Rhodium-catalyzed enantioselective hydrogenation of (1-arylvinyl)phosphonates with TADDOL-based phosphoramidite P,S ligands

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Supporting Information

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1. General information

^{1}H, ^{13}C, ^{31}P and ^{19}F NMR spectra were recorded on Bruker Avance 400, 600 or Agilent 400-MR spectrometers at ambient temperature; ^{13}C and ^{31}P spectra were ^{1}H decoupled. Chemical shifts are reported on the δ-scale in ppm relative to the solvent ($CDCl_3$: δ_C=77.00; CD_3OD: δ_C=49.00) or the residual solvent peak ($CDCl_3$: δ_H=7.25; CD_3OD: δ_H=3.30) as internal standards, or to external 85% H_3PO_4 (δ_P=0) or $CFCl_3$ (δ_F=0). High resolution mass spectra (HRMS) were measured on the AB Sciex TripleTOF 5600+ spectrometer operated in positive ionization mode using electrospray ionization (ESI).

Optical rotations were measured on a A.KRÜSS Optronic GmbH P8000 polarimeter. Enantiomeric excesses of chiral compounds were determined by HPLC on a Stayer instrument with a UV detector at 220 nm using Daicel Chiralcel OD-H and Daicel Chiralpak AD-H columns (see data for individual compounds for details). Racemic compounds were used for comparison. Preparative column chromatography was carried out using Macherey–Nagel silica gel 60 (0.015–0.04 mm). Analytical thin-layer chromatography (TLC) was performed on aluminum backed plates (Merck, TLC Silica gel 60 F_{254}), spots were visualized using 254 nm ultraviolet light. Melting points were found on an Electrothermal 9100 apparatus in sealed capillaries and are uncorrected.

X-ray Crystal Structure Data were collected on a STOE diffractometer with a Pilatus100K detector, focusing mirror collimation Mo Kα (0.7071Å) radiation, plane graphite monochromator, rotation method mode. STOE X-AREA software was used for cells refinement and data reduction. Data collection and image processing was performed with X-Area 1.67 (STOE & Cie GmbH, Darmstadt, Germany, 2013). Intensity data were scaled with LANA (part of X-Area) in order to minimize differences of intensities of symmetry-equivalent reflections (multi-scan method). Structures were solved and refined with SHELX program.[1] Non-hydrogen atoms were refined using the anisotropic full matrix least-square procedure. Molecular geometry calculations (see Tables S2-12) were performed with the SHELX program, and the molecular graphics were prepared using Mercury software. CCDC 2420815, 2420900, and 2207923 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

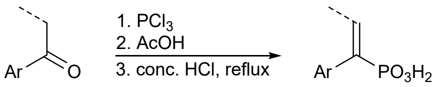
Geometries of vinylphosphonates **3a-r** were optimized using GAUSSIAN16[2] at the B3LYP-D3/6-31+G** level and were considered for calculating the Natural Bond Orbital (NBO) charges,[3] as implemented in the same code using the Gaussian NBO Version 3.1 package.

Dichloromethane (DCM) was distilled over calcium hydride, and 1,2-dimethoxyethane (DME) was distilled over sodium benzophenon ketyl under argon prior to use.

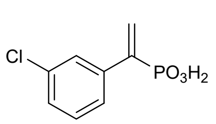
Ligands **L1-16**,[4] $[Rh(COD)_2]BF_4$,[5] dimethyl (1-phenylvinyl)phosphonate (**1**),[6] diethyl (1-phenylvinyl)-phosphonate (**2**),[7] (1-phenylvinyl)phosphonic acid,[8-10] [1-(4-bromophenyl)vinyl]phosphonic acid,[11] [1-(4-chlorophenyl)vinyl]phosphonic acid,[8-10] [1-(4-methylphenyl)vinyl]phosphonic acid,[8-10] [1-(4-isobutylphe-nyl)vinyl]phosphonic acid,[11] [1-(4-diphenyl)vinyl]phosphonic acid,[8] [1-(naphthalen-2-yl)vinyl]phosphonic acid,[8] [1-(naphthalen-1-yl)vinyl]phosphonic acid,[8,9] (*E*)-*N*,*N*-dimethyl-4-(2-nitrovinyl)aniline,[12] (*E*)-1-

methoxy-2-(2-nitrovinyl)benzene,[13] (*E*)-1-methoxy-3-(2-nitrovinyl)benzene,[14,15] (*E*)-1-methoxy-4-(2-nitrovinyl)-benzene,[14,15] (*E*)-2-methoxy-6-(2-nitrovinyl)naphthalene,[15] (*E*)-3-(2-nitrovinyl)-1*H*-indol,[16] (*E*)-(3-nitroallyl)benzene,[15] triisopropyl orthoformate,[17] were obtained as previously described. Other reagents were purchased from commercial suppliers and used as received.

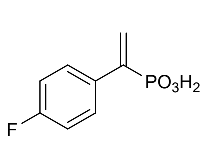
2. Synthesis of (1-arylvinyl)phosphonic acids



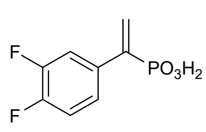
General procedure: Freshly distilled phosphorus trichloride (3.7 ml, 42 mmol, 1.4 equiv.) was slowly added dropwise to the acylated arene (30 mmol, 1 equiv.) under an inert atmosphere. The mixture was stirred for another hour. Glacial acetic acid (5.2 ml, 90 mmol, 3 equiv.) was then added dropwise. The reaction mixture was stirred overnight, then poured onto ice and left for 1 h. The volatile materials were removed on a rotary evaporator at 90°C. The residue was dissolved in boiling concentrated hydrochloric acid and the mixture was refluxed for 3-29 h. The solution was cooled and precipitated solid (1-arylvinyl)phosphonic acid was collected and dried in a vacuum desiccator over NaOH.



[1-(3-Chlorophenyl)vinyl]phosphonic acid. The time of the reflux with conc. HCl was 25 h. The product was obtained as beige flaky crystals in 67% yield; mp 115-117°C, R_f 0.41 (MeOH/$CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 14.4. ^{1}H NMR (400 MHz, CD_3OD, δ): 6.04 (dd, $^2J_{H,H}$=1.4 Hz, $^3J_{H,P}$=43.5 Hz, 1H, *trans*-PC=CH), 6.22 (dd, $^2J_{H,H}$=1.4 Hz, $^3J_{H,P}$=21.5 Hz, 1H, *cis*-PC=CH), 7.31-7.36 (m, 2H, CH_{Ar}), 7.49 (m, 1H, CH_{Ar}), 7.61 (m, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, CD_3OD, δ): 127.13 (d, $^3J_{C,P}$=5.8 Hz, CH_{Ar}), 128.68 (d, $^3J_{C,P}$=5.4 Hz, CH_{Ar}), 129.02 (CH_{Ar}), 130.12 (d, $^2J_{C,P}$=7.0 Hz, H_2C=), 130.87 (CH_{Ar}), 135.17 (CCl_{Ar}), 141.02 (d, $^2J_{CP}$=12.3 Hz, C_{Ar}), 143.43 (d, $^1J_{C,P}$=175.8 Hz, =CP). HRMS (ESI): found 436.9877, calcd. for $[2M + H]^+$ ($C_{16}H_{17}Cl_2O_6P_2$) 436.9872.

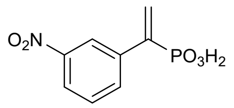


[1-(4-Fluorophenyl)vinyl]phosphonic acid.[11] The time of the reflux with conc. HCl was 10 h. The product was obtained as beige flaky crystals in 58% yield; mp 134°C, R_f 0.34 (MeOH/$CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 15.1 ($^6J_{P,F}$=1.2 Гц). ^{1}H NMR (400 MHz, CD_3OD, δ): 6.00 (br d, $^3J_{H,P}$=44.0 Hz, 1H, *trans*-PC=CH), 6.17 (br d, $^3J_{H,P}$=21.6 Hz, 1H, *cis*-PC=CH), 7.07 (dd, $^3J_{H,H}$=8.8 Hz, $^3J_{H,F}$=8.6 Hz, 2H, CH_{Ar}), 7.59 (ddd, $^3J_{H,H}$=8.8 Hz, $^4J_{H,F}$=5.5 Hz, $^4J_{H,P}$=0.9 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, CD_3OD, δ): 115.98 (d, $^2J_{C,F}$=21.7 Hz, CH_{Ar}), 129.16 (d, $^2J_{C,P}$=7.8 Hz, H_2C=), 130.66 (dd, $^3J_{C,P}$=5.6 Hz, $^3J_{C,F}$=8.1 Hz, CH_{Ar}), 135.17 (dd, $^2J_{C,P}$=12.4 Hz, $^4J_{C,F}$=3.6 Hz, C_{Ar}), 143.43 (d, $^1J_{C,P}$=176.9 Hz, =CP), 164.08 (dd, $^1J_{C,F}$=245.9 Hz, $^5J_{C,P}$=0.7 Hz, CF_{Ar}). ^{19}F NMR (376 MHz, CD_3OD, δ): -116.43 (ddt, $^3J_{H,F}$=8.6 Hz, $^4J_{H,F}$=5.5 Hz, $^6J_{P,F}$=1.2 Hz).

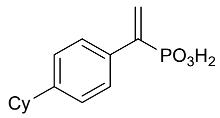


[1-(3,4-Difluorophenyl)vinyl]phosphonic acid. The time of the reflux with conc. HCl was 29 h. The product was obtained as a light grey solid in 56% yield; mp 131-135°C, R_f

0.66 (MeOH/$CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 14.1 ($^{6}J_{P,F}$=1.4 Hz). ^{1}H NMR (400 MHz, CD_3OD, δ): 6.00 (dd, $^{2}J_{H,H}$=1.2 Hz, $^{3}J_{H,P}$=43.3 Hz, 1H, *trans*-PC=CH), 6.21 (dd, $^{2}J_{H,H}$=1.2 Hz, $^{3}J_{H,P}$=21.5 Hz, 1H, *cis*-PC=CH), 7.23 (ddd, $^{3}J_{H,H}$=8.6 Hz, $^{3}J_{H,F}$=10.4 Hz, $^{4}J_{H,F}$=8.5 Hz, 1H, CH_{Ar}), 7.37 (ddddd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,H}$=2.1 Hz, $^{4}J_{H,P}$=1.3 Hz, $^{4}J_{H,F}$=4.1 Hz, $^{5}J_{H,F}$=1.5 Hz, 1H, CH_{Ar}), 7.51 (dddd, $^{4}J_{H,H}$=2.1 Hz, $^{4}J_{H,P}$=1.3 Hz, $^{3}J_{H,F}$=11.8 Hz, $^{4}J_{H,F}$=7.8 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, CD_3OD, δ): 117.74 (dd, $^{3}J_{C,P}$=5.4 Hz, $^{2}J_{C,F}$=18.5 Hz, CH_{Ar}), 118.17 (d, $^{2}J_{C,F}$=17.5 Hz, CH_{Ar}), 125.39 (ddd, $^{3}J_{C,P}$=6.2 Hz, $^{3}J_{C,F}$=6.2 Hz, $^{4}J_{C,F}$=3.6 Hz, CH_{Ar}), 130.00 (d, $^{2}J_{C,P}$=7.4 Hz, H_2C=), 136.26 (ddd, $^{2}J_{C,P}$=12.8 Hz, $^{3}J_{C,F}$=6.3 Hz, $^{4}J_{C,F}$=4.0 Hz, C_{Ar}), 142.61 (d, $^{1}J_{C,P}$=176.9 Hz, =CP), 151.11 (dd, $^{1}J_{C,F}$=246.0 Hz, $^{2}J_{C,F}$=12.6 Hz, CF_{Ar}), 151.40 (ddd, $^{1}J_{C,F}$=247.6 Hz, $^{2}J_{C,F}$=12.5 Hz, $^{5}J_{C,P}$=1.1 Hz, CF_{Ar}). ^{19}F NMR (376 MHz, CD_3OD, δ): -141.63 (ddddd, $^{3}J_{F,F}$=20.8 Hz, $^{3}J_{H,F}$=10.4 Hz, $^{4}J_{H,F}$=7.8 Hz, $^{4}J_{H,F}$=4.1 Hz, $^{6}J_{P,F}$=1.4 Hz, C(4′)F), -140.61 (dddd, $^{3}J_{F,F}$=20.8 Hz, $^{3}J_{H,F}$=11.8 Hz, $^{4}J_{H,F}$=8.5 Hz, $^{5}J_{H,F}$=1.5 Hz, C(3′)F). HRMS (ESI): found 221.0171, calcd. for $[M + H]^+$ ($C_8H_7O_3F_2P$) 221.0174.

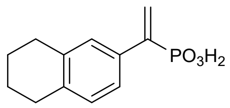


[1-(3-Nitrophenyl)vinyl]phosphonic acid. PCl_3 was added at 80°C, the resulting mixture was stirred at 80°C for 30 min, then cooled to 45°C. After the addition of AcOH, the reaction mixture was stirred at 45°C for 5 h, then left overnight at room temperature. The time of the reflux with conc. HCl was 3 h. After the removal of volatiles, the residue was diluted with toluene (100 ml) and the mixture was refluxed with a Dean-Stark trap for 15 h. The solvent was removed by rotary evaporation and the residue was recrystallized twice from water (the first time using hot filtration). The product was obtained as beige flaky crystals in 54% yield; mp 150-152°C, R_f 0.28 (MeOH/$CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 13.4. ^{1}H NMR (400 MHz, CD_3OD, δ): 6.16 (dd, $^{2}J_{H,H}$=1.2 Hz, $^{3}J_{H,P}$=43.1 Hz, 1H, *trans*-PC=CH), 6.31 (dd, $^{2}J_{H,H}$=1.2 Hz, $^{3}J_{H,P}$=21.5 Hz, 1H, *cis*-PC=CH), 7.61 (dddd, 1H, $^{3}J_{H,H}$=8.3 Hz, $^{3}J_{H,H}$=7.8 Hz, $^{5}J_{H,H}$=0.4 Hz, $^{5}J_{H,P}$=0.8 Hz, 1H, CH_{Ar}), 7.96 (dddd, $^{3}J_{H,H}$=7.8 Hz, $^{4}J_{H,H}$=1.7 Hz, $^{4}J_{H,H}$=0.9 Hz, $^{4}J_{H,P}$=1.5 Hz, 1H, CH_{Ar}), 8.20 (dddd, $^{3}J_{H,H}$=8.3 Hz, $^{4}J_{H,H}$=2.3 Hz, $^{4}J_{H,H}$=0.9 Hz, $^{6}J_{H,P}$=0.9 Hz, 1H, CH_{Ar}), 8.48 (dddd, $^{4}J_{H,H}$=2.3 Hz, $^{4}J_{H,H}$=1.7 Hz, $^{5}J_{H,H}$=0.4 Hz, $^{4}J_{H,P}$=1.3 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, CD_3OD, δ): 123.49 (d, $^{3}J_{C,P}$=5.3 Hz, CH_{Ar}), 123.75 (d, $^{5}J_{C,P}$=0.8 Hz, CH_{Ar}), 130.67 (CH_{Ar}), 131.07 (d, $^{2}J_{C,P}$=7.2 Hz, H_2C=), 134.88 (d, $^{3}J_{C,P}$=5.6 Hz, CH_{Ar}), 140.87 (d, $^{2}J_{C,P}$=12.6 Hz, C_{Ar}), 143.03 (d, $^{3}J_{C,P}$=177.1 Hz, =CP), 149.62 (CN_{Ar}). HRMS (ESI): found 230.0216, calcd. for $[M + H]^+$ ($C_8H_9NO_5P$) 230.0213.

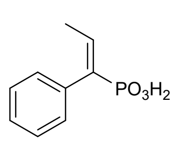


[1-(4-Cyclohexylphenyl)vinyl]phosphonic acid. PCl_3 was added at 80°C, the resulting mixture was stirred at 80°C for 1 h, then cooled to 30°C. After the addition of AcOH, the reaction mixture was stirred at 30°C for 5 h, then left overnight at room temperature. The time of the reflux with conc. HCl was 5 h. The product was obtained as a white solid in 70% yield; mp 173°C, R_f 0.33 (MeOH/$CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 15.7. ^{1}H NMR (400 MHz, CD_3OD, δ): 1.30 (m, 1H, $CH_{2\ Cy}$), 1.36-1.50 (m, 4H, $CH_{2\ Cy}$), 1.75 (m, 1H, $CH_{2\ Cy}$), 1.82-1.85 (m, 4H, $CH_{2\ Cy}$), 2.50 (m, 1H, $CH_{\ Cy}$), 5.98 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=44.4 Hz, 1H, *trans*-PC=CH), 6.13 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=21.7 Hz, 1H, *cis*-PC=CH), 7.19 (d, $^{3}J_{H,H}$=8.1 Hz, 2H, CH_{Ar}), 7.49 (dd, $^{3}J_{H,H}$=8.1 Hz, $^{4}J_{H,P}$=1.2 Hz, 2H,

CH_{Ar}). ^{13}C NMR (101 MHz, CD_3OD, δ): 27.24 ($CH_{2\ Cy}$), 27.97 ($2CH_{2\ Cy}$), 35.62 ($2CH_{2\ Cy}$), 45.71 (CH_{Cy}), 127.75 (CH_{Ar}), 128.34 (d, $^2J_{C,P}$=7.9 Hz, H_2C=), 128.65 (d, $^3J_{C,P}$=5.7 Hz, CH_{Ar}), 136.38 (d, $^2J_{C,P}$=11.9 Hz, C_{Ar}), 144.25 (d, $^1J_{C,P}$=174.3 Hz, =CP), 149.24 (C_{Ar}). HRMS (ESI): found 267.1147, calcd. for $[M + H]^+$ ($C_8H_9NO_5P$) 267.1145.



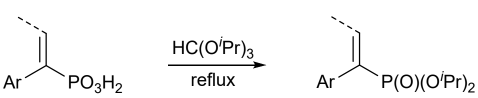
[1-(5,6,7,8-Tetrahydronaphthalen-2-yl)vinyl]phosphonic. PCl_3 was added at 80°C, the resulting mixture was stirred at 80°C for 1 h, then cooled to 35°C. After the addition of AcOH, the reaction mixture was stirred at 35°C for 2.5 h, then left overnight at room temperature. The time of the reflux with conc. HCl was 3 h. The product was obtained as a grayish solid in 74% yield after recrystallization from toluene; mp 188°C, R_f 0.31 ($MeOH/CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 15.9. ^1H NMR (400 MHz, CD_3OD, δ): 1.77 (m, 4H, CH_2), 2.73 (m, 4H, CH_2), 5.95 (dd, $^2J_{H,H}$=1.6 Hz, $^3J_{H,P}$=44.6 Hz, 1H, *trans*-PC=CH), 6.11 (dd, $^2J_{H,H}$=1.6 Hz, $^3J_{H,P}$=21.8 Hz, 1H, *cis*-PC=CH), 6.99 (d, $^3J_{H,H}$=8.4 Hz, 1H, CH_{Ar}) 7.25-7.28 (m, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, CD_3OD, δ): 24.37 ($2CH_2$), 30.10 (CH_2), 30.41 (CH_2), 125.78 (d, $^3J_{C,P}$=5.9 Hz, CH_{Ar}), 128.12 (d, $^2J_{C,P}$=7.9 Hz, H_2C=), 129.19 (d, $^3J_{C,P}$=5.6 Hz, CH_{Ar}), 129.94 (CH_{Ar}), 135.90 (d, $^1J_{C,P}$=12.0 Hz, C_{Ar}), 137.92 (C_{Ar}), 138.11 (C_{Ar}), 144.22 (d, $^1J_{C,P}$=173.4 Hz, =CP). HRMS (ESI): found 239.0834, calcd. for $[M + H]^+$ ($C_{12}H_{16}O_3P$) 239.0832.



(*E*)-(1-Phenylprop-1-en-1-yl)phosphonic acid.[18] The time of the reflux with conc. HCl was 5 h. The mixture of (*E*)- and (*Z*)-isomers (in a ratio of 65% *E* to 35% *Z*) was collected as a white solid in 88% yield. (*E*)-Isomer was isolated by fractional crystallization from chloroform; mp 174°C, R_f 0.74 ($MeOH/CHCl_3$ 2 : 1). ^{31}P NMR (162 MHz, CD_3OD, δ): 16.5. ^1H NMR (400 MHz, CD_3OD, δ): 1.65 (dd, $^3J_{H,H}$=6.9 Hz, $^4J_{H,P}$=3.3 Hz, 3H, CH_3), 6.81 (dq, $^3J_{H,H}$=6.9 Hz, $^3J_{H,P}$=22.6 Hz, 1H, =CH), 7.25 (m, 2H, CH_{Ph}), 7.29 (m, 1H, CH_{Ph}), 7.36 (m, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, CD_3OD, δ): 15.49 (d, $^3J_{C,P}$=18.3 Hz, CH_3), 128.36 (CH_{Ph}), 129.22 (CH_{Ph}), 130.65 (CH_{Ph}), 136.97 (d, $^2J_{C,P}$=10.6 Hz, C_{Ph}), 137.08 (d, $^1J_{C,P}$=180.8 Hz, =CP), 141.04 (d, $^2J_{C,P}$=9.2 Hz, =CHMe).

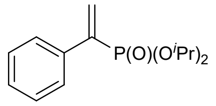
3. Synthesis of diisopropyl (1-arylvinyl)phosphonates

Method A

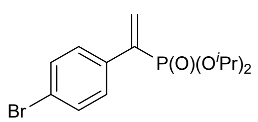


3a-f, h, l-q, s, v

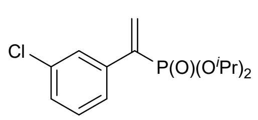
General procedure: A mixture of (1-arylvinyl)phosphonic acid (4 mmol, 1 equiv.) and triisopropyl orthoformate (2.7 ml, 12 mmol, 3 equiv.) was slowly heated under an inert atmosphere, isopropyl formate and propanol-2 being allowed to distil off. After the removal of volatiles, the reaction mixture was heated at 150°C for 3-12 h until the reaction was complete (TLC control). The excess triisopropyl orthoformate was removed under reduced pressure, and the residue was purified by vacuum distillation or by column chromatography to afford pure diisopropyl 1-arylvinylphosphonate as a viscous oil.



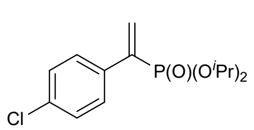
Diisopropyl (1-phenylvinyl)phosphonate (3a). The synthesis was carried out on a 16 mmol scale, the reaction time was 8 h. The product was isolated by vacuum distillation as a colorless viscous oil in 65% yield; bp 114-117°C/0.6 torr. ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.5. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.69 (m, 2H, OCH), 6.12 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=45.6 Hz, 1H, *trans*-PC=CH), 6.33 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.28-7.36 (m, 3H, CH_{Ph}), 7.54 (m, $^{3}J_{H,H}$=8.0 Hz, $^{4}J_{H,H}$=1.3 Hz, $^{4}J_{H,P}$=1.3 Hz, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.54 (d, $^{3}J_{C,P}$=5.0 Hz, CH_3), 23.96 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 70.84 (d, $^{2}J_{C,P}$=5.9 Hz, OCH), 127.43 (d, $^{3}J_{C,P}$=5.7 Hz, CH_{Ph}), 128.16 (CH_{Ph}), 127.97 (d, $^{5}J_{C,P}$=1.1 Hz, CH_{Ph}), 130.99 (d, $^{2}J_{C,P}$=8.0 Hz, H_2C=), 136.91 (d, $^{2}J_{C,P}$=11.7 Hz, C_{Ph}), 140.90 (d, $^{1}J_{C,P}$=175.3 Hz, =CP). HRMS (ESI): found 269.1302, calcd. for $[M + H]^+$ ($C_{14}H_{22}O_3P$) 269.1301.



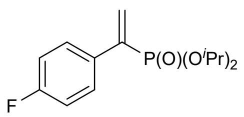
Diisopropyl [1-(4-bromophenyl)vinyl]phosphonate (3b). The reaction time was 10 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 83% yield; R_f 0.25 (EtOAc/petroleum ether 1 : 2), R_f 0.29 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 14.6. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.13 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.24 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.62 (m, 2H, OCH), 6.03 (dd, $^{2}J_{H,H}$=1.5 Hz, $^{3}J_{H,P}$=45.2 Hz, 1H, *trans*-PC=CH), 6.26 (dd, $^{2}J_{H,H}$=1.5 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.35 (dd, $^{3}J_{AB}$=8.9 Hz, $^{4}J_{H,P}$=1.0 Hz, 2H, CH_{Ar}), 7.38 (d, $^{3}J_{AB}$=8.5 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.39 (d, $^{3}J_{C,P}$=4.8 Hz, CH_3), 23.76 (d, $^{3}J_{C,P}$=3.1 Hz, CH_3), 70.76 (d, $^{2}J_{C,P}$=5.9 Hz, OCH), 122.05 (CBr_{Ar}), 128.89 (d, $^{3}J_{C,P}$=5.9 Hz, CH_{Ar}), 131.00 (d, $^{2}J_{C,P}$=8.2 Hz, H_2C=), 131.12 (CH_{Ar}), 135.60 (d, $^{2}J_{C,P}$=11.9 Hz, C_{Ar}), 139.76 (d, $^{1}J_{C,P}$=176.9 Hz, =CP). HRMS (ESI): found 347.0409, calcd. for $[M + H]^+$ ($C_{14}H_{21}BrO_3P$) 347.0406.



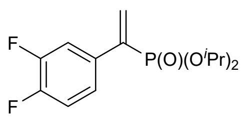
Diisopropyl [1-(3-chlorophenyl)vinyl]phosphonate (3c). The reaction time was 10 h. The product was isolated by column chromatography on silica gel (*i*-PrOH/petroleum ether 1 : 15) as a colorless viscous oil in 82% yield; R_f 0.27 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 14.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.19 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.30 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.67 (m, 2H, OCH), 6.09 (dd, $^{2}J_{H,H}$=1.5 Hz, $^{3}J_{H,P}$=45.0 Hz, 1H, *trans*-PC=CH), 6.33 (dd, $^{2}J_{H,H}$=1.5 Hz, $^{3}J_{H,P}$=21.8 Hz, 1H, *cis*-PC=CH), 7.23 (t, $^{3}J_{H,H}$=8.0 Hz, CH_{Ar}), 7.25 (m, $^{3}J_{H,H}$=8.0 Hz, CH_{Ar}), 7.40 (m, CH_{Ar}), 7.50 (m, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.63 (d, $^{3}J_{C,P}$=4.9 Hz, CH_3) 23.98 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 71.12 (d, $^{2}J_{C,P}$=6.0 Hz, OCH), 125.74 (d, $^{3}J_{C,P}$=5.3 Hz, CH_{Ar}), 127.58 (d, $^{3}J_{C,P}$=6.0 Hz, CH_{Ar}), 128.07 (CH_{Ar}), 129.45 (CH_{Ar}), 131.80 (d, $^{2}J_{C,P}$=7.8 Hz, H_2C=), 134.09 (CCl_{Ar}), 138.77 (d, $^{2}J_{C,P}$=11.9 Hz, C_{Ar}), 140.04 (d, $^{1}J_{C,P}$=177.4 Hz, =CP). HRMS (ESI): found 303.0913, calcd. for $[M + H]^+$ ($C_{14}H_{21}ClO_3P$) 303.0911.



Diisopropyl [1-(4-chlorophenyl)vinyl]phosphonate (3d). The reaction time was 4 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 87% yield; R_f 0.21 (EtOAc/petroleum ether 1 : 2), R_f 0.28 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 14.9. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.30 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 4.67 (m, 2H, OCH), 6.08 (dd, $^2J_{H,H}$=1.4 Hz, $^3J_{H,P}$=45.2 Hz, 1H, *trans*-PC=CH), 6.31 (dd, $^2J_{H,H}$=1.4 Hz, $^3J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.29 (d, $^3J_{AB}$=8.5 Hz, 2H, CH_{Ar}), 7.46 (dd, $^3J_{AB}$=8.5 Hz, $^4J_{H,P}$=1.2 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.64 (d, $^3J_{C,P}$=5.2 Hz, CH_3), 24.01 (d, $^3J_{C,P}$=3.6 Hz, CH_3), 71.06 (d, $^2J_{C,P}$=5.9 Hz, OCH), 128.43 (CH_{Ar}), 128.83 (d, $^3J_{C,P}$=5.7 Hz, CH_{Ar}), 131.25 (d, $^2J_{C,P}$=7.6 Hz, H_2C=), 134.08 (CCl_{Ar}), 135.40 (d, $^2J_{C,P}$=11.6 Hz, C_{Ar}), 139.97 (d, $^1J_{C,P}$=176.9 Hz, =CP). HRMS (ESI): found 303.0909, calcd. for $[M + H]^+$ ($C_{14}H_{21}ClO_3P$) 303.0911.

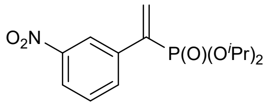


Diisopropyl [1-(4-fluorophenyl)vinyl]phosphonate (3e). The reaction time was 9 h. The product was isolated by column chromatography on silica gel (6-7 vol.% *i*-PrOH in petroleum ether) as a colorless viscous oil in 61% yield; R_f 0.27 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.1 ($^6J_{P,F}$=1.7 Гц). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.19 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 4.69 (m, 2H, OCH), 6.07 (dd, $^2J_{H,H}$=1.2 Hz, $^3J_{H,P}$=45.4 Hz, 1H, *trans*-PC=CH), 6.30 (dd, $^2J_{H,H}$=1.2 Hz, $^3J_{H,P}$=21.8 Hz, 1H, *cis*-PC=CH), 7.02 (dd, $^3J_{H,H}$=8.9 Hz, $^3J_{H,F}$=8.4 Hz, 2H, CH_{Ar}), 7.52 (ddd, $^3J_{H,H}$=8.9 Hz, $^4J_{H,P}$=1.1 Hz, $^4J_{H,F}$=5.4 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.50 (d, $^3J_{C,P}$=5.3 Hz, CH_3), 23.89 (d, $^3J_{C,P}$=3.3 Hz, CH_3), 71.90 (d, $^2J_{C,P}$=5.9 Hz, OCH), 115.05 (d, $^2J_{C,F}$=21.5 Hz, CH_{Ar}), 129.18 (dd, $^3J_{C,P}$=5.5 Hz, $^3J_{C,F}$=8.0 Hz, CH_{Ar}), 130.71 (d, $^2J_{C,P}$=7.7 Hz, H_2C=), 132.88 (dd, $^2J_{C,P}$=12.2 Hz, $^4J_{C,F}$=3.2 Hz, C_{Ar}), 139.87 (d, $^1J_{C,P}$=176.7 Hz, =CP), 162.53 (d, $^1J_{C,F}$=247.7 Hz, CF_{Ar}). ^{19}F NMR (376 MHz, $CDCl_3$, δ): -113.96 (dtt, $^3J_{H,F}$=8.4 Hz, $^4J_{H,F}$=5.4 Hz, $^6J_{P,F}$=1.7 Hz). HRMS (ESI): found 287.1206, calcd. for $[M + H]^+$ ($C_{14}H_{21}FO_3P$) 287.1207.

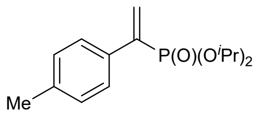


Diisopropyl [1-(3,4-difluorophenyl)vinyl]phosphonate (3f). The reaction time was 8 h. The product was isolated by column chromatography on silica gel (20–33 vol.% EtOAc in petroleum ether) as a colorless viscous oil in 90% yield; R_f 0.30 (EtOAc/petroleum ether 1 : 2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 14.4 ($^6J_{P,F}$=1.7 Гц). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.21 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 4.70 (m, 2H, OCH), 6.08 (dd, $^2J_{H,H}$=1.3 Hz, $^3J_{H,P}$=44.8 Hz, 1H, *trans*-PC=CH), 6.32 (dd, $^2J_{H,H}$=1.3 Hz, $^3J_{H,P}$=21.7 Hz, 1H, *cis*-PC=CH), 7.11 (dddd, $^3J_{H,H}$=8.5 Hz, $^5J_{H,P}$=0.7 Hz, $^3J_{H,F}$=10.1 Hz, $^4J_{H,F}$=8.3 Hz, 1H, CH_{Ar}) 7.26 (ddddd, $^3J_{H,H}$=8.5 Hz, $^4J_{H,H}$=2.2 Hz, $^4J_{H,P}$=1.6 Hz, $^4J_{H,F}$=4.2 Hz, $^5J_{H,F}$=1.1 Hz, 1H, CH_{Ar}), 7.39 (dddd, $^4J_{H,H}$=2.2 Hz, $^4J_{H,P}$=1.2 Hz, $^3J_{H,F}$=11.6 Hz, $^4J_{H,F}$=7.6 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.56 (d, $^3J_{C,P}$=4.9 Hz), 23.90 (d, $^3J_{C,P}$=3.9 Hz, CH_3), 71.14 (d, $^2J_{C,P}$=5.9 Hz, OCH), 116.59 (dd, $^3J_{C,P}$=5.5 Hz, $^2J_{C,F}$=18.4 Hz, CH_{Ar}), 116.99 (d, $^2J_{C,F}$=17.3 Hz, CH_{Ar}), 123.71 (ddd, $^3J_{C,P}$=6.1 Hz, $^3J_{C,F}$=6.1 Hz, $^4J_{C,F}$=3.6 Hz, CH_{Ar}), 131.45 (dd, $^2J_{C,P}$=7.8 Hz, $J_{C,F}$=0.9 Hz, H_2C=), 133.86 (ddd, $^2J_{C,P}$=12.2 Hz, $^3J_{C,F}$=6.2 Hz, $^4J_{C,F}$=4.1 Hz, C_{Ar}), 139.27 (ddd, $^1J_{C,P}$=178.3 Hz, $^4J_{C,F}$=1.5 Hz, $^5J_{C,F}$=0.9 Hz, =CP), 149.78 (dd, $^1J_{C,F}$=247.6 Hz, $^2J_{C,F}$=12.4 Hz, CF_{Ar}), 150.12

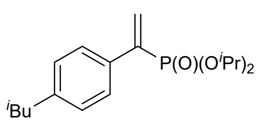
(ddd, $^5J_{C,P}$=1.1 Hz, $^1J_{C,F}$=249.5 Hz, $^2J_{C,F}$=12.4 Hz, CF_{Ar}). ^{19}F NMR (376 MHz, $CDCl_3$, δ): -138.38 (ddddd, $^3J_{F,F}$=21.4 Hz, $^3J_{H,F}$=10.1 Hz, $^4J_{H,F}$=7.6 Hz, $^4J_{H,F}$=4.2 Hz, $^6J_{P,F}$=1.7 Hz, C(4′)F), -137.53 (dddd, $^3J_{F,F}$=21.4 Hz, $^3J_{H,F}$=11.6 Hz, $^4J_{H,F}$=8.3 Hz, $^5J_{H,F}$=1.1 Hz, C(3′)F). HRMS (ESI): found 305.1109, calcd. for $[M + H]^+$ ($C_{14}H_{20}F_2O_3P$) 305.1113.



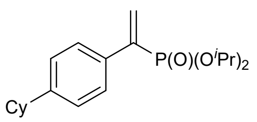
Diisopropyl [1-(3-nitrophenyl)vinyl]phosphonate (3h). The reaction time was 12 h. The product was isolated by column chromatography on silica gel (*i*-PrOH/petroleum ether 1 : 15) as a yellowish viscous oil in 78% yield; R_f 0.24 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 13.9. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.21 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 4.72 (m, 2H, OCH), 6.20 (dd, $^2J_{H,H}$=1.1 Hz, $^3J_{H,P}$=44.6 Hz, 1H, *trans*-PC=CH), 6.44 (dd, $^2J_{H,H}$=1.1 Hz, $^3J_{H,P}$=21.8 Hz, 1H, *cis*-PC=CH), 7.51 (br dd, $^3J_{H,H}$=8.2 Hz, $^3J_{H,H}$=7.8 Hz, 1H, CH_{Ar}), 7.86 (dddd, $^3J_{H,H}$=7.8 Hz, $^4J_{H,H}$=1.7 Hz, $^4J_{H,H}$=0.9 Hz, $^4J_{H,P}$=1.5 Hz, 1H, CH_{Ar}), 8.15 (dddd, $^3J_{H,H}$=8.2 Hz, $^4J_{H,H}$=2.2 Hz, $^4J_{H,H}$=0.9 Hz, $^6J_{H,P}$=0.9 Hz, 1H, CH_{Ar}), 8.40 (ddd, $^4J_{H,H}$=2.2 Hz, $^4J_{H,H}$=1.7 Hz, $^4J_{H,P}$=1.2 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.69 (d, $^3J_{C,P}$=4.8 Hz, CH_3) 23.97 (d, $^3J_{C,P}$=4.0 Hz, CH_3), 71.51 (d, $^2J_{C,P}$=6.1 Hz, OCH), 122.49 (d, $^3J_{C,P}$=5.7 Hz, CH_{Ar}), 122.85 (d, $^5J_{C,P}$=0.9 Hz, CH_{Ar}), 129.27 (CH_{Ar}), 132.87 (d, $^2J_{C,P}$=7.6 Hz, H_2C=), 133.50 (d, $^3J_{C,P}$=5.4 Hz, CH_{Ar}), 138.67 (d, $^2J_{C,P}$=12.1 Hz, CH_{Ar}), 139.43 (d, $^1J_{C,P}$=179.6 Hz, =CP), 148.16 (CN_{Ar}). HRMS (ESI): found 314.1153, calcd. for $[M + H]^+$ ($C_{14}H_{21}NO_5P$) 314.1152.



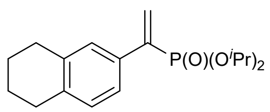
Diisopropyl [1-(4-methylphenyl)vinyl]phosphonate (3l). The reaction time was 10 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 90% yield; R_f 0.36 (EtOAc/petroleum ether 1 : 2), R_f 0.23 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.8. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.31 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 2.34 (s, 3H, CH_3), 4.68 (m, 2H, OCH), 6.10 (dd, $^2J_{H,H}$=1.7 Hz, $^3J_{H,P}$=45.7 Hz, 1H, *trans*-PC=CH), 6.29 (dd, $^2J_{H,H}$=1.7 Hz, $^3J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.13 (d, $^3J_{AB}$=8.0 Hz, 2H, CH_{Ar}), 7.43 (dd, $^3J_{AB}$=8.0 Hz, $^4J_{H,P}$=1.1 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 20.86 (CH_3), 23.39 (d, $^3J_{C,P}$=5.0 Hz, CH_3) 23.81 (d, $^3J_{C,P}$=3.8 Hz, CH_3), 70.55 (d, $^2J_{C,P}$=5.8 Hz, OCH), 127.12 (d, $^3J_{C,P}$=5.8 Hz, CH_{Ar}), 128.70 (CH_{Ar}), 130.02 (d, $^2J_{C,P}$=8.3 Hz, H_2C=), 133.75 (d, $^2J_{C,P}$=11.7 Hz, C_{Ar}), 137.61 (d, $^5J_{C,P}$=1.0 Hz, CMe_{Ar}), 140.45 (d, $^1J_{C,P}$=174.6 Hz, =CP). HRMS (ESI): found 283.1454, calcd. for $[M + H]^+$ ($C_{15}H_{24}O_3P$) 283.1458.



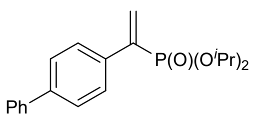
Diisopropyl [1-(4-isobuthylphenyl)vinyl]phosphonate (3m). The reaction time was 10 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 83% yield; R_f 0.39 (EtOAc/petroleum ether 1 : 2), R_f 0.42 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 16.0. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.86 (d, $^3J_{H,H}$=6.6 Hz, 6H, $CH_{3\ i\text{-}Bu}$), 1.15 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.29 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.82 (m, 1H, $CH_{i\text{-}Bu}$), 2.43 (d, $^3J_{H,H}$=7.2 Hz, 2H, $CH_{2\ i\text{-}Bu}$), 4.65 (m, 2H, OCH), 6.08 (dd, $^2J_{H,H}$=1.7 Hz, $^3J_{H,P}$=45.7 Hz, 1H, *trans*-PC=CH), 6.26 (dd, $^2J_{H,H}$=1.7 Hz, $^3J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.08 (d, $^{3}J_{H,H}$=8.0 Hz, 2H, CH_{Ph}), 7.43 (dd, $^{3}J_{H,H}$=8.0 Hz, $^{4}J_{H,P}$=1.3 Hz, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 22.24 ($2CH_{3\ i\text{-Bu}}$), 23.56 (d, $^{3}J_{C,P}$=5.1 Hz, CH_3), 24.02 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 30.08 ($CH_{i\text{-Bu}}$), 44.99 ($CH_{2\ i\text{-Bu}}$), 70.78 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 127.18 (d, $^{3}J_{C,P}$=5.8 Hz, CH_{Ar}), 128.95 (CH_{Ar}), 130.26 (d, $^{2}J_{C,P}$=8.2 Hz, H_2C=), 134.20 (d, $^{2}J_{C,P}$=11.8 Hz, C_{Ar}), 140.69 (d, $^{1}J_{C,P}$=174.4 Hz, =CP), 141.64 (d, $^{5}J_{C,P}$=1.1 Hz, C_{Ar}). HRMS (ESI): found 325.1921, calcd. for $[M + H]^+$ ($C_{18}H_{30}O_3P$) 325.1927.



Diisopropyl [1-(4-cyclohexylphenyl)vinyl]phosphonate (3n). The reaction time was 7 h. The product was isolated by column chromatography on silica gel (*i*-PrOH/petroleum ether 1 : 15) as a colorless viscous oil in 83% yield; R_f 0.29 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.9. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.25 (m, 1H, $CH_{2\ Cy}$), 1.29-1.49 (m, 4H, $CH_{2\ Cy}$), 1.32 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.73 (m, 1H, $CH_{2\ Cy}$), 1.80-1.88 (m, 4H, $CH_{2\ Cy}$), 2.48 (m, 1H, CH_{Cy}), 4.67 (m, 2H, OCH), 6.10 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=45.8 Hz, 1H, *trans*-PC=CH), 6.28 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.16 (d, $^{3}J_{H,H}$=8.1 Hz, 2H, CH_{Ar}), 7.46 (dd, $^{3}J_{H,H}$=8.1 Hz, $^{4}J_{H,P}$=1.2 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.45 (d, $^{3}J_{C,P}$=5.0 Hz, CH_3), 23.89 (br, CH_3), 25.93 ($CH_{2\ Cy}$), 26.64 ($2CH_{2\ Cy}$), 34.15 ($2CH_{2\ Cy}$), 44.05 (CH_{Cy}), 70.63 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 126.53 (CH_{Ar}), 127.24 (d, $^{3}J_{C,P}$=5.9 Hz, CH_{Ar}), 130.07 (d, $^{2}J_{C,P}$=7.9 Hz, H_2C=), 134.13 (d, $^{2}J_{C,P}$=11.6 Hz, C_{Ar}), 140.59 (d, $^{1}J_{C,P}$=173.6 Hz, =CP), 147.88 (C_{Ar}). HRMS (ESI): found 351.2077, calcd. for $[M + H]^+$ ($C_{20}H_{32}O_3P$) 351.2084,.

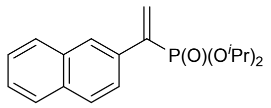


Diisopropyl [1-(5,6,7,8-Tetrahydronaphthalen-2-yl)vinyl]phosphonate (3o). The reaction time was 8 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 89% yield; R_f 0.3 (EtOAc/petroleum ether 1 : 2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 16.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.21 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.33 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.78 (m, 4H, CH_2), 2.75 (m, 4H, CH_2), 4.68 (m, 2H, OCH), 6.09 (dd, $^{2}J_{H,H}$=1.8 Hz, $^{3}J_{H,P}$=45.8 Hz, 1H, *trans*-PC=CH), 6.27 (dd, $^{2}J_{H,H}$=1.8 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.01 (d, $^{3}J_{H,H}$=7.8 Hz, 1H, CH_{Ar}) 7.24-7.27 (m, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.05 ($2CH_2$), 23.61 (d, $^{3}J_{C,P}$=5.0 Hz, CH_3), 24.01 (d, $^{3}J_{C,P}$=3.4 Hz, CH_3), 29.03 (CH_2), 29.35 (CH_2), 70.74 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 124.55 (d, $^{3}J_{C,P}$=5.9 Hz, CH_{Ar}), 128.02 (d, $^{3}J_{C,P}$=6.1 Hz, CH_{Ar}), 128.91 (CH_{Ar}), 130.18 (d, $^{2}J_{C,P}$=8.1 Hz, H_2C=), 133.90 (d, $^{1}J_{C,P}$=11.9 Hz, C_{Ar}), 136.85 (C_{Ar}), 137.16 (C_{Ar}), 140.64 (d, $^{1}J_{C,P}$=174.7 Hz, =CP). HRMS (ESI): found 323.1768, calcd. for $[M + H]^+$ ($C_{18}H_{28}O_3P$) 323.1771.

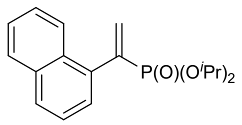


Diisopropyl [1-(4-diphenyl)vinyl]phosphonate (3p). The reaction time was 10 h. The product was isolated by column chromatography on silica gel (*i*-PrOH/petroleum ether 1 : 15) as a yellowish viscous oil in 88% yield; R_f 0.31 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.3. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.22 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.34 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.72 (m, 2H, OCH), 6.19 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=45.5 Hz, 1H, *trans*-PC=CH), 6.36 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.34 (t, $^{3}J_{H,H}$=7.4 Hz, 2H, CH_{Ph}), 7.44 (t, $^{3}J_{H,H}$=7.4 Hz, 1H, CH_{Ph}), 7.56-7.65 (m, 6H, CH_{Ph} and CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.58

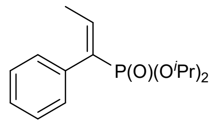
(d, $^{3}J_{C,P}$=4.7 Hz, CH_3), 23.98 (d, $^{3}J_{C,P}$=3.7 Hz, CH_3), 70.98 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 126.85 (2CH_{Ph} and 2CH_{Ar}), 127.35 (CH_{Ph}), 127.83 (d, $^{3}J_{C,P}$=5.8 Hz, 2CH_{Ar}), 128.69 (2CH_{Ph}), 130.90 (d, $^{2}J_{C,P}$=8.5 Hz, H_2C=), 135.71 (d, $^{2}J_{C,P}$=11.9 Hz, C_{Ar}), 140.31 (C_{Ph}), 140.32 (d, $^{1}J_{CP}$=175.6 Hz, =CP), 140.74 (br, C_{Ar}). HRMS (ESI): found 345.1615, calcd. for $[M + H]^+$ ($C_{20}H_{26}O_3P$) 345.1614.



Diisopropyl [1-(naphthalen-2-yl)vinyl]phosphonate (3q). The reaction time was 3 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 83% yield; R_f 0.3 (EtOAc/petroleum ether 1 : 2), R_f 0.27 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.6. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.72 (m, 2H, OCH), 6.23 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=45.5 Hz, 1H, *trans*-PC=CH), 6.42 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.44 (m, 2H, CH_{Ar}), 7.64 (ddd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,H}$=1.6 Hz, $^{4}J_{H,P}$=1.2 Hz, 1H, CH_{Ar}), 7.75-7.87 (m, 3H, CH_{Ar}), 8.06 (br s, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.56 (d, $^{3}J_{C,P}$=5.0 Hz, CH_3), 23.95 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 70.87 (d, $^{2}J_{C,P}$=5.9 Hz, OCH), 125.16 (d, $^{3}J_{C,P}$=6.0 Hz, CH_{Ar}), 126.07 (CH_{Ar}), 126.13 (CH_{Ar}), 126.77 (d, $^{3}J_{C,P}$=5.8 Hz, CH_{Ar}), 127.37 (CH_{Ar}), 127.73 (CH_{Ar}), 128.21 (CH_{Ar}), 131.22 (d, $^{2}J_{C,P}$=8.0 Hz, H_2C=), 132.77 (d, $^{5}J_{C,P}$=0.8 Hz, C_{Ar}), 132.97 (C_{Ar}), 134.12 (d, $^{2}J_{C,P}$=11.9 Hz, C_{Ar}), 140.73 (d, $^{1}J_{C,P}$=175.3 Hz, =CP). HRMS (ESI): found 319.1455, calcd. for $[M + H]^+$ ($C_{18}H_{24}O_3P$) 319.1458.



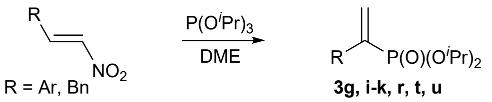
Diisopropyl [1-(naphthalen-1-yl)vinyl]phosphonate (3s). The reaction time was 3 h. The product was isolated by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2) as a colorless viscous oil in 85% yield; R_f 0.3 (EtOAc/petroleum ether 1 : 2), R_f 0.26 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 14.3. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.10 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.22 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.65 (m, 2H, OCH), 5.96 (dd, $^{2}J_{H,H}$=2.1 Hz, $^{3}J_{H,P}$=47.0 Hz, 1H, *trans*-PC=CH), 6.62 (dd, $^{2}J_{H,H}$=2.1 Hz, $^{3}J_{H,P}$=22.4 Hz, 1H, *cis*-PC=CH), 7.43 (t, $^{3}J_{H,H}$=7.5 Hz, 1H, CH_{Ar}) 7.44-7.48 (m, 3H, CH_{Ar}), 7.79 (br d, $^{3}J_{H,H}$=8.1 Hz, 1H, CH_{Ar}), 7.82 (m, 1H, CH_{Ar}), 8.04 (m, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.62 (d, $^{3}J_{C,P}$=5.6 Hz, CH_3), 23.99 (d, $^{3}J_{C,P}$=3.4 Hz, CH_3), 71.03 (d, $^{2}J_{C,P}$=6.3 Hz, OCH), 124.83 (br, CH_{Ar}), 125.69 (CH_{Ar}), 125.81 (CH_{Ar}), 125.92 (br, CH_{Ar}), 126.42 (d, $^{3}J_{C,P}$=4.8 Hz, CH_{Ar}), 127.99 (CH_{Ar}), 128.03 (CH_{Ar}), 131.62 (d, $^{3}J_{C,P}$=5.3 Hz, C_{Ar}), 133.58 (C_{Ar}), 133.62 (d, $^{2}J_{C,P}$=7.0 Hz, H_2C=), 134.89 (d, $^{2}J_{C,P}$=10.0 Hz, C_{Ar}), 140.10 (d, $^{1}J_{C,P}$=180.0 Hz, =CP). HRMS (ESI): found 319.1456, calcd. for $[M + H]^+$ ($C_{18}H_{24}O_3P$) 319.1458.



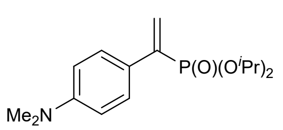
Diisopropyl (*E*)-(1-phenylprop-1-en-1-yl)phosphonate (3v). The reaction time was 10 h. The product was isolated by column chromatography on silica gel (*i*-PrOH/petroleum ether 1 : 20) as a colorless viscous oil in 82% yield; R_f 0.3 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 16.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, OCHC$\underline{H}_3$), 1.26 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, OCHC$\underline{H}_3$), 1.72 (dd, $^{3}J_{H,H}$=6.9 Hz, $^{4}J_{H,P}$=3.4 Hz, 3H, =CHC$\underline{H}_3$), 4.62 (m, 2H, OCH), 6.93 (dq, $^{3}J_{H,H}$=6.9 Hz, $^{3}J_{H,P}$=23.1 Hz, 1H, =CH), 7.23 (m, 2H, CH_{Ph}), 7.27 (m, 1H, CH_{Ph}), 7,33 (m, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.59 (d, $^{3}J_{C,P}$=18.8 Hz, =CH$\underline{C}H_3$), 23.74 (d, $^{3}J_{C,P}$=5.2

Hz, $OCH\underline{C}H_3$), 24.00 (d, $^3J_{C,P}$=2.5 Hz, $OCH\underline{C}H_3$), 70.47 (d, $^2J_{C,P}$=5.8 Hz, OCH), 127.23 (CH_{Ph}), 128.05 (CH_{Ph}), 129.45 (d, $^3J_{C,P}$=5.3 Hz, CH_{Ph}), 133.83 (d, $^1J_{C,P}$=183.0 Hz, =CP), 135.08 (d, $^2J_{C,P}$=10.1 Hz, C_{Ph}), 142.70 (d, $^2J_{C,P}$=10.1 Hz, =CHMe). HRMS (ESI): found 283.1461, calcd. for $[M + H]^+$ ($C_{15}H_{24}O_3P$) 283.1458.

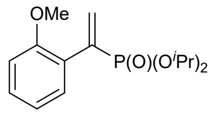
Method B



General procedure: Triisopropyl phosphite (3.3 mmol, 1.1 equiv.) was added to a stirred solution of β-substituted nitroethene (3.0 mmol, 1 equiv.) in absolute DME (7 ml) under argon. The mixture was stirred at room temperature for 48-96 h. Volatile materials were removed on a rotary evaporator and then *in vacuo* (0.05 Torr) at 80°C. The product was isolated by vacuum distillation or column chromatography.

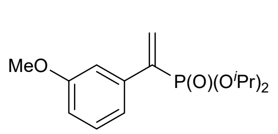


Diisopropyl [1-(4-dimethylaminophenyl)vinyl]phosphonate (3g). The reaction was carried out at 45°C for 48 h. The reaction mixture was then diluted with petroleum ether (10 ml) and filtered through a short pad of Celite to remove unreacted (*E*)-*N*,*N*-dimethyl-4-(2-nitrovinyl)aniline. After the removal of the volatile components *in vacuo*, the product was isolated as an amber viscous oil in 54% yield by column chromatography on silica gel (*i*-PrOH/petroleum ether 1 : 40); R_f 0.21 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 16.8. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.17 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.31 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 2.94 (s, 6H, $N(CH_3)_2$), 4.66 (m, 2H, OCH), 6.03 (dd, $^2J_{H,H}$=1.7 Hz, $^3J_{H,P}$=46.2 Hz, 1H, *trans*-PC=CH), 6.15 (dd, $^2J_{H,H}$=1.7 Hz, $^3J_{H,P}$=22.0 Hz, 1H, *cis*-PC=CH), 6.65 (d, $^3J_{H,H}$=8.8 Hz, 2H, CH_{Ar}), 7.45 (dd, $^3J_{AB}$=8.8 Hz, $^4J_{H,P}$=1.1 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.62 (d, $^3J_{C,P}$=4.9 Hz, CH_3), 24.06 (br, CH_3), 40.27 ($N(CH_3)_2$), 70.61 (d, $^2J_{C,P}$=5.7 Hz, OCH), 111.82 (CH_{Ar}), 124.47 (d, $^2J_{C,P}$=11.5 Hz, C_{Ar}), 127.55 (d, $^2J_{C,P}$=8.6 Hz, H_2C=), 128.25 (d, $^3J_{C,P}$=6.0 Hz, CH_{Ar}), 139.88 (d, $^1J_{C,P}$=172.1 Hz, =CP), 150.21 (CN_{Ar}). HRMS (ESI): found 312.1723, calcd. for $[M + H]^+$ ($C_{16}H_{27}NO_3P$) 312.1723.

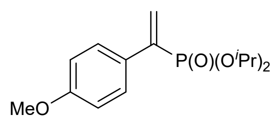


Diisopropyl [1-(2-methoxyphenyl)vinyl]phosphonate (3i). The reaction time was 48 h. The product was isolated as a colorless viscous oil in 78% yield by vacuum distillation; bp 110-114°C/0.05 torr; R_f 0.18 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.2. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 1.27 (d, $^3J_{H,H}$=6.2 Hz, 6H, CH_3), 3.77 (s, 3H, OCH_3), 4.65 (m, 2H, OCH), 6.02 (dd, $^2J_{H,H}$=2.0 Hz, $^3J_{H,P}$=46.8 Hz, 1H, *trans*-PC=CH), 6.42 (dd, $^2J_{H,H}$=2.0 Hz, $^3J_{H,P}$=22.4 Hz, 1H, *cis*-PC=CH), 6.87 (d, $^3J_{H,H}$=8.0 Hz, 1H, CH_{Ar}), 6.90 (m, 1H, CH_{Ar}), 7.24 (m, 1H, CH_{Ar}), 7.32 (ddd, $^3J_{H,H}$=7.5 Hz, $^4J_{H,H}$=1.7 Hz, $^4J_{H,P}$=1.7 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.62 (d, $^3J_{C,P}$=5.6 Hz, CH_3), 24.04 (d, $^3J_{C,P}$=3.2 Hz, CH_3), 55.33 (OCH_3), 70.60 (d, $^2J_{C,P}$=6.0 Hz, OCH), 110.87 (CH_{Ar}), 120.13 (CH_{Ar}), 126.42 (d, $^2J_{C,P}$=11.6 Hz, C_{Ar}), 129.03 (CH_{Ar}), 130.27

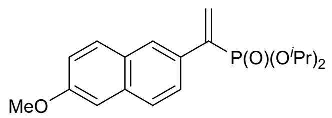
(d, $^{3}J_{C,P}$=4.0 Hz, CH_{Ar}), 133.63 (d, $^{2}J_{C,P}$=7.1 Hz, H_2C=), 137.42 (d, $^{1}J_{C,P}$=179.0 Hz, =CP), 156.63 (d, $^{3}J_{C,P}$=5.7 Hz, CO_{Ar}). HRMS (ESI): found 299.1408, calcd. for $[M + H]^+$ ($C_{15}H_{24}O_4P$) 299.1407.



Diisopropyl [1-(3-methoxyphenyl)vinyl]phosphonate (3j). The reaction time was 48 h. The product was isolated as a colorless viscous oil in 81% yield by vacuum distillation; bp 116-118°C/0.05 torr; R_f 0.21 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.4. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.20 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 3.80 (s, 3H, OCH_3), 4.69 (m, 2H, OCH), 6.12 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=45.4 Hz, 1H, *trans*-PC=CH), 6.32 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 6.85 (ddt, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=0.9 Hz, $^{6}J_{H,P}$=2.5 Hz, 1H, CH_{Ar}), 7.10-7.13 (m, 2H, CH_{Ar}), 7.24 (dt, $^{3}J_{H,H}$=8.2 Hz, $^{5}J_{H,H}$=0.9 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.68 (d, $^{3}J_{C,P}$=5.1 Hz, CH_3), 24.08 (d, $^{3}J_{C,P}$=3.1 Hz, CH_3), 55.18 (OCH_3), 70.97 (d, $^{2}J_{C,P}$=6.0 Hz, OCH), 112.99 (d, $^{3}J_{C,P}$=5.6 Hz, CH_{Ar}), 113.83 (CH_{Ar}), 120.02 (d, $^{3}J_{C,P}$=6.0 Hz, CH_{Ar}), 129.25 (CH_{Ar}), 131.32 (d, $^{2}J_{C,P}$=7.7 Hz, H_2C=), 138.34 (d, $^{2}J_{C,P}$=11.6 Hz, C_{Ar}), 140.63 (d, $^{1}J_{C,P}$=176.0 Hz, =CP), 159.31 (CO_{Ar}). HRMS (ESI): found 299.1408, calcd. for $[M + H]^+$ ($C_{15}H_{24}O_4P$) 299.1407.

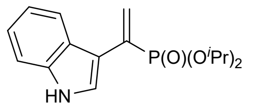


Diisopropyl [1-(4-methoxyphenyl)vinyl]phosphonate (3k). The reaction time was 96 h. The product was isolated as a colorless viscous oil in 52% yield by vacuum distillation; bp 118-120°C/0.05 torr; R_f 0.14 (EtOAc/petroleum ether 1 : 2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.8. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.18 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 3.80 (s, 3H, OCH_3), 4.68 (m, 2H, OCH), 6.06 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=45.7 Hz, 1H, *trans*-PC=CH), 6.24 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 6.86 (d, $^{3}J_{AB}$=8.7 Hz, 2H, CH_{Ar}), 7.49 (dd, $^{3}J_{AB}$=8.7 Hz, $^{4}J_{H,P}$=1.1 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.67 (d, $^{3}J_{C,P}$=5.0 Hz, CH_3), 24.10 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 55.24 (d, $J_{C,P}$=1.4 Hz, OCH_3), 70.88 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 113.64 (CH_{Ar}), 128.76 (d, $^{3}J_{C,P}$=6.0 Hz, CH_{Ar}), 129.32 (d, $^{2}J_{C,P}$=12.1 Hz, C_{Ar}), 129.53 (d, $^{2}J_{C,P}$=8.4 Hz, H_2C=), 140.09 (d, $^{1}J_{C,P}$=174.6 Hz, =CP), 159.53 (d, $^{5}J_{C,P}$=0.9 Hz, CO_{Ar}). HRMS (ESI): found 299.1409, calcd. for $[M + H]^+$ ($C_{15}H_{24}O_4P$) 299.1407.

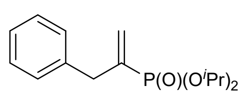


Diisopropyl [1-(6-methoxynaphthalen-2-yl)vinyl]phosphonate (3r). The reaction time was 96 h. The product was isolated as a pale yellowish solid in 80% yield by column chromatography on silica gel (EtOAc/petroleum ether 1 : 2); mp 58°C; R_f 0.32 (EtOAc/petroleum ether 1 : 1). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 15.5. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.19 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.33 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 3.92 (s, 3H, OCH_3), 4.72 (m, 2H, OCH), 6.23 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=45.6 Hz, 1H, *trans*-PC=CH), 6.38 (dd, $^{2}J_{H,H}$=1.6 Hz, $^{3}J_{H,P}$=21.9 Hz, 1H, *cis*-PC=CH), 7.11 (d, $^{4}J_{H,H}$=2.5 Hz, 1H, CH_{Ar}), 7.14 (dd, $^{3}J_{H,H}$=8.8 Hz, $^{4}J_{H,H}$=2.5 Hz, 1H, CH_{Ar}), 7.63 (ddd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,H}$=1.8 Hz, $^{4}J_{H,P}$=1.1 Hz, 1H, CH_{Ar}), 7.70 (br d, $^{3}J_{H,H}$=8.6 Hz, 1H, CH_{Ar}), 7.73 (d, $^{3}J_{H,H}$=8.8 Hz, CH_{Ar}), 7.99 (br s, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.68 (d, $^{3}J_{C,P}$=5.2 Hz, CH_3), 24.08 (d, $^{3}J_{C,P}$=3.4 Hz, CH_3), 52.26 (OCH_3), 70.97 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 105.44 (CH_{Ar}), 119.05 (CH_{Ar}), 125.79 (d, $^{3}J_{C,P}$=5.7 Hz, CH_{Ar}), 126.69 (CH_{Ar}), 126.71 (d, $^{3}J_{C,P}$=5.8 Hz, CH_{Ar}), 128.55 (C_{Ar}), 129.89 (C_{Ar}), 130.68

(d, $^{2}J_{C,P}$=8.3 Hz, H_2C=), 132.00 (d, $^{2}J_{C,P}$=11.9 Hz, C_{Ar}), 134.13 (C_{Ar}), 140.67 (d, $^{1}J_{C,P}$=174.7 Hz, =CP), 157.98 (CO_{Ar}). HRMS (ESI): found 349.1557, calcd. for $[M + H]^+$ ($C_{19}H_{26}O_4P$) 349.1563.



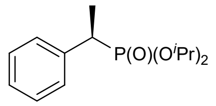
Diisopropyl [1-(1*H*-indol-3-yl)vinyl]phosphonate (3t). The reaction time was 48 h. The product was isolated as an ochre-colored solid in 75% yield by column chromatography on silica gel (EtOAc/petroleum ether 1 : 1); mp 95-96°C; R_f 0.22 (EtOAc/petroleum ether 1 : 1). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 16.3. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.20 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.32 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 4.71 (m, 2H, OCH), 6.33 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=23.1 Hz, 1H, *cis*-PC=CH), 6.40 (dd, $^{2}J_{H,H}$=1.7 Hz, $^{3}J_{H,P}$=47.6 Hz, 1H, *trans*-PC=CH), 7.14-7.22 (m, 2H, CH_{Ar}), 7.40 (m, $^{3}J_{H,H}$=7.8 Hz, 1H, CH_{Ar}), 7.67 (dd, $^{3}J_{H,H}$=2.7 Hz, $^{4}J_{H,P}$=1.2 Hz, 1H, CH_{Ar}), 7.84 (m, $^{3}J_{H,H}$=7.7 Hz, 1H, CH_{Ar}), 9.25 (br s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.70 (d, $^{3}J_{C,P}$=5.3 Hz, CH_3), 24.10 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 71.97 (d, $^{2}J_{C,P}$=5.6 Hz, OCH), 111.45 (d, $^{2}J_{C,P}$=13.0 Hz, C_{Ar}), 111.64 (CH_{Ar}), 119.72 (CH_{Ar}), 120.29 (CH_{Ar}), 122.20 (CH_{Ar}), 125.74 (d, $^{3}J_{C,P}$=12.4 Hz, C_{Ar}), 125.76 (d, $^{3}J_{C,P}$=2.1 Hz, CH_{Ar}), 126.45 (d, $^{2}J_{C,P}$=7.0 Hz, H_2C=), 133.38 (d, $^{1}J_{C,P}$=173.1 Hz, =CP), 136.45 (C_{Ar}). HRMS (ESI): found 308.1413, calcd. for $[M + H]^+$ ($C_{16}H_{23}NO_3P$) 308.1410.



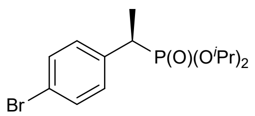
Diisopropyl (3-phenylprop-1-en-2-yl)phosphonate (3u). The reaction time was 96 h. The product was isolated as a colorless oil in 68% yield by column chromatography on silica gel ($Et_2O/CHCl_3$ 1 : 20); R_f 0.19 ($Et_2O/CHCl_3$ 1 : 8). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 17.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.23 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 1.31 (d, $^{3}J_{H,H}$=6.2 Hz, 6H, CH_3), 3.53 (m, 2H, $^{3}J_{H,P}$=10.3 Hz, $PhCH_2$), 4.64 (m, 2H, OCH), 5.44 (m, $^{3}J_{H,P}$=48.0 Hz, 1H, *trans*-PC=CH), 6.08 (m, $^{3}J_{H,P}$=22.5 Hz, 1H, *cis*-PC=CH), 7.17 (m, 2H, CH_{Ph}), 7.21 (m, 1H, CH_{Ph}), 7.29 (m, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 23.75 (d, $^{3}J_{C,P}$=4.9 Hz, CH_3), 24.06 (d, $^{3}J_{C,P}$=3.9 Hz, CH_3), 38.22 (d, $^{2}J_{C,P}$=11.4 Hz, $PhCH_2$), 70.52 (d, $^{2}J_{C,P}$=5.8 Hz, OCH), 126.44 (CH_{Ph}), 128.37 ($2CH_{Ph}$), 129.52 ($2CH_{Ph}$), 129.61 (d, $^{2}J_{C,P}$=10.9 Hz, $=CH_2$), 137.89 (d, $^{3}J_{C,P}$=8.1 Hz, C_{Ph}), 140.61 (d, $^{1}J_{C,P}$=175.3 Hz, =CP). HRMS (ESI): found 283.1461, calcd. for $[M + H]^+$ ($C_{15}H_{24}O_3P$) 283.1458.

4. Rh(I)-catalyzed asymmetric hydrogenation of substrates 3 and characterization of products 6

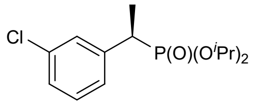
General procedure: All glassware was dried at 200°C for 1.5 h. A sample bottle equipped with a magnetic stir bar was charged with α,β-unsaturated phosphonate **3** (0.40 mmol, 1 equiv.) and placed in a wide-neck Schlenk tube. The tube was sealed with a rubber septum and then evacuated and filled with dry argon three times. In another Schlenk tube, ligand **L3** (1.3 mg, 0.002 mmol, 0.5 mol%) and $[Rh(COD)_2]BF_4$ (0.8 mg, 0.002 mmol, 0.5 mol%) were dissolved in deaerated absolute DCM (4 ml) under dry argon atmosphere. The solution was stirred for 10 min and transferred into the sample bottle using a syringe. The bottle was quickly transported into a stainless-steel autoclave filled with hydrogen. The autoclave was sealed, purged with hydrogen three times, and pressurized with H_2 to 10 atm. The reaction mixture was stirred at room temperature for the time indicated in Table 2. At the end of the experiment, the reaction mixture was evaporated on a rotavapor. The residue was dissolved in $CDCl_3$ and analyzed by ^{31}P NMR spectroscopy to determine the conversion of **3** and the yield of product **6**. The spectrally pure products **6a-r,t,u** were isolated in almost quantitative yields (94-99%) by column chromatography on silica gel, using 2-3 vol.% *i*-PrOH in petroleum ether as an eluent. The enantiomeric excess for the isolated sample was determined by HPLC analysis (see data for individual compounds for details).



Diisopropyl (*R*)-(+)-(1-phenylethyl)phosphonate (6a). Colorless oil, 95% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min, t_R = 10.0 min (minor), 15.8 min (major). $[\alpha]_D^{23}$ = +7.0 (*c* = 1.15, $CHCl_3$) (lit.[6,19] $[\alpha]_D^{20}$ = +6.7 (*c* = 2.0, $CHCl_3$) for 94% *ee* (*R*); $[\alpha]_D^{25}$ = -6.9 (*c* = 1.1, $CHCl_3$) for 95% *ee* (*S*)). R_f 0.3 (EtOAc/petroleum ether 1 : 2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.8. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.94 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.55 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.4 Hz, 3H, CH_3), 3.08 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.7 Hz, 1H, PCH), 4.43 (m, 1H, OCH), 4.61 (m, 1H, OCH), 7.22 (m, 1H, CH_{Ph}), 7.29 (t, $^3J_{H,H}$=7.6 Hz, 2H, CH_{Ph}), 7.34 (m, $^3J_{H,H}$=7.6 Hz, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.82 (d, $^2J_{C,P}$=5.1 Hz, CH_3), 23.27 (d, $^3J_{C,P}$=5.6 Hz, CH_3), 23.88 (d, $^3J_{C,P}$=5.5 Hz, CH_3) 23.94 (d, $^3J_{C,P}$=3.1 Hz, CH_3) 24.18 (d, $^3J_{C,P}$=2.5 Hz, CH_3), 38.99 (d, $^1J_{C,P}$=139.7 Hz, PC), 70.02 (d, $^2J_{C,P}$=7.1 Hz, OCH), 70.73 (d, $^2J_{C,P}$=7.1 Hz, OCH), 126.81 (CH_{Ph}), 128.20 (CH_{Ph}), 128.75 (d, $^3J_{C,P}$=6.4 Hz, CH_{Ph}), 138.32 (d, $^2J_{C,P}$=6.0 Hz, C_{Ph}). HRMS (ESI): found 271.1458, calcd. for $[M + H]^+$ ($C_{14}H_{24}O_3P$) 271.1458.

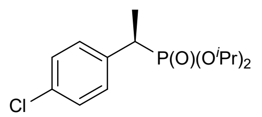


Diisopropyl (*R*)-(+)-[1-(4-bromophenyl)ethyl]phosphonate (6b). Colorless oil, 93% *ee*. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 200, flow rate = 1.5 ml/min, t_R = 11.1 min (major), 12.1 min (minor). $[\alpha]_D^{23}$ = +11.2 (*c* = 1.0, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +18.2 (*c* = 0.6, $CHCl_3$) for 92% *ee* (*R*)). R_f 0.25 (EtOAc/petroleum ether 1 : 2), R_f 0.3 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 27.4. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.99 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.21 (d, $^3J_{H,H}$=6.1 Hz, 3H, CH_3), 1.22 (d, $^3J_{H,H}$=6.1 Hz, 3H, CH_3), 1.25 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.50 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.3 Hz, 3H, CH_3), 3.03 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.8 Hz, 1H, PCH), 4.46 (m, 1H, OCH), 4.60 (m, 1H, OCH), 7.20 (dd, $^3J_{AB}$=8.5 Hz, $^4J_{H,P}$=2.2 Hz, 2H, CH_{Ar}), 7.40 (d, $^3J_{AB}$=8.5 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.69 (d, $^2J_{C,P}$=5.1 Hz, CH_3), 23.46 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.92 (d, $^3J_{C,P}$=5.2 Hz, CH_3) 24.01 (d, $^3J_{C,P}$=3.6 Hz, CH_3) 24.16 (d, $^3J_{C,P}$=3.3 Hz, CH_3), 35.53 (d, $^1J_{C,P}$=140.2 Hz, PCH), 70.26 (d, $^2J_{C,P}$=7.4 Hz, OCH), 70.79 (d, $^2J_{C,P}$=7.2 Hz, OCH), 120.71 (d, $^5J_{C,P}$=4.1 Hz, CBr_{Ar}), 130.44 (d, $^3J_{C,P}$=6.6 Hz, CH_{Ar}), 131.29 (d, $^4J_{C,P}$=2.6 Hz, CH_{Ar}), 137.55 (d, $^2J_{C,P}$=6.7 Hz, C_{Ar}). HRMS (ESI): found 349.0551, calcd. for $[M + H]^+$ ($C_{14}H_{23}BrO_3P$) 349.0563.

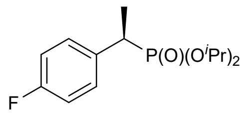


Diisopropyl (*R*)-(+)-[1-(3-chlorophenyl)ethyl]phosphonate (6c). Colorless oil, 95% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 4.2 (minor), 5.6 min (major). $[\alpha]_D^{26}$ = +6.8 (*c* = 1.1, $CHCl_3$). R_f 0.28 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 27.6. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.98

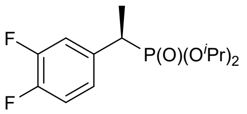
(d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.20 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.21 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.23 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.49 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.3 Hz, 3H, CH_3), 3.02 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.8 Hz, 1H, PCH), 4.44 (m, 1H, OCH), 4.58 (m, 1H, OCH), 7.14-7.22 (m, 3H, CH_{Ar}), 7.28 (m, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.53 (d, $^2J_{C,P}$=5.6 Hz, CH_3), 23.32 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.80 (d, $^3J_{C,P}$=5.5 Hz, CH_3) 23.92 (d, $^3J_{C,P}$=3.5 Hz, CH_3) 24.07 (br, CH_3), 38.74 (d, $^1J_{C,P}$=140.0 Hz, PCH), 70.23 (d, $^2J_{C,P}$=7.0 Hz, OCH), 70.77 (d, $^2J_{C,P}$=6.9 Hz, OCH), 126.88-126.93 (2CH_{Ar}), 129.32 (CH_{Ar}), 128.81 (d, $^3J_{C,P}$=6.5 Hz, CH_{Ar}), 133.88 (CCl_{Ar}), 140.45 (d, $^2J_{C,P}$=6.5 Hz, C_{Ar}). HRMS (ESI): found 305.1069, calcd. for $[M + H]^+$ ($C_{14}H_{23}ClO_3P$) 305.1068.



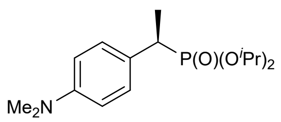
Diisopropyl (*R*)-(+)-[1-(4-chlorophenyl)ethyl]phosphonate (6d). Colorless oil, 94% *ee*. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 300, flow rate = 1.5 ml/min, t_R = 15.8 min (major), 17.0 min (minor). $[\alpha]_D^{24}$ = +10.7 (*c* = 1.11, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +11.9 (*c* = 1.1, $CHCl_3$) for 94% *ee* (*R*)). R_f 0.21 (EtOAc/petroleum ether 1 : 2), R_f 0.29 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 27.9. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.00 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (d, $^3J_{H,H}$=6.1 Hz, 3H, CH_3), 1.23 (d, $^3J_{H,H}$=6.1 Hz, 3H, CH_3), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.51 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.3 Hz, 3H, CH_3), 3.05 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.8 Hz, 1H, PCH), 4.47 (m, 1H, OCH), 4.61 (m, 1H, OCH), 7.25 (br s, 4H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.75 (d, $^2J_{C,P}$=5.1 Hz, CH_3), 23.45 (d, $^3J_{C,P}$=5.4 Hz, CH_3), 23.90 (d, $^3J_{C,P}$=5.2 Hz, CH_3) 24.00 (d, $^3J_{C,P}$=3.6 Hz, CH_3) 24.14 (d, $^3J_{C,P}$=3.3 Hz, CH_3), 38.51 (d, $^1J_{C,P}$=140.3 Hz, PCH), 70.24 (d, $^2J_{C,P}$=7.5 Hz, OCH), 70.75 (d, $^2J_{C,P}$=7.3 Hz, OCH), 128.34 (d, $^4J_{C,P}$=2.6 Hz, CH_{Ar}), 130.07 (d, $^3J_{C,P}$=6.7 Hz, CH_{Ar}), 132.65 (d, $^5J_{C,P}$=3.9 Hz, CCl_{Ar}), 137.09 (d, $^2J_{C,P}$=6.8 Hz, C_{Ar}). HRMS (ESI): found 305.1064, calcd. for $[M + H]^+$ ($C_{14}H_{23}ClO_3P$) 305.1068.



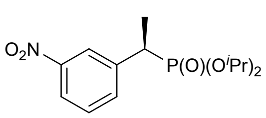
Diisopropyl (*R*)-(+)-[1-(4-fluorophenyl)ethyl]phosphonate (6e). Colorless oil, 89% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 4.8 min (minor), 6.2 min (major). $[\alpha]_D^{26}$ = +4.3 (*c* = 0.9, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +4.6 (*c* = 1.0, $CHCl_3$) for 93% *ee* (*R*)). R_f 0.3 (EtOAc/petroleum ether 1 : 2), R_f 0.28 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.0 ($^6J_{P,F}$=4.7 Hz). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.97 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.52 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.3 Hz, 3H, CH_3), 3.06 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.7 Hz, 1H, PCH), 4.45 (m, 1H, OCH), 4.61 (m, 1H, OCH), 6.98 (dd, $^3J_{H,H}$=8.5 Hz, $^3J_{H,F}$=8.8 Hz, 2H, CH_{Ar}), 7.30 (ddd, $^3J_{H,H}$=8.5 Hz, $^4J_{H,F}$=5.4 Hz, $^4J_{H,P}$=2.2 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.86 (d, $^2J_{C,P}$=4.9 Hz, CH_3), 23.34 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.85 (d, $^3J_{C,P}$=5.2 Hz, CH_3) 23.95 (d, $^3J_{C,P}$=3.6 Hz, CH_3) 24.12 (d, $^3J_{C,P}$=3.3 Hz, CH_3), 38.18 (d, $^1J_{C,P}$=140.6 Hz, PCH), 70.10 (d, $^2J_{C,P}$=7.4 Hz, OCH), 70.69 (d, $^2J_{C,P}$=7.3 Hz, OCH), 114.98 (dd, $^4J_{C,P}$=2.5 Hz, $^2J_{CF}$=21.3 Hz, CH_{Ar}), 130.15 (dd, $^3J_{C,P}$=6.7 Hz, $^3J_{C,F}$=7.9 Hz, CH_{Ar}), 134.06 (dd, $^2J_{C,P}$=6.6 Hz, $^4J_{C,F}$=3.3 Hz, C_{Ar}), 161.76 (dd, $^5J_{C,P}$=3.5 Hz, $^1J_{C,F}$=245.0 Hz, CF_{Ar}). ^{19}F NMR (376 MHz, $CDCl_3$, δ): -116.12 (dtt, $^3J_{H,F}$=8.8 Hz, $^4J_{H,F}$=5.4 Hz, $^6J_{P,F}$=4.7 Hz). HRMS (ESI): found 289.1363, calcd. for $[M + H]^+$ ($C_{14}H_{23}FO_3P$) 289.1363.



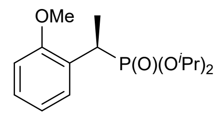
Diisopropyl (*R*)-(+)-[1-(3,4-difluorophenyl)ethyl]phosphonate (6f). Colorless oil, 90% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 4.5 min (minor), 5.3 min (major). $[\alpha]_D^{26}$ = +7.1 (*c* = 1.15, $CHCl_3$). R_f 0.3 (EtOAc/petroleum ether 1 : 2), R_f 0.27 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 27.4 ($^6J_{P,F}$=5.0 Hz). ^1H NMR (400 MHz, $CDCl_3$, δ): 1.04 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (m, 6H, CH_3), 1.27 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.50 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.2 Hz, 3H, CH_3), 3.04 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.7 Hz, 1H, PCH), 4.50 (m, 1H, OCH), 4.62 (m, 1H, OCH), 7.01-7.11 (m, 2H, CH_{Ar}) 7.40 (dddd, $^4J_{H,H}$=2.2 Hz, $^4J_{H,P}$=2.2 Hz, $^3J_{H,F}$=11.5 Hz, $^4J_{H,F}$=7.7 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.71 (d, $^2J_{C,P}$=4.9 Hz, CH_3), 23.45 (d, $^3J_{C,P}$=5.3 Hz, CH_3), 23.85 (d, $^3J_{C,P}$=4.8 Hz, CH_3) 23.94 (d, $^3J_{C,P}$=3.4 Hz, CH_3) 24.08 (d, $^3J_{C,P}$=3.7 Hz, CH_3), 38.20 (ddd, $^1J_{C,P}$=141.1 Hz, $^4J_{C,F}$=3.0 Hz, $^5J_{C,F}$=1.1 Hz, PCH), 70.40 (d, $^2J_{C,P}$=7.4 Hz, OCH), 70.85 (d, $^2J_{C,P}$=7.2 Hz, OCH), 116.81 (dd, $^2J_{C,F}$=17.2 Hz, $^3J_{CP}$=2.3 Hz, CH_{Ar}), 117.51 (dd, $^2J_{C,F}$=17.7 Hz, $^3J_{C,P}$=6.3 Hz, CH_{Ar}), 124.71 (ddd, $^3J_{C,P}$=6.6 Hz, $^2J_{C,F}$=6.6 Hz, $^3J_{C,F}$=3.6 Hz, CH_{Ar}), 135.47 (ddd, $^2J_{C,P}$=6.8 Hz, $^3J_{C,F}$=5.6 Hz, $^4J_{C,F}$=3.8 Hz, C_{Ar}), 149.28 (ddd, $^5J_{C,P}$=3.6 Hz, $^1J_{C,F}$=247.2 Hz, $^2J_{C,F}$=12.6 Hz, CF_{Ar}), 149.94 (ddd, $^4J_{C,P}$=2.9 Hz, $^1J_{C,F}$=247.6 Hz, $^2J_{C,F}$=12.7 Hz, CF_{Ar}). ^{19}F NMR (376 MHz, CD_3Cl, δ): -140.67÷-140.54 (m, C(4′)F), -138.08÷-137.97 (m, C(3′)F). HRMS (ESI): found 307.1266, calcd. for $[M + H]^+$ ($C_{14}H_{22}F_2O_3P$) 307.1269.



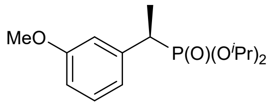
Diisopropyl (*R*)-(+)-[1-(4-dimethylaminophenyl)ethyl]phosphonate (6g). Colorless oil, 93% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 13.1 min (minor), 25.2 min (major). $[\alpha]_D^{26}$ = +8.0 (*c* = 0.9, $CHCl_3$). R_f 0.21 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.3. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.99 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.50 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.4 Hz, 3H, CH_3), 2.91 (s, 6H, $N(CH_3)_2$), 2.99 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.4 Hz, 1H, PCH), 4.43 (m, 1H, OCH), 4.60 (m, 1H, OCH), 6.70 (d, $^3J_{AB}$=8.8 Hz, 2H, CH_{Ar}), 7.20 (dd, $^3J_{AB}$=8.8 Hz, $^4J_{H,P}$=2.3 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.88 (d, $^2J_{C,P}$=4.4 Hz, CH_3), 23.41 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.90 (d, $^3J_{C,P}$=5.2 Hz, CH_3) 23.99 (d, $^3J_{C,P}$=3.5 Hz, CH_3) 24.20 (d, $^3J_{C,P}$=3.1 Hz, CH_3), 37.84 (d, $^1J_{C,P}$=140.2 Hz, PCH), 40.81 ($N(CH_3)_2$), 69.90 (d, $^2J_{C,P}$=7.5 Hz, OCH), 70.63 (d, $^2J_{C,P}$=7.3 Hz, OCH), 112.80 (d, $^4J_{C,P}$=2.2 Hz, CH_{Ar}), 126.25 (d, $^2J_{C,P}$=7.0 Hz, C_{Ar}), 129.30 (d, $^3J_{C,P}$=6.6 Hz, CH_{Ar}), 149.33 (d, $^5J_{C,P}$=2.6 Hz, CN_{Ar}). HRMS (ESI): found 314.1881, calcd. for $[M + H]^+$ ($C_{16}H_{29}NO_3P$) 314.1880.



Diisopropyl (*R*)-(+)-[1-(3-nitrophenyl)ethyl]phosphonate (6h). Colorless oil, 81% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 7.4 min (minor), 8.6 min (major). $[\alpha]_D^{26}$ = +7.1 (*c* = 0.9, $CHCl_3$). R_f 0.24 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.8. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.07 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.25 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.59 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.1 Hz, 3H, CH_3), 3.21 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=23.0 Hz, 1H, PCH), 4.54 (m, 1H, OCH), 4.63 (m, 1H, OCH), 7.47 (m, $^3J_{H,H}$=8.2 Hz, $^3J_{H,H}$=7.7 Hz, 1H, CH_{Ar}), 7.70 (m, $^{3}J_{H,H}$=7.7 Hz, $^{4}J_{H,H}$=2.2 Hz, $^{4}J_{H,H}$=1.1 Hz, $^{5}J_{H,H}$=0.4 Hz, $^{4}J_{H,P}$=1.9 Hz, 1H, CH_{Ar}), 8.09 (dddd, $^{3}J_{H,H}$=8.2 Hz, $^{4}J_{H,H}$=2.1 Hz, $^{4}J_{H,H}$=1.1 Hz, 1H, $^{6}J_{H,P}$=2.1 Hz, CH_{Ar}), 8.16 (m, $^{4}J_{H,H}$=2.2 Hz, $^{4}J_{H,H}$=2.1 Hz, $^{4}J_{H,P}$=2.1 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.40 (d, $^{2}J_{C,P}$=5.1 Hz, CH_3), 23.58 (d, $^{3}J_{C,P}$=4.9 Hz, CH_3), 23.88 (d, $^{3}J_{C,P}$=4.8 Hz, CH_3) 23.98 (d, $^{3}J_{C,P}$=3.9 Hz, CH_3) 24.07 (d, $^{3}J_{C,P}$=3.7 Hz, CH_3), 38.87 (d, $^{1}J_{C,P}$=140.0 Hz, PCH), 70.74 (d, $^{2}J_{C,P}$=7.4 Hz, OCH), 70.99 (d, $^{2}J_{C,P}$=7.3 Hz, OCH), 121.94 (d, $^{5}J_{C,P}$=2.9 Hz, CH_{Ar}), 123.62 (d, $^{3}J_{C,P}$=6.8 Hz, CH_{Ar}), 129.12 (d, $^{4}J_{C,P}$=1.6 Hz, CH_{Ar}), 135.03 (d, $^{3}J_{C,P}$=6.1 Hz, CH_{Ar}), 140.77 (d, $^{2}J_{C,P}$=7.1 Hz, C_{Ar}), 148.08 (CN_{Ar}). HRMS (ESI): found 316.1308, calcd. for $[M + H]^+$ ($C_{14}H_{23}NO_5P$) 316.1310.

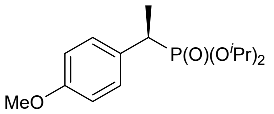


Diisopropyl (*R*)-(+)-[1-(2-methoxyphenyl)ethyl]phosphonate (6i). Colorless oil, 82% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 5.8 min (minor), 17.2 min (major). $[\alpha]_D^{26}$ = +6.5 (*c* = 1.1, $CHCl_3$). R_f 0.25 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 30.0. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.17 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.25 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.45 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{3}J_{H,P}$=18.5 Hz, 3H, CH_3), 3.77 (s, 3H, OCH_3), 3.78 (dq, $^{3}J_{H,H}$=7.4 Hz, $^{2}J_{H,P}$=22.7 Hz, 1H, PCH), 4.39 (m, 1H, OCH), 4.64 (m, 1H, OCH), 6.80 (m, $^{3}J_{H,H}$=8.2 Hz, 1H, CH_{Ar}), 6.90 (m, $^{3}J_{H,H}$=7.7 Hz, $^{3}J_{H,H}$=7.4 Hz, 1H, CH_{Ar}), 7.16 (m, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, $^{4}J_{H,H}$=1.8 Hz, $^{6}J_{H,P}$=1.8 Hz, 1H, CH_{Ar}), 7.48 (m, $^{3}J_{H,H}$=7.7 Hz, $^{4}J_{H,H}$=1.8 Hz, $^{4}J_{H,P}$=2.5 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.86 (d, $^{2}J_{C,P}$=4.7 Hz, CH_3), 23.12 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3), 23.83 (d, $^{3}J_{C,P}$=5.2 Hz, CH_3) 23.97 (d, $^{3}J_{C,P}$=3.4 Hz, CH_3) 24.16 (d, $^{3}J_{C,P}$=3.1 Hz, CH_3), 29.21 (d, $^{1}J_{C,P}$=141.9 Hz, PCH), 55.40 (OCH_3), 69.79 (d, $^{2}J_{C,P}$=7.2 Hz, OCH), 70.48 (d, $^{2}J_{C,P}$=7.2 Hz, OCH), 110.25 (d, $^{4}J_{C,P}$=1.9 Hz, CH_{Ar}), 120.50 (d, $^{4}J_{C,P}$=3.0 Hz, CH_{Ar}), 127.03 (d, $^{2}J_{C,P}$=5.6 Hz, C_{Ar}), 127.59 (d, $^{5}J_{C,P}$=2.9 Hz, CH_{Ar}), 128.93(d, $^{3}J_{C,P}$=4.9 Hz, CH_{Ar}), 156.55 (d, $^{3}J_{C,P}$=8.2 Hz, CO_{Ar}). HRMS (ESI): found 301.1565, calcd. for $[M + H]^+$ ($C_{15}H_{26}O_4P$) 301.1563.

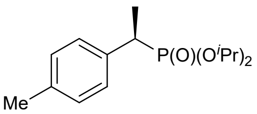


Diisopropyl (*R*)-(+)-[1-(3-methoxyphenyl)ethyl]phosphonate (6j). Colorless oil, 95% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min, t_R = 11.3 min (minor), 20.7 min (major). $[\alpha]_D^{26}$ = +8.0 (*c* = 1.03, $CHCl_3$). R_f 0.25 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.4. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.98 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.23 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.25 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.53 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{3}J_{H,P}$=18.4 Hz, 3H, CH_3), 3.06 (dq, $^{3}J_{H,H}$=7.4 Hz, $^{2}J_{H,P}$=22.6 Hz, 1H, PCH), 3.79 (s, 3H, OCH_3), 4.46 (m, 1H, OCH), 4.62 (m, 1H, OCH), 6.75-6.78 (m, 1H, CH_{Ar}), 6.90-6.94 (m, 2H, CH_{Ar}), 7.20 (ddd, $^{3}J_{H,H}$=8.2 Hz, $^{3}J_{H,H}$=7.4 Hz, $^{5}J_{H,H}$=0.8 Hz, $^{5}J_{H,P}$=0.8 Hz, 1H, CH_{Ar}). ^{13}C NMR (151 MHz, $CDCl_3$, δ): 15.79 (d, $^{2}J_{C,P}$=5.1 Hz, CH_3), 23.23 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3), 23.79 (d, $^{3}J_{C,P}$=5.3 Hz, CH_3) 23.89 (d, $^{3}J_{C,P}$=3.4 Hz, CH_3) 24.09 (d, $^{3}J_{C,P}$=3.1 Hz, CH_3), 38.96 (d, $^{1}J_{C,P}$=139.7 Hz, PCH), 55.01 (OCH_3), 70.00 (d, $^{2}J_{C,P}$=7.4 Hz, OCH), 70.70 (d, $^{2}J_{C,P}$=7.3 Hz, OCH), 112.38 (d, $^{5}J_{C,P}$=3.0 Hz, CH_{Ar}), 114.20 (d, $^{3}J_{C,P}$=6.5 Hz, CH_{Ar}), 121.10 (d, $^{3}J_{C,P}$=6.8 Hz, CH_{Ar}), 129.03 (d, $^{4}J_{C,P}$=2.5 Hz, CH_{Ar}), 139.74 (d,

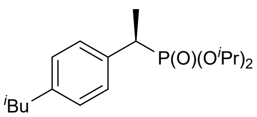
$^{2}J_{C,P}$=6.4 Hz, C_{Ar}), 159.31 (d, $^{4}J_{C,P}$=2.6 Hz, CO_{Ar}). HRMS (ESI): found 301.1564, calcd. for $[M + H]^+$ ($C_{15}H_{26}O_4P$) 301.1563.



Diisopropyl (*R*)-(+)-[1-(4-methoxyphenyl)ethyl]phosphonate (6k). Colorless oil, 95% *ee*. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 200, flow rate = 1.5 ml/min, t_R = 5.5 min (major), 24.2 min (minor). $[\alpha]_D^{23}$ = +8.7 (c = 0.9, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +9.4 (c = 1.1, $CHCl_3$) for 94% *ee* (*R*)). R_f 0.25 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.98 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.51 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{3}J_{H,P}$=18.4 Hz, 3H, CH_3), 3.03 (dq, $^{3}J_{H,H}$=7.4 Hz, $^{2}J_{H,P}$=22.5 Hz, 1H, PCH), 3.78 (s, 3H, OCH_3), 4.43 (m, 1H, OCH), 4.60 (m, 1H, OCH), 6.83 (d, $^{3}J_{H,H}$=8.6 Hz, 2H, CH_{Ar}), 7.26 (dd, $^{3}J_{H,H}$=8.6 Hz, $^{4}J_{H,P}$=2.3 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.99 (d, $^{2}J_{C,P}$=4.7 Hz, CH_3), 23.44 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3), 23.94 (d, $^{3}J_{C,P}$=5.2 Hz, CH_3) 24.04 (d, $^{3}J_{C,P}$=3.5 Hz, CH_3) 24.23 (d, $^{3}J_{C,P}$=3.2 Hz, CH_3), 38.09 (d, $^{1}J_{C,P}$=140.4 Hz, PCH), 55.20 (OCH_3), 69.98 (d, $^{2}J_{C,P}$=7.6 Hz, OCH), 70.65 (d, $^{2}J_{C,P}$=7.3 Hz, OCH), 113.64 (d, $^{4}J_{C,P}$=2.4 Hz, CH_{Ar}), 129.71 (d, $^{3}J_{C,P}$=6.6 Hz, CH_{Ar}), 130.31 (d, $^{2}J_{C,P}$=6.8 Hz, C_{Ar}), 158.47 (d, $^{5}J_{C,P}$=3.4 Hz, CO_{Ar}). HRMS (ESI): found 301.1563, calcd. for $[M + H]^+$ ($C_{15}H_{26}O_4P$) 301.1563.

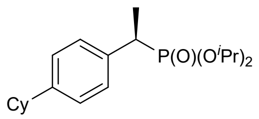


Diisopropyl (*R*)-(+)-[1-(4-methylphenyl)ethyl]phosphonate (6l). Colorless oil, 96% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.0 ml/min, t_R = 9.8 min (minor), 18.6 min (major). $[\alpha]_D^{24}$ = +10.9 (c = 1.0, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +12.6 (c = 1.0, $CHCl_3$) for 93% *ee* (*R*)). R_f 0.3 (EtOAc/petroleum ether 1 : 2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.0. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.97 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (d, $^{3}J_{H,H}$=6.3 Hz, 3H, CH_3), 1.24 (d, $^{3}J_{H,H}$=6.4 Hz, 3H, CH_3), 1.26 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.52 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{3}J_{H,P}$=18.4 Hz, 3H, CH_3), 2.31 (d, $J_{H,P}$=1.8 Hz, 3H, CH_3), 3.04 (dq, $^{3}J_{H,H}$=7.4 Hz, $^{2}J_{H,P}$=22.5 Hz, 1H, PCH), 4.44 (m, 1H, OCH), 4.61 (m, 1H, OCH), 7.09 (d, $^{3}J_{H,H}$=8.0 Hz, 2H, CH_{Ar}), 7.22 (dd, $^{3}J_{H,H}$=8.0 Hz, $^{4}J_{H,P}$=2.2 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.88 (d, $^{2}J_{C,P}$=4.9 Hz, CH_3), 20.92 (CH_3), 23.32 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3), 23.85 (d, $^{3}J_{C,P}$=5.2 Hz, CH_3) 23.96 (d, $^{3}J_{C,P}$=3.5 Hz, CH_3) 24.14 (d, $^{3}J_{C,P}$=3.2 Hz, CH_3), 39.59 (d, $^{1}J_{C,P}$=139.9 Hz, PCH), 69.91 (d, $^{2}J_{C,P}$=7.4 Hz, OCH), 70.55 (d, $^{2}J_{C,P}$=7.3 Hz, OCH), 128.55 (d, $^{3}J_{C,P}$=6.7 Hz, CH_{Ar}), 128.84 (d, $^{4}J_{C,P}$=2.5 Hz, CH_{Ar}), 135.25 (d, $^{2}J_{C,P}$=6.8 Hz, C_{Ar}), 136.27 (d, $^{5}J_{C,P}$=3.4 Hz, CMe_{Ar}). HRMS (ESI): found 285.1611, calcd. for $[M + H]^+$ ($C_{15}H_{26}O_3P$) 285.1614.

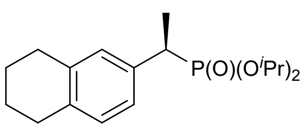


Diisopropyl (*R*)-(+)-[1-(4-isobutylphenyl)ethyl]phosphonate (6m). Colorless oil, 97% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 5.8 min (minor), 13.6 min (major). $[\alpha]_D^{24}$ = +8.4° (c = 1.1, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +8.2 (c = 1.1, $CHCl_3$) for 93% *ee* (*R*)). R_f 0.33 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.2. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.86 (br d, $^{3}J_{H,H}$=6.6 Hz, 6H, $CH_{3\ i\text{-Bu}}$), 0.90 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.21 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.23 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.53 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{3}J_{H,P}$=18.5 Hz, 3H, CH_3), 1.82 (m, 1H, $CH_{i\text{-Bu}}$), 2.43 (br d, $^{3}J_{H,H}$=7.2

Hz, 2H, $CH_{2\ i\text{-}Bu}$), 3.05 (dq, $^3J_{H,H}$=7.2 Hz, $^2J_{H,P}$=22.6 Hz, 1H, PCH), 4.00 (m, 1H, OCH), 4.60 (m, 1H, OCH), 7.06 (d, $^3J_{H,H}$=8.0 Hz, 2H, CH_{Ar}), 7.24 (dd, $^3J_{H,H}$=8.0 Hz, $^4J_{H,P}$=2.2 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.89 (d, $^2J_{C,P}$=4.9 Hz, CH_3), 22.26 ($2CH_{3\ i\text{-}Bu}$), 23.27 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.93 (d, $^3J_{C,P}$=5.1 Hz, CH_3) 24.04 (d, $^3J_{C,P}$=3.5 Hz, CH_3) 24.26 (br s, CH_3), 30.19 ($CH_{i\text{-}Bu}$), 38.61 (d, $^1J_{C,P}$=139.5 Hz, PCH), 44.99 ($CH_{2\ i\text{-}Bu}$), 69.93 (d, $^2J_{C,P}$=7.0 Hz, OCH), 70.75 (d, $^2J_{C,P}$=6.9 Hz, OCH), 128.51 (d, $^3J_{C,P}$=6.5 Hz, CH_{Ar}), 129.00 (CH_{Ar}), 135.44 (d, $^2J_{C,P}$=6.1 Hz, C_{Ar}), 140.26 (C_{Ar}). HRMS (ESI): found 327.2079, calcd. for $[M + H]^+$ ($C_{18}H_{32}O_3P$) 327.2084.

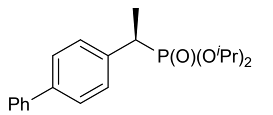


Diisopropyl (*R*)-(+)-[1-(4-cyclohexylphenyl)ethyl]phosphonate (6n). Colorless oil, 99% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 3.9 min (minor), 5.3 min (major). $[\alpha]_D^{23}$ = +10.6 (*c* = 1.0, $CHCl_3$). R_f 0.3 (EtOAc/petroleum ether 1 : 2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.90 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.21 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.22 (m, 1H, $CH_{2\ Cy}$), 1.23 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.31-1.43 (m, 4H, $CH_{2\ Cy}$), 1.53 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.5 Hz, 3H, CH_3), 2.45 (m, 1H, CH_{Cy}), 3.05 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.6 Hz, 1H, PCH), 4.41 (m, 1H, OCH), 4.60 (m, 1H, OCH), 7.12 (d, $^3J_{H,H}$=8.0 Hz, 2H, CH_{Ar}), 7.24 (dd, $^3J_{H,H}$=8.0 Hz, $^4J_{H,P}$=2.2 Hz, 2H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.78 (d, $^2J_{C,P}$=4.9 Hz, CH_3), 23.17 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.86 (d, $^3J_{C,P}$=5.2 Hz, CH_3) 23.98 (d, $^3J_{C,P}$=3.5 Hz, CH_3) 24.20 (d, $^3J_{C,P}$=3.1 Hz, CH_3), 26.12 ($CH_{2\ Cy}$), 26.85 ($2CH_{2\ Cy}$), 34.43 (d, $J_{C,P}$=1.0 Hz, $2CH_{2\ Cy}$), 38.64 (d, $^1J_{C,P}$=139.7 Hz, PCH), 44.14 (d, $J_{C,P}$=0.7 Hz, CH_{Cy}), 69.91 (d, $^2J_{C,P}$=7.5 Hz, OCH), 70.68 (d, $^2J_{C,P}$=7.2 Hz, OCH), 126.61 (d, $^4J_{C,P}$=2.4 Hz, CH_{Ar}), 128.59 (d, $^3J_{C,P}$=6.6 Hz, CH_{Ar}), 135.48 (d, $^2J_{C,P}$=6.6 Hz, C_{Ar}), 146.35 (d, $^5J_{C,P}$=3.3 Hz, C_{Ar}). HRMS (ESI): found 353.2234, calcd. for $[M + H]^+$ ($C_{20}H_{33}O_3P$) 353.2240.

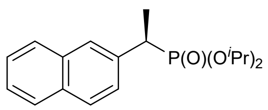


Diisopropyl (*R*)-(+)-[1-(5,6,7,8-Tetrahydronaphthalen-2-yl)ethyl]phosphonate (6o). Colorless oil, 98% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 5.8 min (minor), 13.6 min (major). $[\alpha]_D^{23}$ = +7.3 (*c* = 0.95, $CHCl_3$). R_f 0.3 (EtOAc/petroleum ether 1 : 2), R_f 0.26 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.2. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.01 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.23 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.25 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.51 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.4 Hz, 3H, CH_3), 1.76 (m, 4H, CH_2), 2.72 (m, 4H, CH_2), 3.00 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.5 Hz, 1H, PCH), 4.45 (m, 1H, OCH), 4.61 (m, 1H, OCH), 6.97 (d, $^3J_{H,H}$=7.9 Hz, 1H, CH_{Ar}) 7.01 (dd, $^4J_{H,H}$=2.0 Hz, $^4J_{H,P}$=2.0 Hz, 1H, CH_{Ar}) 7.05 (ddd, $^3J_{H,H}$=7.9 Hz, $^4J_{H,H}$=2.0 Hz, $^4J_{H,P}$=2.0 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.85 (d, $^2J_{C,P}$=5.0 Hz, CH_3), 23.15 (CH_2), 23.19 (CH_2), 23.35 (d, $^3J_{C,P}$=5.6 Hz, CH_3), 23.88 (d, $^3J_{C,P}$=5.3 Hz, CH_3) 24.03 (d, $^3J_{C,P}$=3.4 Hz, CH_3) 24.22(d, $^3J_{C,P}$=3.2 Hz, CH_3), 28.97 (d, $J_{C,P}$=0.7 Гц, CH_2), 29.32 (CH_2), 38.58 (d, $^1J_{C,P}$=139.5 Hz, PCH), 70.00 (d, $^2J_{C,P}$=7.4 Hz, OCH), 70.63 (d, $^2J_{C,P}$=7.2 Hz, OCH), 125.73 (d, $^3J_{C,P}$=6.4 Hz, CH_{Ar}), 128.93 (d, $^4J_{C,P}$=2.6 Hz, CH_{Ar}), 129.40 (d, $^3J_{C,P}$=6.9 Hz, CH_{Ar}), 135.05 (d, $^2J_{C,P}$=6.6 Hz, C_{Ar}), 135.62 (d, $^5J_{C,P}$=3.5 Hz, C_{Ar}), 136.78 (d, $^4J_{C,P}$=2.5 Hz, C_{Ar}). HRMS

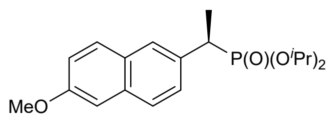
(ESI): found 325.1927, calcd. for $[M + H]^+$ ($C_{18}H_{30}O_3P$) 325.1927. When stored for a long time at room temperature, the substance **6o** crystallizes, forming crystals suitable for X-ray structural analysis.



Diisopropyl (*R*)-(+)-[1-(4-diphenyl)ethyl]phosphonate (6p). Colorless oil, 96% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min, t_R = 15.2 min (minor), 16.9 min (major). $[\alpha]_D^{26}$ = +8.6 (*c* = 0.9, $CHCl_3$). R_f 0.31 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.2. ^1H NMR (400 MHz, $CDCl_3$, δ): 1.00 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.29 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.59 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.4 Hz, 3H, CH_3), 3.14 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.7 Hz, 1H, PCH), 4.49 (m, 1H, OCH), 4.64 (m, 1H, OCH), 7.31 (m, $^3J_{H,H}$=7.4 Hz, 1H, CH_{Ph}), 7.43 (m, 2H, CH_{Ph}), 7.44 (dd, $^3J_{H,H}$=8.4 Hz, $^4J_{H,P}$=2.3 Hz, 2H, CH_{Ar}), 7.54 (d, $^3J_{H,H}$=8.4 Hz, 2H, CH_{Ar}), 7.58 (m, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.74 (d, $^2J_{C,P}$=5.2 Hz, CH_3), 23.32 (d, $^3J_{C,P}$=5.5 Hz, CH_3), 23.87 (d, $^3J_{C,P}$=5.4 Hz, CH_3) 23.99 (d, $^3J_{C,P}$=3.1 Hz, CH_3) 24.16 (br, CH_3), 38.67 (d, $^1J_{C,P}$=139.6 Hz, PCH), 70.09 (d, $^2J_{C,P}$=7.1 Hz, OCH), 70.72 (d, $^2J_{C,P}$=7.1 Hz, OCH), 126.83 (d, $^4J_{C,P}$=2.6 Hz, $2CH_{Ar}$), 126.86 ($2CH_{Ph}$), 127.08 (CH_{Ph}), 128.63 (CH_{Ph}), 129.03 (d, $^3J_{C,P}$=6.6 Hz, $2CH_{Ar}$), 137.37 (d, $^2J_{CP}$=6.7 Hz, C_{Ar}), 139.61 (br, C_{Ar}), 140.70 (C_{Ph}). HRMS (ESI): found 347.1770, calcd. for $[M + H]^+$ ($C_{20}H_{27}O_3P$) 347.1771.

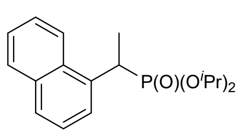


Diisopropyl (*R*)-(+)-[1-(naphthalen-2-yl)ethyl]phosphonate (6q). Colorless oil, 97% *ee*. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 200, flow rate = 1.0 ml/min, t_R = 34.9 min (major), 39.7 min (minor). $[\alpha]_D^{24}$ = +11.8 (*c* = 0.94, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +8.0 (*c* = 1.0, $CHCl_3$) for 91% *ee* (*R*)). R_f 0.3 (EtOAc/petroleum ether 1 : 2), R_f 0.27 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.2. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.93 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.21 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.25 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.64 (dd, $^3J_{H,H}$=7.4 Hz, $^3J_{H,P}$=18.3 Hz, 3H, CH_3), 3.26 (dq, $^3J_{H,H}$=7.4 Hz, $^2J_{H,P}$=22.7 Hz, 1H, PCH), 4.44 (m, 1H, OCH), 4.63 (m, 1H, OCH), 7.44 (m, 2H, CH_{Ar}), 7.51 (ddd, $^3J_{H,H}$=8.6 Hz, $^4J_{H,H}$=1.7 Hz, $^4J_{H,P}$=1.7 Hz, 1H, CH_{Ar}), 7.76-7.82 (m, 4H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.85 (d, $^2J_{C,P}$=5.3 Hz, CH_3), 23.33 (d, $^3J_{C,P}$=5.6 Hz, CH_3), 23.86 (d, $^3J_{C,P}$=5.4 Hz, CH_3) 23.97 (d, $^3J_{C,P}$=3.7 Hz, CH_3) 24.12 (d, $^3J_{C,P}$=2.6 Hz, CH_3), 39.11 (d, $^1J_{C,P}$=139.5 Hz, PCH), 70.09 (d, $^2J_{C,P}$=7.0 Hz, OCH), 70.67 (d, $^2J_{C,P}$=7.1 Hz, OCH), 125.51 (CH_{Ar}), 125.86 (CH_{Ar}), 127.05 (d, $^3J_{C,P}$=5.3 Hz, CH_{Ar}), 127.29 (d, $^3J_{C,P}$=8.5 Hz, CH_{Ar}), 127.47 (CH_{Ar}), 127.61 (CH_{Ar}), 127.69 (CH_{Ar}), 132.36 (C_{Ar}), 133.23 (C_{Ar}), 135.88 (d, $^2J_{C,P}$=6.9 Hz, C_{Ar}). HRMS (ESI): found 321.1614, calcd. for $[M + H]^+$ ($C_{18}H_{26}O_3P$) 321.1614.

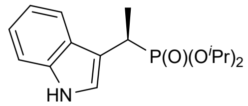


Diisopropyl (*R*)-(+)-[1-(6-methoxynaphthalen-2-yl)ethyl]phosphonate (6r). White solid, 96% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min, t_R = 18.9 min (minor), 34.2 min (major). $[\alpha]_D^{24}$ = +15.2 (*c* = 1.0, $CHCl_3$) (lit.[19] $[\alpha]_D^{20}$ = +15.4 (*c* = 1.0, $CHCl_3$) for 92% *ee* (*R*)). Mp 82-84°C; R_f 0.32 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 28.4. ^1H NMR (400 MHz, $CDCl_3$, δ): 0.92 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.21 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.24 (d, $^3J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d,

$^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.62 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{3}J_{H,P}$=18.4 Hz, 3H, CH_3), 3.22 (dq, $^{3}J_{H,H}$=7.3 Hz, $^{2}J_{H,P}$=22.7 Hz, 1H, PCH), 4.42 (m, 1H, OCH), 4.62 (m, 1H, OCH), 7.10 (br s, 1H, CH_{Ar}), 7.11 (dd, $^{3}J_{H,H}$=8.8 Hz, $^{4}J_{H,H}$=2.4 Hz, 1H, CH_{Ar}), 7.47 (ddd, $^{3}J_{H,H}$=8.5 Hz, $^{4}J_{H,H}$=1.5 Hz, $^{4}J_{H,P}$=1.5 Hz, 1H, CH_{Ar}), 7.67 (d, $^{3}J_{H,H}$=8.8 Hz, 1H, CH_{Ar}), 7.69 (d, $^{3}J_{H,H}$=8.5 Hz, 1H, CH_{Ar}), 7.70 (br s, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 15.94 (d, $^{2}J_{C,P}$=5.0 Hz, CH_3), 23.39 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3), 23.93 (d, $^{3}J_{C,P}$=5.2 Hz, CH_3) 24.03 (d, $^{3}J_{C,P}$=3.4 Hz, CH_3) 24.20 (d, $^{3}J_{C,P}$=3.1 Hz, CH_3), 38.92 (d, $^{1}J_{C,P}$=139.8 Hz, PCH), 55.21 (OCH_3), 70.08 (d, $^{2}J_{C,P}$=7.5 Hz, OCH), 70.70 (d, $^{2}J_{C,P}$=7.2 Hz, OCH), 105.47 (CH_{Ar}), 118.74 (CH_{Ar}), 126.60 (d, $^{4}J_{C,P}$=1.7 Hz, CH_{Ar}), 127.17 (d, $^{3}J_{C,P}$=8.3 Hz, CH_{Ar}), 127.60 (d, $^{3}J_{CP}$=5.2 Hz, CH_{Ar}), 129.16 (CH_{Ar}), 128.78 (d, $J_{C,P}$=2.3 Hz, C_{Ar}), 133.50 (d, $J_{C,P}$=2.3 Hz, C_{Ar}), 133.51 (d, $^{2}J_{C,P}$=6.8 Hz, C_{Ar}), 157.43 (CO_{Ar}). HRMS (ESI): found 351.1714, calcd. for $[M + H]^+$ ($C_{19}H_{28}O_4P$) 351.1720.

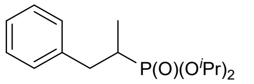


Diisopropyl [1-(naphthalen-1-yl)ethyl]phosphonate (6s). Colorless oil, 5% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 6.0 min (minor), 15.6 min (major). R_f 0.31 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.1. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.55 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.13 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.26 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.27 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.68 (dd, $^{3}J_{H,H}$=7.3 Hz, $^{3}J_{H,P}$=18.3 Hz, 3H, CH_3), 4.02 (dq, $^{3}J_{H,H}$=7.3 Hz, $^{2}J_{H,P}$=23.2 Hz, 1H, PCH), 4.32 (m, 1H, OCH), 4.67 (m, 1H, OCH), 7.44-7.48 (m, 2H, CH_{Ar}) 7.51 (m, 1H, CH_{Ar}), 7.72-7.75 (m, 2H, CH_{Ar}), 7.84 (dd, $^{3}J_{H,H}$=8.0 Hz, J=1.4 Hz, 1H, CH_{Ar}), 8.11 (d, $^{3}J_{H,H}$=8.5 Hz, 1H, CH_{Ar}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 16.57 (d, $^{2}J_{C,P}$=5.0 Hz, CH_3), 22.88 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3), 23.97 (d, $^{3}J_{C,P}$=5.3 Hz, CH_3) 24.05 (d, $^{3}J_{C,P}$=3.5 Hz, CH_3) 24.21 (d, $^{3}J_{C,P}$=3.1 Hz, CH_3), 32.80 (br d, $^{1}J_{CP}$=140.4 Hz, PCH), 70.05 (d, $^{2}J_{C,P}$=7.5 Hz, OCH), 70.93 (d, $^{2}J_{C,P}$=7.4 Hz, OCH), 123.45 (CH_{Ar}), 125.35 (CH_{Ar}), 125.37 (d, $J_{C,P}$=4.8 Hz, CH_{Ar}), 125.85 (CH_{Ar}), 126.03 (d, $J_{C,P}$=6.4 Hz, CH_{Ar}), 127.26 (d, $J_{C,P}$=3.3 Hz, CH_{Ar}), 128.78 (d, $J_{C,P}$=0.8 Hz, CH_{Ar}), 131.87 (d, $J_{C,P}$=7.4 Hz, C_{Ar}), 133.82 (d, $J_{C,P}$=1.7 Hz, C_{Ar}), 134.89 (d, $J_{C,P}$=6.1 Hz, C_{Ar}). HRMS (ESI): found 321.1610, calcd. for $[M + H]^+$ ($C_{18}H_{26}O_3P$) 321.1614.

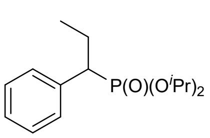


Diisopropyl (*R*)-(+)-[1-(1*H*-indol-3-yl)ethyl]phosphonate (6t). White solid, 47% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 9.6 min (minor), 21.3 min (major). $[\alpha]_D^{26}$ = +3.9 (c = 1.2, $CHCl_3$). Mp 85-87°C; R_f 0.35 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 29.8. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.75 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.20 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.30 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.33 (d, $^{3}J_{H,H}$=6.2 Hz, 3H, CH_3), 1.60 (dd, $^{3}J_{H,H}$=7.4 Hz, $^{3}J_{H,P}$=18.3 Hz, 3H, CH_3), 3.45 (dq, $^{3}J_{H,H}$=7.4 Hz, $^{2}J_{H,P}$=22.0 Hz, 1H, PCH), 4.43 (m, 1H, OCH), 4.72 (m, 1H, OCH), 7.04 (dd, $^{3}J_{H,H}$=2.9 Hz, $^{4}J_{H,P}$=2.9 Hz, 1H, CH_{Ar}), 7.08 (ddd, $^{3}J_{H,H}$=7.8 Hz, $^{3}J_{H,H}$=7.0 Hz, $^{4}J_{H,H}$=1.0 Hz, 1H, CH_{Ar}), 7.14 (ddd, $^{3}J_{H,H}$=7.9 Hz, $^{3}J_{H,H}$=7.0 Hz, $^{4}J_{H,H}$=1.1 Hz, 1H, CH_{Ar}), 7.33 (br. d, $^{3}J_{H,H}$=7.9 Hz, 1H, CH_{Ar}), 7.66 (br d, $^{3}J_{H,H}$=7.8 Hz, 1H, CH_{Ar}), 9.49 (br s, 1H, NH). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 16.25 (d, $^{2}J_{C,P}$=3.8 Hz, CH_3), 23.20 (d, $^{3}J_{C,P}$=3.8 Hz, CH_3), 23.20 (d, $^{3}J_{C,P}$=5.3 Hz, CH_3) 24.04 (d, $^{3}J_{C,P}$=5.5 Hz, CH_3) 24.09 (d, $^{3}J_{C,P}$=4.0 Hz, CH_3), 29.57 (d, $^{1}J_{C,P}$=144.8 Hz), 70.10 (d, $^{2}J_{C,P}$=7.6 Hz, OCH), 70.95 (d, $^{2}J_{C,P}$=7.4 Hz, OCH), 111.20 (CH_{Ar}), 112.38 (d, $^{2}J_{C,P}$=7.6 Hz,

C_{Ar}), 119.07 (CH_{Ar}), 119.28 (CH_{Ar}), 121.74 (CH_{Ar}), 122.93 (d, $^3J_{C,P}$=6.9 Hz, CH_{Ar}), 127.10 (d, $^3J_{C,P}$=6.5 Hz, C_{Ar}), 135.92 (C_{Ar}). HRMS (ESI): found 310.1570, calcd. for $[M + H]^+$ ($C_{16}H_{25}NO_3P$) 310.1567.

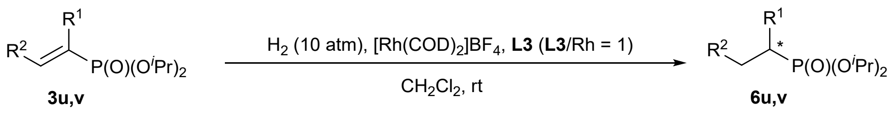


Diisopropyl (1-phenylpropan-2-yl)phosphonate (6u). Colorless oil, 13% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 5.8 min (minor), 15.3 min (major). R_f 0.35 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 32.5. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 1.02 (dd, $^3J_{H,H}$=7.1 Hz, $^3J_{P,H}$=18.5 Hz, 3H, PCHC$\underline{H}_3$), 1.31-1.34 (m, 12H, OCHC$\underline{H}_3$), 2.00 (m, $^3J_{H,H}$=$^3J_{H,H}$=7.1 Hz, $^3J_{H,H}$=3.2 Hz, $^2J_{P,H}$=24.0 Hz, 1H, PCH), 2.42 (ddd, $^2J_{H,H}$=13.6 Hz, $^3J_{H,H}$=7.1 Hz, $^3J_{P,H}$=11.6 Hz, 1H, $PhCH_2$), 3.22 (ddd, $^2J_{H,H}$=13.6 Hz, $^3J_{H,H}$=3.2 Hz, $^3J_{P,H}$=9.4 Hz, 1H, $PhCH_2$), 4.73 (m, 2H, OCH), 7.16 (d, $^3J_{H,H}$=7.5 Hz, 2H, CH_{Ph}), 7.20 (t, $^3J_{H,H}$=7.1 Hz, 1H, CH_{Ph}), 7.28 (t, $^3J_{H,H}$=7.3 Hz, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 12.49 (d, $^2J_{P,C}$=6.3 Hz, PCH$\underline{C}H_3$), 23.96-24.13 (m, 4OCH$\underline{C}H_3$), 33.54 (d, $^1J_{P,C}$=142.3 Hz, PCH), 36.13 (br, $PhCH_2$), 69.82 (d, $^2J_{P,C}$=6.6 Hz, OCH), 126.16 (CH_{Ph}), 128.29 ($2CH_{Ph}$), 128.99 ($2CH_{Ph}$), 139.59 (d, $^3J_{P,C}$=17.2 Hz, C_{Ph}). HRMS (ESI): found 285.1617, calcd. for $[M + H]^+$ ($C_{15}H_{26}O_3P$) 285.1614.



Diisopropyl (+)-(1-phenylpropyl)phosphonate (6v). Colorless oil, 46% yield, 55% *ee*. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min, t_R = 4.3 min (minor), 6.1 min (major). $[\alpha]_D^{23}$ = +2.1° (*c* = 0.95, $CHCl_3$). R_f 0.38 (*i*-PrOH/petroleum ether 1 : 10). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 27.6. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.81 (dt, $^3J_{H,H}$=7.3 Hz, $^4J_{P,H}$=0.6 Hz, $CH_2C\underline{H}_3$), 0.85 (d, $^3J_{H,H}$=6.2 Hz, 3H, CHC$\underline{H}_3$), 1.19 (d, $^3J_{H,H}$=6.2 Hz, 3H, CHC$\underline{H}_3$), 1.26 (d, $^3J_{H,H}$=6.2 Hz, 3H, CHC$\underline{H}_3$), 1.27 (d, $^3J_{H,H}$=6.2 Hz, 3H, CHC$\underline{H}_3$), 1.92 (m,1H, CH_2), 2.13 (m, 1H, CH_2), 2.79 (ddd, $^3J_{H,H}$=3.9 Hz, $^3J_{H,H}$=11.3 Hz, $^2J_{P,H}$=22.3 Hz, 1H, PCH), 4.38 (m, 1H), 4.64 (m, 1H), 7.19-7.24 (m, 1H, CH_{Ph}), 7.25-7.32 (m, 4H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 12.52 (d, $^3J_{C,P}$=16.5 Hz, $CH_2\underline{C}H_3$), 23.13 (d, $^3J_{C,P}$=5.6 Hz, CHC$\underline{H}_3$), 23.32 (d, $^2J_{C,P}$=3.2 Hz, CH_2), 23.94 (d, $^3J_{C,P}$=5.6 Hz, CHC$\underline{H}_3$), 23.99 (d, $^3J_{C,P}$=5.5 Hz, CHC$\underline{H}_3$), 24.24 (d, $^3J_{C,P}$=4.5 Hz, CHC$\underline{H}_3$), 47.09 (d, $^1J_{C,P}$=138.9 Hz, PCH), 69.82 (d, $^2J_{C,P}$=7.4 Hz, OCH), 70.81 (d, $^2J_{C,P}$=7.2 Hz, OCH), 126.81 (d, $^5J_{C,P}$=1.7 Hz, CH_{Ph}), 128.21 (CH_{Ph}), 129.41 (d, $^3J_{C,P}$=6.4 Hz, CH_{Ph}), 136.43 (d, $^2J_{C,P}$=6.4 Hz, C_{Ph}). HRMS (ESI): found 285.1617, calcd. for $[M + H]^+$ ($C_{15}H_{26}O_3P$) 285.1614.

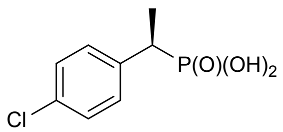
Table S1. L3/[Rh(COD)$_2$]BF$_4$-catalyzed asymmetric hydrogenation of α,β-unsaturated phosphonates 3u,v[a]



Entry	Substrate	R^1	R^2	S/C	Time [h]	Conversion [%][b]	*ee* [%][c]
1	**3u**	Bn	H	200	3	24	10
2					24	100	13
3	**3v**	Ph	Me	200	3	<1	n/d[d]
4				20	16	50	55

[a] The catalyst precursor was prepared *in situ* from [Rh(COD)$_2$]BF$_4$ and the ligand **L3** (**L3**/Rh = 1); reactions were carried out with substrate **3** (0.4 mmol) in CH_2Cl_2 (4 mL) at the specified substrate/catalyst ratio (S/C) for the indicated time. [b] Conversions were determined by ^{31}P NMR analysis of the crude reaction mixture. [c] Determined by chiral HPLC. [d] Not determined because of low conversion.

5. Synthesis of (*R*)-(+)-[1-(4-chlorophenyl)ethyl]phosphonic acid ((*R*)-(+)-7)



A solution of **6d** (126 mg, 0.413 mmol) in a mixture of water (150 µl) and conc. HCl (150 µl) was heated under reflux for 16 h. Volatile materials were thoroughly removed on a rotary evaporator and then *in vacuo* (0.05 Torr). The spectrally pure product (*R*)-(+)-**7** was obtained in quantitative yield (91 mg) as a white solid; $[\alpha]_D^{23}$ = +6.7 (*c* = 1.1, MeOH) (lit.[20] $[\alpha]_D^{20}$ = -6.5 (*c* = 1.1, MeOH) for 94% *ee* (*S*)). ^{31}P NMR (162 MHz, CD_3OD, δ): 29.3. ^{1}H NMR (400 MHz, CD_3OD, δ): 1.57 (dd, $^3J_{H,H}$=7.6 Hz, $^3J_{P,H}$=18.0 Hz, CH_3), 3.17 (dd, $^3J_{H,H}$=7.6 Hz, $^2J_{P,H}$=22.4 Hz, CH), 7.32 (d, $^3J_{H,H}$=8.4 Hz, 2H, CH_{Ar}), 7.37 (d, $^3J_{H,H}$=8.4 Hz, 2H, CH_{Ar}). Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of petroleum ether into a solution of the product in chloroform.

6. Synthesis and characterization of [Rh(COD)L3]BF_4

A solution of $[Rh(COD)_2]BF_4$ (40.6 mg, 0.100 mmol) and **L3** (66.2 mg, 0.100 mmol) in absolute DCM (3 ml) was stirred for 30 min at room temperature under an inert atmosphere. The solution was then concentrated under reduced pressure to a volume of ~1 ml and added dropwise to absolute petroleum ether (10 ml). The resulting precipitate was filtered off, washed with petroleum ether and dried *in vacuo*. The product was obtained as a mustard yellow solid (92.0 mg, 96% yield); $[\alpha]_D^{23}$ = -37.8 (*c* = 0.77, CH_2Cl_2). ^{31}P NMR (162 MHz, $CDCl_3$, δ): 96.3 (d, $^2J_{P,Rh}$ = 232.2). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.23 (s, 3H, CH_3), 0.32 (s, 3H, CH_3), 1.45 (br m, 1H, $CH_{2\ COD}$), 1.90 (br m, 2H, $CH_{2\ COD}$), 2.03 (br m, 2H, $CH_{2\ COD}$), 2.29 (br m, 1H, $CH_{2\ COD}$), 2.41 (s, 3H, SCH_3), 2.51 (br m, 1H, $CH_{2\ COD}$), 2.71 (m, 1H, $CH_{2\ COD}$), 2.99 (ddd, $^3J_{H,H}$ = 11.9 Hz, $^2J_{H,H}$ = 11.3 Hz, $^3J_{H,H}$ = 4.3 Hz, 1H, SCH_2), 3.05 (dd, $^2J_{H,H}$ = 11.3 Hz, $^3J_{H,H}$ = 4.0 Hz, 1H, SCH_2), 3.21 (ddd, $^3J_{P,H}$ = 27.8 Hz, $^2J_{H,H}$ = 15.2 Hz, $^3J_{H,H}$ = 4.3 Hz, 1H, NCH_2), 4.24 (br m, 1H, =CH(COD)), 4.53 (dddd, $^2J_{H,H}$ = 15.2 Hz, $^3J_{P,H}$ = 13.4 Hz, $^3J_{H,H}$ = 11.9 Hz, $^3J_{H,H}$ = 4.0 Hz, 1H, NCH_2), 4.91 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, OCH), 5.07 (br m, 1H, =CH_{COD}), 5.22 (d, $^3J_{H,H}$ = 7.8 Hz, 1H, OCH), 5.44 (br m, 1H, =CH_{COD}), 5.61 (br m, 1H, =CH_{COD}), 6.04 (br d, $^3J_{H,H}$ = 6.8 Hz, 2H, CH_{Ph}), 6.17 (dd, $^3J_{H,H}$ = 8.0 Hz, $^4J_{H,H}$ = 0.9 Hz, 2H, CH_{Ph}), 6.88 (t, $^3J_{H,H}$ = 7.8 Hz, 2H, CH_{Ph}), 7.00-7.02 (m, 2H, CH_{Ph}), 7.06 (t, $^3J_{H,H}$ = 7.4 Hz, 1H, CH_{Ph}), 7.15-7.22 (m, 5H, CH_{Ph}), 7.30 (t, $^3J_{H,H}$ = 7.3 Hz, 1H, CH_{Ph}), 7.54-7.60 (m, 6H, CH_{Ph}), 7.65 (t, $^3J_{H,H}$ = 7.4 Hz, 2H, CH_{Ph}), 7.78 (d, $^3J_{H,H}$ = 7.3 Hz, 2H, CH_{Ph}). ^{13}C NMR (101 MHz, $CDCl_3$, δ): 14.80 (d, *J* = 3.9 Hz, SCH_3), 26.24 (CH_3), 26.34 (CH_3), 28.44 ($CH_{2\ COD}$), 28.90 ($CH_{2\ COD}$), 29.57 (d, *J* = 3.3 Hz, $CH_{2\ COD}$), 33.15 ($CH_{2\ COD}$), 38.30 (SCH_2), 52.46 (d, *J* = 36.0 Hz, NCH_2), 79.28 (d, *J* = 2.8 Hz, OCH), 79.55 (d, *J* = 2.2 Hz, OCH), 79.69 (d, *J* = 11.1 Hz, =CH_{COD}), 88.09 (d, *J* = 2.7 Hz, CPh_2), 89.14 (d, *J* = 11.15 Hz, =CH_{COD}), 89.84 (d, *J* = 20.8 Hz, CPh_2), 102.90 (dd, *J* = 14.3 Hz, *J* = 5.7 Hz, =CH_{COD}), 109.32 (dd, *J* = 12.3 Hz, *J* = 5.9 Hz, =CH_{COD}), 115.52 (CMe_2), 126.89 (CH_{Ph}), 127.26 (CH_{Ph}), 127.41 (CH_{Ph}), 127.41 (CH_{Ph}), 127.45 (CH_{Ph}), 127.48 (CH_{Ph}), 127.71 (CH_{Ph}), 127.76 (CH_{Ph}), 128.40 (CH_{Ph}), 128.77 (CH_{Ph}), 129.00 (CH_{Ph}), 129.03 (CH_{Ph}), 129.39 (br, CH_{Ph}), 130.70 (CH_{Ph}), 139.58 (d, *J* = 6.2 Hz, C_{Ph}), 139.79 (d, *J* = 7.3 Hz, C_{Ph}), 140.58 (d, *J* = 7.9 Hz, C_{Ph}), 143.75 (C_{Ph}), 143.85 (C_{Ph}). HRMS (ESI): found 872.2410, calcd. for $[M + H]^+$ ($C_{48}H_{52}NO_4PRhS$) 872.2406.

Single crystals suitable for X-ray diffraction analysis were grown by slow diffusion of diethyl ether into a solution of [Rh(COD)**L3**]BF_4 in CH_2Cl_2.

7. References

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8. X-Ray structure determinations

Crystallographic study of the product 6o

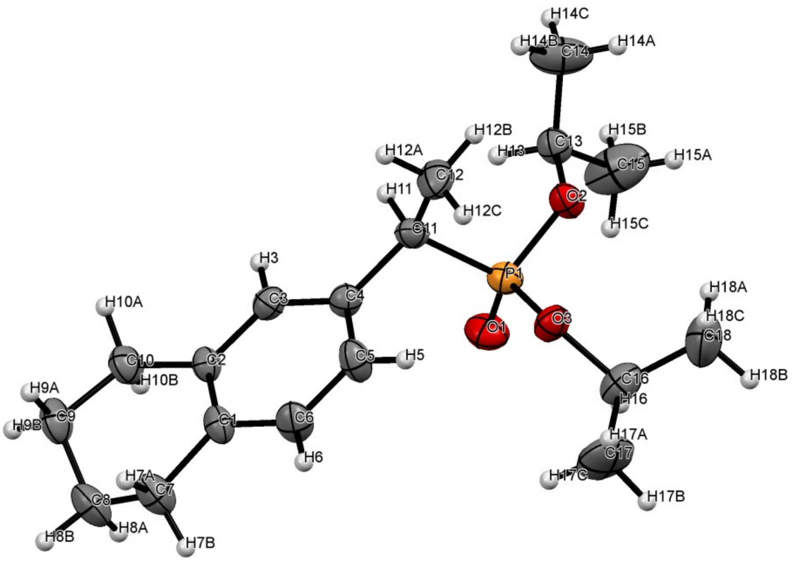


Table S2. Crystal data and structure refinement for **6o**.

CCDC number	2420900	
Empirical formula	$C_{18}H_{29}O_3P$	
Formula weight	324.38	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 8.9119(8) Å	α = 90°.
	b = 11.3949(7) Å	β = 90°.
	c = 18.6150(11) Å	γ = 90°.
Volume	1890.4(2) Å ^{3}	
Z	4	
Density (calculated)	1.140 Mg/m^3	
Absorption coefficient	0.155 mm^{-1}	
F(000)	704	
Theta range for data collection	2.096 to 28.238°.	
Index ranges	-11<=h<=11, -15<=k<=14, -24<=l<=24	
Reflections collected	50009	
Independent reflections	4607 [R(int) = 0.1778]	
Completeness to theta = 25.242°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4607 / 0 / 205	
Goodness-of-fit on F^2	0.652	
Final R indices [I>2sigma(I)]	R1 = 0.0426, wR2 = 0.0619	
R indices (all data)	R1 = 0.1853, wR2 = 0.0779	
Absolute structure parameter	-0.29(14)	
Extinction coefficient	0.0030(5)	
Largest diff. peak and hole	0.141 and -0.159 e·Å $^{-3}$	

Table S3. Bond lengths [Å] and angles [°] for **6o**.

P(1)-O(1)	1.461(3)	C(1)-C(7)	1.499(5)
P(1)-O(3)	1.572(3)	C(2)-C(3)	1.387(5)
P(1)-O(2)	1.573(3)	C(2)-C(10)	1.516(5)
P(1)-C(11)	1.804(4)	C(3)-C(4)	1.399(5)
O(2)-C(13)	1.469(5)	C(3)-H(3)	0.9300
O(3)-C(16)	1.445(5)	C(4)-C(5)	1.368(5)
C(1)-C(2)	1.373(5)	C(4)-C(11)	1.507(5)
C(1)-C(6)	1.397(5)	C(5)-C(6)	1.380(5)

C(5)-H(5)	0.9300	C(8)-C(7)-H(7A)	109.2
C(6)-H(6)	0.9300	C(1)-C(7)-H(7B)	109.2
C(7)-C(8)	1.521(5)	C(8)-C(7)-H(7B)	109.2
C(7)-H(7A)	0.9700	H(7A)-C(7)-H(7B)	107.9
C(7)-H(7B)	0.9700	C(9)-C(8)-C(7)	111.0(4)
C(8)-C(9)	1.485(6)	C(9)-C(8)-H(8A)	109.4
C(8)-H(8A)	0.9700	C(7)-C(8)-H(8A)	109.4
C(8)-H(8B)	0.9700	C(9)-C(8)-H(8B)	109.4
C(9)-C(10)	1.510(6)	C(7)-C(8)-H(8B)	109.4
C(9)-H(9A)	0.9700	H(8A)-C(8)-H(8B)	108.0
C(9)-H(9B)	0.9700	C(8)-C(9)-C(10)	110.6(4)
C(10)-H(10A)	0.9700	C(8)-C(9)-H(9A)	109.5
C(10)-H(10B)	0.9700	C(10)-C(9)-H(9A)	109.5
C(11)-C(12)	1.532(5)	C(8)-C(9)-H(9B)	109.5
C(11)-H(11)	0.9800	C(10)-C(9)-H(9B)	109.5
C(12)-H(12A)	0.9600	H(9A)-C(9)-H(9B)	108.1
C(12)-H(12B)	0.9600	C(9)-C(10)-C(2)	113.4(4)
C(12)-H(12C)	0.9600	C(9)-C(10)-H(10A)	108.9
C(13)-C(15)	1.458(6)	C(2)-C(10)-H(10A)	108.9
C(13)-C(14)	1.481(6)	C(9)-C(10)-H(10B)	108.9
C(13)-H(13)	0.9800	C(2)-C(10)-H(10B)	108.9
C(14)-H(14A)	0.9600	H(10A)-C(10)-H(10B)	107.7
C(14)-H(14B)	0.9600	C(4)-C(11)-C(12)	112.8(3)
C(14)-H(14C)	0.9600	C(4)-C(11)-P(1)	112.0(3)
C(15)-H(15A)	0.9600	C(12)-C(11)-P(1)	112.0(3)
C(15)-H(15B)	0.9600	C(4)-C(11)-H(11)	106.5
C(15)-H(15C)	0.9600	C(12)-C(11)-H(11)	106.5
C(16)-C(18)	1.480(6)	P(1)-C(11)-H(11)	106.5
C(16)-C(17)	1.490(6)	C(11)-C(12)-H(12A)	109.5
C(16)-H(16)	0.9800	C(11)-C(12)-H(12B)	109.5
C(17)-H(17A)	0.9600	H(12A)-C(12)-H(12B)	109.5
C(17)-H(17B)	0.9600	C(11)-C(12)-H(12C)	109.5
C(17)-H(17C)	0.9600	H(12A)-C(12)-H(12C)	109.5
C(18)-H(18A)	0.9600	H(12B)-C(12)-H(12C)	109.5
C(18)-H(18B)	0.9600	C(15)-C(13)-O(2)	109.5(4)
C(18)-H(18C)	0.9600	C(15)-C(13)-C(14)	113.8(4)
O(1)-P(1)-O(3)	116.06(18)	O(2)-C(13)-C(14)	107.4(3)
O(1)-P(1)-O(2)	114.25(17)	C(15)-C(13)-H(13)	108.7
O(3)-P(1)-O(2)	101.51(15)	O(2)-C(13)-H(13)	108.7
O(1)-P(1)-C(11)	114.85(19)	C(14)-C(13)-H(13)	108.7
O(3)-P(1)-C(11)	102.31(18)	C(13)-C(14)-H(14A)	109.5
O(2)-P(1)-C(11)	106.25(17)	C(13)-C(14)-H(14B)	109.5
C(13)-O(2)-P(1)	121.2(2)	H(14A)-C(14)-H(14B)	109.5
C(16)-O(3)-P(1)	122.8(3)	C(13)-C(14)-H(14C)	109.5
C(2)-C(1)-C(6)	118.8(4)	H(14A)-C(14)-H(14C)	109.5
C(2)-C(1)-C(7)	122.6(4)	H(14B)-C(14)-H(14C)	109.5
C(6)-C(1)-C(7)	118.6(4)	C(13)-C(15)-H(15A)	109.5
C(1)-C(2)-C(3)	119.7(4)	C(13)-C(15)-H(15B)	109.5
C(1)-C(2)-C(10)	120.9(4)	H(15A)-C(15)-H(15B)	109.5
C(3)-C(2)-C(10)	119.4(4)	C(13)-C(15)-H(15C)	109.5
C(2)-C(3)-C(4)	122.4(4)	H(15A)-C(15)-H(15C)	109.5
C(2)-C(3)-H(3)	118.8	H(15B)-C(15)-H(15C)	109.5
C(4)-C(3)-H(3)	118.8	O(3)-C(16)-C(18)	109.5(4)
C(5)-C(4)-C(3)	116.5(4)	O(3)-C(16)-C(17)	107.4(4)
C(5)-C(4)-C(11)	122.8(4)	C(18)-C(16)-C(17)	113.6(5)
C(3)-C(4)-C(11)	120.7(4)	O(3)-C(16)-H(16)	108.8
C(4)-C(5)-C(6)	122.3(4)	C(18)-C(16)-H(16)	108.8
C(4)-C(5)-H(5)	118.8	C(17)-C(16)-H(16)	108.8
C(6)-C(5)-H(5)	118.8	C(16)-C(17)-H(17A)	109.5
C(5)-C(6)-C(1)	120.3(4)	C(16)-C(17)-H(17B)	109.5
C(5)-C(6)-H(6)	119.9	H(17A)-C(17)-H(17B)	109.5
C(1)-C(6)-H(6)	119.9	C(16)-C(17)-H(17C)	109.5
C(1)-C(7)-C(8)	112.1(4)	H(17A)-C(17)-H(17C)	109.5
C(1)-C(7)-H(7A)	109.2	H(17B)-C(17)-H(17C)	109.5

C(16)-C(18)-H(18A)	109.5	C(16)-C(18)-H(18C)	109.5
C(16)-C(18)-H(18B)	109.5	H(18A)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18B)	109.5	H(18B)-C(18)-H(18C)	109.5

Table S4. Torsion angles [°] for **6o**.

O(1)-P(1)-O(2)-C(13)	45.8(4)
O(3)-P(1)-O(2)-C(13)	171.5(3)
C(11)-P(1)-O(2)-C(13)	-81.9(3)
O(1)-P(1)-O(3)-C(16)	41.0(4)
O(2)-P(1)-O(3)-C(16)	-83.5(4)
C(11)-P(1)-O(3)-C(16)	166.8(3)
C(6)-C(1)-C(2)-C(3)	0.2(6)
C(7)-C(1)-C(2)-C(3)	-178.2(4)
C(6)-C(1)-C(2)-C(10)	179.3(4)
C(7)-C(1)-C(2)-C(10)	0.9(6)
C(1)-C(2)-C(3)-C(4)	0.7(6)
C(10)-C(2)-C(3)-C(4)	-178.5(4)
C(2)-C(3)-C(4)-C(5)	-1.3(6)
C(2)-C(3)-C(4)-C(11)	179.4(4)
C(3)-C(4)-C(5)-C(6)	1.3(7)
C(11)-C(4)-C(5)-C(6)	-179.5(4)
C(4)-C(5)-C(6)-C(1)	-0.5(7)
C(2)-C(1)-C(6)-C(5)	-0.2(6)
C(7)-C(1)-C(6)-C(5)	178.2(4)
C(2)-C(1)-C(7)-C(8)	15.6(6)
C(6)-C(1)-C(7)-C(8)	-162.8(4)
C(1)-C(7)-C(8)-C(9)	-47.3(6)
C(7)-C(8)-C(9)-C(10)	63.1(5)
C(8)-C(9)-C(10)-C(2)	-45.4(5)
C(1)-C(2)-C(10)-C(9)	14.0(6)
C(3)-C(2)-C(10)-C(9)	-166.9(4)
C(5)-C(4)-C(11)-C(12)	-55.5(6)
C(3)-C(4)-C(11)-C(12)	123.6(4)
C(5)-C(4)-C(11)-P(1)	71.9(5)
C(3)-C(4)-C(11)-P(1)	-108.9(4)
O(1)-P(1)-C(11)-C(4)	50.9(4)
O(3)-P(1)-C(11)-C(4)	-75.7(3)
O(2)-P(1)-C(11)-C(4)	178.2(3)
O(1)-P(1)-C(11)-C(12)	178.8(3)
O(3)-P(1)-C(11)-C(12)	52.2(3)
O(2)-P(1)-C(11)-C(12)	-53.9(3)
P(1)-O(2)-C(13)-C(15)	-102.8(4)
P(1)-O(2)-C(13)-C(14)	133.2(3)
P(1)-O(3)-C(16)-C(18)	100.8(4)
P(1)-O(3)-C(16)-C(17)	-135.5(4)

Crystallographic study of the substance (*R*)-(+)-7

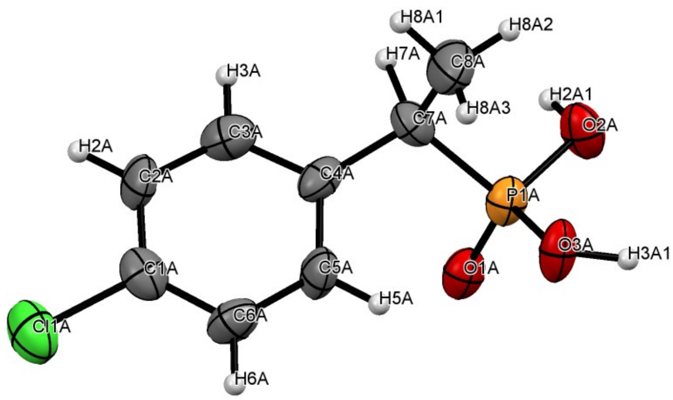


Table S5. Crystal data and structure refinement for (*R*)-(+)-**7**.

CCDC number	2207923	
Empirical formula	$C_8H_{10}ClO_3P$	
Formula weight	220.58	
Temperature	295(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	I 2	
Unit cell dimensions	a = 15.5220(10) Å	α = 90°.
	b = 5.6987(4) Å	β = 94.618(10)°.
	c = 26.800(3) Å	γ = 90°.
Volume	2362.9(3) $Å^3$	
Z	8	
Density (calculated)	1.240 Mg/m^3	
Absorption coefficient	0.435 mm^{-1}	
F(000)	912	
Theta range for data collection	2.546 to 28.351°.	
Index ranges	-18<=h<=20, -7<=k<=7, -35<=l<=35	
Reflections collected	16165	
Independent reflections	5274 [R(int) = 0.0968]	
Completeness to theta = 25.242°	99.9 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5274 / 1 / 246	
Goodness-of-fit on F^2	0.466	
Final R indices [I>2sigma(I)]	R1 = 0.0442, wR2 = 0.0736	
R indices (all data)	R1 = 0.2280, wR2 = 0.0988	
Absolute structure parameter	0.26(16)	
Largest diff. peak and hole	0.141 and -0.132 $e·Å^{-3}$	

Table S6. Bond lengths [Å] and angles [°] for (*R*)-(+)-**7**.

Cl(1A)-C(1A)	1.755(9)	C(4A)-C(7A)	1.502(11)
P(1A)-O(1A)	1.496(6)	C(5A)-C(6A)	1.362(12)
P(1A)-O(2A)	1.540(5)	C(5A)-H(5A)	0.9300
P(1A)-O(3A)	1.541(5)	C(6A)-H(6A)	0.9300
P(1A)-C(7A)	1.786(9)	C(7A)-C(8A)	1.537(11)
O(2A)-H(2A1)	0.9839	C(7A)-H(7A)	1.26(6)
O(3A)-H(3A1)	0.9727	C(8A)-H(8A1)	0.9600
C(1A)-C(2A)	1.381(13)	C(8A)-H(8A2)	0.9600
C(1A)-C(6A)	1.383(12)	C(8A)-H(8A3)	0.9600
C(2A)-C(3A)	1.387(12)	Cl(1B)-C(1B)	1.739(10)
C(2A)-H(2A)	0.9300	P(1B)-O(2B)	1.509(5)
C(3A)-C(4A)	1.383(11)	P(1B)-O(3B)	1.557(5)
C(3A)-H(3A)	0.9300	P(1B)-O(1B)	1.567(5)
C(4A)-C(5A)	1.400(11)	P(1B)-C(7B)	1.768(10)

O(1B)-H(1B1)	0.9764
O(3B)-H(3B1)	0.9746
C(1B)-C(6B)	1.342(14)
C(1B)-C(2B)	1.376(14)
C(2B)-C(3B)	1.386(14)
C(2B)-H(2B)	0.9300
C(3B)-C(4B)	1.341(11)
C(3B)-H(3B)	0.9300
C(4B)-C(5B)	1.367(11)
C(4B)-C(7B)	1.518(12)
C(5B)-C(6B)	1.353(12)
C(5B)-H(5B)	0.9300
C(6B)-H(6B)	0.9300
C(7B)-C(8B)	1.524(13)
C(7B)-H(7B)	0.86(4)
C(8B)-H(8B1)	0.9600
C(8B)-H(8B2)	0.9600
C(8B)-H(8B3)	0.9600
O(1A)-P(1A)-O(2A)	112.8(3)
O(1A)-P(1A)-O(3A)	113.4(3)
O(2A)-P(1A)-O(3A)	107.2(3)
O(1A)-P(1A)-C(7A)	111.2(4)
O(2A)-P(1A)-C(7A)	106.3(4)
O(3A)-P(1A)-C(7A)	105.4(4)
P(1A)-O(2A)-H(2A1)	106.7
P(1A)-O(3A)-H(3A1)	108.0
C(2A)-C(1A)-C(6A)	122.2(9)
C(2A)-C(1A)-Cl(1A)	118.0(9)
C(6A)-C(1A)-Cl(1A)	119.8(10)
C(1A)-C(2A)-C(3A)	116.6(9)
C(1A)-C(2A)-H(2A)	121.7
C(3A)-C(2A)-H(2A)	121.7
C(4A)-C(3A)-C(2A)	123.9(9)
C(4A)-C(3A)-H(3A)	118.0
C(2A)-C(3A)-H(3A)	118.0
C(3A)-C(4A)-C(5A)	116.0(9)
C(3A)-C(4A)-C(7A)	119.8(9)
C(5A)-C(4A)-C(7A)	124.2(8)
C(6A)-C(5A)-C(4A)	122.5(9)
C(6A)-C(5A)-H(5A)	118.8
C(4A)-C(5A)-H(5A)	118.8
C(5A)-C(6A)-C(1A)	118.7(9)
C(5A)-C(6A)-H(6A)	120.6
C(1A)-C(6A)-H(6A)	120.6
C(4A)-C(7A)-C(8A)	109.4(7)
C(4A)-C(7A)-P(1A)	113.3(7)
C(8A)-C(7A)-P(1A)	111.6(6)
C(4A)-C(7A)-H(7A)	105(3)
C(8A)-C(7A)-H(7A)	107(3)
P(1A)-C(7A)-H(7A)	110(3)
C(7A)-C(8A)-H(8A1)	109.5
C(7A)-C(8A)-H(8A2)	109.5
H(8A1)-C(8A)-H(8A2)	109.5
C(7A)-C(8A)-H(8A3)	109.5
H(8A1)-C(8A)-H(8A3)	109.5
H(8A2)-C(8A)-H(8A3)	109.5
O(2B)-P(1B)-O(3B)	115.1(3)
O(2B)-P(1B)-O(1B)	112.7(3)
O(3B)-P(1B)-O(1B)	105.5(3)
O(2B)-P(1B)-C(7B)	110.8(4)
O(3B)-P(1B)-C(7B)	102.9(4)
O(1B)-P(1B)-C(7B)	109.3(4)
P(1B)-O(1B)-H(1B1)	106.5
P(1B)-O(3B)-H(3B1)	107.4
C(6B)-C(1B)-C(2B)	119.3(10)
C(6B)-C(1B)-Cl(1B)	120.4(12)
C(2B)-C(1B)-Cl(1B)	120.2(13)
C(1B)-C(2B)-C(3B)	120.0(10)
C(1B)-C(2B)-H(2B)	120.0
C(3B)-C(2B)-H(2B)	120.0
C(4B)-C(3B)-C(2B)	119.7(10)
C(4B)-C(3B)-H(3B)	120.2
C(2B)-C(3B)-H(3B)	120.2
C(3B)-C(4B)-C(5B)	119.2(9)
C(3B)-C(4B)-C(7B)	119.7(10)
C(5B)-C(4B)-C(7B)	121.0(10)
C(6B)-C(5B)-C(4B)	121.5(10)
C(6B)-C(5B)-H(5B)	119.2
C(4B)-C(5B)-H(5B)	119.2
C(1B)-C(6B)-C(5B)	120.1(11)
C(1B)-C(6B)-H(6B)	120.0
C(5B)-C(6B)-H(6B)	120.0
C(4B)-C(7B)-C(8B)	115.4(9)
C(4B)-C(7B)-P(1B)	113.9(7)
C(8B)-C(7B)-P(1B)	110.3(7)
C(4B)-C(7B)-H(7B)	102(4)
C(8B)-C(7B)-H(7B)	106(4)
P(1B)-C(7B)-H(7B)	109(4)
C(7B)-C(8B)-H(8B1)	109.5
C(7B)-C(8B)-H(8B2)	109.5
H(8B1)-C(8B)-H(8B2)	109.5
C(7B)-C(8B)-H(8B3)	109.5
H(8B1)-C(8B)-H(8B3)	109.5
H(8B2)-C(8B)-H(8B3)	109.5

Table S7. Torsion angles [°] for (*R*)-(+)-**7**.

C(6A)-C(1A)-C(2A)-C(3A)	-1.4(15)
Cl(1A)-C(1A)-C(2A)-C(3A)	179.2(7)
C(1A)-C(2A)-C(3A)-C(4A)	-1.1(15)
C(2A)-C(3A)-C(4A)-C(5A)	2.0(14)
C(2A)-C(3A)-C(4A)-C(7A)	-178.4(9)
C(3A)-C(4A)-C(5A)-C(6A)	-0.5(14)
C(7A)-C(4A)-C(5A)-C(6A)	179.9(9)
C(4A)-C(5A)-C(6A)-C(1A)	-1.9(15)
C(2A)-C(1A)-C(6A)-C(5A)	2.9(15)
Cl(1A)-C(1A)-C(6A)-C(5A)	-177.8(8)
C(3A)-C(4A)-C(7A)-C(8A)	96.0(9)
C(5A)-C(4A)-C(7A)-C(8A)	-84.4(10)

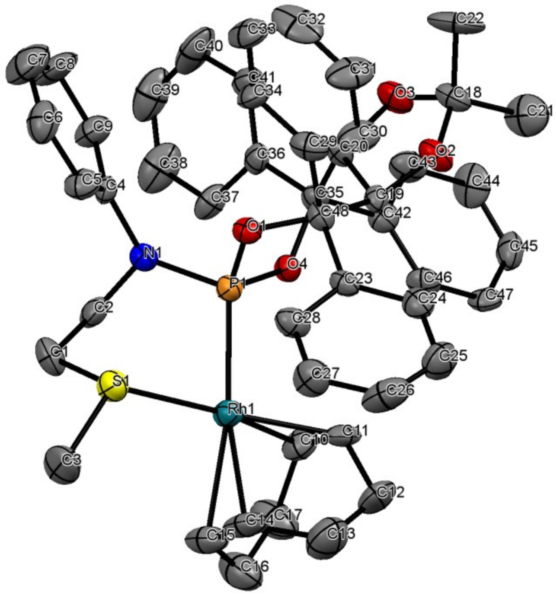
C(3A)-C(4A)-C(7A)-P(1A)	-138.8(7)
C(5A)-C(4A)-C(7A)-P(1A)	40.7(11)
O(1A)-P(1A)-C(7A)-C(4A)	42.1(7)
O(2A)-P(1A)-C(7A)-C(4A)	165.3(6)
O(3A)-P(1A)-C(7A)-C(4A)	-81.2(7)
O(1A)-P(1A)-C(7A)-C(8A)	166.1(6)
O(2A)-P(1A)-C(7A)-C(8A)	-70.8(7)
O(3A)-P(1A)-C(7A)-C(8A)	42.8(7)
C(6B)-C(1B)-C(2B)-C(3B)	-4.1(16)
Cl(1B)-C(1B)-C(2B)-C(3B)	177.4(8)
C(1B)-C(2B)-C(3B)-C(4B)	2.9(15)
C(2B)-C(3B)-C(4B)-C(5B)	-0.6(14)
C(2B)-C(3B)-C(4B)-C(7B)	178.9(9)
C(3B)-C(4B)-C(5B)-C(6B)	-0.5(14)
C(7B)-C(4B)-C(5B)-C(6B)	180.0(9)
C(2B)-C(1B)-C(6B)-C(5B)	3.0(16)
Cl(1B)-C(1B)-C(6B)-C(5B)	-178.5(8)
C(4B)-C(5B)-C(6B)-C(1B)	-0.7(15)
C(3B)-C(4B)-C(7B)-C(8B)	147.9(9)
C(5B)-C(4B)-C(7B)-C(8B)	-32.6(12)
C(3B)-C(4B)-C(7B)-P(1B)	-83.0(10)
C(5B)-C(4B)-C(7B)-P(1B)	96.5(10)
O(2B)-P(1B)-C(7B)-C(4B)	172.3(7)
O(3B)-P(1B)-C(7B)-C(4B)	-64.2(9)
O(1B)-P(1B)-C(7B)-C(4B)	47.6(9)
O(2B)-P(1B)-C(7B)-C(8B)	-56.1(8)
O(3B)-P(1B)-C(7B)-C(8B)	67.5(8)
O(1B)-P(1B)-C(7B)-C(8B)	179.2(7)

Table S8. Hydrogen bonds for (*R*)-(+)-**7** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(2A)-H(2A1)...O(2B)#1	0.98	1.80	2.582(6)	133.5
O(3A)-H(3A1)...O(2B)#2	0.97	1.64	2.529(7)	149.8
O(1B)-H(1B1)...O(1A)#3	0.98	1.60	2.542(6)	159.4
O(3B)-H(3B1)...O(1A)#4	0.97	2.01	2.580(8)	114.9
O(3B)-H(3B1)...O(2A)#5	0.97	2.65	3.414(8)	135.7
C(2B)-H(2B)...Cl(1A)#3	0.93	2.88	3.784(11)	163.7

Symmetry transformations used to generate equivalent atoms:
#1 x-1/2,y+1/2,z-1/2 #2 x-1/2,y-1/2,z-1/2 #3 -x+1/2,y-1/2,-z+1/2
#4 -x+1/2,y+1/2,-z+1/2 #5 x+1/2,y+1/2,z+1/2

Crystallographic study of the catalyst precursor [Rh(COD)L3]BF_4



Hydrogen atoms, the BF_4^- counteranion and solvate molecules of CH_2Cl_2 are omitted for clarity.

Table S9. Crystal data and structure refinement for [Rh(COD)**L3**]BF_4.

CCDC number	2420900	
Empirical formula	C51 H55 B Cl9 F4 N O4 P Rh S	
Formula weight	1317.76	
Temperature	295(2) K	
Wavelength	0.71068 Å	
Crystal system	Orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 16.8778(8) Å	α = 90°.
	b = 16.9391(8) Å	β = 90°.
	c = 20.3030(7) Å	γ = 90°.
Volume	5804.5(4) Å^3	
Z	4	
Density (calculated)	1.508 Mg/m^3	
Absorption coefficient	0.828 mm^{-1}	
F(000)	2680	
Theta range for data collection	2.405 to 28.633°.	
Index ranges	-22<=h<=22, -22<=k<=22, -26<=l<=26	
Reflections collected	80977	
Independent reflections	14049 [R(int) = 0.1356]	
Completeness to theta = 25.240°	99.8 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	14049 / 34 / 657	
Goodness-of-fit on F^2	0.770	
Final R indices [I>2sigma(I)]	R1 = 0.0591, wR2 = 0.1048	
R indices (all data)	R1 = 0.2525, wR2 = 0.1450	
Absolute structure parameter	-0.01(3)	
Largest diff. peak and hole	0.564 and -0.443 e·Å^{-3}	

Table S10. Bond lengths [Å] and angles [°] for [Rh(COD)**L3**]BF_4.

Rh(1)-C(11)	2.158(13)	Rh(1)-S(1)	2.355(3)
Rh(1)-C(10)	2.165(11)	P(1)-O(1)	1.591(8)
Rh(1)-C(14)	2.254(13)	P(1)-O(4)	1.614(6)
Rh(1)-P(1)	2.270(3)	P(1)-N(1)	1.654(9)
Rh(1)-C(15)	2.284(14)	S(1)-C(3)	1.788(12)

S(1)-C(1)	1.810(13)	C(25)-C(26)	1.336(17)
O(1)-C(48)	1.477(12)	C(25)-C(24)	1.400(17)
O(2)-C(19)	1.411(11)	C(25)-H(25)	0.9300
O(2)-C(18)	1.448(13)	C(24)-H(24)	0.9300
O(3)-C(18)	1.385(14)	C(26)-C(27)	1.378(19)
O(3)-C(20)	1.417(11)	C(26)-H(26)	0.9300
O(4)-C(35)	1.445(11)	C(27)-C(28)	1.361(17)
N(1)-C(2)	1.428(14)	C(27)-H(27)	0.9300
N(1)-C(4)	1.460(12)	C(28)-H(28)	0.9300
C(1)-C(2)	1.496(14)	C(29)-C(34)	1.363(16)
C(1)-H(1A)	0.9700	C(29)-C(30)	1.379(16)
C(1)-H(1B)	0.9700	C(29)-C(48)	1.555(15)
C(2)-H(2A)	0.9700	C(30)-C(31)	1.367(18)
C(2)-H(2B)	0.9700	C(30)-H(30)	0.9300
C(3)-H(3A)	0.9600	C(31)-C(32)	1.30(2)
C(3)-H(3B)	0.9600	C(31)-H(31)	0.9300
C(3)-H(3C)	0.9600	C(32)-C(33)	1.362(19)
C(4)-C(5)	1.359(13)	C(32)-H(32)	0.9300
C(4)-C(9)	1.361(13)	C(33)-C(34)	1.374(17)
C(5)-C(6)	1.365(16)	C(33)-H(33)	0.9300
C(5)-H(5)	0.9300	C(34)-H(34)	0.9300
C(6)-C(7)	1.368(18)	C(35)-C(36)	1.518(14)
C(6)-H(6)	0.9300	C(35)-C(42)	1.552(14)
C(7)-C(8)	1.321(19)	C(36)-C(41)	1.376(15)
C(7)-H(7)	0.9300	C(36)-C(37)	1.398(15)
C(8)-C(9)	1.374(16)	C(37)-C(38)	1.349(17)
C(8)-H(8)	0.9300	C(37)-H(37)	0.9300
C(9)-H(9)	0.9300	C(38)-C(39)	1.32(2)
C(10)-C(11)	1.325(16)	C(38)-H(38)	0.9300
C(10)-C(17)	1.527(18)	C(39)-C(40)	1.35(2)
C(10)-H(10)	0.9300	C(39)-H(39)	0.9300
C(11)-C(12)	1.502(17)	C(40)-C(41)	1.379(19)
C(11)-H(11)	0.9300	C(40)-H(40)	0.9300
C(12)-C(13)	1.465(18)	C(41)-H(41)	0.9300
C(12)-H(12A)	0.9700	C(42)-C(43)	1.373(14)
C(12)-H(12B)	0.9700	C(42)-C(46)	1.365(16)
C(13)-C(14)	1.47(2)	C(43)-C(44)	1.404(18)
C(13)-H(13A)	0.9700	C(43)-H(43)	0.9300
C(13)-H(13B)	0.9700	C(44)-C(45)	1.362(15)
C(14)-C(15)	1.34(2)	C(44)-H(44)	0.9300
C(14)-H(14)	0.9300	C(45)-C(47)	1.351(17)
C(15)-C(16)	1.511(19)	C(45)-H(45)	0.9300
C(15)-H(15)	0.9300	C(46)-C(47)	1.367(15)
C(16)-C(17)	1.386(18)	C(46)-H(46)	0.9300
C(16)-H(16A)	0.9700	C(47)-H(47)	0.9300
C(16)-H(16B)	0.9700	Cl(1)-C(60)	1.74(3)
C(17)-H(17A)	0.9700	Cl(2)-C(60)	1.61(2)
C(17)-H(17B)	0.9700	Cl(3)-C(60)	1.76(3)
C(18)-C(21)	1.491(16)	C(60)-H(60)	0.9800
C(18)-C(22)	1.547(15)	C(61)-Cl(5)	1.71(2)
C(19)-C(20)	1.501(13)	C(61)-Cl(6)	1.731(16)
C(19)-C(48)	1.572(13)	C(61)-Cl(4)	1.85(2)
C(19)-H(19)	0.9800	C(61)-H(61)	0.9800
C(20)-C(35)	1.518(14)	C(611)-Cl(51)	1.63(2)
C(20)-H(20)	0.9800	C(611)-Cl(61)	1.78(2)
C(21)-H(21A)	0.9600	C(611)-Cl(41)	1.87(2)
C(21)-H(21B)	0.9600	C(611)-H(611)	0.9801
C(21)-H(21C)	0.9600	F(1)-B(1)	1.31(2)
C(22)-H(22A)	0.9600	F(2)-B(1)	1.27(2)
C(22)-H(22B)	0.9600	F(3)-B(1)	1.34(3)
C(22)-H(22C)	0.9600	F(4)-B(1)	1.39(3)
C(23)-C(24)	1.367(16)	C(80)-Cl(9)	1.65(3)
C(23)-C(28)	1.363(14)	C(80)-Cl(8)	1.68(2)
C(23)-C(48)	1.505(14)	C(80)-Cl(7)	1.78(2)

C(80)-H(80)	0.9800
C(801)-Cl(81)	1.64(3)
C(801)-Cl(91)	1.68(3)
C(801)-Cl(71)	2.01(3)
C(801)-H(801)	0.9801
C(11)-Rh(1)-C(10)	35.7(4)
C(11)-Rh(1)-C(14)	80.0(5)
C(10)-Rh(1)-C(14)	92.1(5)
C(11)-Rh(1)-P(1)	97.0(3)
C(10)-Rh(1)-P(1)	96.1(4)
C(14)-Rh(1)-P(1)	161.2(6)
C(11)-Rh(1)-C(15)	88.0(5)
C(10)-Rh(1)-C(15)	79.3(5)
C(14)-Rh(1)-C(15)	34.4(5)
P(1)-Rh(1)-C(15)	164.4(5)
C(11)-Rh(1)-S(1)	168.8(4)
C(10)-Rh(1)-S(1)	155.5(4)
C(14)-Rh(1)-S(1)	96.2(4)
P(1)-Rh(1)-S(1)	83.16(12)
C(15)-Rh(1)-S(1)	94.8(4)
O(1)-P(1)-O(4)	105.2(4)
O(1)-P(1)-N(1)	96.9(4)
O(4)-P(1)-N(1)	111.9(4)
O(1)-P(1)-Rh(1)	120.4(3)
O(4)-P(1)-Rh(1)	110.7(3)
N(1)-P(1)-Rh(1)	111.0(3)
C(3)-S(1)-C(1)	100.4(6)
C(3)-S(1)-Rh(1)	115.6(5)
C(1)-S(1)-Rh(1)	105.8(4)
C(48)-O(1)-P(1)	127.3(6)
C(19)-O(2)-C(18)	108.5(9)
C(18)-O(3)-C(20)	111.8(9)
C(35)-O(4)-P(1)	131.1(6)
C(2)-N(1)-C(4)	113.9(9)
C(2)-N(1)-P(1)	114.7(8)
C(4)-N(1)-P(1)	129.1(8)
C(2)-C(1)-S(1)	109.0(9)
C(2)-C(1)-H(1A)	109.9
S(1)-C(1)-H(1A)	109.9
C(2)-C(1)-H(1B)	109.9
S(1)-C(1)-H(1B)	109.9
H(1A)-C(1)-H(1B)	108.3
N(1)-C(2)-C(1)	115.4(11)
N(1)-C(2)-H(2A)	108.4
C(1)-C(2)-H(2A)	108.4
N(1)-C(2)-H(2B)	108.4
C(1)-C(2)-H(2B)	108.4
H(2A)-C(2)-H(2B)	107.5
S(1)-C(3)-H(3A)	109.5
S(1)-C(3)-H(3B)	109.5
H(3A)-C(3)-H(3B)	109.5
S(1)-C(3)-H(3C)	109.5
H(3A)-C(3)-H(3C)	109.5
H(3B)-C(3)-H(3C)	109.5
C(5)-C(4)-C(9)	118.4(10)
C(5)-C(4)-N(1)	121.6(10)
C(9)-C(4)-N(1)	120.0(10)
C(4)-C(5)-C(6)	119.5(12)
C(4)-C(5)-H(5)	120.3
C(6)-C(5)-H(5)	120.3
C(5)-C(6)-C(7)	122.2(13)
C(5)-C(6)-H(6)	118.9
C(7)-C(6)-H(6)	118.9
C(8)-C(7)-C(6)	117.3(14)
C(8)-C(7)-H(7)	121.3
C(6)-C(7)-H(7)	121.3
C(7)-C(8)-C(9)	122.0(14)
C(7)-C(8)-H(8)	119.0
C(9)-C(8)-H(8)	119.0
C(4)-C(9)-C(8)	120.3(12)
C(4)-C(9)-H(9)	119.8
C(8)-C(9)-H(9)	119.8
C(11)-C(10)-C(17)	125.4(13)
C(11)-C(10)-Rh(1)	71.8(8)
C(17)-C(10)-Rh(1)	109.0(8)
C(11)-C(10)-H(10)	117.3
C(17)-C(10)-H(10)	117.3
Rh(1)-C(10)-H(10)	89.2
C(10)-C(11)-C(12)	126.1(14)
C(10)-C(11)-Rh(1)	72.5(8)
C(12)-C(11)-Rh(1)	111.9(9)
C(10)-C(11)-H(11)	116.9
C(12)-C(11)-H(11)	116.9
Rh(1)-C(11)-H(11)	85.5
C(13)-C(12)-C(11)	117.2(13)
C(13)-C(12)-H(12A)	108.0
C(11)-C(12)-H(12A)	108.0
C(13)-C(12)-H(12B)	108.0
C(11)-C(12)-H(12B)	108.0
H(12A)-C(12)-H(12B)	107.2
C(12)-C(13)-C(14)	117.2(13)
C(12)-C(13)-H(13A)	108.0
C(14)-C(13)-H(13A)	108.0
C(12)-C(13)-H(13B)	108.0
C(14)-C(13)-H(13B)	108.0
H(13A)-C(13)-H(13B)	107.2
C(15)-C(14)-C(13)	123.4(16)
C(15)-C(14)-Rh(1)	74.0(9)
C(13)-C(14)-Rh(1)	108.8(9)
C(15)-C(14)-H(14)	118.3
C(13)-C(14)-H(14)	118.3
Rh(1)-C(14)-H(14)	87.1
C(14)-C(15)-C(16)	124.6(17)
C(14)-C(15)-Rh(1)	71.6(9)
C(16)-C(15)-Rh(1)	109.7(9)
C(14)-C(15)-H(15)	117.7
C(16)-C(15)-H(15)	117.7
Rh(1)-C(15)-H(15)	88.8
C(17)-C(16)-C(15)	116.1(13)
C(17)-C(16)-H(16A)	108.3
C(15)-C(16)-H(16A)	108.3
C(17)-C(16)-H(16B)	108.3
C(15)-C(16)-H(16B)	108.3
H(16A)-C(16)-H(16B)	107.4
C(16)-C(17)-C(10)	119.1(13)
C(16)-C(17)-H(17A)	107.5
C(10)-C(17)-H(17A)	107.5
C(16)-C(17)-H(17B)	107.5
C(10)-C(17)-H(17B)	107.5
H(17A)-C(17)-H(17B)	107.0
O(3)-C(18)-O(2)	106.3(10)
O(3)-C(18)-C(21)	112.1(11)
O(2)-C(18)-C(21)	108.7(10)
O(3)-C(18)-C(22)	111.1(12)
O(2)-C(18)-C(22)	106.3(10)
C(21)-C(18)-C(22)	111.9(12)
O(2)-C(19)-C(20)	105.6(8)
O(2)-C(19)-C(48)	108.1(8)

C(20)-C(19)-C(48)	112.1(8)
O(2)-C(19)-H(19)	110.3
C(20)-C(19)-H(19)	110.3
C(48)-C(19)-H(19)	110.3
O(3)-C(20)-C(19)	104.0(8)
O(3)-C(20)-C(35)	112.7(8)
C(19)-C(20)-C(35)	112.5(9)
O(3)-C(20)-H(20)	109.1
C(19)-C(20)-H(20)	109.1
C(35)-C(20)-H(20)	109.1
C(18)-C(21)-H(21A)	109.5
C(18)-C(21)-H(21B)	109.5
H(21A)-C(21)-H(21B)	109.5
C(18)-C(21)-H(21C)	109.5
H(21A)-C(21)-H(21C)	109.5
H(21B)-C(21)-H(21C)	109.5
C(18)-C(22)-H(22A)	109.5
C(18)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(18)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(24)-C(23)-C(28)	116.9(11)
C(24)-C(23)-C(48)	123.1(10)
C(28)-C(23)-C(48)	119.7(11)
C(26)-C(25)-C(24)	118.6(13)
C(26)-C(25)-H(25)	120.7
C(24)-C(25)-H(25)	120.7
C(23)-C(24)-C(25)	122.0(10)
C(23)-C(24)-H(24)	119.0
C(25)-C(24)-H(24)	119.0
C(25)-C(26)-C(27)	120.8(14)
C(25)-C(26)-H(26)	119.6
C(27)-C(26)-H(26)	119.6
C(28)-C(27)-C(26)	119.1(11)
C(28)-C(27)-H(27)	120.5
C(26)-C(27)-H(27)	120.5
C(27)-C(28)-C(23)	122.5(12)
C(27)-C(28)-H(28)	118.7
C(23)-C(28)-H(28)	118.7
C(34)-C(29)-C(30)	121.1(13)
C(34)-C(29)-C(48)	121.6(13)
C(30)-C(29)-C(48)	117.3(13)
C(31)-C(30)-C(29)	117.0(14)
C(31)-C(30)-H(30)	121.5
C(29)-C(30)-H(30)	121.5
C(32)-C(31)-C(30)	123.0(16)
C(32)-C(31)-H(31)	118.5
C(30)-C(31)-H(31)	118.5
C(31)-C(32)-C(33)	120.5(16)
C(31)-C(32)-H(32)	119.8
C(33)-C(32)-H(32)	119.8
C(32)-C(33)-C(34)	119.8(15)
C(32)-C(33)-H(33)	120.1
C(34)-C(33)-H(33)	120.1
C(29)-C(34)-C(33)	118.7(13)
C(29)-C(34)-H(34)	120.7
C(33)-C(34)-H(34)	120.7
O(4)-C(35)-C(36)	110.4(9)
O(4)-C(35)-C(20)	107.8(8)
C(36)-C(35)-C(20)	113.8(9)
O(4)-C(35)-C(42)	104.8(8)
C(36)-C(35)-C(42)	108.6(9)
C(20)-C(35)-C(42)	111.1(9)
C(41)-C(36)-C(37)	117.0(11)
C(41)-C(36)-C(35)	123.4(12)
C(37)-C(36)-C(35)	119.5(11)
C(38)-C(37)-C(36)	120.0(14)
C(38)-C(37)-H(37)	120.0
C(36)-C(37)-H(37)	120.0
C(39)-C(38)-C(37)	122.4(18)
C(39)-C(38)-H(38)	118.8
C(37)-C(38)-H(38)	118.8
C(38)-C(39)-C(40)	120(2)
C(38)-C(39)-H(39)	120.1
C(40)-C(39)-H(39)	120.1
C(39)-C(40)-C(41)	120.3(19)
C(39)-C(40)-H(40)	119.8
C(41)-C(40)-H(40)	119.8
C(36)-C(41)-C(40)	120.4(15)
C(36)-C(41)-H(41)	119.8
C(40)-C(41)-H(41)	119.8
C(43)-C(42)-C(46)	117.9(10)
C(43)-C(42)-C(35)	119.2(11)
C(46)-C(42)-C(35)	122.7(10)
C(42)-C(43)-C(44)	118.0(13)
C(42)-C(43)-H(43)	121.0
C(44)-C(43)-H(43)	121.0
C(45)-C(44)-C(43)	123.0(15)
C(45)-C(44)-H(44)	118.5
C(43)-C(44)-H(44)	118.5
C(47)-C(45)-C(44)	117.9(14)
C(47)-C(45)-H(45)	121.1
C(44)-C(45)-H(45)	121.1
C(47)-C(46)-C(42)	123.3(10)
C(47)-C(46)-H(46)	118.4
C(42)-C(46)-H(46)	118.4
C(45)-C(47)-C(46)	120.0(12)
C(45)-C(47)-H(47)	120.0
C(46)-C(47)-H(47)	120.0
O(1)-C(48)-C(23)	109.9(8)
O(1)-C(48)-C(29)	105.6(9)
C(23)-C(48)-C(29)	111.3(9)
O(1)-C(48)-C(19)	105.6(8)
C(23)-C(48)-C(19)	112.6(9)
C(29)-C(48)-C(19)	111.3(8)
Cl(2)-C(60)-Cl(1)	113.3(14)
Cl(2)-C(60)-Cl(3)	114(2)
Cl(1)-C(60)-Cl(3)	108.6(14)
Cl(2)-C(60)-H(60)	106.8
Cl(1)-C(60)-H(60)	106.8
Cl(3)-C(60)-H(60)	106.8
Cl(5)-C(61)-Cl(6)	112.5(11)
Cl(5)-C(61)-Cl(4)	99.1(9)
Cl(6)-C(61)-Cl(4)	106.1(11)
Cl(5)-C(61)-H(61)	112.7
Cl(6)-C(61)-H(61)	112.7
Cl(4)-C(61)-H(61)	112.7
Cl(51)-C(611)-Cl(61)	120.4(18)
Cl(51)-C(611)-Cl(41)	106.8(17)
Cl(61)-C(611)-Cl(41)	91.1(15)
Cl(51)-C(611)-H(611)	112.1
Cl(61)-C(611)-H(611)	112.1
Cl(41)-C(611)-H(611)	112.1
F(2)-B(1)-F(1)	119.9(16)
F(2)-B(1)-F(3)	110(2)
F(1)-B(1)-F(3)	109(2)
F(2)-B(1)-F(4)	112(3)

F(1)-B(1)-F(4)	106(2)	Cl(7)-C(80)-H(80)	109.3
F(3)-B(1)-F(4)	98.2(15)	Cl(81)-C(801)-Cl(91)	114.4(19)
Cl(9)-C(80)-Cl(8)	112.3(18)	Cl(81)-C(801)-Cl(71)	103(2)
Cl(9)-C(80)-Cl(7)	113.0(14)	Cl(91)-C(801)-Cl(71)	95.6(14)
Cl(8)-C(80)-Cl(7)	103.4(13)	Cl(81)-C(801)-H(801)	114.0
Cl(9)-C(80)-H(80)	109.3	Cl(91)-C(801)-H(801)	114.0
Cl(8)-C(80)-H(80)	109.3	Cl(71)-C(801)-H(801)	114.0

Table S11. Torsion angles [°] for [Rh(COD)**L3**]BF_4.

O(4)-P(1)-O(1)-C(48)	-53.0(8)
N(1)-P(1)-O(1)-C(48)	-168.0(7)
Rh(1)-P(1)-O(1)-C(48)	72.7(8)
O(1)-P(1)-O(4)-C(35)	-38.7(9)
N(1)-P(1)-O(4)-C(35)	65.4(10)
Rh(1)-P(1)-O(4)-C(35)	-170.2(8)
O(1)-P(1)-N(1)-C(2)	-152.5(7)
O(4)-P(1)-N(1)-C(2)	98.0(8)
Rh(1)-P(1)-N(1)-C(2)	-26.2(8)
O(1)-P(1)-N(1)-C(4)	9.3(9)
O(4)-P(1)-N(1)-C(4)	-100.1(9)
Rh(1)-P(1)-N(1)-C(4)	135.6(8)
C(3)-S(1)-C(1)-C(2)	-157.5(10)
Rh(1)-S(1)-C(1)-C(2)	-36.9(10)
C(4)-N(1)-C(2)-C(1)	-75.7(13)
P(1)-N(1)-C(2)-C(1)	89.0(12)
S(1)-C(1)-C(2)-N(1)	-45.1(14)
C(2)-N(1)-C(4)-C(5)	90.8(13)
P(1)-N(1)-C(4)-C(5)	-71.2(13)
C(2)-N(1)-C(4)-C(9)	-88.7(12)
P(1)-N(1)-C(4)-C(9)	109.3(11)
C(9)-C(4)-C(5)-C(6)	3.7(17)
N(1)-C(4)-C(5)-C(6)	-175.9(11)
C(4)-C(5)-C(6)-C(7)	-1(2)
C(5)-C(6)-C(7)-C(8)	-3(3)
C(6)-C(7)-C(8)-C(9)	5(3)
C(5)-C(4)-C(9)-C(8)	-2(2)
N(1)-C(4)-C(9)-C(8)	178.0(13)
C(7)-C(8)-C(9)-C(4)	-3(3)
C(17)-C(10)-C(11)-C(12)	4(2)
Rh(1)-C(10)-C(11)-C(12)	104.7(14)
C(17)-C(10)-C(11)-Rh(1)	-100.7(12)
C(10)-C(11)-C(12)-C(13)	-76(2)
Rh(1)-C(11)-C(12)-C(13)	8(2)
C(11)-C(12)-C(13)-C(14)	10(3)
C(12)-C(13)-C(14)-C(15)	61(2)
C(12)-C(13)-C(14)-Rh(1)	-22(2)
C(13)-C(14)-C(15)-C(16)	-1(2)
Rh(1)-C(14)-C(15)-C(16)	101.6(13)
C(13)-C(14)-C(15)-Rh(1)	-102.3(13)
C(14)-C(15)-C(16)-C(17)	-83(2)
Rh(1)-C(15)-C(16)-C(17)	-2(2)
C(15)-C(16)-C(17)-C(10)	22(3)
C(11)-C(10)-C(17)-C(16)	50(2)
Rh(1)-C(10)-C(17)-C(16)	-30(2)
C(20)-O(3)-C(18)-O(2)	0.7(12)
C(20)-O(3)-C(18)-C(21)	119.4(11)
C(20)-O(3)-C(18)-C(22)	-114.5(11)
C(19)-O(2)-C(18)-O(3)	11.8(12)
C(19)-O(2)-C(18)-C(21)	-109.1(12)
C(19)-O(2)-C(18)-C(22)	130.3(11)
C(18)-O(2)-C(19)-C(20)	-18.9(10)
C(18)-O(2)-C(19)-C(48)	-139.0(9)

C(18)-O(3)-C(20)-C(19)	-12.0(12)
C(18)-O(3)-C(20)-C(35)	-134.1(10)
O(2)-C(19)-C(20)-O(3)	18.6(10)
C(48)-C(19)-C(20)-O(3)	136.2(9)
O(2)-C(19)-C(20)-C(35)	140.9(8)
C(48)-C(19)-C(20)-C(35)	-101.6(10)
C(28)-C(23)-C(24)-C(25)	-0.4(18)
C(48)-C(23)-C(24)-C(25)	172.7(11)
C(26)-C(25)-C(24)-C(23)	-3(2)
C(24)-C(25)-C(26)-C(27)	4(2)
C(25)-C(26)-C(27)-C(28)	-3(2)
C(26)-C(27)-C(28)-C(23)	0(2)
C(24)-C(23)-C(28)-C(27)	1.4(18)
C(48)-C(23)-C(28)-C(27)	-171.9(11)
C(34)-C(29)-C(30)-C(31)	-0.1(18)
C(48)-C(29)-C(30)-C(31)	178.0(11)
C(29)-C(30)-C(31)-C(32)	0(2)
C(30)-C(31)-C(32)-C(33)	0(3)
C(31)-C(32)-C(33)-C(34)	0(2)
C(30)-C(29)-C(34)-C(33)	-0.2(17)
C(48)-C(29)-C(34)-C(33)	-178.2(10)
C(32)-C(33)-C(34)-C(29)	0.4(18)
P(1)-O(4)-C(35)-C(36)	-76.7(11)
P(1)-O(4)-C(35)-C(20)	48.2(12)
P(1)-O(4)-C(35)-C(42)	166.6(7)
O(3)-C(20)-C(35)-O(4)	154.8(8)
C(19)-C(20)-C(35)-O(4)	37.5(11)
O(3)-C(20)-C(35)-C(36)	-82.5(11)
C(19)-C(20)-C(35)-C(36)	160.3(8)
O(3)-C(20)-C(35)-C(42)	40.5(12)
C(19)-C(20)-C(35)-C(42)	-76.7(11)
O(4)-C(35)-C(36)-C(41)	147.2(10)
C(20)-C(35)-C(36)-C(41)	25.8(14)
C(42)-C(35)-C(36)-C(41)	-98.5(12)
O(4)-C(35)-C(36)-C(37)	-36.5(12)
C(20)-C(35)-C(36)-C(37)	-157.9(9)
C(42)-C(35)-C(36)-C(37)	77.8(11)
C(41)-C(36)-C(37)-C(38)	-2.3(16)
C(35)-C(36)-C(37)-C(38)	-178.8(10)
C(36)-C(37)-C(38)-C(39)	2(2)
C(37)-C(38)-C(39)-C(40)	-1(3)
C(38)-C(39)-C(40)-C(41)	0(3)
C(37)-C(36)-C(41)-C(40)	1.9(16)
C(35)-C(36)-C(41)-C(40)	178.2(11)
C(39)-C(40)-C(41)-C(36)	-1(2)
O(4)-C(35)-C(42)-C(43)	159.3(10)
C(36)-C(35)-C(42)-C(43)	41.4(14)
C(20)-C(35)-C(42)-C(43)	-84.5(13)
O(4)-C(35)-C(42)-C(46)	-24.9(14)
C(36)-C(35)-C(42)-C(46)	-142.8(11)
C(20)-C(35)-C(42)-C(46)	91.3(13)
C(46)-C(42)-C(43)-C(44)	1.5(18)
C(35)-C(42)-C(43)-C(44)	177.5(12)
C(42)-C(43)-C(44)-C(45)	0(2)
C(43)-C(44)-C(45)-C(47)	0(3)
C(43)-C(42)-C(46)-C(47)	-1.8(18)
C(35)-C(42)-C(46)-C(47)	-177.7(10)
C(44)-C(45)-C(47)-C(46)	0(2)
C(42)-C(46)-C(47)-C(45)	1.0(18)
P(1)-O(1)-C(48)-C(23)	-68.9(10)
P(1)-O(1)-C(48)-C(29)	170.9(7)
P(1)-O(1)-C(48)-C(19)	52.8(10)
C(24)-C(23)-C(48)-O(1)	148.9(10)
C(28)-C(23)-C(48)-O(1)	-38.2(13)

C(24)-C(23)-C(48)-C(29)	-94.4(12)
C(28)-C(23)-C(48)-C(29)	78.5(13)
C(24)-C(23)-C(48)-C(19)	31.4(14)
C(28)-C(23)-C(48)-C(19)	-155.7(10)
C(34)-C(29)-C(48)-O(1)	-24.5(13)
C(30)-C(29)-C(48)-O(1)	157.4(9)
C(34)-C(29)-C(48)-C(23)	-143.8(11)
C(30)-C(29)-C(48)-C(23)	38.1(13)
C(34)-C(29)-C(48)-C(19)	89.7(13)
C(30)-C(29)-C(48)-C(19)	-88.4(12)
O(2)-C(19)-C(48)-O(1)	155.8(8)
C(20)-C(19)-C(48)-O(1)	39.8(11)
O(2)-C(19)-C(48)-C(23)	-84.2(11)
C(20)-C(19)-C(48)-C(23)	159.8(9)
O(2)-C(19)-C(48)-C(29)	41.6(12)
C(20)-C(19)-C(48)-C(29)	-74.4(12)

Table S12. Hydrogen bonds for [Rh(COD)**L3**]BF_4 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2A)...F(1)	0.97	2.45	3.322(16)	149.6
C(3)-H(3B)...F(1)#1	0.96	2.45	3.209(16)	136.1
C(5)-H(5)...S(1)	0.93	3.00	3.638(13)	126.8
C(21)-H(21C)...Cl(51)#2	0.96	2.89	3.51(3)	122.9
C(61)-H(61)...F(4)	0.98	2.16	3.11(2)	164.6
C(611)-H(611)...F(4)	0.98	2.18	3.11(2)	158.8

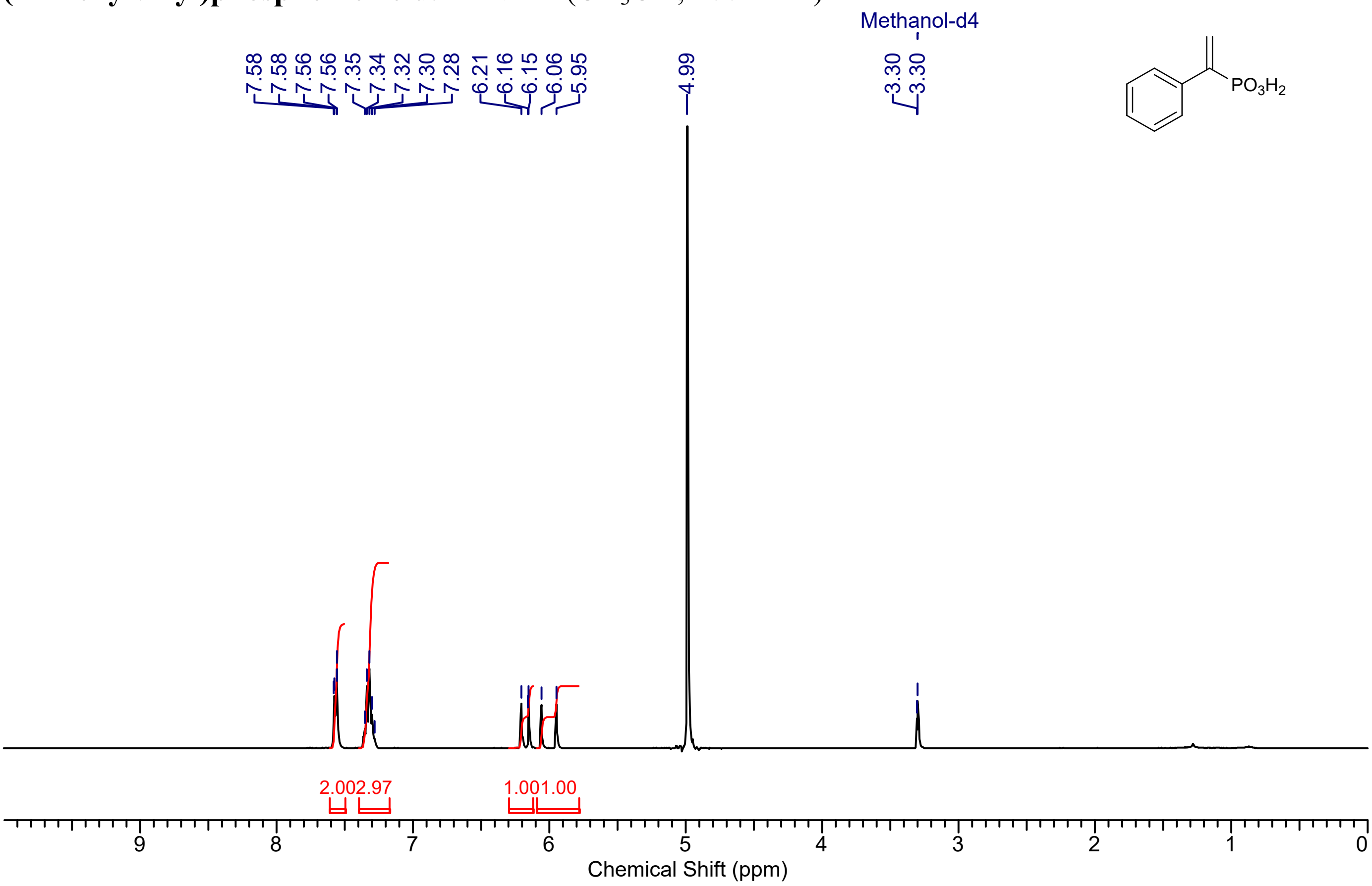
Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y-1/2,-z+1/2   #2 -x+1,y+1/2,-z+1/2

9. NBO atomic charges on the α-carbon atoms

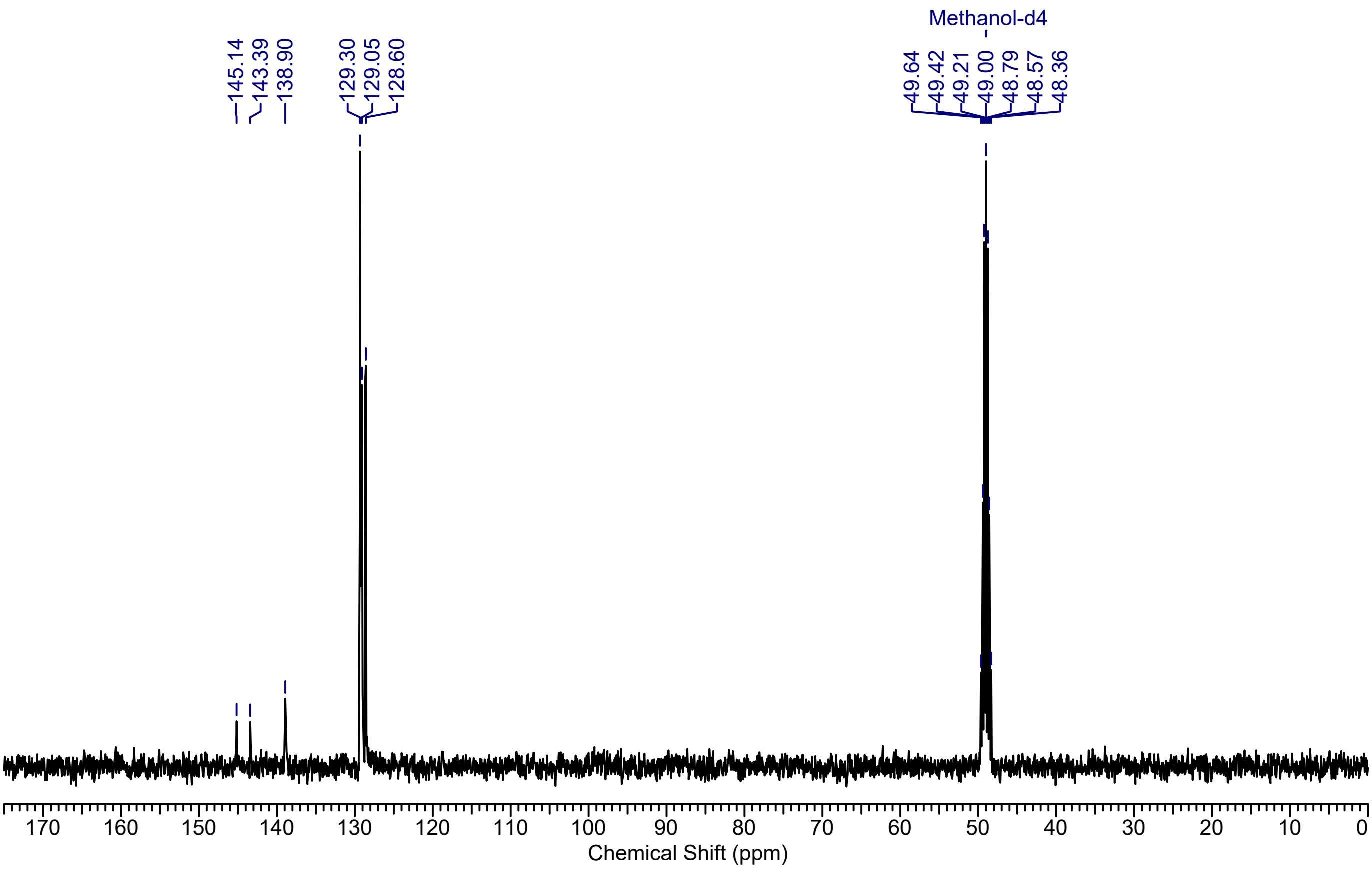
Diisopropyl (1-arylvinyl)phosphonate **3**	Charge [e]
6a	-0.4447
6b	-0.4462
6c	-0.4474
6d	-0.4466
6e	-0.4448
6f	-0.4479
6g	-0.4391
6h	-0.4524
6i	-0.4515
6j	-0.4442
6k	-0.4417
6l	-0.4430
6m	-0.4433
6n	-0.4428
6o	-0.4417
6p	-0.4451
6q	-0.4441
6r	-0.4427
6s	-0.4458
6t	-0.4394

10. ¹H and ¹³C NMR spectra

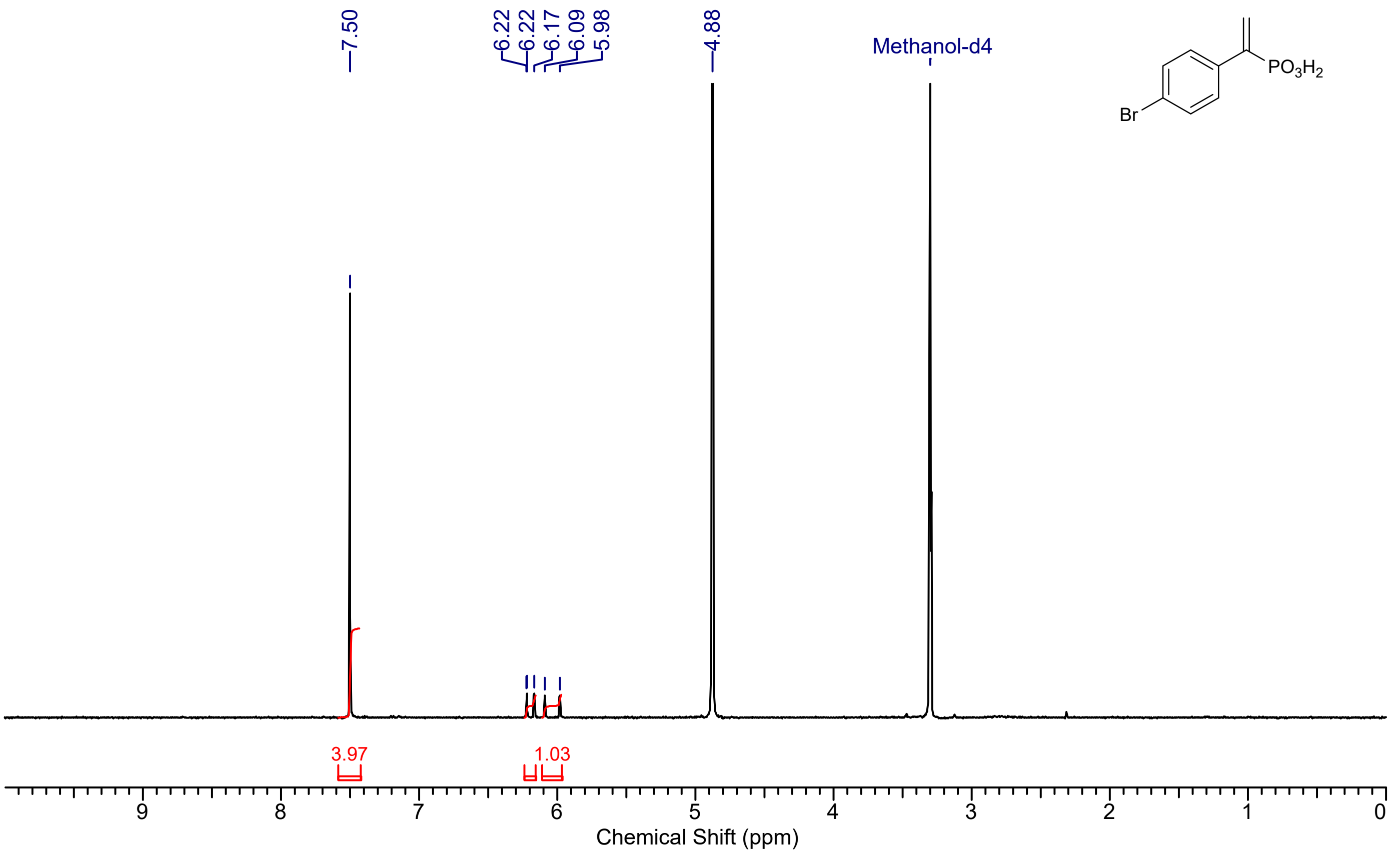
(1-Phenylvinyl)phosphonic acid: ¹H NMR (CD_3OD, 400 MHz)



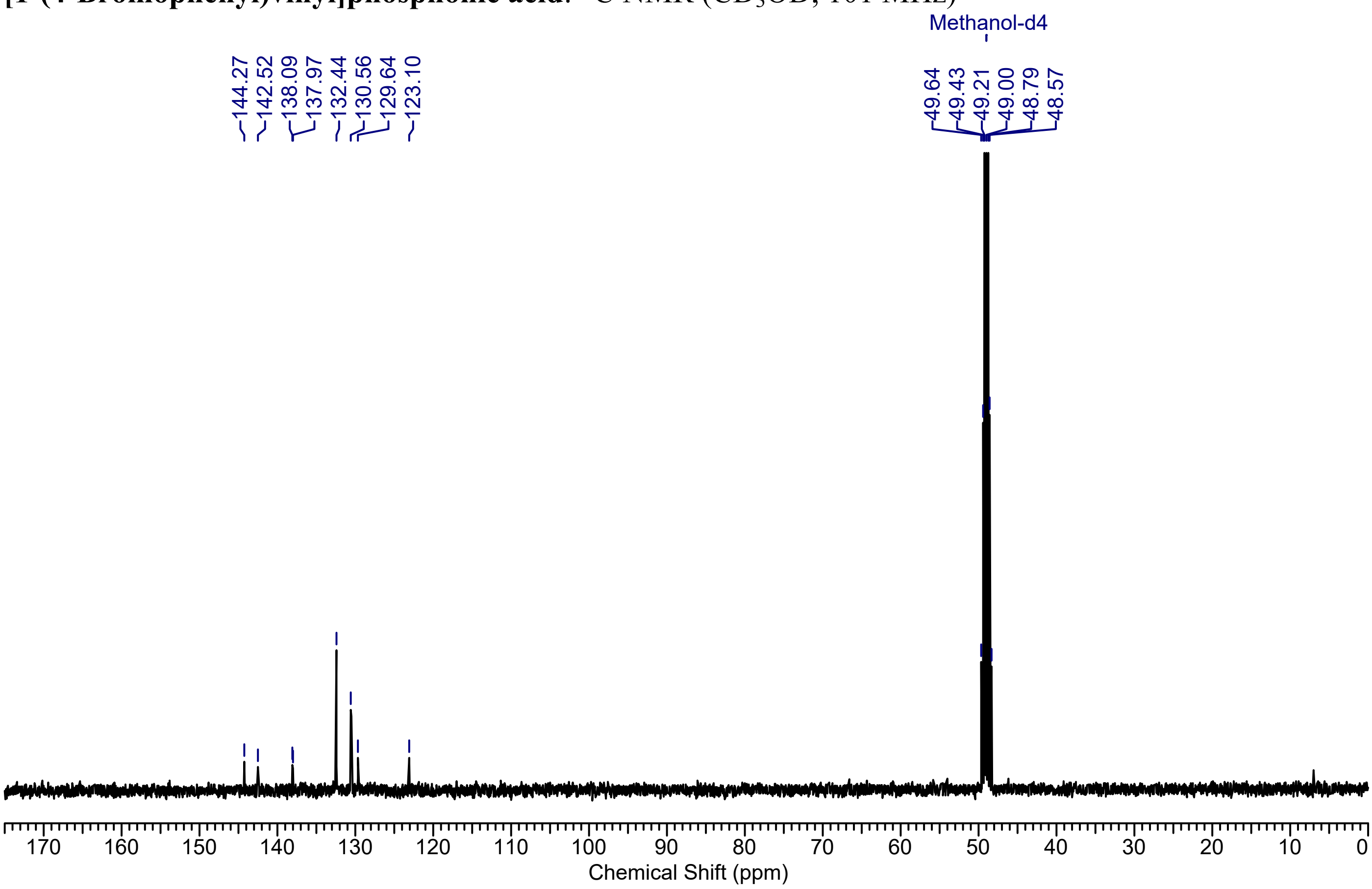
(1-Phenylvinyl)phosphonic acid: ¹³C NMR (CD_3OD, 101 MHz)



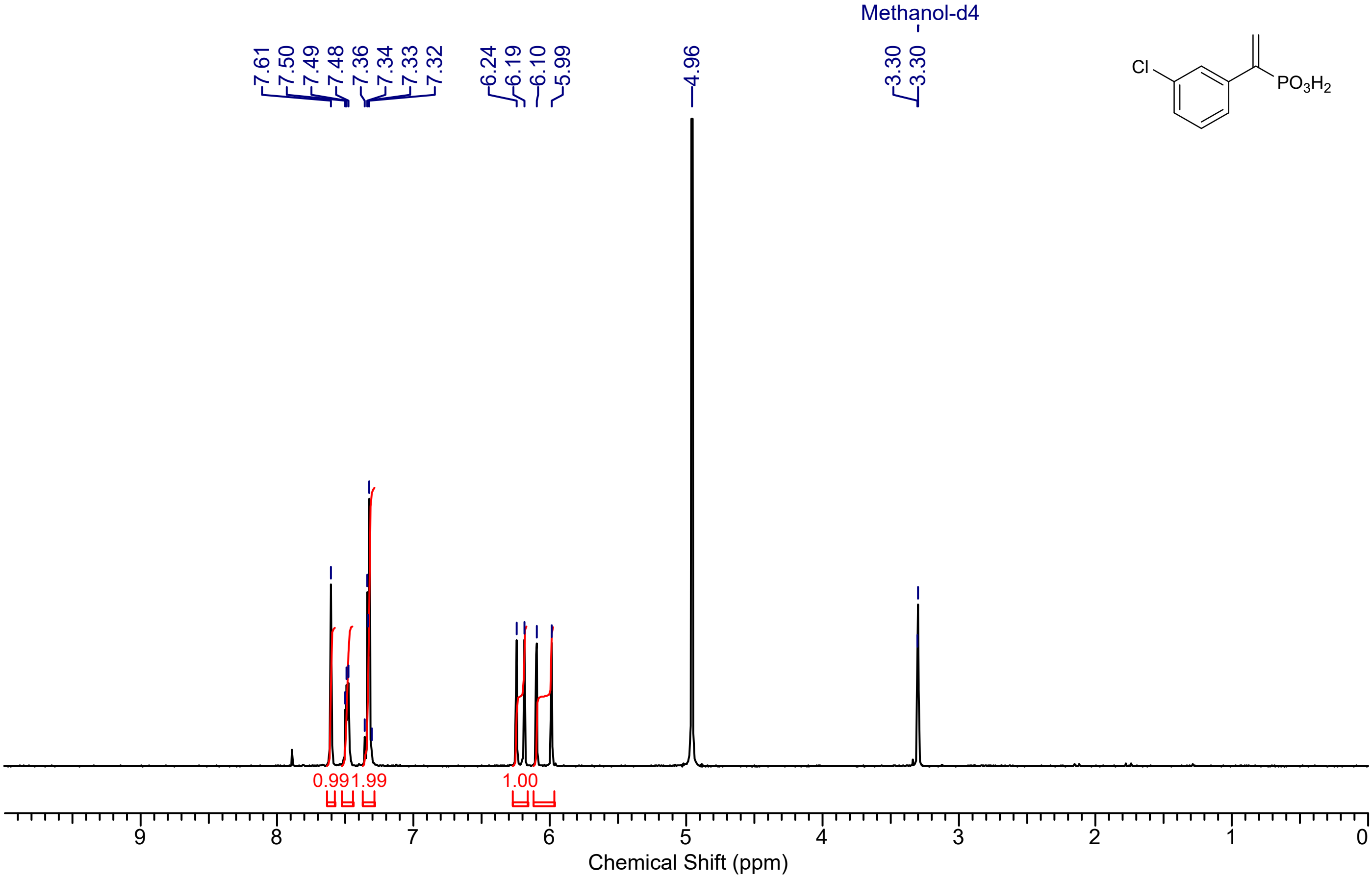
[1-(4-Bromophenyl)vinyl]phosphonic acid: ^1H NMR (CD_3OD, 400 MHz)



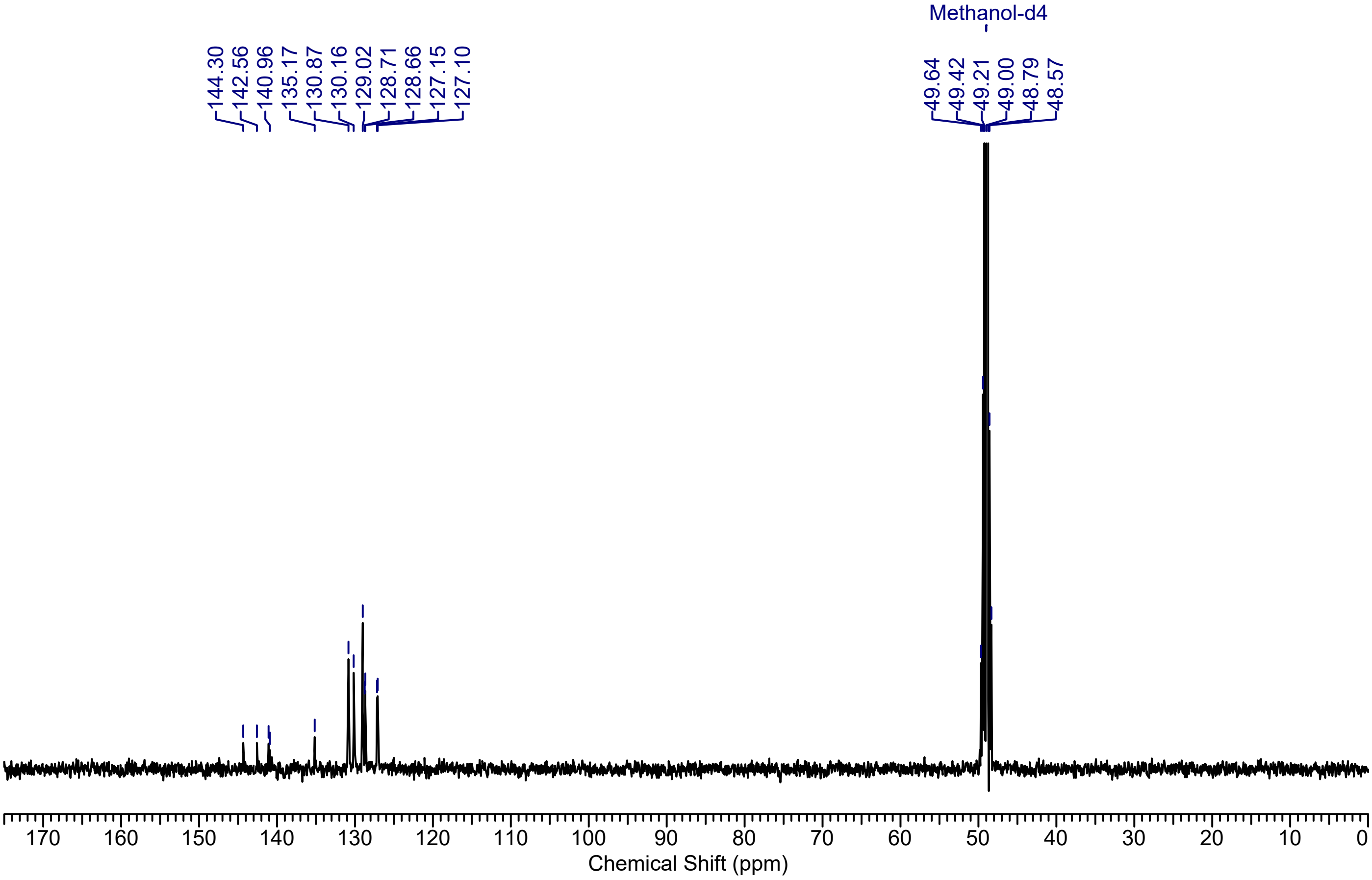
[1-(4-Bromophenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



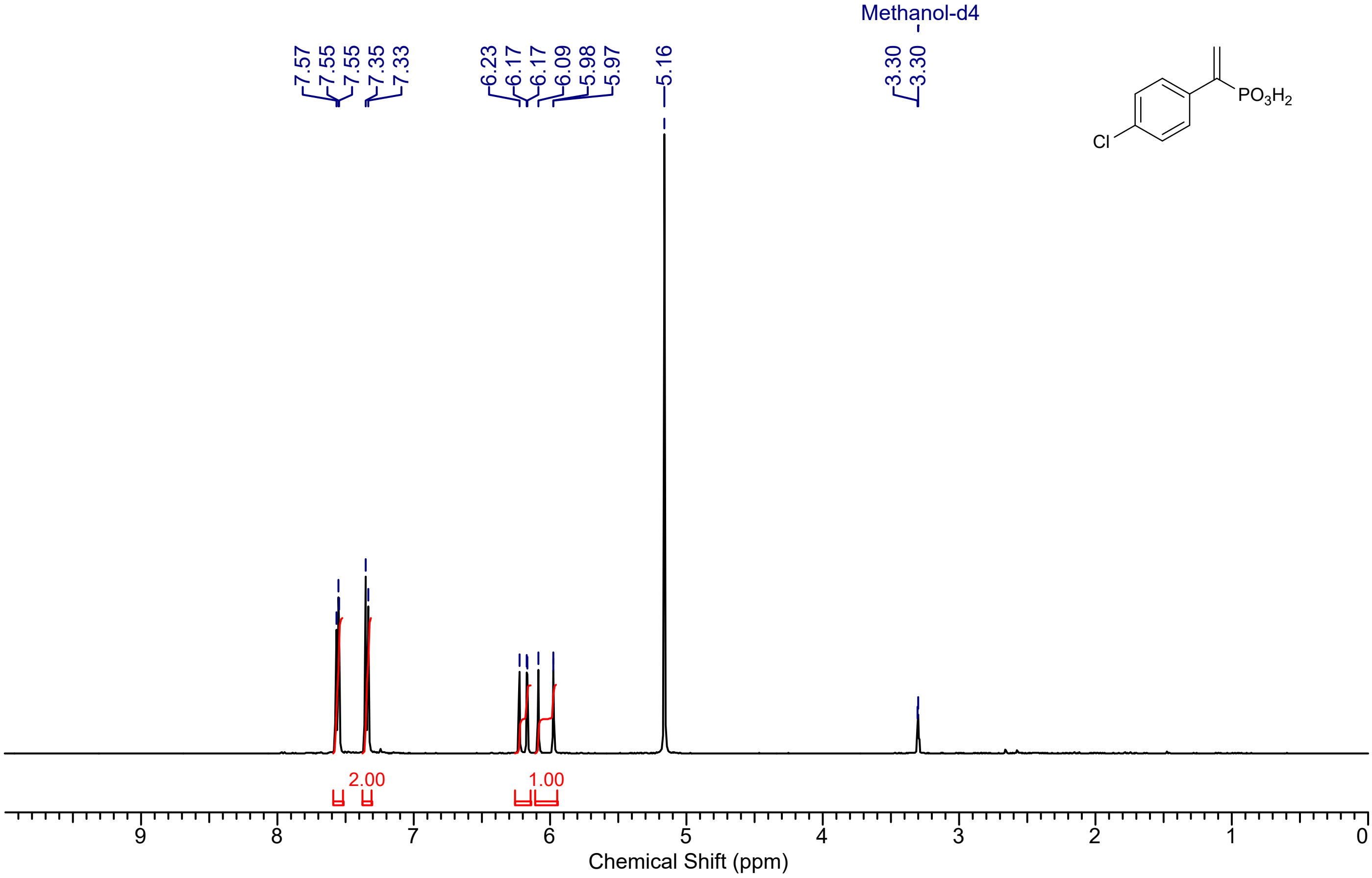
[1-(3-Chlorophenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



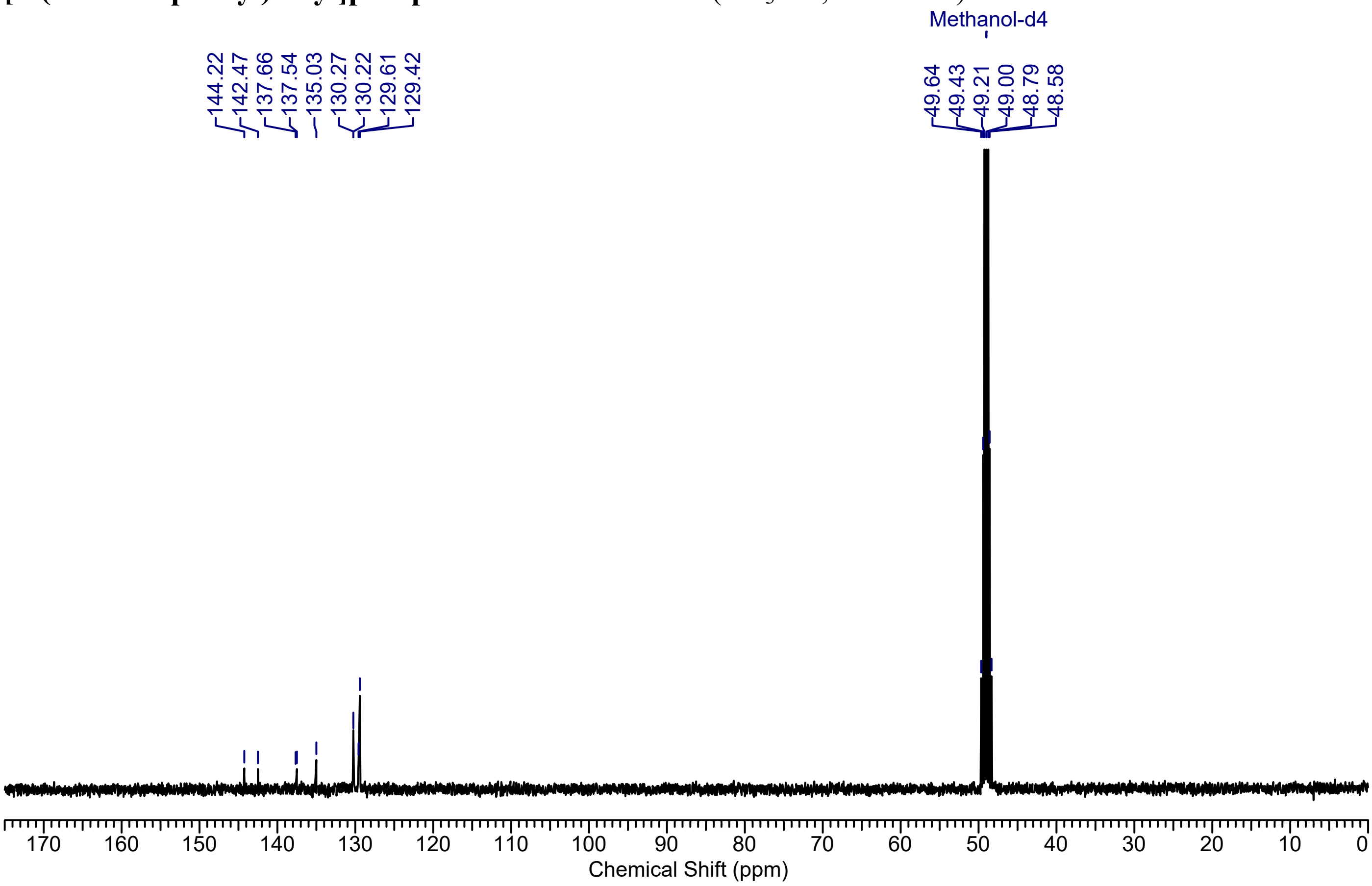
[1-(3-Chlorophenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



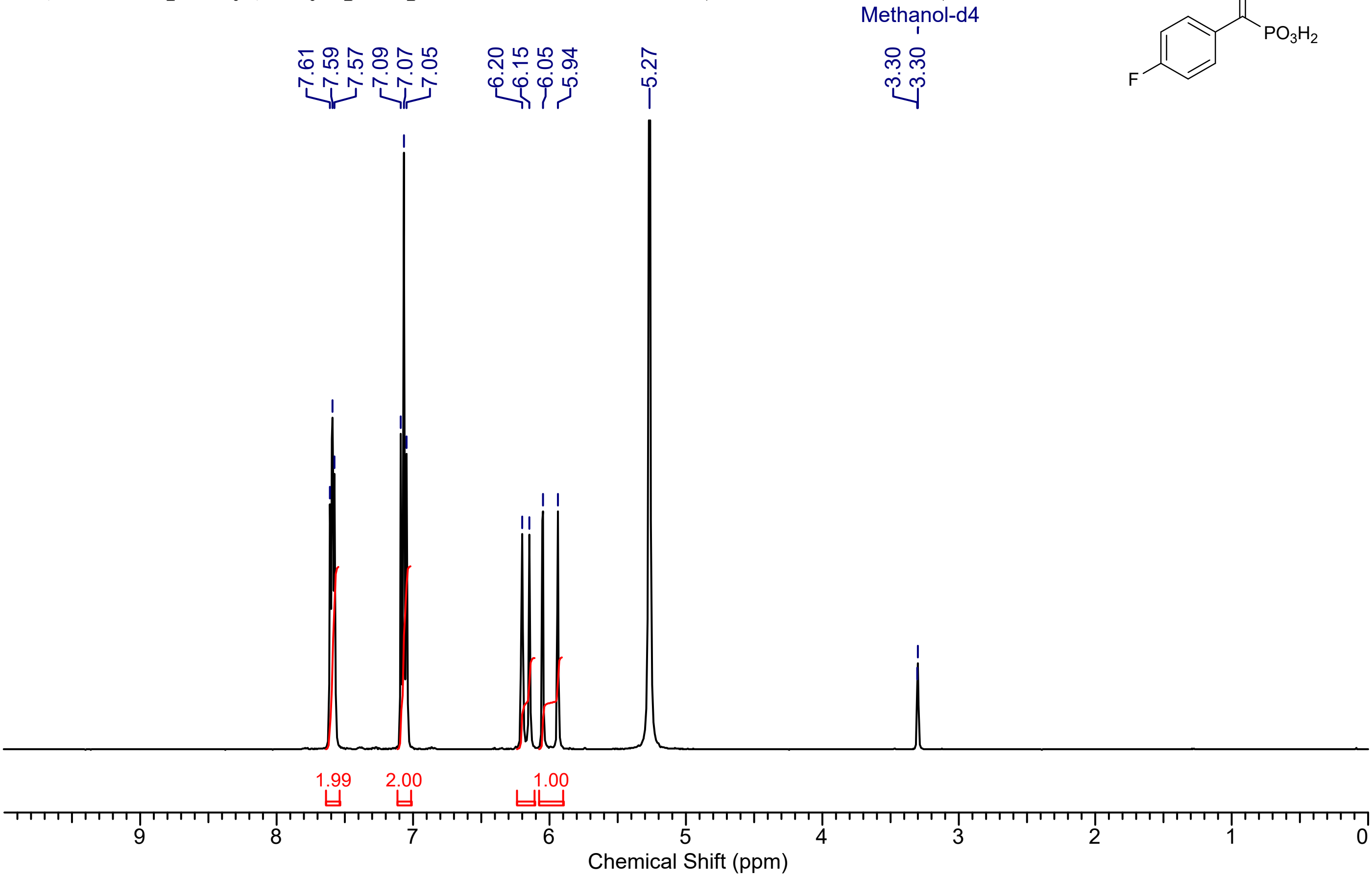
[1-(4-Chlorophenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



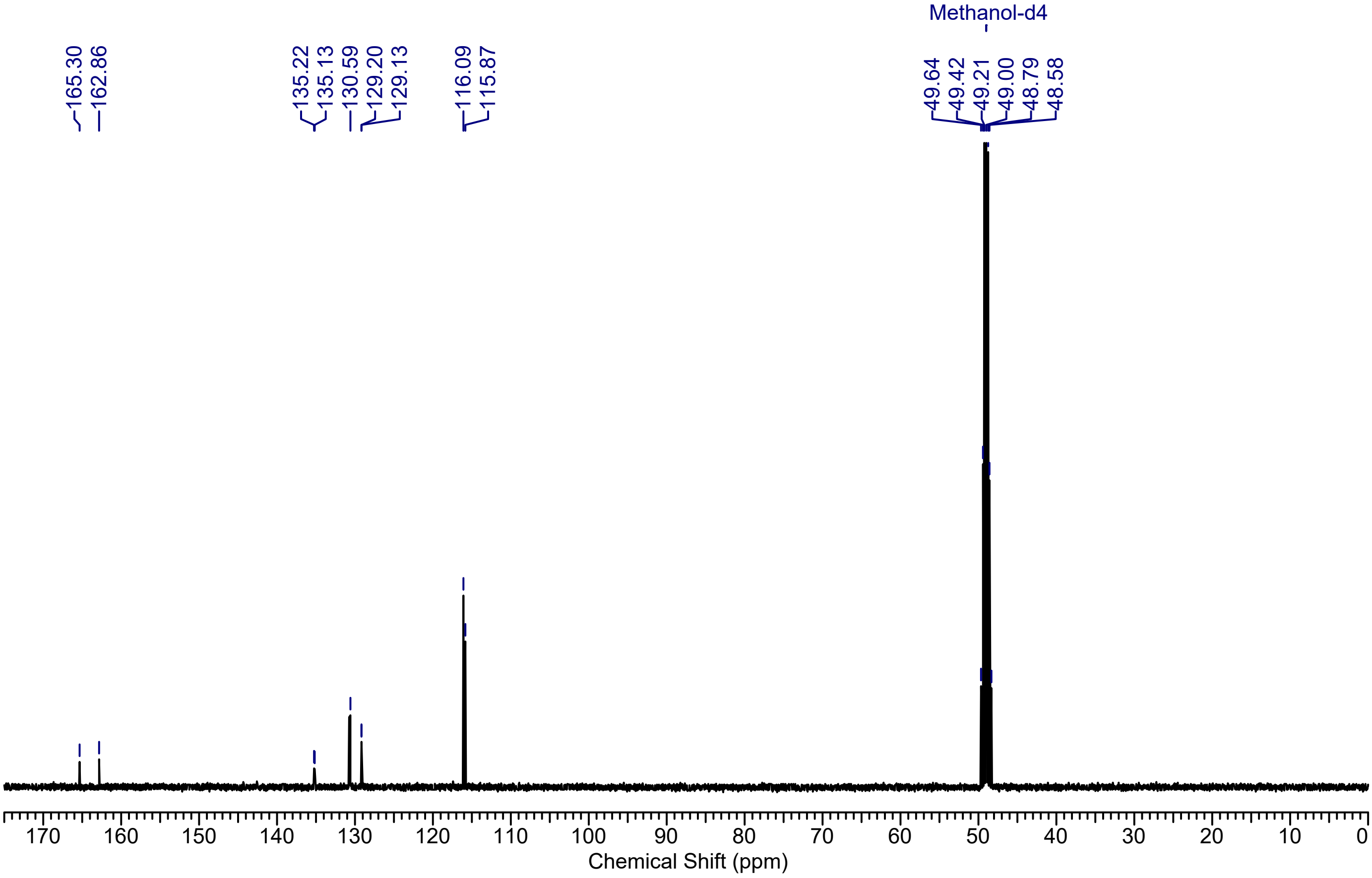
[1-(4-Chlorophenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



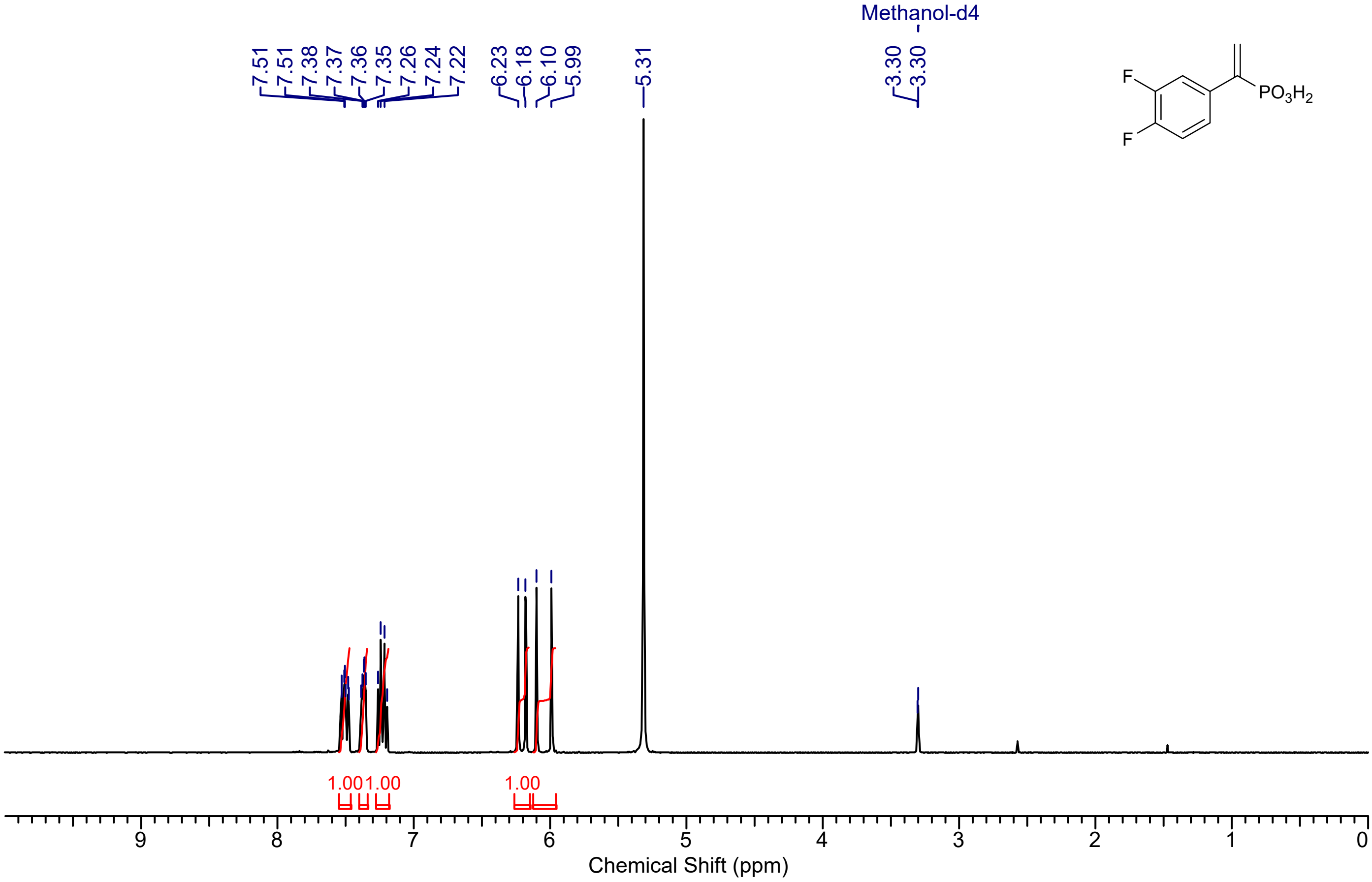
[1-(4-Fluorophenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



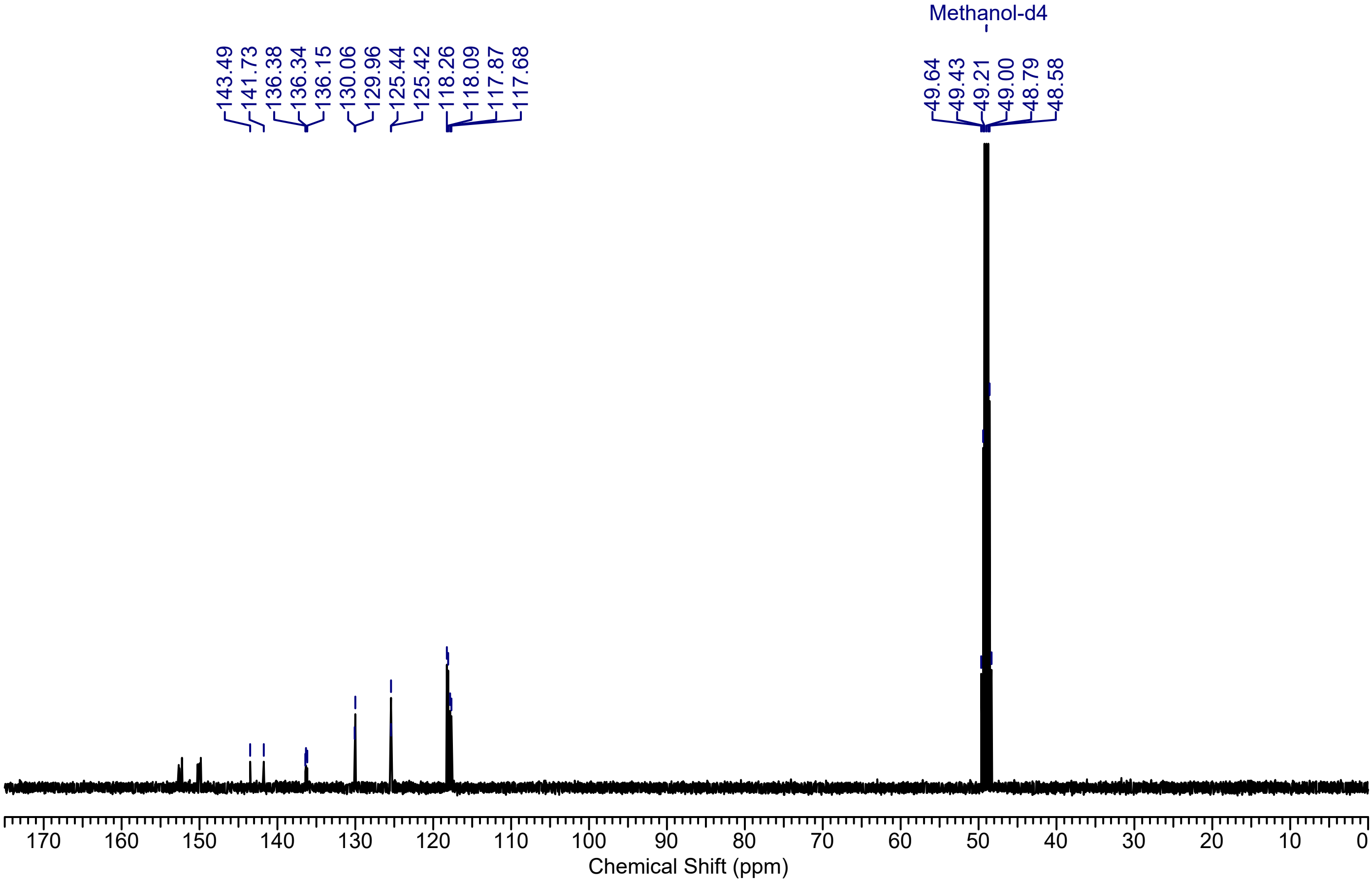
[1-(4-Fluorophenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



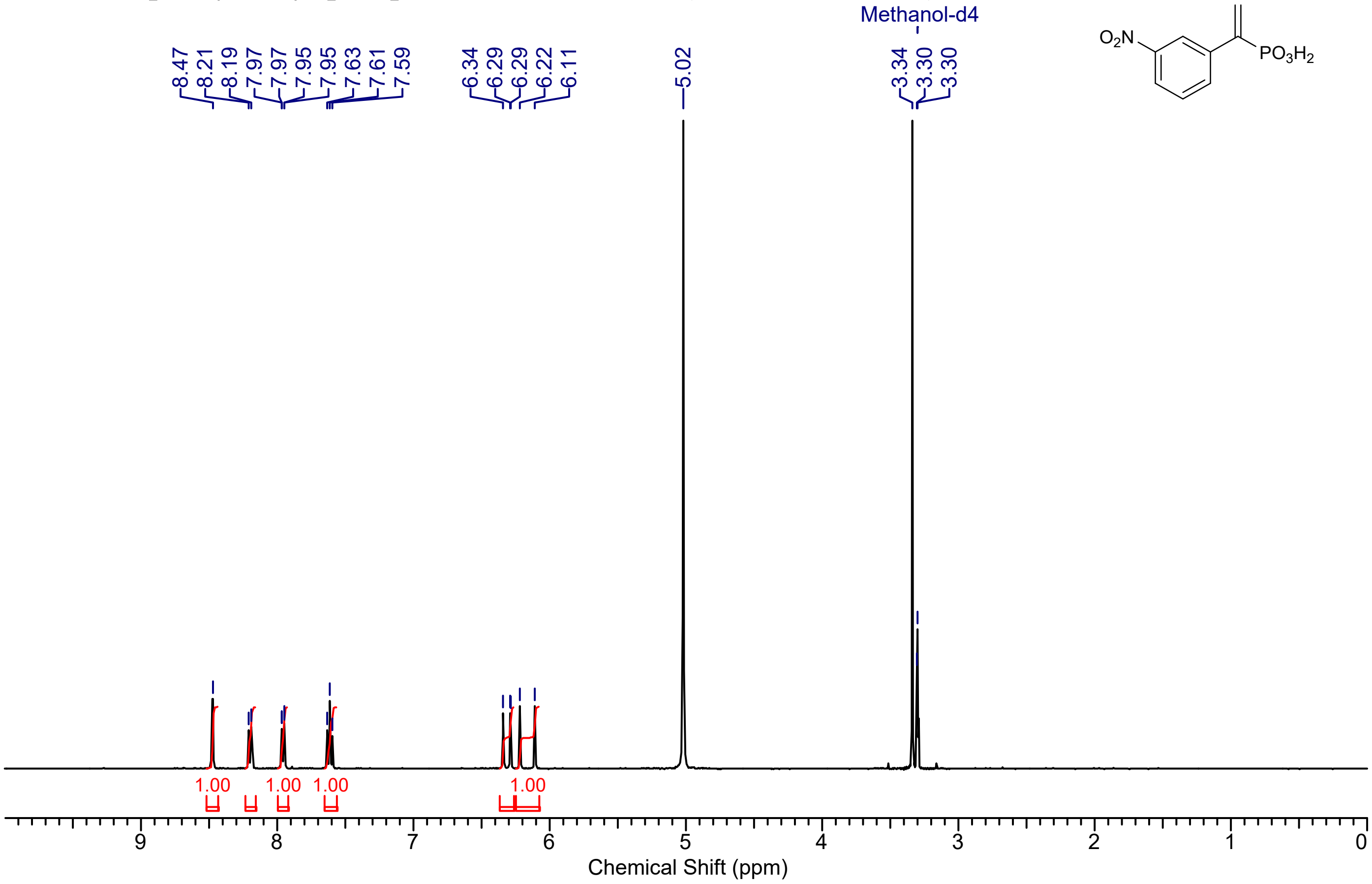
[1-(3,4-Difluorophenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



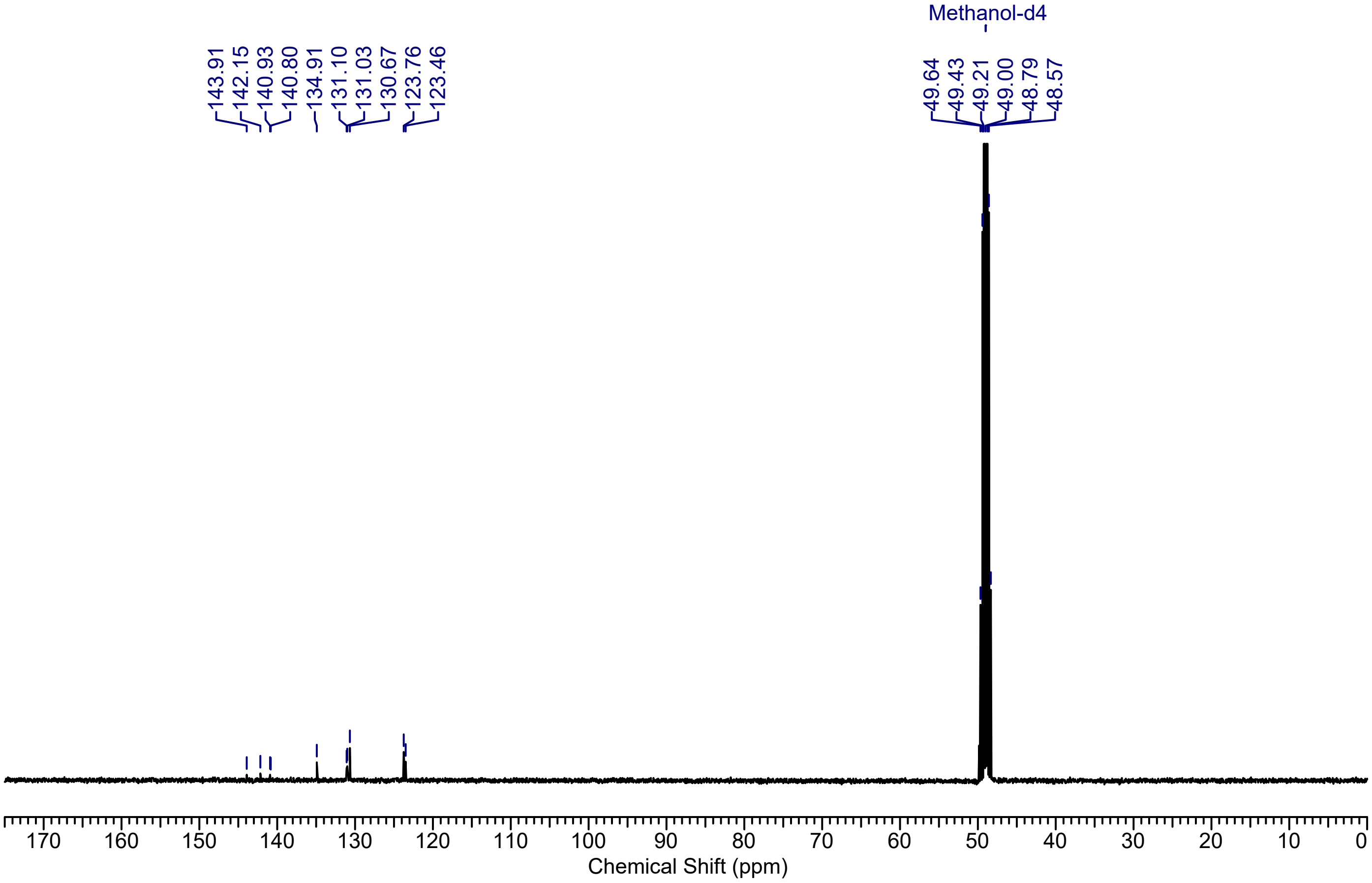
[1-(3,4-Difluorophenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



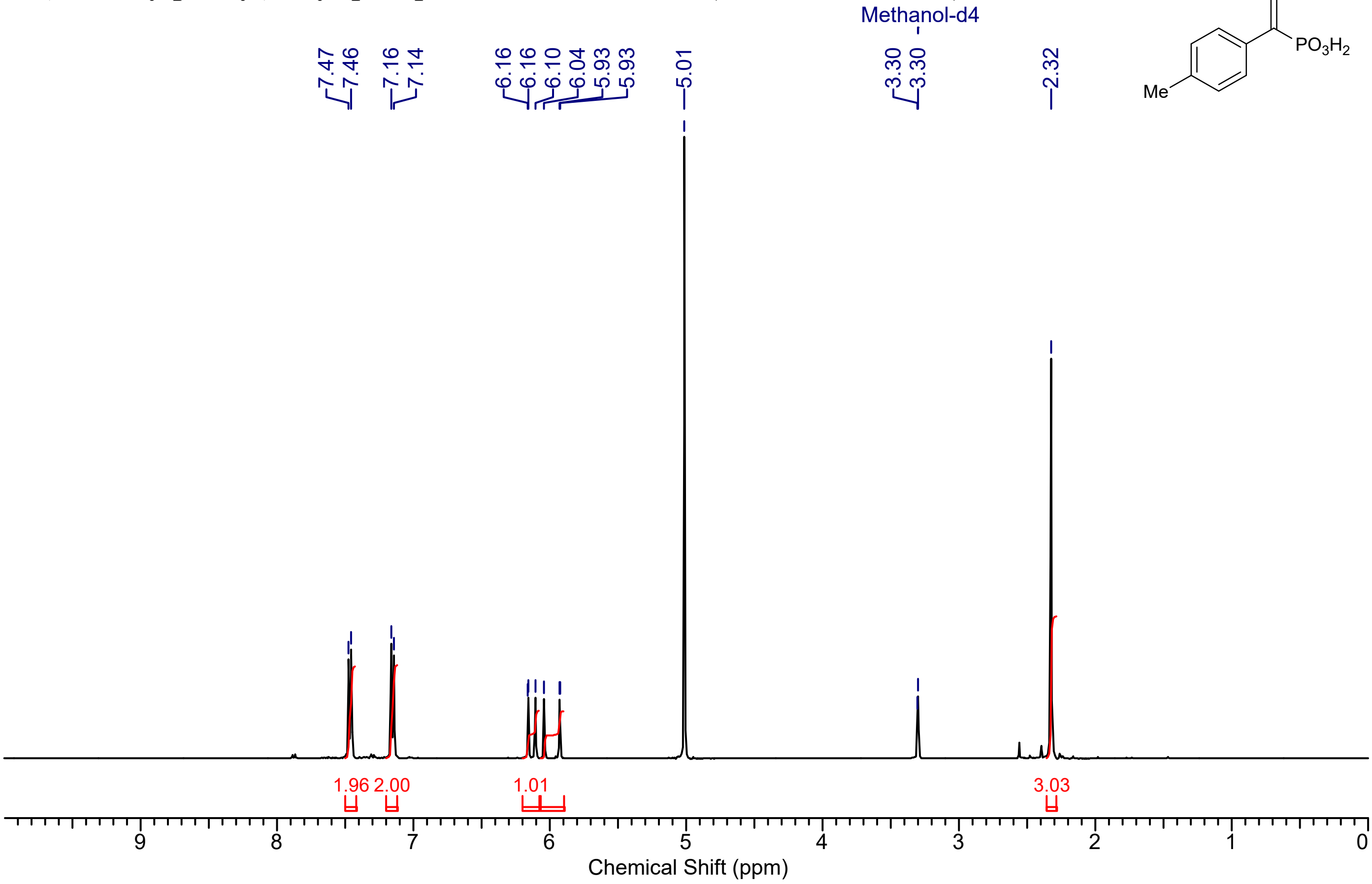
[1-(3-Nitrophenyl)vinyl]phosphonic acid: ¹H NMR (CD_3OD, 400 MHz)



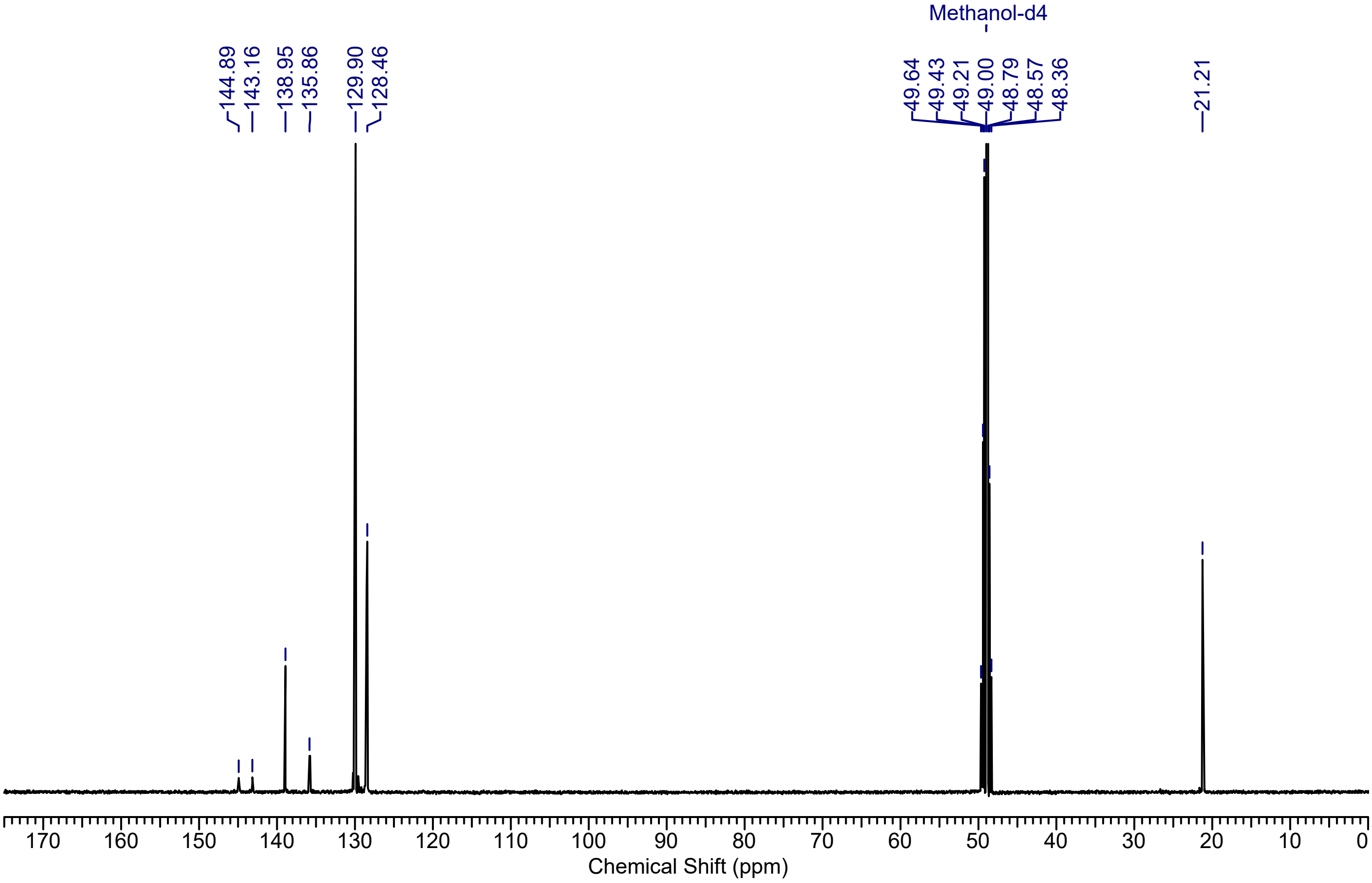
[1-(3-Nitrophenyl)vinyl]phosphonic acid: ¹³C NMR (CD_3OD, 101 MHz)



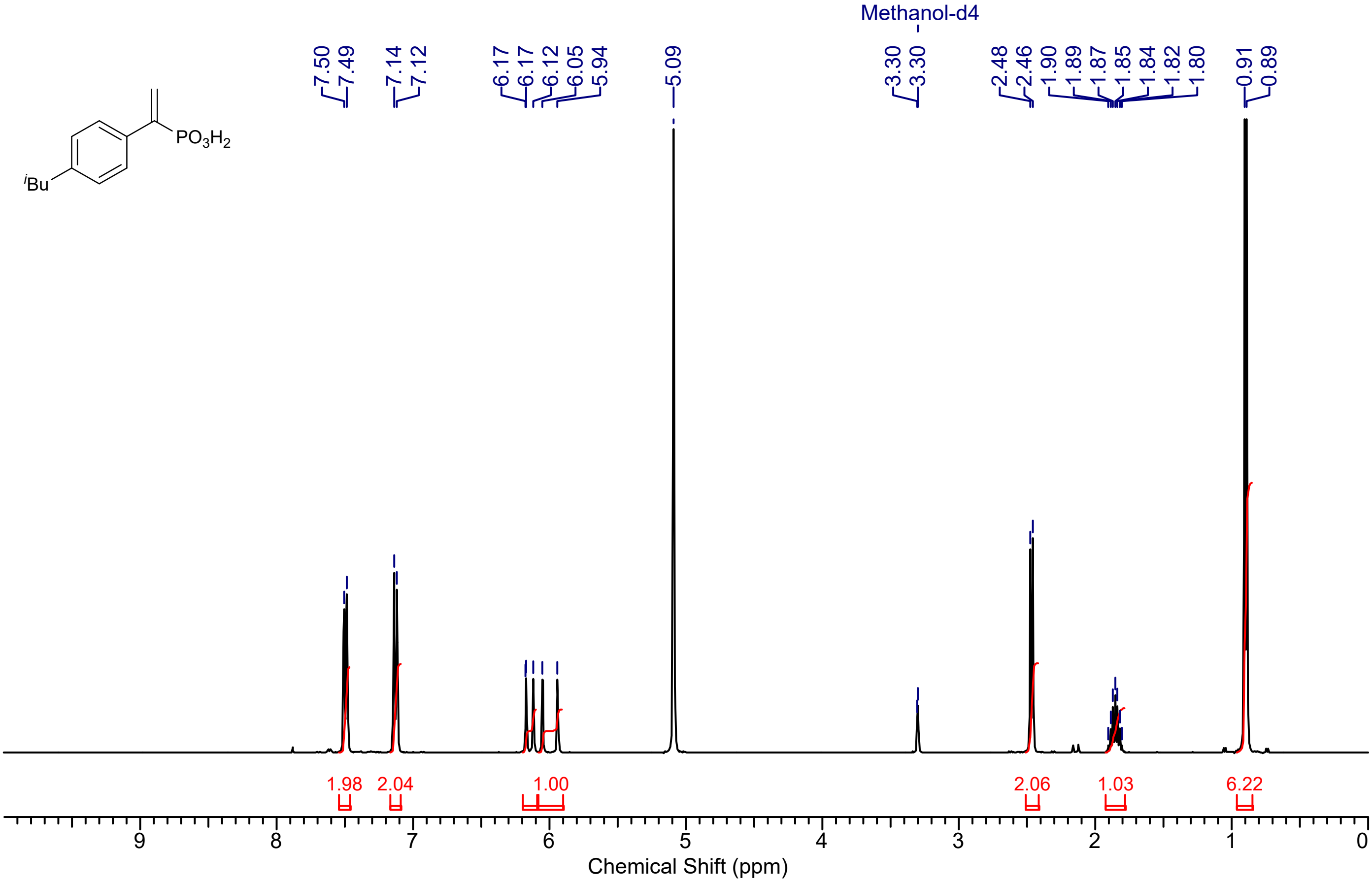
[1-(4-Methylphenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



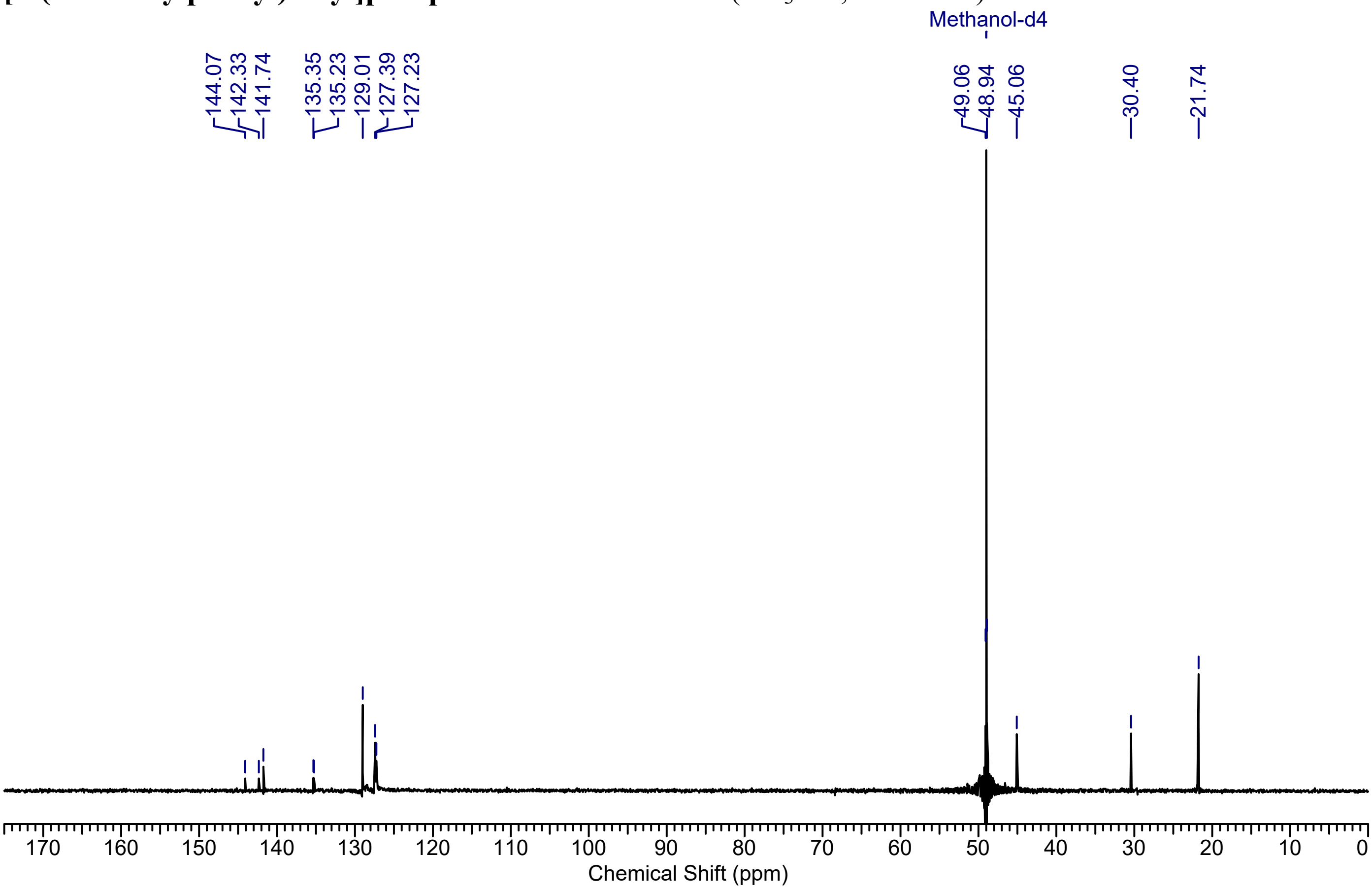
[1-(4-Methylphenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



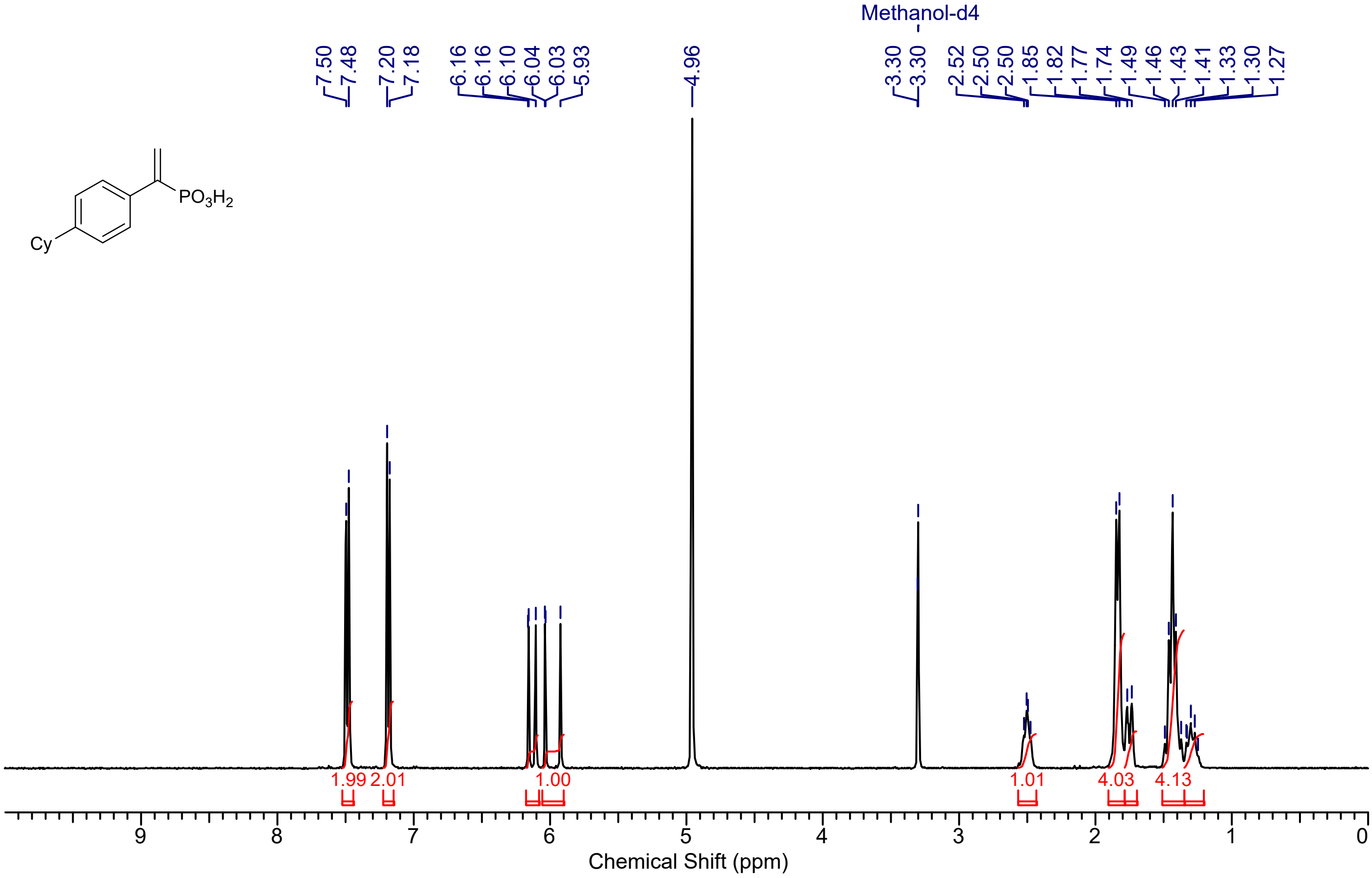
[1-(4-Isobutylphenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



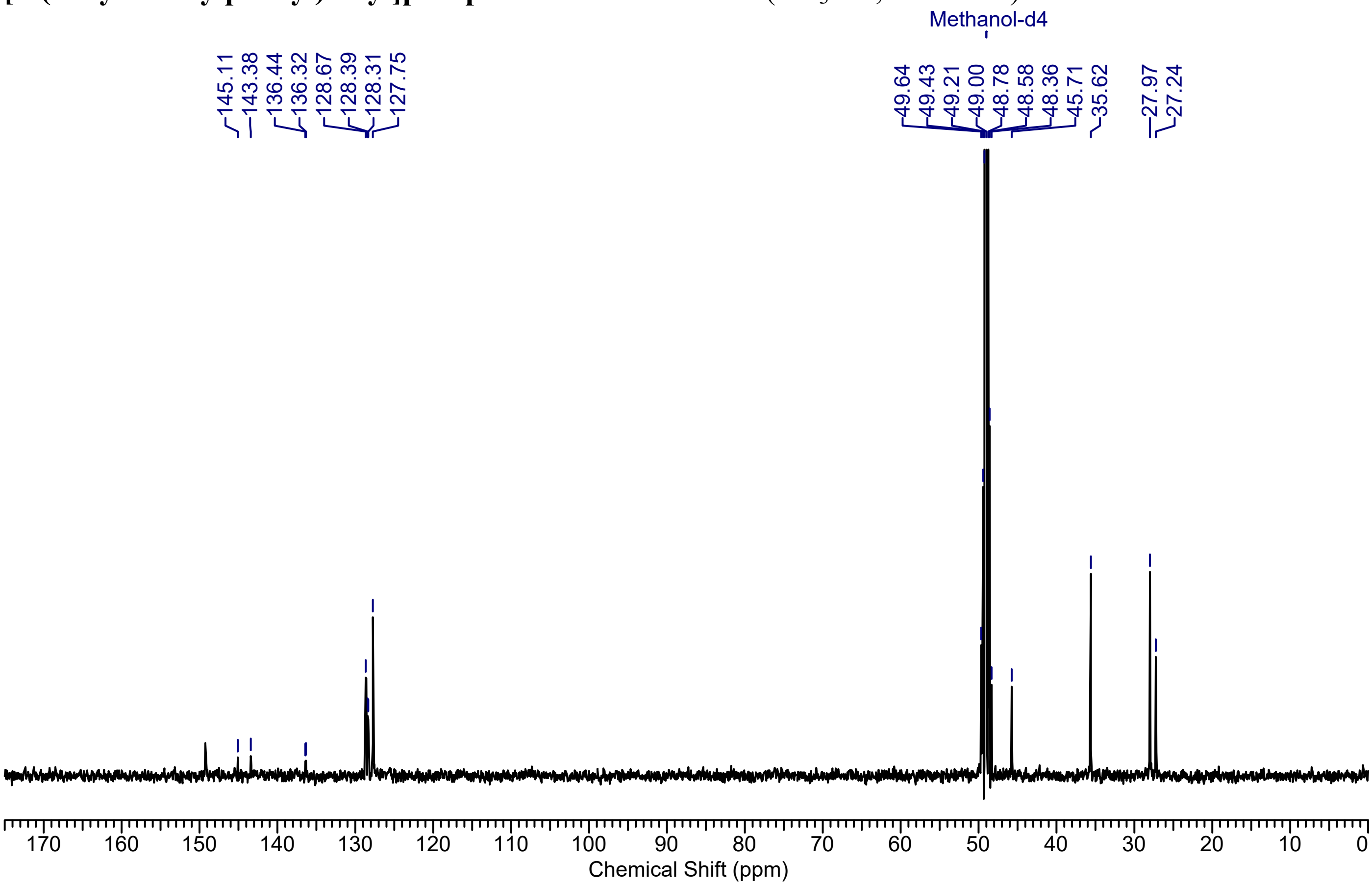
[1-(4-Isobutylphenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



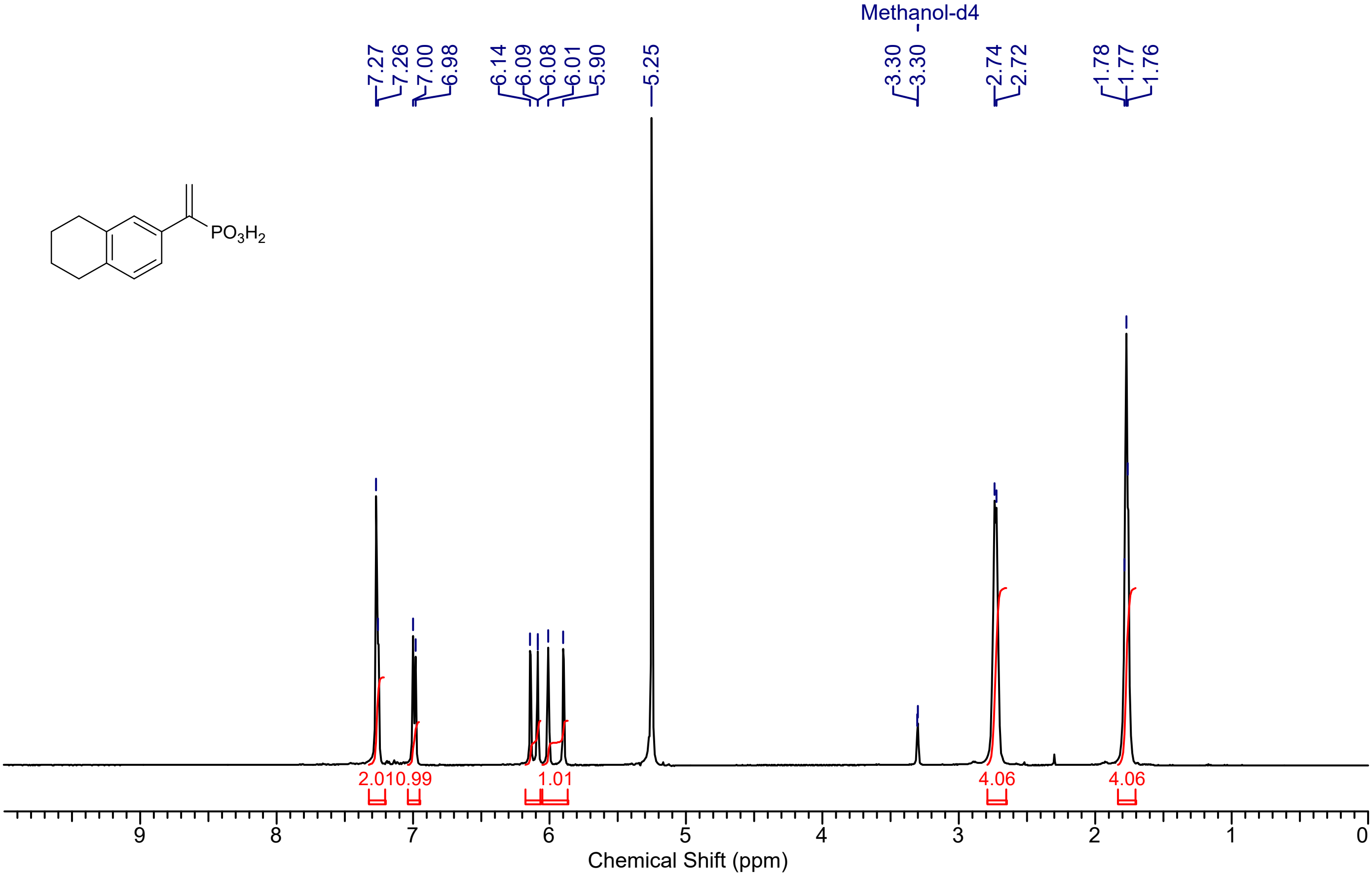
[1-(4-Cyclohexylphenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



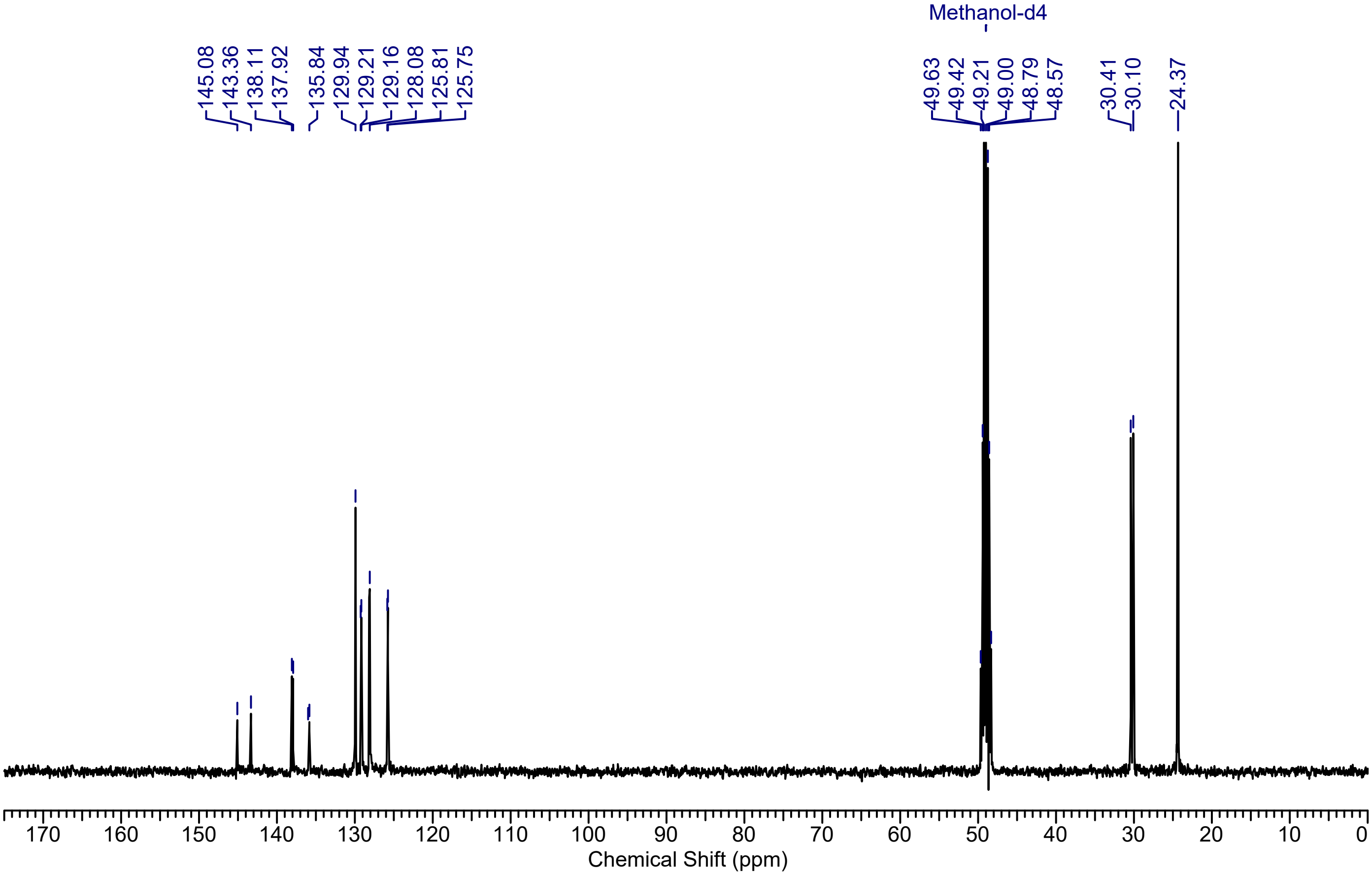
[1-(4-Cyclohexylphenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



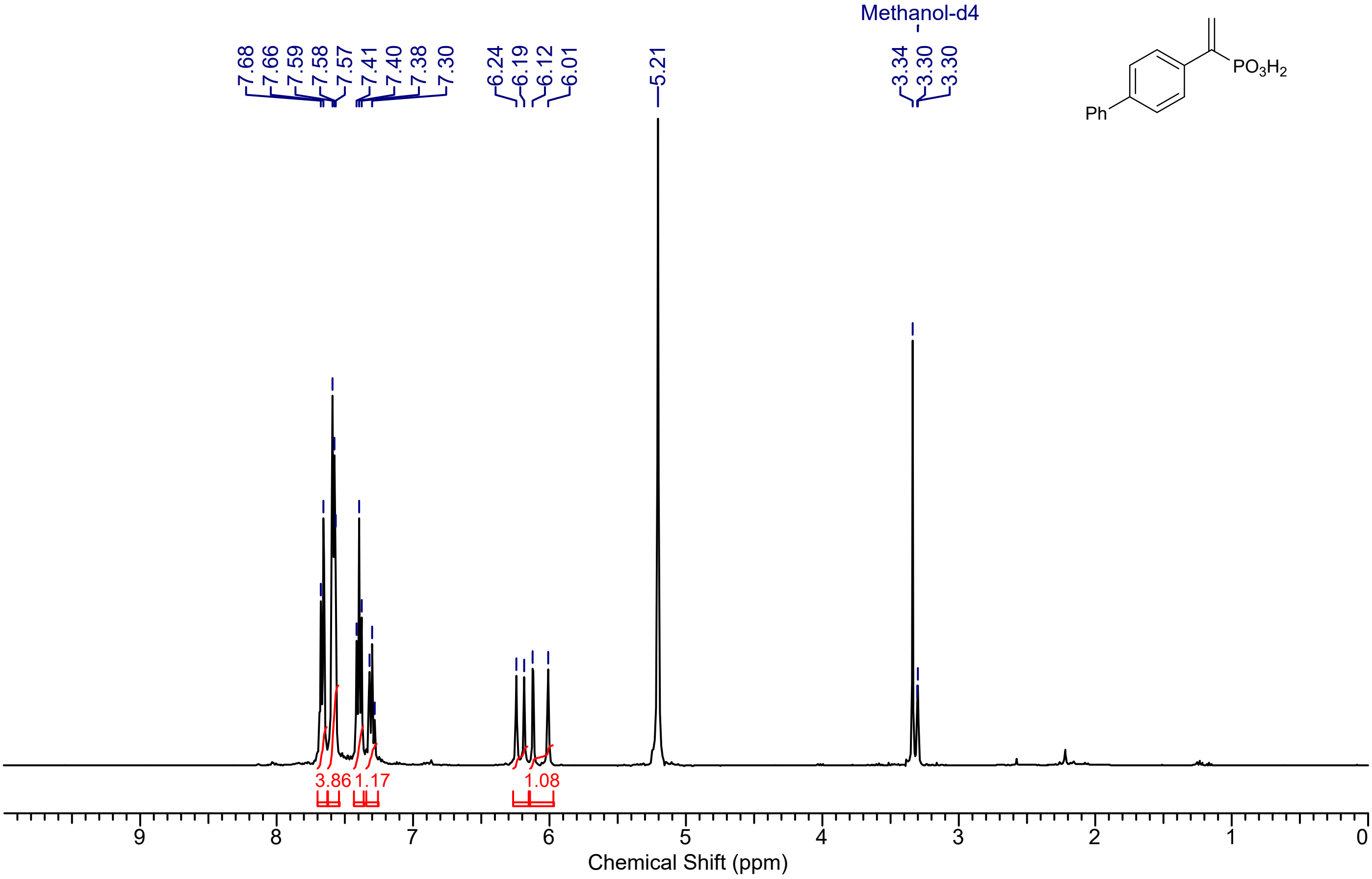
(1-(5,6,7,8-Tetrahydronaphthalen-2-yl)vinyl)phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



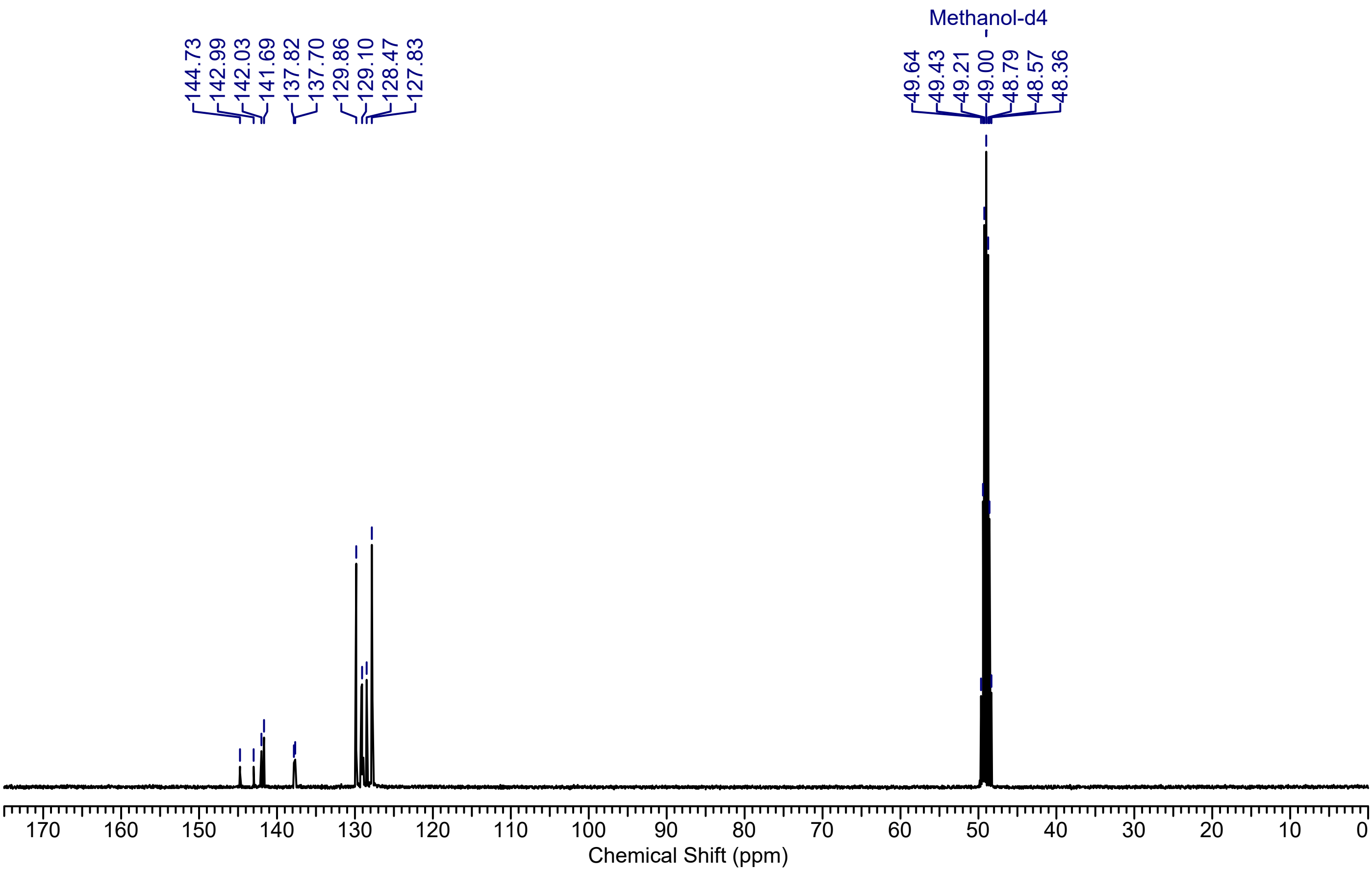
(1-(5,6,7,8-Tetrahydronaphthalen-2-yl)vinyl)phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



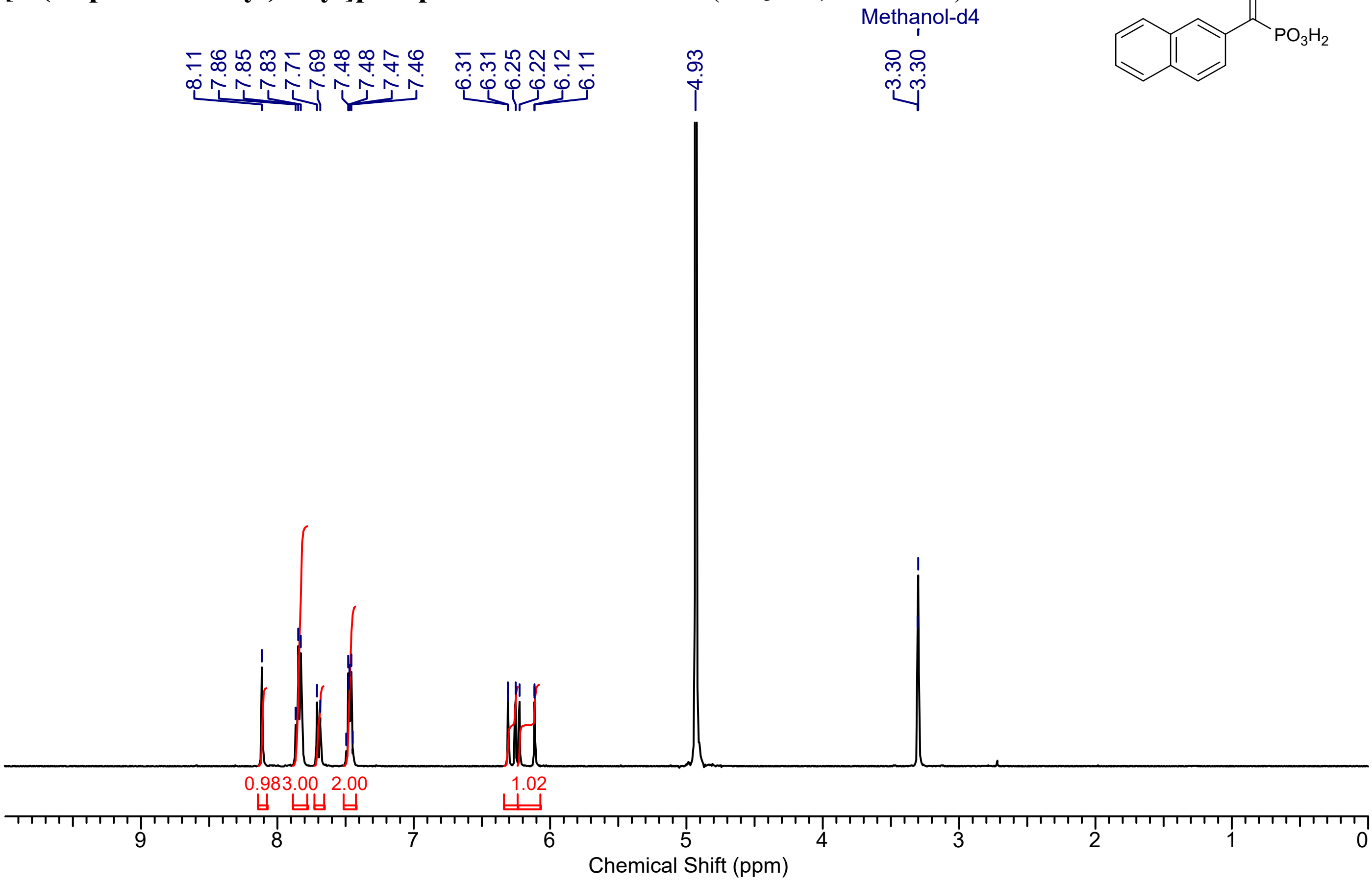
[1-(4-Diphenyl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



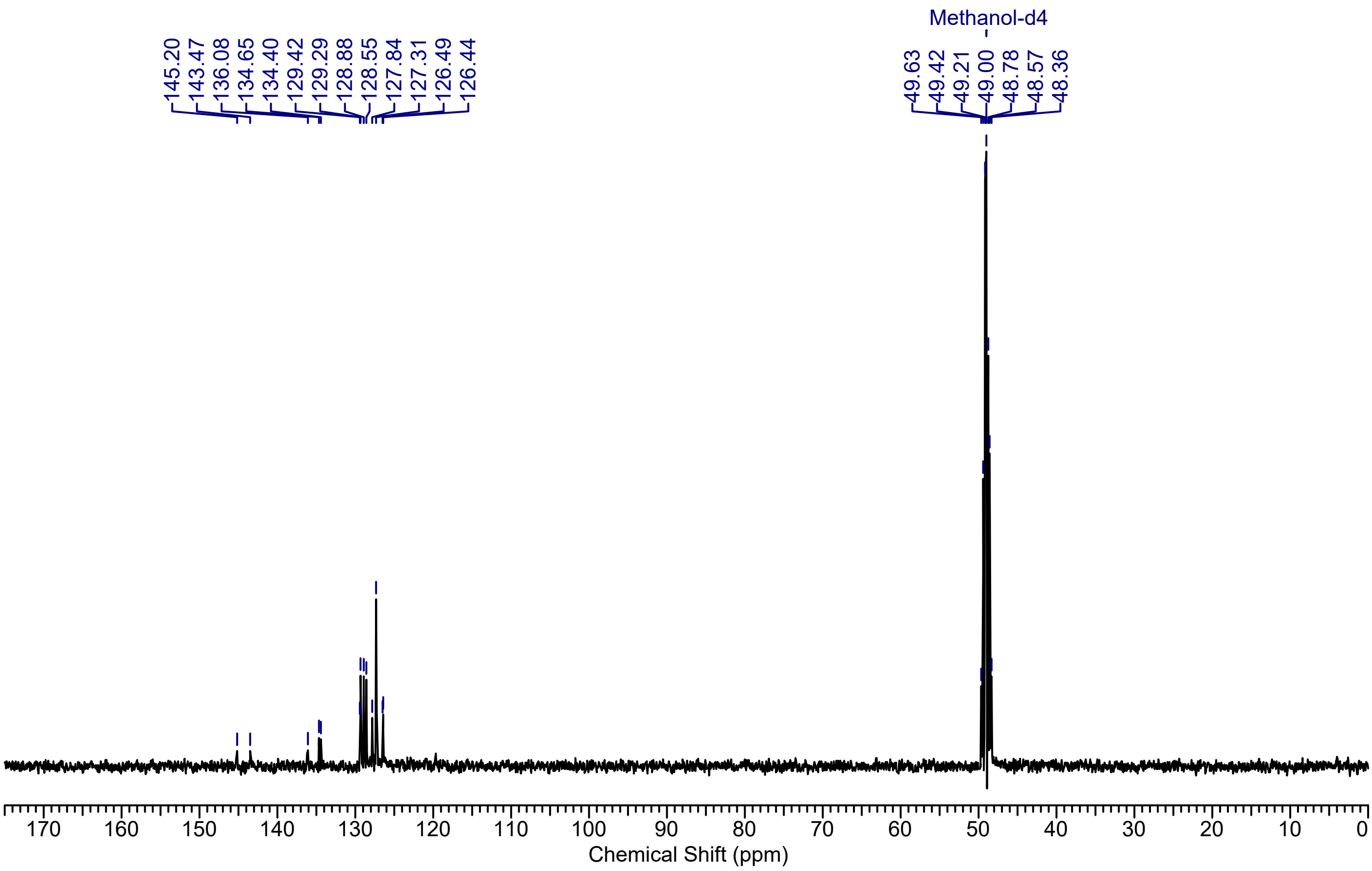
[1-(4-Diphenyl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



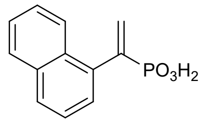
[1-(Naphthalen-2-yl)vinyl]phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)

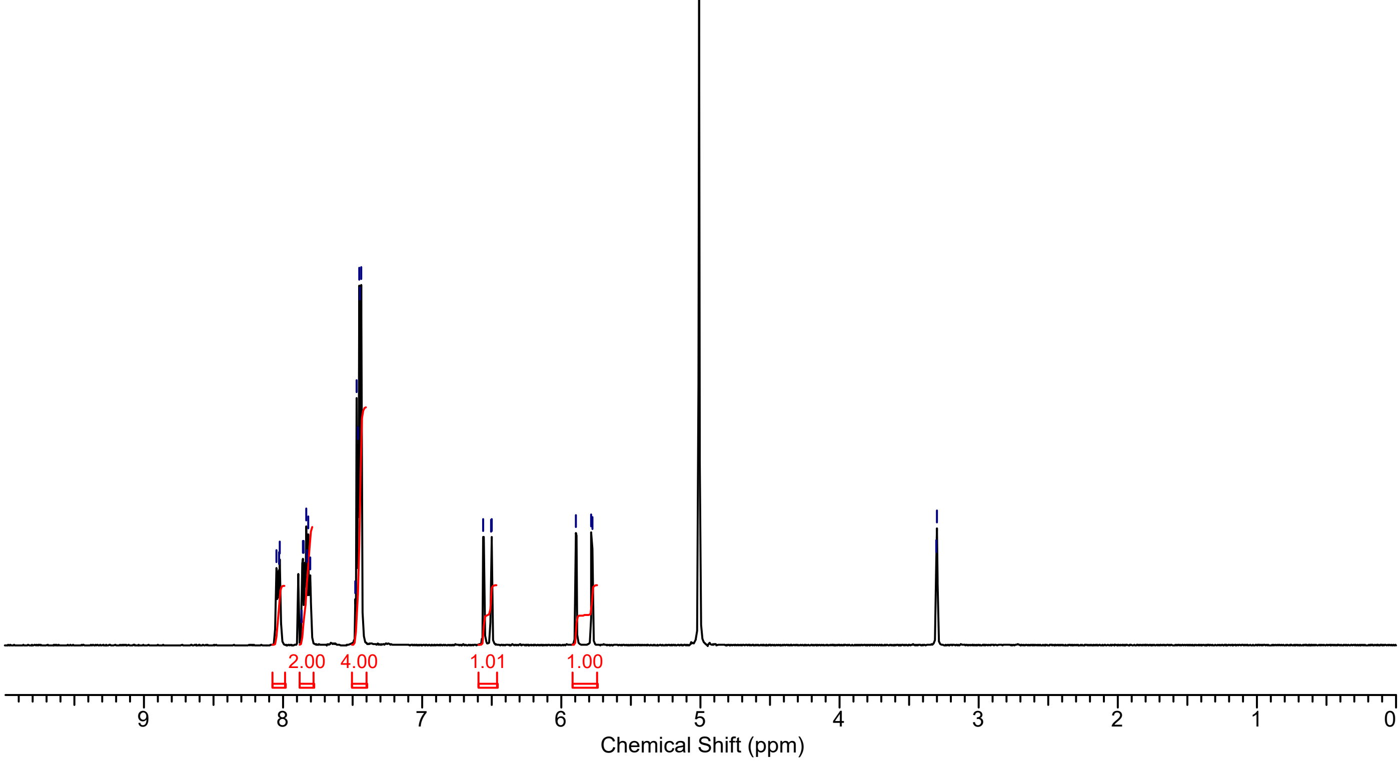


[1-(Naphthalen-2-yl)vinyl]phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)

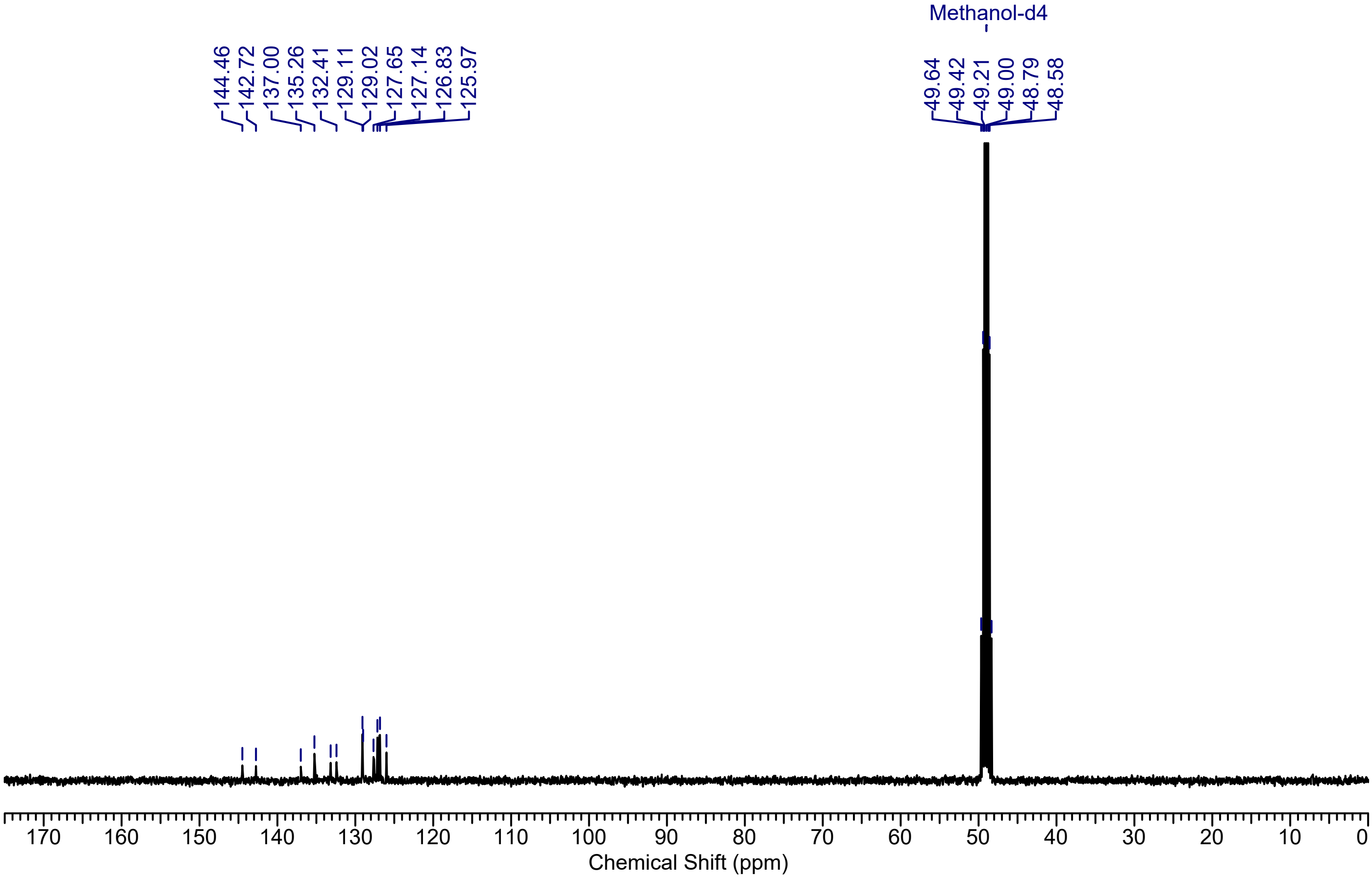


[1-(Naphthalen-1-yl)vinyl]phosphonic acid: [1]H NMR (CD_3OD, 400 MHz)

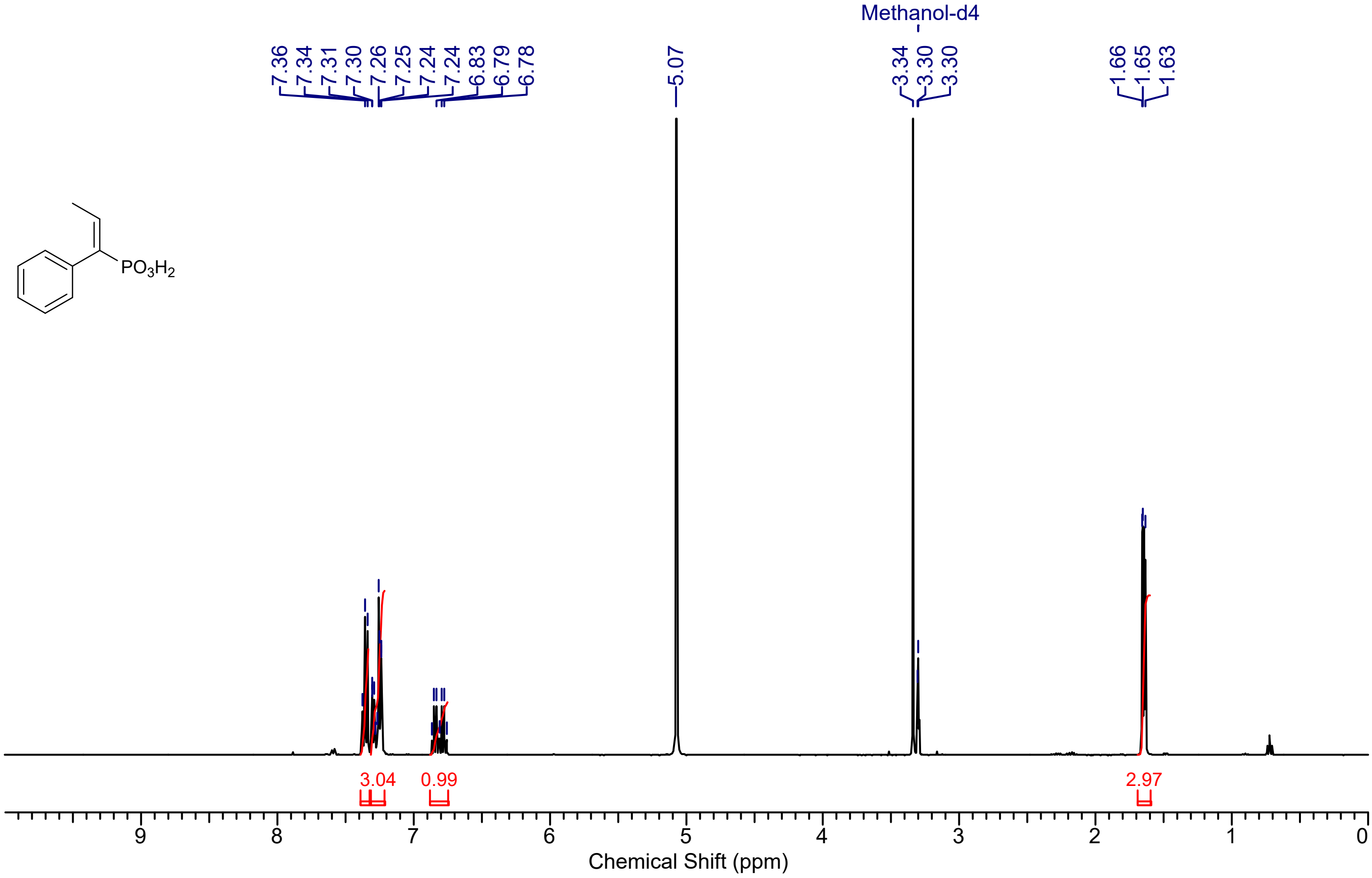




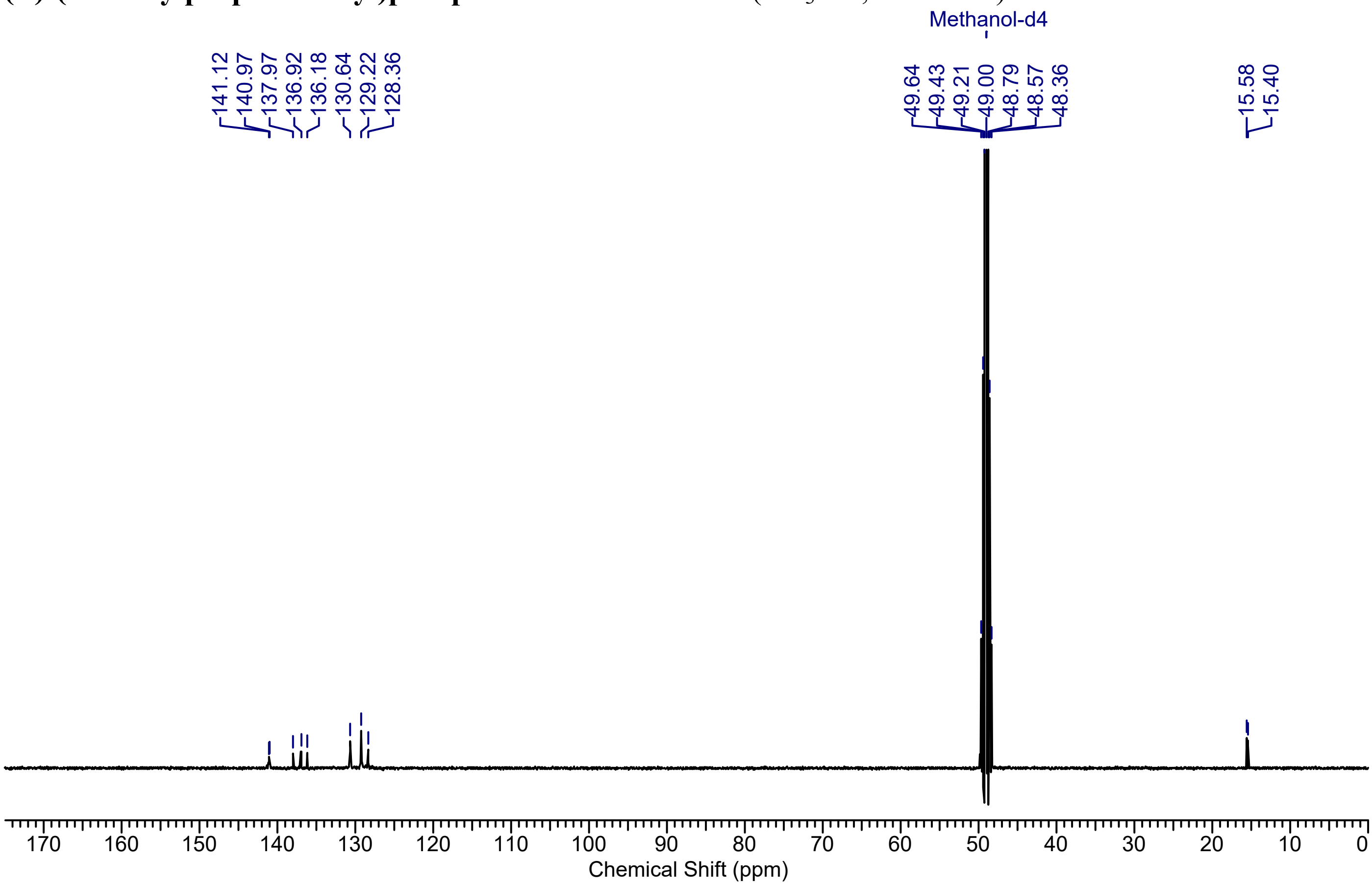
[1-(Naphthalen-1-yl)vinyl]phosphonic acid: [13]C NMR (CD_3OD, 101 MHz)



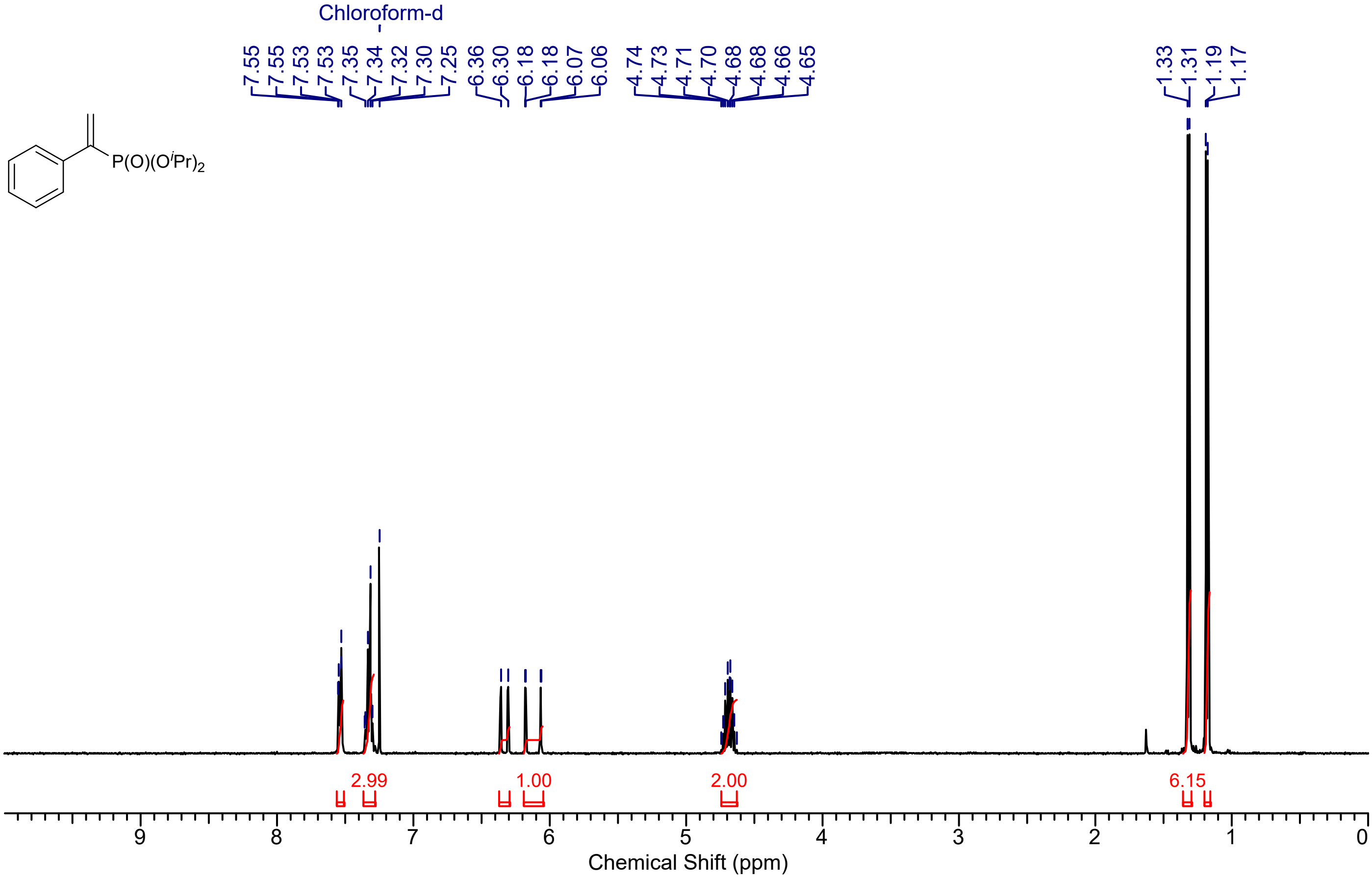
(*E*)-(1-Phenylprop-1-en-1-yl)phosphonic acid: ^{1}H NMR (CD_3OD, 400 MHz)



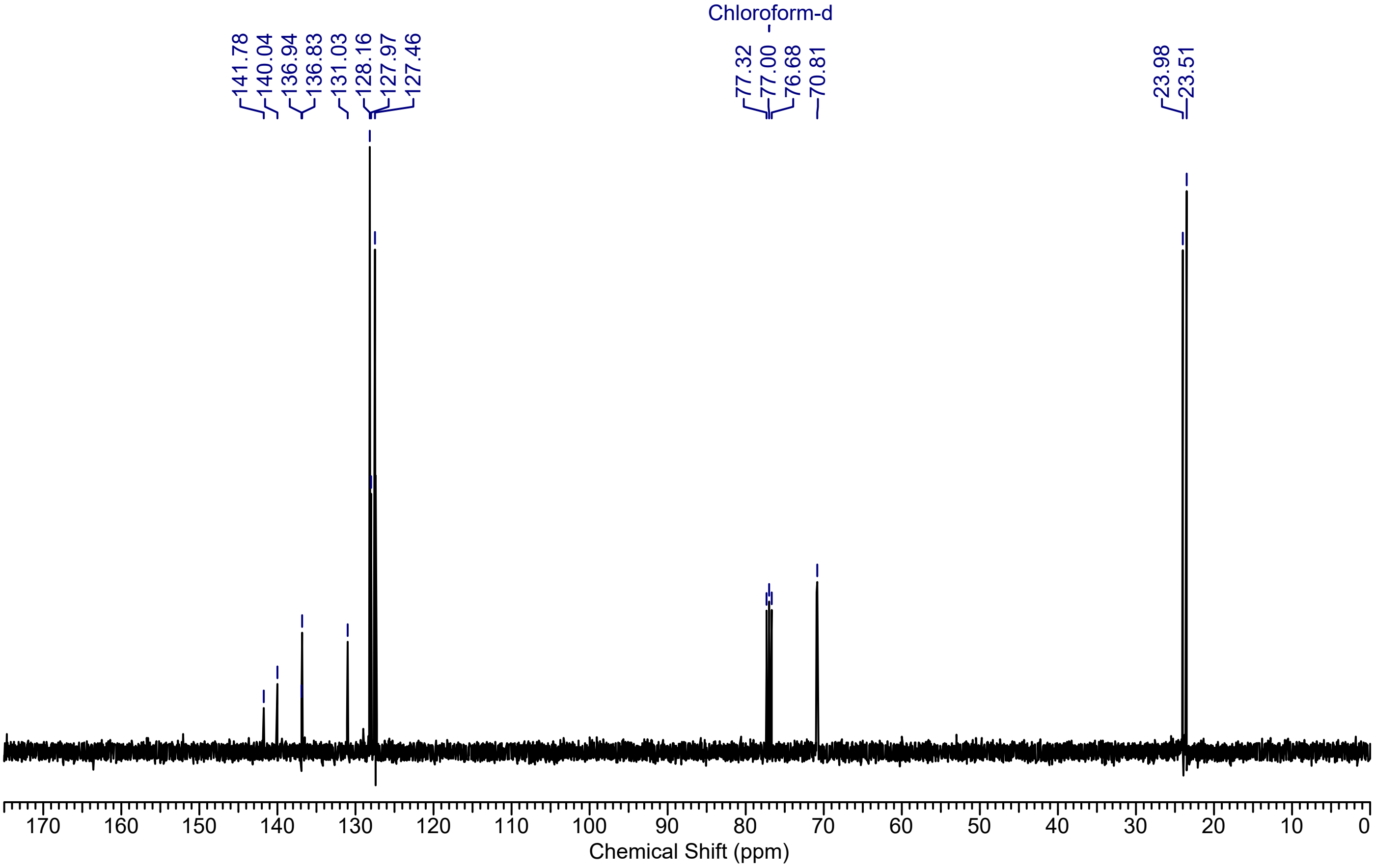
(*E*)-(1-Phenylprop-1-en-1-yl)phosphonic acid: ^{13}C NMR (CD_3OD, 101 MHz)



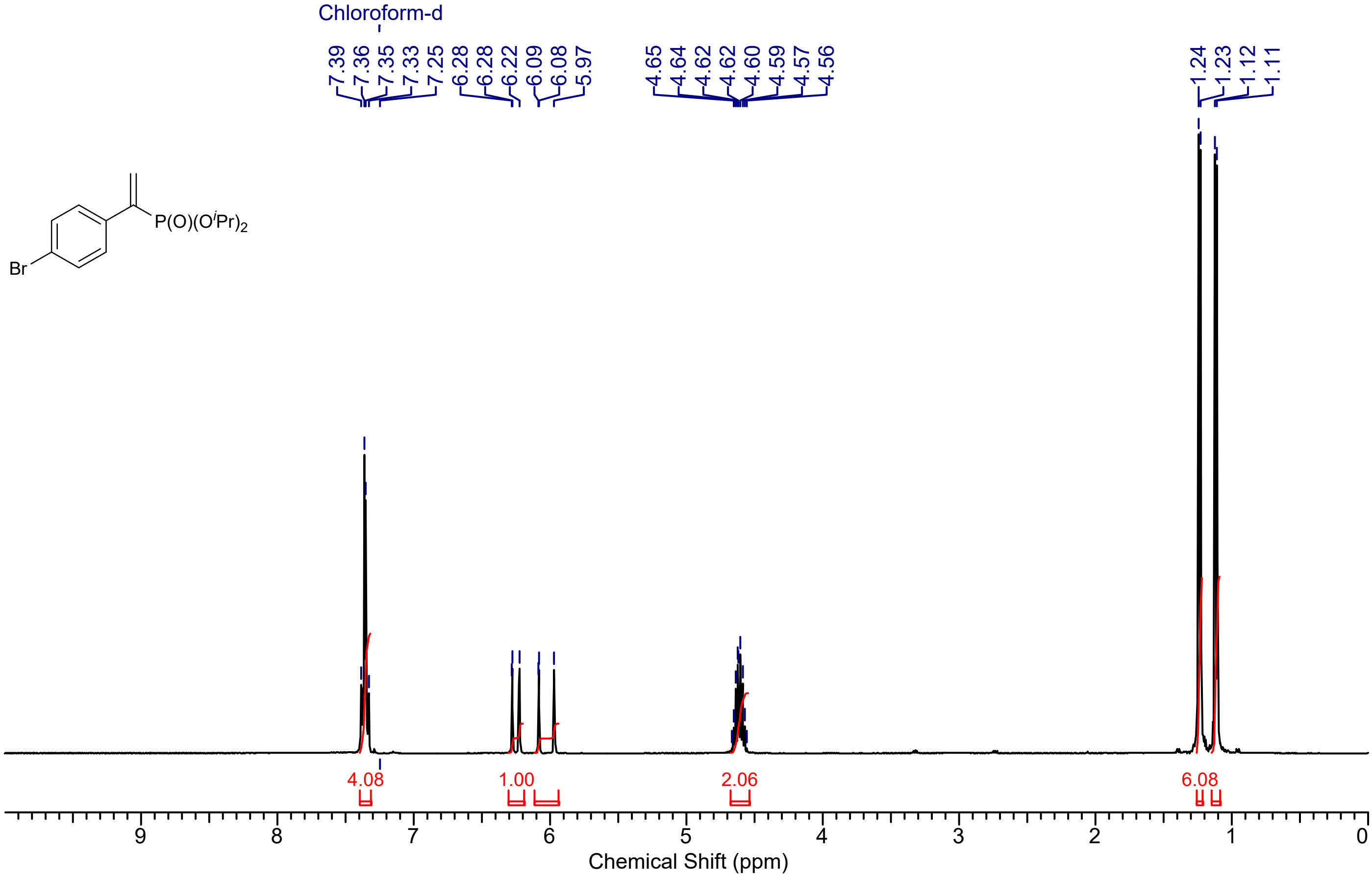
3a: ^{1}H NMR ($CDCl_3$, 400 MHz)



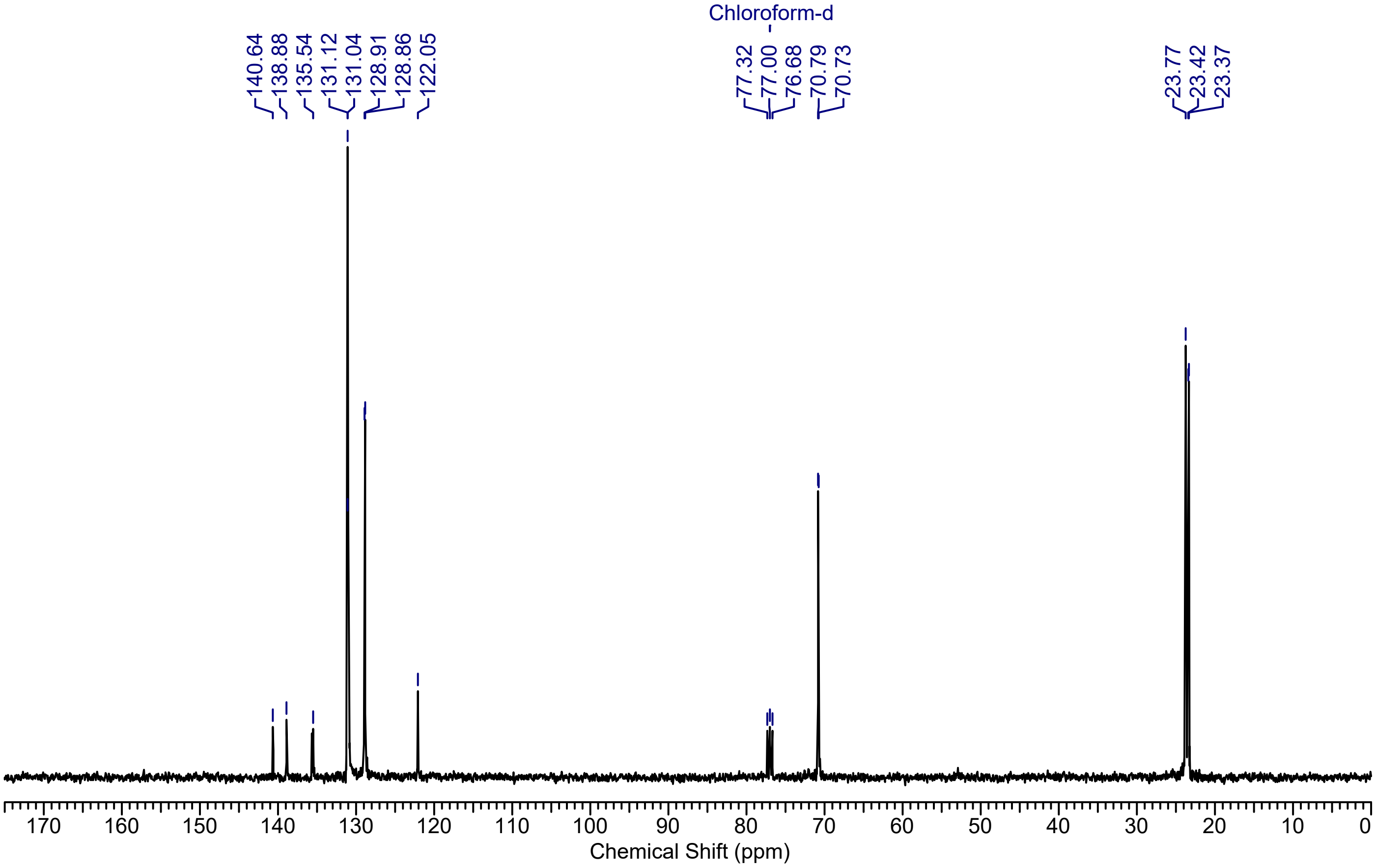
3a: ^{13}C NMR ($CDCl_3$, 101 MHz)



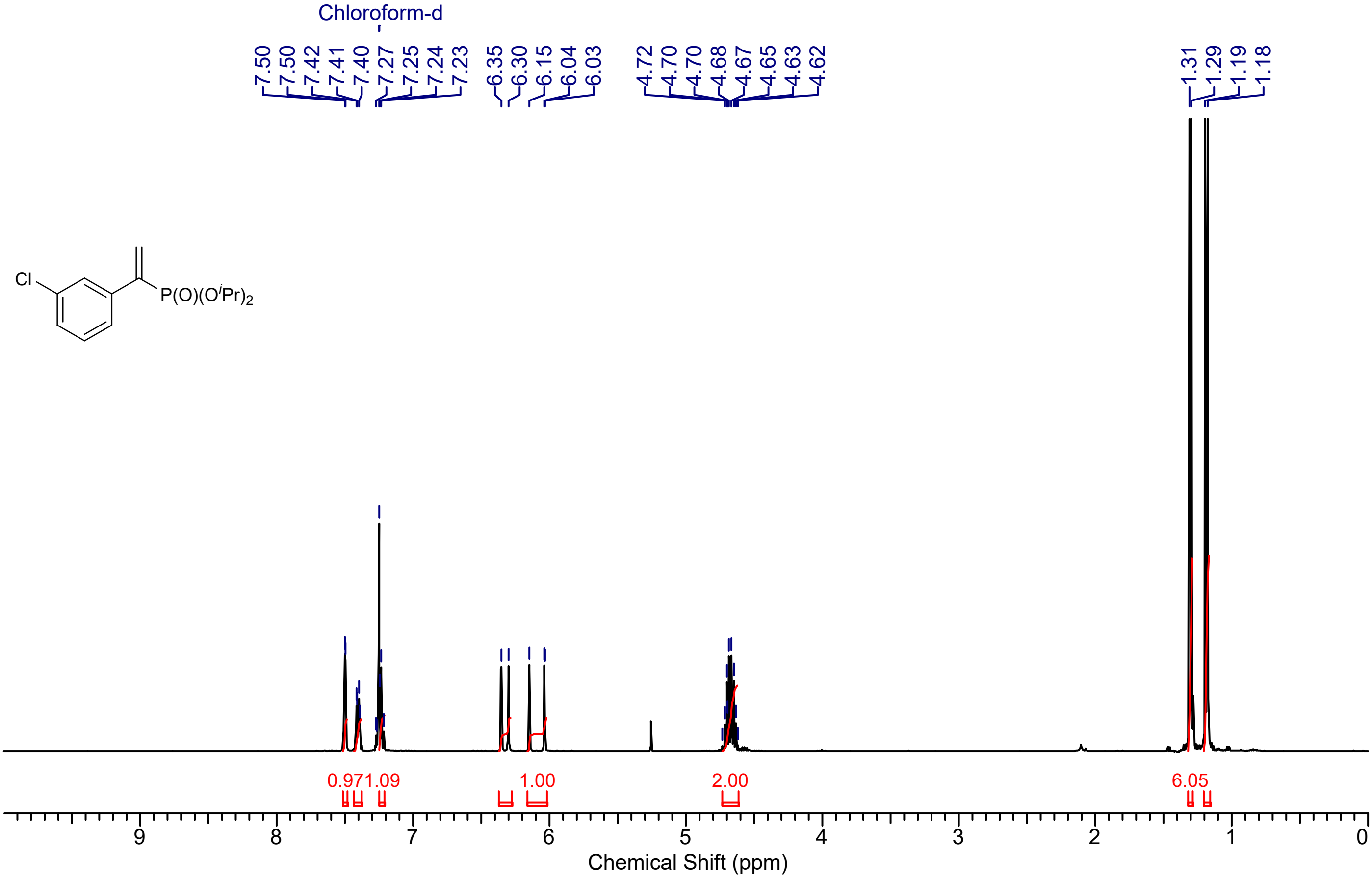
3b: ^{1}H NMR ($CDCl_3$, 400 MHz)



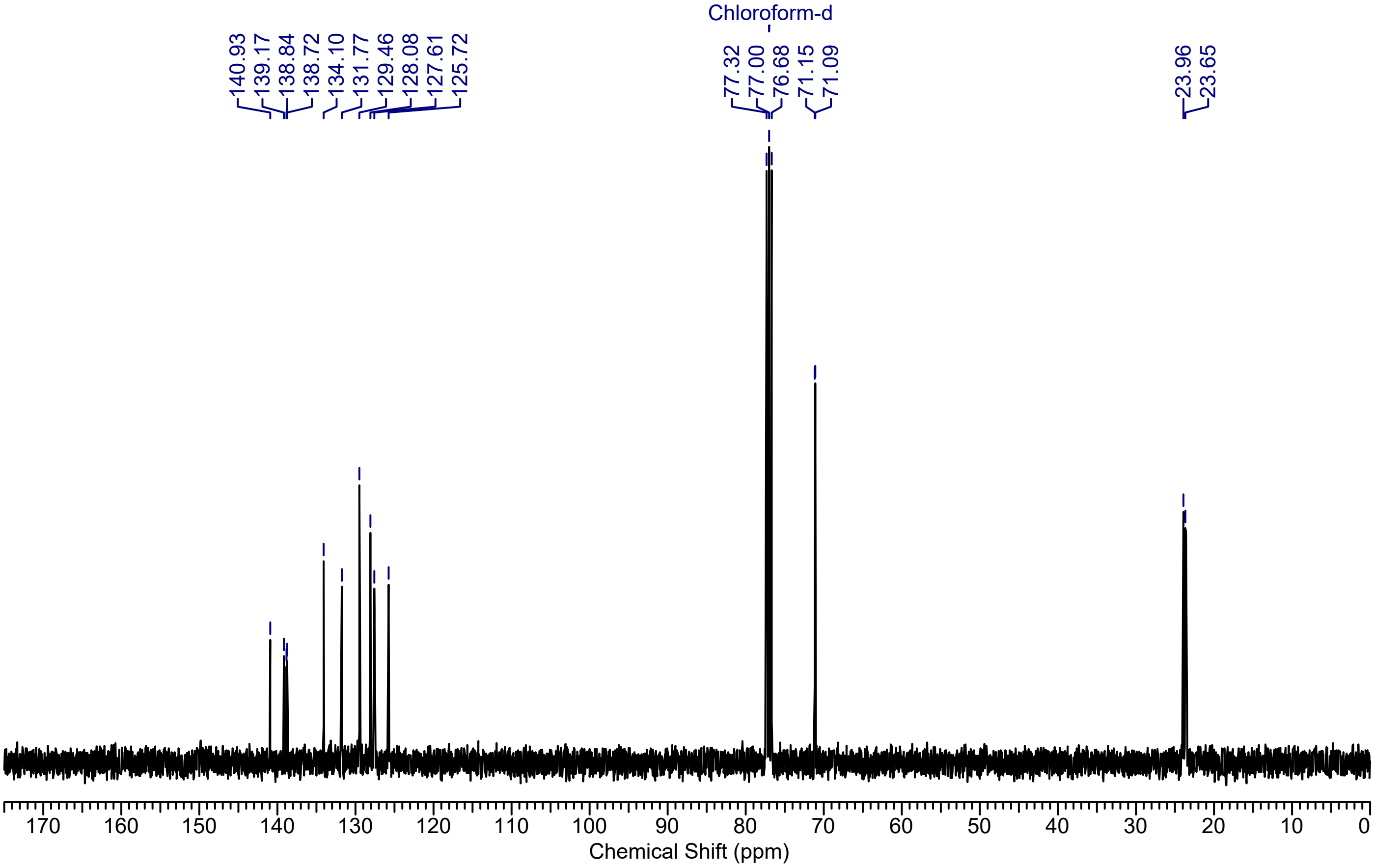
3b: ^{13}C NMR ($CDCl_3$, 101 MHz)



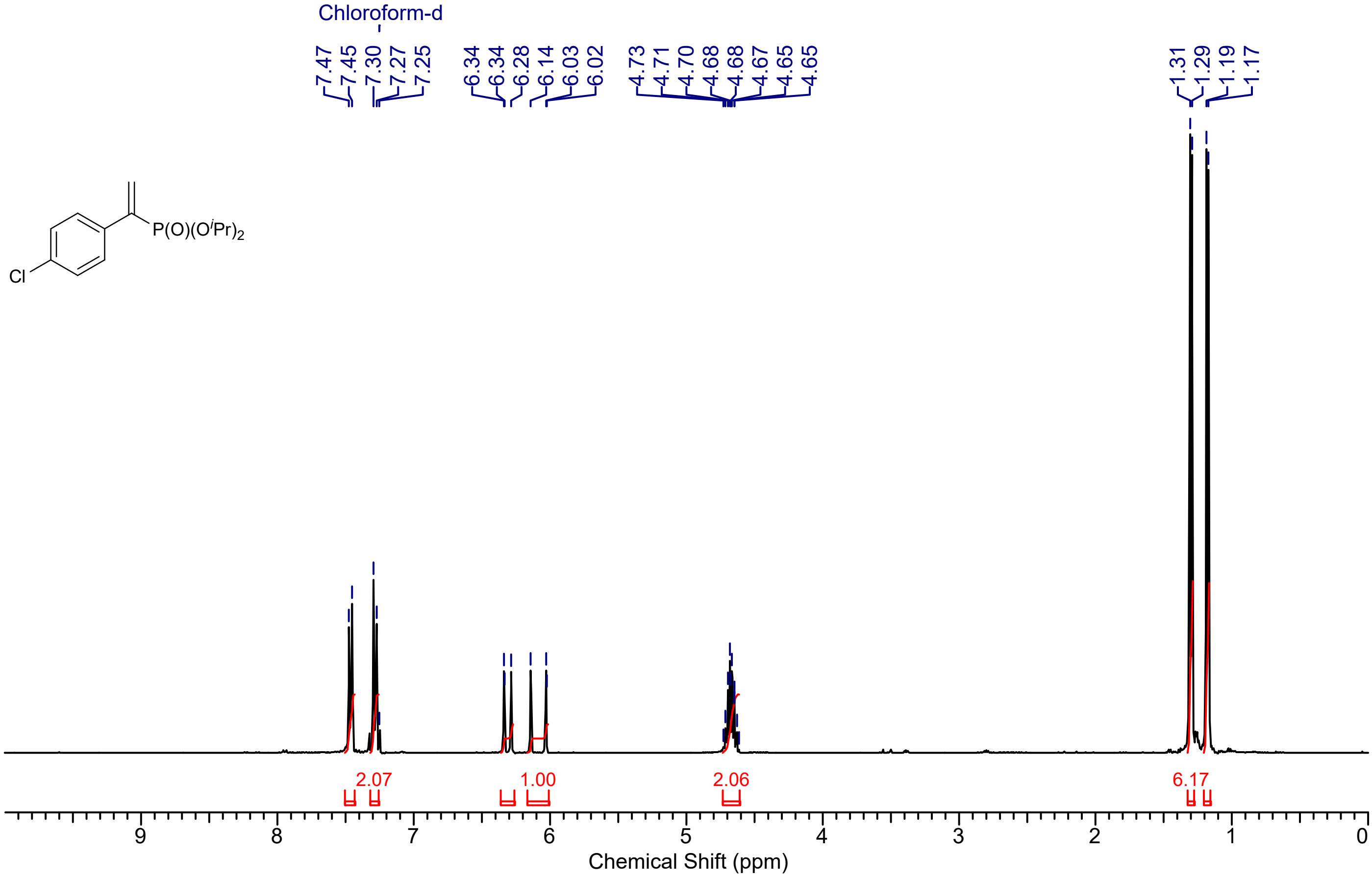
3c: ^{1}H NMR ($CDCl_3$, 400 MHz)



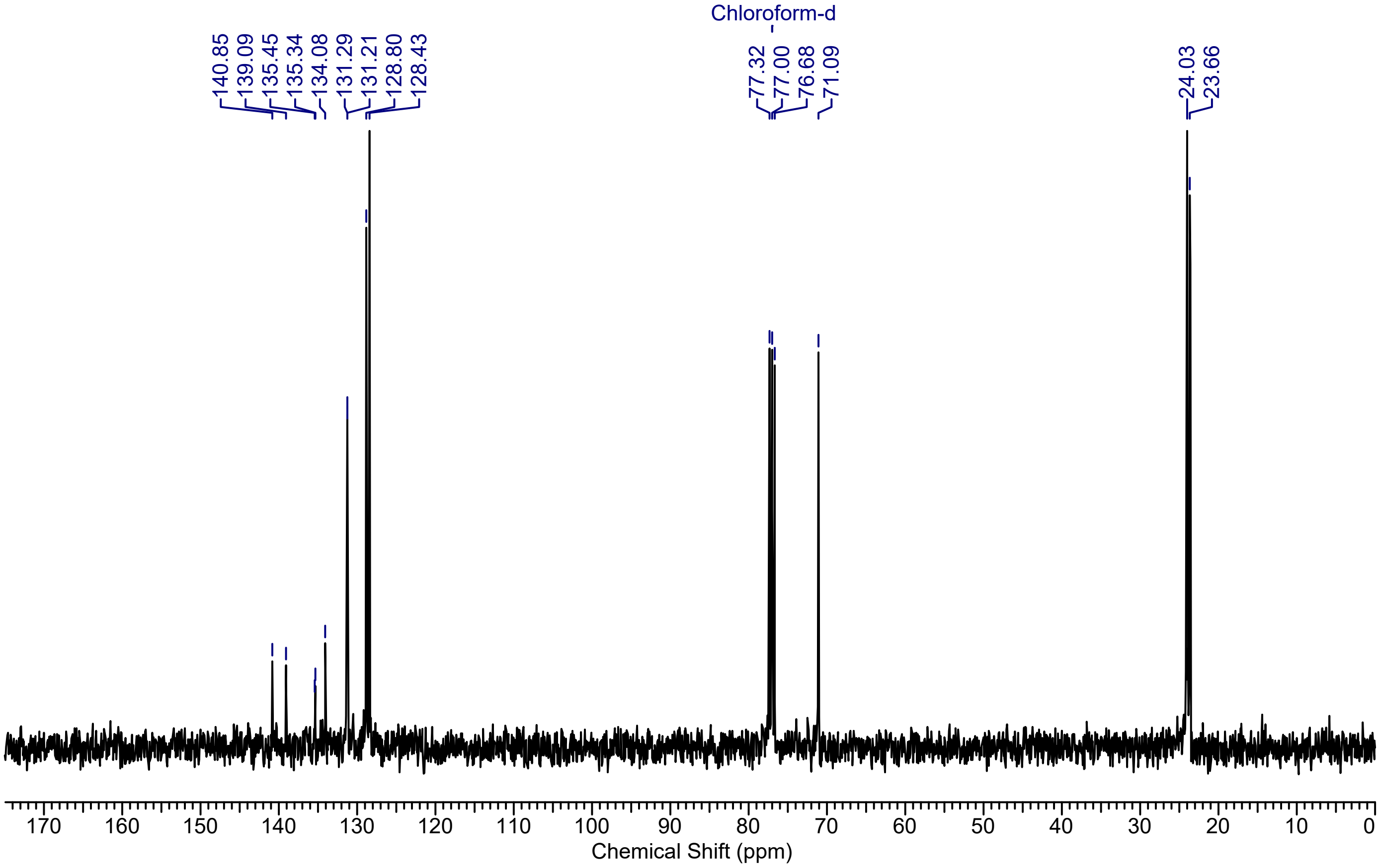
3c: ^{13}C NMR ($CDCl_3$, 101 MHz)



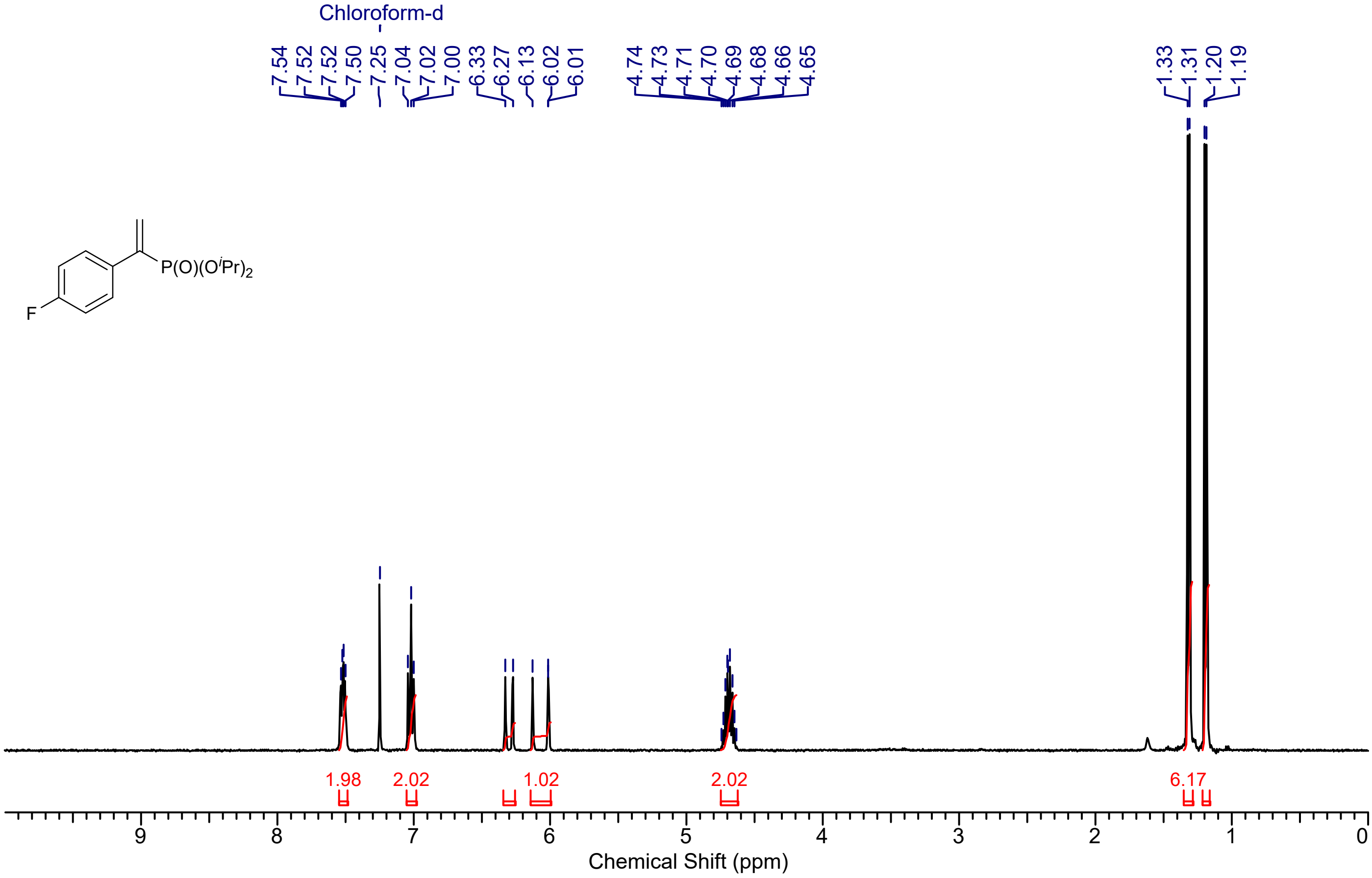
3d: ^{1}H NMR ($CDCl_3$, 400 MHz)



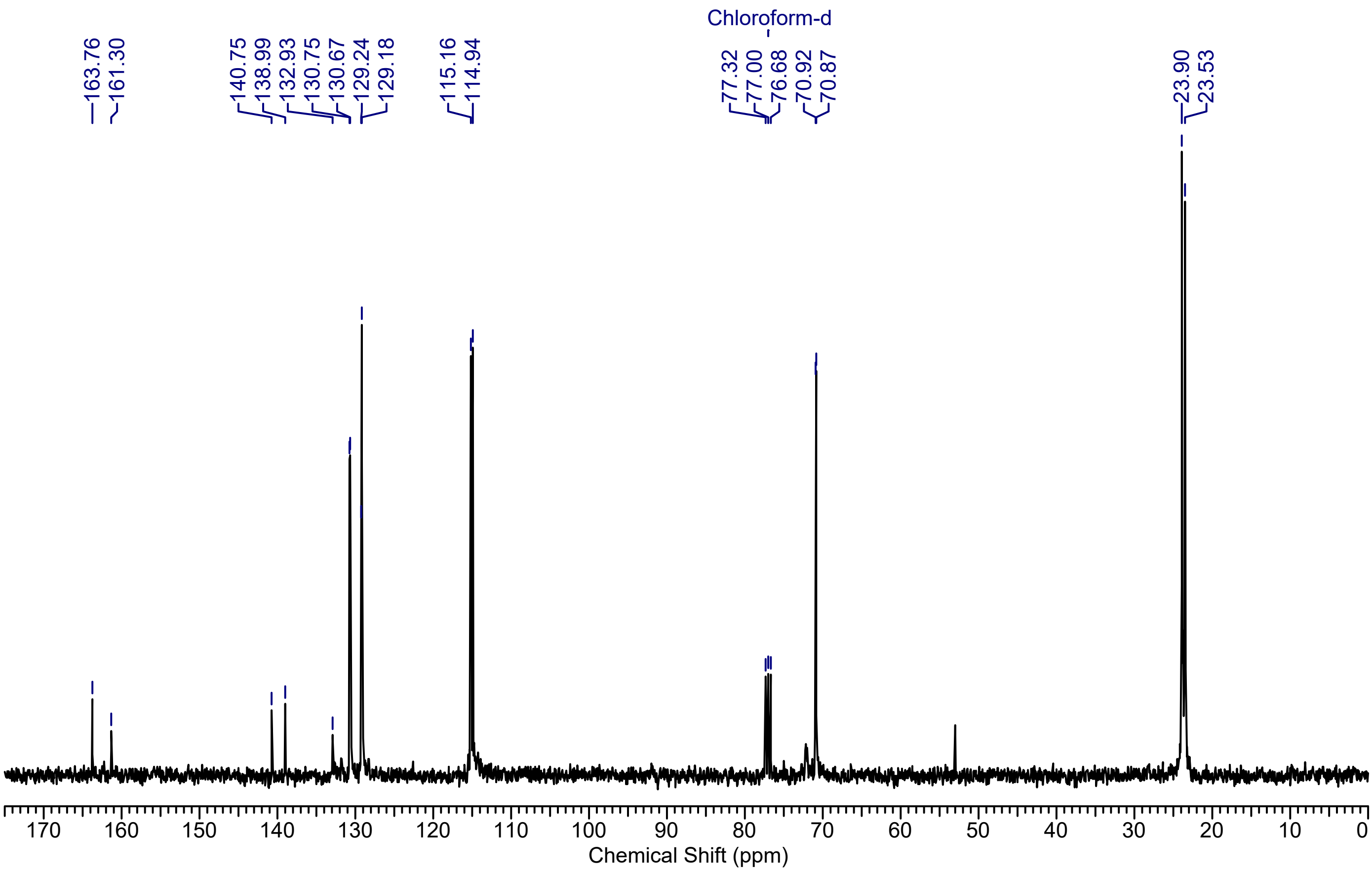
3d: ^{13}C NMR ($CDCl_3$, 101 MHz)



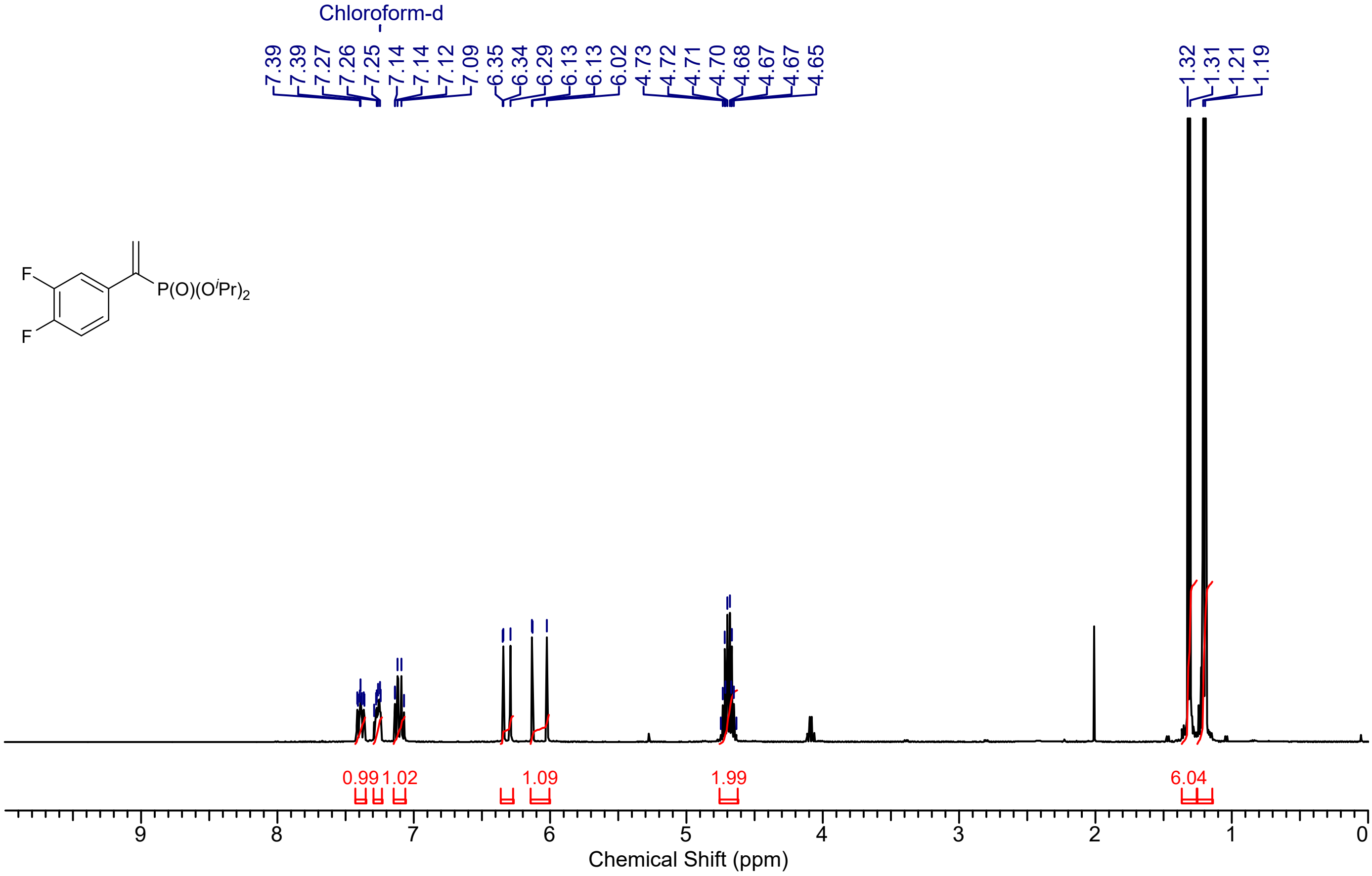
3e: ^{1}H NMR ($CDCl_3$, 400 MHz)



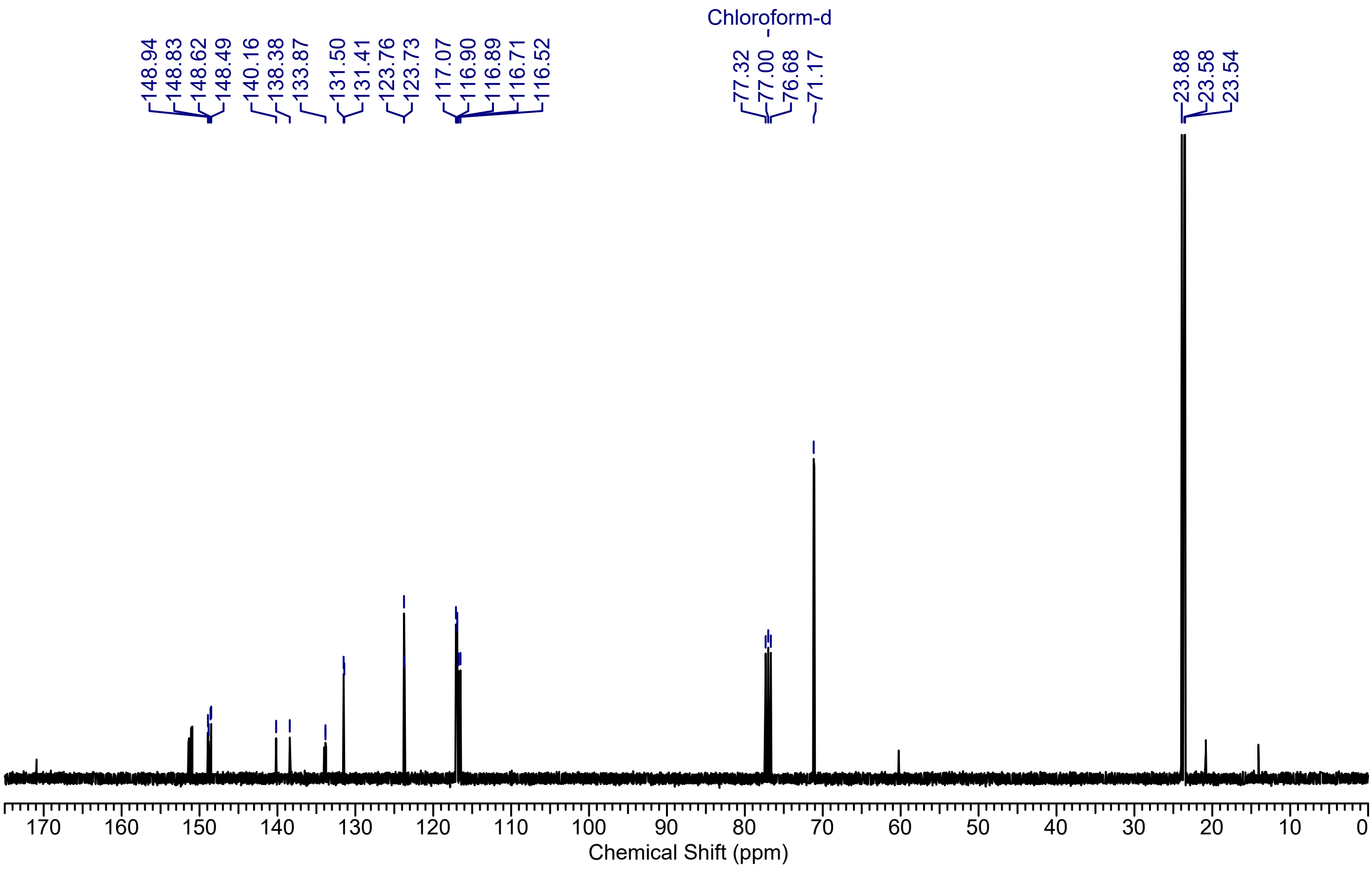
3e: ^{13}C NMR ($CDCl_3$, 101 MHz)



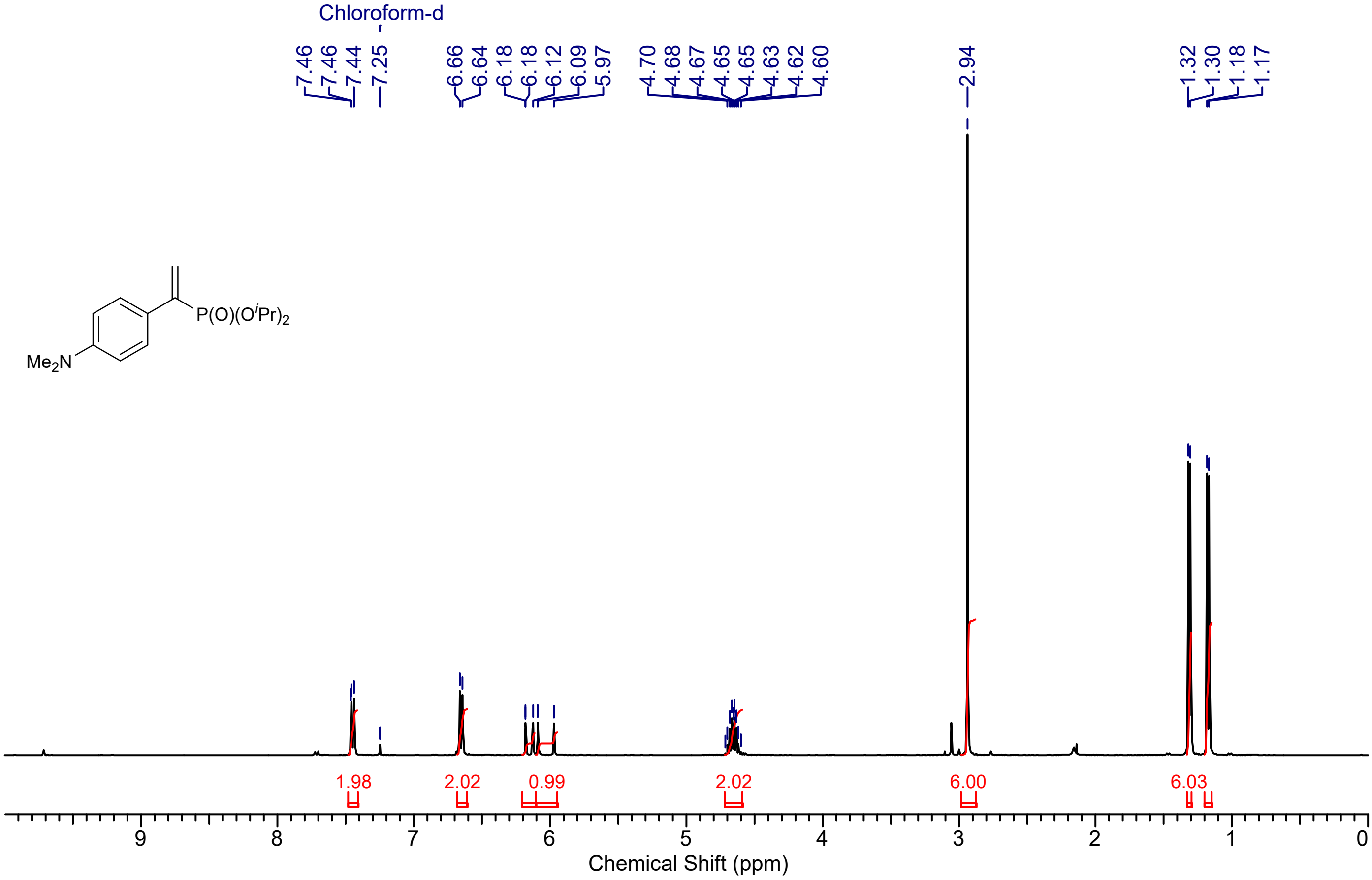
3f: ^{1}H NMR ($CDCl_3$, 400 MHz)



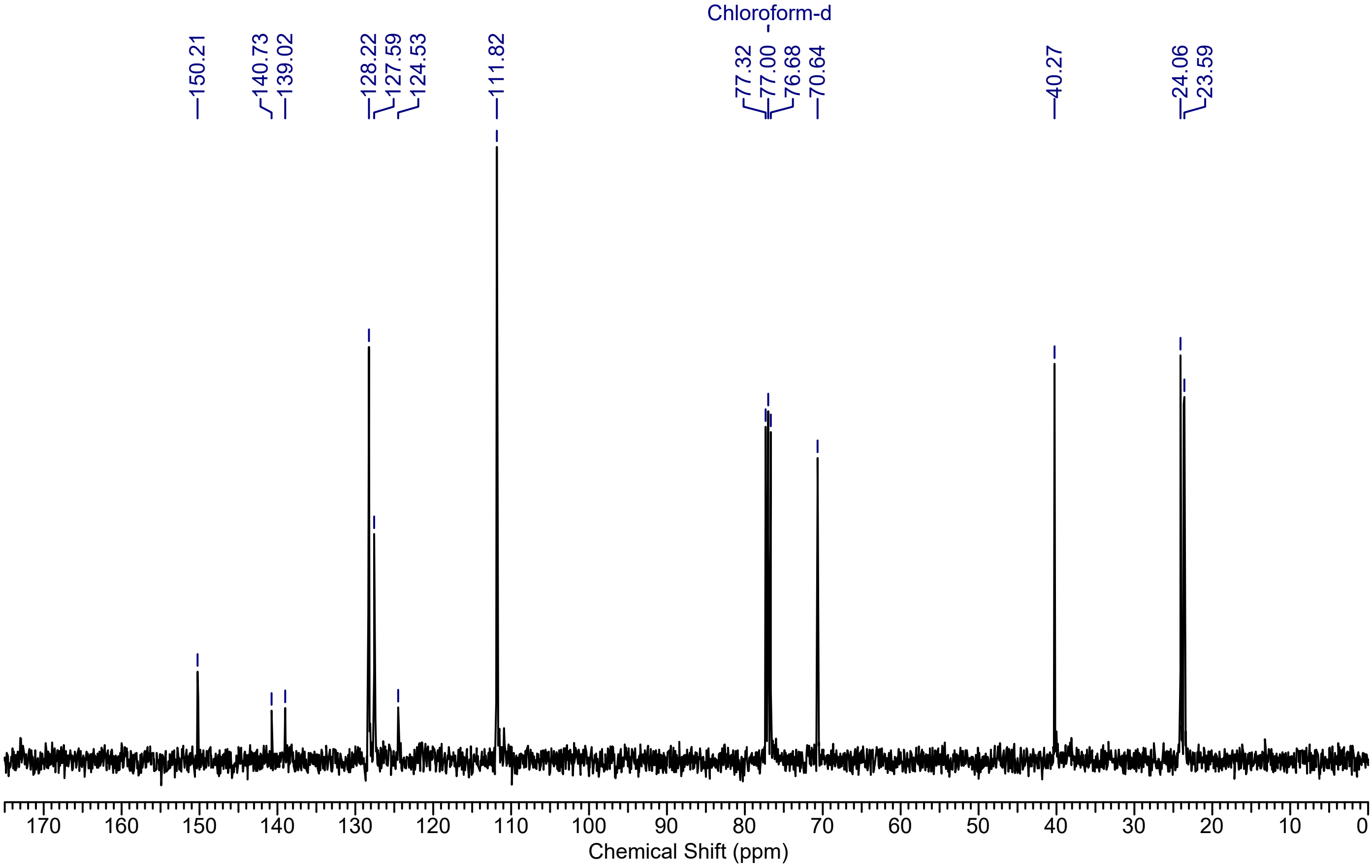
3f : ^{13}C NMR ($CDCl_3$, 101 MHz)



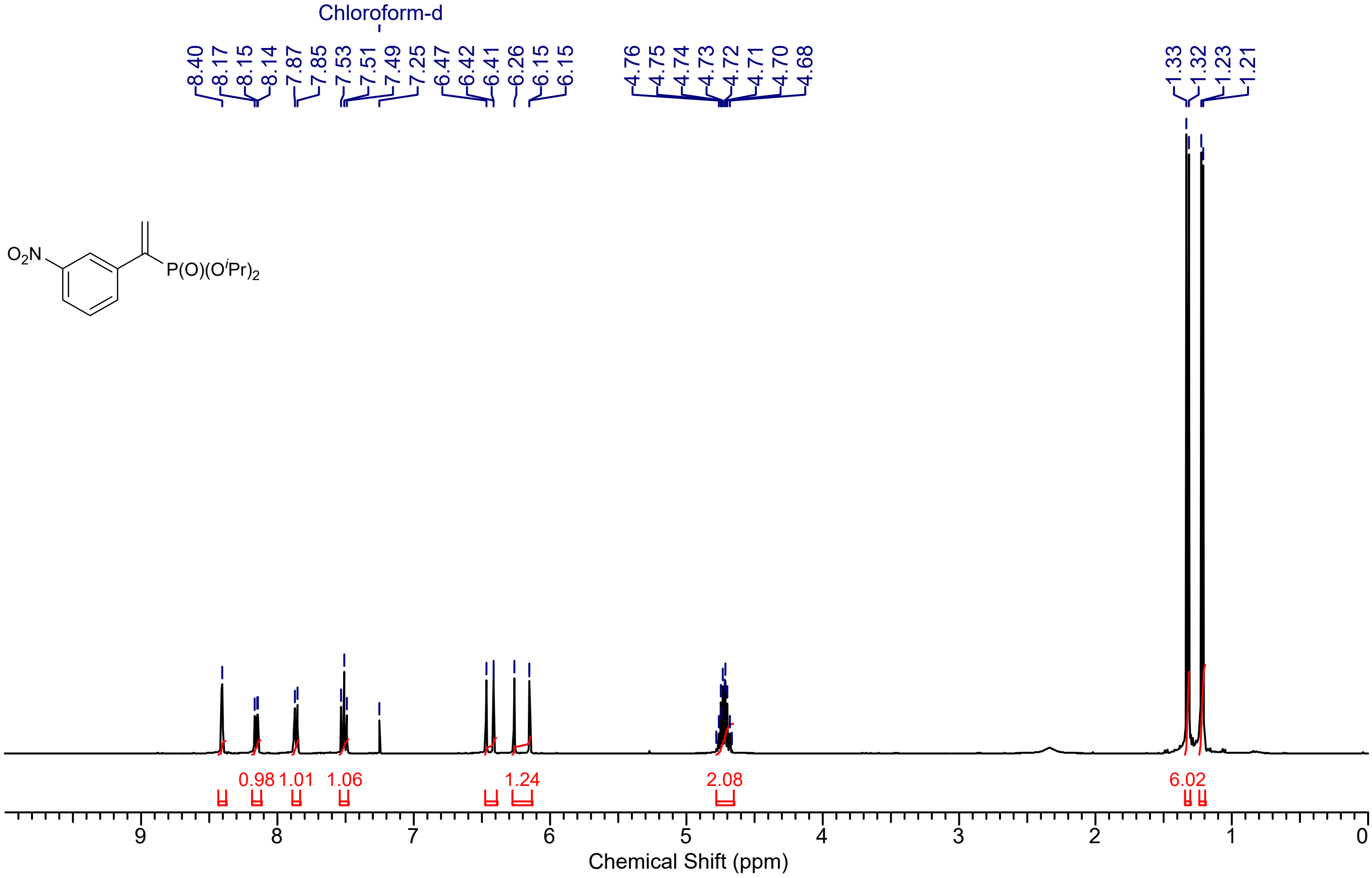
3g: ^{1}H NMR ($CDCl_3$, 400 MHz)



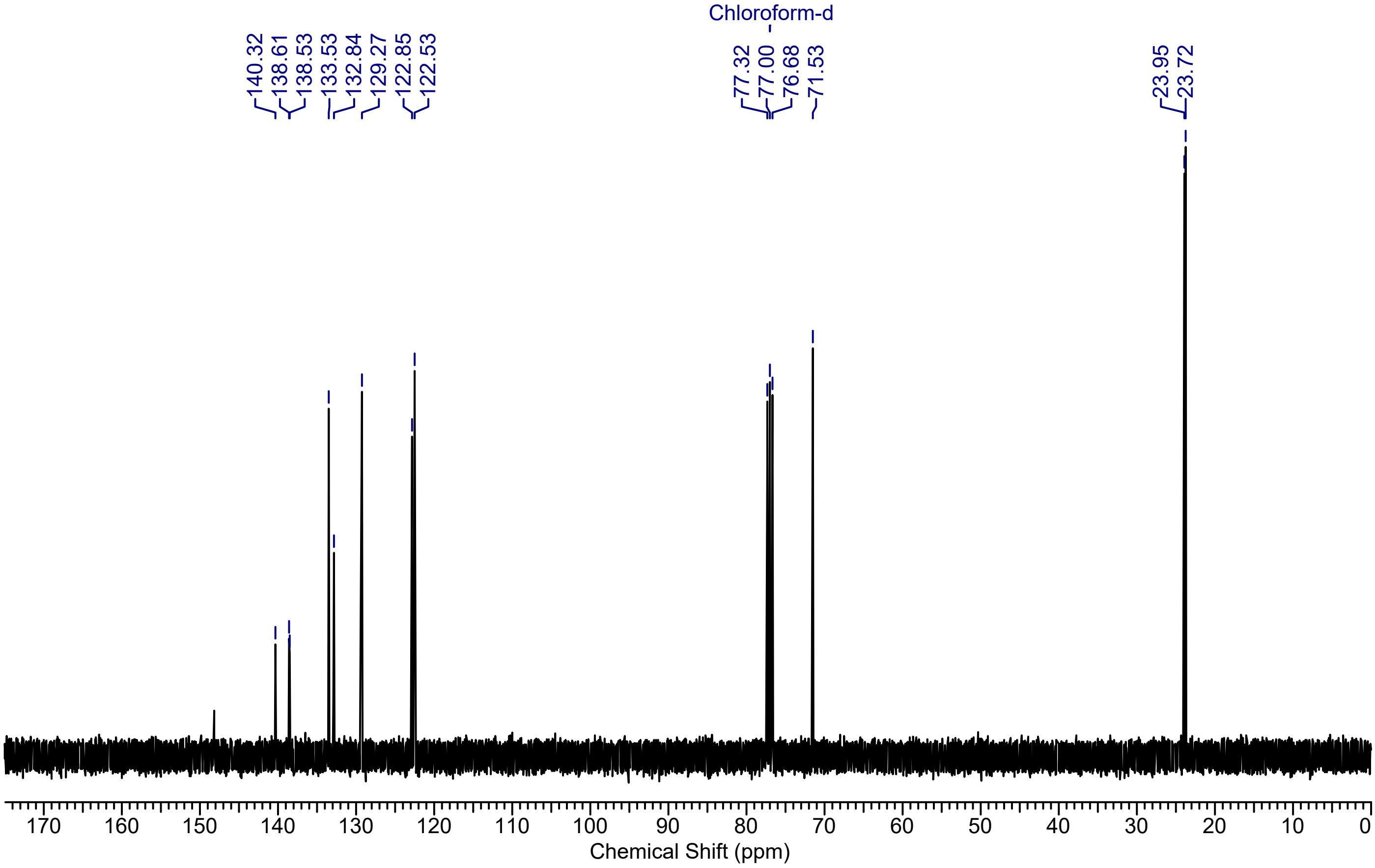
3g: ^{13}C NMR ($CDCl_3$, 101 MHz)



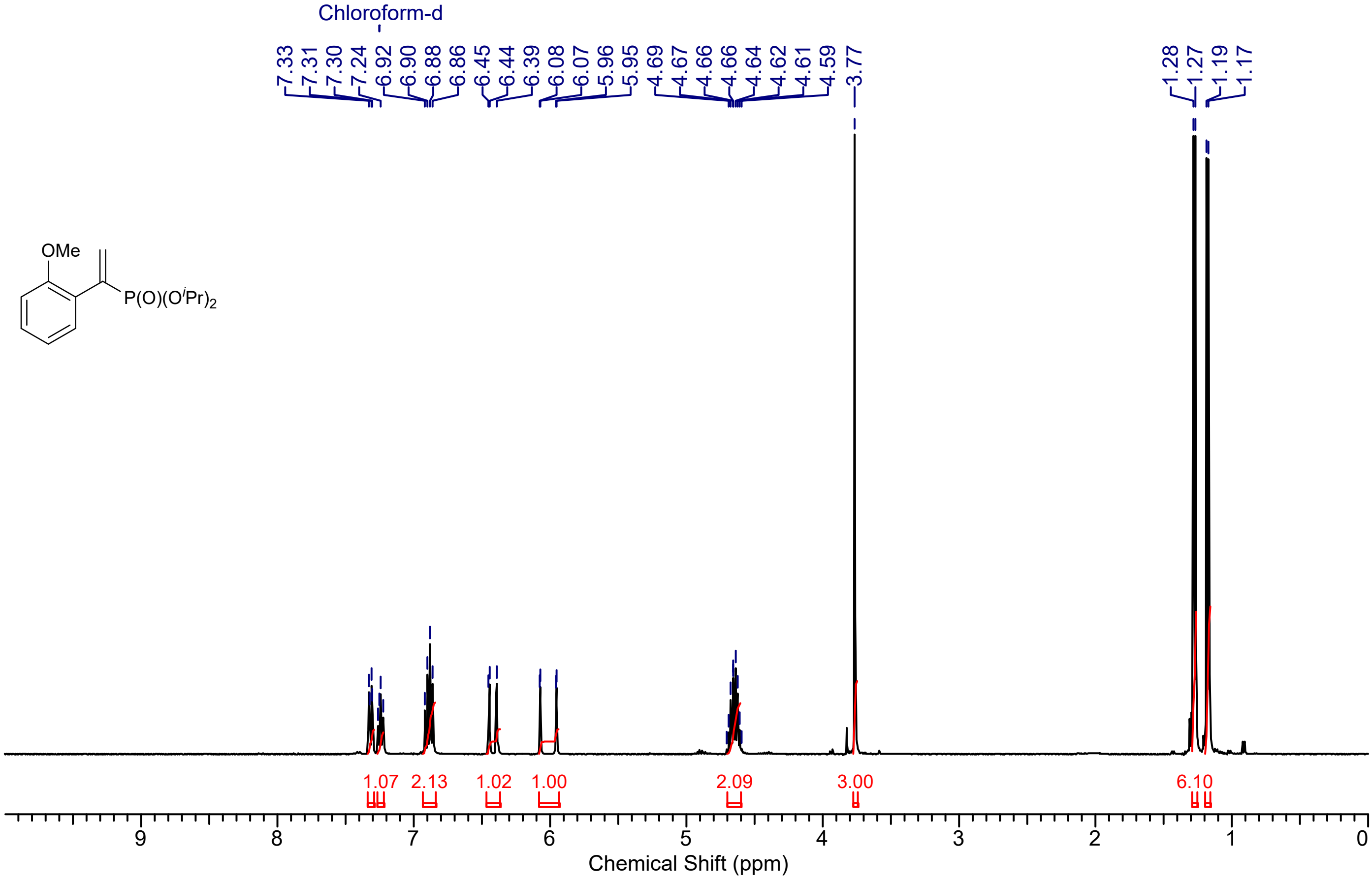
3h: ^{1}H NMR ($CDCl_3$, 400 MHz)



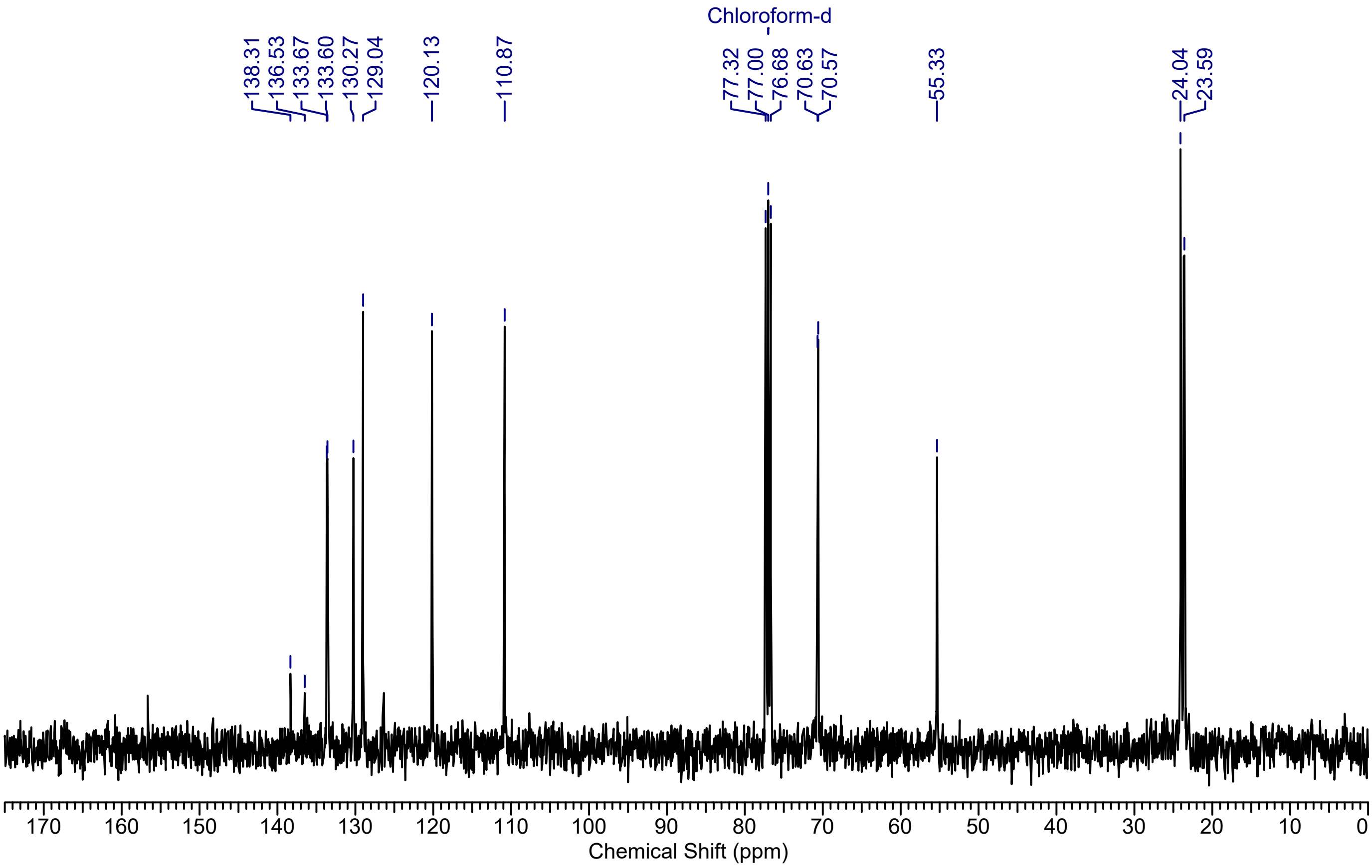
3h: ^{13}C NMR ($CDCl_3$, 101 MHz)



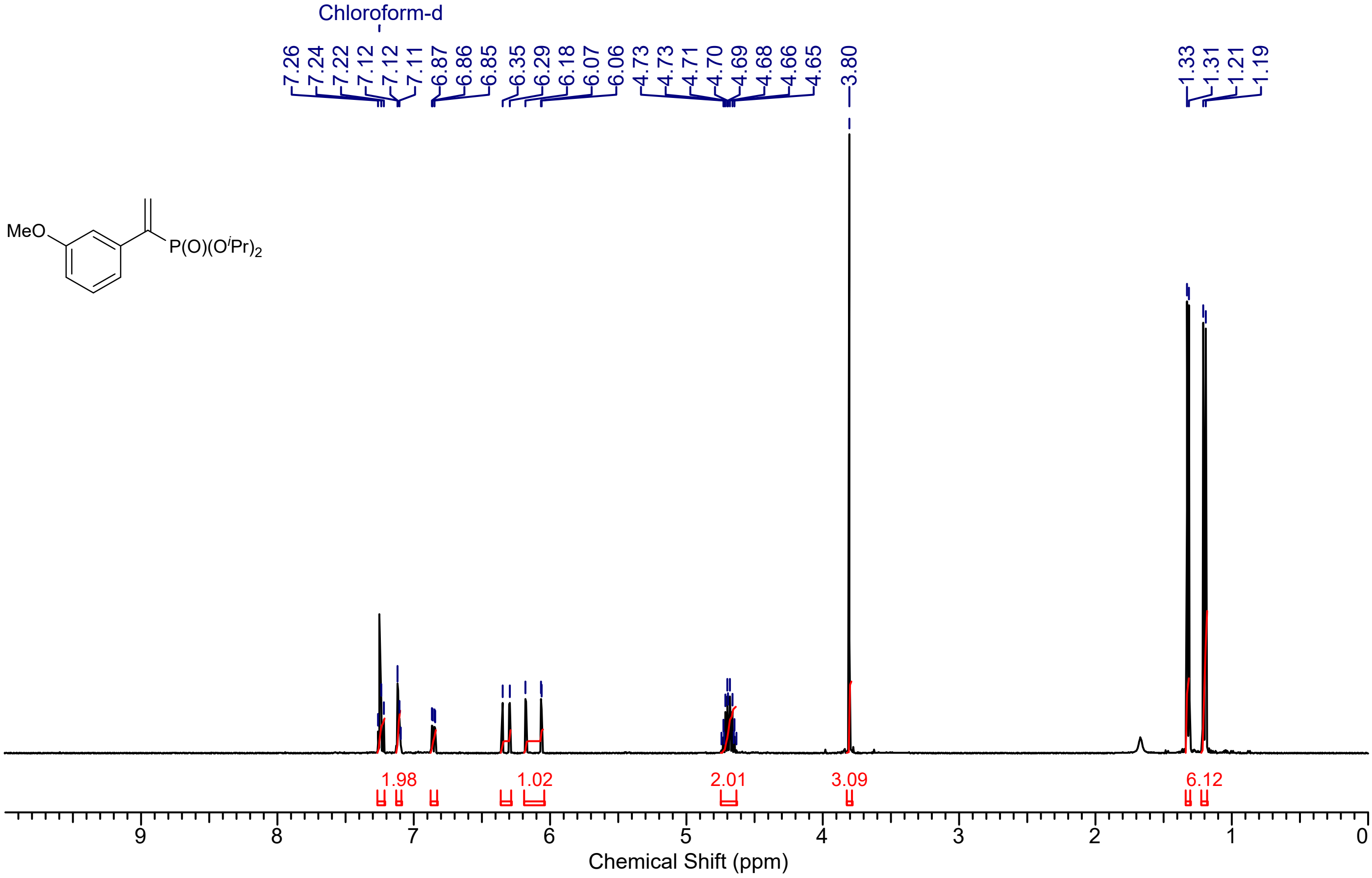
3i: ^{1}H NMR ($CDCl_3$, 400 MHz)



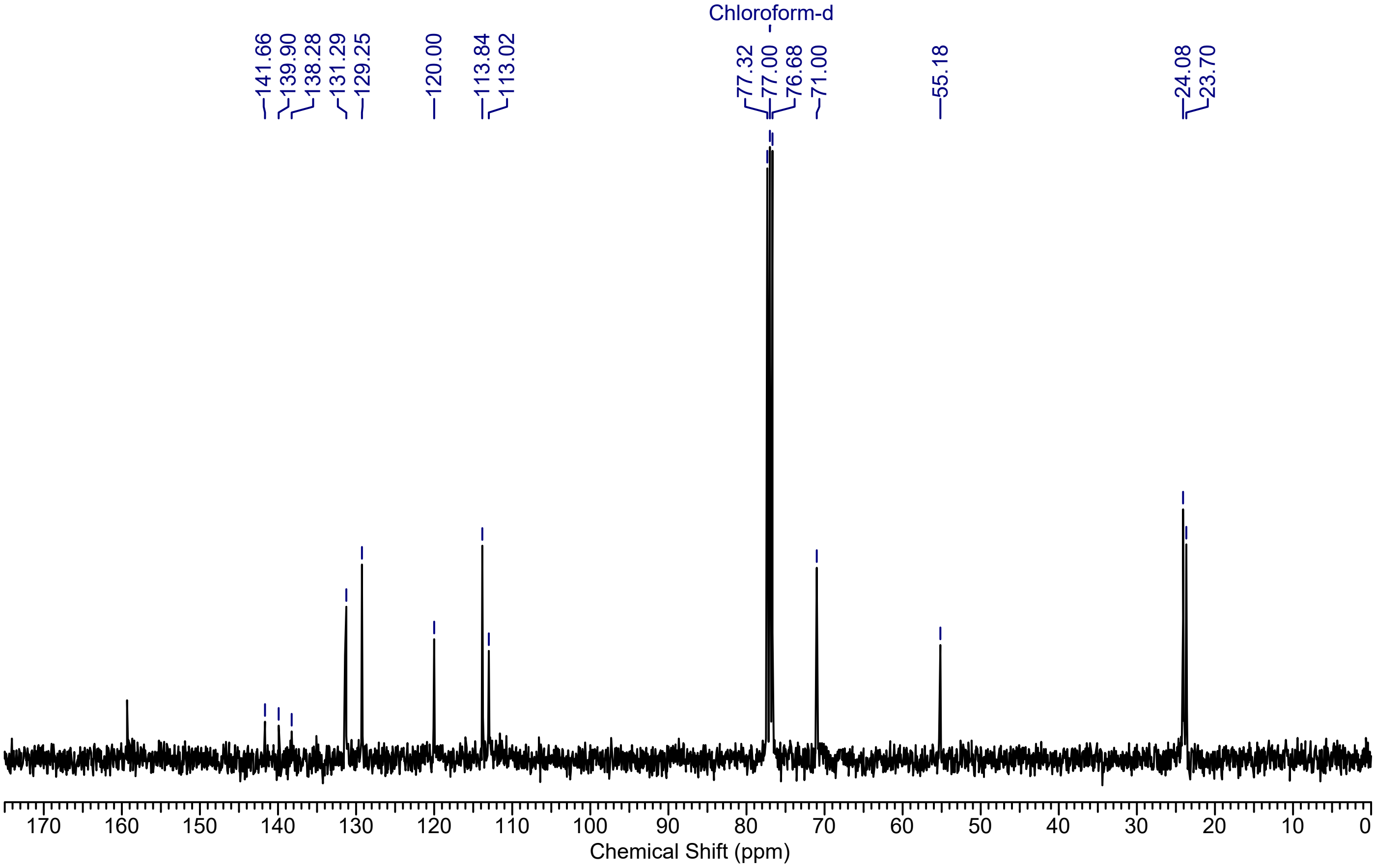
3i: ^{13}C NMR ($CDCl_3$, 101 MHz)



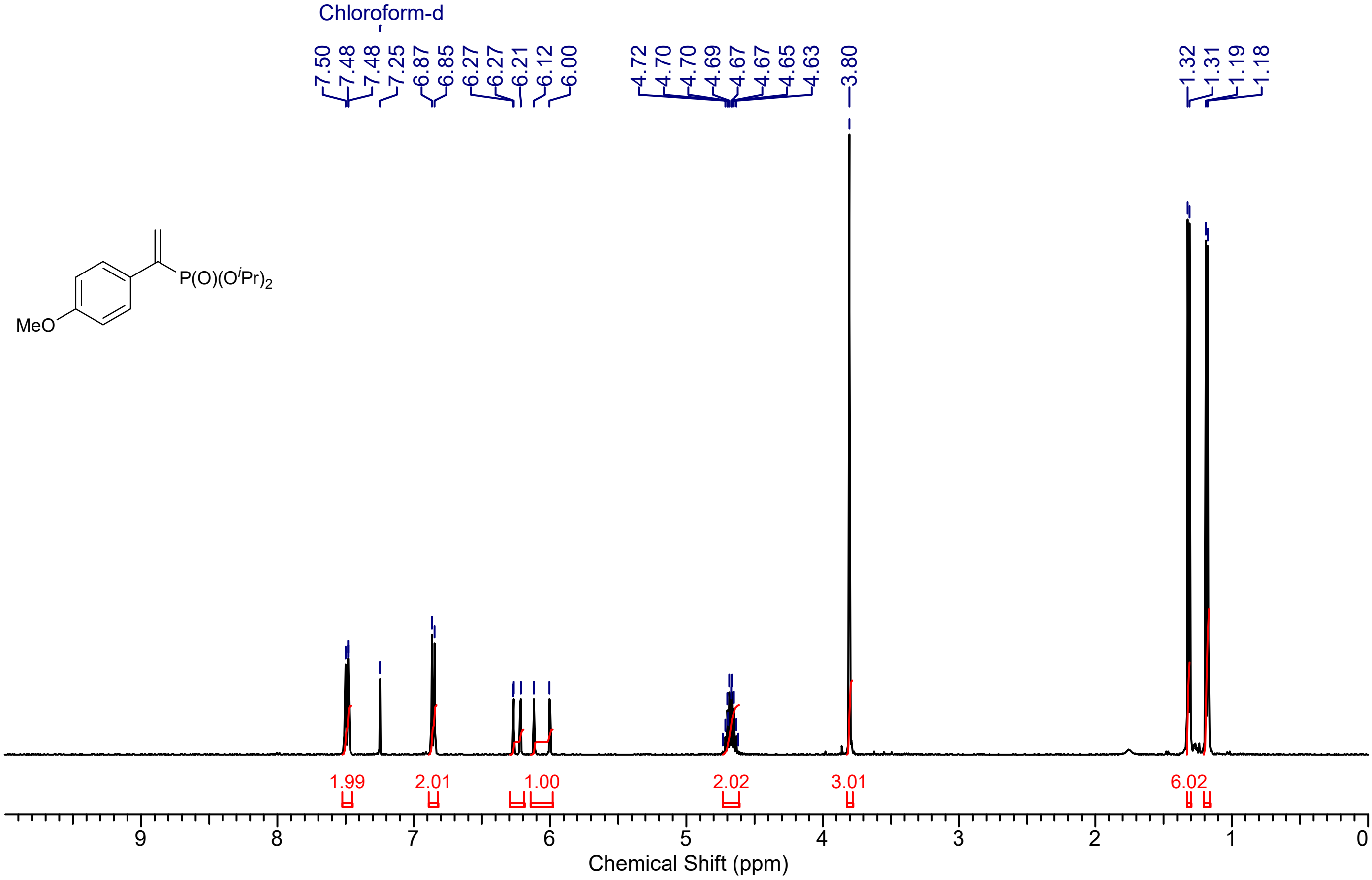
3j: ^{1}H NMR ($CDCl_3$, 400 MHz)



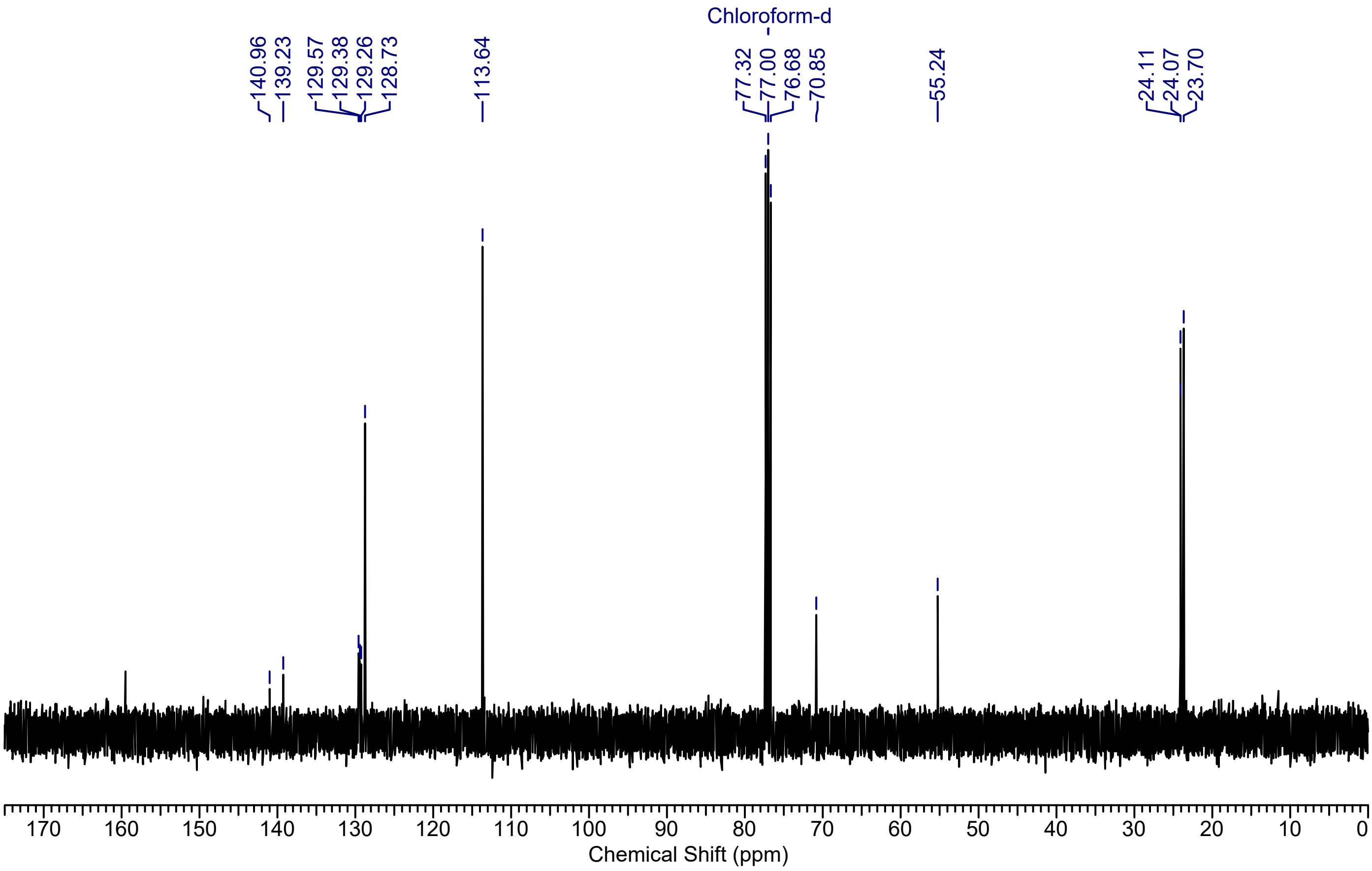
3j: ^{13}C NMR ($CDCl_3$, 101 MHz)



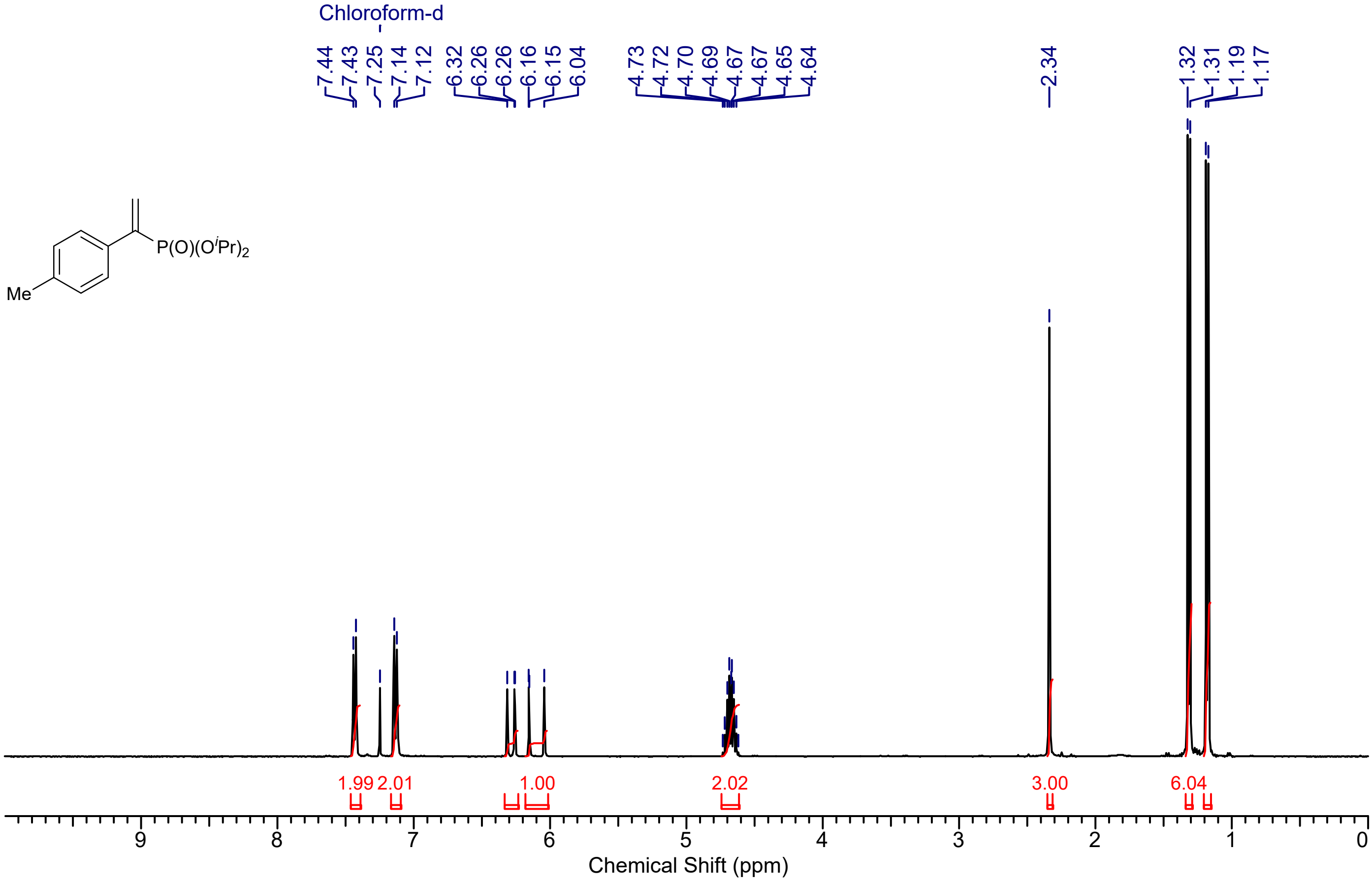
3k: ^{1}H NMR ($CDCl_3$, 400 MHz)



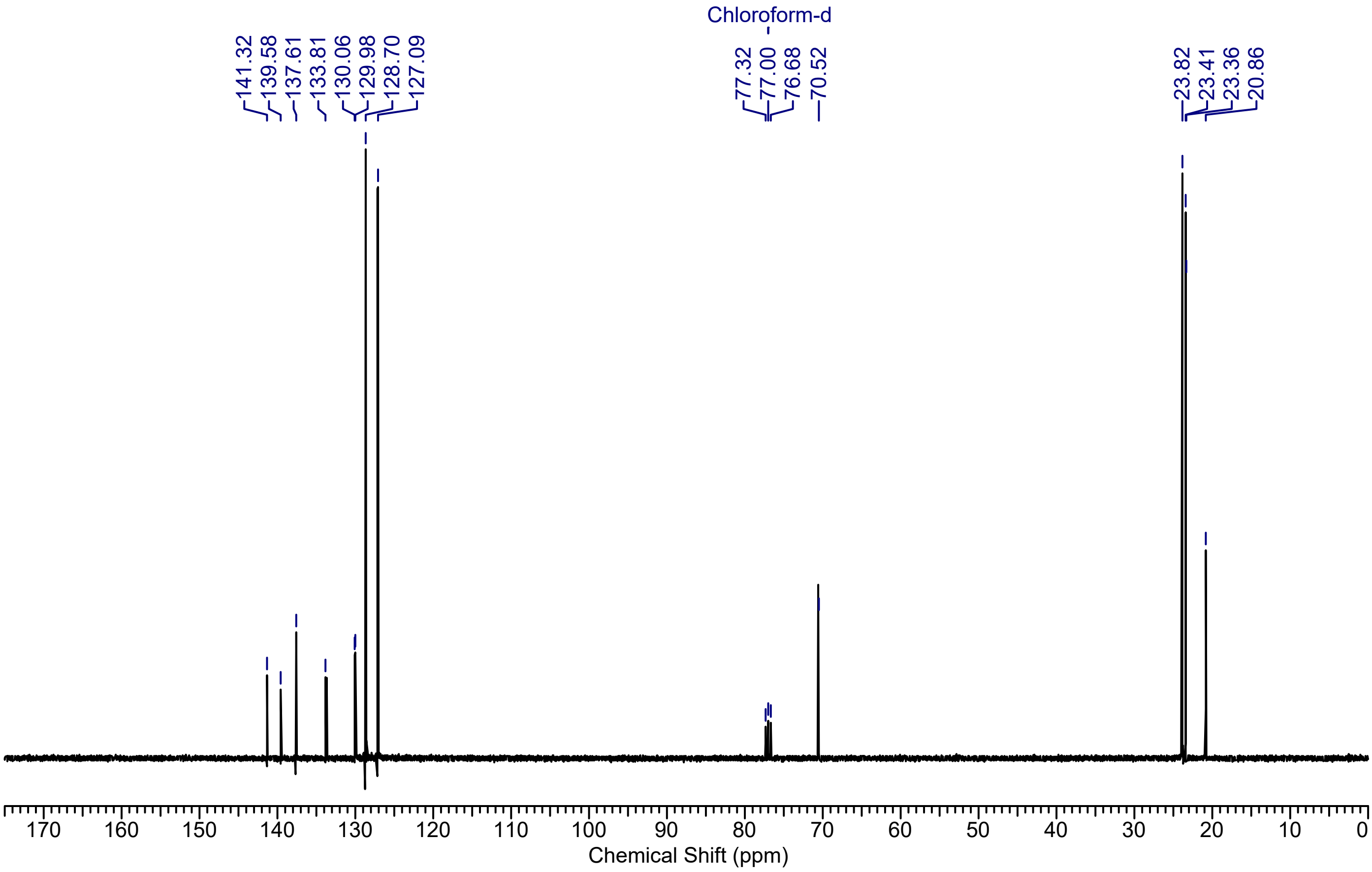
3k: ^{13}C NMR ($CDCl_3$, 101 MHz)



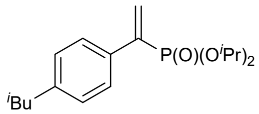
3l: ^{1}H NMR ($CDCl_3$, 400 MHz)

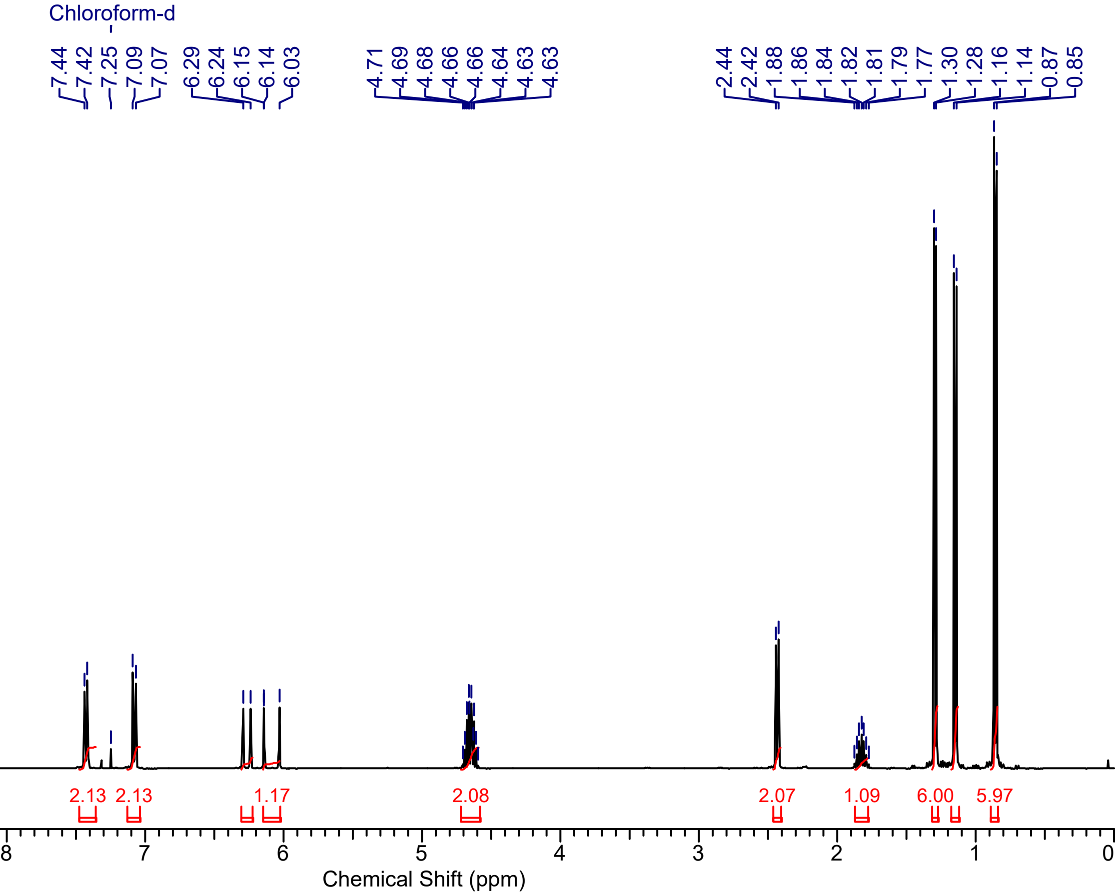


3l: ^{13}C NMR ($CDCl_3$, 101 MHz)

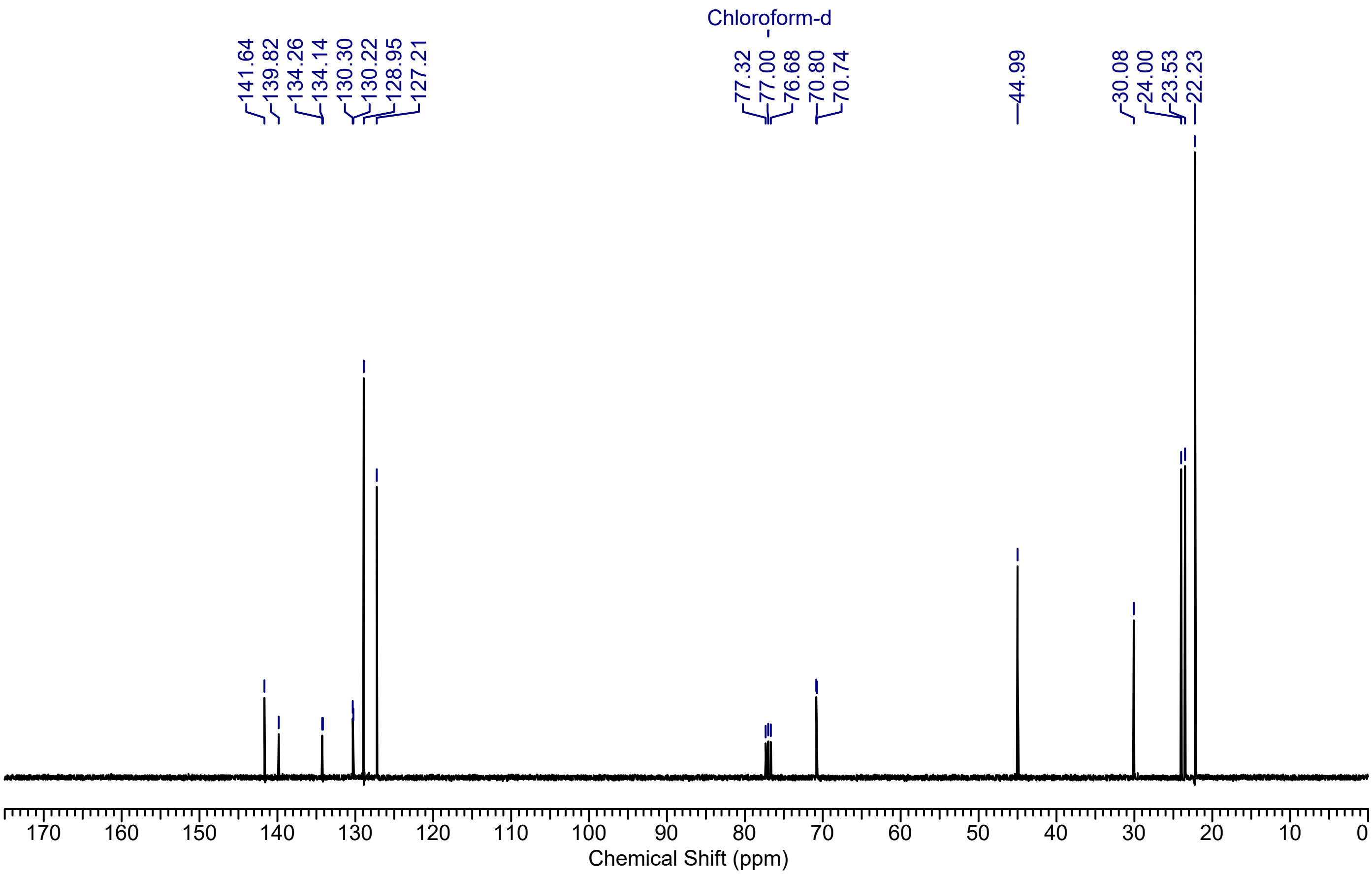


3m: ^{1}H NMR ($CDCl_3$, 400 MHz)

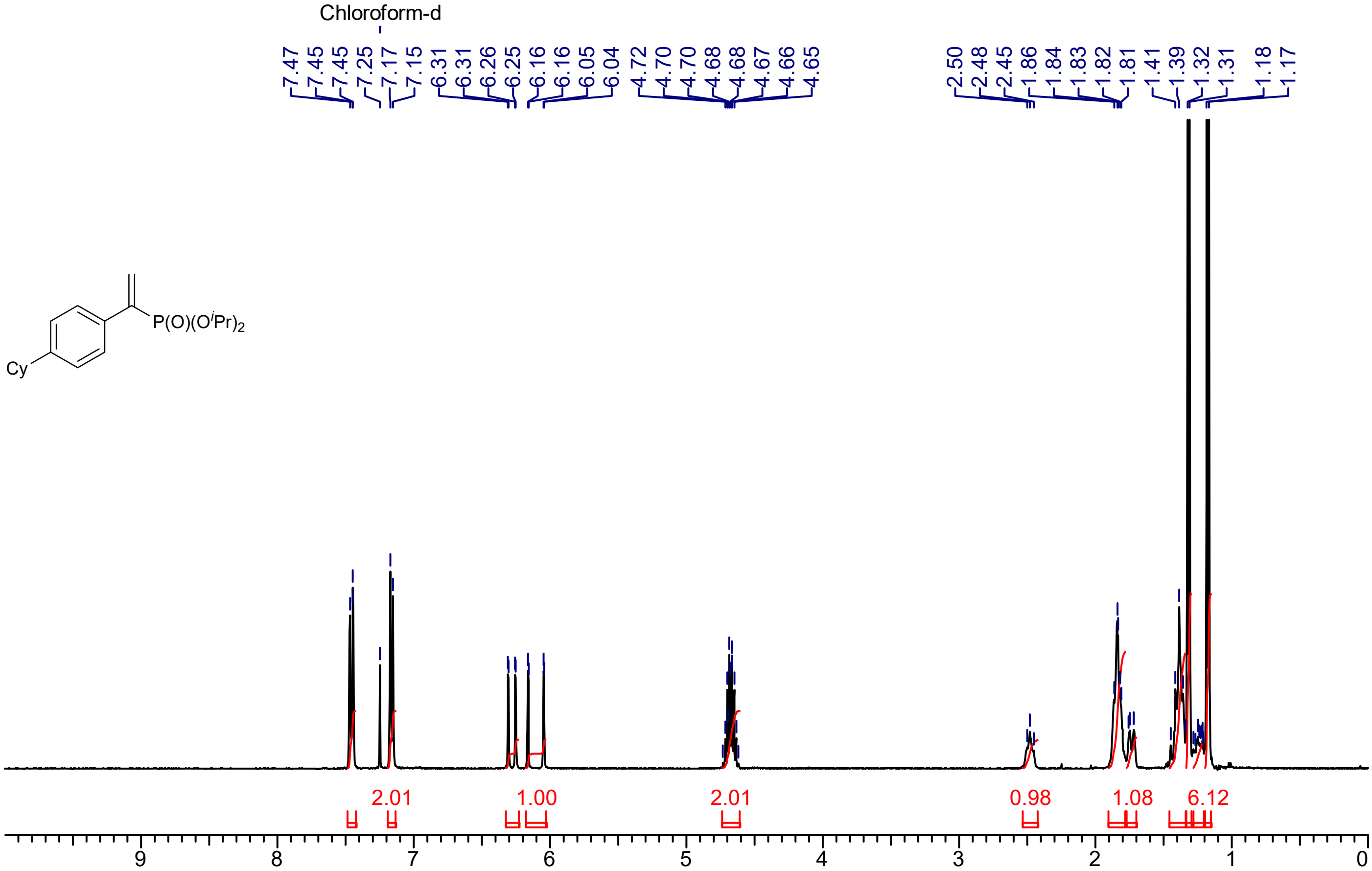




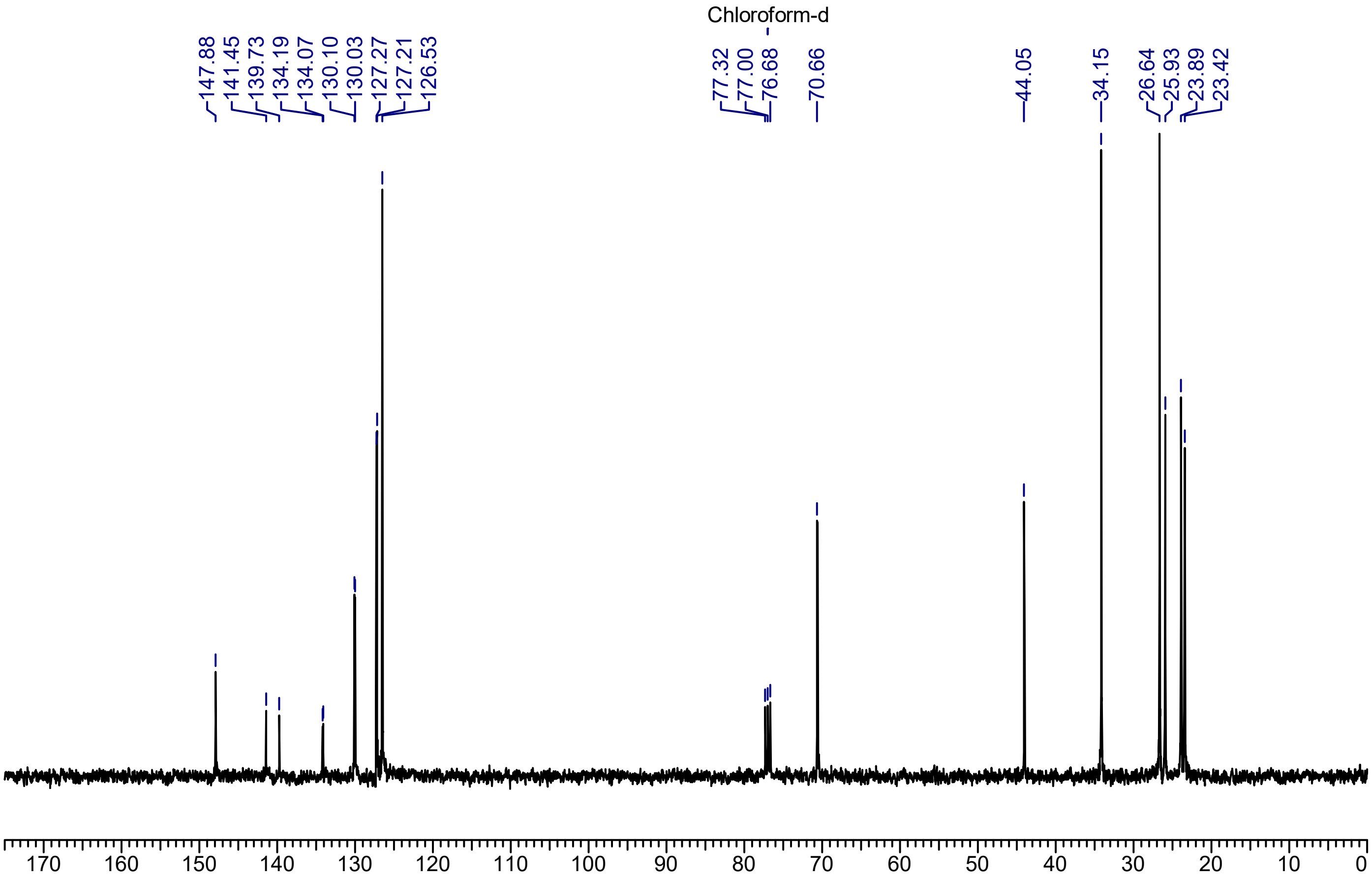
3m: ^{13}C NMR ($CDCl_3$, 101 MHz)



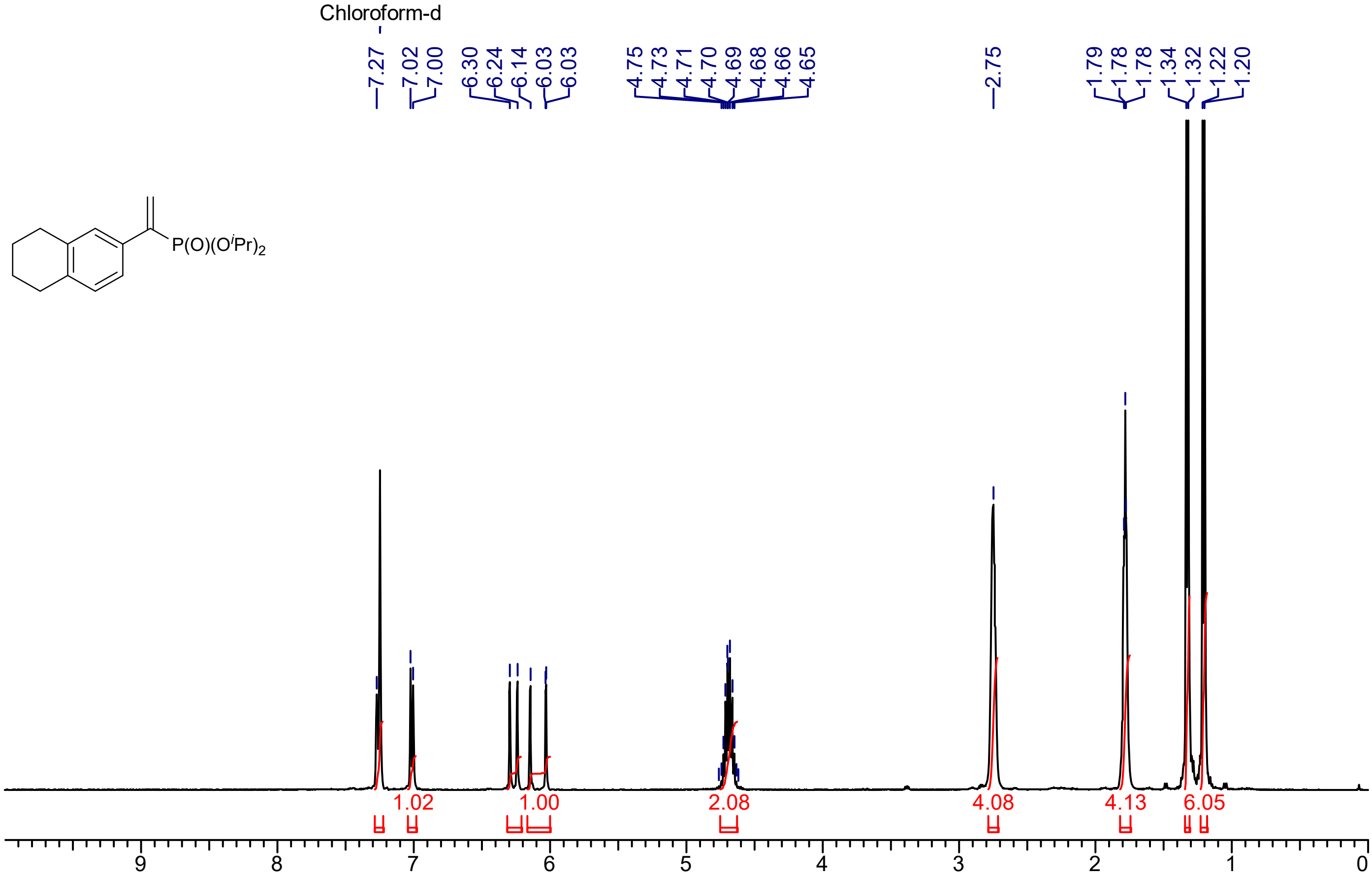
3n: ^{1}H NMR ($CDCl_3$, 400 MHz)



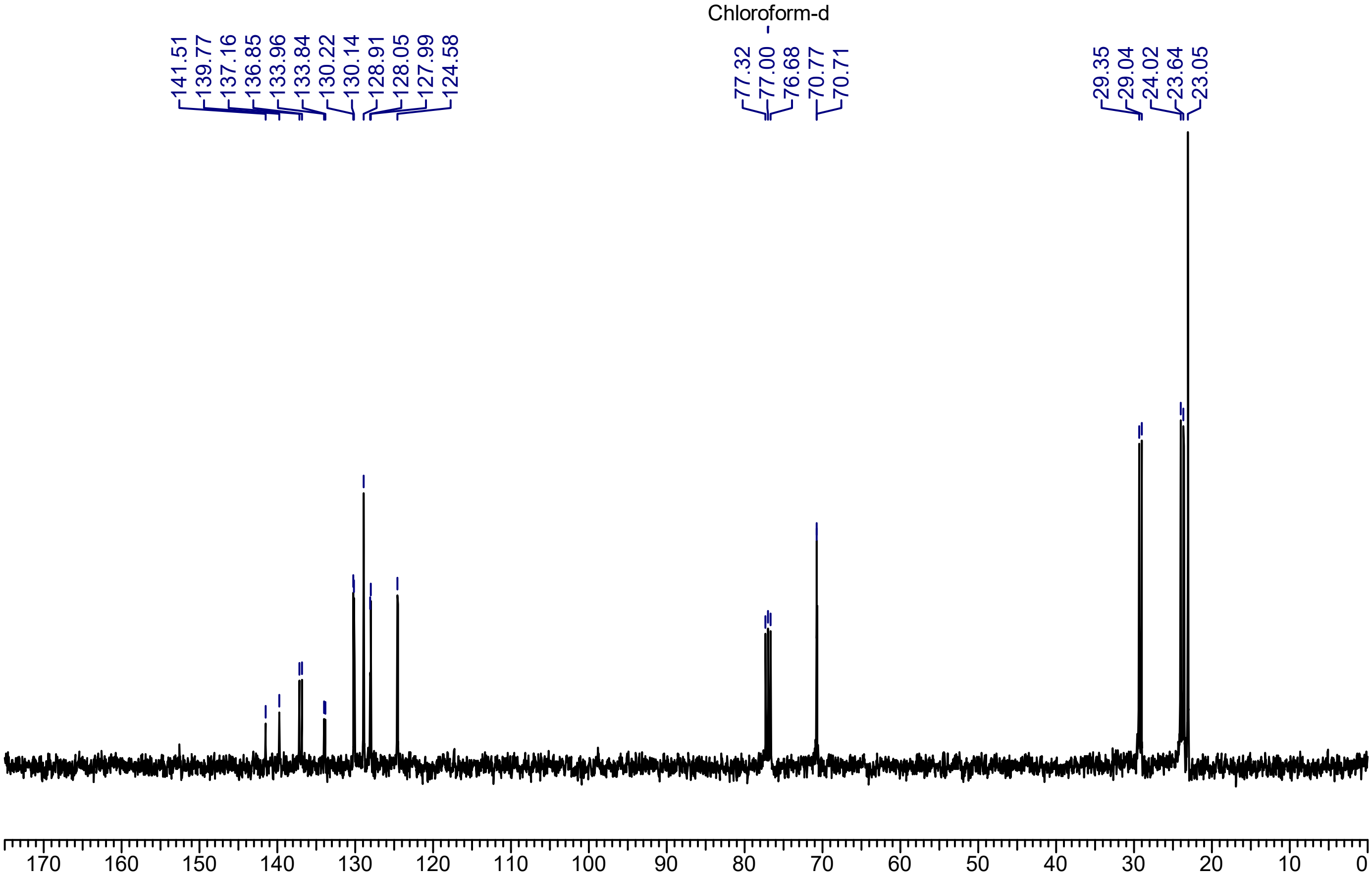
3n: ^{13}C NMR ($CDCl_3$, 101 MHz)



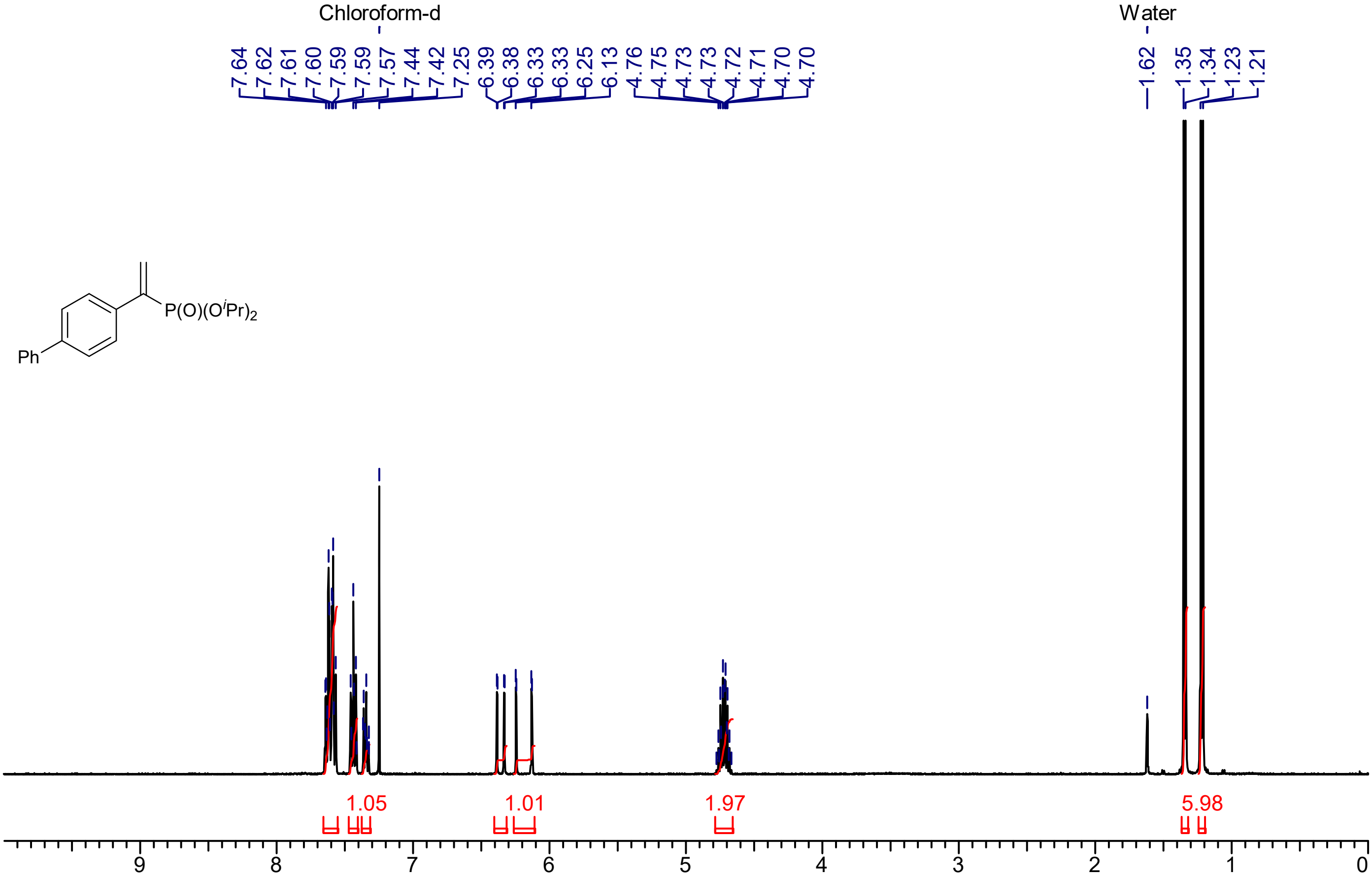
3o: ^{1}H NMR ($CDCl_3$, 400 MHz)



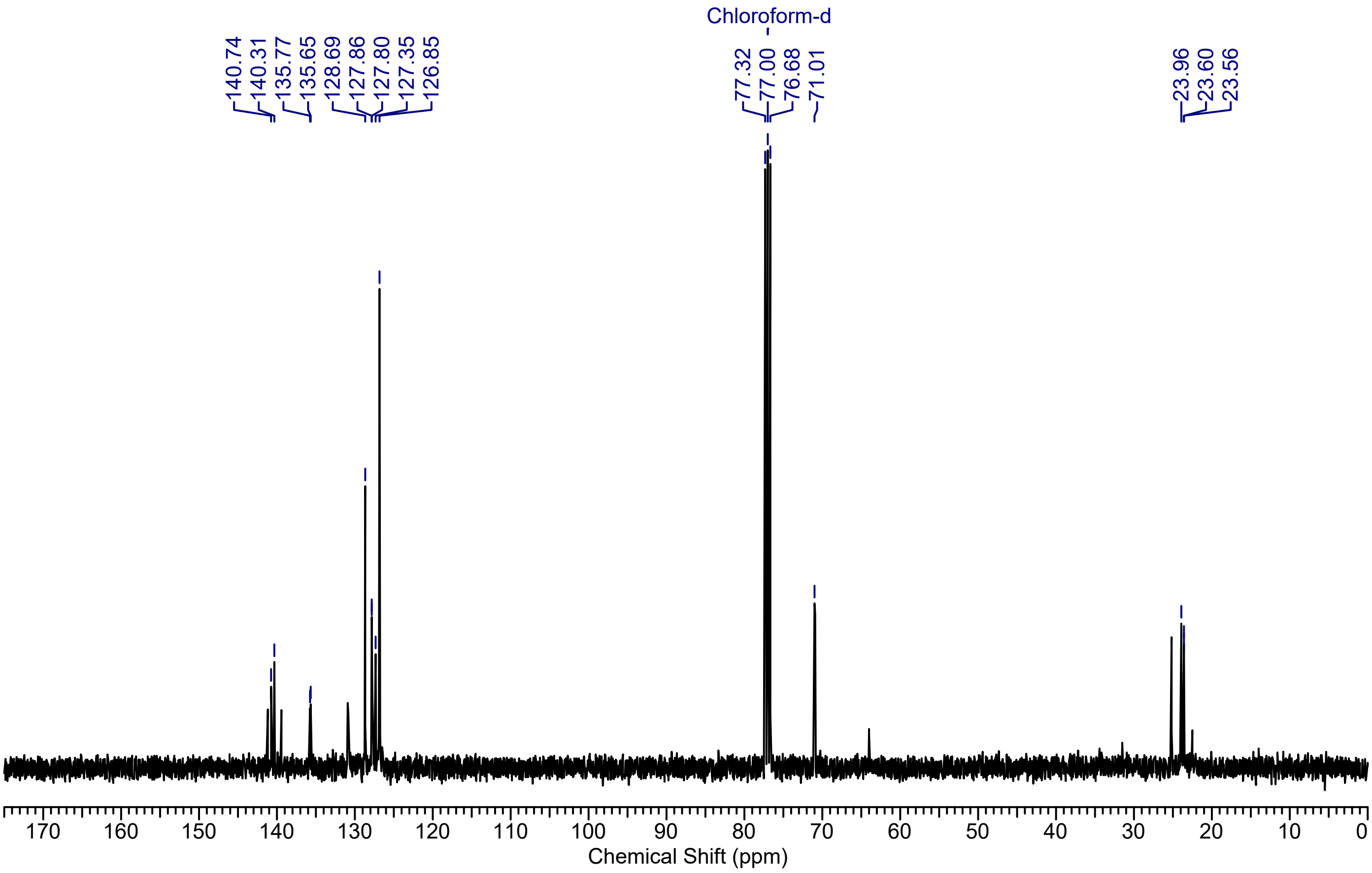
3o: ^{13}C NMR ($CDCl_3$, 101 MHz)



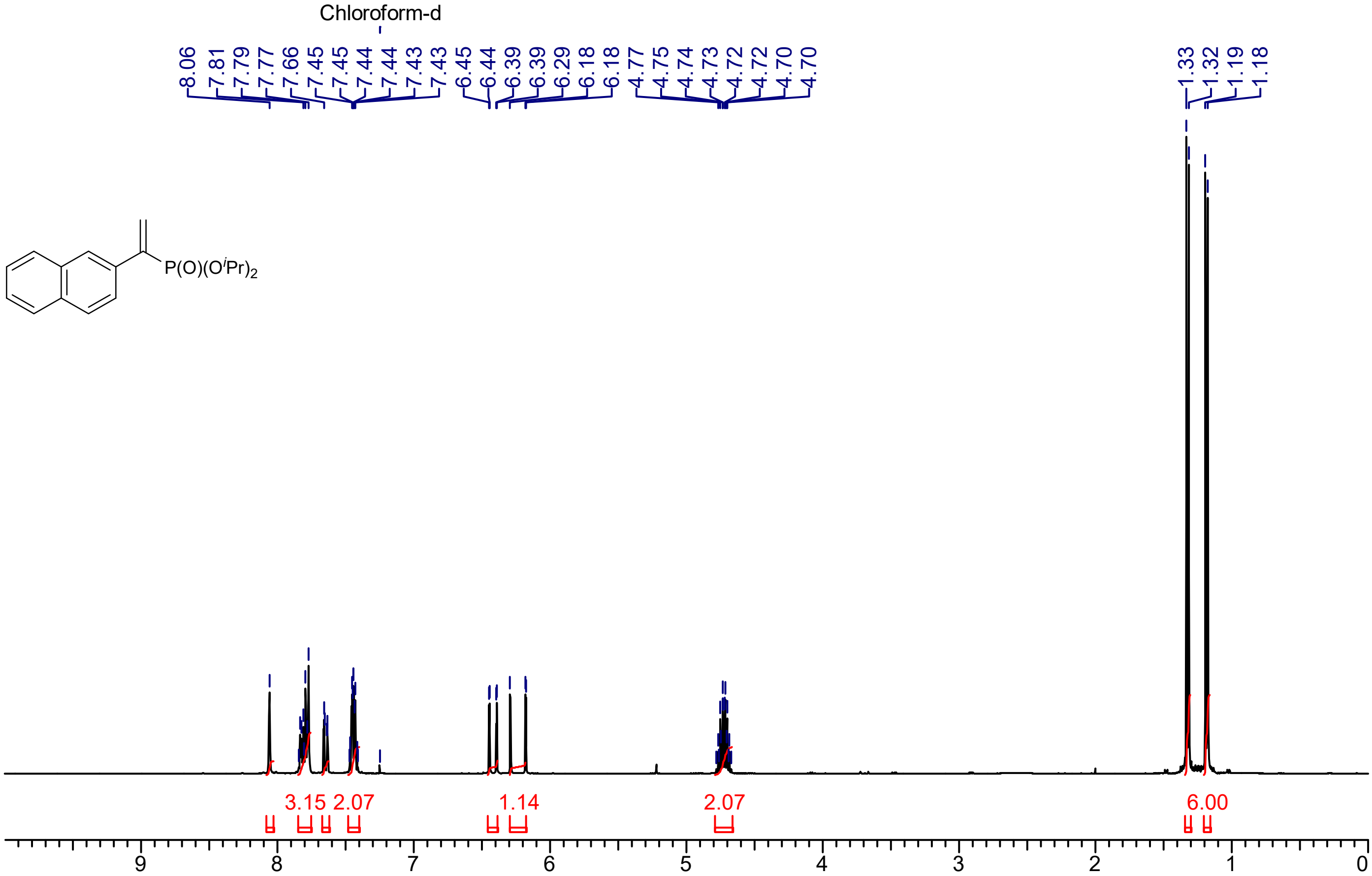
3p: ^{1}H NMR ($CDCl_3$, 400 MHz)



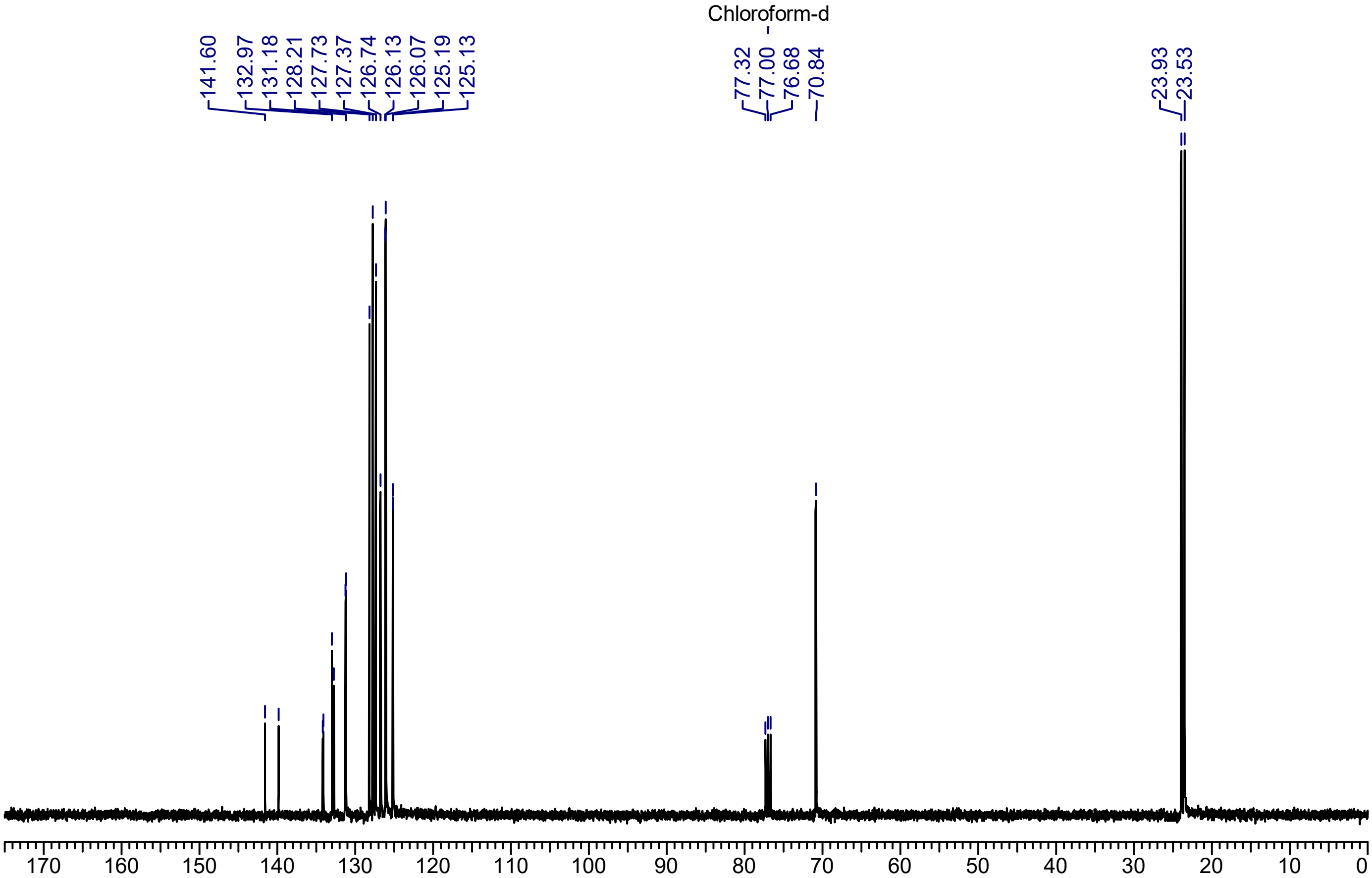
3p: ^{13}C NMR ($CDCl_3$, 101 MHz)



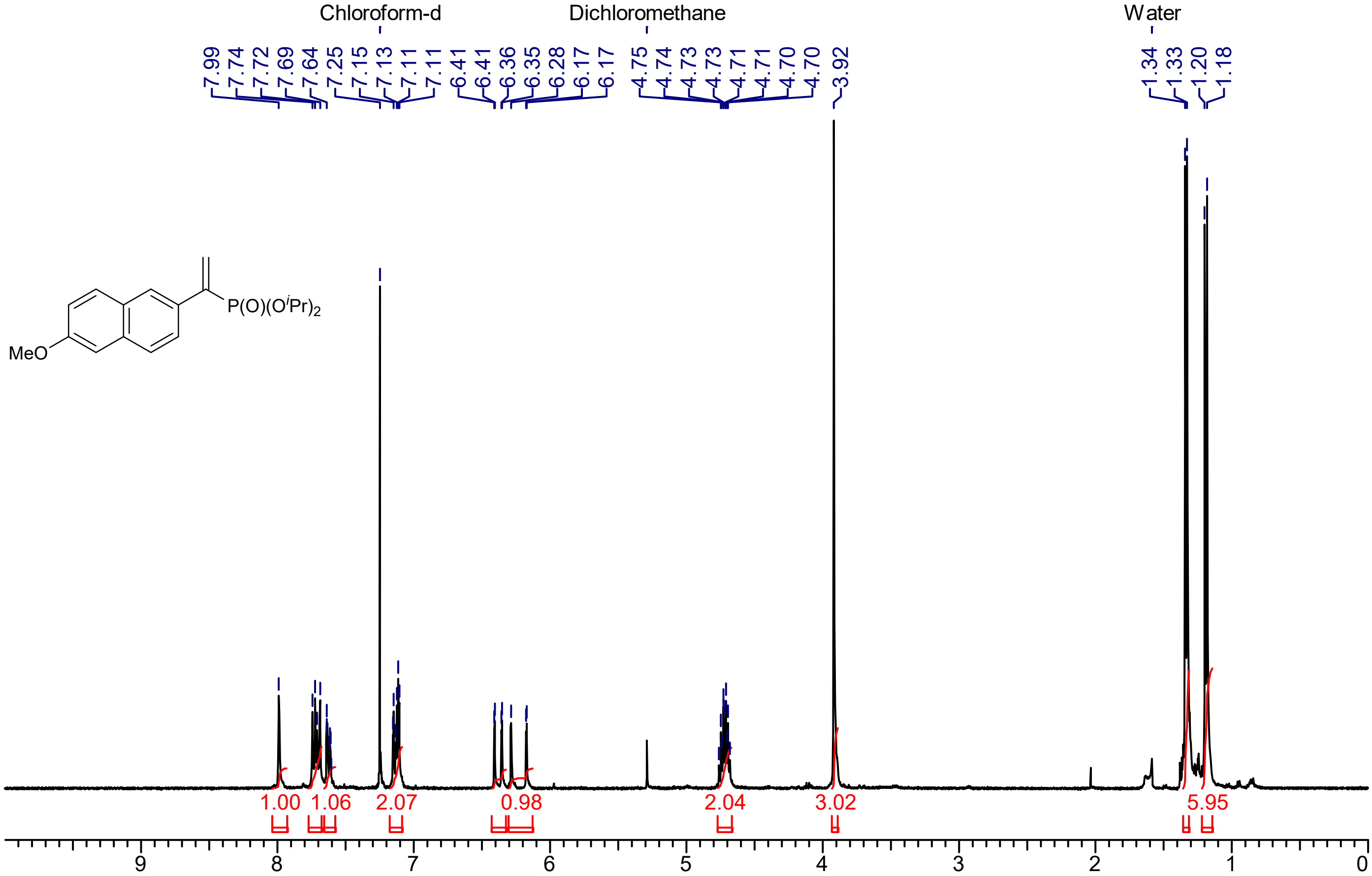
3q: ^{1}H NMR ($CDCl_3$, 400 MHz)



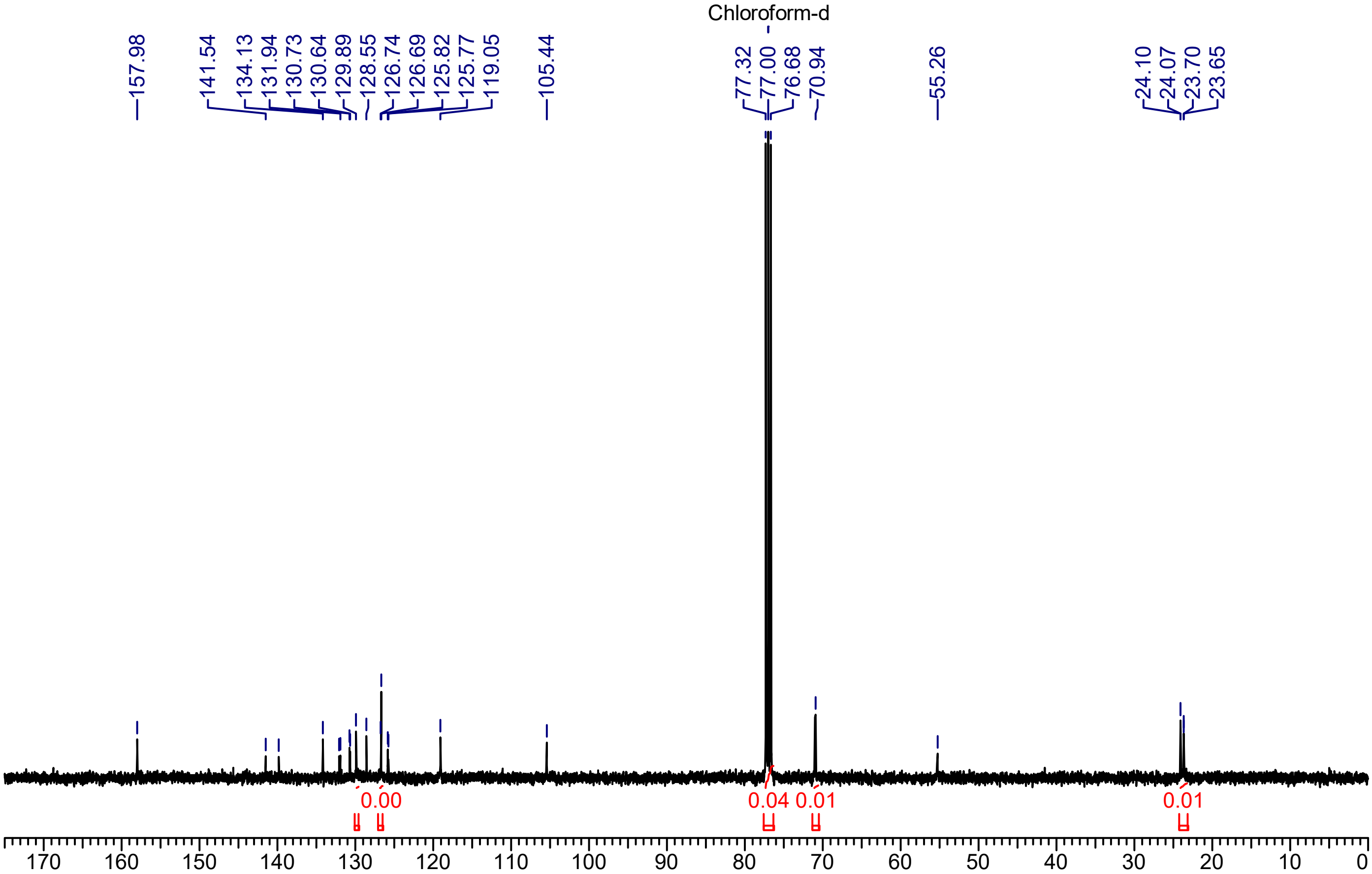
3q: ^{13}C NMR ($CDCl_3$, 101 MHz)



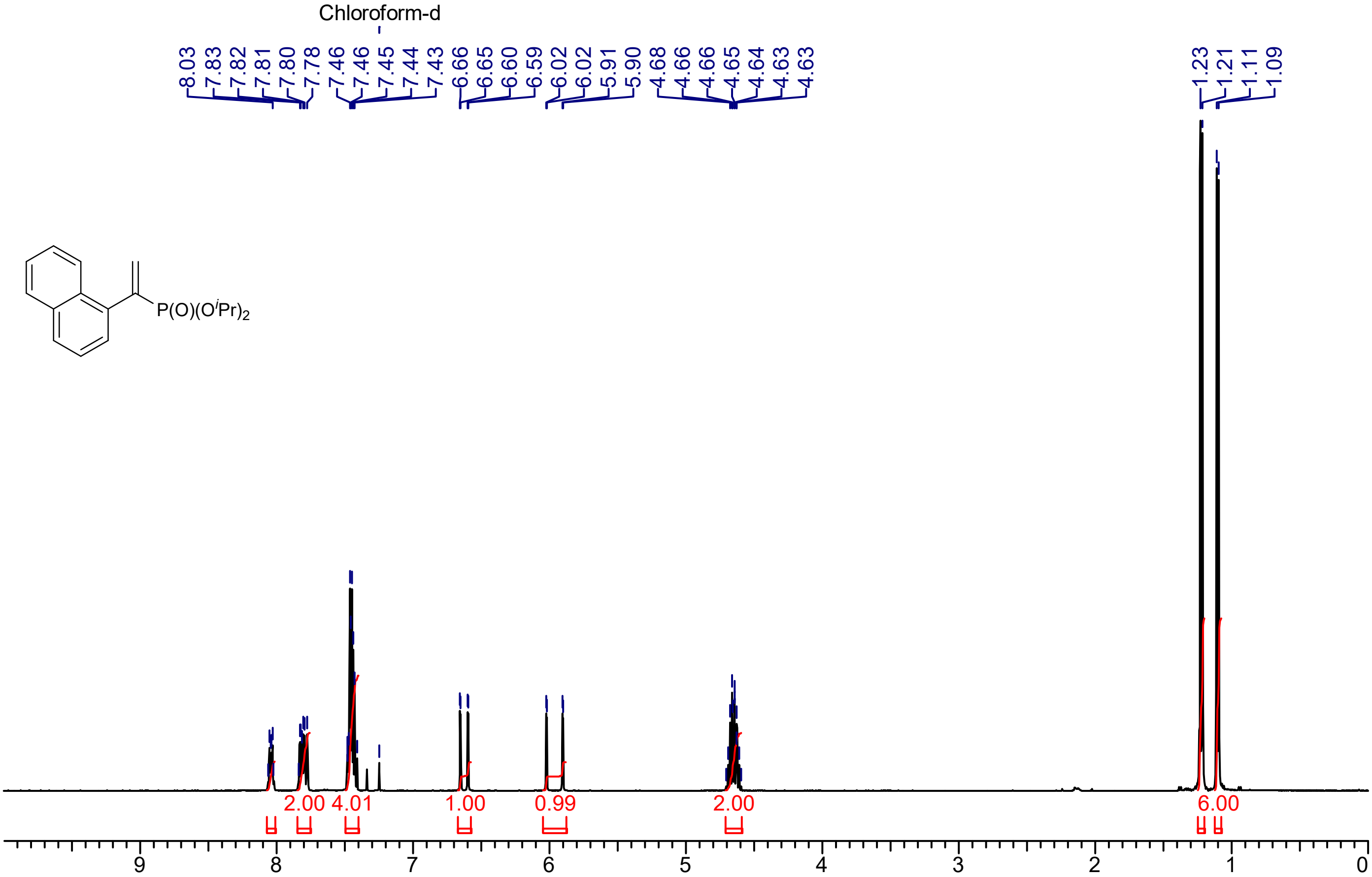
3r: ^{1}H NMR ($CDCl_3$, 400 MHz)



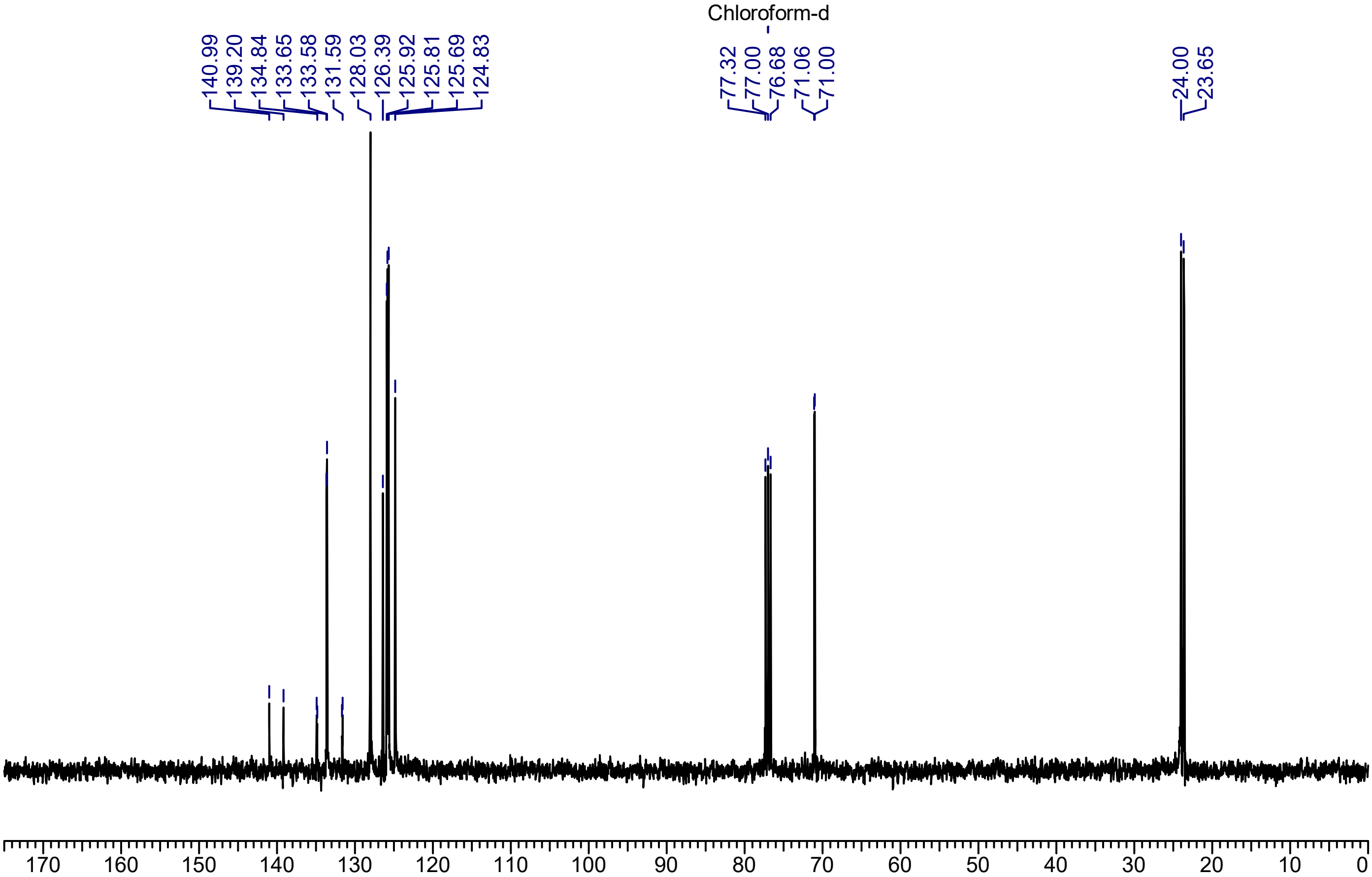
3r: ^{13}C NMR ($CDCl_3$, 101 MHz)



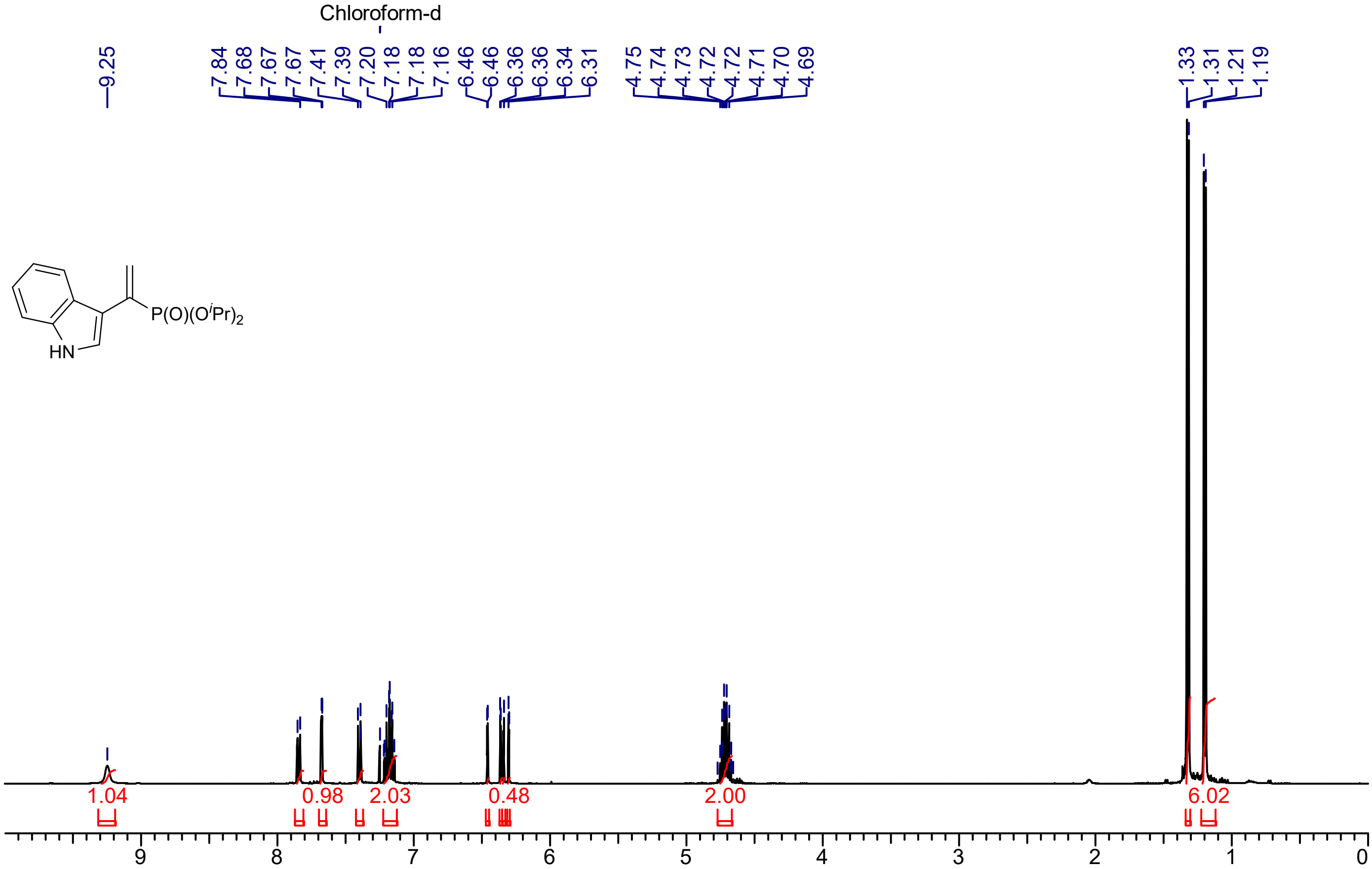
3s: ^{1}H NMR ($CDCl_3$, 400 MHz)



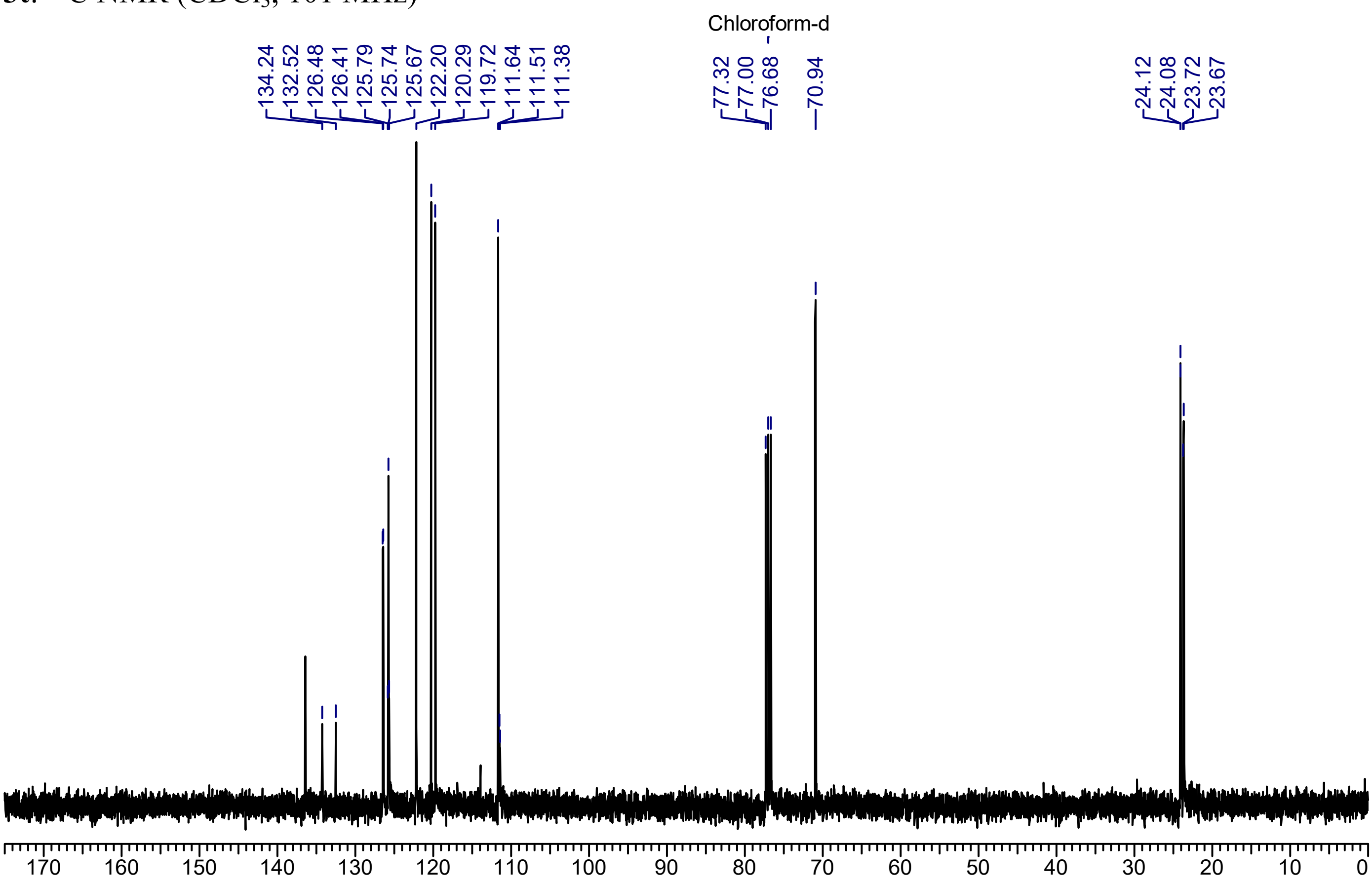
3s: ^{13}C NMR ($CDCl_3$, 101 MHz)



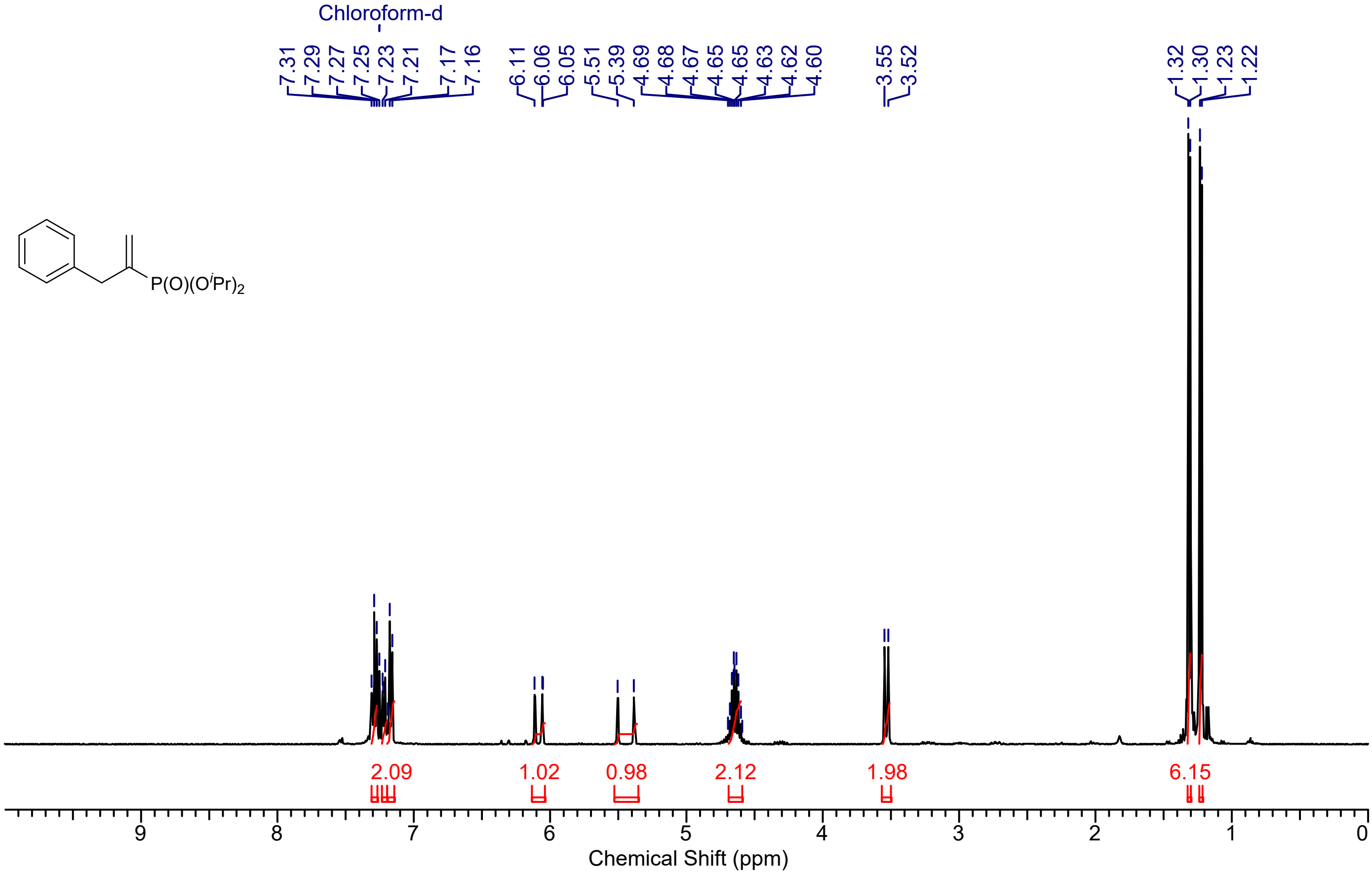
3t: ^{1}H NMR ($CDCl_3$, 400 MHz)



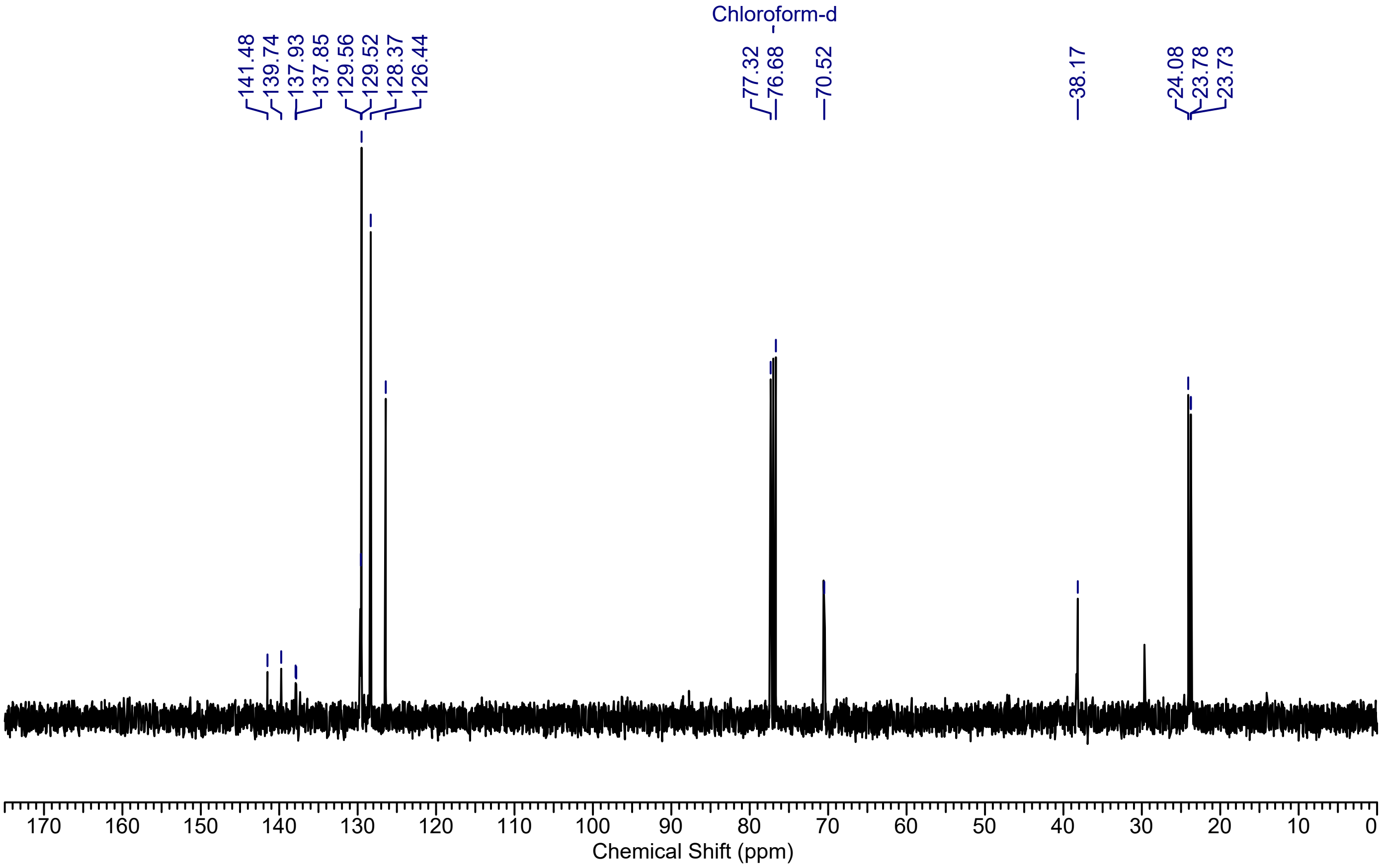
3t: ^{13}C NMR ($CDCl_3$, 101 MHz)



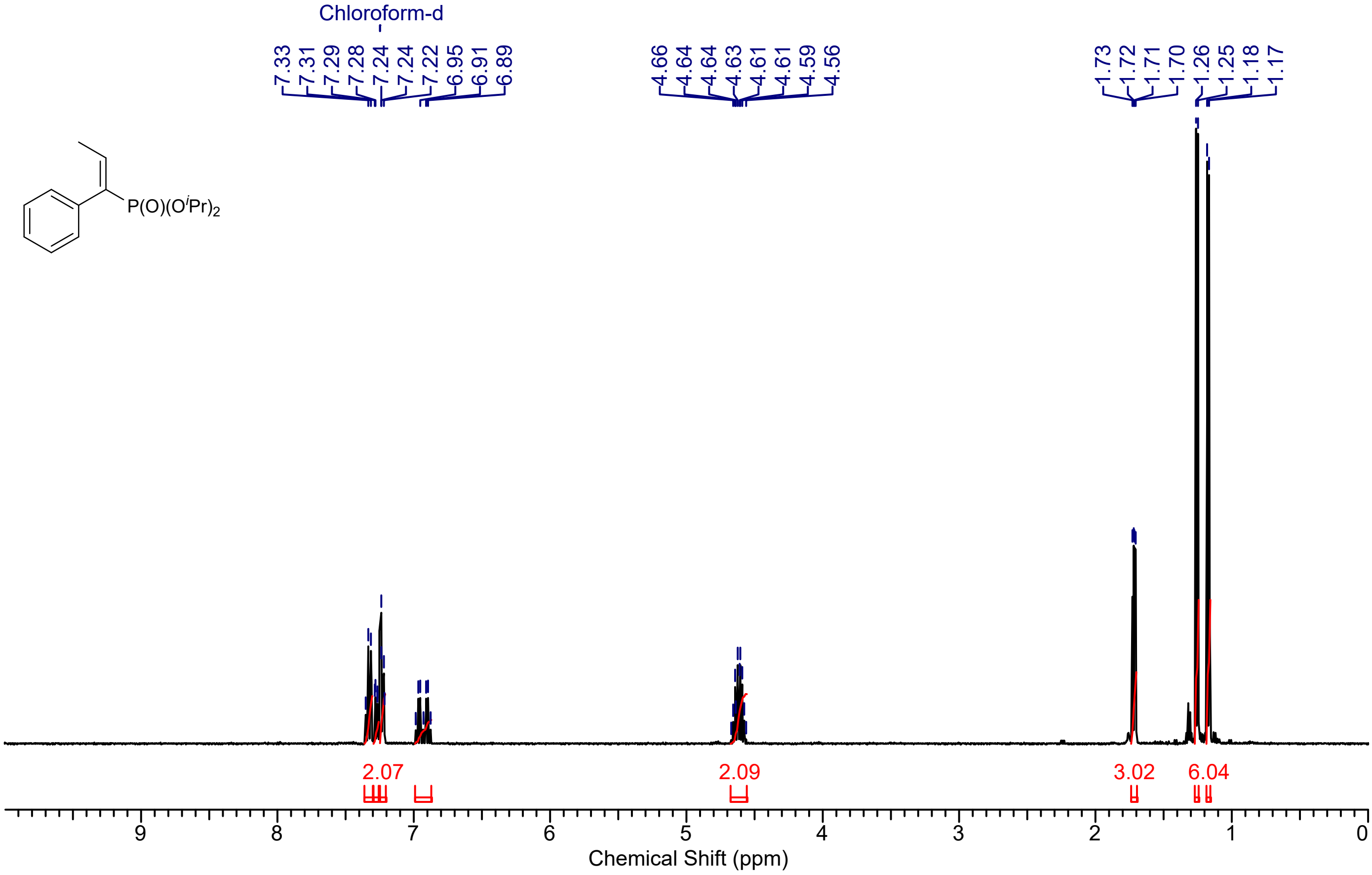
3u: ^{1}H NMR ($CDCl_3$, 400 MHz)



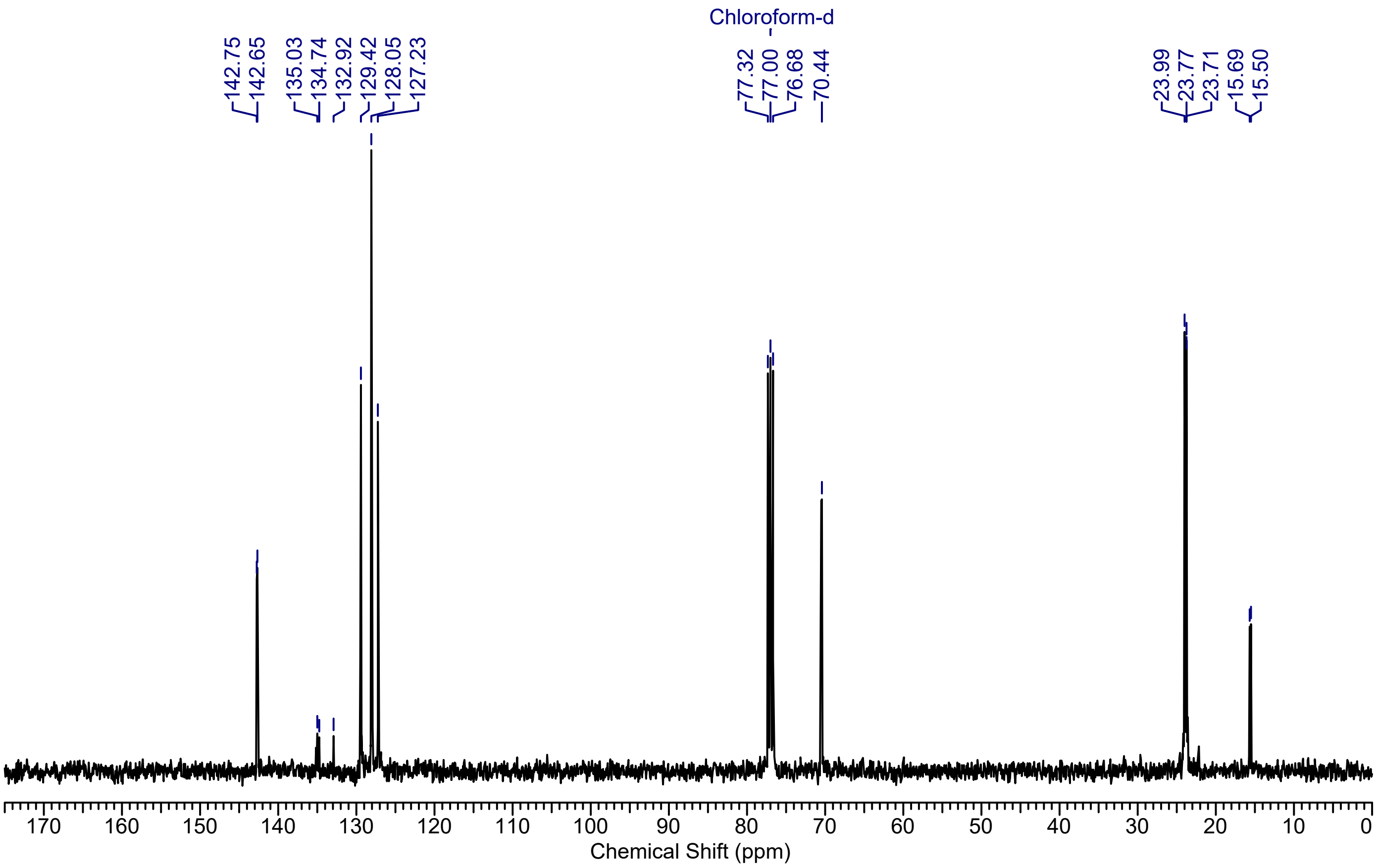
3u: ^{13}C NMR ($CDCl_3$, 101 MHz)



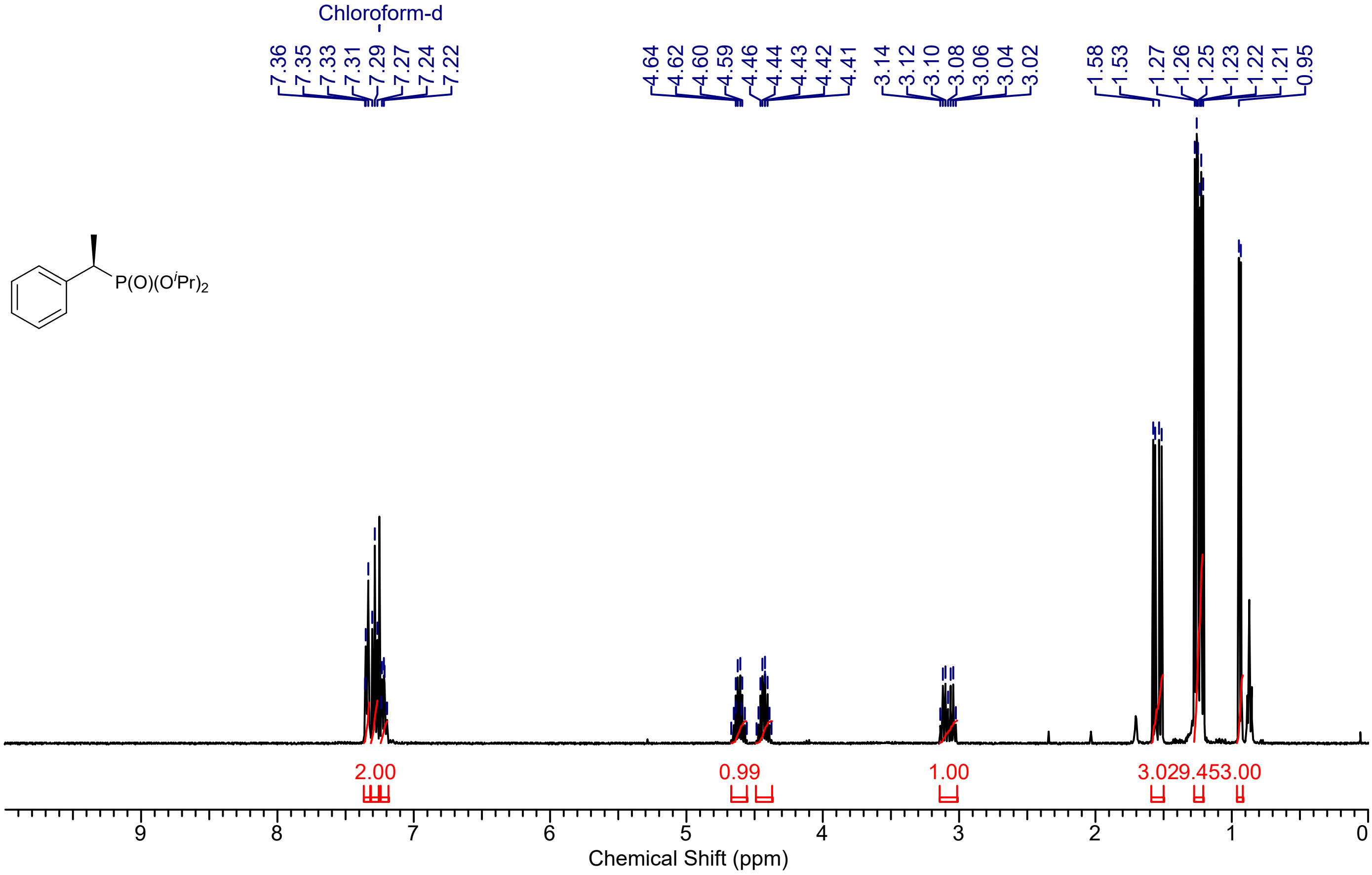
3v: ^{1}H NMR ($CDCl_3$, 400 MHz)



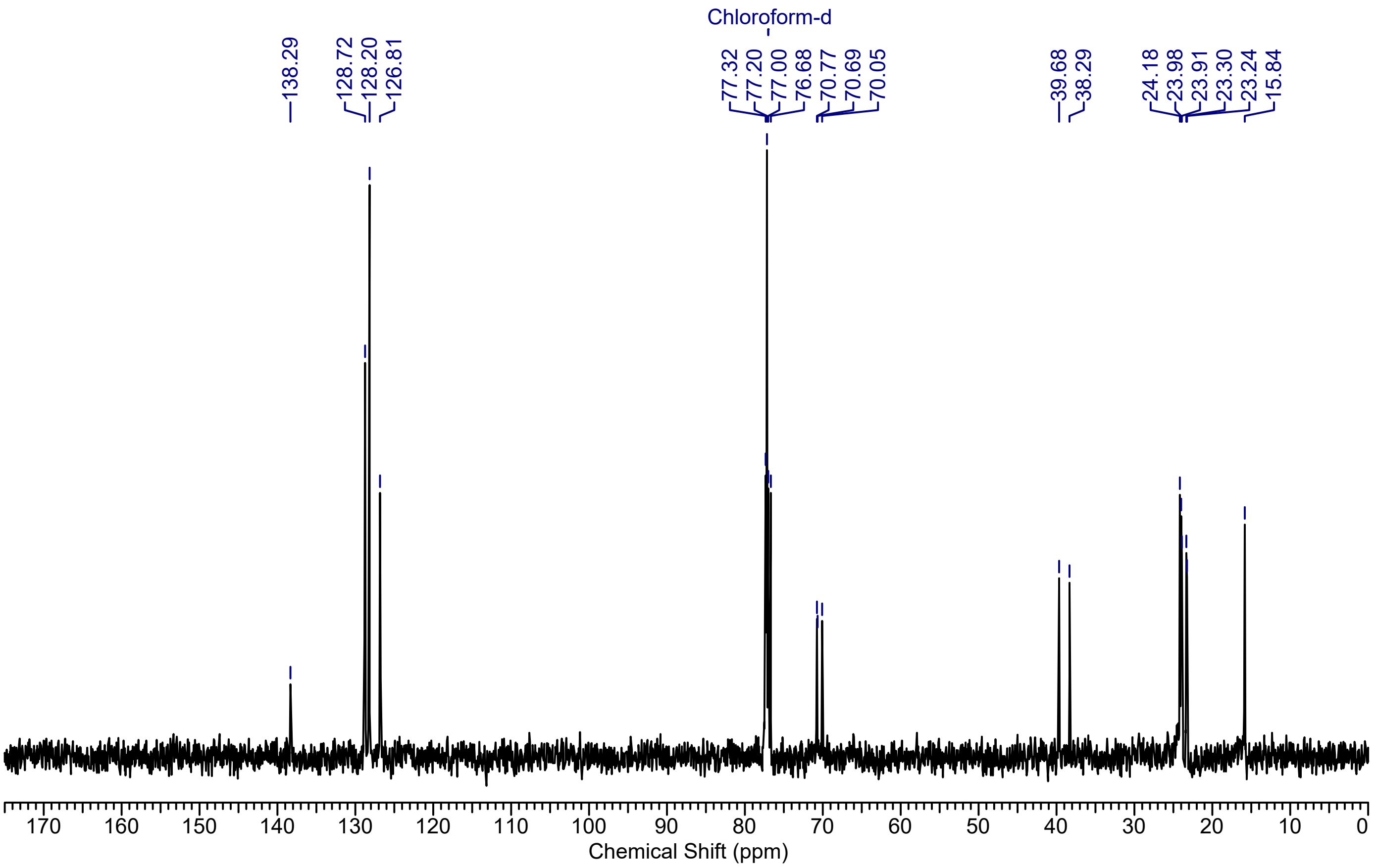
3v: ^{13}C NMR ($CDCl_3$, 101 MHz)



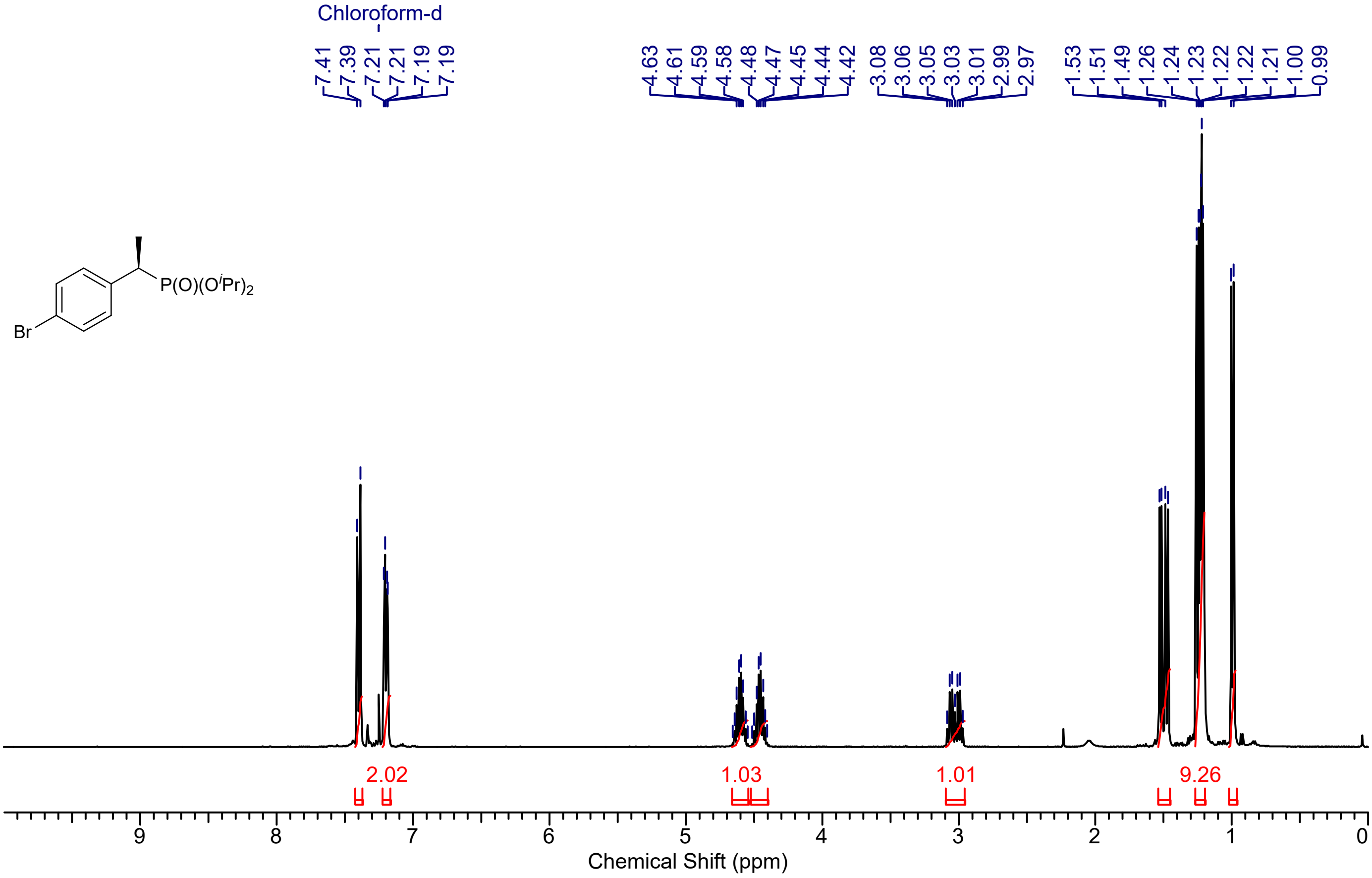
6a: ^{1}H NMR ($CDCl_3$, 400 MHz)



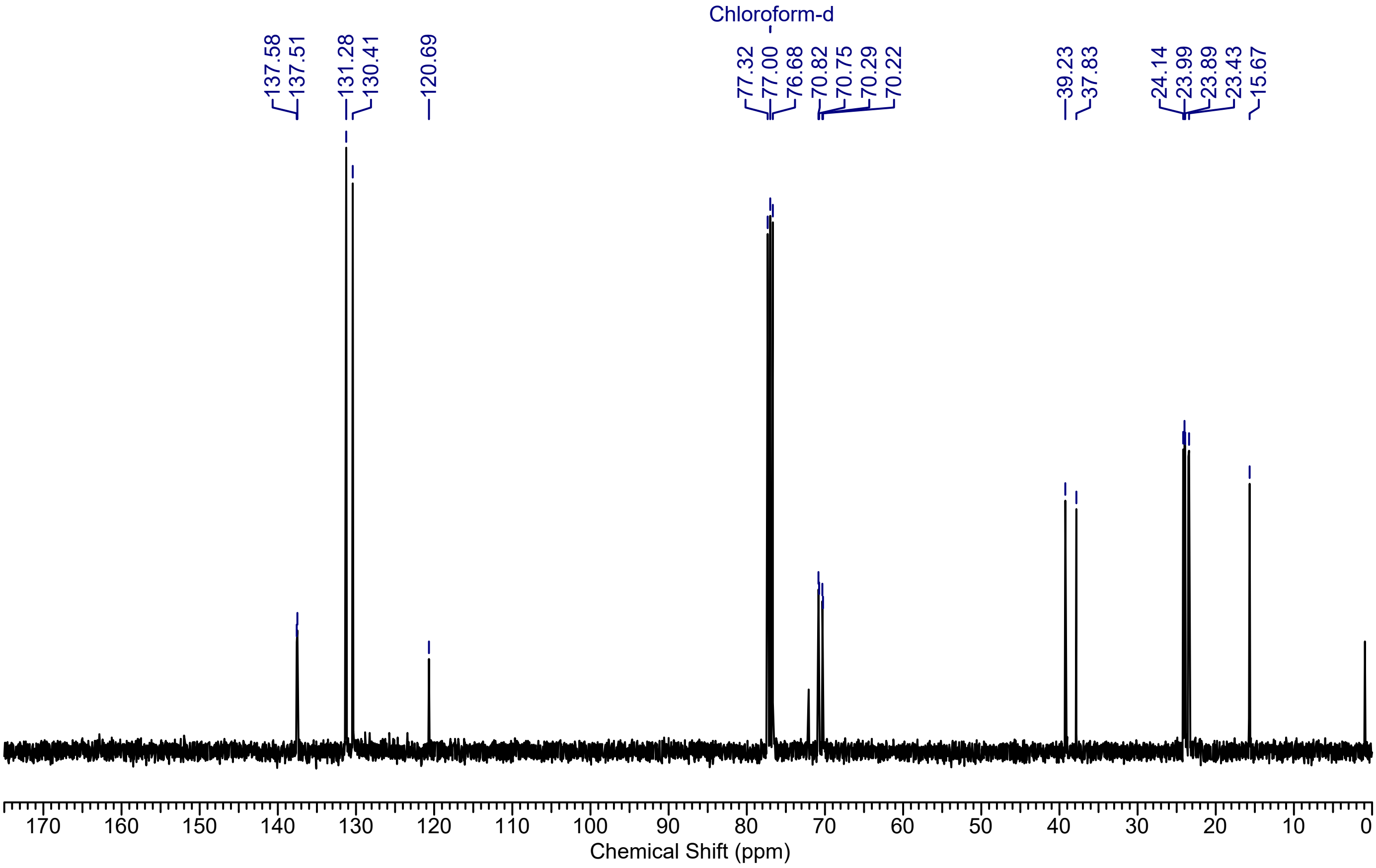
6a: ^{13}C NMR ($CDCl_3$, 101 MHz)



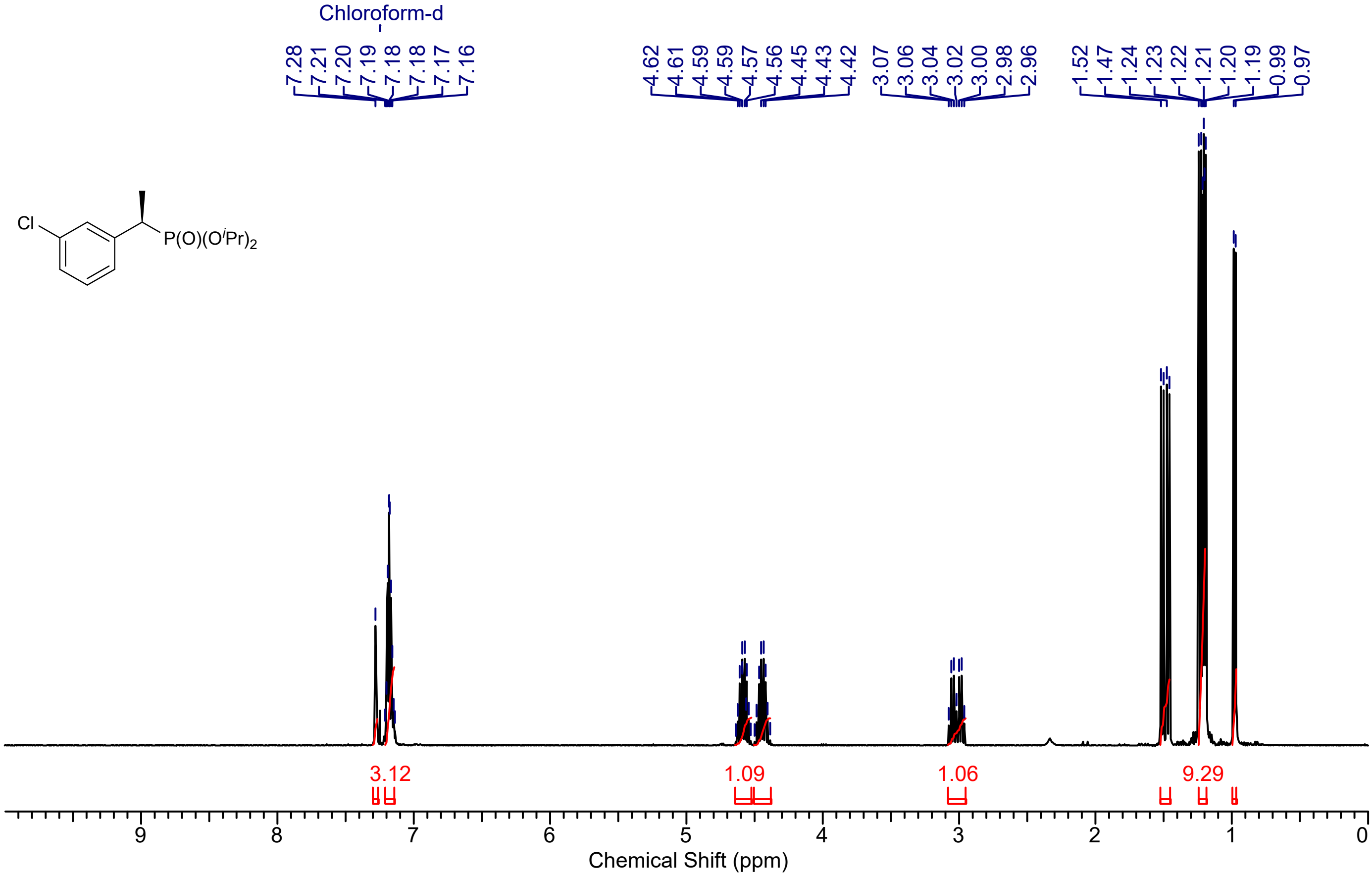
6b: ^{1}H NMR (CDCl$_3$, 400 MHz)



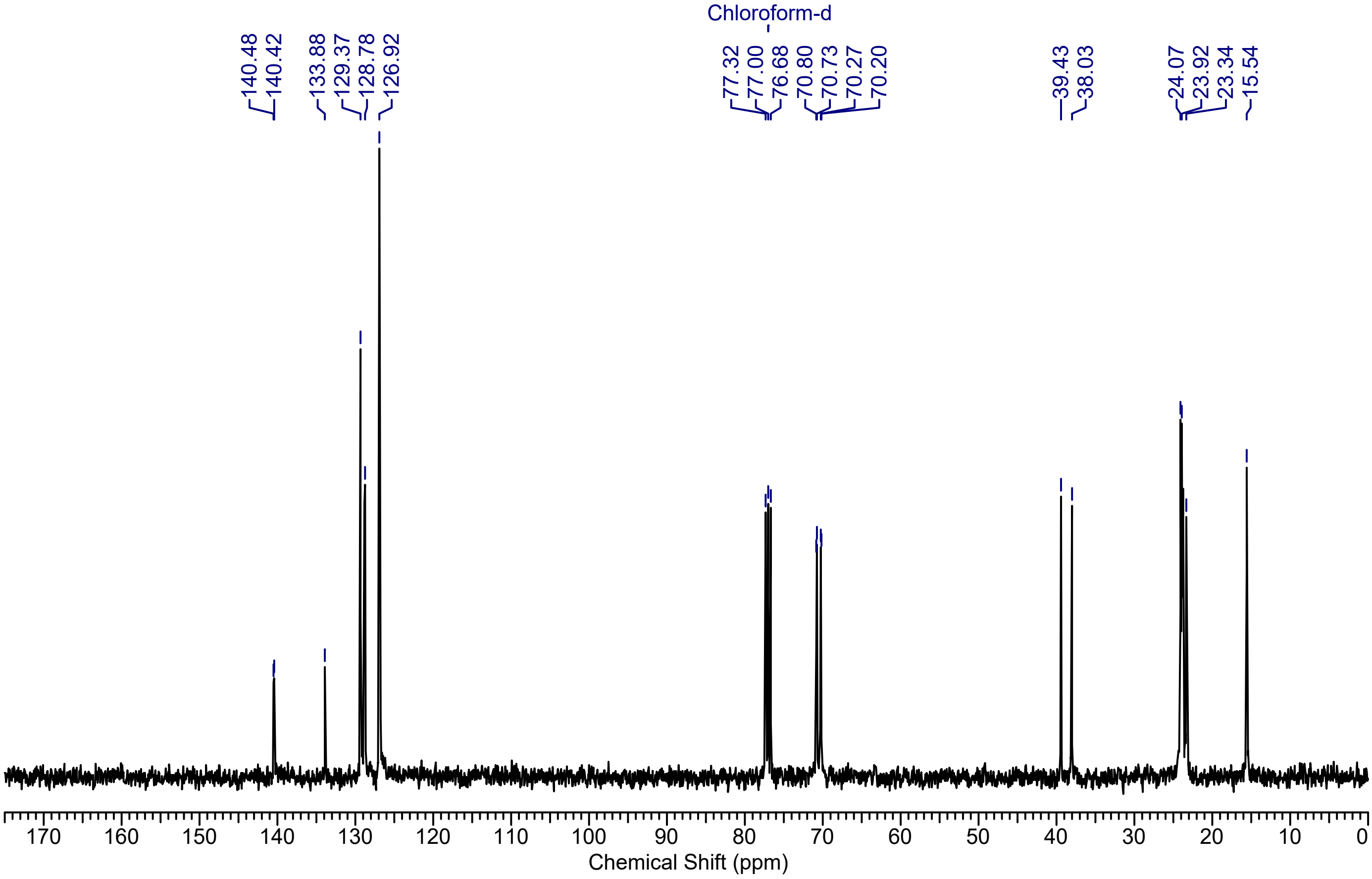
6b: ^{13}C NMR (CDCl$_3$, 101 MHz)



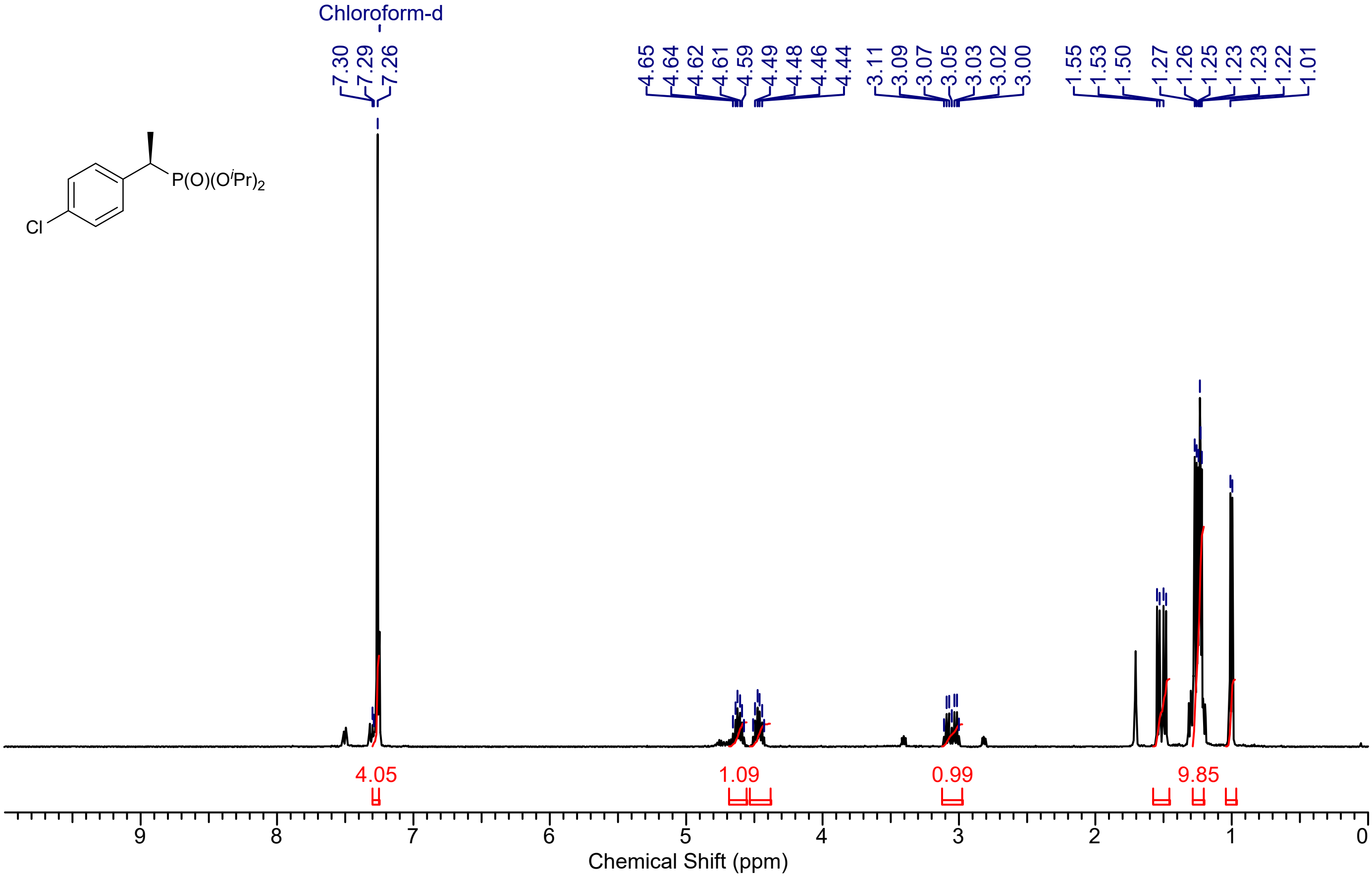
6c: ^{1}H NMR ($CDCl_3$, 400 MHz)



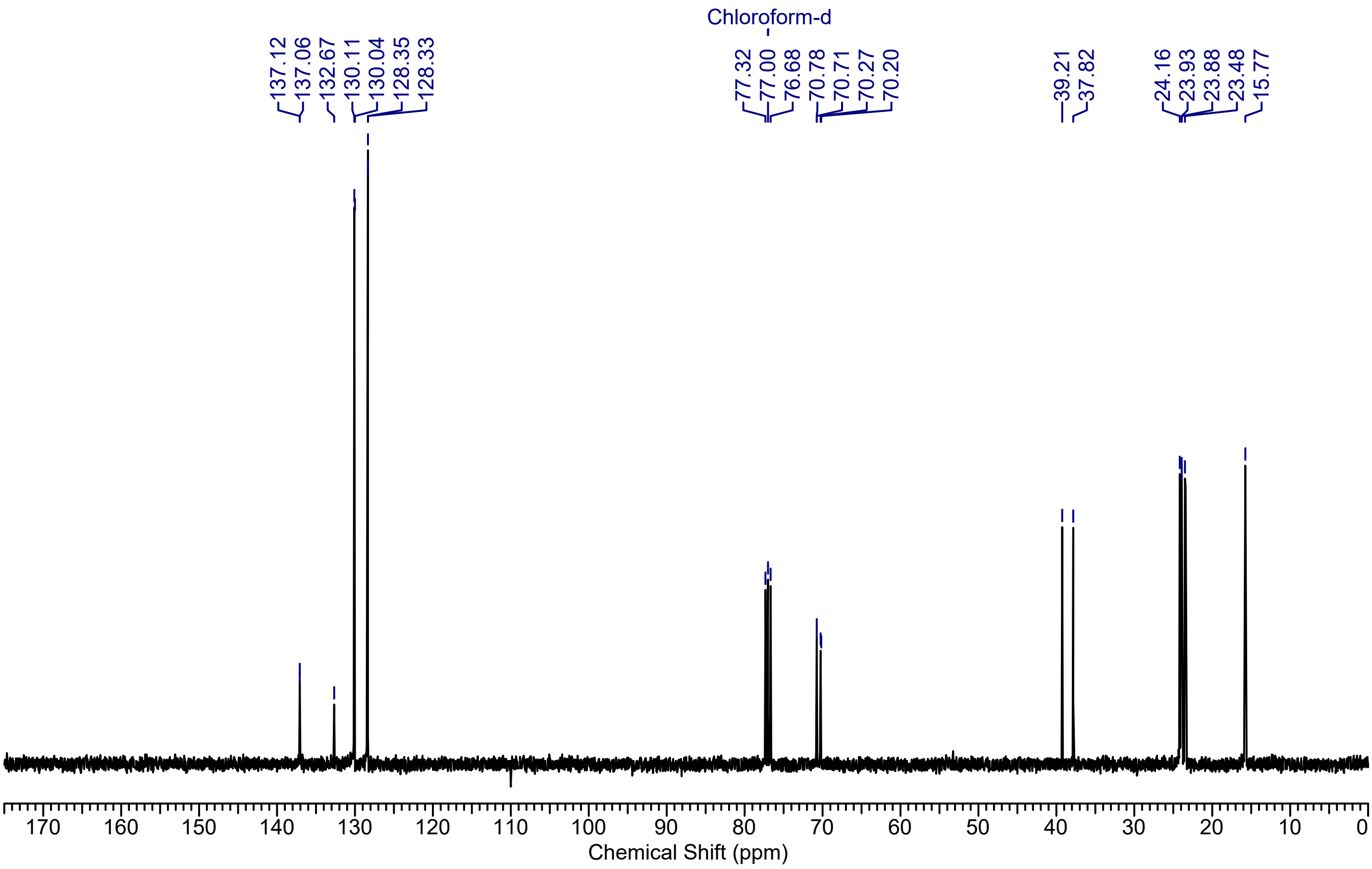
6c: ^{13}C NMR ($CDCl_3$, 101 MHz)



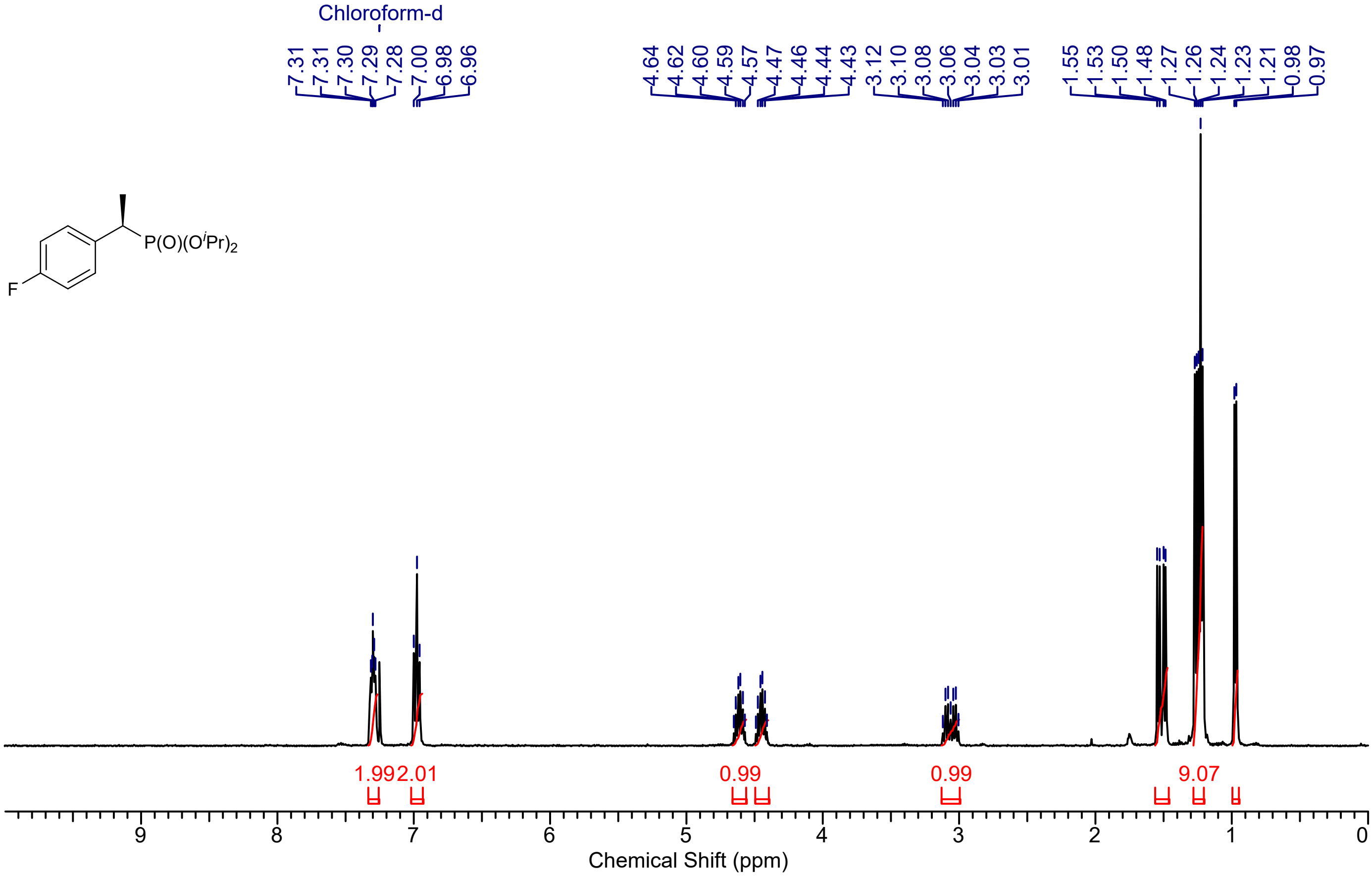
6d: [1]H NMR ($CDCl_3$, 400 MHz)



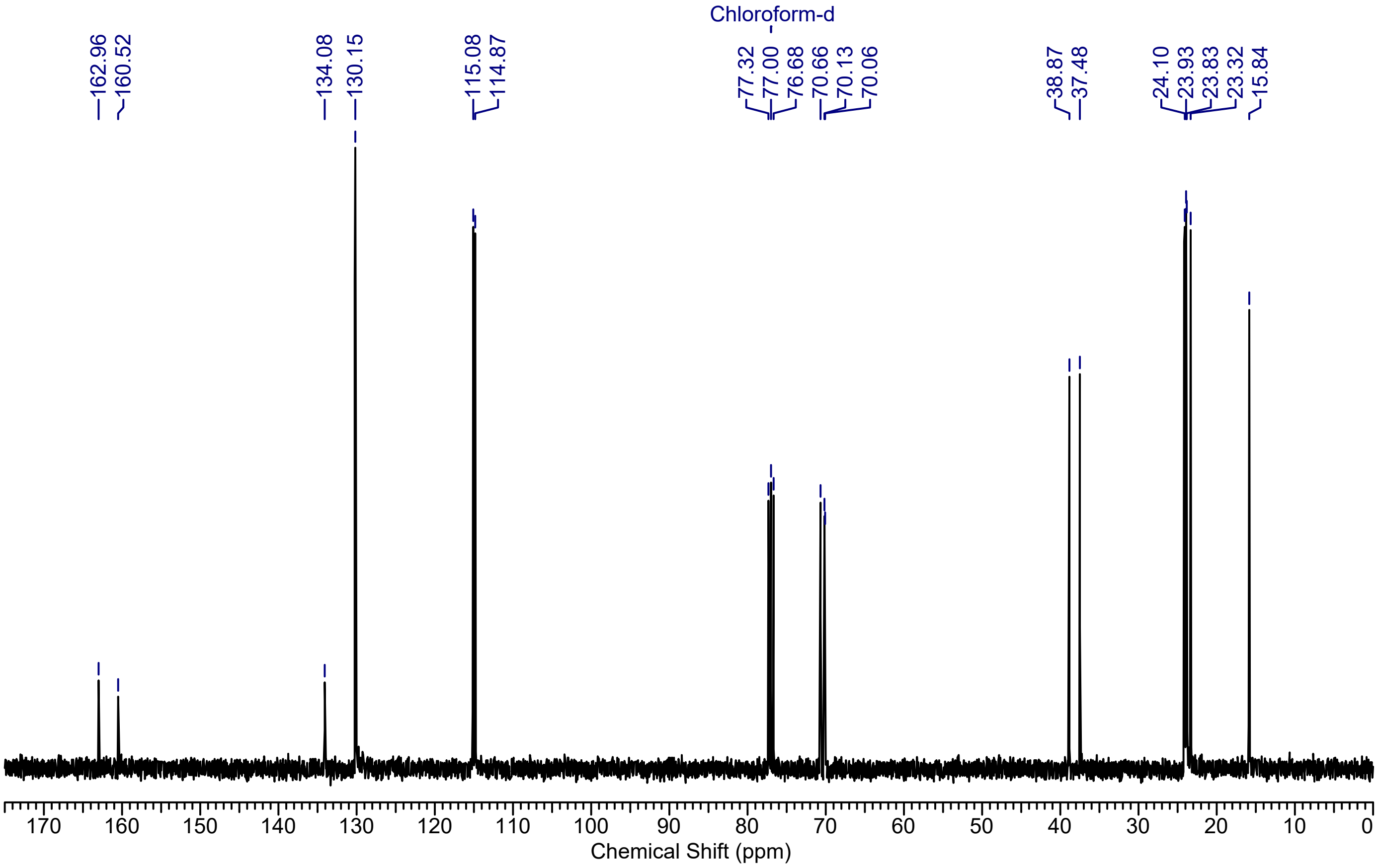
6d: [13]C NMR ($CDCl_3$, 101 MHz)



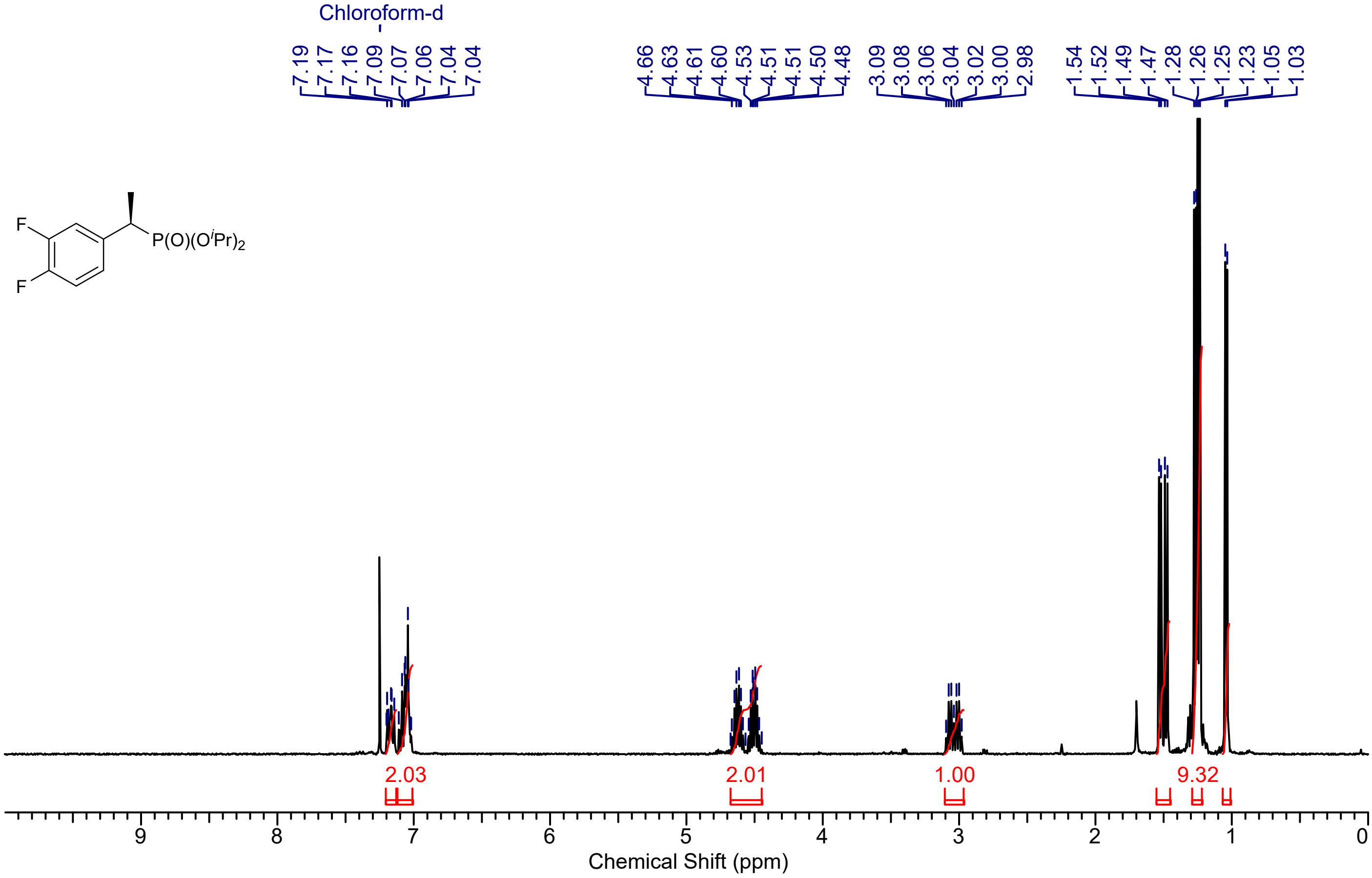
6e: ^{1}H NMR ($CDCl_3$, 400 MHz)



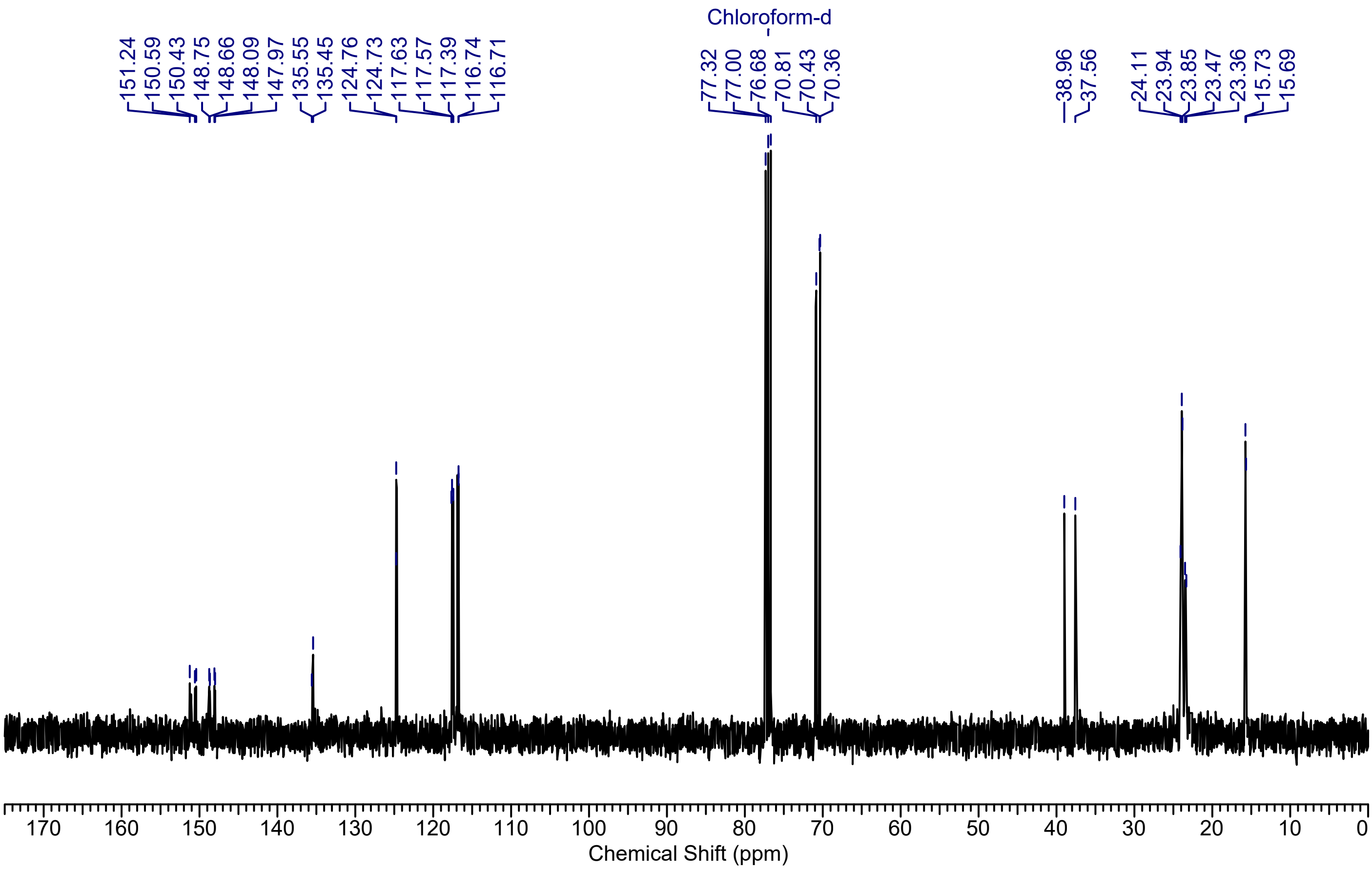
6e: ^{13}C NMR ($CDCl_3$, 101 MHz)



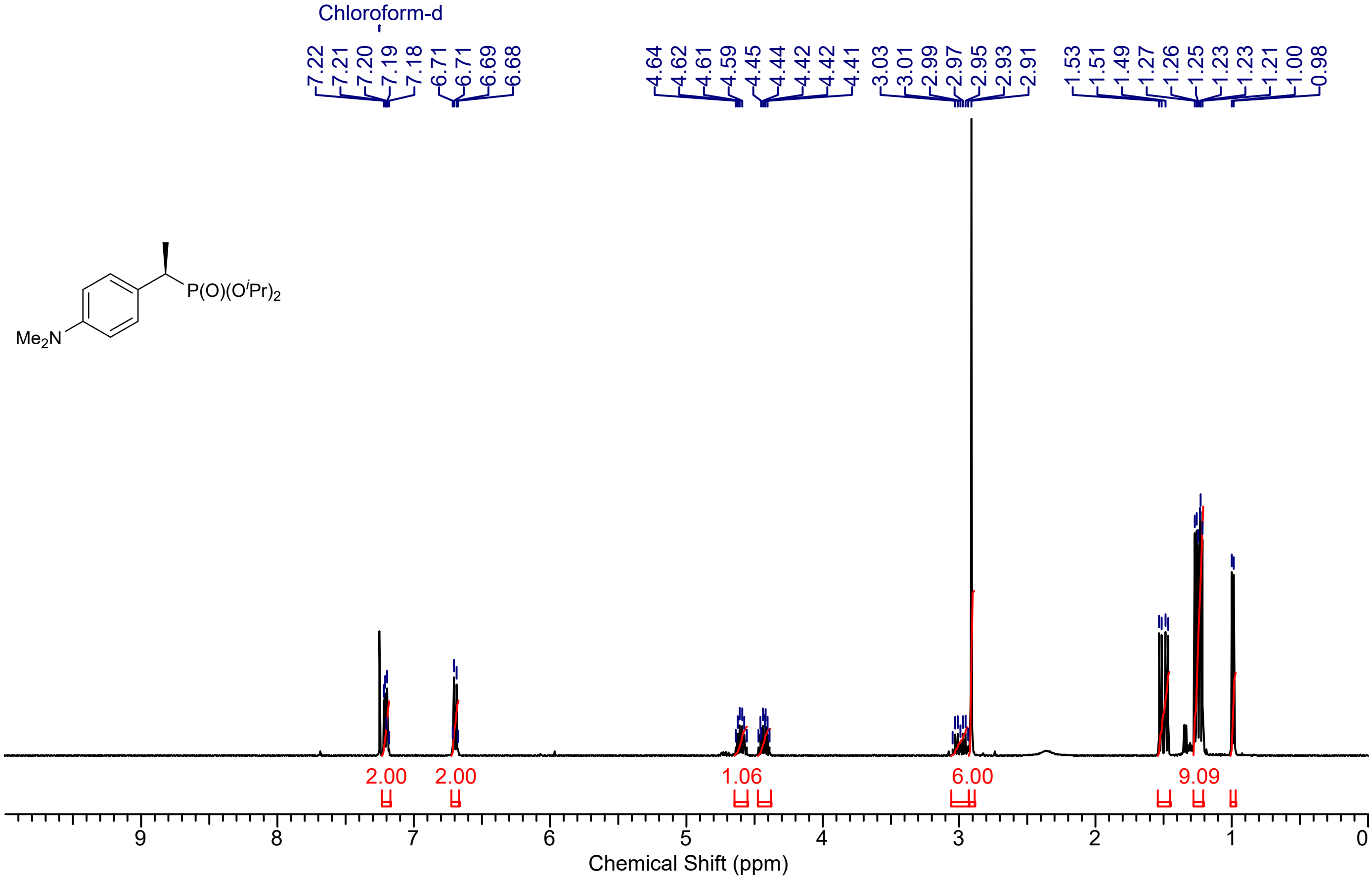
6f: ^{1}H NMR ($CDCl_3$, 400 MHz)



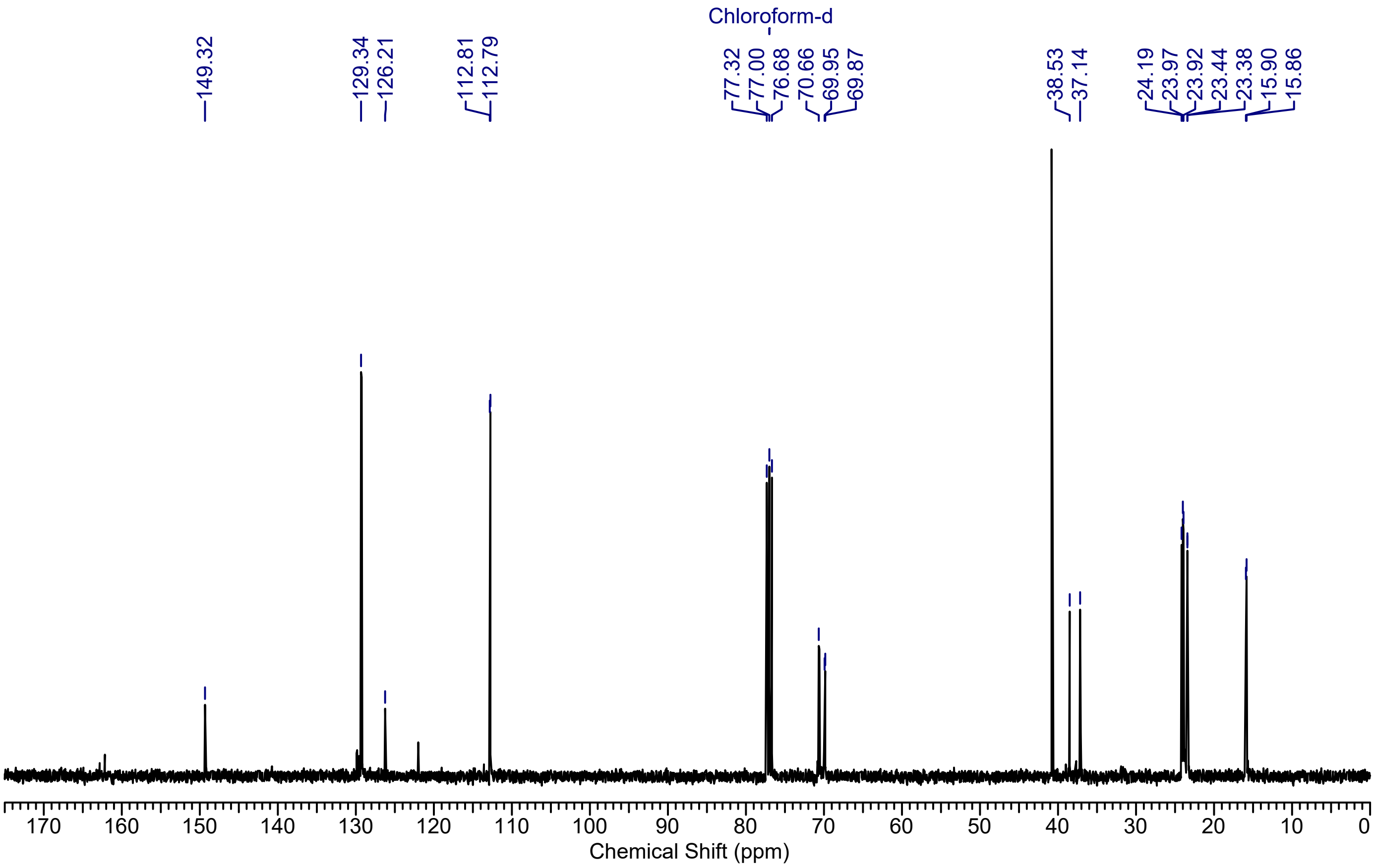
6f: ^{13}C NMR ($CDCl_3$, 101 MHz)



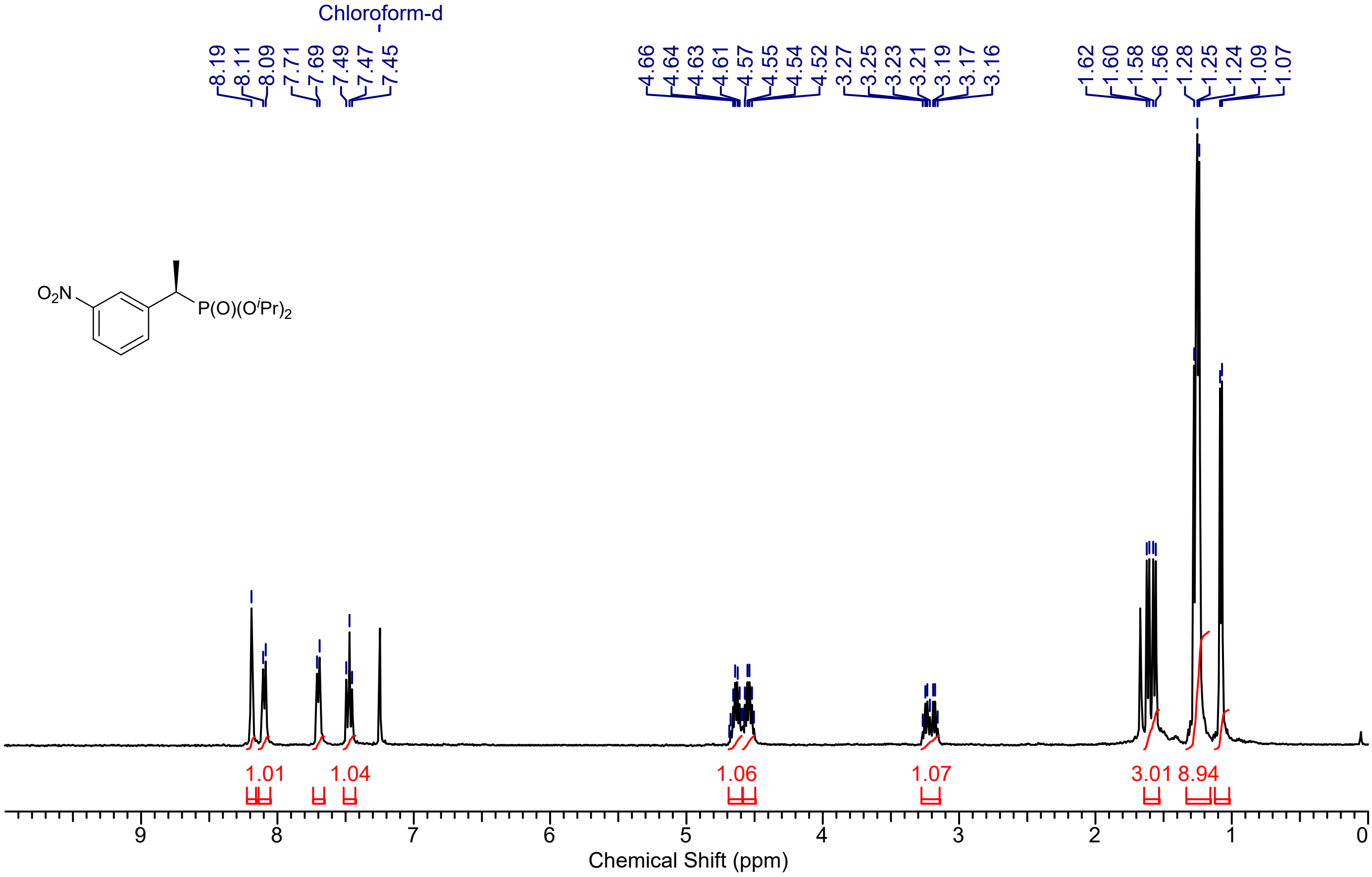
6g: ^{1}H NMR ($CDCl_3$, 400 MHz)



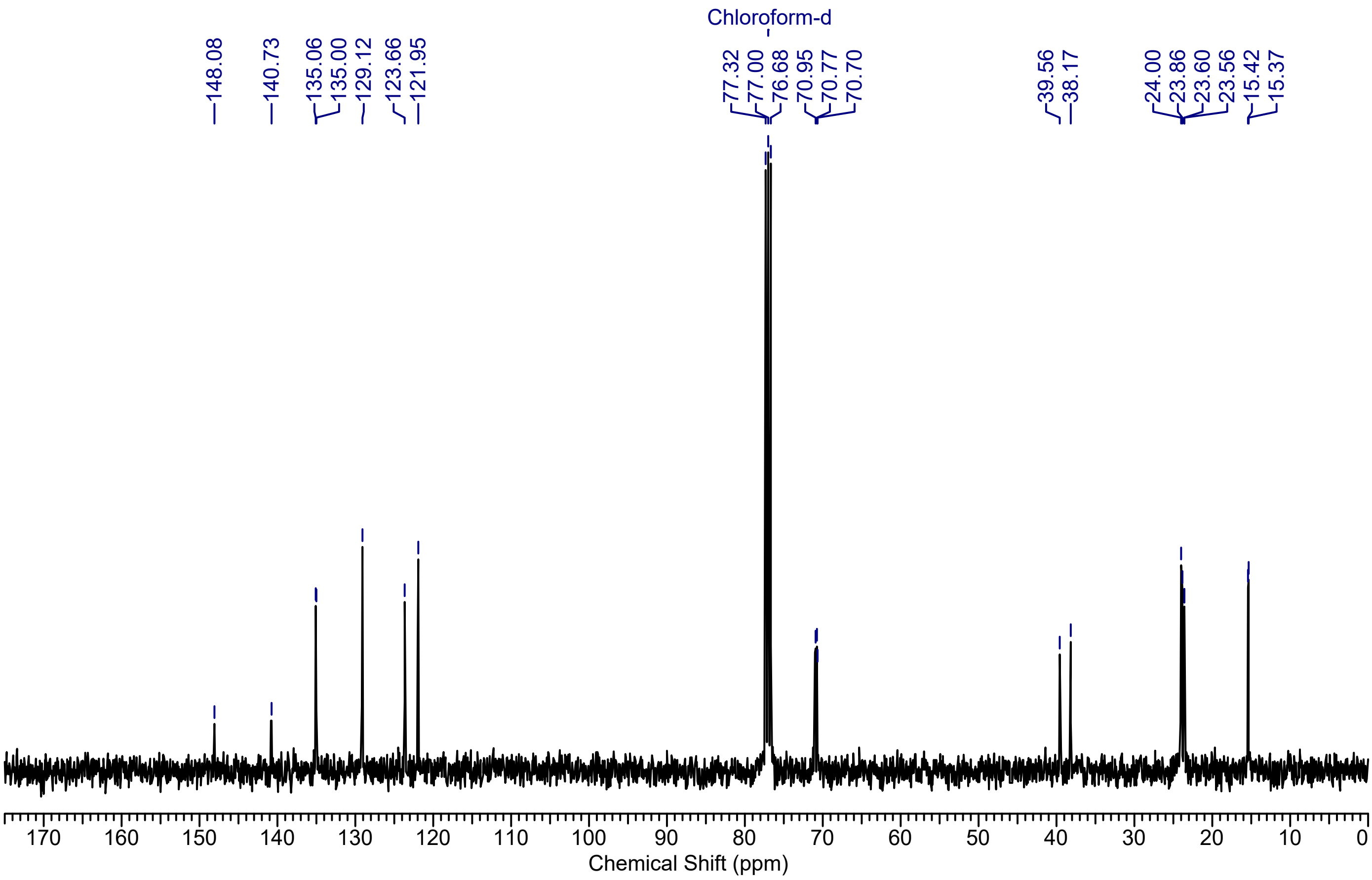
6g: ^{13}C NMR ($CDCl_3$, 101 MHz)



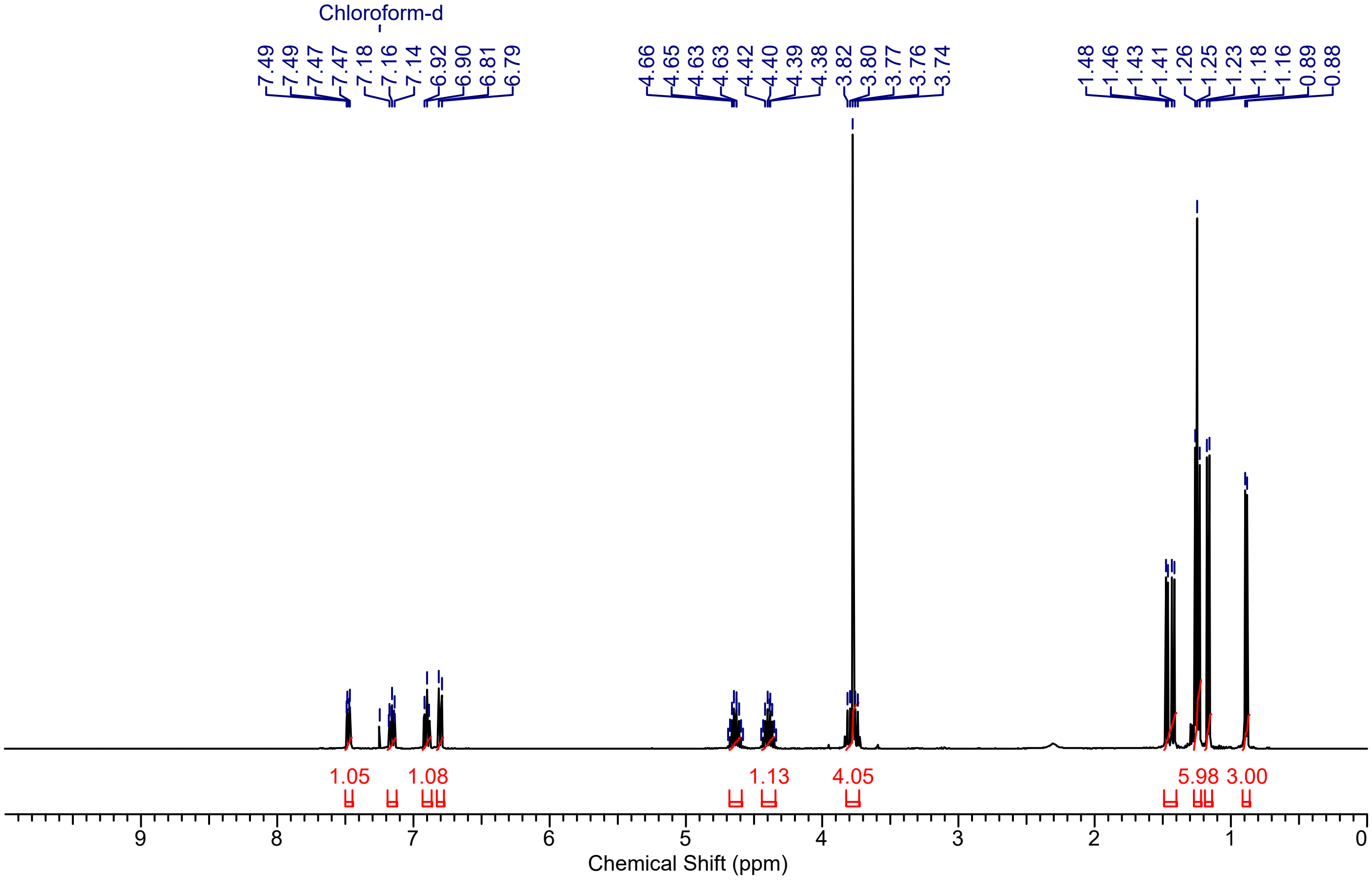
6h: ^{1}H NMR ($CDCl_3$, 400 MHz)



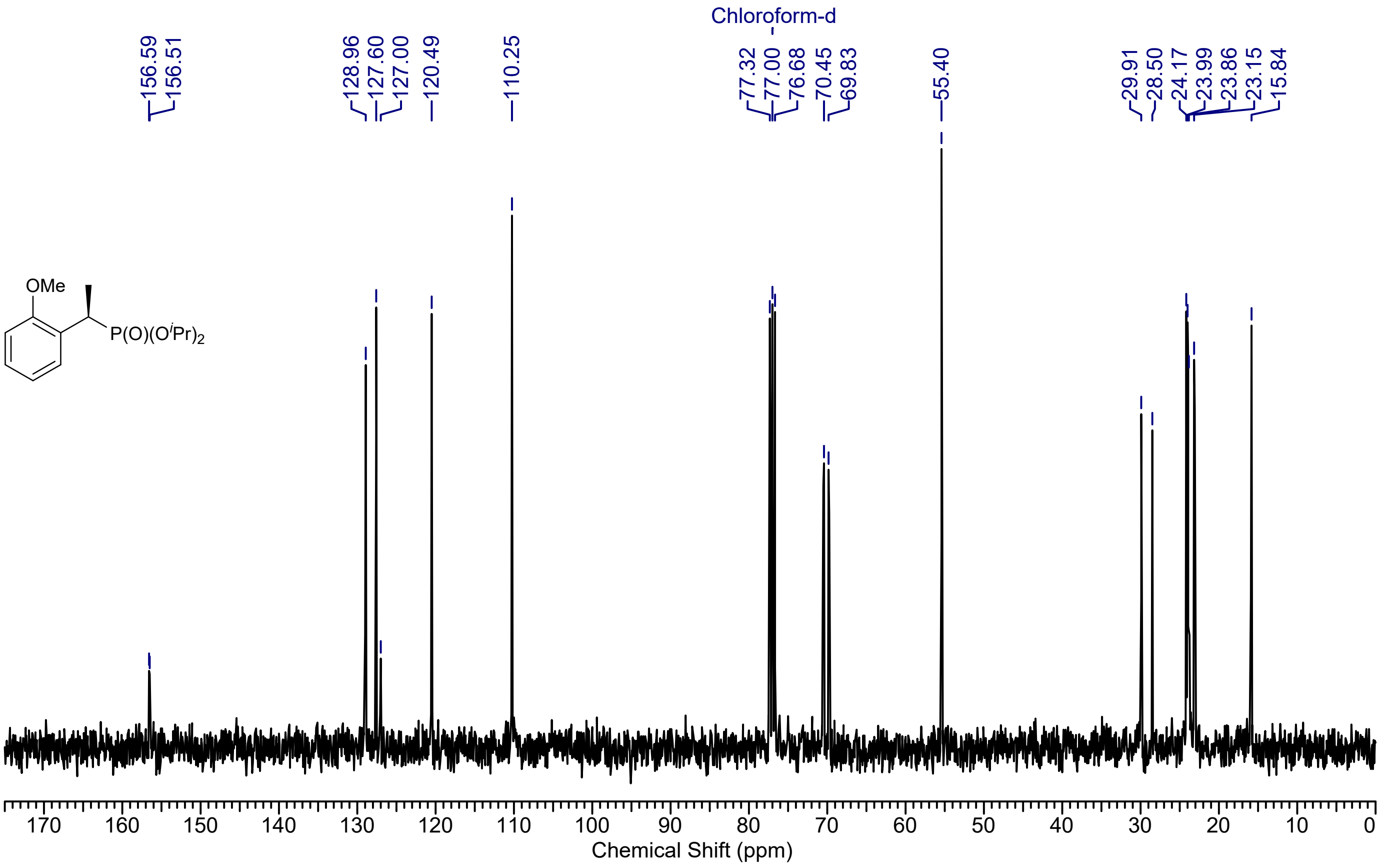
6h: ^{13}C NMR ($CDCl_3$, 101 MHz)



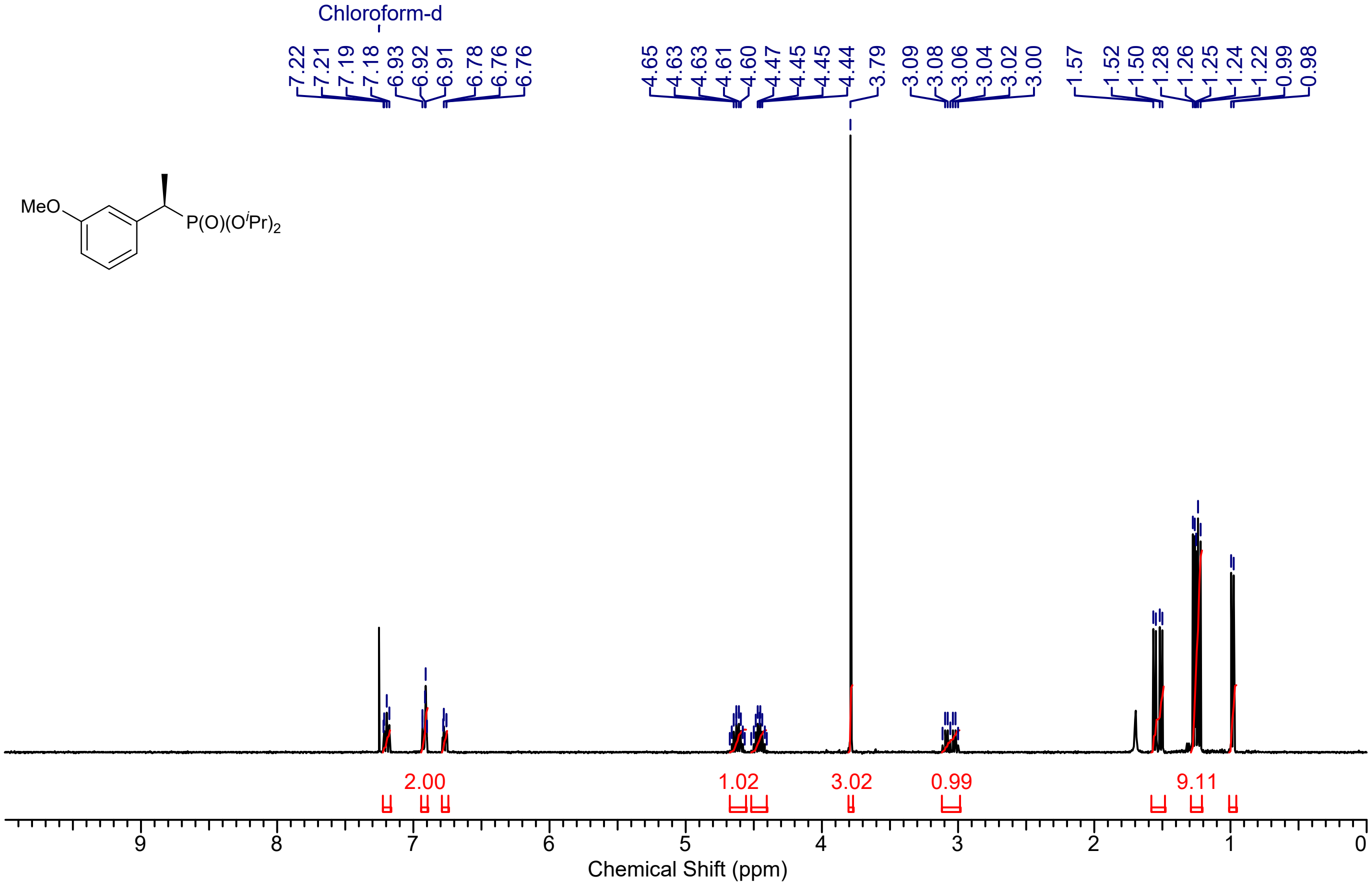
6i: ^{1}H NMR ($CDCl_3$, 400 MHz)



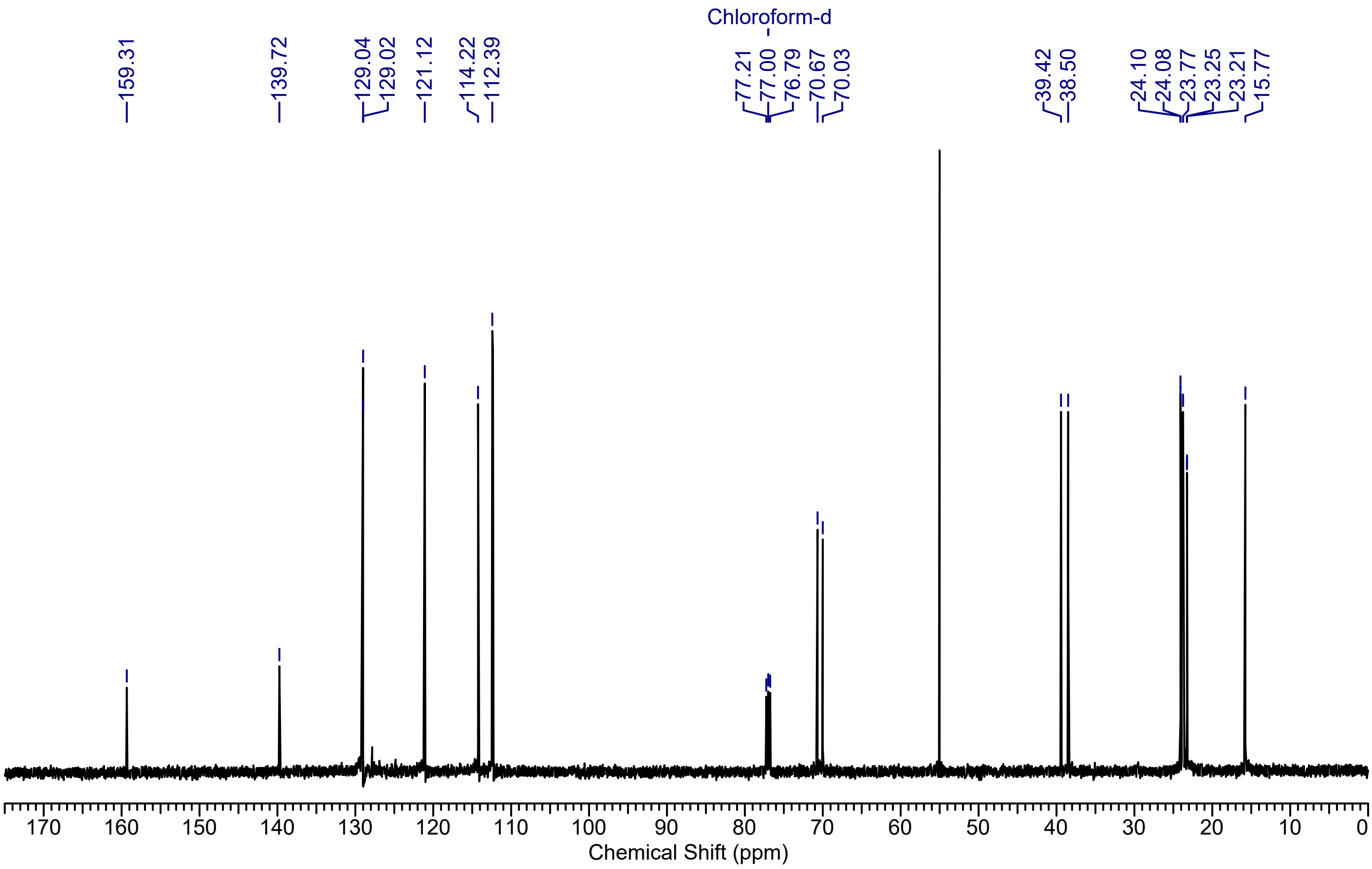
6i: ^{13}C NMR ($CDCl_3$, 101 MHz)



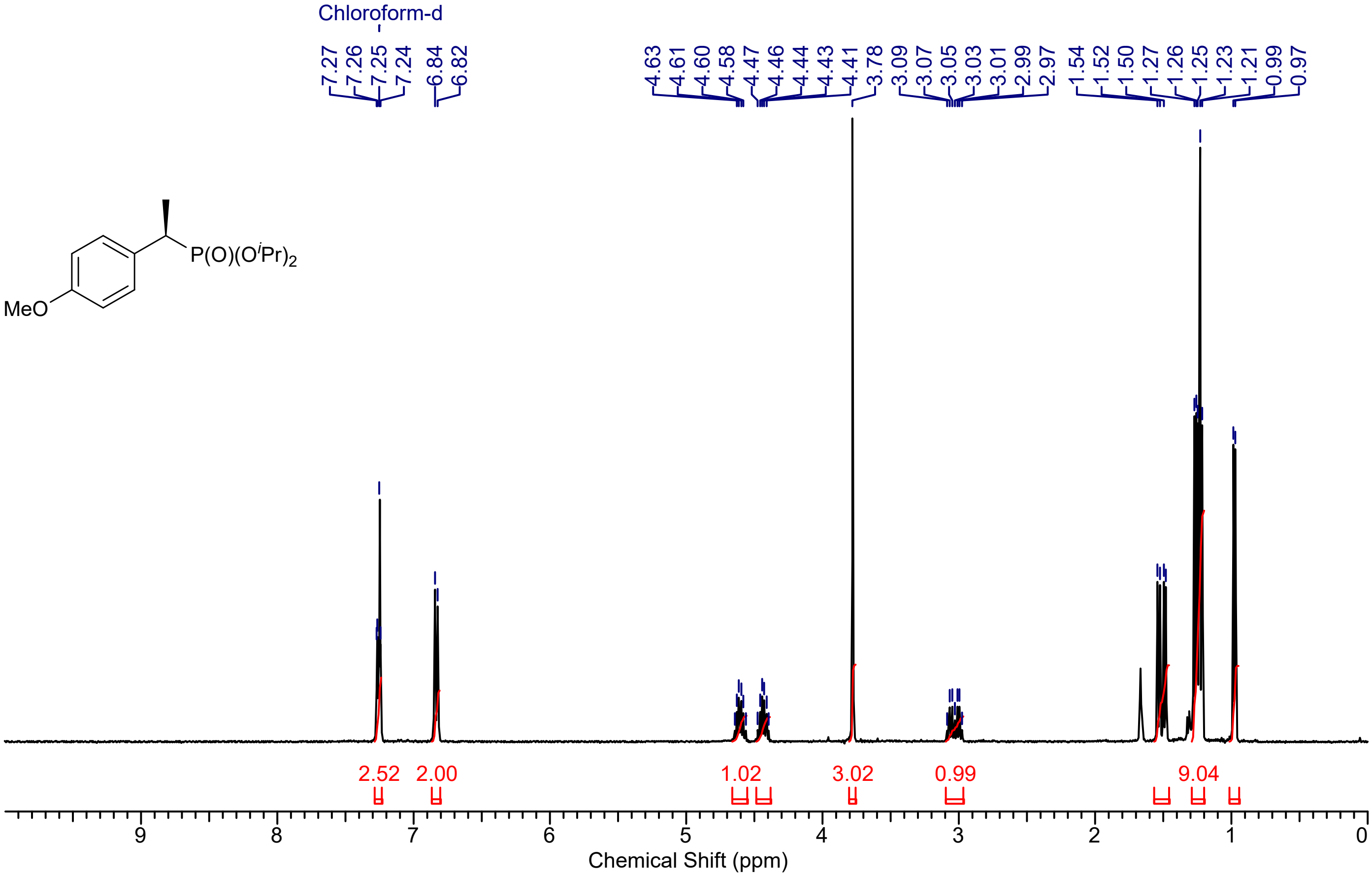
6j: ^{1}H NMR ($CDCl_3$, 400 MHz)



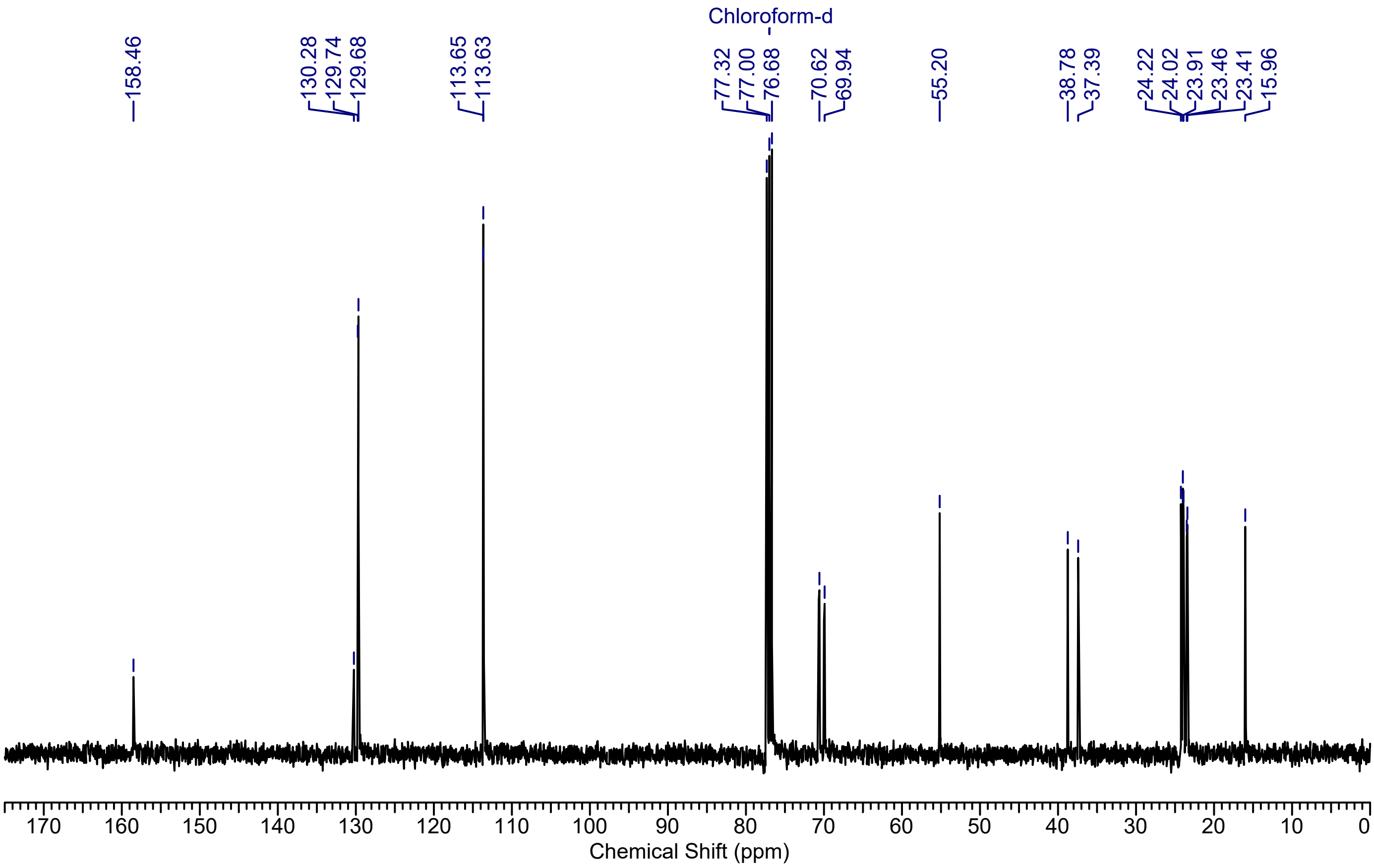
6j: ^{13}C NMR ($CDCl_3$, 151 MHz)



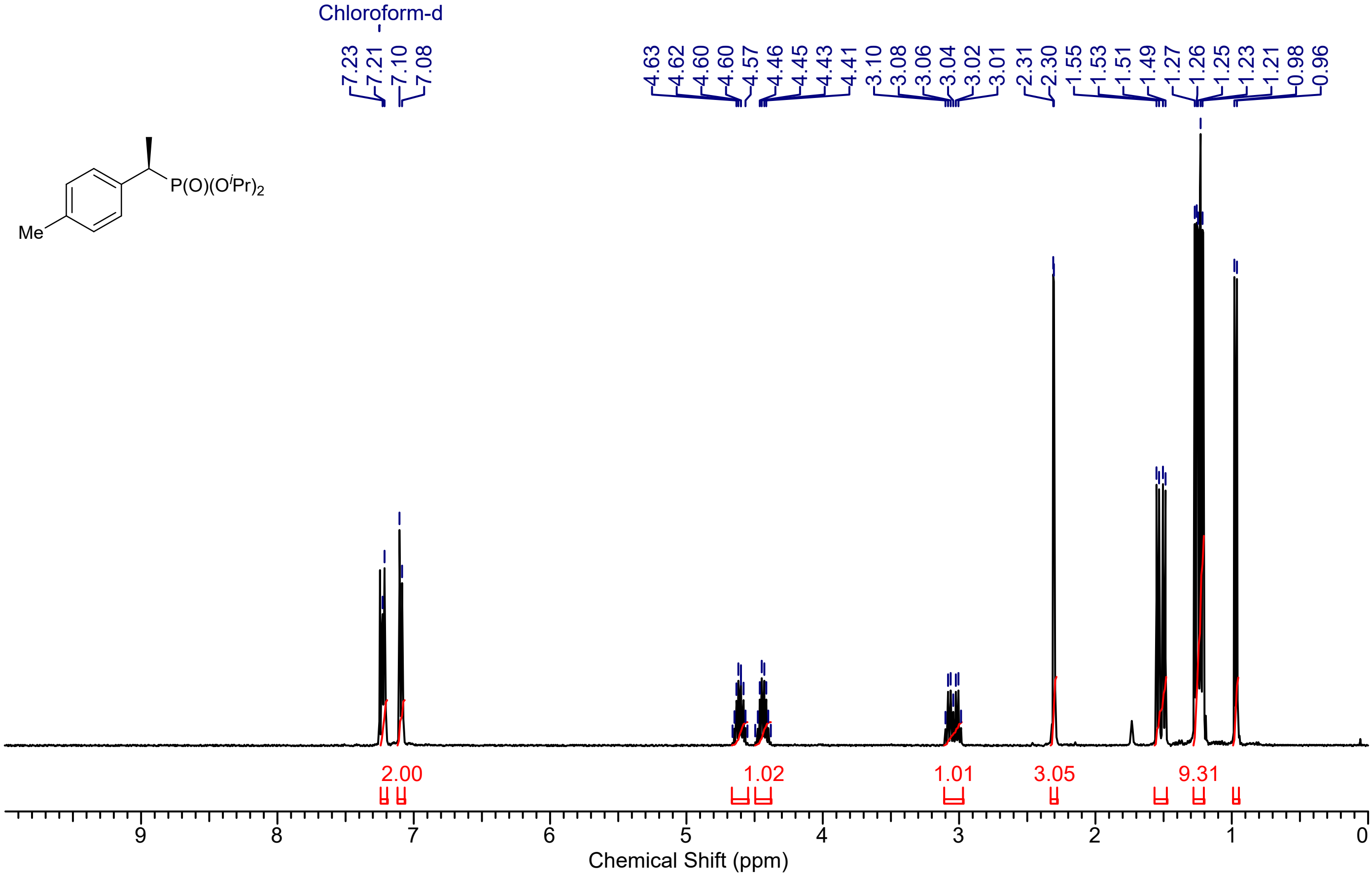
6k: ^{1}H NMR ($CDCl_3$, 400 MHz)



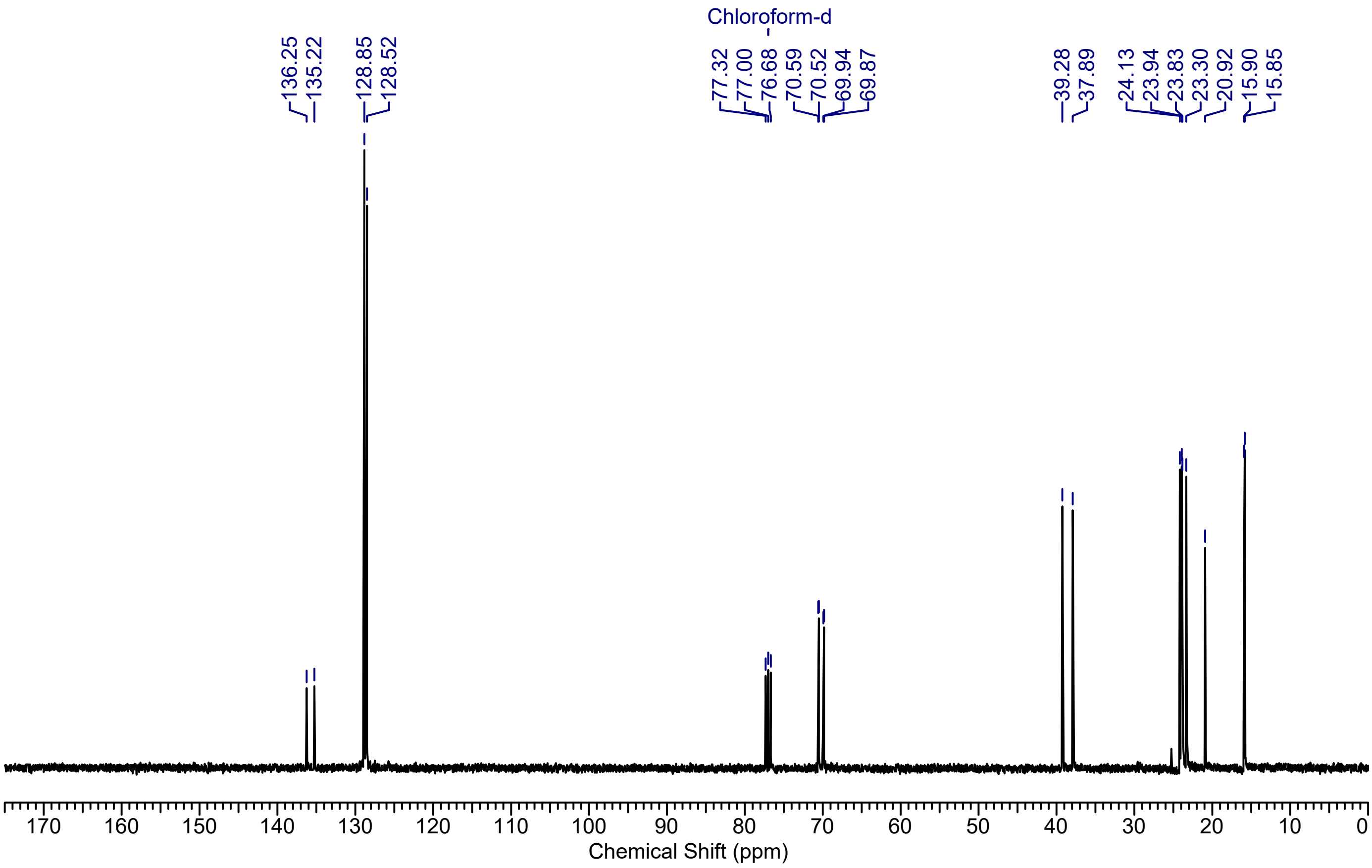
6k: ^{13}C NMR ($CDCl_3$, 101 MHz)



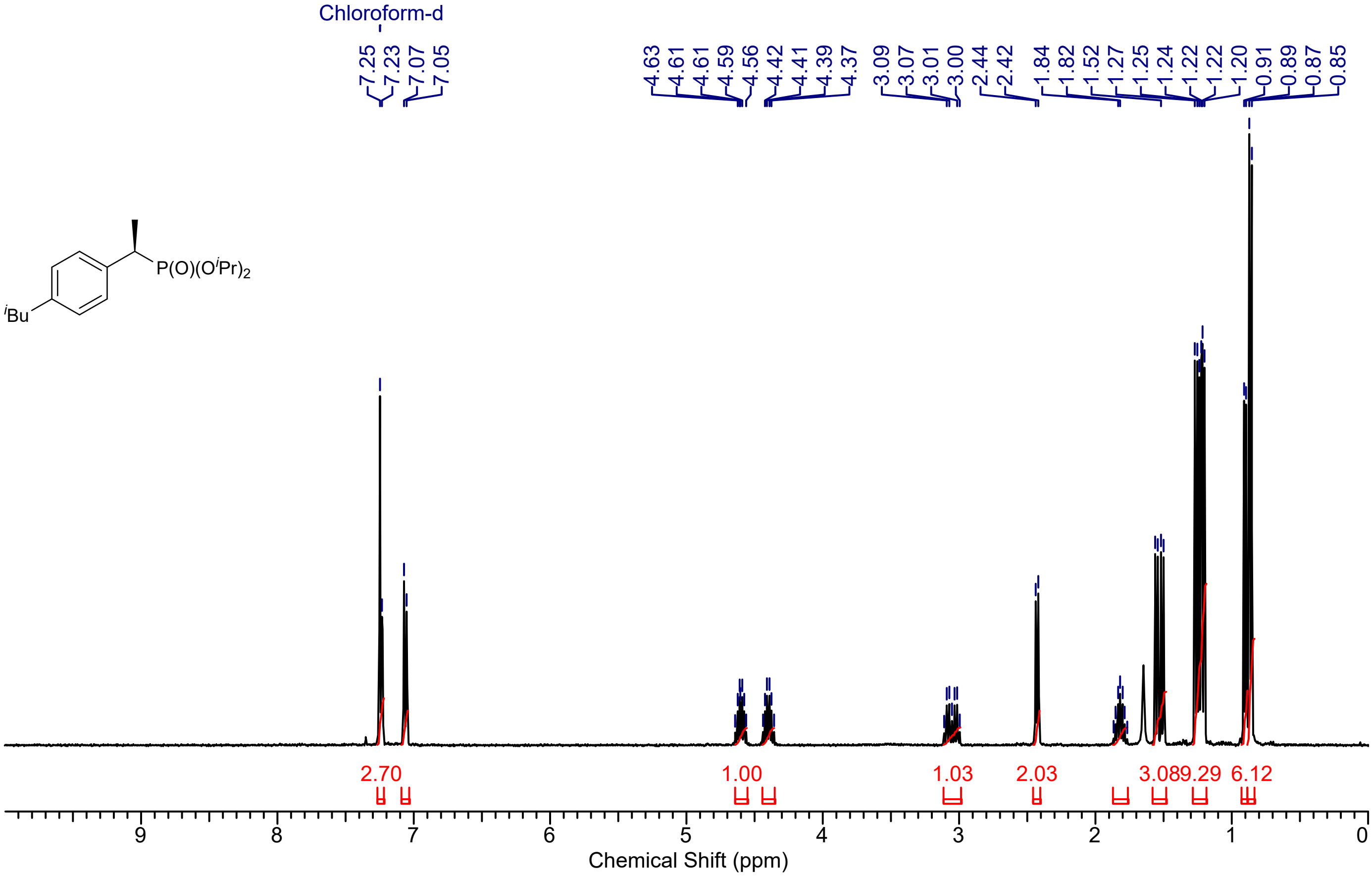
6l: ^{1}H NMR ($CDCl_3$, 400 MHz)



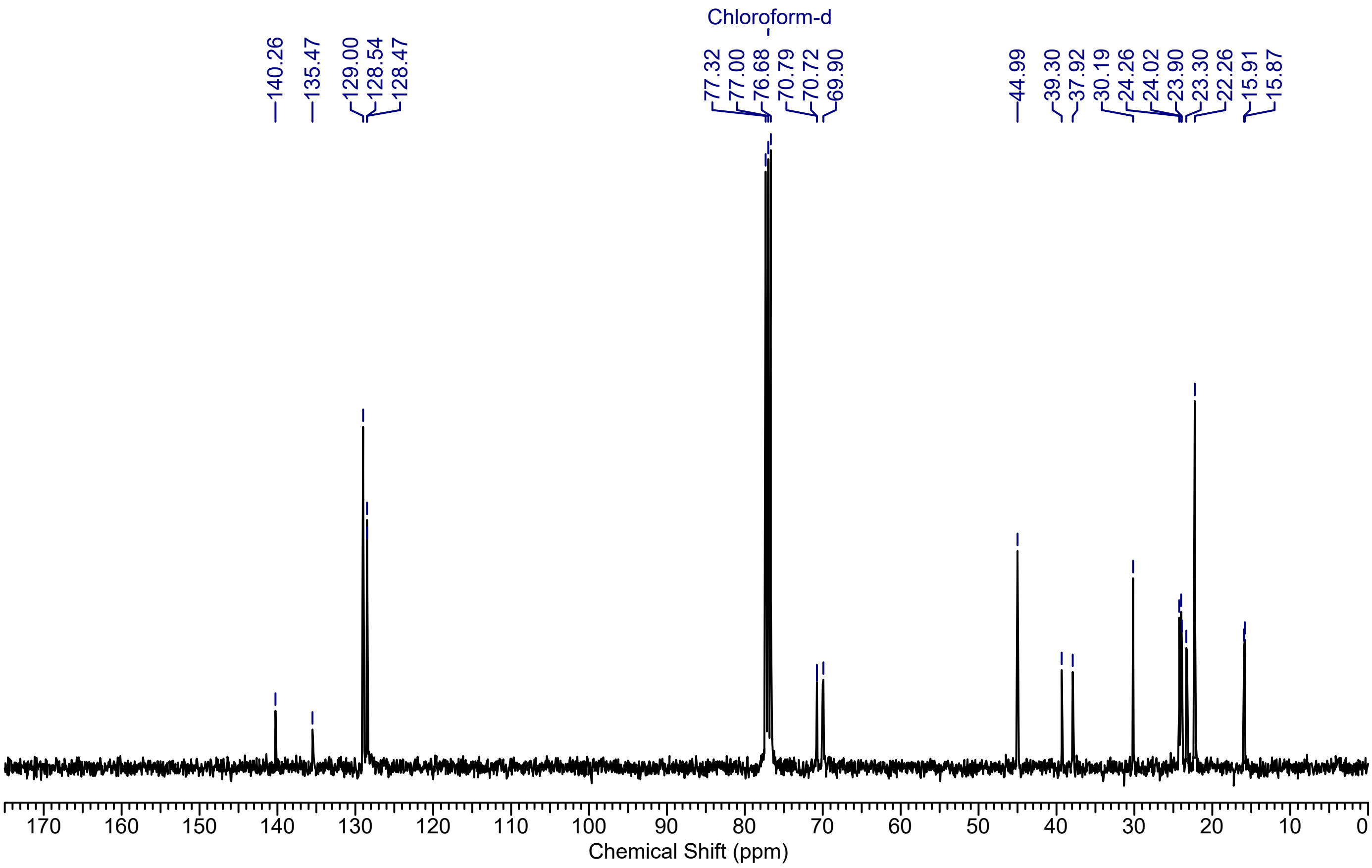
6l: ^{13}C NMR ($CDCl_3$, 101 MHz)



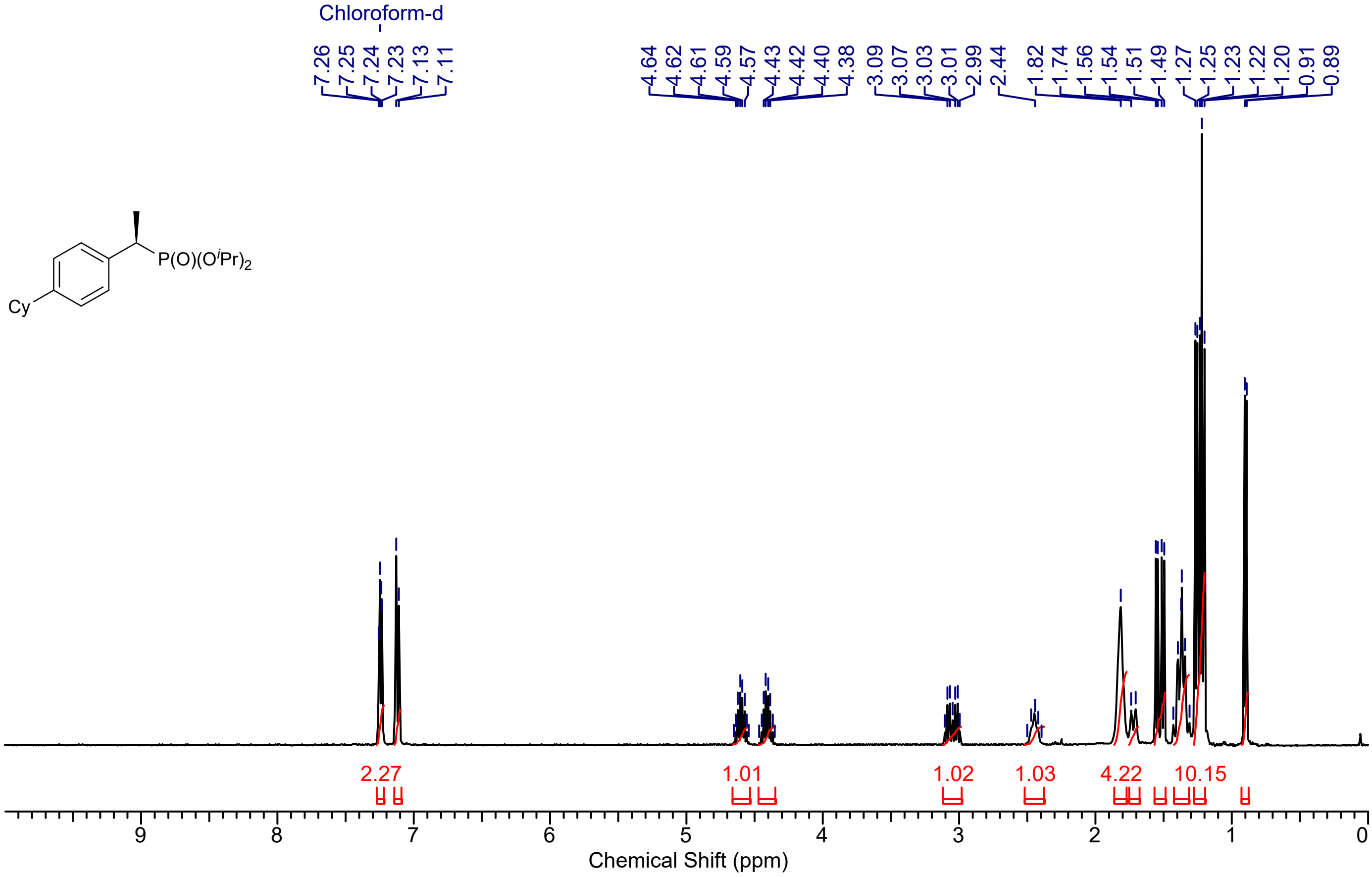
6m: ^{1}H NMR ($CDCl_3$, 400 MHz)



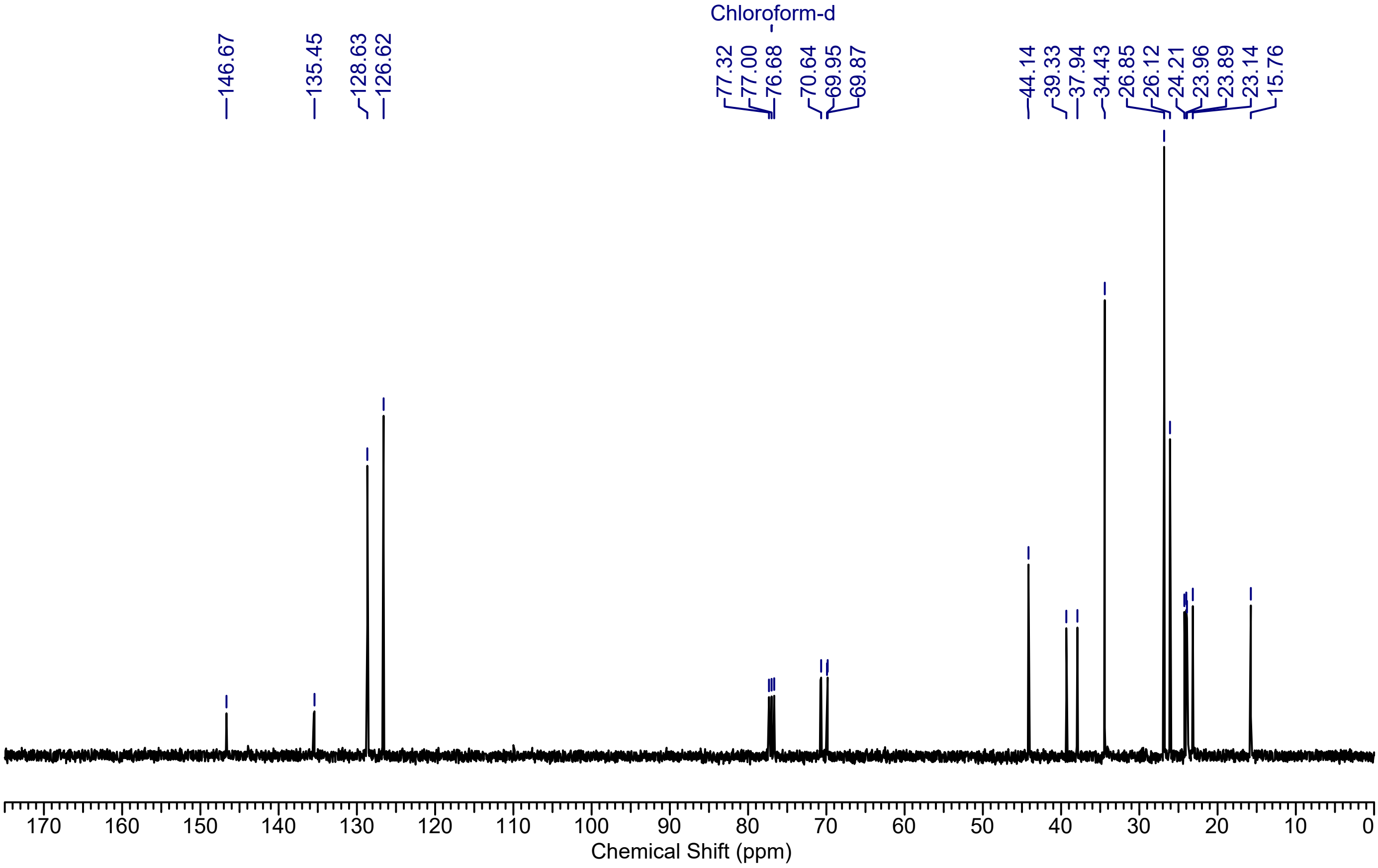
6m: ^{13}C NMR ($CDCl_3$, 101 MHz)



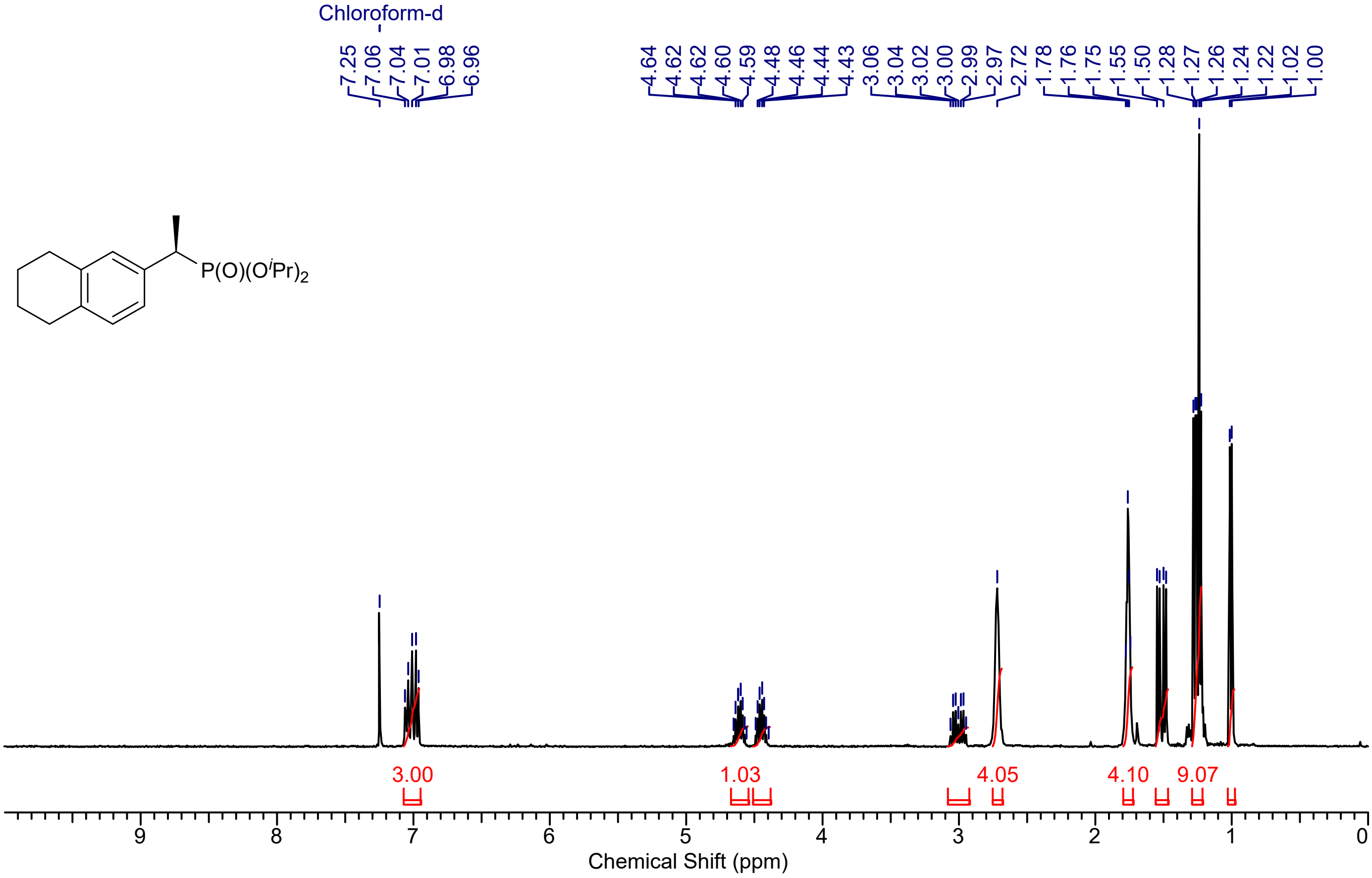
6n: ^{1}H NMR ($CDCl_3$, 400 MHz)



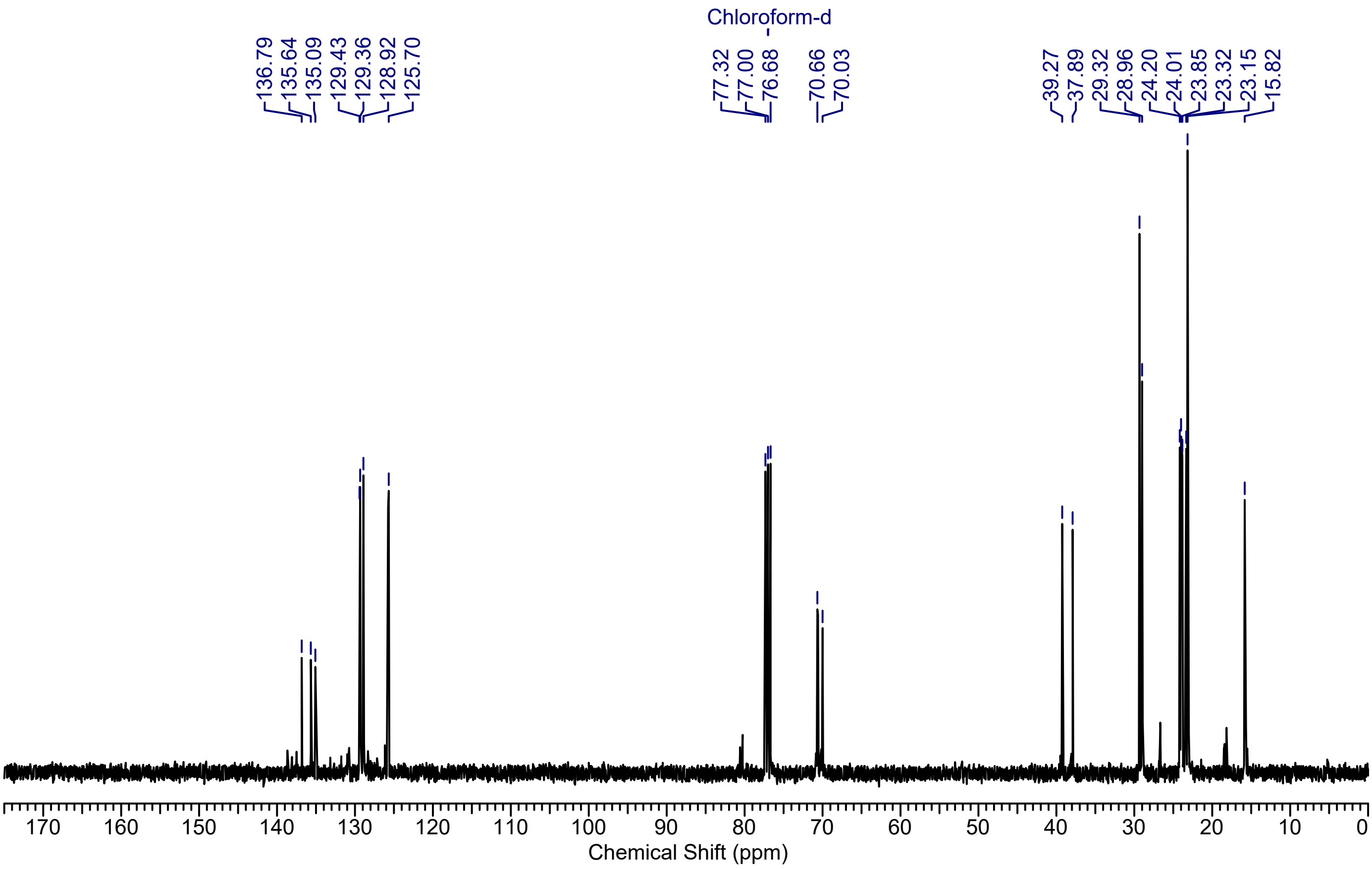
6n: ^{13}C NMR ($CDCl_3$, 101 MHz)



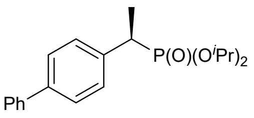
6o: ^{1}H NMR ($CDCl_3$, 400 MHz)

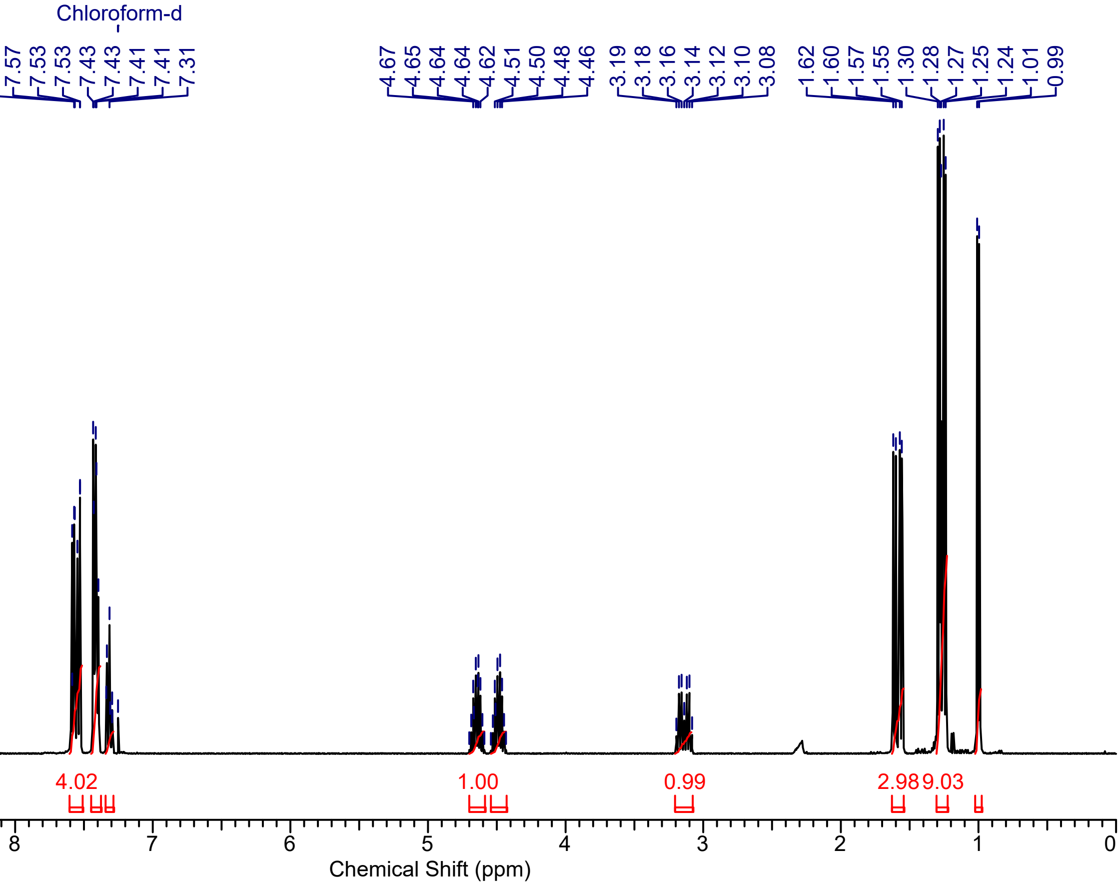


6o: ^{13}C NMR ($CDCl_3$, 101 MHz)

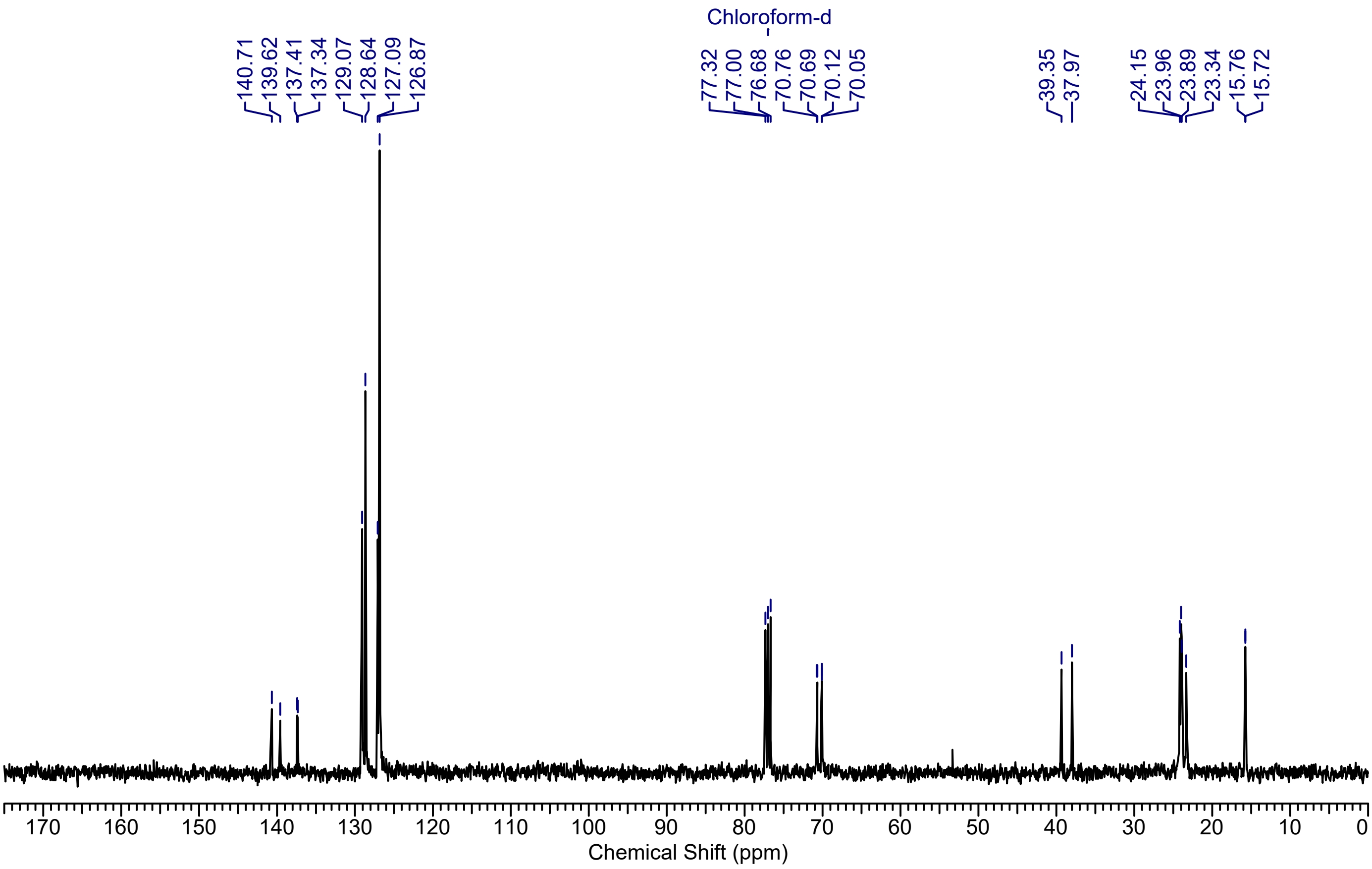


6p: ^{1}H NMR ($CDCl_3$, 400 MHz)

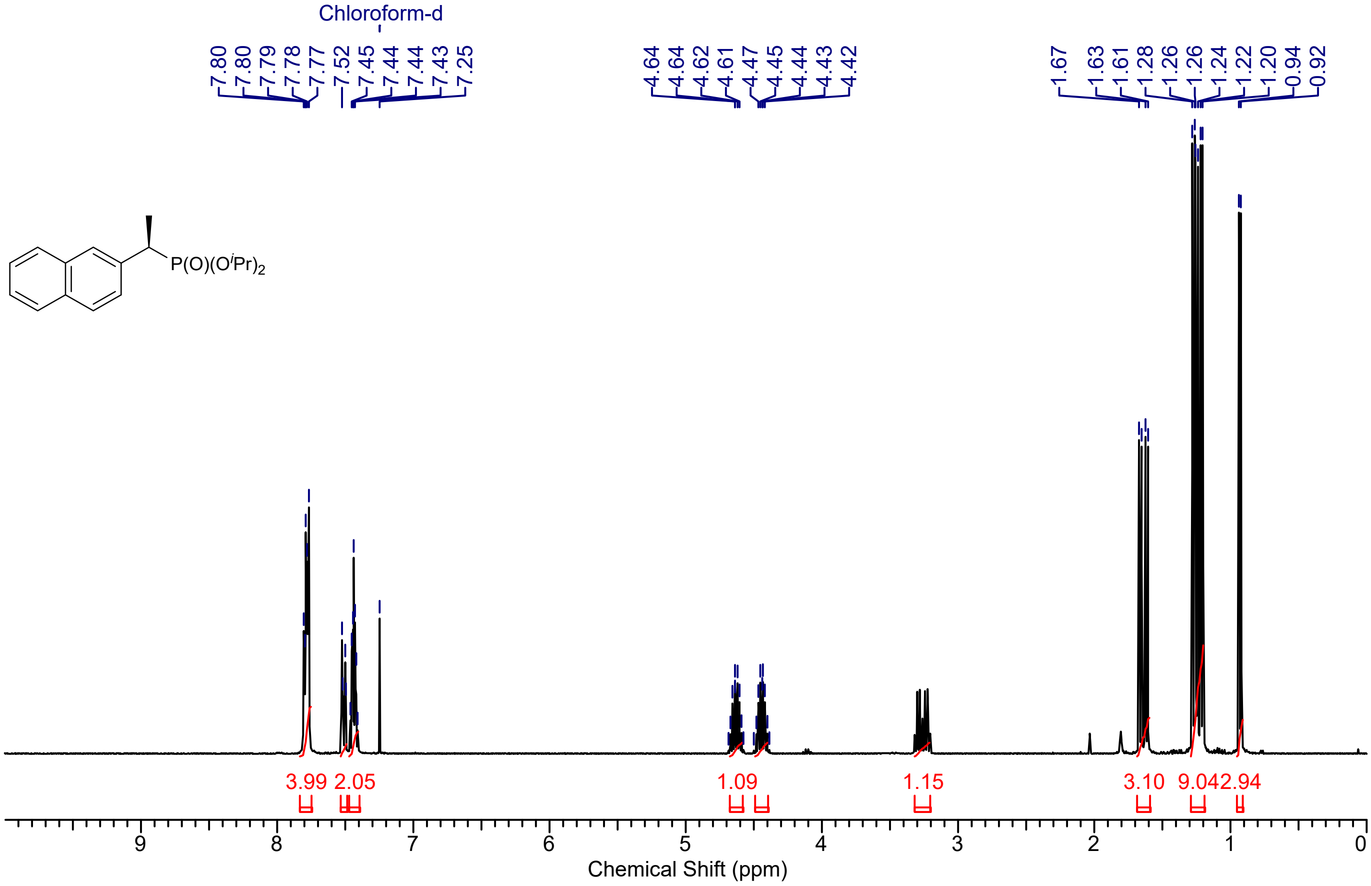




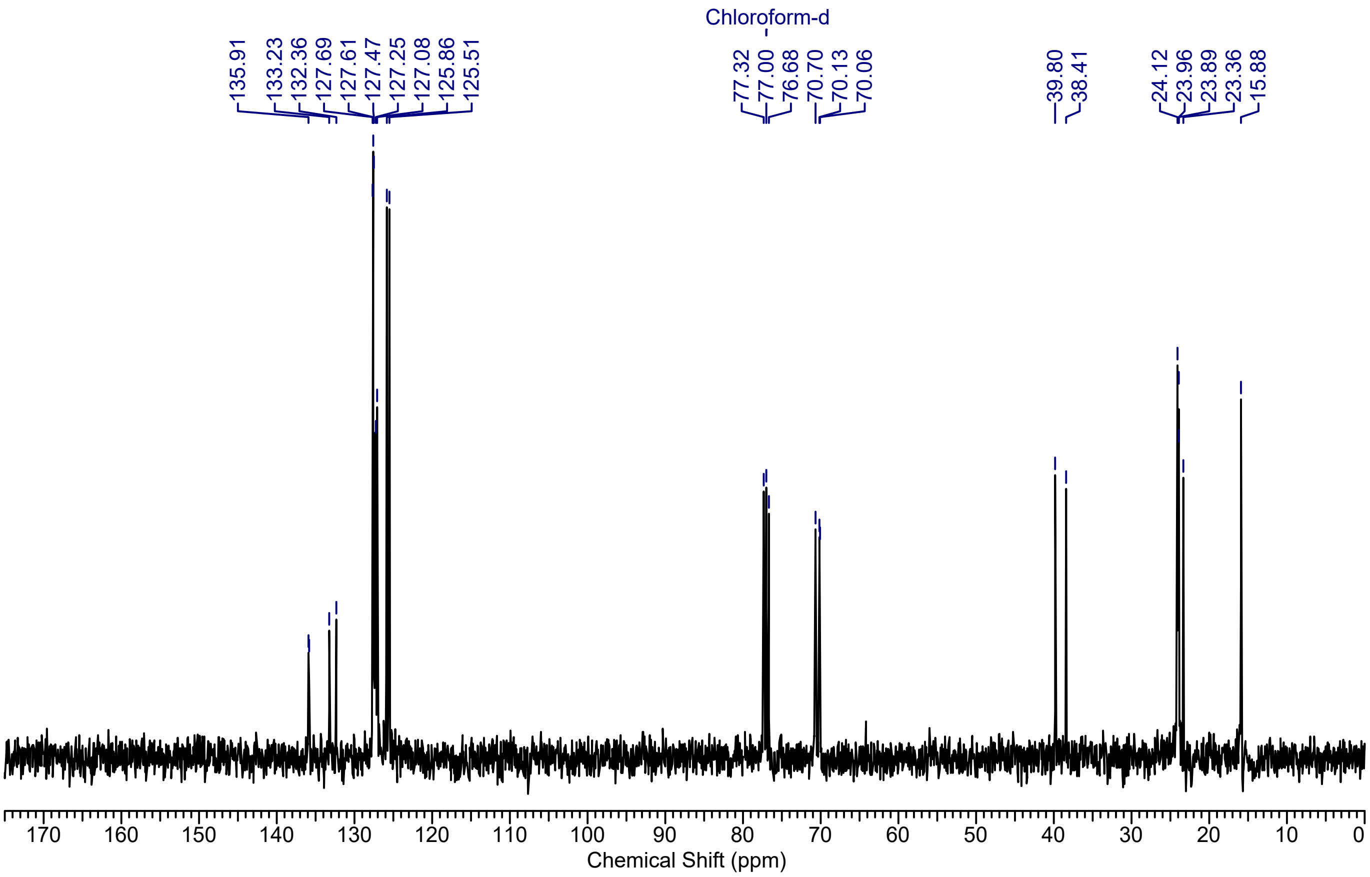
6p: ^{13}C NMR ($CDCl_3$, 101 MHz)



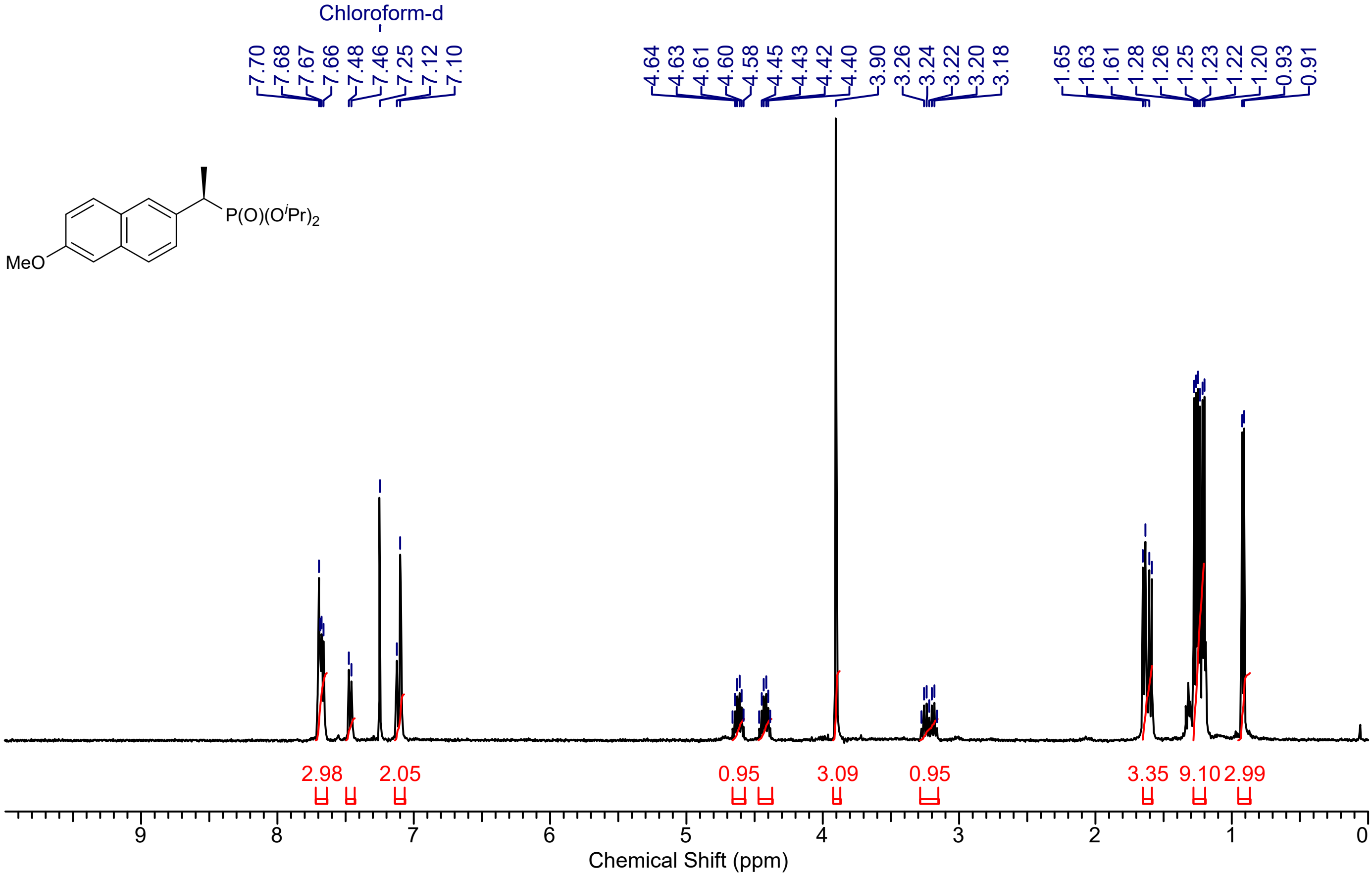
6q: ^{1}H NMR ($CDCl_3$, 400 MHz)



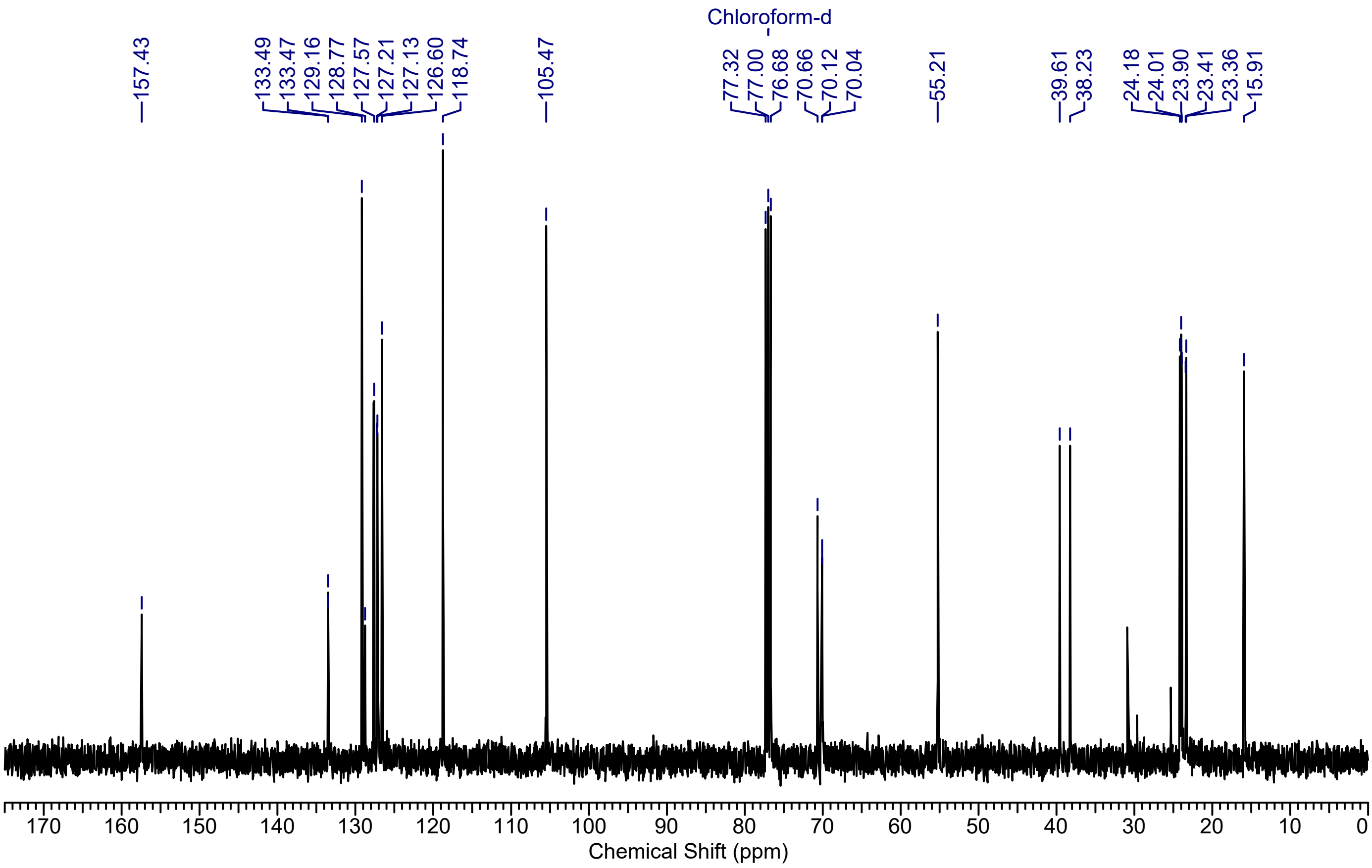
6q: ^{13}C NMR ($CDCl_3$, 101 MHz)



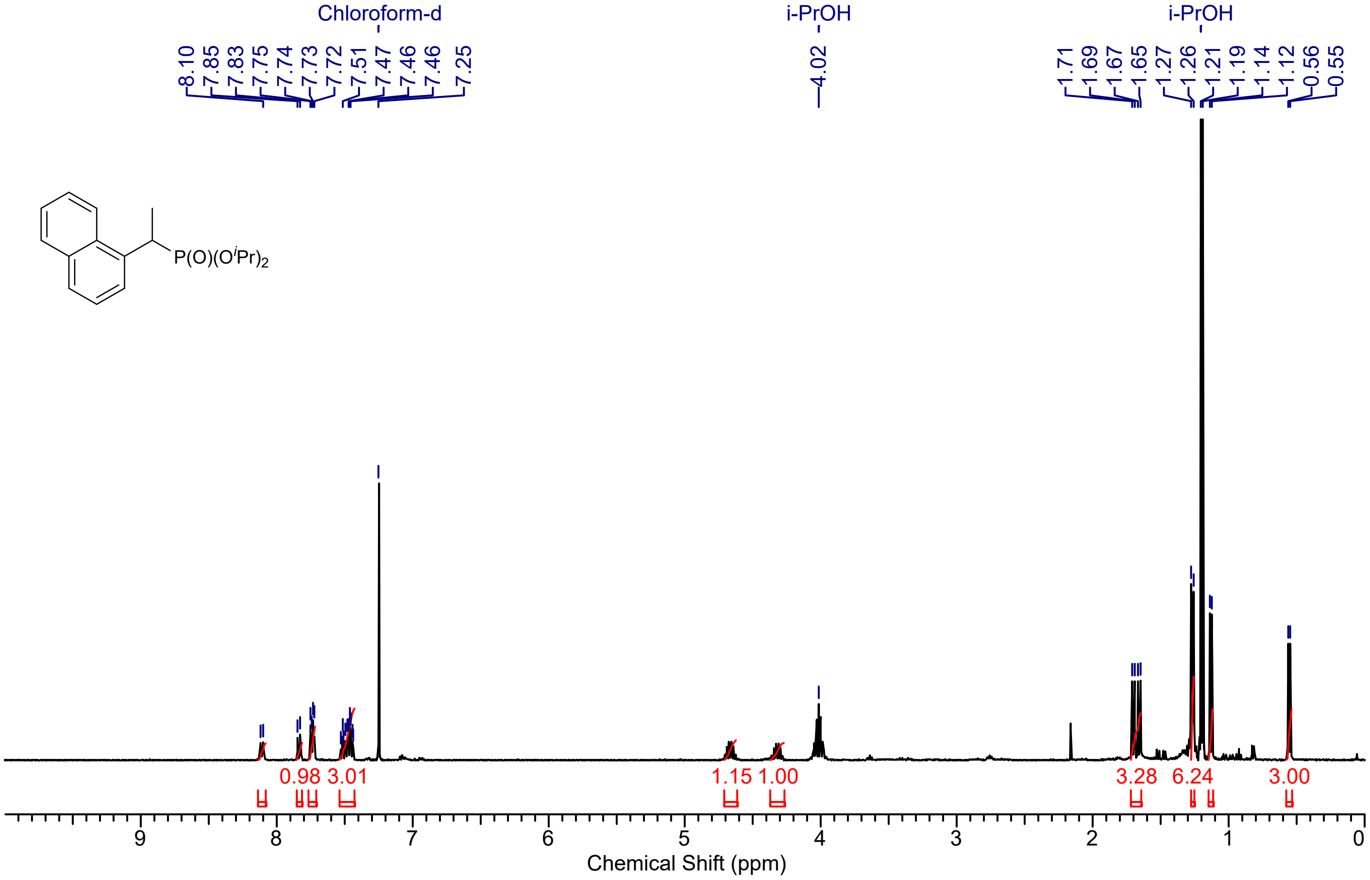
6r: ^{1}H NMR ($CDCl_3$, 400 MHz)



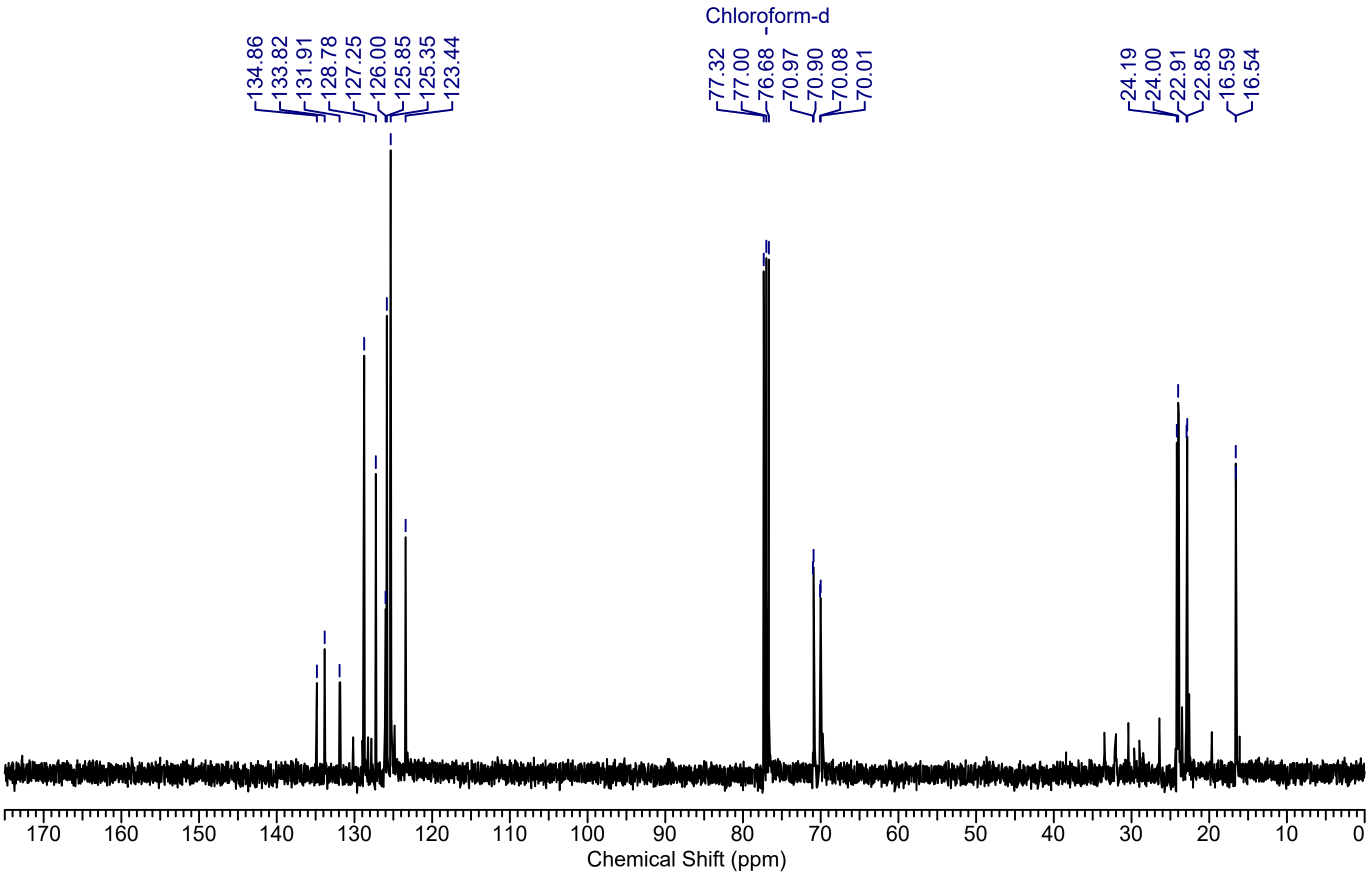
6r: ^{13}C NMR ($CDCl_3$, 101 MHz)



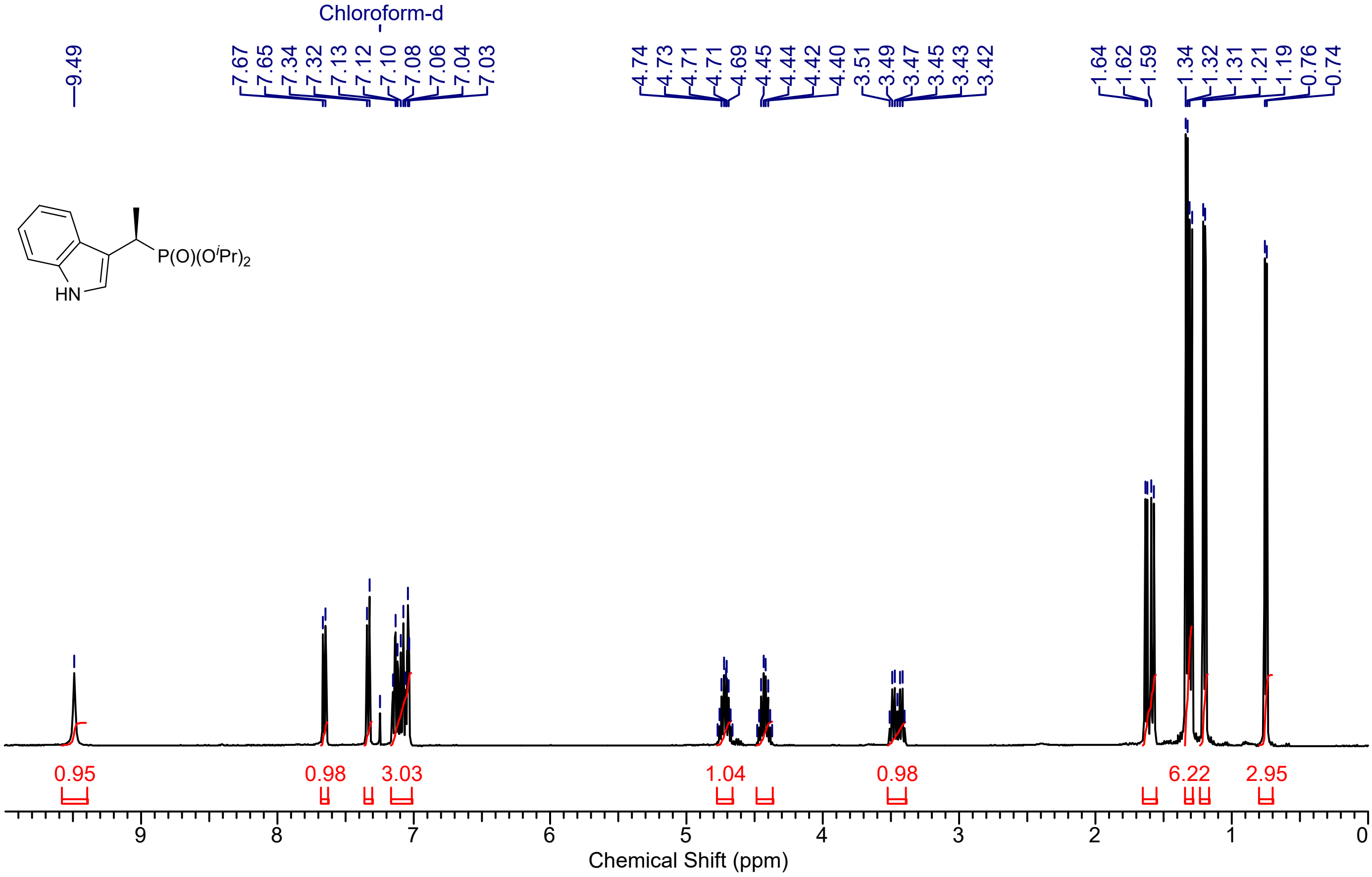
6s: ^{1}H NMR ($CDCl_3$, 400 MHz)



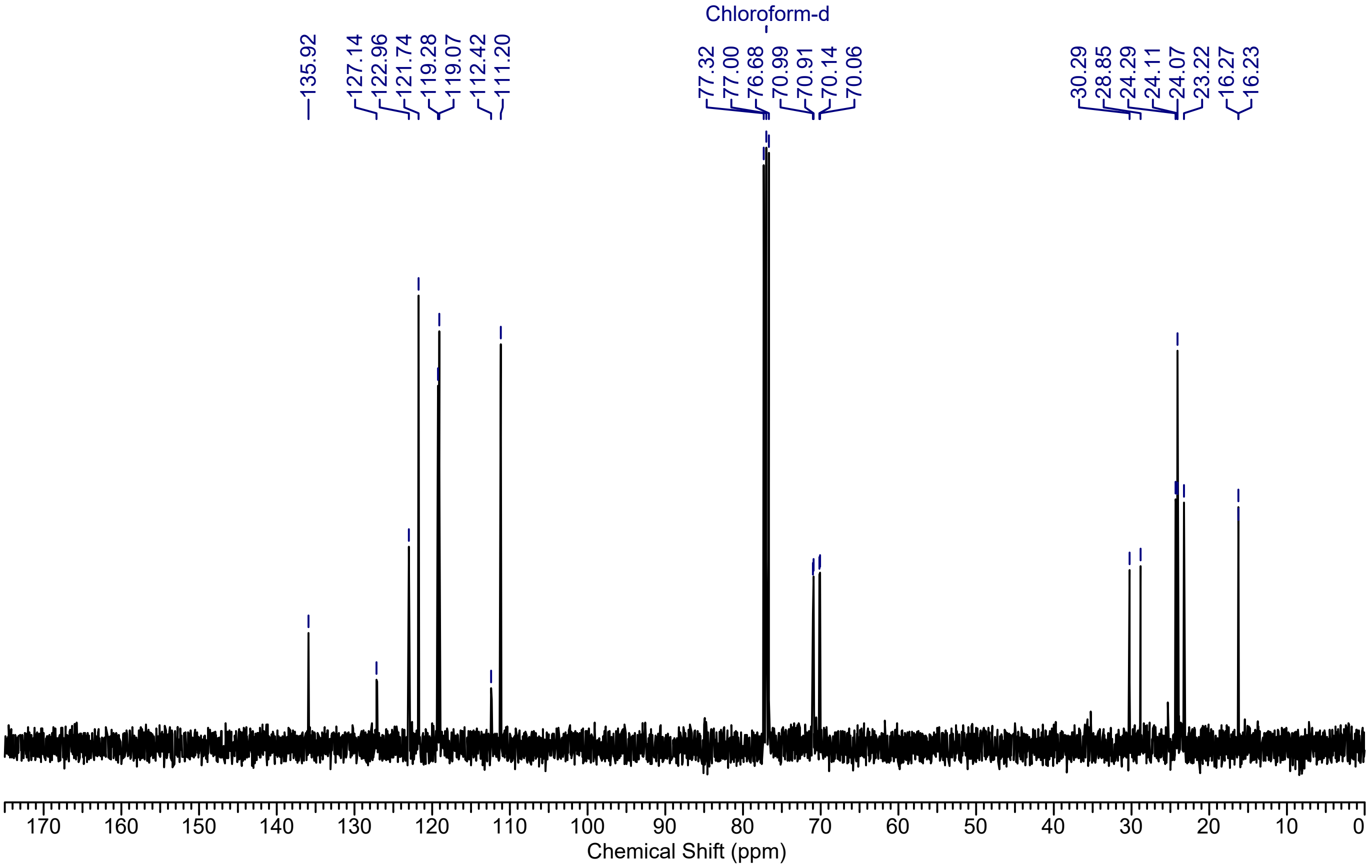
6s: ^{13}C NMR ($CDCl_3$, 101 MHz)



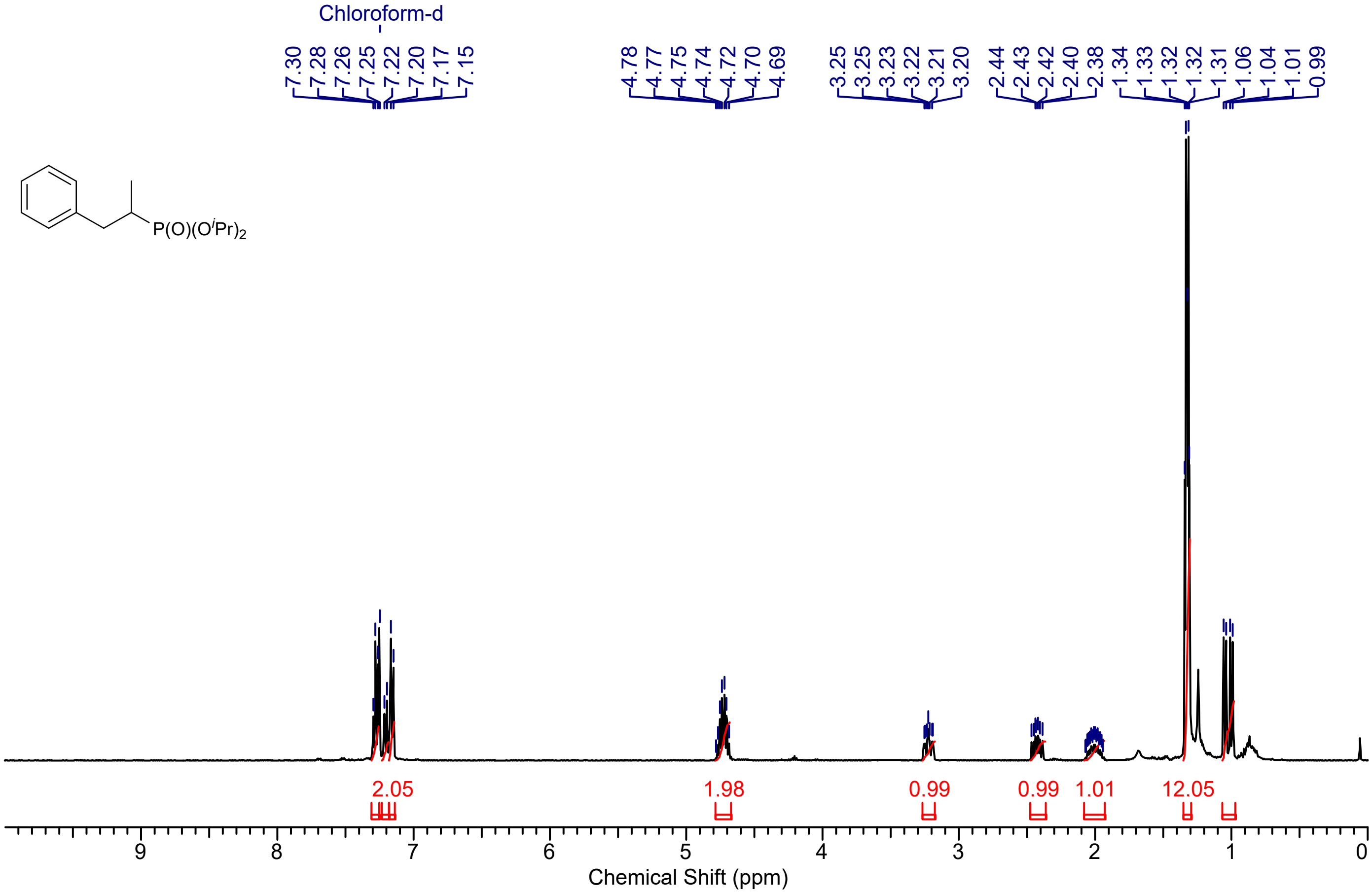
6t: ^{1}H NMR ($CDCl_3$, 400 MHz)



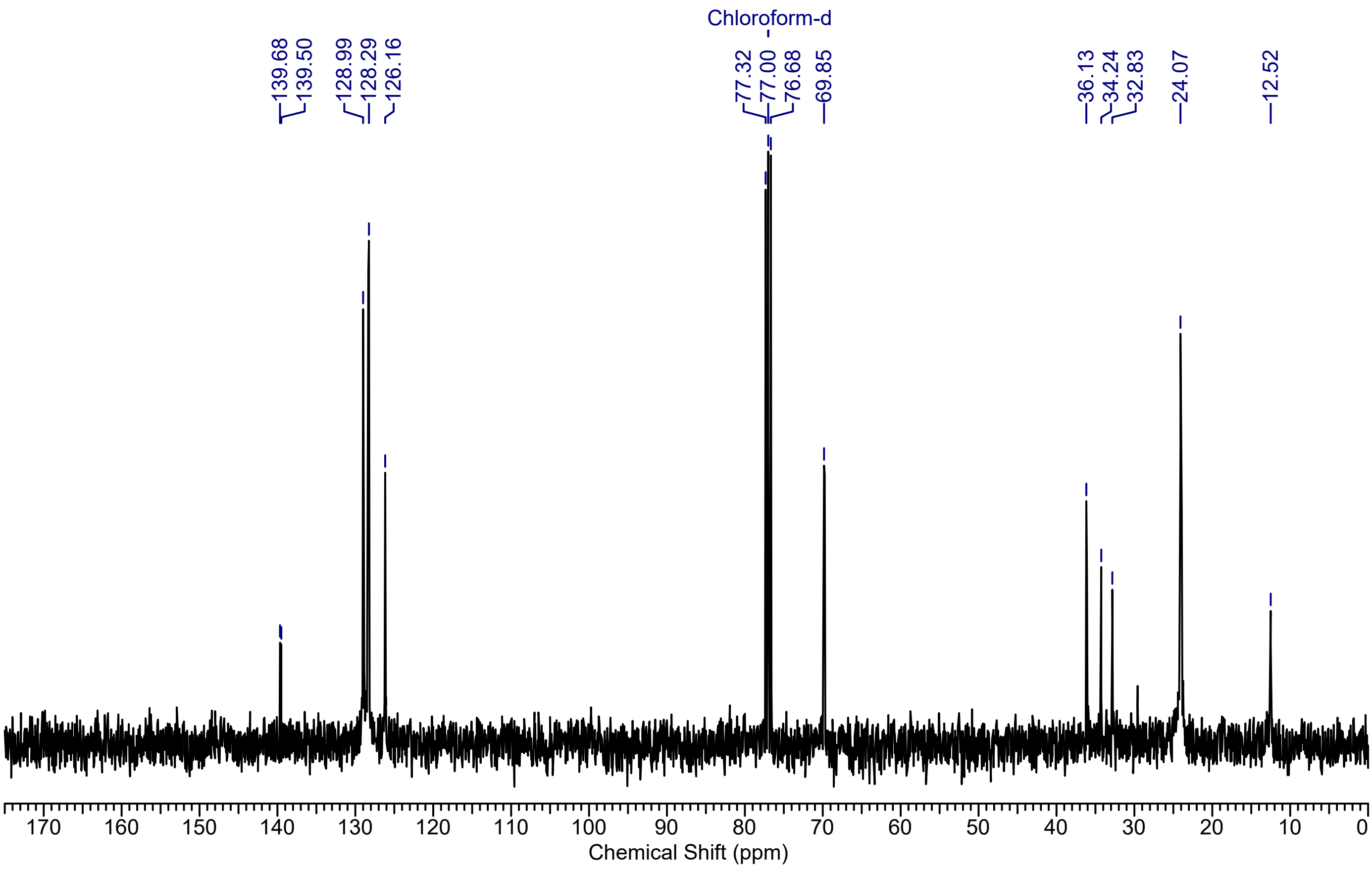
6t: ^{13}C NMR ($CDCl_3$, 101 MHz)



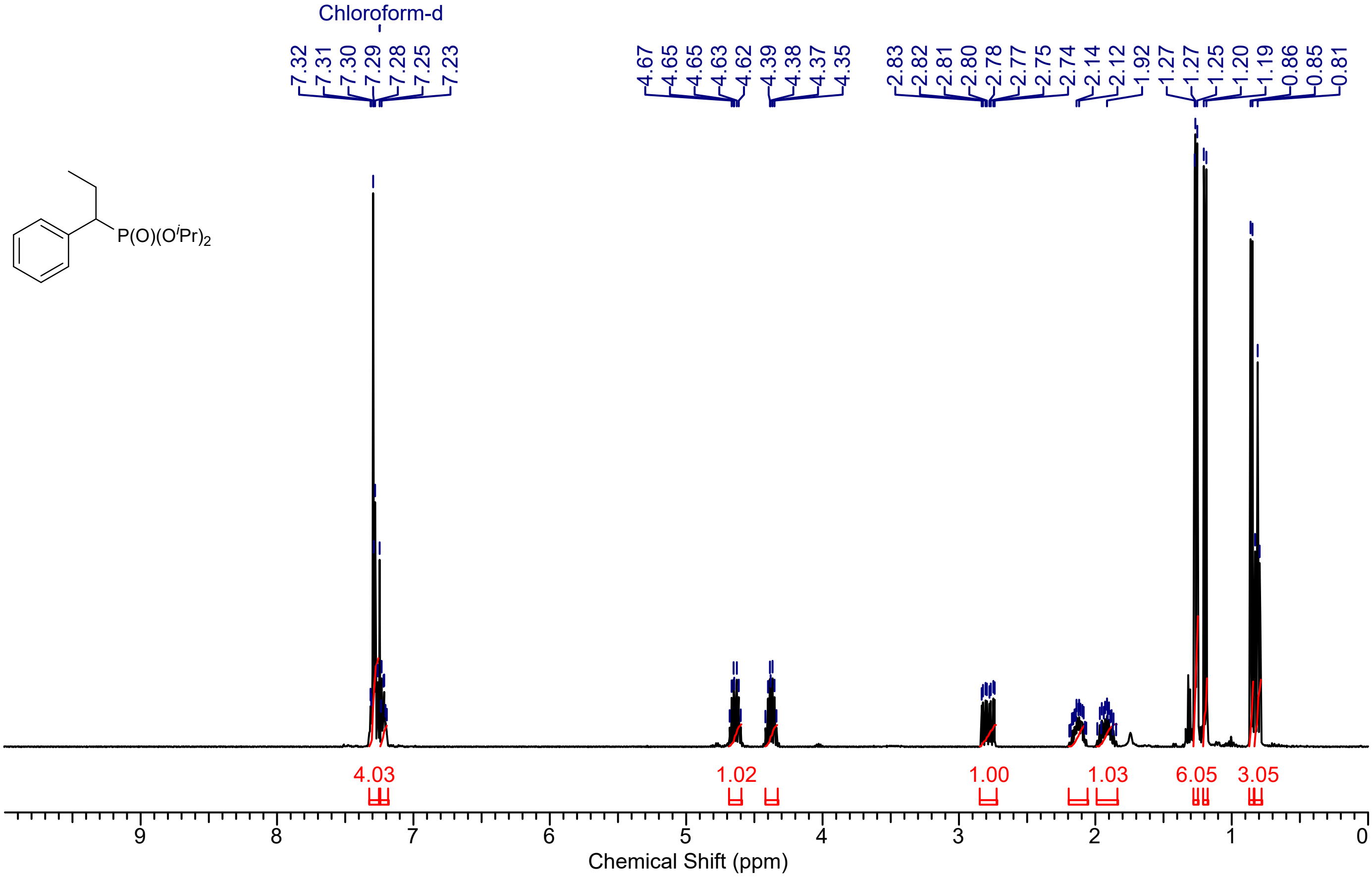
6u: ^{1}H NMR ($CDCl_3$, 400 MHz)



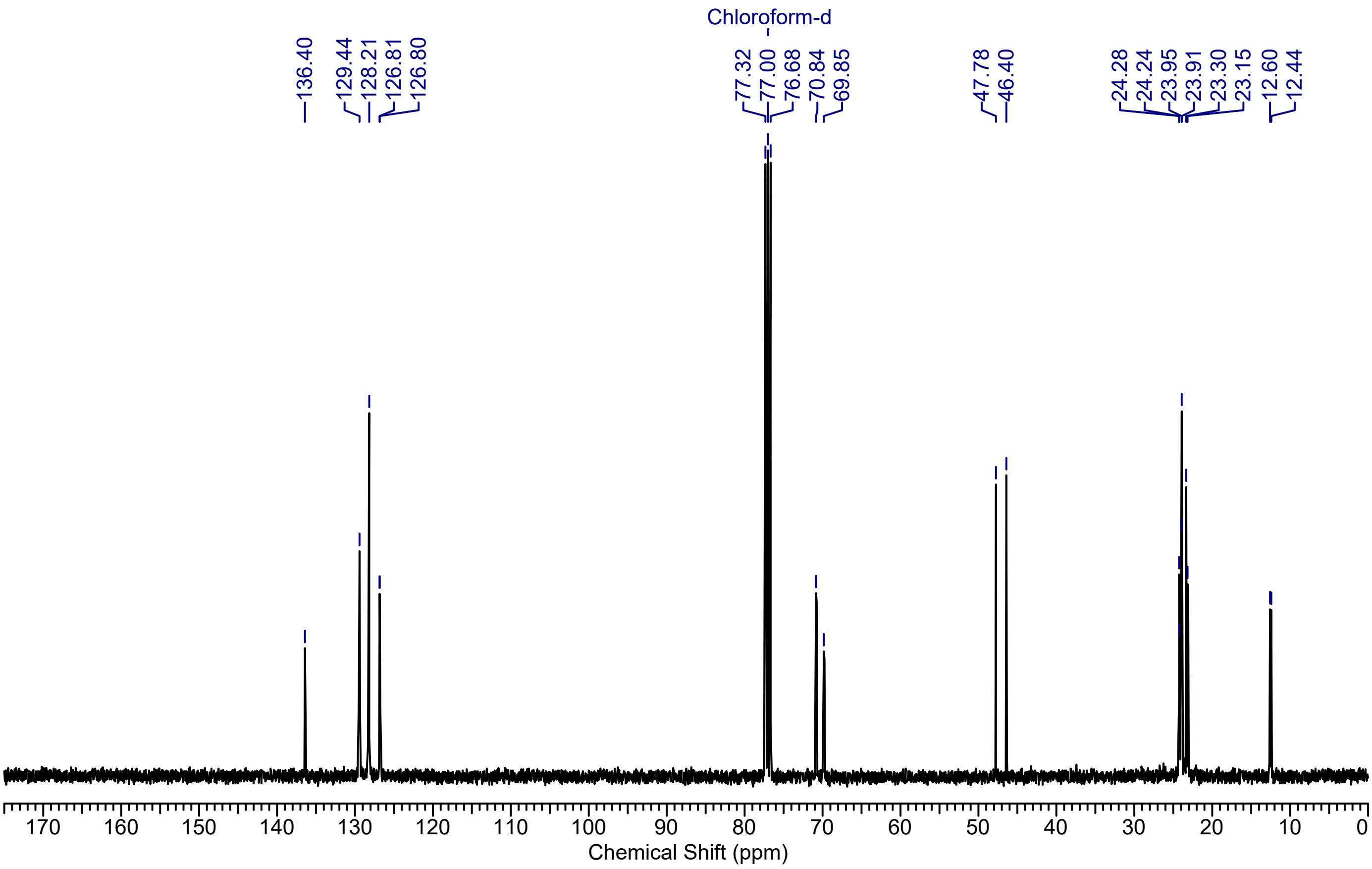
6u: ^{13}C NMR ($CDCl_3$, 101 MHz)



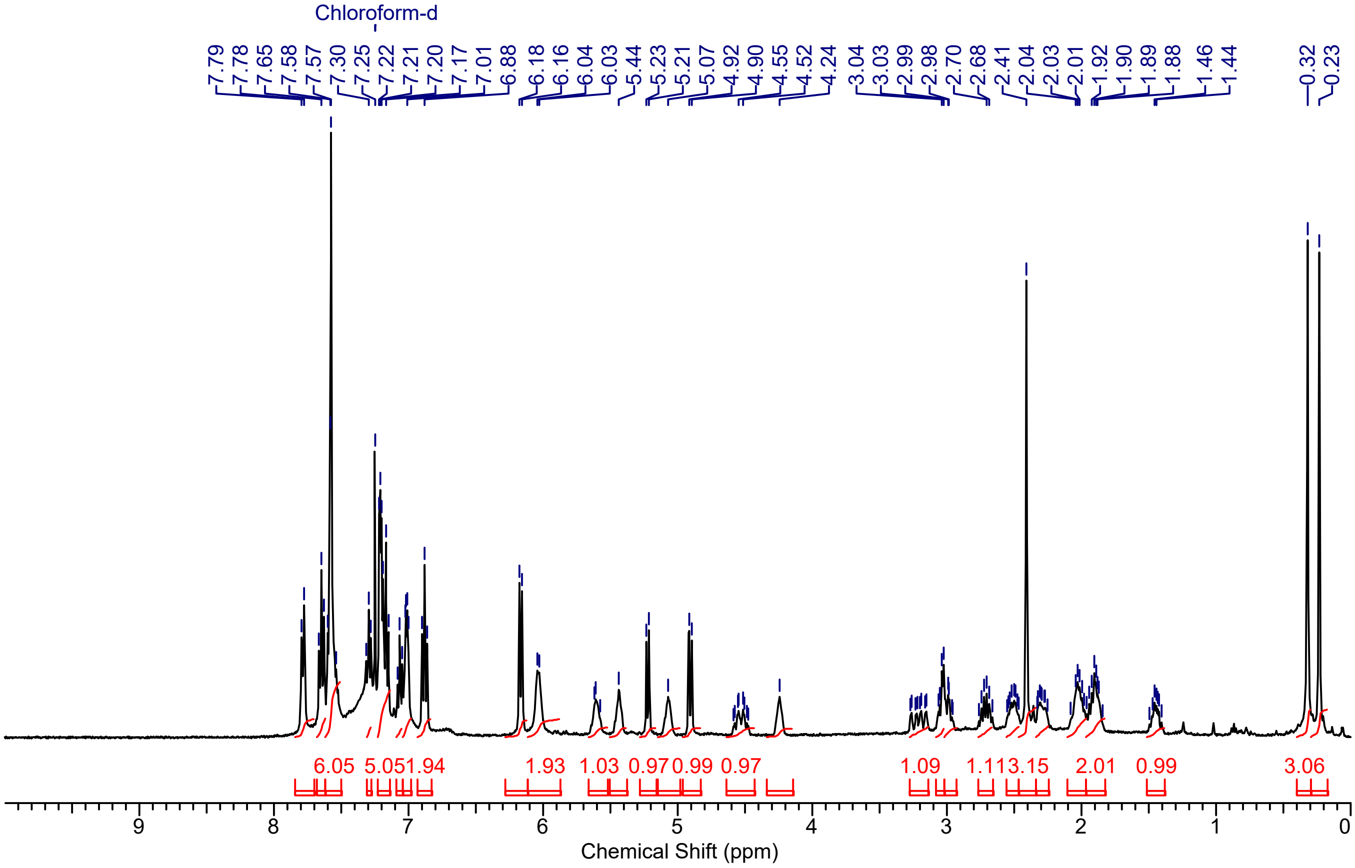
6v: ^{1}H NMR ($CDCl_3$, 400 MHz)



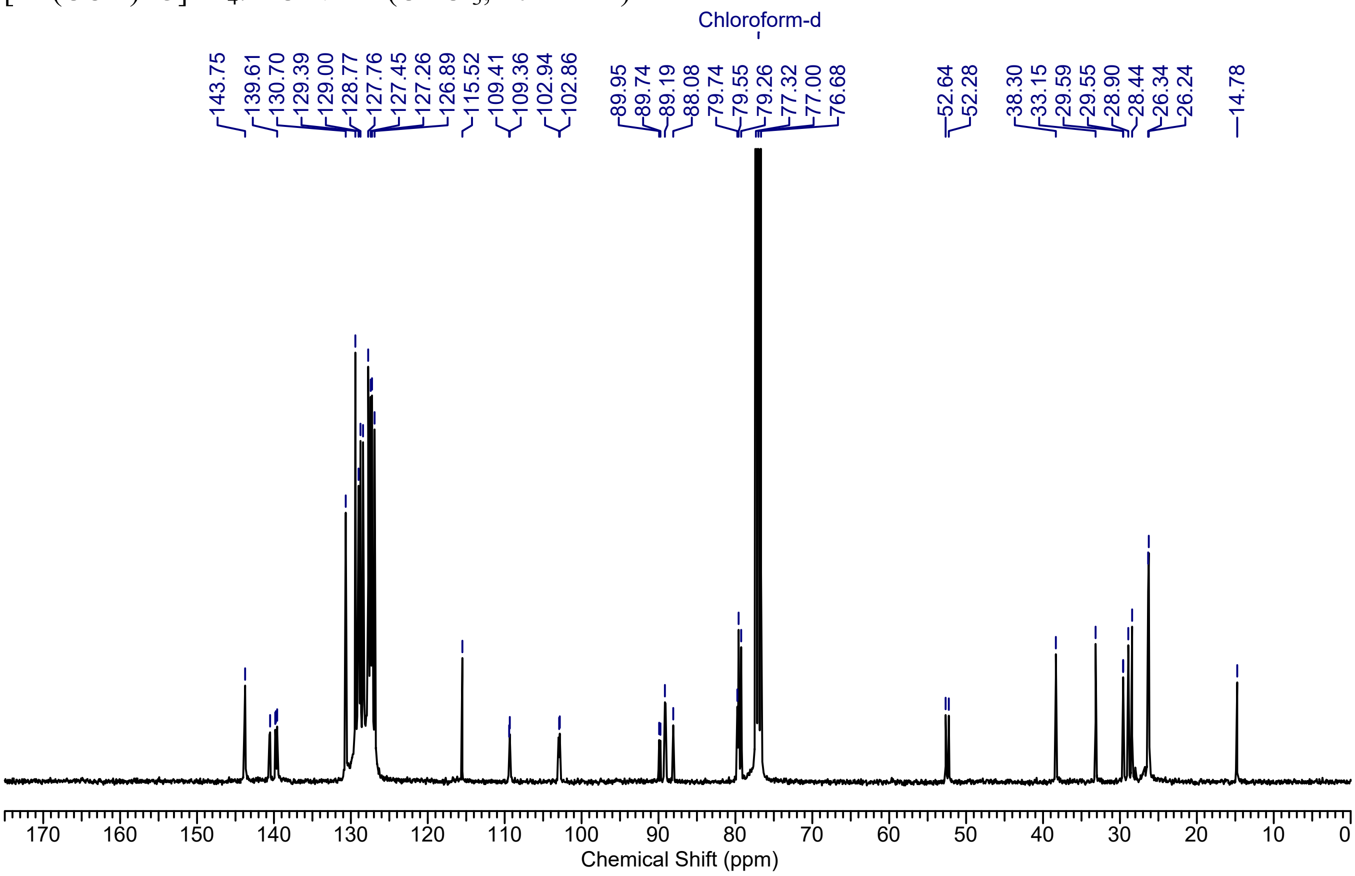
6v: ^{13}C NMR ($CDCl_3$, 101 MHz)



[Rh(COD)**L3**]BF_4: ^{1}H NMR ($CDCl_3$, 400 MHz)

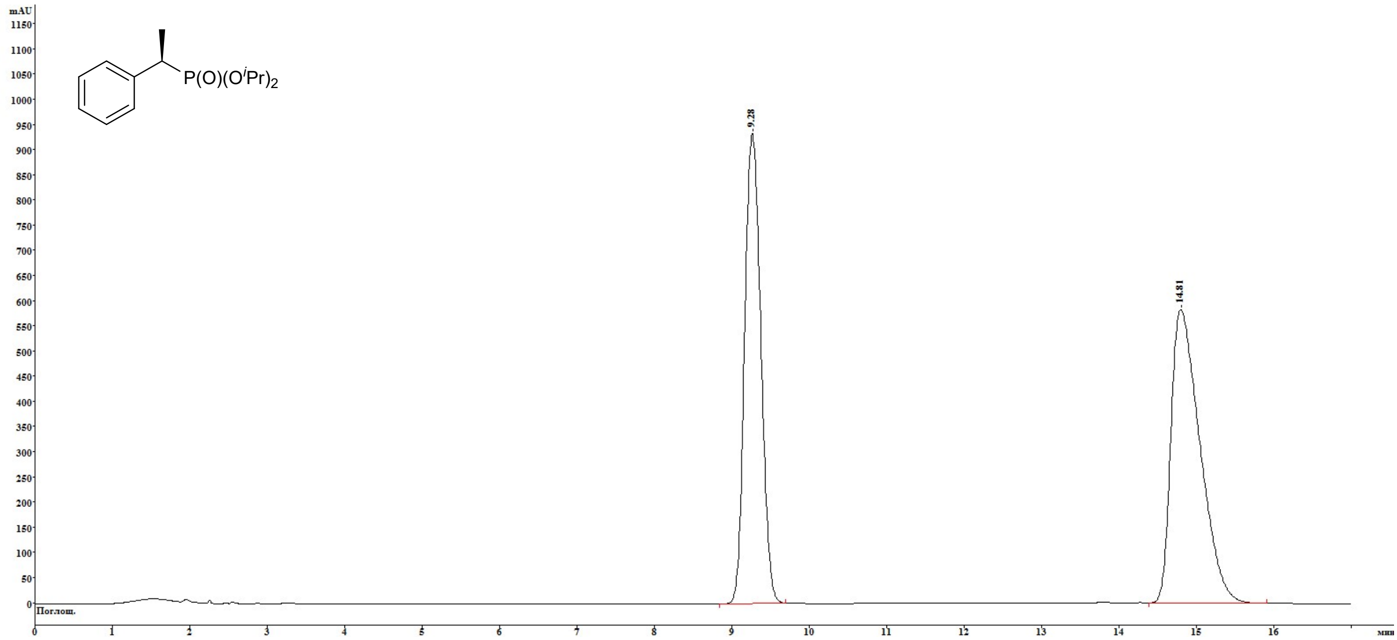


[Rh(COD)**L3**]BF_4: ^{13}C NMR ($CDCl_3$, 101 MHz)

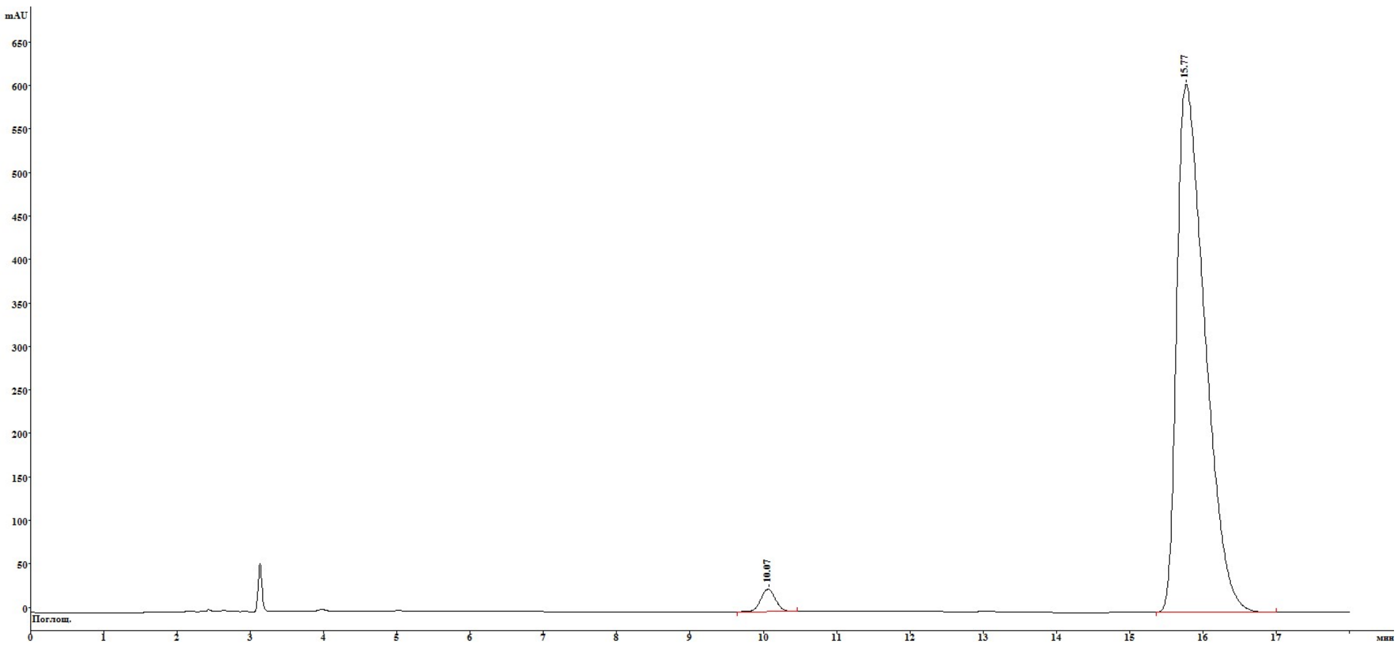


11. HPLC data

6a. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min.

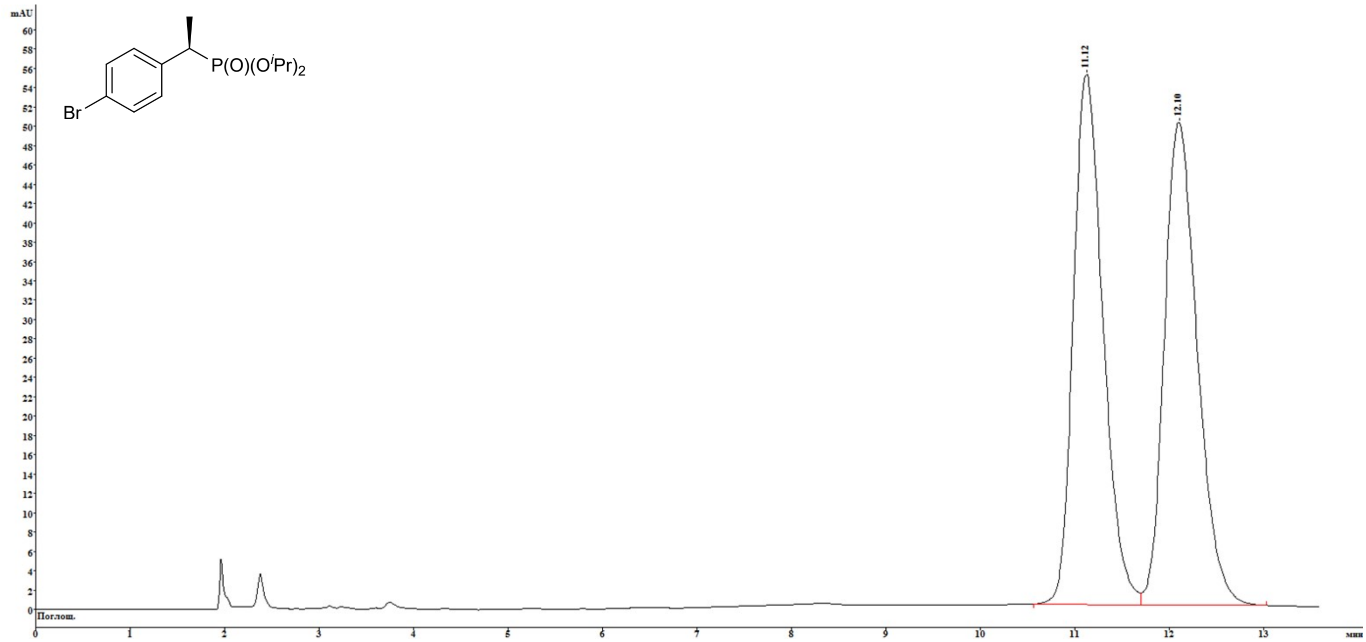


№	Retention time	Area	Area, %
1	9.28	13560	47.22
2	14.81	15154	52.78

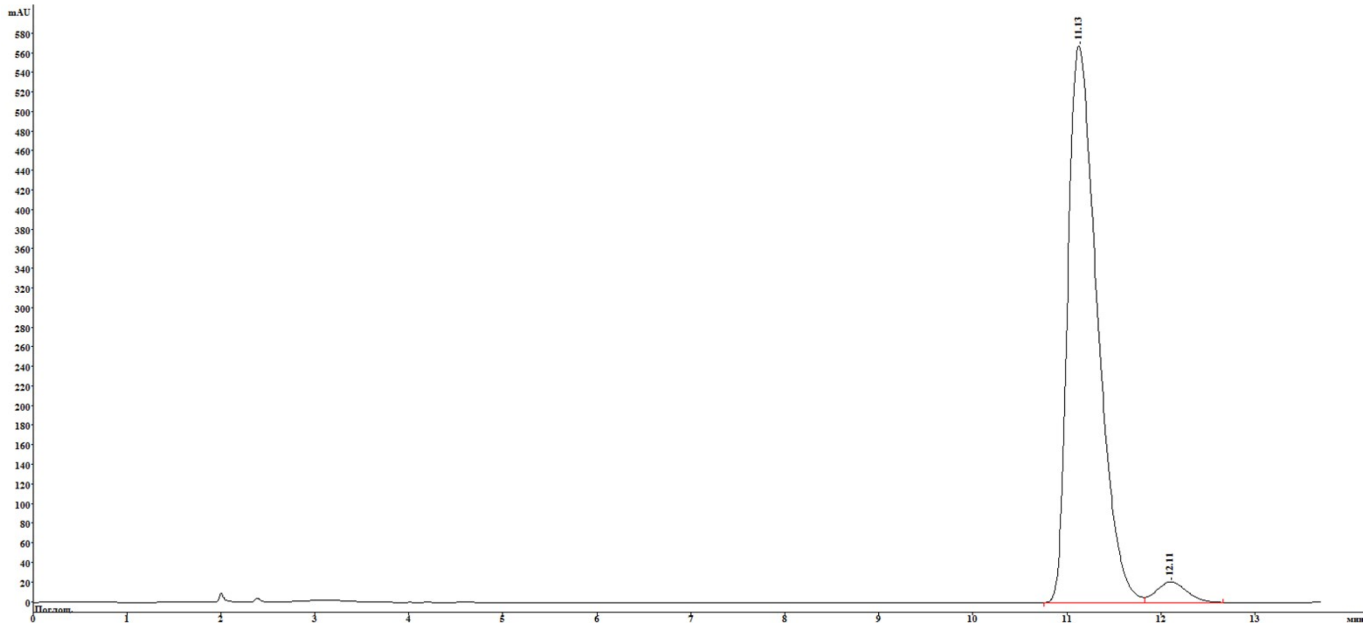


№	Retention time	Area	Area, %
1	10.07	365	2.22
2	15.77	16074	97.78

6b. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 200, flow rate = 1.5 ml/min.

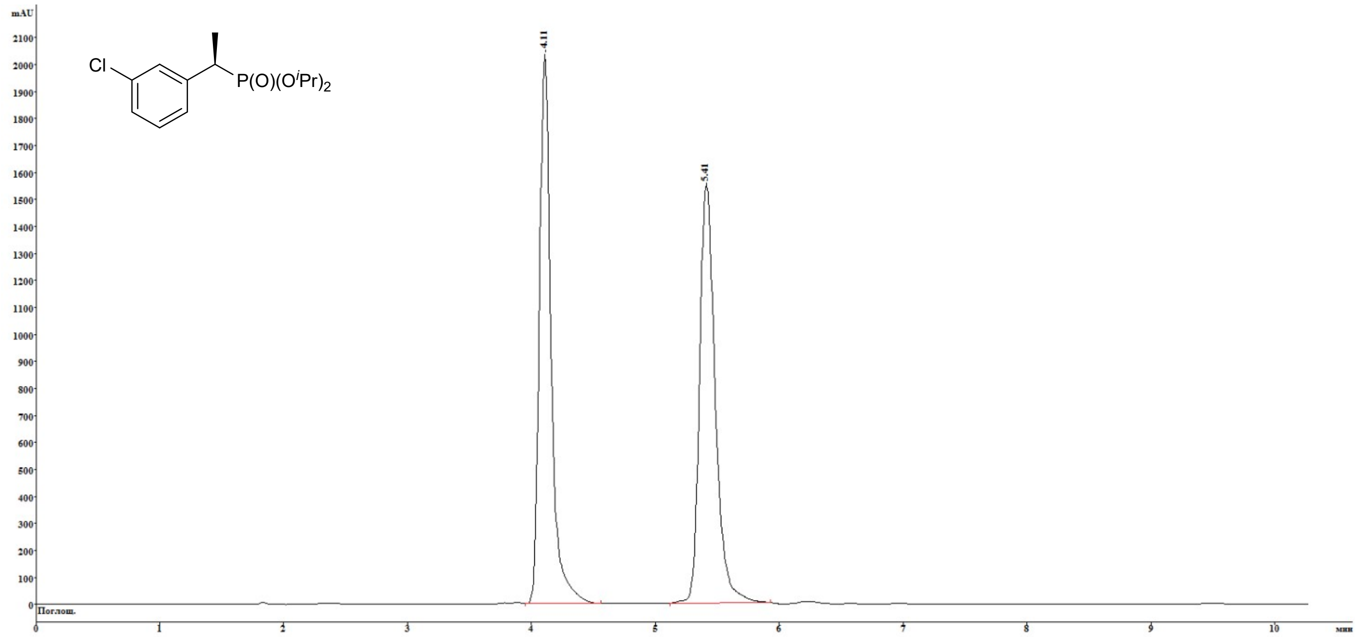


№	Retention time	Area	Area, %
1	11.12	1195	49.69
2	12.10	1210	50.31

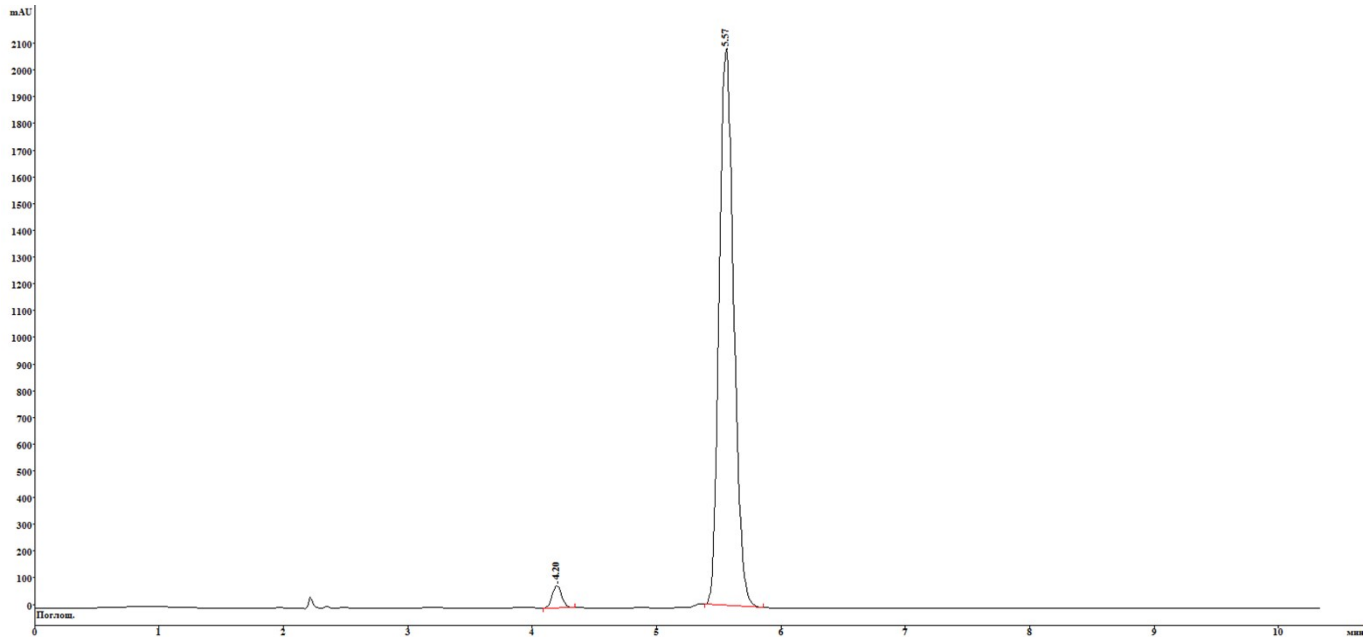


№	Retention time	Area	Area, %
1	11.13	12312	96.32
2	12.11	471	3.68

6c. HPLC conditions: Chiralpak AD-H, *i*-PrOH/hexane 5 : 95, flow rate = 1.5 ml/min.

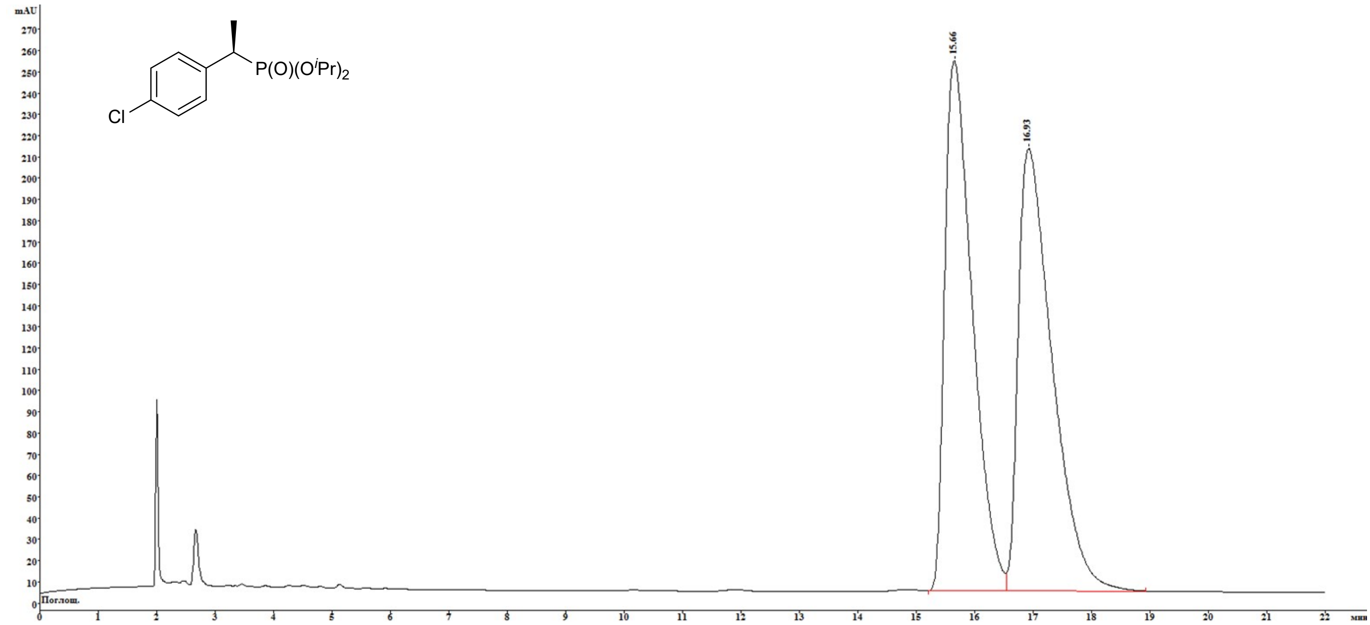


№	Retention time	Area	Area, %
1	4.11	12704	49.92
2	5.41	12742	50.07

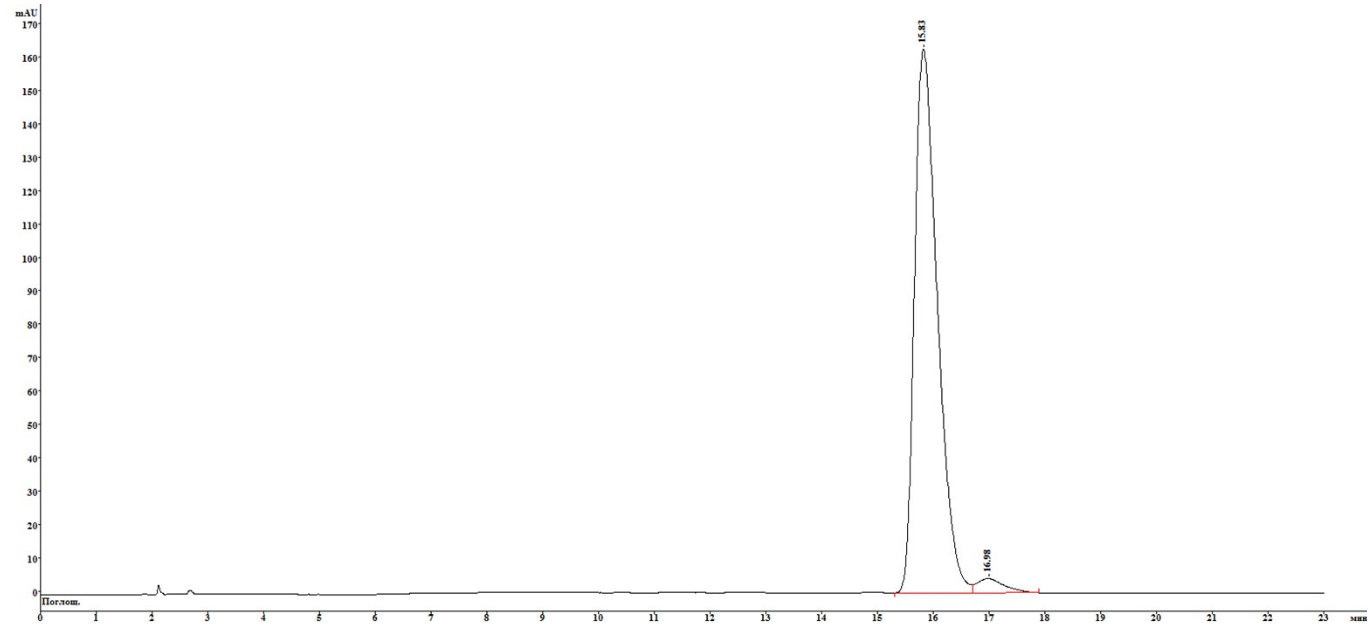


№	Retention time	Area	Area, %
1	4.20	440	2.53
2	5.57	16977	97.47

6d. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 300, flow rate = 1.5 ml/min.

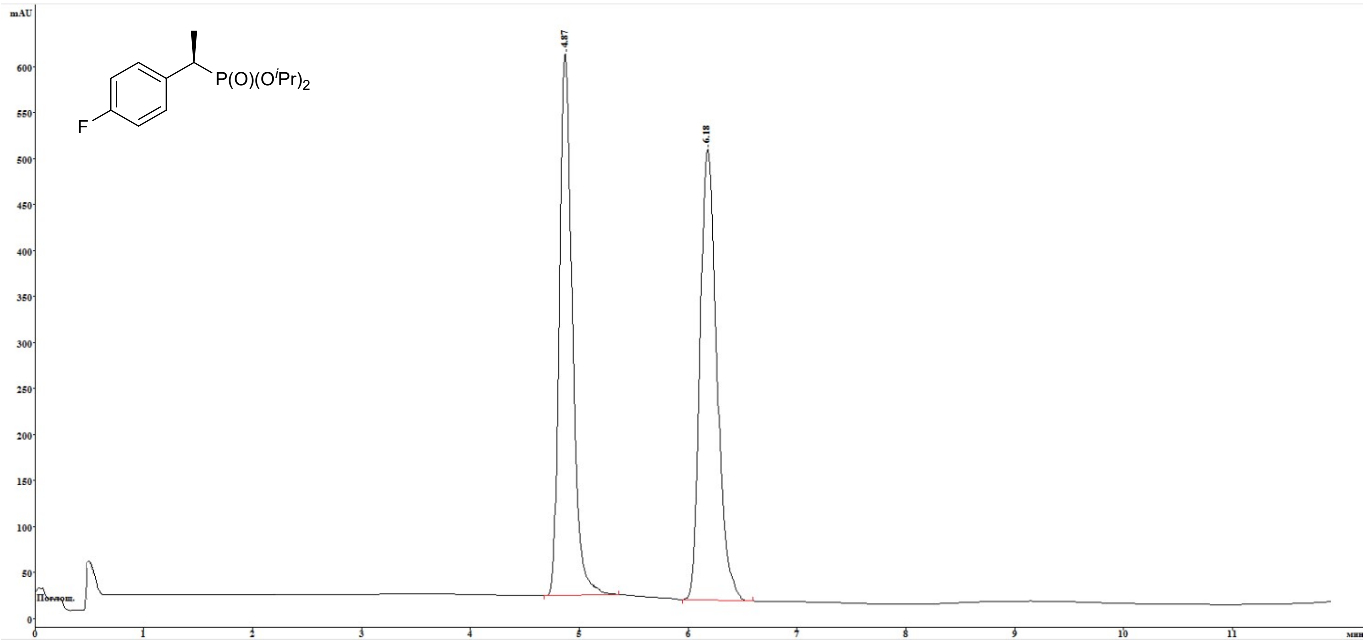


№	Retention time	Area	Area, %
1	15.66	8190	49.25
2	16.93	8438	50.75

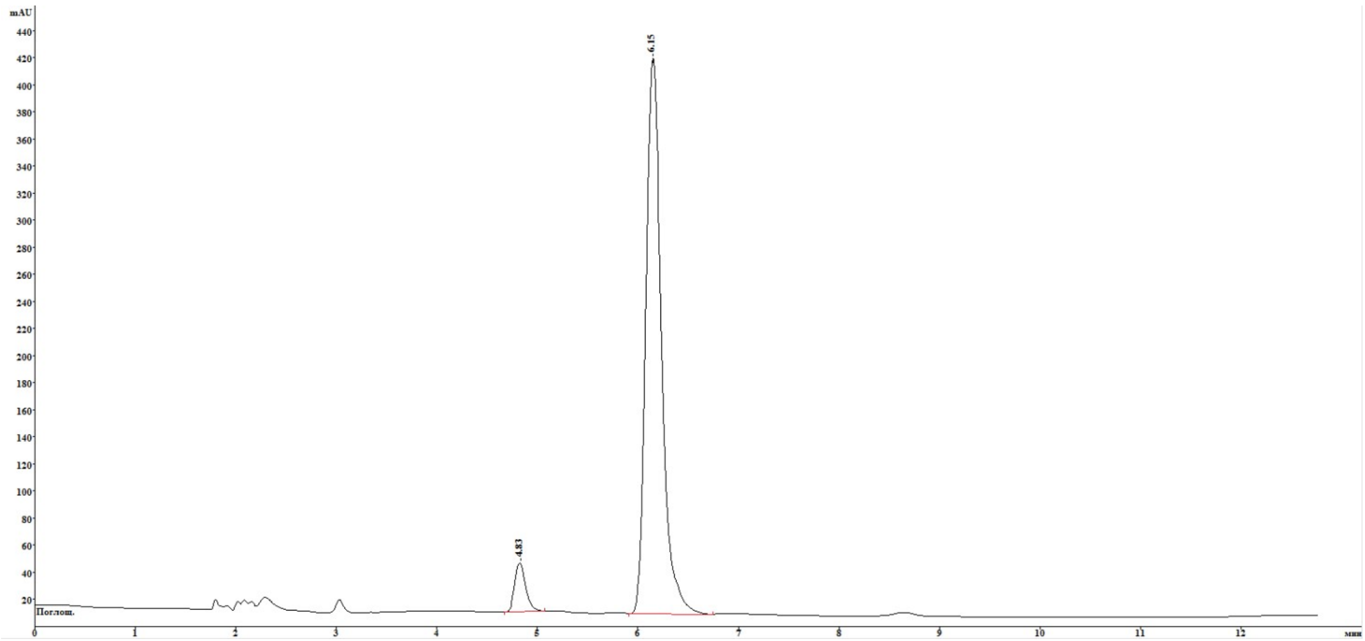


№	Retention time	Area	Area, %
1	15.83	4656	96.96
2	16.98	146	3.04

6e. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

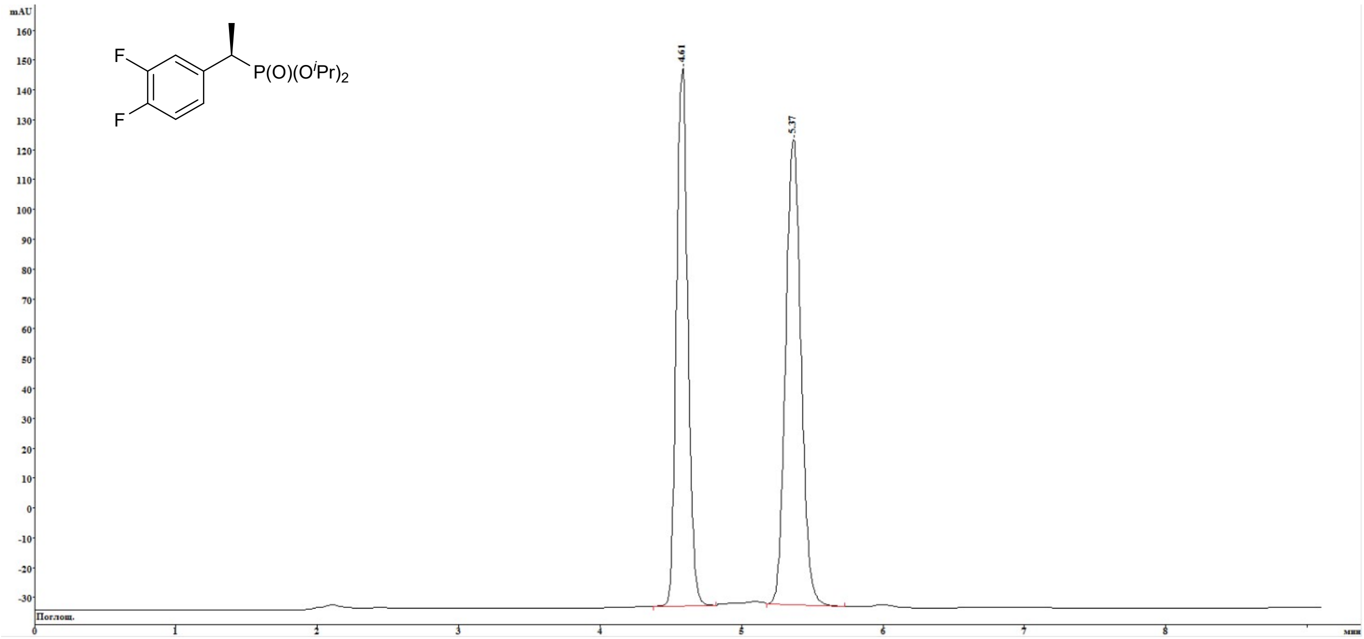


№	Retention time	Area	Area, %
1	4.87	4658	48.47
2	6.18	4953	51.53

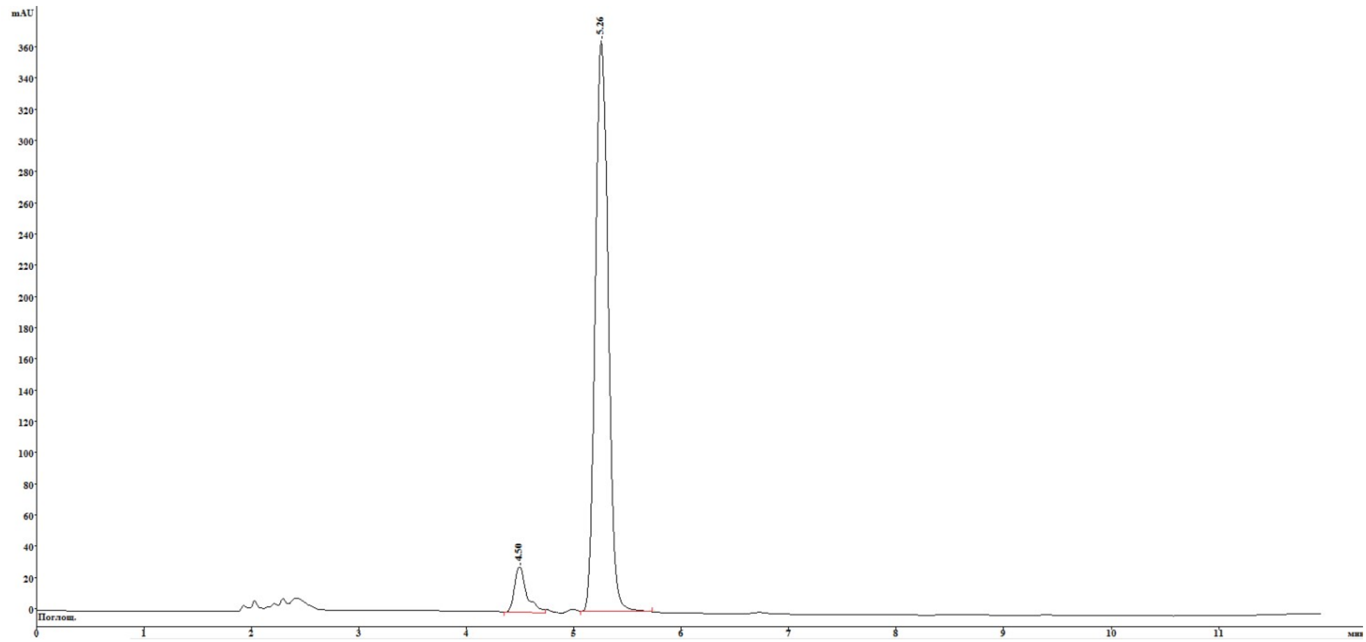


№	Retention time	Area	Area, %
1	4.83	263	5.61
2	6.15	4425	94.39

6f. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

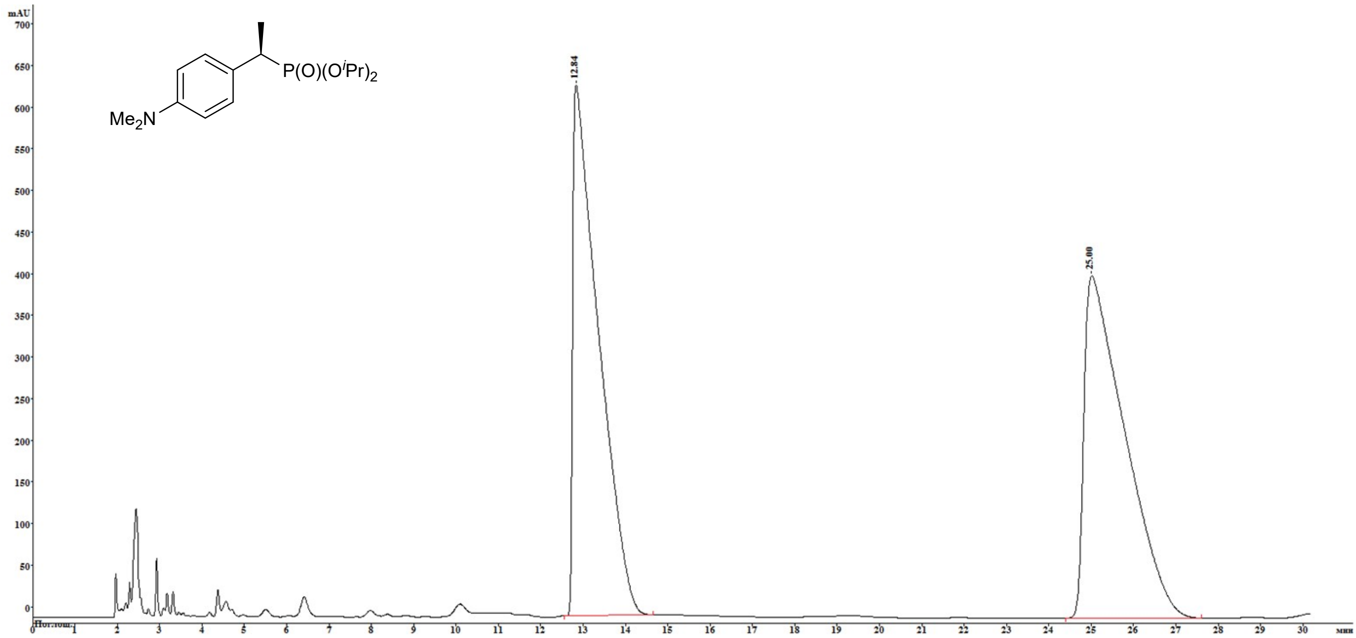


№	Retention time	Area	Area, %
1	4.61	1019	46.51
2	5.37	1172	53.49

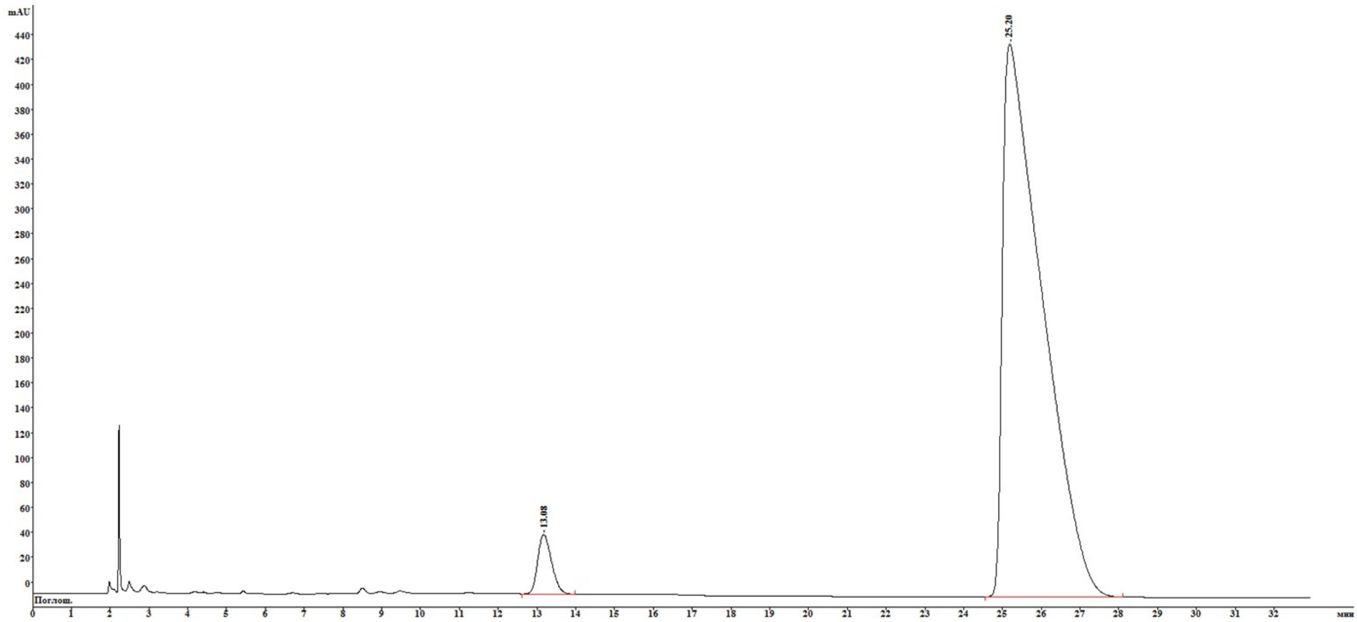


№	Retention time	Area	Area, %
1	4.50	242	5.27
2	5.26	4350	94.73

6g. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

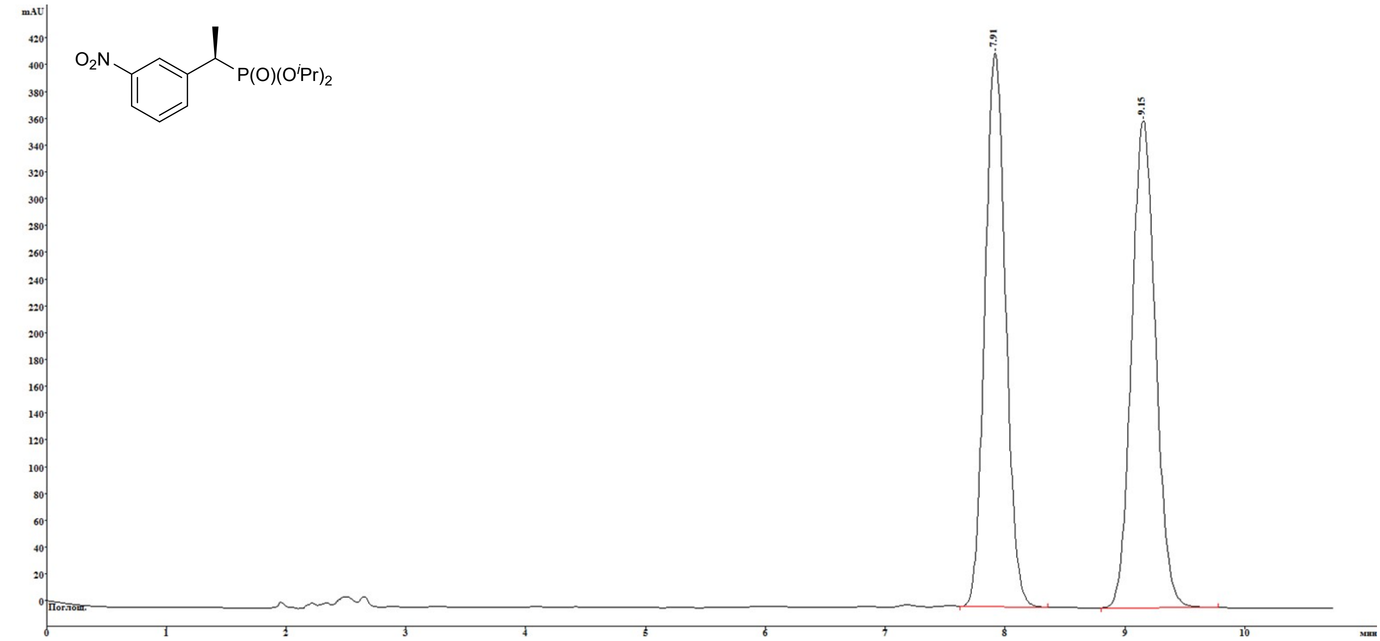


№	Retention time	Area	Area, %
1	12.84	22994	49.05
2	25.00	23888	50.95

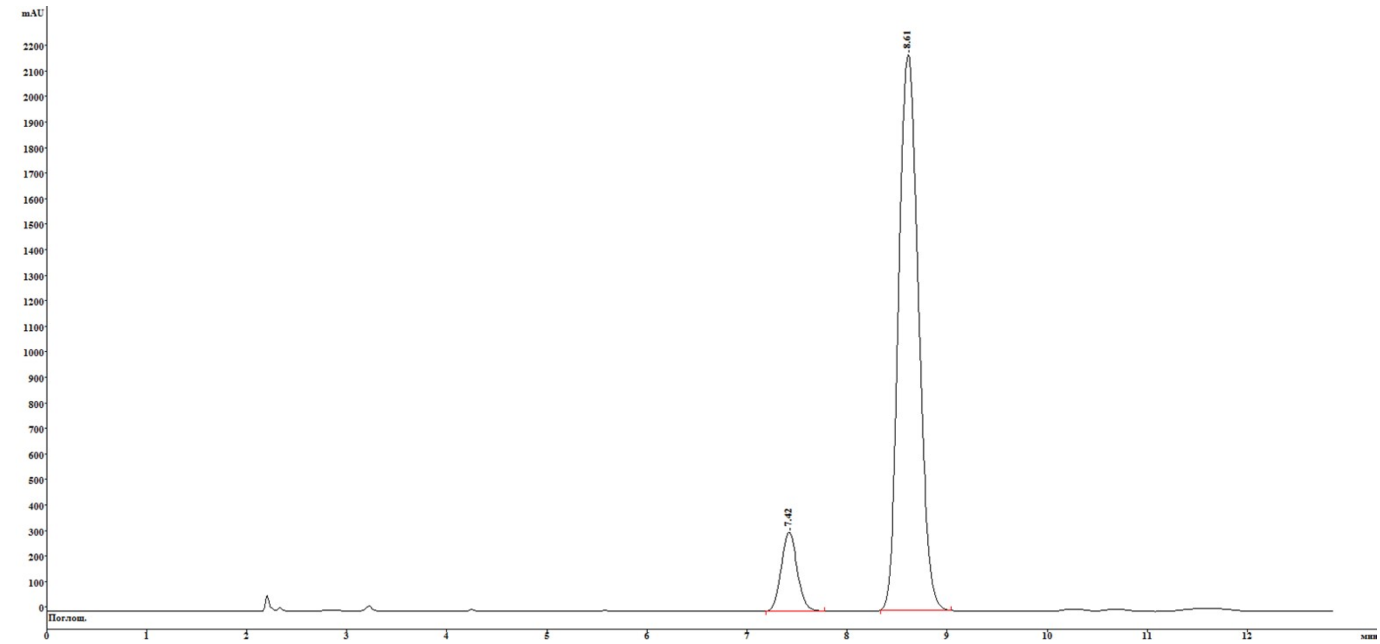


№	Retention time	Area	Area, %
1	13.08	234	3.58
2	25.20	6305	96.42

6h. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

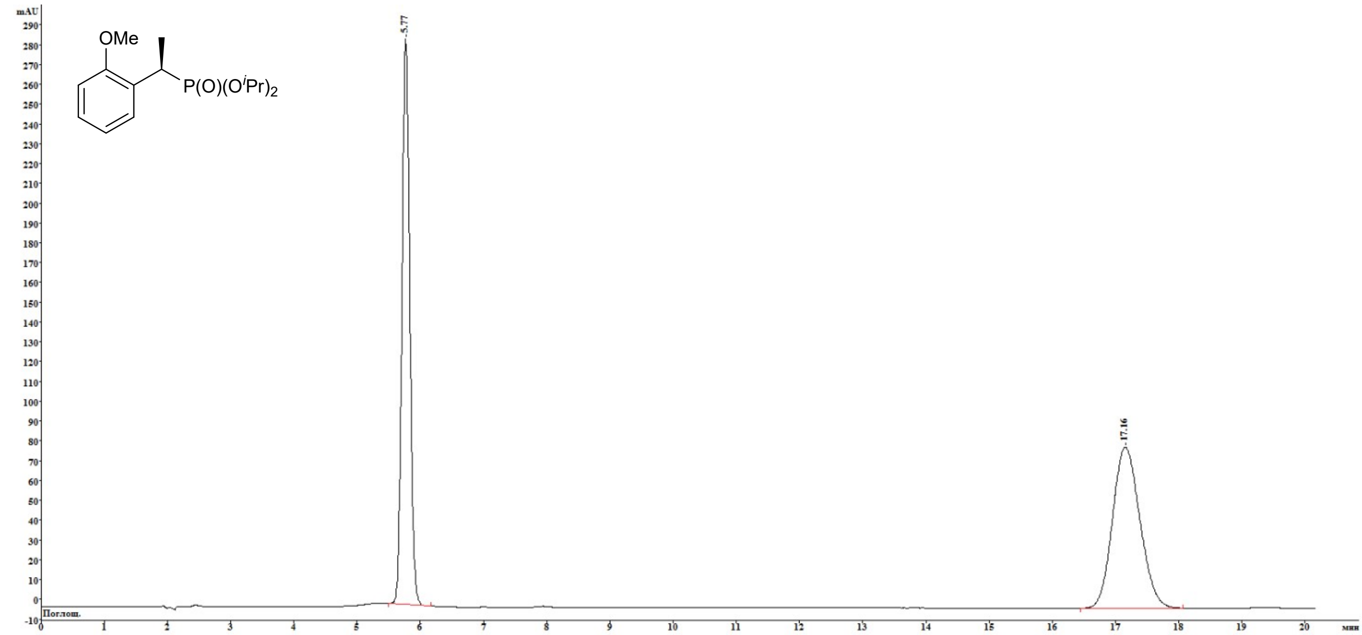


№	Retention time	Area	Area, %
1	7.91	4956	49.51
2	9.15	5054	50.49

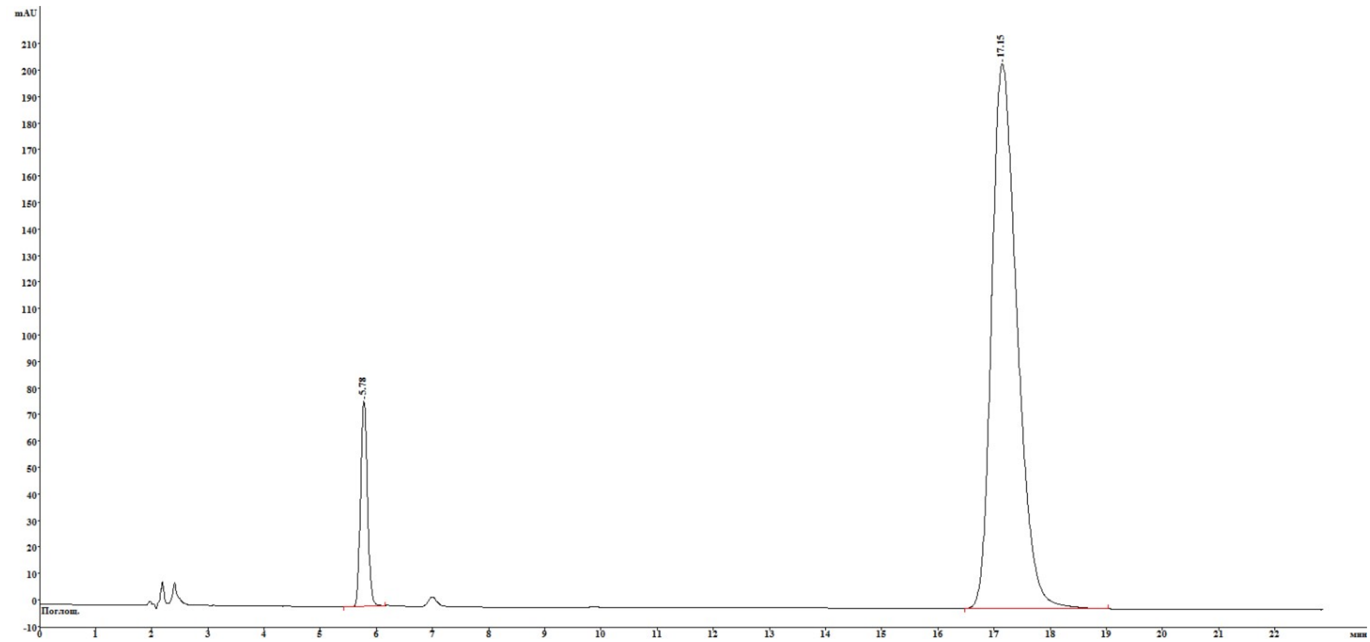


№	Retention time	Area	Area, %
1	7.42	3457	9.58
2	8.61	32610	90.42

6i. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

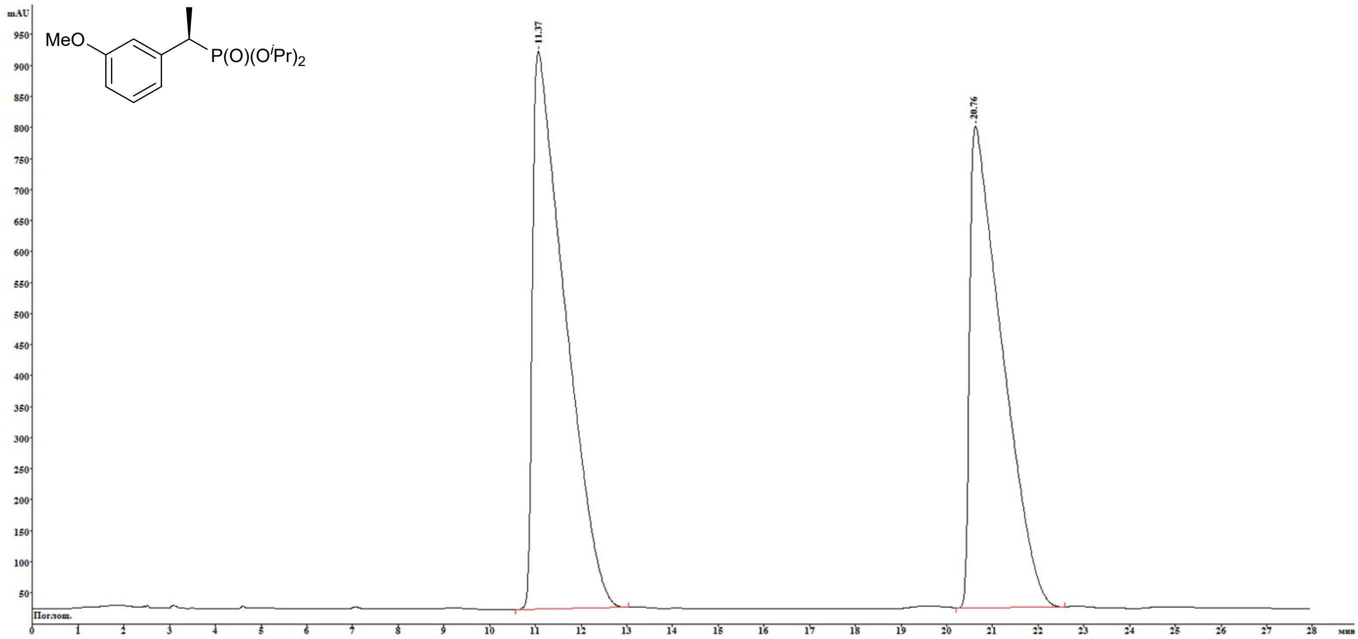


№	Retention time	Area	Area, %
1	5.77	9617	49.31
2	17.46	9888	50.69

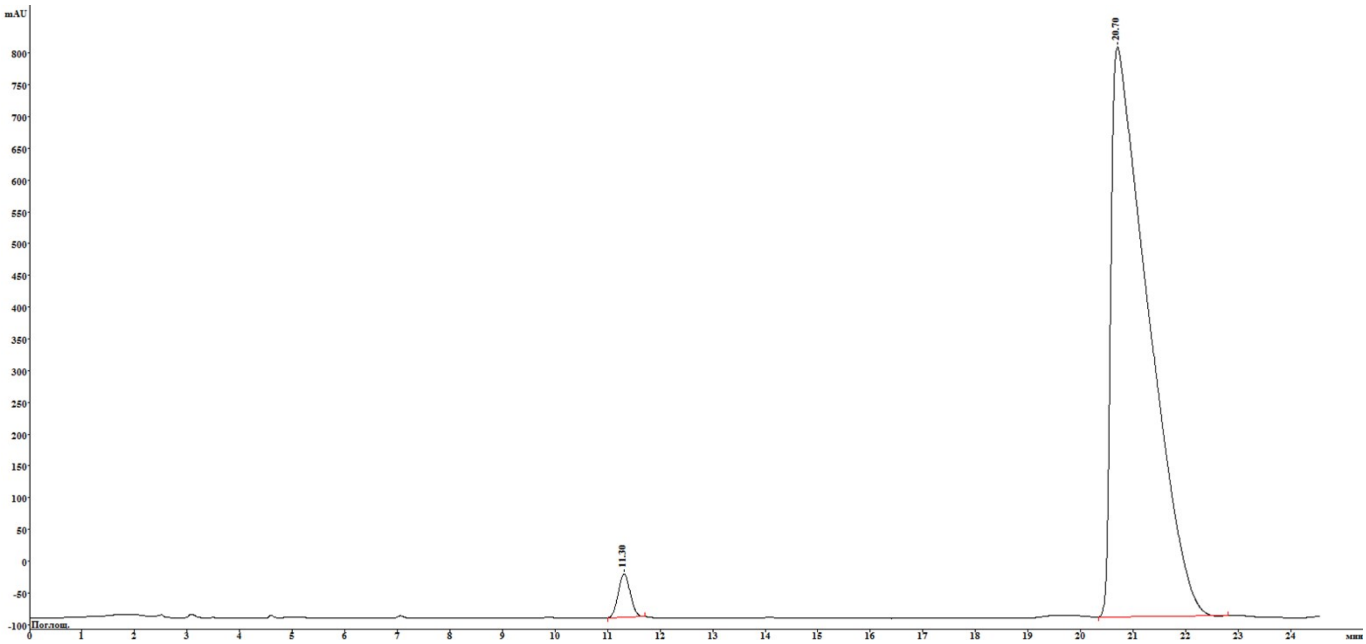


№	Retention time	Area	Area, %
1	5.78	658	9.23
2	17.15	6473	90.77

6j. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min.

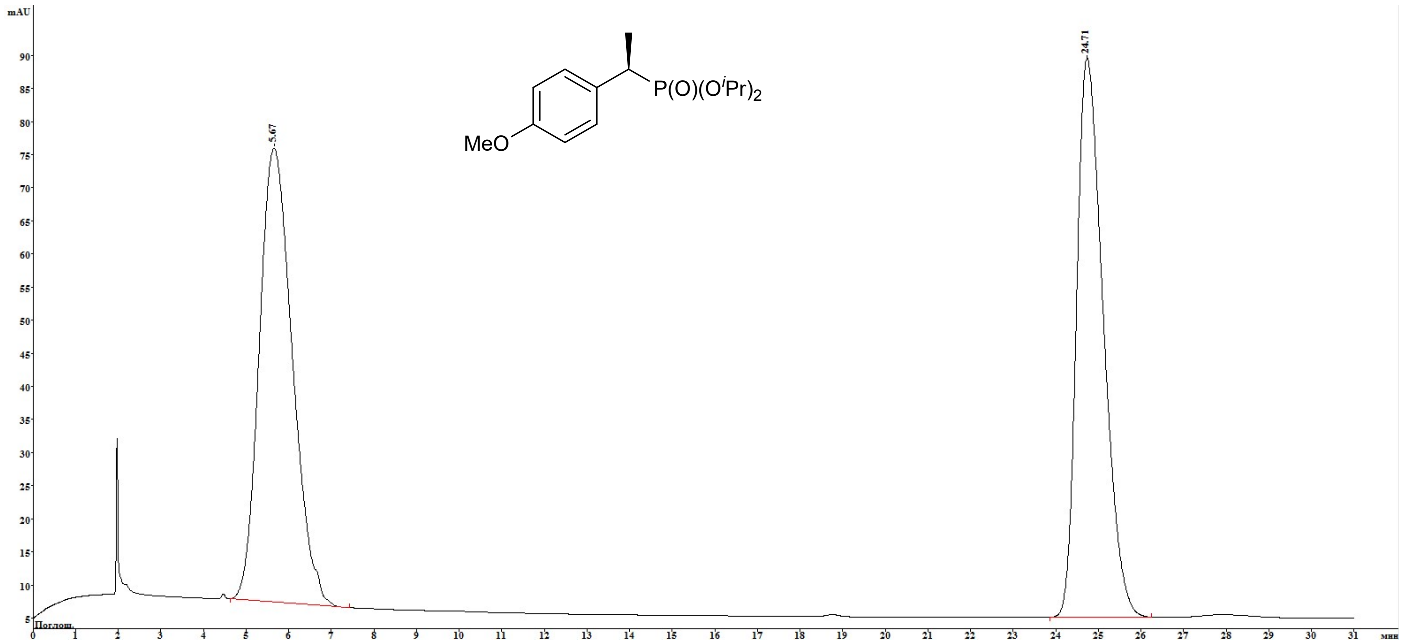


№	Retention time	Area	Area, %
1	11.37	50877	51.11
2	20.76	48659	48.89

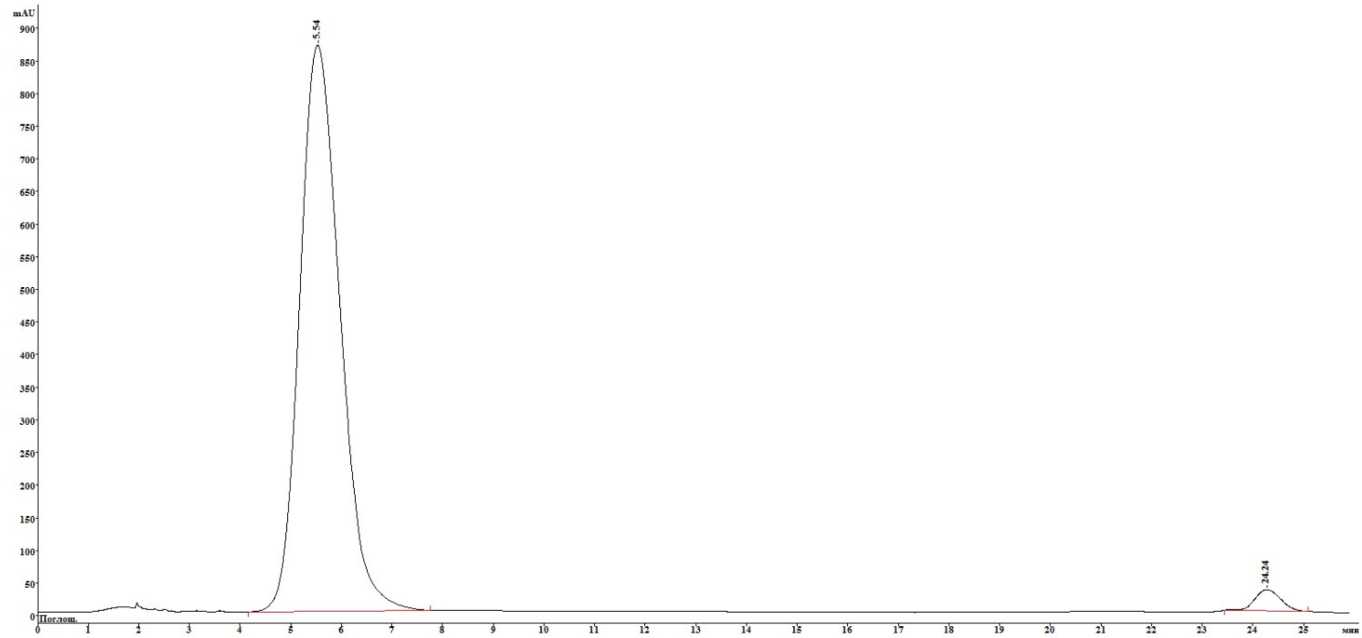


№	Retention time	Area	Area, %
1	11.30	1074	2.38
2	20.70	43979	97.62

6k. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 200, flow rate = 1.5 ml/min.

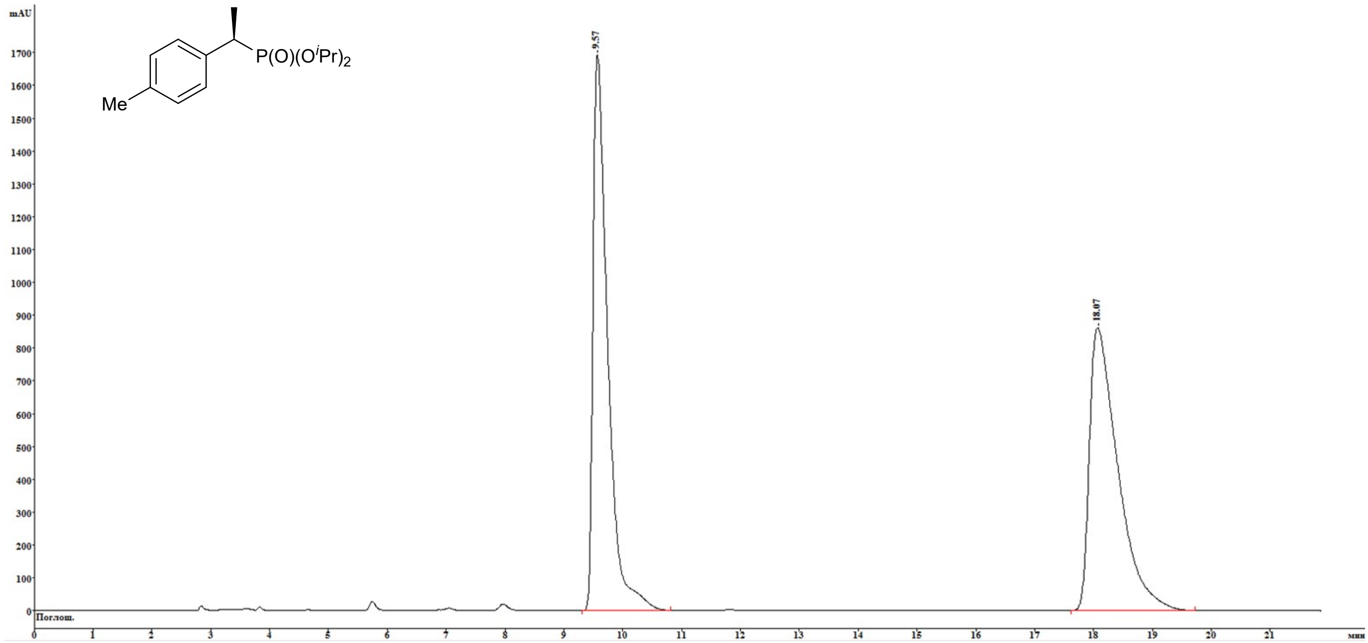


№	Retention time	Area	Area, %
1	5.67	3663	50.07
2	24.71	3653	49.93

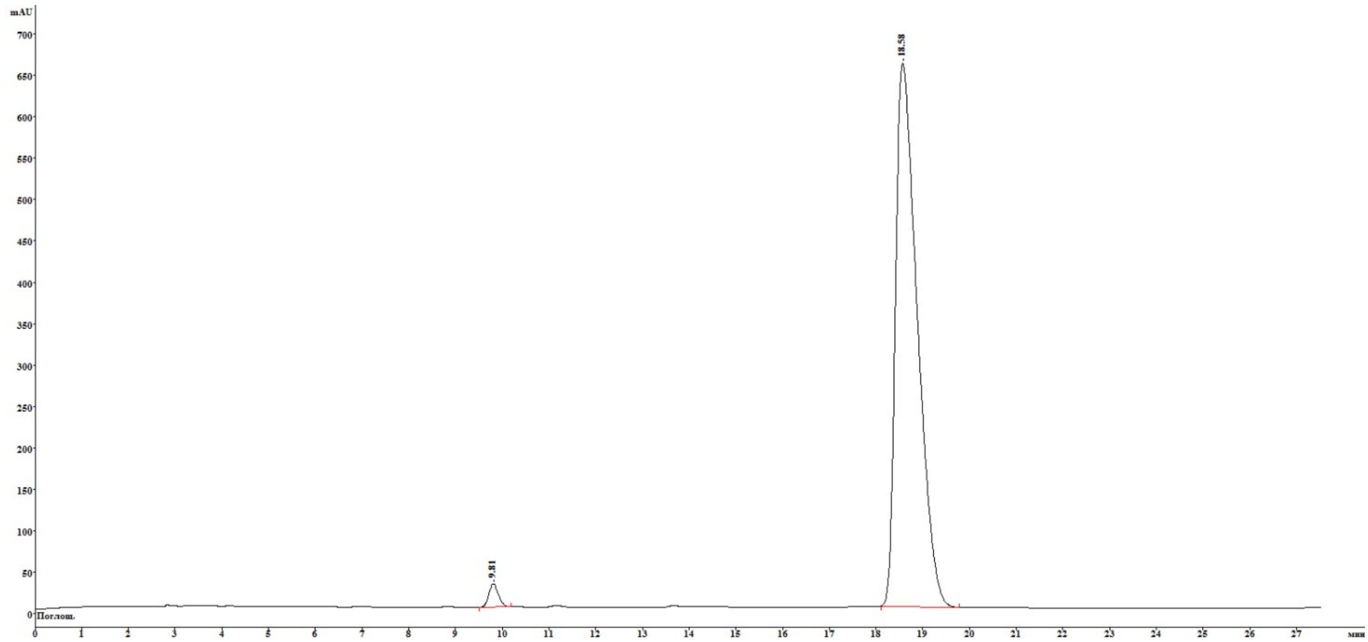


№	Retention time	Area	Area, %
1	5.54	45322	97.38
2	24.24	1219	2.62

6l. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.0 ml/min.

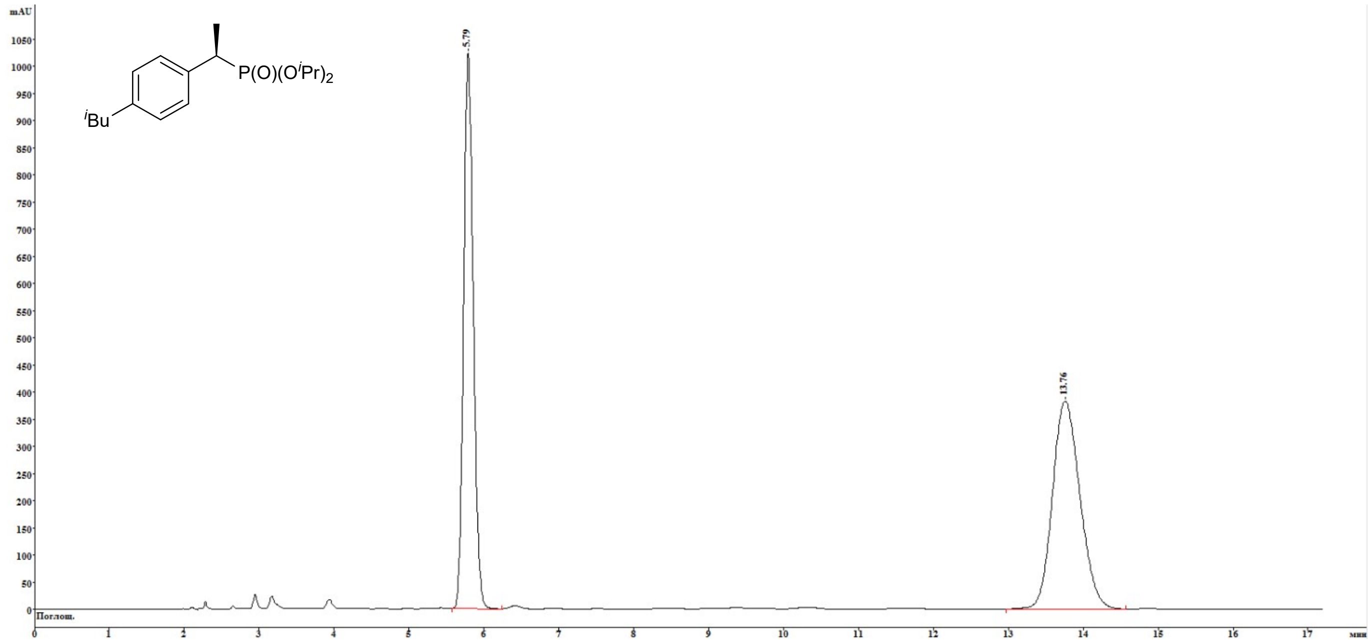


№	Retention time	Area	Area, %
1	9.57	29210	50.02
2	18.07	28968	49.98

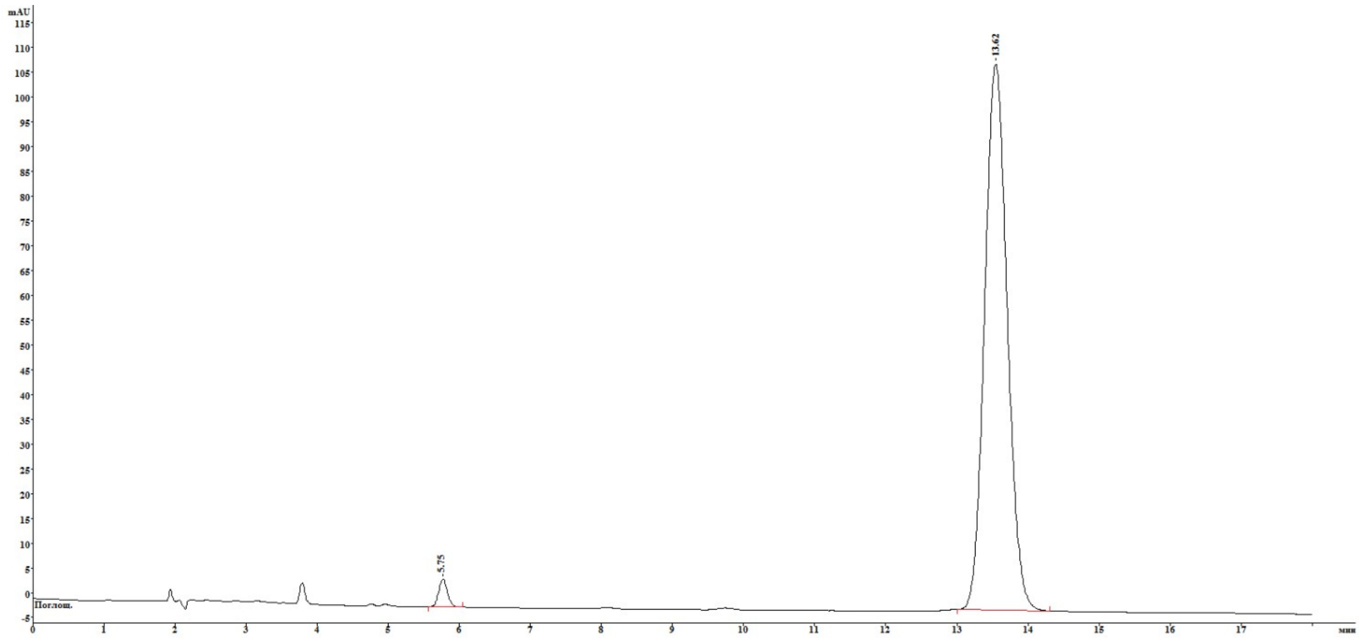


№	Retention time	Area	Area, %
1	9.81	396	1.84
2	18.58	7171	98.16

6m. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

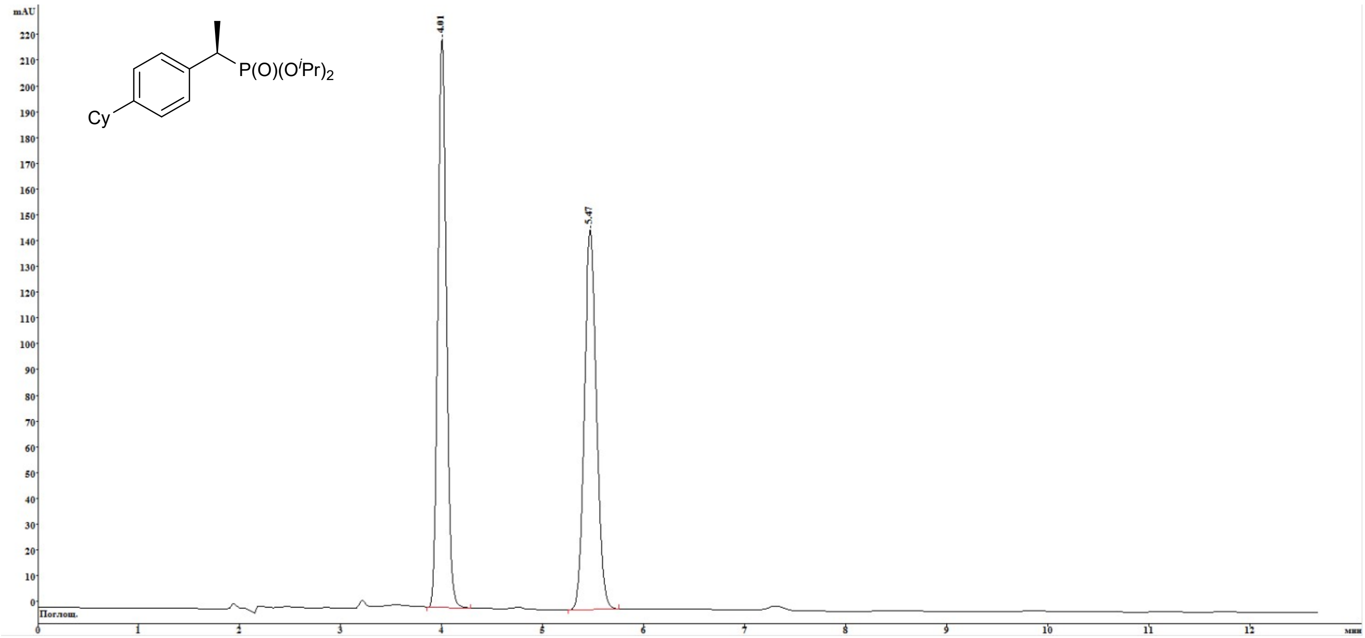


№	Retention time	Area	Area, %
1	5.79	9207	48.56
2	13.76	9754	51.44

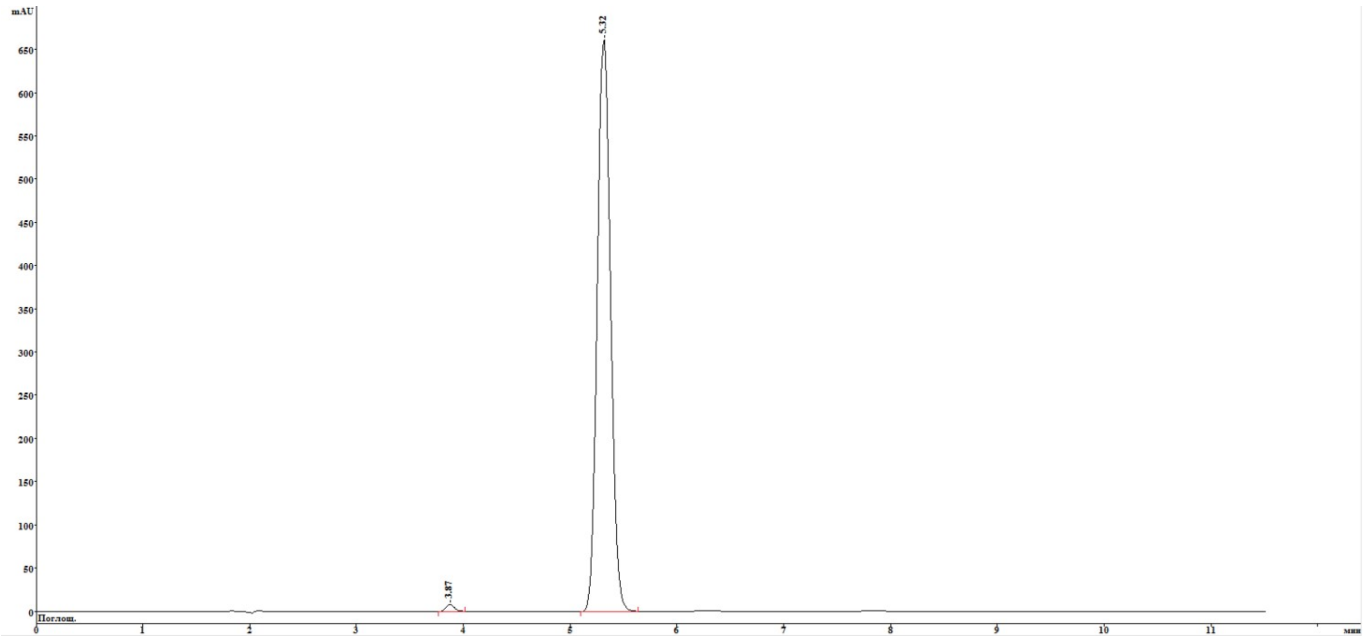


№	Retention time	Area	Area, %
1	5.75	43	1.65
2	13.62	2564	98.35

6n. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

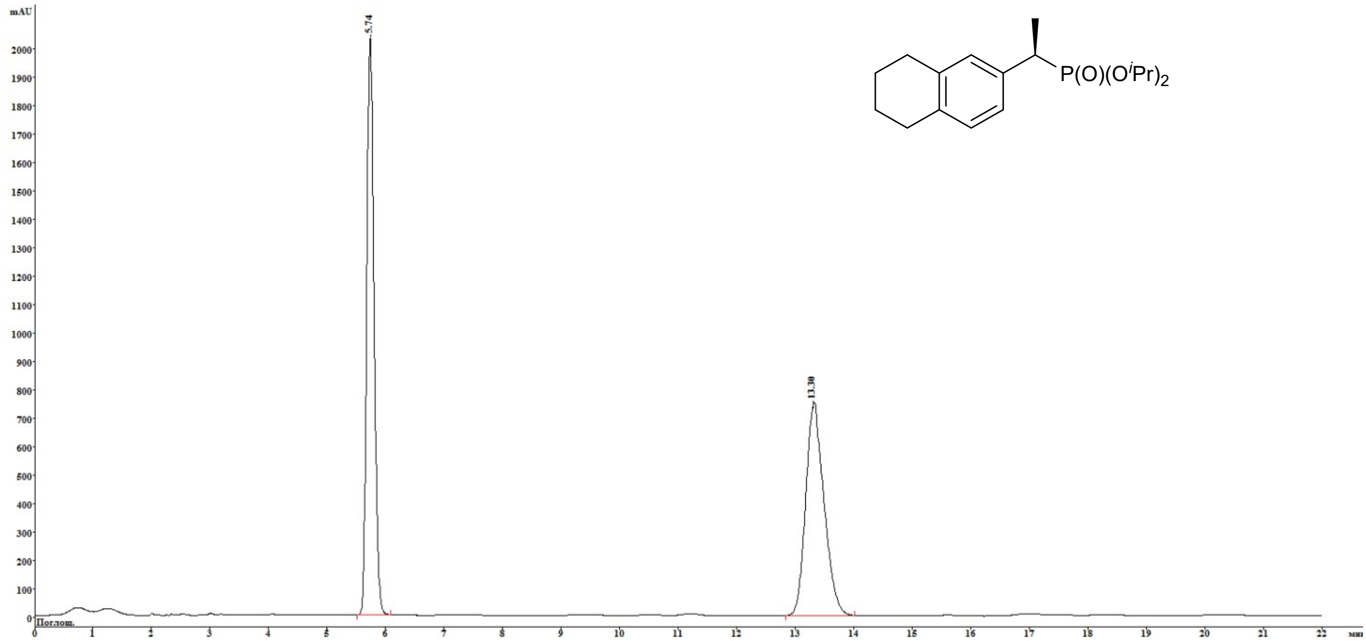


№	Retention time	Area	Area, %
1	4.01	4633	51.22
2	5.47	4412	48.78

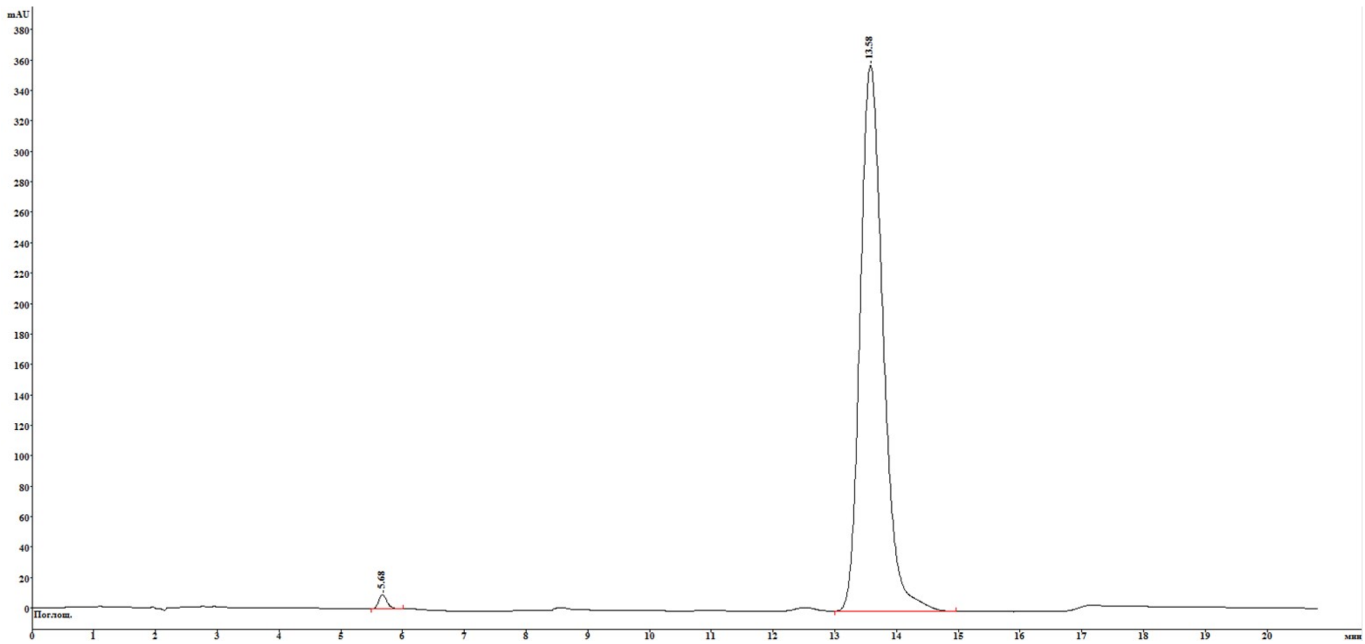


№	Retention time	Area	Area, %
1	3.87	45	0.58
2	5.32	7713	99.42

6o. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

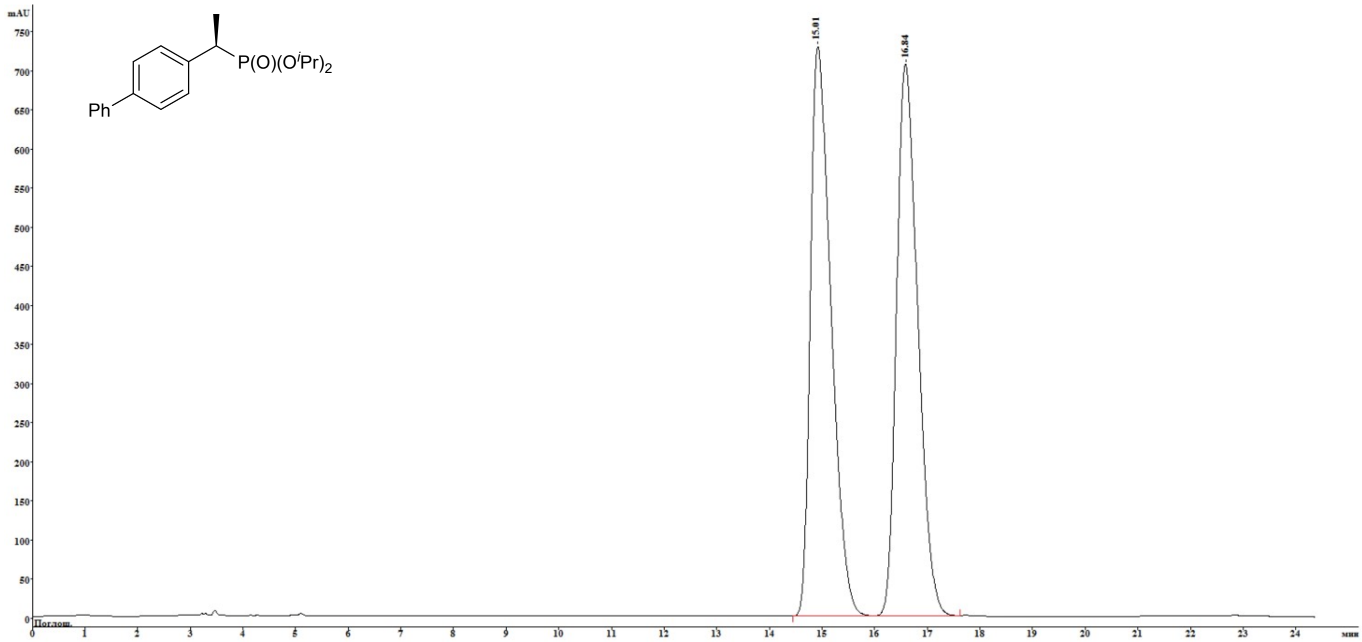


№	Retention time	Area	Area, %
1	5.74	14883	48.63
2	13.30	15721	51.37

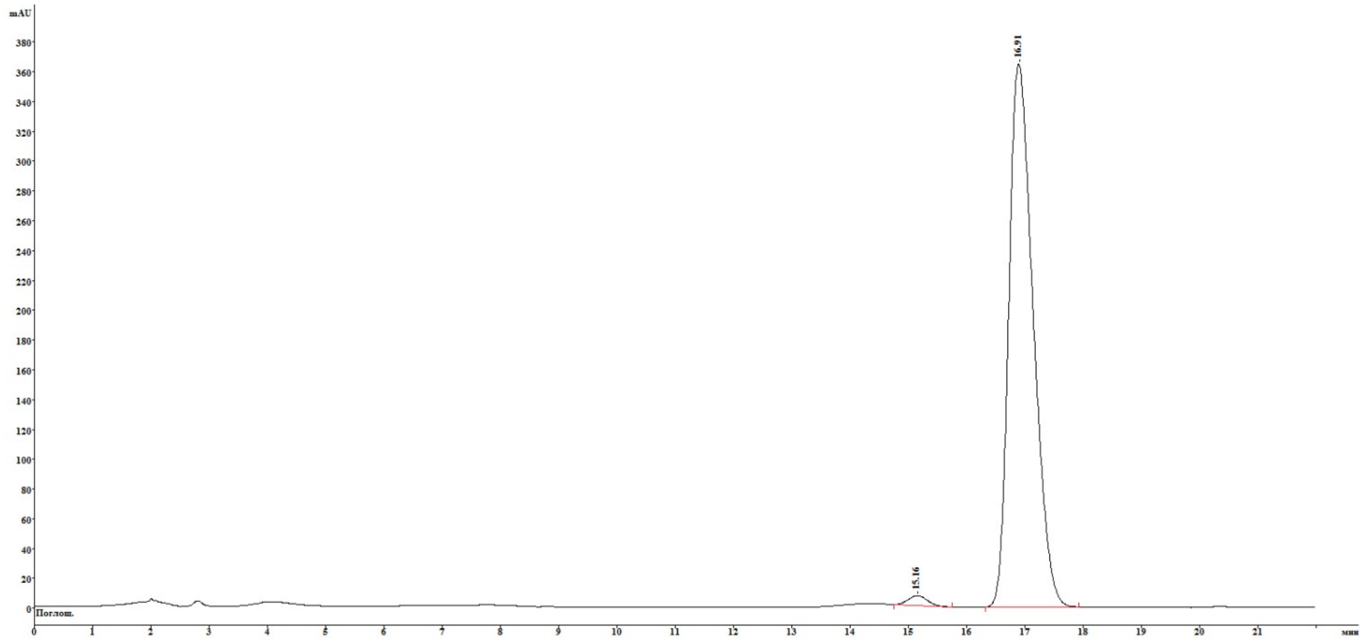


№	Retention time	Area	Area, %
1	5.68	90	0.97
2	13.58	9226	99.03

6p. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min.

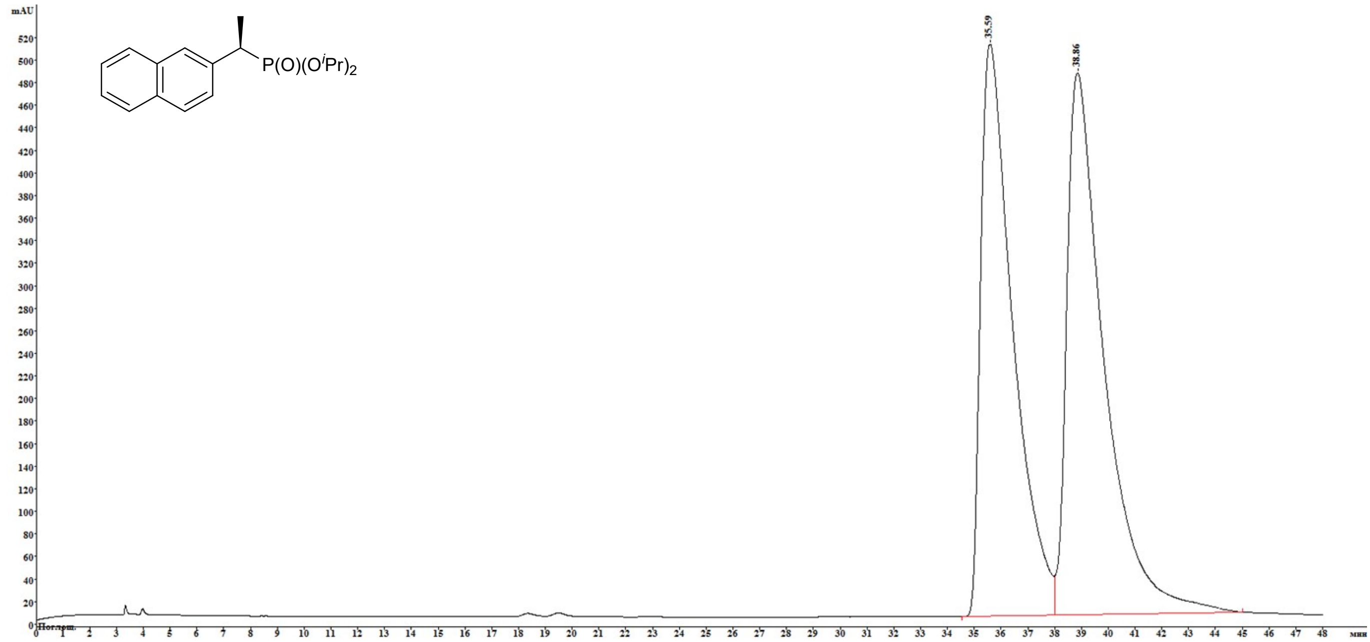


№	Retention time	Area	Area, %
1	15.01	16112	51.06
2	16.84	15443	48.94

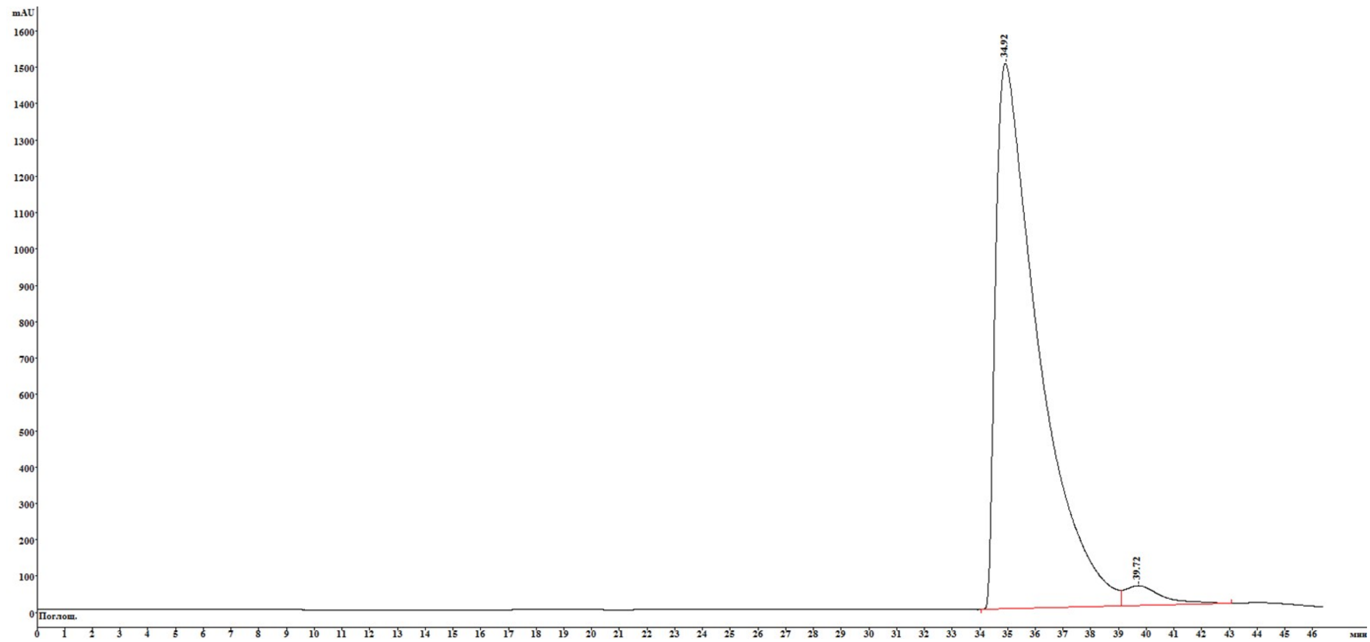


№	Retention time	Area	Area, %
1	15.16	36	2.22
2	16.91	1586	97.78

6q. HPLC conditions: Chiralcel OD-H, *i*-PrOH/*n*-hexane 1 : 200, flow rate = 1.0 ml/min.

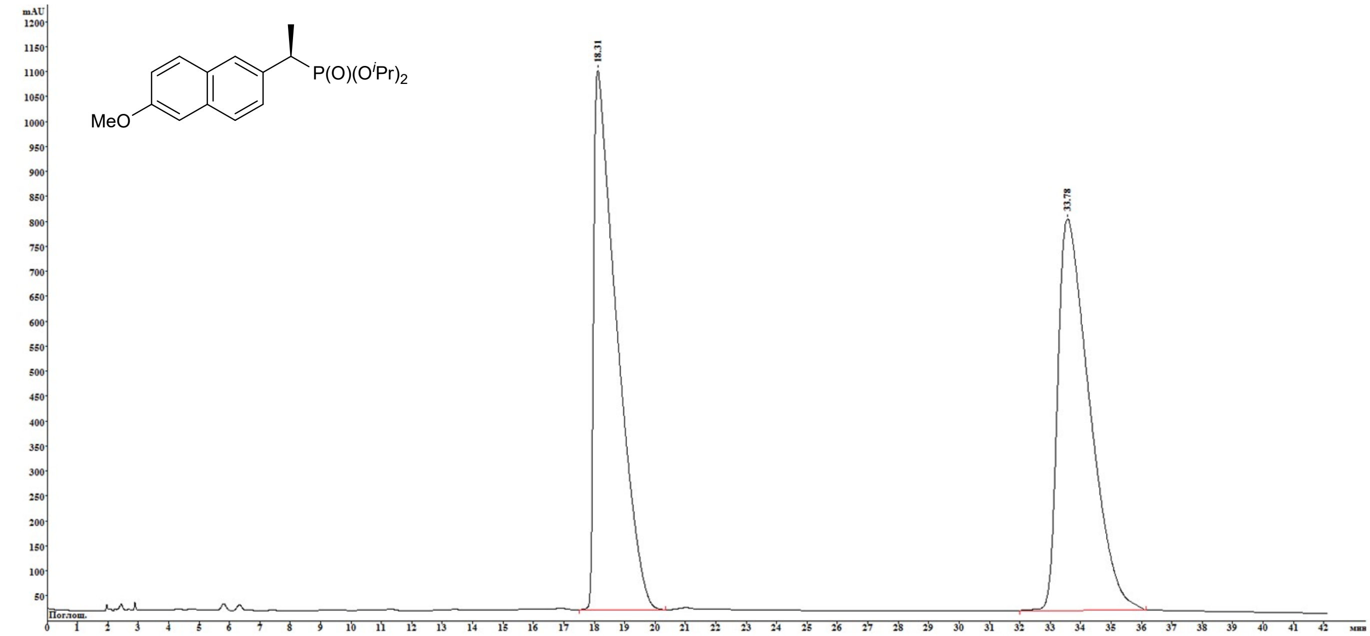


№	Retention time	Area	Area, %
1	35.59	43241	48.55
2	38.86	45824	51.45

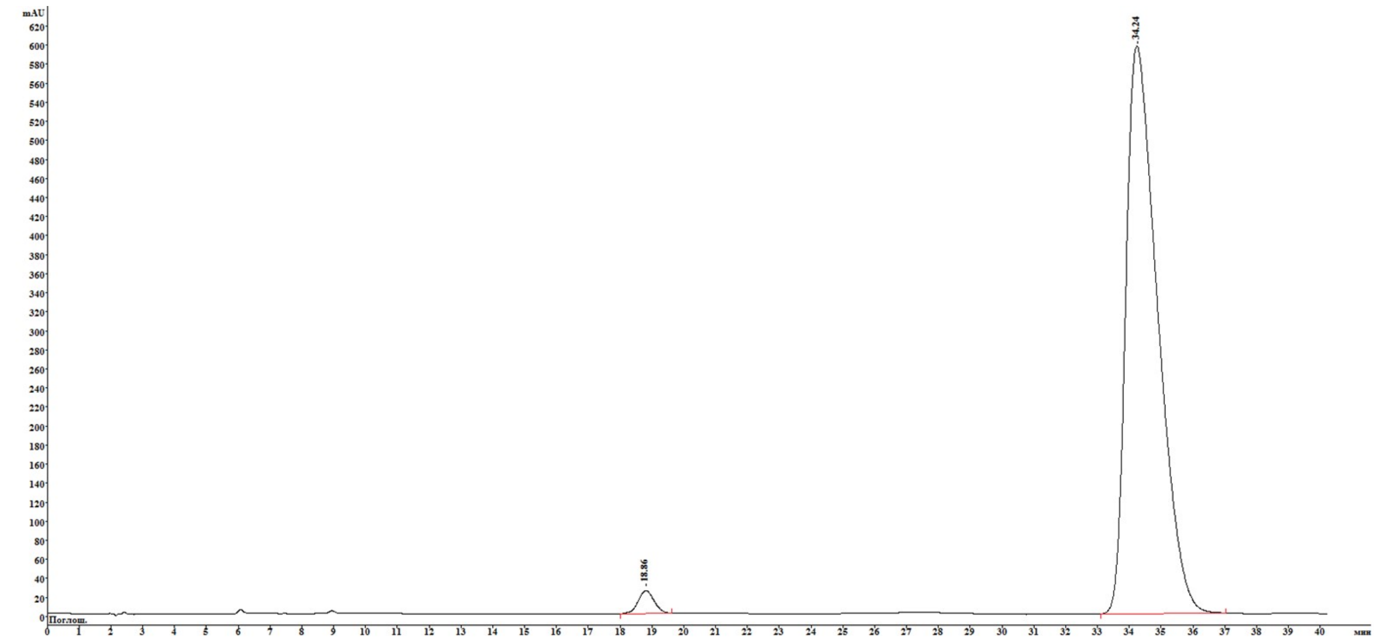


№	Retention time	Area	Area, %
1	34.92	161032	98.47
2	39.72	2502	1.53

6r. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 2 : 98, flow rate = 1.5 ml/min.

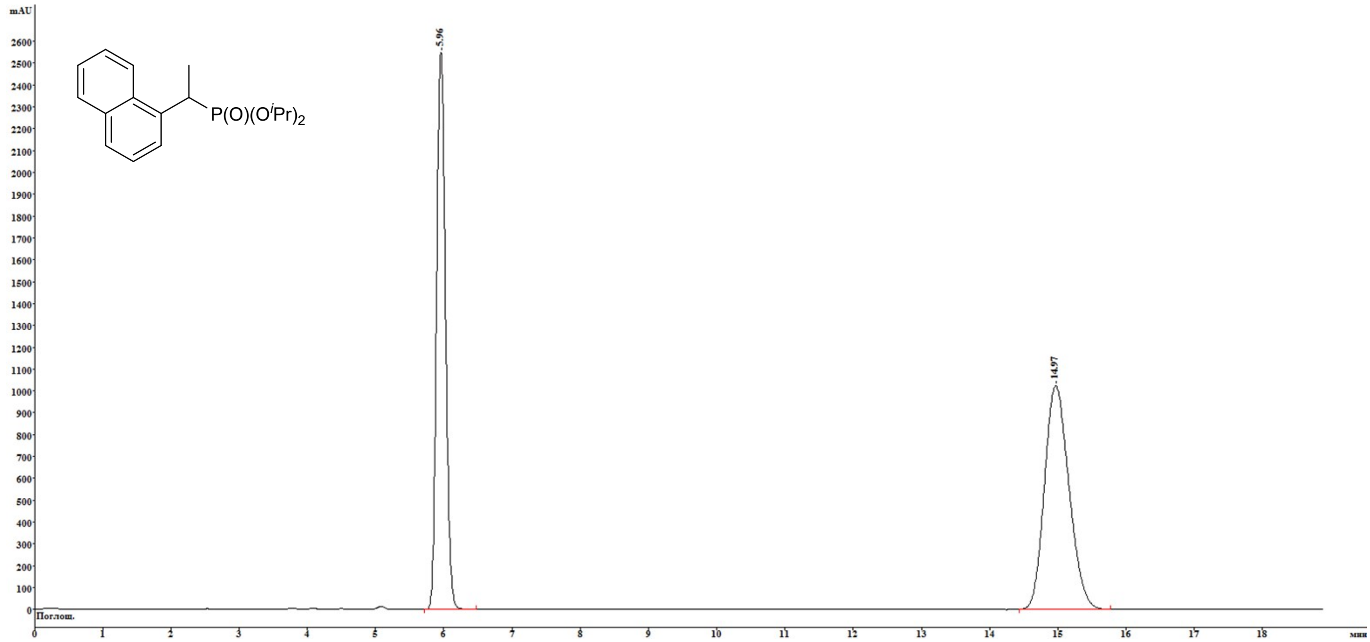


№	Retention time	Area	Area, %
1	18.31	56005	49.33
2	33.78	57531	50.67

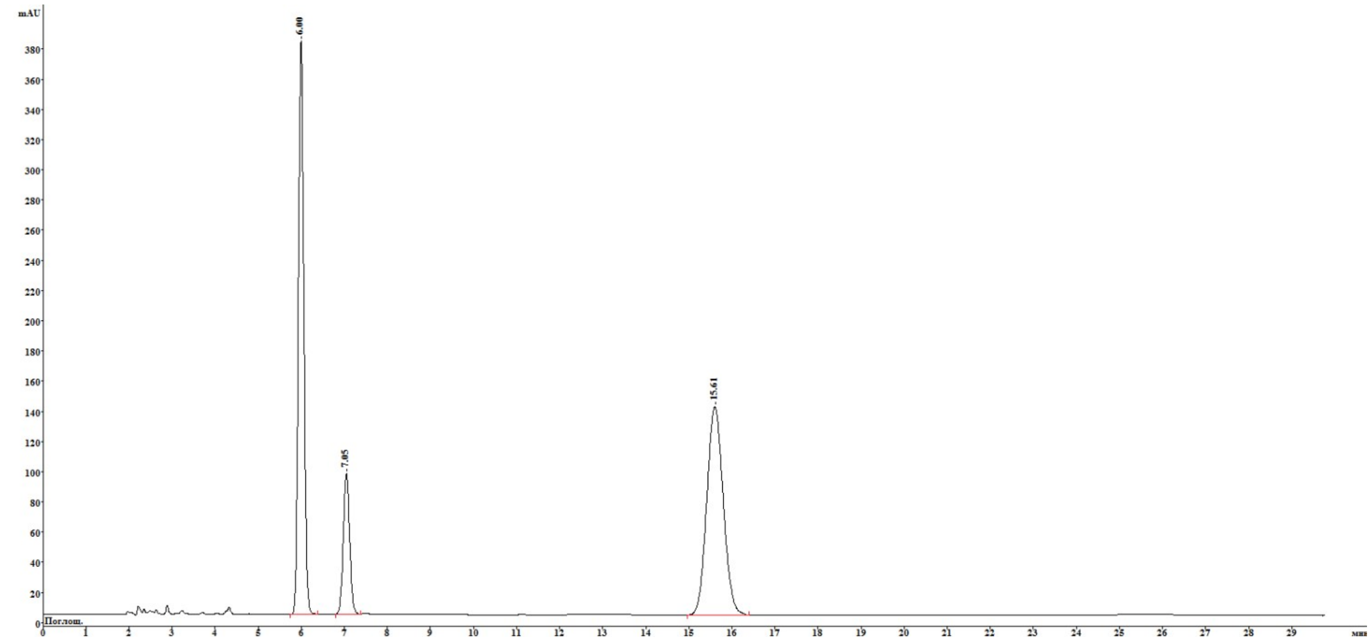


№	Retention time	Area	Area, %
1	18.86	770	1.83
2	34.24	41174	98.17

6s. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

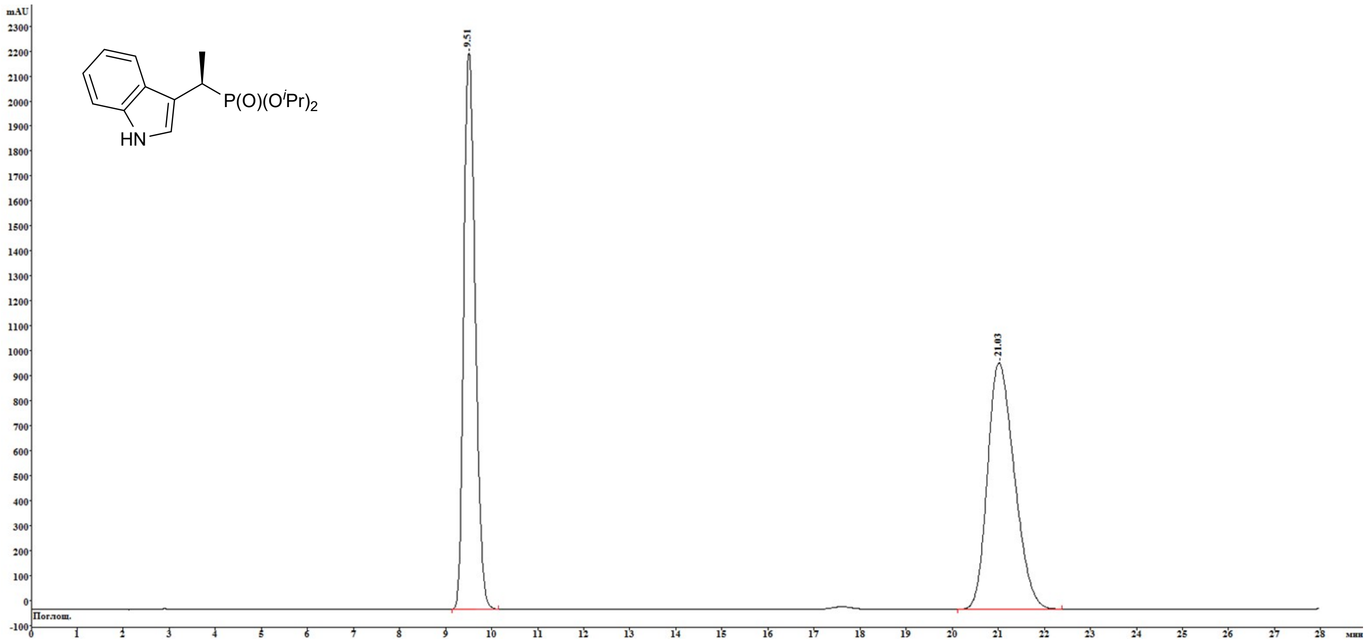


№	Retention time	Area	Area, %
1	5.96	23381	47.75
2	14.97	25590	52.25

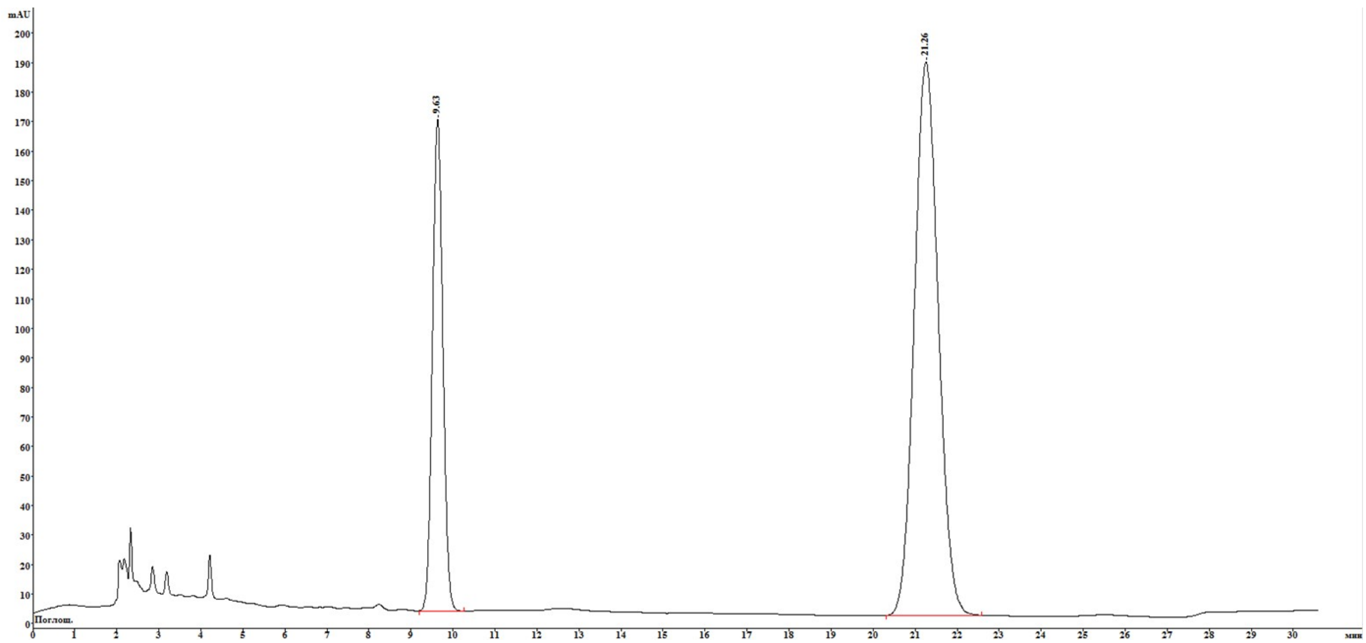


№	Retention time	Area	Area, %
1	6.00	1012	47.36
2	15.61	1125	52.64

6t. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

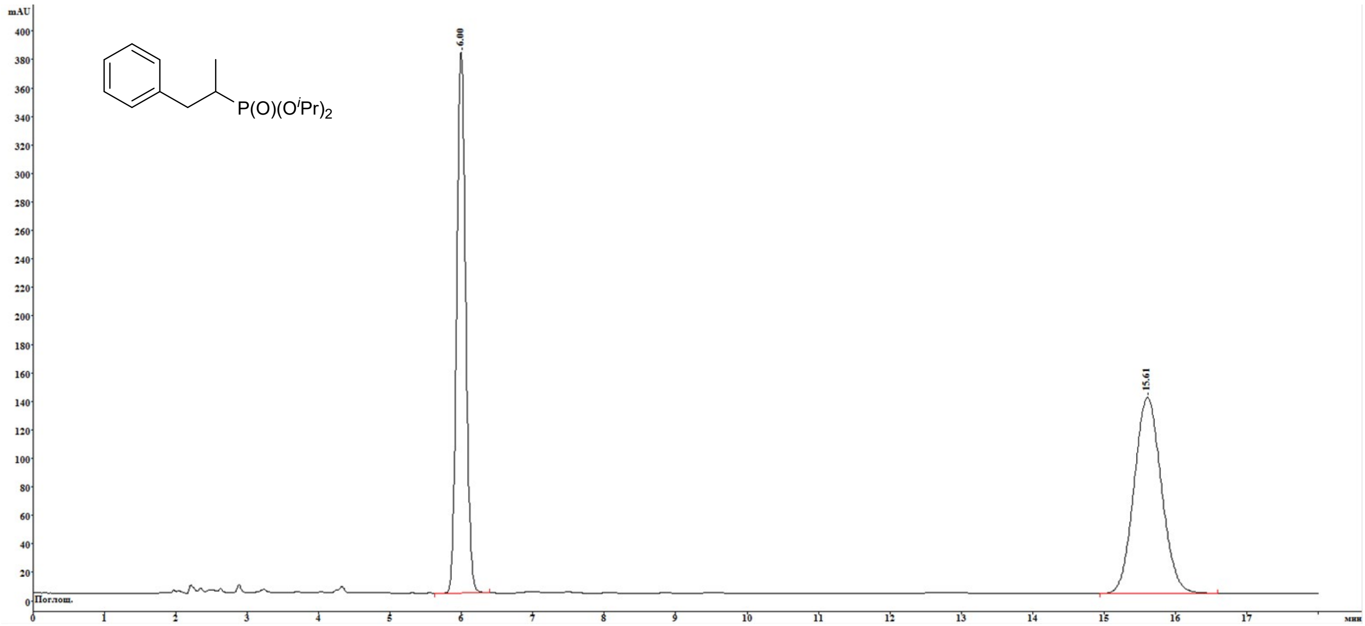


№	Retention time	Area	Area, %
1	9.51	38726	49.02
2	21.03	40280	50.98

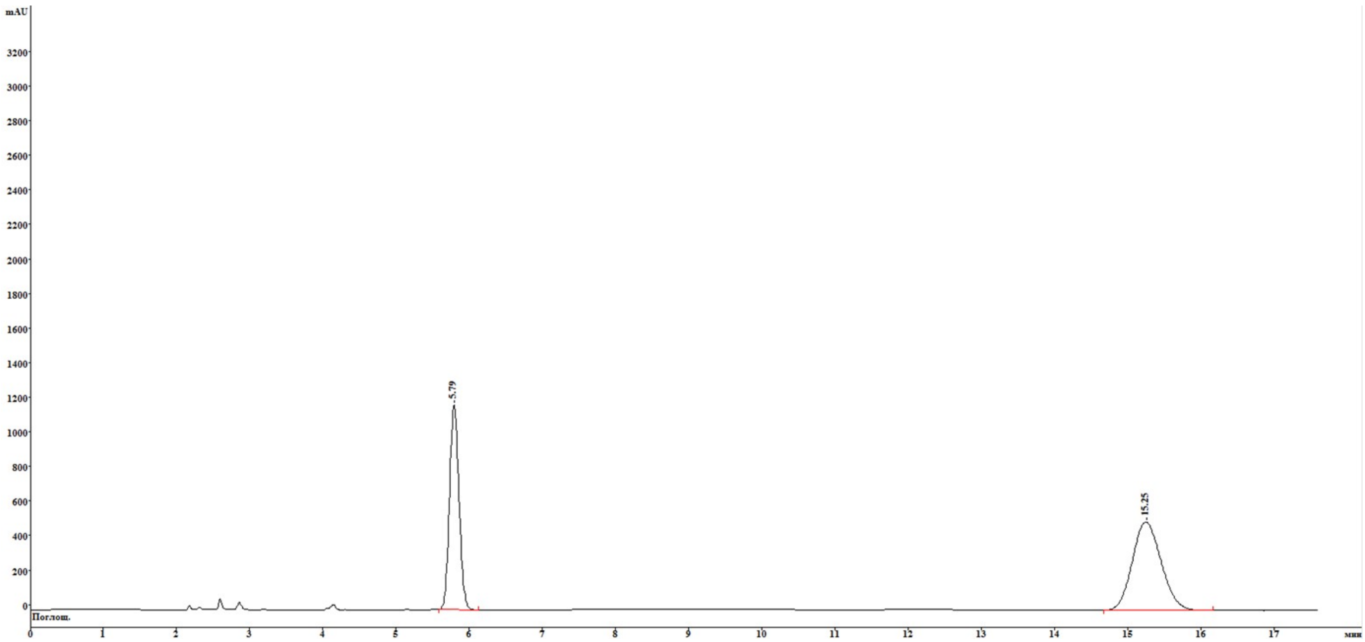


№	Retention time	Area	Area, %
1	9.63	2701	26.66
2	21.26	7429	73.34

6u. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.

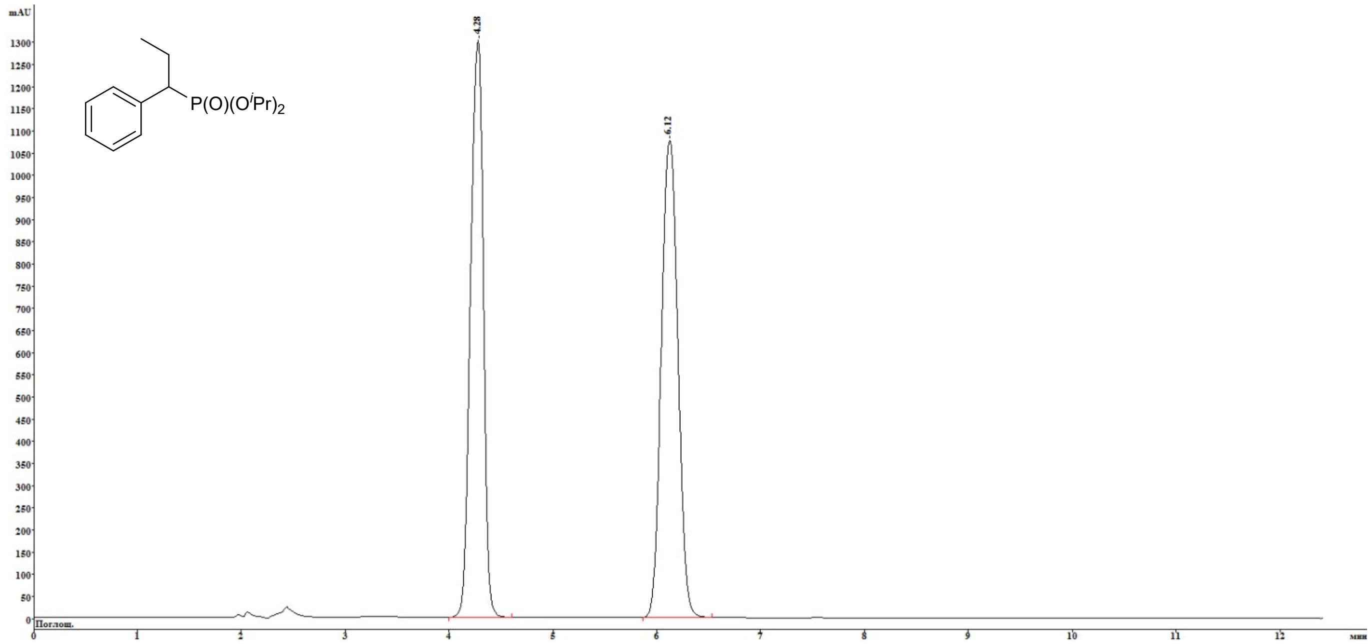


№	Retention time	Area	Area, %
1	6.00	3423	48.55
2	15.61	3628	51.45

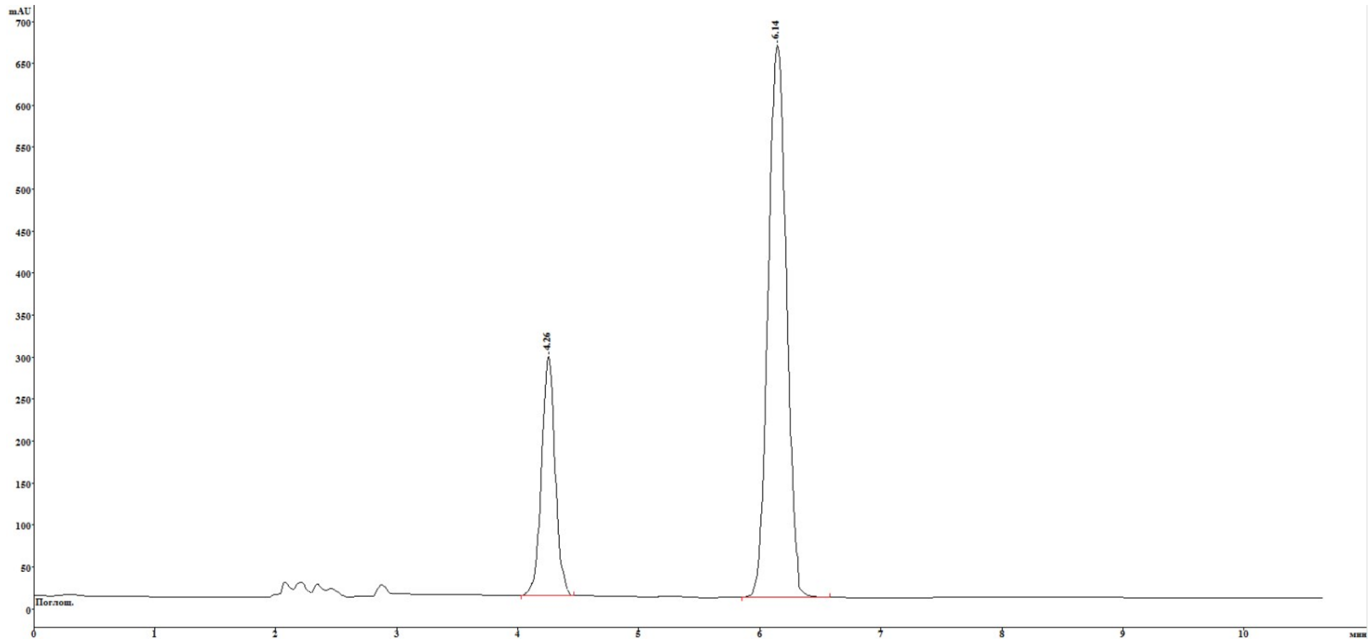


№	Retention time	Area	Area, %
1	5.79	10706	43.30
2	15.25	14021	56.70

6v. HPLC conditions: Chiralpak AD-H, *i*-PrOH/*n*-hexane 5 : 95, flow rate = 1.5 ml/min.



№	Retention time	Area	Area, %
1	4.28	11198	48.37
2	6.12	11955	51.63



№	Retention time	Area	Area, %
1	4.26	1981	22.29
2	6.14	6907	77.71