Supporting Information

Resolution of aryl-*H*-phosphinates applied in the synthesis of P-stereogenic compounds including a Brønsted acid NMR solvating agent

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1. General methods (instruments)

The (*S*)-alanine, 2-amino-1-phenylethanol (**8**), 2-amino-1-phenylpropan-1-ol (**7**), 2-amino-3-phenylpropan-1-ol (**10**), benzyl alcohol, (*S*)-1,1′-bi(2-naphthol), (1*S*)-3-bromocamphor-10-sulfonic acid, (1*S*)-10-camphorsulphonic acid, carbon tetrachloride, (*R*)-2-chloromandelic acid, (+)-cinchonine, *c*-heptanol, *c*-hexanol, *O*,*O*′-dibenzoyl-(*R*,*R*)-tartaric acid, *O*,*O*′-di-(4-toluoyl)-(*R*,*R*)-tartaric acid, iodomethane, (1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexanol, methyl-*c*-hexanol, 1-naphthylethylamine (**6**), *n*-butyllithium solution (2.5 M in hexane), (*R*)-phencyphos hydrate, (*S*)-phenylalanine, (*S*)-1-phenylethylamine, (*S*)-α-phenylglycine, phenylglycinol (**9**), phenyl-*H*-phosphinic acid (**4**), sodium hydride, sulfur, (*R*,*R*)-tartric acid and *t*-butanol were purchased from Merck Chemicals Ltd. The 2-adamantanol, 4-bromoanisole, 4-bromobenzotrifluoride, 1-bromonapthalene, 2-bromonapthalene, 2-bromotoluene, 3-bromotoluene, 4-bromotoluene, *c*-pentanol, 2,4-dimethyl-3-pentanol, *N*-(3-dimethylaminopropyl)-*N*′-ethylcarbodiimide hydrochloride (EDC·HCl) and 2,4,6- triisopropylbenzenesulfonyl chloride were purchased from Fluorochem Ltd. The 1-adamantanol and *t*-butylmagnesium chloride solution (2M in THF) were purchased from Tokyo Chemical Industry Ltd. The 5% Rh/C catalyst was purchased from Alfa Aesar - Thermo Fisher Scientific Inc.

The calcium hydrogen *O*,*O*′-dibenzoyl-(*R*,*R*)-tartrate, calcium hydrogen *O*,*O*′-di-(4-toluoyl)-(*R*,*R*)-tartrate,[1,2] diethyl (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate, ((4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis(diphenylmethanol) [(*R*,*R*)-**2a**], ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(diphenylmethanol) [(*R*,*R*)-**2b**],[3] ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(bis(4-(*tert*-butyl)phenyl)methanol) [(*R*,*R*)-**2c**],[4] ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(di(naphthalen-1-yl)methanol) [(*R*,*R*)-**2e**],[3] ((2*R*,3*R*,10*R*,11*R*)-1,4,9,12-tetraoxadispiro[4.2.4^8.2^5]tetradecane-2,3,10,11-tetrayl)tetrakis(diphenylmethanol) [(*R*,*R*)-**2g**],[5] dicloro-adamantyloxyphosphine (**5**),[6] *t*-butyl-phenylphosphine oxide (**11**), *c*-hexyl-phenylphosphine-oxide (**12**) and butyl-phenylphosphine-oxide (**13**)[7] were synthesized as described in the literature, and their analytical data were identical to the ones reported.

The solvents were purchased from Merck Chemicals Ltd., and they were purified according to the standard procedures.[8] Dry solvents were stored over 3Å or 4Å molecular sieves.

The ^{31}P, ^{19}F, ^{13}C, ^{1}H NMR spectra were taken on a Bruker AV-300 or DRX-500 spectrometer operating at 121.5, 282.4, 75.5 and 300 or 202.5, 470.6, 125.8 and 500 MHz, respectively. The chemical shifts (δ) are given in parts per million (ppm). The chemical shifts (δ) for ^{1}H and ^{13}C in $CDCl_3$ and referenced to 7.26 and 77.16 ppm, respectively. 85% Solution of H_3PO_4 was the external reference for ^{31}P NMR chemical shifts. Coupling constants are expressed in Hertz (Hz). The following abbreviations are used: s = singlet, bs = broad singlet, d = doublet, t = triplet, q = quadruplet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets.

The exact mass measurements were performed using an Agilent 6230C TOF LCMS System with Agilent Jet Stream source in positive ESI mode (Buffer: ammonium-formate in water / acetonitrile; Drying gas: 325 °C; Capillary: 3000 V; Fragmentor 100 V).

LCMS measurements were performed using an Agilent 1100 and Agilent 6130 LCMS system in positive and negative electrospray mode.

The stainless steel autoclave was a product of Technoclave Inc (Hungary).

Melting points were obtained on a melting point apparatus and are uncorrected.

Thin layer chromatography (TLC) was performed on Merck pre-coated Silica gel 60 F_{254} aluminium plates with realization by UV irradiation.

Column chromatography was performed on Silica gel 60 with a particle size of 0.063-0.200 mm supplied by Merck. Flash column chromatography was performed using a Combi-Flash® (Teledyne ISCO) using gradient elution in normal (Silica gel column; hexane−ethyl acetate).

The syntheses involving organometallic reagents were carried out under a nitrogen atmosphere in *Schlenk*-type reaction vessels.[9]

The enantiomeric excess (*ee*) values of compounds **1a-o** and **3a-d** were determined by chiral HPLC on a Perkin Elmer Series 200 instrument using normal phase mode equipped with Kromasil® 5-Amycoat, Phenomenex Lux ® 5µm Amylose-2, Phenomenex Lux ® 5µm Cellulose-1, Phenomenex Lux ® 5µm Cellulose-2 or Phenomenex Lux ® 3µm Cellulose-4 columns. All columns had the dimensions of 250 × 4.6 mm. A mixture of hexane-ethanol was used as the eluent with a flow rate of 0.8 mL/min (T = 20°C, UV detector α = 254 nm). The exact chromatographic parameters of the normal phase chiral HPLC are detailed in Table S12.

The enantiomeric excess (*ee*) values of **3f** were determined by ^{31}P NMR using 6.2 mg (20 µmol) of the analyte, 3.9 µL (30 µmol) (*S*)-1-phenylethylamine as CSA and 750 µL $CDCl_3$ as solvent.

Optical rotations were determined on a Perkin–Elmer 341 polarimeter.

For the single crystal structure determination, the intensity data were collected on a Rigaku RAXIS-RAPID II diffractometer (using graphite monochromator; Mo-Kα radiation, λ= 0.71075Å) in case of crystals. The crystals were measured with fiber. Crystal Clear (developed

by Rigaku Company) software were used for data collection and refinement.[10] Numerical and empirical absorption corrections were applied to the data.[11] The structures were solved by direct methods. Anisotropic full-matrix least-squares refinements were performed on F^2 for all non-hydrogen atoms. Hydrogen atoms bonded to C atoms were placed in calculated positions and refined in a riding-model approximation. The computer programs used for the structure solution, refinement and analysis of the structures were Shelx,[12,13] Sir2014,[14] Wingx,[15] Platon,[16-18] and Crystal Explorer.[19-21] Details of crystallographic data, data collection and refinement for the crystals are collected in Table S11.

2. Preparation of racemic *H*-phosphinates (1a-p) and TADDOL-derivatives [(*R*,*R*)-2d and (*R*,*R*)-2f)

2.1. Preparation of phenyl-*H*-phosphinates (1a-j)

2.1.1. Preparation of 1-adamantyl phenyl-*H*-phosphinate (1a) (Representative procedure I.)

The phenyl-*H*-phosphinates (**1a-j**) were synthesized by a modified procedure of *Morales et. al.*[22]

To a solution of 8.0 g (56.3 mmol) of phenyl-*H*-phosphinic acid (**4**) and 8.6 g (56.3 mmol) of 1-adamantanol in 160 mL of anhydrous DCM, 21.6 g (113 mmol) of EDC·HCl was added in 10 portions over 30 min under nitrogen atmosphere at 25°C. The resulting solution was stirred at this temperature for an additional 2 hours. Then, it was washed with 2 M HCl solution (2 × 160 mL), and the aqueous phases were combined and extracted with DCM (3 × 160 mL). The organic layers were combined, dried (Na_2SO_4) and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 12.4 g (80%) of 1-adamantyl phenyl-*H*-phosphinate (**1a**) as a white solid.

mp.: 70-72°C; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 14.3 (δ_{lit} 14.1);[23] ^1H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 553.6, 1H), 7.82 – 7.74 (m, 2H), 7.59 – 7.45 (m, 3H), 2.22 (bs, 3H), 2.14 (bs, 6H), 1.66 (bs, 6H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 132.6 (d, J = 3.0), 131.9 (d, J = 137.9), 131.0 (d, J = 11.6), 128.6 (d, J = 13.9), 82.8 (d, J = 8.5), 44.3 (d, J = 4.7), 35.8, 31.3; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}O_2P$ 277.1357; Found 277.1354.

2.1.2. Preparation of 2-adamantyl phenyl-*H*-phosphinate (1b)

The 2-adamantyl phenyl-*H*-phosphinate (**1b**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 1.1 g (7.0 mmol) of 2-adamantanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.7 g (90%) of 2-adamantyl phenyl-*H*-phosphinate (**1b**) as a dense clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 21.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 – 7.78 (m, 2H), 7.68 (d, *J* = 557.2, 1H), 7.60 – 7.57 (m, 1H), 7.52 – 7.49 (m, 2H), 4.66 – 4.63 (m, 1H), 2.19 – 2.03 (m, 4H), 1.91 – 1.81 (m, 4H), 1.76 – 1.68 (m, 4H), 1.63 – 1.52 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 133.0 (d, *J* = 2.9), 131.0 (d, *J* = 11.8), 130.9 (d, *J* = 134.2), 128.8 (d, *J* = 13.9), 80.8 (d, *J* = 6.7), 37.4, 36.4, 33.9 (d, *J* = 3.9), 33.5 (d, *J* = 3.6), 31.4, 31.3, 27.3, 27.0, 26.9; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}O_2P$ 277.1357; Found 277.1353.

2.1.3. Preparation of *c*-pentyl phenyl-*H*-phosphinate (1c)

The *c*-pentyl phenyl-*H*-phosphinate (**1c**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.64 mL (7.0 mmol) of *c*-pentanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to hexane – EtOAc 50% : 50%) to give 1.3 g (85%) of *c*-pentyl phenyl-*H*-phosphinate (**1c**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 22.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.58 (d, *J* = 559.6, 1H), 7.59 – 7.56 (m, 1H), 7.49 (td, *J* = 7.58, 3.44, 2H), 4.95 – 4.90 (m, 1H), 1.97 – 1.72 (m, 6H), 1.66 – 1.54 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 133.0 (d, *J* = 2.9), 131.0 (d, *J* = 11.7), 130.6 (d, *J* = 133.0), 128.8 (d, *J* = 13.8), 80.0 (d, *J* = 6.8), 34.4 (d, *J* = 4.8), 34.1 (d, *J* = 4.2), 23.2, 23.1; HRMS (ESI/TOF) m/z: $[M + Na]^+$ Calcd for $C_{11}H_{15}NaO_2P$ 233.0707; Found 233.0702.

2.1.4. Preparation of *c*-hexyl phenyl-*H*-phosphinate (1d)

The *c*-hexyl phenyl-*H*-phosphinate (**1d**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.73 mL (7.0 mmol) of *c*-hexanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution,

100% hexane to 100% EtOAc) to give 1.5 g (97%) of *c*-hexyl phenyl-*H*-phosphinate (**1d**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 22.0 (δ_{lit} 22.0);[24] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 – 7.76 (m, 2H), 7.63 (d, *J* = 559.0, 1H), 7.59 – 7.56 (m, 1H), 7.51 – 7.47 (m, 2H), 4.47 – 4.40 (m, 1H), 2.04 – 1.99 (m, 1H), 1.92 – 1.87 (m, 1H), 1.78 – 1.49 (m, 5H), 1.39 – 1.21 (m, 3H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 133.0 (d, *J* = 3.0), 131.0 (d, *J* = 11.8), 130.8 (d, *J* = 133.4), 128.8 (d, *J* = 13.8), 76.3 (d, *J* = 6.5), 34.0 (d, *J* = 4.2), 33.6 (d, *J* = 3.7), 25.2, 23.7; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{12}H_{18}O_2P$ 225.1044; Found 225.1039.

2.1.5. Preparation of (1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexyl phenyl-*H*-phosphinate (1e)

The (1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1e**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 1.1 g (7.0 mmol) of (1*R*,2*S*,5*R*)-menthol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to hexane – EtOAc 50% : 50%) to give 1.9 g (94%) of (1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1e**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (Diastereomer A, 202.5 MHz, $CDCl_3$) δ 24.6 (δ_{lit} 25.2);[25] $^{31}P\{^{1}H\}$ NMR (Diastereomer B, 202.5 MHz, $CDCl_3$) δ 21.2 (δ_{lit} 21.9);[25] ^{1}H NMR (Diastereomer A, 500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H, overlap), 7.65 (d, *J* = 552.9, 1H), 7.60 – 7.56 (m, 1H, overlap), 7.52 – 7.48 (m, 2H, overlap), 4.31 – 4.21 (m, 1H, overlap), 2.30 – 2.07 (m, 2H, overlap), 1.71 – 1.64 (m, 2H, overlap), 1.51 – 1.36 (m, 2H, overlap), 1.31 – 1.20 (m, 1H, overlap), 1.08 – 0.85 (m, 11H, overlap); ^{1}H NMR (Diastereomer B, 500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H, overlap), 7.67 (d, *J* = 556.2, 1H), 7.60 – 7.56 (m, 1H, overlap), 7.52 – 7.48 (m, 2H, overlap), 4.31 – 4.21 (m, 1H, overlap), 2.30 – 2.07 (m, 2H, overlap), 1.71 – 1.64 (m, 2H, overlap), 1.51 – 1.36 (m, 2H, overlap), 1.31 – 1.20 (m, 1H, overlap), 1.08 – 0.85 (m, 8H, overlap); 0.67 (d, *J* = 6.9, 3H); $^{13}C\{^{1}H\}$ NMR (Diastereomers A and B, 125.8 MHz, $CDCl_3$) δ 133.0 (d, *J* = 3.3 Hz), 133.0 (d, *J* = 3.0 Hz), 131.2 (d, *J* = 135.1 Hz), 130.9 (d, *J* = 12.0 Hz), 130.8 (d, *J* = 11.8 Hz), 130.7 (d, *J* = 134.5 Hz), 128.8 (d, *J* = 14.1 Hz), 79.1 (d, *J* = 7.1 Hz), 77.8 (d, *J* = 7.2 Hz), 48.9 (d, *J* = 6.1 Hz), 48.7 (d, *J* = 6.1 Hz), 43.7, 42.6 (d, *J* = 1.7 Hz), 34.1, 34.1, 31.8, 31.7, 25.9, 25.7, 23.1, 22.1, 22.0, 21.1, 21.0, 15.9, 15.7; HRMS (ESI/TOF) m/z: $[M + Na]^+$ Calcd for $C_{16}H_{26}O_2P$ 303.1490; Found 303.1486.

2.1.6. Preparation of *c*-heptyl phenyl-*H*-phosphinate (1f)

The *c*-heptyl phenyl-*H*-phosphinate (**1f**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.85 mL (7.0 mmol) of *c*-heptanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.6 g (95%) of *c*-heptyl phenyl-*H*-phosphinate (**1f**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 22.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.75 (m, 2H), 7.61 (d, J = 558.0, 1H), 7.59 – 7.56 (m, 1H), 7.51 – 7.47 (m, 2H), 4.65 – 4.58 (m, 1H), 2.08 – 2.02 (m, 1H), 1.97 – 1.78 (m, 3H), 1.74 – 1.34 (m, 8H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 133.0 (d, J = 3.0), 131.0 (d, J = 11.8), 130.8 (d, J = 133.5), 128.8 (d, J = 13.8), 78.9 (d, J = 6.8), 36.2 (d, J = 4.1), 35.8 (d, J = 3.6), 28.1, 22.3 (d, J = 3.8); HRMS (ESI/TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{19}NaO_2P$ 261.1020; Found 261.1016.

2.1.7. Preparation of 1-methyl-*c*-hexyl phenyl-*H*-phosphinate (1g)

The (1-methyl-*c*-hexyl) phenyl-*H*-phosphinate (**1g**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.88 mL (7.0 mmol) of 1-methyl-*c*-hexanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to hexane – EtOAc 50% :50%) to give 0.72 g (43%) of 1-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1g**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 14.5; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, J = 550.5, 1H), 7.79 – 7.74 (m, 2H), 7.56 – 7.52 (m, 1H), 7.49 – 7.45 (m, 2H), 2.07 – 2.01 (m, 2H), 1.72 – 1.46 (m, 11H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 132.6 (d, J = 2.9), 132.0 (d, J = 139.5), 130.8 (d, J = 11.7), 128.7 (d, J = 13.9), 85.0 (d, J = 8.4), 39.3 (d, J = 4.5), 38.7 (d, J = 5.1), 28.0, 25.2, 22.5, 22.3; HRMS (ESI/TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{19}NaO_2P$ 261.1020; Found 261.1016.

2.1.8. Preparation of *t*-butyl phenyl-*H*-phosphinate (1h)

The *t*-butyl phenyl-*H*-phosphinate (**1h**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.67 mL (7.0 mmol) of *t*-butanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution,

100% hexane to 100% EtOAc) to give 1.1 g (80%) of *t*-butyl phenyl-*H*-phosphinate (**1h**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 15.2; (δ_{lit} 15.2);[26] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 – 7.73 (m, 2H), 7.73 (d, *J* = 552.7, 1H), 7.57 – 7.54 (m, 1H), 7.50 – 7.46 (m, 2H), 1.56 (s, 9H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 132.7 (d, *J* = 3.1), 131.7 (d, *J* = 138.7), 130.9 (d, *J* = 11.6), 128.7 (d, *J* = 14.0), 83.3 (d, *J* = 8.2), 30.5 (d, *J* = 4.7); HRMS (ESI/TOF) m/z: $[2 \times M + H]^+$ Calcd for $C_{20}H_{31}O_4P$ 397.1698; Found 397.1697.

2.1.9. Preparation of 2,4-dimethyl-pent-3-yl phenyl-*H*-phosphinate (1i)

The 2,4-dimethyl-pent-3-yl phenyl-*H*-phosphinate (**1i**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.99 mL (7.0 mmol) of 2,4-dimethyl-3-pentanol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.4 g (81%) of 2,4-dimethyl-pent-3-yl phenyl-*H*-phosphinate (**1i**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 26.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 14.0, 7.5, 2H), 7.70 (d, *J* = 556.8, 1H), 7.58 (t, *J* = 7.5, 1H), 7.52 – 7.48 (m, 2H), 4.08 (dt, *J* = 11.6, 5.6, 1H), 2.08 – 2.01 (m, 1H), 1.98 – 1.91 (m, 1H), 1.02 (d, *J* = 6.7, 6H), 0.94 (d, *J* = 6.7, 6H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 132.9 (d, *J* = 2.8), 131.5 (d, *J* = 136.2), 130.7 (d, *J* = 11.6), 128.8 (d, *J* = 14.0), 88.4 (d, *J* = 8.2), 30.8 (d, *J* = 3.3), 30.4 (d, *J* = 3.2), 20.4, 20.0, 17.8, 17.7; HRMS (ESI/TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{21}NaO_2P$ 263.1177; Found 263.1171.

2.1.10. Preparation of benzyl phenyl-*H*-phosphinate (1j)

The benzyl phenyl-*H*-phosphinate (**1j**) was prepared according to Representative Procedure I. described in Section 2.1.1. by reacting 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**), 0.73 mL (7.0 mmol) of benzyl alcohol and 2.7 g (14.0 mmol) of EDC·HCl in 20 mL of anhydrous DCM. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.4 g (86%) of benzyl phenyl-*H*-phosphinate (**1j**) as a clear oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 25.0 (δ_{lit} 25.6);[27] ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 – 7.76 (m, 2H), 7.64 (d, *J* = 566.1, 1H), 7.62 – 7.58 (m, 1H), 7.52 – 7.48 (m, 2H), 7.40 – 7.33 (m, 5H), 5.18 – 5.05 (m, 2H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 135.7 (d, *J* = 6.7), 133.3 (d, *J* = 3.0), 131.1 (d, *J* = 11.9), 129.8 (d, *J* = 131.9), 128.9 (d, *J* = 14.1), 128.8, 128.8, 128.2, 67.3

(d, J = 6.3); HRMS (ESI/TOF) m/z: $[M + Na]^+$ Calcd for $C_{13}H_{13}NaO_2P$ 255.0551; Found 255.0546.

2.2. Preparation of 1-adamantyl aryl-*H*-phosphinates (1k-p)

2.2.1. Preparation of 1-adamantyl (2-methylphenyl)-*H*-phosphinate (1k) (Representative Procedure II.)

The 1-adamantyl *H*-phosphinates (**1k-p**) were synthesized by a modified procedure of *Leclaire, Giordano et. al.*[6]

Under nitrogen atmosphere, a solution of 10 mmol of (2-methylphenyl)magnesium bromide in 15 mL of anhydrous THF was added dropwise over 4 hours to a solution of 2.5 g (10 mmol) of dichloro-1-adamantyloxyphosphine (**5**) in 5 mL of anhydrous THF at -50°C. [The (2-methylphenyl)magnesium bromide was prepared by from 1.2 mL (10 mmol) of 2-bromotoluene and 0.27 g (11 mmol) of Mg in 15 mL of anhydrous THF.] The reaction mixture was stirred for 1 hour at -50°C. Then, it was allowed to warm to 25°C, and it was stirred overnight. After that, 10 mL of water was added at 0°C, and the reaction mixture was stirred for 30 min at the same temperature. The phases were separated, the aqueous layer was extracted with DCM (3 × 20 mL). The organic layers were combined, dried (Na_2SO_4) and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 2.0 g (69%) of 1-adamantyl (2-methylphenyl)-*H*-phosphinate (**1k**) as a white solid.

mp.: 49-50°C; $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 15.2 (δ_{lit} 15.2);[6] ^1H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, J = 547.4, 1H), 7.81 – 7.76 (m, 1H), 7.44 – 7.40 (m, 1H), 7.31 – 7.27 (m, 1H), 7.23 – 7.21 (m, 1H), 2.55 (s, 3H), 2.21 (bs, 3H), 2.14 (bs, 6H), 1.65 (bs, 6H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$) δ 140.9 (d, J = 10.6), 132.5 (d, J = 2.8), 131.7 (d, J = 13.0), 131.1 (d, J = 12.1), 130.0 (d, J = 136.9), 125.8 (d, J = 14.4), 82.7 (d, J = 8.5), 44.2 (d, J = 4.7), 35.9, 31.9, 20.2 (d, J = 6.7); HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}O_2P$ 291.1514; Found 291.1513.

2.2.2. Preparation of 1-adamantyl (3-methylphenyl)-*H*-phosphinate (1l)

The 1-adamantyl (3-methylphenyl)-*H*-phosphinate (**1l**) was prepared according to Representative Procedure II. described in Section 2.2.1. by reacting 2.5 g (10 mmol) of dichloro-1-adamantyloxyphosphine (**5**) in 5 mL of anhydrous THF with 10 mmol of (3-methylphenyl)magnesium bromide in 15 mL of anhydrous THF at -50°C.

[The (3-methylphenyl)magnesium bromide was prepared by from 1.2 mL (10 mmol) of 3-bromotoluene and 0.27 g (11 mmol) of Mg in 15 mL of anhydrous THF.] The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 2.1 g (74%) of 1-adamantyl (3-methylphenyl)-*H*-phosphinate (**1l**) as a white solid.

mp.: 82-84°C; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 14.7; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 551.9, 1H), 7.59 – 7.52 (m, 2H), 7.38 – 7.33 (m, 2H), 2.39 (s, 3H), 2.20 (bs, 3H), 2.13 (d, *J* = 3.0, 6H), 1.65 (t, *J* = 3.1, 6H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 138.5 (d, *J* = 13.8), 133.4 (d, *J* = 3.1), 131.7 (d, *J* = 137.5), 131.4 (d, *J* = 11.7), 128.6 (d, *J* = 14.7), 128.0 (d, *J* = 11.7), 82.6 (d, *J* = 8.6), 44.3 (d, *J* = 4.7), 35.8, 31.3, 21.5; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}O_2P$ 291.1514; Found 291.1510.

2.2.3. Preparation of 1-adamantyl (4-methylphenyl)-*H*-phosphinate (1m)

The 1-adamantyl (4-methylphenyl)-*H*-phosphinate (**1m**) was prepared according to Representative Procedure II. described in Section 2.2.1. by reacting 2.5 g (10 mmol) of dichloro-1-adamantyloxyphosphine (**5**) in 5 mL of anhydrous THF with 10 mmol of (4-methylphenyl)magnesium bromide in 15 mL of anhydrous THF at -50°C. [The (4-methylphenyl)magnesium bromide was prepared by from 1.2 mL (10 mmol) of 4-bromotoluene and 0.27 g (11 mmol) of Mg in 15 mL of anhydrous THF.] The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.7 g (59%) of 1-adamantyl (4-methylphenyl)-*H*-phosphinate (**1m**) as a white solid.

mp.: 85-87°C; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 14.6; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 552.5, 1H), 7.65 (dd, *J* = 13.7, 7.8 2H), 7.28 (dd, *J* = 8.0, 3.3, 2H), 2.40 (s, 3H), 2.20 (bs, 3H), 2.12 (bs, 6H), 1.65 (bs, 6H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 143.1 (d, *J* = 3.0), 131.0 (d, *J* = 12.1), 129.4 (d, *J* = 14.4), 128.8 (d, *J* = 140.2), 82.5 (d, *J* = 8.5), 44.3 (d, *J* = 4.7), 35.9, 31.3, 21.8; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}O_2P$ 291.1514; Found 291.1513.

2.2.4. Preparation of 1-adamantyl (4-methoxyphenyl)-*H*-phosphinate (1n)

The 1-adamantyl (4-methoxyphenyl)-*H*-phosphinate (**1n**) was prepared according to Representative Procedure II. described in Section 2.2.1. by reacting 2.5 g (10 mmol) of dichloro-1-adamantyloxyphosphine (**5**) in 5 mL of anhydrous THF with 10 mmol of

(4-methoxyphenyl)magnesium bromide in 15 mL of anhydrous THF at -50°C. [The (4-methoxyphenyl)magnesium bromide was prepared by from 1.3 mL (10 mmol) of 4-bromoanisol and 0.27 g (11 mmol) of Mg in 15 mL of anhydrous THF.] The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.5 g (50%) of 1-adamantyl (4-methoxyphenyl)-*H*-phosphinate (**1n**) as a white solid.

mp.: 101-104°C; $^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 14.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, *J* = 553.0, 1H), 7.72 – 7.67 (m, 2H), 6.98 – 6.96 (m, 2H), 3.84 (s, 3H), 2.20 (s, 3H), 2.11 (d, *J* = 3.0, 6H), 1.65 (t, *J* = 3.1, 6H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 163.1 (d, *J* = 3.1), 133.0 (d, *J* = 12.9), 123.3 (d, *J* = 144.3), 114.2 (d, *J* = 14.8), 82.4 (d, *J* = 8.4), 55.5, 44.3 (d, *J* = 4.6), 35.9, 31.2 HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{17}H_{24}O_3P$ 307.1463; Found 307.1457.

2.2.5. Preparation of 1-adamantyl (1-naphthyl)-*H*-phosphinate (1o)

The 1-adamantyl (1-naphthyl)-*H*-phosphinate (**1o**) was prepared according to Representative Procedure II. described in Section 2.2.1. by reacting 2.5 g (10 mmol) of dichloro-1-adamantyloxyphosphine (**5**) in 5 mL of anhydrous THF with 10 mmol of (1-naphthyl)magnesium bromide in 15 mL of anhydrous THF at -50°C. [The (1-naphthyl)magnesium bromide was prepared by from 1.4 mL (10 mmol) of 1-bromonaphthalene and 0.27 g (11 mmol) of Mg in 15 mL of anhydrous THF.] The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.8 g (57%) of 1-adamantyl (1-naphthyl)-*H*-phosphinate (**1o**) as a dense oil.

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$) δ 16.0; ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.4, 1H), 8.12 (d, *J* = 554.6, 1H), 8.10 – 8.03 (m, 2H), 7.92 – 7.90 (m, 1H), 7.63 – 7.54 (m, 3H), 2.22 – 2.18 (m, 9H), 1.66 (bs, 6H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 133.6 (d, *J* = 10.6), 133.5 (d, *J* = 3.1), 132.5 (d, *J* = 10.5), 131.9 (d, *J* = 12.8), 129.1 (d, *J* = 1.9), 128.0 (d, *J* = 135.1), 127.5, 126.6, 125.3 (d, *J* = 7.3), 124.9 (d, *J* = 16.4), 83.4 (d, *J* = 8.4), 44.3 (d, *J* = 4.6), 35.9, 31.3; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}O_2P$ 349.1333; Found 349.1326.

2.2.6. Preparation of 1-adamantyl *t*-butyl-*H*-phosphinate (1p)

The 1-adamantyl *t*-butyl-*H*-phosphinate (**1p**) was prepared according to Representative Procedure II. described in Section 2.2.1. by reacting 2.5 g (10 mmol) of dichloro-1-

adamantyloxyphosphine (**5**) in 5 mL of anhydrous THF with 5 mL (10 mmol) of 2M THF solution of (*t*-butyl)magnesium chloride at -50°C. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 1.8 g (71%) of 1-adamantyl *t*-butyl-*H*-phosphinate (**1p**) as a white solid.

mp.: 78-80°C; $^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$) δ 37.7 (δ_{lit} 37.5);[6] ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.88 (d, *J* = 509.8, 1H), 2.19 (bs, 3H), 2.03 (bs, 6H), 1.63 (s, 6H), 1.08 (d; *J* = 17.6, 9H); $^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$) δ 81.0 (d, *J* = 10.2), 44.0 (d, *J* = 4.3), 35.9, 31.2, 30.8 (d, *J* = 100.0), 23.0; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{26}O_2P$ 257.1670; Found 257.1669.

2.3. Preparation of TADDOL-derivatives (2d and 2f)

2.3.1. Preparation of (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(bis(4-(trifluoromethyl)phenyl)methanol [(*R*,*R*-2d] (Representative Procedure III.)

The TADDOL-derivatives (**2d** and **2f**) were synthesized by a modified procedure of *Seebach et. al.*[3]

Under nitrogen atmosphere, 2.5 g (8.7 mmol) of diethyl (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate in 15 mL of anhydrous THF was added to a solution of 44 mmol of (4-trifluoromethylphenyl)magnesium bromide in 35 mL of anhydrous THF over 30 min at 0°C. [The (4-trifluoromethylphenyl)magnesium bromide was prepared by from 6.2 mL (44 mmol) of 4-bromobenzotrifluoride and 1.2 g (48 mmol) of Mg in 35 mL of anhydrous THF.] The reaction mixture was refluxed for 4 hours, then it was allowed to cool to 25°C, and it was stirred overnight at the same temperature. Then 40 mL of saturated NH_4Cl and 20 mL of water was added. The phases were separated, and the aqueous layer was extracted with DCM (3 × 40 mL). The organic layers were combined, dried (Na_2SO_4) and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% $CHCl_3$) to give 4.9 g (72%) of ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(bis(4-(trifluoromethyl)phenyl)methanol) [(*R*,*R*-**2d**] as a white solid.

mp.: 178°C; $[\alpha]_D^{25}$ = –53.2 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (q, *J* = 8.6, 8H), 7.54 (d, *J* = 8.4, 4H), 8.28 (d, *J* = 8.3, 4H), 4.49 (s, 2H), 4.32 (s, 2H), 1.48 – 1.44 (m, 4H), 1.34 – 1.19 (m, 6H); $^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$) δ 148.6, 146.0, 130.3 (q, *J* = 32.6), 130.2 (q, *J* = 32.6), 128.8, 128.0, 125.5 (q, *J* = 3.7), 124.7 (q, *J* = 3.8), 124.2 (q, *J* = 272.2), 124.0 (q, *J* = 272.1), 111.0, 80.5, 78.0, 36.7, 24.9, 24.0; ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.5, -62.8.

2.3.2. Preparation of ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(di(naphthalen-2-yl)methanol) [(*R*,*R*)-2f]

The ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(di(naphthalen-2-yl)methanol) [(*R*,*R*)-**2f**] was prepared according to Representative Procedure III. described in Section 2.3.1. by reacting 2.5 g (8.7 mmol) of diethyl (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-dicarboxylate in 15 mL of anhydrous THF with 44 mmol of (2-naphthyl)magnesium bromide in 35 mL of anhydrous THF at 0°C. [The (2-naphthyl)magnesium bromide was prepared by from 9.1 g (44 mmol) of 2-bromonaphthalene and 1.2 g (48 mmol) of Mg in 35 mL of anhydrous THF.] The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% $CHCl_3$) to give 4.7 g (77%) of ((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(di(naphthalen-2-yl)methanol) [(*R*,*R*)-**2f**] as a white solid.
mp.: 197°C; $[\alpha]_D^{25}$ = –121.9 (*c* = 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.18 (s, 2H), 7.99 (s, 2H), 7.87 – 7.86 (m, 4H), 7.79 – 7.66 (m, 8H), 7.57 – 7.40 (m, 10H), 7.29 (dd, *J* = 8.8, 1.9, 2H), 4.90 (s, 2H), 4.43 (d, *J* = 7.9, 2H), 1.57 – 1.45 (m, 4H), 1.39 – 1.27 (m, 6H); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$) δ 142.9, 140.7, 132.9, 132.8, 132.8, 132.8, 128.8, 128.7, 128.0, 127.6, 127.5, 127.4, 127.2, 126.8, 126.3 (overlapping), 126.2, 126.1, 126.1, 126.1, 110.4, 81.1, 78.9, 36.9, 25.2, 24.2.

3. Representative resolution procedures and data

It was observed over the course of this research project that even the residual water content of the solvent may influence the outcome of the resolution in a negative manner. Thus, all solvents used for resolution were dried according to the standard procedures. Dry solvents were stored over molecular sieves 3Å or 4Å.

3.1. Resolving agent screening for the enantioseparation of 1-adamantyl phenyl-*H*-phosphinate (1a)

10 mg (0.036 mmol) of 1-Adamantyl phenyl-*H*-phosphinate (**1a**) was added to the hot solution of the corresponding resolving agent (0.5 equivalent, 0.018 mmol). Generally 30-100 μL was used from the corresponding solvent, but this amount was adjusted in a few instances to obtain a clear solution of the resolving agent.
The solution containing racemic **1a** and the corresponding resolving agent was allowed to cool to 25°C, and the diastreomers were allowed to crystallize without agitation. If crystals were

formed in the period of 1-7 days, they were collected by filtration. The enantiomeric mixture of 1-adamantyl phenyl-*H*-phosphinate (**1a**) was liberated by preparative TLC from *c.a.* 3 mg of the corresponding diastereomer. The enantiomeric excess values were measured by HPLC on a chiral stationary phase. Results are summarized in Fig. S1 and Table S1.

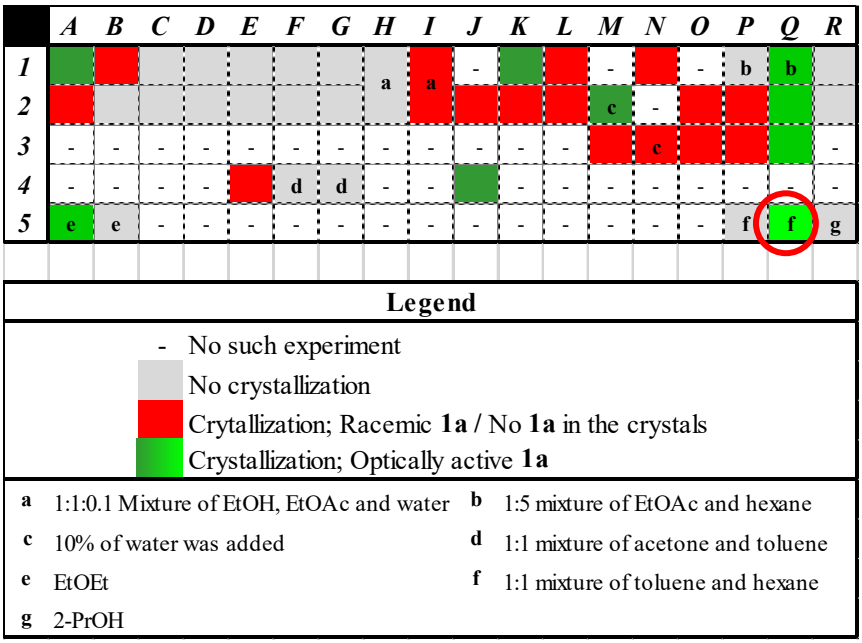


Fig. S1: 'Heat map'[28] of the resolving agent screening for the enantioseparation of 1-adamantyl phenyl-*H*-phosphinate (**1a**); resolving agents A-R and solvents 1-5 can be found in Table S1; the brightness of the green color indicates the relative ee values in the range of 2-39%; the best result is marked with a red circle.

Table S1: Resolving agents and solvents used during screening.

A: (*R*)-mandelic acid	**1**: EtOAc
B: (*R*)-2-chloromandelic acid	**2**: EtOH
C: (1*S*)-10-camphorsulphonic acid	**3**: MeOH
D: (1*S*)-3-bromocamphor-10-sulfonic acid	**4**: acetone
E: (*R*,*R*)-tartric acid	**5**: miscellaneous solvents, see footnote
F: *O*,*O*′-dibenzoyl-(*R*,*R*)-tartaric acid	
G: *O*,*O*′-di-(4-toluoyl)-(*R*,*R*)-tartaric acid	
H: calcium hydrogen *O*,*O*′-dibenzoyl-(*R*,*R*)-tartrate	
I: calcium hydrogen *O*,*O*′-di-(4-toluoyl)-(*R*,*R*)-tartrate	
J: (*R*)-phencyphos hydrate	
K: (*S*)-1-phenylethylamine	
L: (+)-cinchonine	
M: (*S*)-alanine	
N: (*S*)-α-phenylglycine	
O: (*S*)-phenylalanine	
P: (4*R*,5*R*)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)bis (diphenylmethanol) (TADDOL)	
Q: (2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis (diphenylmethanol) (spiro-TADDOL)	
R: (*S*)-1,1′-Bi(2-naphthol) (BINOL)	

3.2. Resolution of 1-adamantyl phenyl-*H*-phosphinate (1a) with 1-naphthyl-spiro-TADDOL [(*R*,*R*)-2e] (Representative procedure)

0.28 g (1.0 mmol) of Racemic 1-adamantyl phenyl-*H*-phosphinate (**1a**) and 0.70 g (1.0 mmol) of 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**] were dissolved in 5.3 mL of hot toluene, and then 5.3 mL of hexane was added. Colorless crystalline diastereomeric complex of (*R*)-**1a**·(*R*,*R*)-**2e** appeared immediately. After standing at 25°C for 3 hours, the crystals were separated by filtration, washed with 1.8 mL of hexane to give 0.47 g (95%) of (*R*)-**1a**·(*R*,*R*)-**2e** with a *de* of 81%. The diastereomeric complex (*R*)-**1a**·(*R*,*R*)-**2e** was purified by recrystallization from a mixture of 5.3 mL of toluene and 5.3 mL of hexane according to the procedure described above to afford 0.36 g (74%) of the (*R*)-**1a**·(*R*,*R*)-**2e** with a *de* of 99% (Scheme 3; Table S3, Entry 12). The (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] was recovered from the diastereomer by flash column chromatography (silica gel, gradient elution, DCM to DCM – MeOH 95:5) to give 0.098 g (71%) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of 99%.

The resolution of 1-adamantyl phenyl-*H*-phosphinate (**1a**) with TADDOL derivatives [(*R*,*R*)-**2a-g**] (Fig. S2) were performed according to this representative procedure (Tables S2 and S3). When ethanol, 2-propanol or water was used as solvent, the corresponding diastereomer crystallized upon cooling. The crystals were washed with the corresponding solvent (Table S3, Entries 7-9). The resolution of *H*-phosphinates (**1b-p**) with 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**] were performed according to this representative procedure. All conditions and results can be found in Tables S4 and S5. Scheme 3 shows the selected results.

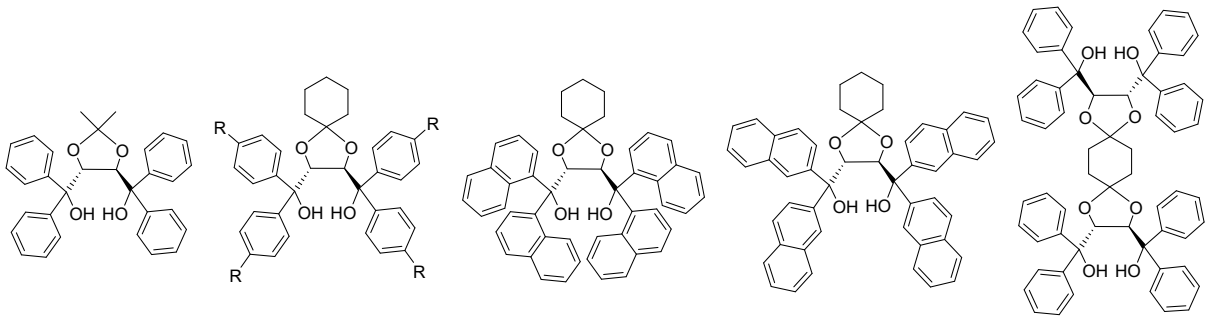


Fig. S2: TADDOL-derivatives [(*R*,*R*)-**2a-g**] used as resolving agents for the enantioseparation of 1-adamantyl phenyl-*H*-phosphinate (**1a**).

Table S2. Resolution of 1-adamantyl phenyl-*H*-phosphinate (**1a**) with TADDOL derivatives [(*R*,*R*)-**2a-g**].

Entry	Resolving agent	Eq.	Solvents[a]	Diastereomeric complex[b]	Yield[c,f] (%)	*ee*[d,f] (%)	S[e,f] (-)	Abs. Config.[g]
1	TADDOL (**2a**)	0.5	2.5×toluene 2.5×hexane	no complex	-	-	-	-
2	TADDOL (**2a**)	0.5	5×toluene 5×hexane	no complex	-	-	-	-
3	spiro-TADDOL (**2b**)[h]	0.5	5×toluene 5×hexane	(**1a**)·spiro-TADDOL	(73) **38**	(60) **96**	(0.44) **0.36**	(*R*)
4	4-*t*-Bu-spiro-TADDOL (**2c**)	0.5	2.5×toluene 2.5×hexane	no complex	-	-	-	-
5	4-*t*-Bu-spiro-TADDOL (**2c**)	0.5	5×toluene 5×hexane	no complex	-	-	-	-
6	4-CF_3-spiro-TADDOL (**2d**)	0.5	2.5×toluene 2.5×hexane	no complex	-	-	-	-
7	4-CF_3-spiro-TADDOL (**2d**)	0.5	5×toluene 5×hexane	no complex	-	-	-	-
8	1-naphthyl-spiro-TADDOL (**2e**)	0.5	5×toluene 5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(85) **72**	(72) **95**	(0.61) **0.68**	(*R*)
9	2-naphthyl-spiro-TADDOL (**2f**)	0.5	2.5×toluene 2.5×hexane	no complex	-	-	-	-
10	2-naphthyl-spiro-TADDOL (**2f**)	0.5	5×toluene 5×hexane	no complex	-	-	-	-
11	bis-spiro-TADDOL (**2g**)	0.25	2.5×toluene 2.5×hexane	no complex	-	-	-	-
12	bis-spiro-TADDOL (**2g**)	0.25	5×toluene 5×hexane	no complex	-	-	-	-

[a]Mixture of solvents for the crystallization and recrystallizations [mL of solvent/g of resolving agent].
[b]The ratio of *H*-phosphinate (**1**) and the resolving agent was determined by ^{1}H NMR.
[c]The yield of the diastereomer was calculated based on the half of the racemic *H*-phosphinate (**1**) that is regarded to be 100% for each antipode.
[d]Determined by HPLC using a chiral stationary phase.
[e]Resolving capability, also known as the Fogassy parameter [S (-) = (Yield [%] /100)×(*ee* [%]/100)].[29]
[f]The results obtained after the first crystallization are shown in parentheses, while the results obtained after one recrystallization are shown in boldface.
[g]Absolute configuration of the *H*-phosphinate (**1**) was determined by X-ray analysis.
[h]The diastereomer was purified by two recrystallizations.

Table S3. Resolution of 1-adamantyl-phenyl-*H*-phosphinate (**1a**) with 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**].

Entry	Eq.	Solvents[a]	Diastereomeric complex[b]	Yield[c,f] (%)	*ee*[d,f] (%)	S[e,f] (-)	Abs. Config.[g]
1	0.5	5×toluene 5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(85) **72**	(72) **95**	(0.61) **0.68**	(*R*)
2	0.5	5×*p*-xylene 5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(64) **42**	(82) **98**	(0.53) **0.41**	(*R*)
3	0.5	5×cymene 5×hexane	no complex	-	-	-	-
4	0.5	5×anisole 5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(59) **35**	(93) **99**	(0.52) **0.35**	(*R*)
5	0.5	5×toluene	(**1a**)·1-naphthyl-spiro-TADDOL	(66) **48**	(88) **99**	(0.59) **0.47**	(*R*)
6	0.5	2×EtOAc 10×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(59)	(77)	(0.46)	(*R*)
7	0.5	6×2-PrOH	(**1a**)·1-naphthyl-spiro-TADDOL$_2$	(32)	(4)	(0.01)	(*S*)
8	0.5	6×EtOH	1-naphthyl-spiro-TADDOL	-	-	-	-
9	0.5	15×H_2O	(**1a**)·1-naphthyl-spiro-TADDOL	(87)	(4)	(0.03)	(*S*)
10	1	5×toluene 5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(98) **77**	(77) **96**	(0.75) **0.74**	(*R*)
11	1	2.5×toluene	(**1a**)·1-naphthyl-spiro-TADDOL	(88) **66**	(82) **99**	(0.73) **0.66**	(*R*)
12	1	7.5×toluene 7.5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(95) **74**	(81) **99**	(0.77) **0.74**	(*R*)
13	1	10×toluene 10×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(91) **61**	(86) **99**	(0.78) **0.61**	(*R*)
14[h]	1	7.5×toluene 7.5×hexane	(**1a**)·1-naphthyl-spiro-TADDOL	(93) **75**	(84) **99**	(0.78) **0.75**	(*R*)

[a-g]See Table S2.

[h]The resolution was performed on a gram-scale.

Table S4. Resolution of alkyl phenyl-*H*-phosphinates (**1b-j**) with 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**].

Entry	RO	Solvents[a]	Diastereomeric complex[b]	Yield[c] (%)	*ee*[d] (%)	S[e,f] (-)	Abs. Config.[g]
1	2-AdO (**1b**)	7.5×toluene 7.5×hexane	(**1b**)·1-naphthyl-spiro-TADDOL	(103) **84**	(75) **96**	(0.77) **0.80**	(*R*)
2	2-AdO (**1b**)	10×toluene 10×hexane	(**1b**)·1-naphthyl-spiro-TADDOL	(92) **62**	(78) **98**	(0.72) **0.60**	(*R*)
3	*c*-PentO (**1c**)	7.5×toluene 7.5×hexane	(**1c**)·1-naphthyl-spiro-TADDOL	(93) **68**	(84) **98**	(0.78) **0.67**	(*R*)
4	*c*-HexO (**1d**)	7.5×toluene 7.5×hexane	(**1d**)·1-naphthyl-spiro-TADDOL	(86) **65**	(92) **>99**	(0.79) **0.65**	(*R*)
5	(−)-MentO (**1e**)	7.5×toluene 7.5×hexane	(**1e**)·1-naphthyl-spiro-TADDOL	(55)	(96)	(0.53)	(R_P)
6	*c*-HeptO (**1f**)	7.5×toluene 7.5×hexane	(**1f**)·1-naphthyl-spiro-TADDOL	(86) **64**	(91) **>99**	(0.78) **0.64**	(*R*)
7[h]	(1-Me)-*c*-HexO (**1g**)	5×toluene 5×hexane	(**1g**)·1-naphthyl-spiro-TADDOL	(49)	(62)	(0.30)	(*R*)[i]
8[h]	(1-Me)-*c*-HexO (**1g**)	7.5×toluene 7.5×hexane	(**1g**)·1-naphthyl-spiro-TADDOL	(44)	(96)	(0.42)	(*R*)
9	*t*-BuO (**1h**)	7.5×toluene 7.5×hexane	(**1h**)·1-naphthyl-spiro-TADDOL	(65) **30**	(84) **99**	(0.54) **0.30**	(*S*)
10	2,4-di-*Me*-PentO (**1i**)	7.5×toluene 7.5×hexane	no complex	-	-	-	-
11	BnO (**1j**)	7.5×toluene 7.5×hexane	(**1j**)·1-naphthyl-spiro-TADDOL	(67) **37**	(94) **>99**	(0.63) **0.37**	(*R*)
12	BnO (**1j**)	5×toluene 5×hexane	(**1j**)·1-naphthyl-spiro-TADDOL	(82) **49**	(81) **>99**	(0.66) **0.49**	(*R*)

[a-g]See Table S2. [h] The crystallization(s) were performed at 0°C. [i] The assignation of absolute P-configuration is ambiguous.

Table S5. Resolution of 1-adamantyl *H*-phosphinates (**1k-p**) with 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**] under optimized conditions.

Entry	Y	Solvents[a]	Diastereomeric complex[b]	Yield[c,f] (%)	*ee*[d,f] (%)	S[e,f] (-)	Abs. Config.[g]
1	2-Me-C_6H_4 (**1k**)	7.5×toluene 7.5×hexane	(**1k**)·1-naphthyl-spiro-TADDOL	(82) **53**	(80) **98**	(0.66) **0.52**	(*R*)
2[h]	3-Me-C_6H_4 (**1l**)	7.5×toluene 7.5×hexane	(**1l**)·1-naphthyl-spiro-TADDOL	(71) **24**	(64) **91**	(0.45) **0.21**	(*R*)[i]
3	4-Me-C_6H_4 (**1m**)	7.5×toluene 7.5×hexane	(**1m**)·1-naphthyl-spiro-TADDOL	(87) **65**	(94) **>99**	(0.81) **0.65**	(*R*)
4	4-MeO-C_6H_4 (**1n**)	7.5×toluene 7.5×hexane	no complex				
5	1-Naph (**1o**)	7.5×toluene 7.5×hexane	no complex				
6	*t*-Bu (**1p**)	7.5×toluene 7.5×hexane	no complex	-	-	-	-

[a-g]See Table S2 [h] The crystallization(s) were performed at 0°C. [i] The assignation of absolute P-configuration is ambiguous..

(*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**]: $[\alpha]_D^{25}$ = +44.5 (*c* = 0.7, $CHCl_3$, *ee* = 99%, R_P) $[\alpha]_D^{25}$(lit) = +44.3 (*c* = 1.07, $CHCl_3$, *ee* = 98%, R_P);[6] Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 7.6 min (*S*)-(−)-**1a**, t_{R2} 13.8 min (*R*)-(+)-**1a**.

(*R*)-2-admantyl phenyl-*H*-phosphinate [(*R*)-**1b**]: $[\alpha]_D^{25}$ = +31.7 (*c* = 3.6, $CHCl_3$, *ee* = 97%, R_P); Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 7.5 min (*S*)-(−)-**1b**, t_{R2} 14.1 min (*R*)-(+)-**1b**.

(*R*)-*c*-pentyl phenyl-*H*-phosphinate [(*R*)-**1c**]: $[\alpha]_D^{25}$ = +36.2 (*c* = 1.4, $CHCl_3$, *ee* = 98%, R_P); Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 7.6 min (*R*)-(+)-**1c**, t_{R2} 9.0 min (*S*)-(−)-**1c**.

(*R*)-*c*-hexyl phenyl-*H*-phosphinate [(*R*)-**1d**]: $[\alpha]_D^{25}$ = +42.3 (*c* = 4.1, $CHCl_3$, *ee* = 99%, R_P); Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 7.6 min (*R*)-(+)-**1d**, t_{R2} 9.8 min (*S*)-(−)-**1d**.

(R_P)-(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexyl phenyl-*H*-phosphinate [(R_P)-**1e**]: $[\alpha]_D^{25}$ = −33.9 (*c* = 2.0, $CHCl_3$, *de* = 96%, R_P), $[\alpha]_D^{25}$(lit)= −35.5 ($CHCl_3$, *de* = 95%, R_P);[30] Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (85:15), t_{R1} 7.5 min (S_P)-**1e**, t_{R2} 10.1 min (R_P)-**1e**.

(*R*)-*c*-heptyl phenyl-*H*-phosphinate [(*R*)-**1f**]: $[\alpha]_D^{25}$ = +37.6 (*c* = 1.3, $CHCl_3$, *ee* = 99%, R_P); Chiral HPLC: Phenomenex Lux 3 μm Cellulose-4 column, hexane/ethanol (50:50), t_{R1} 6.2 min (*S*)-(−)-**1f**, t_{R2} 8.6 min (*R*)-(+)-**1f**.

(*R*)-1-methyl-*c*-hexyl phenyl-*H*-phosphinate [(*R*)-**1g**]: $[\alpha]_D^{25}$ = +28.2 (*c* = 2.5, $CHCl_3$, *ee* = 96%, R_P); Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 6.4 min, (*S*)-(−)-**1g**, t_{R2} 8.9 min (*R*)-(+)-**1g**.

(*S*)-*t*-butyl phenyl-*H*-phosphinate [(*S*)-**1h**]: $[\alpha]_D^{25}$ = −37.0 (*c* = 2.0, $CHCl_3$, *ee* = 99%, S_P); Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 5.5 min, (*S*)-(−)-**1h**, t_{R2} 6.6 min (*R*)-(+)-**1h**.

(*R*)-benzyl phenyl-*H*-phosphinate [(*R*)-**1j**]: $[\alpha]_D^{25}$ = −1.5 (*c* = 1.5, $CHCl_3$, *ee* = 99%, R_P); Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 10.5 min, (*R*)-(−)-**1j**, t_{R2} 13.6 min (*S*)-(+)-**1j**.

(*R*)-1-admantyl (2-methyl-phenyl)-*H*-phosphinate [(*R*)-**1k**]: $[\alpha]_D^{25}$ = +28.5 (*c* = 1.6, $CHCl_3$, *ee* = 98%, R_P), $[\alpha]_D^{25}$(lit) = +25.1 (*c* = 1.0, $CHCl_3$, *ee* = 99%, R_P);[6] Chiral HPLC: Phenomenex Lux 5 μm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 6.8 min (*S*)-(−)-**1k**, t_{R2} 10.6 min (*R*)-(+)-**1k**.

(*R*)-1-admantyl (3-methyl-phenyl)-*H*-phosphinate [(*R*)-**1l**]: $[\alpha]_D^{25}$ = +32.0 (*c* = 1.7, $CHCl_3$, *ee* = 91%, R_P); Chiral HPLC: Phenomenex Lux 5 µm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 8.4 min (*S*)-(−)-**1l**, t_{R2} 10.0 min (*R*)-(+)-**1l**.
(*R*)-1-admantyl (4-methyl-phenyl)-*H*-phosphinate [(*R*)-**1m**]: $[\alpha]_D^{25}$ = +34.2 (*c* = 1.4, $CHCl_3$, *ee* = 99%, R_P); Chiral HPLC: Phenomenex Lux 5 µm Cellulose-2 column, hexane/ethanol (50:50), t_{R1} 8.9 min (*S*)-(−)-**1m**, t_{R2} 16.1 min (*R*)-(+)-**1m**.

4. Gram-scale resolution of 1-adamantyl phenyl-*H*-phosphinate (1a) with 1-naphthyl-spiro-TADDOL [(*R*,*R*)-2e]

4.0 g (14.5 mmol) of Racemic 1-adamantyl phenyl-*H*-phosphinate (**1a**) and 10.2 g (14.5 mmol) of 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**] were dissolved in 75 mL of hot toluene, and then 75 mL of hexane was added. Colorless crystalline diastereomeric complex of (*R*)-**1a**·(*R*,*R*)-**2e** appeared immediately. After standing at 25°C for 3 hours, the crystals were separated by filtration, washed with 25 mL of hexane to give 6.6 g (93%) of (*R*)-**1a**·(*R*,*R*)-**2e** with a *de* of 84%. The diastereomeric complex (*R*)-**1a**·(*R*,*R*)-**2e** was purified by recrystallization from a mixture of 75 mL of toluene and 75 mL of hexane according to the procedure described above to afford 5.3 g (75%) of the (*R*)-**1a**·(*R*,*R*)-**2e** with a *de* of 99% (Scheme 3; Table S3, Entry 14). The (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] was recovered from the diastereomer by flash column chromatography (silica gel, gradient elution, DCM to DCM – MeOH 95:5) to give 1.4 g (72%) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of 99%.

5. Recrystallization of enantiomeric mixtures of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-1a]

The enantiomeric mixtures of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**] were prepared either by the decomposition of the corresponding diastereomeric complex, or by mixing the racemate (**1a**) and the (*R*)-enantiomer [(*R*)-**1a**].
Under nitrogen atmosphere 31 mg (0.11 mmol) of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of 22%, was dissolved in 50 µL of EtOAc at 25°C. The solution was kept at -20°C for 24 hours then crystals were separated by filtration, washed with 25 µL of cold hexane to afford 16 mg (51%) of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of

21%. The mother liquor was evaporated to afford 15 mg (48%) of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of 23% (Table S6, Entry 2).

The recrystallization of enantiomeric mixtures with different *ee* were performed according to this representative procedure. Table S6 and Fig. S3 contain the results.

Table S6. Recrystallization of enantiomeric mixtures of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**].

Entry	ee_0[a] (%)	$ee_{crystal}$[a] (%)	$Y_{crystal}$ (%)	$ee_{mother\ liquor}$[a] (%)	$Y_{mother\ liquor}$ (%)
1	8	**4**	49	**11**	45
2	22	**21**	51	**23**	48
3	31	**29**	45	**33**	53
4	39	**82**	41	**12**	56
5	59	**85**	59	**26**	41
6	82	**93**	68	**54**	31

[a]Determined by HPLC using a chiral stationary phase.

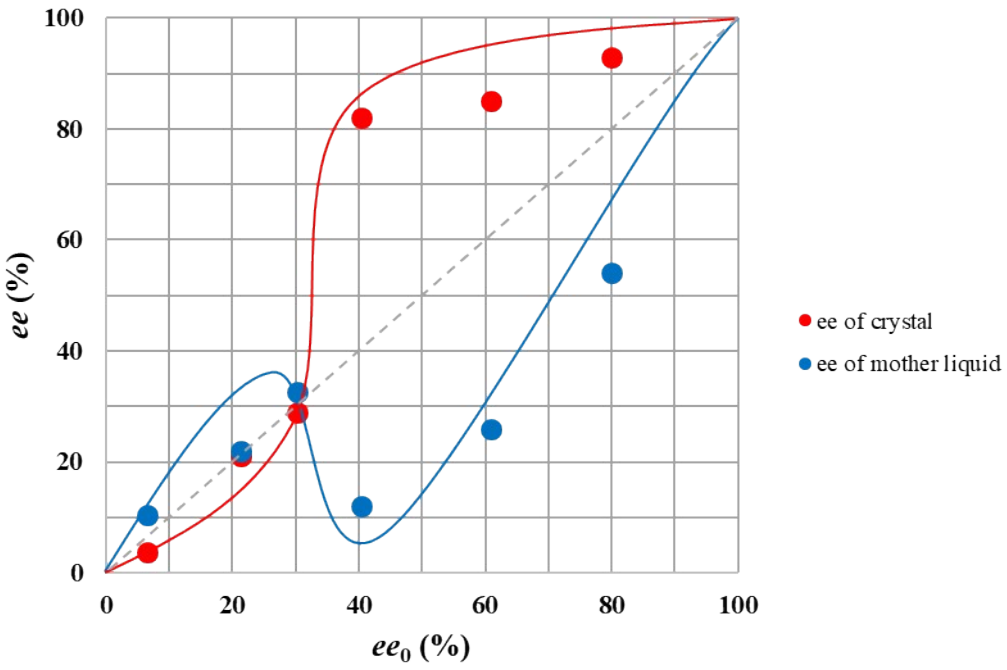


Fig. S3. ee_0 – *ee* Diagram of the recrystallization of enantiomeric mixtures of (*R*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**].

6. Decomposition of the diastereomeric complex (*R*)-1a·(*R*,*R*)-2e

100 mg (0.10 mmol) of (*R*)-**1a**·(*R*,*R*)-**2e** diastereomeric complex was dissolved in 0.43 mL of hot ethanol. Colorless crystalline complex of [(*R*,*R*)-**2e**]·EtOH appeared immediately. After standing at 25°C for 16 hours, the crystals were separated by filtration, washed with 0.10 mL of ethanol to give 70 mg (91%) of [(*R*,*R*)-**2e**]·EtOH (Table S7, Entry 1). The remaining mother liquor was evaporated, and redissolved in DCM, and filtered through a small plug of silica gel with DCM, to elute (*R*,*R*)-**2e**. Then the silica gel was washed with DCM – MeOH 95:5, to give 27 mg (0.097 mmol) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of 99%.
The decomposition of the diastereomeric complex (*R*)-**1a**·(*R*,*R*)-**2e** with MeOH or EtOH and hexane were performed according to this representative procedure. Results are summarized in Table S7.

Table S7. Decomposition of the diastereomeric complex (*R*)-**1a**·(*R*,*R*)-**2e**.

Entry	Solvent[a]	Crystallization temp (°C)	Yield of EtOH·[(*R*,*R*)-**2e**] (%)
1	6×EtOH	25	91
2	6×MeOH	25	mixture of (*R*)-**1a** and (*R*,*R*)-**2e**
3	6×EtOH 3×hexane	25	mixture of (*R*)-**1a** and (*R*,*R*)-**2e**
4	3×EtOH	25	65
5	9×EtOH	25	mixture of (*R*)-**1a** and (*R*,*R*)-**2e**
6	6×EtOH	0	80
7	6×EtOH	-20	61

[a]Mixture of solvents for the crystallization [mL of solvent/g of (*R*,*R*)-**2e**].

7. Complete procedure for the preparation of (*R*)- and (*S*)-1-adamantyl phenyl-*H*-phosphinate [(*R*)-1a and (*S*)-1a]

To a solution of 1.0 g (7.0 mmol) of phenyl-*H*-phosphinic acid (**4**) and 1.1 g (7.0 mmol) of 1-adamantanol in 20 mL of anhydrous DCM, 2.7 g (17.0 mmol) of EDC·HCl was added in 4 portions over 20 min under nitrogen atmosphere at 25°C. The resulting solution was stirred at this temperature for an additional 2 hours. Then, it was washed with 2 M HCl solution (2 × 20 mL), and the acidic phases were combined and extracted with DCM (3 × 20 mL). The combined organic layers were dried (Na_2SO_4) and evaporated to give 2.0 g of crude 1-adamantyl phenyl-*H*-phosphinate (**1a**) as white solid. The 1-adamantyl phenyl-*H*-phosphinate (**1a**) content of the crude product was 85% according to ^{31}P NMR.

2.0 g of the Crude product [*c.a.* 6.2 mmol of **1a**] and 4.35 g (6.2 mmol) of 1-naphthyl-spiro-TADDOL [(*R*,*R*)-**2e**] were dissolved in 33 mL of hot toluene, and then 33 mL of hexane was added. Colorless crystalline diastereomeric complex of (*R*)-**1a**·(*R*,*R*)-**2e** appeared immediately. After standing at 25°C for 3 hours, the crystals were separated by filtration, washed with 11 mL of hexane to give 2.54 g (2.6 mmol) of (*R*)-**1a**·(*R*,*R*)-**2e** with a *de* of 83%. The diastereomeric complex (*R*)-**1a**·(*R*,*R*)-**2e** was purified by recrystallization from a mixture of 33 mL of toluene and 33 mL of hexane according to the procedure described above to afford 1.94 g (63%) of the (*R*)-**1a**·(*R*,*R*)-**2e** with a *de* of 99%.

The resulting crystalline diastereomer (*R*)-**1a**·(*R*,*R*)-**2e** (1.94 g) was dissolved in 8.4 mL of hot ethanol. Colorless crystalline complex of [(*R*,*R*)-**2e**]·EtOH appeared immediately. After standing at 25°C for 16 hours, the crystals were separated by filtration, washed with 1.4 mL of ethanol to give 1.31 g (1.86 mmol) of [(*R*,*R*)-**2e**]·EtOH. The remaining mother liquor was evaporated, redissolved in DCM, and filtered through a small plug of silica gel with DCM, to elute the remaining (*R*,*R*)-**2e**. Then, the column was washed with DCM – MeOH 95:5, to give 0.52 g (61%) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] with an *ee* of 99%.

The mother liquor of the original resolution procedure was evaporated to give 4.89 g of the (*S*)-**1a**·(*R*,*R*)-**2e** diastereomer with a *de* of 60%. The crystals were dissolved in 18 mL of hot ethanol. Colorless crystalline complex of [(*R*,*R*)-**2e**]·EtOH appeared immediately. After standing at 25°C for 16 hours, crystals were separated by filtration, washed with 4.0 mL of ethanol to give 2.90 g (4.11 mmol) of [(*R*,*R*)-**2e**]·EtOH. The resulting mother liquid was evaporated, redissolved in DCM, and filtered on a small plug of silica gel with DCM, to elute the remaining [(*R*,*R*)-**2e**]. Then the silica gel was washed with DCM – MeOH 95:5, to give 0.97 g (3.51 mmol) of (*S*)-1-adamantyl phenyl-*H*-phosphinate [(*S*)-**1a**] with an *ee* of 60%. The resulting solid was

recrystallized from 1.7 mL of EtOAc at -20°C to give 0.35 g (41%) of (*S*)-1-admantyl phenyl-*H*-phosphinate [(*S*)-**1a**] with an *ee* of 91% (Scheme 4).

8. Racemization studies of enantiopure alkyl phenyl-*H*-phosphinates [(*R*)-1a, (*R*)-1b, (*R*)-1d or (*R*)-1j]

28 mg (0.10 mmol) of (*R*)-1-Adamantyl phenyl-*H*-phosphinate [(*R*)-**1a**] was dissolved in 0.40 mL of anhydrous toluene in a pressure tube under nitrogen atmosphere. The solution was stirred for 8 days at 25°C or for 3 days at 110°C. Samples were taken from the reaction mixture after 1, 3 and 8 days as it is indicated in Table S8. After taking the given samples, the headspace of the pressure tube was evacuated and filled with nitrogen gas three times.

The thermal racemization of 2-adamantyl, cyclohexyl- or benzyl phenyl-*H*-phosphinate [(*R*)-**1b**, (*R*)-**1d** or (*R*)-**1j**] was conducted according to this representative procedure. Table S8 contains the results.

Table S8. Racemization of optically active alkyl phenyl-*H*-phosphinates [(*R*)-**1a**, (*R*)-**1b**, (*R*)-**1d** or (*R*)-**1j**]

Entry	RO	T (°C)	t (day)	ee_0 (%)[a]	*ee* (%)[a]
1	1-AdO (**1a**)	25	1	99	99
2	1-AdO (**1a**)	25	3	99	99
3	1-AdO (**1a**)	25	8	99	99
4	1-AdO (**1a**)	110	3	99	96
5	2-AdO (**1b**)	110	3	98	93
6	*c*-HexO (**1d**)	25	1	99	99
7	*c*-HexO (**1d**)	25	3	99	99
8	*c*-HexO (**1d**)	25	8	99	99
9	*c*-HexO (**1d**)	110	3	99	decomposition
10	BnO (**1j**)	25	1	99	99
11	BnO (**1j**)	25	3	99	99
12	BnO (**1j**)	25	8	99	94
13	BnO (**1j**)	110	3	99	decomposition

[a]Determined by HPLC using a chiral stationary phase.

9. Stereospecific transformations of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-1a]

9.1. Preparation of (*R*)-(2-methoxyphenyl)-phenylphosphine oxide [(*R*)-3a]

Under nitrogen atmosphere, 0.51 mL (1.3 mmol) of *n*-butyllithium (2.5 M hexane solution) was added dropwise to a mixture of 0.14 mL (1.3 mmol) of anisole and 0.19 mL (1.3 mmol) of TMEDA in 1.5 mL of anhydrous Et_2O over 10 min at 0°C. The reaction mixture was stirred at 25°C for 4 hours. The resulting white suspension was cooled to -50°C, and 0.14 g (0.51 mmol) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] in 1.5 mL of anhydrous Et_2O was added over 15 min. The reaction mixture was stirred at -50°C for 4 hours, then it was allowed to warm to 0°C, and stirred for another 30 min at this temperature. Then 2 mL of saturated NH_4Cl solution and 2 mL of water were added. Phases were separated, and the aqueous layer was extracted with DCM (3 × 1 mL). The organic layers were combined, dried (Na_2SO_4), and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 105 mg (89%) of (*R*)-(2-methoxyphenyl)-phenylphosphine oxide [(*R*)-**3a**] with an *ee* of 95% as a white solid.

mp.: 97-98°C (mp_{lit}: 101–103°C);[31] $[\alpha]_D^{25}$ = +48.8 (*c* = 1.0, $CHCl_3$, *ee* = 95%, R_P) ($[\alpha]_D^{25}$(lit) = +40.9 (*c* = 0.91, $CHCl_3$, ee = 67%, R_P),[4] Chiral HPLC: Phenomenex Lux 5 μm Cellulose-1 column, hexane/ethanol (85:15), t_{R1} 10.8 min (*S*)-**3a**, t_{R2} 15.4 min (*R*)-**3a**; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 12.5 (δ_{lit} 14.4);[31] ^1H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 499.0, 1H), 7.81–7.70 (m, 3H), 7.54–7.43 (m, 4H), 7.11–7.08 (m, 1H), 6.92–6.89 (m, 1H), 3.77 (s, 3H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 160.8 (d, *J* = 3.8), 134.5 (d, *J* = 1.9), 133.2 (d, *J* = 7.1), 132.3 (d, *J* = 104.5), 132.1 (d, *J* = 3.0), 130.6 (d, *J* = 11.8), 128.6 (d, *J* = 13.1), 121.2 (d, *J* = 12.1), 119.6 (d, *J* = 101.9), 110.9 (d, *J* = 6.1), 55.6; HRMS (ESI/TOF) *m*/*z*: $[M + H]^+$ Calcd for $C_{13}H_{14}O_2P$ 233.0731; Found 233.0733.

9.2. Preparation of (*R*)-(2-methoxyphenyl)-methyl-phenylphosphine oxide [(*R*)-3b]

Under nitrogen atmosphere, 0.51 mL (1.3 mmol) of *n*-butyllithium (2.5 M hexane solution) was added dropwise to a mixture of 0.14 mL (1.3 mmol) of anisole and 0.19 mL (1.3 mmol) of TMEDA in 1.5 mL of anhydrous Et_2O over 10 min at 0°C. The reaction mixture was stirred at

25°C for 4 hours. The resulting white suspension was cooled to -50°C, and 0.14 g (0.51 mmol) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] in 1.5 mL of anhydrous Et_2O was added over 15 min. The reaction mixture was stirred at -50°C for 4 hours, then it was allowed to warm to 0°C, and stirred for another 30 min at this temperature. Then 0.13 mL of MeI in 1.5 mL of mL of anhydrous Et_2O was added over 10 min at 0°C, and the reaction mixture was stirred for another 30 min at the same temperature. Then 2 mL of saturated NH_4Cl solution and 2 mL of water were added. Phases were separated, and the aqueous layer was extracted with DCM (3 × 1 mL). The organic layers were combined, dried (Na_2SO_4), and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, 100% hexane to 100% EtOAc) to give 95 mg (75%) of (*R*)-(2-methoxyphenyl)-methyl-phenylphosphine oxide [(*R*)-**3b**] with an *ee* of 93% as a white solid. The enantiomeric mixture of (*R*)-**3b** was dissolved in 95 µL of EtOAc and cooled to -78°C for 3 hours. The crystals were separated by filtration to give 17 mg of (*R*)-(2-methoxyphenyl)-methyl-phenylphosphine oxide [(*R*)-**3b**] with an *ee* of 75%. The mother liquid was evaporated to give 78 mg (62%) of (*R*)-(2-methoxyphenyl)-methyl-phenylphosphine oxide [(*R*)-**3b**] with an *ee* of 97% as a white solid.

mp.: 82-84°C ($mp_{lit.}$: 81-83°C);[32] $[\alpha]_D^{25}$ = +20.8 (*c* = 1.0, $CHCl_3$, *ee* = 97%, *R*) ($[\alpha]_D^{25}$(lit) = +30.4 (*c* = 0.55, $CHCl_3$, ee = 96%, *R*),[32] Chiral HPLC: Kromasil 5-Amycoat column, hexane/ethanol (85:15), t_{R1} 11.5 min (*S*)-**3b**, t_{R2} 14.5 min (*R*)-**3b**; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 28.5 (δ_{lit} 29.4);[32] ^1H NMR (500 MHz, $CDCl_3$) δ 7.97 – 7.93 (m, 1H), 7.75 – 7.71 (m, 2H), 7.51 – 7.39 (m, 4H), 7.11 – 7.08 (m, 1H), 6.89 – 6.86 (m, 1H), 3.72 (s, 3H), 2.07 (d, *J* = 14.1, 3H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$) δ 160.0 (d, *J* = 4.2), 135.1 (d, *J* = 103.9), 134.0 (d, *J* = 3.6), 134.0, 131.4 (d, *J* = 2.8), 130.4 (d, *J* = 10.1), 128.3 (d, *J* = 12.2), 121.5 (d, *J* = 100.2), 121.2 (d, *J* = 11.0), 111.0 (d, *J* = 6.5), 55.4, 16.3 (d, *J* = 75.2); HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{16}O_2P$ 247.0888; Found 247.0883.

9.3. Preparation of (*R*)-*c*-hexyl-(2-methoxyphenyl)-methylphosphine-oxide [(*R*)-3c]

To 122 mg (0.49 mmol) of (*R*)-phenyl-(2-methoxyphenyl)-methylphosphine oxide [(*R*)-**3b**] (*ee* 97%) in 30 mL of MeOH was added 50 mg of 5% Rh/C catalyst, then (*R*)-**3b** was hydrogenated in a 80 mL stainless steel autoclave equipped with a magnetic stirrer (stirring speed: 1200 rpm), at 20 bar and 95°C for 24 h. After finishing the hydrogen uptake, the catalyst was filtered and washed with MeOH (2×5 mL). After removing the solvent under *vacuum*, the crude product was purified by column chromatography (silica gel, gradient elution, acetone to acetone - 2-

PrOH=90:10) to afford 100 mg (80%) of (*R*)-cyclohexyl-(2-methoxyphenyl)-methylphosphine oxide [(*R*)-**3c**] with an *ee* of 96% a dense oil.

$[\alpha]_D^{25}$ = +30.0 (*c* = 2.4, $CHCl_3$, *ee* = 96%, R_P) ($[\alpha]_D^{25}$(lit) = +63.3 (c = 0.5, MeOH, R_P),[33] Chiral HPLC: Phenomenex Lux 5 µm Amylose-2 column, hexane/ethanol (85:15), t_{R1} 12.1 min (*S*)-**3c**, t_{R2} 16.9 min (*R*)-**3c**;$^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 40.5; ^1H NMR (500 MHz, $CDCl_3$) δ 7.95 – 7.91 (m, 1H), 7.50 – 7.46 (m, 1H), 7.10 – 7.07 (m, 1H), 6.90 (dd, *J* = 8.3, 5.1, 1H), 3.86 (s, 3H), 1.98 – 1.92 (m, 2H), 1.90 – 1.85 (m, 1H), 1.72 – 1.55 (m, 6H), 1.39 – 1.11 (m, 5H); $^{13}C\{^1H\}$ NMR (75.5 MHz, $CDCl_3$) δ 159.3 (d, *J* = 4.8), 134.9 (d, *J* = 4.5), 133.4 (d, *J* = 2.2), 121.1 (d, *J* = 10.1), 120.4 (d, *J* = 90.4), 110.3 (d, *J* = 6.5), 55.3, 38.0 (d, *J* = 73.1), 26.4 (d, *J* = 13.8), 25.8 (d, *J* = 1.6), 24.9 (d, *J* = 3.3), 24.5 (d, *J* = 3.1), 13.8 (d, *J* = 68.8); HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{14}H_{22}O_2P$ 253.1357; Found 253.1354.

9.4. Preparation of (*R*)-1-adamantyl-phenylphosphonamidate [(*R*)-3d]

0.50 g (1.8 mmol) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] was dissolved in 10 mL of MeCN under nitrogen atmosphere, it was cooled to 0°C. 2.3 mL of CCl_4, 0.63 mL (4.5 mmol) of NEt_3 were added in one portion, which was followed by the controlled addition of 1.1 mL of NH_4OH solution (28%) over 5 min each at 0°C. The reaction was stirred at 0°C for 1 hour, then it was allowed to warm to 25°C and stirred for 16 hours. 10 mL of Water was added, the phases were separated, and the aqueous layer was extracted with EtOAc (3 × 10 mL). The organic layers were combined, dried (Na_2SO_4), and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, EtOAc to EtOAc – MeOH 98:2) to give 0.47 g (90%) (*R*)-1-adamantyl-phenylphosphonamidate [(*R*)-**3d**] with an *ee* of 99% as a white solid.

mp.: 148-150°C; $[\alpha]_D^{25}$ = −15.4 (c = 1.0, $CHCl_3$, *ee* = 99%, R_P); Chiral HPLC: Phenomenex Lux 5 µm Amylose-2 column, hexane/ethanol (50:50), t_{R1} 6.1 min (*R*)-**3d**, t_{R2} 10.7 min (*S*)-**3d**; $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 18.0; ^1H NMR (500 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 13.2, 7.4, 2H), 7.49 – 7.39 (m, 3H), 2.94 (bs, 2H), 2.14 – 2.10 (m, 9H), 1.61 (bs, 6H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$) δ 135.0 (d, *J* = 174.4), 131.4 (d, *J* = 3.1), 131.1 (d, *J* = 10.1), 128.3 (d, *J* = 14.3), 82.4 (d, *J* = 8.2), 44.4 (d, *J* = 4.1), 35.9, 31.3; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{23}NO_2P$ 292.1466; Found 292.1463.

9.5. Preparation of (*R*)-*N*-(1-adamantyl-phenylphosphonyl)-2,4,6-triisopropylbenzenesulfonamide [(*R*)-3e]

Under argon atmosphere, 0.12 g of 60% (w/w %) NaH dispersion (74 mg of NaH, 3.1 mmol) was washed with anhydrous THF (2 × 2.0 mL), 2.0 mL of anhydrous THF was added then. To this suspension, 0.30 g (1.0 mmol) of (*R*)-1-adamantyl-phenylphosphonamidate [(*R*)-**3d**] in 2.0 mL of anhydrous THF was added dropwise over 10 min at 0 °C, and the reaction mixture was stirred for 45 min at this temperature. Then, 0.47 g (1.6 mmol) of 2,4,6-triisopropylbenzenesulfonyl chloride in 2.0 mL of anhydrous THF was added dropwise over 10 min at 0 °C, and the reaction mixture was stirred for 20 min at this temperature. The reaction mixture was allowed to warm to 25 °C, and it was stirred for 16 hours. Then, 6 mL of saturated NH_4Cl solution and 4 mL of water were added. Phases were separated, and the aqueous layer was extracted with DCM (3 × 10 mL). The organic layers were combined, dried (Na_2SO_4), and evaporated. The crude product was purified by flash column chromatography (silica gel, gradient elution, DCM to DCM − MeOH 90:10) to give 0.47 g (84%) of (*R*)-*N*-(1-adamantyl-phenylphosphonyl)-2,4,6-triisopropylbenzenesulfonamide [(*R*)-**3e**] as a white solid.
mp.: 88-89°C; $[\alpha]_D^{25}$ = +6.8 (*c* = 0.6, $CHCl_3$, *R*); $^{31}P\{^1H\}$ NMR (202.5 MHz, $CDCl_3$) δ 7.2; ^1H NMR (500 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 14.1, 7.6, 2H), 7.35 (t, *J* = 7.4, 1H), 7.24 – 7.20 (m, 2H), 7.04 (s, 2H), 4.22 – 4.10 (m, 2H), 2.89 – 2.81 (m, 1H), 1.99 (bs, 9H), 1.49 (bs, 6H), 1.22 (d, J = 6.9, 6H), 1.17 – 1.15 (m, 12H); $^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$) δ 152.7, 149.6, 135.0, 131.9 (d, *J* = 3.2), 131.7 (d, *J* = 10.7), 128.6 (d, *J* = 102.0), 127.9 (d, *J* = 15.6), 123.4, 85.9 (d, *J* = 8.9), 44.0 (d, *J* = 4.1), 35.7, 34.2, 31.3, 29.7, 24.9, 24.7, 23.7, 23.7; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{31}H_{45}NO_4PS$ 558.2807; Found 558.2802.

9.6. Preparation of (*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-3f]

0.38 mL (2.7 mmol) of NEt_3 and 0.13 g (0.51 mmol) of S_8 were added to a solution of 0.75 g (2.7 mmol) of (*R*)-1-admantyl phenyl-*H*-phosphinate [(*R*)-**1a**] in 4 mL diethyl-ether at 25°C. The reaction was stirred for 16 hours under nitrogen atmosphere at room temperature. Then the solvent was evaporated, and the resulting salt was re-dissolved in 8 mL of EtOAc. The remaining sulfur was filtered and washed with EtOAc (2 × 1 mL). In order to liberate the corresponding phosphonothioic acid [(*S*)-**3f**], 6 mL of 1M $NaHSO_4$ was added to the EtOAc solution. Phases were separated, and the aqueous layer was extracted with EtOAc (3 × 6 mL).

The organic layers were combined, dried (Na_2SO_4), and evaporated to give 0.75 g (90%) of (*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-**3f**] with an *ee* of 99% as a yellow solid.
mp.: 87-89°C; $[\alpha]_D^{25} = -5.6$ (*c* = 1.1, $CHCl_3$, *ee* = 99%, S_P); The enantiomeric excess of (*S*)-**3f** was determined by ^{31}P NMR using 6.2 mg (20 μmol) of the analyte, 3.9 μL (30 μmol) (*S*)-1-phenylethylamine as CSA and 750 μL $CDCl_3$ as solvent; $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$) δ 69.2; ^1H NMR (500 MHz, $CDCl_3$) δ 7.92 – 7.87 (m, 2H), 7.49 – 7.46 (m, 1H), 7.43 – 7.39 (m, 2H), 7.05 (bs, 1H), 2.26 – 2.19 (m, 6H), 2.15 (bs, 3H), 1.65 – 1.58 (m, 6H);$^{13}C\{^1H\}$ NMR (125.8 MHz, $CDCl_3$) δ 136.8 (d, *J* = 156.9), 131.6 (d, *J* = 3.2), 130.3 (d, *J* = 11.9), 128.2 (d, *J* = 15.4), 85.2 (d, *J* = 10.4), 44.0 (d, *J* = 4.2), 35.9, 31.4; HRMS (ESI/TOF) m/z: $[M + H]^+$ Calcd for $C_{16}H_{22}O_2PS$ 309.1078; Found 309.1074.

10. Application of (*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-3f] as NMR chiral solvating agent

5.8 mg (19 μmol) of (*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-**3f**] and 3.0 μL (19 μmol) of 1-naphthylethylamine (**6**) were dissolved in 0.75 mL of $CDCl_3$ in an NMR tube, then the ^1H NMR of the mixture was measured. The same procedure was used in case of the other analytes (**7-13**).
In case of **6** no baseline separation was achieved in toluene-d_8, acetone-d_6, DMSO-d_6, EtOH-d_6 and MeOH-d_4. However, it was found that CD_3CN, CD_2Cl_2 and $CDCl_3$ can be used as solvents. The amount of the (*S*)-**3f** was also investigated, and it was found that 1 – 1.5 eq. of (*S*)-**3f** at 25 mM in $CDCl_3$ should be used for the best peak separation. Tables S9 and S10 contain selected regions of the ^1H NMR spectra.

Table S9. The use of (*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-**3f**] as chiral NMR solvating agent for 1-naphthylethylamine (**6**) and amino alcohols (**7-10**).

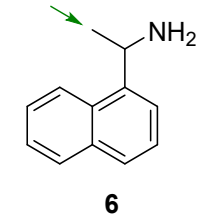
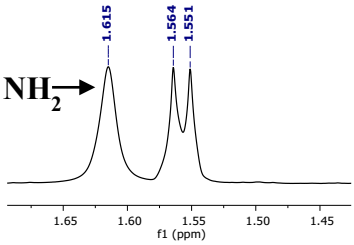
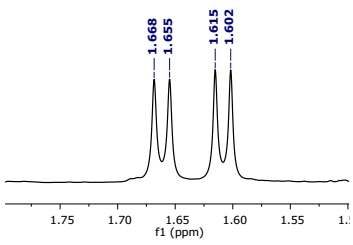
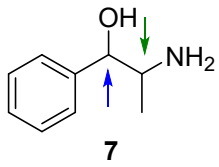
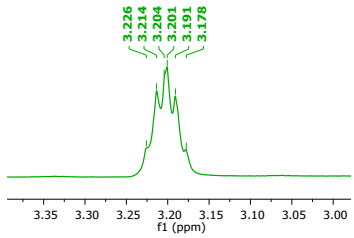
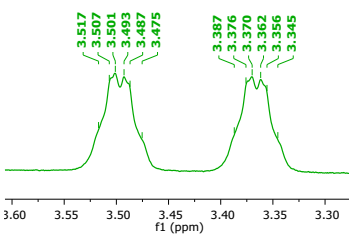
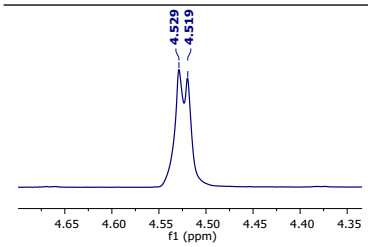
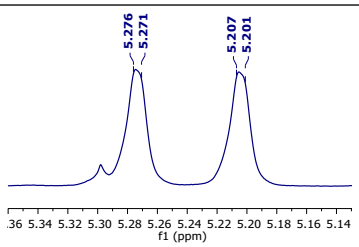
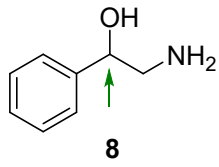
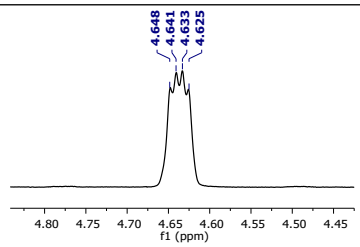
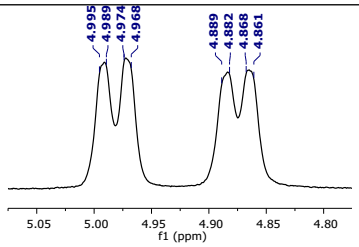
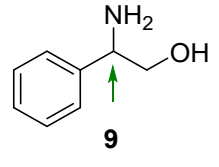
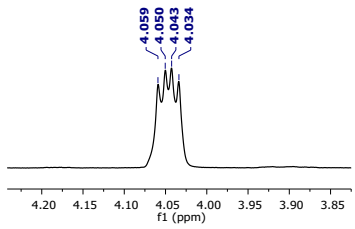
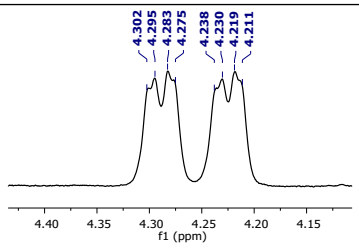
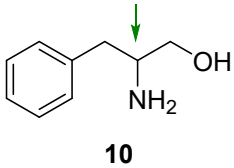
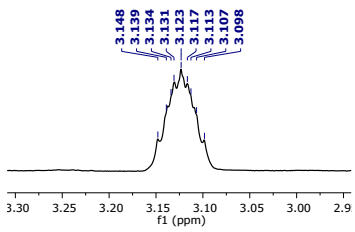
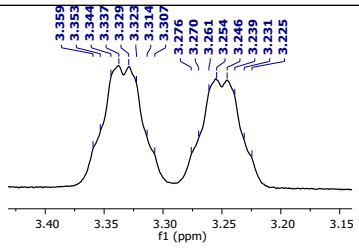
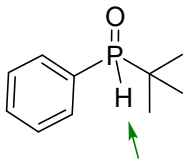
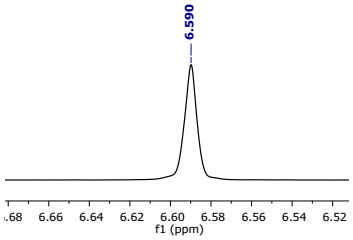
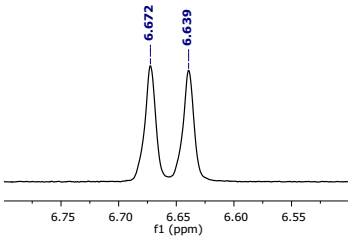
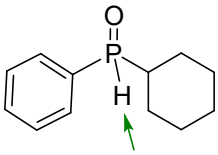
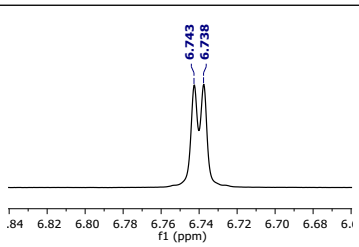
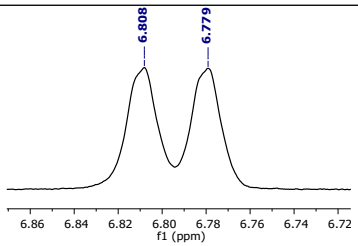
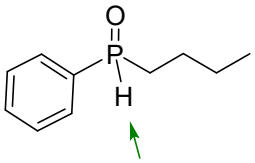
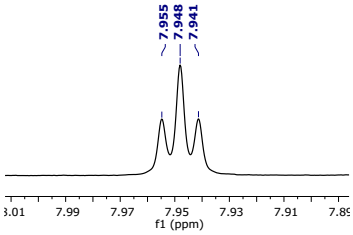
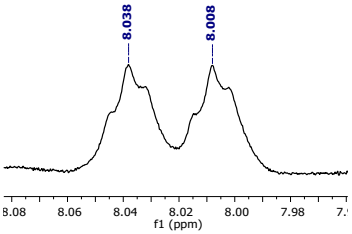
Entry	Analyte	^{1}H of analyte	^{1}H of analyte in the presence of 1 eq. of (*S*)-**3f**	Δδ (ppm)
1	 **6**			0.053
2	 **7**			0.131
				0.069
3	 **8**			0.107
4	 **9**			0.064
5	 **10**			0.083

Table S10. The use of (*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-**3f**] as chiral NMR solvating agent for secondary phosphine oxides (**11-13**).

Entry	Analyte	^{1}H of analyte	^{1}H of analyte in the presence of 1 eq. of (*S*)-**3f**	Δδ (ppm)
1	 **11**			0.033
2	 **12**			0.029
3	 **13**			0.030

11.X-ray measurements

In all instances, X-ray quality crystals were prepared by slowly diffusing hexane to the toluene solution of the corresponding diastereomeric complex.

Crystallographic information of the measured crystals:

Crystal structure data are deposited at the Cambridge Crystallographic Data Centre under CCDC 2143598-2143607.

[(*R*)-**1a**·(*R*,*R*)-**2e**]*:* C_{73} H_{71} O_6 P, *Fwt.*: 1075.26, colourless, chunk, size: 0.50 x 0.40 x 0.40 mm, orthorhombic, space group *P* 2_1 2_1 2_1, *a* = 10.3422(7)Å, *b* = 23.1822(17)Å, *c* = 23.8390(18)Å, α = 90°, β = 90°, γ = 90°, *V* = 5716(1)Å^3, *T* = 103(2)K, *Z*= 4, *F*(000) = 2288, D_x = 1.250 Mg/m^3, μ 0.104mm^{-1}.

A crystal of [(*R*)-**1a**·(*R*,*R*)-**2e**] was mounted on a glass fiber. Cell parameters were determined by least-squares using 40690 (3.11 ≤ θ ≤ 27.41°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.108 ≤ θ ≤ 25.350[1].

A total of 75348 reflections were collected of which 10434were unique [*R*(int) = 0.1701, *R(*σ) = 0.0946]; intensities of 6380 reflections were greater than 2σ(*I*). Completeness to θ = 0.997.

An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.7230 and 1.0000).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0866 and wR^2 = 0.1287 for 1332 [I>2σ(I)] and R_1 = 0.1501 and wR^2 = 0.1479 for all (10434) intensity data, (number of parameters = 699, goodness-of-fit = 1.103, the maximum and mean shift/esd is 0.002 and 0.000). The absolute structure parameter is 0.11(9). (Friedel coverage: 0.803, Friedel fraction max.: 0.999, Friedel fraction full: 0.999).

The maximum and minimum residual electron density in the final difference map was 0.26 and -0.18e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.02993.1546P)^2+3.1546P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1b**·(*R*,*R*)-**2e**]*:* C_{73} H_{71} O_6 P, *Fwt.*: 1075.26, colourless, needle, size: 0.50 x 0.10 x 0.10 mm, orthorhombic, space group *P* 2_1 2_1 2_1, *a* = 10.2809(13)Å, *b* = 22.954(3)Å, *c* = 23.721(3)Å, α =

90°, β = 90°, γ = 90°, V = 5597.8(12)Å^3, T = 103(2)K, Z= 4, F(000) = 2288, D_x = 1.276 Mg/m^3, μ 0.106mm^{-1}.

A crystal of [(*R*)-**1b**·(*R*,*R*)-**2e**] was mounted on a glass fiber. Cell parameters were determined by least-squares using 62643 (3.13 ≤ θ ≤ 25.29°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.129 ≤ θ ≤ 23.532[1].

A total of 114437 reflections were collected of which 8286were unique [R(int) = 0.2025, R(σ) = 0.0883]; intensities of 6257 reflections were greater than 2σ(I). Completeness to θ = 0.996.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.988724 and 0.998178).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0743 and wR^2 = 0.1356 for 1332 [I>2σ(I)] and R_1 = 0.1044 and wR^2 = 0.1461 for all (8286) intensity data, (number of parameters = 688, goodness-of-fit = 1.072, the maximum and mean shift/esd is 0.000 and 0.000). The absolute structure parameter is -0.03(8). (Friedel coverage: 0.790, Friedel fraction max.: 0.998, Friedel fraction full: 0.998).

The maximum and minimum residual electron density in the final difference map was 0.33 and -0.19e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.05841.2195P)^2+1.2195P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1c**·(*R*,*R*)-**2e**]*:* C_{68} H_{65} O_6 P, *Fwt.*: 1009.17, colourless, block, size: 0.50 x 0.10 x 0.10 mm, orthorhombic, space group P 2_1 2_1 2_1, a = 10.2844(10)Å, b = 22.511(3)Å, c = 22.695(2)Å, α = 90°, β = 90°, γ = 90°, V = 5254(1)Å^3, T = 103(2)K, Z= 4, F(000) = 2144, D_x = 1.276 Mg/m^3, μ 0.109mm^{-1}.

A crystal of [(*R*)-**1c**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 30821 (3.24 ≤ θ ≤ 25.33°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.228 ≤ θ ≤ 21.964[1].

A total of 43009 reflections were collected of which 6392were unique [R(int) = 0.1544, R(σ) = 0.0863]; intensities of 4811 reflections were greater than 2σ(I). Completeness to θ = 0.996.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.991439 and 0.996990).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).
Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0668 and wR^2 = 0.1191 for 1332 [I>2σ(I)] and R_1 = 0.0965 and wR^2 = 0.1306 for all (6392) intensity data, (number of parameters = 713, goodness-of-fit = 1.065, the maximum and mean shift/esd is 0.001 and 0.000). The absolute structure parameter is -0.05(12). (Friedel coverage: 0.776, Friedel fraction max.: 0.999, Friedel fraction full: 0.999).
The maximum and minimum residual electron density in the final difference map was 0.21 and -0.18e.Å^{-3}.
The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.03223.4327P)^2+3.4327P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1d**·(*R*,*R*)-**2e**]*:* $C_{68.5}$ $H_{66.5}$ O_6 P, *Fwt.*: 1017.04, colourless, chunk, size: 0.45 x 0.15 x 0.15 mm, orthorhombic, space group $P\,2_1\,2_1\,2_1$, a = 10.2836(19)Å, b = 23.126(4)Å, c = 23.684(4)Å, α = 90°, β = 90°, γ = 90°, V = 5633(2)Å^3, T = 103(2)K, Z= 4, F(000) = 2163, D_x = 1.199 Mg/m^3, μ 0.102mm^{-1}.
A crystal of [(*R*)-**1d**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 126744 (3.185 ≤ θ ≤ 27.46°) reflections.
Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.124 ≤ θ ≤ 21.491[1].
A total of 192117 reflections were collected of which 6451 were unique [R(int) = 0.1849, R(σ) = 0.0489]; intensities of 5814 reflections were greater than 2σ(I). Completeness to θ = 0.996.
A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.990194 and 0.996229).
The structure was solved by direct methods[10,11] (and subsequent difference syntheses).
Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0679 and wR^2 = 0.1359for 1332 [I>2σ(I)] and R_1 = 0.0773 and wR^2 = 0.1398 for all (6451) intensity data, (number of parameters = 696, goodness-of-fit = 1.154, the maximum and mean shift/esd is 0.000 and 0.000). The absolute structure parameter is 0.17(7). (Friedel coverage: 0.775, Friedel fraction max.: 0.999, Friedel fraction full: 0.999).
The maximum and minimum residual electron density in the final difference map was 0.31 and -0.21e.Å^{-3}.
The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.05842.3001P)^2+2.3001P]$ where $P = (F_o^2+2F_c^2)/3$.

[(R_P)-**1e**·(*R*,*R*)-**2e**]*:* C66 H67 O6 P, *Fwt.*: 987.16, colourless, needle, size: 0.40 x 0.07 x 0.04 mm, orthorhombic, space group $P\,2_1\,2_1\,2_1$, a = 10.1392(9)Å, b = 21.9837(19)Å, c = 23.902(2)Å, α = 90°, β = 90°, γ = 90°, V = 5328(1)Å^3, T = 103(2)K, Z= 4, F(000) = 2104, D_x = 1.231 Mg/m^3, μ 0.106mm^{-1}.

A crystal of [(R_P)-**1e**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 47728 (3.16 ≤ θ ≤ 27.42°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.158 ≤ θ ≤ 25.350[1].

A total of 114772 reflections were collected of which 9729 were unique [R(int) = 0.3192, R(σ) = 0.1354]; intensities of 6069 reflections were greater than 2σ(I). Completeness to θ = 0.997.

An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.4445 and 1.0000).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.1080 and wR^2 = 0.1278 for 1332 [I>2σ(I)] and R_1 = 0.1706 and wR^2 = 0.1464 for all (9729) intensity data, (number of parameters = 711, goodness-of-fit = 1.118, the maximum and mean shift/esd is 0.000 and 0.000). The absolute structure parameter is -0.05(13). (Friedel coverage: 0.799, Friedel fraction max.: 0.999, Friedel fraction full: 0.999).

The maximum and minimum residual electron density in the final difference map was 0.22 and -0.25e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.01353.9024P)^2+3.9024P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1f**·(*R*,*R*)-**2e**]*:* C_{70} H_{69} O_6 P, *Fwt.*: 1037.22, colourless, block, size: 0.400 x 0.250 x 0.200 mm, orthorhombic, space group $P\,2_1\,2_1\,2_1$, a = 10.2103(10)Å, b = 22.6629(18)Å, c = 23.531(2)Å, α = 90°, β = 90°, γ = 90°, V = 5445(1)Å^3, T = 103(2)K, Z= 4, F(000) = 2208, D_x = 1.265 Mg/m^3, μ 0.107mm^{-1}.

A crystal of [(*R*)-**1f**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 39803 (3.16 ≤ θ ≤ 27.475°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.159 ≤ θ ≤ 25.351[1].

A total of 61727 reflections were collected of which 9769 were unique [R(int) = 0.1373, R(σ)

= 0.0915]; intensities of 7176 reflections were greater than 2σ(*I*). Completeness to θ = 0.981.
A(n) numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.988662 and 0.996401).
The structure was solved by direct methods[10,11] (and subsequent difference syntheses).
Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0653 and wR^2 = 0.1101for 1332 [I>2σ(I)] and R_1 = 0.1001 and wR^2 = 0.1207 for all (9769) intensity data, (number of parameters = 701, goodness-of-fit = 1.031, the maximum and mean shift/esd is 0.001 and 0.000). The absolute structure parameter is 0.02(7). (Friedel coverage: 0.798, Friedel fraction max.: 0.980, Friedel fraction full: 0.980).
The maximum and minimum residual electron density in the final difference map was 0.24 and -0.29e.Å^{-3}.
The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.04421.3054P)^2+1.3054P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*S*)-**1h**·(*R*,*R*)-**2e**]*:* C_{60} H_{57} O_6 P, *Fwt.*: 905.02, colourless, chunk, size: 0.60 x 0.40 x 0.20 mm, orthorhombic, space group $P\,2_1\,2_1\,2_1$, a = 10.3472(9)Å, b = 18.8991(16)Å, c = 24.1084(19)Å, α = 90°, β = 90°, γ = 90°, V = 4716(1)Å^3, T = 103(2)K, Z= 4, F(000) = 1920, D_x = 1.275 Mg/m^3, μ 0.113mm^{-1}.
A crystal of [(*S*)-**1h**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 62017 (3.04 ≤ θ ≤ 27.555°) reflections.
Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.039 ≤ θ ≤ 25.351[1].
A total of 94536 reflections were collected of which 8594 were unique [R(int) = 0.1053, R(σ) = 0.0584]; intensities of 6273 reflections were greater than 2σ(*I*). Completeness to θ = 0.994.
A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.984771 and 0.990183).
The structure was solved by direct methods[10,11] (and subsequent difference syntheses).
Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0776 and wR^2 = 0.1469 for 1332 [I>2σ(I)] and R_1 = 0.1114 and wR^2 = 0.1636 for all (8594) intensity data, (number of parameters = 613, goodness-of-fit = 1.085, the maximum and mean shift/esd is 0.001 and 0.000). The absolute structure parameter is 0.18(5). (Friedel coverage: 0.793, Friedel fraction max.: 0.993, Friedel fraction full: 0.993).
The maximum and minimum residual electron density in the final difference map was 0.30 and

-0.22e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.04833.2355P)^2+3.2355P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1j**·(*R*,*R*)-**2e**]*:* C_{70} H_{63} O_6 P, *Fwt.*: 1031.17, colourless, chunk, size: 0.40 x 0.15 x 0.15 mm, orthorhombic, space group *P* 2_1 2_1 2_1, *a* = 10.1883(9)Å, *b* = 22.4173(19)Å, *c* = 23.625(2)Å, α = 90°, β = 90°, γ = 90°, *V* = 5395.8(8)Å^3, *T* = 103(2)K, *Z*= 4, *F*(000) = 2184, D_x = 1.269 Mg/m^3, μ 0.107mm^{-1}.

A crystal of [(*R*)-**1j**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 46300 (3.16 ≤ θ ≤ 27.44°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.162 ≤ θ ≤ 25.350[1].

A total of 68488 reflections were collected of which 9860 were unique [*R*(int) = 0.1168, *R(*σ) = 0.0734]; intensities of 7253 reflections were greater than 2σ(*I*). Completeness to θ = 0.997.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.988785 and 0.996190).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0597 and wR^2 = 0.1040for 1332 [I>2σ(I)] and R_1 = 0.0905 and wR^2 = 0.1134 for all (9860) intensity data, (number of parameters = 701, goodness-of-fit = 1.025, the maximum and mean shift/esd is 0.001 and 0.000). The absolute structure parameter is 0.29(6). (Friedel coverage: 0.801, Friedel fraction max.: 0.999, Friedel fraction full: 0.999).

The maximum and minimum residual electron density in the final difference map was 0.17 and -0.22e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.04760.5665P)^2+0.5665P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1k**·(*R*,*R*)-**2e**]*:* $C_{70.50}$ H_{69} O_6 P, *Fwt.*: 1043.22, colourless, platelet, size: 0.45 x 0.15 x 0.15 mm, orthorhombic, space group *P* 2_1 2_1 2_1, *a* = 10.2836(19)Å, *b* = 23.126(4)Å, *c* = 23.684(4)Å, α = 90°, β = 90°, γ = 90°, *V* = 5633(2)Å^3, *T* = 103(2)K, *Z*= 4, *F*(000) = 2220, D_x = 1.230 Mg/m^3, μ 0.104mm^{-1}.

A crystal of [(*R*)-**1k**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by

least-squares using 26801 (3.125 ≤ θ ≤ 25.53°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.124 ≤ θ ≤ 21.491[1]. A total of 47515 reflections were collected of which 6432were unique [*R*(int) = 0.2255, *R(*σ) = 0.1273]; intensities of 4477 reflections were greater than 2σ(*I*). Completeness to θ = 0.993.

An empirical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.2899 and 1.0000).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.1196 and wR^2 = 0.2756 for 1332 [I>2σ(I)] and R_1 = 0.1650 and wR^2 = 0.3109 for all (6432) intensity data, (number of parameters = 689, goodness-of-fit = 1.116, the maximum and mean shift/esd is 0.001 and 0.000). The absolute structure parameter is 0.4(2). (Friedel coverage: 0.774, Friedel fraction max.: 0.995, Friedel fraction full: 0.995).

The maximum and minimum residual electron density in the final difference map was 0.55 and -0.28e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.120800P)^2+17.6425P]$ where $P = (F_o^2+2F_c^2)/3$.

[(*R*)-**1m**·(*R*,*R*)-**2e**]*:* $C_{74}H_{73}O_6P$, *Fwt.*: 1089.29, colourless, block, size: 0.40 x 0.17 x 0.15 mm, orthorhombic, space group $P\,2_1\,2_1\,2_1$, a = 10.3398(9)Å, b = 23.222(2)Å, c = 23.718(2)Å, α = 90°, β = 90°, γ = 90°, V = 5695(1)Å^3, T = 103(2)K, Z= 4, F(000) = 2320, D_x = 1.270 Mg/m^3, μ 0.105mm^{-1}.

A crystal of [(*R*)-**1m**·(*R*,*R*)-**2e**] was mounted on a fiber. Cell parameters were determined by least-squares using 63144 (3.115 ≤ θ ≤ 27.425°) reflections.

Intensity data were collected on a(n) Rigaku RAXIS-RAPID II diffractometer (monochromator; Mo-*K*α radiation, λ = 0.71075Å) at 103(2) K in the range 3.117 ≤ θ ≤ 25.351[1]. A total of 102295 reflections were collected of which 10408 were unique [*R*(int) = 0.1637, *R(*σ) = 0.0940]; intensities of 8299 reflections were greater than 2σ(*I*). Completeness to θ = 0.997.

A numerical absorption correction was applied to the data (the minimum and maximum transmission factors were 0.5599 and 1.0000).

The structure was solved by direct methods[10,11] (and subsequent difference syntheses).

Anisotropic full-matrix least-squares refinement[12] on F^2 for all non-hydrogen atoms yielded R_1 = 0.0690 and wR^2 = 0.1170 for 1332 [I>2σ(I)] and R_1 = 0.0929 and wR^2 = 0.1251 for all (

10408) intensity data, (number of parameters = 738, goodness-of-fit = 1.077, the maximum and mean shift/esd is 0.002 and 0.000). The absolute structure parameter is 0.12(8). (Friedel coverage: 0.804, Friedel fraction max.: 0.999, Friedel fraction full: 0.999).

The maximum and minimum residual electron density in the final difference map was 0.23 and -0.29e.Å^{-3}.

The weighting scheme applied was $w = 1/[\sigma^2(F_o^2)+(0.04262.0874P)^2+2.0874P]$ where $P = (F_o^2+2F_c^2)/3$.

Table S11: Summary of crystallographic data, data collections, structure determination and refinement for the corresponding diastereomers.

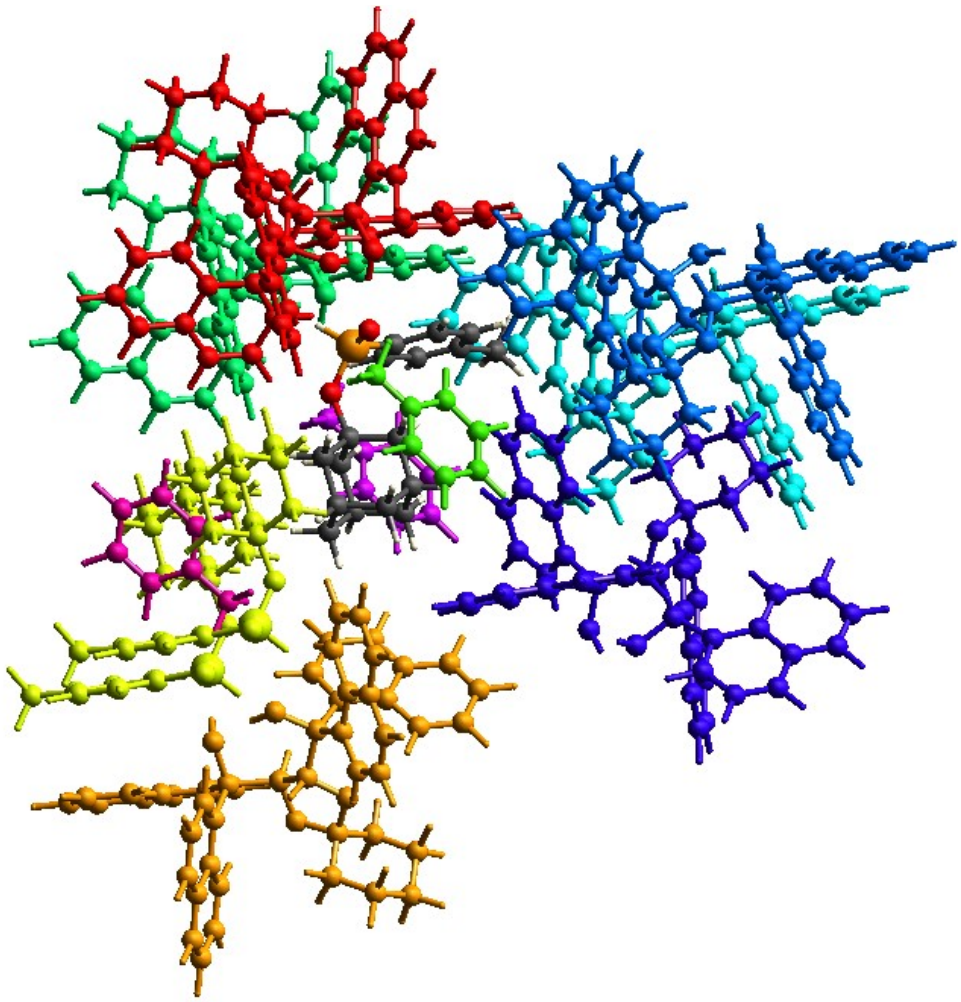
Number	[(*R*)-**1a**·(*R*,*R*)-**2e**]	[(*R*)-**1b**·(*R*,*R*)-**2e**]	[(*R*)-**1c**·(*R*,*R*)-**2e**]	[(*R*)-**1k**·(*R*,*R*)-**2e**]
CCDC	2143598	2143599	2143600	2143601
Empirical formula	C50 H42 O4 C7 H8 C16 H21 O2 P	C50 H42 O4 C7 H8 C16 H21 O2 P	C50 H42 O4 C7 H8 C11 H15 O2 P	C50 H42 O4 C7 H8 C17 H22 O2 P
Formula weight	1075.26	1075.26	1009.17	1043.22
Temperature	103(2)	103(2)	103(2)	103(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$	$P\,2_1\,2_1\,2_1$
Unit cell dimensions	*a* =10.3422(7)Å *b* =23.1822(17)Å *c* =23.8390(18)Å α =90° β =90° γ =90°	*a* =10.2809(13)Å *b* =22.954(3)Å *c* =23.721(3)Å α =90° β =90° γ =90°	*a* =10.2844(10)Å *b* =22.511(3)Å *c* =22.695(2)Å α =90° β =90° γ =90°	*a* =10.2836(19)Å *b* =23.126(4)Å *c* =23.684(4)Å α =90° β =90° γ =90°
Volume	5716(1)Å^3	5598(1)Å^3	5254(1)Å^3	5633(2)Å^3
Z, Z'	4, 1	4, 1	4, 1	4, 1
Density (calculated)	1.250 Mg/m^3	1.276 Mg/m^3	1.276 Mg/m^3	1.230 Mg/m^3
Absorption coefficient, μ	0.104 mm^{-1}	0.106 mm^{-1}	0.109 mm^{-1}	0.104 mm^{-1}
F(000)	2288	2288	2144	2220
Crystal colour	colourless	colourless	colourless	colourless
Crystal description	chunk	needle	block	platelet
Crystal size	0.50 x 0.40 x 0.40 mm	0.50 x 0.10 x 0.10 mm	0.50 x 0.100 x 0.10 mm	0.45 x 0.15 x 0.10 mm
Absorption correction	empirical	numerical	numerical	empirical
Max. and min. transmission	0.7230 and 1.0000	0.988724 and 0.998178	0.991439 and 0.996990	0.2899 and 1.0000
θ–range for data collection	3.108 ≤ θ ≤ 25.350°	3.129 ≤ θ ≤ 23.532°	3.228 ≤ θ ≤ 21.964°	3.124 ≤ θ ≤ 21.491°
Index ranges	-12 ≤ *h* ≤12; -27≤ *k* ≤27; -28 ≤ *l* ≤28	-11 ≤ *h* ≤11; -25≤ *k* ≤25; -26 ≤ *l* ≤26	-10 ≤ *h* ≤10; -23≤ *k* ≤23; -23 ≤ *l* ≤23	-10 ≤ *h* ≤10; -23≤ *k* ≤23; -24 ≤ *l* ≤24
Reflections collected	75348	114437	43009	47515
Completeness to 2θ	0.997	0.996	0.996	0.993
Absolute structure parameter	0.11(9)	-0.03(8)	-0.05(12)	0.4(2)
Friedel coverage	0.803	0.790	0.776	0.774
Friedel fraction max.	0.999	0.998	0.999	0.995
Friedel fraction full	0.999	0.998	0.999	0.995
Independent reflections	10434 [*R*(int) =0.1701]	8286 [*R*(int) =0.2025]	6392 [*R*(int) =0.1544]	6432 [*R*(int) =0.2255]
Reflections *I*>2σ(*I*)	6380	6257	4811	4477
Data / restraints / parameters	10434 /15 /699	8286 /4 /688	6392 /12 /713	6432 /1 /689
Goodness-of-fit on *F*2	1.103	1.072	1.065	1.116
Final *R* indices [*I*>2σ(*I*)]	R_1 =0.0866, wR^2 =0.1287	R_1 =0.0743, wR^2 =0.1356	R_1 =0.0668, wR^2 =0.1191	R_1 =0.1196, wR^2 =0.2756
R indices (all data)	R_1 =0.1501, wR^2 =0.1479	R_1 =0.1044, wR^2 =0.1461	R_1 =0.0965, wR^2 =0.1306	R_1 =0.1650, wR^2 =0.3109
Max. and mean shift/esd	0.002;0.000	0.000;0.000	0.001;0.000	0.001;0.000
Largest diff. peak and hole	0.26;-0.18 e.Å^{-3}	0.33;-0.19 e.Å^{-3}	0.21;-0.18 e.Å^{-3}	0.55;-0.28 e.Å^{-3}

Table S11 (continued): Summary of crystallographic data, data collections, structure determination and refinement for the corresponding diastereomers.

Number	[(*R*)-**1m**·(*R*,*R*)-**2e**]	[(*S*)-**1h**·(*R*,*R*)-**2e**]	[(*R*)-**1d**·(*R*,*R*)-**2e**]	[(R_P)-**1e**·(*R*,*R*)-**2e**]
CCDC	2143602	2143603	2143604	2143605
Empirical formula	C50 H42 O4 C7 H8 C14 H23 O2 P	C50 H42 O4 C10 H15 O2 P	C50 H42 O4 C7 H8 C12 H18 O2 P	C50 H42 O4 C16 H25 O2 P
Formula weight	1089.29	905.02	1017.04	987.16
Temperature	103(2)	103(2)	103(2)	103(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1
Unit cell dimensions	*a* =10.3398(9)Å *b* =23.222(2)Å *c* =23.718(2)Å α =90° β =90° γ =90°	*a* =10.3472(9)Å *b* =18.8991(16)Å *c* =24.1084(19)Å α =90° β =90° γ =90°	*a* =10.2836(19)Å *b* =23.126(4)Å *c* =23.684(4)Å α =90° β =90° γ =90°	*a* =10.1392(9)Å *b* =21.9837(19)Å *c* =23.902(2)Å α =90° β =90° γ =90°
Volume	5695(1)Å^3	4714.5(7)Å^3	5633(2)Å^3	5328(1)Å^3
Z, Z'	4, 1	4, 1	4, 1	4, 1
Density (calculated)	1.270 Mg/m^3	1.275 Mg/m^3	1.199 Mg/m^3	1.231 Mg/m^3
Absorption coefficient, μ	0.105 mm^{-1}	0.113 mm^{-1}	0.102 mm^{-1}	0.106 mm^{-1}
F(000)	2320	1920	2163	2104
Crystal colour	colourless	colourless	colourless	colourless
Crystal description	block	chunk	chunk	needle
Crystal size	0.40 x 0.17 x 0.15 mm	0.60 x 0.40x 0.200 mm	0.45 x 0.15 x 0.15 mm	0.40 x 0.07 x 0.04 mm
Absorption correction	numerical	numerical	numerical	empirical
Max. and min. transmission	0.5599 and 1.0000	0.984771 and 0.990183	0.990194 and 0.996229	0.4445 and 1.0000
θ–range for data collection	3.117 ≤ θ ≤ 25.351°	3.039 ≤ θ ≤ 25.351°	3.124 ≤ θ ≤ 21.491°	3.158 ≤ θ ≤ 25.350°
Index ranges	-12 ≤ *h* ≤12; -27≤ *k* ≤27; -28 ≤ *l* ≤28	-12 ≤ *h* ≤12; -22≤ *k* ≤22; -29 ≤ *l* ≤29	-10 ≤ *h* ≤10; -23≤ *k* ≤23; -24 ≤ *l* ≤24	-12 ≤ *h* ≤12; -26≤ *k* ≤26; -28 ≤ *l* ≤28
Reflections collected	102295	94536	192117	114772
Completeness to 2θ	0.997	0.994	0.996	0.997
Absolute structure parameter	0.12(8)	0.18(5)	0.17(7)	-0.05(13)
Friedel coverage	0.804	0.793	0.775	0.799
Friedel fraction max.	0.999	0.993	0.999	0.999
Friedel fraction full	0.999	0.993	0.999	0.999
Independent reflections	10408 [*R*(int) =0.1637]	8594 [*R*(int) =0.1053]	6451 [*R*(int) =0.1849]	9729 [*R*(int) =0.3192]
Reflections *I*>2σ(*I*)	8299	6273	5814	6069
Data / restraints / parameters	10408 /0 /738	8594 /2 /613	6451 /7 /696	9729 /6 /711
Goodness-of-fit on *F*2	1.077	1.085	1.154	1.118
Final *R* indices [*I*>2σ(*I*)]	R_1 =0.0690, wR^2 =0.1170	R_1 =0.0776, wR^2 =0.1469	R_1 =0.0679, wR^2 =0.1359	R_1 =0.1080, wR^2 =0.1278
R indices (all data)	R_1 =0.0929, wR^2 =0.1251	R_1 =0.1114, wR^2 =0.1636	R_1 =0.0773, wR^2 =0.1398	R_1 =0.1706, wR^2 =0.1464
Max. and mean shift/esd	0.002;0.000	0.001;0.000	0.000;0.000	0.000;0.000
Largest diff. peak and hole	0.23;-0.29 e.Å^{-3}	0.30;-0.22 e.Å^{-3}	0.31;-0.21 e.Å^{-3}	0.22;-0.25 e.Å^{-3}

Table S11 (continued): Summary of crystallographic data, data collections, structure determination and refinement for the corresponding diastereomers.

Number	[(*R*)-**1f**·(*R*,*R*)-**2e**]	[(*R*)-**1j**·(*R*,*R*)-**2e**]
CCDC	2143606	2143607
Empirical formula	C50 H42 O4 C7 H8 C13 H19 O2 P	C50 H42 O4 C7 H8 C13 H13 O2 P
Formula weight	1037.22	1031.17
Temperature	103(2)	103(2)
Radiation and wavelength	Mo-Kα, λ =0.71075Å	Mo-Kα, λ =0.71075Å
Crystal system	orthorhombic	orthorhombic
Space group	*P* 2_1 2_1 2_1	*P* 2_1 2_1 2_1
Unit cell dimensions	*a* =10.2103(10)Å *b* =22.6629(18)Å *c* =23.531(2)Å α =90° β =90° γ =90°	*a* =10.1883(9)Å *b* =22.4173(19)Å *c* =23.625(2)Å α =90° β =90° γ =90°
Volume	5445.0(8)Å^3	5396(1)Å^3
Z, Z'	4, 1	4, 1
Density (calculated)	1.265 Mg/m^3	1.269 Mg/m^3
Absorption coefficient, μ	0.107 mm^{-1}	0.107 mm^{-1}
F(000)	2208	2184
Crystal colour	colourless	colourless
Crystal description	block	chunk
Crystal size	0.40 x 0.25 x 0.20 mm	0.40 x 0.15 x 0.15 mm
Absorption correction	numerical	numerical
Max. and min. transmission	0.988662 and 0.996401	0.988785 and 0.996190
θ–range for data collection	3.159 ≤ θ ≤ 25.351°	3.162 ≤ θ ≤ 25.350°
Index ranges	-12 ≤ *h* ≤12; -27≤ *k* ≤26; -28 ≤ *l* ≤28	-12 ≤ *h* ≤12; -27≤ *k* ≤27; -28 ≤ *l* ≤28
Reflections collected	61727	68488
Completeness to 2θ	0.981	0.997
Absolute structure parameter	0.02(7)	0.29(6)
Friedel coverage	0.798	0.801
Friedel fraction max.	0.980	0.999
Friedel fraction full	0.980	0.999
Independent reflections	9769 [*R*(int) =0.1373]	9860 [*R*(int) =0.1168]
Reflections *I*>2σ(*I*)	7176	7253
Data / restraints / parameters	9769 /0 /701	9860 /0 /701
Goodness-of-fit on *F*2	1.031	1.025
Final *R* indices [*I*>2σ(*I*)]	R_1 =0.0653, wR^2 =0.1101	R_1 =0.0597, wR^2 =0.1040
R indices (all data)	R_1 =0.1001, wR^2 =0.1207	R_1 =0.0905, wR^2 =0.1134
Max. and mean shift/esd	0.001;0.000	0.001;0.000
Largest diff. peak and hole	0.24;-0.29 e.Å^{-3}	0.17;-0.22 e.Å^{-3}

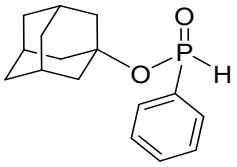


	N	Symop	R	Electron Density	E_ele	E_pol	E_dis	E_rep	E_tot
	1	-	7.46	B3LYP/6-31G(d,p)	-75.6	-21.9	-67.6	110.1	-87
	1	-	9.47	B3LYP/6-31G(d,p)	-7.2	-1.2	-50.8	28.1	-35.4
	1	-	9	B3LYP/6-31G(d,p)	-5.7	-2.1	-28.9	16.8	-22.3
	1	-	10.5	B3LYP/6-31G(d,p)	-5.6	-1.6	-23.1	12.4	-19.6
	1	-	11.3	B3LYP/6-31G(d,p)	-4.1	-0.6	-26.7	14.8	-18.9
	1	-	11.1	B3LYP/6-31G(d,p)	-5.7	-1	-26.5	18.9	-18.2
	2	x+1/2, -y+1/2, -z	9.48	B3LYP/6-31G(d,p)	-1.3	-0.3	-13.3	5.7	-9.7
	1	-	7.85	B3LYP/6-31G(d,p)	-1.3	-0.3	-13.3	5.7	-9.7
	1	-	5.38	B3LYP/6-31G(d,p)	-1.4	-0.3	-1.5	0	-3
	1	-	5.33	B3LYP/6-31G(d,p)	0	nan	0	0	nan

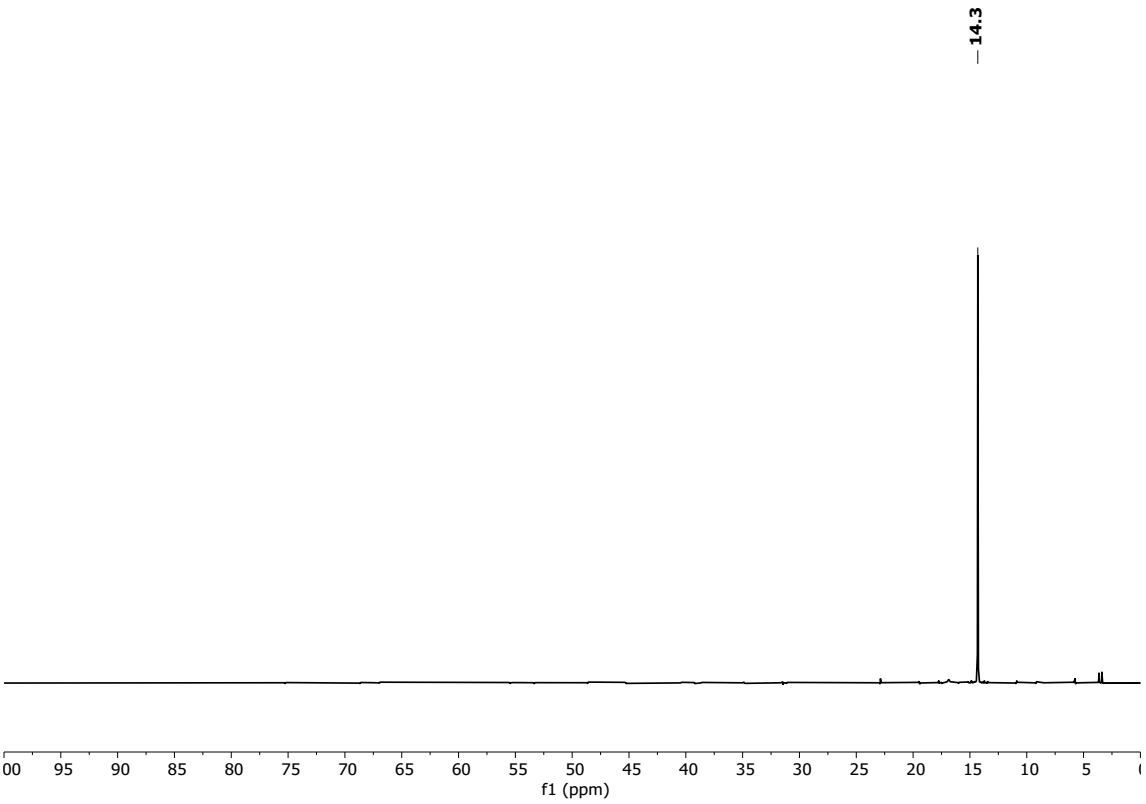
Fig. S4. The calculated total energy and its particles are shown between the molecules in the crystal lattices of the diastereomer incorporating 1-adamantyl (4-methylphenyl)-*H*-phosphinate [(*R*)-**1m**] and (*R*,*R*)-(1-naphthyl)-spiro-TADDOL [(*R*,*R*)-**2e**]. Total energies (E_tot) is reported by the DFT interaction energy calculation, which are the sum of the coulomb interactions (E_ele), polar interactions (E_pol), dispersion interactions (E_dis) and the repulsive (E_rep) interactions. The four energy components are scaled in the total Energy (E_tot=1.057*E_ele+0.740*E_pol+0.871*E_dis+0.618*E_rep). The interaction energies were investigated for a 3.8 Å cluster around the selected phosphorous derivatives. All fragment molecules were completed around the phosphorous molecule.

^{31}P, ^{19}F, ^{1}H and ^{13}C NMR spectra of the compounds prepared

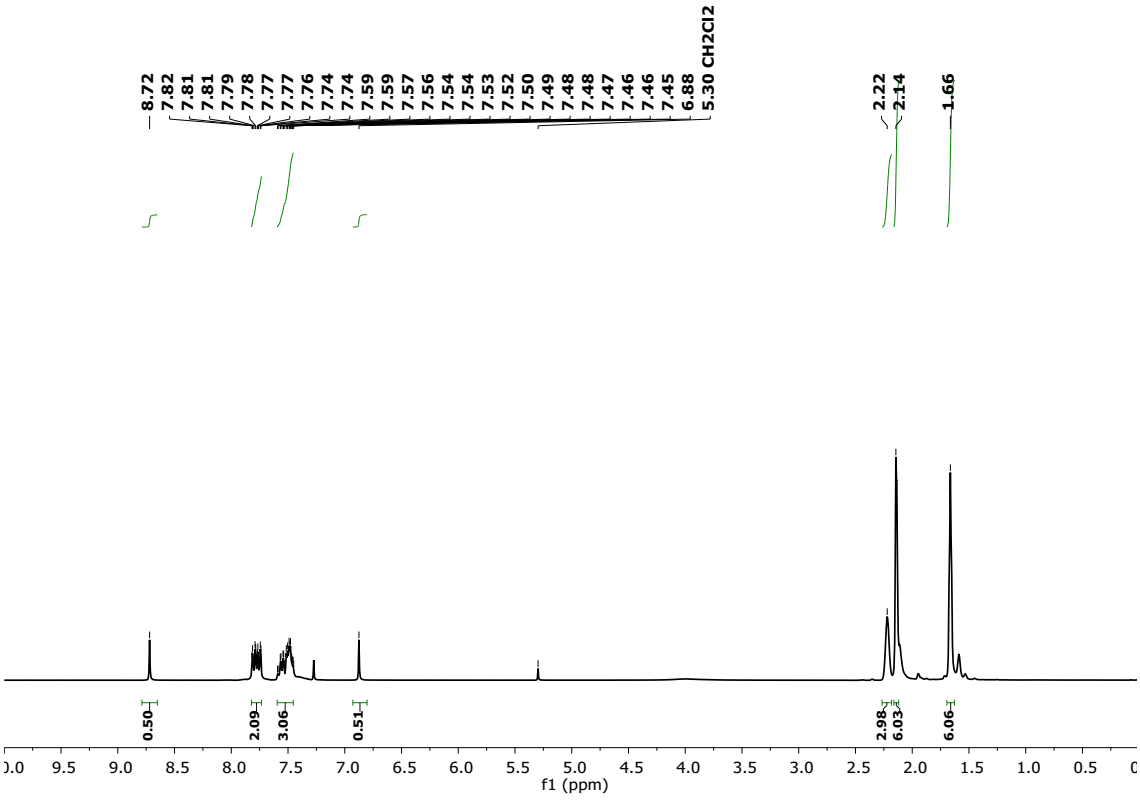
1-adamantyl phenyl-*H*-phosphinate (**1a**)



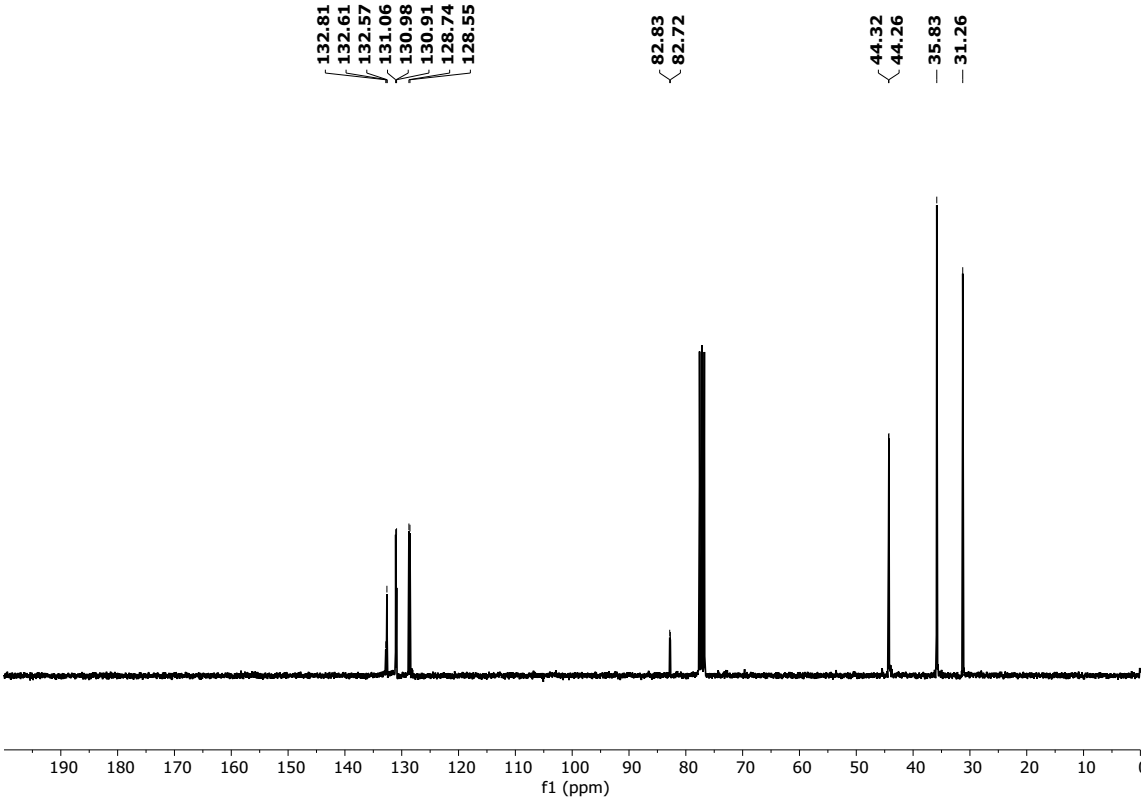
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$)



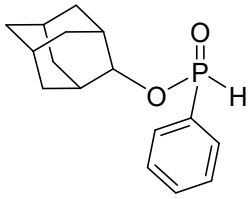
^{1}H NMR (300 MHz, $CDCl_3$)



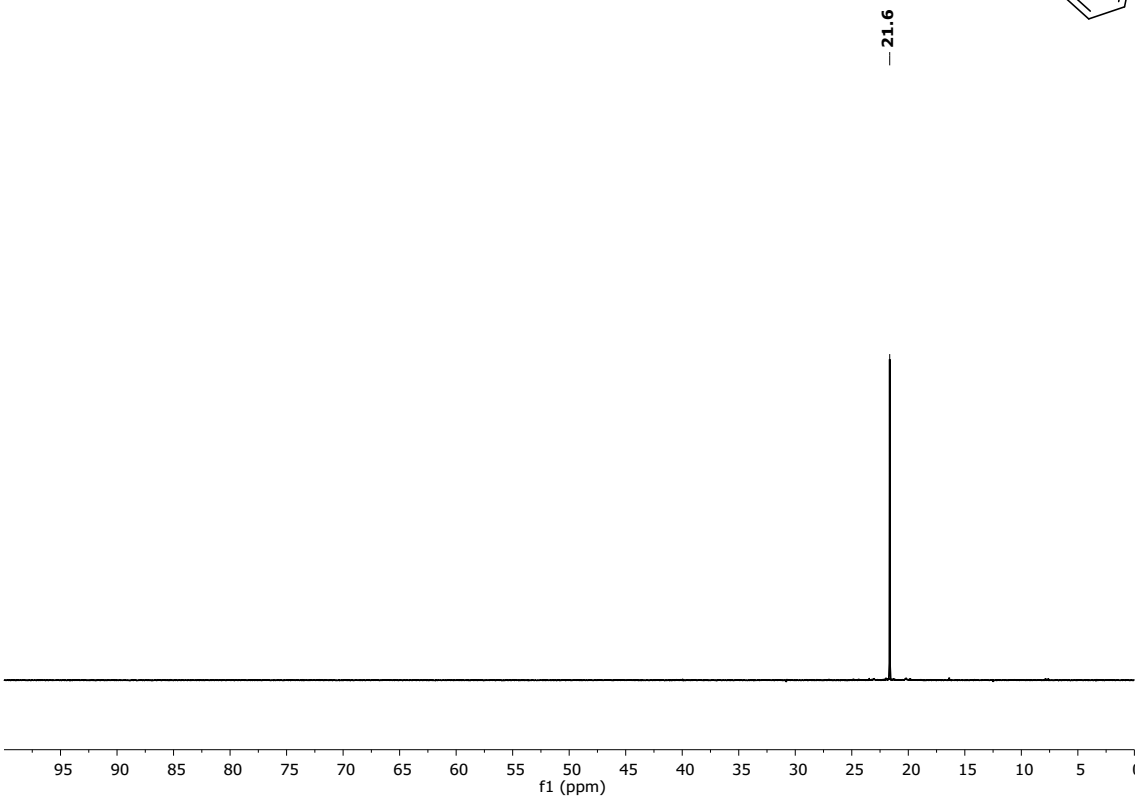
$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$)



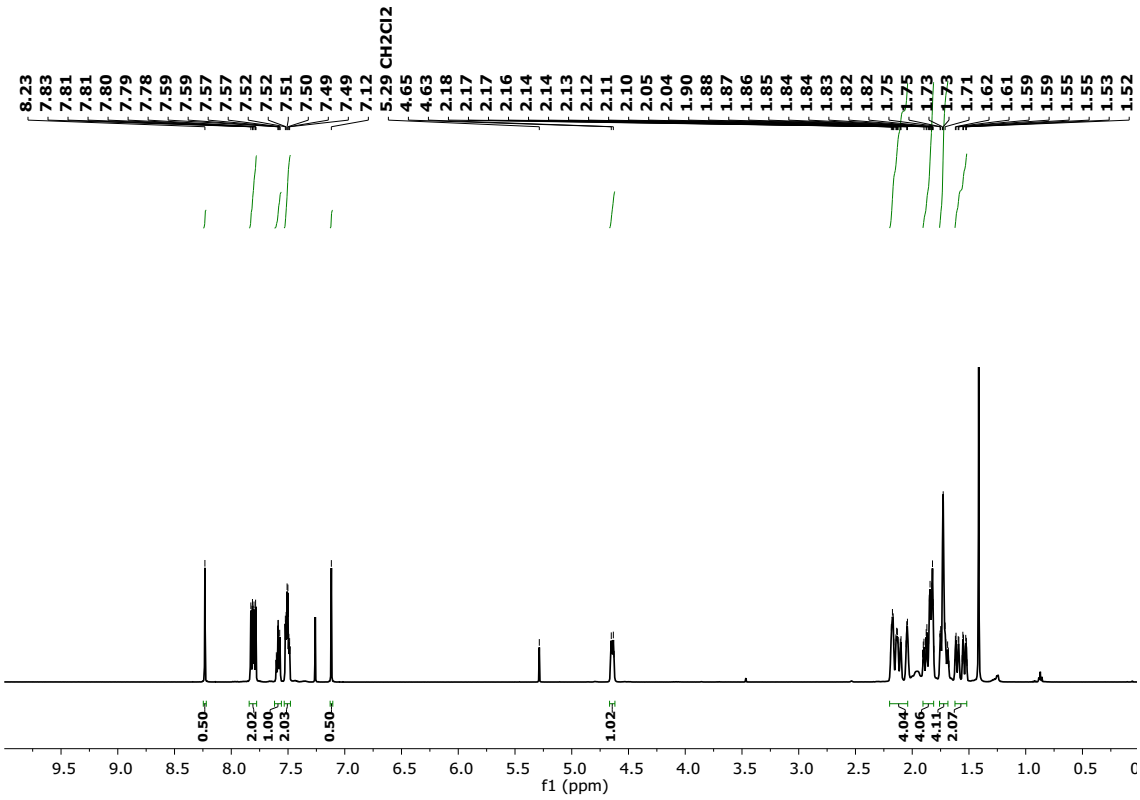
2-adamantyl phenyl-*H*-phosphinate (**1b**)



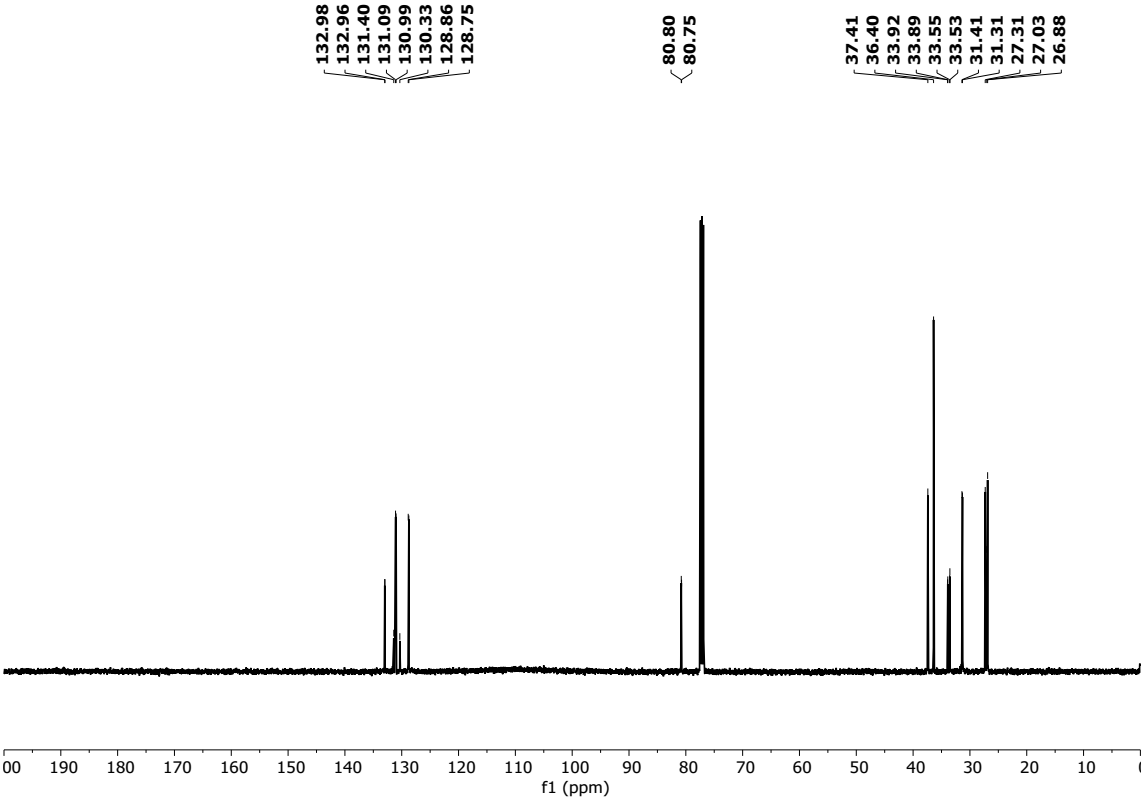
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



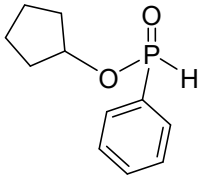
^{1}H NMR (500 MHz, $CDCl_3$)



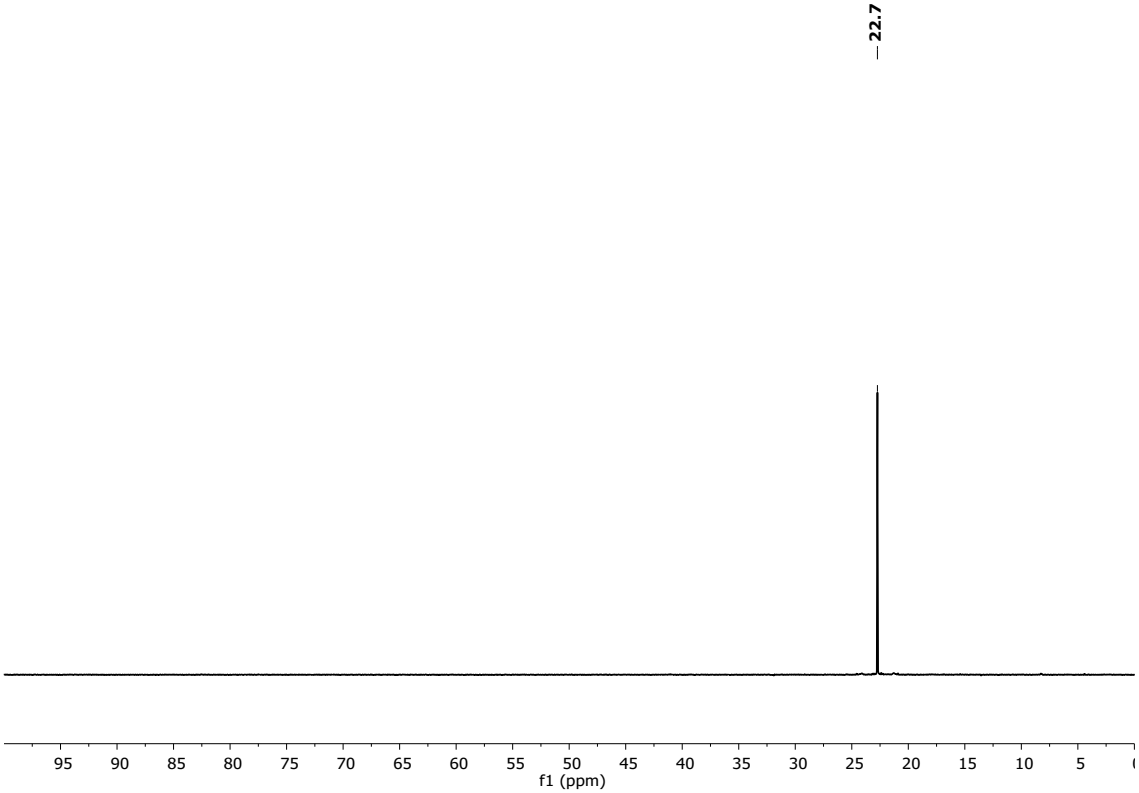
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



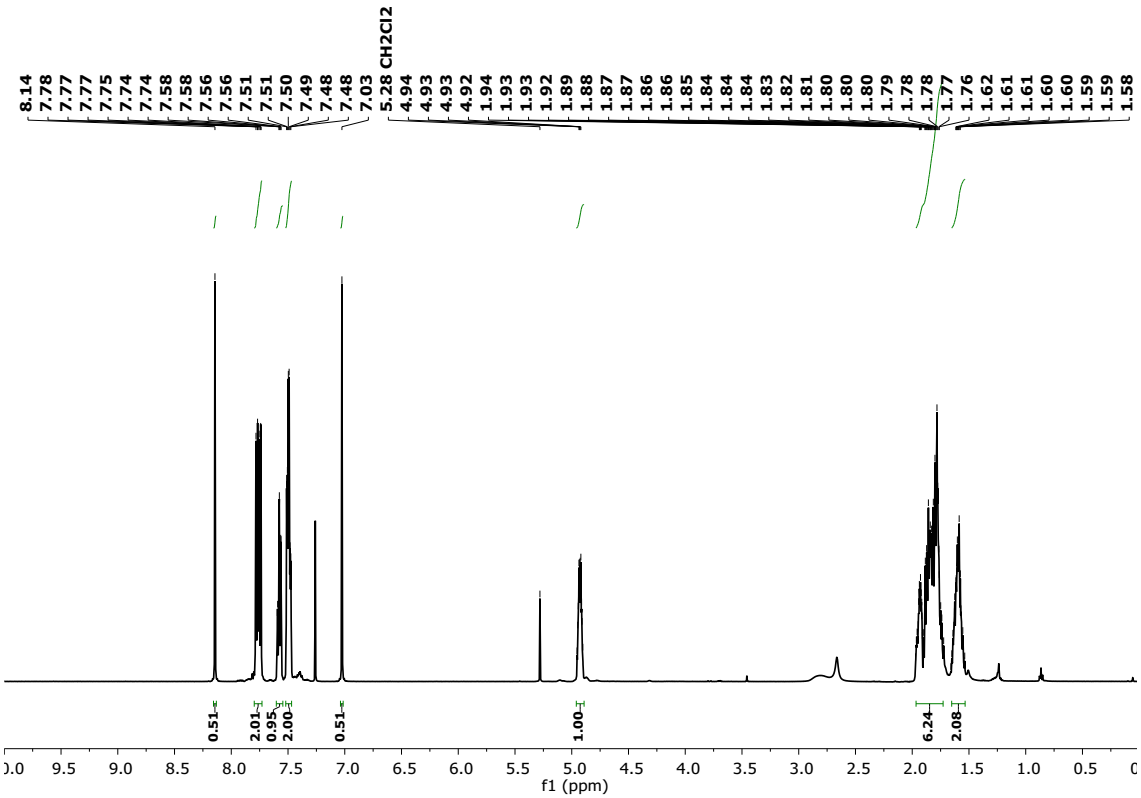
c-pentyl phenyl-*H*-phosphinate (**1c**)



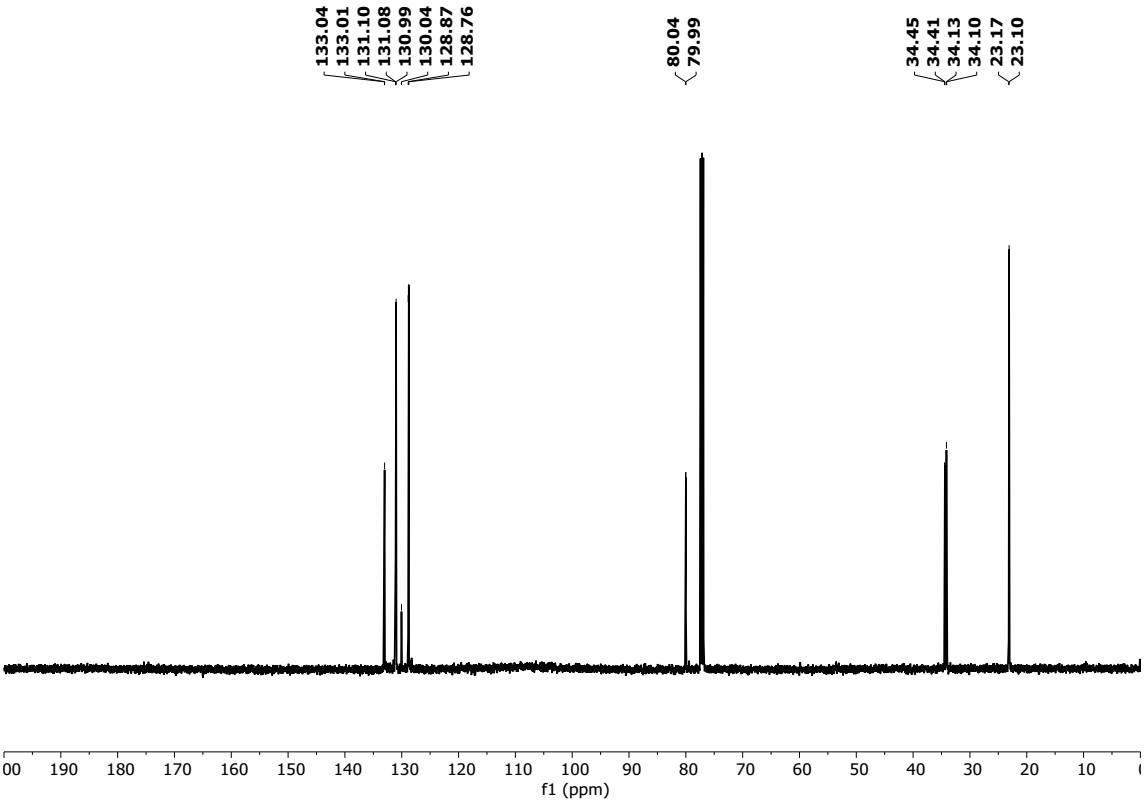
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



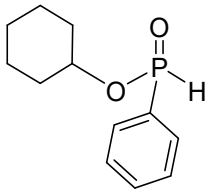
^{1}H NMR (500 MHz, $CDCl_3$)



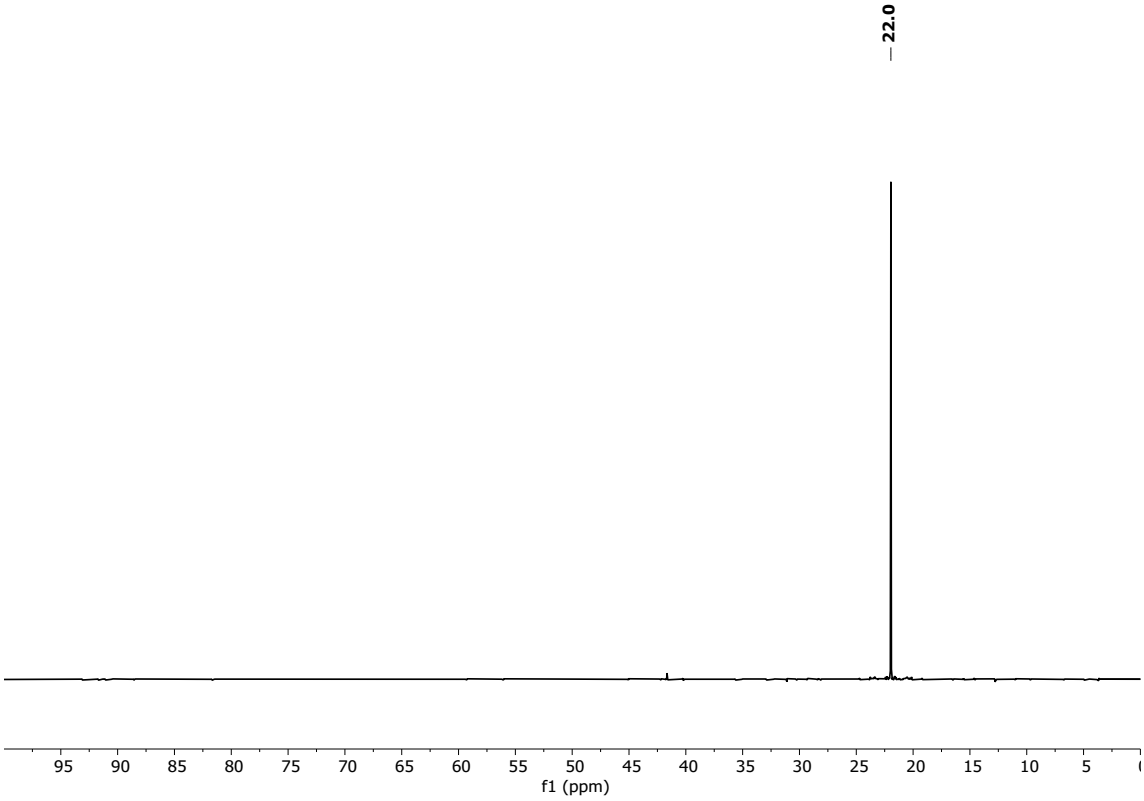
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



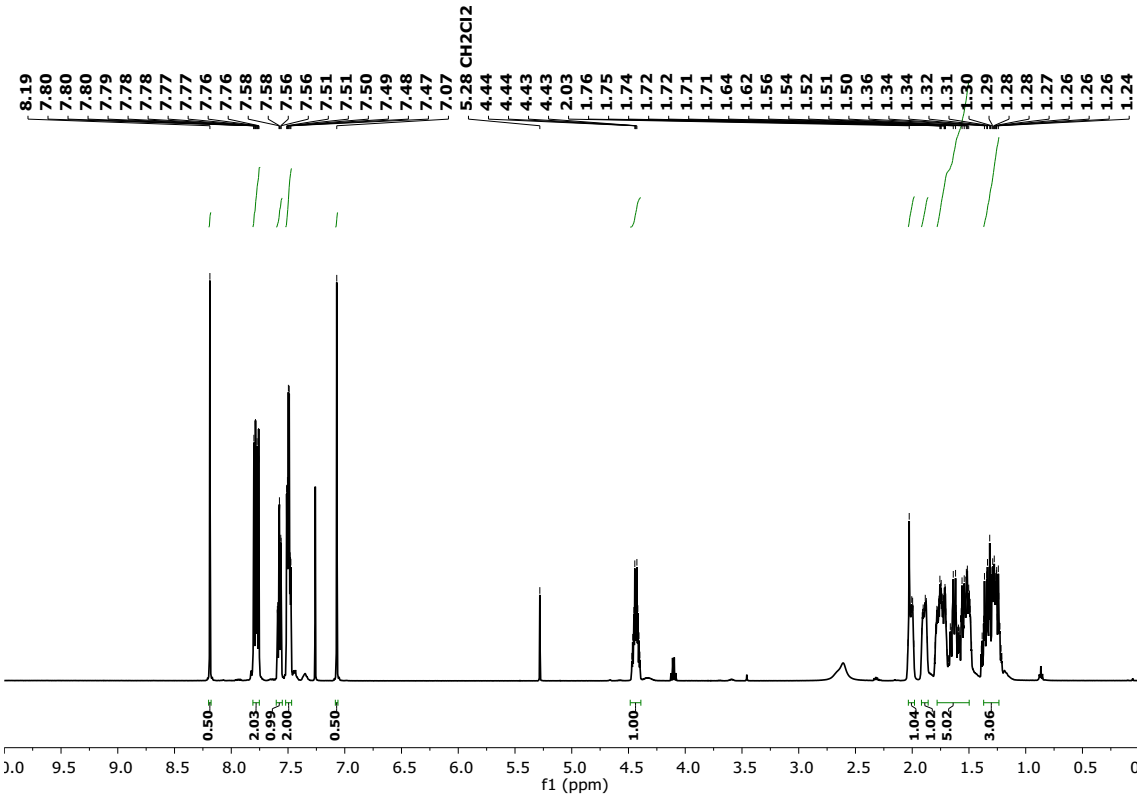
c-hexyl phenyl-*H*-phosphinate (**1d**)



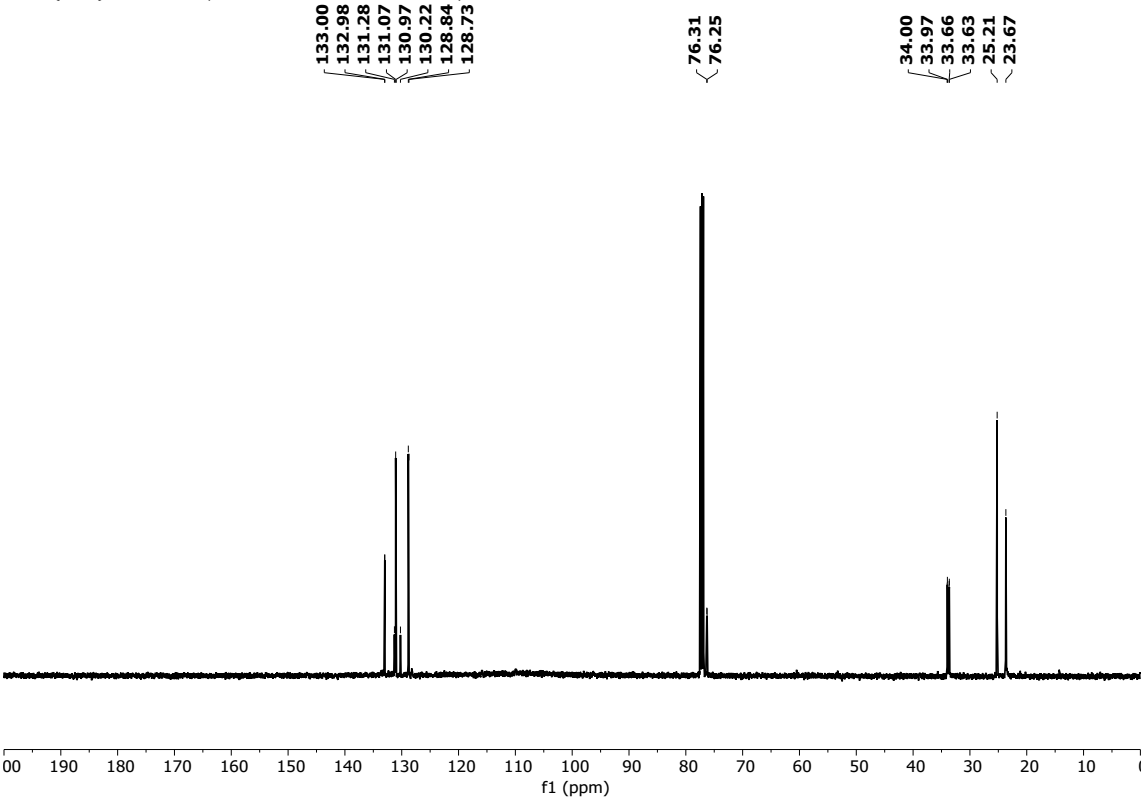
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

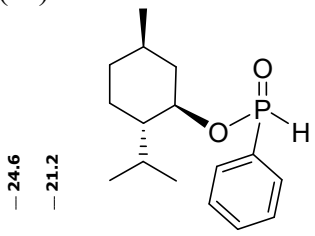


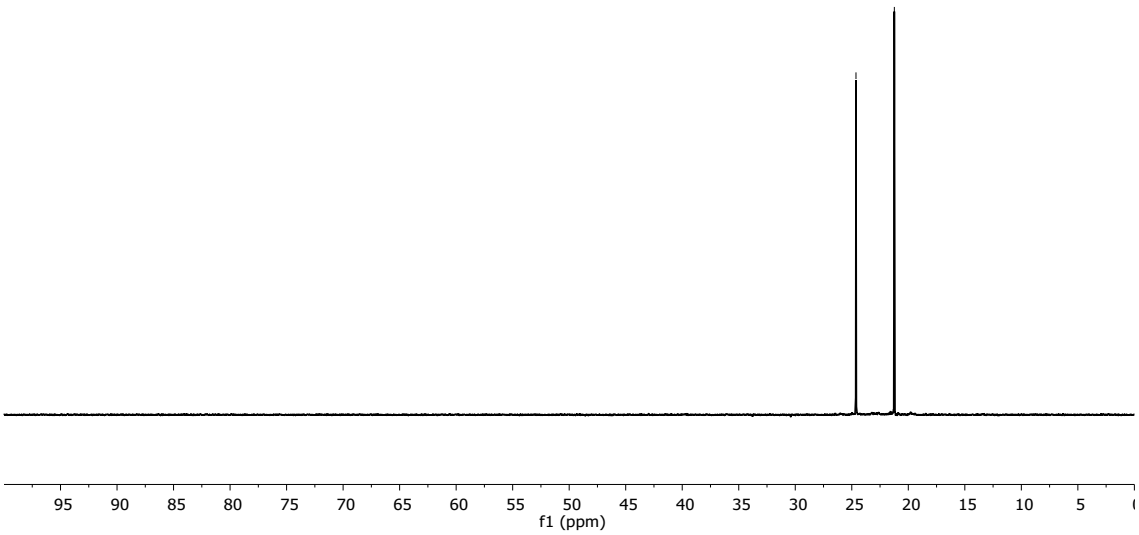
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



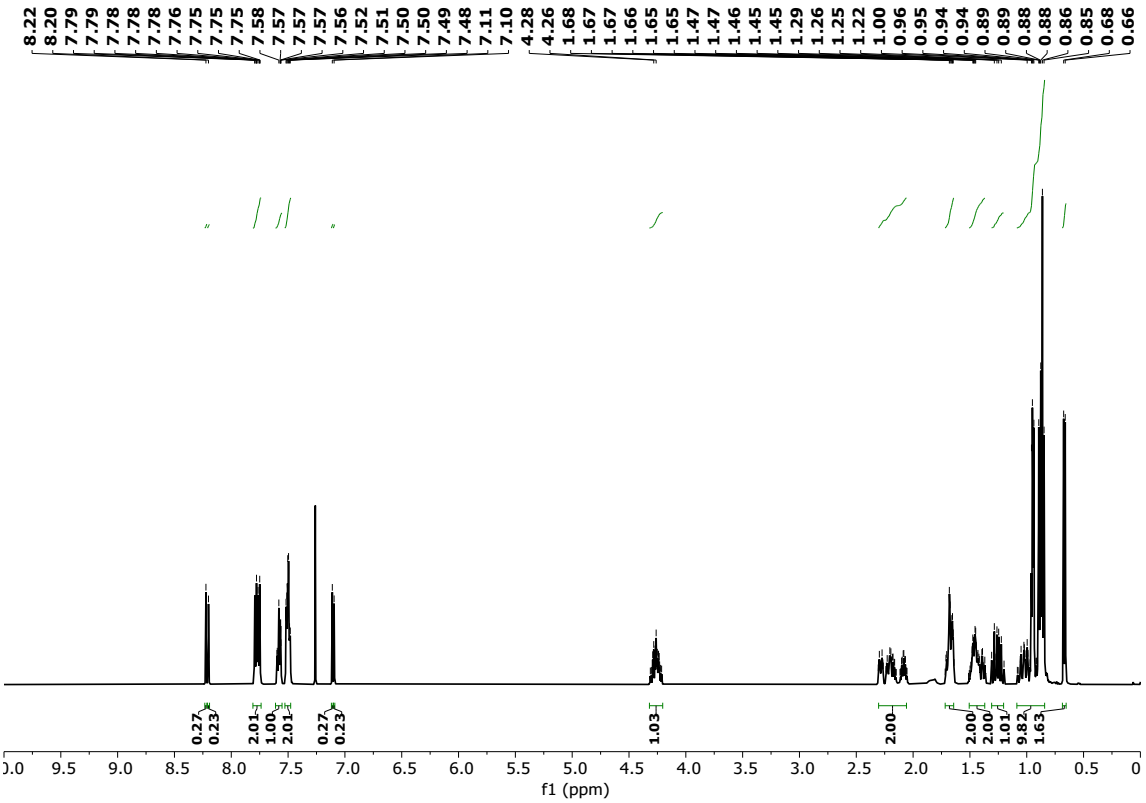
(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1e**)

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)

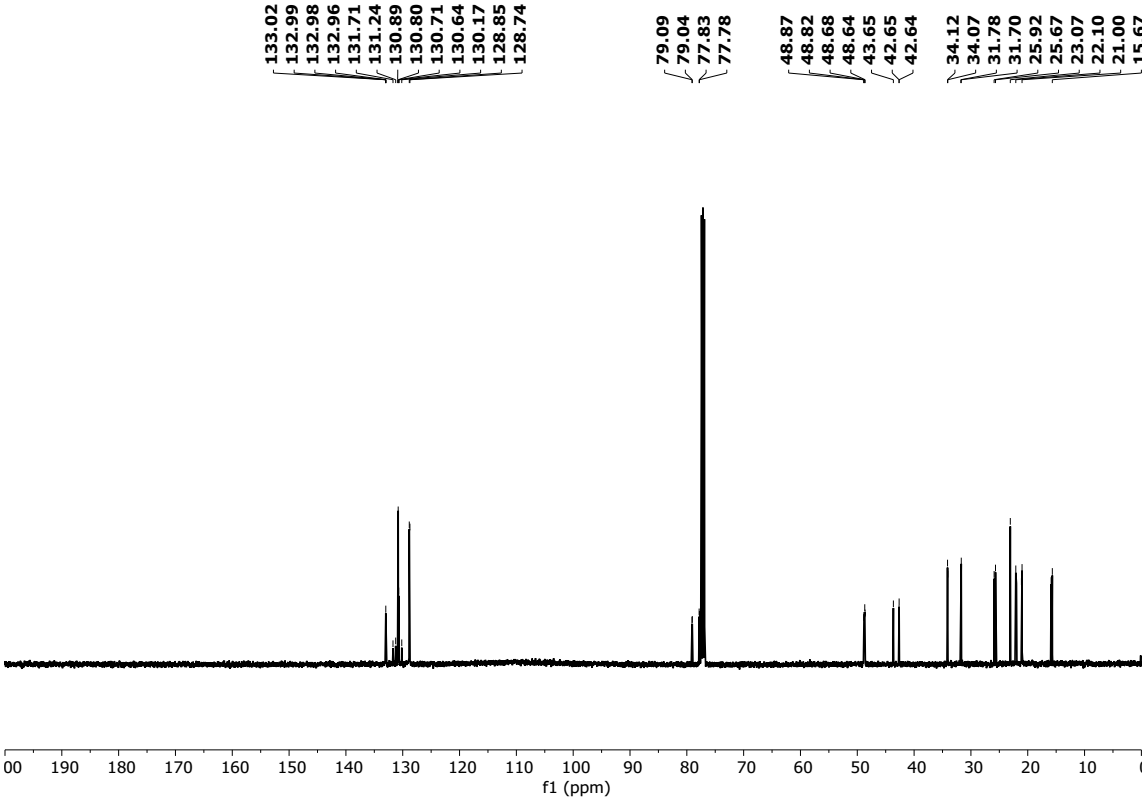




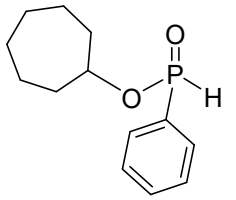
^{1}H NMR (500 MHz, $CDCl_3$)



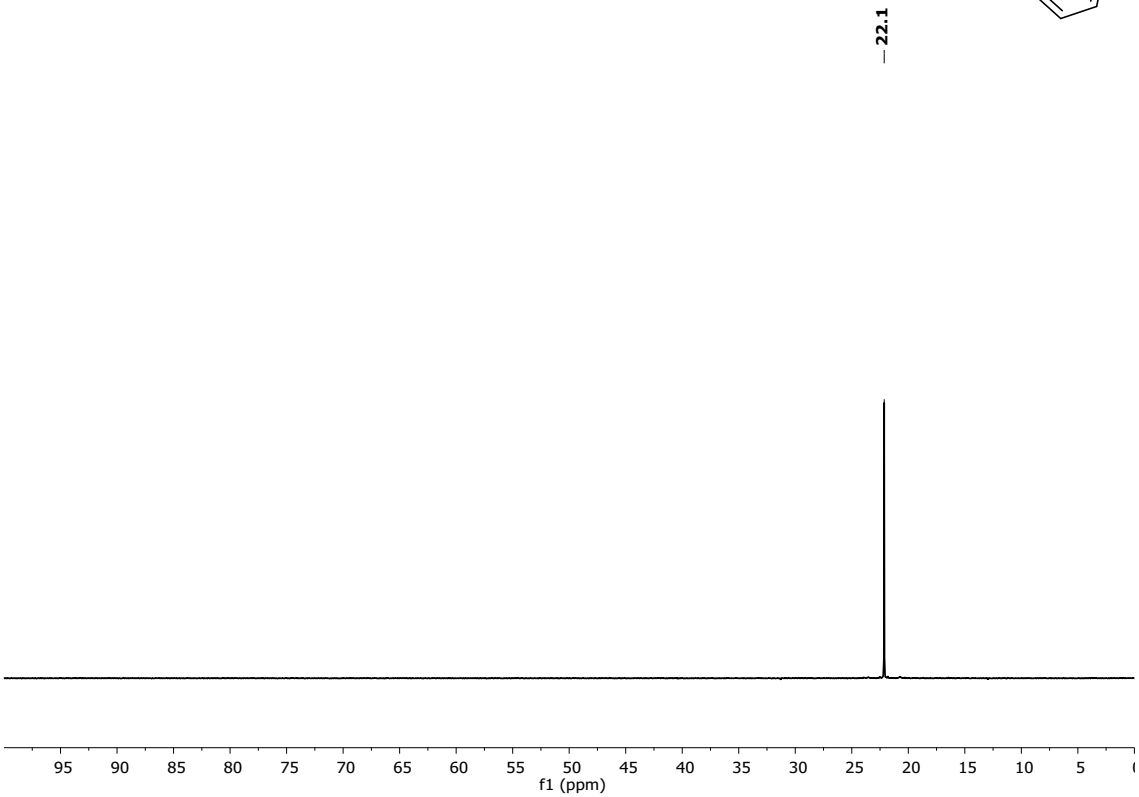
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



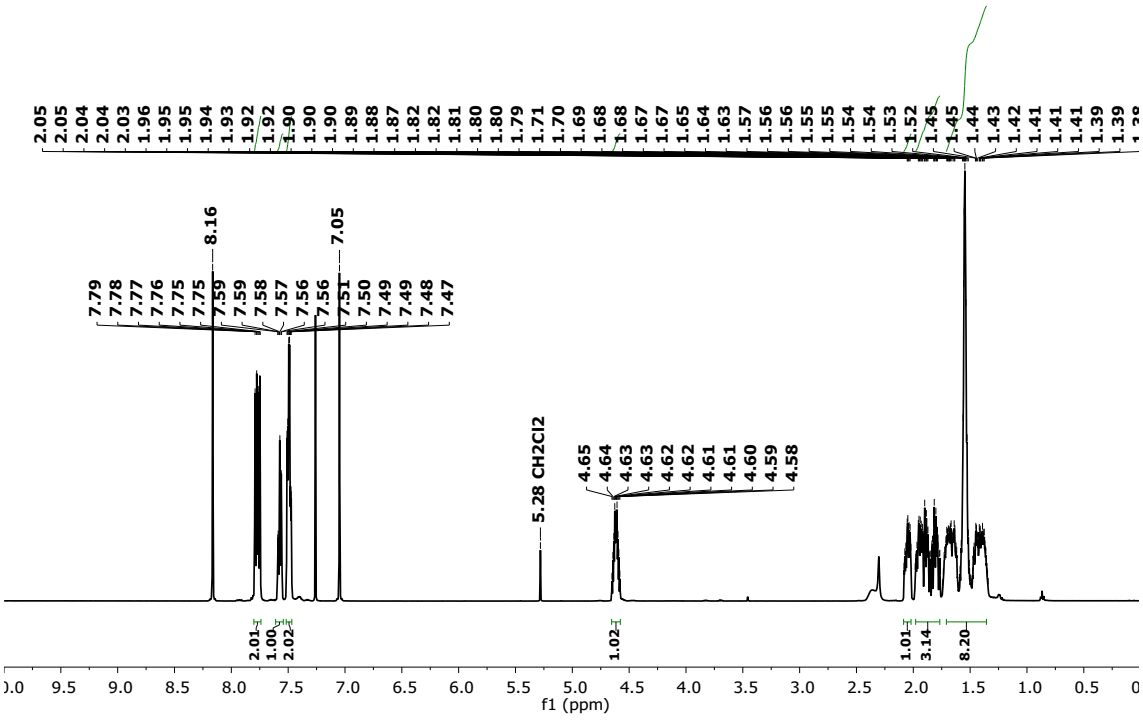
c-heptyl phenyl-*H*-phosphinate (**1f**)



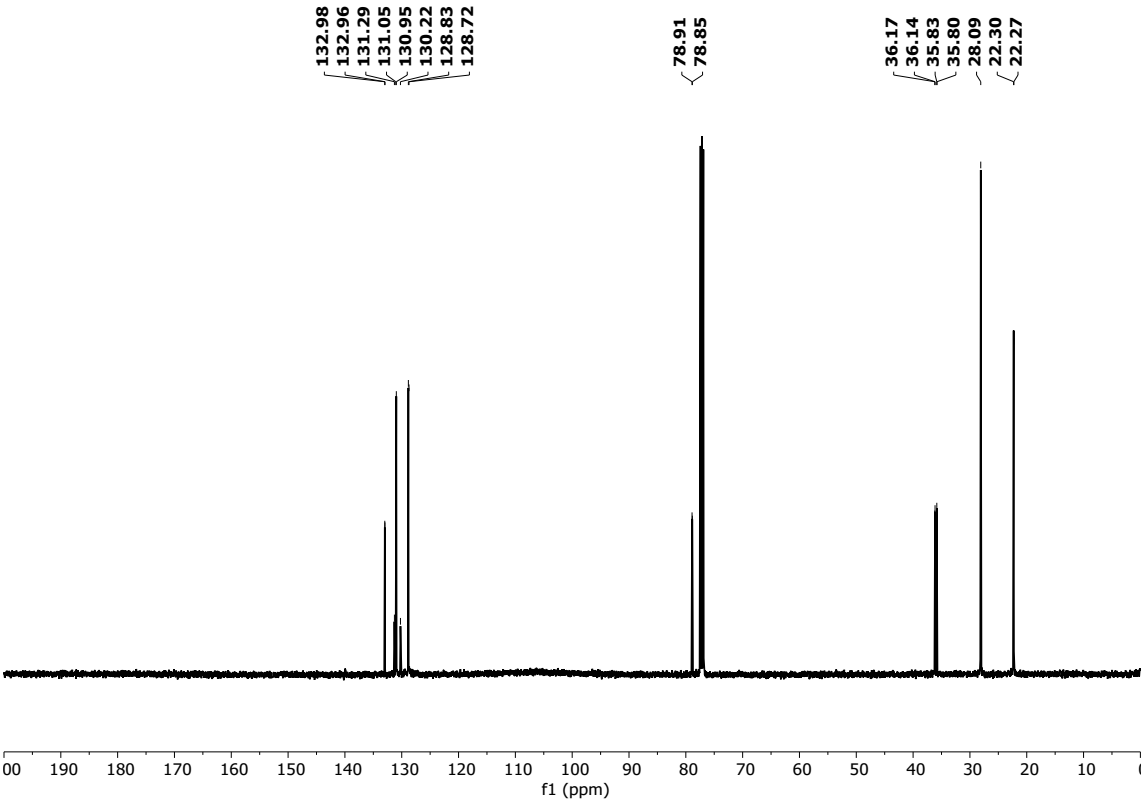
$^{1}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



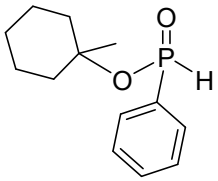
^{1}H NMR (500 MHz, $CDCl_3$)



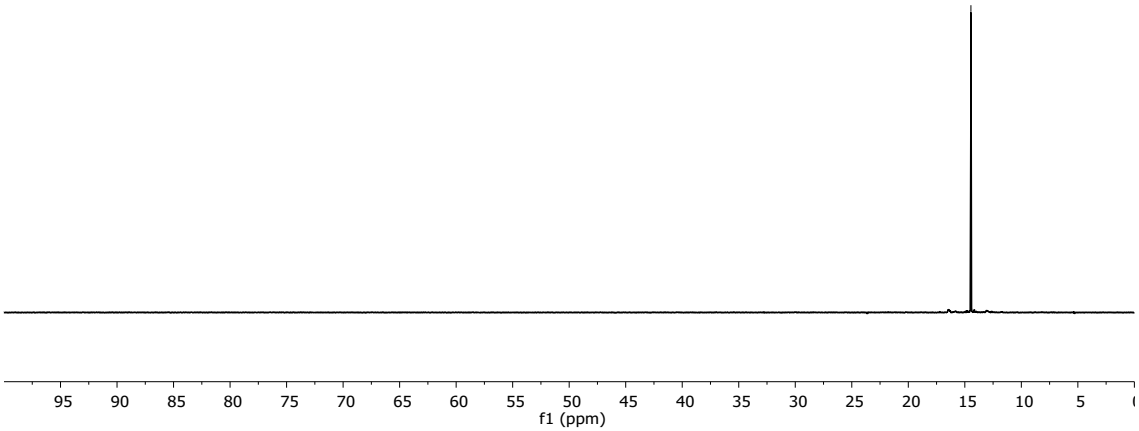
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



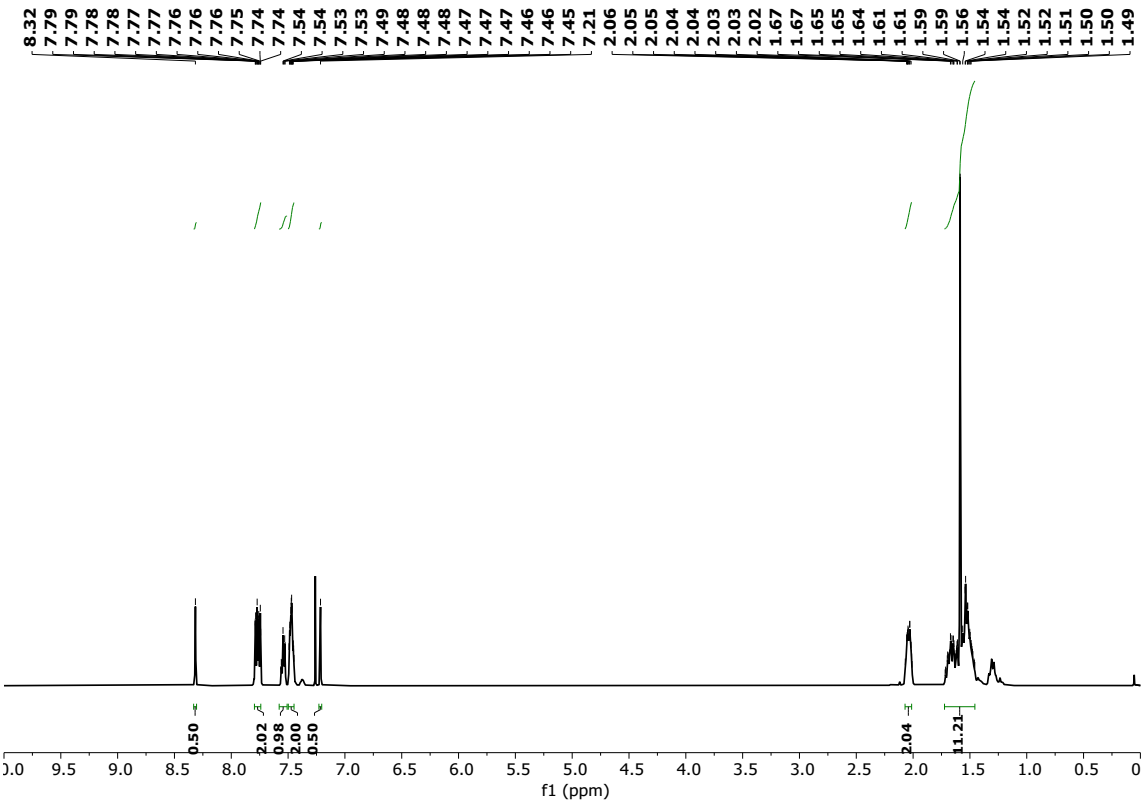
1-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1g**)



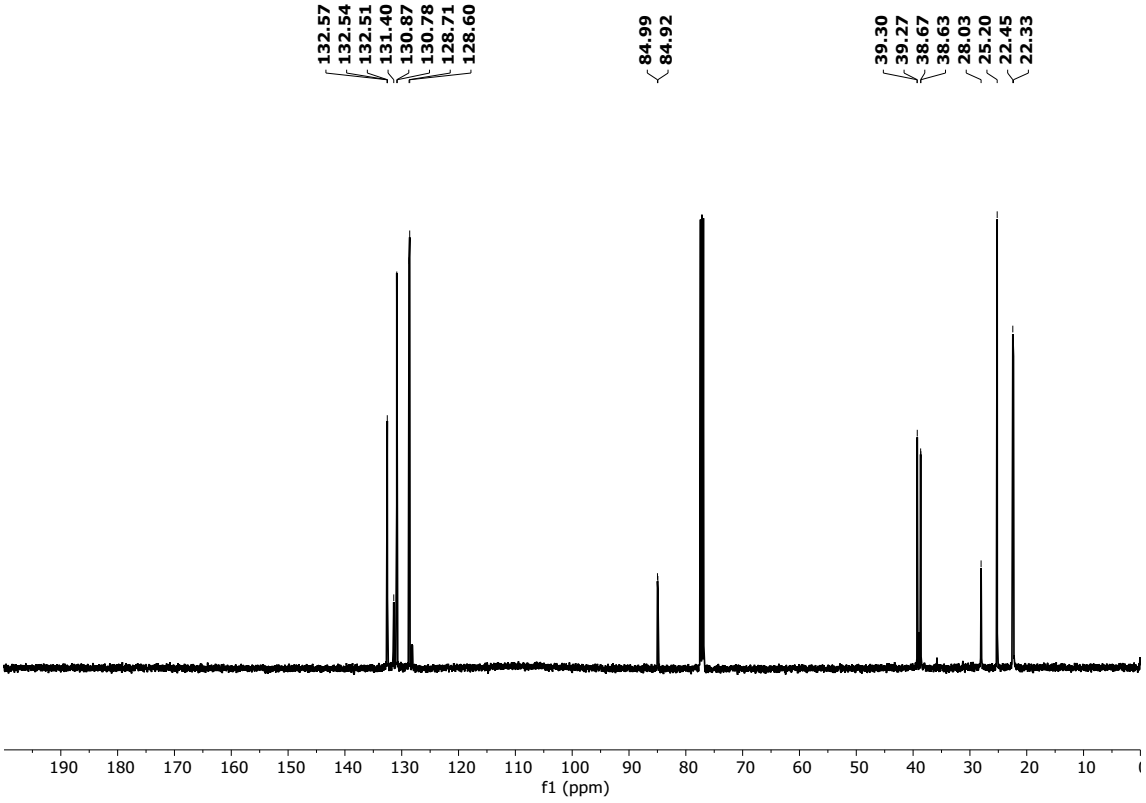
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



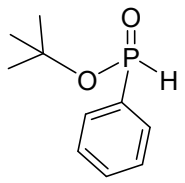
^{1}H NMR (500 MHz, $CDCl_3$)



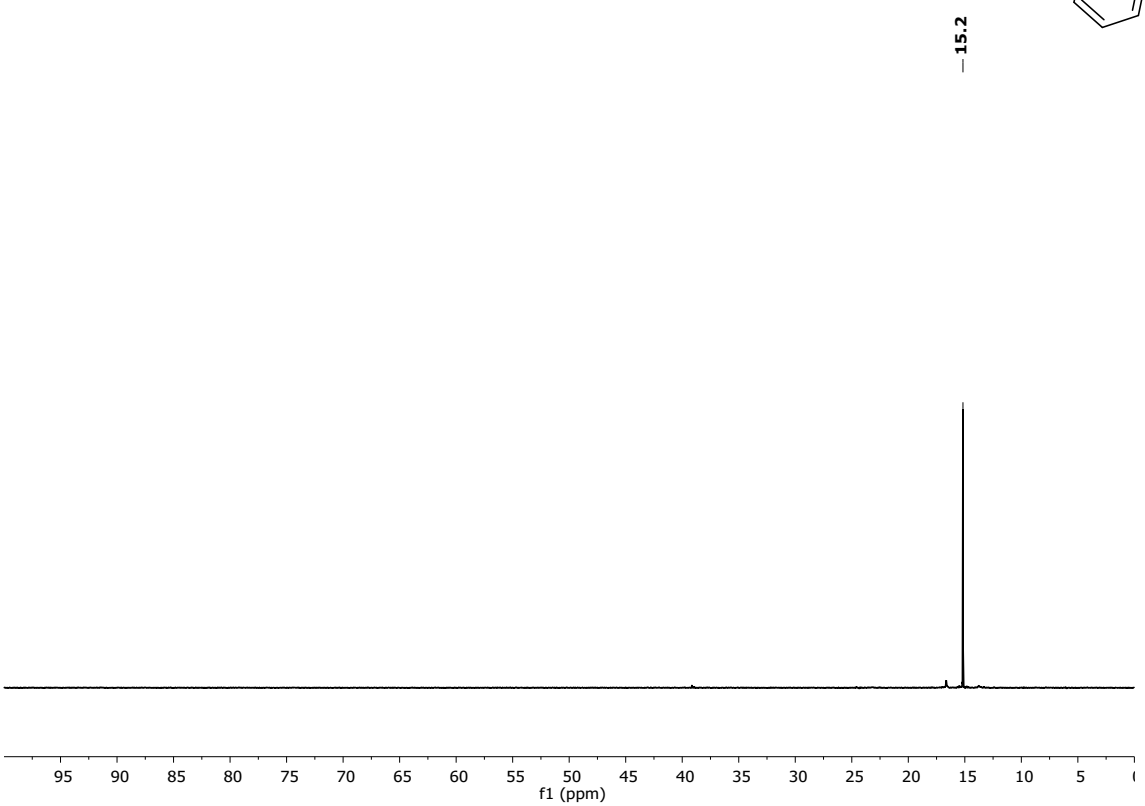
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



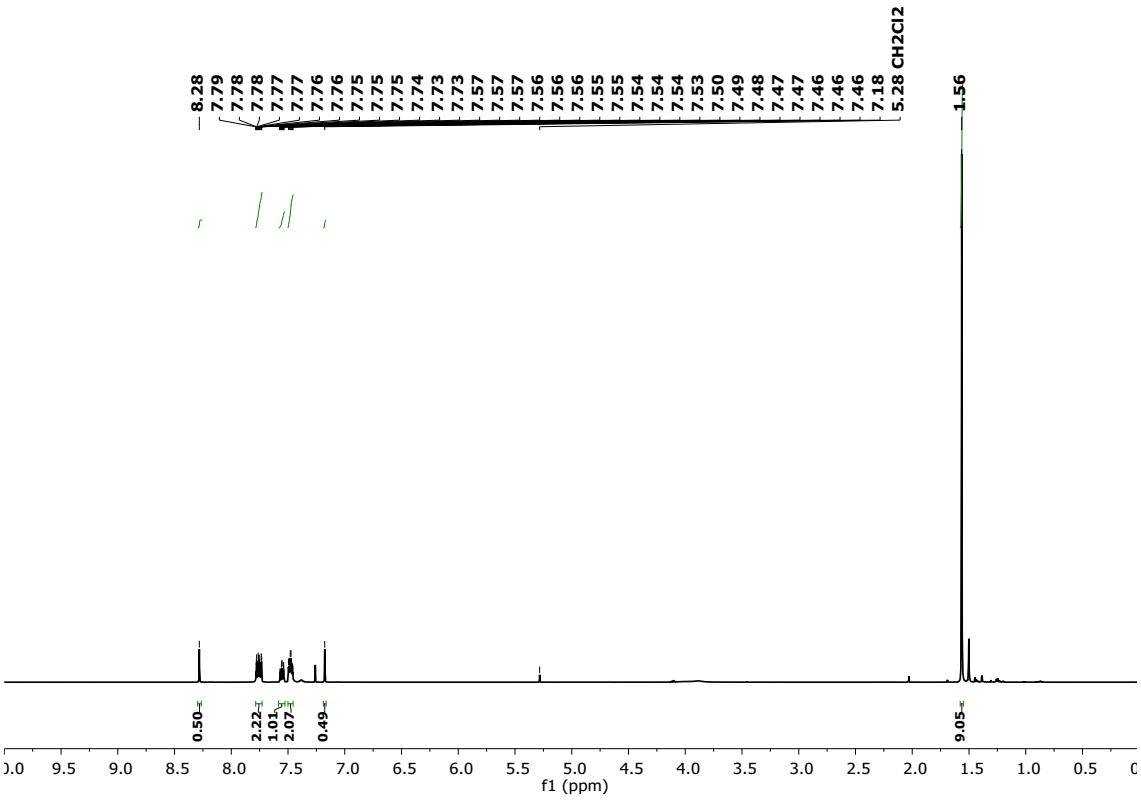
t-butyl phenyl-*H*-phosphinate (**1h**)



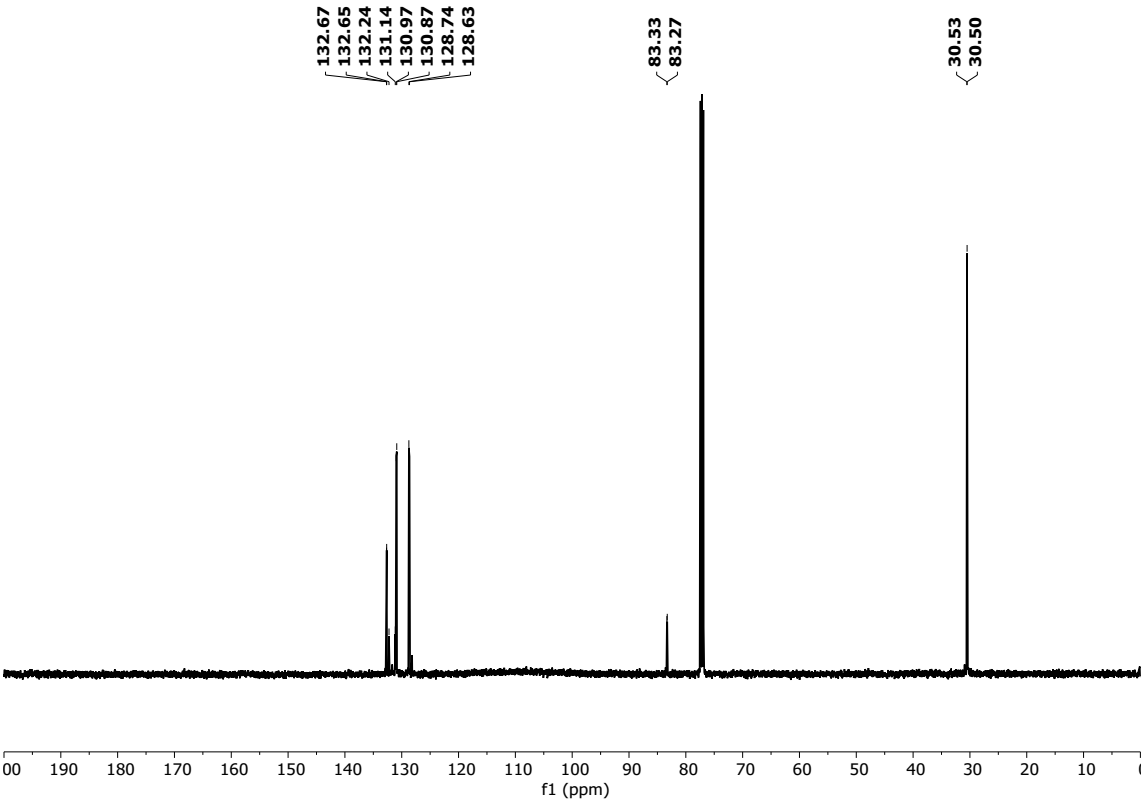
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



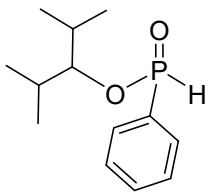
^{1}H NMR (500 MHz, $CDCl_3$)



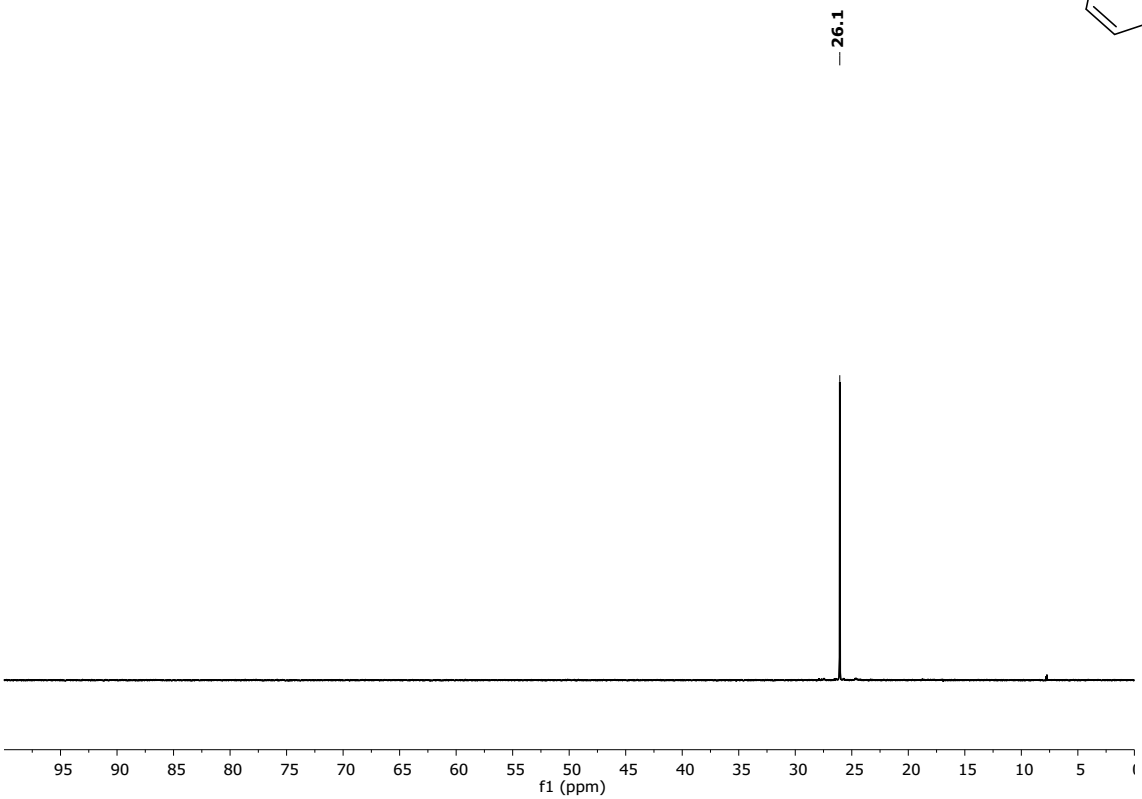
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



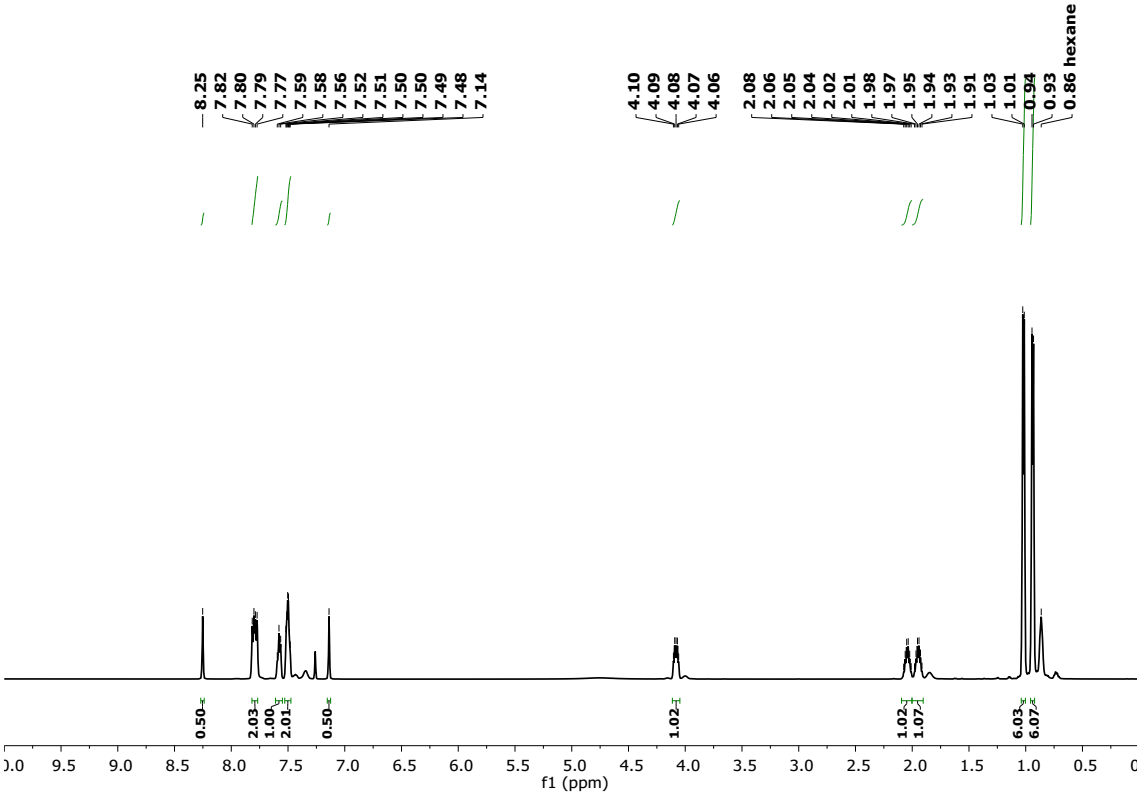
2,4-dimethyl-pent-3-yl phenyl-*H*-phosphinate (**1i**)



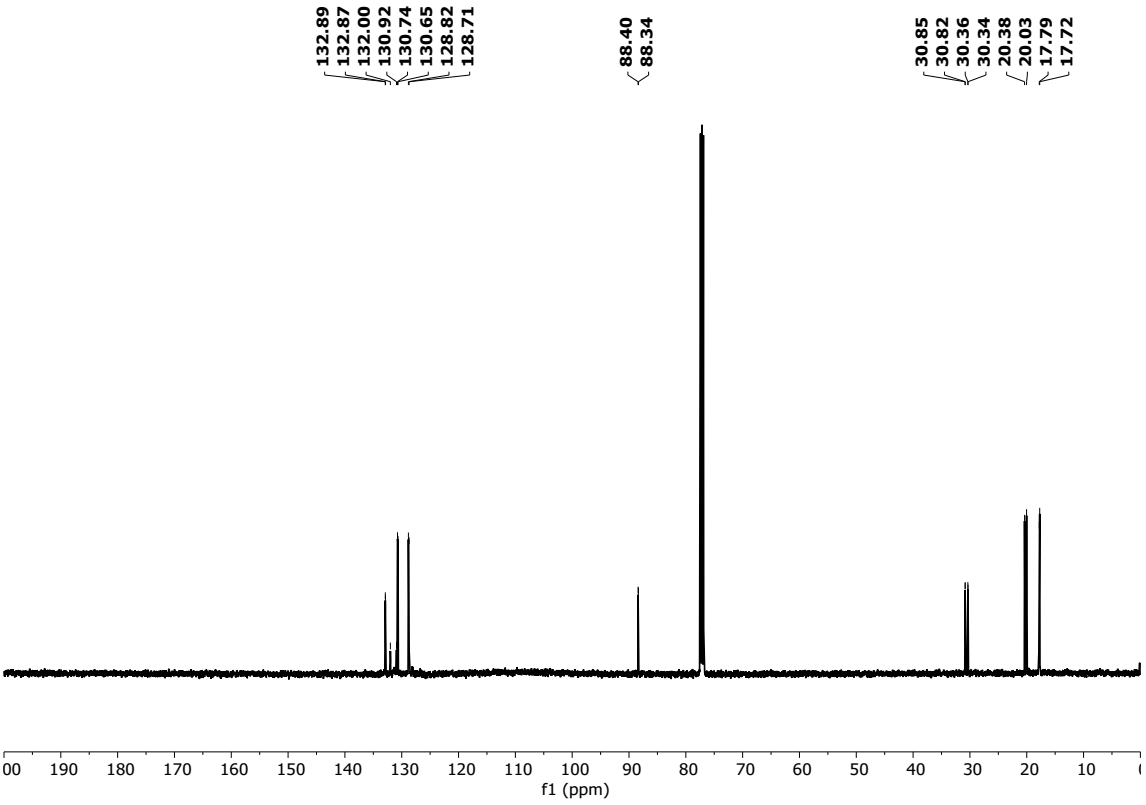
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



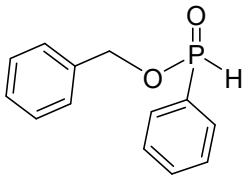
^{1}H NMR (500 MHz, $CDCl_3$)



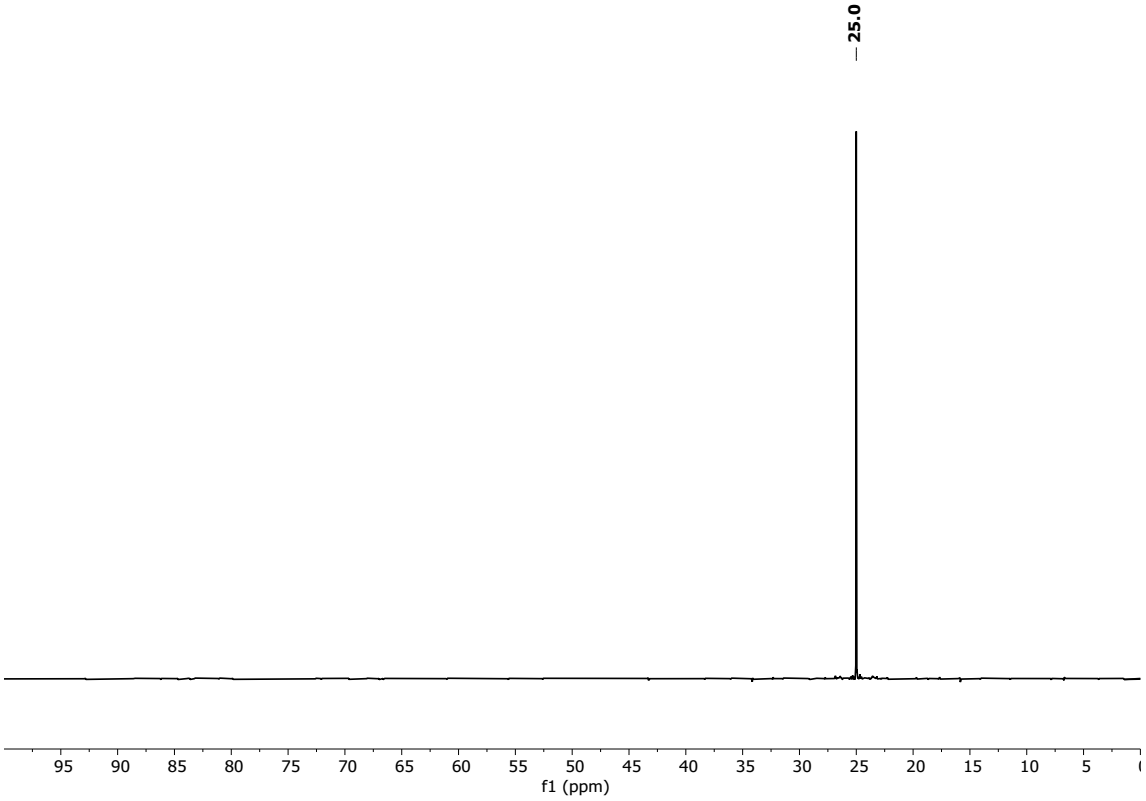
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



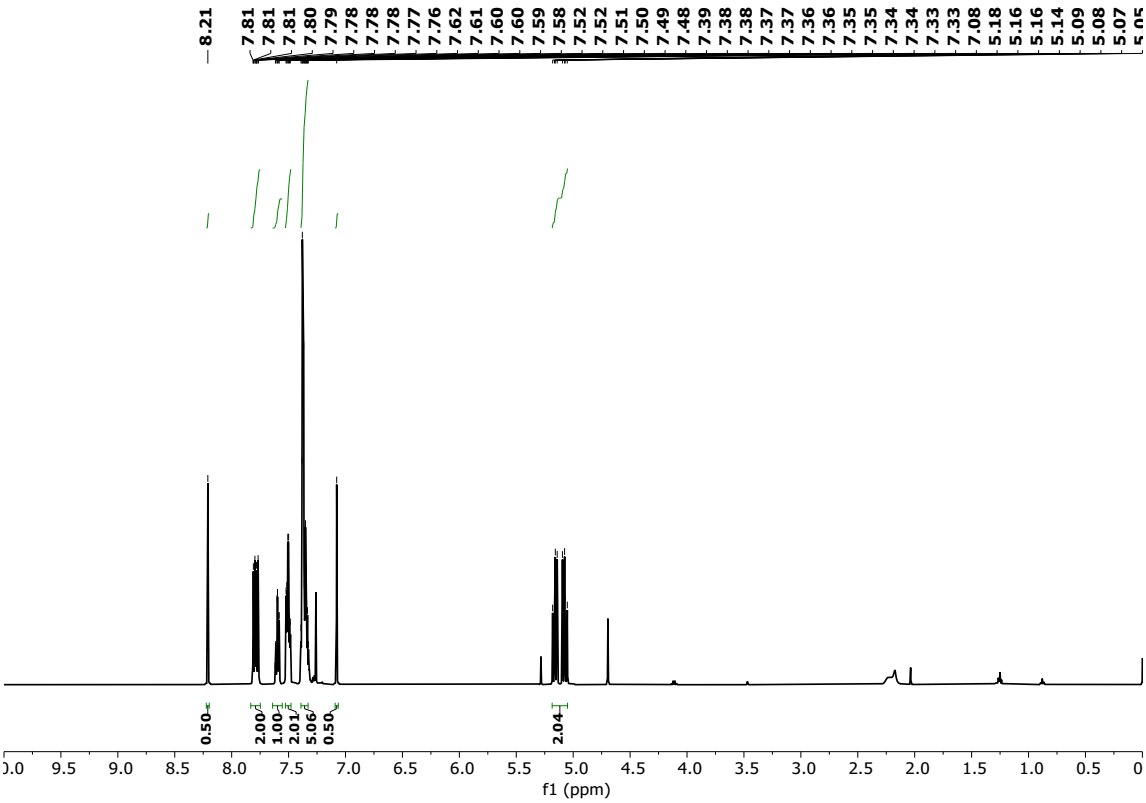
benzyl phenyl-*H*-phosphinate (**1j**)



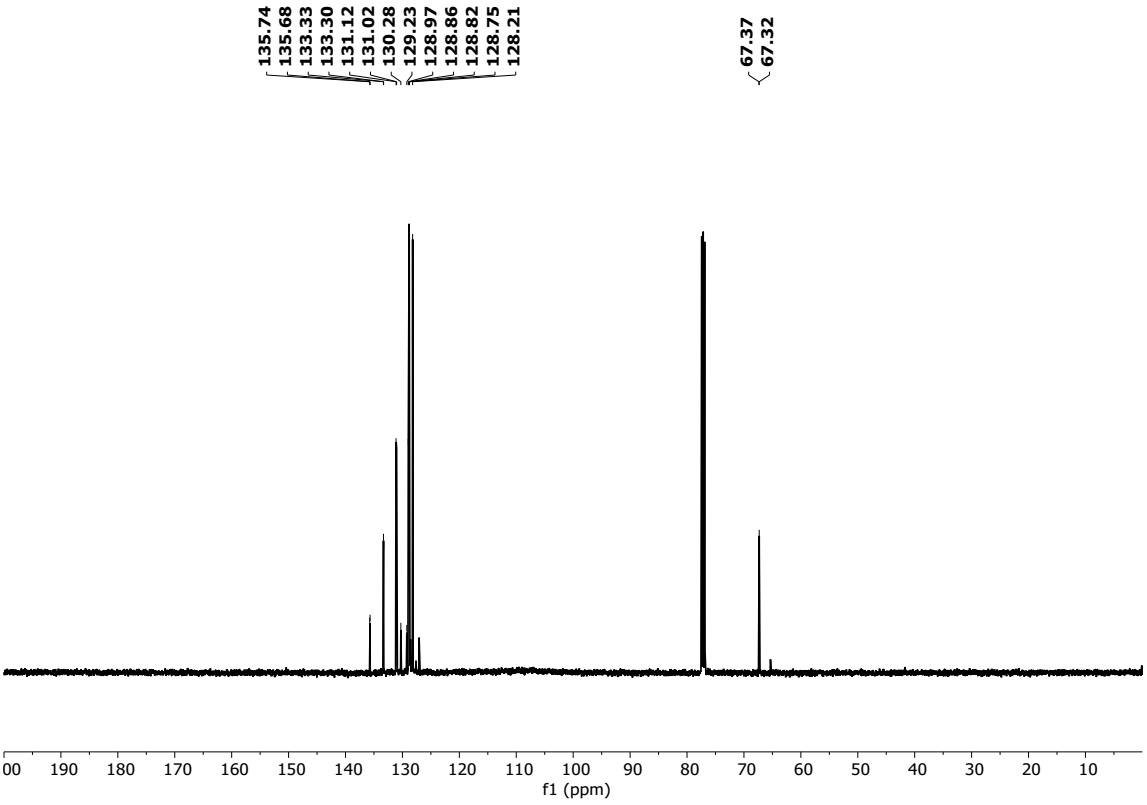
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



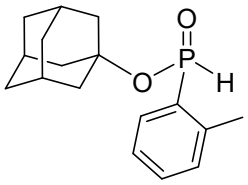
^{1}H NMR (500 MHz, $CDCl_3$)



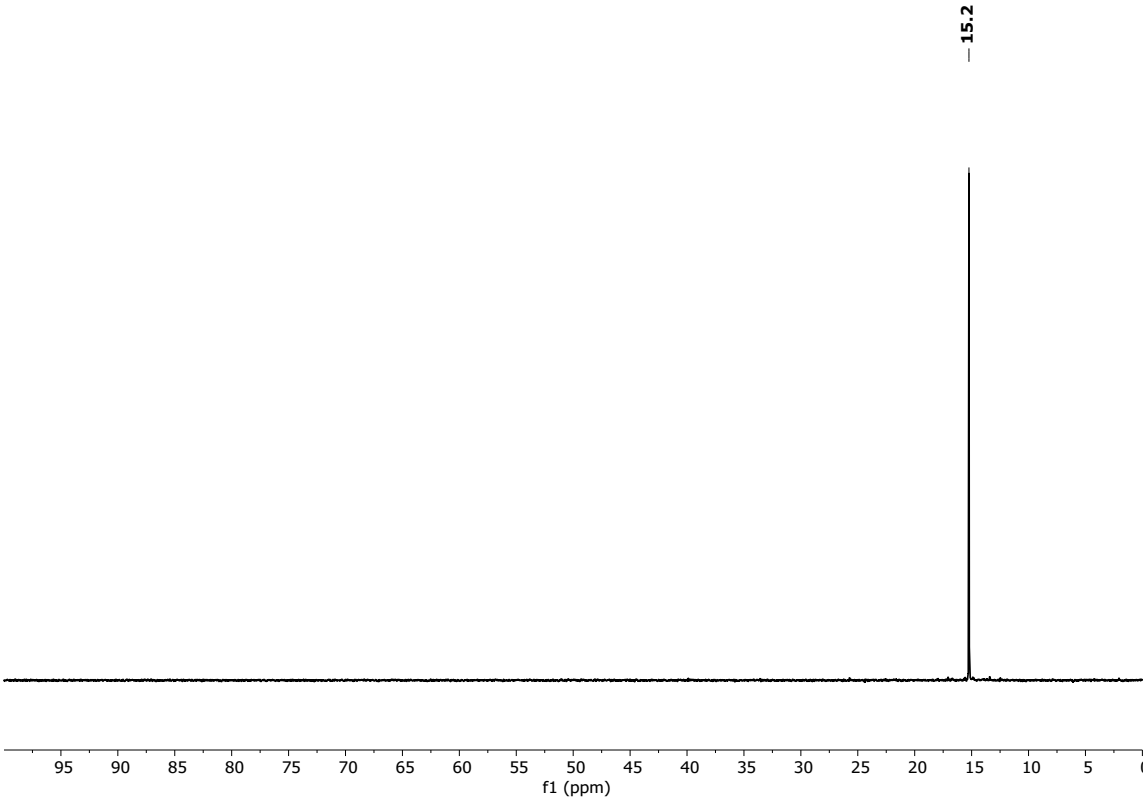
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



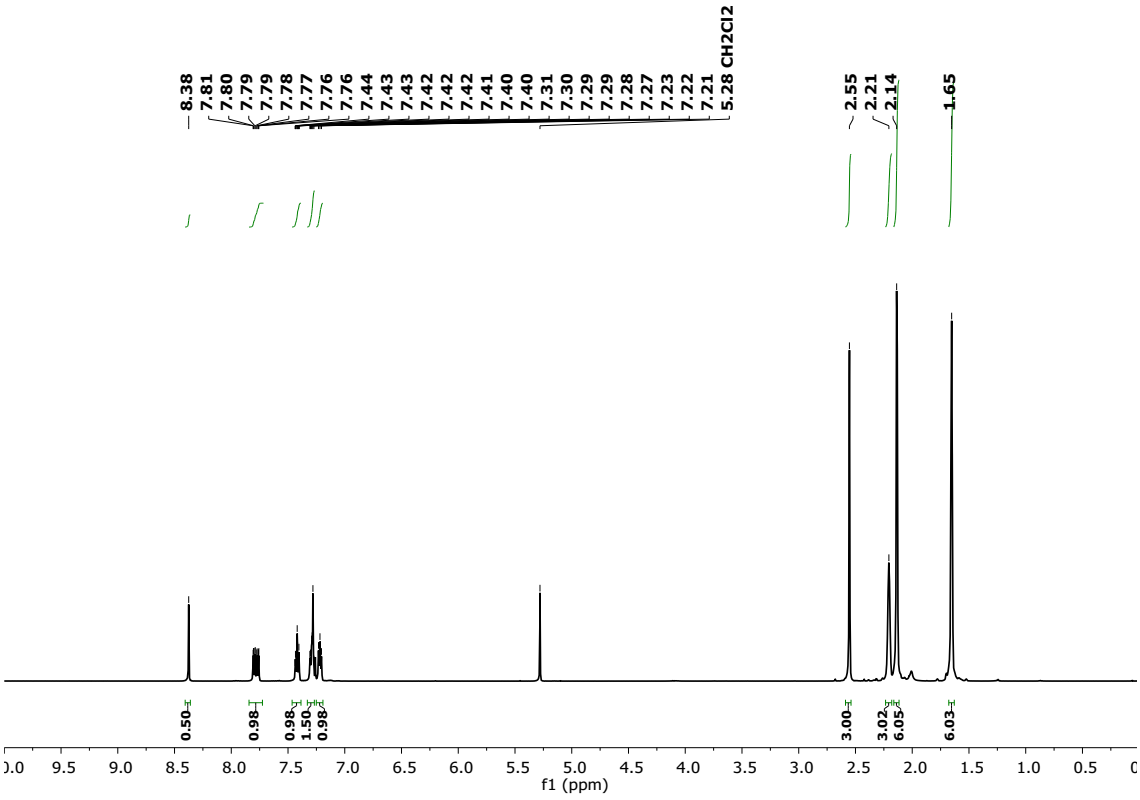
1-adamantyl (2-methylphenyl)-*H*-phosphinate (**1k**)



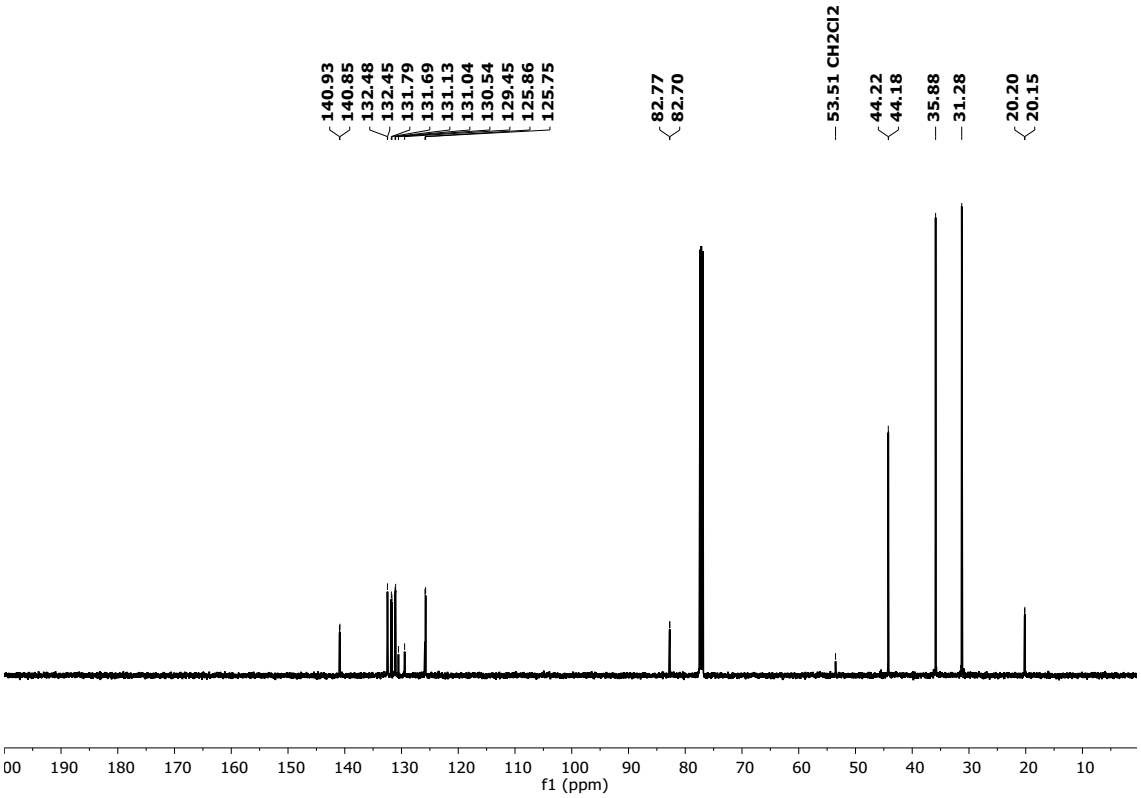
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



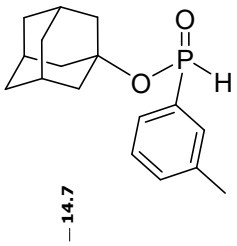
^{1}H NMR (500 MHz, $CDCl_3$)



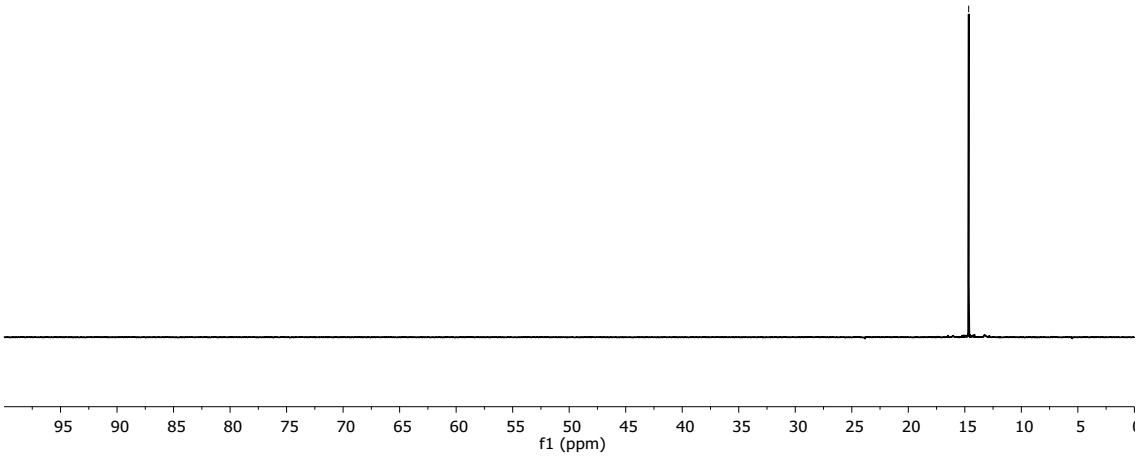
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



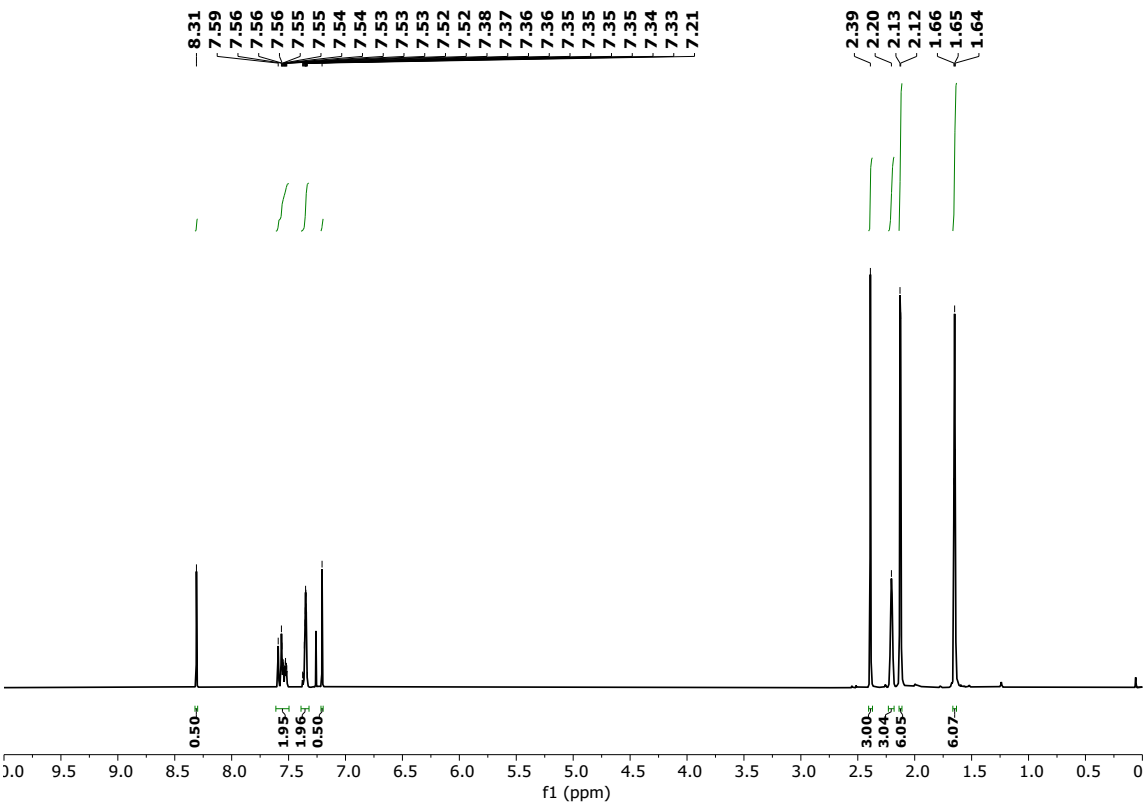
1-adamantyl (3-methylphenyl)-*H*-phosphinate (**1l**)



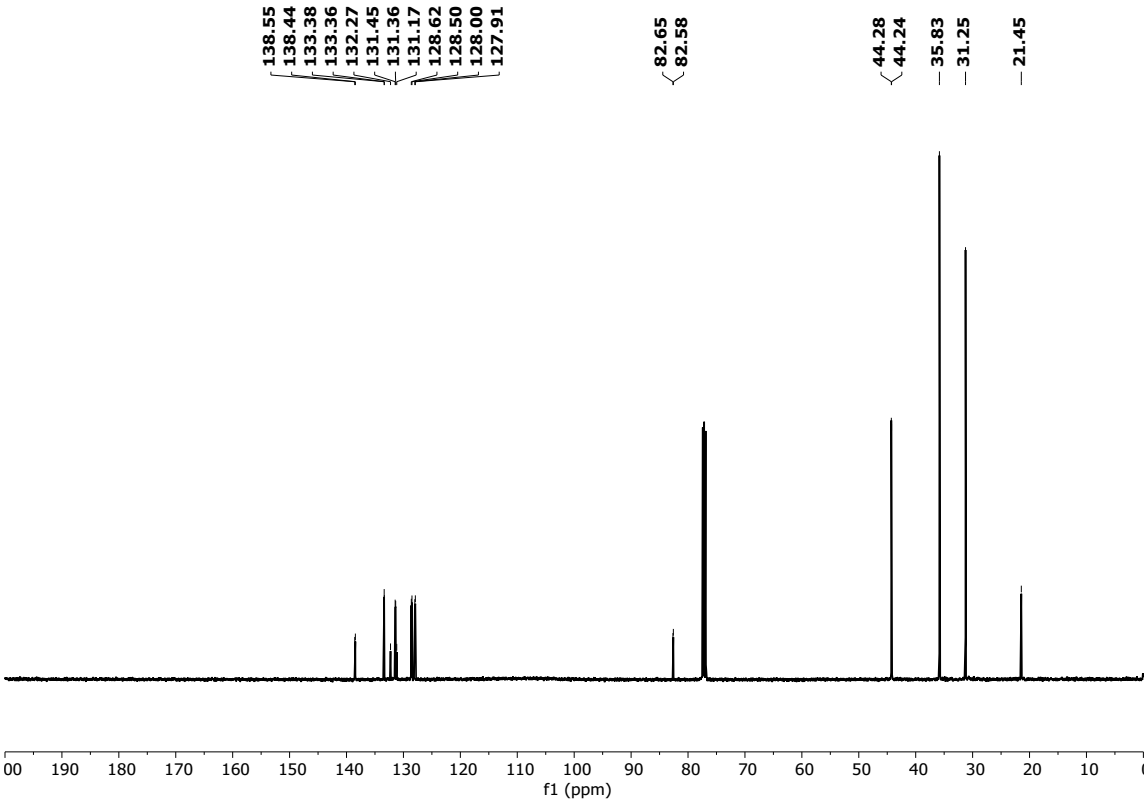
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



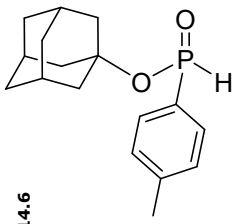
^{1}H NMR (500 MHz, $CDCl_3$)



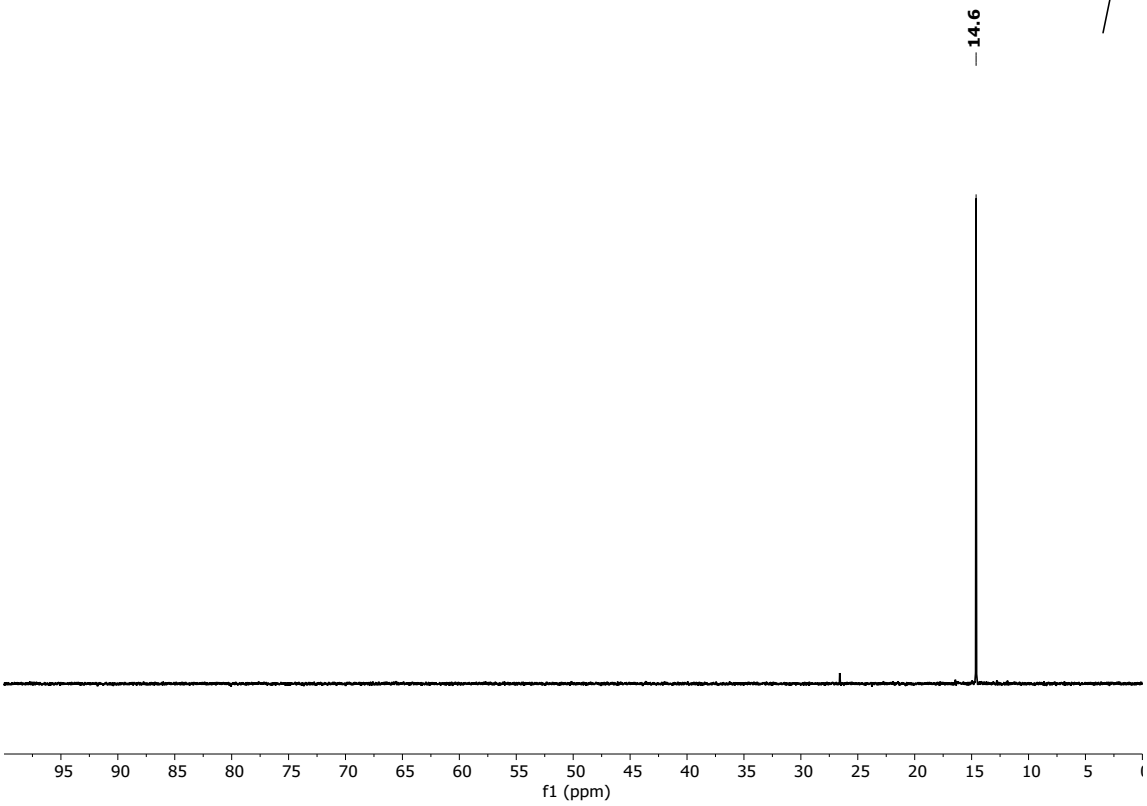
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



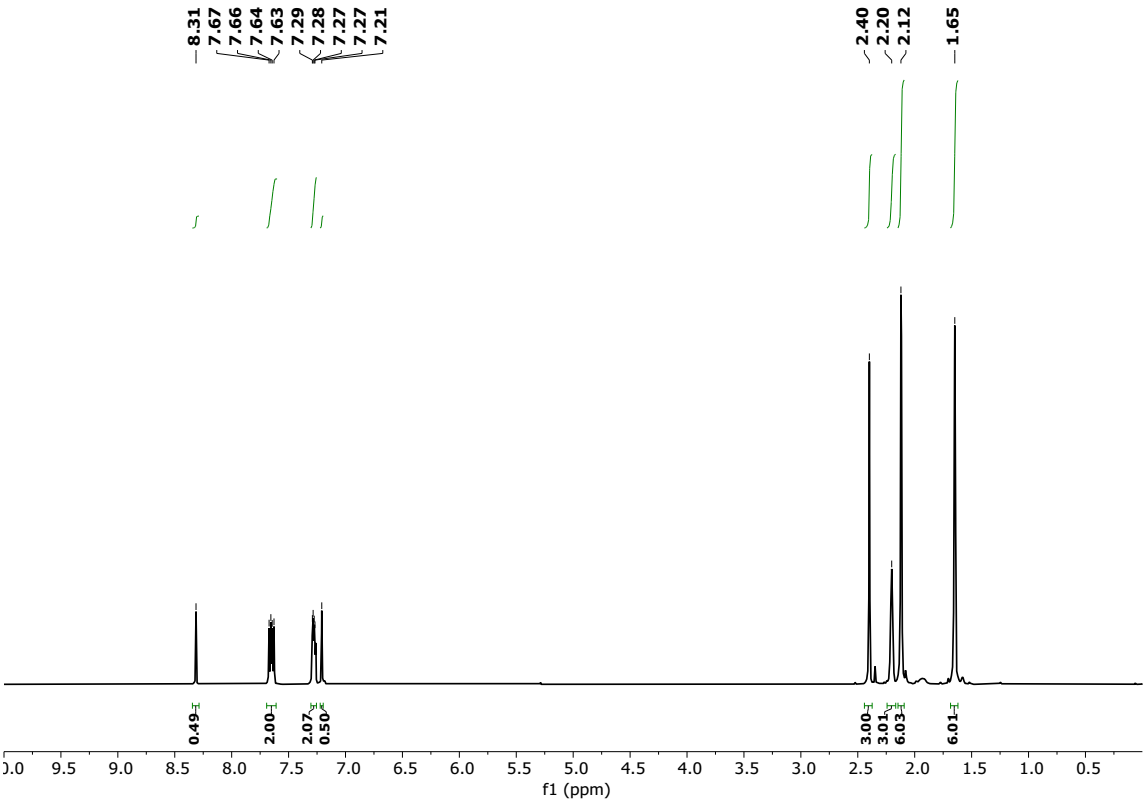
1-adamantyl (4-methylphenyl)-*H*-phosphinate (**1m**)



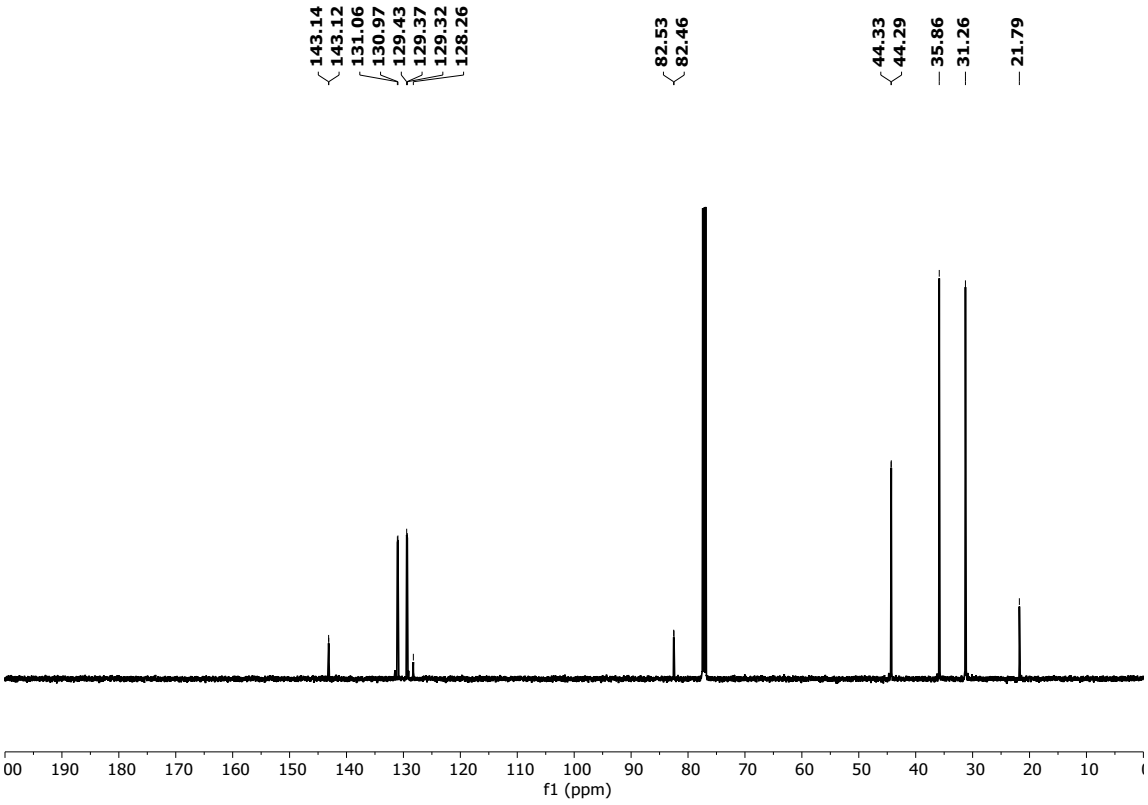
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



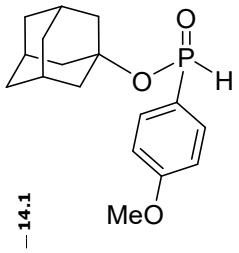
^{1}H NMR (500 MHz, $CDCl_3$)



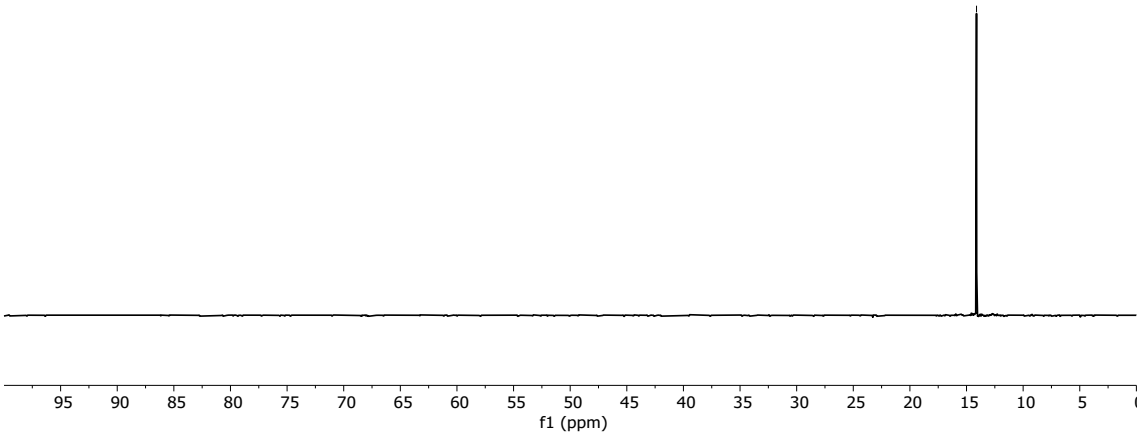
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



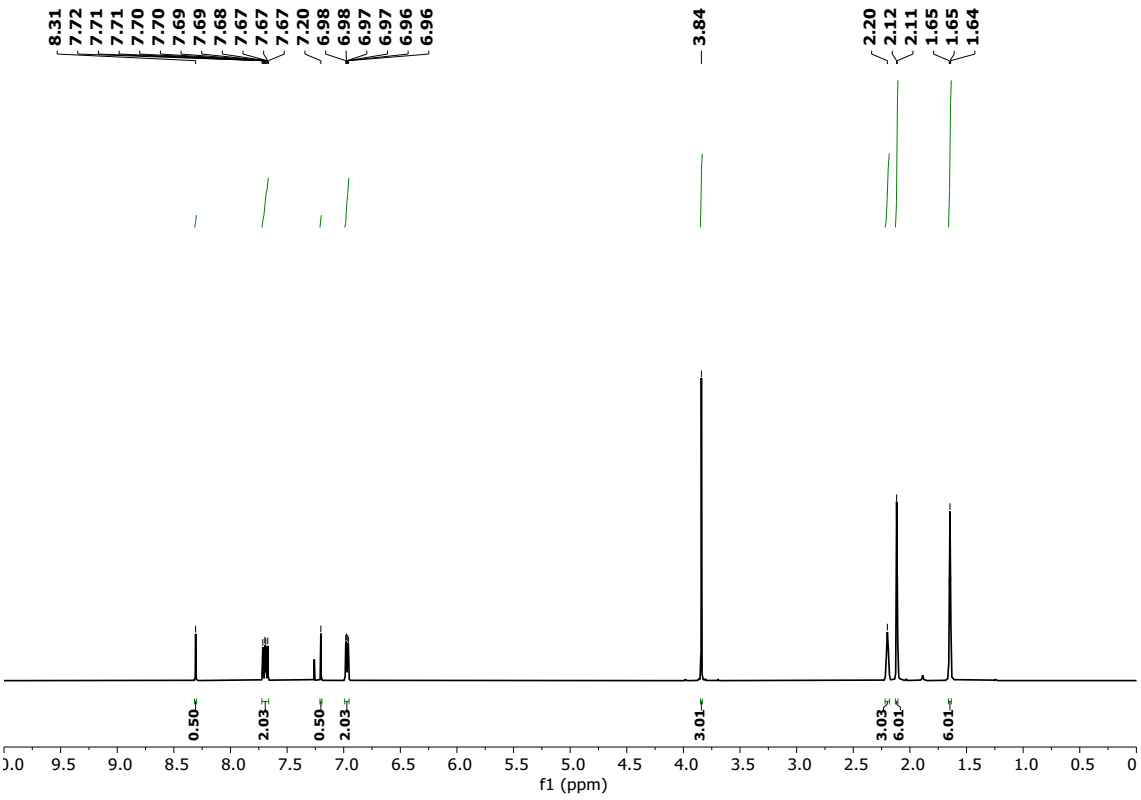
1-adamantyl (4-methoxyphenyl)-*H*-phosphinate (**1n**)



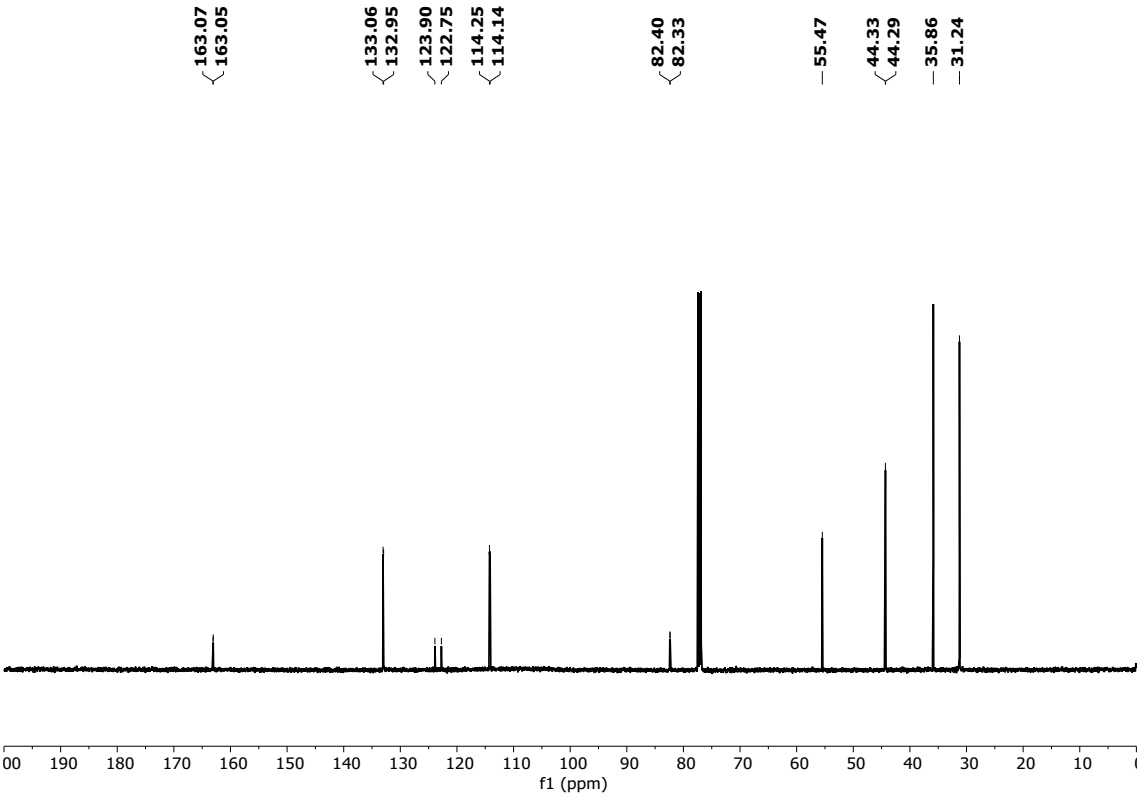
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



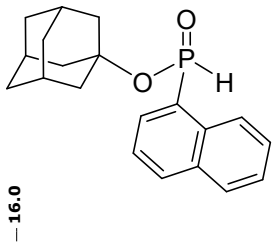
^{1}H NMR (500 MHz, $CDCl_3$)



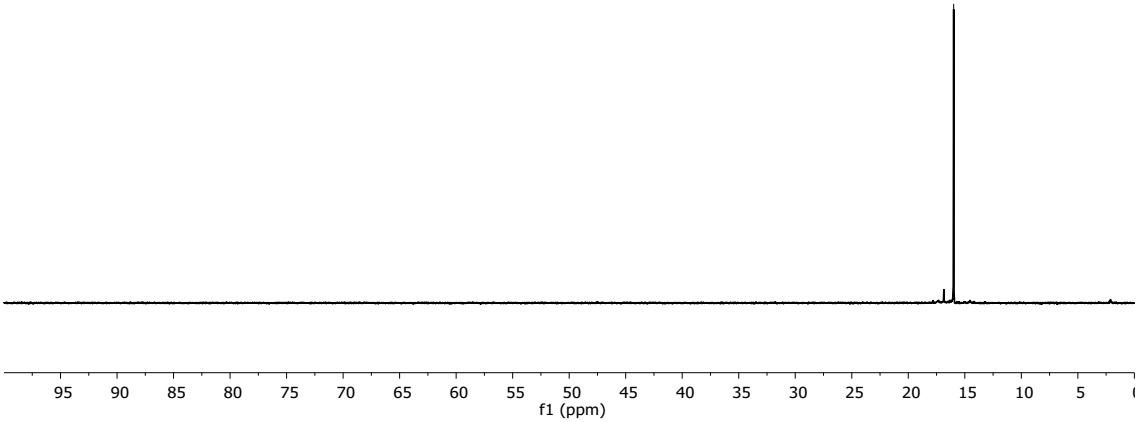
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



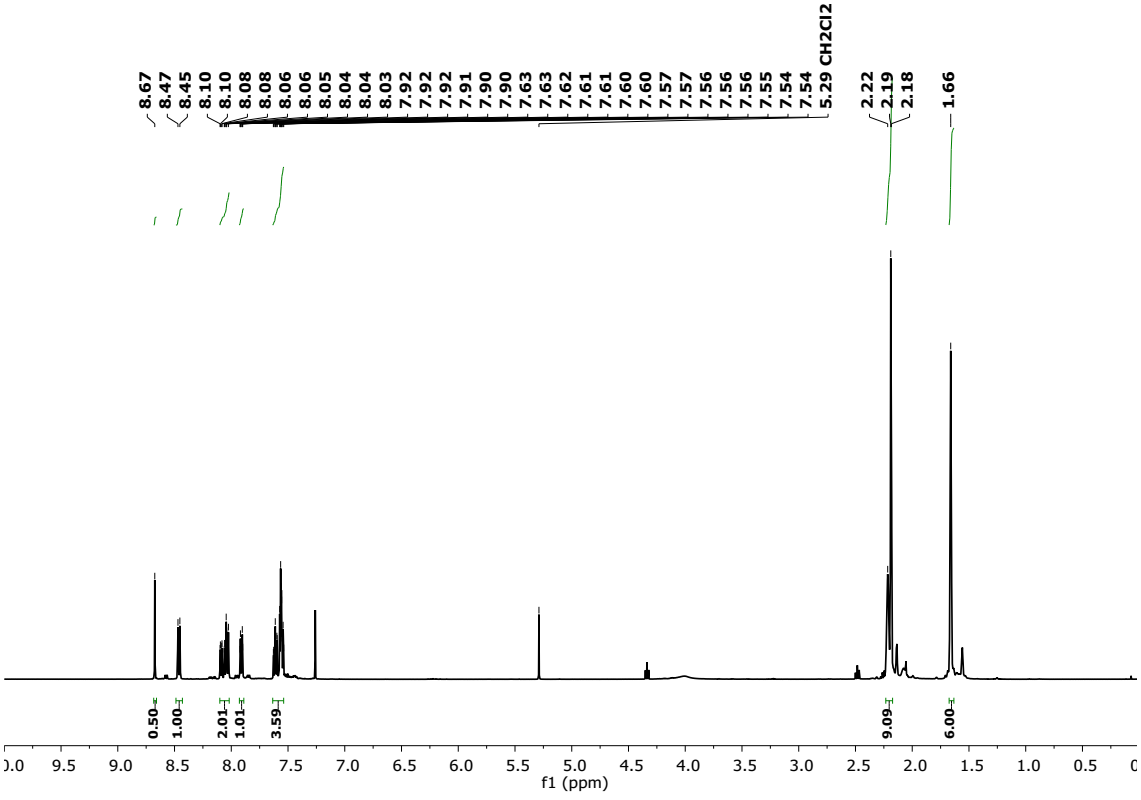
1-adamantyl (1-naphthyl)-*H*-phosphinate (**1o**)



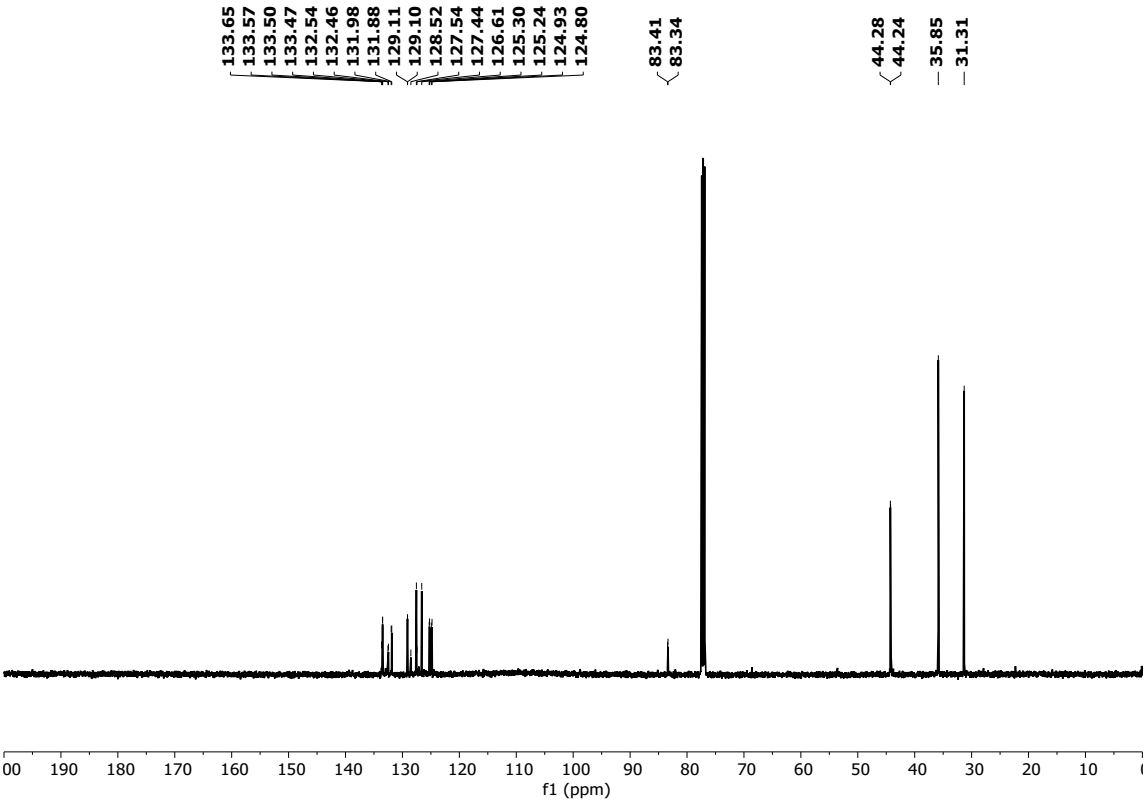
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



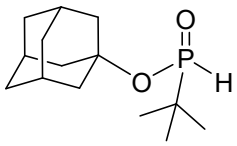
^{1}H NMR (500 MHz, $CDCl_3$)



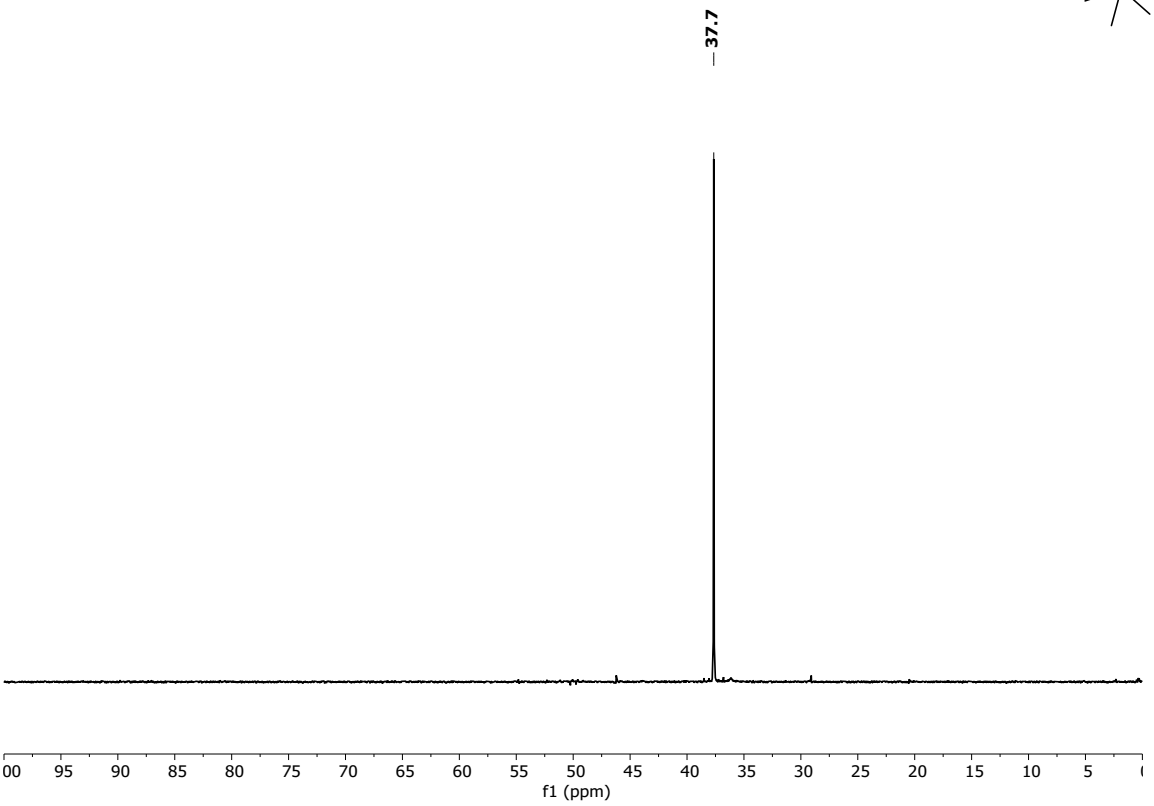
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



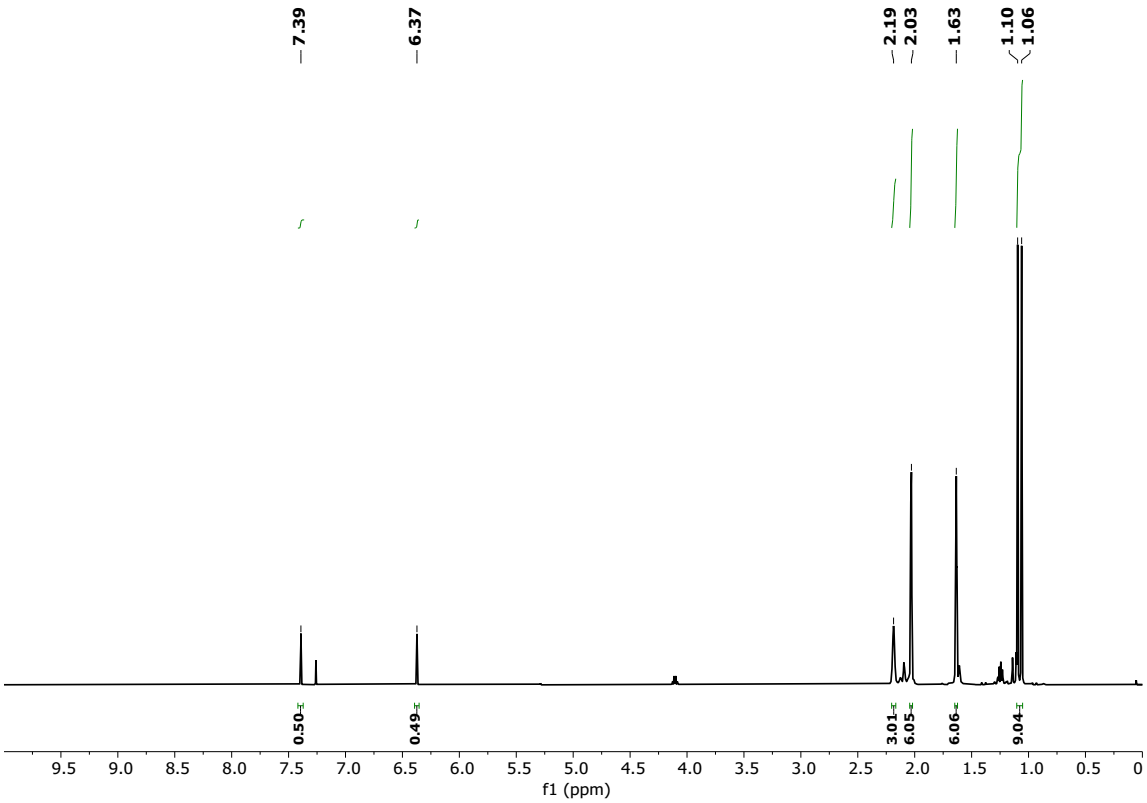
1-adamantyl *t*-butyl-*H*-phosphinate (**1p**)



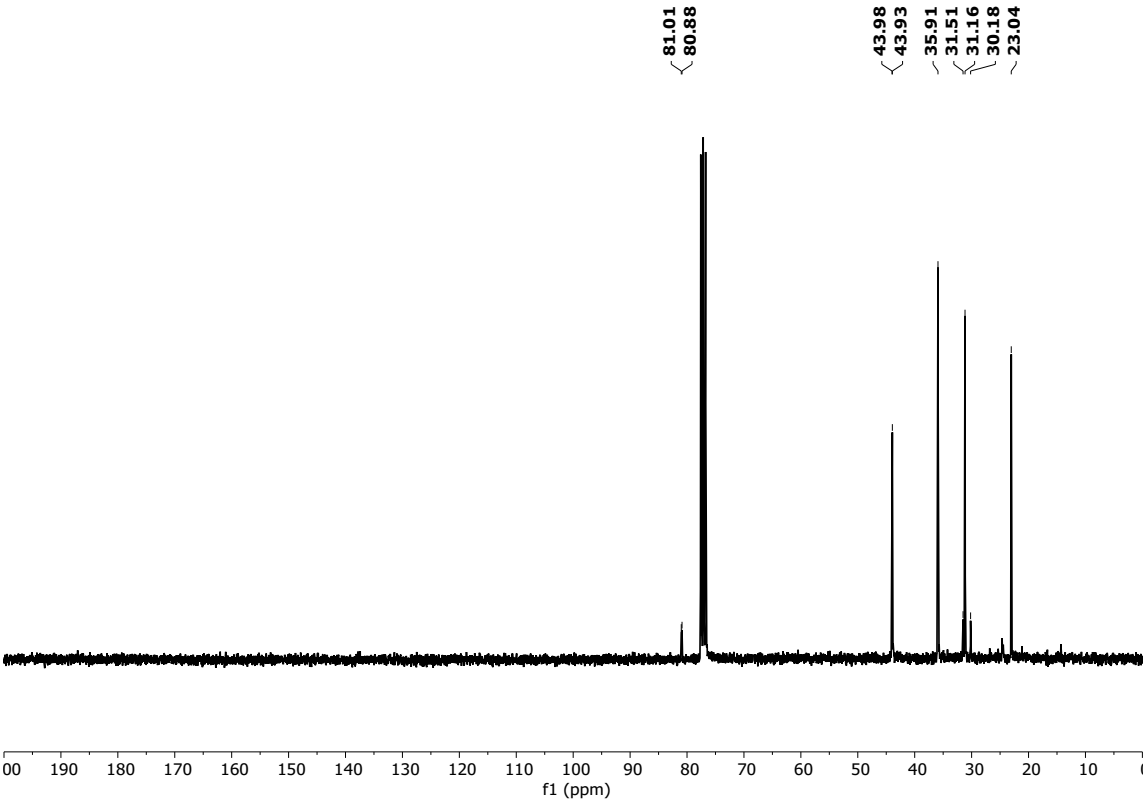
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$)



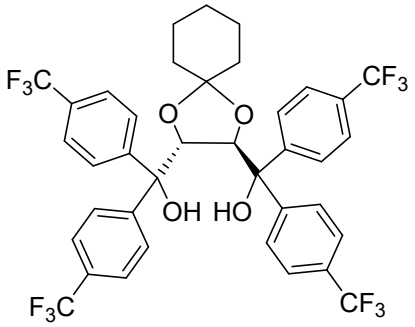
^{1}H NMR (500 MHz, $CDCl_3$)



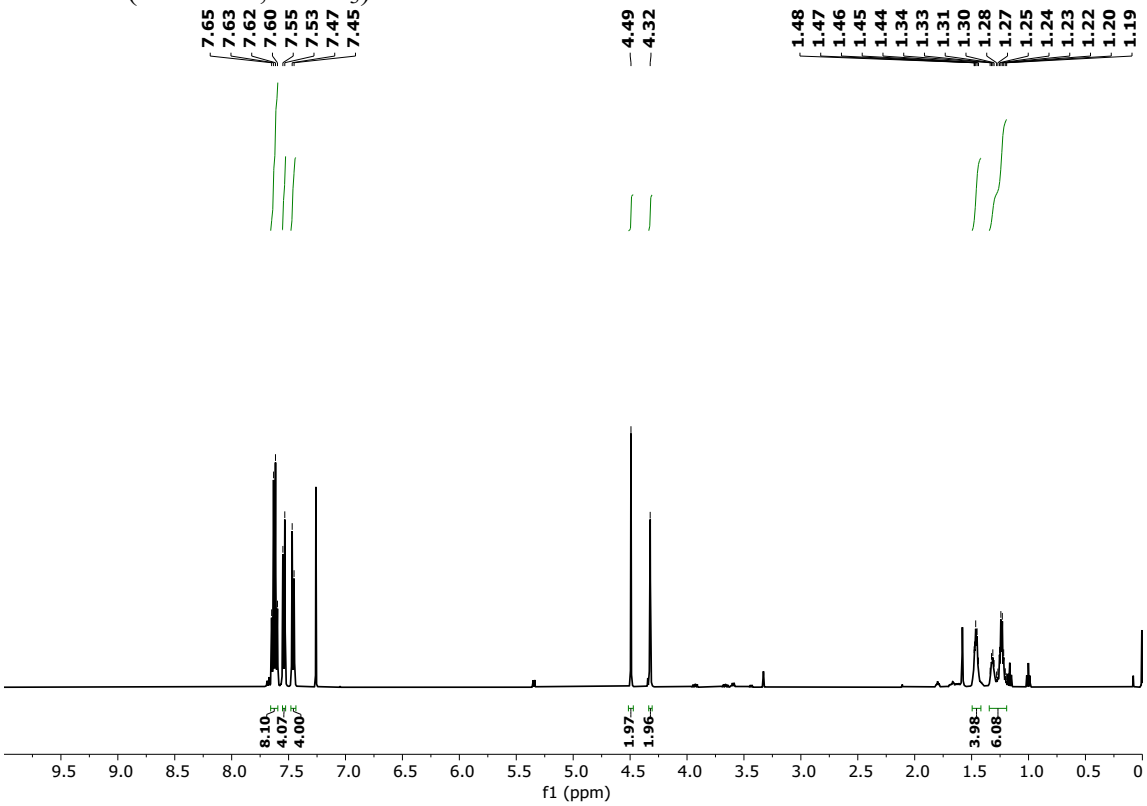
$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$)



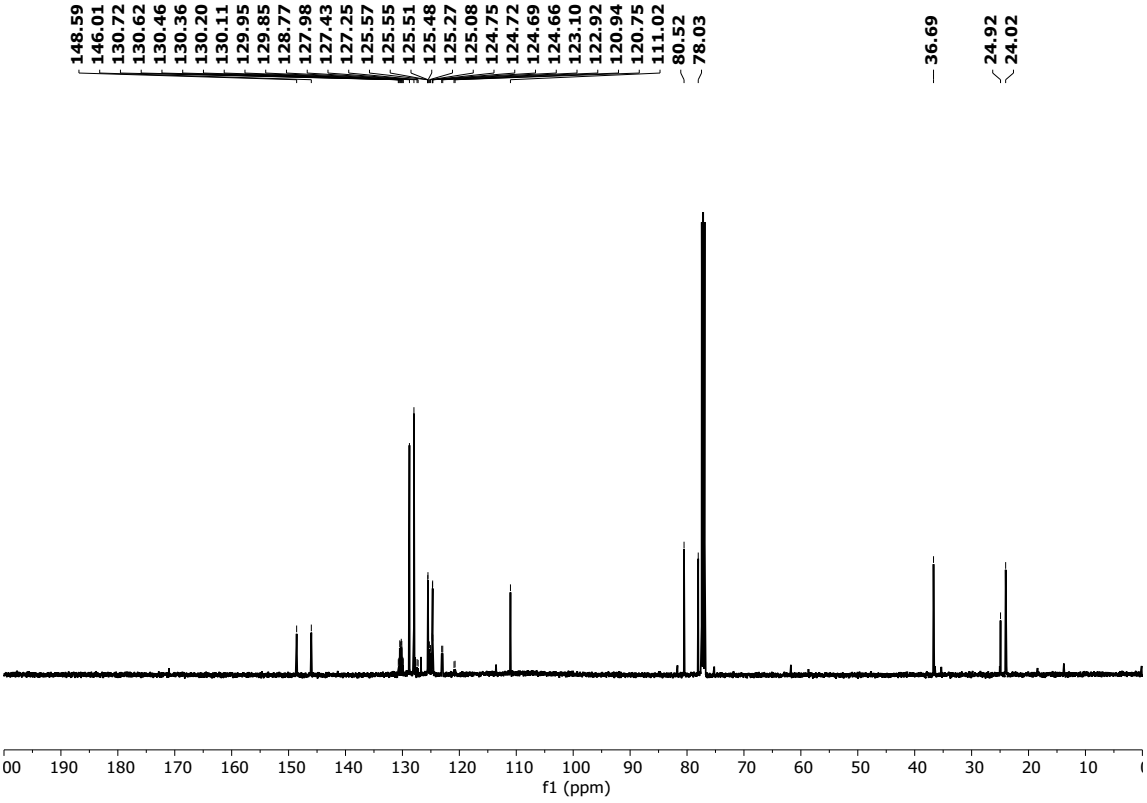
((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(bis(4-(trifluoromethyl)phenyl)methanol) [(*R*,*R*-**2d**]



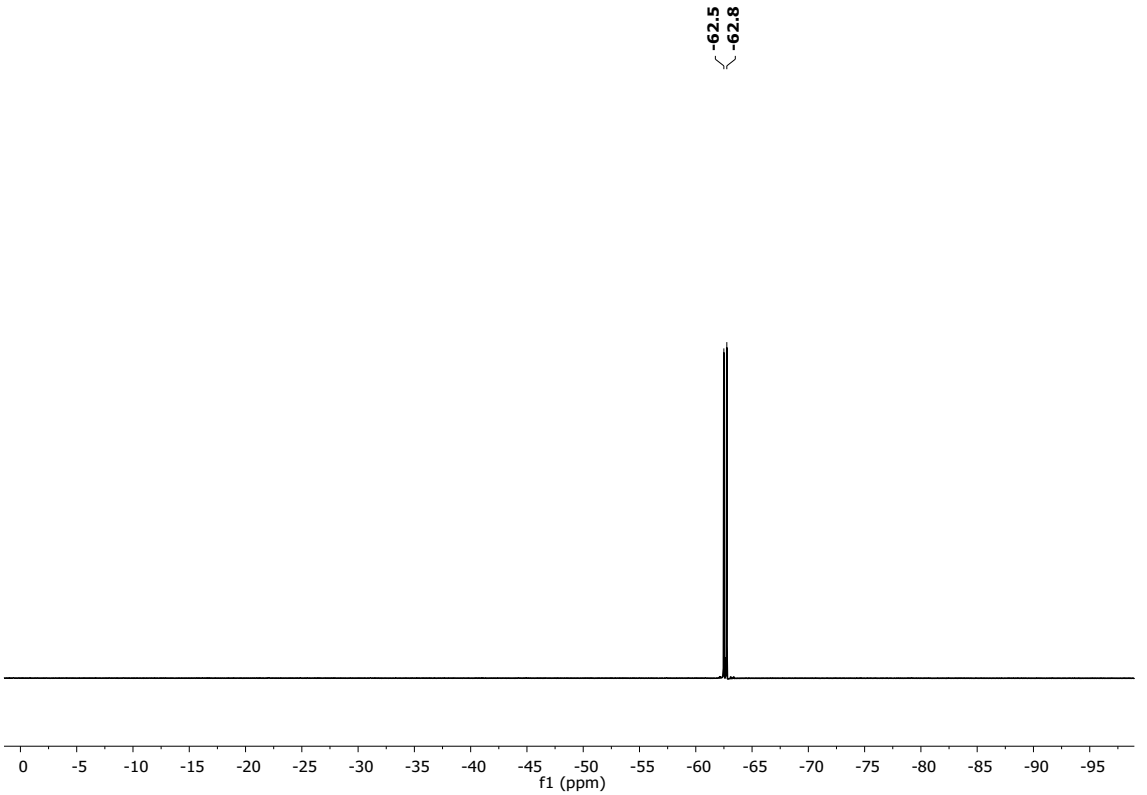
^{1}H NMR (500 MHz, $CDCl_3$)



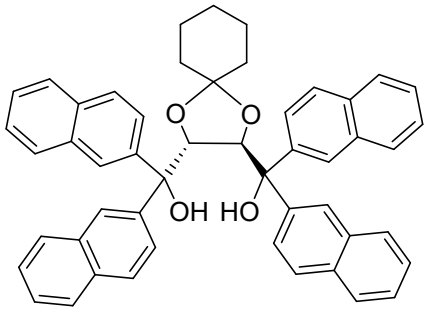
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



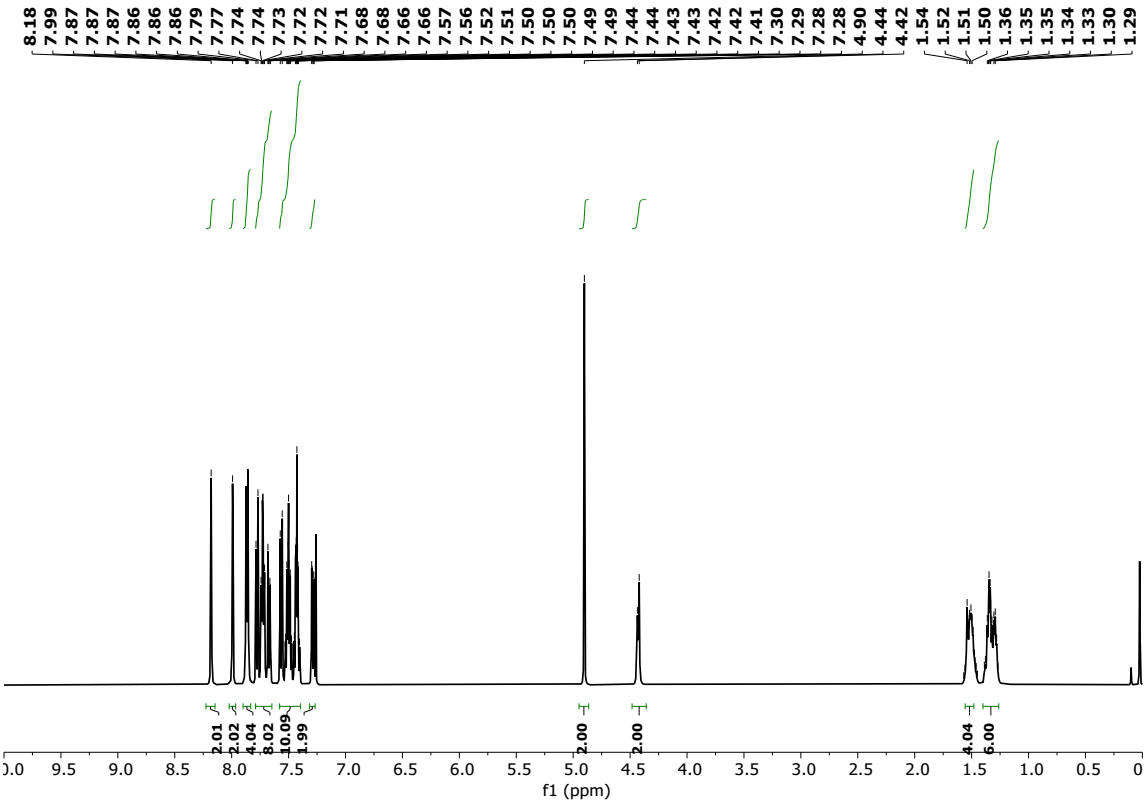
^{19}F NMR (282 MHz, $CDCl_3$)



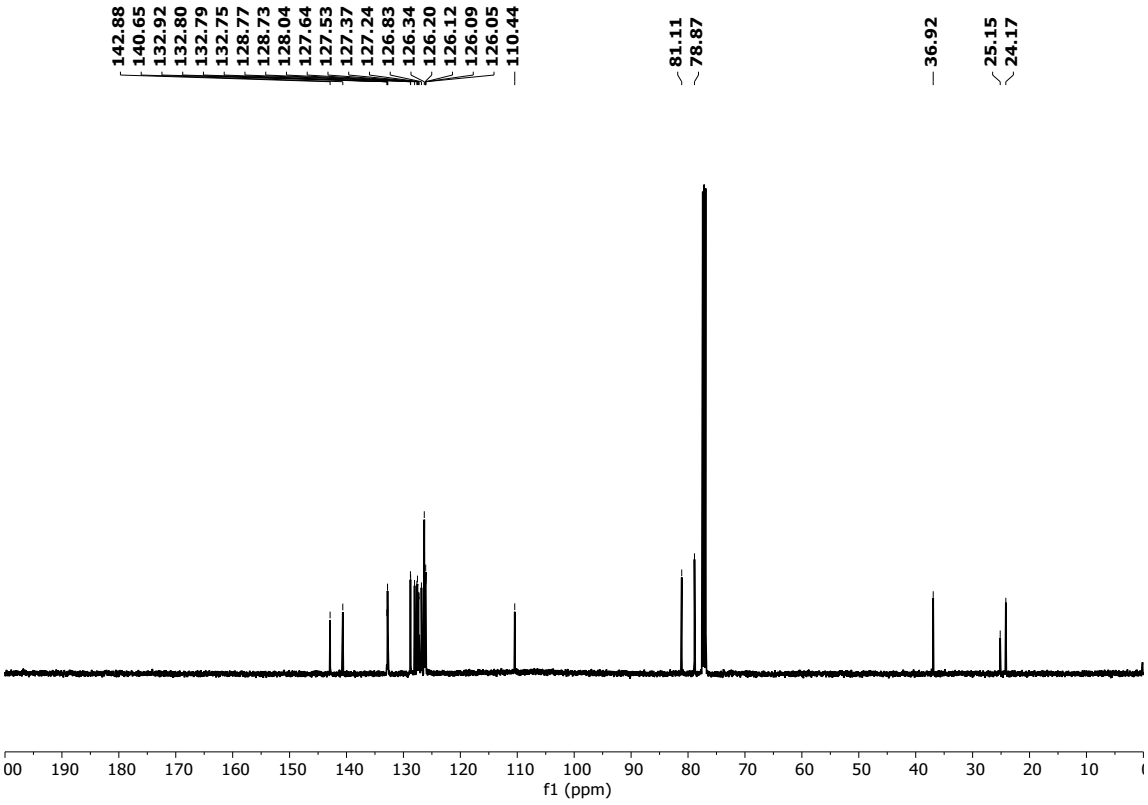
((2*R*,3*R*)-1,4-dioxaspiro[4.5]decane-2,3-diyl)bis(di(naphthalen-2-yl)methanol) [(*R*,*R*)-**2f**]



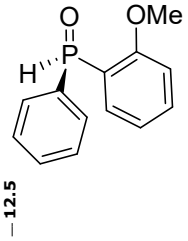
^{1}H NMR (500 MHz, $CDCl_3$)



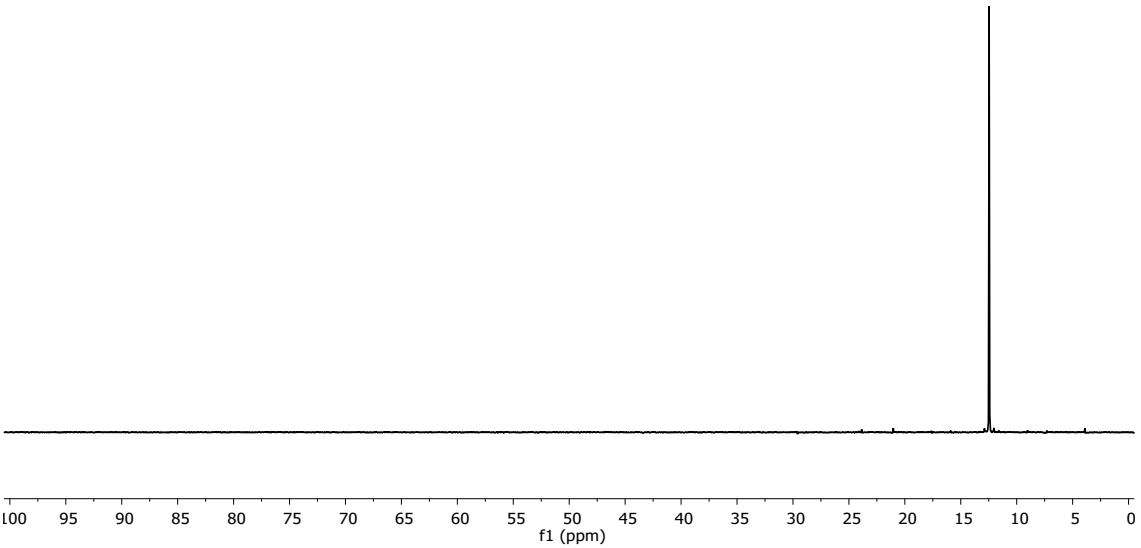
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



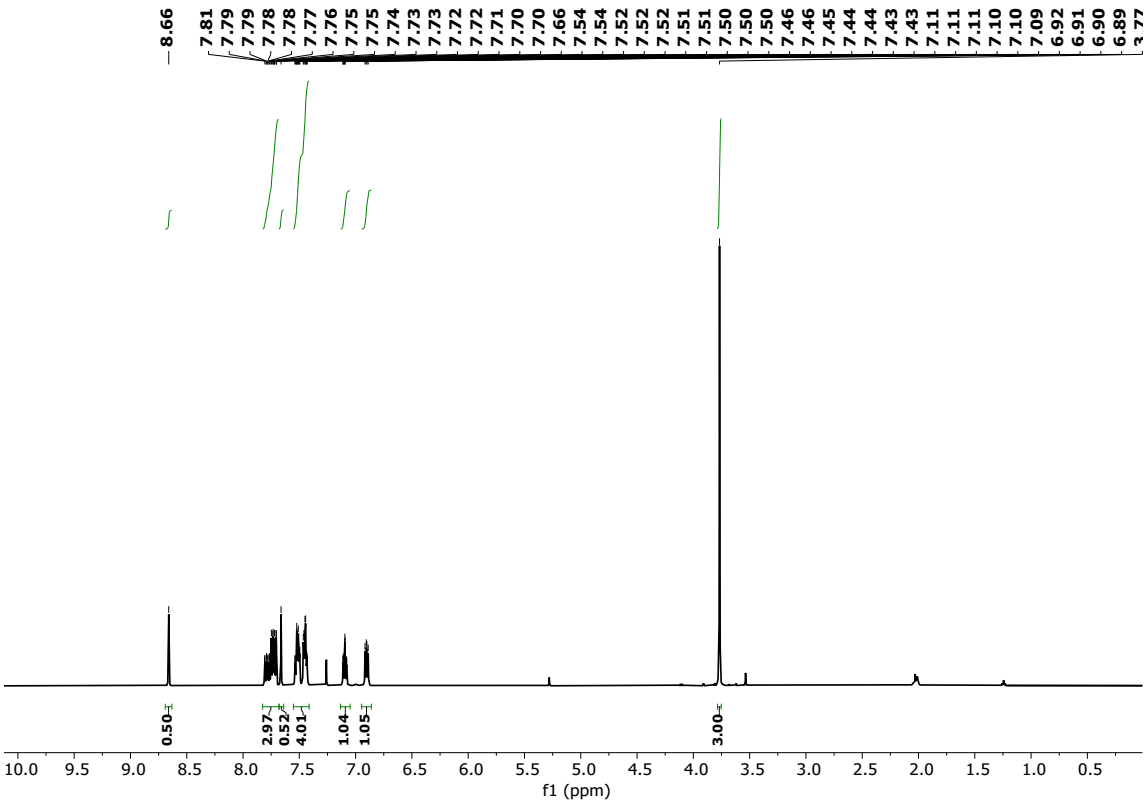
(*R*)-(2-methoxyphenyl)-phenylphosphine oxide [(*R*)-**3a**]



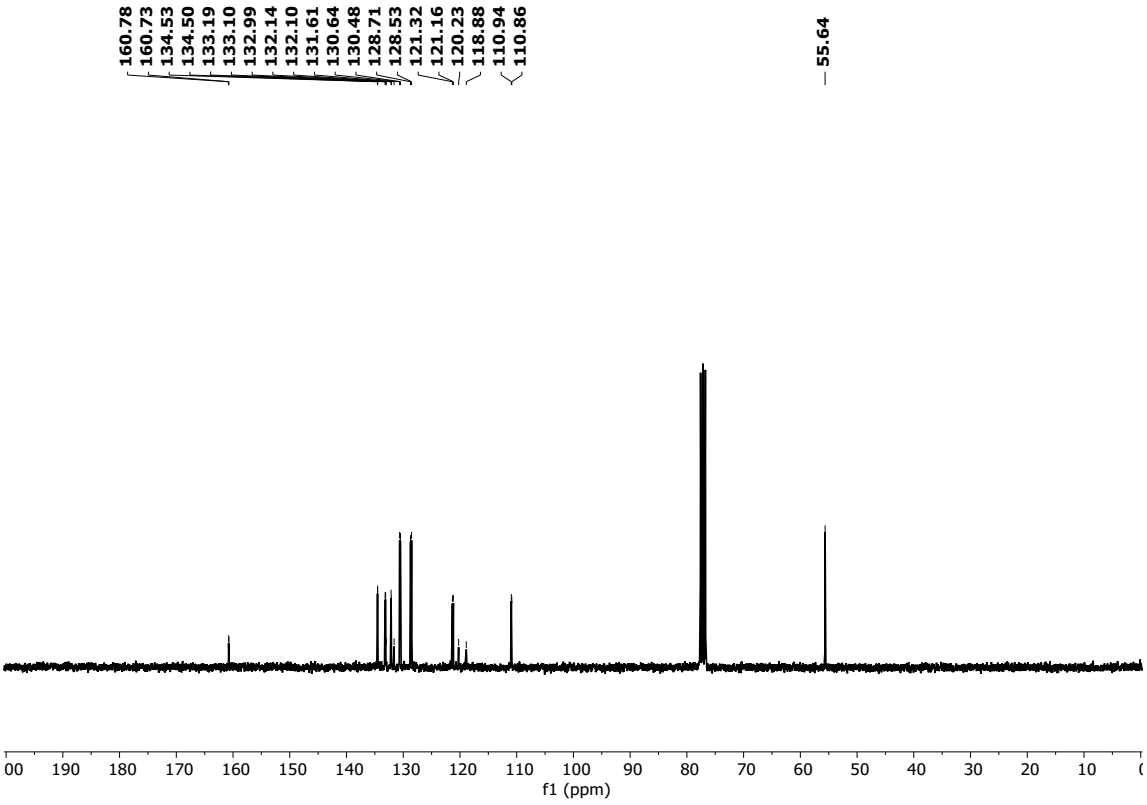
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$)



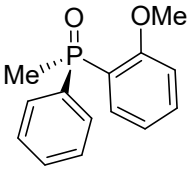
^{1}H NMR (500 MHz, $CDCl_3$)



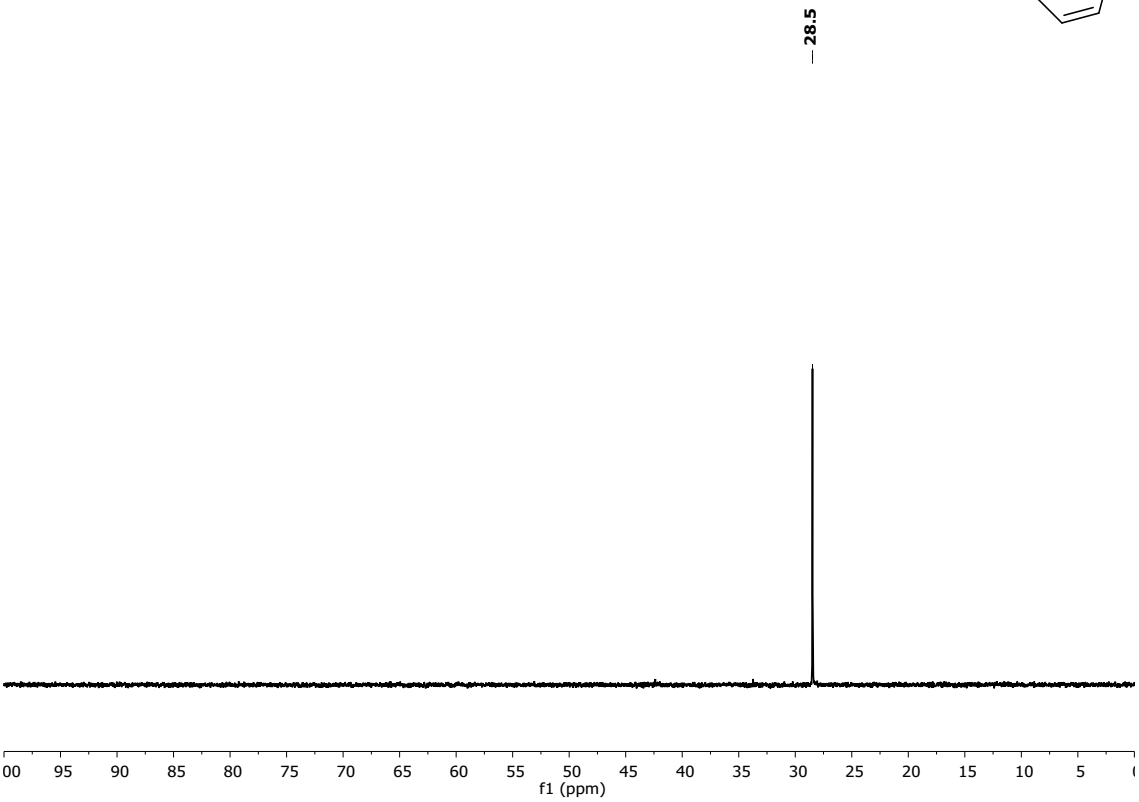
$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$)



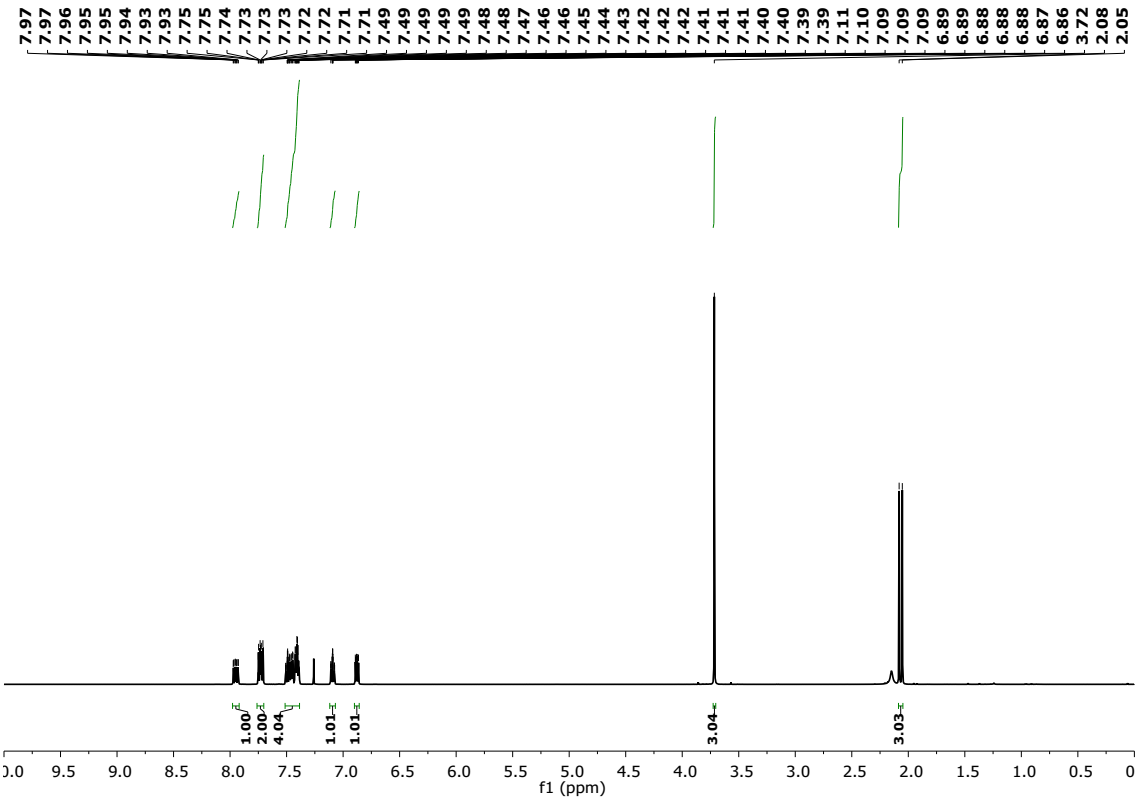
(*R*)-(2-methoxyphenyl)-methyl-phenylphosphine oxide [(*R*)-**3b**]



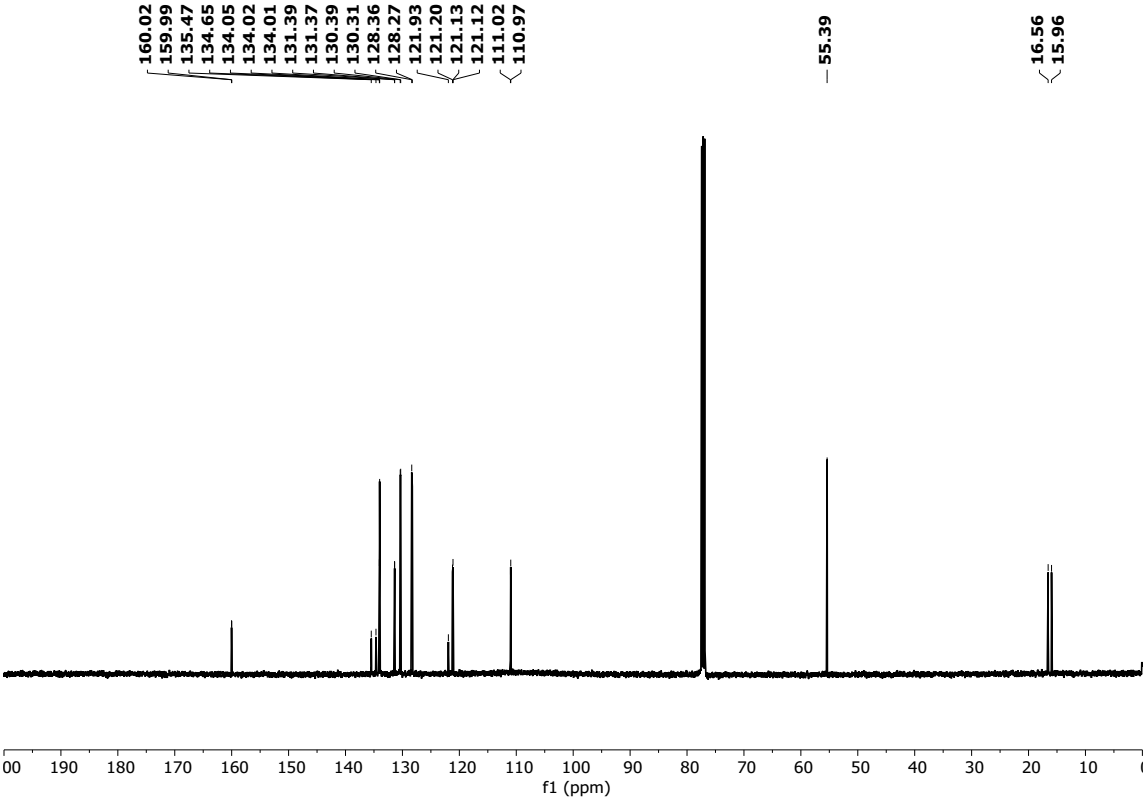
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$)



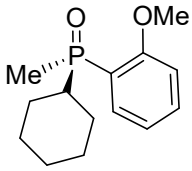
^{1}H NMR (500 MHz, $CDCl_3$)



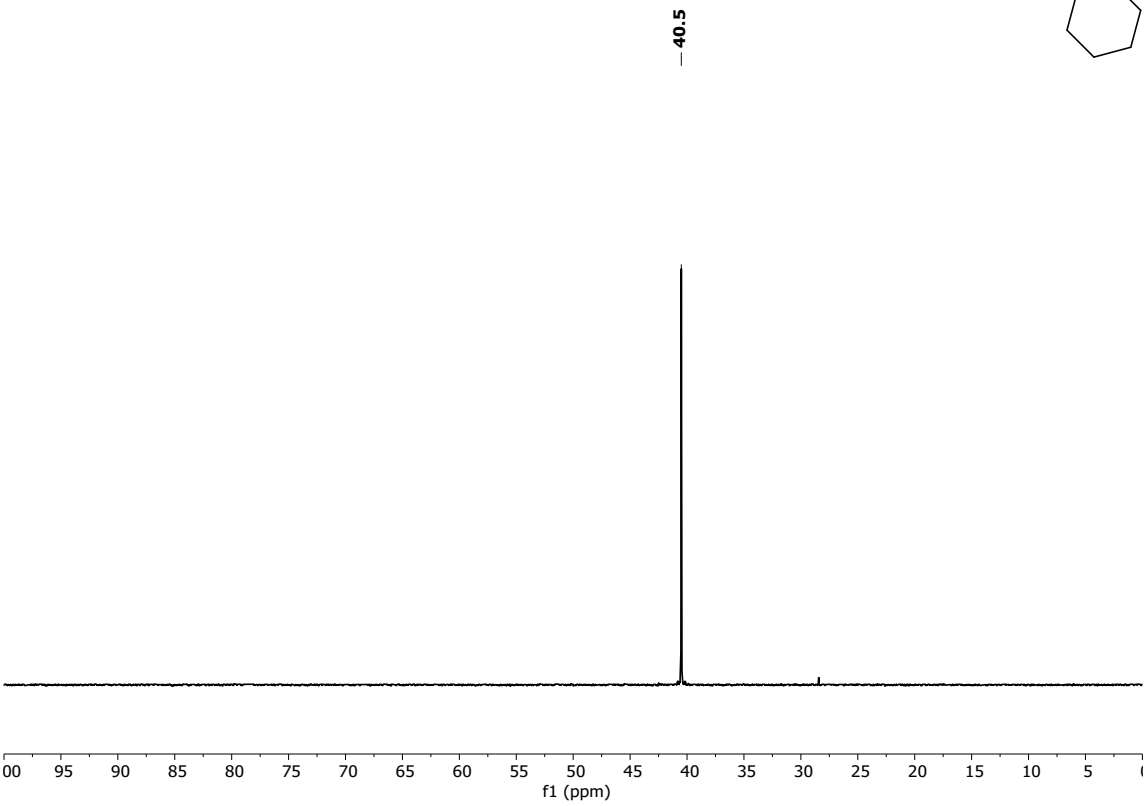
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



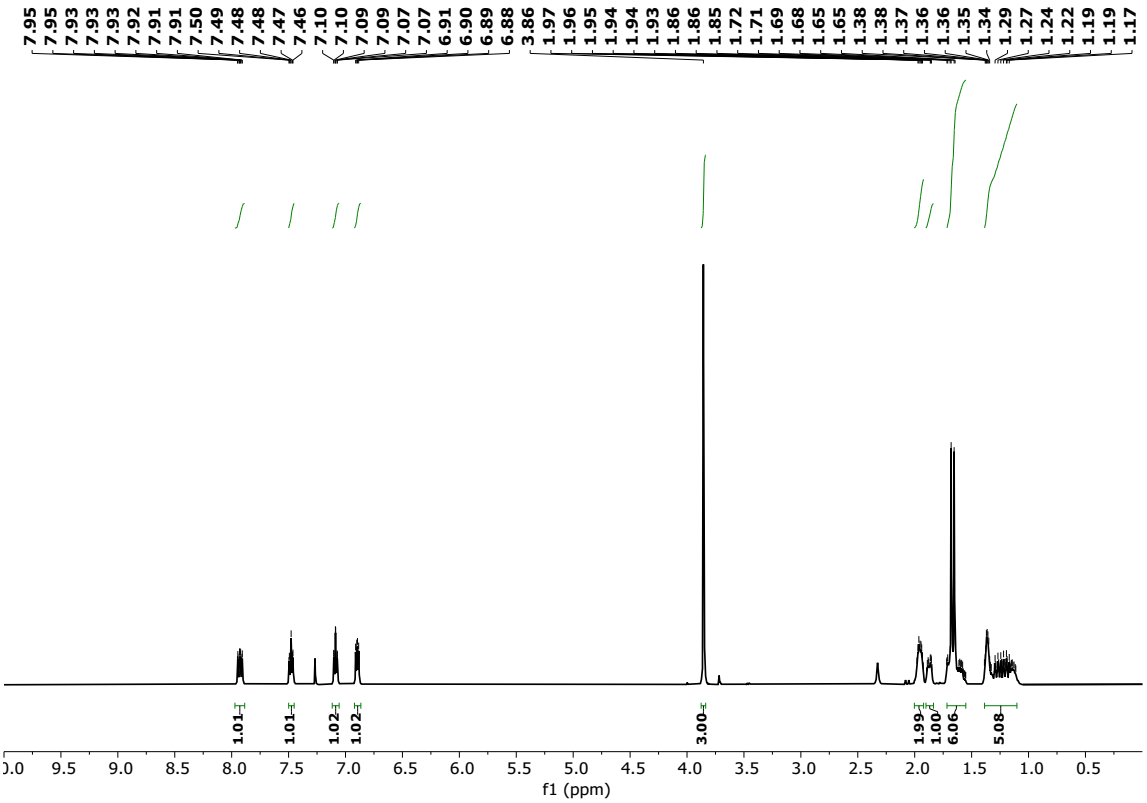
(*R*)-cyclohexyl-(2-methoxyphenyl)-methylphosphine oxide [(*R*)-**3c**]



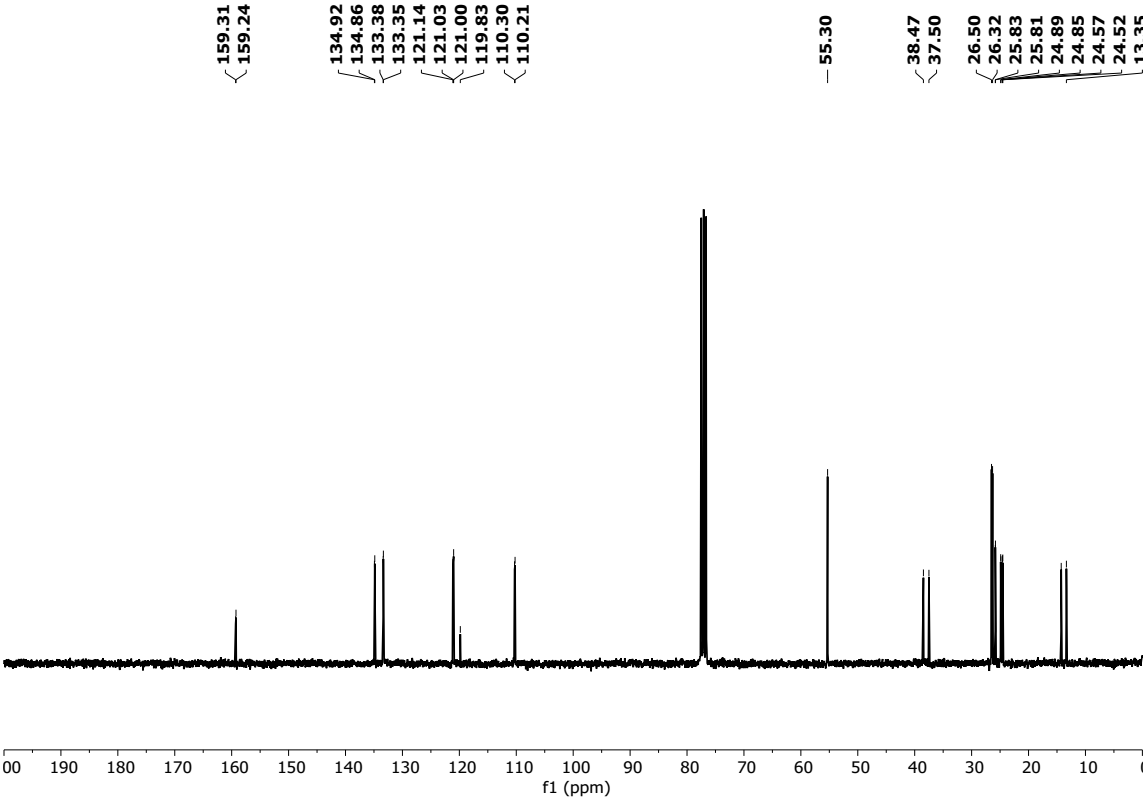
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

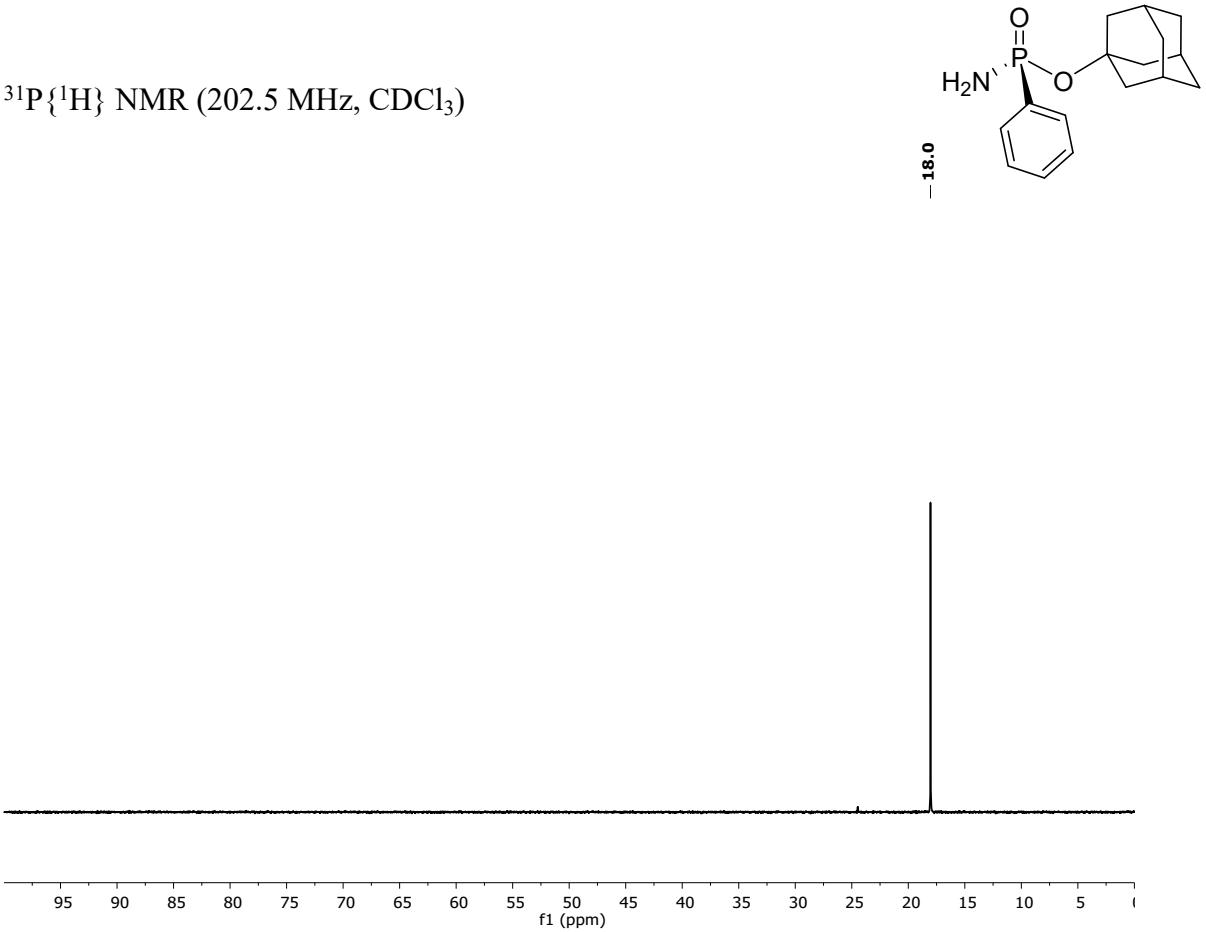


$^{13}C\{^{1}H\}$ NMR (75.5 MHz, $CDCl_3$)

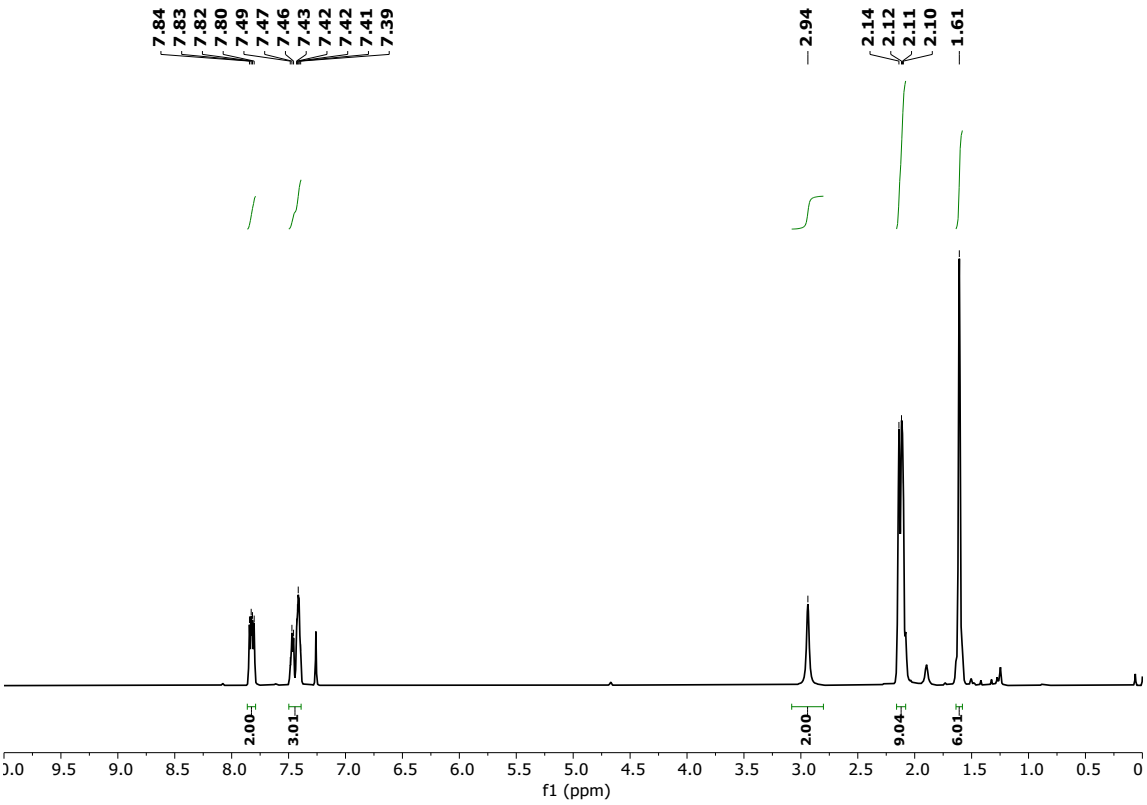


(*R*)-1-adamantyl-phenylphosphonamidate [(*R*)-**3d**]

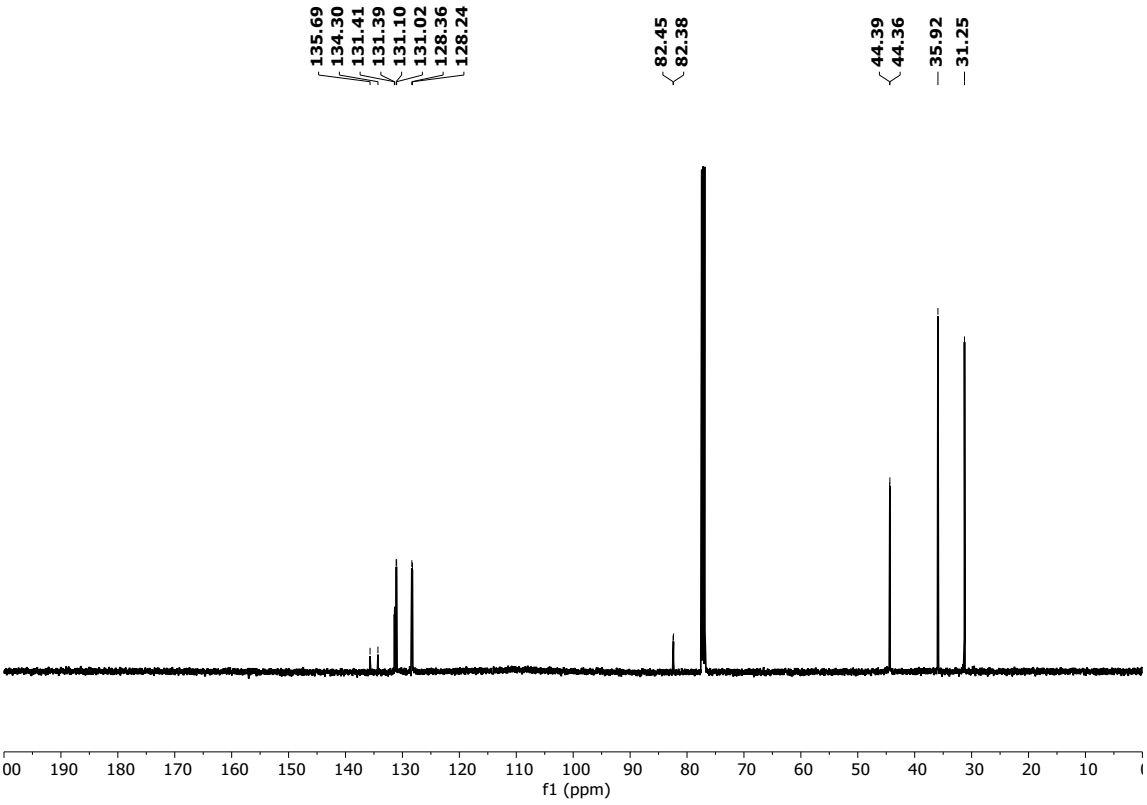
$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

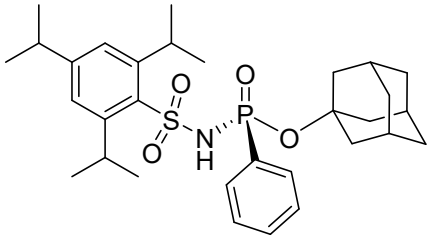


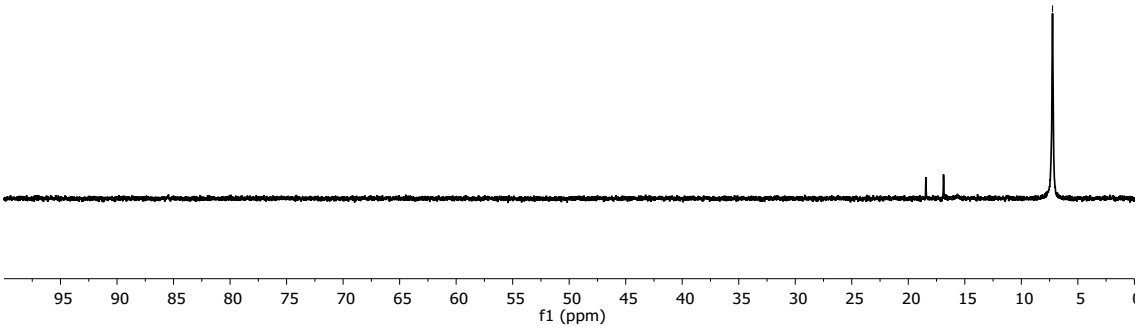
$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



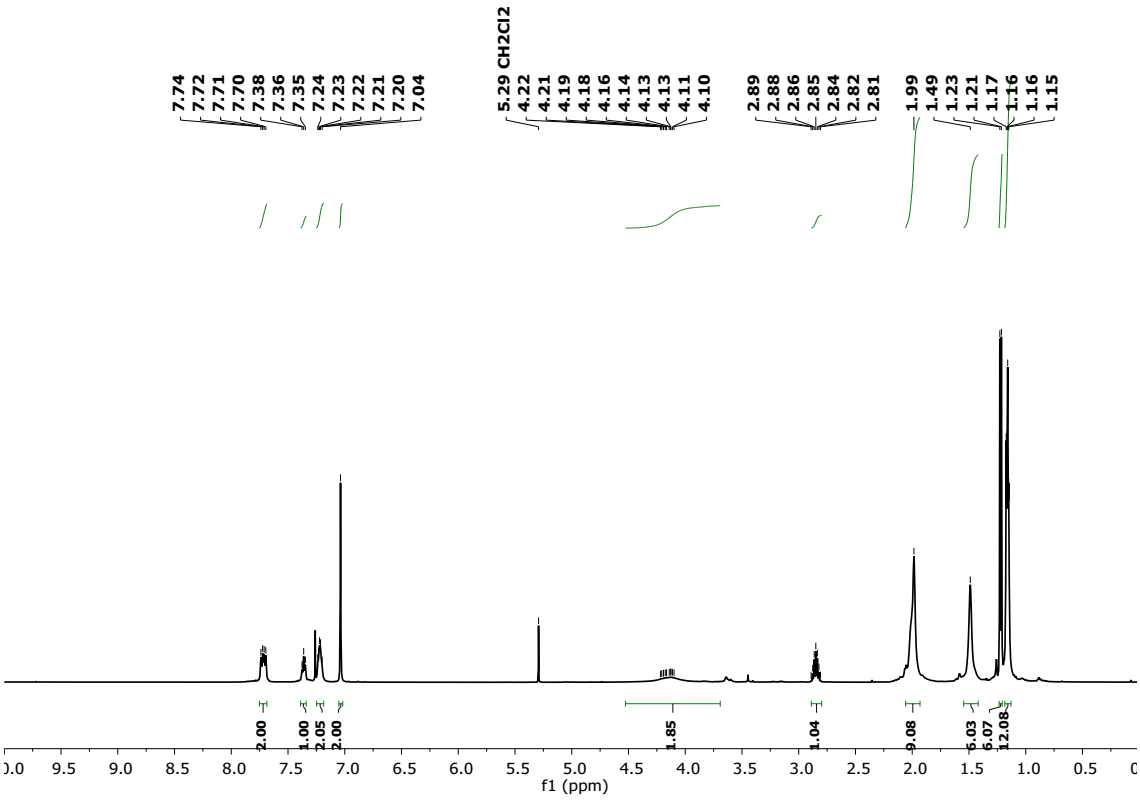
(*R*)-*N*-(1-adamantyl-phenylphosphonyl)-2,4,6-triisopropylbenzenesulfonamide [(*R*)-**3e**]

$^{31}P\{^{1}H\}$ NMR (202.5 MHz, $CDCl_3$)

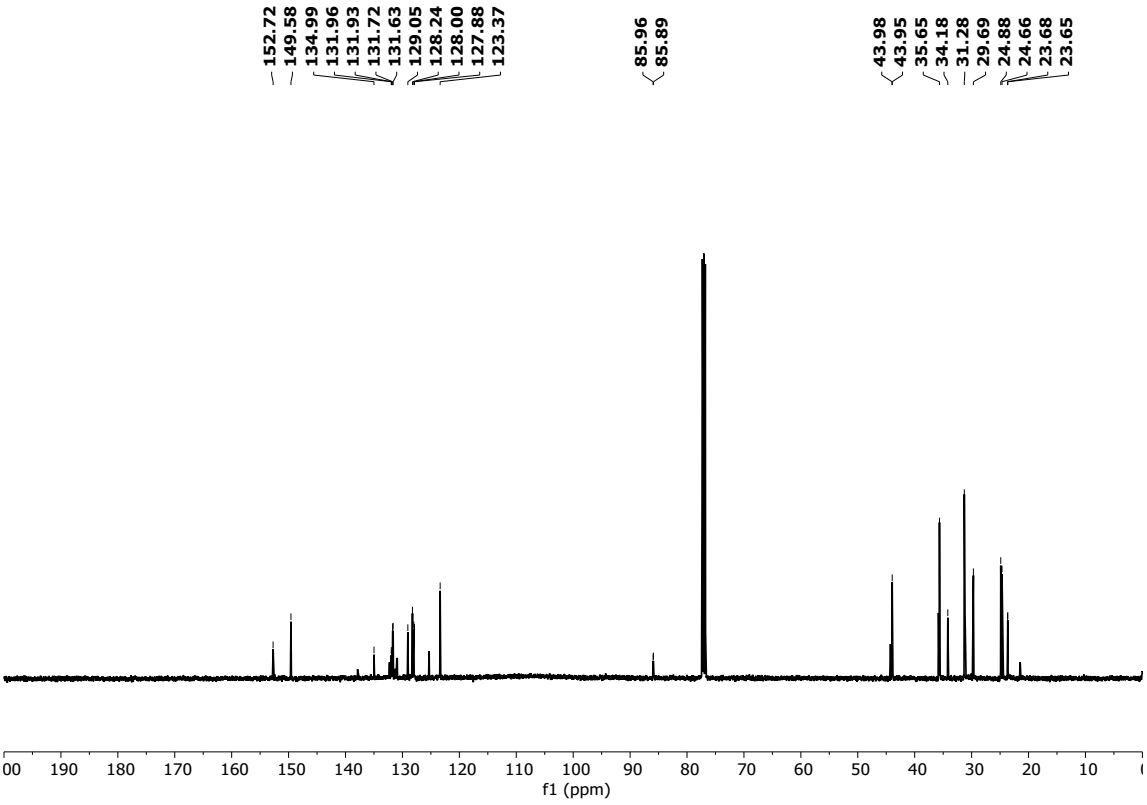




^{1}H NMR (500 MHz, $CDCl_3$)

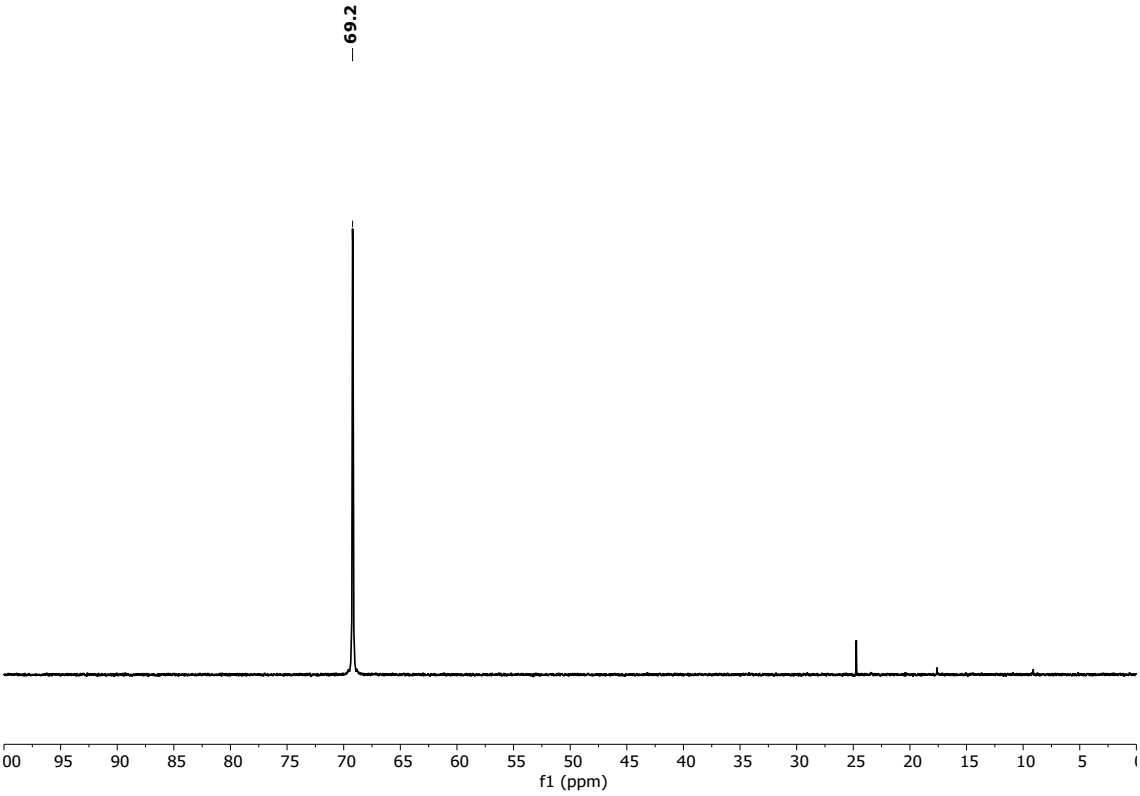


$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)

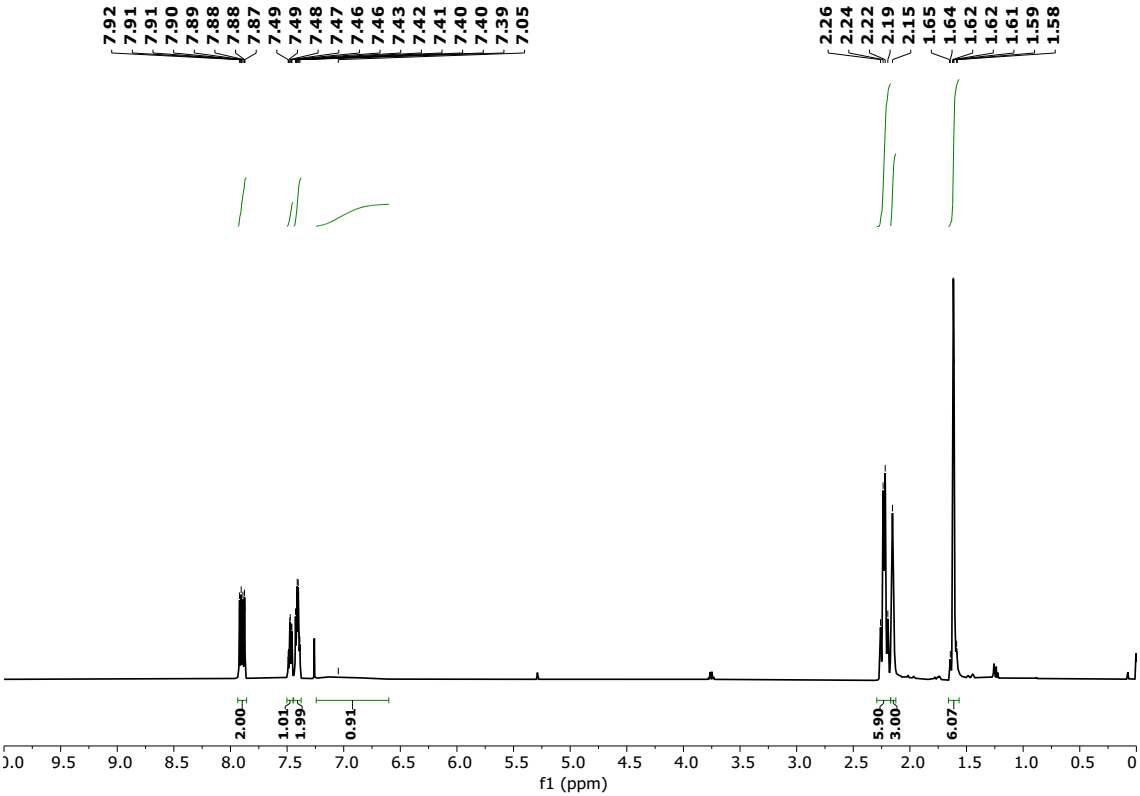


(*S*)-1-adamantyl-phenylphosphonothioic acid [(*S*)-**3f**]

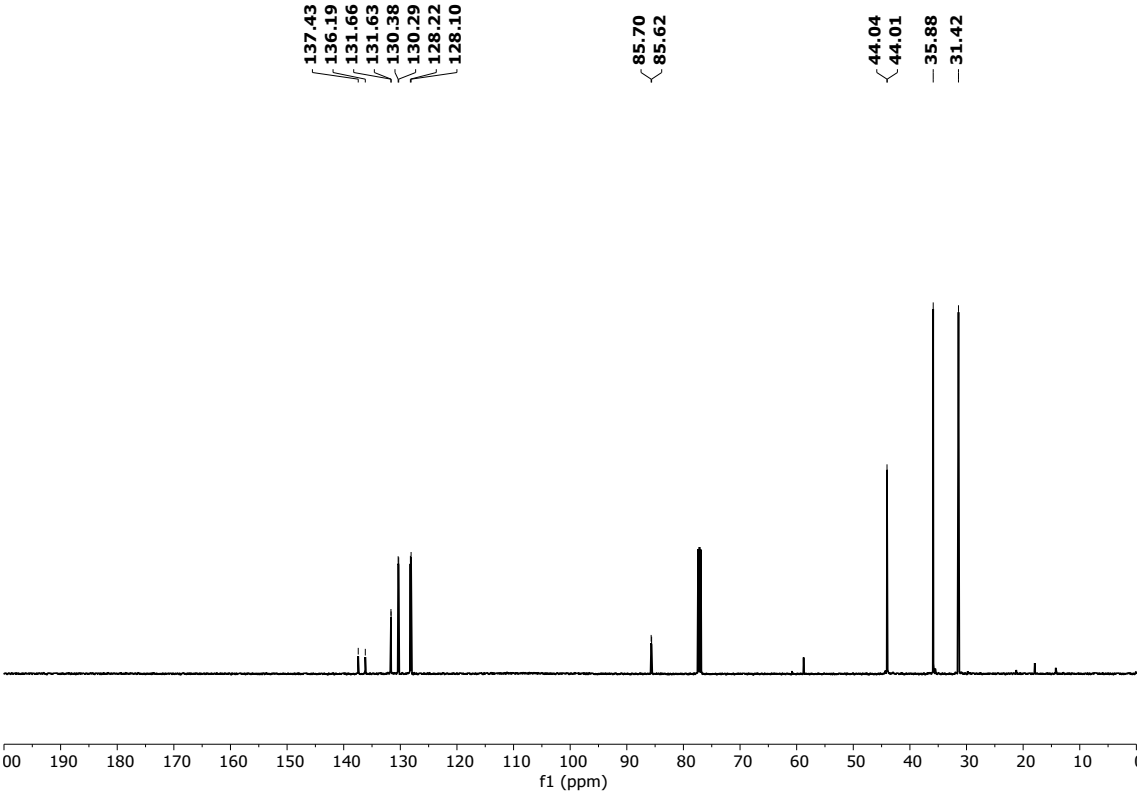
$^{31}P\{^{1}H\}$ NMR (121.5 MHz, $CDCl_3$)



^{1}H NMR (500 MHz, $CDCl_3$)

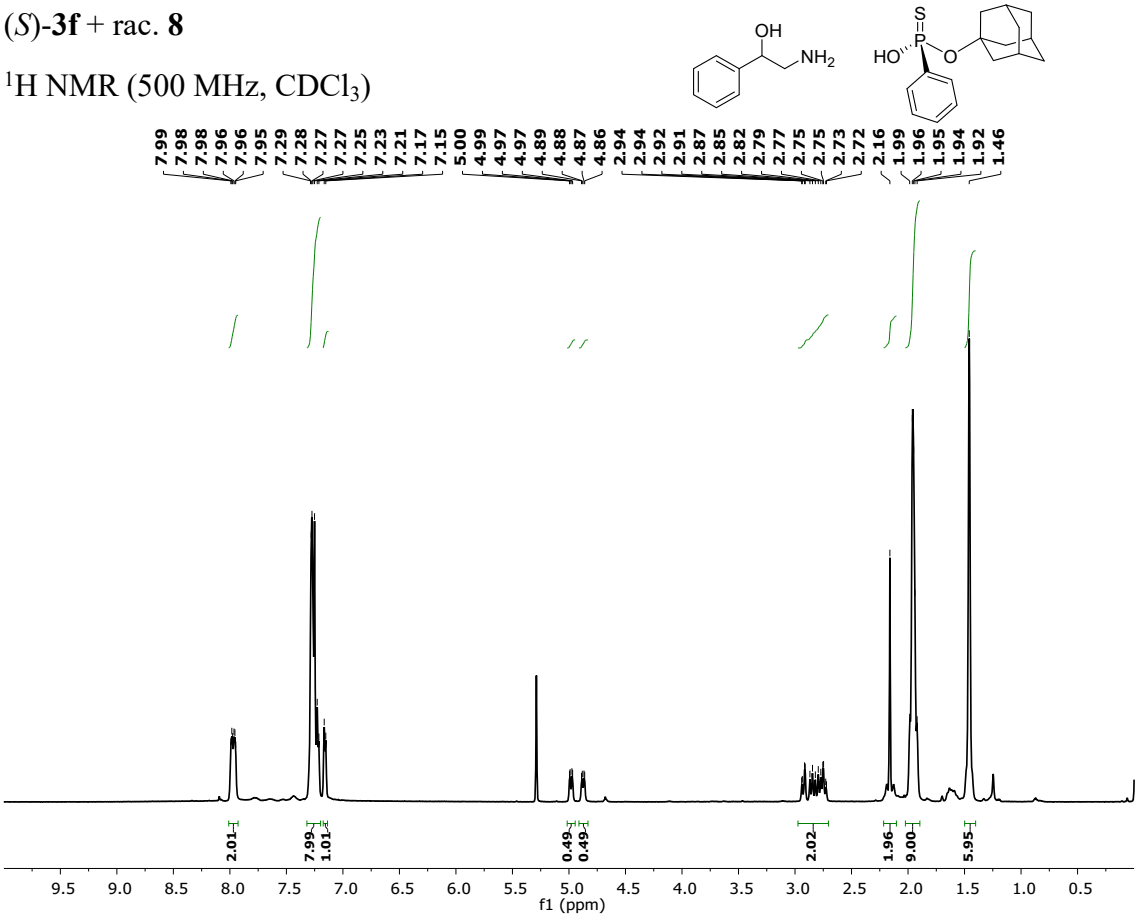


$^{13}C\{^{1}H\}$ NMR (125.8 MHz, $CDCl_3$)



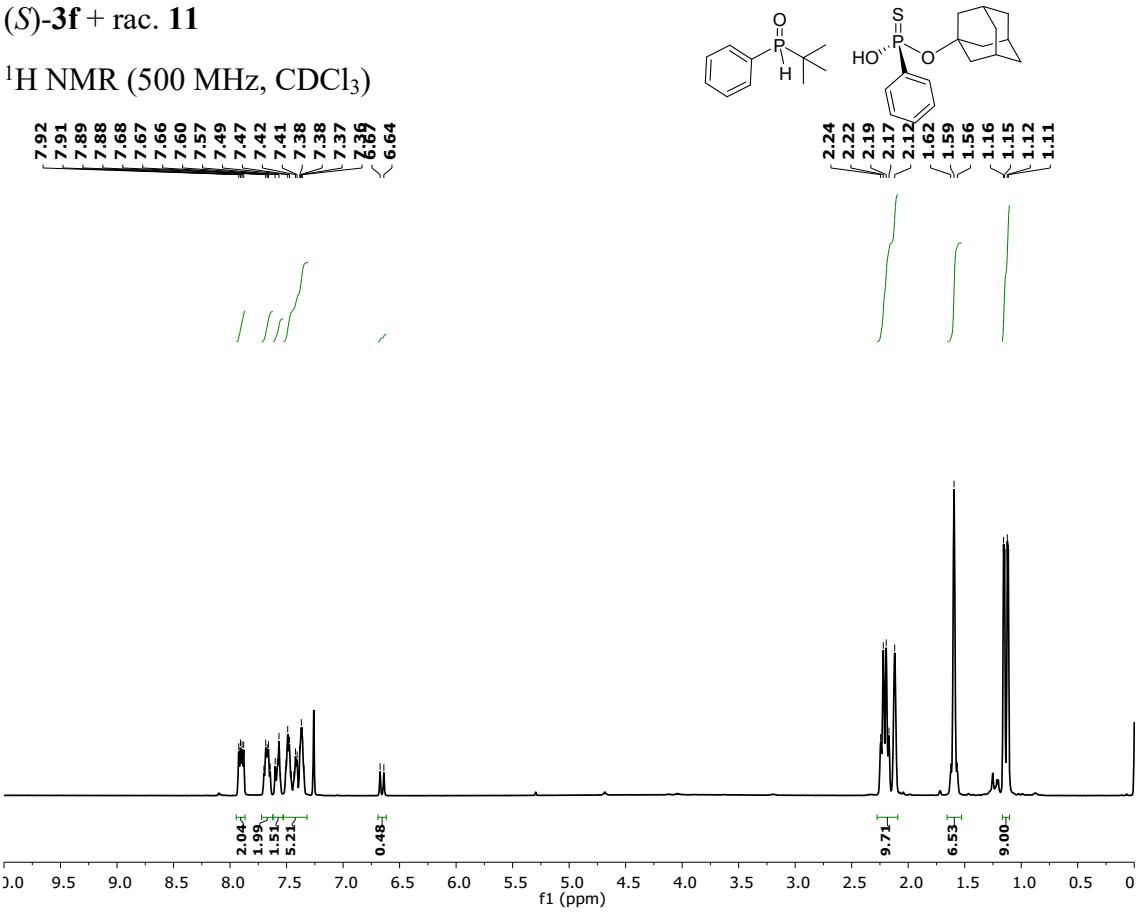
(*S*)-**3f** + rac. **8**

^{1}H NMR (500 MHz, $CDCl_3$)



(*S*)-**3f** + rac. **11**

^{1}H NMR (500 MHz, $CDCl_3$)



HPLC traces of the optically active compounds

Table S12 HPLC parameters for the *ee* determination of **1a-o** and **3a-d**.

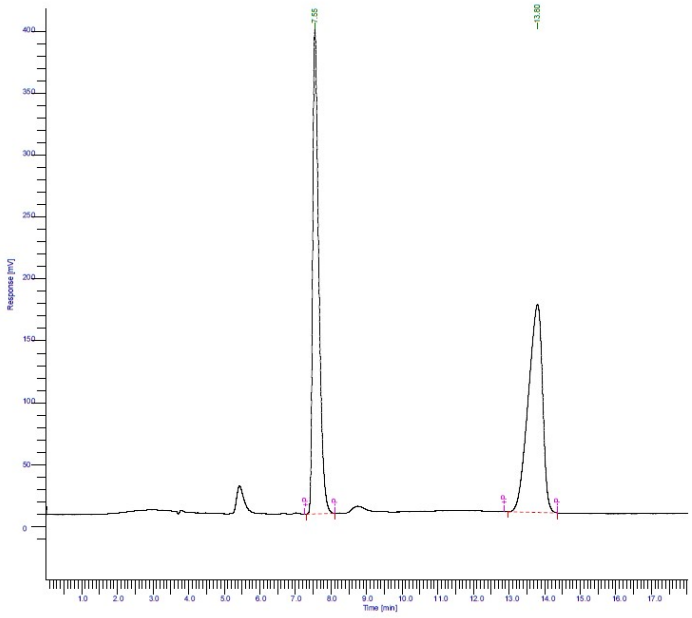
Compound	Column	Hexane : Ethanol ratio	Retention time 1 (min)	Enantiomer 1	Retention time 2 (min)	Enantiomer 2
1a	Amylose-2[a]	50:50	7.6	(*S*), (−)	13.8	(*R*), (+)
1b	Amylose-2[a]	50:50	7.5	(*S*), (−)	14.1	(*R*), (+)
1c	Amylose-2[a]	50:50	7.6	(*R*), (+)	9.0	(*S*), (−)
1d	Amylose-2[a]	50:50	7.6	(*R*), (+)	9.8	(*S*), (−)
1e	Amylose-2[a]	85:15	7.5	(S_P)	10.1	(R_P)
1f	Cellulose-4[b]	50:50	6.2	(*S*), (−)	8.6	(*R*), (+)
1g	Amylose-2[a]	50:50	6.4	(*S*), (−)	8.9	(*R*), (+)
1h	Amylose-2[a]	50:50	5.5	(*S*), (−)	6.6	(*R*), (+)
1i	Amylose-2[a]	50:50	5.5	-	6.2	-
1j	Amylose-2[a]	50:50	10.5	(*R*), (−)	13.6	(*S*), (+)
1k	Amylose-2[a]	50:50	6.8	(*S*), (−)	10.6	(*R*), (+)
1l	Amylose-2[a]	50:50	8.4	(*S*), (−)	10.0	(*R*), (+)
1m	Cellulose-2[c]	50:50	8.9	(*S*), (−)	16.1	(*R*), (+)
1n	Amylose-2[a]	50:50	9.0	-	27.5	-
1o	Cellulose-2[c]	50:50	8.5	-	11.6	-
3a	Cellulose-1[d]	85:15	10.8	(*S*), (−)	15.4	(*R*), (+)
3b	Amycoat[e]	85:15	11.5	(*S*), (−)	14.5	(*R*), (+)
3c	Amylose-2[a]	85:15	12.1	(*S*), (−)	16.9	(*R*), (+)
3d	Amylose-2[a]	50:50	6.1	(*R*), (−)	10.7	(*S*), (+)

[a] Phenomenex Lux ® 5µm Amylose-2 column
[b] Phenomenex Lux ® 3µm Cellulose-4 column
[c] Phenomenex Lux ® 5µm Cellulose-2 column
[d] Phenomenex Lux ® 5µm Cellulose-1 column
[e] Kromasil ® 5-Amycoat column

1-adamantyl phenyl-*H*-phosphinate (**1a**)

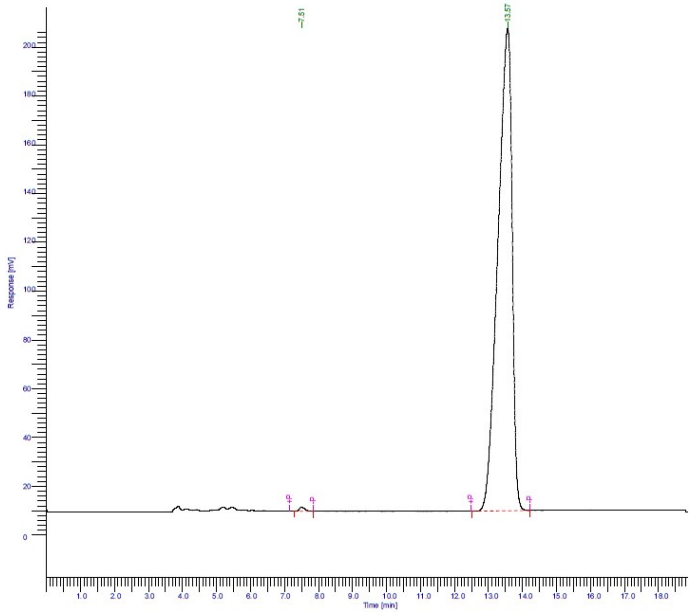
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.548	4663239.90	391840.61	49.85	49.85	*BB	11.9009
2	13.801	4690666.03	168118.18	50.15	50.15	*BB	27.9010
		9353905.93	559958.78	100.00	100.00		



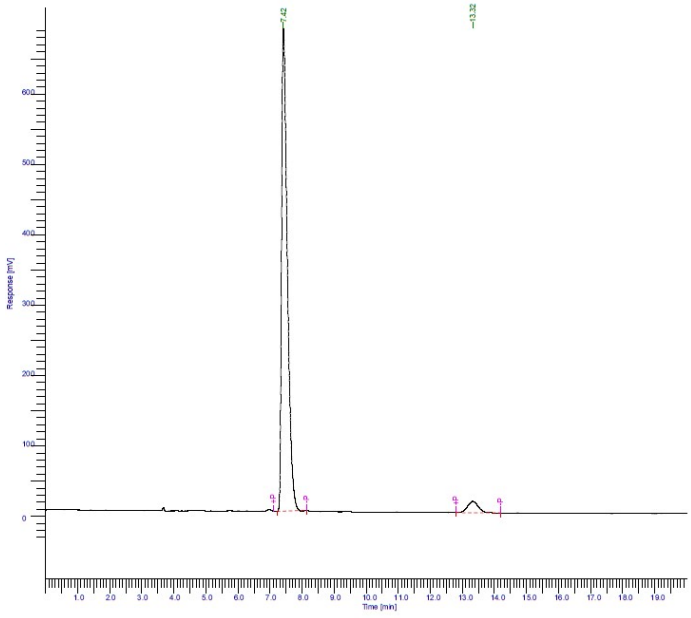
(*R*)-**1a** (Table S3, Entry 12; Scheme 3)

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.507	19398.65	1785.01	0.34	0.34	*BB	10.8675
2	13.565	5732781.05	197891.35	99.66	99.66	*BB	28.9693
		5752179.70	199676.36	100.00	100.00		



(*S*)-**1a** (Scheme 4)

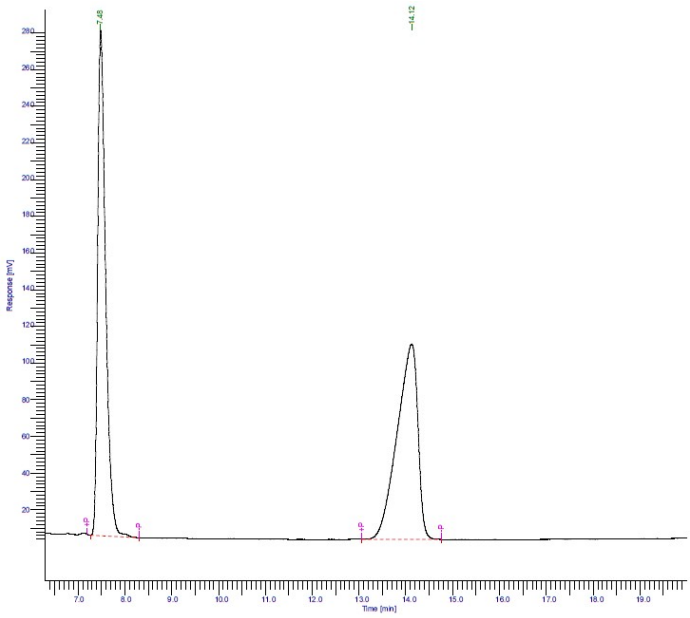
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.417	8527418.27	686098.97	95.73	95.73	*BB	12.4288
2	13.323	380189.26	16146.94	4.27	4.27	*BB	23.5456
		8907607.53	702245.91	100.00	100.00		



2-adamantyl phenyl-*H*-phosphinate (**1b**)

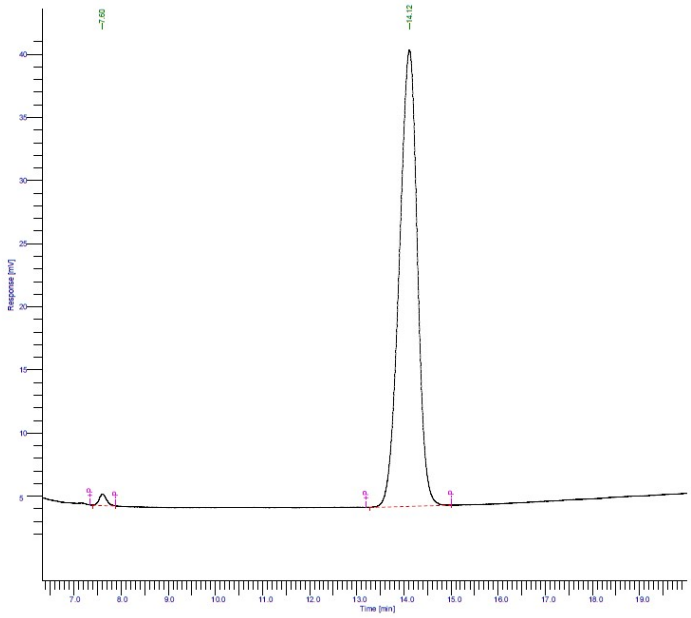
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.483	3264639.35	275556.38	49.92	49.92	*BB	11.8474
2	14.125	3275055.88	106559.47	50.08	50.08	*BB	30.7345
		6539695.23	382115.85	100.00	100.00		



(*R*)-**1b** (Table S4, Entry 2; Scheme 3)

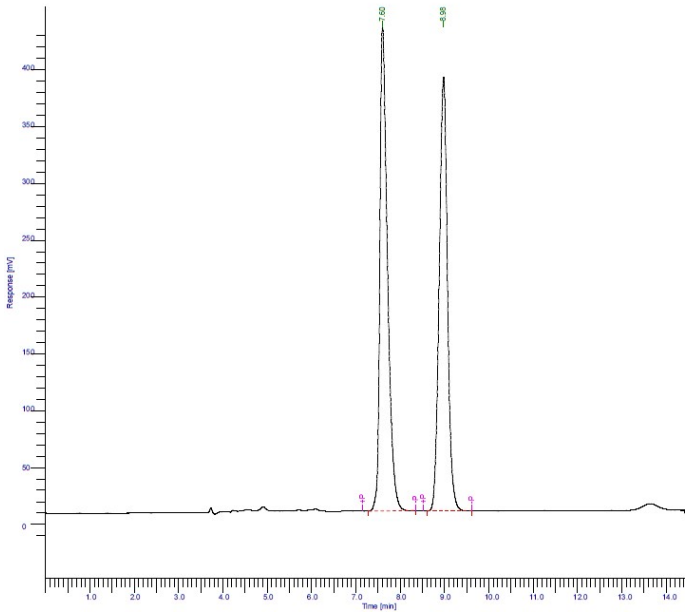
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.598	9911.62	908.06	1.02	1.02	*BB	10.9151
2	14.119	959831.03	36129.33	98.98	98.98	*BB	26.5665
		969742.64	37037.39	100.00	100.00		


7.60
14.12
Response [mV]
Time [min]

c-pentyl phenyl-*H*-phosphinate (**1c**)

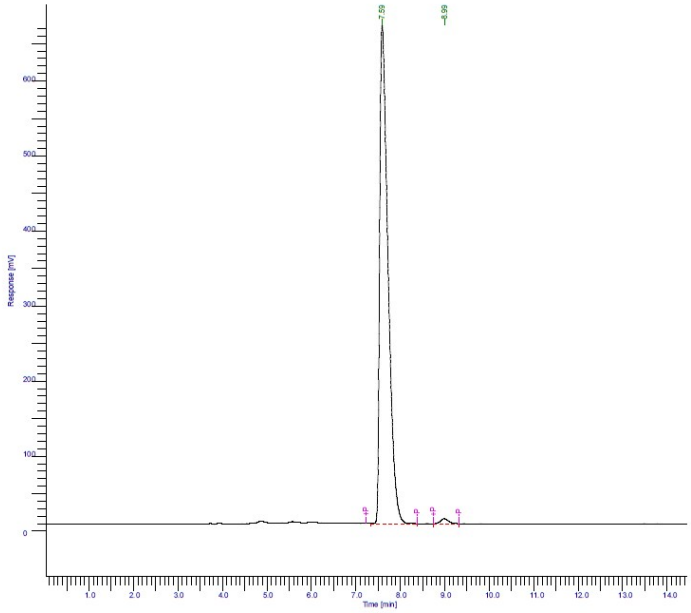
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.599	5101378.26	425774.72	50.73	50.73	*BB	11.9814
2	8.977	4954262.82	381561.74	49.27	49.27	*BB	12.9842
		10055641.07	807336.46	100.00	100.00		



(*R*)-**1c** (Table S4, Entry 3; Scheme 3)

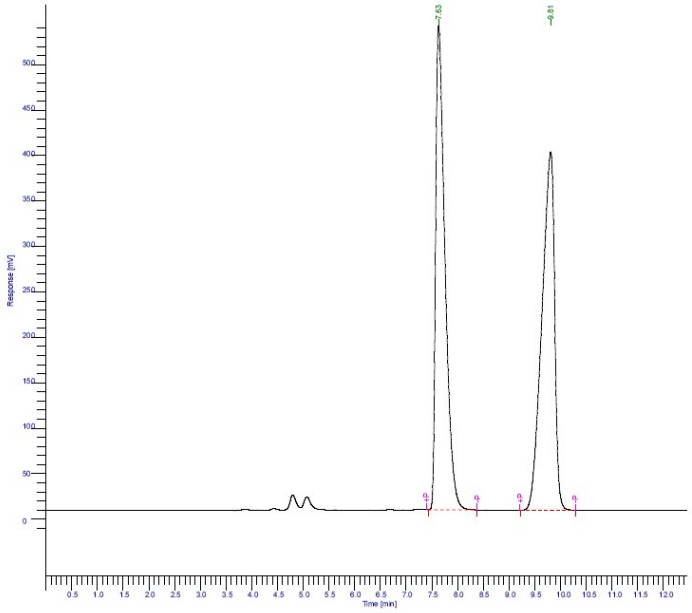
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.593	8596931.14	664360.26	99.06	99.06	*BB	12.9402
2	8.992	81174.24	6527.15	0.94	0.94	*BB	12.4364
		8678105.38	670887.41	100.00	100.00		


7.59
8.99
Response [mV]
600
500
400
300
200
100
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
Time [min]

c-hexyl phenyl-*H*-phosphinate (**1d**)

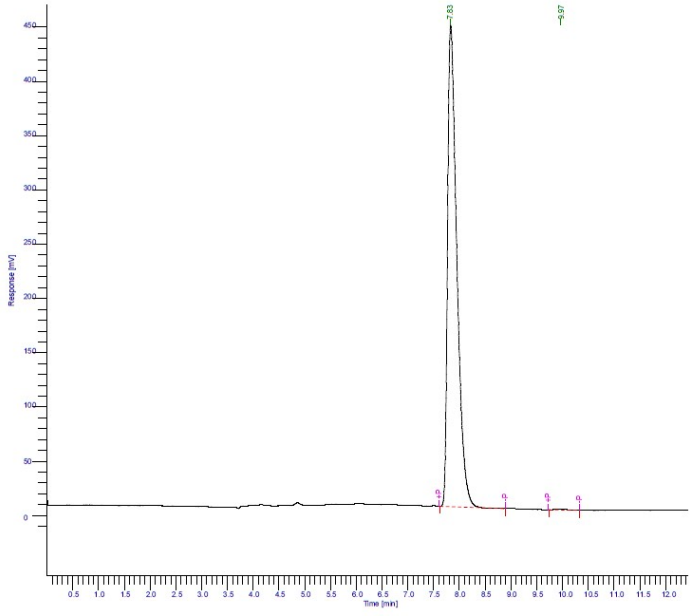
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.630	6725882.64	532900.14	49.90	49.90	*BB	12.6213
2	9.809	6753020.68	394242.94	50.10	50.10	*BB	17.1291
		13478903.32	927143.09	100.00	100.00		



(*R*)-**1d** (Table S4, Entry 4; Scheme 3)

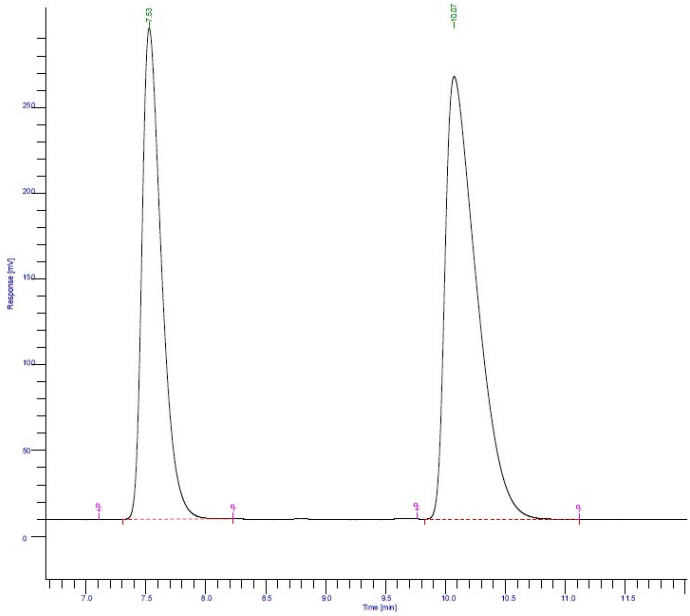
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.831	5527330.81	443594.70	99.80	99.80	*BB	12.4603
2	9.970	11002.55	807.11	0.20	0.20	*BB	13.6321
		5538333.35	444401.81	100.00	100.00		


7.83
9.97
Response [mV]
Time [min]

(1*R*,2*S*,5*R*)-2-isopropyl-5-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1e**)

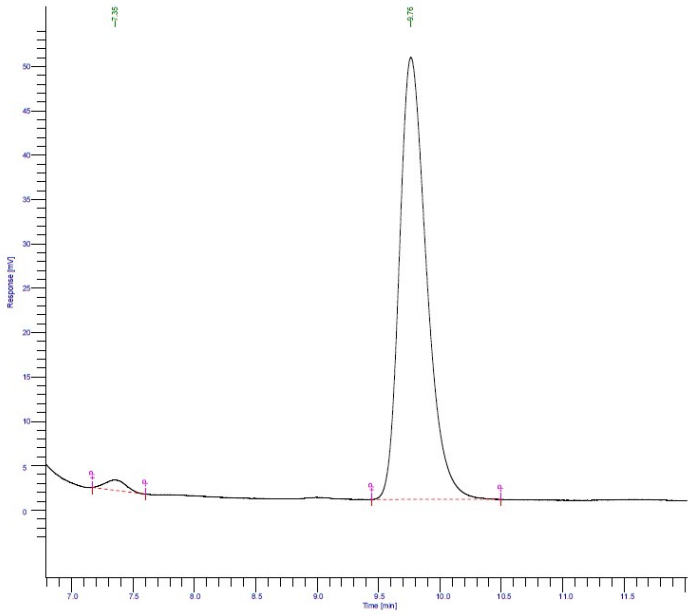
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.527	3250716.69	286238.66	40.89	40.89	*BB	11.3567
2	10.074	4699877.01	258048.21	59.11	59.11	*BB	18.2132
		7950593.71	544286.87	100.00	100.00		



(R_P)-**1e** (Table S4, Entry 5; Scheme 3)

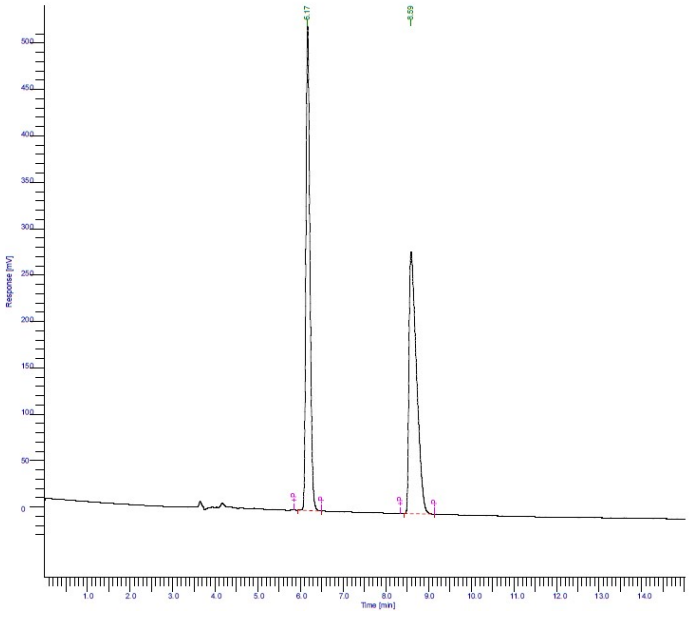
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.352	14076.99	1166.83	1.81	1.81	*BB	12.0643
2	9.763	763207.18	49832.31	98.19	98.19	*BB	15.3155
		777284.16	50999.14	100.00	100.00		


7.35
9.76
Response [mV]
Time [min]

c-heptyl phenyl-*H*-phosphinate (**1f**)

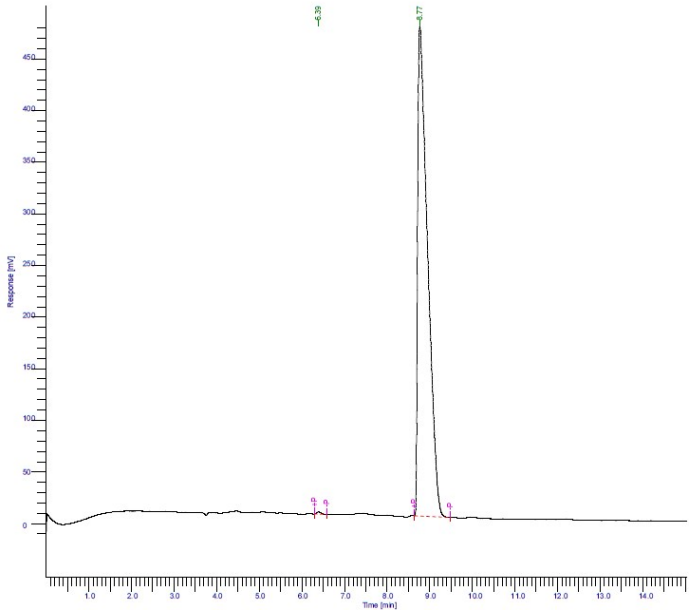
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.167	3398492.69	522456.57	49.62	49.62	*BB	6.5048
2	8.591	3451169.62	282295.74	50.38	50.38	*BB	12.2254
		6849662.31	804752.31	100.00	100.00		



(*R*)-**1f** (Table S4, Entry 6; Scheme 3)

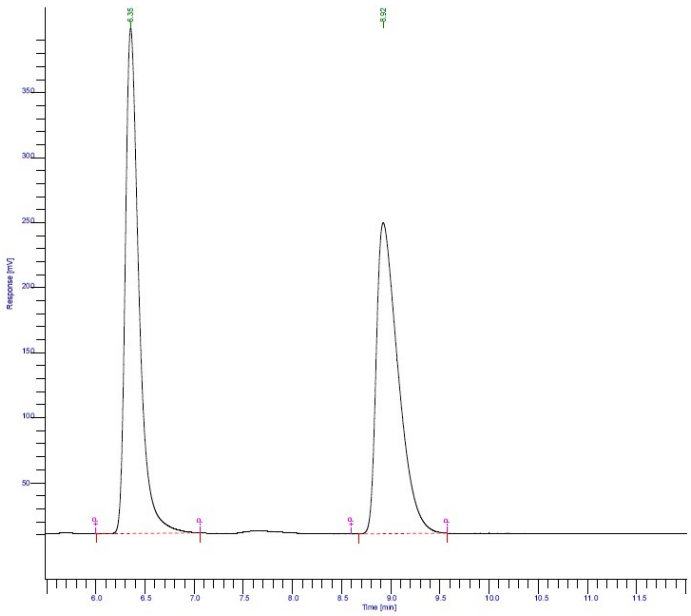
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.393	13864.67	2193.29	0.18	0.18	*BB	6.3214
2	8.767	7640664.10	474442.76	99.82	99.82	*BB	16.1045
		7654528.76	476636.06	100.00	100.00		


6.39
8.77
Response [mV]
Time [min]

1-methyl-*c*-hexyl phenyl-*H*-phosphinate (**1g**)

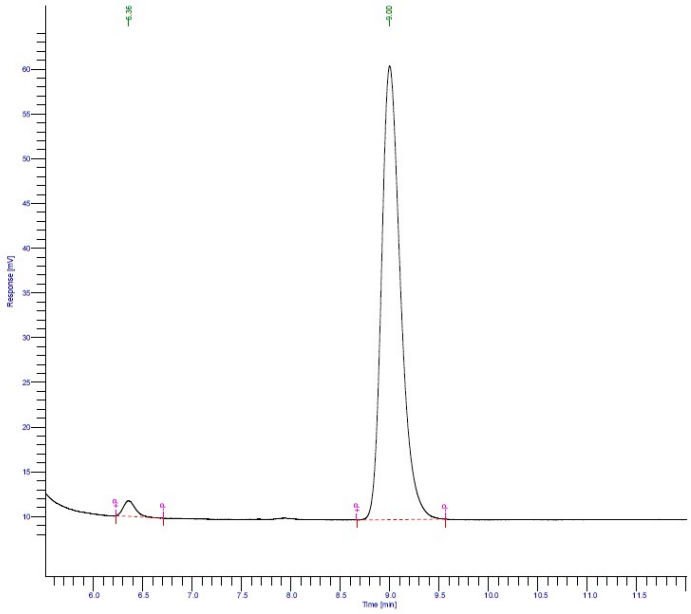
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.353	3760592.75	388415.66	50.57	50.57	*BB	9.6819
2	8.922	3675755.46	238939.09	49.43	49.43	*BB	15.3837
		7436348.20	627354.75	100.00	100.00		



(*R*)-**1g** (Table S4, Entry 8; Scheme 3)

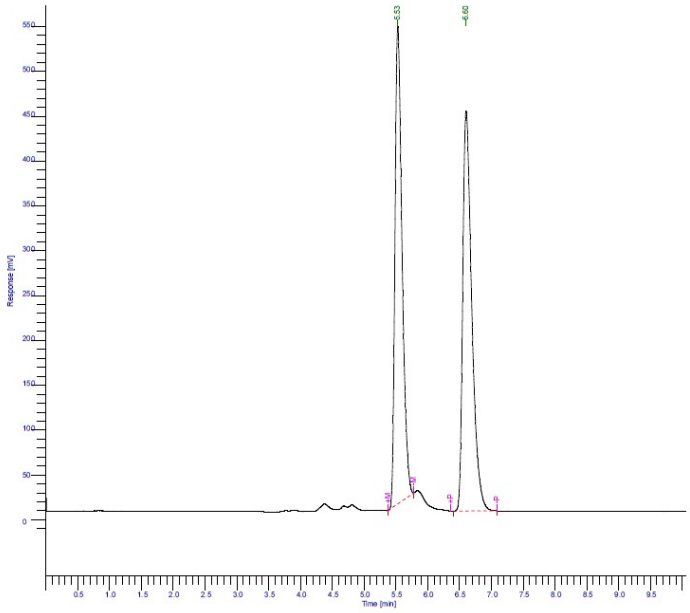
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.356	14761.79	1745.72	2.14	2.14	*BB	8.4560
2	8.999	675926.58	50688.18	97.86	97.86	*BB	13.3350
		690688.37	52433.90	100.00	100.00		


6.36
9.00
Response [mV]
Time [min]

t-butyl phenyl-*H*-phosphinate (**1h**)

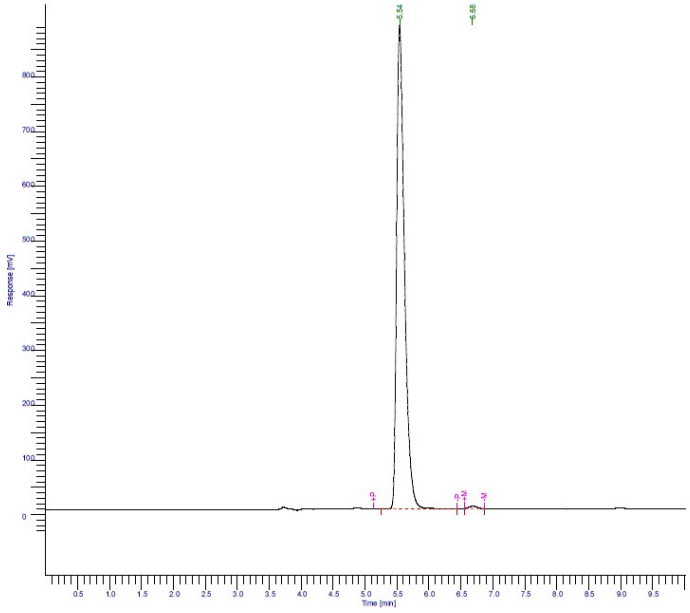
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	5.529	4133793.23	532879.99	48.40	48.40	*BB	7.7575
2	6.603	4407665.06	446176.24	51.60	51.60	*BB	9.8788
		8541458.29	979056.23	100.00	100.00		



(*S*)-**1h** (Table S4, Entry 9; Scheme 3)

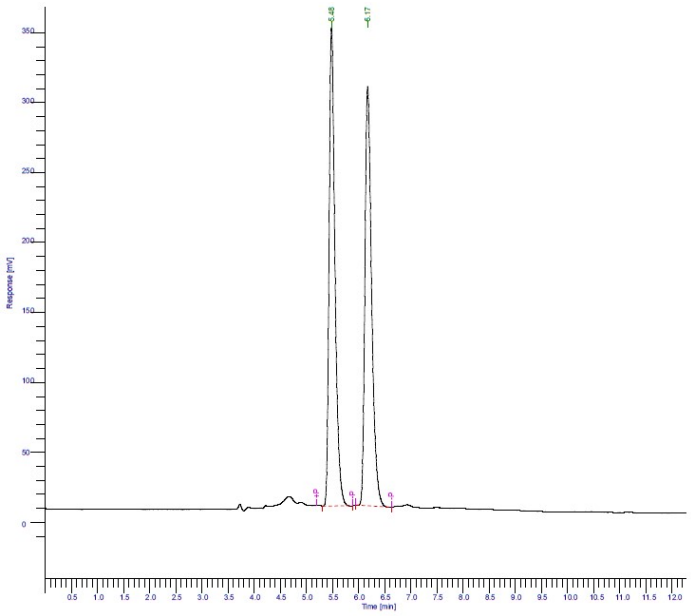
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	5.541	7511633.76	884197.17	99.49	99.49	*BB	8.4954
2	6.684	38262.37	4339.48	0.51	0.51	*BB	8.8173
		7549896.13	888536.65	100.00	100.00		


5.54
6.68
Response [mV]
Time [min]

2,4-dimethyl-pent-3-yl phenyl-*H*-phosphinate (**1i**)

Racemic

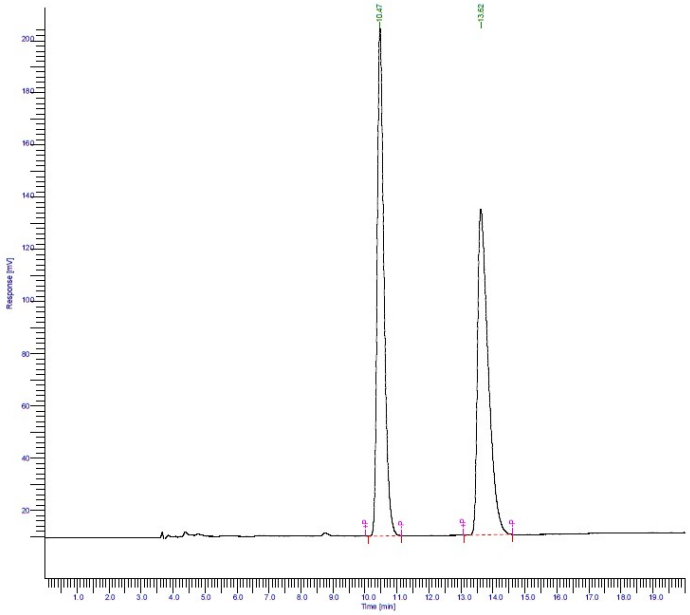
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	5.481	2677404.46	342033.21	50.09	50.09	*BB	7.8279
2	6.173	2668165.77	299660.60	49.91	49.91	*BB	8.9040
		5345570.23	641693.81	100.00	100.00		



benzyl phenyl-*H*-phosphinate (**1j**)

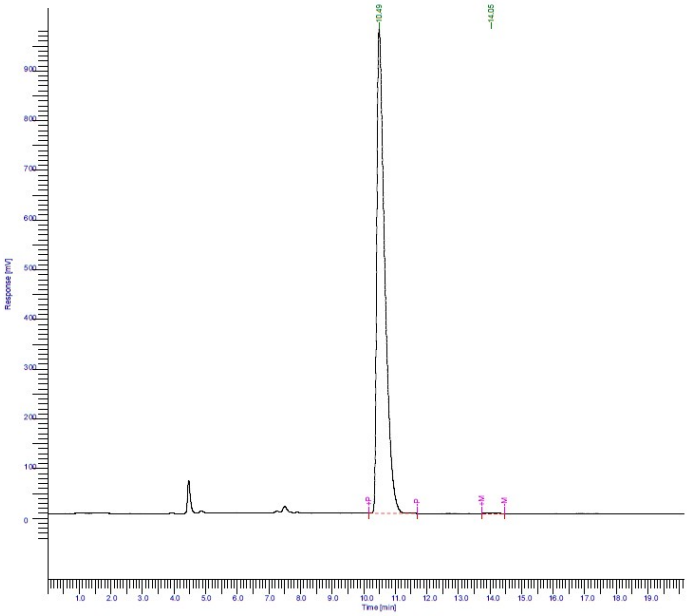
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	10.467	2872469.08	194541.30	49.95	49.95	*BB	14.7653
2	13.621	2877954.85	124806.12	50.05	50.05	*BB	23.0594
		5750423.93	319347.42	100.00	100.00		



(*R*)-**1j** (Table S4, Entry 12; Scheme 3)

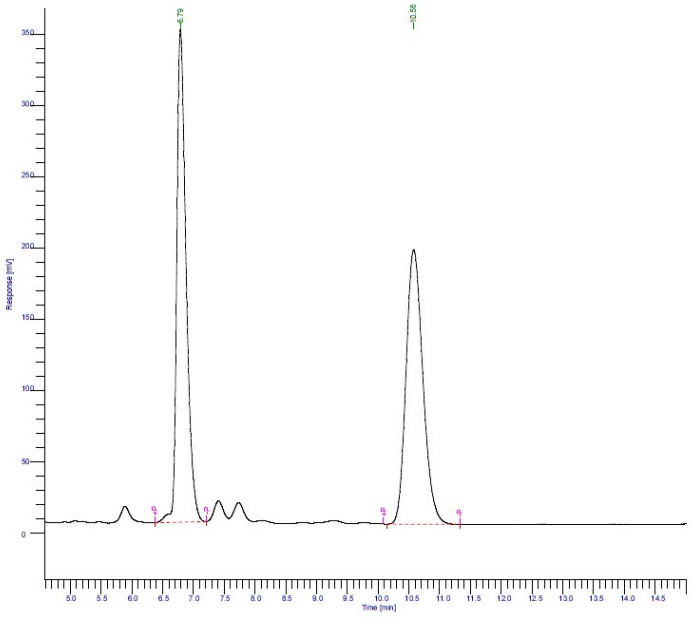
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	10.491	17085257.30	974942.94	99.83	99.83	*BB	17.5244
2	14.051	29634.25	1571.41	0.17	0.17	*BB	18.8583
		17114891.55	976514.36	100.00	100.00		


10.49
14.05
Response [mV]
Time [min]

1-adamantyl (2-methylphenyl)-*H*-phosphinate (**1k**)

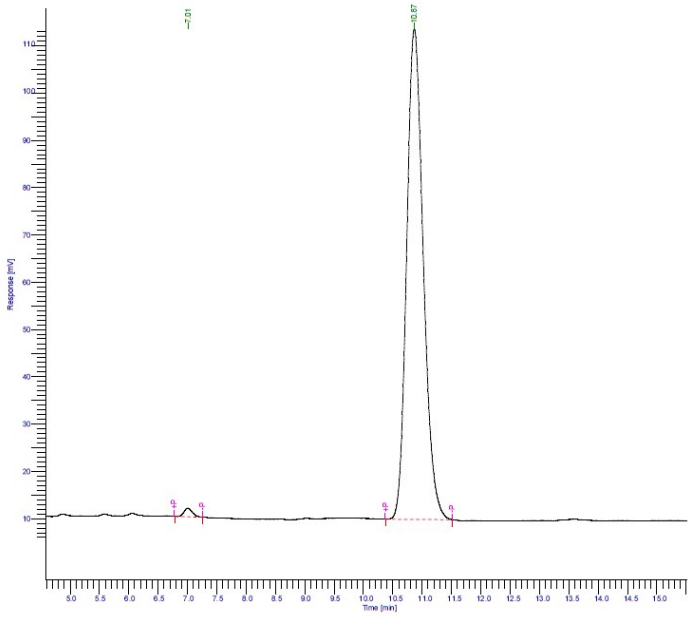
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.788	3653033.00	346468.65	49.93	49.93	*BB	10.5436
2	10.578	3663717.77	192912.08	50.07	50.07	*BB	18.9916
		7316750.77	539380.73	100.00	100.00		



(*R*)-**1k** (Table S5, Entry 1; Scheme 3)

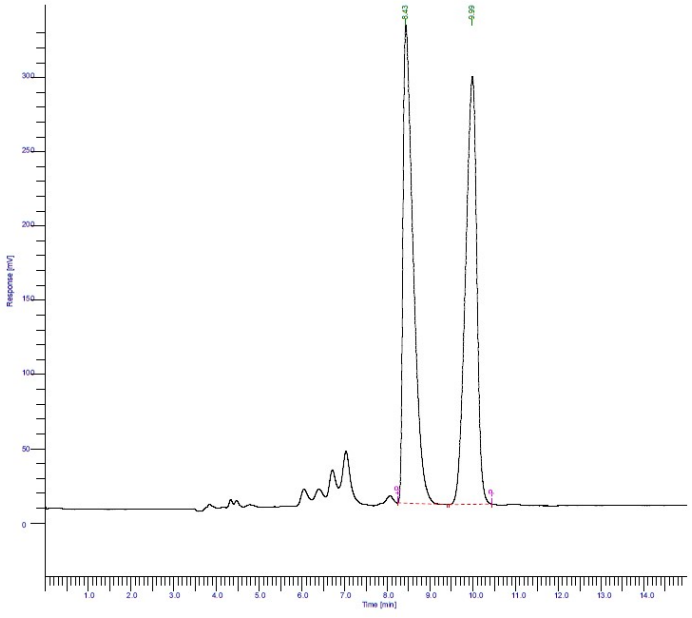
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	7.006	18188.05	1828.98	0.88	0.88	*BB	9.9444
2	10.866	2037460.11	103728.73	99.12	99.12	*BB	19.6422
		2055648.17	105557.71	100.00	100.00		


7.01
10.57
Response [mV]
Time [min]

1-adamantyl (3-methylphenyl)-*H*-phosphinate (**1l**)

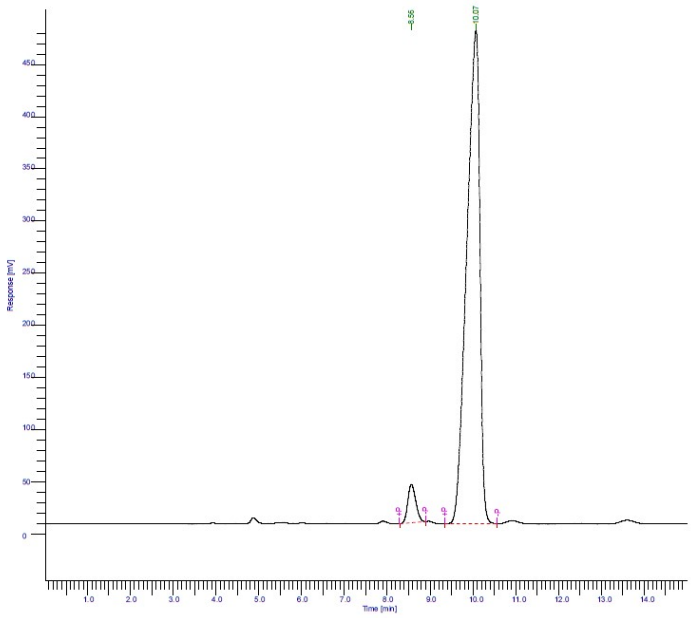
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.431	5322356.26	321685.02	50.25	50.25	BB	16.5452
2	9.988	5270062.81	288202.97	49.75	49.75	*BB	18.2859
		10592419.07	609887.98	100.00	100.00		



(*R*)-**1l** (Table S5, Entry 2; Scheme 3)

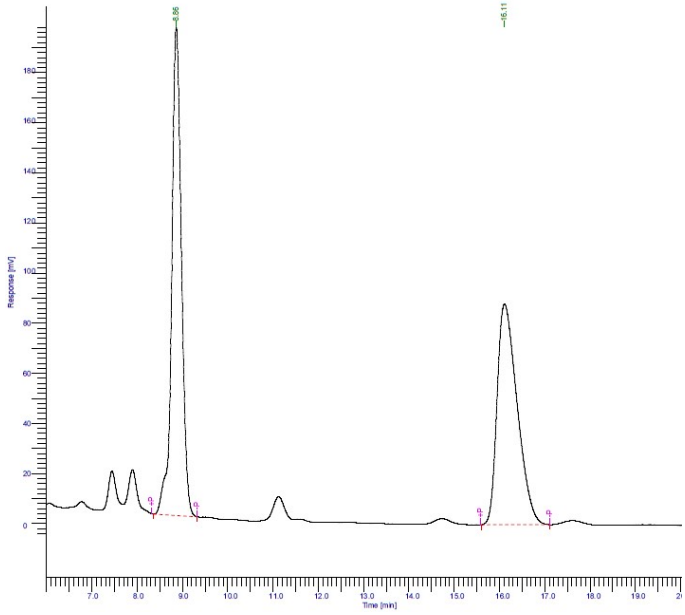
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.564	473851.85	36847.33	4.52	4.52	*BB	12.8599
2	10.073	10014006.61	473229.05	95.48	95.48	*BB	21.1610
		10487858.46	510076.37	100.00	100.00		


8.55
10.07
Response [mV]
Time [min]

1-adamantyl (4-methylphenyl)-*H*-phosphinate (**1m**)

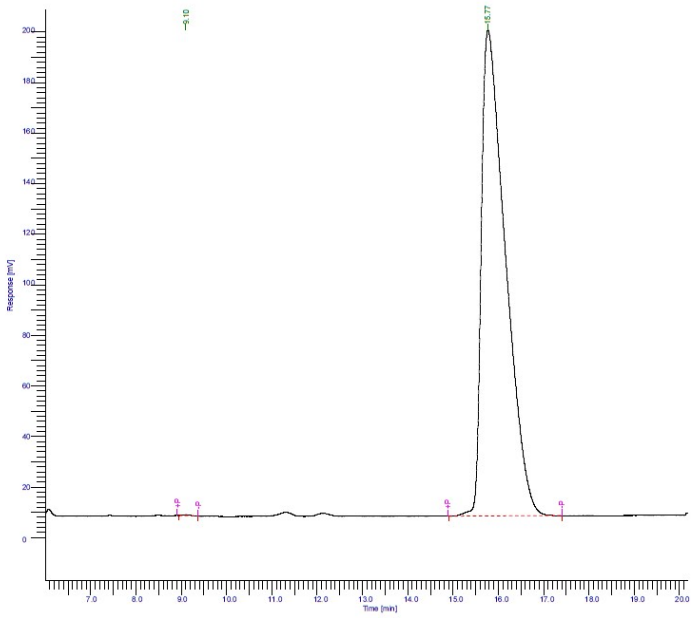
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.861	2895924.29	194936.76	51.66	51.66	*BB	14.8557
2	16.108	2709458.70	88098.88	48.34	48.34	*BB	30.7547
		5605382.99	283035.65	100.00	100.00		



(*R*)-**1m** (Table S5, Entry 3; Scheme 3)

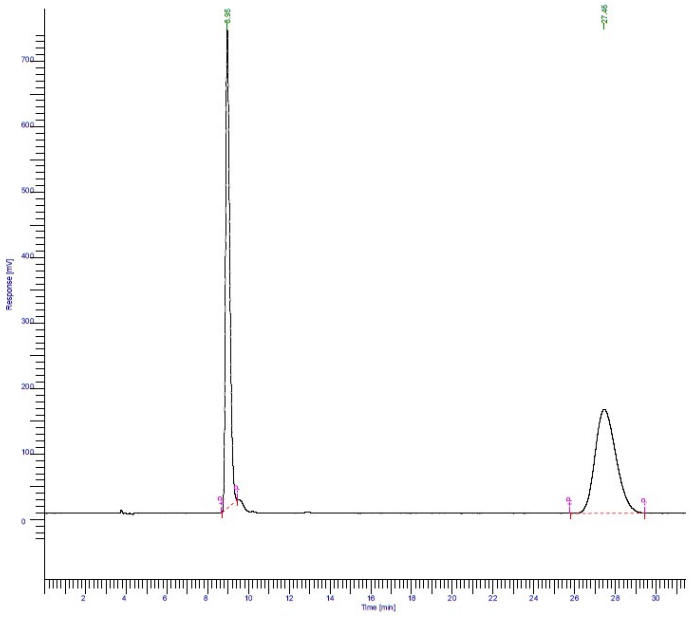
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	9.100	4130.47	349.84	0.06	0.06	*BB	11.8067
2	15.773	7072927.66	192242.14	99.94	99.94	*BB	36.7918
		7077058.12	192591.98	100.00	100.00		


9.10
15.77
Response [mV]
Time [min]

1-adamantyl (4-methoxyphenyl)-*H*-phosphinate (**1n**)

Racemic

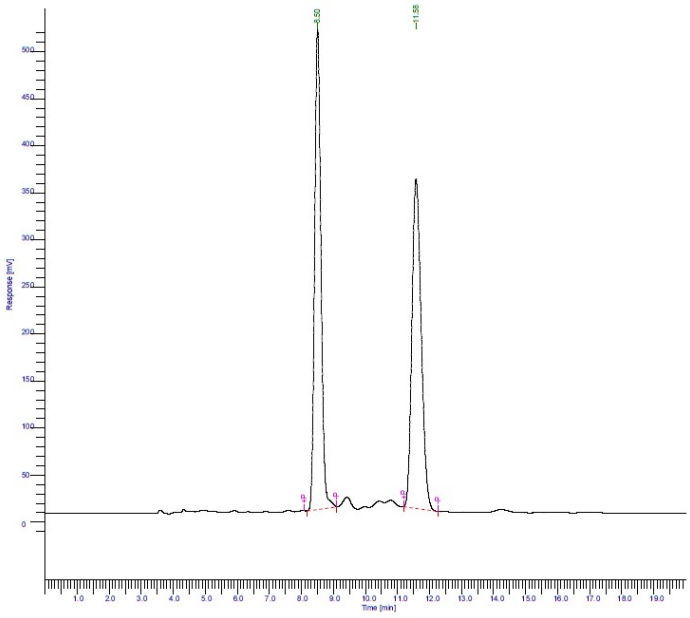
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.952	10323180.41	731715.44	47.74	47.74	*BB	14.1082
2	27.455	11301862.90	158468.88	52.26	52.26	*BB	71.3191
		21625043.31	890184.32	100.00	100.00		



1-adamantyl 1-naphthyl-*H*-phosphinate (**1o**)

Racemic

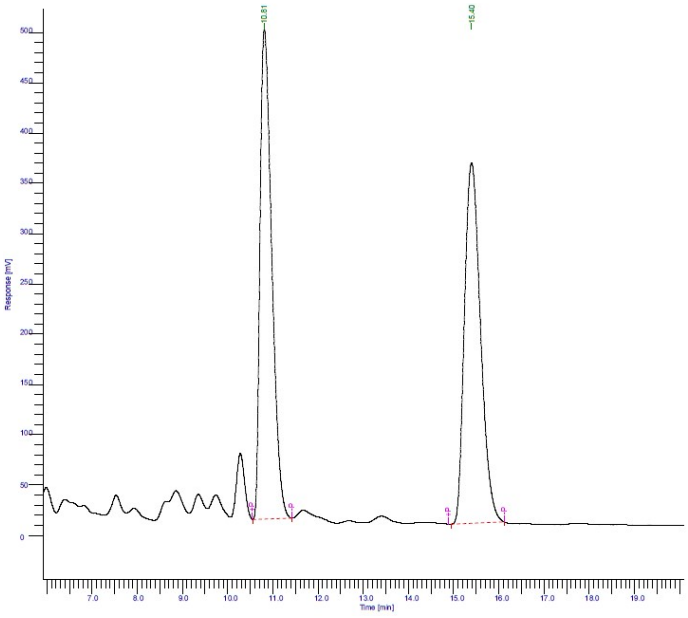
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	8.503	7021550.98	510547.55	49.94	49.94	*BB	13.7530
2	11.577	7037572.45	350385.41	50.06	50.06	*BB	20.0852
		14059123.43	860932.96	100.00	100.00		



(2-methoxylphenyl)-phenylphosphine oxide (**3a**)

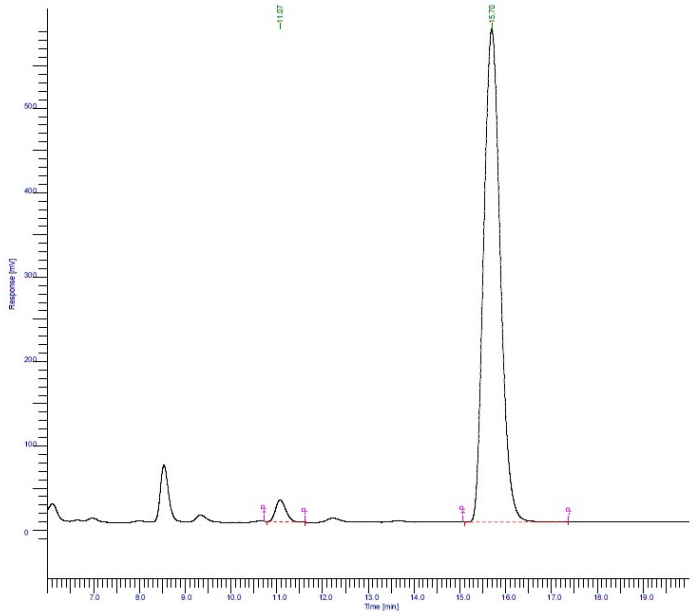
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	10.810	8782304.23	486920.14	49.82	49.82	*BB	18.0364
2	15.395	8846850.67	358610.06	50.18	50.18	*BB	24.6698
		17629154.89	845530.20	100.00	100.00		



(*R*)-**3a** (Scheme 5)

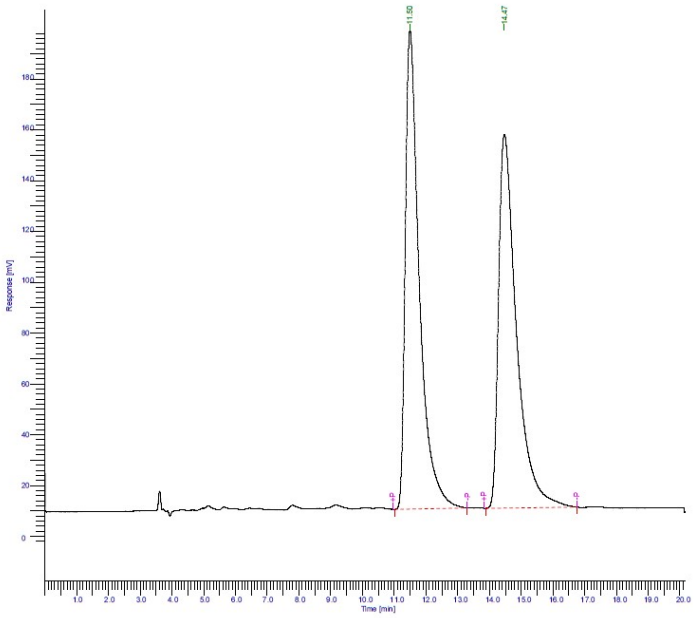
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	11.074	405637.53	25992.47	2.70	2.70	*BB	15.6060
2	15.696	14637766.30	583603.61	97.30	97.30	*BB	25.0817
		15043403.83	609596.08	100.00	100.00		


11.27
15.70
Response [mV]
500
400
300
200
100
0
7.0
8.0
9.0
10.0
11.0
12.0
13.0
14.0
15.0
16.0
17.0
18.0
19.0
Time [min]

(2-methoxyphenyl)-methyl-phenylphosphine oxide (**3b**)

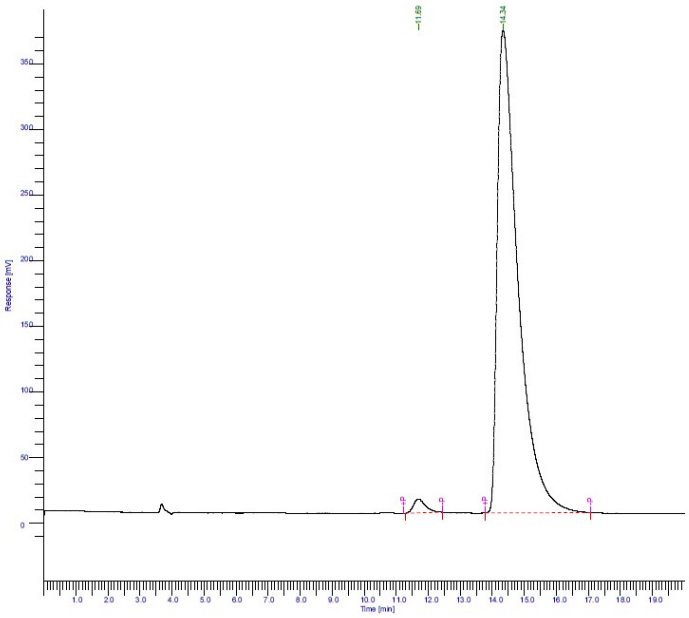
Racemic

Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	11.498	5784253.79	188498.35	50.11	50.11	*BB	30.6860
2	14.471	5758503.18	147231.28	49.89	49.89	*BB	39.1120
		11542756.97	335729.63	100.00	100.00		



(*R*)-**3b** (Scheme 5)

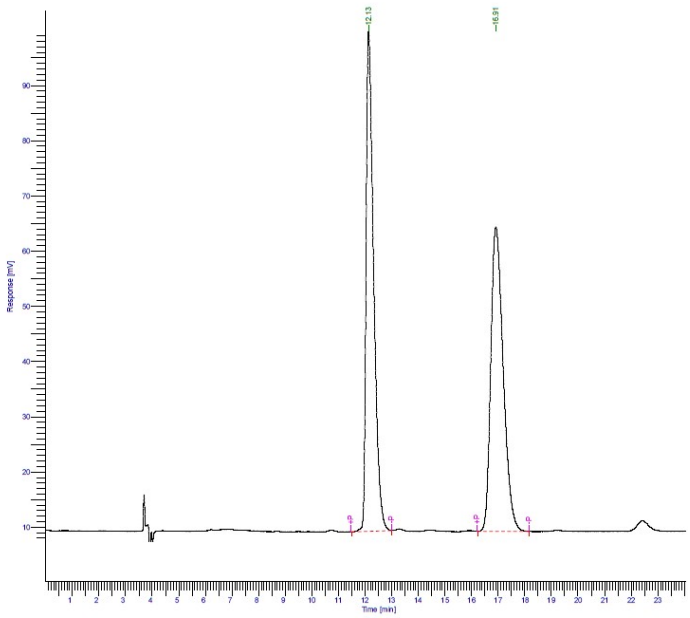
Peak #	Time [min]	Area [μV·s]	Height [μV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	11.693	269526.65	10460.02	1.61	1.61	*BB	25.7673
2	14.336	16429609.92	367707.63	98.39	98.39	*BB	44.6812
		16699136.57	378167.65	100.00	100.00		


11.69
14.34
Response [mV]
Time [min]

c-hexyl-(2-methoxyphenyl)-methylphosphine-oxide (**3c**)

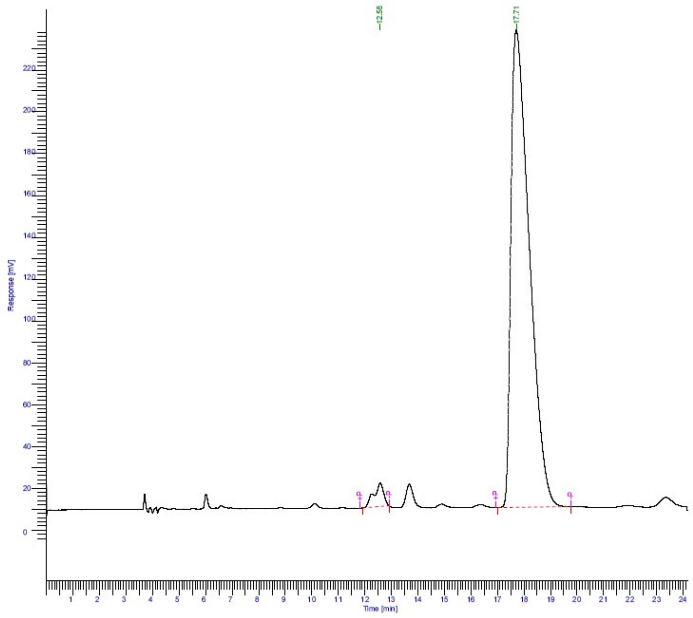
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.132	1776952.09	90585.83	49.94	49.94	*BB	19.6162
2	16.913	1781192.38	55145.41	50.06	50.06	*BB	32.2999
		3558144.48	145731.24	100.00	100.00		



(*R*)-**3c** (Scheme 5)

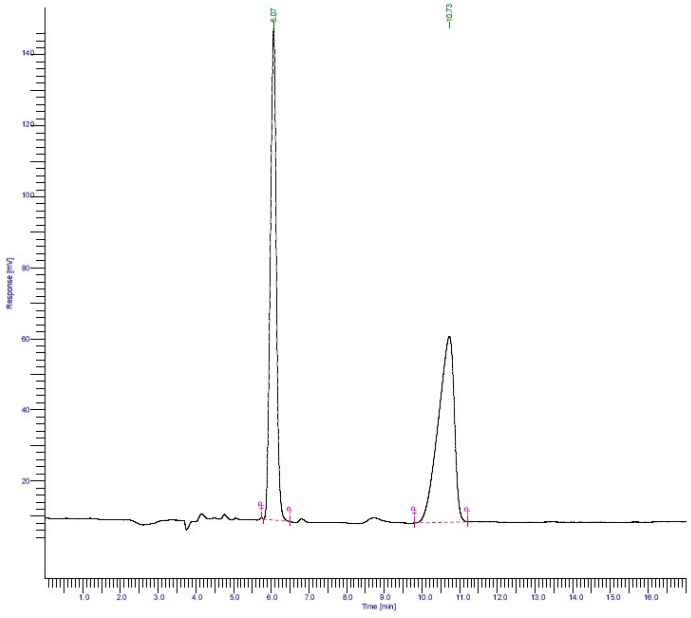
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	12.581	288926.36	11072.72	2.56	2.56	*BB	26.0935
2	17.707	10981744.91	228218.94	97.44	97.44	*BB	48.1193
		11270671.26	239291.66	100.00	100.00		


12.58
17.71
Response [mV]
Time [min]

1-adamantyl-phenylphosphonamidate (**3d**)

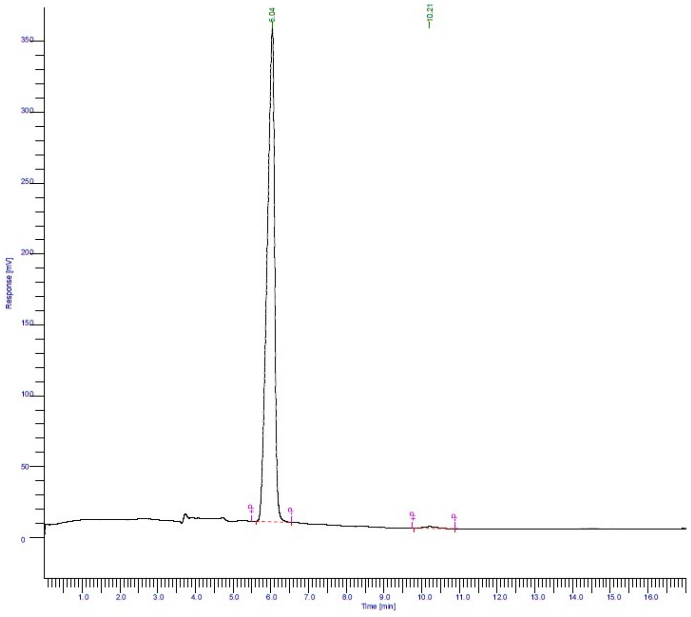
Racemic

Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.065	1525698.74	138581.45	49.64	49.64	*BB	11.0094
2	10.727	1547982.84	52443.44	50.36	50.36	*BB	29.5172
		3073681.58	191024.89	100.00	100.00		



(*R*)-**3d** (Scheme 5)

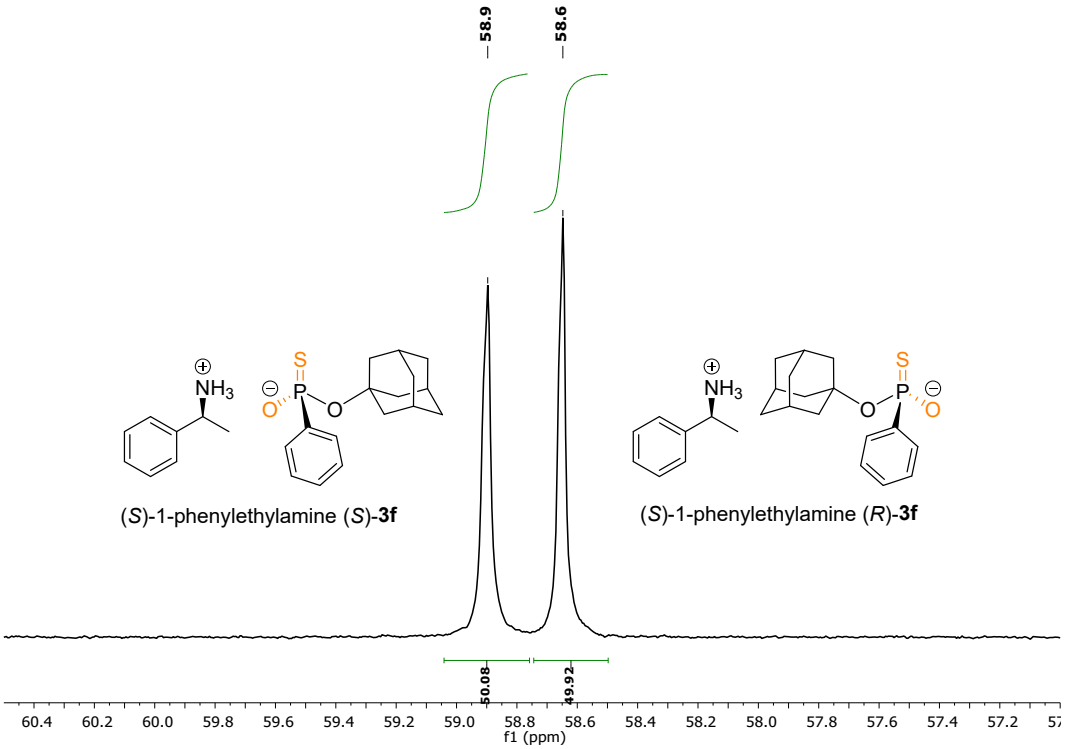
Peak #	Time [min]	Area [µV·s]	Height [µV]	Area [%]	Norm. Area [%]	BL	Area/Height [s]
1	6.040	4802478.93	348279.10	99.35	99.35	*BB	13.7892
2	10.208	31475.38	1296.66	0.65	0.65	*BB	24.2743
		4833954.31	349575.75	100.00	100.00		


6.04
10.21
Response [mV]
Time [min]

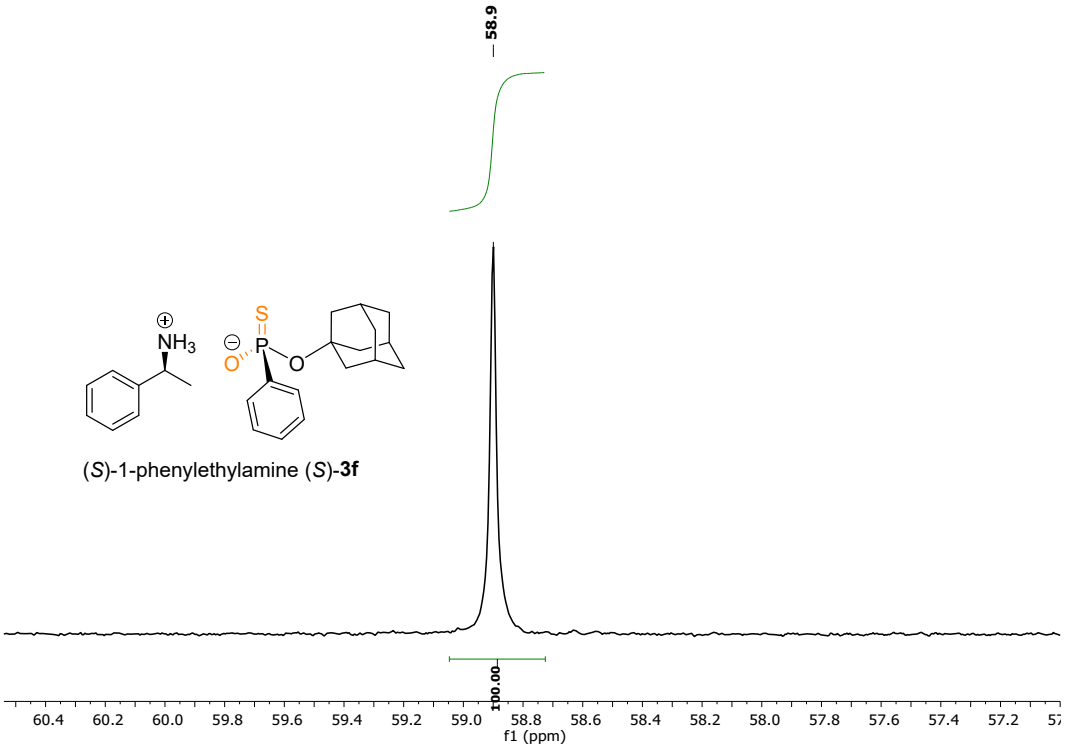
1-adamantyl-phenylphosphonothioic acid (**3f**)

The enantiomeric excess (*ee*) values of **3f** were determined by ^{31}P NMR using 6.2 mg (20 µmol) of the analyte, 3.9 µL (30 µmol) (*S*)-1-phenylethylamine as CSA and 750 µL $CDCl_3$ as solvent.

Racemic **3f** + (*S*)-phenylethylamine



(*S*)-**3f** + (*S*)-phenylethylamine



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