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Exploiting Self-Assembly for Ligand-Scaffold Optimization: Substrate-Tailored Ligands for Efficient Catalytic Asymmetric Hydroboration

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Exploiting Self-Assembly for Ligand-Scaffold Optimization: Substrate-Tailored Ligands for Efficient Catalytic Asymmetric Hydroboration

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Summary: A self-assembled ligand library (**SAL XY**) affords a wide range of *R*/*S* ratios in Rh-catalyzed asymmetric hydroboration (nbd = 2,5norbornadiene, R* is a chiral substituent). Ligand-scaffold optimization reveals “substrate-tailored” ligands that afford high regio- and enantioselectivity for a variety of *ortho*-substituted styrene derivatives.

Keywords: asymmetric synthesis, combinatorial chemistry, hydroboration, self-assembly, stereoselective catalysis

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Supporting information for this article follows the text; it is also available at http://www.angewandte.org or from the author.

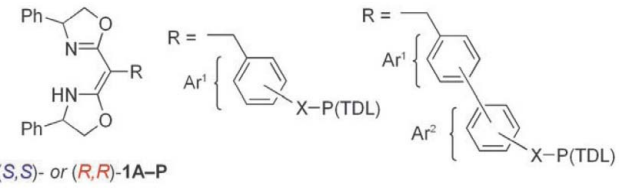
Rhodium-catalyzed hydroboration has attracted much interest, in part owing to the complementary regio-and diastereoselectivity obtained with certain substrates compared to the uncatalyzed process.[1, 2] The novel regiocontrol is exemplified in the rhodium-catalyzed hydroborations of vinyl arenes, which, in contrast to the uncatalyzed reaction, introduce boron at the benzylic position. For example, styrene affords 1-phenylethanol after hydroboration and oxidation. Several catalyst systems exhibit both high regio-and enantioselectivity for the catalytic asymmetric hydroboration of styrene and some of its substituted derivatives.[3] However, the reaction is sensitive to both steric and electronic factors, and for the reactions of *ortho*-substituted styrene derivatives, an important subclass ofthese substrates, high levels of enantioselection have proved elusive.[4] Herein, we report the use of self-assembled ligands (SALs) for the catalytic asymmetric hydroboration ofa family of *ortho*-substituted styrene derivatives varying in steric and electronic character.

Several strategies for preparing novel ligands by self-assembly have emerged as promising approaches to unsolved problems in catalysis.[5,6] We reported a novel method for the in situ preparation of chiral ligand libraries by chirality-directed self-assembly, a strategy by which the topography at the catalytic site is varied over a wide range by subtle changes in the ligand scaffold.[7]

Bifunctional subunits (*S*,*S*)- and (*R*,*R*)-**1A–P** exploit a chiral bisoxazoline to direct the self-assembly, substituted with a series of phenylmethyl or biphenylmethyl tethers terminating in a phosphite ligating group derived from TADDOL[8] ((4*R*,5*R*)-α,α,α′,α′-tetraphenyl-2,2-dimethyl-1,3dioxolan-4,5-dimethanol, TDL). The subunits differ with respect to the tether substitution pattern (Table 1).

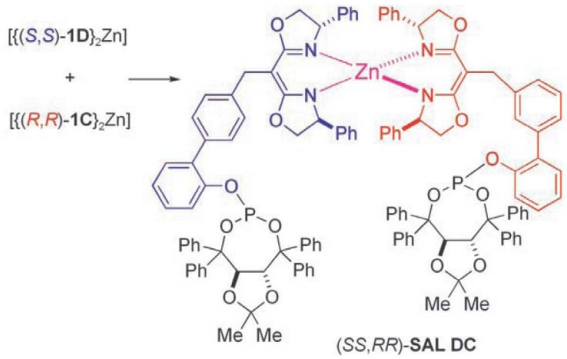
A mixture of (*S*,*S*)-and (*R*,*R*)-**1A–P** readily undergoes chirality-directed self-assembly upon addition of zinc(II) to yield the heterodimeric (*SS*,*RR*)-SALs.[9] In the present study, we found it convenient to first prepare the (*S*,*S*)- and (*R*,*R*) homodimers from **1A–P**, which upon mixing rapidly equilibrate to the (*SS*,*RR*)-heterodimer. For example, mixing [{(*S*,*S*)-**1D**}$_2$Zn] with [{(*R*,*R*)-**1C**}$_2$Zn] affords (*SS*,*RR*)-**SAL DC** (Scheme 1). The latter can be isolated; however, the SALs and their derived catalyst systems are typically generated in situ and used without isolation.[10] Combining various pairs of (*S*,*S*)- and (*R*,*R*)-**1A–P** quickly affords a library of unique (*SS*,*RR*)-**SAL XY** differing only in scaffold structure.

Table 1: TADDOL-derived subunits (*S*,*S*)-and (*R*,*R*)-**1A–P** are used to form (*SS*,*RR*)-**SAL XY** by chirality-directed self-assembly.

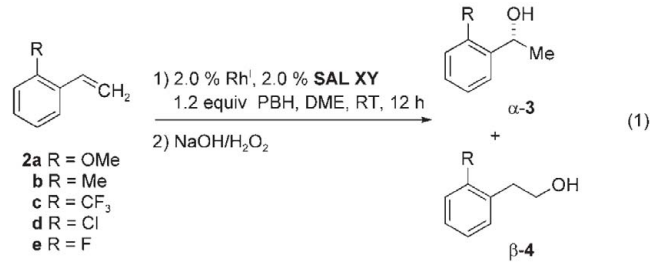


(*S*,*S*)- *or* (*R*,*R*)-**1A–P**

	X = O			X = CH_2O	
Ar^2	1,3-Ar^1	1,4-Ar^1	Ar^2	1,3-Ar^1	1,4-Ar^1
—	**A**	**B**	—	**I**	**J**
1,2-	**C**	**D**	1,2-	**K**	**L**
1,3-	**E**	**F**	1.3-	**M**	**N**
1,4-	**G**	**H**	1,4-	**O**	**P**



Scheme 1. Heterodimer (*SS*,*RR*)-**SAL DC** is readily prepared by ligand exchange of the appropriate homodimers.



(1)

The hydroboration of 2-methoxystyrene (**2a**) with pinacolborane (PBH) was screened using [{Rh(nbd)Cl}$_2$] (nbd = 2,5-norbornadiene) in combination with 162 in situ prepared **SAL XY** [Eq. (1), DME = dimethoxyethane].[11] Remarkably, this readily accessible, focused ligand library affords *R*:*S* enantiomeric ratios ranging from 98:2 to 35:65 (Figure 1).[12] Analysis of these data reveals that with few exceptions the most efficient catalysts combine SALs containing only phenyl phosphite subunits **1A–H** (65 to 96% *ee* (*R*)). The SALs containing only benzyl phosphite subunits (**1I–P**) afford lower levels of enantioselectivity (30 % *ee* (*S*) to 40% *ee* (*R*)). Mixed phenyl/benzyl combinations tend to fall in between.

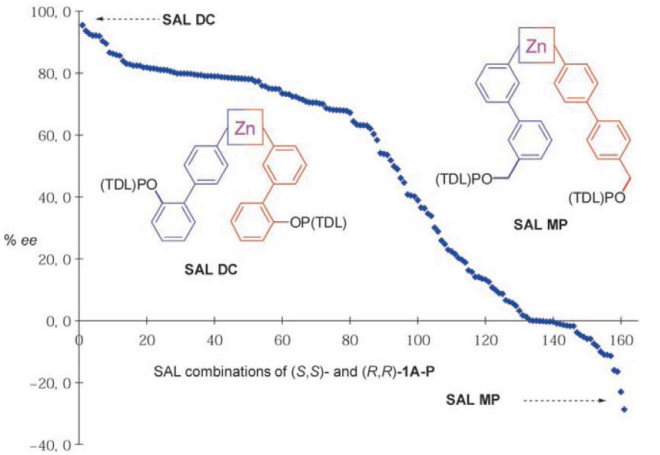


Figure 1. Wide variation in enantioselectivity is observed for the SAL/[{Rh(nbd)Cl}$_2$]-catalyzed asymmetric hydroboration of 2-methoxystyrene (2a) as a function of ligand scaffold.

Varying the catalyst precursor reveals other remarkable features of the role of scaffold structure in catalyst optimization. The nature of the Rh^I catalyst precursor can be an important factor in catalytic asymmetric hydroboration.[13] Having obtained data using [{Rh(nbd)Cl}$_2$], the reaction of 2-methoxystyrene (**2a**) was carried out using [Rh(nbd)$_2$BF$_4$] in combination with each of the 64 possible SALs from derived from subunits **1A–H**. As summarized in Table 2, different optimal ligand scaffolds were found for each catalyst precursor. **SAL DC** (96% *ee*) was best for [{Rh(nbd)Cl}$_2$] while **SAL HC** (95% *ee*) proved best for [Rh(nbd)$_2$BF$_4$]. It is interesting to note that while subunit (*R*,*R*)-**1C** is present in both optimal SALs, the SAL combination containing only **1C** (i.e., the pseudo-C_2-symmetric **SAL CC**) is less effective with either catalyst precursor. In addition, **SAL DC** is more selective than its closely related diastereomer **SAL CD**, and **SAL HC** is more selective than its corresponding diastereomer **SAL CH**.

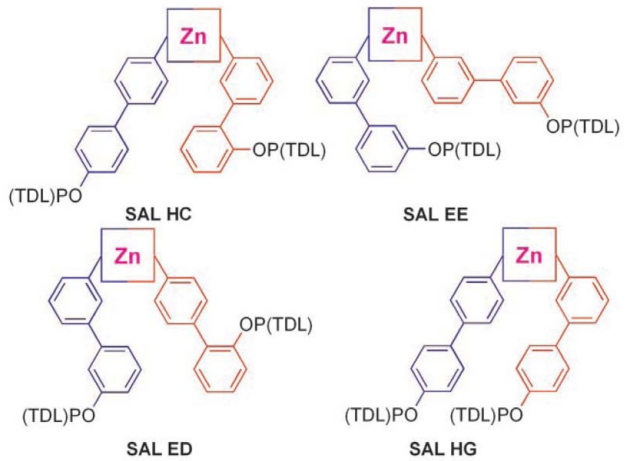
Table 2: {Rh^{I}Cl} and {Rh^{I}BF$_4$} catalyst precursors require different ligand scaffolds for the hydroboration of 2-methoxystyrene (**2a**).[a]

Ligand	[{Rh(nbd)Cl}$_2$]	[Rh(nbd)$_2$BF$_4$]
SAL DC	96 (98)	78 (96)
SAL HC	86 (94)	95 (98)
SAL CC	75 (88)	84 (97)
SAL CD	92 (94)	—
SAL CH	—	86 (97)
SAL DD	79 (90)	—
SAL HH	—	93 (94)

[a] Conditions: see Equation (1). The results listed indicate % *ee* (% α-isomer).

Prior studies have shown that the efficiency of rhodium-catalyzed asymmetric hydroboration is quite sensitive to steric and electronic factors in the substrate.[14] The availability of a range of different SAL scaffolds proves useful for the rapid optimization of different catalysts for individual substrates. High regio- and enantioselectivity can be obtained for each substrate within the series of *ortho*-substituted styrene derivatives **2a–e** using in situ generated [(**SAL XY**)Rh(nbd)BF$_4$] catalysts derived from the subunits **1A–H**.[15] The best results for each substrate are highlighted in Table 3 (entries in boldface); these results are for preparative reactions run on a 1-mmol or greater scale. The regio-and enantioselectivities found in preparative reactions are similar to those obtained under the screening conditions (± 1–2%); the yields of isolated product range from 82–98%. For comparison, Table 3 also gives the results achieved using two equivalents of (TDL)POPh (53–81 % *ee*), the monodentate chiral phosphite moiety present in

Table 3: Different ligand scaffolds are used to achieve optimal results for substrates **2a–e** with [(**SAL XY**)Rh(nbd)BF$_4$] catalysts.[a]



Ligand	3a (R = OMe)	3b (R = Me)	3c (R = CF3)	3d (R= Cl)	3e (R= F)
SAL HC	**94 (99)**[b]	87 (86)	66 (66)	78 (96)	76 (88)
SAL EE	66 (93)	**91 (95)**[b]	76 (49)	73 (87)	**91 (92)**[b]
SAL ED	75 (96)	85 (93)	**91 (95)**[b]	68 (67)	68 (78)
SAL HG	91 (95)	87 (81)	53 (72)	**93 (92)**[b]	77 (73)
(TDL)POPh	81 (91)	73 (78)	69 (73)	77 (83)	53 (76)
literature[c]	82 (99)	92 (93)	83 (97)	69 (93)	72 (92)

[a] Conditions: see Equation (1).The results indicate % *ee* (% α-isomer). [b] Reaction run on a 1-mmol scale. [c] The best results previously reported for each substrate; see reference [7] for details.

each SAL, as well as the best results previously reported for each substrate. For substrates **2a** (R = OMe) and **2c–e** (R = CF_3, Cl, F), the SAL identified is the most selective catalyst reported to date. For **2b** (R = Me), the best SAL and literature results are nearly equivalent.

The importance of the heterodimeric zinc complex as a structural element for the SALs is further illustrated by comparing three diastereomeric ligands derived from (*S*,*S*)and (*R*,*R*)-**1E**. Even though the ligating groups and tethers are identical in all three zinc complexes, the results obtained in the hydroboration of 2-methylstyrene (**2b**) vary significantly. In contrast to the (*SS*,*RR*)-heterodimer, **SAL EE** (91% *ee*,95% α-**3b**), the diastereomeric (*SS*,*SS*)- and (*RR*,*RR*)-homodimers, that is, [{(*S*,*S*)-1E}$_2$Zn] and [{(*R*,*R*)1E}$_2$Zn], exhibit low reactivity and lower selectivity: 87% *ee* (84% α-**3b**) and 79% *ee* (82 % α-**3b**), respectively.

In summary, a series of TADDOL phosphite-bearing SALs, readily prepared in combinatorial arrays by chirality-directed self-assembly, provides a focused ligand library for Rh^I-catalyzed hydroboration. These SALs exhibit the unique feature of achieving high enantioselectivity through the subtle manipulation ofthe chiral catalytic pocket by small systematic changes in the ligand scaffold, an approach not available with classic ligand designs. The ligands differ only in scaffold structure, yet the enantioselectivity obtained in catalytic asymmetric hydroboration of 2-methoxystyrene varies from 96% *ee* favoring the *R*-configuration to 30 % ee favoring *S*. {Rh^ICl} and {Rh^IBF_4} catalyst precursors and different substrates require different ligand scaffolds to achieve success. Nevertheless, {(**SAL XY**)Rh^I} catalysts afford high regioselectivity (92–99% α3) and enantioselectivity (91–96% *ee*) across a series of ortho-substituted styrenes varying in electronic character and steric demand. Thus, a facile method of self-assembly is exploited to fine tune catalysts by ligand scaffold optimization, improving substrate generality in a reaction that has thus far exhibited rather limited substrate scope. Studies directed toward understanding the structural basis for the wide variation in selectivity as a function of ligand scaffold (i.e. the structure–activity relationship of these ligands) are in progress.

Experimental Section

[(**SAL HC**)Rh(nbd)BF_4]-catalyzed asymmetric hydroboration of 2-methoxystyrene: A solution of [{(*S*,*S*)-**1H**}$_2$Zn] (10.0 mg, 1.4×10^{-2} mmol) and [{(*R*,*R*)-**1C**}$_2$Zn] (10.0 mg, 1.4×10^{-2} mmol) in CH_2Cl_2 (10 mL) was stirred at ambient temperature (10 min), and then a solution of [Rh(nbd)$_2BF_4$] (9.7 mg, 2.6×10^{-2} mmol) in CH_2Cl_2 (5 mL) was added. The resulting mixture was stirred at ambient temperature (0.5 h), after which the volatile solvent was removed under vacuum. The residue was dissolved in DME (10 mL), stirred (0.5 h), and then a solution of 2-methoxystyrene (**2a**, 174.0 mg, 1.30 mmol) in DME (2.0 mL) and powdered 4-Å molecular sieves (ca. 0.5 g) were added. The resulting mixture was cooled (0 °C) and a solution of pinacolborane (199.0 mg, 1.56 mmol) in DME (4.0 mL) added dropwise. The reaction mixture was gradually warmed to room temperature and stirred (12 h). Afterwards, the mixture was again cooled (0 °C) and quenched by the addition of MeOH (10 mL), NaOH(aq) (3.0 m, 15 mL), and H_2O_2 (aq) (1 mL of a 30% solution). The ice bath was removed, and the resulting mixture stirred (3 h, RT) and then filtered. The filtrate was extracted with diethyl ether (3 × 15 mL) and the combined organics were dried (anhydrous Na_2SO_4), filtered, and concentrated. Chromatography on silica (10% 1:9 EtOAc/Hex) gives 1-(2-methoxyphenyl)ethanol (**3a**, 194 mg, 98%) as a clear oil: capillary GC analysis (J&W Scientific 30m × 0.25mm ID Cyclosil *β*, 120 °C (1 min hold) to 130° at 18 min^{-1} then to 165° at 28 min^{-1}) found peaks at 21.19 (97.2%, (*R*)-**3a**) and 23.55 (2.8%, (*S*)-**3a**); ^{1}H NMR (400 MHz, $CDCl_3$): δ =7.39 (1H, dd, J =7.5, 1.4 Hz), 7.37–7.26 (1H, dt, J =8.2, 1.6 Hz), 7.00 (1 H, t, J =7.5 Hz), 6.90 (1 H, d, J =8.2 Hz), 5.15–5.11 (1H, q, J =13.0, 6.5 Hz), 3.88 (3H, s) 1.53 ppm (3H, d, J =6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 133.6, 128.2, 126.1, 120.8, 110.4, 66.4, 55.3, 23.0 ppm; $[\alpha]_D^{25}$ = +25.8° (c =1.4 g(100mL)$^{-1}$, $CHCl_3$).

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[10] (*SS*,*RR*)-**SAL DC** was combined with [{Rh(nbd)Cl}$_2$] to generate the heterobimetallic complex [(**SAL DC**)Rh(nbd)Cl]. Its ^{31}P NMR spectrum, obtained after addition of a stoichiometric amount of 1,10-phenanthroline (see reference [2i]), shows a doublet at δ = 112.8 ppm ($J_{P,Rh}$ = 250 Hz)

[11] In contrast to the results found using pinacol borane, the use of catechol borane gave low levels of asymmetric induction.

[12] The regioselectivity also varies as a function of SAL scaffold structure, but to a lesser extent (70–99% α-**3**), with {Rh^{I}BF$_4$} catalysts generally affording higher regioselectivity. We find no strong correlation between regio- and enantioselectivity, however, there seems to be a loose correlation between enantioselectivity and conversion/yield under the conditions examined.

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[15] While [Rh(nbd)$_2$BF$_4$] is an effective catalyst precursor, other complexes can give comparable or superior results for substrates in Table 3. For example, slightly higher enantioselectivity can be obtained for 2-methoxystryene (96 % *ee*, 98% α-**3a**) using [{Rh(nbd)Cl}$_2$] and SAL (*SS*,*RR*)-**SAL DC** and for 2 (trifluoromethyl)styrene (94% *ee*, 92% α-**3c**) using [Rh(cod)$_2$OTf] using (*SS*,*RR*)-**SAL CH**.

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Exploiting self-assembly for ligand scaffold optimization: "Substrate-tailored" ligands for catalytic asymmetric hydroboration.

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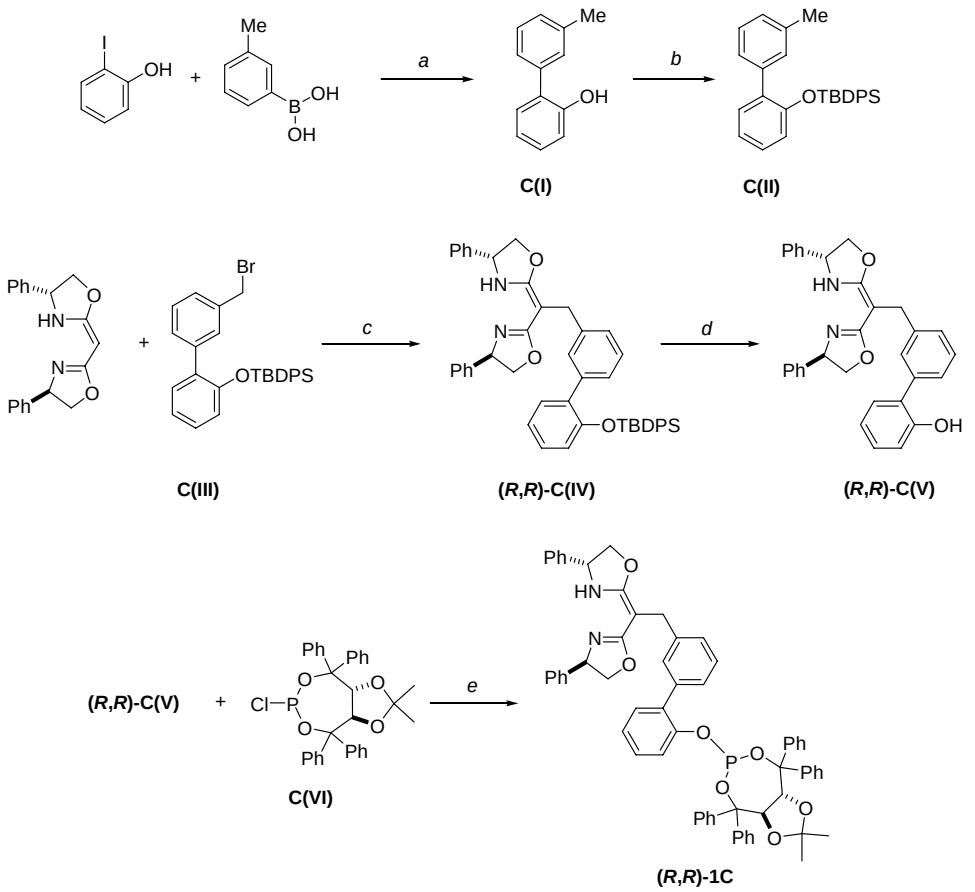
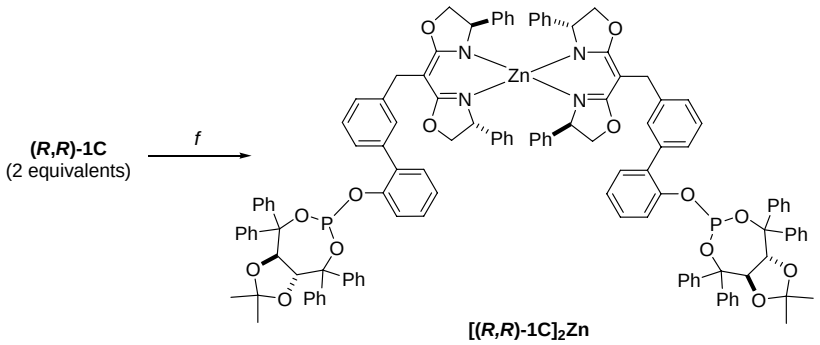
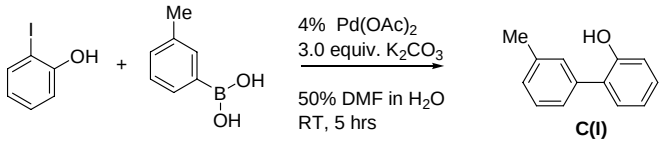
All reactions are carried out under an atmosphere of dry nitrogen and use dry, degassed solvents unless noted otherwise. All solvents, 2-susbtituted styrene derivatives, PCl_3 (99.999%), and pinacolborane were obtained from Aldrich Chemicals and used without further purification. For the hydroboration reaction, DME (Aldrich) was stored over activated 4A sieves and used without further purification. THF was distilled from sodium/benzophenone prior to use. $[Rh(cod)Cl]_2$ was purchased from Strem Chemicals, Inc. $Rh(nbd)_2BF_4$ was purchased from Alfa Aesar. NMR spectra were recorded on 300 or 400 MHz Bruker Avance NMR spectrometers.

The syntheses of (*R*,*R*)- and (*S*,*S*)-**1A-H** follow the route illustrated by the preparation of the homodimer [(*R*,*R*)-**1C**]$_2$Zn via the following scheme.





a) 4% $Pd(OAc)_2$, 3.0 equiv. K_2CO_3, 1:1 DMF:H_2O, RT 5 h. *b*) 1.1 equiv. TBDPSCl, 4.0 equiv. imidazole, DMF, 0°C to RT, 12 h. *c*) 1) 1.0 equiv. NaHMDS, THF, -78 °C, 2 h, 2) 1.0 equiv. **C(III)**, -78 °C to RT, 12h. *d*) 1.0 equiv. TBAF, THF, RT, 10 h. *e*) 1.2 equiv. (*R*)-**C(VI)**, 20 equiv. TEA, 5% DMAP, THF, RT, 12h. *f*) 1.0 equiv. $Zn(OAc)_2$, 1:1 DCM:MeOH, RT, 5 min.



***a*. Preparation of C(I) (*adapted from the procedure of Cowart, et al.*)[1].** To a 500 mL round-bottom flask was added 2-iodophenol (11.0 g, 50.0 mmol), 3-toluyl boronic acid (7.48 g, 55.0 mmol), and palladium acetate (0.455 g, 2.03 mmol). The mixture was dissolved in DMF (150 mL) and stirred at room temperature. Potassium carbonate (20.7 g, 150 mmol) was dissolved in 150 mL of degassed water, and then added via cannula transfer. The resulting mixture was stirred at room temperature (5 h). Afterwards, the mixture was extracted ethyl acetate (3 x 100 mL) and the combined organic layers dried (anhydrous magnesium sulfate) and concentrated via rotovap. The residue was chromatographed on flash silica (ca 150 g, 10 % ethyl acetate in hexanes) giving **C(I)** (8.90 g, 96 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.35 (1H, m), 7.32-7.25 (5H, m), 7.05-7.00 (2H, m), 2.46 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 139.1, 137.2, 130.3, 130.0, 129.9, 129.3, 129.1, 128.7, 126.2, 120.9, 115.9, 21.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M+), 184.0888; found, 184.0886 *m/z*.

D(I) (8.30 g, 90 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.38 (2H, m), 7.34-7.30 (2H, m), 7.28-7.25 (2H, m), 7.03-6.99 (2H, m), 2.45 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 137.7, 134.3, 130.4, 130.1, 129.1, 129.1, 128.3, 121.0, 116.0, 21.3 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M+), 184.0888; found, 184.0893 *m/z*.

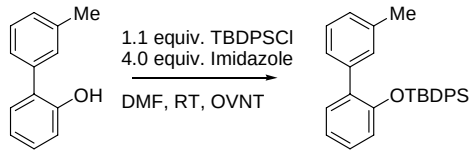
E(I) (9.10 g, 98 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.26 (4H, m), 7.21-7.18 (2H, m), 7.09-7.07 (1H, dd, *J* = 4.1 Hz, 2.4 Hz), 6.86-6.81 (1H, ddd, *J* = 13.6, 2.5, 0.9 Hz), 2.42 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.8, 143.2, 140.8, 138.5, 130.1, 128.8, 128.4, 128.0, 127.0, 124.3, 120.0, 114.3, 21.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M+), 184.0888; found, 184.0882 *m/z*.

G(I) (9.00 g, 97 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (2H, d, *J* = 8.6 Hz),

[1] M. Cowart, R. Faghih, M. P. Curtis, G. A. Gfesser, Y. L. Bennani, L. A. Black, L. Pan, K. C. Marsh, J. P. Sullivan, T. A. Esbenshade, G. B. Fox, A. A. Hancock , *J. Med. Chem.* **2005**, *48*, 38-55.

7.39-7.28 (3H, m), 6.92 (2H, d, *J* = 8.7 Hz), 2.44 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 140.8, 138.6, 134.4, 128.9, 128.7, 127.8, 127.7, 124.0, 115.9, 21.7 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M+), 184.0888; found, 184.0886 *m/z*.

H(I) (8.10 g, 88 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (4H, t, *J* = 8.7 Hz), 7.25 (2H, d, *J* = 7.9 Hz), 6.92 (2H, d, *J* = 8.7 Hz), 2.41 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 137.9, 136.5, 134.1, 129.5, 128.2, 126.6, 115.6, 21.1 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{13}H_{12}O$ (M+), 184.0888; found, 184.0883 *m/z*.



C(I) **C(II)**

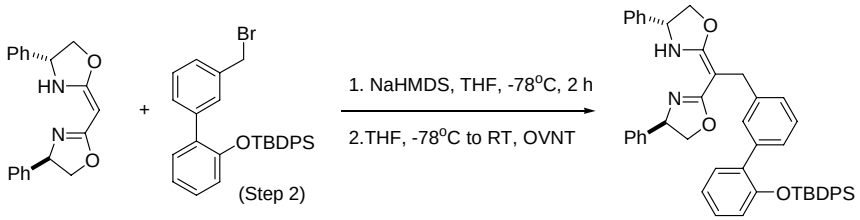
***b*. Preparation of C(II).** To a cooled (0 ^{o}C) solution of **C(I)** (8.50 g, 46.1 mmol) and imidazole (9.35 g, 137 mmol) in DMF (130 mL) was added TBDPSCl (14.2 mL, 55.0 mmol) dropwise over 15 minutes. Upon complete addition, the cooling bath was removed and solution was stirred at ambient temperature overnight. Afterwards, water (ca 50 mL) was added the mixture extracted ether (3 x 100 mL). The combined organic layers were dried (anhydrous magnesium sulfate), filtered and concentrated via rotovap. The residue was chromatographed on flash silica (ca 150 g, 5.0 % ethyl acetate in hexanes) to give **C(II)** (18.3 g, 98 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68-7.63 (4H, dd, *J* = 9.6, 1.9 Hz), 7.46-7.28 (10H, m), 7.18 (1H, d, *J* = 7.2 Hz), 6.96-6.88 (2H, m), 6.54-6.50 (1H, dd, *J* = 7.7, 1.5 Hz), 2.43 (3H, s), 0.88 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5, 139.1, 137.2, 135.6, 134.9, 133.2, 133.0, 130.9, 129.9, 129.3, 128.0, 127.8, 127.6, 126.9, 121.3, 119.8, 26.3, 21.6, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2217 *m/z*.

D(II) (17.5 g, 93 %) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69-7.66 (4H, dd, *J* = 9.6 Hz, 1.8 Hz), 7.45-7.36 (11H, m), 6.96-6.86 (2H, m), 6.57-6.51 (1H, dd, *J* = 7.9, 1.3 Hz), 2.45 (3H, s), 0.89 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 136.4, 135.6, 135.3, 134.9, 133.0, 130.9, 129.9, 129.8, 129.7, 128.7, 127.8, 121.3, 119.9, 26.7, 21.4, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2215 *m/z*.

E(II) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (4H, dd, *J* = 7.9 Hz, 1.3 Hz), 7.49-7.38 (6H, m), 7.25 (1H, d, *J* = 7.8 Hz), 7.20-7.10 (5H, m), 6.98 (1H, t, *J* = 2.0 Hz), 6.80-6.75 (1H, ddd, *J* = 8.0, 2.4, 1.0 Hz), 2.38 (3H, s), 1.16 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.0, 142.5, 140.9, 138.2, 135.7, 133.1, 130.0, 129.5, 129.4, 128.6, 128.0, 127.9, 124.2, 120.0, 118.7, 118.6, 26.7, 21.5, 19.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSiLi$ $[(M+Li)^+]$, 429.2226; found, 429.2216 *m/z*.

G(II) (17.9 g, 95 %) as clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (4H, dd, *J* = 7.9 Hz, 1.4 Hz), 7.48-7.30 (11H, m), 7.10 (1H, d, *J* = 7.0 Hz), 6.87-6.82 (2H, dd, *J* = 9.6, 2.4 Hz), 2.40 (3H, s), 1.15 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.2, 140.8, 138.2, 135.6, 134.1, 133.0, 129.9, 128.6, 127.9, 127.8, 127.5, 127.4, 123.8, 119.9, 26.6, 21.6, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSi$ [(M+)], 429.2066; found, 429. 2070 *m/z*.

H(II) (16.3 g, 87 %) as white solid: mp 105-106 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.73 (5H, m), 7.48-7.39 (9H, m), 7.20 (2H, d, *J* = 7.9 Hz), 6.87-6.81 (2H, dd, *J* = 6.5, 2.0 Hz), 2.37 (3H, s), 1.15 ppm (9H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.0, 138.0, 135.6, 134.9, 130.0, 129.7, 129.4, 127.9, 127.8, 127.7, 126.6, 119.9, 26.6, 21.1, 19.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{29}H_{30}OSi$ [(M+)], 429.2066; found, 429. 2079 *m/z*.



C(III) **C(IV)**

***c*. Preparation of (*R*,*R*)-C(IV). Step *i*: Preparation of bromide C(III).** A solution of **C(II)** (5.50 g, 13.6 mmol), NBS (2.42 g, 13.6 mmol) and AIBN (111 mg, 0.68 mmol) dry benzene (100 mL) was heated at reflux for 6 hours. The reaction was monitored by TLC for disappearance of starting material. Afterwards, the reaction mixture was cooled to room temperature during which time a solid separates. The mixture is filtered and the filtrate concentrated via rotovap. Hexane was added to the residue and the resulting precipitates were removed via filtration. The filtrate was concentrated via rotovap to give bromide **C(III)**, which was used without further purification.

Step *ii*: Preparation of substituted box derivative (*R*,*R*)-C(IV). To a stirred, cooled (-78 °C) solution of 2,2'-methylenebis[(4*R*)-4-phenyl-4,5-dihydro-2-oxazole] (4.00 g, 13.1 mmol) in dry THF (10 mL) was added dropwise a solution of sodium bis(trimethylsilyl) amide (13.1 mL of a 1.0 *M* solution in THF, 13.1 mmol). The resulting mixture was stirred (-78 °C, 2 h) then a solution of crude bromide **C(III)** (ca. 13.6 mmol) in a dry THF (15 mL) was added dropwise. The resulting reaction mixture was allowed to slowly warm to room temperature and stirred for a total of 12 h. The reaction was quenched by the addition of satd aq. NH_4Cl and extracted with CH_2Cl_2 (2 x 120 mL). The combined organic extracts were washed with brine, dried (Na_2SO_4) and concentrated via rotovap. Flash chromatography on silica (95:5 CH_2Cl_2:MeOH) affords **(*R*,*R*)-C(IV)** (7.78 g, 82 %) as a colorless solid: mp 89-90 °C; $[\alpha]_D^{25}$ = +24.2 (c = 0.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56-7.54 (2H, m), 7.45-7.22 (17H, m), 7.08 (2H, dd, *J* = 7.9, 7.8 Hz), 6.92-6.90 (2H, m), 6.57-6.54 (2H, m), 5.28 and 5.20 (2H, overlapping t, *J*= 10.0, 10.0 Hz), 4.68 and 4.65 (2H, overlapping dd, *J*= 10.1, 10.1 Hz), 4.17 (1H, dd, *J* = 8.2, 8.1 Hz), 4.13-4.08 (2H, m), 3.57-3.46 (2H, m), 0.87 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 152.5, 142.2, 139.5, 137.7, 135.5, 132.91, 132.88, 132.85, 130.9, 130.6, 129.9, 128.9, 128.7, 128.6, 128.13, 128.07, 127.8, 127.63, 127.57, 126.8, 126.7, 126.5, 121.3, 119.8, 75.5, 75.2, 69.72, 69.70, 41.5, 36.0, 26.34, 19.4 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ [$(M+H)^+$], 727.3356; found, 727.3349 *m/z*.

(*R*,*R*)-D(IV) (8.11 g, 85 %) as a colorless solid: mp 84-85 °C; $[\alpha]_D^{25}$ = +28.0 (c = 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.65 (5H, m), 7.63-7.58 (2H, m), 7.44-7.24 (14H, m), 7.12 (2H, dd, *J* = 8.1, 8.0 Hz), 6.97-6.87 (2H, m), 6.55 (1H, dd, *J* = 8.0, 7.9 Hz), 5.28 and

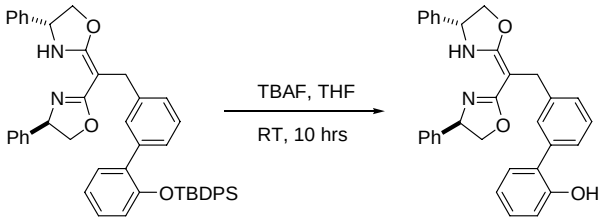
5.22 (2H, overlapping t, *J*= 10.0, 10.0 Hz), 4.71 and 4.68 (2H, overlapping dd, *J*= 10.4, 10.3 Hz), 4.21 (1H, dd, *J* = 8.1, 8.1 Hz), 4.17-4.10 (2H, m), 3.59-3.51 (2H, m), 0.88 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.6, 152.6, 142.2, 142.2, 137.7, 136.7, 135.6, 132.91, 132.89, 132.7, 131.0, 130.2, 130.0, 128.9, 128.8, 128.1, 127.9, 127.7, 127.6, 126.8, 126.6, 121.4, 120.0, 75.5, 75.3, 69.80, 69.78, 41.6, 35.9, 26.5, 19.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ [$(M+H)^+$], 727.3356; found, 727.3373 *m/z*.

(*R*,*R*)-E(IV) (8.32 g, 88 %) as a colorless solid: mp 82-83 ^oC; $[\alpha]_D^{25}$ = +21.0 (c = 1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (4H, m), 7.49-7.22 (19H, m), 7.17-7.08 (2H, m), 7.01-6.96 (2H, m), 6.76 (1H, dd, *J* = 7.9, 7.8 Hz), 5.25-5.19 (2H, m), 4.67 and 4.65 (2H, overlapping dd, *J*= 10.1, 10.3 Hz), 4.17 (1H, dd, *J* = 8.2, 8.2 Hz), 4.08-4.01 (2H, m), 3.50-3.38 (2H, m), 1.16 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.49, 165.46, 156.0, 142.1, 142.0, 141.1, 138.4, 135.69, 135.66, 133.0, 130.1, 129.6, 129.0, 128.9, 128.8, 128.7, 128.1, 128.0, 127.7, 127.6, 126.74, 126.72, 126.5, 125.5, 120.0, 118.7, 75.5, 75.2, 69.74, 69.69, 41.5, 36.0, 26.7, 19.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ $(M+H)^+$, 727.3356; found, 727.3342 *m/z* [$(M+H)^+$].

(*S*,*S*)-E(IV) (8.18 g, 86 %) as a colorless solid: mp 82-83 ^oC; $[\alpha]_D^{25}$ = -20.1 (c = 2.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.75 (4H, m), 7.48-7.22 (19H, m), 7.15-7.06 (2H, m), 7.01-6.95 (2H, m), 6.76 (1H, dd, *J* = 7.9 Hz, 7.9 Hz), 5.26-5.20 (2H, m), 4.67 and 4.64 (2H, overlapping dd, *J*= 10.2, 10.2 Hz), 4.18 (1H, dd, *J* = 8.3, 8.3 Hz), 4.08-4.00 (2H, m), 3.51-3.38 (2H, m), 1.15 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.51, 165.47, 156.0, 142.2, 142.1, 141.2, 138.5, 135.7, 135.7, 133.0, 130.1, 129.6, 129.5, 129.0, 128.9, 128.8, 128.7, 128.2, 128.0, 127.7, 127.6, 126.8, 126.5, 125.5, 120.0, 118.7, 75.5, 75.2, 69.8, 69.7, 41.6, 36.0, 26.7, 19.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ $(M+H)^+$, 727.3356; found, 727.3349 *m/z* [$(M+H)^+$].

(*R*,*R*)-G(IV) (8.51 g, 89 %) as a colorless solid: mp 91-92 ^oC; $[\alpha]_D^{25}$ = +20.2 (c = 1.8, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.73 (5H, m), 7.49-7.18 (19H, m), 7.17-7.08 (2H, m), 7.05-6.96 (2H, m), 6.69 (1H, d, *J* = 8.4 Hz), 5.26-5.15 (2H, m), 4.69 and 4.61 (2H, overlapping dd, *J*= 10.0, 10.3 Hz), 4.15 (1H, dd, *J* = 7.9, 7.9 Hz), 4.10-4.03 (2H, m), 3.53-3.40 (2H, m), 1.16 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (2C), 155.3, 142.13, 142.05, 141.1, 138.5, 135.6, 133.9, 133.0, 130.1, 129.0, 128.9, 128.8, 128.7, 128.0, 127.9, 127.7, 127.65, 127.63, 127.5, 126.74, 126.72, 120.1, 75.5, 75.2, 69.73, 69.68, 41.5, 36.1, 26.7, 19.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ [$(M+H)^+$], 727.3356; found, 727.3361 *m/z*.

(*S*,*S*)-H(IV) (8.54 g, 79 %) as a colorless solid: mp 96-98 ^oC; $[\alpha]_D^{25}$ = -30.8 (c = 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80-7.78 (4H, m), 7.49-7.17 (19H, m), 6.96-6.94 (2H, m), 6.89-6.87 (2H, m), 5.32 and 5.19 (2H, overlapping t, *J*= 10.0, 10.1 Hz), 4.69 and 4.66 (2H, overlapping dd, *J*= 8.5, 8.5 Hz), 4.19 (1H, dd, *J* = 8.2, 8.2 Hz), 4.12-4.05 (2H, m), 3.52-3.39 (2H, m), 1.15 ppm (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.4, 155.3, 142.2, 142.0, 139.4, 136.4, 135.7, 133.7, 133.0, 130.1, 129.6, 128.8, 128.7, 128.0, 127.9, 127.7, 127.6, 126.9, 126.8, 126.7, 120.2, 75.5, 75.2, 69.73, 69.70, 41.5, 35.6, 26.8, 19.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{48}H_{47}N_2O_3Si$ [$(M+H)^+$], 727.3356; found, 727.3351 *m/z*.



C(IV) **C(V)**

***d*. Preparation of (*R*,*R*)-C(V).** To a solution of (*R*,*R*)-**C(IV)** (8.00 g, 11.0 mmol) dry THF (100 mL) was added dropwise tetrabutylammonium fluoride (TBAF, 11.0 mL of a 1.0 *M* solution in THF, 11.0 mmol). After 10 h, the mixture was partitioned between CH_2Cl_2 (80 mL)-water (80 mL). The organic layer was dried (Na_2SO_4) and concentrated. Chromatography on silica gel (90:10 CH_2Cl_2:MeOH) gave **(*R*,*R*)-C(V)** (4.90 g, 91%) as a colorless solid: mp 124-126 ^{0}C; $[\alpha]_D^{25}$ = 18.8 (c = 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.20 (14H, m), 7.02-6.96 (4H, m), 5.24 and 5.20 (2H, overlapping t, *J* = 10.8, 10.8 Hz), 4.71 and 4.66 (2H, overlapping dd, *J* = 8.5, 8.5 Hz), 4.19 (1H, dd, *J* = 8.2, 8.1 Hz), 4.14-4.07 (2H, m), 3.55-3.43 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.7, 153.3, 141.9, 141.8, 138.3, 138.2, 130.4, 130.0, 129.1, 128.81, 128.77, 128.71, 128.2, 128.1, 127.8, 127.7, 127.6, 126.72, 126.69, 120.3, 116.3, 75.5, 75.3, 69.4 (2C), 41.3, 35.8 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ [$(M+H)^+$], 489.2178; found, 489.2180 *m/z*.

(*R*,*R*)-D(V) (5.17 g, 96%) as a colorless solid: mp 120-122 ^{0}C; $[\alpha]_D^{25}$ = 18.7 (c = 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.50-7.41 (4H, dd, *J* = 19.6, 8.1 Hz), 7.36-7.19 (10H, m), 7.04 (2H, dd, *J* = 7.8, 7.0 Hz), 7.01 (1H, dd, *J* = 8.6, 8.4 Hz), 6.93 (1H, d, *J* = 8.0 Hz), 5.27-5.21 (2H, m), 4.74 and 4.68 (2H, overlapping dd, *J* = 8.5, 8.3 Hz), 4.22 (2H, dd, *J* = 8.2, 8.1 Hz), 4.13 (1H, dd, *J* = 8.5, 8.5 Hz), 3.54-3.43 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.9, 153.7, 141.8, 141.7, 136.9, 136.5, 130.5, 129.5, 129.3, 128.82, 128.78, 128.6, 128.2, 127.8, 127.7, 126.8, 126.7, 120.2, 116.3, 75.6, 75.4, 69.41, 69.38, 41.3, 35.6 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ [$(M+H)^+$], 489.2178; found, 489.2170 *m/z*.

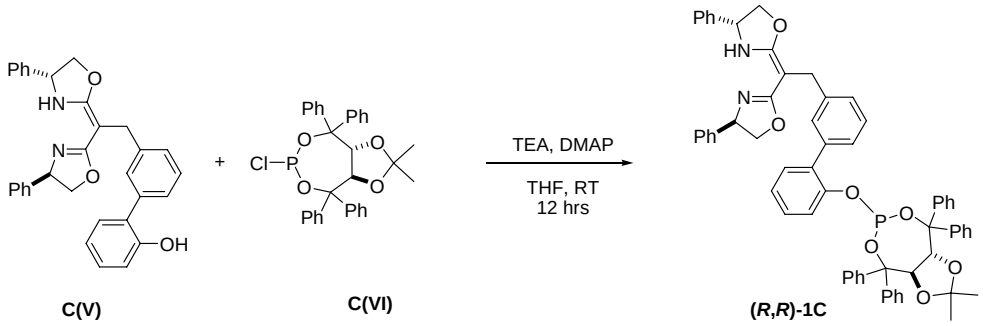
(*R*,*R*)-E(V) (5.00 g, 93%) as a colorless solid: mp 113-114 ^{0}C; $[\alpha]_D^{25}$ = 22.5 (c = 1.1, CH_2Cl_2); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.54 (1H, s), 7.44 (1H, d, *J* = 7.6 Hz), 7.36-7.11 (12H, m), 7.05-7.03 (2H, m), 6.97-6.94 (2H, m), 6.66 (1H, dd, *J* = 8.2, 8.0 Hz), 5.26-5.20 (2H, m), 4.72-4.66 (2H, m), 4.23-4.17 (2H, m), 4.09 (1H, dd, *J* = 8.0, 8.0 Hz), 3.56-3.43 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.1 (2C), 157.4, 142.3, 141.7, 141.6, 141.5, 137.9, 129.6, 129.0, 128.9, 128.8, 128.0, 127.8, 127.7, 126.72, 126.68, 126.4, 125.8, 118.5, 114.64, 114.58, 75.7, 75.4, 69.3, 69.2, 41.4, 35.8 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ [$(M+H)^+$], 489.2178; found, 489.2165 *m/z*.

(*S*,*S*)-E(V) (5.00 g, 93%) as a colorless solid: mp 113-114 ^{0}C; $[\alpha]_D^{25}$ = -19.3 (c = 1.3, CH_2Cl_2); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.53 (1H, s), 7.45 (1H, d, *J* = 7.6 Hz), 7.36-7.10 (12H, m), 7.05-7.02 (2H, m), 6.97-6.94 (2H, m), 6.67 (1H, dd, *J* = 8.7, 8.1 Hz), 5.25-5.20 (2H, m), 4.72-4.67 (2H, m), 4.23-4.16 (2H, m), 4.09 (1H, dd, *J* = 8.3, 8.3 Hz), 3.56-3.43 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.09, 166.07, 157.4, 142.3, 141.7, 141.6, 141.5, 137.9, 129.6, 129.0, 128.9, 128.8, 128.0, 127.8, 127.7, 126.73, 126.69, 126.4, 125.8, 118.5, 114.64, 114.59,

75.7, 75.4, 69.32, 69.25, 41.4, 35.8 ppm;. HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ [$(M+H)^+$], 489.2178; found, 489.2171 *m/z*.

(*R,R*)-G(V) (4.88 g, 91%) as a colorless solid: mp 110-111 ^{0}C; $[\alpha]_D^{25}$ = 29.8 (c = 0.7, CH_2Cl_2); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.45-7.43 (2H, m), 7.37-7.20 (13H, m), 6.99-6.96 (2H, m), 6.65 (2H, dd, *J* = 8.4, 8.4 Hz), 5.27-5.22 (2H, m), 4.75-4.69 (2H, m), 4.24 and 4.20 (2H, overlapping dd, *J* = 8.2, 7.8 Hz), 4.13 (1H, dd, *J* = 8.5, 8.5 Hz), 3.54-3.47 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 166.1, 156.7, 141.7, 141.5, 141.4, 137.9, 132.1, 129.0, 128.9, 128.8, 128.1, 127.9, 127.8, 127.3, 127.2, 126.8, 126.7, 125.3, 115.9, 75.6, 75.5, 69.3, 69.2, 41.4, 35.9 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ [$(M+H)^+$], 489.2178; found, 489.2176 *m/z*.

(*S,S*)-H(V) (5.10 g, 95%) as a colorless solid: mp 129-130 ^{0}C; $[\alpha]_D^{25}$ = -33.8 (c = 2.0, CH_2Cl_2); ^{1}H NMR (400 MHz,$CDCl_3$) δ 7.38-7.30 (9H, m), 7.26-7.19 (5H, m), 7.01 (2H, dd, *J* = 8.8, 7.4 Hz), 6.46 (2H, d, *J* = 8.6 Hz), 5.30 and 5.24 (2H, overlapping t, *J*= 10.0, 10.1 Hz), 4.80 and 4.74 (2H, overlapping dd, *J*= 8.5, 8.5 Hz), 4.29 (1H, dd, *J* = 8.2, 8.2 Hz), 4.25 and 4.19 (2H, overlapping dd, *J* = 8.5, 8.5 Hz), 3.56-3.41 ppm (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.0, 165.9, 156.6, 141.6, 141.2, 139.6, 135.4, 131.6, 129.4, 129.1, 128.8, 128.7, 127.8, 127.7, 126.9, 126.7, 126.5, 116.1, 75.7, 75.5, 69.3, 69.2, 41.7, 35.3 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{32}H_{29}N_2O_3$ [$(M+H)^+$], 489.2178; found, 489.2167 *m/z*.



C(V) **C(VI)** **(*R,R*)-1C**

***e*. Preparation of (*R,R*)-1C (*adapted from the procedure of Kranich et al.*)** [2] **.** (*R,R*)-TADDOL)PCl ((*R*)-**C(VI)**) was prepared according to the published procedure.[3] To a solution of **(*R,R*)-C(V)** (300 mg, 0.61 mmol), Et_3N (1.70 mL, 12.2 mmol), and DMAP (3.7 mg, 0.03 mmol) in dry THF (15 mL) was added dropwise a solution of (*R,R*)-TADDOL)PCl ((*R*)-**C(VI)**) (389 mg, 0.73 mmol) in dry THF (7 mL). The resulting milky suspension was stirred at room temperature (ca. 12 h) and then filtered under nitrogen through a short pad of celite. The celite was washed with degassed THF and the combined filtrates concentrated to dryness on a vacuum line using care to insure the product is keep oxygen-free. Rapid chromatography of the residue on a short column of silica gel using degassed solvent (95:5 CH_2Cl_2:MeOH) afforded **(*R,R*)-1C** (482 mg, 80%) as a colorless solid: mp 131-132 ^{0}C; $[\alpha]_D^{25}$ = -105.5 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42-7.17 (36H, m), 7.04-6.98 (2H, m), 5.24-5.13 (2H, m), 5.07 (2H, s), 4.63-4.57 (2H, m), 4.12 (1H, dd, *J* = 8.1, 8.1 Hz), 4.04-4.00 (2H,

[2] R. Kranich, K. Eis, O. Geis, S. Mühle, J. W. Bats, H.-G. Schmalz. *Chem.Eur. J.* **2000**, *6*, 2874-2894.
[3] J. Sakaki, W. B. Schweizer, D. Seebach, *Helv. Chim. Acta* **1993**, *76*, 2654-2665.

m), 3.36 (2H, d, J = 8.1 Hz), 1.00 (3H, s), 0.36 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.53, 165.45, 148.8, 145.6, 145.2, 142.15, 142.10, 141.29, 141.26, 140.7, 138.5, 137.8, 134.4, 130.8, 130.6, 128.7, 128.65, 128.62, 128.5, 128.2, 128.1, 128.06, 127.8, 127.6, 127.51, 127.48, 127.45, 127.40, 127.32, 127.30, 127.2, 127.1, 127.0, 126.9, 126.7, 124.2, 122.3, 122.2, 113.1, 85.6 (d, J_{CP} = 8.0 Hz), 83.2, 82.2 (d, J_{CP} = 15.2 Hz), 81.0 (d, J_{CP} = 4.0 Hz), 75.3, 75.1, 69.6, 69.5, 41.2, 35.8, 27.2, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.4 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3830 *m/z*.

(*R*,*R*)-1D (461 mg, 77%) as a colorless solid: mp 138-139 ^{0}C; $[\alpha]_D^{25}$ = -158.0 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44-7.12 (36H, m), 7.04-7.02 (2H, m), 5.23-5.18 (2H, m), 5.10 (2H, s), 4.66-4.60 (2H, m), 4.17 (1H, dd, J = 8.2, 8.2 Hz), 4.12-4.05 (2H, m), 3.57-3.45 (2H, m), 0.98 (3H, s), 0.39 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.47, 149.0, 145.5, 145.2, 142.1, 142.0, 141.39, 141.36, 140.7, 136.7, 136.6, 134.03, 134.01, 130.8, 130.1, 128.7, 128.69, 128.66, 128.2, 128.1, 127.8, 127.76, 127.6, 127.53, 127.50, 127.29, 127.26, 127.17, 127.07 126.99, 126.72, 126.70, 124.2, 122.1, 122.0, 113.2, 86.0 (d, J_{CP} = 8.9 Hz), 83.3, 82.1 (d, J_{CP} = 14.5 Hz), 80.9 (d, J_{CP} = 4.5 Hz), 75.4, 75.2, 69.7, 69.6, 41.4, 35.6, 27.1, 25.8 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.9 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3840 *m/z*.

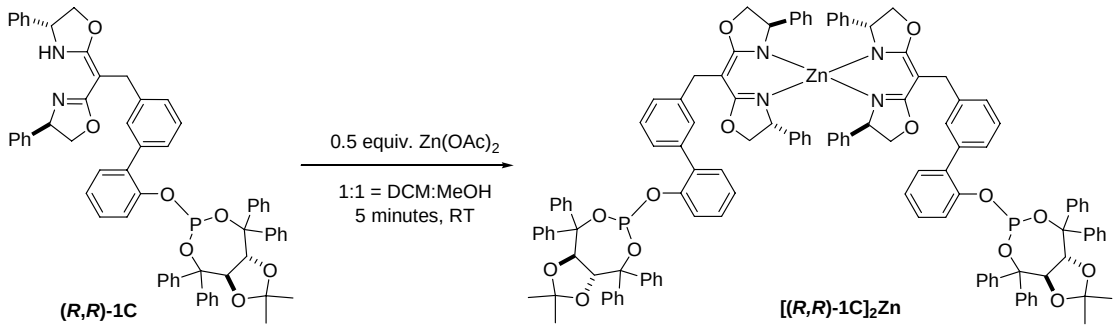
(*R*,*R*)-1E (527 mg, 88%) as a colorless solid: mp 125-126 ^{0}C; $[\alpha]_D^{25}$ = -75.2 (c = 0.6, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65-7.62 (2H, m), 7.58-7.51 (5H, m), 7.48 (3H, s), 7.38-7.15 (24H, m), 7.05-7.03 (2H, m), 6.73 (1H, s), 6.56 (1H, dd, J = 7.8, 1.2 Hz), 5.68 (1H, d, J = 8.3 Hz), 5.27 and 5.23 (2H, overlapping dd, J = 8.2, 8.2 Hz), 5.14 (1H, d, J = 8.3 Hz), 4.71 and 4.66 (2H, overlapping dd, J = 9.9, 9.6 Hz), 4.20 (1H, dd, J = 8.2, 5.6 Hz), 4.17-4.08 (2H, m), 3.59-3.48 (2H, m), 0.87 (3H, s), 0.69 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.44, 165.41, 152.5 (d, J_{CP} = 6.6 Hz), 146.0, 142.1, 142.0, 141.96, 141.4, 141.3, 140.7, 138.5, 129.3, 129.2, 128.9, 128.7, 128.65, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.16, 127.14, 126.9, 126.8, 126.7. 126.6, 126.4, 125.6, 121.9, 118.6, 118.5, 118.5, 118.4, 113.0, 86.6 (d, J_{CP} = 11.0 Hz), 85.2 (d, J_{CP} = 7.1 Hz), 82.3 (d, J_{CP} = 10.2 Hz), 80.2 (d, J_{CP} = 5.1 Hz), 75.4, 75.2, 69.7, 69.6, 41.5, 36.0 26.8, 26.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.0 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3835 *m/z*.

(*S*,*S*)-1E (540 mg, 90%) as a colorless solid: mp 123-124 ^{0}C; $[\alpha]_D^{25}$ = -74.0 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64-7.62 (2H, m), 7.57-7.51 (7H, m), 7.47 (1H, s), 7.41-7.16 (24H, m), 7.05-7.03 (2H, m), 6.72 (1H, s), 6.56 (1H, dd, J = 7.8, 1.2 Hz), 5.67 (1H, d, J = 8.3 Hz), 5.27 and 5.23 (2H, overlapping dd, J = 8.2, 8.2 Hz), 5.14 (1H, d, J = 8.3 Hz), 4.71 and 4.66 (2H, overlapping dd, J = 9.9, 9.6 Hz), 4.21 (1H, dd, J = 8.2, 5.6 Hz), 4.17-4.08 (2H, m), 3.59-3.48 (2H, m), 0.86 (3H, s), 0.65 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.44, 165.39, 152.5 (d, J_{CP} = 6.6 Hz), 146.0, 142.1, 142.04, 141.96, 141.4, 141.3, 140.7, 138.5, 129.5, 129.3, 129.1, 128.9, 128.7, 128.69, 128.65, 128.2, 128.1, 127.9, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 126.7. 126.6, 126.4, 125.6, 122.1, 121.9, 118.6, 118.5, 118.5, 118.4, 113.0, 86.6 (d, J_{CP} = 11.5 Hz), 85.2 (d, J_{CP} = 7.9 Hz), 82.3 (d, J_{CP} = 10.1 Hz), 80.2 (d, J_{CP} = 4.5 Hz), 75.4, 75.2, 69.7, 69.6, 41.5, 36.0 26.7, 26.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.0 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3833 *m/z*.

(*R*,*R*)-1G (500 mg, 83%) as a colorless solid: mp 134-135 ^{0}C; $[\alpha]_D^{25}$ = -98.5 (c = 0.4,

CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.63 (2H, m), 7.59-7.52 (7H, m), 7.46-7.22 (24H, m), 7.04-7.02 (2H, m), 6.59 (2H, d, *J* = 7.9 Hz), 5.65 (1H, d, *J* = 8.2 Hz), 5.28 (2H, m), 5.15 (1H, d, *J* = 8.3 Hz), 4.73-4.68 (2H, m), 4.19 (1H, dd, *J* = 8.2, 8.2 Hz), 4.16-4.09 (2H, m), 3.59-3.46 (2H, m), 0.85 (3H, s), 0.70 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5 (2C), 151.7 (d, J_{CP} = 5.6 Hz), 145.97, 145.93, 142.0, 141.97, 141.3, 140.9, 138.5, 136.0, 129.2, 129.0, 128.95, 128.8, 128.7, 128.67, 128.2, 128.1, 128.0, 127.8, 127.7, 127.6, 127.5, 127.4, 127.3, 127.2, 127.19, 127.17, 126.7, 126.67, 126.64, 126.4, 125.3, 120.1, 120.06, 113.1, 86.8 (d, J_{CP} = 11.7 Hz), 85.2 (d, J_{CP} = 6.9 Hz), 82.3 (d, J_{CP} = 9.9 Hz), 80.2 (d, J_{CP} = 5.2 Hz), 75.5, 75.2, 69.7, 69.6, 41.4, 36.0, 26.7, 26.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 136.4 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3789 *m/z*.

(*S*,*S*)-1H (572 mg, 95%) as a colorless solid: mp 139-141 ^{0}C; $[\alpha]_D^{25}$ = -87.5 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.65 (2H, m), 7.60-7.51 (8H, m), 7.47-7.21 (24H, m), 6.99-6.97 (2H, m), 6.65 (2H, d, *J* = 8.1 Hz), 5.66 (1H, d, *J* = 8.4 Hz), 5.30-5.23 (2H, m), 5.16 (1H, d, *J* = 8.3 Hz), 4.74 and 4.70 (2H, overlapping dd, *J* = 8.6, 8.5 Hz), 4.22 (1H, dd, *J* = 8.2, 8.2 Hz), 4.16-4.09 (2H, m), 3.57-3.44 (2H, m), 0.84 (3H, s), 0.71 ppm (3H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.3, 151.6 (d, J_{CP} = 5.4 Hz), 146.0, 142.1, 141.9, 141.3, 139.1, 136.7, 135.9, 129.6, 129.2, 128.9, 128.74, 128.71, 128.6, 128.2, 128.0, 127.8, 127.78 127.63, 127.60, 127.5, 127.4, 127.3, 127.2, 127.17, 127.0, 126.8, 126.7, 126.66, 126.4, 120.3, 120.2, 113.1, 86.8 (d, J_{CP} = 10.9 Hz), 85.1 (d, J_{CP} = 7.4 Hz), 82.3 (d, J_{CP} = 10.6 Hz), 80.2 (d, J_{CP} = 5.2 Hz), 75.5, 75.2, 69.7, 69.6, 41.4, 35.5, 26.7, 26.5 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.5 ppm; HRMS (FAB, 3-NBA matrix) calcd. for $C_{63}H_{56}N_2O_7P$ [$(M+H)^+$], 983.3825; found, 983.3813 *m/z*.



***f*. Preparation of [(*R*,*R*)-1C]$_2$Zn.** To a solution of (*R*,*R*)-**1C** (400 mg, 0.41 mmol) in dry degassed dichloromethane (5.0 mL) was added dropwise a solution of $Zn(OAc)_2$ (37.6 mg, 0.21 mmol) in dry degassed methanol (5.0 mL). The resulting solution was stirred at room temperature for ca. 5 minutes and then vacuum was applied to reduce a volume by approximately half. Dry degassed methanol (30.0 mL) was added to the resulting solution resulting in the formation of a milky suspension. This suspension was filtered and residue was washed with dry degassed methanol (3 x 7.0 mL). Residue was dried under vacuum (< 1 torr) to afford **[(*R*,*R*)-1C]$_2$Zn** (398 mg, 96 %) as a white solid: mp 161-162 ^{0}C; $[\alpha]_D^{25}$ = -175.9 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43-7.37 (14H, m), 7.30-7.18 (41H, m), 7.10-7.02, (14H, m), 6.83-6.79 (7H, m), 5.09-5.04 (4H, m), 4.51-4.42 (4H, m), 4.14-4.06 (4H, m), 3.78-3.53 (9H, m), 1.00 (6H, s), 0.36 ppm (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 171.3, 149.0, 145.7, 145.3, 144.6, 141.5, 141.46, 140.7, 137.6, 135.3, 130.9, 130.1, 129.6, 129.2, 128.8, 128.7, 128.6, 128.4, 128.2, 128.1, 127.9, 127.8, 127.7, 127.6, 127.5, 127.4, 127.36, 127.31, 127.25,

127.0, 126.99, 126.90, 126.7, 126.6, 124.2, 122.3, 122.2, 113.1, 85.8 (d, J_{CP} = 7.9 Hz), 83.1, 82.3 (d, J_{CP} = 14.8 Hz), 80.9 (d, J_{CP} = 3.8 Hz), 73.3, 68.0, 66.8, 66.4, 31.4, 27.2, 25.8, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.3 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [(M+H)$^+$], 2029.6863; found: 2029.6843 *m/z*.

[(*R*,*R*)-1D]$_2$Zn (366 mg, 88 %) as a white solid: mp 158-159 ^{0}C; $[\alpha]_D^{25}$ = -184.7 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45-7.04 (69H, m), 6.86-6.83 (7H, m), 5.09-5.08 (4H, m), 4.56-4.52 (4H, m), 4.21-4.17 (4H, m), 3.77-3.64 (10H, m), 0.94 (6H, s), 0.35 ppm (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 171.3, 149.0, 145.7, 145.3, 143.5, 141.5, 141.5, 141.4, 140.8, 135.07, 135.05, 134.9, 130.9, 129.4, 129.2, 128.87, 128.85, 128.79, 128.5, 128.3, 128.0, 127.8, 127.7, 127.59, 127.55, 127.50, 127.4, 127.3, 127.28, 127.1, 127.0, 126.7, 124.3, 122.4, 122.3, 113.2, 85.9 (d, J_{CP} = 8.9 Hz), 83.1, 82.3 (d, J_{CP} = 14.7 Hz), 80.8 (d, J_{CP} = 3.9 Hz), 73.3, 68.0, 66.9, 66.4, 31.2, 27.2, 25.8, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 134.6 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [(M+H)$^+$], 2029.6863; found: 2029.6839 *m/z*.

[(*R*,*R*)-1E]$_2$Zn (405 mg, 97 %) as a white solid: mp 164-165 ^{0}C; $[\alpha]_D^{25}$ = -204.3 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (5H, m), 7.76-7.53 (14H, m), 7.44-7.19 (42H, m), 7.12-7.06 (8H, m), 6.85-6.83 (7H, m), 5.70 (2H, d, *J* = 8.2 Hz), 5.17 (2H, d, *J* = 8.2 Hz), 4.61-4.56 (4H, m), 4.36-4.32 (4H, m), 3.85-3.73 (10H, m), 0.87 (6H, s), 0.71 ppm (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.4, 171.3, 152.5 (d, J_{CP} = 6.5 Hz), 146.04, 146.02, 145.99, 145.5, 145.4, 143.2, 141.4, 141.3, 140.0, 132.5, 130.1, 129.2, 128.8, 128.4, 128.35, 128.33, 128.2, 128.15, 128.0, 127.7, 127.5, 127.47, 127.42, 127.37, 127.31, 127.2, 127.18, 127.15, 126.7, 124.1, 122.1, 118.7, 118.6, 118.3, 118.2, 113.1, 86.6 (d, J_{CP} = 10.8 Hz), 85.2 (d, J_{CP} = 6.9 Hz), 82.3 (d, J_{CP} = 10.5 Hz), 80.3 (d, J_{CP} = 4.5 Hz), 73.5, 68.0, 66.90, 66.87, 31.6, 26.8, 26.4, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.3 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [(M+H)$^+$], 2029.6863; found: 2029.6854 *m/z*.

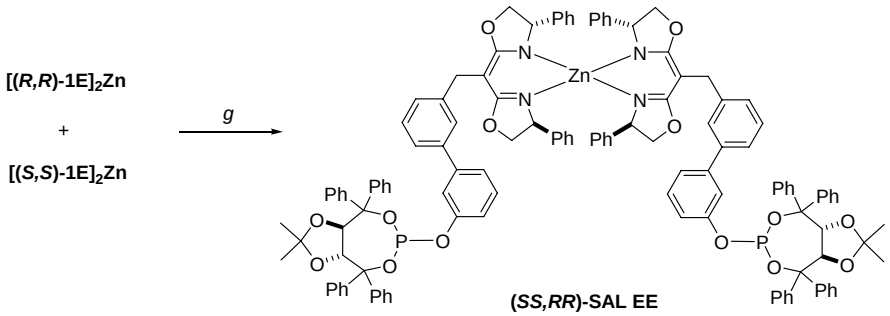
[(*S*,*S*)-1E]$_2$Zn (397 mg, 95 %) as a white solid: mp 163-165 ^{0}C; $[\alpha]_D^{25}$ = +99.0 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66-7.64 (5H, m), 7.76-7.53 (14H, m), 7.42-7.19 (36H, m), 7.10-7.05 (10H, m), 6.85-6.83 (8H, m), 5.70 (2H, d, *J* = 8.2 Hz), 5.17 (2H, d, *J* = 8.2 Hz), 4.63-4.56 (4H, m), 4.38-4.32 (4H, m), 3.83-3.73 (10H, m), 0.87 (6H, s), 0.71 ppm (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 171.3, 152.5 (d, J_{CP} = 6.4 Hz), 146.04, 146.01, 145.4, 144.7, 143.4, 143.2, 143.0, 141.4, 141.3, 140.2, 140.0, 129.2, 128.8, 128.7, 128.4, 128.2, 128.0, 127.9, 127.8, 127.7, 127.5, 127.46, 127.42, 127.3, 127.2, 127.18, 126.8, 126.7, 124.2, 124.0, 122.1, 118.6, 118.5, 118.2, 118.1, 113.1, 86.6 (d, J_{CP} = 10.8 Hz), 85.2 (d, J_{CP} = 6.9 Hz), 82.3 (d, J_{CP} = 10.5 Hz), 80.3 (d, J_{CP} = 4.5 Hz), 73.5, 68.0, 66.90, 66.86, 31.6, 26.8, 26.4, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.3 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [(M+H)$^+$], 2029.6863; found: 2029.6887 *m/z*.

[(*R*,*R*)-1G]$_2$Zn (401 mg, 96 %) as a white solid: mp 151-153 ^{0}C; $[\alpha]_D^{25}$ = -146.1 (c = 0.2, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61-7.54 (15H, m), 7.47-7.22 (43H, m), 7.11-7.04 (10H, m), 6.85 (8H, d, *J* = 6.7 Hz) , 5.67 (2H, d, *J* = 8.4 Hz), 5.43 (2H, d, *J* = 2.8 Hz), 5.18 (2H, d, *J* = 8.2 Hz), 4.63-4.57 (4H, m), 4.41-4.35 (4H, m), 3.86-3.79 (8H, m), 0.85 (6H, s), 0.70 ppm (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 171.3, 151.4 (d, J_{CP} = 10.5 Hz), 146.0, 145.6, 145.4, 141.4, 140.2, 137.1, 132.5, 130.1, 129.2, 129.16, 128.8, 128.4, 128.35, 128.33, 128.2, 128.18, 128.11, 128.0, 127.9, 127.8, 127.6, 127.4, 127.3, 127.2, 127.19, 127.0, 126.7, 123.9,

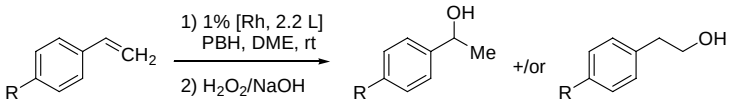
123.8, 120.1, 120.0, 119.94, 119.89, 113.2, 86.6 (d, J_{CP} = 11.0 Hz), 85.1 (d, J_{CP} = 6.9 Hz), 82.2 (d, J_{CP} = 10.5 Hz), 80.2 (d, J_{CP} = 4.8 Hz), 73.5, 68.0, 66.9, 66.8, 31.5, 26.6, 26.5, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.8 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [$(M+H)^+$], 2029.6863; found: 2029.6901 *m/z*.

[(*S*,*S*)-1H]$_2$Zn (388 mg, 93 %) as a white solid: mp 180-181 ^{0}C; $[\alpha]_D^{25}$ = +78.2 (c = 0.3, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62-7.54 (16H, m), 7.51-7.46 (6H, m), 7.45-7.25 (33H, m), 7.20-7.12 (14H, m), 6.94-6.88 (7H, m), 5.64 (2H, d, *J* = 8.2 Hz), 5.17 (2H, d, *J* = 8.2 Hz), 4.66-4.62 (4H, m), 4.42-4.38 (4H, m), 3.87-3.70 (10H, m), 0.85 (6H, s), 0.72 ppm (6H, s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 171.3, 151.2 (d, J_{CP} = 5.7 Hz), 146.0, 144.2, 143.8, 143.4, 142.9, 141.4, 141.35, 137.5, 136.8, 132.5, 130.1, 129.2, 128.8, 128.5, 128.47, 128.24, 128.18 128.0, 127.9, 127.6, 127.5, 127.4, 127.3, 127.2, 127.18, 126.8, 126.5, 120.2, 120.1, 120.04, 119.98, 113.0, 86.7 (d, J_{CP} = 11.2 Hz), 85.0 (d, J_{CP} = 6.7 Hz), 82.2 (d, J_{CP} = 10.6 Hz), 80.2 (d, J_{CP} = 5.1 Hz), 73.4, 68.0, 67.0, 66.9, 31.1, 26.7, 26.5, 25.7 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.8 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [$(M+H)^+$], 2029.6863, found: 2029.6933 *m/z*.

The heterodimeric SALs can be isolated but are usually generated via in situ and used without isolation. Representative characterization data for the heterodimeric (*SS*,*RR*)-SAL **2(EE)** is given below.



***g*. Preparation of (*SS*,*RR*)-SAL EE.** Solutions of **[(*R*,*R*)-1E]$_2$Zn** (200 mg, 0.10 mmol) and **[(*S*,*S*)-1E]$_2$Zn** (200 mg, 0.10 mmol), each in dry degassed dimethoxyethane (1.00 mL) were mixed at room temperature. After ca. 5 minutes, the solvents were evaporated and residue dried under vacuum (< 1 torr) to afford (*SS*,*RR*)-**SAL EE** (398 mg, 99 %) as a white solid: mp 178-179 ^{0}C; $[\alpha]_D^{25}$ = -80.5 (c = 0.1, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (4H, d, *J* = 7.4 Hz), 7.62-7.59 (13H, m), 7.50-7.17 (47H, m), 7.06-7.05, (8H, m), 5.07 (2H, dd, *J* = 9.0, 8.8 Hz), 5.19, (4H, d, *J* = 8.2 Hz), 4.12-4.08 (4H, m), 3.91-3.75 (8H, m), 3.39-3.38 (2H, m), 0.87 (6H, d, *J* = 7.3 Hz), 0.74 ppm (6H, d, *J* = 5.2 Hz);^{13}C NMR (100 MHz, CDCl3) δ 169.8, 152.5, 146.0, 145.8, 144.2, 143.3, 142.1, 142.0, 141.4, 140.1, 129.4, 129.3, 129.2, 129.0, 128.8, 128.7, 128.5, 128.2, 128.0, 127.8, 127.6, 127.5, 127.45, 127.33, 127.28, 127.2, 127.1, 127.0, 126.7, 126.69, 124.0 122.1, 118.9, 118.82, 118.79, 118.71, 118.49, 118.42, 118.40, 118.3, 113.11, 113.07, 86.7 (d, J_{CP} = 4.4 Hz), 86.5 (d, J_{CP} = 10.4 Hz), 85.2 (d, J_{CP} = 8.2 Hz), 85.1 (d, J_{CP} = 6.7 Hz), 82.4 (d, J_{CP} = 4.4 Hz), 82.2 (d, J_{CP} = 5.9 Hz), 80.38 (d, J_{CP} = 5.9 Hz), 80.26 (d, J_{CP} = 6.9 Hz), 73.0, 65.7, 65.68, 65.14, 65.12, 31.6, 26.80, 26.76, 26.72, 26.5, 26.4 ppm; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.3 ppm; HRMS (FAB) calcd for $C_{126}H_{111}N_4O_{14}P_2Zn$ [$(M+H)^+$], 2029.6863; found: 2029.6951 *m/z*.



General procedure employed for the preparative scales reactions reported in Table 3 illustrated for the preparation of 1-(2-methoxyphenyl)ethanol 3a. A solution of ((*S*,*S*)-**1H**)$_2$Zn (10.0 mg, 1.4 x 10^{-2} mmol) and ((*R*,*R*)-**1C**)$_2$Zn (10.0 mg, 1.4 x 10^{-2} mmol) in DCM (10 mL) was stirred at ambient temperature (RT, ca. 10 min.) and then a solution of Rh(nbd)$_2$BF$_4$ (9.7 mg, 2.6 x 10^{-2} mmol) in DCM (5 mL) was added. The resulting mixture was stirred at ambient temperature (0.5 h) after which the volatile solvent was removed under vacuum. The residue was dissolved in DME (10 mL), stirred (0.5 h) and then a solution of 2-methoxystyrene (**2a**, 174.0 mg, 1.30 mmol) in DME (2.0 mL) and powdered 4Å molecular sieves (ca. 0.5 g) were added. The resulting mixture was cooled (0 ^{o}C) and a solution of pinacolborane (199.0 mg, 1.56 mmol) in DME (4.0 mL) added dropwise. The reaction mixture was gradually warmed to RT and stirred (12 h). Afterwards, the mixture was re-cooled (0 ^{o}C), and quenched by the addition of MeOH (10 mL), aq. NaOH (3.0 M, 15 mL), and aq. H_2O_2 (1 mL of a 30% solution). The ice bath was removed, the resulting mixture stirred (3 h, RT) and then filtered. The filtrate was extracted with ether (3 x 15 mL) and the combined organics dried (anhyd. Na_2SO_4), filtered and concentrated. Chromatography on silica (10% EtOAc/Hex) gives 1-(2-methoxyphenyl)ethanol (**3a**, 194 mg, 98%) as a clear oil: capillary GC analysis (J&W Scientific 30 m x 0.25 mm ID Cyclosil β, 120 ^{o}C (1 min hold) to 130^o @ 1^o/min then to 165^o @ 2^o/min) found peaks at 21.19 (97.2%, (*R*)-**3a**) and 23.55 (2.8%, (*S*)-**3a**); $[\alpha]_D^{25}$ = +25.8 (c = 1.4, $CHCl_3$) (lit.[4] $[\alpha]_D^{25}$ = +23.7 (91% ee (*R*)) (c = 1.4, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (1H, dd, *J* = 7.5, 1.4 Hz), 7.31 (1H, dt, *J* = 8.2, 1.6 Hz), 7.00 (1H, t, *J* = 7.5 Hz), 6.90 (1H, d, *J* = 8.2 Hz), 5.13 (1H, q, *J* = 13.0, 6.5 Hz), 3.88 (3H, s) 1.53 ppm (3H, d, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) 156.5, 133.6, 128.2, 126.1, 120.8, 110.4, 66.4, 55.3, 23.0 ppm; $[\alpha]_D^{25}$ = +25.8^o (c = 1.4, $CHCl_3$).

(*R*)-1-(2-methylphenyl)ethanol (3b). The title compound was prepared via the general procedure: The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(2-methoxyphenyl)ethanol (**3b**, 166 mg, 94%) as a clear oil: (J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 ^{o}C (1 min hold) to 130^o @ 1^o/min then 165^o @ 2^o/min) found peaks at 17.86 (97.2%, (*R*)-**3b**) and 18.78 (2.80%, (*S*)-**3b**); $[\alpha]_D^{25}$ = +62.1 (c = 0.83, EtOH) (lit.[5] $[\alpha]_D^{25}$ = -64.3 (99% ee (*S*)) (c = 1.04, EtOH)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (1H, d, *J* = 7.5 Hz), 7.27 (1H, t, *J* = 6.4 Hz), 7.23-7.15 (2H, m), 5.16 (1H, q, *J* = 6.4 Hz), 2.37 (3H, s) 1.49 ppm (3H, d, *J* = 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 134.2, 130.4, 127.2, 126.4, 124.5, 66.8, 23.9, 18.9 ppm.

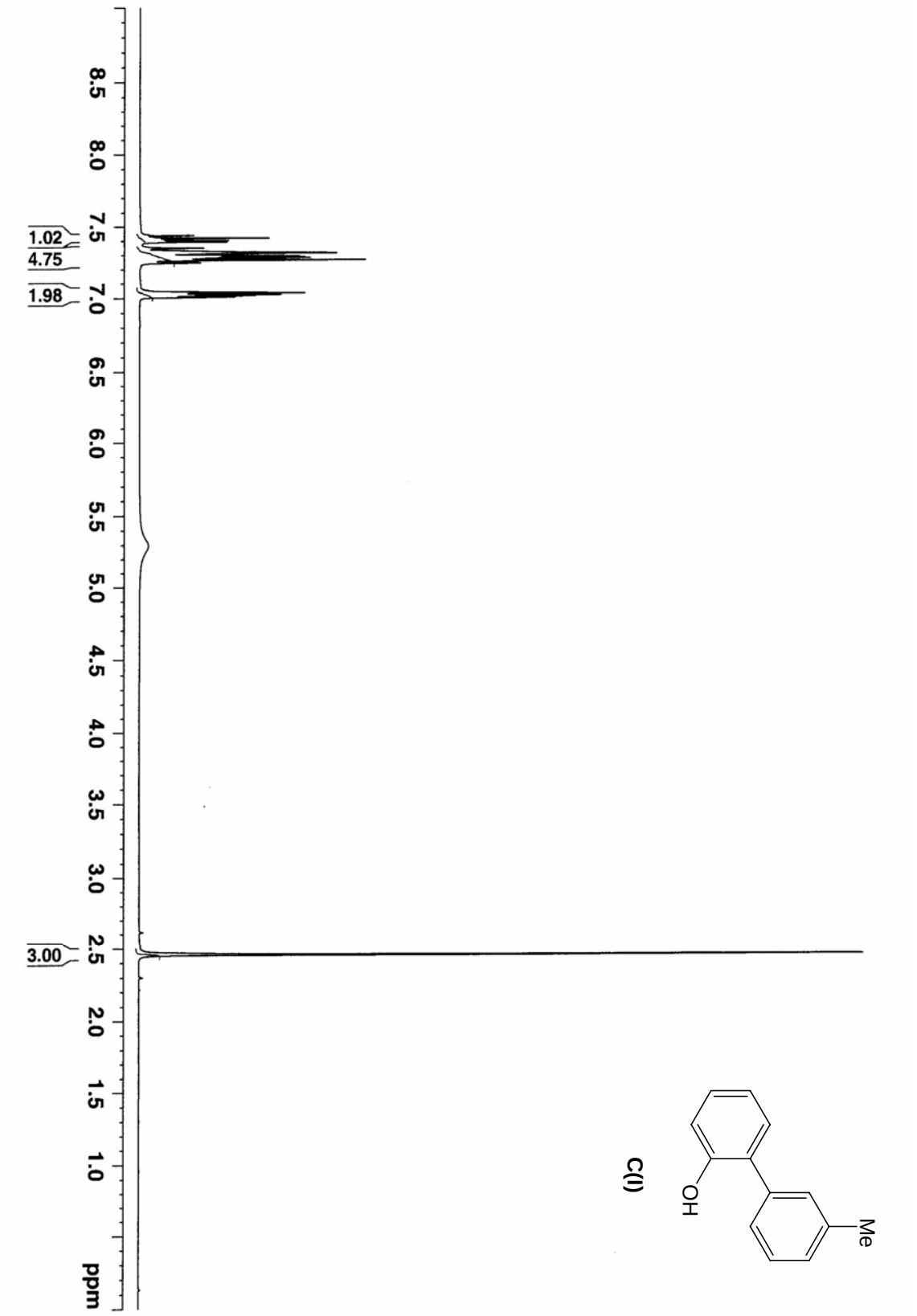
(*R*)-1-(2-trifluoromethylphenyl)ethanol (3c). The title compound was prepared via the general procedure. The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(2-trifluoromethylphenyl)ethanol (**3c**, 202 mg, 82%) as a clear oil: (J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 ^{o}C (1 min hold) to 130^o @ 1^o/min then 165^o @ 2^o/min) found peaks at 17.86 (95.6%, (*R*)-**3c**) and 18.78 (4.40%, (*S*)-**3c**) ; $[\alpha]_D^{25}$ = +25.8 (c = 1.0,

[4] Y.-J. Cherng, J.-M. Fang, T.-J. Lu, *J. Org. Chem.* **1999**, *64*, 3207-3212.
[5] K. Nakamura, T. Matsuda, *J. Org. Chem.* **1998**, *63*, 8957-8964.

MeOH) (lit. $[\alpha]_D^{22}$ = -28.4 (99% ee (*S*)) (c = 1.26, MeOH)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (1H, d, *J* = 7.8 Hz), 7.64-7.60 (2H, m), 7.39 (2H, 1H, t, *J* = 6.4 Hz), 5.36 (1H, q, *J* = 5.6, 1.0 Hz), 1.51 ppm (3H, d, *J* = 6.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.1, 132.3, 127.3, 127.1 , 126.4 (d, J_{CF} = 30.2 Hz), 125.2 (q, J_{CF} = 5.8 Hz), 124.4 (d, J_{CF} = 273.8 Hz), 65.6 (d, J_{CF} = 2.2 Hz), 25.4 ppm.

(*R*)-1-(2-chlorophenyl)ethanol (3d). The title compound was prepared via the general procedure: The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(2-chlorophenyl)ethanol (**3d**, 193 mg, 95%) as a clear oil: (J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 ^{o}C (1 min hold) to 130^o @ 1^o/min then 165^o @ 2^o/min) found peaks at 21.52 (96.4%, (*R*)-**3d**) and 24.77 (3.6%, (*S*)-**3d**); $[\alpha]_D^{25}$ = +60.3 (c = 1.0, $CHCl_3$) (lit. $[\alpha]_D^{25}$ = -62.7 (99% ee (*S*)) (c = 0.894, $CHCl_3$)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (1H, dd, *J* = 7.7, 1.6 Hz), 7.35-7.28 (2H, m), 7.20 (1H, td, *J* = 7.7, 1.6 Hz), 5.28 (1H, q, *J* = 6.3, 2.8 Hz), 2.37 (3H, s) 1.49 ppm (3H, d, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.1, 131.6, 129.4, 128.4, 127.2, 126.4, 66.9, 23.5 ppm.

(*R*)-1-(2-fluorophenyl)ethanol (3e). The crude product was purified by chromatography on silica (10% EtOAc/Hex) to give 1-(2-fluorophenyl)ethanol (**3e**, 158 mg, 87%) as a clear oil: (J&W Scientific 30.0 m x 0.25 mm ID Cyclosil β, 120 ^{o}C (1 min hold) to 130^o @ 1^o/min then 165^o @ 2^o/min) found peaks at 17.86 (95.3%, (*R*)-**3e**) and 18.78 (4.70%, (*S*)-**3e**); $[\alpha]_D^{25}$ = +39.8 (c = 0.5, MeOH) (lit. $[\alpha]_D^{25}$ = -44.5 (99% ee (*S*)) (c = 0.782, MeOH)); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (1H, t, *J* = 5.8 Hz), 7.28-7.24 (1H, m), 7.17 (1H, t, *J* = 7.5 Hz), 7.07-7.02 (1H, m), 5.24 (1H, dq, *J* = 6.9, 2.5 Hz), 2.37 (3H, s) 1.54 ppm (3H, d, *J* = 6.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7 (d, J_{CF} = 254.3 Hz), 132.7 (d, J_{CF} = 13.3 Hz), 128.7 (d, J_{CF} = 8.2 Hz), 126.6 (d, J_{CF} = 4.5 Hz), 124.3 (d, J_{CF} = 3.4 Hz), 115.2 (d, J_{CF} = 1.8 Hz), 64.3 (d, J_{CF} = 3.1 Hz), 24.0 ppm.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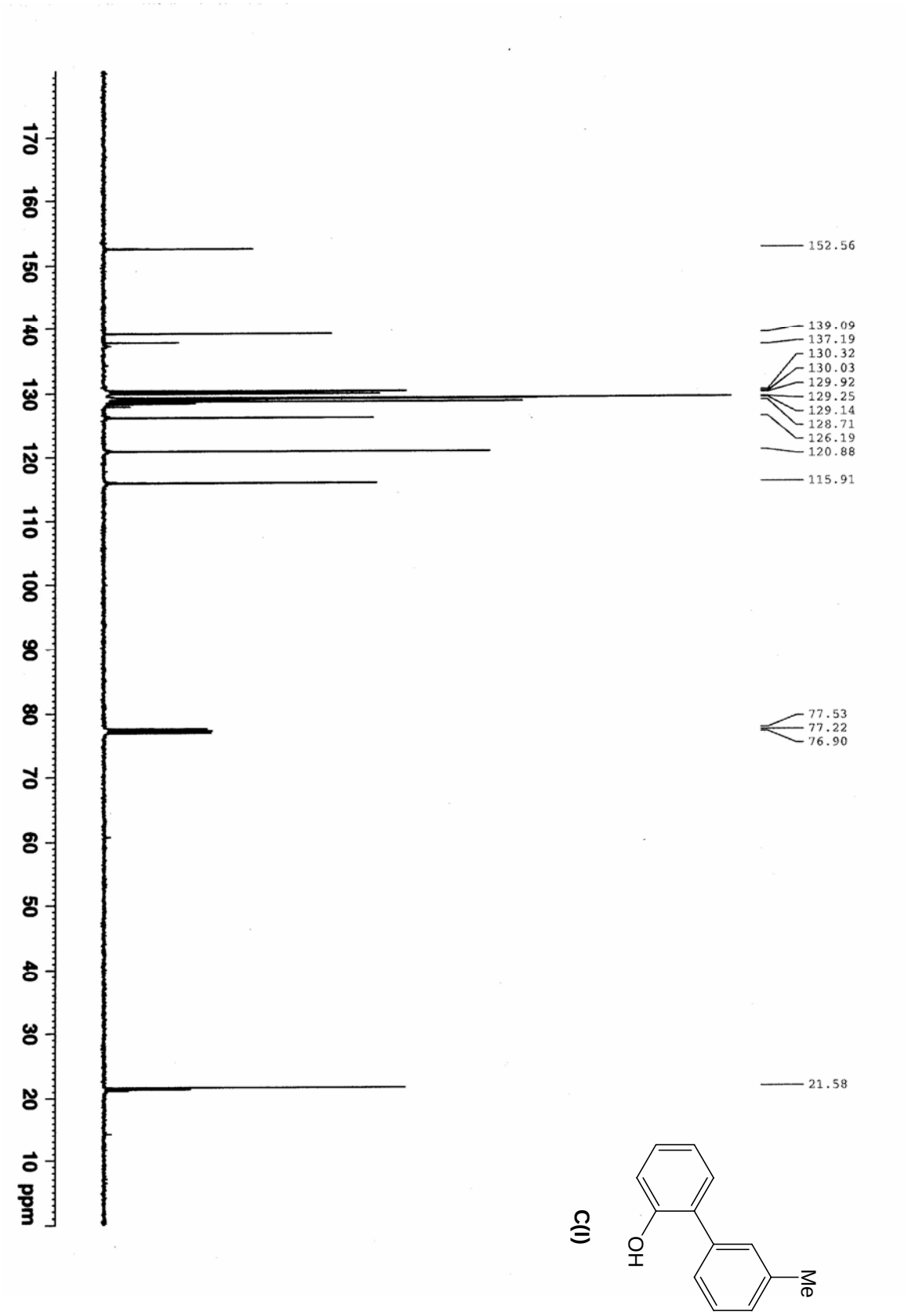
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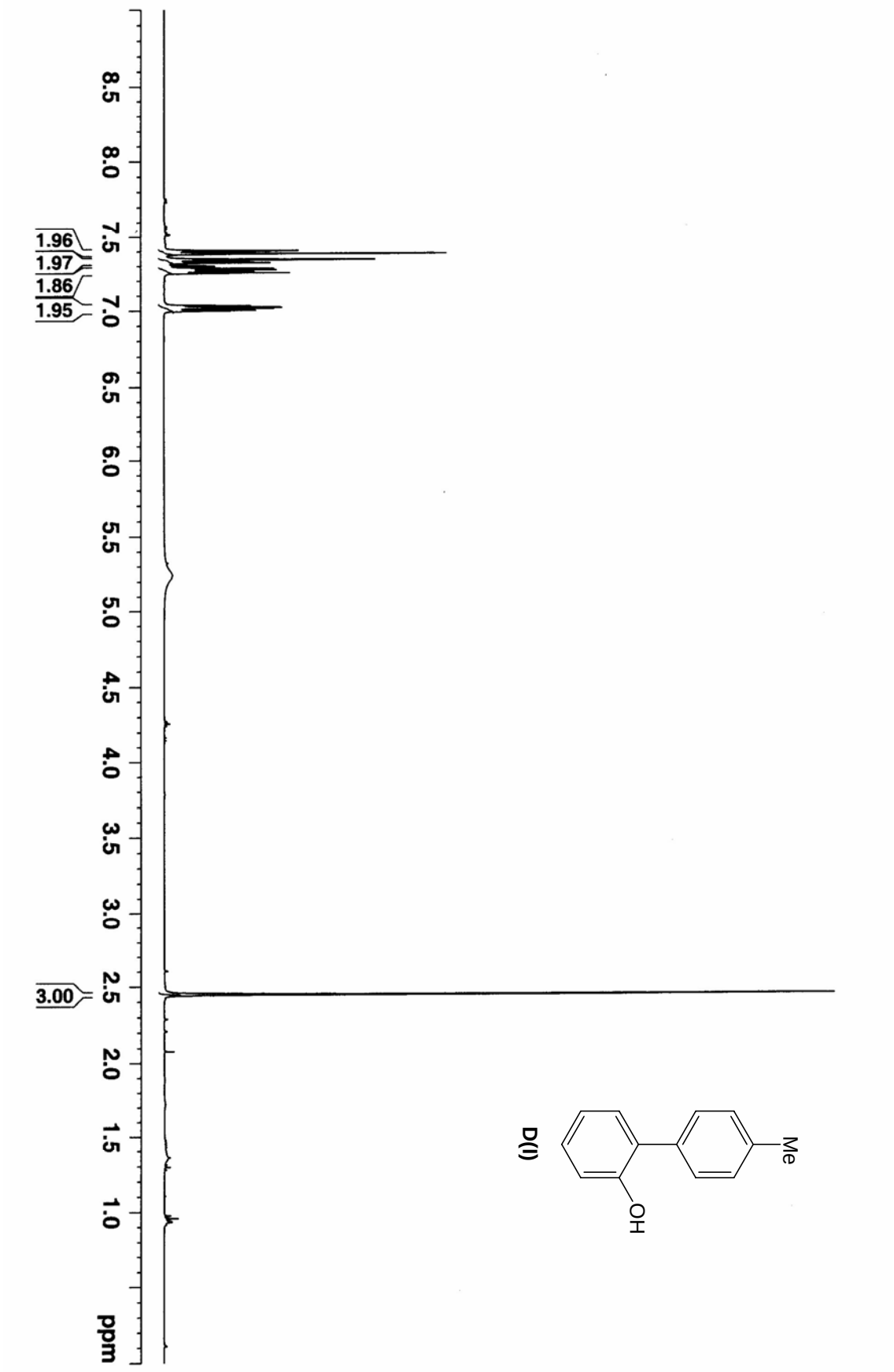
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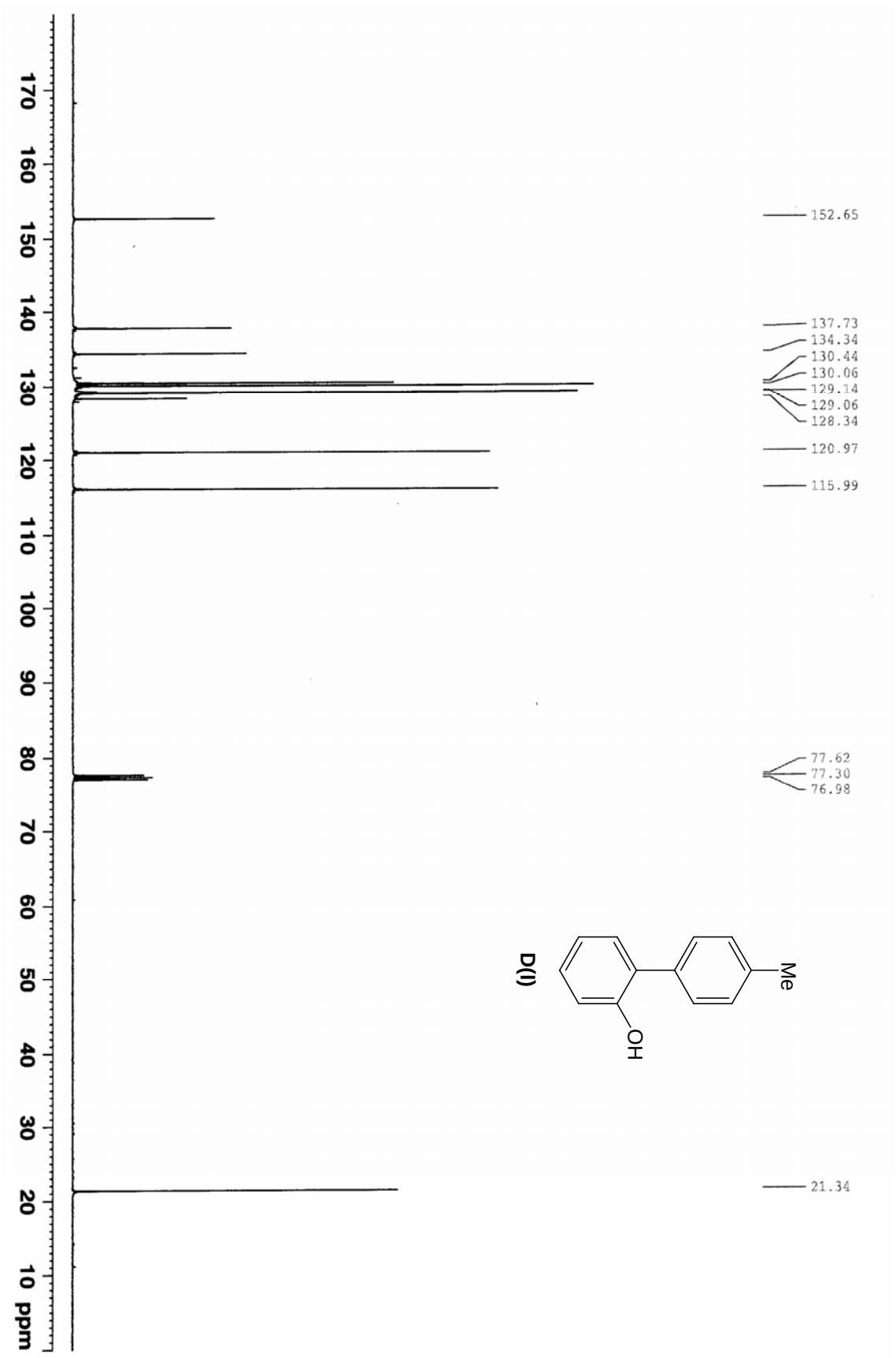
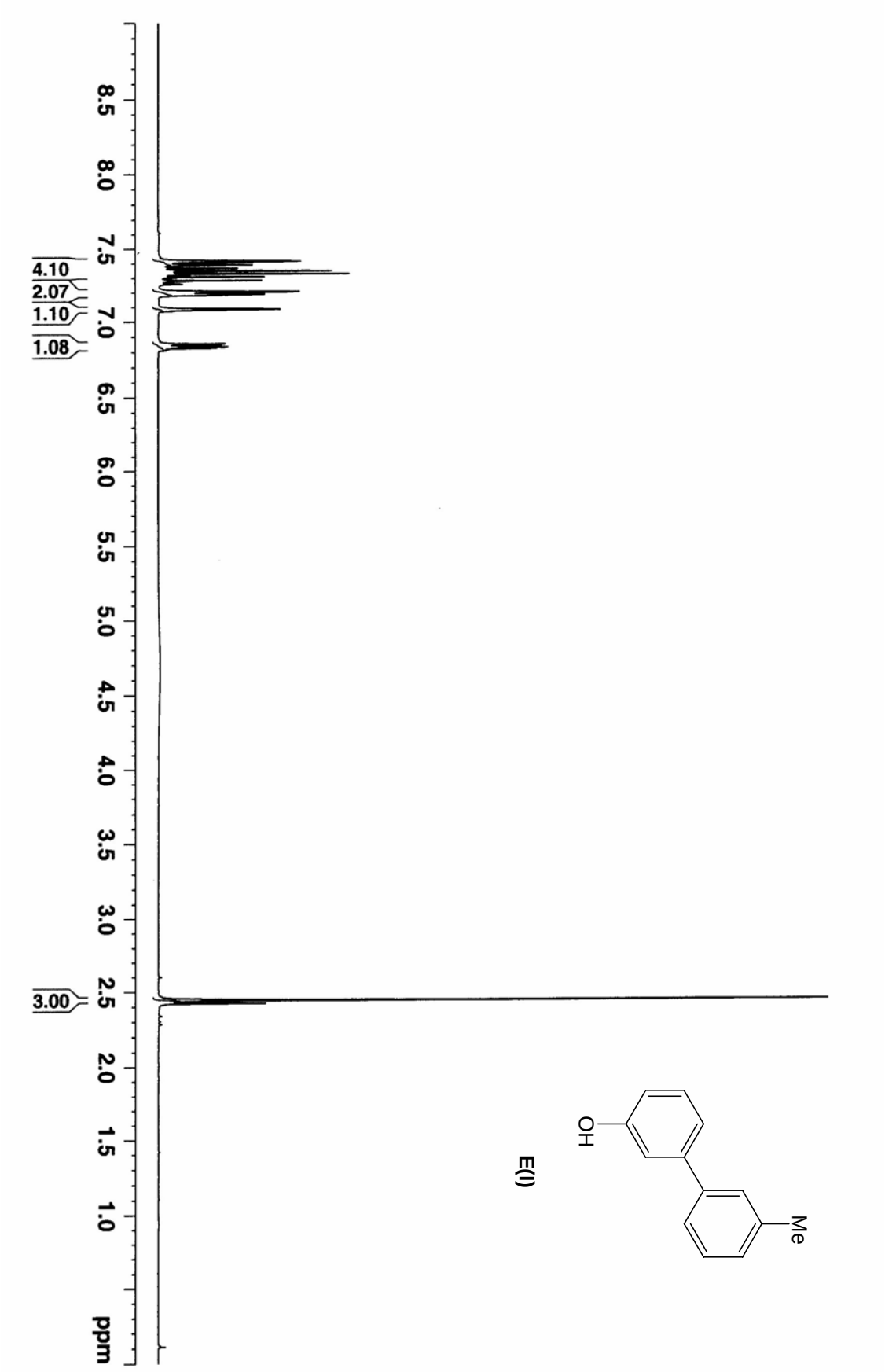
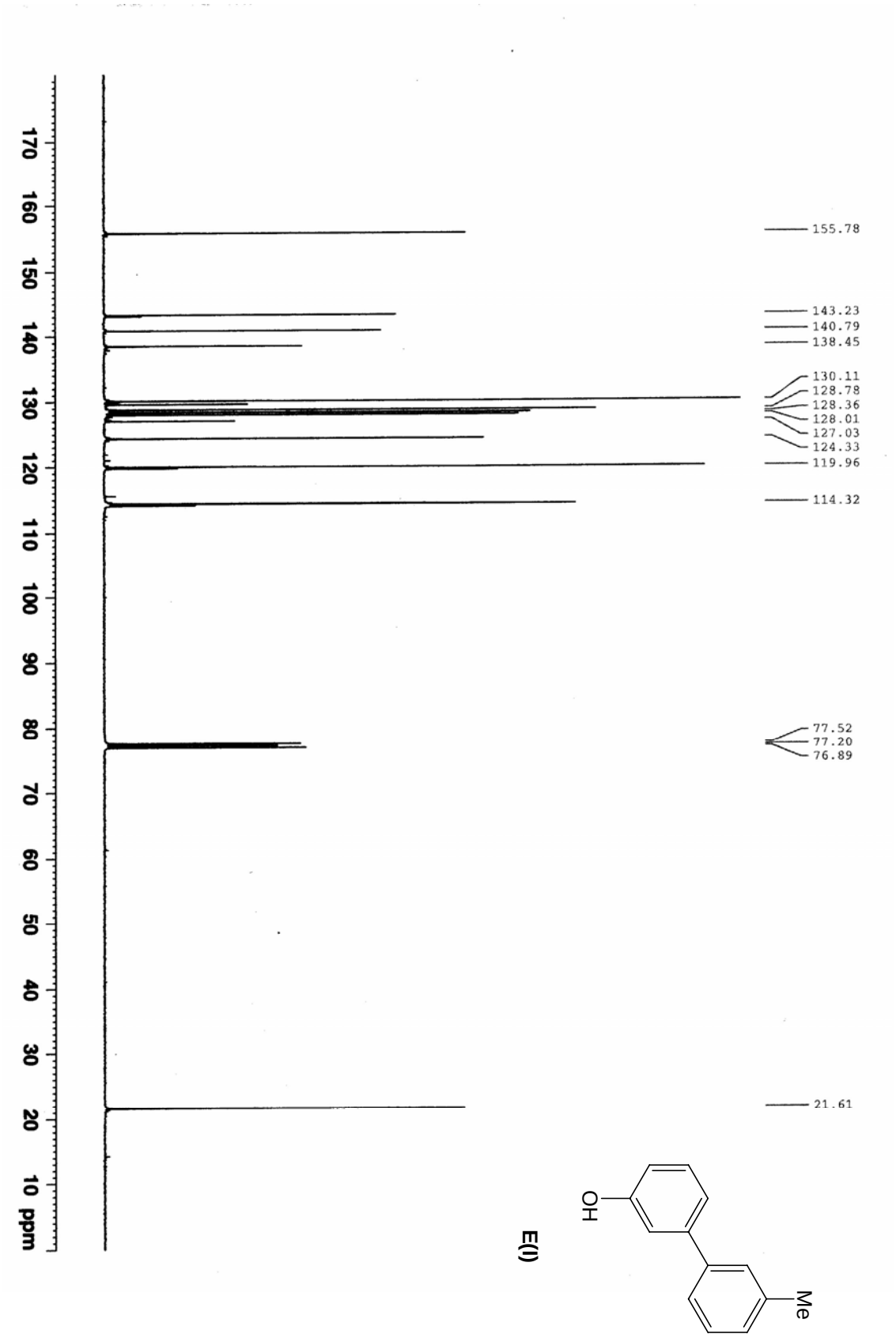
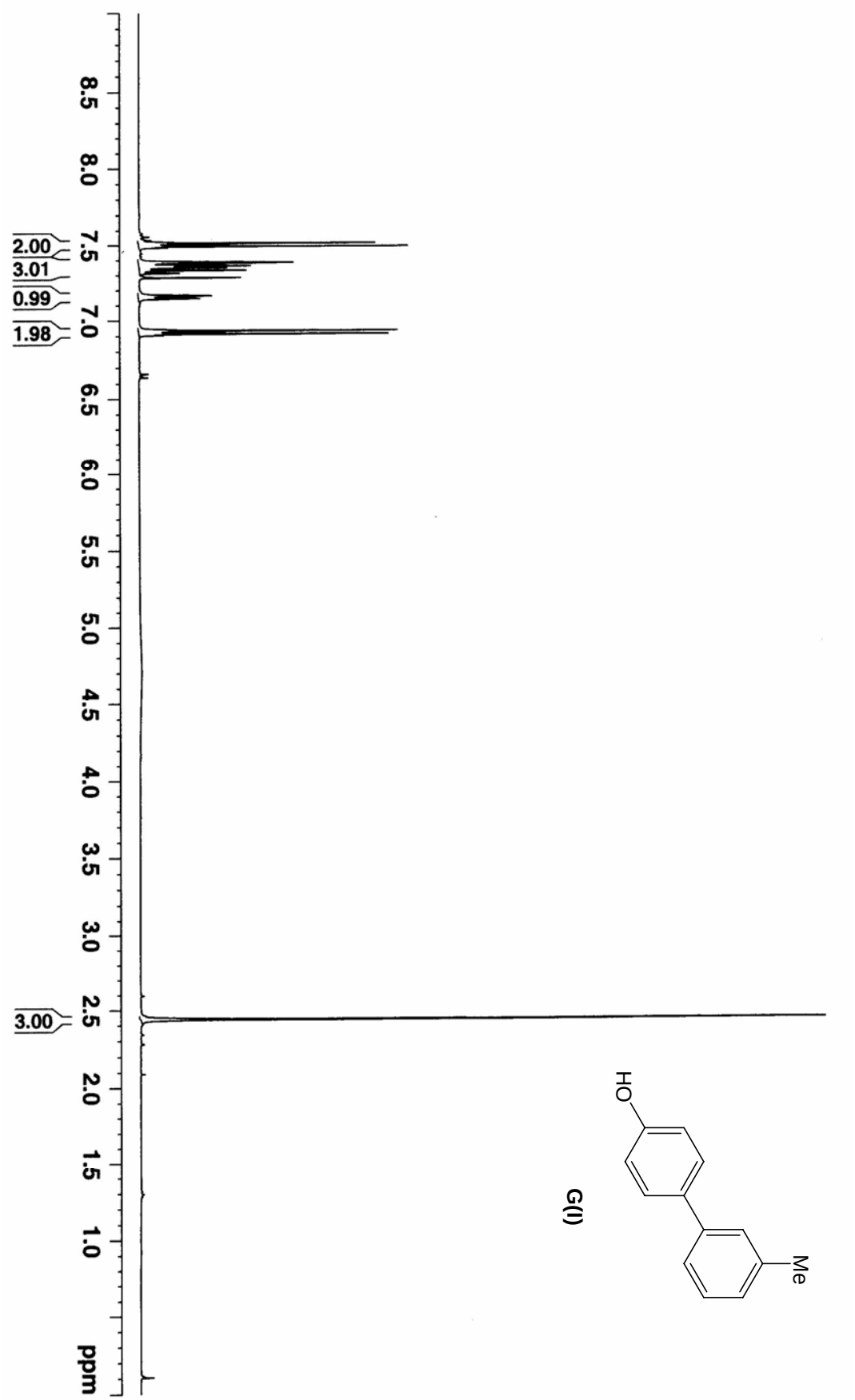
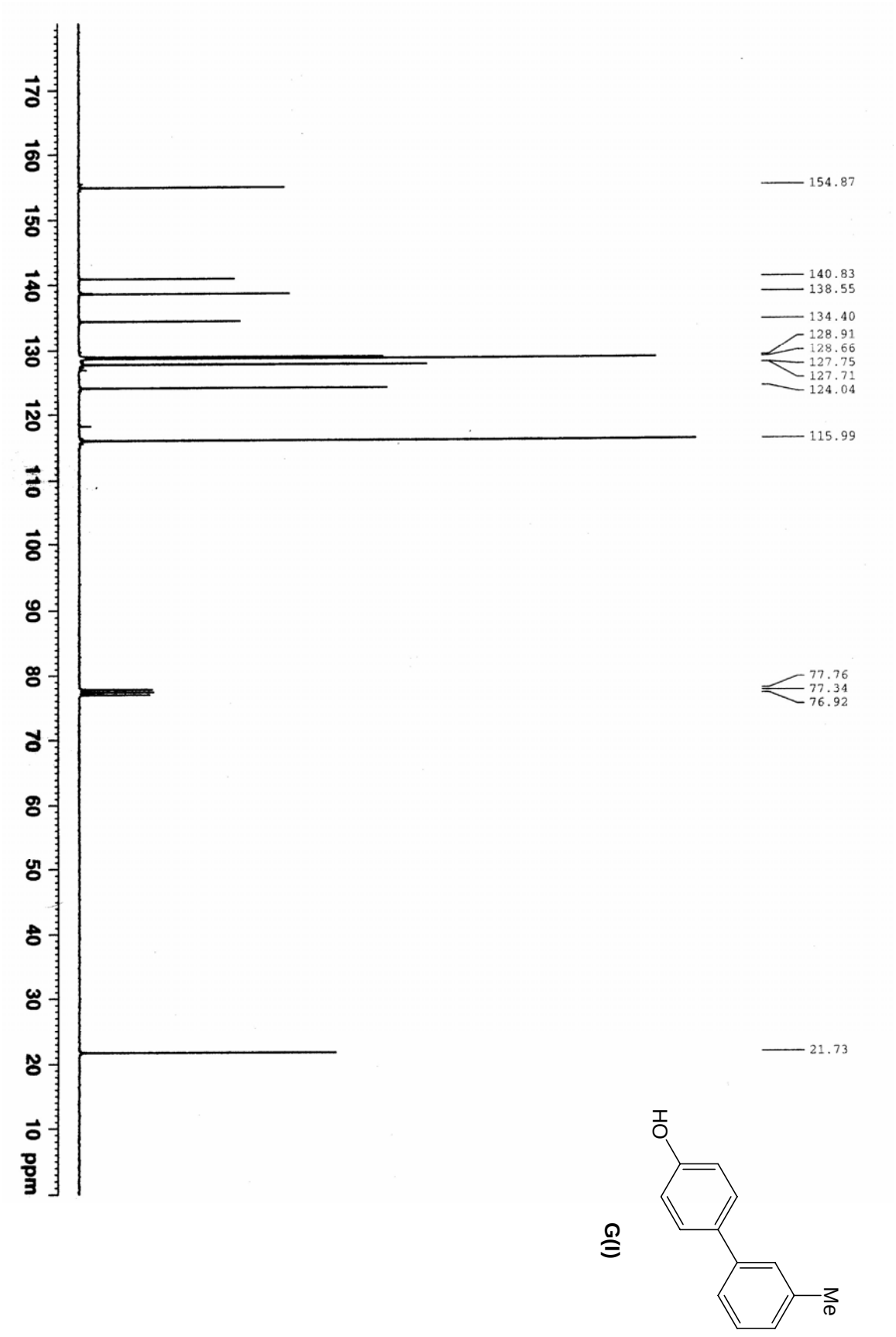
Me
OH

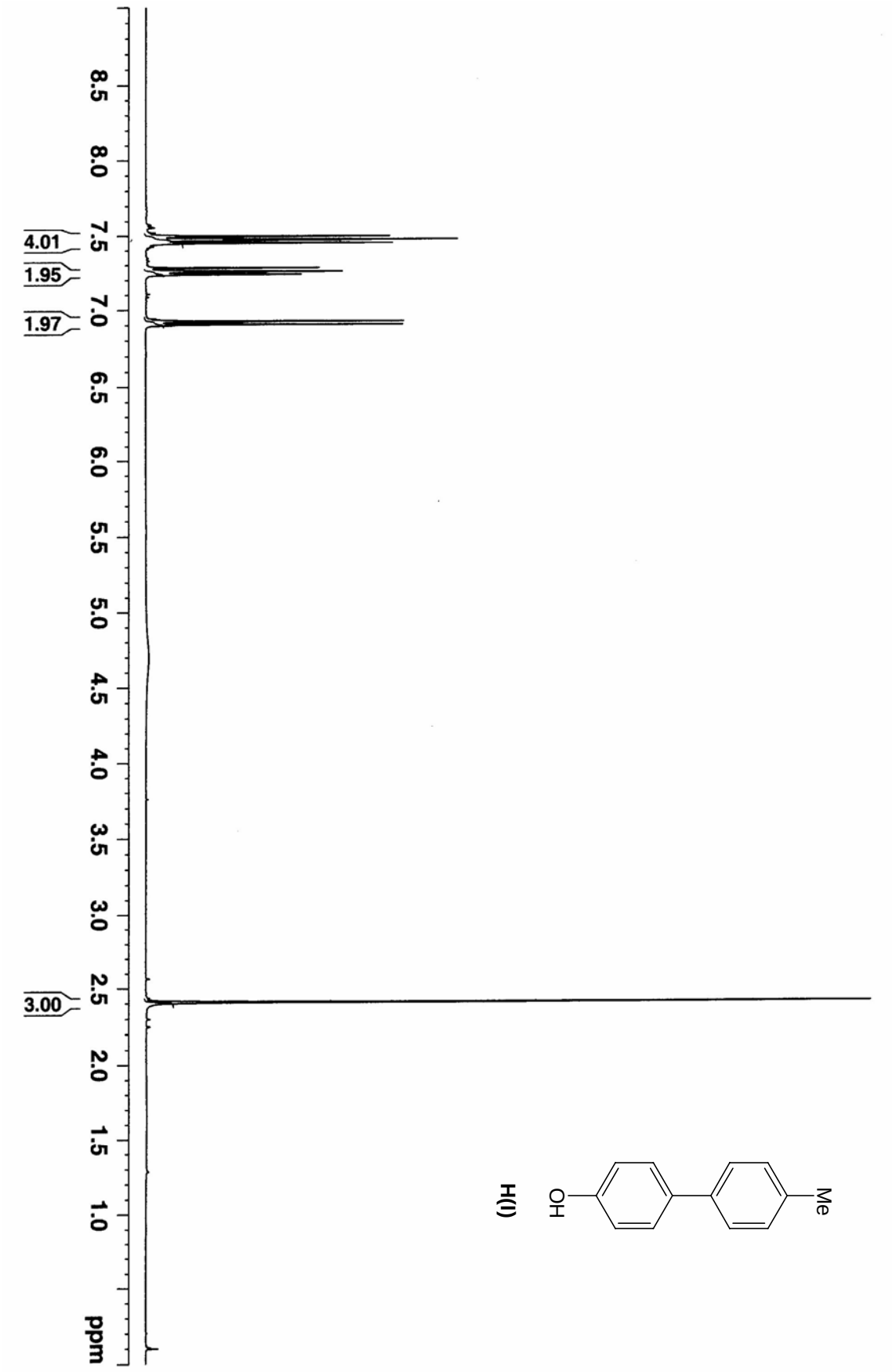

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
152.65
137.73
134.34
130.44
130.06
129.14
129.06
128.34
120.97
115.99
77.62
77.30
76.98
21.34
D(l)
Me
OH

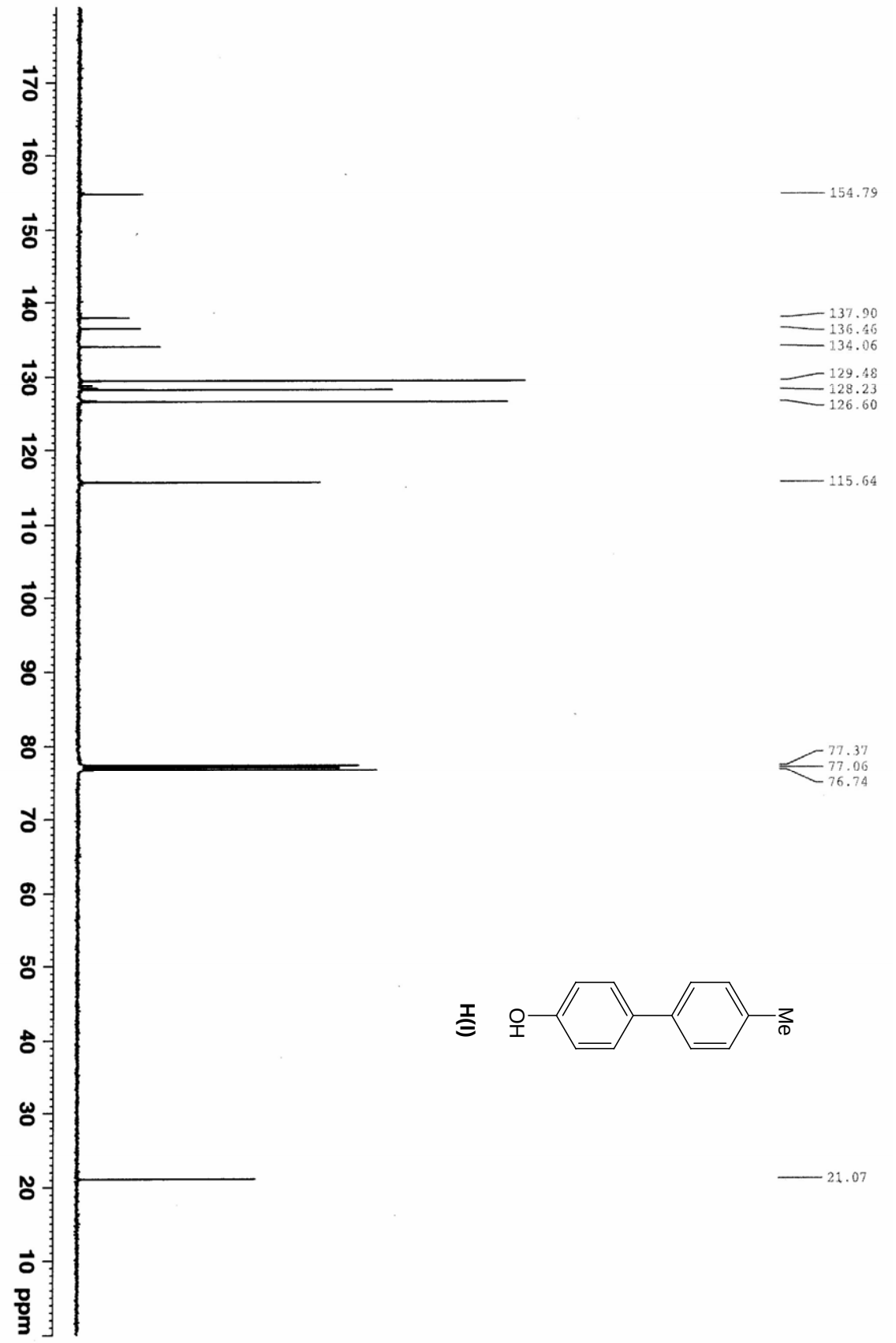

4.10
2.07
1.10
1.08
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
E(I)
OH
Me

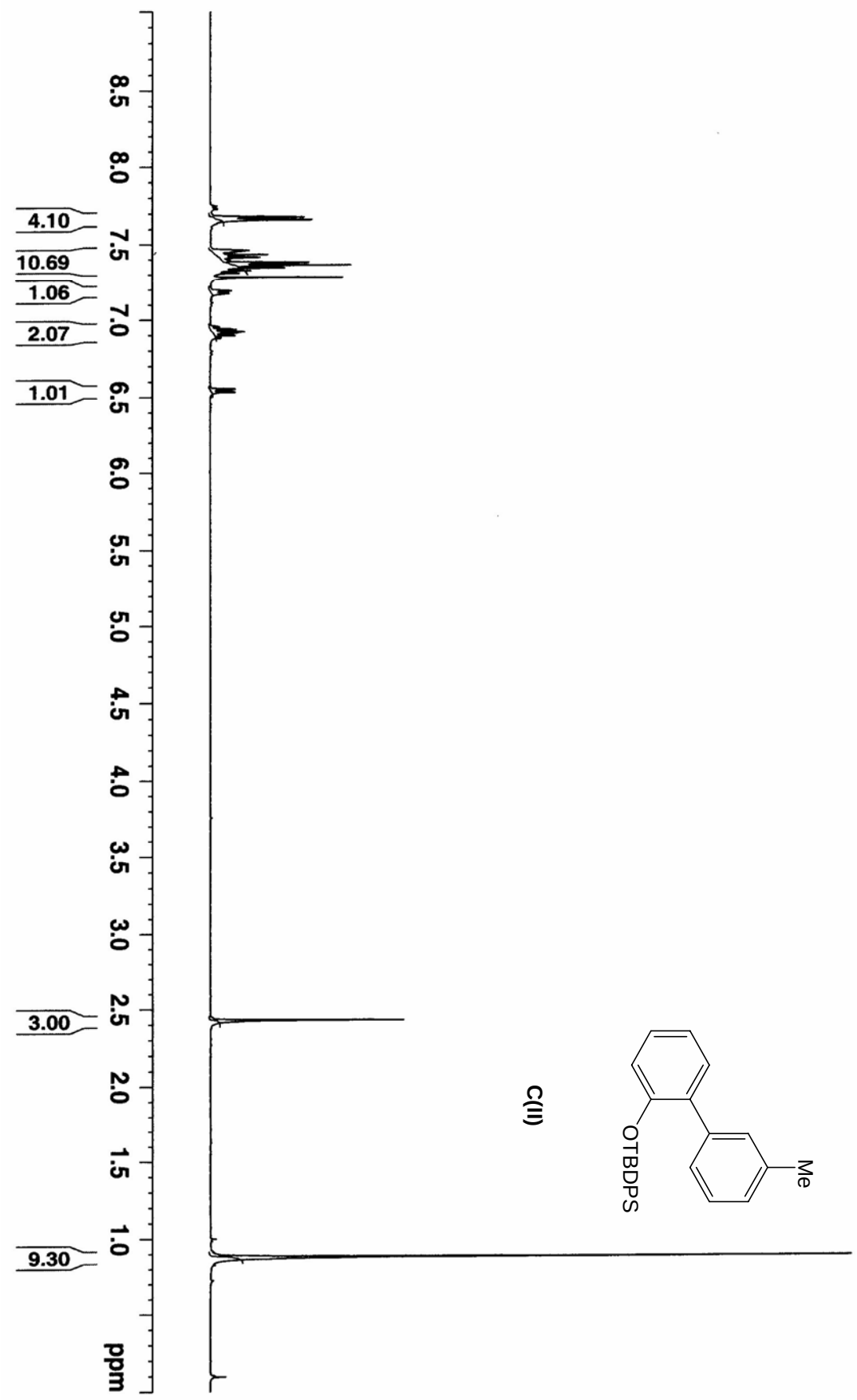

155.78
143.23
140.79
138.45
130.11
128.78
128.36
128.01
127.03
124.33
119.96
114.32
77.52
77.20
76.89
21.61
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
E(I)
OH
Me

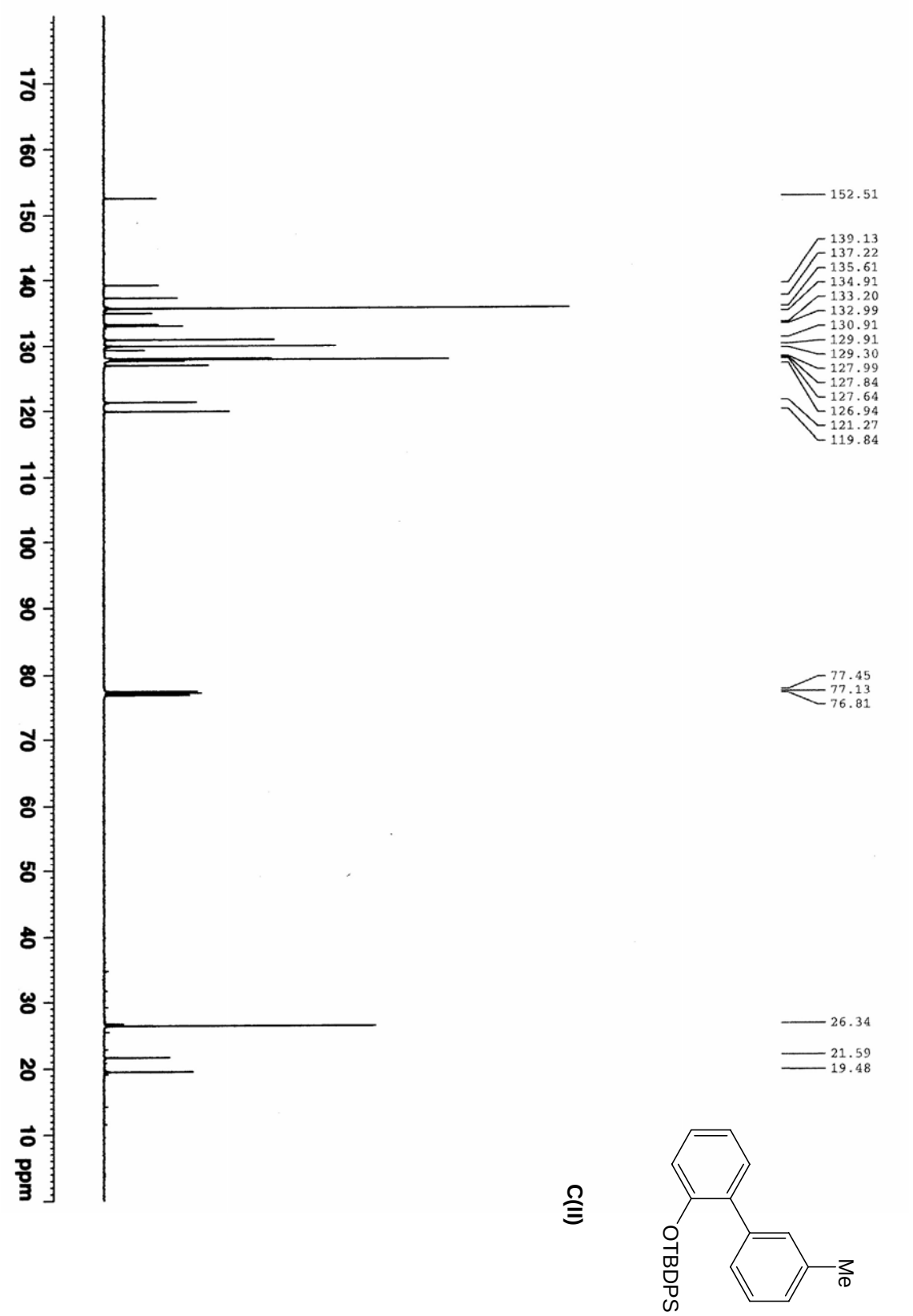

2.00
3.01
0.99
1.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
HO
Me
G(I)

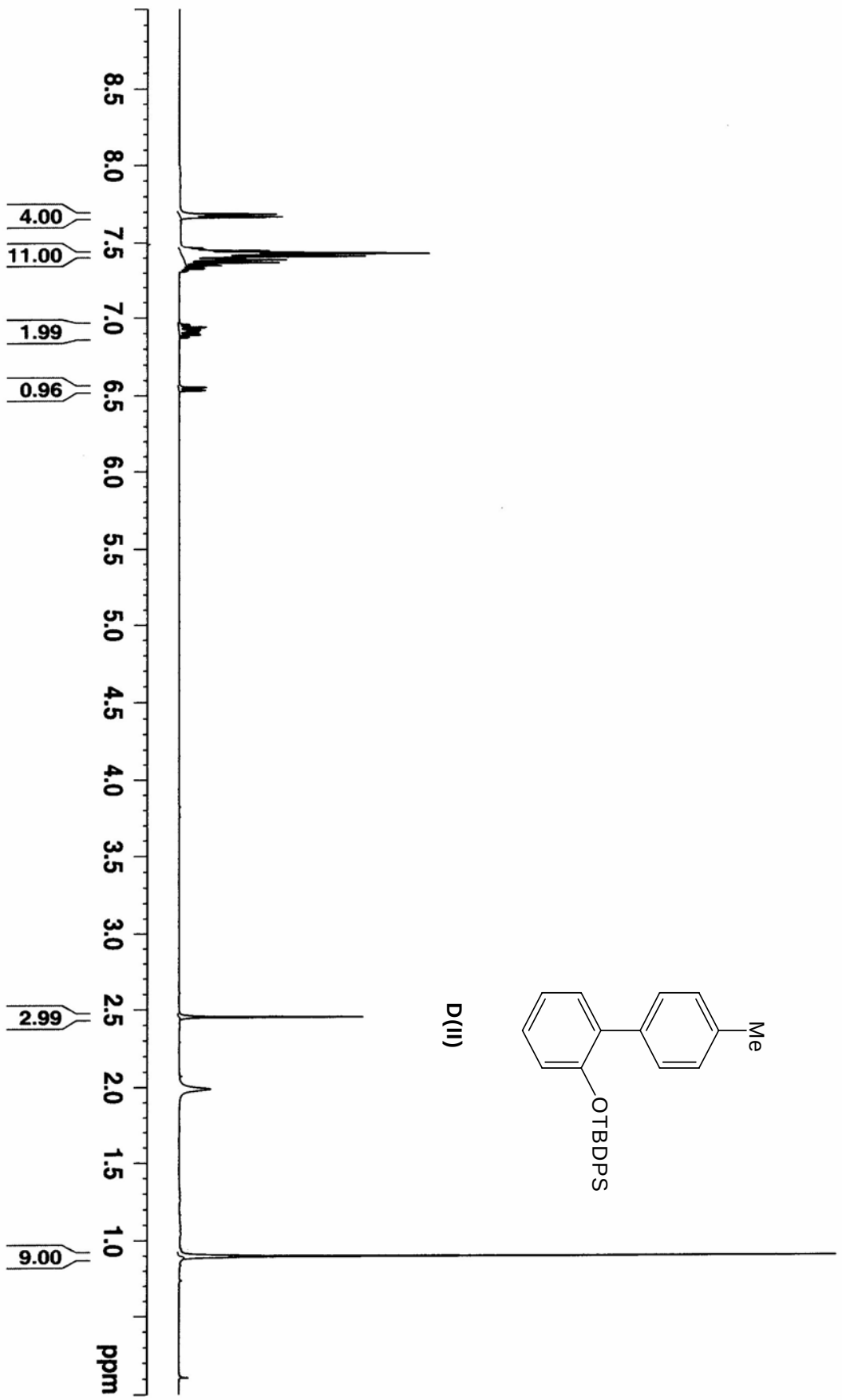

154.87
140.83
138.55
134.40
128.91
128.66
127.75
127.71
124.04
115.99
77.76
77.34
76.92
21.73
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
HO
Me
G(I)

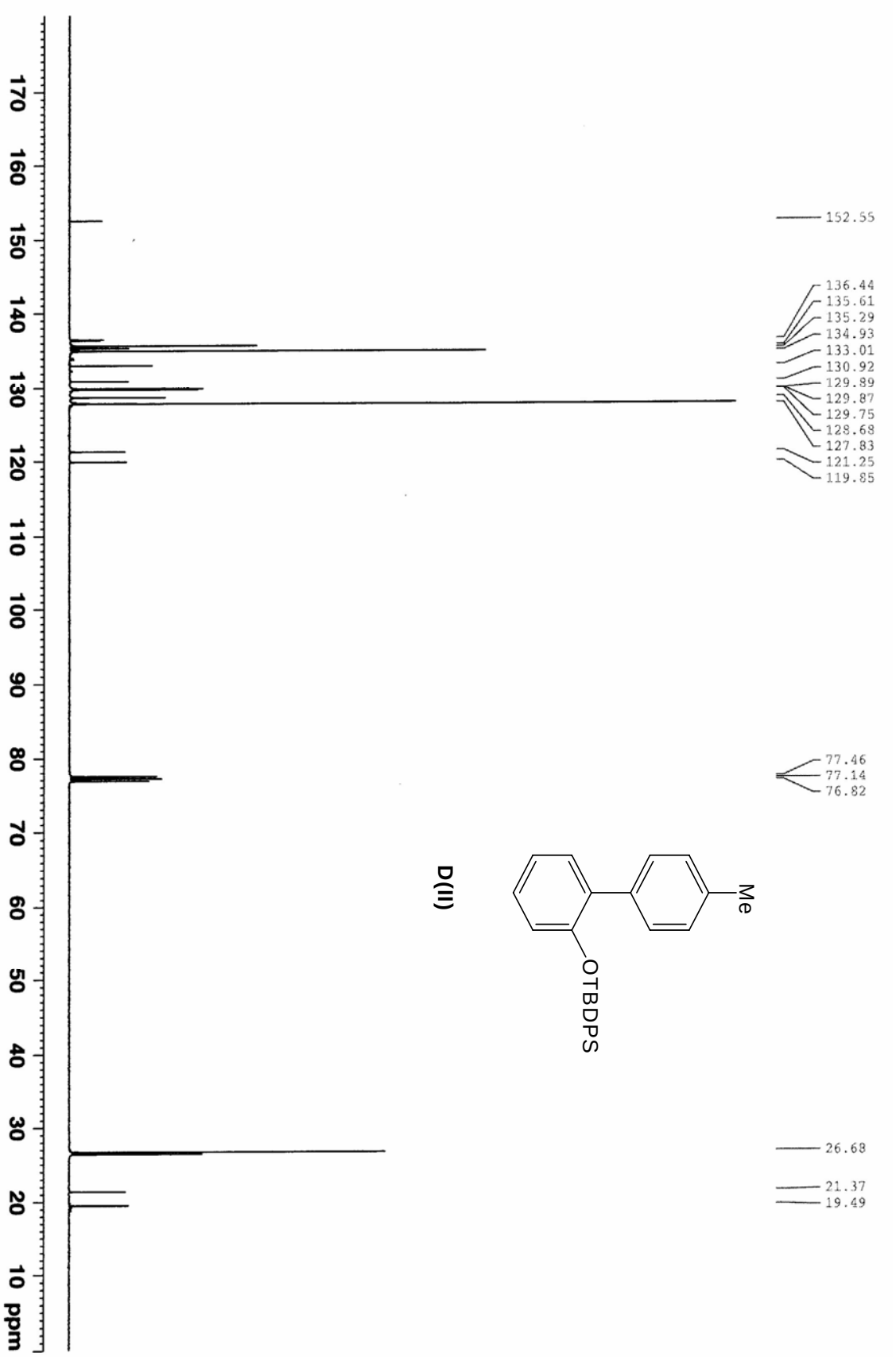

4.01
1.95
1.97
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
H(I)
OH
Me

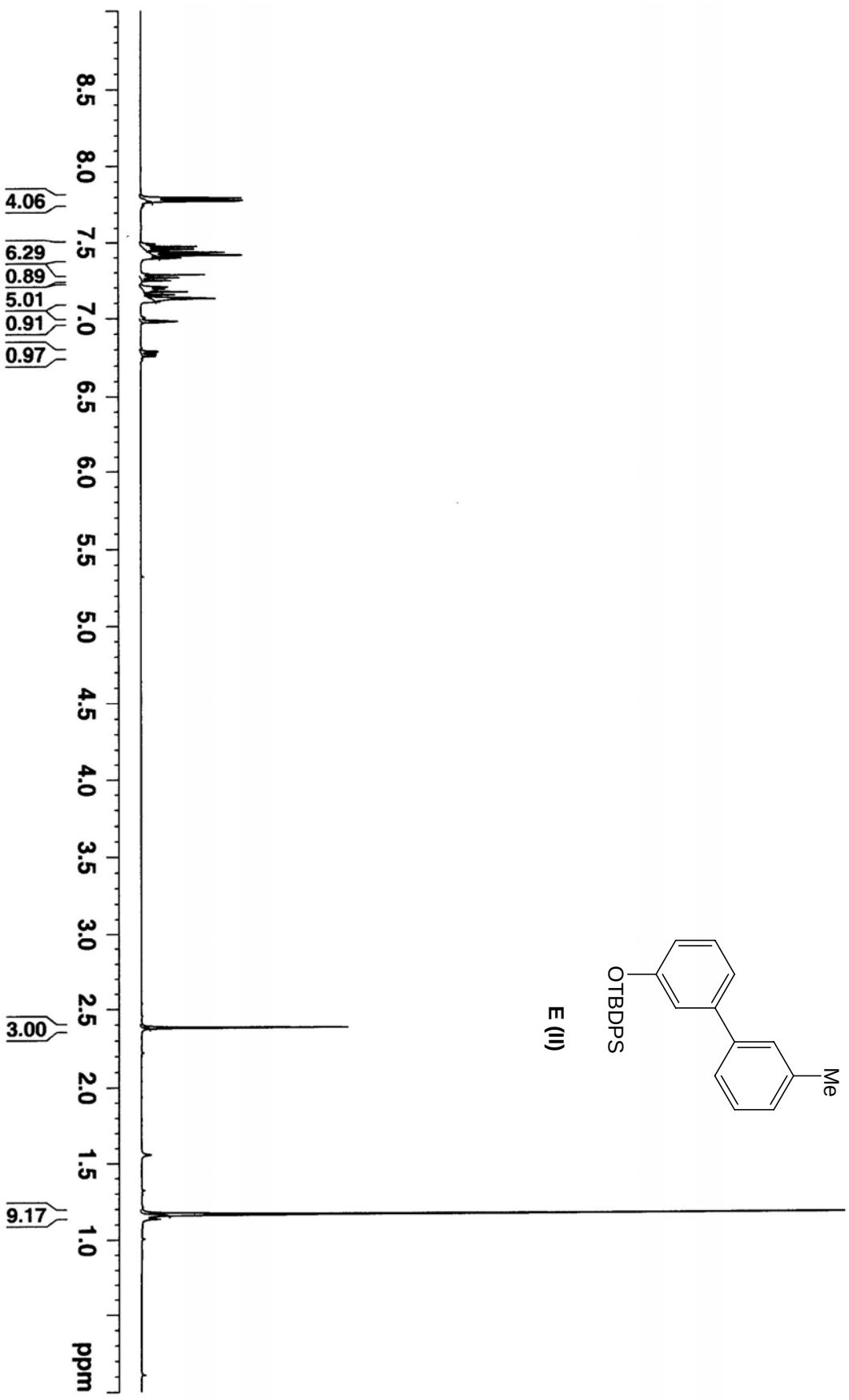

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
154.79
137.90
136.46
134.06
129.48
128.23
126.60
115.64
77.37
77.06
76.74
21.07
H(I)
OH
Me

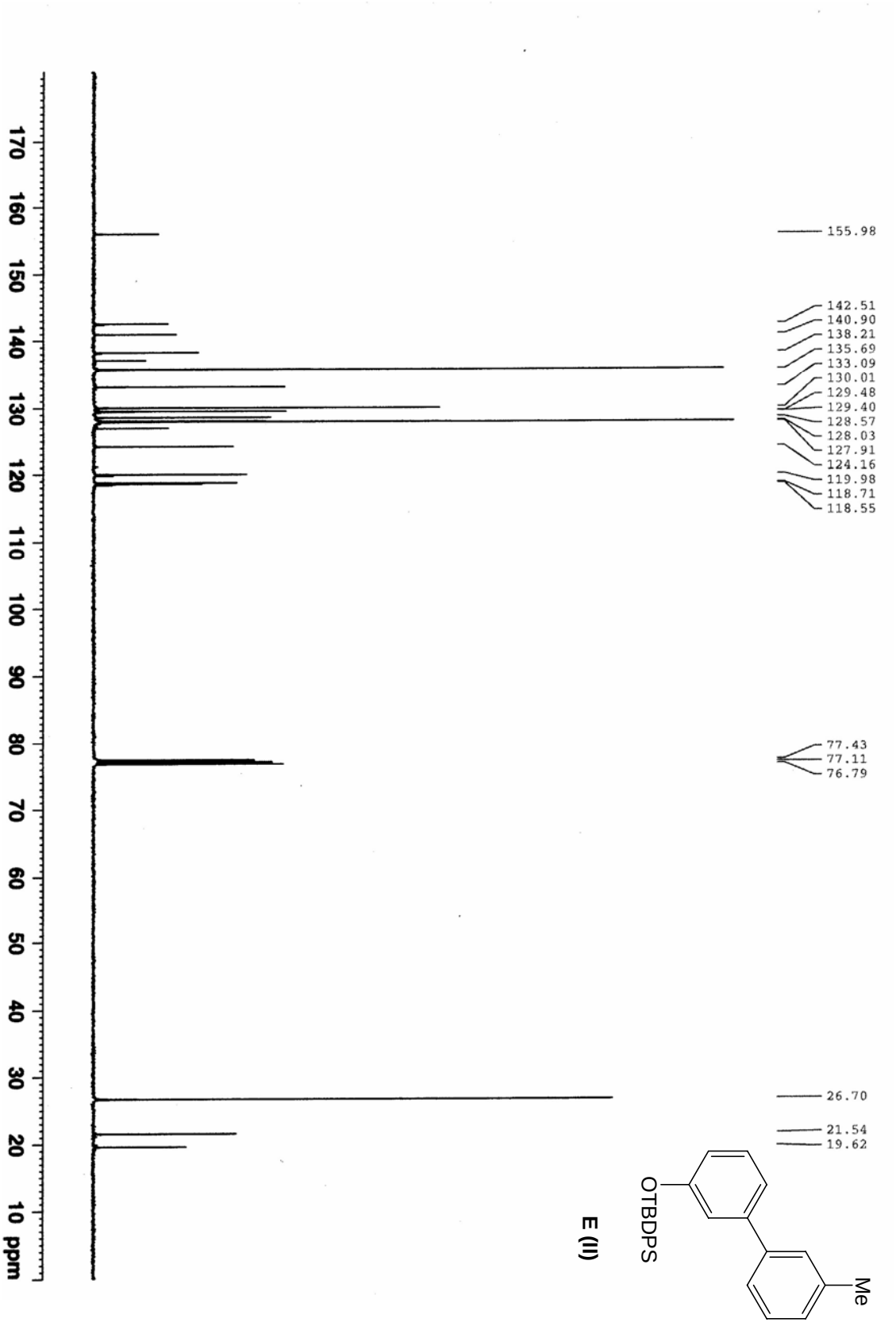

4.10
10.69
1.06
2.07
1.01
3.00
9.30
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
C(II)
OTBDPS
Me

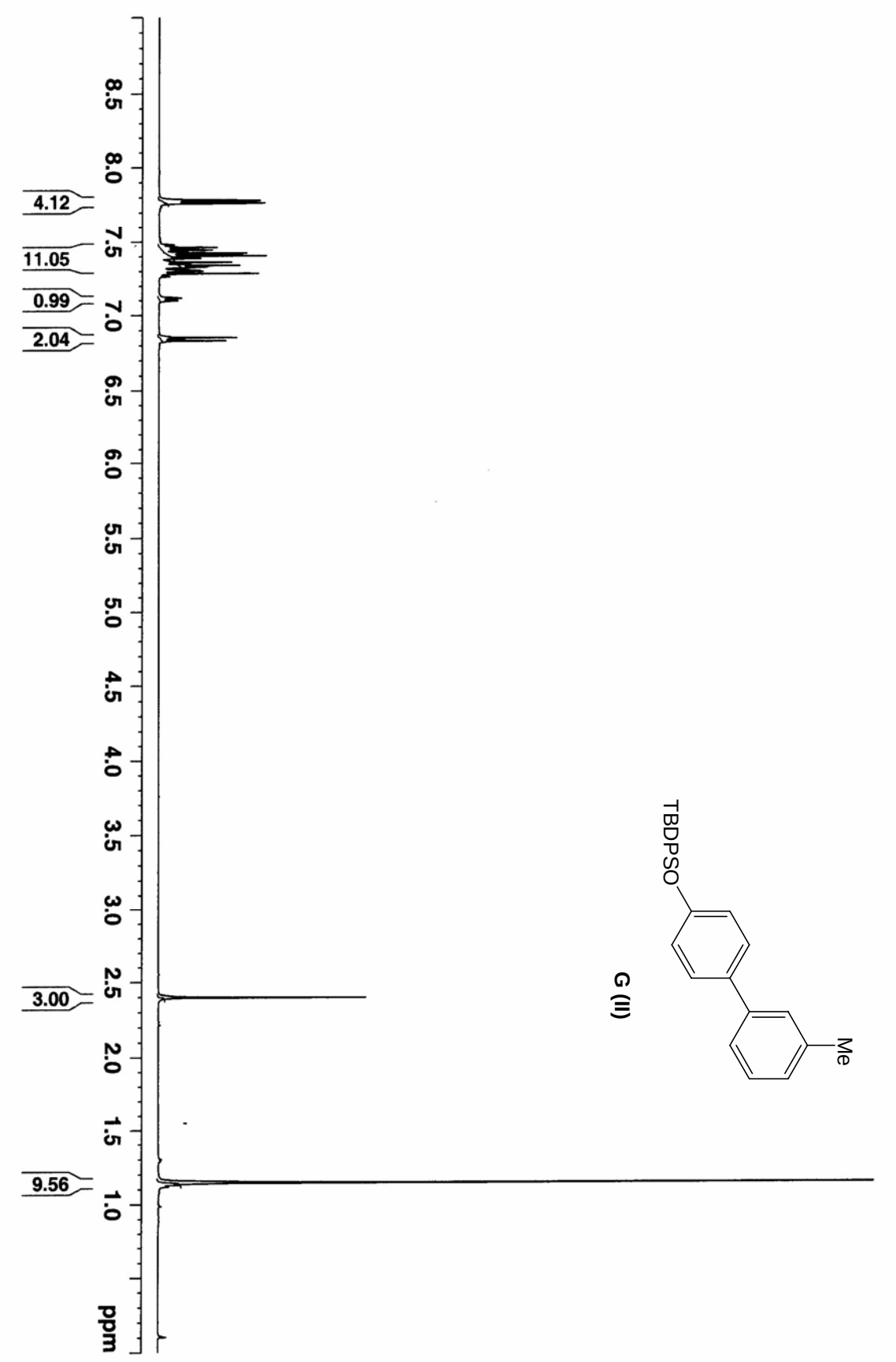

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
152.51
139.13
137.22
135.61
134.91
133.20
132.99
130.91
129.91
129.30
127.99
127.84
127.64
126.94
121.27
119.84
77.45
77.13
76.81
26.34
21.59
19.48
C(II)
OTBDPS
Me

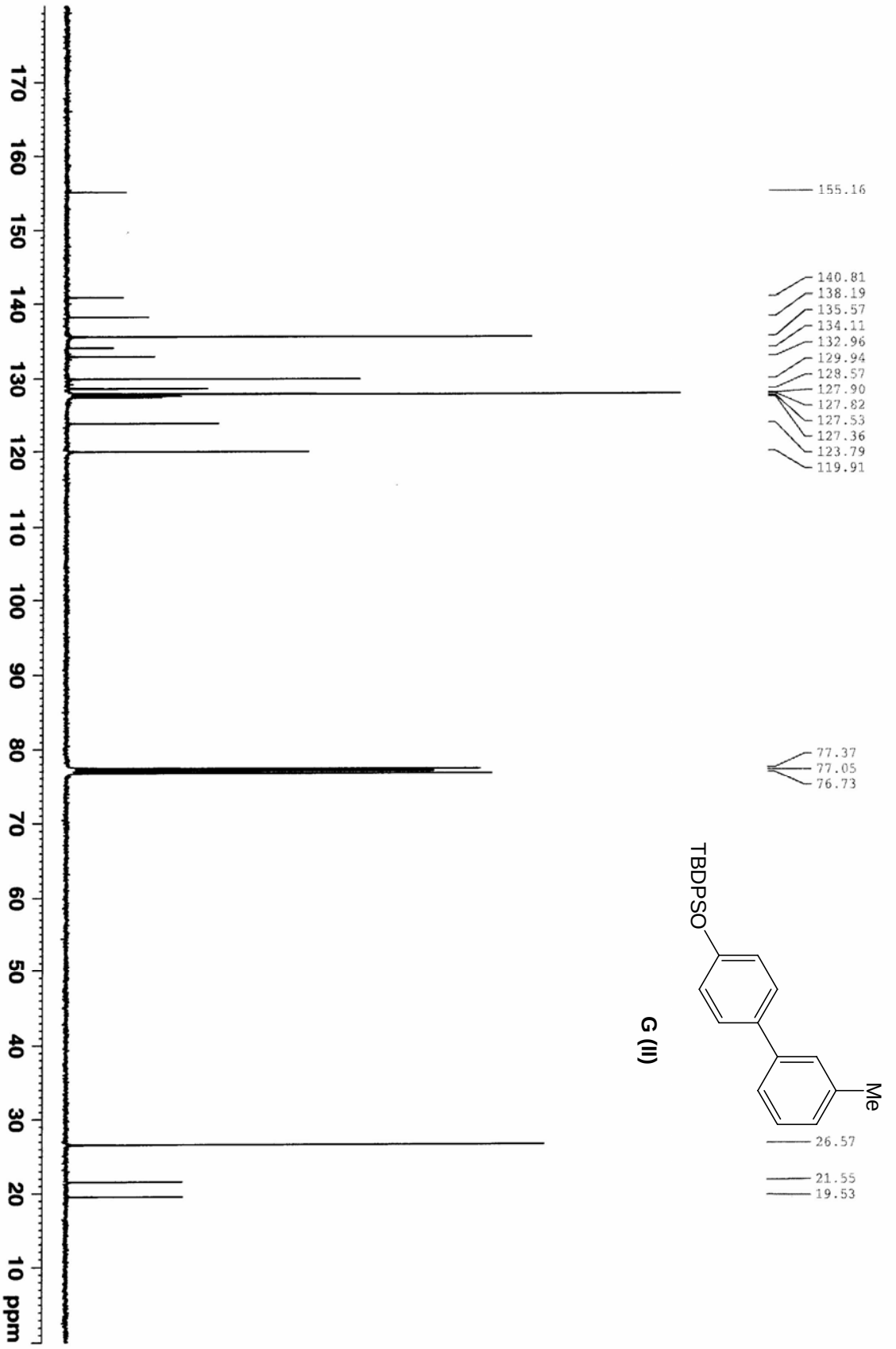

4.00
11.00
1.99
0.96
2.99
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
D(II)
Me
OTBDPS

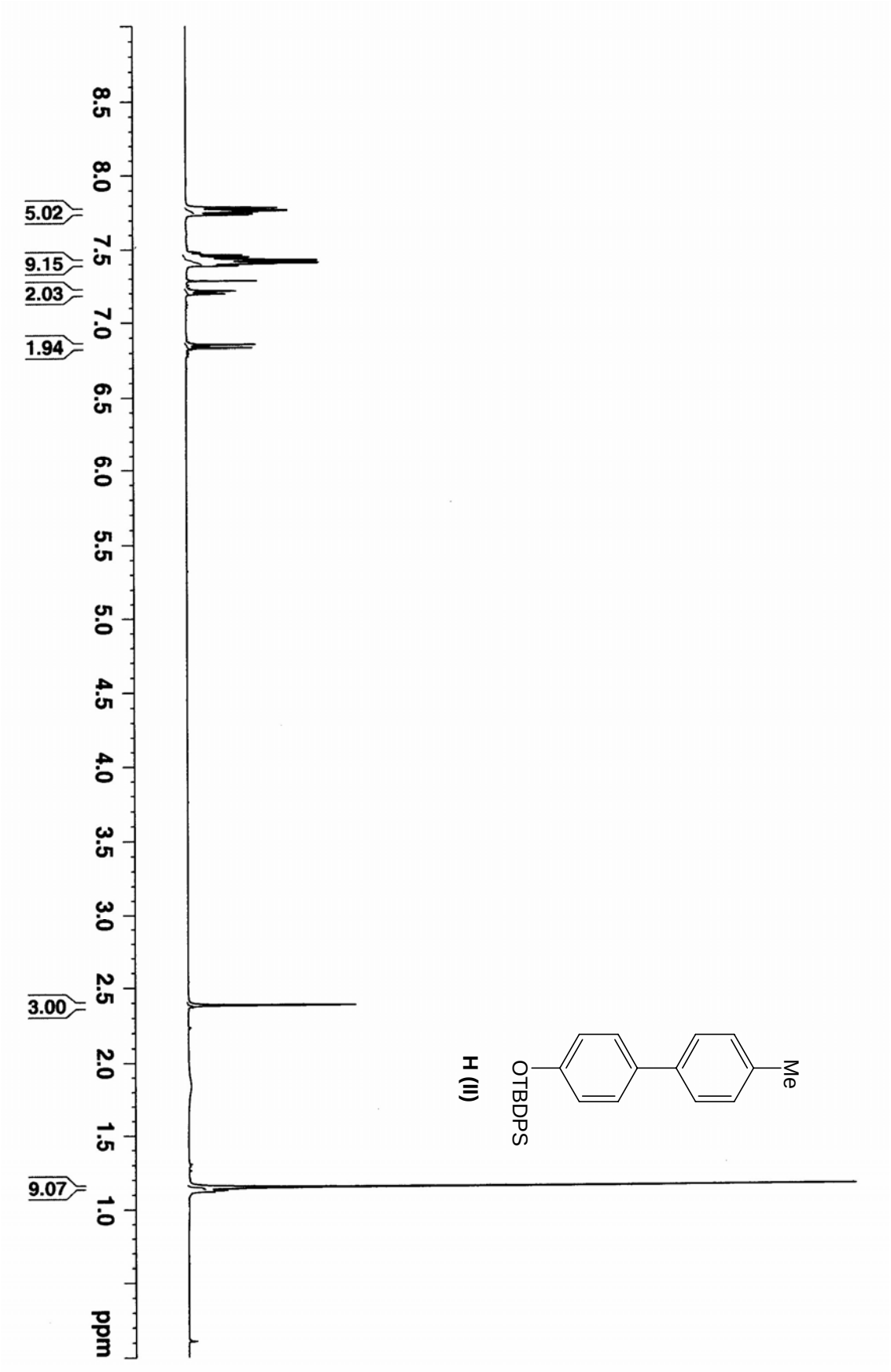

152.55
136.44
135.61
135.29
134.93
133.01
130.92
129.89
129.87
129.75
128.68
127.83
121.25
119.85
77.46
77.14
76.82
26.68
21.37
19.49
D(II)
Me
OTBDPS
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

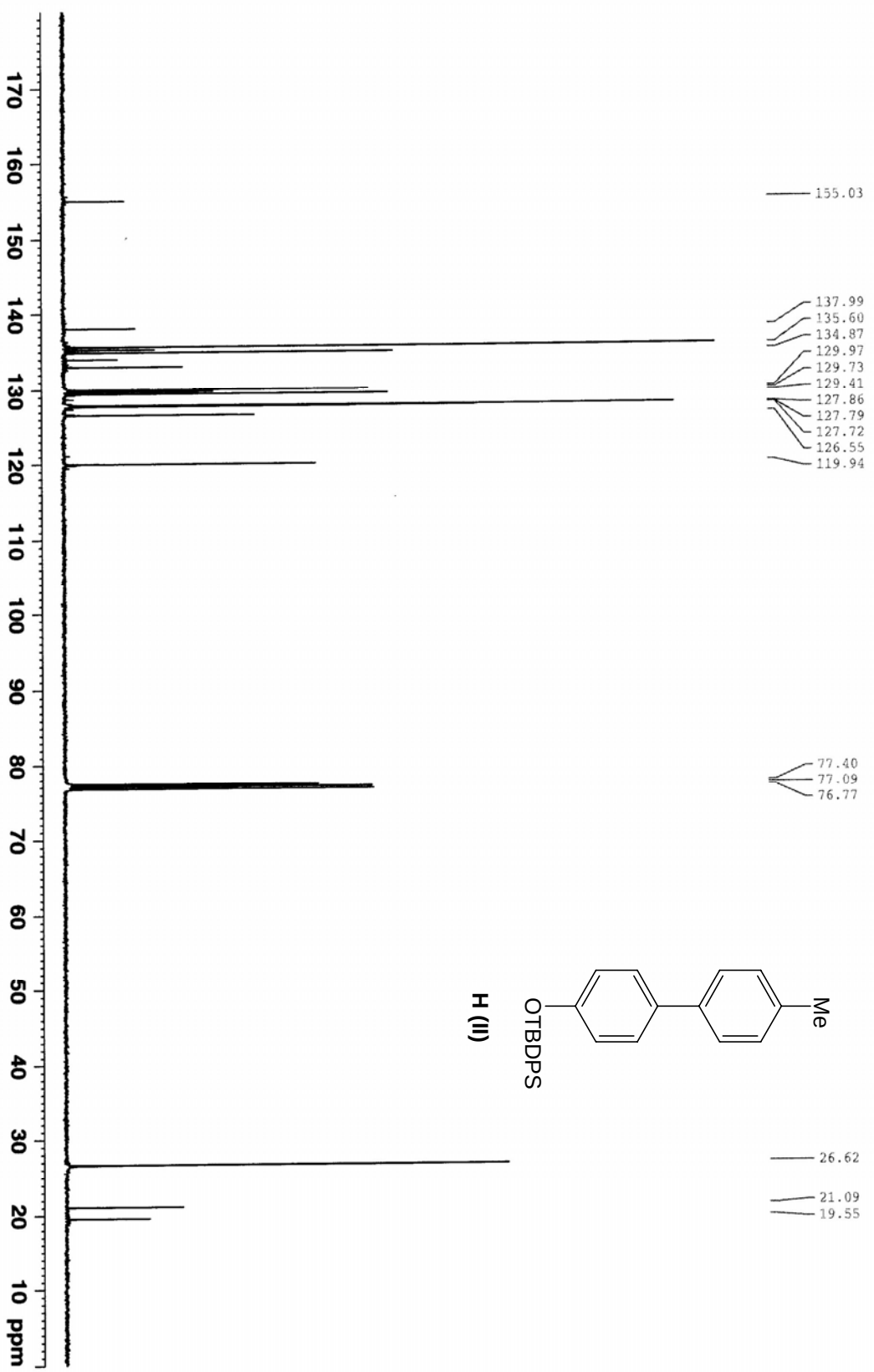

4.06
6.29
0.89
5.01
0.91
0.97
3.00
9.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
E (II)
OTBDPS
Me

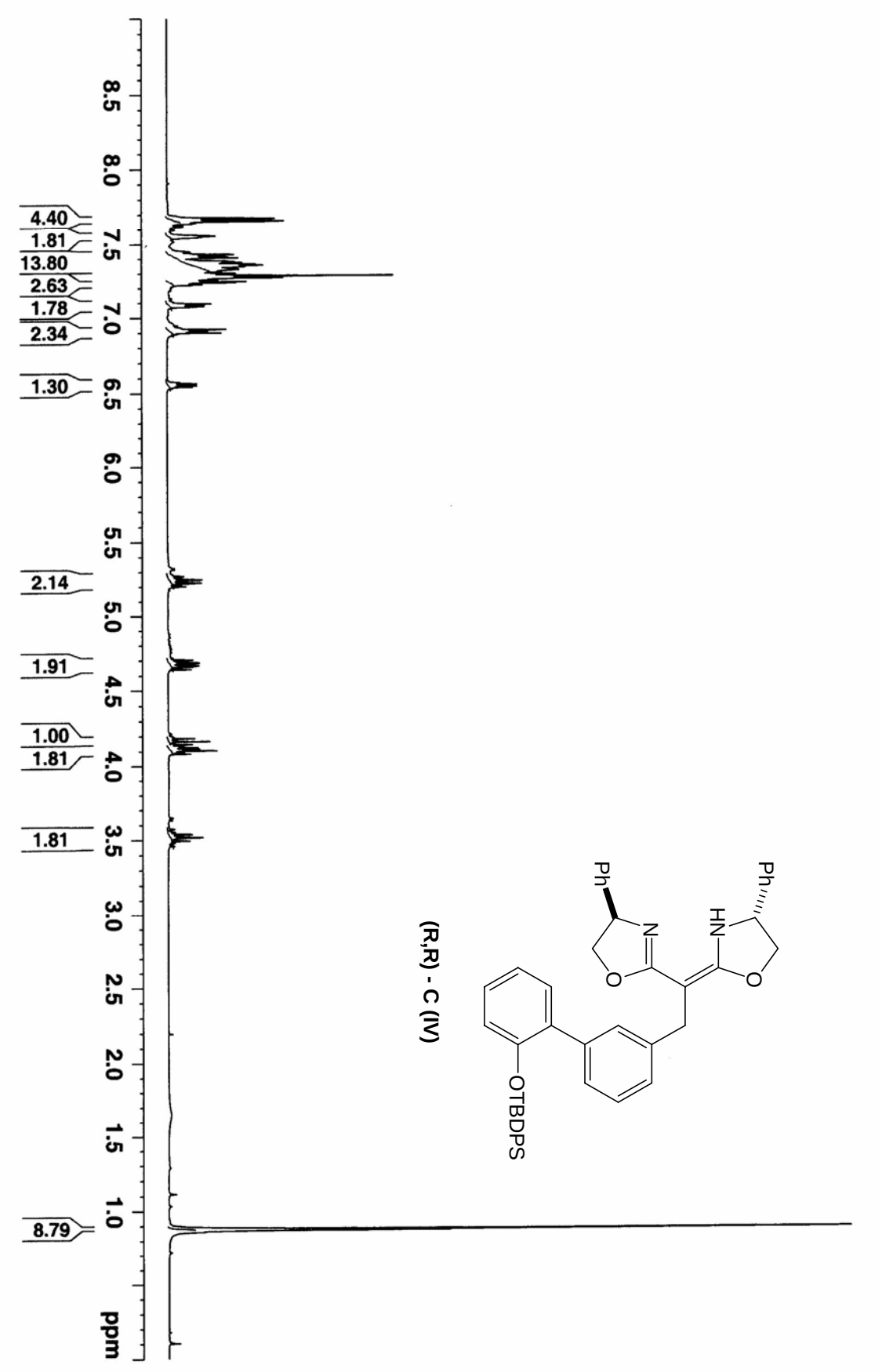

155.98
142.51
140.90
138.21
135.69
133.09
130.01
129.48
129.40
128.57
128.03
127.91
124.16
119.98
118.71
118.55
77.43
77.11
76.79
26.70
21.54
19.62
E (II)
OTBDPS
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

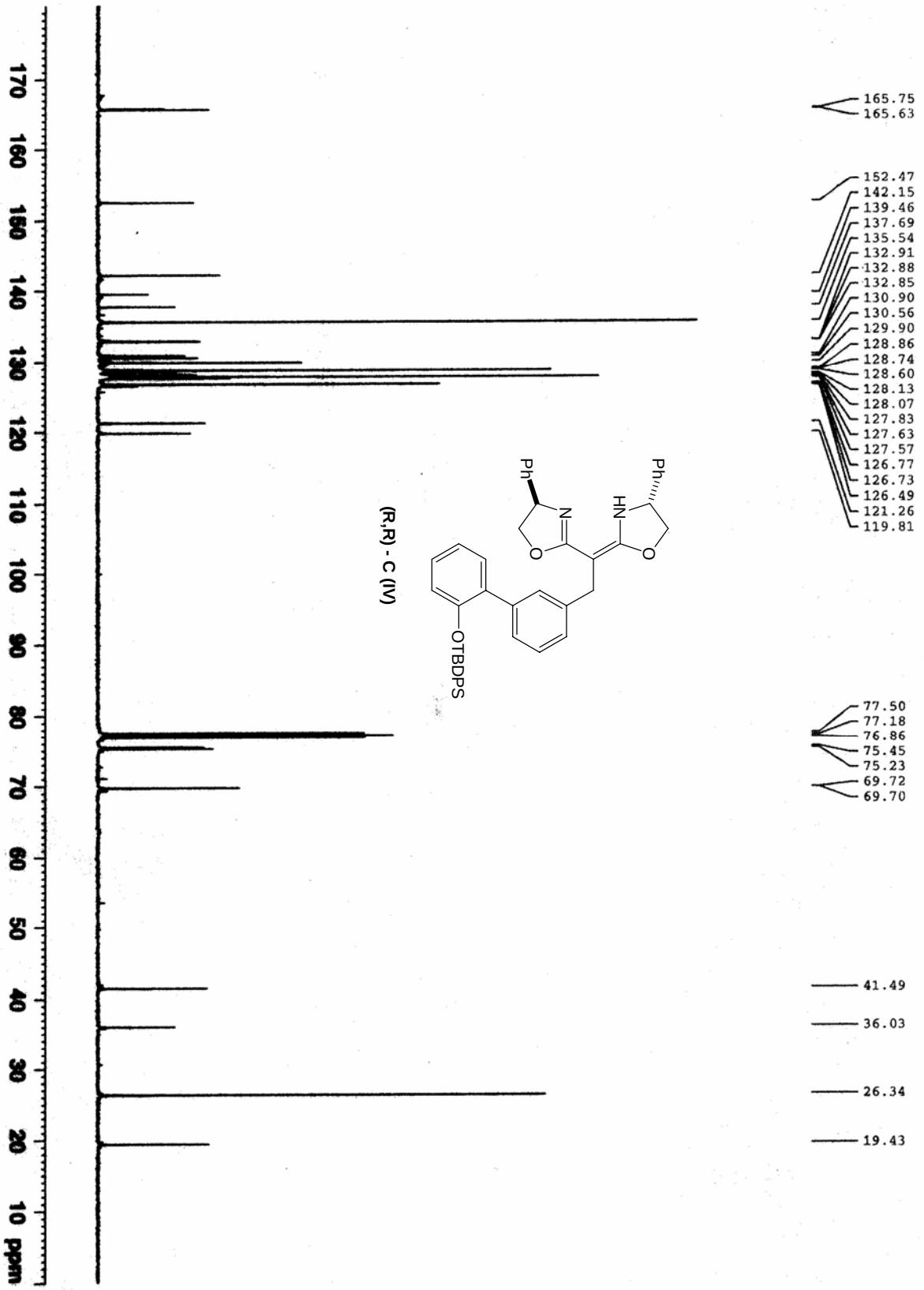

4.12
11.05
0.99
2.04
3.00
9.56
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
TBDPSO
Me
G (II)

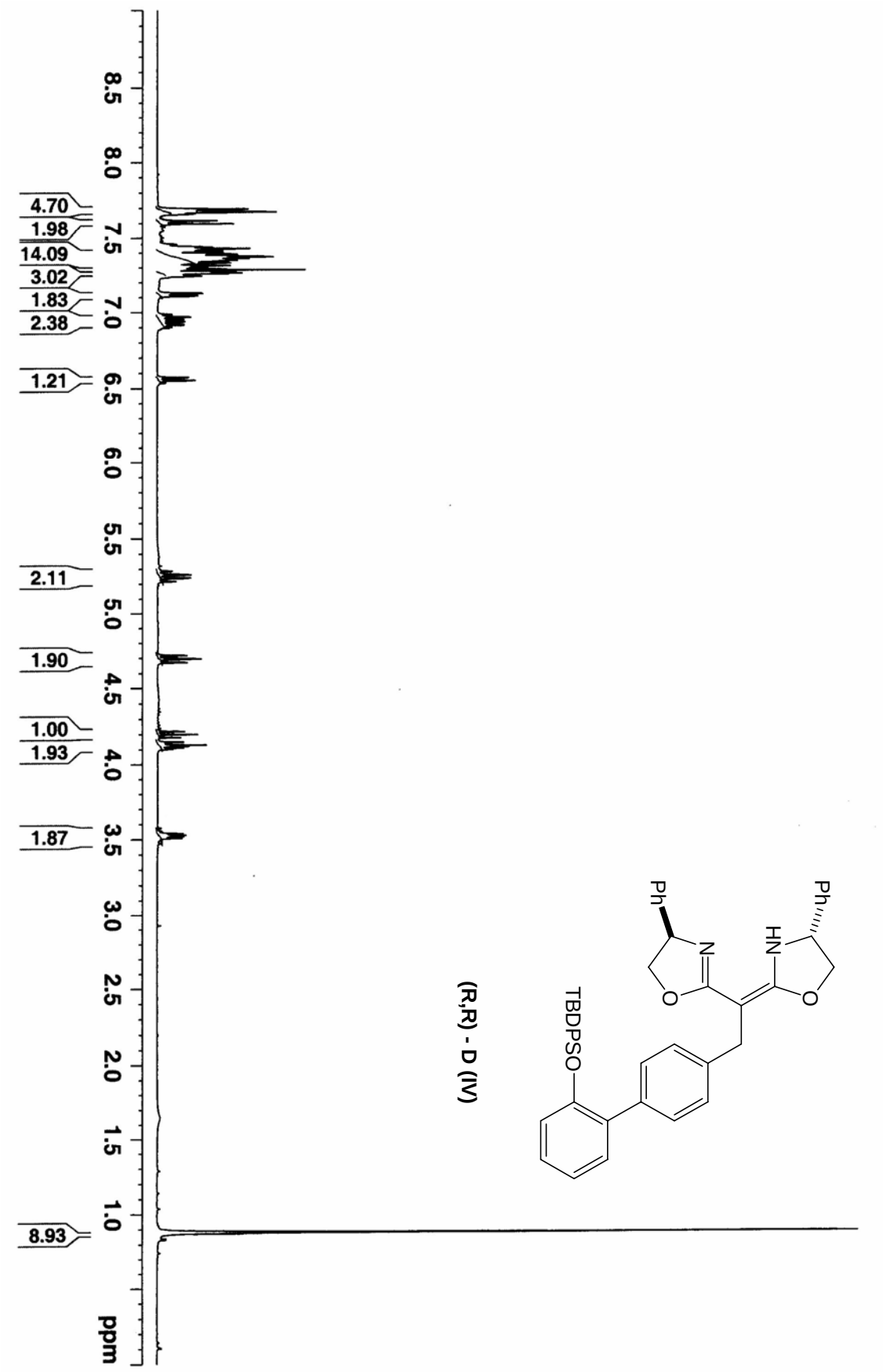

155.16
140.81
138.19
135.57
134.11
132.96
129.94
128.57
127.90
127.82
127.53
127.36
123.79
119.91
77.37
77.05
76.73
TBDPSO
Me
26.57
21.55
19.53
G (II)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

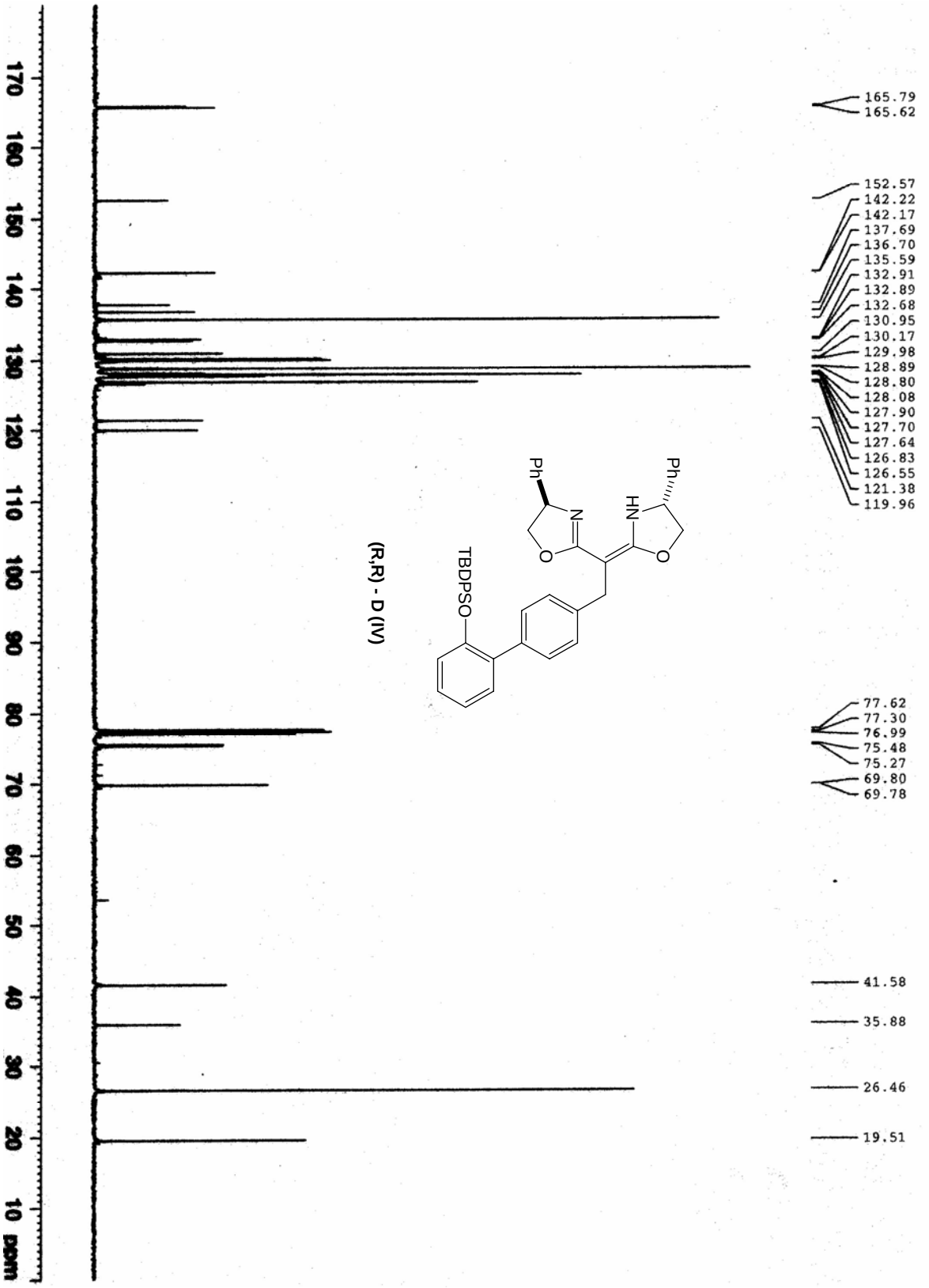

5.02
9.15
2.03
1.94
3.00
9.07
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
H (II)
OTBDPS
Me

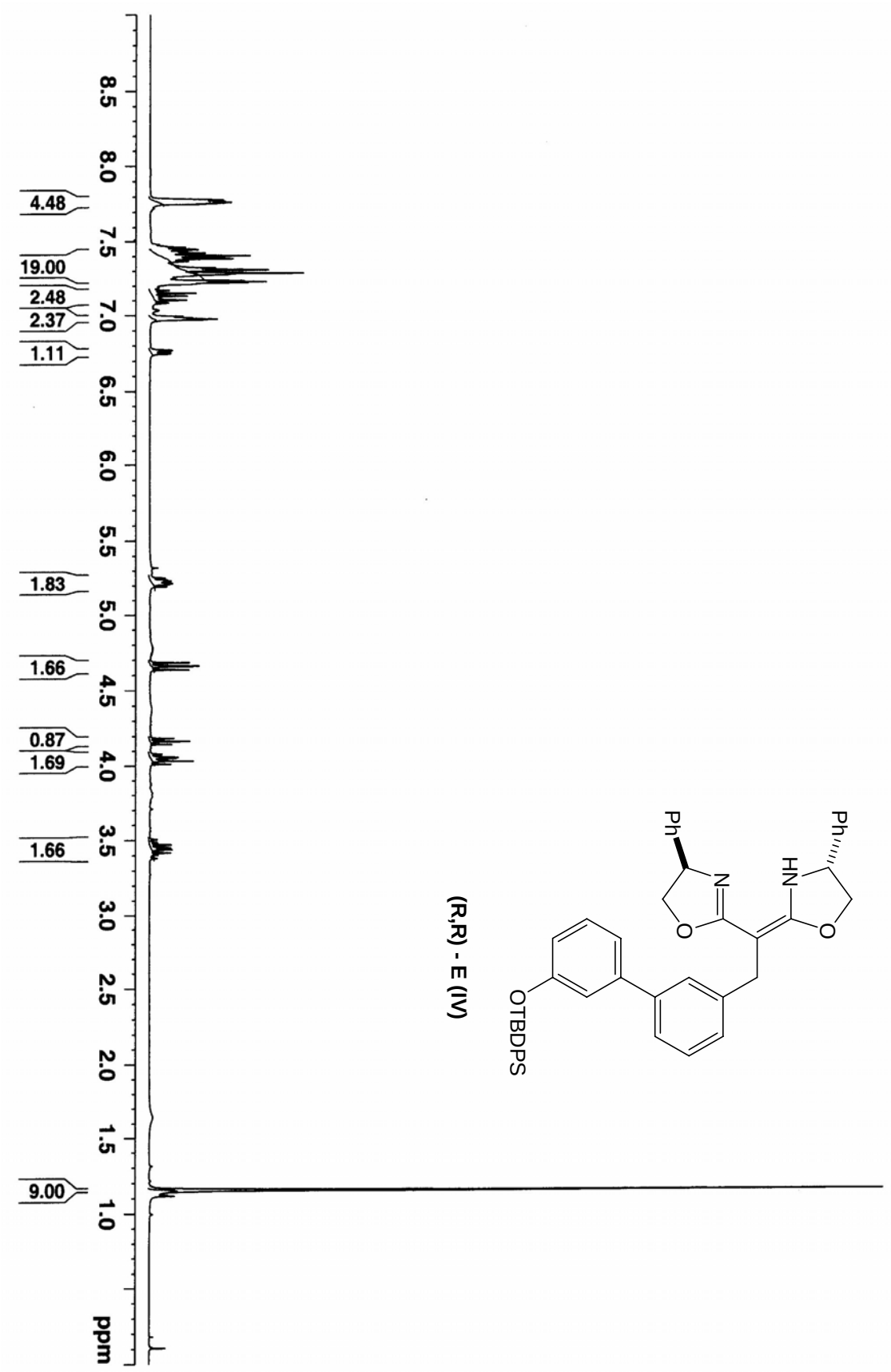

155.03
137.99
135.60
134.87
129.97
129.73
129.41
127.86
127.79
127.72
126.55
119.94
77.40
77.09
76.77
26.62
21.09
19.55
H (II)
OTBDPS
Me
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


4.40
1.81
13.80
2.63
1.78
2.34
1.30
2.14
1.91
1.00
1.81
1.81
8.79
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - C (IV)
Ph
N
O
HN
Ph
O
OTBDPS


165.75
165.63
152.47
142.15
139.46
137.69
135.54
132.91
132.88
132.85
130.90
130.56
129.90
128.86
128.74
128.60
128.13
128.07
127.83
127.63
127.57
126.77
126.73
126.49
121.26
119.81
77.50
77.18
76.86
75.45
75.23
69.72
69.70
41.49
36.03
26.34
19.43
ppm
(R,R) - C (IV)
Ph
N
O
HN
Ph
O
OTBDPS


4.70
1.98
14.09
3.02
1.83
2.38
1.21
2.11
1.90
1.00
1.93
1.87
8.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - D (IV)
TBDPSO
Ph
N
O
HN
O
Ph


165.79
165.62
152.57
142.22
142.17
137.69
136.70
135.59
132.91
132.89
132.68
130.95
130.17
129.98
128.89
128.80
128.08
127.90
127.70
127.64
126.83
126.55
121.38
119.96
77.62
77.30
76.99
75.48
75.27
69.80
69.78
41.58
35.88
26.46
19.51
ppm
(R,R) - D (IV)
TBDPSO
Ph
Ph
N
HN
O
O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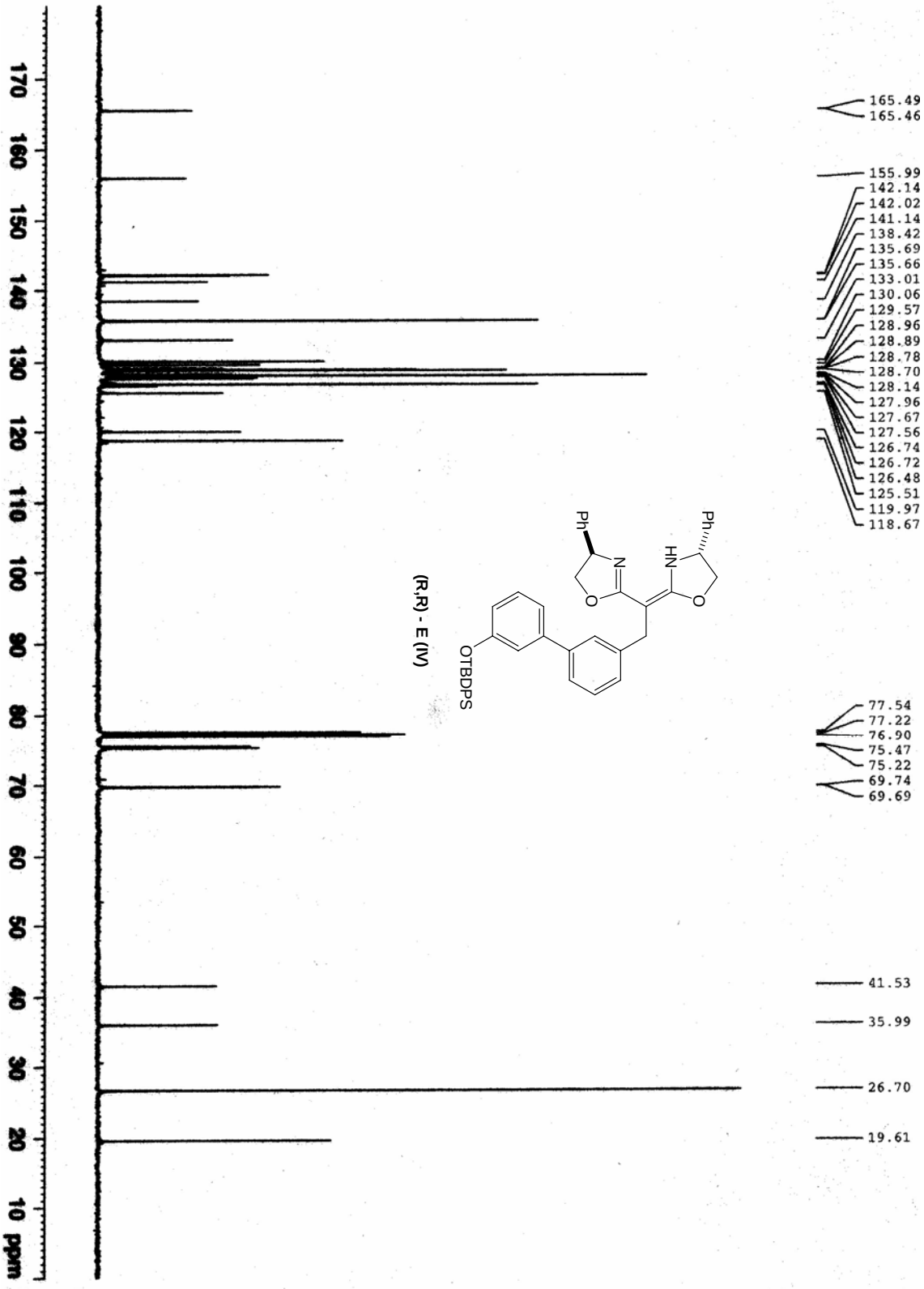
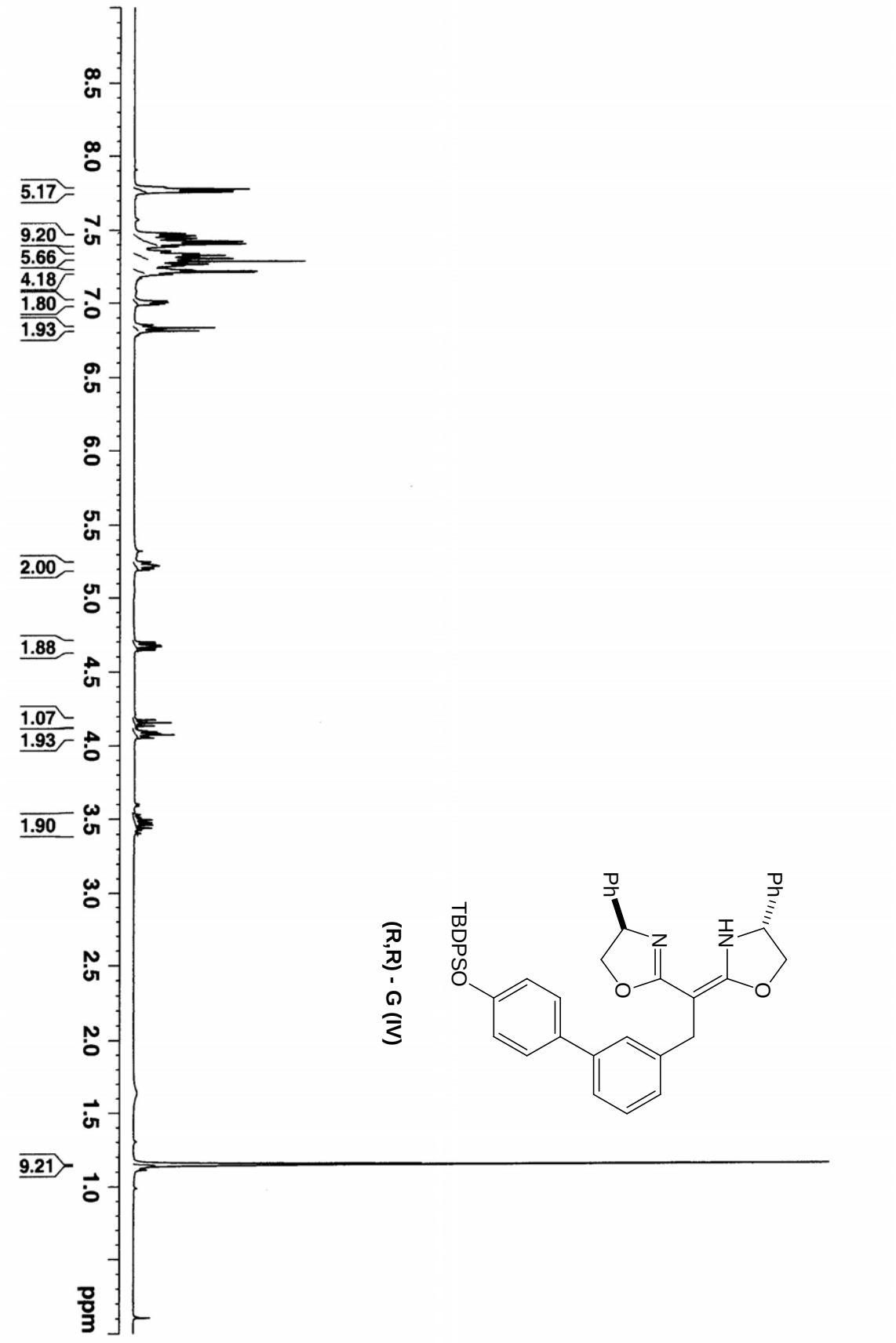
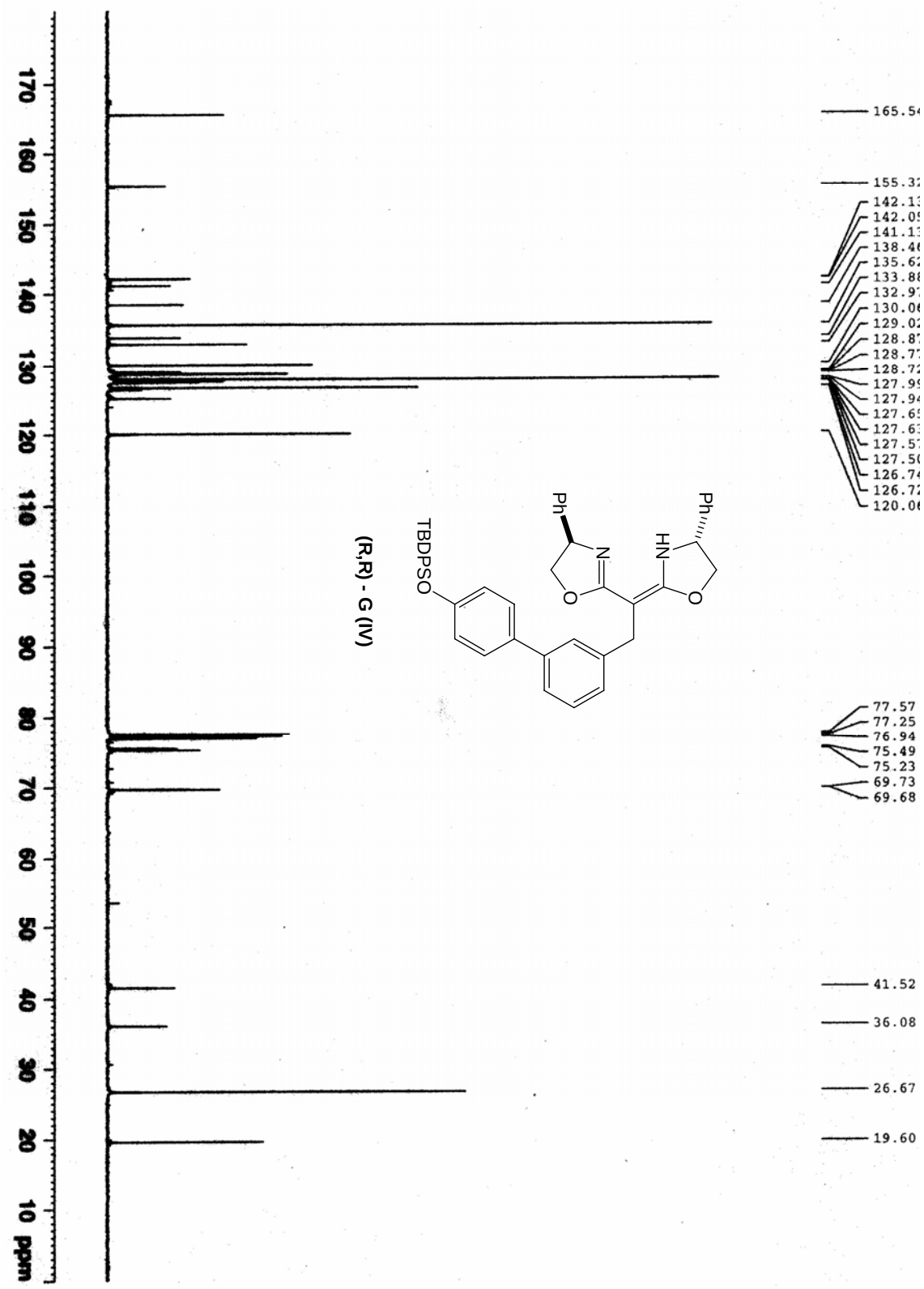
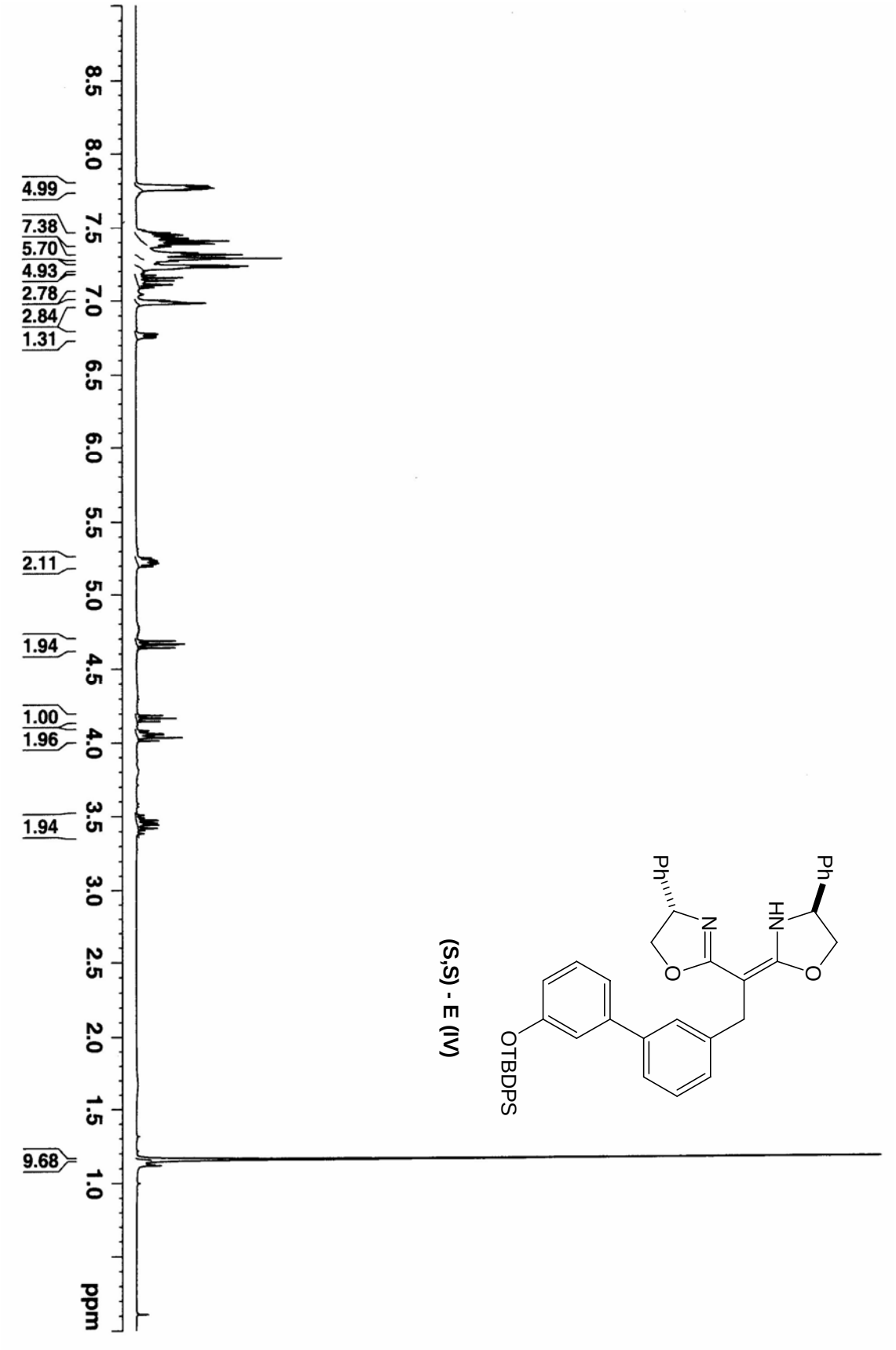
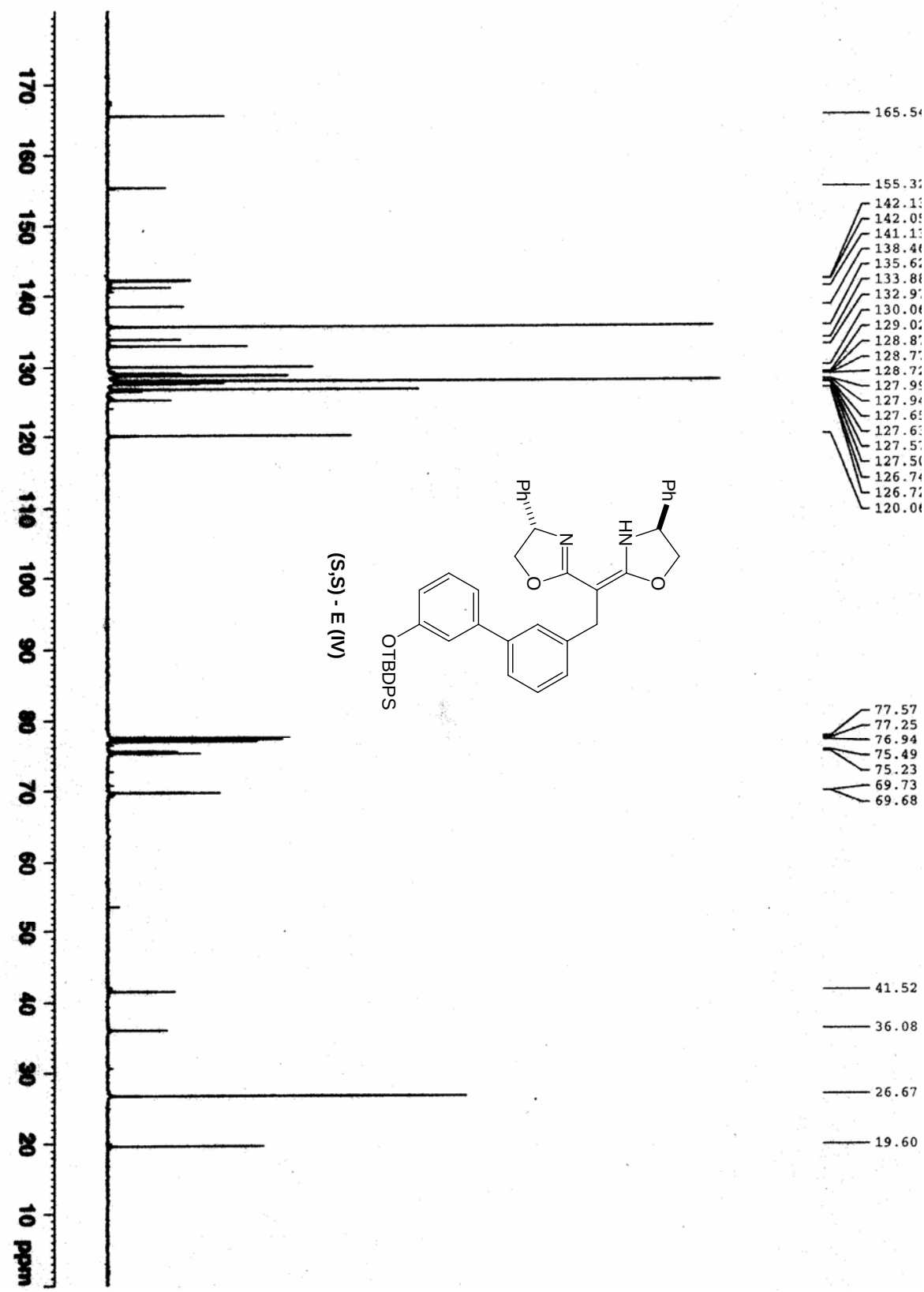
19.00
2.48
2.37
1.11
1.83
1.66
0.87
1.69
1.66
9.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - E (IV)
Ph
N
O
HN
Ph
O
OTBDPS

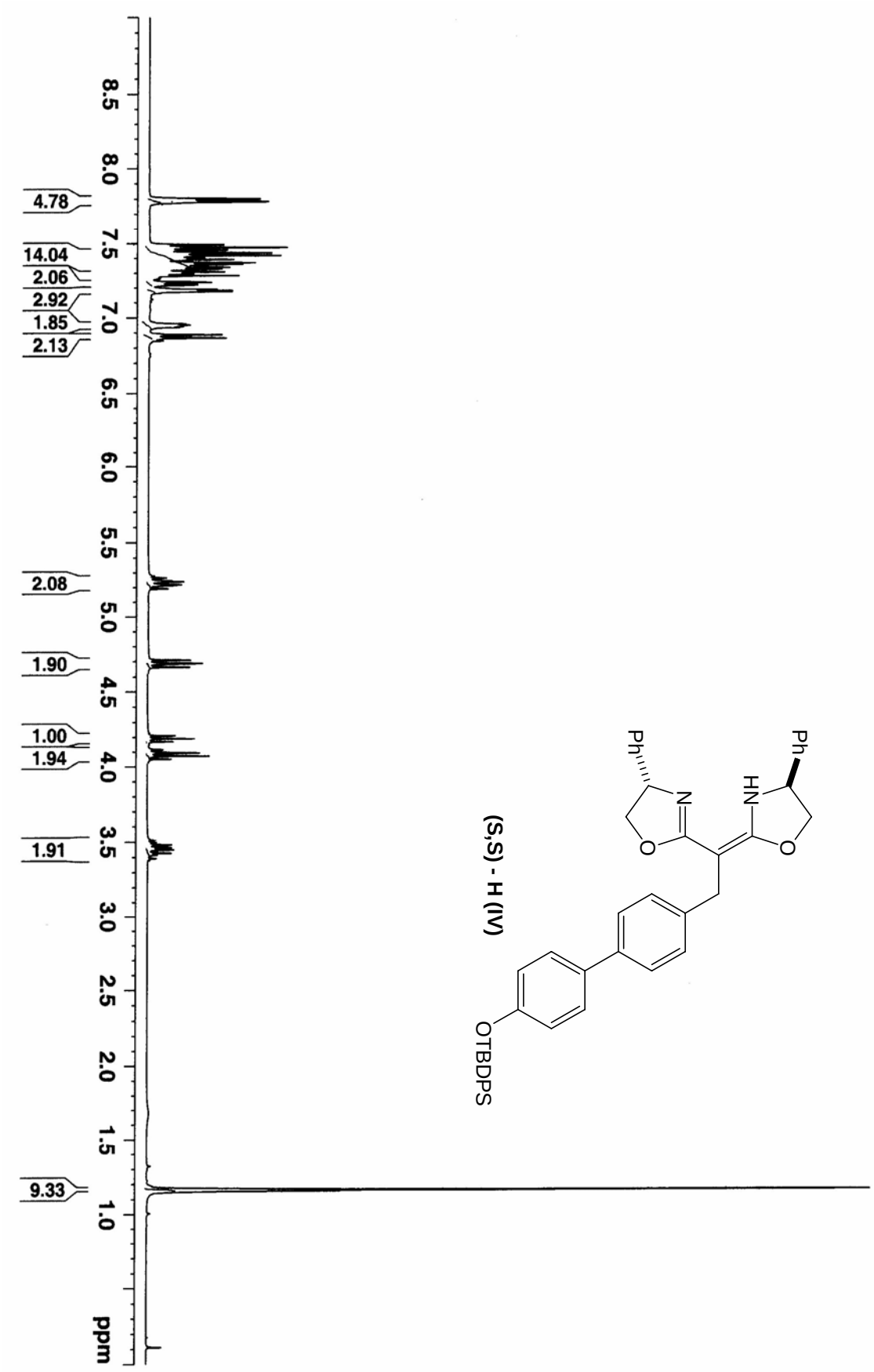

165.49
165.46
155.99
142.14
142.02
141.14
138.42
135.69
135.66
133.01
130.06
129.57
128.96
128.89
128.78
128.70
128.14
127.96
127.67
127.56
126.74
126.72
126.48
125.51
119.97
118.67
77.54
77.22
76.90
75.47
75.22
69.74
69.69
41.53
35.99
26.70
19.61
ppm
(R,R) - E (IV)
Ph
N
O
HN
Ph
O
OTBDPS

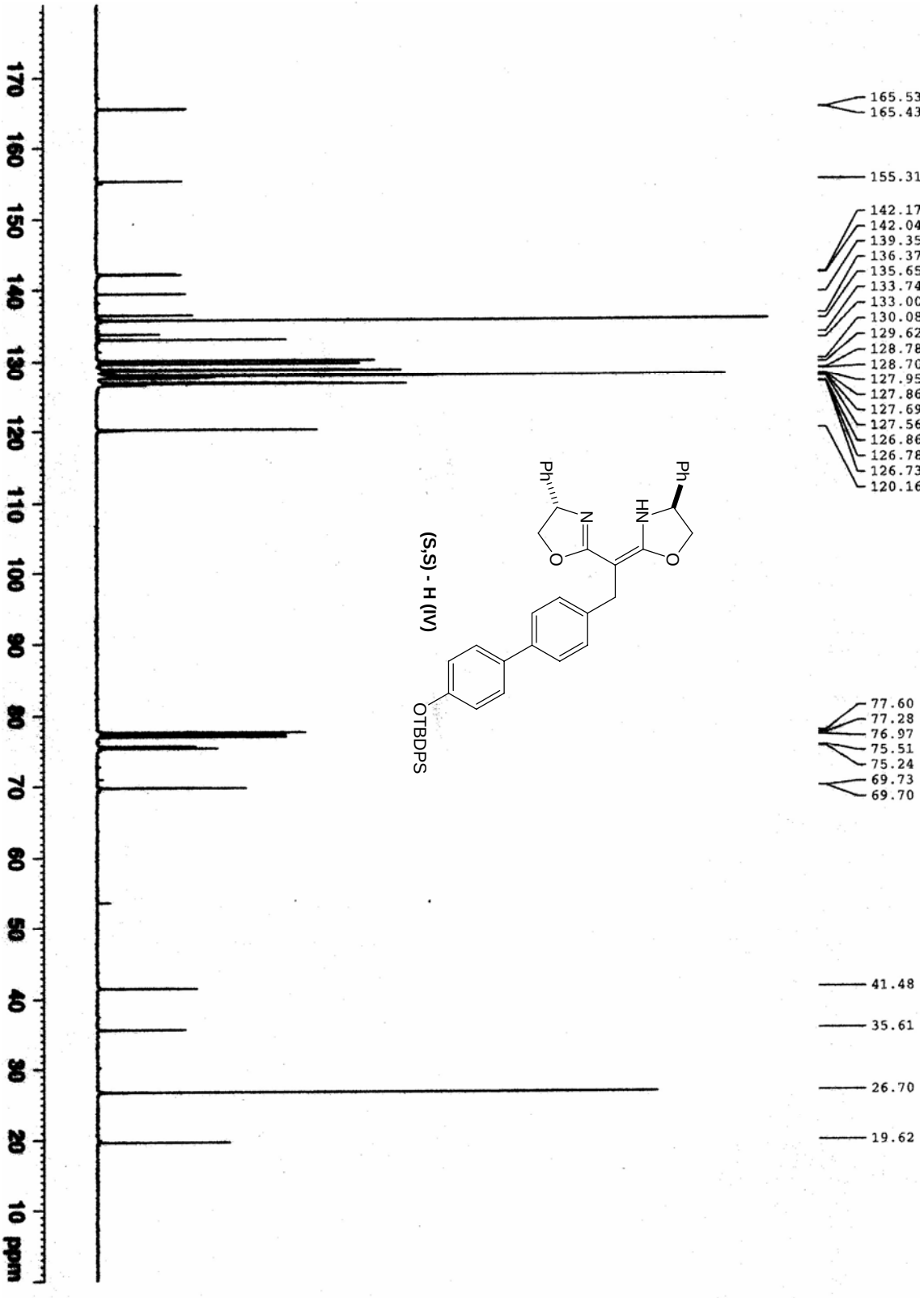

5.17
9.20
5.66
4.18
1.80
1.93
2.00
1.88
1.07
1.93
1.90
9.21
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - G (IV)
TBDPSO
Ph
N
O
HN
O
Ph


165.54
155.32
142.13
142.09
141.13
138.46
135.62
133.88
132.97
130.06
129.02
128.87
128.77
128.72
127.99
127.94
127.65
127.63
127.57
127.50
126.74
126.72
120.06
77.57
77.25
76.94
75.49
75.23
69.73
69.68
41.52
36.08
26.67
19.60
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
(R,R) - G (IV)
TBDPSO
Ph
N
O
HN
Ph
O


4.99
7.38
5.70
4.93
2.78
2.84
1.31
2.11
1.94
1.00
1.96
1.94
9.68
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(S,S) - E (IV)
Ph
HN
N
O
O
Ph
OTBDPS


(S,S) - E (IV)
Ph
N
O
HN
Ph
O
OTBDPS
165.54
155.32
142.13
142.05
141.11
138.46
135.62
133.88
132.97
130.06
129.02
128.87
128.77
128.72
127.99
127.94
127.65
127.61
127.57
127.50
126.74
126.72
120.06
77.57
77.25
76.94
75.49
75.23
69.73
69.68
41.52
36.08
26.67
19.60
ppm


4.78
14.04
2.06
2.92
1.85
2.13
2.08
1.90
1.00
1.94
1.91
9.33
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(S,S) - H (IV)
Ph
N
O
HN
Ph
O
OTBDPS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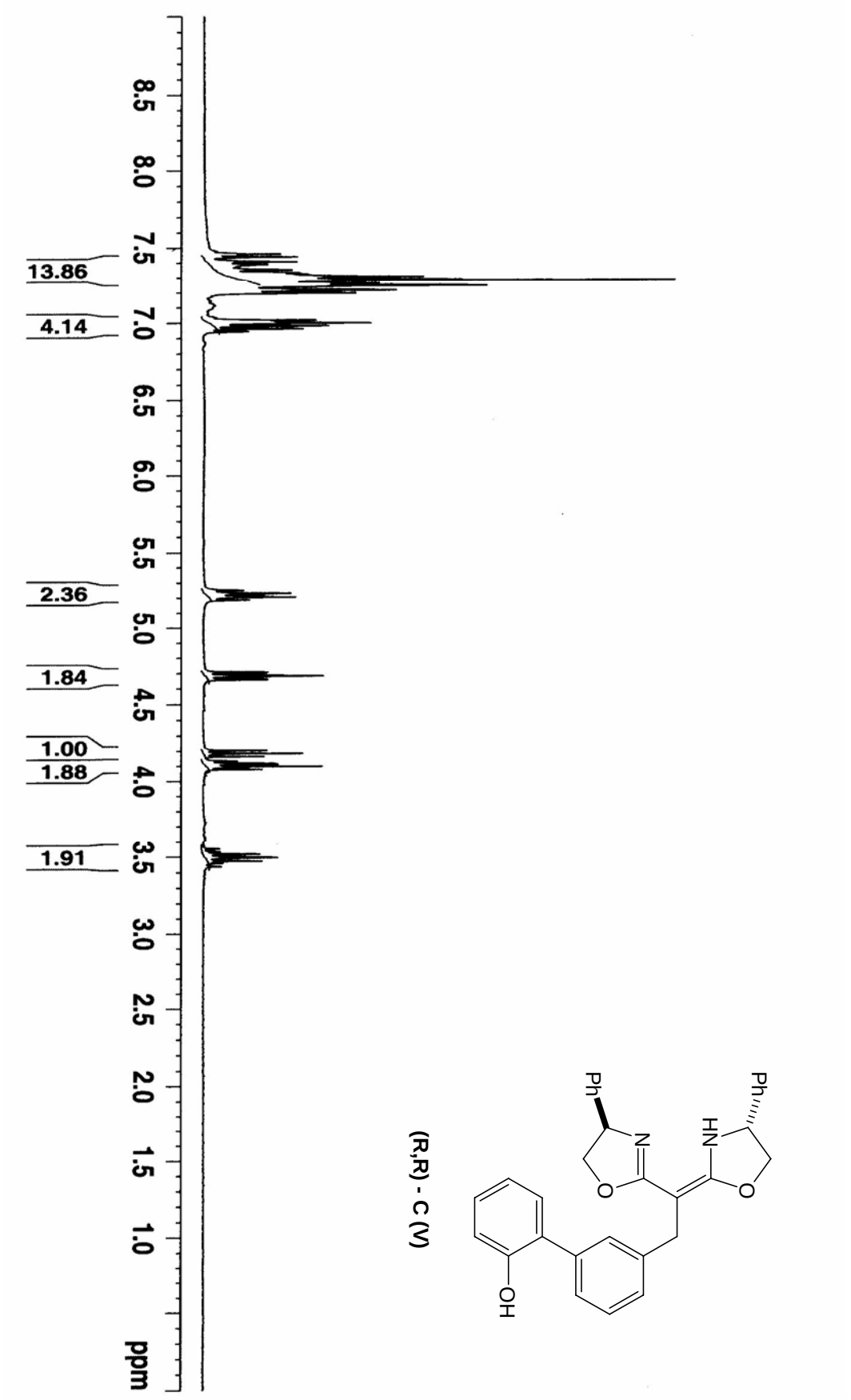
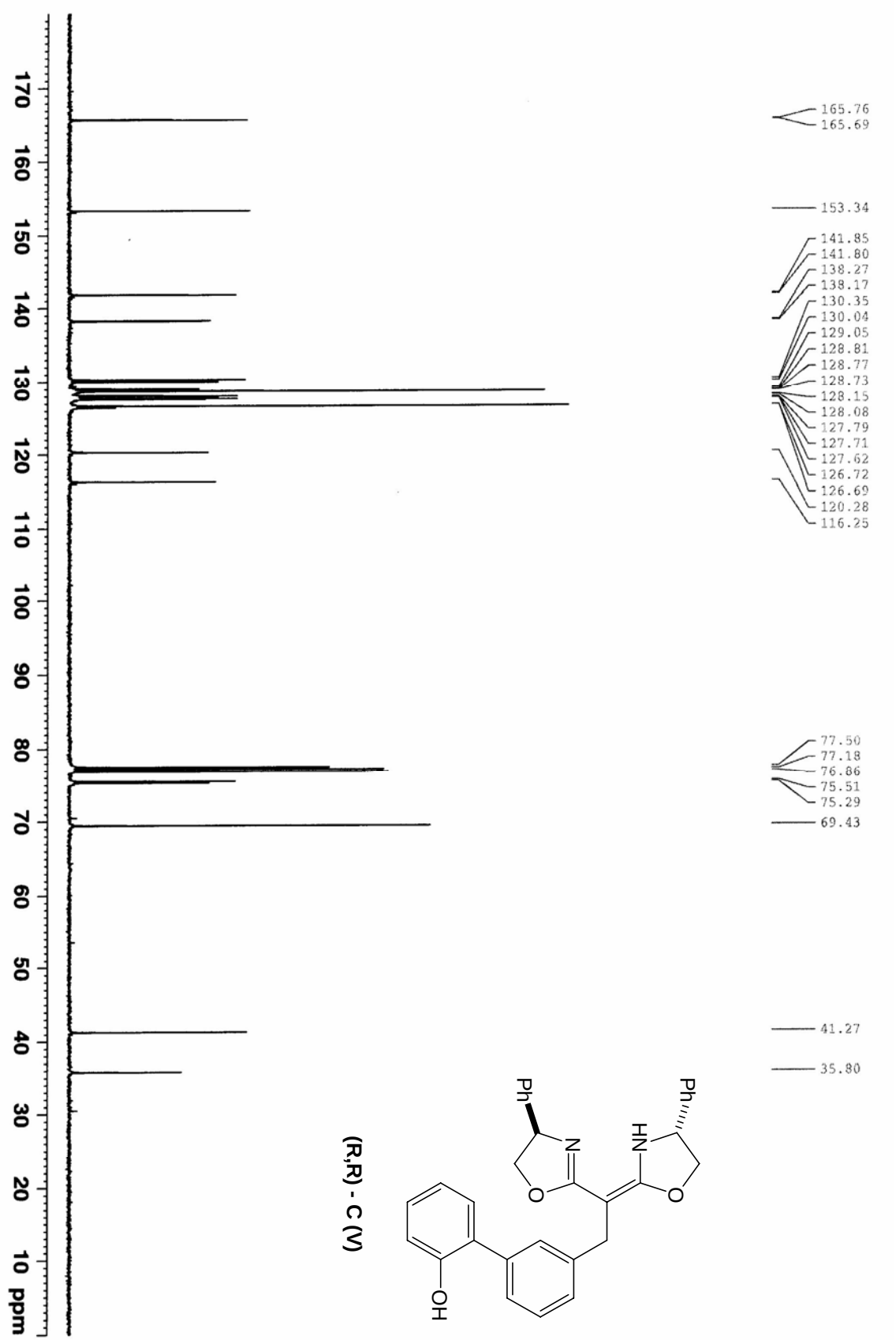
165.43
155.31
142.17
142.04
139.35
136.37
135.65
133.74
133.00
130.08
129.62
128.78
128.70
127.95
127.86
127.69
127.56
126.86
126.78
126.73
120.16
77.60
77.28
76.97
75.51
75.24
69.73
69.70
41.48
35.61
26.70
19.62
ppm
(S,S) - H (IV)
Ph
Ph
N
HN
O
O
OTBDPS


13.86
4.14
2.36
1.84
1.00
1.88
1.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - C (V)
Ph
N
O
HN
Ph
O
OH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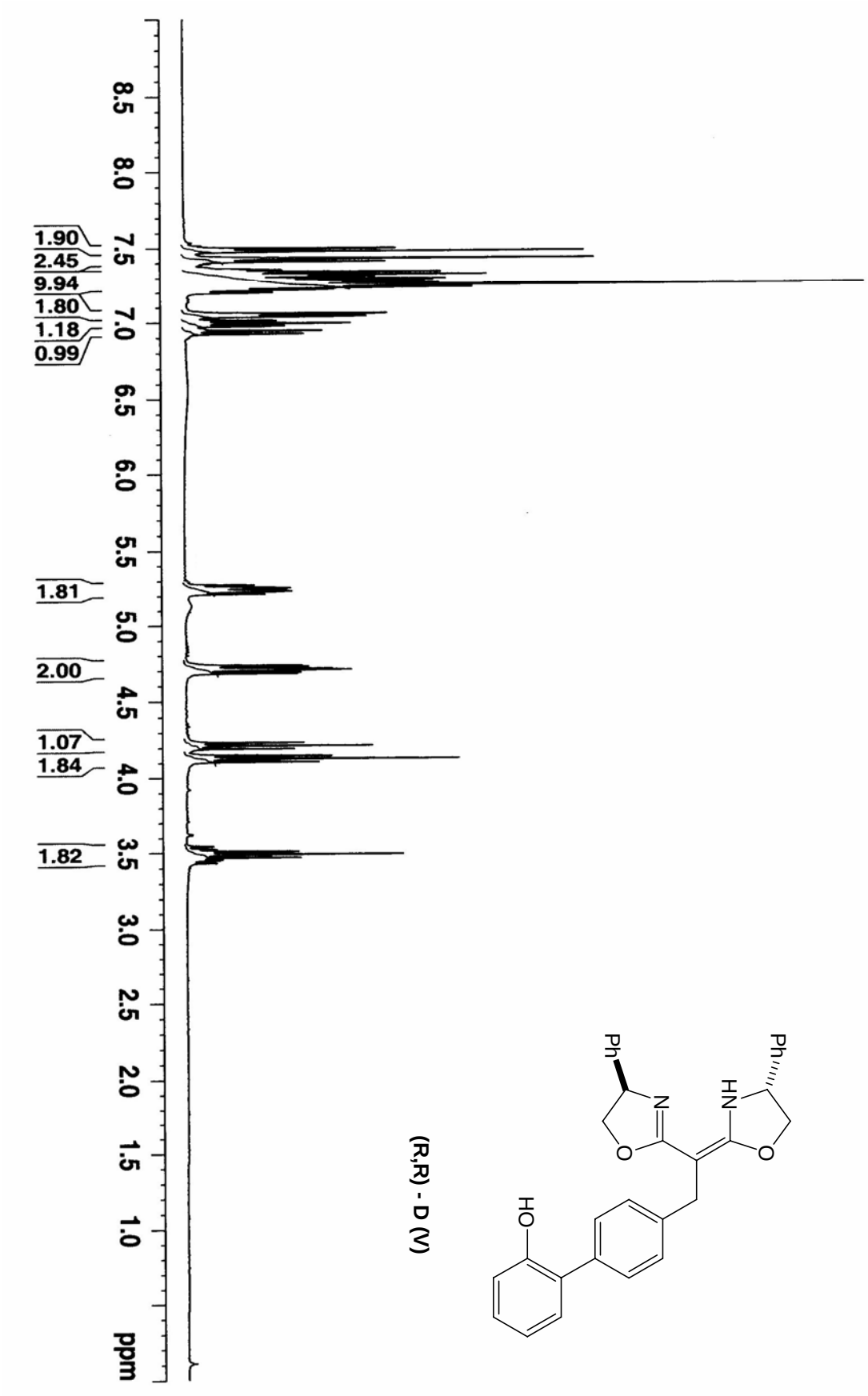
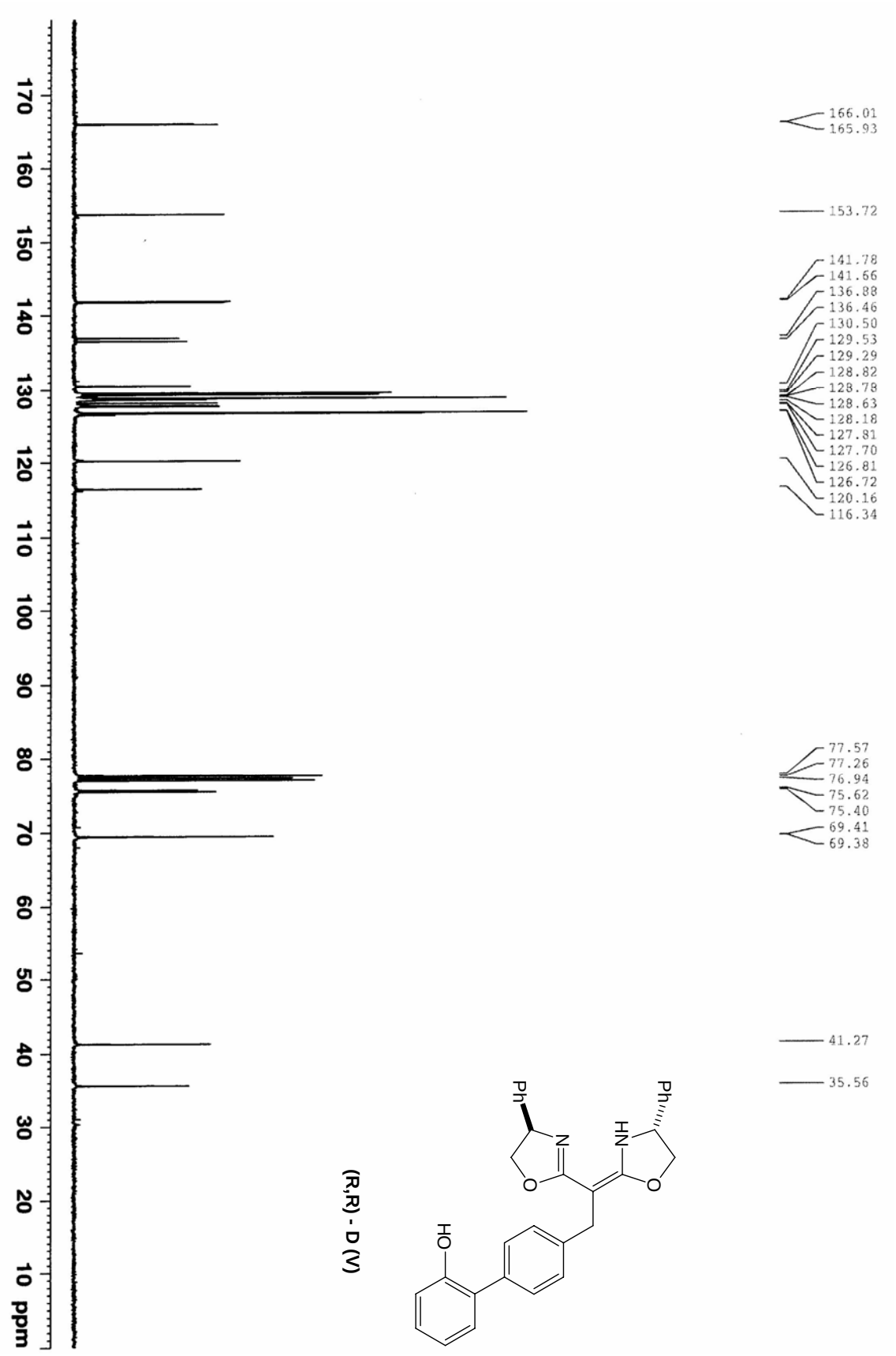
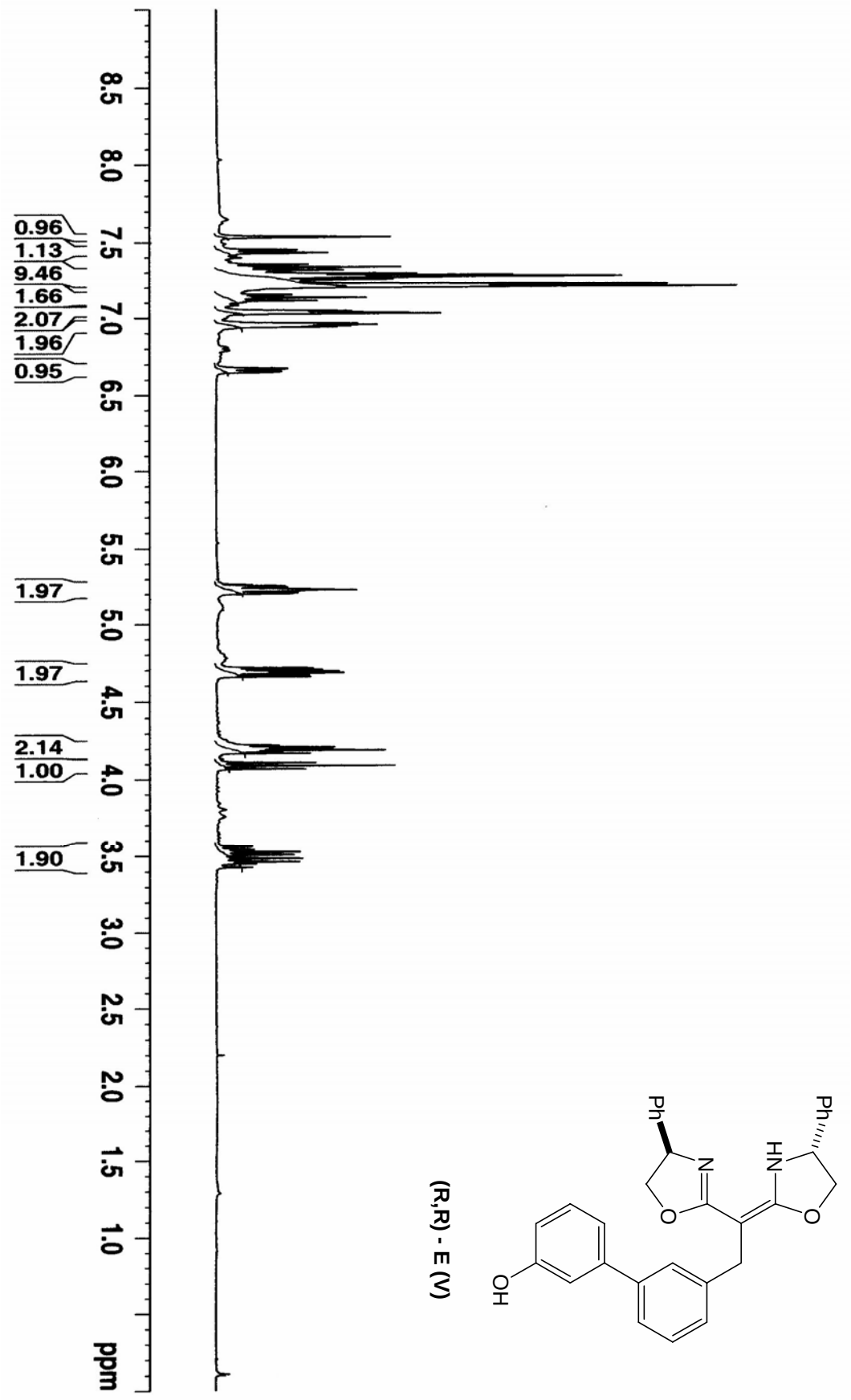
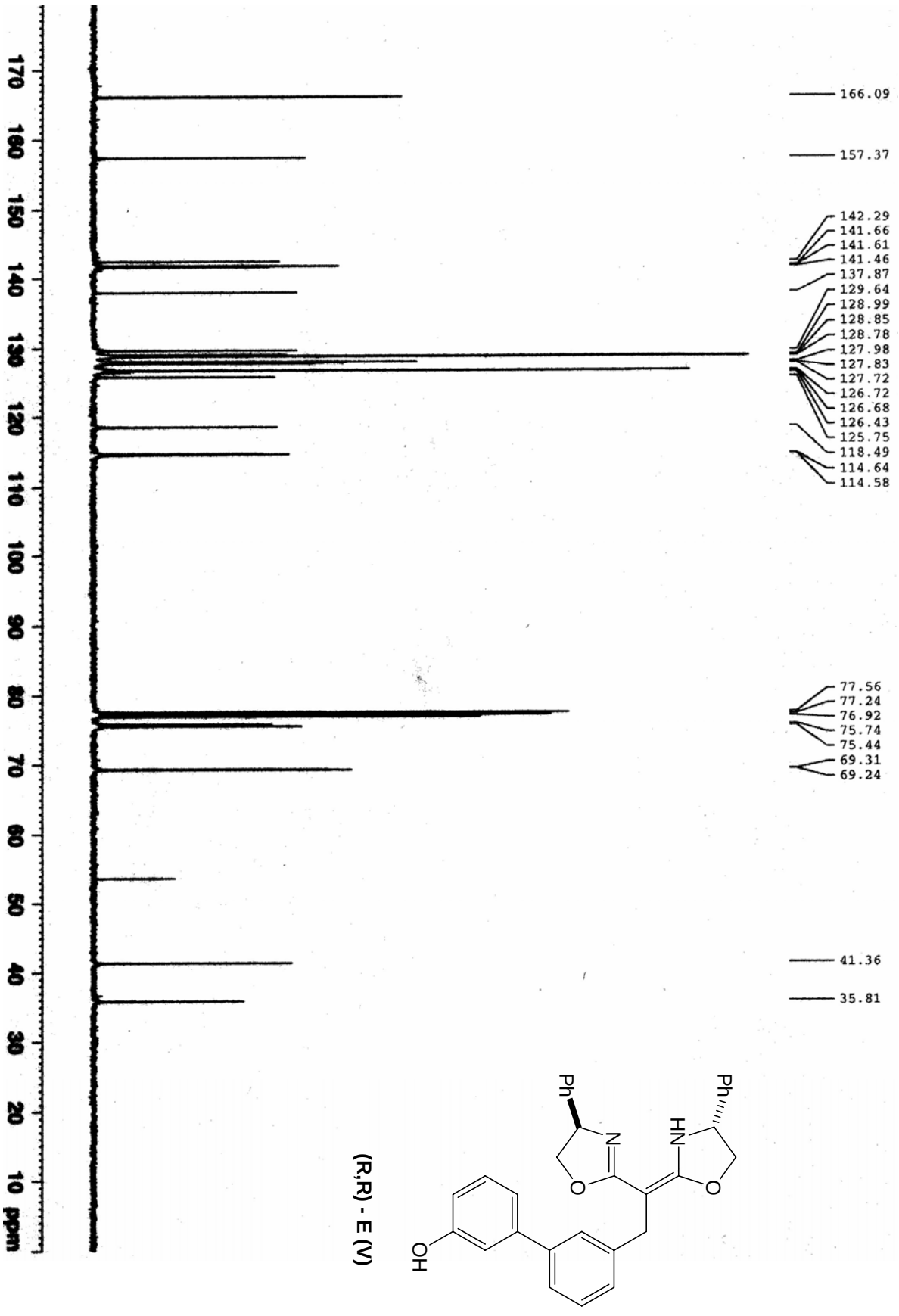
165.69
153.34
141.85
141.80
138.27
138.17
130.35
130.04
129.05
128.81
128.77
128.73
128.15
128.08
127.79
127.71
127.62
126.72
126.69
120.28
116.25
77.50
77.18
76.86
75.51
75.29
69.43
41.27
35.80
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
(R,R) - C (V)
Ph
N
O
HN
Ph
O
OH

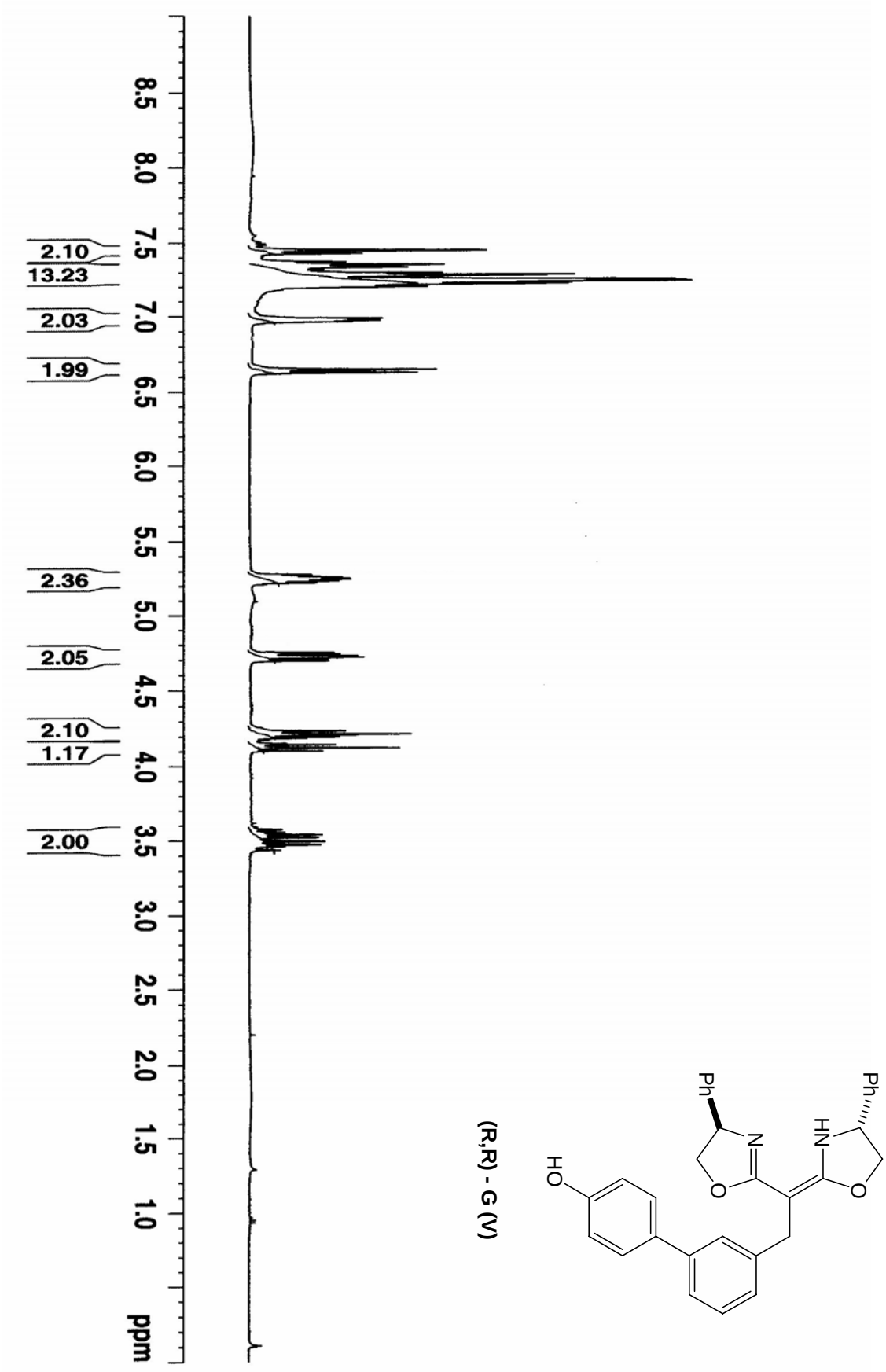

1.90
2.45
9.94
1.80
1.18
0.99
1.81
2.00
1.07
1.84
1.82
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
Ph
N
O
HN
Ph
O
HO

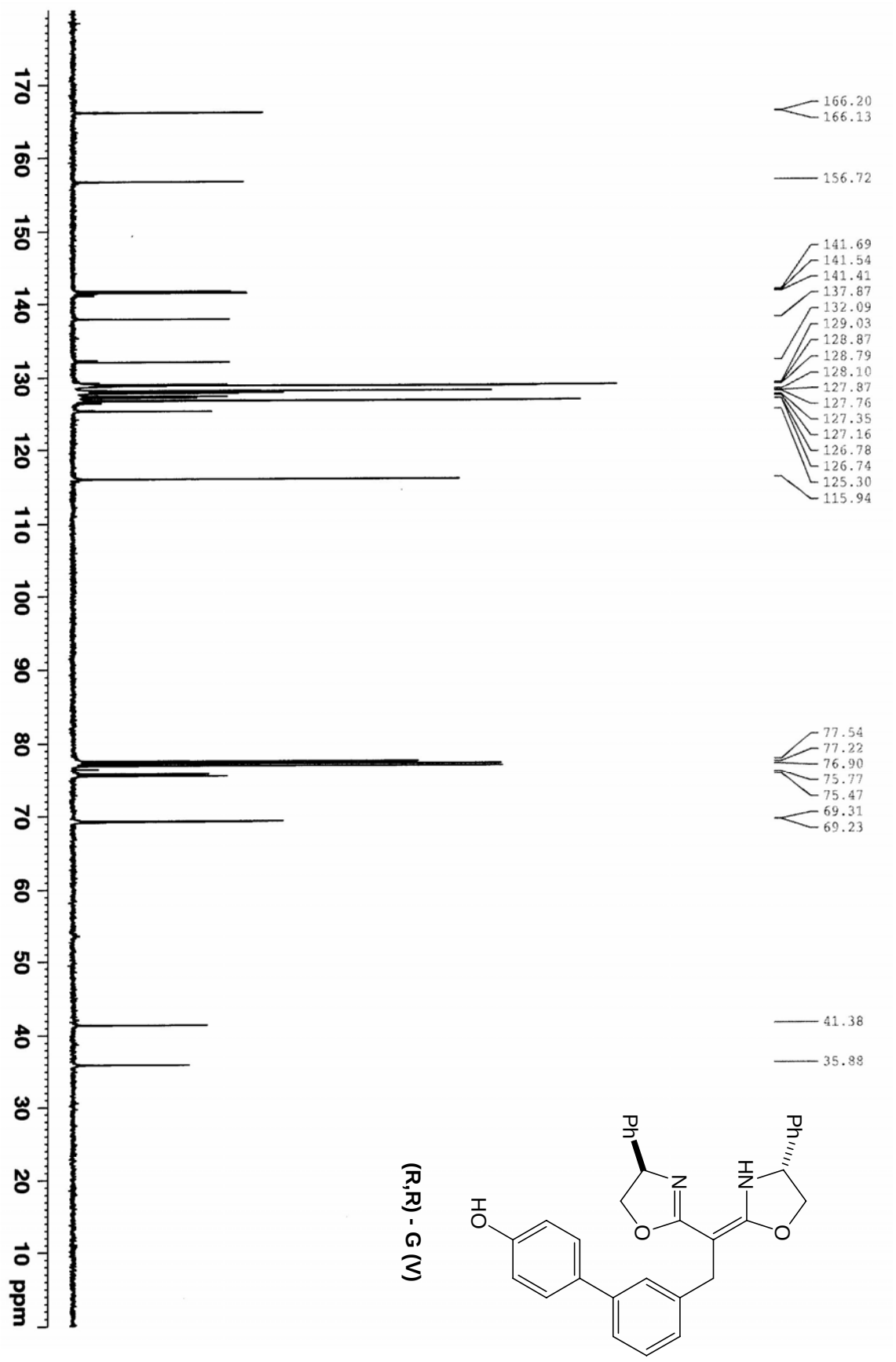
(R,R) - D (V)

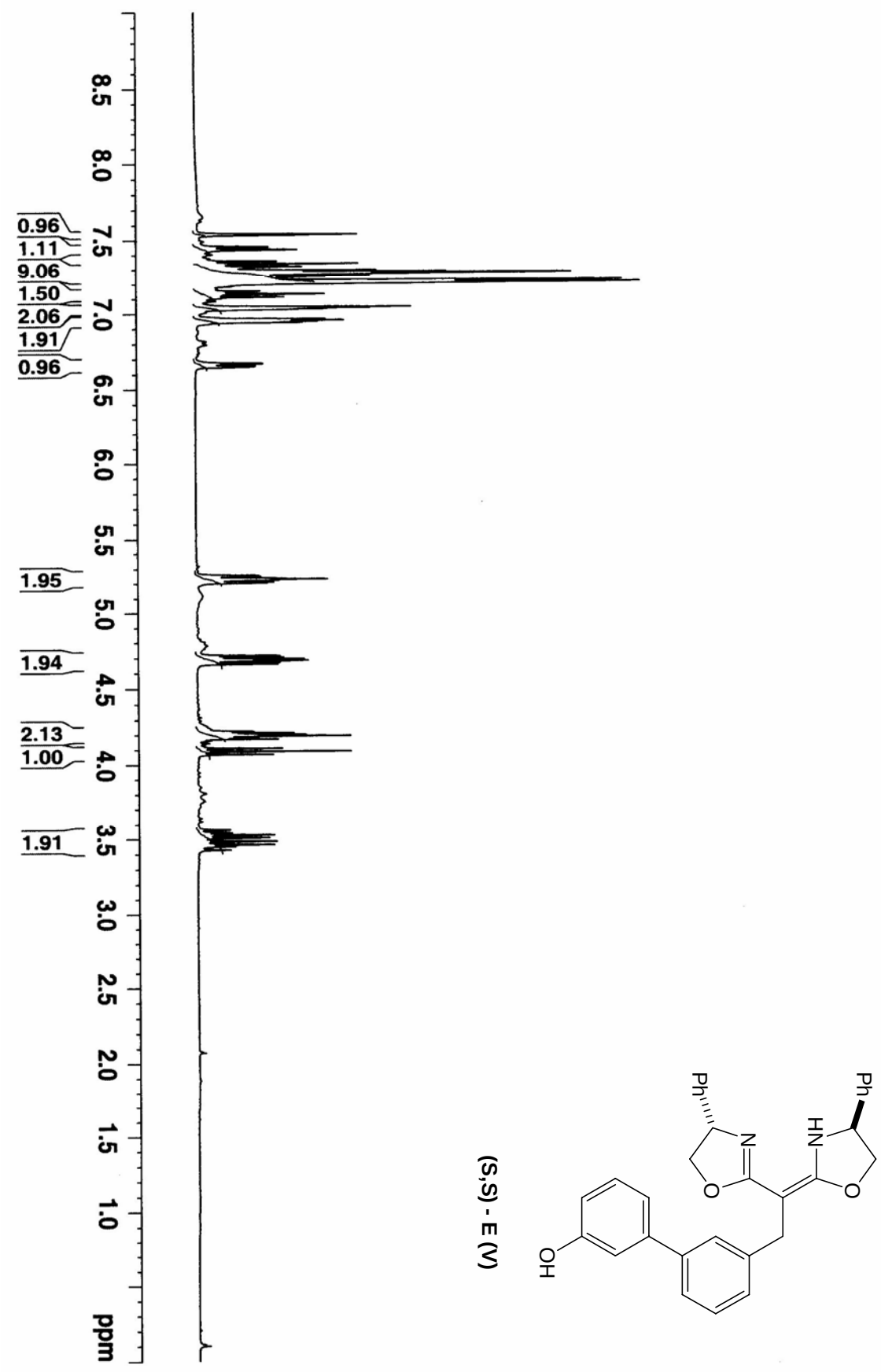

166.01
165.93
153.72
141.78
141.66
136.88
136.46
130.50
129.53
129.29
128.82
128.78
128.63
128.18
127.81
127.70
126.81
126.72
120.16
116.34
77.57
77.26
76.94
75.62
75.40
69.41
69.38
41.27
35.56
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
(R,R) - D (V)
Ph
N
O
HN
Ph
O
HO

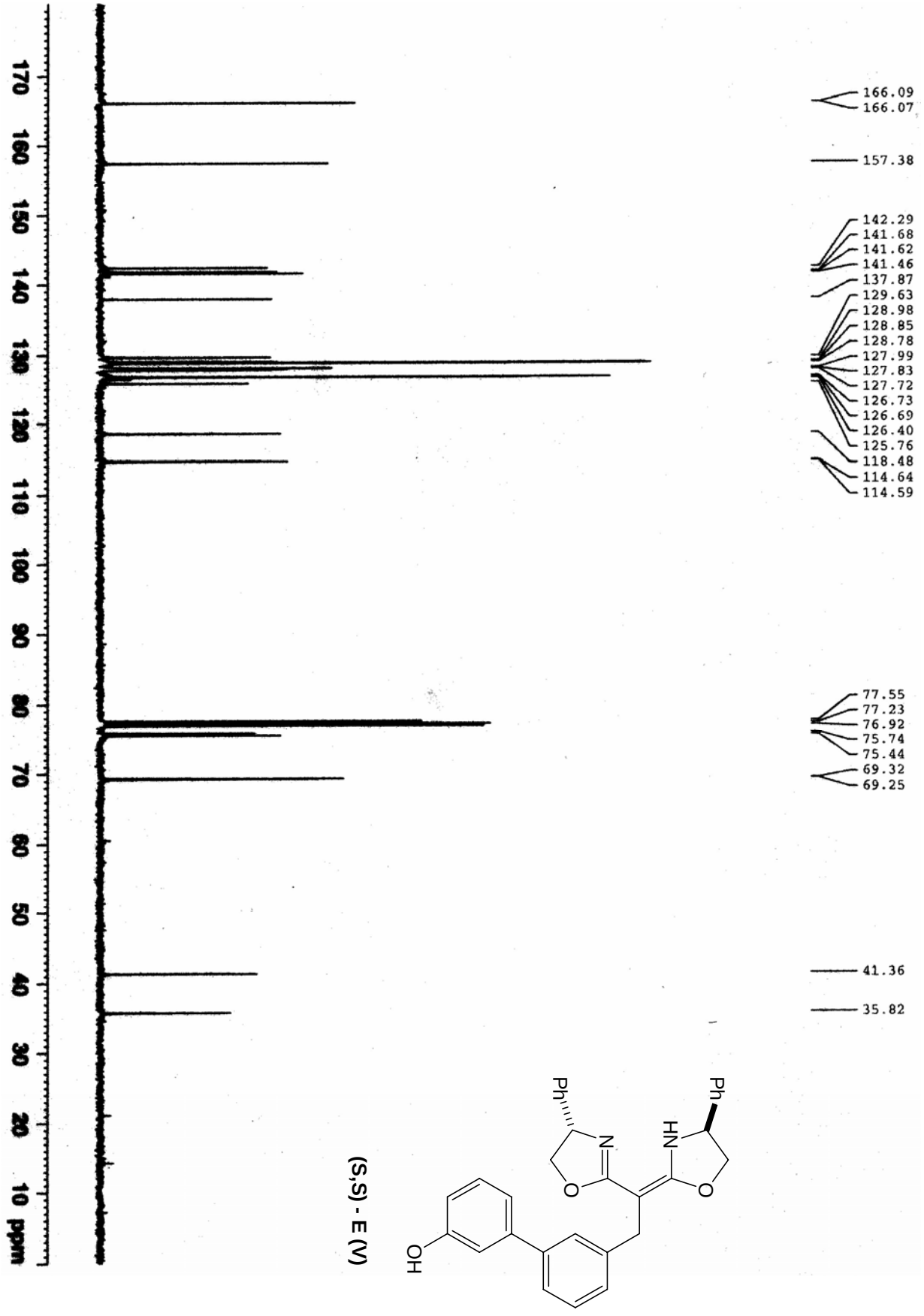

0.96
1.13
9.46
1.66
2.07
1.96
0.95
1.97
1.97
2.14
1.00
1.90
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - E (V)
Ph
N
O
HN
Ph
O
OH

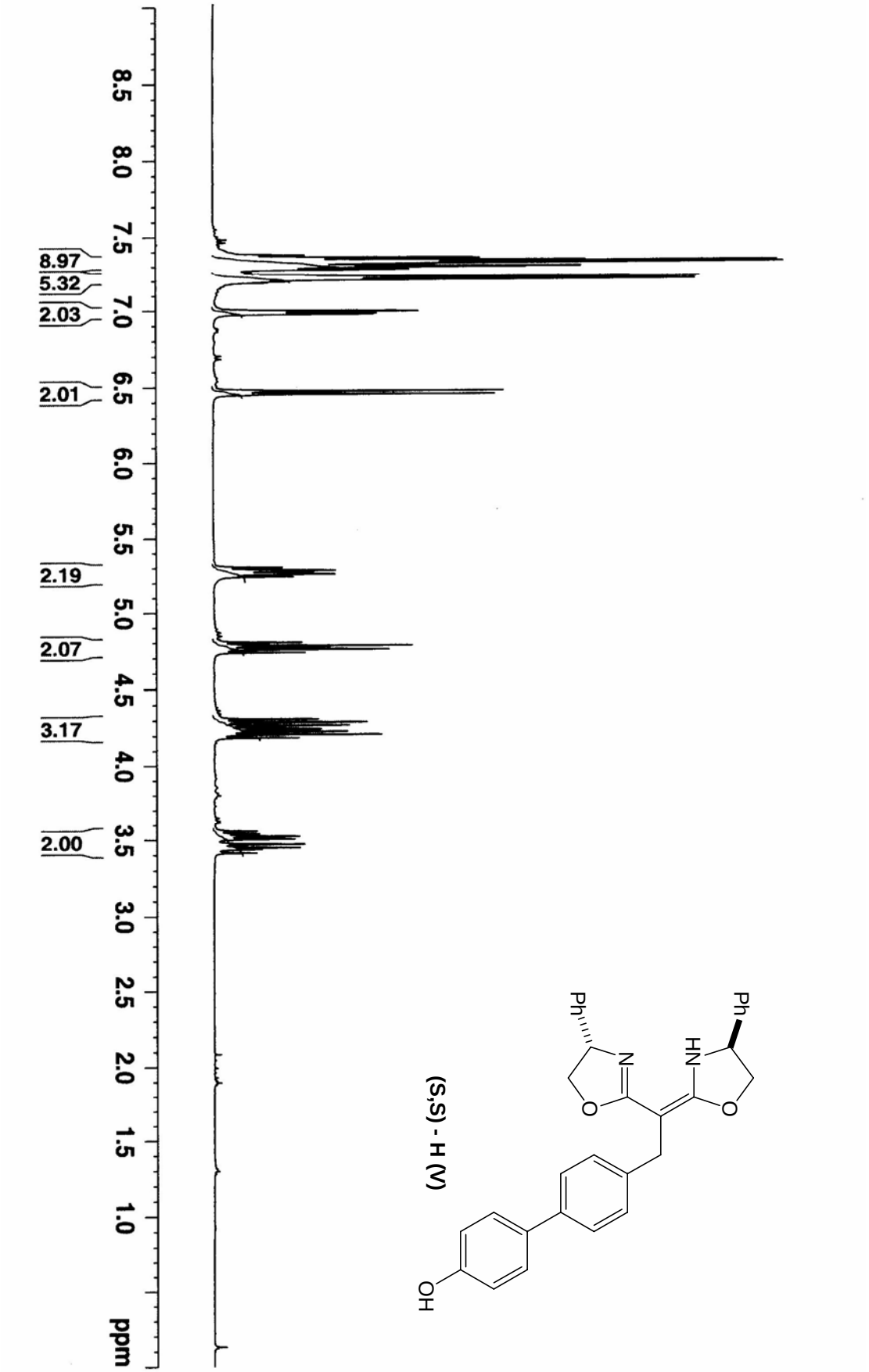

166.09
157.37
142.29
141.66
141.61
141.46
137.87
129.64
128.99
128.85
128.78
127.98
127.83
127.72
126.72
126.68
126.43
125.75
118.49
114.64
114.58
77.56
77.24
76.92
75.74
75.44
69.31
69.24
41.36
35.81
ppm
(R,R) - E (V)
Ph
N
O
HN
Ph
O
OH

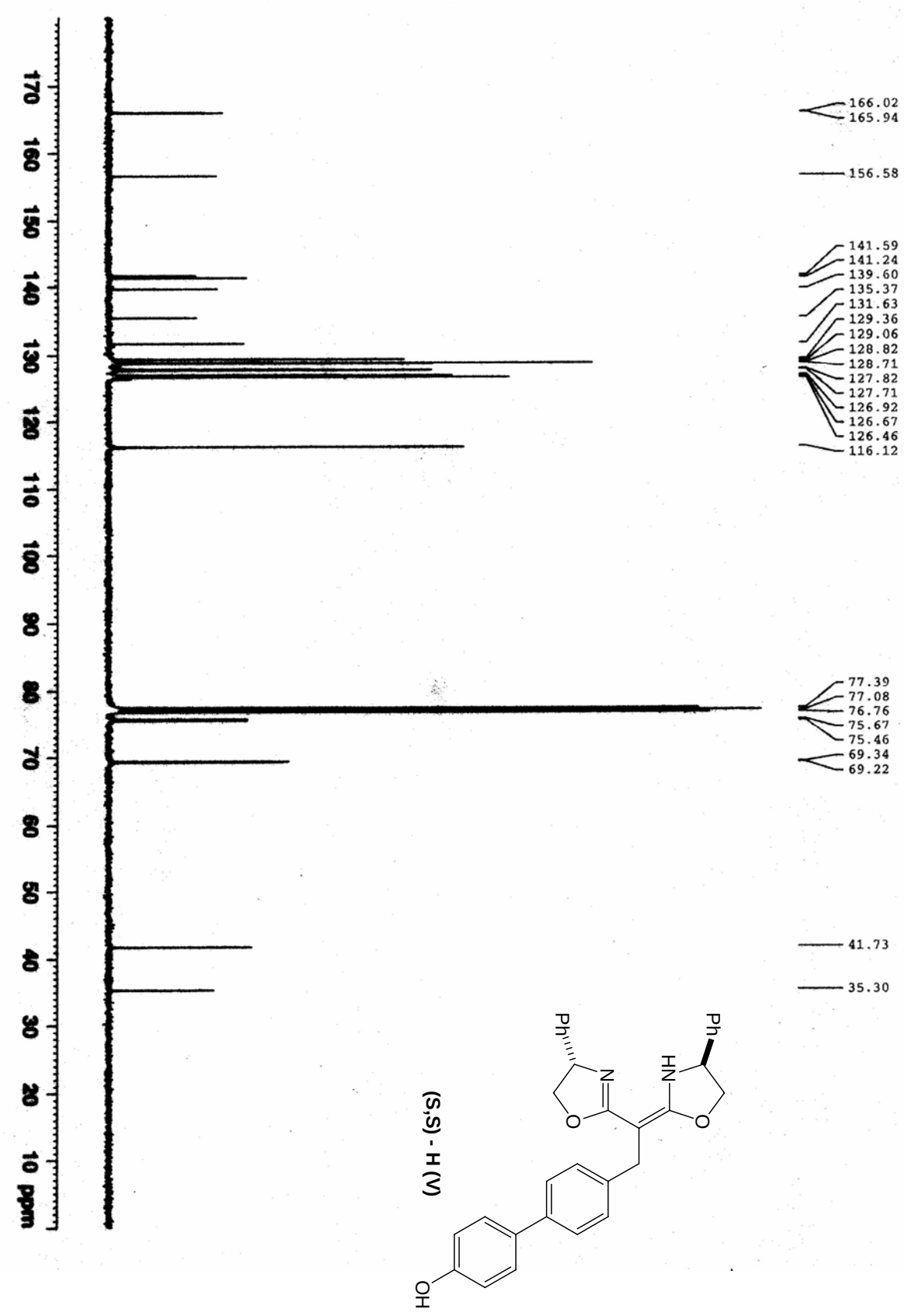

2.10
13.23
2.03
1.99
2.36
2.05
2.10
1.17
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R,R) - G (V)
HO
Ph
N
O
HN
Ph
O

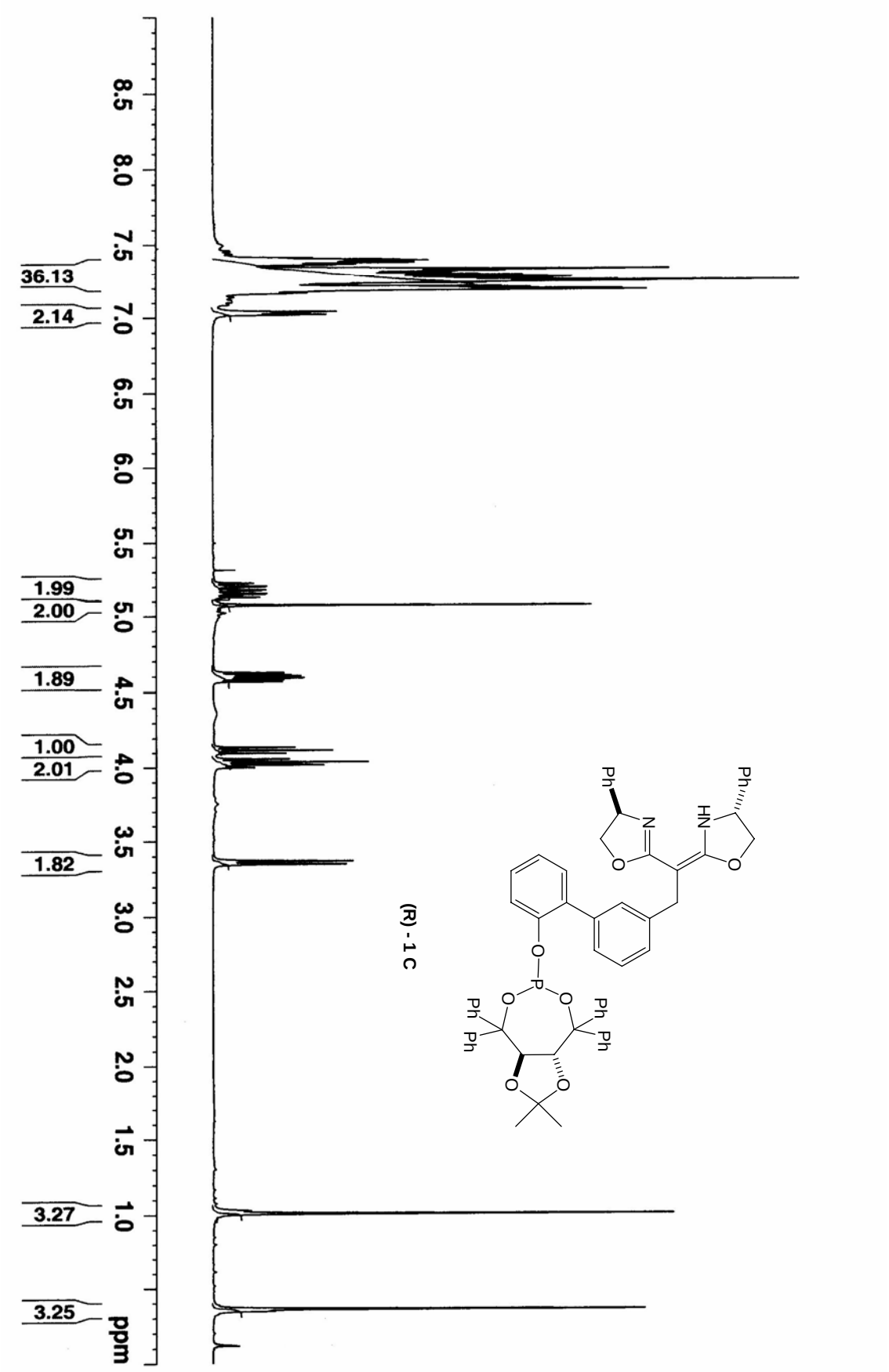

166.20
166.13
156.72
141.69
141.54
141.41
137.87
132.09
129.03
128.87
128.79
128.10
127.87
127.76
127.35
127.16
126.78
126.74
125.30
115.94
77.54
77.22
76.90
75.77
75.47
69.31
69.23
41.38
35.88
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
(R,R) - G (V)
Ph
N
O
HN
Ph
O
HO

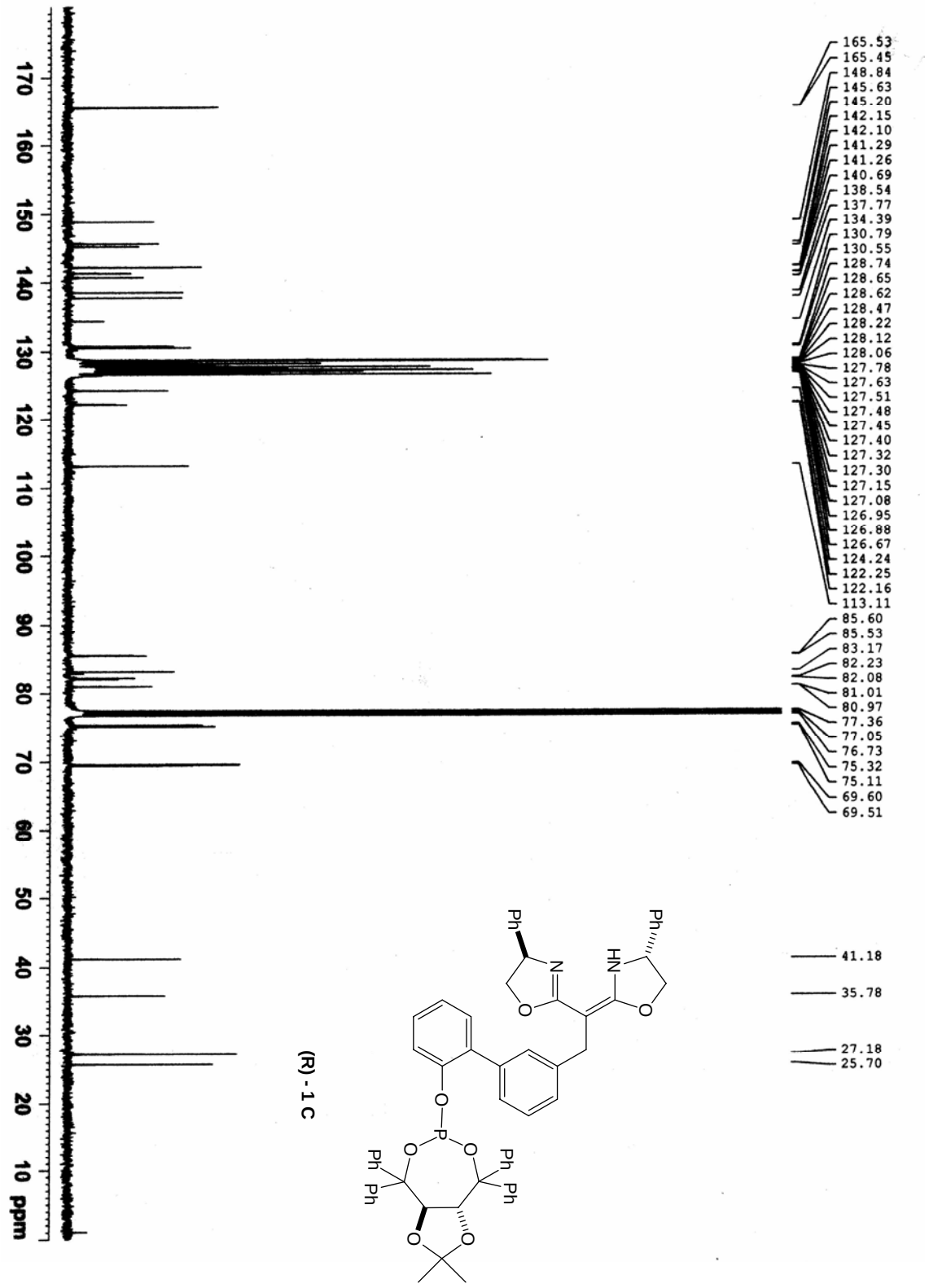

0.96
1.11
9.06
1.50
2.06
1.91
0.96
1.95
1.94
2.13
1.00
1.91
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(S,S) - E (V)
Ph
N
O
HN
Ph
O
OH

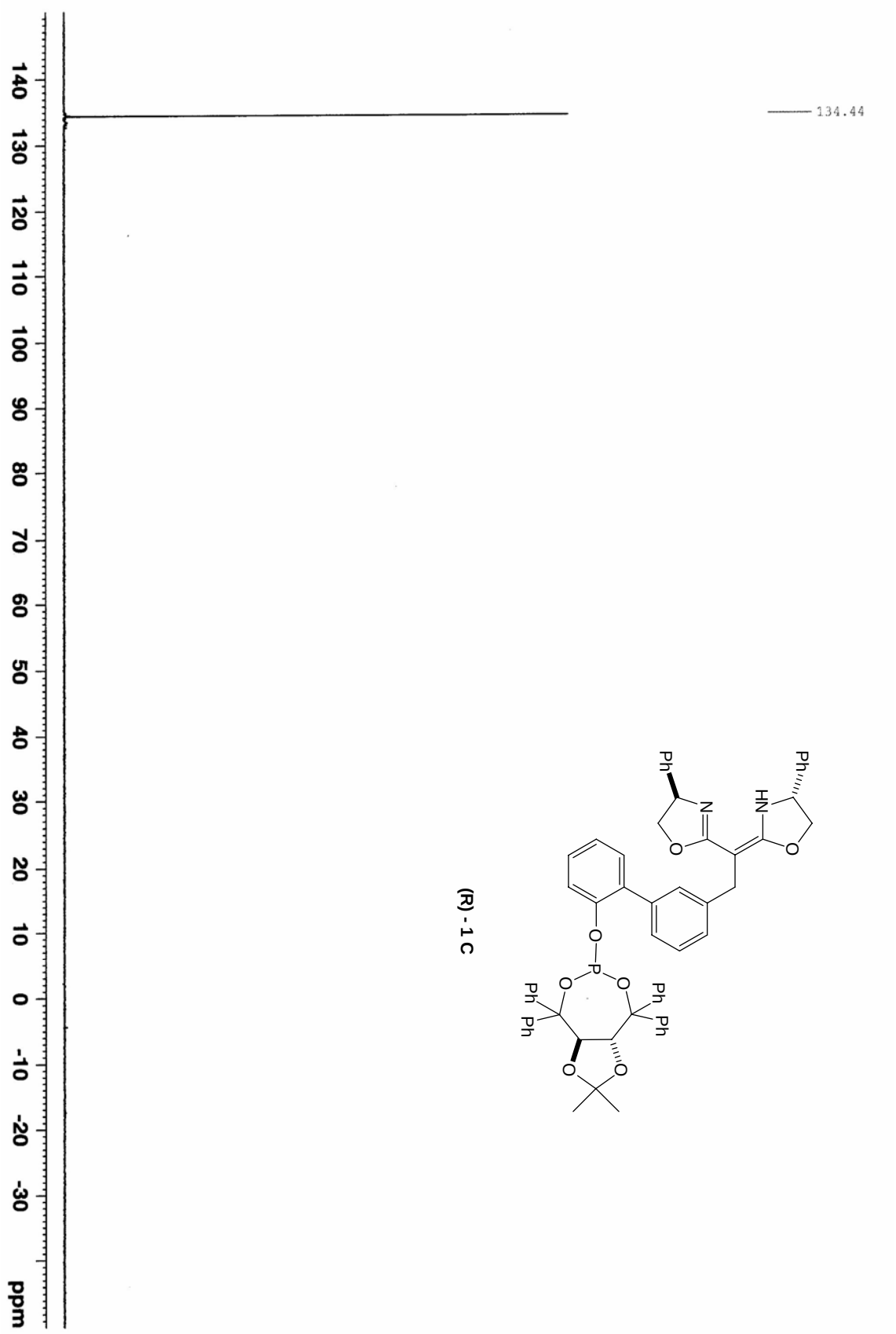

166.09
166.07
157.38
142.29
141.68
141.62
141.46
137.87
129.63
128.98
128.85
128.78
127.99
127.83
127.72
126.73
126.69
126.40
125.76
118.48
114.64
114.59
77.55
77.23
76.92
75.74
75.44
69.32
69.25
41.36
35.82
ppm
(S,S) - E (V)
Ph
N
O
HN
Ph
O
OH


8.97
5.32
2.03
2.01
2.19
2.07
3.17
2.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(S,S) - H (V)
Ph
N
O
HN
Ph
O
OH

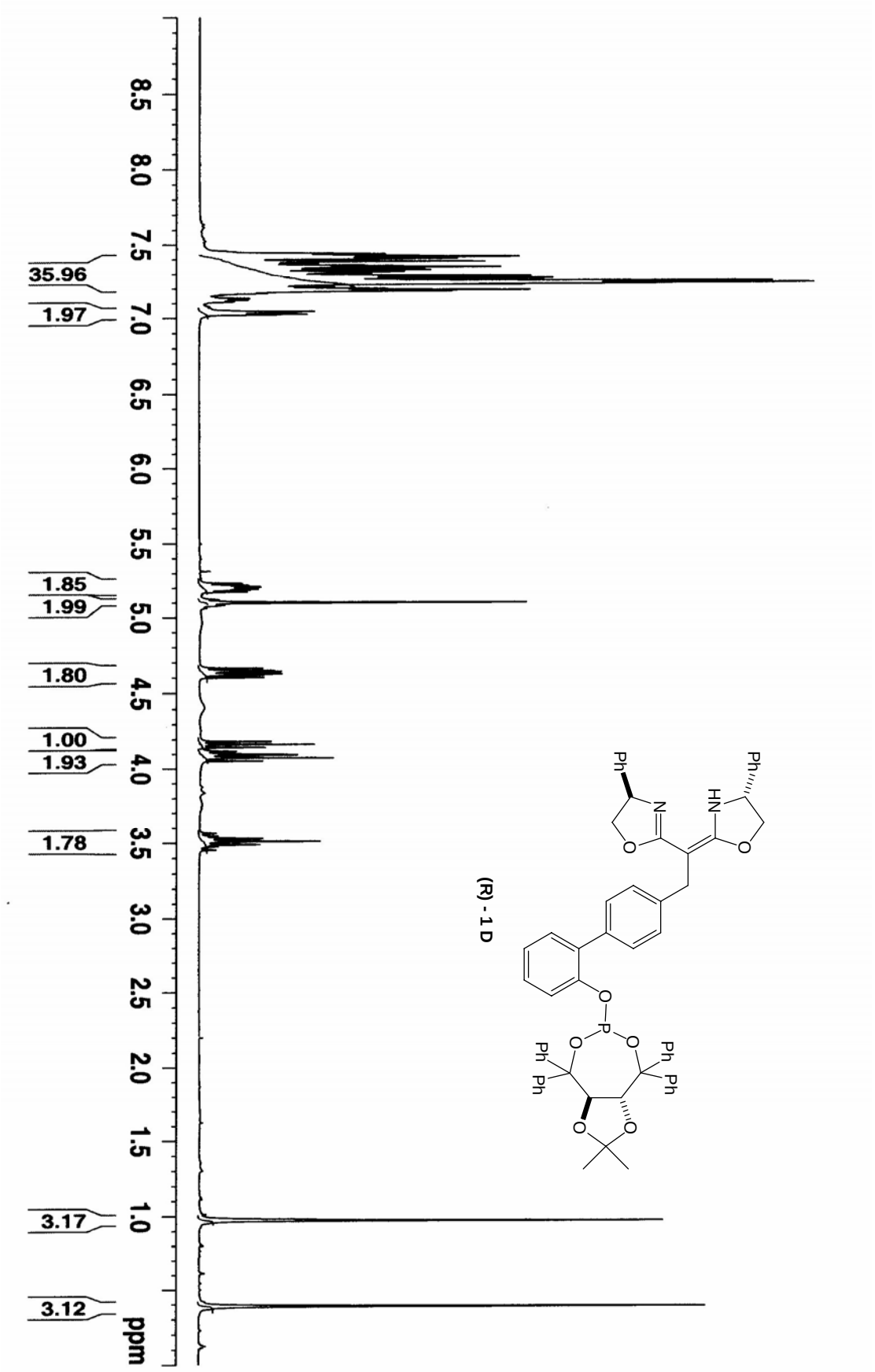

166.02
165.94
156.58
141.59
141.24
139.60
135.37
131.63
129.36
129.06
128.82
128.71
127.82
127.71
126.92
126.67
126.46
116.12
77.39
77.08
76.76
75.67
75.46
69.34
69.22
41.73
35.30
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10 ppm
(S,S) - H (V)
Ph
N
O
HN
Ph
O
OH

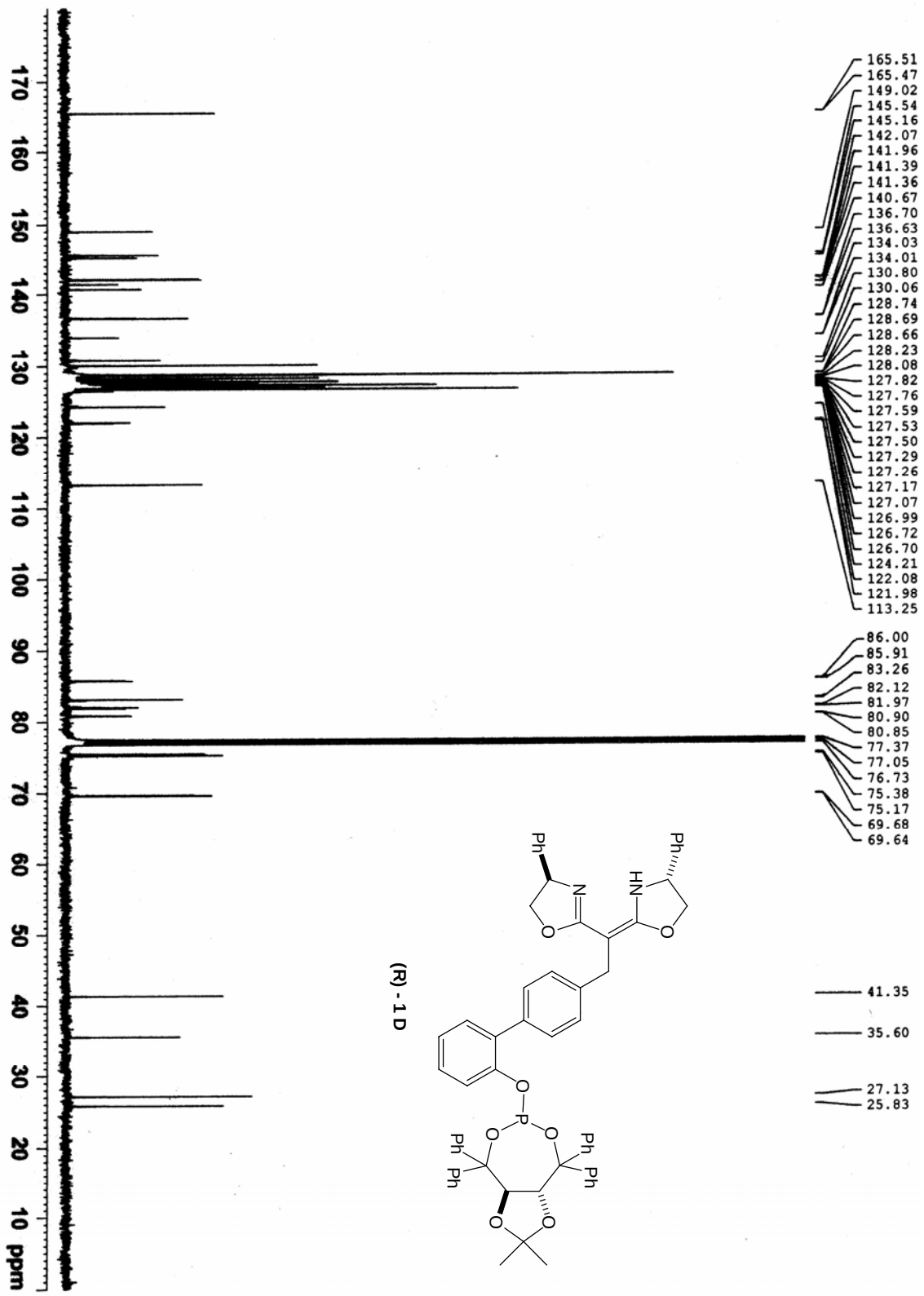

36.13
2.14
1.99
2.00
1.89
1.00
2.01
1.82
3.27
3.25
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R) - 1 C
Ph
N
HN
O
P
Ph Ph
Ph Ph

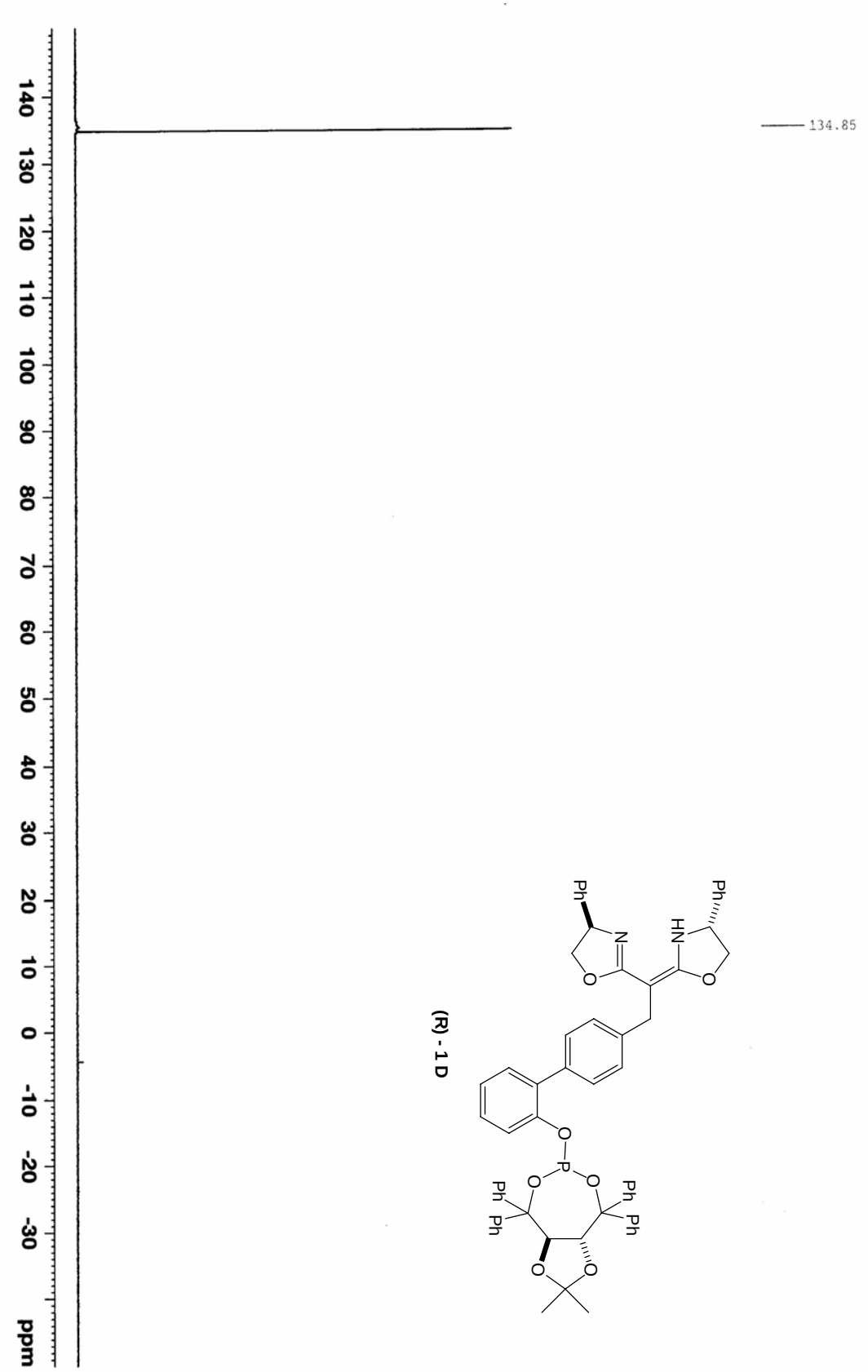

165.53
165.45
148.84
145.63
145.20
142.15
142.10
141.29
141.26
140.69
138.54
137.77
134.39
130.79
130.55
128.74
128.65
128.62
128.47
128.22
128.12
128.06
127.78
127.63
127.51
127.48
127.45
127.40
127.32
127.30
127.15
127.08
126.95
126.88
126.67
124.24
122.25
122.16
113.11
85.60
85.53
83.17
82.23
82.08
81.01
80.97
77.36
77.05
76.73
75.32
75.11
69.60
69.51
41.18
35.78
27.18
25.70
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
(R) - 1 C
Ph
N
HN
Ph
O
O
O
O
R
O
O
Ph
Ph
Ph
Ph
O
O


134.44
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm
Ph
N
HN
Ph
O
O
O
P
O
O
Ph Ph
Ph Ph
O
O

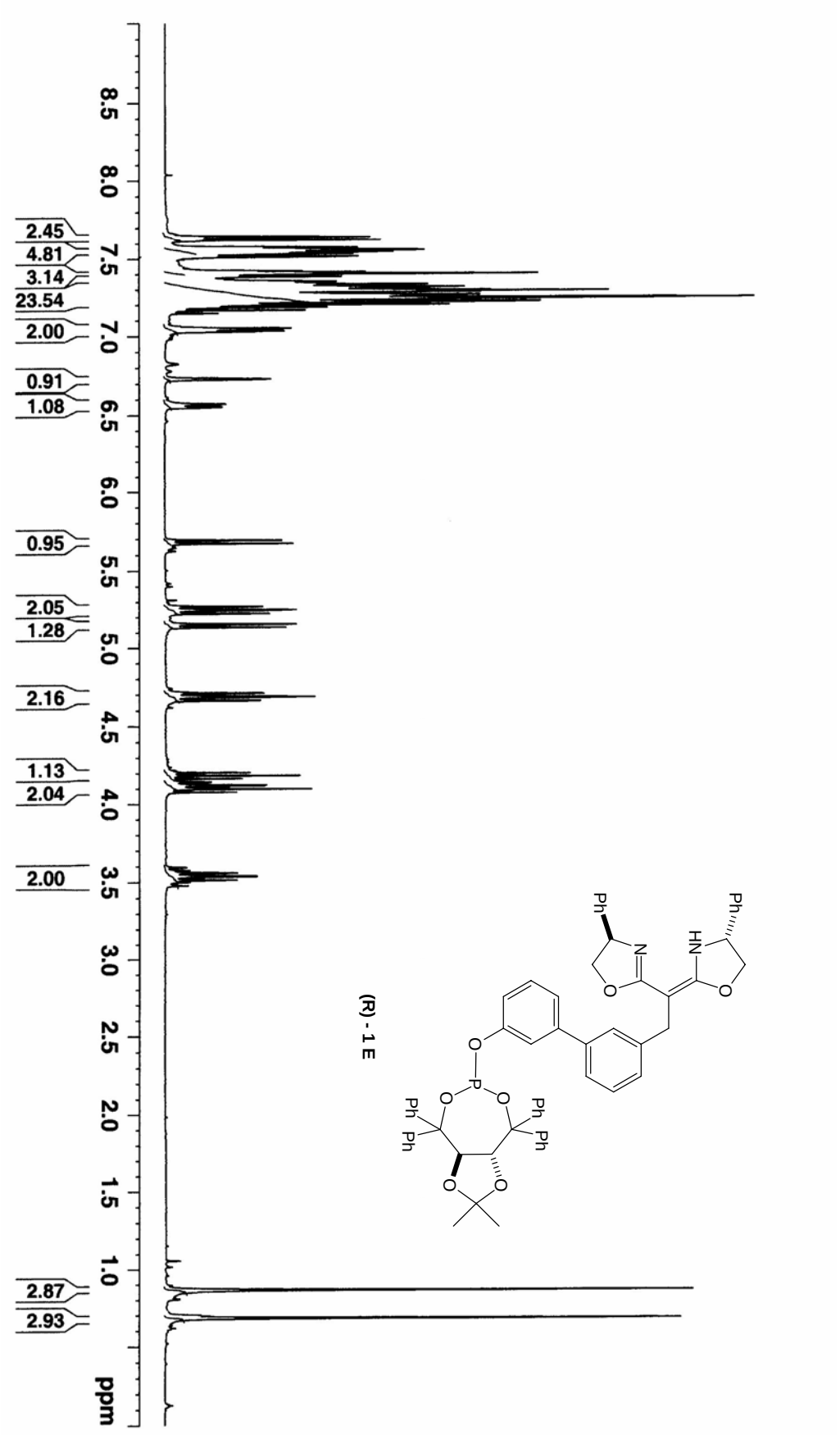
(R) - 1 C

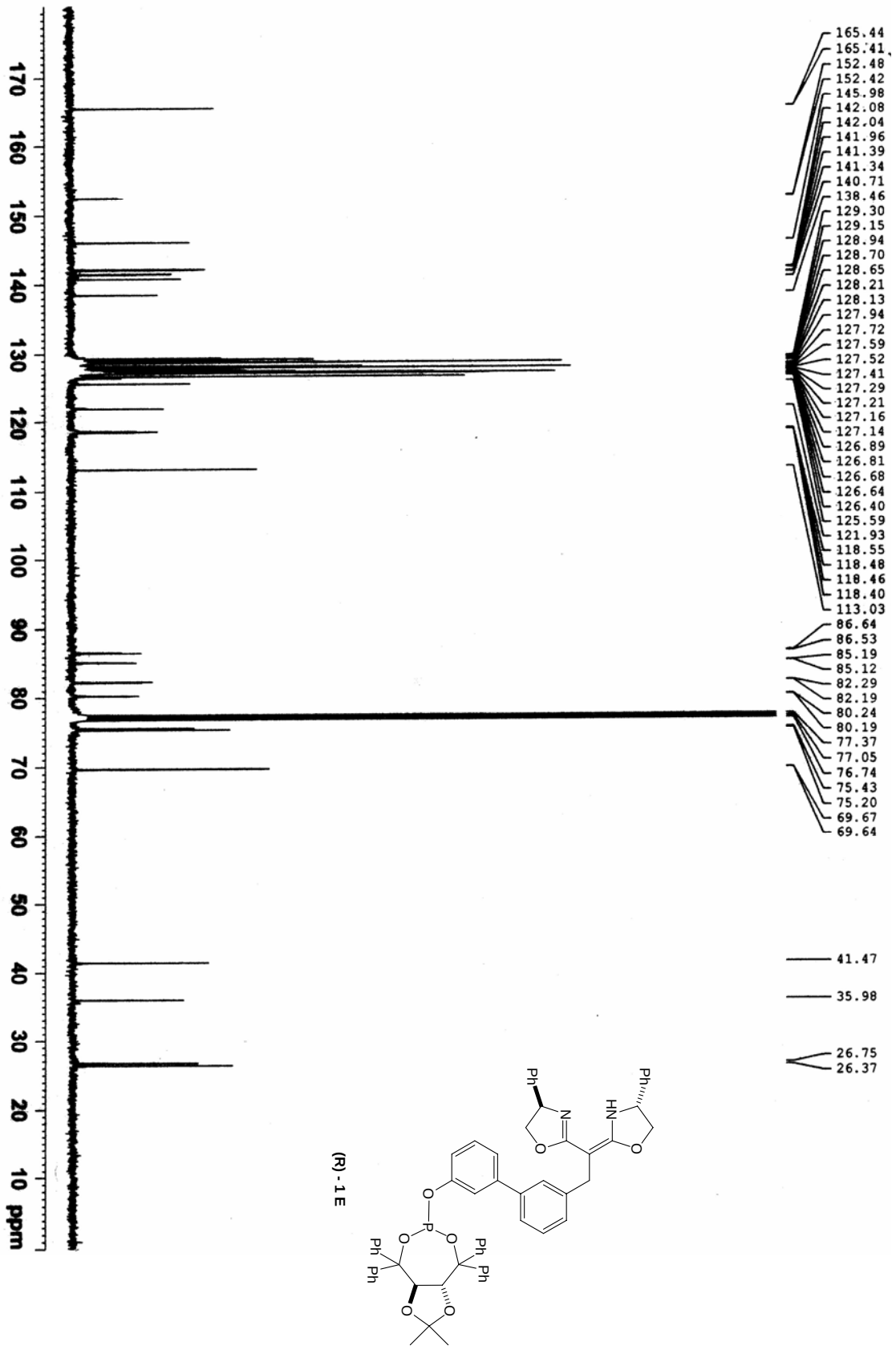

35.96
1.97
1.85
1.99
1.80
1.00
1.93
1.78
3.17
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R) - 1 D
Ph
N
HN
O
P
Ph
Ph
Ph
Ph

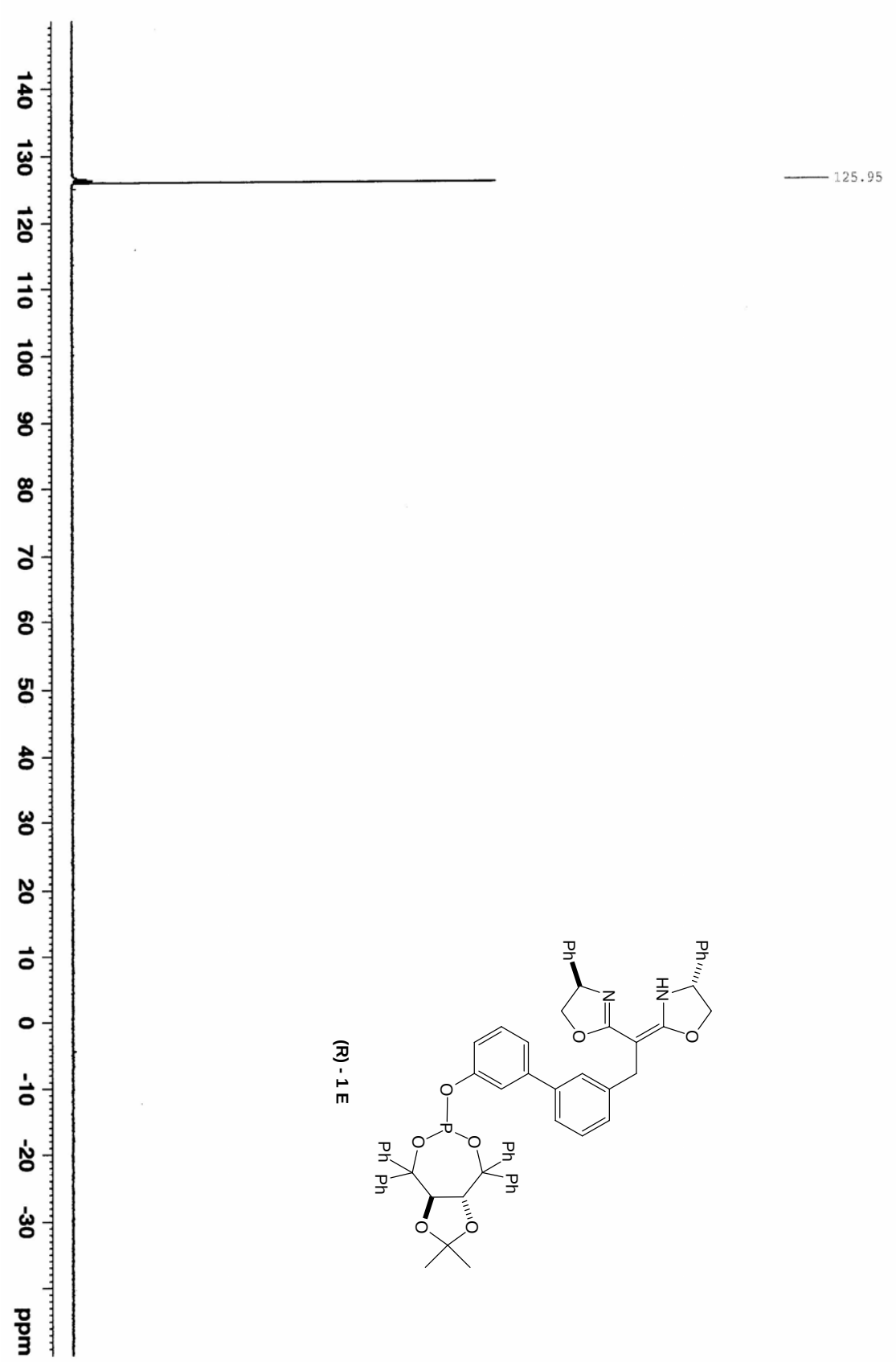

165.51
165.47
149.02
145.54
145.16
142.07
141.96
141.39
141.36
140.67
136.70
136.63
134.03
134.01
130.80
130.06
128.74
128.69
128.66
128.23
128.08
127.82
127.76
127.59
127.53
127.50
127.29
127.26
127.17
127.07
126.99
126.72
126.70
124.21
122.08
121.98
113.25
86.00
85.91
83.26
82.12
81.97
80.90
80.85
77.37
77.05
76.73
75.38
75.17
69.68
69.64
41.35
35.60
27.13
25.83
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
(R) - 1 D
Ph
N
O
HN
Ph
O
O
P
O
O
Ph
Ph
Ph
Ph
O
O

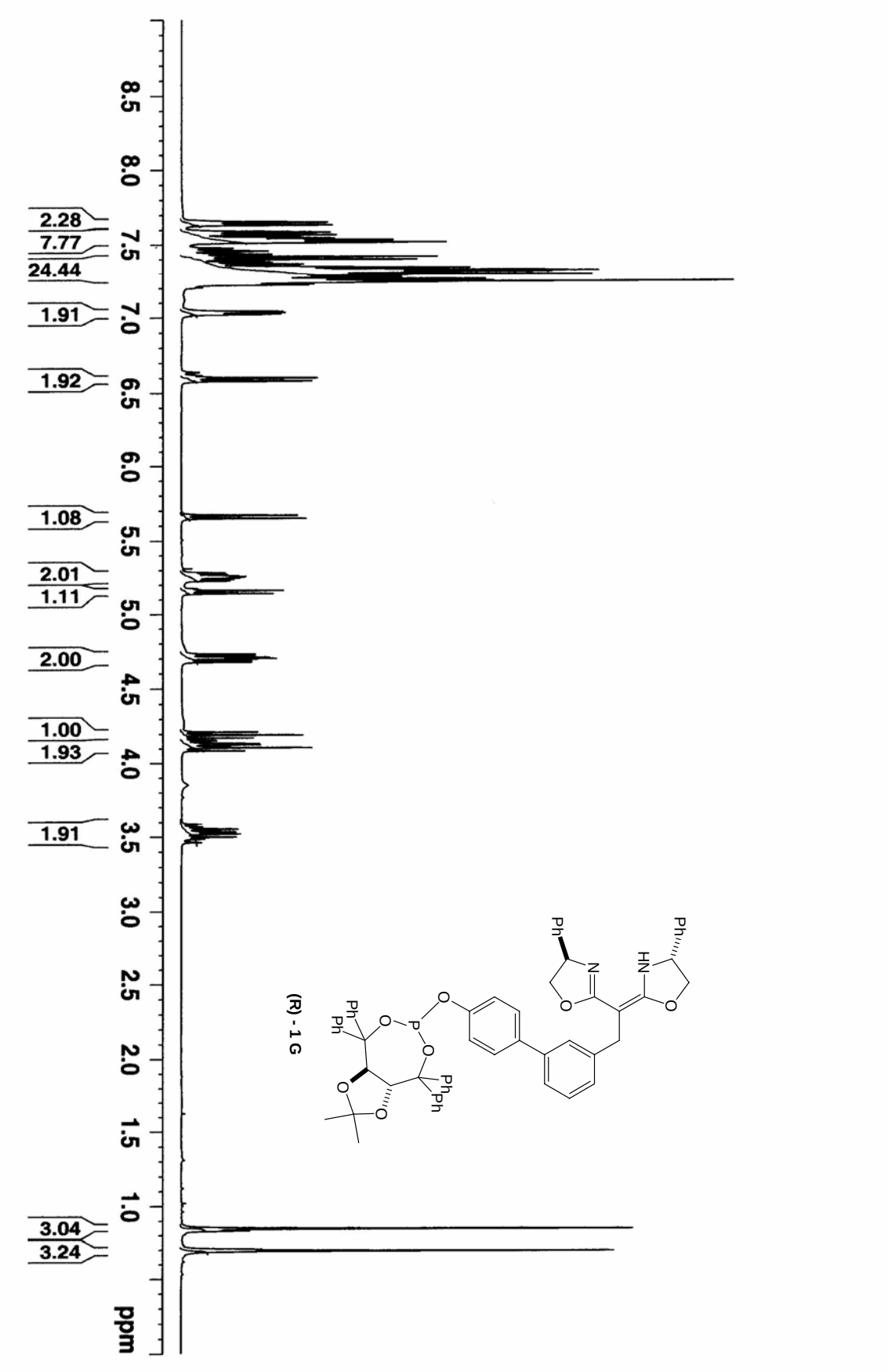

134.85
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm
Ph
N
O
HN
Ph
O
O
O
P
O
O
Ph
Ph
Ph
Ph
O
O

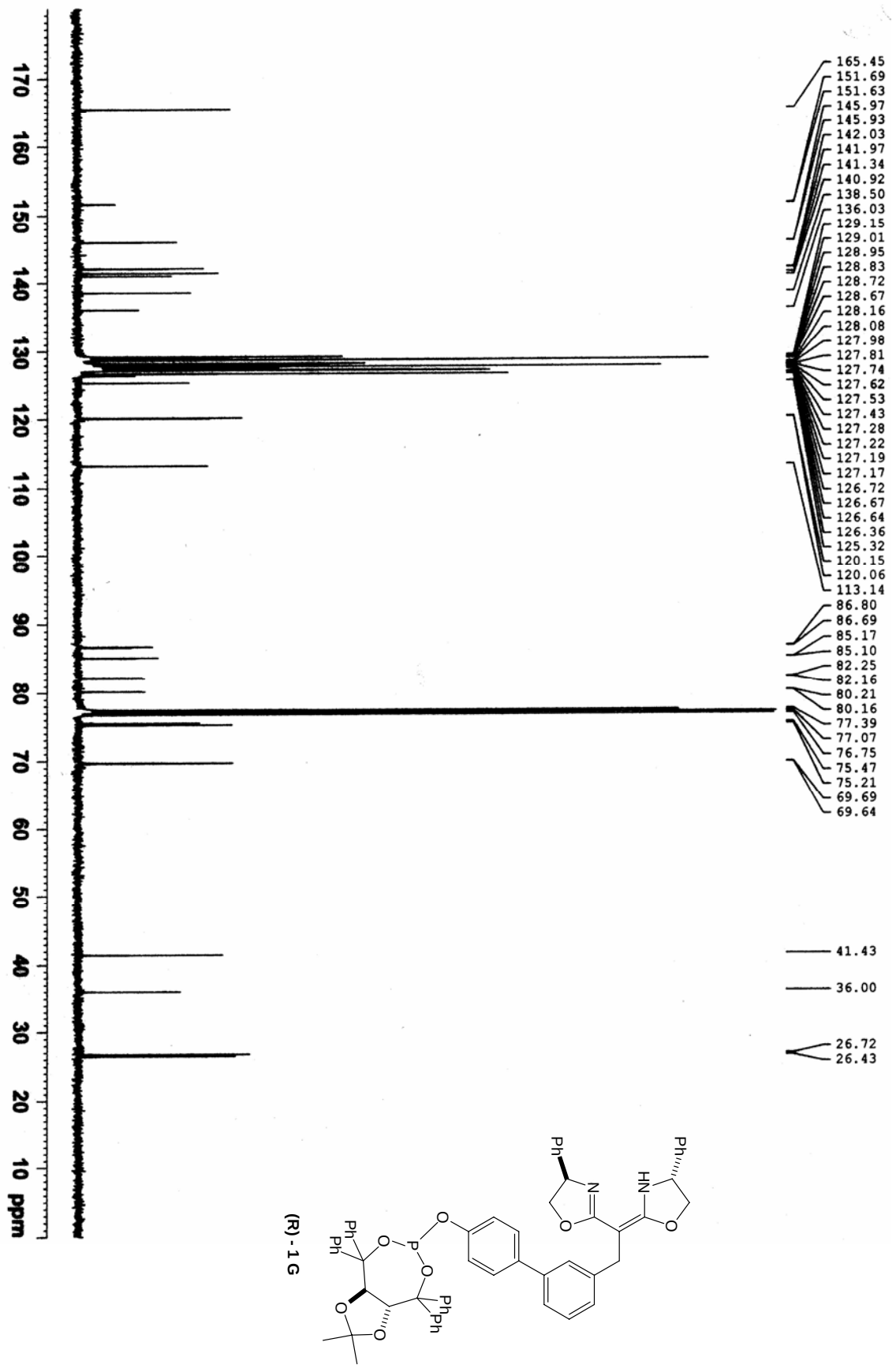
(R) - 1 D

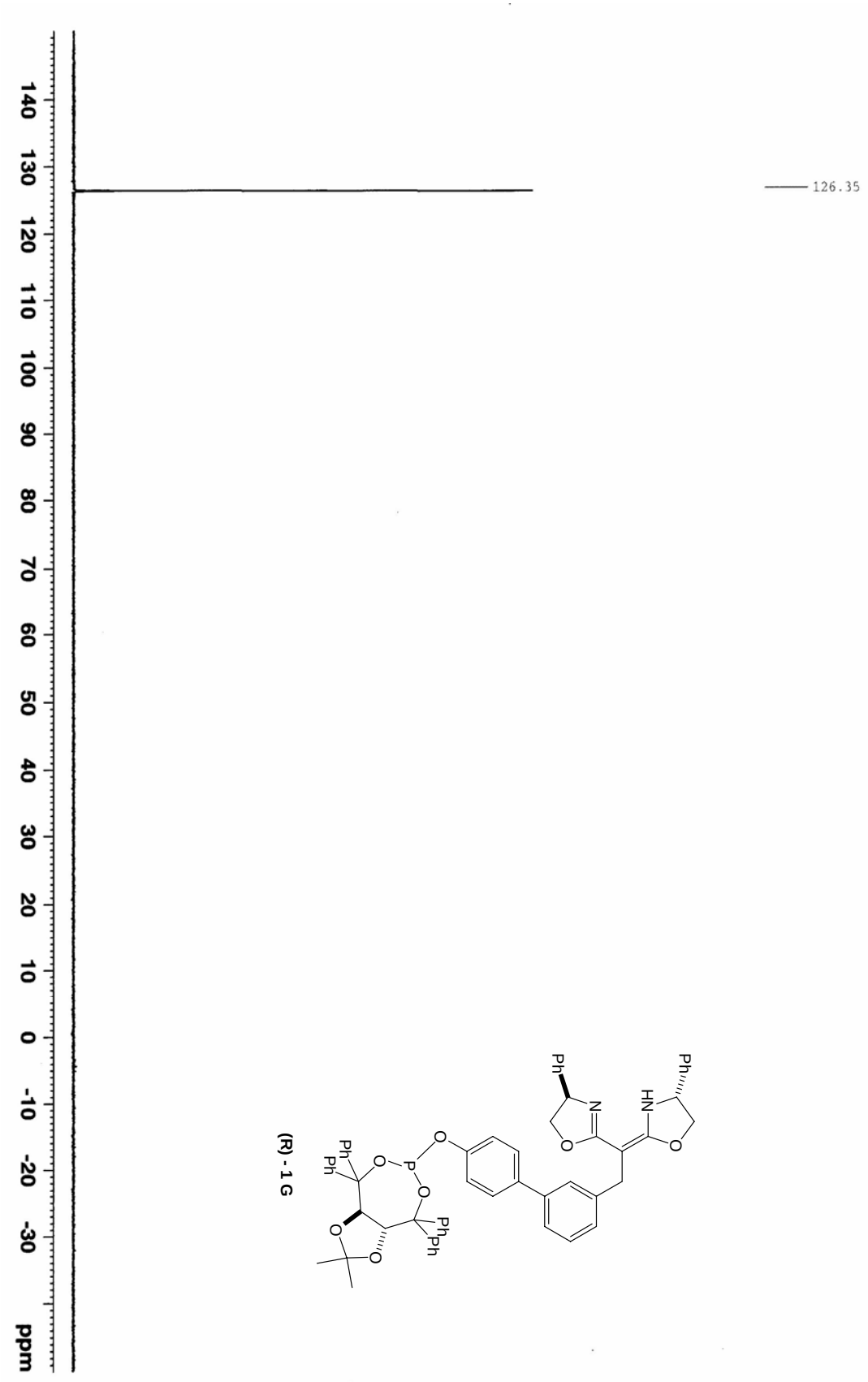

2.45
4.81
3.14
23.54
2.00
0.91
1.08
0.95
2.05
1.28
2.16
1.13
2.04
2.00
2.87
2.93
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(R) - 1 E
Ph
N
O
HN
Ph
O
O
P
O
O
Ph
Ph
Ph
Ph
O
O

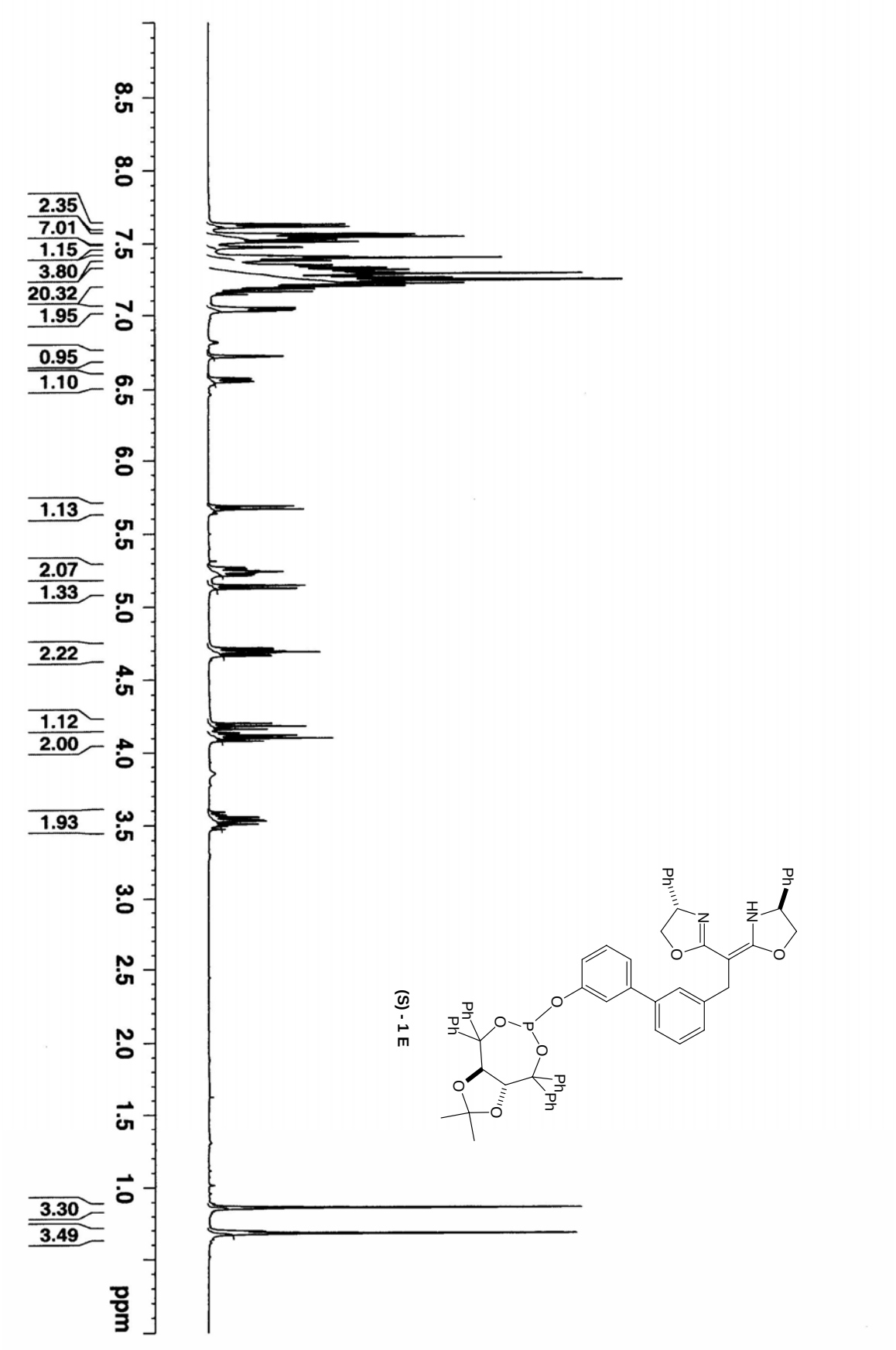

165.44
165.41
152.48
152.42
145.98
142.08
142.04
141.96
141.39
141.34
140.71
138.46
129.30
129.15
128.94
128.70
128.65
128.21
128.13
127.94
127.72
127.59
127.52
127.41
127.29
127.21
127.16
127.14
126.89
126.81
126.68
126.64
126.40
125.59
121.93
118.55
118.48
118.46
118.40
113.03
86.64
86.53
85.19
85.12
82.29
82.19
80.24
80.19
77.37
77.05
76.74
75.43
75.20
69.67
69.64
41.47
35.98
26.75
26.37
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
(R)-1E

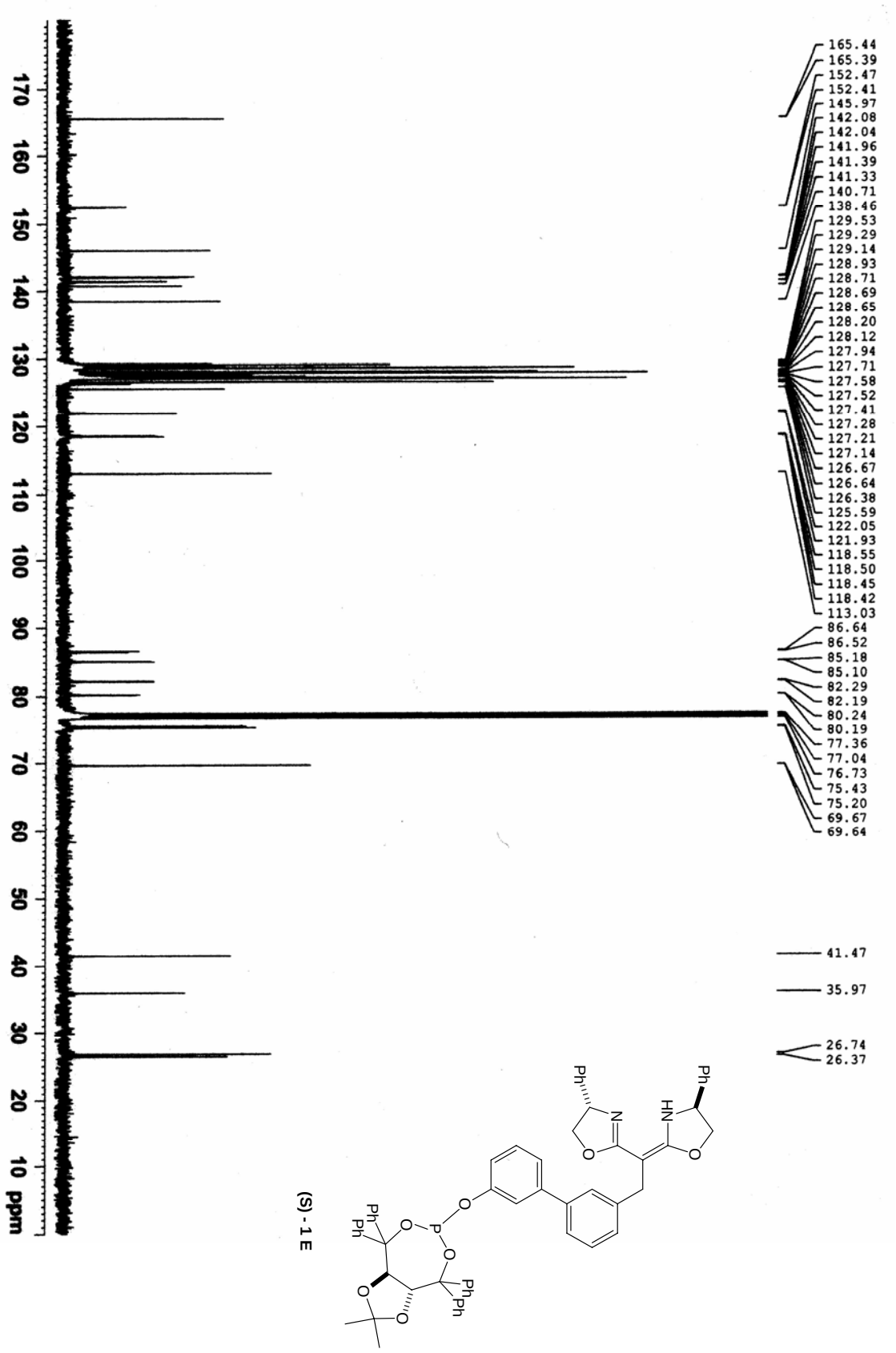

125.95
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm
(R) - 1 E
Ph
N
O
HN
Ph
O
O
P
O
O
Ph
Ph
Ph
Ph
O
O

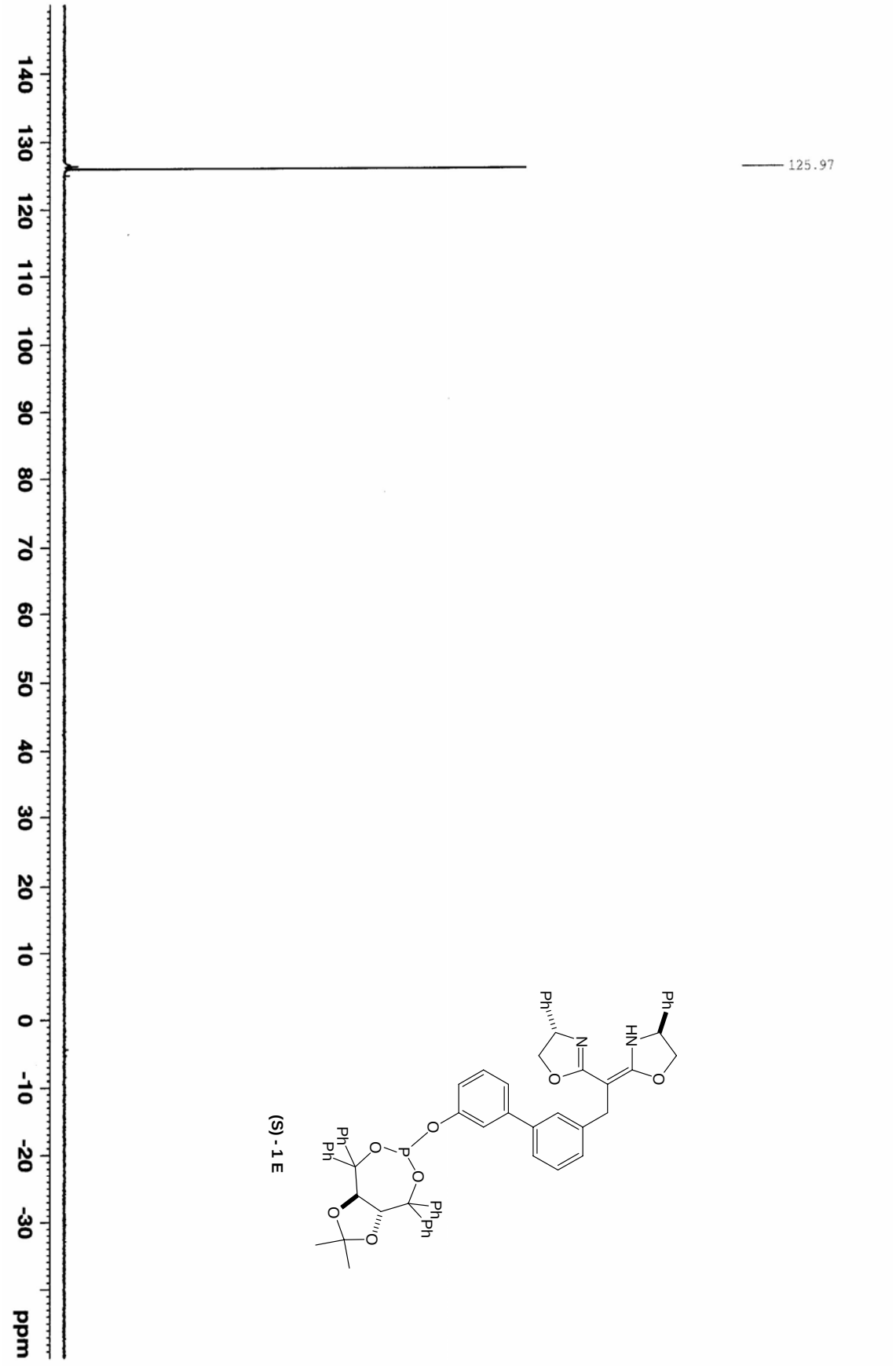

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
2.28
7.77
24.44
1.91
1.92
1.08
2.01
1.11
2.00
1.00
1.93
1.91
3.04
3.24
(R) - 1G

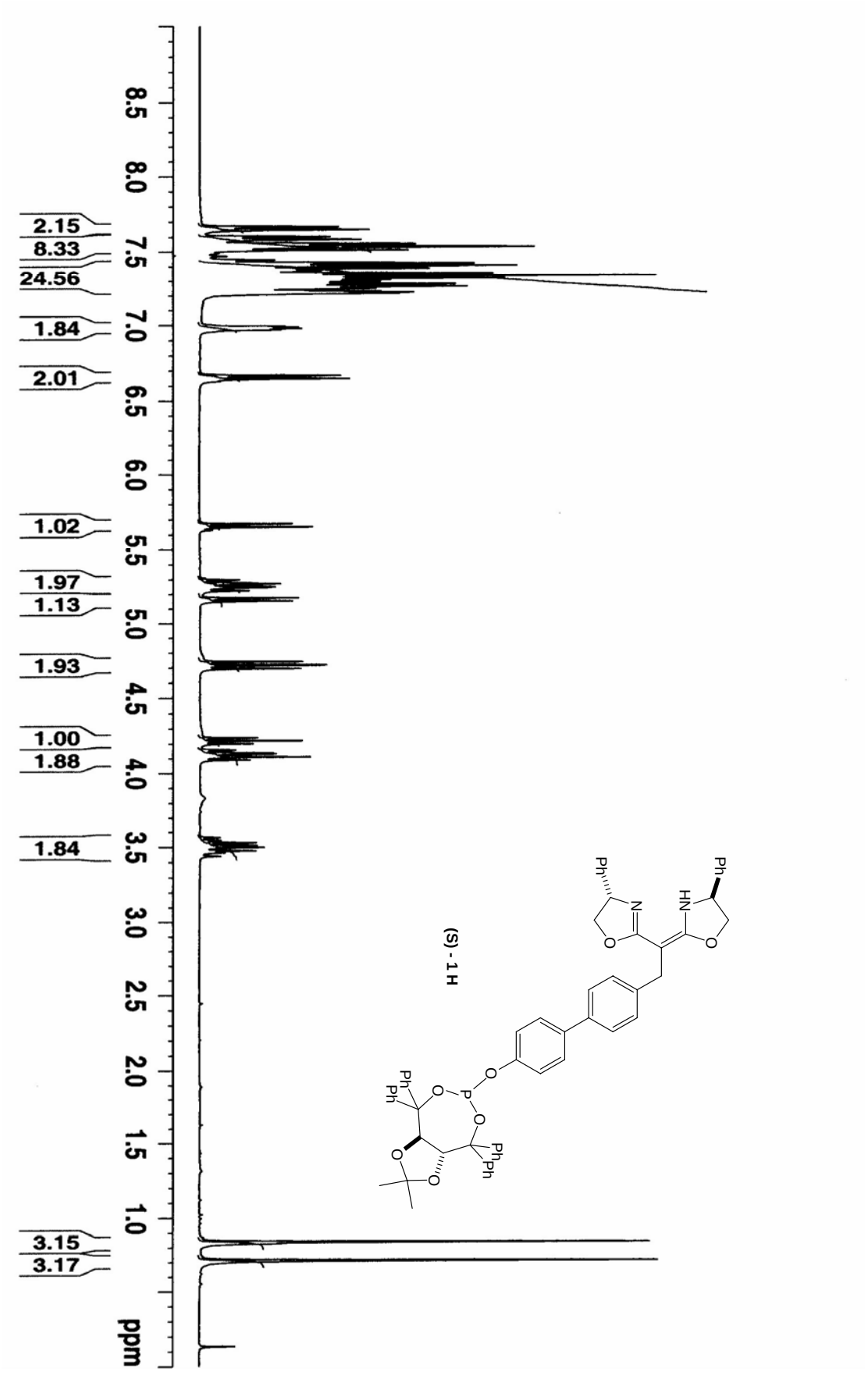

165.45
151.69
151.63
145.97
145.93
142.03
141.97
141.34
140.92
138.50
136.03
129.15
129.01
128.95
128.83
128.72
128.67
128.16
128.08
127.98
127.81
127.74
127.62
127.53
127.43
127.28
127.22
127.19
127.17
126.72
126.67
126.64
126.36
125.32
120.15
120.06
113.14
86.80
86.69
85.17
85.10
82.25
82.16
80.21
80.16
77.39
77.07
76.75
75.47
75.21
69.69
69.64
41.43
36.00
26.72
26.43
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
(R)-1G
Ph
Ph
Ph
Ph
Ph
Ph
N
HN
O
O
O
O
O
O
O
O
P

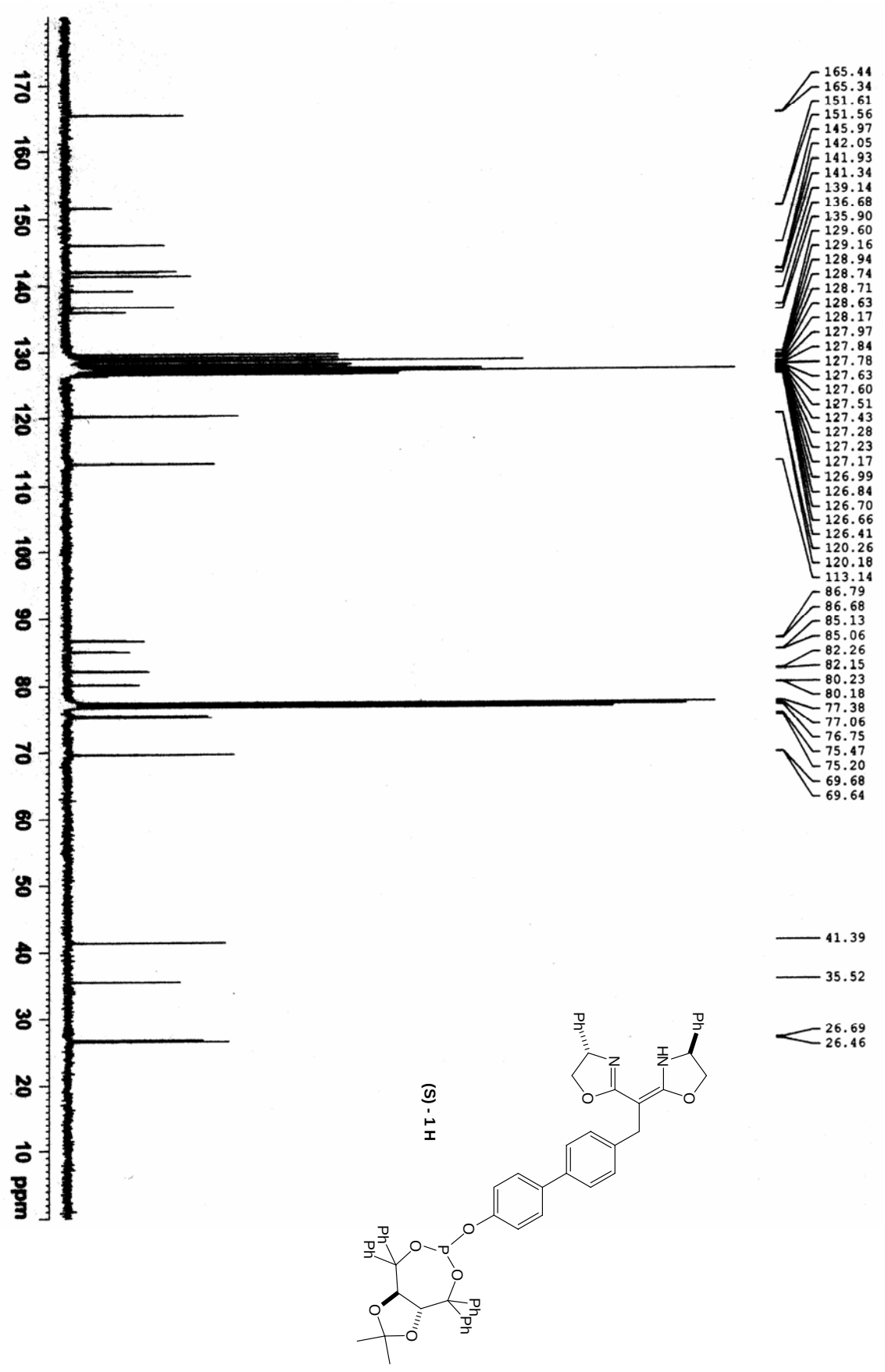

126.35
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm
(R) - 1 G
Ph
Ph
O
P
O
O
O
O
Ph
Ph
Ph
N
O
HN
O
Ph

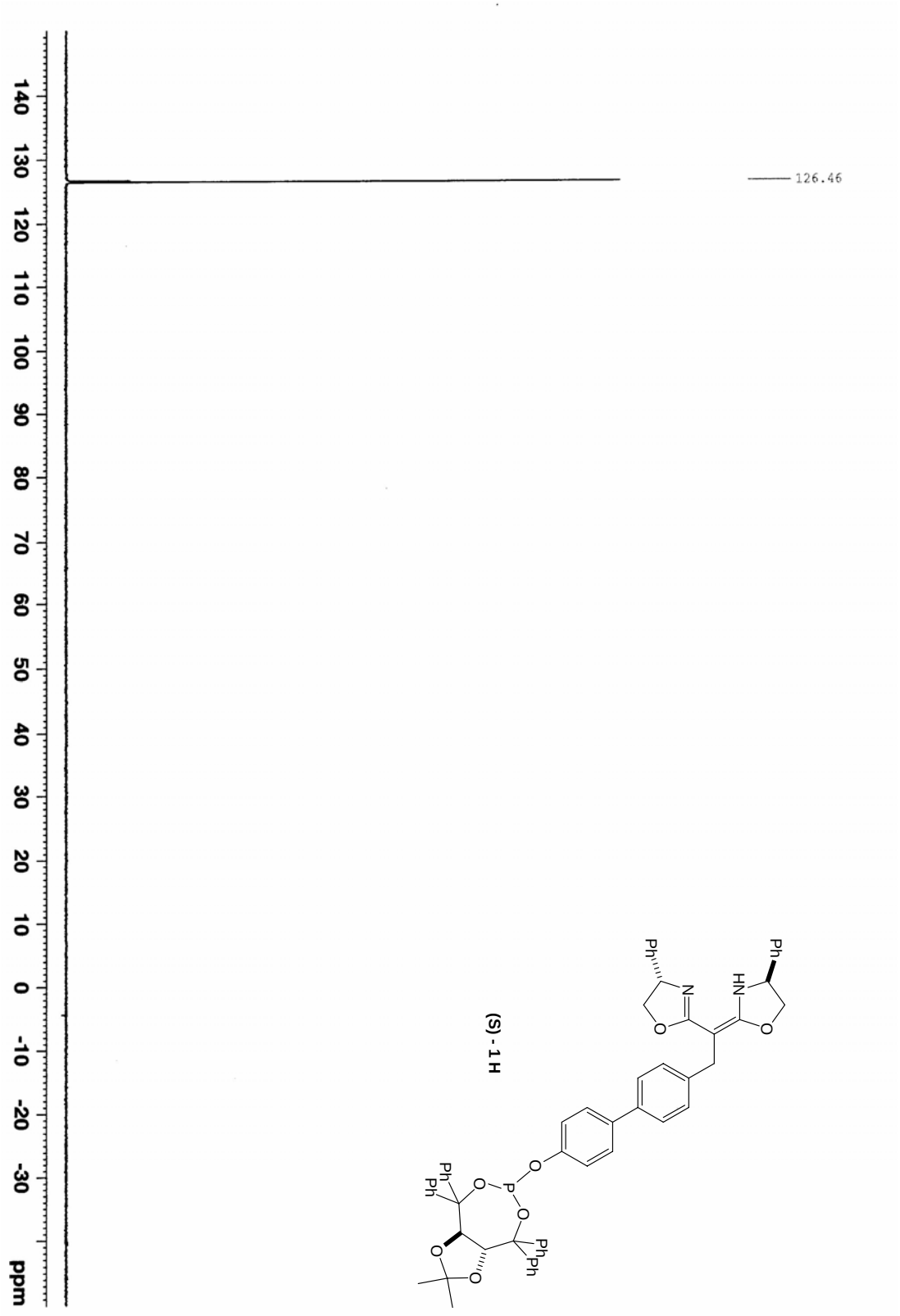

2.35
7.01
1.15
3.80
20.32
1.95
0.95
1.10
1.13
2.07
1.33
2.22
1.12
2.00
1.93
3.30
3.49
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(S) - 1 E
Ph
HN
N
O
P

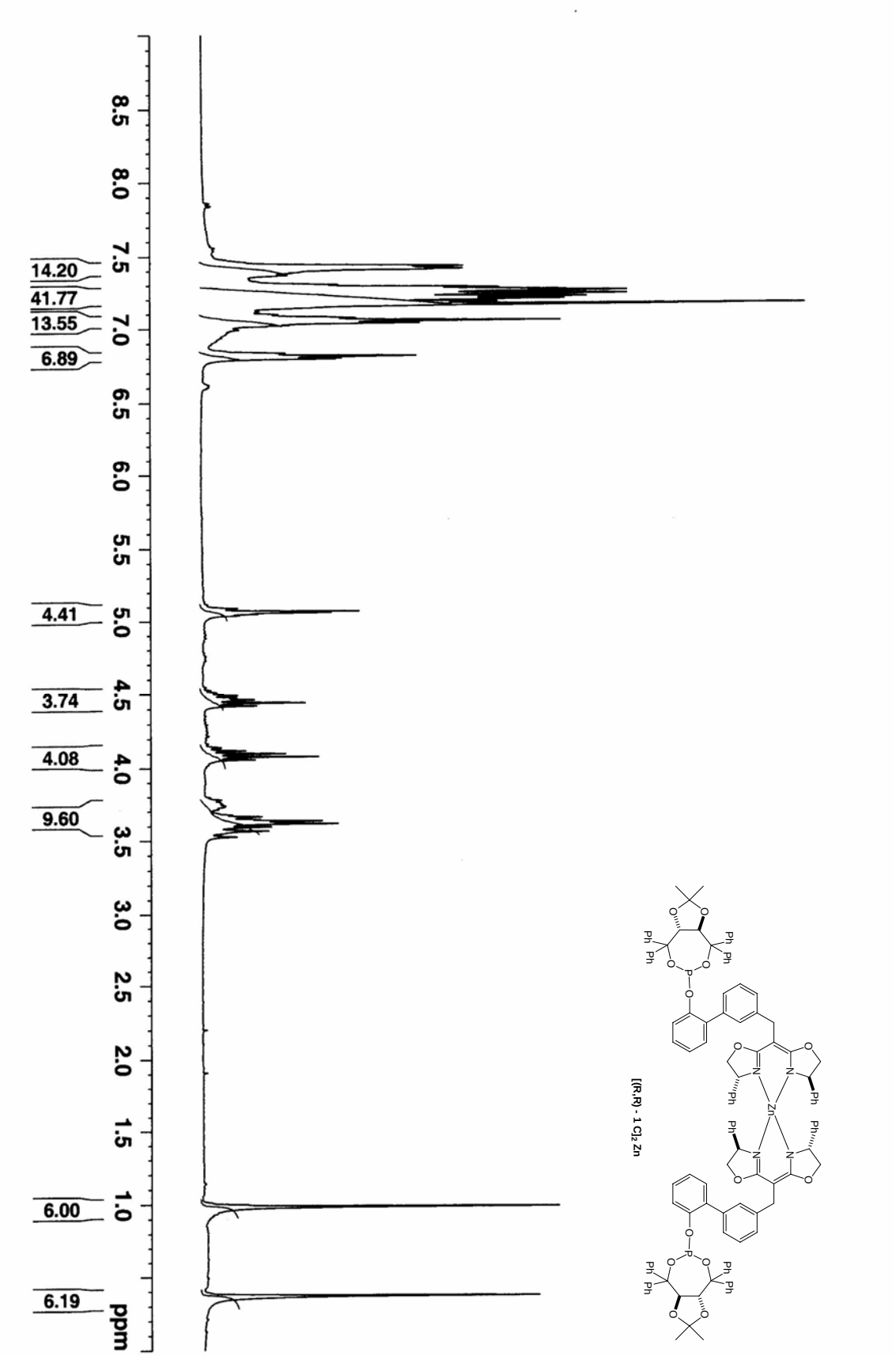

165.44
165.39
152.47
152.41
145.97
142.08
142.04
141.96
141.39
141.33
140.71
138.46
129.53
129.29
129.14
128.93
128.71
128.69
128.65
128.20
128.12
127.94
127.71
127.58
127.52
127.41
127.28
127.21
127.14
126.67
126.64
126.38
125.59
122.05
121.93
118.55
118.50
118.45
118.42
113.03
86.64
86.52
85.18
85.10
82.29
82.19
80.24
80.19
77.36
77.04
76.73
75.43
75.20
69.67
69.64
41.47
35.97
26.74
26.37
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
(S)-1E

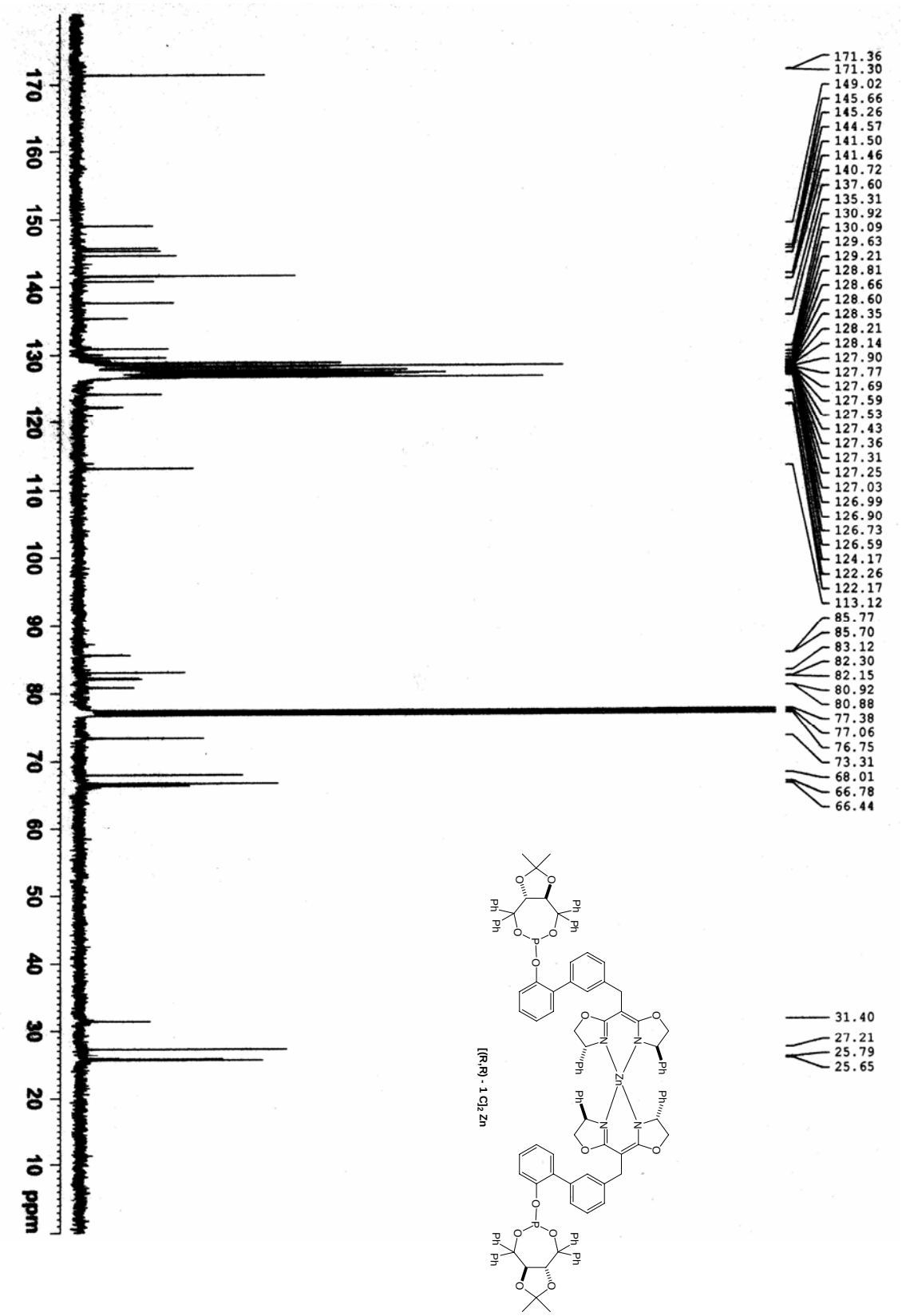

125.97
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
ppm
(S) - 1 E
Ph
Ph
N
HN
Ph
O
O
O
P
O
O
O
O
Ph
Ph
Ph
Ph

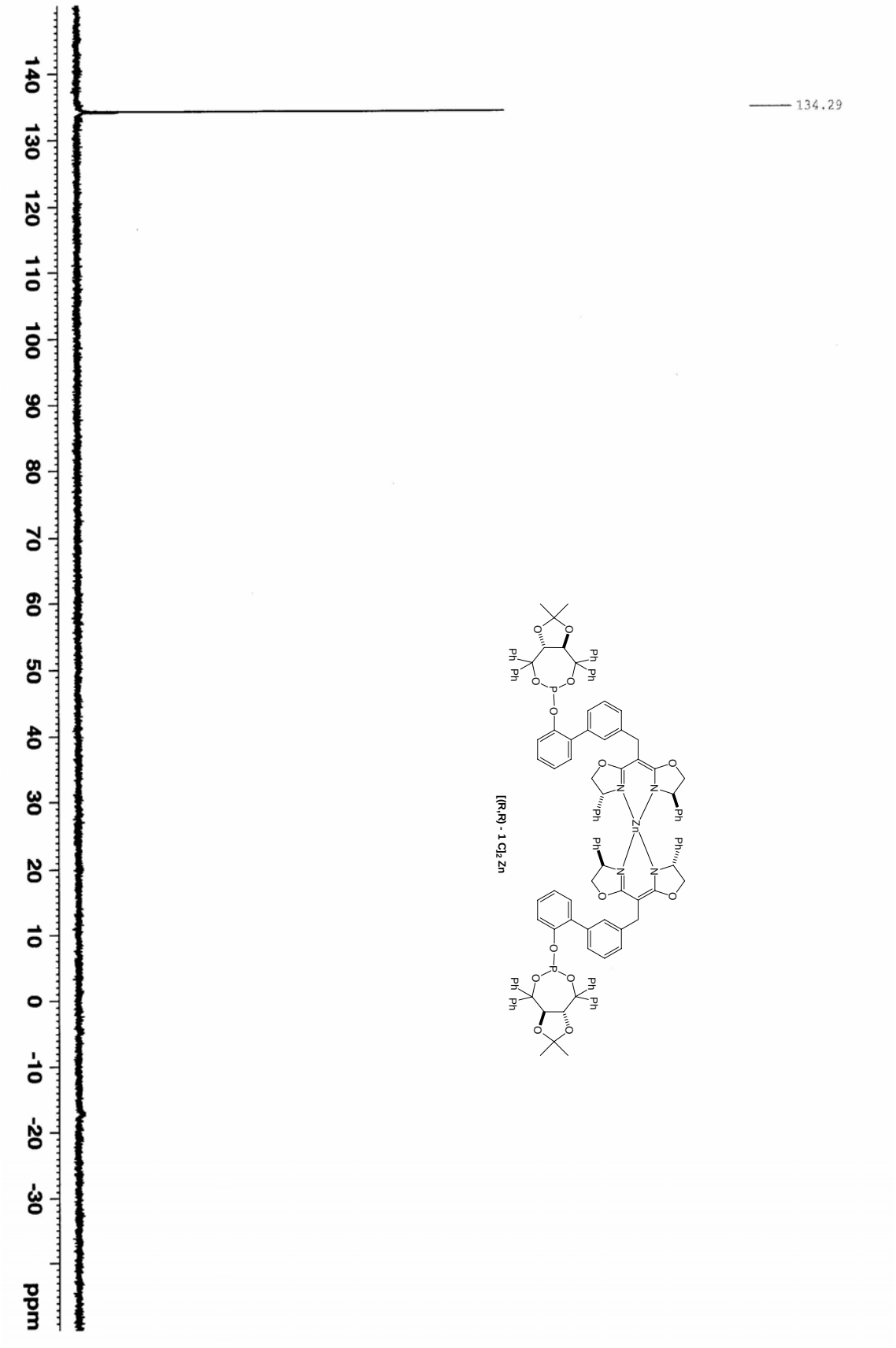

2.15
8.33
24.56
1.84
2.01
1.02
1.97
1.13
1.93
1.00
1.88
1.84
3.15
3.17
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
(S) - 1 H
Ph
N
HN
O
P

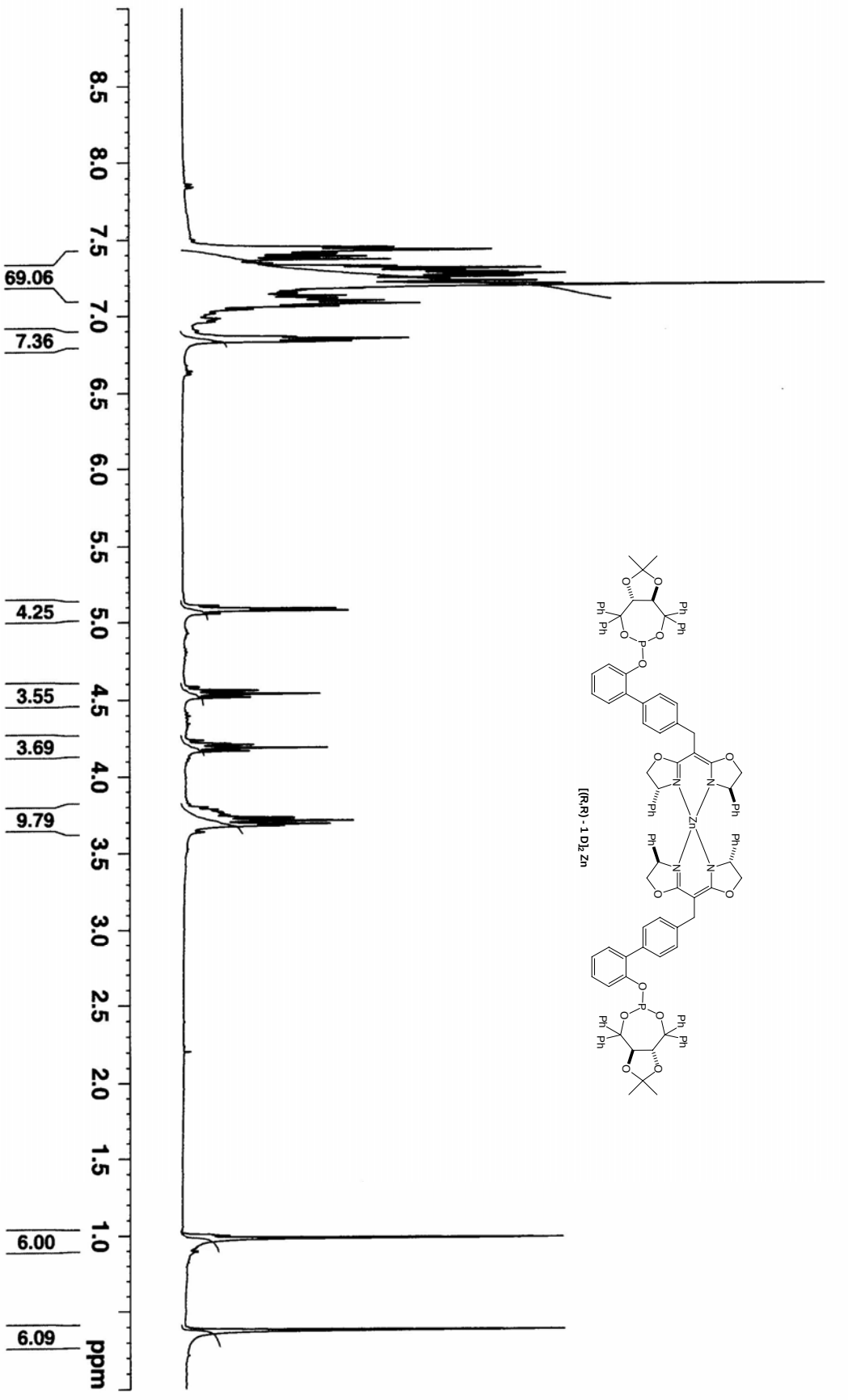

165.44
165.34
151.61
151.56
145.97
142.05
141.93
141.34
139.14
136.68
135.90
129.60
129.16
128.94
128.74
128.71
128.63
128.17
127.97
127.84
127.78
127.63
127.60
127.51
127.43
127.28
127.23
127.17
126.99
126.84
126.70
126.66
126.41
120.26
120.18
113.14
86.79
86.68
85.13
85.06
82.26
82.15
80.23
80.18
77.38
77.06
76.75
75.47
75.20
69.68
69.64
41.39
35.52
26.69
26.46
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
(S) - 1 H
Ph
N
O
HN
Ph
O
O
P
O
O
Ph
Ph
Ph
Ph
O
O

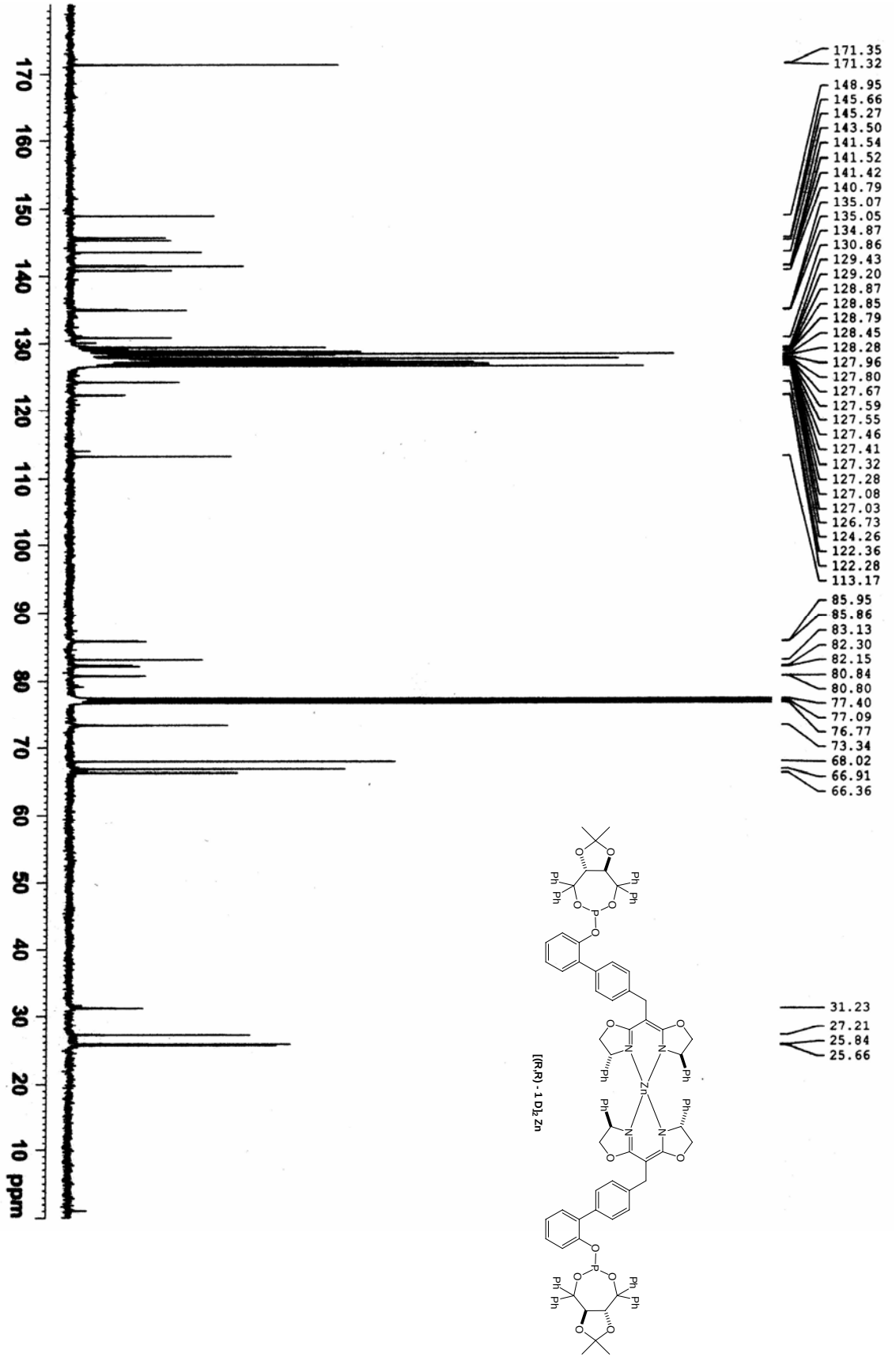

126.46
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 ppm
(S) - 1 H
Ph
Ph
N
HN
O
O
O
P
O
O
O
O
Ph
Ph
Ph
Ph

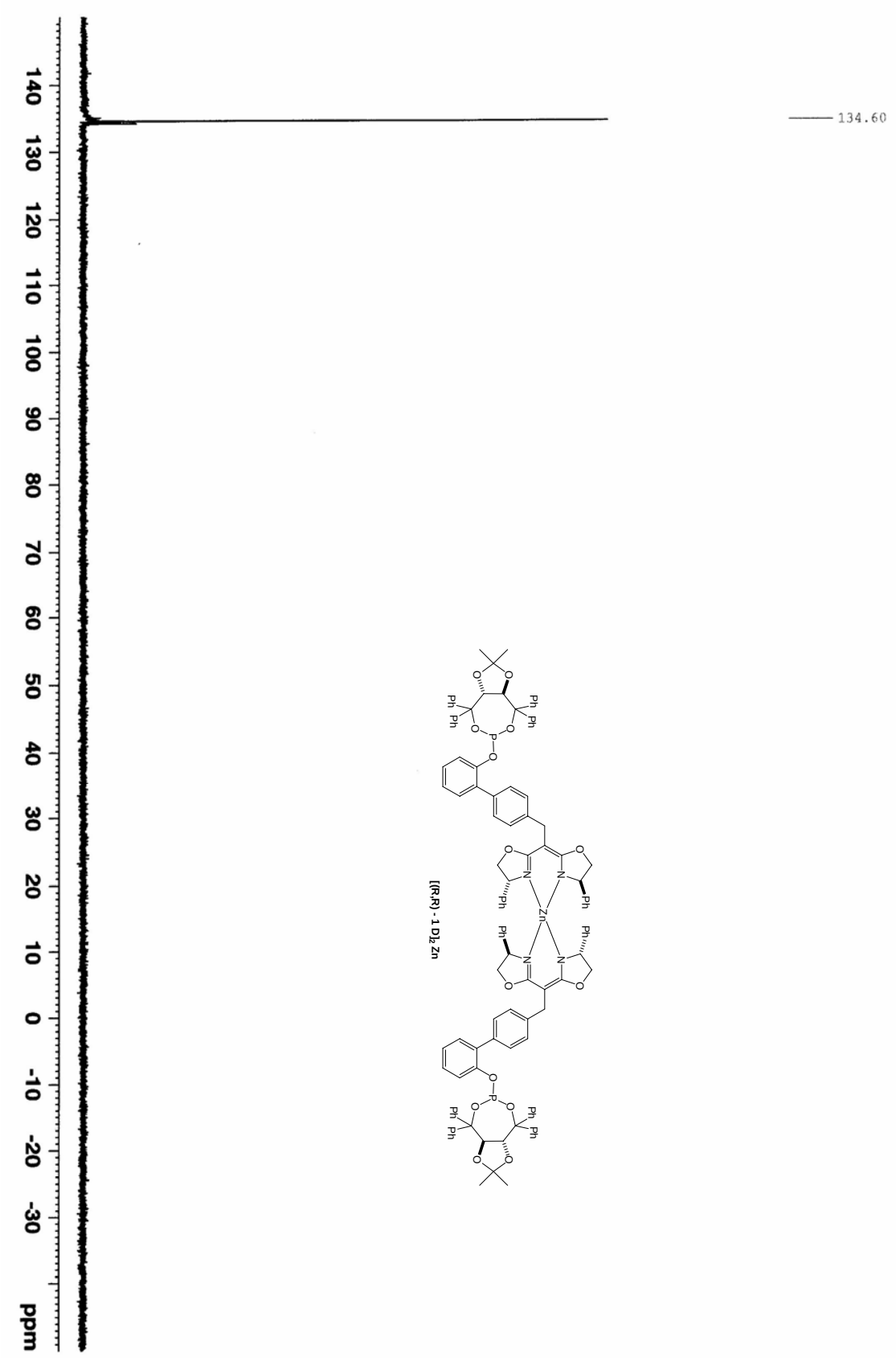

14.20
41.77
13.55
6.89
4.41
3.74
4.08
9.60
6.00
6.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
[(R,R) - 1 Cl2 Zn

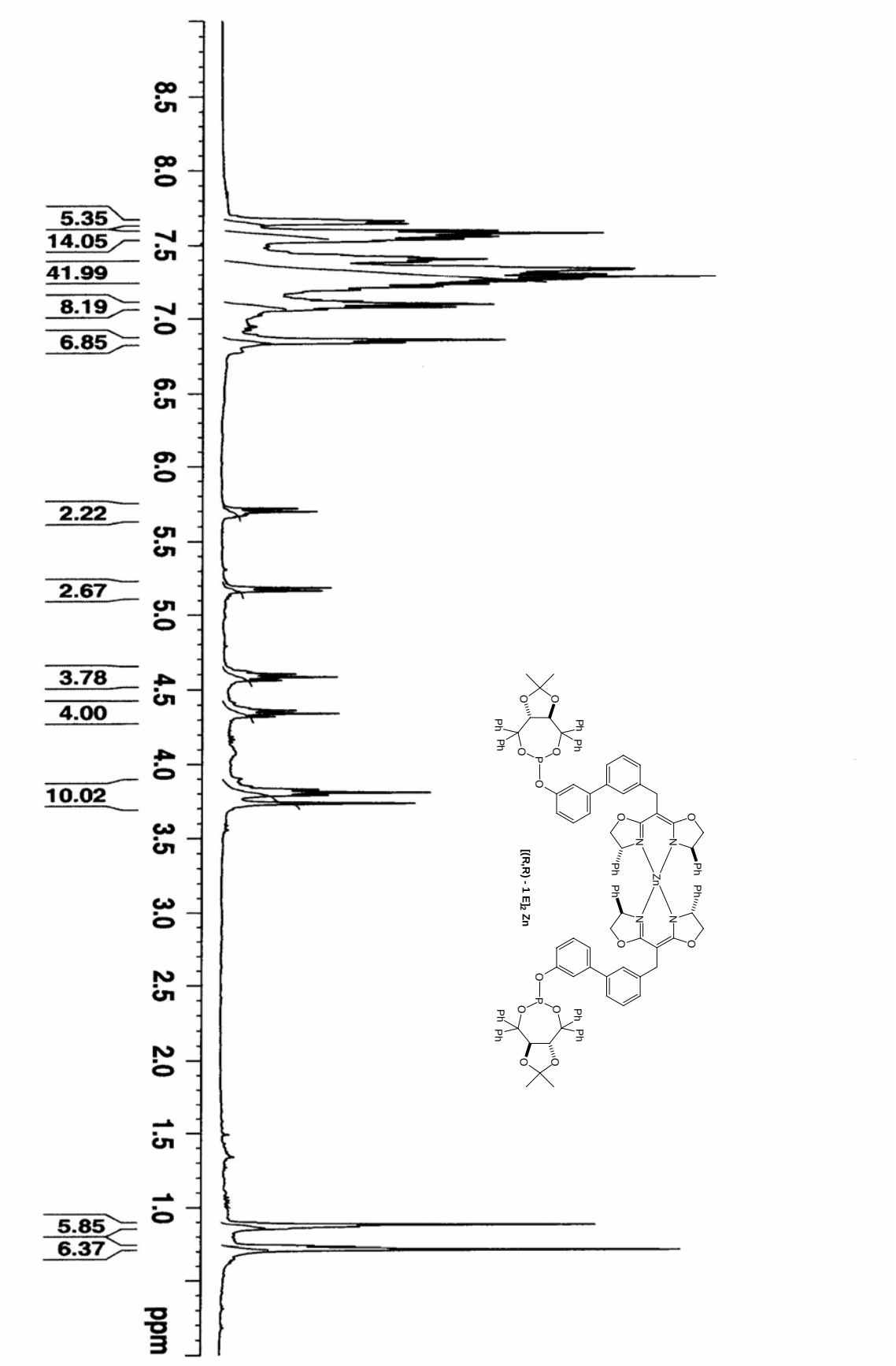

171.36
171.30
149.02
145.66
145.26
144.57
141.50
141.46
140.72
137.60
135.31
130.92
130.09
129.63
129.21
128.81
128.66
128.60
128.35
128.21
128.14
127.90
127.77
127.69
127.59
127.53
127.43
127.36
127.31
127.25
127.03
126.99
126.90
126.73
126.59
124.17
122.26
122.17
113.12
85.77
85.70
83.12
82.30
82.15
80.92
80.88
77.38
77.06
76.75
73.31
68.01
66.78
66.44
31.40
27.21
25.79
25.65
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
[(R,R) - 1 Cl]2 Zn

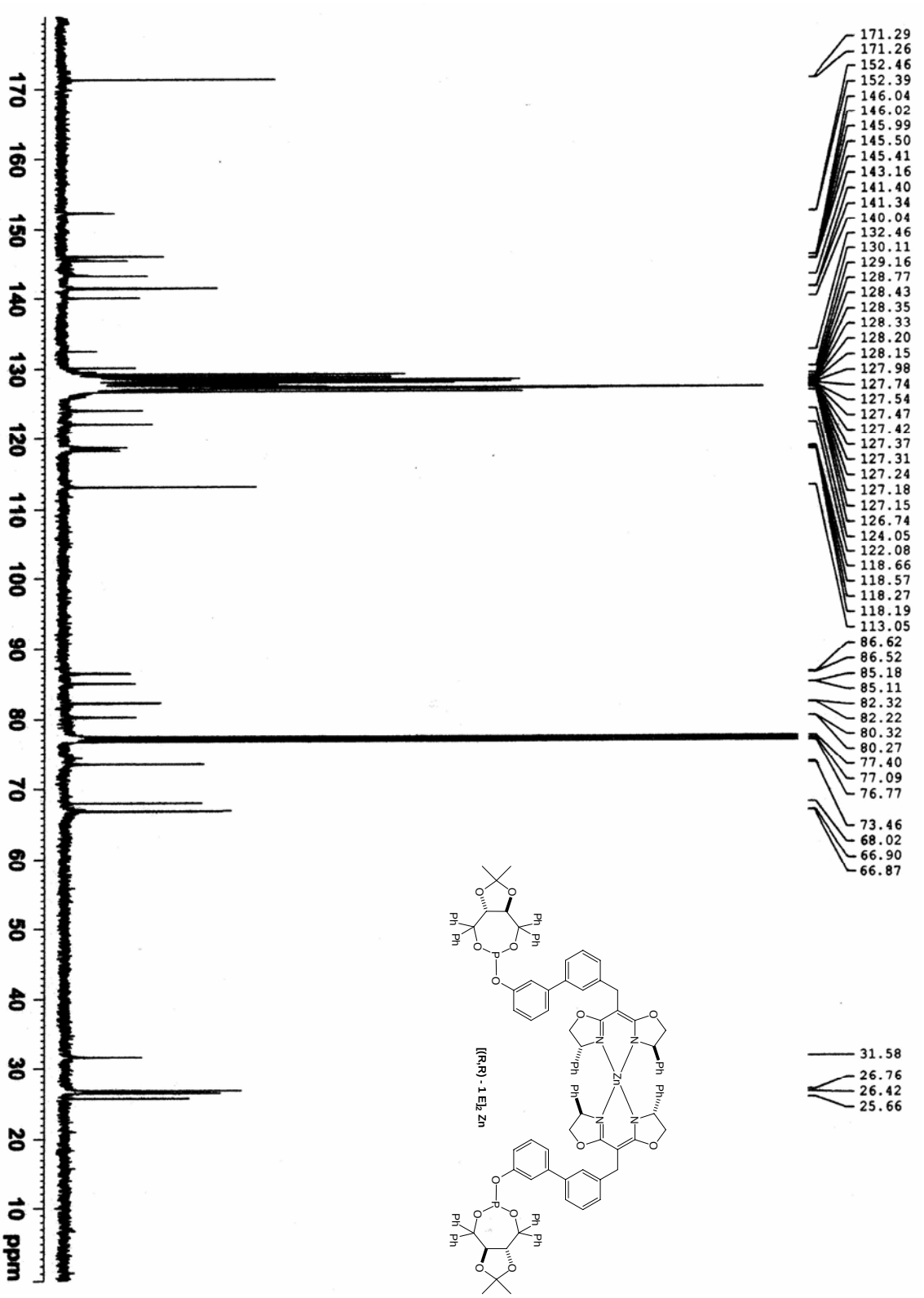

134.29
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm
[(R,R) - 1 Cl]2 Zn

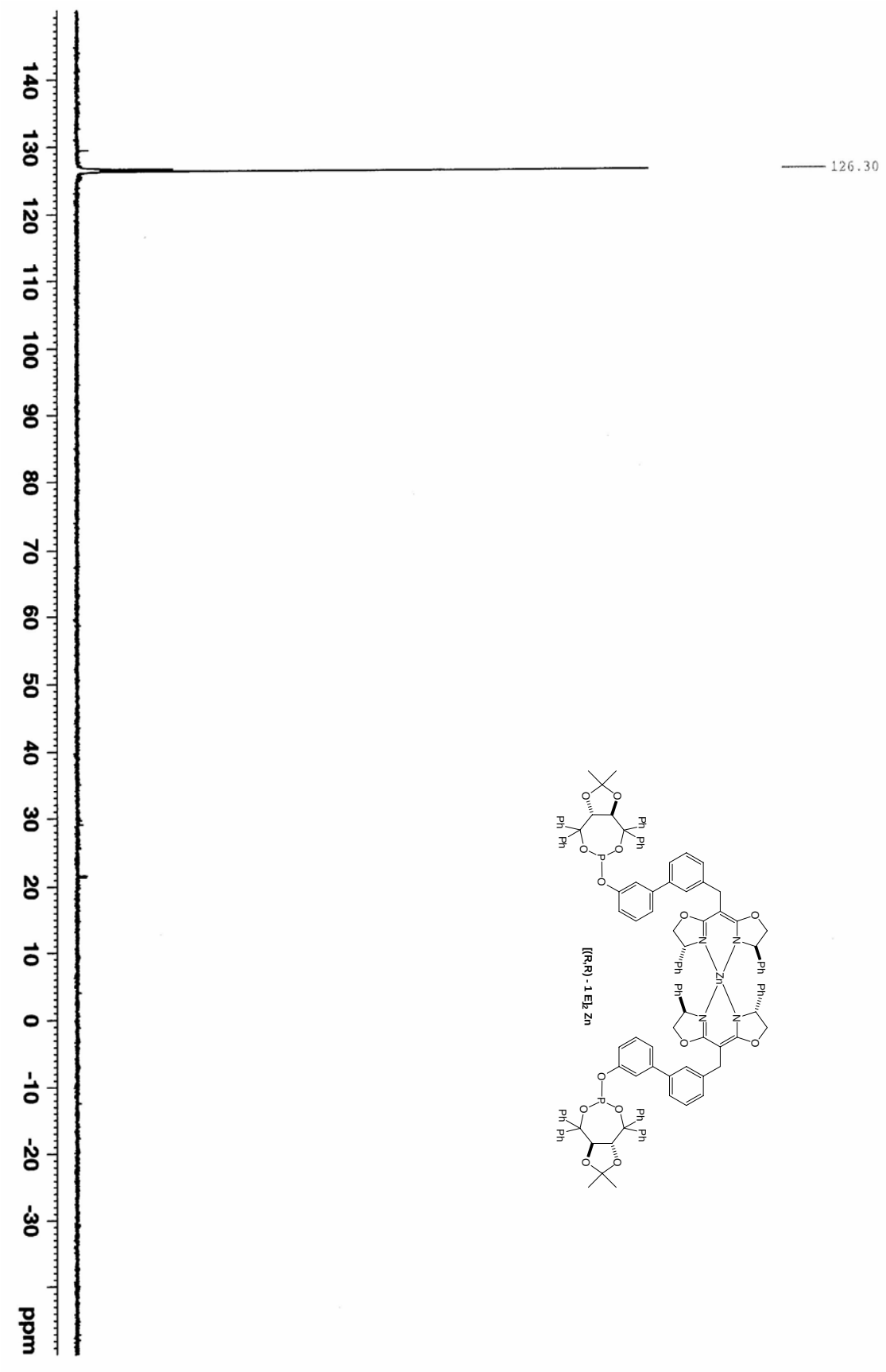

8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
69.06
7.36
4.25
3.55
3.69
9.79
6.00
6.09
[(R,R) - 1 D]2 Zn

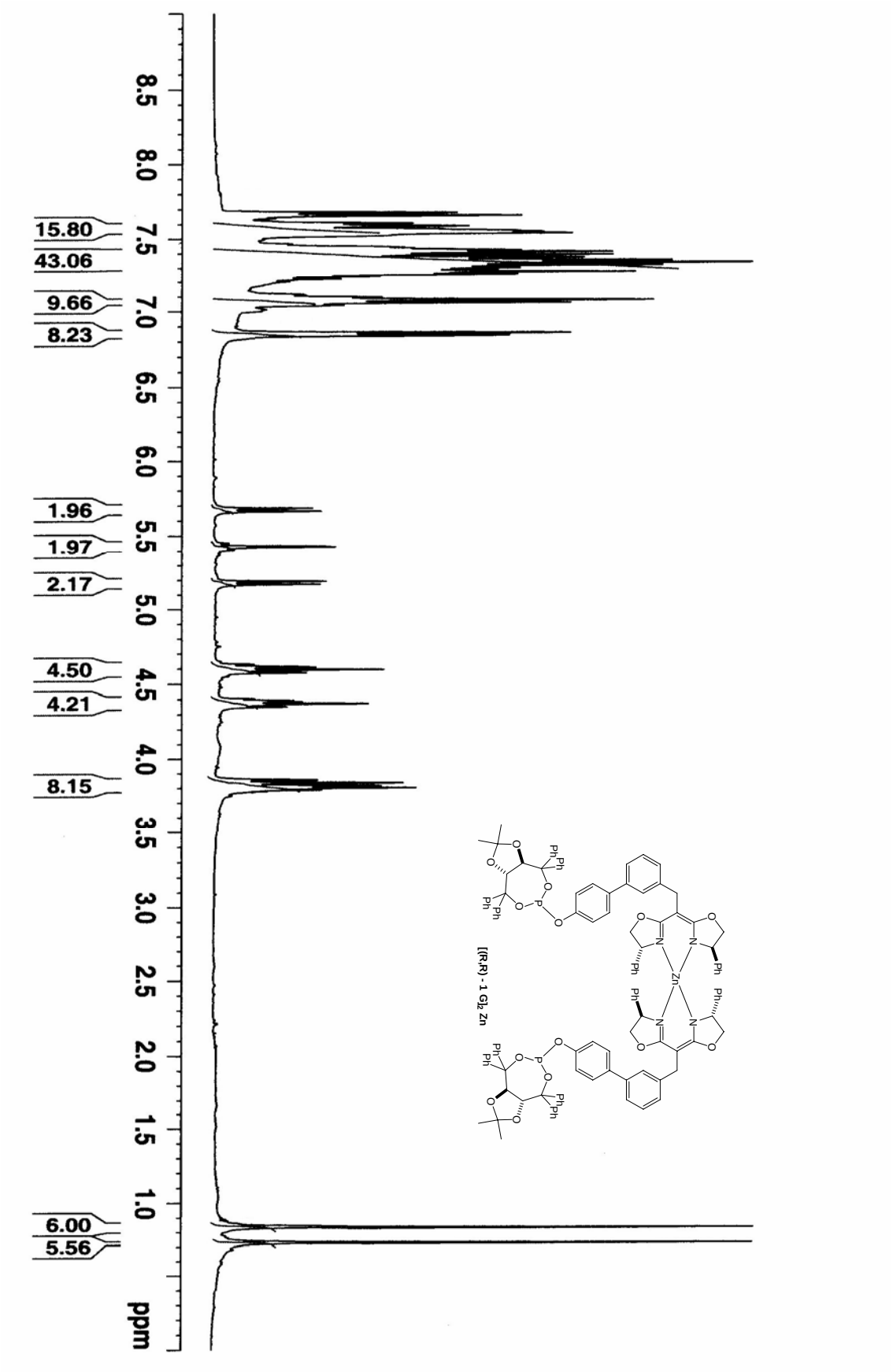

171.35
171.32
148.95
145.66
145.27
143.50
141.54
141.52
141.42
140.79
135.07
135.05
134.87
130.86
129.43
129.20
128.87
128.85
128.79
128.45
128.28
127.96
127.80
127.67
127.59
127.55
127.46
127.41
127.32
127.28
127.08
127.03
126.73
124.26
122.36
122.28
113.17
85.95
85.86
83.13
82.30
82.15
80.84
80.80
77.40
77.09
76.77
73.34
68.02
66.91
66.36
31.23
27.21
25.84
25.66
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
[(R,R) - 1 D]2 Zn

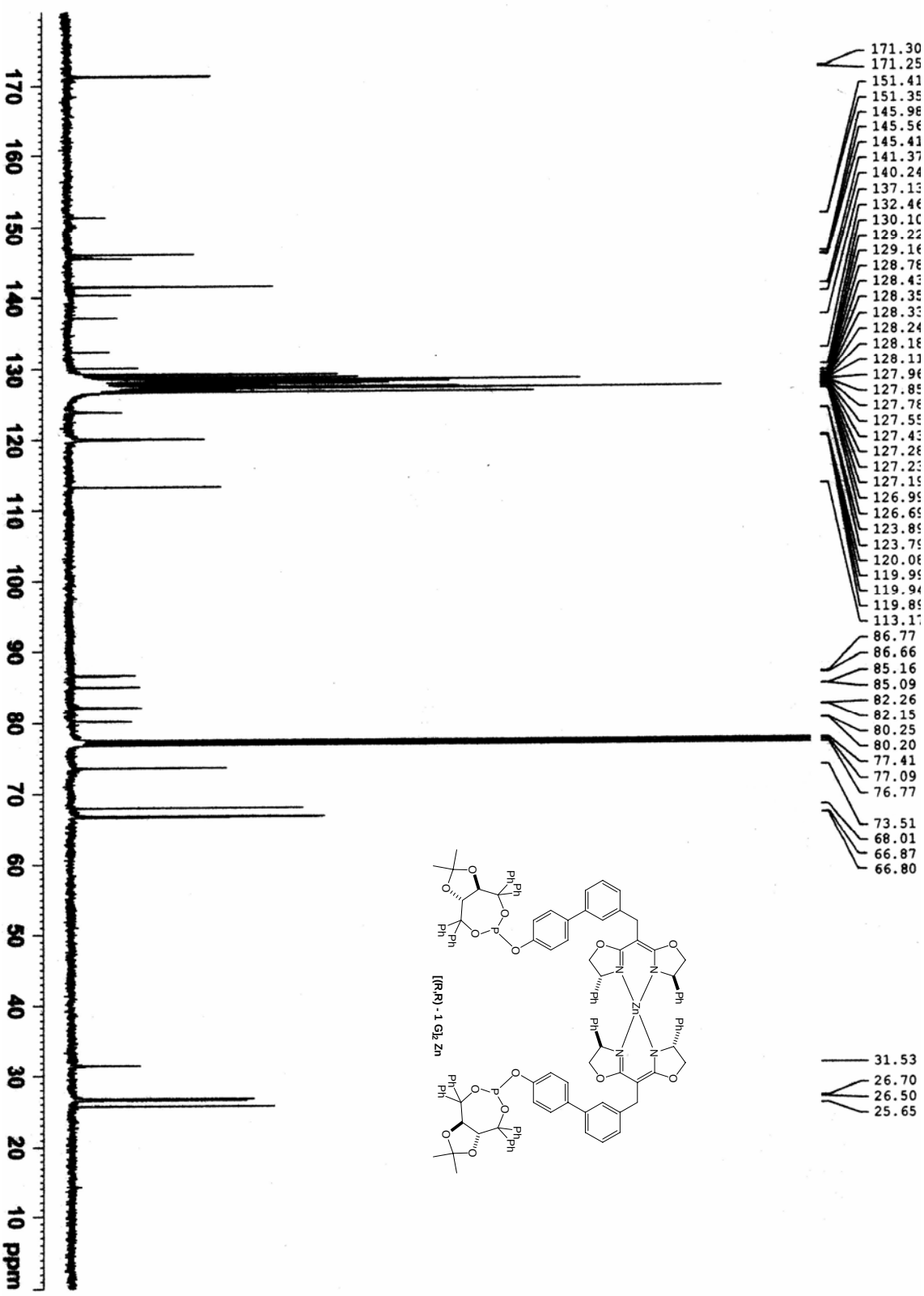

134.60
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
ppm
[(R,R) - 1 D]2 Zn

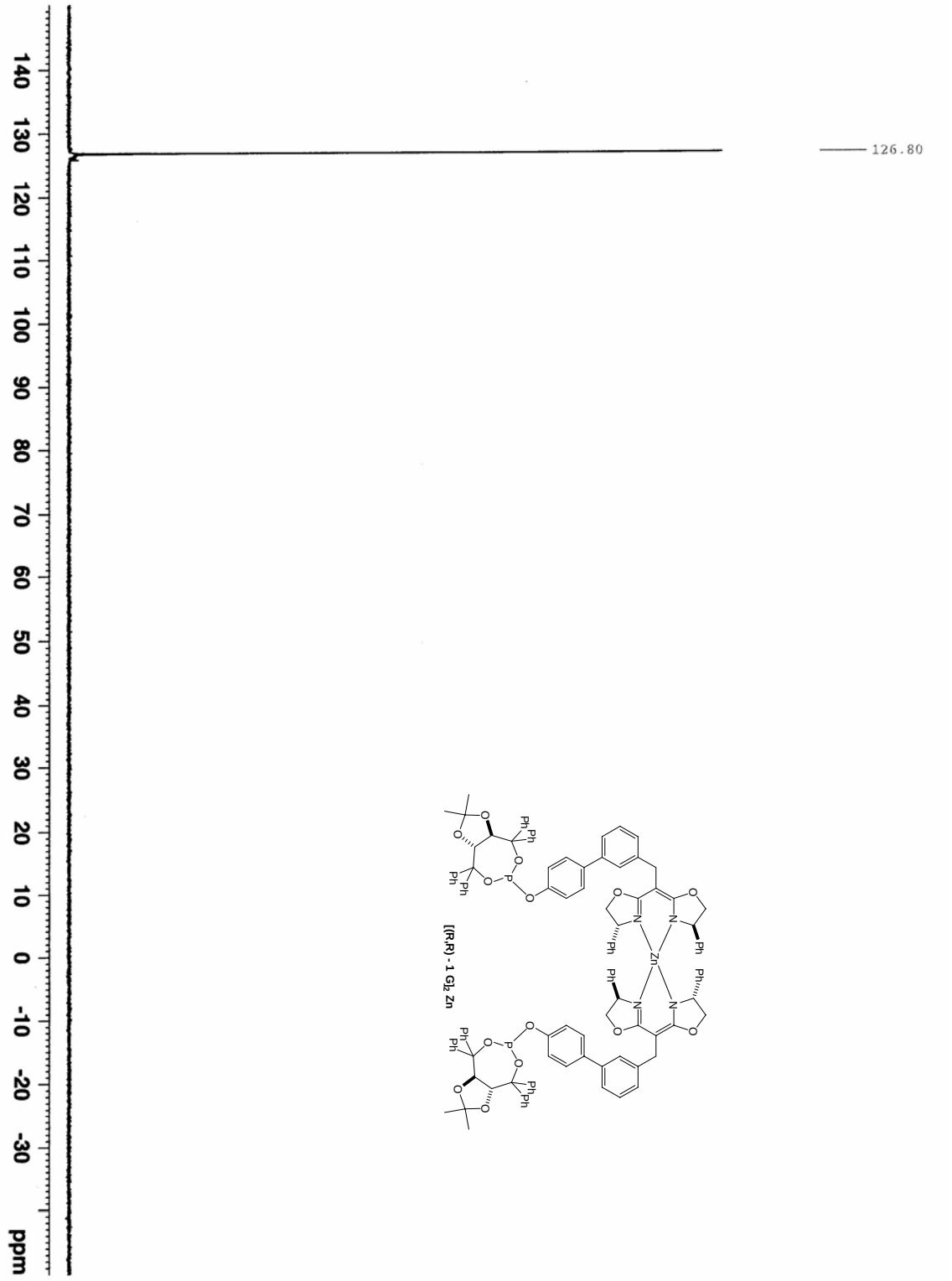

5.35
14.05
41.99
8.19
6.85
2.22
2.67
3.78
4.00
10.02
5.85
6.37
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
[(R,R) - 1 Et2 Zn

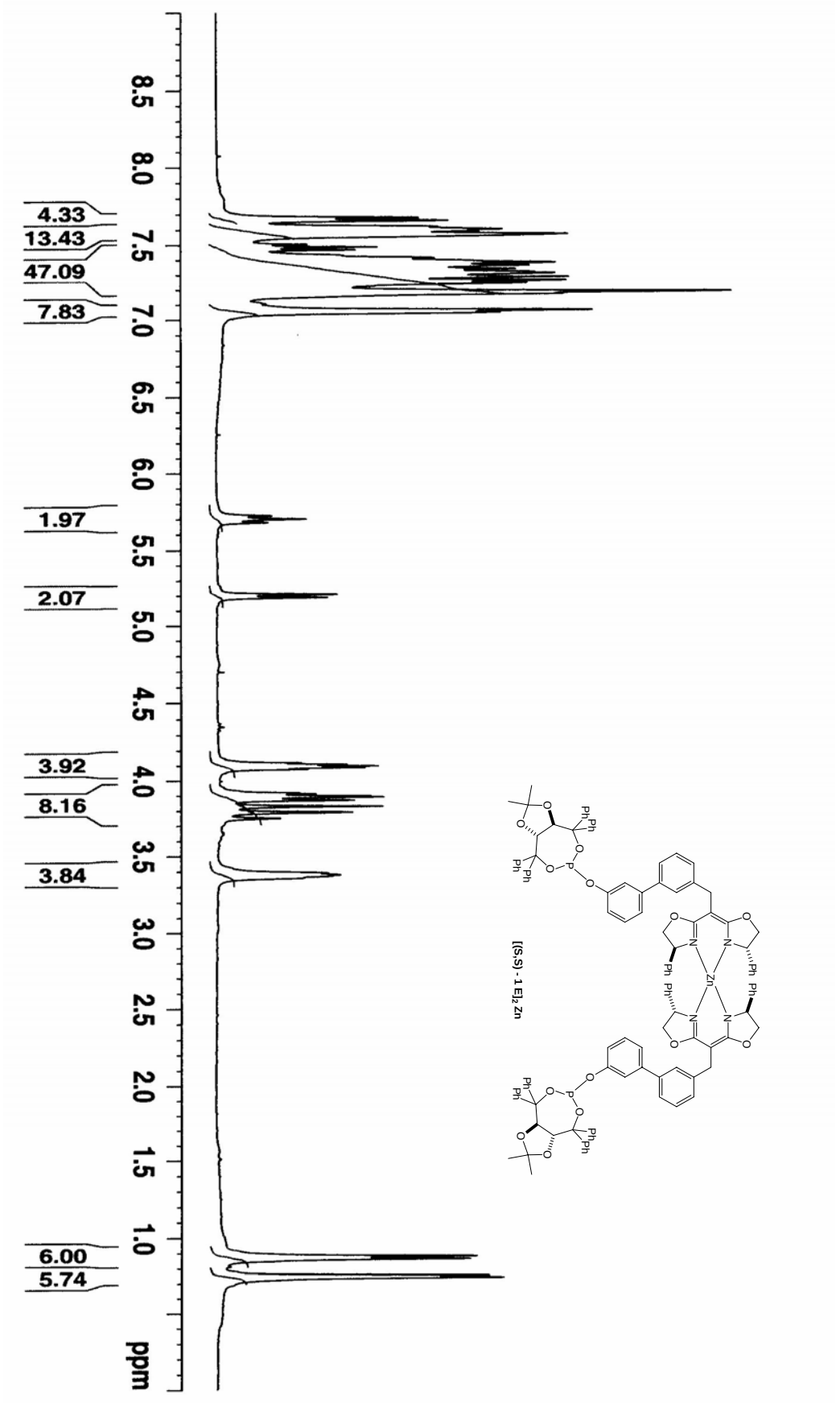

171.29
171.26
152.46
152.39
146.04
146.02
145.99
145.50
145.41
143.16
141.40
141.34
140.04
132.46
130.11
129.16
128.77
128.43
128.35
128.33
128.20
128.15
127.98
127.74
127.54
127.47
127.42
127.37
127.31
127.24
127.18
127.15
126.74
124.05
122.08
118.66
118.57
118.27
118.19
113.05
86.62
86.52
85.18
85.11
82.32
82.22
80.32
80.27
77.40
77.09
76.77
73.46
68.02
66.90
66.87
31.58
26.76
26.42
25.66
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
[(R,R) - 1 E]2 Zn

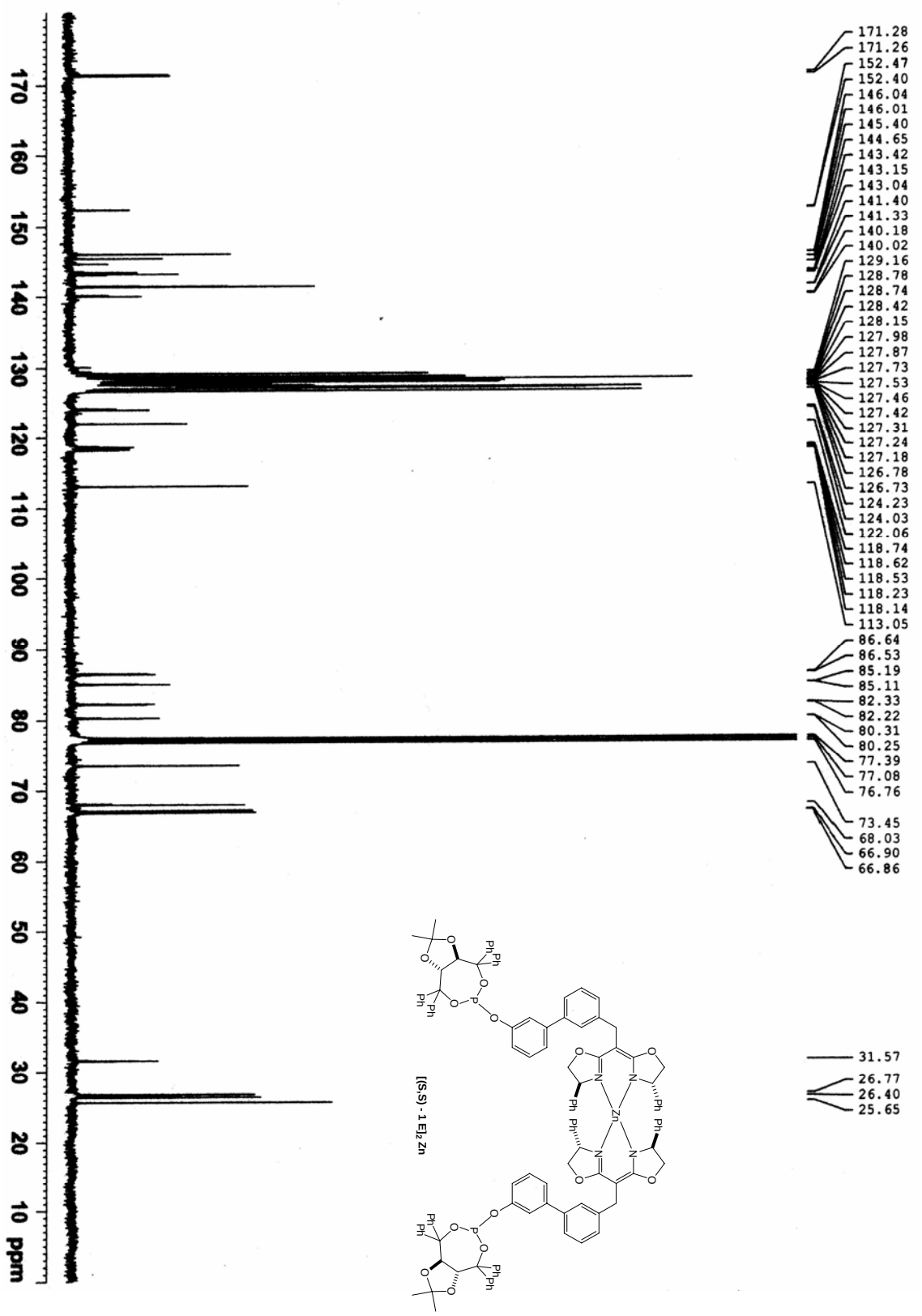

126.30
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm
[(R,R) - 1 E]2 Zn

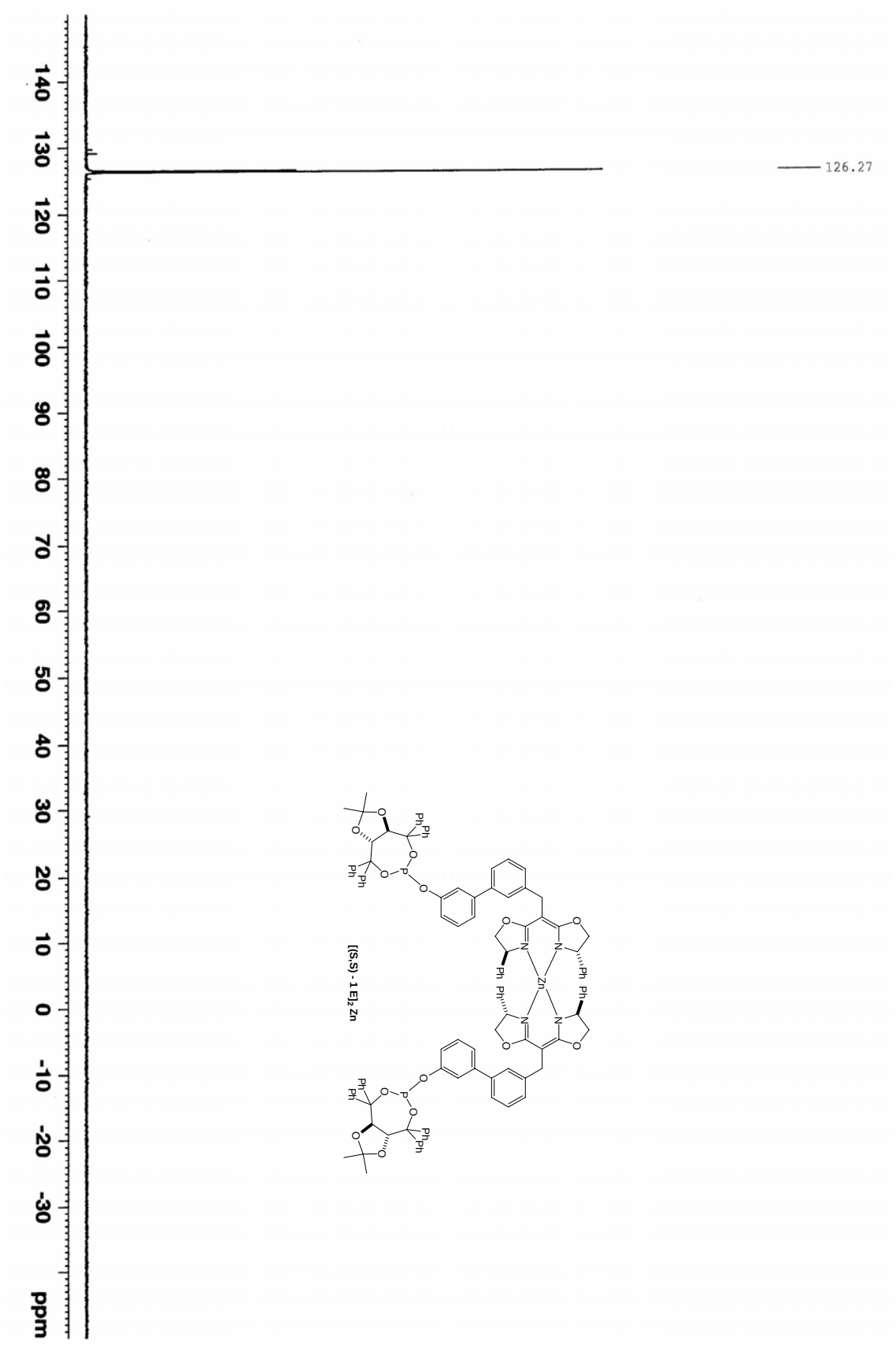

15.80
43.06
9.66
8.23
1.96
1.97
2.17
4.50
4.21
8.15
6.00
5.56
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
[(R,R) - 1 G]2 Zn

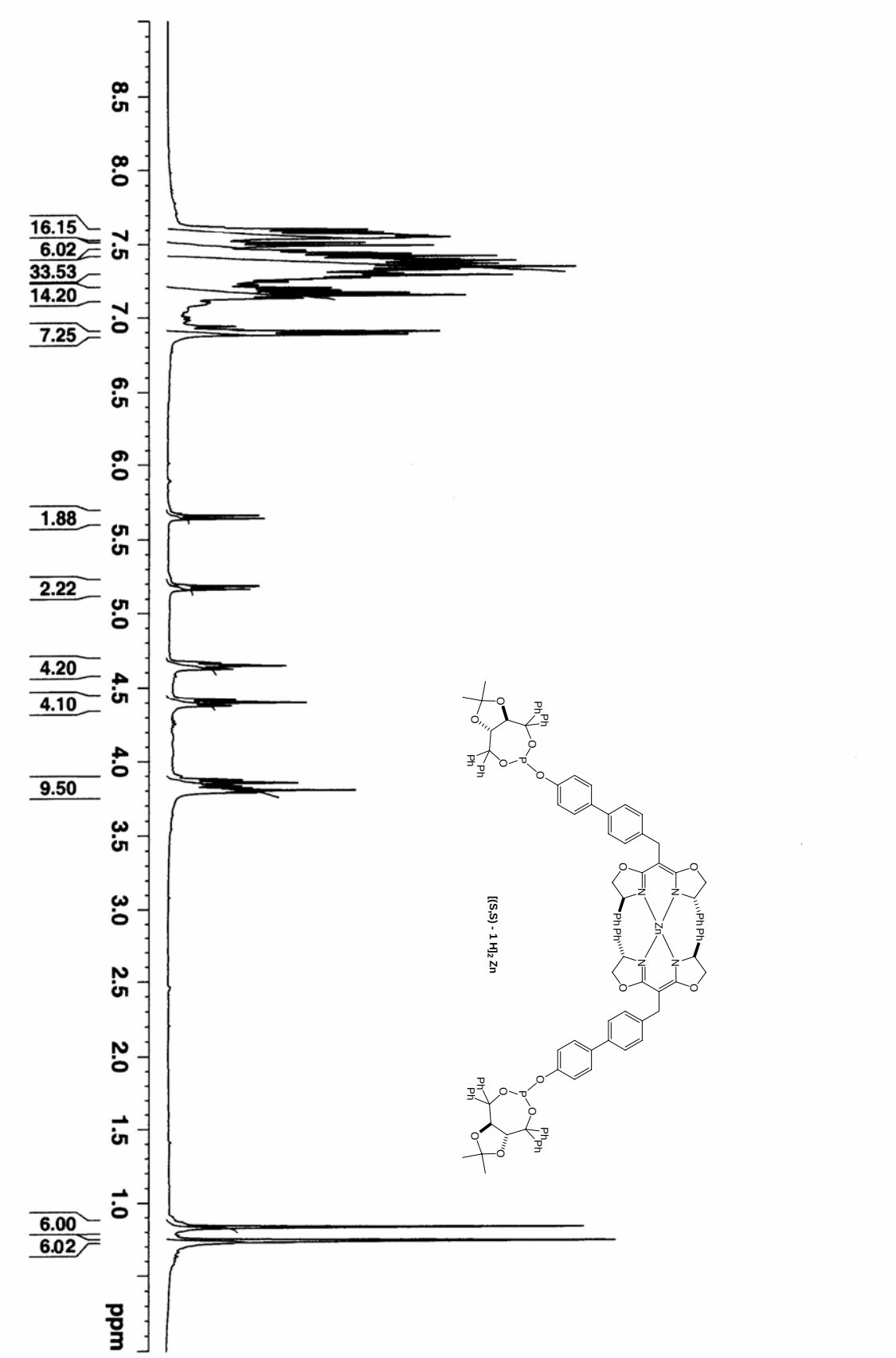

171.30
171.25
151.41
151.35
145.98
145.56
145.41
141.37
140.24
137.13
132.46
130.10
129.22
129.16
128.78
128.43
128.35
128.33
128.24
128.18
128.11
127.96
127.85
127.78
127.55
127.43
127.28
127.23
127.19
126.99
126.69
123.89
123.79
120.08
119.99
119.94
119.89
113.17
86.77
86.66
85.16
85.09
82.26
82.15
80.25
80.20
77.41
77.09
76.77
73.51
68.01
66.87
66.80
31.53
26.70
26.50
25.65
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
[(R,R) - 1 G]2 Zn

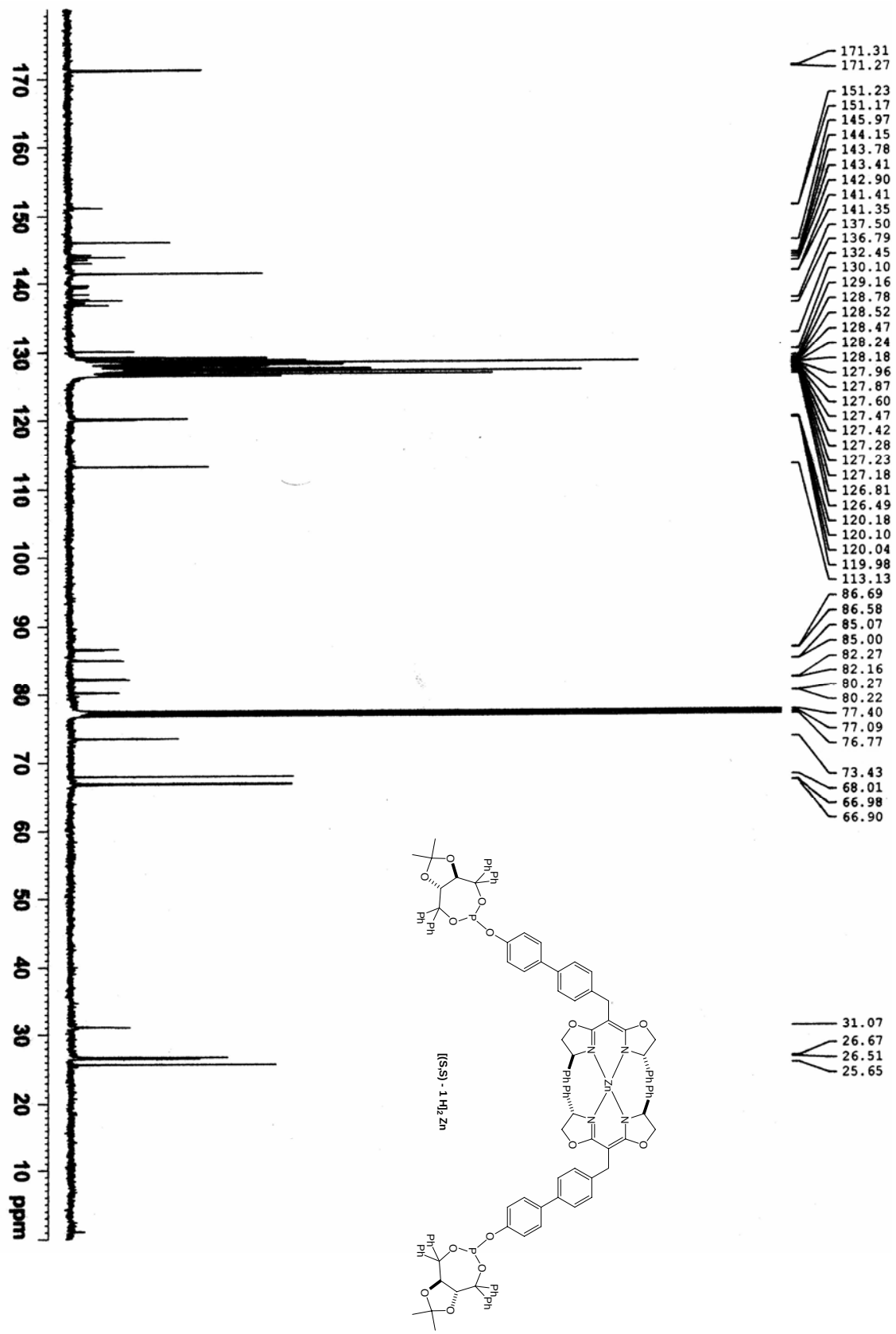

126.80
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm
[(R,R) - 1 G]2 Zn

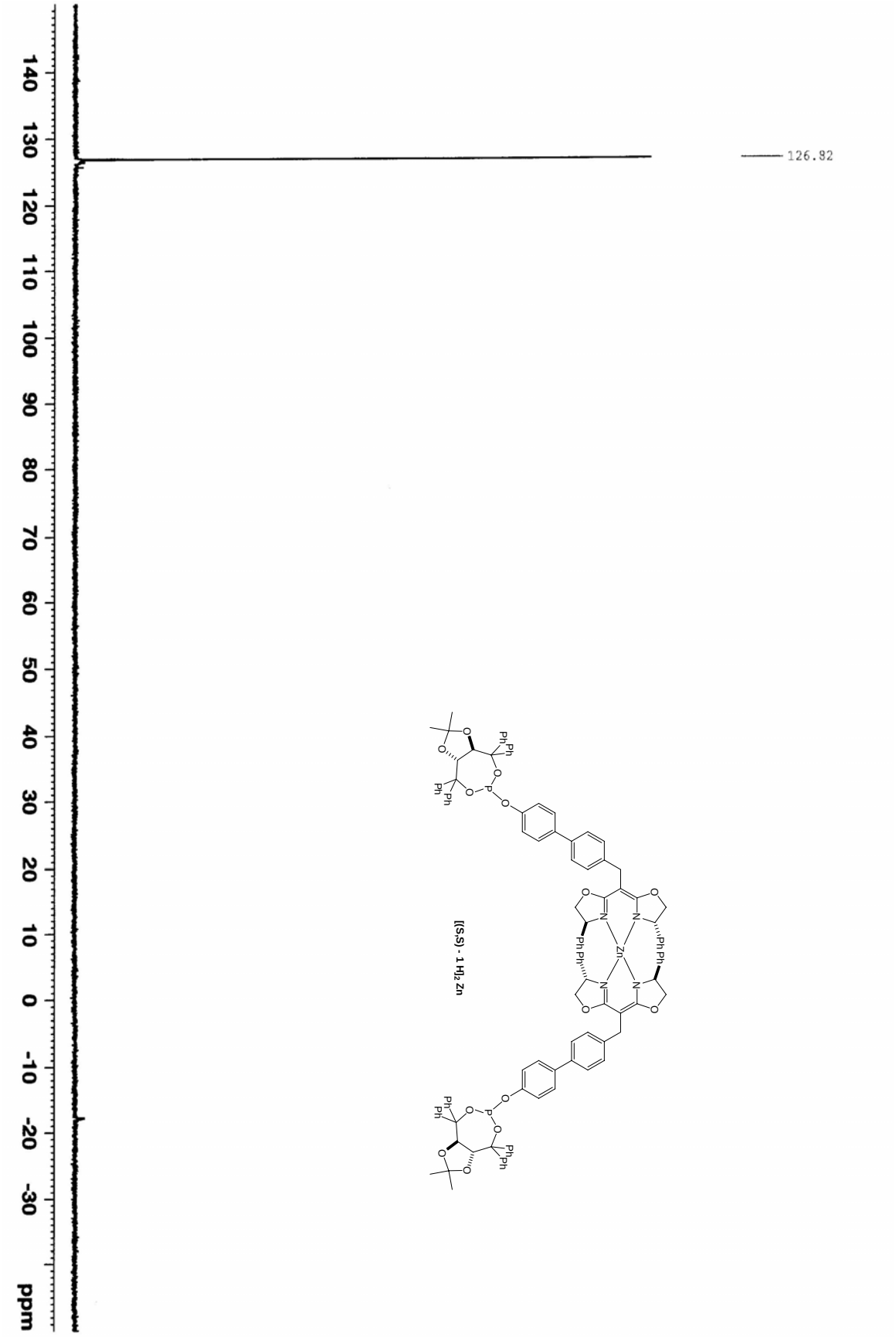

4.33
13.43
47.09
7.83
1.97
2.07
3.92
8.16
3.84
6.00
5.74
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
[(S,S) - 1 E]2 Zn

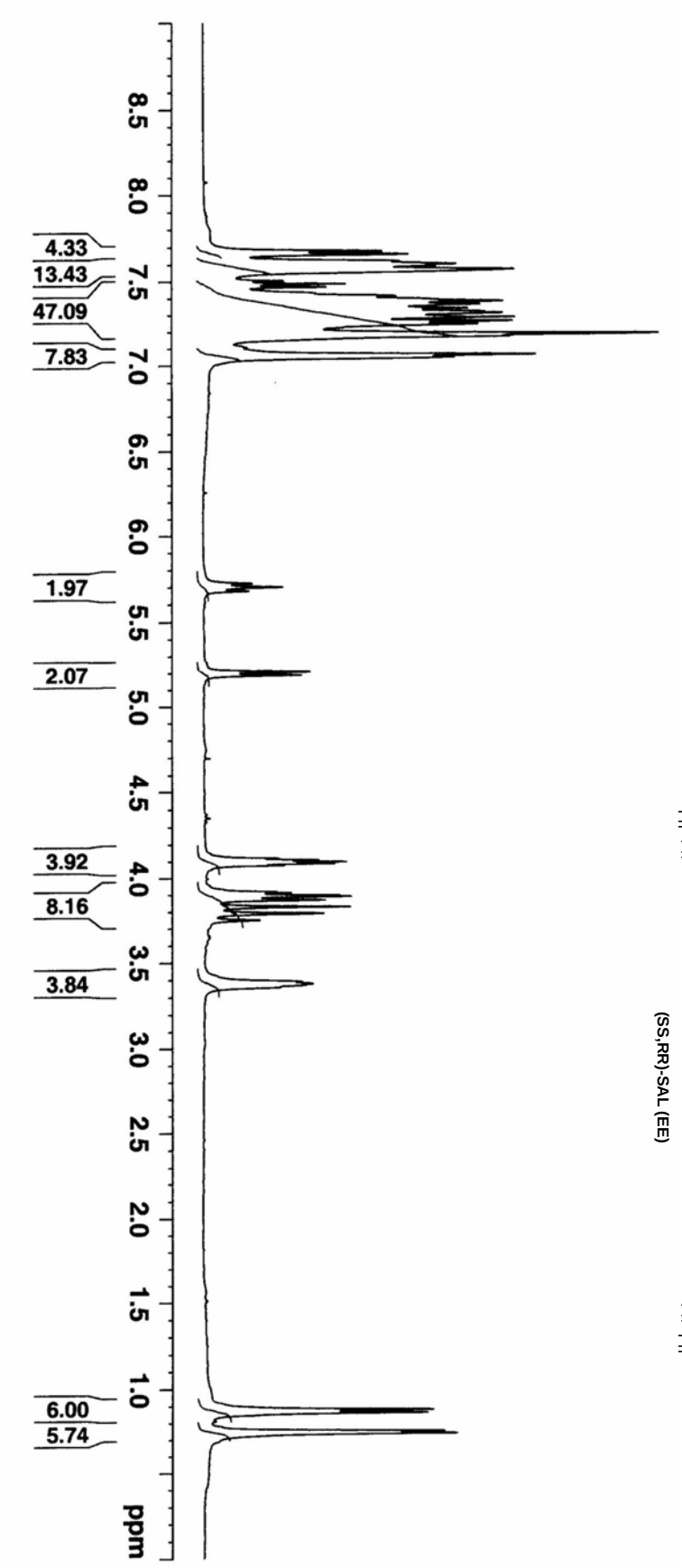

171.28
171.26
152.47
152.40
146.04
146.01
145.40
144.65
143.42
143.15
143.04
141.40
141.33
140.18
140.02
129.16
128.78
128.74
128.42
128.15
127.98
127.87
127.73
127.53
127.46
127.42
127.31
127.24
127.18
126.78
126.73
124.23
124.03
122.06
118.74
118.62
118.53
118.23
118.14
113.05
86.64
86.53
85.19
85.11
82.33
82.22
80.31
80.25
77.39
77.08
76.76
73.45
68.03
66.90
66.86
31.57
26.77
26.40
25.65
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm
[(S,S) - 1 E]2 Zn

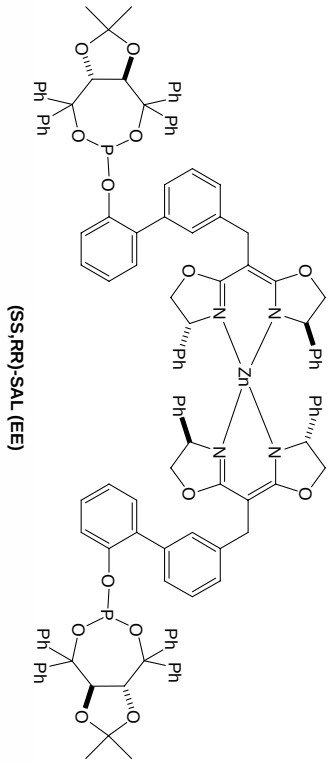

126.27
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm
[(S,S)-1-Et]2Zn


16.15
6.02
33.53
14.20
7.25
1.88
2.22
4.20
4.10
9.50
6.00
6.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
[(S,S) - 1 H]2 Zn

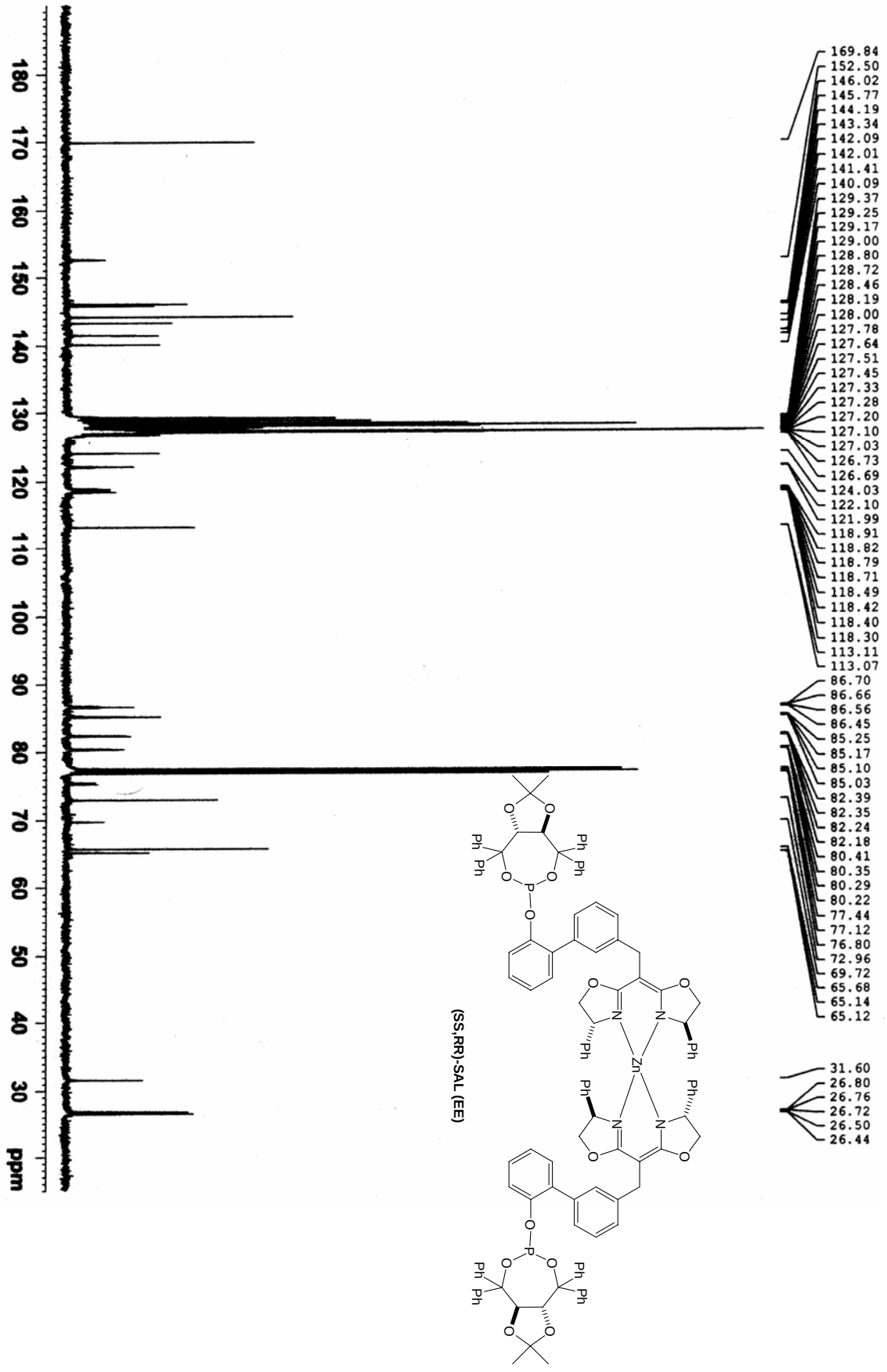

171.31
171.27
151.23
151.17
145.97
144.15
143.78
143.41
142.90
141.41
141.35
137.50
136.79
132.45
130.10
129.16
128.78
128.52
128.47
128.24
128.18
127.96
127.87
127.60
127.47
127.42
127.28
127.23
127.18
126.81
126.49
120.18
120.10
120.04
119.98
113.13
86.69
86.58
85.07
85.00
82.27
82.16
80.27
80.22
77.40
77.09
76.77
73.43
68.01
66.98
66.90
31.07
26.67
26.51
25.65
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
[(S,S) - 1 H]2 Zn

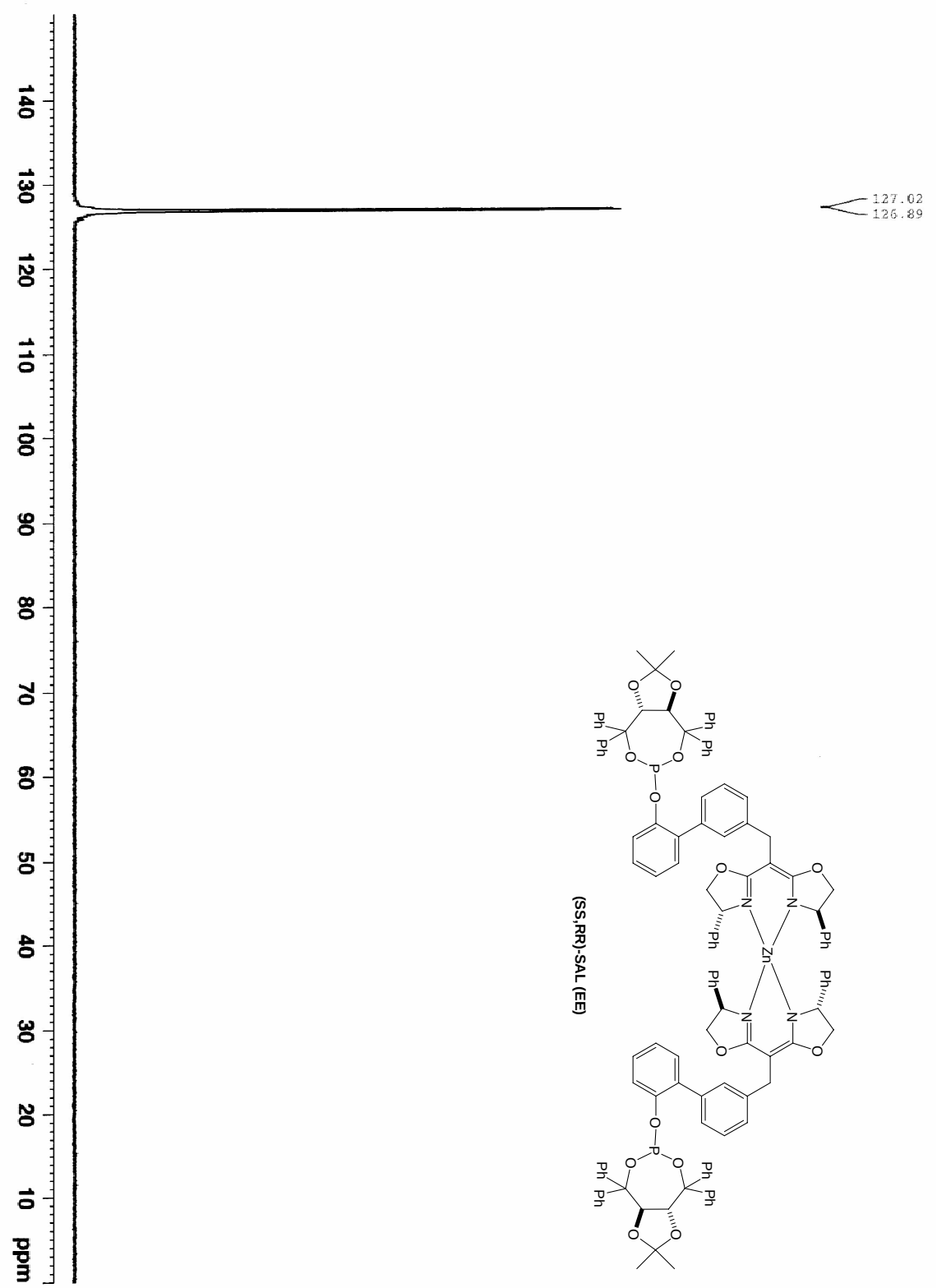

126.82
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
ppm
[(S,S) - 1 H2 Zn

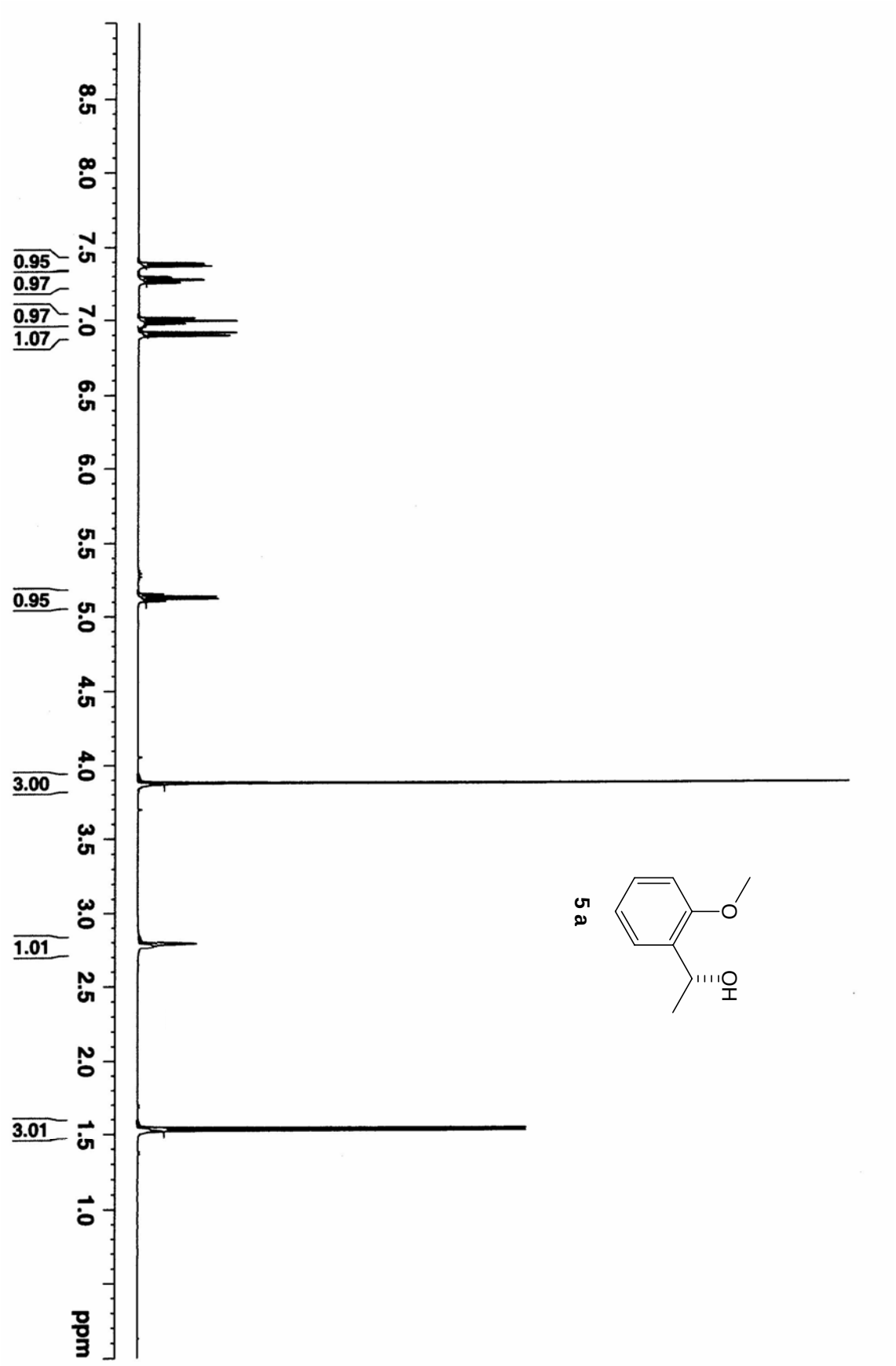

4.33
13.43
47.09
7.83
1.97
2.07
3.92
8.16
3.84
6.00
5.74
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm

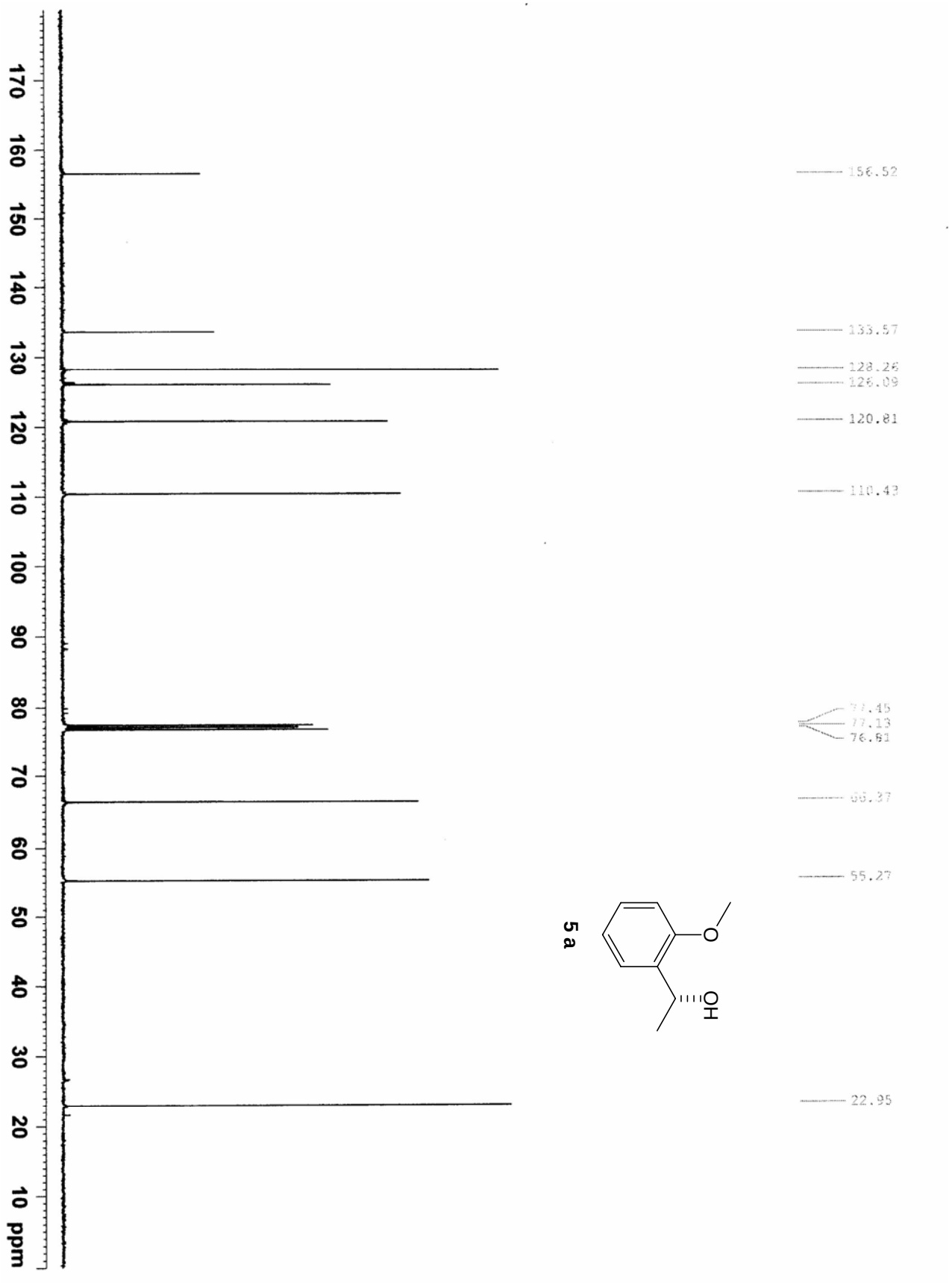


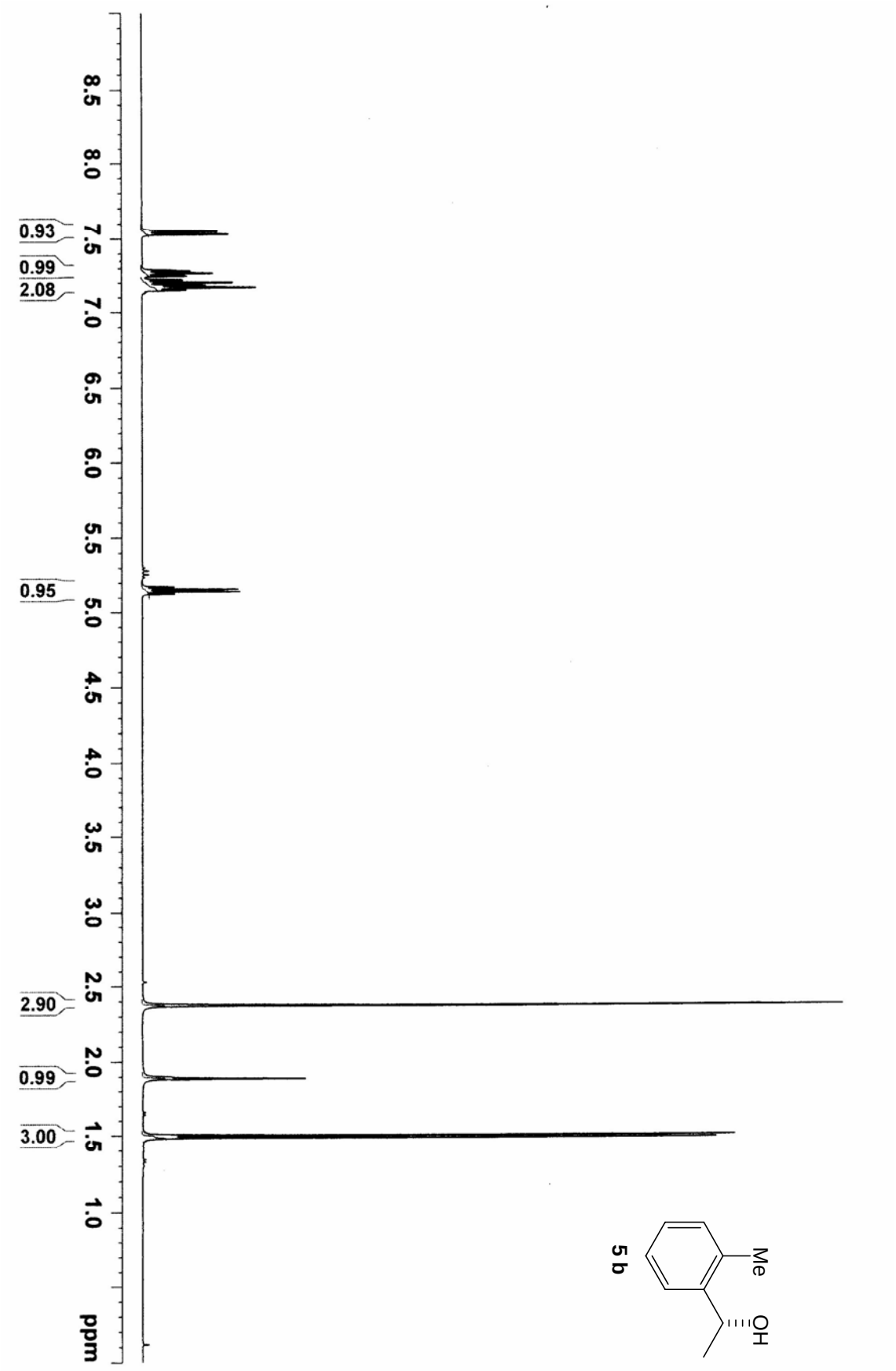
(SS,RR)-SAL (EE)

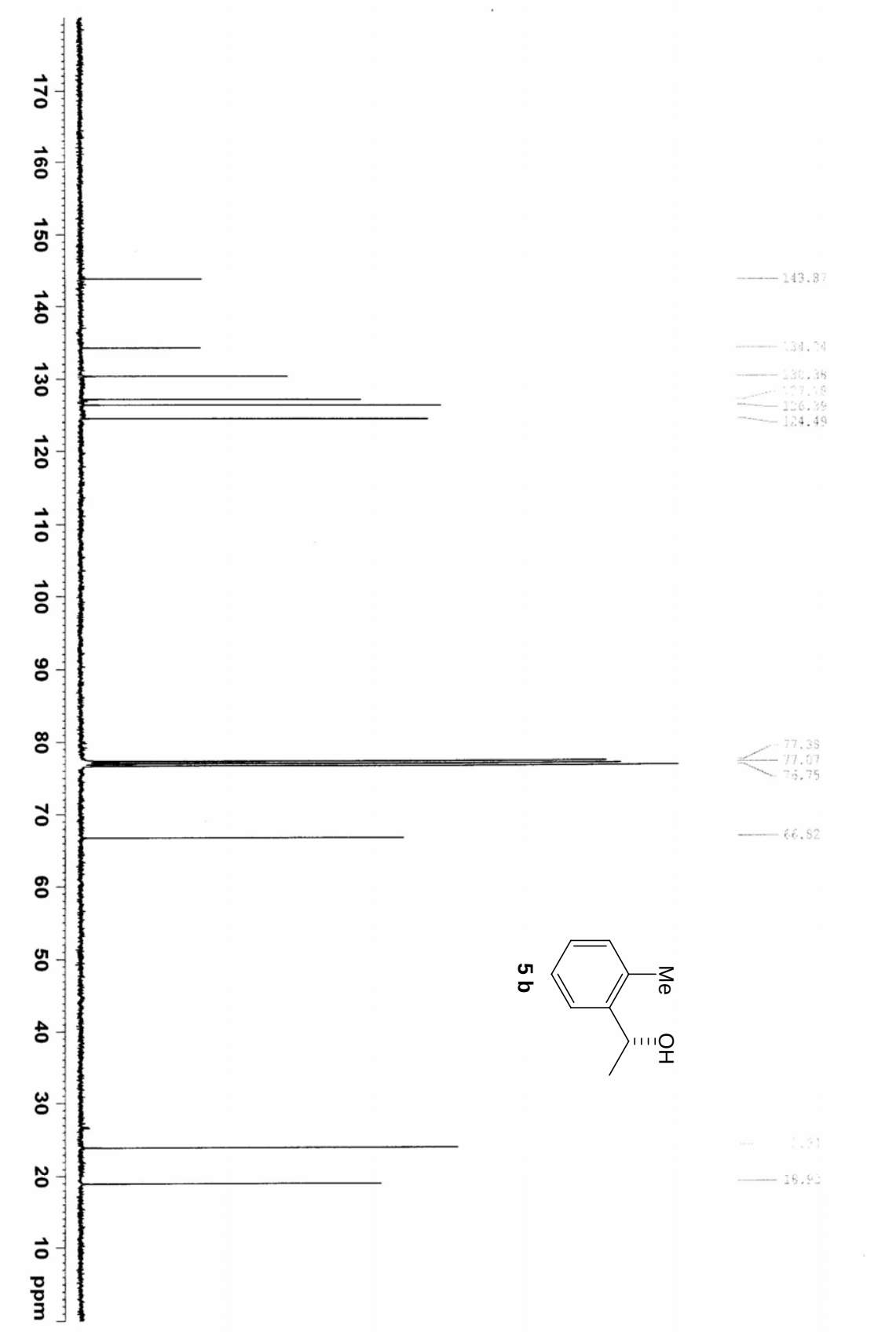

169.84
152.50
146.02
145.77
144.19
143.34
142.09
142.01
141.41
140.09
129.37
129.25
129.17
129.00
128.80
128.72
128.46
128.19
128.00
127.78
127.64
127.51
127.45
127.33
127.28
127.20
127.10
127.03
126.73
126.69
124.03
122.10
121.99
118.91
118.82
118.79
118.71
118.49
118.42
118.40
118.30
113.11
113.07
86.70
86.66
86.56
86.45
85.25
85.17
85.10
85.03
82.39
82.35
82.24
82.18
80.41
80.35
80.29
80.22
77.44
77.12
76.80
72.96
69.72
65.68
65.14
65.12
31.60
26.80
26.76
26.72
26.50
26.44
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
ppm
(SS,RR)-SAL (EE)

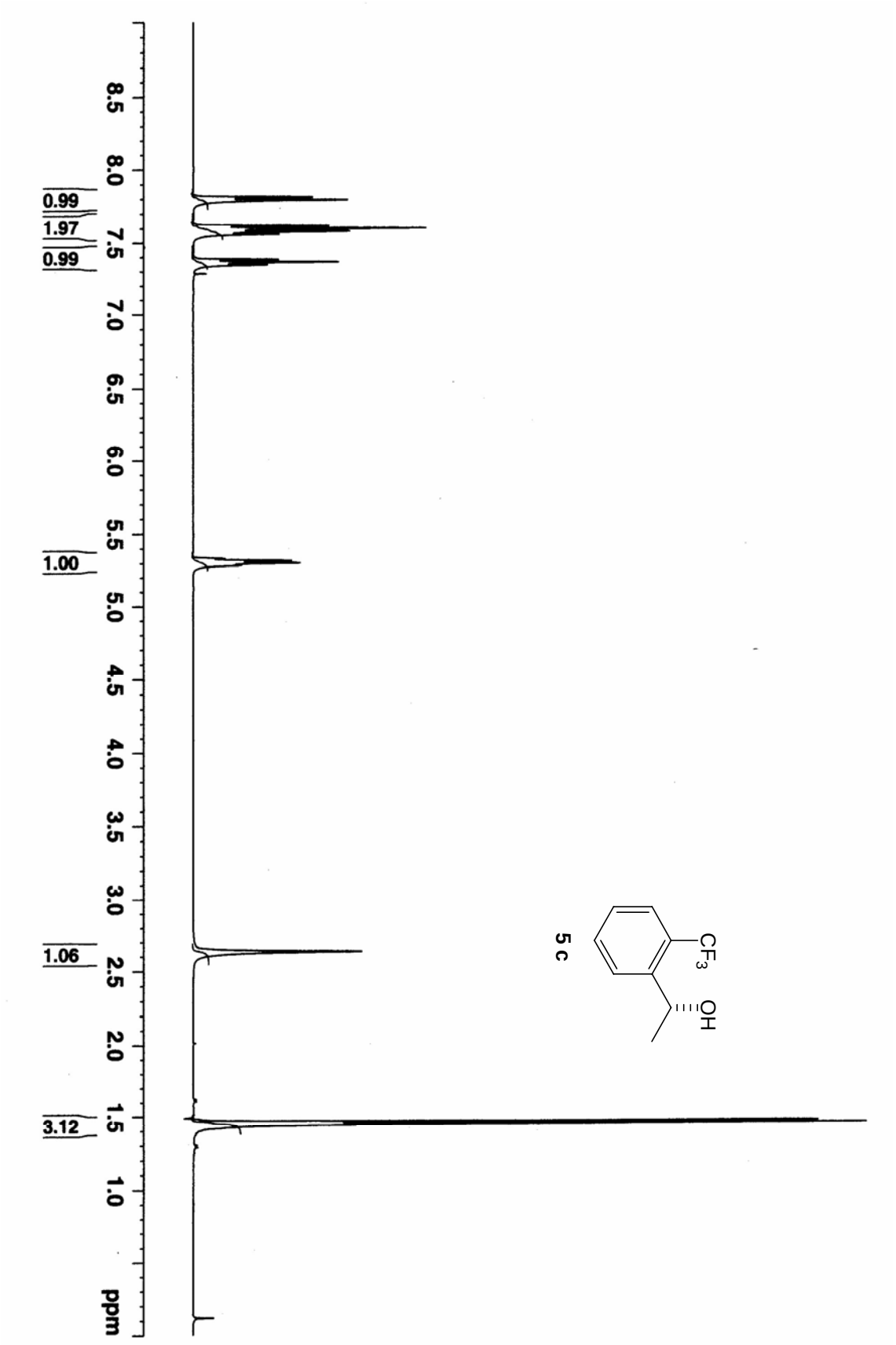

127.02
126.89
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
(SS,RR)-SAL (EE)

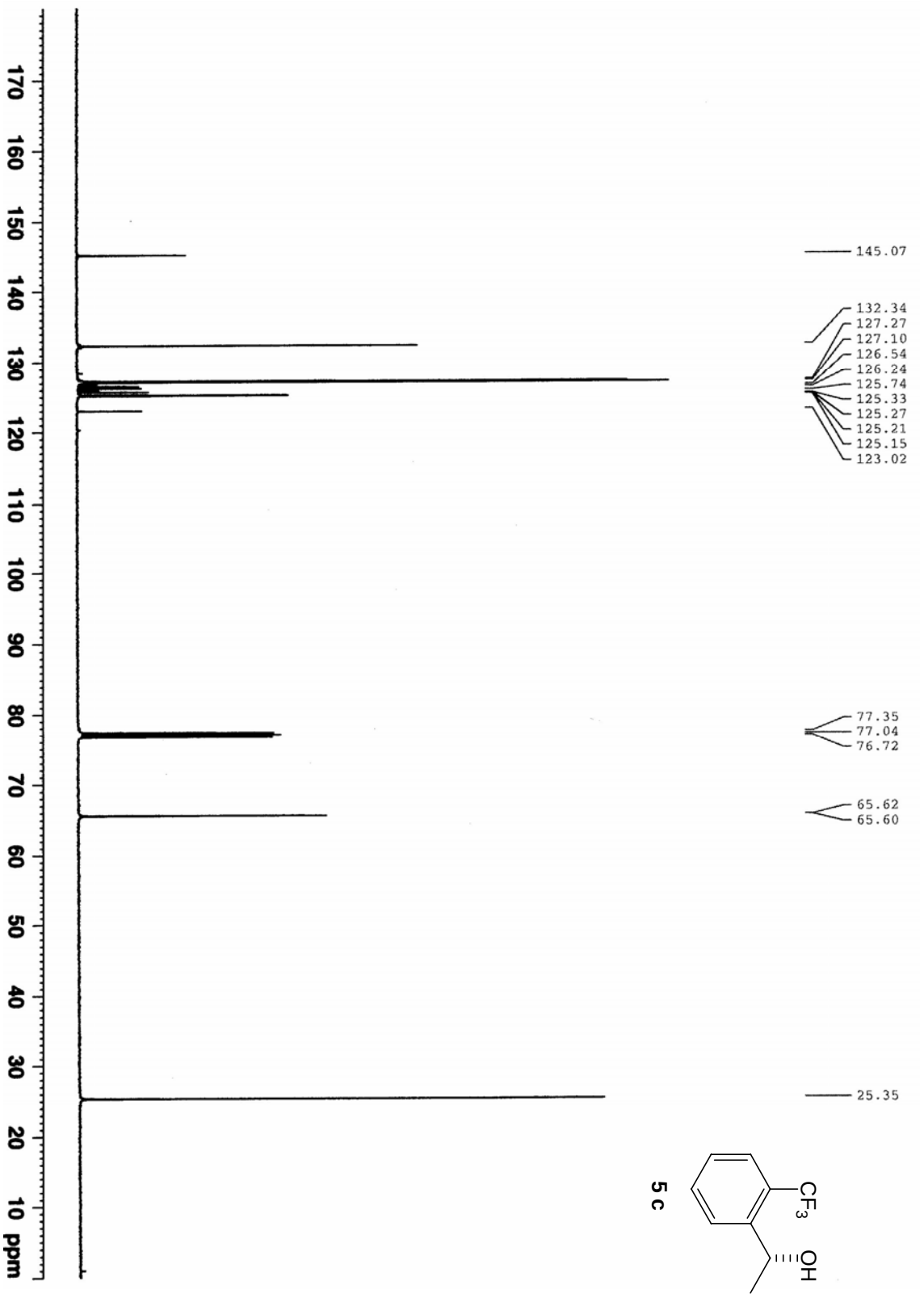

0.95
0.97
0.97
1.07
0.95
3.00
1.01
3.01
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5 a
O
OH

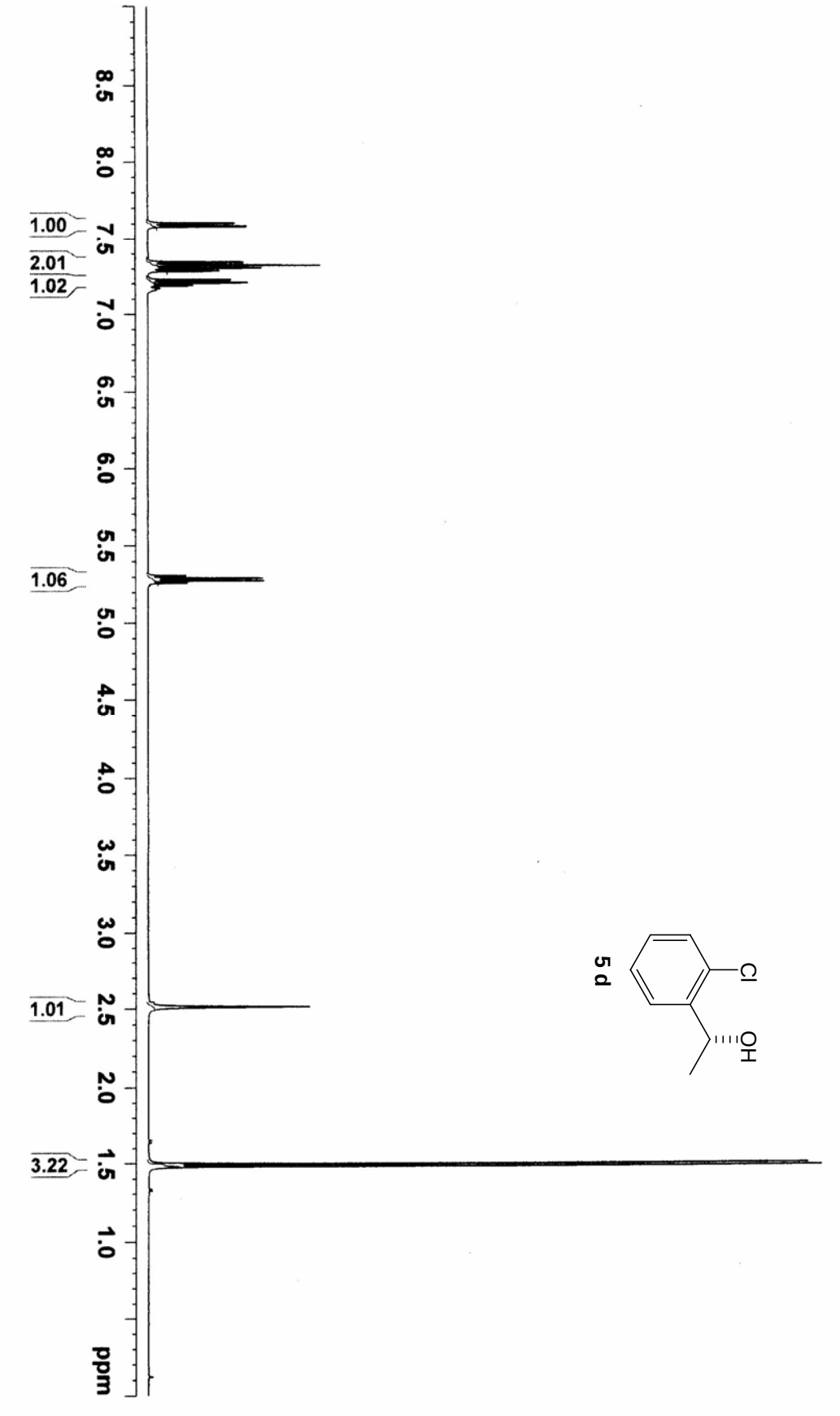

156.52
133.57
128.26
126.09
120.81
110.43
77.46
77.13
76.81
68.37
55.27
22.95
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
5a
O
OH

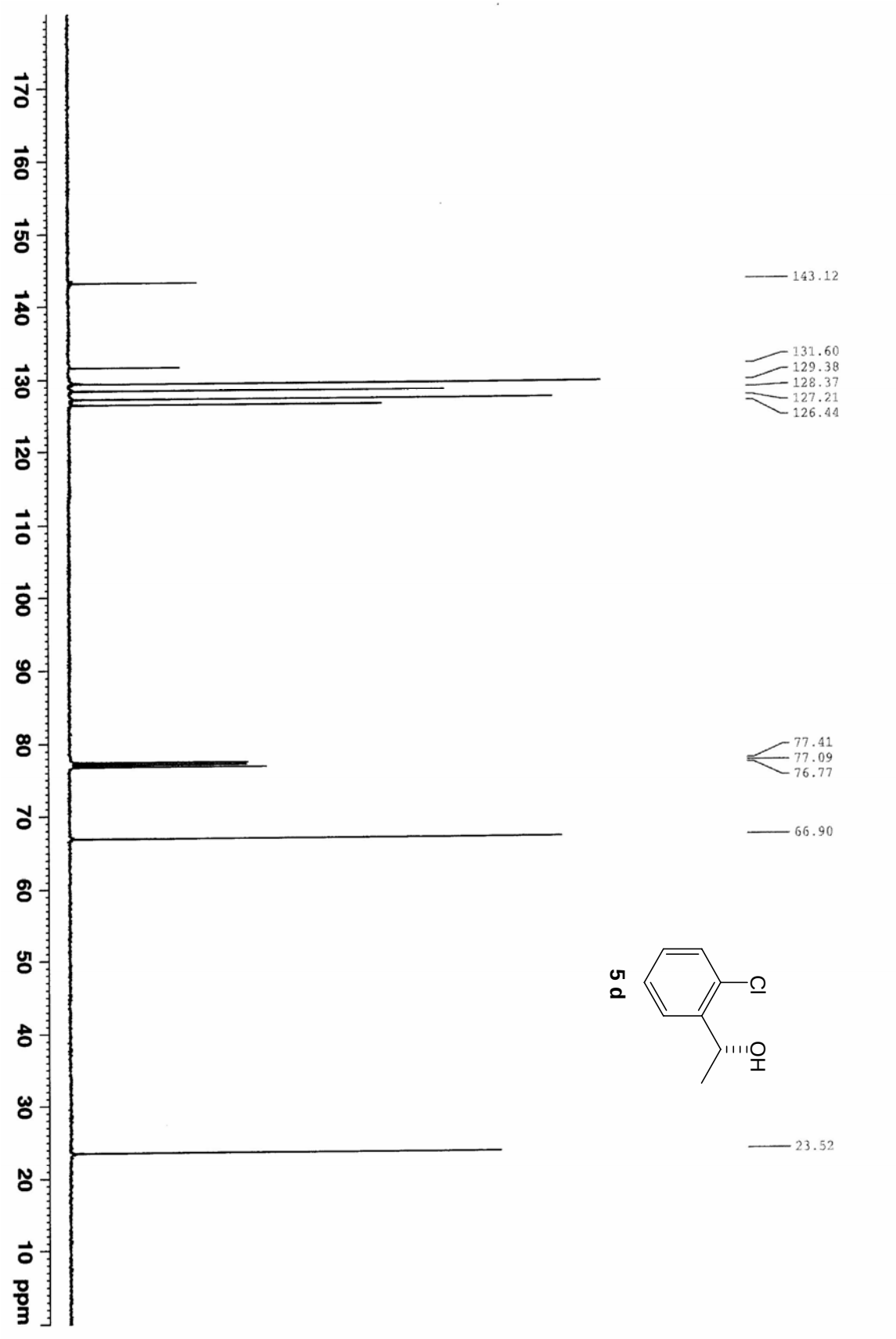

0.93
0.99
2.08
0.95
2.90
0.99
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5 b
Me
OH

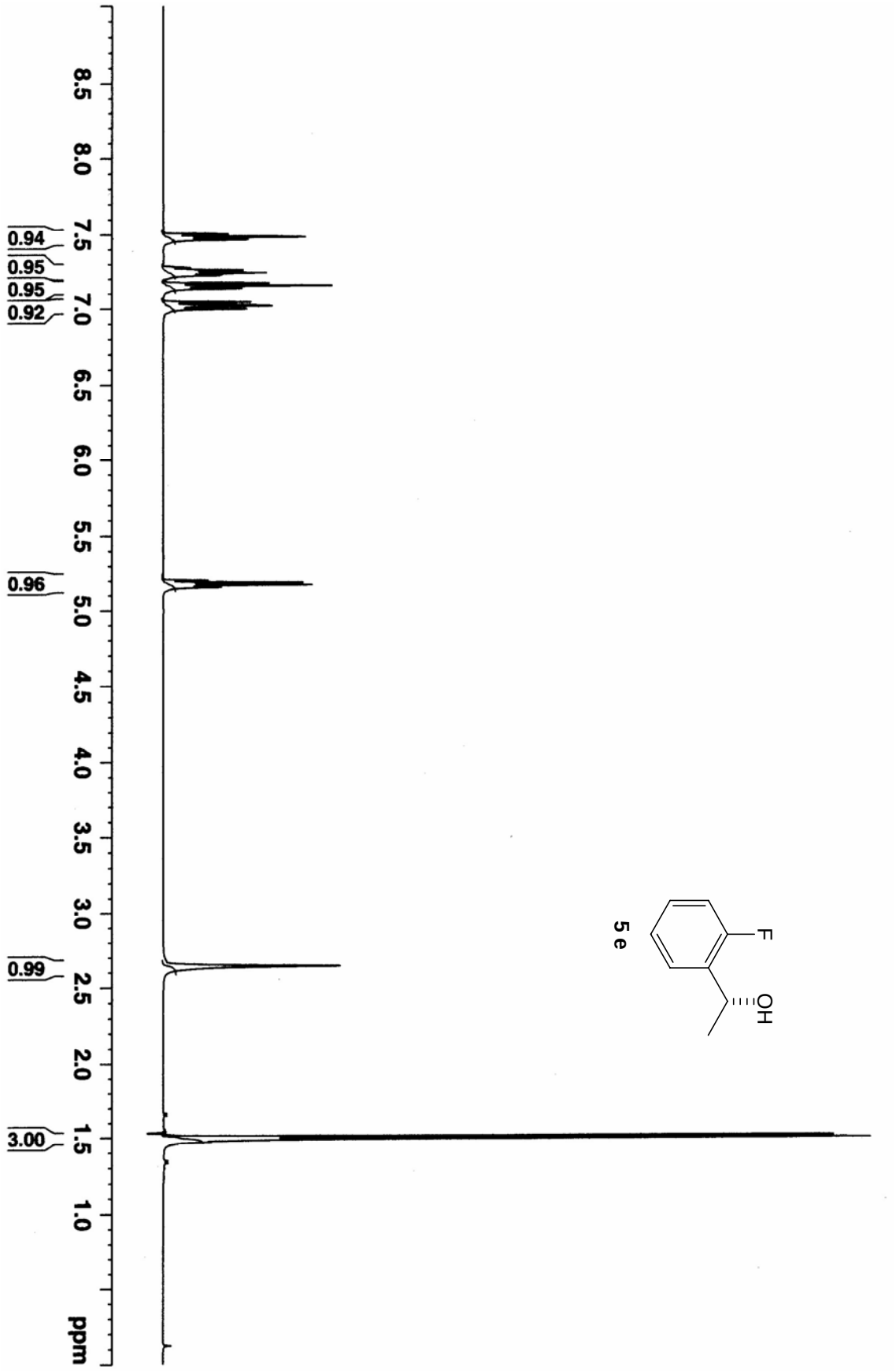

170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
143.87
134.54
130.38
127.16
126.39
124.49
77.38
77.07
76.75
66.82
23.91
18.93
5 b
Me
OH

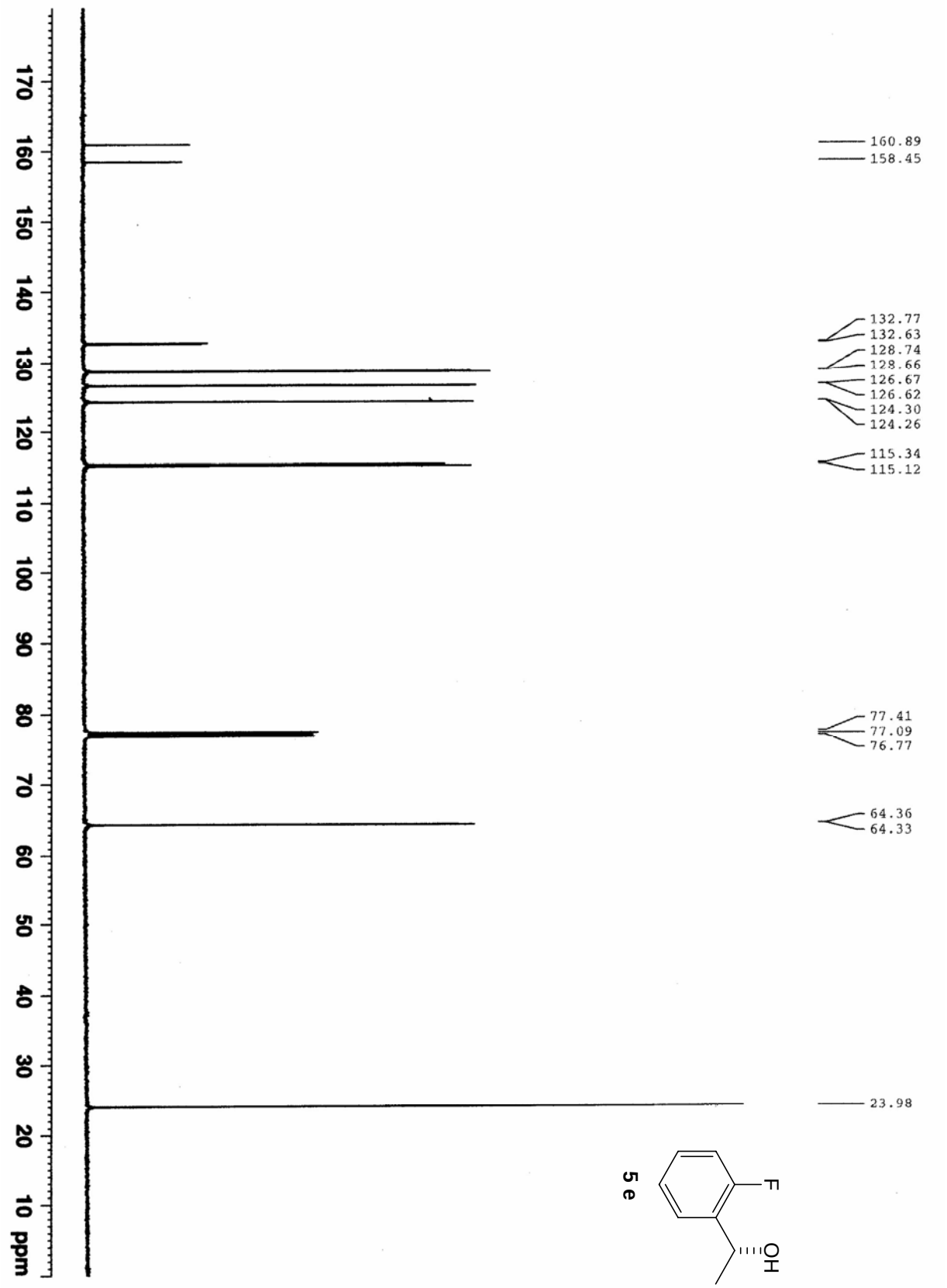

0.99
1.97
0.99
1.00
1.06
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5 c
CF3
OH


170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
145.07
132.34
127.27
127.10
126.54
126.24
125.74
125.33
125.27
125.21
125.15
123.02
77.35
77.04
76.72
65.62
65.60
25.35
5c
CF3
OH


1.00
2.01
1.02
1.06
1.01
3.22
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
5 d
Cl
OH


143.12
131.60
129.38
128.37
127.21
126.44
77.41
77.09
76.77
66.90
23.52
5 d
Cl
OH
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
ppm
0.94
0.95
0.95
0.92
0.96
0.99
3.00
5 e
F
OH


160.89
158.45
132.77
132.63
128.74
128.66
126.67
126.62
124.30
124.26
115.34
115.12
77.41
77.09
76.77
64.36
64.33
23.98
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm
5 e
F
OH