Enantioselective Synthesis of *trans*-Aryl- and Heteroaryl-Substituted Cyclopropylboronates by Copper(I)-Catalyzed Reactions of Allylic Phosphates with a Diboron Derivative

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1. General and Materials.

NMR spectra were recorded on a Varian Gemini 2000 (^{1}H: 300 MHz, ^{13}C:75.4 MHz) spectrometer. ^{1}H NMR chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS and are referenced relative to TMS (δ 0.00 ppm). Chemical shifts for carbon atoms are reported in parts per million downfield of TMS and are referenced to the carbon resonance of the solvent ($CDCl_3$: δ 77.2 ppm). GLC analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. HPLC analyses were carried out using Hitachi Elite LaChrome HPLC system with L-2400 UV detector. High-resolution mass spectra were recorded on a JEOL JMS-700TZ, JMS-T100L, JMS-T100GC, Thermo Fisher Scientific LTQ-Orbitrap XL, and Thermo Fisher Scientific Exactive mass spectrometers at the Center for Instrumental Analysis, Hokkaido University. Melting points were determined on a micro melting point apparatus (Yanaco: MP-500D) using micro cover glass. All reactions were performed under a nitrogen atmosphere, using oven-dried glassware unless otherwise indicated. Column chromatography was performed using silica gel (Kanto Chemical Co., 60Å, 40-100 μm) unless otherwise indicated.

Materials were obtained from commercial suppliers and purified by the standard procedures unless otherwise noted. Solvents for reactions were purchased from commercial suppliers, degassed via three freeze-pump-thaw cycles, and further dried on MS 4A. Bis(pinacolato)diboron was purchased from AllyChem, Co., Ltd, China. (*R*,*R*)-QuinoxP* was provided from Nippon Chemical Industrial Co. and used as received. (*R*,*R*)-*i*-Pr-DuPhos, copper(I) chloride (Reagent Plus grade) and THF solution of potassium *tert*-butoxide (1.0 M or 1.2 M) were purchased from Aldrich Chemical Co. and used as received. Other phosphine ligands were purchased from appropriate commercial suppliers.

3-Aryl substituted propargylic alcohols were prepared from the corresponding aryl iodide and propargyl alcohol via Sonogashira coupling reaction.[1] All (*Z*)-3-aryl allylic alcohols, except (*Z*)-3-(2-thiophenyl)prop-2-en-1-ol, were prepared from the corresponding propargylic alcohols according to the reported method for the preparation of (*Z*)-3-phenyl-2-propenol[2] through Ni-catalyzed stereoselective hydrogenation [$Ni(OAc)_2 \cdot 4H_2O/NaBH_4$/1,2-diaminoethane/$H_2$]. The *E*-configured allylic alcohols in the crude products were removed by careful silica gel column chromatography (ethyl acetate/hexane). (*Z*)-3-(2-thiophenyl)prop-2-en-1-ol was prepared via hydrogenation of the corresponding propargylic alcohol in the presence of Lindlar catalyst[3] and further purified by crystallization from CH_2Cl_2/hexane.

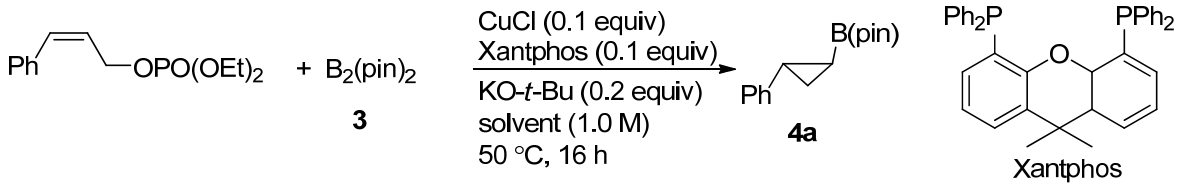
2. General Experimental Procedure.

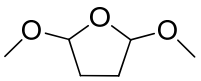
A typical procedure for the copper(I)-catalyzed enantioselective synthesis of cyclopropylboronates (Table 2) is shown as followings:

In a glove box filled with nitrogen, bis(pinacolato)diboron **3** (122 mg, 0.48 mmol), CuCl (2.0 mg, 0.02 mmol), (*R*,*R*)-*i*-Pr-DuPhos (10.0 mg, 0.024 mmol) and toluene (1.2 mL) were added into a vial tube with a magnetic stirrer bar. The tube was sealed with a screw cap equipped with a rubber septum and removed out of the glove box. The mixture was stirred at room temperature for ca. 30 min to form a clear yellow solution. After an allylic phosphate **2** (0.4 mmol) was added using a syringe, a THF solution of potassium *tert*-butoxide (1.2 M, 0.4 mmol) was then added dropwise with stirring at room temperature. After the reaction was complete, the reaction mixture was passed through a Florisil short column (hexane : ethyl acetate = 80:20). After evaporation under reduced pressure, the residue was subjected to silica gel column chromatography to obtain the product (typically, hexane : ethyl acetate = 95 : 5).

3. Detailed Investigation on Impact of Reaction Conditions and Catalysts.

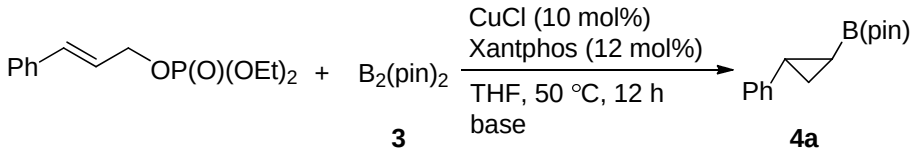
Table S1. **Solvent Effect on the Cyclopropylboronate Formation** [a]



entry	solvent	GC conv. (%)	GC yield (%)
1	THF	85	63
2	Et_2O	62	46
3	dioxane	75	54
4	DME	68	47
5		76	50
6	CH_2ClCH_2Cl	21	9
7	CH_2Cl_2	6	trace
8	CH_3CN	27	14
9	acetone	38	17
10	DMI	66	36

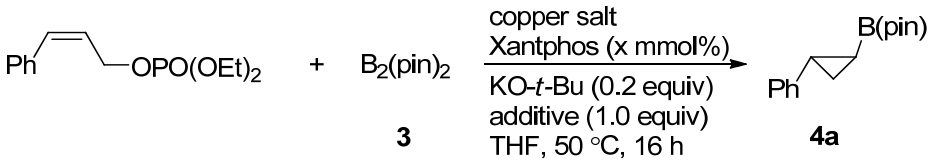
[a] Phosphate (0.2 mmol), **3** (0.3 mmol), CuCl (0.02 mmol), Xantphos (0.02 mmol), KO-*t*-Bu (1.0 M THF solution, 0.04 mmol), solvent (0.2 mL).

Table S2. Effect of Base on the Cyclopropylboronate Formation [a]



entry	additives	GC conv. (%)	GC yield (%)
1	LiCl	60	9
2	NaOAc	99	73
3	NaOMe	98	25
4	NaO-*t*-Bu	98	77
5	$CsCO_3$	92	71
6	K_3PO_4	60	41
7	Et_3N	73	57

Table S3. **Effect of Copper(I) Salt and Base on the Cyclopropylboronate Formation** [a]

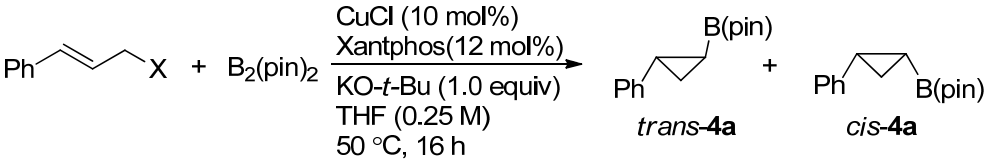


entry	copper salt	mol%	additive	x (mol%)	phosphate concentration (mol/L)	GC yield (%)
1	CuCl	10	NaOAc	10	0.5	75
2	CuCl	10	KO-*t*-Bu	10	0.5	77
3	CuCl	10	KO-*t*-Bu	12	0.5	78
4	CuCl	10	KO-*t*-Bu	12	0.25	78
5	CuCl	5	KO-*t*-Bu	10	0.5	64
6	CuCl	10	LiO-*t*-Bu	12	0.25	34
7	CuI	10	NaOAc	10	1.0	30
8	CuI	10	NaO-*t*-Bu	10	1.0	58
9	CuOAc	10	NaO-*t*-Bu	10	0.5	76
10	CuOAc	5	NaOAc	10	0.5	39

11	CuOAc	5	none	10	0.5	11
12	$(CuOTf)_2$·toluene	5	KO-*t*-Bu	12	0.25	67
13	$(CuOTf)_2$·toluene	5	LiO-*t*-Bu	12	0.25	30
14	$Cu(CH_3CN)_4$·PF_6	10	KO-*t*-Bu	12	0.25	57
15	$Cu(CH_3CN)_4$·PF_6	10	LiO-*t*-Bu	12	0.25	19
16[a]	Cu(O-*t*-Bu)	5	none	5	0.25	3

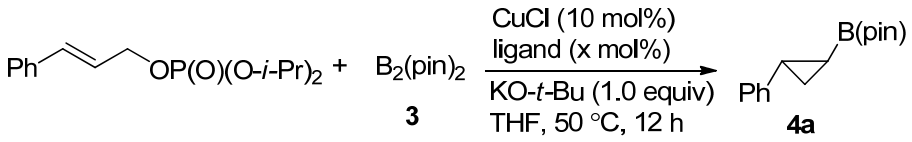
[a] Toluene was used as solvent, rt, 20 h.

Table S4. Effect of Leaving Group in the Reaction



entry	X	yield(%)	*trans*/*cis*
1	$OP(O)(OEt)_2$	80	>99:1
2	$OP(O)(O\text{-}i\text{-}Pr)_2$	89	>99:1
3	OCO_2Me	49	>99:1
4	$OCOCF_3$	0	-
5	Cl	<1	-

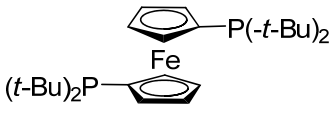
Table S5. **Effect of Achiral Phosphine Ligands in the Copper(I)-catalyzed Reaction** [a]



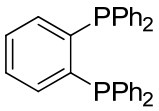
entry	ligand	x (mol%)	GC yield (%)	*trans*/*cis*[b]
1	PPh_3	24	14	93:7
2	PCy_3	24	26	99:1
3	PBu_3	24	40	96:4
4	$P(t\text{-}Bu)_3$	24	20	97:3
5	dppe	12	34	93:7
6	dppp	12	52	94:6
7	dppb	12	11	94:6
8	dpph	12	2	nd

9	dppf	12	25	94:4
10	dtbpf	12	4	90:10
11	BDP	12	85	97:3

[a] Phosphate (0.2 mmol), **3** (0.3 mmol), CuCl (0.02 mmol), THF (0.6 mL). [b] Determined by GC.

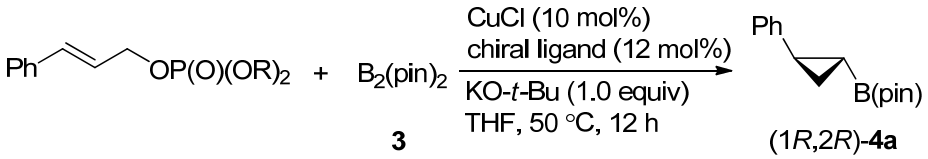


dtbpf



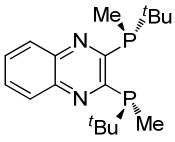
BDP

Table S6. **Effect of Chiral Phosphine Ligands in the Reaction of (*E*)-Configured Substrates**

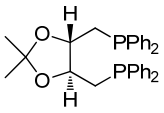


entry	R	ligand	yield (%)	*trans*/*cis* (ee)
1	Et	(*R*,*R*)-QuinoxP*	36	>99:1
2	Et	(*R*)-Segphos	20	97:3
3	*i*-Pr	(*S*,*S*)-DIOP	79	98:2 (–49 % ee for trans)
4	*i*-Pr	TANGPHOS	13	89:11
5	*i*-Pr	L1	trace	nd
6	*i*-Pr	(2*S*,3*S*)-ChiralPhos	10	93:7
7	*i*-Pr	(*R*)-SDP	trace	nd
8	*i*-Pr	L2	10	88:22
9	*i*-Pr	(*R*,*R*)-Me-BPE	trace	nd
10	*i*-Pr	(*R*)-(*S*)-PPF-P-*t*-Bu_2	16	49:51
11	*i*-Pr	(*S*)-PHANEPhos	trace	nd
12	*i*-Pr	(*R*)-C_3-TunePhos	23	91:9
13	*i*-Pr	(*R*)-BINAP	4	67:33
14	*i*-Pr	(*R*)-DTBM-Segphos	trace	nd
15	*i*-Pr	(*S*,*S*)-Reetz-Diphosphonite	2	nd
16	*i*-Pr	(*R*,*S*)-NMe_2-PPh_2-Mandyphos	trace	nd

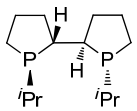
17	*i*-Pr	(*R*)-Ph-MeOBIPHEP	7	71:29
18	*i*-Pr	(*R*,*R*)-BDPP	49	84:16 (–40% ee for trans)
19	*i*-Pr	(*S*)-BINAPHANE	27	81:19
20	*i*-Pr	Trost ligand	trace	nd
21	*i*-Pr	(*R*,*R*)-Me-DuPhos	33	73:27
22	*i*-Pr	(*R*,*R*)-Et-DuPhos	23	63:37
23	CH_2Ph	(*R*,*R*)-QuinoxP*	76	75:25 (73% ee for trans)
24	CH_2Ph	(*R*,*R*)-*i*-Pr-DuPhos	87	7:93 (25% ee for trans)



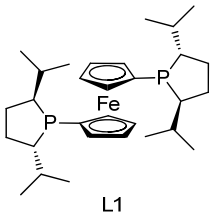
(*R*,*R*)-QuinoxP*



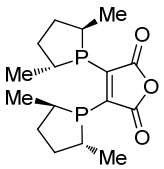
(*S*,*S*)-DIOP



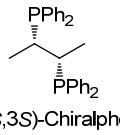
(*S*,*S*,*R*,*R*)-TANGPHOS



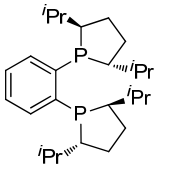
L1



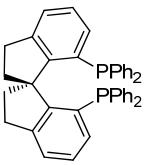
L2



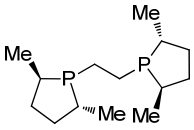
(2*S*,3*S*)-Chiralphos



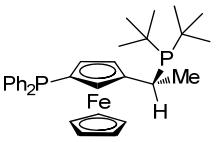
(*R*,*R*)-*i*-Pr-DuPhos



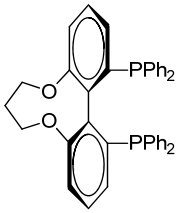
(*S*)-SDP



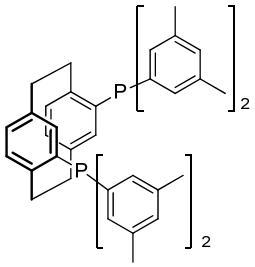
(*R*,*R*)-Me-BPE



(*R*)-(*S*)-PPF-P^{t}Bu$_2$



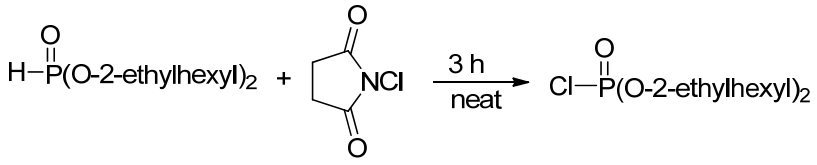
(*R*)-C$_3$-TunePhos



(*S*)-PHANEPhos

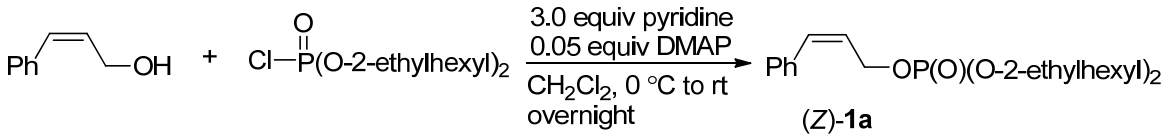
4. Substrate Synthesis and Characterization.

4.1. Preparation of bis(2-ethylhexyl) phosphorochloridate.



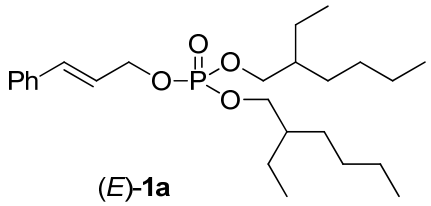
N-chlorosuccinimide (36 mmol, 4.807 g) was added to a dry 50 ml round bottom flask equipped with a magnetic stirrer bar and capped with a septum. The flask was evacuated and filled with argon using a vacuum line through a needle. The flask was cooled to –78 °C and bis(2-ethylhexyl) phosphonate (30 mmol, 9.193 g) was added dropwise. The flask was removed from the cooling bath and stirred at room temperature for 3 h. It should be careful that the reaction is strongly exthothermic and that the flask should be connected to an argon line. The material was then diluted with dry hexane and filtrated through a cannula. The solid residue was washed twice with hexane. The combined solution was concentrated under reduced pressure to yield the product in 97% yield as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.85–0.95 (m, 12H), 1.20–1.49 (m, 16H), 1.56–1.69 (m, 2H), 4.02–4.19 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9 (d, ^{5}J = 2.3 Hz, CH_3), 14.0 (CH_3), 22.9 (CH_2), 23.2 (CH_2), 28.9 (d, ^{4}J = 2.3 Hz, CH_2), 29.9 (CH_2), 39.9 (d, ^{3}J = 8.6 Hz, *C*H), 71.8 (d, ^{2}J = 8.0 Hz, CH_2). HRMS–ESI (*m/z*): $[M+H]^+$ calcd. for $C_{16}H_{35}ClO_3P$ 341.20123, found 341.20195.

4.2 Synthesis of (*Z*)-1a, (*E*)-1a, (*E)*-2a, (*Z*)-1a–o.



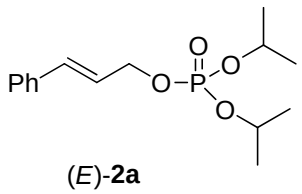
In a 50 ml dry two-neck flask equipped with a magnetic bar was added DMAP (0.042 mmol, 51 mg). The flask was then evacuated and back-filled with argon three times. Dry dichloromethane (10 ml), pyridine (24.9 mmol, 2.0 ml) and (*Z*)-3-phenylpropenol (8.3 mmol, 1.114 g) were added in turn to the flask. The reaction mixture was cooled to 0 °C and then bis(2-ethylhexyl) phosphorochloridate (8.3 mmol, 2.286 g) was added dropwise. After the reaction was slowly warmed to room temperature through overnight with stirring, it was quenched with water (10 ml) at 0 °C. The organic layer was separated and the water layer was extracted with hexane (3×15 ml). The combined organic layer was then washed with water (50 ml). The solution was concentrated *in vacuo*, which afforded an oil that was

purified by flash chromatography (10:90 ethyl acetate : hexane) to give (*Z*)-**1a** (2.68 g, 74%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–0.92 (m, 12H), 1.22–1.45 (m, 16H), 1.48–1.60 (m, 2H), 3.91–3.97 (m, 4H), 4.82 (ddd, *J* = 8.3, 6.6, 1.7 Hz, 2H), 5.88 (dt, *J* = 11.8, 6.3 Hz, 1H), 6.67 (d, *J* = 11.8 Hz, 1H), 7.18–7.22 (m, 2H), 7.25–7.39 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9 (*C*H_3), 14.1 (*C*H_3), 23.0 (*C*H_2), 23.3 (*C*H_2), 28.9 (d, ^{4}J = 1.1 Hz, *C*H_2), 29.9 (*C*H_2), 40.2 (d, ^{3}J = 7.4 Hz, *C*H), 64.2 (d, ^{2}J = 5.7 Hz, *C*H_2), 69.9 (d, ^{2}J = 6.3 Hz, *C*H_2), 126.8 (d, ^{3}J = 7.4 Hz, *C*H), 127.9 (*C*H), 128.6 (*C*H), 129.0 (*C*H), 133.1 (d, ^{4}J = 1.1 Hz, *C*H), 136.1 (*C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{43}ClO_4NaP$ 461.27967, found 461.27900.



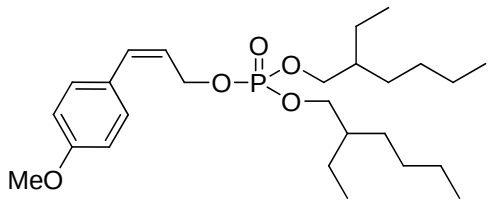
(*E*)-**1a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–0.92 (m, 12H), 1.18–1.50 (m, 16H), 1.51–1.62 (m, 2H), 3.88–4.05 (m, 4H), 4.70 (ddd, *J* = 8.0, 6.3, 1.0 Hz, 2H), 6.31 (dt, *J* = 15.8, 6.3 Hz, 1H), 6.68 (d, *J* = 15.8 Hz, 1H), 7.23–7.42 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.3, 28.9, 29.9, 40.2 (d, *J* = 7.4 Hz), 68.0 (d, *J* = 5.3 Hz), 69.9 (d, *J* = 6.4 Hz), 123.9 (d, *J* = 6.7 Hz), 126.9, 128.4, 128.9, 134.0, 136.3. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{43}O_4NaP$ 461.27967, found 461.27877.



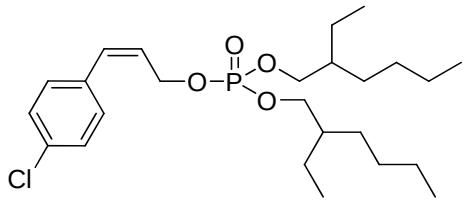
(*E*)-**2a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 1.35 (m, 12H), 4.61–4.73 (m, 4H), 6.31 (dt, *J* = 15.9, 6.0 Hz, 1H), 6.68 (d, *J* = 16.0 Hz, 1H), 7.23–7.42 (m, 5H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 23.7 (d, *J* = 5.0 Hz, *C*H_3), 67.7 (d, *J* = 5.6 Hz), 72.5 (d, *J* = 6.0 Hz), 124.0 (d, *J* = 7.4 Hz), 126.8, 128.3, 128.8, 133.6, 136.3. HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{15}H_{23}O_4P$ 298.13340, found 298.13316.



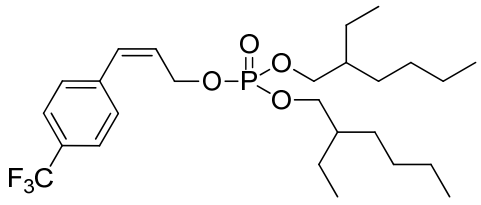
(*Z*)-**1b**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–0.93 (m, 12H), 1.20–1.48 (m, 16H), 1.48–1.61 (m, 2H), 3.82 (s, 3H), 3.83–4.01 (m, 4H), 4.82 (ddd, *J* = 8.1, 6.6, 1.6 Hz, 2H), 5.77 (dt, *J* = 11.5, 6.5 Hz, 1H), 6.60 (d, *J* = 11.5 Hz, 1H), 6.85–6.91 (m, 2H), 7.12–7.18 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.3, 28.9 (d, *J* = 0.9 Hz), 29.9, 40.1 (d, *J* = 7.3 Hz), 55.4, 64.3 (d, *J* = 5.3 Hz), 69.9 (d, *J* = 6.6 Hz), 114.0, 125.0 (d, *J* = 7.3 Hz), 128.8 130.3, 132.7, 159.4. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{45}O_5NaP$ 491.29023, found 491.28999.



(*Z*)-**1c**

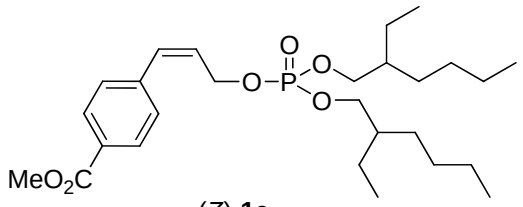
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79–0.97 (m, 12H), 1.18–1.47 (m, 16H), 1.48–1.61 (m, 2H), 3.88–4.01 (m, 4H), 4.77 (ddd, *J* = 8.1, 6.6, 1.6 Hz, 2H), 5.90 (dt, *J* = 11.7, 6.6 Hz, 1H), 6.61 (d, *J* = 11.7 Hz, 1H), 7.11–7.17 (m, 2H), 7.30–7.35 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.3, 28.9 (d, *J* = 1.1 Hz), 29.9, 40.1 (d, *J* = 7.4 Hz), 63.9 (d, *J* = 5.1 Hz), 70.0 (d, *J* = 6.4 Hz), 127.5 (d, *J* = 7.2 Hz), 128.8, 130.2, 132.0 (d, *J* = 1.1 Hz), 133.8, 134.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{42}O_4ClNaP$ 495.24069, found 495.23988.



(*Z*)-**1d**

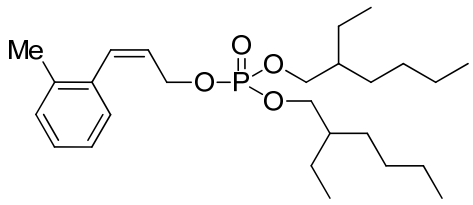
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80–0.97 (m, 12H), 1.18–1.47 (m, 16H), 1.48–1.61 (m, 2H), 3.88–4.01 (m, 4H), 4.78 (ddd, *J* = 8.1, 6.7, 1.6 Hz, 2H), 6.00 (dt, *J* = 11.8, 6.7 Hz, 1H), 6.69 (d, *J* = 11.8

Hz, 1H), 7.32 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.1, 23.3, 28.9 (d, J = 1.1 Hz), 29.9, 40.1 (d, J = 7.4 Hz), 63.8 (d, J = 5.1 Hz), 70.0 (d, J = 6.4 Hz), 124.3 (q, J = 271.5 Hz), 125.6 (q, J = 11.3 Hz), 128.9, 129.0, 129.2, 131.8, 139.6 (d, J = 1.6 Hz). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{42}O_4F_3NaP$ 529.26705, found 529.26610.



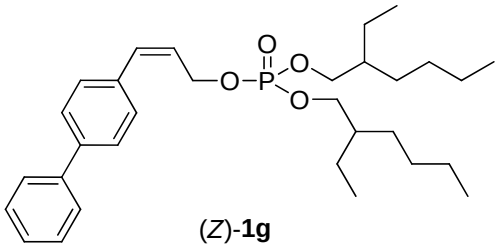
(*Z*)-**1e**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–0.92 (m, 12H), 1.20–1.47 (m, 16H), 1.46–1.60 (m, 2H), 3.93 (s, 3H), 3.91–3.99 (m, 4H), 4.80 (ddd, J = 8.1, 6.4, 1.6 Hz, 2H), 5.98 (dt, J = 11.8, 6.4 Hz, 1H), 6.69 (d, J = 11.8 Hz, 1H), 7.24–7.29 (m, 2H), 8.00–8.05 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.3, 28.9, 29.9, 40.1 (d, J = 7.4 Hz), 52.3, 63.9 (d, J = 5.1 Hz), 70.0 (d, J = 6.3 Hz), 128.9 (d, J = 7.4 Hz), 128.9, 129.4, 130.0, 132.1, 140.6, 167.0. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{27}H_{45}O_6NaP$ 519.28515, found 519.28425.



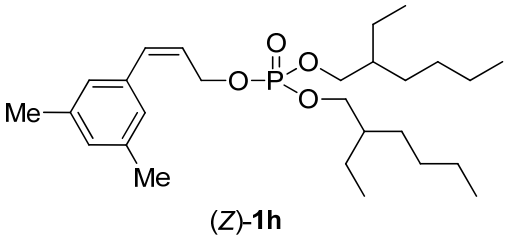
(*Z*)-**1f**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.84–0.92 (m, 12H), 1.14–1.47 (m, 16H), 1.47–1.60 (m, 2H), 2.27 (s, 3H), 3.86–3.99 (m, 4H), 4.67 (ddd, J = 8.0, 6.6, 1.4 Hz, 2H), 5.92 (dt, J = 11.4, 6.6 Hz, 1H), 6.73 (d, J = 11.4 Hz, 1H), 7.03–7.09 (m, 2H), 7.12–7.21 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 19.9, 23.0, 23.3, 28.9, 29.9, 40.1 (d, J = 7.4 Hz), 64.2 (d, J = 5.1 Hz), 69.9 (d, J = 6.4 Hz), 125.9, 126.8 (d, J = 7.2 Hz), 128.1, 129.1, 130.2, 132.6, 135.1, 136.5. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{26}H_{45}O_4NaP$ 475.29532, found 475.29449.



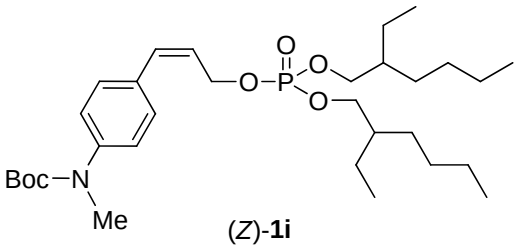
(*Z*)-**1g**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (bt, *J* = 7.4 Hz, 12H), 1.15–1.46 (m, 16H), 1.48–1.64 (m, 2H), 3.96 (bt, *J* = 5.5 Hz, 4H), 4.87 (ddd, *J* = 8.0, 6.6, 1.7 Hz, 2H), 5.90 (dt, *J* = 11.7, 6.4 Hz, 1H), 6.70 (d, *J* = 11.6 Hz, 1H), 7.25–7.49 (m, 5H), 7.56–7.64 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 10.7 (*C*H_3), 13.9 (*C*H_3), 22.8 (*C*H_2), 23.1 (*C*H_2), 28.7 (*C*H_2), 29.7 (*C*H_2), 39.9 (d, ^{3}J = 6.9 Hz, *C*H), 64.1 (d, ^{2}J = 5.7 Hz, *C*H_2), 69.8 (d, ^{2}J = 6.3 Hz, *C*H_2), 126.7 (d, ^{3}J = 7.4 Hz, *C*H), 127.0 (*C*H), 127.1 (*C*H), 127.5 (*C*H), 128.9 (*C*H), 129.3 (*C*H), 132.4 (*C*H), 134.9 (*C*), 140.5 (*C*), 140.6 (*C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{31}H_{47}O_4PNa$, 537.31042; found, 537.31001.



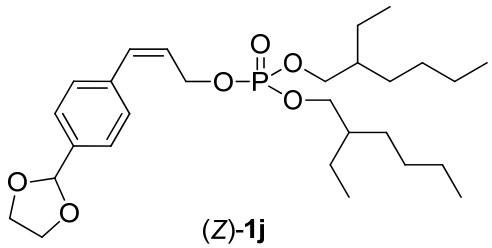
(*Z*)-**1h**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (bt, *J* = 7.4 Hz, 12H), 1.18–1.46 (m, 16H), 1.49–1.64 (m, 2H), 2.31 (s, 6H), 3.94 (bt, *J* = 5.5 Hz, 4H), 4.83 (ddd, *J* = 8.0, 6.3, 1.7 Hz, 2H), 5.82 (dt, *J* = 11.8, 6.3 Hz, 1H), 6.60 (d, *J* = 11.8 Hz, 1H), 6.80 (s, 2H), 6.93 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 10.7 (*C*H_3), 13.9 (*C*H_3), 21.1 (*C*H_3), 22.8 (*C*H_2), 23.1 (*C*H_2), 28.7 (d, ^{4}J = 1.1 Hz, *C*H_2), 29.7 (*C*H_2), 39.9 (d, ^{3}J = 7.4 Hz, *C*H), 64.1 (d, ^{2}J = 5.2 Hz, *C*H_2), 69.6 (d, ^{2}J = 6.3 Hz, CH_2), 126.3 (d, ^{3}J = 7.4 Hz, *C*H), 126.6 (*C*H), 129.3 (*C*H), 132.92 (d, ^{4}J = 1.1 Hz, *C*H), 135.8 (*C*), 137.9 (*C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{27}H_{47}O_4PNa$, 489.31042; found, 489.31000.



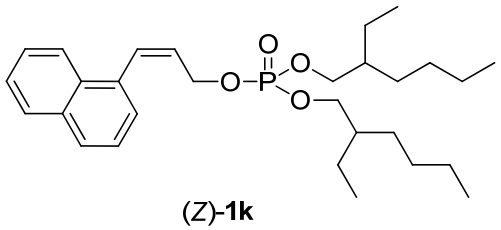
(*Z*)-**1i**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.88 (bt, J = 7.1 Hz, 12H), 1.18–1.44 (m, 16H), 1.46 (s, 9H), 1.49–1.64 (m, 2H), 3.26 (s, 3H), 3.95 (bt, 4H), 4.82 (ddd, J = 8.0, 6.5, 1.6 Hz, 2H), 5.85 (dt, J = 11.8, 6.5 Hz, 1H), 6.62 (d, J = 11.8 Hz, 1H), 7.13–7.26 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 10.7 (CH_3), 13.9 (CH_3), 22.8 (CH_2), 23.1 (CH_2), 28.2 (CH_3), 28.7 (CH_2), 29.7 (CH_2), 37.0 (CH_3), 39.9 (d, ^3J = 7.4 Hz, *C*H), 64.0 (d, ^2J = 5.2 Hz, CH_2), 69.7 (d, ^2J = 6.9 Hz, CH_2), 80.4 (*C*), 125.2 (*C*H), 126.4 (d, ^3J = 6.9 Hz, *C*H), 129.0 (*C*H), 132.2 (*C*H), 132.8 (*C*), 143.2 (*C*), 154.7 (*C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{31}H_{54}NO_6PNa$, 590.35810; found, 590.35747.



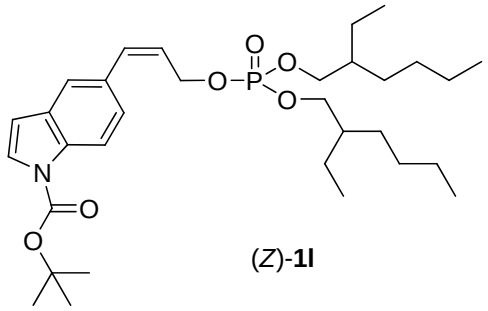
(*Z*)-**1j**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.83–0.94 (m, 12H), 1.17–1.46 (m, 16H), 1.49–1.61 (m, 2H), 3.86–4.01 (m, 4 H), 4.01–4.17 (m, 4H), 4.80 (ddd, J = 8.0, 6.6, 1.7 Hz, 2H), 5.82 (s, 1H), 5.89 (dt, J = 11.8, 6.3 Hz, 1H), 6.66 (d, J = 11.8 Hz, 1H), 7.22 (d, J = 8.3 Hz, 2H), 7.47 (d, J = 8.3 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 10.7 (CH_3), 13.8 (CH_3), 22.8 (CH_2), 23.0 (CH_2), 28.7 (d, ^4J = 1.1 Hz, CH_2), 29.7 (CH_2), 39.9 (d, ^3J = 7.4 Hz, *C*H), 63.9 (d, ^2J = 5.2 Hz, CH_2), 65.2 (CH_2), 69.7 (d, ^2J = 6.3 Hz, CH_2), 103.3 (*C*H), 126.5 (*C*H), 127.1 (d, ^3J = 6.9 Hz, *C*H), 128.7 (*C*H), 132.4 (*C*H), 136.7 (*C*), 137.4 (*C*). HRMS–ESI (*m/z*): $[M+Na]^+$ calcd for $C_{28}H_{47}O_6PNa$, 533.30025; found, 533.29975.



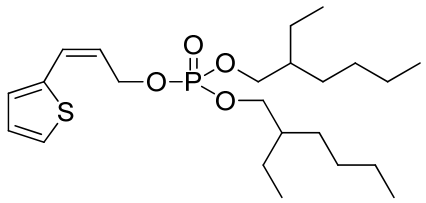
(*Z*)-**1k**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.76–0.91 (m, 12H), 1.12–1.42 (m, 16H), 1.42–1.56 (m, 2H), 3.83–3.96 (m, 4H), 4.69 (ddd, J = 8.0, 6.6, 1.4 Hz, 2H), 6.15 (dt, J = 11.4, 6.6 Hz, 1H), 7.20 (d, J = 11.4 Hz, 1H), 7.24–7.29 (m, 1H), 7.41–7.45 (m, 1H), 7.48–7.55 (m, 2H), 7.81 (d, J = 8.3 Hz, 1H), 7.83–7.90 (m, 1H), 7.92–7.98 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.2, 28.9 (d, J = 1.1 Hz), 29.9, 40.1 (d, J = 7.4 Hz), 64.3 (d, J = 5.4 Hz), 69.9 (d, J = 6.4 Hz), 124.9, 125.4, 126.3, 126.5, 126.9, 128.4 (d, J = 7.2 Hz), 128.6, 128.7, 131.6, 131.8, 133.0, 133.8. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{29}H_{45}O_4NaP$ 511.29532, found 511.29445.



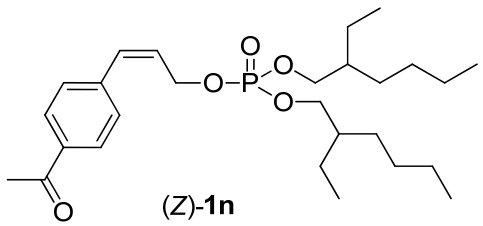
(*Z*)-**1l**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.87 (t, *J* = 7.3 Hz, 12H), 1.20–1.47 (m, 16H), 1.48–1.60 (m, 2H), 1.68 (s, 9H), 3.88–4.00 (m, 4H), 4.88 (ddd, *J* = 8.0, 6.5, 1.6 Hz, 2H), 5.86 (dt, *J* = 11.8, 6.6 Hz, 1H), 6.56 (dd, *J* = 3.8, 0.5 Hz, 1H), 6.77 (d, *J* = 11.8 Hz, 1H), 7.15 (dd, *J* = 8.6, 1.6 Hz, 1H), 7.37–7.39 (m, 1H), 7.61 (d, *J* = 3.6 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.3, 28.2, 28.9, 29.9, 40.1 (d, *J* = 7.4 Hz), 64.4 (d, *J* = 5.6 Hz), 69.9 (d, *J* = 6.3 Hz), 84.0, 107.5, 115.2, 121.3, 125.5, 125.8 (d, *J* = 7.3 Hz), 126.8, 130.7, 130.9, 133.5, 134.7, 149.9. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{32}H_{52}O_6NNaP$ 600.34299, found 600.34252.



(*Z*)-**1m**

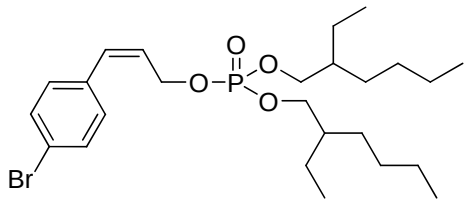
^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, *J* = 8.2 Hz, 12H), 1.20–1.48 (m, 16H), 1.48–1.66 (m, 2H), 3.96 (t, *J* = 6.0 Hz, 4H), 4.92 (ddd, *J* = 8.8, 6.7, 1.4 Hz, 2H), 5.77 (dt, *J* = 13.0, 6.7 Hz, 1H), 6.67 (d, *J* = 13.0 Hz, 1H), 6.96–7.00 (m, 1H), 7.00–7.05 (m, 1H), 7.32 (d, *J* = 5.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9, 14.1, 23.0, 23.3, 28.9, 29.9, 40.2 (d, *J* = 7.3 Hz), 64.5 (d, *J* = 5.6 Hz), 70.0 (d, *J* = 6.6 Hz), 124.4, 125.2 (d, *J* = 7.7 Hz), 126.8, 127.6, 128.5, 139.1. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{23}H_{41}O_4NaPS$ 467.23609, found 467.23512.



(*Z*)-**1n**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.80–0.98 (m, 12H), 1.20–1.46 (m, 16H), 1.48–1.62 (m, 2H), 2.61 (s, 3H), 3.88–4.20 (m, 4H), 4.81 (ddd, *J* = 7.8, 6.4, 1.7 Hz, 2H), 5.99 (dt, *J* = 11.8, 6.6 Hz, 1H), 6.69 (d, *J* = 11.8 Hz, 1H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.9,

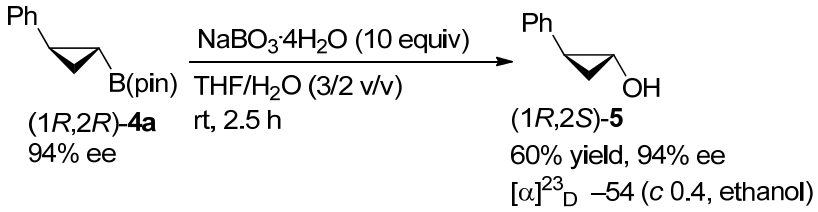
14.1, 23.0, 23.3, 26.7, 28.9 (d, J = 1.1 Hz), 29.9, 40.1 (d, J = 7.3 Hz), 63.9 (d, J = 5.2 Hz), 70.0 (d, J = 6.3 Hz), 128.7, 129.0 (d, J = 7.4 Hz), 129.1, 132.0, 136.3, 140.8, 197.8. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{27}H_{45}O_5NaP$ 503.29023, found 503.28950.



(*Z*)-**1o**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.79–0.96 (m, 12H), 1.20–1.47 (m, 16H), 1.48–1.61 (m, 2H), 3.90–3.97 (m, 4H), 4.76 (ddd, J = 8.1, 6.6, 1.6 Hz, 2H), 5.91 (dt, J = 11.7, 6.6 Hz, 1H), 6.59 (d, J = 11.7 Hz, 1H), 7.05–7.10 (m, 2H), 7.45–7.51 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 10.2, 14.1, 23.0, 23.3, 28.9 (d, J = 1.1 Hz), 29.9, 40.1 (d, J = 7.3 Hz), 63.9 (d, J = 5.6 Hz), 70.0 (d, J = 6.3 Hz), 122.0, 127.6 (d, J = 7.2 Hz), 130.5, 131.8, 132.0, 134.9. HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{25}H_{42}O_4BrNaP$ 539.19018, found 539.18929.

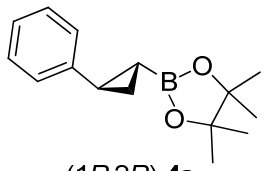
5. Determination of Absolute Configuration of *trans*-4a.



The absolute configuration of *trans*-**4a** was determined by comparing the optical rotation of the cyclopropyl alcohol obtained by oxidation. The spectral data were identical with those reported.[4] Yield 60%. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.05 (q, *J* = 6.3 Hz, 1H), 1.28 (ddd, *J* = 9.6, 6.3, 2.5 Hz, 1H), 2.11 (ddd, *J* = 9.6, 6.3, 2.5 Hz, 1H), 2.23 (br, 1H), 3.62 (ddd, *J* = 6.5, 3.5, 2.6 Hz, 1H). 6.98–7.04 (m, 2H), 7.13–7.21 (m, 1H), 7.23–7.29 (m, 2H). $[\alpha]^{23.0}_D$ –54 (*c* 0.4, ethanol, 94% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, 2-PrOH/Hexane = 5/95, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*S*)-**5** t_R = 30.5 min, (1*S*,2*R*)-**5** t_R = 26.6 min).

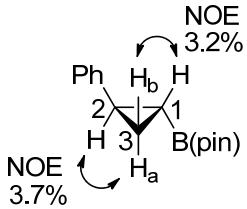
6. **Characterization Data for Cyclopropylboronates.**

4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-phenylcyclopropyl)]1,3,2-dioxaborolane.



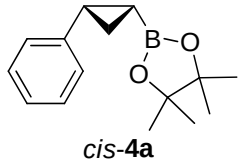
(1*R*,2*R*)-**4a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.30 (ddd, *J* = 9.8, 6.8, 5.4 Hz, 1H), 1.00 (ddd, *J* = 9.8, 5.4, 3.7 Hz, 1H), 1.16 (ddd, *J* = 8.1, 6.8, 3.6 Hz, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 2.10 (dt, *J* = 8.1, 5.4 Hz, 1H), 7.05–7.17 (m, 3H), 7.21–7.28 (m, 2H). NOEs were observed between resonances of H-1 and H-3b, H-2 and H-3a.



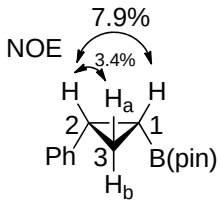
^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.1, 22.0, 24.8, 24.8, 83.3, 125.8, 125.9, 128.5, 143.7. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{15}H_{21}BO_2$ 244.16346, found 244.16310. $[\alpha]^{26}_D$ –175.8 (*c* 1.085, $CHCl_3$, 94% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, hexane, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4a** t_R = 18.2 min, (1*S*,2*S*)-**4a** t_R = 16.3 min).

4,4,5,5-Tetramethyl-2-(2-phenylcyclopropyl)-1,3,2-dioxaborolane.



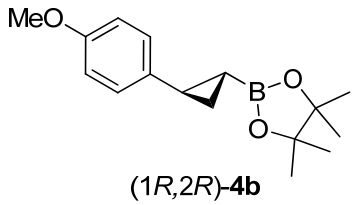
cis-**4a**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.44 (ddd, *J* = 10.1, 9.3, 7.3 Hz, 1H), 0.88 (s, 6H), 1.01 (s, 6H), 1.10 (ddd, *J* = 9.3, 8.0, 4.2 Hz, 1H), 1.28 (ddd, *J* = 7.1, 6.1, 4.2 Hz, 1H), 2.35 (ddd, *J* = 10.1, 7.8, 6.1 Hz, 1H), 7.08–7.16 (m, 1H), 7.18–7.31 (m, 4H). NOEs were observed between resonances of H-2 and H-1, H-2 and H-3a.



^{13}C NMR (75.4 MHz, $CDCl_3$): δ 3.4 (br), 8.9, 21.8, 24.5, 24.8, 83.1, 126.0, 127.9, 129.1, 141.0. HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{15}H_{21}BO_2$ 244.16346, found 244.16352. $[\alpha]^{22.6}_D$ +17.6 (*c* 0.98, $CHCl_3$, 27% ee). The ee value was determined by HPLC analysis (CHIRALPAK IC, 2-PrOH/Hexane = 0.1/99.9, 0.5 mL/min, UV detector at 220 nm, 40 °C, t_{minor} = 11.3 min, t_{major} = 12.3 min). The absolute configuration of this compound could not be determined because the C–B bond oxidation resulted in fast decomposition of the alcohol derivative.

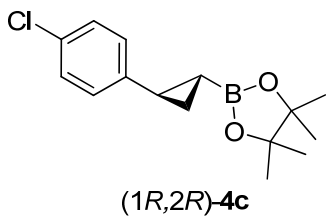
2-[(1*R*,2*R*)-2-(4-Methoxyphenyl)cyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4b**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.22 (ddd, *J* = 9.8, 6.6, 5.6 Hz, 1H), 0.93 (ddd, *J* = 9.6, 5.4, 3.7 Hz, 1H), 1.11 (ddd, *J* = 8.1, 6.8, 3.6 Hz, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 2.07 (dt, *J* = 8.1, 5.4 Hz, 1H), 3.77 (s, 3H), 6.76–6.82 (m, 2H), 6.99–7.05 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 5.5 (br), 14.6, 21.3, 24.8, 24.8, 55.4, 83.3, 114.0, 127.0, 135.6, 158.0. HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{16}H_{23}BO_3$ 274.17402, found 274.17399. $[\alpha]^{26.0}_D$ –152.5 (*c* 1.055, $CHCl_3$, 94% ee). The ee value was determined by HPLC analysis (CHIRALPAK IC, 2-PrOH/Hexane = 0.25/99.75, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4b** t_R = 16.8 min, (1*S*,2*S*)-**4b** t_R = 24.6 min).

2-[(1*R*,2*R*)-2-(4-Chlorophenyl)cyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.

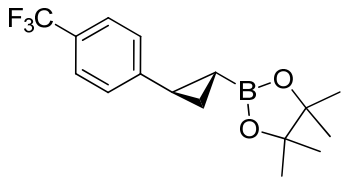


(1*R*,2*R*)-**4c**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.25 (ddd, *J* = 9.8, 6.8, 5.6 Hz, 1H), 0.96 (ddd, *J* = 9.8, 5.2, 3.8 Hz, 1H), 1.16 (ddd, *J* = 8.1, 6.9, 3.8 Hz, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 2.07 (dt, *J* = 8.1, 5.4 Hz, 1H), 6.97–7.03 (m, 2H), 7.17–7.23 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 6.2 (br), 15.1, 21.4, 24.77, 24.80, 83.4, 127.3, 128.5, 131.3, 142.2. HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{15}H_{20}BClO_2$ 278.12449,

found 278.12453. $[\alpha]^{26.0}_{D}$ –155.7 (*c* 0.87, $CHCl_3$, 84% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, hexane, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4c** t_R = 13.0 min, (1*S*,2*S*)-**4c** t_R = 14.5 min).

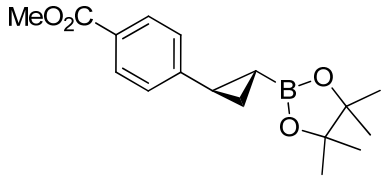
4,4,5,5-Tetramethyl-2-{(1*R*,2*R*)-2-[4-(trifluoromethyl)phenyl]cyclopropyl-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4d**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.35 (ddd, *J* = 9.8, 7.0, 5.6 Hz, 1H), 1.04 (ddd, *J* = 9.8, 5.2, 3.9 Hz, 1H), 1.19–1.32 (m, 1H), 1.25 (s, 6H), 1.26 (s, 6H), 2.14 (dt, *J* = 8.0, 5.2 Hz, 1H), 7.16 (d, *J* = 8.2 Hz, 2H), 7.48 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 6.7 (br), 15.6, 21.8, 24.78, 24.82, 83.6, 124.6 (q, *J* = 272.0 Hz), 125.4 (q, *J* = 3.8 Hz), 128.0 (q, *J* = 32.5 Hz), 126.1, 148.1 (q, *J* = 1.1 Hz). HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{16}H_{20}BF_3O_2$ 312.15084, found 312.15085. mp 41.8–44.0 °C. $[\alpha]^{26.0}_{D}$ –122.4 (*c* 0.63, $CHCl_3$, 82% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, hexane, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4d** t_R = 11.0 min, (1*S*,2*S*)-**4d** t_R = 12.2 min).

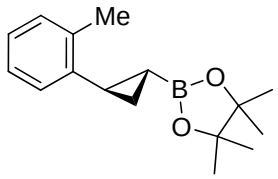
Methyl 4-[(1*R*,2*R*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]benzoate.



(1*R*,2*R*)-**4e**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.37 (ddd, *J* = 9.9, 6.9, 5.5 Hz, 1H), 1.07 (ddd, *J* = 9.9, 5.2, 3.8 Hz, 1H), 1.24 (s, 6H), 1.26 (s, 6H), 1.19–1.30 (m, 1H), 2.13 (dt, *J* = 8.0, 5.3 Hz, 1H), 3.89 (s, 3H), 7.09–7.14 (m, 2H), 7.88–7.93 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.8, 22.1, 24.8, 52.1, 83.5, 125.7, 127.6, 129.9, 149.7, 167.5. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{17}H_{23}BO_4$ 302.16894, found 302.16861. mp 55.5–69.2 °C. $[\alpha]^{26.0}_{D}$ –132.9 (*c* 0.91, $CHCl_3$, 64% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, 2-PrOH/Hexane = 1:99, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4e** t_R = 11.6 min, (1*S*,2*S*)-**4e** t_R = 12.7 min).

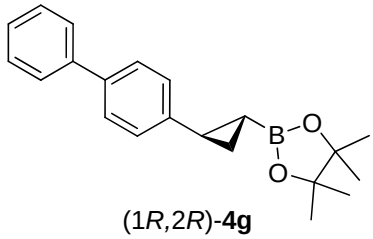
4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-(o-tolyl)cyclopropyl]-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4f**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.16 (dt, *J* = 9.6, 6.2 Hz, 1H), 1.02 (ddd, *J* = 9.7, 5.7, 3.4 Hz, 1H), 1.13 (ddd, *J* = 8.0, 6.5, 3.5 Hz, 1H), 1.26 (s, 12H), 2.09 (dt, *J* = 8.0, 5.8 Hz, 1H), 2.40 (s, 3H), 6.98–7.02 (m, 1H), 7.07–7.16 (m, 3H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 12.3, 19.7, 20.4, 24.7, 24.8, 83.3, 125.7, 126.0, 126.1, 129.8, 138.2, 141.2. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{16}H_{23}BO_2$ 258.17911, found 258.17899. mp 60.8–68.8 °C. $[\alpha]^{26.0}_D$ –103.1 (*c* 0.99, $CHCl_3$, 94% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, Hexane, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4f** t_R = 18.1 min, (1*S*,2*S*)-**4f** t_R = 20.2 min).

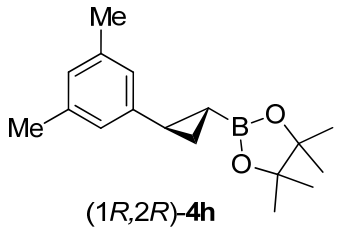
4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-(4-phenylphneyl)cyclopropyl]-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4g**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.35 (ddd, *J* = 9.6, 6.6, 5.6 Hz, 1H), 1.01–1.09 (m, 1H), 1.05 (ddd, *J* = 9.9, 5.5, 3.9 Hz, 1H), 1.25 (s, 6H), 1.26 (s, 6H), 2.15 (dt, *J* = 8.0, 5.5 Hz, 1H), 7.15 (d, *J* = 8.3 Hz, 2H), 7.23–7.64 (m, 7H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 6.1 (br, *C*H), 15.0 (*C*H_2), 21.5 (*C*H), 24.6 (*C*H_3), 24.7 (*C*H_3), 83.2 (*C*), 126.1 (*C*H), 127.0 (*C*H), 127.01 (*C*H), 127.06 (*C*H), 128.8 (*C*H), 138.6 (*C*), 141.2 (*C*), 147.3 (*C*). $[\alpha]^{21}_D$ –149.8 (*c* 0.995, $CHCl_3$, 86% ee), mp 86°C. HRMS–ESI (*m/z*): $[M]^+$ calcd for $C_{21}H_{25}BO_2$, 320.19476; found, 320.19479. The ee value of 86% was determined by chiral HPLC analysis (CHIRALCEL OD-3, hexane/2-propanol 99.75/0.25, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4g**: t_R = 23.5 min. (1*S*,2*S*)-**4g**: t_R = 32.4 min.).

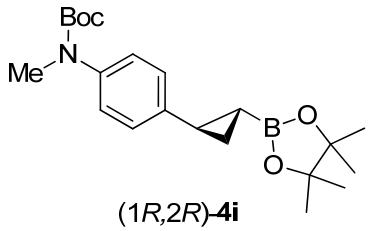
4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-(3,5-dimethylphenyl)cyclopropyl]-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4h**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.27 (ddd, *J* = 9.6, 6.9, 5.5 Hz, 1H), 0.98 (ddd, *J* = 9.7, 5.2, 3.7 Hz, 1H), 1.08–1.20 (m, 1H), 1.23 (s, 6H), 1.25 (s, 6H), 1.99–2.08 (m, 1H), 2.26 (s, 6H), 6.71 (s, 2H), 6.78 (s, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 5.3 (br, *C*H), 14.6 (*C*H_2), 21.1 (*C*H_3), 21.6 (*C*H), 24.5 (*C*H_3), 24.6 (*C*H_3), 83.1 (*C*), 123.6 (*C*H), 127.3 (*C*H), 137.8 (*C*), 143.4 (*C*). $[\alpha]^{23}_D$ –147.6 (*c* 0.975, $CHCl_3$, 94% ee). HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{17}H_{26}BO_2$, 273.20258; found, 273.20205. The ee value of 94% was determined by chiral HPLC analysis (CHIRALCEL OD-3, hexane, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4h**: t_R = 13.4 min. (1*S*,2*S*)-**4h**: t_R = 16.2 min.).

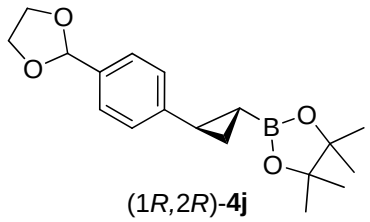
4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-[4-(*N*-Boc-*N*-methylamino)phenyl]cyclopropyl-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4i**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.27 (ddd, *J* = 9.7, 6.8, 5.6 Hz, 1H), 0.98 (ddd, *J* = 9.7, 5.3, 3.8 Hz, 1H) 1.11–1.20 (m, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 1.43 (s, 9H), 2.08 (dt, *J* = 8.3, 5.4 Hz, 1H), 3.22 (s, 3H), 6.98–7.14 (m, 4H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 5.6 (br, *C*H), 14.8 (*C*H_2), 21.3 (*C*H), 24.57 (*C*H_3), 24.61 (*C*H_3), 28.23 (*C*H_3), 37.3 (*C*H_3), 80.1 (*C*), 83.2 (*C*), 125.5 (*C*H), 125.8 (*C*H), 140.6 (*C*), 141.5 (*C*), 155.0 (*C*). $[\alpha]^{23}_D$ –90.5 (*c* 0.935, $CHCl_3$, 89% ee,). MS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{21}H_{32}BNO_4$, 374.25026; found, 374.25006. The ee value of 89% was determined by chiral HPLC analysis (CHIRALCEL IC, hexane/2-propanol 99/1, 40 °C, (1*R*,2*R*)-**4i**: t_R = 29.4 min. (1*S*,2*S*)-**4i**: t_R = 33.7 min.).

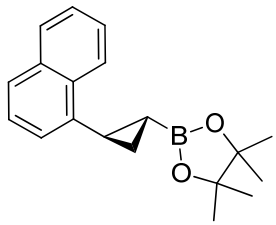
2-{(1*R*,2*R*)-2-[4-(1,3-Dioxolan-2-yl)phenyl]cyclopropyl}-4,4,5,5-tetramethyl-1,3,2-dioxaborolane



(1*R*,2*R*)-**4j**

^{1}H NMR (300 MHz, $CDCl_3$, δ): 0.30 (ddd, *J* = 9.7, 6.8, 5.5 Hz, 1H), 0.96–1.04 (m, 1H), 1.12–1.21 (m, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 2.11 (dt, *J* = 8.1, 5.4 Hz, 1H), 3.91–4.18 (m, 4H), 5.78 (s, 1H), 7.09 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$, δ): 5.8 (br, *C*H), 15.0 (*C*H_2), 21.6 (*C*H), 24.5 (*C*H_3), 24.6 (*C*H_3), 65.1 (*C*H_2), 83.1 (*C*), 103.7 (*C*H), 125.7 (*C*H), 126.4 (*C*H), 135.2 (*C*), 144.7 (*C*). $[\alpha]^{22}_{D}$ –127.9° (*c* 1.03, $CHCl_3$, 86% ee). HRMS–ESI (*m/z*): $[M+H]^+$ calcd for $C_{18}H_{26}BO_4$, 317.19241; found, 317.19150. Anal. Calcd for $C_{18}H_{25}BO_4$: C, 68.37; H, 7.97. Found: C, 68.11; H, 8.13. The ee value of 86% was determined by chiral HPLC analysis (CHIRALCEL OD-3, hexane/2-propanol 99.5/0.5, 40 °C, (1*R*,2*R*)-**4j**: t_R = 22.7 min. (1*S*,2*S*)-**4j**: t_R = 27.3 min.).

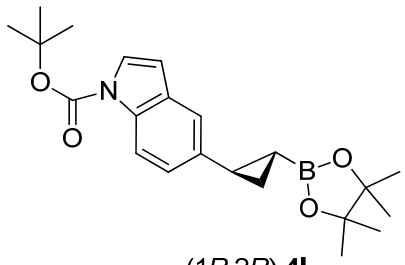
4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-(naphthalen-1-yl)cyclopropyl]-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4k**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.37 (dt, *J* = 9.6, 6.2 Hz, 1H), 1.09 (ddd, *J* = 9.6, 5.6, 3.4 Hz, 1H), 1.28 (m, 1H), 1.31 (s, 12H), 2.59 (dt, *J* = 8.1, 5.9 Hz, 1H), 7.24–7.29 (m, 1H), 7.34–7.40 (m, 1H), 7.45–7.57 (m, 2H), 7.70 (d, *J* = 8.0 Hz, 1H), 7.82–7.87 (m, 1H), 8.33–8.38 (m, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 12.3, 19.8, 24.63, 24.64, 83.2, 123.5, 124.4, 125.5, 125.6, 125.8, 126.7, 128.5, 133.4, 133.5, 138.9. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{19}H_{23}BO_2$ 294.17911, found 294.17897. $[\alpha]^{26.0}_{D}$ –58.2 (*c* 1.085, $CHCl_3$, 91% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, 2-PrOH/Hexane = 0.5/99.5, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4k** t_R = 17.4 min, (1*S*,2*S*)-**4k** t_R = 15.7 min).

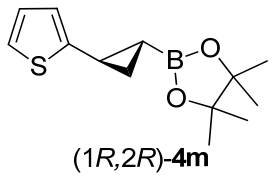
***tert*-Butyl 5-[(1*R*,2*R*)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]-1H-indole-1-carboxylate.**



(1*R*,2*R*)-**4l**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.32 (ddd, *J* = 9.7, 6.8, 5.7 Hz, 1H), 1.03 (ddd, *J* = 9.7, 5.3, 3.7 Hz, 1H), 1.16 (ddd, *J* = 7.9, 6.9, 3.7 Hz, 1H), 1.25 (s, 6H), 1.26 (s, 6H), 1.66 (s, 9H), 2.21 (dt, *J* = 8.1, 5.5 Hz, 1H), 6.48 (dd, *J* = 3.8, 0.5 Hz, 1H), 7.04 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.28 (d, *J* = 1.7 Hz, 1H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.98 (d, *J* = 8.5 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 14.9, 22.0, 24.80, 24.83, 28.3, 83.3, 83.6, 107.3, 115.1, 118.2, 122.8, 126.3, 131.0, 133.8, 137.9, 150.1. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–ESI (*m/z*): $[M+Na]^+$ calcd. for $C_{22}H_{30}BNNaO_4$ 406.21656, found 406.21662. $[\alpha]^{26.0}_D$ –117.6 (*c* 0.95, $CHCl_3$, 92% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, 2-PrOH/Hexane = 0.5/99.5, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4l** t_R = 11.7 min, (1*S*,2*S*)-**4l** t_R = 13.2 min).

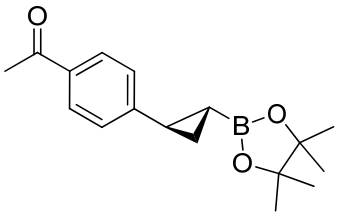
4,4,5,5-Tetramethyl-2-[(1*R*,2*R*)-2-(thiophen-2-yl)cyclopropyl]-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4m**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.34 (ddd, *J* = 9.9, 6.9, 5.5 Hz, 1H), 1.02 (ddd, *J* = 9.9, 5.2, 3.6 Hz, 1H), 1.17 (ddd, *J* = 8.0, 7.0, 3.6 Hz, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 2.31 (dt, *J* = 8.0, 5.4 Hz, 1H), 6.78 (dt, *J* = 3.5, 1.0 Hz, 1H), 6.87 (dd, *J* = 5.0, 3.5 Hz, 1H), 7.03 (dd, *J* = 5.0, 1.0 Hz, 1H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.8, 17.5, 24.8, 83.4, 122.2, 123.0, 126.9, 148.5. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{13}H_{19}BO_2S$ 250.11988, found 250.11976. $[\alpha]^{26.0}_D$ –160.4 (*c* 1.06, $CHCl_3$, 92% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, Hexane, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4m** t_R = 16.1 min, (1*S*,2*S*)-**4m** t_R = 17.5 min).

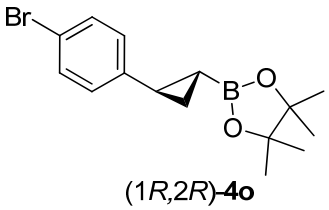
1-{4-[(1*R*,2*R*)-2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)cyclopropyl]}2phenylethanone.



(1*R*,2*R*)-**4n**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.38 (ddd, *J* = 9.8, 7.0, 5.5 Hz, 1H), 1.08 (ddd, *J* = 9.8, 5.1, 3.8 Hz, 1H), 1.20–1.27 (m, 1H), 1.25 (s, 6H), 1.26 (s, 6H), 2.15 (dt, *J* = 8.0, 5.3 Hz, 1H), 2.57 (s, 3H), 7.11–7.16 (m, 2H), 7.82–7.87 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.9, 22.1, 24.80, 24.82, 26.6, 83.6, 125.8, 128.8, 135.0, 150.0, 198.1. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{17}H_{23}BO_3$ 286.17402, found 286.17406. $[\alpha]^{25.3}_D$ –163.6 (*c* 0.365, $CHCl_3$, 85% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, 2-PrOH/Hexane = 1.5/98.5, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4n** t_R = 14.6 min, (1*S*,2*S*)-**4n** t_R = 13.9 min).

2-[(1*R*,2*R*)-2-(4-Bromophenyl)cyclopropyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.



(1*R*,2*R*)-**4o**

^{1}H NMR (300 MHz, $CDCl_3$): δ 0.26 (ddd, *J* = 9.9, 6.9, 5.4 Hz, 1H), 0.96 (ddd, *J* = 9.8, 5.4, 3.7 Hz, 1H), 1.16 (ddd, *J* = 8.2, 7.0, 3.7 Hz, 1H), 1.24 (s, 6H), 1.25 (s, 6H), 2.06 (dt, *J* = 8.2, 5.4 Hz, 1H), 6.91–6.97 (m, 2H), 7.32–7.37 (m, 2H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 15.1, 21.5, 24.78, 24.81, 83.5, 119.2, 127.7, 131.5, 142.8. The carbon directly attached to the boron atom was not detected, likely due to quadropolar relaxation.[4,5,6] HRMS–EI (*m/z*): $[M]^+$ calcd. for $C_{15}H_{20}BBrO_2$ 322.07397, found 322.07311. $[\alpha]^{26.0}_D$ –74.6 (*c* 0.155, $CHCl_3$, >50% ee). The ee value was determined by HPLC analysis (CHIRALCEL OD-3, Hexane, 0.5 mL/min, UV detector at 220 nm, 40 °C, (1*R*,2*R*)-**4o** t_R = 14.1 min, (1*S*,2*S*)-**4o** t_R = 16.1 min (overlapped with a peak from a side product).

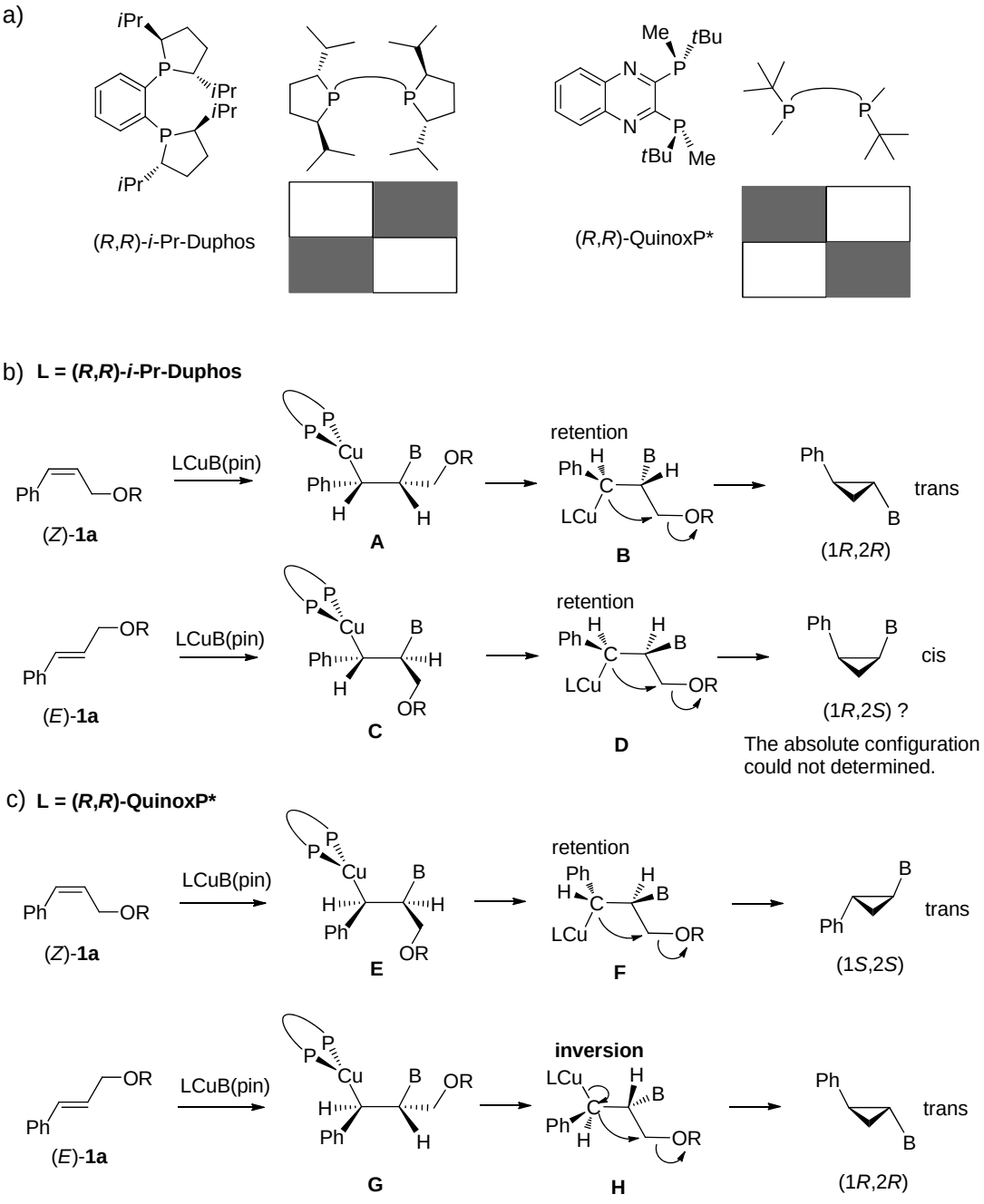
7. Possible Explanation on the Stereoselectivity in the reaction of (*Z*)- and (*E*)-1a.

The chiral environments created by (*R*,*R*)-*i*-Pr-DuPhos in the copper(I) catalyst intermediate is opposite to those with (*R*,*R*)-QuinoxP* or (*R*,*R*)-Me-DuPhos (Figure S1a). This explains the absolute configuration of the product **4a** in Table 1 (main text): the product with (*R*,*R*)-*i*-Pr-DuPhos [(1*R*,2*R*)-**4a**, Table 1, entries 1–3] shows the opposite configuration those with (*R*,*R*)-QuinoxP*or (*R*,*R*)-Me-DuPhos [(1*S*,2*S*)-**4a**, Table 1, entries 4, 5, 9].

The further explanation on the stereochemical outcomes in the main text was illustrated in Figure S1b and S1c. In the reaction of (*Z*)-**1a**, the borylcopper(I) species with (*R*,*R*)-*i*-Pr-DuPhos ligand first approaches to the (*Z*)-**1a** substrate such that the steric interaction between the ligand and phenyl group in (*Z*)-**1a** is minimized, affording the alkylcopper(I) intermediate **A** (Figure S1b). This intermediate **A** next undergoes intramolecular nucleophilic substitution (**B**) with retention of the configuration in terms of the carbon atom on the copper center to produce (1*R*,2*R*)-**4a** (94% ee). In the case of the reaction of (*E*)-**1a**, the borylcopper(I) intermediate reacts with (*E*)-**1a** to afford **C** with the favored steric interaction with the phenyl group. It is reasonable to suppose that the subsequent intramolecular nucleophilic substitution (**D**) proceeds with the retention of the configuration at the α-carbon center. This explains the cis product formation (Scheme 1, *cis*-**4a** (27% ee), the absolute configuration could not be determined).

The reaction between the catalyst with (*R*,*R*)-QuinoxP* and (*Z*)-**1a** proceeds similarly: the steric interaction between the ligand and phenyl group is minimized. The resultant intermediate **E** undergoes intramolecular nucleophilic substitution (**F**) with retention of the configuration to afford (1*S*,2*S*)-**4a**. In the case of (*E*)-**1a**, the inversion of the stereochemistry of the α-carbon atom in the alkylcopper product **H** should take place during the cyclization process. Despite the rationale for the difference between (*R*,*R*)-*i*-Pr-DuPhos and (*R*,*R*)-QuinoxP* in their stereoselectivity at the cyclization step is not clear at this stage, this assumption can explain the stereochemical outcome observed in our results. The similar stereoselectivity switching of the copper(I) catalyst containing (*R*,*R*)-QuinoxP* ligand was observed in the reaction of silyl-substituted allylic carbonates.[1b]

Figure S1.


a)
(R,R)-i-Pr-Duphos
(R,R)-QuinoxP*
b) L = (R,R)-i-Pr-Duphos
LCuB(pin)
retention
trans
(Z)-1a
A
B
(1R,2R)
LCuB(pin)
retention
cis
(E)-1a
C
D
(1R,2S) ?
The absolute configuration could not determined.
c) L = (R,R)-QuinoxP*
LCuB(pin)
retention
trans
(Z)-1a
E
F
(1S,2S)
LCuB(pin)
inversion
trans
(E)-1a
G
H
(1R,2R)

8. References.

(1) Nakamura, K.; Takenaka, K.; Ohno, A. *Tetrahedron: Asymmetry* **1998**, *9*, 4429.

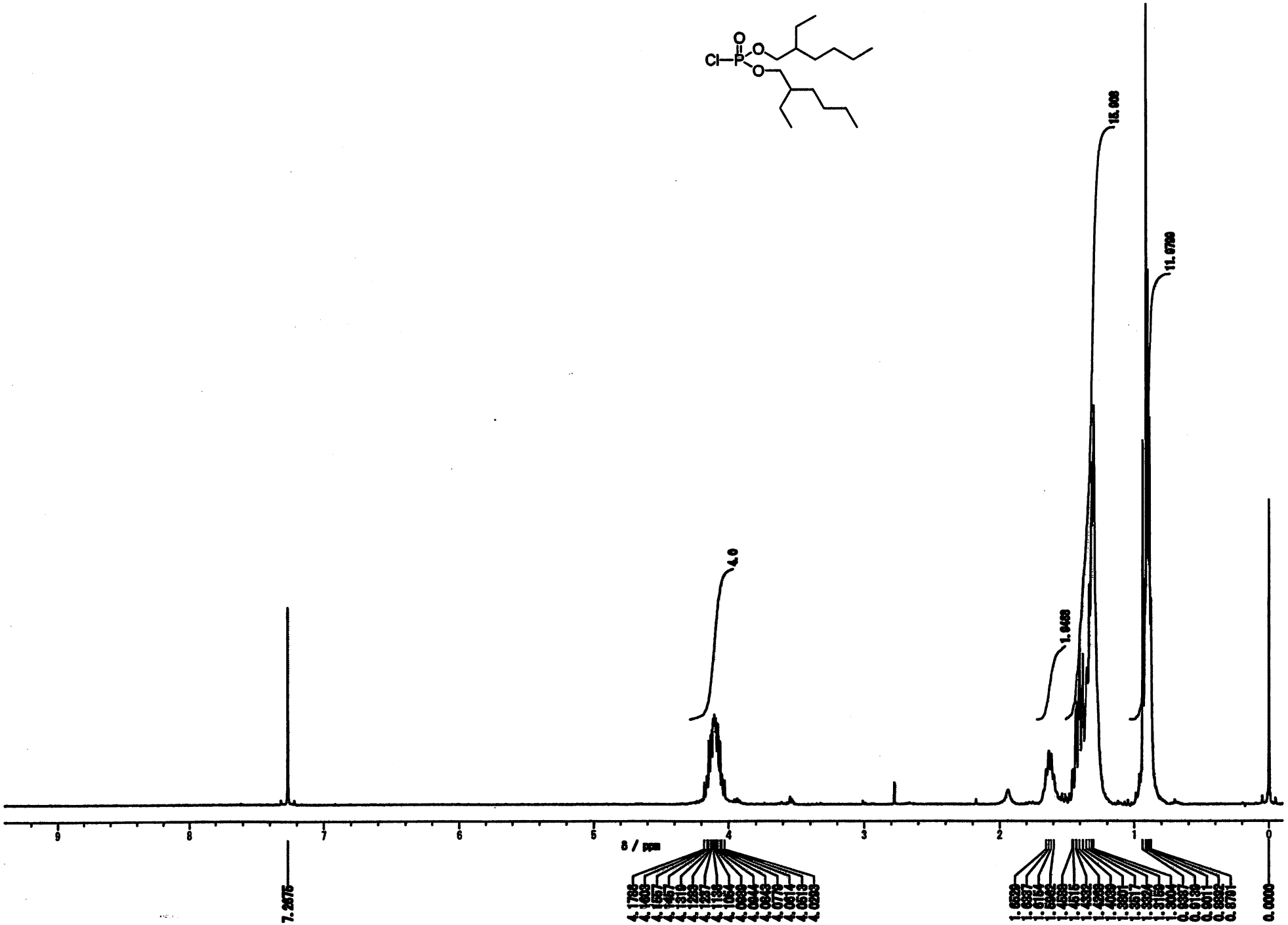
(2) Charette, A. B.; Molinaro, C.; Brochu, C. *J. Am. Chem. Soc.* **2001**, *123*, 12168. The procedure was described in the Supporting Information of this paper.

(3) de Sousa, P. T., Jr.; Taylor, R. J. K. *Journal of Brazilian Chemical Society* **1993**, *4*, 64.

(4) Ito H.; Kosaka, Y.; Nonoyama K.; Sasaki, Y.; Sawamura, Y. *Angew. Chem. Int. Ed.* **2008**, *47*, 7424.

(5) Wrackmeyer, B. *Prog. Nucl. Magn. Reson. Spectrosc.* **1979**, *12*, 227.

(6) Pelz, N. F.; Woodward, A. R.; Burks, H. E.; Sieber, J. D.; Morken, J. P. *J. Am. Chem. Soc.* **2004**, *126*, 16328.


Cl
P
O
O
O
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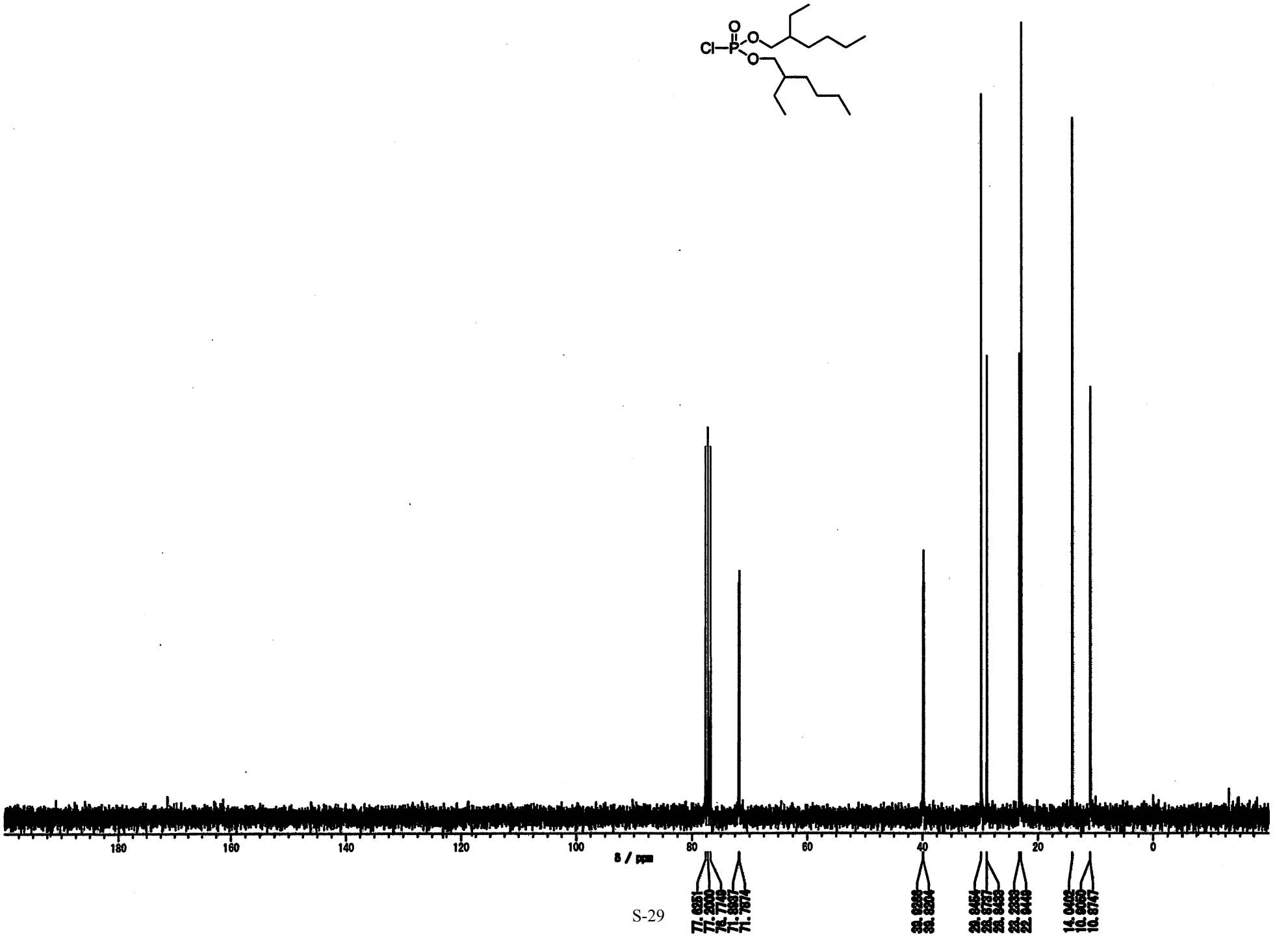
15.000
11.6799
7.2676
0.0000
9
8
7
6
5
4
3
2
1
0
δ / ppm


Cl
P
O
O
O
180
160
140
120
100
80
60
40
20
0
δ / ppm
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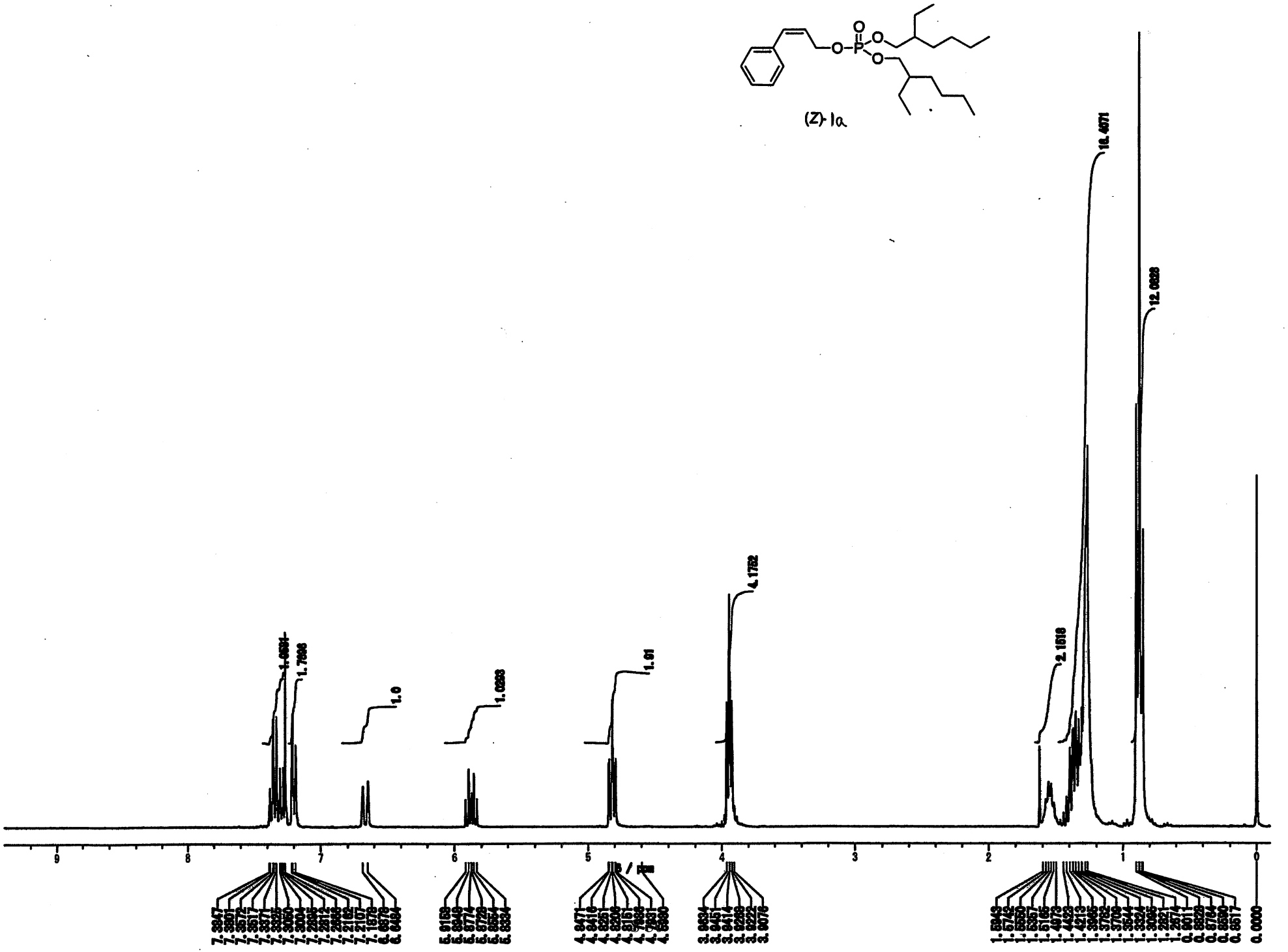
77.2000
76.7149
71.8857
71.7874
39.9286
39.8204
29.9464
29.6757
29.6483
23.2333
22.9448
14.0402
10.9080
10.8747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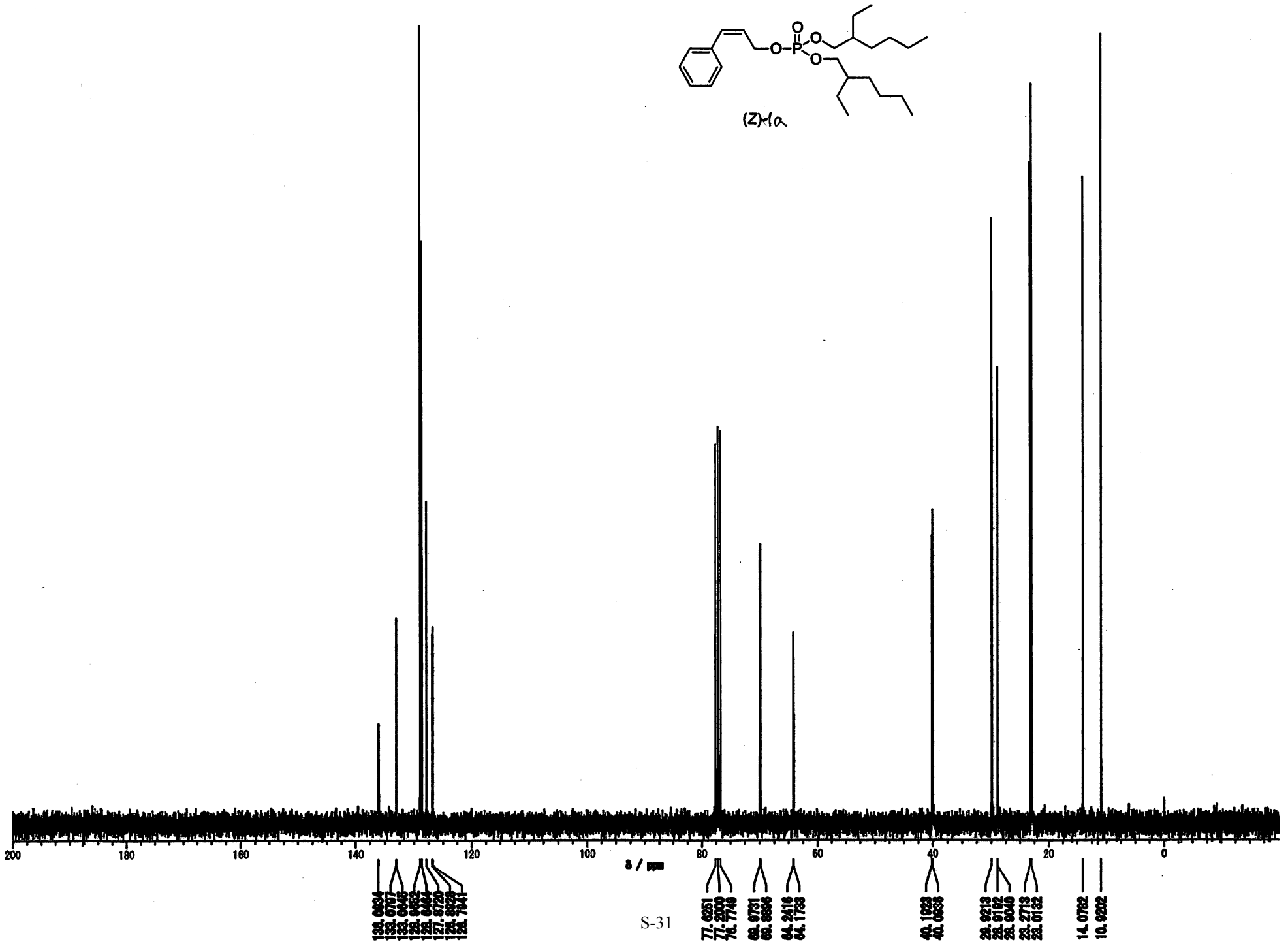
4.1752
2.1516
18.4071
12.0000
f1 / ppm


(Z)-1a
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
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133.0767
133.0445
128.9652
128.6404
127.6750
126.8928
126.7641
77.6951
77.2000
76.7749
69.6781
69.6886
64.2416
64.1783
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40.0838
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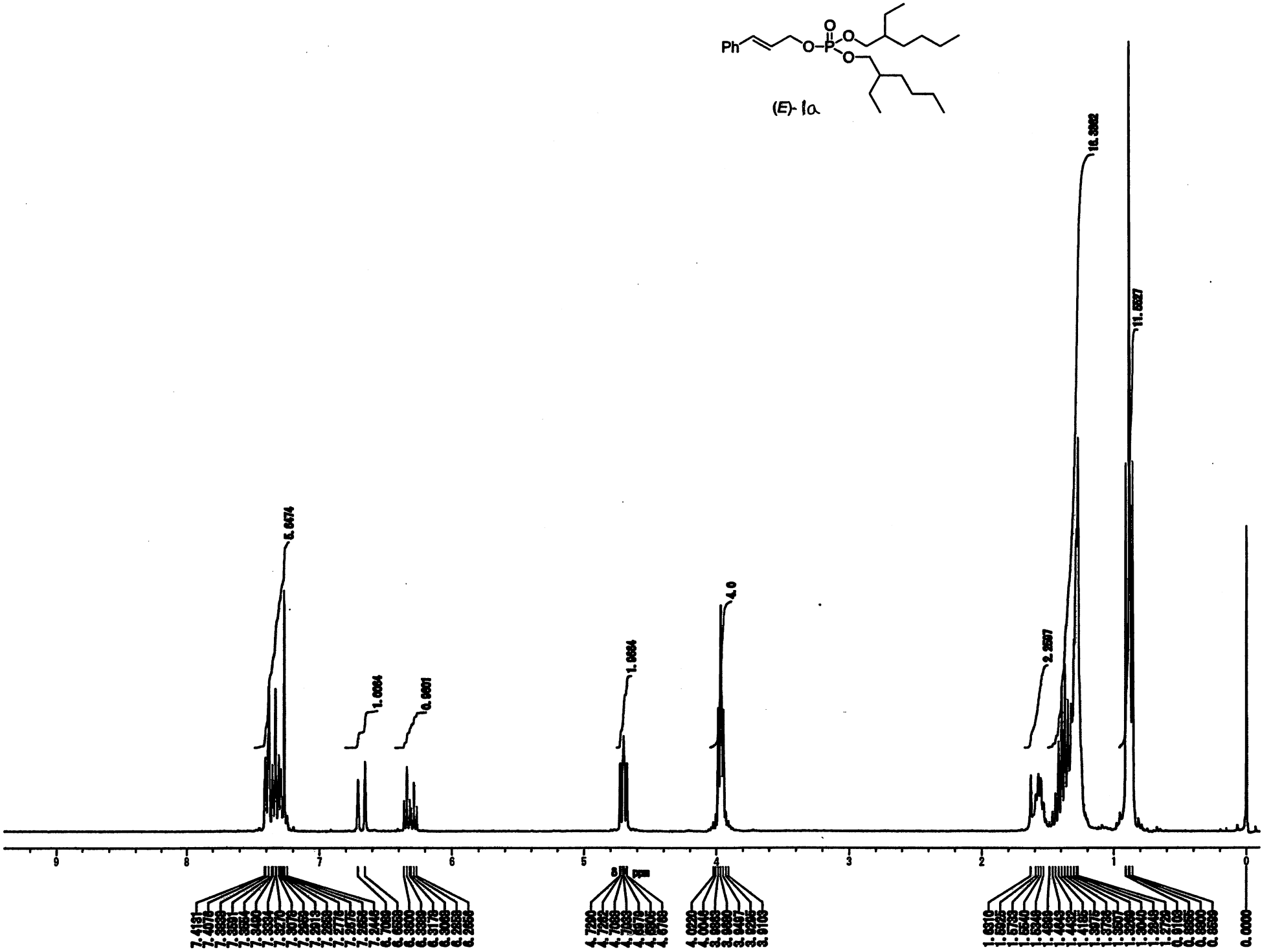
29.6192
29.0040
23.2713
22.6132
14.0782
10.9282


Ph
O
O
P
O
O
(E)-1a
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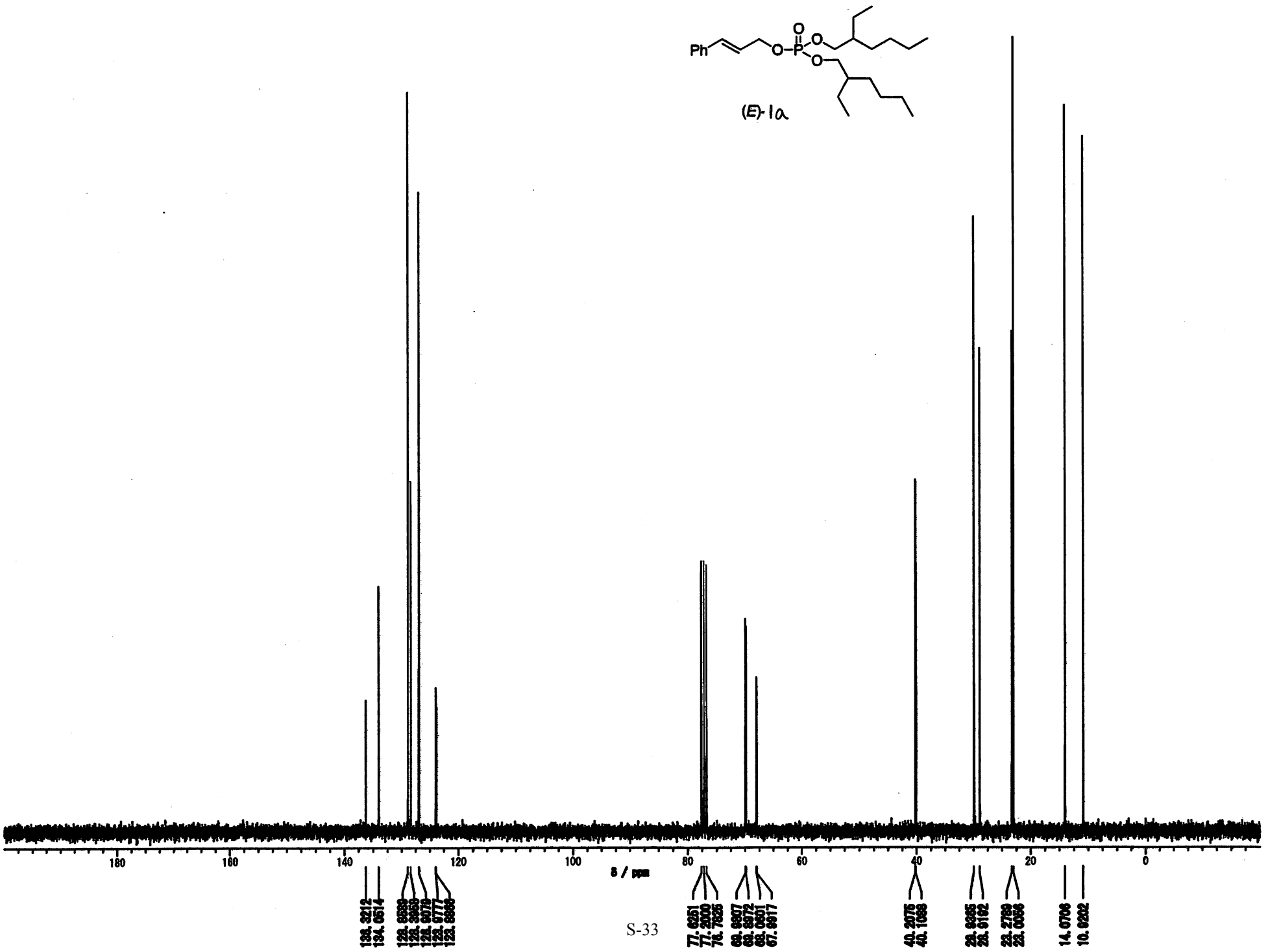
0.9801
1.0084
4.0
2.2937
16.3882
11.8927
9
8
7
6
5
4
3
2
1
0
f1 ppm


Ph
O
O
O
O
(E)-1a
180
160
140
120
100
80
60
40
20
0
δ / ppm
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134.0514
128.6539
128.3858
126.6070
123.5777
123.0868
77.6251
77.2000
76.7825
69.9807
69.8572
68.0601
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40.1088
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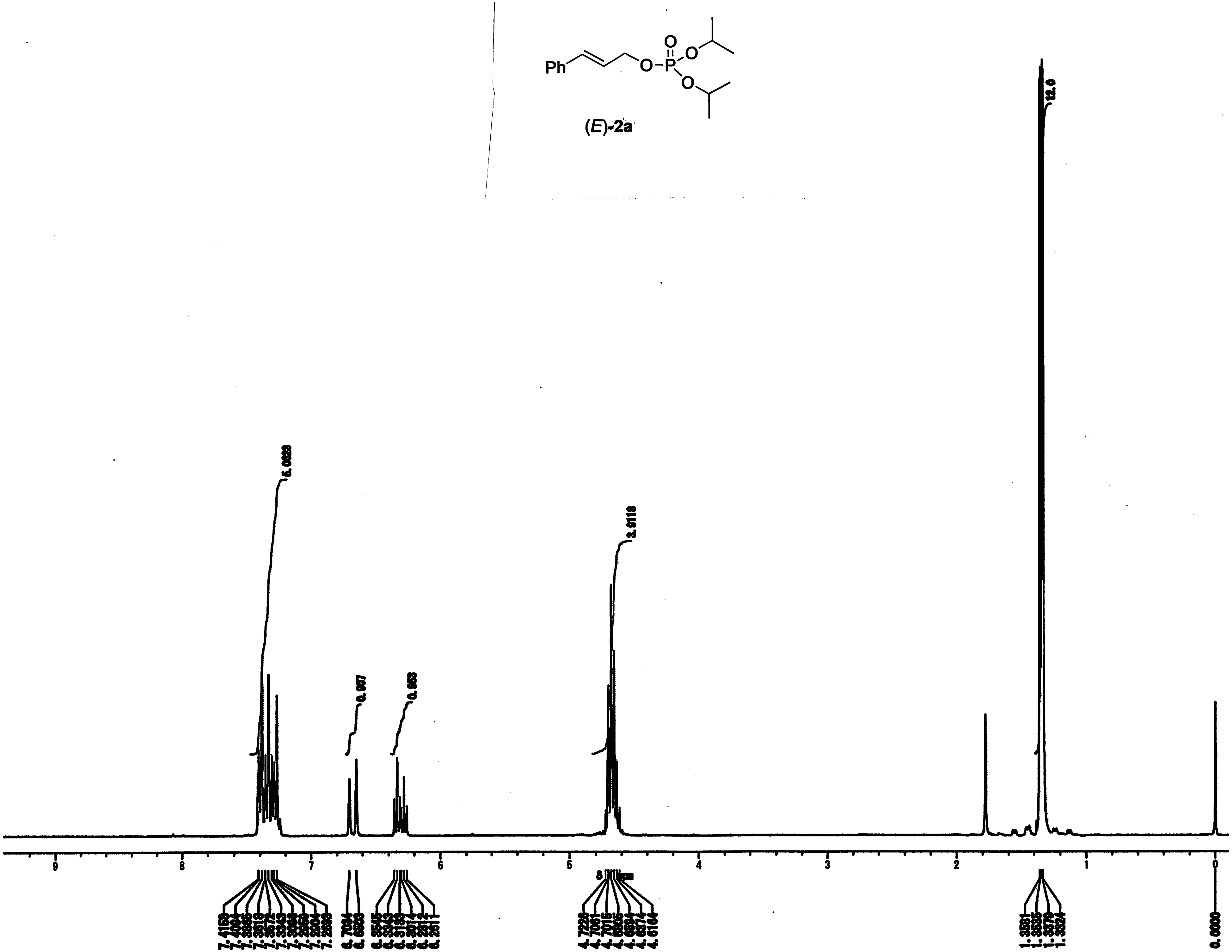
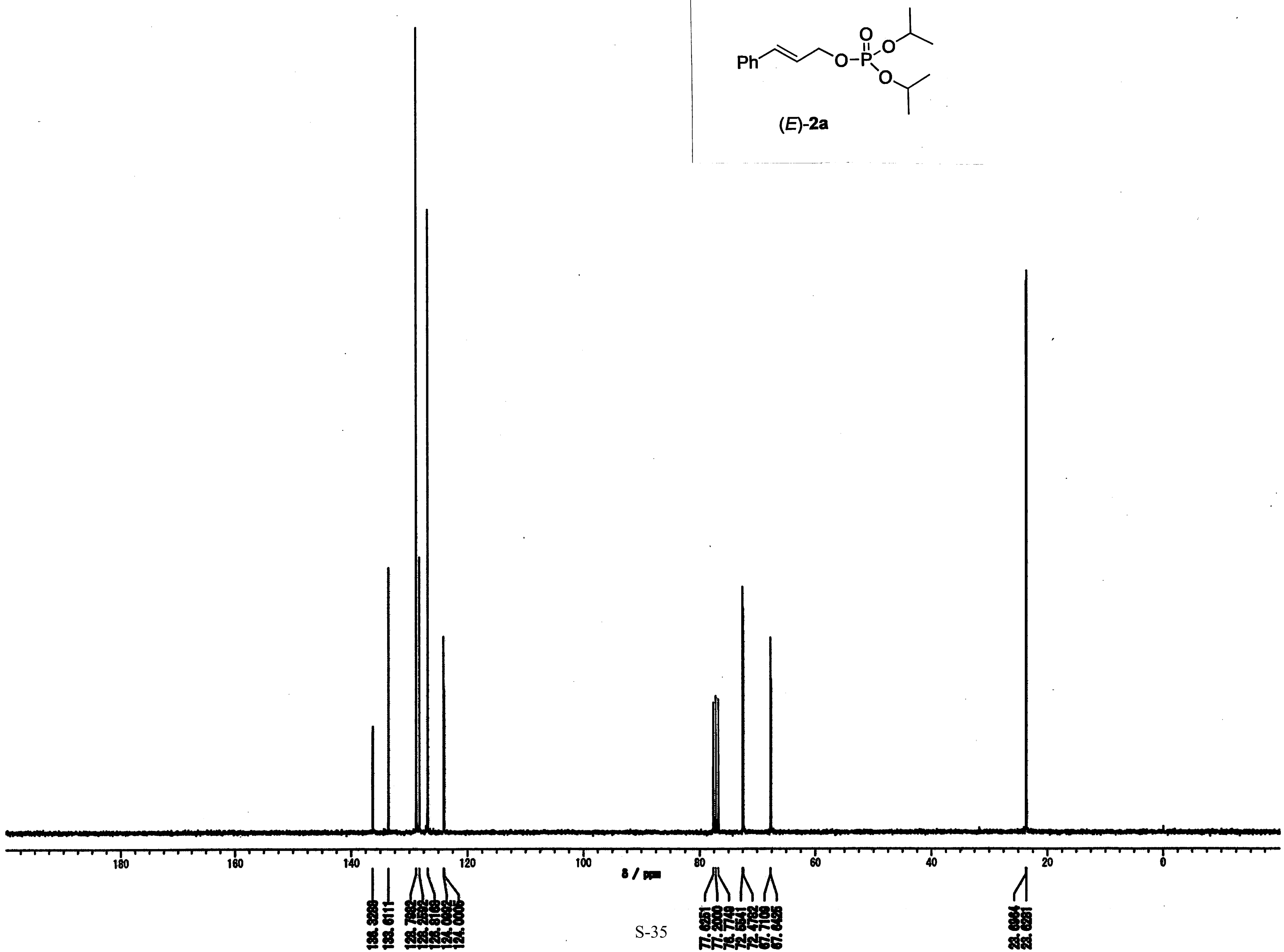
22.2789
22.0058
14.0706
10.9202


Ph
O
P
(E)-2a
9
8
7
6
5
4
3
2
1
0



Ph
O
P
(E)-2a
180
160
140
120
100
δ / ppm
80
60
40
20
0
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133.6111
128.7682
128.2862
126.8168
124.0902
124.0005
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77.2000
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67.7106
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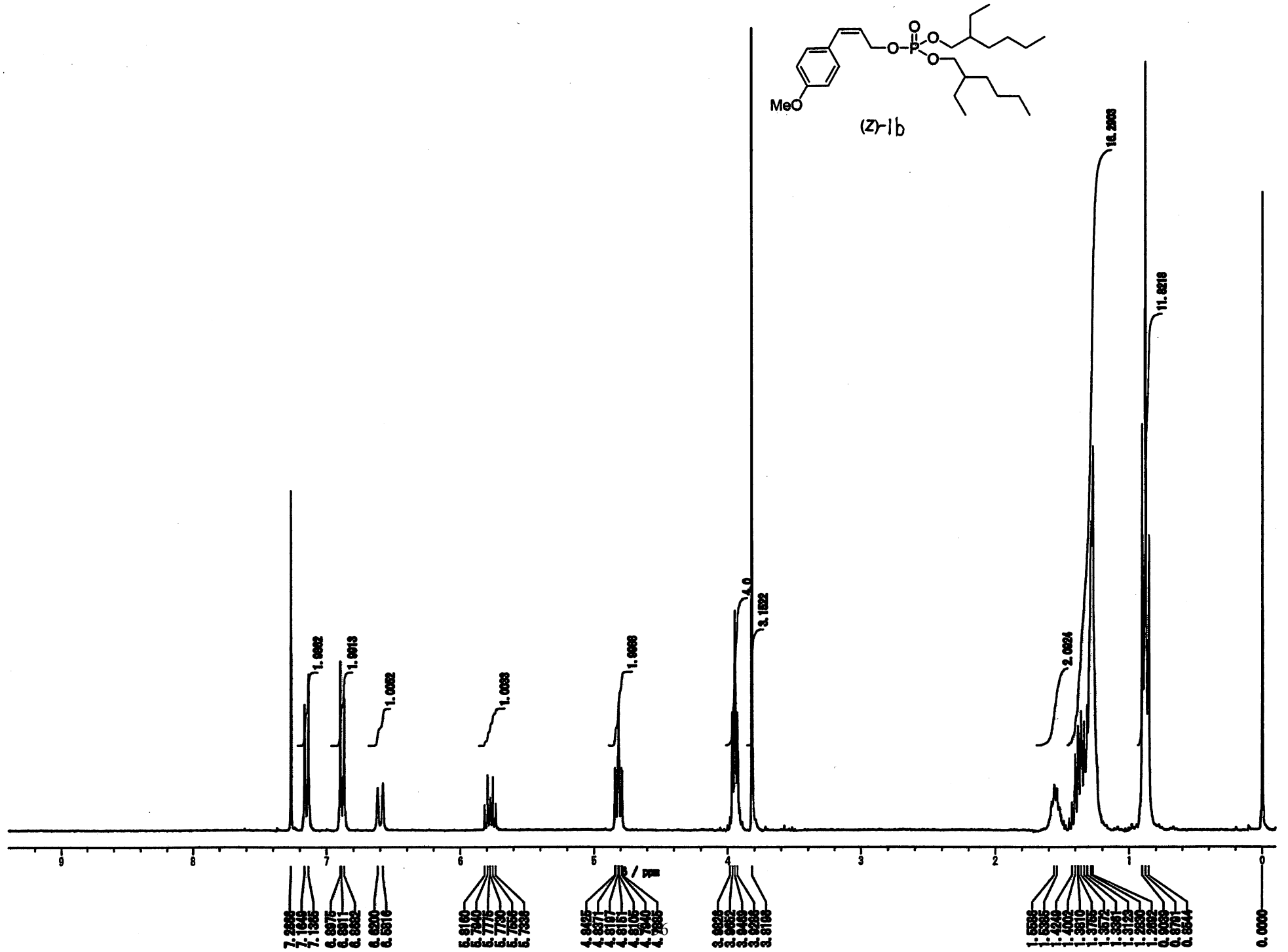
23.6964
23.6281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(Z)-1b
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1.0002
1.0003
1.0008
4.0
3.1822
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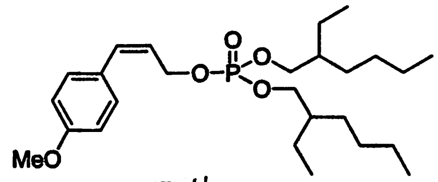
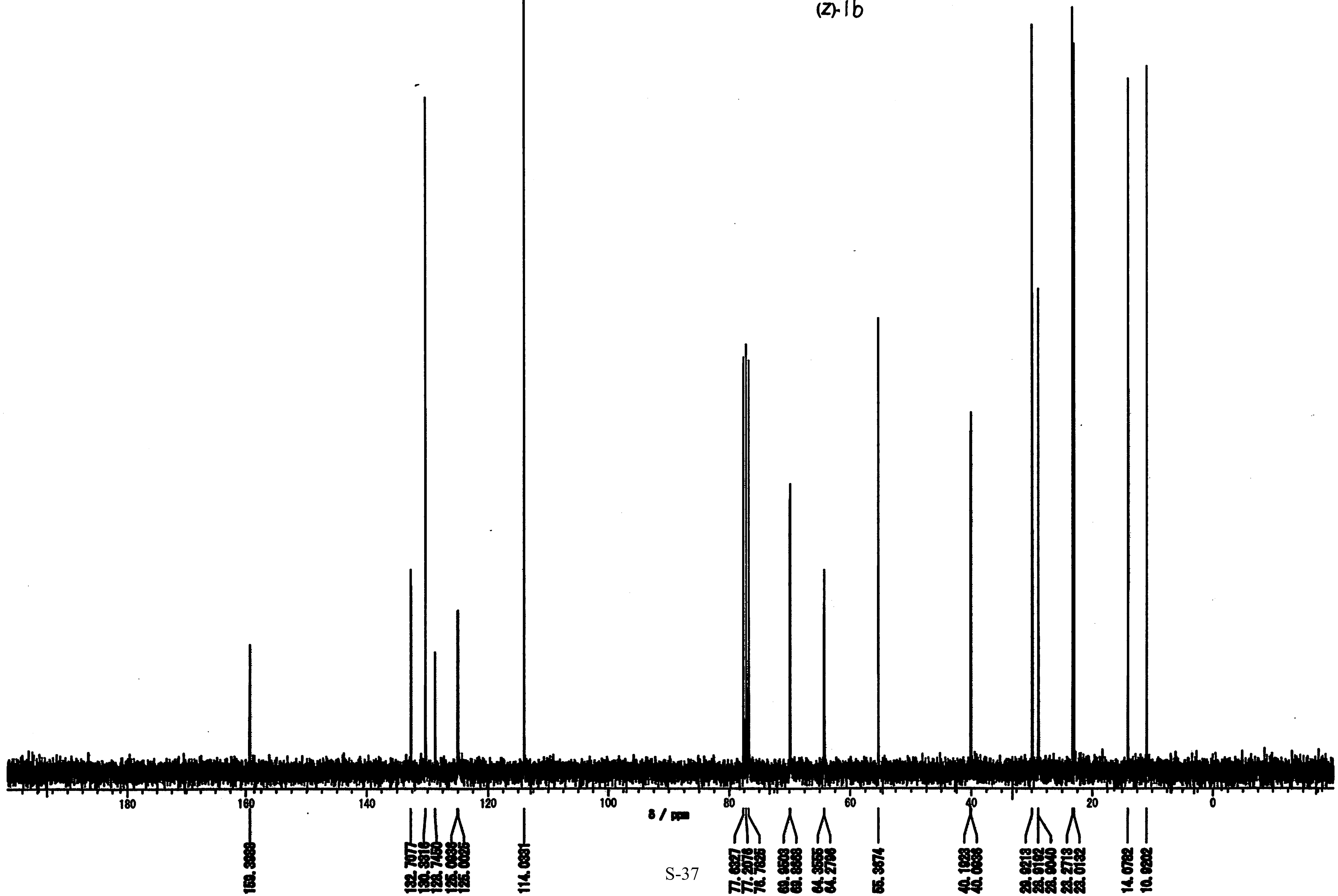
14.2903
11.8218
9
8
7
6
5
4
3
2
1
0
f1 / ppm



(Z)-1b



180
160
140
120
100
δ / ppm
80
60
40
20
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130.3316
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125.0838
125.0026
114.0381
77.6327
77.2076
76.7826
69.9508
69.8868
64.3555
64.2796
55.3674
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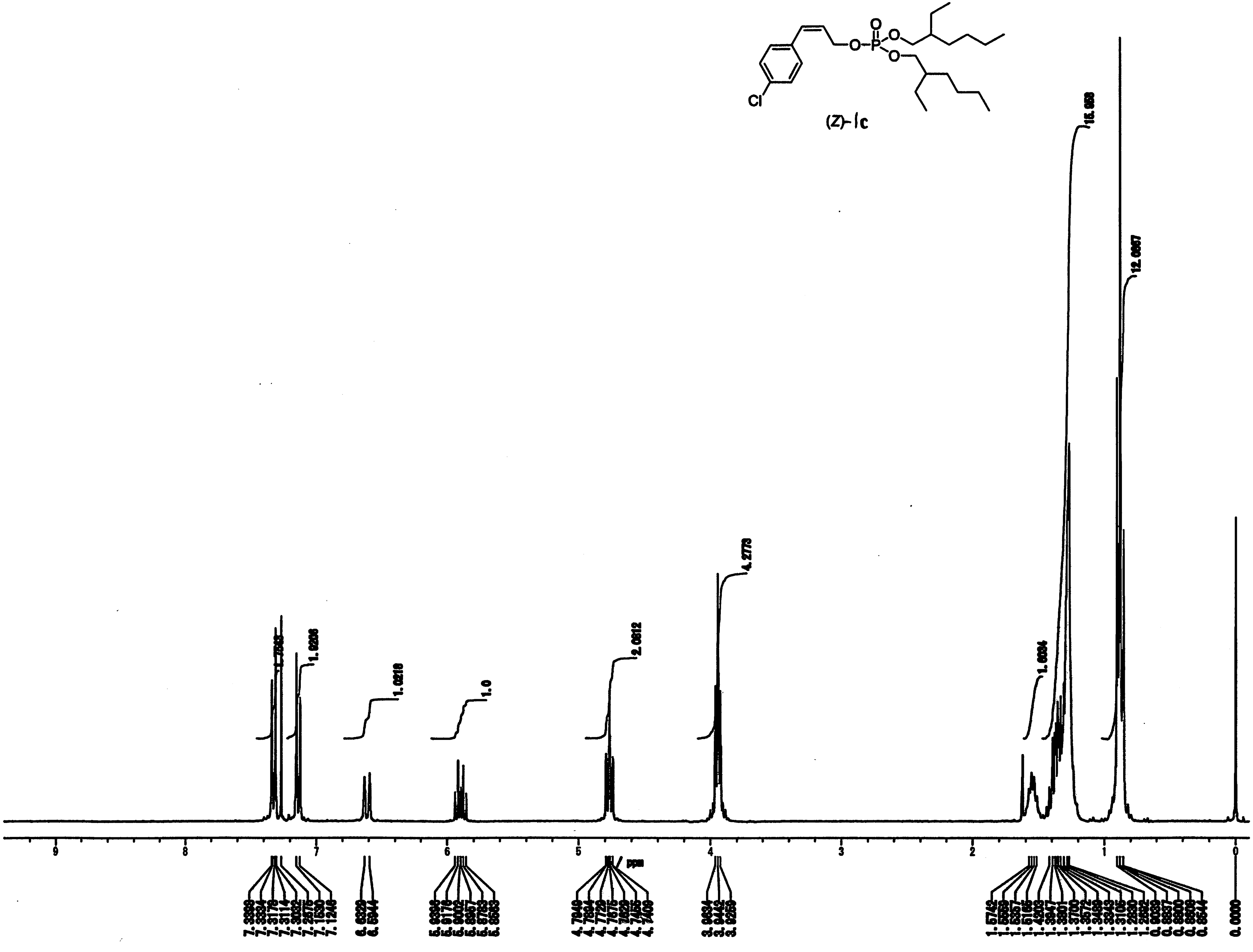
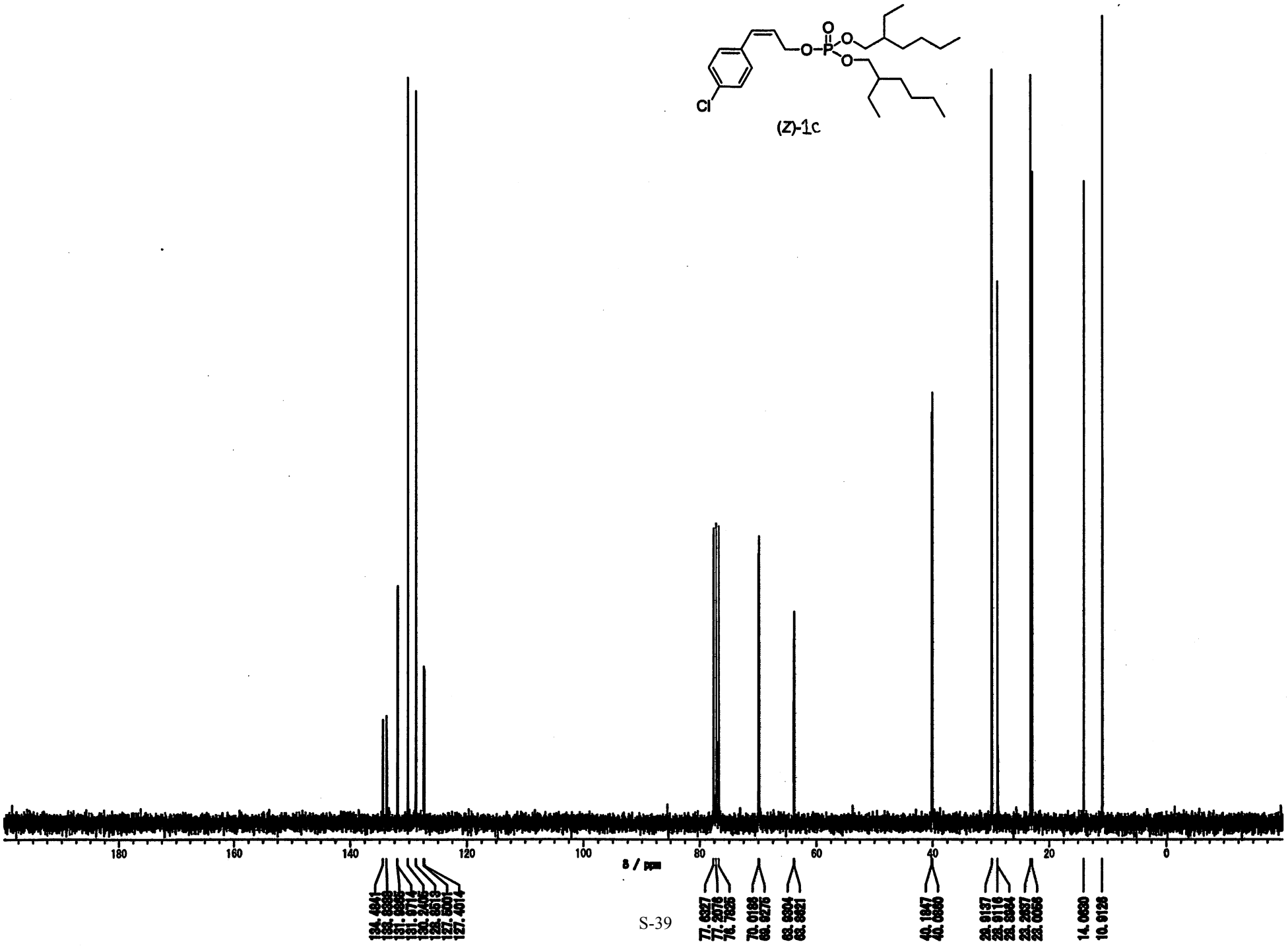
40.0838
29.9213
28.9192
28.9040
23.2713
23.0132
14.0782
10.9202



(Z)-1c
Cl
ppm
9
8
7
6
5
4
3
2
1
0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O
P
O
O
O
180
160
140
120
100
80
60
40
20
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δ / ppm
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133.8369
131.9965
131.6774
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77.2576
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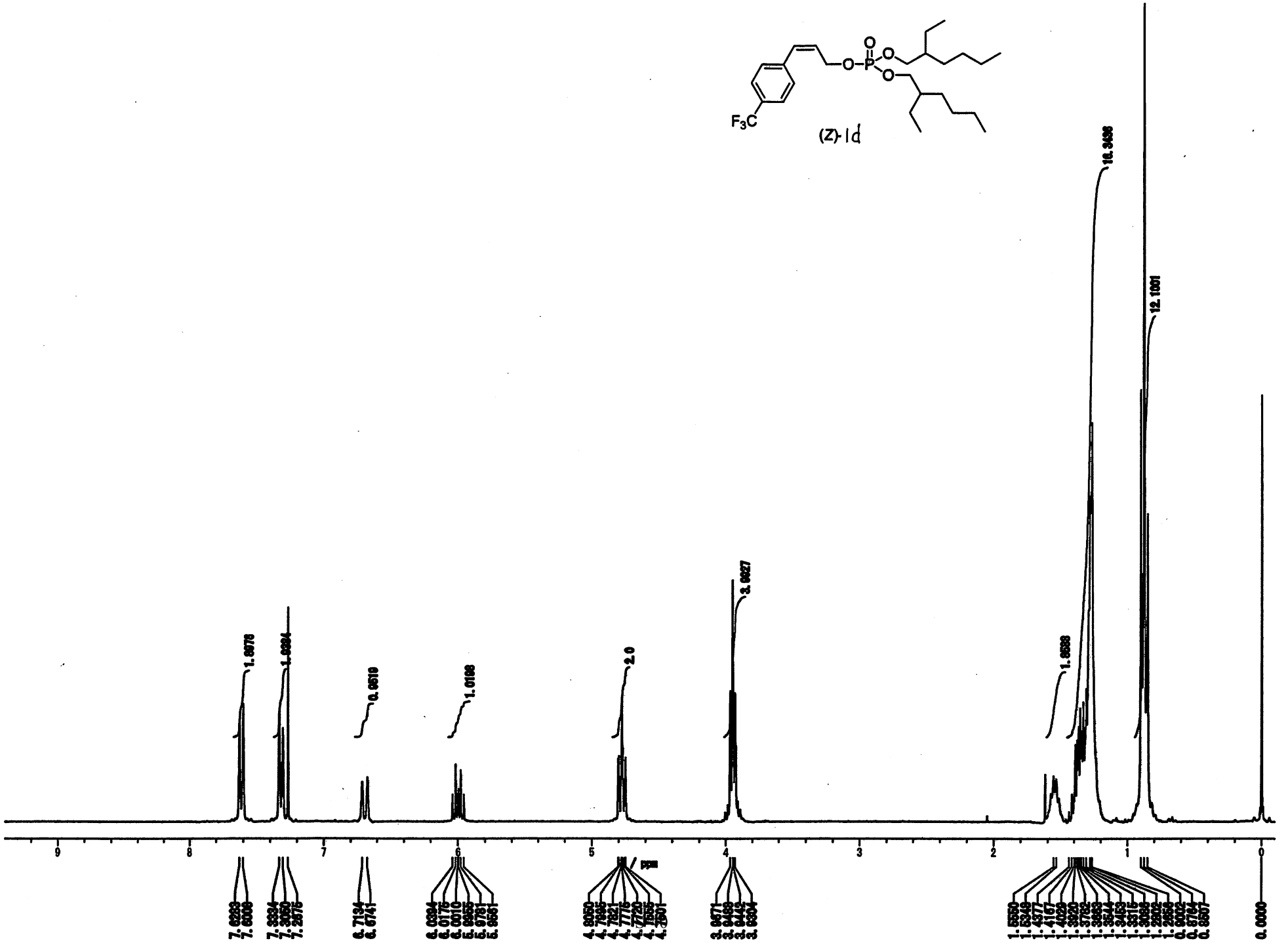
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P
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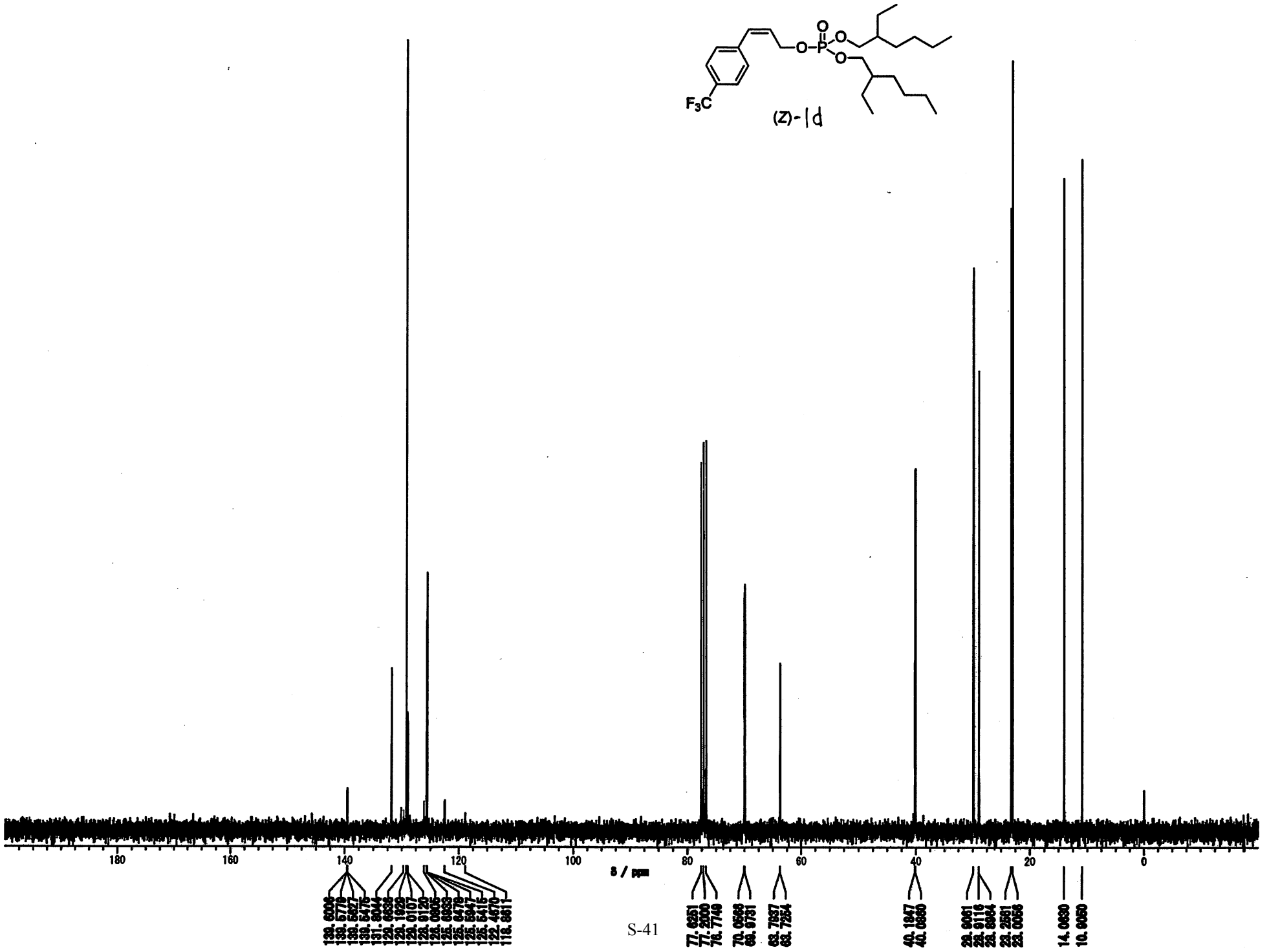
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F3C
O
O
O
O
P
180
160
140
120
100
80
60
40
20
0
δ / ppm
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138.6779
138.6627
138.5476
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128.8838
128.1929
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128.0120
125.9805
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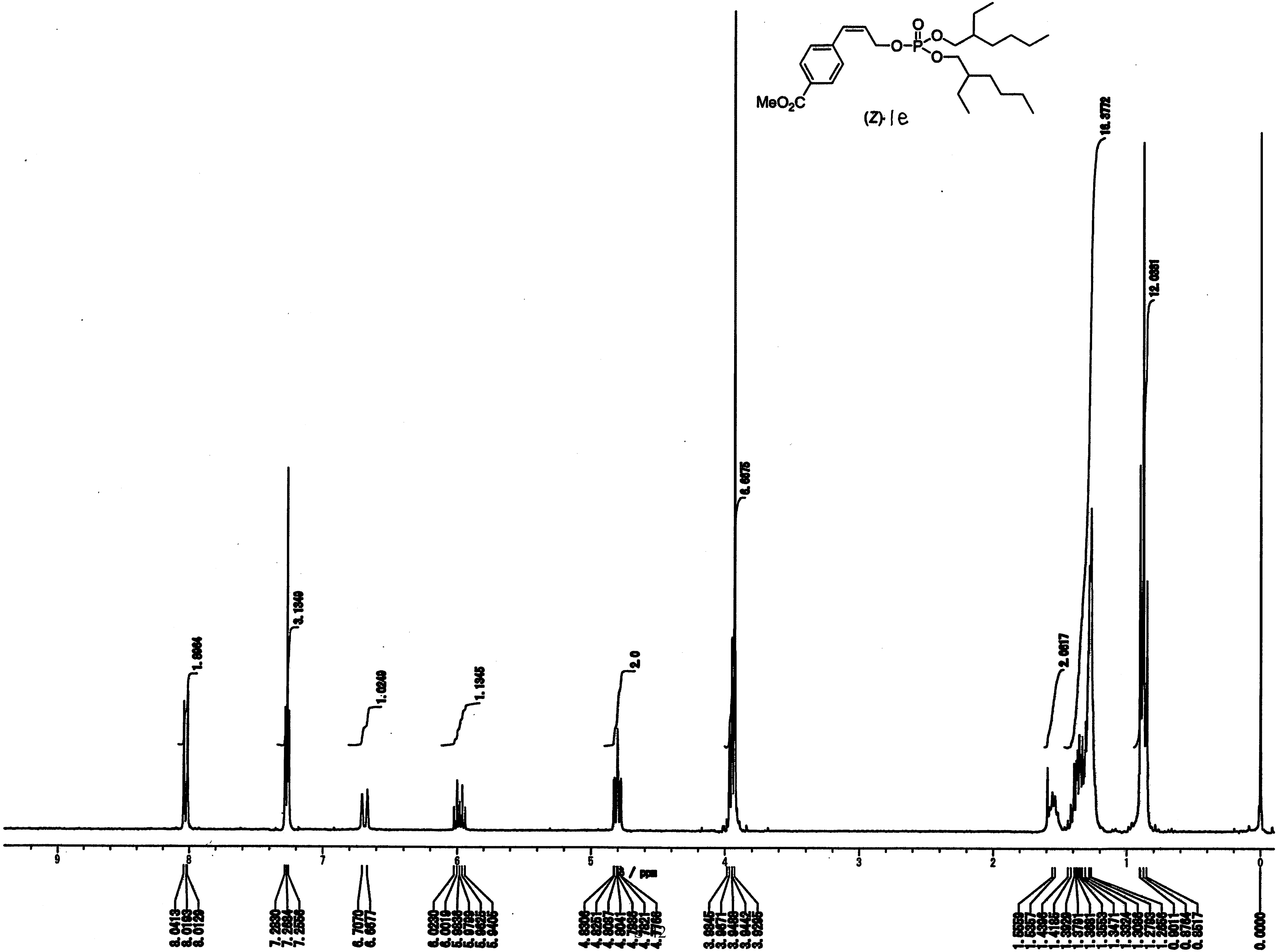
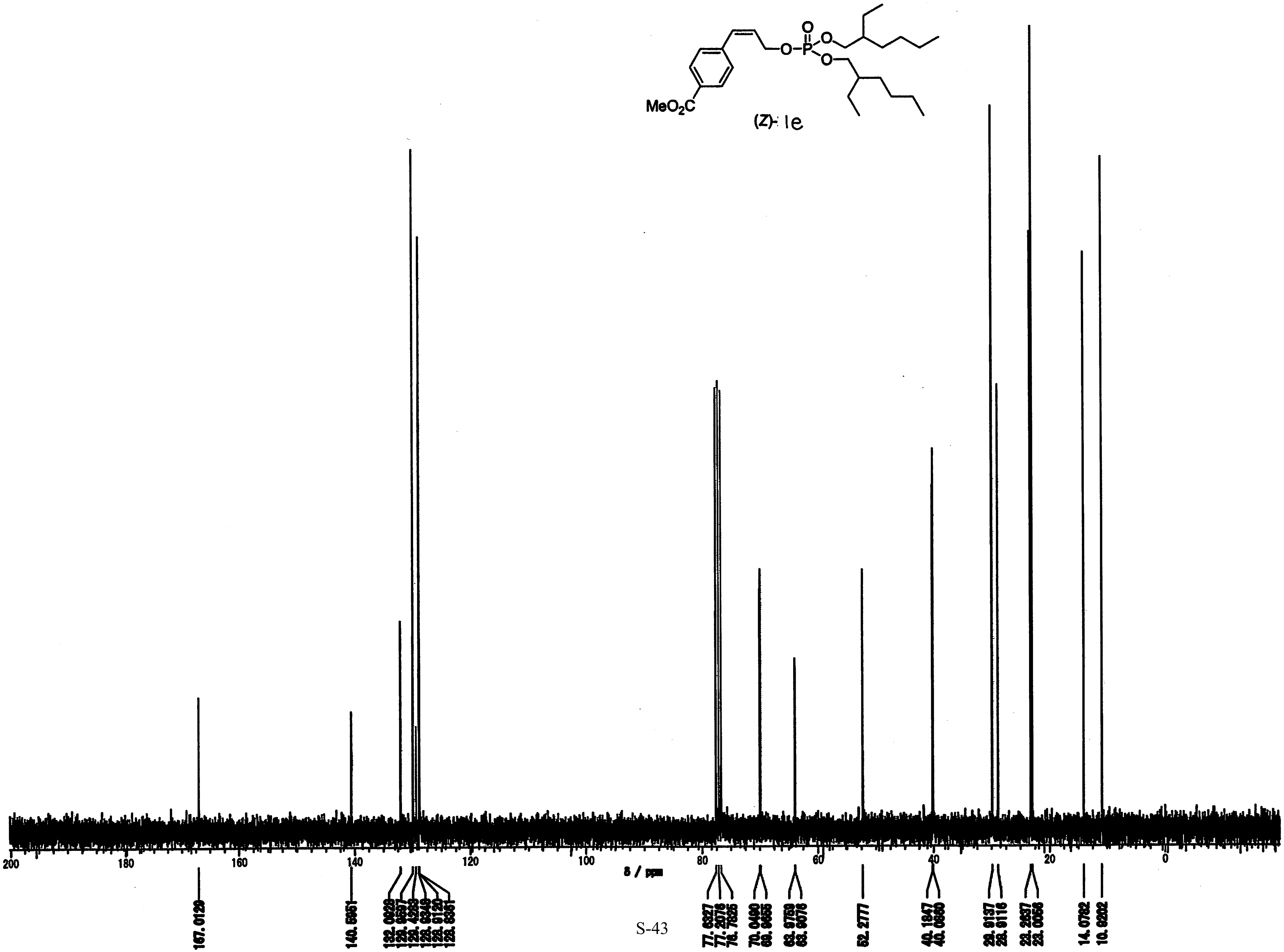
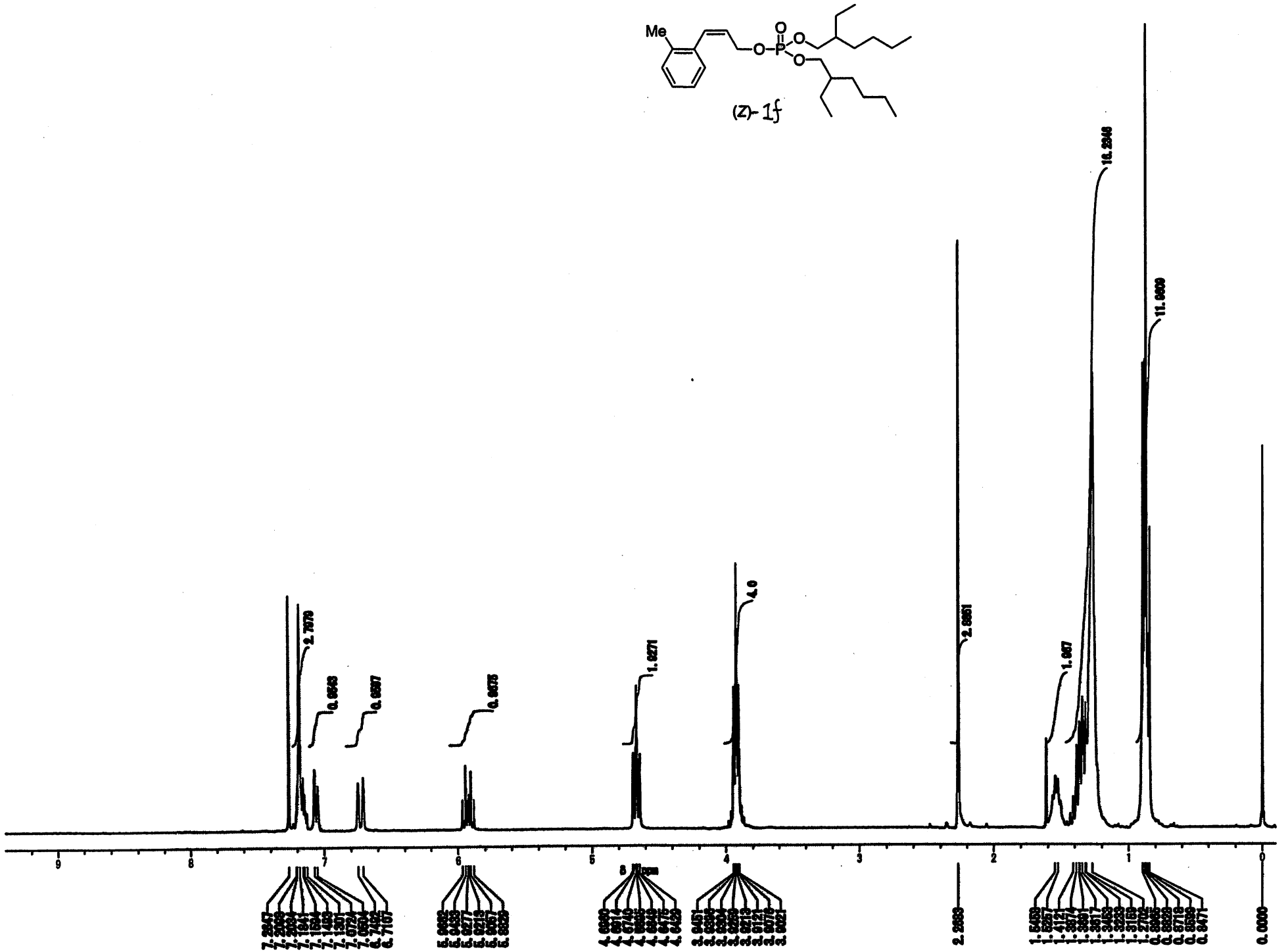
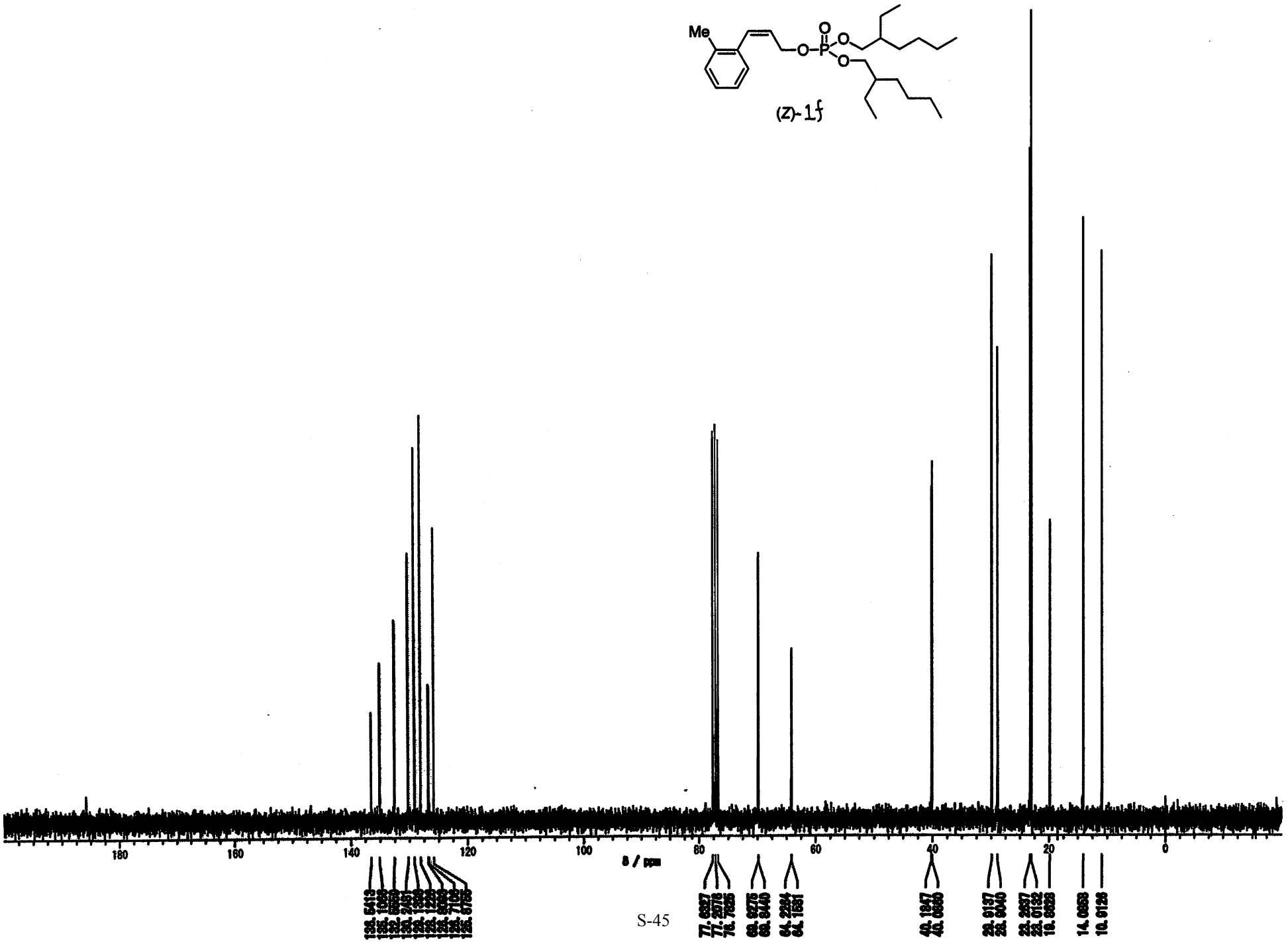
125.6478
125.6047
125.5416
122.4570
118.8611
77.6351
77.2000
76.7749
70.0568
68.9751
63.7937
63.7254
40.1947
40.0860
29.9061
29.9116
23.8934
23.2561
23.0056
14.0630
10.9050



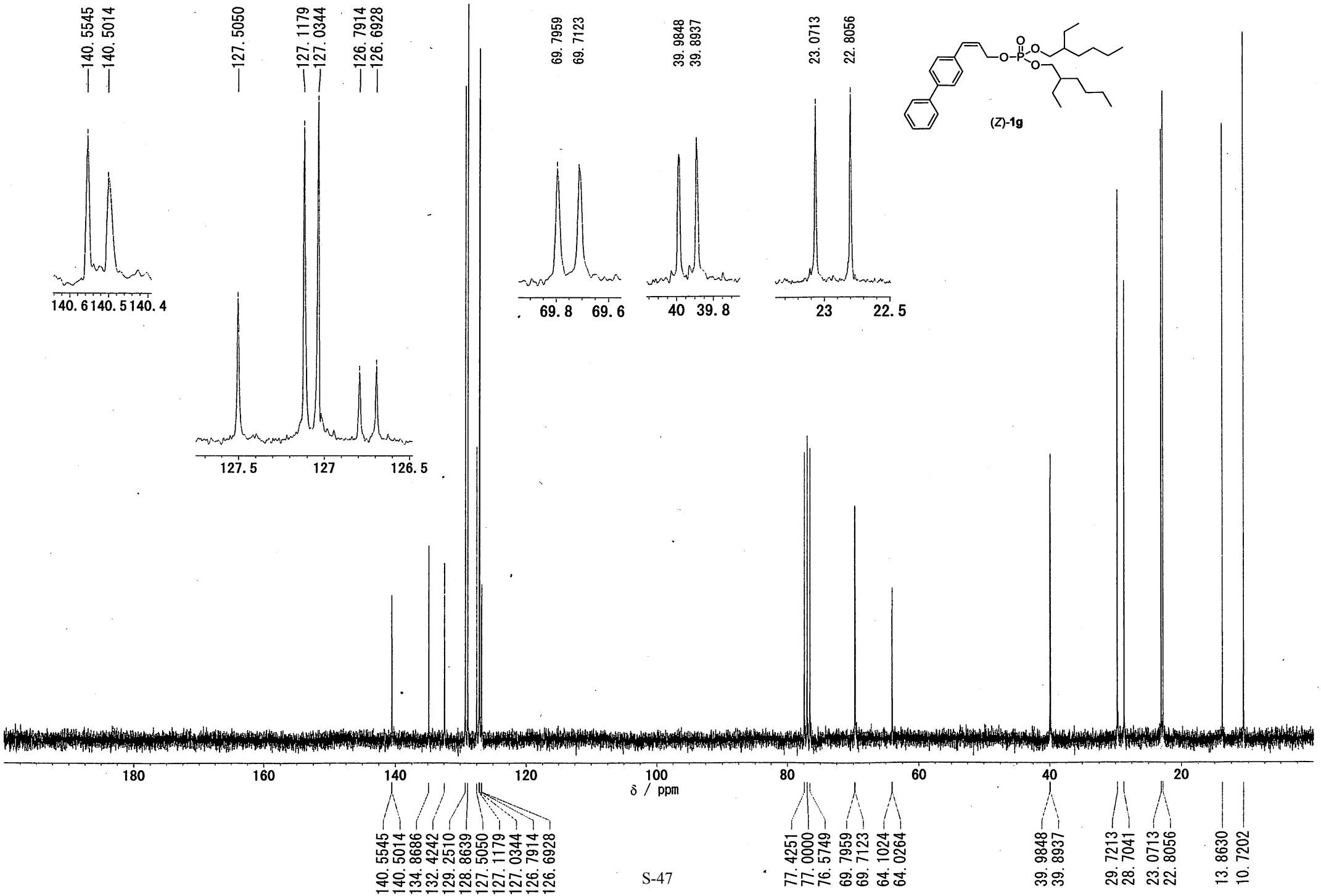
MeO2C
(Z)-1e
δ / ppm
1.8864
3.1349
1.0249
1.1345
2.0
6.0676
2.0617
16.5772
12.0881
8.0413
8.0193
8.0129
7.2630
7.2604
7.2556
6.7070
6.6677
0.0000

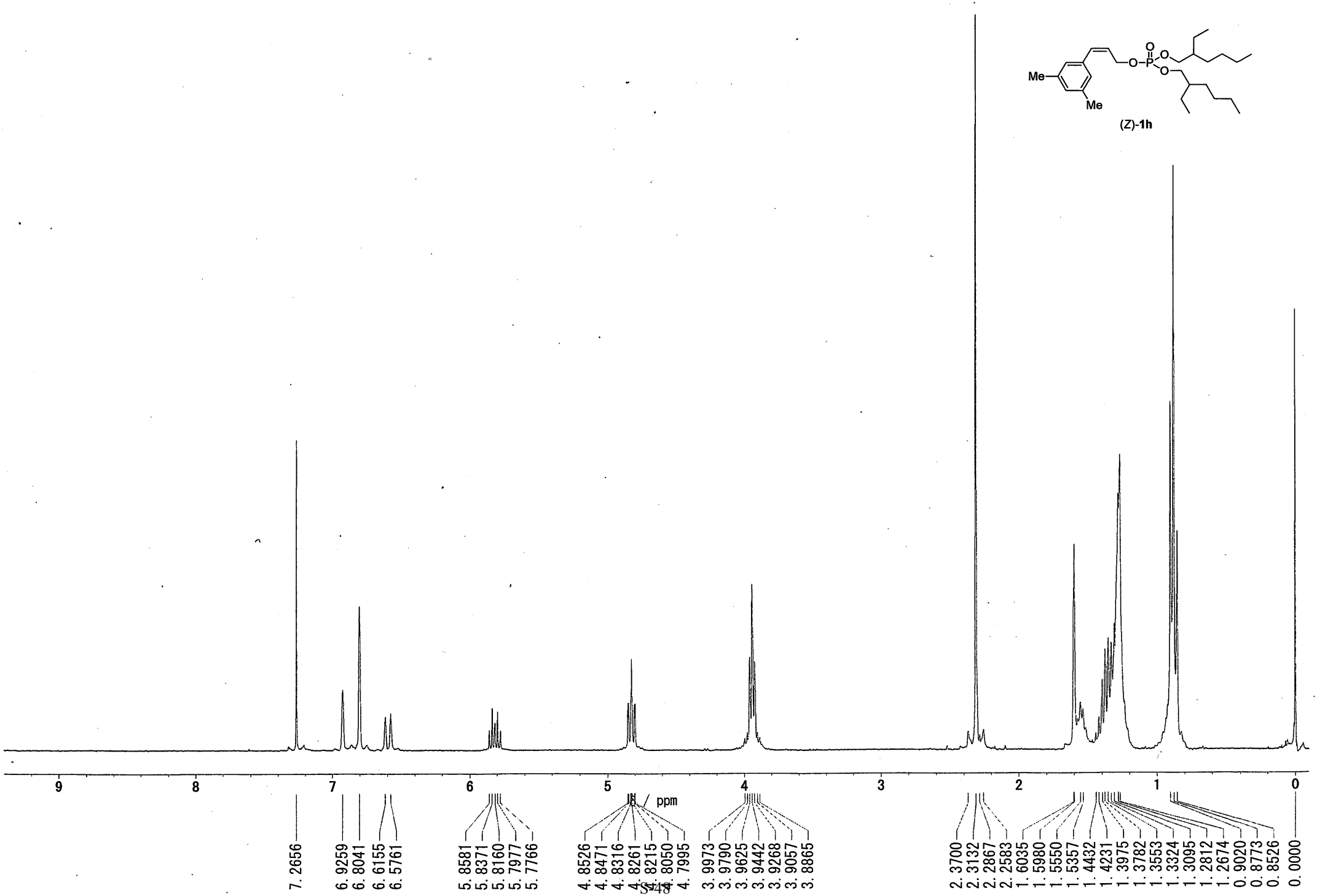

MeO2C
O
P
(Z)-1e
200
180
160
140
120
100
δ / ppm
80
60
40
20
0
167.0120
140.5951
132.0928
129.9597
129.4283
128.6949
128.6120
128.5361
77.6327
77.2076
76.7825
70.0490
69.9655
63.9759
63.9076
52.2777
40.1847
40.0860
29.9137
28.9116
23.2637
23.0056
14.0782
10.9202

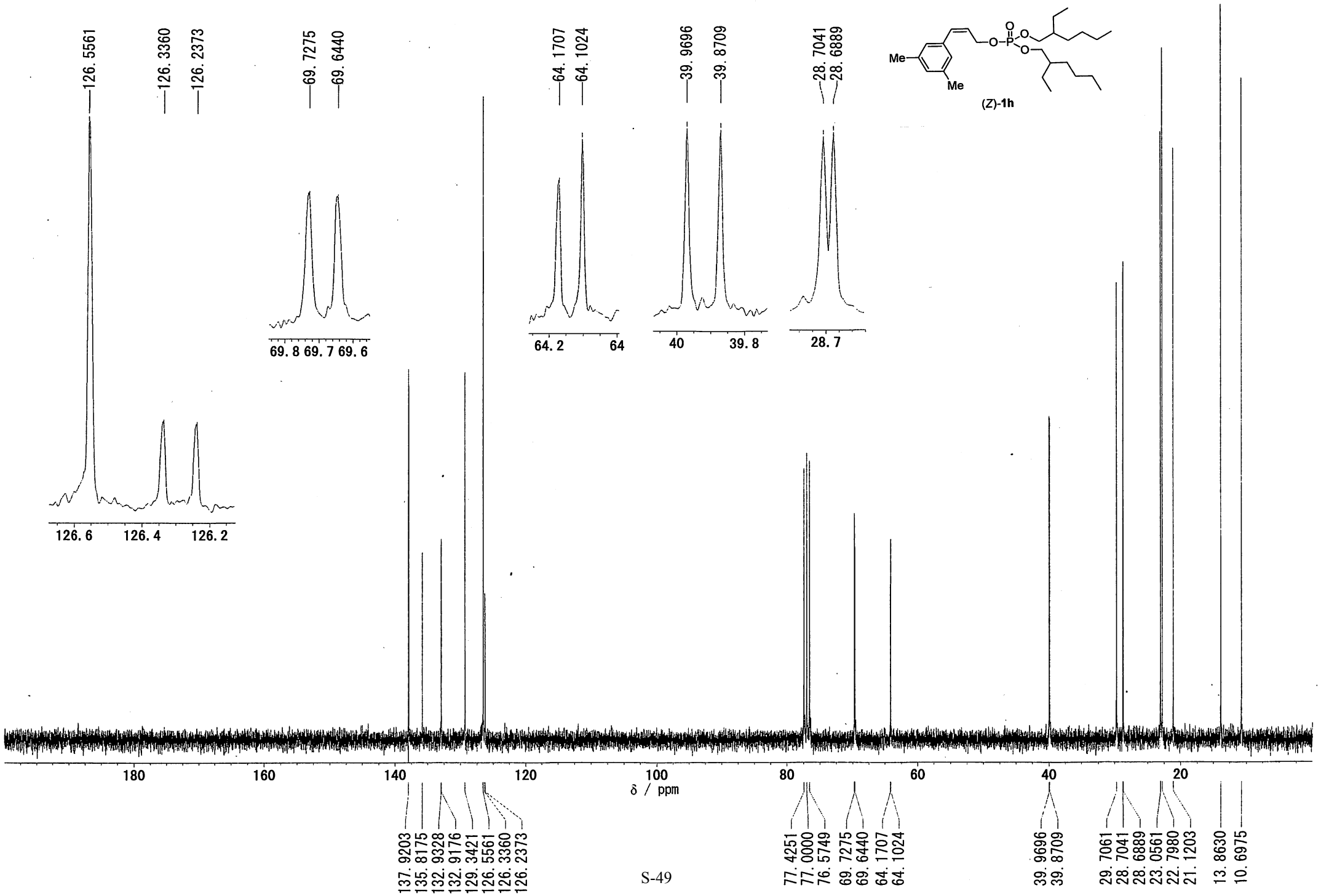

Me
O
O
P
O
O
(Z)-1f
2.7978
0.9543
0.9997
0.9675
1.9271
4.0
2.9931
1.967
18.2946
11.9999
0.0000

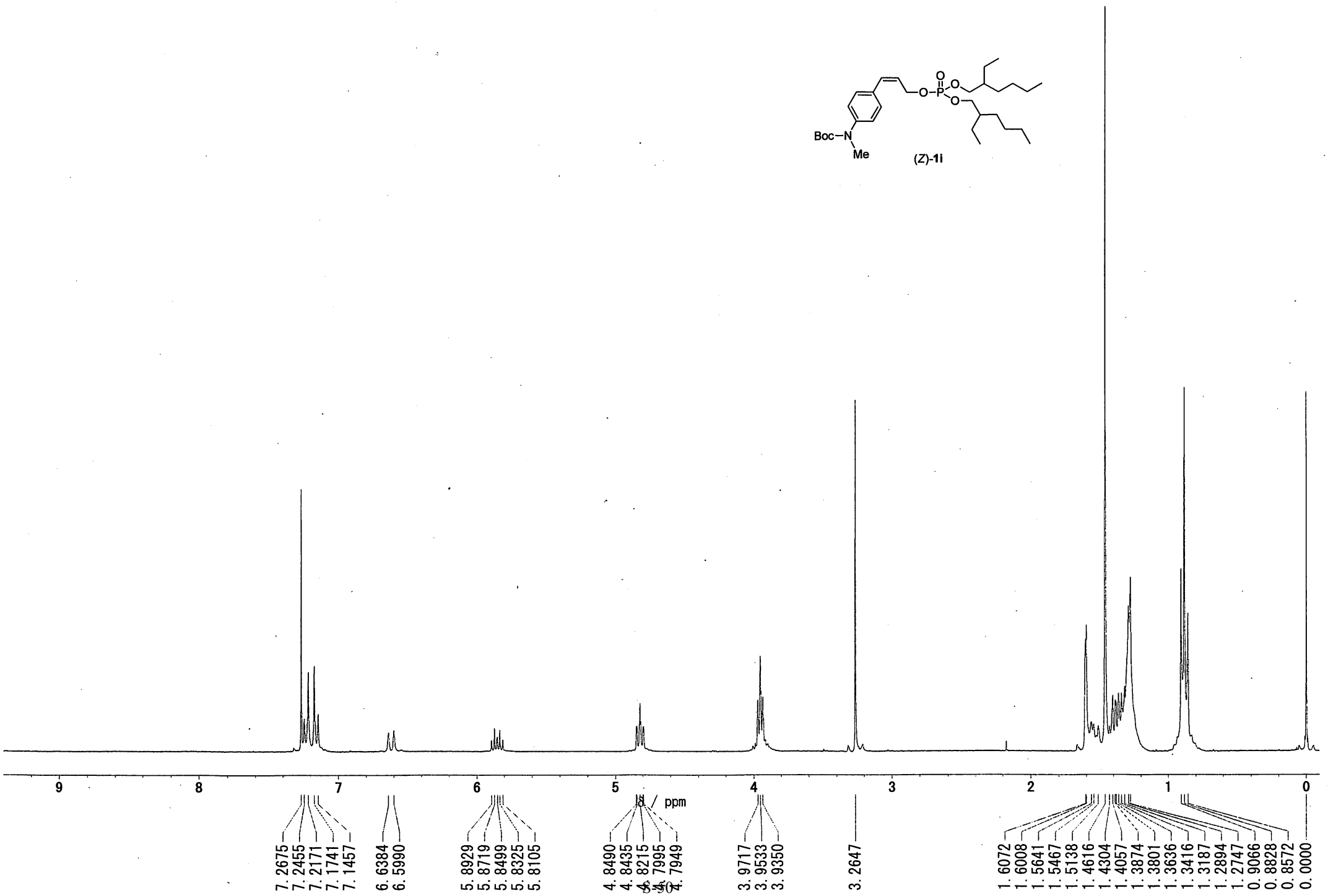

Me
O
O
P
O
O
(Z)-1f
180
160
140
120
100
80
60
40
20
0
δ / ppm

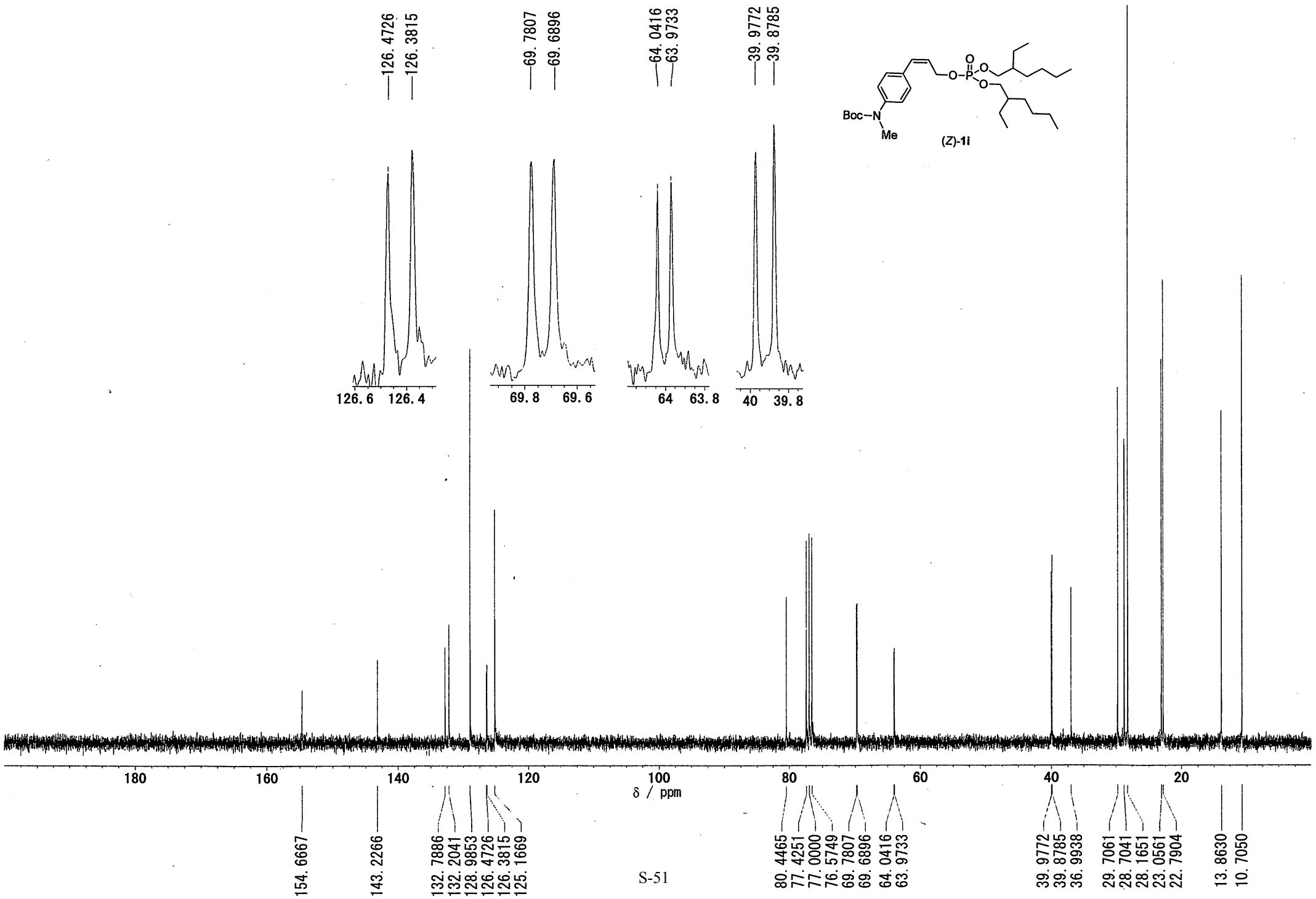
(Z)-1g
δ / ppm
7.6182
7.6127
7.6054
7.5990
7.5898
7.5852
7.5779
7.5193
7.4799
7.4744
7.4561
7.4515
7.4305
7.3902
7.3856
7.3810
7.3691
7.3618
7.3536
7.3371
7.2986
7.2711
7.2656
6.7162
6.6777
5.9442
5.9231
5.9021
5.8838
5.8618
4.9002
4.8947
4.8783
4.8728
4.8682
4.8517
4.8462
4.0147
3.9964
3.9790
3.9607
3.9414
3.9231
3.9039
2.1758
1.5660
1.5458
1.4762
1.4506
1.4295
1.4048
1.3855
1.3791
1.3617
1.3398
1.3169
1.2857
1.2702
0.9441
0.9231
0.9048
0.8800
0.8553
0.8141
0.0705
0.0110
0.0000
-0.0110


140.5545
140.5014
127.5050
127.1179
127.0344
126.7914
126.6928
69.7959
69.7123
39.9848
39.8937
23.0713
22.8056
(Z)-1g
δ / ppm
140.5545
140.5014
134.8686
132.4242
129.2510
128.8639
127.5050
127.1179
127.0344
126.7914
126.6928
77.4251
77.0000
76.5749
69.7959
69.7123
64.1024
64.0264
39.9848
39.8937
29.7213
28.7041
23.0713
22.8056
13.8630
10.7202

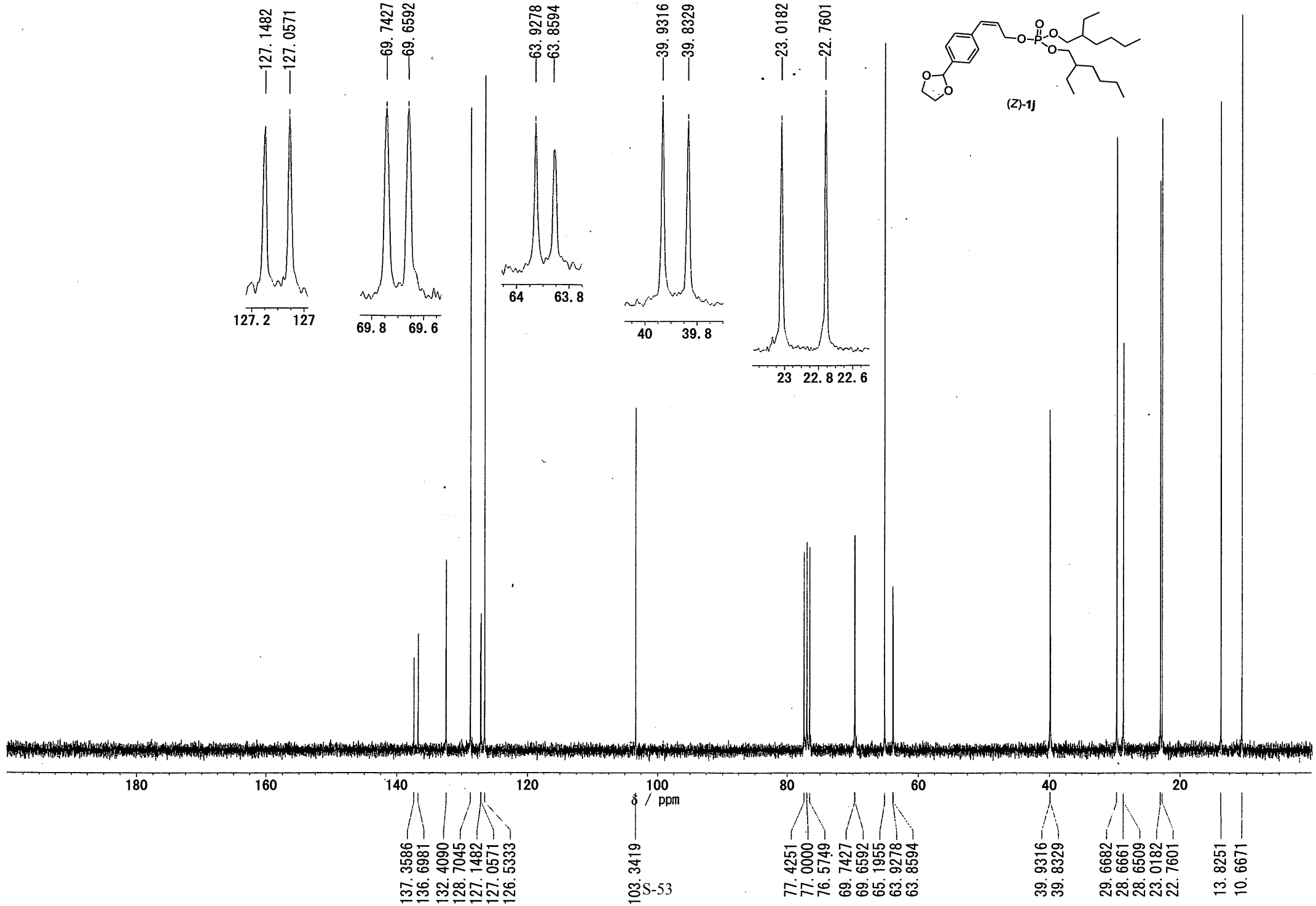

Me
Me
(Z)-1h
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2656
6.9259
6.8041
6.6155
6.5761
5.8581
5.8371
5.8160
5.7977
5.7766
4.8526
4.8471
4.8316
4.8261
4.8215
4.8050
4.7995
3.9973
3.9790
3.9625
3.9442
3.9268
3.9057
3.8865
2.3700
2.3132
2.2867
2.2583
1.6035
1.5980
1.5550
1.5357
1.4432
1.4231
1.3975
1.3782
1.3553
1.3324
1.3095
1.2812
1.2674
0.9020
0.8773
0.8526
0.0000

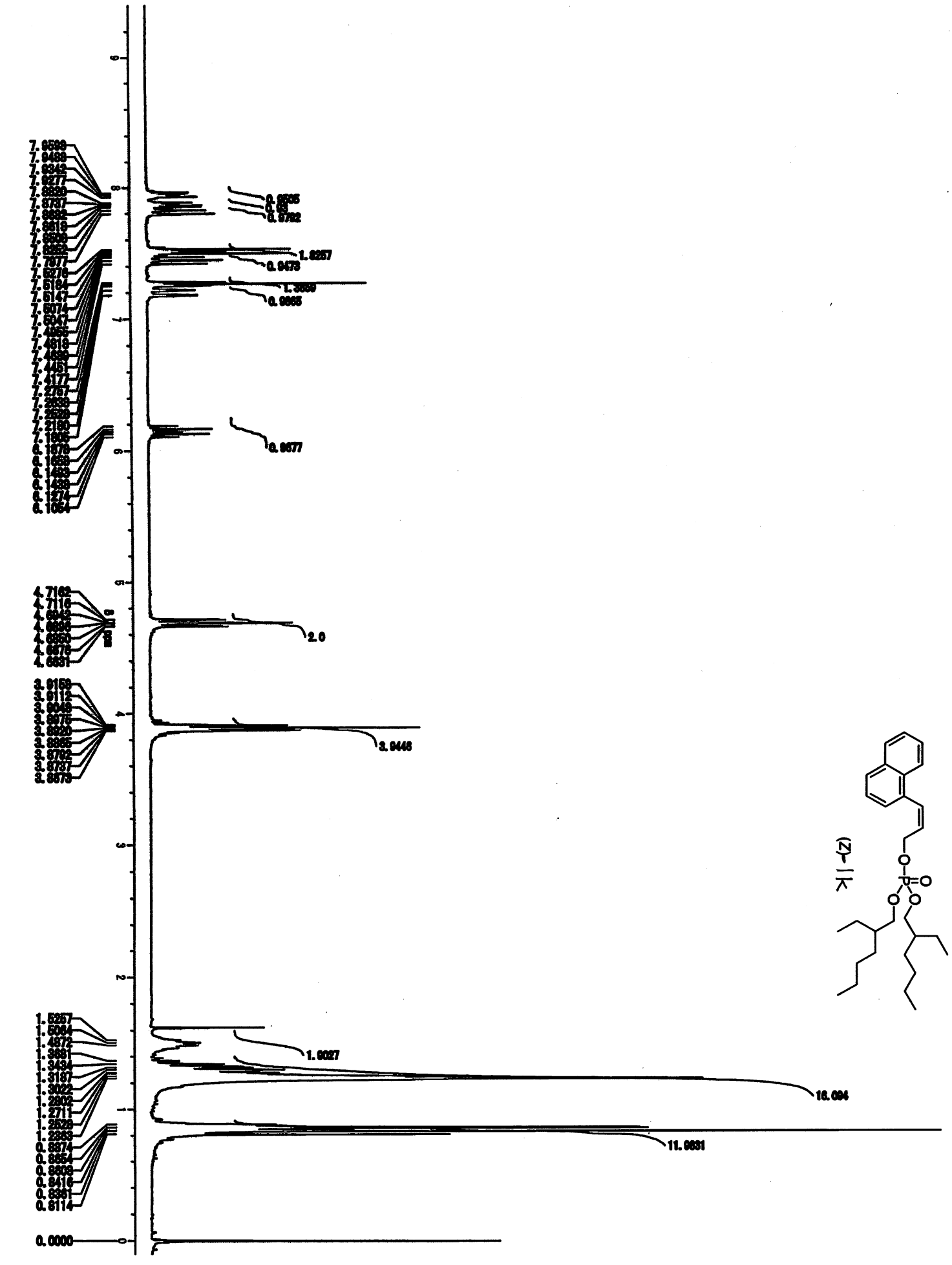

126.5561
126.3360
126.2373
69.7275
69.6440
64.1707
64.1024
39.9696
39.8709
28.7041
28.6889
Me
Me
(Z)-1h
126.6
126.4
126.2
69.8 69.7 69.6
64.2
64
40
39.8
28.7
δ / ppm
137.9203
135.8175
132.9328
132.9176
129.3421
126.5561
126.3360
126.2373
77.4251
77.0000
76.5749
69.7275
69.6440
64.1707
64.1024
39.9696
39.8709
29.7061
28.7041
28.6889
23.0561
22.7980
21.1203
13.8630
10.6975

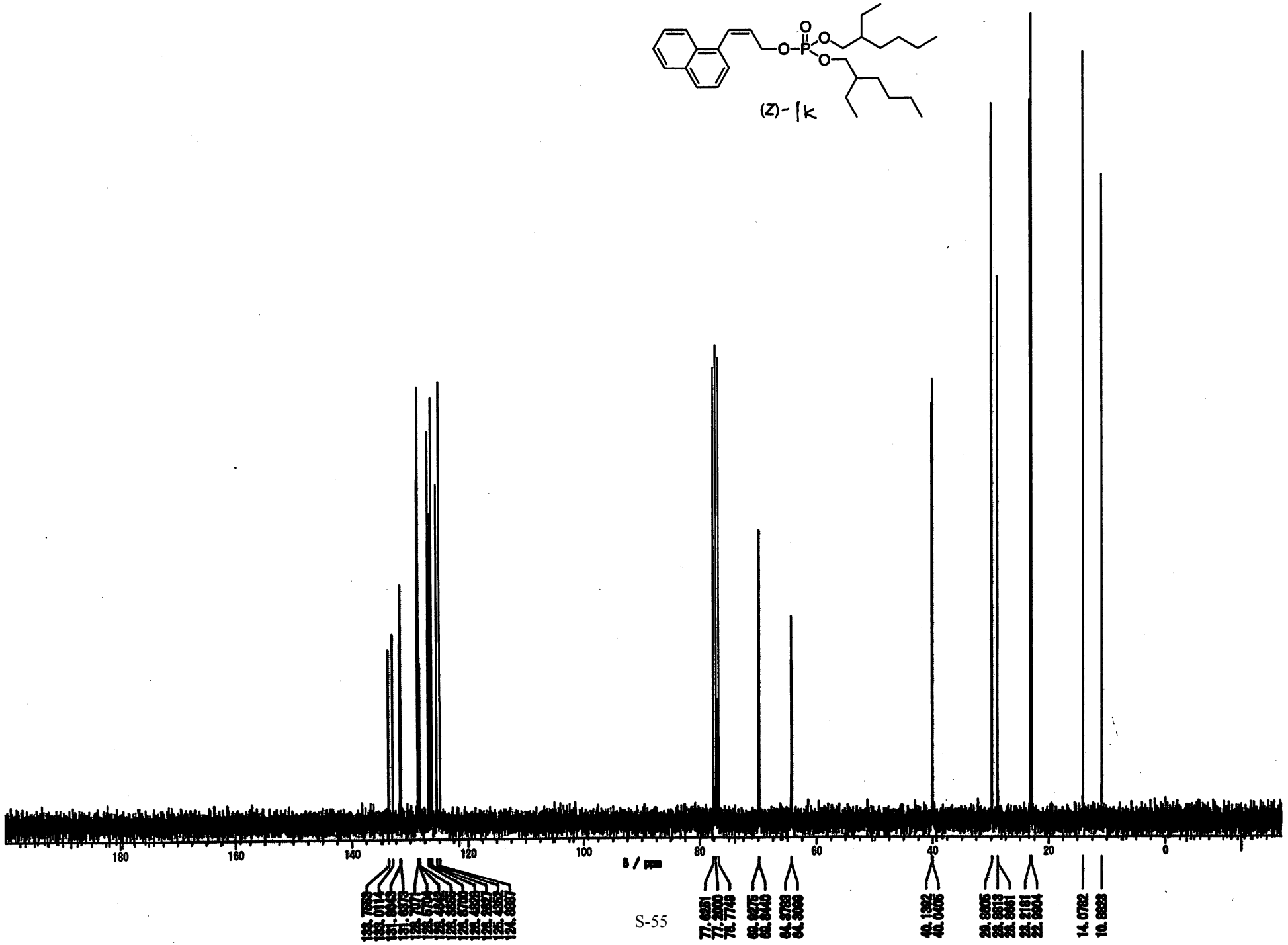

Boc–N
Me
(Z)-1i
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2675
7.2455
7.2171
7.1741
7.1457
6.6384
6.5990
5.8929
5.8719
5.8499
5.8325
5.8105
4.8490
4.8435
4.8215
4.7995
4.7949
3.9717
3.9533
3.9350
3.2647
1.6072
1.6008
1.5641
1.5467
1.5138
1.4616
1.4304
1.4057
1.3874
1.3801
1.3636
1.3416
1.3187
1.2894
1.2747
0.9066
0.8828
0.8572
0.0000

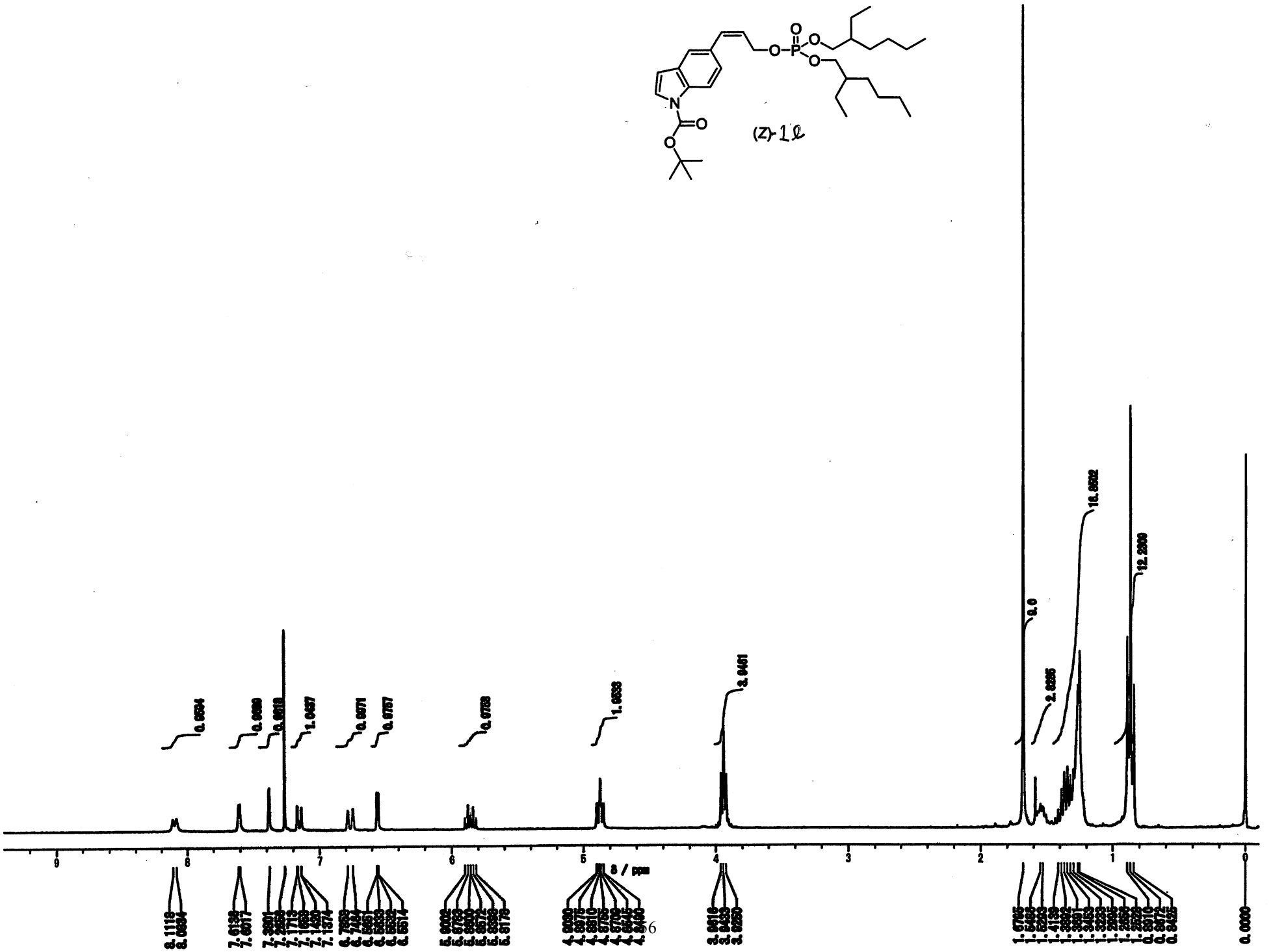

126.4726
126.3815
69.7807
69.6896
64.0416
63.9733
39.9772
39.8785
Boc–N
Me
(Z)-1i
126.6
126.4
69.8
69.6
64
63.8
40
39.8
180
160
140
120
100
80
60
40
20
δ / ppm
154.6667
143.2266
132.7886
132.2041
128.9853
126.4726
126.3815
125.1669
80.4465
77.4251
77.0000
76.5749
69.7807
69.6896
64.0416
63.9733
39.9772
39.8785
36.9938
29.7061
28.7041
28.1651
23.0561
22.7904
13.8630
10.7050

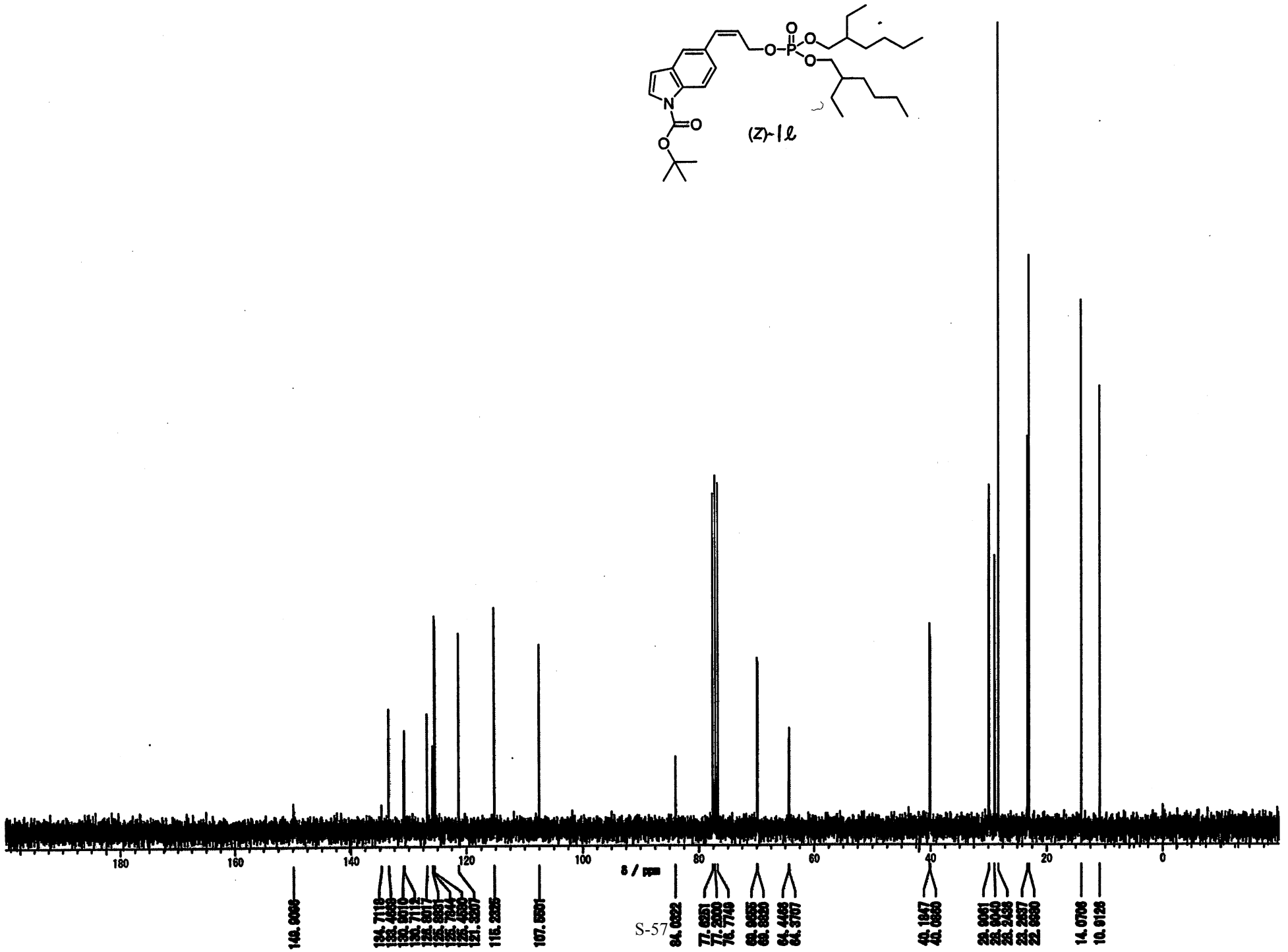
(Z)-1j
δ1 / ppm
9
8
7
6
5
4
3
2
1
0
7.4836
7.4561
7.2675
7.2327
7.2052
6.6841
6.6448
5.9341
5.9131
5.8911
5.8737
5.8517
5.8215
4.8288
4.8233
4.8068
4.8023
4.7968
4.7803
4.7748
4.1603
4.1383
4.1337
4.1283
4.1218
4.1136
4.0962
4.0834
4.0660
4.0587
4.0522
4.0467
4.0403
4.0202
4.0010
3.9817
3.9634
3.9579
3.9451
3.9396
3.9259
3.9204
3.9066
3.8874
1.6273
1.5595
1.5394
1.4442
1.4231
1.3984
1.3801
1.3727
1.3562
1.3343
1.3114
1.2848
1.2711
0.9029
0.8837
0.8782
0.8608
0.8535
0.8214
0.0000

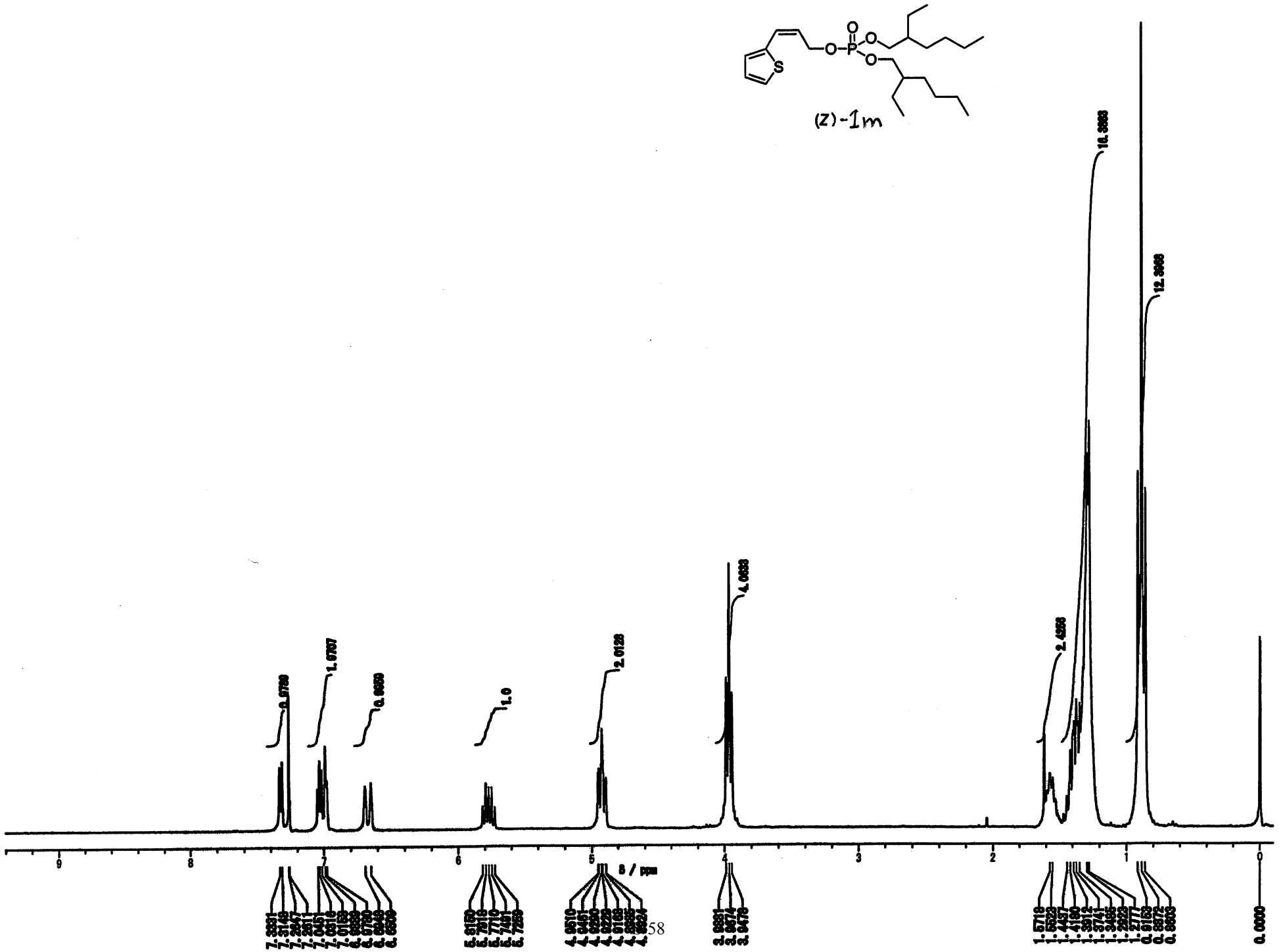

127.1482
127.0571
69.7427
69.6592
63.9278
63.8594
39.9316
39.8329
23.0182
22.7601
(Z)-1j
127.2
127
69.8
69.6
64
63.8
40
39.8
23
22.8
22.6
180
160
140
120
100
80
60
40
20
δ / ppm
137.3586
136.6981
132.4090
128.7045
127.1482
127.0571
126.5333
103.3419
77.4251
77.0000
76.5749
69.7427
69.6592
65.1955
63.9278
63.8594
39.9316
39.8329
29.6682
28.6661
28.6509
23.0182
22.7601
13.8251
10.6671

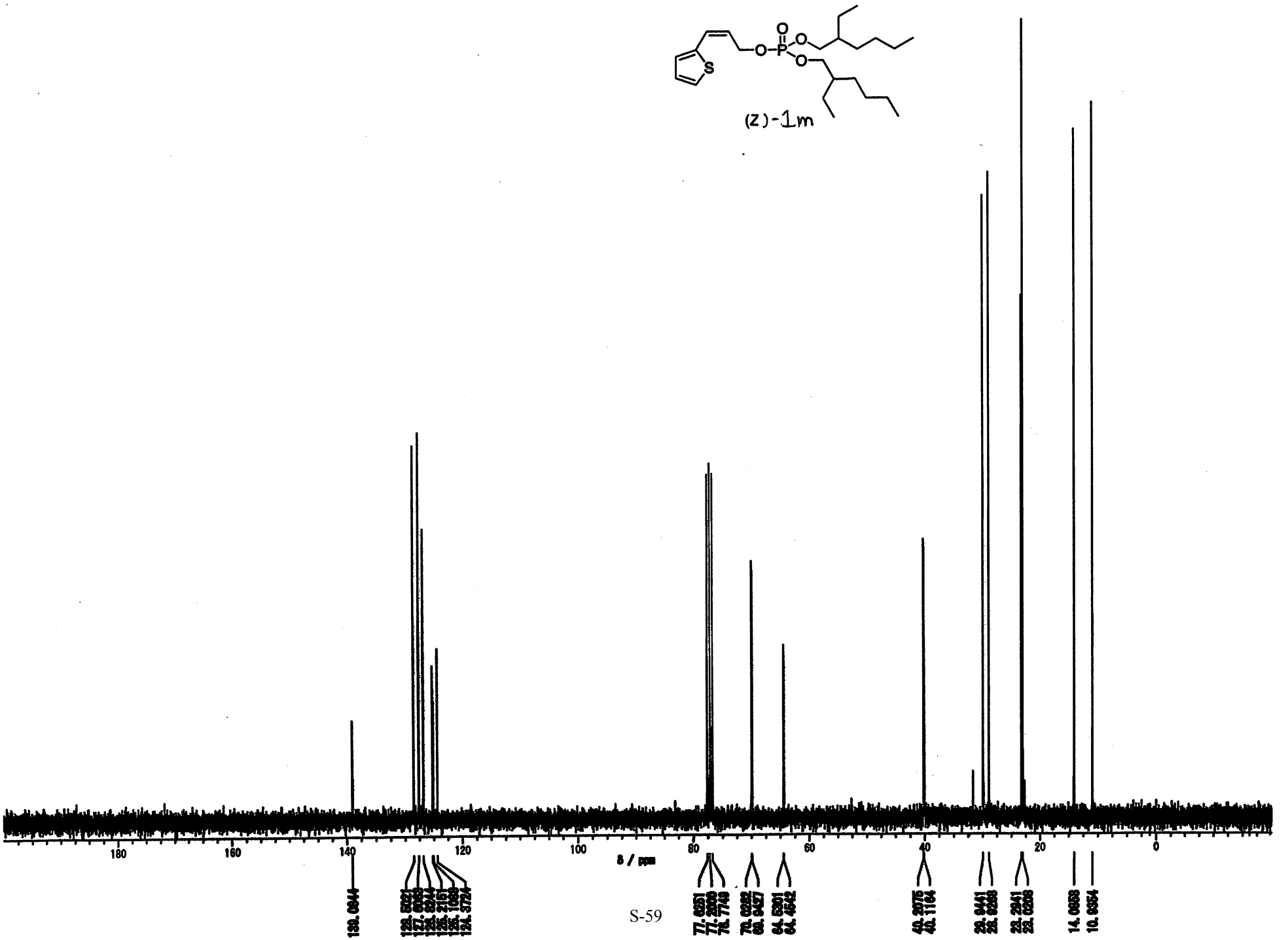

(Z)-1k

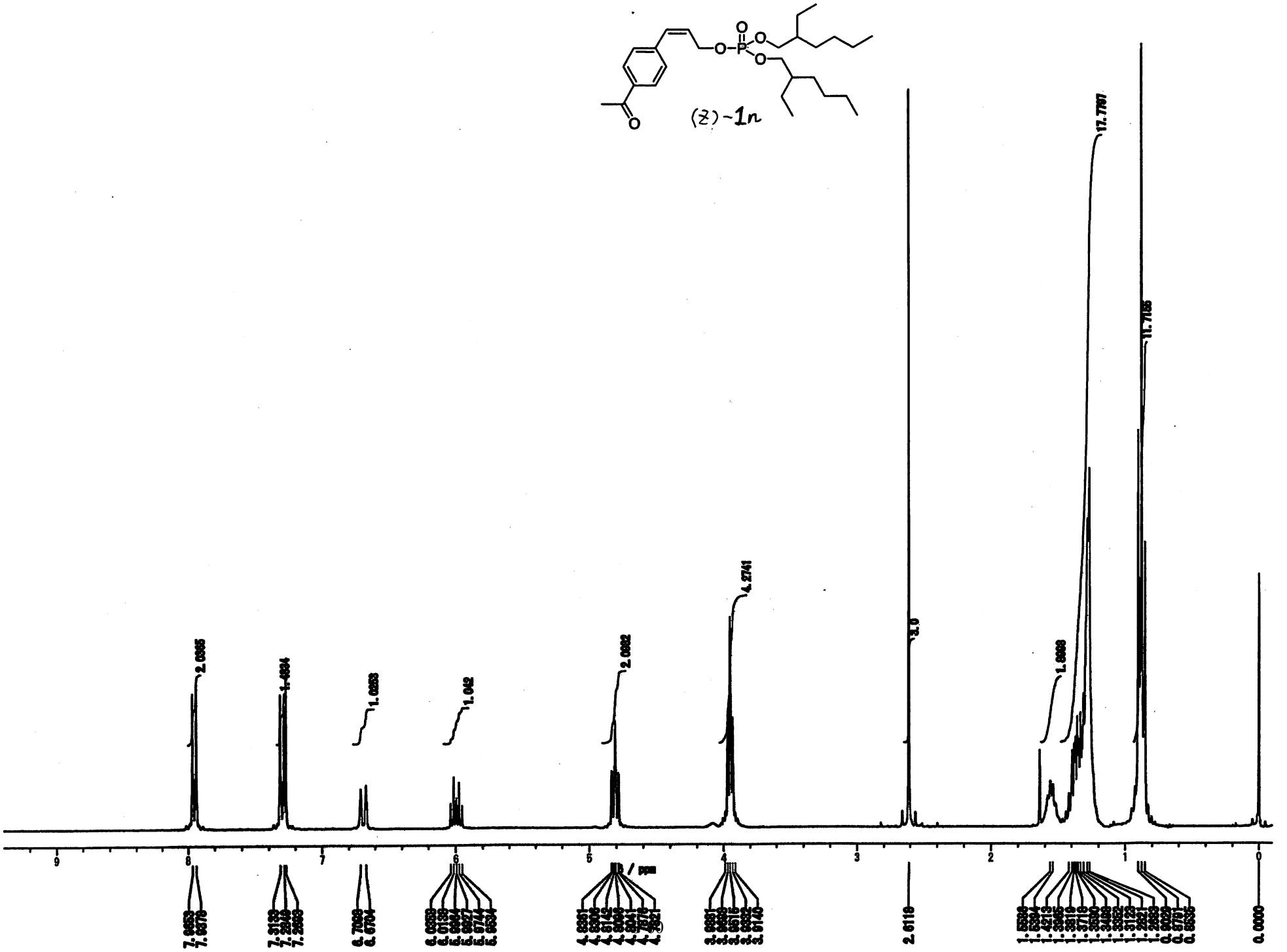

(Z)-1k
180
160
140
120
100
δ / ppm
80
60
40
20
0
77.6351
77.2000
76.7749
68.9275
68.8440
64.3783
64.3059
40.1392
40.0405
29.8805
29.8513
29.8351
23.2161
22.6904
14.0782
10.8823

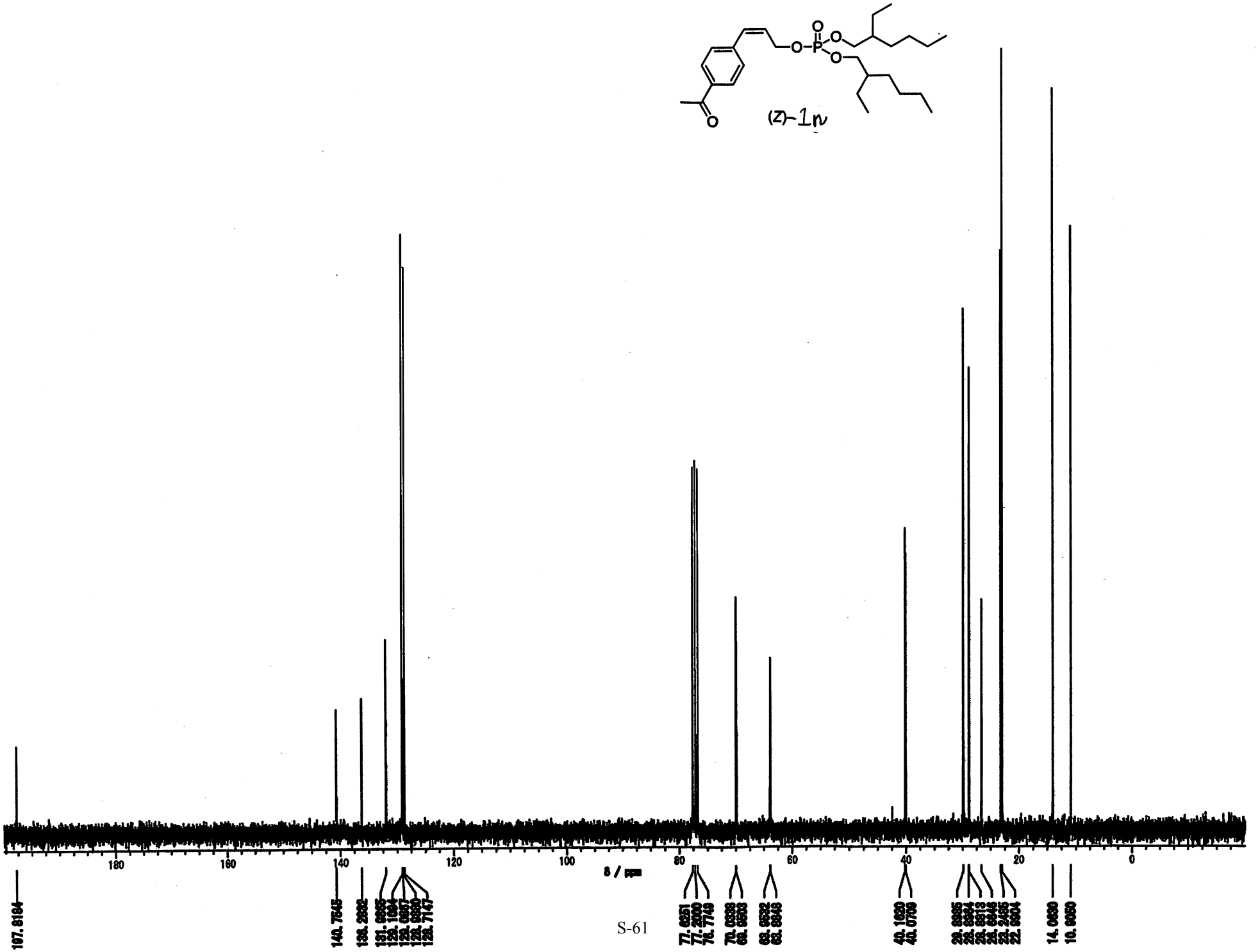

(Z)-1l
δ / ppm

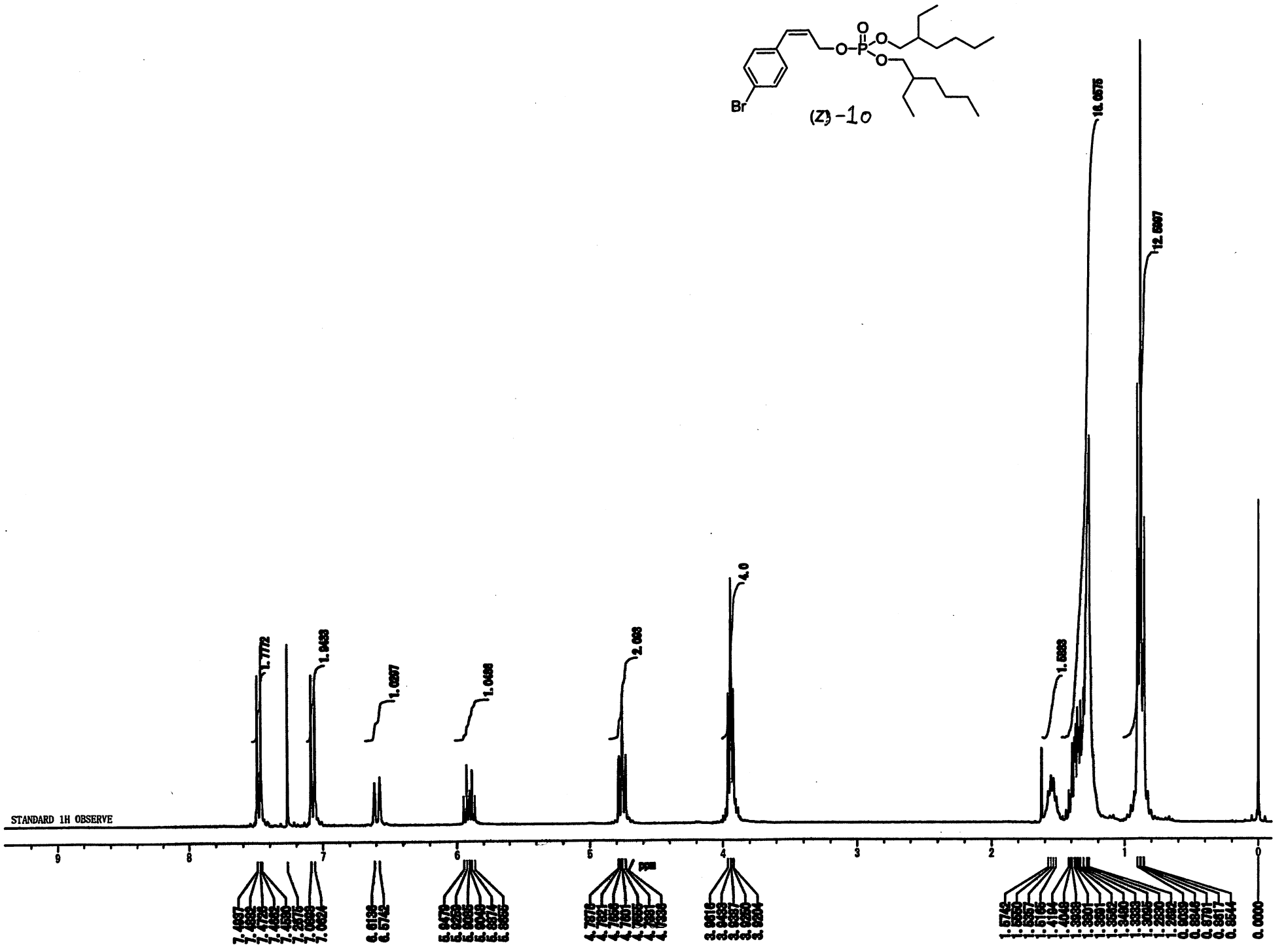

(Z)-1ℓ
δ / ppm

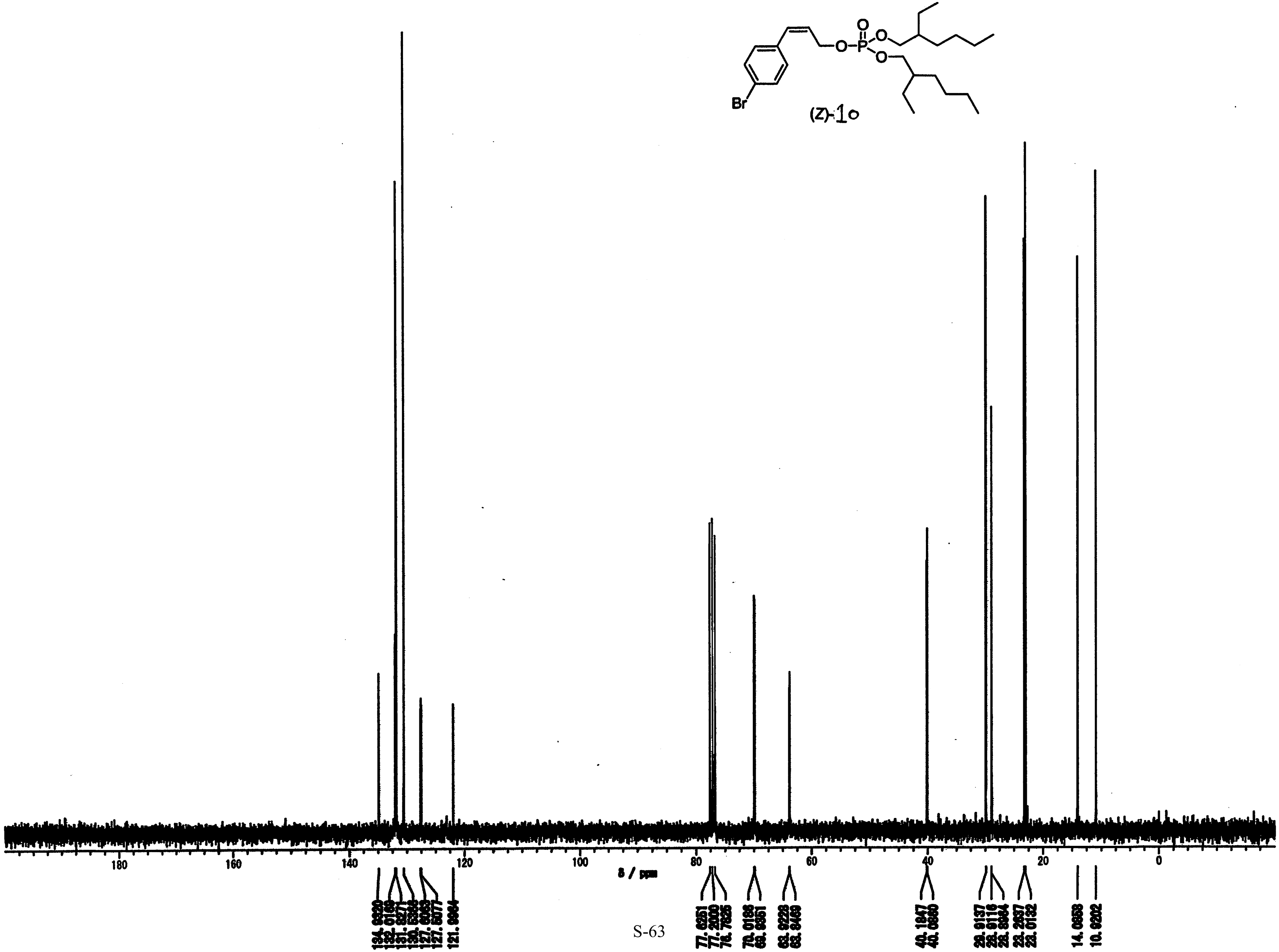

(Z)-1m
δ / ppm

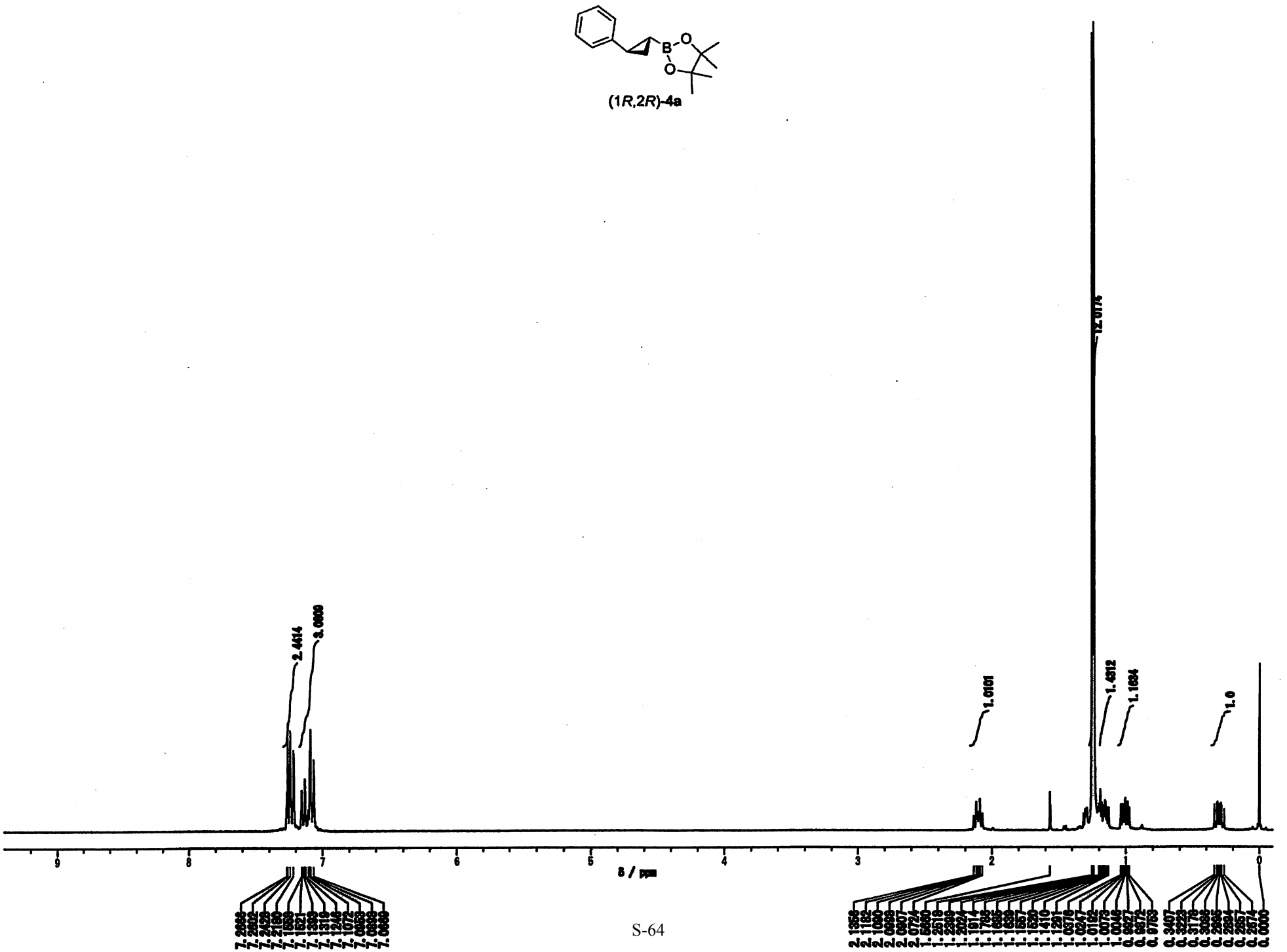

(z)-1m
δ / ppm

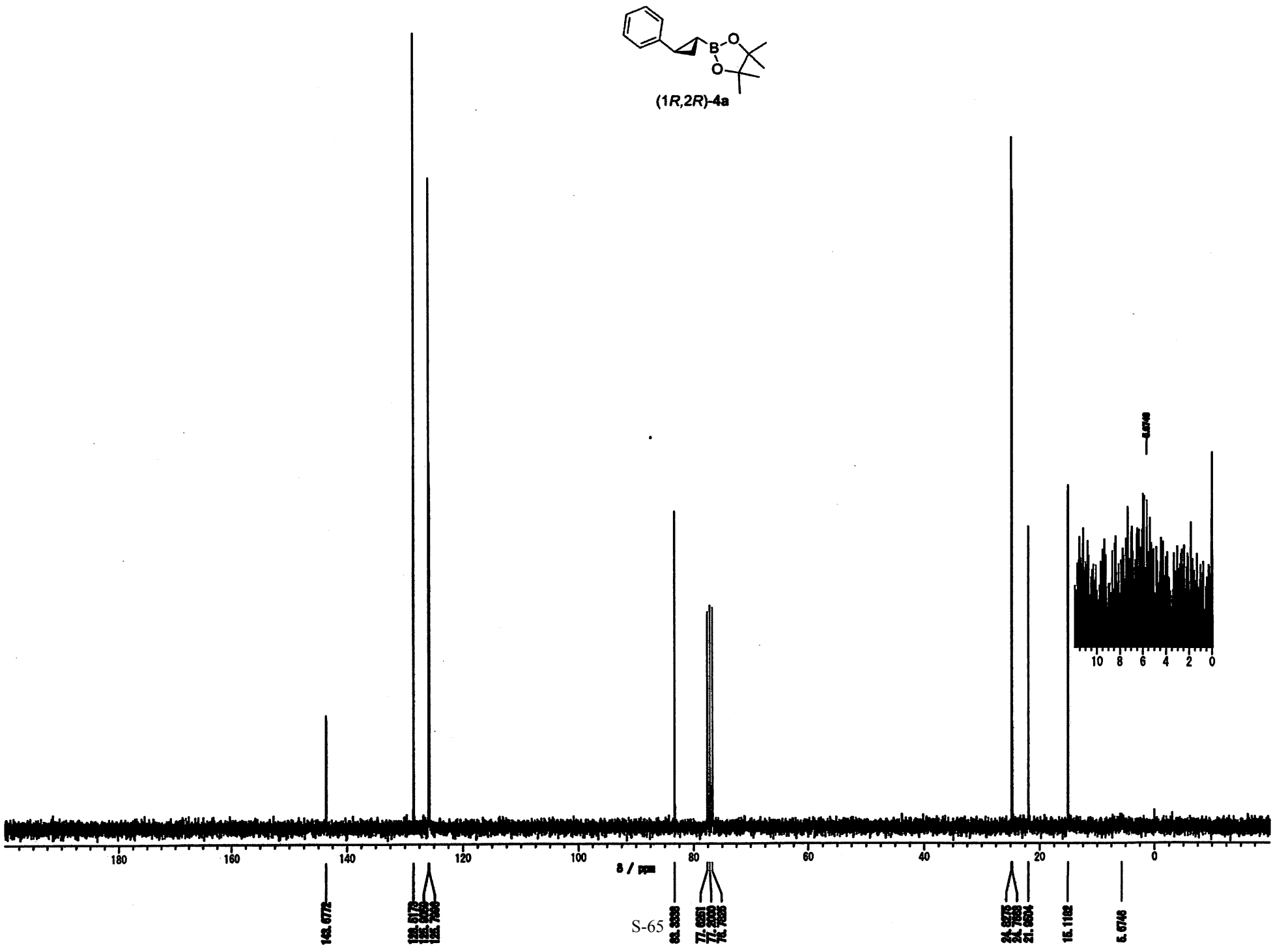

(Z)-1n
2.0065
1.4834
1.0263
1.042
2.0032
4.2741
3.0
1.9003
17.7997
11.7185
9
8
7
6
5
4
3
2
1
0
f1 / ppm
2.6110
0.0000

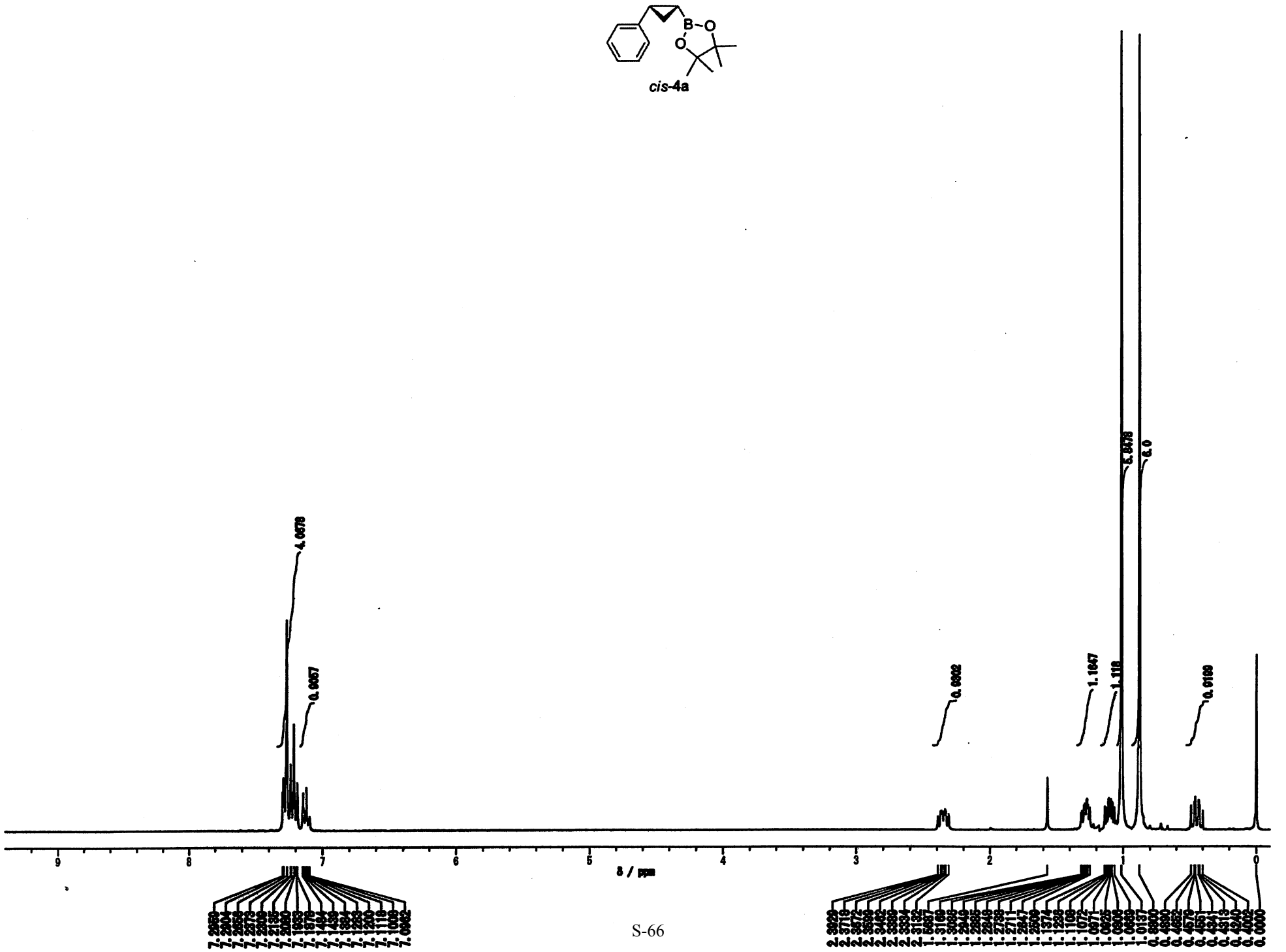

(Z)-1n
δ / ppm

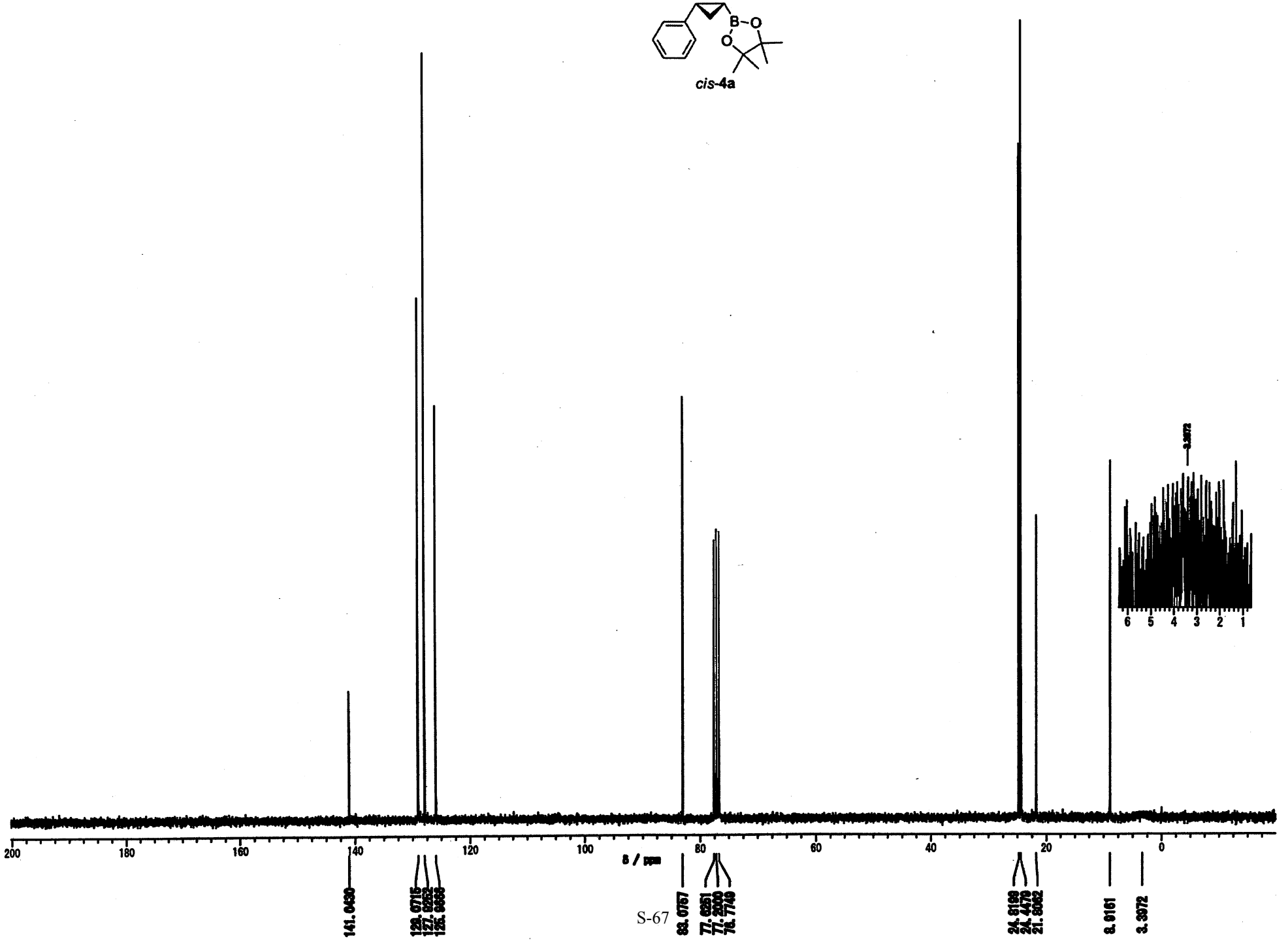

Br
(Z)-1o
STANDARD 1H OBSERVE
16.0675
12.5997
4.0
2.003
1.8433
1.7772
1.0297
1.0088
1.6883
PPM

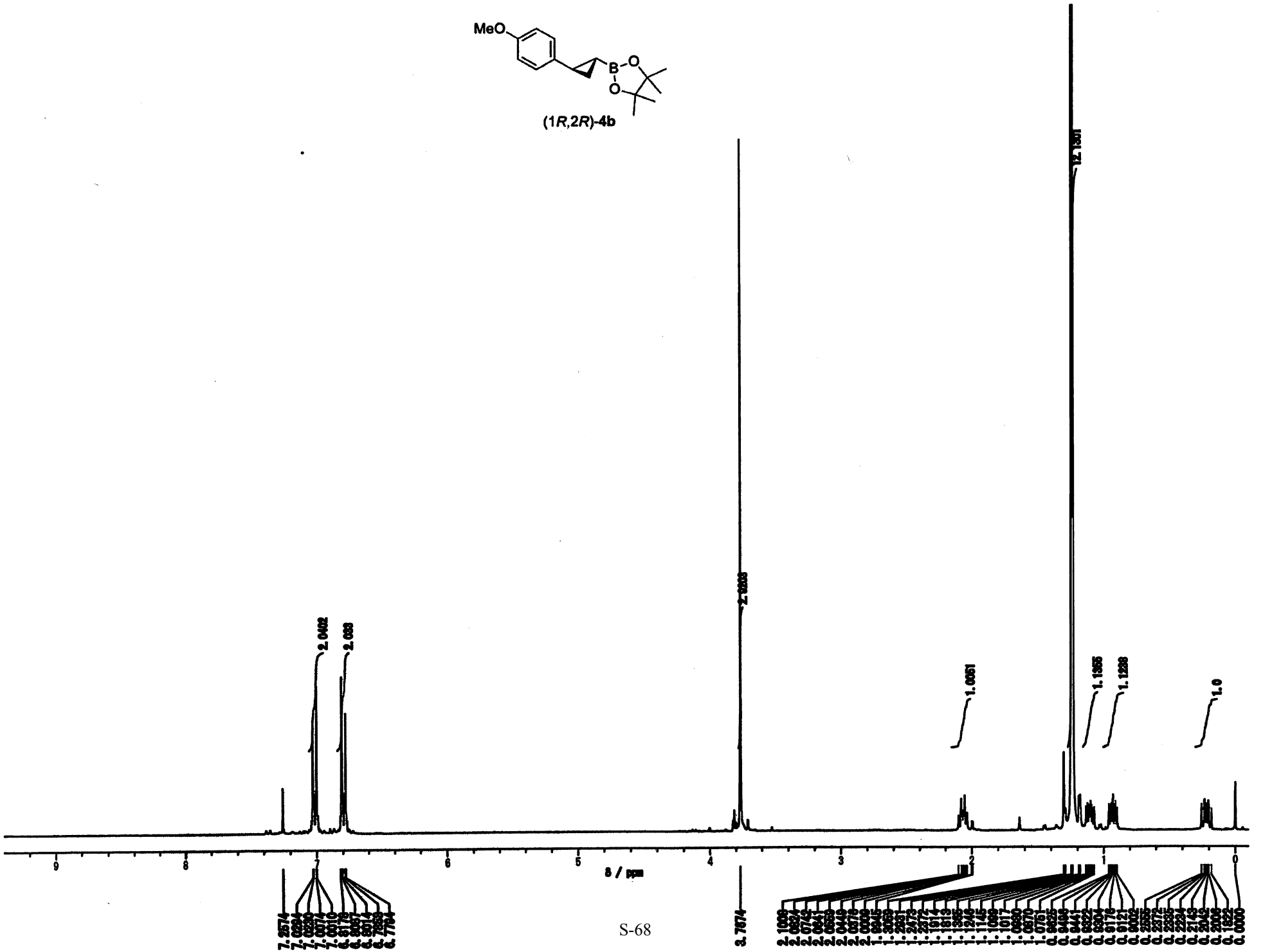

Br
O
P
(Z)-10
180
160
140
120
100
80
60
40
20
0
δ / ppm
10.9202

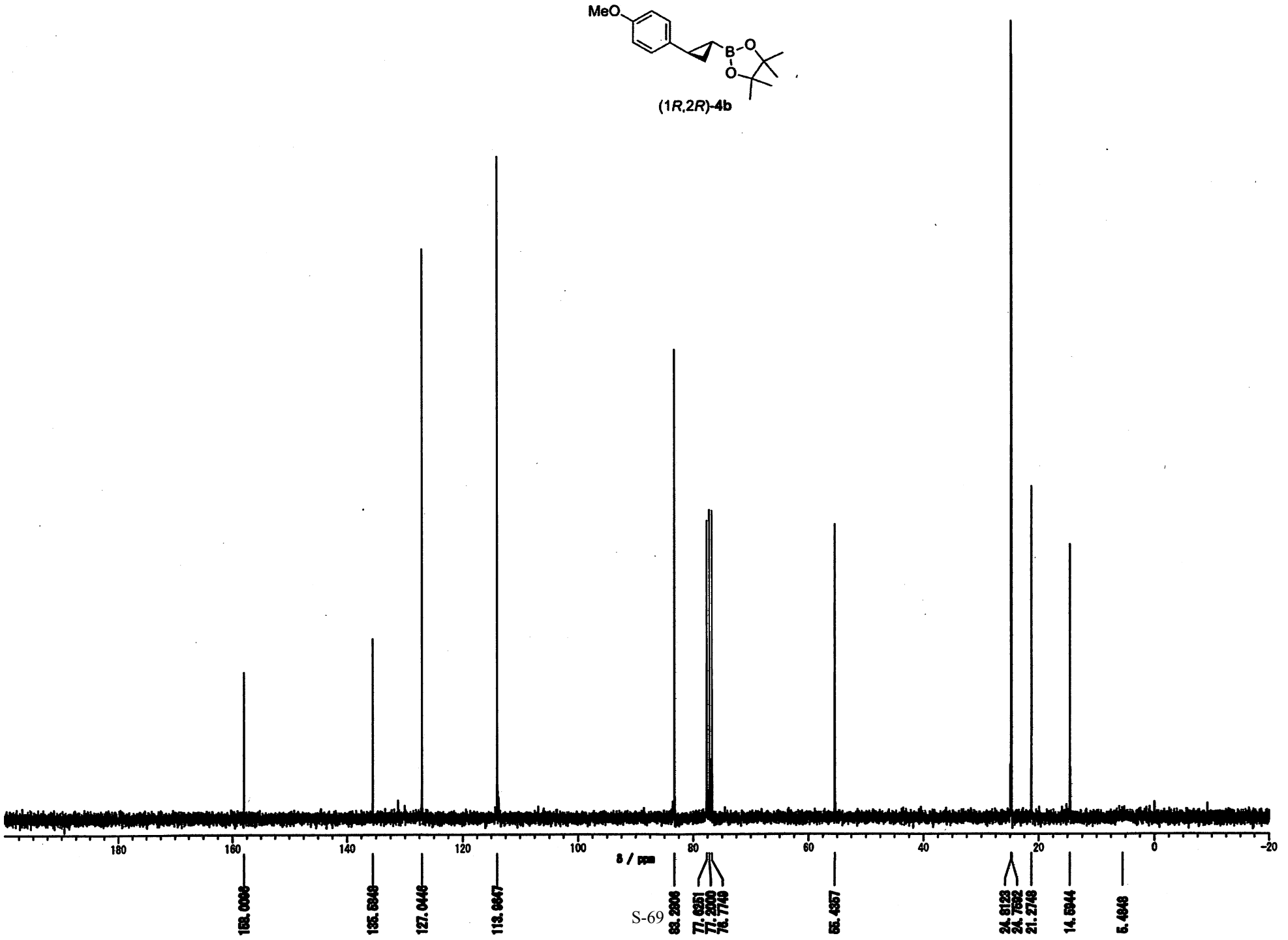

(1R,2R)-4a
2.4414
3.0000
12.0174
1.0101
1.4312
1.1694
1.0
δ / ppm

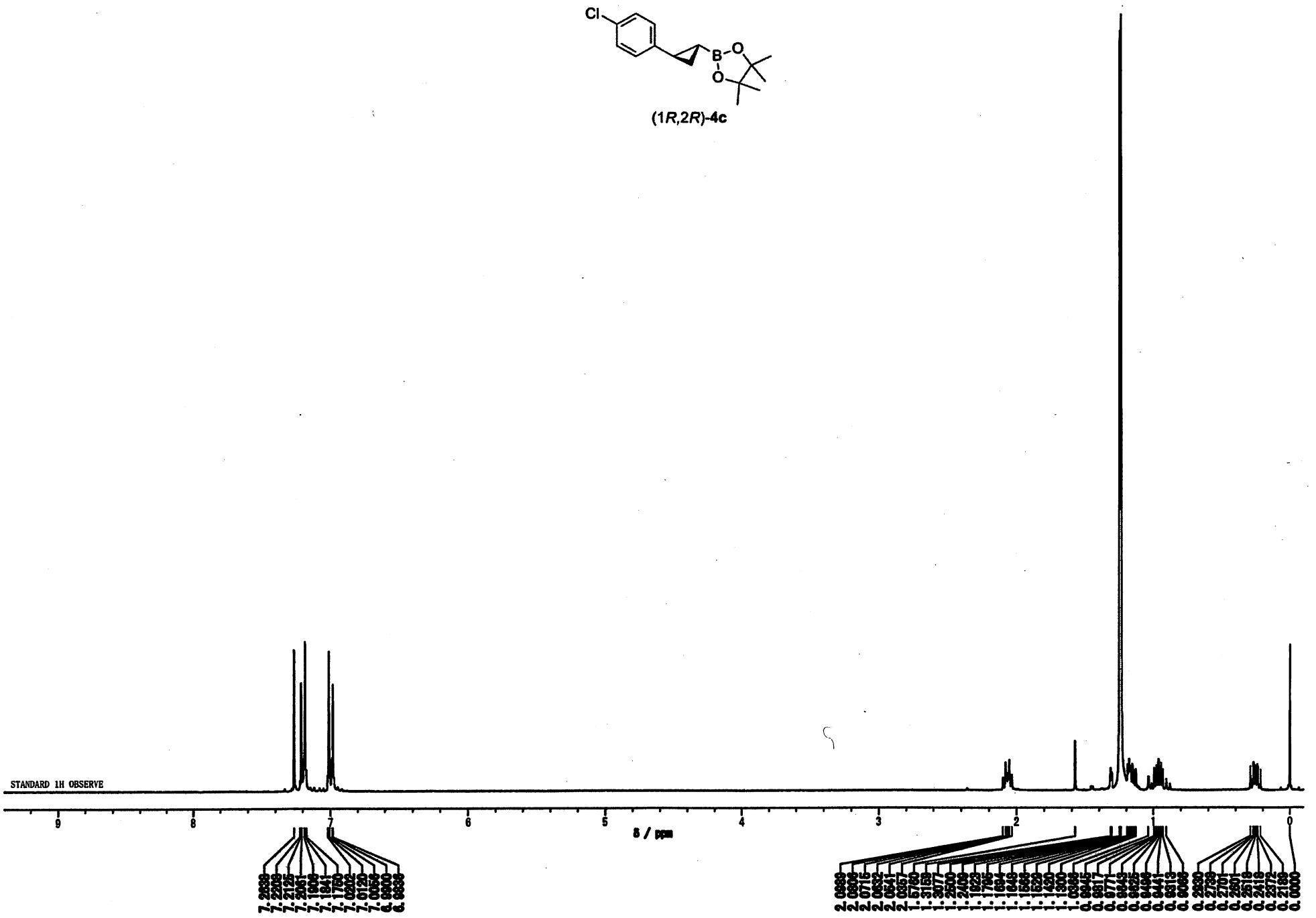

(1R,2R)-4a
B
O
O
180
160
140
120
100
80
60
40
20
0
δ / ppm
10 8 6 4 2 0

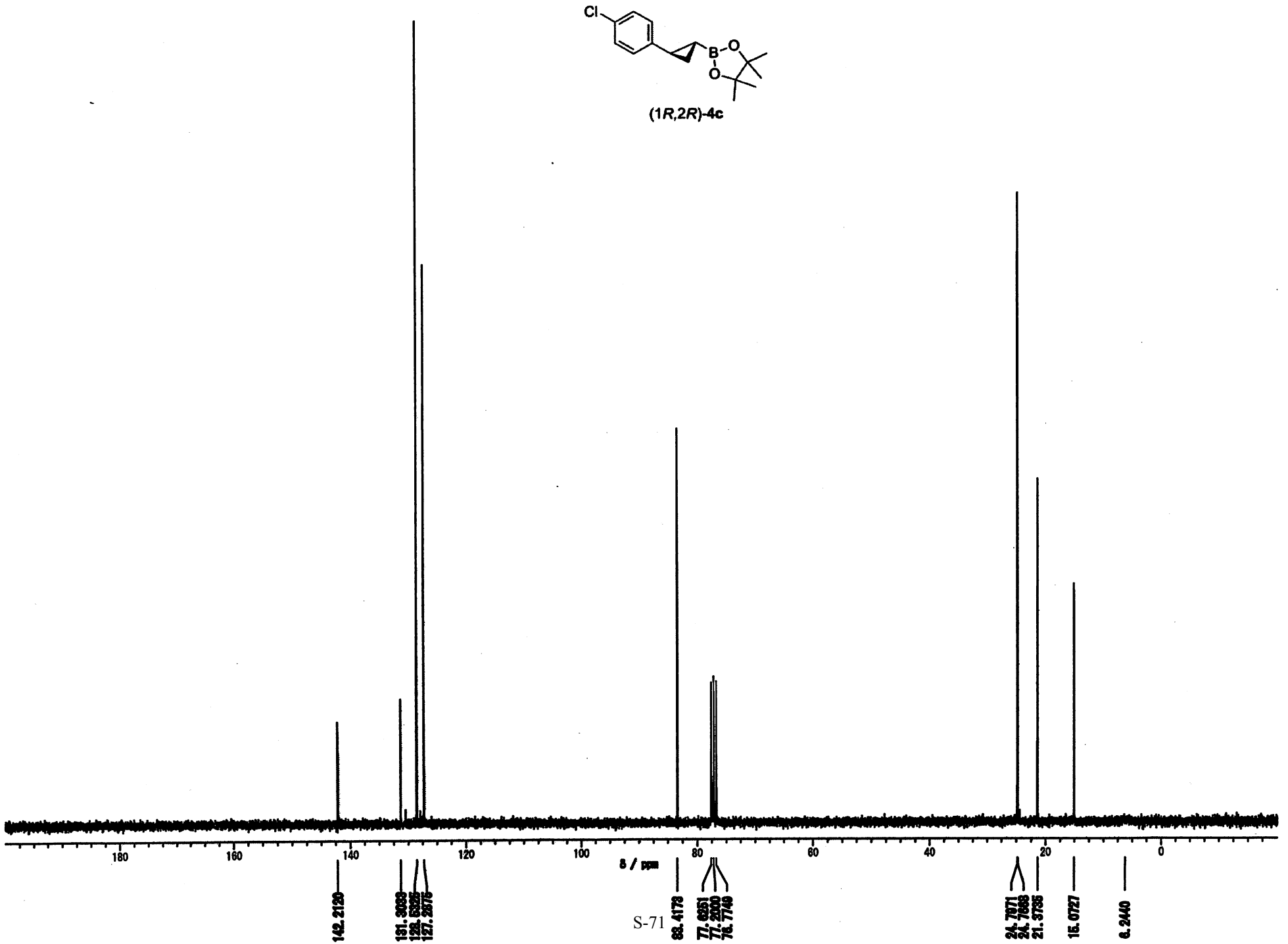

cis-4a
4.0578
2.0057
0.9802
1.1847
1.118
5.8478
6.0
0.9199
9
8
7
6
5
4
3
2
1
0
δ / ppm

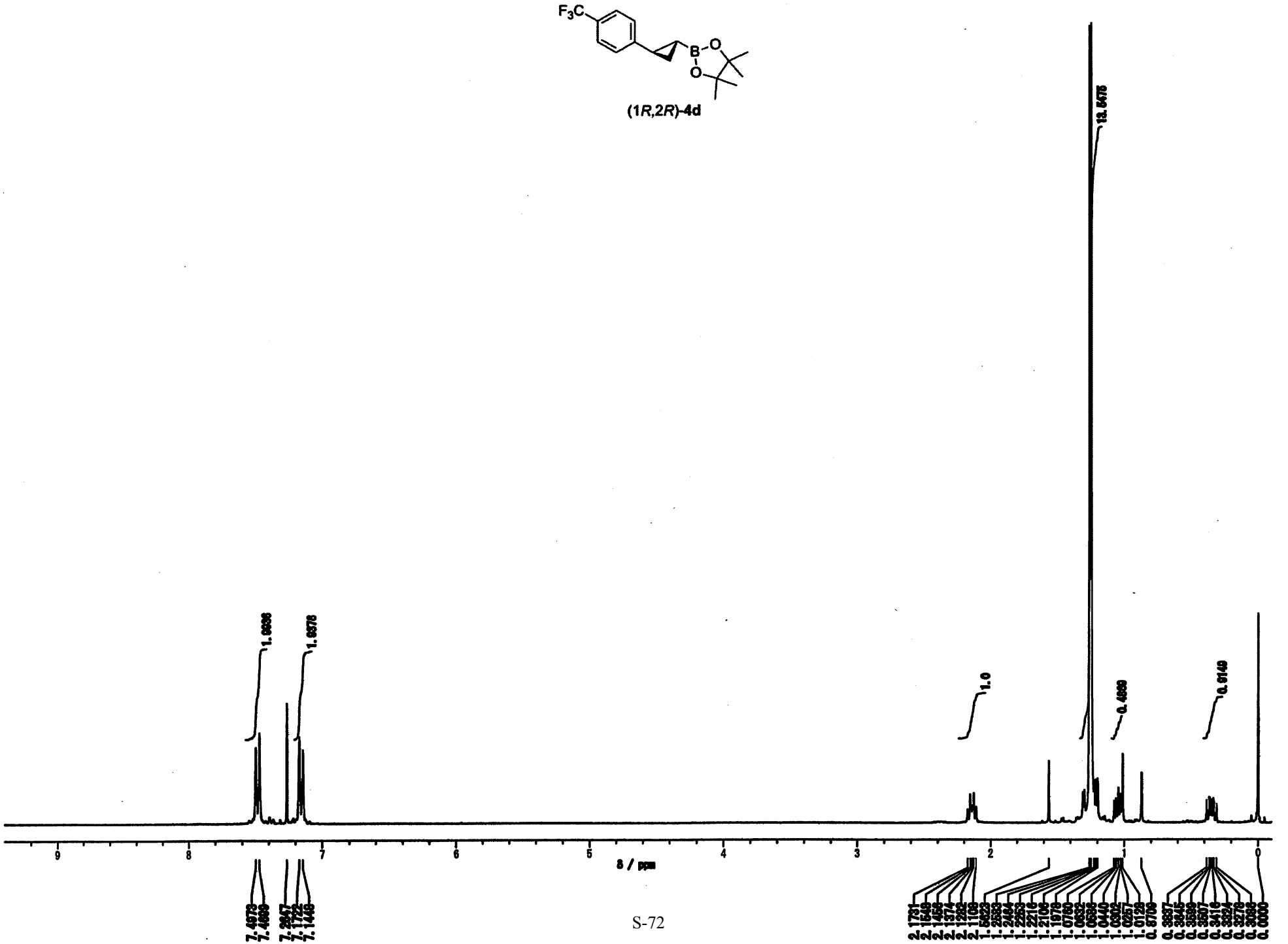

cis-4a
200
180
160
140
120
100
δ / ppm
80
60
40
20
0
6
5
4
3
2
1
141.0430
129.0715
127.9252
125.9668
83.0767
77.6281
77.2000
76.7748
24.8199
24.4479
21.8062
8.9161
3.3972

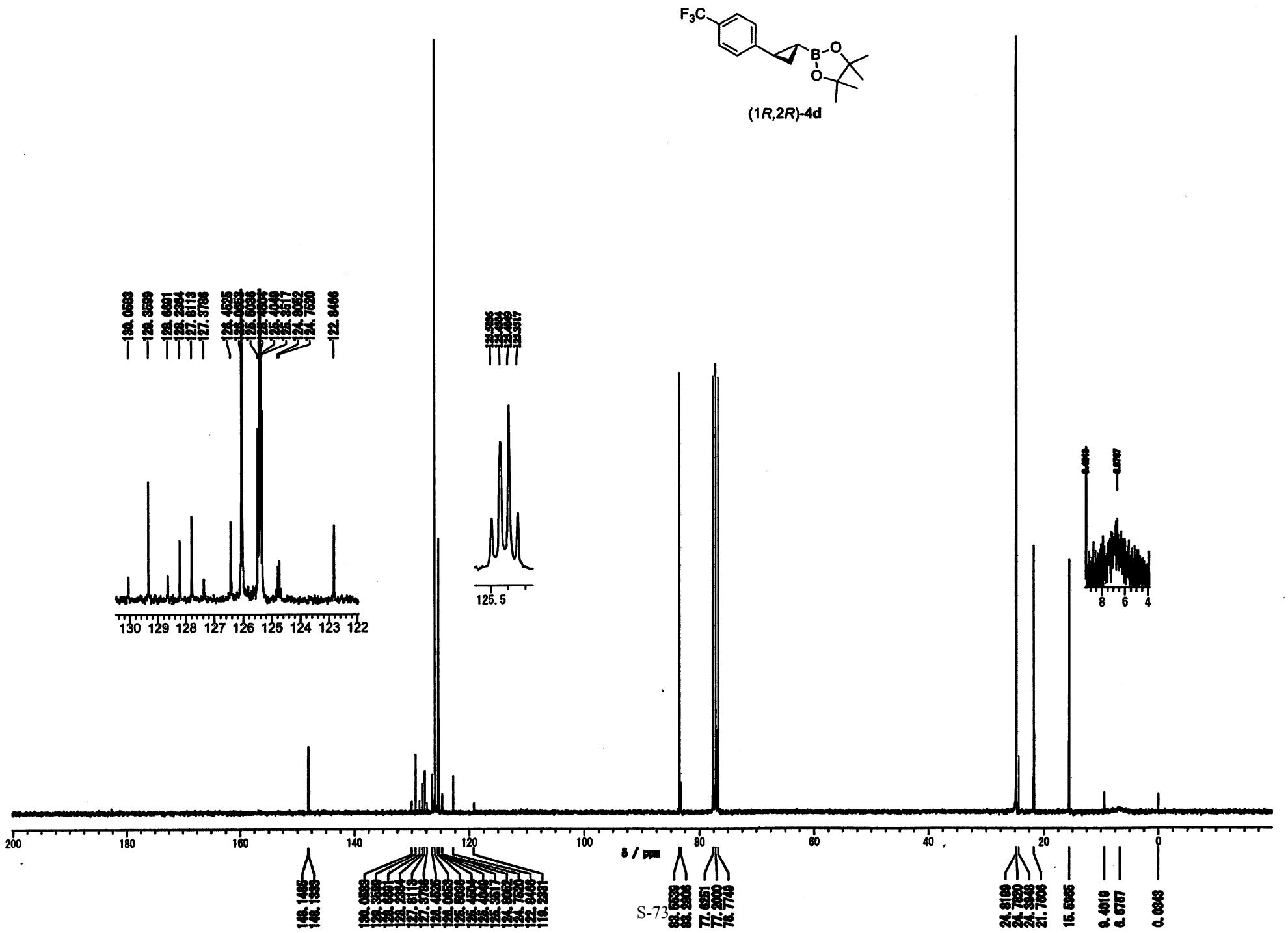

MeO
B
O
O
(1R,2R)-4b
2.0402
2.0000
1.0051
1.1365
1.1228
1.0
δ / ppm

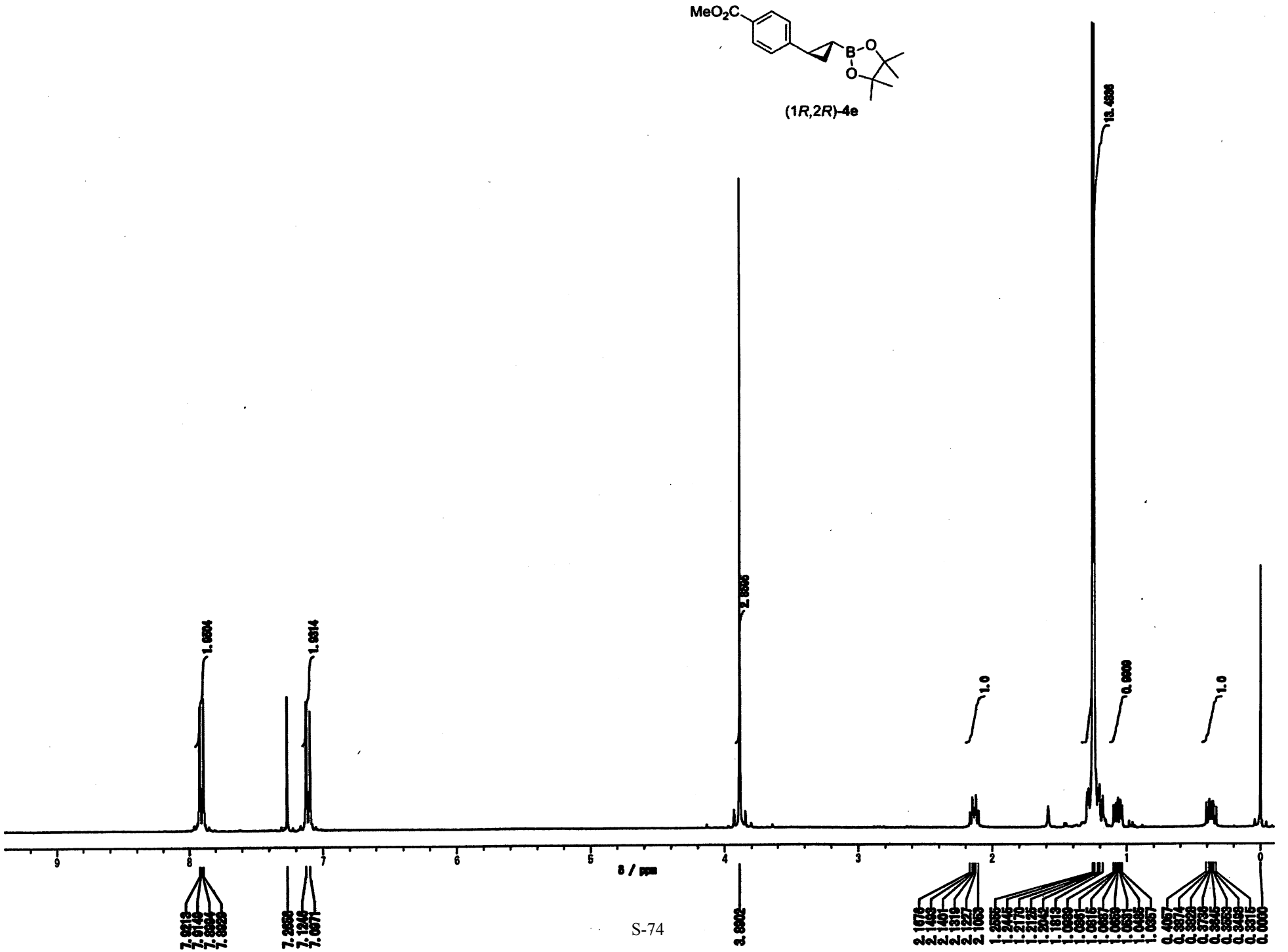

MeO
B
O
O
(1R,2R)-4b
180
160
140
120
100
80
60
40
20
0
-20
δ / ppm
163.0066
135.5848
127.0446
113.9847
83.2806
77.6251
77.2000
76.7749
55.4357
24.8123
24.7632
21.2748
14.6944
5.4948

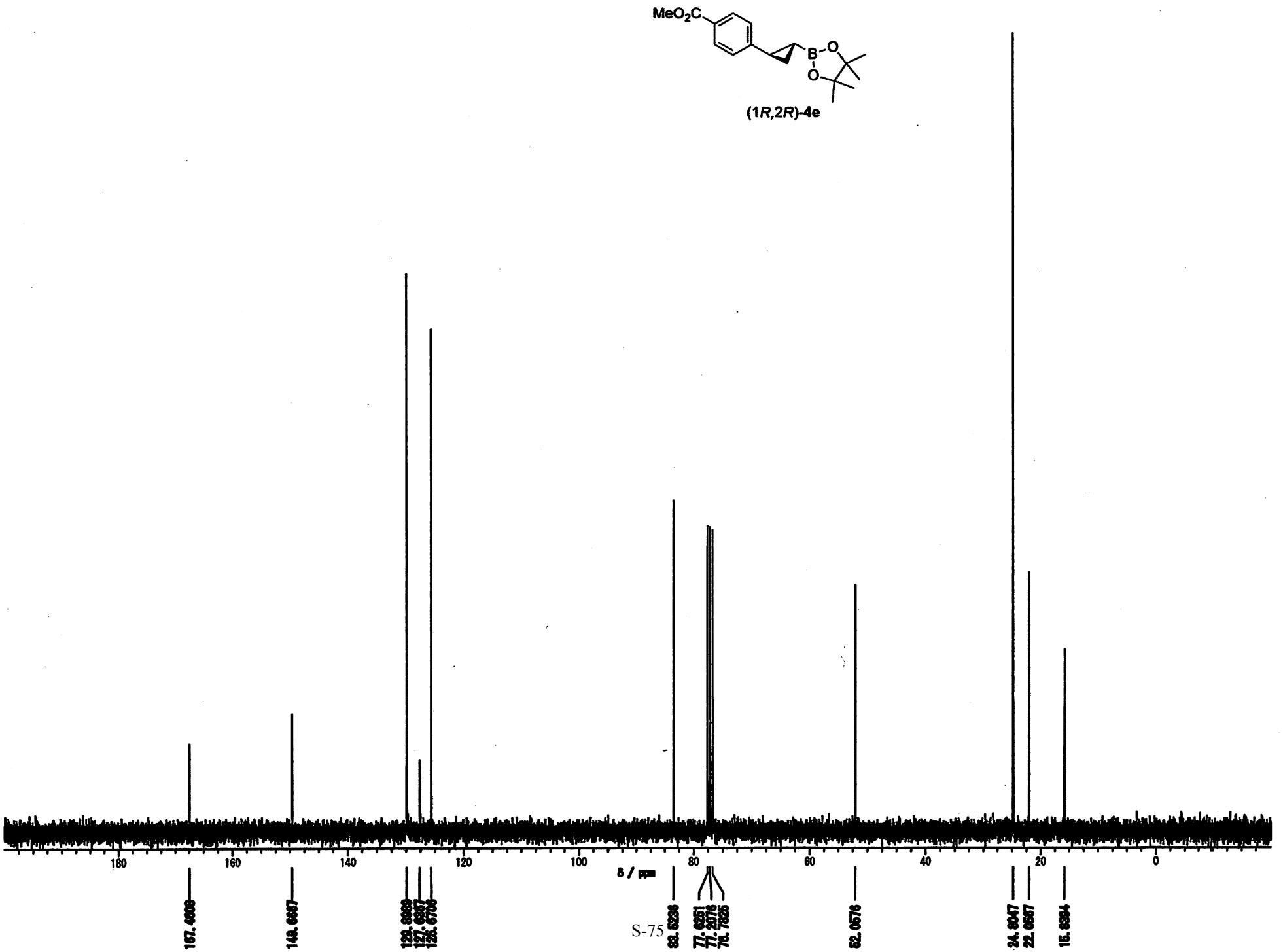

Cl
B
O
O
(1R,2R)-4c
STANDARD 1H OBSERVE
9
8
7
6
5
4
3
2
1
0
δ / ppm

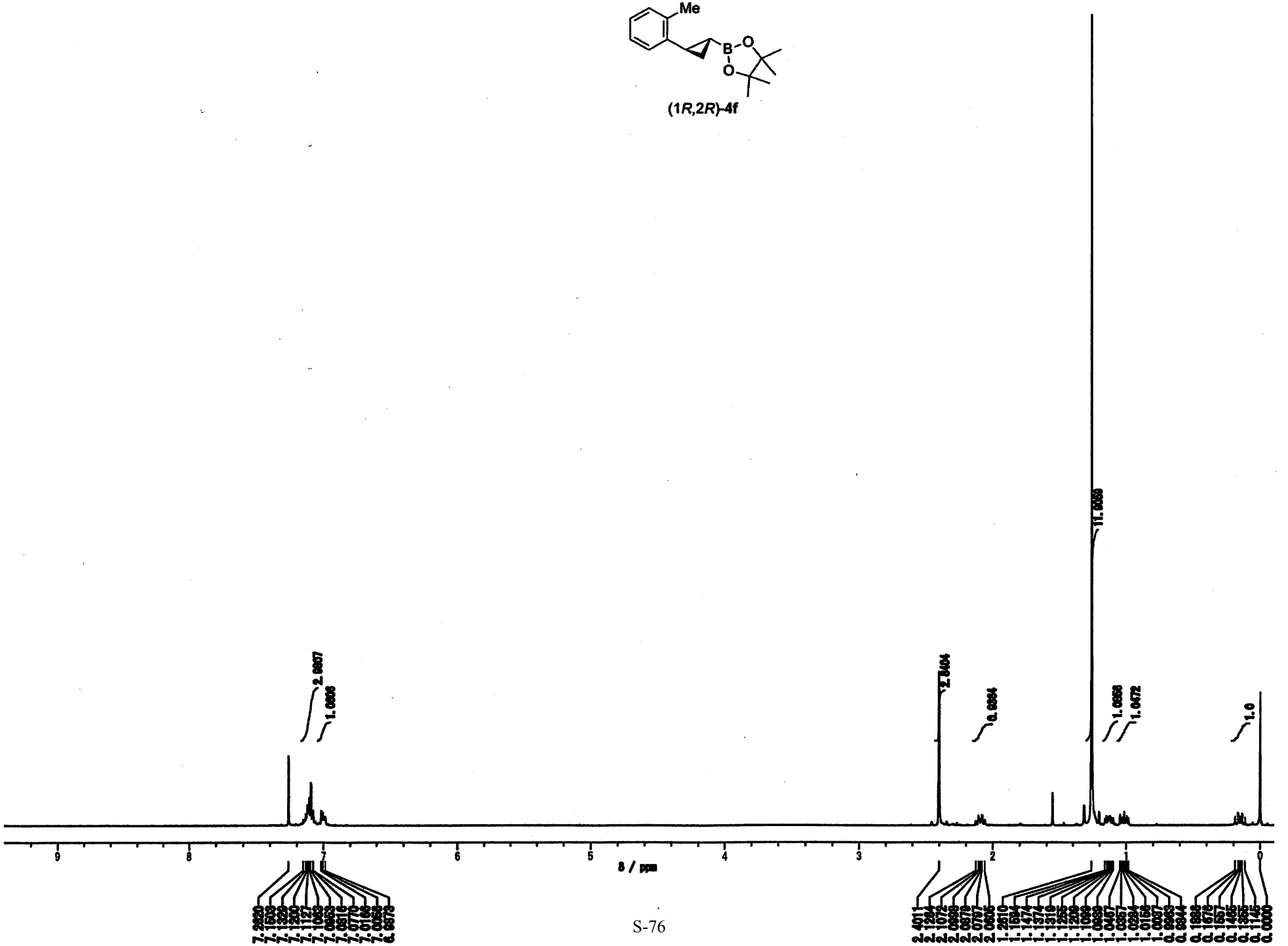

Cl
B
O
O
(1R,2R)-4c
180
160
140
120
100
δ / ppm
80
60
40
20
0
142.2120
131.9069
128.6325
127.2575
83.4178
77.6251
77.2000
76.7749
24.7071
24.7068
21.3736
15.0727
6.2440

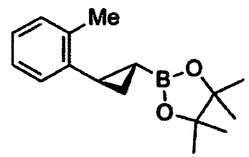

F3C
B
O
O
(1R,2R)-4d
18.5476
1.0000
1.0
0.4869
0.9149
7.4973
7.4869
7.2947
7.1722
7.1448
δ / ppm


F3C
B
O
O
(1R,2R)-4d
130. 0583
128. 3539
128. 6691
128. 2394
127. 8113
127. 3788
126. 4525
125. 6038
125. 4046
125. 3517
124. 8062
124. 7620
122. 8466
123. 3295
123. 4804
123. 4049
123. 3317
125.5
130 129 128 127 126 125 124 123 122
8 6 4
200 180 160 140 120 100 80 60 40 20 0
δ / ppm
83. 6539
83. 2806
77. 6251
77. 2000
76. 7749
24. 9169
24. 7620
24. 3948
21. 7606
15. 6365
9. 4019
6. 6767
0. 0343

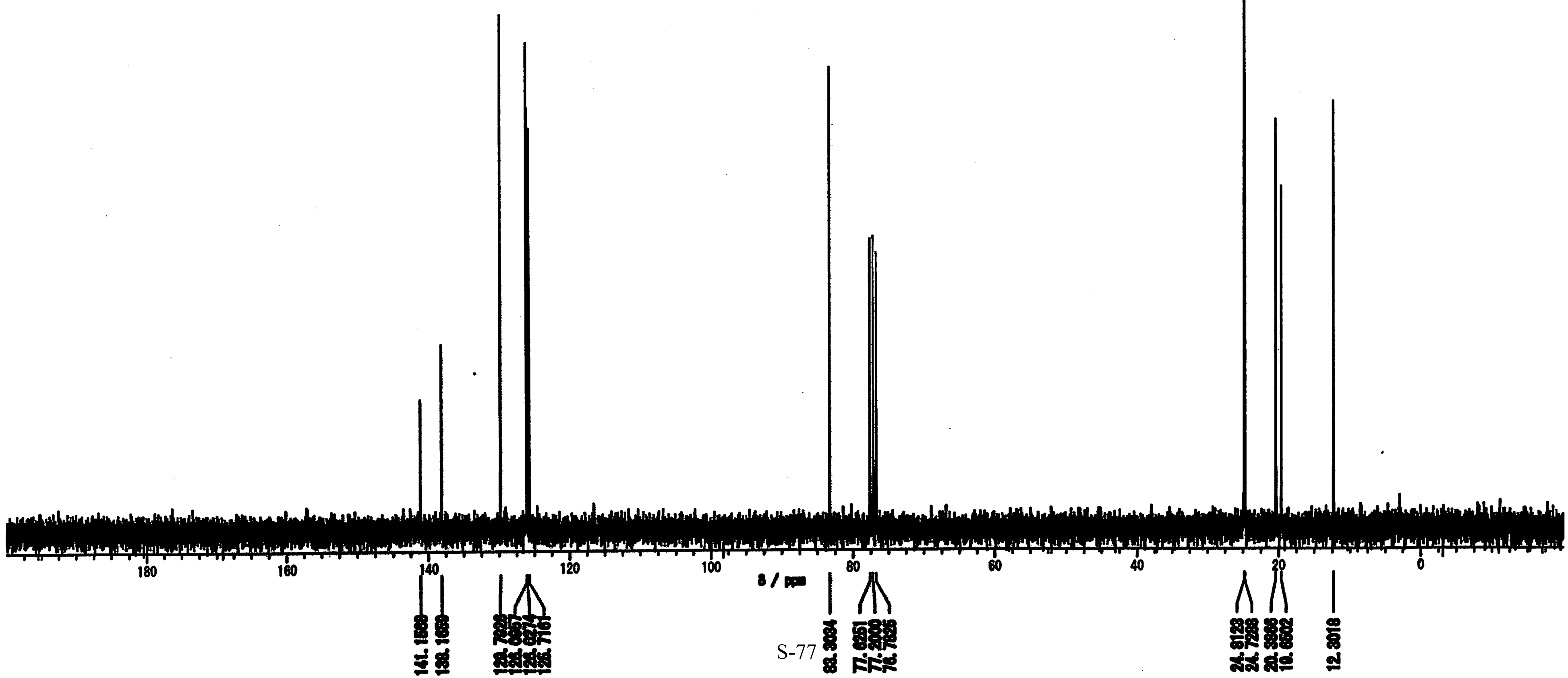

MeO2C
B
O
O
(1R,2R)-4e
1.0
1.0
δ / ppm

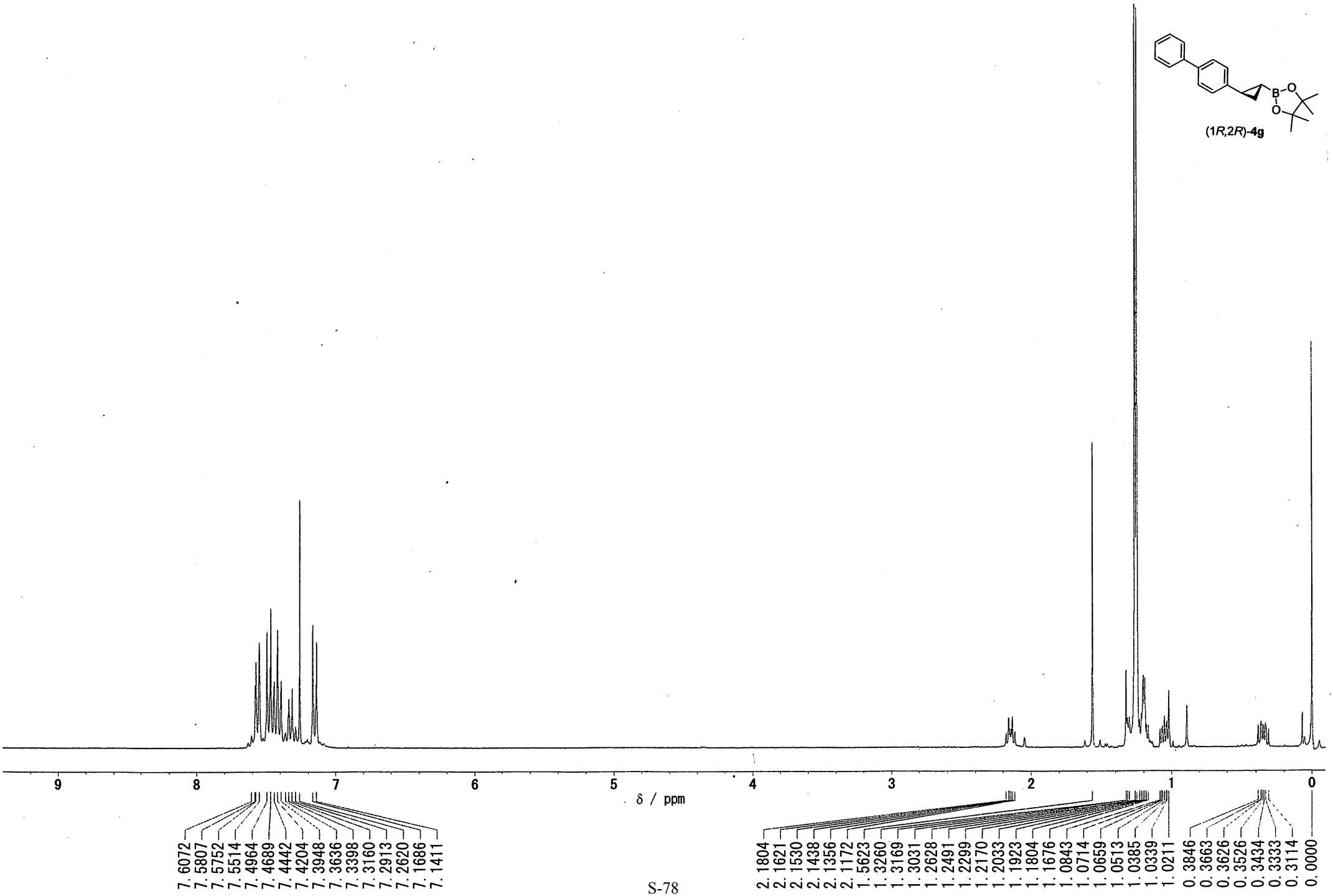

MeO2C
B
O
O
(1R,2R)-4e
180
160
140
120
100
80
60
40
20
0
δ / ppm
167.4008
149.6657
129.8936
127.6957
127.2076
126.6706
83.5238
77.6251
77.2076
76.7825
62.0576
24.9047
22.0557
15.8394

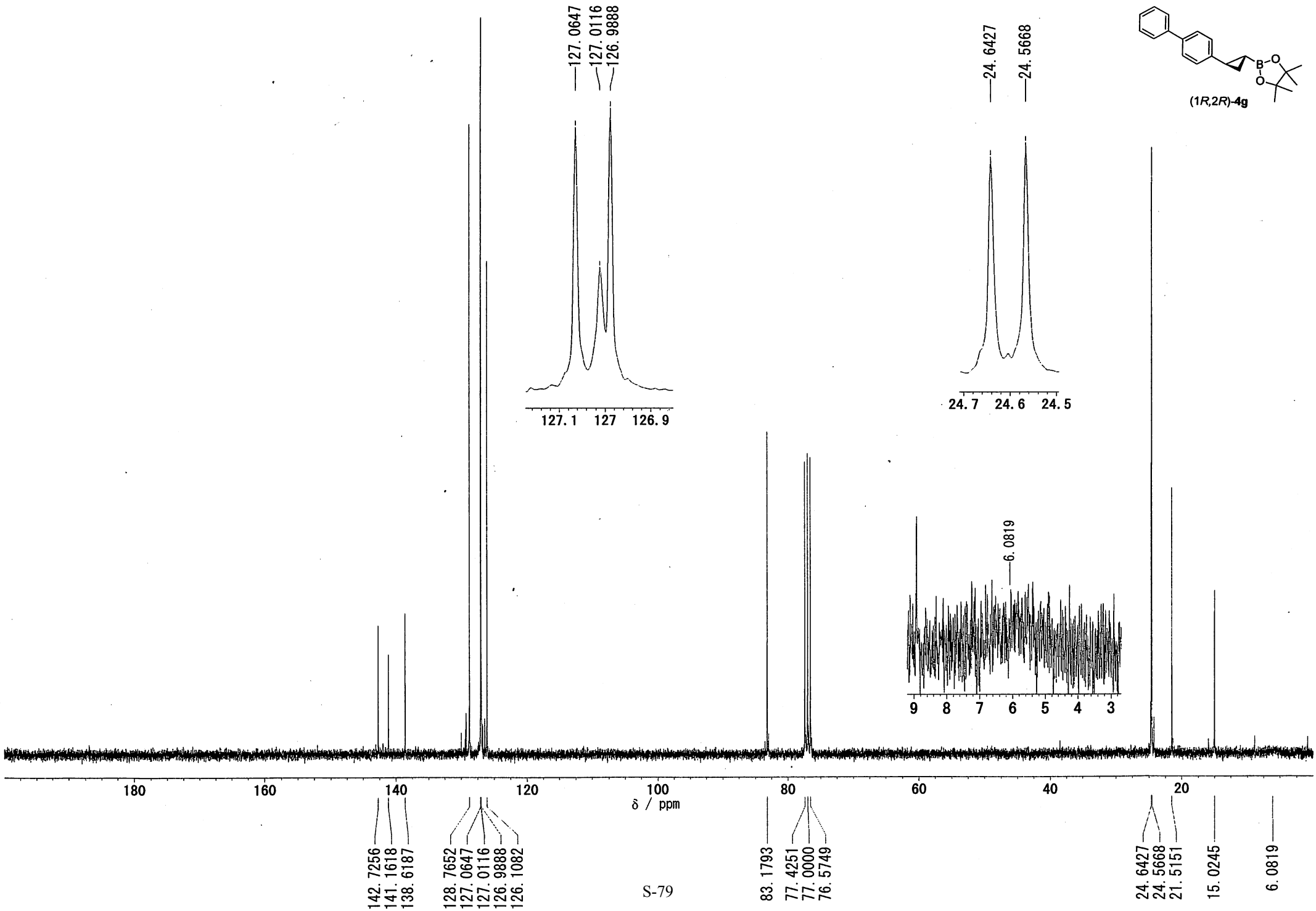

Me
B
O
O
(1R,2R)-4f
2.9897
1.0006
2.8404
0.9394
11.6068
1.0558
1.0472
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

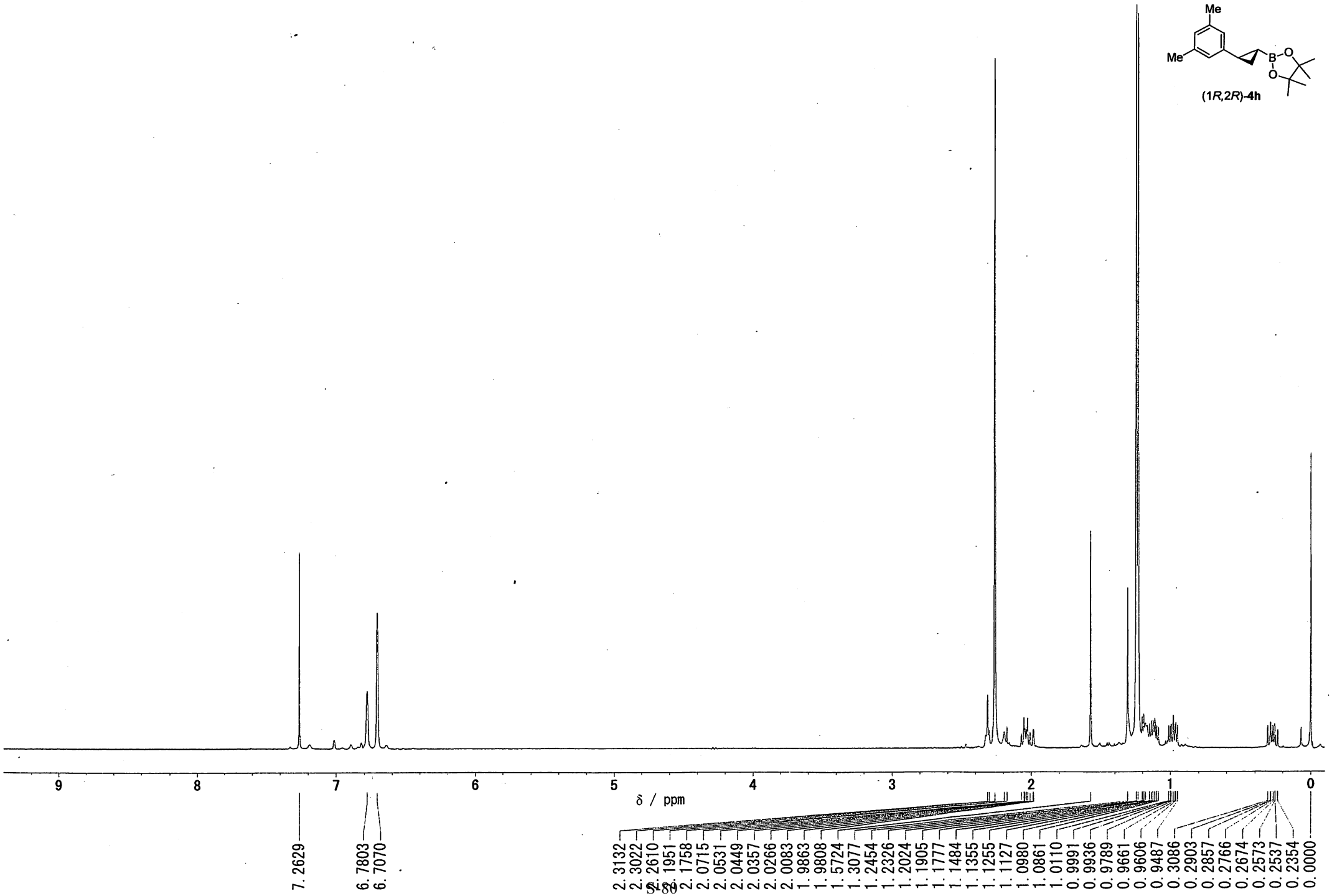

Me
B
O
O

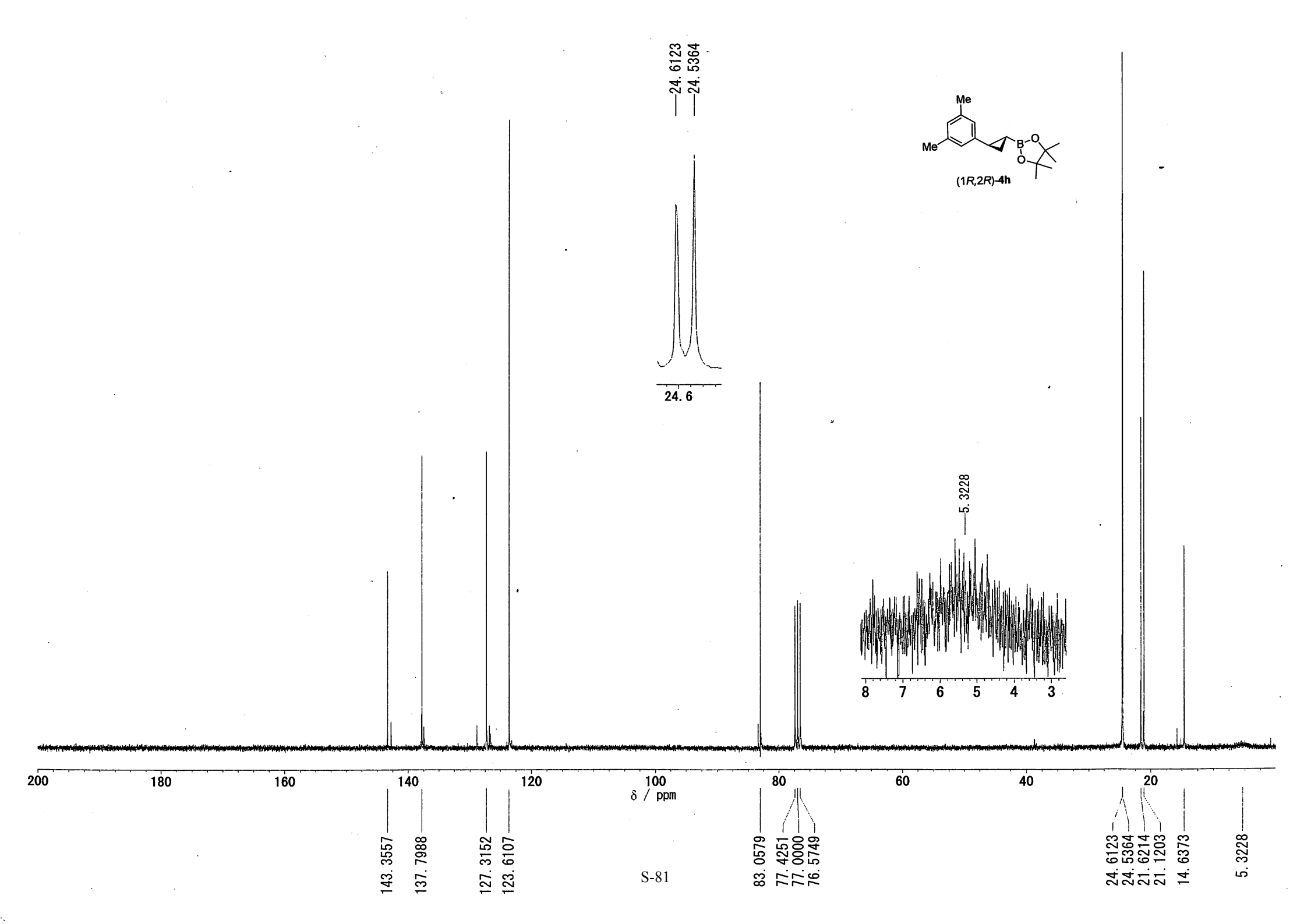
(1*R*,2*R*)-4f

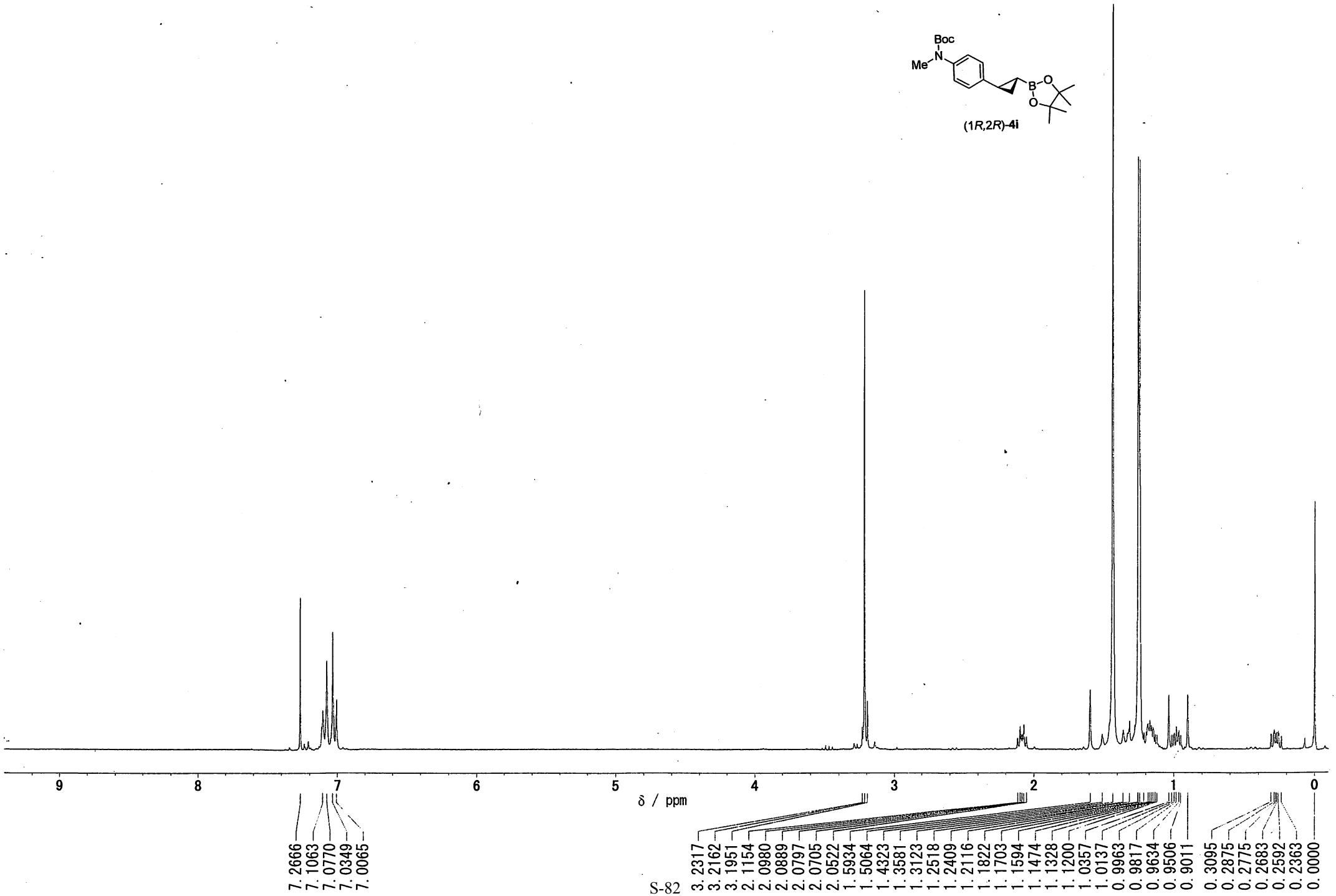

180
160
140
120
100
δ / ppm
80
60
40
20
0
141.1568
138.1659
129.7628
126.0957
126.0274
125.7161
83.3034
77.6351
77.2000
76.7625
24.8123
24.7288
20.3866
19.6502
12.3018

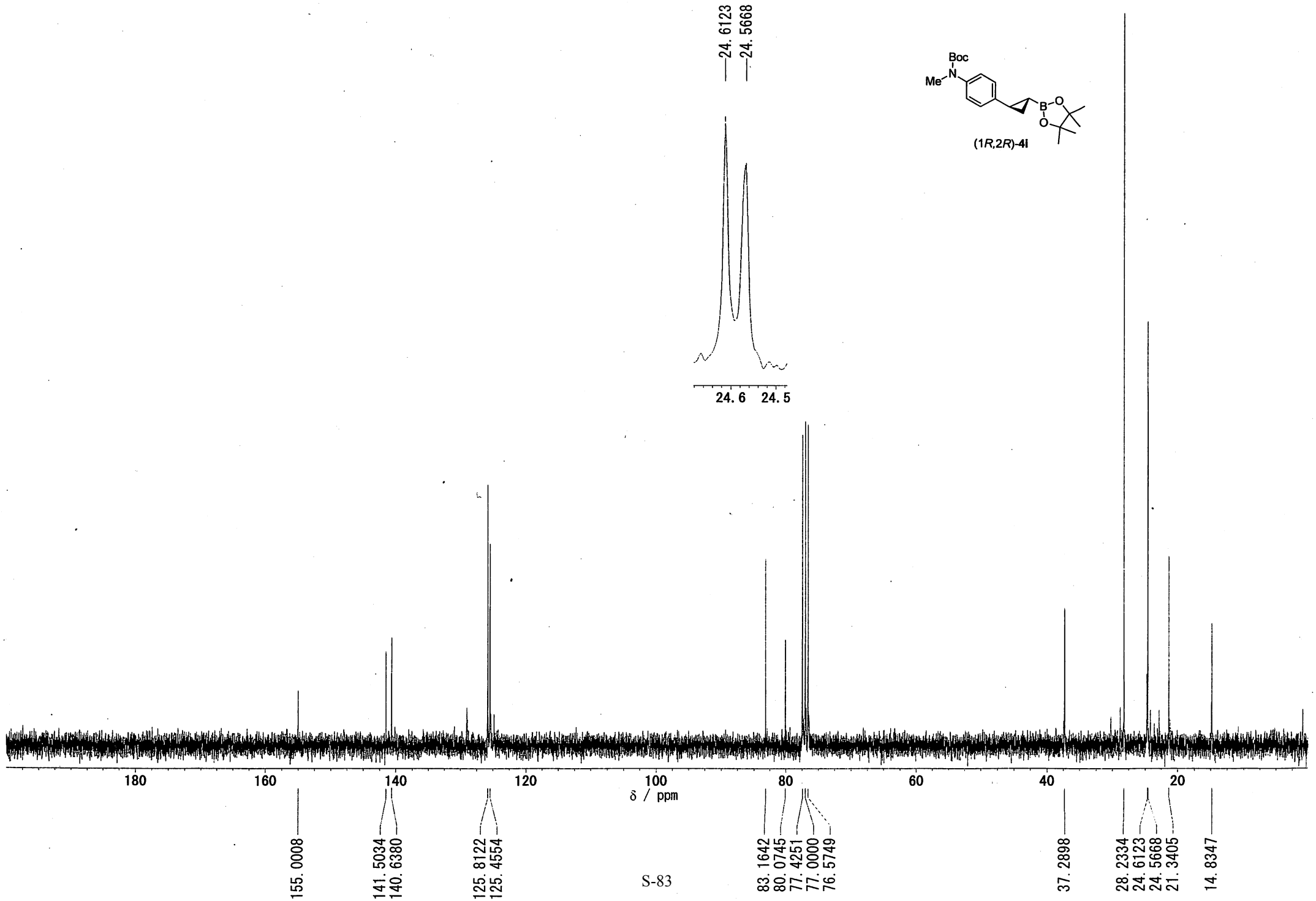

(1R,2R)-4g
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.6072
7.5807
7.5752
7.5514
7.4964
7.4689
7.4442
7.4204
7.3948
7.3636
7.3398
7.3160
7.2913
7.2620
7.1686
7.1411
2.1804
2.1621
2.1530
2.1438
2.1356
2.1172
1.5623
1.3260
1.3169
1.3031
1.2628
1.2491
1.2299
1.2170
1.2033
1.1923
1.1804
1.1676
1.0843
1.0714
1.0659
1.0513
1.0385
1.0339
1.0211
0.3846
0.3663
0.3626
0.3526
0.3434
0.3333
0.3114
0.0000

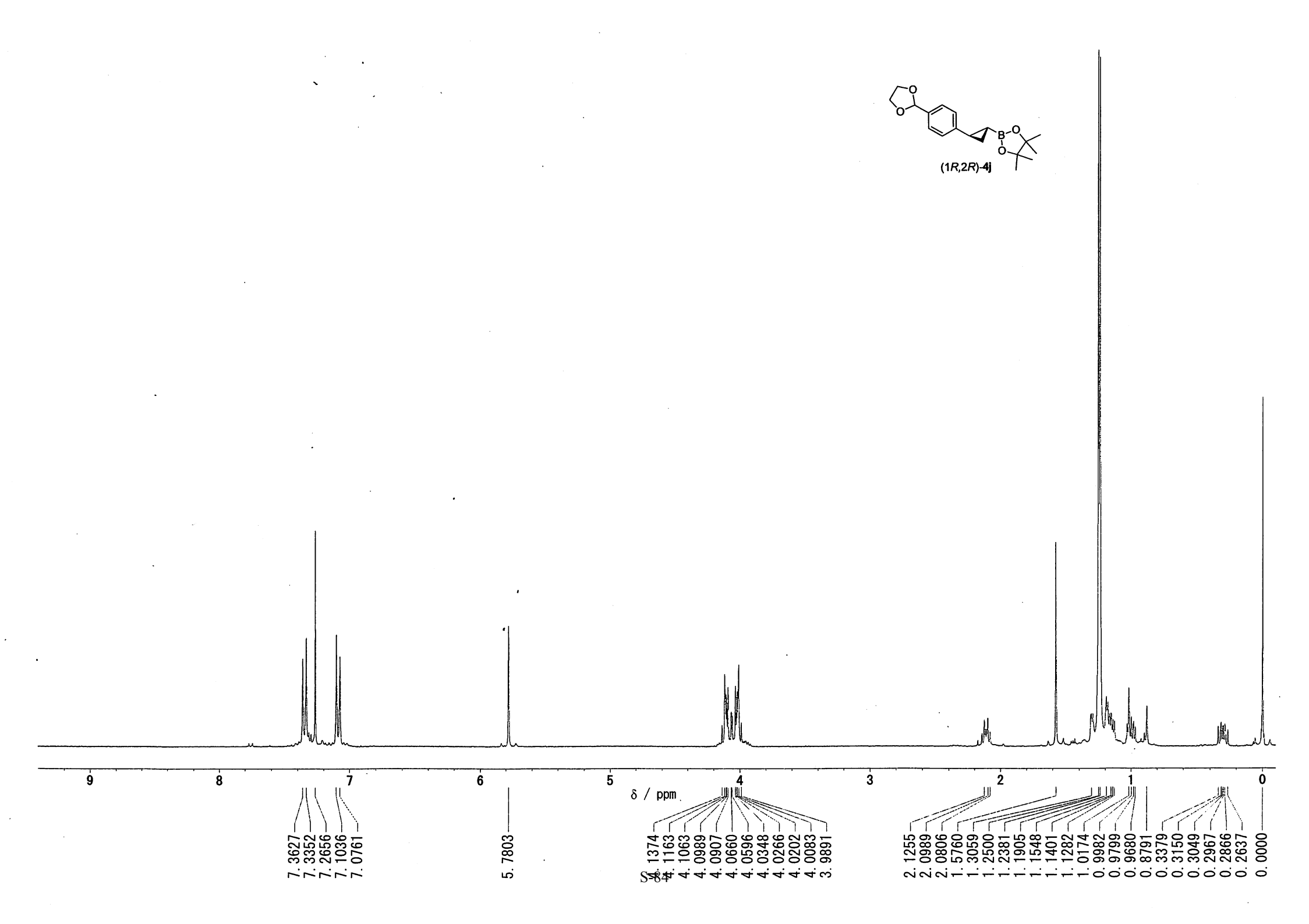

127.0647
127.0116
126.9888
24.6427
24.5668
(1R,2R)-4g
6.0819
δ / ppm
142.7256
141.1618
138.6187
128.7652
127.0647
127.0116
126.9888
126.1082
83.1793
77.4251
77.0000
76.5749
24.6427
24.5668
21.5151
15.0245
6.0819

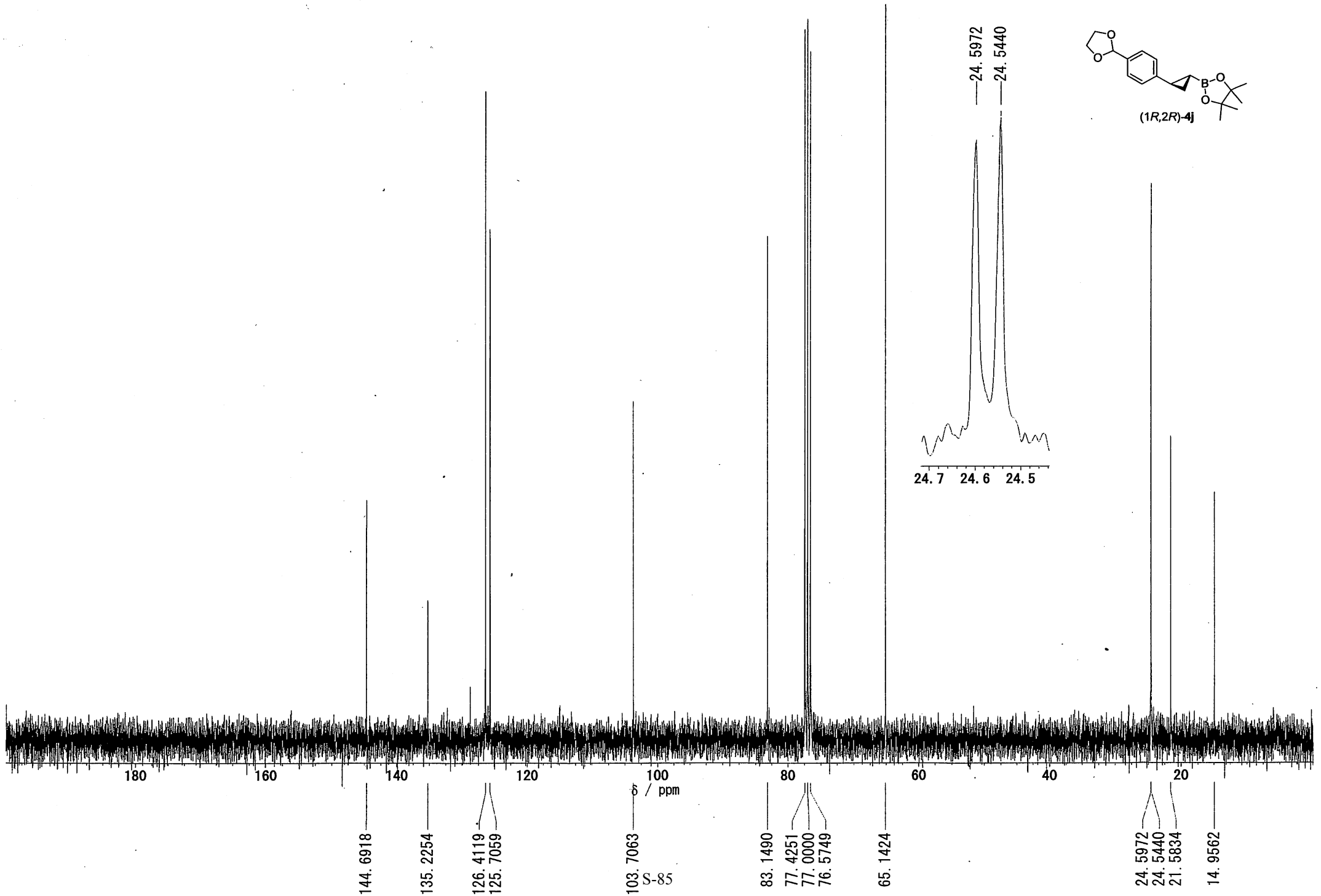

Me
Me
B
O
O
(1R,2R)-4h
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2629
6.7803
6.7070
2.3132
2.3022
2.2610
2.1951
2.1758
2.0715
2.0531
2.0449
2.0357
2.0266
2.0083
1.9863
1.9808
1.5724
1.3077
1.2454
1.2326
1.2024
1.1905
1.1777
1.1484
1.1355
1.1255
1.1127
1.0980
1.0861
1.0110
0.9991
0.9936
0.9789
0.9661
0.9606
0.9487
0.3086
0.2903
0.2857
0.2766
0.2674
0.2573
0.2537
0.2354
0.0000

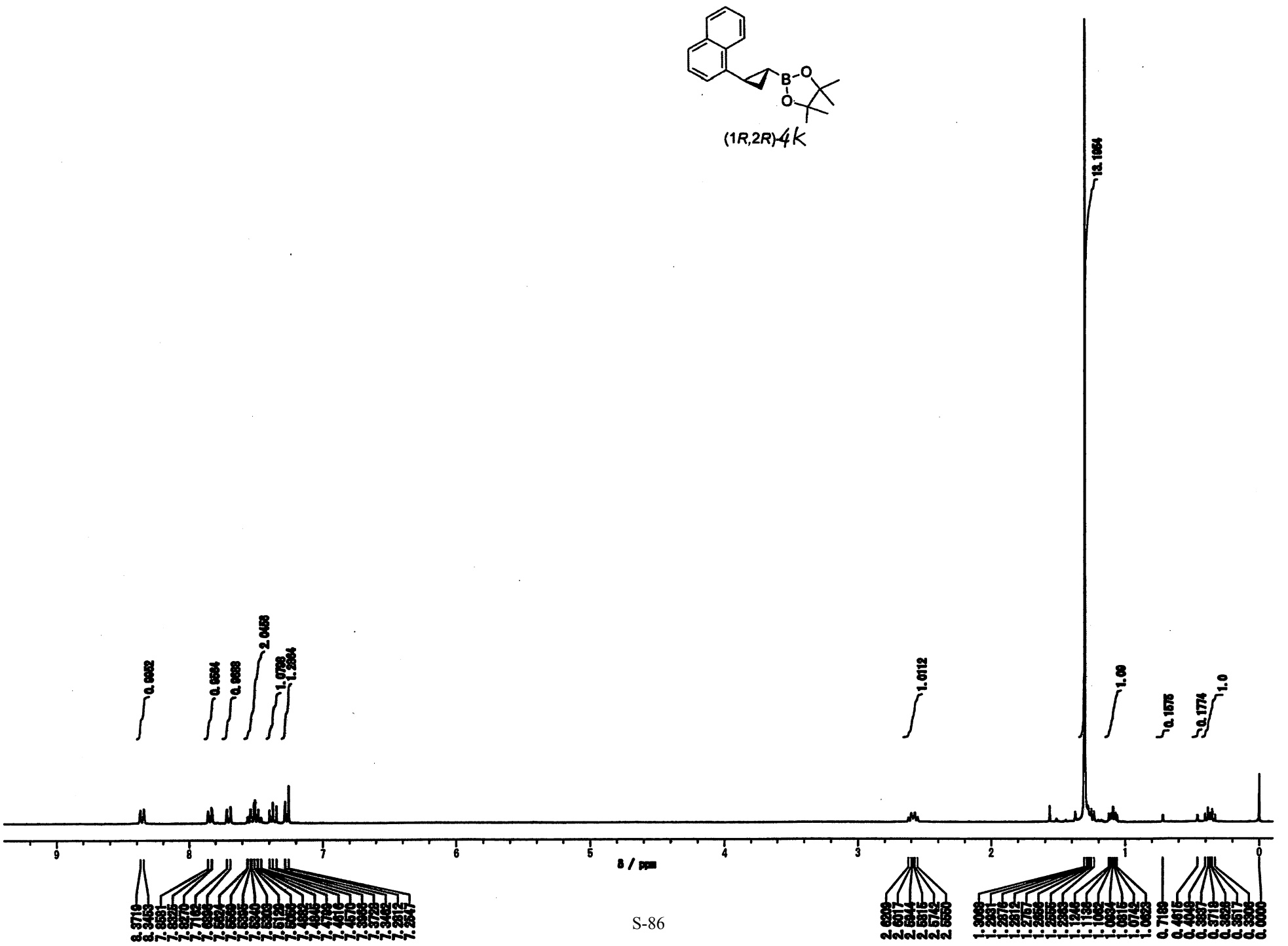

24.6123
24.5364
Me
Me
B
O
O
(1R,2R)-4h
24.6
5.3228
8
7
6
5
4
3
200
180
160
140
120
100
80
60
40
20
δ / ppm
143.3557
137.7988
127.3152
123.6107
83.0579
77.4251
77.0000
76.5749
24.6123
24.5364
21.6214
21.1203
14.6373
5.3228

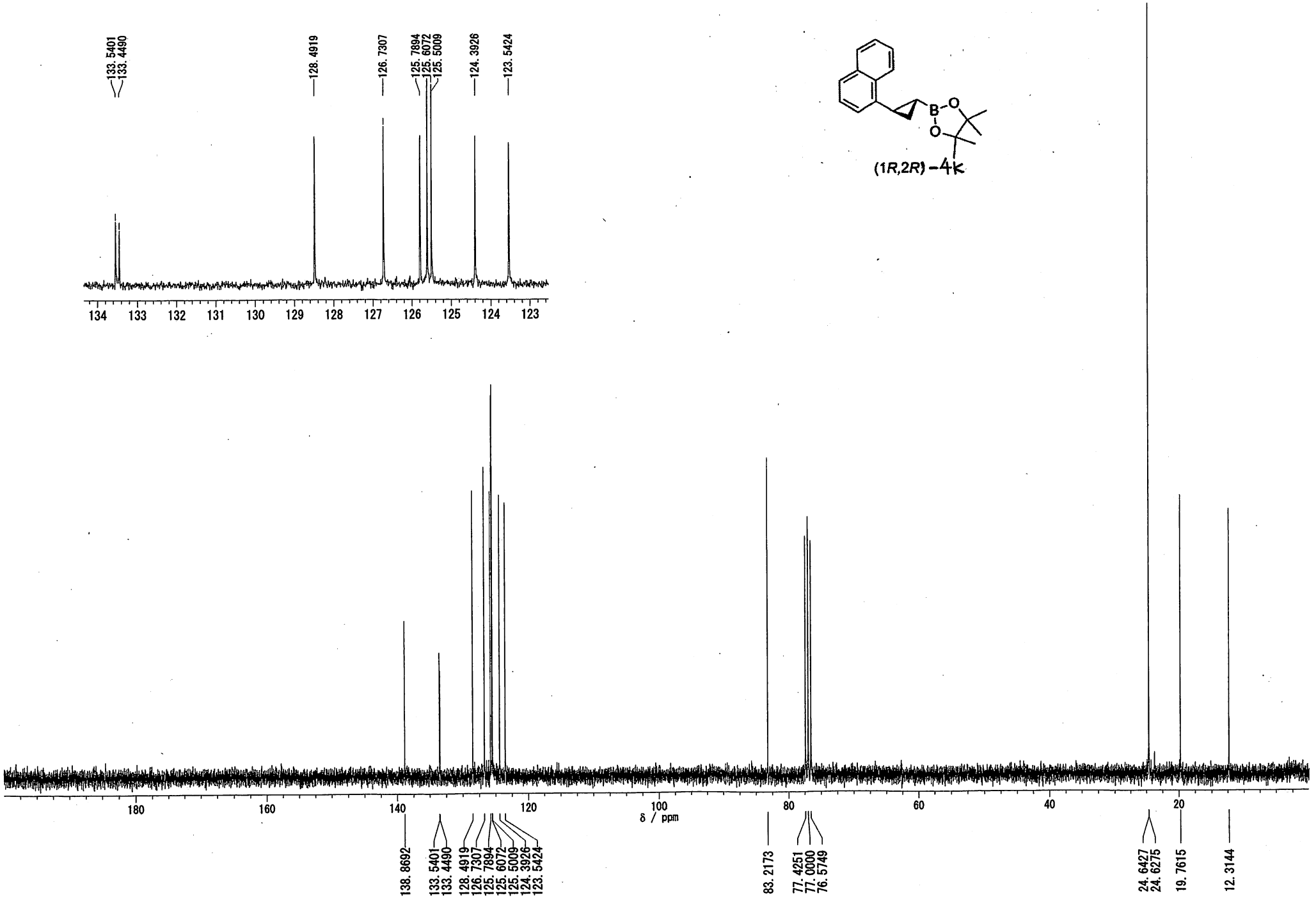

Boc
N
Me
B
O
O
(1R,2R)-4i
9
8
7
6
5
4
3
2
1
0
δ / ppm
7.2666
7.1063
7.0770
7.0349
7.0065
3.2317
3.2162
3.1951
2.1154
2.0980
2.0889
2.0797
2.0705
2.0522
1.5934
1.5064
1.4323
1.3581
1.3123
1.2518
1.2409
1.2116
1.1822
1.1703
1.1594
1.1474
1.1328
1.1200
1.0357
1.0137
0.9963
0.9817
0.9634
0.9506
0.9011
0.3095
0.2875
0.2775
0.2683
0.2592
0.2363
0.0000

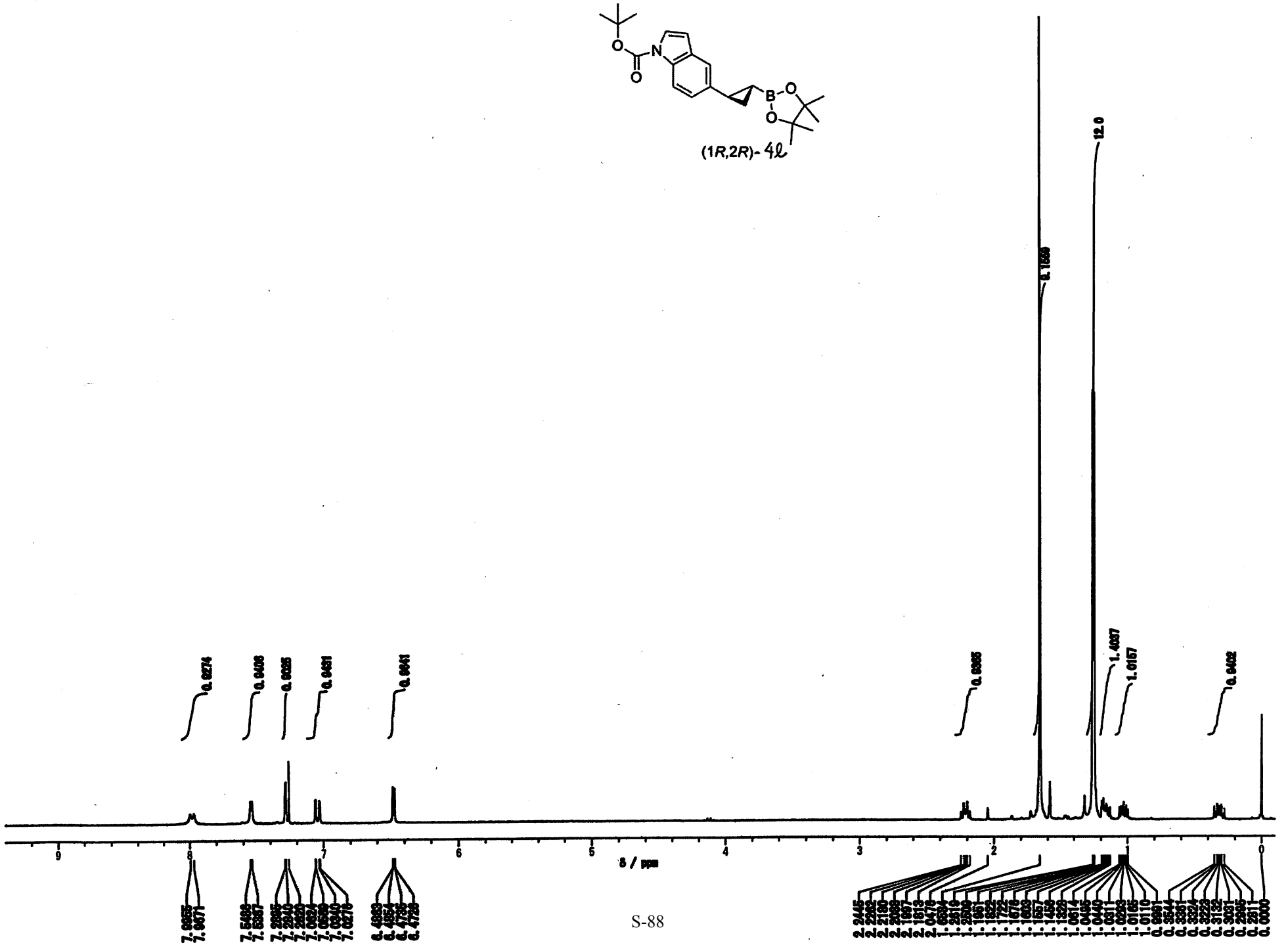

24.6123
24.5668
Boc
N
Me
B
O
O
(1R,2R)-4l
24.6
24.5
180
160
140
120
100
80
60
40
20
δ / ppm
155.0008
141.5034
140.6380
125.8122
125.4554
83.1642
80.0745
77.4251
77.0000
76.5749
37.2898
28.2334
24.6123
24.5668
21.3405
14.8347

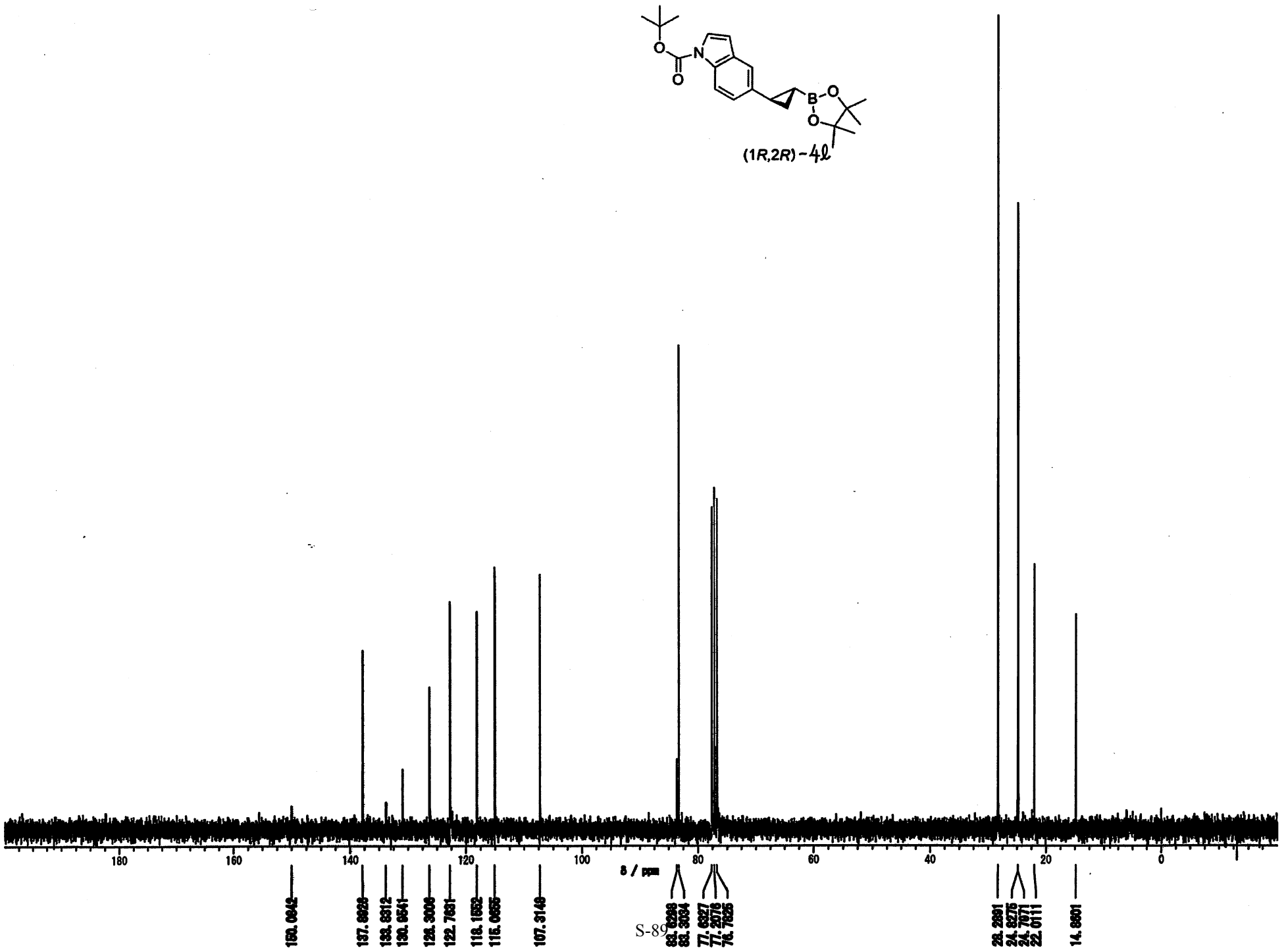

(1R,2R)-4j
δ / ppm
7.3627
7.3352
7.2656
7.1036
7.0761
5.7803
4.1374
4.1163
4.1063
4.0989
4.0907
4.0660
4.0596
4.0348
4.0266
4.0202
4.0083
3.9891
2.1255
2.0989
2.0806
1.5760
1.3059
1.2500
1.2381
1.1905
1.1548
1.1401
1.1282
1.0174
0.9982
0.9799
0.9680
0.8791
0.3379
0.3150
0.3049
0.2967
0.2866
0.2637
0.0000

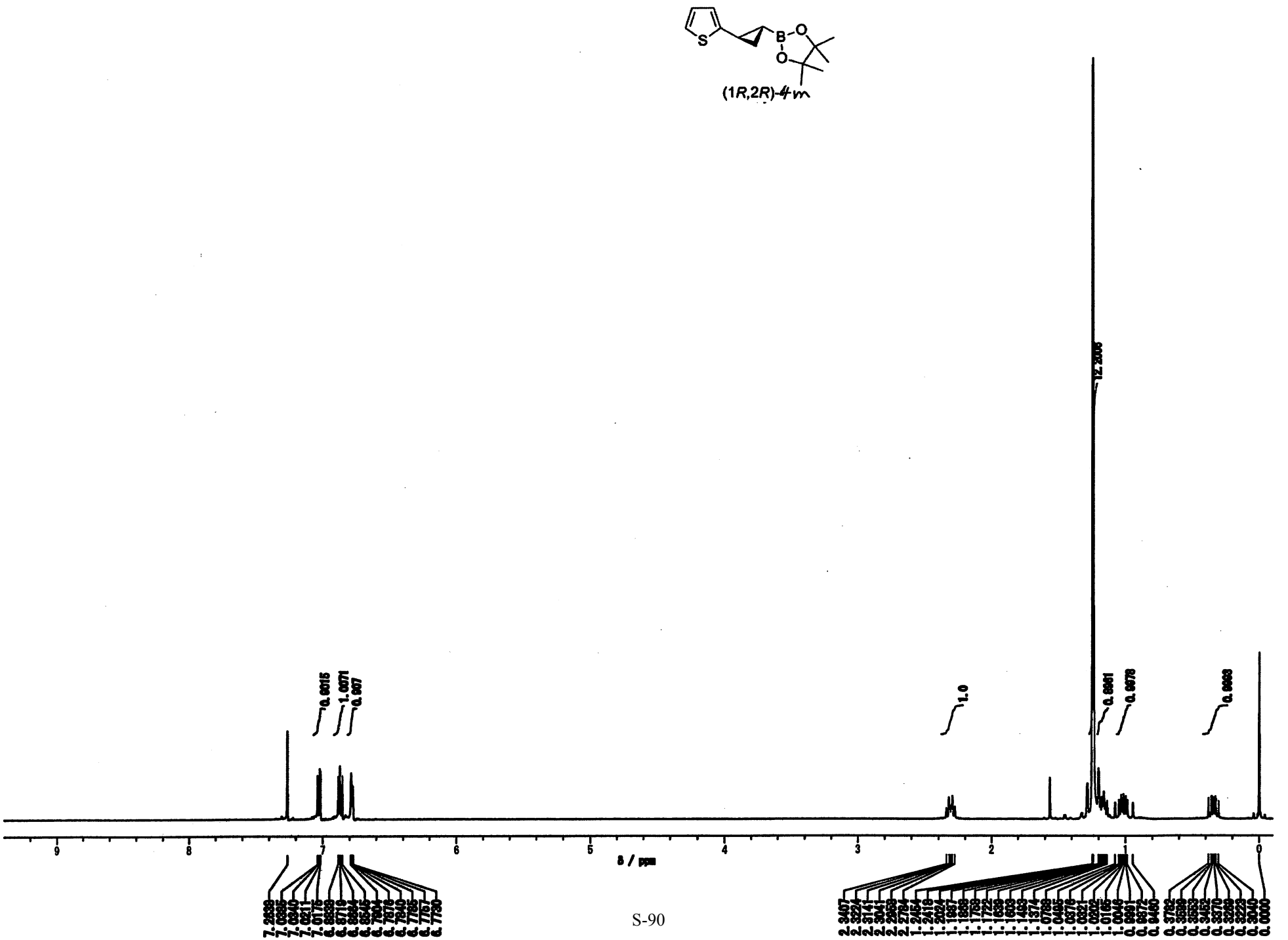

24.5972
24.5440
(1R,2R)-4j
24.7
24.6
24.5
180
160
140
120
100
80
60
40
20
δ / ppm
144.6918
135.2254
126.4119
125.7059
103.7063
83.1490
77.4251
77.0000
76.5749
65.1424
24.5972
24.5440
21.5834
14.9562

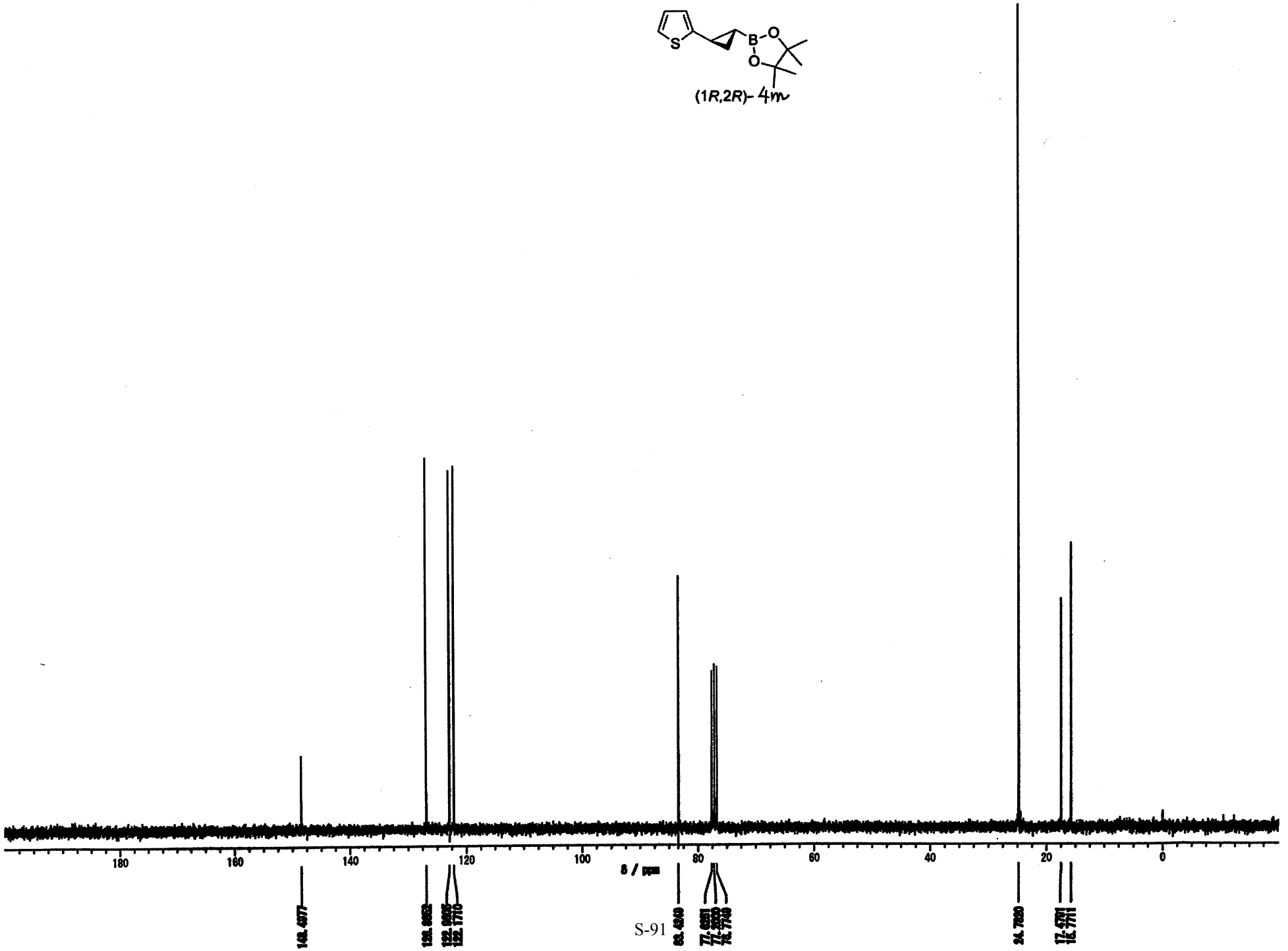

(1R,2R)-4k
B
O
O
0.9932
0.9934
0.9993
2.0458
1.0799
1.2884
1.0112
13.1664
1.00
0.1675
0.1774
1.0
9
8
7
6
5
4
3
2
1
0
δ / ppm

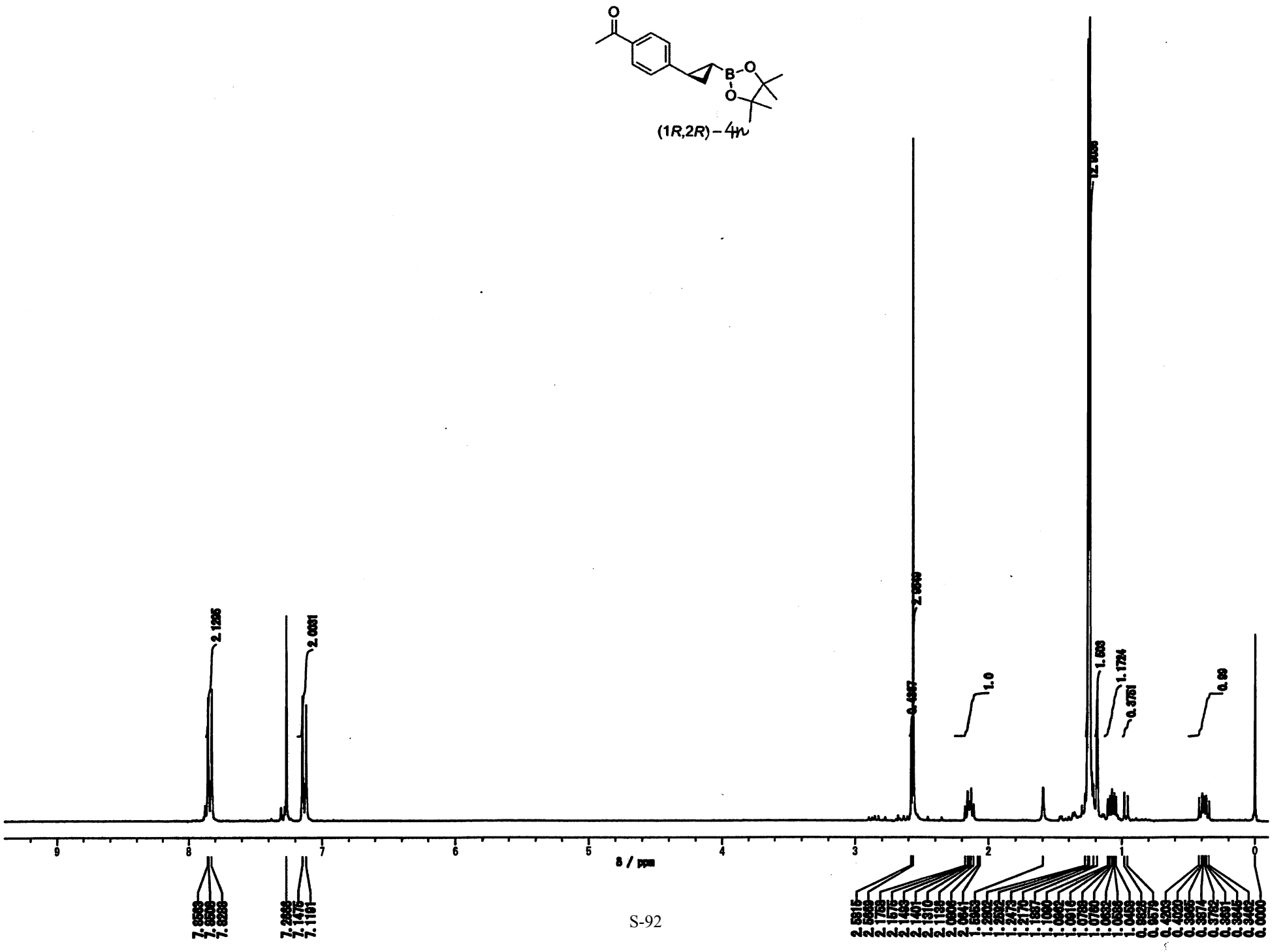

133.5401
133.4490
128.4919
126.7307
125.7894
125.6072
125.5009
124.3926
123.5424
134 133 132 131 130 129 128 127 126 125 124 123
(1R,2R)-4k
δ / ppm
180 160 140 120 100 80 60 40 20
138.8692
133.5401
133.4490
128.4919
126.7307
125.7894
125.6072
125.5009
124.3926
123.5424
83.2173
77.4251
77.0000
76.5749
24.6427
24.6275
19.7615
12.3144

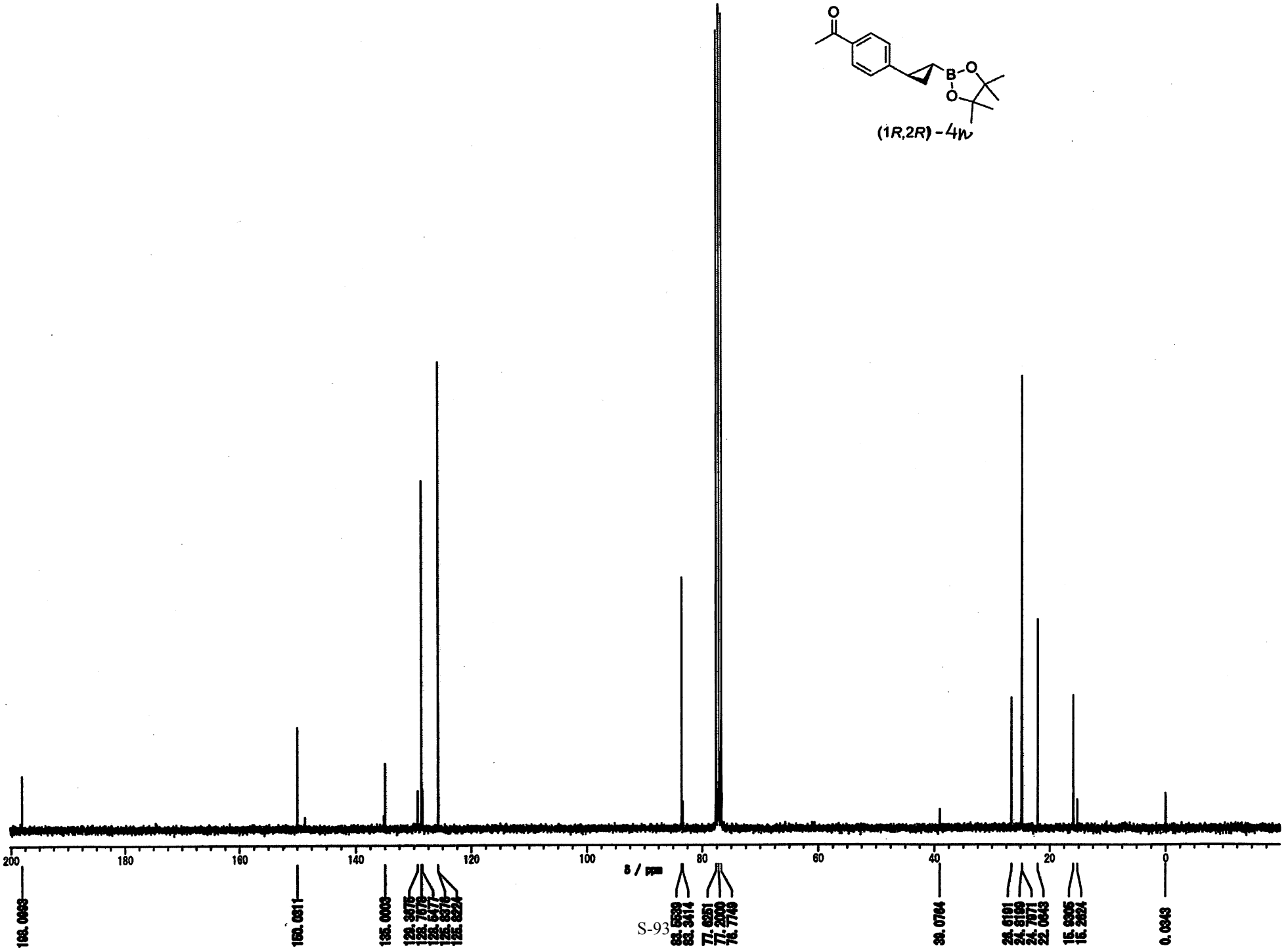

(1R,2R)-4l
δ / ppm

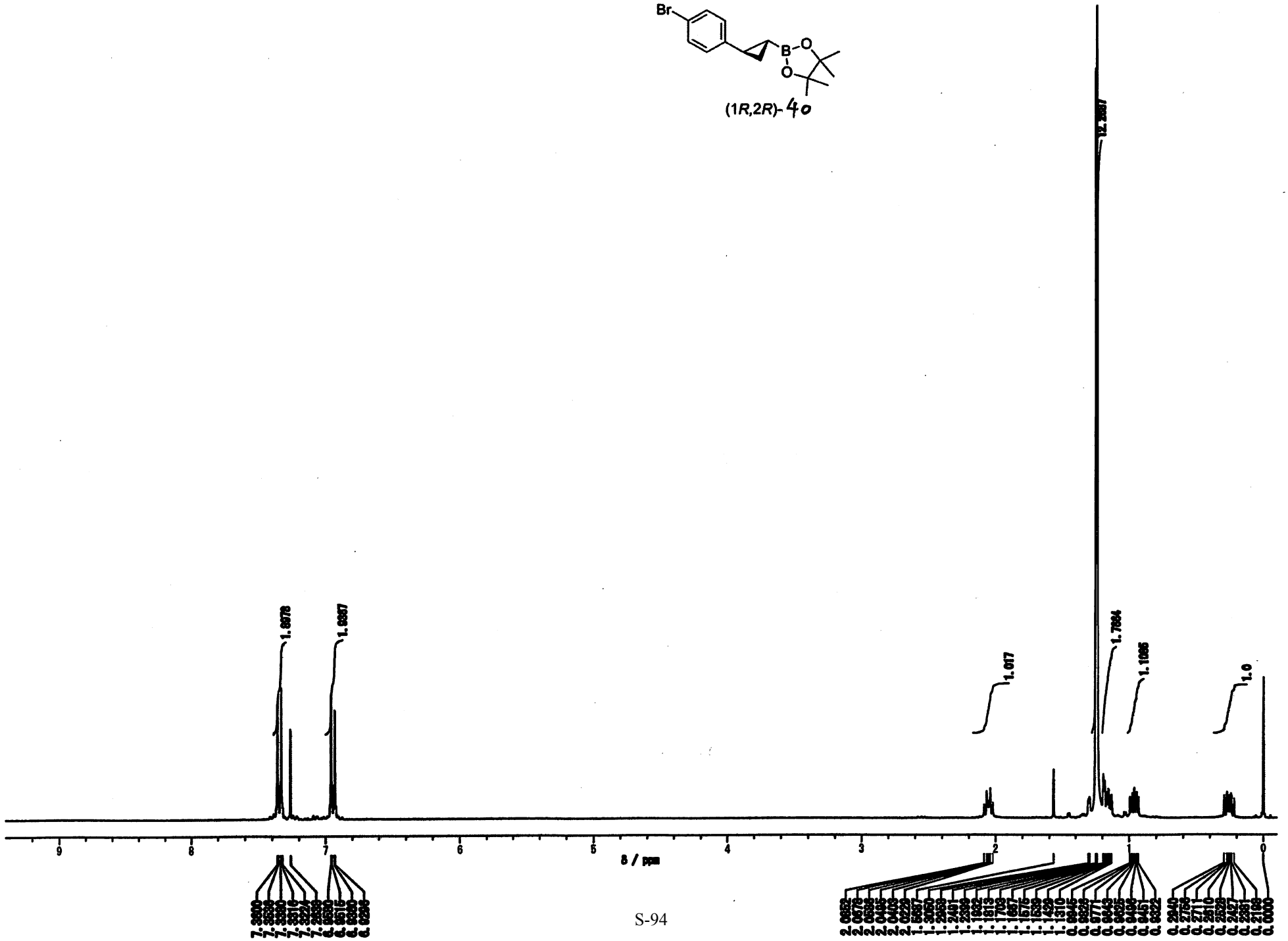

(1R,2R)-4l
180
160
140
120
100
80
60
40
20
0
δ / ppm
150.0042
137.8928
133.6912
130.6641
128.3006
122.7631
118.1632
115.0655
107.3148
83.6298
83.3034
77.6327
77.2076
76.7825
28.2891
24.8276
24.7971
22.0111
14.6801

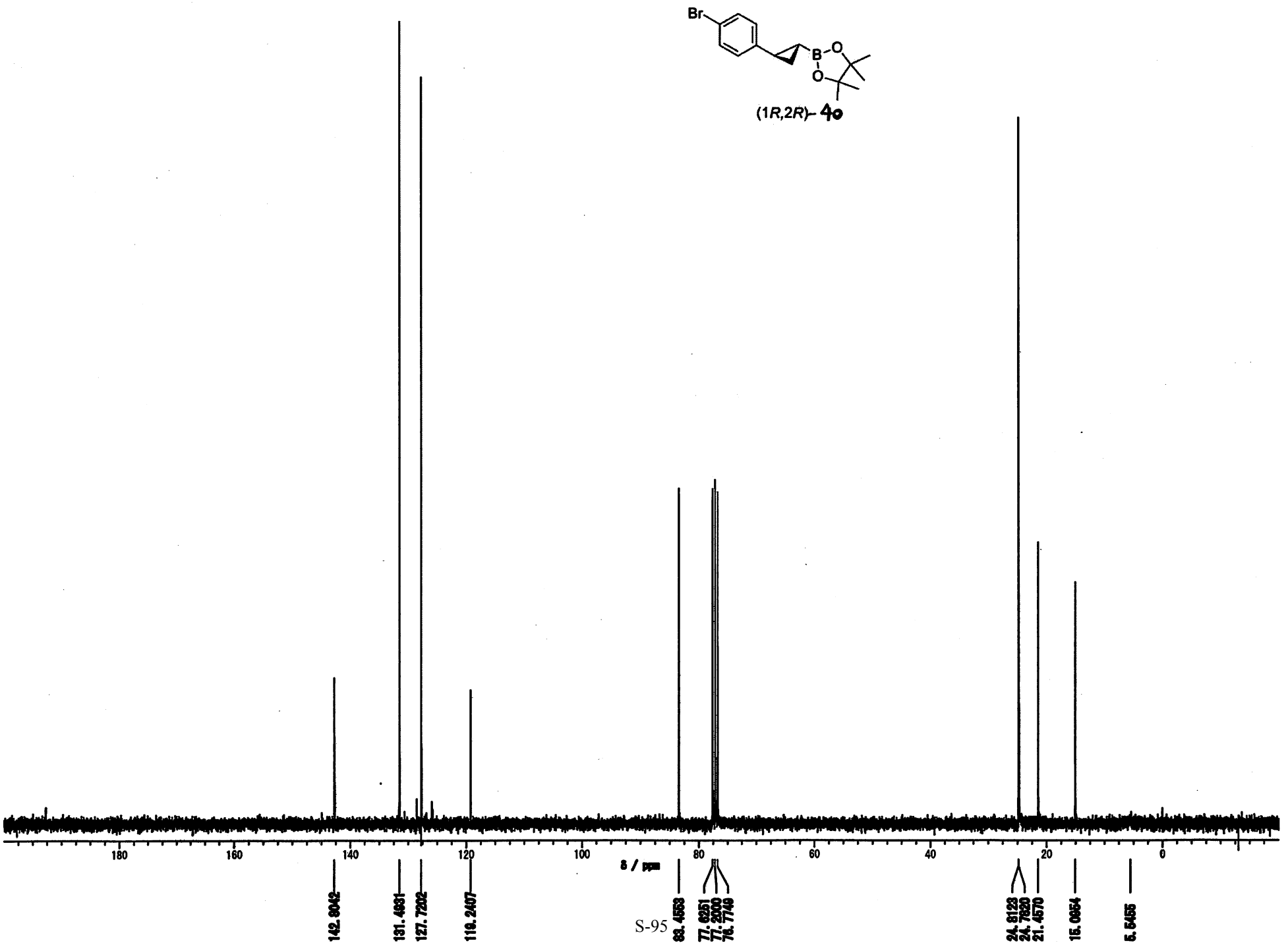

(1R,2R)-4m
S
B
O
O
12.2000
1.0
0.9961
0.9978
0.9993
1.0071
0.9977
0.9915
δ / ppm


(1R,2R)-4m
180
160
140
120
100
80
60
40
20
0
δ / ppm


(1R,2R)-4m
δ / ppm


(1R,2R)-4w
200
180
160
140
120
100
80
60
40
20
0
δ / ppm
198.0068
169.0811
135.0003
129.3675
128.7078
128.6477
126.6376
125.8224
83.6539
83.3414
77.6251
77.2000
76.7748
30.0764
26.6101
24.6159
24.7671
22.0043
15.9305
15.2824
0.0343


Br
B
O
O
(1R,2R)-4o
1.6978
1.6957
1.017
1.7004
1.1005
1.0
δ / ppm


Br
B
O
O
(1R,2R)-4o
180
160
140
120
100
80
60
40
20
0
δ / ppm
142.8042
131.4631
127.7202
119.2407
83.4553
77.6251
77.2000
76.7748
24.8123
24.7820
21.4670
15.0864
5.6455