Supporting information for

Consecutive Dynamic Resolutions of Phosphine Oxides

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A) General information

a) Solvents and Reagents

All solvents used for extraction, filtration and chromatography were of commercial grade, and used without further purification. Anhydrous methanol, and acetonitrile were sourced from Sigma-Aldrich or Acros and stored under dinitrogen.

Reagents were purchased from Sigma-Aldrich, TCI, Alfa-Aesar or Acros and used without further purification.

b) Analysis

^{1}H-, ^{13}C- and ^{31}P-NMR were recorded on a Varian AMX400 (^{1}H: 400, ^{13}C: 101, ^{31}P: 160 MHz) and Varian AMX200 (^{1}H: 200, ^{13}C: 51, ^{31}P: 80 MHz) using $CDCl_3$ or MeOD as solvent, unless specified otherwise. Chemical shift values are reported in ppm with the solvent resonance as the internal standard ($CHCl_3$: δ = 7.27 ppm for ^{1}H, δ = 77.1 ppm for ^{13}C, MeOD: δ = 3.31, 4.87 ppm for ^{1}H, δ = 49.0 ppm for ^{13}C). Data is reported as follows: chemical shifts (δ in ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants *J* (Hz), and integration.

Enantiomeric excess was determined by chiral HPLC analysis using a Shimadzu LC-10AD*VP* HPLC equipped with a Shimadzu SPD-M10A*VP* diode array detector and CHIRALPAK AD or AD-H columns.

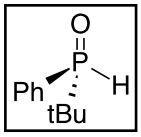
High Resolution Mass Spectrometry was performed using a ThermoScientific LTQ Oribitrap XL spectrometer.

Optical rotations were measured on a *Schmidt + Haensch* polarimeter (Polartronic MH8)

with a 10 cm cell (*c* given in mg/1 mL).

B) Experimental procedures

(*R*)-*tert*-butyl(phenyl)phosphine oxide



Racemic synthesis

0.4 mol *t*-butylmagnesiumchloride (1 M in 2-Me-THF, 400 ml) was cooled under N_2 to -15°C and dichlorophenylphosphine (27.1 ml, 200 mmol) in 2-Me-THF (25 ml) was added over 2 h. To avoid over-alkylation it is crucial to keep the temperature below -10 °C during the addition of Grignard reagent. Subsequently, the mixture was stirred for an andditional hour and allowed to warm up to RT.

The slurry was hydrolyzed by slowly adding 25% sulfuric acid (340 ml, 1.6 mol) and the layers were separated. The aqueous layer was extracted with choloroform (5x50 ml) and the combined organic layers dried ($MgSO_4$).

After removing the solvents in vacuo *tert*-butyl(phenyl)phosphine oxide (34.8 g, 191 mmol, 96 % yield) was obtained as white needles. For further purification the product can be recrystallized from diethyl ether or MTBE.

Resolution by diastereomeric complex formation

(-)-(*R,R*)-dibenzoyltartaric acid (590 mg, 1.65 mmol) and *tert*-butyl(phenyl)phosphine oxide (250 mg, 1.37 mmol) were dissolved in little as possible refluxing acetone/benzene (1:4) or diisopropyl ether/toluene (1:1). The mixture was slowly cooled (kept in the oil bath) down to RT to give the (R)-SPO-DBTA complex as big colourless crystals. These were filtered off and dissolved in 1 M NaOH (10 ml) and $CHCl_3$ (10 ml). The layers were separated and the aq. phase was extracted with $CHCl_3$ (5 x 5 ml). The combined organic layers were dried and the solvent removed under reduced pressure to give (*R*)-*tert*-butyl(phenyl)phosphine oxide (115 mg, 0.63 mmol, 46% yield).

The (S)-enantionmer of the SPO can be obtained from the mother liquor in the same manner as described above. Alternatively (*S,S*)-dibenzoyltartaric acid can be used as resolving agent to yield (*S*)-*tert*-butyl(phenyl)phosphine oxide.

Crystallization induced asymmetric transformation

Racemic tert-butyl(phenyl)phosphine oxide was prepared as described above.

(−)-(*R,R*)-dibenzoyltartaric acid (590 mg, 1.65 mmol) and *tert*-butyl(phenyl)phosphine oxide (250 mg, 1.372 mmol) were dissolved at 50°C in diisopropyl ether (20 ml). Subsequently iodine (5 mg, 0.020 mmol) was added. The initial slightly yellow mixture bleached after few minutes and a white precipitate was formed. The mixture was stirred for 16 h at 70°C.

The precipitate was filtered off at 70°C and the white solid was dissolved in 1 M NaOH and $CHCl_3$ (10 ml each). The layers were separated and the aq. layer extracted with $CHCl_3$ (5 x 10 ml). The combined organic layers were dried (PS-filter) and the solvent removed under reduced pressure to give (*R*)-*tert*-butyl(phenyl)phosphine oxide (230 mg, 1.32 mmol, 92 % yield)

^{1}H-NMR: (200 MHz, MeOD) ∂ (ppm) = 7.82 – 7.40 (m, 5H), 7.04 (d, $^{1}J_{HP}$ = 452.7 Hz, 1H), 1.15 (d, $^{3}J_{HCCP}$ = 16.6 Hz, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 132.4 (d, $^{4}J_{CCCCP}$ = 2.8 Hz), 130.8 (d, $^{2}J_{CCP}$ = 9.9 Hz), 128.9 (d, $^{1}J_{CP}$ = 90.0 Hz), 128.2 (d, $^{3}J_{CCCP}$ = 11.8 Hz), 31.9 (d, $^{1}J_{PC}$ = 69.2 Hz), 23.4 (d, $^{2}J_{CCP}$ = 2.1 Hz).

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 47.3.

HRMS: 183.0861 (calc), 183.0931 (found)

Mp: 51 °C

HPLC: t_1 ((*S*)-SPO) = 11.8 min, t_2 ((*R*)-SPO) = 16.5 min, Chiralpak AD-H, heptane/2-propanol 90:10, flow: 1.0 ml/min

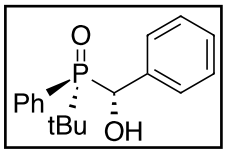
t_1 ((*S*)-SPO) = 18.3 min, t_2 ((*R*)-SPO) = 25.5 min, Chiralpak AD-H, heptane/2-propanol 90:10, flow: 0.5 ml/min

General procedure for tert-butyl(hydroxymethyl)phenylphosphine oxides

(*R*)-tert-butyl(phenyl)phosphine oxide (100 mg, 0.55 mmol) was dissolved in 0.05 M NaOH(aq) (5 ml) at RT and the corresponding aldehyde (0.66 mmol, 1.2 eq) was added to form a white precipitate within several minutes of vigorously stirring.

The mixture was heated to the indicated temperature for 16 h. After cooling down, the mixture was filtered and the residue washed with water (5 ml) and MTBE (5 ml) to give the corresponding tert-butyl(hydroxymethyl)phenylphosphine oxide.

(*R*)-*tert*-butyl((*R*)-hydroxy(phenyl)methyl)(phenyl)phosphine oxide



^{1}H-NMR: (400 MHz, MeOD) ∂ (ppm) = 7.77 (t, *J* = 8.5 Hz, 2H), 7.55 – 7.27 (m, 5H), 7.20 – 7.09 (m, 3H), 5.59 (s, 1H), 1.26 (d, $^{3}J_{HCCP}$ = 14.5 Hz, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 137.8 (d, *J* = 1.9 Hz), 131.6 (d, *J* = 7.6 Hz), 131.5 (d, *J* = 2.8 Hz), 129.2 (d, *J* = 84.5 Hz), 128.0 (d, *J* = 4.7 Hz), 127.8 (d, *J* = 10.5 Hz), 127.3 (d, *J* = 1.9 Hz), 72.2 (d, *J* = 78.2 Hz), 33.7 (d, *J* = 63.4 Hz), 24.5.

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 48.8

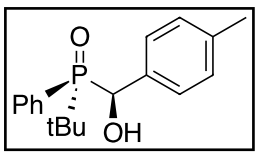
HRMS: 289.1352 (calc), 289.1350 (found)

Mp: 154 °C

Elemental analysis: C: 70.82 %, H: 7.34 % (calc), C: 70.47 %, H: 7.27 % (found)

$[\alpha]^{20}_{D}$ = –29.4 (c = 6.67, MeOH)

(*R*)-*tert*-butyl((*S*)-hydroxy(p-tolyl)methyl)(phenyl)phosphine oxide



^{1}H-NMR: (400 MHz, MeOD) ∂ (ppm) = 7.95-7.90 (m, 2H); 7.47-7.45 (m, 3H); 7.20 (dd, J = 8.0, 1.5 Hz, 2H); 6.99 (d, J = 7.9 Hz, 2H), 5.51 (d, $^{2}J_{HCP}$ = 9.3 Hz, 1H); 2.23 (s, 3H); 1.25 (d, $^{3}J_{HCCP}$ = 14.3 Hz, 9H)

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 137.2 (*J* = 2.4 Hz), 134.9 (*J* = 1.7 Hz), 132.5 (*J* = 7.7 Hz), 131.6 (*J* = 2.7 Hz), 129.1 (*J* = 88.4 Hz), 128.0 (*J* = 1.9 Hz), 127.5 (*J* = 10.7 Hz),

127.3 (J = 4.4 Hz), 126.7, 71.5 (J = 81.4 Hz), 33.1 (J = 63.0 Hz), 24.1, 19.7

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 47.4

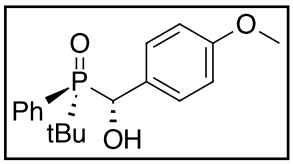
HRMS: 303.1508 (calc), 303.1506 (found)

Mp: 161-163 °C

Elemental analysis: C: 71.50 %, H: 7.67 % (calc), C: 70.98 %, H: 7.68 % (found)

$[\alpha]^{20}_{D}$ = –149.7 (c = 6.67, MeOH)

(*R*)-*tert*-butyl((*R*)-hydroxy(4-methoxyphenyl)methyl)(phenyl)phosphine oxide



^{1}H-NMR: (200 MHz, MeOD) ∂ (ppm) = 7.75 (t, J = 8.32, 2H), 7.44 - 7.30 (m, 5H), 6.72 (m, 2H), 5.56 (s, 1 H), 3.70 (s, 3H), 1.28 (d, $^{3}J_{HCCP}$ = 14.5 Hz, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 159.4 (d, J = 2.1 Hz), 131.6 (d, J = 7.5 Hz), 131.4 (d, J = 2.7 Hz), 129.3 (d, J = 4.9 Hz), 129.3 (d, J = 84.7 Hz), 128.7 (d, J = 4.4 Hz), 127.8 (d, J = 10.5 Hz), 112.8 (d, J = 1.6 Hz), 71.5 (d, J = 79.5 Hz), 54.1, 33.6 (d, J= 62.8 Hz), 24.5.

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 47.4

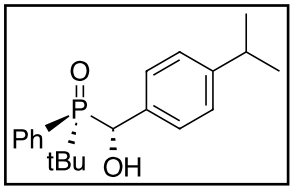
HRMS: 319.1458 (calc), 319.1456 (found)

Mp: 131 °C

Elemental analysis: C: 67.49 % H: 7.23 % calc: 67,91 % H: 7.28 %

$[\alpha]^{20}_{D}$ = –49.2 (c = 6.67, MeOH)

(*R*)-*tert*-butyl((*R*)-hydroxy(4-isopropylphenyl)methyl)(phenyl)phosphine oxide



^{1}H-NMR: (400 MHz, MeOD) ∂ (ppm) = 7.81 - 7.68 (m, 2H), 7.53 - 7.38 (m, 3H), 7.32 - 7.19 (m, 2H), 7.07 - 7.01 (m, 2H), 5.57 (s, 1H), 2.78 (dt, J = 14.0, 7.1 Hz, 1H), 1.25 (d, $^{3}J_{PCCH}$ = 14.5 Hz, 9H), 1.14 (dt, J = 6.0, 3.9 Hz, 6H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 135.2 (d, J = 18.4 Hz), 132.7 (d, J = 9.0 Hz), 131.6

(d, *J* = 7.4 Hz), 131.5 (d, *J* = 2.8 Hz), 128.5 (d, *J* = 68.2 Hz), 128.0 (d, *J* = 4.8 Hz), 127.8 (d, *J* = 10.5 Hz), 125.4 (d, *J* = 1.8 Hz), 72.0 (d, *J* = 78.8 Hz), 33.6, 33.16 (d, *J* = 42.3 Hz), 24.5, 22.9 (d, *J* = 5.8 Hz).

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 47.9

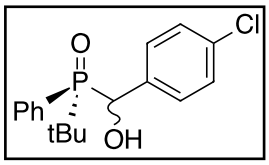
HRMS: 331.1821 (calc), 331.1816 (found)

Mp: 156 °C

Elemental analysis: C: 72.70 %, H: 8.24 % (calc), C: 72.36 %, H: 8.30 % (found)

$[\alpha]^{20}_{D}$ = –72.6 (c = 6.67, MeOH)

(*R*)-*tert*-butyl((*RS*)-(4-chlorophenyl)(hydroxy)methyl)(phenyl)phosphine oxide



^{1}H-NMR: (400 MHz, MeOD) ∂ (ppm) = 7.99 – 7.69 (m, 5H), 7.64 – 7.39 (m, 7H), 7.38 – 7.10 (m, 6H), 5.60 (s, 1H), 5.55 (d, $^{2}J_{HCP}$ = 10.7 Hz, 1H), 1.29 (d, $^{3}J_{HCCP}$ = 14.4 Hz, 9 H), 1.27 (d, $^{3}J_{HCCP}$ = 14.7 Hz, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 136.8 (d, *J* = 23.1), 136.8 (d, *J* = 23.4), 132.5 (d, J = 7.7), 131.8 (d, *J* = 2.8), 131.8 (d, *J* = 2.8), 131.6 (d, *J* = 2.8), 131.6 (d, *J* = 7.5), 129.5 (d, *J* = 4.6), 128.7 (d, *J* = 4.1), 127.9 (d, *J* = 10.6), 127.5 (d, *J* = 10.8), 127.4 (d, *J* = 1.9), 127.3 (d, *J* = 2.2), 71.6 (d, *J* = 78.2), 71.2 (d, *J* = 80.9), 33.8 (d, *J* = 56.6), 33.2 (d, *J* = 56.6), 24.5, 24.0.

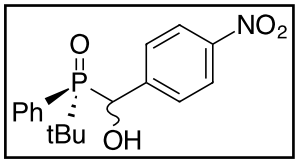
^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 47.6, 46.9

HRMS: 345.0782 ([M+Na] calc), 345.0780 ([M+Na] found)

Mp: 188 °C

Elemental analysis: C: 63.26 %, H: 6.25 % (calc), C: 63.37 %, H: 6.13 % (found)

(*R*)-*tert*-butyl((*RS*)-hydroxy(4-nitrophenyl)methyl)(phenyl)phosphine oxide



1H-NMR: (400 MHz, MeOD) ∂ (ppm) = 8.42 – 7.01 (m, 20 H), 5.78 (s, 1H), 5.73 (d, $^{2}J_{HCP}$ = 12.7 Hz, 1H), 1.36 (d, $^{3}J_{HCCP}$ = 14.7 Hz, 9H), 1.30 (d, *J* = 14.9, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 132.5 (d, *J* = 7.8 Hz), 131.9 (d, *J* = 2.8 Hz), 131.9 (d, *J* = 2.7 Hz), 131.6 (d, *J* = 7.6 Hz), 128.8 (d, *J* = 4.2 Hz), 128.1 (d, *J* = 10.7 Hz), 127.8 (d, *J* = 3.7 Hz), 127.6 (d, *J* = 10.9 Hz), 127.1 (d, *J* = 81.5 Hz), 71.9 (d, *J* = 76.2 Hz), 71.50 (d, *J* = 81.6 Hz), 34.4, 33.2, 24.5, 24.0

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 47.5, 46.7

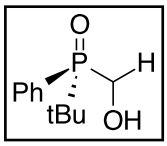
HRMS: 356.1022 ([M+Na] calc), 356.1018 ([M+Na] found)

Mp: 183 °C (decomp)

Elemental analysis: C: 61.26 %, H: 6.05 %, N: 4.20 % (calc), C: 60.97 %, H: 5.99 %, N: 4.19 % (found)

$[\alpha]^{20}_{D}$ = –142.0 (c = 6.67, MeOH)

(*R*)-*tert*-butyl(hydroxymethyl)(phenyl)phosphine oxide



^{1}H-NMR: (400 MHz, $CDCl_3$) ∂ (ppm) = 7.73 – 7.68 (m, 2H), 7.53 – 7.44 (m, 3H), 4.33 (dd, *J* = 70.6, 14.3 Hz, 2H), 1.16 (d, $^{3}J_{HCCP}$ = 14.5 Hz, 9H).

^{13}C-NMR: (101 MHz, $CDCl_3$) ∂ (ppm) = 131.8 , 131.6 (d, *J* = 7.8 Hz), 128.7 (d, *J* = 85.4 Hz), 128.3 (d, *J* = 10.6 Hz), 57.4 (d, *J* = 72.3 Hz), 32.5 (d, *J* = 64.7 Hz), 24.6.

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 46.4

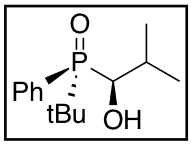
HRMS: 213.1039 (calc), 213.1037 (found)

Mp: 137°C

Elemental analysis: C: 62.25 %, H: 8.07 % (calc), C: 62.36 %, H: 8.12 % (found)

$[\alpha]^{20}_{D}$ = +4.8 (c = 6.67, MeOH)

(*R*)-*tert*-butyl((*S*)-1-hydroxy-2-methylpropyl)(phenyl)phosphine oxide



^{1}H-NMR: (400 MHz, MeOD) ∂ (ppm) = 8.13 – 7.87 (m, 2H), 7.71 – 7.32 (m, 3H), 4.24 (dd, *J* = 7.9, 4.9 Hz, 1H), 2.31 – 1.92 (m, 1H), 1.21 (d, $^{3}J_{HCCP}$ = 14.0 Hz, 9H), 1.00 (d, *J* = 6.9 Hz, 3H), 0.73 (d, *J* = 6.7, 3H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 132.4 (d, *J* = 7.6 Hz), 131.5 (d, *J* = 2.8 Hz), 128.8

(d, J = 80.8 Hz), 127.6 (d, J = 10.5 Hz), 72.8 (d, J = 83.3 Hz), 32.8 (d, J = 64.6 Hz), 30.2 (d, J = 2.6 Hz), 23.8, 19.5 (d, J = 8.1 Hz), 16.7 (d, J = 5.4 Hz).

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 43.7

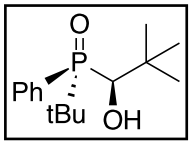
HRMS: 277.1328 ([M+Na] calc), 277.1326 ([M+Na] found)

Mp: 143 °C

Elemental analysis: C: 66.12 %, H: 9.12 % (calc), C: 66.08 %, H: 9.15 % (found)

$[\alpha]^{20}_{D}$ = +33.0 (c = 6.67, MeOH)

(*R*)-*tert*-butyl((*S*)-1-hydroxy-2,2-dimethylpropyl)(phenyl)phosphine oxide



1H-NMR: (400 MHz, MeOD) ∂ (ppm) = 8.17 – 8.00 (m, 2H), 7.71 – 7.32 (m, 3H), 4.17 (d, $^{2}J_{HCP}$ = 7.9 Hz, 1H), 1.20 (d, $^{3}J_{HCCP}$ = 13.8 Hz, 9H), 0.92 (s, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 133.1 (d, J = 7.4 Hz), 131.2 (d, J = 2.8 Hz), 129.9 (d, J = 81.1 Hz), 127.3 (d, J = 10.5 Hz), 75.1 (d, J = 83.3 Hz), 36.5 (d, J = 1.8 Hz), 33.3 (d, J = 65.1 Hz), 26.3 (d, J = 4.6 Hz), 24.1.

^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 44.9.

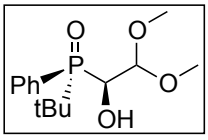
HRMS: 269.1665 (calc), 269.1652 (found)

Mp: 131 °C

Elemental analysis: C: 67.14 %, H: 9.39 % (calc), C: 67.12 %, H: 9.47 % (found)

$[\alpha]^{20}_{D}$ = +34.5 (c = 6.67, MeOH)

(*R*)-tert-butyl((*S*)-1-hydroxy-2,2-dimethoxyethyl)(phenyl)phosphine oxide



1H-NMR: (400 MHz, MeOD) ∂ (ppm) = 7.77 – 7.74 (m, 2H), 7.56 – 7.50 (m, 3H), 4.57 (dd, J = 7.3, 4.1 Hz, 1H), 4.50 (dd, J = 7.3, 3.6 Hz, 1H), 3.39 (s, 3H), 3.00 (s, 3H), 1.22 (d,$^{3}J_{HCCP}$ = 14.6 Hz, 9H).

^{13}C-NMR: (101 MHz, MeOD) ∂ (ppm) = 131.1 (d, J = 2.8 Hz), 130.9 (d, J = 7.9 Hz), 130.3 (d, J = 86.2 Hz), 127.7 (d, J = 10.9), 103.7 (d, J = 5.6 Hz), 69.9 (d, J = 79.8 Hz), 54.6, 53.1,

33.4 (d, J = 66.8), 24.0.

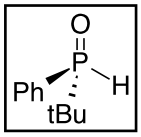
^{31}P-NMR: (162 MHz, MeOD) ∂ (ppm) = 48.6.

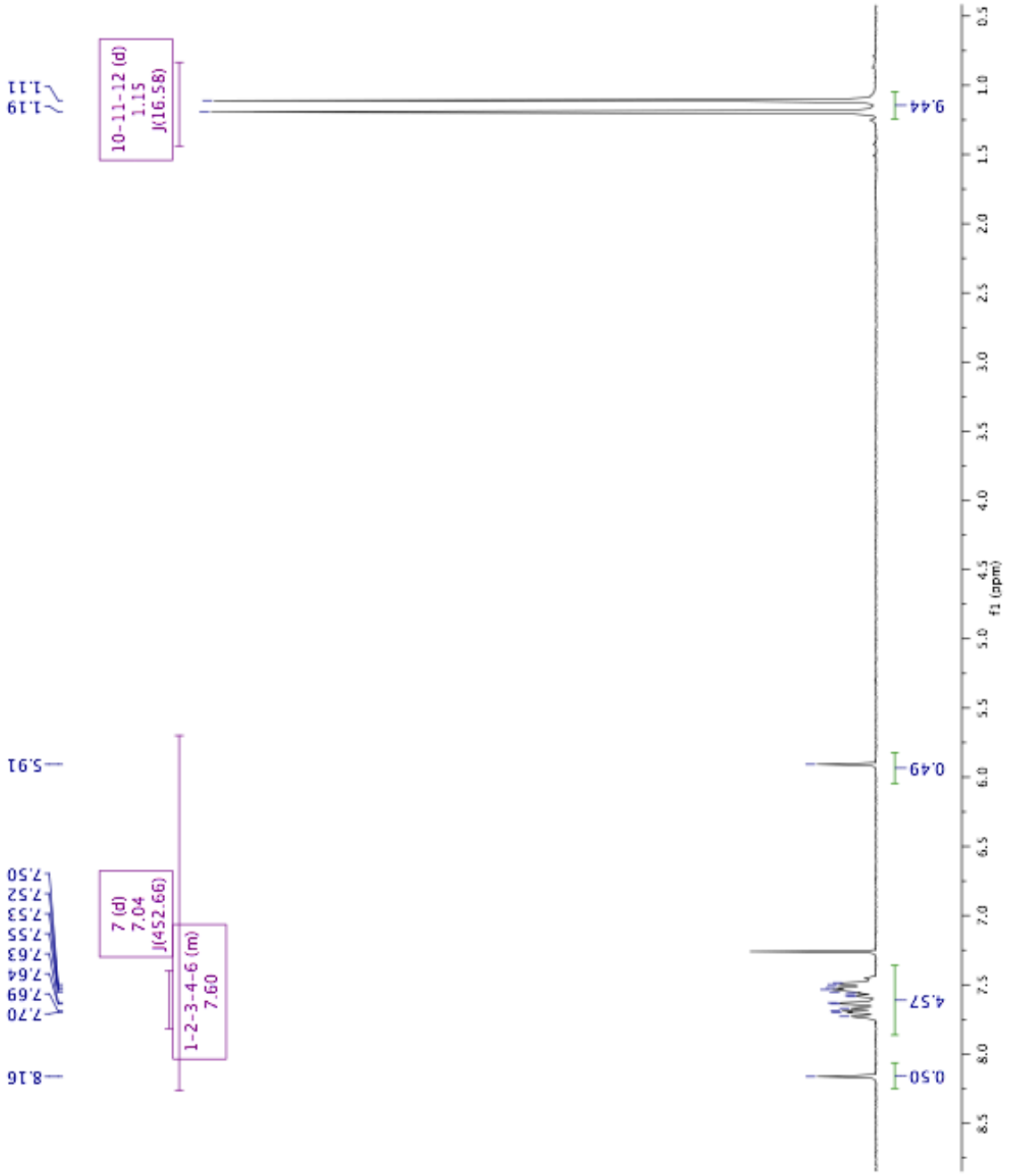
HRMS: 287.1407 (calc), 287.1407 (found)

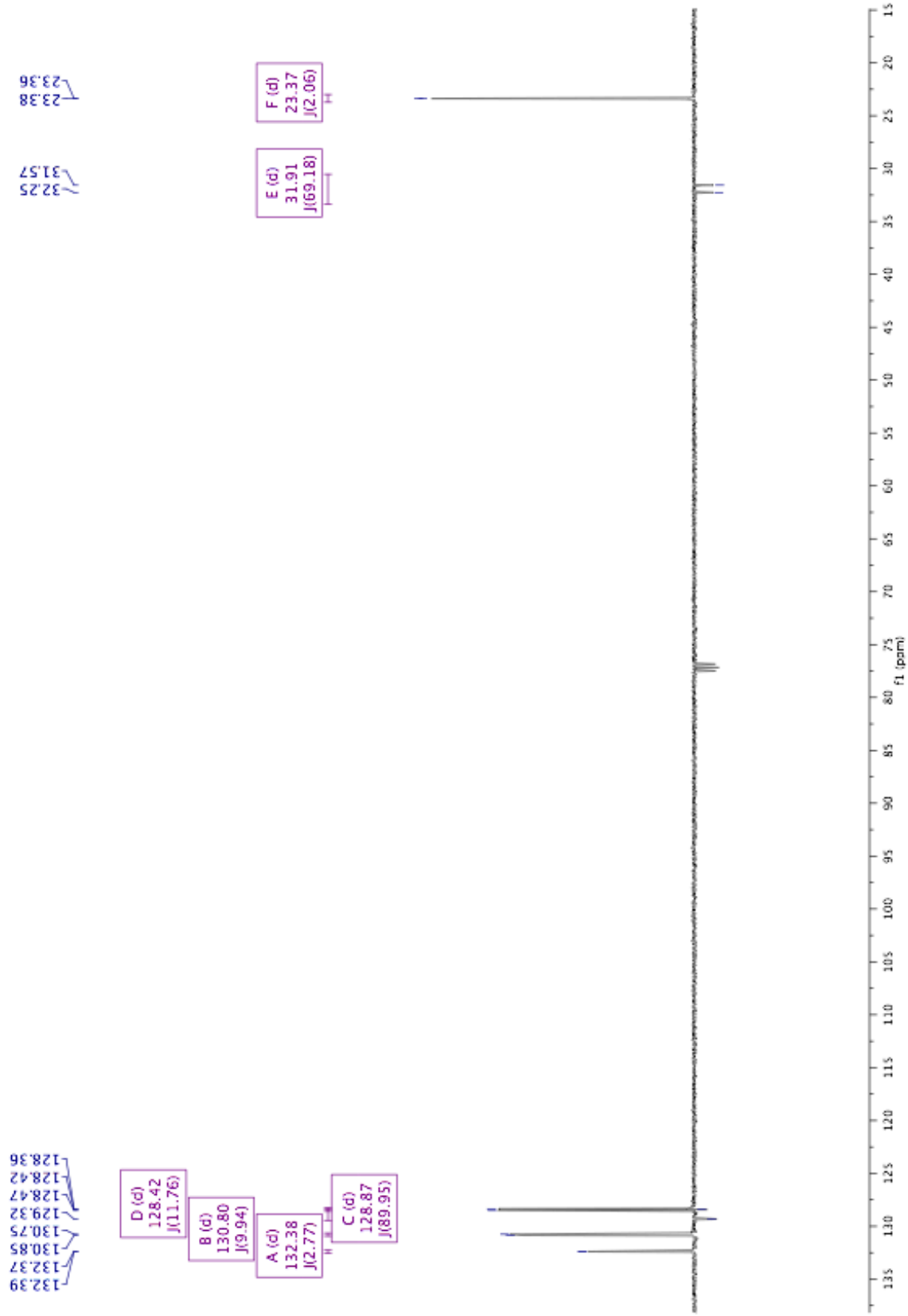
Mp: 133 °C

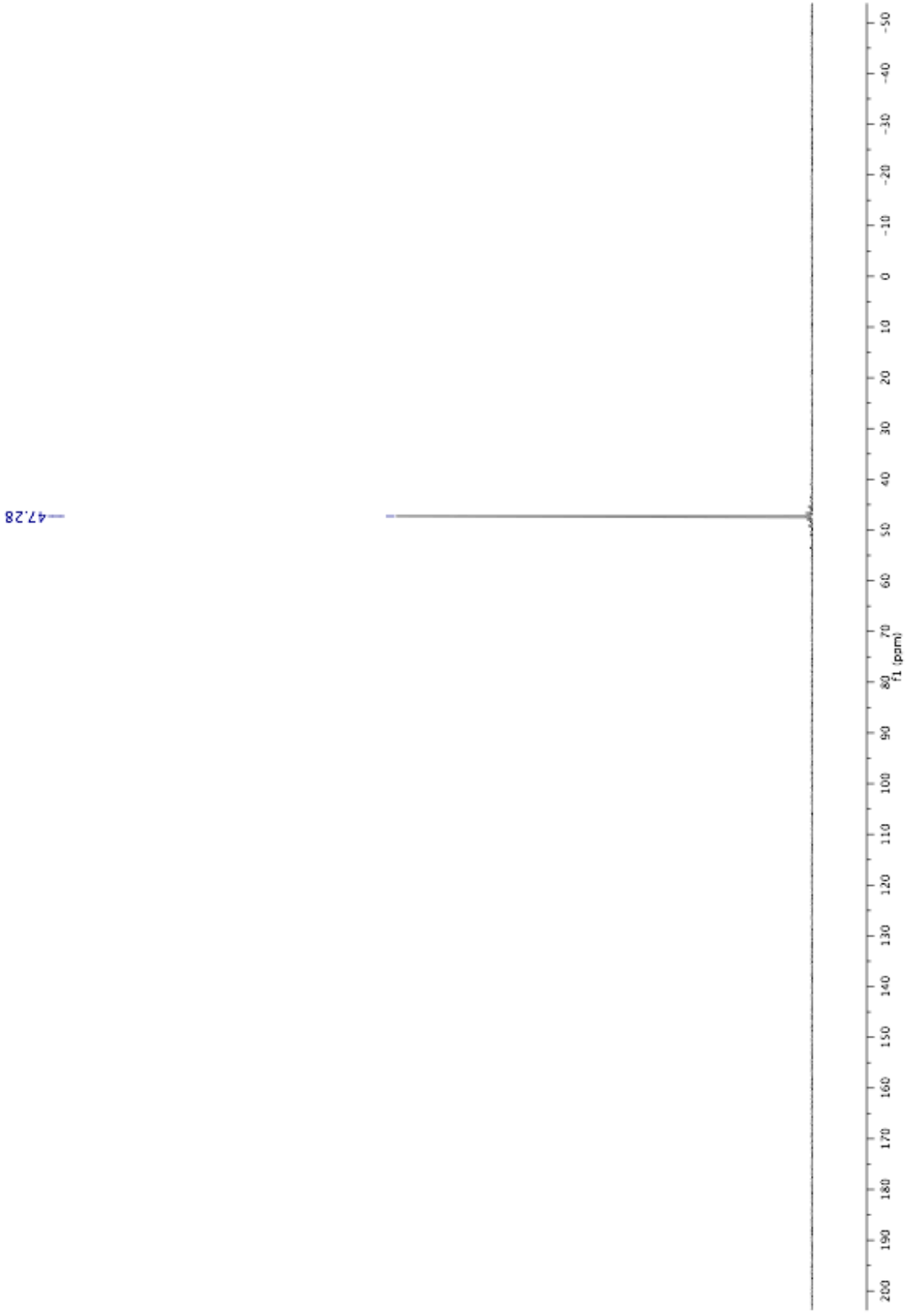
C) NMR-Spectra

(*R*)-*tert*-butyl(phenyl)phosphine oxide

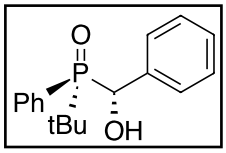


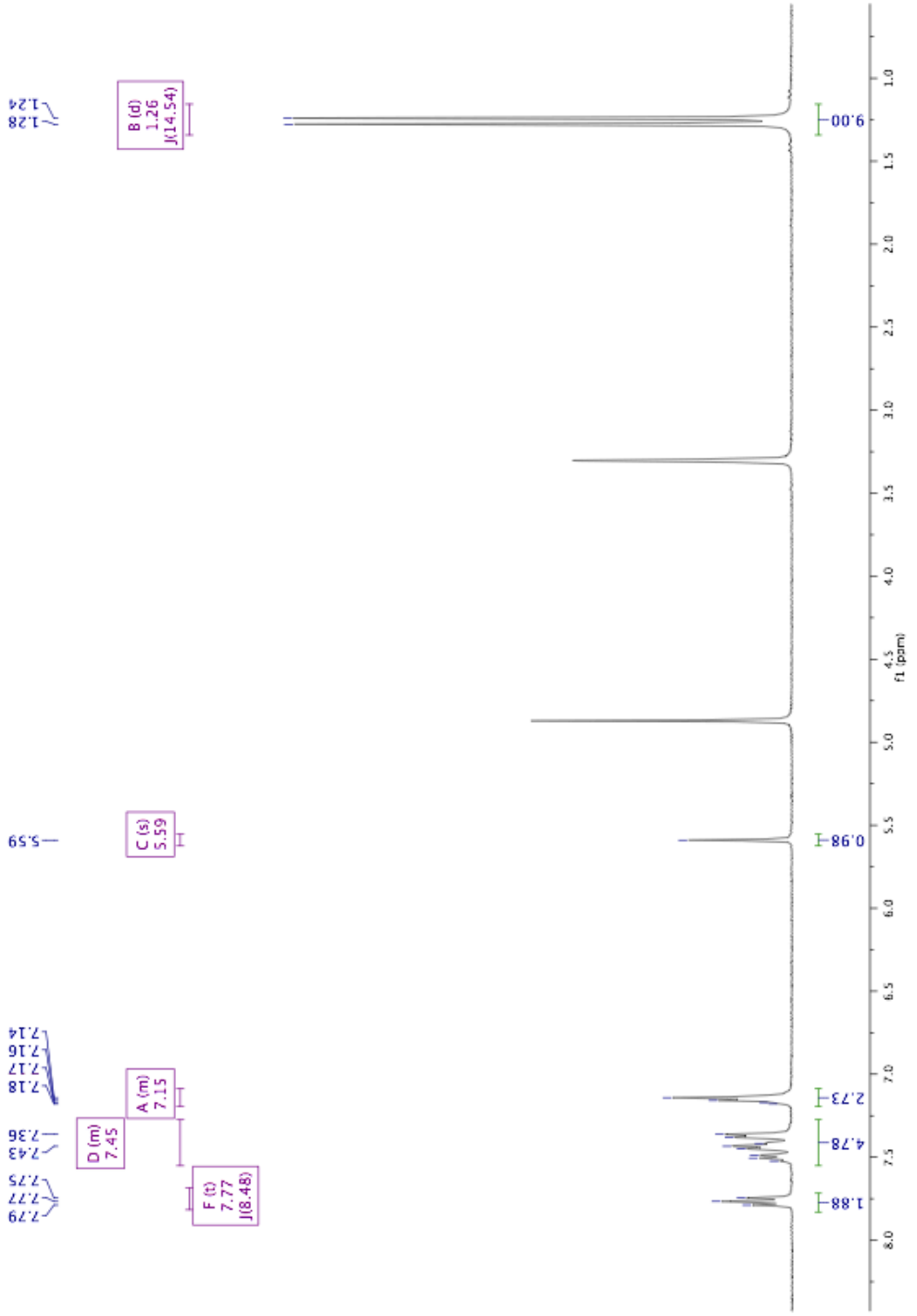


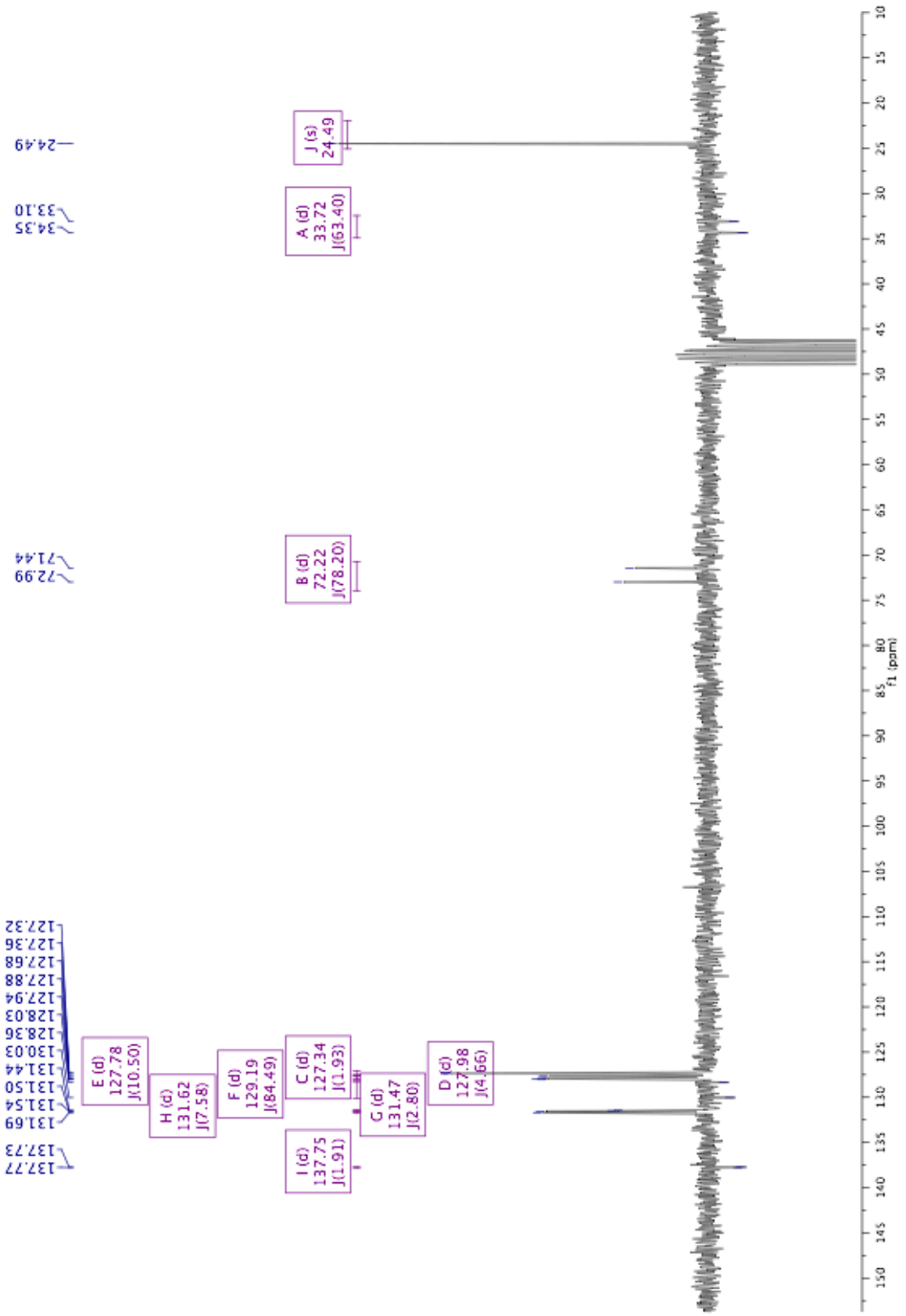


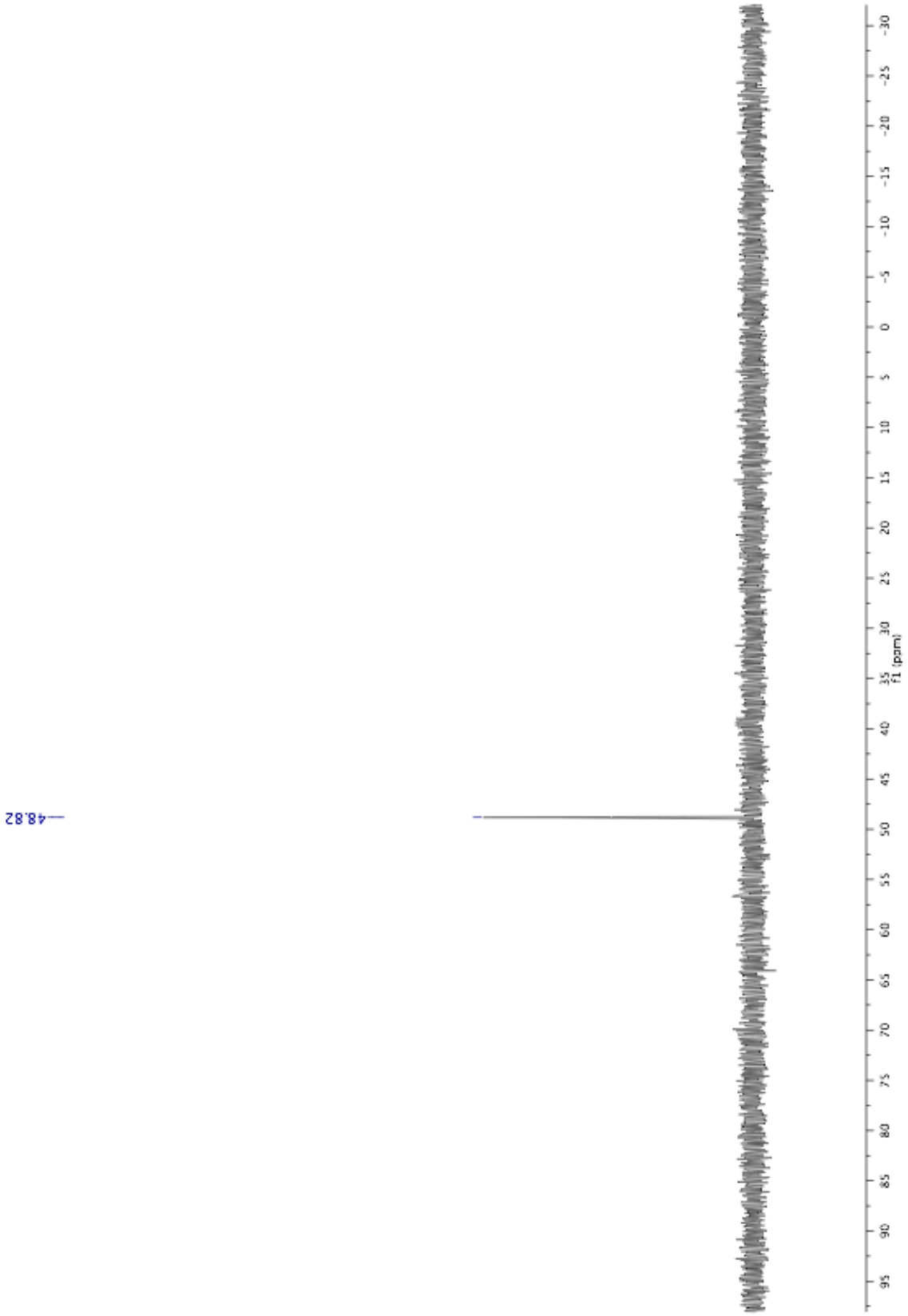


(*R*)-*tert*-butyl((*R*)-hydroxy(phenyl)methyl)(phenyl)phosphine oxide

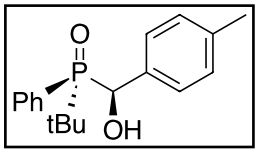


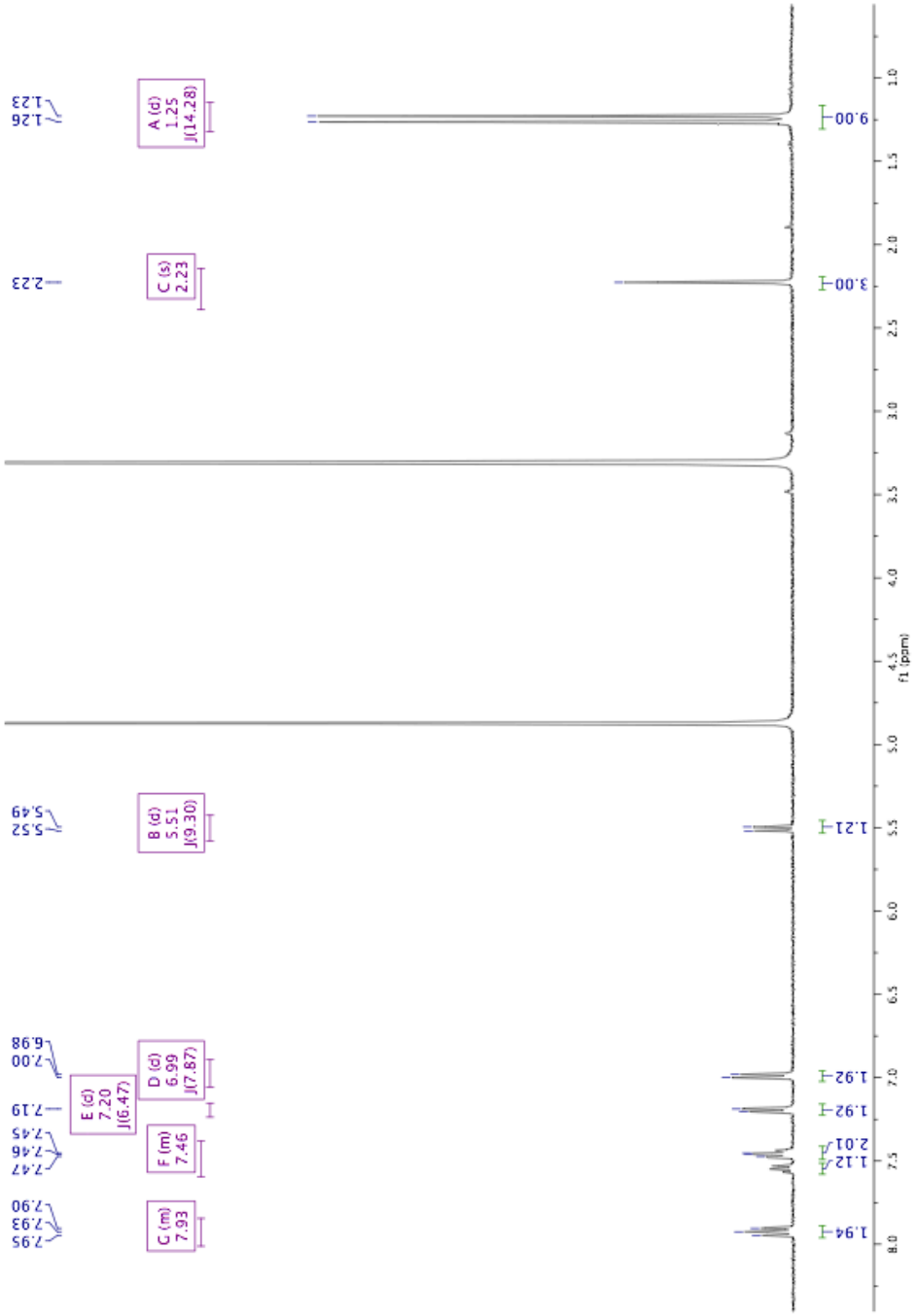


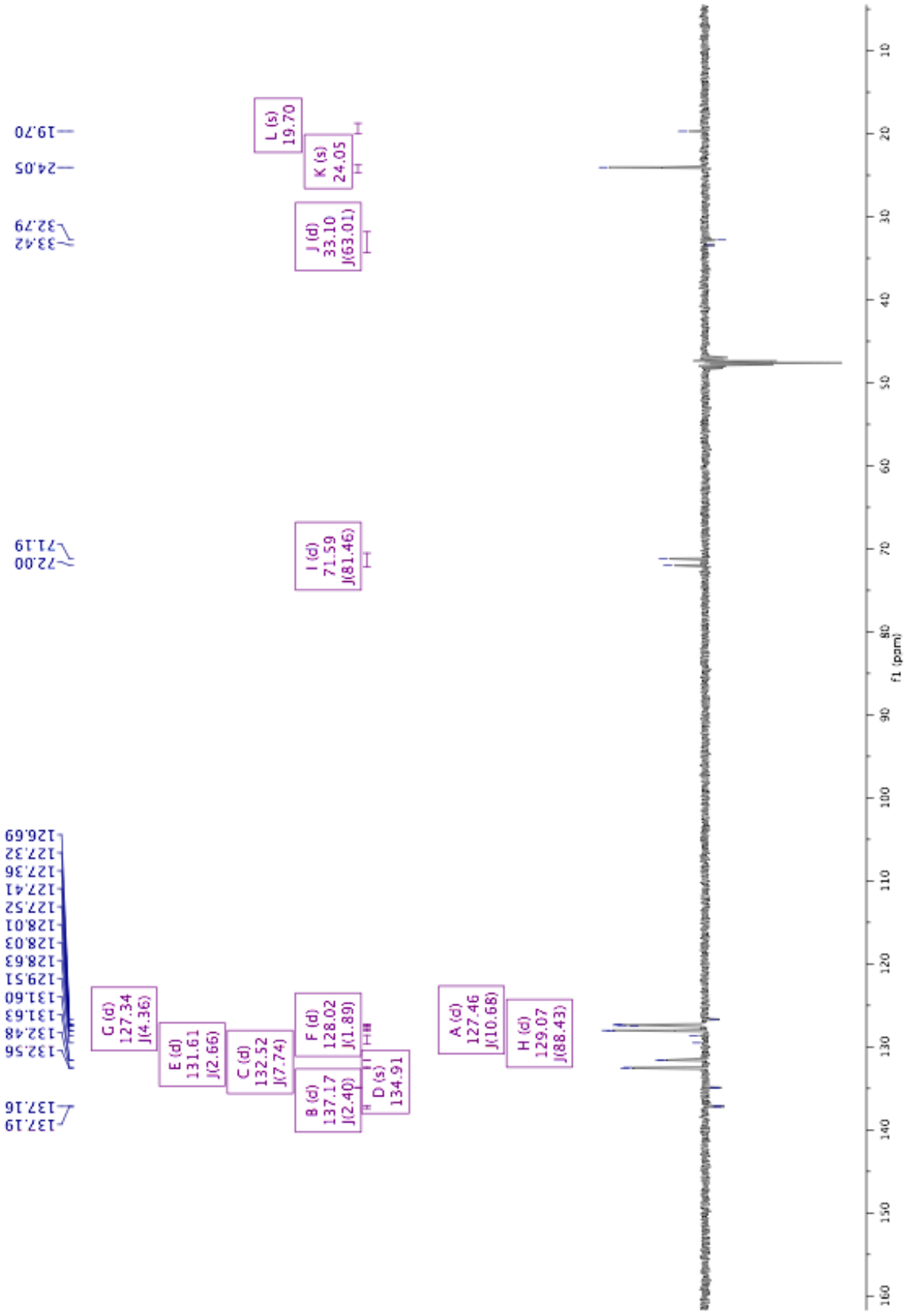

24.49
33.10
34.35
71.44
72.99
127.32
127.36
127.68
127.88
127.94
128.03
128.36
130.03
131.44
131.50
131.54
131.69
137.73
137.77
J (s)
24.49
A (d)
33.72
J(63.40)
B (d)
72.22
J(78.20)
E (d)
127.78
J(10.50)
H (d)
131.62
J(7.58)
F (d)
129.19
J(84.49)
C (d)
127.34
J(1.93)
I (d)
137.75
J(1.91)
G (d)
131.47
J(2.80)
D (d)
127.98
J(4.66)
f1 (ppm)

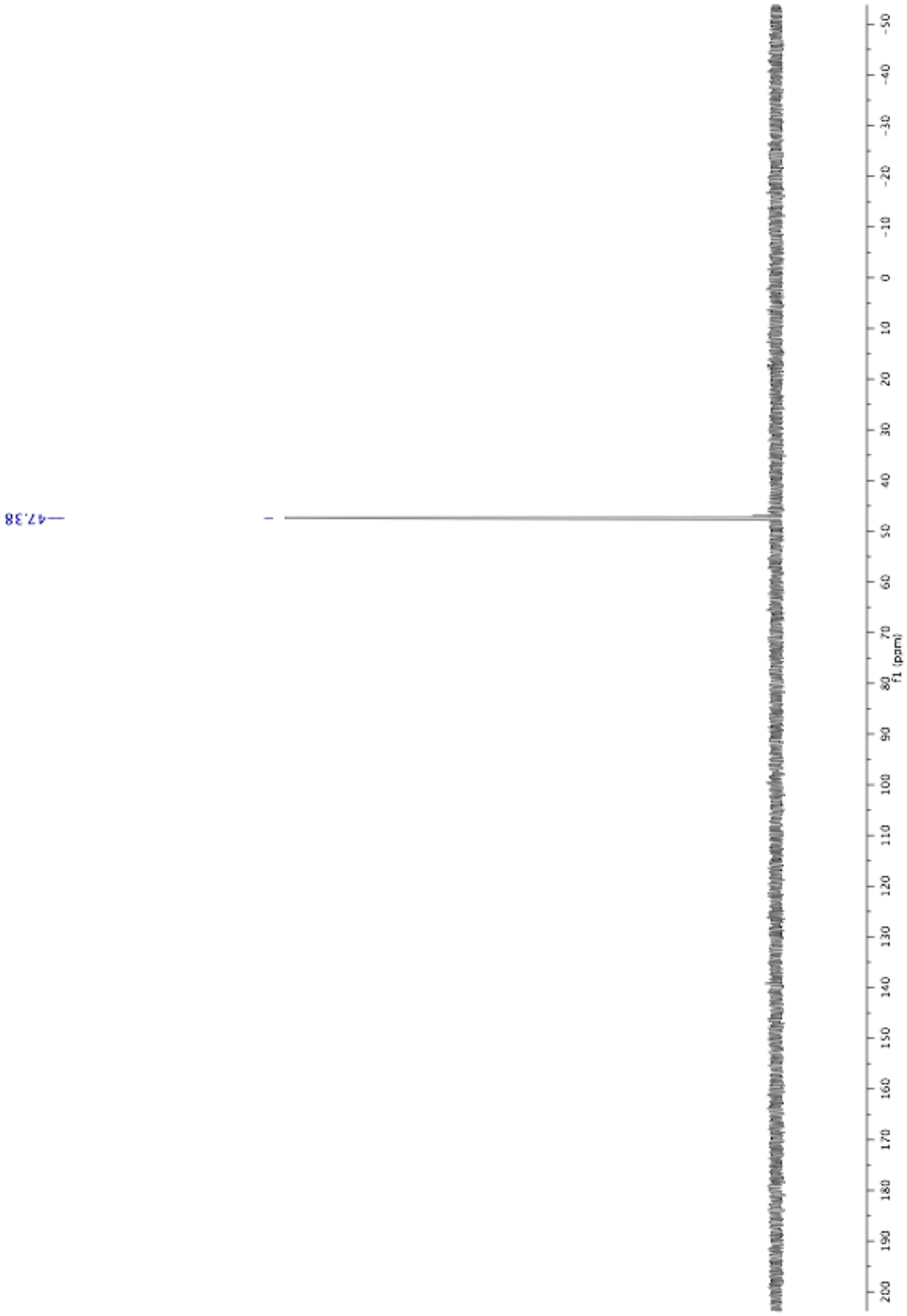

48.82
f1 (ppm)

(*R*)-*tert*-butyl((*S*)-hydroxy(p-tolyl)methyl)(phenyl)phosphine oxide

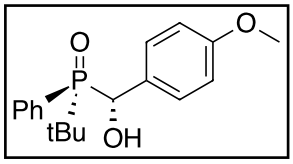


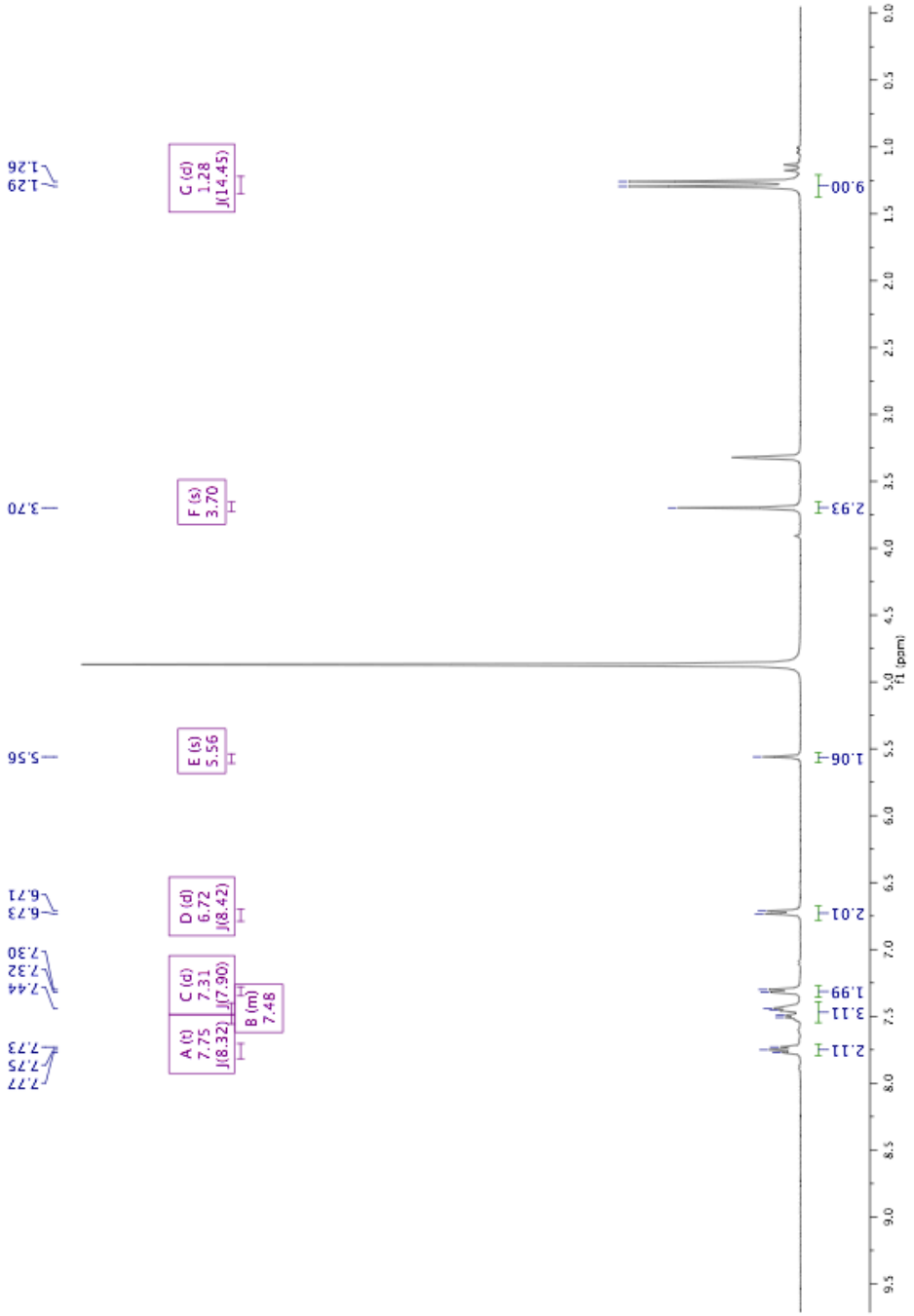


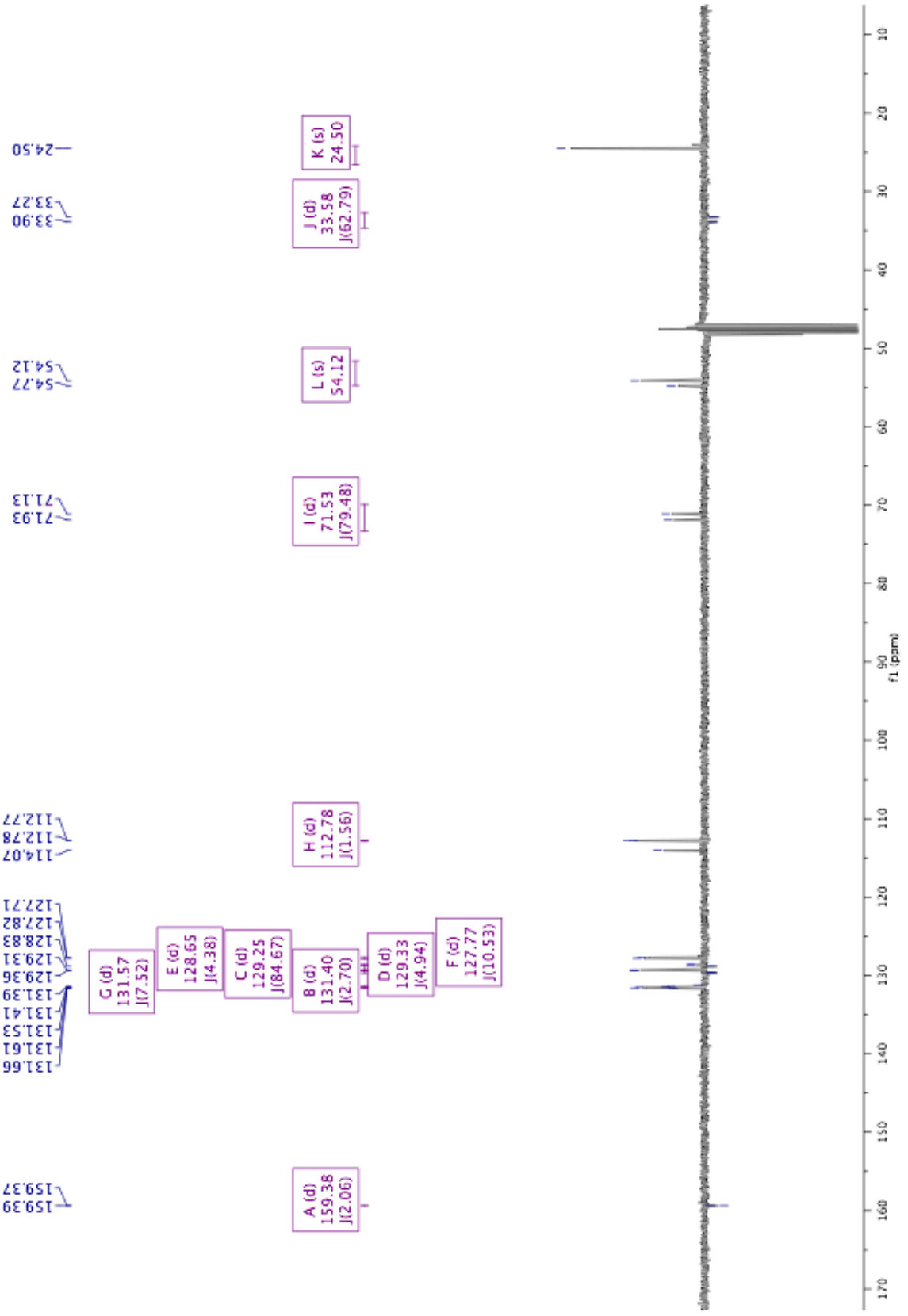


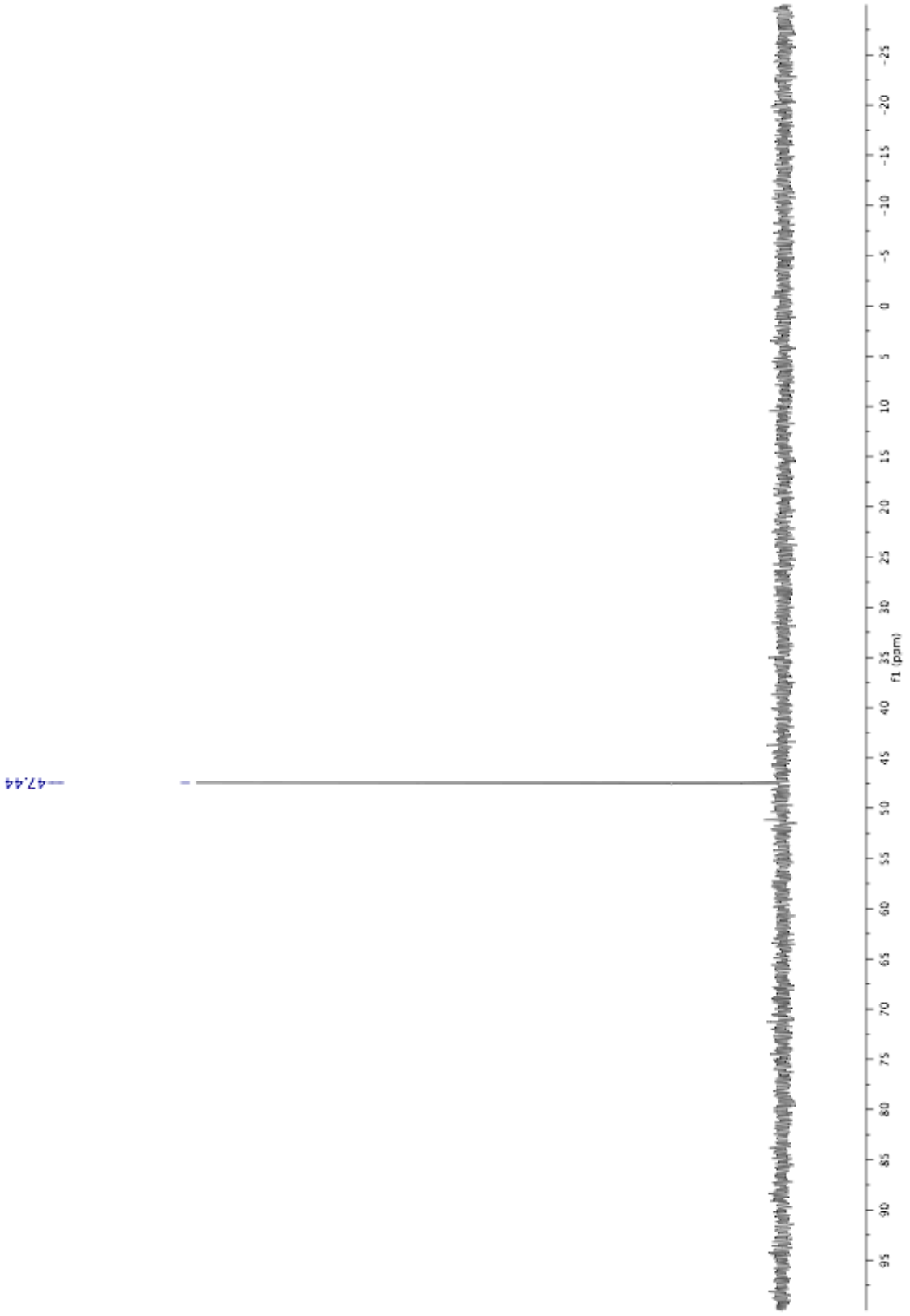

47.38
f1 (ppm)

(*R*)-*tert*-butyl((*R*)-hydroxy(4-methoxyphenyl)methyl)(phenyl)phosphine oxide

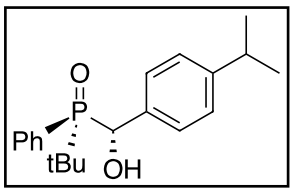


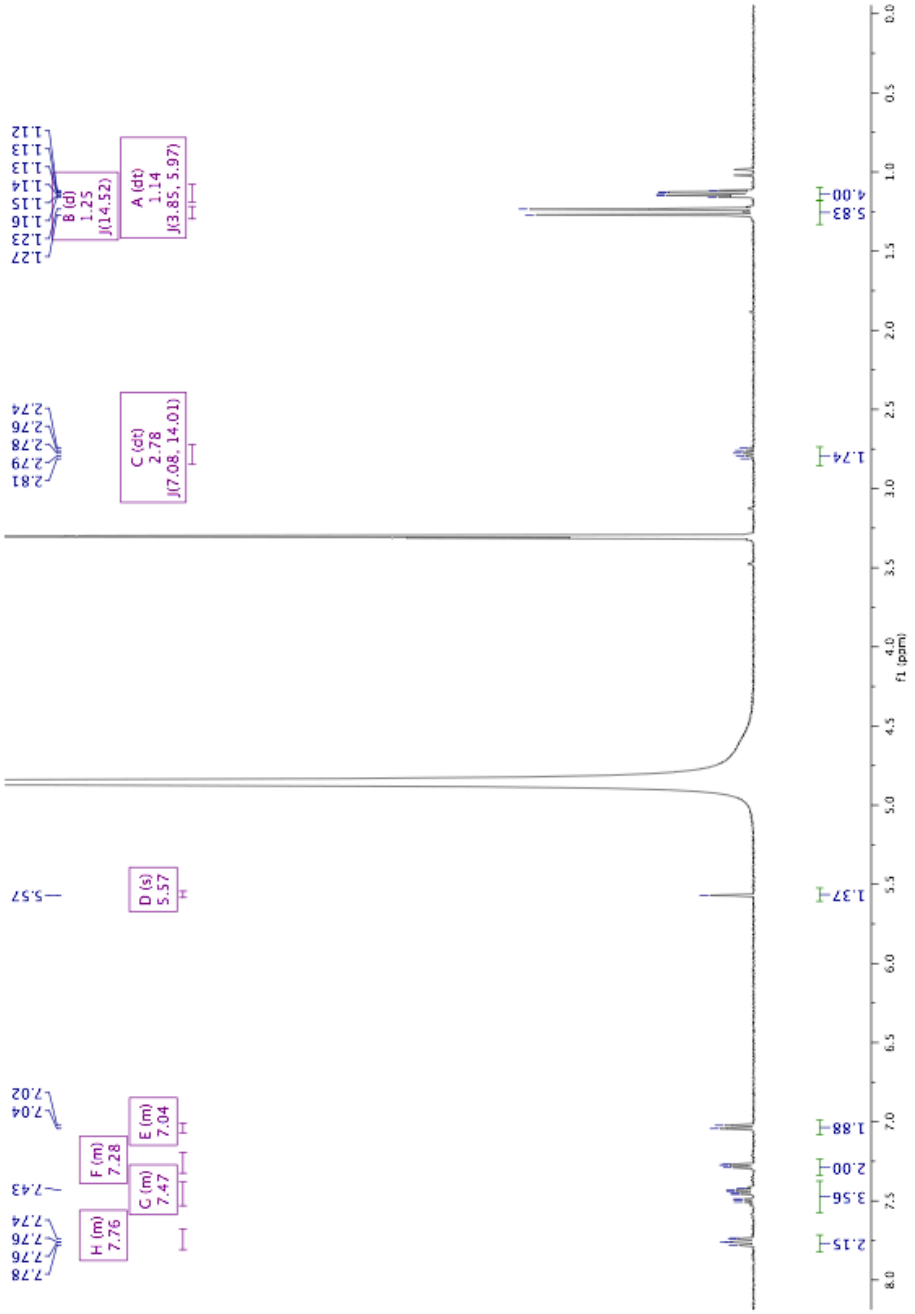


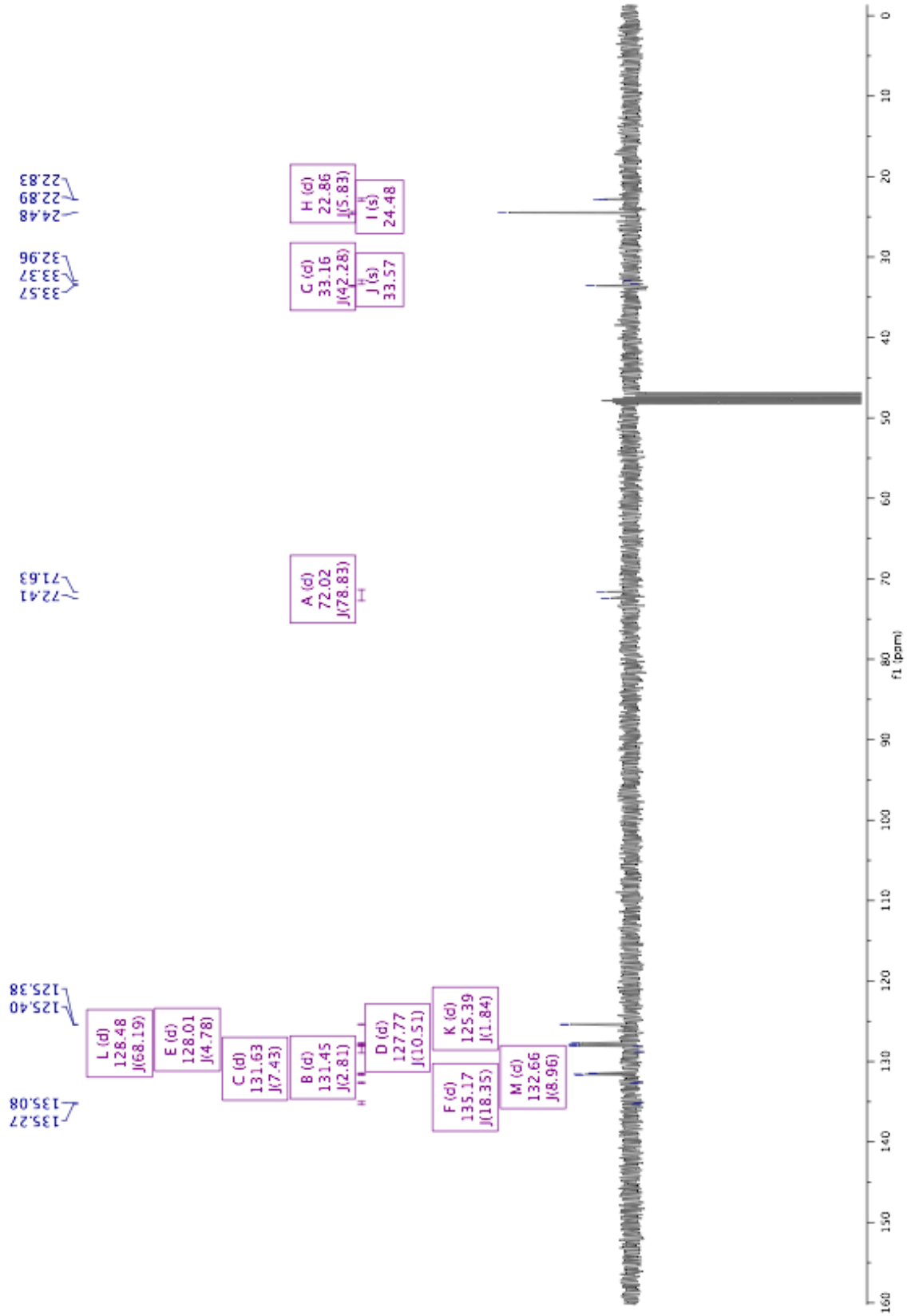


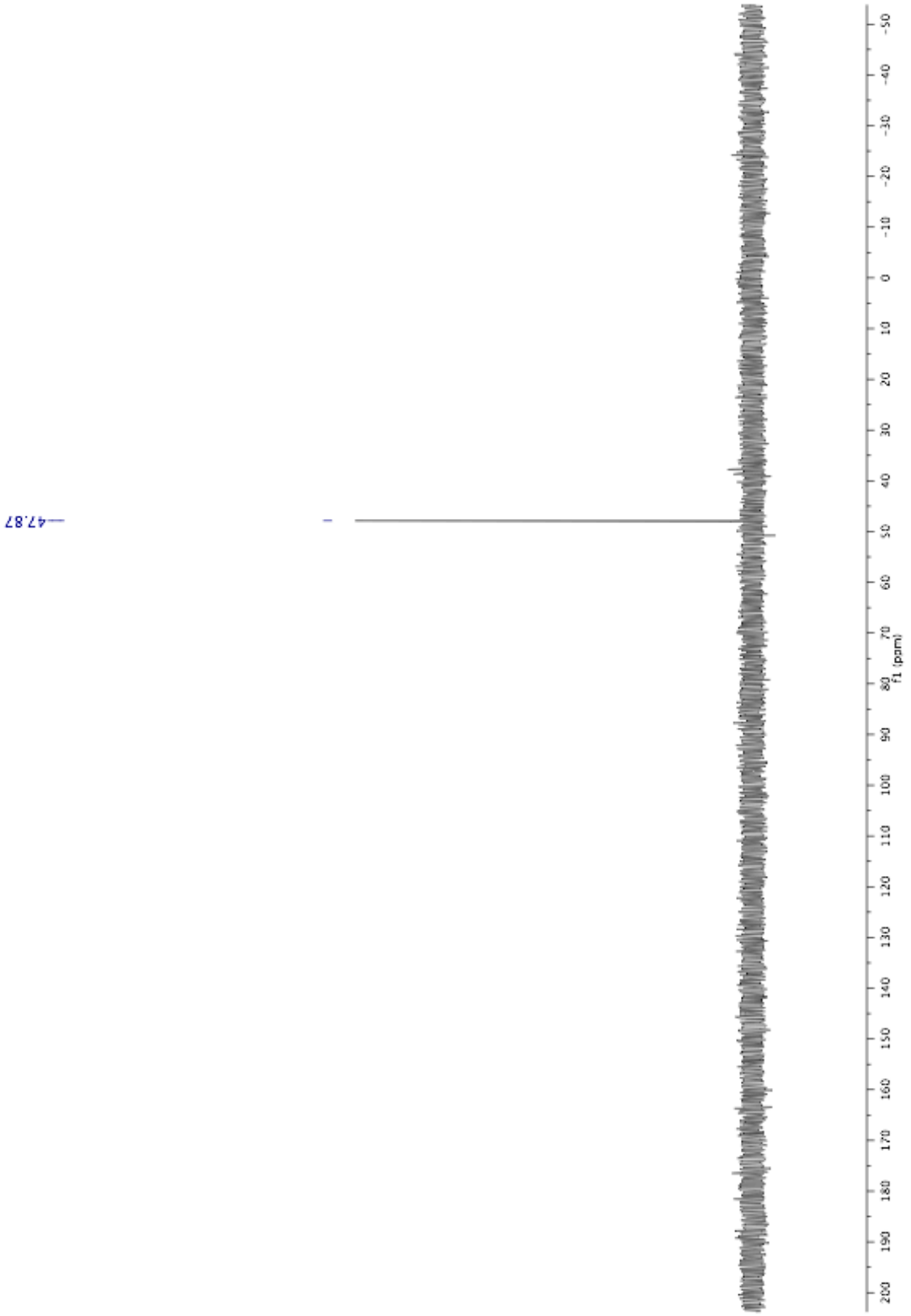


(*R*)-*tert*-butyl((*R*)-hydroxy(4-isopropylphenyl)methyl)(phenyl)phosphine oxide

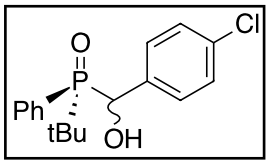


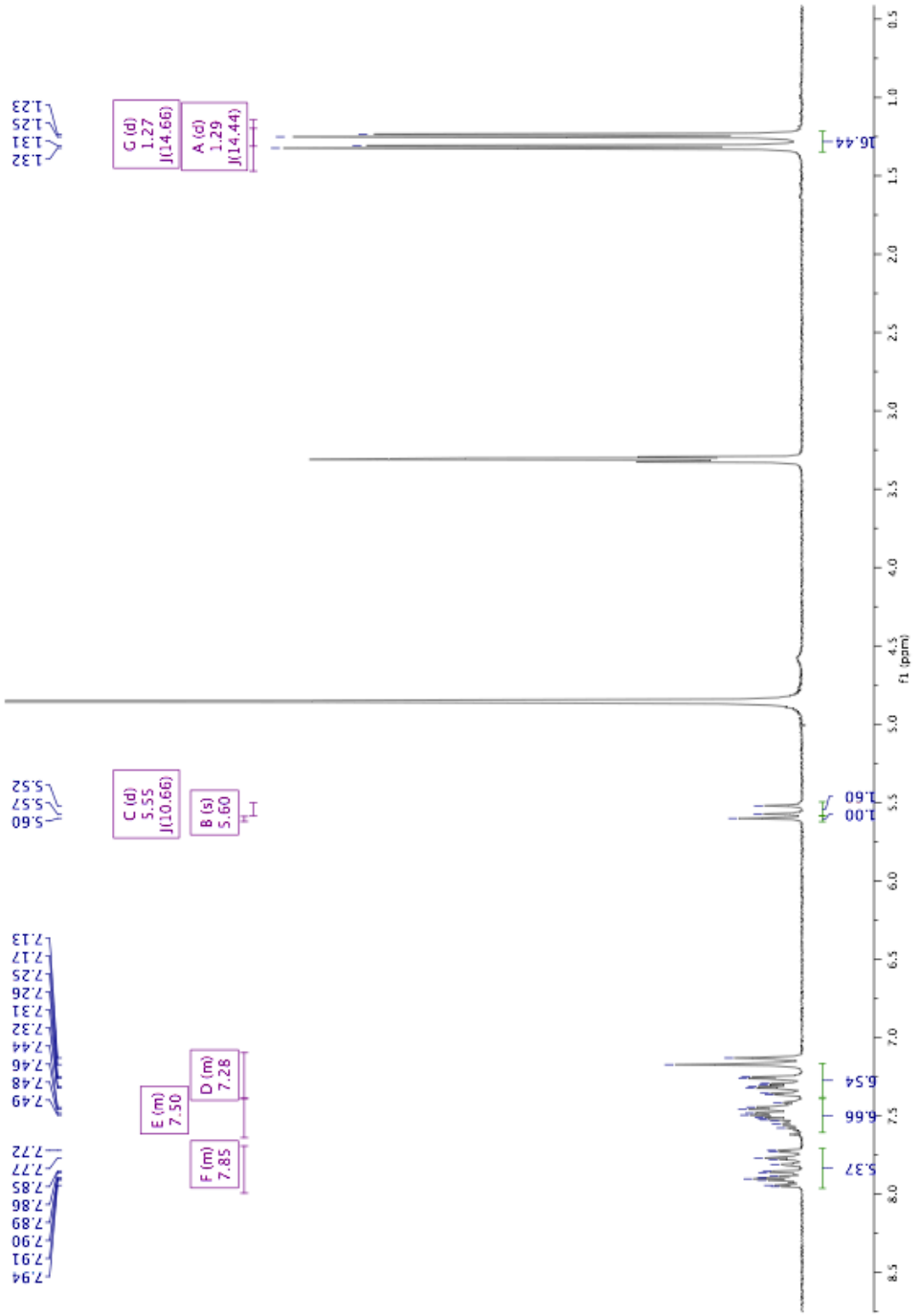


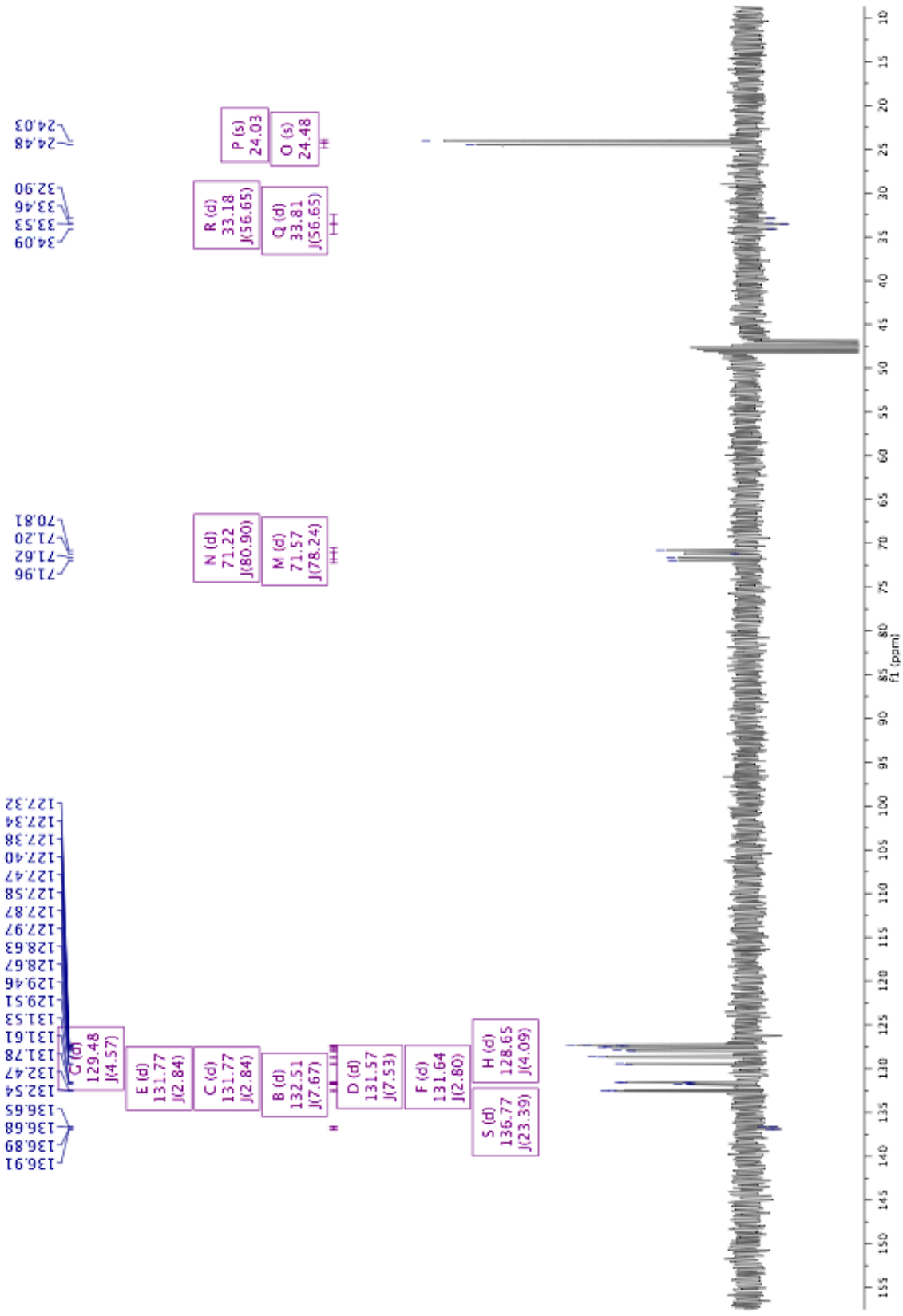

135.27
135.08
125.40
125.38
72.41
71.63
33.57
33.37
32.96
24.48
22.89
22.83
L (d)
128.48
J(68.19)
E (d)
128.01
J(4.78)
C (d)
131.63
J(7.43)
B (d)
131.45
J(2.81)
D (d)
127.77
J(10.51)
K (d)
125.39
J(1.84)
F (d)
135.17
J(18.35)
M (d)
132.66
J(8.96)
A (d)
72.02
J(78.83)
G (d)
33.16
J(42.28)
J (s)
33.57
H (d)
22.86
J(5.83)
I (s)
24.48
f1 (ppm)

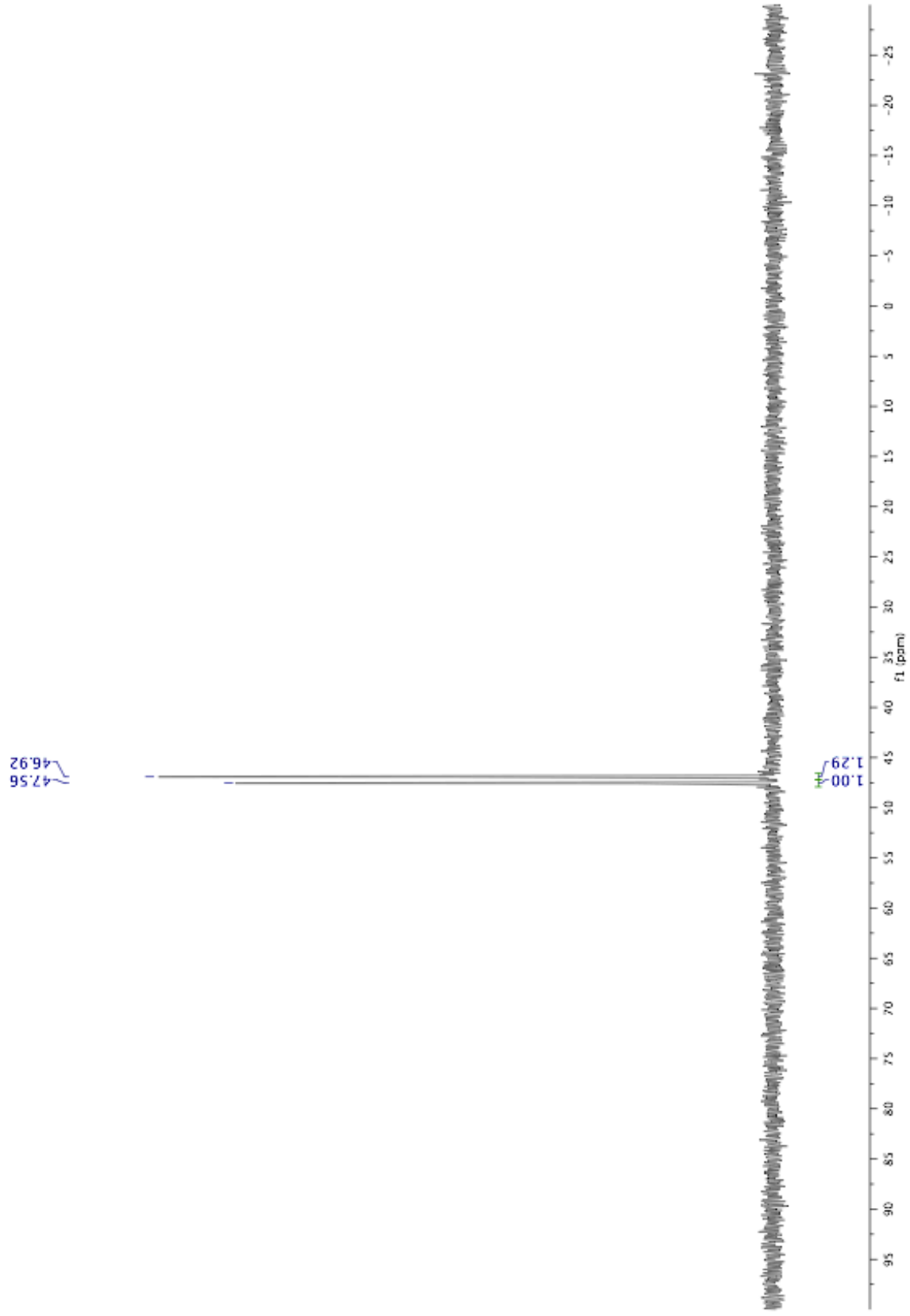

47.87
f1 (ppm)

(*R*)-*tert*-butyl((*RS*)-(4-chlorophenyl)(hydroxy)methyl)(phenyl)phosphine oxide

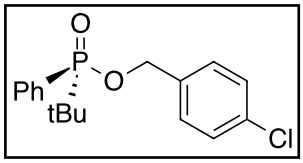


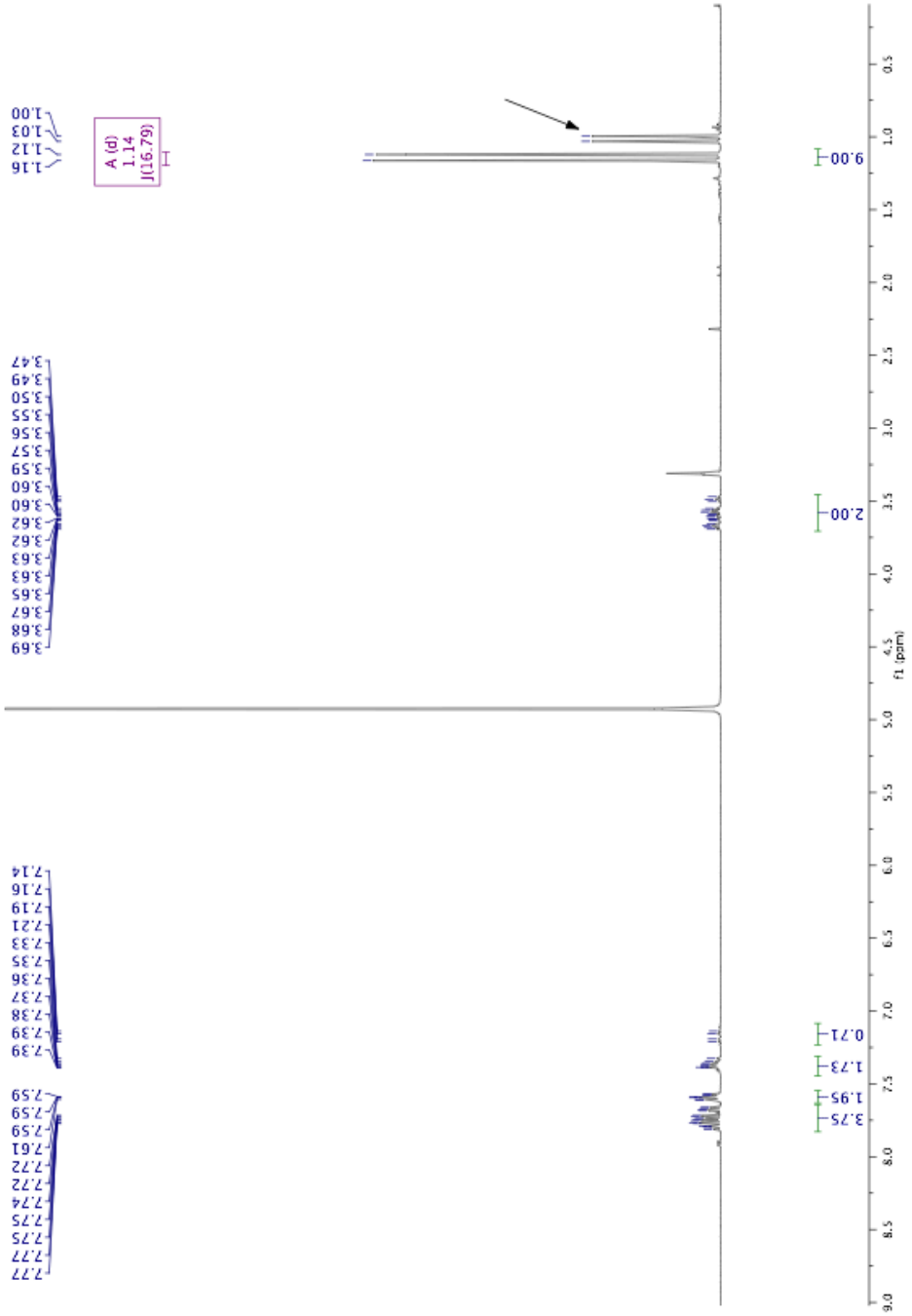


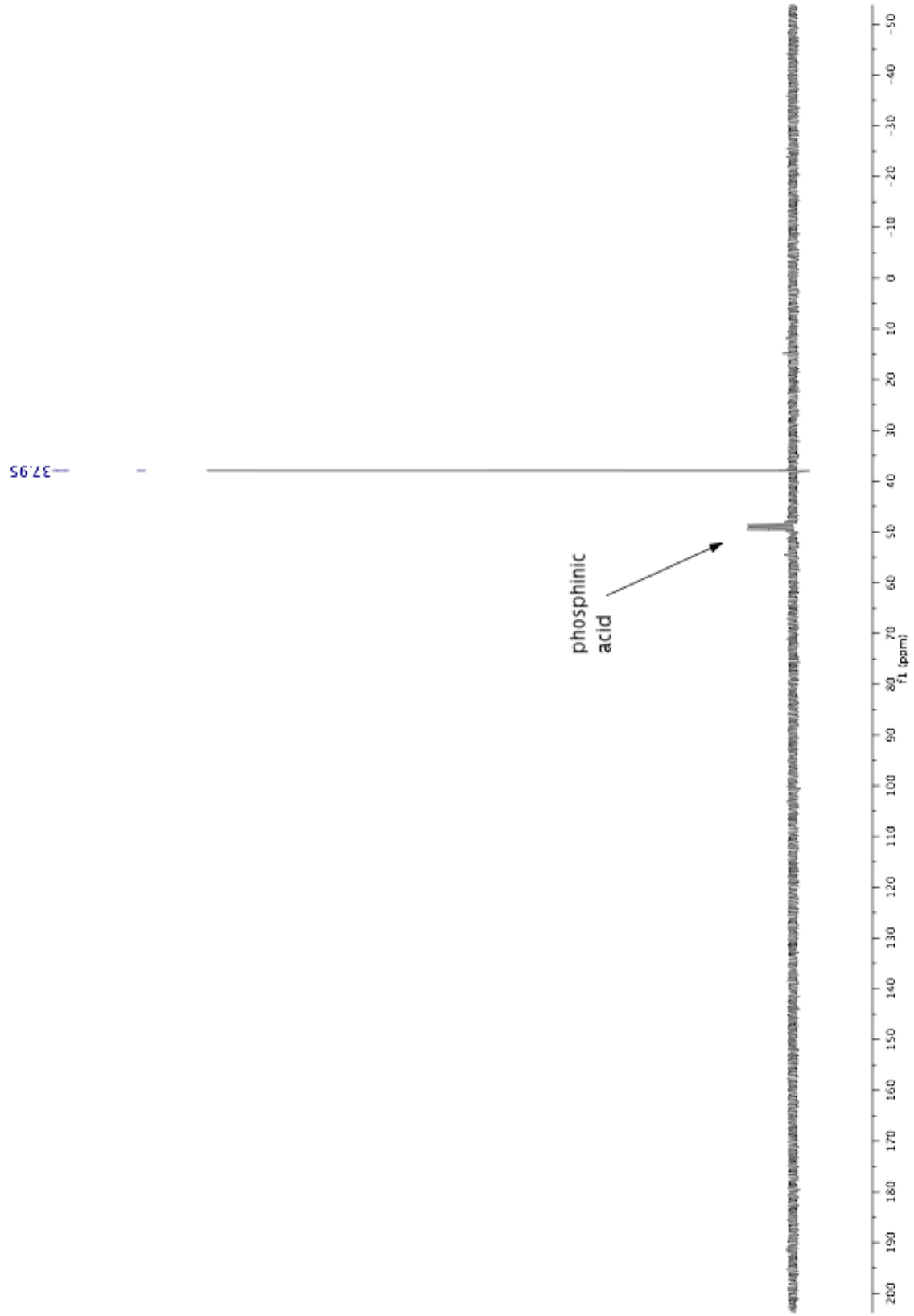

24.48
24.03
32.90
33.46
33.53
34.09
70.81
71.20
71.62
71.96
127.32
127.34
127.38
127.40
127.47
127.58
127.87
127.97
128.63
128.67
129.46
129.51
131.53
131.61
131.78
132.47
132.54
136.65
136.68
136.89
136.91
G (d) 129.48 J(4.57)
E (d) 131.77 J(2.84)
C (d) 131.77 J(2.84)
B (d) 132.51 J(7.67)
D (d) 131.57 J(7.53)
F (d) 131.64 J(2.80)
H (d) 128.65 J(4.09)
S (d) 136.77 J(23.39)
R (d) 33.18 J(56.65)
Q (d) 33.81 J(56.65)
P (s) 24.03
O (s) 24.48
N (d) 71.22 J(80.90)
M (d) 71.57 J(78.24)
f1 (ppm)


47.56
46.92
1.00
1.29
f1 (ppm)

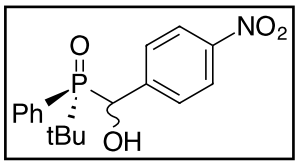
(S)-4-chlorobenzyl tert-butyl(phenyl)phosphinate

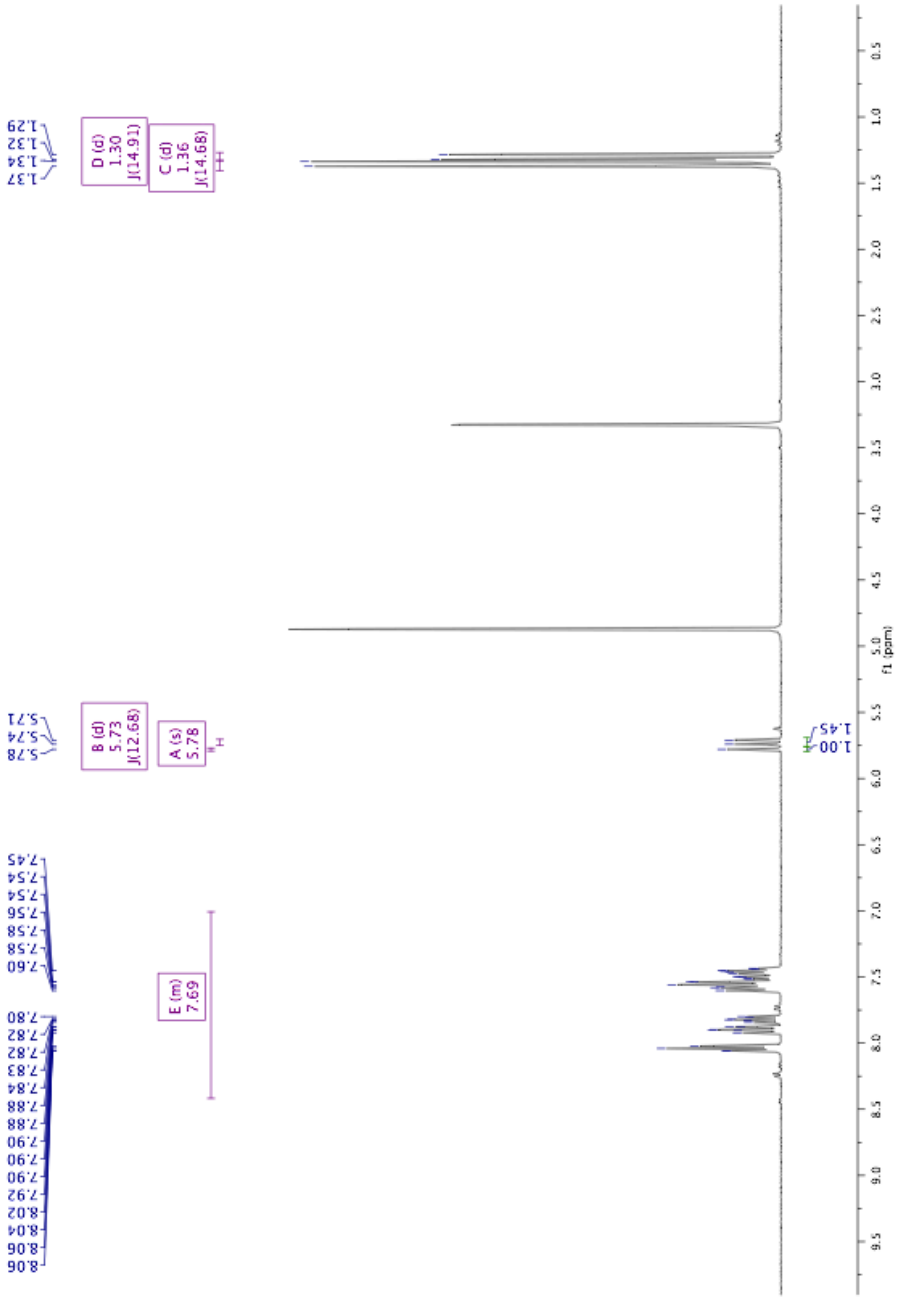


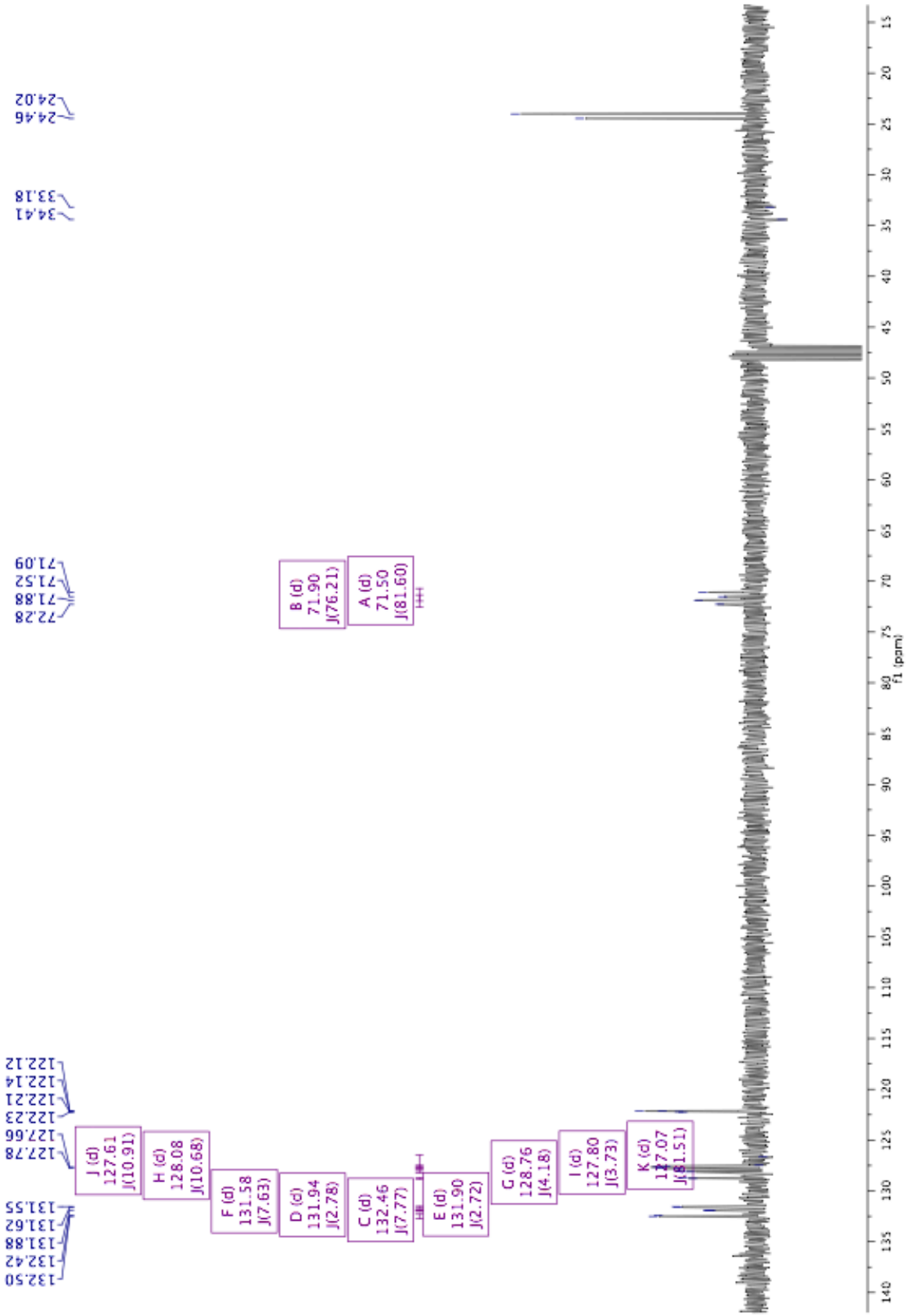


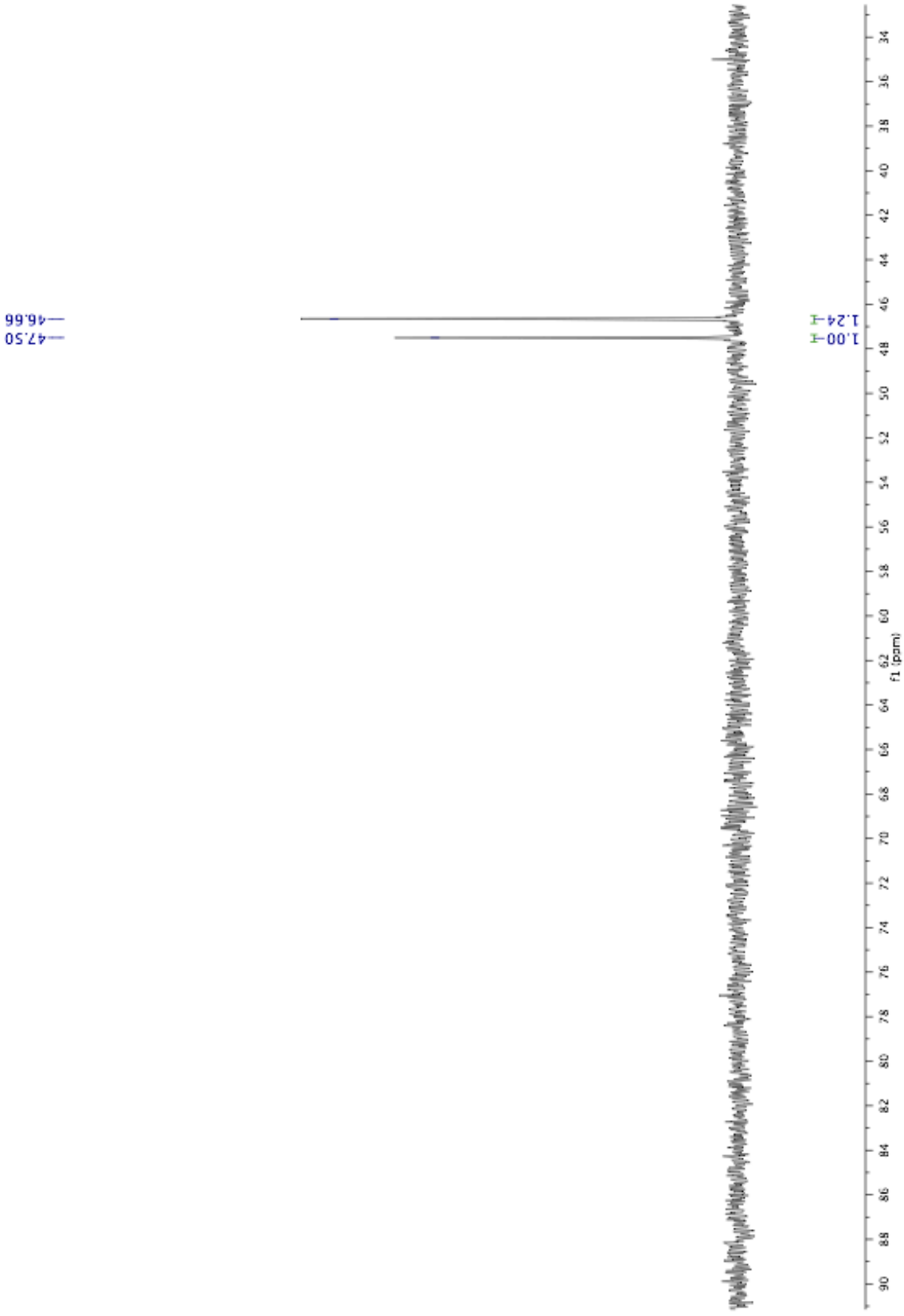

37.95
phosphinic
acid
f1 (ppm)

(*R*)-*tert*-butyl((*RS*)-hydroxy(4-nitrophenyl)methyl)(phenyl)phosphine oxide

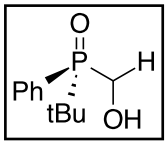


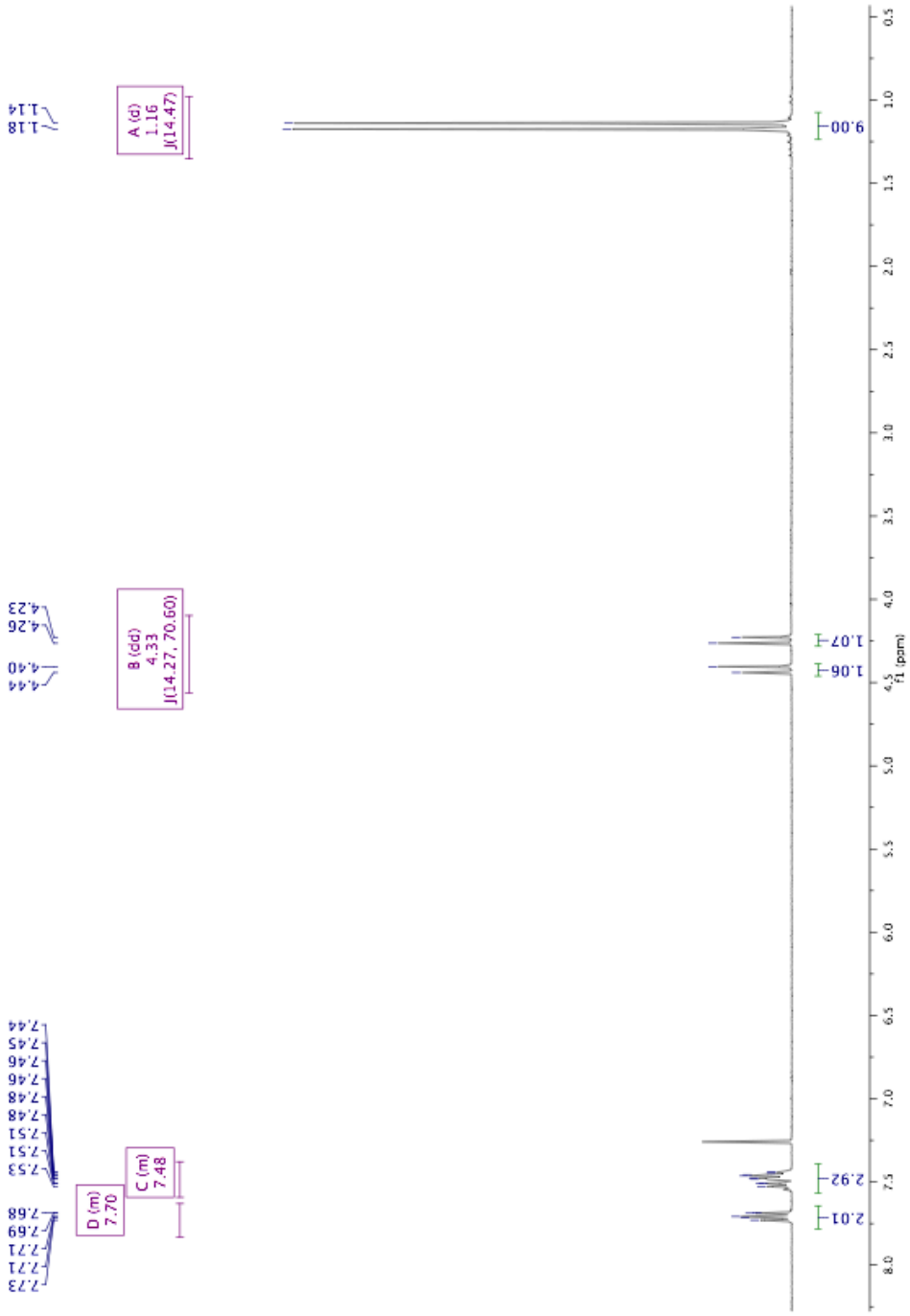


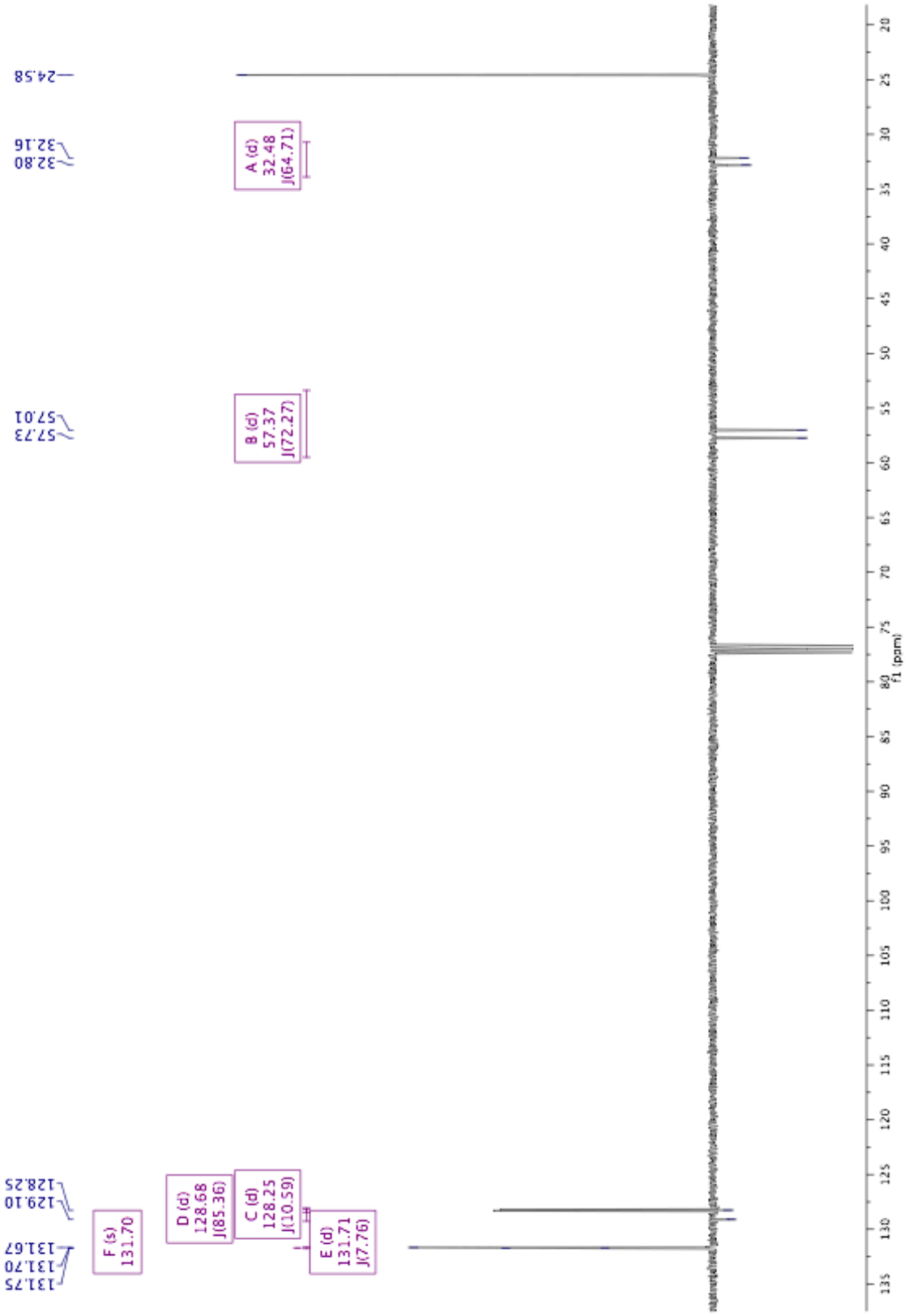

24.02
24.46
33.18
34.41
71.09
71.52
71.88
72.28
B (d)
71.90
J(76.21)
A (d)
71.50
J(81.60)
122.12
122.14
122.21
122.23
127.66
127.78
J (d)
127.61
J(10.91)
H (d)
128.08
J(10.68)
F (d)
131.58
J(7.63)
D (d)
131.94
J(2.78)
C (d)
132.46
J(7.77)
E (d)
131.90
J(2.72)
G (d)
128.76
J(4.18)
I (d)
127.80
J(3.73)
K (d)
127.07
J(81.51)
131.55
131.62
131.88
132.42
132.50
f1 (ppm)

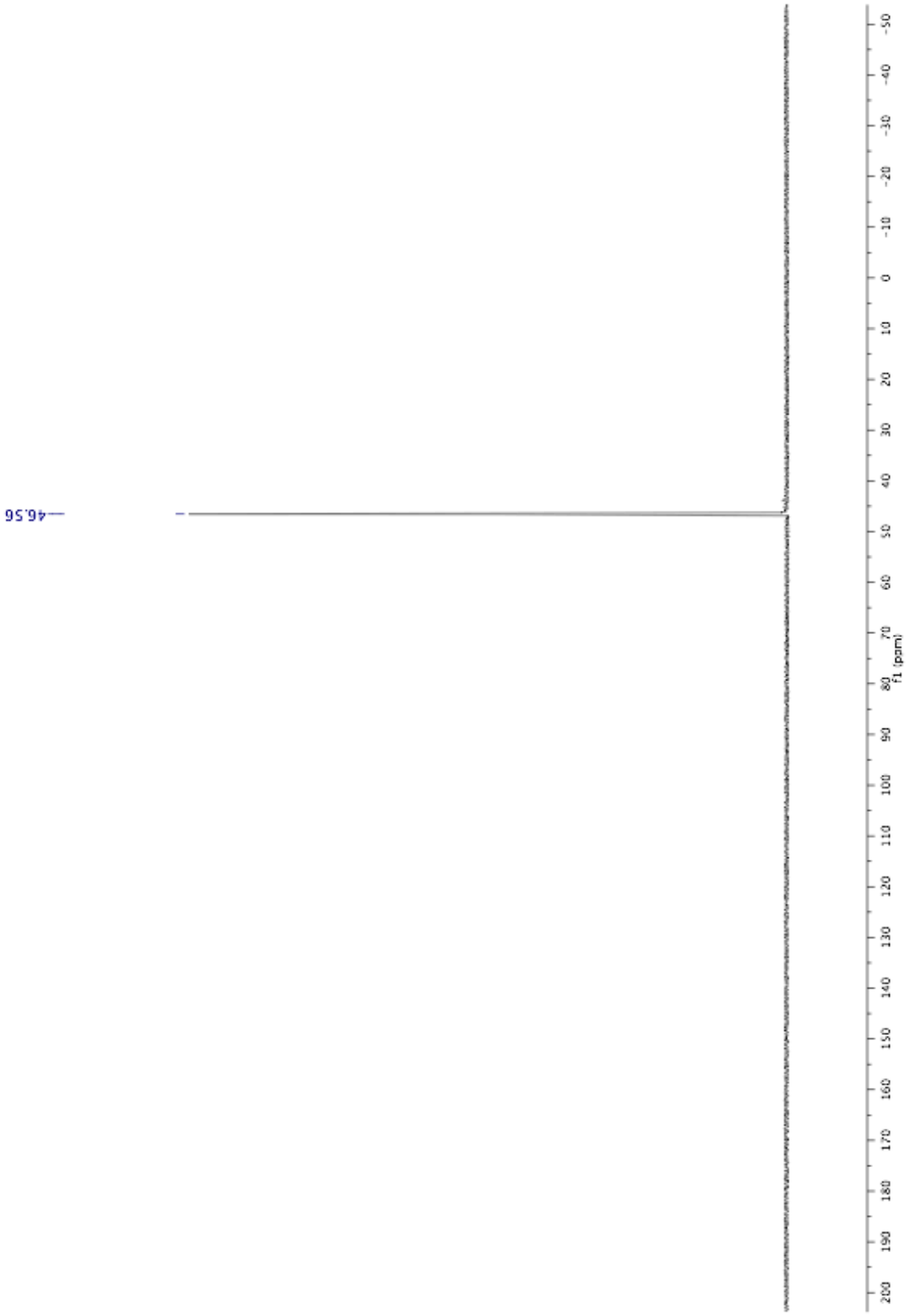

46.66
47.50
1.24
1.00
f1 (ppm)

(*R*)-*tert*-butyl(hydroxymethyl)(phenyl)phosphine oxide

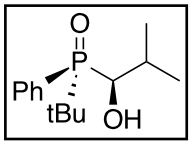


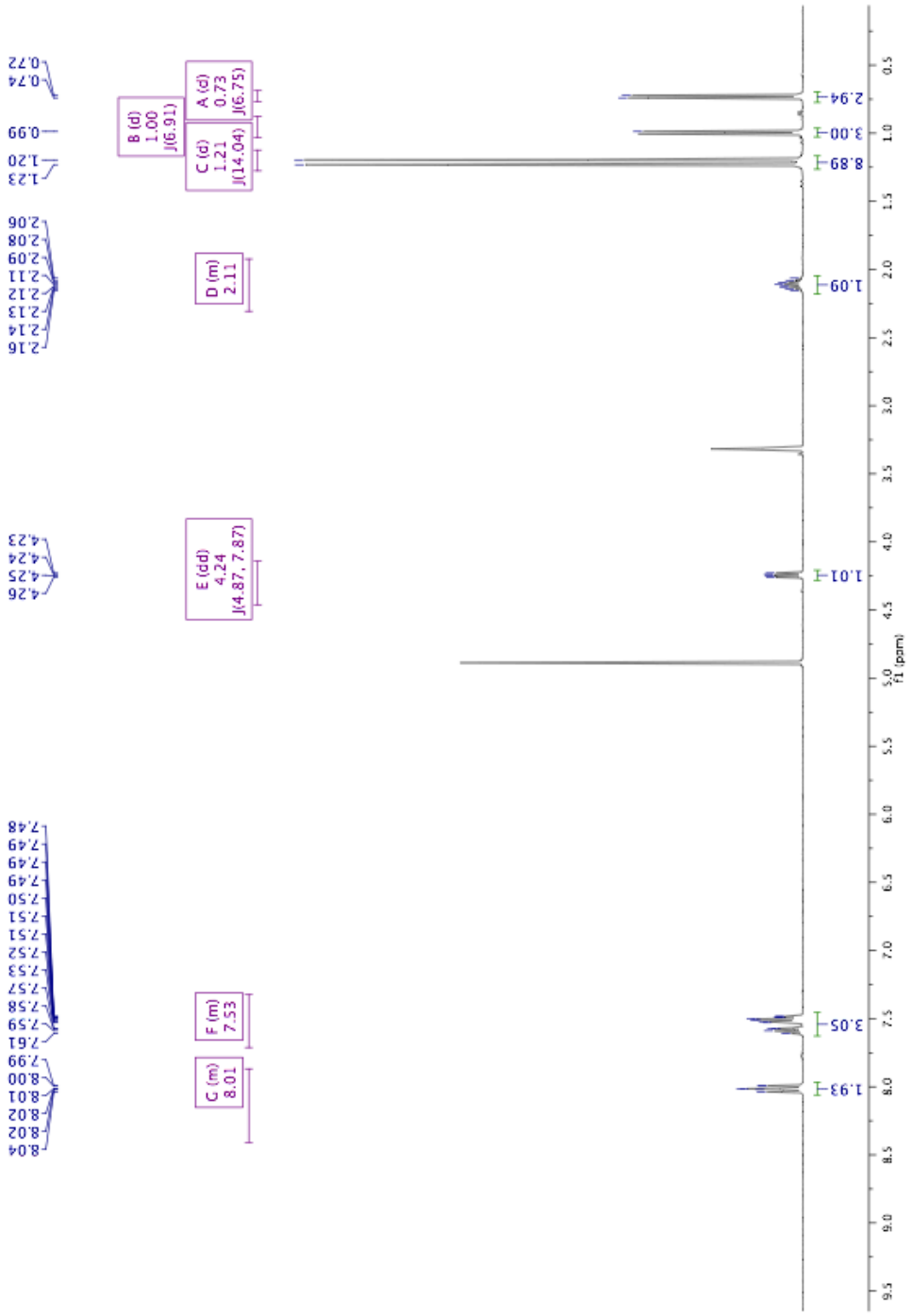


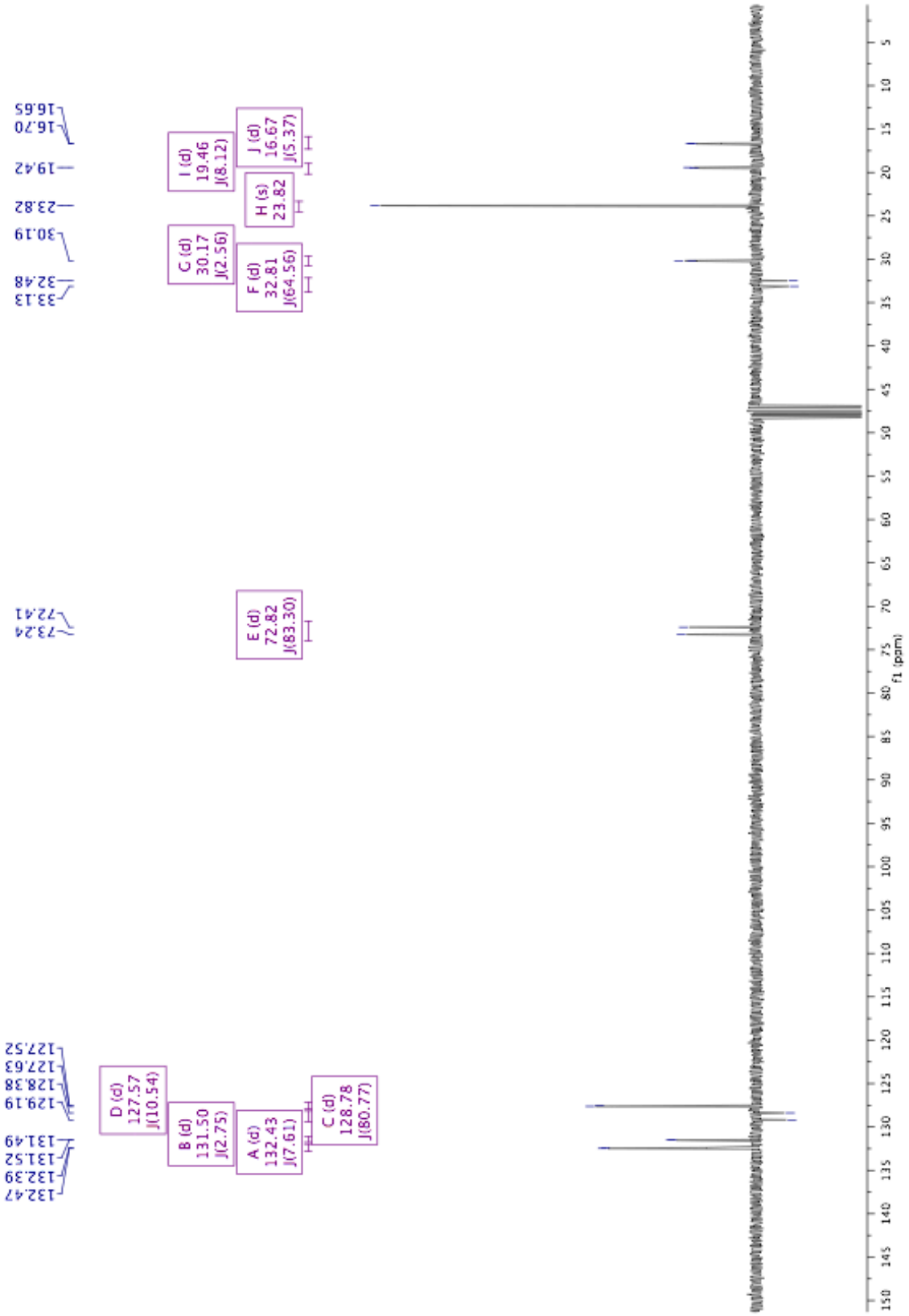

24.58
32.80
32.16
A (d)
32.48
J(64.71)
57.73
57.01
B (d)
57.37
J(72.27)
131.75
131.70
131.67
129.10
128.25
F (s)
131.70
D (d)
128.68
J(85.36)
C (d)
128.25
J(10.59)
E (d)
131.71
J(7.76)
f1 (ppm)

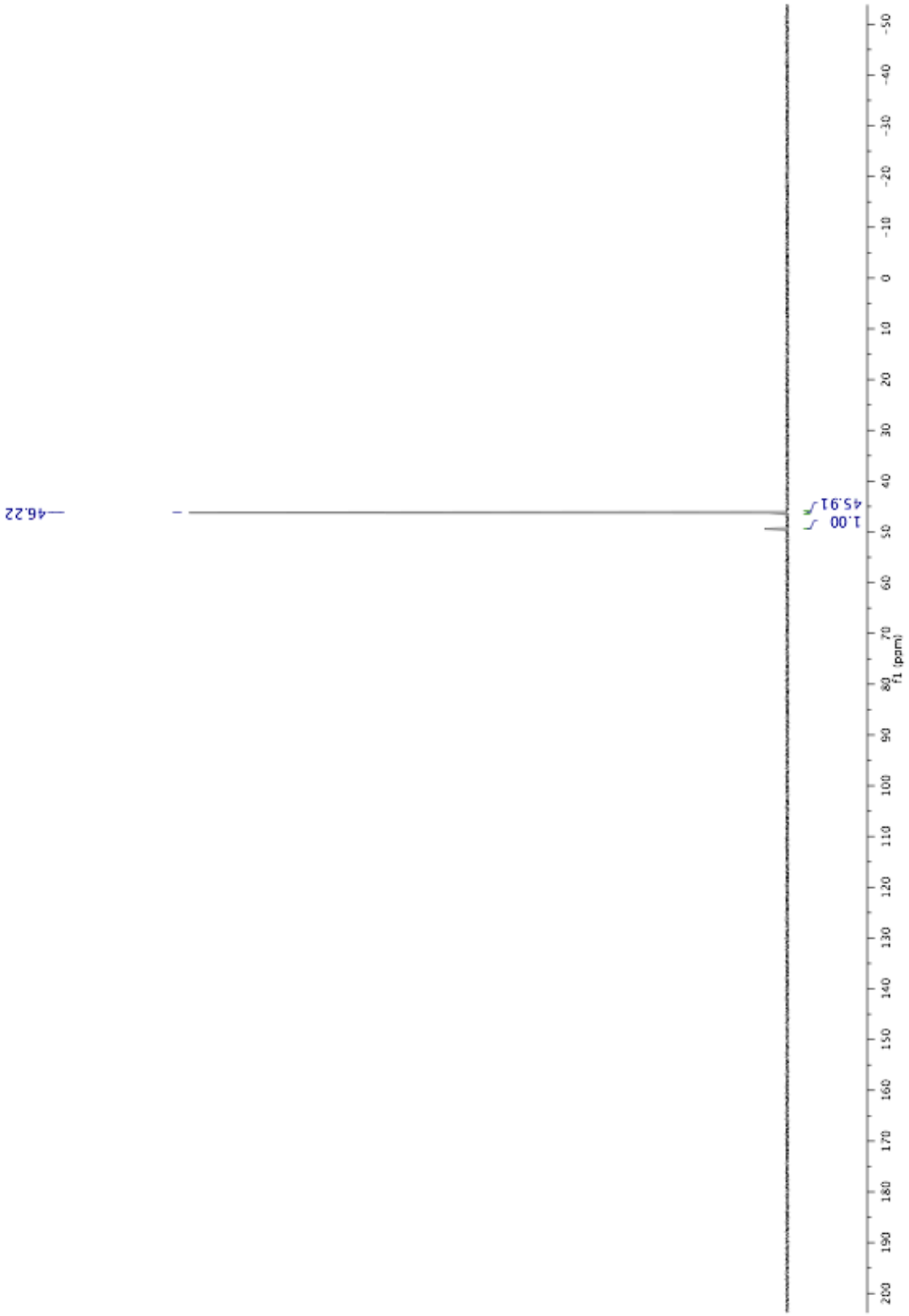

46.56
f1 (ppm)

(*R*)-*tert*-butyl((*S*)-1-hydroxy-2-methylpropyl)(phenyl)phosphine oxide

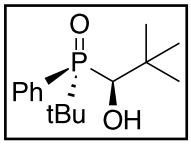


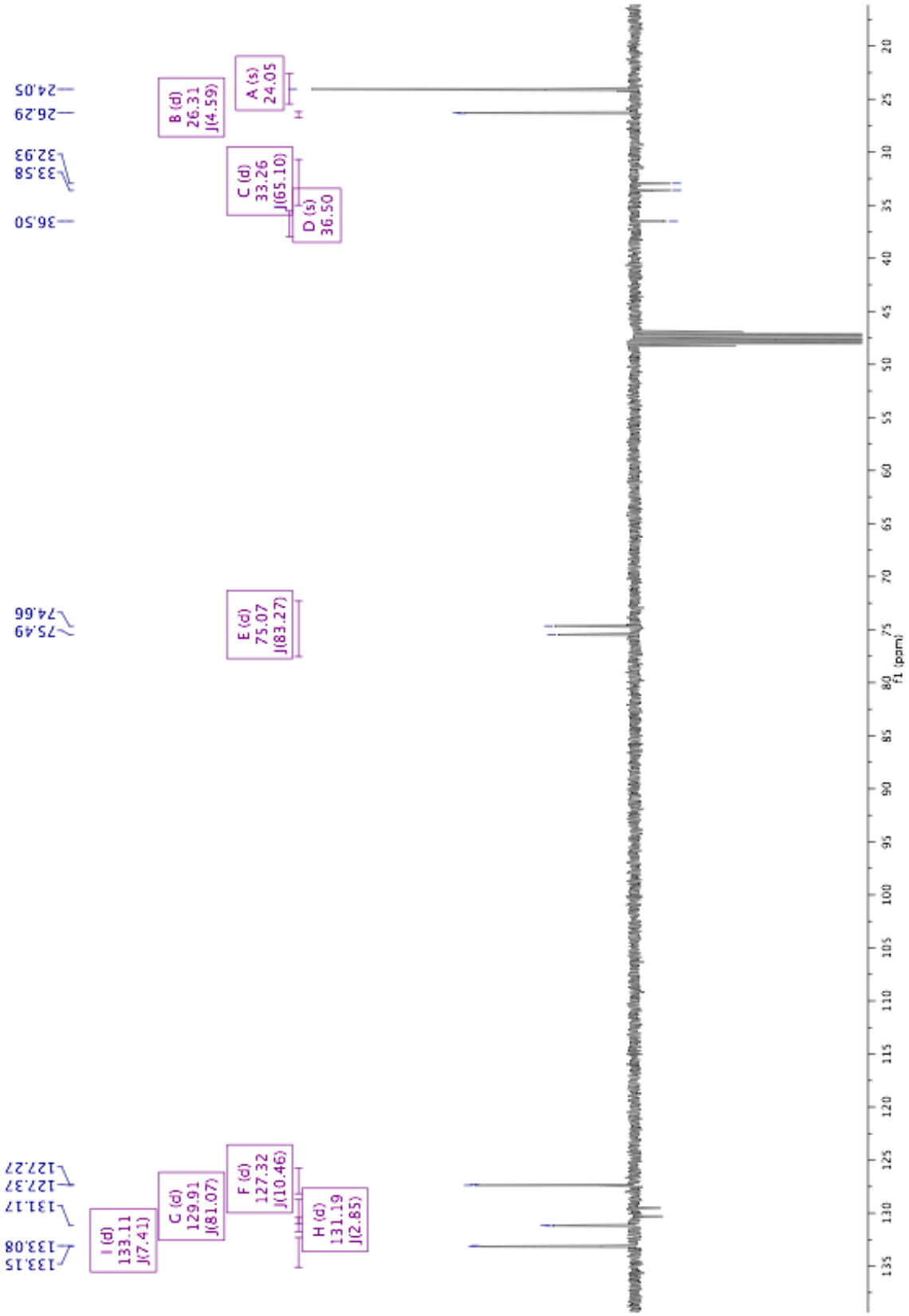



16.65
16.70
19.42
23.82
30.19
32.48
33.13
72.41
73.24
127.52
127.63
128.38
129.19
131.49
131.52
132.39
132.47
I (d) 19.46 J(8.12)
J (d) 16.67 J(5.37)
H (s) 23.82
C (d) 30.17 J(2.56)
F (d) 32.81 J(64.56)
E (d) 72.82 J(83.30)
D (d) 127.57 J(10.54)
B (d) 131.50 J(2.75)
A (d) 132.43 J(7.61)
C (d) 128.78 J(80.77)
f1 (ppm)


46.22
45.91
1.00
f1 (ppm)

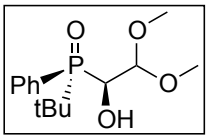
(*R*)-*tert*-butyl((*S*)-1-hydroxy-2,2-dimethylpropyl)(phenyl)phosphine oxide

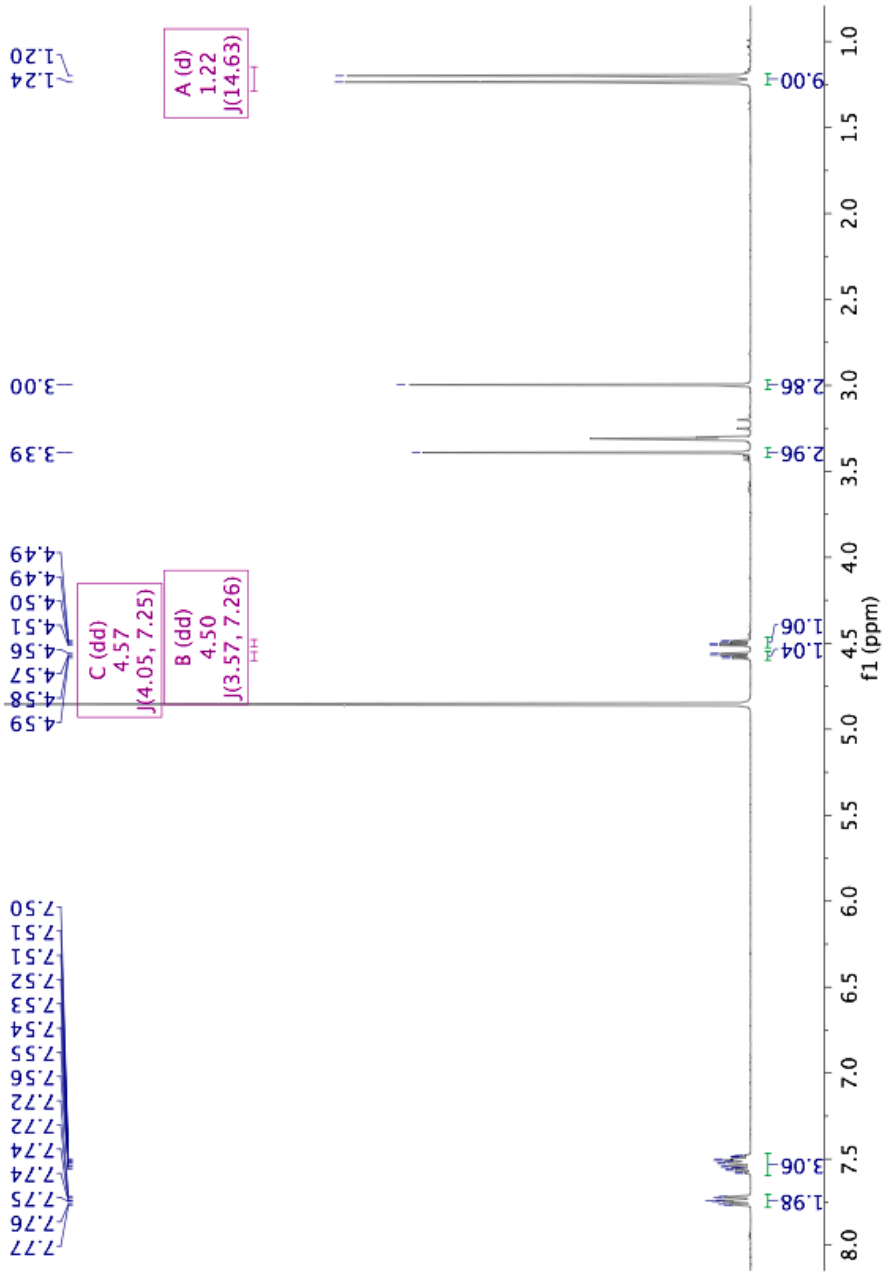


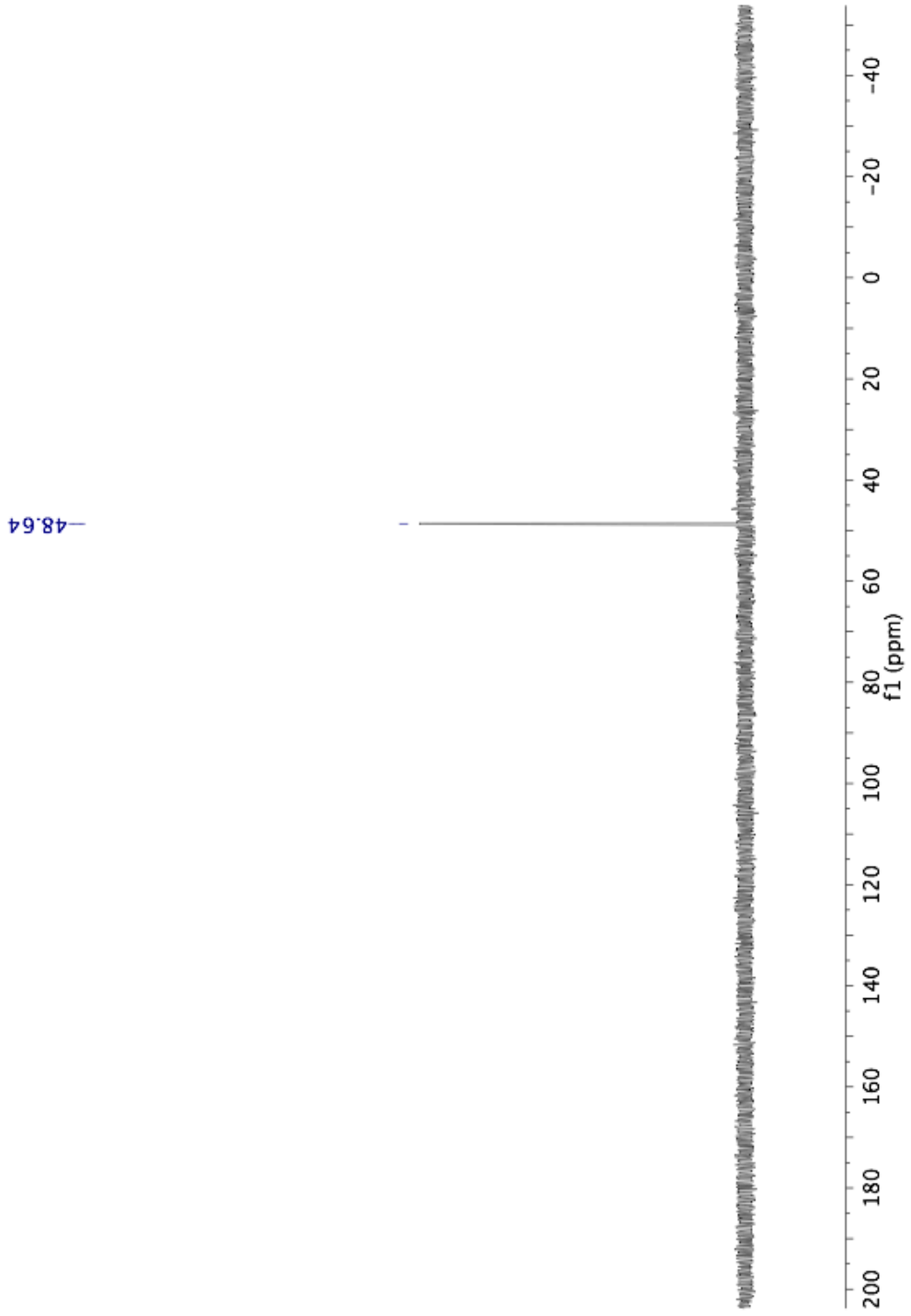

A (s)
24.05
B (d)
26.31
J(4.59)
C (d)
33.26
J(65.10)
D (s)
36.50
E (d)
75.07
J(83.27)
F (d)
127.32
J(10.46)
G (d)
129.91
J(81.07)
H (d)
131.19
J(2.85)
I (d)
133.11
J(7.41)
24.05
26.29
32.93
33.58
36.50
74.66
75.49
127.27
127.37
131.17
133.08
133.15
f1 (ppm)

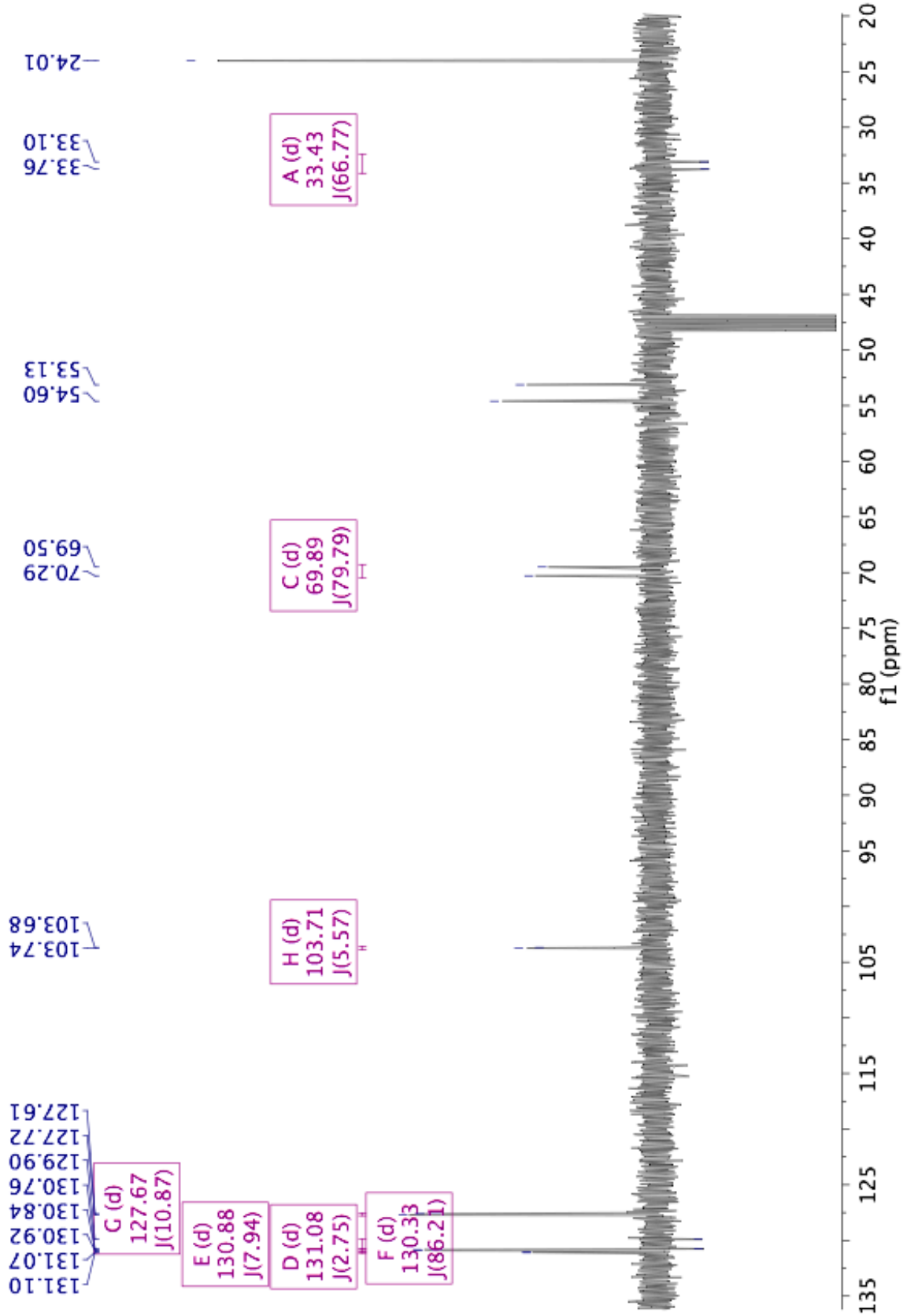

44.95
f1 (ppm)

(*R*)-tert-butyl((*S*)-1-hydroxy-2,2-dimethoxyethyl)(phenyl)phosphine oxide





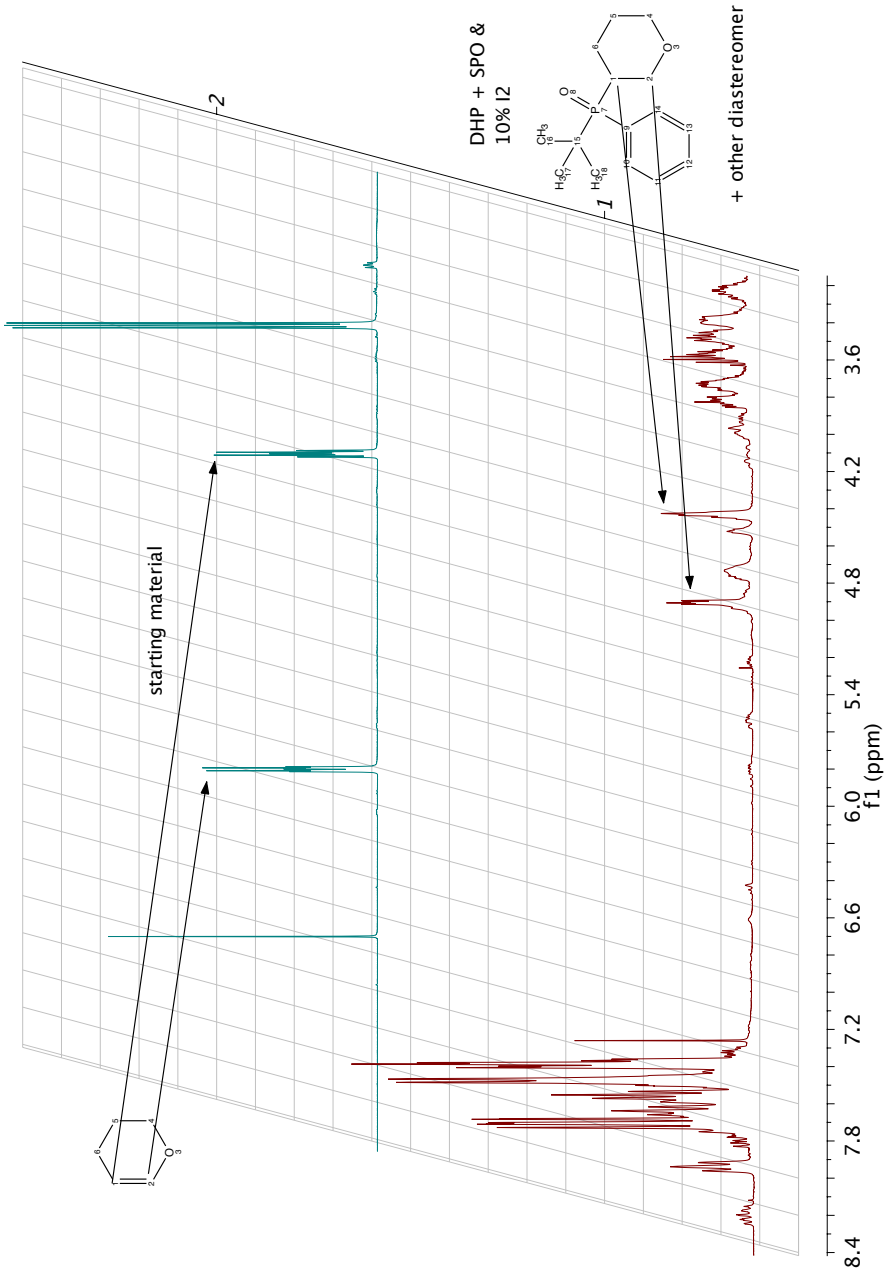

48.64
200
180
160
140
120
100
80
60
40
20
0
-20
-40
f1 (ppm)


24.01
33.10
33.76
53.13
54.60
69.50
70.29
103.68
103.74
127.61
127.72
129.90
130.76
130.84
130.92
131.07
131.10
A (d)
33.43
J(66.77)
C (d)
69.89
J(79.79)
H (d)
103.71
J(5.57)
F (d)
130.33
J(86.21)
D (d)
131.08
J(2.75)
E (d)
130.88
J(7.94)
G (d)
127.67
J(10.87)
f1 (ppm)

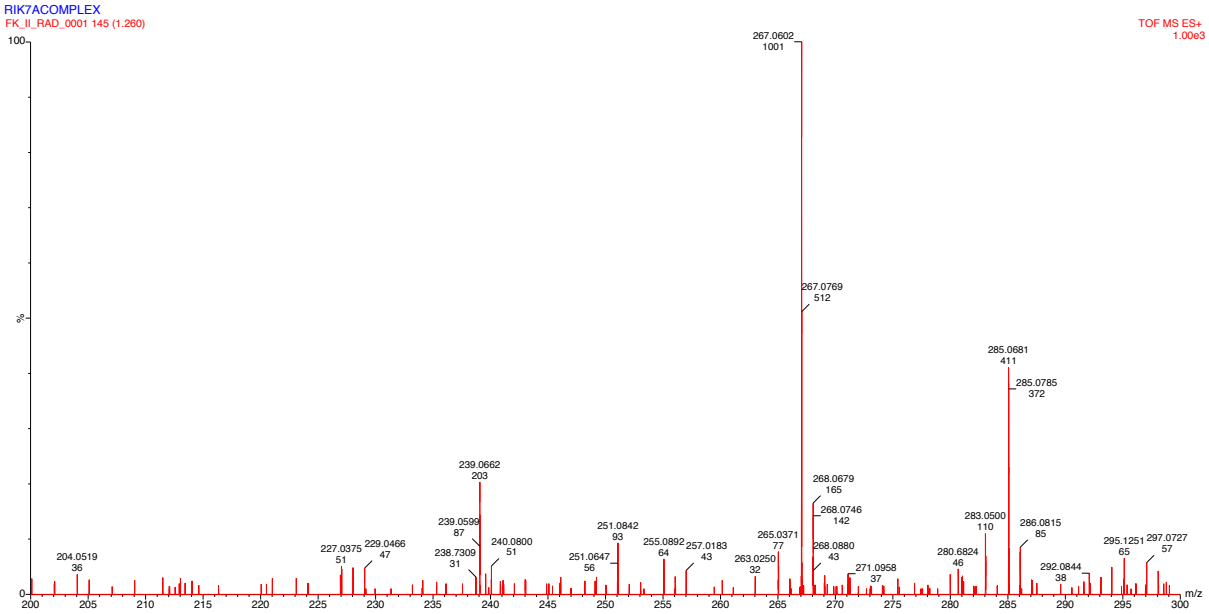
D) Radical trapping experiments

a) Dihydropyran

1 eq. SPO was dissolved in diisopropyl ether and 10 mol% iodine were added. The mixture was stirred until the orange/yellow colour completely disappeared. Subsequently 1 eq dihydropyran was added and the solution heated to 50°C for 16h.

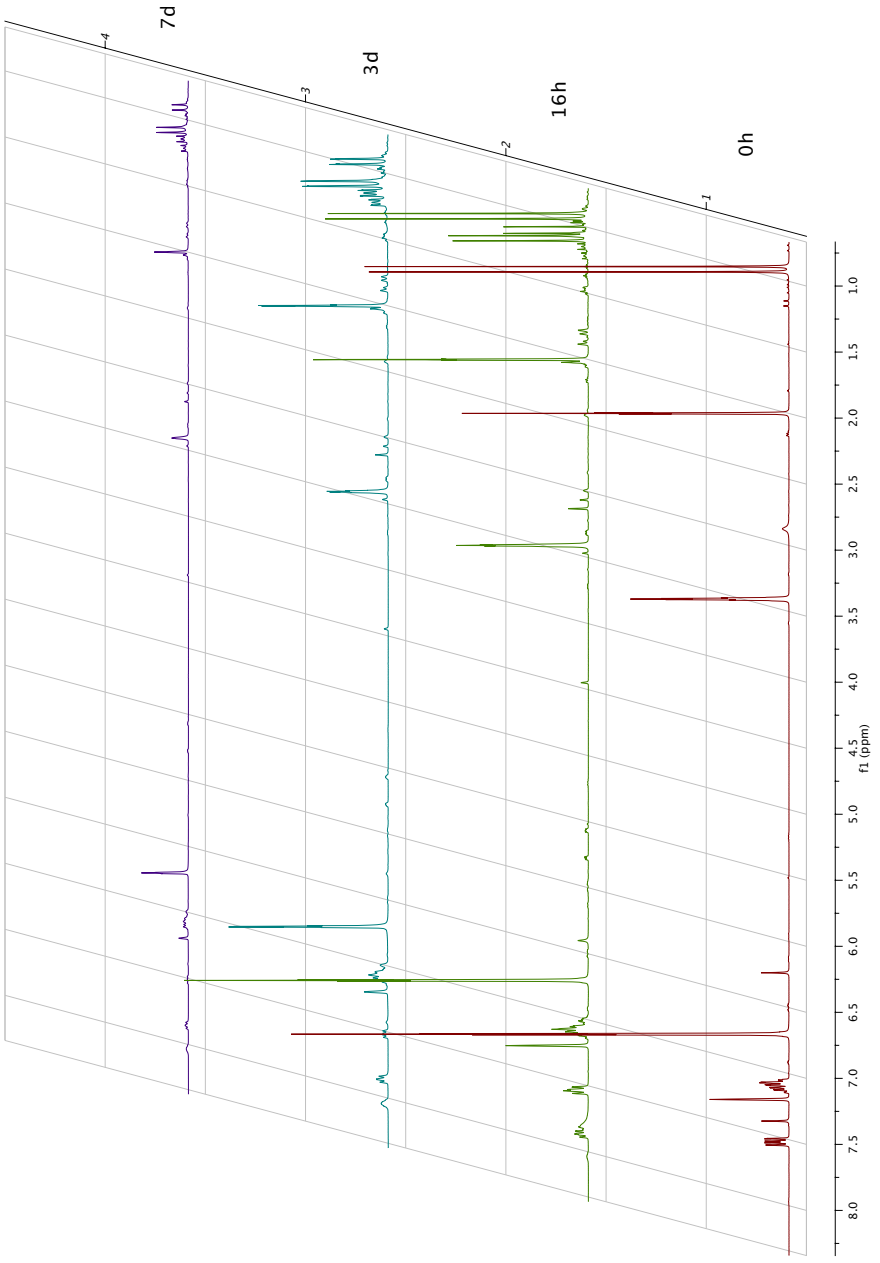


HRMR: 267.1514 ([M+] calc), 267.0602 ([M+] found)



b) Norbornadiene

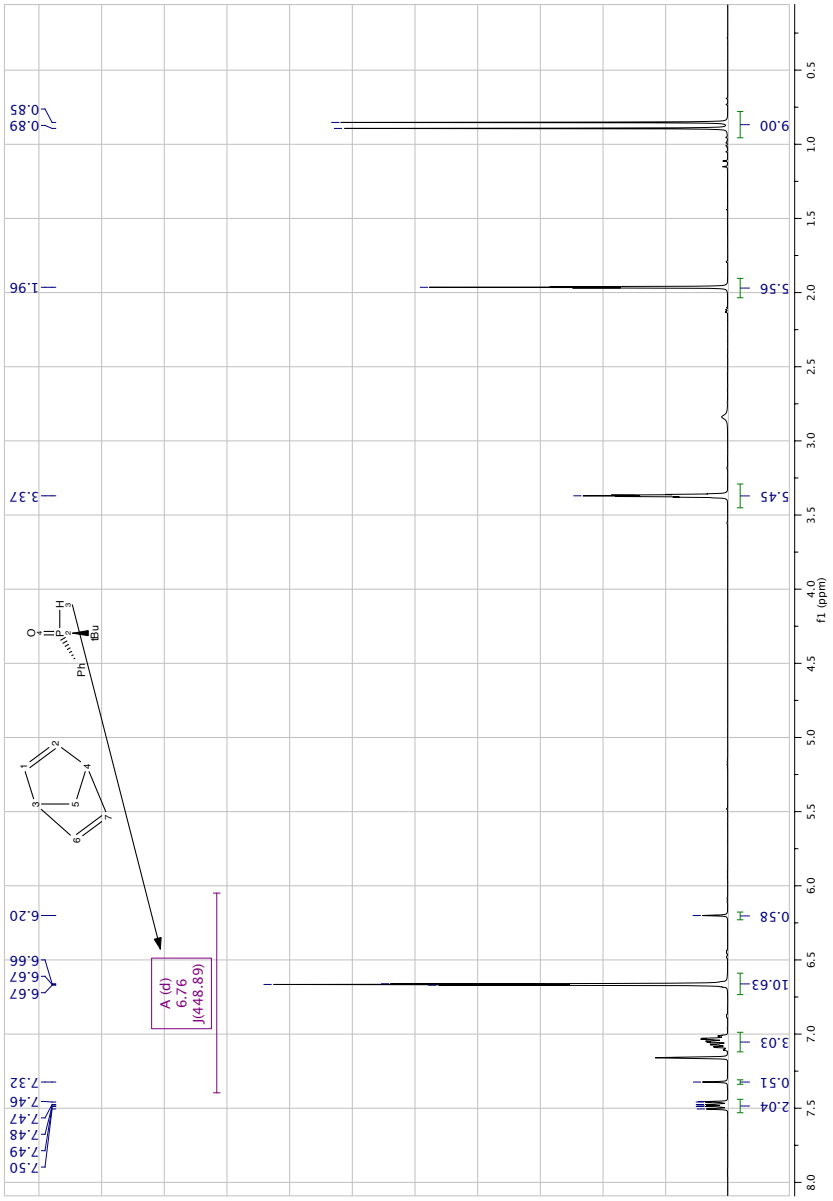
1 eq. SPO was dissolved in diisopropyl ether and 10 mol% iodine were added. The mixture was stirred until the orange/yellow colour completely disappeared. Subsequently 2.5 eq norbornadiene were added and the solution heated to 50°C for 7d.



control experiment:

1 eq. SPO was dissolved in diisopropyl ether and no iodine was added. Subsequently 2.5 eq norbornadiene were added and the solution heated to 50°C for 16h.

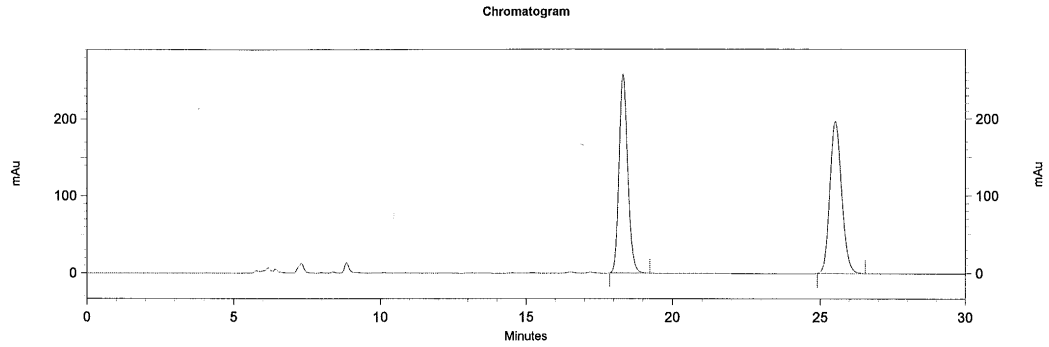
after 16h @ 50°C



E) HPLC-traces

a) Classical resolution

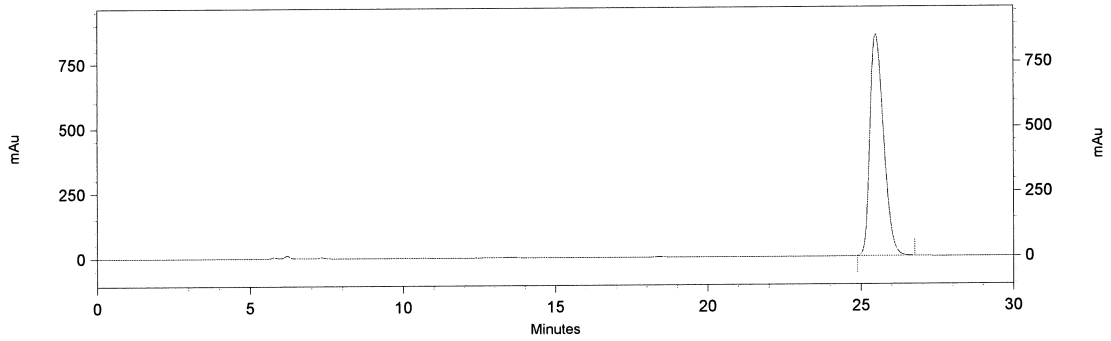
racemic *tert*-butyl(phenyl)phosphine oxide



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,316 Minutes	18,316	5304757	48,757
2	Peak @ 25,512 Minutes	25,512	5575169	51,243
Totals			10879926	100,000

(*R*)-*tert*-butyl(phenyl)phosphine oxide (classical resolution)

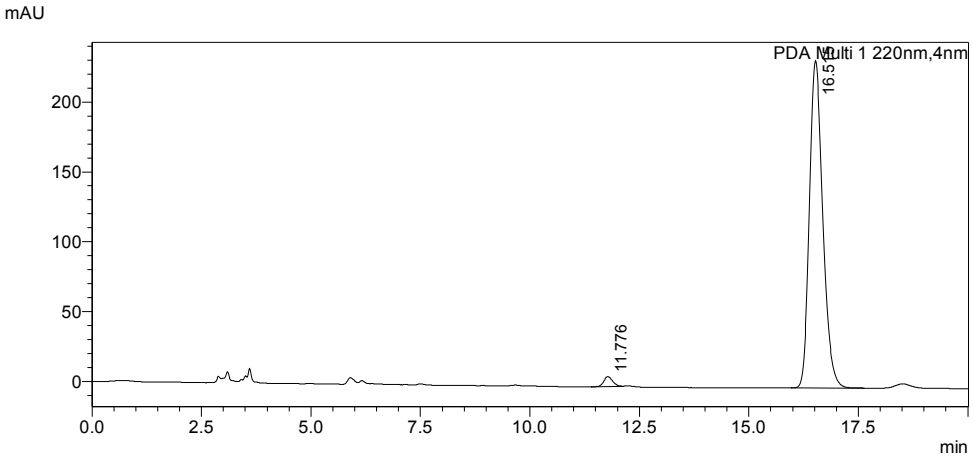


1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,484 Minutes	25,484	26557223	100,000

b) CIAT

(*R*)-*tert*-butyl(phenyl)phosphine oxide (CIAT, before recrystallization) (flow 1.0 ml/min)



<Peak Table>

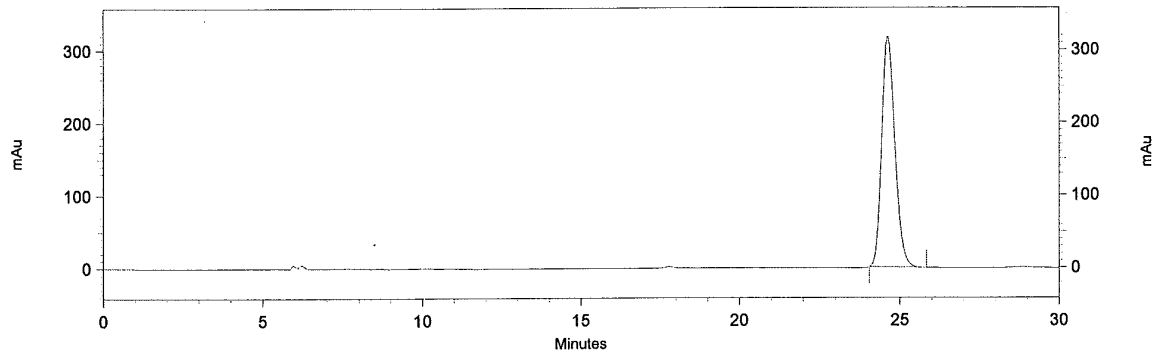
AD2

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
Total							

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	11.776	98778	7087	1.945			
2	16.515	4979204	234227	98.055			
Total		5077983	241313				

(*R*)-*tert*-butyl(phenyl)phosphine oxide (CIAT, after single recrystallization) (flow 0.5 ml/min)



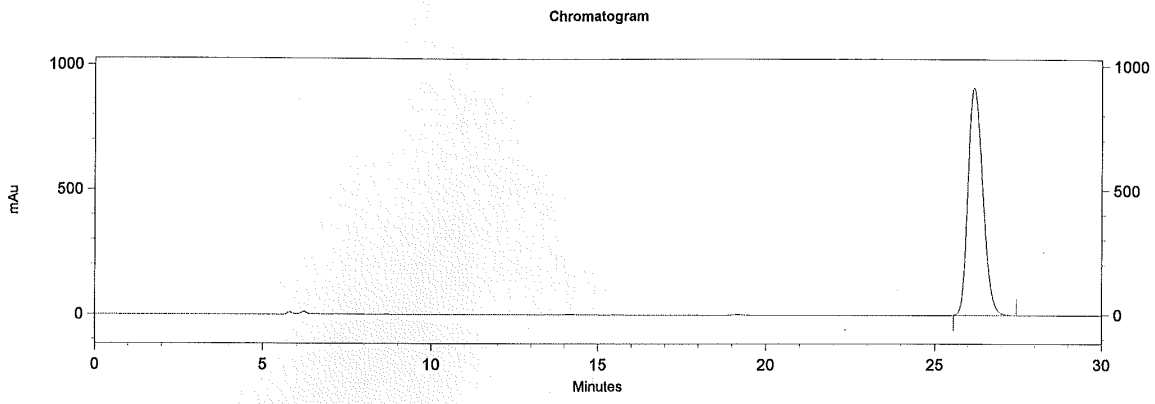
1: 220 nm,
10 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 24,616 Minutes	24,616	9050752	100,000

c) Racemization studies of SPO, bases

For all spectra enantiopure (R)-SPO was used as starting material.

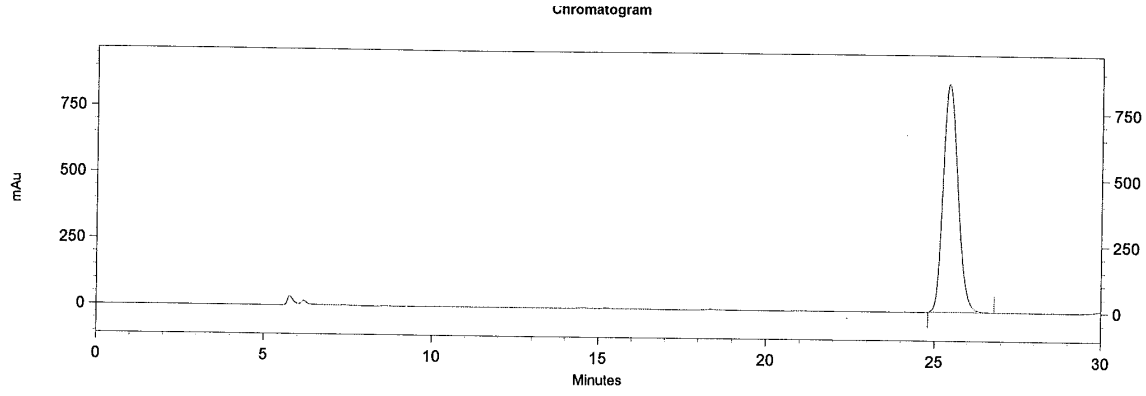
after 16h @ RT in 0.05M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 26,164 Minutes	26,164	28068542	100,000
Totals			28068542	100,000

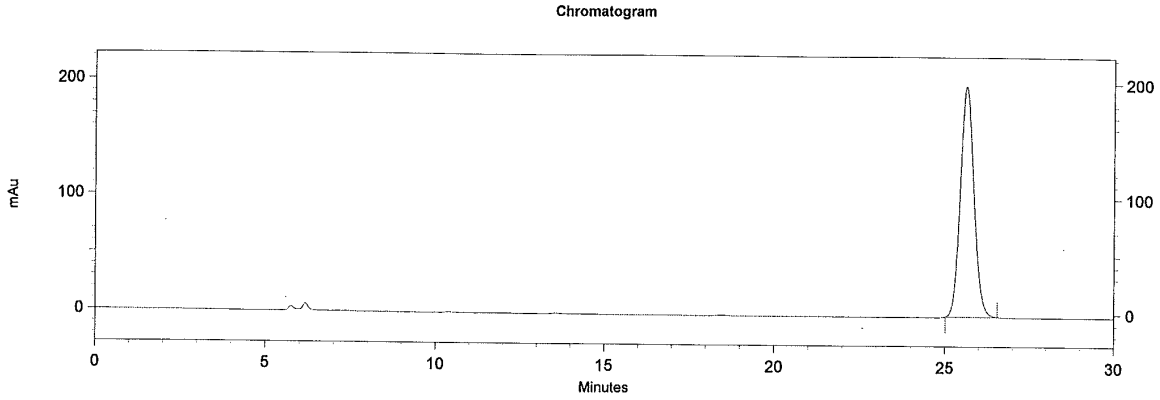
after 16h @ RT in 1M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,396 Minutes	25,396	26692300	100,000
Totals			26692300	100,000

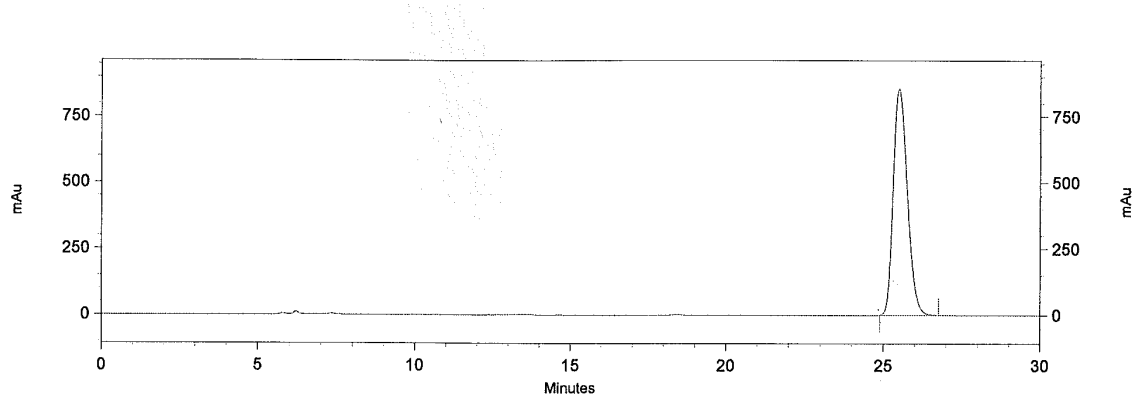
after 24h @ RT in 1M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,616 Minutes	25,616	5624484	100,000
Totals			5624484	100,000

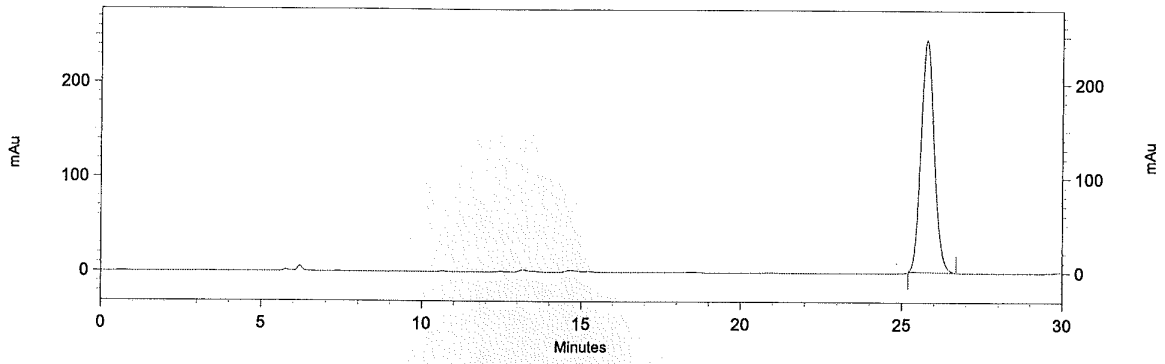
after 16h @ 50°C in 1M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,484 Minutes	25,484	26557223	100,000

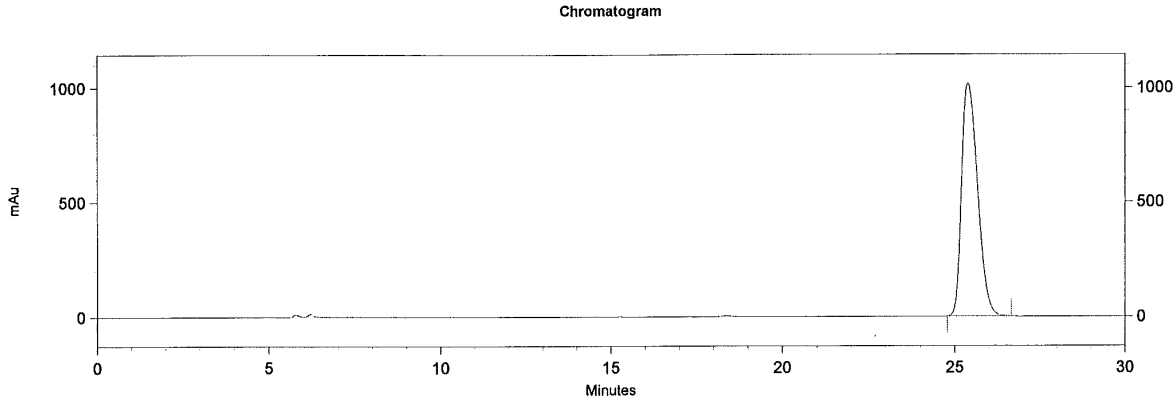
after 3d @ 50°C in 1M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,596 Minutes	25,760	7009850	100,000

after 16h @ reflux in 1M NaOH

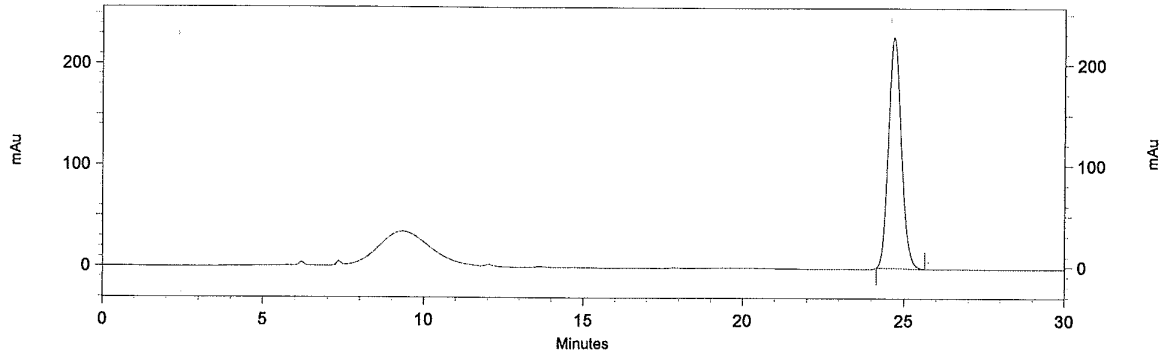


1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,380 Minutes	25,380	33025980	100,000

Totals			33025980	100,000

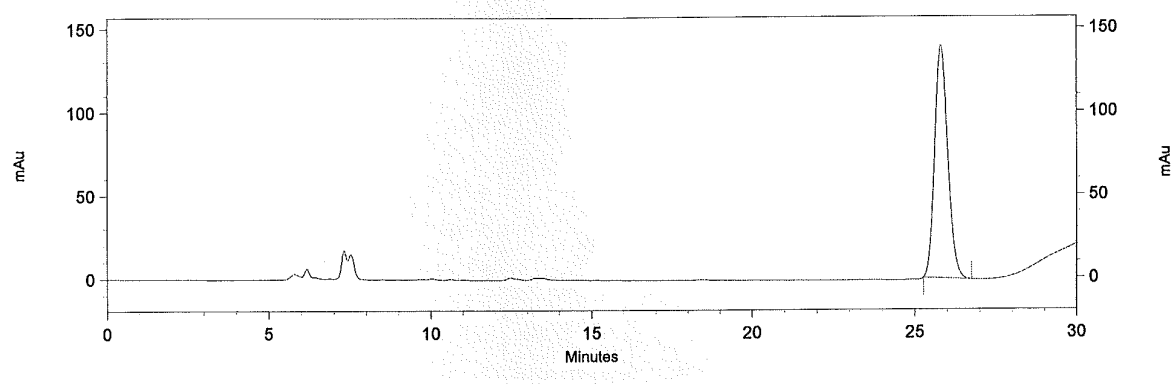
after 3d @ reflux in 1M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,596 Minutes	24,688	6298006	100,000

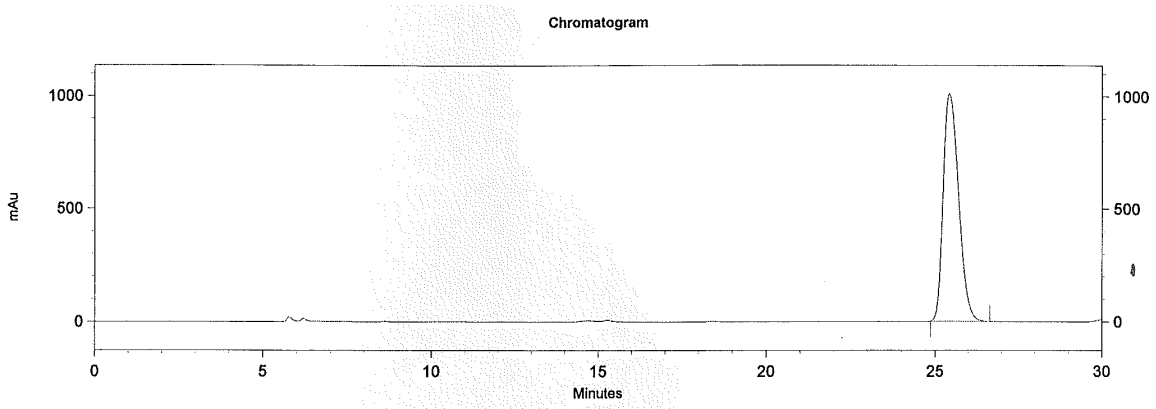
after 16h @ reflux in 3M NaOH



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,596 Minutes	25,800	3942048	100,000

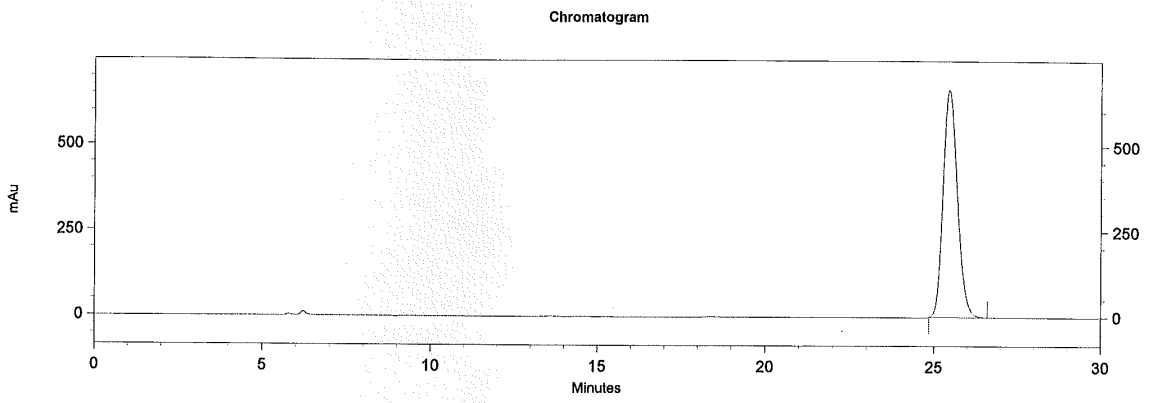
after 16h @ RT in $NH_{3(aq)}$



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent

after 16h @ RT in 1M LiOH

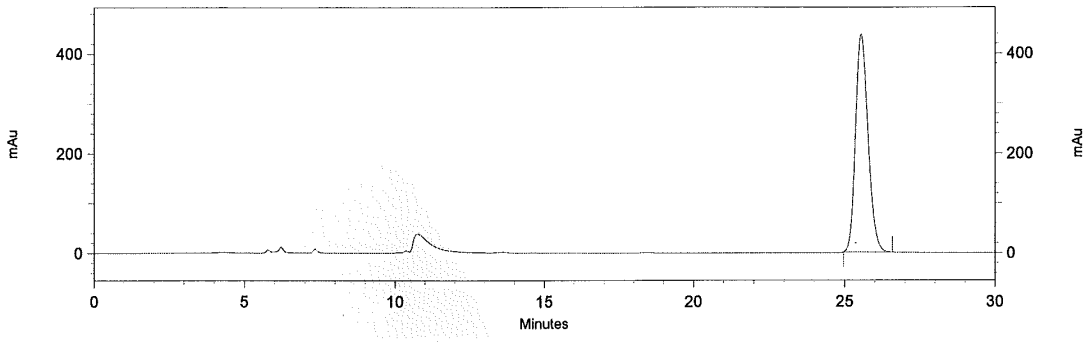


1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 25,436 Minutes	25,436	19901163	100,000
Totals			19901163	100,000

d) Racemization studies of SPO, acids

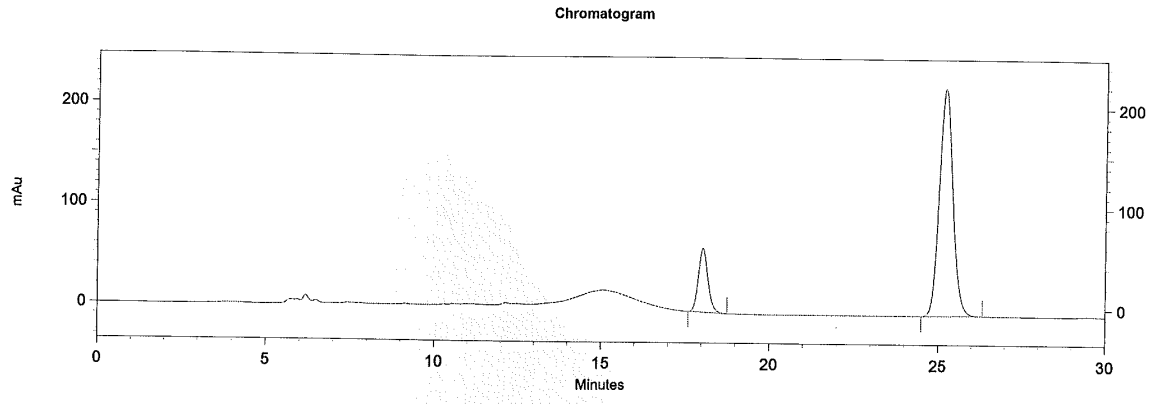
after 3d @ 50°C in 1M HCl



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1		25,536	12673402	100,000

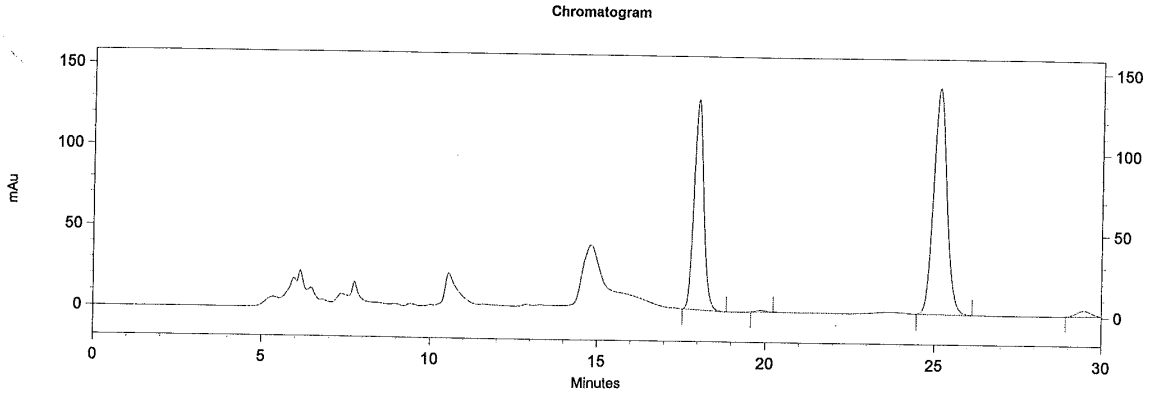
after 3d @ 50°C in 6M HCl



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,032 Minutes	18,032	1252790	16,372
2	Peak @ 25,184 Minutes	25,184	6399212	83,628
Totals			7652002	100,000

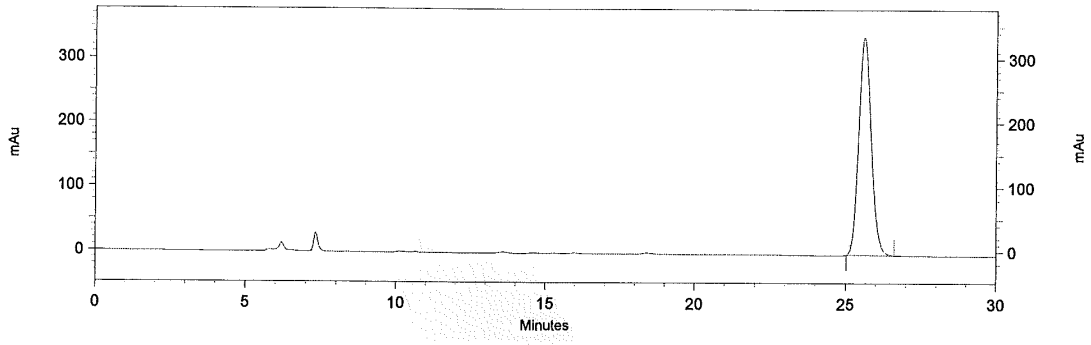
after 3d @ 50°C in concentrated HCl



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,032 Minutes	17,984	2594846	39,237
3	Peak @ 25,184 Minutes	25,116	3883769	58,728
Totals			6478615	97,965

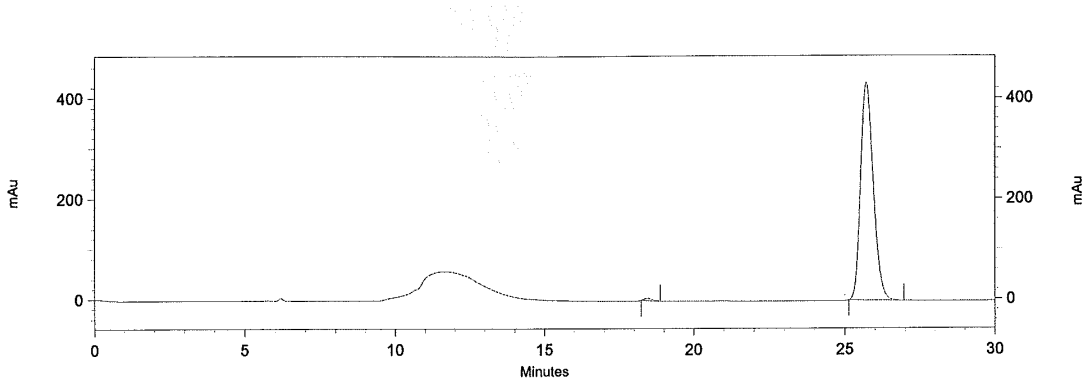
after 16h @ 50°C in Amberlyst/PhMe



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1		25,596	9727343	100,000

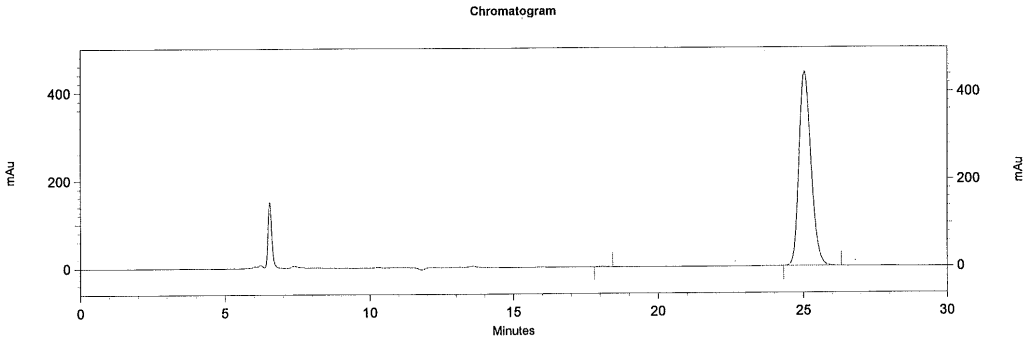
after 3d @ 50°C in Amberlyst/PhMe



1: 220 nm,
10 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1		18,452	81066	0,636
2		25,716	12662126	99,364

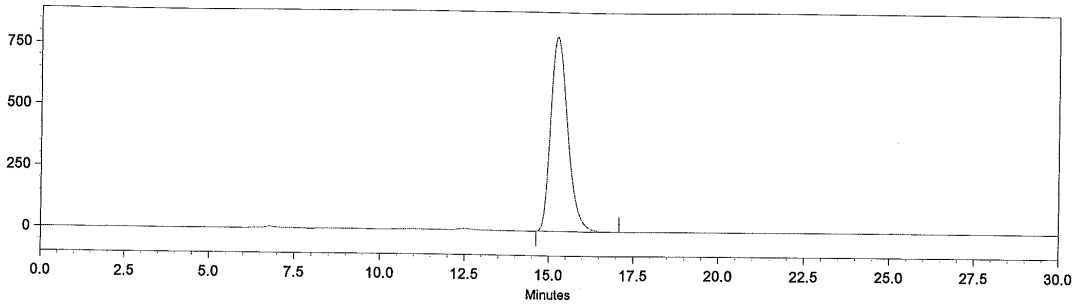
after 3d @ 50°C in TFA/PhMe



1: 220 nm,
2 nm Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,032 Minutes	18,056	20595	0,161
2	Peak @ 25,184 Minutes	25,036	12790784	99,839
Totals			12811379	100,000

after 3d @ 50°C in $Zn(OTf)_2$/PhMe

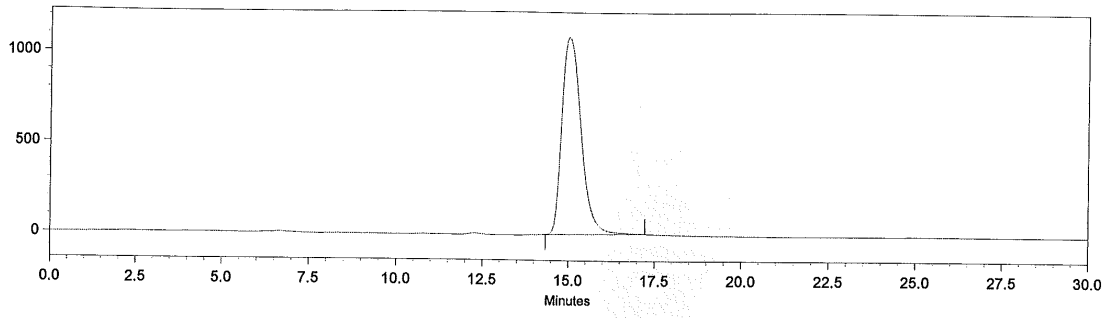


: 220 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	15.232	28137338	100.00
Totals			28137338	100.00

Peak: 1

after 3d @ 50°C in $CeSO_4$/PhMe

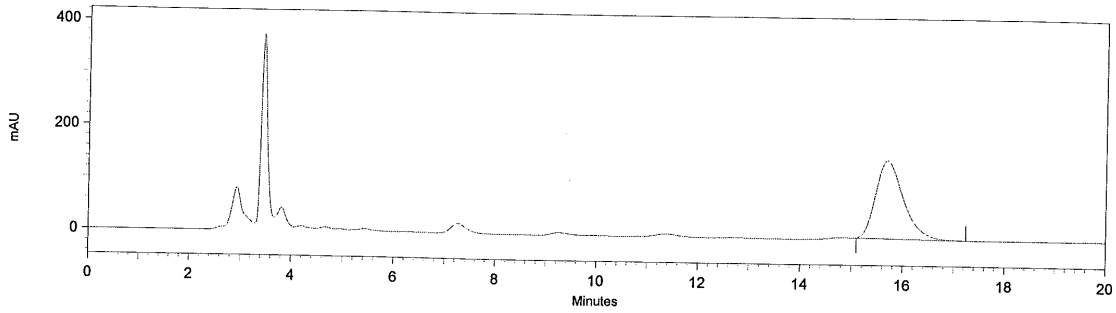


: 220 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	14.997	42559234	100.00
Totals			42559234	100.00

Peak: 1

after 3d @ 50°C in $NiCl_2$/PhMe



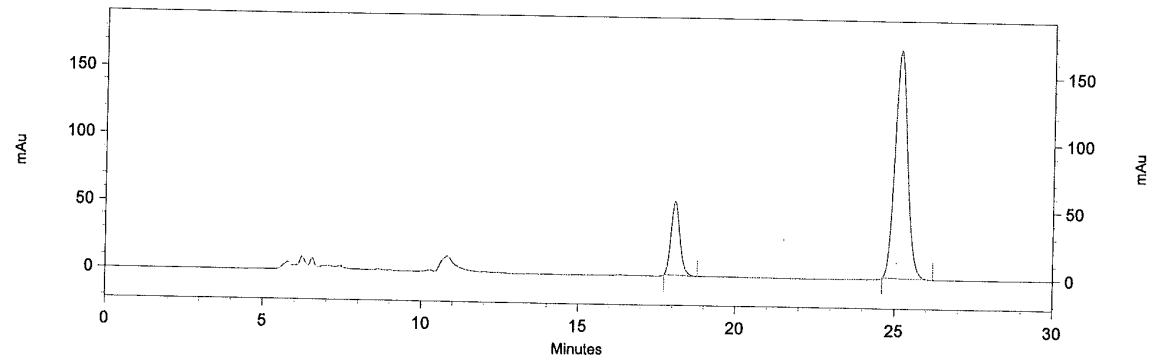
1: 220 nm, 8 nm

Pk #	Name	Retention Time	Area	Area Percent
1	1	15.691	5585552	100.00
Totals			5585552	100.00

Peak: 2

e) Racemization studies of SPO, iodine

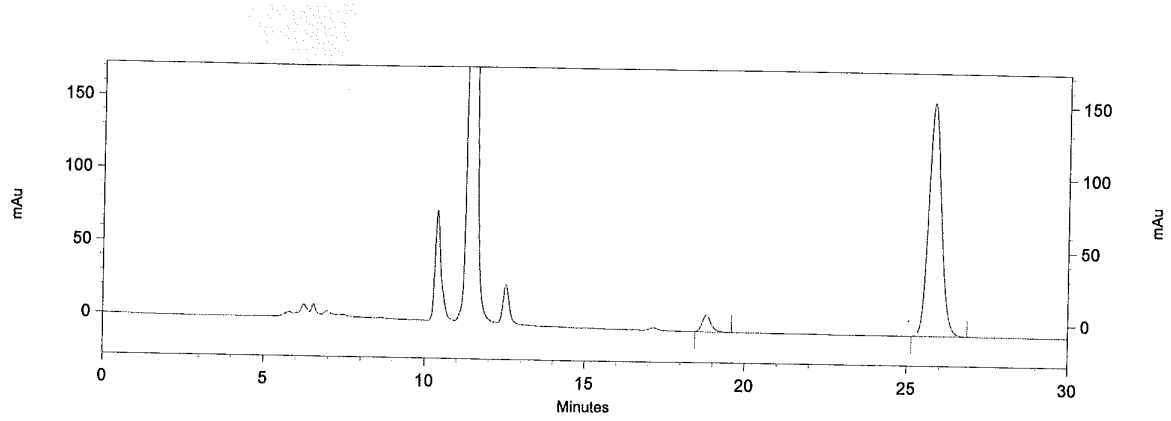
after 16h @ RT in MeCN with 10% I_2



1: 220 nm,
10 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1	Peak @ 18,068 Minutes	18,068	1074493	18,669
2	Peak @ 25,136 Minutes	25,136	4681089	81,331

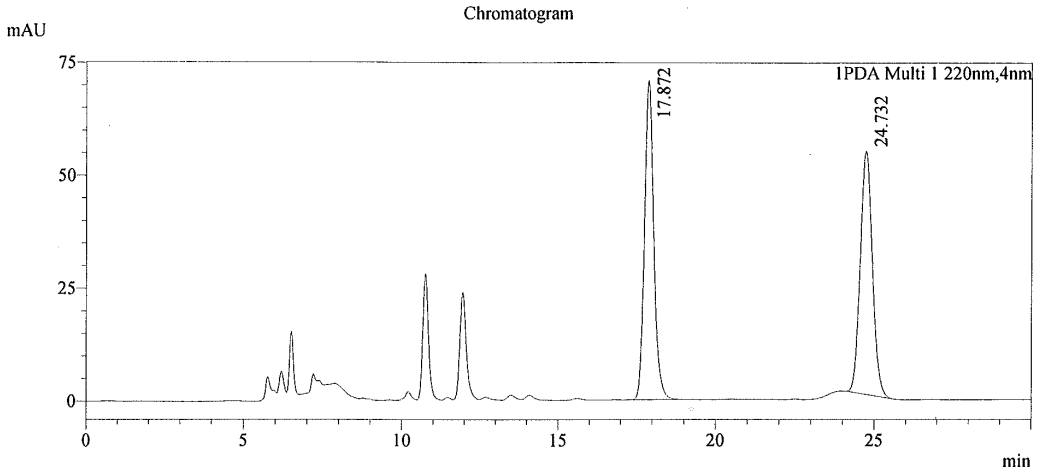
after 16h @ RT in EtOH with 10% I_2



1: 220 nm,
10 nm
Results

Pk #	Name	Retention Time	Area	Area Percent
1		18,804	220298	4,780
2		25,808	4388210	95,220

after 16h @ reflux in PhMe with 10% I_2

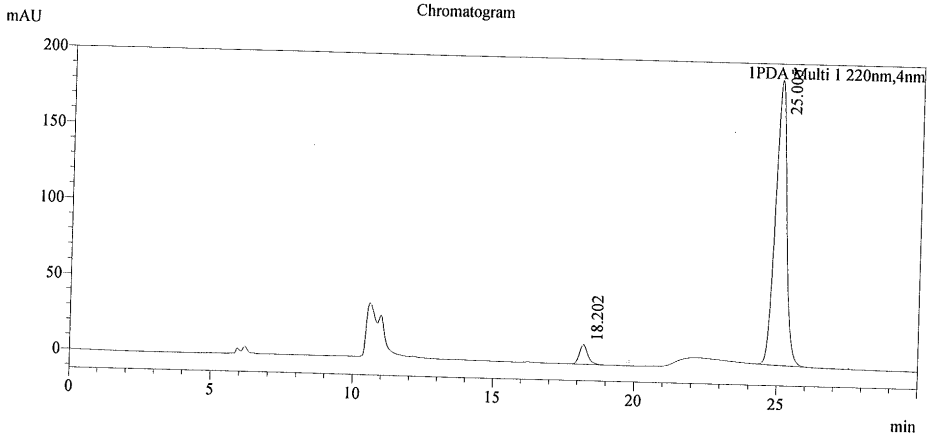


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.872	1455196	70801	50.043			
2	24.732	1452680	54066	49.957			
Total		2907876	124866				

after 16h @ RT in DIPE with 10% I_2

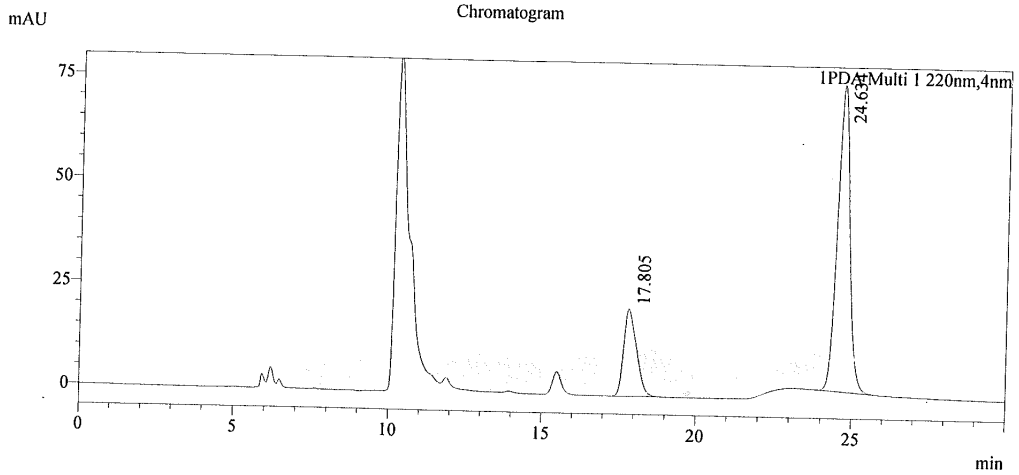


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	18.202	263882	12846	4.796			
2	25.005	5237683	188066	95.204			
Total		5501565	200912				

after 16h @ 50°C in DIPE with 10% I_2

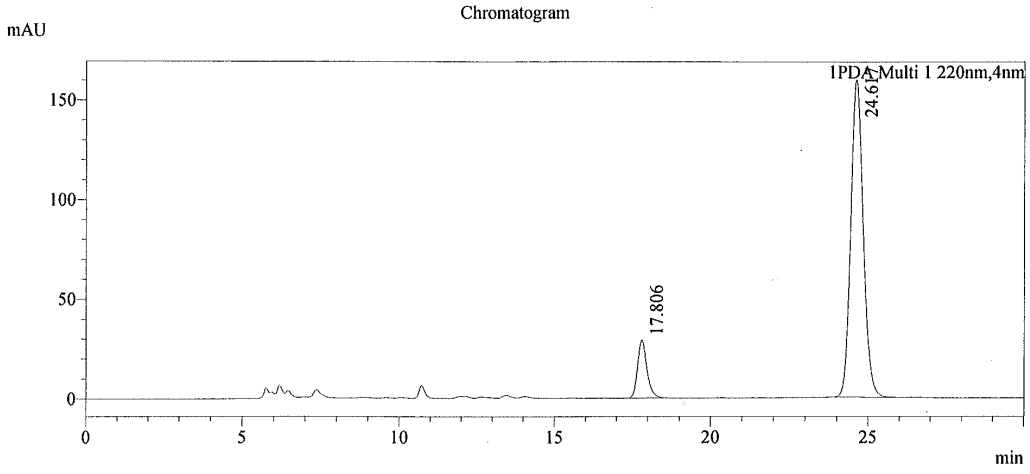


Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.805	604914	21088	22.606			
2	24.634	2070982	73899	77.394			
Total		2675896	94987				

after 16h @ reflux in DIPE with 1% I_2



Peak Table

PDA Ch1 220nm

Peak#	Ret. Time	Area	Height	Conc.	Unit	Mark	Name
1	17.806	606687	29152	12.093			
2	24.617	4410119	159658	87.907			
Total		5016806	188810				

NMR

F) Density-Functional Computations

a) Computational Details

Calculations were performed in Gaussian 09[SI1] using the B3LYP density functional, which has previously been shown to perform well for pentacoordinate silicon and phosphorus compounds.[SI2] Structures were fully optimized using the 6-31G(d,p) full-electron double-zeta polarized basis set for H, C, O, and P; for I the LANL2DZ effective core potential and valence basis set were used with an additional Cartesian set of d polarization functions as defined by Huzinaga[SI3] (hereafter denoted basis set S). An ultrafine integration grid was applied in combination with tight convergence criteria for SCF and geometry. Where applicable, the redundant internal coordinates were edited to improve performance, removing angles and dihedrals relating to nearly collinear bonds. Nonspecific solvation effects of diisopropyl ether (DIPE) were treated with the polarizable continuum model using radii and non-electrostatic terms from the recent SMD solvation model,[SI4] which is recommended for computing ΔG of solvation. The nature of each stationary point was confirmed by a frequency calculation, which also afforded a thermochemical analysis. The correction for the Gibbs free energy was reevaluated for the experimental reaction temperature of 343 K. Subsequent single-point energies were calculated with the 6-311G(2d) triple-zeta doubly polarized basis set for I[SI5] and 6-311+G(2d,p) (including a set of diffuse functions) for all other elements, hereafter denoted basis set L.

Hypothetically, racemization could occur through stereomutation of pentacoordinate phosphorane intermediate ^{t}BuPhP(H)(I)OH, generated by nucleophilic addition of HI to the phosphite. However, for all possible stereoisomers geometry optimization led instead to I^- adducts of the tetrahedral hydroxyphosphonium species ^{t}BuPhP(H)OH$^+$ at the B3LYP/S/SMD(DIPE) level of theory.[SI6]

We also considered anionic pentacoordinate species ^{t}BuPhP(H)(I)O$^-$ and their neutral radical analogues, hypothetical adducts of ^{t}BuPhP(H)O with I^- and I•, respectively. However, the geometry optimizations invariably afforded loosely bound iodide–phosphite ion–molecule and radical–molecule complexes, except in two cases where the [^{t}Bu• PhP(H)(I)O] radical–molecule complex was obtained. Thus, five-coordinate organophosphorus species can be excluded as intermediates for the phosphite racemization.

b) Optimized Energies and Thermochemistry

Table S1. B3LYP/L/SMD(DIPE)//B3LYP/S/SMD(DIPE) results in Hartree (S_{tot} in cal mol^{-1} K^{-1}).

	E_{Opt}	ZPE	H_{corr}	S_{tot}	G_{corr}	G_{corr}(343K)	E_{SP}
^{t}BuPhP(H)O	−806.732077220	0.227687	0.241463	111.280	0.188590	0.180363	−806.890979523
^{t}BuPhPOH	−806.724115996	0.227978	0.242282	112.761	0.188706	0.180363	−806.877470778
^{t}BuPhP(I)O	−817.547211408	0.219328	0.234833	122.742	0.176514	0.167445	−7725.847092610
Radical mechanism:							
I•	−11.3658298621	0.000000	0.002360	41.806	−0.017503	−0.020516	−6919.50683418

^{t}BuPhPO•	−806.094255362	0.216903	0.230789	113.815	0.176712	0.168306	−806.250670434
[^{t}BuPhPO• TS]‡	−806.073991246	0.216480	0.229864	111.488	0.176892	0.168661	−806.232551783
[(^{t}BuPhPO)$_2$H• A]‡	−1612.81471409	0.441357	0.469758	185.236	0.381746	0.367946	−1613.12515770
[(^{t}BuPhPO)$_2$H• B]‡	−1612.81380304	0.441210	0.469748	188.436	0.380216	0.366186	−1613.12457868
HI addition mechanism:							
^{t}BuPhP(H)OHI	−818.751600250	0.239247	0.255533	130.600	0.193481	0.183836	−7727.04912032
^{t}BuPhP(H)OHI'	−818.749666406	0.238868	0.255267	131.341	0.192862	0.183164	−7727.04669066
^{t}BuPhP(HI)OH	−818.740769146	0.238746	0.255785	134.982	0.191650	0.181686	−7726.03794222

c) Relative Gibbs Free Energies

Table S2. B3LYP/L/SMD(DIPE)//B3LYP/S/SMD(DIPE) calculated relative Gibbs free energies at 343 K in kcal mol^{-1}.

Reaction equation	B3LYP/S	B3LYP/L//S
^{t}BuPhP(H)O → ^{t}BuPhPOH	5.00	8.48
^{t}BuPhP(I)O → ^{t}BuPhPO• + I•	42.34	43.88
^{t}BuPhPO• → [^{t}BuPhPO• TS]‡	12.94	11.59
R-^{t}BuPhPO• + *S*-^{t}BuPhP(H)O → [(^{t}BuPhPO)$_2$H• A]‡	19.39	22.45
R-^{t}BuPhPO• + *R*-^{t}BuPhP(H)O → [(^{t}BuPhPO)$_2$H• B]‡	18.85	21.70
^{t}BuPhP(H)OHI → ^{t}BuPhP(H)OHI'	0.79	1.10
→ ^{t}BuPhP(HI)OH	5.45	5.67

d) Assessment of Multireference Character

Radical species, among others, may exhibit significant multireference character, for which the purely single-reference Hartee-Fock approximation fails badly. This would compromise the use of hybrid functionals as these have some HF exchange contribution mixed in (20% in the case of B3LYP). For dissociation reactions the extent of multireference character can be estimated with the B_1 diagnostic:[SI7]

$$B_1 = (BE_{\mathrm{BLYP}} - BE_{\mathrm{B1LYP//BLYP}}) / n$$

where BE is the reaction energy for breaking n bonds, calculated with the BLYP vs the B1LYP functional using BLYP-optimized geometries.

In analogy, the energetics of the radical processes were recalculated at the B1LYP/S//BLYP/S level of theory; in Table S3 the BLYP Gibbs free energy corrections were included to enable direct comparison with Table S2.

Table S1: B1LYP/S//BLYP/S calculated Gibbs free energies of dissociation or of activation in kcal mol^{-1}.

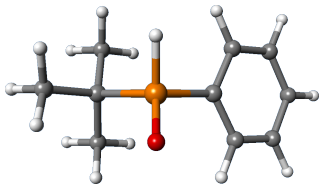
Reaction equation	BLYP	B1LYP//BLYP	|BLYP − B1LYP|[a]
^{t}BuPhP(I)O → ^{t}BuPhPO• + I•	43.66	43.09	0.57
^{t}BuPhPO• → [^{t}BuPhPO• TS]‡	12.28	13.73	1.45
R-^{t}BuPhPO• + *S*-^{t}BuPhP(H)O → [(^{t}BuPhPO)$_2$H• A]‡	11.96	15.34	3.38
R-^{t}BuPhPO• + *R*-^{t}BuPhP(H)O → [(^{t}BuPhPO)$_2$H• B]‡	12.70	16.22	3.52

[a] This quantity is equivalent to B_1 as the BLYP Gibbs free energy corrections cancel out.

Comparing the BLYP and B1LYP//BLYP relative Gibbs free energies mutually as well as with the B3LYP results in Table S2, it is obvious that the HF exchange contribution affects the energetics by significantly less than the 10 kcal mol^{-1} limit suggested for B_1 to reasonably distinguish single-reference systems. This indicates that the investigated radical species have little multireference character and that hybrid functionals such as B3LYP are appropriate to model their energetics.

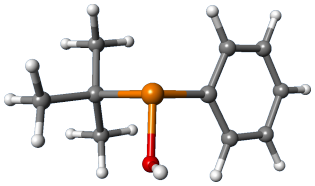
G) Optimized Structures

^{t}BuPhP(H)O (C_1, $N_{imag} = 0$)



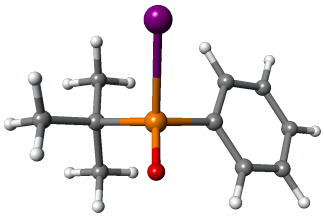
P	0.222403386131	−1.246800861491	−0.652188715220
H	0.133792159483	−1.080208678465	−2.061715918525
O	0.309410496011	−2.673503755769	−0.173781649033
C	−1.278689659222	−0.373586261600	−0.090283491501
C	−3.595459912139	0.920681985789	0.805031948513
C	−1.929337658432	0.560381207623	−0.909598275719
C	−1.808766141718	−0.666982881384	1.175106320792
C	−2.960609678052	−0.018703113212	1.620966155129
C	−3.081562666010	1.207577600198	−0.461332714701
H	−1.544056387340	0.777437537347	−1.902452380726
H	−1.328012808590	−1.414090740806	1.799526988536
H	−3.366500268081	−0.251639775390	2.601147999436
H	−3.581536179364	1.927317883799	−1.102972884888
H	−4.494872159306	1.421540427296	1.151680163946
C	1.720162424150	−0.211988174287	−0.248407831484
C	2.931732269697	−0.954618236022	−0.846837407564
H	3.035750378069	−1.958055119541	−0.424968099788
H	3.850742563690	−0.396160701135	−0.633214295738
H	2.849313324573	−1.051948316472	−1.935716782795
C	1.864523175112	−0.109045041436	1.280226065437
H	1.921126789456	−1.099053625200	1.743381943777
H	1.027710754585	0.433244424831	1.732411796529
H	2.784917874302	0.431646445243	1.530387628810
C	1.592656673664	1.184696926638	−0.879583657925
H	1.469480885302	1.132604874915	−1.967523556649
H	2.504772384152	1.760440462189	−0.682623765780
H	0.750908979880	1.748817506343	−0.466668582871

^{t}BuPhPOH (C_1, $N_{imag} = 0$)



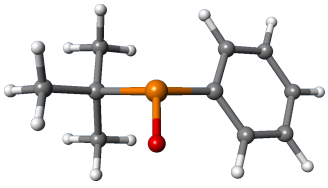
P	−0.743062685466	−0.914508599701	−0.965359769311
O	−0.556718317543	−0.100549297074	−2.433553638077
H	−0.688107896417	−0.730436268243	−3.155671994229
C	0.979321629087	−0.815964557298	−0.301340281959
C	3.597452483976	−0.802172033846	0.726109629767
C	1.975026873853	−0.024855167517	−0.894887761385
C	1.321912189792	−1.618533115680	0.799355526883
C	2.618078826665	−1.603275320502	1.317050354440
C	3.274112992638	−0.018930402128	−0.384364085556
H	1.726604988467	0.576341958659	−1.763653776285
H	0.574574300788	−2.267693784236	1.249937831427
H	2.865848497912	−2.225920430161	2.172320780478
H	4.035253766676	0.598296066725	−0.854284228969
H	4.609323412513	−0.797179753096	1.121553232696
C	−1.660261600032	0.451551915043	−0.014411247896
C	−1.769058632141	0.024723179028	1.459391003199
H	−2.239434230986	−0.959805688753	1.566858286444
H	−2.387604332858	0.744920663249	2.009278797199
H	−0.791115474714	−0.010130948287	1.949682548460
C	−3.067862418928	0.519382029423	−0.638553190275
H	−3.593954399012	−0.438666161837	−0.557051947619
H	−3.023387081011	0.792281978828	−1.697467098215
H	−3.671536112866	1.276331691799	−0.122628995917
C	−0.971788246036	1.819488116573	−0.128835925597
H	−1.578375150911	2.586253193946	0.370541229229
H	−0.850267935034	2.119605814964	−1.173821890915
H	0.015027551588	1.819447920122	0.343807611983

^{t}BuPhP(I)O (C_1, $N_{imag} = 0$)



P	0.220931706231	−0.541956595261	1.260742667762
O	0.343425267454	0.131466349258	2.595415267934
C	−1.294483206181	−0.036880525676	0.372861833506
C	−3.600531961798	0.916091551051	−0.890236669305
C	−1.817581194014	−0.712509195155	−0.739961230709
C	−1.941263440600	1.110497812224	0.857927646609
C	−3.090589952764	1.583798927315	0.223866932882
C	−2.964418317898	−0.231912652174	−1.369913963680
H	−1.347863611950	−1.621195328651	−1.101435598055
H	−1.546926851584	1.617121990496	1.732420272787
H	−3.589159504819	2.469911920910	0.605384731597
H	−3.367521701916	−0.760395255828	−2.228680718367
H	−4.497093689210	1.283899271481	−1.380744516339
C	1.737747659820	−0.286765575380	0.179715216067
C	2.962913838872	−0.780659878127	0.969018838128
H	3.030250683164	−0.301153705839	1.949252237549
H	3.871412834156	−0.536460193952	0.406968656251
H	2.940667458538	−1.864354043076	1.116323663696
C	1.828300218007	1.242568244501	−0.026835156441
H	1.904327344818	1.775565038854	0.924564139937
H	0.968210612700	1.635288058723	−0.577940899791
H	2.727589854195	1.463724188483	−0.612953524115
C	1.641163227079	−0.997448414042	−1.177511405306
H	1.554806640721	−2.082404869695	−1.070077267016
H	2.556053007225	−0.793378607310	−1.745791442287
H	0.798960125185	−0.635838461580	−1.773936610329
I	−0.029330045431	−3.046620051550	1.501554897036

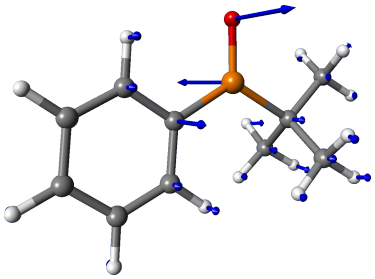
^{t}BuPhPO• (C_1, $N_{imag} = 0$)



P	0.788863135955	−0.591828729451	−0.723683592693
O	1.085293476854	−2.078468057005	−0.568327667963
C	−0.947650067680	−0.211992431505	−0.279175629706
C	−3.643465870757	0.262338954910	0.321812842387
C	−1.559378129406	0.992314664235	−0.665415693471
C	−1.708724206894	−1.189139990665	0.384264776705
C	−3.048088338257	−0.947413556178	0.687610668313
C	−2.898760989364	1.229670101683	−0.357278445903
H	−0.996068892514	1.740453270178	−1.215395180858
H	−1.244686848502	−2.132380218664	0.654446431069
H	−3.628162504484	−1.704184373400	1.208198399250
H	−3.363611638340	2.164644941931	−0.656585587085

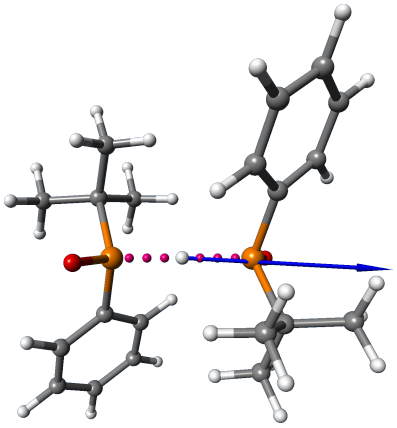
H	−4.687741515858	0.447345119179	0.556584124934
C	1.967402783981	0.470582170028	0.316608792985
C	3.387209554421	0.134624382117	−0.172061194338
H	3.596609716236	−0.935777013879	−0.092618996926
H	4.122878056991	0.671222135228	0.438920705695
H	3.536842271248	0.433472971937	−1.215251279557
C	1.800324041553	0.072373613826	1.794824546678
H	2.006918318054	−0.990944827491	1.947235570512
H	0.790471901786	0.282473291253	2.161020708765
H	2.504925657799	0.646646873625	2.410037684470
C	1.672936498855	1.964406707625	0.119044138537
H	1.736163724470	2.260339769030	−0.933828889709
H	2.415650848853	2.553790552011	0.670546022861
H	0.686582015002	2.244556679443	0.499372745048

[^{t}**BuPhPO• TS**]‡ (C_1, N_{imag} = 1: 384.1627 i cm^{-1})



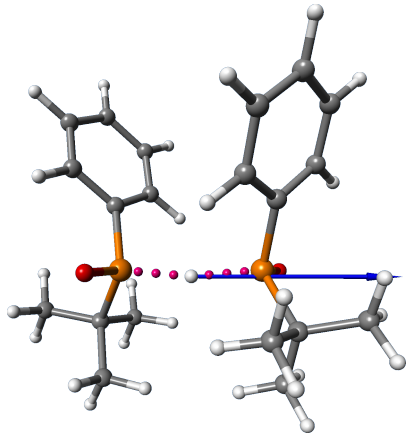
P	0.692443427615	−0.776823661755	−0.000001902269
O	0.985743449239	−2.269484239566	−0.000004212870
C	−0.996274251167	−0.231265496017	−0.000001046046
C	−3.726335019283	0.474679688034	−0.000000288107
C	−1.390628760693	1.127956429517	0.000001095382
C	−2.002050986724	−1.229216249703	−0.000002710339
C	−3.344942678123	−0.872038493001	−0.000002316310
C	−2.740219170407	1.466196431332	0.000001445854
H	−0.648319527639	1.917492210929	0.000002456404
H	−1.714919654249	−2.275386287295	−0.000004294786
H	−4.101873474980	−1.651585808136	−0.000003601298
H	−3.023375734535	2.515164364994	0.000003045615
H	−4.777291286558	0.747043583714	−0.000000025330
C	2.098987462555	0.470691323218	−0.000000026553
C	2.035493896905	1.343006743635	1.270313191277
H	1.108000338005	1.917173504071	1.341464043576
H	2.866483584490	2.059196690881	1.256587542655
H	2.127356121967	0.736803015992	2.176365043547
C	2.035493479393	1.343011238355	−1.270310164636
H	1.107999795882	1.917178056237	−1.341458838517
H	2.127355607268	0.736810682774	−2.176364157374
H	2.866483040201	2.059201282689	−1.256582195039
C	3.397670140672	−0.356765505694	−0.000001675986
H	3.477171315515	−0.993681823341	0.884743440535
H	4.248448219213	0.334505345400	−0.000000766674
H	3.477170895435	−0.993679017264	−0.884748850905

[(^{t}**BuPhPO)$_2$H• A**]‡ (C_1, N_{imag} = 1: 1235.1597 i cm^{-1})



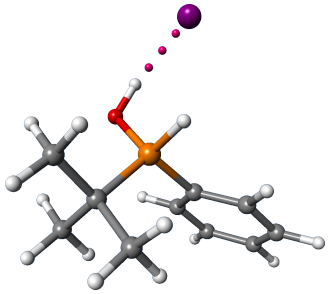
P	−0.128755892532	−0.494019603803	1.741709279235
O	0.048485692284	−1.952256929329	2.118139172500
C	−1.808174861107	0.124972041563	2.114606554675
C	−4.413367395832	0.975568131987	2.694364408164
C	−2.336742024750	1.264964221409	1.484694170739
C	−2.605642799762	−0.598930628145	3.015564222477
C	−3.900112492234	−0.169923530956	3.307568295966
C	−3.633665729610	1.687907701226	1.780313762633
H	−1.749533977922	1.813768092121	0.754007061004
H	−2.206631896425	−1.497364775333	3.476192939763
H	−4.509099295318	−0.731307671671	4.010457840885
H	−4.036181810934	2.569876628336	1.290711968019
H	−5.422940912496	1.306579543696	2.920794111599
C	1.138334898312	0.640240402552	2.550293903293
C	2.526792865486	0.092368381517	2.172002313530
H	2.646288868694	−0.948249385964	2.486722719820
H	3.301679097898	0.689578635299	2.667291329256
H	2.707196678101	0.144863646870	1.093264852233
C	0.941177350936	0.566168003482	4.076680002777
H	1.033587203553	−0.460352278532	4.444160231753
H	−0.036904921075	0.952346457036	4.380514311668
H	1.708580663732	1.172897481994	4.573408520213
C	0.979957144814	2.087309540590	2.055869312439
H	1.056448917575	2.170427315639	0.966727848430
H	1.777045160363	2.703681921633	2.488866111561
H	0.025255838904	2.522607309091	2.364509226568
H	−0.013673858495	−0.165973588939	0.060157307724
P	0.051168400152	0.312928920395	−1.585820513090
O	−0.258175824480	1.788302794282	−1.757879666101
C	1.771054712625	−0.087566117459	−2.064189279176
C	4.432914667867	−0.581735152581	−2.787844355706
C	2.415456022978	−1.261079480104	−1.637129586129
C	2.481661996795	0.847261787823	−2.834343406623
C	3.803991917856	0.595707903473	−3.199345350587
C	3.739453950491	−1.506668802064	−2.003797790825
H	1.893595015673	−1.980002950553	−1.012273164613
H	1.991985316644	1.767667464922	−3.137029127346
H	4.344687914458	1.320019069202	−3.802027913537
H	4.230676033817	−2.416375479942	−1.670794349280
H	5.463729108066	−0.775157842536	−3.070613085196
C	−1.132138122388	−0.808825983640	−2.529414642360
C	−2.555400073495	−0.430797427265	−2.079064274581
H	−2.760198582447	0.630532441879	−2.244408014310
H	−3.285128797949	−1.013097679871	−2.654110827507
H	−2.720272867876	−0.648101474741	−1.018784054447
C	−0.962705090291	−0.523392387583	−4.034139348895
H	−1.147500211775	0.529760364343	−4.266851041290
H	0.039810760434	−0.782768535466	−4.388589599261
H	−1.683341127364	−1.125611165450	−4.601408929100
C	−0.853353090059	−2.289668955955	−2.227045595344
H	−0.933186935135	−2.519174098586	−1.159191449443
H	−1.593669665564	−2.907950652651	−2.748947270077
H	0.135482058807	−2.601953623241	−2.574549144101

[(ᵗBuPhPO)$_2$H• B]‡ (C_1, N_{imag} = 1: 1255.0922 *i* cm^{-1})



P	−1.217765040045	1.259755484742	0.705189060941
O	−0.725441931620	2.685921113333	0.549098346775
C	−1.998492205518	0.620696114538	−0.819539827398
C	−3.150199392455	−0.272918174521	−3.211968749276
C	−2.136648472104	−0.755163547416	−1.068140349262
C	−2.418213742419	1.542864448785	−1.791670108503
C	−2.997594370947	1.095957556309	−2.978748800873
C	−2.715019068483	−1.196335361473	−2.258995134074
H	−1.782441320040	−1.485581166152	−0.346609399614
H	−2.281077334964	2.604859849866	−1.612589259388
H	−3.326096181030	1.815518371179	−3.723422602391
H	−2.816663131623	−2.261614936484	−2.444738746415
H	−3.598110673118	−0.619520572871	−4.138980483523
C	−2.421059206431	1.050659634686	2.140836279811
C	−2.763327435754	−0.430981793885	2.364298182412
H	−3.297051693845	−0.861886938043	1.512472111837
H	−3.417480823263	−0.521763493798	3.239859387783
H	−1.873919648477	−1.040472408936	2.555945955350
C	−3.693701543162	1.857722895750	1.819520100080
H	−4.211400248184	1.469576557934	0.936985690881
H	−3.465466927768	2.913966349481	1.647098354764
H	−4.387966067644	1.797618550446	2.666979371541
C	−1.731313737302	1.636817161174	3.385657754856
H	−0.829855482126	1.075877413114	3.654910316418
H	−2.415970314175	1.589095304336	4.240745188401
H	−1.447677748367	2.681571117248	3.232494697841
H	0.045211801251	0.119893721960	0.947477266818
P	1.296277524835	−1.056809614174	0.890015705969
O	0.806953518015	−2.473617417545	1.122206457383
C	1.949378810051	−0.812766749235	−0.800141455987
C	2.902099460382	−0.535019347496	−3.420040583759
C	2.054507009532	0.460817405124	−1.383931081979
C	2.300710334308	−1.946550603253	−1.550273554078
C	2.781299335809	−1.805405792867	−2.851686598421
C	2.533849160191	0.595494557757	−2.687531238216
H	1.750752741237	1.347344392787	−0.834947859631
H	2.188161703066	−2.932404674247	−1.109665855139
H	3.057517164424	−2.686745143628	−3.423669930232
H	2.610463534534	1.583265965420	−3.132605016612
H	3.272899338791	−0.427077508555	−4.435404805237
C	2.605961791503	−0.518484789177	2.134063398485
C	2.021192060352	−0.779728061534	3.533601189515
H	1.736482315022	−1.827749450913	3.660134500545
H	2.770051591807	−0.533326336447	4.295639312704
H	1.138183703871	−0.161703380337	3.728842188374
C	3.857296194880	−1.391473844694	1.918967873608
H	3.626423357452	−2.455831034053	2.025325853973
H	4.300744225991	−1.233142378234	0.931131090638
H	4.615019366066	−1.134991793066	2.669884347539
C	2.950424355569	0.969878079145	1.965345971808
H	2.072902051699	1.616136815205	2.072855138922
H	3.670063663255	1.263303504014	2.739158711223
H	3.411833626971	1.176968948700	0.995622632814

ᵗBuPhP(H)OHI (C_1, N_{imag} = 0)



P	0.638818104926	−0.512455772945	−0.701983561385
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C	−0.658161493459	−0.968306635786	0.454452902808
C	−2.652263133719	−1.630702744810	2.283533406597
C	−0.308618325955	−1.466948457606	1.719244307326
C	−2.008458748434	−0.814002242068	0.100589667650
C	−3.000809820274	−1.147490984823	1.019863681469
C	−1.309876139606	−1.791927145625	2.632457377956
H	0.733909085103	−1.614342024882	1.986138421675
H	−2.281634841533	−0.457913466590	−0.887596709046
H	−4.045659224035	−1.038092899433	0.746982957078
H	−1.041669828297	−2.182477631602	3.608959502847
H	−3.429915693293	−1.892905469667	2.994509495519
C	1.077935623381	1.279484568748	−0.675524983247
C	1.475344675041	1.651224486743	0.766624253135
H	0.644778603002	1.529688322044	1.467906109992
H	1.776335263897	2.703899264155	0.785390503518
H	2.324864533537	1.060572787844	1.125942977988
C	2.273455657759	1.466495962981	−1.632407651331
H	2.016364417881	1.206160488441	−2.662164469067
H	3.138258271281	0.866527392825	−1.329731862664
H	2.575113323167	2.518929209645	−1.613124858836
C	−0.131895563500	2.110402242533	−1.143261941525
H	−0.993134550405	1.987250439916	−0.479568326792
H	−0.434355924855	1.851335866291	−2.161792419418
H	0.145665172513	3.169727606491	−1.134552562563
O	0.247611306697	−0.860631612168	−2.200377592152
H	0.402739583888	−1.844795823479	−2.417964823873
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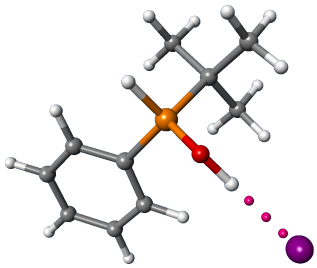
ᵗBuPhP(H)OHI' (C_1, N_{imag} = 0)



P	1.064815231090	−0.341677966605	0.424348974821
H	1.955241734706	0.405802299290	1.204039669392
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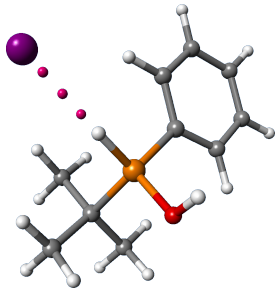
C	−2.979100479239	0.196531876567	2.519574941242
C	−0.681069393521	0.863138818827	2.188020193707
C	−1.606840304627	−1.010853566501	0.933545487650
C	−2.826433351409	−0.827797562495	1.581950347904
C	−1.908956698786	1.040277812034	2.823129525715
H	0.153522417546	1.511745768122	2.438634192197
H	−1.491586749843	−1.820608674880	0.218855302287
H	−3.655574961383	−1.490923520759	1.357001063184
H	−2.025213917852	1.828800939303	3.559963693038
H	−3.932558019130	0.332007879054	3.021290587925
C	1.144779521633	0.393213858757	−1.273024627219
C	0.044192465642	−0.186426346676	−2.179126130375
H	0.133981840711	−1.269984456907	−2.297928839501
H	0.138360451368	0.268175855893	−3.171082655170
H	−0.957293867064	0.040933939527	−1.802983821490

C	0.961673609635	1.916283318605	−1.102638151488
H	1.737205473289	2.359076074650	−0.468335387390
H	−0.018062098514	2.171267860727	−0.686749411311
H	1.033802453981	2.385586148851	−2.089327301039
C	2.543226743976	0.074101393165	−1.840122961217
H	2.691196119000	−0.999547405494	−1.979669519367
H	3.346540541941	0.455479467216	−1.199931640358
H	2.639537892545	0.558141156861	−2.817515625334
O	1.650701500077	−1.813094338744	0.508574355958
H	1.177262442024	−2.560349744333	0.001495885586
I	0.197991171615	−4.321802903609	−1.105745559116

^{t}BuPhP(HI)OH (C_1, N_{imag} = 0)



P	0.985894262519	0.272709653993	0.330136562721
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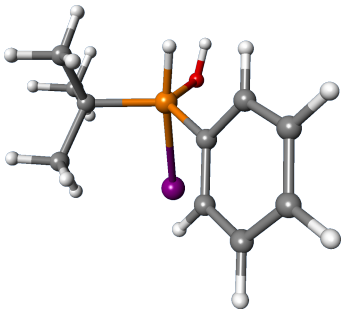
C	−0.595725807647	0.109124116001	1.161354721205
C	−3.026079497339	−0.218413840351	2.481773827891
C	−0.853458929815	−1.080256549467	1.864449043247
C	−1.551229226564	1.140838094578	1.131353158390
C	−2.763919273242	0.970429433144	1.793705017461
C	−2.074920645984	−1.239123962648	2.518177237297
H	−0.105104426203	−1.866338705055	1.911339961987
H	−1.345560953998	2.069754414697	0.608564277139
H	−3.503169117282	1.765083850899	1.776931283668
H	−2.275325201143	−2.155811977152	3.063412284029
H	−3.973307493615	−0.344896926731	2.997562690440
C	0.950621361129	0.098772900628	−1.503275593064
C	0.371677240223	−1.299744316196	−1.802226787411
H	0.959827827536	−2.096493246917	−1.335910735800
H	0.396410395665	−1.459099191544	−2.885280668397
H	−0.667707380094	−1.393297206105	−1.473944631794
C	0.086221569748	1.201420526818	−2.138856269292
H	0.465491831825	2.202254800588	−1.913062195139
H	−0.957542215348	1.138066310266	−1.817414219676
H	0.105969530504	1.074650044055	−3.226604784134
C	2.413711880177	0.191528238849	−1.987187296535
H	3.045592234478	−0.572024124022	−1.522921781130
H	2.849324189637	1.174097448303	−1.786935201788
H	2.430891870658	0.028290917336	−3.069870484604
O	1.598030940259	1.751735043917	0.586853399796
H	1.870267189932	1.904247595024	1.508585289010
I	3.318835405282	−2.638639613053	1.862352416683

^{t}BuPhP(H)(I)OH at B3LYP/S (C_1, N_{imag} = 0)



P	0.9578828740	−0.5195755403	0.3198267509
H	1.4506065196	0.6603022385	0.9642954118
C	−0.6635547399	−0.3793649405	1.1834316204
C	−3.0636685662	0.0490901725	2.5716407449
C	−0.6940913490	0.4402145681	2.3252653910
C	−1.8526860493	−0.9798474285	0.7440870384
C	−3.0450165644	−0.7528777449	1.4288821795
C	−1.8844922293	0.6412929354	3.0229615174
H	0.2136382353	0.9215753175	2.6767161836
H	−1.8354394021	−1.6394621211	−0.1148110781
H	−3.9600497379	−1.2167754571	1.0736886049
H	−1.8888191992	1.2643585373	3.9121629436
H	−3.9935965772	0.2096603229	3.1092000976
C	1.0833622348	0.2567536043	−1.4313661671
C	−0.1492835935	−0.0331001099	−2.3002761795
H	−0.2811830995	−1.1008798331	−2.4764469657
H	−0.0127690245	0.4622986263	−3.2683695181
H	−1.0635943186	0.3652882469	−1.8496768507
C	1.1964584076	1.7808223008	−1.2142457861
H	2.1038550755	2.0562299600	−0.6689057992
H	0.3339360884	2.1844477348	−0.6736252488
H	1.2330709875	2.2732421726	−2.1919527431
C	2.3645975119	−0.2828789829	−2.0887595488
H	2.3094357608	−1.3631643984	−2.2376284102
H	3.2560910324	−0.0614636457	−1.4927381085
H	2.4883152945	0.1997571521	−3.0648978107
O	2.2123177201	−1.4136008040	0.9379569490
H	2.7617347679	−0.8266229441	1.4873052526
I	0.4229409404	−3.1957209394	−0.6837204710

H) X-Ray Structures

a) X-ray crystal structure determination of (R)-tert-butyl((S)-hydroxy(p-tolyl)methyl)(phenyl)phosphine oxide

$C_{18}H_{23}O_2P$, Fw = 302.33, colourless needle, 0.48 × 0.18 × 0.06 mm^3, monoclinic, $P2_1$ (no. 4), a = 8.8020(7), b = 10.1477(8), c = 10.3699(8) Å, β = 114.980(2) º, V = 839.59(11) Å^3, Z = 2, D_x = 1.196 g/cm^3, μ = 0.17 mm^{-1}. 11820 Reflections were measured on a Bruker Kappa ApexII diffractometer with sealed tube and Triumph monochromator (λ = 0.71073 Å) at a temperature of 150(2) K up to a resolution of $(\sin \theta/\lambda)_{max}$ = 0.65 Å^{-1}. Intensity data were integrated with the Saint software.[SI8] Absorption correction and scaling was performed with SADABS[SI9] based on multiple measured reflections (correction range 0.69-0.75). 3775 Reflections were unique (R_{int} = 0.026), of which 3256 were observed [I>2σ(I)]. The structure was solved with Direct Methods using the program SHELXS-97[SI10]. Least-squares refinement was performed with SHELXL-97[SI10] against F^2 of all reflections. Non-hydrogen atoms were refined freely with anisotropic displacement parameters. All hydrogen atoms were located in difference Fourier maps. The hydrogen atom of the O-H group was refined freely with an isotropic displacement parameter, C-H hydrogen atoms were refined with a riding model. 199 Parameters were refined with one restraint (floating origin). R1/wR2 [I > 2σ(I)]: 0.0328 / 0.0737. R1/wR2 [all refl.]: 0.0461 / 0.0795. S = 1.023. Flack parameter[SI11] x = 0.03(8). Residual electron density between -0.17 and 0.32 e/Å^3. Geometry calculations and checking for higher symmetry was performed with the PLATON program[SI12].

CCDC 953762 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S2: Hydrogen bonding geometry in (R)-tert-butyl((S)-hydroxy(p-tolyl)methyl)(phenyl)phosphine oxide

D-H...A	D-H [Å]	H...A [Å]	D....A [Å]	D-H...A [º]
O2-H2...O1^i	0.85(2)	1.77(3)	2.6042(19)	168(2)

Symmetry operation *i*: 1-x, y+0.5, -z.

By intermolecular hydrogen bonding, the molecules form an infinite one-dimensional chain along the *b*-axis.

I) References

[SI1] *Gaussian 09, Revision A.02*, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[SI2] a) E. P. A. Couzijn, D. W. F. van den Engel, J. C. Slootweg, F. J. J. de Kanter, A. W. Ehlers, M. Schakel, K. Lammertsma, *J. Am. Chem. Soc.* **2009**, *131*, 3741–3751; b) E. P. A. Couzijn, J. C. Slootweg, A. W. Ehlers, K. Lammertsma, *J. Am. Chem. Soc.* **2010**, *132*, 18127–18140.

[SI3] S. Huzinaga, J. Anzelm, M. Klobukowski, E. Radzio-Andzelm, Y. Sakai, H. Tatewaki in *Gaussian Basis Sets for Molecular Calculations*, Elsevier, Amsterdam, **1984**.

[SI4] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B* **2009**, *113*, 6378–6396.

[SI5] M. N. Glukhovtsev, A. Pross, M. P. McGrath, L. Radom, *J. Chem. Phys.* **1995**, *103*, 1878–1885.

[SI6] At the B3LYP/S level of theory (i.e. without solvation) only one stereoisomer could be located, having a trigonal bipyramidal geometry around phosphorus with the hydrogen and iodine atoms in the apical positions. However, full racemization via stereomutations would involve at least four other trigonal bipyramidal configurational isomers;[40] as these appear not to exist, such a pathway must be discarded.

[SI7] N. E. Schultz, Y. Zhao, D. G. Truhlar, *J. Phys. Chem. A* **2005**, *109*, 11127–11143.

[SI8] Bruker (2001). SAINT-Plus. Bruker AXS Inc., Madison, Wisconsin, USA.

[SI9] Sheldrick, G. M. (1999). SADABS: Area-Detector Absorption Correction, Universität Göttingen, Germany.

[SI10] G. M. Sheldrick, Acta Cryst. 2008, A64, 112-122.

[SI11] H. D. Flack, Acta Cryst. 1983, A39, 876-881.

[SI12] A.L. Spek, Acta Cryst. (2009). D65, 148-155.