Synthesis

Reviews and Full Papers in Chemical Synthesis

Supporting Information

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Supporting Information

Two-Step Transesterification of Phosphates, Phosphorothioates, and Phosphonates with a Binaphthyl Group for the Synthesis of *P*-Chirogenic Phosphates and Phosphonates

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1. X-ray structure analysis: The single crystal of **5i** suitable for X-ray diffraction was obtained by slow diffusion of hexane into EtOAc solution of **5i**. The single-crystal X-ray diffraction analyses of **5i** was carried out at the BL02B1 beam line of the SPring-8 synchrotron. All frame images (PILATUS3X CdTe 1M, Dectris) were converted to the SFRM format using *Henkankun-R*.[1] Data reduction was performed using Bruker SAINT. Structures were solved by direct methods (*SHELXT*-2014)[2] and refined against F^2 by weighted full-matrix least-squares (*SHELXL*-2014).[3] Crystallographic data of **5i** was deposited at the CCDC under reference number CCDC-2191785. Crystal data and measurement descriptions are summarized Table S1.

The single crystals of (S_{ax}, S_p)-**9c** and (R_{ax}, R_p)-**9c** suitable for X-ray diffraction were obtained by slow diffusion of hexane into toluene solution of them. Single-crystal X-ray diffraction experiment for them was carried out at XtaLAB Synergy-i. A wavelength of λ = 1.54184 Å and single crystals of 0.15 × 0.04 × 0.02 ((S_{ax}, S_p)-**9c**) and 0.10 × 0.10 × 0.10 ((R_{ax}, R_p)-**9c**) mm^3 were used. Data reduction was performed using CrysAlisPro 1.171.41.122a (Rigaku OD). Structures were solved by direct methods (*SHELXT*)[2)] and refined against F^2 by weighted full-matrix least-squares (*SHELXL*)[3)]. Crystal data and measurement descriptions are summarized Tables S2 and S3. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre: Deposition numbers CCDC-2181071 for (S_{ax}, S_p)-**9c** and CCDC-2181072 for (R_{ax}, R_p)-**9c**. Crystal data and measurement descriptions are summarized Table S2 and S3.

Table S1. Crystal Data and Structure Refinement for **5i**

	13_TM01_0m_a
Crystal data	
Chemical formula	$C_{33}H_{35}O_9PS$
M_r	638.64
Crystal system, space group	*Monoclinic*, $P2_1$
Temperature (K)	100
a, *b*, *c* (Å)	8.9472 (5), 26.2523 (13), 13.4716 (7)
β (°)	90.056 (1)
V (Å^3)	3164.3 (3)
Z	4

Radiation type	Synchrotron, λ = 0.81063 Å
μ (mm^{-1})	0.29
Crystal size (mm)	0.01 × 0.01 × 0.01
Diffractometer	Dectris PILATUS-CdTe
Absorption correction	–
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30822, 9350, 9121
R_{int}	0.036
θ_{max} (°)	27.5
$(\sin\theta/\lambda)_{max}$ ($Å^{-1}$)	0.570
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.040, 0.112, 1.20
No. of reflections	9350
No. of parameters	805
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rangle_{max}$, $\Delta\rangle_{min}$ (e $Å^{-3}$)	0.49, -0.42
Absolute structure	Flack x determined using 3993 quotients [(I+)-(I-)]/[(I+)+(I-)] .[4]
Absolute structure parameter	0.032 (15)

Table S2. Crystal Data and Structure Refinement for (S_{ax}, S_p)-**9c**

	inoue20220317s_auto
Crystal data	
Chemical formula	$C_{25}H_{25}O_4P$
M_r	420.42

Crystal system, space group	*Orthorhombic*, $P2_12_12_1$
Temperature (K)	123
a, *b*, *c* (Å)	9.9829 (3), 11.4652 (3), 18.5624 (5)
V (Å^3)	2124.58 (10)
Z	4
Radiation type	Cu *K*a
m (mm^{-1})	1.39
Crystal size (mm)	0.15 × 0.04 × 0.02
Data collection	
Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction	Gaussian *CrysAlis PRO* 1.171.41.122a (Rigaku Oxford Diffraction, 2021) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.882, 1.000
No. of measured, independent and observed [$I > 2s(I)$] reflections	7961, 3298, 3024
R_{int}	0.034
$(\sin q/l)_{max}$ (Å^{-1})	0.602
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, *S*	0.038, 0.084, 1.04

No. of reflections	3298
No. of parameters	275
H-atom treatment	H-atom parameters constrained
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	0.20, -0.33
Absolute structure	Flack x determined using 939 quotients [(I+)-(I-)]/[(I+)+(I-)].[4]
Absolute structure parameter	-0.008 (18)

Table S3. Crystal Data and Structure Refinement for (R_{ax}, R_p)-**9c**

	inoue20220317_auto
Crystal data	
Chemical formula	$C_{25}H_{25}O_4P$
M_r	420.42
Crystal system, space group	Orthorhombic, $P2_12_12_1$
Temperature (K)	123
a, *b*, *c* (Å)	9.9626 (4), 11.4931 (4), 18.7069 (7)
V (Å^3)	2141.96 (14)
Z	4
Radiation type	Cu *K*a
m (mm^{-1})	1.37
Crystal size (mm)	0.10 × 0.10 × 0.10
Data collection	

Diffractometer	XtaLAB Synergy, Single source at home/near, HyPix3000
Absorption correction	Gaussian *CrysAlis PRO* 1.171.41.122a (Rigaku Oxford Diffraction, 2021) Numerical absorption correction based on gaussian integration over a multifaceted crystal model Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.
T_{min}, T_{max}	0.930, 1.000
No. of measured, independent and observed [$I > 2s(I)$] reflections	8282, 3526, 3132
R_{int}	0.043
$(\sin q/l)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2s(F^2)]$, $wR(F^2)$, S	0.058, 0.162, 1.05
No. of reflections	3526
No. of parameters	275
H-atom treatment	H-atom parameters constrained
$D\rho_{max}$, $D\rho_{min}$ (e Å^{-3})	0.68, -0.46
Absolute structure	Flack x determined using 1079 quotients [(I+)-(I-)]/[(I+)+(I-)] (Parsons, Flack and Wagner, Acta Cryst. B69 (2013) 249-259).
Absolute structure parameter	-0.02 (2)

2. Experimental procedures and spectroscopic data of the starting materials

(S_{ax})- 4-(Cyclohexyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide ((S_{ax})-**1a**)

To a THF solution (2 mL) of (S_{ax})-4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (0.36 g, 1.0 mmol) was added cyclohexanol (0.11 mL, 1.0 mmol) and Et_3N (0.28 mL, 2.0 mmol) under Ar atmosphere. The resulting solution was stirred under reflux for 2 h and it was extracted with Et_2O. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 3) to give (S_{ax})-4-(cyclohexyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (0.29 g, 0.67 mmol, 67%) as a white solid.: mp: 230–236 °C; IR (ATR): 1376, 1297, 1078, 1015, 963, 887, 816, 717, 596, 565, 484, 432 cm^{-1}; ^1H NMR ($CDCl_3$): δ 1.21–1.28 (m, 2H), 1.30–1.45 (m, 2H), 1.67–1.89 (m, 4H), 1.99–2.01 (m, 1H), 2.07–2.14 (m, 1H), 4.70–4.77 (m, 1H), 7.26–7.30 (m, 2H), 7.31–7.33 (m, 1H), 7.35–7.39 (m, 1H), 7.44–7.55 (m, 3H), 7.58–7.60 (m, 1H), 7.93–7.95 (m, 2H), 7.99–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 23.5, 23.6, 25.0, 33.3, 33.6, 80.2, 120.4, 120.9, 121.4, 121.6, 125.8, 126.8, 127.1, 127.3, 128.5, 128.6, 131.0, 131.5, 131.7, 131.9, 132.4, 132.4, 146.5, 146.6, 147.6, 147.7; ^{31}P NMR ($CDCl_3$): δ 2.89; MS (EI) m/z 430 (M^+): HRMS Calcd for $C_{26}H_{23}O_4P$:430.1334; found: 430.1336.

(S_{ax})-4-(Cyclohexyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide ((S_{ax})-**3a**)

To a THF solution (2 mL) of the (S_{ax})-4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (0.42 g, 1.0 mmol) was added cyclohexanol (0.11 mL, 1.0 mmol) and Et_3N (0.28 mL, 2.0 mmol) under Ar atmosphere. The resulting solution was stirred under reflux 4 h and extracted with Et_2O. The organic layer was dried over magnesium sulfate, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 3) to give (S_{ax})-4-(cyclohexyloxy)dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide (0.48 g, 0.97 mmol, 99%) as a white solid.: mp: 98–103 °C; ^1H NMR ($CDCl_3$): δ 1.20–1.27 (m, 1H), 1.33–1.41 (m, 1H), 1.42–1.48 (m, 1H), 1.51–1.73 (m, 4H), 1.77–1.80 (m, 1H), 1.98–2.00 (m, 1H), 2.15–2.17 (m, 1H), 4.85–4.95 (m, 1H), 7.26–7.32 (m, 2H), 7.37–7.50 (m, 5H), 7.60 (d, J = 9.16 Hz, 1H), 7.95 (d, J = 8.59 Hz, 2H), 8.00 (d, J = 8.59 Hz, 1H), 8.05 (d, J = 9.16 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ 23.6, 25.1, 32.9, 81.8, 120.8, 121.6, 122.1, 122.6, 125.8, 126.7, 126.8, 127.2, 127.4, 128.5, 128.6, 130.8, 131.1, 131.7, 132.1, 132.6(d, J = 6.0 Hz), 146.4, 146.5, 148.1, 148.2; ^{31}P NMR($CDCl_3$): δ 77.7; ^{77}Se

NMR ($CDCl_3$): δ -323.4 ($J_{P\text{-}Se}$ = 1010 Hz); MS(EI) m/z 494 (M^+): HRMS Calcd for $C_{26}H_{23}O_3PSe$: 494.0550, Found: 494.0550.

(S_{ax})-4-Ethoxydinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide ((S_{ax})-**1b**)
a white solid.: mp: 209–212 °C; ^1H NMR ($CDCl_3$): δ 1.40 (t, J = 7.2 Hz, 3H), 4.32–4.43 (m, 2H), 7.26–7.39 (m, 4H), 7.45–7.53 (m, 3H), 7.58–7.60 (m, 1H), 7.93–7.96 (m, 2H), 8.00–8.04 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 16.4, 66.1, 120.3, 120.8, 121.4, 121.5, 125.9, 126.9, 127.1, 127.3, 128.5, 128.6, 131.2, 131.6, 131.7, 132.0, 132.3, 132.4, 146.4, 146.5, 147.5, 147.6; ^{31}P NMR ($CDCl_3$): δ 3.5; MS (EI) m/z 376 (M^+): HRMS Calcd for $C_{22}H_{17}O_4P$: 376.0864, Found: 376.0869.

(S_{ax})-4-Ethoxydinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide ((S_{ax})-**2b**)
To a dichloromethane solution (5 mL) of the (R_{ax})-4-chlorodinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (0.38 g, 1.0 mmol) and DMAP (0.24 g, 2.0 mmol) was added EtOH (0.040 mL, 1.0 mmol) under Ar atmosphere. The resulting solution was stirred at room temperature for 2 h and extracted with Et_2O. The organic layer was dried over magnesium sulfide, filtered, and concentrated *in vacuo*. The mixture was purified by column chromatography on silica gel (EtOAc : hexane = 1 : 8) to give (R_{ax})-4-ethoxydinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide (0.27 g, 0.70 mmol, 69%) as a white solid.: mp: 175–180 °C; ^1H NMR ($CDCl_3$): δ 1.40 (t, J = 7.2 Hz, 3H), 4.34–4.50 (m, 2H), 7.27–7.33 (m, 2H), 7.36–7.49 (m, 5H), 7.56–7.58 (m, 1H), 7.94–8.05 (m, 4H); ^{13}C NMR ($CDCl_3$): δ 16.2, 66.6, 120.6, 121.4, 121.9, 122.3, 125.9, 126.7, 126.8, 127.2, 127.3, 128.5, 128.6, 131.0, 131.2, 131.7, 132.0, 132.5, 146.4, 146.5, 148.0, 148.1; ^{31}P NMR ($CDCl_3$): δ 75.1; MS (EI) m/z 392 (M^+): HRMS Calcd for $C_{22}H_{17}O_3PS$: 392.4088; Found: 392.0630.

(S_{ax})-4-Methoxydinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-sulfide ((S_{ax})-**2c**)
a white solid.: mp: 178–182 °C; ^1H NMR ($CDCl_3$): δ 3.99 (d, J = 13.9 Hz, 3H), 7.27–7.32 (m, 2H), 7.36–7.40 (m, 2H), 7.44–7.50 (m, 3H), 7.56–7.61 (m, 1H), 7.93–7.96 (m, 2H), 7.99–8.05 (m, 2H); ^{13}C NMR ($CDCl_3$): δ 56.2 (d, J = 4.7 Hz, O<u>C</u>H$_3$), 120.5, 121.2, 121.9, 122.2, 125.9, 126.8, 126.9, 127.2, 127.3, 128.6, 128.7, 131.1, 131.3, 131.8, 132.0, 132.5, 146.4, 146.5, 148.0, 148.2; ^{31}P NMR ($CDCl_3$): δ 76.9; MS (EI) m/z 378 (M^+): HRMS Calcd for $C_{21}H_{15}O_3PS$: 378.0480; Found: 378.0476.

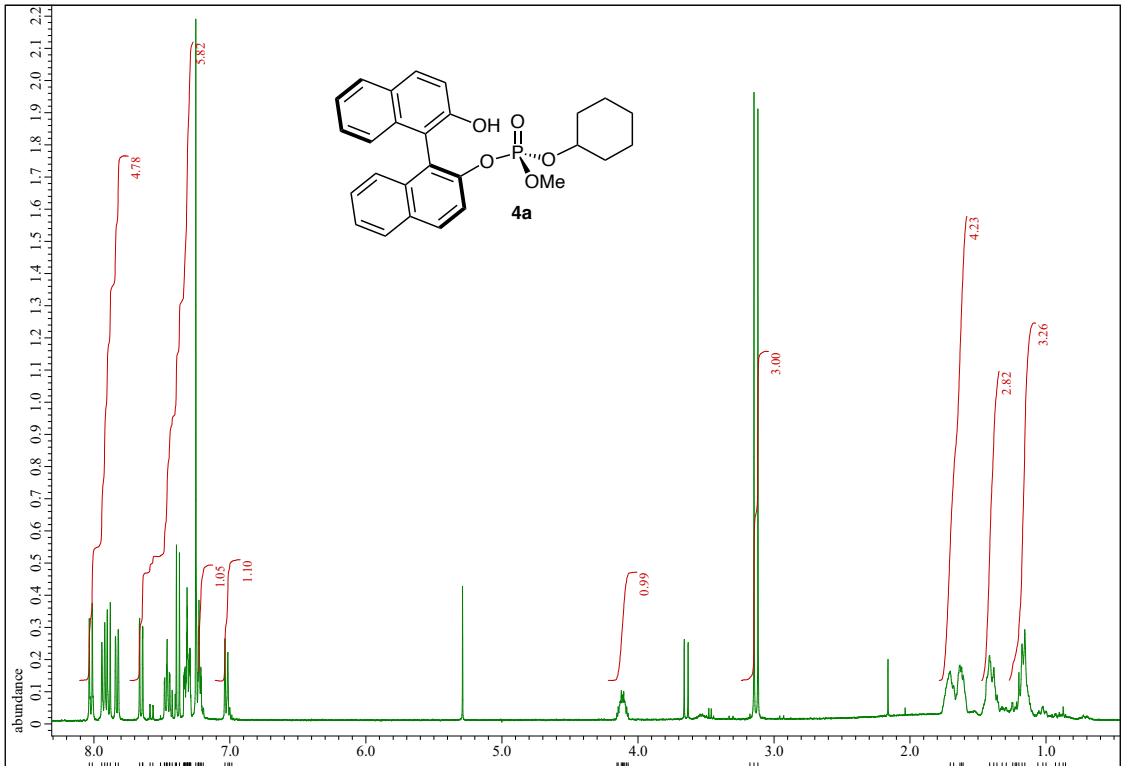
(S_{ax})-4-Butyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide ((S_{ax})**-8a**)

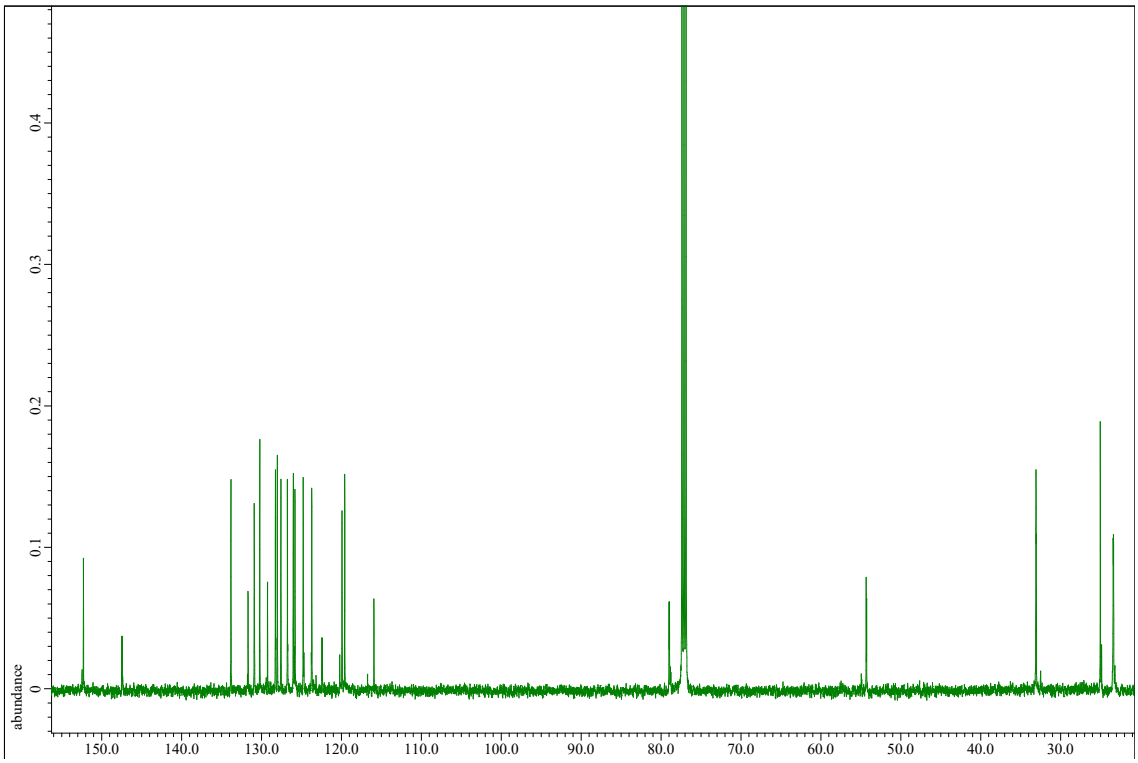
To a CH_2Cl_2 solution (4.70 mL) of (S_{ax})-4-Butyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-selenide[5] (1.06 g, 2.35 mmol) was added 35% H_2O_2 (0.62 mL), and the mixture was stirred for 3 h at room temperature. The resulting solution was poured onto water, and it was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$ and concentrated. The crude product was purified by chromatography on silica gel (hexane:EtOAc = 2:1, Rf = 0.31) to give (S_{ax})-4-butyldinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepine 4-oxide (0.78 g, 86%) as a white solid. mp: 153-155 ℃; IR (ATR): 2359, 1716, 1698, 1652, 1558, 1540, 1507, 1456, 1268, 1223, 1071 cm^{-1}; ^1H NMR ($CDCl_3$): δ 0.93 (t, J = 7.2 Hz, 3H), 1.41-1.50 (m, 2H), 1.73-1.87 (m, 2H), 1.90-2.03 (m, 2H), 7.27-7.58 (m, 7H), 7.57 (d, J = 7.6 Hz, 1H), 7.94 (m, 2H), 8.02 (d, J = 8.5 Hz, 2H); ^{31}P NMR ($CDCl_3$): δ 43.79 (s); MS(EI)m/z 388 (M^+); HRMS Calcd for $C_{24}H_{21}O_3P$: 388.1228, Found: 388.1229.

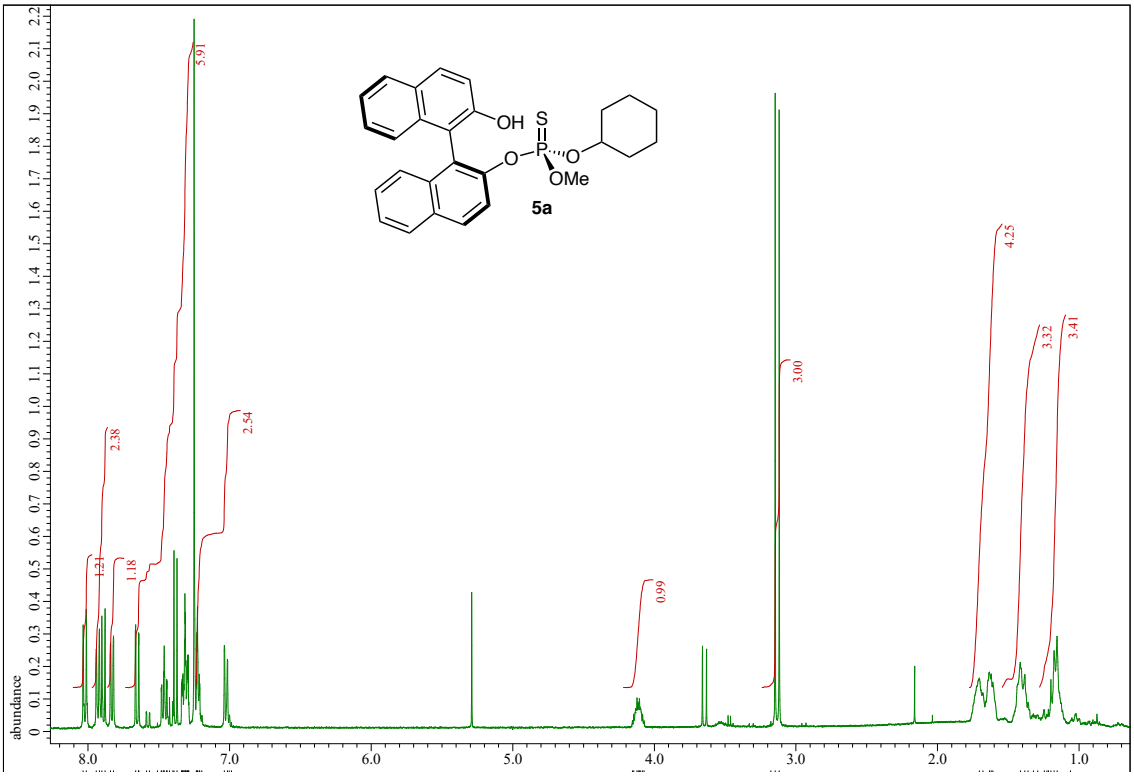
3. References

1. *Henkankun-R* is software for the conversion from Dectris-PILATUS and EIGER frames to the SFRM format, and is written in C# and Python codes by Shikama, S.; Nishino, R.; Minoura, M. November, 2018, available at SPring-8.
2. Sheldrick, G. M. *Acta Crystallogr. Sect. A*, **2015**, *71*, 3.
3. Sheldrick G. M. *Acta Crystallogr. Sect. C*, **2015**, *71*, 3.
4. Parsons, S.; Flack, H. D.; Wagner, T. *Acta Crystallogr. Sect. B*, **2013**, *69* 249.
5. Murai, T.; Maekawa, Y.; Hirai, Y.; Kuwabara, K.; Minoura, M. *RSC. Adv.* **2016**, *6*, 15180.

4. ^{1}H and ^{13}C NMR spectra



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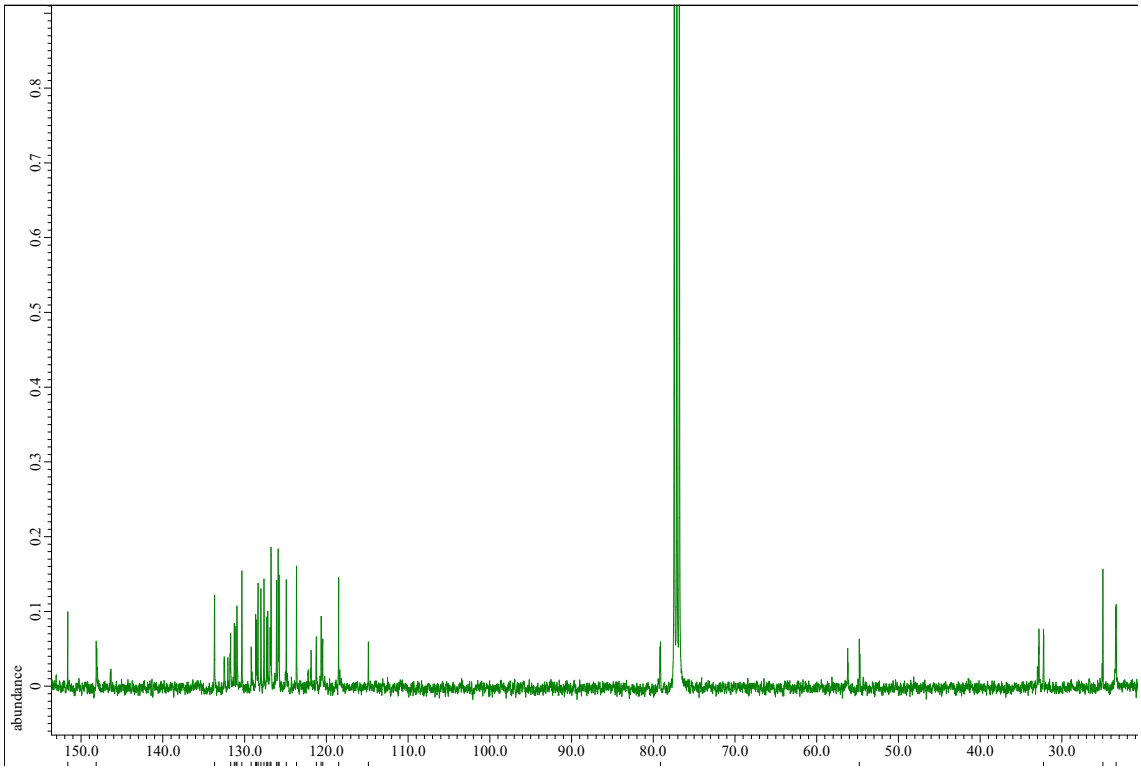
abundance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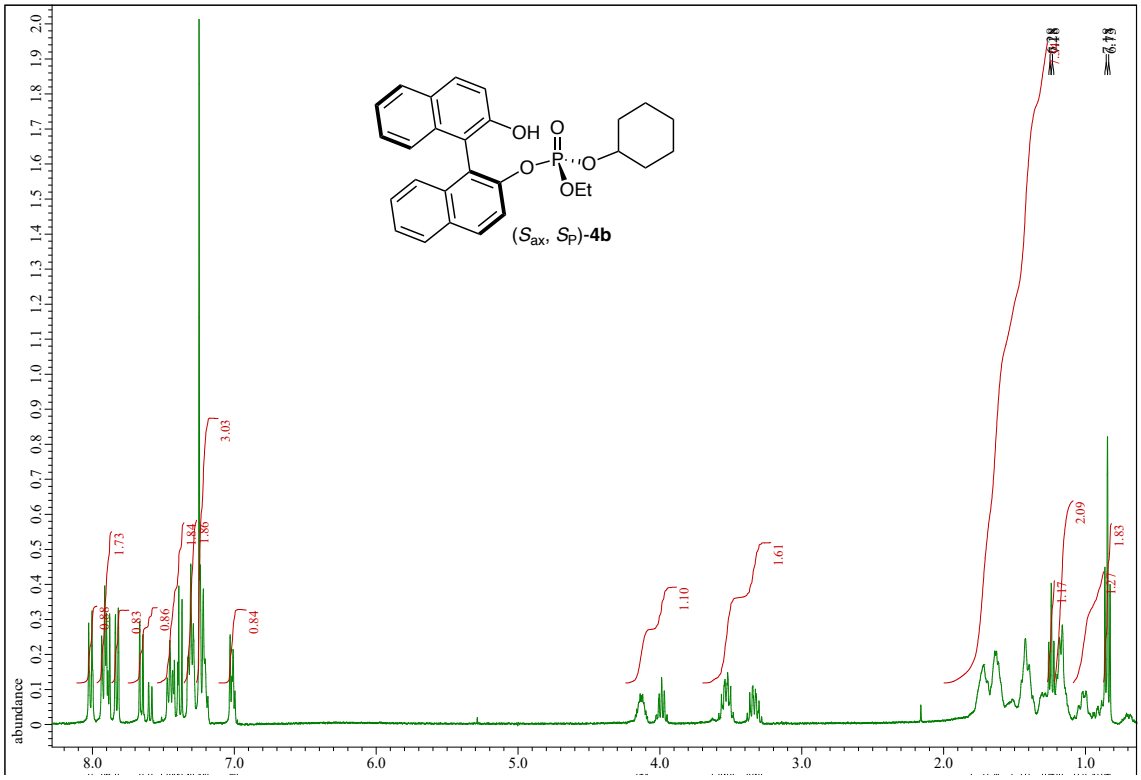
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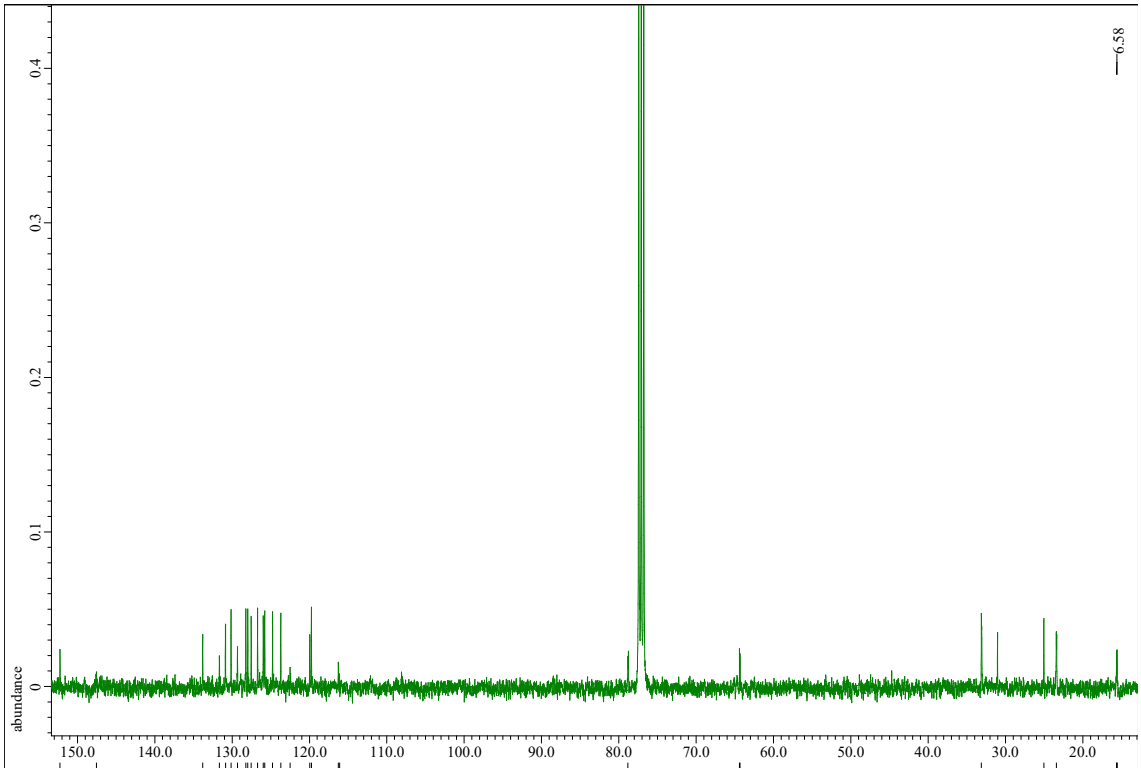
1.83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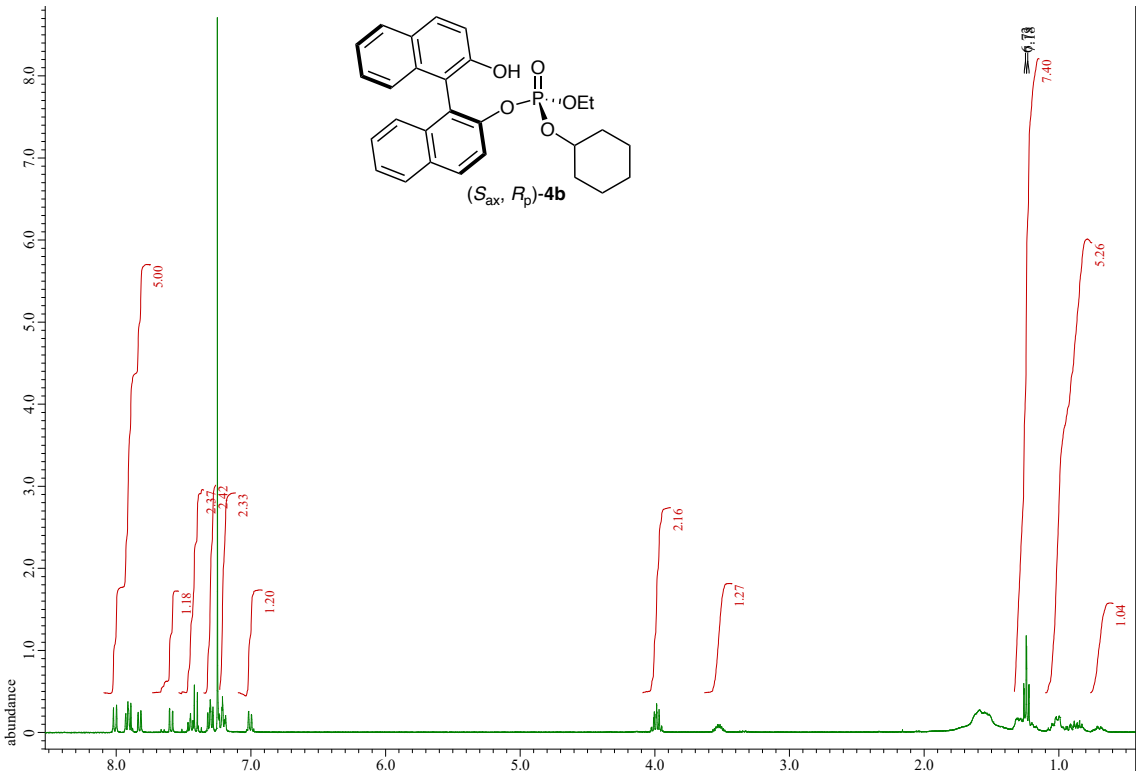
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(S_{ax}, R_p)-**4b**
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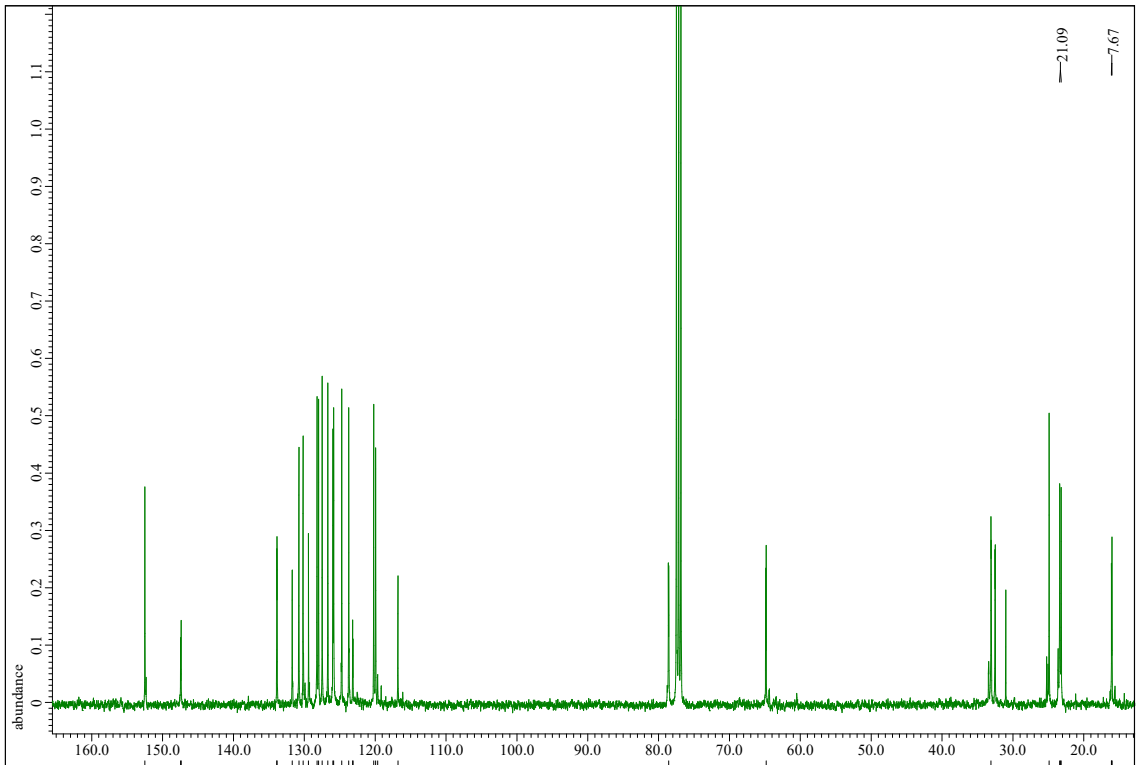
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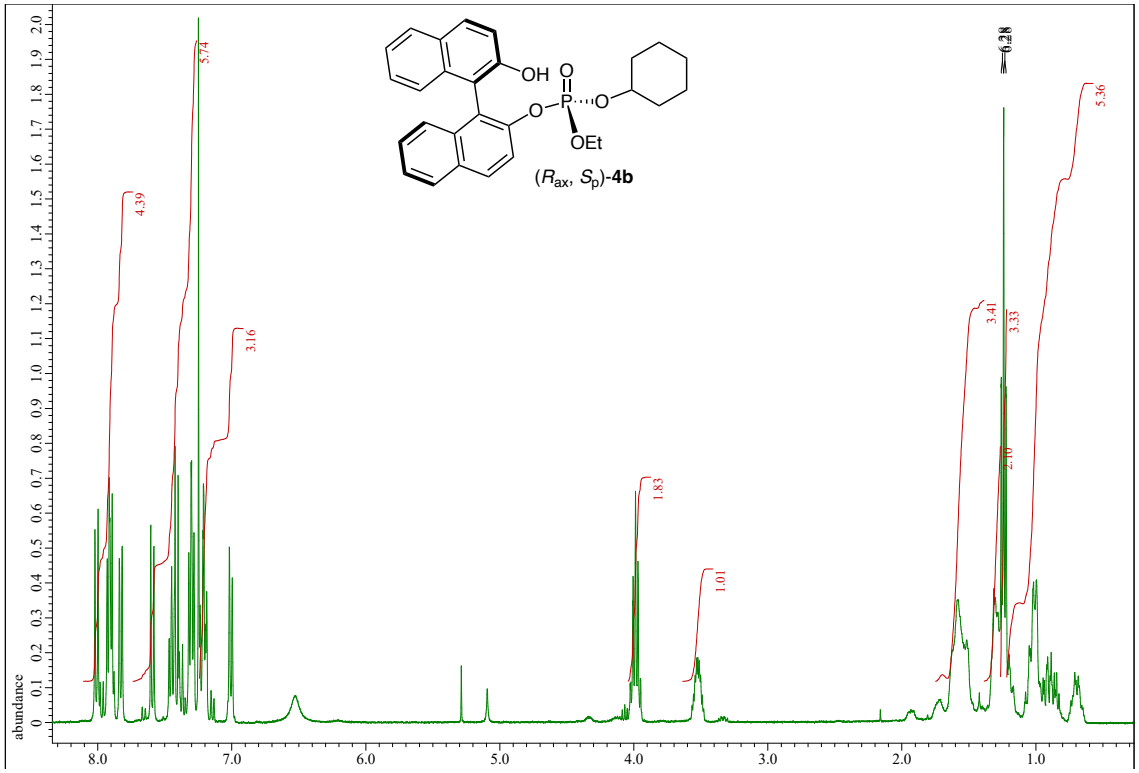
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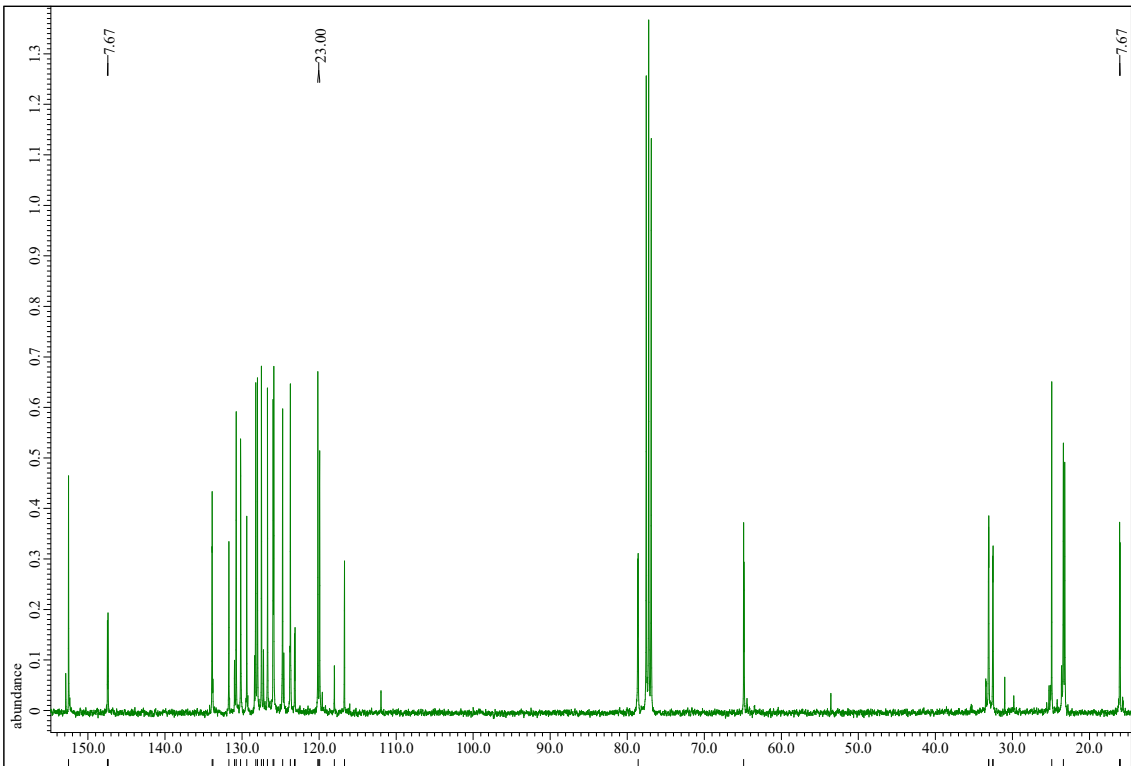
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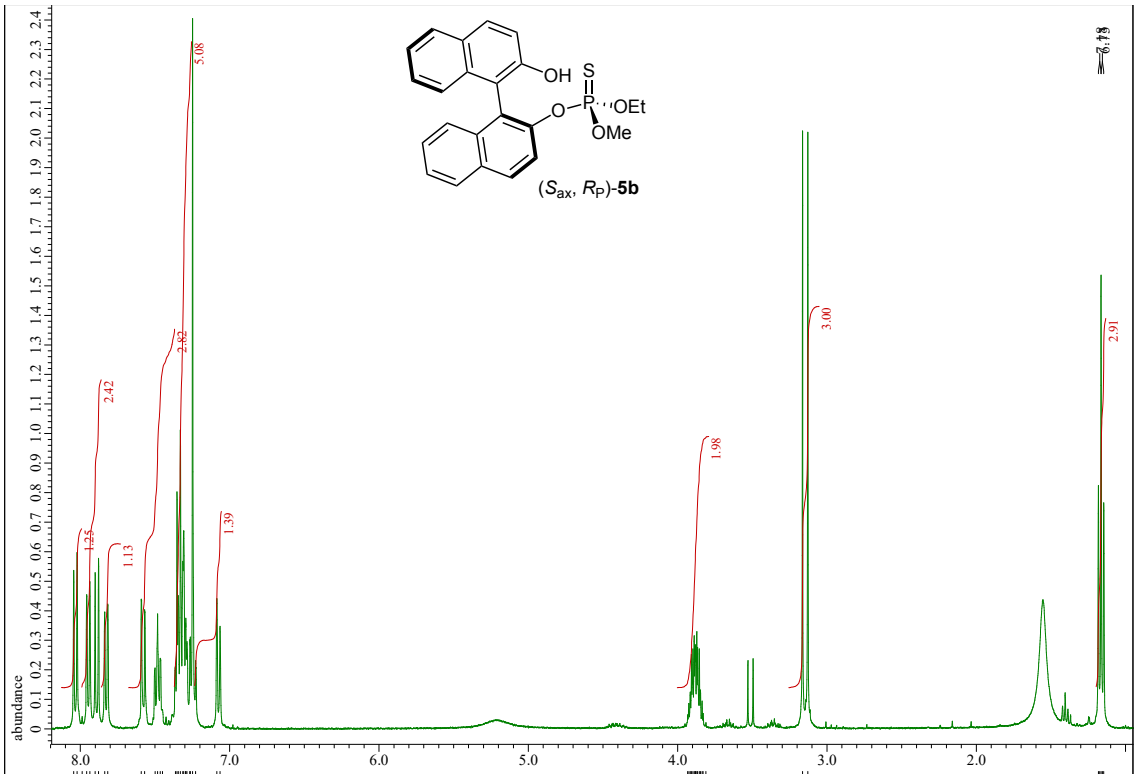
OH
S
P
O
OEt
OMe
(S_{ax}, R_P)-**5b**
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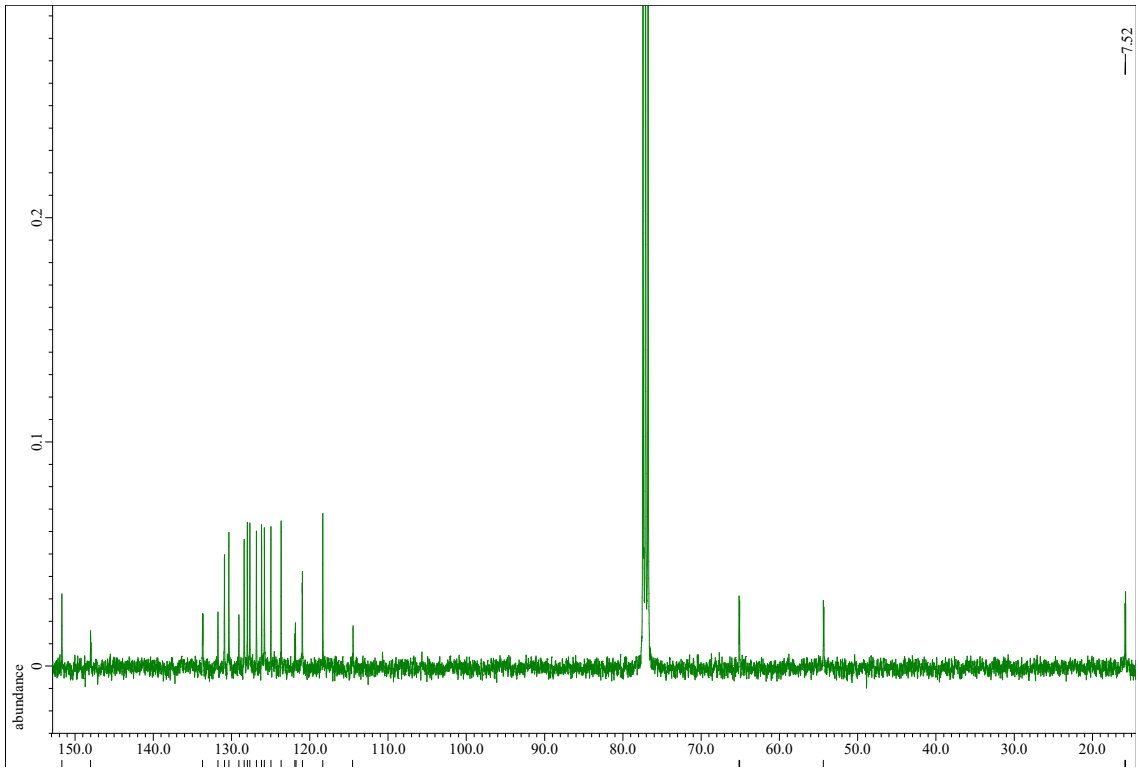
3.00
2.91
abundance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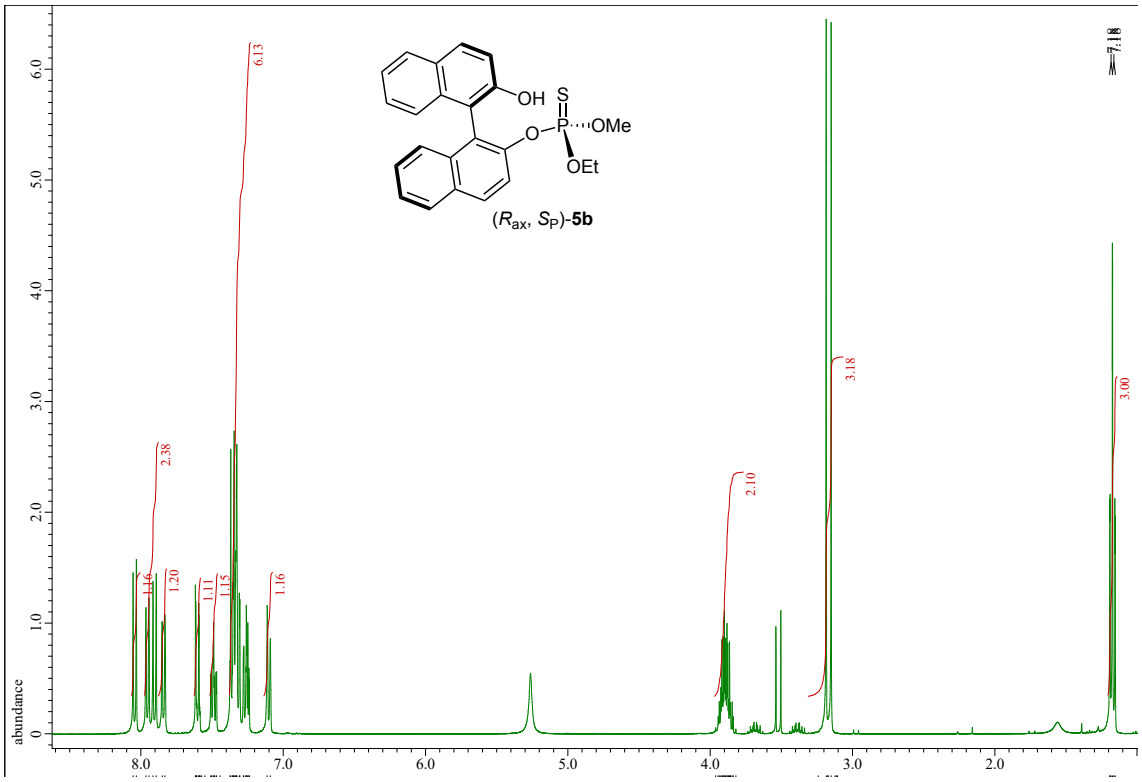
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S
O
P
OMe
OEt
(R_{ax}, S_P)-**5b**
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1.16
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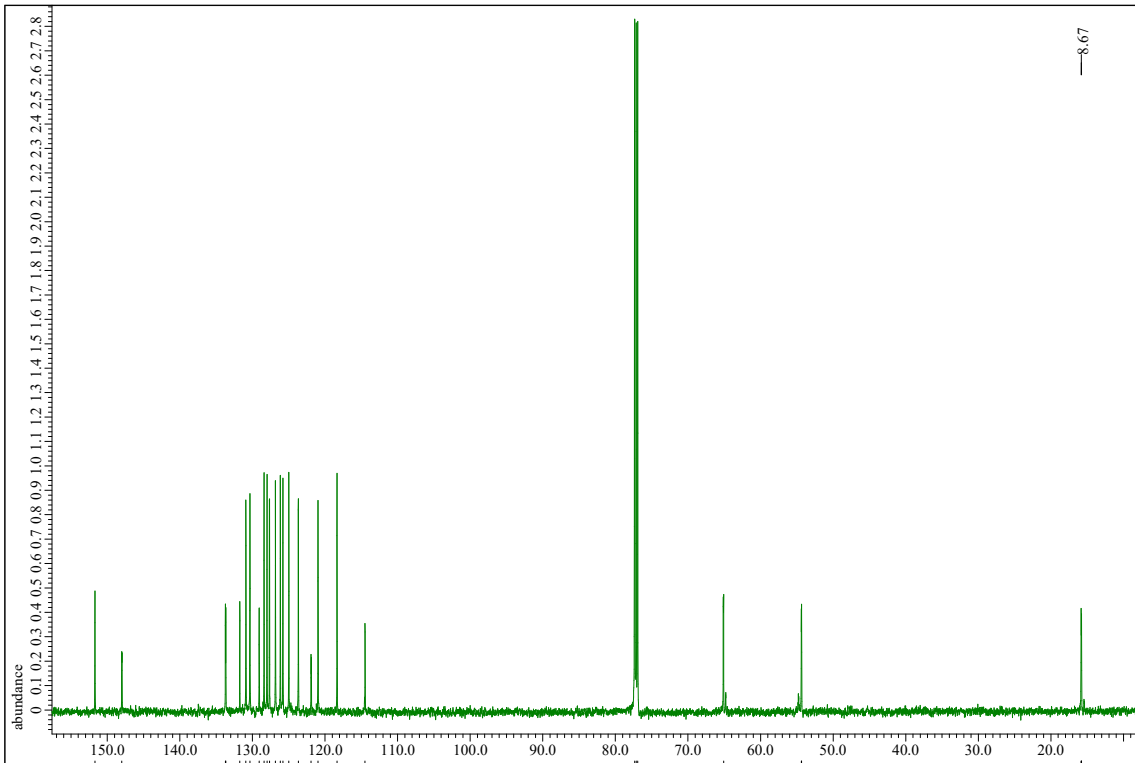
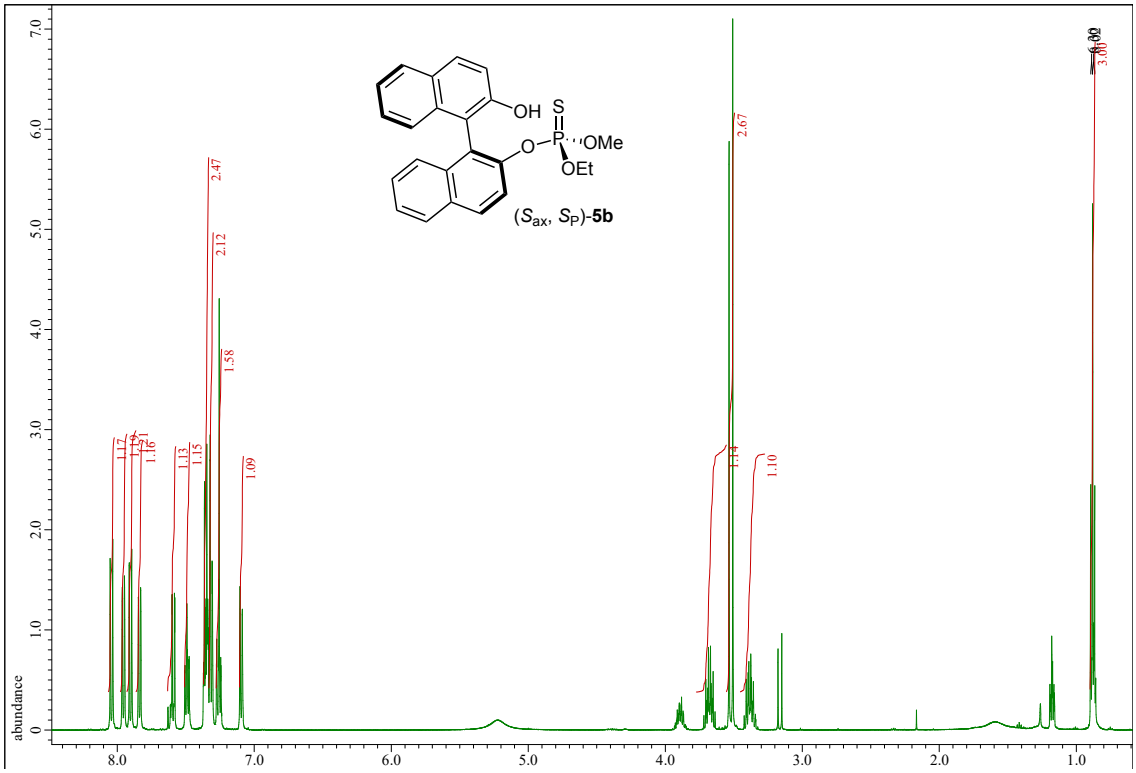
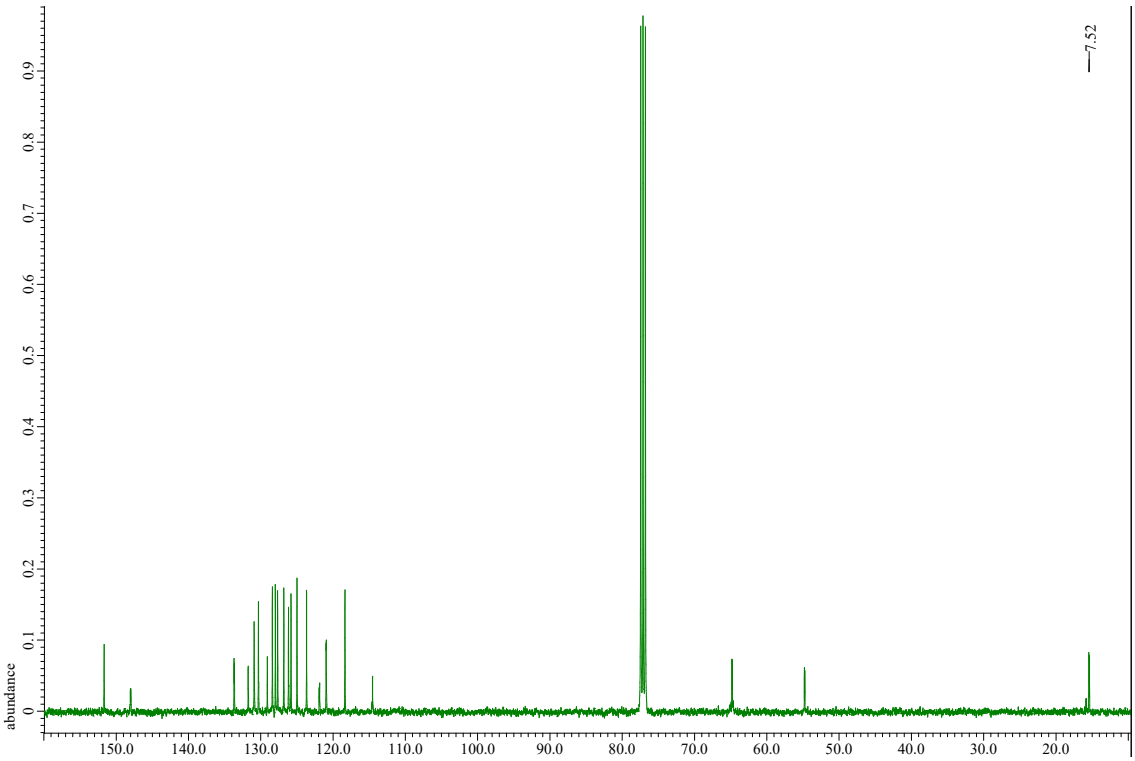
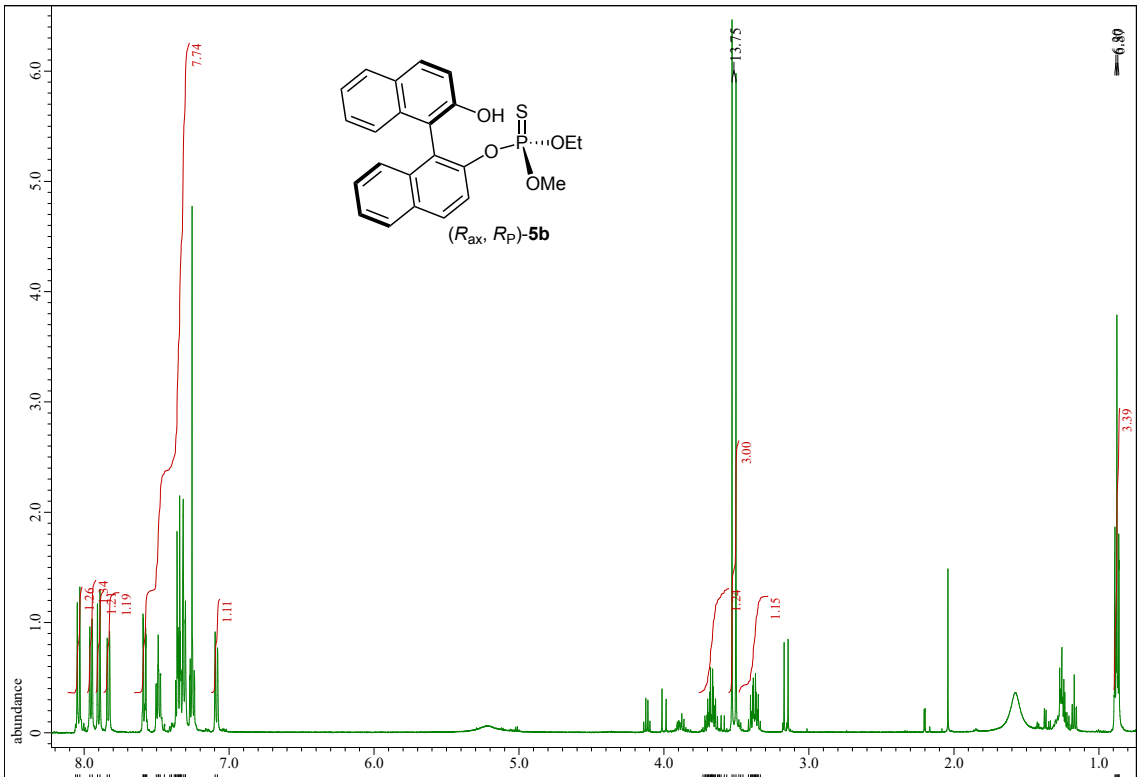
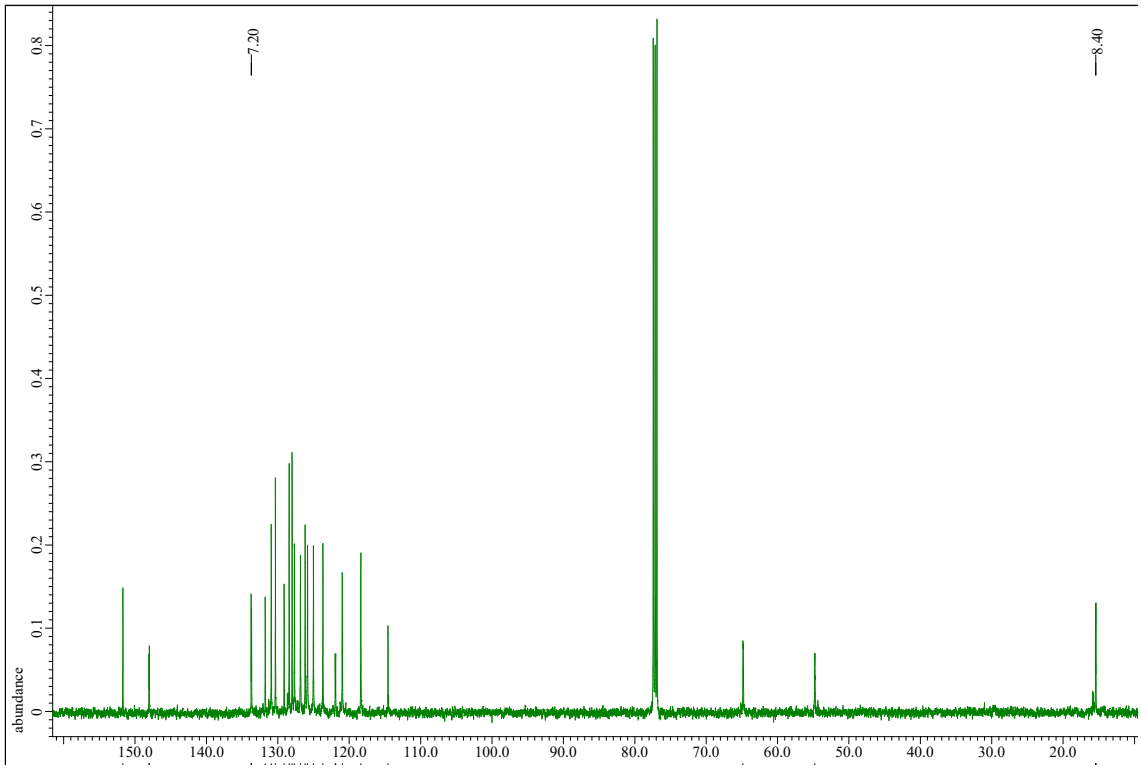
1.15
1.16
2.10
3.18
3.00
abundance

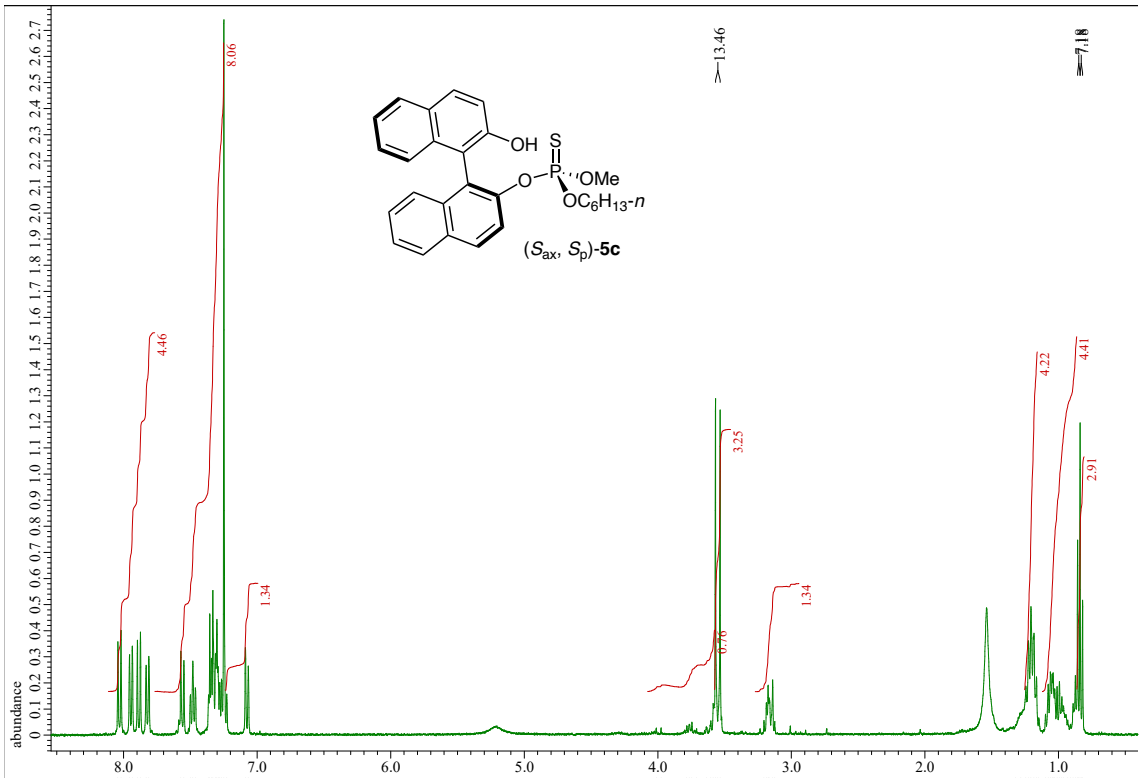

8.67
abundance

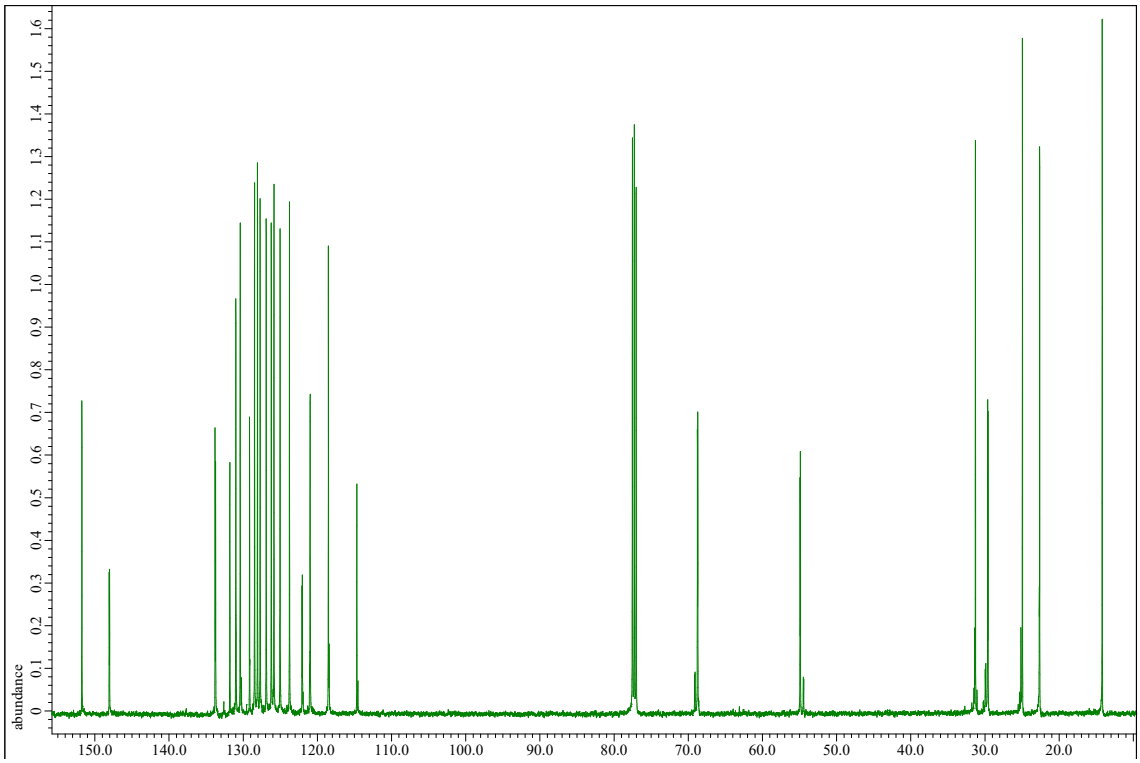

OH
S
O
P
OMe
OEt
(S_{ax}, S_P)-**5b**
2.47
2.12
1.58
1.09
2.67
1.10
3.00
abundance

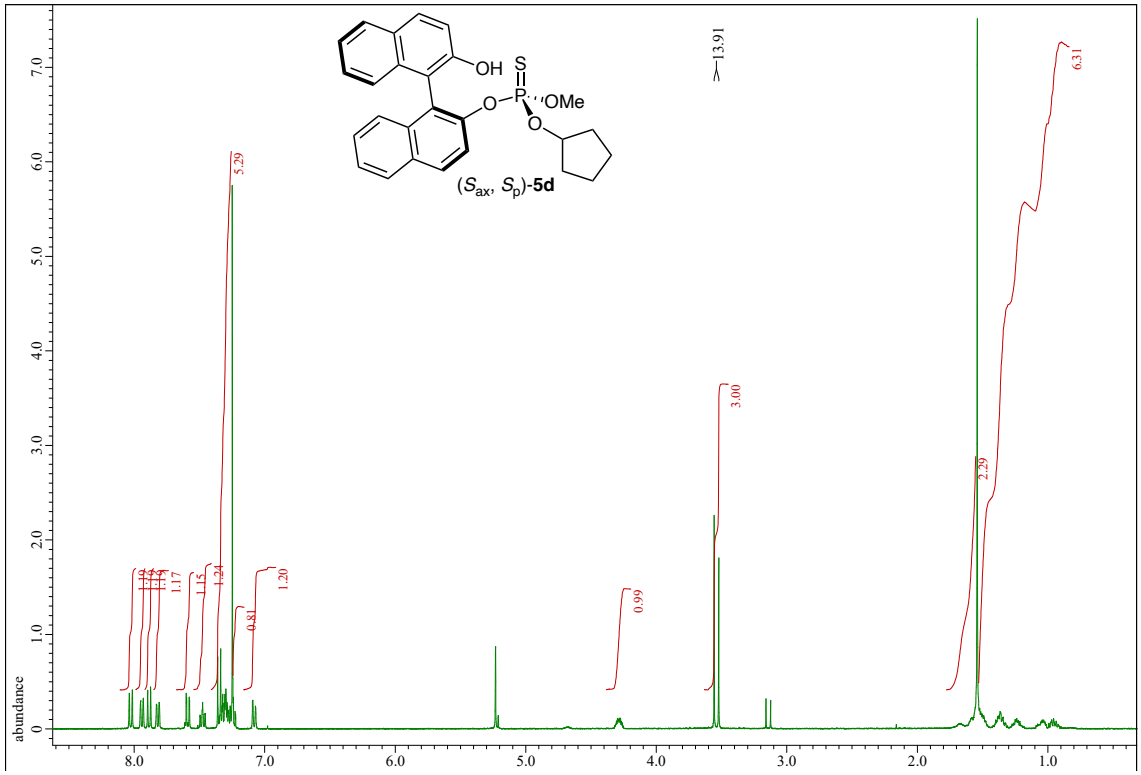

7.52
abundance

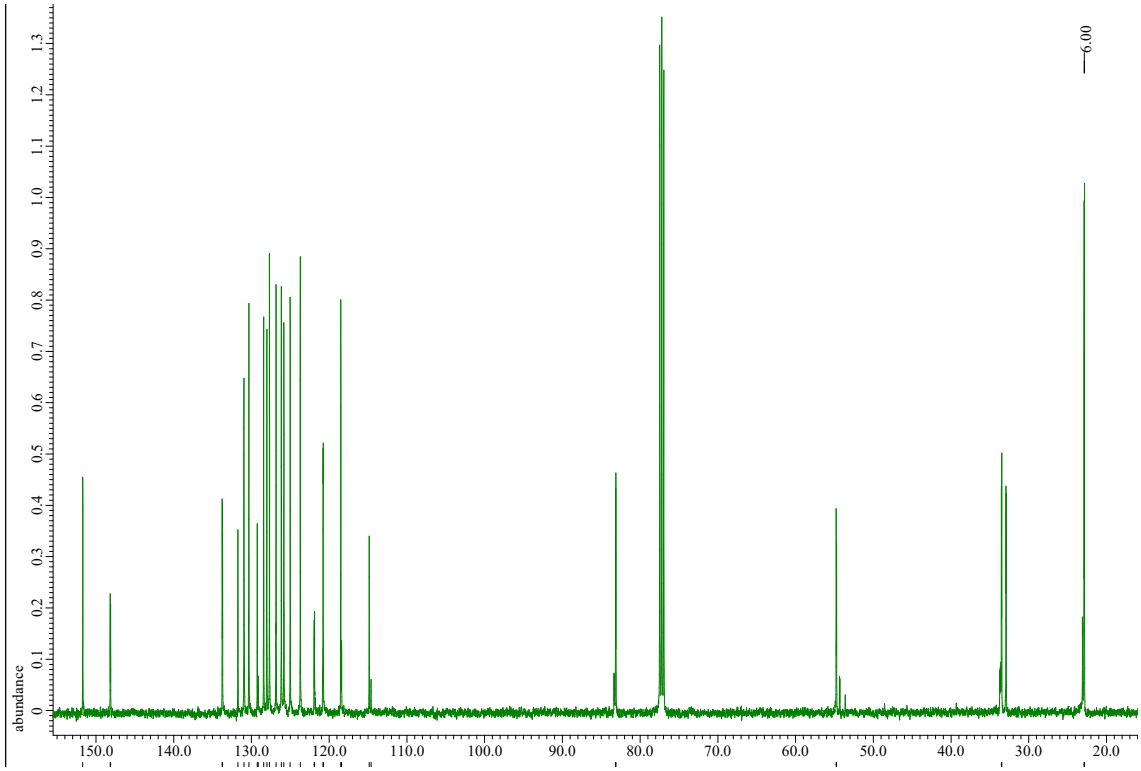

OH
S
O
P
OEt
OMe
(R_{ax}, R_P)-**5b**
7.74
13.75
6.80
3.39
3.00
1.26
1.24
1.19
1.11
1.24
1.15
abundance

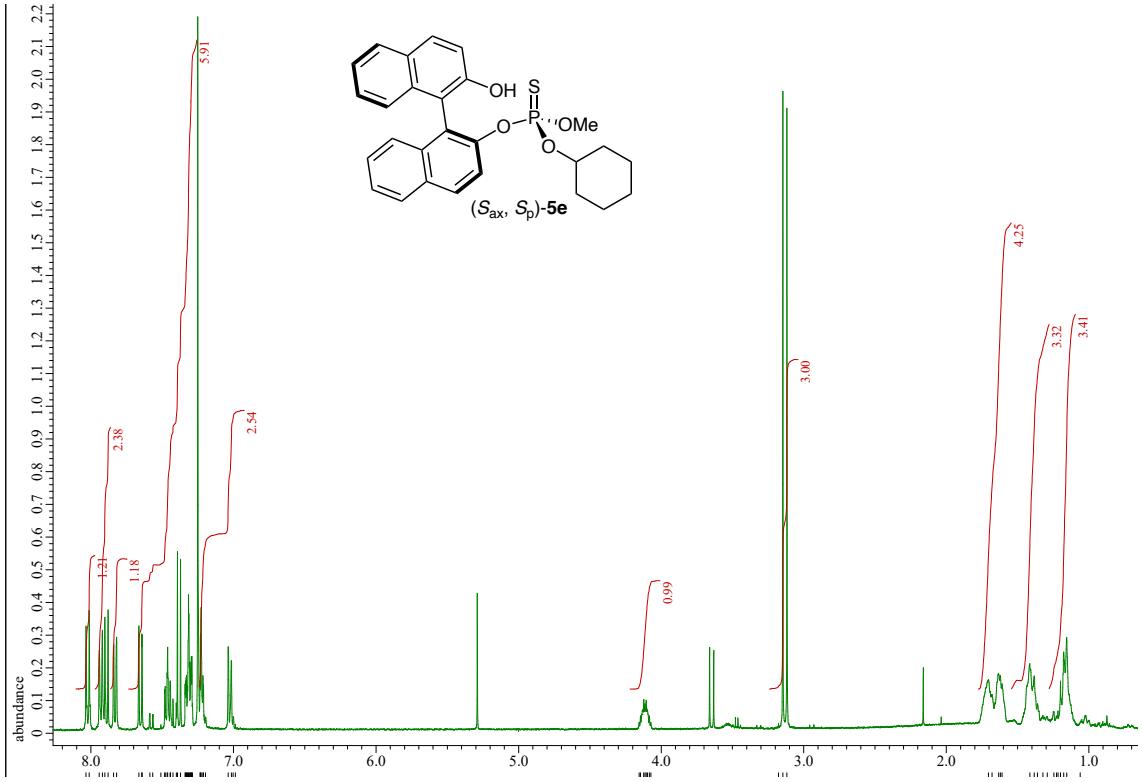

7.20
8.40
abundance

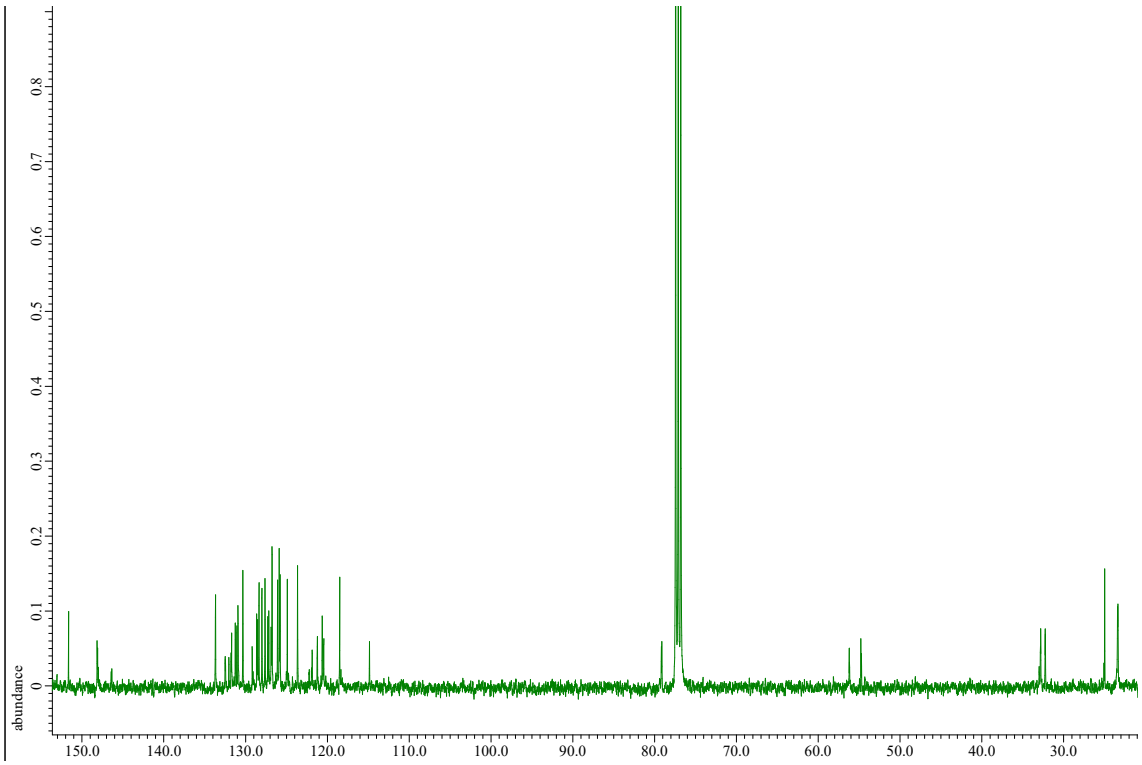

OH
S
O
P
OMe
OC6H13-n
(Sax, Sp)-5c
8.06
4.46
1.34
13.46
3.25
0.76
1.34
4.22
4.41
2.91
abundance

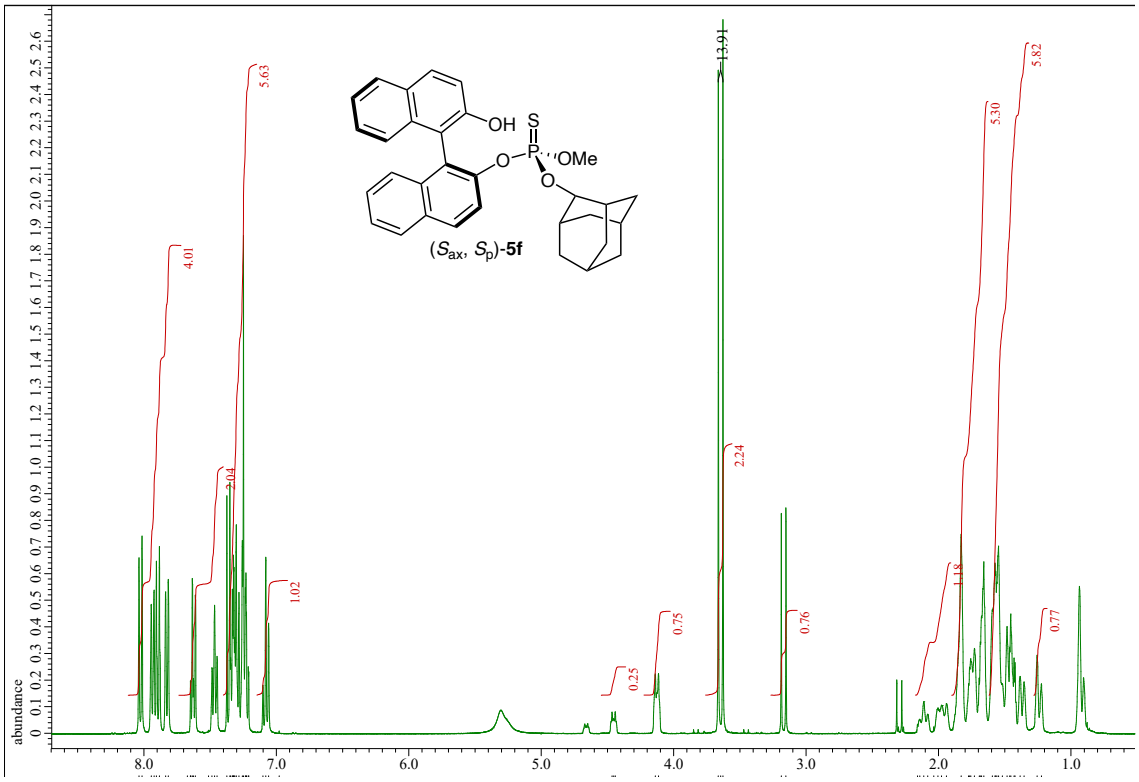

abundance

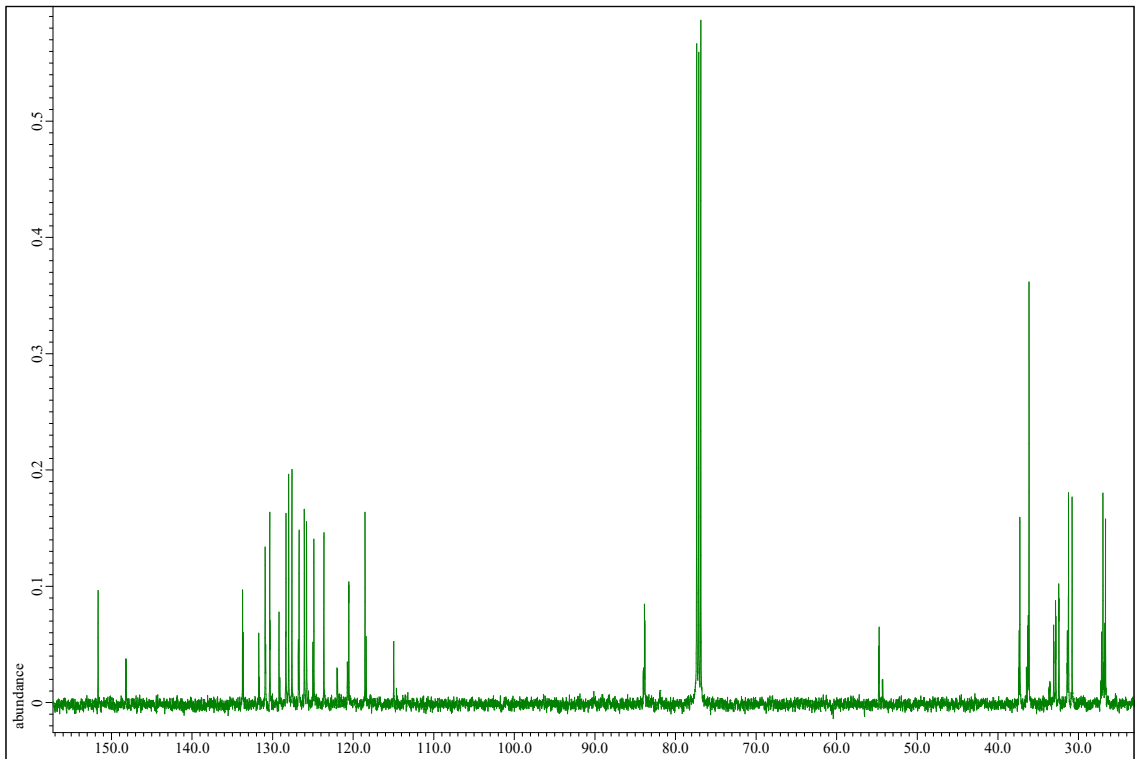

OH
S
O
P
OMe
O
(S_{ax}, S_p)-5d
13.91
6.31
5.29
3.00
2.29
1.20
1.17
1.15
1.14
1.13
1.12
0.99
0.81
abundance

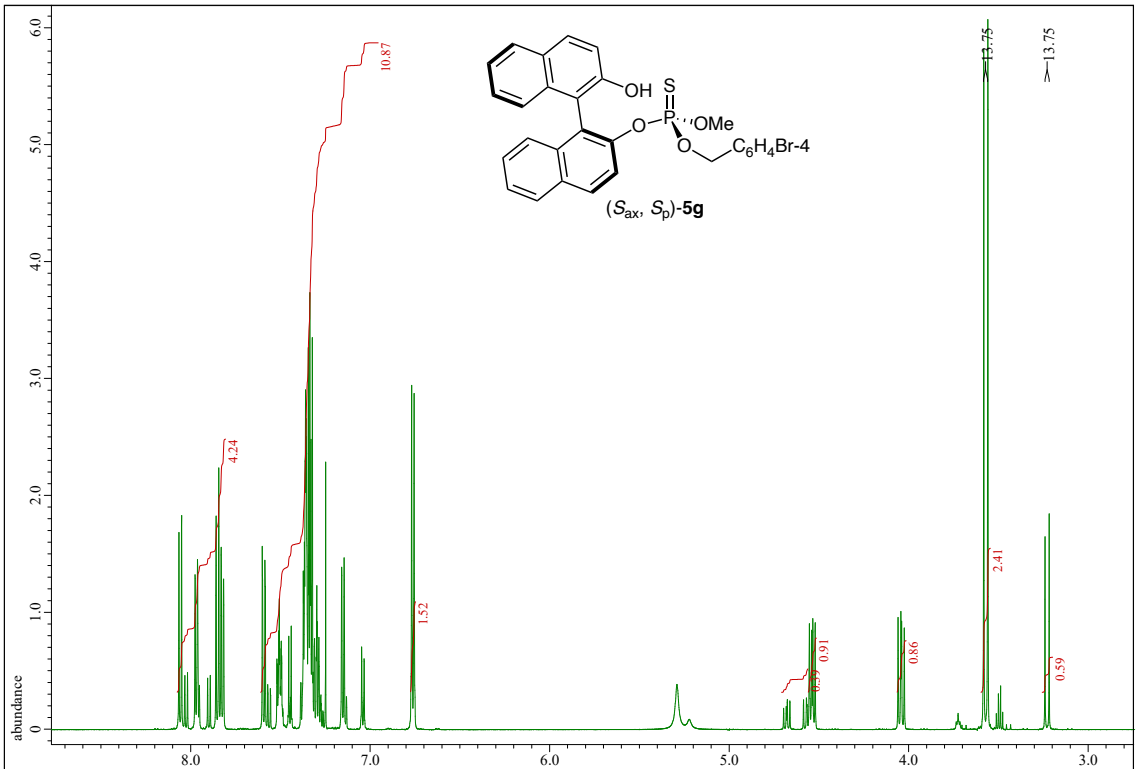

6.00
abundance

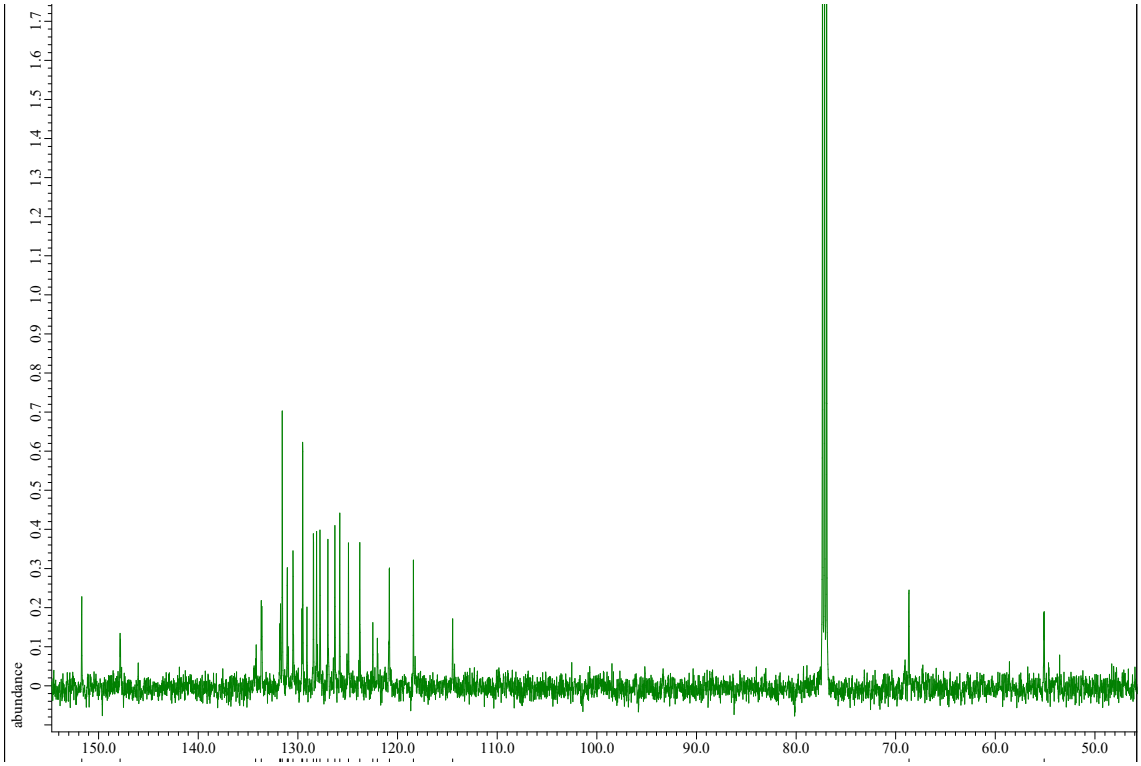

OH
S
P
OMe
O
O
(S_{ax}, S_p)-**5e**
5.91
2.38
1.21
1.18
2.54
0.99
3.00
4.25
3.32
3.41
abundance

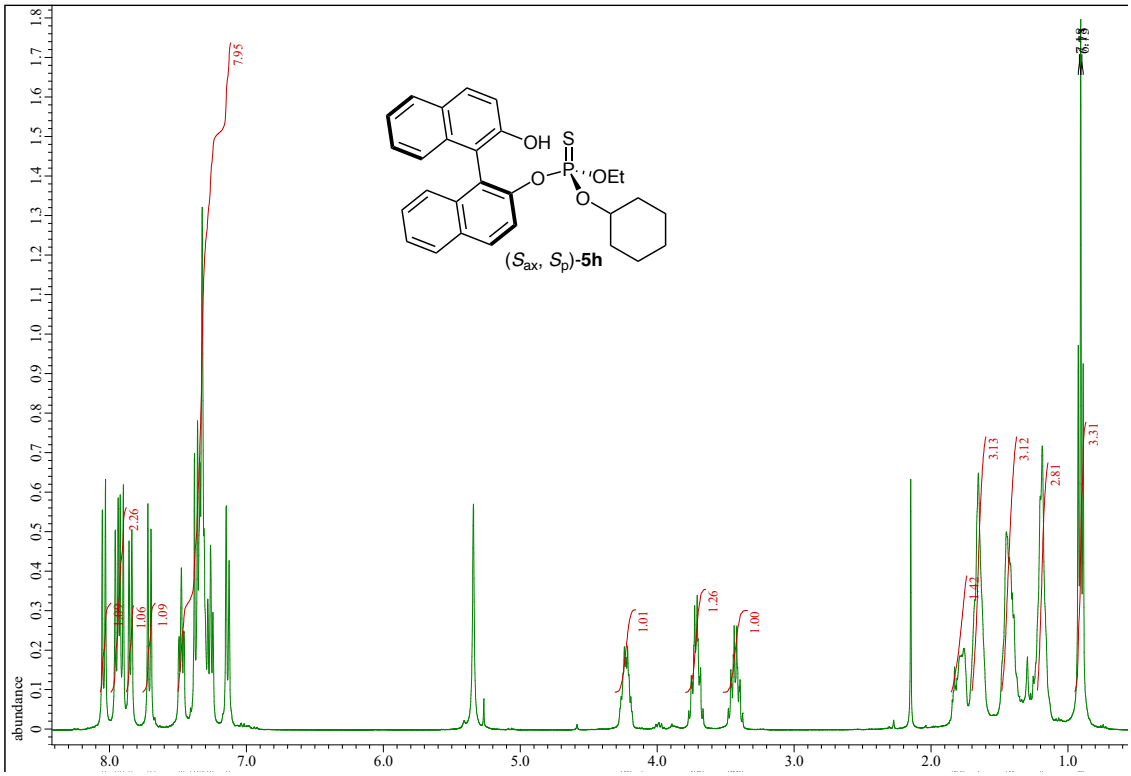

abundance

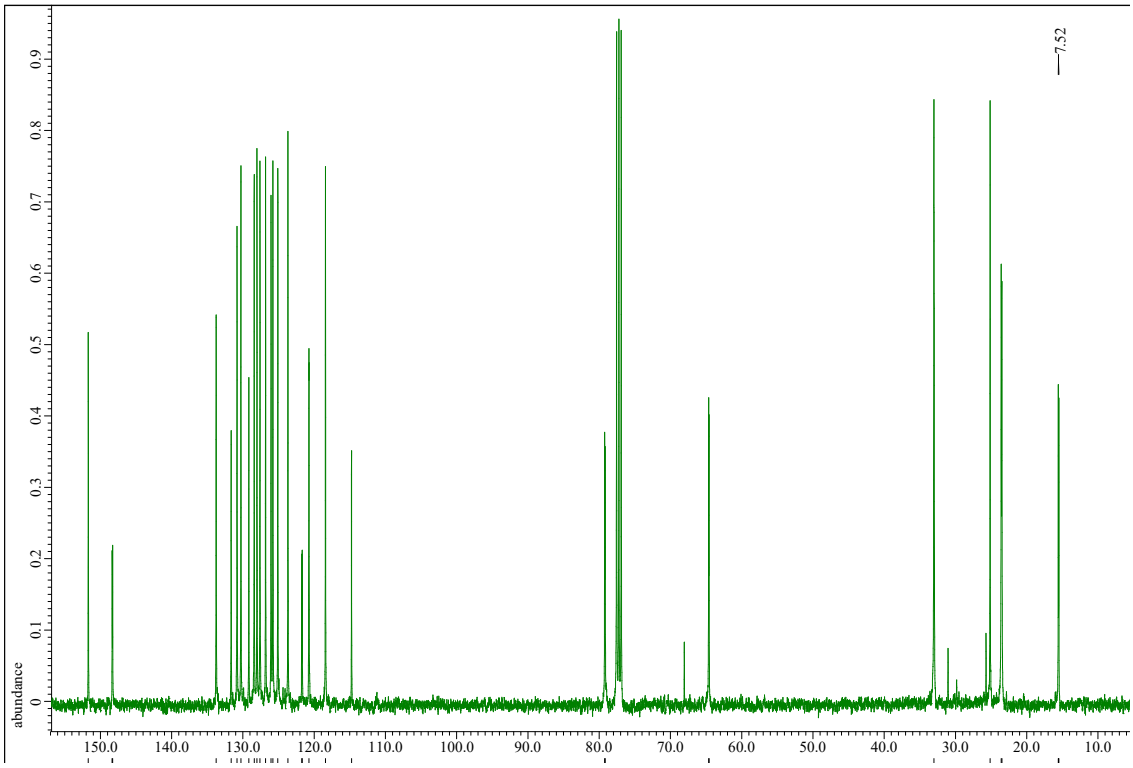

OH
S
P
OMe
O
O
O
(S_{ax}, S_p)-5f
4.01
2.04
5.63
1.02
0.25
0.75
13.91
2.24
0.76
1.18
5.30
5.82
0.77
abundance

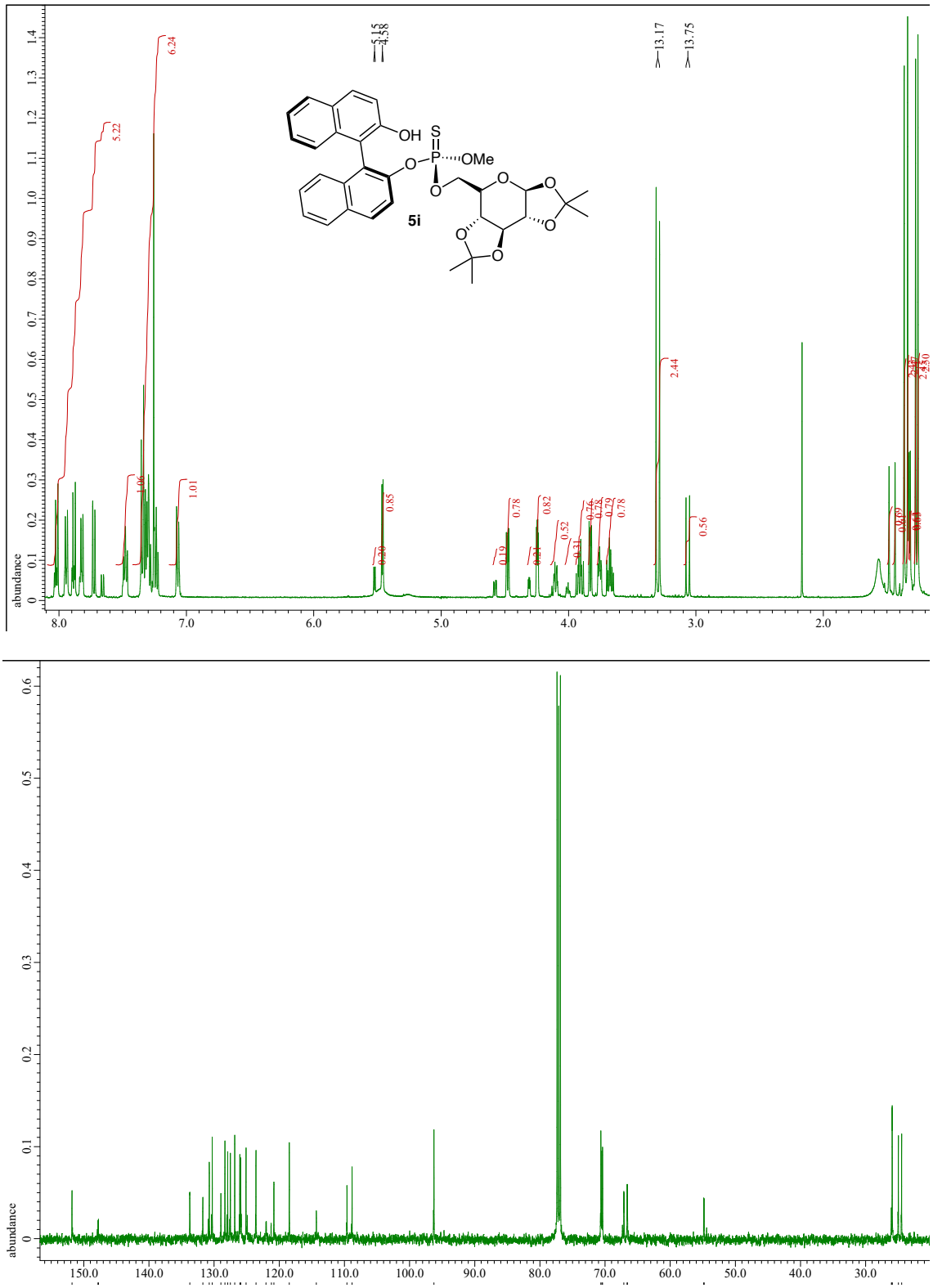

abundance

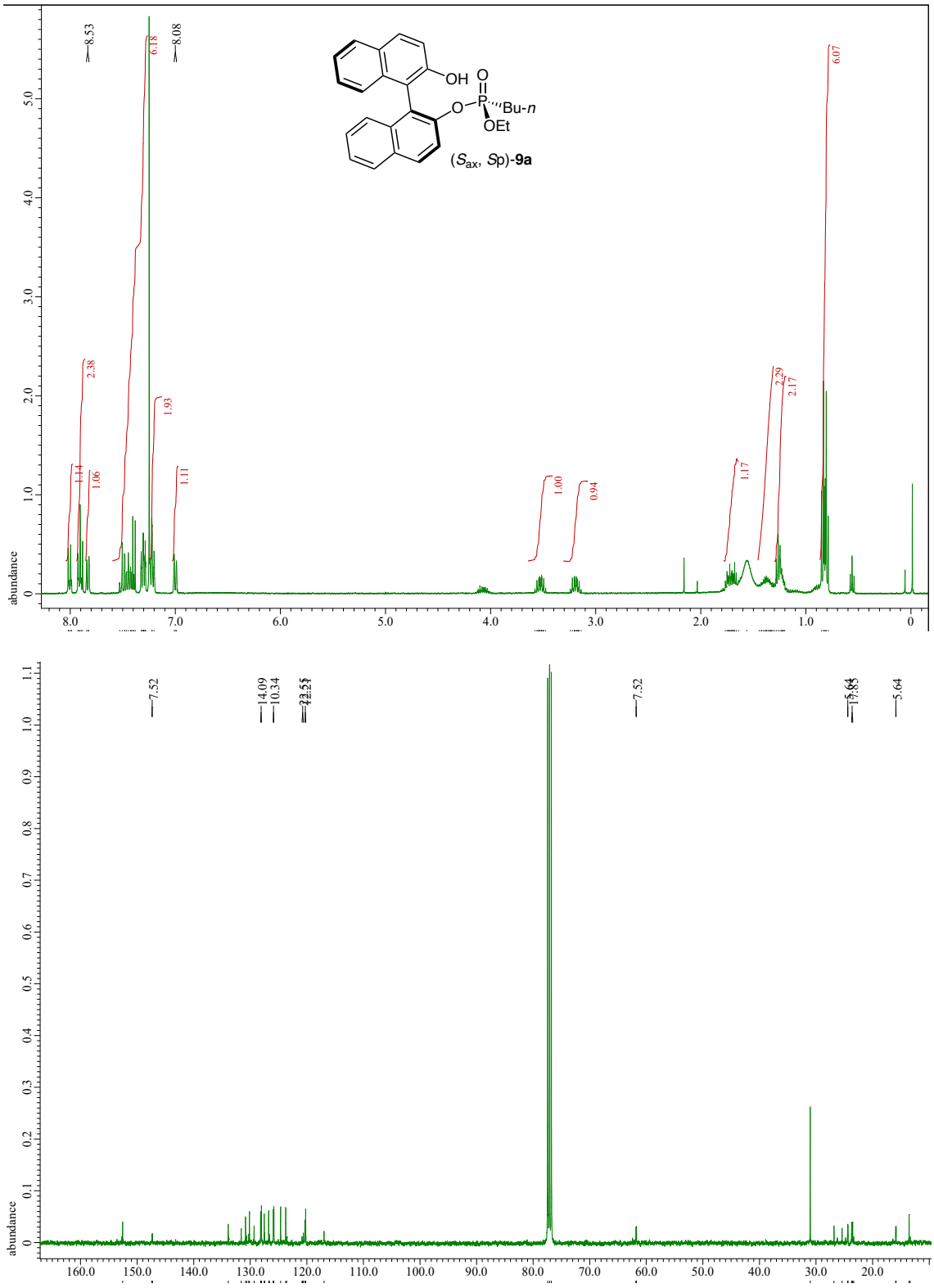

OH
S
O
P
OMe
O
C6H4Br-4
(Sax, Sp)-5g
10.87
4.24
1.52
0.91
0.86
2.41
0.59
13.75
abundance

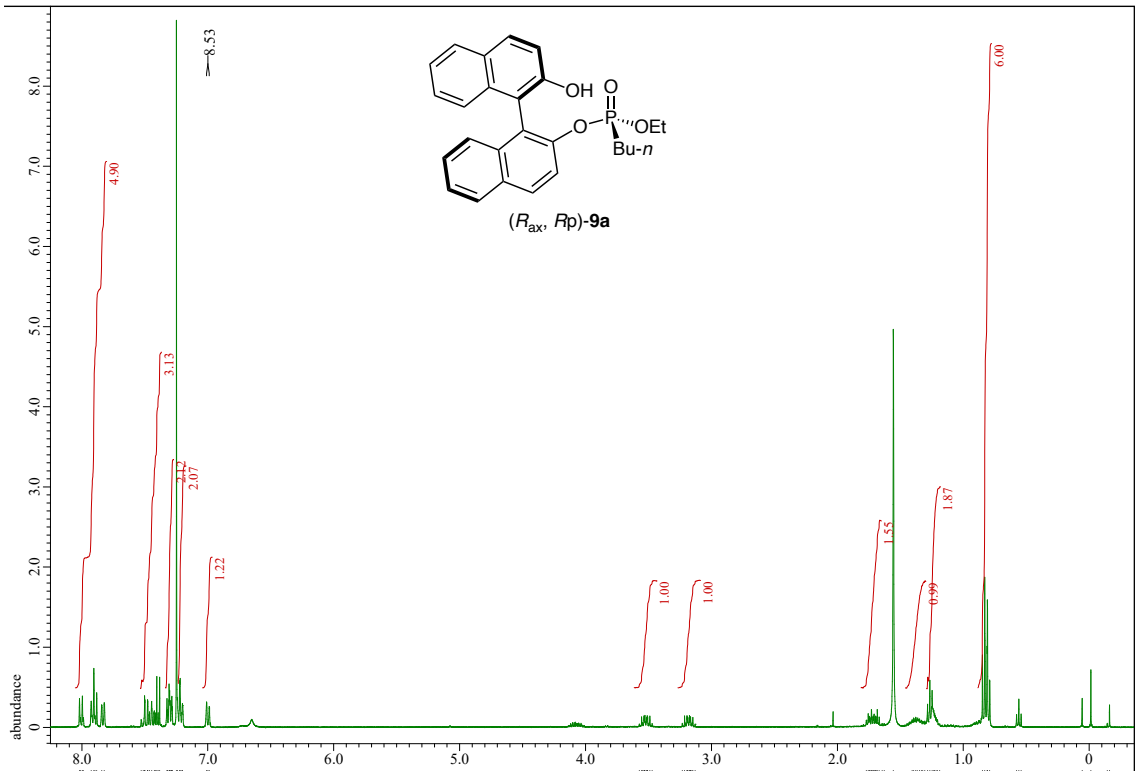

abundance


OH
S
O
P
OEt
O
(S_{ax}, S_p)-5h
abundance
7.95
2.26
1.06
1.09
1.01
1.26
1.00
3.13
3.12
2.81
3.31

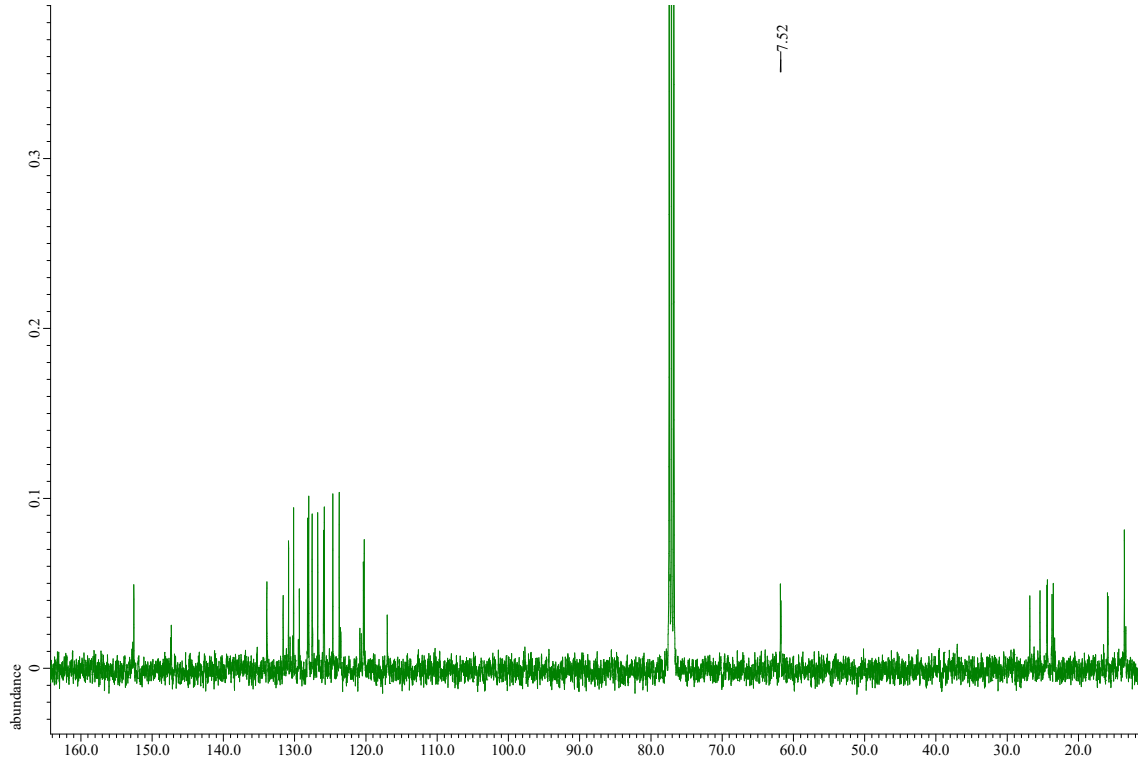

abundance
7.52

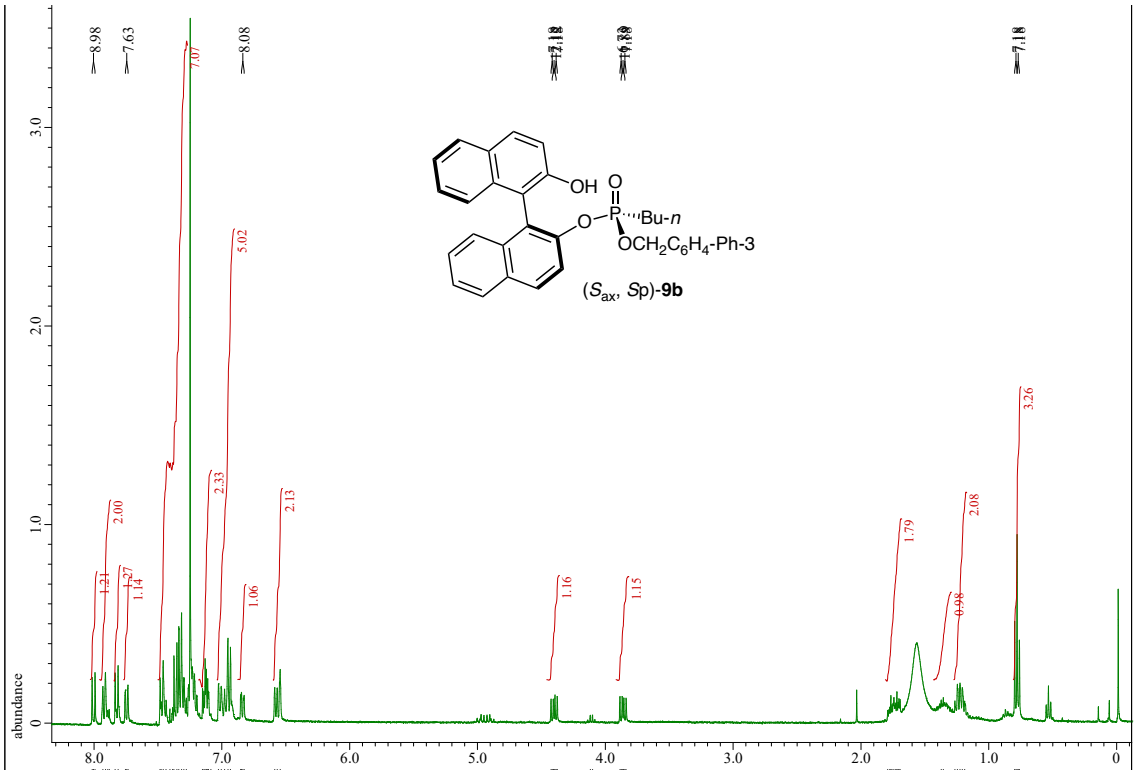

5i
OH
S
P
OMe
O
abundance
5.22
6.24
1.01
0.85
0.78
0.82
0.52
0.56
2.44
13.17
13.75
8.0
7.0
6.0
5.0
4.0
3.0
2.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0

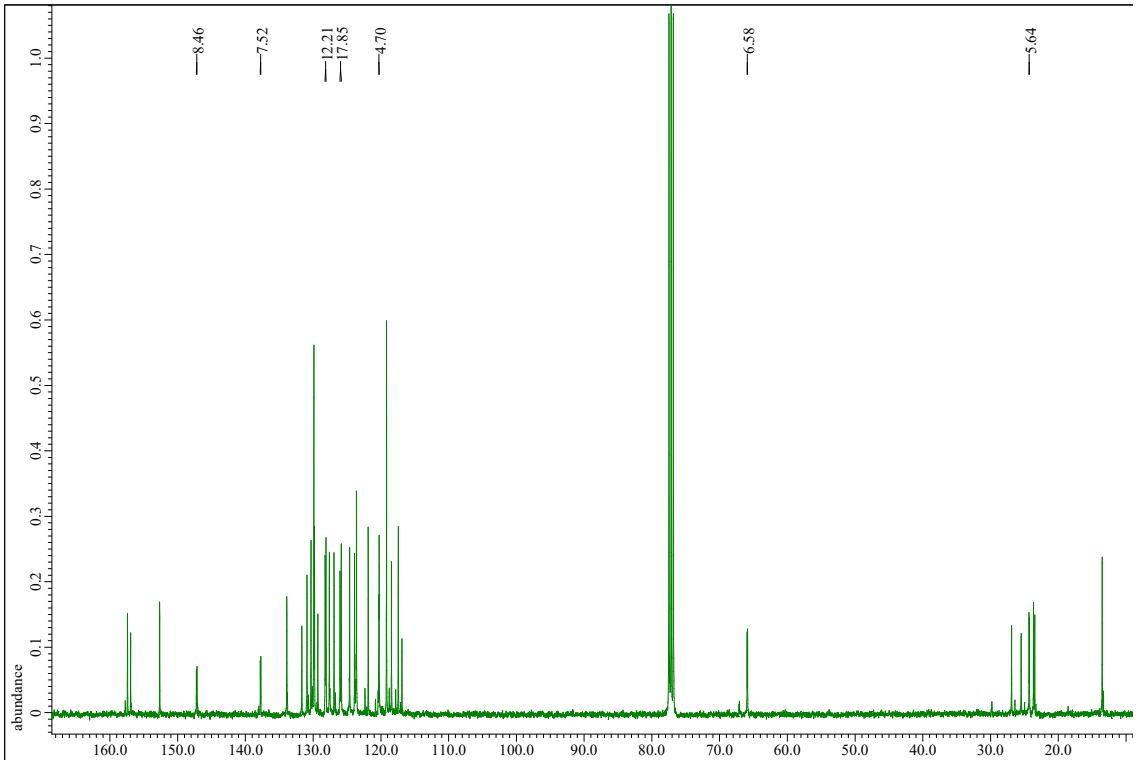

8.53
6.18
8.08
6.07
2.38
1.93
2.29
2.17
1.14
1.06
1.11
1.00
0.94
1.17
OH
O
O
P
''Bu-n
OEt
(Sax, Sp)-9a
abundance
7.52
14.09
10.34
7.52
5.64
abundance

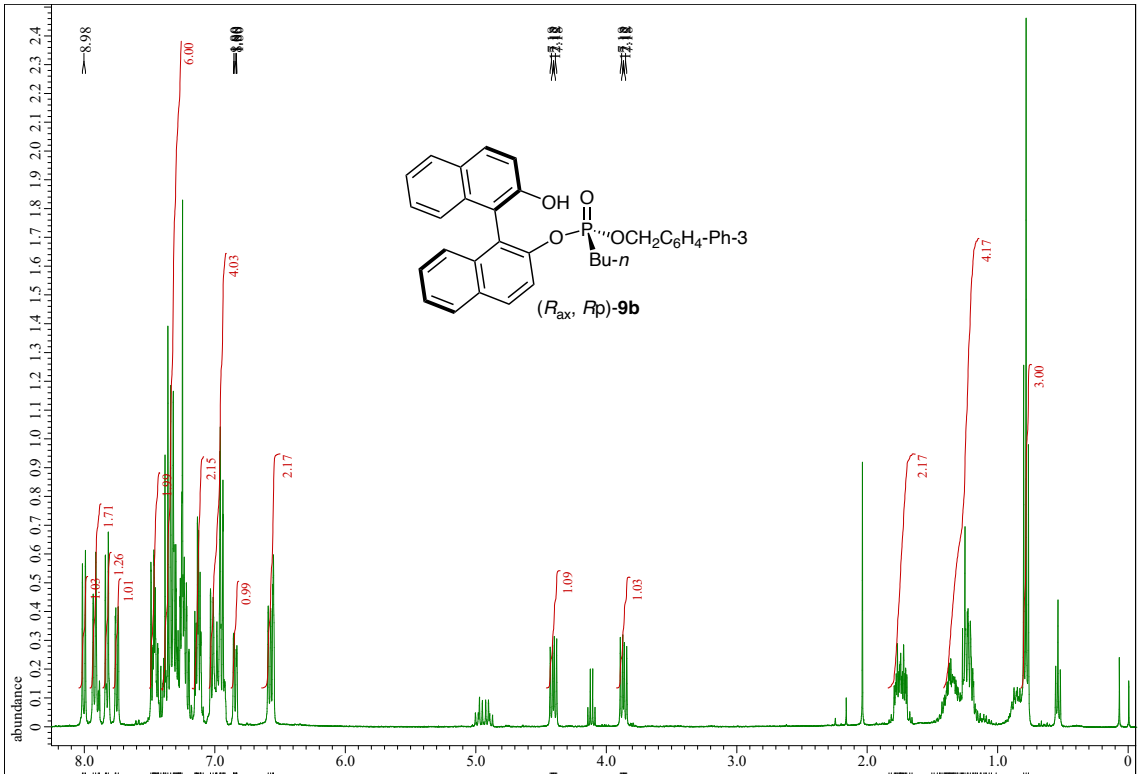

8.53
4.90
3.13
2.12
2.07
1.22
1.00
1.00
1.55
0.99
1.87
6.00
OH
O
O
P
OEt
Bu-n
abundance

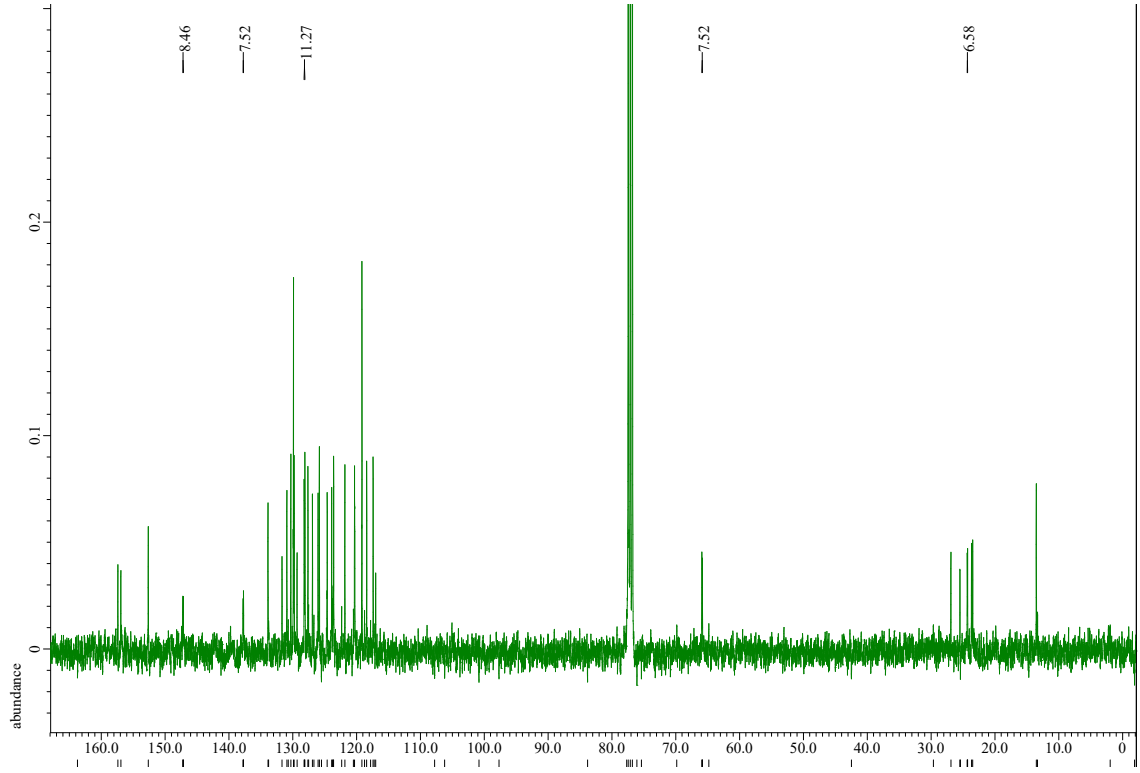
(R_{ax}, Rp)-**9a**

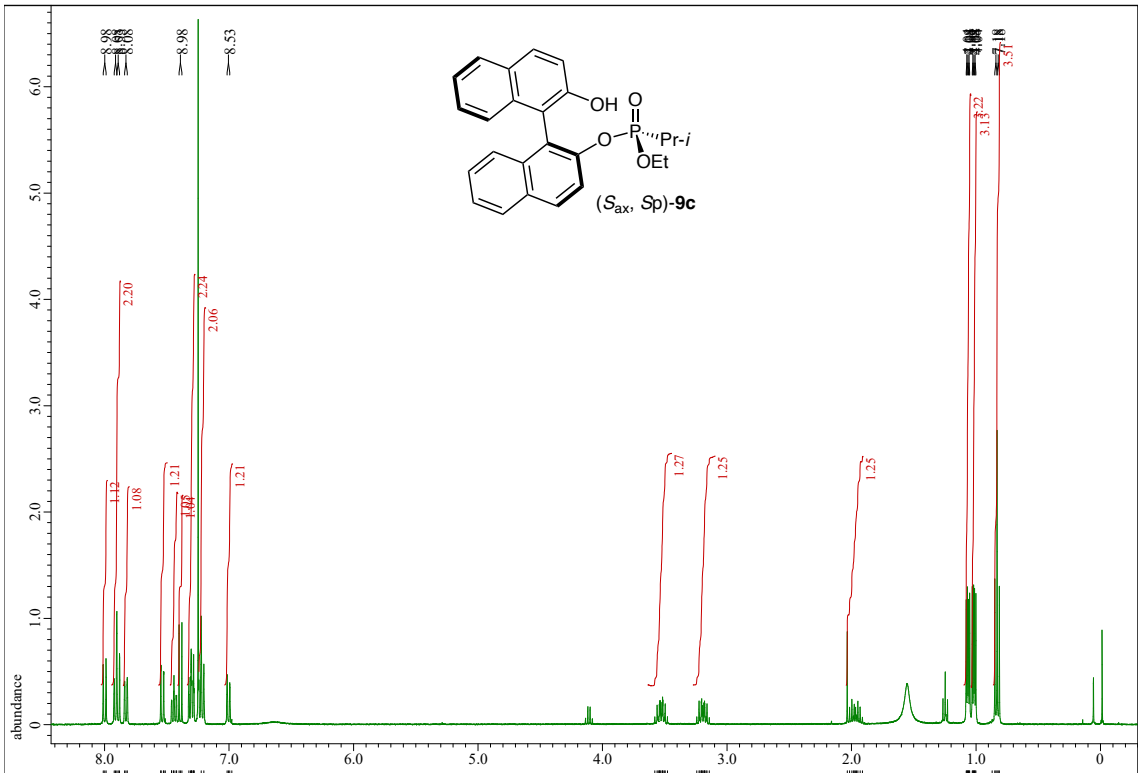

7.52
abundance

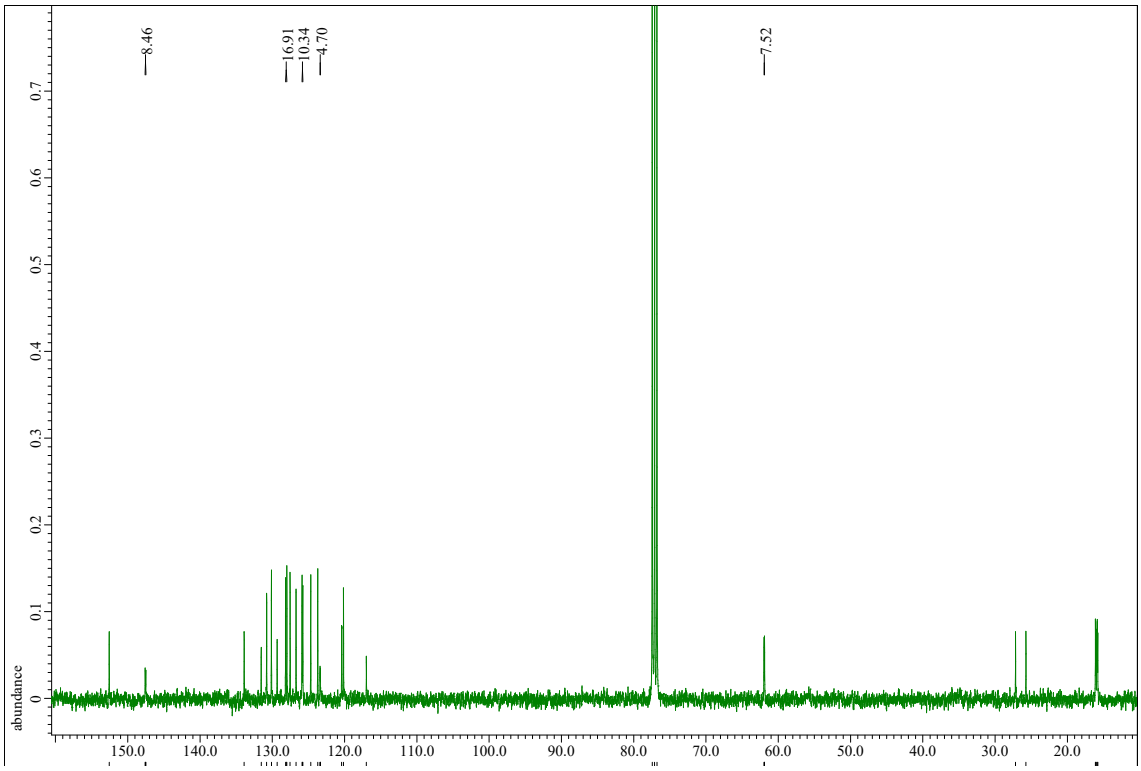

8.98
7.63
7.07
8.08
5.02
2.33
2.13
2.00
1.21
1.27
1.14
1.06
1.16
1.15
1.79
2.08
0.98
3.26
OH
O
P
Bu-n
OCH2C6H4-Ph-3
(Sax, Sp)-9b
abundance

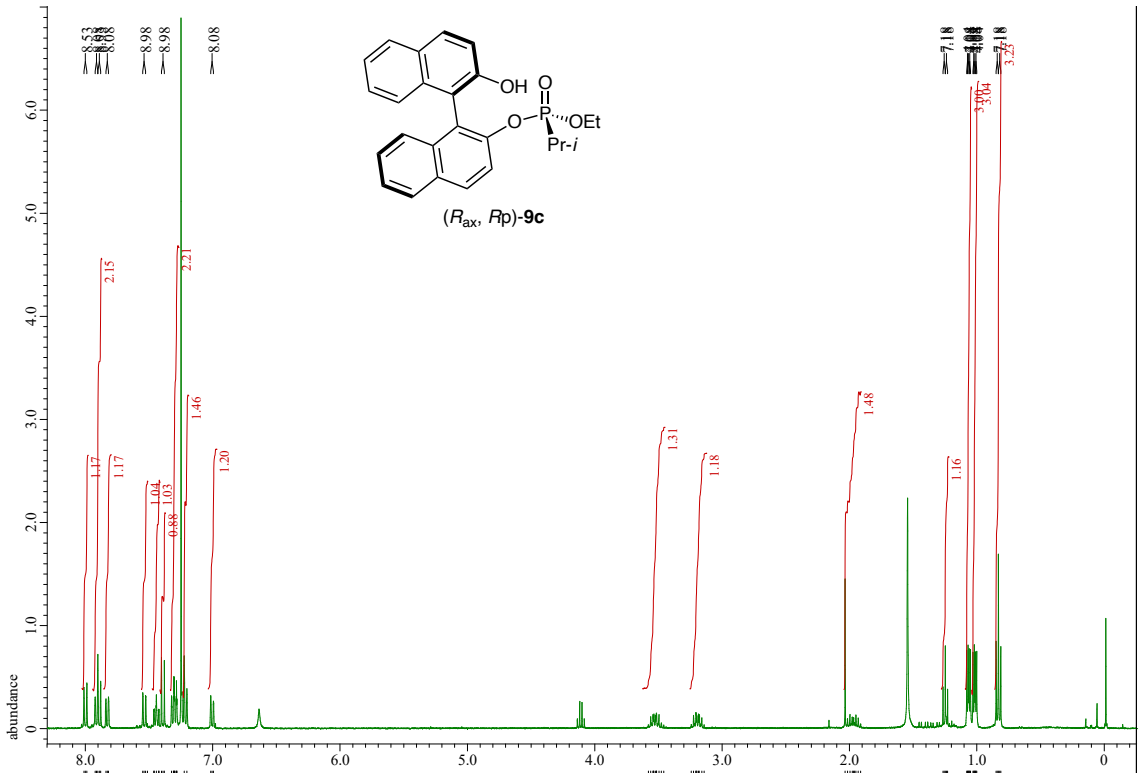

8.46
7.52
12.21
17.85
4.70
6.58
5.64
abundance

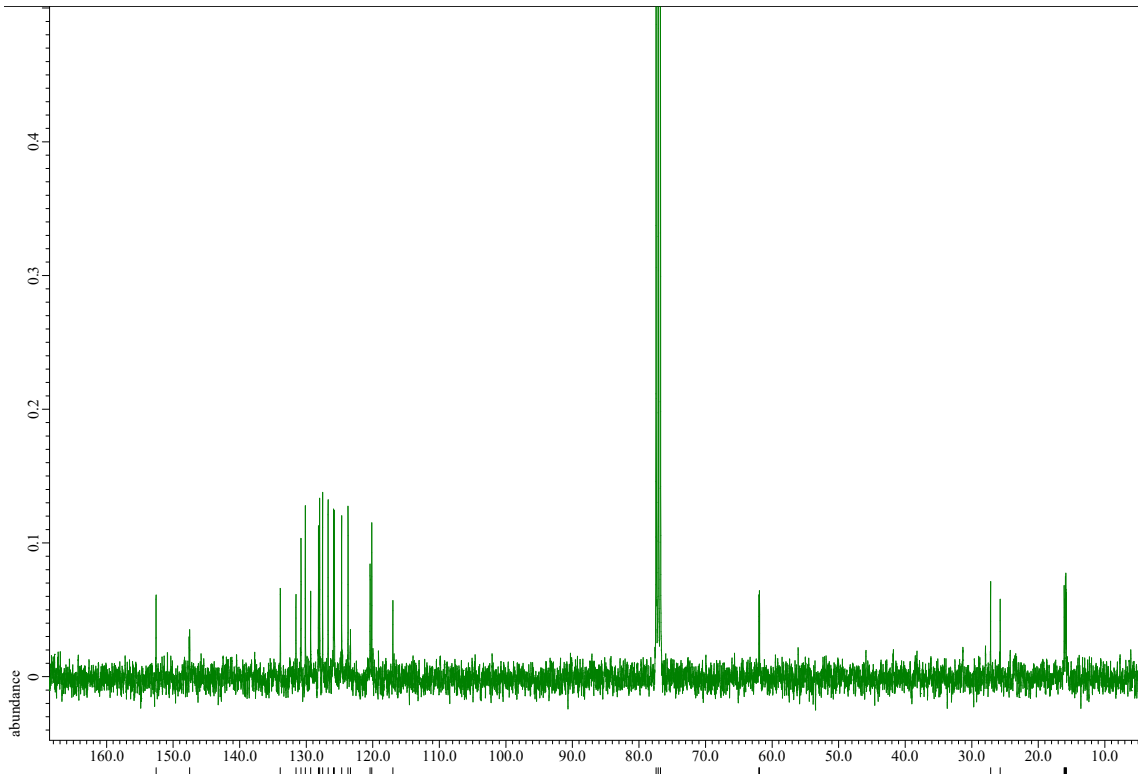

8.98
6.00
4.03
2.15
2.17
1.93
1.71
1.63
1.26
1.01
0.99
1.09
1.03
4.17
2.17
3.00
OH
O
O
P
OCH2C6H4-Ph-3
Bu-n
(Rax, Rp)-9b
abundance

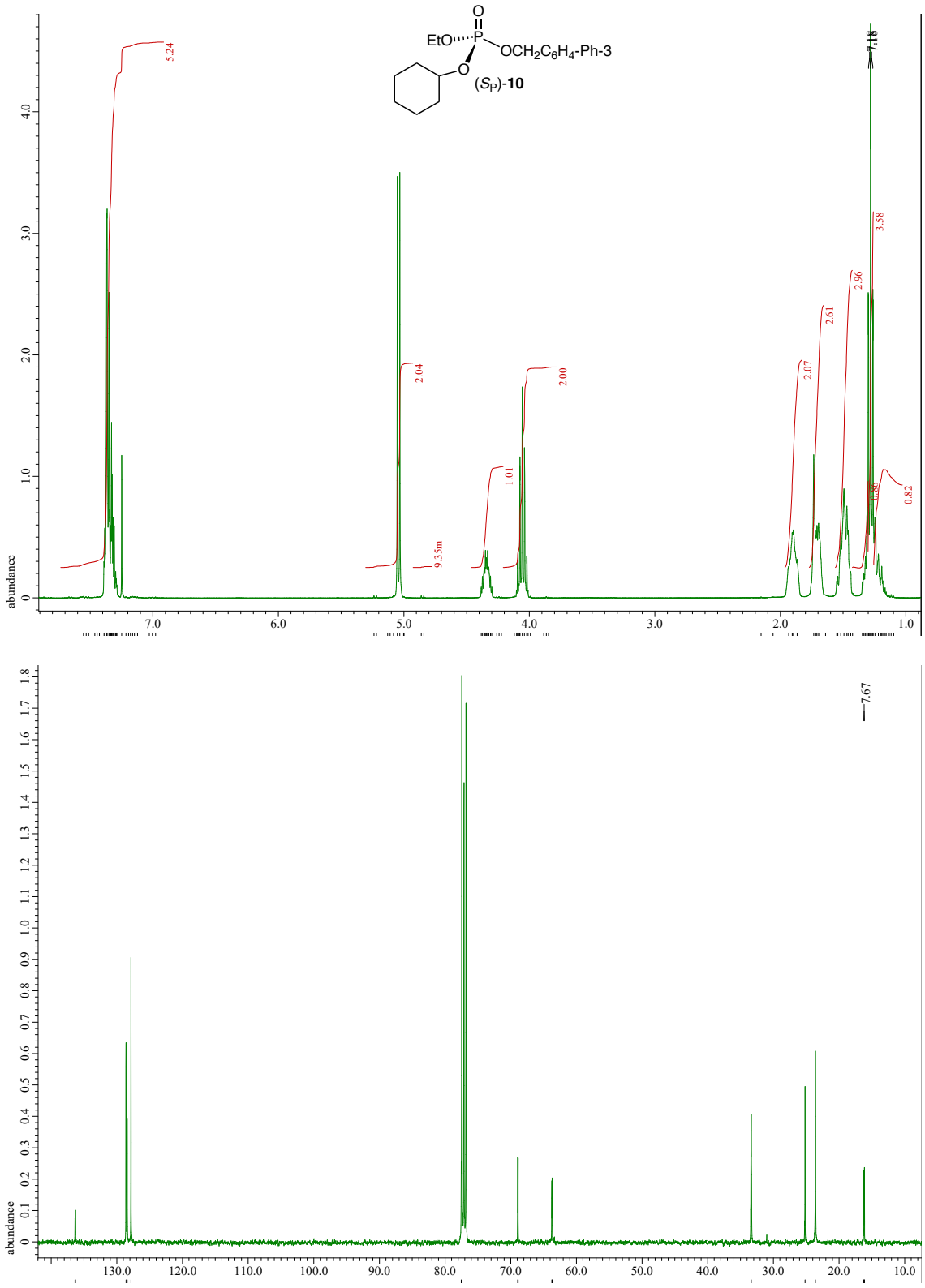

8.46
7.52
11.27
7.52
6.58
abundance

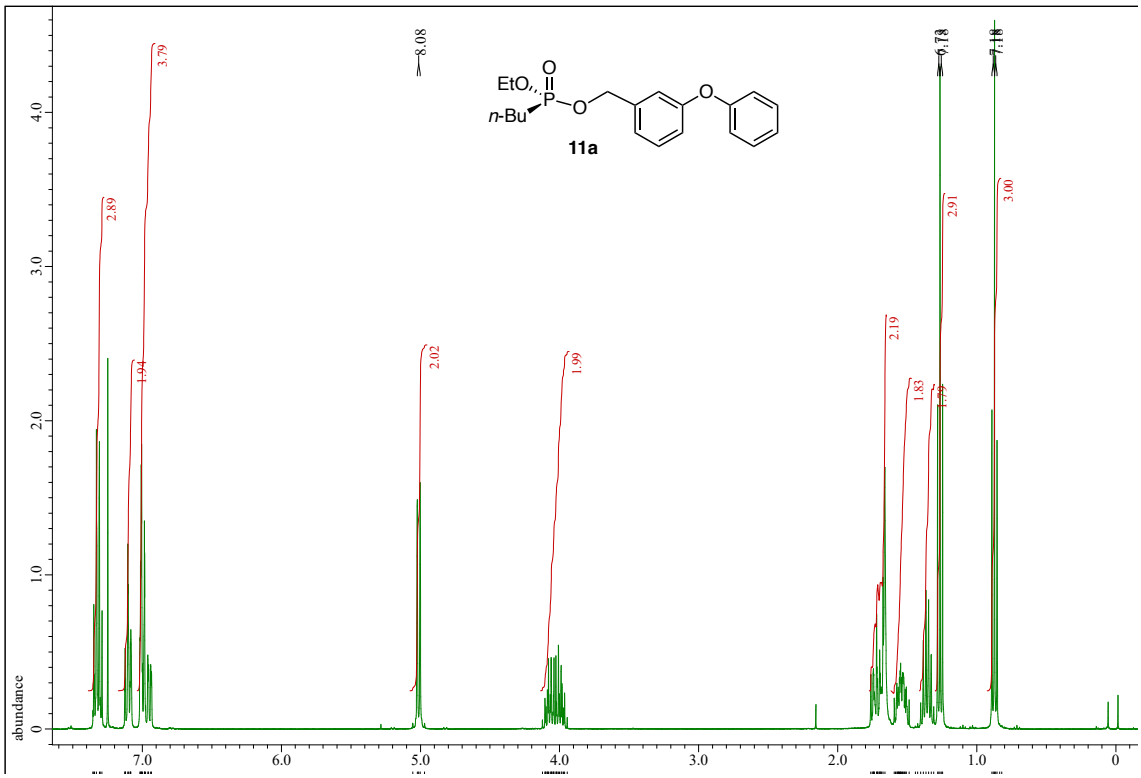

OH
O
O
P
Pr-i
OEt
(Sax, Sp)-9c
abundance

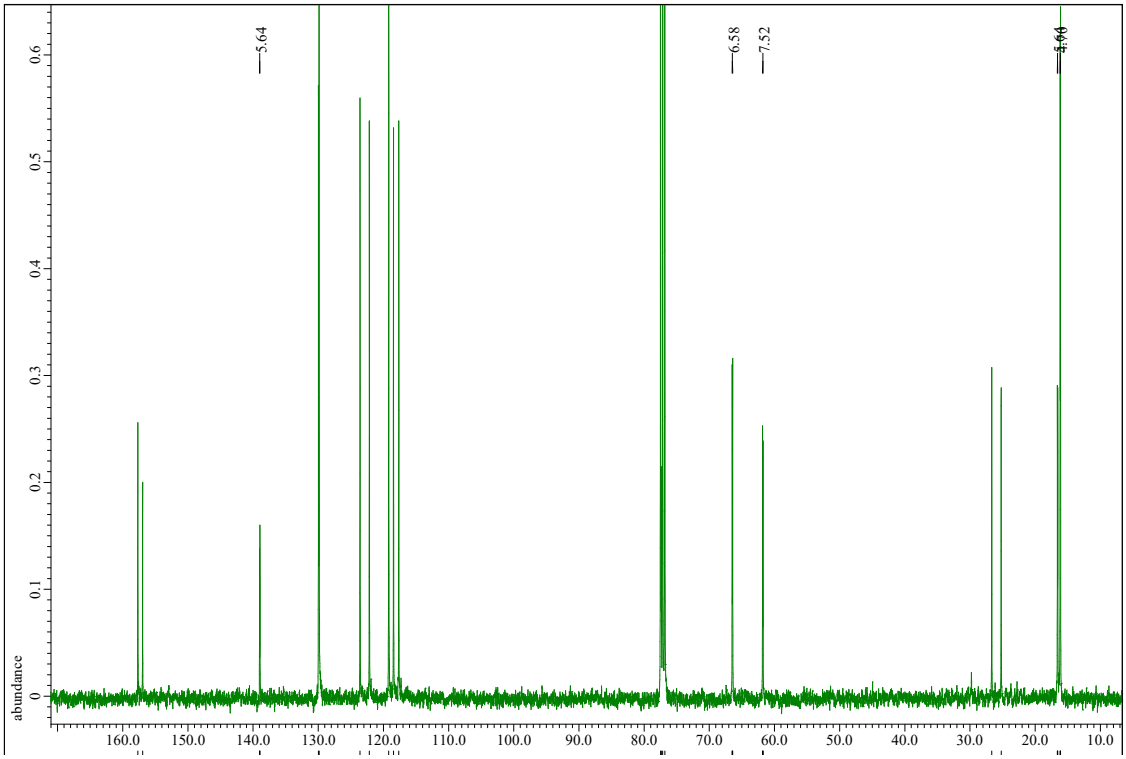

abundance

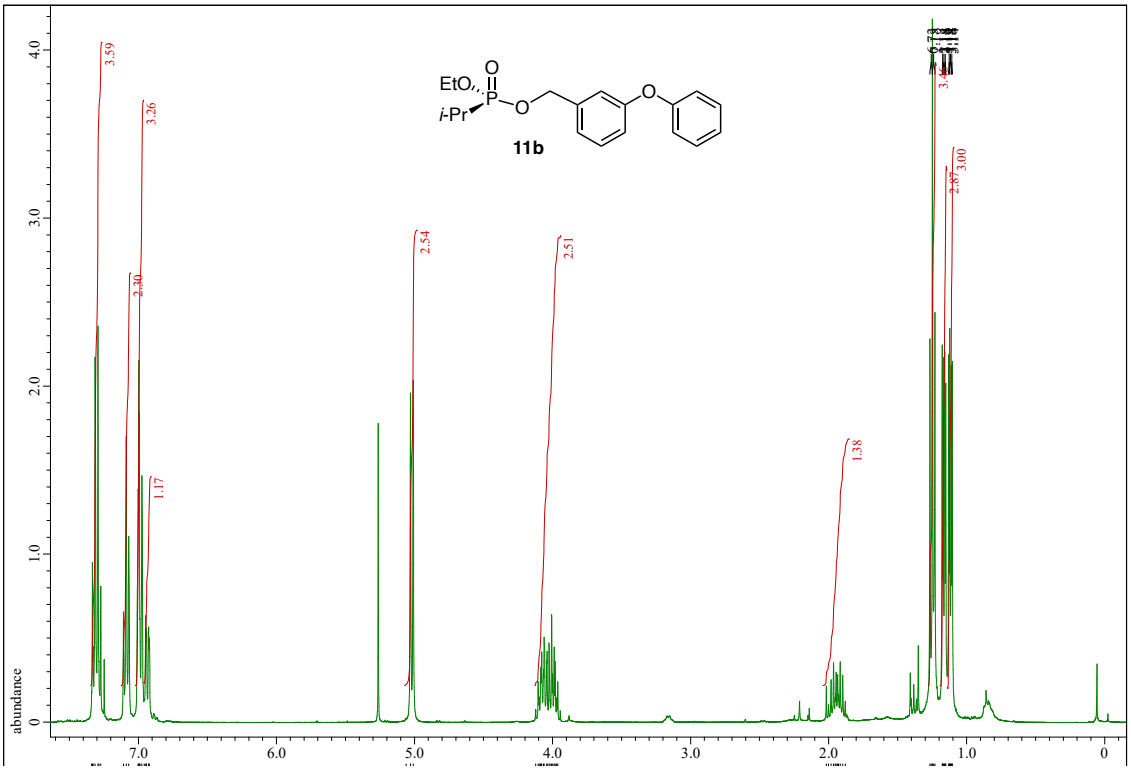

OH
O
O
P
OEt
Pr-i
(Rax, Rp)-9c
abundance

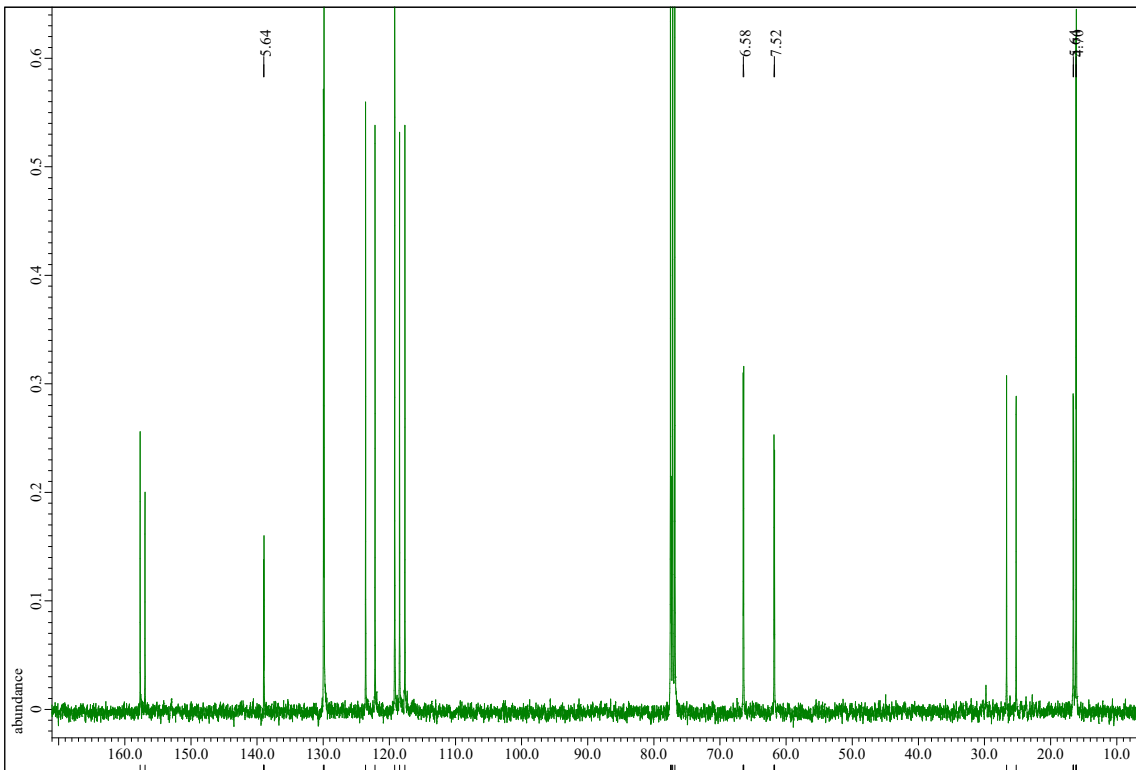

abundance


EtO
P
O
OCH2C6H4-Ph-3
O
(SP)-10
5.24
2.04
9.35m
1.01
2.00
2.07
2.61
2.96
3.58
0.82
7.67
abundance


8.08
3.79
2.89
1.94
2.02
1.99
2.19
1.83
2.91
3.00
EtO
O
P
O
n-Bu
O
11a
abundance

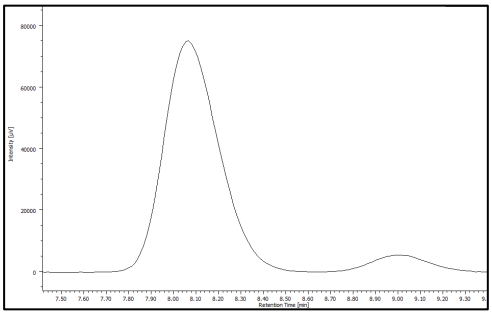

5.64
6.58
7.52
abundance


EtO
O
P
O
i-Pr
O
11b
3.59
3.26
2.30
1.17
2.54
2.51
1.38
3.00
abundance


5.64
6.58
7.52
4.60
abundance

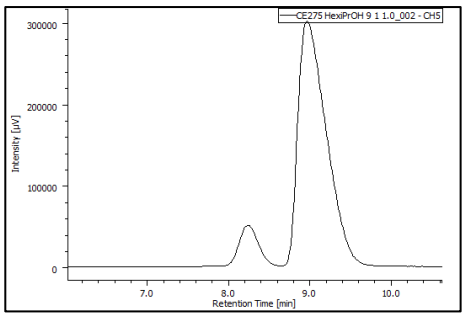
5. Charts of high performance liquid chromatography

Enantiomeric ratio was determined by HPLC analysis with DAICEL CHIRALPACK IH.



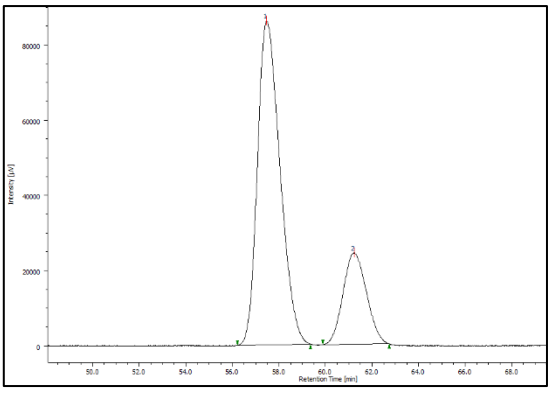
Chiral HPLC (CHIRALPAK IH, hexane/*i*PrOH = 9/1, 1 ml/min)

The result of entry 3 in Table 3, (R_p)- and (S_p)-**10** from (R_{ax}, S_P)-**4b** (>95:5)



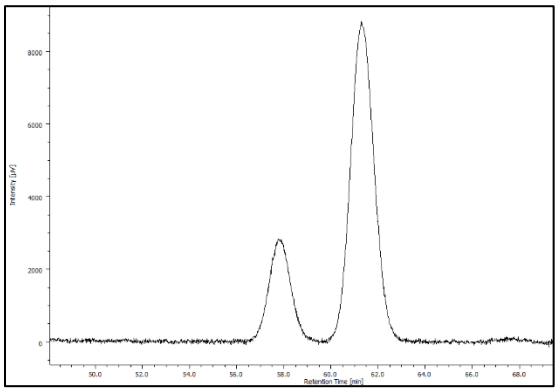
Chiral HPLC (CHIRALPAK IH, hexane/*i*PrOH = 9/1, 1.0 ml/min)

The result of entry 4 in Table 3, (R_p)- and (S_p)-**10** from (R_{ax}, R_P)-**4b** (5:>95)



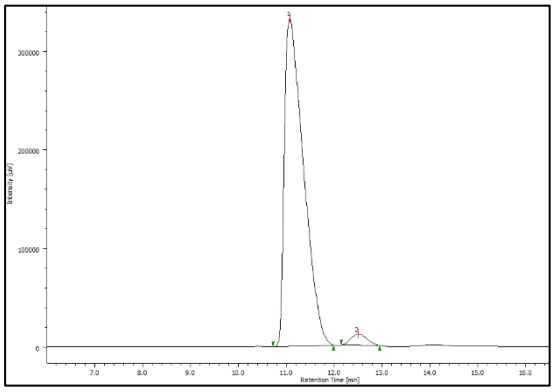
Chiral HPLC (CHIRALPAK IC, hexane : *i*-PrOH = 95 : 5, 0.5 mL/min)

The result in Scheme 8, (R_p)- and (S_p)-**11a** from (S_{ax}, R_P)-**9a** (76:23)



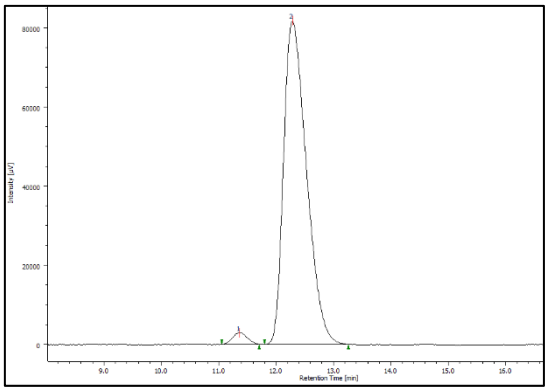
Chiral HPLC (CHIRALPAK IC, hexane : *i*-PrOH = 95 : 5, 0.5 mL/min)

The result in Scheme 8, (R_p)- and (S_p)-**11a** from (R_{ax}, S_P)-**9a** (87:16)



Chiral HPLC (CHIRALPAK IH, hexane ; *i*-PrOH = 90 : 10, 1 mL/min)

The result in Scheme 8, (R_p)- and (S_p)-**11b** from (S_{ax}, R_P)-**9b** (>95:5)



Chiral HPLC (CHIRALPAK IH, hexane ; *i*-PrOH = 90 : 10, 1 mL/min)

The result in Scheme 8, (R_p)- and (S_p)-**11b** from (R_{ax}, S_P)-**9b** (>95:5)