-P(4)-C(86)-C(87)	-104.8(9)
N(4)-P(4)-C(86)-C(87)	17.8(10)
C(92)-P(4)-C(86)-C(87)	133.4(9)
C(91)-C(86)-C(87)-C(88)	-0.1(16)
P(4)-C(86)-C(87)-C(88)	177.7(9)
C(86)-C(87)-C(88)-C(89)	-0.5(18)
C(87)-C(88)-C(89)-C(90)	0.7(18)
C(88)-C(89)-C(90)-C(91)	-0.3(17)
C(87)-C(86)-C(91)-C(90)	0.4(16)

P(4)-C(86)-C(91)-C(90)	-177.4(9)
C(89)-C(90)-C(91)-C(86)	-0.3(18)
O(4)-P(4)-C(92)-C(93)	-176.6(8)
N(4)-P(4)-C(92)-C(93)	58.9(9)
C(86)-P(4)-C(92)-C(93)	-51.9(9)
O(4)-P(4)-C(92)-C(97)	8.0(8)
N(4)-P(4)-C(92)-C(97)	-116.6(7)
C(86)-P(4)-C(92)-C(97)	132.6(7)
C(97)-C(92)-C(93)-C(94)	-2.7(15)
P(4)-C(92)-C(93)-C(94)	-178.2(8)
C(92)-C(93)-C(94)-C(95)	0.8(17)
C(93)-C(94)-C(95)-C(96)	1.0(17)
C(94)-C(95)-C(96)-C(97)	-0.8(16)
C(95)-C(96)-C(97)-C(92)	-1.2(15)
C(93)-C(92)-C(97)-C(96)	2.9(14)
P(4)-C(92)-C(97)-C(96)	178.5(7)

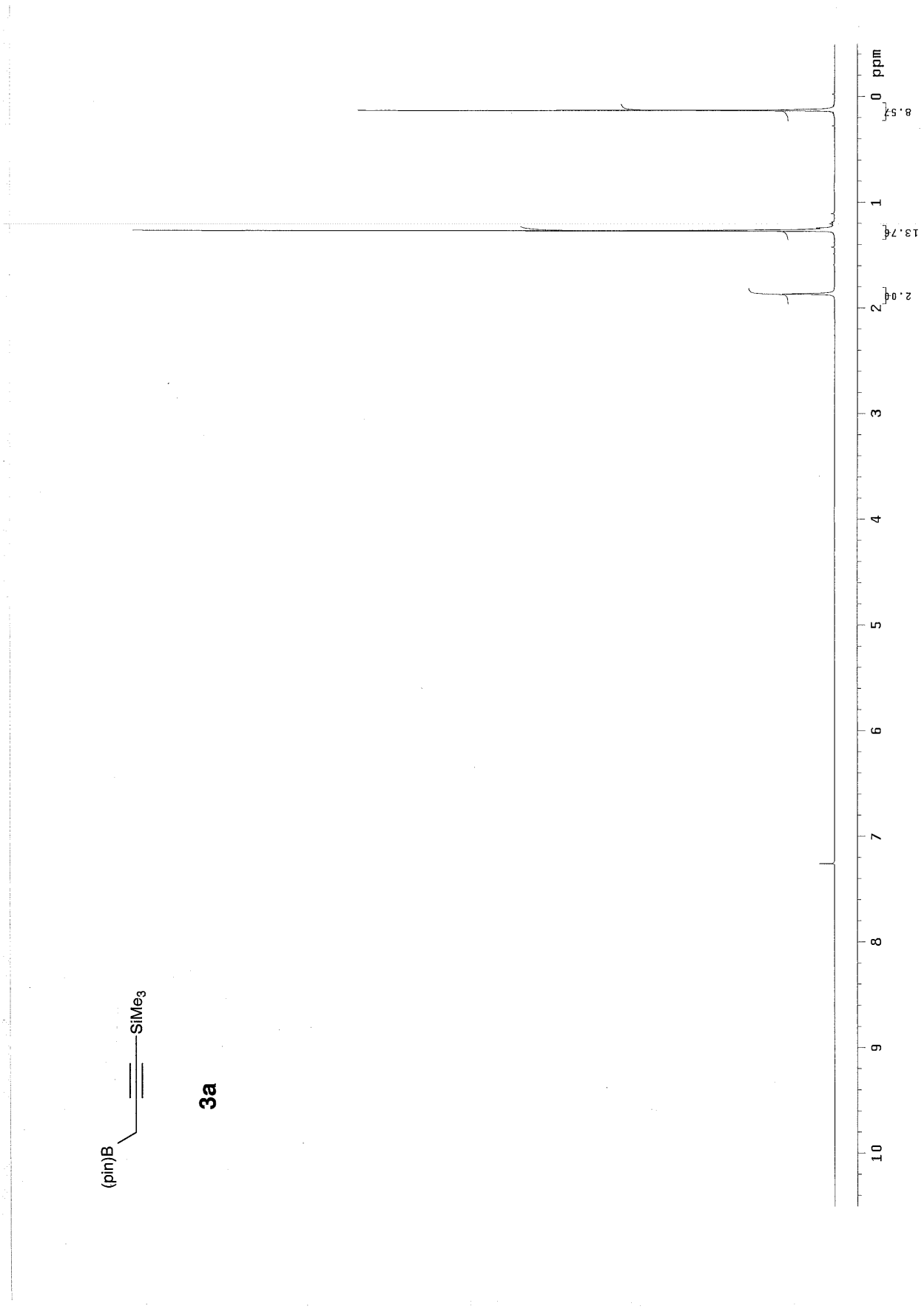
Symmetry transformations used to generate equivalent atoms:

Table S25. Hydrogen bonds for $C_{25}H_{27}BrNOPSi$ [Å and °]

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
N(1)-H(1N)...O(1)#1	0.88	2.39	3.009(11)	127.4
N(2)-H(2N)...O(2)#2	0.88	2.40	3.050(10)	130.5
N(3)-H(3N)...O(4)#3	0.88	2.36	2.997(11)	129.4
N(4)-H(4N)...O(3)	0.88	2.34	2.980(10)	129.6

Symmetry transformations used to generate equivalent atoms:

#1 -x,y-1/2,-z+1 #2 -x+2,y-1/2,-z+2 #3 x,y-1,z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3a
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6
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8
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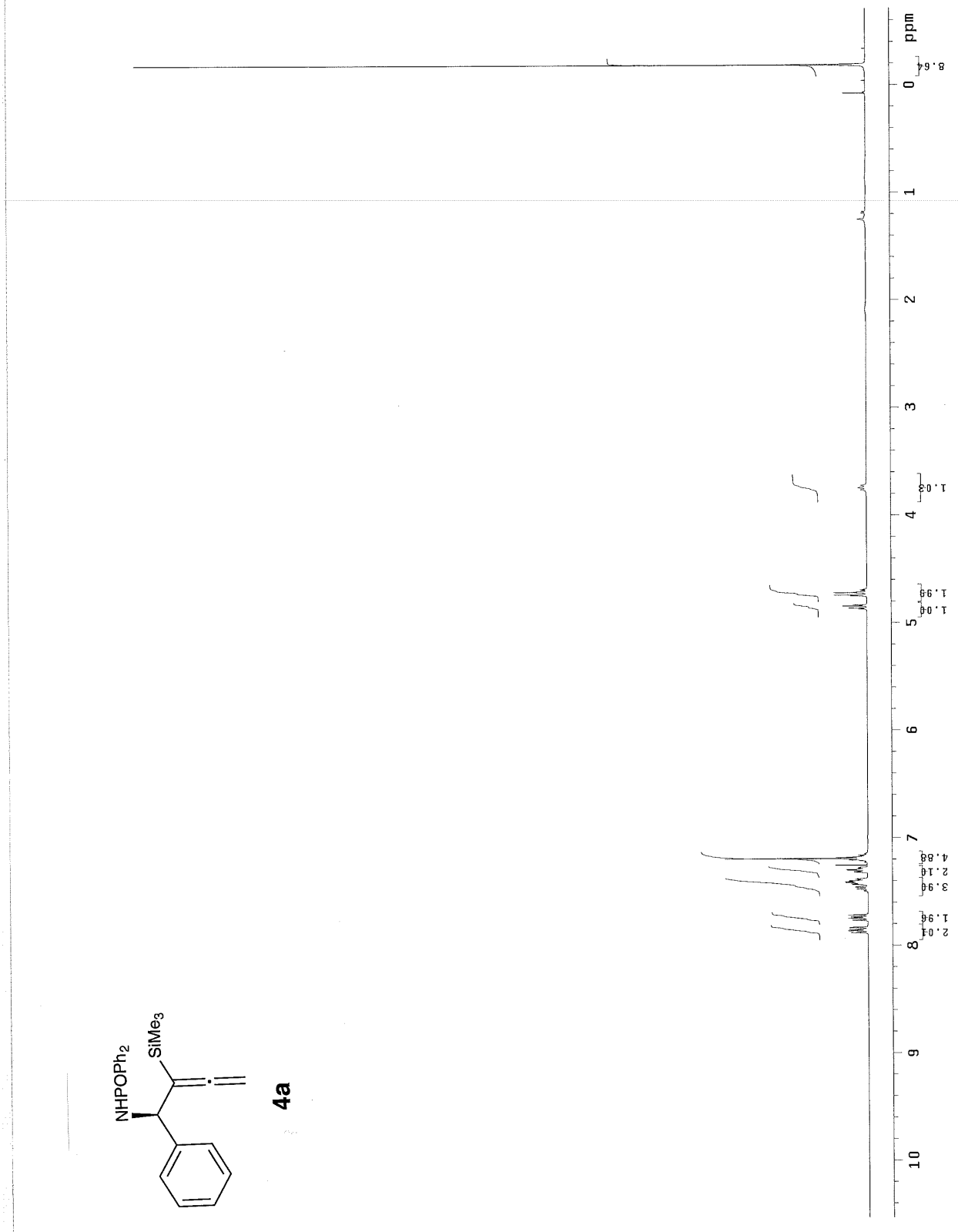
2.00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SiMe3
4a
ppm
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2
3
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6
7
8
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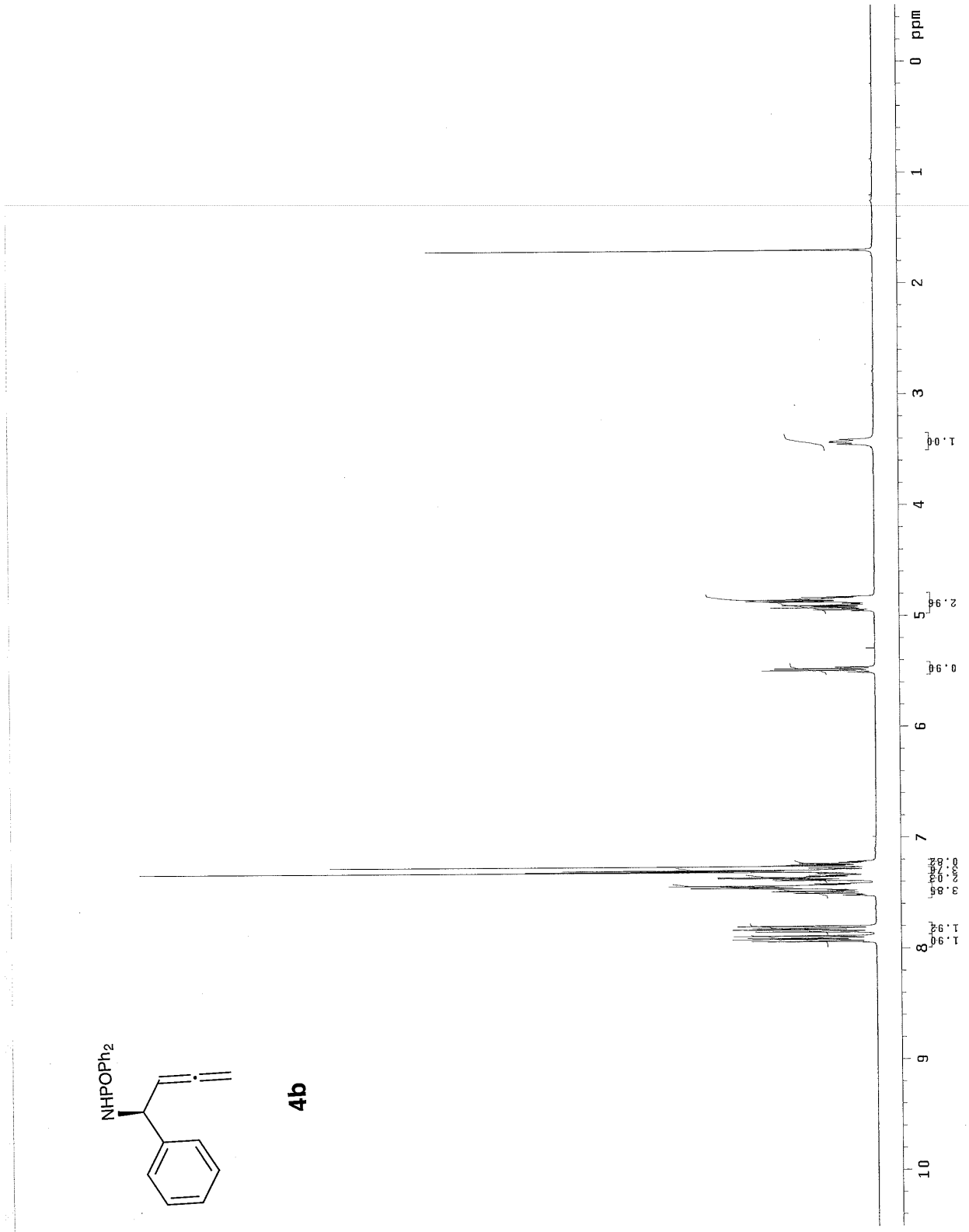
4.88
2.10
3.96
2.01
1.96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4b
ppm
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2
3
4
5
6
7
8
9
10
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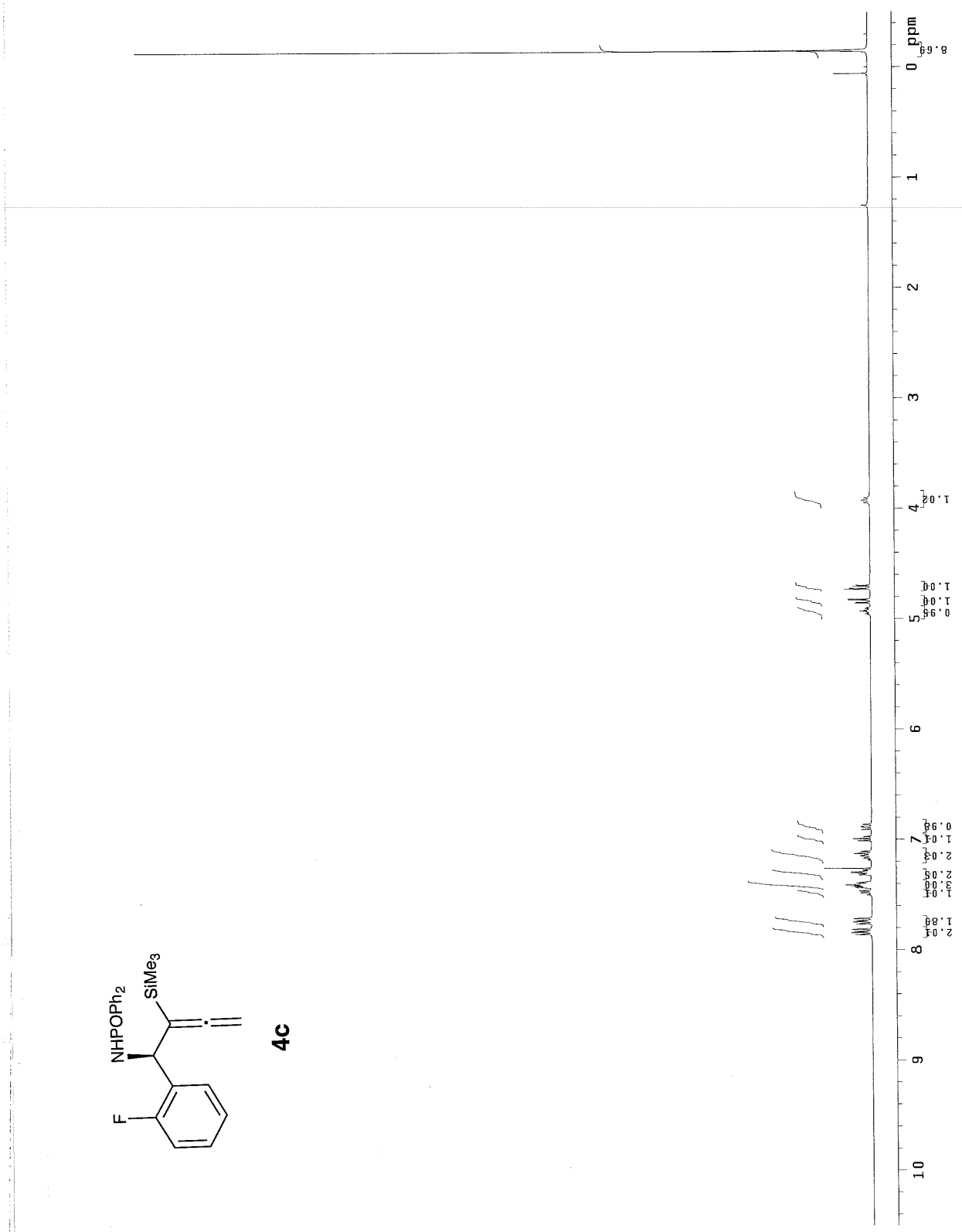
0.96
3.83
2.03
2.00
1.94
1.90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0.93
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1.03
1.83
2.01
ppm
0
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2
3
4
5
6
7
8
9
10

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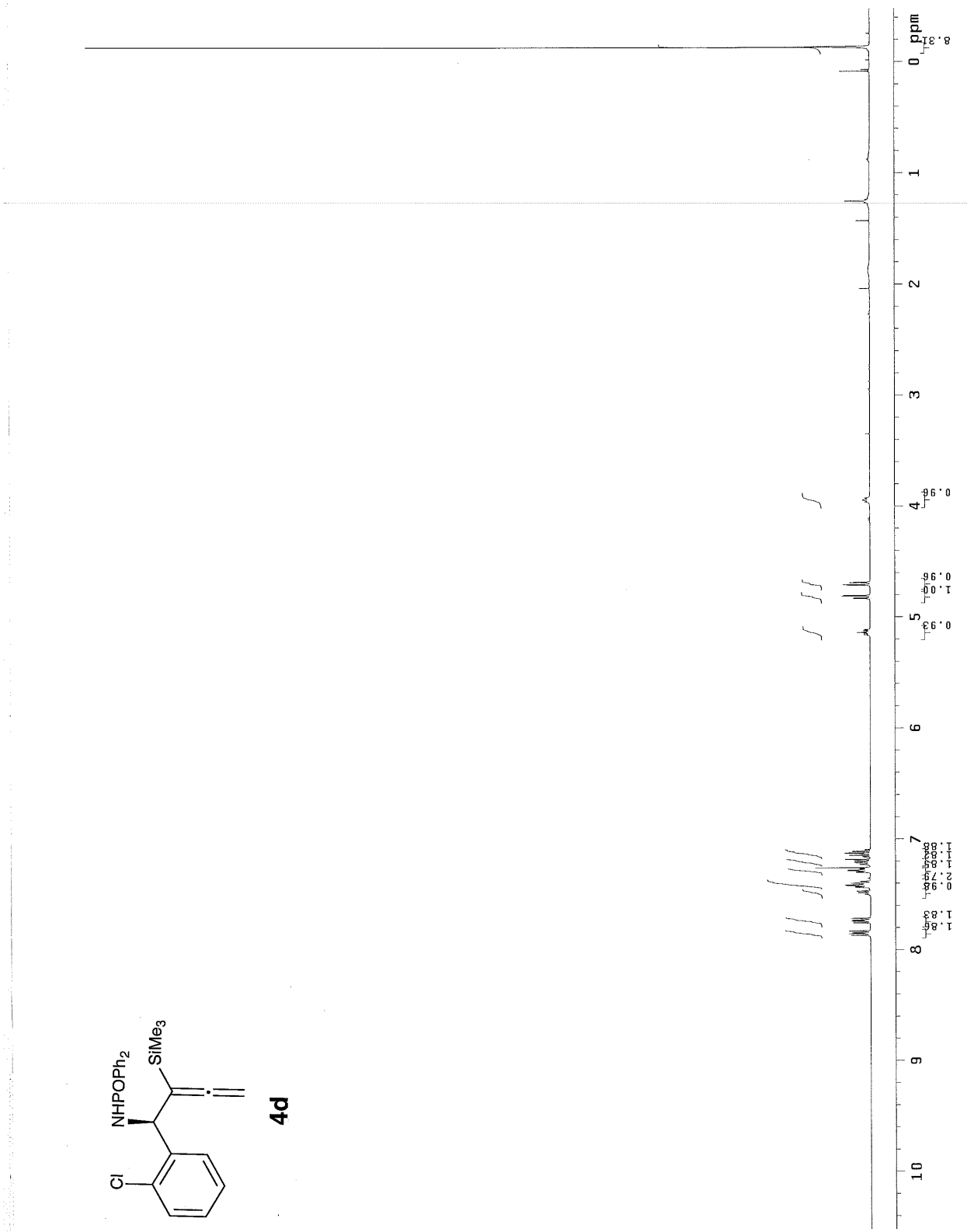
SiMe3
F

4c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Cl
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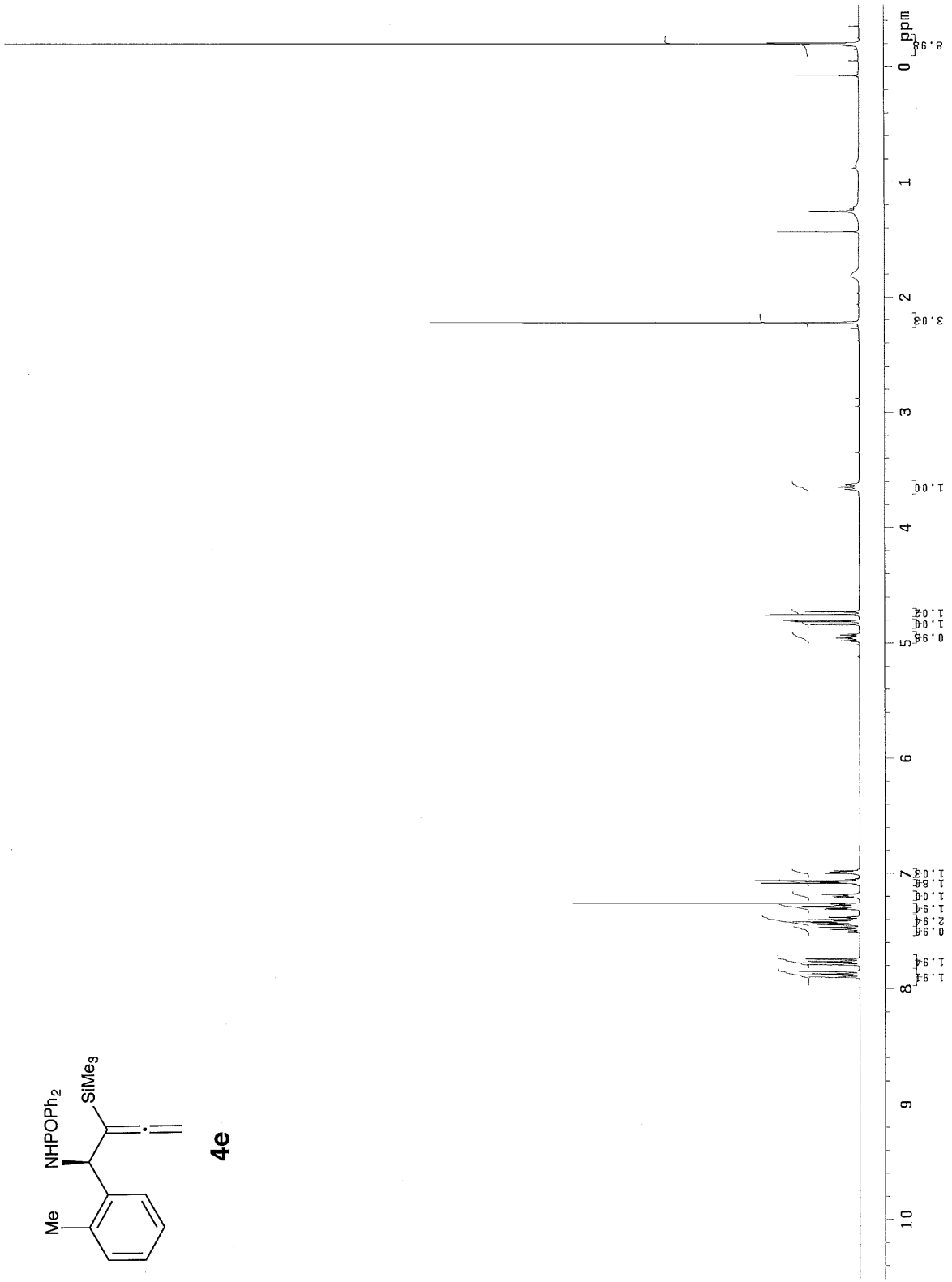
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Me
4e
ppm
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3
4
5
6
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8
9
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3.04
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1.02
1.00
0.98
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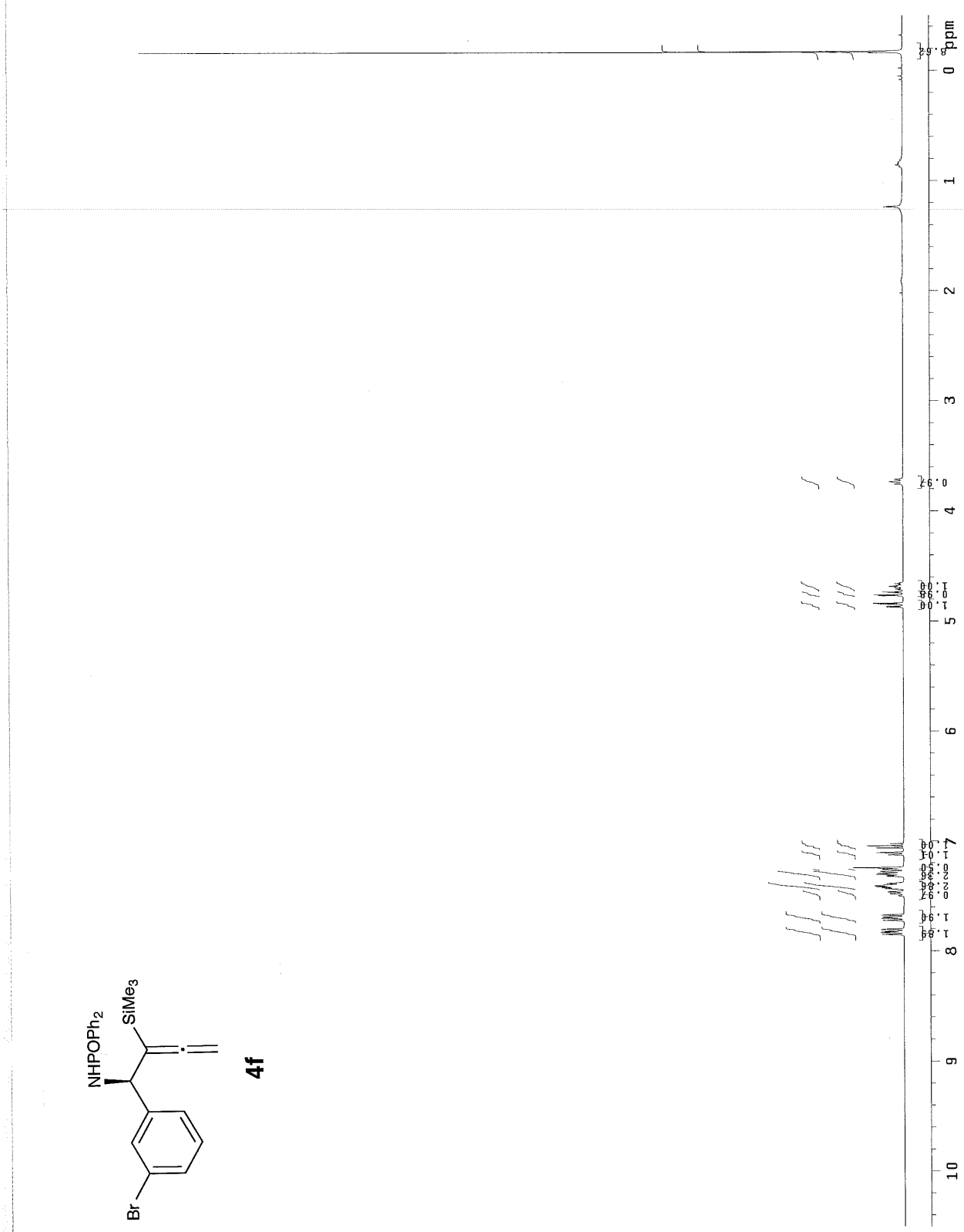
1.94
2.94
0.98
1.94
1.91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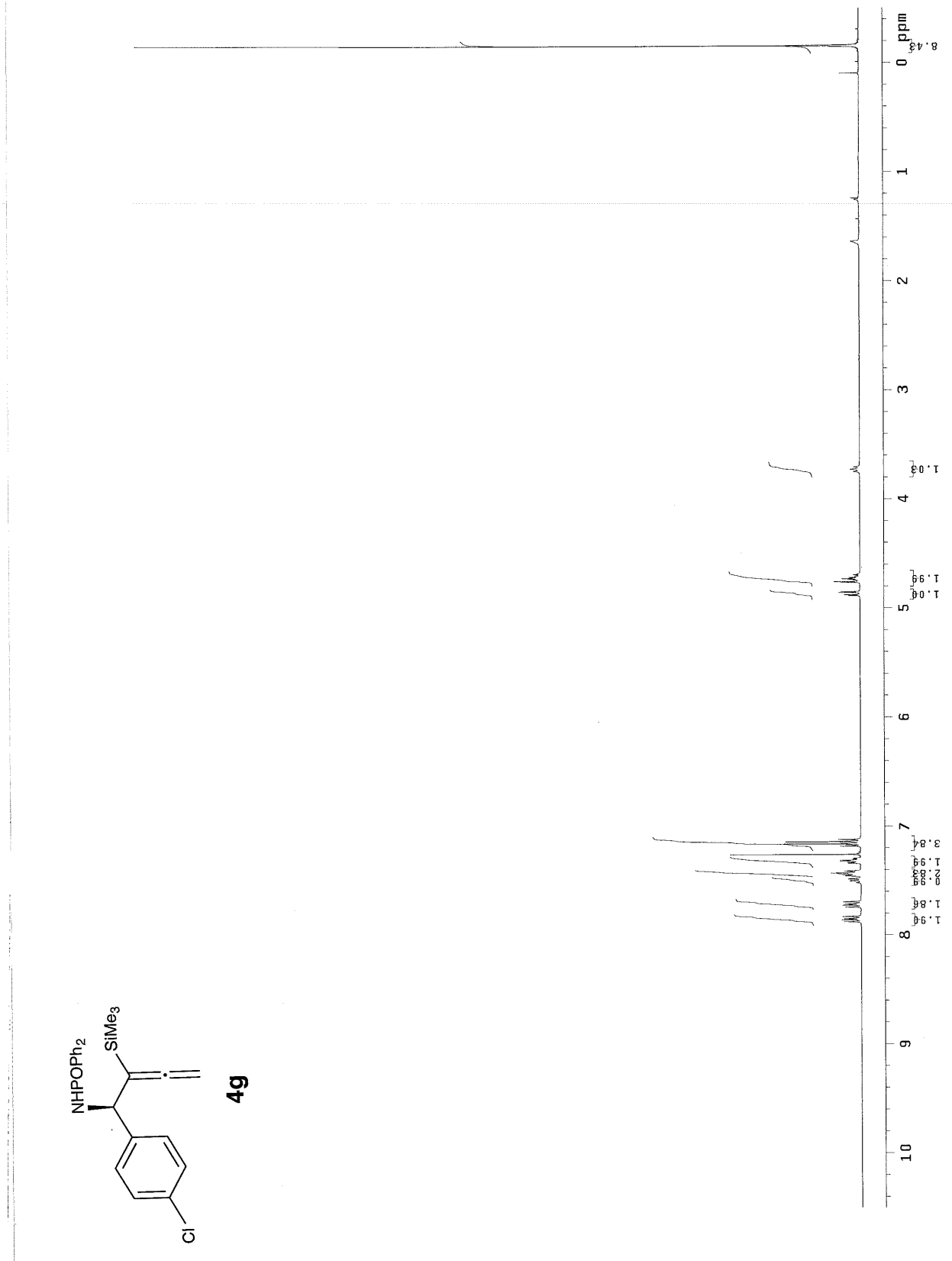
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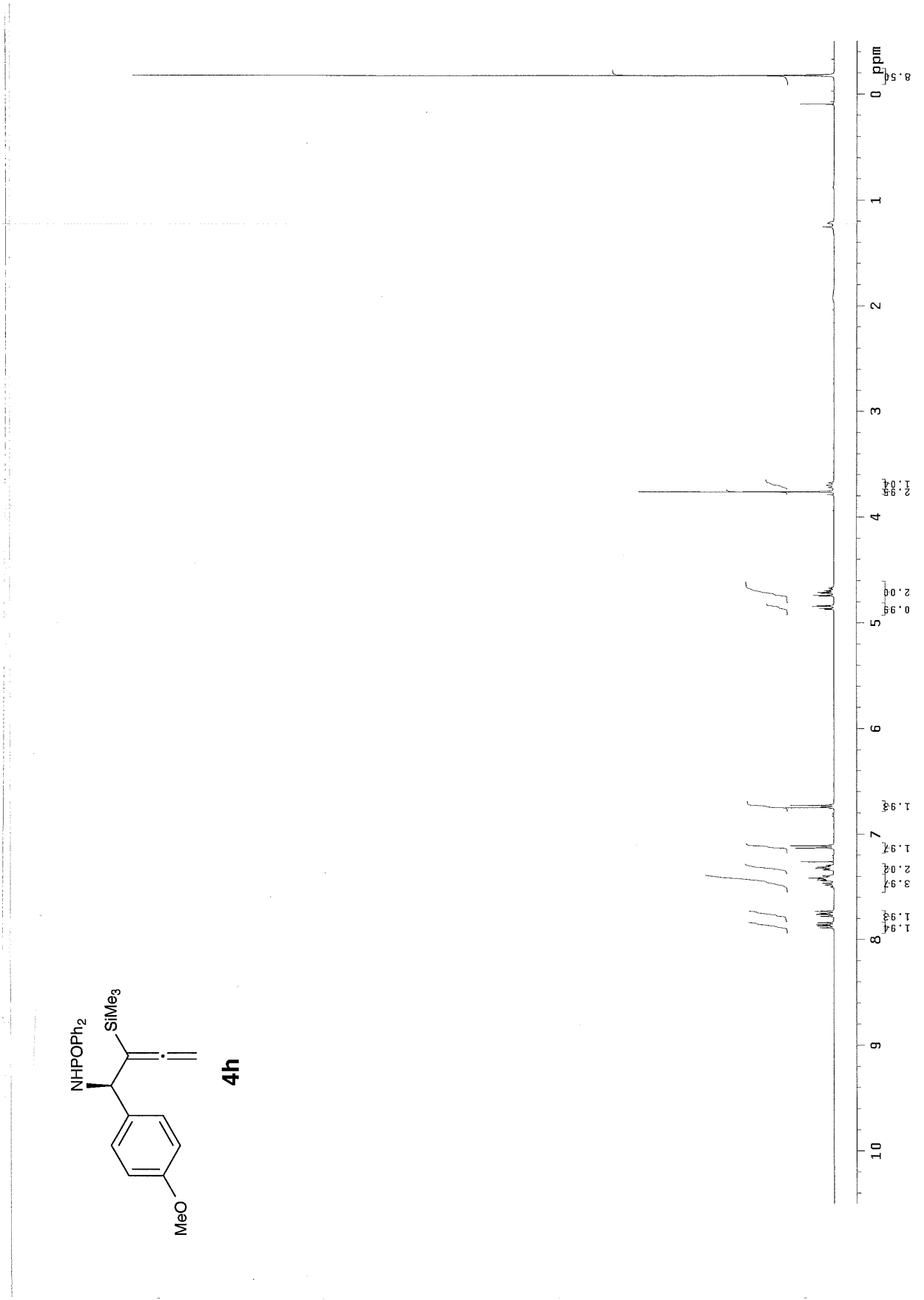
ppm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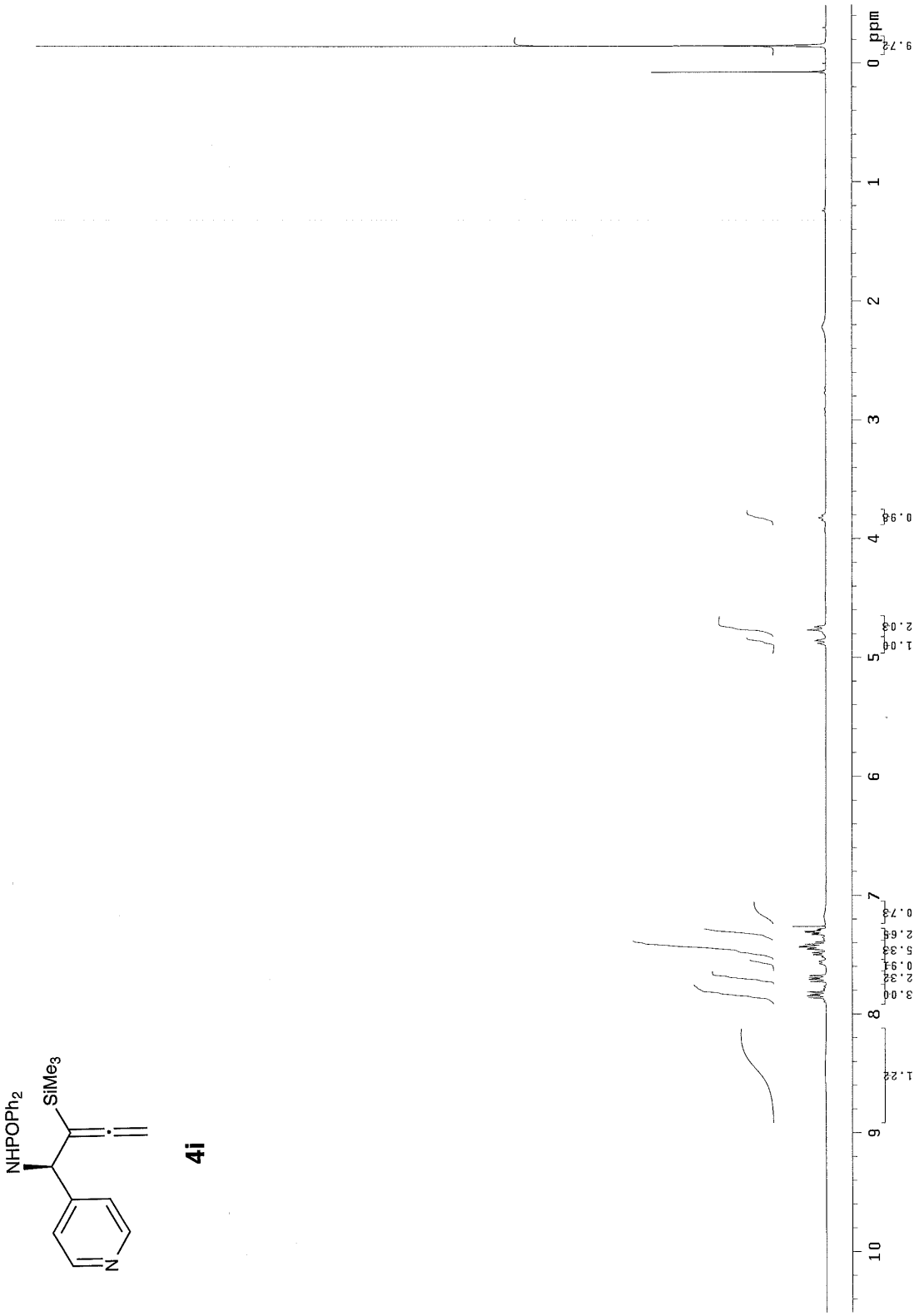
3.97
1.94
1.94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N
4i
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3
4
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6
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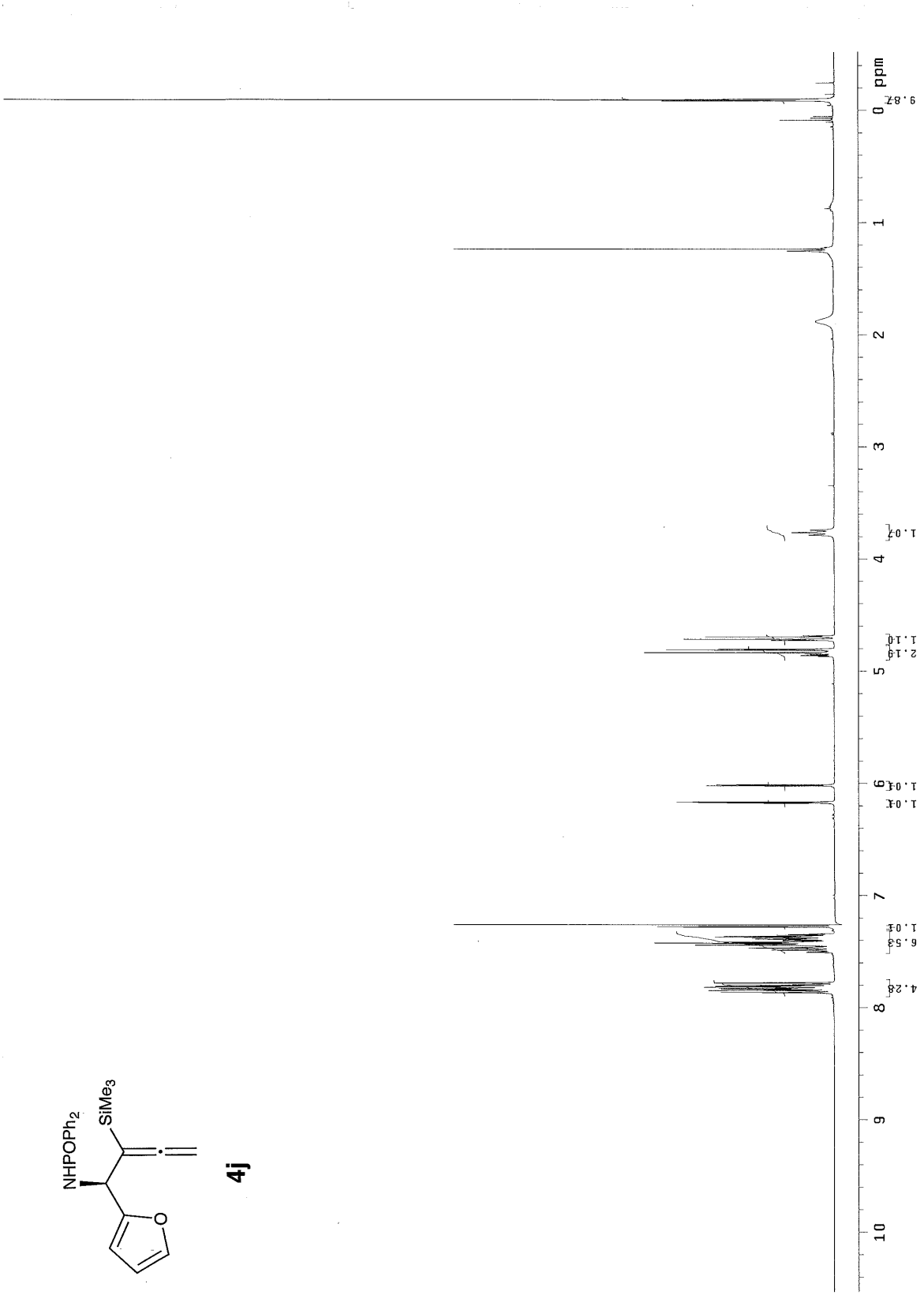
1.22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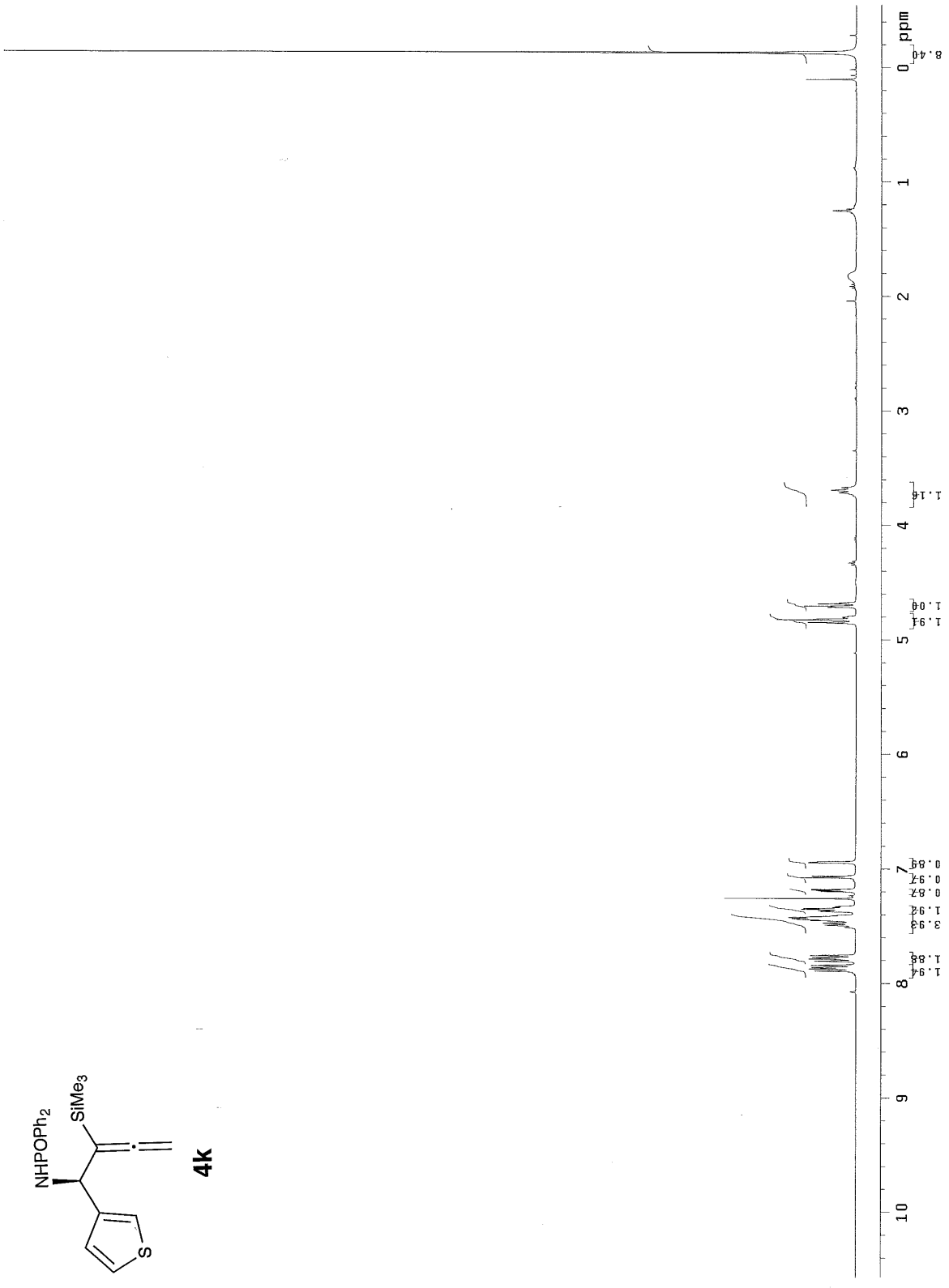
1.01
1.01
6.53
1.01
4.28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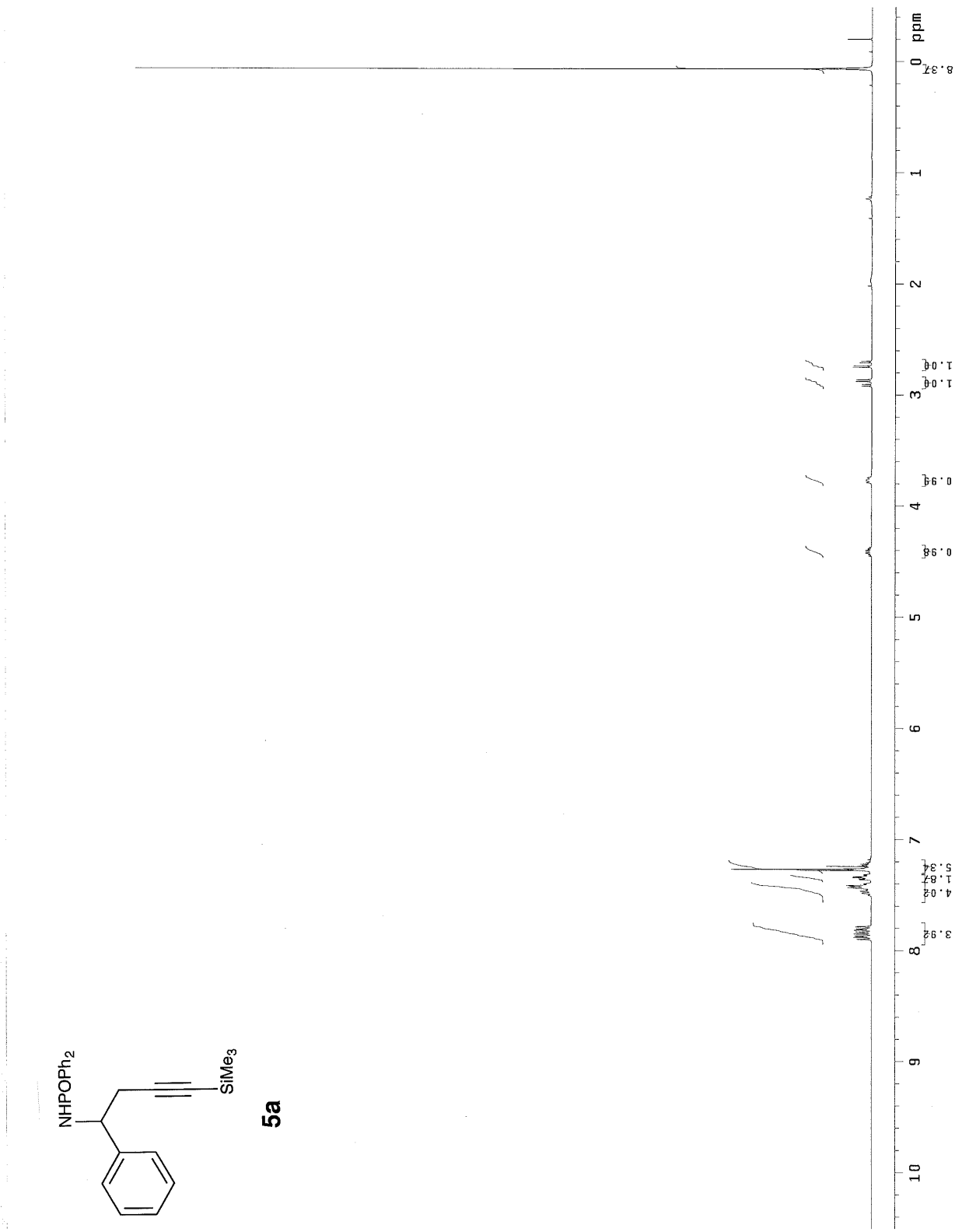
1.94
1.88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5a
ppm
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8
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0.94
0.93
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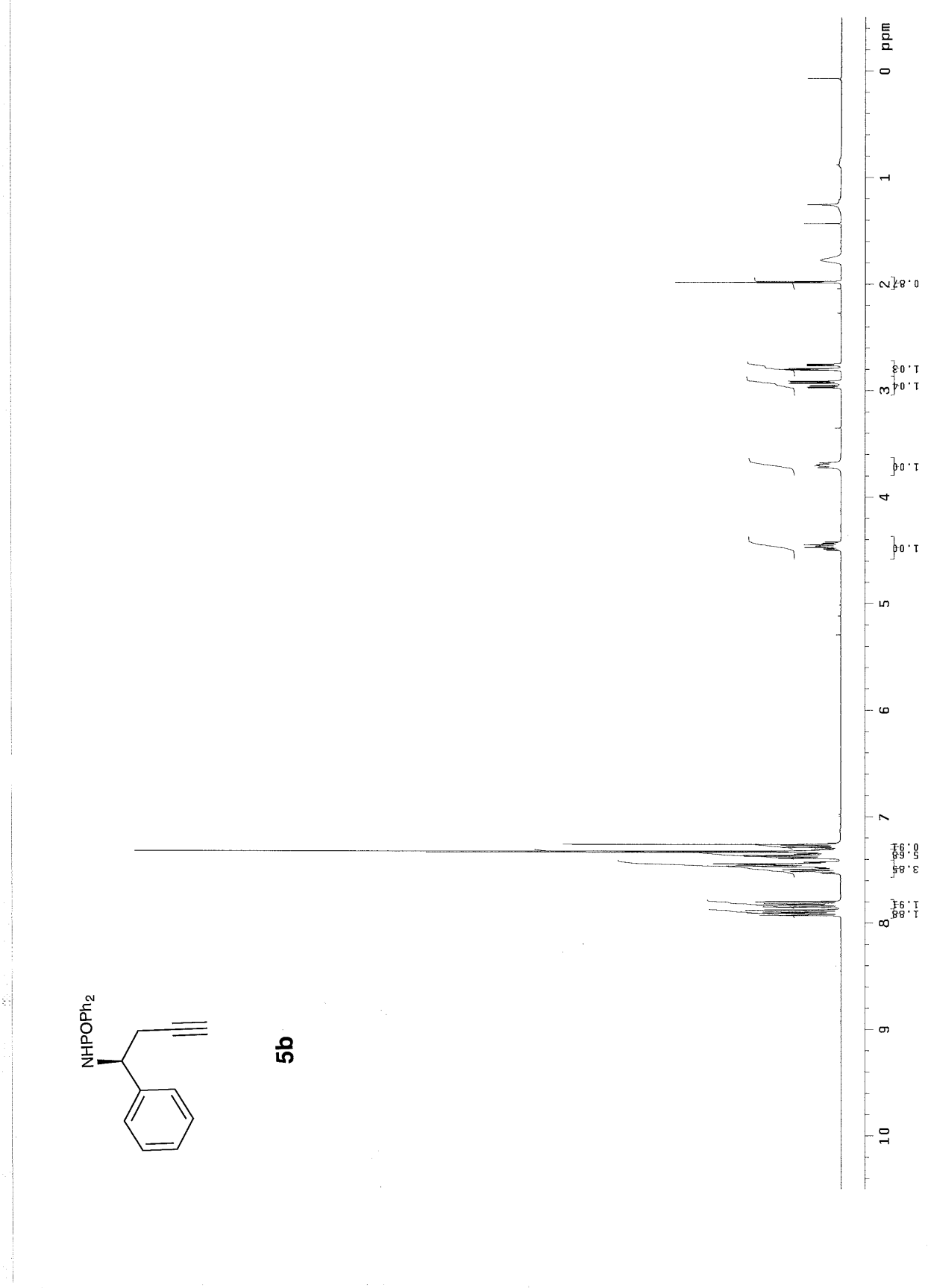
4.02
3.92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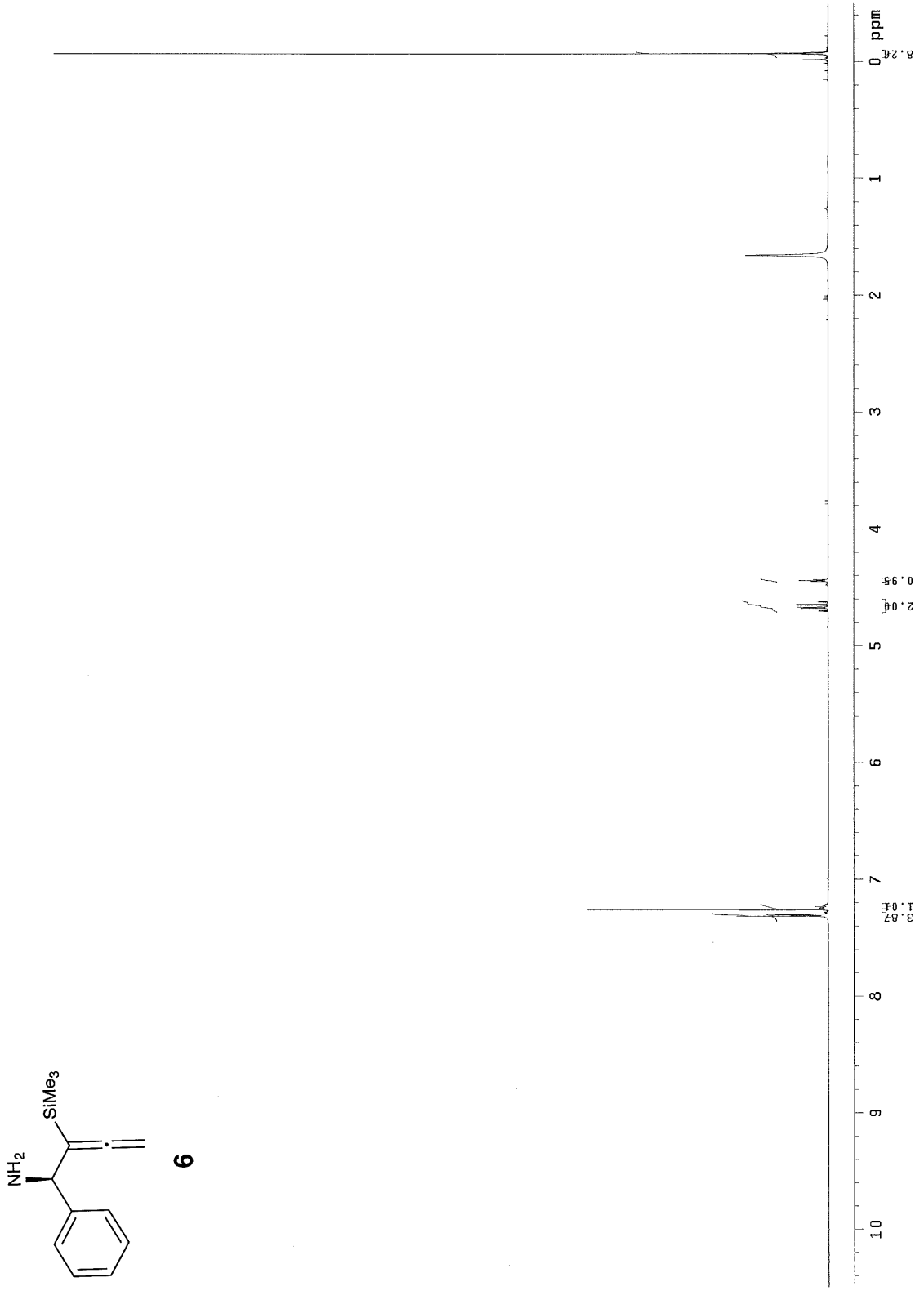

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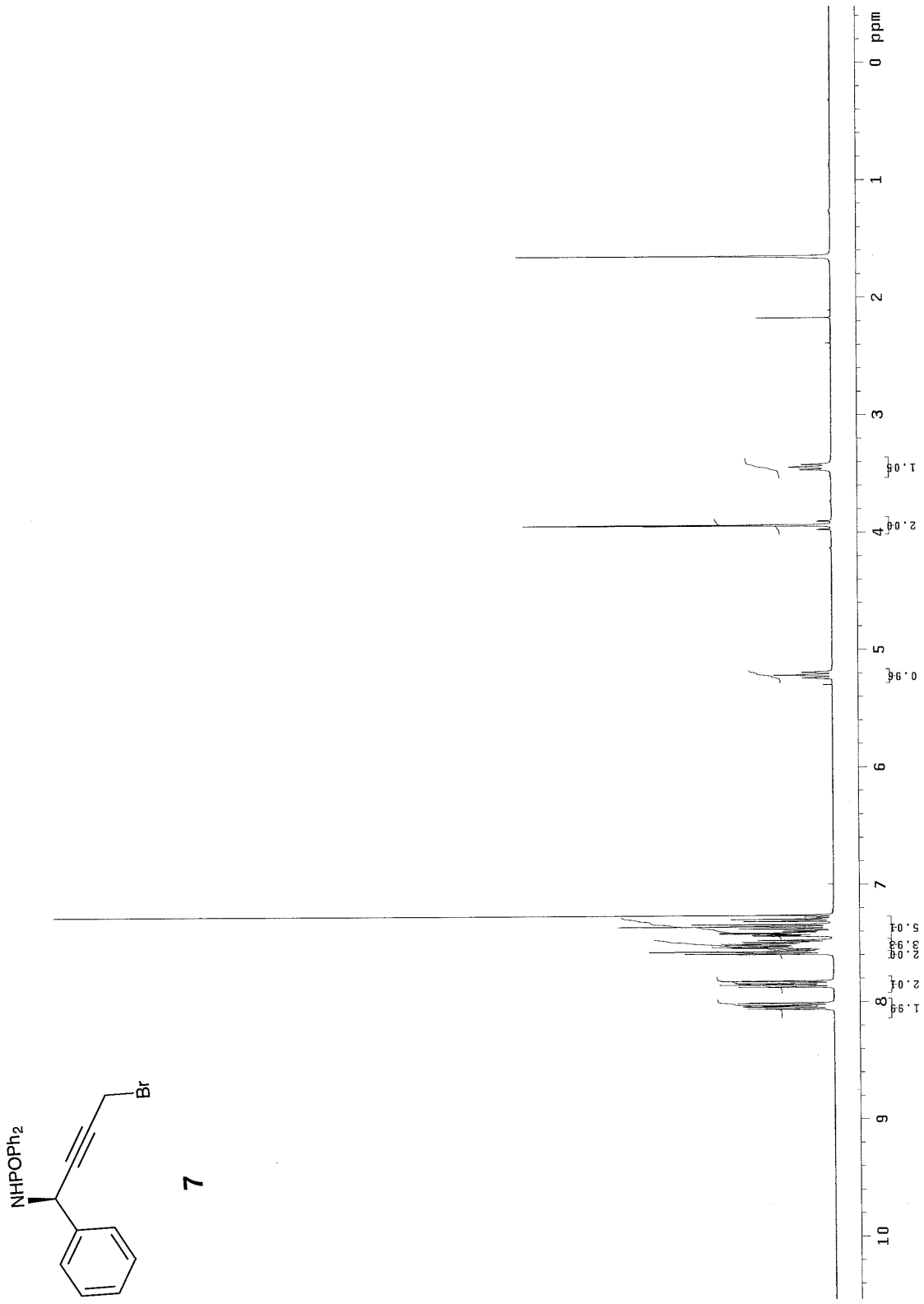
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ppm
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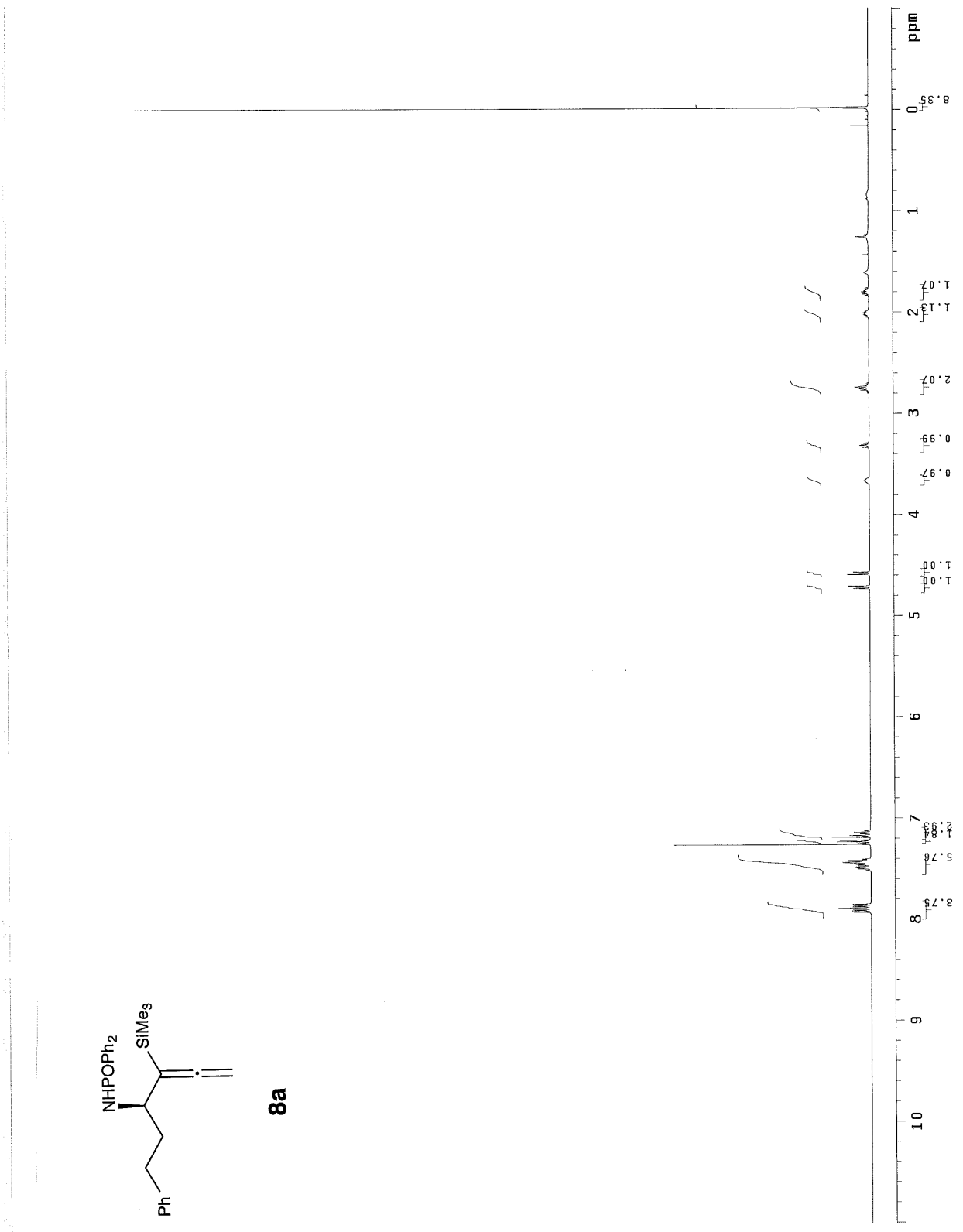
1.99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Ph
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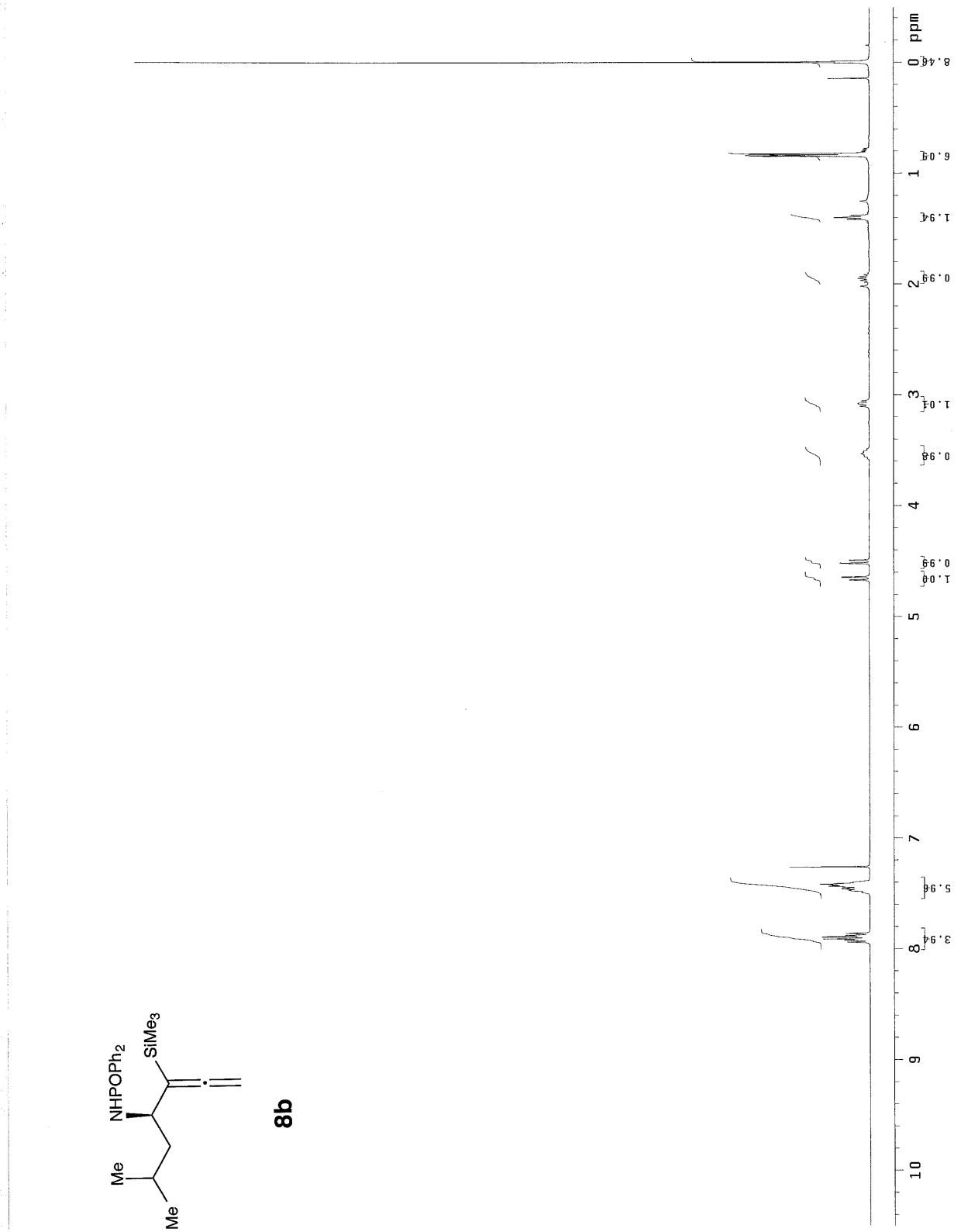
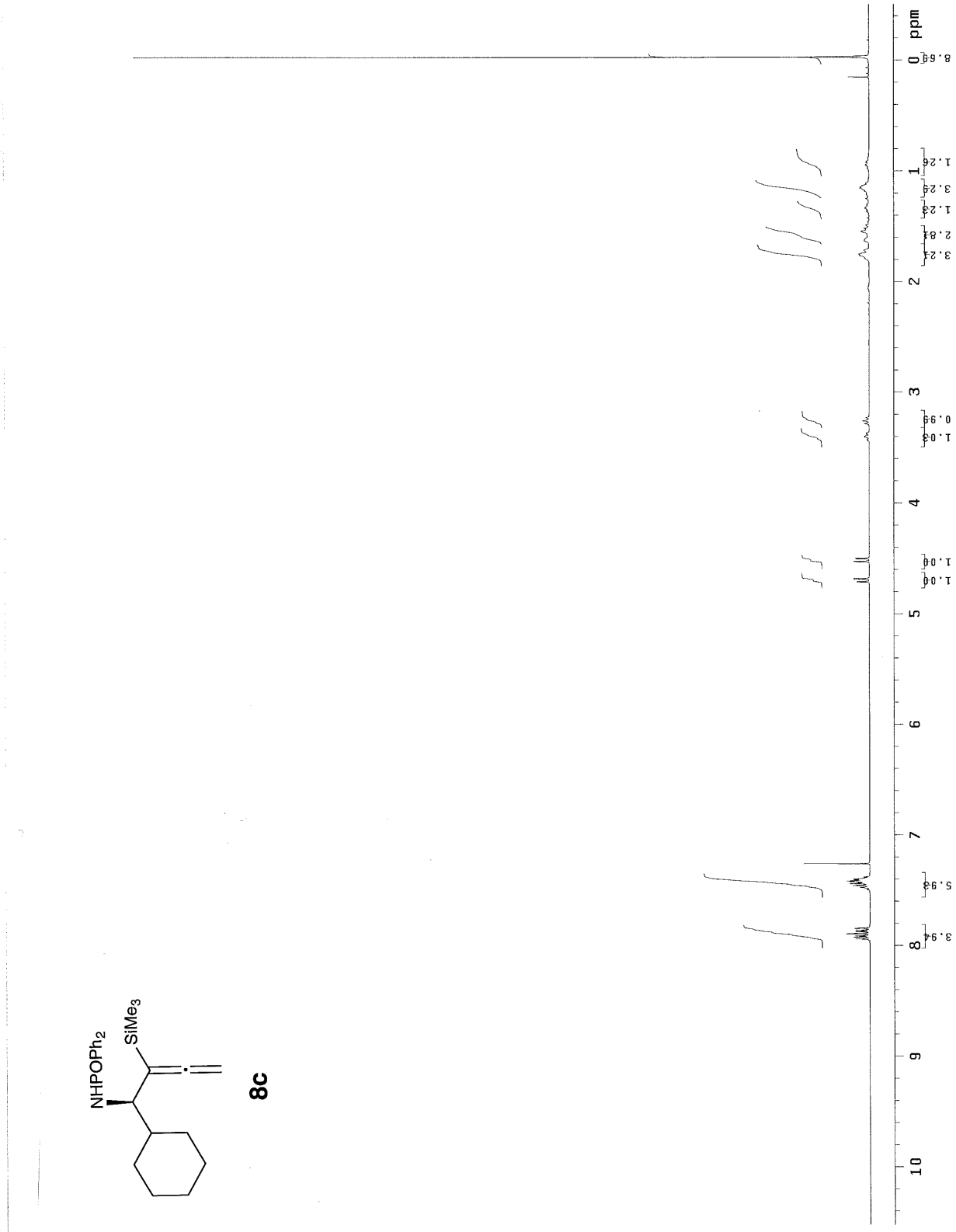
1.84
5.78
3.75


NHPOPh2
SiMe3
Me
Me
8b
ppm
8.46
6.09
1.94
0.99
1.01
0.98
0.99
1.00
5.96
3.94


NHPOPh2
SiMe3
8c
ppm
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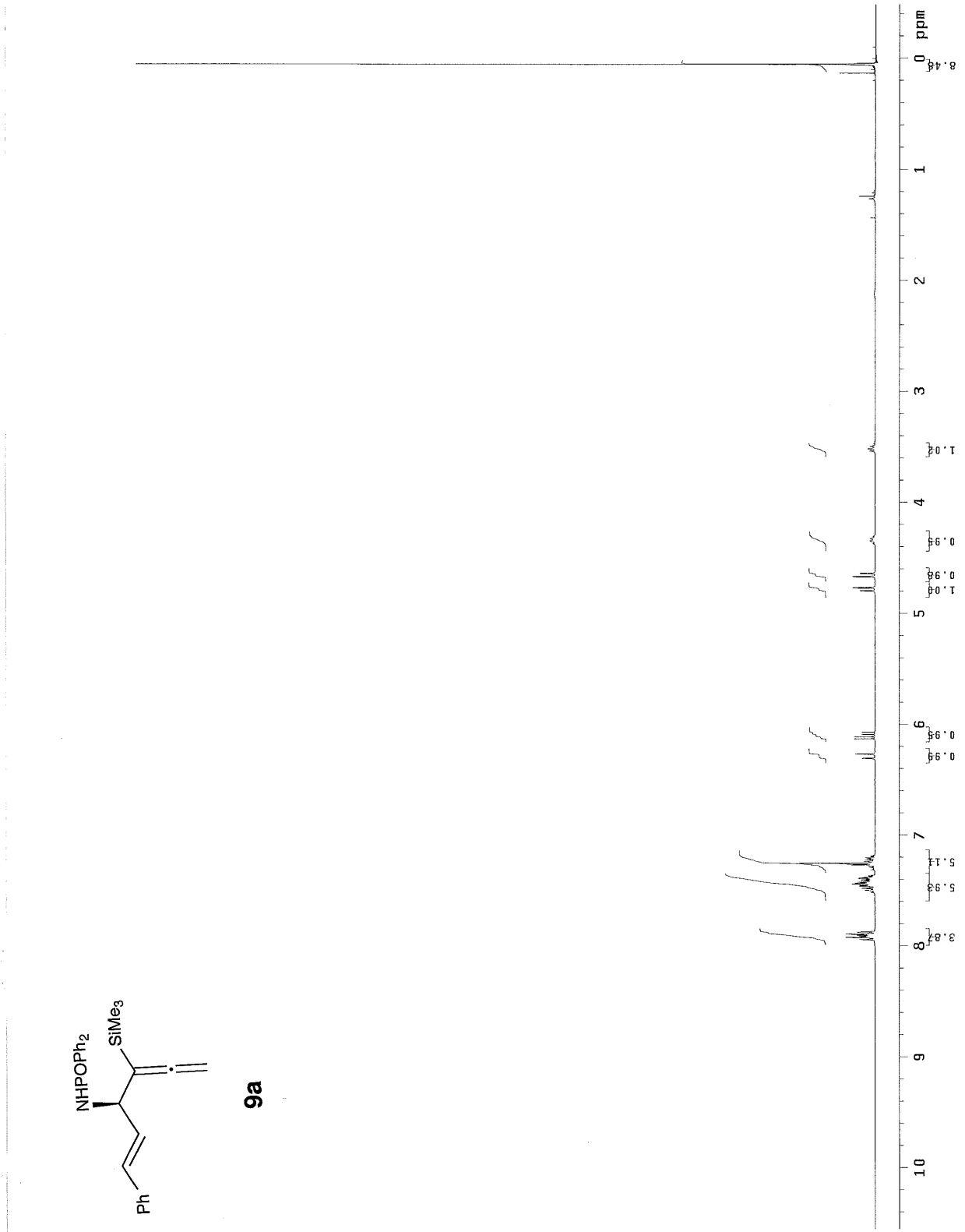
1.26
3.25
1.23
2.81
3.21
0.99
1.03
1.00
1.00
5.93
3.94


NHPOPh2
SiMe3
Ph
9a
ppm
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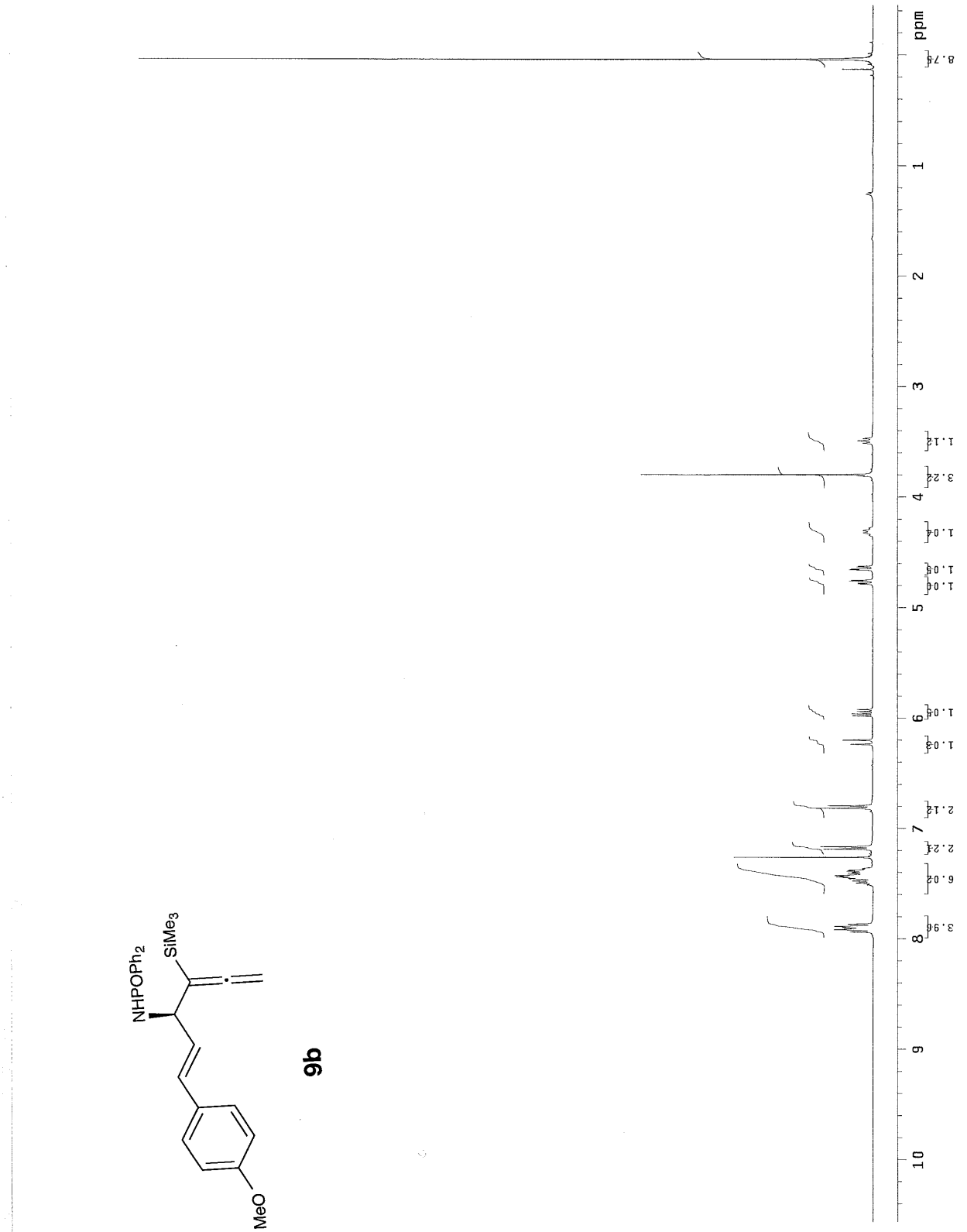
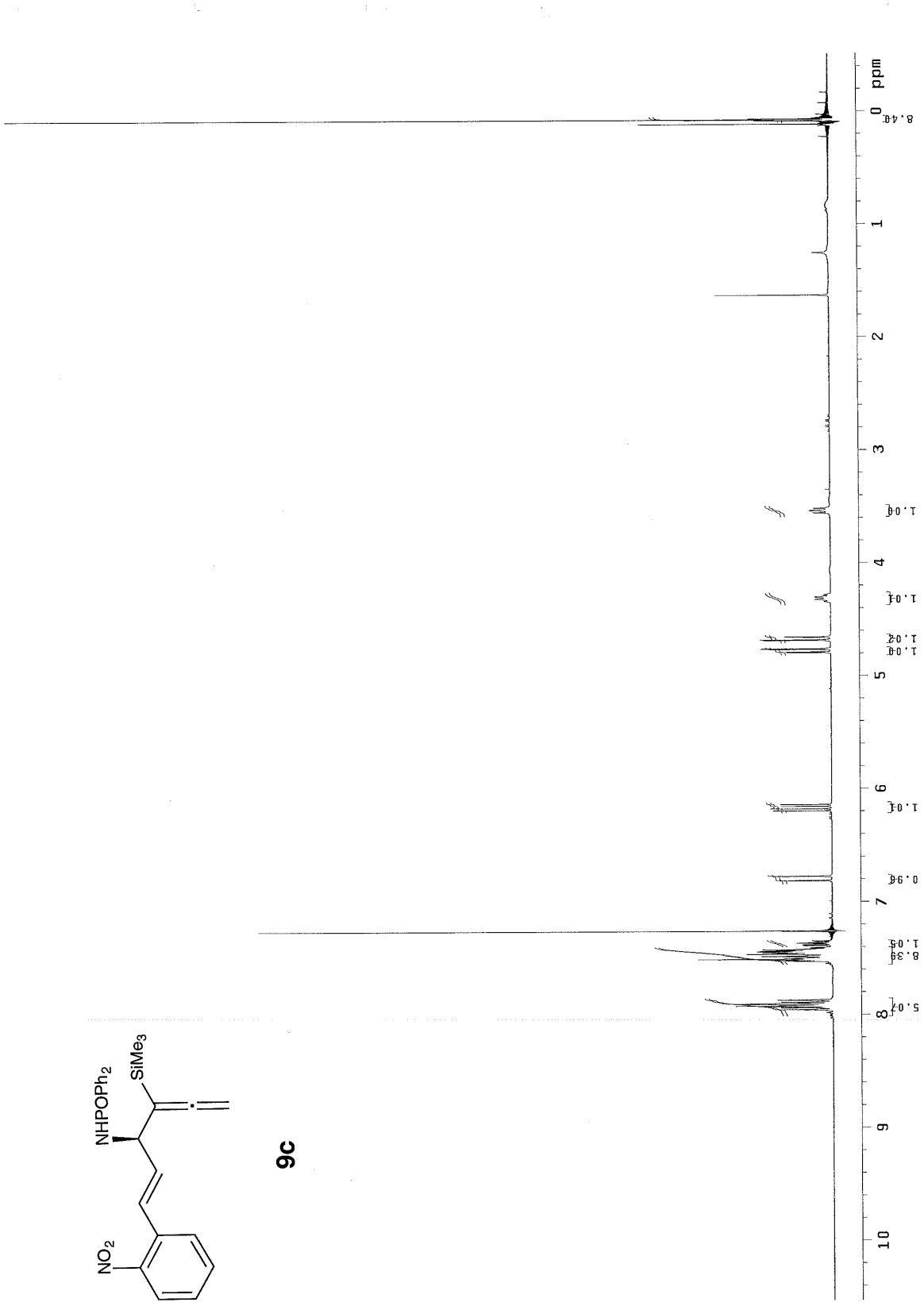
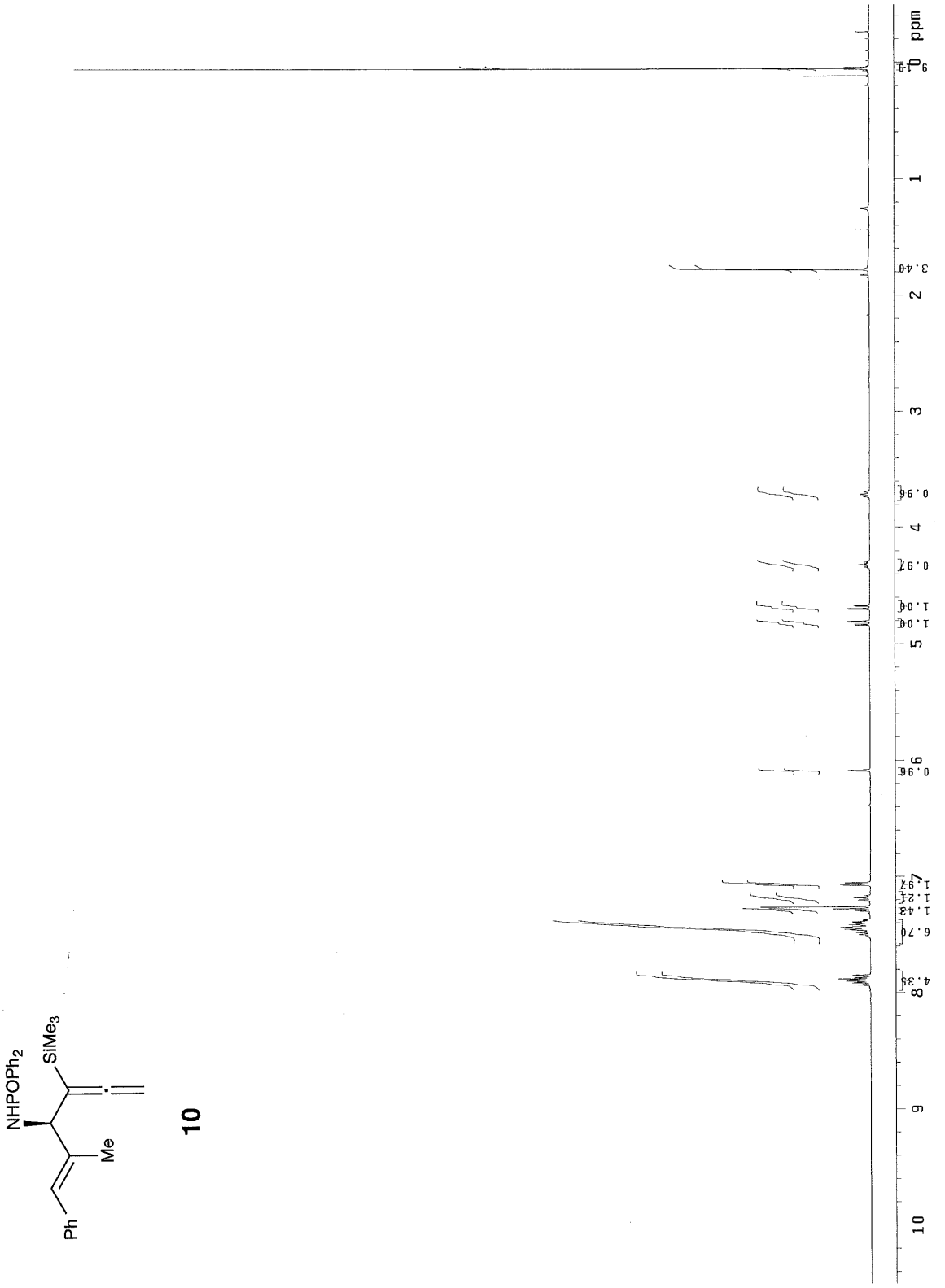
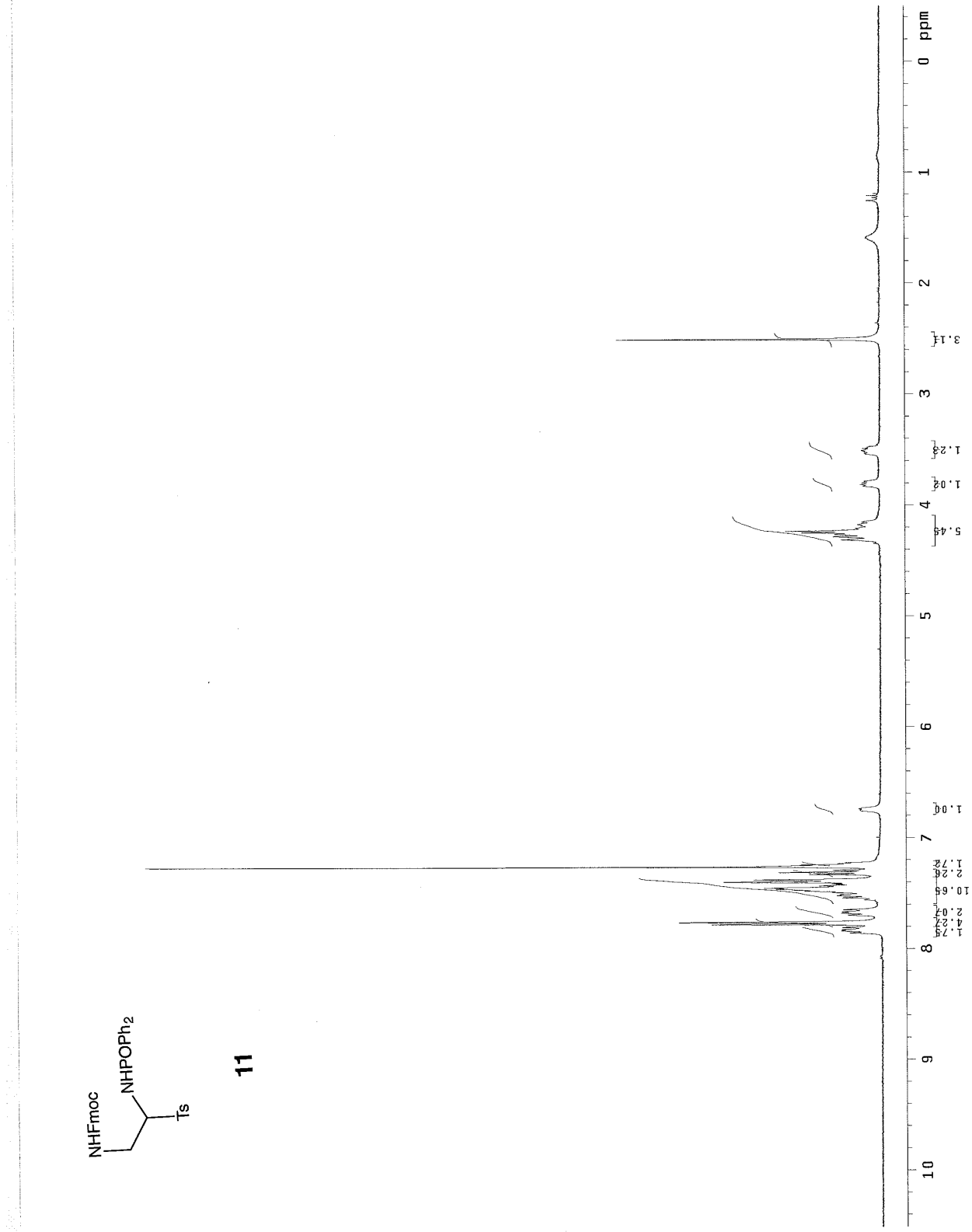
1.02
0.95
0.96
1.00
0.99
0.95
5.11
5.93
3.87


NHPOPh2
SiMe3
MeO
ppm
8.76
1.12
3.22
1.04
1.06
1.06
1.04
1.03
2.12
2.22
6.02
3.96

9b


NHPOPh2
SiMe3
NO2
9c
ppm
0
1
2
3
4
5
6
7
8
9
10
8.44
1.04
1.04
1.02
1.04
1.04
0.96
8.34
1.05
5.04


NHPOPh2
SiMe3
Me
Ph
10
ppm
0
1
2
3
4
5
6
7
8
9
10
4.38
6.76
1.43
1.21
1.97
0.96
1.00
1.00
0.97
0.96
3.40


NHFmoc
NHPOPh2
Ts
11
ppm
0
1
2
3
4
5
6
7
8
9
10
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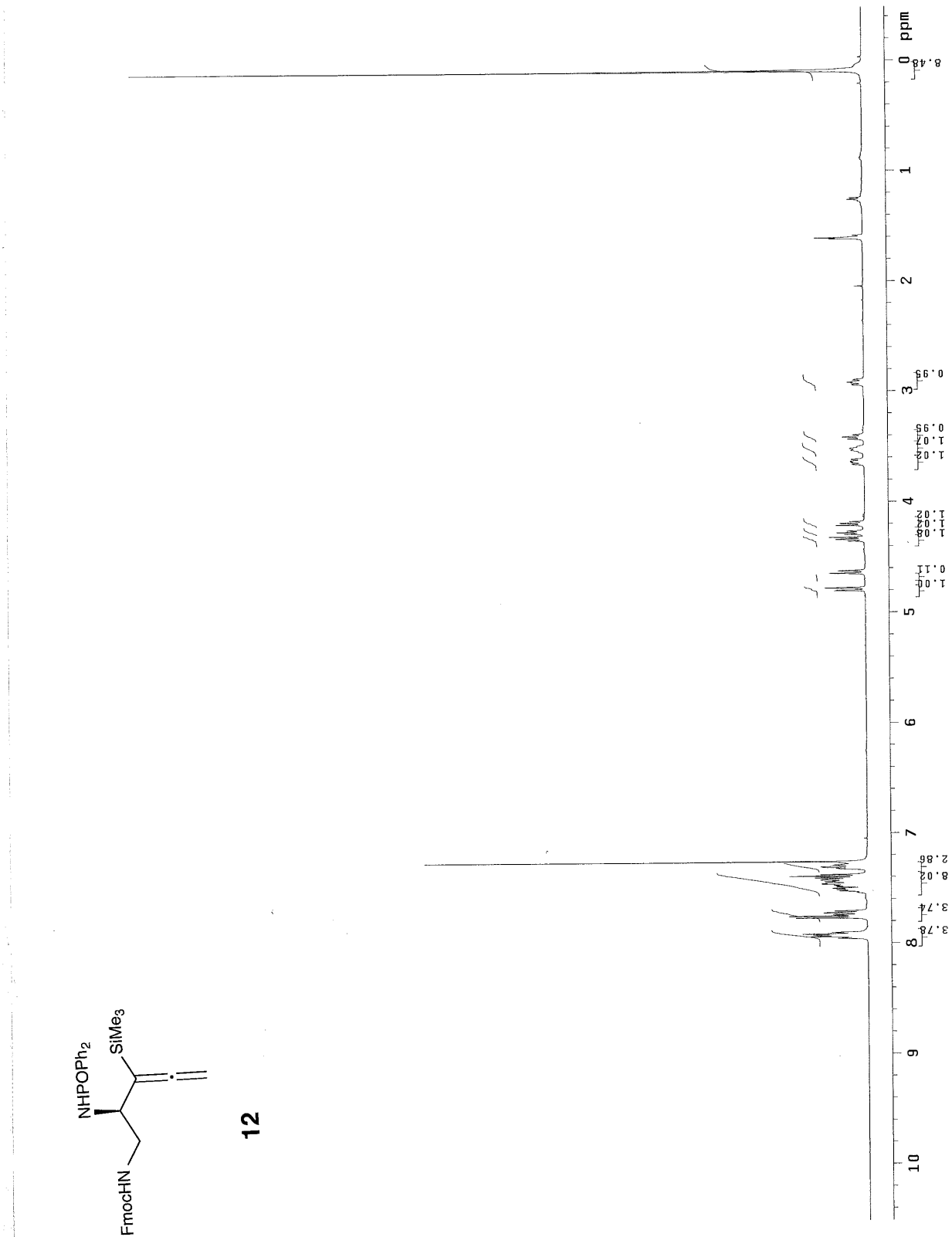
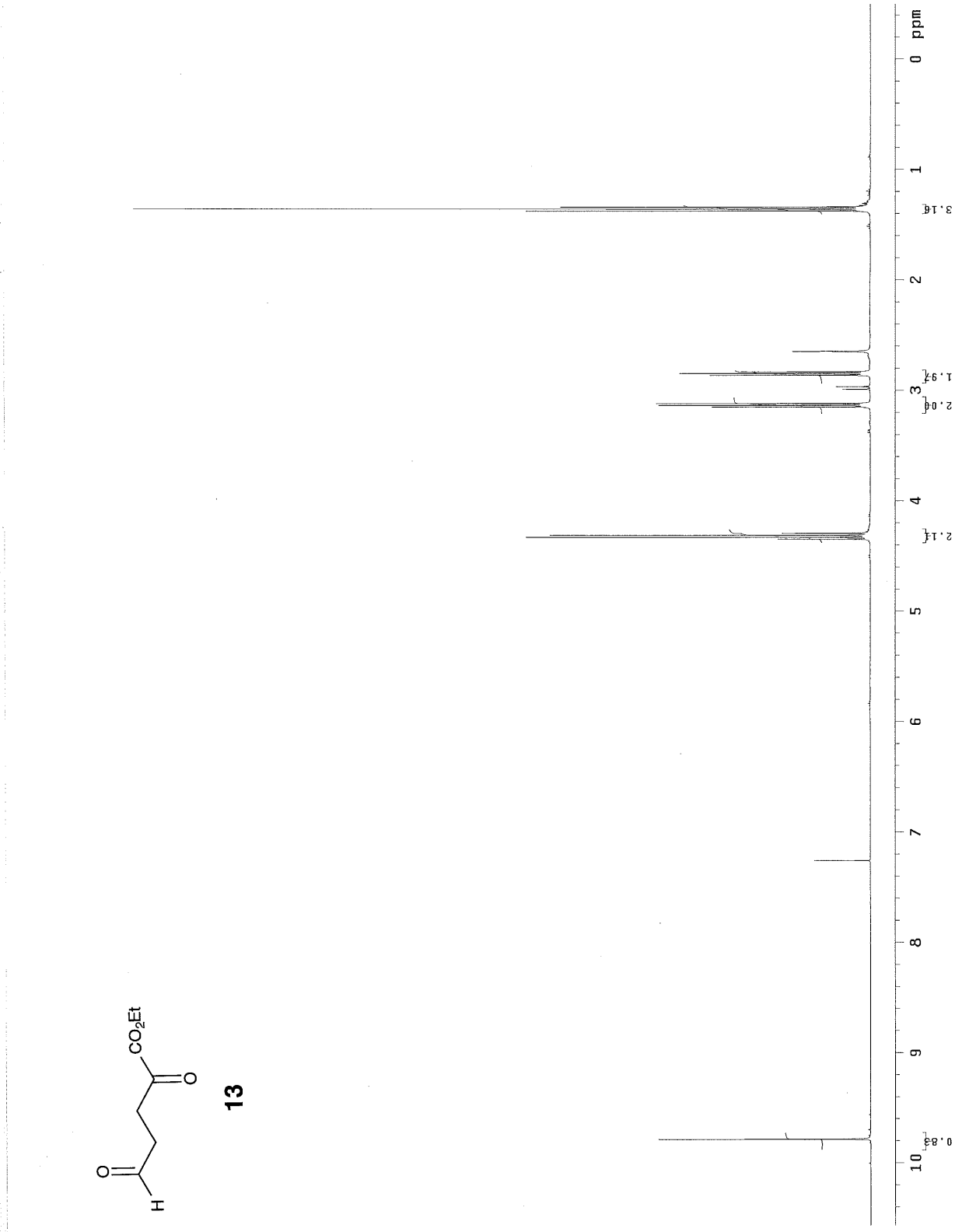
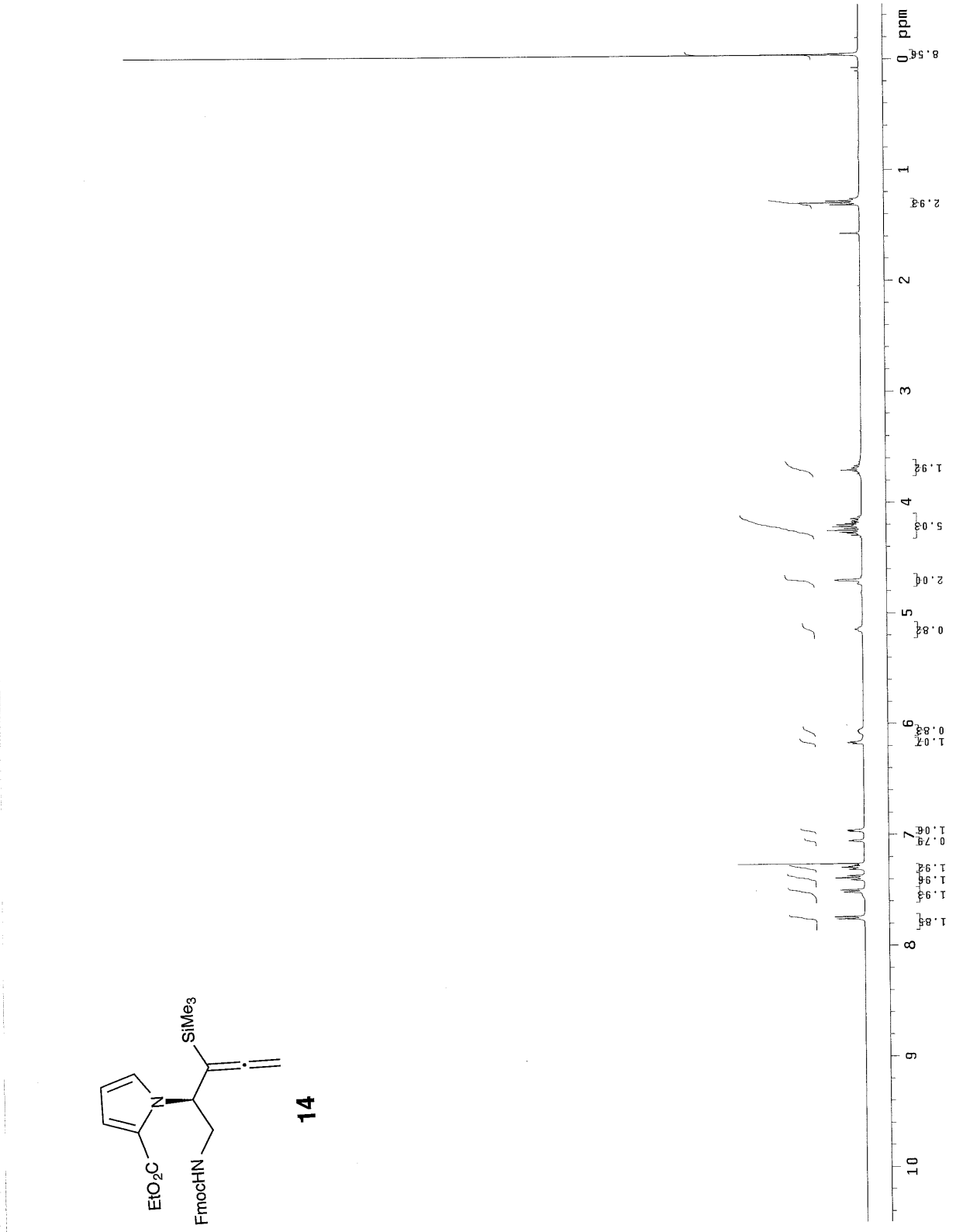
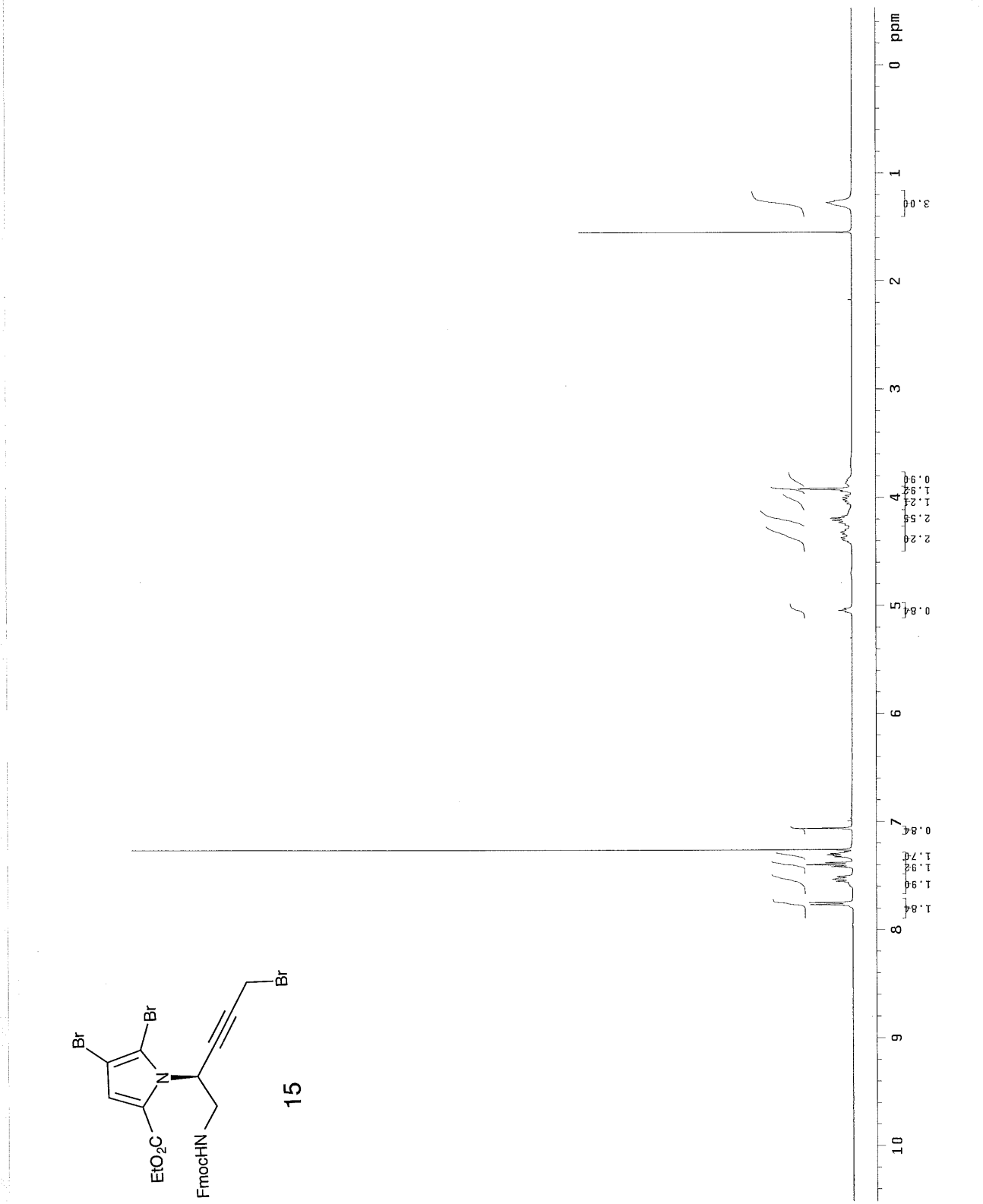
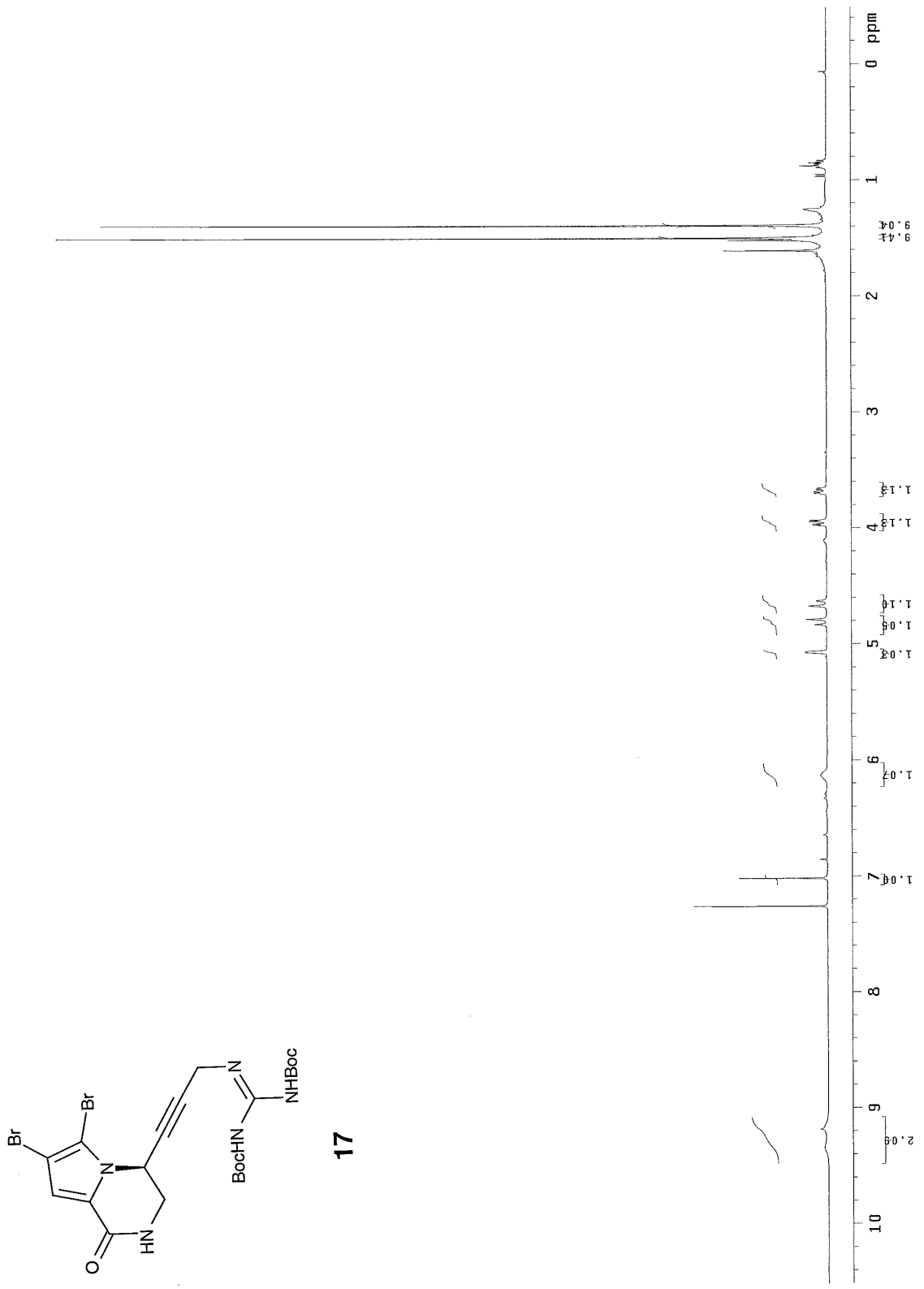
1.23
1.02
5.45
1.00
1.78
2.24
10.65
2.07
4.27
1.79

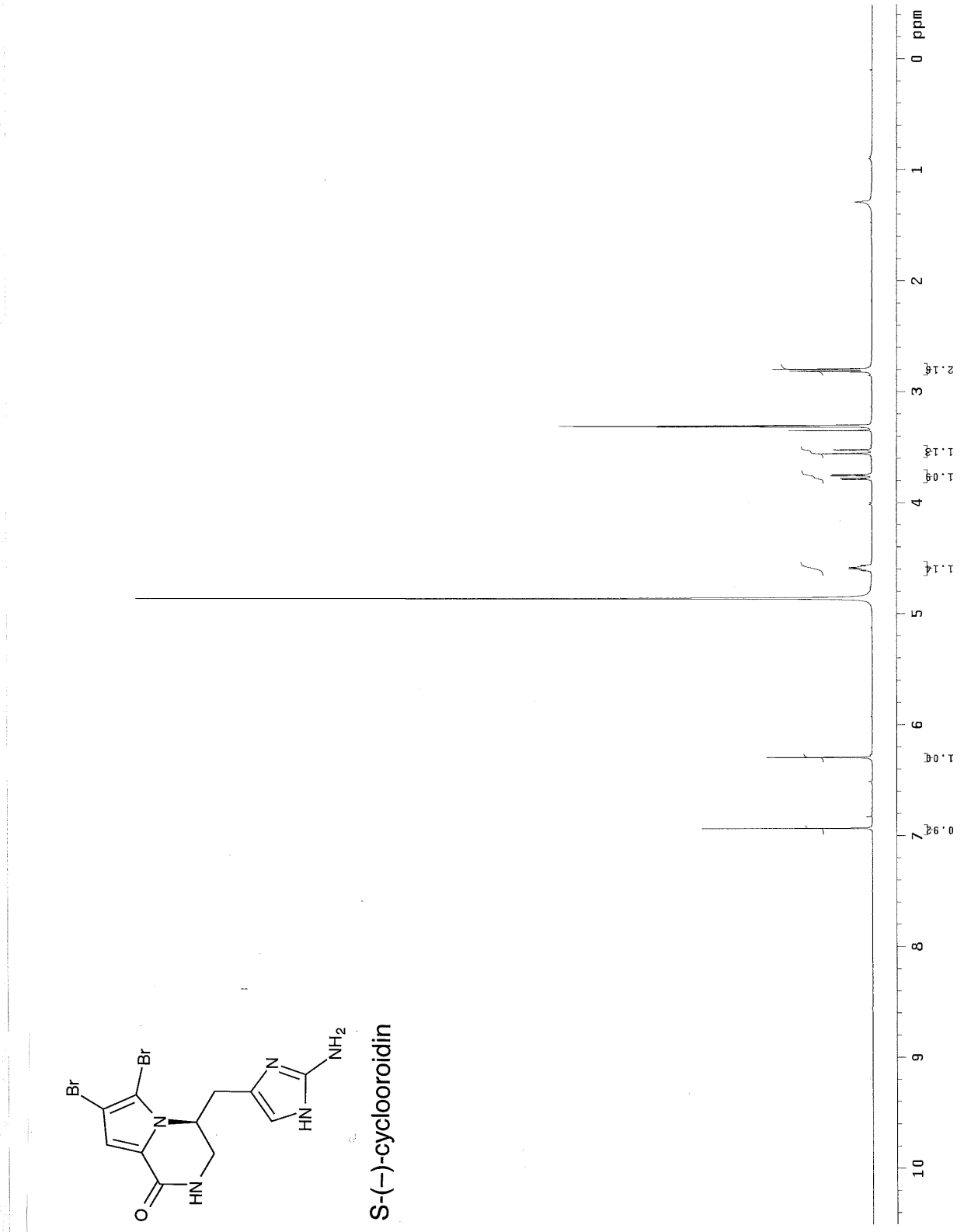

NHPOPh2
SiMe3
FmocHN
12
ppm


CO2Et
O
O
H
13
ppm
0
1
2
3
4
5
6
7
8
9
10
3.16
1.97
2.00
2.11
0.83


SiMe3
N
EtO2C
FmocHN
14
ppm
0
1
2
3
4
5
6
7
8
9
10
8.56
2.93
1.94
5.03
2.04
0.84
1.07
0.84
1.04
0.79
1.94
1.96
1.94
1.85


Br
Br
Br
N
EtO2C
FmocHN
15
ppm
0
1
2
3
4
5
6
7
8
9
10
3.00
2.20
2.55
1.21
1.92
0.90
0.84
1.84
1.90
1.92
1.76
0.84


Br
Br
N
HN
O
BocHN
N
NHBoc
17
ppm
0
1
2
3
4
5
6
7
8
9
10
9.41
9.04
1.13
1.13
1.16
1.05
1.03
1.07
1.08
2.05


Br
Br
N
HN
O
N
HN
NH2
S-(−)-cyclooroidin
ppm
0
1
2
3
4
5
6
7
8
9
10
2.16
1.12
1.00
1.14
1.00
0.92

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