

Supporting Information

Asymmetric Carbolithiation of Conjugated Enynes. A Flow Microreactor Enables the Use of Configurationally Unstable Intermediates Before They Epimerize.

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1. General Remarks.

HPLC analysis was performed on a HITACHI Ezchrom ELITE ver. 3.1.8J with a diode array detector using Daicel Chiralpack AD-H or Daicel Chiralcel OD-H (0.46 mm x 25 cm). ^1H and ^{13}C NMR spectra were recorded on Varian MERCURYplus-400 (^1H 400 MHz, ^{13}C 100 MHz) spectrometer with Me_4Si or CHCl_3 as a standard in CDCl_3 unless otherwise noted. EI mass spectra were recorded on a JEOL JMS-SX102A spectrometer. ESI and APCI mass spectra were recorded on a JEOL JMS-T100CS spectrometer. Optical rotation was measured by JASCO DIP-1000 polarimeter. Stainless steel (SUS304) T-shaped micromixers with inner diameter of 250 μm and 500 μm were manufactured by Sanko Seiki Co., Inc. Stainless steel (SUS316) microtube reactors with inner diameter of 1000 μm were purchased from GL Sciences. The micromixers and the microtube reactors were connected with stainless steel fittings (GL Sciences, 1/16 OUV). The flow microreactor was dipped in a cooling bath to control the temperature. Solutions were introduced to the flow microreactor using syringe pumps, Harvard Model 11 Plus or Harvard PHD 2000, equipped with gastight syringes purchased from SGE.

2. Material.

THF from Kanto Chemical Co., Inc., Toluene from Aldrich Ltd., and DMF from Nakarai Tesque were purchased as a dry solvent and were used without further purification. *N,N,N',N'*-tetramethylethylenediamine (TMEDA), I_2 , Phenylacetylene, 3-methoxyphenylacetylene, 4-chlorophenylacetylene, $\text{Pd}(\text{PPh}_3)_4$, CuI, triethylamine, NaH, 4-phenylbut-3-yn-2-one, chlorodimethyl ether, *n*-BuLi, *s*-BuLi, HexLi, EtLi, (-)-sparteine (**1a**), (*R,R*)-(-)-2,3-dimethoxy-1,4-bis(dimethylamino)butane (**1b**), 2,2-bis((4*S*)-(-)-4-isopropylloxazoline)propane (**1c**), (*S*)-(-)-*N*, α -dimethylbenzylamine (**1d**), (*S*)-(-)-1-methyl-2-pyrrolidine methanol (**1e**), 1-phenyl-1-octyne, methanol, chlorotrimethylsilane, tributyltin chloride, benzophenone, phenyl isocyanate, 4,4'-dibromobenzophenone are commercially available. 4-Phenylbut-1-en-3-yne (**2b**) and vinyl *N,N*-diisopropylcarbamate were synthesized according to the literature.^{1,2}

3. Preparation of Substrates.

Preparation of 1-Iode-1-ethenyl *N,N*-Diisopropylcarbamate. *s*-BuLi (1.04 M in cyclohexane/hexane, 180 mmol, 173 mL) was added dropwise to a solution of TMEDA (21.1g, 181 mmol) in THF (150 mL) at -78 °C. After stirring for 10 min, vinyl *N,N*-diisopropylcarbamate (25.5 g, 149 mmol) was added dropwise to the mixture. After stirring for 70 min, a solution of I₂ (49.8g, 196 mmol) in THF (200 mL) was added to the solution, the reaction mixture was stirred for 30 min. HCl (1M) was added to the resulting solution at -78 °C and the reaction mixture was warmed to room temperature. The mixture was extracted with Et₂O three times. The combined organic phase was washed with sat. aq Na₂S₂O₃ two times, and dried over Na₂SO₄. The filtrate was evaporated and the residue was subjected to silica gel chromatography (hexane/ethyl acetate 90/10 to 80/20) to afford 1-iodo-1-ethenyl *N,N*-diisopropylcarbamate (**4d**) (22.7 g, 51%). ¹H NMR (400 MHz, CDCl₃) δ 1.22-1.32 (m, 12H), 3.66-4.16 (m, 2H), 5.47 (d, *J* = 2.4 Hz, 1H), 5.80 (d, *J* = 2.4 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 20.3 and 21.5, 46.2 and 47.2, 102.2, 117.7, 151.1. HRMS (ESI) *m/z* calcd for C₉H₁₆O₂NINa⁺ [M+Na]⁺: 320.0118., found 320.0122

Preparation of 1-Phenylbut-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2a**).** Phenylacetylene (6.04 g, 59.1 mmol) was added dropwise to a solution of 1-iodo-1-ethenyl *N,N*-Diisopropylcarbamate (15.9 g, 53.5 mmol), Pd(PPh₃)₄ (1.87 g, 1.62 mmol), CuI (839 mg, 4.41 mmol), and triethylamine (10.8 g, 107 mmol) in dry THF (150 mL). The reaction mixture was stirred at room temperature for 3 hours and then it was filtered through Celite. The filtrate was evaporated under the reduced pressure. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 97/3 to 90/10) to afford 1-phenylbut-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (12.5 g, 86%). ¹H NMR (400 MHz, CDCl₃) δ 1.10-1.45 (m, 12H), 3.69-4.21 (m, 2H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 7.28-7.35 (m, 3H), 7.43-7.49 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 20.2 and 21.3, 45.8 and 46.7, 83.8, 88.7, 110.6, 121.9, 128.1, 128.6, 131.6, 136.6, 152.6. HRMS (ESI) *m/z* calcd for C₁₇H₂₁O₂NNa⁺ [M+Na]⁺: 294.1465., found 294.1462

Preparation of 1-Phenyl-3-(methoxymethoxy)-but-3-en-1-yne (2c**).** 4-phenylbut-3-yne-2-one (8.70 g, 60.3 mmol) was added dropwise to a solution of NaH (6.00 g, 250 mmol) in dry DMF (400 mL) over 1 hour at 0 °C. The reaction mixture was stirred at 0 °C for 1 hour and then chlorodimethyl ether was added dropwise to the

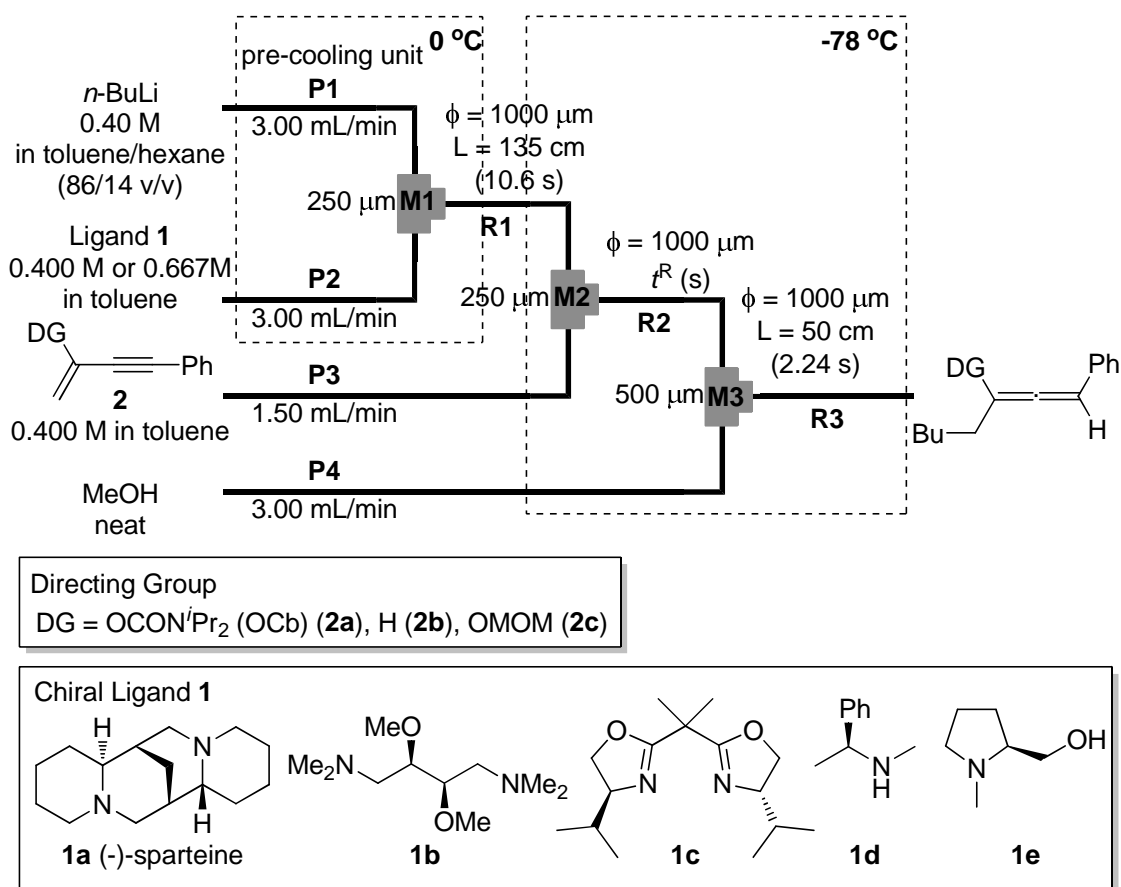
reaction solution over 1 hour. After stirring for 1 hour at 0 °C, Sat. aq. NH₄Cl was added to the reaction solution. The mixture was extracted with EtOAc three times. The combined organic phase was dried over Na₂SO₄. The filtrate was evaporated and the residue was subjected to silica gel chromatography (hexane/ethyl acetate 97/3 to 90/10) to afford 1-phenyl-3-(methoxymethoxy)-but-3-en-1-yne (2.44 g, 21%). ¹H NMR (400 MHz, CDCl₃) δ 3.48 (d, *J* = 0.8 Hz, 3H), 4.83 (dd, *J* = 1.6, 0.8 Hz, 1H), 4.93 (dd, *J* = 1.8, 0.6 Hz, 1H), 5.08 (d, *J* = 0.8 Hz, 2H), 7.28-7.37 (m, 3H), 7.44-7.52 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 56.2, 83.6, 89.1, 94.0, 99.7, 121.9, 128.3, 128.8, 131.7, 142.1. HRMS (APCI) *m/z* calcd for C₁₂H₁₃O₂⁺ [M+H]⁺: 189.0910, found 189.0912.

Preparation of 1-(4-Chlorophenyl)but-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2d). 4-Chlorophenylacetylene (1.60 g, 11.7 mmol) in THF (10 mL) was added dropwise to a solution of 1-iodo-1-ethenyl *N,N*-Diisopropylcarbamate (3.16 g, 10.6 mmol), Pd(PPh₃)₄ (381 mg, 0.330 mmol), CuI (172 mg, 0.903 mmol), and triethylamine (2.18 g, 21.5 mmol) in dry THF (30 mL). The reaction mixture was stirred at room temperature for 16 hours and then it was filtered through Celite. The filtrate was evaporated under the reduced pressure. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 95/5 to 90/10) to afford 1-(4-chlorophenyl)but-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (2.14 g, 66%). ¹H NMR (400 MHz, CDCl₃) δ 1.09-1.48 (m, 12H), 3.70-4.20 (m, 2H), 5.27 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 7.25-7.31 (m, 3H), 7.35-7.41 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 20.1 and 21.2, 45.8 and 46.6, 84.7, 87.4, 110.9, 120.3, 128.4, 132.7, 134.6, 136.3, 152.3. HRMS (ESI) *m/z* calcd for C₁₇H₂₀O₂NCINa⁺ [M+Na]⁺: 328.1075, found 328.1083.

Preparation of 1-(3-Methoxyphenyl)but-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2e). 3-Methoxyphenylacetylene (9.48 g, 71.7 mmol) in THF (40 mL) was added dropwise to a solution of 1-iodo-1-ethenyl *N,N*-Diisopropylcarbamate (16.7 g, 56.2 mmol), Pd(PPh₃)₄ (2.27 g, 1.97 mmol), CuI (978 mg, 5.13 mmol), and triethylamine (13.2 g, 130 mmol) in dry THF (200 mL). The reaction mixture was stirred at room temperature for 3 hours and then it was filtered through Celite. The filtrate was evaporated under the reduced pressure. The crude product was purified by silica gel chromatography (hexane/ethyl acetate 97/3 to 90/10) to afford 1-(3-methoxyphenyl)but-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (10.6 g, 63%). ¹H NMR (400 MHz, CDCl₃) δ 1.09-1.45 (m, 12H), 3.80 (s, 3H), 3.70-4.20 (m, 2H), 5.26 (d, *J* = 1.2 Hz, 1H), 5.33 (d, *J* = 1.2 Hz, 1H), 6.89 (ddd, *J* = 8.3, 2.7, 1.1 Hz,

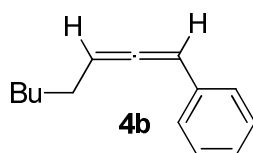
1H), 6.99 (dd, $J = 2.8, 1.2$ Hz, 1H), 7.06 (dd, $J = 7.6, 1.2$ Hz, 1H), 7.22 (dd, $J = 8.2, 8.2$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 20.2 and 21.3, 45.9 and 46.7, 55.1, 83.6, 88.6, 110.7, 115.3, 116.4, 122.9, 124.1, 129.2, 136.5, 152.6., 159.1. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{23}\text{O}_3\text{NNa}^+$ $[\text{M}+\text{Na}]^+$: 324.1570., found 324.1577

4. Typical Procedure for Carbolithiation of Conjugated Enynes (**2**) Having a Directing Group with *n*-BuLi in the Presence of a Chiral Ligand (**1**) Using a Flow Microreactor.



A flow microreactor consisting of three T-shaped micromixers (**M1** ($\phi = 250 \mu\text{m}$), **M2** ($\phi = 250 \mu\text{m}$) and **M3** ($\phi = 500 \mu\text{m}$)), three microtube reactors (**R1** ($\phi = 1000 \mu\text{m}$, $L = 135 \text{ cm}$ (25 cm at 0°C , 10 cm at ambient temperature, and 100 cm at -78°C), **R2** ($\phi = 1000 \mu\text{m}$, $L = 3.5 \text{ cm}$ to 200 cm) and **R3** ($\phi = 1000 \mu\text{m}$, $L = 50 \text{ cm}$)), and four tube pre-cooling units (**P1-P4** ($\phi = 1000 \mu\text{m}$, $L = 50 \text{ cm}$)) was used. The flow microreactor was dipped in a cooling bath (0°C and -78°C). A solution of *n*-BuLi (0.40 M) in toluene/hexane (86/14 v/v, flow rate: 3.00 mL min^{-1}) and a solution of ligand **1** (0.400 M or 0.667 M) in toluene (flow rate: 3.00 mL min^{-1}) were introduced to **M1** by syringe

pumps. The resulting solution was passed through **R1** and was mixed with a solution of 3-directing group-substituted-4-phenyl-but-1-en-3-yne (**2**) (0.400 M) in toluene (flow rate: 3.00 mL min⁻¹) in **M2**. The resulting solution was passed through **R2** and was mixed with methanol (neat) (flow rate: 3.00 mL min⁻¹) in **M3**. The resulting solution was passed through **R3**. After a steady state was reached, the product solution was collected for 30 s while being quenched with Sat. aq. NH₄Cl and was analyzed by HPLC. HPLC yield was calibrated with acetophenone or methyl benzoate as an internal standard. The crude mixture was extracted with Et₂O three times and dried over Na₂SO₄. The filtrate was evaporated and the residue was purified by silica gel chromatography. The results are summarized in Table S-1.



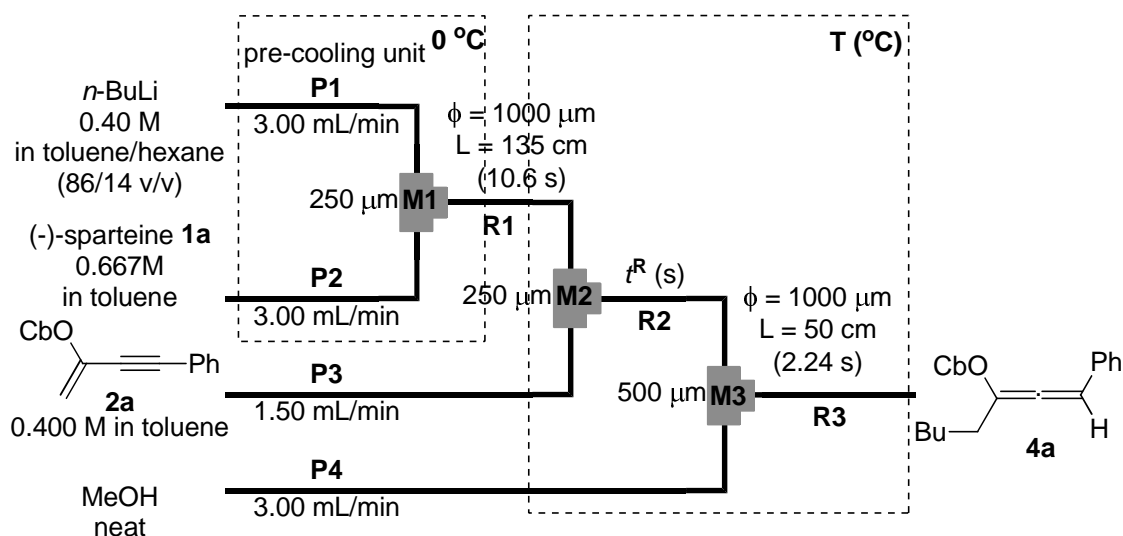
1-Phenylbuta-1,3-diene (4b). 83% HPLC yield (internal standard: methyl benzoate). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm × 25 cm); eluent: hexane; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 6.0, 6.6 min). [α]_D²⁹ -58.4 (c 2.28, CH₂Cl₂, er 61:39). ¹H NMR (400 MHz, CDCl₃) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.22-1.40 (m, 4H), 1.42-1.54 (m, 2H), 2.08-2.17 (m, 2H), 5.56 (dd, *J* = 13.2, 6.6 Hz, 1H), 6.08-6.15 (m, 1H), 7.14-7.22 (m, 1H), 7.26-7.33 (m, 4H). ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 22.5, 28.7, 28.8, 31.4, 94.5, 95.0, 126.5, 128.5, 135.1, 205.1. Some signals were overlapped. HRMS (EI) *m/z* calcd for C₁₄H₁₈: 186.1409, found 186.1409.

Table S-1. Enantioselective Carbolithiation of **2** with *n*-BuLi in the Presence of Various Ligands in a Flow Microreactor System.

entry	substrate	ligand	product	<i>t</i> ^R (s)	yield (%) ^a	
					product (er)	SM
1	2a	1a	4a	12.6	91 (88:12)	4
2 ^b	2a	1a	4a	12.6	82 (93:7)	10
3 ^b	2b	1a	4b	0.220	38 (61:39), 7 ^c	57
4 ^b	2b	1a	4b	0.785	53 (62:38), 9 ^c	40
5 ^b	2b	1a	4b	3.14	66 (60:40), 11 ^c	25
6 ^b	2b	1a	4b	12.6	83 (61:39), 14 ^c	1
7 ^b	2c	1a	4c	12.6	0	91
8	2a	1b	4a	12.6	57 (52:48)	36
9	2a	1c	4a	12.6	<1 (45:55)	88
10	2a	1d	4a	12.6	<1 (34:66)	98
11	2a	1e	4a	12.6	0	>99

^a Determined by chiral HPLC. Enantiomer ratio (er) is shown in parenthesis. ^b **1a** (0.67 M in toluene, 3.0 mL/min). ^c Yield of 1-phenyl-1-octyne.

5. Typical Procedure for Carbolithiation of 1-Phenylbut-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2a**) with *n*-BuLi in the Presence of (-)-Sparteine (**1**) Using a Flow Microreactor.**

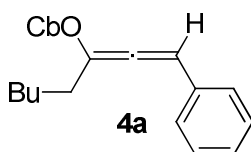


A flow microreactor consisting of three T-shaped micromixers (**M1** ($\phi = 250 \mu\text{m}$), **M2** ($\phi = 250 \mu\text{m}$) and **M3** ($\phi = 500 \mu\text{m}$)), three microtube reactors (**R1** ($\phi = 1000 \mu\text{m}$, $L = 135 \text{ cm}$ (25 cm at 0 °C, 10 cm at ambient temperature, and 100 cm at -78 °C), **R2** ($\phi = 500 \mu\text{m}$ or $1000 \mu\text{m}$, $L = 3.5 \text{ cm}$ to 400 cm) and **R3** ($\phi = 1000 \mu\text{m}$, $L = 50 \text{ cm}$)), and four tube pre-cooling units (**P1-P4** ($\phi = 1000 \mu\text{m}$, $L = 50 \text{ cm}$)) was used. The flow microreactor was dipped in a cooling bath (0 °C and T °C). A solution of *n*-BuLi (0.40 M) in toluene/hexane (86/14 v/v, flow rate: 3.00 mL min^{-1}) and a solution of (-)-sparteine **1a** (0.667 M) in toluene (flow rate: 3.00 mL min^{-1}) were introduced to **M1** by syringe pumps. The resulting solution was passed through **R1** and was mixed with a solution of 1-phenylbut-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (**2a**) (0.400 M) in toluene (flow rate: 3.00 mL min^{-1}) in **M2**. The resulting solution was passed through **R2** and was mixed with methanol (neat) (flow rate: 3.00 mL min^{-1}) in **M3**. The resulting solution was passed through **R3**. After a steady state was reached, the product solution was collected for 30 s while being quenched with Sat. aq. NH_4Cl and was analyzed by HPLC. HPLC yield was calibrated with acetophenone as an internal standard. The crude mixture was extracted with Et_2O three times and dried over Na_2SO_4 . The filtrate was evaporated and the residue was purified by silica gel chromatography. The results are summarized in Table S-2.

Table S-2. Effects of Temperature and Residence Time of **R2** on the Yield and the Enantiomer composition (ec) of **4a**.

T (°C)	microtube reactor R2			SM (%)	product (%)	ec (%)
	ϕ (μm)	L (cm)	t^R (s)			
-78	500	3.5	0.0550	84	17	95
-78	1000	3.5	0.220	84	18	94
-78			0.785	75	27	94
-78			3.14	42	58	94
-78			12.6	10	82	93
-78			25.1	0	91	91
-78 ^a			50.2	0	92	86
-68	500	3.5	0.0550	46	54	93
-68	1000	3.5	0.220	47	55	92
-68			0.785	30	71	93
-68			3.14	4	98	90
-68			12.6	0	99	85
-68			25.1	0	99	77
-68 ^a			50.2	0	99	68
-48	500	3.5	0.0550	25	73	85
-48	1000	3.5	0.220	25	73	83
-48			0.785	7	91	73
-48			3.14	0	99	61
-48			12.6	0	97	56
-48			25.1	0	95	56
-48 ^a			50.2	0	99	56
-28	500	3.5	0.0550	8	90	68
-28	1000	3.5	0.220	0	99	57
-28			0.785	0	99	56
-28			3.14	0	99	56
-28			12.6	0	99	56
-28			25.1	0	99	56
-28 ^a			50.2	0	99	56

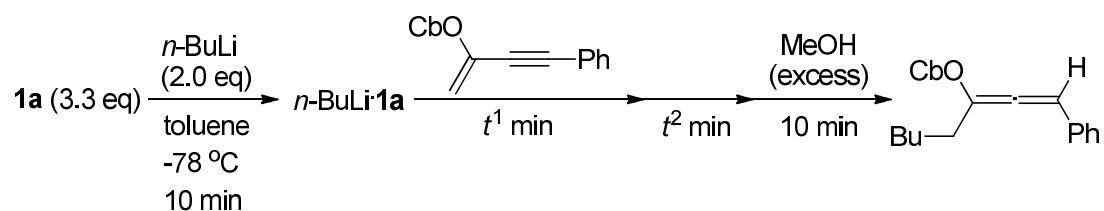
^a Flow rates of all solutions were a half of the standard ones.



1-Phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4a). 91% HPLC yield; 76% Isolated yield (75.3 mg) purified by silica gel chromatography (hexane/ethyl acetate 95/5 to 90/10). HPLC analysis (column: Daicel Chiralpack AD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 5.5, 6.4 min). $[\alpha]_D^{25}$ -128.0 (*c* 0.650, CH_2Cl_2 , er 91:9). ^1H NMR (400 MHz, CDCl_3) δ 0.86 (t, J = 7.2 Hz, 3H), 1.14-1.42 (m, 16H), 1.44-1.56 (m, 2H), 2.30-2.46 (m, 2H), 3.60-4.28 (m, 2H), 6.58 (t, J = 3.0 Hz, 1H), 7.20-7.26 (m, 1H), 7.29-7.36 (m, 2H), 7.42-7.47 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 14.0, 20.6 and 21.5, 22.4, 26.0, 31.2,

32.2, 45.5 and 46.8, 103.8, 127.5, 127.6, 127.7, 128.6, 134.5, 153.4, 197.6. HRMS (EI) m/z calcd for $C_{21}H_{31}O_2N$: 329.2355, found 329.2355.

6. Typical Procedure for Carbolithiation of 1-Phenylbut-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2a) with *n*-BuLi in the Presence of (-)-Sparteine (1) Using a Batch Macroreactor.



A solution of *n*-BuLi (0.400 M, 1.50 mL) in toluene/hexane (86/14 v/v) was added dropwise to a solution of (-)-sparteine (**1a**) (0.667 M, 1.50 mL) in toluene in a 20 mL round-bottomed flask at -78 °C under argon. After the mixture was stirred for 10 min, a solution of 1-phenylbut-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (**2a**) (0.400 M, 0.75 mL) in toluene was added dropwise (t^1 min). After the mixture was stirred for t^2 (min), methanol (neat M, 1.50 mL) was added dropwise (1.0 min) to the reaction solution. After stirring for 10 min, the product solution was quenched by sat. aq. NH_4Cl and was analyzed by HPLC. The results are summarized in Table S-3.

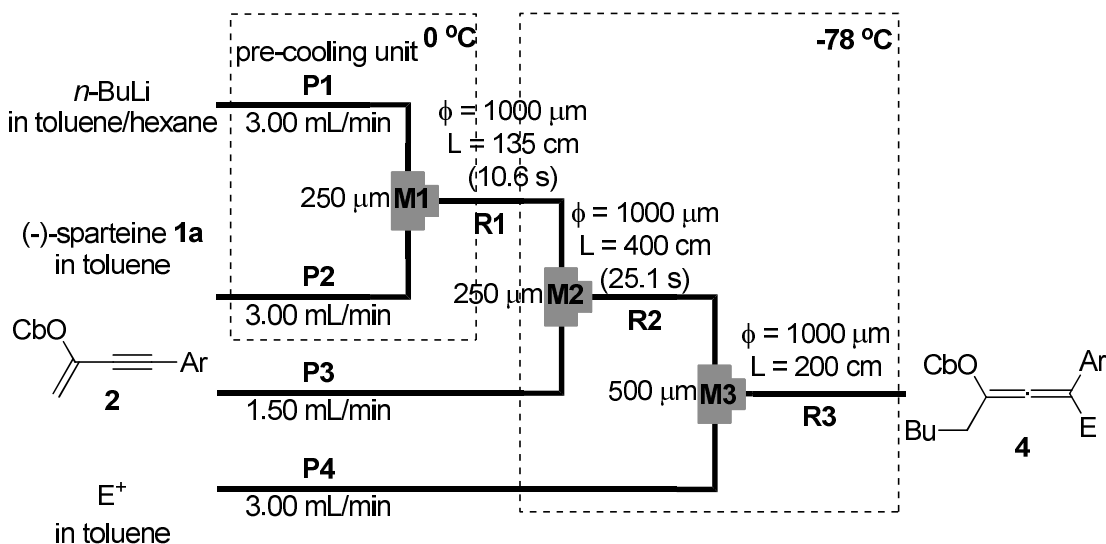
Table S-3. The Carbolithiation Reaction in a Batch Macroreactor.

entry	t^1 (min)	t^2 (min)	Yield (%)	er
1	1.0	5.0	94	63:27
2	1.0	20.0	93	58:42
3	1 (s)	24 (s)	99	61:39

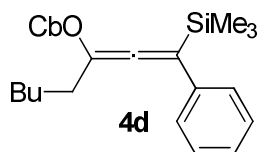
7. Hoffman Test (Reaction of 0.10 eq or 1.5 eq of Chiral Organolithium intermediate (3a) with Me_3SiCl). A solution of *n*-BuLi (2.76 M, 217 μ L) in toluene/hexane (86/14 v/v) was added dropwise to a solution of (-)-sparteine (**1a**) (0.200 M, 3.00 mL) in toluene at -78 °C under argon. After the mixture was stirred for 10 min, a solution of 1-phenylbut-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (**2a**) (0.400 M, 1.50 mL) in toluene was added dropwise (2 min). After the mixture was stirred for 30 min, chlorotrimethylsilane (6.5 mg, 0.0600 mmol or 97.0 mg, 0.893 mmol) was added dropwise to the reaction solution. After stirring for 30 min, the product solution was quenched by sat. aq. $NaHCO_3$. The mixture was extracted with Et_2O three times and dried over Na_2SO_4 . The filtrate was evaporated and the residue was subjected to silica

gel chromatography (hexane/ethyl acetate 99/1 to 96/4) to afford 1-trimethylsilyl-1-phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (**4d**) (15.4 mg, 6% or 177.4 mg, 74%).

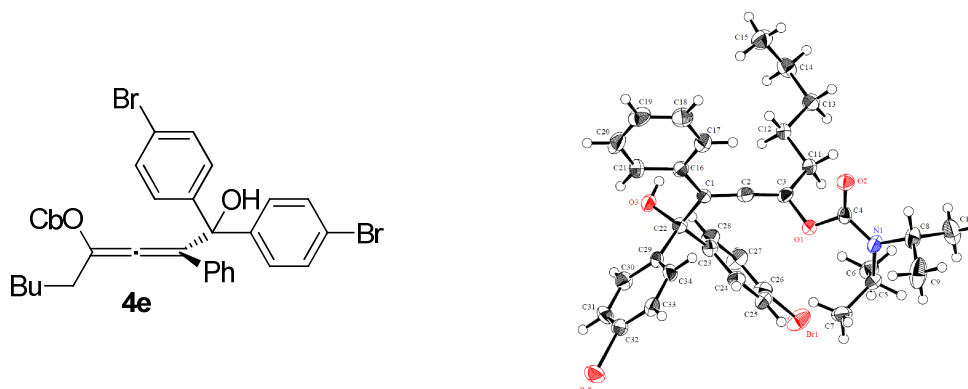
8. Typical Procedure for Reactions with Electrophiles.



A flow microreactor consisting of three T-shaped micromixers (**M1** ($\phi = 250 \mu\text{m}$), **M2** ($\phi = 250 \mu\text{m}$) and **M3** ($\phi = 500 \mu\text{m}$)), three microtube reactors (**R1** ($\phi = 1000 \mu\text{m}$, $L = 135 \text{ cm}$ (25 cm at 0 °C, 10 cm at ambient temperature, and 100 cm at -78 °C), **R2** ($\phi = 1000 \mu\text{m}$, 400 cm) and **R3** ($\phi = 1000 \mu\text{m}$, $L = 200 \text{ cm}$)), and four tube pre-cooling units (**P1-P4** ($\phi = 1000 \mu\text{m}$, $L = 50 \text{ cm}$)) was used. The flow microreactor was dipped in a cooling bath (0 °C and -78 °C). A solution of alkyllithium (flow rate: 3.00 mL min⁻¹) and a solution of (-)-sparteine **1a** in toluene (flow rate: 3.00 mL min⁻¹) were introduced to **M1** by syringe pumps. The resulting solution was passed through **R1** and was mixed with a solution of 1-phenylbut-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (**2a**) in toluene (flow rate: 3.00 mL min⁻¹) in **M2**. The resulting solution was passed through **R2** and was mixed with a solution of electrophile (flow rate: 3.00 mL min⁻¹ or 4.00 mL min⁻¹) in **M3**. The resulting solution was passed through **R3**. After a steady state was reached, the product solution was collected for 30 s while being quenched with Sat. aq. NH₄Cl or Sat. aq. NaHCO₃. and was analyzed by HPLC. The crude mixture was extracted with Et₂O three times and dried over Na₂SO₄. The filtrate was evaporated and the residue was purified by silica gel chromatography.

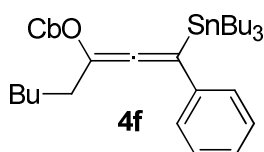


1-Trimethylsilyl-1-phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4d). Reaction condition: *n*-BuLi (0.400 M in toluene/hexane (86/14 v/v)), (-)-sparteine (0.667 M in toluene), **2a** (0.400 M in toluene), and Me₃SiCl (2.00 M in toluene, 3.0 mL/min). 70% Isolated yield (84.0 mg) purified by silica gel chromatography (hexane/ethyl acetate 97/3 to 95/5). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm × 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 3.3, 6.1 min). [α]_D²⁷ +51.5 (*c* 0.97, CH₂Cl₂, er 91:9). ¹H NMR (400 MHz, CDCl₃) δ 0.26-0.29 (m, 9H), 0.89 (t, *J* = 7.0 Hz, 3H), 1.15-1.40 (m, 16H), 1.40-1.52 (m, 2H), 2.24-2.44 (m, 2H), 3.50-4.38 (m, 2H), 7.17-7.26 (m, 1H), 7.28-7.35 (m, 2H), 7.42-7.48 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ -0.3, 13.9, 20.8, 22.4, 26.2, 31.4, 31.7, 45.5, 113.4, 125.4, 126.7, 128.1, 128.3, 137.4, 153.9, 203.5. HRMS (ESI) *m/z* calcd for C₂₄H₃₉O₂NNaSi⁺ [M+Na]⁺: 424.2642, found 424.2637.



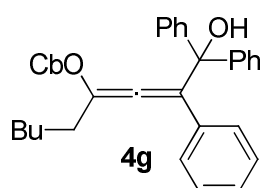
1,1-Bis(4-bromophenyl)-1-hydroxy-2-phenylnona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4e). Reaction condition: *n*-BuLi (0.200 M in toluene/hexane (93/7 v/v)), (-)-sparteine (0.333 M in toluene), **2a** (0.200 M in toluene), and 4,4'-dibromobenzophenone (0.400 M in THF/HMPA (93/7 v/v), 4.0 mL/min). 50% Isolated yield (49.7 mg) purified by silica gel chromatography (hexane/ethyl acetate 95/5 to 90/10). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm × 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 4.5, 11.8 min). [α]_D²⁸ -4.4 (*c* 0.57, CH₂Cl₂, er 88:12). ¹H NMR (400 MHz, CDCl₃) δ 0.87 (t, *J* = 6.6 Hz, 3H), 1.12-1.51 (m, 18H), 2.23 (t, *J* = 7.6 Hz, 2H), 3.66-4.13 (m, 2H), 5.39 (s, 1H), 7.12-7.17 (m, 5H), 7.26-7.32 (m, 2H), 7.34-7.40 (m, 6H). ¹³C NMR (100

MHz, CDCl₃) δ 13.9, 20.3 and 21.4, 22.4, 26.0, 31.2, 32.2, 45.9 and 47.0, 80.5, 121.1, 121.2, 122.2, 127.4, 128.0, 128.3, 129.1, 129.7, 129.8, 130.70, 130.73, 135.1, 144.1, 144.3, 153.1, 197.0. HRMS (ESI) m/z calcd for C₃₄H₃₉O₃NBr₂Na⁺ [M+Na]⁺: 690.1189, found 690.1193. The absolute configuration of the major stereoisomer of **4e** was determined by a X-ray analysis with anomalous dispersion technique. Table of atomic coordinates, anisotropic displacement parameters, bond lengths, bond angles, and torsion angles are listed at the section 10.



1-Tributylstannyl-1-phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4f).

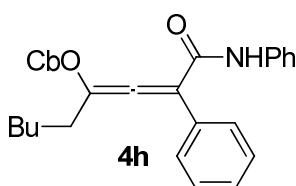
Reaction condition: *n*-BuLi (0.40 M in toluene/hexane (86/14 v/v)), (-)-sparteine (0.667 M in toluene), **2a** (0.40 M in toluene), and Bu₃SiCl (0.80 M in THF, 3.0 mL/min). 68% Isolated yield (126.4 mg) purified by silica gel chromatography (hexane/ethyl acetate 97/3 to 95/5). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 3.2, 3.8 min). $[\alpha]_D^{28} +17.6$ (*c* 1.79, CH₂Cl₂, er 87:13). ¹H NMR (400 MHz, CDCl₃) δ 0.81-0.90 (m, 12H), 0.98-1.40 (m, 28H), 1.41-1.62 (m, 8H), 2.28-2.45 (m, 2H), 3.58-4.32 (m, 2H), 7.15-7.21 (m, 1H), 7.27-7.34 (m, 2H), 7.37-7.42 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 11.2, 13.6, 13.9, 21.2, 22.5, 26.5, 27.2, 28.9, 31.5, 32.0, 46.7, 111.4, 123.7, 126.6, 128.4, 128.5, 138.7, 154.0, 200.0. HRMS (ESI) m/z calcd for C₃₃H₅₇O₂NNaSn⁺ [M+Na]⁺: 642.3303, found 642.3314.



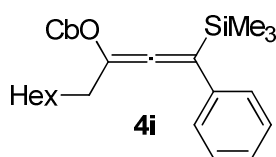
1-Hydroxy-1,1,2-triphenylnona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4g).

Reaction condition: *n*-BuLi (0.200 M in toluene/hexane (93/7 v/v)), (-)-sparteine (0.333 M in toluene), **2a** (0.200 M in toluene), and benzophenone (0.800 M in toluene/HMPA (86/14 v/v), 3.0 mL/min). 64% HPLC yield; 53% Isolated yield (40.9 mg) purified by silica gel chromatography (hexane/ethyl acetate 98/2 to 90/10). HPLC analysis (column: Daicel Chiralpack AD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 16.2, 20.9 min). $[\alpha]_D^{28} +26.2$ (*c* 0.69,

CH₂Cl₂, er 88:12). ¹H NMR (400 MHz, CDCl₃) δ 0.85 (t, *J* = 6.6 Hz, 3H), 1.14-1.47 (m, 18H), 2.22 (t, *J* = 7.6 Hz, 2H), 3.64-4.18 (m, 2H), 5.05 (s, 1H), 7.09-7.30 (m, 11H), 7.41-7.46 (m, 2H), 7.48-7.54 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 13.9, 20.3 and 21.5, 22.4, 25.9, 31.2, 32.2, 45.7 and 46.9, 81.1, 123.0, 126.8, 127.0, 127.1, 127.5, 127.8, 128.0, 128.1, 128.3, 129.2, 135.5, 145.1, 145.5, 153.4, 196.9. Some signals were overlapped. HRMS (ESI) *m/z* calcd for C₃₄H₄₁O₃NNa⁺ [M+Na]⁺: 534.2979, found 534.2974.

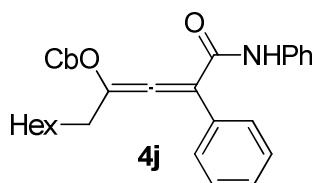


1-Oxo-2-phenyl-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4h). Reaction condition: *n*-BuLi (0.200 M in toluene/hexane (93/7 v/v)), (-)-sparteine (0.333 M in toluene), **2a** (0.200 M in toluene), and phenyl isocyanate (0.800 M in toluene/HMPA (85/15 v/v), 3.0 mL/min). 91% HPLC yield. HPLC analysis (column: Daicel Chiralpack AD-H (4.6 mm × 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 19.0, 23.1 min). [α]_D²⁶ +66.4 (*c* 1.22, CH₂Cl₂, er 92:8). ¹H NMR (400 MHz, CDCl₃) δ 0.83 (t, *J* = 7.2 Hz, 3H), 1.18-1.41 (m, 16H), 1.53-1.64 (m, 2H), 2.35-2.49 (m, 2H), 3.85-4.14 (m, 2H), 7.05-7.11 (m, 1H), 7.27-7.40 (m, 5H), 7.57-7.62 (m, 2H), 7.78-7.84 (m, 2H), 10.6 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 13.8, 20.3 and 21.2 and 21.3, 22.2, 25.7, 31.0, 32.4, 46.3 and 47.1, 114.1, 119.2, 123.4, 127.0, 128.07, 128.14, 128.7, 128.8, 132.9, 139.4, 152.9, 163.7, 199.4. C₂₈H₃₆O₃N₂Na⁺ [M+Na]⁺: 471.2618, found 471.2613.

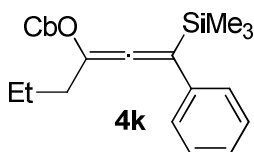


1-Trimethylsilyl-1-phenyldeca-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4i). Reaction condition: HexLi (0.400 M in toluene/hexane (83/17 v/v)), (-)-sparteine (0.667 M in toluene), **2a** (0.400 M in toluene), and Me₃SiCl (2.00 M in toluene, 3.0 mL/min). 68% Isolated yield (87.2 mg) purified by silica gel chromatography (hexane/ethyl acetate 99/1 to 95/5). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm × 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 3.3, 9.5 min). [α]_D²⁷ +46.0 (*c* 0.97, CH₂Cl₂, er 91:9). ¹H NMR (400 MHz,

CDCl₃) δ 0.25-0.32 (m, 9H), 0.85 (t, *J* = 6.6 Hz, 3H), 1.16-1.40 (m, 20H), 1.41-1.52 (m, 2H), 2.30-2.44 (m, 2H), 3.46-4.38 (m, 2H), 7.17-7.27 (m, 1H), 7.28-7.35 (m, 2H), 7.42-7.48 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ -0.3, 14.0, 20.9, 22.6, 26.5, 29.1, 29.2, 31.7, 45.6, 113.4, 125.4, 126.7, 128.1, 128.3, 137.5, 153.9, 203.6. HRMS (ESI) *m/z* calcd for C₂₆H₄₃O₂NNaSi⁺ [M+Na]⁺: 452.2955, found 452.2948.

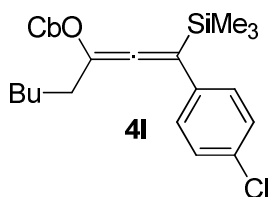


1-Oxo-2-phenyl-1-(phenylamino)undeca-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4j). Reaction condition: HexLi (0.200 M in toluene/hexane (87/13 v/v)), (-)-sparteine (0.333 M in toluene), **2a** (0.200 M in toluene), and phenyl isocyanate (0.800 M in toluene/HMPA (85/15 v/v), 3.0 mL/min). 62% HPLC yield; 53% Isolated yield (37.6 mg) purified by silica gel chromatography (hexane/ethyl acetate 95/5 to 90/10). HPLC analysis (column: Daicel Chiralpack AD-H (4.6 mm × 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 10.9, 20.8 min). [α]_D²⁶ +43.5 (*c* 1.03, CH₂Cl₂, er 91:9). ¹H NMR (400 MHz, CDCl₃) δ 0.82 (t, *J* = 7.2 Hz, 3H), 2.11, 1.12-1.42 (m, 20H), 1.52-1.63 (m, 2H), 2.38-2.45 (m, 2H), 3.85-4.14 (m, 2H), 7.05-7.15 (m, 1H), 7.28-7.40 (m, 5H), 7.57-7.62 (m, 2H), 7.78-7.84 (m, 2H), 10.6 (bs, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 14.0, 20.4 and 21.3 and 21.4, 22.5, 26.1, 28.88, 28.94, 31.7, 32.5, 46.4 and 47.1, 114.1, 119.3, 123.5, 127.1, 128.1, 128.2, 128.7, 128.9, 132.9, 139.4, 153.0, 163.8, 199.4. C₃₀H₄₀O₃N₂Na⁺ [M+Na]⁺: 499.2931, found 499.2924.

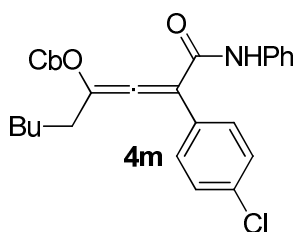


1-Trimethylsilyl-1-phenylhex-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4k). Reaction condition: EtLi (0.100 M in toluene/benzene/cyclohexane (80/18/2 v/v/v)), (-)-sparteine (0.167 M in toluene), **2a** (0.100 M in toluene), and Me₃SiCl (0.500 M in toluene, 3.0 mL/min). 50% Isolated yield (27.9 mg) purified by silica gel chromatography (hexane/ethyl acetate 91/9 to 96/4). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm × 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 3.4, 5.3 min). [α]_D²⁸ +73.6 (*c* 0.66, CH₂Cl₂, er 96:4). ¹H NMR (400 MHz, CDCl₃) δ 0.24-0.31 (m, 9H), 0.96 (t, *J* = 7.6 Hz, 3H),

1.15-1.30 (m, 12H), 1.42-1.55 (m, 2H), 2.28-2.43 (m, 2H), 3.30-4.50 (m, 2H), 7.17-7.23 (m, 1H), 7.28-7.35 (m, 2H), 7.42-7.48 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ -0.3, 13.8, 19.8, 21.0, 33.8, 45.4 and 46.4, 113.3, 125.1, 126.6, 128.0, 128.3, 137.4, 153.9, 203.5. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{35}\text{O}_2\text{NNaSi}^+$ $[\text{M}+\text{Na}]^+$: 396.2320, found 396.2329.

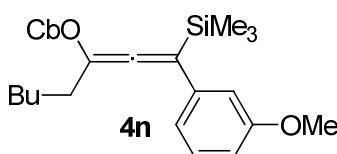


1-(4-Chlorophenyl)-1-trimethylsilylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4l). Reaction condition: *n*-BuLi (0.400 M in toluene/hexane (86/14 v/v)), (-)-sparteine (0.667 M in toluene), **2d** (0.400 M in toluene), and Me_3SiCl (2.00 M in toluene, 3.0 mL/min). 74% Isolated yield (97.2 mg) purified by silica gel chromatography (hexane/ethyl acetate 97/3 to 92/8). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 5.4, 5.9 min). $[\alpha]_D^{28}$ +72.6 (*c* 1.07, CH_2Cl_2 , er 91:9). ^1H NMR (400 MHz, CDCl_3) δ 0.24-0.29 (m, 9H), 0.84 (t, J = 6.8 Hz, 3H), 1.14-1.51 (m, 18H), 2.26-2.42 (m, 2H), 3.40-4.40 (m, 2H), 7.23-7.30 (m, 2H), 7.35-7.41 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ -0.3, 13.9, 20.6 and 21.3, 22.4, 26.1, 31.4, 31.7, 45.3 and 46.7, 112.4, 125.5, 128.5, 129.3, 132.5, 136.0, 153.8, 203.9. HRMS (ESI) m/z calcd for $\text{C}_{24}\text{H}_{38}\text{O}_2\text{NCINaSi}^+$ $[\text{M}+\text{Na}]^+$: 458.2253, found 458.2249.

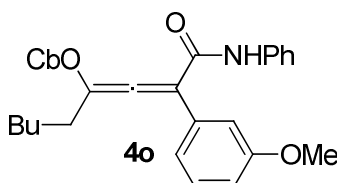


2-(4-Chlorophenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4m). Reaction condition: *n*-BuLi (0.200 M in toluene/hexane (93/7 v/v)), (-)-sparteine (0.333 M in toluene), **2d** (0.200 M in toluene), and phenyl isocyanate (0.800 M in toluene/HMPA (85/15 v/v), 3.0 mL/min). 74% HPLC yield. HPLC analysis (column: Daicel Chiralpack AD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 98/2; flow rate: 1.0 mL/min; detection wavelength: 254 nm; T_R = 10.7, 17.9 min). $[\alpha]_D^{28}$ +46.9 (*c* 0.67, CH_2Cl_2 , er 93:7). ^1H NMR (400 MHz, CDCl_3)

δ 0.82 (t, $J = 7.2$ Hz, 3H), 1.18-1.41 (m, 16H), 1.50-1.62 (m, 2H), 2.35-2.49 (m, 2H), 3.82-4.15 (m, 2H), 7.05-7.11 (m, 1H), 7.28-7.37 (m, 4H), 7.52-7.58 (m, 2H), 7.76-7.82 (m, 2H), 10.6 (bs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.8, 20.4 and 21.27 and 21.31, 22.2, 25.7, 31.0, 32.4, 46.4 and 47.2, 113.1, 119.3, 123.6, 127.5, 128.3, 128.7, 130.2, 131.4, 134.0, 139.2, 152.9, 163.4, 199.5. $\text{C}_{28}\text{H}_{35}\text{O}_3\text{N}_2\text{ClNa}^+$ $[\text{M}+\text{Na}]^+$: 505.2228, found 505.2227.



1-(3-methoxyphenyl)-1-trimethylsilylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4n). Reaction condition: *n*-BuLi (0.400 M in toluene/hexane (86/14 v/v)), (-)-sparteine (0.667 M in toluene), **2e** (0.400 M in toluene), and Me_3SiCl (2.00 M in toluene, 3.0 mL/min). 67% Isolated yield (80.6 mg) purified by silica gel chromatography (hexane/ethyl acetate 96/4 to 90/10). HPLC analysis (column: Daicel Chiralcel OD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; $T_R = 3.4, 4.7$ min). $[\alpha]_D^{25} +53.1$ (c 0.96, CH_2Cl_2 , ν 95:5). ^1H NMR (400 MHz, CDCl_3) δ 0.28-0.32 (m, 9H), 0.87 (t, $J = 7.2$ Hz, 3H), 1.18-1.42 (m, 16H), 1.43-1.54 (m, 2H), 2.30-2.46 (m, 2H), 3.54-4.34 (m, 2H), 3.84 (s, 3H), 6.75-6.82 (m, 1H), 7.01-7.06 (m, 1H), 7.09-7.14 (m, 1H), 7.20-7.29 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ -0.3, 13.9, 20.7, 22.4, 26.1, 31.3, 31.7, 45.4 and 46.4, 55.1, 112.8, 113.28, 113.33, 120.5, 125.3, 129.1, 138.9, 153.9, 159.6, 203.7. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{41}\text{O}_3\text{N}_2\text{NaSi}^+$ $[\text{M}+\text{Na}]^+$: 454.2748, found 454.2744.



2-(3-Methoxyphenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4o). Reaction condition: *n*-BuLi (0.200 M in toluene/hexane (93/7 v/v)), (-)-sparteine (0.333 M in toluene), **2e** (0.200 M in toluene), and phenyl isocyanate (0.800 M in toluene/HMPA (85/15 v/v), 3.0 mL/min). 74% HPLC yield; 55% Isolated yield (39.4 mg) purified by silica gel chromatography (hexane/ethyl acetate 90/10 to 85/15). HPLC analysis (column: Daicel Chiralpack AD-H (4.6 mm \times 25 cm); eluent: hexane/2-PrOH = 99/1; flow rate: 1.0 mL/min; detection wavelength: 254 nm; $T_R = 19.9$,

25.6 min). $[\alpha]_D^{25} +54.8$ (c 1.89, CH_2Cl_2 , er 91:9). ^1H NMR (400 MHz, CDCl_3) δ 0.82 (t, $J = 7.2$ Hz, 3H), 1.18-1.42 (m, 16H), 1.50-1.66 (m, 2H), 2.34-2.49 (m, 2H), 3.81 (s, 3H), 3.85-4.13 (m, 2H), 6.83-6.89 (m, 1H), 7.04-7.12 (m, 1H), 7.15-7.22 (m, 2H), 7.23-7.37 (m, 3H), 7.77-7.84 (m, 2H), 10.6 (bs, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 13.9, 20.4 and 21.3 and 21.4, 22.3, 25.8, 31.1, 32.5, 46.4 and 47.2, 55.2, 114.0, 114.1, 114.2, 119.4, 121.4, 123.5, 127.1, 128.7, 129.1, 134.3, 139.4, 153.0, 159.4, 163.7, 199.5. $\text{C}_{29}\text{H}_{38}\text{O}_4\text{N}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 501.2724, found 501.2715.

9. Typical Procedure for Synthesis of Racemic Allene Products. A solution of *n*-BuLi (2.76 M in hexane, 1.92 mmol, 696 μL) was added dropwise to a solution of TMEDA (223 mg, 1.92 mmol) and 1-phenylbut-3-en-1-yn-1-yl *N,N*-diisopropylcarbamate (434 mg, 1.60 mmol) in toluene (9.0 mL) at -78 $^\circ\text{C}$ under argon. After the mixture was stirred for 10 min, a solution of chlorotrimethylsilane (261 mg, 2.4 mmol) was added. After stirring for 10 min, the product solution was quenched by sat. aq. NaHCO_3 . The mixture was extracted with Et_2O three times. The combined organic phase was dried over Na_2SO_4 . The filtrate was evaporated and the residue was subjected to silica gel chromatography (hexane/ethyl acetate 97/3 to 95/5) to afford racemic 1-trimethylsilyl-1-phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (**4d**) (359 mg, 56%).

10. X-ray Data for 1,1-Bis(4-bromophenyl)-1-hydroxy-2-phenylnona-2,3-dien-4-yl *N,N*-diisopropyl-carbamate (4e). $\text{C}_{34}\text{H}_{39}\text{Br}_2\text{NO}_3$, $M = 669.50$, monoclinic, space group $P2_1$ (No. 4), $a = 10.9694(8)$ \AA , $b = 11.956(1)$ \AA , $c = 12.111(1)$ \AA , $V = 1578.7(3)$ \AA^3 , $Z = 2$, $D_c = 1.408$ g/cm^3 . Intensity data were measured on a Rigaku RAXIS imaging plate area detector with graphite-monochromated $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54187$ \AA). The data were collected at -120 ± 1 $^\circ\text{C}$ to a maximum 2θ value of 136.4° . Of the 15071 reflections that were collected, 5353 were unique ($R_{\text{int}} = 0.0423$); equivalent reflections were merged. The structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically. The final cycle of full-matrix least-squares refinement on F was based on 5353 observed reflections ($I > 2.00\sigma(I)$) and 367 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of $R = 0.0366$ ($R_w = 0.0880$). The standard deviation of an observation of unit weight was 1.11. All calculations were performed using the CrystalStructure crystallographic software package.

Table S-4. Atomic Coordinates and $B_{\text{iso}}/B_{\text{eq}}$.

atom	x	y	z	B_{eq}
Br1	0.70160(3)	0.59312(4)	0.08041(3)	4.02(1)
Br2	-0.09105(3)	0.25873(3)	-0.09582(3)	3.43(1)
O1	0.5818(2)	0.1716(2)	0.3115(2)	2.08(4)
O2	0.6472(2)	0.0316(2)	0.4299(2)	2.58(4)
O3	0.2154(2)	0.4807(2)	0.3725(2)	2.49(4)
N1	0.7342(2)	0.0598(3)	0.2683(2)	2.33(5)
C1	0.3123(3)	0.2959(3)	0.3903(3)	2.02(5)
C2	0.4274(3)	0.2617(3)	0.3958(2)	2.13(5)
C3	0.5429(3)	0.2382(3)	0.3980(3)	2.10(5)
C4	0.6566(3)	0.0824(3)	0.3431(3)	2.10(5)
C5	0.7516(3)	0.1328(3)	0.1715(3)	2.52(6)
C6	0.7914(3)	0.2506(4)	0.2067(3)	3.00(6)
C7	0.6425(3)	0.1297(4)	0.0821(3)	3.10(7)
C8	0.8114(3)	-0.0422(3)	0.2852(3)	3.03(7)
C9	0.7846(4)	-0.1225(4)	0.1884(5)	4.8(1)
C10	0.9466(4)	-0.0130(4)	0.3057(4)	4.19(8)
C11	0.6453(3)	0.2859(3)	0.4764(3)	2.47(6)
C12	0.6024(3)	0.3552(3)	0.5700(3)	2.43(6)
C13	0.7114(3)	0.3897(3)	0.6529(3)	2.67(6)
C14	0.6759(3)	0.4656(3)	0.7456(3)	3.09(7)
C15	0.5835(4)	0.4136(4)	0.8149(3)	3.90(8)
C16	0.2228(3)	0.2403(3)	0.4566(3)	2.24(6)
C17	0.2606(3)	0.1495(4)	0.5252(3)	3.08(7)
C18	0.1807(3)	0.0974(4)	0.5889(3)	3.71(7)
C19	0.0608(4)	0.1321(4)	0.5870(3)	3.63(8)
C20	0.0216(3)	0.2220(4)	0.5192(3)	3.53(8)
C21	0.0998(3)	0.2755(4)	0.4551(3)	2.82(6)
C22	0.2709(3)	0.3955(3)	0.3125(3)	2.00(5)
C23	0.3797(3)	0.4435(3)	0.2570(3)	2.08(5)
C24	0.4299(3)	0.3848(3)	0.1744(3)	2.29(5)
C25	0.5265(3)	0.4269(3)	0.1221(3)	2.37(5)
C26	0.5716(3)	0.5312(3)	0.1534(3)	2.56(6)
C27	0.5246(3)	0.5920(4)	0.2352(3)	3.23(6)
C28	0.4279(3)	0.5477(3)	0.2877(3)	2.77(6)
C29	0.1741(3)	0.3575(3)	0.2178(3)	2.04(5)
C30	0.0996(3)	0.4376(3)	0.1615(3)	2.51(6)
C31	0.0207(3)	0.4086(3)	0.0679(3)	2.70(6)
C32	0.0166(3)	0.2993(3)	0.0325(3)	2.33(6)
C33	0.0879(3)	0.2178(3)	0.0871(3)	2.35(6)
C34	0.1669(3)	0.2485(3)	0.1813(3)	2.33(5)
H3O	0.2634	0.4991	0.4285	2.99
H5	0.8218	0.0998	0.1367	3.03
H6A	0.7266	0.2864	0.2437	3.6
H6B	0.8063	0.2941	0.1409	3.6

H6C	0.8669	0.247	0.258	3.6
H7A	0.5701	0.1602	0.1121	3.71
H7B	0.6264	0.0523	0.0584	3.71
H7C	0.6609	0.1747	0.0184	3.71
H8	0.7886	-0.0807	0.3533	3.63
H9A	0.8092	-0.0883	0.1208	5.71
H9B	0.6966	-0.1391	0.1778	5.71
H9C	0.8307	-0.192	0.2042	5.71
H10A	0.9611	0.0344	0.3719	5.03
H10B	0.9712	0.0273	0.2412	5.03
H10C	0.995	-0.0818	0.3171	5.03
H11A	0.6973	0.3333	0.4337	2.96
H11B	0.6968	0.2237	0.5091	2.96
H12A	0.5436	0.3111	0.6087	2.92
H12B	0.5595	0.4229	0.5387	2.92
H13A	0.751	0.3215	0.6865	3.21
H13B	0.7723	0.4289	0.6124	3.21
H14A	0.7508	0.4851	0.7951	3.71
H14B	0.6411	0.5359	0.7123	3.71
H15A	0.615	0.3418	0.8449	4.68
H15B	0.5057	0.4016	0.7683	4.68
H15C	0.5701	0.4639	0.8763	4.68
H17	0.3427	0.1234	0.5279	3.7
H18	0.209	0.0364	0.635	4.46
H19	0.0062	0.0955	0.6309	4.36
H20	-0.0609	0.2469	0.5171	4.24
H21	0.0707	0.3367	0.4095	3.38
H24	0.3972	0.3135	0.1529	2.75
H25	0.5605	0.385	0.0663	2.84
H27	0.5574	0.6635	0.2558	3.87
H28	0.3951	0.5891	0.3445	3.32
H30	0.1025	0.5128	0.187	3.01
H31	-0.0297	0.4636	0.0291	3.24
H33	0.0839	0.1426	0.0617	2.82
H34	0.2163	0.193	0.2206	2.8

$$B_{eq} = 8/3 \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos \gamma + 2U_{13}(aa^*cc^*)\cos \beta + 2U_{23}(bb^*cc^*)\cos \alpha)$$

Table S-5. Anisotropic Displacement Parameters.

atom	U ₁₁	U ₂₂	U ₃₃	U ₁₂	U ₁₃	U ₂₃
Br1	0.0480(2)	0.0566(3)	0.0522(3)	-0.0214(2)	0.0235(2)	-0.0088(2)
Br2	0.0360(2)	0.0609(3)	0.0310(2)	-0.0084(2)	-0.0067(2)	-0.0005(2)
O1	0.0221(9)	0.035(2)	0.0219(9)	0.0037(9)	0.0051(8)	0.0009(9)
O2	0.032(1)	0.038(2)	0.029(1)	0.003(1)	0.0070(9)	0.008(1)
O3	0.025(1)	0.039(2)	0.031(1)	0.0033(9)	0.0039(8)	-0.009(1)
N1	0.026(2)	0.033(2)	0.032(2)	0.005(1)	0.010(1)	0.002(1)
C1	0.022(2)	0.034(2)	0.021(2)	0.001(2)	0.002(1)	-0.004(2)

C2	0.028(2)	0.032(2)	0.020(2)	-0.001(2)	0.003(1)	0.001(2)
C3	0.022(2)	0.037(2)	0.023(2)	0.002(2)	0.006(1)	0.004(2)
C4	0.020(2)	0.032(2)	0.028(2)	-0.003(2)	0.003(1)	-0.003(2)
C5	0.032(2)	0.038(2)	0.028(2)	-0.001(2)	0.011(2)	0.003(2)
C6	0.034(2)	0.042(2)	0.040(2)	-0.007(2)	0.011(2)	0.003(2)
C7	0.045(2)	0.047(3)	0.026(2)	-0.002(2)	0.007(2)	-0.002(2)
C8	0.036(2)	0.033(2)	0.047(2)	0.012(2)	0.013(2)	0.003(2)
C9	0.037(2)	0.047(3)	0.098(4)	0.003(2)	0.009(2)	-0.029(3)
C10	0.039(2)	0.050(3)	0.068(3)	0.011(2)	-0.006(2)	-0.006(2)
C11	0.021(2)	0.046(3)	0.027(2)	-0.001(2)	0.004(1)	-0.004(2)
C12	0.023(2)	0.042(2)	0.027(2)	0.002(2)	0.001(2)	-0.004(2)
C13	0.026(2)	0.044(2)	0.031(2)	-0.002(2)	0.001(2)	-0.004(2)
C14	0.040(2)	0.035(2)	0.040(2)	0.000(2)	-0.007(2)	-0.009(2)
C15	0.054(2)	0.058(3)	0.038(2)	0.003(2)	0.010(2)	-0.012(2)
C16	0.024(2)	0.038(2)	0.023(2)	-0.003(2)	0.002(1)	-0.005(2)
C17	0.032(2)	0.052(3)	0.034(2)	0.003(2)	0.009(2)	0.004(2)
C18	0.048(2)	0.051(3)	0.044(2)	-0.004(2)	0.013(2)	0.013(2)
C19	0.042(2)	0.060(3)	0.039(2)	-0.017(2)	0.015(2)	-0.001(2)
C20	0.026(2)	0.059(3)	0.051(2)	-0.006(2)	0.012(2)	-0.011(2)
C21	0.024(2)	0.047(3)	0.037(2)	-0.002(2)	0.006(2)	-0.002(2)
C22	0.021(2)	0.030(2)	0.025(2)	0.000(2)	0.003(1)	-0.003(2)
C23	0.022(2)	0.030(2)	0.026(2)	0.002(2)	0.000(1)	0.001(2)
C24	0.031(2)	0.029(2)	0.027(2)	-0.002(2)	0.003(2)	-0.003(2)
C25	0.031(2)	0.032(2)	0.028(2)	0.002(2)	0.009(2)	-0.002(2)
C26	0.028(2)	0.040(2)	0.031(2)	-0.009(2)	0.007(2)	0.003(2)
C27	0.037(2)	0.040(2)	0.047(2)	-0.011(2)	0.011(2)	-0.012(2)
C28	0.033(2)	0.036(2)	0.038(2)	-0.007(2)	0.010(2)	-0.010(2)
C29	0.017(2)	0.036(2)	0.025(2)	0.001(2)	0.004(1)	-0.000(2)
C30	0.034(2)	0.026(2)	0.035(2)	0.002(2)	0.001(2)	0.000(2)
C31	0.032(2)	0.035(2)	0.035(2)	0.004(2)	-0.003(2)	0.008(2)
C32	0.021(2)	0.041(2)	0.026(2)	-0.006(2)	0.001(2)	-0.001(2)
C33	0.025(2)	0.031(2)	0.034(2)	0.001(2)	0.005(2)	-0.006(2)
C34	0.027(2)	0.031(2)	0.030(2)	0.006(2)	0.001(1)	0.000(2)

The general temperature factor expression: $\exp(-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl))$

Table S-6. Bond Lengths (Å).

atom	atom	distance	atom	atom	distance
Br1	C26	1.908(4)	Br2	C32	1.908(3)
O1	C3	1.419(4)	O1	C4	1.373(4)
O2	C4	1.229(4)	O3	C22	1.426(4)
N1	C4	1.337(4)	N1	C5	1.491(5)
N1	C8	1.486(5)	C1	C2	1.322(4)
C1	C16	1.492(5)	C1	C22	1.554(5)
C2	C3	1.295(4)	C3	C11	1.501(4)
C5	C6	1.522(5)	C5	C7	1.522(5)

C8	C9	1.519(6)	C8	C10	1.518(5)
C11	C12	1.520(5)	C12	C13	1.531(4)
C13	C14	1.528(5)	C14	C15	1.519(6)
C16	C17	1.402(5)	C16	C21	1.412(4)
C17	C18	1.379(6)	C18	C19	1.378(6)
C19	C20	1.391(6)	C20	C21	1.377(5)
C22	C23	1.544(4)	C22	C29	1.543(4)
C23	C24	1.386(5)	C23	C28	1.388(5)
C24	C25	1.387(5)	C25	C26	1.380(5)
C26	C27	1.374(5)	C27	C28	1.400(5)
C29	C30	1.388(5)	C29	C34	1.376(5)
C30	C31	1.391(4)	C31	C32	1.375(5)
C32	C33	1.372(5)	C33	C34	1.404(4)

Table S-7. Bond Lengths Involving Hydrogens (Å).

atom	atom	distance	atom	atom	distance
O3	H3O	0.84	C5	H5	1
C6	H6A	0.98	C6	H6B	0.98
C6	H6C	0.98	C7	H7A	0.98
C7	H7B	0.98	C7	H7C	0.98
C8	H8	1	C9	H9A	0.98
C9	H9B	0.98	C9	H9C	0.98
C10	H10A	0.98	C10	H10B	0.98
C10	H10C	0.98	C11	H11A	0.99
C11	H11B	0.99	C12	H12A	0.99
C12	H12B	0.99	C13	H13A	0.99
C13	H13B	0.99	C14	H14A	0.99
C14	H14B	0.99	C15	H15A	0.98
C15	H15B	0.98	C15	H15C	0.98
C17	H17	0.95	C18	H18	0.95
C19	H19	0.95	C20	H20	0.95
C21	H21	0.95	C24	H24	0.95
C25	H25	0.95	C27	H27	0.95
C28	H28	0.95	C30	H30	0.95
C31	H31	0.95	C33	H33	0.95
C34	H34	0.95			

Table S-8. Bond Angles (°).

atom	atom	atom	angle	atom	atom	atom	angle
C3	O1	C4	116.7(2)	C4	N1	C5	124.1(3)
C4	N1	C8	117.9(3)	C5	N1	C8	117.9(3)
C2	C1	C16	121.1(3)	C2	C1	C22	118.7(3)
C16	C1	C22	120.2(3)	C1	C2	C3	174.2(4)
O1	C3	C2	118.8(3)	O1	C3	C11	114.5(3)
C2	C3	C11	126.3(3)	O1	C4	O2	121.1(3)
O1	C4	N1	112.0(3)	O2	C4	N1	126.9(3)
N1	C5	C6	112.3(3)	N1	C5	C7	112.7(3)

C6	C5	C7	113.6(3)	N1	C8	C9	110.7(3)
N1	C8	C10	111.4(3)	C9	C8	C10	111.9(4)
C3	C11	C12	114.0(3)	C11	C12	C13	110.6(3)
C12	C13	C14	113.5(3)	C13	C14	C15	113.8(3)
C1	C16	C17	119.7(3)	C1	C16	C21	123.0(3)
C17	C16	C21	117.3(3)	C16	C17	C18	121.1(4)
C17	C18	C19	121.4(4)	C18	C19	C20	118.3(4)
C19	C20	C21	121.4(4)	C16	C21	C20	120.5(4)
O3	C22	C1	110.5(3)	O3	C22	C23	110.5(3)
O3	C22	C29	107.0(3)	C1	C22	C23	111.2(3)
C1	C22	C29	110.9(3)	C23	C22	C29	106.7(3)
C22	C23	C24	120.9(3)	C22	C23	C28	120.5(3)
C24	C23	C28	118.5(3)	C23	C24	C25	122.1(3)
C24	C25	C26	118.1(3)	Br1	C26	C25	119.2(3)
Br1	C26	C27	119.2(3)	C25	C26	C27	121.6(3)
C26	C27	C28	119.4(4)	C23	C28	C27	120.2(4)
C22	C29	C30	118.8(3)	C22	C29	C34	121.8(3)
C30	C29	C34	119.1(3)	C29	C30	C31	120.5(3)
C30	C31	C32	119.1(3)	Br2	C32	C31	119.5(3)
Br2	C32	C33	118.7(3)	C31	C32	C33	121.8(3)
C32	C33	C34	118.3(3)	C29	C34	C33	121.1(3)

Table S-9. Bond Angles Involving Hydrogens ($^{\circ}$).

atom	atom	atom	angle	atom	atom	atom	angle
C22	O3	H3O	109	N1	C5	H5	106
C6	C5	H5	106	C7	C5	H5	106
C5	C6	H6A	109	C5	C6	H6B	109
C5	C6	H6C	109	H6A	C6	H6B	109
H6A	C6	H6C	109	H6B	C6	H6C	109
C5	C7	H7A	109	C5	C7	H7B	109
C5	C7	H7C	109	H7A	C7	H7B	109
H7A	C7	H7C	109	H7B	C7	H7C	109
N1	C8	H8	108	C9	C8	H8	108
C10	C8	H8	108	C8	C9	H9A	109
C8	C9	H9B	109	C8	C9	H9C	109
H9A	C9	H9B	109	H9A	C9	H9C	109
H9B	C9	H9C	109	C8	C10	H10A	109
C8	C10	H10B	109	C8	C10	H10C	109
H10A	C10	H10B	109	H10A	C10	H10C	109
H10B	C10	H10C	109	C3	C11	H11A	109
C3	C11	H11B	109	C12	C11	H11A	109
C12	C11	H11B	109	H11A	C11	H11B	108
C11	C12	H12A	110	C11	C12	H12B	110
C13	C12	H12A	110	C13	C12	H12B	110
H12A	C12	H12B	108	C12	C13	H13A	109
C12	C13	H13B	109	C14	C13	H13A	109
C14	C13	H13B	109	H13A	C13	H13B	108

C13	C14	H14A	109	C13	C14	H14B	109
C15	C14	H14A	109	C15	C14	H14B	109
H14A	C14	H14B	108	C14	C15	H15A	109
C14	C15	H15B	109	C14	C15	H15C	109
H15A	C15	H15B	109	H15A	C15	H15C	109
H15B	C15	H15C	109	C16	C17	H17	119
C18	C17	H17	119	C17	C18	H18	119
C19	C18	H18	119	C18	C19	H19	121
C20	C19	H19	121	C19	C20	H20	119
C21	C20	H20	119	C16	C21	H21	120
C20	C21	H21	120	C23	C24	H24	119
C25	C24	H24	119	C24	C25	H25	121
C26	C25	H25	121	C26	C27	H27	120
C28	C27	H27	120	C23	C28	H28	120
C27	C28	H28	120	C29	C30	H30	120
C31	C30	H30	120	C30	C31	H31	120
C32	C31	H31	120	C32	C33	H33	121
C34	C33	H33	121	C29	C34	H34	119
C33	C34	H34	119				

Table S-10. Possible Hydrogen Bonds.

Donor	H	Acceptor	D...A	D-H	H...A	D-H...A
O3	H3O	O2 ¹	2.752(3)	0.84	1.92	170.71

Symmetry Operators: (1) -X+1,Y+1/2,-Z+1

Table S-11. Intermolecular Contacts Less than 3.6 Å.

atom	atom	distance	atom	atom	distance
Br1	C33 ¹	3.565(3)	O2	O3 ²	2.752(3)
O2	C1 ²	3.559(4)	O2	C12 ²	3.455(4)
O2	C22 ²	3.545(4)	C6	C32 ³	3.471(5)
C17	C27 ²	3.596(5)			

Symmetry Operators:

(1) -X+1,Y+1/2,-Z (2) -X+1,Y+1/2-1,-Z+1 (3) X+1,Y,Z

Table S-12. Intermolecular Contacts Less than 3.60 Å Involving Hydrogens.

atom	atom	distance	atom	atom	distance
Br1	H9B ¹	3.414	Br1	H9C ¹	3.223
Br1	H15C ²	3.128	Br1	H18 ³	3.543
Br1	H31 ⁴	3.446	Br1	H33 ⁵	3.122
Br2	H6B ⁶	3.223	Br2	H7C ⁶	3.341
Br2	H9C ⁵	3.326	Br2	H10C ⁵	3.543
Br2	H13A ⁷	3.082	Br2	H14A ⁷	3.402
Br2	H15A ⁷	3.374	Br2	H30 ⁸	3.139
O1	H14B ⁹	2.922	O1	H15B ⁹	3.474
O2	H3O ⁹	1.919	O2	H12A ⁹	3.367
O2	H12B ⁹	2.676	O2	H14B ⁹	3.429
O2	H15B ⁹	3.178	O2	H28 ⁹	2.904

O3	H8 ³	3.407	O3	H11B ³	3.334
O3	H19 ¹⁰	2.788	N1	H15B ⁹	3.231
C1	H14B ⁹	3.408	C2	H14B ⁹	3.058
C3	H14B ⁹	3.333	C3	H28 ⁹	3.591
C4	H3O ⁹	2.98	C4	H12B ⁹	3.473
C4	H14B ⁹	3.308	C4	H15B ⁹	3.023
C7	H15C ⁹	3.143	C8	H15B ⁹	3.531
C9	H15B ⁹	3.296	C10	H13B ¹¹	3.208
C11	H20 ⁴	3.24	C11	H28 ⁹	3.263
C12	H17 ³	3.495	C12	H28 ⁹	3.345
C13	H10C ¹²	3.22	C13	H17 ³	3.56
C13	H20 ⁴	3.574	C14	H34 ³	2.975
C15	H7A ³	3.555	C15	H7B ³	3.344
C15	H9B ³	3.147	C15	H25 ¹³	3.102
C15	H27 ⁹	3.431	C16	H8 ³	3.155
C17	H12B ⁹	3.489	C17	H13B ⁹	3.12
C17	H14B ⁹	3.46	C17	H27 ⁹	3.142
C18	H9C ³	3.564	C18	H10A ⁶	3.446
C18	H11A ⁹	3.452	C18	H13B ⁹	3.248
C18	H27 ⁹	3.349	C19	H9C ³	3.401
C19	H10A ⁶	2.953	C20	H6C ⁶	3.433
C20	H8 ³	3.402	C20	H10A ⁶	2.897
C20	H10C ³	3.09	C20	H11B ⁶	3.551
C21	H6C ⁶	3.315	C21	H8 ³	3.034
C21	H10A ⁶	3.362	C21	H10C ³	3.498
C24	H7B ⁵	3.457	C25	H7B ⁵	3.004
C25	H15C ²	3.098	C26	H7B ⁵	3.182
C26	H7C ⁵	3.549	C26	H15C ²	3.449
C26	H18 ³	3.316	C27	H12A ³	3.363
C27	H15A ³	3.446	C27	H17 ³	3.093
C27	H18 ³	3.231	C28	H12A ³	3.391
C28	H17 ³	3.3	C30	H19 ¹⁰	3.446
C31	H6B ⁶	2.941	C31	H6C ⁶	3.57
C31	H9A ⁵	3.107	C31	H33 ¹⁴	3.348
C32	H5 ⁶	3.528	C32	H6B ⁶	2.779
C32	H6C ⁶	3.398	C32	H9A ⁵	3.113
C32	H9C ⁵	3.479	C33	H5 ⁶	3.356
C33	H6B ⁶	3.354	C33	H6C ⁶	3.377
C33	H10B ⁶	3.293	C33	H14A ⁹	3.514
C33	H31 ⁸	3.38	C34	H6C ⁶	3.518
C34	H10B ⁶	3.532	C34	H14A ⁹	3.279
C34	H14B ⁹	3.458	H3O	H8 ³	2.925
H3O	H11B ³	2.811	H3O	H19 ¹⁰	3.181
H5	H31 ¹⁵	3.591	H5	H33 ⁴	3.151
H6A	H18 ³	3.37	H6B	H31 ⁴	3.118
H6C	H20 ⁴	3.15	H6C	H21 ⁴	2.934
H7A	H15B ⁹	3.552	H7A	H15C ⁹	2.818
H7B	H15B ⁹	3.229	H7B	H15C ⁹	2.601

H7B	H25 ¹⁵	3.13	H7C	H15A ²	2.903
H8	H15B ⁹	3.403	H8	H21 ⁹	3.259
H9A	H31 ¹⁵	3.241	H9B	H15A ⁹	3.406
H9B	H15B ⁹	2.43	H9B	H15C ⁹	3.175
H9B	H27 ¹⁶	3.019	H9C	H19 ⁹	3.585
H9C	H27 ¹⁶	3.575	H10A	H13B ¹¹	3.171
H10A	H19 ⁴	3.206	H10A	H20 ⁴	3.115
H10A	H21 ⁹	3.594	H10B	H13B ¹¹	3.367
H10B	H14A ¹¹	3.169	H10B	H31 ¹⁵	3.49
H10B	H33 ⁴	2.959	H10B	H34 ⁴	3.371
H10C	H13A ¹¹	3.022	H10C	H13B ¹¹	2.604
H10C	H14A ¹¹	3.332	H10C	H20 ⁹	2.903
H10C	H21 ⁹	3.6	H11A	H17 ³	3.534
H11A	H18 ³	2.799	H11A	H20 ⁴	2.921
H11B	H20 ⁴	2.664	H11B	H28 ⁹	2.672
H12A	H27 ⁹	2.727	H12A	H28 ⁹	2.78
H12B	H17 ³	2.783	H13A	H20 ⁴	3.195
H13A	H28 ⁹	3.208	H13B	H17 ³	3.069
H13B	H18 ³	3.288	H13B	H20 ⁴	3.144
H14A	H31 ¹⁷	3.518	H14A	H33 ³	3.024
H14A	H34 ³	2.522	H14B	H17 ³	3.115
H14B	H34 ³	2.521	H15A	H25 ¹³	2.859
H15A	H27 ⁹	3.016	H15B	H25 ¹³	3.598
H15B	H27 ⁹	2.937	H15C	H25 ¹³	2.5
H17	H27 ⁹	2.766	H17	H28 ⁹	3.137
H18	H27 ⁹	3.142	H19	H21 ¹⁸	3.23
H19	H30 ¹⁸	2.801	H31	H33 ¹⁴	2.448

Symmetry Operators:

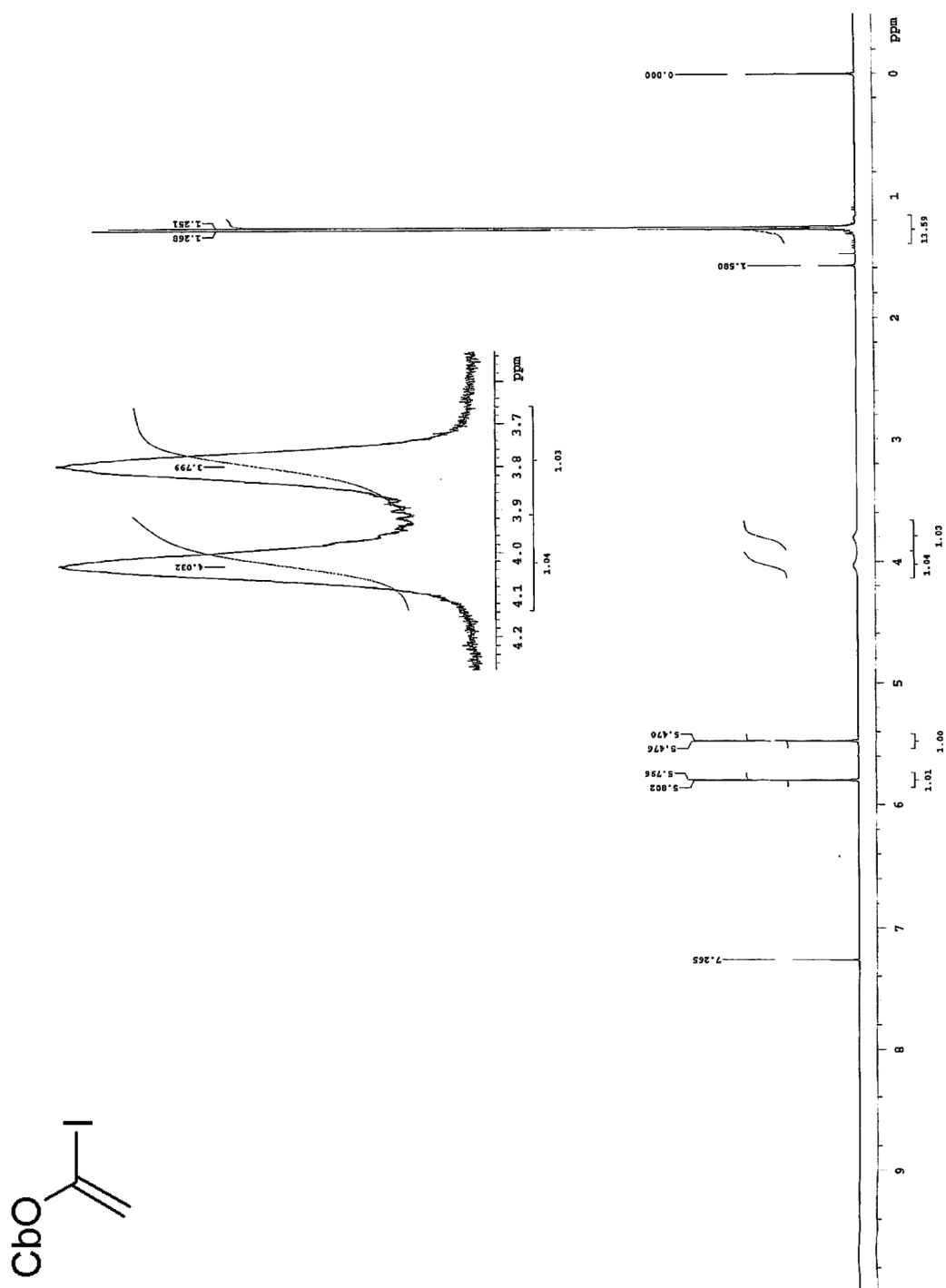
(1) X,Y+1,Z (2) X,Y,Z-1 (3) -X+1,Y+1/2,-Z+1 (4) X+1,Y,Z (5) -X+1,Y+1/2,-Z (6) X-1,Y,Z (7) X-1,Y,Z-1 (8) -X,Y+1/2-1,-Z (9) -X+1,Y+1/2-1,-Z+1 (10) -X,Y+1/2,-Z+1 (11) -X+2,Y+1/2-1,-Z+1 (12) -X+2,Y+1/2,-Z+1 (13) X,Y,Z+1 (14) -X,Y+1/2,-Z (15) -X+1,Y+1/2-1,-Z (16) X,Y-1,Z (17) X+1,Y,Z+1 (18) -X,Y+1/2-1,-Z+1

11. Complete Reference 6n in the Text. Lee, C.-C.; Sui, G.; Elizarov, A.; Shu, C. J.; Shin, Y.-S.; Dooley, A. N.; Huang, J.; Daridon, A.; Wyatt, P.; Stout, D.; Kolb, H. C.; Witte, O. N.; Satyamurthy, N.; Heath, J. R.; Phelps, M. E.; Quake, S. R.; Tseng, H.-R. *Science* **2005**, *310*, 1793.

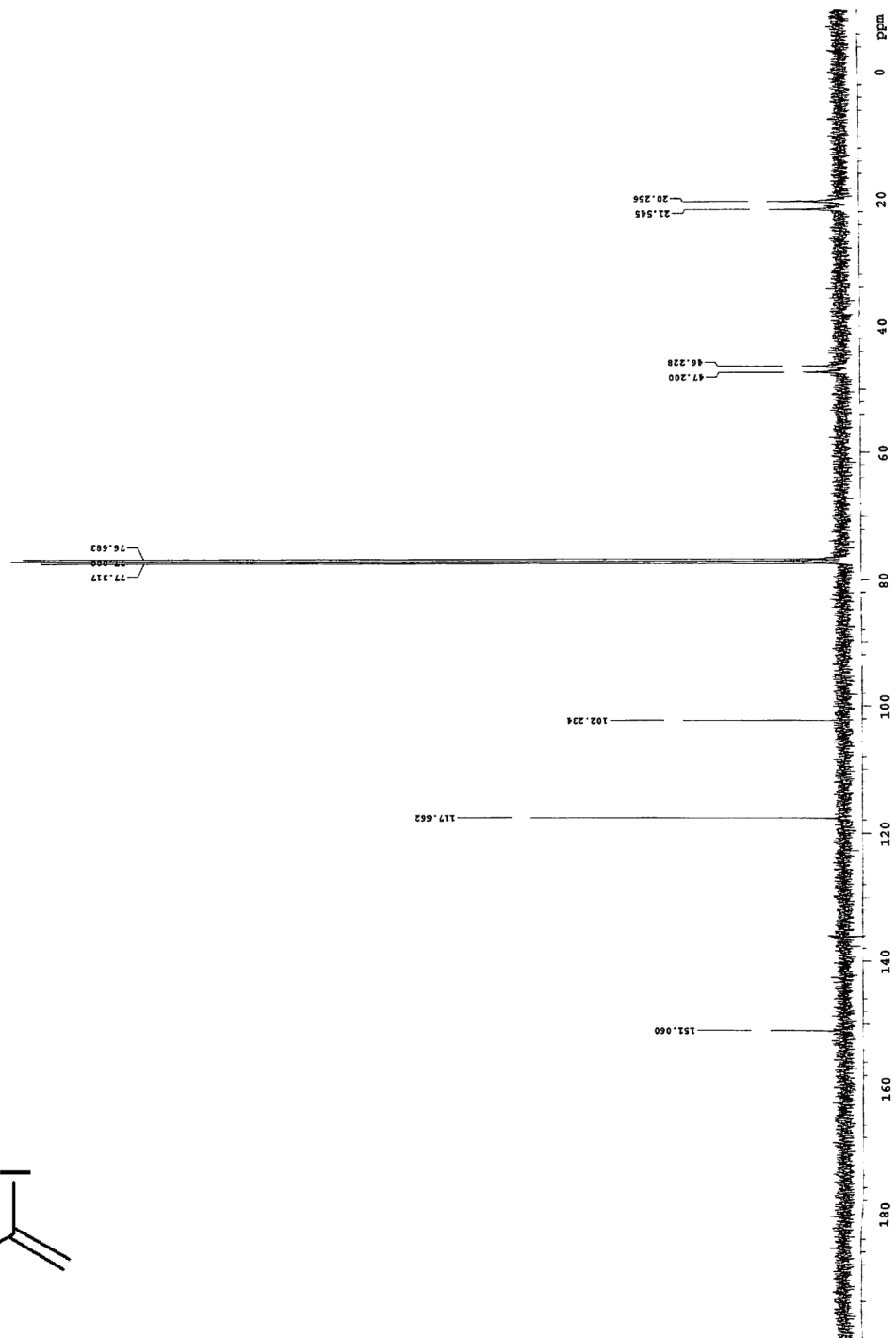
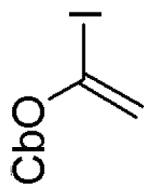
12. References.

1. Tomida, Y.; Nagaki, A.; Yoshida, J. *Org. Lett.* **2009**, *11*, 3614.
2. Siemer, M.; Fröhlich, R.; Hoppe, D. *Synthesis.* **2008**, 2264.

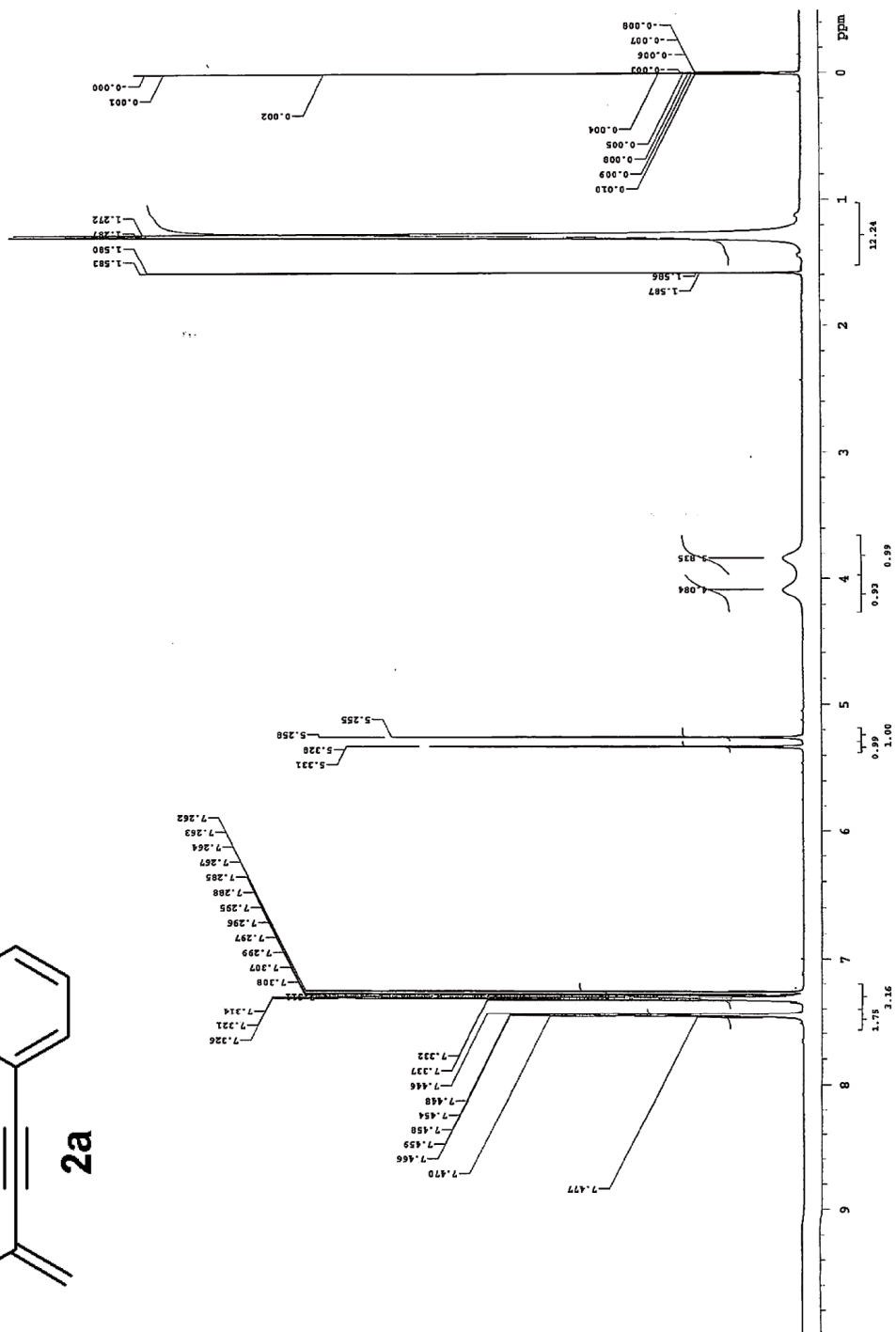
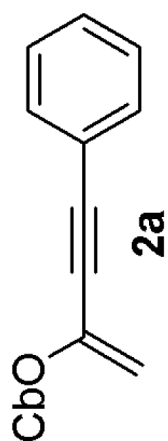
13. ¹H and ¹³C NMR Spectra.



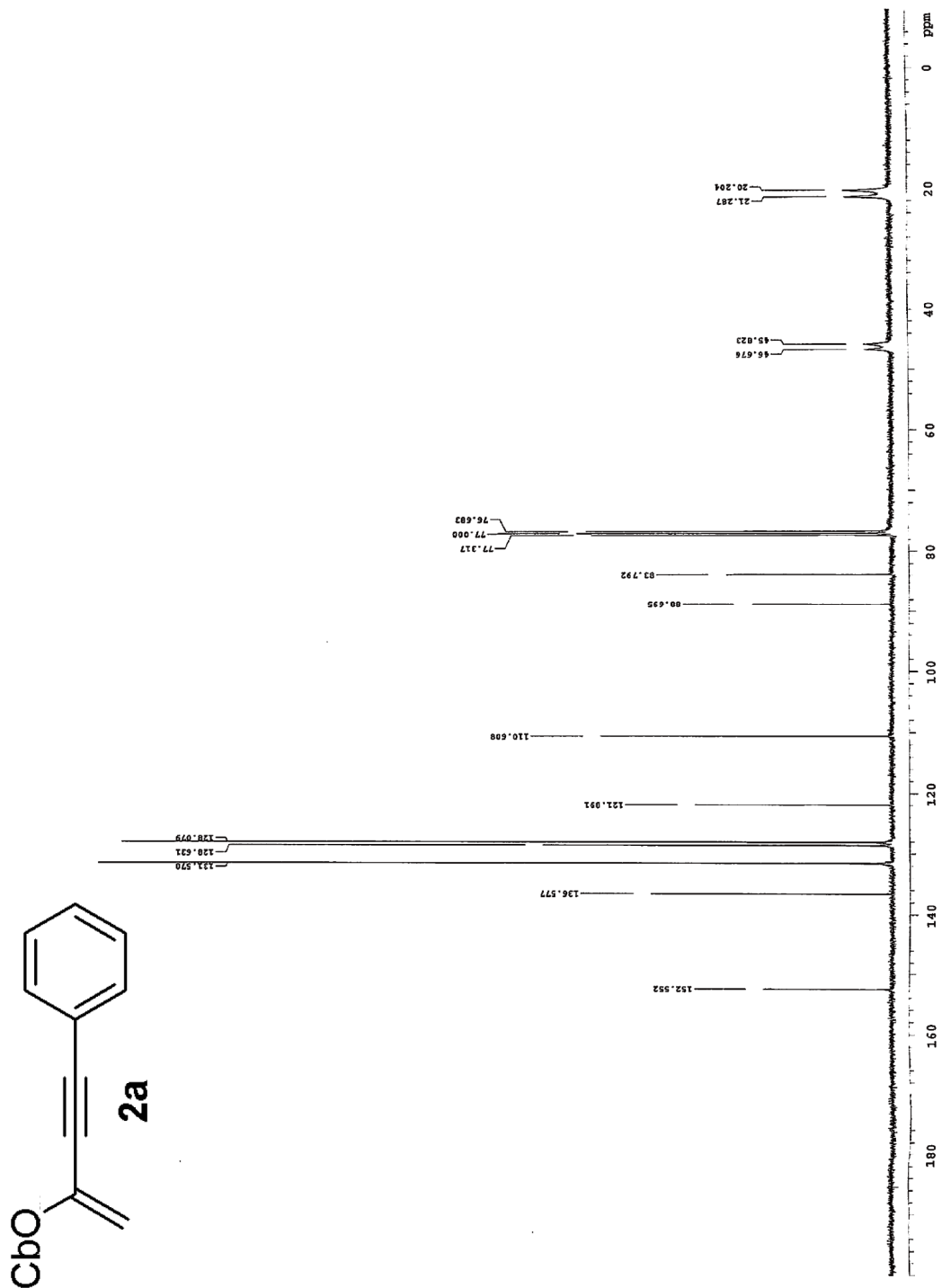
¹H NMR spectrum of 1-Iodo-1-ethenyl *N,N*-Diisopropylcarbamate



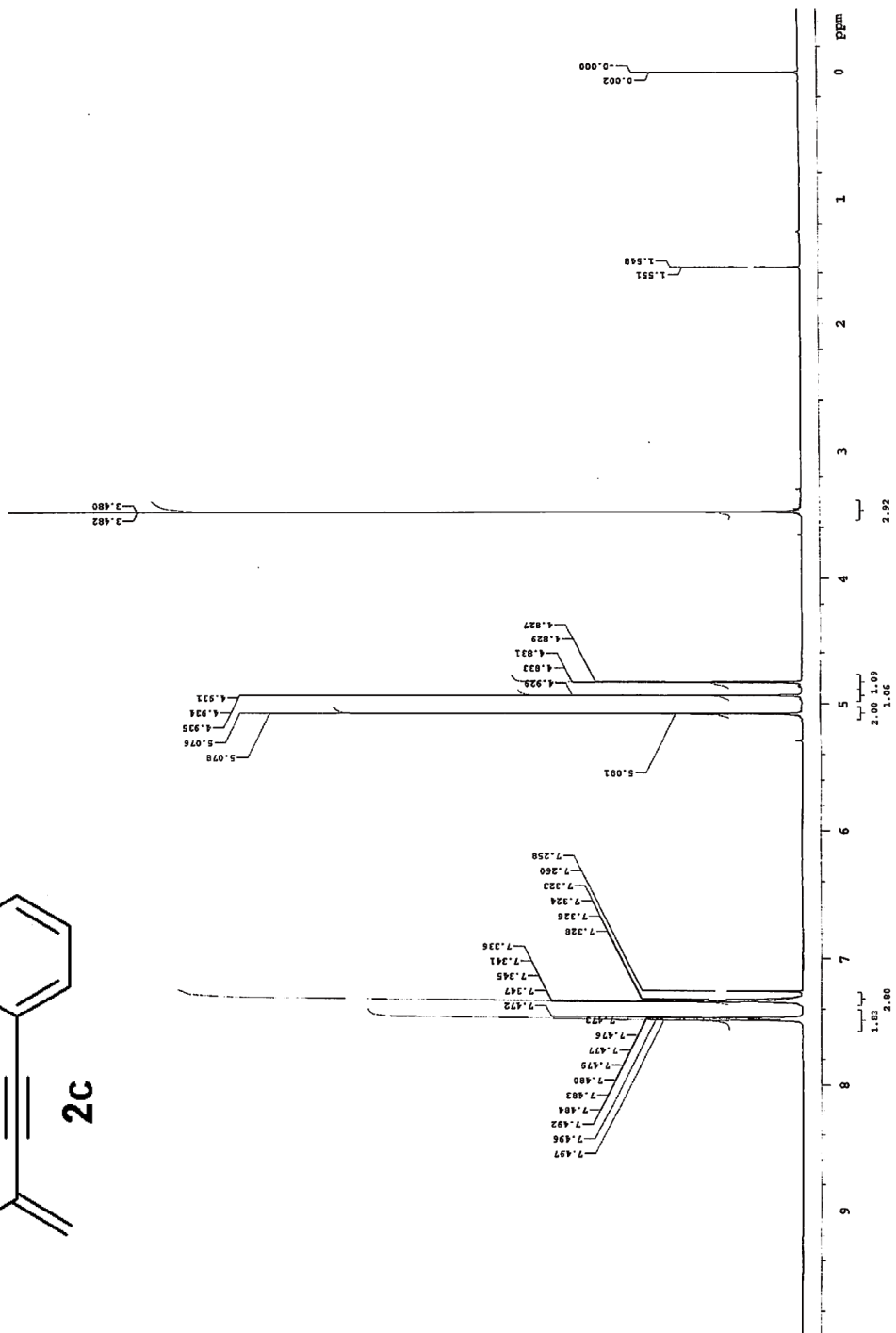
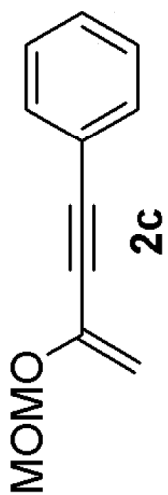
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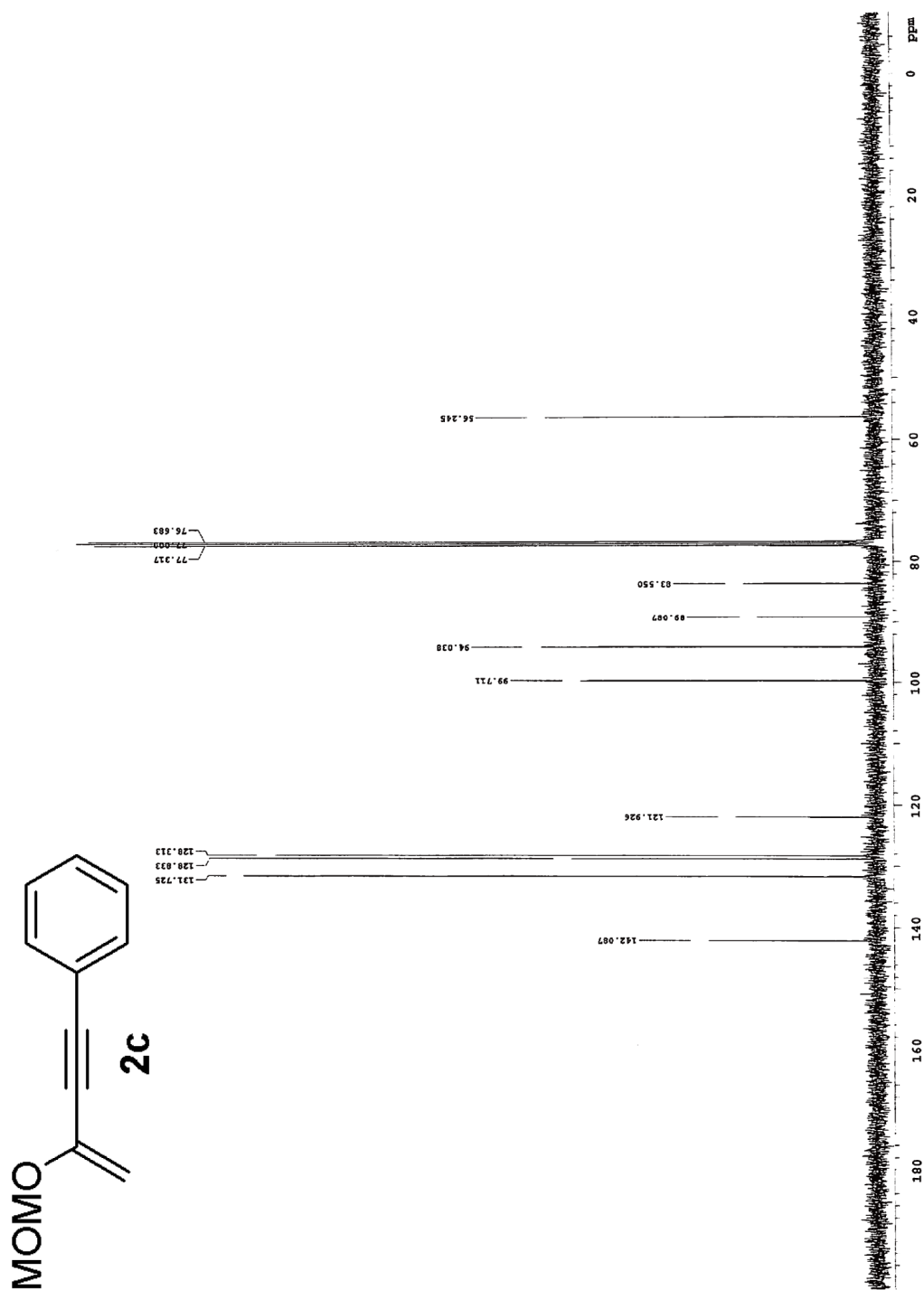
¹H NMR spectrum of 1-Phenylbut-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2a)



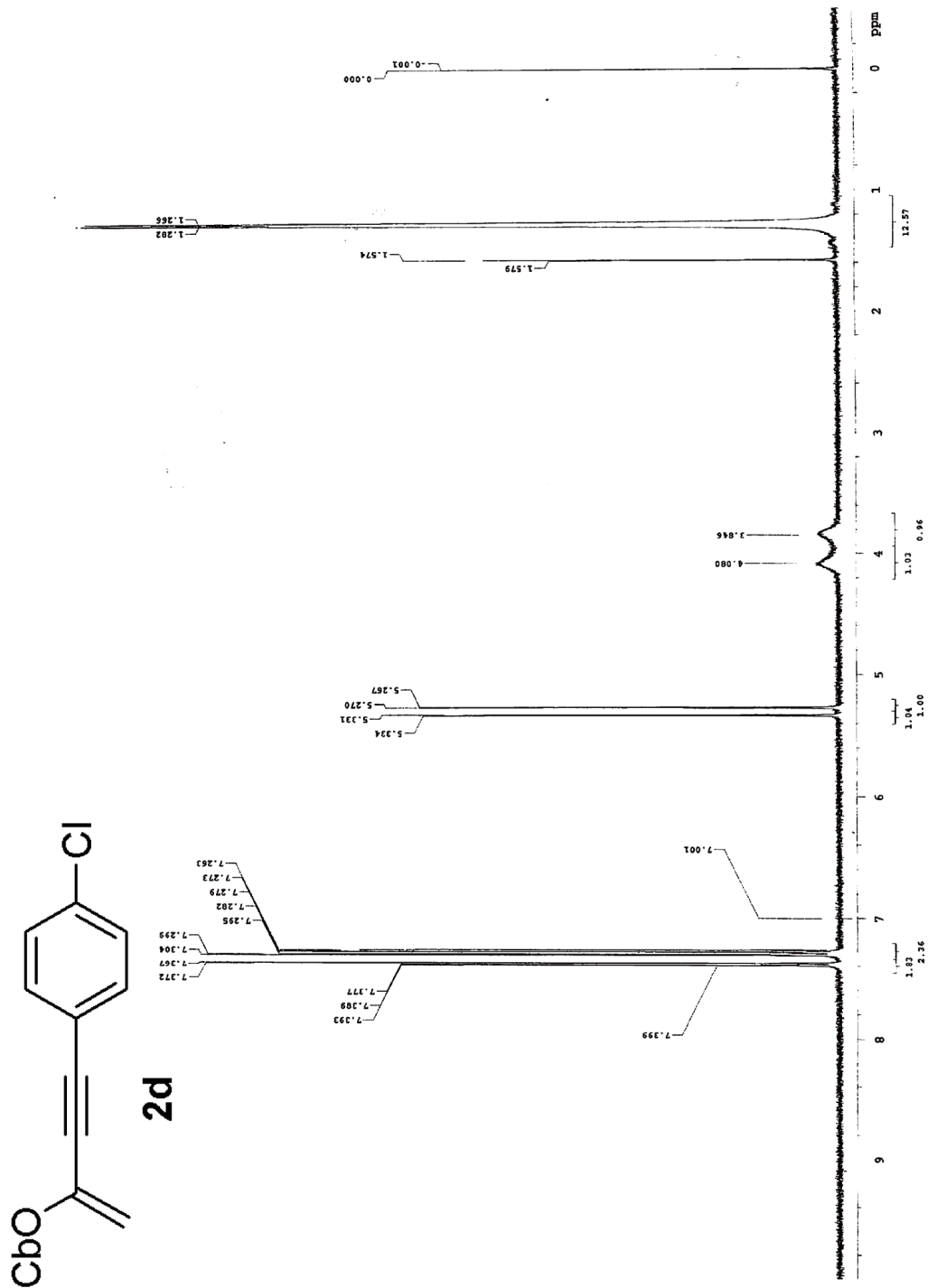
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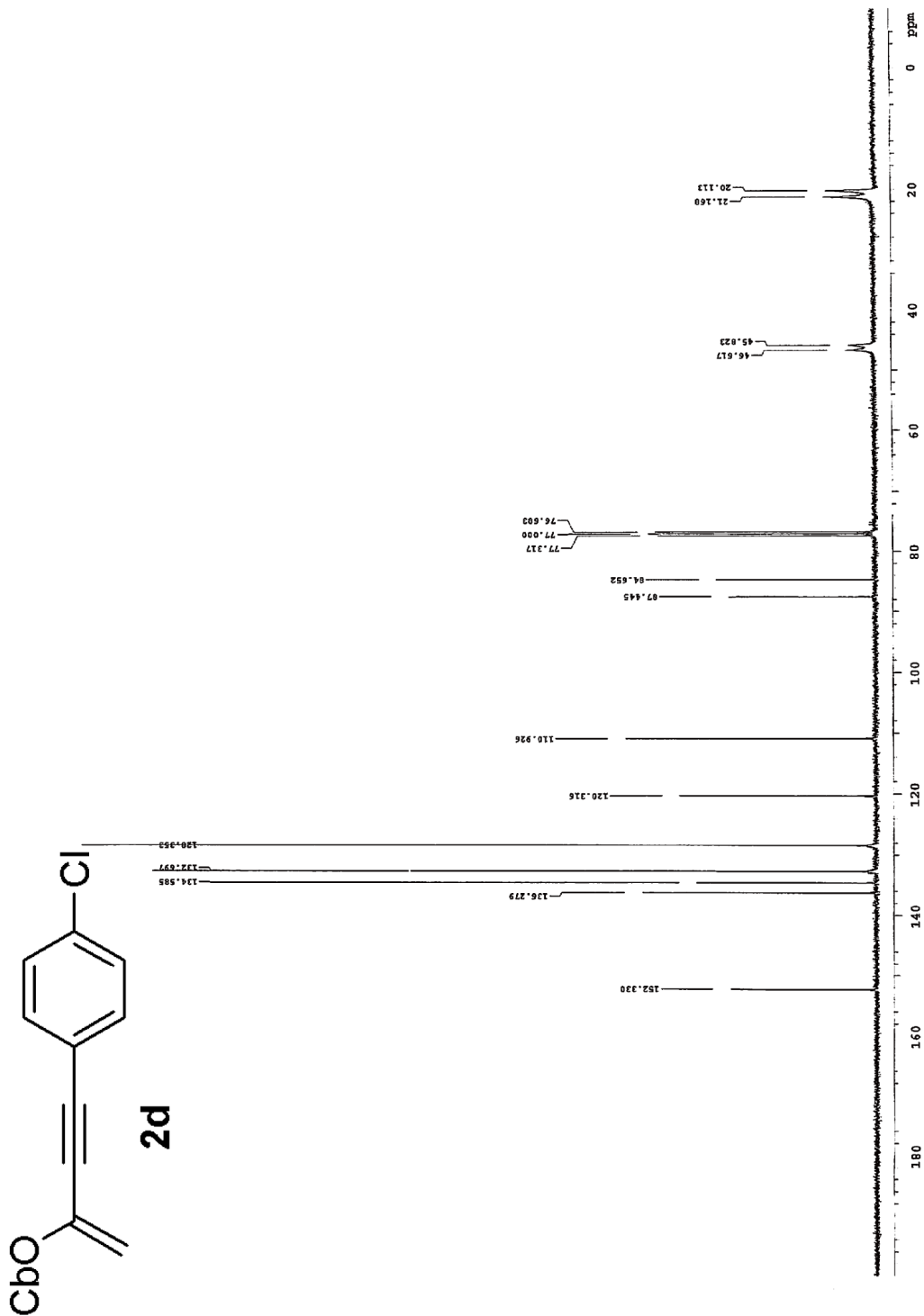
¹H NMR spectrum of 1-Phenyl-3-(methoxymethoxy)-but-3-en-1-yne (2c)



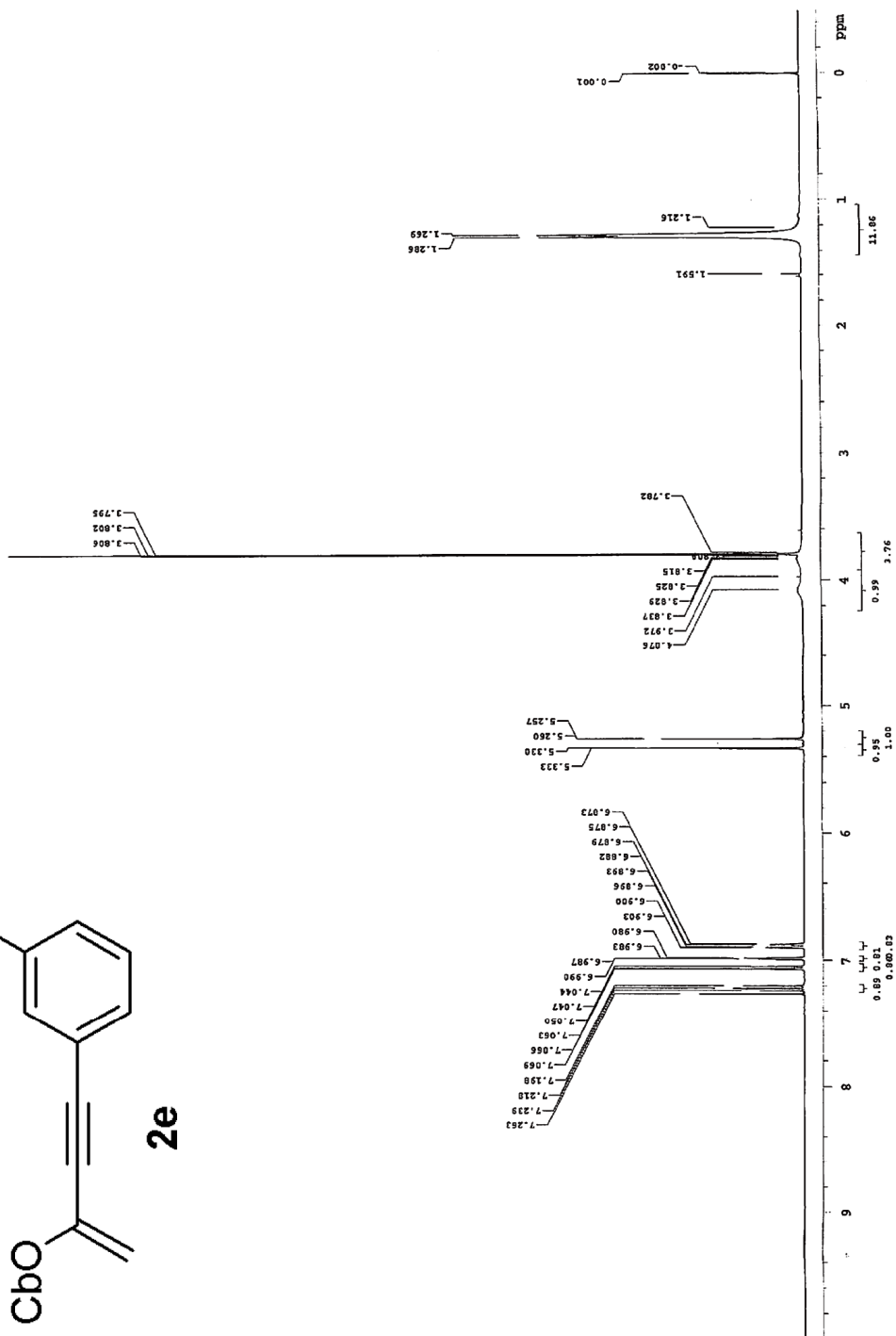
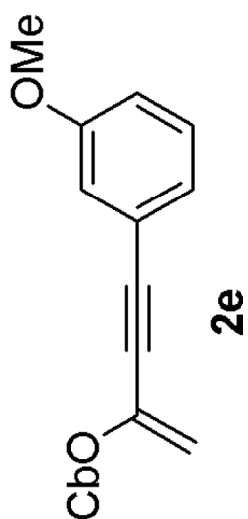
¹³C NMR spectrum of 1-Phenyl-3-(methoxymethoxy)-but-3-en-1-yne (2c)



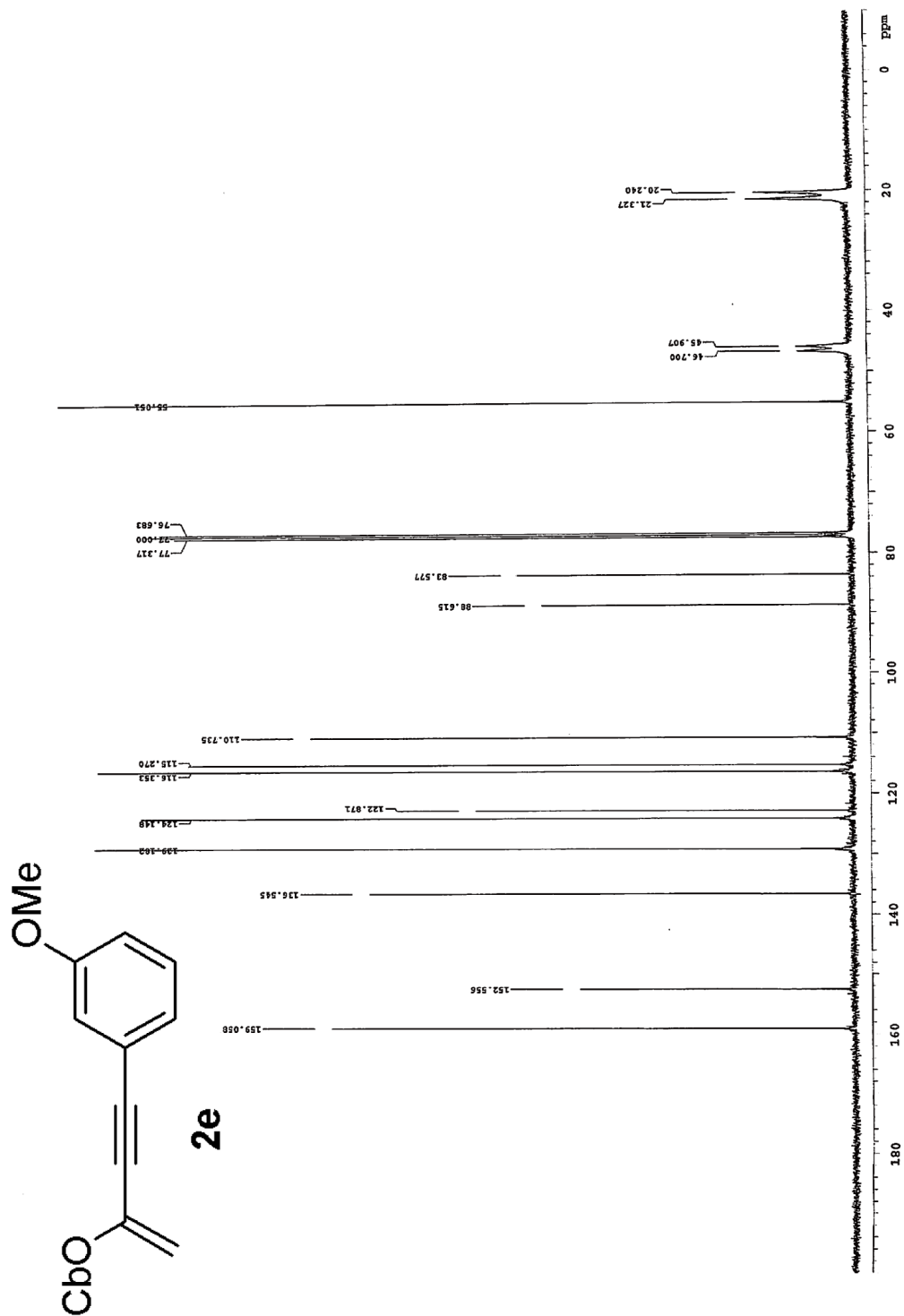
¹H NMR spectrum of 1-(4-Chlorophenyl)but-3-en-1-yn-1-yl
N,N-Diisopropylcarbamate (2d)



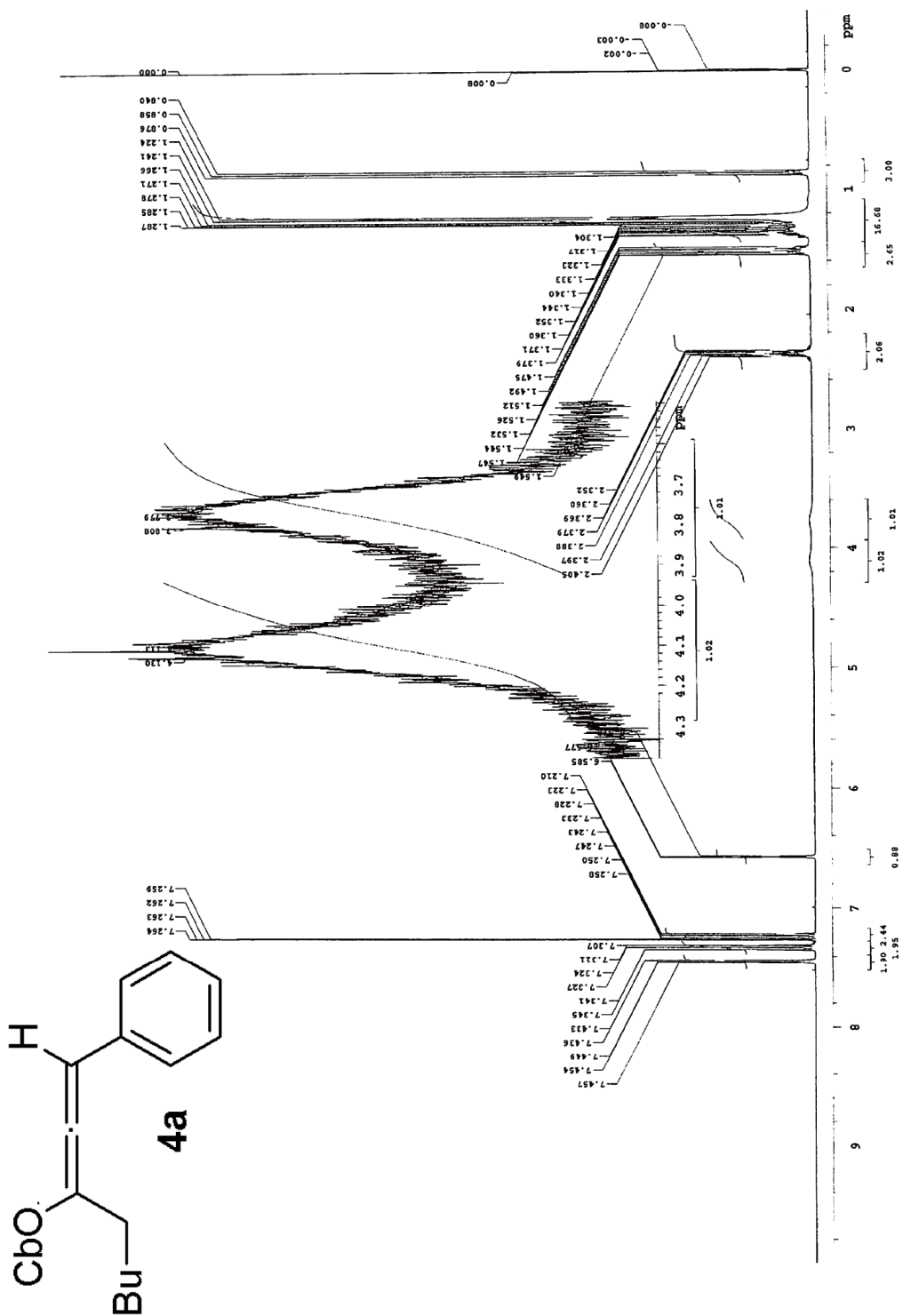
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N,N-Diisopropylcarbamate (2d)



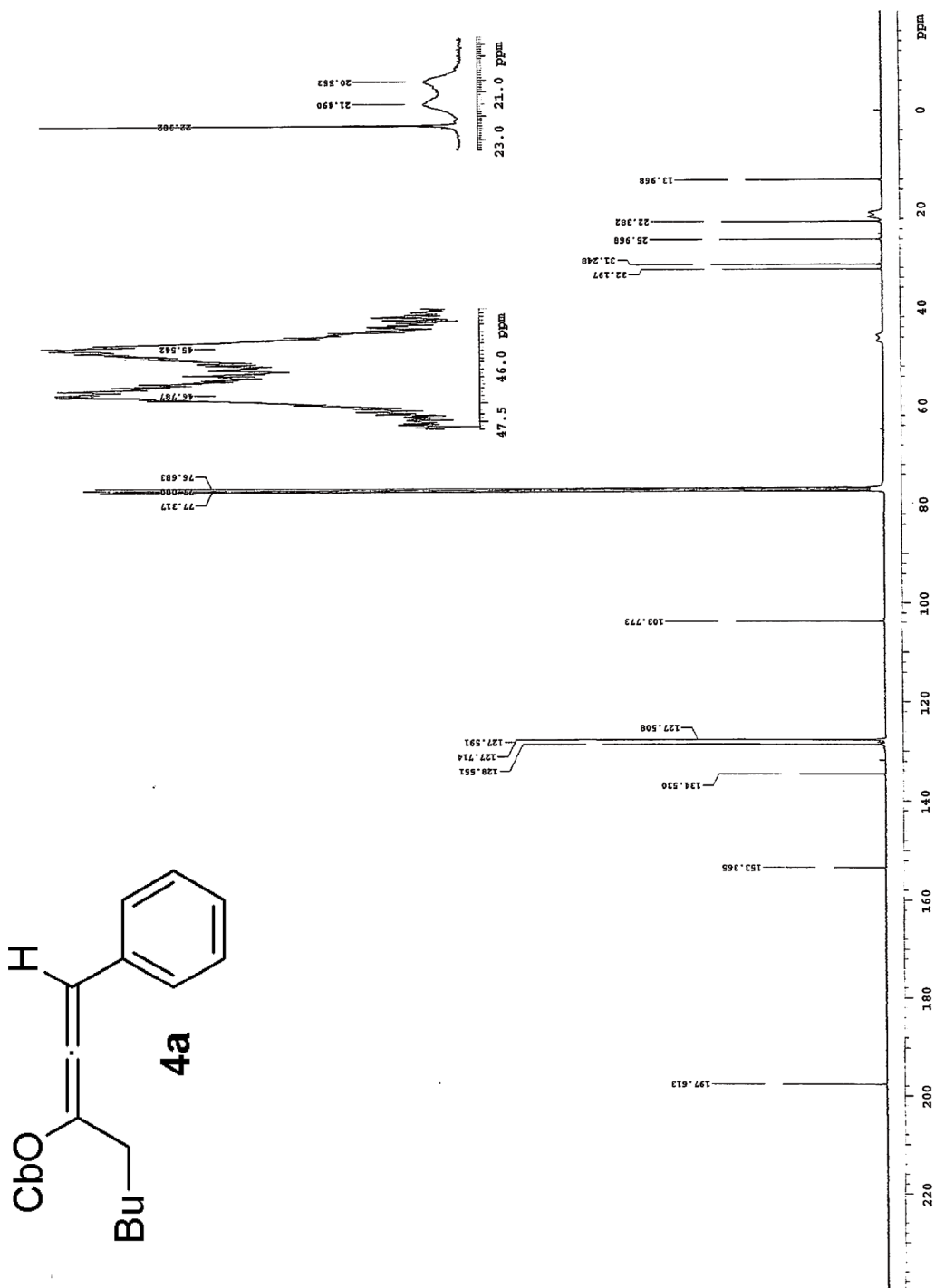
¹H NMR spectrum of 1-(3-Methoxyphenyl)but-3-en-1-yn-1-yl *N,N*-Diisopropylcarbamate (2e)



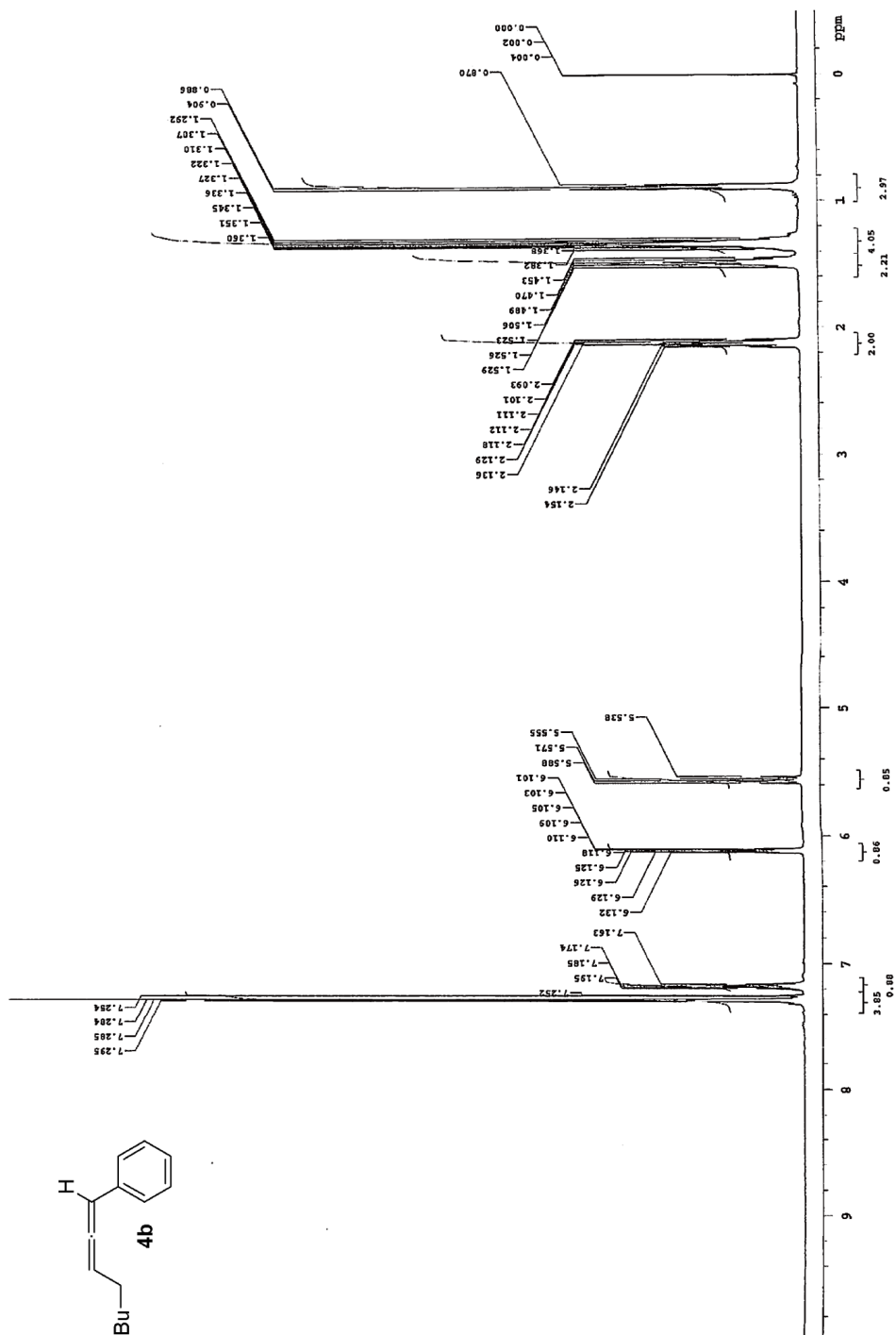
¹³C NMR spectrum of 1-(3-Methoxyphenyl)but-3-en-1-yn-1-yl
N,N-Diisopropylcarbamate (**2e**)



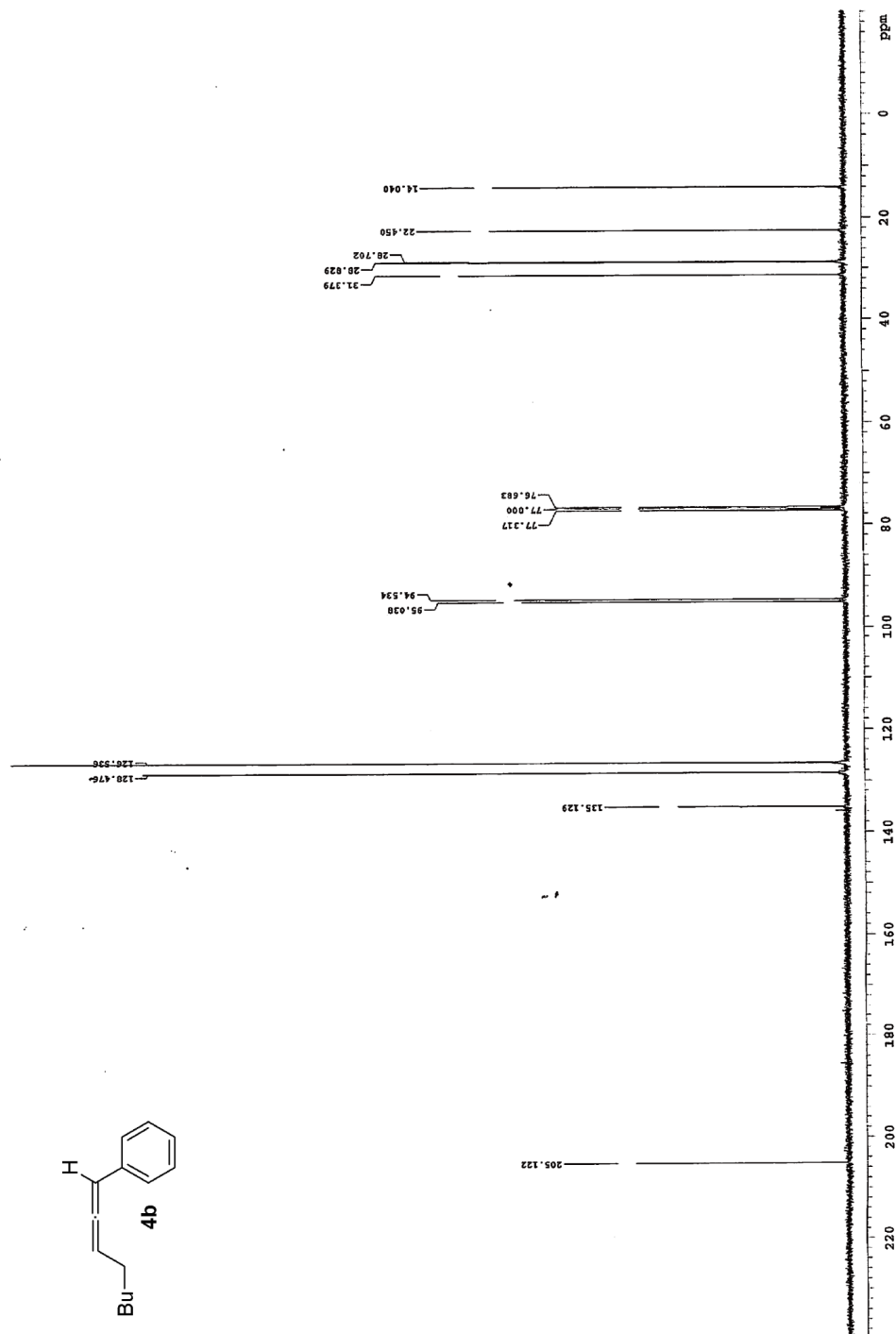
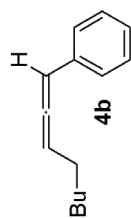
¹H NMR spectrum of 1-Phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4a)



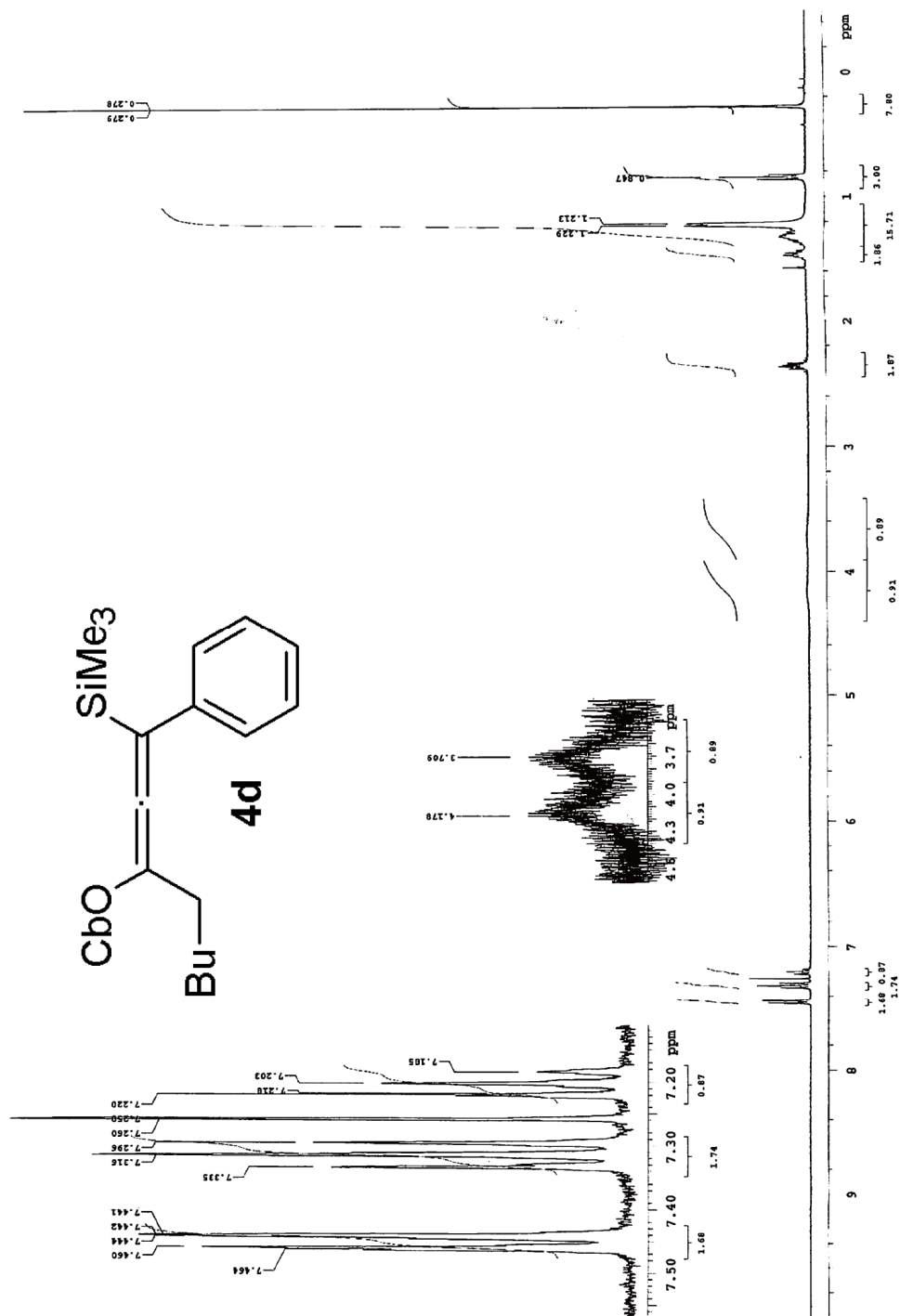
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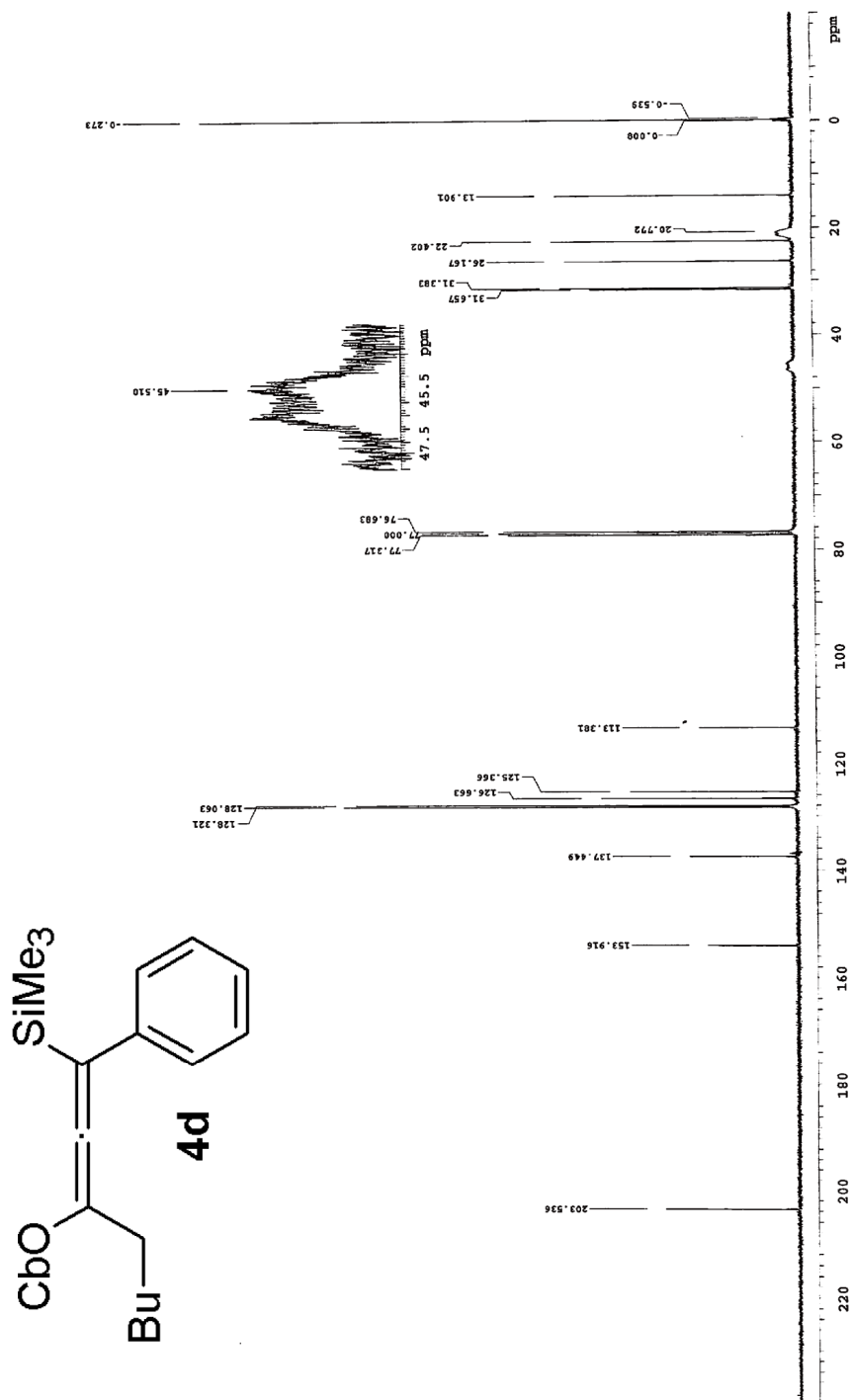
¹H NMR spectrum of 1-Phenylbuta-1,2-diene (4b)



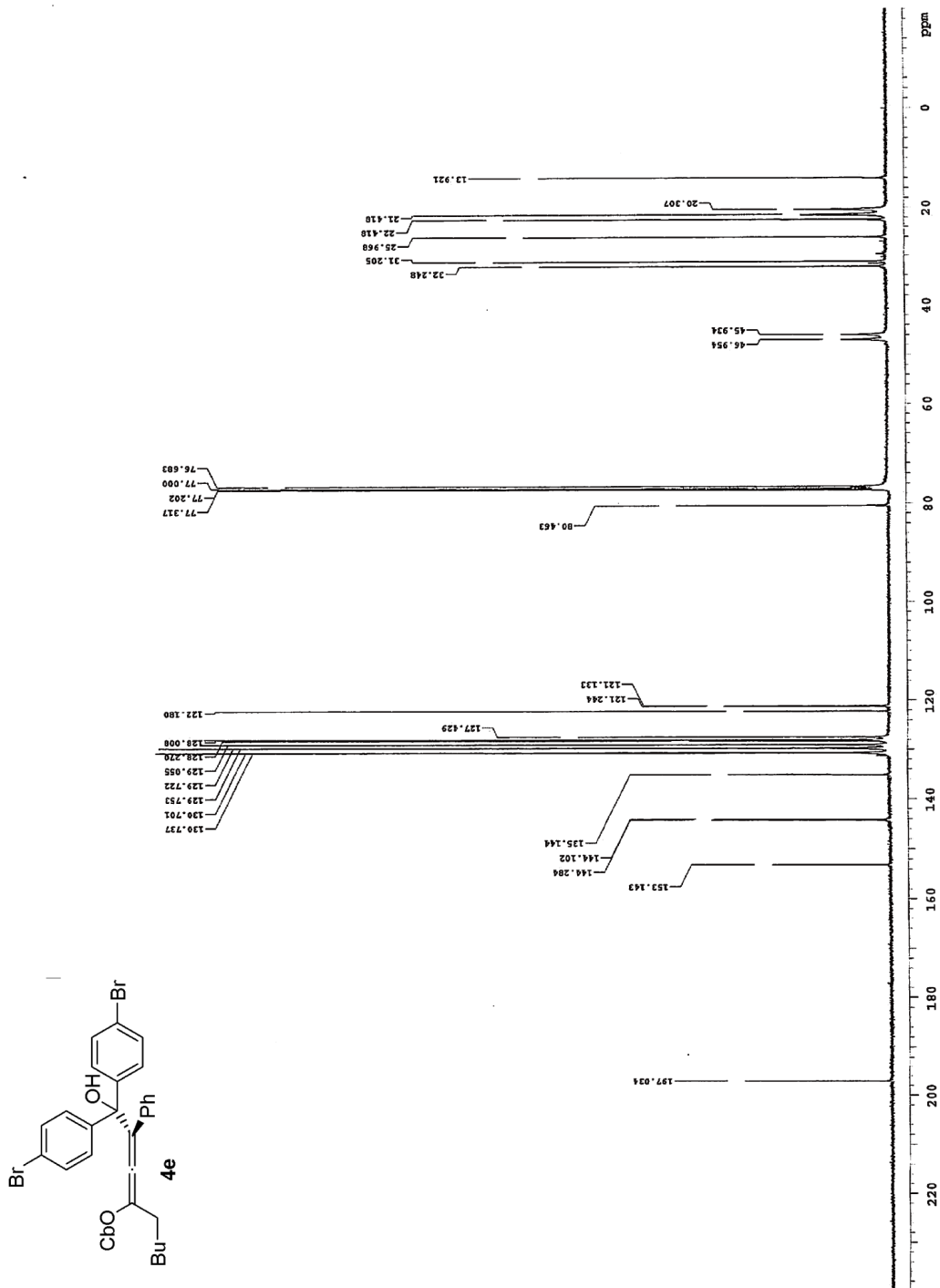
¹³C NMR spectrum of 1-Phenylbuta-1,2-diene (4b)



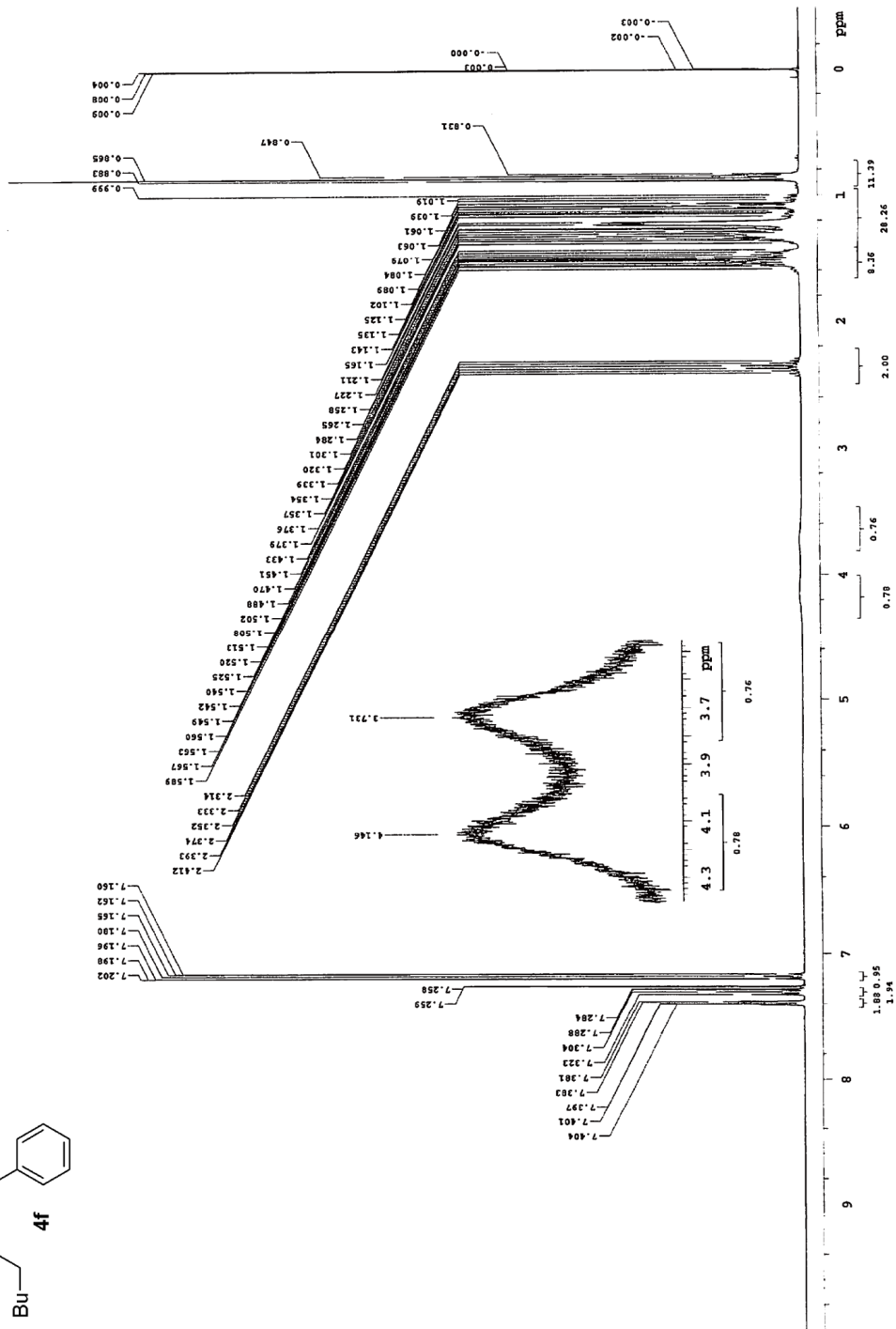
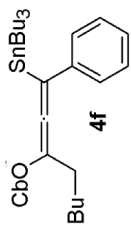
¹H NMR spectrum of 1-Trimethylsilyl-1-phenylocta-1,2-dien-3-yl
N,N-diisopropylcarbamate (4d)



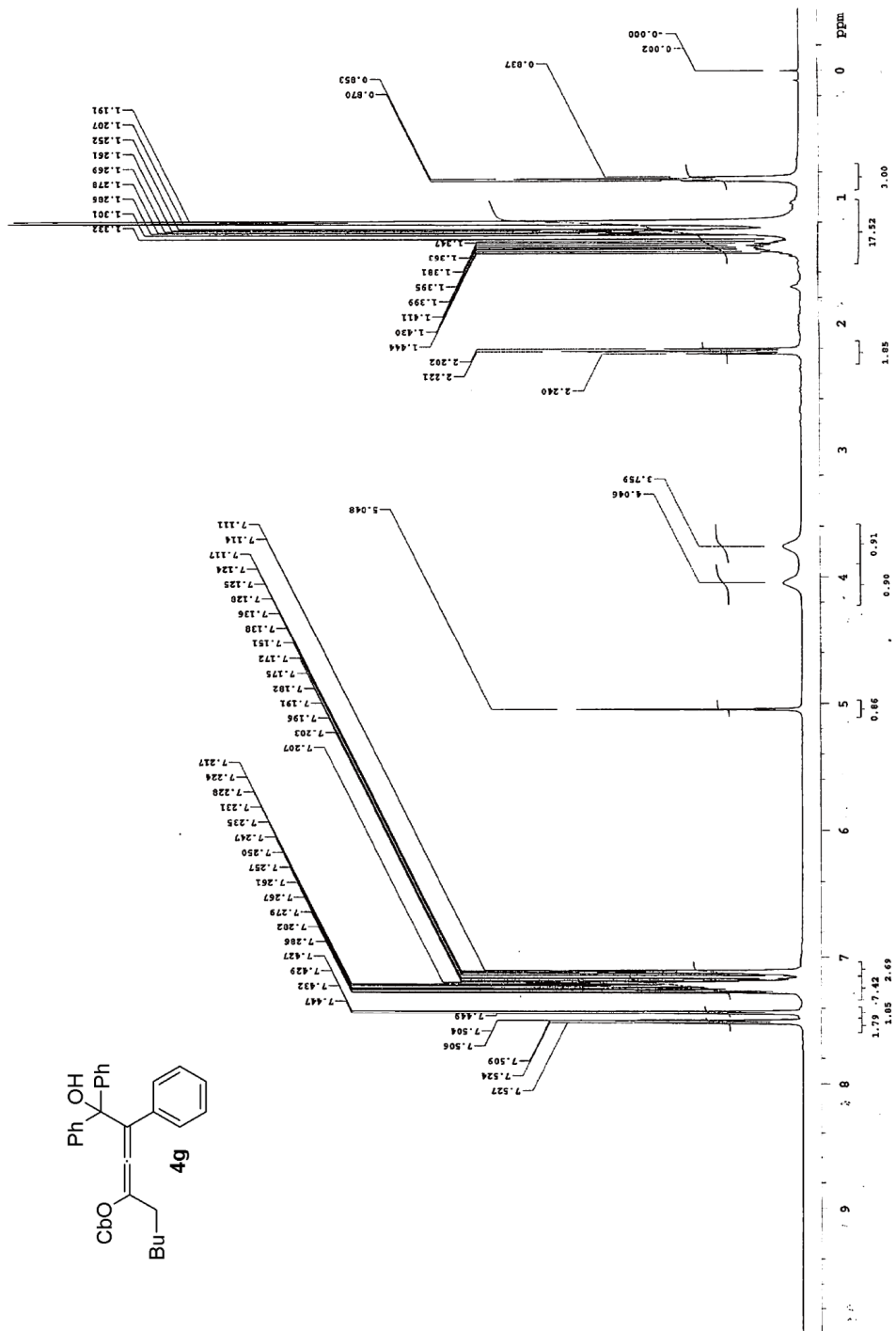
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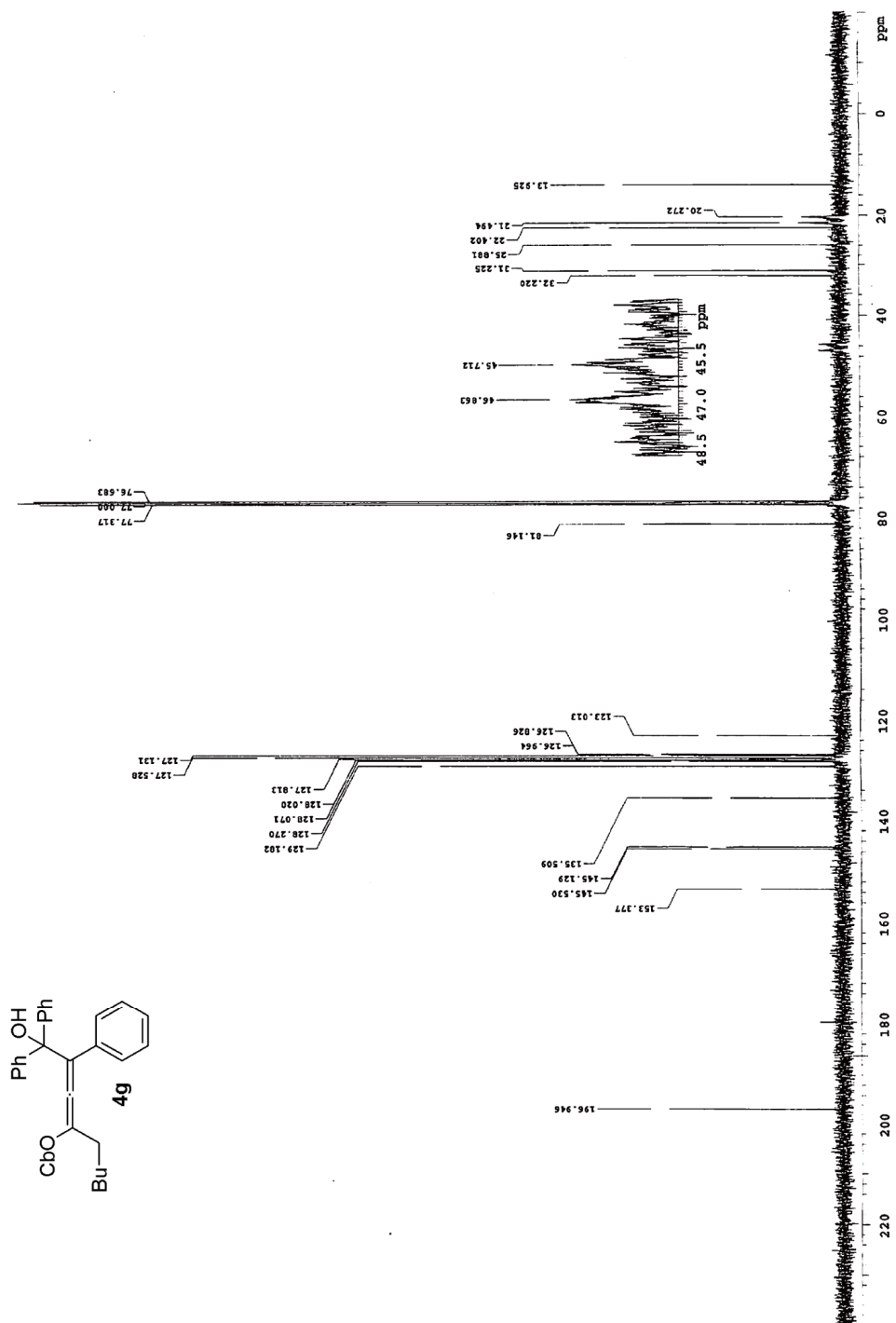
¹³C NMR spectrum of 1,1-Bis(4-bromophenyl)-1-hydroxy-2-phenylnona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4e)



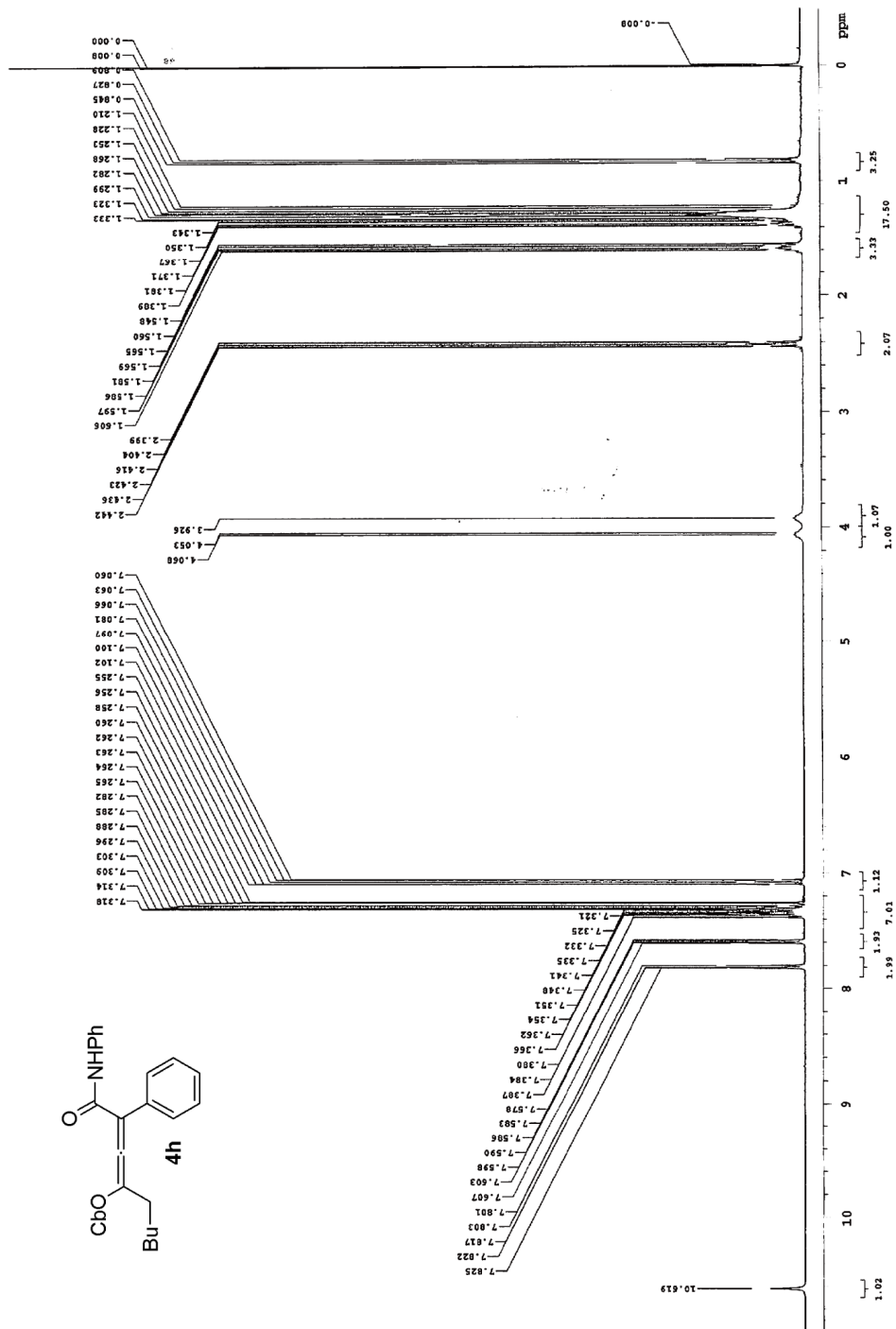
**¹H NMR spectrum of 1-Tributylstannyl-1-phenylocta-1,2-dien-3-yl
N,N-diisopropylcarbamate (4f)**



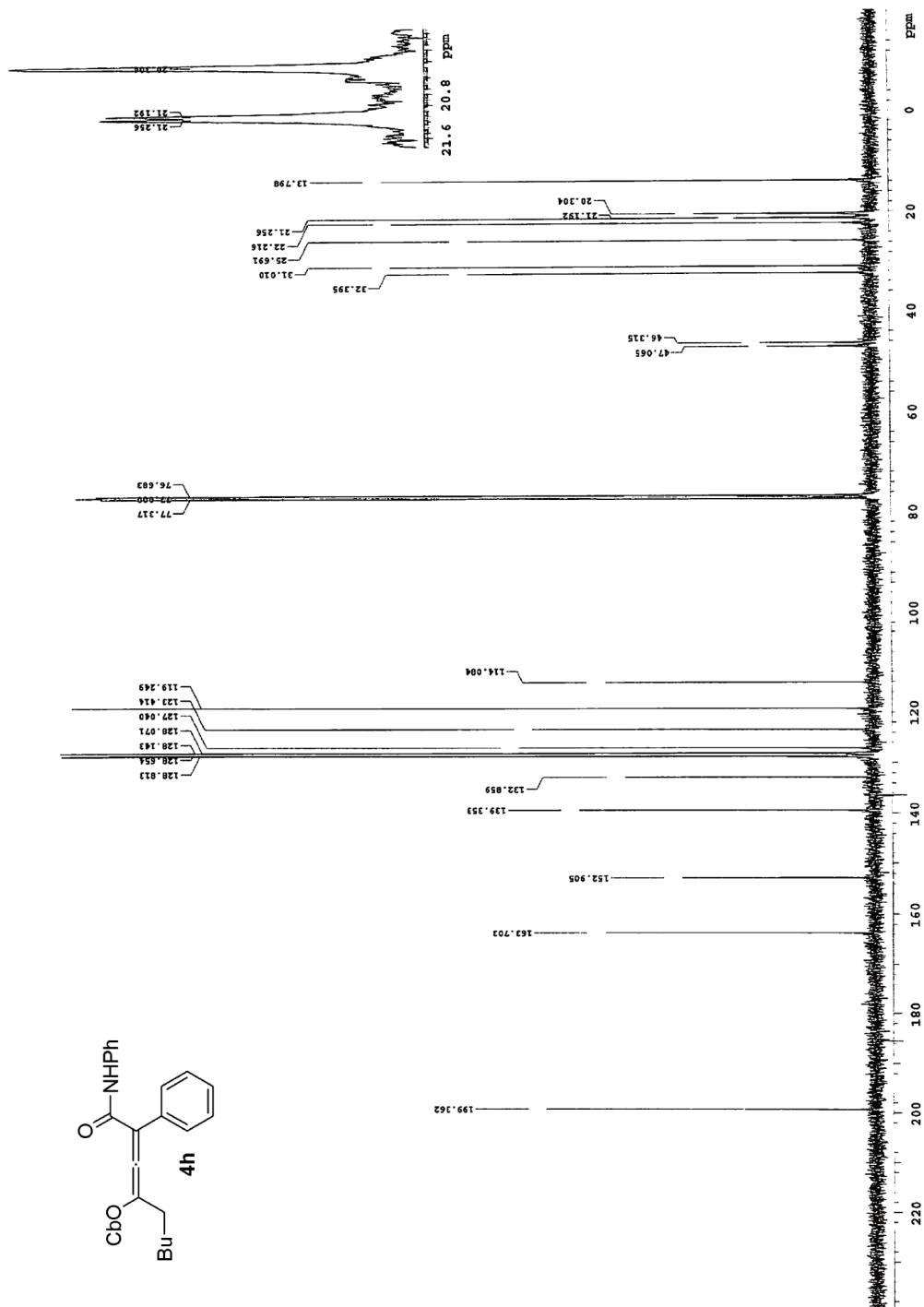
¹H NMR spectrum of 1-Hydroxy-1,1,2-triphenylnona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4g)



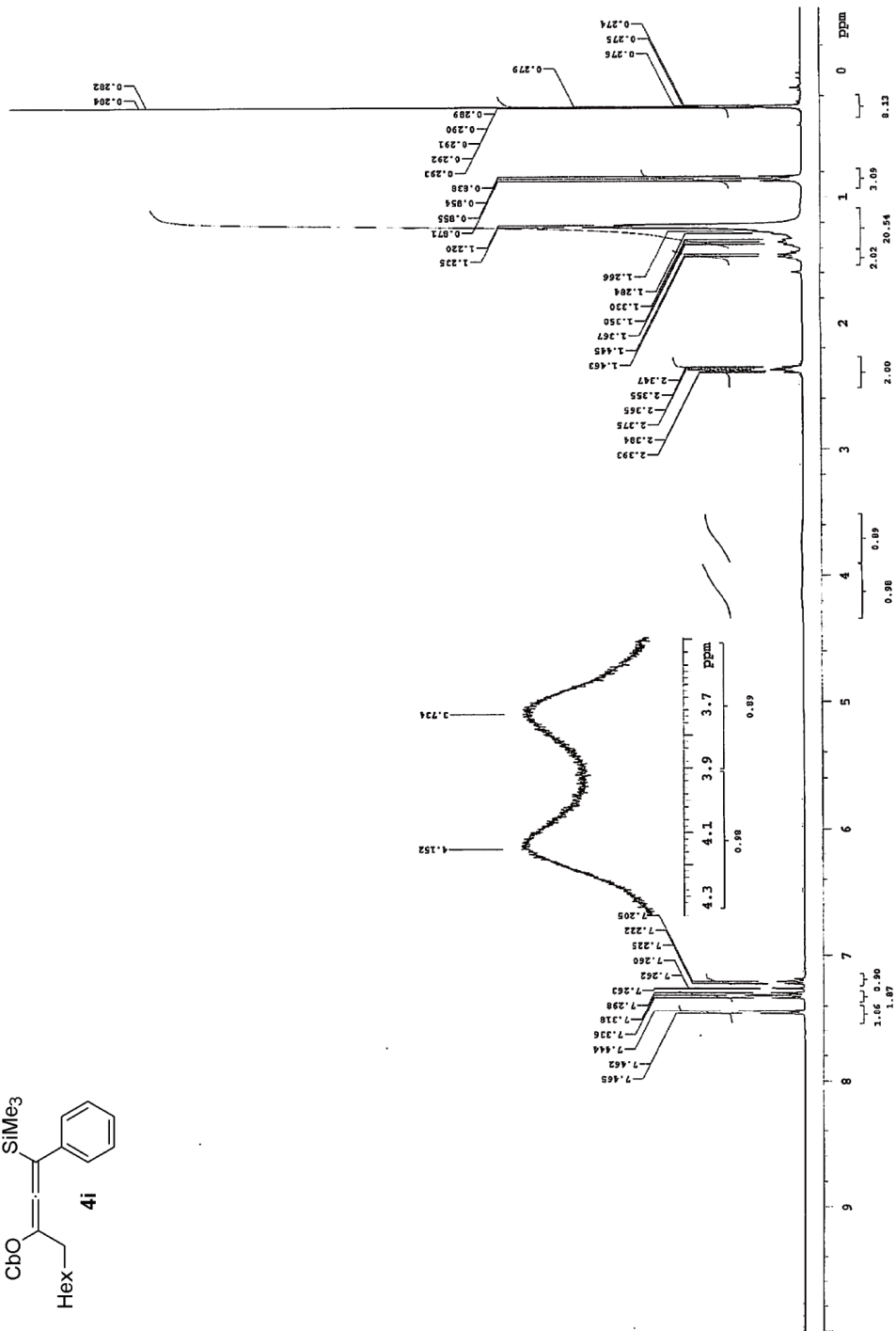
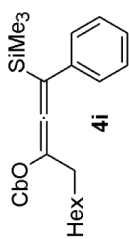
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N,N-diisopropylcarbamate (4g)



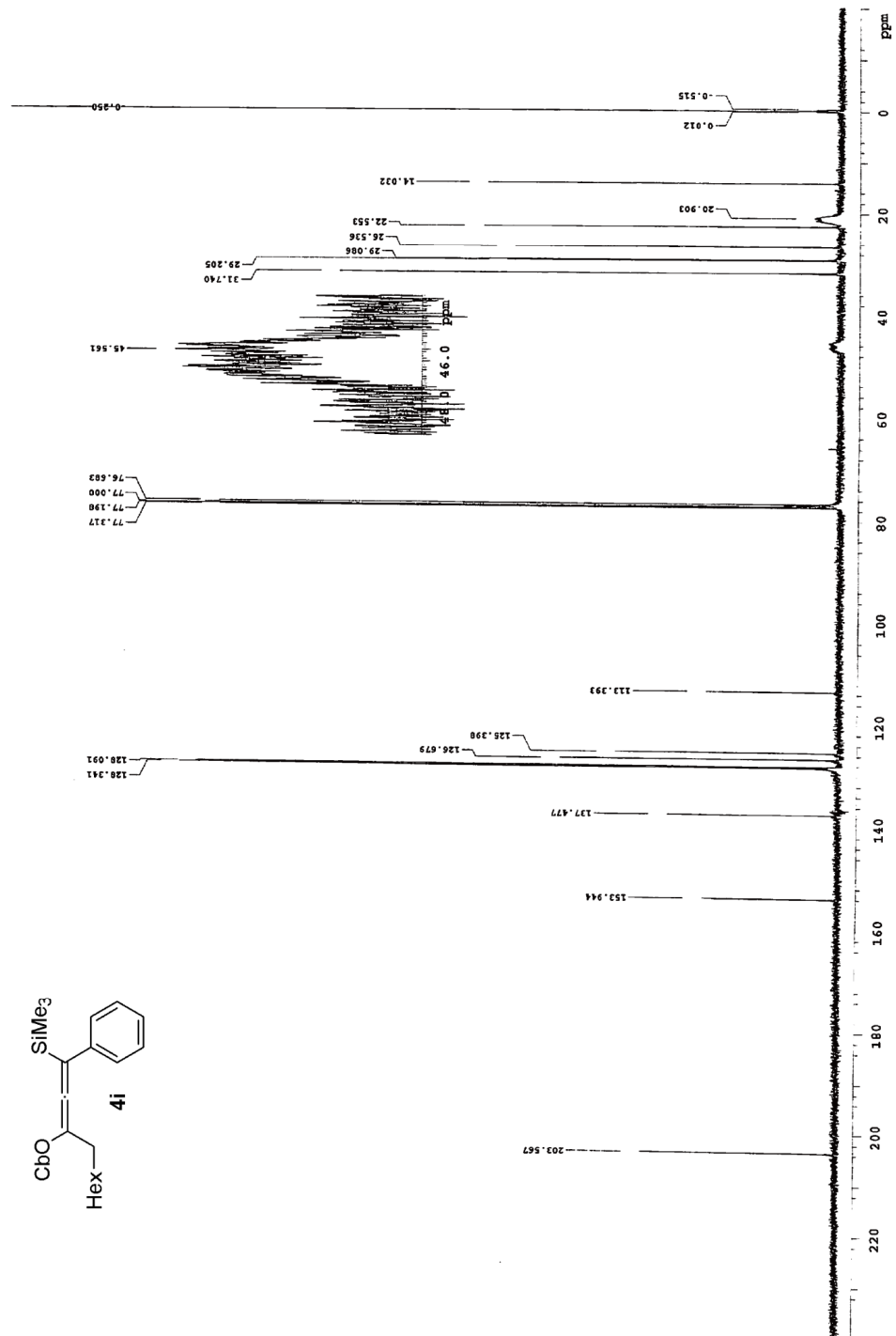
¹H NMR spectrum of 1-Oxo-2-phenyl-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4h)



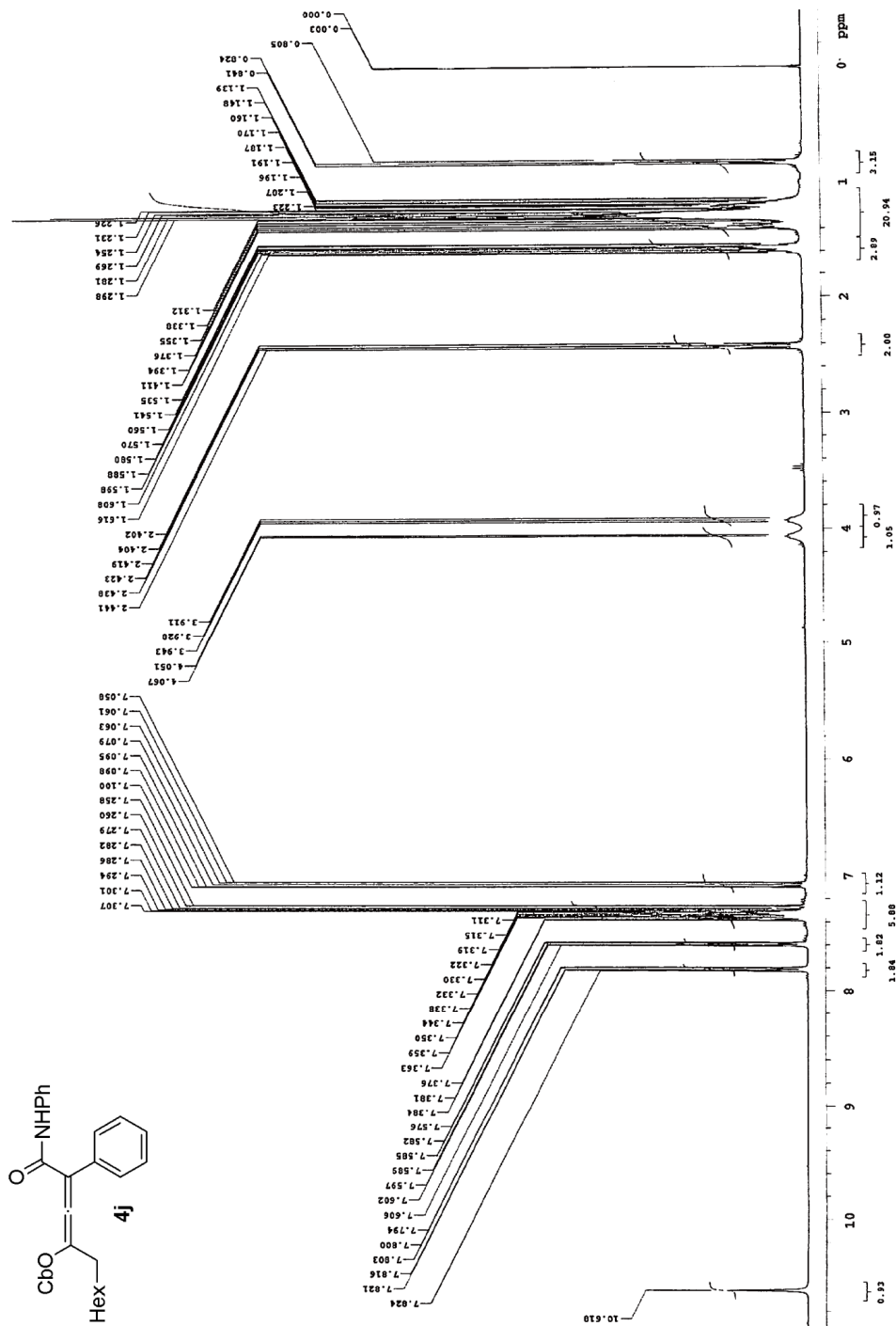
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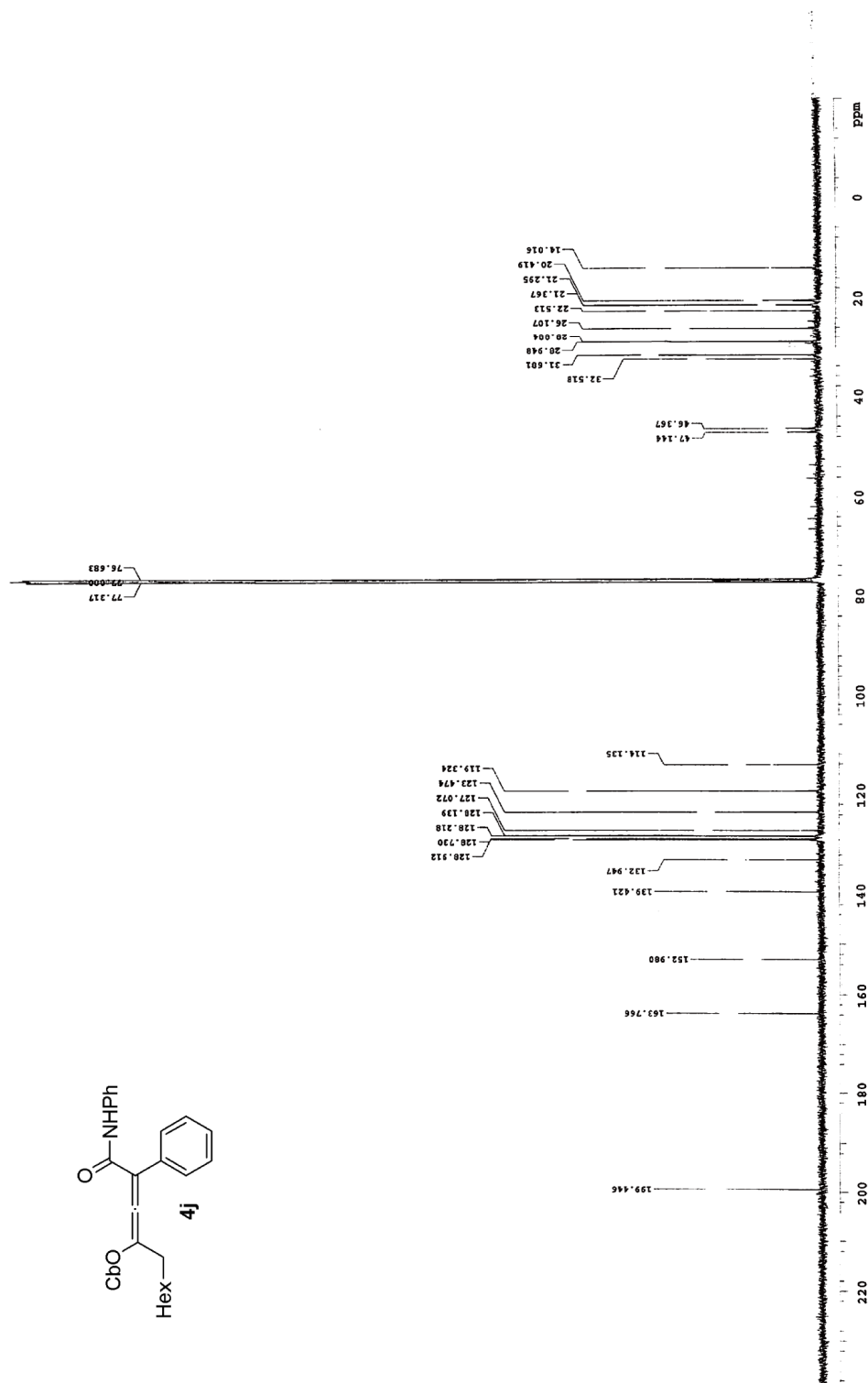
¹H NMR spectrum of 1-Trimethylsilyl-1-phenyldeca-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4i)



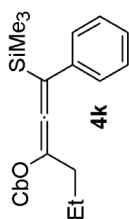
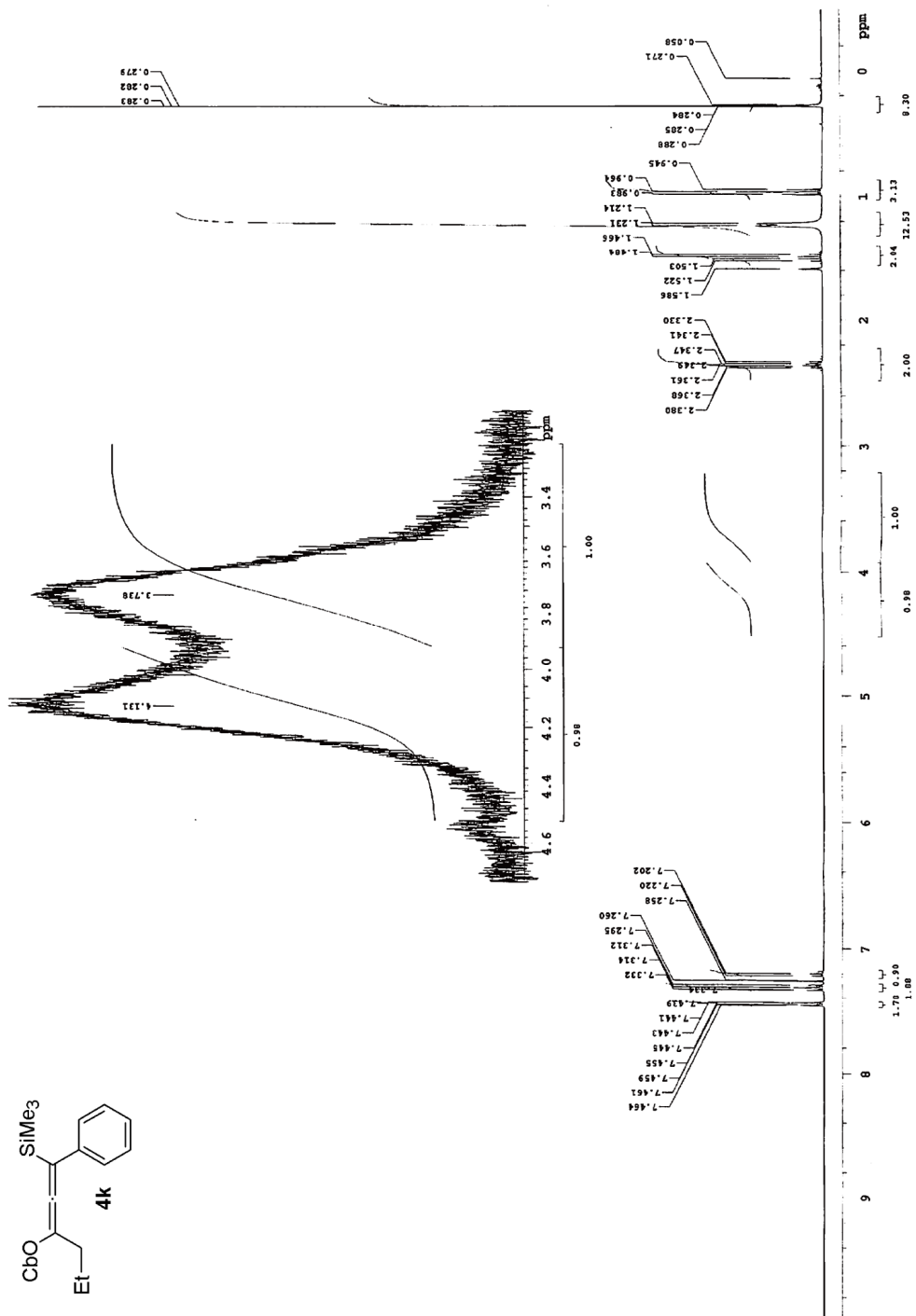
¹³C NMR spectrum of 1-Trimethylsilyl-1-phenyldeca-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4i)



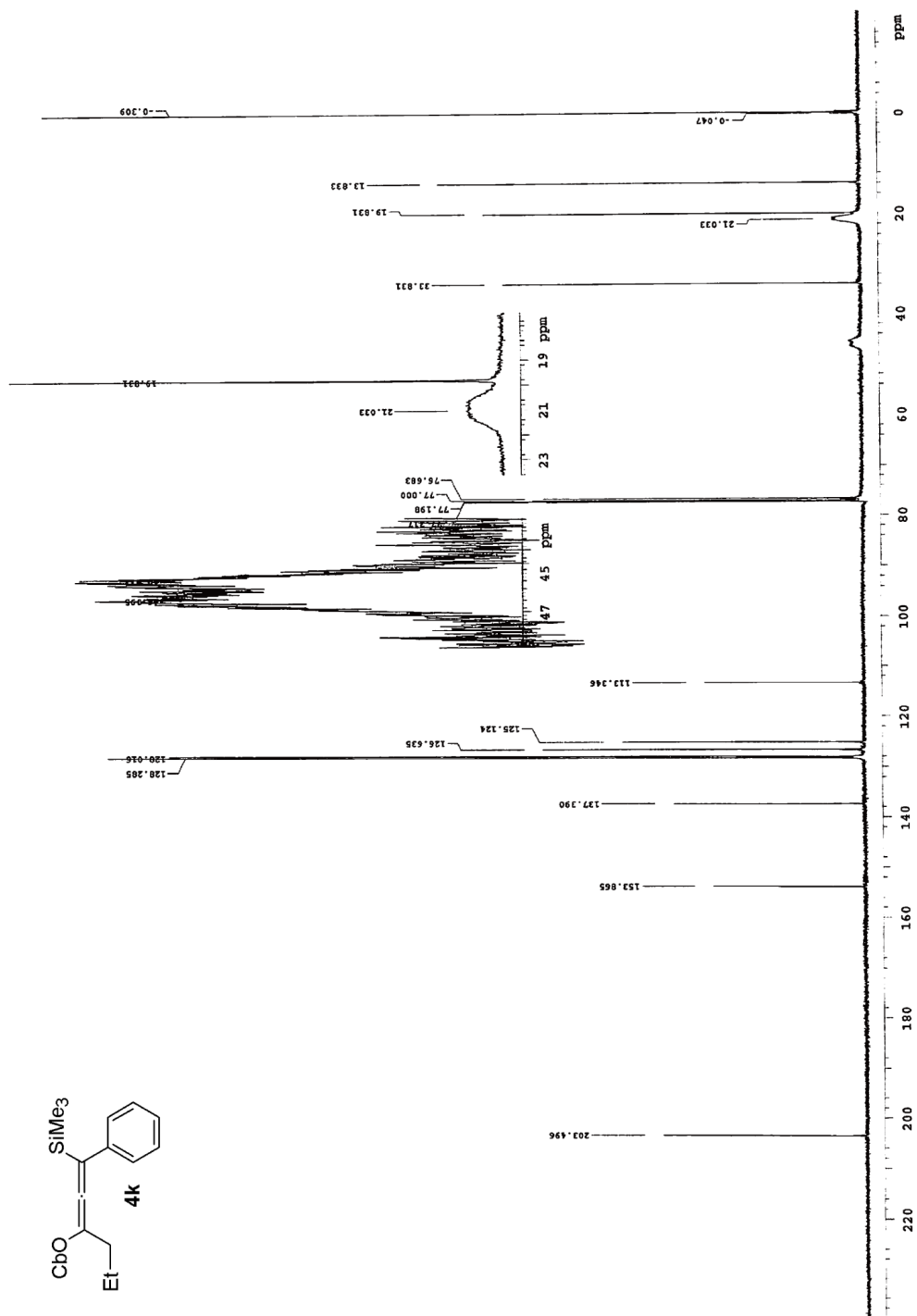
¹H NMR spectrum of 1-Oxo-2-phenyl-1-(phenylamino)undeca-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4j)



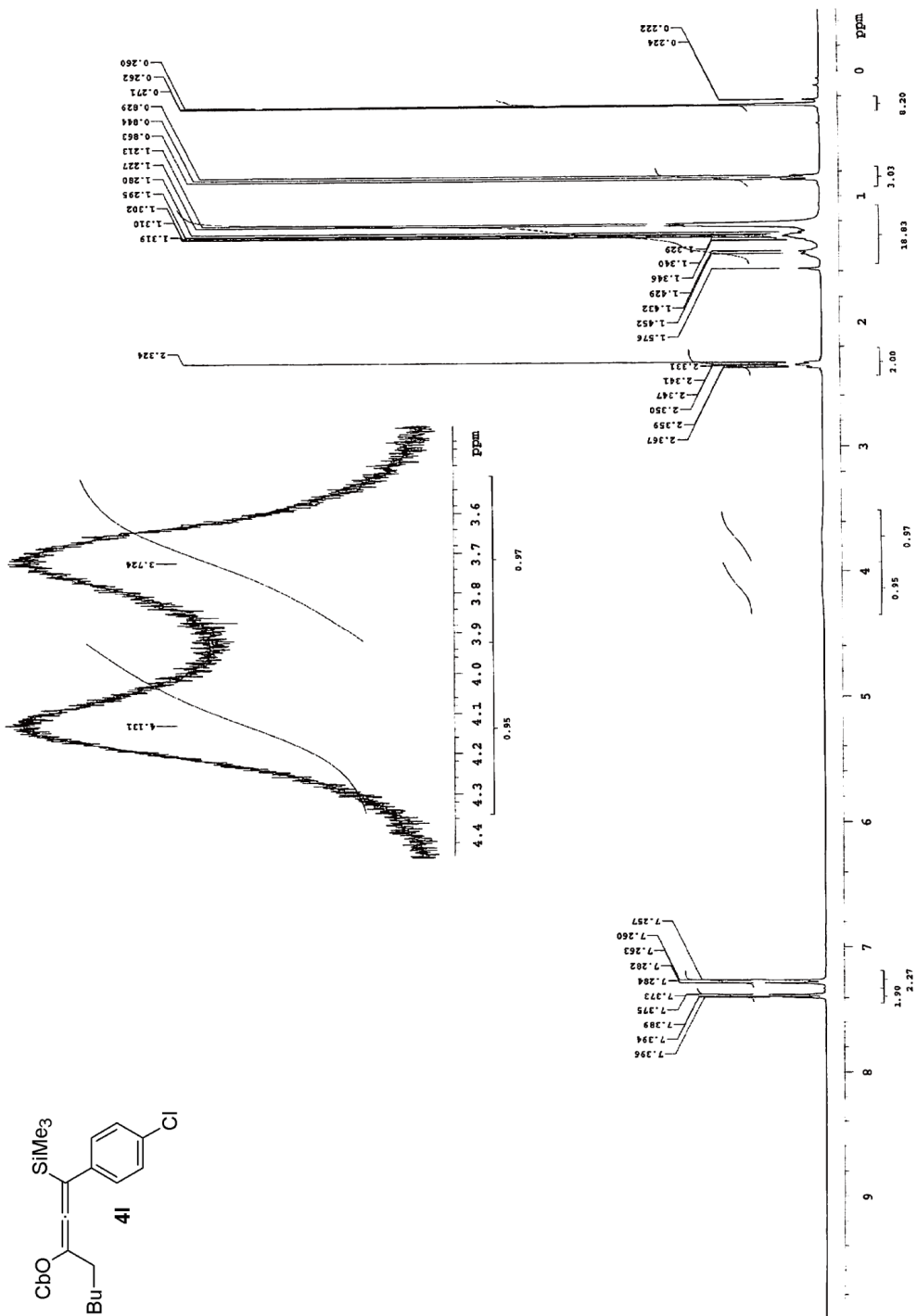
¹³C NMR spectrum of 1-Oxo-2-phenyl-1-(phenylamino)undeca-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4j)



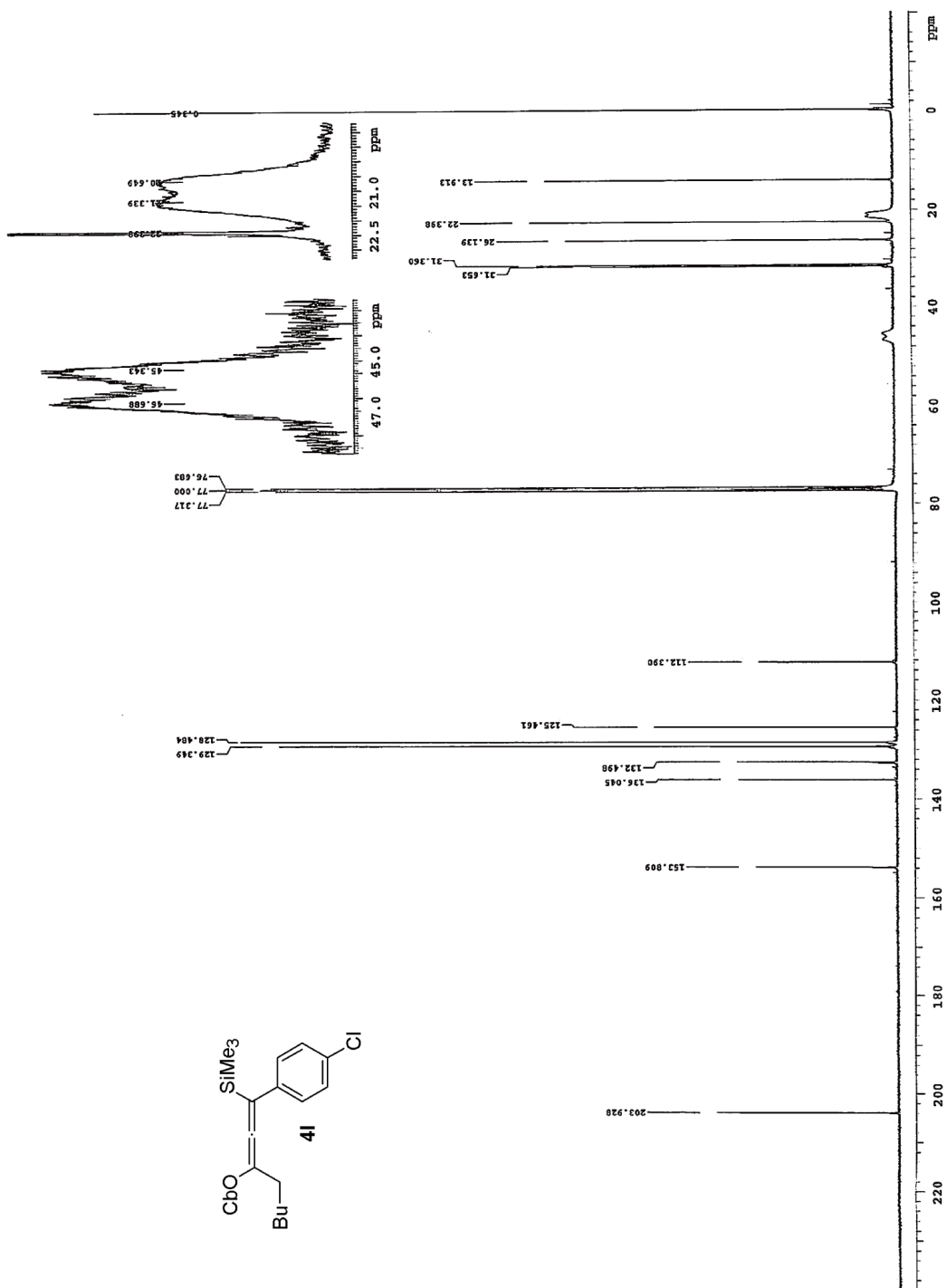
¹H NMR spectrum of 1-Trimethylsilyl-1-phenylhex-1,2-dien-3-yl
N,N-diisopropylcarbamate (4k)



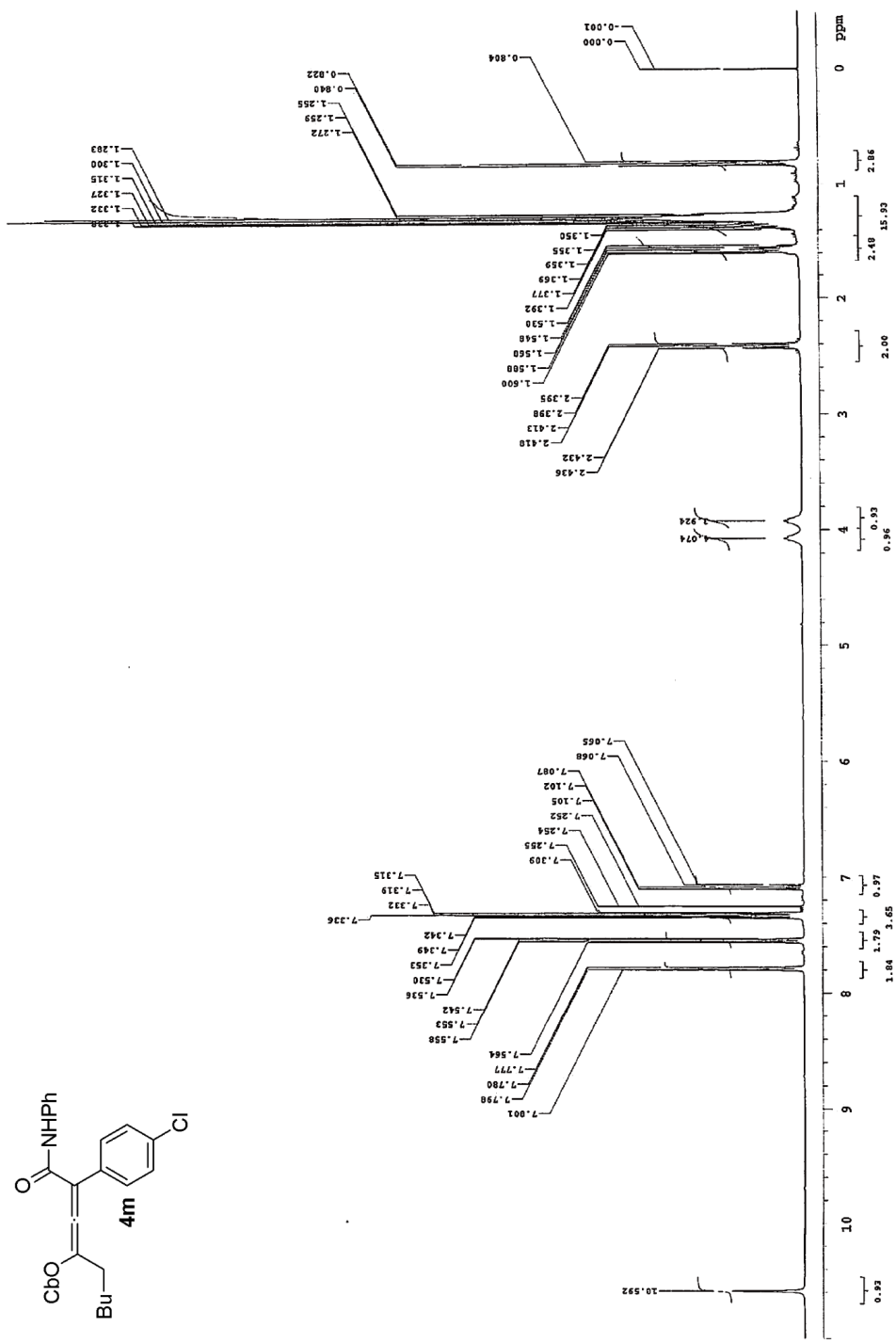
¹³C NMR spectrum of 1-Trimethylsilyl-1-phenylhex-1,2-dien-3-yl
N,N-diisopropylcarbamate (4k)



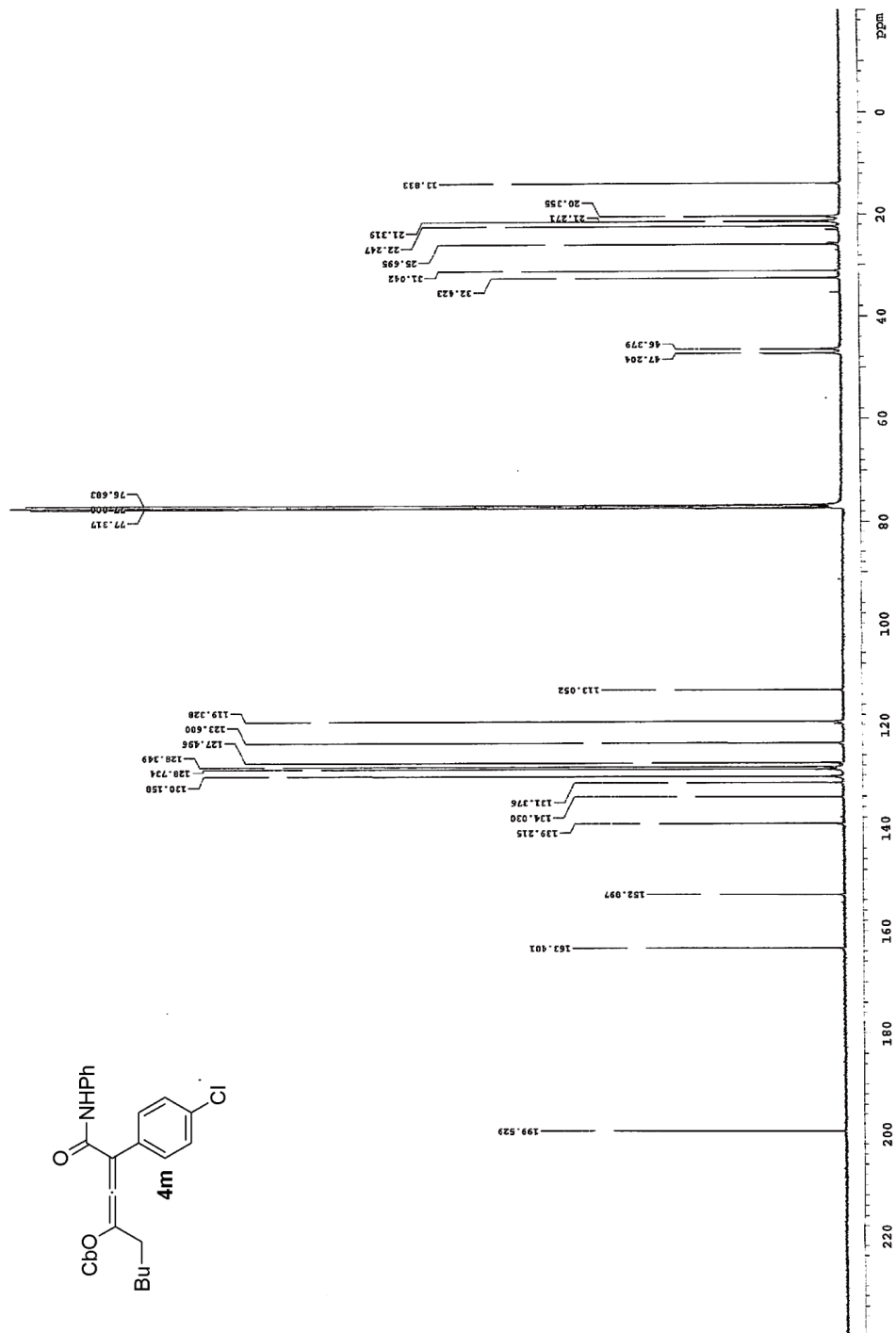
¹H NMR spectrum of 1-(4-Chlorophenyl)-1-trimethylsilylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4l)



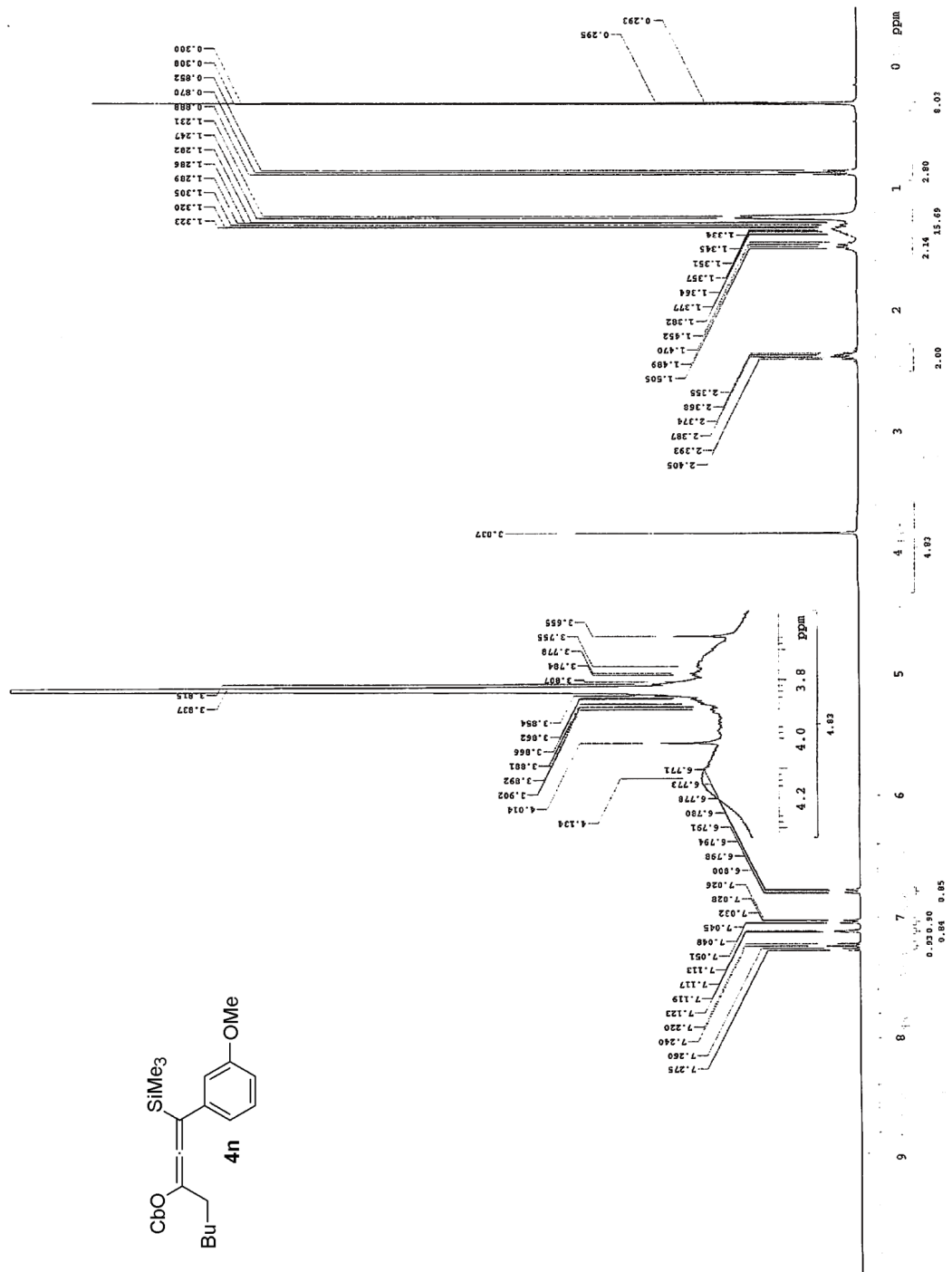
¹³C NMR spectrum of 1-(4-Chlorophenyl)-1-trimethylsilylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4I)



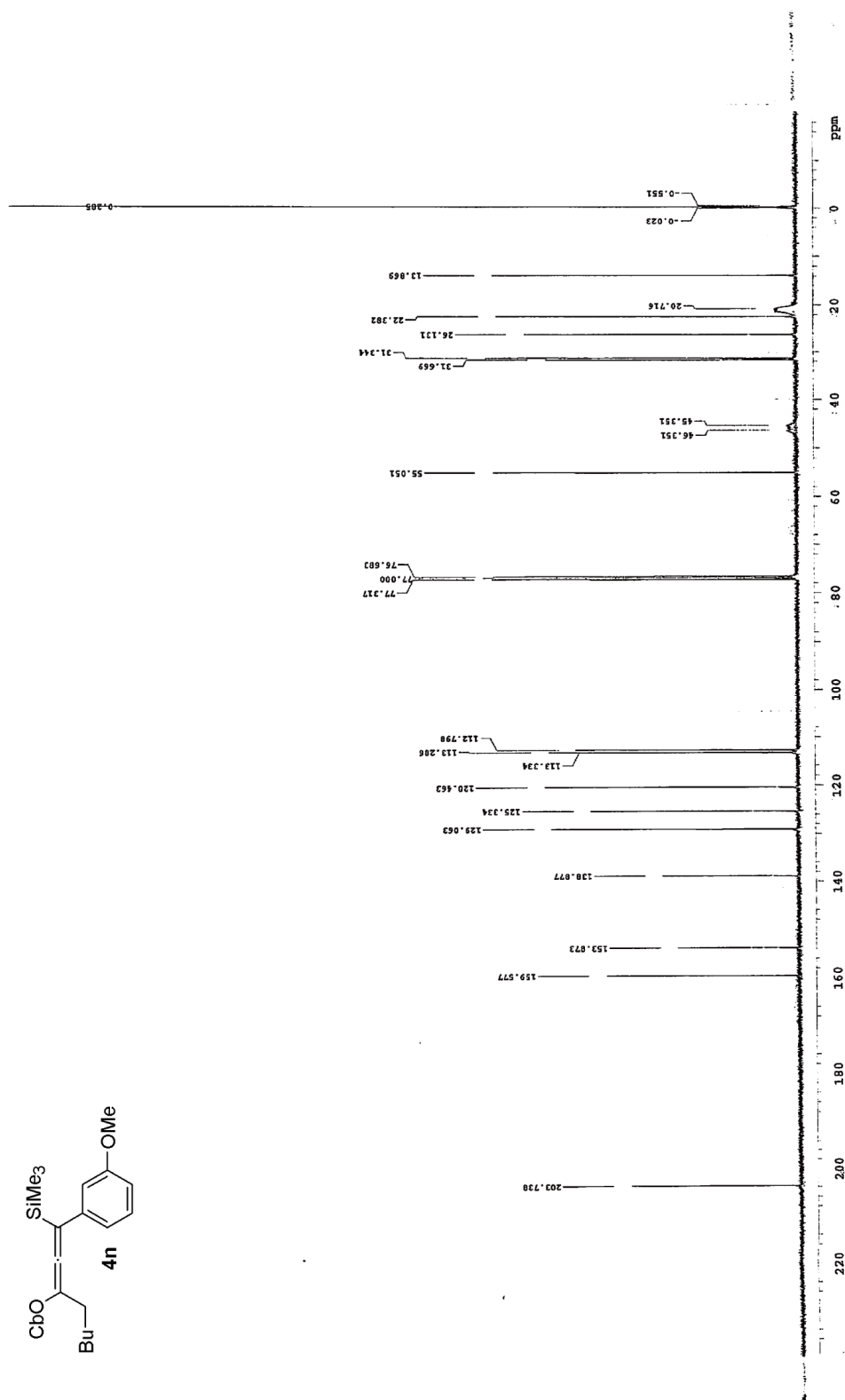
¹H NMR spectrum of 2-(4-Chlorophenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4m)



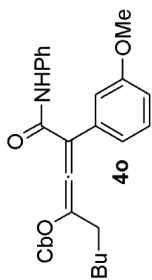
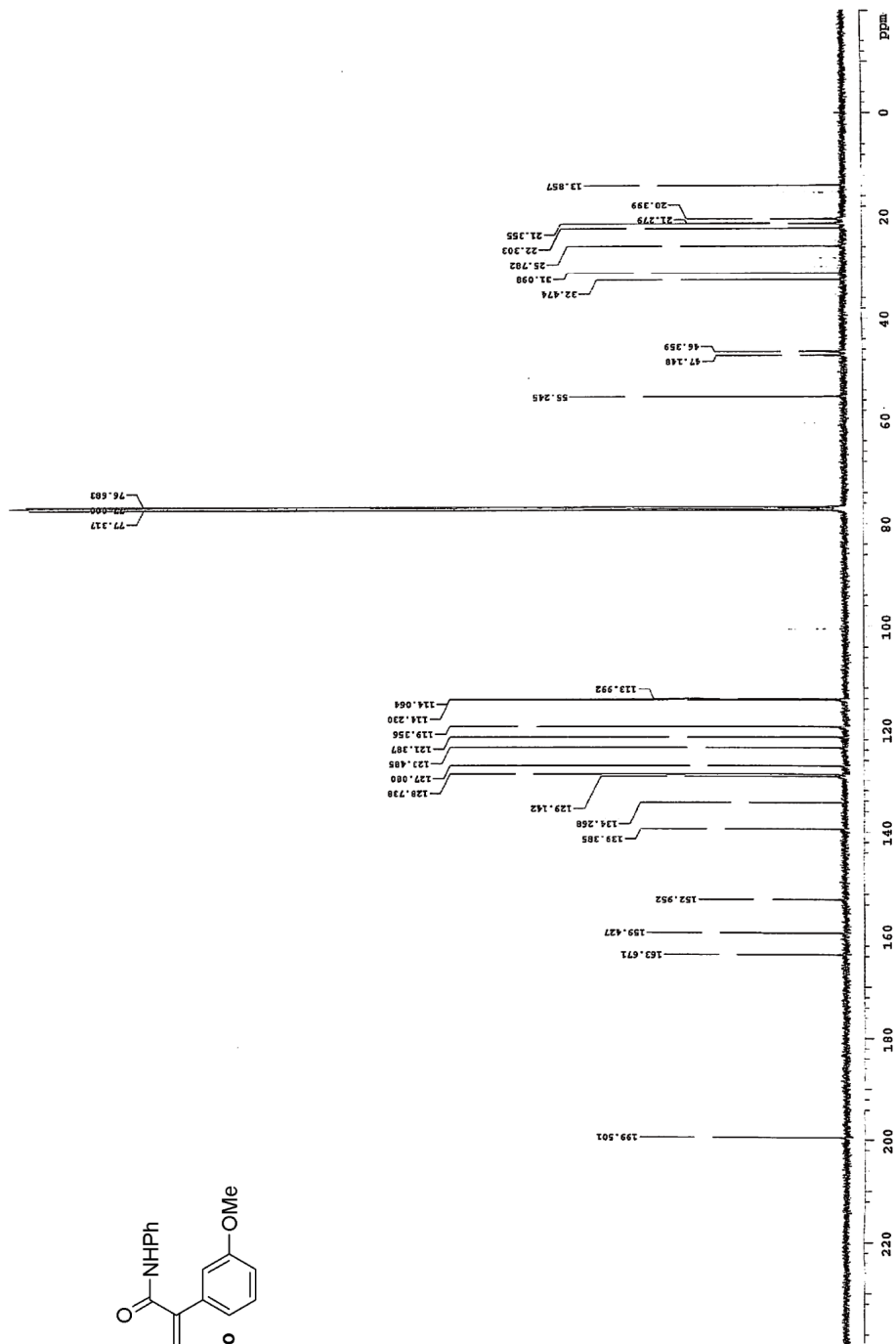
¹³C NMR spectrum of 2-(4-Chlorophenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4m)



¹H NMR spectrum of 1-(3-methoxyphenyl)-1-trimethylsilylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4n)

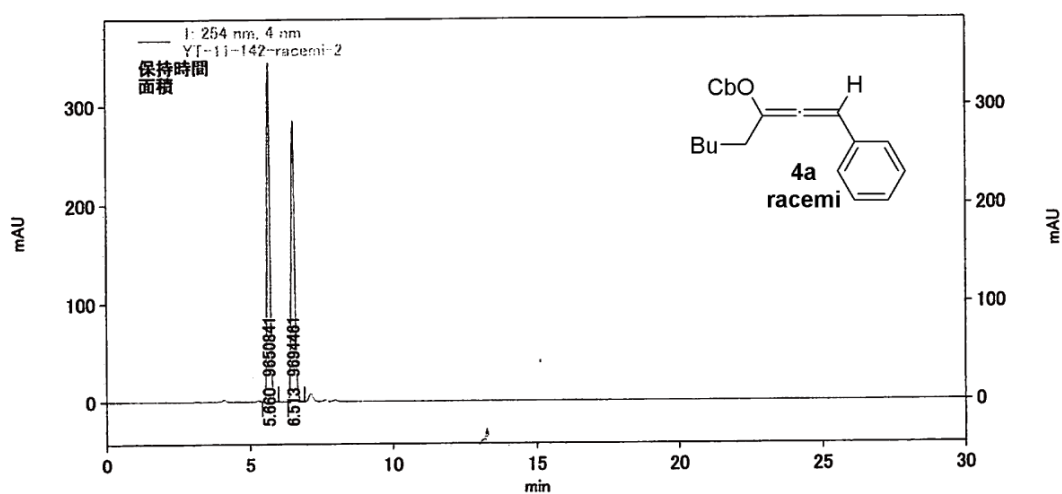


¹³C NMR spectrum of 1-(3-methoxyphenyl)-1-trimethylsilylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4n)



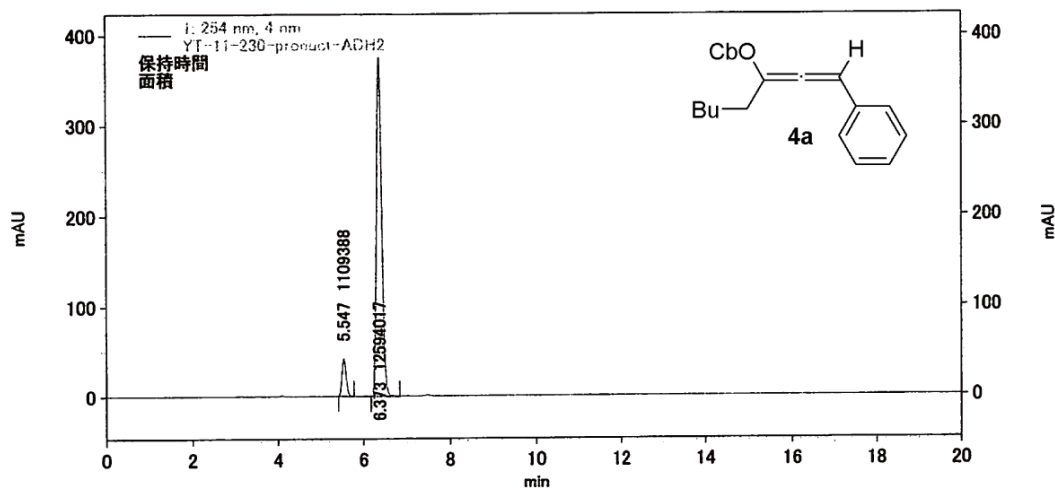
¹³C NMR spectrum of 2-(3-Methoxyphenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4o)

14. HPLC Chromatograms.



1: 254 nm, 4 nm
nm結果

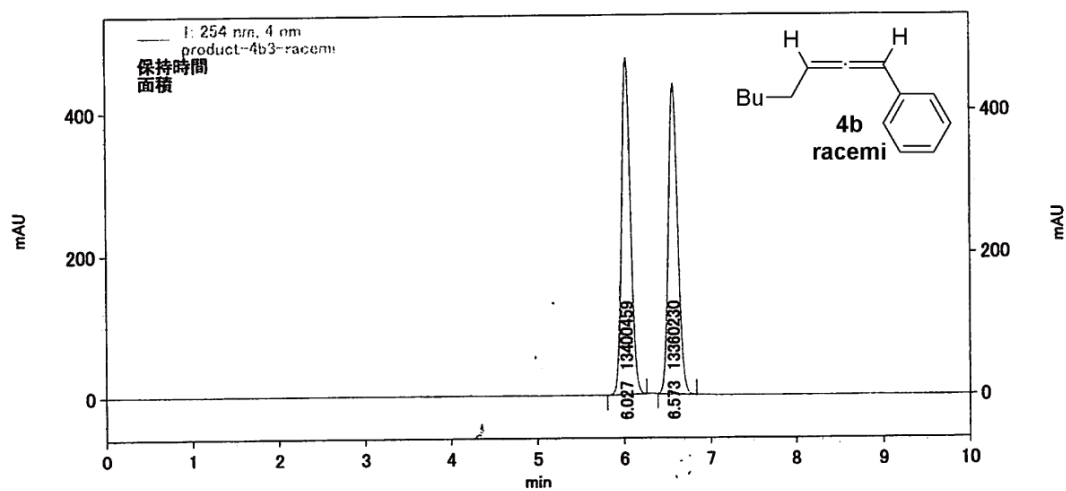
Pk #	保持時間	面積	高さ	ペーサインコード
1	5.66	9650841	1380013	BB
2	6.51	9694461	1143133	BI
トータル		19345302	2523146	



1: 254 nm, 4 nm
nm結果

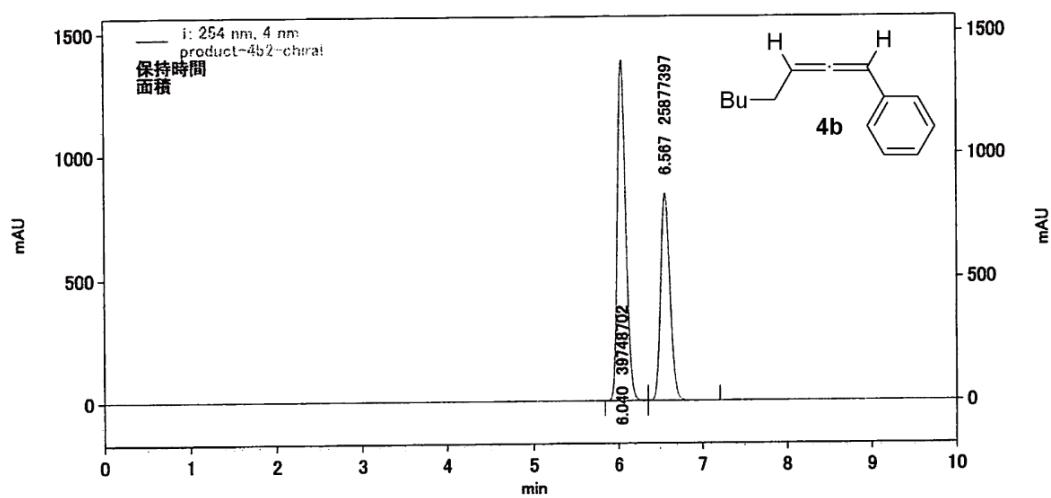
Pk #	保持時間	面積	高さ	ペーサインコード
1	5.55	1109388	165891	BB
2	6.37	12594017	1505275	BB
トータル		13703405	1671166	

HPLC Chromatogram of 1-Phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4a)



1: 254 nm, 4 nm
結果

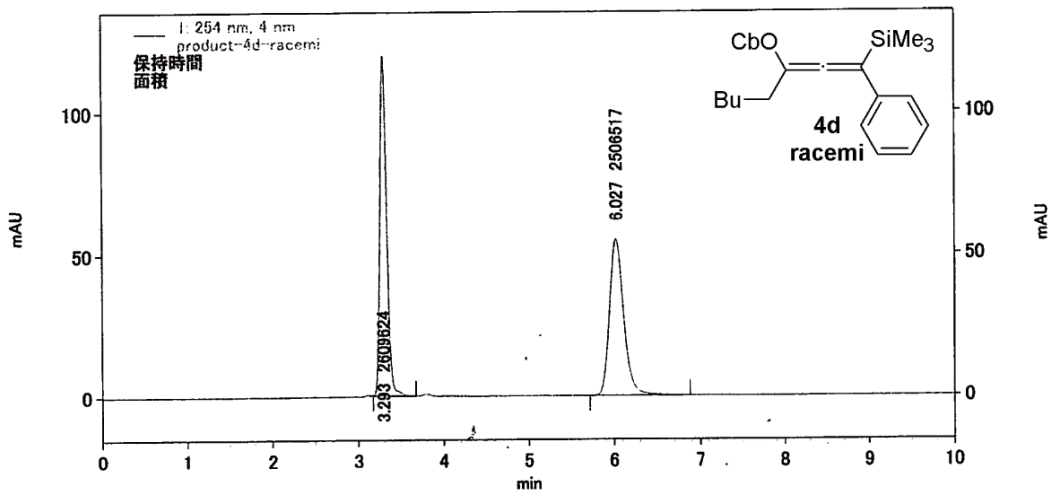
Pk #	保持時間	面積	高さ	ピークコード
1	6.03	13400459	1900261	B1
2	6.57	13360230	1752227	B1
トータル		26760689	3652488	



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	6.04	39748702	5546227	BV
2	6.57	25877397	3362843	VB
トータル		65626099	8909070	

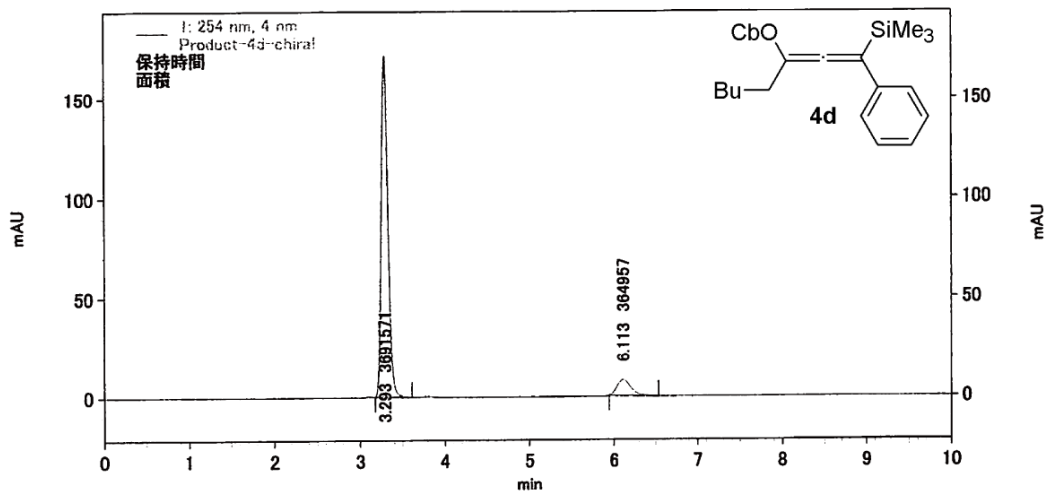
HPLC Chromatogram of 1-Phenylocta-1,2-diene (4b)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピーク名
1	3.29	2609624	479951	II
2	6.03	2506517	219943	BI

トータル		5116141	699894	
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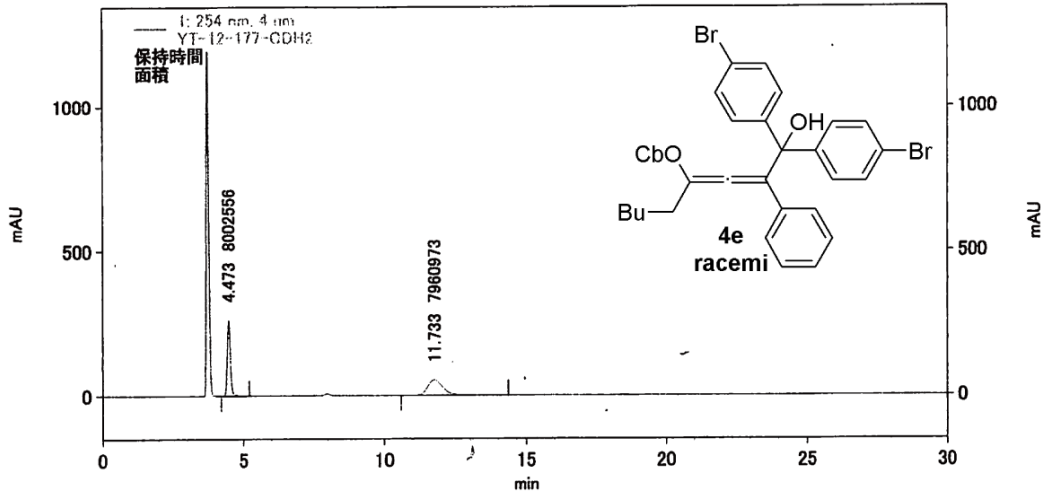


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピーク名
1	3.29	3691571	686926	BB
2	6.11	364957	32116	BB

トータル		4056528	719042	
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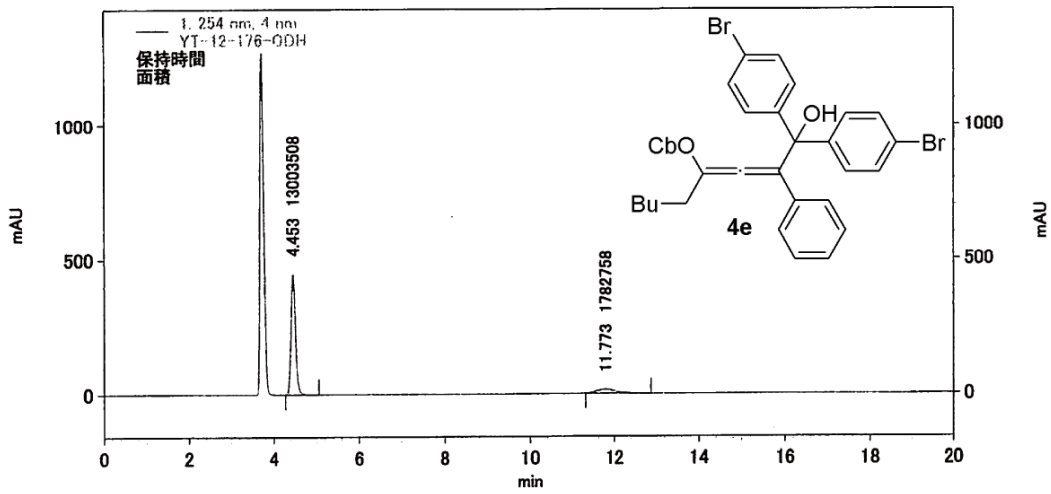
HPLC Chromatogram of 1-Trimethylsilyl-1-phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4d)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ペーシングコード
1	4.47	8002556	1051321	BI
2	11.73	7960973	214121	BB

トータル	面積	高さ
	15963529	1265442

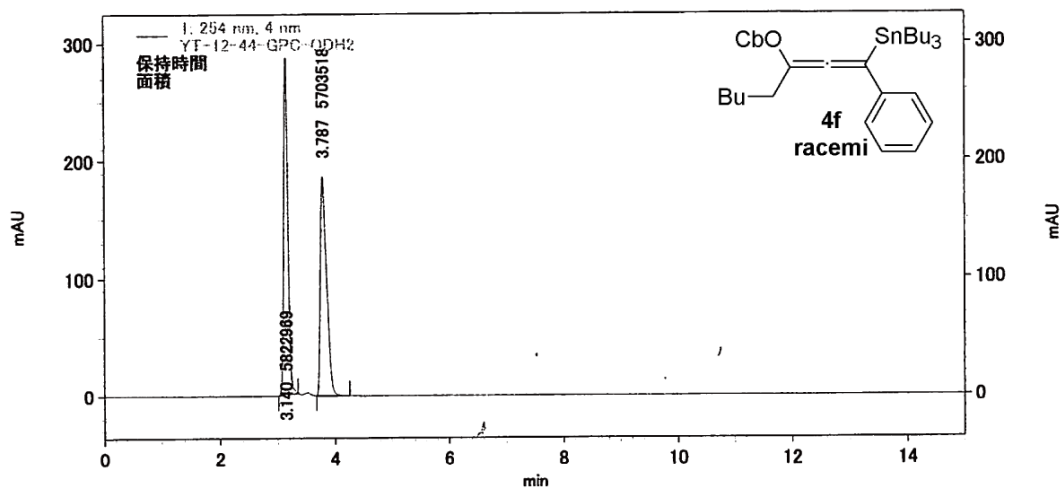


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ペーシングコード
1	4.45	13003508	1785345	BB
2	11.77	1782758	52140	BB

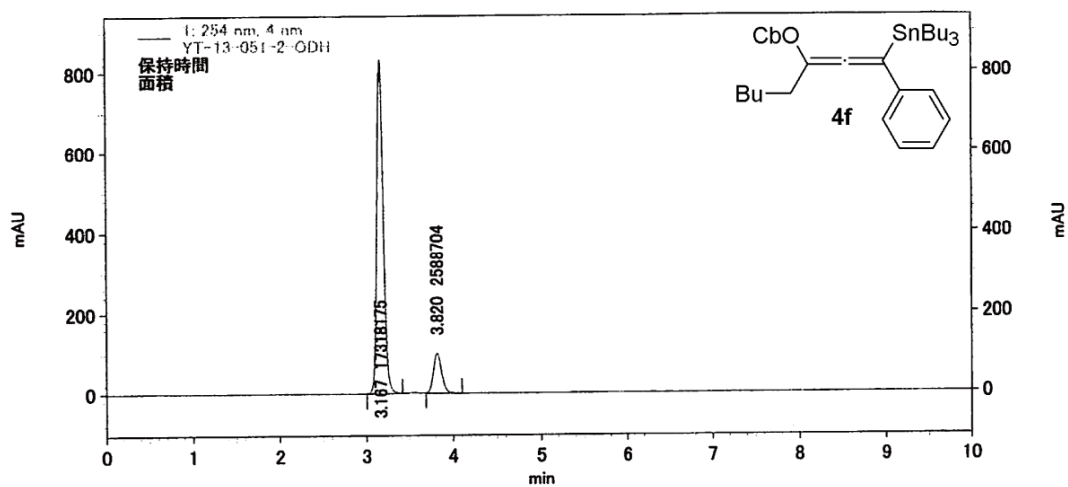
トータル	面積	高さ
	14786266	1837485

HPLC Chromatogram of 1,1-Bis(4-bromophenyl)-1-hydroxy-2-phenylnona-2,3-dien-4-yl *N,N*-diisopropyl- carbamate (4e)



1: 254 nm, 4 nm
結果

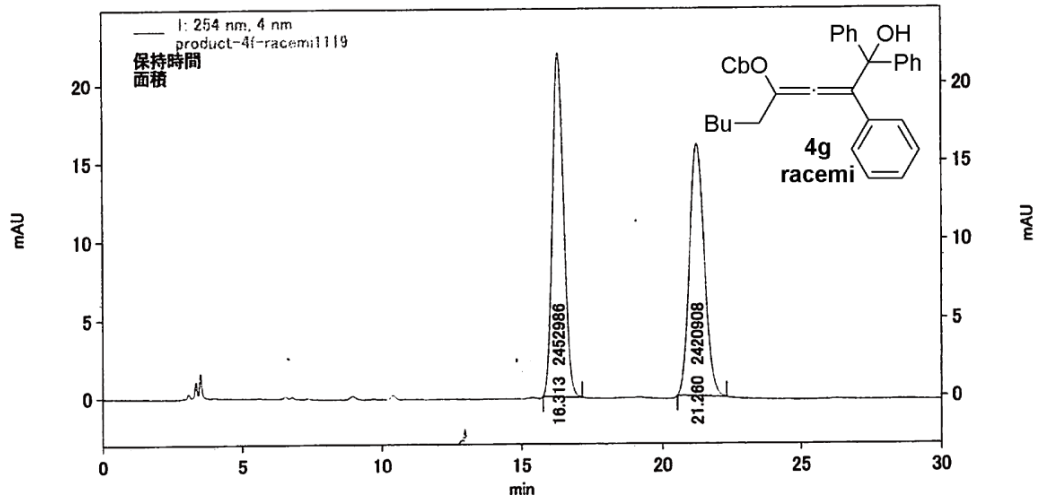
Pk #	保持時間	面積	高さ	ピーク名
1	3.14	5822969	1149796	B1
2	3.79	5703518	745655	BB
トータル		11526487	1895451	



1: 254 nm, 4 nm
結果

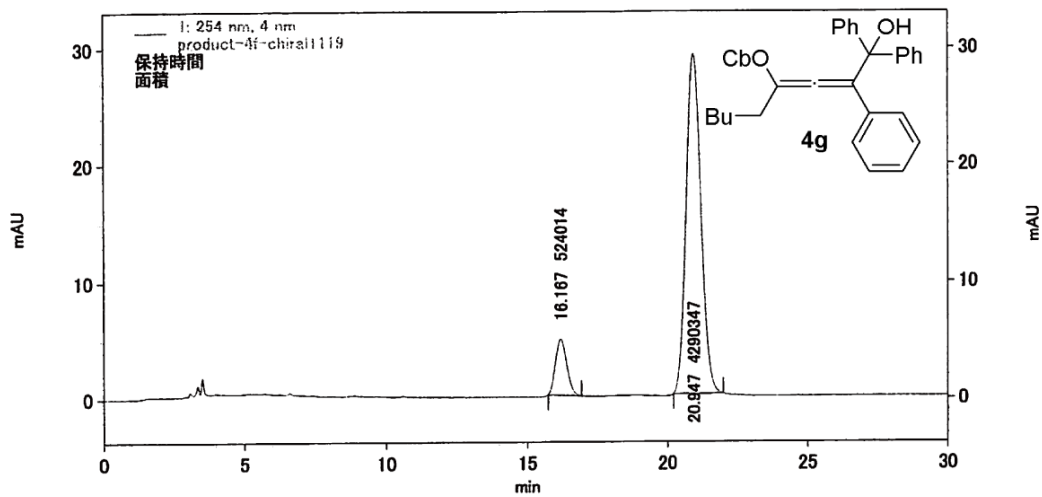
Pk #	保持時間	面積	高さ	ピーク名
1	3.17	17318175	3340387	B1
2	3.82	2588704	402635	BB
トータル		19906879	3743022	

HPLC Chromatogram of 1-Tributylstannyl-1-phenylocta-1,2-dien-3-yl *N,N*-diisopropylcarbamate (4f)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	16.31	2452986	88099	BB
2	21.26	2420908	64428	BB

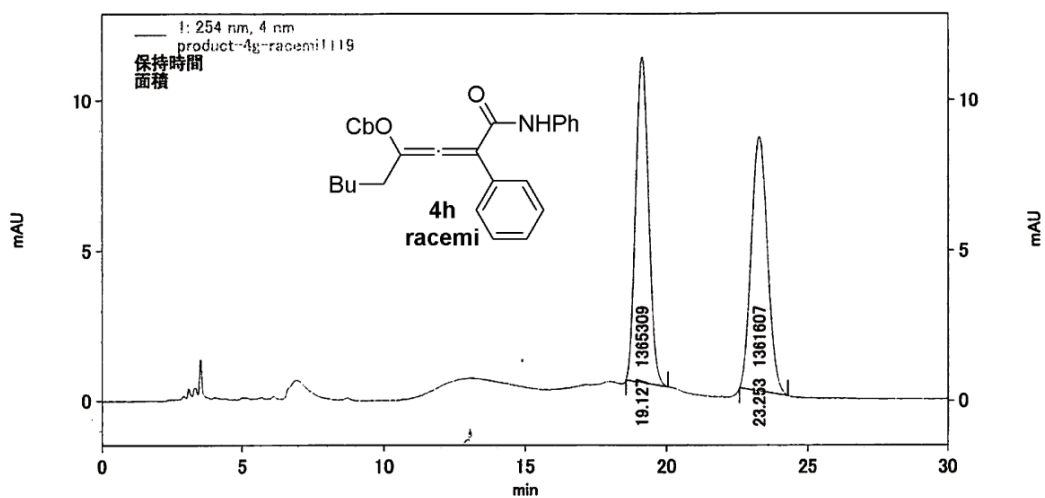


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	16.17	524014	19394	BB
2	20.95	4290347	116504	BB

トータル		4814361	135898	
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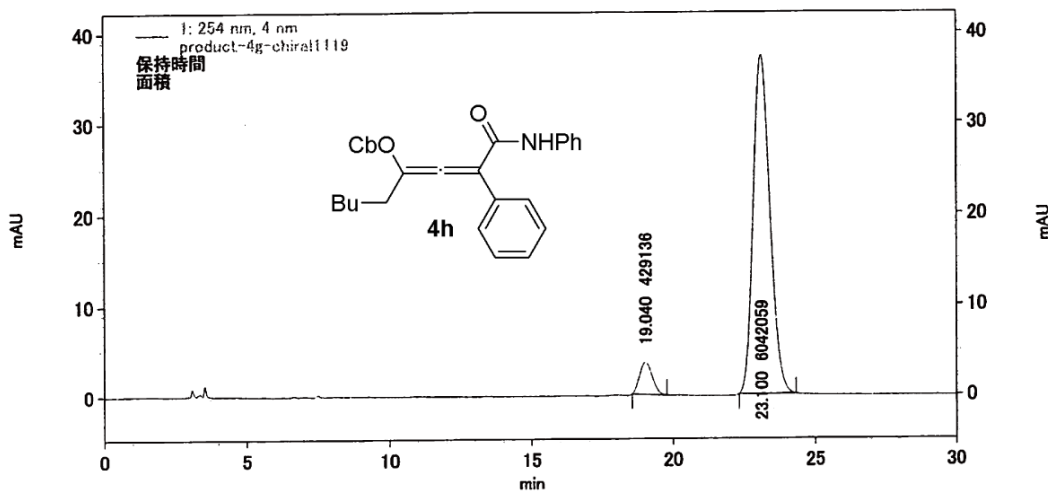
HPLC Chromatogram of 1-Hydroxy-1,1,2-triphenylnona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4g)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	19.13	1365309	43399	BB
2	23.25	1361607	33830	BB

トータル		2726916	77229	
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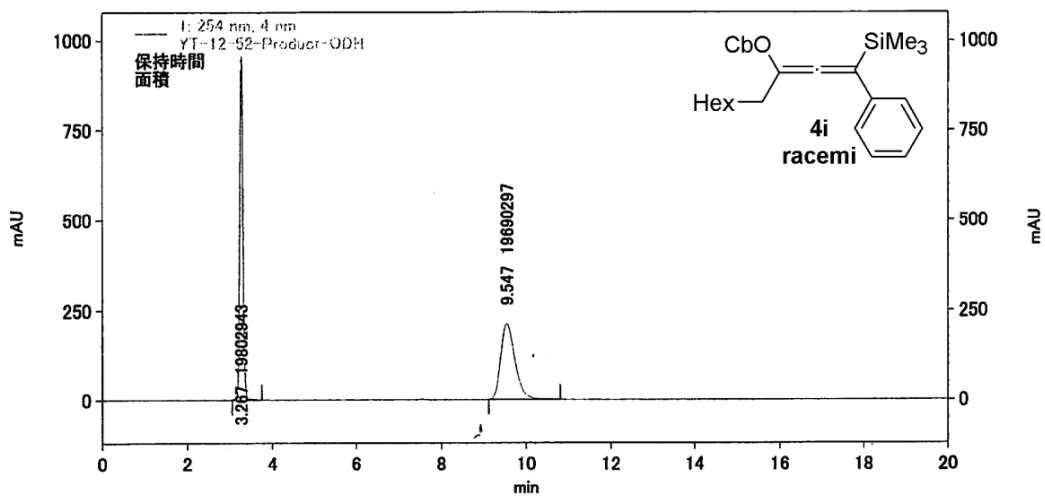


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	19.04	429136	14063	BB
2	23.10	6042059	149513	BB

トータル		6471195	163576	
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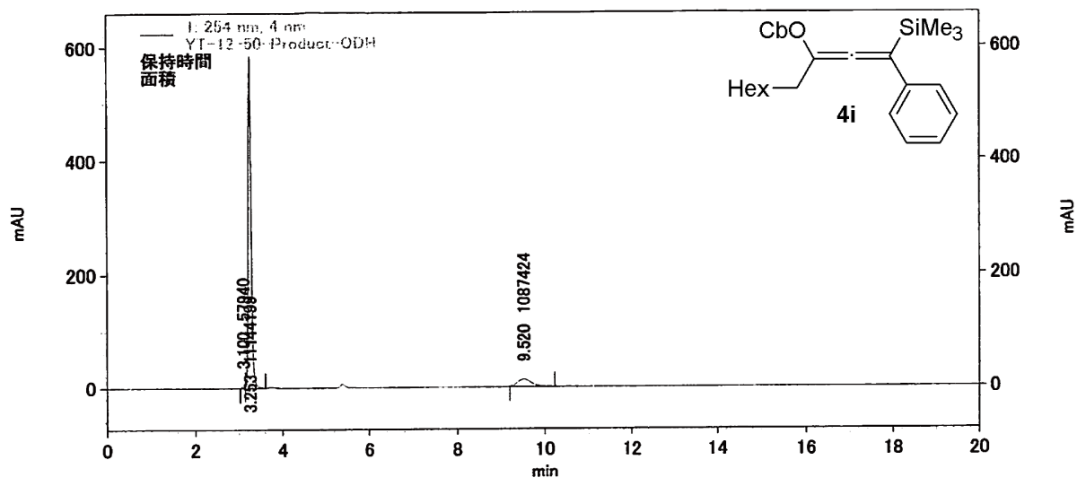
**HPLC Chromatogram of 1-Oxo-2-phenyl-1-(phenylamino)nona-2,3-dien-4-yl
N,N-diisopropylcarbamate (4h)**



1: 254 nm, 4
nm結果

Pk #	保持時間	面積	高さ	ヘーラインコード
1	3.27	19802943	3830544	BB
2	9.55	19690297	851106	BB

トータル		39493240	4681650	
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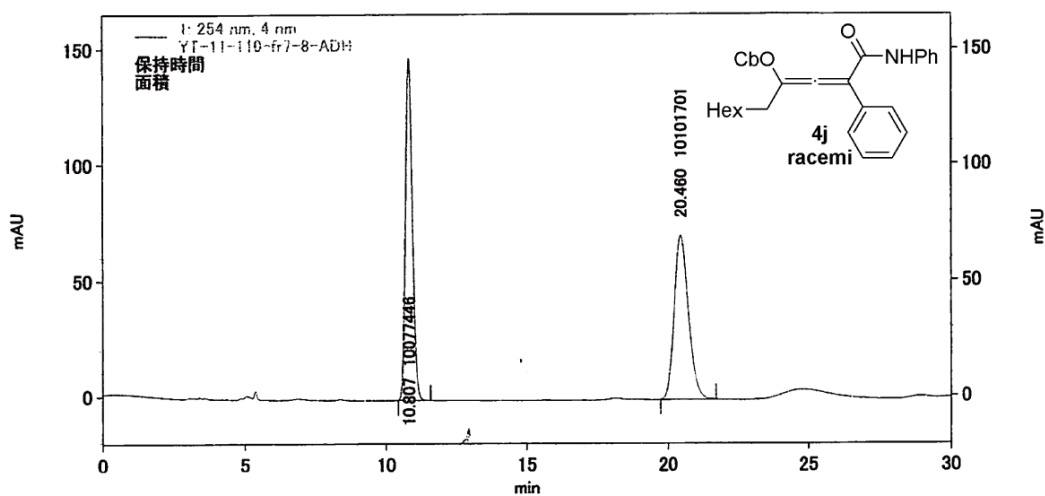


1: 254 nm, 4
nm結果

Pk #	保持時間	面積	高さ	ヘーラインコード
1	3.10	57940	13689	BV
2	3.25	11144199	2343239	VB
3	9.52	1087424	50205	BB

トータル		12289563	2407133	
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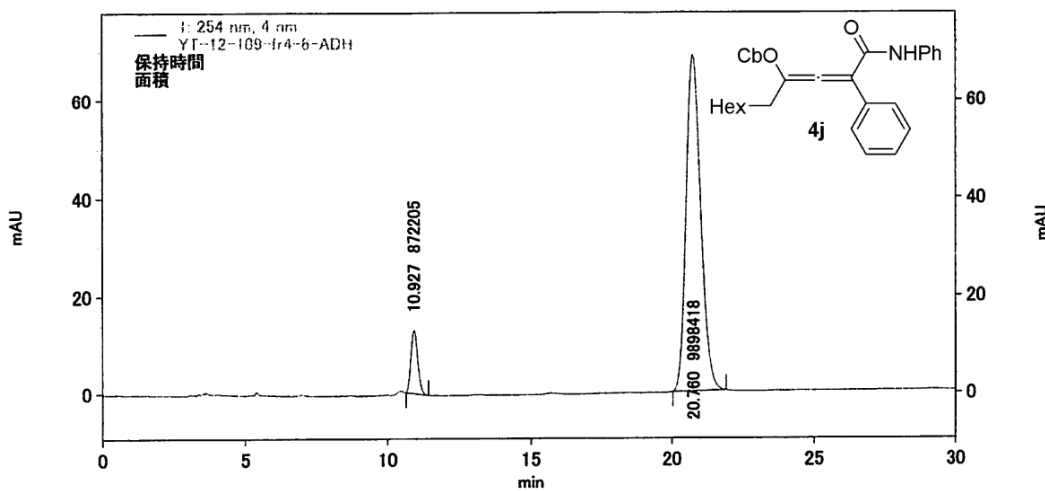
HPLC Chromatogram of 1-Trimethylsilyl-1-phenyldeca-1,2-dien-3-yl
N,N-diisopropylcarbamate (4i)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピーク名
1	10.81	10077446	592167	BB
2	20.46	10101701	282873	BB

トータル		20179147	875040	
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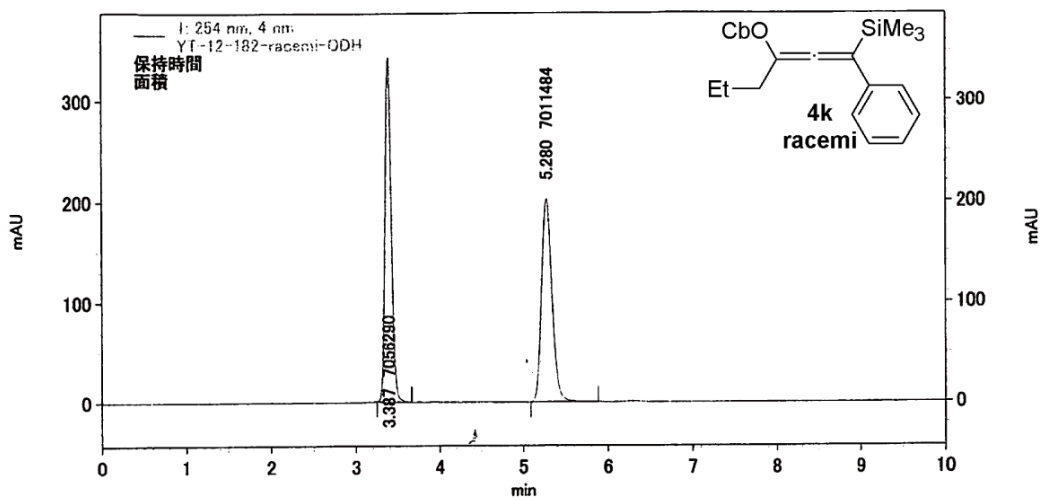


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピーク名
1	10.93	872205	52486	BB
2	20.76	9898418	275646	BB

トータル		10770623	328132	
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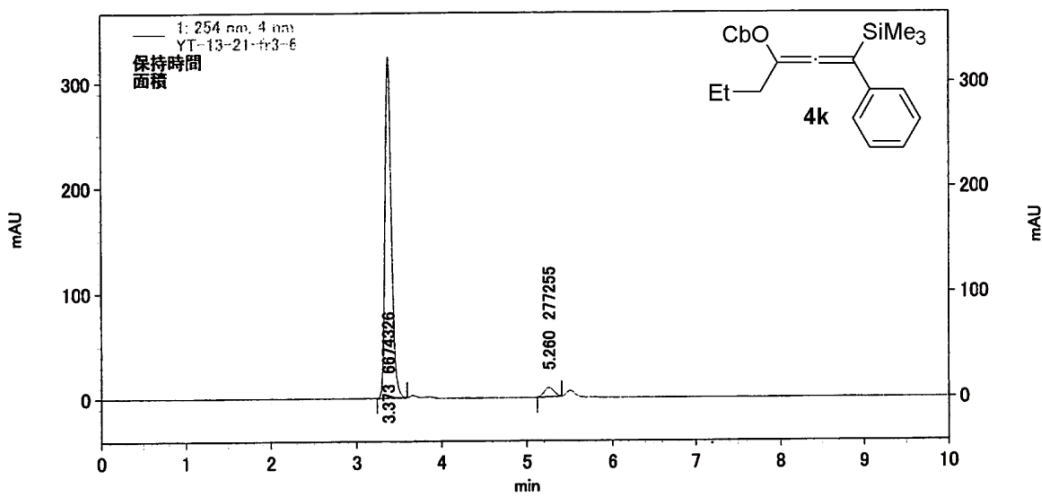
**HPLC Chromatogram of 1-Oxo-2-phenyl-1-(phenylamino)undeca-2,3-dien-4-yl
N,N-diisopropylcarbamate (4j)**



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	3.39	7056290	1374226	BB
2	5.28	7011484	809774	BB

トータル		14067774	2184000	
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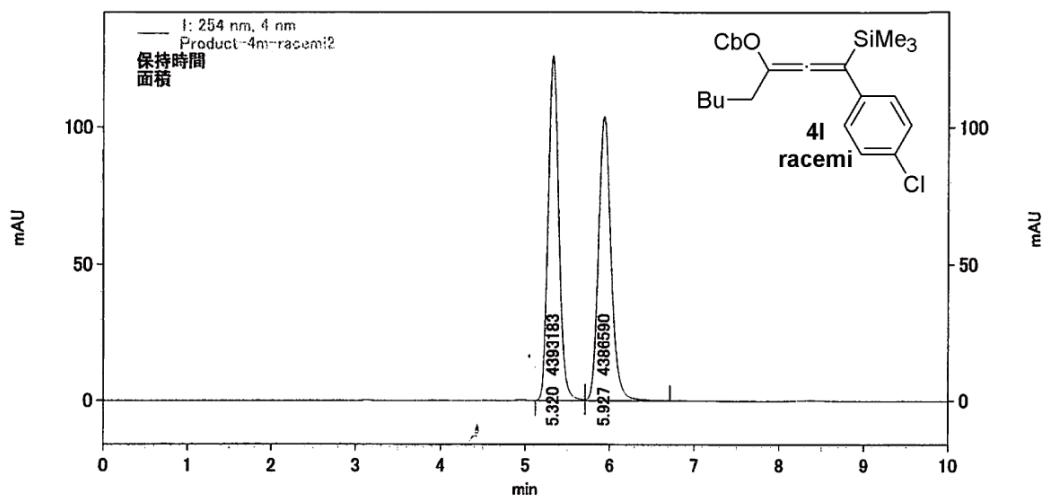


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	3.37	6674326	1300178	BI
2	5.26	277255	34748	BB

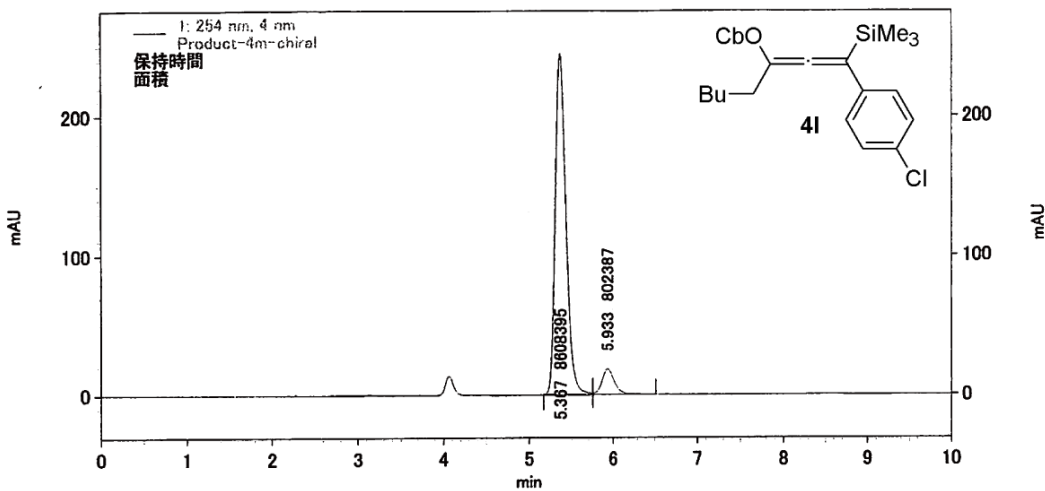
トータル		6951581	1334926	
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**HPLC Chromatogram of 1-Trimethylsilyl-1-phenylhex-1,2-dien-3-yl
N,N-diisopropylcarbamate (4k)**



1: 254 nm, 4 nm
結果

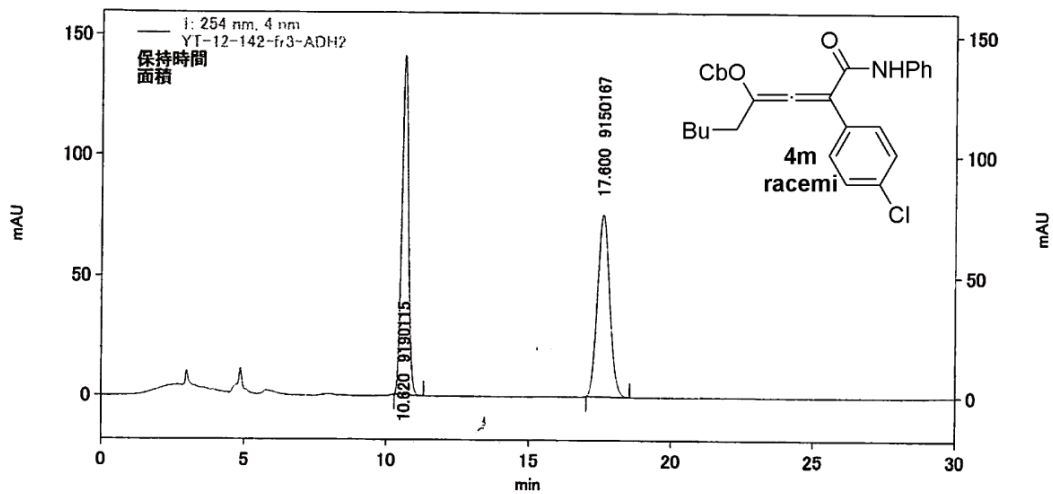
Pk #	保持時間	面積	高さ	ピーク名
1	5.32	4393183	505680	BV
2	5.93	4386590	416634	VB
トータル		8779773	922314	



1: 254 nm, 4 nm
結果

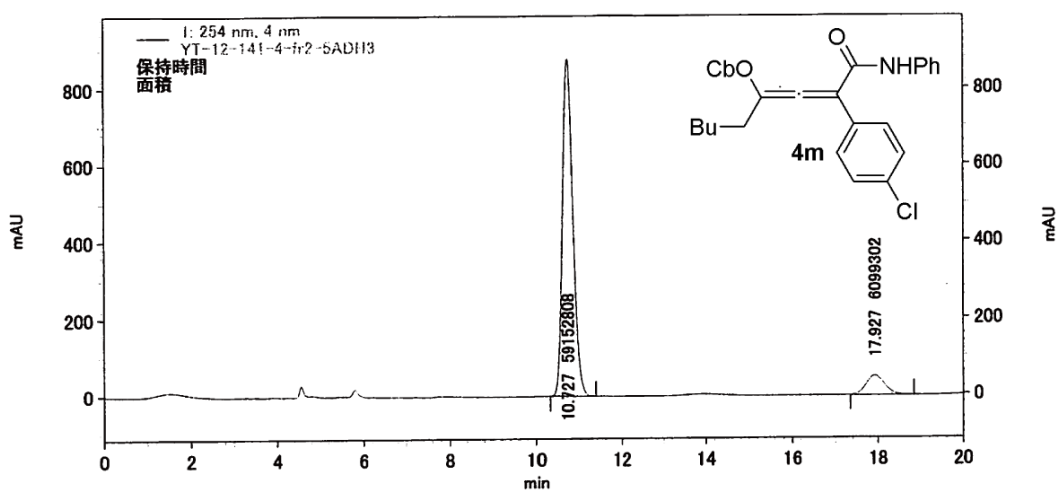
Pk #	保持時間	面積	高さ	ピーク名
1	5.37	8608395	979877	BV
2	5.93	802387	73755	VB
トータル		9410782	1053632	

**HPLC Chromatogram of 1-(4-Chlorophenyl)-1-trimethylsilylocta-1,2-dien-3-yl
N,N-diisopropylcarbamate (4I)**



1: 254 nm, 4 nm
結果

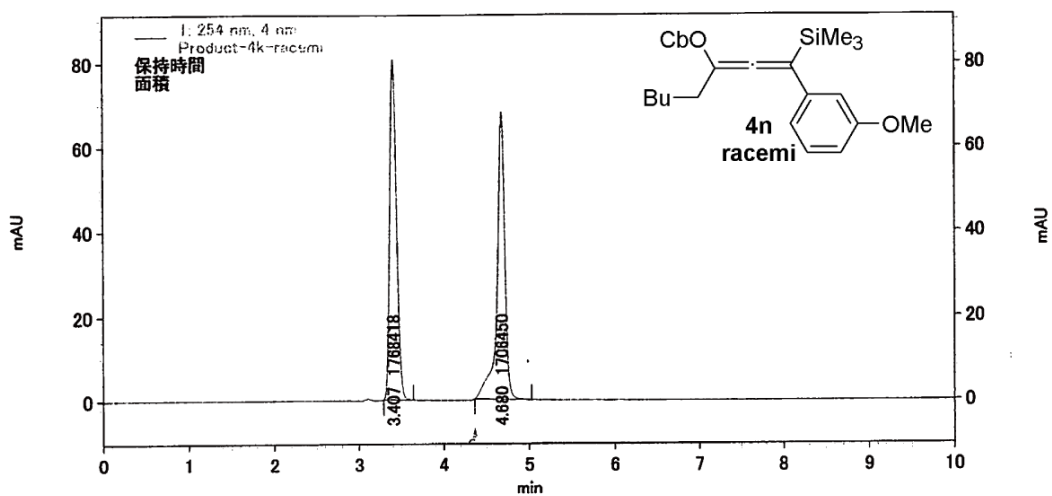
Pk #	保持時間	面積	高さ	ピーク名
1	10.62	9190115	565476	BB
2	17.60	9150167	303105	BB
トータル		18340282	868581	



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピーク名
1	10.73	59152808	3520447	BB
2	17.93	6099302	201893	BB
トータル		65252110	3722340	

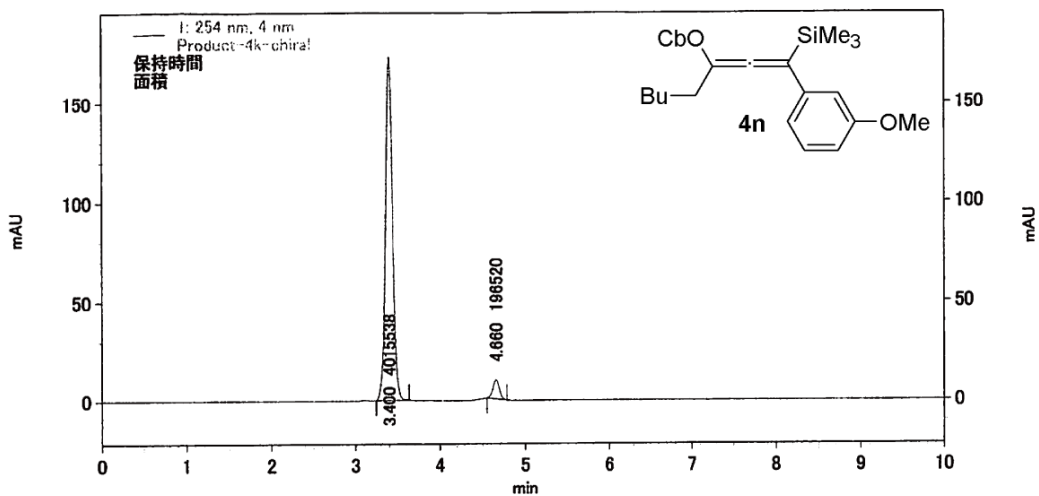
HPLC Chromatogram of 2-(4-Chlorophenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4m)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ヘーラインコート
1	3.41	1768418	323412	BB
2	4.68	1706450	272358	BB

トータル		3474868	595770	
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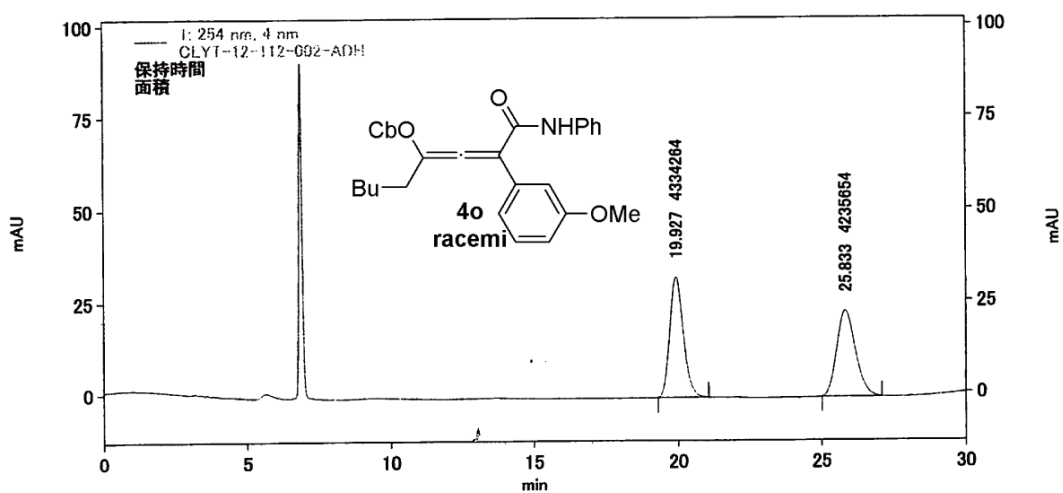


1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ヘーラインコート
1	3.40	4015538	693419	BB
2	4.66	196520	38400	BB

トータル		4212058	731819	
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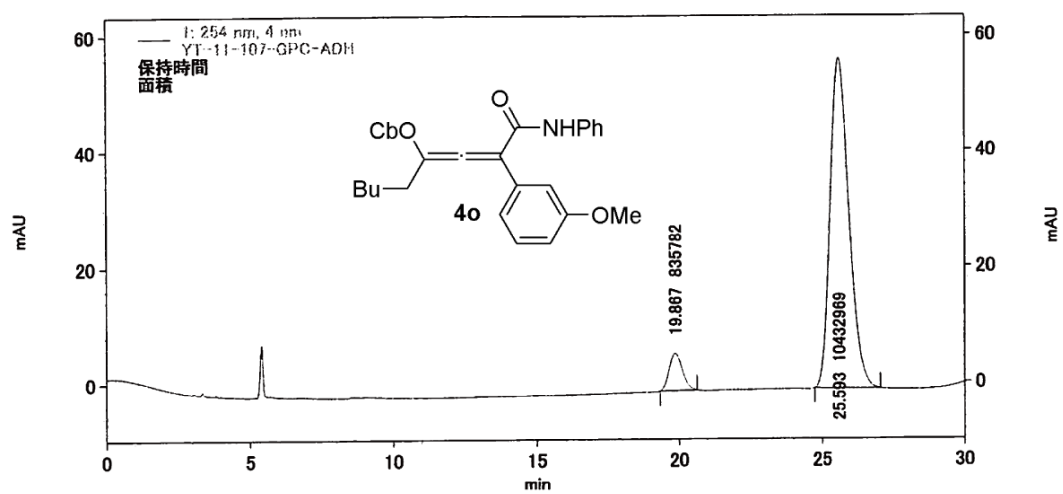
HPLC Chromatogram of 1-(3-methoxyphenyl)-1-trimethylsilylocta-1,2-dien-3-yl
N,N-diisopropylcarbamate (4n)



1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	19.93	4334264	130942	BB
2	25.83	4235654	93667	BB

トータル		8569918	224609	
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1: 254 nm, 4 nm
結果

Pk #	保持時間	面積	高さ	ピークコード
1	19.87	835782	26025	BB
2	25.59	10432969	228080	BB

トータル		11268751	254105	
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HPLC Chromatogram of 2-(3-Methoxyphenyl)-1-oxo-1-(phenylamino)nona-2,3-dien-4-yl *N,N*-diisopropylcarbamate (4o)