Supporting Information

Construction of P-stereogenic phosphine oxides via Lewis base-catalyzed enantioselective O-Boc protection

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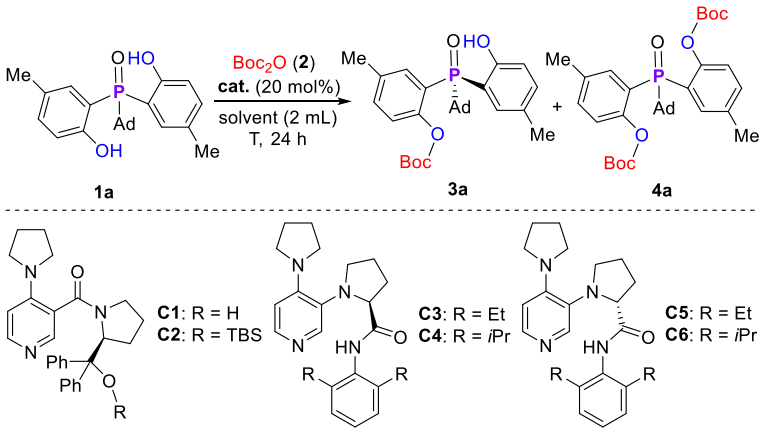
General Information

Commercially available materials were used as received. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker AV 400 (400 MHz) spectrometer. Chemical shifts were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ 0.00) or chloroform (δ = 7.26, singlet). ^{1}H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), dd (doublet of doublets); m (multiplets), and etc. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m) or broad (br). Carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker AV 400 (101 MHz) spectrometer. High resolution mass spectral analysis (HRMS) was performed on Waters Xevo G2-S QTof mass spectrometer. The determination of ee was performed via chiral HPLC analysis using Waters Empower 3 HPLC system. X-ray crystallography analysis was performed on Bruker X8 APEX X-ray diffractionmeter. Analytical thin-layer chromatography (TLC) was carried out on with GF 254 silica gel coated plates. Flash column chromatography was carried out using 200−300 mesh silica gel. Melting points are uncorrected. Bisphenols **1**[1] and DMAP analogue **C6**[2] were synthesized according to reported methods.

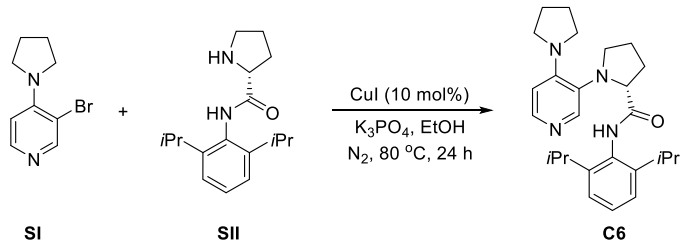
Optimization of reaction conditions:[a]



Entry	**Cat.**	Solvent	T (°C)	Yield of **3a** (%)[b]	Yield of **4a** (%)[b]	er of **3a**[c]
1	**C1**	CH_2Cl_2	-20	68	30	37:63
2	**C2**	CH_2Cl_2	-20	64	20	55.5:44.5
3	**C3**	CH_2Cl_2	-20	63	34	10:90
4	**C4**	CH_2Cl_2	-20	60	38	5:95
5	**C5**	CH_2Cl_2	-20	59	38	92:8
6	**C6**	**CH_2Cl_2**	**-20**	**60**	**39**	**97.5:2.5**
7	**C6**	$CHCl_3$	-20	58	40	97:3
8	**C6**	toluene	-20	22	33	85:15
9	**C6**	THF	-20	54	7	85.5:14.5
10	**C6**	EtOAc	-20	11	69	80:20
11	**C6**	CH_2Cl_2	0	51	49	93:7
12	**C6**	CH_2Cl_2	-40	70	14	93.5:6.5
13[d]	**C6**	CH_2Cl_2	-20	82	4	85:15
14[e]	**C6**	CH_2Cl_2	-20	90	7	88.5:11.5
15[f]	**C6**	CH_2Cl_2	-20	87	10	90:10
16[g]	**C6**	CH_2Cl_2	-20	80	16	92:8
17[h]	**C6**	CH_2Cl_2	-20	74	22	94:6
18[i]	**C6**	CH_2Cl_2	-20	70	26	95:5
19[j]	**C6**	CH_2Cl_2	-20	47	47	98.5:1.5
20[k]	**C6**	CH_2Cl_2	-20	33	66	99:1
21[d]	**C6**	CH_2Cl_2	-40	77	2	90:10
22[e]	**C6**	CH_2Cl_2	-40	75	3	91.5:8.5

[a] Reaction conditions unless otherwise specified: **1a** (0.2 mmol), **2** (0.3 mmol), **cat.** (0.04 mmol), solvent (2 mL) at -20 °C for 24 h. [b] Isolated yield based on **1a**. [c] Enantiomeric ratio of **3a**, determined *via* chiral-phase HPLC analysis. [d] 0.18 mmol of **2** was used. [e] 0.20 mmol of **2** was used. [f] 0.22 mmol of **2** was used. [g] 0.24 mmol of **2** was used. [h] 0.26 mmol of **2** was used. [i] 0.28 mmol of **2** was used. [j] 0.32 mmol of **2** was used. [k] 0.34 mmol of **2** was used. THF = Tetrahydrofuran.

Preparation of catalyst C6:

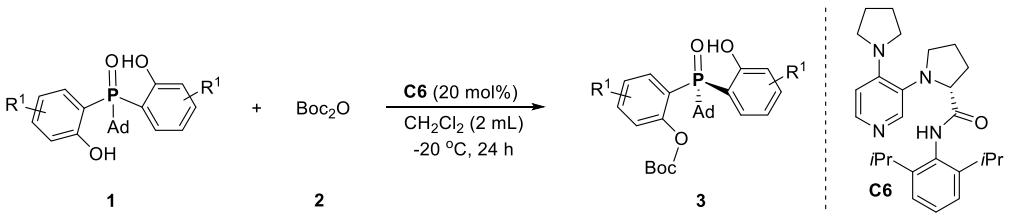


SI **SII** **C6**

Following Xie's procedure[2]: To a dry 120 mL Schlenk tube equipped with a magnetic stir bar, were added CuI (171.4 mg, 0.9 mmol, 0.1 equiv), K_3PO_4 (3.82 g, 18 mmol, 2.0 equiv), and D-prolinamide **SII**[4] (2.47 g, 9 mmol, 1.0 equiv). The tube was sealed with a septum, evacuated and refilled with nitrogen (3 cycles). Subsequently, a solution of 3-bromopridine **SI**[3] (3.07 g, 13.5 mmol, 1.5 equiv) in EtOH (72 mL) was introduced, and the reaction mixture was stirred at 80 °C (oil bath temperature) for 24 hours. Upon completion, the mixture was cooled to room temperature and concentrated under reduced pressure. The residue was dissolved in EtOAc, washed with brine, dried over $NaSO_4$, and concentrated. Purification by flash column chromatography using CH_2Cl_2/MeOH (v/v) = 20/1 as eluent afforded the desired catalyst **C6** (2.14 g, 5.1 mmol, 57% yield).

Note: The racemic catalyst that used for HPLC analysis was synthesized by mixing L-proline-derived catalyst **C4** and D-proline-derived catalyst **C6** in a 1:1 ratio.

General procedure for the catalytic synthesis of products 3:

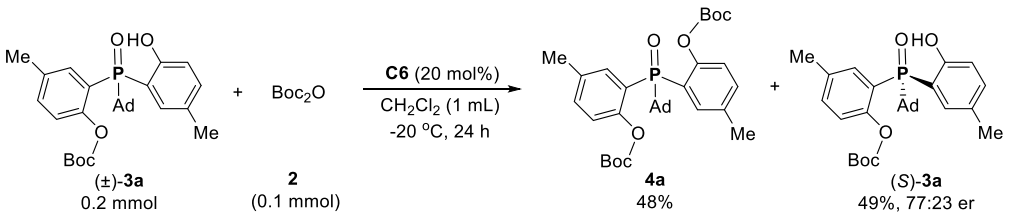


1 **2** **3**

To a dry 10 mL Schlenk tube equipped with a magnetic stir bar, were added **C6** (16.8 mg, 0.04 mmol, 0.2 equiv), bisphenol **1** (0.2 mmol, 1.0 equiv), and CH_2Cl_2 (2.0 mL). The tube was sealed with a septum, and the reaction mixture was cooled to -20 °C and stirred for 30 minutes. Subsequently, Boc_2O **2** (70 μL, 65.4 mg, 0.3 mmol) was introduced, and the reaction was allowed to proceed at -20 °C for another 24 hours. Upon completion, the mixture was directly purified by flash column chromatography using petroleum ether/EtOAc (v/v) = 10/1~5/1 as eluent to afford the desired product **3**.

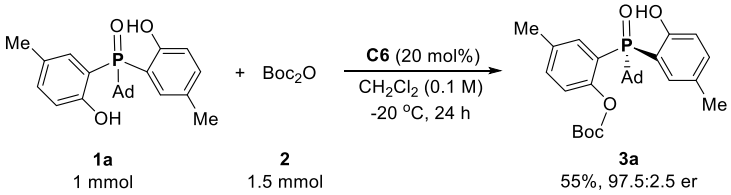
Note: The corresponding racemic product was prepared under identical conditions using DMAP as the catalyst.

Kinetic resolution of racemic 3a:



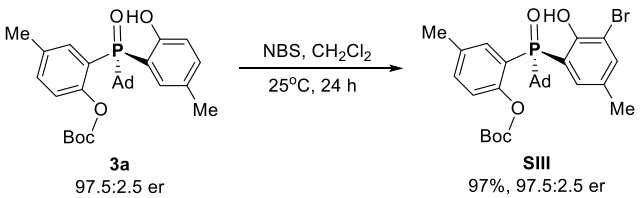
To a dry 10 mL Schlenk tube equipped with a magnetic stir bar, were added **C6** (8.4 mg, 0.02 mmol, 0.2 equiv), racemic **3a** (99.2 mg, 0.2 mmol, 2.0 equiv), and CH_2Cl_2 (1.0 mL). The tube was sealed with a septum, and the reaction mixture was cooled to -20 °C and stirred for 30 minutes. Subsequently, Boc_2O **2** (23.0 μL, 0.1 mmol, 1.0 equiv) was introduced, and the reaction was allowed to proceed at -20 °C for another 24 hours. Upon completion, the mixture was directly purified by flash column chromatography using petroleum ether/EtOAc (v/v) = 10/1 as eluent to afford product **4a** (56.9 mg, 48% yield based on racemic **3a**) and (*S*)-**3a** (48.5 mg, 49% yield based on racemic **3a**, 77:23 er).

1 mmol scale preparation of 3a:



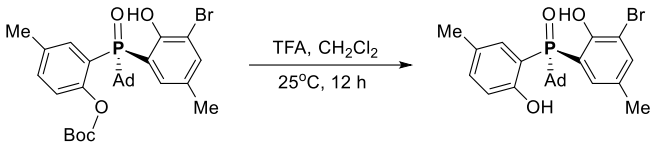
To a dry 50 mL round-bottom flask equipped with a magnetic stir bar, were added **C6** (84.1 mg, 0.2 mmol, 0.2 equiv), **1a** (396.2 mg, 1.0 mmol, 1.0 equiv), and CH_2Cl_2 (10.0 mL). The flask was sealed with a septum, and the reaction mixture was cooled to -20 °C and stirred for 30 minutes. Subsequently, Boc_2O **2** (0.35 mL, 1.5 mmol, 1.5 equiv) was introduced, and the reaction was allowed to proceed at -20 °C for another 24 hours. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography using petroleum ether/EtOAc (v/v) = 10/1 as eluent to afford the desired product **3a** (276.2 mg, 0.55 mmol, 55% yield, 97.5:2.5 er).

Synthetic transformation of 3a:



To a dry 10 mL Schlenk tube equipped with a magnetic stir bar, were added **3a** (49.6 mg, 0.1 mmol, 1.0 equiv), N-bromosuccinimide (21.2 mg, 0.12 mmol, 1.2 equiv), and CH_2Cl_2 (2.0 mL). The tube was sealed with a septum, and the reaction mixture was stirred at 25 °C and for 24 hours. Upon completion, the mixture was directly purified

by flash column chromatography using petroleum ether/EtOAc (v/v) = 10/1 as eluent to afford the desired product **SIII** (56.0 mg, 0.097 mmol, 97% yield, 97.5:2.5 er).

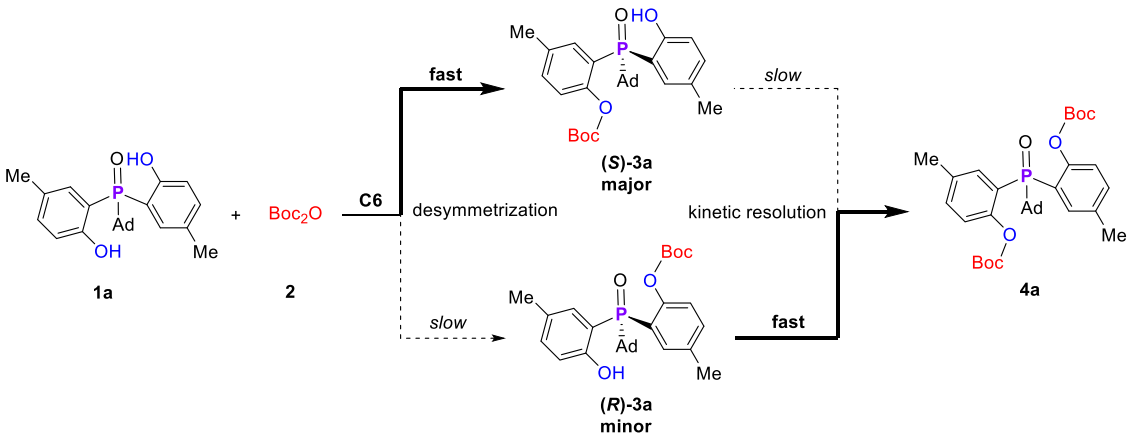


SIII
97.5:2.5 er

5
72%, 97.5:2.5 er

To a dry 10 mL Schlenk tube equipped with a magnetic stir bar, were added **SIII** (56.0 mg, 0.097 mmol, 1.0 equiv), CH_2Cl_2 (1.0 mL), and trifluoroacetic acid (97 μL, 1.26 mmol, 13 equiv). The tube was sealed with a septum, and the reaction mixture was stirred at 25 °C and for 12 hours. Upon completion, the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography using petroleum ether/EtOAc (v/v) = 10/1 as eluent to afford the desired product **5** (33.1 mg, 0.07 mmol, 72% yield, 97.5:2.5 er).

Proposed reaction phthway:



We propose that the overall process involves an initial desymmetrization of prochiral **1a**, followed by a subsequent kinetic resolution of the mono-O-Boc product **3a** (Scheme C2). In this context, excess Boc_2O can further react with the minor enantiomer (*R*)-**3a**, converting it into the di-O-Boc-protected byproduct **4a**. This secondary transformation enhances the enantiomeric ratio of **3a** but concurrently diminishes its isolated yield.

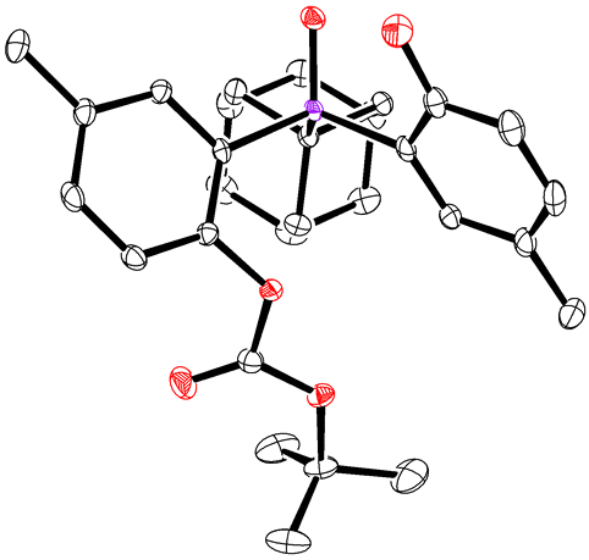
References cited in the SI:

1. (a) G.-H. Yang, Y. Li, X. Li and J.-P. Cheng, *Chem. Sci.*, 2019, **10**, 4322–4327; (b) Q.-H. Huang, Q.-Y. Zhou, C. Yang, L. Chen, J.-P. Cheng and X. Li, *Chem. Sci.*, 2021, **12**, 4582–4587; (c) H.-L. Hu, S. Fang, X. Luo, J. He, J.-H. Wu, Z. Su, Z. Xu and T. Wang, *Org. Lett.*, 2025, **27**, 109–114.
2. L. Cao, X.-P. Zhang, M.-S. Xie and H.-M. Guo, *J. Org. Chem.*, 2023, **88**, 341–346.
3. T. Yamamoto , R. Murakami and M. Suginome, *J. Am. Chem. Soc.*, 2017, **139**, 2557–2560.
4. V. K. Vyas and B. M. Bhanage, *Asian J. Org. Chem.*, 2018, **7**, 346–349.

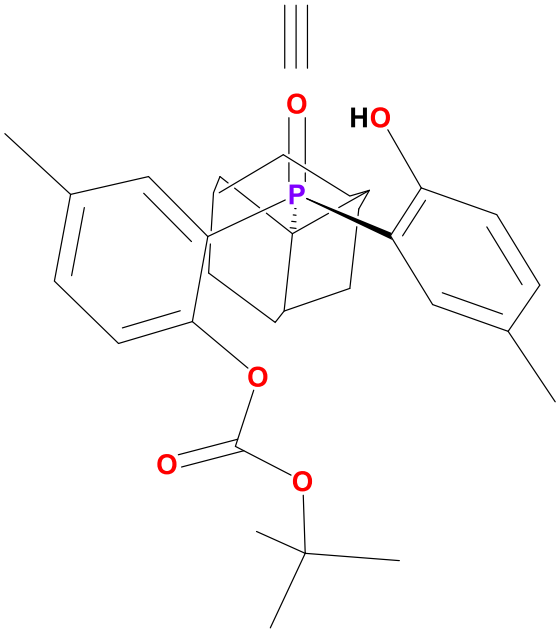
X-ray structure of product 3a (ellipsoid contour at 30% probability)

Absolute configurations of the products **3** were assigned based on the crystal X-ray structures of **3a**. CCDC 2541536 (**3a**, obtained as colorless needles *via* evaporation of a petroleum ether/CH_2Cl_2 solution) contains the supplementary X-ray crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Figure S1. ORTEP diagram of 3a with ellipsoid contour at 30% probability level



CCDC 2541536

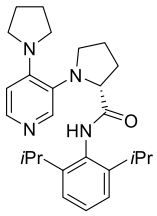


3a

Table S1. Crystal data and structure refinement for 3a.

Identification code	WYK_3A_170K
Empirical formula	$C_{29}H_{37}O_5P$
Formula weight	496.55
Temperature/K	169.99(10)
Crystal system	monoclinic
Space group	$P2_1$
a/Å	8.50930(10)
b/Å	17.3102(3)
c/Å	8.9737(2)
α/°	90
β/°	92.984(2)
γ/°	90
Volume/Å^3	1320.01(4)
Z	2
ρcalcg/cm^3	1.249
μ/mm-1	1.217
F(000)	532.0
Crystal size/mm^3	0.15 × 0.13 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	9.87 to 146.808
Index ranges	$-10 \leq h \leq 6$, $-19 \leq k \leq 21$, $-10 \leq l \leq 11$
Reflections collected	8902
Independent reflections	4815 [R_{int} = 0.0379, R_{sigma} = 0.0495]
Data/restraints/parameters	4815/1/322
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0419, wR_2 = 0.1094
Final R indexes [all data]	R_1 = 0.0435, wR_2 = 0.1117
Largest diff. peak/hole / e Å^{-3}	0.43/-0.31
Flack parameter	0.006(16)

Characterization of products:

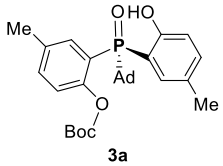


C6

(R)-N-(2,6-Diisopropylphenyl)-1-(4-(pyrrolidin-1-yl)pyridin-3-yl)pyrrolidine-2-carboxamide (C6)[2]

Following the above procedure, **SI** (3.07 g, 13.5 mmol) and **SII** (2.47 g, 9 mmol) was reacted at 80 °C for 24 hours to give **C6** as a white solid, 2.14 g, 57% yield, 99.5:0.5 er, obtained by the purification with flash column chromatography on silica gel using CH_2Cl_2/MeOH (v/v) = 20/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (s, 1H), 8.18 (s, 1H), 8.14 (s, 1H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.09 (d, *J* = 7.7 Hz, 2H), 6.68 (s, 1H), 4.34 (t, *J* = 7.8 Hz, 1H), 3.73 – 3.58 (m, 1H), 3.42 (dd, *J* = 9.6, 6.9 Hz, 2H), 3.37 – 3.31 (m, 2H), 2.86 – 2.79 (m, 1H), 2.57 (dd, *J* = 12.6, 7.1 Hz, 1H), 2.21 (dd, *J* = 12.6, 7.5 Hz, 1H), 2.06 (t, *J* = 7.8 Hz, 2H), 1.91 (t, *J* = 6.6 Hz, 4H), 1.16 (d, *J* = 76.3 Hz, 14H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.4, 151.1, 146.2, 145.4, 143.1, 130.8, 128.1, 123.2, 110.7, 65.7, 54.7, 49.7, 30.8, 28.5, 24.9, 24.1, 23.4. Proton and Carbon NMR was consistent with literature data[2]. HPLC (Daicel CHIRALPAK® AD-H, isopropanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 254 nm) tR = 4.7 min (major), 5.9 min (minor).

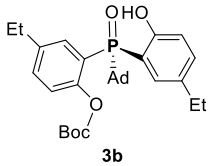


3a

2-((S)-(Adamantan-1-yl)(2-hydroxy-5-methylphenyl)phosphoryl)-4-methylphenyl tert-butyl carbonate (3a)

Following the general procedure, **1a** (79.2 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 °C for 24 hours to give **3a** as a white solid, 59.5 mg, 60% yield, 97.5:2.5 er, mp: 160-162 °C, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.67 (s, 1H), 7.92 (dd, *J* = 11.8, 2.5 Hz, 1H), 7.41 (dd, *J* = 12.4, 2.5 Hz, 1H), 7.34 (dd, *J* = 8.4, 2.4 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.79 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H), 2.03 (d, *J* = 5.4 Hz, 9H), 1.73 (s, 6H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.5, 162.4, 150.7, 149.6, 149.5, 135.2, 135.1, 134.8, 134.7, 134.6, 134.6, 133.8, 133.8, 131.5, 131.4, 126.9, 126.8, 122.7, 122.6, 122.1, 121.3, 118.3, 118.2, 109.7, 108.8, 84.0, 39.3, 38.6, 36.3, 34.9, 27.6, 27.6, 27.5, 20.9, 20.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.6. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{29}H_{38}O_5P^+$ 497.2451, found 497.2448. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 12.8 min (major), 16.9 min (minor).

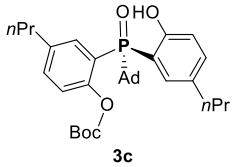


3b

2-((S)-(Adamantan-1-yl)(5-ethyl-2-hydroxyphenyl)phosphoryl)-4-ethylphenyl tert-butyl carbonate (3b)

Following the general procedure, **1b** (84.8 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3b** as a white solid, 58.7 mg, 56% yield, 96.5:3.5 er, mp: 179-180 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.74 (s, 1H), 7.94 (dd, *J* = 12.0, 2.4 Hz, 1H), 7.46 (dd, *J* = 12.6, 2.4 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.81 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.70 (q, *J* = 7.6 Hz, 2H), 2.59 (dq, *J* = 15.0, 7.2 Hz, 2H), 2.02 (d, *J* = 5.2 Hz, 9H), 1.72 (s, 6H), 1.53 (s, 9H), 1.25 (t, *J* = 7.6 Hz, 3H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.6, 162.6, 150.9, 149.7, 149.7, 141.3, 141.2, 133.7, 133.7, 133.5, 133.4, 133.4, 132.6, 132.5, 130.5, 130.4, 122.8, 122.7, 122.1, 121.3, 118.3, 118.2, 109.6, 108.7, 84.0, 39.3, 38.6, 36.3, 35.0, 28.2, 28.0, 27.6, 27.6, 27.5, 16.0, 15.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{31}H_{42}O_5P^+$ 525.2764, found 525.2778. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 9.3 min (major), 10.5 min (minor).



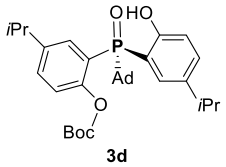
3c

2-((S)-(Adamantan-1-yl)(2-hydroxy-5-propylphenyl)phosphoryl)-4-propylphenyl tert-butyl carbonate (3c)

Following the general procedure, **1c** (90.4 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3c** as a yellow oil, 70.7 mg, 64% yield, 96.5:3.5 er, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 7.91 (d, *J* = 9.5 Hz, 1H), 7.44 (d, *J* = 12.4 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.81 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.63 (t, *J* = 7.7 Hz, 2H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.02 (d, *J* = 5.3 Hz, 9H), 1.71 (s, 6H), 1.68 – 1.59 (m, 4H), 1.54 (s, 9H), 0.93 (dt, *J* = 11.1, 7.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 162.7, 150.9, 149.8, 149.7, 139.9, 139.8, 134.3, 134.2, 134.0, 134.0, 133.1, 133.1, 131.8, 131.7, 131.1, 131.0, 122.7, 122.7, 122.0, 121.2, 118.2, 118.2, 109.4, 108.5, 84.0, 77.2, 39.3, 38.6, 37.3, 37.1, 36.3, 35.0, 27.6, 27.5, 24.6, 24.4, 13.7, 13.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{33}H_{46}O_5P^+$ 553.3077, found 553.3081. HPLC (Daicel CHIRALPAK® IC,

isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 28.1 min (minor), 33.6 min (major).

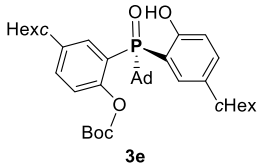


3d

2-((S)-(Adamantan-1-yl)(2-hydroxy-5-isopropylphenyl)phosphoryl)-4-isopropylphenyl tert-butyl carbonate (3d)

Following the general procedure, **1d** (90.4 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3d** as a white solid, 67.3 mg, 61% yield, 96:4 er, mp: 166-168 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.78 (s, 1H), 7.96 (dd, *J* = 12.2, 2.4 Hz, 1H), 7.50 (dd, *J* = 12.7, 2.4 Hz, 1H), 7.40 (dd, *J* = 8.4, 2.5 Hz, 1H), 7.24 (dd, *J* = 8.5, 4.8 Hz, 2H), 6.83 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.97 (h, *J* = 6.9 Hz, 1H), 2.85 (p, *J* = 6.9 Hz, 1H), 2.02 (d, *J* = 5.4 Hz, 9H), 1.72 (s, 6H), 1.55 (s, 10H), 1.27 – 1.21 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 162.7, 151.1, 149.8, 149.8, 145.9, 145.8, 138.1, 138.0, 132.5, 132.4, 131.8, 131.8, 131.1, 131.1, 129.2, 129.1, 122.9, 122.8, 122.2, 121.4, 118.2, 118.1, 109.5, 108.6, 84.1, 39.3, 38.6, 36.4, 35.1, 33.6, 33.2, 27.7, 27.6, 24.4, 23.9, 23.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.8. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{33}H_{46}O_5P^+$ 553.3077, found 553.3074. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 5/95, flow rate = 1.0 mL/min, λ = 220 nm) tR = 11.1 min (major), 12.3 min (minor).



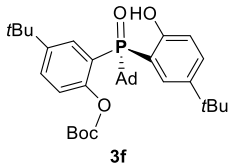
3e

2-((S)-(Adamantan-1-yl)(5-cyclohexyl-2-hydroxyphenyl)phosphoryl)-4-cyclohexylphenyl tert-butyl carbonate (3e)

Following the general procedure, **1e** (106.4 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3e** as a white solid, 76.8 mg, 60% yield, 95.5:4.5 er, mp: 115-117 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 7.90 (dd, *J* = 12.2, 2.4 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.23 (dd, *J* = 8.4, 4.7 Hz, 2H), 6.82 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.59 – 2.50 (m, 1H), 2.48 – 2.38 (m, 1H), 2.01 (d, *J* = 5.4 Hz, 10H), 1.90 – 1.81 (m, 8H), 1.72 (s, 7H), 1.54 (s, 10H), 1.41 – 1.21 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 162.7, 151.1, 150.0, 150.0, 145.1, 145.0, 137.4, 137.3, 132.7, 132.6, 132.2, 132.2, 131.5, 131.5, 129.3, 129.2, 122.9, 122.9, 122.3, 121.4, 118.2, 118.2, 109.5, 108.5, 83.9, 43.8, 43.4, 39.3, 38.6, 36.4, 35.1, 34.9, 34.3, 34.1, 27.7, 27.6, 26.8, 26.8, 26.7, 26.0, 25.9. ^{31}P NMR

(162 MHz, $CDCl_3$) δ 49.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{39}H_{54}O_5P^+$ 633.3703, found 633.3708. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 5/95, flow rate = 1.0 mL/min, λ = 220 nm) tR = 13.2 min (minor), 14.3 min (major).

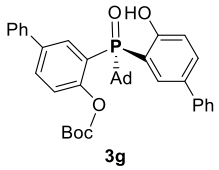


3f

2-((S)-(Adamantan-1-yl)(5-(tert-butyl)-2-hydroxyphenyl)phosphoryl)-4-(tert-butyl)phenyl tert-butyl carbonate (3f)

Following the general procedure, **1f** (96.0 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3f** as a yellow oil, 75.4 mg, 65% yield, 92.5:7.5 er, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.77 (s, 1H), 8.06 (dd, *J* = 12.7, 2.5 Hz, 1H), 7.61 (dd, *J* = 12.9, 2.5 Hz, 1H), 7.55 (dd, *J* = 8.6, 2.7 Hz, 1H), 7.40 (d, *J* = 8.8 Hz, 1H), 7.22 (dd, *J* = 8.6, 4.8 Hz, 1H), 6.84 (dd, *J* = 8.8, 4.7 Hz, 1H), 2.03 (d, *J* = 5.3 Hz, 9H), 1.71 (s, 6H), 1.55 (s, 9H), 1.32 (s, 9H), 1.29 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.3, 162.3, 151.3, 150.0, 149.9, 148.2, 140.5, 140.4, 131.2, 131.2, 130.9, 130.8, 130.2, 130.2, 127.9, 127.8, 122.9, 122.8, 122.1, 121.3, 117.9, 117.9, 109.3, 108.3, 84.1, 39.2, 38.5, 36.4, 35.2, 34.7, 34.1, 31.5, 31.3, 27.7, 27.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 49.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{35}H_{50}O_5P^+$ 581.3390, found 581.3381. HPLC (Daicel CHIRALPAK® AD-H, isopropanol/n-hexane = 5/95, flow rate = 1.0 mL/min, λ = 220 nm) tR = 4.8 min (major), 5.4 min (minor).



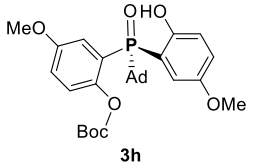
3g

3-((S)-(Adamantan-1-yl)(4-hydroxy-[1,1'-biphenyl]-3-yl)phosphoryl)-[1,1'-biphenyl]-4-yl tert-butyl carbonate (3g)

Following the general procedure, **1g** (104.0 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3g** as a white solid, 52.1 mg, 42% yield, 80.5:19.5 er, mp: 177-179 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.90 (s, 1H), 8.40 (dd, *J* = 11.9, 2.3 Hz, 1H), 7.85 (dd, *J* = 12.7, 2.2 Hz, 1H), 7.77 (dd, *J* = 8.5, 2.4 Hz, 1H), 7.66 – 7.55 (m, 3H), 7.52 (d, *J* = 7.0 Hz, 2H), 7.48 – 7.34 (m, 6H), 7.29 (t, *J* = 7.4 Hz, 1H), 6.99 (dd, *J* = 8.6, 4.6 Hz, 1H), 2.10 (d, *J* = 25.0 Hz, 9H), 1.75 (s, 6H), 1.41 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 164.2, 151.3, 151.3, 150.8, 140.4, 139.3, 138.5, 138.5, 133.0, 133.0, 132.8, 132.7, 131.8, 131.8, 131.4, 131.3, 129.6, 129.5, 128.9, 128.8, 127.8, 127.1, 126.7, 126.6, 123.6, 123.5, 122.9, 122.1, 119.0, 118.9, 110.6, 109.6, 84.4, 39.4, 38.7, 36.3, 35.1, 27.6,

27.5, 27.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{39}H_{42}O_5P^+$ 621.2764, found 621.2759. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 11.9 min (major), 17.8 min (minor).

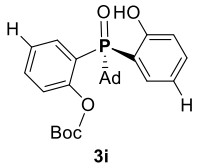


3h

2-((S)-(Adamantan-1-yl)(2-hydroxy-5-methoxyphenyl)phosphoryl)-4-methoxyphenyl tert-butyl carbonate (3h)

Following the general procedure, **1h** (85.6 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3h** as a white solid, 41.2 mg, 39% yield, 93:7 er, mp: 174-176 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 5/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (dd, *J* = 12.5, 3.1 Hz, 1H), 7.22 – 7.16 (m, 2H), 7.05 (dd, *J* = 9.0, 3.1 Hz, 1H), 6.97 (dd, *J* = 9.1, 3.0 Hz, 1H), 6.83 (dd, *J* = 9.0, 5.2 Hz, 1H), 3.84 (s, 3H), 3.76 (s, 3H), 2.03 (d, *J* = 5.2 Hz, 9H), 1.72 (s, 6H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 156.6, 156.5, 151.2, 151.1, 151.0, 145.1, 145.1, 124.2, 124.1, 123.2, 122.4, 120.3, 120.3, 119.1, 119.1, 119.0, 118.9, 118.6, 118.6, 115.8, 115.7, 109.8, 108.9, 84.1, 55.8, 39.4, 38.7, 36.3, 34.9, 27.6, 27.5, 27.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.2. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{29}H_{38}O_7P^+$ 529.2350, found 529.2347. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm) tR = 11.2 min (major), 15.1 min (minor).



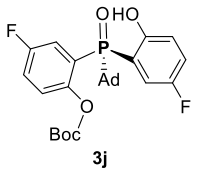
3i

2-((S)-(Adamantan-1-yl)(2-hydroxyphenyl)phosphoryl)phenyl tert-butyl carbonate (3i)

Following the general procedure, **1i** (73.6 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3i** as a white solid, 34.4 mg, 37% yield, 94.5:5.5 er, mp: 129-131 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.85 (s, 1H), 8.13 – 8.04 (m, 1H), 7.59 – 7.52 (m, 2H), 7.38 – 7.29 (m, 3H), 6.88 (dd, *J* = 8.4, 4.4 Hz, 1H), 6.83 (td, *J* = 7.5, 3.1 Hz, 1H), 2.04 (d, *J* = 5.3 Hz, 9H), 1.72 (s, 6H), 1.52 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 164.8, 152.1, 152.1, 150.5, 134.3, 134.2, 133.7, 133.7, 133.3, 133.3, 131.6, 131.5, 125.3, 125.2, 123.1, 123.1, 122.6, 121.7, 118.6, 118.5, 118.0, 117.9, 110.1, 109.2, 84.1, 39.3, 38.6, 36.3, 34.9, 27.6, 27.6, 27.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.4. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{27}H_{34}O_5P^+$ 469.2138, found 469.2132. HPLC (Daicel

CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 16.0 min (major), 18.3 min (minor).

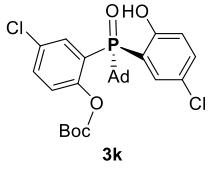


3j

2-((S)-(Adamantan-1-yl)(5-fluoro-2-hydroxyphenyl)phosphoryl)-4-fluorophenyl tert-butyl carbonate (3j)

Following the general procedure, **1j** (80.8 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3j** as a yellow solid, 42.2 mg, 42% yield, 82.5:17.5 er, mp: 174-175 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.58 (s, 1H), 7.83 (ddd, *J* = 11.8, 8.5, 3.1 Hz, 1H), 7.47 – 7.33 (m, 2H), 7.26 (d, *J* = 3.9 Hz, 1H), 7.14 – 7.07 (m, 1H), 6.85 (dt, *J* = 9.3, 4.9 Hz, 1H), 2.07 – 1.98 (m, 9H), 1.72 (d, *J* = 14.5 Hz, 6H), 1.55 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.1, 150.3, 147.4, 147.4, 124.4, 124.3, 124.2, 123.1, 121.5, 121.5, 121.3, 121.3, 121.2, 121.0, 121.0, 120.5, 120.4, 120.2, 120.2, 119.9, 119.9, 119.9, 119.8, 117.4, 117.3, 117.2, 117.1, 108.5, 84.9, 39.6, 38.9, 36.2, 34.8, 27.5, 27.4. ^{19}F NMR (377 MHz, $CDCl_3$) δ -115.3 (d, *J* = 2.8 Hz), -124.3 (d, *J* = 5.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.6 (dd, *J* = 5.3, 2.8 Hz). HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{27}H_{32}F_2O_5P^+$ 505.1950, found 505.1951. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 7.7 min (major), 10.0 min (minor).



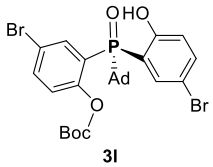
3k

2-((S)-(Adamantan-1-yl)(5-chloro-2-hydroxyphenyl)phosphoryl)-4-chlorophenyl tert-butyl carbonate (3k)

Following the general procedure, **1k** (87.0 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3k** as a yellow solid, 41.8 mg, 39% yield, 77.5:22.5 er, mp: 165-166 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/CH_2Cl_2 (v/v) = 1/2 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.83 (s, 1H), 8.10 (dd, *J* = 11.6, 2.7 Hz, 1H), 7.67 (dd, *J* = 12.2, 2.6 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.7 Hz, 1H), 7.37 – 7.29 (m, 2H), 6.84 (dd, *J* = 8.9, 4.8 Hz, 1H), 2.07 – 1.98 (m, 9H), 1.74 (s, 6H), 1.57 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 163.5, 150.1, 149.9, 149.9, 134.4, 134.3, 134.1, 134.1, 133.5, 133.5, 131.4, 131.3, 130.8, 130.7, 124.0, 124.0, 123.8, 123.1, 123.0, 122.9, 120.3, 120.3, 110.8, 109.9, 85.2, 39.7, 39.0, 36.2, 34.8, 27.7, 27.5, 27.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 46.0. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{27}H_{32}Cl_2O_5P^+$ 537.1359, found 537.1368. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0

mL/min, λ = 220 nm) tR = 6.8 min (major), 8.4 min (minor).

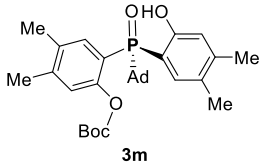


3l

2-((S)-(Adamantan-1-yl)(5-bromo-2-hydroxyphenyl)phosphoryl)-4-bromophenyl tert-butyl carbonate (3l)

Following the general procedure, **1l** (104.8 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 °C for 24 hours to give **3l** as a yellow solid, 47.8 mg, 38% yield, 81.5:18.5 er, mp: 171-173 °C, obtained by the purification with flash column chromatography on silica gel using petroleum ether/CH_2Cl_2 (v/v) = 1/2 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.87 (s, 1H), 8.24 (dd, *J* = 11.5, 2.5 Hz, 1H), 7.78 (dd, *J* = 12.0, 2.5 Hz, 1H), 7.67 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.44 (dd, *J* = 9.3, 2.8 Hz, 1H), 7.31 – 7.26 (m, 1H), 6.79 (dd, *J* = 8.9, 4.8 Hz, 1H), 2.08 – 1.97 (m, 9H), 1.74 (s, 6H), 1.58 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.0, 163.9, 150.5, 150.5, 150.0, 137.2, 137.2, 136.9, 136.9, 136.5, 136.5, 133.6, 133.5, 124.4, 124.3, 124.2, 123.4, 120.8, 120.7, 119.0, 118.9, 111.5, 110.6, 110.2, 110.0, 85.3, 39.8, 39.1, 36.2, 34.9, 27.7, 27.5, 27.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 45.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{27}H_{32}Br_2O_5P^+$ 625.0349, found 625.0357. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 6.8 min (major), 9.2 min (minor).



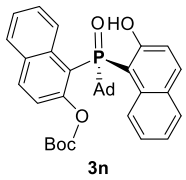
3m

2-((S)-(Adamantan-1-yl)(2-hydroxy-4,5-dimethylphenyl)phosphoryl)-4,5-dimethylphenyl tert-butyl carbonate (3m)

Following the general procedure, **1m** (84.8 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 °C for 24 hours to give **3m** as a yellow oil, 71.2 mg, 68% yield, 96:4 er, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.62 (s, 1H), 7.83 (d, *J* = 11.6 Hz, 1H), 7.33 (d, *J* = 12.1 Hz, 1H), 7.05 (d, *J* = 4.6 Hz, 1H), 6.68 (d, *J* = 4.5 Hz, 1H), 2.28 (s, 6H), 2.18 (d, *J* = 4.4 Hz, 6H), 2.01 (d, *J* = 5.2 Hz, 9H), 1.72 (s, 6H), 1.53 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 162.7, 151.0, 149.6, 149.6, 143.0, 143.0, 142.6, 142.6, 135.0, 134.9, 134.0, 133.9, 131.8, 131.7, 126.1, 126.0, 123.9, 123.8, 119.5, 119.2, 119.1, 118.6, 107.2, 106.2, 83.8, 39.2, 38.5, 36.4, 34.9, 27.7, 27.6, 27.5, 20.0, 20.0, 19.3, 19.0. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.5. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{31}H_{42}O_5P^+$ 525.2764, found 525.2771. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 13.4 min

(major), 15.3 min (minor).

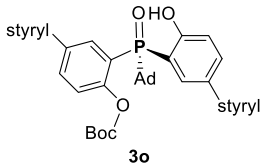


3n

1-((S)-(Adamantan-1-yl)(2-hydroxynaphthalen-1-yl)phosphoryl)naphthalen-2-yl tert-butyl carbonate (3n)

Following the general procedure, **1n** (93.6 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 °C for 24 hours to give **3n** as a white solid, 18.2 mg, 16% yield, 99:1 er, mp: 107-108 °C, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.61 (s, 1H), 8.78 (d, *J* = 12.9 Hz, 1H), 8.21 (d, *J* = 14.2 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76 (dd, *J* = 11.8, 6.4 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.44 (t, *J* = 7.5 Hz, 1H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.12 (d, *J* = 47.6 Hz, 9H), 1.75 (s, 6H), 1.51 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 159.9, 150.7, 147.8, 147.7, 137.1, 137.0, 136.8, 136.8, 135.4, 135.4, 133.8, 133.7, 130.1, 130.0, 129.0, 128.9, 128.8, 128.1, 127.3, 126.7, 126.6, 126.2, 123.3, 121.7, 120.8, 120.3, 120.3, 114.0, 113.1, 112.0, 112.0, 84.3, 39.7, 39.0, 36.3, 35.2, 27.6, 27.6, 27.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.0. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. for $C_{35}H_{38}O_5P^+$ 569.2451, found 569.2460. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 30/70, flow rate = 1.0 mL/min, λ = 220 nm) tR = 39.6 min (minor), 72.1 min (major).



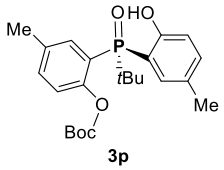
3o

2-((S)-(Adamantan-1-yl)(2-hydroxy-5-((E)-styryl)phenyl)phosphoryl)-4-((E)-styryl)phenyl tert-butyl carbonate (3o)

Following the general procedure, **1o** (114.4 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 °C for 24 hours to give **3o** as a white solid, 57.8 mg, 43% yield, 88:12 er, mp: 142-144 °C, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 12.11 (s, 1H), 8.42 (dd, *J* = 12.2, 2.3 Hz, 1H), 7.87 – 7.76 (m, 3H), 7.62 (dd, *J* = 14.4, 7.2 Hz, 4H), 7.47 (q, *J* = 7.2 Hz, 5H), 7.43 – 7.34 (m, 4H), 7.19 – 7.06 (m, 2H), 7.06 – 7.03 (m, 1H), 2.21 (d, *J* = 5.6 Hz, 9H), 1.88 (s, 6H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.6, 164.5, 150.8, 150.6, 137.4, 136.7, 134.9, 134.8, 132.6, 132.6, 130.9, 130.7, 130.6, 130.2, 128.7, 128.6, 128.2, 128.0, 127.9, 127.8, 127.3, 126.8, 126.6, 126.3, 123.4, 123.3, 122.6, 119.2, 119.1, 84.6, 39.5, 38.8, 36.3, 35.0, 27.6, 27.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 48.0. HRMS (ESI-TOF) *m/z*: [M + H]$^+$ calcd. for $C_{43}H_{46}O_5P^+$ 673.3077, found 673.3095. HPLC (Daicel CHIRALPAK®

ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 27.0 min (major), 32.8 min (minor).

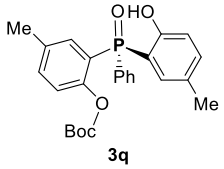


3p

(S)-tert-Butyl (2-(tert-butyl(2-hydroxy-5-methylphenyl)phosphoryl)-4-methylphenyl) carbonate (3p)

Following the general procedure, **1p** (63.6 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3p** as a white solid, 36.1 mg, 43% yield, 91:9 er, mp: 150-151 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.52 (s, 1H), 7.87 (dd, *J* = 11.8, 2.9 Hz, 1H), 7.35 (d, *J* = 9.1 Hz, 1H), 7.25 (d, *J* = 12.4 Hz, 1H), 7.17 (dd, *J* = 8.4, 4.8 Hz, 2H), 6.80 (dd, *J* = 8.5, 4.6 Hz, 1H), 2.40 (s, 3H), 2.25 (s, 3H), 1.50 (s, 9H), 1.34 (d, *J* = 15.9 Hz, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.2, 162.2, 150.8, 149.9, 149.9, 135.2, 135.1, 134.7, 134.7, 134.2, 134.1, 134.0, 134.0, 131.2, 131.1, 127.1, 127.0, 123.2, 123.1, 122.8, 122.0, 118.2, 118.1, 110.6, 109.7, 84.0, 36.1, 35.4, 27.6, 25.1, 20.9, 20.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 52.1. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{23}H_{32}O_5P^+$ 419.1982, found 419.1978. HPLC (Daicel CHIRALPAK® IA, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 5.1 min (minor), 5.8 min (major).



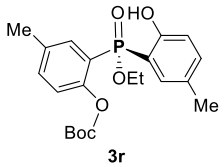
3q

(S)-tert-Butyl (2-((2-hydroxy-5-methylphenyl)(phenyl)phosphoryl)-4-methylphenyl) carbonate (3q)

Following the general procedure, **1q** (67.6 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3q** as a yellow oil, 38.4 mg, 44% yield, 90:10 er, obtained by the purification with flash column chromatography on silica gel using petroleum ether/acetone (v/v) = 5/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H), 7.68 (dd, *J* = 13.0, 7.0 Hz, 2H), 7.61 – 7.53 (m, 2H), 7.51 – 7.44 (m, 2H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.24 – 7.16 (m, 2H), 7.07 (d, *J* = 14.3 Hz, 1H), 6.87 (dd, *J* = 8.4, 5.1 Hz, 1H), 2.36 (s, 3H), 2.20 (s, 3H), 1.31 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.9, 161.9, 150.3, 150.0, 150.0, 135.7, 135.6, 135.3, 135.3, 134.7, 134.7, 134.4, 134.3, 132.4, 132.4, 132.3, 132.0, 131.9, 131.4, 131.3, 128.7, 128.6, 127.9, 127.8, 123.8, 123.0, 123.0, 122.8, 118.2, 118.2, 110.7, 109.7, 83.6, 27.4, 20.9, 20.5. ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{25}H_{28}O_5P^+$ 439.1669, found 439.1664. HPLC (Daicel CHIRALPAK® IA, isopropanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm) tR = 6.7 min

(minor), 7.8 min (major).

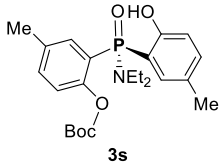


3r

(R)-tert-Butyl (2-(ethoxy(2-hydroxy-5-methylphenyl)phosphoryl)-4-methylphenyl) carbonate (3r)

Following the general procedure, **1r** (61.2 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3r** as a white solid, 36.9 mg, 45% yield, 92:8 er, mp: 112-113 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/acetone (v/v) = 5/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 10.59 (s, 1H), 7.75 (dd, *J* = 13.0, 2.2 Hz, 1H), 7.37 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.19 (dd, *J* = 8.5, 2.2 Hz, 1H), 7.14 – 7.06 (m, 2H), 6.85 (dd, *J* = 8.5, 6.0 Hz, 1H), 4.29 – 4.16 (m, 1H), 4.12 – 3.99 (m, 1H), 2.40 (s, 3H), 2.20 (s, 3H), 1.52 (s, 9H), 1.38 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 160.7, 151.1, 150.3, 150.3, 135.8, 135.8, 135.7, 135.6, 134.7, 134.7, 133.4, 133.3, 131.3, 131.2, 128.3, 128.2, 124.0, 123.3, 123.2, 122.6, 117.6, 117.5, 111.6, 110.3, 83.7, 61.6, 61.6, 27.6, 20.8, 20.3, 16.4, 16.3. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{21}H_{28}O_6P^+$ 407.1618, found 407.1620. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 20/80, flow rate = 1.0 mL/min, λ = 220 nm) tR = 8.0 min (major), 8.7 min (minor).



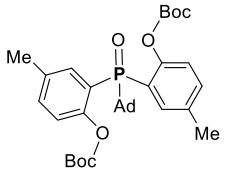
3s

(S)-tert-Butyl (2-((diethylamino)(2-hydroxy-5-methylphenyl)phosphoryl)-4-methylphenyl) carbonate (3s)

Following the general procedure, **1s** (66.6 mg, 0.2 mmol) and **2** (70 μL, 0.3 mmol) was reacted at -20 ºC for 24 hours to give **3s** as a white solid, 61.9 mg, 71% yield, 91.5:8.5 er, mp: 105-107 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.39 (br, 1H), 7.98 – 7.86 (m, 1H), 7.55 (d, *J* = 14.2 Hz, 1H), 7.34 (d, *J* = 8.3 Hz, 1H), 7.15 (dd, *J* = 8.4, 5.3 Hz, 2H), 6.78 (dd, *J* = 8.7, 5.6 Hz, 1H), 3.11 (ddt, *J* = 27.5, 14.1, 7.2 Hz, 4H), 2.38 (s, 3H), 2.27 (s, 3H), 1.58 (s, 9H), 1.14 (t, *J* = 7.0 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 161.6, 150.9, 149.1, 135.9, 135.8, 135.7, 135.6, 135.3, 135.2, 134.2, 134.2, 132.7, 132.6, 127.5, 127.3, 123.1, 122.6, 122.5, 121.8, 117.6, 117.5, 111.4, 110.1, 83.7, 38.9, 38.8, 27.7, 20.8, 20.4, 13.7, 13.7. ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.7. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{23}H_{33}NO_5P^+$ 434.2091, found 434.2097. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 12.7 min

(major), 13.8 min (minor).

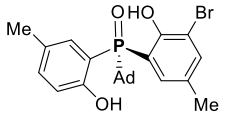


4a

(Adamantan-1-yl)phosphoryl)bis(4-methyl-2,1-phenylene) di-tert-butyl bis(carbonate) (4a)

Following the above procedure, racemic **3a** (99.2 mg, 0.2 mmol) and **2** (23 μL, 0.1 mmol) was reacted at -20 ºC for 24 hours to give **4a** as a white solid, 56.9 mg, 48% yield, mp: 182-184 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 11.9 Hz, 2H), 7.29 (d, *J* = 8.2 Hz, 2H), 7.14 (dd, *J* = 8.3, 4.5 Hz, 2H), 2.34 (s, 6H), 2.07 (d, *J* = 51.0 Hz, 9H), 1.76 (q, *J* = 11.7 Hz, 6H), 1.42 (s, 18H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 149.6, 134.8, 134.7, 134.2, 134.1, 133.0, 133.0, 124.4, 123.5, 122.5, 122.4, 83.0, 38.7, 37.9, 36.5, 35.8, 28.2, 28.1, 27.6, 20.9. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.9. HRMS (ESI-TOF) *m/z*: $[M + H]^+$ calcd. for $C_{34}H_{46}O_7P^+$ 597.2976, found 597.2978.

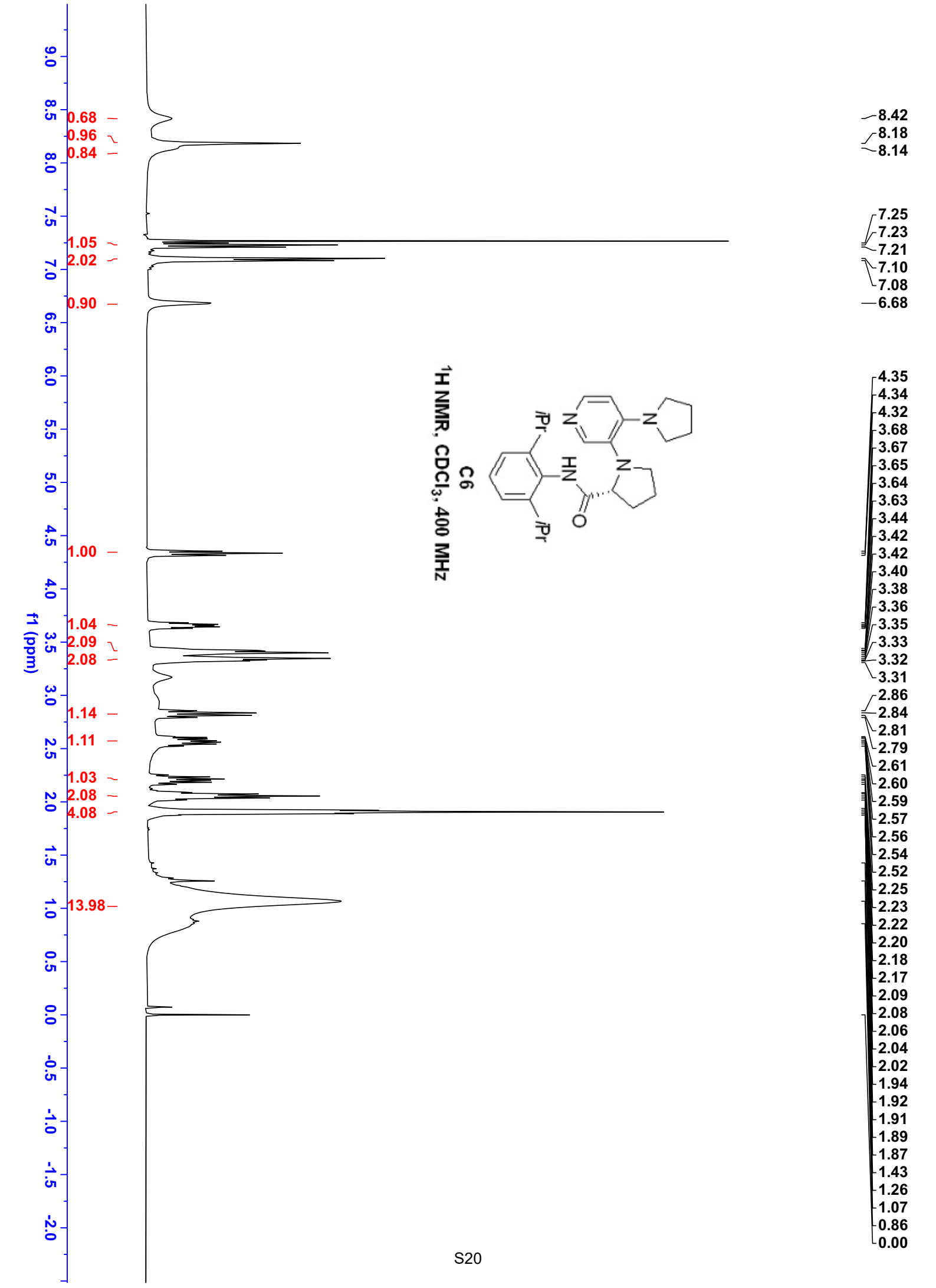


5

(R)-(Adamantan-1-yl)(3-bromo-2-hydroxy-5-methylphenyl)(2-hydroxy-5-methylphenyl)phosphine oxide (5)[1a,b]

Following the above procedure, **SI** (56.0 mg, 0.097 mmol) and trifluoroacetic acid (97 μL, 1.26 mmol) was reacted at 25 ºC for 12 hours to give **5** as a white solid, 33.1 mg, 72% yield, 97.5:2.5 er, mp: 187-189 ºC, obtained by the purification with flash column chromatography on silica gel using petroleum ether/EtOAc (v/v) = 10/1 as eluent.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.79 (s, 1H), 7.53 (d, *J* = 1.9 Hz, 1H), 7.24 (dd, *J* = 8.5, 2.0 Hz, 1H), 7.16 (td, *J* = 11.5, 2.1 Hz, 2H), 6.85 (dd, *J* = 8.5, 4.7 Hz, 1H), 2.31 (s, 3H), 2.30 (s, 3H), 2.08 – 1.97 (m, 9H), 1.78 – 1.68 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.4, 158.4, 150.6, 149.6, 149.6, 137.7, 137.7, 135.3, 135.2, 134.5, 134.5, 134.1, 134.1, 130.8, 130.7, 128.2, 128.1, 122.9, 122.8, 121.6, 120.8, 111.9, 111.8, 111.4, 110.5, 84.2, 39.4, 38.7, 36.2, 34.9, 27.6, 27.5, 27.4, 20.9, 20.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 47.8. HPLC (Daicel CHIRALPAK® ID, isopropanol/n-hexane = 10/90, flow rate = 1.0 mL/min, λ = 220 nm) tR = 11.0 min (minor), 14.7 min (major).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6.5
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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
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0.90
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2.09
2.08
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2.08
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2.18
2.17
2.09
2.08
2.06
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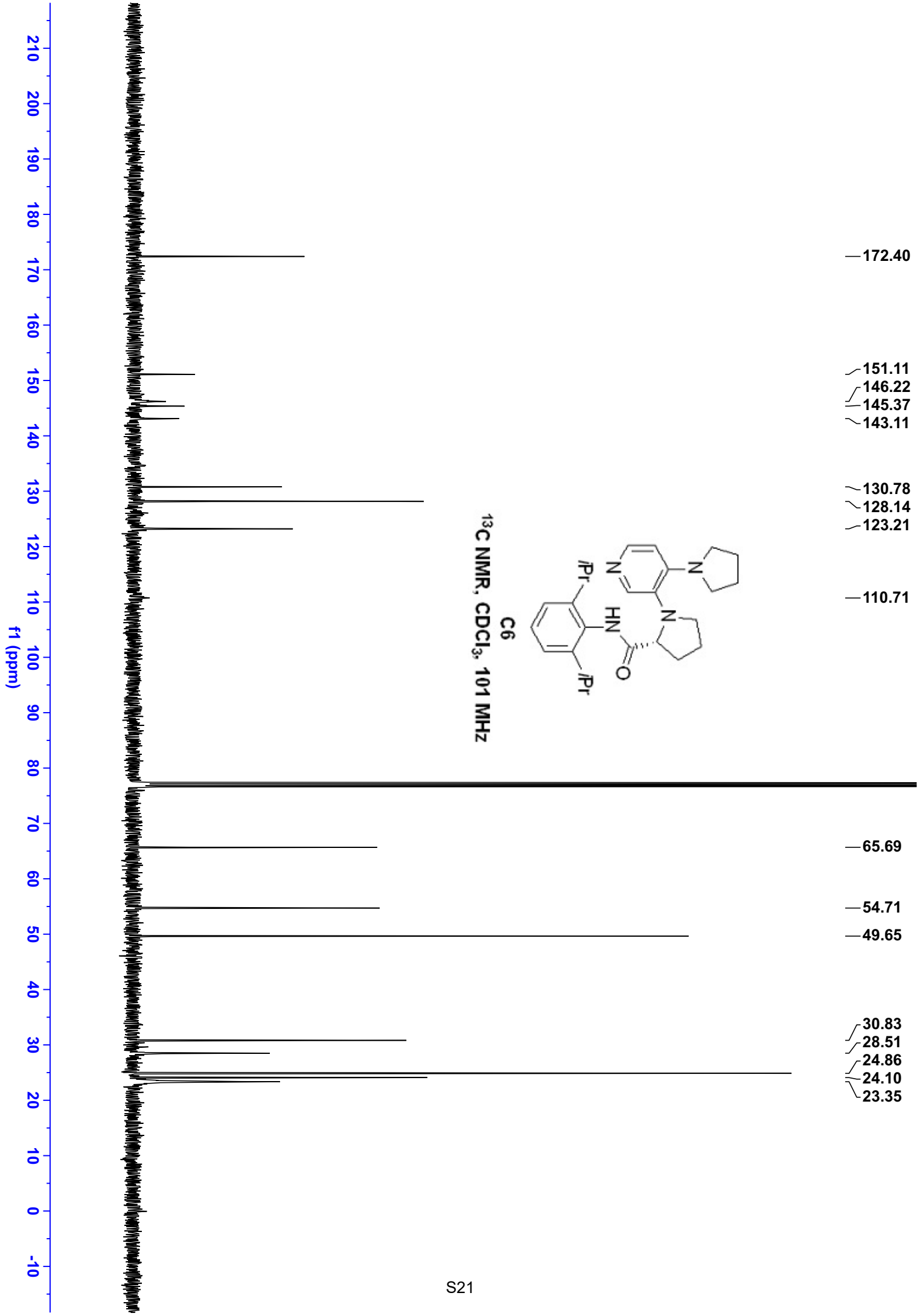
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28.51
24.86
24.10
23.35
f1 (ppm)
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190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
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10
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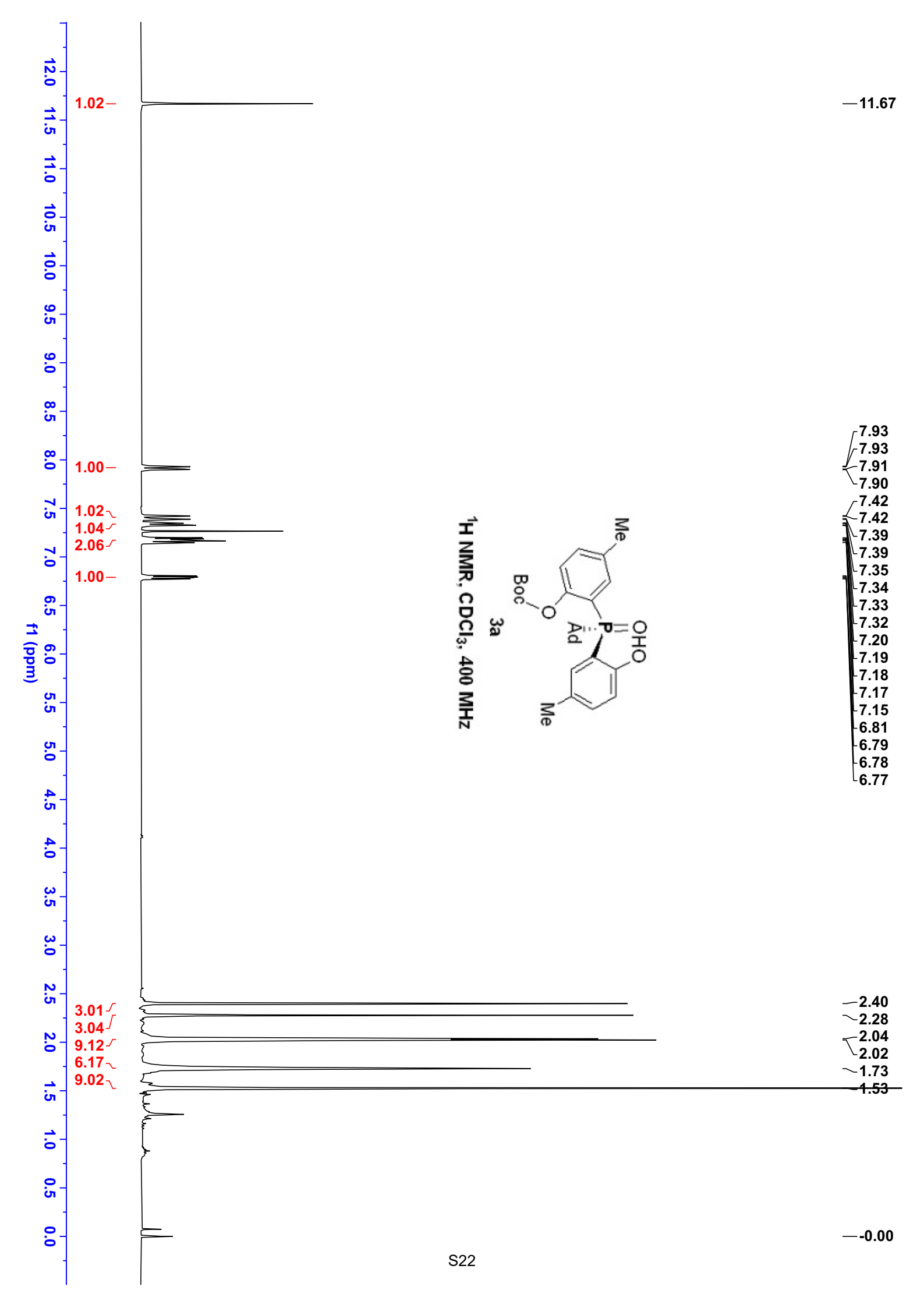
C6
13C NMR, CDCl3, 101 MHz
iPr
iPr
HN
O
N
N
N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1.02
1.04
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3.04
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9.02
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7.15
6.81
6.79
6.78
6.77
2.40
2.28
2.04
2.02
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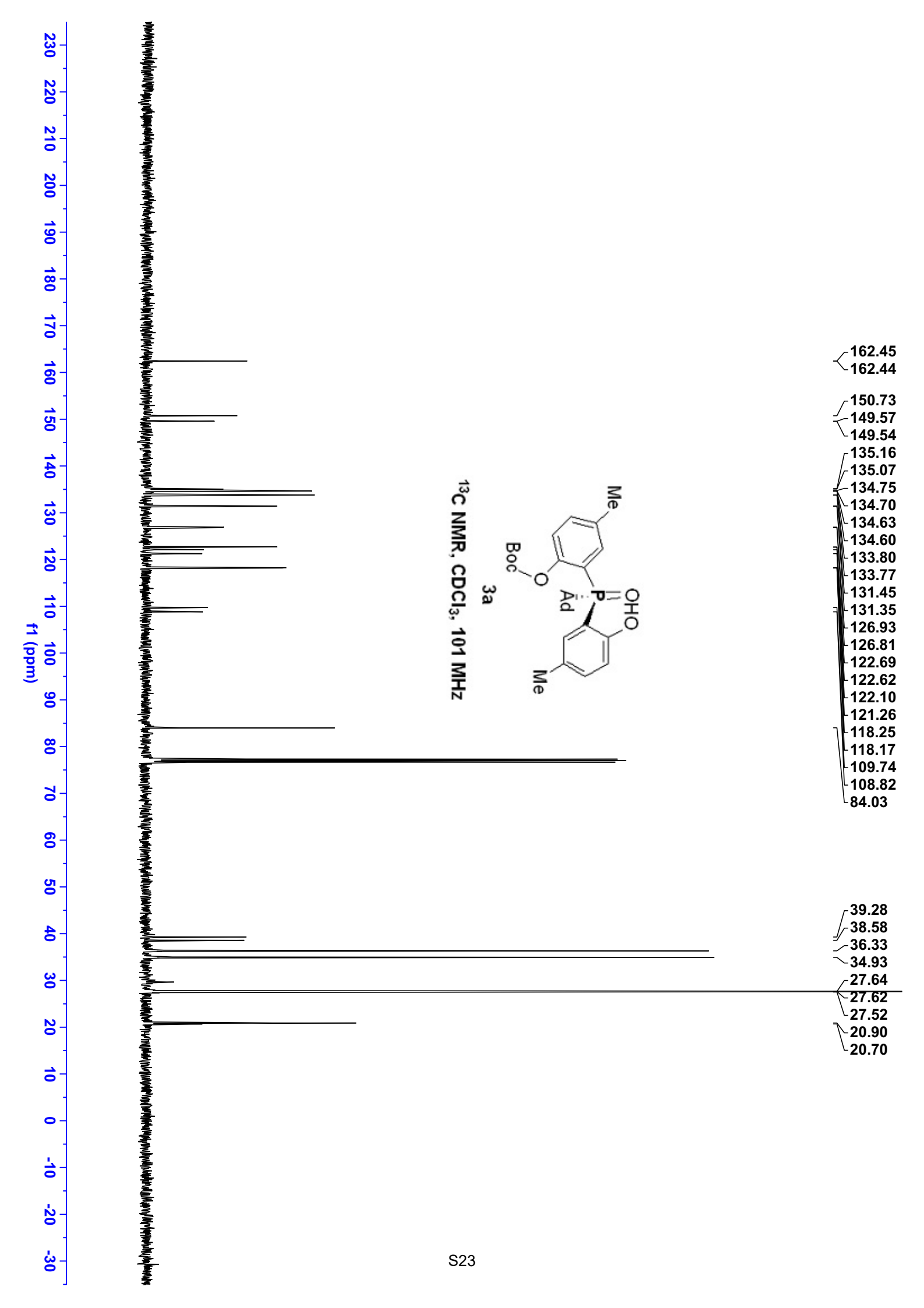
Me
Boc
O
P
Ad
OHO
Me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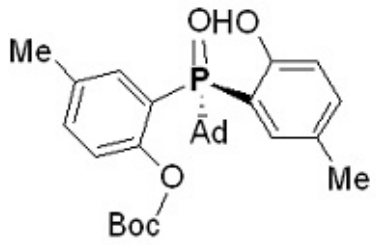
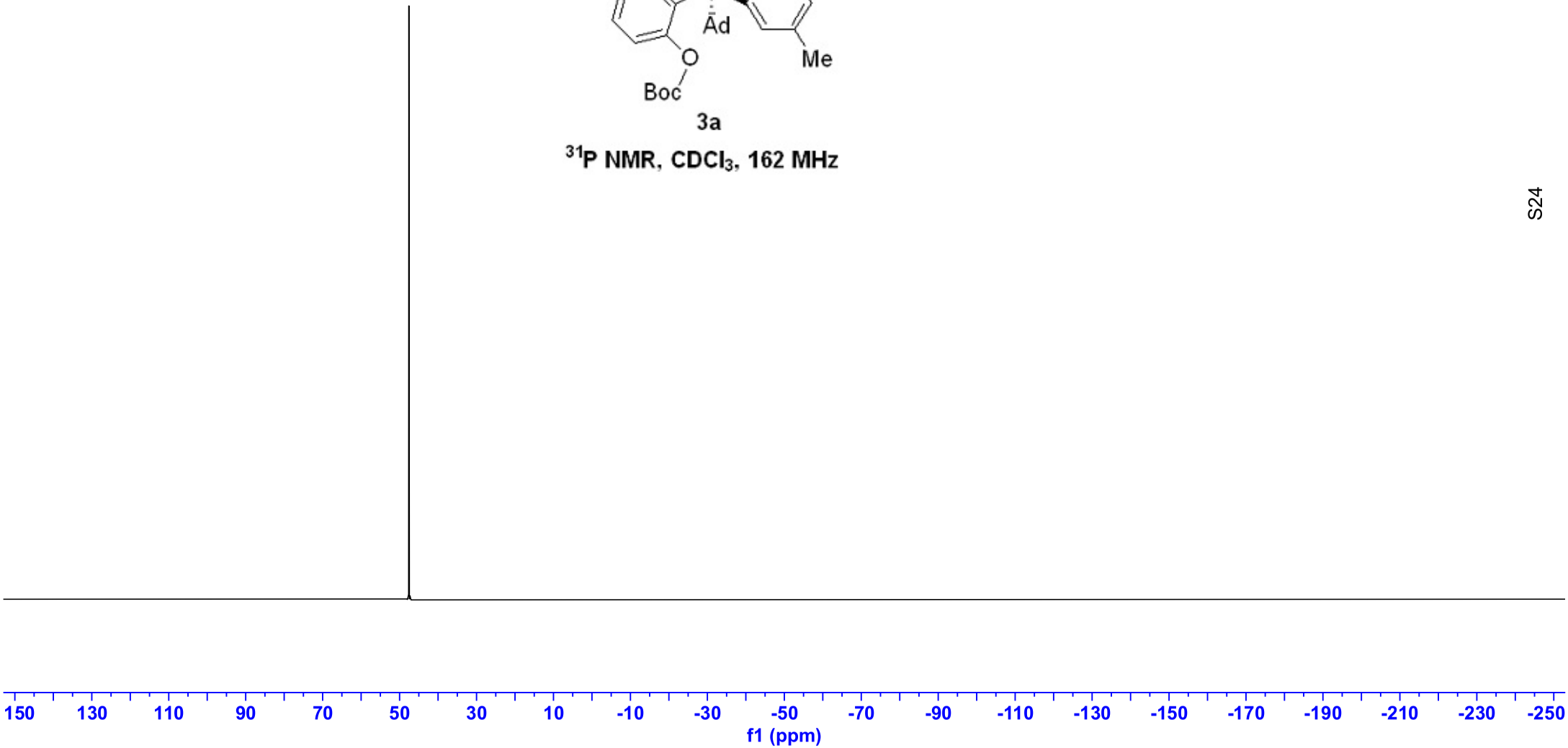
122.62
122.10
121.26
118.25
118.17
109.74
108.82
84.03
39.28
38.58
36.33
34.93
27.64
27.62
27.52
20.90
20.70
Me
Boc
O
P
Ad
OHO
Me
3a
13C NMR, CDCl3, 101 MHz
f1 (ppm)

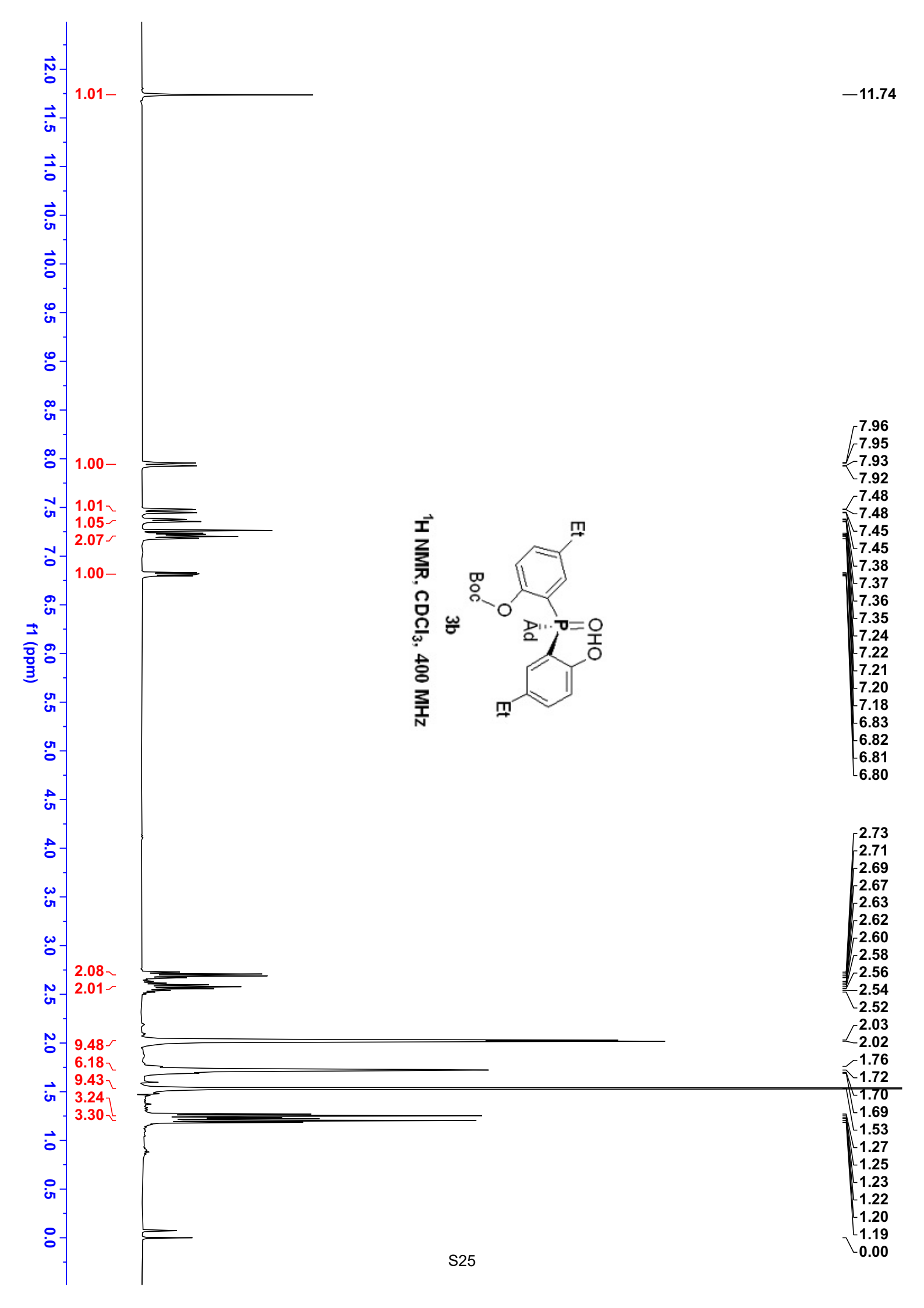
47.59

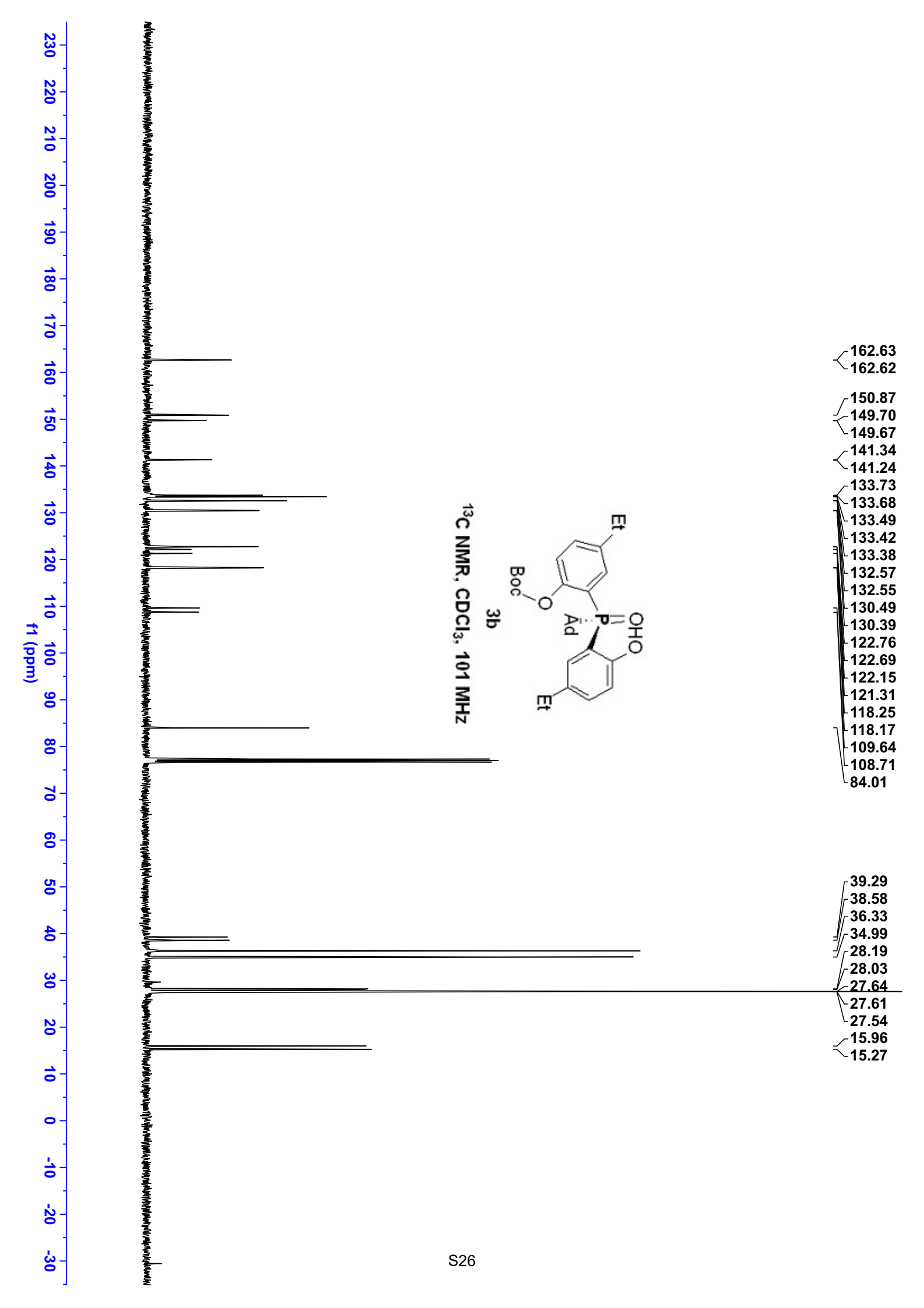


3a

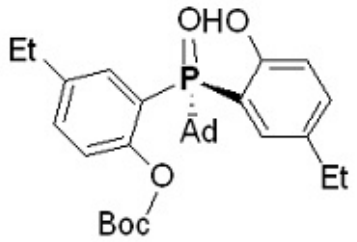
^{31}P NMR, $CDCl_3$, 162 MHz




1.01
1.00
1.01
1.05
2.07
1.00
2.08
2.01
9.48
6.18
9.43
3.24
3.30
11.74
7.96
7.95
7.93
7.92
7.48
7.48
7.45
7.45
7.38
7.37
7.36
7.35
7.24
7.22
7.21
7.20
7.18
6.83
6.82
6.81
6.80
2.73
2.71
2.69
2.67
2.63
2.62
2.60
2.58
2.56
2.54
2.52
2.03
2.02
1.76
1.72
1.70
1.69
1.53
1.27
1.25
1.23
1.22
1.20
1.19
0.00
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3b
Et
Boc
O
P
Ad
OHO
Et

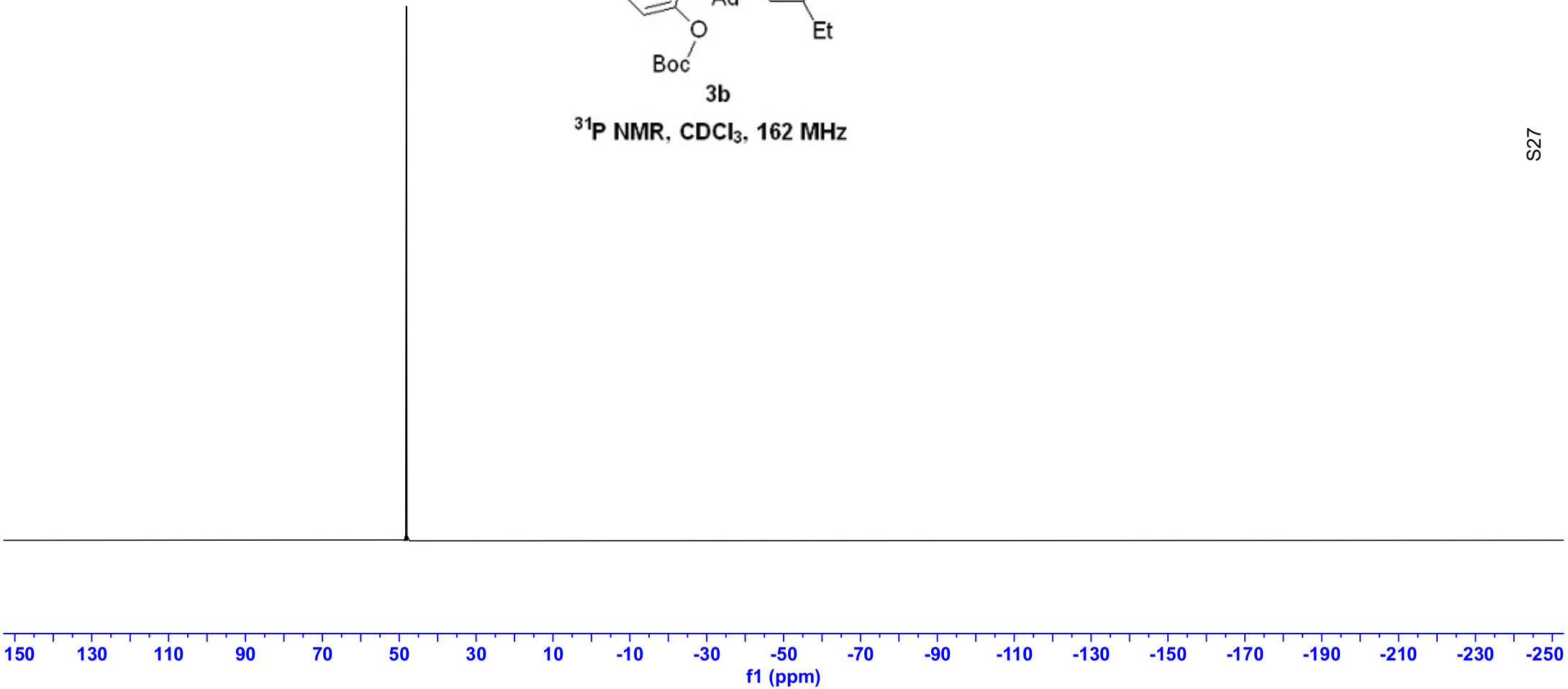

f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
^{13}C NMR, $CDCl_3$, 101 MHz
3b
Et
Boc
O
Ad
P
OHO
Et
162.63
162.62
150.87
149.70
149.67
141.34
141.24
133.73
133.68
133.49
133.42
133.38
132.57
132.55
130.49
130.39
122.76
122.69
122.15
121.31
118.25
118.17
109.64
108.71
84.01
39.29
38.58
36.33
34.99
28.19
28.03
27.64
27.61
27.54
15.96
15.27

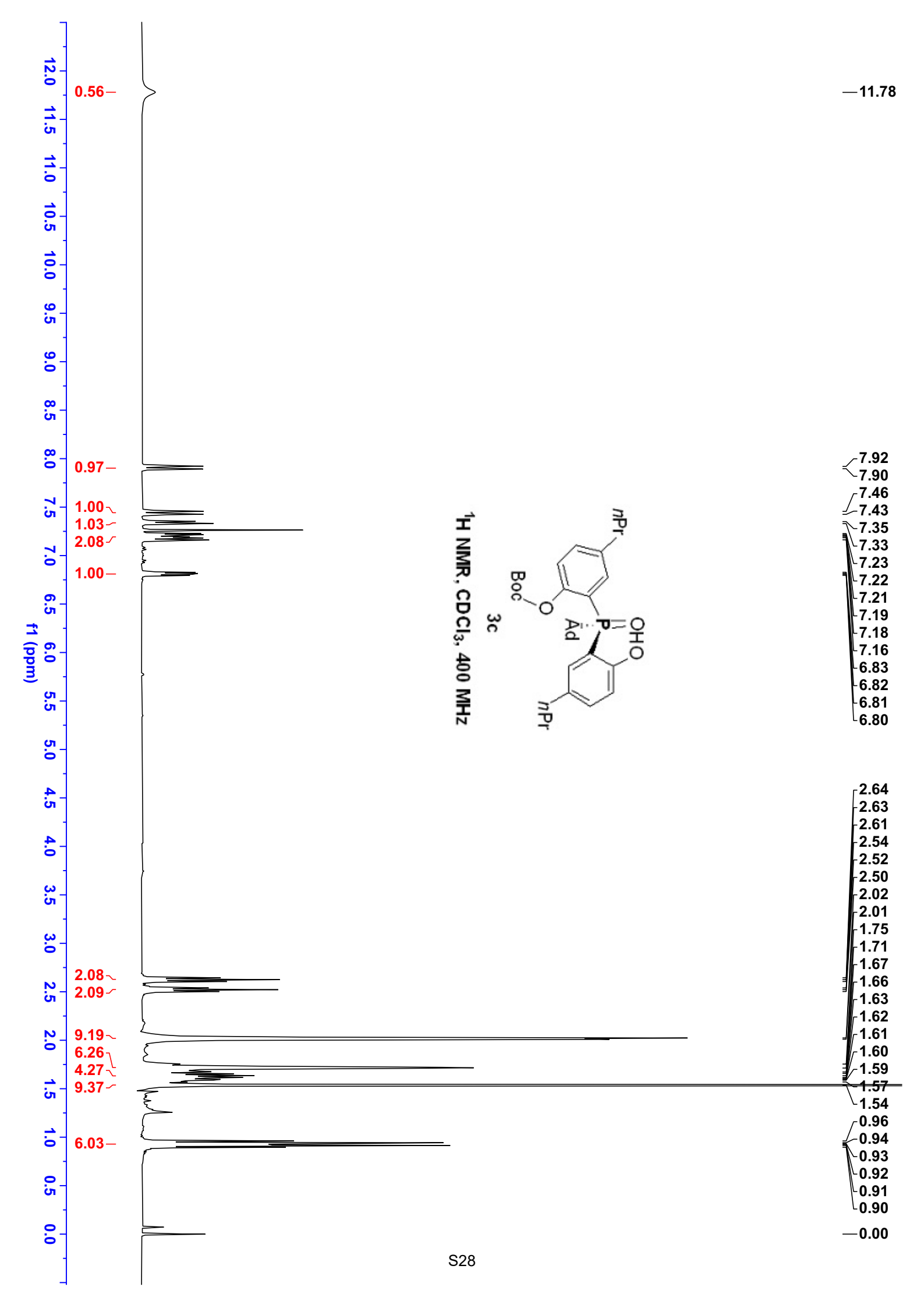
48.15

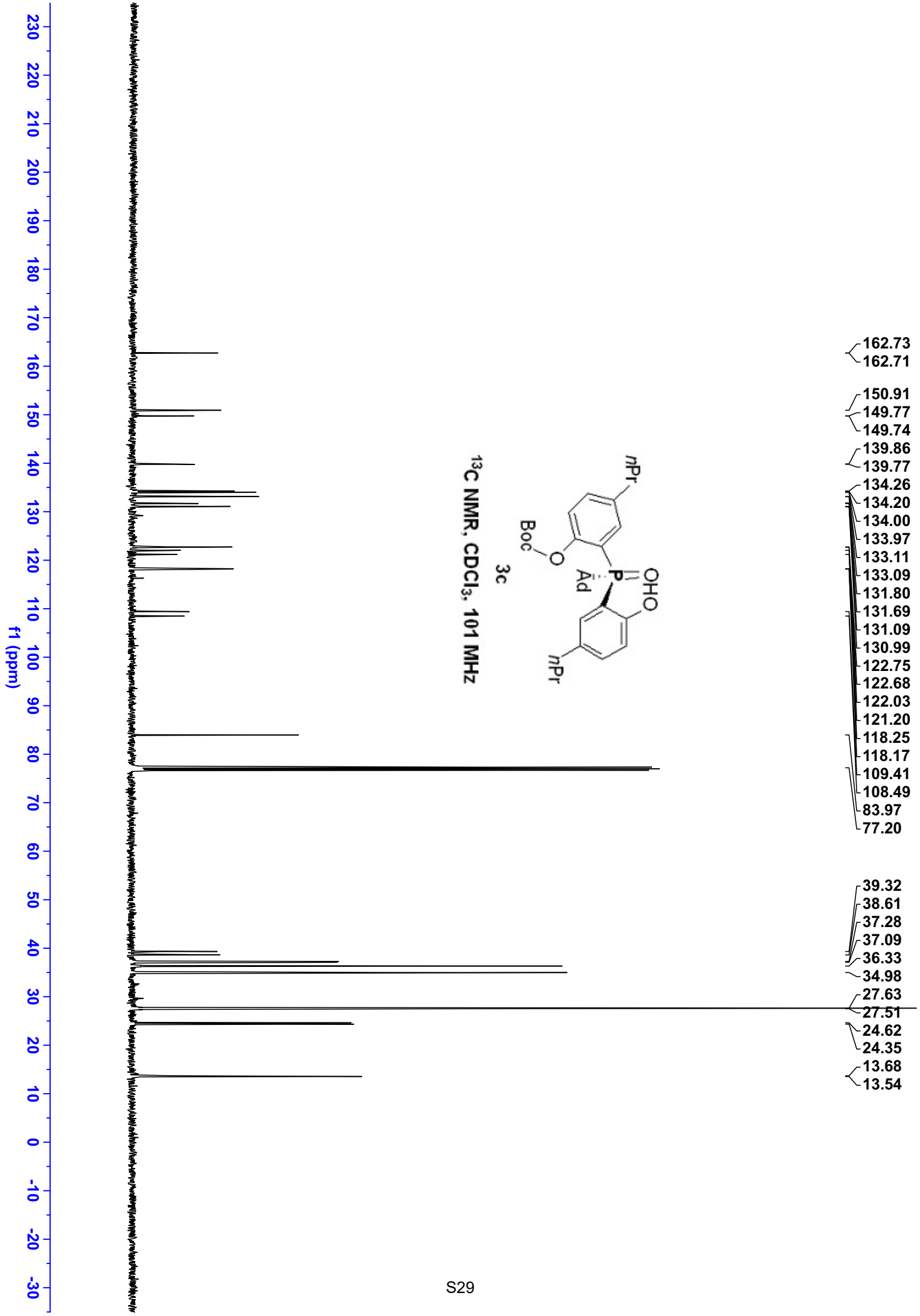


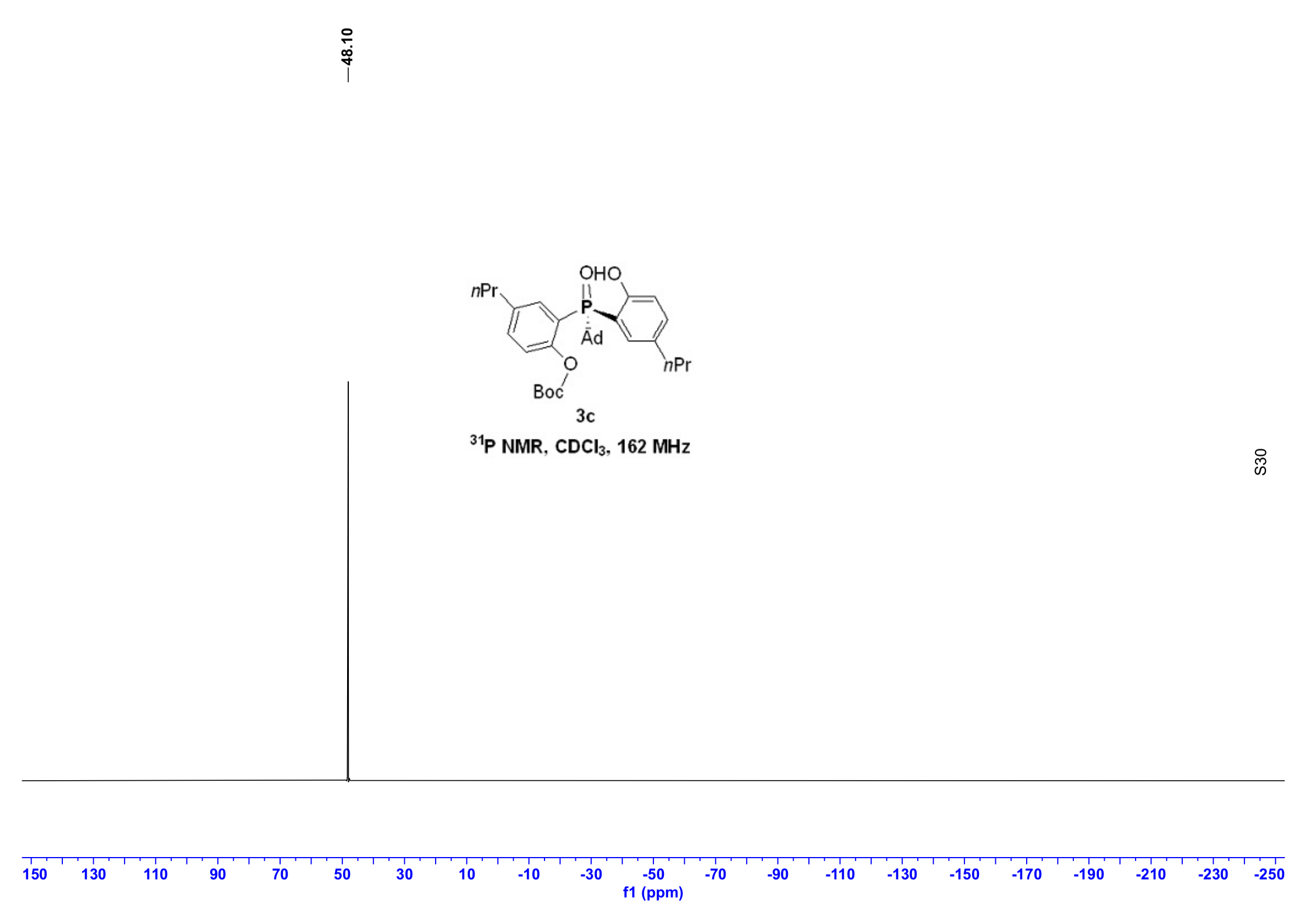
3b

^{31}P NMR, $CDCl_3$, 162 MHz



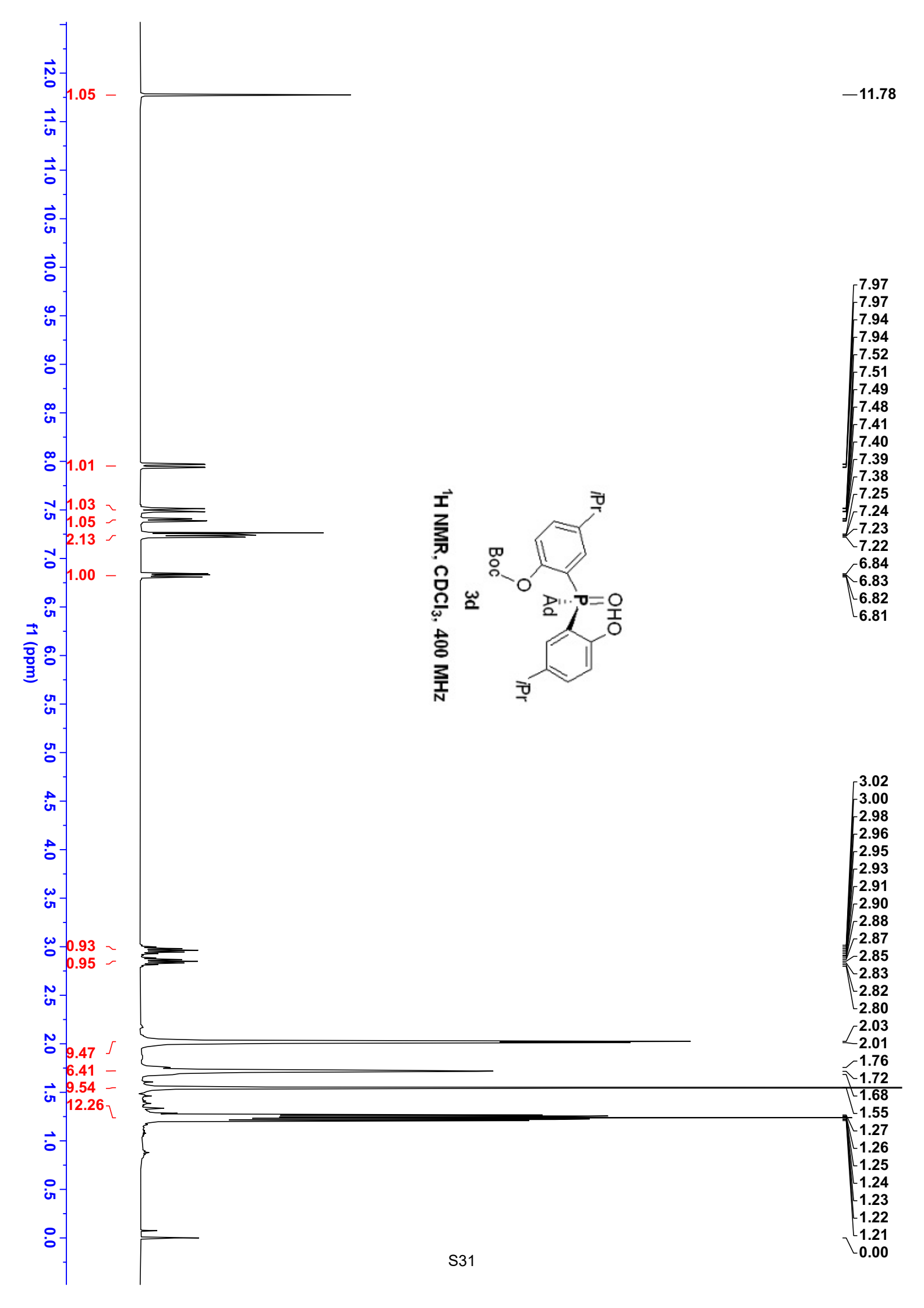

0.56
0.97
1.00
1.03
2.08
1.00
2.08
2.09
9.19
6.26
4.27
9.37
6.03
11.78
7.92
7.90
7.46
7.43
7.35
7.33
7.23
7.22
7.21
7.19
7.18
7.16
6.83
6.82
6.81
6.80
2.64
2.63
2.61
2.54
2.52
2.50
2.02
2.01
1.75
1.71
1.67
1.66
1.63
1.62
1.61
1.60
1.59
1.57
1.54
0.96
0.94
0.93
0.92
0.91
0.90
0.00
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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
0.5
0.0
^{1}H NMR, CDCl$_3$, 400 MHz
3c
nPr
Boc
O
P
Ad
OHO
nPr

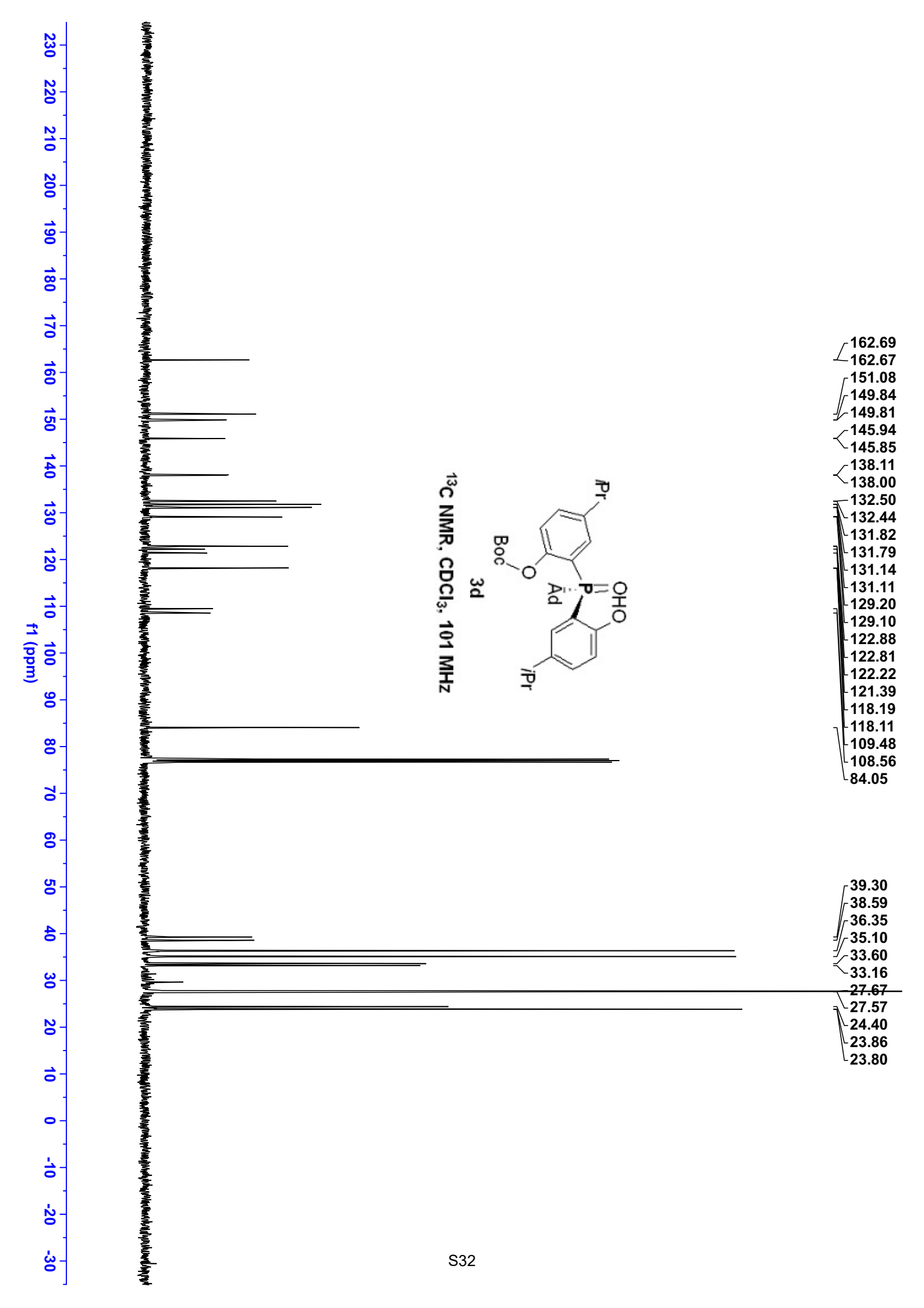

f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
^{13}C NMR, CDCl$_3$, 101 MHz
3c
nPr
Boc
O
P
Ad
OHO
nPr
162.73
162.71
150.91
149.77
149.74
139.86
139.77
134.26
134.20
134.00
133.97
133.11
133.09
131.80
131.69
131.09
130.99
122.75
122.68
122.03
121.20
118.25
118.17
109.41
108.49
83.97
77.20
39.32
38.61
37.28
37.09
36.33
34.98
27.63
27.51
24.62
24.35
13.68
13.54



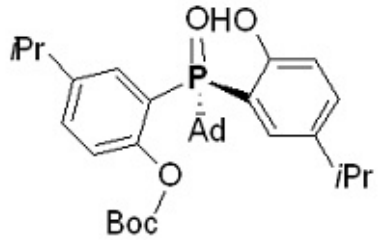
3c

^{31}P NMR, $CDCl_3$, 162 MHz


1.05
1.01
1.03
1.05
2.13
1.00
0.93
0.95
9.47
6.41
9.54
12.26
f1 (ppm)
11.78
7.97
7.97
7.94
7.94
7.52
7.51
7.49
7.48
7.41
7.40
7.39
7.38
7.25
7.24
7.23
7.22
6.84
6.83
6.82
6.81
3.02
3.00
2.98
2.96
2.95
2.93
2.91
2.90
2.88
2.87
2.85
2.83
2.82
2.80
2.03
2.01
1.76
1.72
1.68
1.55
1.27
1.26
1.25
1.24
1.23
1.22
1.21
0.00
^{1}H NMR, CDCl$_3$, 400 MHz
3d
iPr
Boc
O
P
Ad
OHO
iPr

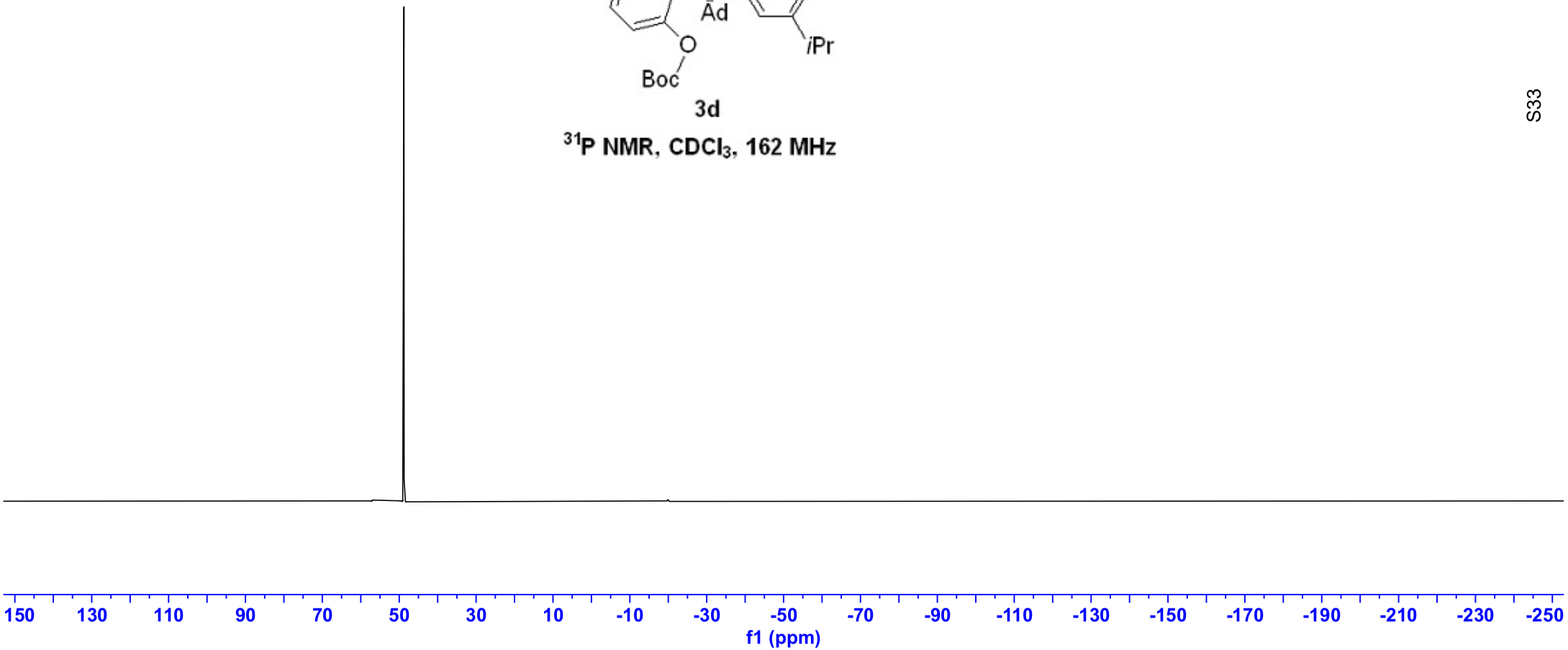

162.69
162.67
151.08
149.84
149.81
145.94
145.85
138.11
138.00
132.50
132.44
131.82
131.79
131.14
131.11
129.20
129.10
122.88
122.81
122.22
121.39
118.19
118.11
109.48
108.56
84.05
39.30
38.59
36.35
35.10
33.60
33.16
27.67
27.57
24.40
23.86
23.80
iPr
Boc
O
P
Ad
OHO
iPr
3d
13C NMR, CDCl3, 101 MHz
f1 (ppm)

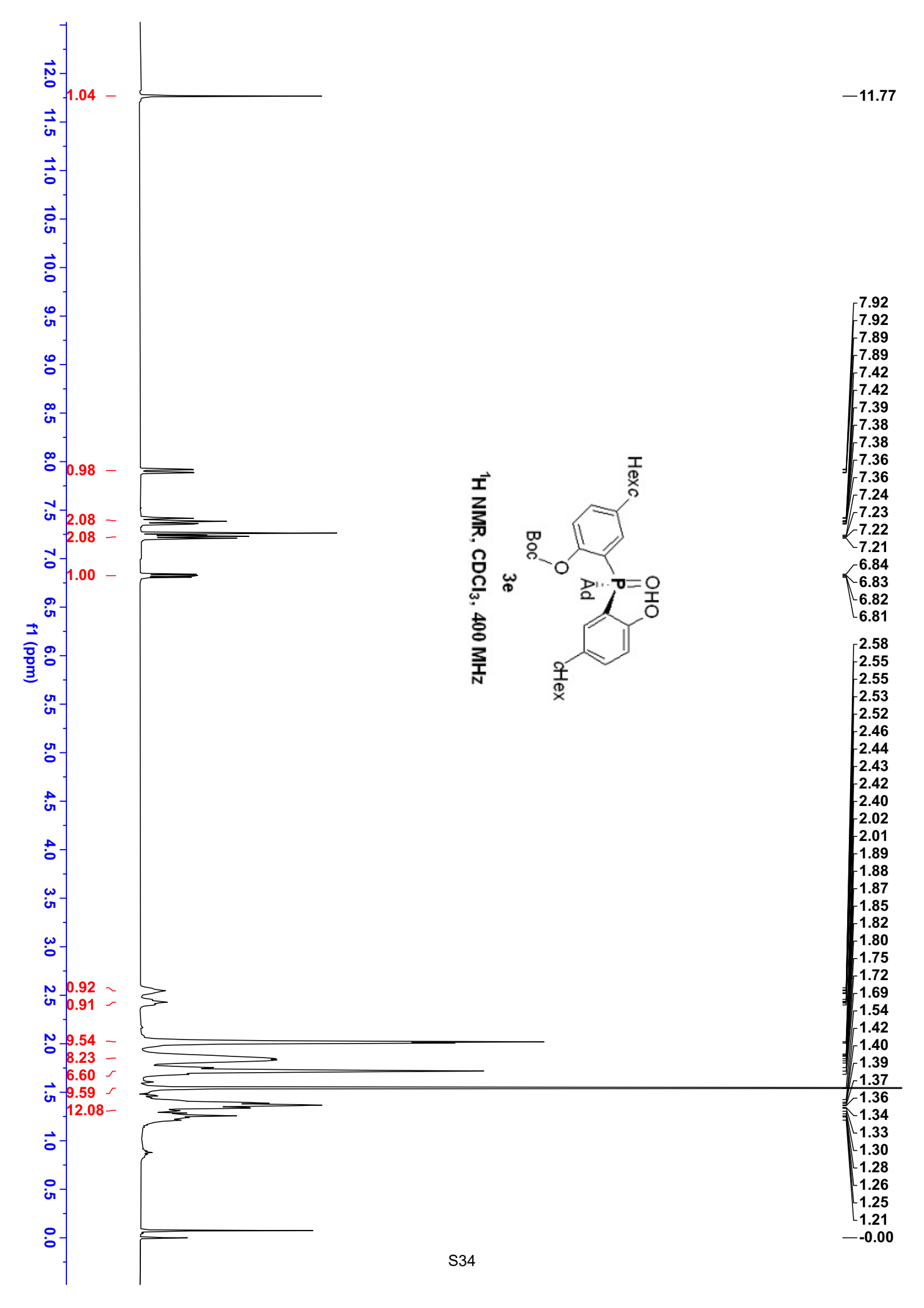
48.77

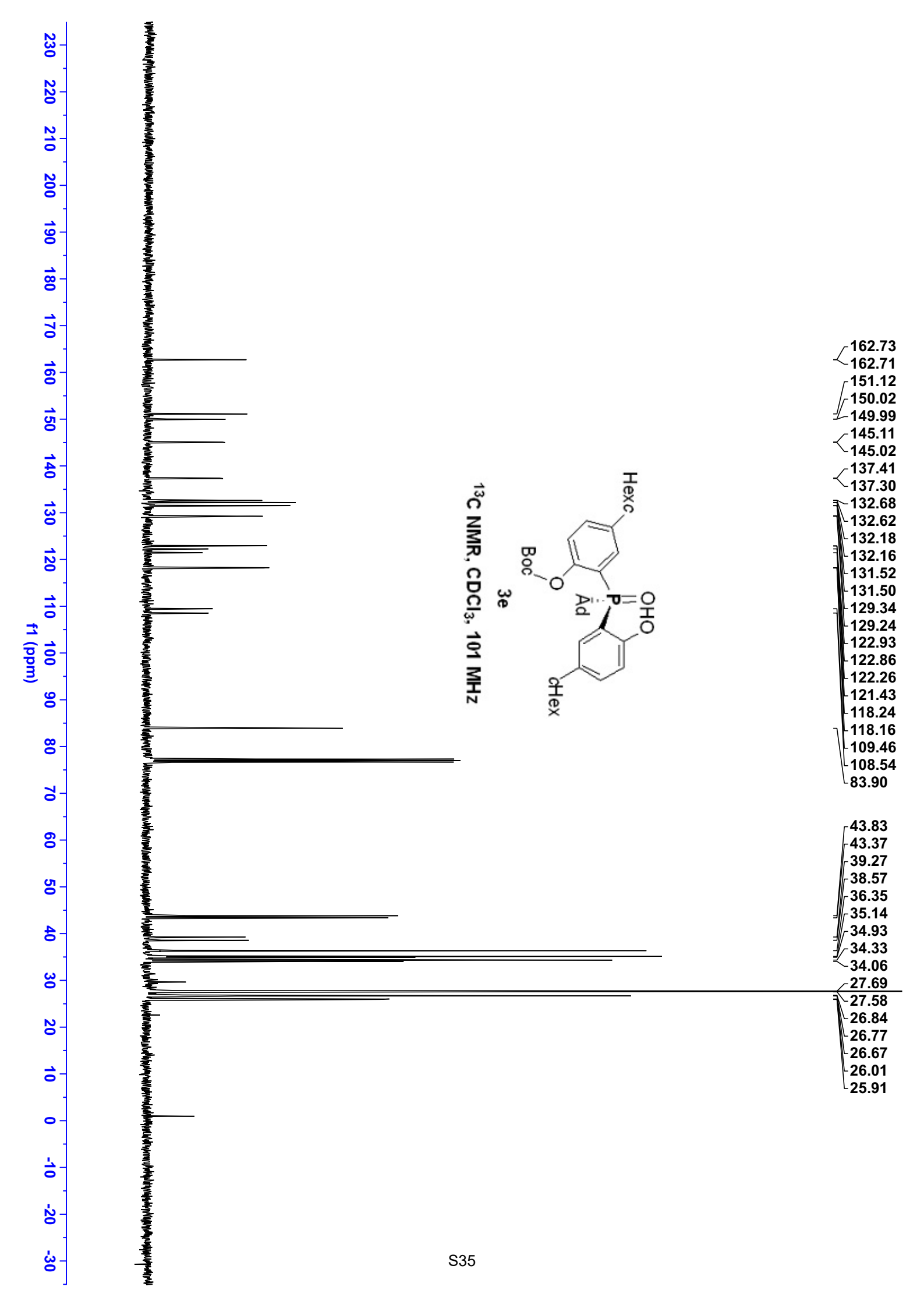


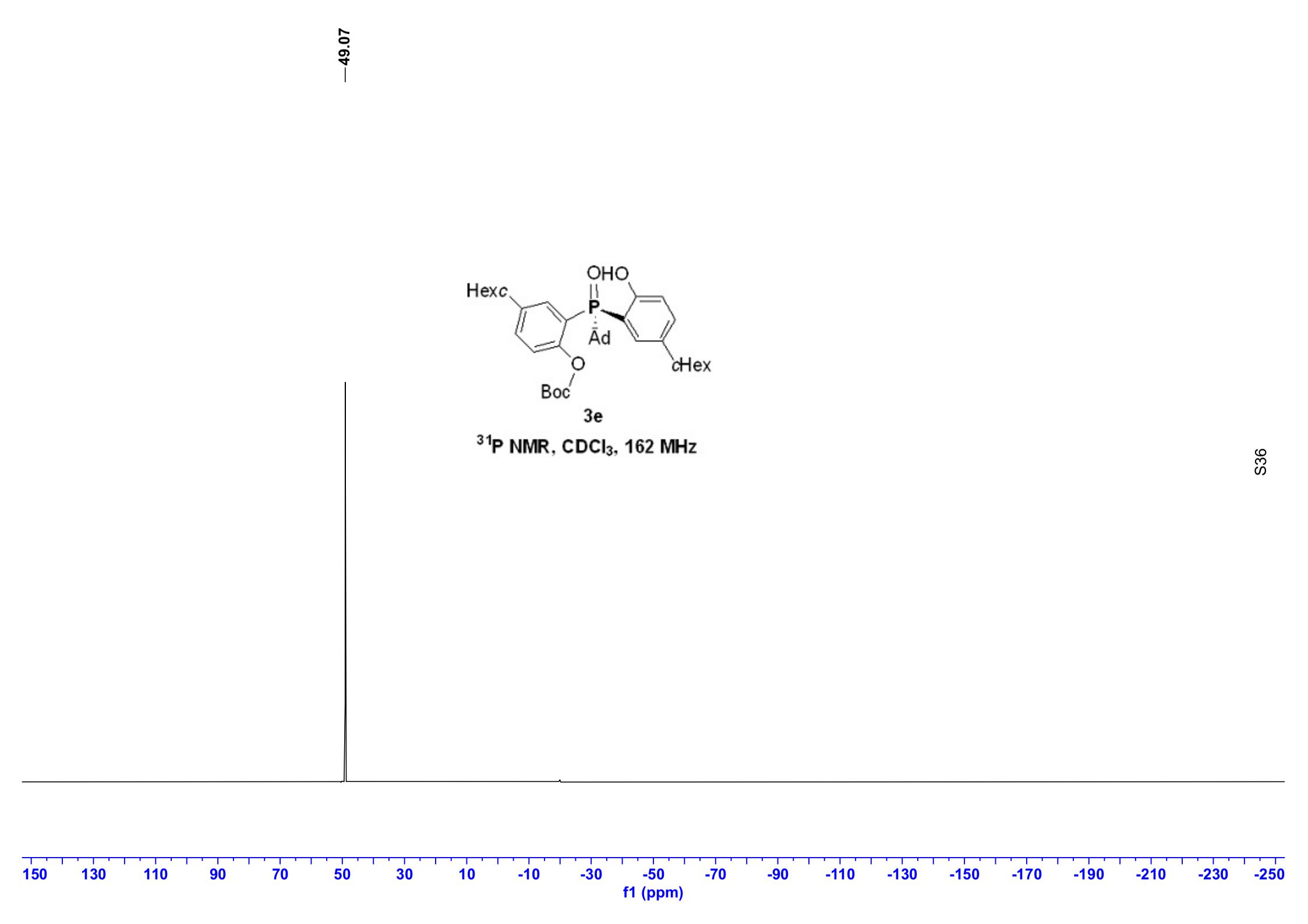
3d

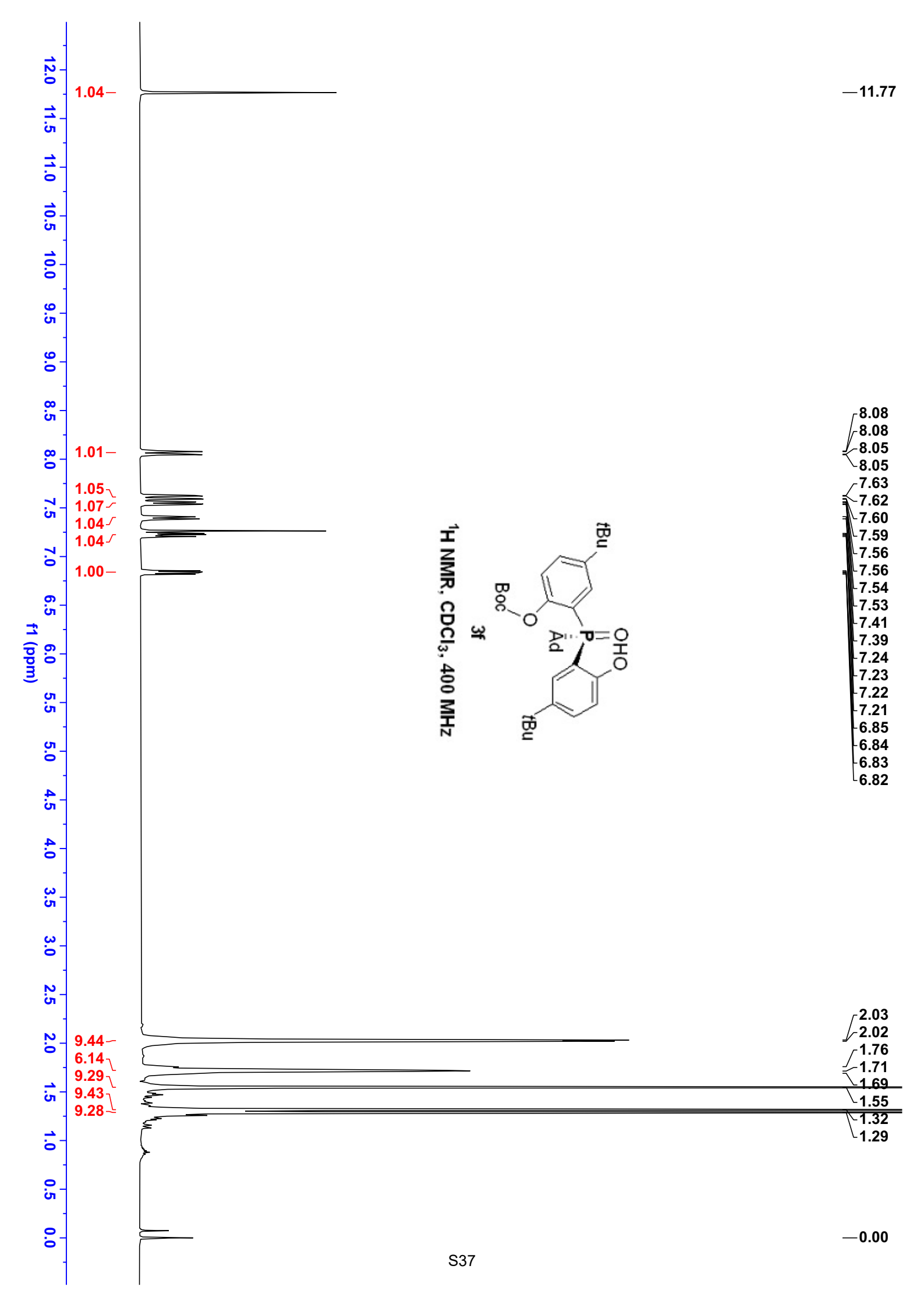
^{31}P NMR, $CDCl_3$, 162 MHz

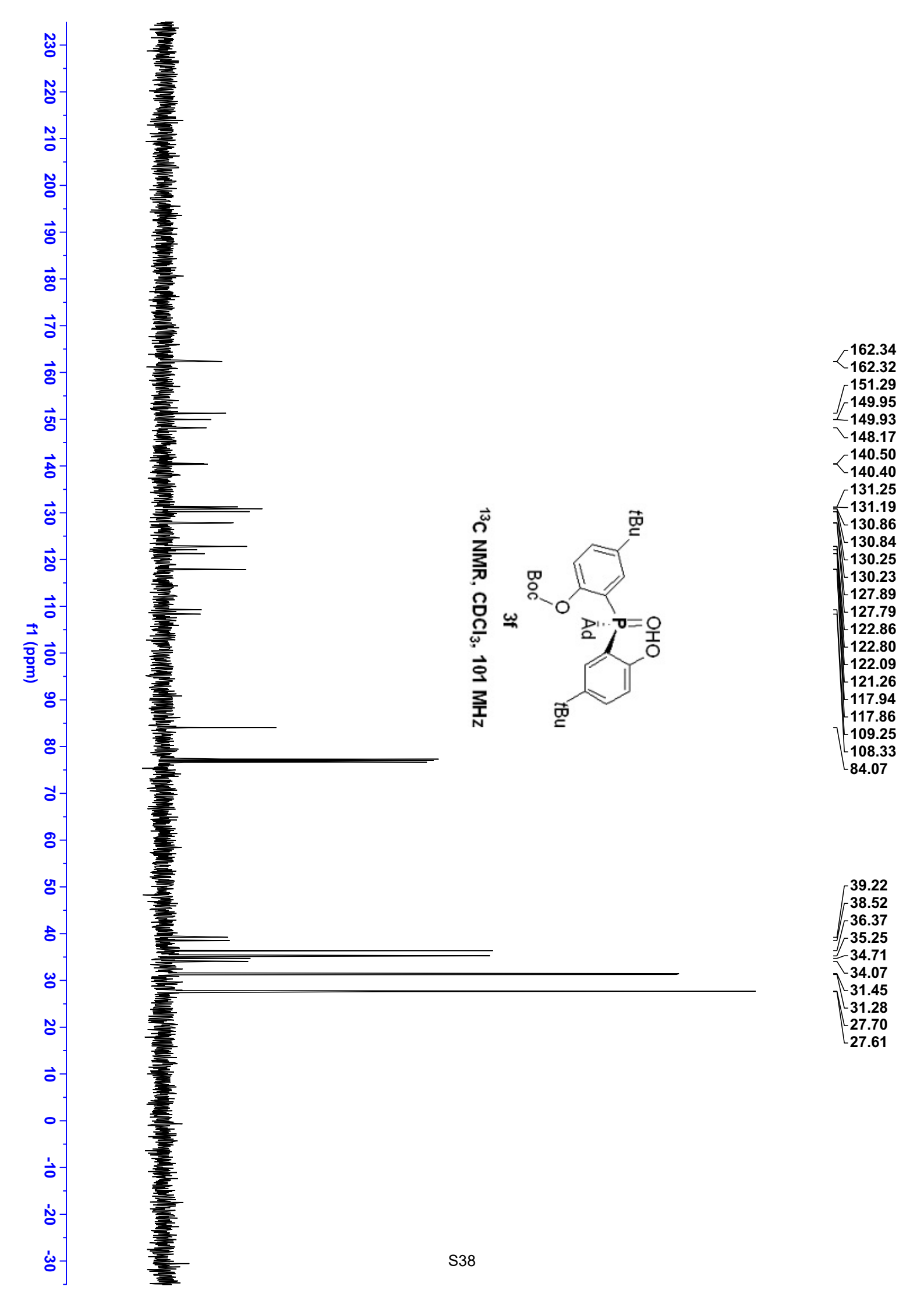


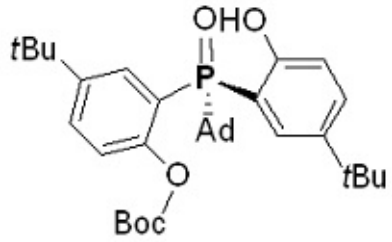

1.04
0.98
2.08
2.08
1.00
0.92
0.91
9.54
8.23
6.60
9.59
12.08
11.77
7.92
7.92
7.89
7.89
7.42
7.42
7.39
7.38
7.38
7.36
7.36
7.24
7.23
7.22
7.21
6.84
6.83
6.82
6.81
2.58
2.55
2.55
2.53
2.52
2.46
2.44
2.43
2.42
2.40
2.02
2.01
1.89
1.88
1.87
1.85
1.82
1.80
1.75
1.72
1.69
1.54
1.42
1.40
1.39
1.37
1.36
1.34
1.33
1.30
1.28
1.26
1.25
1.21
-0.00
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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
0.5
0.0
^{1}H NMR, CDCl$_3$, 400 MHz
3e
Hexc
Boc
O
P
Ad
OHO
cHex


f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
162.73
162.71
151.12
150.02
149.99
145.11
145.02
137.41
137.30
132.68
132.62
132.18
132.16
131.52
131.50
129.34
129.24
122.93
122.86
122.26
121.43
118.24
118.16
109.46
108.54
83.90
43.83
43.37
39.27
38.57
36.35
35.14
34.93
34.33
34.06
27.69
27.58
26.84
26.77
26.67
26.01
25.91
Hexc
Boc
O
P
Ad
OHO
cHex
3e
13C NMR, CDCl3, 101 MHz


49.07
OHO
Hexc
P
Ad
O
cHex
Boc
3e
31P NMR, CDCl3, 162 MHz
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)

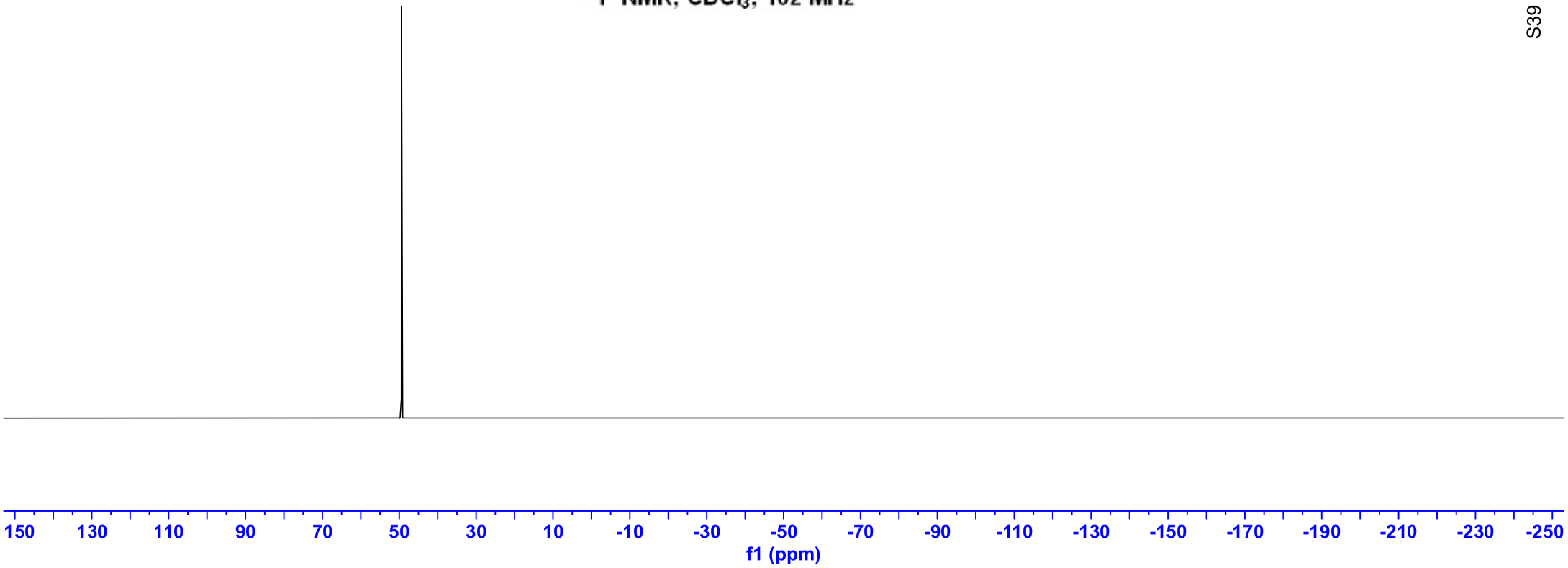

1.04
1.01
1.05
1.07
1.04
1.04
1.00
9.44
6.14
9.29
9.43
9.28
11.77
8.08
8.08
8.05
8.05
7.63
7.62
7.60
7.59
7.56
7.56
7.54
7.53
7.41
7.39
7.24
7.23
7.22
7.21
6.85
6.84
6.83
6.82
2.03
2.02
1.76
1.71
1.69
1.55
1.32
1.29
0.00
f1 (ppm)
12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
^{1}H NMR, CDCl$_3$, 400 MHz
3f
tBu
Boc
O
P
Ad
OHO
tBu

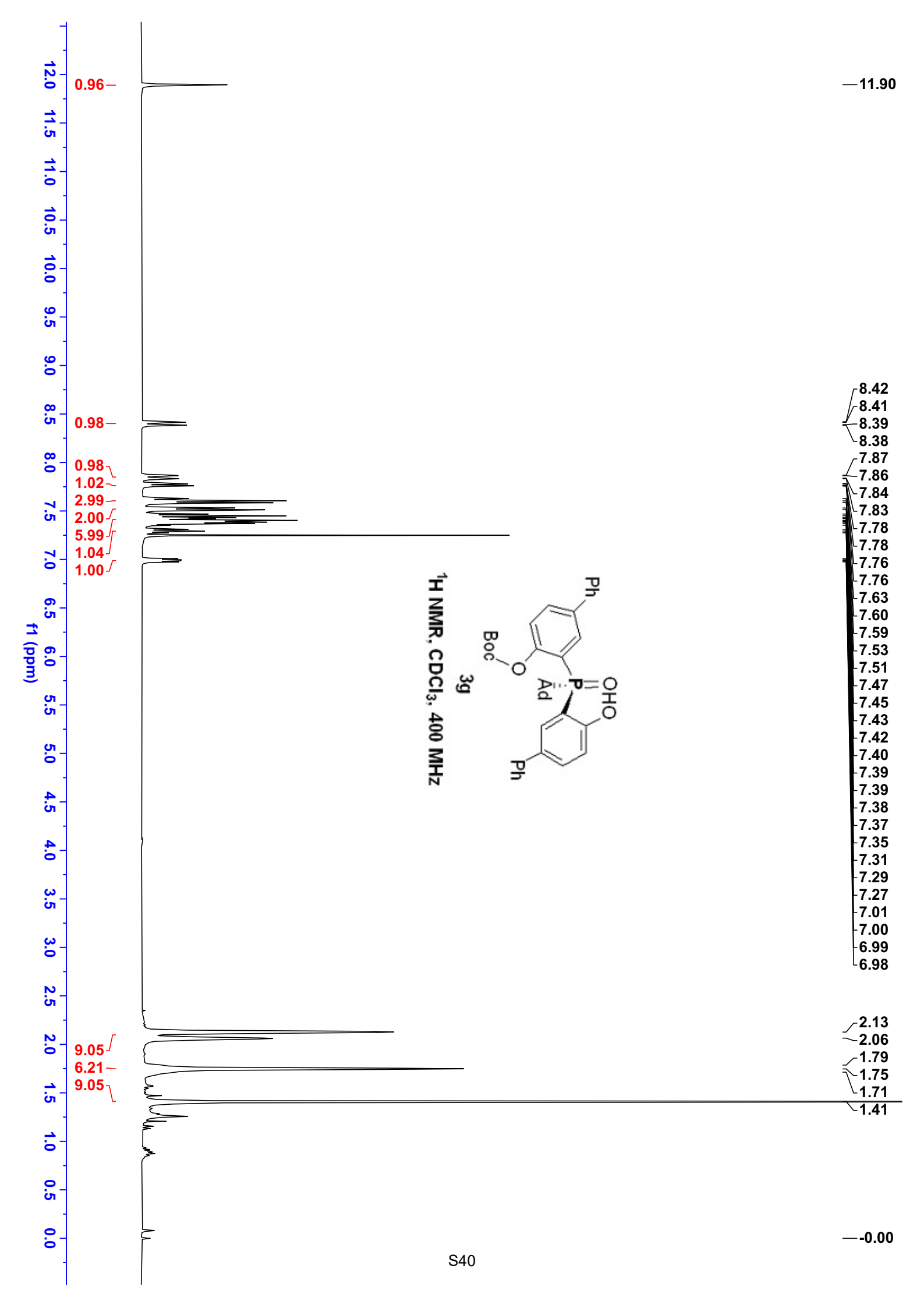

f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
162.34
162.32
151.29
149.95
149.93
148.17
140.50
140.40
131.25
131.19
130.86
130.84
130.25
130.23
127.89
127.79
122.86
122.80
122.09
121.26
117.94
117.86
109.25
108.33
84.07
39.22
38.52
36.37
35.25
34.71
34.07
31.45
31.28
27.70
27.61
tBu
Boc
O
P
Ad
OHO
tBu
3f
13C NMR, CDCl3, 101 MHz

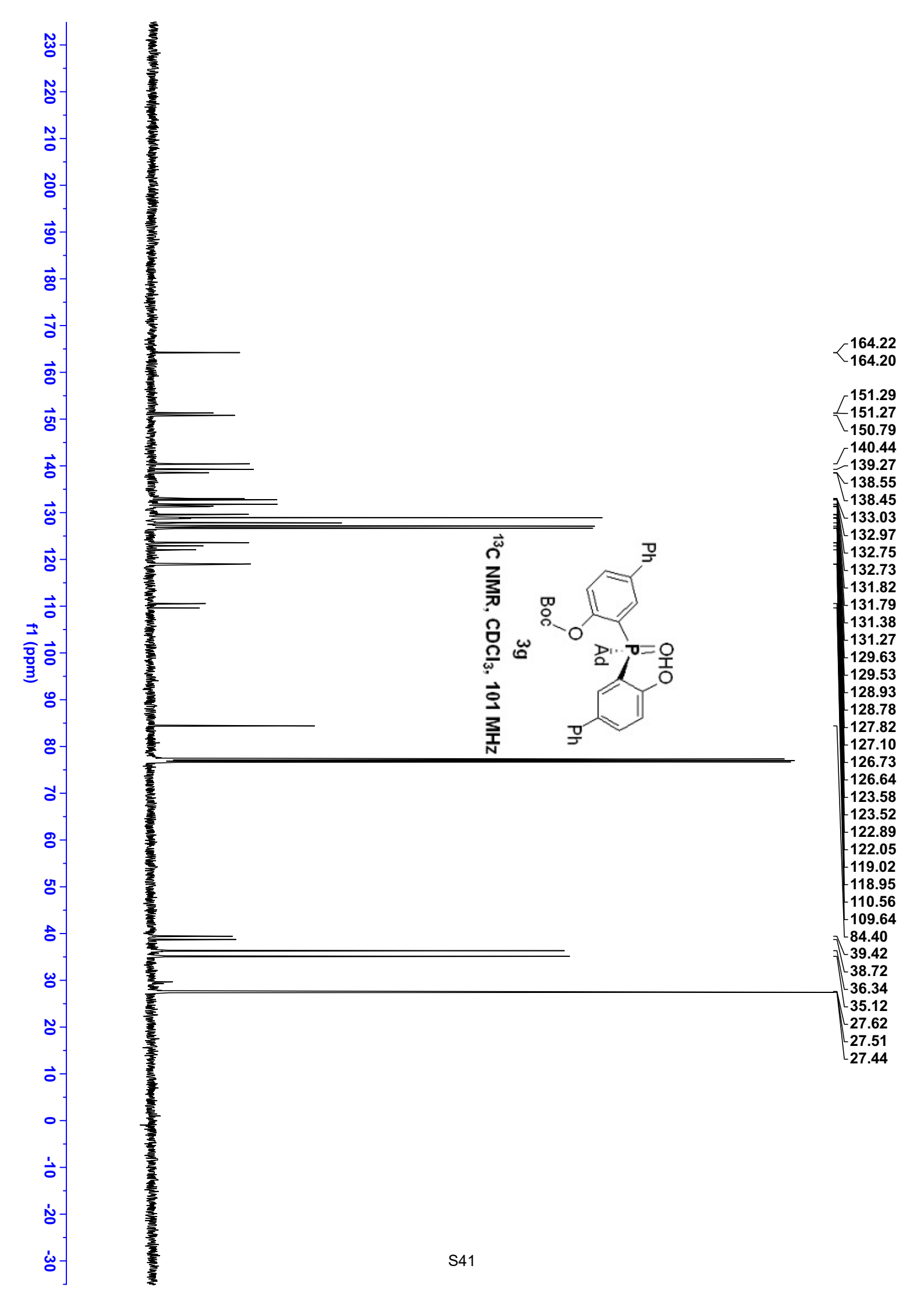


3f

^{31}P NMR, $CDCl_3$, 162 MHz

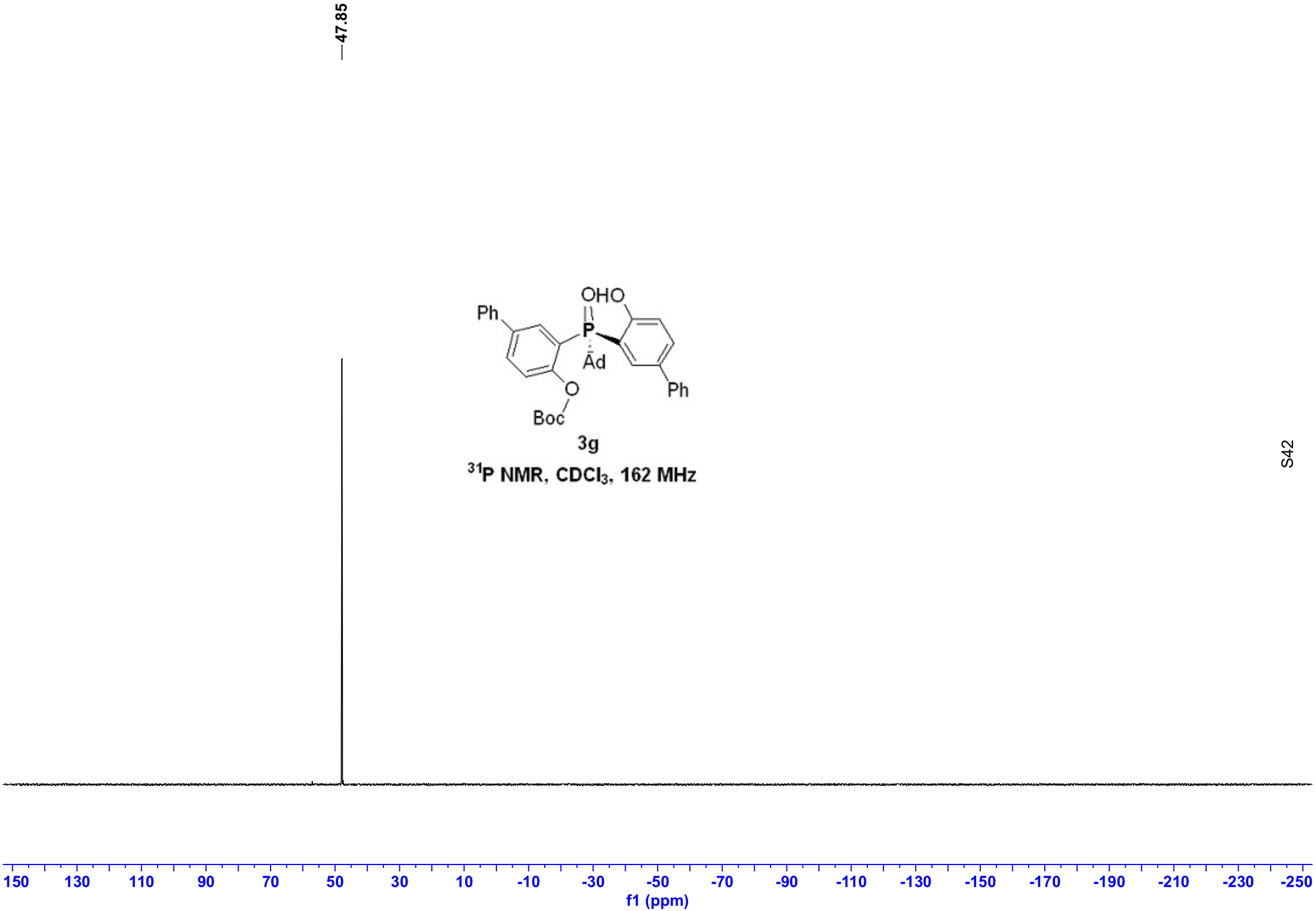


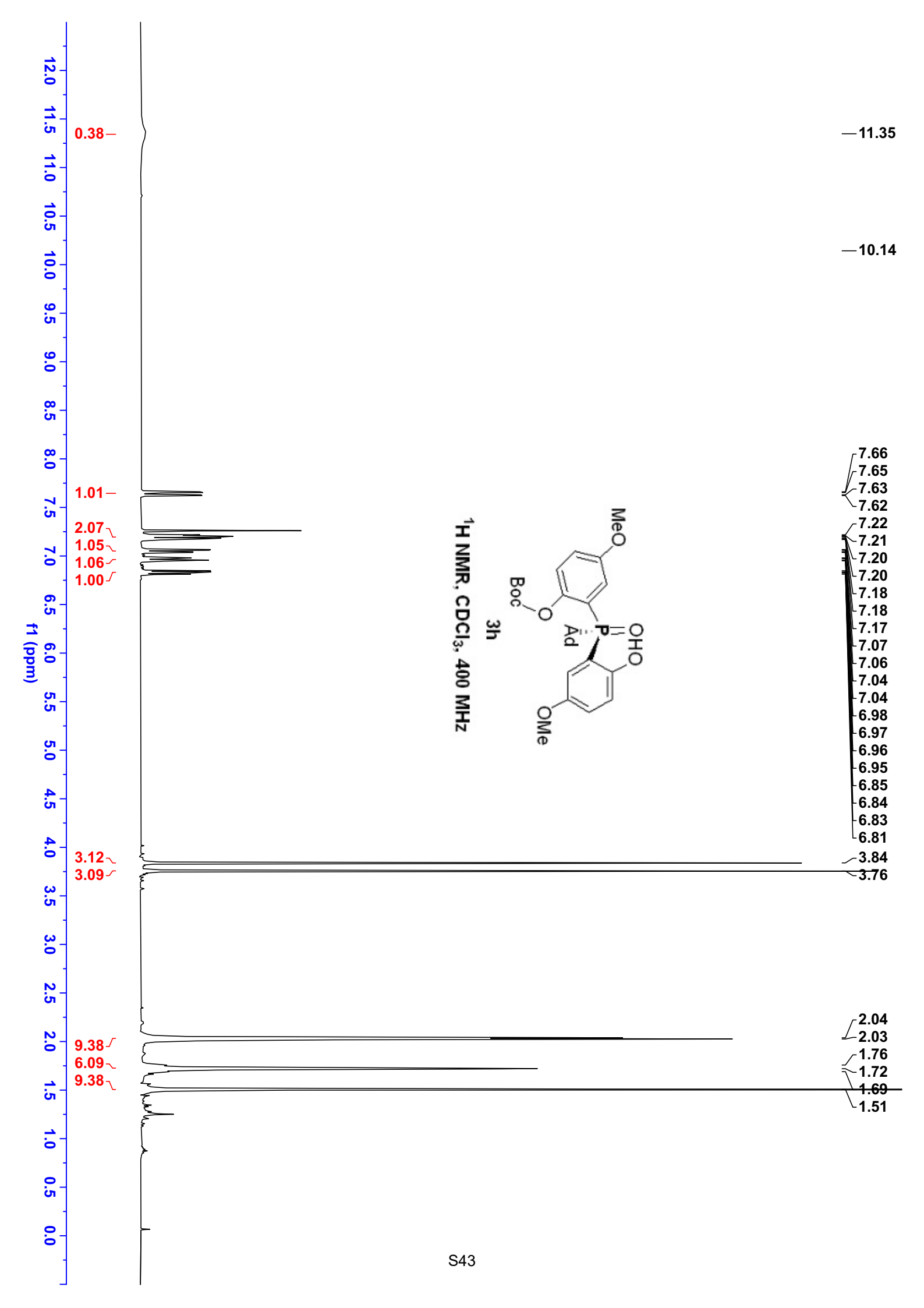

f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
0.96
0.98
0.98
1.02
2.99
2.00
5.99
1.04
1.00
9.05
6.21
9.05
11.90
8.42
8.41
8.39
8.38
7.87
7.86
7.84
7.83
7.78
7.78
7.76
7.76
7.63
7.60
7.59
7.53
7.51
7.47
7.45
7.43
7.42
7.40
7.39
7.39
7.38
7.37
7.35
7.31
7.29
7.27
7.01
7.00
6.99
6.98
2.13
2.06
1.79
1.75
1.71
1.41
-0.00
Ph
Boc
O
P
Ad
OHO
Ph
3g
1H NMR, CDCl3, 400 MHz

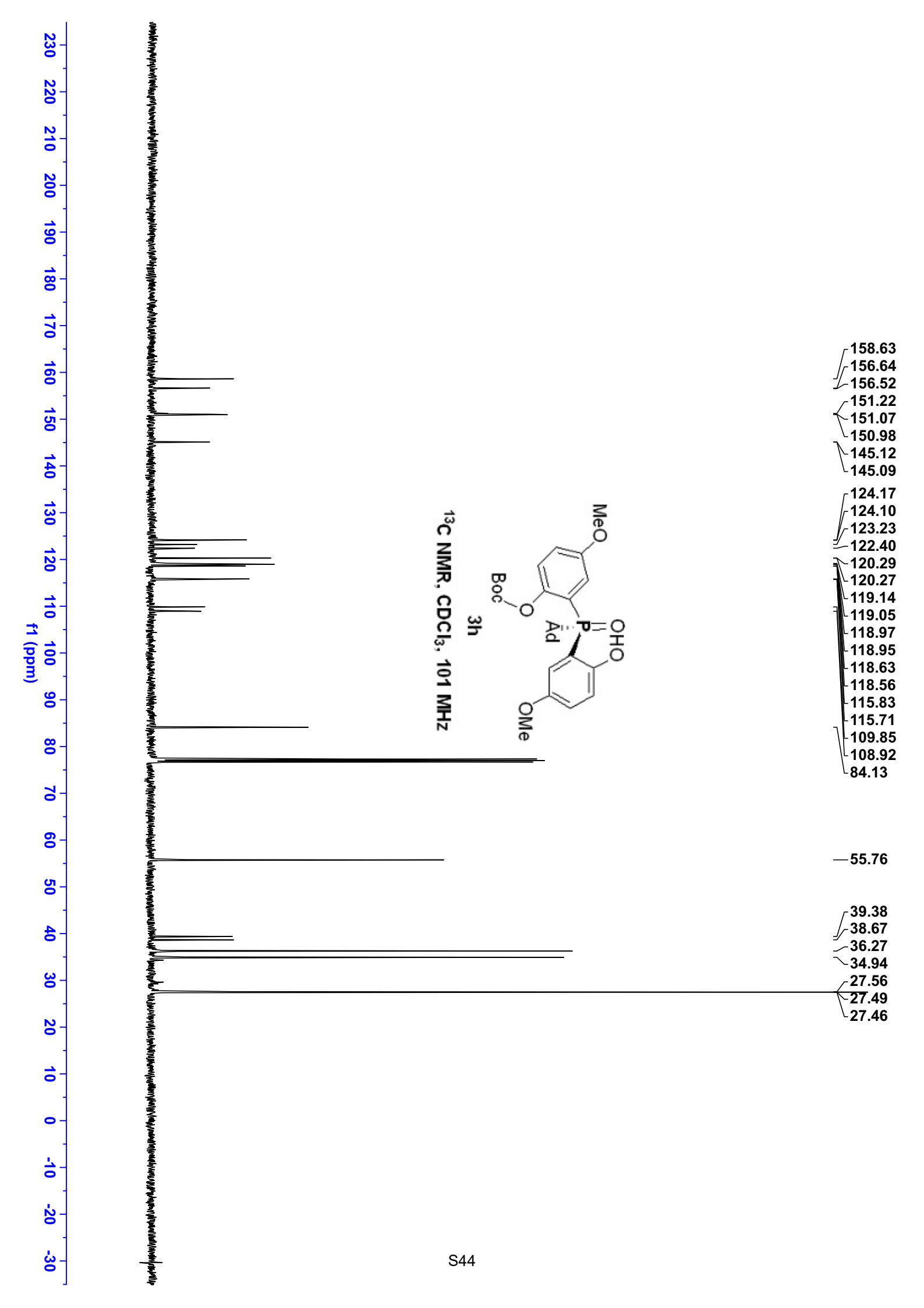

164.22
164.20
151.29
151.27
150.79
140.44
139.27
138.55
138.45
133.03
132.97
132.75
132.73
131.82
131.79
131.38
131.27
129.63
129.53
128.93
128.78
127.82
127.10
126.73
126.64
123.58
123.52
122.89
122.05
119.02
118.95
110.56
109.64
84.40
39.42
38.72
36.34
35.12
27.62
27.51
27.44
^{13}C NMR, CDCl$_3$, 101 MHz
3g
Ph
Boc
O
P
Ad
OHO
Ph
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30

3g

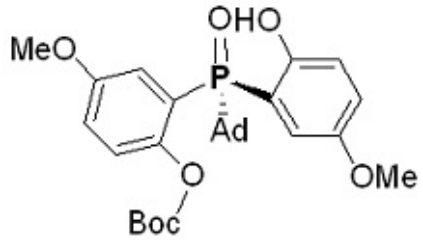
^{31}P NMR, $CDCl_3$, 162 MHz




f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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
0.5
0.0
0.38
1.01
2.07
1.05
1.06
1.00
3.12
3.09
9.38
6.09
9.38
11.35
10.14
7.66
7.65
7.63
7.62
7.22
7.21
7.20
7.20
7.18
7.18
7.17
7.07
7.06
7.04
7.04
6.98
6.97
6.96
6.95
6.85
6.84
6.83
6.81
3.84
3.76
2.04
2.03
1.76
1.72
1.69
1.51
^{1}H NMR, CDCl$_3$, 400 MHz
3h
MeO
Boc
O
P
Ad
OHO
OMe


158.63
156.64
156.52
151.22
151.07
150.98
145.12
145.09
124.17
124.10
123.23
122.40
120.29
120.27
119.14
119.05
118.97
118.95
118.63
118.56
115.83
115.71
109.85
108.92
84.13
55.76
39.38
38.67
36.27
34.94
27.56
27.49
27.46
MeO
Boc
O
P
Ad
OHO
OMe
3h
13C NMR, CDCl3, 101 MHz
f1 (ppm)

47.15

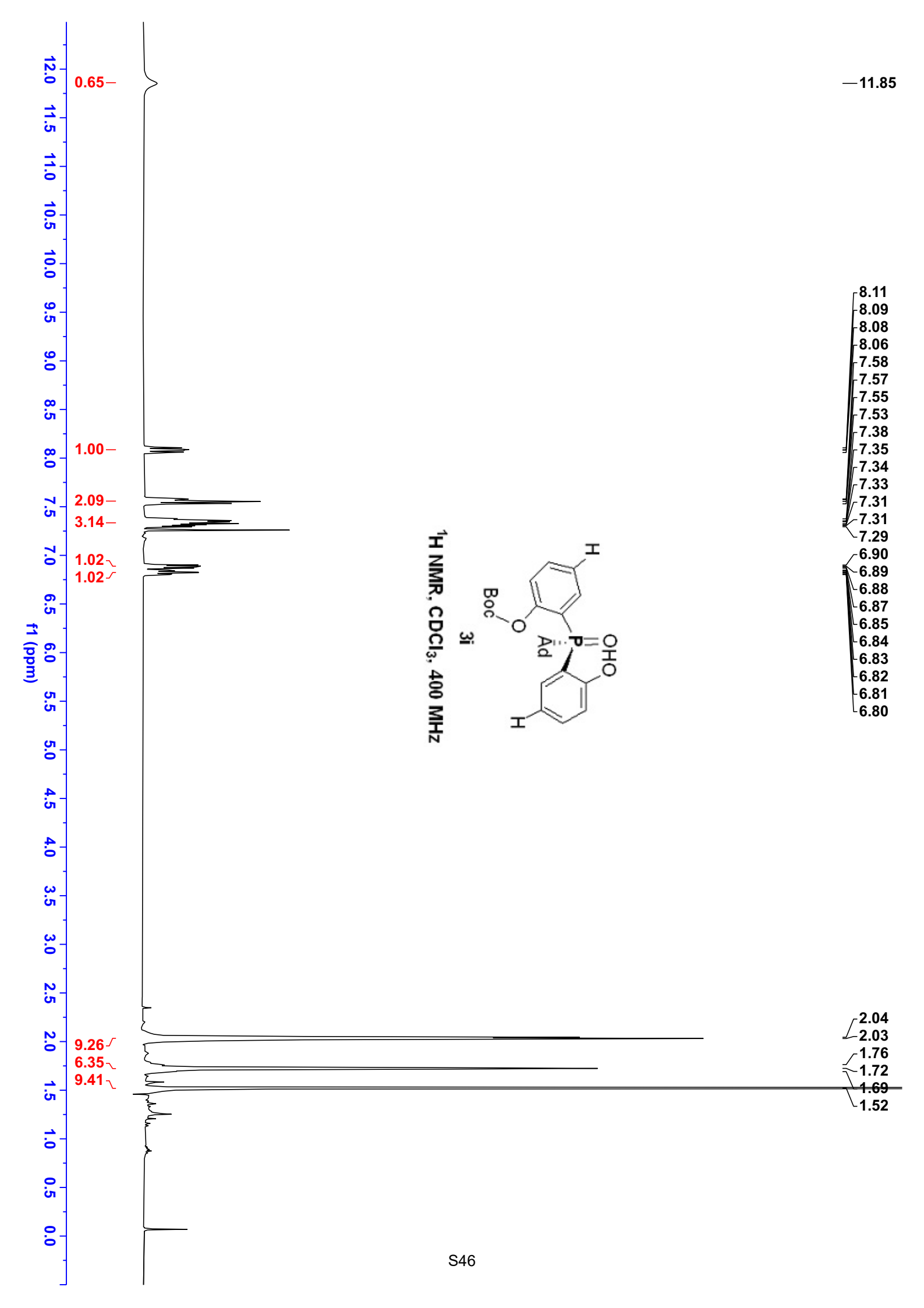


3h

^{31}P NMR, $CDCl_3$, 162 MHz

150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -250

f1 (ppm)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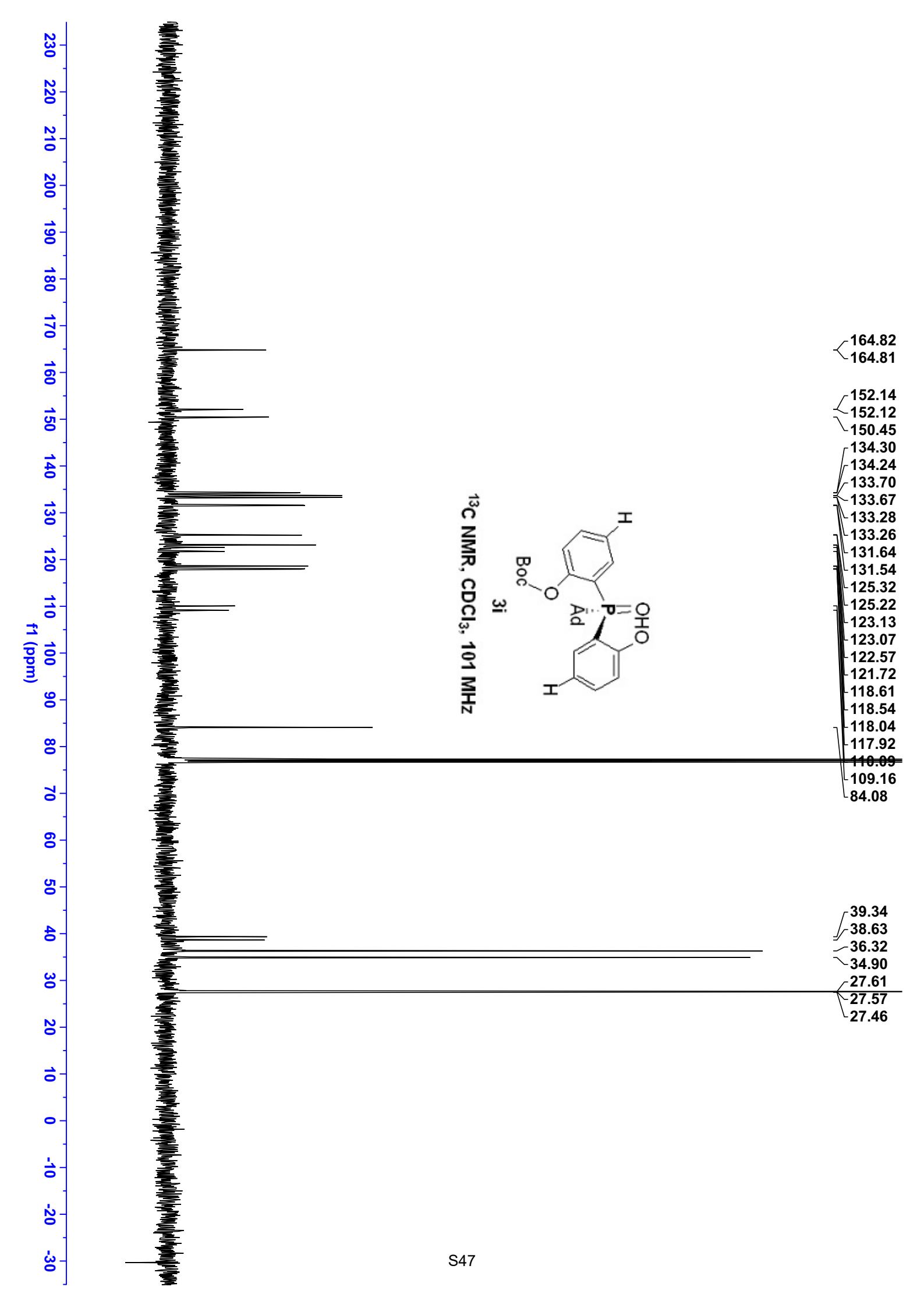
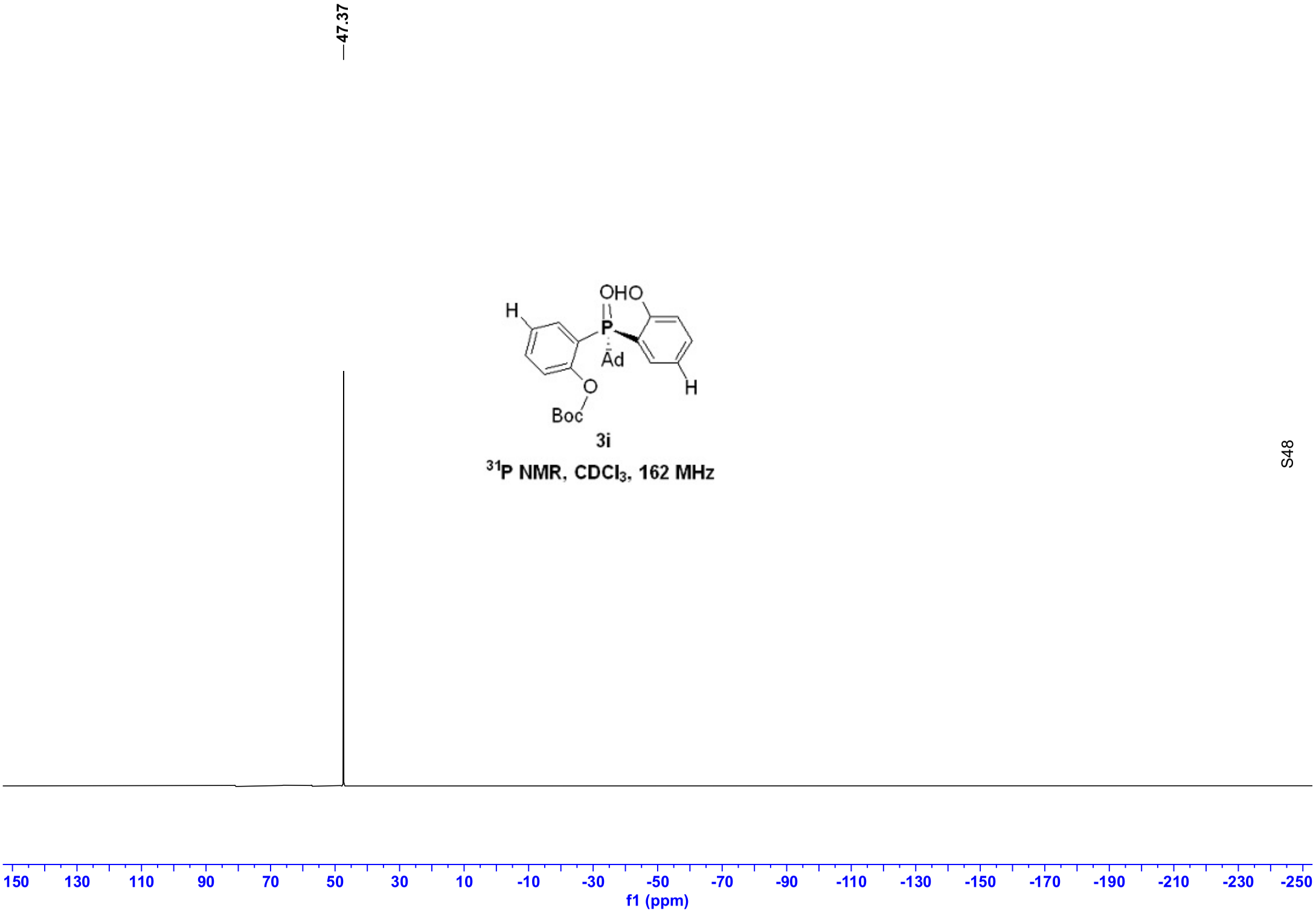
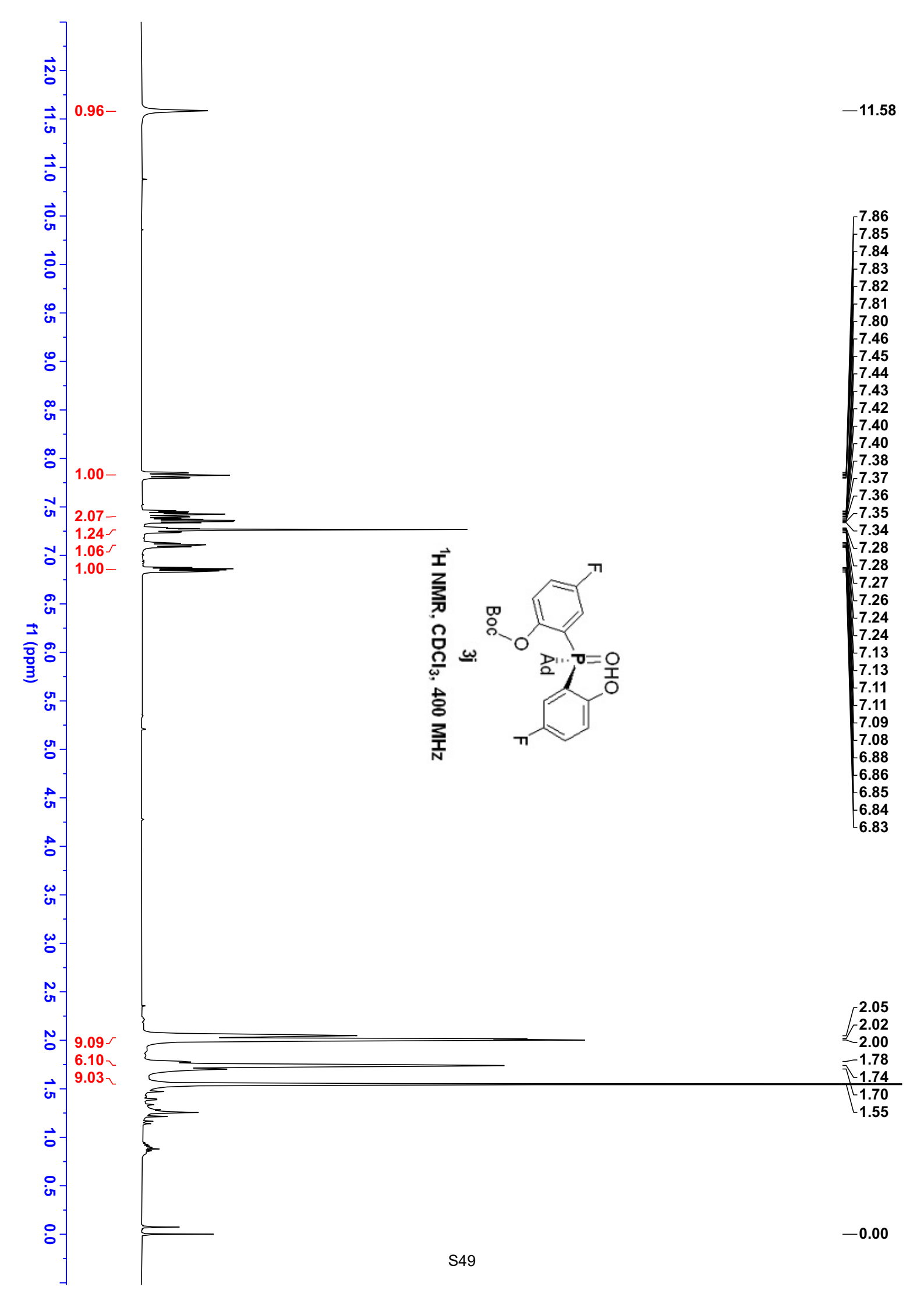
1.00
2.09
3.14
1.02
1.02
9.26
6.35
9.41
11.85
8.11
8.09
8.08
8.06
7.58
7.57
7.55
7.53
7.38
7.35
7.34
7.33
7.31
7.31
7.29
6.90
6.89
6.88
6.87
6.85
6.84
6.83
6.82
6.81
6.80
2.04
2.03
1.76
1.72
1.69
1.52
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
^{1}H NMR, CDCl$_3$, 400 MHz
3i
Boc
O
P
Ad
OHO
H
H

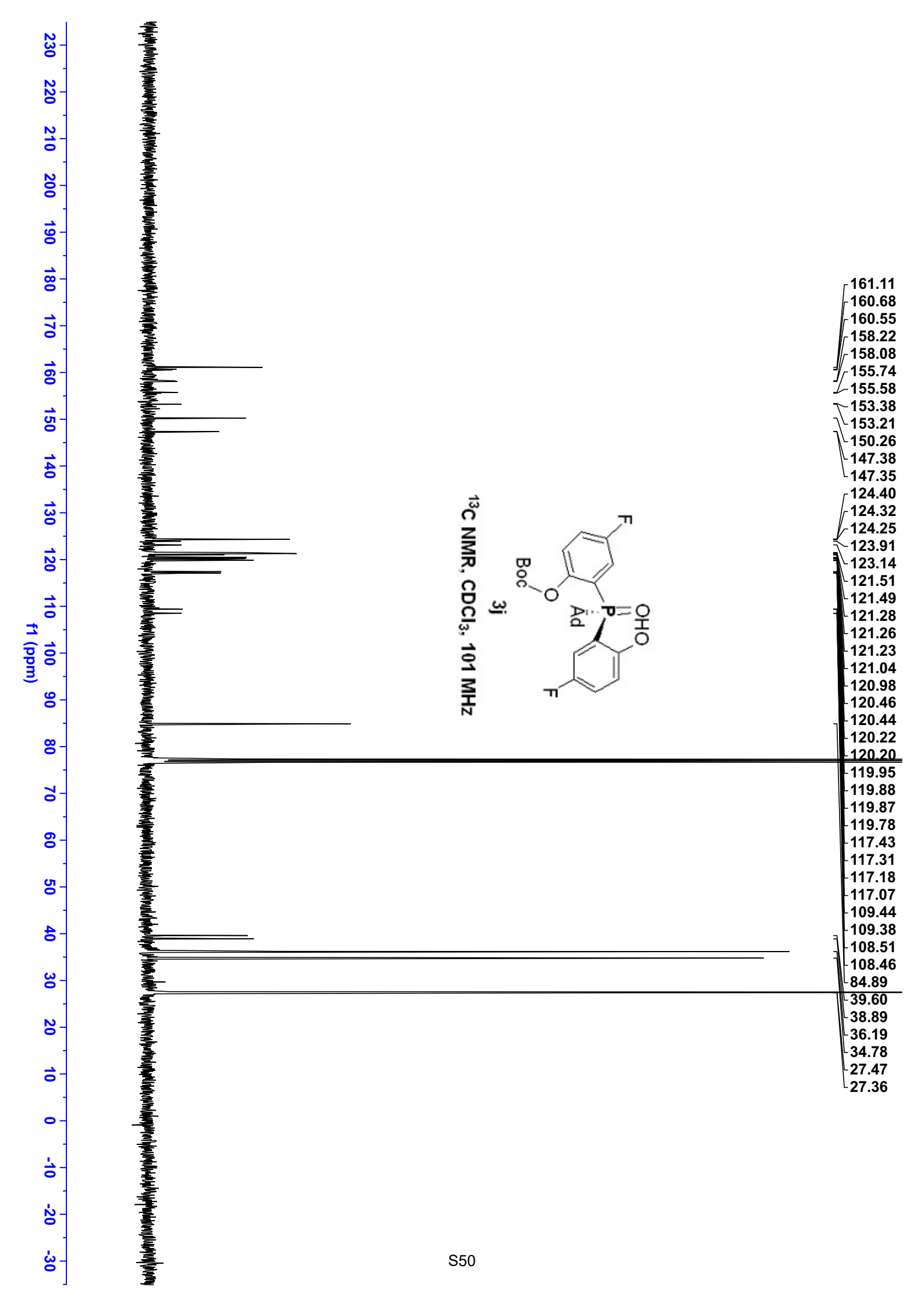

164.82
164.81
152.14
152.12
150.45
134.30
134.24
133.70
133.67
133.28
133.26
131.64
131.54
125.32
125.22
123.13
123.07
122.57
121.72
118.61
118.54
118.04
117.92
110.09
109.16
84.08
39.34
38.63
36.32
34.90
27.61
27.57
27.46
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
^{13}C NMR, CDCl$_3$, 101 MHz
3i
Boc
O
P
Ad
OHO
H
H

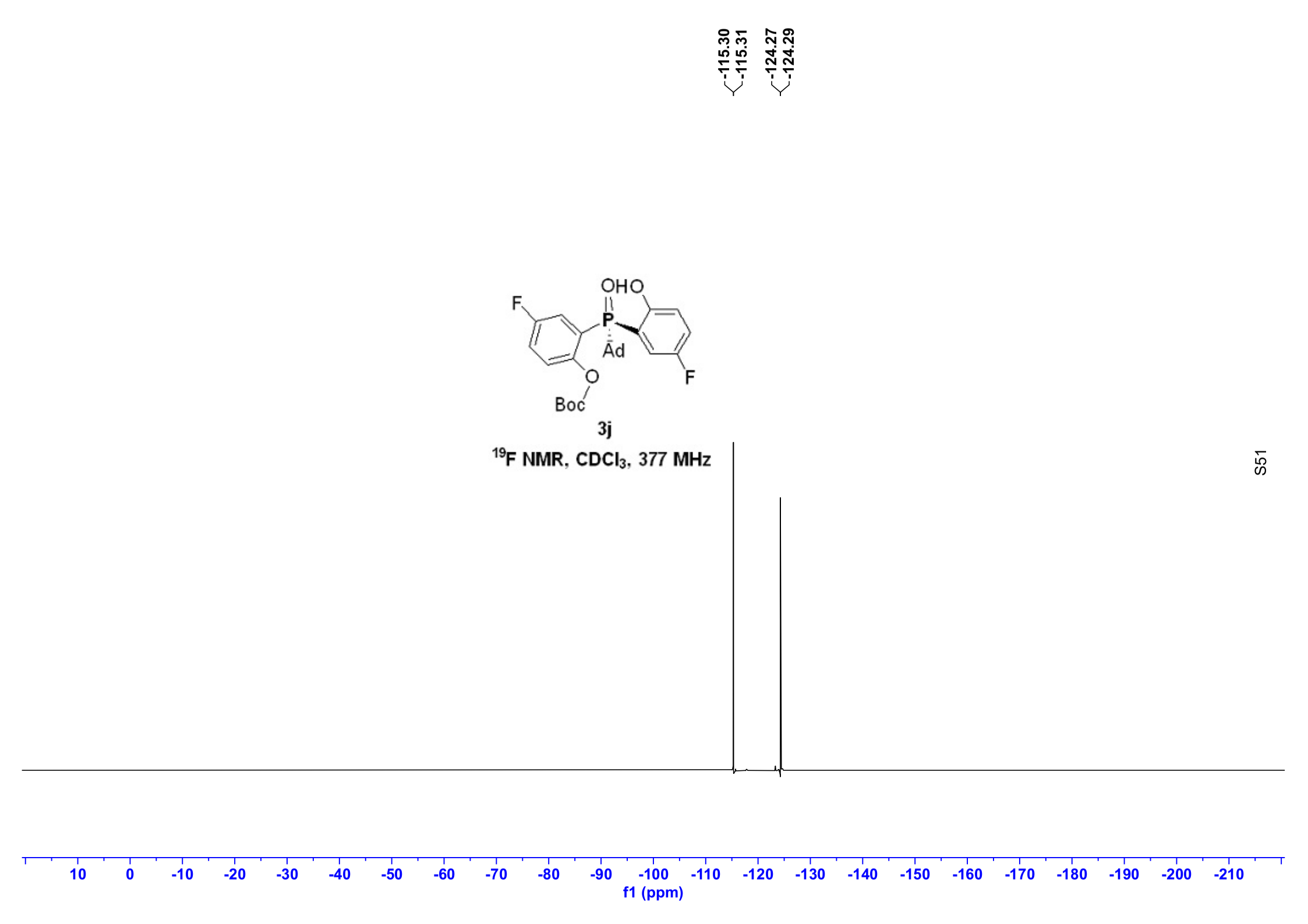
3i

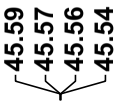
^{31}P NMR, $CDCl_3$, 162 MHz

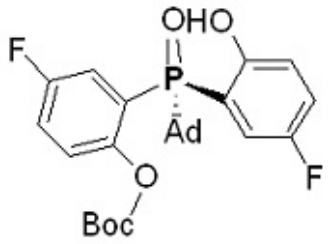



0.96
1.00
2.07
1.24
1.06
1.00
9.09
6.10
9.03
11.58
7.86
7.85
7.84
7.83
7.82
7.81
7.80
7.46
7.45
7.44
7.43
7.42
7.40
7.40
7.38
7.37
7.36
7.35
7.34
7.28
7.28
7.27
7.26
7.24
7.24
7.13
7.13
7.11
7.11
7.09
7.08
6.88
6.86
6.85
6.84
6.83
2.05
2.02
2.00
1.78
1.74
1.70
1.55
0.00
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
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
0.5
0.0
^{1}H NMR, CDCl$_3$, 400 MHz
3j
F
Boc
O
P
Ad
OHO
F


161.11
160.68
160.55
158.22
158.08
155.74
155.58
153.38
153.21
150.26
147.38
147.35
124.40
124.32
124.25
123.91
123.14
121.51
121.49
121.28
121.26
121.23
121.04
120.98
120.46
120.44
120.22
120.20
119.95
119.88
119.87
119.78
117.43
117.31
117.18
117.07
109.44
109.38
108.51
108.46
84.89
39.60
38.89
36.19
34.78
27.47
27.36
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
F
Boc
O
P
Ad
OHO
F
3j
13C NMR, CDCl3, 101 MHz

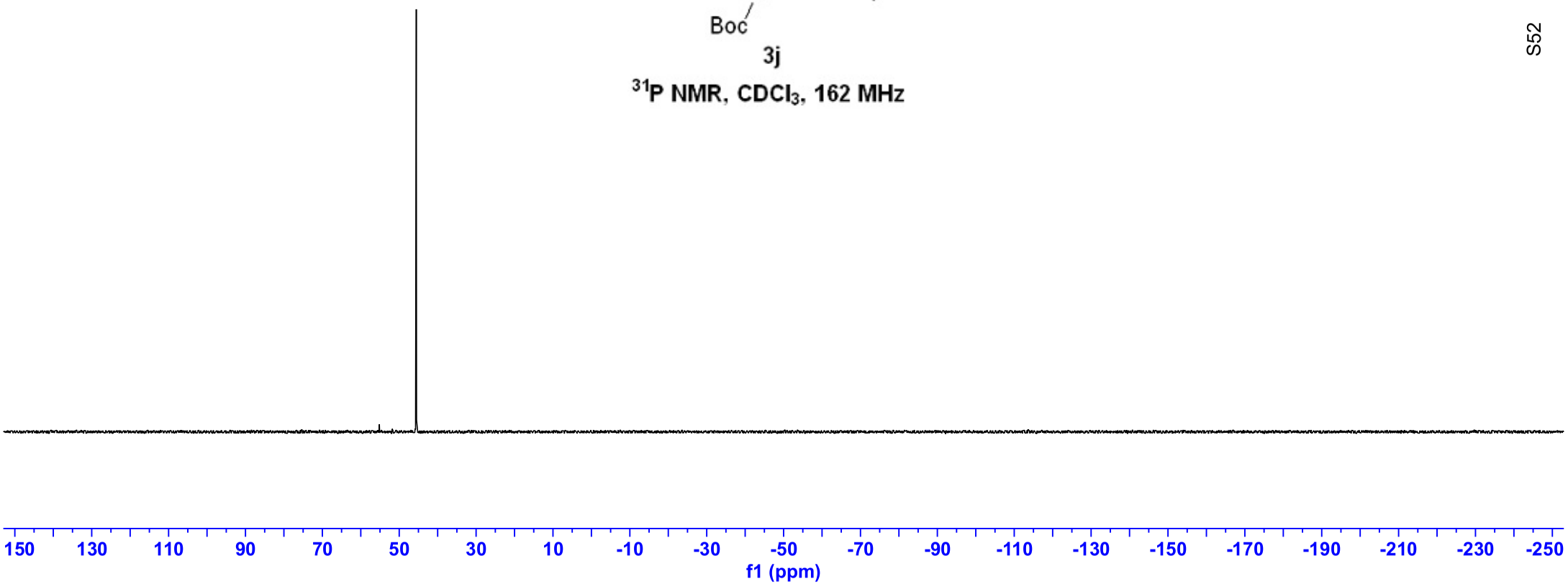

-115.30
-115.31
-124.27
-124.29
OH
O
F
P
Ad
O
F
Boc
3j
^{19}F NMR, $CDCl_3$, 377 MHz
S51
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

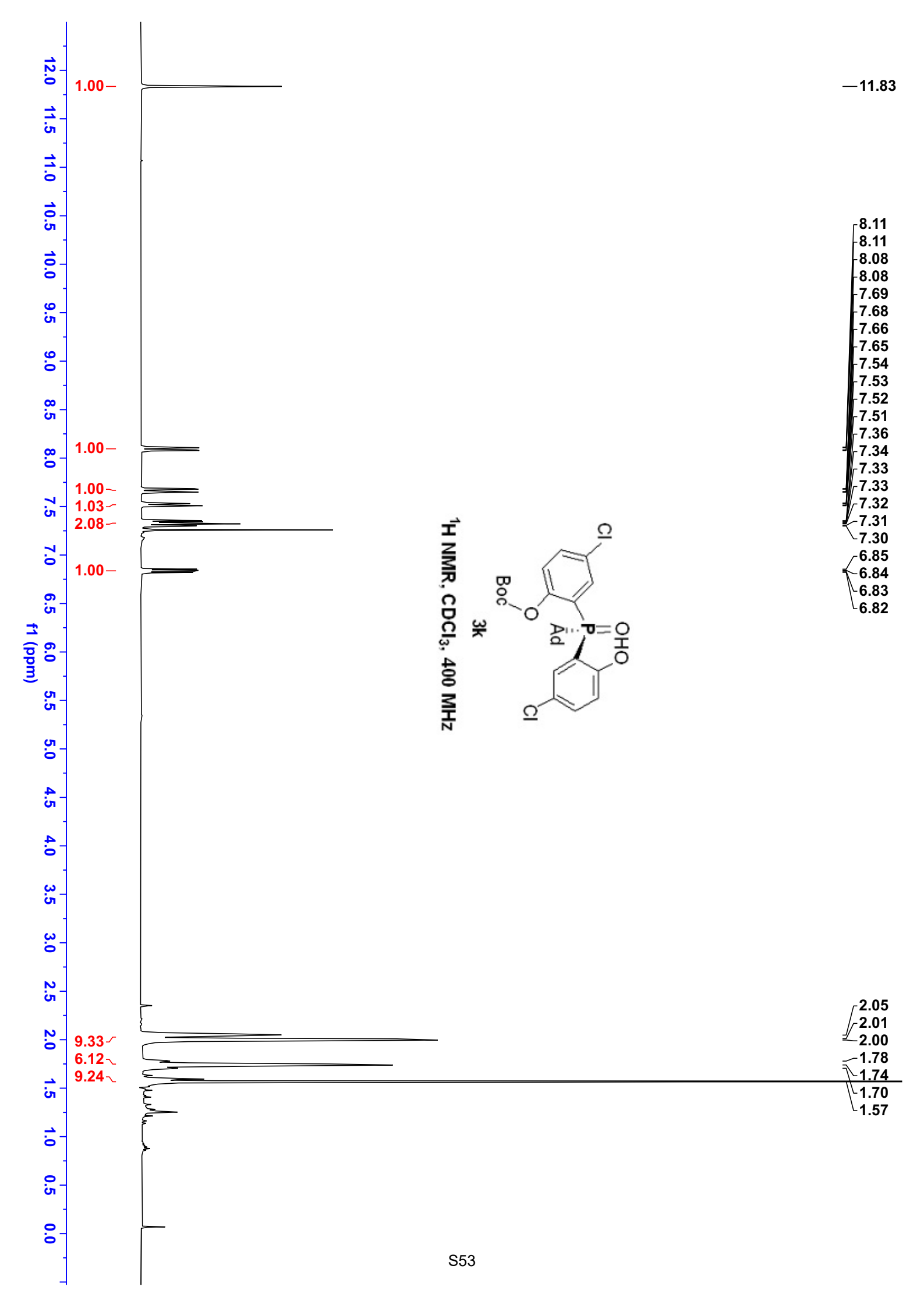


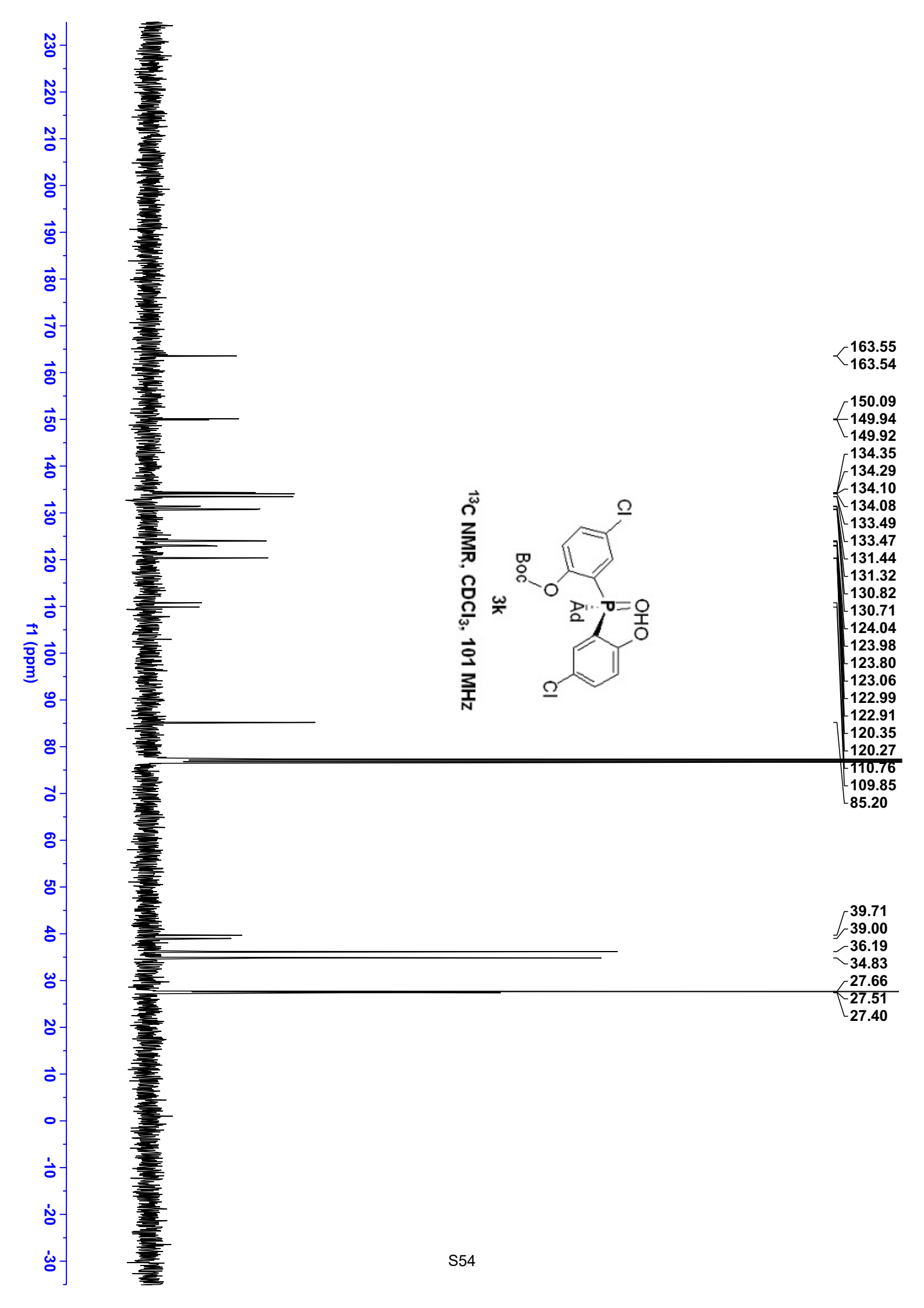


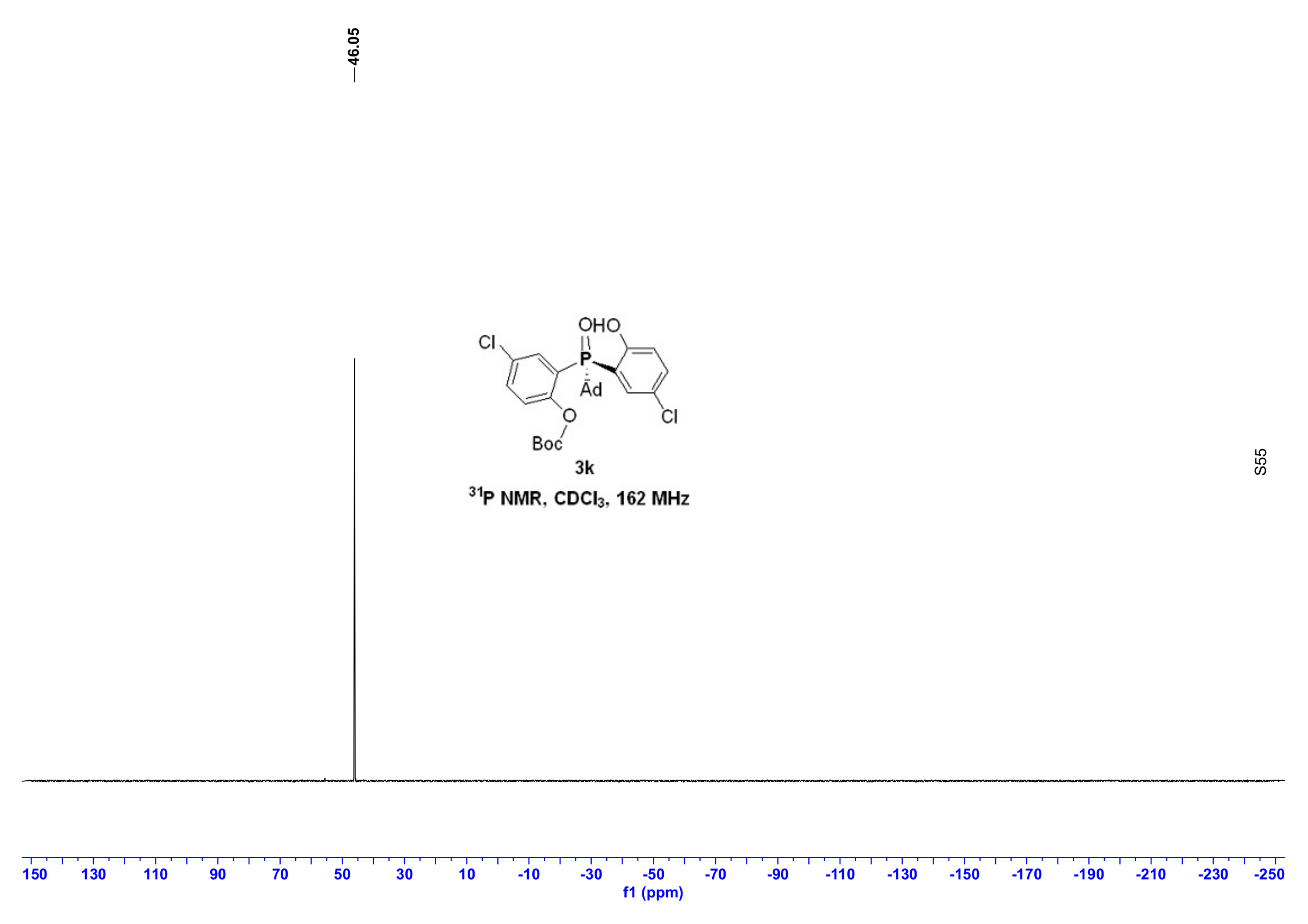
3j

^{31}P NMR, $CDCl_3$, 162 MHz



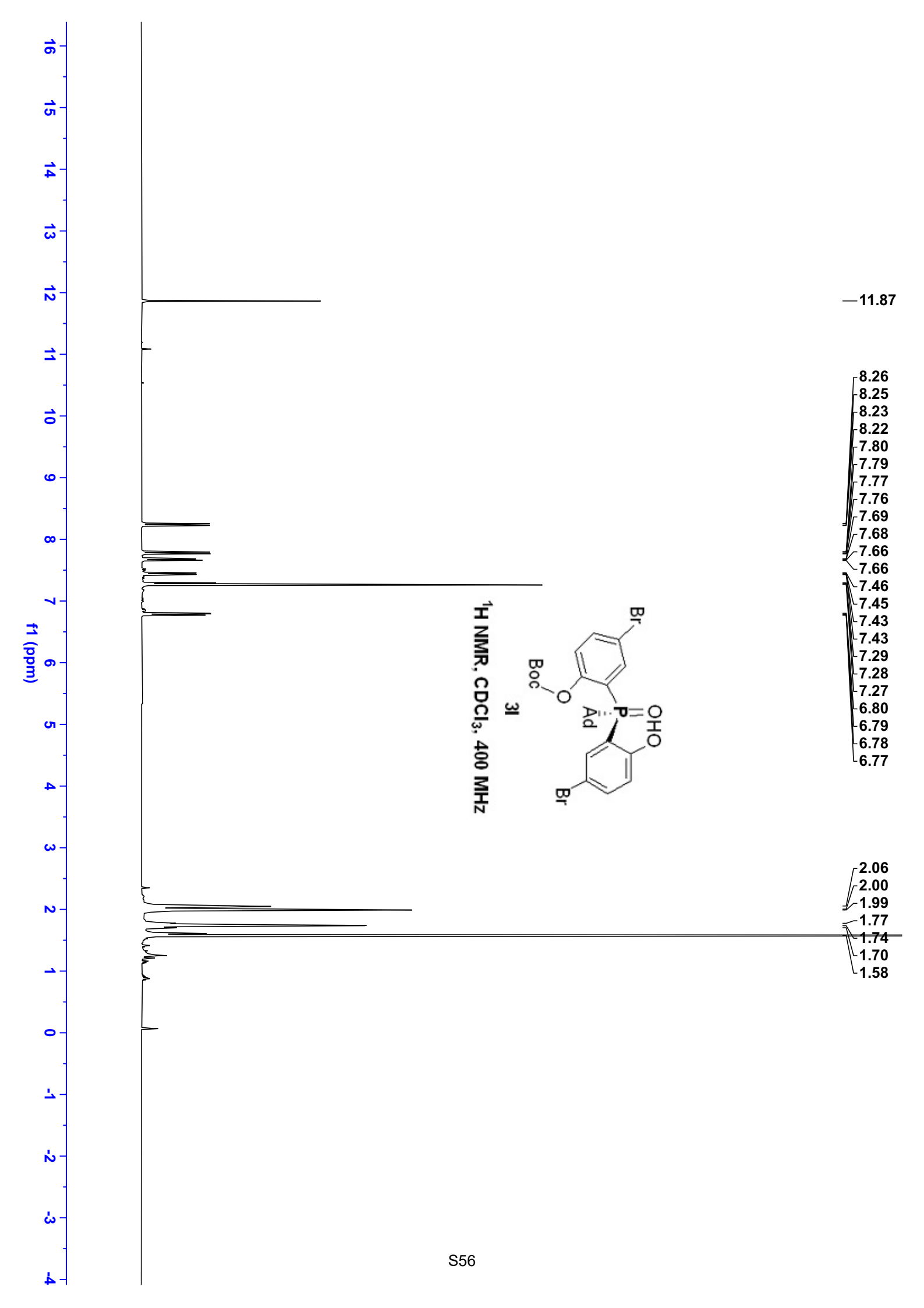

1.00
1.00
1.00
1.03
2.08
1.00
9.33
6.12
9.24
11.83
8.11
8.11
8.08
8.08
7.69
7.68
7.66
7.65
7.54
7.53
7.52
7.51
7.36
7.34
7.33
7.33
7.32
7.31
7.30
6.85
6.84
6.83
6.82
2.05
2.01
2.00
1.78
1.74
1.70
1.57
f1 (ppm)
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Cl
Boc
O
P
Ad
OHO
Cl
3k
^{1}H NMR, CDCl$_3$, 400 MHz

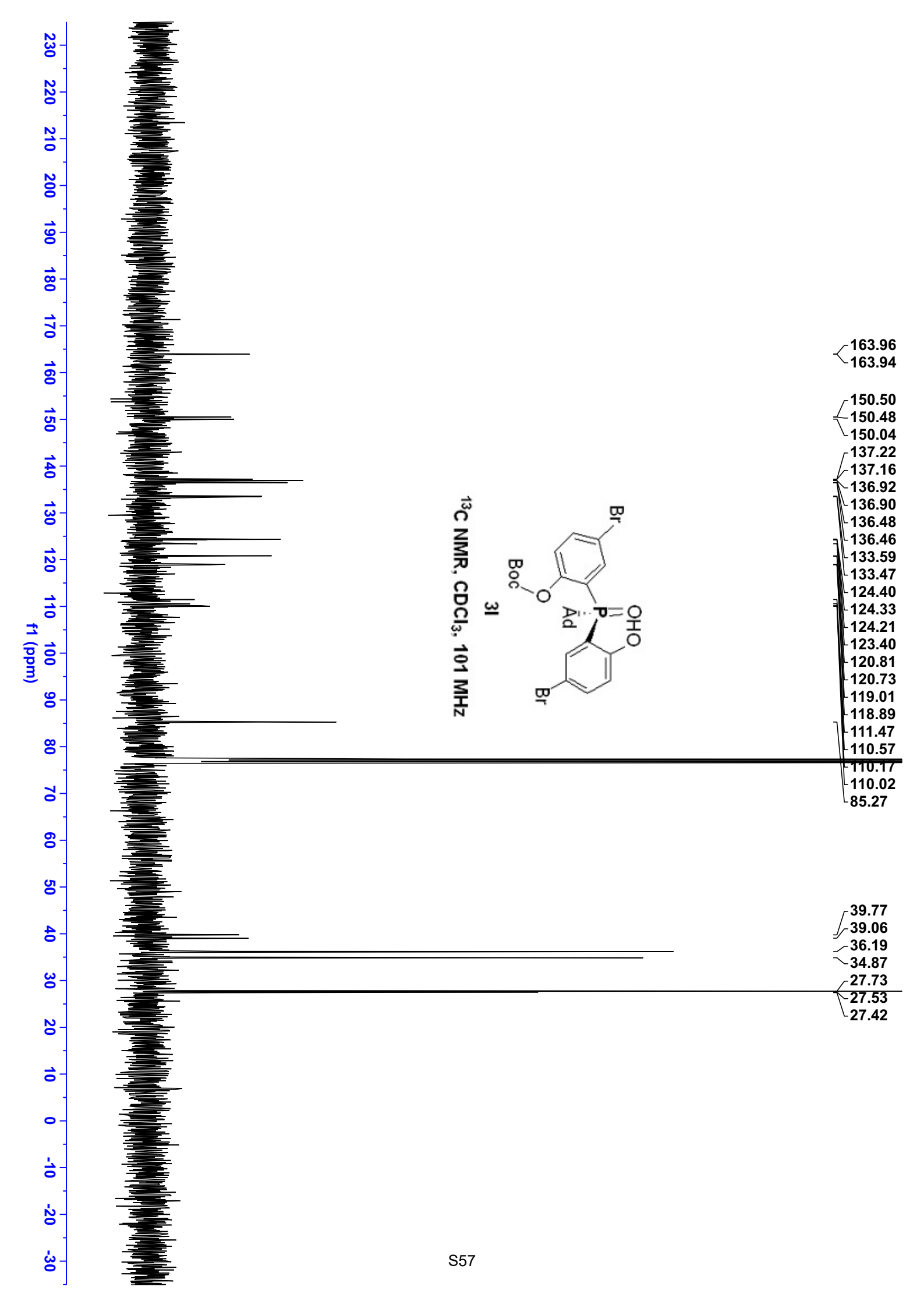

163.55
163.54
150.09
149.94
149.92
134.35
134.29
134.10
134.08
133.49
133.47
131.44
131.32
130.82
130.71
124.04
123.98
123.80
123.06
122.99
122.91
120.35
120.27
110.76
109.85
85.20
39.71
39.00
36.19
34.83
27.66
27.51
27.40
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
^{13}C NMR, CDCl$_3$, 101 MHz
3k
Cl
Boc
O
P
Ad
OHO
Cl



3k

^{31}P NMR, $CDCl_3$, 162 MHz


11.87
8.26
8.25
8.23
8.22
7.80
7.79
7.77
7.76
7.69
7.68
7.66
7.66
7.46
7.45
7.43
7.43
7.29
7.28
7.27
6.80
6.79
6.78
6.77
2.06
2.00
1.99
1.77
1.74
1.70
1.58
f1 (ppm)
16
15
14
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
-3
-4
^{1}H NMR, CDCl$_3$, 400 MHz
3l
Br
Boc
O
P
Ad
OHO
Br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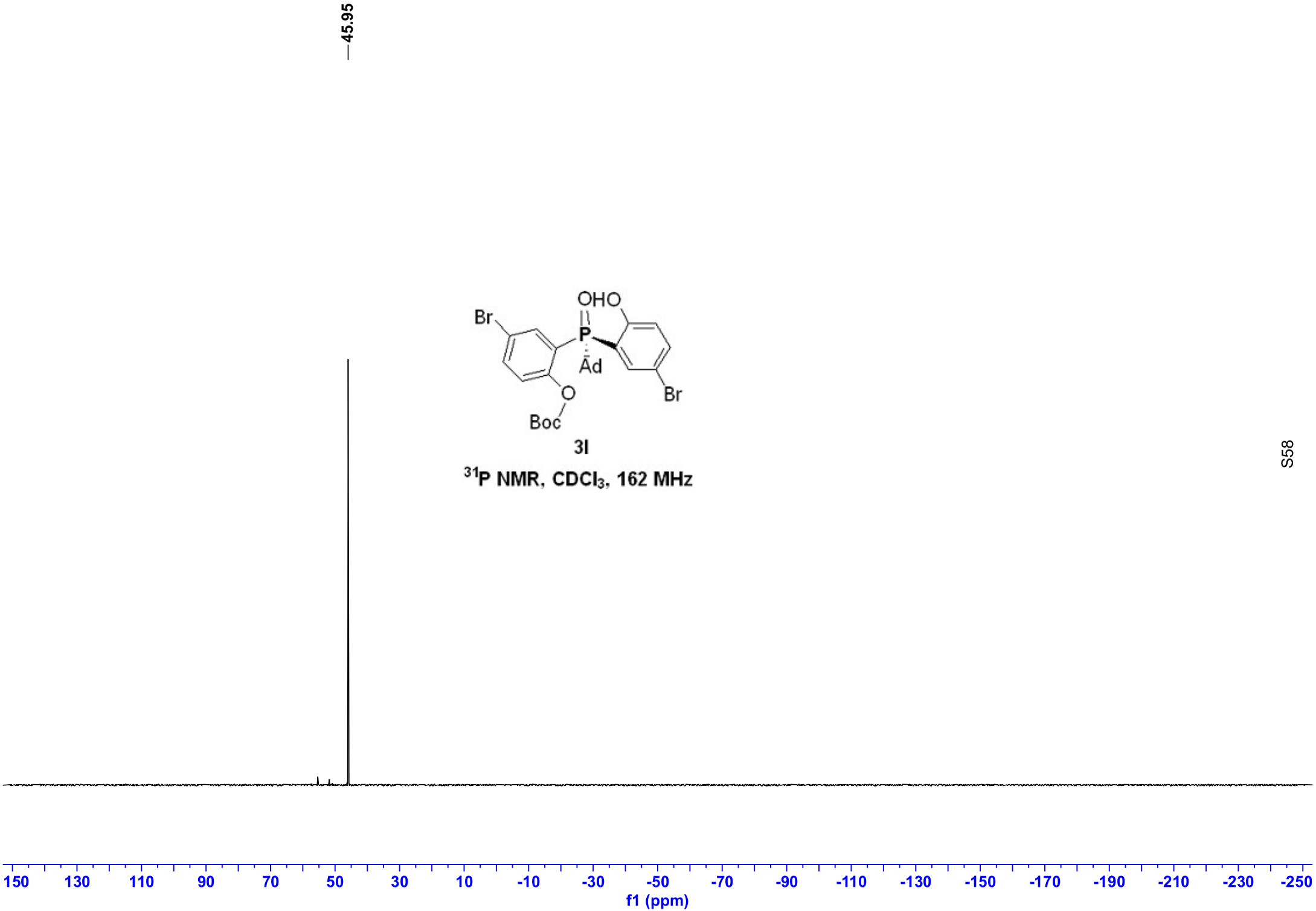
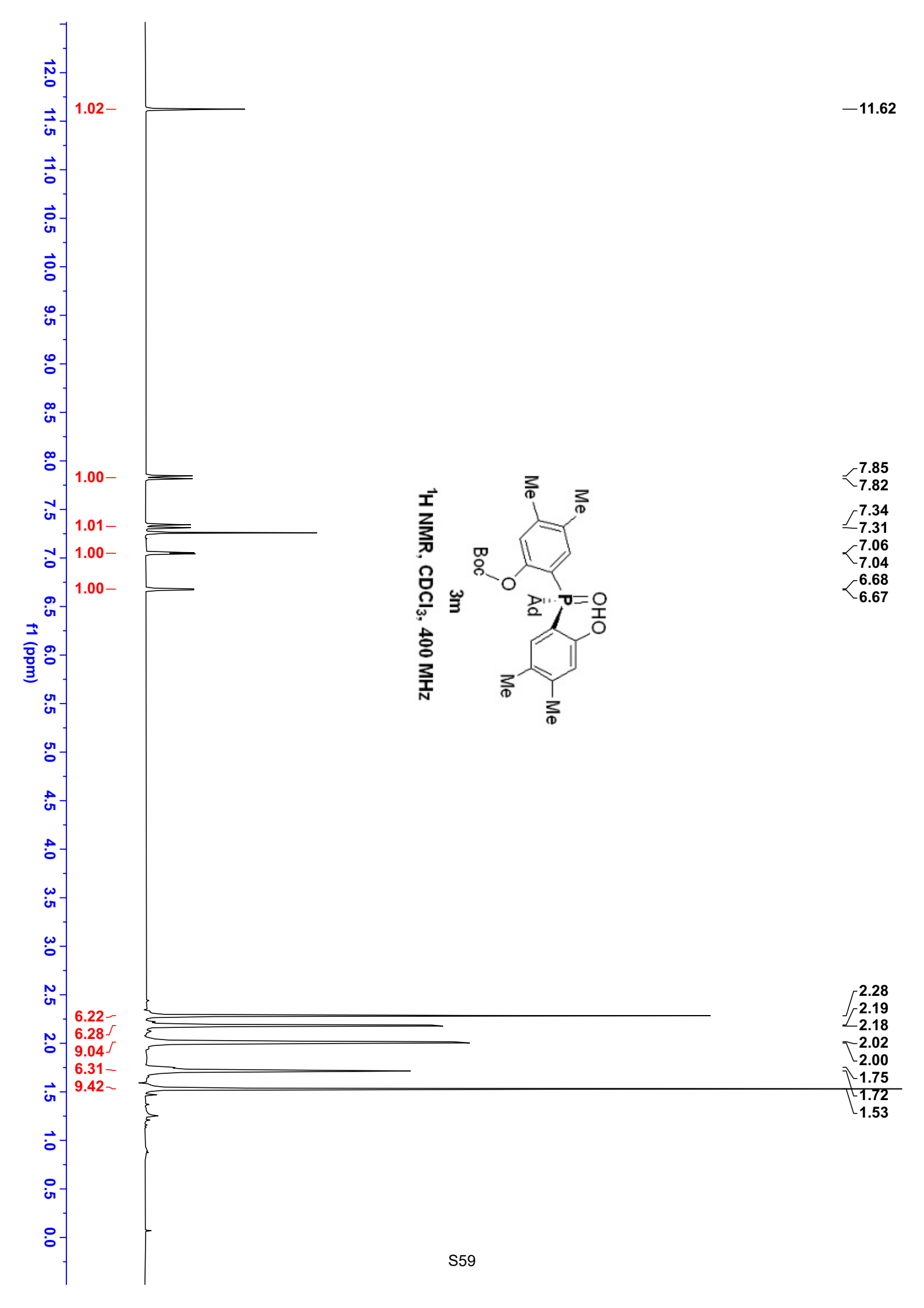
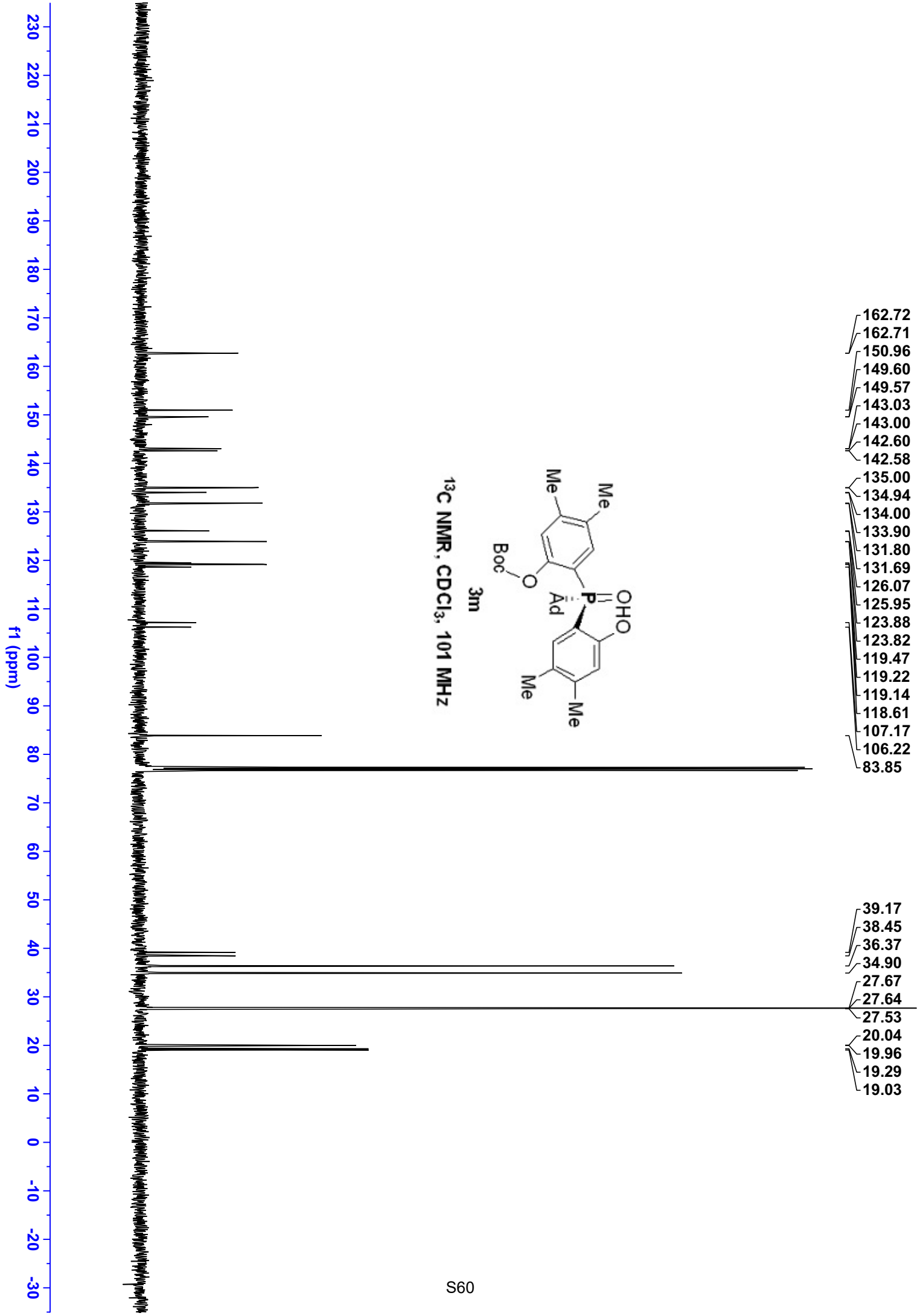
163.94
150.50
150.48
150.04
137.22
137.16
136.92
136.90
136.48
136.46
133.59
133.47
124.40
124.33
124.21
123.40
120.81
120.73
119.01
118.89
111.47
110.57
110.17
110.02
85.27
39.77
39.06
36.19
34.87
27.73
27.53
27.42
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
Br
Boc
O
P
Ad
OHO
Br
3l
13C NMR, CDCl3, 101 MHz

3l

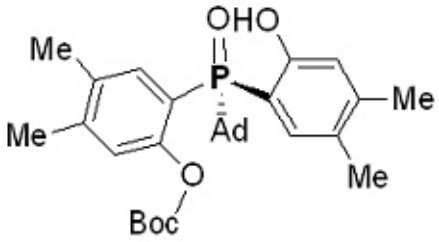
^{31}P NMR, $CDCl_3$, 162 MHz




1.02
1.00
1.01
1.00
1.00
6.22
6.28
9.04
6.31
9.42
11.62
7.85
7.82
7.34
7.31
7.06
7.04
6.68
6.67
2.28
2.19
2.18
2.02
2.00
1.75
1.72
1.53
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3m
Me
Me
Boc
O
P
Ad
OHO
Me
Me

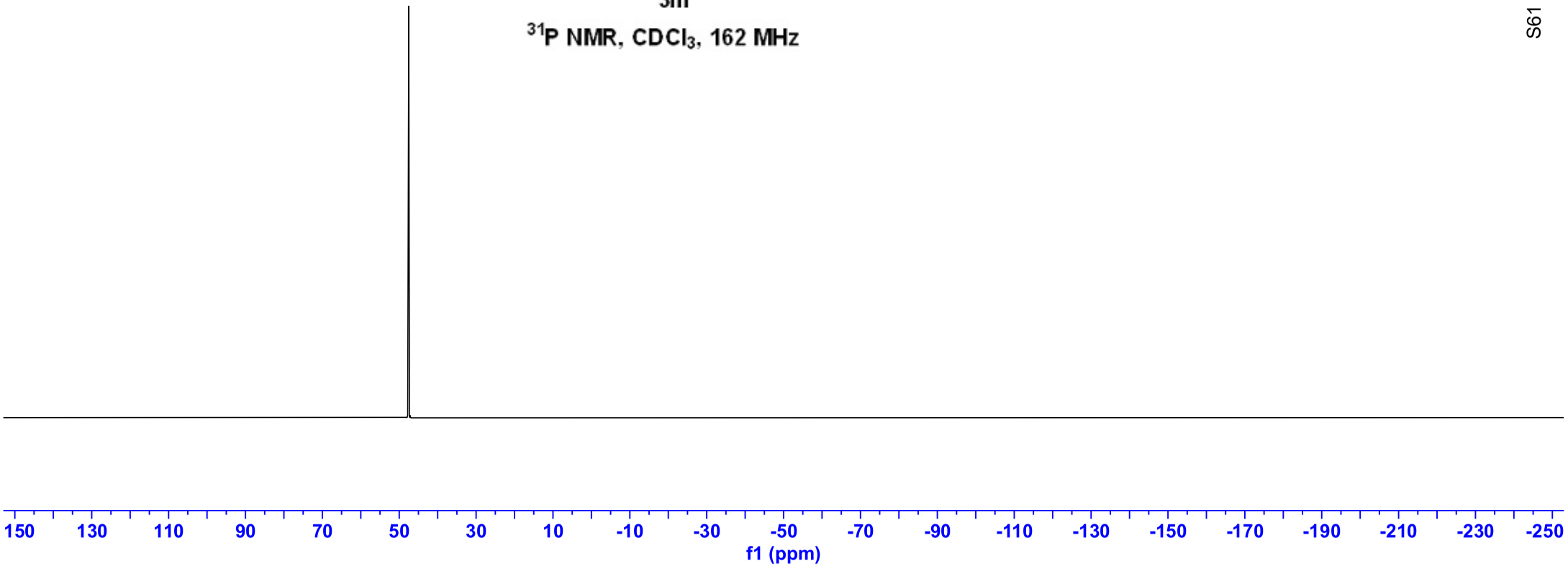

f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
162.72
162.71
150.96
149.60
149.57
143.03
143.00
142.60
142.58
135.00
134.94
134.00
133.90
131.80
131.69
126.07
125.95
123.88
123.82
119.47
119.22
119.14
118.61
107.17
106.22
83.85
39.17
38.45
36.37
34.90
27.67
27.64
27.53
20.04
19.96
19.29
19.03
^{13}C NMR, CDCl$_3$, 101 MHz
3m
Me
Me
Boc
O
P
Ad
OHO
Me
Me

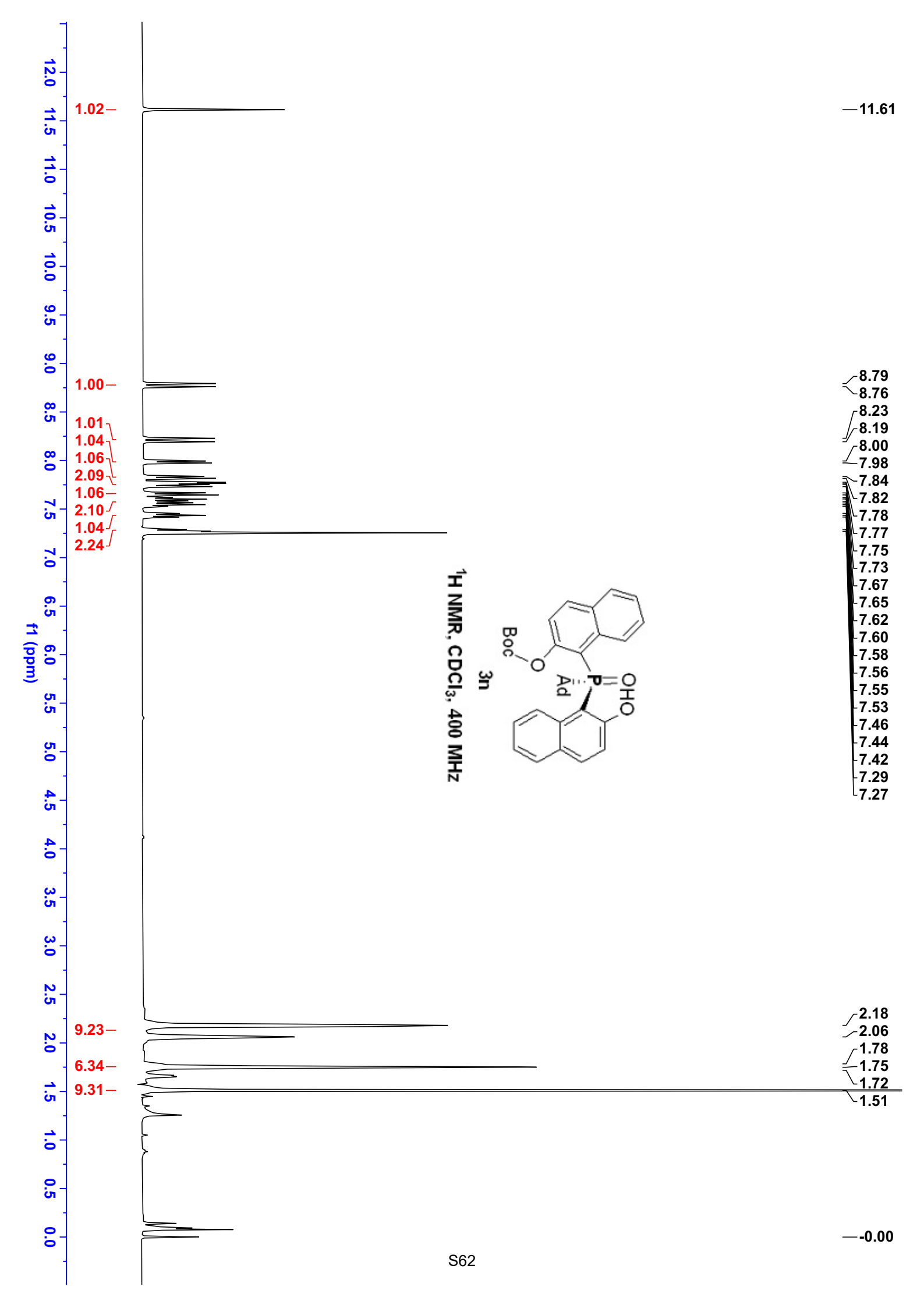
47.52

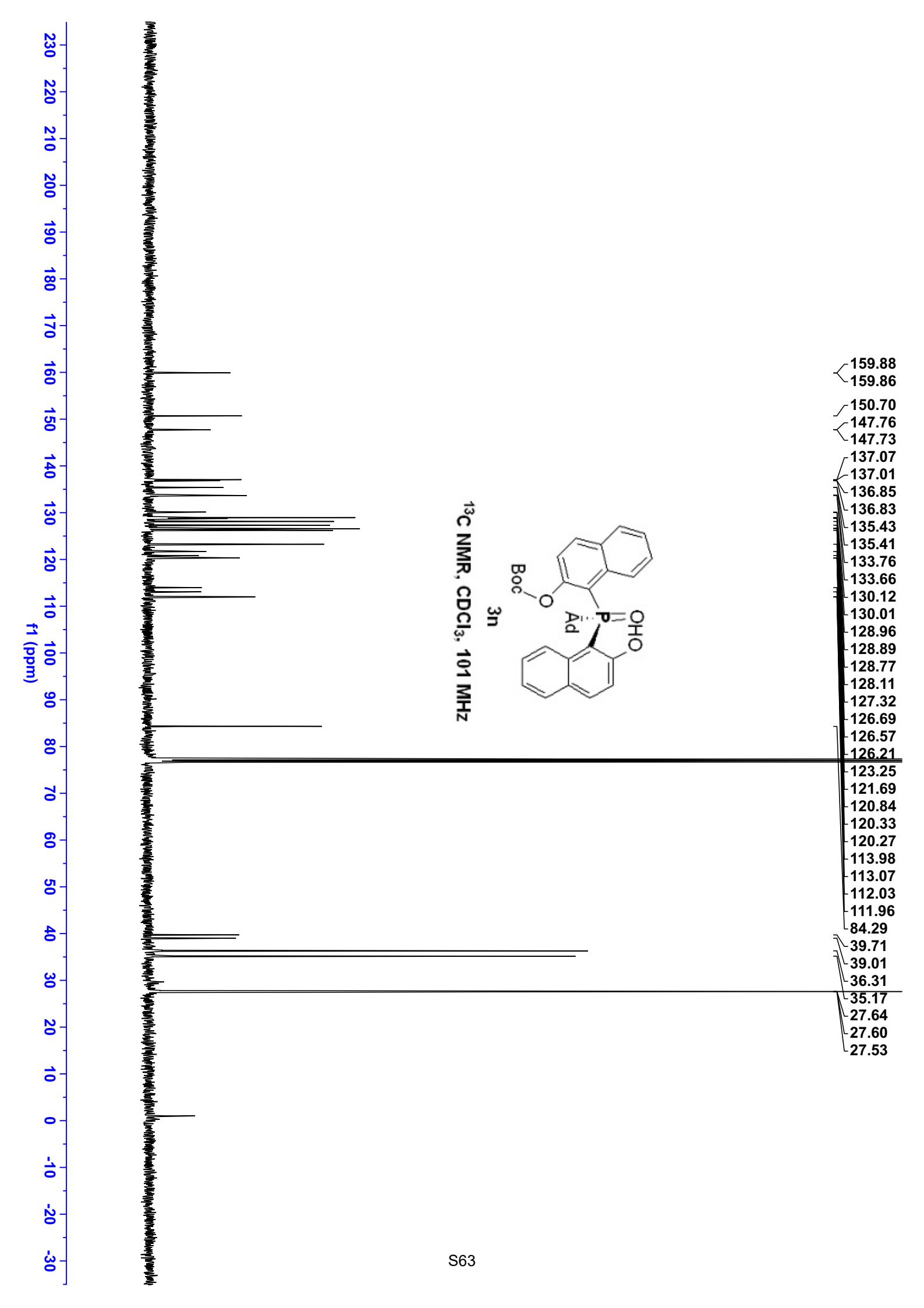


3m

^{31}P NMR, $CDCl_3$, 162 MHz

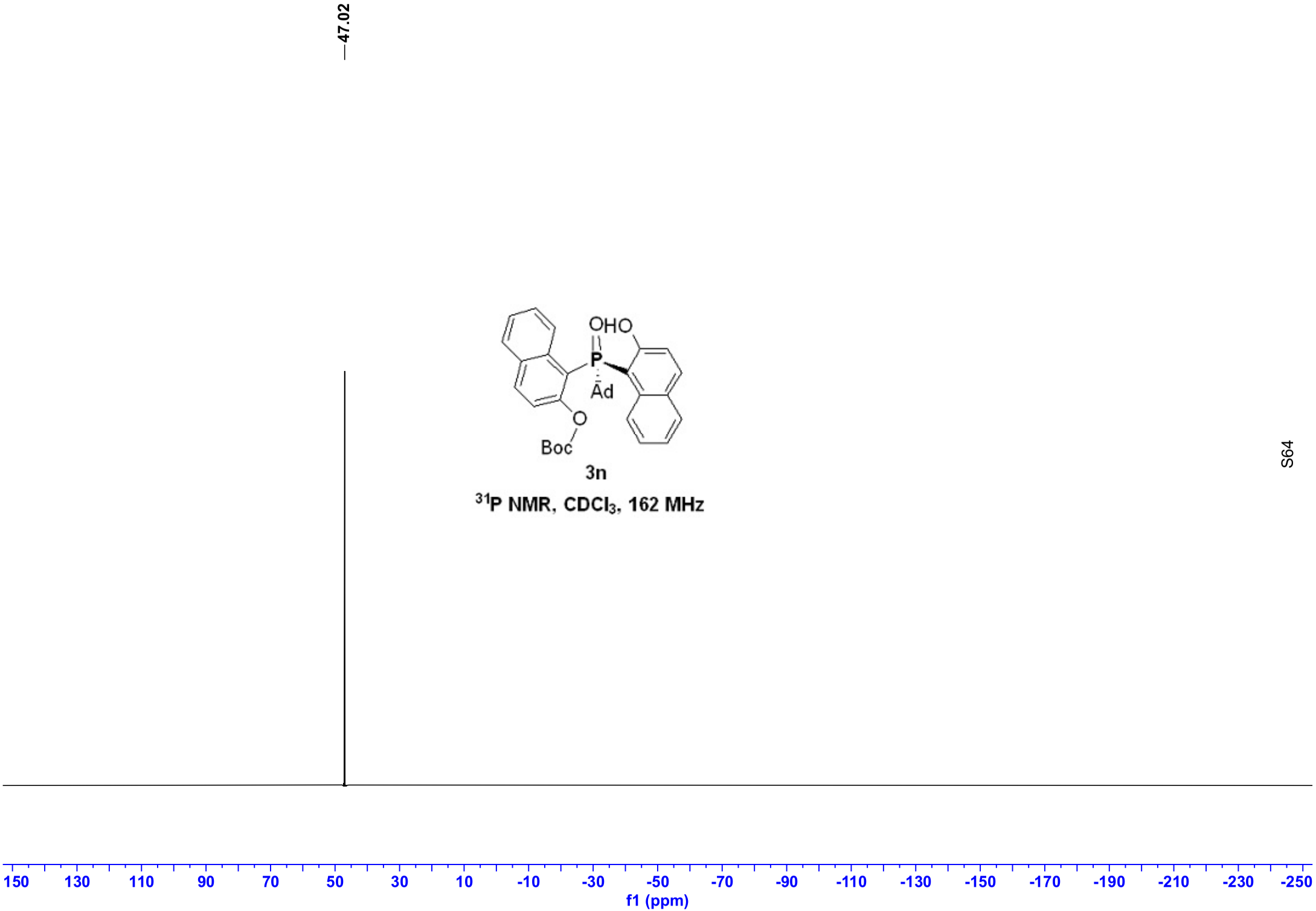


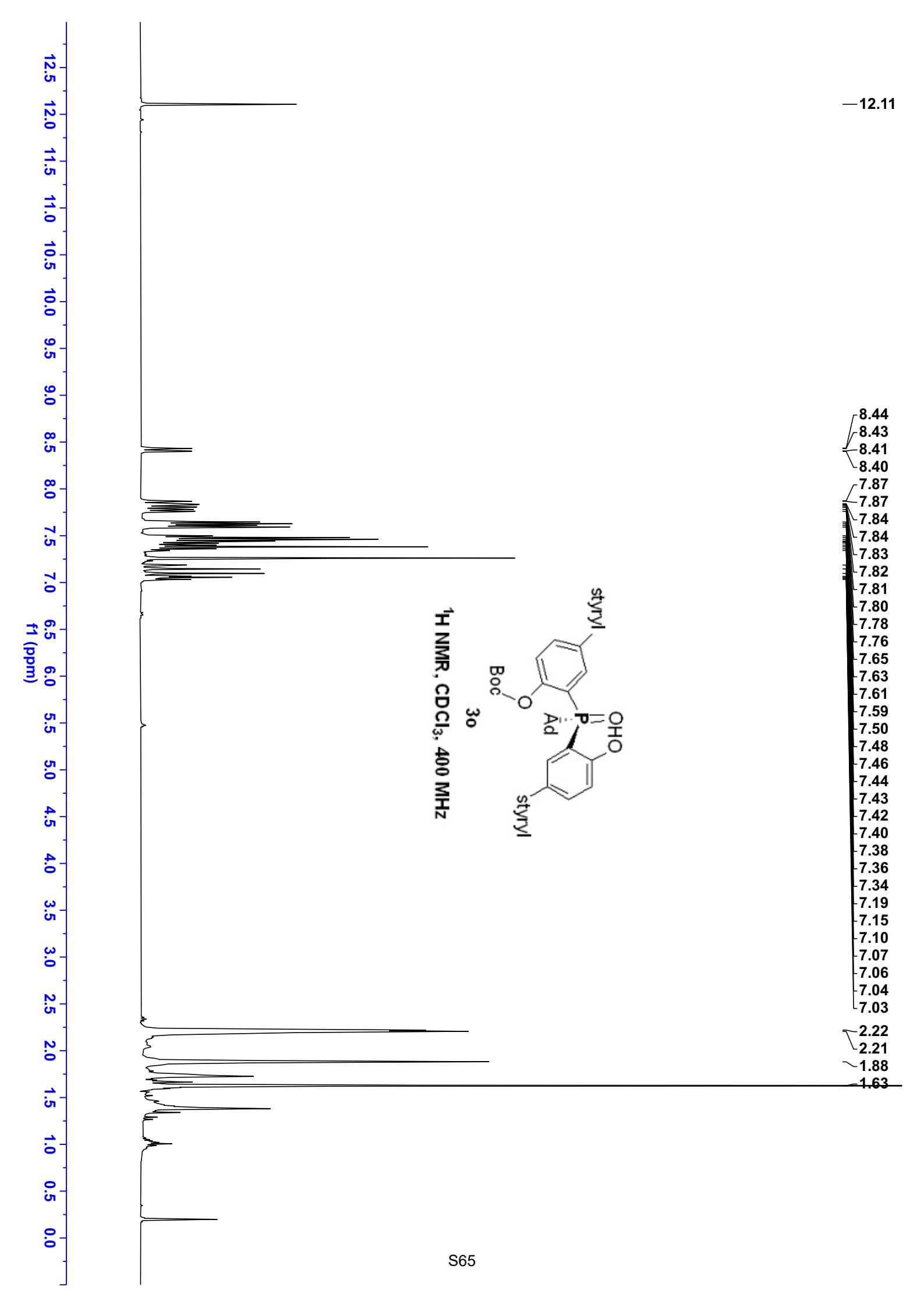

1.02
1.00
1.01
1.04
1.06
2.09
1.06
2.10
1.04
2.24
9.23
6.34
9.31
11.61
8.79
8.76
8.23
8.19
8.00
7.98
7.84
7.82
7.78
7.77
7.75
7.73
7.67
7.65
7.62
7.60
7.58
7.56
7.55
7.53
7.46
7.44
7.42
7.29
7.27
2.18
2.06
1.78
1.75
1.72
1.51
-0.00
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3n
Boc
O
P
Ad
OHO

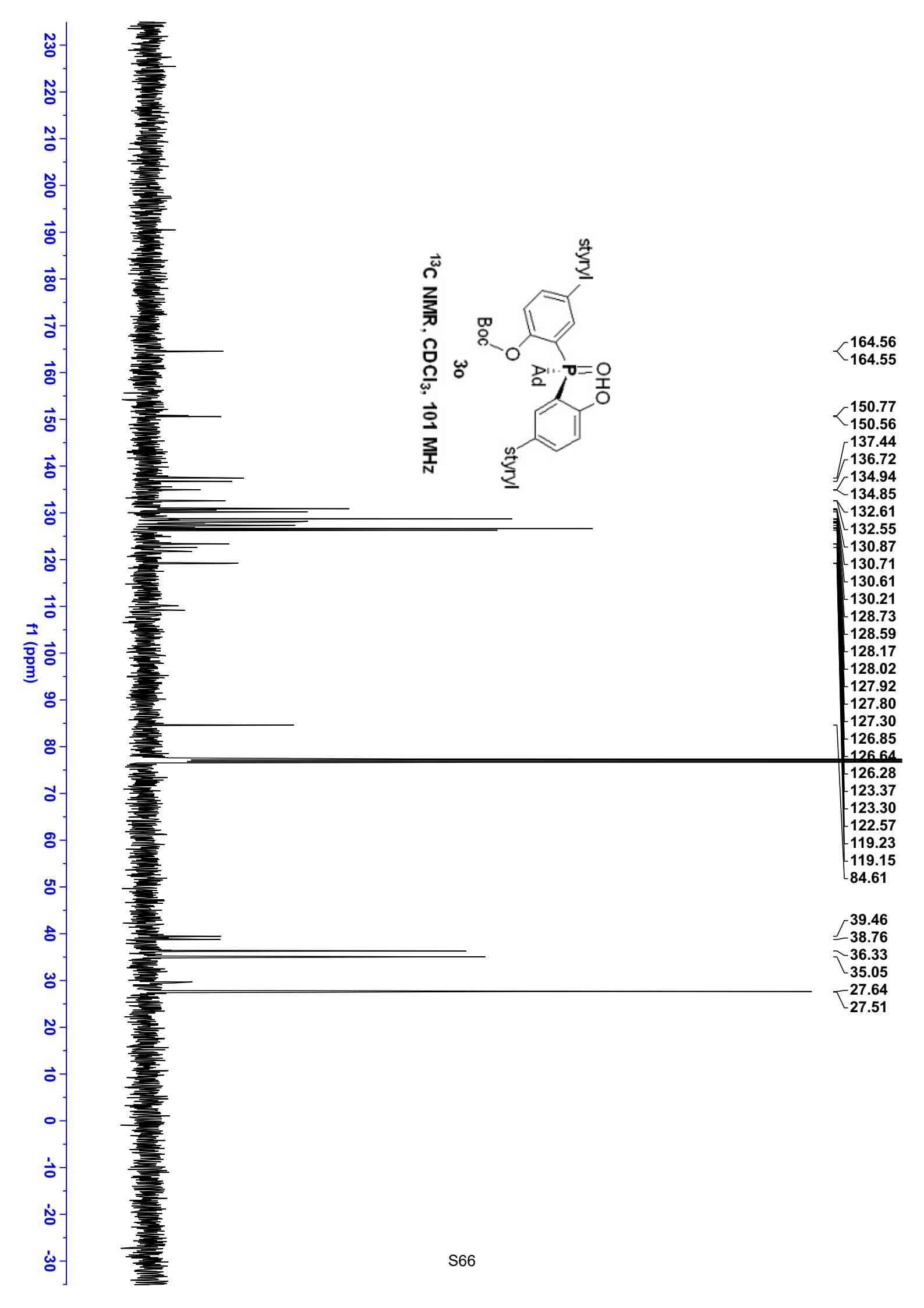

159.88
159.86
150.70
147.76
147.73
137.07
137.01
136.85
136.83
135.43
135.41
133.76
133.66
130.12
130.01
128.96
128.89
128.77
128.11
127.32
126.69
126.57
126.21
123.25
121.69
120.84
120.33
120.27
113.98
113.07
112.03
111.96
84.29
39.71
39.01
36.31
35.17
27.64
27.60
27.53
Boc
O
P
Ad
OHO
3n
13C NMR, CDCl3, 101 MHz
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30

3n

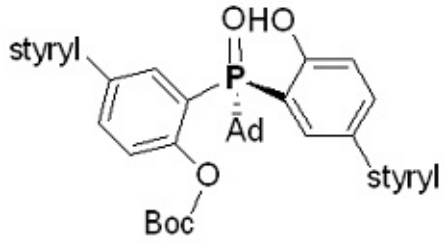
^{31}P NMR, $CDCl_3$, 162 MHz




12.11
8.44
8.43
8.41
8.40
7.87
7.87
7.84
7.84
7.83
7.82
7.81
7.80
7.78
7.76
7.65
7.63
7.61
7.59
7.50
7.48
7.46
7.44
7.43
7.42
7.40
7.38
7.36
7.34
7.19
7.15
7.10
7.07
7.06
7.04
7.03
2.22
2.21
1.88
1.63
styryl
Boc
O
P
Ad
OHO
styryl
3o
^{1}H NMR, CDCl$_3$, 400 MHz
f1 (ppm)

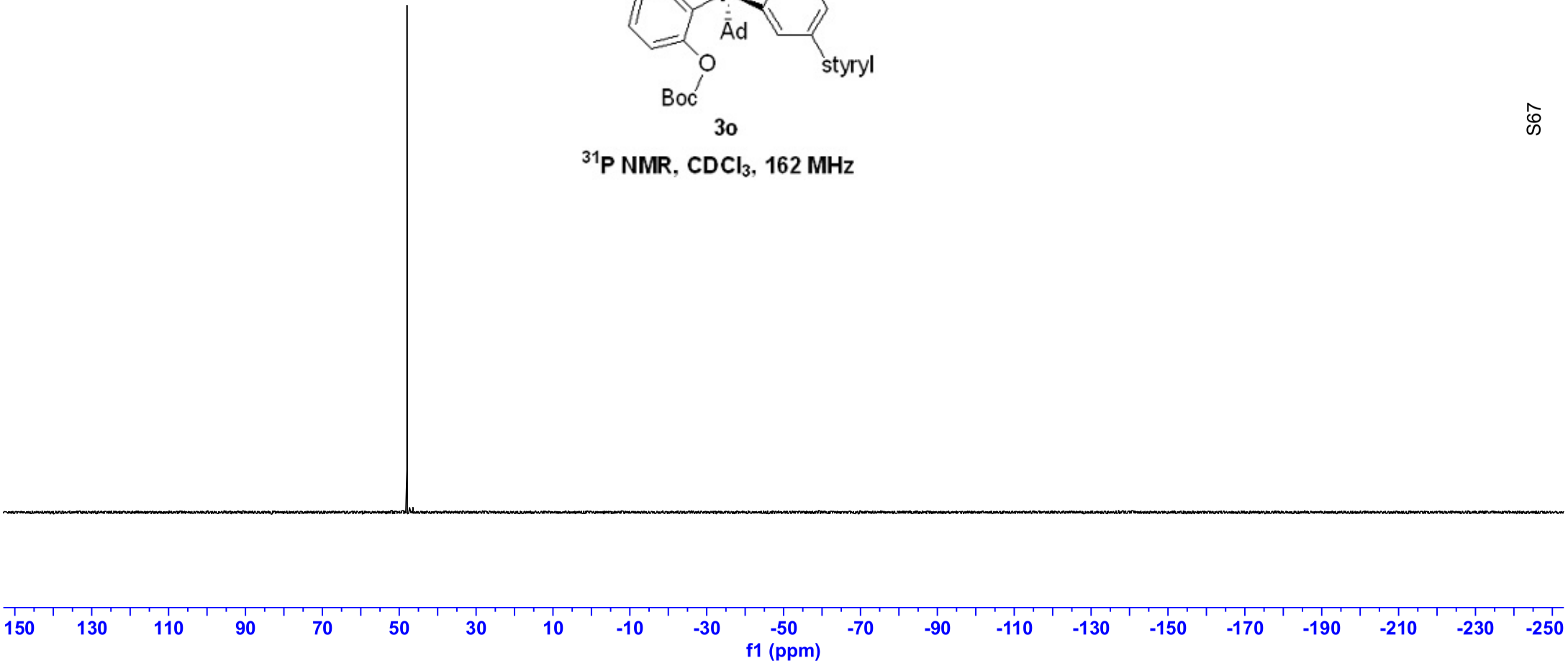

styryl
Boc
O
P
Ad
OHO
styryl
3o
^{13}C NMR, CDCl$_3$, 101 MHz
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
164.56
164.55
150.77
150.56
137.44
136.72
134.94
134.85
132.61
132.55
130.87
130.71
130.61
130.21
128.73
128.59
128.17
128.02
127.92
127.80
127.30
126.85
126.64
126.28
123.37
123.30
122.57
119.23
119.15
84.61
39.46
38.76
36.33
35.05
27.64
27.51

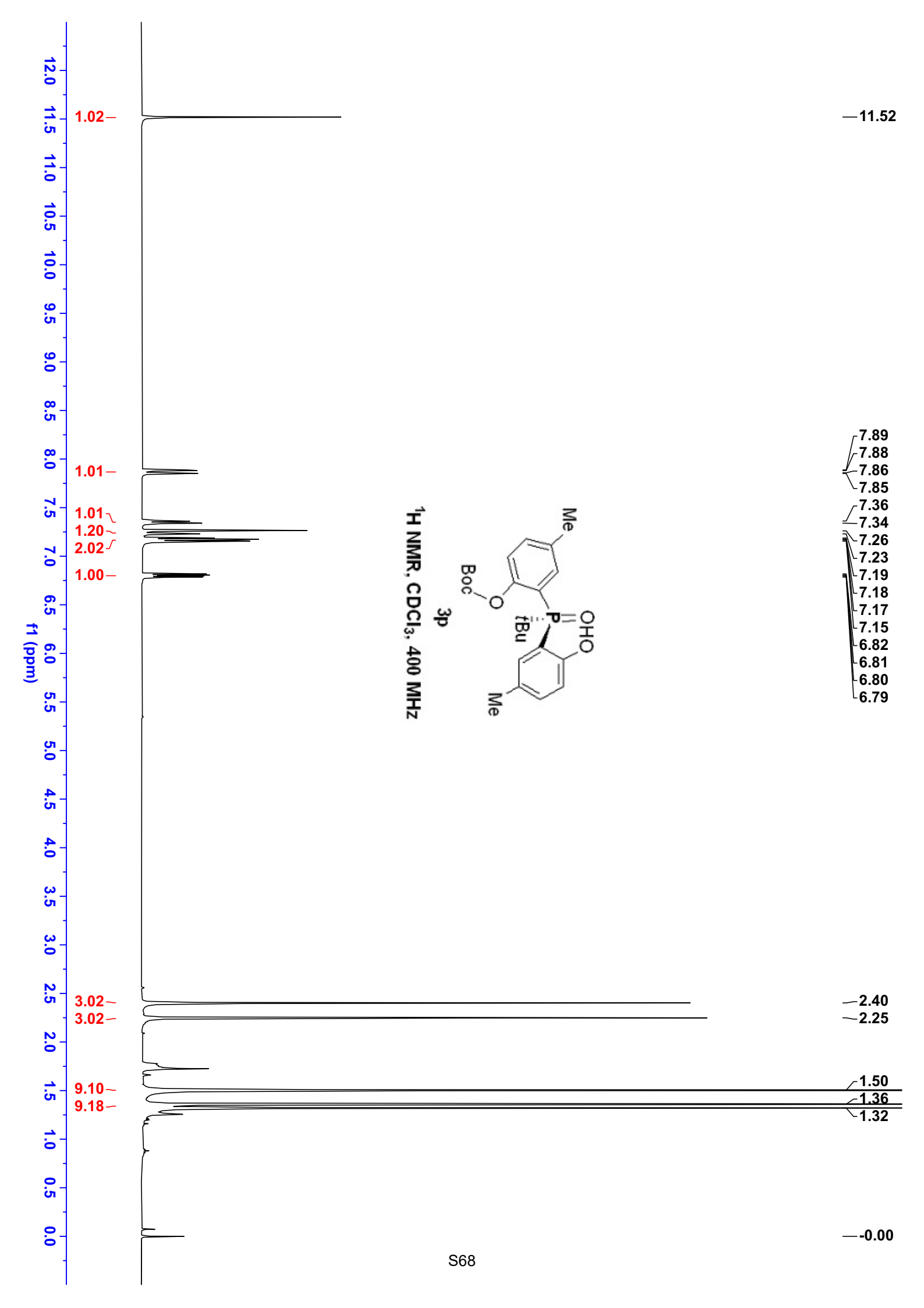
47.98

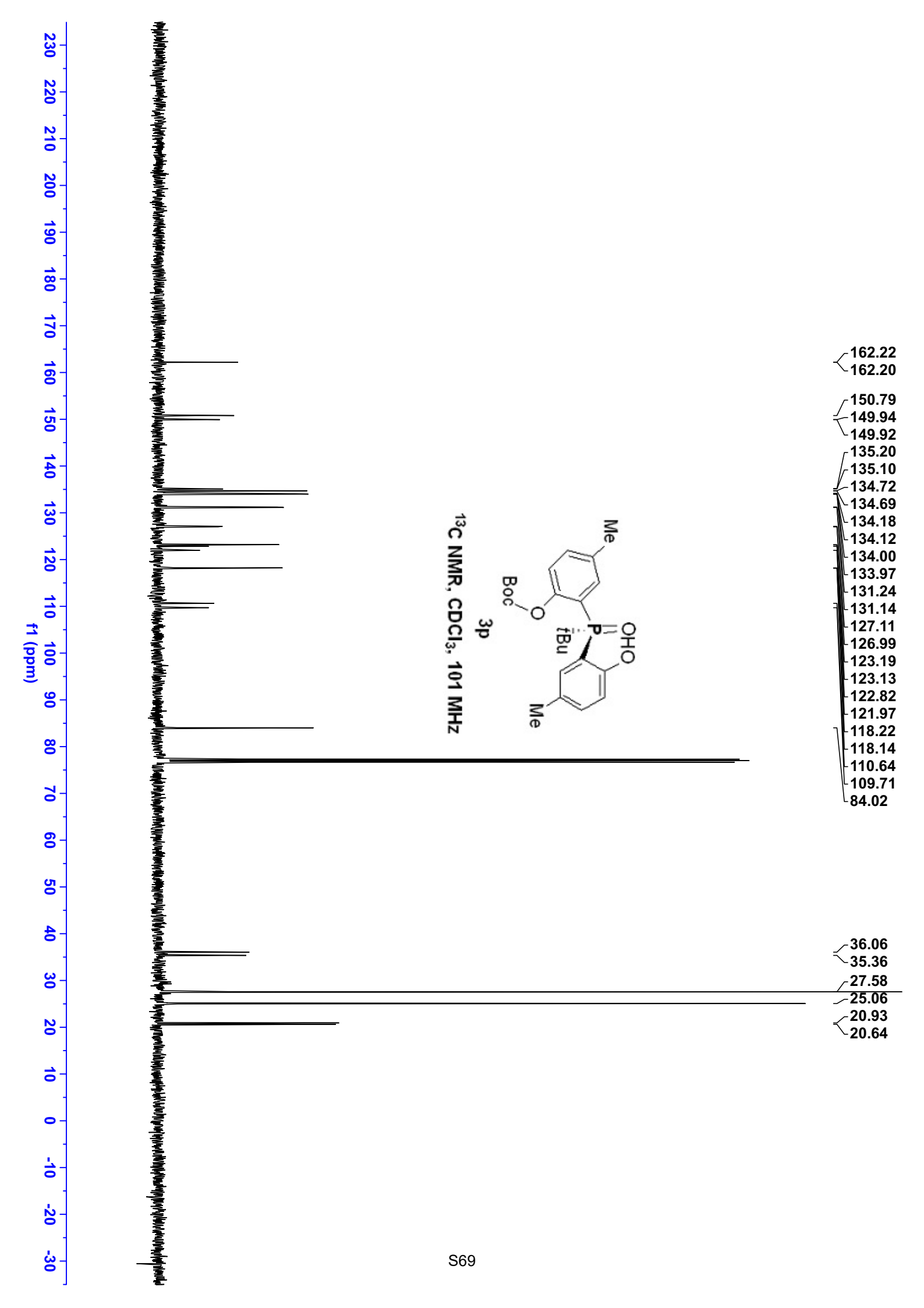


3o

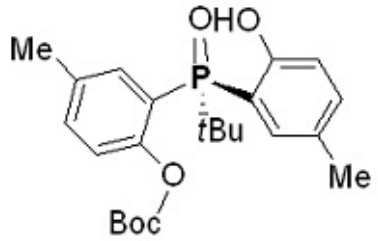
^{31}P NMR, $CDCl_3$, 162 MHz




1.02
1.01
1.01
1.20
2.02
1.00
3.02
3.02
9.10
9.18
11.52
7.89
7.88
7.86
7.85
7.36
7.34
7.26
7.23
7.19
7.18
7.17
7.15
6.82
6.81
6.80
6.79
2.40
2.25
1.50
1.36
1.32
-0.00
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3p
Me
Boc
O
P
tBu
OHO
Me

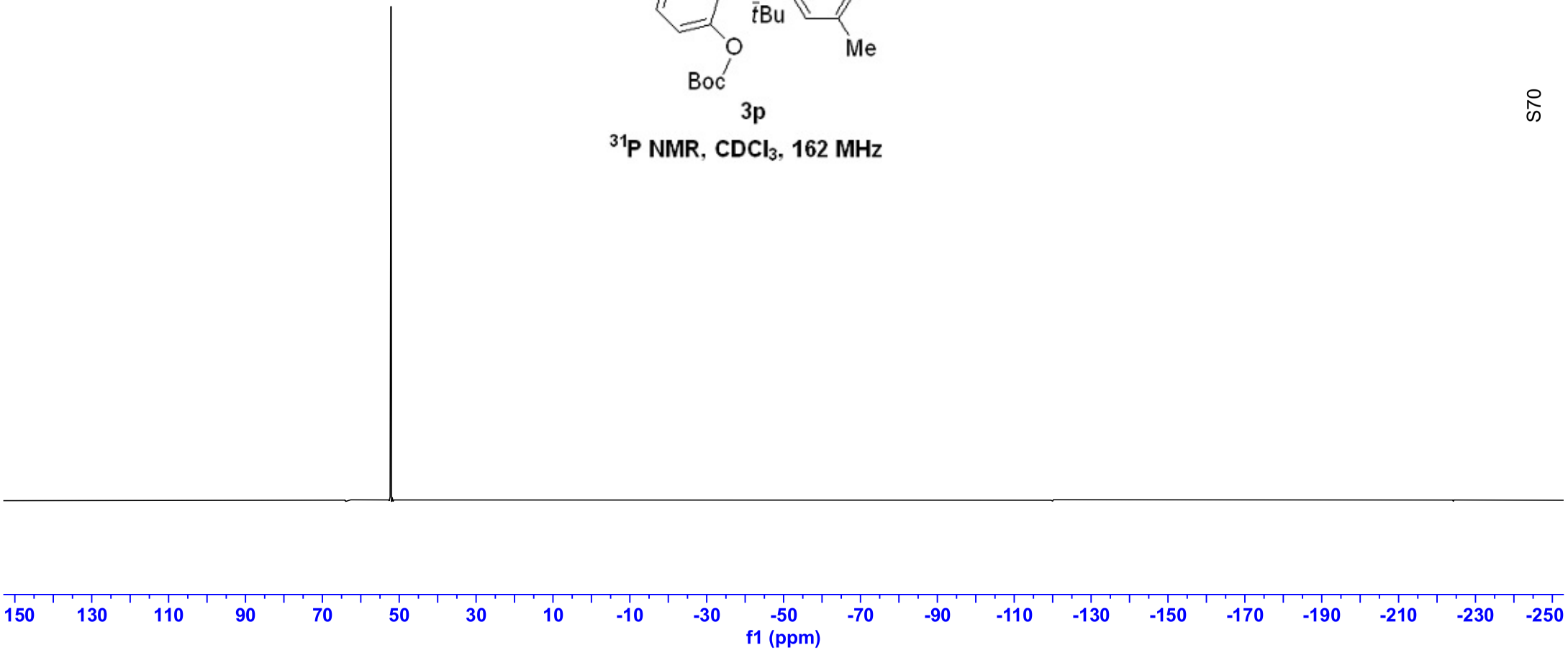

f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
^{13}C NMR, CDCl$_3$, 101 MHz
3p
Me
Boc
O
P
tBu
OHO
Me
162.22
162.20
150.79
149.94
149.92
135.20
135.10
134.72
134.69
134.18
134.12
134.00
133.97
131.24
131.14
127.11
126.99
123.19
123.13
122.82
121.97
118.22
118.14
110.64
109.71
84.02
36.06
35.36
27.58
25.06
20.93
20.64

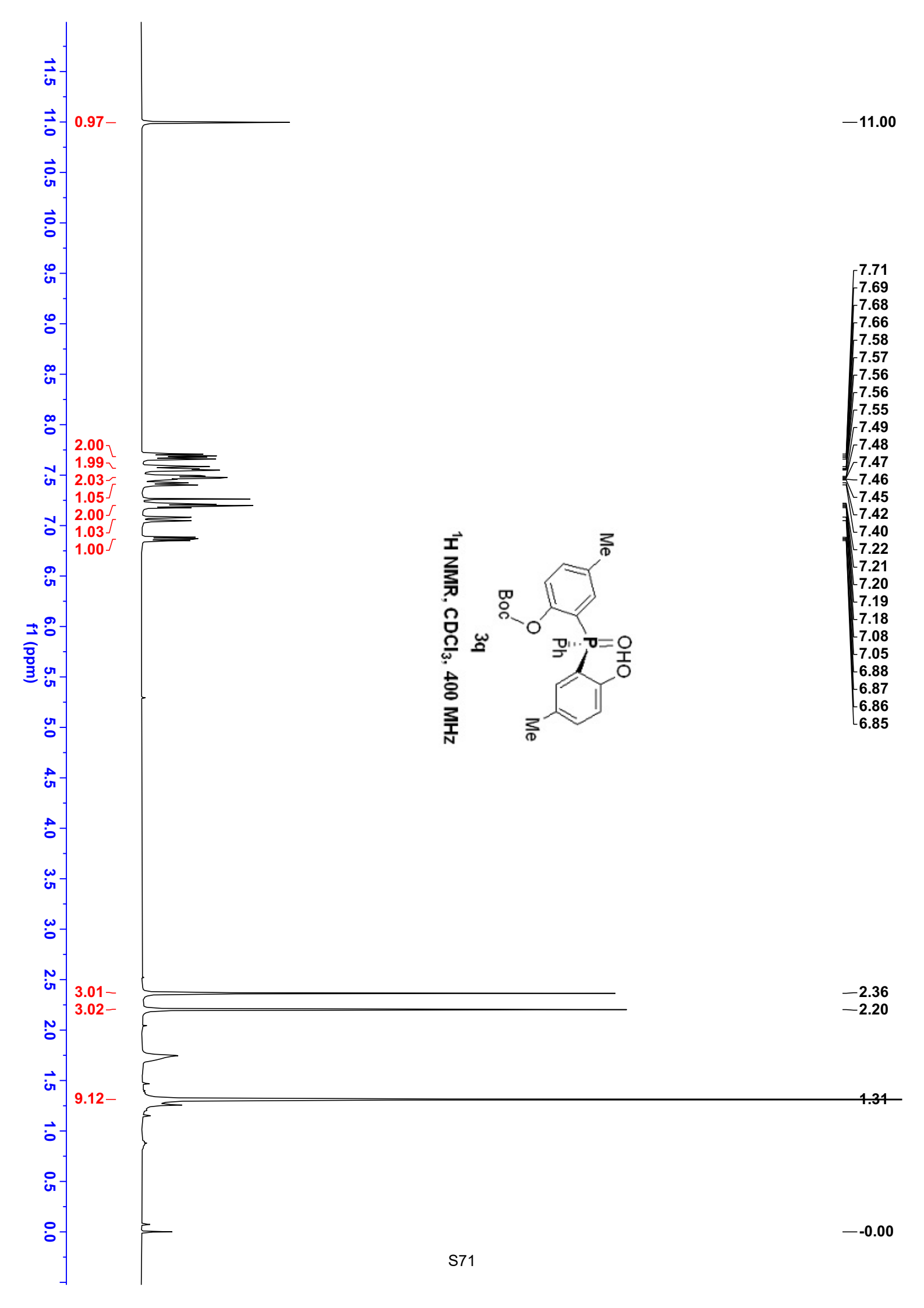
52.12

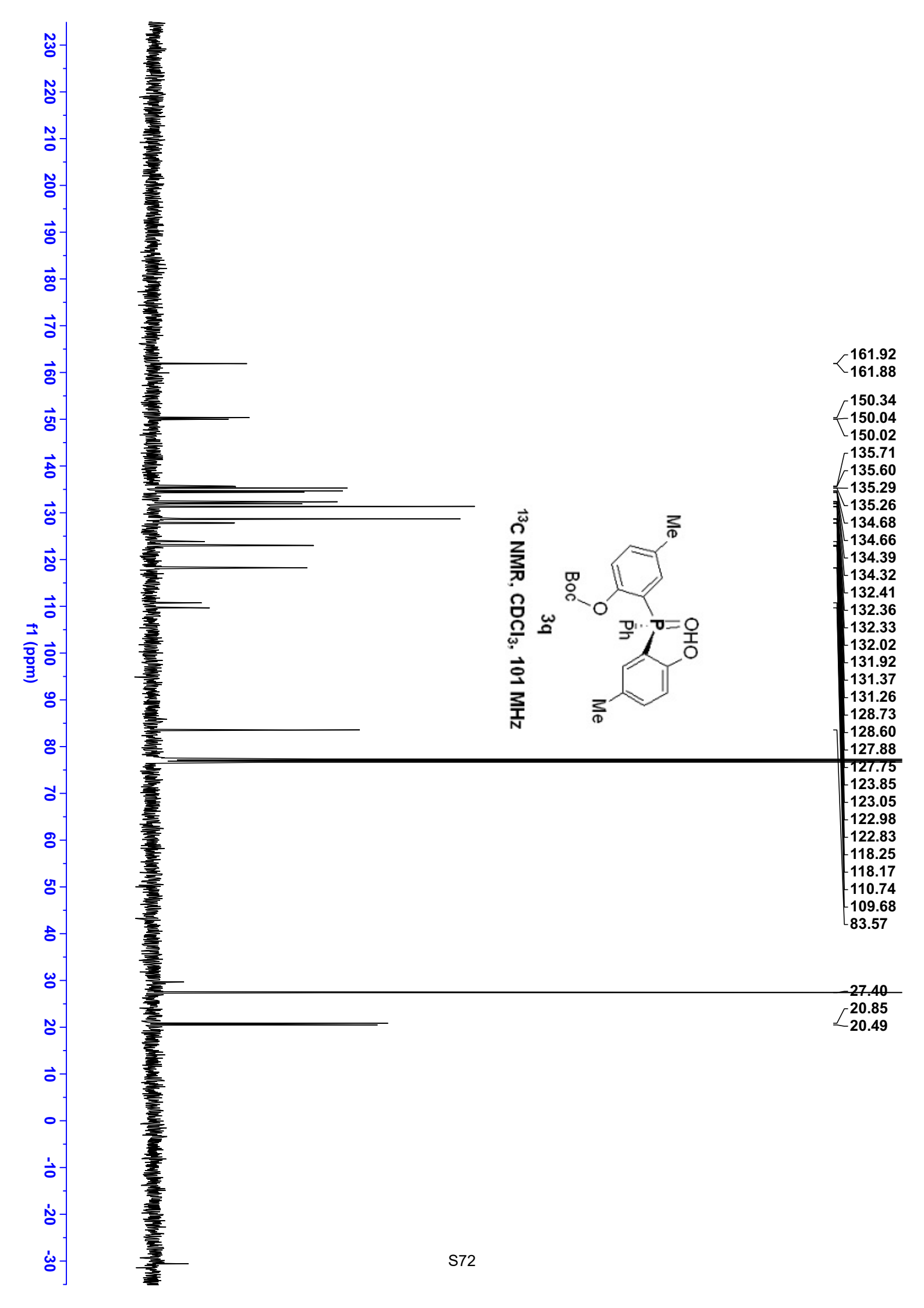


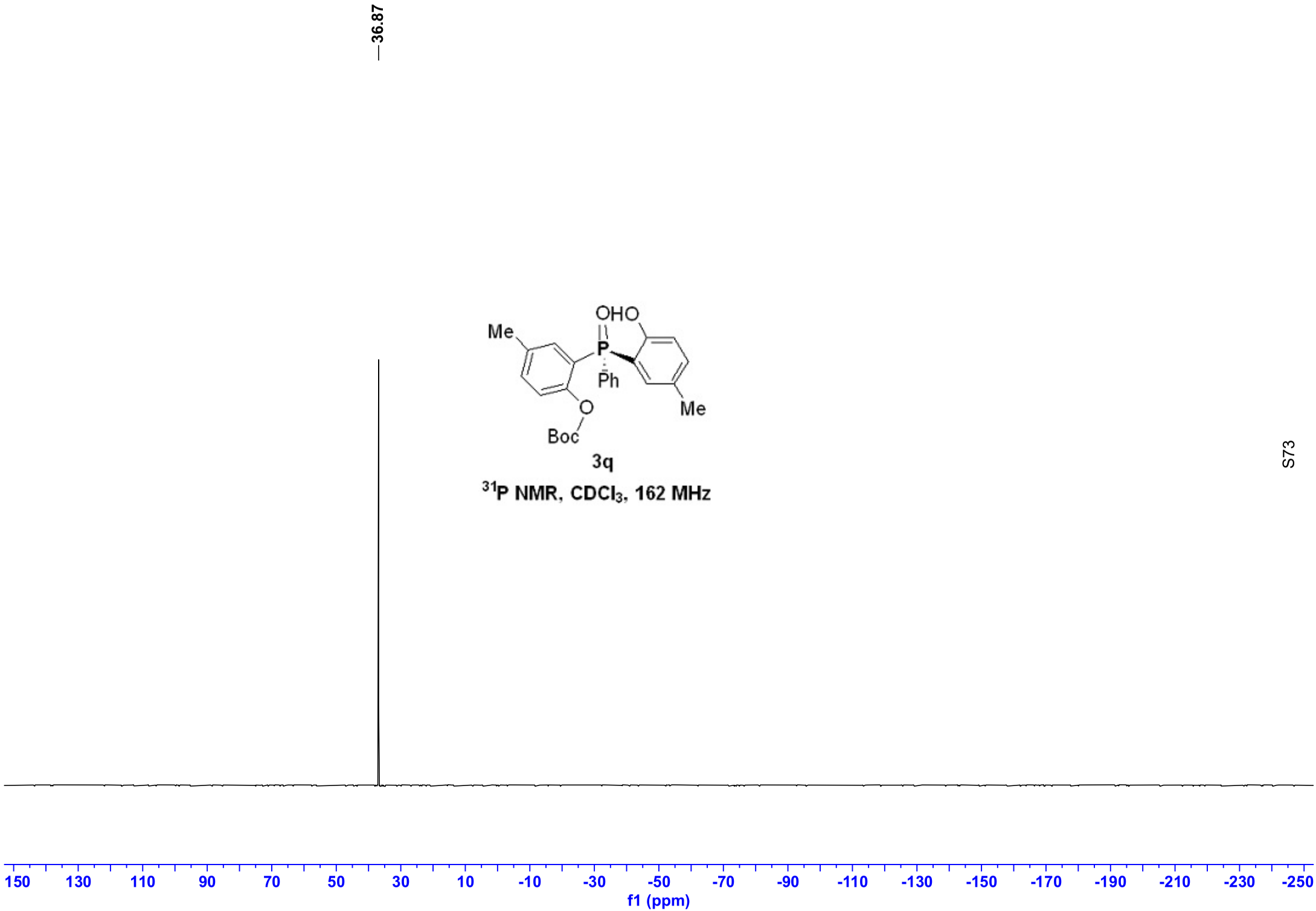
3p

^{31}P NMR, $CDCl_3$, 162 MHz



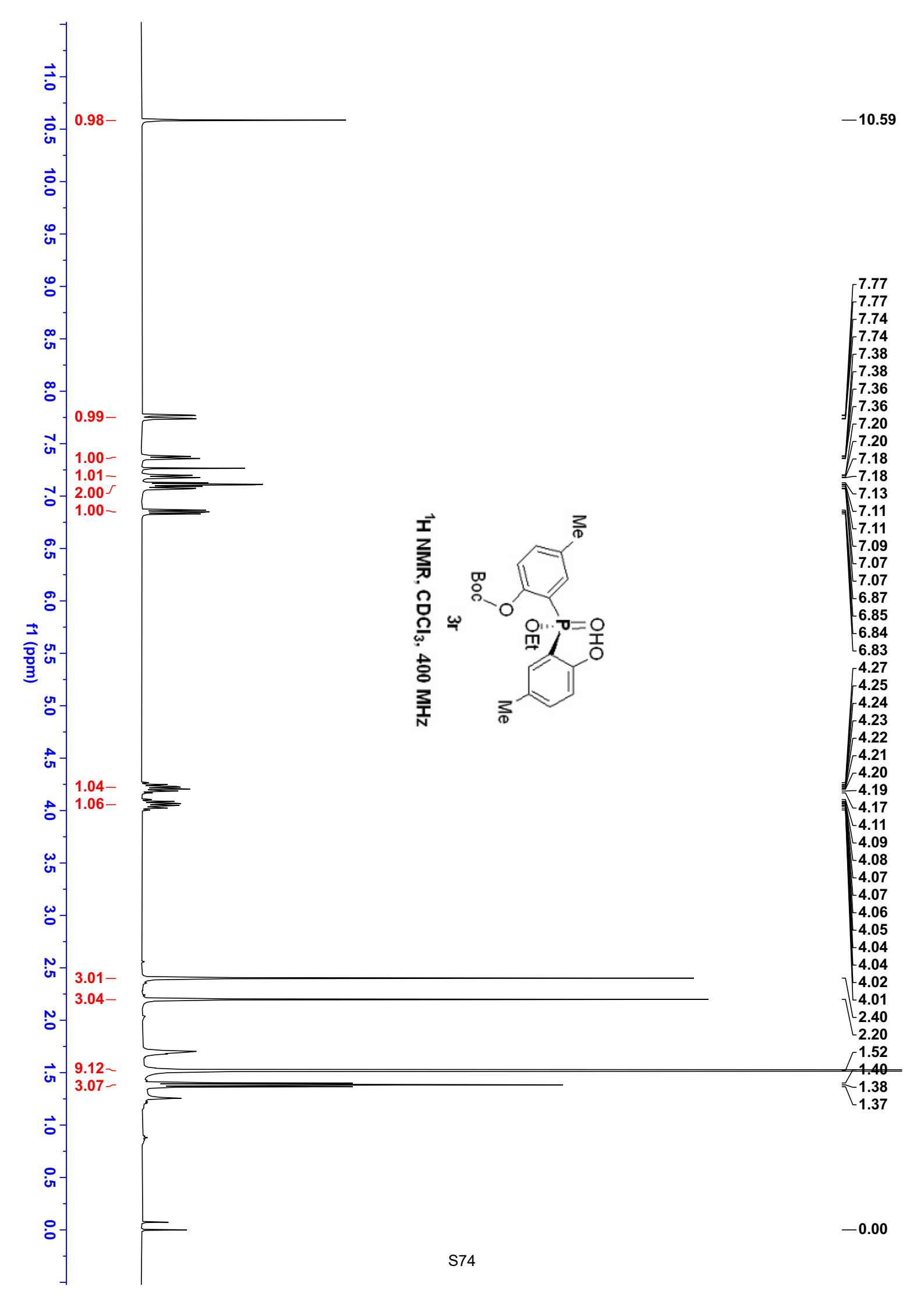

0.97
2.00
1.99
2.03
1.05
2.00
1.03
1.00
3.01
3.02
9.12
11.00
7.71
7.69
7.68
7.66
7.58
7.57
7.56
7.56
7.55
7.49
7.48
7.47
7.46
7.45
7.42
7.40
7.22
7.21
7.20
7.19
7.18
7.08
7.05
6.88
6.87
6.86
6.85
2.36
2.20
1.31
-0.00
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3q
Me
Boc
O
P
Ph
OHO
Me

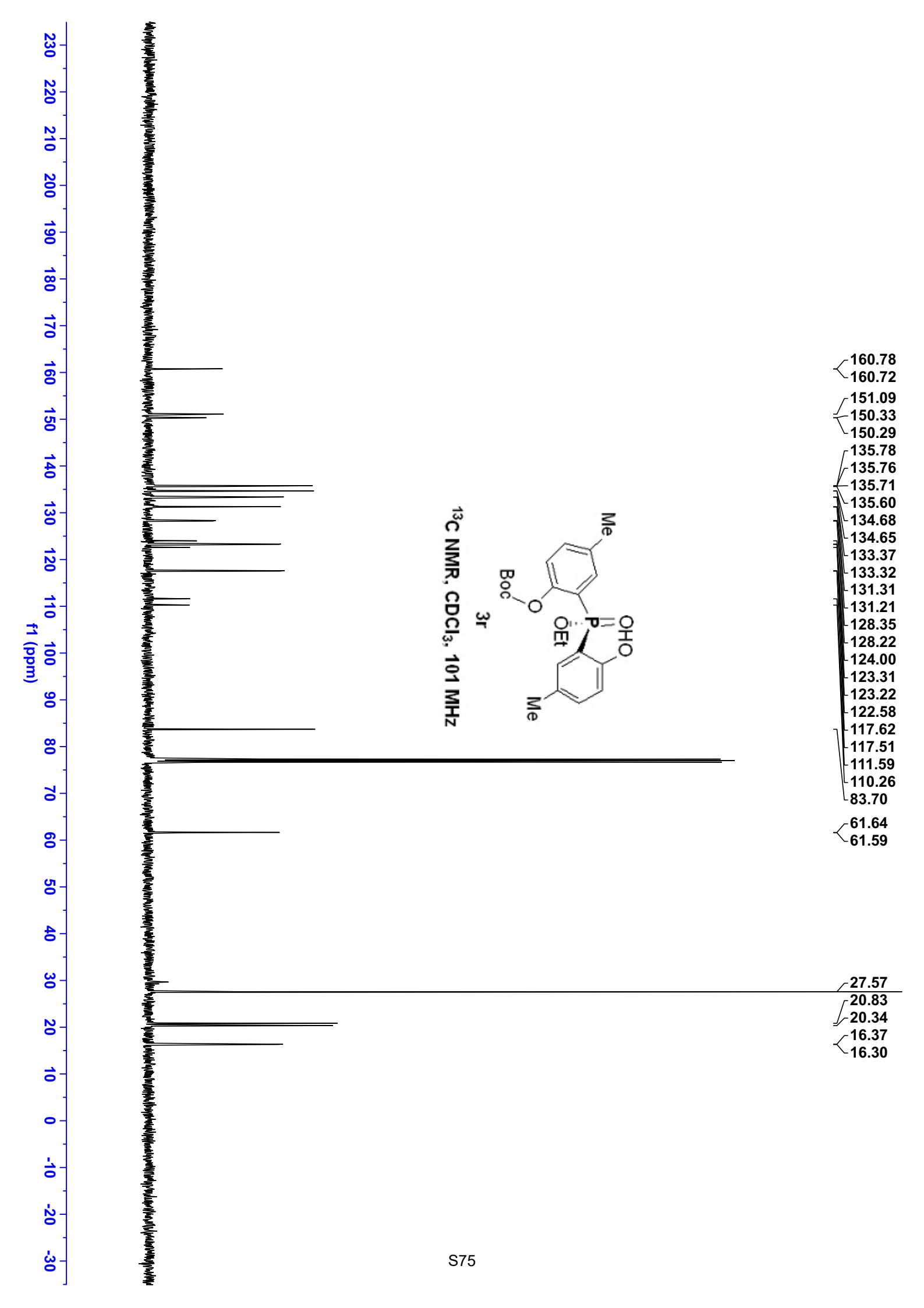

161.92
161.88
150.34
150.04
150.02
135.71
135.60
135.29
135.26
134.68
134.66
134.39
134.32
132.41
132.36
132.33
132.02
131.92
131.37
131.26
128.73
128.60
127.88
127.75
123.85
123.05
122.98
122.83
118.25
118.17
110.74
109.68
83.57
27.40
20.85
20.49
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
Me
Boc
O
P
Ph
OHO
Me
3q
13C NMR, CDCl3, 101 MHz

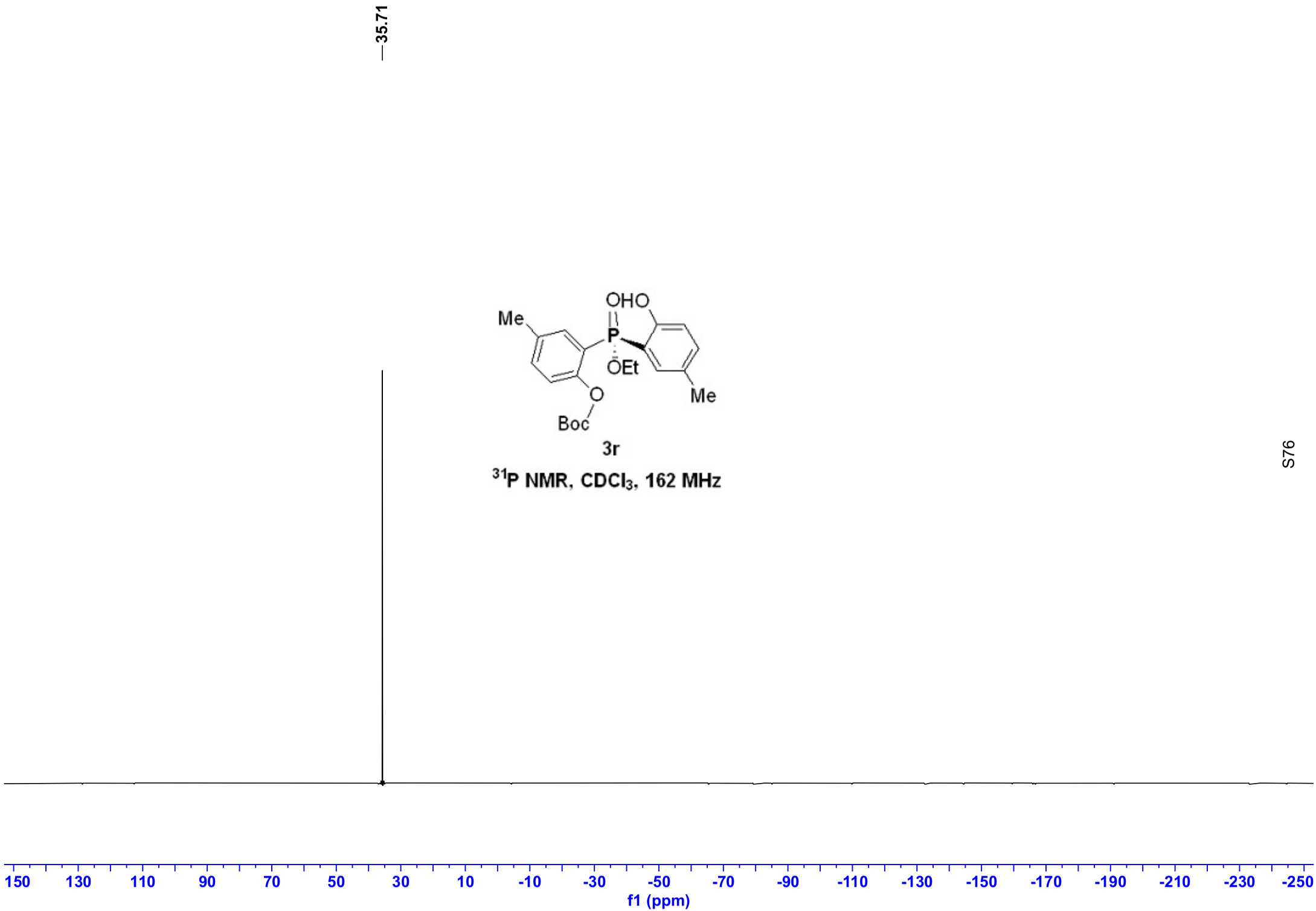


3q

^{31}P NMR, $CDCl_3$, 162 MHz

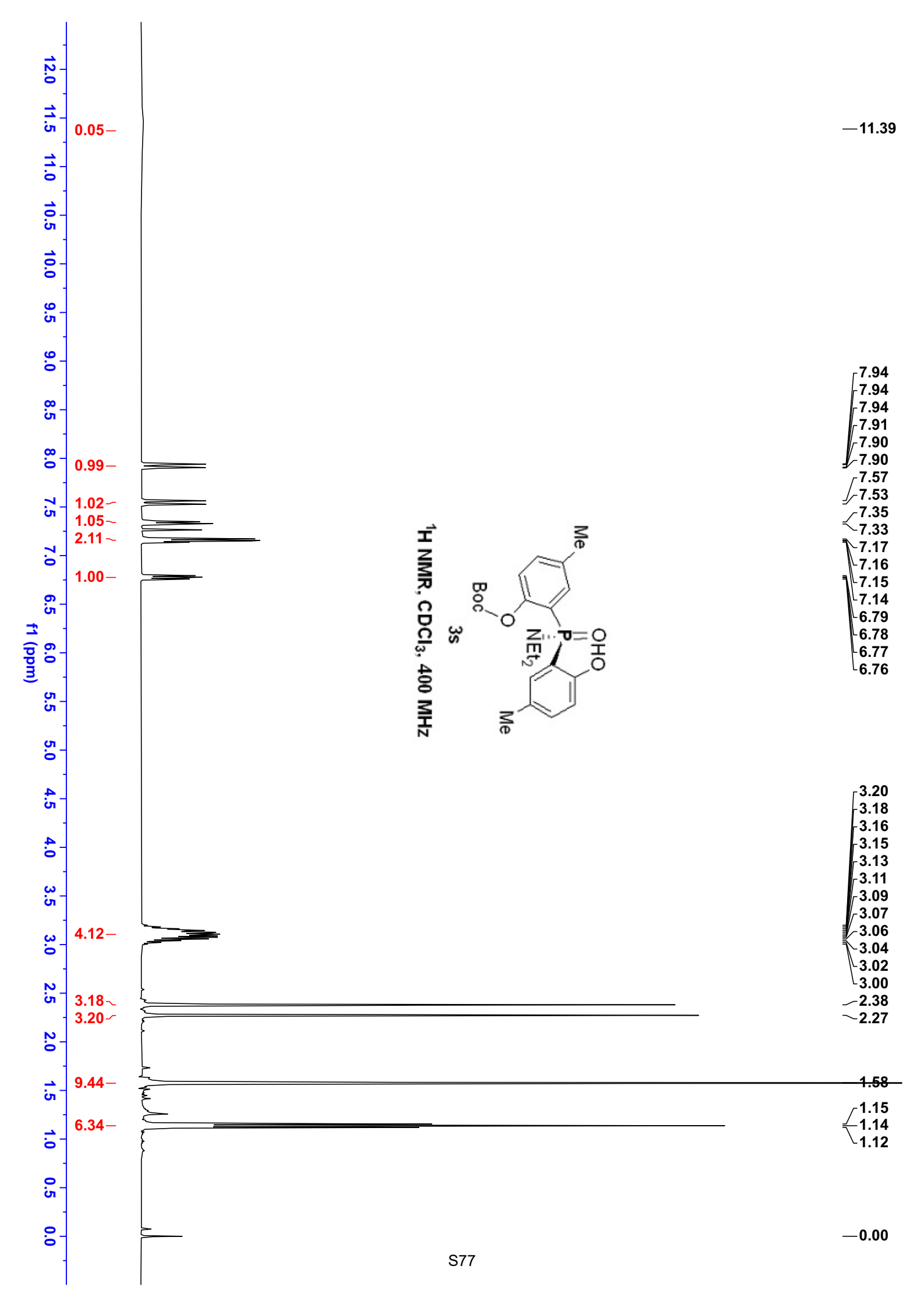

0.98
0.99
1.00
1.01
2.00
1.00
1.04
1.06
3.01
3.04
9.12
3.07
10.59
7.77
7.77
7.74
7.74
7.38
7.38
7.36
7.36
7.20
7.20
7.18
7.18
7.13
7.11
7.11
7.09
7.07
7.07
6.87
6.85
6.84
6.83
4.27
4.25
4.24
4.23
4.22
4.21
4.20
4.19
4.17
4.11
4.09
4.08
4.07
4.07
4.06
4.05
4.04
4.04
4.02
4.01
2.40
2.20
1.52
1.40
1.38
1.37
0.00
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3r
Me
Boc
O
P
OEt
OHO
Me

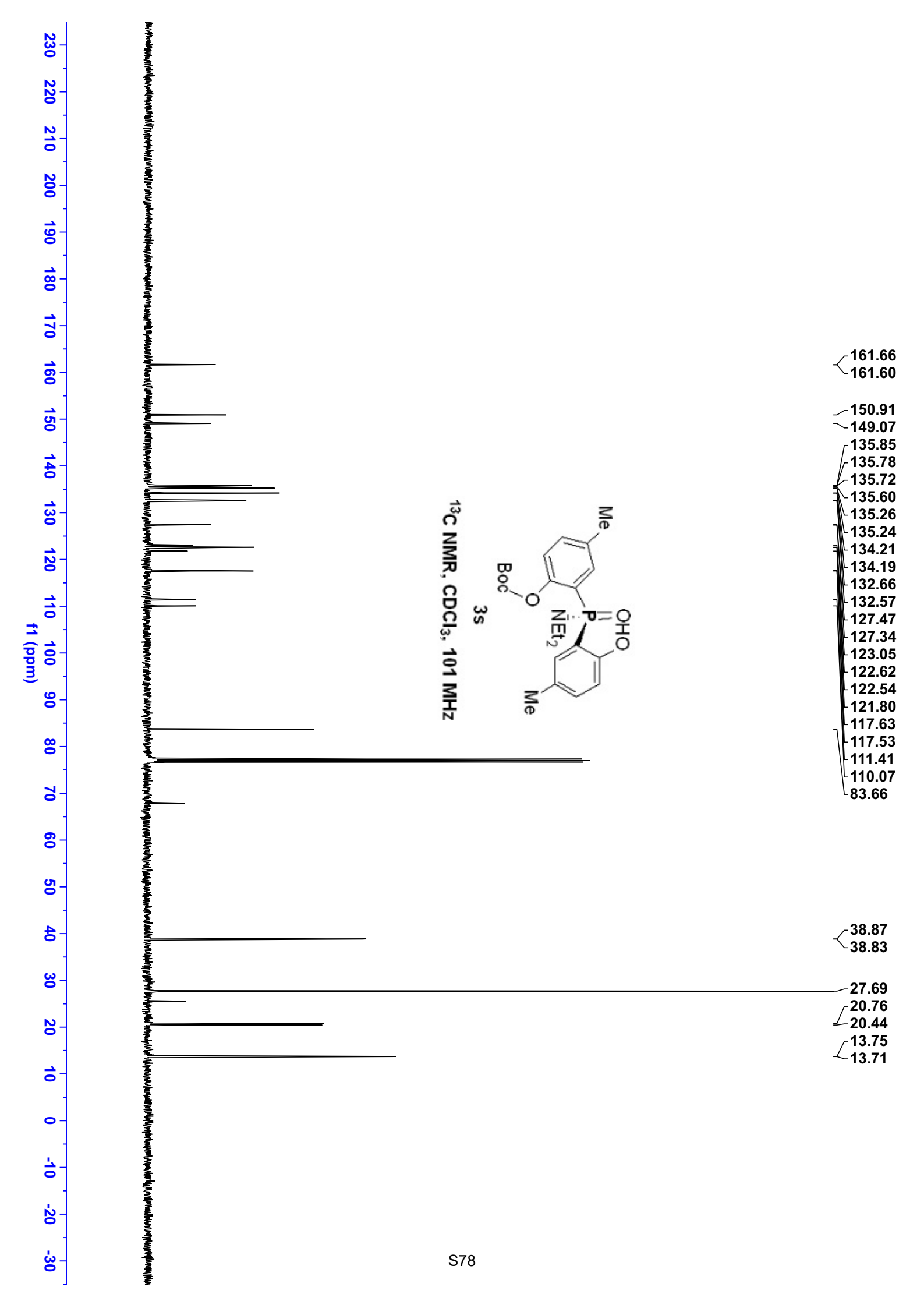

160.78
160.72
151.09
150.33
150.29
135.78
135.76
135.71
135.60
134.68
134.65
133.37
133.32
131.31
131.21
128.35
128.22
124.00
123.31
123.22
122.58
117.62
117.51
111.59
110.26
83.70
61.64
61.59
27.57
20.83
20.34
16.37
16.30
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
^{13}C NMR, CDCl$_3$, 101 MHz
3r
Me
Boc
O
P
OEt
OHO
Me

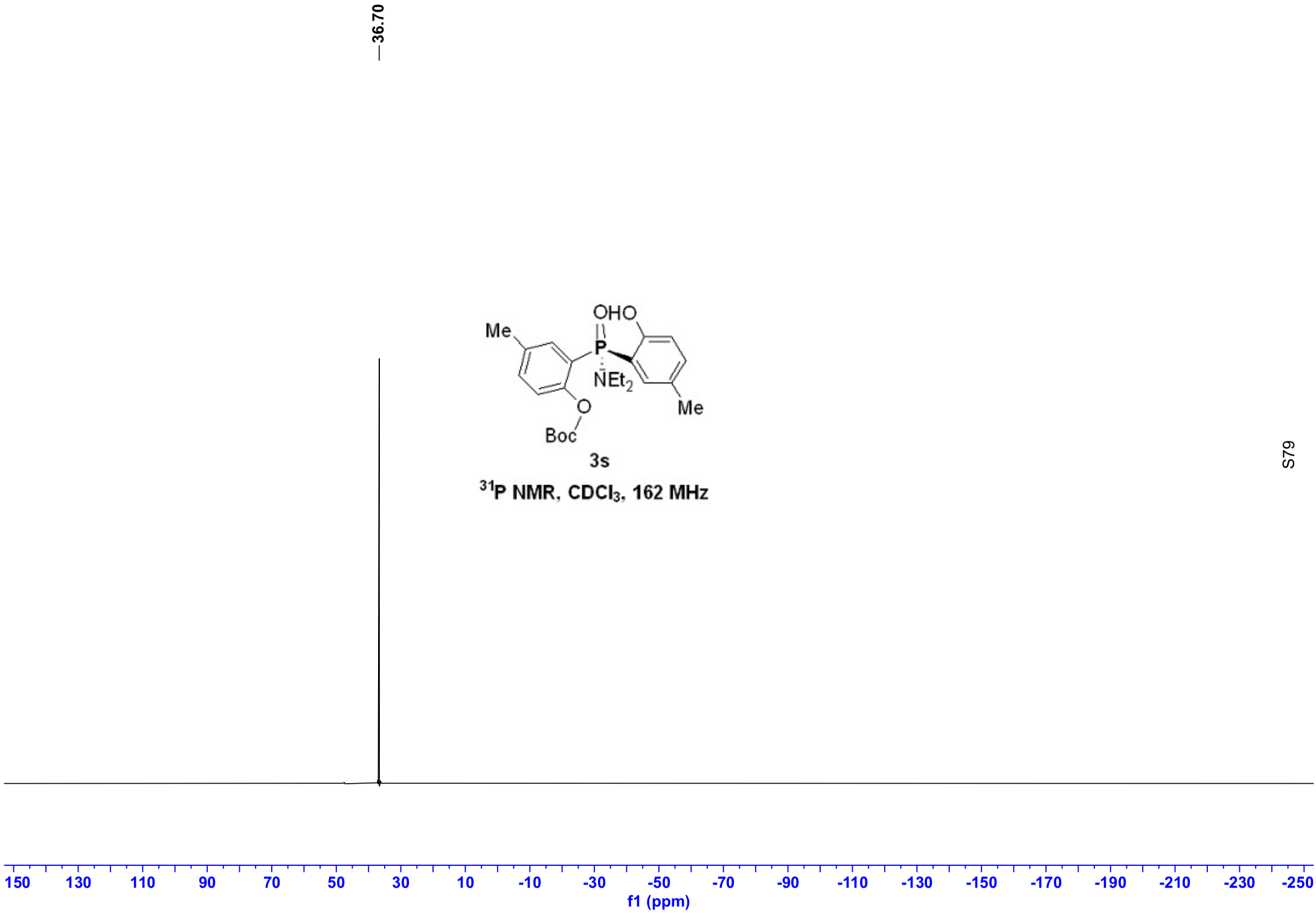


3r

^{31}P NMR, $CDCl_3$, 162 MHz

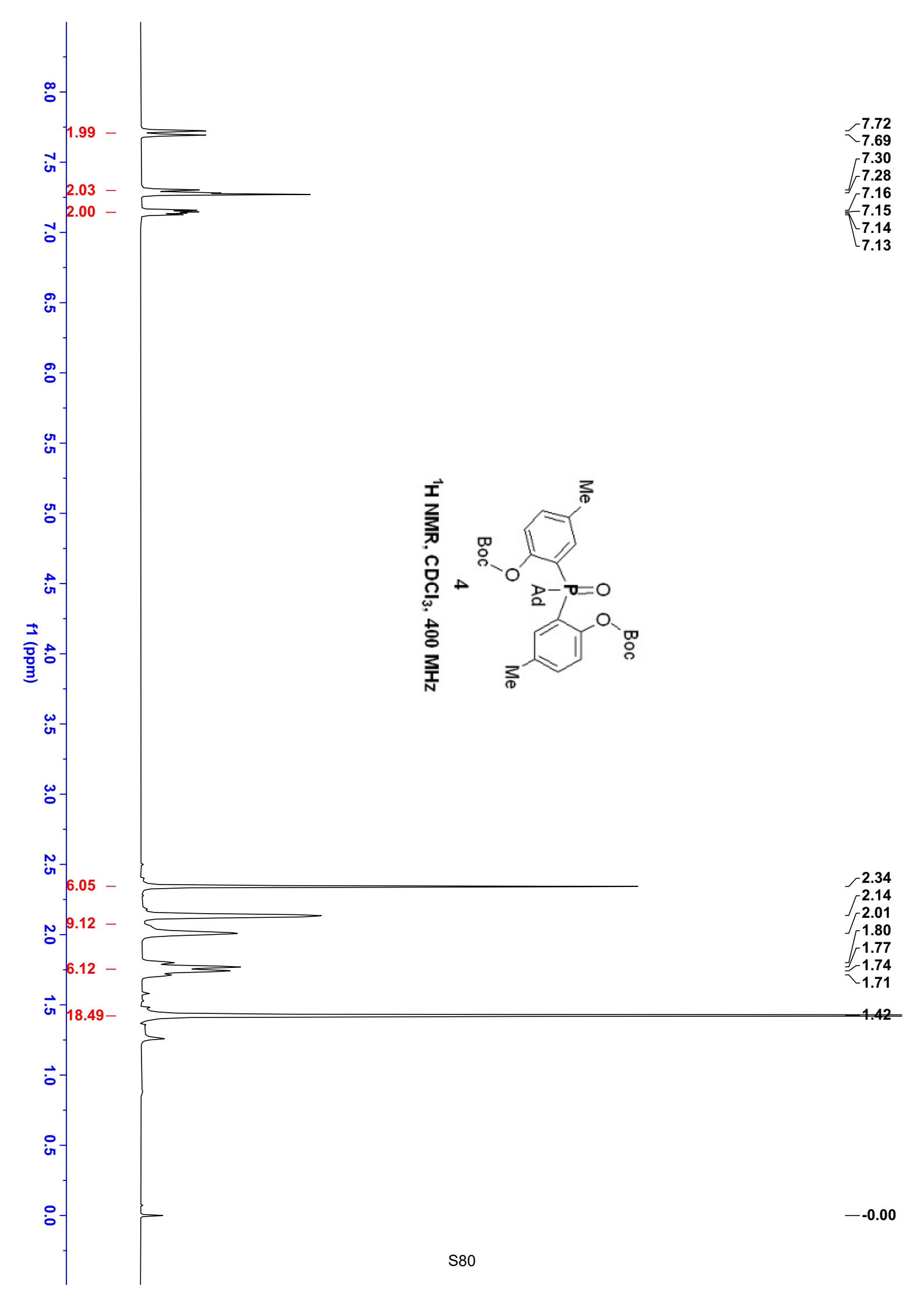

0.05
0.99
1.02
1.05
2.11
1.00
4.12
3.18
3.20
9.44
6.34
11.39
7.94
7.94
7.94
7.91
7.90
7.90
7.57
7.53
7.35
7.33
7.17
7.16
7.15
7.14
6.79
6.78
6.77
6.76
3.20
3.18
3.16
3.15
3.13
3.11
3.09
3.07
3.06
3.04
3.02
3.00
2.38
2.27
1.58
1.15
1.14
1.12
0.00
f1 (ppm)
^{1}H NMR, CDCl$_3$, 400 MHz
3s
Me
Boc
O
P
OHO
NEt$_2$
Me

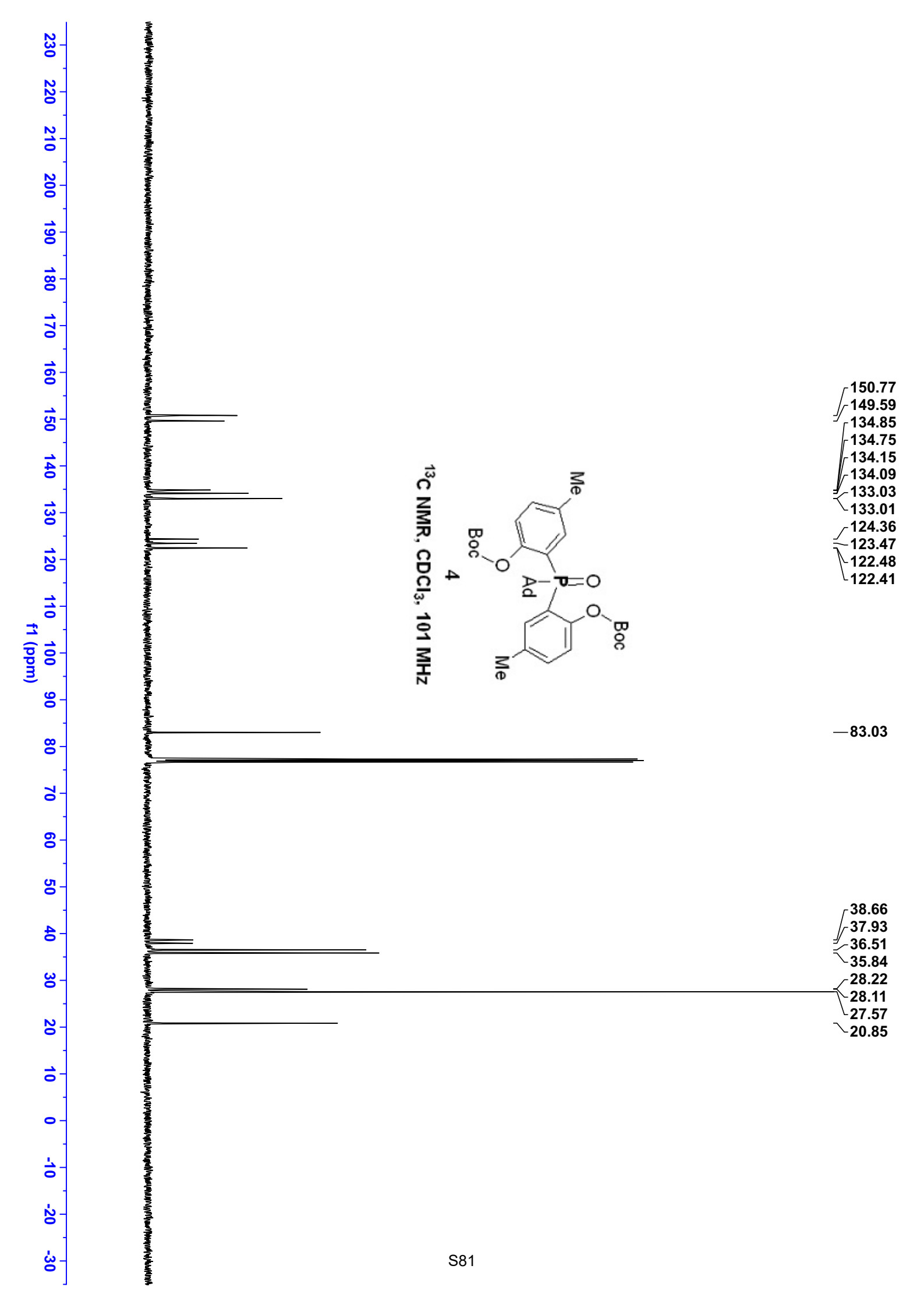

161.66
161.60
150.91
149.07
135.85
135.78
135.72
135.60
135.26
135.24
134.21
134.19
132.66
132.57
127.47
127.34
123.05
122.62
122.54
121.80
117.63
117.53
111.41
110.07
83.66
38.87
38.83
27.69
20.76
20.44
13.75
13.71
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
^{13}C NMR, $CDCl_3$, 101 MHz
3s
Me
Boc
O
P
OHO
NEt_2
Me

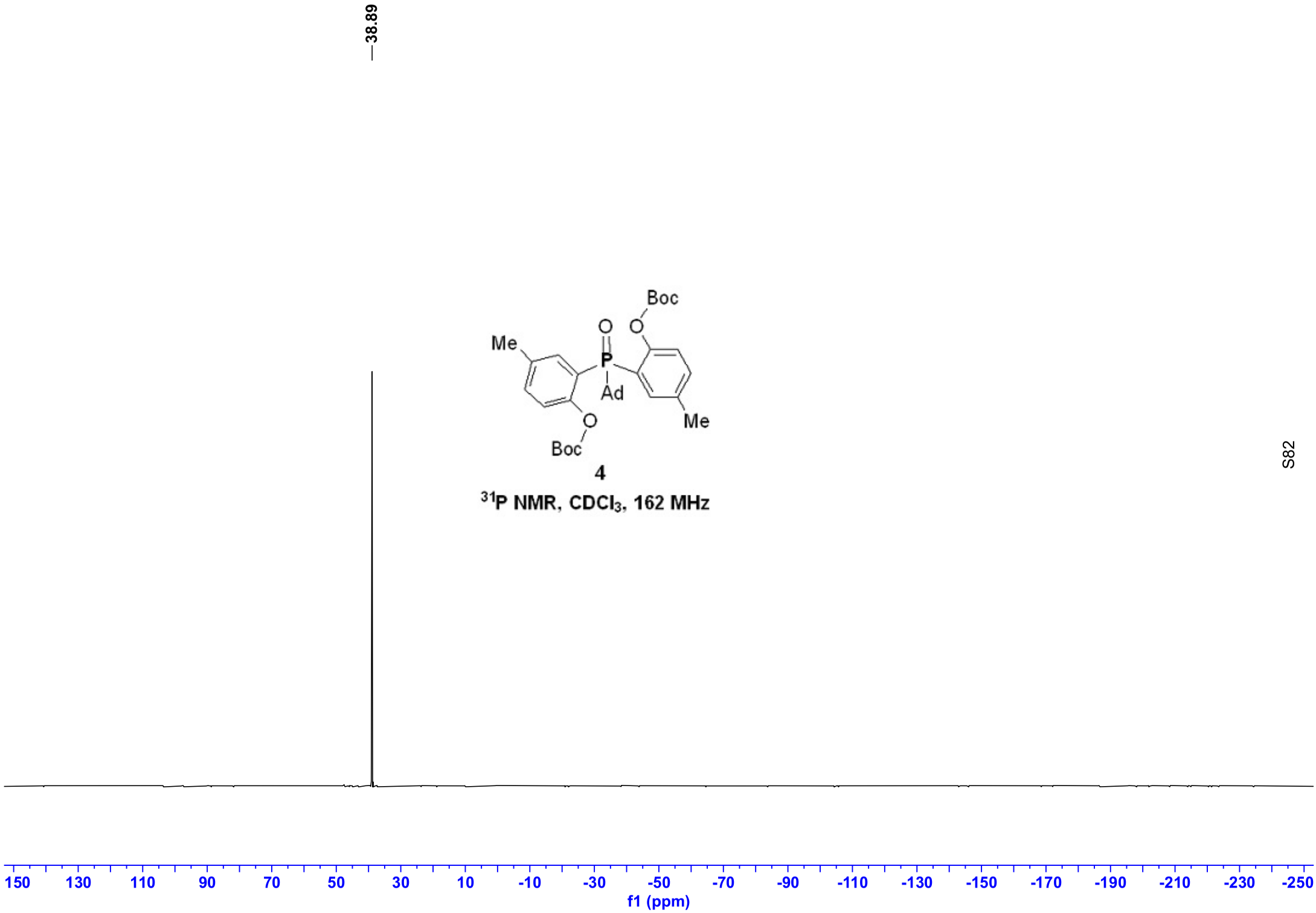


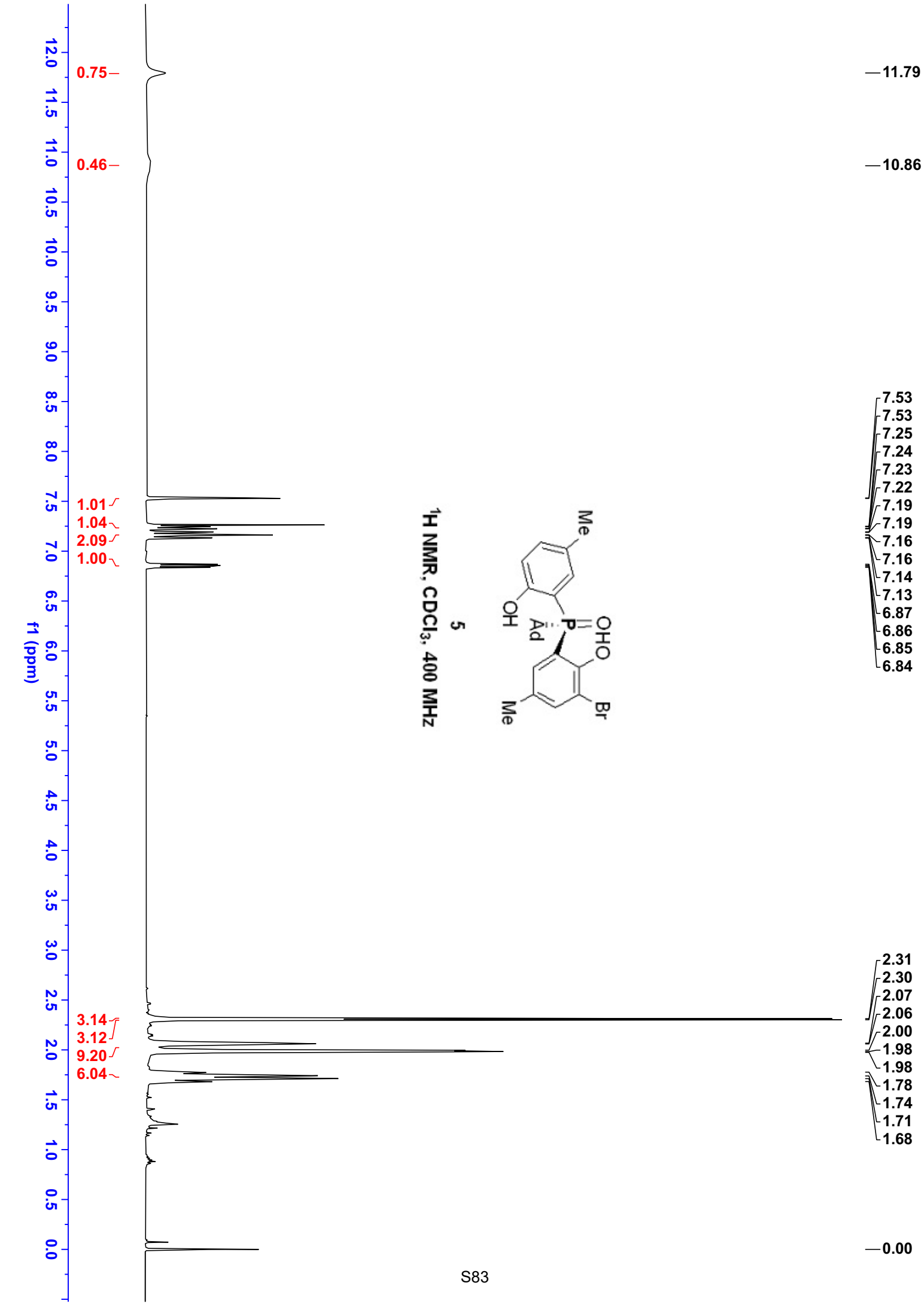
3s

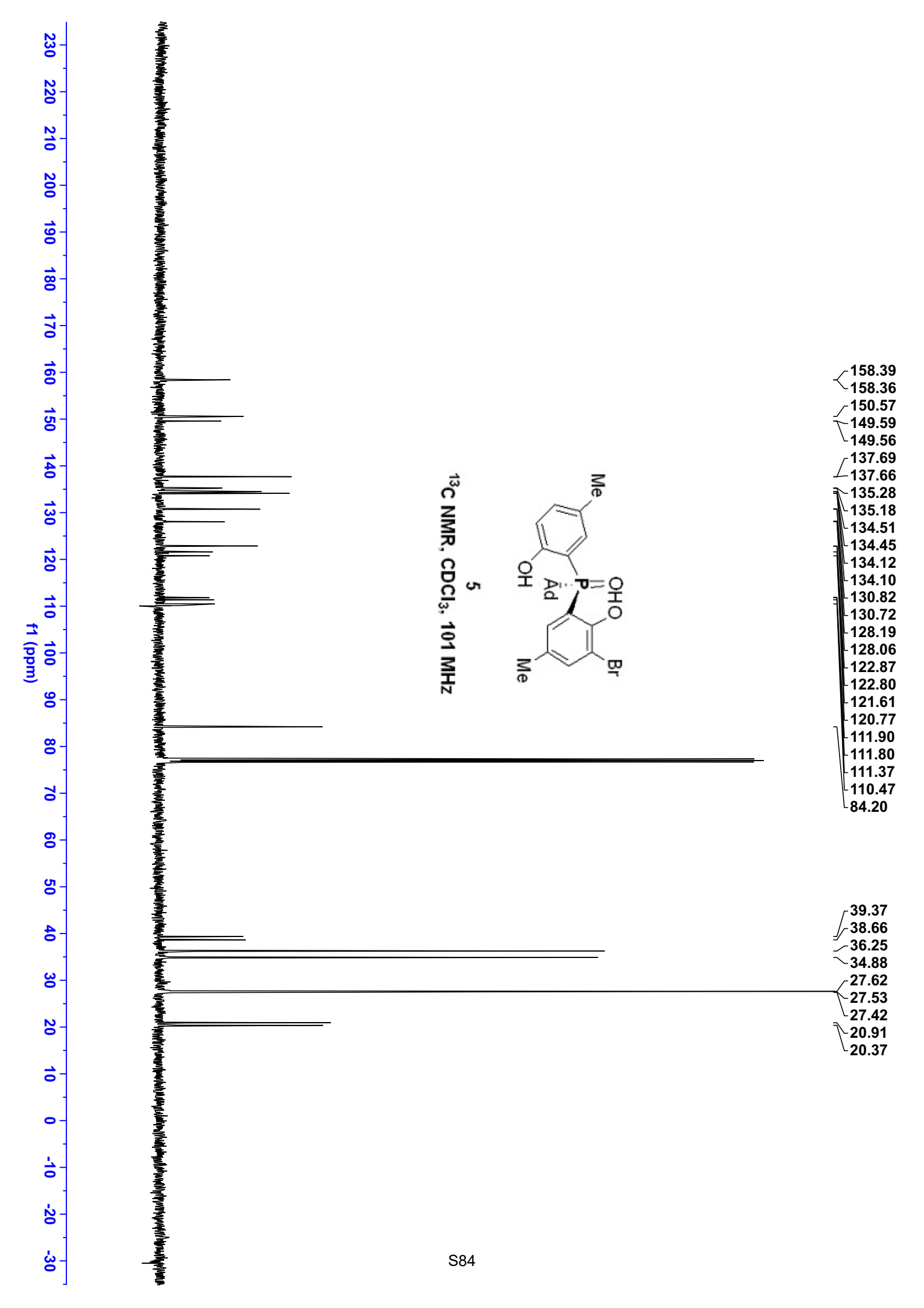
^{31}P NMR, $CDCl_3$, 162 MHz


1.99
2.03
2.00
6.05
9.12
6.12
18.49
7.72
7.69
7.30
7.28
7.16
7.15
7.14
7.13
2.34
2.14
2.01
1.80
1.77
1.74
1.71
1.42
-0.00
Me
Boc
O
Ad
P
O
O
Boc
Me
4
^{1}H NMR, CDCl$_3$, 400 MHz
f1 (ppm)
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
0.5
0.0

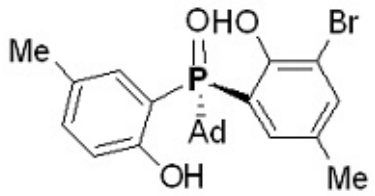

150.77
149.59
134.85
134.75
134.15
134.09
133.03
133.01
124.36
123.47
122.48
122.41
83.03
38.66
37.93
36.51
35.84
28.22
28.11
27.57
20.85
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30
Me
Boc
O
P
Ad
O
O
Boc
Me
4
13C NMR, CDCl3, 101 MHz


38.89
Boc
O
O
Me
P
Ad
Me
O
Boc
4
31P NMR, CDCl3, 162 MHz
150
130
110
90
70
50
30
10
-10
-30
-50
-70
-90
-110
-130
-150
-170
-190
-210
-230
-250
f1 (ppm)


0.75
0.46
1.01
1.04
2.09
1.00
3.14
3.12
9.20
6.04
11.79
10.86
7.53
7.53
7.25
7.24
7.23
7.22
7.19
7.19
7.16
7.16
7.14
7.13
6.87
6.86
6.85
6.84
2.31
2.30
2.07
2.06
2.00
1.98
1.98
1.78
1.74
1.71
1.68
0.00
f1 (ppm)
5
^{1}H NMR, CDCl$_3$, 400 MHz
Me
OH
Ad
P
OHO
Br
Me

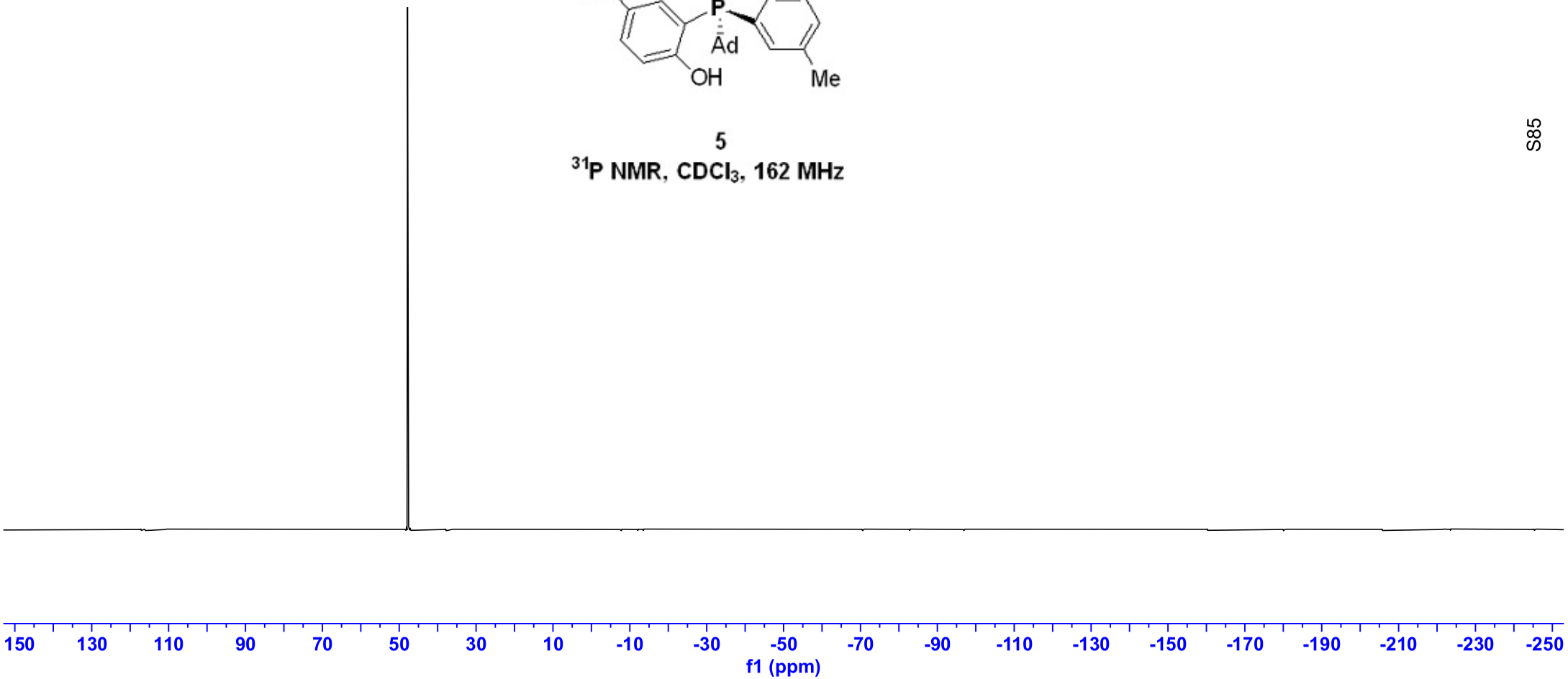

158.39
158.36
150.57
149.59
149.56
137.69
137.66
135.28
135.18
134.51
134.45
134.12
134.10
130.82
130.72
128.19
128.06
122.87
122.80
121.61
120.77
111.90
111.80
111.37
110.47
84.20
39.37
38.66
36.25
34.88
27.62
27.53
27.42
20.91
20.37
Me
OH
P
Ad
OHO
Br
Me
5
13C NMR, CDCl3, 101 MHz
f1 (ppm)

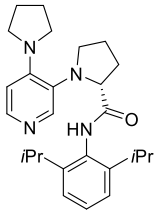
47.84



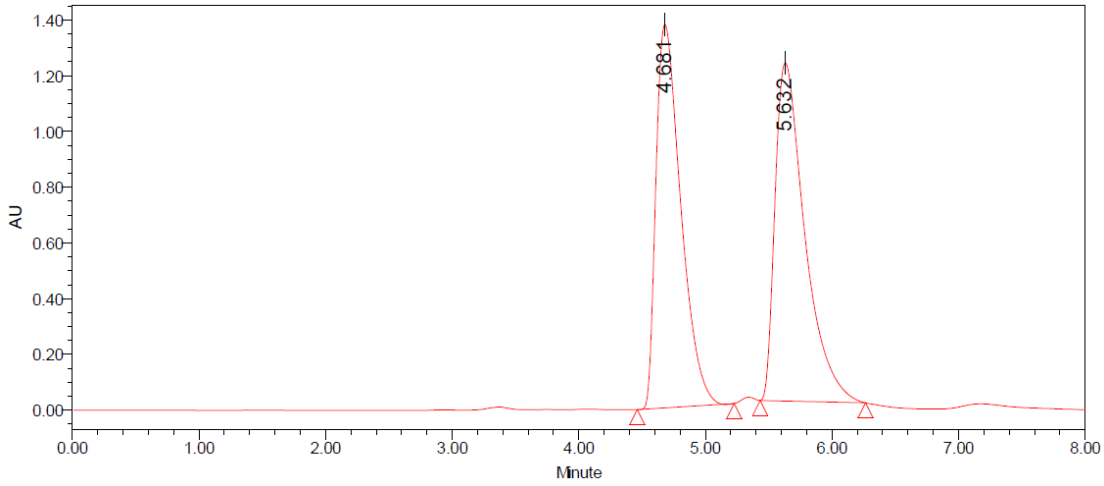
5

^{31}P NMR, $CDCl_3$, 162 MHz

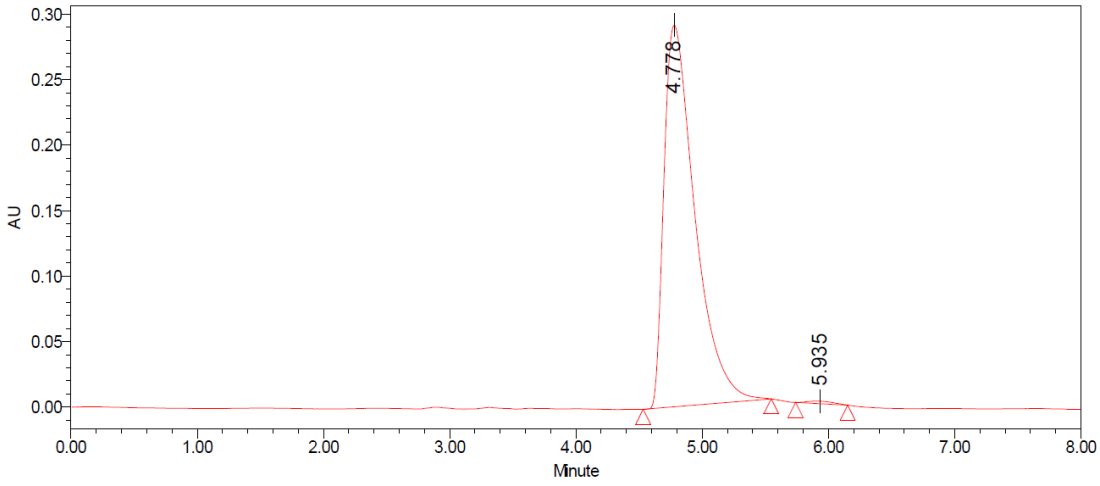




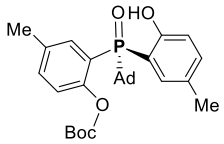
C6



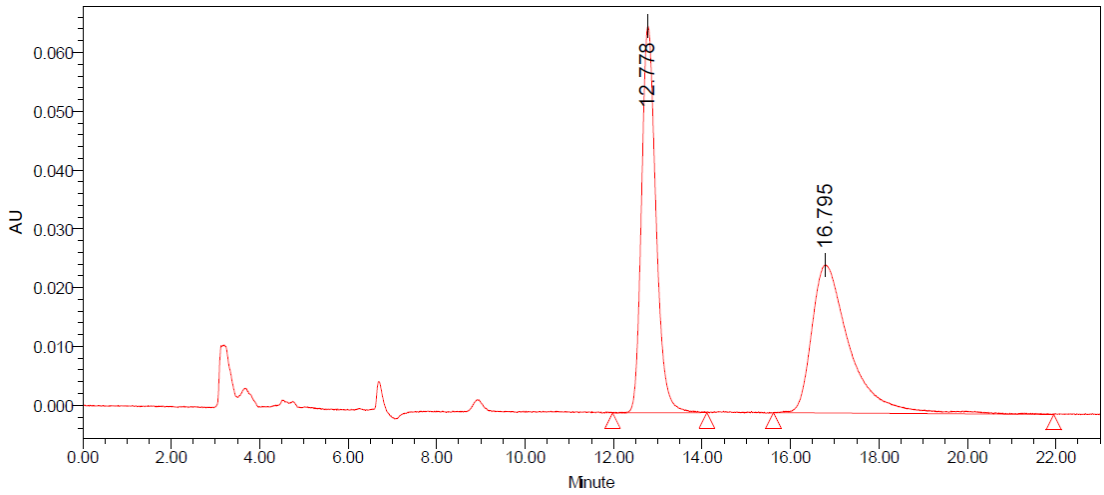
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	4.681	18760001	48.60	1375426	53.13	4.462	5.227
2	5.632	19837301	51.40	1213189	46.87	5.433	6.265



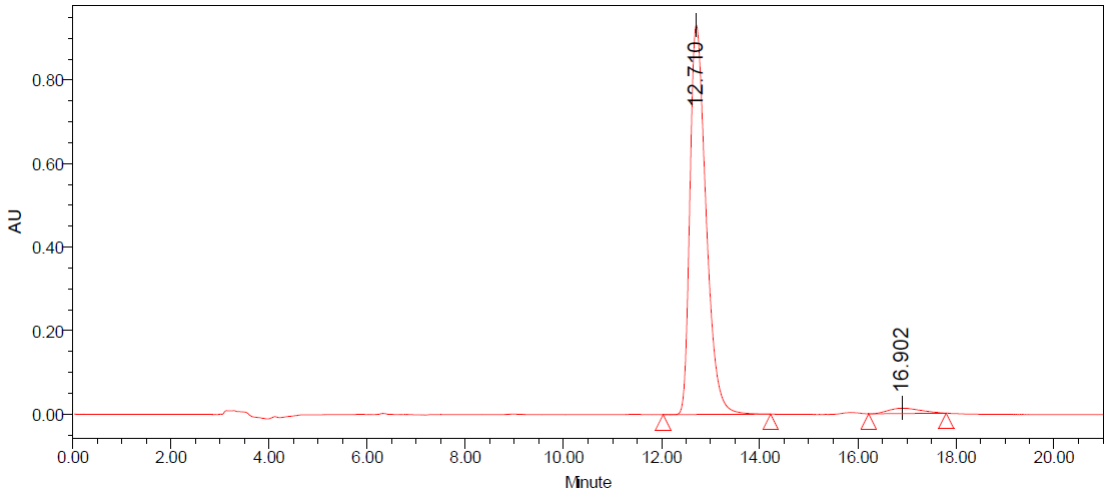
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	4.778	4969410	99.46	291325	99.33	4.532	5.547
2	5.935	27182	0.54	1970	0.67	5.740	6.152



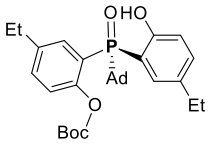
3a



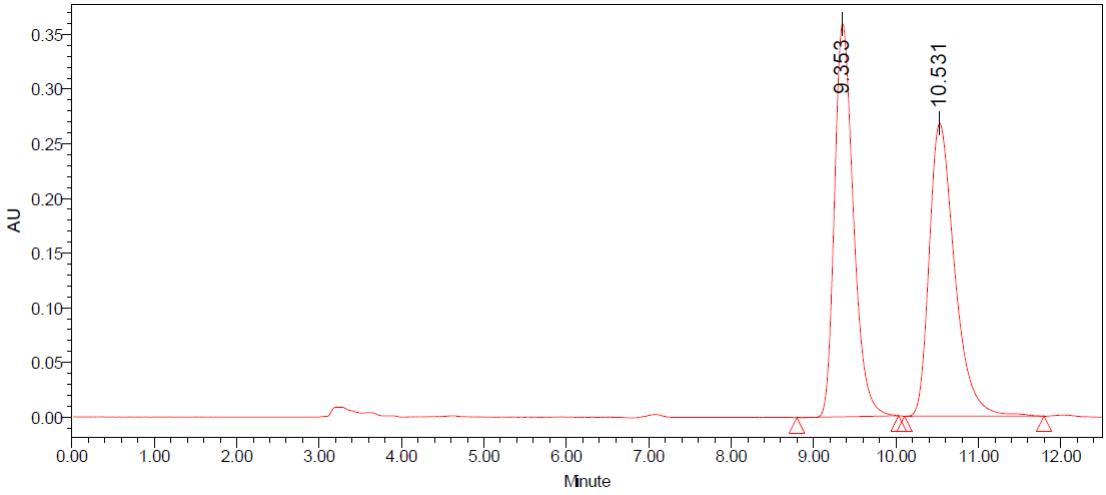
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.778	1497499	49.93	65778	72.27	11.980	14.110
2	16.795	1501549	50.07	25235	27.73	15.617	21.953



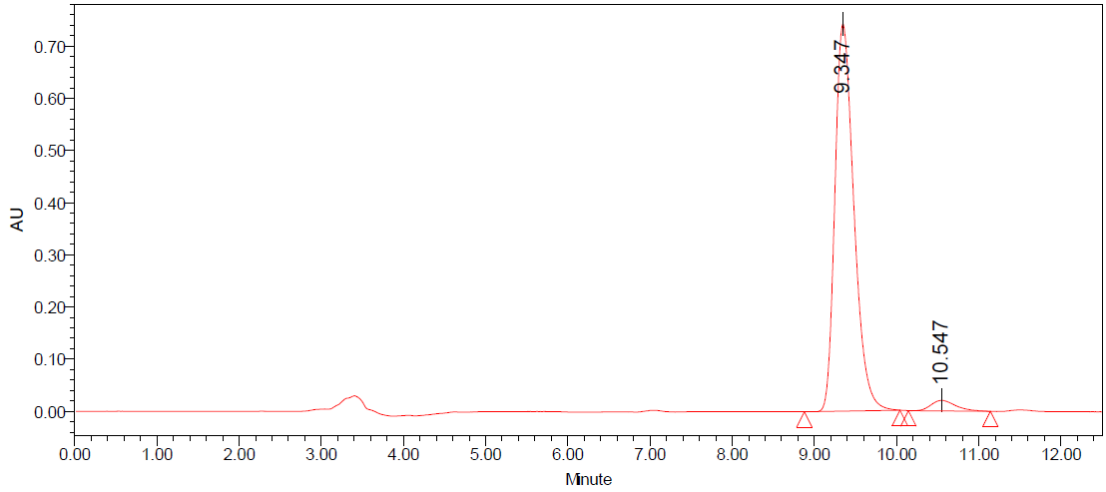
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.710	21282204	97.31	932099	98.63	12.033	14.222
2	16.902	589405	2.69	12910	1.37	16.220	17.802



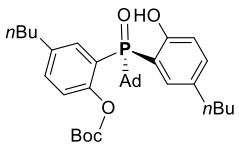
3b



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	9.353	5735916	49.95	359311	57.27	8.797	10.032
2	10.531	5748320	50.05	268059	42.73	10.103	11.795



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	9.347	11931953	96.59	742172	97.35	8.877	10.042
2	10.547	421031	3.41	20242	2.65	10.143	11.142



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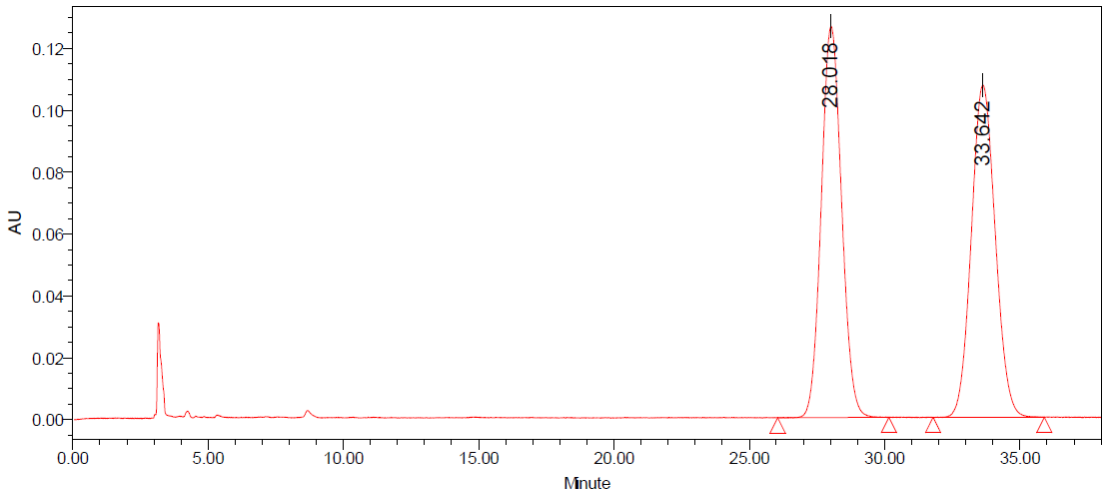
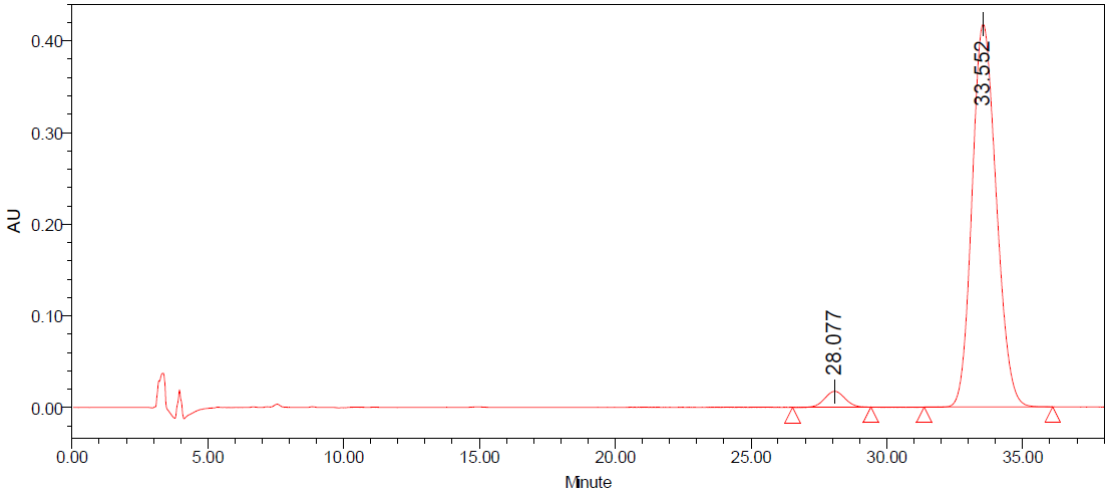
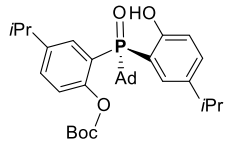


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	28.018	6604617	50.00	126570	54.09	26.050	30.162
2	33.642	6605097	50.00	107426	45.91	31.792	35.902



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	28.077	888547	3.32	17365	3.99	26.532	29.413
2	33.552	25877947	96.68	417731	96.01	31.375	36.112



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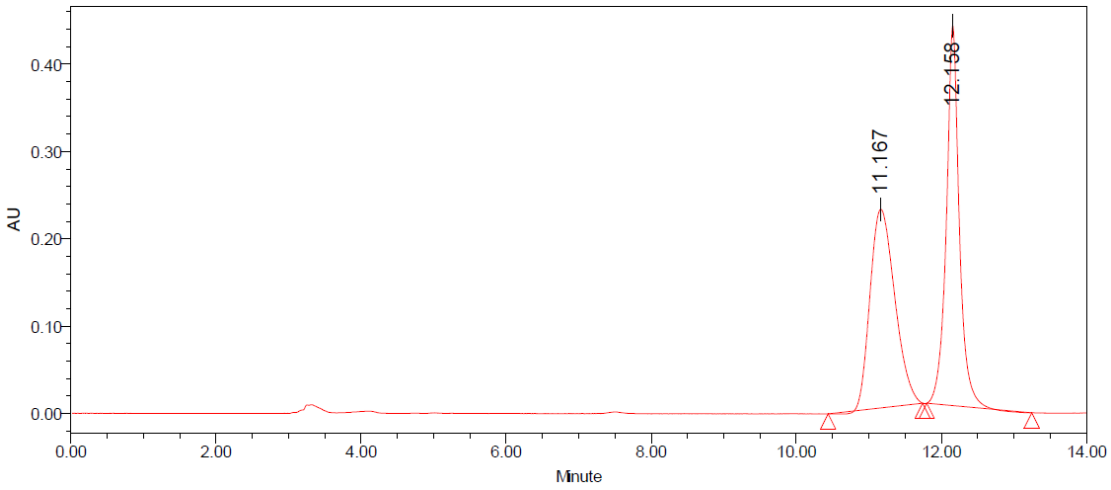
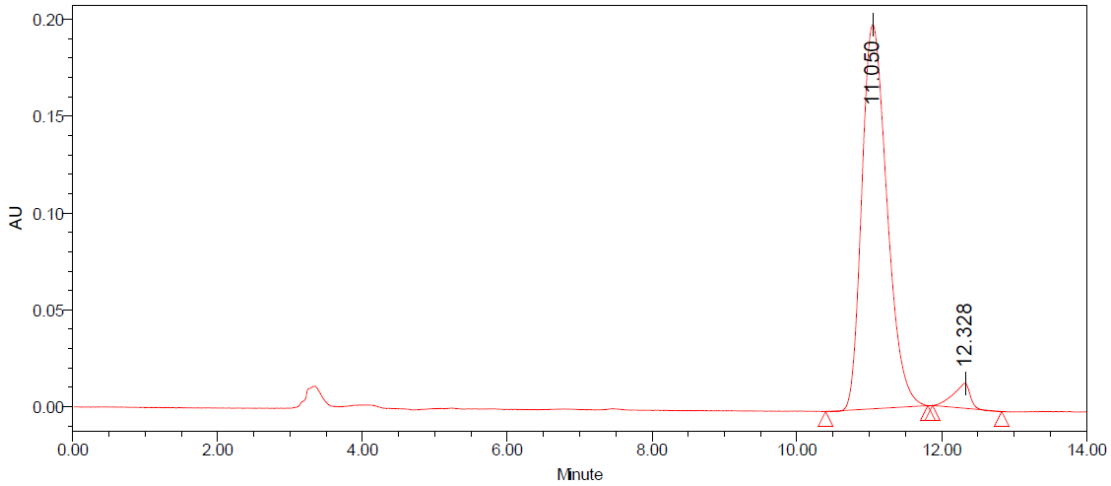
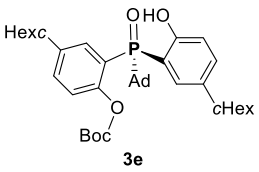


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	11.167	5437712	49.90	227519	34.32	10.438	11.743
2	12.158	5460196	50.10	435374	65.68	11.798	13.247



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	11.050	4786457	95.76	198265	93.81	10.398	11.810
2	12.328	211817	4.24	13084	6.19	11.875	12.830



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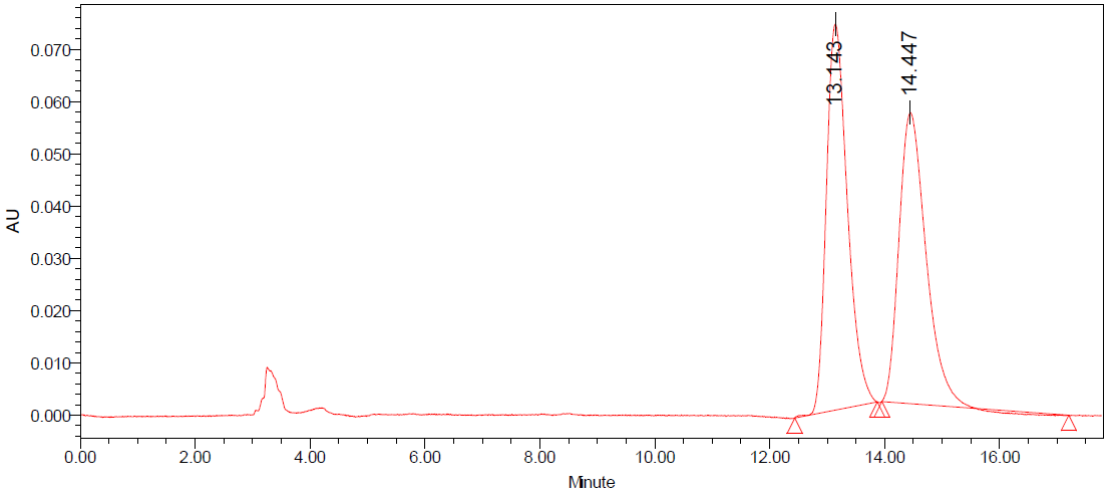
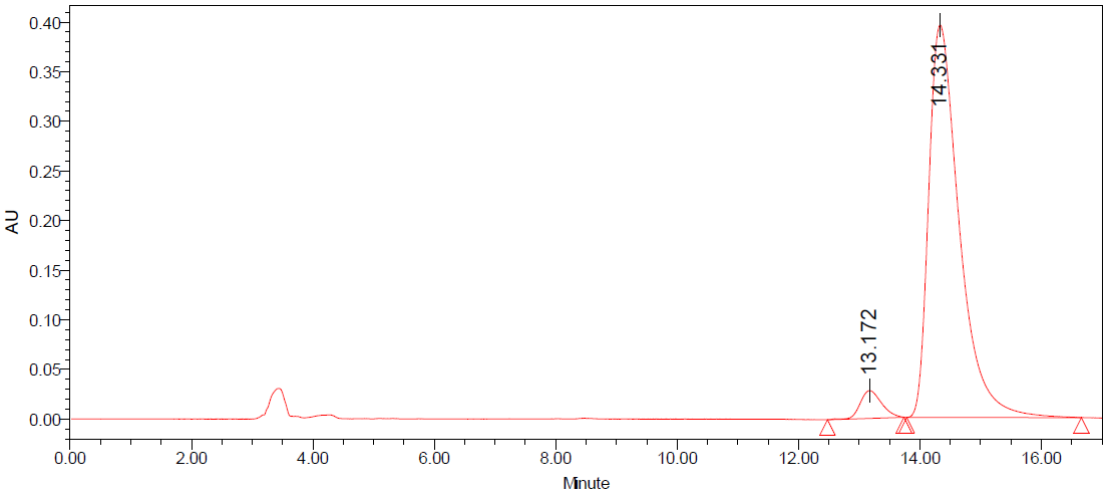
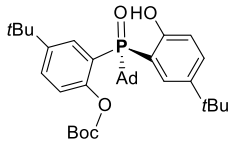


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	13.143	1886936	50.42	73871	56.99	12.437	13.873
2	14.447	1855424	49.58	55747	43.01	13.952	17.205



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	13.172	679295	4.68	27974	6.61	12.477	13.738
2	14.331	13847914	95.32	395491	93.39	13.783	16.660



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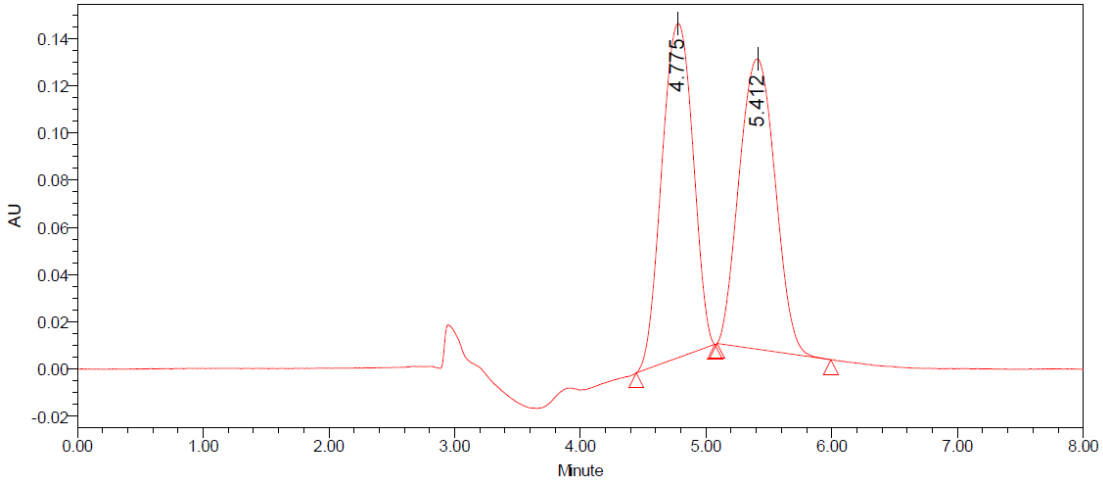
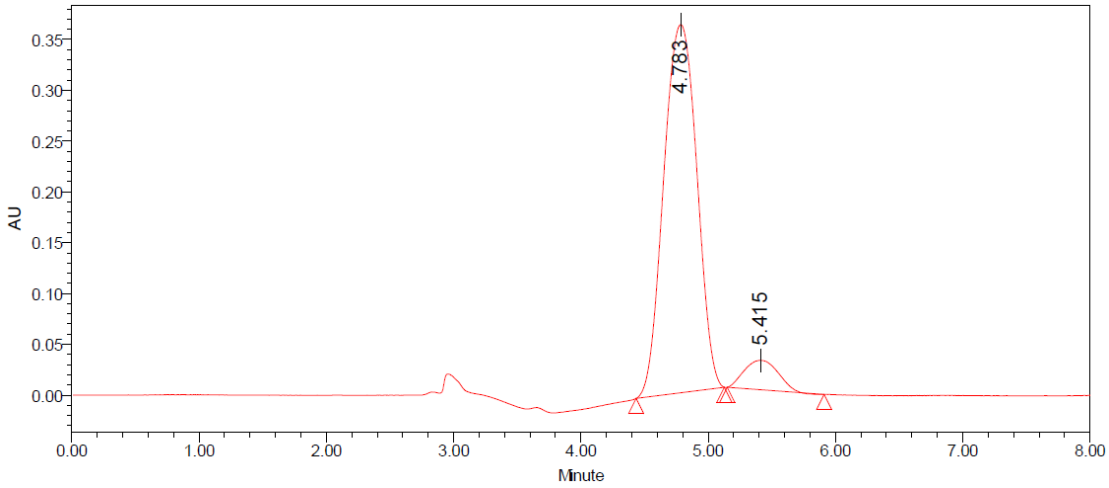
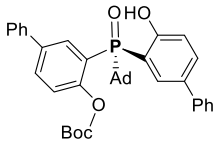


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	4.775	2440120	49.95	141409	53.51	4.445	5.070
2	5.412	2445459	50.05	122874	46.49	5.088	5.993



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	4.783	6563315	92.35	362191	92.58	4.435	5.127
2	5.415	543974	7.65	29018	7.42	5.150	5.912



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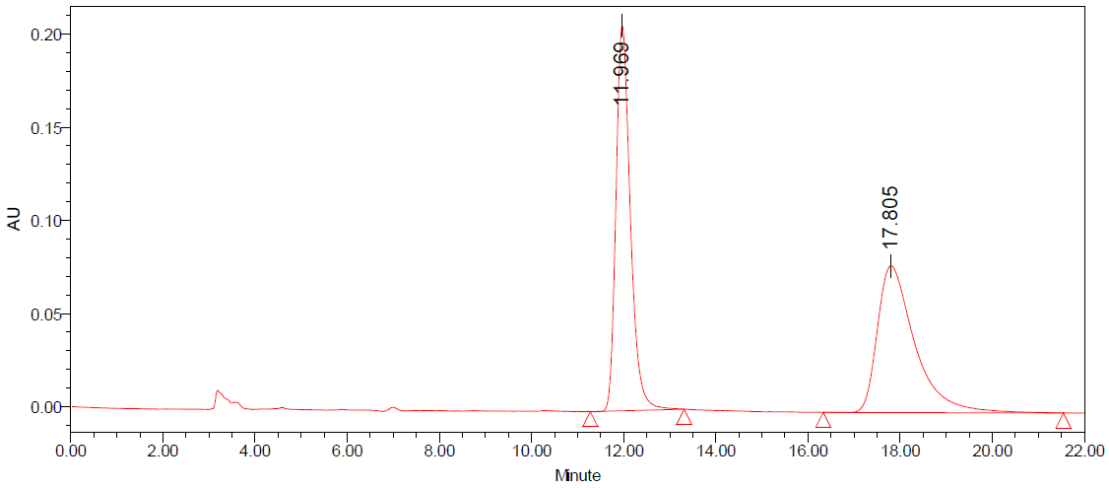
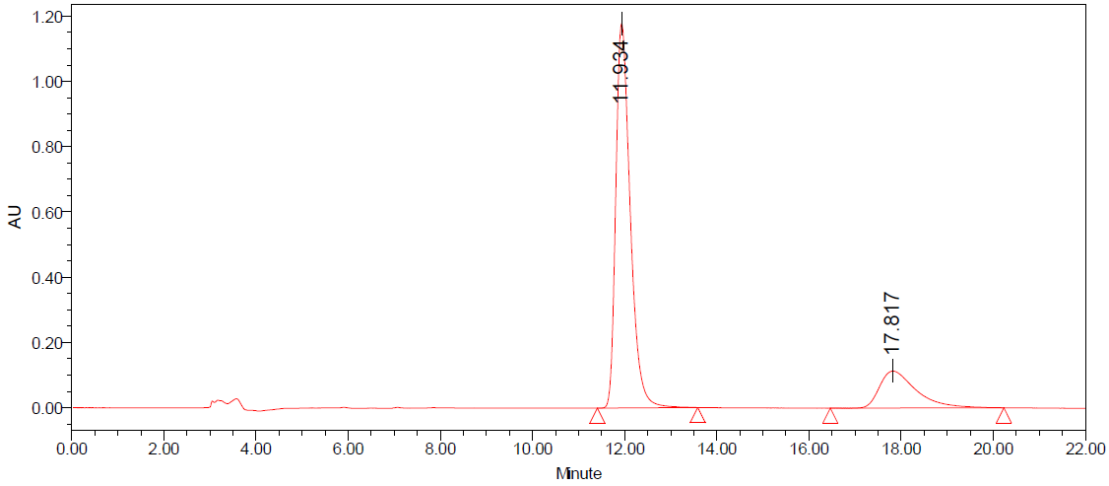
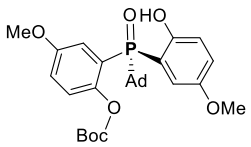


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	11.969	4487338	50.24	206708	72.41	11.273	13.313
2	17.805	4444017	49.76	78743	27.59	16.333	21.545



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	11.934	25639772	80.44	1177853	91.23	11.407	13.585
2	17.817	6233025	19.56	113195	8.77	16.465	20.230



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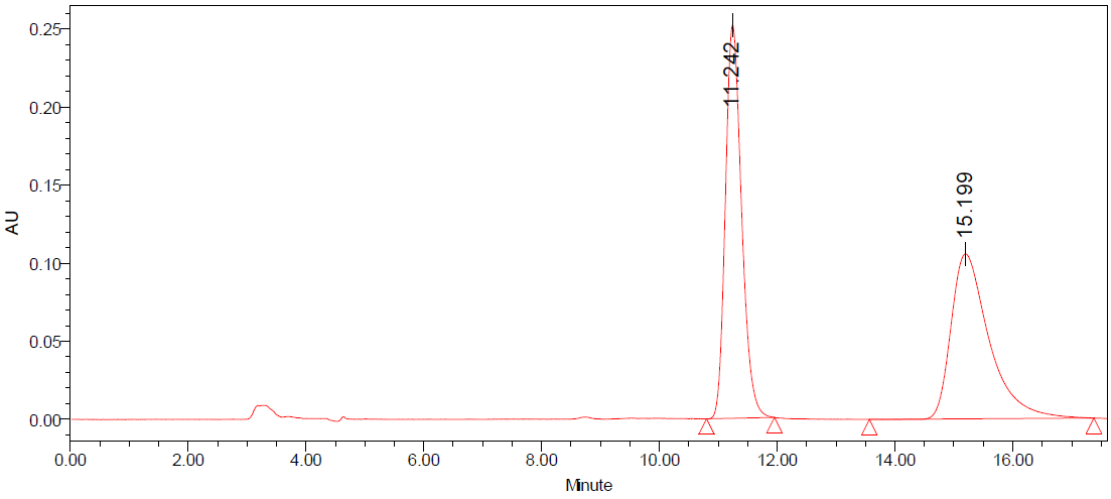
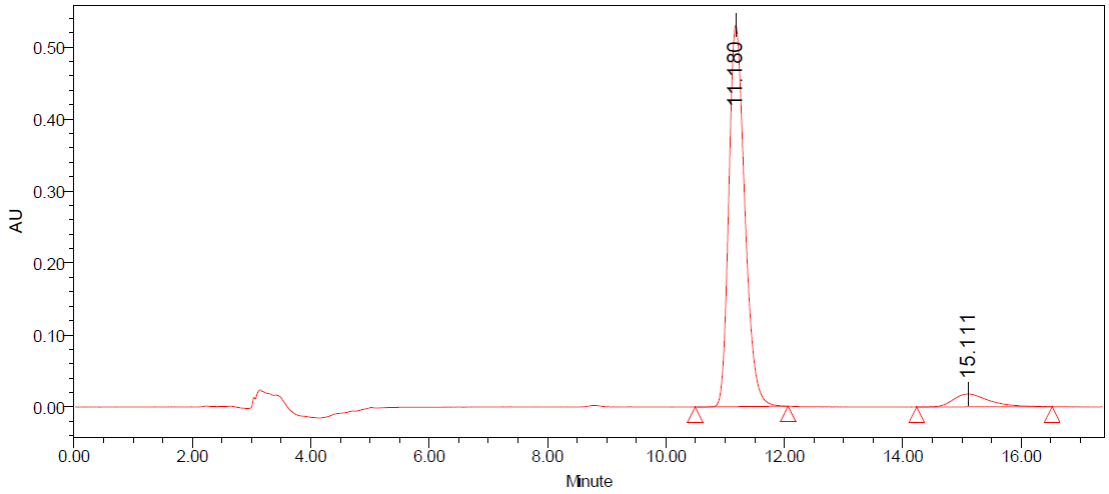
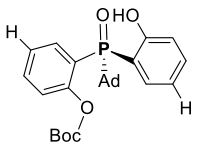


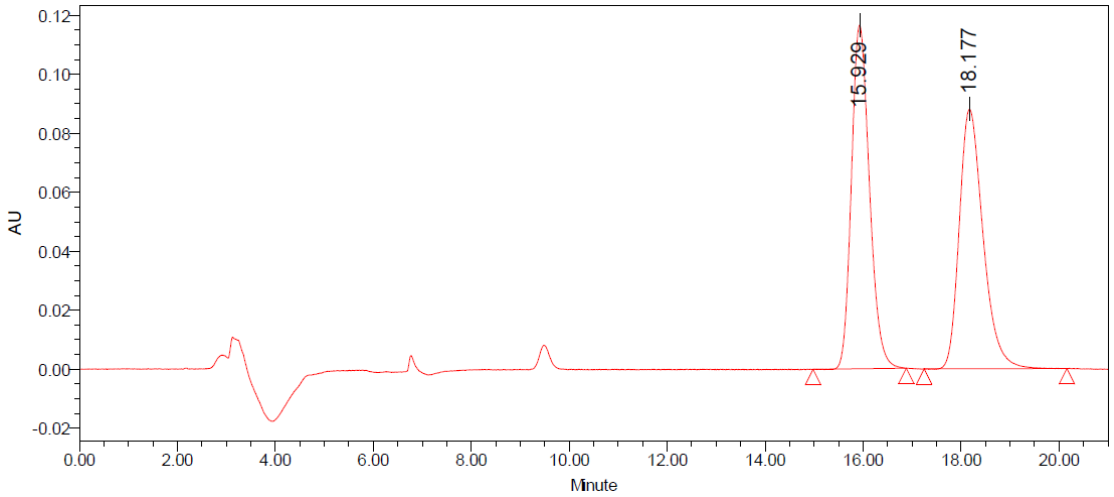
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	11.242	4819973	50.39	251795	70.44	10.802	11.953
2	15.199	4745772	49.61	105681	29.56	13.565	17.378



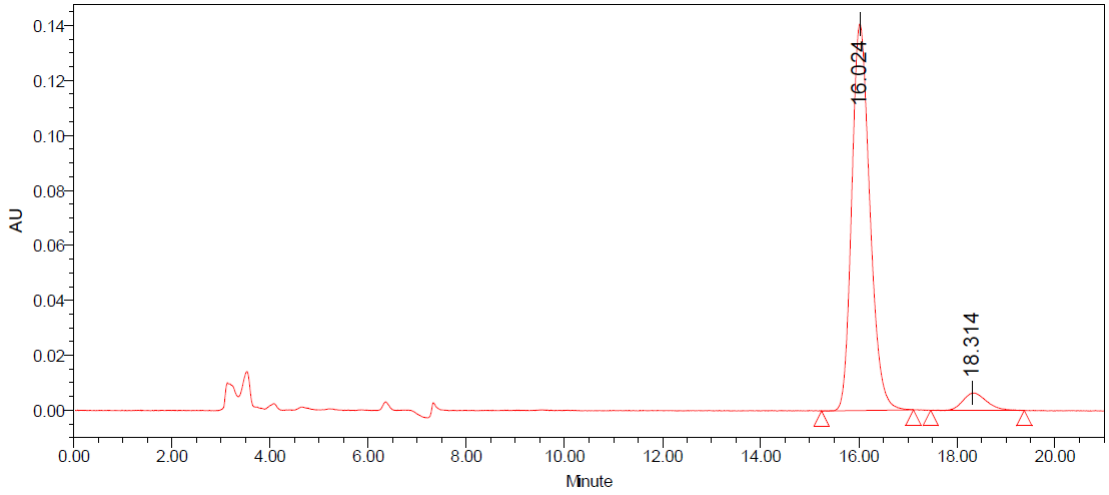
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	11.180	9950293	93.01	530242	96.73	10.492	12.063
2	15.111	748317	6.99	17922	3.27	14.235	16.525



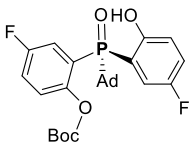
3i



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	15.929	2980617	50.12	116552	56.96	14.980	16.883
2	18.177	2965982	49.88	88055	43.04	17.247	20.160



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	16.024	3602026	94.51	140585	95.71	15.242	17.113
2	18.314	209380	5.49	6309	4.29	17.465	19.373



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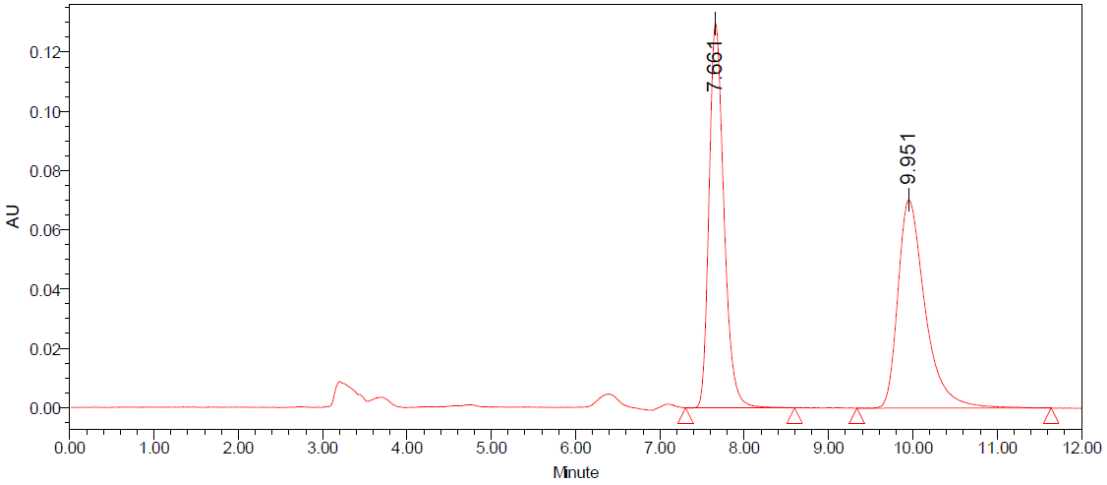
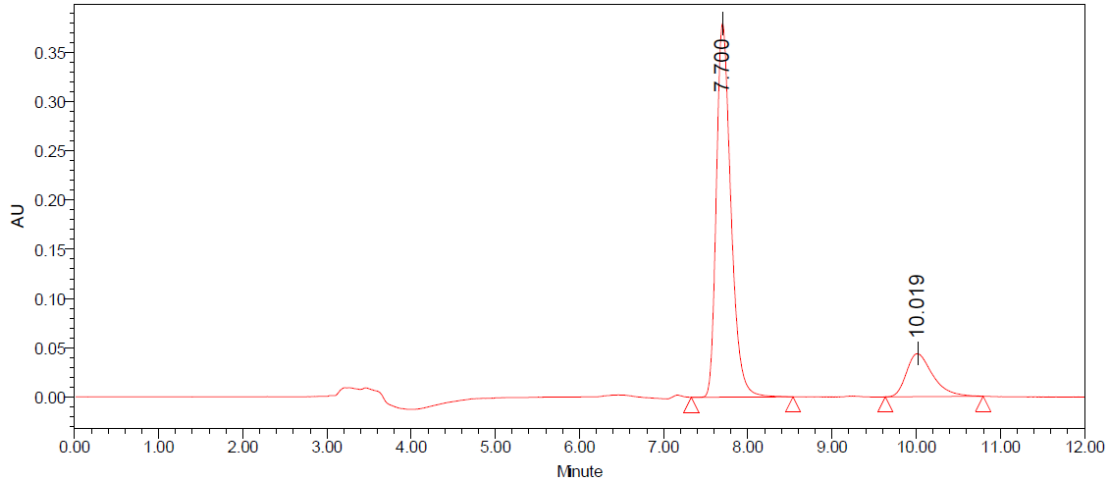
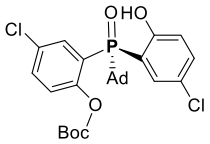


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	7.661	1589412	50.24	129721	64.86	7.305	8.598
2	9.951	1574210	49.76	70282	35.14	9.335	11.640



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	7.700	4560832	82.74	379640	89.67	7.328	8.537
2	10.019	951377	17.26	43721	10.33	9.633	10.795



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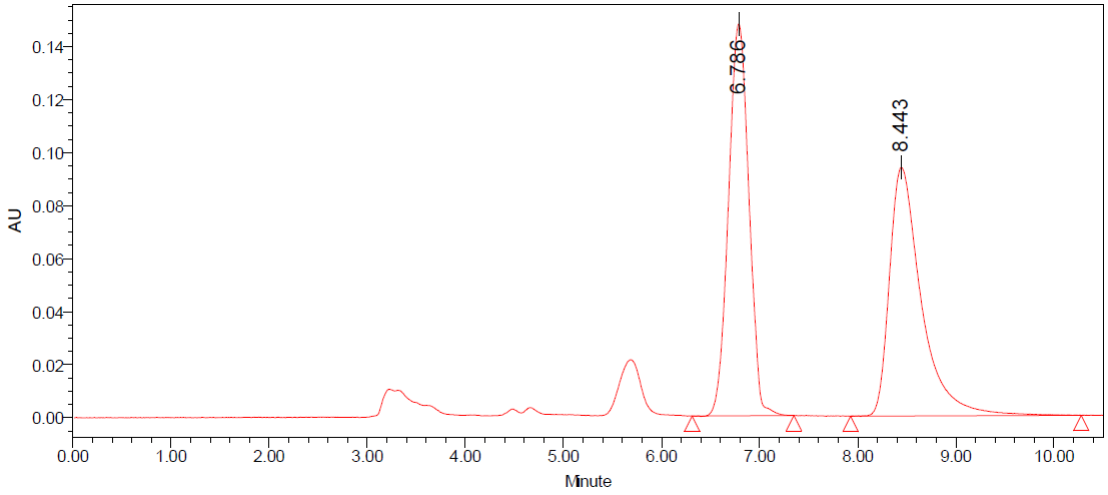
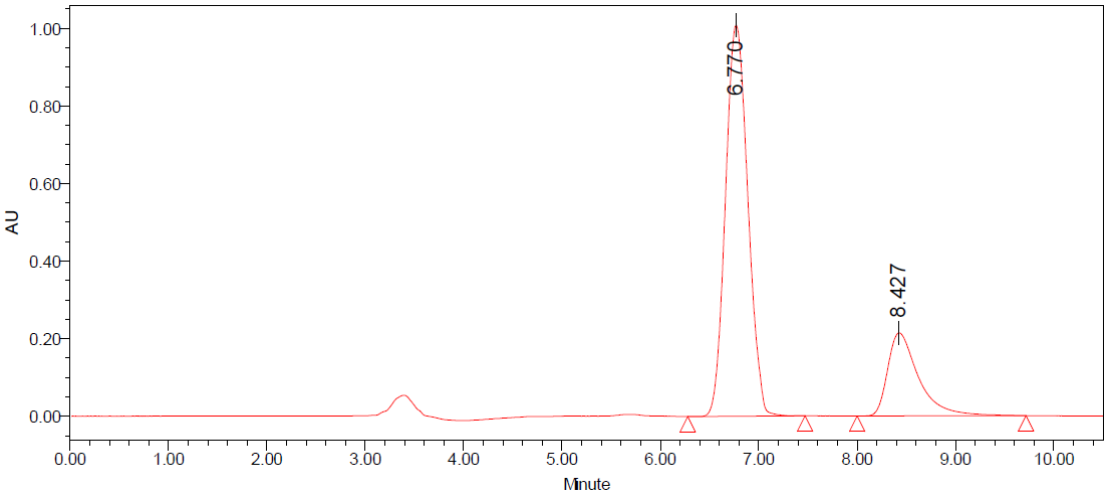
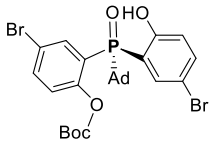


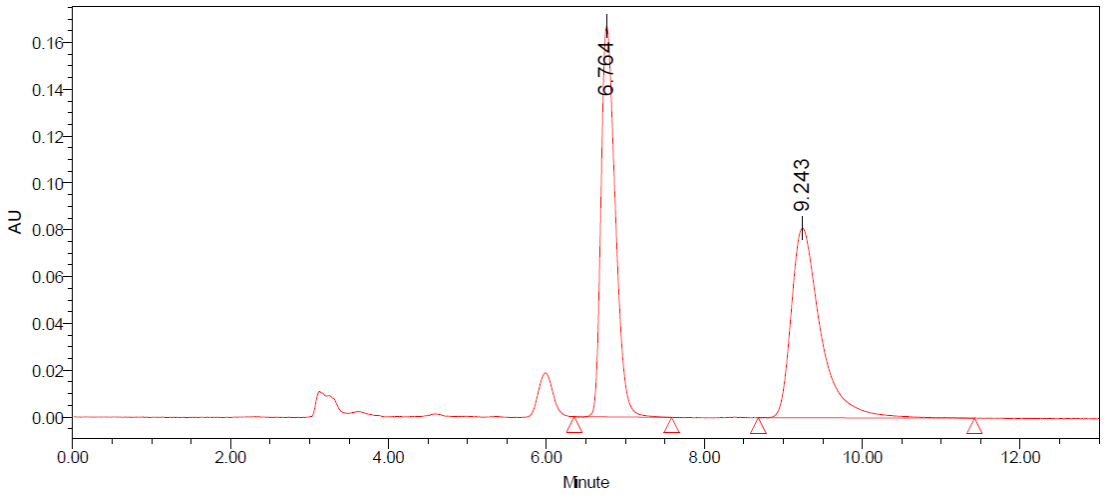
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	6.786	2139101	50.21	147718	61.20	6.312	7.348
2	8.443	2120928	49.79	93669	38.80	7.927	10.278



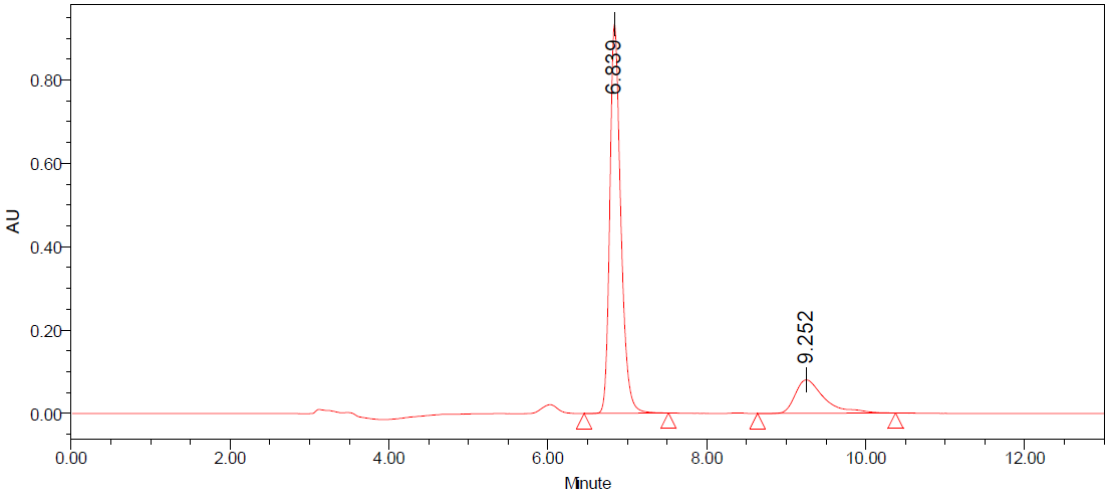
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	6.770	15948972	77.41	1008373	82.50	6.278	7.472
2	8.427	4654068	22.59	213926	17.50	8.000	9.717



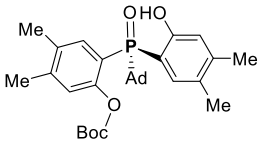
3l



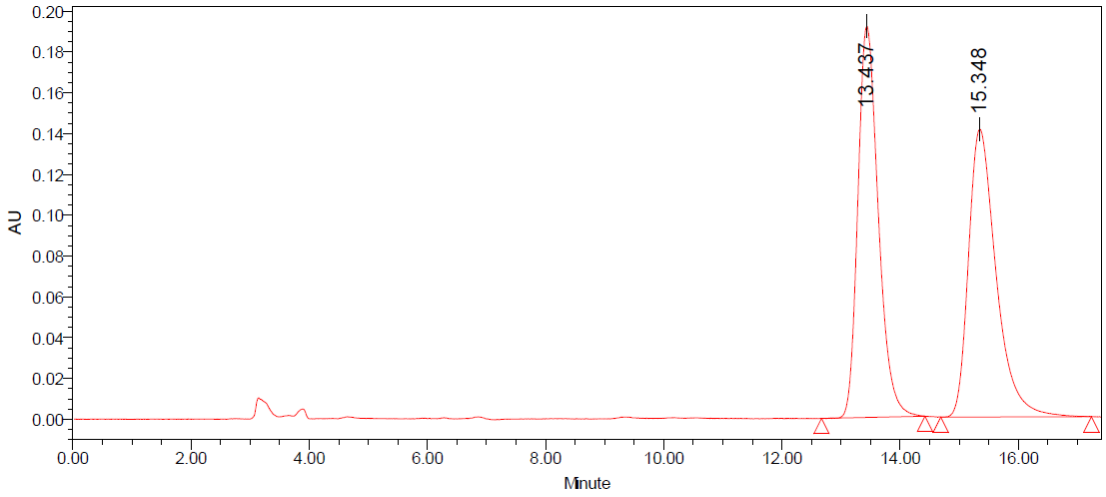
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	6.764	2102838	50.11	166927	67.30	6.353	7.587
2	9.243	2093342	49.89	81104	32.70	8.683	11.423



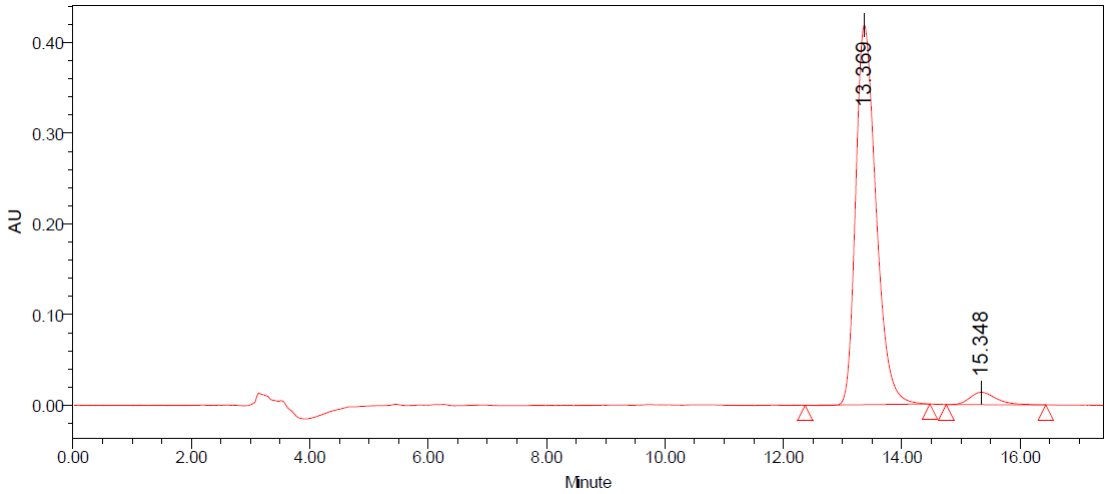
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	6.839	8950385	81.46	933271	92.09	6.457	7.518
2	9.252	2037031	18.54	80158	7.91	8.640	10.377



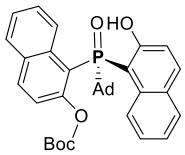
3m



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	13.437	4604423	50.09	191706	57.63	12.670	14.420
2	15.348	4587347	49.91	140954	42.37	14.687	17.238



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	13.369	9985400	95.97	418235	96.84	12.368	14.473
2	15.348	419530	4.03	13637	3.16	14.750	16.433



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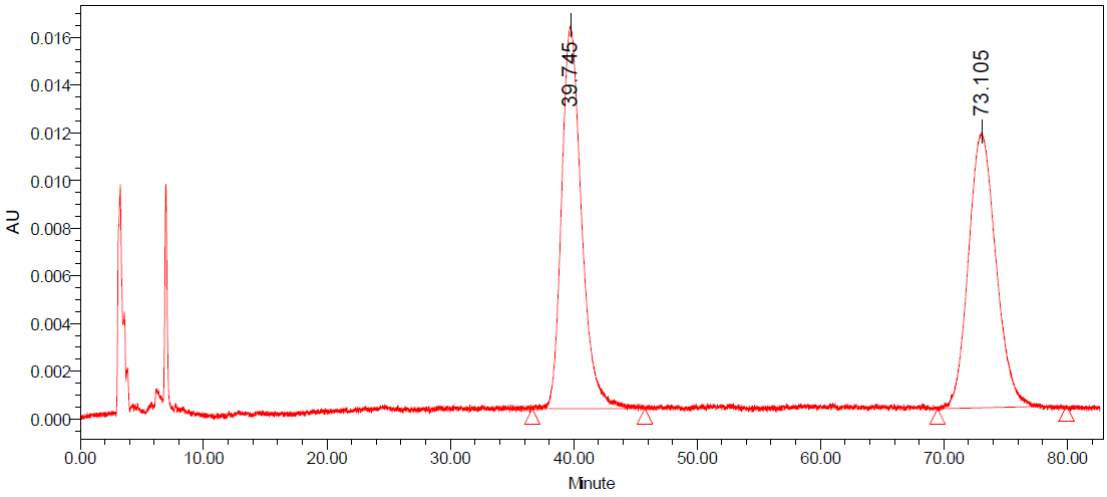
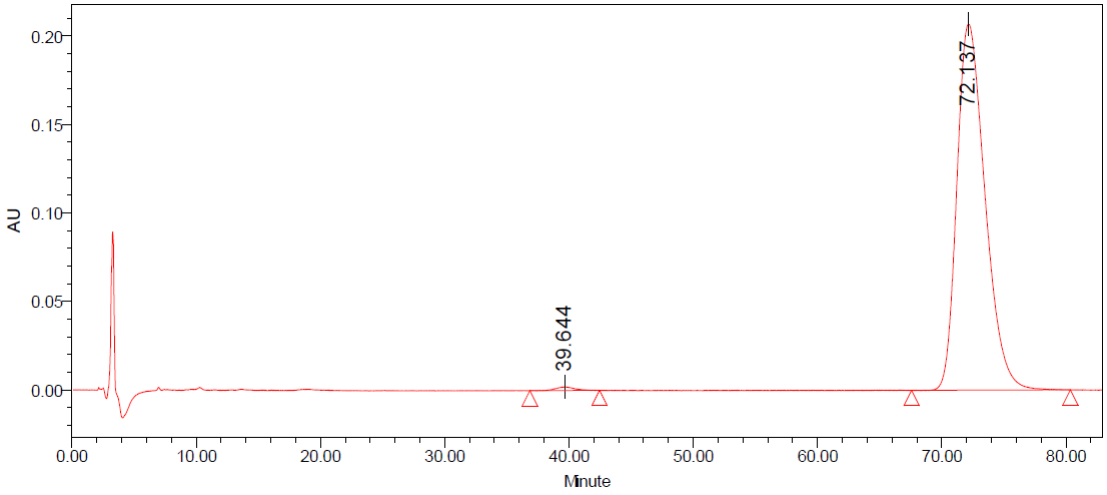
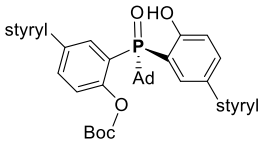


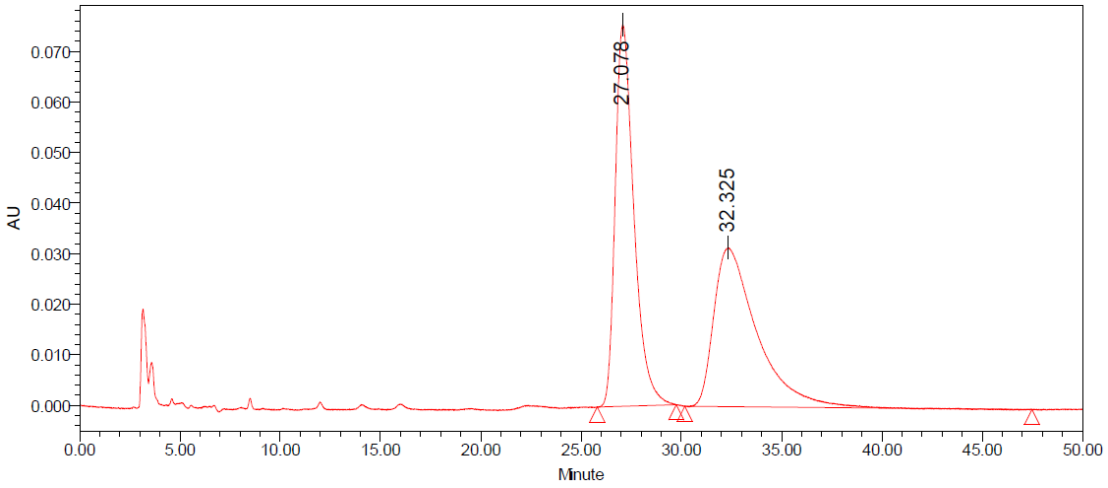
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	39.745	1806487	50.17	16085	58.12	36.642	45.773
2	73.105	1794490	49.83	11589	41.88	69.485	79.935



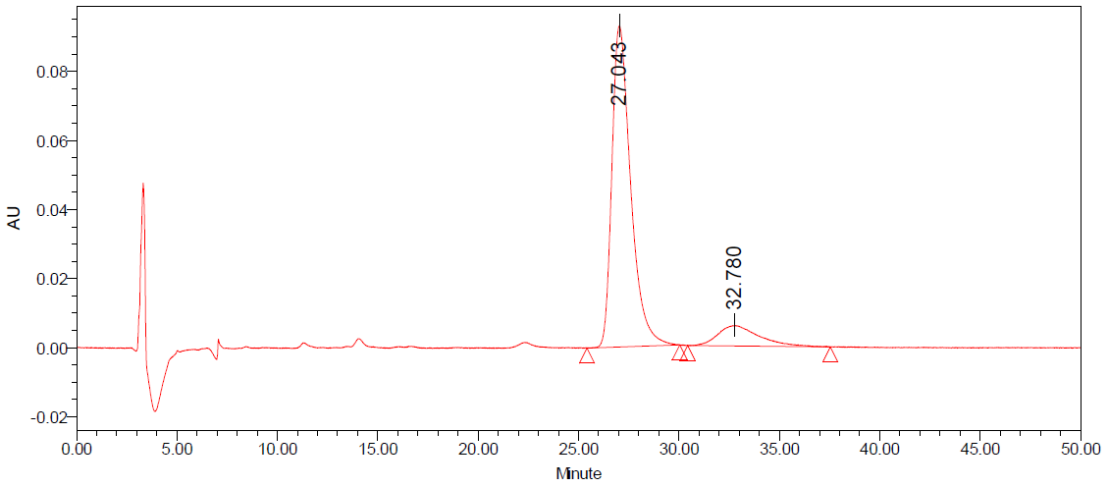
	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	39.644	212497	0.65	2026	0.97	36.852	42.455
2	72.137	32586411	99.35	206855	99.03	67.567	80.357



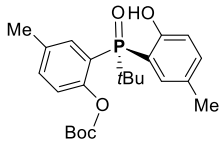
3o



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	27.078	4880759	50.93	75441	70.62	25.807	29.750
2	32.325	4702769	49.07	31389	29.38	30.168	47.485



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	27.043	6054217	87.77	93075	93.99	25.415	30.043
2	32.780	843265	12.23	5947	6.01	30.428	37.535



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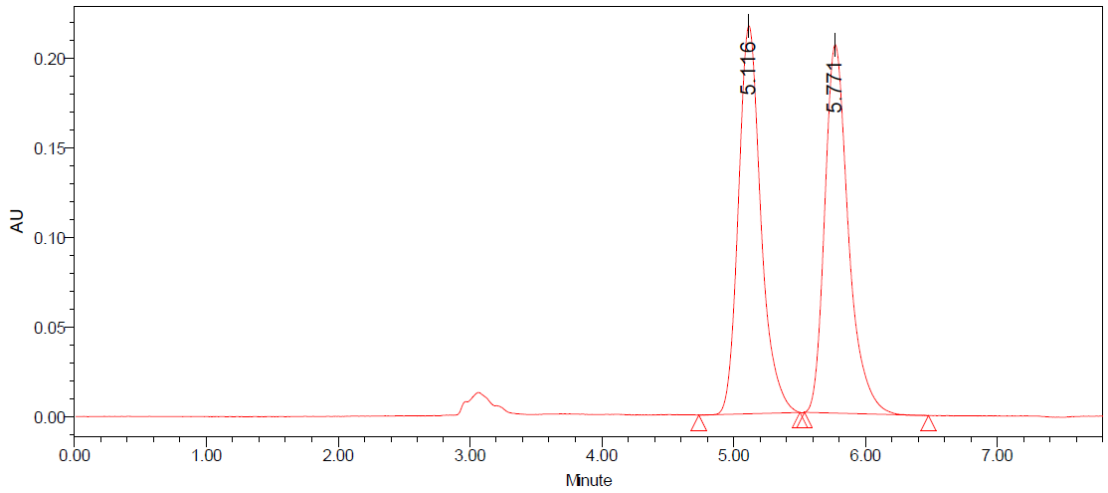
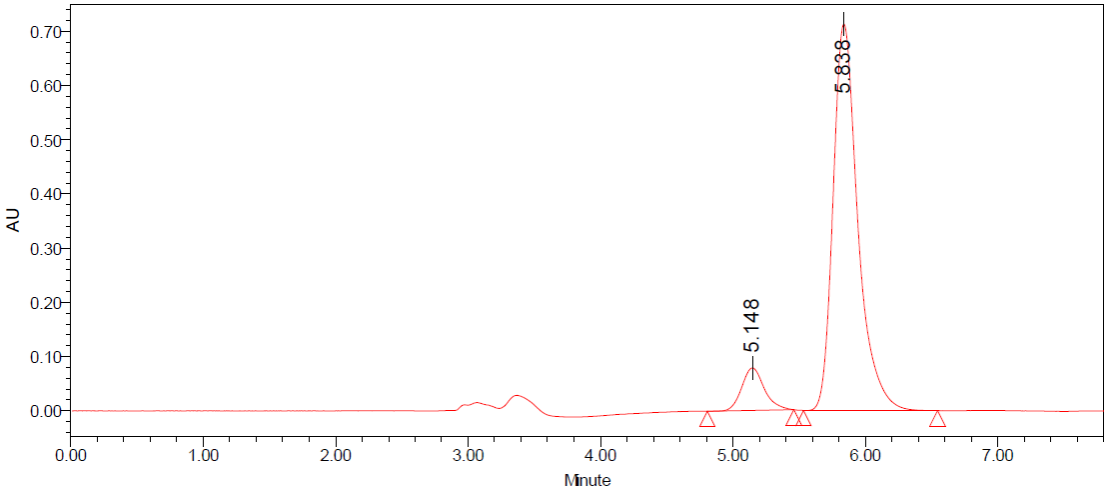
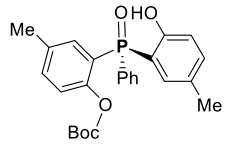


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	5.116	2573643	50.00	216418	51.28	4.737	5.503
2	5.771	2573275	50.00	205616	48.72	5.538	6.478



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	5.148	928234	9.10	78384	9.90	4.807	5.460
2	5.838	9268779	90.90	713013	90.10	5.533	6.545



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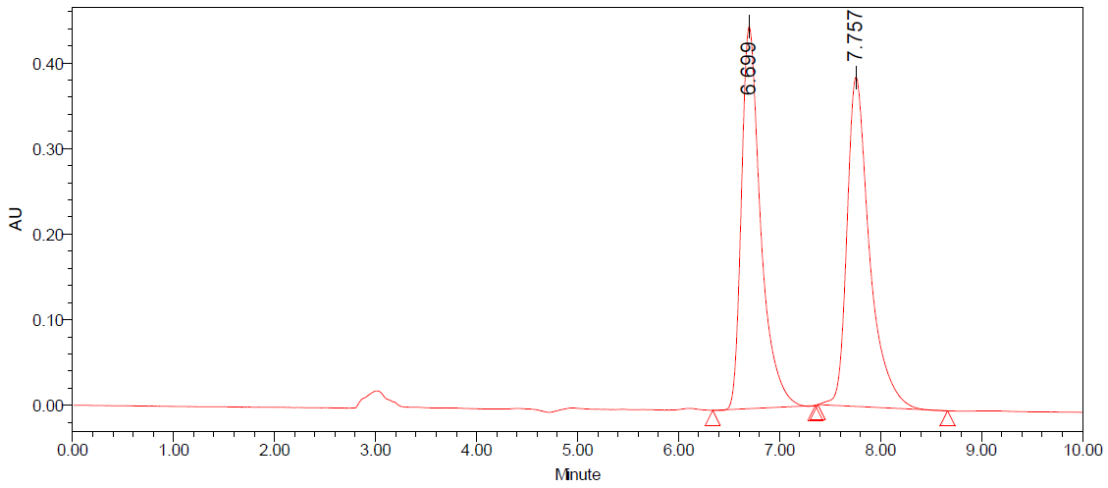
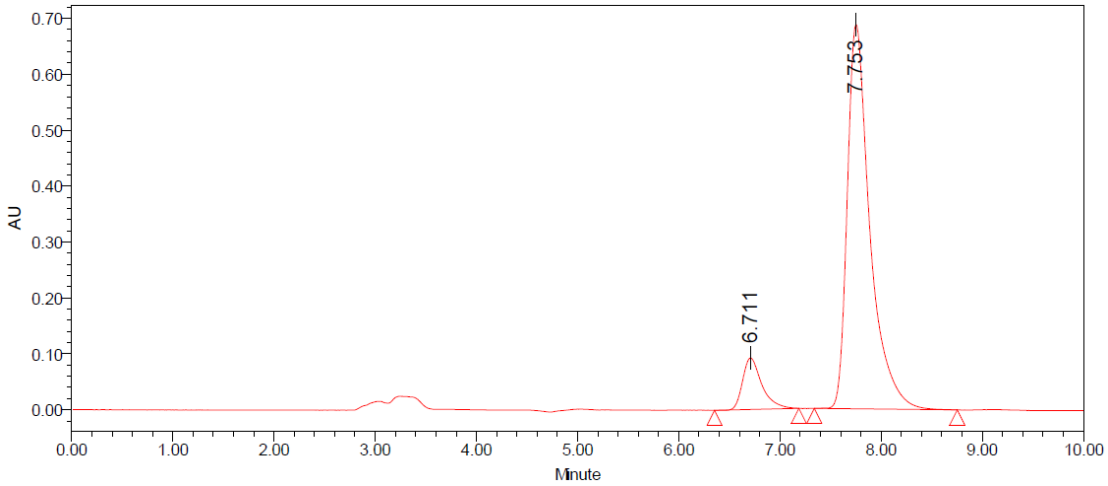
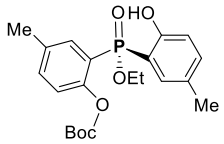


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	6.699	5932139	49.82	446605	53.71	6.338	7.355
2	7.757	5973830	50.18	384965	46.29	7.378	8.665



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	6.711	1215175	10.22	92180	11.83	6.353	7.187
2	7.753	10673792	89.78	686966	88.17	7.340	8.753



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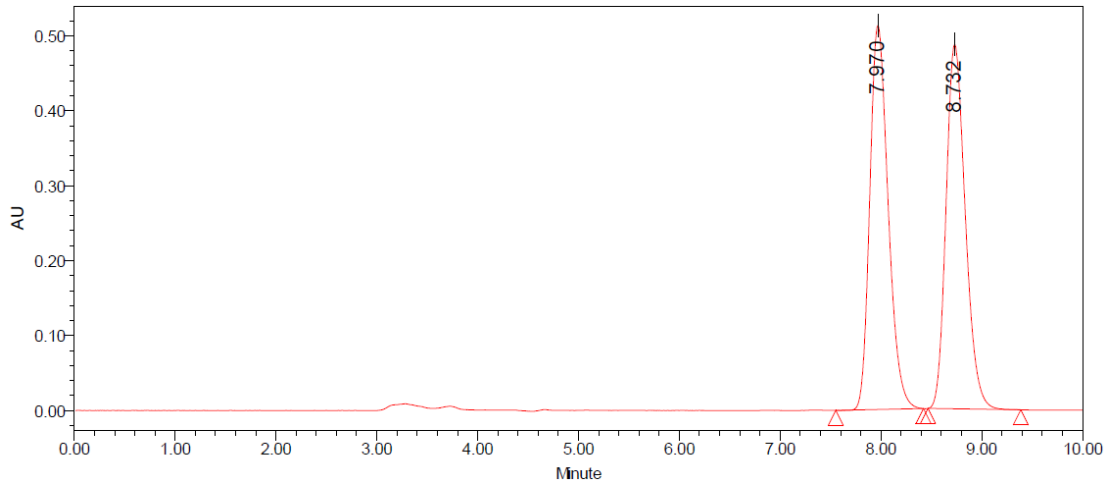
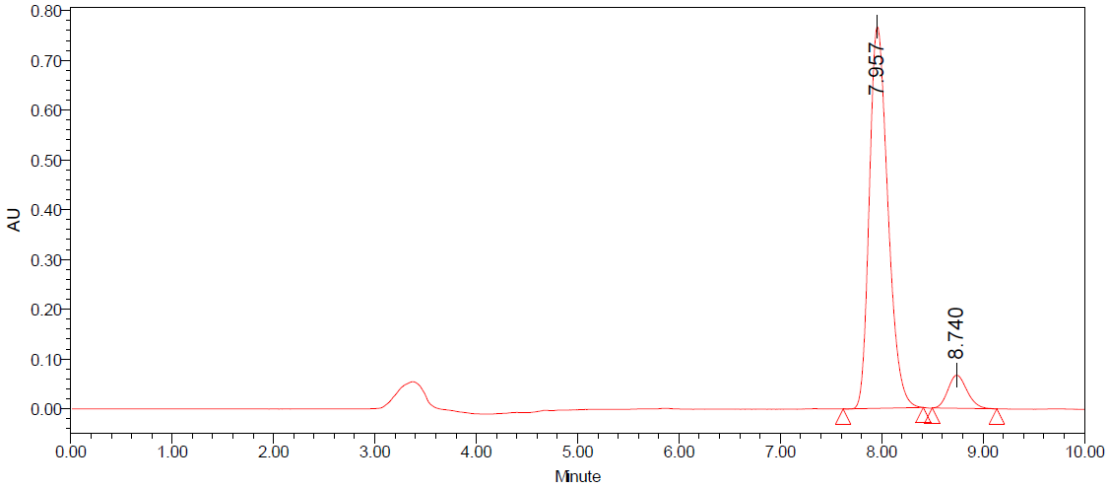
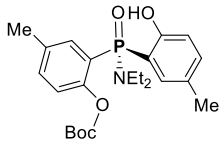


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	7.970	6491110	50.15	512392	51.32	7.552	8.422
2	8.732	6452901	49.85	486128	48.68	8.467	9.387



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	7.957	9752833	91.82	766818	92.01	7.620	8.410
2	8.740	868927	8.18	66587	7.99	8.498	9.135



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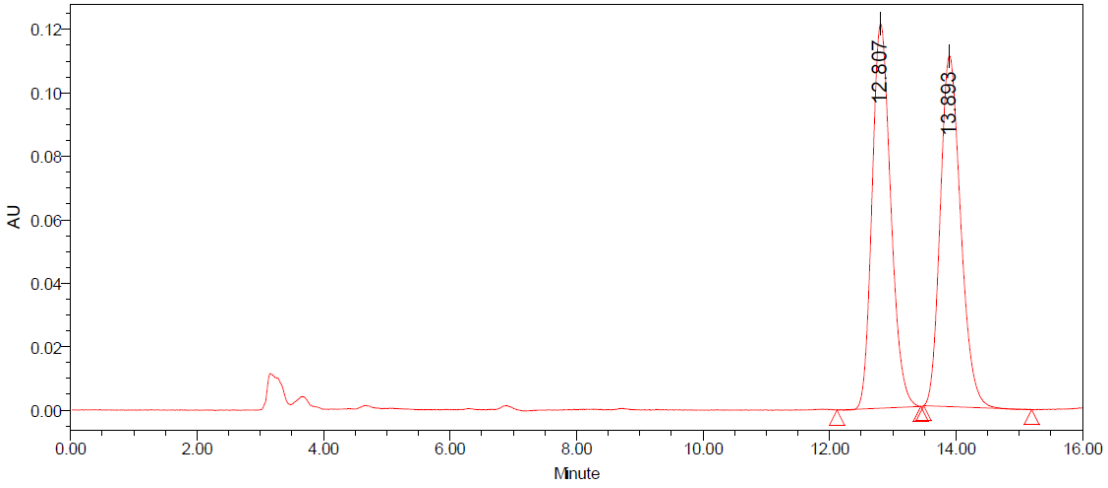
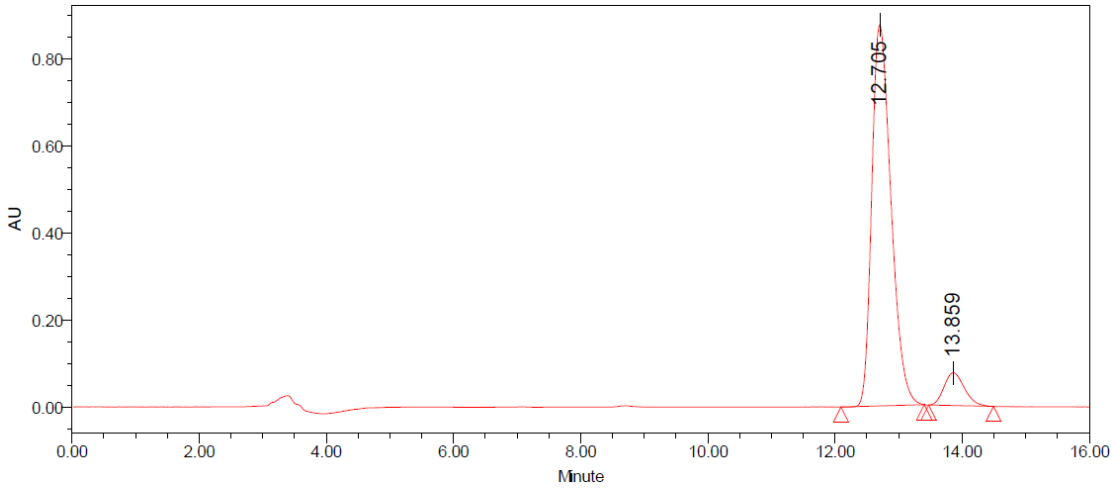
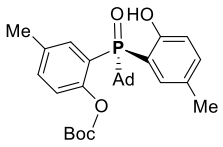


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.807	2486994	50.06	121185	52.29	12.117	13.445
2	13.893	2480639	49.94	110563	47.71	13.490	15.197

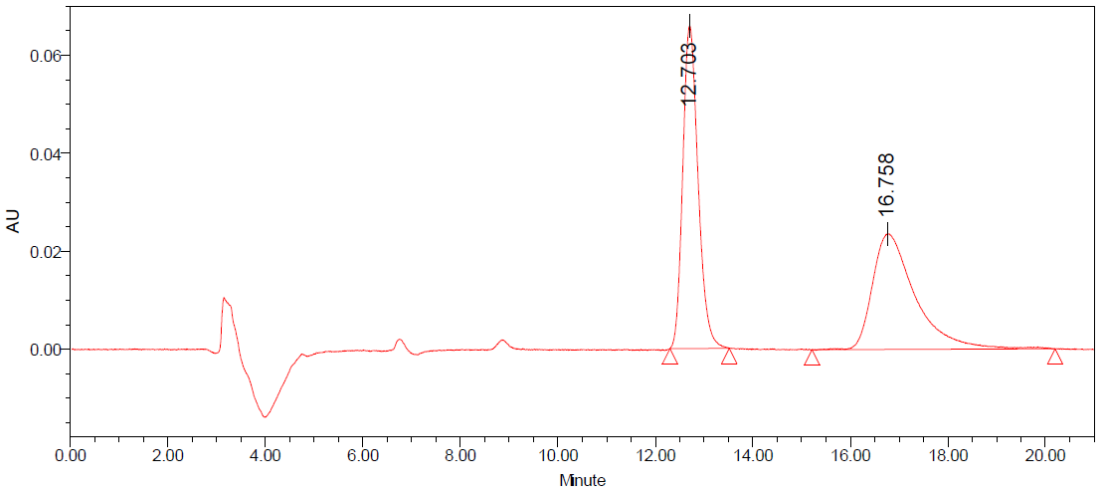


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.705	18394932	91.67	875776	92.08	12.093	13.403
2	13.859	1671271	8.33	75337	7.92	13.473	14.493

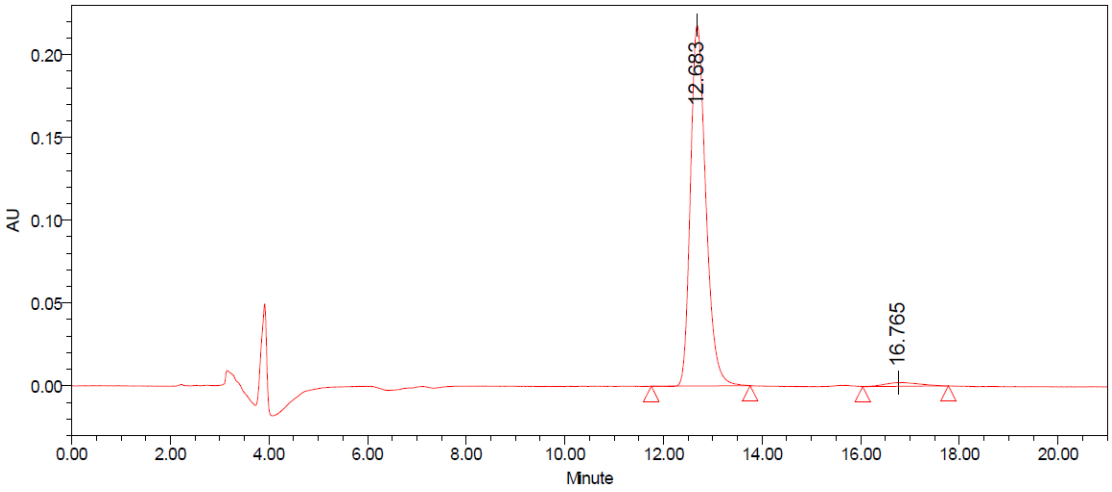


3a

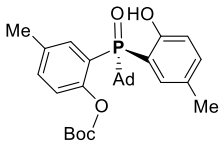
1 mmol scale



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.703	1438049	50.01	65810	73.61	12.298	13.515
2	16.758	1437504	49.99	23591	26.39	15.213	20.202

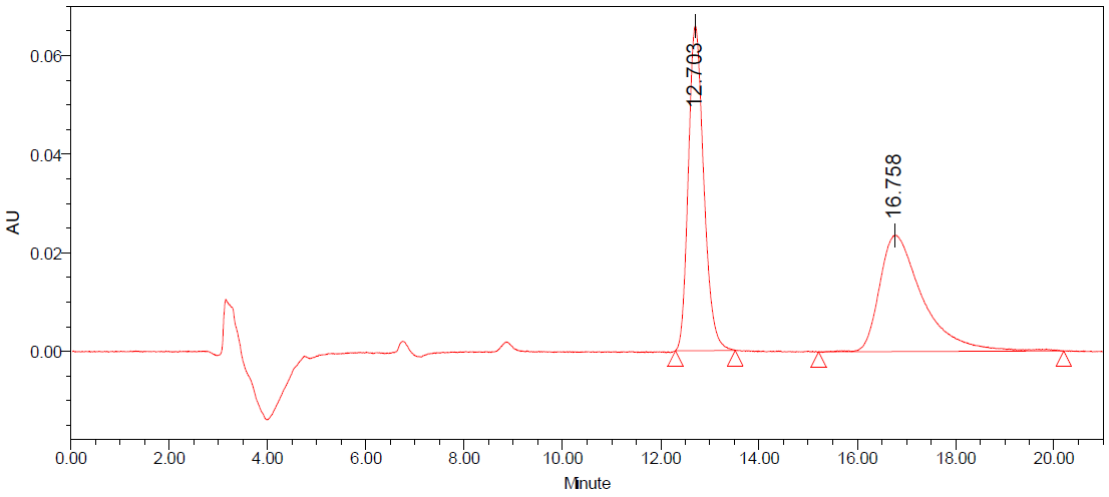


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.683	4728019	97.68	217902	98.94	11.753	13.758
2	16.765	112445	2.32	2331	1.06	16.040	17.778

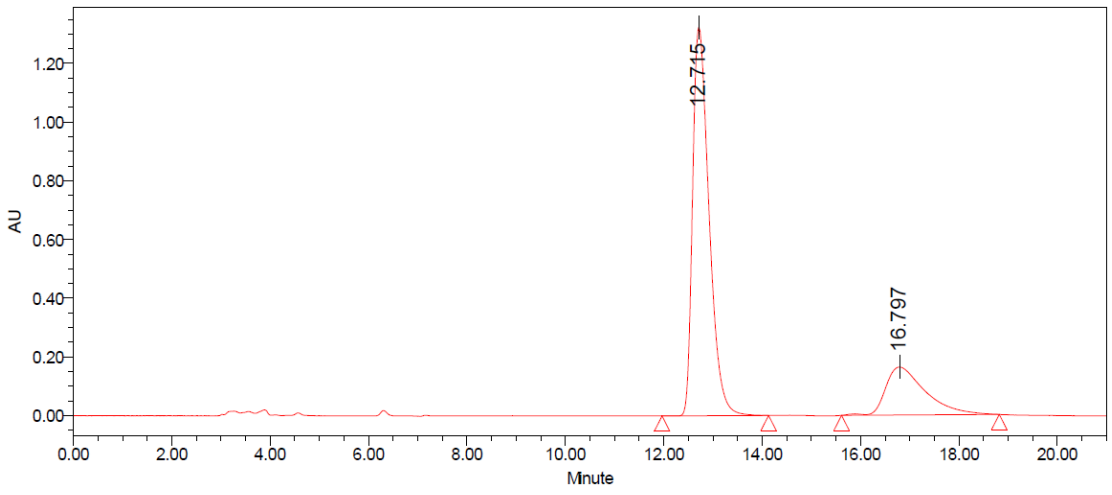


3a

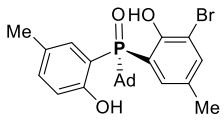
kinetic resolution



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.703	1438049	50.01	65810	73.61	12.298	13.515
2	16.758	1437504	49.99	23591	26.39	15.213	20.202



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	12.715	30730501	77.05	1324131	89.01	11.965	14.130
2	16.797	9155017	22.95	163496	10.99	15.615	18.822



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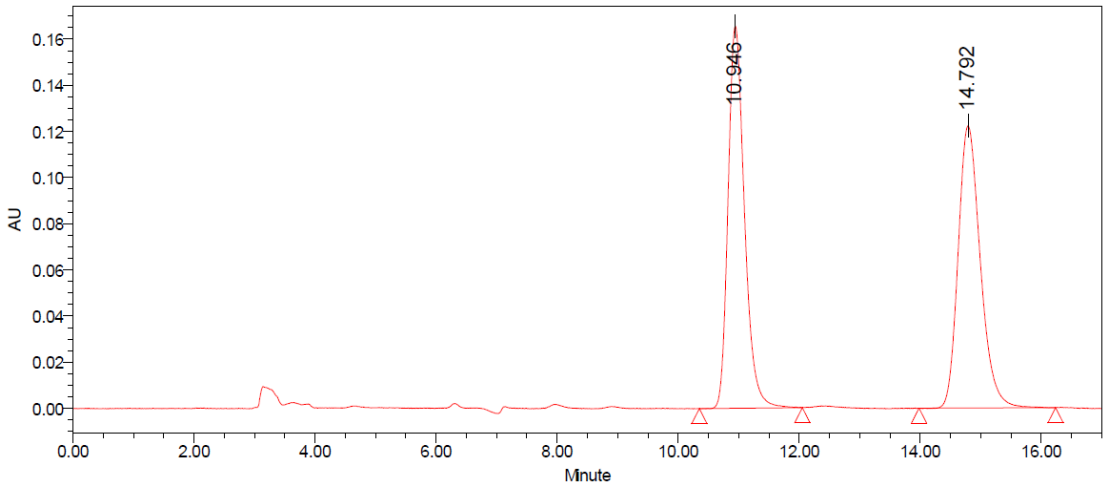
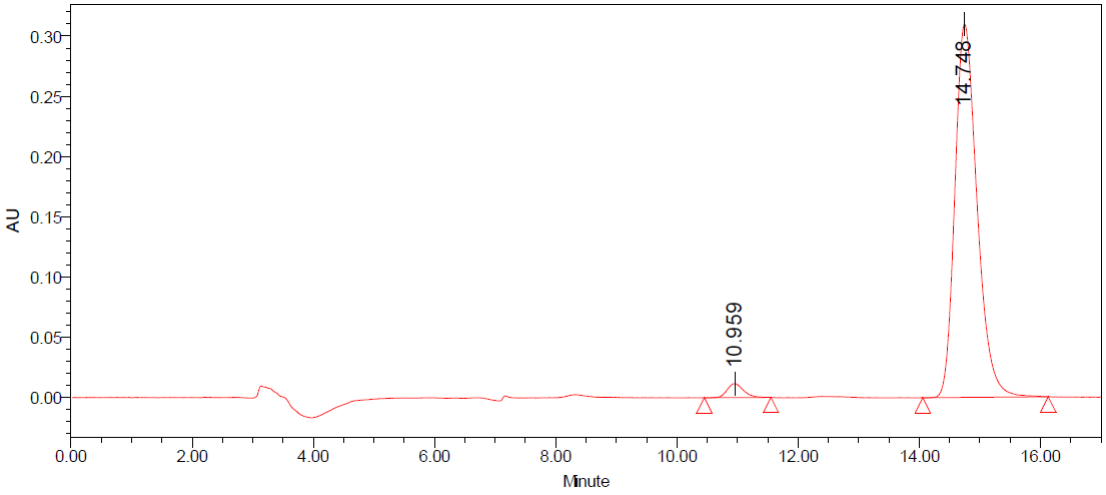


	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	10.946	3114361	49.98	165724	57.51	10.350	12.052
2	14.792	3116491	50.02	122421	42.49	13.982	16.238



	RT (Min)	Area (μU*s)	% Area	Height (μU)	% Height	Start Time (Min)	End Time (Min)
1	10.959	215441	2.66	11614	3.61	10.452	11.552
2	14.748	7884745	97.34	309863	96.39	14.058	16.128