H-Bond Directed Photocatalytic Site-Selective α-C-H Functionalization of Alcohols with *p*-Quinone Methides

Sabhya Sandha[a] and Chandra Bhushan Tripathi[a, b] *

[a] Medicinal & Process Chemistry Division, CSIR-Central Drug Research Institute, Lucknow-226031, India.

[b] Academy of Scientific and Innovative Research (AcSIR), Ghaziabad-201002, India.

Email: chandra.tripathi.cdri@csir.res.in

SUPPORTING INFORMATION

A. General Information:

Infrared (FT-IR) spectra were recorded on PerkinElmer Spectrometer, ν_{max} in cm^{-1}. Bands are characterized as broad (br), strong (s), medium (m), weak (w). ^{1}H-NMR spectra were recorded on a BRUKER-AV400 (400 MHz) and BRUKER-AV500 (500 MHz) spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard ($CDCl_3$: δ 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, q = quartet, br = broad, m = multiplet), coupling constants (Hz), and integration. ^{13}C-NMR spectra were recorded on a BRUKER-AV400 (100 MHz) and BRUKER-AV500 (125 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm relative to tetramethylsilane, with the solvent resonance as the internal standard ($CDCl_3$: δ 77.16). ^{31}P-NMR spectra were recorded on a BRUKER-AV400 (162 MHz) and BRUKER-AV500 (202 MHz) spectrometer. ^{19}F-NMR spectra were recorded on a BRUKER-AV400 (376 MHz) spectrometer. Mass spectra were measured with a Q-TOF microspectrometer. Melting points were measured using ANALAB μ-Thermocal 10 melting point apparatus in an open glass capillary, and values are uncorrected. Unless otherwise noted, all reactions have been carried out with dried solvents under an atmosphere of nitrogen. Oven-dried glassware (100 °C) was used with standard vacuum line techniques. All workup and purification were carried out with reagent-grade solvents in air. Thin-layer chromatography was performed using Merck silica gel 60 F_{254} pre-coated plates (0.25 mm). Column chromatography was performed using silica gel (230-400 mesh) and neutral alumina. The photochemical reactions were carried out in a 5 mL flat-bottom, headspace vial obtained from Merck (Product No. 27197) and with 455 nm Kessil LED Light (Product no. PR160L-370 Gen 2) placed at a distance of 4 cm in the manner depicted below:

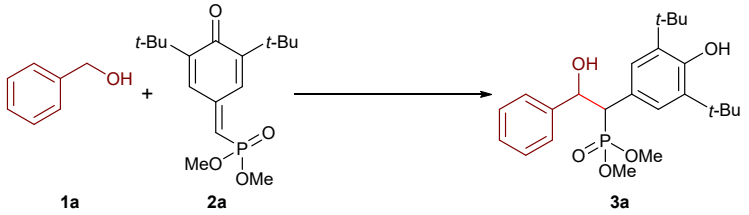
B. Starting preparation:

The alcohol starting material used in this study were obtained from commercial sources.

The *p*-quinone methides (*p*-QM) used in this study were synthesized by following the reported literature procedure and the spectral data are in agreement with the literature.[1]

C. Optimization of reaction conditions:

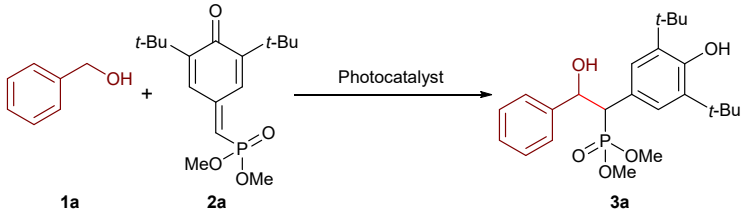
Screening of Different Additives:



Additive	Reaction Conditions	Yield (%)
Na_2CO_3	AQ (20 mol%), Na_2CO_3, CH_3CN, 25 °C, 12 h, 390 nm	10
Diphenyl phosphate	AQ (10 mol%), DPP, (10 mol%), Acetone, 25 °C, 12 h, 390 nm	39
Diphenyl phosphate	AQ (10 mol%), DPP, (10 mol%), 1,4-dioxane, 25 °C, 12 h, 390 nm	< 5
Diphenyl phosphate	AQ (10 mol%), DPP, (10 mol%), EtOAc, 25 °C, 12 h, 390 nm	16
Diphenyl phosphate	AQ (10 mol%), DPP, (10 mol%), PhMe, 25 °C, 12 h, 390 nm	16
Diphenyl phosphate	AQ (10 mol%), DPP, (10 mol%), CH_3CN:H_2O (9:1), 25 °C, 12 h, 390 nm	35

AQ: Anthraquinone

Screening of different photocatalyst:



Photocatalyst	Reaction Conditions	Yield (%)
DDQ	DDQ (20 mol%), TBN (20 mol%), CH_3CN, 25 °C, 12 h, 455 nm	< 5
Thioxanthone	Thioxanthone (20 mol%), CH_3CN, 25 °C, 12 h, 390 nm	< 5
4-CzIPN	4-CzIPN (5 mol%), PhSH (25 mol%), Acetone, 25 °C, 18 h, 455 nm	< 5
TBADT	TBADT (1 mol%), CH_3CN, 25 °C, 12 h, 390 nm	20
Xanthone	Xanthone (10 mol%), tert-amyl alcohol, 25 °C, 16 h, 370 nm	< 5
Benzophenone	Benzophenone (10 mol%), tert-amyl alcohol, 25 °C, 16 h, 370 nm	< 5

Determination of diastereomeric ratio:

In this work, the diastereomeric ratio is assigned based on the isolated product, as assigning the dr from crude NMR proved difficult due to overlapping impurity peaks with the product NMR peaks.

D. General procedure for photocatalytic α-C-H-functionalization of alcohols with *p*-quinone methides:

In an oven-dried 5 mL reaction vial, **alcohol** (0.1 mmol, 1.0 equiv.), **2** (0.15 mmol, 0.15 equiv.), and **anthraquinone** (0.005 mmol, 5 mol%) were taken. The reaction vial was covered with a rubber septum and *tert*-amyl alcohol (0.1M) was added. The reaction mixture was degassed with nitrogen by freeze-thaw (three times) and the solution was irradiated with 370 nm LED for 16 h. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography furnished **3.**

Note: Two batches of 0.1 mmol with corresponding alcohol were conducted, and the combined yield is reported.

For products **5c**-**5f**, two batches of 0.1 mmol scale with *p*-QM **2a** (1.0 equiv.) and corresponding alcohol (0.1 M) were conducted, and the combined yield is reported.

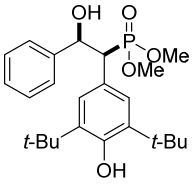
Assignment of relative configuration: The relative configuration of *syn*-**3a** was initially assigned by analyzing the ^{1}H-NMR spectra and coupling constant of signals at 5.40 (dd, J = 6.3, 4.4 Hz, 1H) and 3.24 (dd, J = 22.8, 4.2 Hz, 1H) ppm, which was reaffirmed by single crystal X-ray diffraction analysis.

For other diastereomer, by analyzing the ^{1}H-NMR spectra and coupling constant of peaks at 5.13 (dd, J = 11.7, 9.2 Hz, 1H) and 3.30 (dd, J = 19.6, 9.1Hz, 1H) ppm the relative configuration was assigned as *anti*-**3a**.

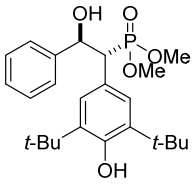
The relative configurations in other products were assigned in analogy to *syn*-**3a** and *anti*-**3a**.

Dimethyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-phenylethyl) phosphonate (3a): Combined yield: (74 mg, 0.170 mmol, 85% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *anti*- **3a** as a colorless oil (42 mg, 0.096 mmol, 48% yield). The residual mixture obtained after isolation of *anti*-**3a** was repurified by column chromatography over neutral alumina with 87:13 Hexane/Acetone to obtain *syn*-**3a** as a white solid (32 mg, 0.074 mmol, 37% yield).

syn-**3a: m.p.** 139-141˚C. **FT-IR (thin film):** 3379 (br), 2954 (s), 1385 (m), 1040 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.21- 7.16 (m, 3H), 7.09-7.05 (m, 2H), 6.94 (s, 2H), 5.40 (dd, *J* = 6.3, 4.4 Hz, 1H), 5.12 (s, 1H), 3.65 (d, *J* = 10.8 Hz, 3H), 3.43 (d, *J* = 10.5 Hz, 3H), 3.24 (dd, *J* = 22.8, 4.2 Hz, 1H), 1.34 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.4, 141.3 (d, *J* = 11.8 Hz), 135.6, 127.8, 127.45, 127.37, 126.5, 121.8, 73.2, 54.1 (d, *J* = 6.7 Hz), 52.3 (d, *J* = 7.2 Hz), 52.1 (d, *J* = 134.7 Hz), 34.3, 30.4. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.79. **HRMS (ESI)** m/z: Calcd. for $C_{24}H_{35}NaO_5P$ $[M + Na]^+$: 457.2115; Found 457.2121.



anti-**3a: FT-IR (thin film):** 3356 (br), 2953 (s), 1227 (s), 1044 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.15-7.08 (m, 3H), 7.06-7.02 (m, 2H), 6.84 (s, 2H), 5.13 (dd, *J* = 11.7, 9.2 Hz, 1H), 5.04 (s, 1H), 3.70 (d, *J* = 10.8 Hz, 3H), 3.59 (d, *J* = 10.5 Hz, 3H), 3.30 (dd, *J* = 19.6, 9.1 Hz, 1H), 1.31 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 152.9, 141.9, 135.8, 127.8, 127.5, 126.7, 126.6 (d, *J* = 7.1 Hz), 124.1, 75.7, 53.7 (d, *J* = 7.1 Hz), 52.92 (d, *J* = 6.8 Hz), 52.96 (d, *J* = 132.9 Hz), 34.3, 30.3. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 30.68. **HRMS (ESI)** m/z: Calcd. for $C_{24}H_{35}NaO_5P$ $[M + Na]^+$: 457.2115; Found 457.2123.



Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(*p*-tolyl)ethyl) phosphonate (3b): Combined yield: (54 mg, 0.120 mmol, 60% yield, 1.4:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**3b** as a colorless oil (32 mg, 0.071 mmol, 36% yield). The residual mixture obtained after isolation of *anti*-**3b** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3b** as a white solid (22 mg, 0.049 mmol, 24% yield).

syn-**3b: m.p.** 106-109˚C. **FT-IR (thin film):** 3368 (br), 2953 (s), 1045 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.02- 6.95 (m, 4H), 6.94 (s, 2H), 5.39-5.34 (m, 1H), 5.11 (s, 1H), 3.64 (d, *J* = 10.8 Hz, 3H), 3.43 (d, *J* = 10.5 Hz, 3H), 3.22 (dd, *J* = 22.8, 4.2 Hz, 1H), 2.27 (s, 3H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 148.4 (d, *J* = 1.7 Hz), 133.3 (d, *J* = 11.5 Hz), 131.9, 130.6, 123.5, 122.4 (d, *J* = 7.8 Hz), 121.4, 116.9 (d, *J* = 3.4 Hz), 68.1, 49.0 (d, *J* = 6.6 Hz), 47.3 (d, *J* = 7.3 Hz), 47.1 (d, *J* = 134.4 Hz), 29.3, 25.3, 16.2. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 29.87. **HRMS** (**ESI**) m/z: Calcd. for $C_{25}H_{37}NaO_5P$ $[M + Na]^+$: 471.2271; Found 471.2274.

anti-**3b: FT-IR (thin film):** 3371 (br), 2952 (s), 1063 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: 6.92 (s, 4H), 6.82 (s, 2H), 5.09 (dd, *J* = 11.5, 9.4 Hz, 1H), 5.03 (s, 1H), 3.70 (d, *J* = 10.8 Hz, 3H), 3.59 (d, *J* = 10.5 Hz, 3H), 3.28 (dd, *J* = 19.5, 9.1 Hz, 1H), 2.22 (s, 3H), 1.31 (s, 18H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: 152.9, 139.0 (d, *J* = 14.1Hz), 136.9, 135.8, 128.5, 126.6, 126.5, 124.3 (d, *J* = 5.9 Hz), 75.6, 53.6 (d, *J* = 7.1 Hz), 52.9 (d, *J* = 132.8 Hz), 52.8 (d, *J* = 6.8 Hz), 52.9 (d, *J* = 132.8 Hz), 34.3, 30.3, 21.1. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.83. **HRMS** (**ESI**) m/z: Calcd. for $C_{25}H_{37}NaO_5P$ $[M + Na]^+$: 471.2271; Found 471.2277.

Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(4-methoxyphenylethyl) phosphonate (3c): Combined yield: (75 mg, 0.161 mmol, 81% yield, 1.1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**3c** as a colorless oil (39 mg, 0.084 mmol, 42% yield). The residual mixture obtained after isolation of *anti*-**3c** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3c** as a white solid (36 mg, 0.077 mmol, 39% yield).

syn-**3c: m.p.** 94-97˚C. **FT-IR (thin film)**: 3375 (br), 2955 (s), 1244 (m), 1040 **(s)** cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.01 (d, *J* = 8.6 Hz, 2H), 6.97 (s, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 5.36-5.32 (m, 1H), 5.13 (s, 1H), 3.75 (s, 3H), 3.63 (d, *J* = 10.8 Hz, 3H), 3.41 (d, *J* = 10.5 Hz, 3H), 3.20 (dd, *J* = 22.7, 4.6 Hz, 1H), 1.36 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 159.1, 153.4, 135.7, 133.5 (d, *J* = 11.5 Hz), 127.8, 127.4 (d, *J* = 7.9 Hz), 122.1 (d, *J* = 4.0 Hz), 113.3, 72.9, 55.4, 54.0 (d, *J* = 7.1 Hz), 52.3 (d, *J* = 7.2 Hz), 52.2 (d, *J* = 134.1 Hz), 34.4, 30.4. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 29.74. **HRMS** (**ESI**) m/z: Calcd. for $C_{25}H_{37}NaO_6P$ $[M + Na]^+$: 487.2220; Found 487.2224.

anti-**3c: FT-IR (thin film)**: 3369 (br), 2953 (s), 1242 (m), 1042 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 6.96 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 1.6 Hz, 2H), 6.65 (d, *J* = 8.7 Hz, 2H), 5.09 (dd, *J* = 11.2, 9.3 Hz, 1H), 5.04 (s, 1H), 4.23 (s, 1H), 3.70 (d, *J* = 10.8 Hz, 3H), 3.69 (s, 3H), 3.59 (d, *J* = 10.5 Hz, 3H), 3.26 (dd, *J* = 19.5, 9.2 Hz, 1H), 1.31 (s, 18H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: 158.9, 152.9, 135.8, 134.2 (d, *J* = 14.4 Hz), 127.8, 126.5 (d, *J* = 7.3 Hz), 124.3 (d, *J* = 6.0 Hz), 113.2, 75.3 (d, *J* = 2.4 Hz), 55.3, 53.6 (d, *J* = 7.1 Hz), 53.0 (d, *J* = 132.6 Hz), 52.8 (d, *J* = 6.9 Hz), 34.3, 30.3. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 30.80. **HRMS** (**ESI**) m/z: Calcd. For $C_{25}H_{37}NaO_6P$ $[M + Na]^+$: 487.2220; Found 487.2224.

Dimethyl(2-(4-(benzyloxy)phenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3d): Combined yield: (59 mg, 0.109 mmol, 54% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**3d** as a colorless oil (25 mg, 0.046 mmol, 23% yield). The residual mixture obtained after isolation of *anti*-**3d** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3d** as a white solid (34 mg, 0.063 mmol, 31% yield).

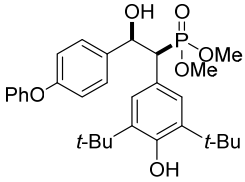
syn-**3d: m.p.** 150-154˚C. **FT-IR (thin film)**: 3374 (br), 2955 (s), 1238 (m), 1041 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.42-7.28 (m, 5H), 7.02 (d, *J* = 8.2 Hz, 2H), 6.98 (s, 2H), 6.82 (d, *J* = 8.2 Hz, 2H), 5.37-5.31 (m, 1H), 5.13 (s, 1H), 5.02 (s, 2H), 3.61 (d, *J* = 10.8 Hz, 3H), 3.40 (d, *J* = 10.5 Hz, 3H), 3.21 (dd, *J* = 22.7, 4.5 Hz, 1H), 1.36 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 158.2, 153.4, 137.2, 135.7, 133.8 (d, *J* = 11.1 Hz), 131.9, 128.7, 128.0, 127.8, 127.5, 127.4 (d, *J* = 7.7 Hz), 122.1, 114.3, 72.9, 70.1, 54.0 (d, *J* = 6.7 Hz), 52.3 (d, *J* = 7.3 Hz), 52.2 (d, *J* = 134.3 Hz), 34.4, 30.4. **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 29.67. **HRMS** (**ESI**) m/z: Calcd. for $C_{31}H_{41}NaO_6P$ $[M + Na]^+$: 563.2533; Found 563.2531.

anti-**3d: FT-IR (thin film)**: 3403 (br), 2926 (s), 1227 (m), 1040 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.29-7.19 (m, 5H), 6.88 (d, *J* = 8.2 Hz, 2H), 6.75 (s, 2H), 6.64 (d, *J* = 8.1 Hz, 2H), 5.04-4.97 (m, 1H), 4.96 (s, 1H), 4.87 (s, 2H), 4.15 (s, 1H), 3.61 (d, *J* = 10.8 Hz, 3H), 3.50 (d, *J* = 10.5 Hz, 3H), 3.18 (dd, *J* = 19.5, 9.1 Hz, 1H), 1.23 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 157.2, 151.9, 136.1, 134.8, 133.5 (d, *J* = 14.3 Hz), 127.6, 127.0, 126.8, 126.5, 125.6 (d, *J* = 7.1 Hz), 123.30, 123.26, 113.2, 74.2, 69.0, 52.6 (d, *J* = 7.1 Hz), 52.0 (d, *J* = 132.7 Hz), 51.9 (d,

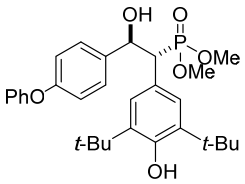
J = 6.9 Hz), 33.3, 29.4. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 30.78. **HRMS** (**ESI**) m/z: Calcd. for $C_{31}H_{41}NaO_6P$ $[M + Na]^+$: 563.2533; Found 563.2530.

Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(4-phenoxyphenyl)ethyl) phosphonate (3e): Combined yield: (83 mg, 0.158 mmol, 79% yield, 2.6:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 88:12 Hexane/Acetone furnished *syn*-**3e** as a white solid (60 mg, 0.114 mmol, 57% yield). The residual mixture obtained after isolation of *syn*-**3e** was repurified by column chromatography over neutral alumina with 90:10 Hexane/Acetone to obtain *anti*-**3e** as a colorless oil (23 mg, 0.044 mmol, 22% yield).

syn-**3e: FT-IR (thin film)**: 3435 (br), 2953 (s), 1228 (s), 1039 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.37- 7.31 (m, 2H), 7.13- 7.07 (m, 2H), 7.00 (d, *J* = 7.9 Hz, 2H), 6.93-6.88 (m, 3H), 6.87- 6.80 (m, 2H), 5.70 (d, *J* = 6.4 Hz, 1H), 5.06 (s, 1H), 4.04 (s, 1H), 3.72 (d, *J* = 10.8 Hz, 3H), 3.55 (d, *J* = 2.4 Hz, 0.6H), 3.49 (d, *J* = 10.5 Hz, 3.4 H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 157.3, 153.2, 152.4, 135.2, 132.4 (d, *J* = 14.7 Hz), 129.9, 128.6, 128.1, 127.5 (d, *J* = 8.2 Hz), 123.3, 123.2, 121.8, 118.4, 118.1, 67.8, 53.9 (d, *J* = 6.6 Hz), 52.6 (d, *J* = 7.2 Hz), 48.3 (d, *J* = 133.8 Hz), 34.3, 30.4. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.94. **HRMS** (**ESI**) m/z: Calcd. for $C_{30}H_{40}O_6P$ $[M + H]^+$: 527.2558; Found 527.2563.



anti-**3e: FT-IR (thin film)**: 3370 (br), 2953 (s), 1231 (s), 1041 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.49 (d, *J* = 7.4 Hz, 1H), 7.29- 7.25 (m, 2H), 7.14 -7.02 (m, 5H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.67 (d, *J* = 8.0 Hz, 1H), 5.47 (dd, *J* = 18.0, 7.4 Hz, 1H), 5.07 (s, 1H), 3.66 (dd, *J* = 20.8, 7.4 Hz, 1H), 3.59 (d, *J* = 10.9 Hz, 3H), 3.45 (d, *J* = 10.5 Hz, 3H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: δ 157.1, 153.9, 153.1, 135.7, 133.4 (d, *J* = 10.8 Hz), 129.8, 128.6, 128.4, 126.6 (d, *J* = 7.2 Hz), 124.9 (d, *J* = 5.2 Hz), 123.4, 123.3, 118.6, 118.3, 71.1, 53.7 (d, *J* = 6.9 Hz), 52.4 (d, *J* = 7.0 Hz), 51.0 (d, *J* = 133.5 Hz), 34.4, 30.4. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.69. **HRMS** (**ESI**) m/z: Calcd. for $C_{30}H_{39}NaO_6P$ $[M + Na]^+$: 549.2377; Found 549.2382.



Dimethyl(2-(4-bromophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3f): Combined yield: (65 mg, 0.126 mmol, 63% yield, 1.2:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *anti*-**3f** as a colorless oil (36 mg, 0.070 mmol, 35% yield). The residual mixture obtained after isolation of *anti*-**3f** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3f** as a white solid (29 mg, 0.056 mmol, 28% yield).

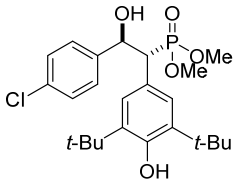
syn-**3f: m.p.** 130-133˚C.**FT-IR (thin film)**: 3382 (br), 2953 (s), 1231 (m), 1042 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 8.3 Hz, 2H), 6.94 (d, *J* = 8.3 Hz, 2H), 6. 91 (s, 2H), 5.39-5.35 (m, 1H), 5.14 (s, 1H), 3.69 (d, *J* = 10.9 Hz, 3H), 3.44 (d, *J* = 10.5 Hz, 3H), 3.16 (dd, *J* = 23.0, 3.9 Hz, 1H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.1 (d, *J* = 2.4 Hz), 141.2 (d, *J* = 14.8 Hz), 136.0, 130.8, 128.4, 126.5 (d, *J* = 7.3 Hz), 123.7 (d, *J* = 6.1 Hz), 121.3, 75.1 (d, *J* = 2.4 Hz), 53.7 (d, *J* = 7.1 Hz), 53.0 (d, *J* = 6.7 Hz), 52.9 (d, *J* = 133.6 Hz), 34.3, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 29.56. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}BrO_5P$ $[M + H]^+$: 513.1400; Found 513.1403.

anti-**3f: FT-IR (thin film)**: 3360 (br), 2954 (s), 1224 (m), 1051 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.23 (d, *J* = 8.3 Hz, 2H), 6.89 (d, *J* = 8.3 Hz, 2H), 6.79 (s, 2H), 5.08 (dd, *J* = 10.7, 9.7 Hz, 2H), 3.71 (d, *J* = 10.9 Hz, 3H), 3.60 (d, *J* = 10.5 Hz, 3H), 3.21 (dd, *J* = 19.5, 9.2 Hz, 1H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: 153.5, 140.4 (d, *J* = 12.7 Hz), 135.7, 130.8, 128.2, 127.3 (d, *J* = 7.7 Hz), 121.4, 121.2, 72.6, 54.3 (d, *J* = 6.6 Hz), 52.3 (d, *J* = 3.9 Hz), 51.8 (d, *J* = 137.9 Hz), 34.3, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.39. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}BrO_5P$ $[M + H]^+$: 513.1400; Found 513.1406.

Dimethyl(2-(4-chlorophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3g): Combined yield: (65 mg, 0.138 mmol, 69% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *syn*-**3g** as a white solid (29 mg, 0.062 mmol, 31% yield). The residual mixture obtained after isolation of *syn*-**3g** was repurified by column chromatography over neutral alumina with 87:13 Hexane/Acetone to obtain *anti*-**3g** as a colorless oil (36 mg, 0.076 mmol, 38% yield).

syn-**3g: m.p.** 111-115˚C. **FT-IR (thin film)**: 3387 (br), 2921 (s), 1384 (s), 1044 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.16 (d, *J* = 8.4 Hz, 2H), 7.00 (d, *J* = 8.4 Hz, 2H), 6.92 (d, *J* = 1.4 Hz, 2H), 5.38 (dd, *J* = 6.0, 4.1 Hz, 1H), 5.13 (s, 1H), 3.69 (d, *J* = 10.9 Hz, 3H), 3.43 (d, *J* = 10.6 Hz, 3H), 3.17 (dd, *J* = 23.0, 4.0 Hz, 1H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.5 (d, *J* = 1.8 Hz), 139.9, 139.8, 135.7, 133.1, 127.9 (d, *J* = 2.5 Hz), 127.3 (d, *J* = 8.0 Hz), 121.4 (d, *J* = 3.6 Hz), 72.6, 54.3 (d, *J* = 7.1 Hz), 52.3 (d, *J* = 7.3 Hz), 51.9 (d, *J* = 135 Hz), 34.3, 30.3. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 29.56. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}ClO_5P$ $[M + H]^+$: 469.1906; Found 469.1912.

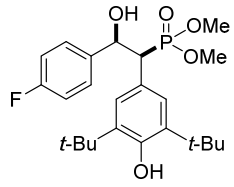
anti-**3g: FT-IR (thin film)**: 3368 (br), 2953 (s), 1051 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**:



δ 7.09 (d, *J* = 8.4 Hz, 2H), 6.96 (d, *J* = 8.4 Hz, 2H), 6.81 (s, 2H), 5.10 (dd, *J* = 11.3, 9.4 Hz, 2H), 3.71 (d, *J* = 10.8 Hz, 3H), 3.62 (d, *J* = 10.5 Hz, 3H), 3.21 (dd, *J* = 19.6, 9.1 Hz, 1H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.1 (d, *J* = 2.6 Hz), 140.6 (d, *J* = 14.8 Hz), 136.0, 133.1, 128.0, 127.9, 126.5 (d, *J* = 7.2 Hz), 123.8 (d, *J* = 5.9 Hz), 75.1 (d, *J* = 2.5 Hz), 53.7 (d, *J* = 7.0 Hz), 52.99 (d, *J* = 133.3 Hz), 52.96 (d, *J* = 6.8 Hz), 34.3, 30.3. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 30.33. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}ClO_5P$ $[M + H]^+$: 469.1906; Found 469.1912.

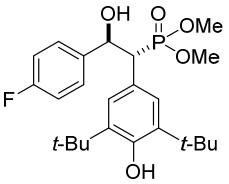
Dimethyl(2-(4-flororphenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3h): Combined yield: (57 mg, 0.126 mmol, 63% yield, 1.5:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *syn*-**3h** as a white solid (18 mg, 0.039 mmol, 20% yield). The residual mixture obtained after isolation of *syn*-**3h** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *anti*-**3h** as a colorless oil (26 mg, 0.057 mmol, 29% yield). Note: During purification of *anti*-**3h**, a brown oil (13 mg, 0.028 mmol, 14% yield) containing the mixture of diastereomers was also obtained.

syn-**3h: m.p.** 105-109˚C. **FT-IR (thin film)**: 3393 (br), 2921 (s), 1384 (s), 1044 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**:



δ 7.04 (dd, *J* = 8.4, 5.6 Hz, 2H), 6.94 (s, 2H), 6.88 (t, *J* = 8.6 Hz, 2H), 5.38 (t, *J* = 5.0 Hz 1H), 5.14 (s, 1H), 3.67 (d, *J* = 10.9 Hz, 3H), 3.42 (d, *J* = 10.5 Hz, 3H), 3.17 (dd, *J* = 22.9, 4.2 Hz, 1H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 162.2 (d, *J* = 243.4 Hz), 153.5, 137.0 (d, *J* = 12.7 Hz), 135.8, 128.2 (d, *J* = 7.8 Hz), 127.4 (d, *J* = 7.7 Hz), 121.6, 114.6 (d, *J* = 21.1 Hz), 72.6, 54.2 (d, *J* = 6.6 Hz), 52.3 (d, *J* = 7.3 Hz), 52.1 (d, *J* = 134.9 Hz), 34.4, 30.4. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 29.57. **^{19}F-NMR (471 MHz, $CDCl_3$)**: δ –115.50. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{34}FNaO_5P$ $[M + Na]^+$: 475.2021; Found 475.2024.

anti-**3h: FT-IR (thin film)**: 3373 (br), 2952 (s), 1225 (s), 1050 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**:

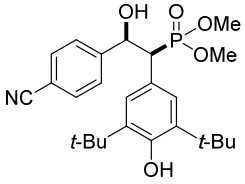


δ 7.01 (dd, *J* = 8.3, 5.5 Hz, 2H), 6.84-6.78 (m, 4H), 5.16-5.09 (m, 1H), 5.07 (s, 1H), 3.71 (d, *J* = 10.8 Hz, 3H), 3.62 (d, *J* = 10.5 Hz, 3H), 3.23 (dd, *J* = 19.5, 9.2 Hz, 1H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 162.1 (d, *J* = 243.7 Hz), 153.0 (d, *J* = 2.1 Hz), 137.8 (d, *J* = 14.6 Hz), 135.9, 128.3 (d, *J* = 8.1 Hz), 126.5 (d, *J* = 7.2 Hz), 123.9 (d, *J* = 5.9 Hz), 114.6 (d, *J* = 21.1 Hz), 75.0 (d, *J* = 2.5 Hz), 53.7 (d, *J* = 7.3 Hz), 53.1 (d, *J* = 133.3 Hz), 52.9 (d, *J* = 7.1

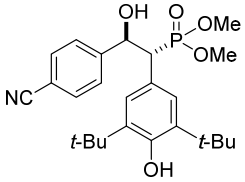
Hz), 34.3, 30.3. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 30.44. **^{19}F-NMR (471 MHz, $CDCl_3$)**: δ –115.46. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{34}FNaO_5P$ $[M + Na]^+$: 475.2021; Found 475.2024.

Dimethyl(2-(4-cyanophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3i): Combined yield: (25 mg, 0.054 mmol, 27% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *anti*-**3i** as a colorless oil (08 mg, 0.017 mmol, 09% yield). The residual mixture obtained after isolation of *anti*-**3i** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3i** as a white solid (10 mg, 0.022 mmol, 11% yield). Note: During purification of *syn*-**3i**, a brown oil (07 mg, 0.015 mmol, 7% yield) containing the mixture of diastereomers was also obtained.

syn-**3i: m.p.** 115-120˚C. **FT-IR (thin film)**: 3385 (br), 2923 (s), 1384 (s), 1042 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.47 (d, *J* = 8.3 Hz, 2H), 7.18 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 1,4 Hz, 2H), 5.45 (dd, *J* = 5.8, 3.8 Hz, 1H), 5.14 (s, 1H), 4.06 (s, 1H), 3.73 (d, *J* = 10.9 Hz, 3H), 3.44 (d, *J* = 10.5 Hz, 3H), 3.18 (dd, *J* = 23.2, 3.7 Hz, 1H), 1.33 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.6, 146.8 (d, *J* = 13.4 Hz), 135.9, 131.6, 127.3, 127.2, 120.9, 118.9, 111.0, 72.6, 54.5 (d, *J* = 6.6 Hz), 52.4 (d, *J* = 7.5 Hz), 51.5 (d, *J* = 135.6 Hz), 34.3, 30.4. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 29.17. **HRMS** (**ESI**) m/z: Calcd. for $C_{25}H_{35}NO_5P$ $[M + H]^+$: 460.2247; Found 460.2255.



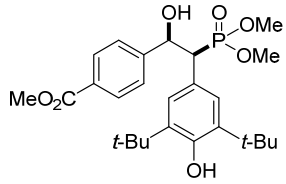
anti-**3i: FT-IR (thin film)**: 3436 (s), 2923 (s), 1384 (s), 1044 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.42 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.82 (s, 2H), 5.22-5.14 (m, 1H), 5.11 (s, 1H), 4.75 (s, 1H), 3.70 (d, *J* = 10.9 Hz, 3H), 3.63 (d, *J* = 10.6 Hz, 3H), 3.21 (dd, *J* = 19.8, 9.1 Hz, 1H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.3, 147.5 (d, *J* = 14.6 Hz), 136.3, 131.6, 127.5, 126.4 (d, *J* = 7.2 Hz), 123.3, 118.8, 111.2, 75.1, 53.9 (d, *J* = 6.2 Hz), 53.0 (d, *J* = 6.8 Hz), 52.8 (d, *J* = 134.2 Hz), 34.4, 30.3. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 29.67. **HRMS** (**ESI**) m/z: Calcd. for $C_{25}H_{35}NO_5P$ $[M + H]^+$: 460.2247; Found 460.2255.



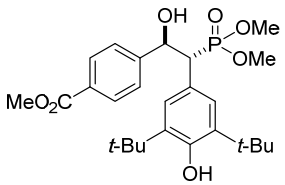
Methyl-4-(2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-(dimethoxyphosphoryl)-1-hydroxyethyl) benzoate (3j): Combined yield: (50 mg, 0.102 mmol, 51% yield, 1.1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *anti*-**3j** as a colorless oil (24 mg, 0.049 mmol, 24% yield). The residual mixture obtained after isolation of *anti*-**3j** was repurified by column chromatography

over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3j** as a brown solid (26 mg, 0.053 mmol, 27% yield).

syn-**3j: m.p.** 166-170˚C. **FT-IR (thin film)**: 3384 (br), 2924 (s), 1383 (s), 1039 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.86 (d, *J* = 8.2 Hz, 2H), 7.16 (d, *J* = 8.2 Hz, 2H), 6.93 (s, 2H), 5.48-5.42 (m, 1H), 5.12 (s, 1H), 3.88 (s, 3H), 3.85 (s, 1H), 3.69 (d, *J* = 10.8 Hz, 3H), 3.42 (d, *J* = 10.5 Hz, 3H), 3.23 (dd, *J* = 23.1, 3.9 Hz, 1H), 1.33 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 167.1, 153.5, 146.6 (d, *J* = 12.4 Hz), 135.8, 129.2, 127.3 (d, *J* = 7.6 Hz), 126.5, 121.3, 72.8, 54.3 (d, *J* = 6.8 Hz), 52.3 (d, *J* = 7.3 Hz), 52.1, 51.7 (d, *J* = 135.1 Hz), 34.3, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 29.42. **HRMS** (**ESI**) m/z: Calcd. for $C_{26}H_{38}O_7P$ $[M + H]^+$: 493.2350; Found 493.2359.

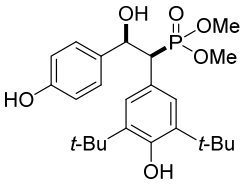


anti-**3j: FT-IR (thin film)**: 3432 (br), 2953 (s), 1719 (s), 1042 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.80 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.85 (s, 2H), 5.19 (dd, *J* = 11.9, 9.3 Hz, 1H), 5.07 (s, 1H), 4.61 (s, 1H), 3.86 (s, 3H), 3.69 (d, *J* = 10.8 Hz, 3H), 3.59 (d, *J* = 10.5 Hz, 3H), 3.28 (dd, *J* = 19.7, 8.9 Hz, 1H), 1.31 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 167.0, 153.2, 147.3 (d, *J* = 13.9 Hz), 136.1, 129.22, 129.16, 126.7, 126.5 (d, *J* = 7.0 Hz), 123.7 (d, *J* = 6.2 Hz), 75.2, 53.8 (d, *J* = 6.9 Hz), 52.9 (d, *J* = 7.1 Hz), 52.8 (d, *J* = 132.9 Hz), 52.1, 34.3, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.09. **HRMS** (**ESI**) m/z: Calcd. for $C_{26}H_{38}O_7P$ $[M + H]^+$: 493.2350; Found 493.2356.



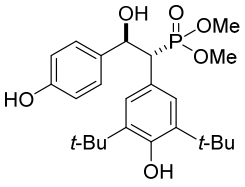
Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(4-hydroxyphenyl)ethyl) phosphonate (3k): Combined yield: (46 mg, 0.102 mmol, 51% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 80:20 Hexane/ Ethyl acetate furnished *syn*-**3k** as a white solid (26 mg, 0.058 mmol, 29% yield) and with 75:25 Hexane/ Ethyl acetate as eluent provided *anti*-**3k** as a white solid (20 mg, 0.044 mmol, 22% yield).

syn-**3k: m.p.** 138-142˚C. **FT-IR (thin film)**: 3361 (br), 2952 (s), 1443 (s), 1046 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.06-6.99 (m, 4H), 6.69 (d, *J* = 8.2 Hz, 2H), 5.32-5.26 (m, 1H), 5.15 (s, 1H), 3.55 (d, *J* = 10.9 Hz, 3H), 3.37 (d, *J* = 10.4 Hz, 3H), 3.25 (dd, *J* = 22.6, 5.4 Hz, 1H), 1.38 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 155.8, 153.5, 135.9, 132.9, 128.2, 127.2 (d, *J* = 7.4 Hz), 122.4, 114.9, 73.3, 54.0 (d, *J* = 6.8 Hz), 52.5 (d, *J* = 134.7 Hz), 52.4 (d, *J* = 7.5



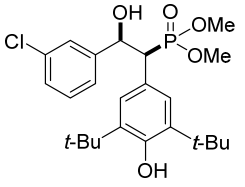
Hz), 34.4, 30.4. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 29.26. **HRMS (ESI)** m/z: Calcd. for $C_{24}H_{35}NaO_6P$ $[M + Na]^+$:473.2063; Found 473.2064.

anti-**3k: m.p.** 149-154˚C. **FT-IR (thin film)**: 3364 (br), 2925 (s), 1045 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 6.91 (d, *J* = 8.3 Hz, 2H), 6.84 (s, 2H), 6.59 (d, *J* = 8.3 Hz, 2H), 5.12-5.06 (m, 1H), 5.05 (s, 1H), 3.71 (d, *J* = 10.8 Hz, 3H), 3.58 (d, *J* = 10.5 Hz, 3H), 3.28 (dd, *J* = 19.7, 9.0 Hz, 1H), 1.32 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 155.3, 152.9, 135.8, 133.9, 128.0, 126.6 (d, *J* = 7.1 Hz), 124.1, 114.8, 75.2, 53.7 (d, *J* = 5.9 Hz), 52.94 (d, *J* = 6.2 Hz), 52.91 (d, *J* = 133.1 Hz), 34.3, 30.4. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 30.78. **HRMS (ESI)** m/z: Calcd. for $C_{24}H_{35}NaO_6P$ $[M + Na]^+$:473.2063; Found 473.2068.

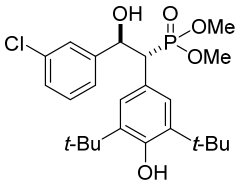


Dimethyl(2-(3-chlorophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3l): Combined yield: (43 mg, 0.092 mmol, 46% yield, 1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *anti*-**3l** as a colorless oil (21 mg, 0.045 mmol, 22% yield). The residual mixture obtained after isolation of *anti*-**3l** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3l** as a white solid (22 mg, 0.047 mmol, 24% yield).

syn-**3l: m.p.** 173-177˚C. **FT-IR (thin film)**: 3438 (br), 2924 (s), 2383 (s), 1042 (s)cm^{-1}. **^{1}H -NMR (500 MHz, $CDCl_3$)**: δ 7.15-7.09 (m, 2H), 7.01 (s, 1H), 6.99-6.95 (m, 1H), 6.92 (d, *J* = 1.2 Hz, 2H), 5.38 (dd, *J* = 6.4, 3.8 Hz, 1H), 5.13 (s, 1H), 3.72 (d, *J* = 10.8 Hz, 3H), 3.46 (d, *J* = 10.6 Hz, 3H), 3.19 (dd, *J* = 23.1, 3.8 Hz, 1H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.5, 143.3, 135.8, 133.9, 129.0, 127.5, 127.3 (d, *J* = 7.9 Hz), 126.9, 124.6, 121.3 (d, *J* = 3.6 Hz), 72.6, 54.3 (d, *J* = 7.1 Hz), 52.4 (d, *J* = 7.3 Hz), 51.7 (d, *J* = 135.0 Hz), 34.4, 30.4. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 29.57. **HRMS (ESI)** m/z: Calcd. for $C_{24}H_{35}ClO_5P$ $[M + H]^+$: 469.1906; Found 469.1911.

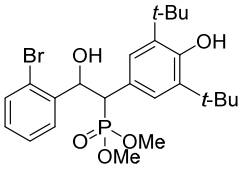


anti-**3l: FT-IR (thin film)**: 3345 (br), 2950 (s), 1044 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.09-7.03 (m, 2H), 6.97 (s, 1H), 6.96-6.93 (m, 1H), 6.83 (s, 2H), 5.13-5.06 (m, 2H), 3.72 (d, *J* = 10.8 Hz, 3H), 3.64 (d, *J* = 10.5 Hz, 3H), 3.22 (dd, *J* = 19.5, 9.1 Hz, 1H), 1.33 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 144.1 (d, *J* = 14.5 Hz), 136.1 (d, *J* = 1.4 Hz), 133.7, 129.1, 127.5, 127.0, 126.5 (d, *J* = 7.2 Hz), 124.7, 123.7 (d, *J* = 6.3 Hz), 75.2 (d, *J* = 2.5 Hz), 53.7 (d, *J* = 7.1 Hz), 52.99 (d, *J* = 6.9 Hz), 52.97 (d, *J* = 133.5 Hz), 34.3, 30.3. **^{31}P-NMR (202**

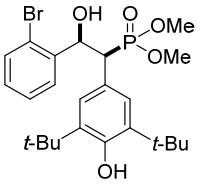


MHz, $CDCl_3$): δ 30.23. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}ClO_5P$ $[M + H]^+$: 469.1906; Found 469.1911.

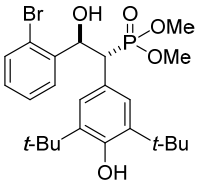
Dimethyl(2-(2-bromophenyl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3m): Combined yield: (42 mg, 0.082 mmol, 41% yield, 2.4:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *syn*-**3m** as a white solid (30 mg, 0.058 mmol, 29% yield). The residual mixture obtained after isolation of *syn*-**3m** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *anti*-**3m** as a colorless oil (12 mg, 0.023 mmol, 12% yield).



syn-**3m: m.p.** 159-163˚C. **FT-IR (thin film)**: 3341 (s), 2921 (m), 1385 (s), 759 (m) cm^{-1}. **^{1}H-NMR (400 MHz, Acetone-d_6)**: δ 7.52 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.06 (dt, *J* = 7.5, 1.7 Hz, 1H), 6.97 (t, *J* = 8.1 Hz, 1H), 6.91 (s, 2H), 6.81 (dd, *J* = 7.9, 1.6 Hz, 1H), 5.87 (s, 1H), 5.70 (dd, *J* = 5.9, 2.1 Hz, 1H), 4.93 (s, 1H), 3.82 (d, *J* = 10.6 Hz, 3H), 3.61 (d, *J* = 10.6 Hz, 3.5H), 3.55 (d, *J* = 2.5 Hz, 0.5H), 1.31 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 139.7 (d, *J* = 15.5 Hz), 135.2, 131.9, 129.3, 128.6, 127.5 (d, *J* = 8.4 Hz), 126.7, 121.2, 120.8, 71.6, 54.2 (d, *J* = 6.6 Hz), 52.8 (d, *J* = 7.1 Hz), 47.1 (d, *J* = 134.9 Hz), 34.2, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.83. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}BrO_5P$ $[M + H]^+$: 513.1400; Found 513.1403.



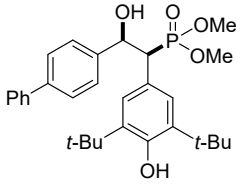
anti-**3m: FT-IR (thin film)**: 3436 (br), 2952 (s), 1384 (s), 1037 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.68 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.37-7.28 (m, 2H), 7.10-7.01 (m, 3H), 5.84 (s, 1H), 5.59 (dd, *J* = 13.4, 8.9 Hz, 1H), 5.16 (s, 1H), 3.68 (d, *J* = 10.8 Hz, 3H), 3.58 (dd, *J* = 20.0, 8.9 Hz, 1H), 3.49 (d, *J* = 10.5 Hz, 3H), 1.33 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 141.4, 135.7, 132.6, 128.9, 128.7, 127.4, 126.7 (d, *J* = 7.0 Hz), 124.1, 122.9, 74.3, 53.9 (d, *J* = 7.2 Hz), 52.5 (d, *J* = 6.8 Hz), 50.5 (d, *J* = 133.3 Hz), 34.4, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.21. **HRMS** (**ESI**) m/z: Calcd. for $C_{24}H_{35}BrO_5P$ $[M + H]^+$: 513.1400; Found 513.1403.



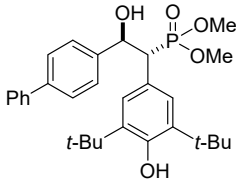
Dimethyl(2-([1,1'-biphenyl]-4-yl)-1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (3n): Combined yield: (96 mg, 0.188 mmol, 94% yield, 1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**3n** as a colorless oil (42 mg, 0.082 mmol, 41% yield). The residual mixture obtained after isolation of *anti*-**3n** was repurified by column chromatography over neutral alumina with 89:11 Hexane/Acetone to obtain *syn*-**3n** as a white solid (34 mg, 0.066 mmol, 33% yield). Note:

During purification of *syn*-**3n**, a white solid (20 mg, 0.039 mmol, 20% yield) containing the mixture of diastereomers was also obtained.

syn-**3n: m.p.** 125-128˚C. **FT-IR (thin film)**: 3371 (br), 2955 (s), 1039 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.53 (d, *J* = 7.5 Hz, 2H), 7.45-7.39 (m, 4H), 7.35- 7.29 (m, 1H), 7.15 (d, *J* = 8.1 Hz, 2H), 6.97 (s, 2H), 5.46 (dd, *J* = 6.1, 4.4 Hz, 1H), 5.13 (s, 1H), 3.68 (d, *J* = 10.8 Hz, 3H), 3.46 (d, *J* = 10.5 Hz, 3H), 3.28 (dd, *J* = 22.8, 4.1 Hz, 1H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.4 (d, *J* = 1.8 Hz), 141.1, 140.5, 140.4, 135.6, 128.8, 127.4 (d, *J* = 7.9 Hz), 127.3, 127.1, 126.9, 126.6, 121.8 (d, *J* = 3.5 Hz), 73.0, 54.1 (d, *J* = 6.9 Hz), 52.3 (d, *J* = 7.3 Hz), 52.0 (d, *J* = 134.8 Hz), 34.3, 30.4. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 29.80. **HRMS** (**ESI**) m/z: Calcd. for $C_{30}H_{39}NaO_5P$ $[M + Na]^+$: 533.2428; Found 533.2437.



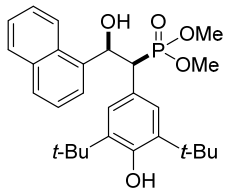
anti-**3n: FT-IR (thin film)**: 3369 (br), 2954 (s), 1041 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.48 (d, *J* = 7.5 Hz, 2H), 7.41-7.34 (m, 4H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 8.1 Hz, 2H), 6.87 (s, 2H), 5.21- 5.15 (m, 1H), 5.05 (s, 1H), 4.41 (s, 1H), 3.73 (d, *J* = 10.8 Hz, 3H), 3.62 (d, *J* = 10.5 Hz, 3H), 3.34 (dd, *J* = 19.5, 9.1 Hz, 1H), 1.31 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.0, 141.15, 141.09, 140.4, 135.9, 128.8, 127.3, 127.15, 127.10, 126.64, 126.60, 124.1 (d, *J* = 5.9 Hz), 75.6, 53.7 (d, *J* = 7.0 Hz), 52.96 (d, *J* = 133.2 Hz), 52.91 (d, *J* = 6.8 Hz), 34.3, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.68. **HRMS** (**ESI**) m/z: Calcd. for $C_{30}H_{39}NaO_5P$ $[M + Na]^+$: 533.2428; Found 533.2435.



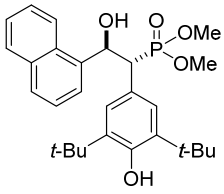
Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(naphthalen-1-yl)ethyl) phosphonate (3o): Combined yield: (89 mg, 0.184 mmol, 92% yield, 1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**3o** as a colorless oil (21 mg, 0.043 mmol, 22% yield). The residual mixture obtained after isolation of *anti*-**3o** was repurified by column chromatography over neutral alumina with 89:11 Hexane/Acetone to obtain *syn*-**3o** as a white solid (44 mg, 0.091 mmol, 46% yield). Note: During purification of *syn*-**3o**, a yellow oil (24 mg, 0.049 mmol, 24% yield) containing the mixture of diastereomers was also obtained.

syn-**3o: m.p.** 183-187˚C. **FT-IR (thin film)**: 3438 (br), 2954 (s), 1619 (m), 1040 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 8.02 (d, *J* = 8.4 Hz, 1H), 7.86 (d, *J* = 7.9 Hz, 1H), 7.67 (d, *J* = 8.1 Hz, 1H), 7.57- 7.53 (m, 1H), 7.51- 7.46 (m, 1H), 7.19- 7.15 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.66 (s, 2H), 6.25 (dd, *J* = 7.2, 2.4 Hz, 1H), 5.05 (s, 1H), 3.84 (d, *J* = 10.8 Hz, 3H), 3.56 (d, *J*

= 10.6 Hz, 3H), 3.51 (dd, *J* = 23.0, 2.6 Hz, 1H), 1.24 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 136.2 (d, *J* = 13.5 Hz), 135.2, 133.6, 129.7, 129.1, 127.6, 127.3 (d, *J* = 8.4 Hz), 126.2, 125.2, 125.1, 124.7, 122.5, 121.4, 69.2, 54.3 (d, *J* = 6.9 Hz), 52.4 (d, *J* = 7.2 Hz), 49.5 (d, *J* = 135.1 Hz), 34.2, 30.3. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 31.13. **HRMS** (**ESI**) m/z: Calcd. for $C_{28}H_{37}NaO_5P$ [M + Na]$^+$: 507.2271; Found 507.2276.

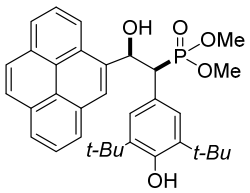


anti-**3o: FT-IR (thin film)**: 3353 (br), 2952 (s), 1631 (m), 1039 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 8.02- 7.95 (m, 1H), 7.76- 7.71 (m, 1H), 7.65 (d, *J* = 8.1 Hz. 1H), 7.51 (d, *J* = 7.1 Hz, 1H), 7.38- 7.32 (m, 3H), 6.87 (s, 2H), 5.86 (dd, *J* = 15.2, 8.0 Hz, 1H), 4.92 (s, 1H), 4.52 (s, 1H), 3.71 (d, *J* = 8.0 Hz, 0.6H), 3.67 (d, *J* = 10.9 Hz, 3.6H), 3.57 (d, *J* = 10,5 Hz, 3H), 1.22 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 152.9, 137.9, 135.6, 133.7, 130.8, 128.7, 128.2, 126.34, 126.28, 125.7, 125.2, 125.1, 124.5, 123.6, 73.5, 53.7 (d, *J* = 6.9 Hz), 52.7 (d, *J* = 7.1 Hz), 52.0 (d, *J* = 133.3 Hz), 34.2, 30.2. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.86. **HRMS** (**ESI**) m/z: Calcd. for $C_{28}H_{37}NaO_5P$ [M + Na]$^+$: 507.2271; Found 507.2278.

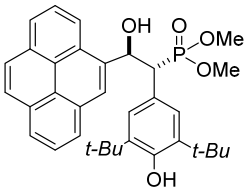


Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(pyren-1-yl)ethyl) phosphonate (3p): Combined yield: (30 mg, 0.061 mmol, 30% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone furnished *anti*-**3p** as a brown solid (15 mg, 0.027 mmol, 13% yield). The residual mixture obtained after isolation of *anti*-**3p** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3p** as a white solid (19 mg, 0.034 mmol, 17% yield).

syn-**3p: m.p.** 206-210˚C. **FT-IR (thin film)**: 3374 (br), 2951 (m), 1611 (m), 1384 (s), 1040 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 8.29 (d, *J* = 9.3 Hz, 1H), 8.19 (t, *J* = 7.2 Hz, 2H), 8.16 (d, *J* = 9.2 Hz, 1H), 8.04-7.99 (m, 2H), 7.96 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 8.0 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 6.67 (s, 2H), 6.56 (dd, *J* = 6.8, 2.9 Hz, 1H), 5.05 (s, 1H), 3.82 (d, *J* = 10.8 Hz, 3H), 3.62 (d, *J* = 3.0 Hz, 0.5H), 3.55 (d, *J* = 10.6 Hz, 3.5H), 1.16 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.3, 135.3, 134.6 (d, *J* = 13.4 Hz), 134.5, 131.4, 130.7, 130.6, 127.9, 127.6, 127.4 (d, *J* = 8.2 Hz), 127.1, 126.7, 125.9, 125.4, 125.11, 125.07, 124.8, 124.6, 124.4, 122.2, 121.4, 69.8, 54.4 (d, *J* = 6.9 Hz), 52.5 (d, *J* = 7.2 Hz), 50.5 (d, *J* = 134.6 Hz), 34.1, 30.2. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 30.75. **HRMS** (**ESI**) m/z: Calcd. for $C_{34}H_{39}NaO_5P$ [M + Na]$^+$: 581.2428; Found 5812435.

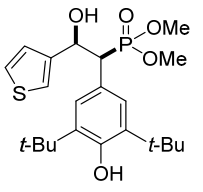


anti-**3p: m.p.** 195-200˚C. **FT-IR (thin film)**: 3436 (br), 2923 (s), 1619 (m), 1383 (s), 1042(s) cm^{-1}. **^{1}H-NMR (400 MHz, CDCl$_3$)**: δ 8.16-8.06 (m, 5H), 8.02-7.87 (m, 4H), 6.81 (s, 2H), 6.26-6.17 (m, 1H), 4.74 (s, 1H), 4.66 (d, *J* = 3.2 Hz, 1H), 3.76-3.67 (m, 4H), 3.63 (d, *J* = 10.5 Hz, 3H), 1.04 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 152.8, 135.8 (d, *J* = 13.4 Hz), 135.5, 131.3, 130.8, 130.6, 128.3, 127.4, 127.3, 127.2, 126.4, 126.3, 125.9, 125.2, 124.9, 124.8, 124.7, 124.5, 124.1, 122.9, 72.8, 53.8 (d, *J* = 7.8 Hz), 52.9 (d, *J* = 133.1 Hz), 52.8 (d, *J* = 6.5 Hz), 34.0, 29.9. **^{31}P-NMR** (**162 MHz, CDCl$_3$**): δ 30.90. **HRMS** (**ESI**) m/z: $C_{34}H_{39}NaO_5P$ [M + Na]$^+$: 581.2428; Found 5812433.

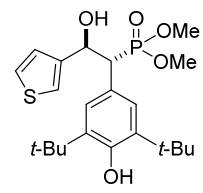


Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-(thiophen-3-yl)ethyl) phosphonate (3q): Combined yield: (57 mg, 0.129 mmol, 65% yield, 1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**3q** as a white solid (20 mg, 0.045 mmol, 23% yield). The residual mixture obtained after isolation of *anti*-**3q** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**3q** as a white solid (22 mg, 0.049 mmol, 25% yield). Note: During purification of *syn*-**3q**, a white solid (15 mg, 0.034 mmol, 17% yield) containing the mixture of diastereomers was also obtained.

syn-**3q: m.p.** 127-131˚C. **FT-IR (thin film)**: 3376 (br), 2953 (s), 1384 (s), 1039 (s) cm^{-1}. **^{1}H-NMR (500 MHz, CDCl$_3$)**: δ 7.18-7.13 (m, 1H), 7.01 (s, 2H), 6.96-6.94 (m, 1H), 6.79 (d, *J* = 4.9 Hz, 1H), 5.49 (dd, *J* = 6.7, 4.4 Hz, 1H), 5.14 (s, 1H), 3.67 (d, *J* = 10.8 Hz, 3H), 3.43 (d, *J* = 10.5 Hz, 3H), 3.25 (dd, *J* = 22.9, 4.2 Hz, 1H), 1.37 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 153.5, 142.6 (d, *J* = 12.2 Hz), 135.7, 127.3 (d, *J* = 7.7 Hz), 126.0, 125.0, 122.2, 121.9, 70.1, 54.1 (d, *J* = 6.6 Hz), 52.3 (d, *J* = 7.1 Hz), 51.7 (d, *J* = 134.7 Hz), 34.4, 30.4. **^{31}P-NMR** (**202 MHz, CDCl$_3$**): δ 29.61. **HRMS** (**ESI**) m/z: Calcd. for $C_{22}H_{33}NaO_5PS$ [M + Na]$^+$: 463.1679; Found 463.1678.



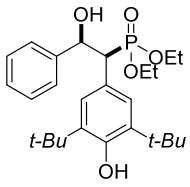
anti-**3q: m.p.** 130-135˚C. **FT-IR (thin film)**: 3428 (br), 2920 (s), 1701 (s), 1384 (s) cm^{-1}. **^{1}H-NMR (500 MHz, CDCl$_3$)**: δ 7.08 (dd, *J* = 4.9, 3.0 Hz, 1H), 6.92 (d, *J* = 1.3 Hz, 2H), 6.86 (d, *J* = 2.4 Hz, 1H), 6.73 (d, *J* = 5.0 Hz, 1H), 5.25 (dd, *J* = 12.2, 8.8 Hz, 1H), 5.09 (s, 1H), 3.69 (d, *J* = 10.8 Hz, 3H), 3.57 (d, *J* = 10.5 Hz, 3H), 3.29 (dd, *J* = 19.7, 8.8 Hz, 1H), 1.35 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 153.1, 143.6 (d, *J* = 14.1 Hz), 135.9, 126.4 (d, *J* = 7.2 Hz), 125.8, 125.0, 124.3 (d, *J* = 6.1 Hz), 121.6, 72.1 (d, *J* = 2.6 Hz), 53.7 (d, *J* = 6.9 Hz), 52.8 (d, *J* = 7.0 Hz), 52.6 (d,



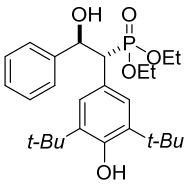
J = 132.9 Hz), 34.4, 30.4. **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 30.32. **HRMS** (**ESI**) m/z: Calcd. for $C_{22}H_{33}NaO_5PS$ $[M + Na]^+$: 463.1679; Found 463.1679.

Diethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-phenylethyl)phosphonate (4a): Combined yield: (66 mg, 0.142 mmol, 71% yield, 1.1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *anti*-**4a** as a colorless oil (32 mg, 0.069 mmol, 34% yield). The residual mixture obtained after isolation of *anti*-**4a** was repurified by column chromatography over neutral alumina with 88:12 Hexane/Acetone to obtain *syn*-**4a** as a white solid (34 mg, 0.074 mmol, 37% yield).

syn-**4a: m.p.** 100-104˚C. **FT-IR (thin film)**: 3637 (m), 3375 (br), 2926 (s), 1035 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.22-7.15 (m, 3H), 7.13-7.09 (m, 2H), 6.95 (d, *J* = 1.2 Hz, 2H), 5.40 (dd, *J* = 6.6, 4.5 Hz, 1H), 5.11 (s, 1H), 4.06-3.98 (m, 2H), 3.93-3.85 (m, 1H), 3.69-3.60 (m, 1H), 3.22 (dd, *J* = 22.8, 4.4 Hz, 1H), 1.34 (s, 18H), 1.25 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.3, 141.4 (d, *J* = 11.4 Hz), 135.6, 127.8, 127.42, 127.36, 126.7, 122.2 (d, *J* = 3.5 Hz), 73.3, 63.4 (d, *J* = 7.1 Hz), 61.7 (d, *J* = 7.2 Hz), 52.4 (d, *J* = 134.5 Hz), 34.3, 30.4, 16.4 (d, *J* = 5.9 Hz), 16.1 (d, *J* = 6.0 Hz). **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 27.46. **HRMS** (**ESI**) m/z: Calcd. for $C_{26}H_{40}O_5P$ $[M + H]^+$: 463.2608; Found 463.2615.



anti-**4a: FT-IR (thin film)**: 3371 (br), 2956 (s), 1439 (m), 1035 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.16-7.05 (m, 5H), 6.86 (s, 2H), 5.14 (dd, *J* = 12.6, 8.8 Hz, 1H), 5.02 (s, 1H), 4.08-3.93 (m, 4H), 3.27 (dd, *J* = 19.7, 8.8 Hz, 1H), 1.31 (s. 18H), 1.22 (t, *J* = 7.05 Hz, 3H), 1.18 (t, *J* = 7.1 Hz, 3H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: δ 152.9, 142.1 (d, *J* = 13.5 Hz), 135.7, 127.8, 127.3, 126.73, 126.62, 124.4 (d, *J* = 5.8 Hz), 75.6, 62.9 (d, *J* = 6.9 Hz), 62.4 (d, *J* = 6.7 Hz), 53.3 (d, *J* = 132.2 Hz), 34.3, 30.3, 16.4 (d, *J* = 4.1 Hz). **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 28.23. **HRMS** (**ESI**) m/z: Calcd. for $C_{26}H_{40}O_5P$ $[M + H]^+$: 463.2608; Found 463.2618.



Dibutyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-phenylethyl) phosphonate (4b): Combined yield: (68 mg, 0.131 mmol, 65% yield, 1.3:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Ethyl acetate furnished *syn*-**4b** as a colorless liquid (29 mg, 0.056 mmol, 28% yield) and with 85:15 Hexane/ Ethyl acetate as eluent provided *anti*-**4b** as a white solid (39 mg, 0.075 mmol, 37% yield).

syn-**4b: FT-IR (thin film)**: 3390 (br), 2954 (s), 1384 (m), 1027 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.21-7.15 (m, 3H), 7.09 (dd, *J* = 7.4, 2.0 Hz, 2H), 6.94 (d, *J* = 1.1 Hz, 2H), 5.39 (dd, *J* = 6.6, 4.3 Hz, 1H), 5.09 (s, 1H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.84-3.77 (m, 1H), 3.60-3.53 (m, 1H), 3.22 (dd, *J* = 22.7, 4.2 Hz, 1H), 1.60-1.53 (m, 2H), 1.34 (s, 18H), 1.29-1.22 (m, 4H), 1.13-1.03 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H), 0.73 (t, *J* = 7.4 Hz, 3H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.3 (d, *J* = 1.8 Hz), 141.4 (d, *J* = 11.8 Hz), 135.5, 127.8, 127.4 (d, *J* = 7.9 Hz), 127.37, 126.6, 122.2 (d, *J* = 3.5 Hz), 73.3, 67.1 (d, *J* = 7.2 Hz), 65.4 (d, *J* = 7.5 Hz), 52.3 (d, *J* = 134.5 Hz), 34.3, 32.6 (d, *J* = 5.7 Hz), 32.3 (d, *J* = 6.2 Hz), 30.4, 18.9, 18.6, 13.7, 13.6. **^{31}P-NMR** (**202 MHz, $CDCl_3$**): δ 27.40. **HRMS** (**ESI**) m/z: Calcd. for $C_{30}H_{48}O_5P$ $[M + H]^+$: 519.3234; Found 519.3241.

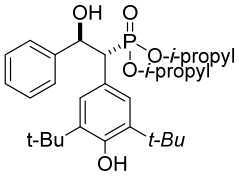
anti-**4b: m.p.** 80-84˚C. **FT-IR (thin film)**: 3428 (br), 2955 (s), 1384 (m), 1027 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.17-7.05 (m, 5H), 6.85 (s, 2H), 5.13 (dd, *J* = 12.7, 8.8 Hz, 1H), 5.01 (s, 1H), 4.01-3.86 (m, 4H), 3.28 (dd, *J* = 19.7, 8.7 Hz, 1H), 1.59-1.45 (m, 4H), 1.31 (s, 18H), 1.27-1.24 (m, 4H), 0.85 (t, *J* = 7.4 Hz, 6H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 152.8, 142.1 (d, *J* = 13.5 Hz), 135.6, 127.8, 127.3, 126.7, 126.6 (d, *J* = 6.8 Hz), 124.5 (d, *J* = 6.3 Hz), 75.6, 66.6 (d, *J* = 7.2 Hz), 66.1 (d, *J* = 6.9 Hz), 53.2 (d, *J* = 131.9 Hz), 34.3, 32.6, 32.54, 32.49, 30.4, 30.3, 18.8, 13.7. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 28.12. **HRMS** (**ESI**) m/z: Calcd. for $C_{30}H_{48}O_5P$ $[M + H]^+$: 519.3234; Found 519.3240.

Diisopropyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-phenylethyl) phosphonate (4c): Combined yield: (55 mg, 0.112 mmol, 56% yield, 1.5:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 94:6 Hexane/Ethyl acetate furnished *syn*-**4c** as a colorless oil (22 mg,0.045 mmol, 22% yield) and with 93:7 Hexane/Ethyl acetate as eluent provided *anti*-**4c** as a white solid (33 mg, 0.067 mmol, 33% yield).

syn-**4c: FT-IR (thin film)**: 3403 (br), 2927 (s), 1383 (s) cm^{-1}. **^{1}H-NMR (500 MHz, $CDCl_3$)**: δ 7.19-7.13 (m, 3H), 7.09-7.04 (m, 2H), 6.93 (s, 2H), 5.43-5.35 (m, 1H), 5.07 (s, 1H), 4.75-4.66 (m, 1H), 4.45-4.33 (m, 1H), 3.93 (s, 1H), 3.14 (dd, *J* = 23.1, 2.8 Hz, 1H), 1.33 (s, 18H), 1.28 (d, *J* = 5.8 Hz, 6H), 1.18 (d, *J* = 5.7 Hz, 3H), 0.63 (d, *J* = 5.8 Hz, 3H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 141.4, 135.5, 128.2, 127.7, 127.5 (d, *J* = 7.9 Hz), 127.2, 126.6, 73.3, 72.3 (d, *J* = 7.2 Hz), 70.4 (d, *J* = 7.5 Hz), 52.7 (d, *J* = 135.9 Hz), 34.3, 30.4, 24.6, 24.12 (d, *J* = 3.4 Hz),

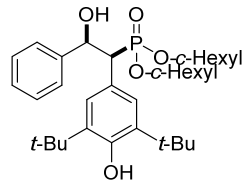
24.09, 22.7 (d, *J* = 6.4 Hz). **^{31}P-NMR (202 MHz, $CDCl_3$)**: δ 26.29. **HRMS (ESI)** m/z: Calcd. for $C_{28}H_{44}O_5P$ $[M + H]^+$: 491.2921; Found 491.2924.

anti-**4c: m.p.** 128-131˚C. **FT-IR (thin film)**: 3423 (br), 2955 (s), 1383 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.14-7.04 (m, 5H), 6.84 (s, 2H), 5.11 (dd, *J* = 12.3, 8.9 Hz, 1H), 4.99 (s, 1H), 4.72-4.59 (m, 2H), 3.19 (dd, *J* = 19.6, 8.9 Hz, 1H), 1.31 (s, 18H), 1.28 (d, *J* = 6.2 Hz, 3H), 1.22 (t, *J* = 5.8 Hz, 6H), 1.09 (d, *J* = 6.2 Hz, 3H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 152.7, 142.2 (d, *J* = 14.2 Hz), 135.5, 127.7, 127.2, 126.8, 126.7, 124.7 (d, *J* = 6.2 Hz), 75.6 (d, *J* = 2.4 Hz), 71.9 (d, *J* = 7.3 Hz), 71.2 (d, *J* = 7.2 Hz), 53.9 (d, *J* = 133.3 Hz), 34.3, 30.3, 24.5 (d, *J* = 2.8 Hz), 24.0 (d, *J* = 3.1 Hz), 23.9, 23.6 (d, *J* = 5.7 Hz). **^{31}P-NMR (162 MHz, $CDCl_3$)**: δ 26.67. **HRMS (ESI)** m/z: Calcd. for $C_{28}H_{44}O_5P$ $[M + H]^+$: 491.2921; Found 491.2927.

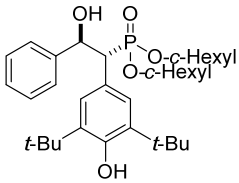


Dicyclohexyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-phenylethyl) phosphonate (4d): Combined yield: (50 mg, 0.088 mmol, 44% yield, 1.7:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 92:8 Hexane/Ethyl acetate furnished *syn*-**4d** as a colorless oil (18 mg, 0.032 mmol, 16% yield) and with 91:9 Hexane/Ethyl acetate as eluent provided *anti*-**4d** as a white solid (32 mg, 0.056 mmol, 28% yield).

syn-**4d: FT-IR (thin film)**: 3403 (br), 2927 (s), 1383 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.19-7.13 (m, 3H), 7.08-7.03 (m, 2H), 6.93 (s, 2H), 5.42 (dd, *J* = 6.8, 3.5 Hz, 1H), 5.05 (s, 1H), 4.49-4.37 (m, 1H), 4.13-4.05 (m, 1H), 3.99 (s, 1H), 3.16 (dd, *J* = 23.2, 3.3 Hz, 1H), 1.96-1.69 (m, 6H), 1.66-1.46 (m, 9H), 1.33 (s, 18H), 1.13-0.91 (m, 5H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 141.5, 135.4, 127.7, 127.6 (d, *J* = 7.8 Hz), 127.2, 126.6, 122.4, 75.4, 73.2, 52.8 (d, *J* = 135.3 Hz), 34.3, 33.9, 33.8, 32.6, 30.4, 29.5, 25.3 (d, *J* = 15.6 Hz), 23.7, 23.6, 14.3. **^{31}P-NMR (162MHz, $CDCl_3$)**: δ 26.27. **HRMS (ESI)** m/z: Calcd. for $C_{34}H_{52}O_5P$ $[M + H]^+$: 571.3547; Found 571.3558.



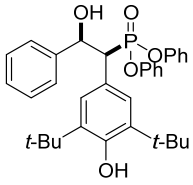
anti-**4d: m.p.** 114-117˚C. **FT-IR (thin film)**: 3423 (br), 2955 (s), 1383 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.13-7.04 (m, 5H), 6.84 (s, 2H), 5.13 (dd, *J* = 11.7, 9.3 Hz, 1H), 4.98 (s, 1H), 4.85 (s, 1H), 4.41-4.31 (m, 2H), 3.22 (dd, *J* = 19.6, 8.9 Hz, 1H), 1.90-1.83 (m, 1H), 1.81-1.70 (m, 3H), 1.66-1.57 (m, 5H), 1.51-1.38 (m, 7H), 1.31 (s, 18H), 1.23-1.16 (m, 4H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 152.7 (d, *J* = 2.4 Hz), 142.2 (d, *J* = 13.9 Hz), 135.5, 127.7, 127.2, 126.83, 126.76 (d, *J* = 7.1 Hz), 124.8 (d, *J* = 6.4 Hz), 76.6 (d, *J* = 7.4 Hz), 75.9 (d, *J* = 7.2 Hz), 75.6,



54.1 (d, *J* = 133.4 Hz), 34.3, 34.1, 33.6 (d, *J* = 3.5 Hz), 33.4 (d, *J* = 4.6 Hz), 32.0, 30.5, 30.3, 29.5, 25.2 (d, *J* = 4.1 Hz), 23.7, 23.5, 14.2. **^{31}P-NMR (162 MHz, CDCl$_3$)**: δ 26.51. **HRMS** (**ESI**) m/z: Calcd. for $C_{34}H_{51}NaO_5P$ [M + Na]$^+$: 593.3367; Found 593.3373.

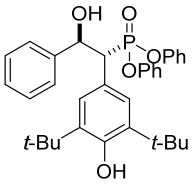
Diphenyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-phenylethyl) phosphonate (4e): Combined yield: (52 mg, 0.093 mmol, 46% yield, 1.7:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 97:3 Hexane/Ethyl acetate furnished *syn*-**4e** as a colorless oil (19 mg,0.034 mmol, 17% yield) and with 96:4 Hexane/Ethyl acetate as eluent provided *anti*-**4e** as a white solid (33 mg, 0.059 mmol, 29% yield).

syn-**4e: FT-IR (thin film)**: 3375 (br), 2954 (s), 1388 (s) cm^{-1}. **^{1}H-NMR (400 MHz, CDCl$_3$)**:



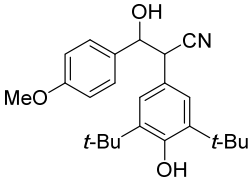
δ 7.34-7.28 (m, 2H), 7.25-7.16 (m, 6H), 7.13-7.05 (m, 4H), 7.03-6.97 (m, 3H), 6.58 (d, *J* = 7.8 Hz, 2H), 5.61-5.54 (m, 1H), 5.12 (s, 1H), 3.62 (dd, *J* = 22.9, 3.9 Hz, 1H), 3.37 (s, 1H), 1.30 (s, 18H). **^{13}C{^{1}H}-NMR (100 MHz, CDCl$_3$)**: δ 153.7 (d, *J* = 2.4 Hz), 150.8 (d, *J* = 9.3 Hz), 150.2 (d, *J* = 10.2 Hz), 140.9 (d, *J* = 11.3 Hz), 135.9, 129.8, 129.3, 128.0, 127.8 (d, *J* = 8.2 Hz), 127.6, 126.8, 125.4, 124.8, 120.9 (d, *J* = 3.9 Hz), 120.8 (d, *J* = 4.4 Hz), 120.4 (d, *J* = 4.3 Hz), 73.4, 52.9 (d, *J* = 134.3 Hz), 34.3, 30.3. **^{31}P-NMR (162MHz, CDCl$_3$)**: δ 19.76. **HRMS** (**ESI**) m/z: Calcd. for $C_{34}H_{39}NaO_5P$ [M + Na]$^+$: 581.2427; Found 581.2432.

anti-**4e: m.p.** 110-115˚C. **FT-IR (thin film)**: 3406 (br), 2954 (s), 1386 (s), 1198 (s) cm^{-1}. **^{1}H-NMR (500 MHz, CDCl$_3$)**:



δ 7.29 (t, *J* = 7.9 Hz, 2H), 7.19-7.08 (m, 10H), 7.06 (t, *J* = 7.3 Hz, 1H), 6.87 (s, 2H), 6.81 (d, *J* = 8.0 Hz, 2H), 5.35 (dd, *J* = 11.9, 9.0 Hz, 1H), 5.05 (s, 1H), 3.64 (dd, *J* = 20.3, 8.9 Hz, 1H), 1.27 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 153.2 (d, *J* = 2.6 Hz), 150.8 (d, *J* = 9.5 Hz), 150.4 (d, *J* = 9.3 Hz), 141.8 (d, *J* = 13.8 Hz), 135.9, 129.7, 129.5, 127.9, 127.6, 126.9 (d, *J* = 7.8 Hz), 126.7, 125.3, 124.9, 123.3 (d, *J* = 6.2 Hz), 121.0 (d, *J* = 4.3 Hz), 120.4 (d, *J* = 4.6 Hz), 75.8 (d, *J* = 2.6 Hz), 53.7 (d, *J* = 133.0 Hz), 34.3 30.3. **^{31}P-NMR (202 MHz, CDCl$_3$)**: δ 21.03. **HRMS** (**ESI**) m/z: Calcd. for $C_{34}H_{39}NaO_5P$ [M + Na]$^+$: 581.2427; Found 581.2429.

2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-hydroxy-3-(4-methoxyphenyl) propanenitrile

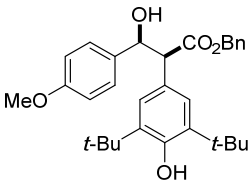


(4f): Purification by column chromatography over 230-400 silica gel mesh with 96:4 Hexane/THF as eluent furnished a colorless oil containing the diastereomeric mixture (42 mg, 0.11 mmol, 55% yield, 1.3:1 dr). **FT-IR (thin film)**: 3420 (br), 3155 (s), 2243 (m), 2956 (s), 1394 (s) cm^{-1}. **^{1}H-NMR (500 MHz, CDCl$_3$)**: δ 7.19 (d, *J* = 8.6 Hz, 1H), 7.12 (d, *J* = 8.5 Hz,

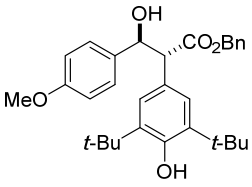
1H), 6.92 (s, 1H), 6.89-6.85 (m, 2H), 6.83 (d, *J* = 8.6 Hz, 1H), 5.27 (s, 0.55H), 5.23 (s, 0.42H), 4.88-4.82 (m, 1H), 4.01 (d, *J* = 6.7 Hz, 0.56H), 3.91 (d, *J* = 6.2 Hz, 0.43H), 3.81 (s, 1.69H), 3.79 (s, 1.25H), 1.39 (s, 9.8H), 1.37 (s, 7.7H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 160.0, 159.9, 154.1, 153.9, 136.6, 136.4, 131.9, 131.3, 128.1, 127.7, 125.5, 125.2, 122.9, 122.6, 119.6, 119.4, 113.9, 76.4, 76.0, 55.5, 47.5, 46.8, 34.5, 34.4, 30.2. **HRMS** (**ESI–**) m/z: Calcd. for $C_{24}H_{30}NO_3$ $[M - H]^-$: 380.2231; Found 380.2230.

Benzyl-2-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-hydroxy-3-(4methoxyphenyl) propanoate (4g): Combined yield: (63 mg, 0.128 mmol, 64% yield, 1.5:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 96:4 Hexane/Ethyl acetate furnished *anti*-**4g** as a brown solid (25 mg, 0.051 mmol, 26% yield) and with 95:5 Hexane/Ethyl acetate as eluent provided *syn*-**4g** as a colorless oil (38 mg, 0.077 mmol, 38% yield).

syn-**4g: FT-IR (thin film)**: 3414 (br), 2951 (s), 1725 (m), 1391 (s) cm^{-1}. **^{1}H-NMR (500 MHz, CDCl$_3$)**: δ 7.34-7.26 (m, 5H), 6.94 (d, *J* = 8.5 Hz, 2H), 6.74 (s, 2H), 6.71 (d, *J* = 8.5 Hz, 2H), 5.21 (q, *J* = 12.4 Hz, 2H), 5.06 (s, 1H), 5.02 (d, *J* = 9.0 Hz, 1H), 3.79 (d, *J* = 9.0 Hz, 1H), 3.74 (s, 3H), 3.05 (s, 1H), 1.29 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 173.8, 159.1, 153.1, 135.9, 135.8, 133.5, 128.6, 128.2, 128.1, 127.9, 125.8, 125.3, 113.4, 76.7, 66.7, 60.1, 55.3, 34.3, 30.3. **HRMS** (**ESI**) m/z: Calcd. for $C_{31}H_{38}NaO_5$ $[M + Na]^+$: 513.2611; Found 513.2609.



anti-**4g: m.p.** 100-103˚C. **FT-IR (thin film)**: 3440 (s), 2954 (s), 1726 (m), 1245 (m) cm^{-1}. **^{1}H-NMR (500 MHz, CDCl$_3$)**: δ 7.26-7.20 (m, 5H), 7.16 (s, 2H), 6.99 (d, *J* = 4.2 Hz, 2H), 6.80 (d, *J* = 7.9 Hz, 2H), 5.19 (s, 1H), 5.12 (d, *J* = 8.3 Hz, 1H), 5.01 (d, *J* = 12.3 Hz, 1H), 4.83 (d, *J* = 12.3 Hz, 1H), 3.80 (s, 1H), 3.78 (s, 3H), 2.29 (s, 1H), 1.39 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, CDCl$_3$)**: δ 172.3, 159.5, 153.9, 136.3, 135.7, 133.2, 128.5, 128.3, 128.1, 128.0, 125.8, 125.3, 113.8, 75.3, 66.4, 60.4, 55.4, 34.5, 30.4. **HRMS** (**ESI**) m/z: Calcd. for $C_{31}H_{38}NaO_5$ $[M + Na]^+$: 513.2611; Found 513.2610.



Dimethyl((3,5-di-*tert*-butyl-4-hydroxyphenyl)(1-hydroxycyclohexyl)methyl phosphonate (5a): yield: (16 mg, 0.037 mmol, 18% yield). Purification by column chromatography over 230-400 silica gel mesh with 97:03 DCM/Ethyl acetate as eluent to obtain the colorless oil product.

FT-IR (thin film): 3382 (br), 2925 (s), 1386 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.17 (s, 2H), 5.14 (s, 1H), 3.75-3.69 (m, 1H), 3.63 (d, *J* = 10.4 Hz, 3H), 3.50 (d, *J* = 9.6 Hz, 3H), 2.56 (s, 1H), 2.36-2.25 (m, 1H), 1.42 (s, 18H), 1.39-1.37 (m, 1H), 1.28-1.24 (m, 3H), 1.08 (s, 2H), 1.01 (d, *J* = 7.2 Hz, 3H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: δ 153.1, 135.8, 127.9 (d, *J* = 7.9 Hz), 125.1, 73.8 (d, *J* = 12.2 Hz), 65.1 (d, *J* = 141.2 Hz), 53.5 (d, *J* = 7.2 Hz), 52.8 (d, *J* = 7.2 Hz), 44.5 (d, *J* = 8.1 Hz), 43.2, 34.5, 30.5, 26.9, 24.8, 14.4 (d, *J* = 5.4 Hz). **^{31}P-NMR (162MHz, $CDCl_3$)**: δ 33.55. **HRMS (ESI)** m/z: Calcd. for $C_{23}H_{40}O_5P$ $[M + H]^+$: 427.2608; Found 427.2610.

Dimethyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxyethyl) phosphonate (5b): Purification by column chromatography over 230-400 silica gel mesh with 85:15 Hexane/Acetone as eluent provided a white solid (44 mg, 0.122 mmol, 61% yield).

m.p. 122-125˚C.**FT-IR (thin film)**: 3389 (br), 2955 (s), 1041 (s), 767 (m) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.12 (d, *J* = 1.7 Hz, 2H), 5.19 (s, 1H), 4.22-4.11 (m, 1H), 4.06-3.94 (m, 1H), 3.71 (d, *J* = 10.7 Hz, 3H), 3.54 (d, *J* = 10.5 Hz, 3H), 3.27 (dt, *J* = 21.5, 6.9 Hz, 1H), 2.54 (s, 1H), 1.43 (s, 18H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.5, 136.4, 125.9 (d, *J* = 6.6 Hz), 123.9 (d, *J* = 6.5 Hz), 62.9, 53.6 (d, *J* = 6.9 Hz), 52.7 (d, *J* = 7.1 Hz), 46.9 (d, *J* = 133.7 Hz), 34.5, 30.4. **^{31}P-NMR (162MHz, $CDCl_3$)**: δ 29.74. **HRMS (ESI)** m/z: Calcd. for $C_{18}H_{31}NaO_5P$ $[M + Na]^+$: 381.1802; Found 381.1816.

Dimethyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxypropyl) phosphonate (5c): Combined yield: (56 mg, 0.150 mmol, 75% yield, 1.1:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 86:14 Hexane/Acetone furnished *syn*-**5c** as a colorless oil (29 mg, 0.078 mmol, 39% yield) and with 86:14 Hexane/Acetone as eluent to obtain *anti*-**5c** as a white solid (27 mg, 0.072 mmol, 36% yield).

syn-**5c: FT-IR (thin film)**: 3381 (br), 2954 (s), 1041 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.20 (s, 2H), 5.18 (s, 1H), 4.43 (s, 1H), 3.73 (d, *J* = 10.3 Hz, 3H), 3.35 (d, *J* = 9.9 Hz, 3H), 3.07-2.91 (m, 2H), 1.43 (s, 18H), 1.24 (d, *J* = 13.4 Hz, 3H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.5, 136.2, 127.1 (d, *J* = 7.1 Hz), 122.9, 67.1, 53.9 (d, *J* = 6.9 Hz), 52.2 (d, *J* = 7.2 Hz), 51.2 (d, *J* = 133.7 Hz), 34.5, 30.5, 21.2 (d, *J* = 10.2 Hz). **^{31}P-NMR (162MHz, $CDCl_3$)**: δ 30.06 (s). **HRMS (ESI)** m/z: Calcd. for $C_{19}H_{34}O_5P$ $[M + H]^+$: 373.2139; Found 373.2148.

anti-**5c: m.p.** 140-143˚C. **FT-IR (thin film)**: 3407 (br), 2924 (s), 1043 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.02 (d, *J* = 2.1 Hz, 2H), 5.16 (s, 1H), 4.43-4.32 (m, 1H), 3.83 (s, 1H), 3.69 (d, *J* = 10.8 Hz, 3H), 3.52 (d, *J* = 10.4 Hz, 3H), 2.98 (dd, *J* = 20.2, 8.8 Hz, 1H), 1.42 (s, 18H), 1.08 (dd, *J* = 6.1, 0.8 Hz, 3H). **^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)**: δ 153.2, 136.2, 126.1 (d, *J* = 6.8 Hz), 124.8 (d, *J* = 7.3 Hz), 68.3, 53.6 (d, *J* = 6.9 Hz), 52.73 (d, *J* = 7.1 Hz), 52.69 (d, *J* = 132.5 Hz), 34.4, 30.5, 22.1 (d, *J* = 13.6 Hz). **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 30.67. **HRMS** (**ESI**) m/z: Calcd. for $C_{19}H_{34}O_5P$ $[M + H]^+$: 373.2139; Found 373.2148.

Dimethyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxybutyl) phosphonate (5d): Combined yield: (21 mg, 0.054 mmol, 27% yield, 6.6:1 dr). Purification by column chromatography over 230-400 silica gel mesh with 87:13 Hexane/Acetone furnished *syn*-**5d** as a colorless oil (03 mg, 0.007 mmol, 04% yield) a minor diastereomer and with 86:14 Hexane/Acetone as eluent to obtain *anti*-**5d** as a white solid (18 mg, 0.046 mmol, 23% yield) a major diastereomer.

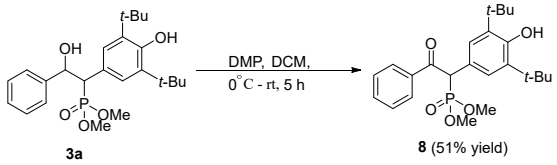
syn-**5d: FT-IR (thin film)**: 3394 (br), 2952 (m), 1045 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.21 (s, 2H), 5.16 (s, 1H), 4.20-4.09 (m, 1H), 3.74 (d, *J* = 10.6 Hz, 3H), 3.35 (d, *J* = 10.3 Hz, 3H), 3.19 (s, 1H), 3.06 (d, *J* = 24.4 Hz, 1H), 1.49-1.45 (m, 2H), 1.43 (s, 18H), 0.94 (t, *J* = 7.2 Hz, 3H). **^{31}P-NMR** (**162MHz, $CDCl_3$**): δ 30.77. **HRMS** (**ESI**) m/z: Calcd. for $C_{20}H_{37}O_5P$ $[M + H]^+$: 387.2295; Found 387.2301.

anti-**5d: m.p.** 145-148˚C. **FT-IR (thin film)**: 3405 (br), 2926 (s), 1042 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.05 (d, *J* = 1.8 Hz, 2H), 5.16 (s, 1H), 4.19-4.07 (m, 1H), 3.69 (d, *J* = 10.8 Hz, 3H), 3.48 (d, *J* = 10.4 Hz, 3H), 3.07 (dd, *J* = 20.7, 8.7 Hz, 1H), 1.42 (s, 18H), 1.34-1.26 (m, 2H), 0.90 (t, *J* = 7.3 Hz, 3H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: δ 153.2 (d, *J* = 3.3 Hz), 136.2 (d, *J* = 2.3 Hz), 126.2 (d, *J* = 6.7 Hz), 124.9 (d, *J* = 7.4 Hz), 73.1 (d, *J* = 4.1 Hz), 53.7 (d, *J* = 7.1 Hz), 52.6 (d, *J* = 6.9 Hz), 50.8 (d, *J* = 132.8 Hz), 34.5, 30.5, 28.2 (d, *J* = 12.4 Hz), 9.5. **^{31}P-NMR** (**162 MHz, $CDCl_3$**): δ 31.03. **HRMS** (**ESI**) m/z: Calcd. for $C_{20}H_{37}O_5P$ $[M + H]^+$: 387.2295; Found 387.2300.

Dimethyl(1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-hydroxy-2-methylpropyl) phosphonate (5e): Purification by column chromatography over 230-400 silica gel mesh with 88:12 Hexane/Acetone as eluent furnished a colorless oil (32 mg, 0.083 mmol, 41% yield).

FT-IR (thin film): 3414 (br), 2954 (s), 1040 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.19 (s, 2H), 5.16 (s, 1H), 4.09 (s, 1H), 3.70 (d, *J* = 10.7 Hz, 3H), 3.38 (d, *J* = 10.2 Hz, 3H), 3.11 (d, *J* = 23.4 Hz, 1H), 1.42 (s, 18H), 1.26 (s, 6H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: δ 153.3, 135.8, 127.3, 124.8, 72.2, 55.2 (d, *J* = 130.3 Hz), 53.7 (d, *J* = 6.3 Hz), 52.1 (d, *J* = 6.2 Hz), 34.5, 30.5, 28.3 (d, *J* = 8.7 Hz). **^{31}P-NMR (162MHz, $CDCl_3$)**: δ 30.83. **HRMS (ESI)** m/z: Calcd. for $C_{20}H_{36}O_5P$ $[M + H]^+$: 387.2295; Found 387.2308.

E. Synthesis of β-ketophosphonate (8):

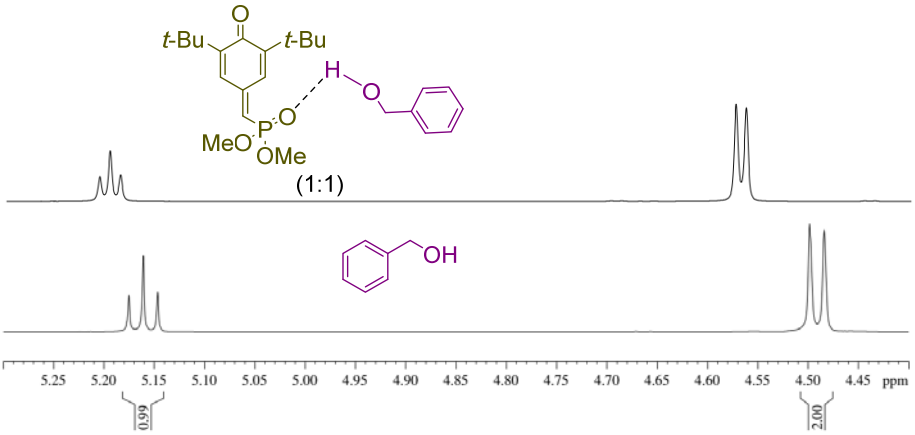


Dimethyl (1-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-2-oxo-2-phenylethyl) phosphonate (8): In an oven dried 25 mL two neck round bottom flask, DMP (dess-Martin Periodinane) (0.10 mmol., 2.0 equiv.) was added. The flask was cooled to 0° C and a solution of *anti*-**3a** (0.05 mmol., 1.0 equiv.) in CH_2Cl_2 (2.0 mL) was added. After addition, the resulting mixture was stirred at 25 °C for 5h. The reaction mixture was concentrated under reduced pressure. Purification by column chromatography over 230-400 silica gel mesh using 86:14 Hexane/Acetone as eluent furnished a colorless oil (11 mg, 0.025 mmol, 51% yield). **FT-IR (thin film)**: 3413 (br), 2955 (s), 1677 (s), 1042 (s) cm^{-1}. **^{1}H-NMR (400 MHz, $CDCl_3$)**: δ 7.97 (d, *J* = 7.3 Hz, 2H), 7.53 (t, *J* = 7.4 Hz, 1H), 7.46-7.40 (m, 2H), 7.30 (d, *J* = 2.4 Hz, 2H), 5.29 (d, *J* = 21.9 Hz, 1H), 5.20 (s, 1H), 3.73 (d, *J* = 10.8 Hz, 3H), 3.67 (d, *J* = 10.8 Hz, 3H), 1.42 (s, 18H). **^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)**: δ 194.2 (d, *J* = 4.9 Hz), 153.8 (d, *J* = 4.5 Hz), 136.8 (d, *J* = 5.9 Hz), 136.4 (d, *J* = 2.7 Hz), 133.4, 129.1, 128.7, 126.5 (d, *J* = 6.1 Hz), 121.4 (d, *J* = 9.2 Hz), 53.9 (d, *J* = 5.1 Hz), 53.8 (d, *J* = 6.1 Hz), 53.6 (d, *J* = 138.2 Hz), 34.5, 30.4. **^{31}P-NMR (162MHz, $CDCl_3$)**: δ 23.08. **HRMS (ESI)** m/z: Calcd. for $C_{24}H_{34}O_5P$ $[M + H]^+$: 433.2138; Found 433.2150.

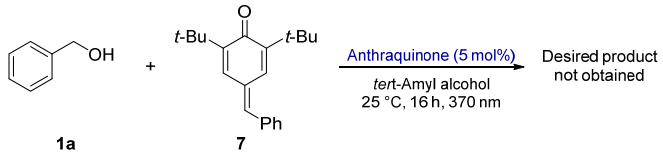
F. Mechanistic studies and control experiments:

(i). H-bonding interaction between substrate-

Reaction faciliated by H- bonding interaction between substrate:

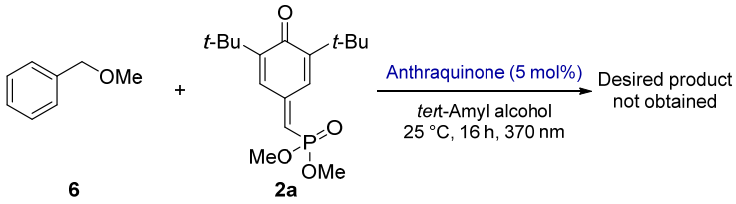


To gain mechanistic insight, the ^{1}H-NMR titration was conducted between benzyl alcohol **(1a)** and *p*-QM **2a**. An equimolar mixture of both components, showed a downfield shift in the NMR which showed the possibility of H-bonding interaction between both substrates.



In an oven dried 5 mL reaction vial, **1a** (10.8 mg, 0.1 mmol, 1.0 equiv.), **7** (44.2 mg, 0.15 mmol, 1.5 equiv.) and **anthraquinone** (1.0 mg, 0.005 mmol, 5 mol%) were taken. The reaction vial was covered with a rubber septum and *tert*-amyl alcohol (0.1M) was added. The reaction mixture was degassed with Nitrogen by freeze-thaw (three times) and the solution was irradiated with 370 nm LED. Under these conditions, the desired product was not obtained and thus demonstrating the critical role of suitable group on *p*-QM.

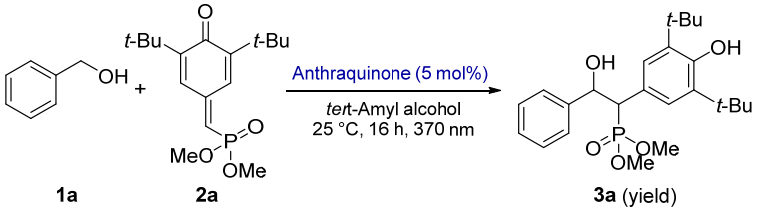
(ii). Role of hydroxy group in the reaction-



In an oven dried 5 mL reaction vial, **6** (12.2 mg, 0.1 mmol, 1.0 equiv.), **2a** (48.9 mg, 0.15 mmol, 1.5 equiv.) and **anthraquinone** (01 mg, 0.005 mmol, 5 mol%) were taken. The reaction vial was covered with a rubber septum and *tert*-amyl alcohol (0.1M) was added. The reaction mixture was degassed with Nitrogen by freeze-thaw (three times) and the solution was

irradiated with 370 nm LED. No α-functionalized was product obtained and thus demonstrating the critical role of the hydroxy group.

(iii). Light ON-OFF experiment:

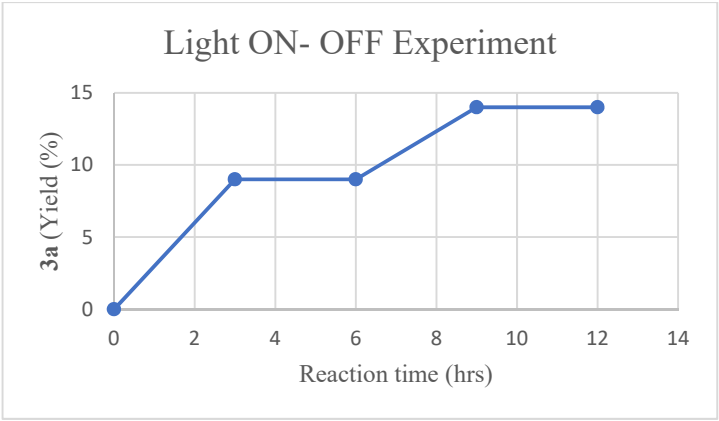


1a **2a** **3a** (yield)

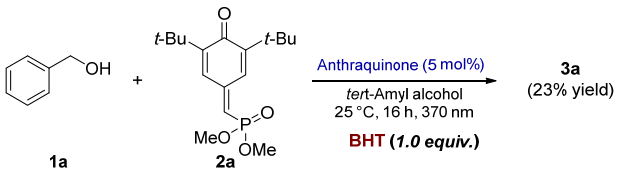
In an oven dried 5 mL reaction vial, **1a** (10.8 mg, 0.1 mmol, 1.0 equiv.), **2a** (48.9 mg, 0.15 mmol, 1.5 equiv.) and **anthraquinone** (1.0 mg, 0.005 mmol, 5 mol%) were taken. The reaction vial was covered with a rubber septum and *tert*-amyl alcohol (0.1M) was added. The reaction mixture was degassed with Nitrogen by freeze-thaw (three times) and the solution was irradiated with 370 nm LED at fixed intervals. The reaction proceeded only in the presence of light and the continuous irradiation is essential for the reaction.

Conditions	Yield (%)[b]
3h, ON	09
3h, ON — 3h, OFF	09
3h, ON — 3h, OFF — 3h, ON	14
3h, ON — 3h, OFF — 3h, ON — 3h, OFF	14

[a]Reaction condition: **1a** (0.1 mmol, 0.1 equiv.), **2a** (0.15 mmol, 1.5 equiv.), AQ (5 mol%), [b] Isolated yield.

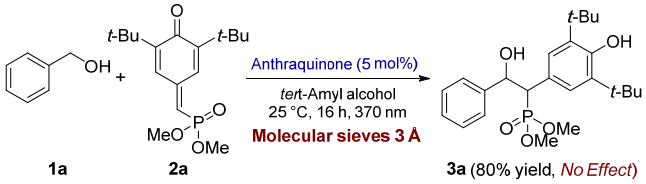


(iv). Reaction with radical trapping agent:



In an oven dried 5 mL reaction vial, **1a** (10.8 mg, 0.1 mmol, 1.0 equiv.), **2a** (48.9 mg, 0.15 mmol,1.5 equiv.), **anthraquinone** (1.0 mg, 0.005 mmol, 5 mol%) and **BHT** (0.1 mmol, 1.0 equiv.) were taken. The reaction vial was covered with a rubber septum and (0.1 M) *tert*-amyl alcohol was added. The reaction mixture was degassed with Nitrogen by freeze-thaw (three times) and the solution was irradiated with 370 nm LED. The reaction furnished **3a** with a reduced yield of 23% and suggesting that the reaction proceeds through a radical pathway.

(v). Effect of molecular sieves in the reaction:



To check the possibility of H-transfer from the moisture, the optimal reaction was conducted in the presence of 3A° molecular sieve. The reaction was unaffected by the use of molecular sieves and thus suggesting no role of residual moisture.

G. X-Ray data:

Crystallization: Crystals of compound *syn*-**3a** were grown from the solvents CH_2Cl_2-Hexane by slow evaporation method.

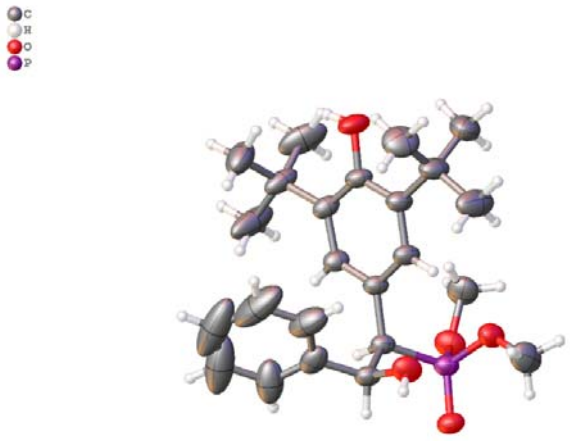


Figure 1 ORTEP diagram drawn with 50% ellipsoid probability for non-H atoms of the crystal structure of compound *syn*-**3a** determined at 295.15 K.

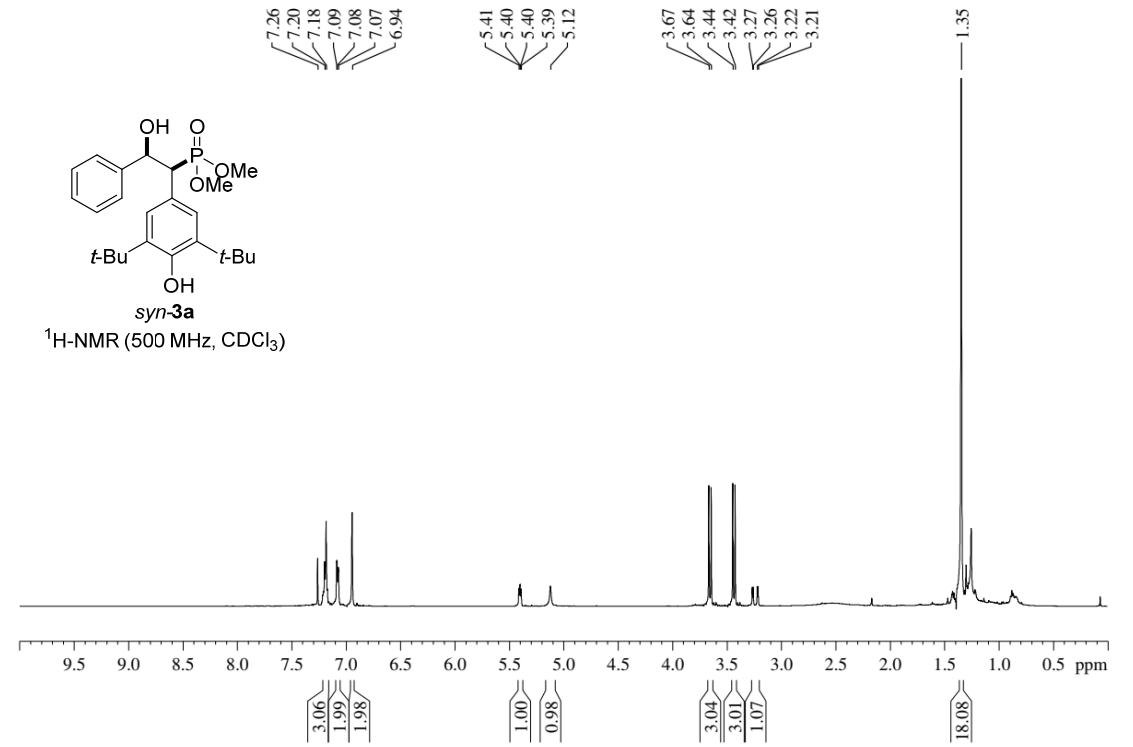
Table 1 Crystal data and structure refinement details for *syn*-**3a.**

Compound	*syn*-**3a**
Identification code	XRF24062025B_auto
Empirical formula	$C_{24}H_{35}O_5P$
Formula weight	434.513
Temperature/K	296.06(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	9.61485(13)
b/Å	16.6523(2)
c/Å	16.0640(2)
α/°	90
β/°	94.6663(12)
γ/°	90
Volume/Å^3	2563.49(6)
Z	4
ρ_{calc}g/cm^3	1.126
μ/mm^{-1}	1.185
F(000)	940.1
Crystal size/mm^3	0.15 × 0.1 × 0.06
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.66 to 155.88
Index ranges	$-12 \le h \le 11$, $-20 \le k \le 13$, $-20 \le l \le 19$
Reflections collected	18209
Independent reflections	5210 [R_{int} = 0.0321, R_{sigma} = 0.0270]
Data/restraints/parameters	5210/0/281
Goodness-of-fit on F^2	1.046
Final R indexes [I>=2σ (I)]	R_1 = 0.0512, wR_2 = 0.1409
Final R indexes [all data]	R_1 = 0.0601, wR_2 = 0.1462
Largest diff. peak/hole / e Å^{-3}	0.30/-0.54

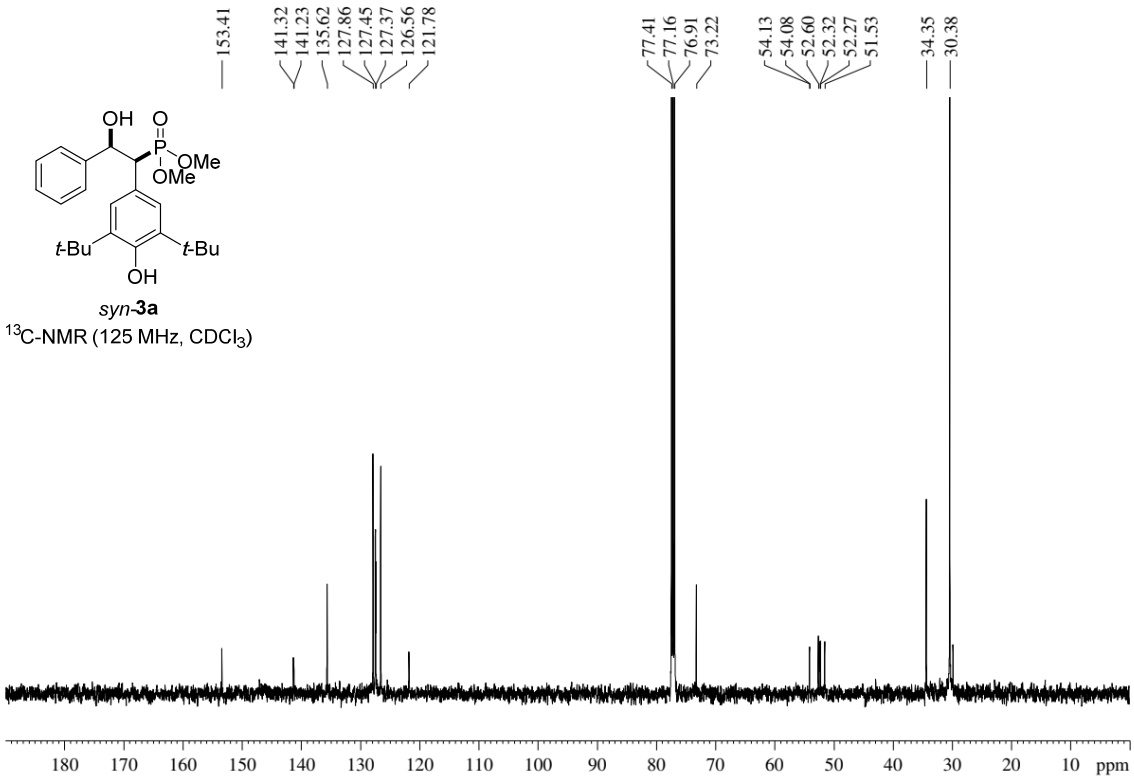
H. References:

(1). (a) J. Jose, A. Yadav and C. B. Tripathi, *Chem. Commun.*, 2024, **60**, 11315-11318. (b) A. Yadav, D. Kumar, M. K. Mishra, Deeksha and C. B. Tripathi, *J. Org. Chem.*, 2021, **86**, 2000-2011.

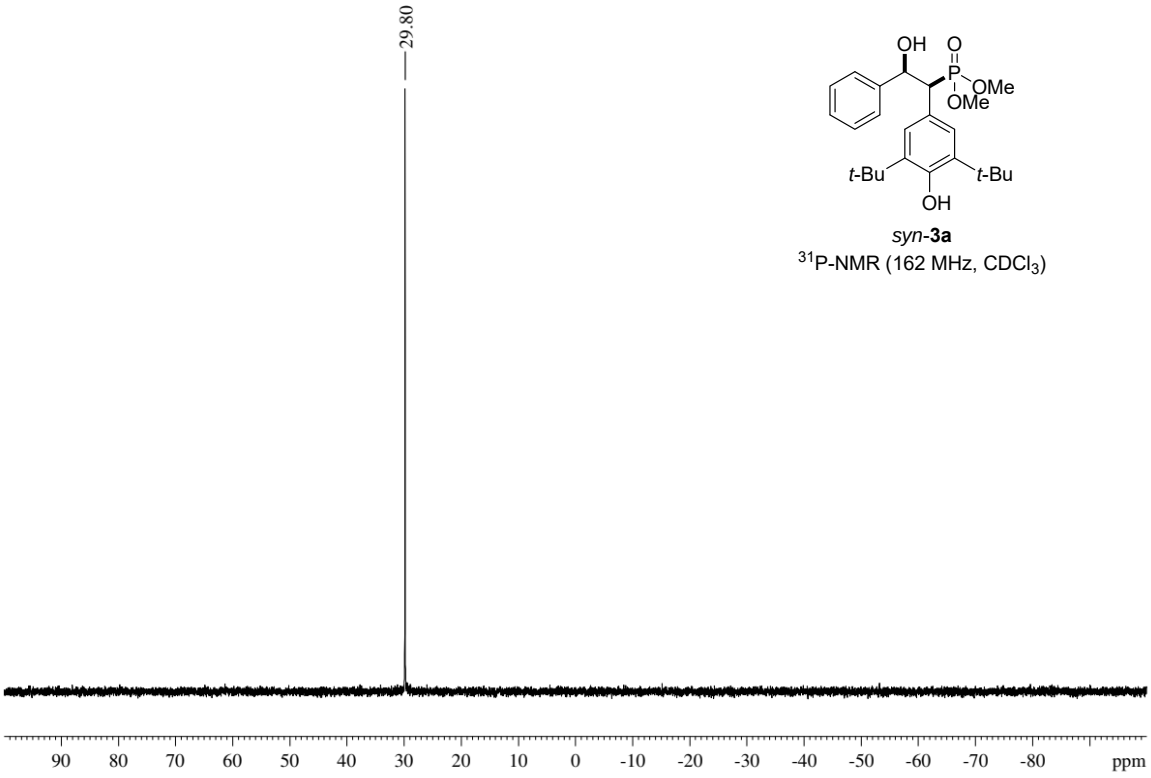
I. Spectra of compounds:



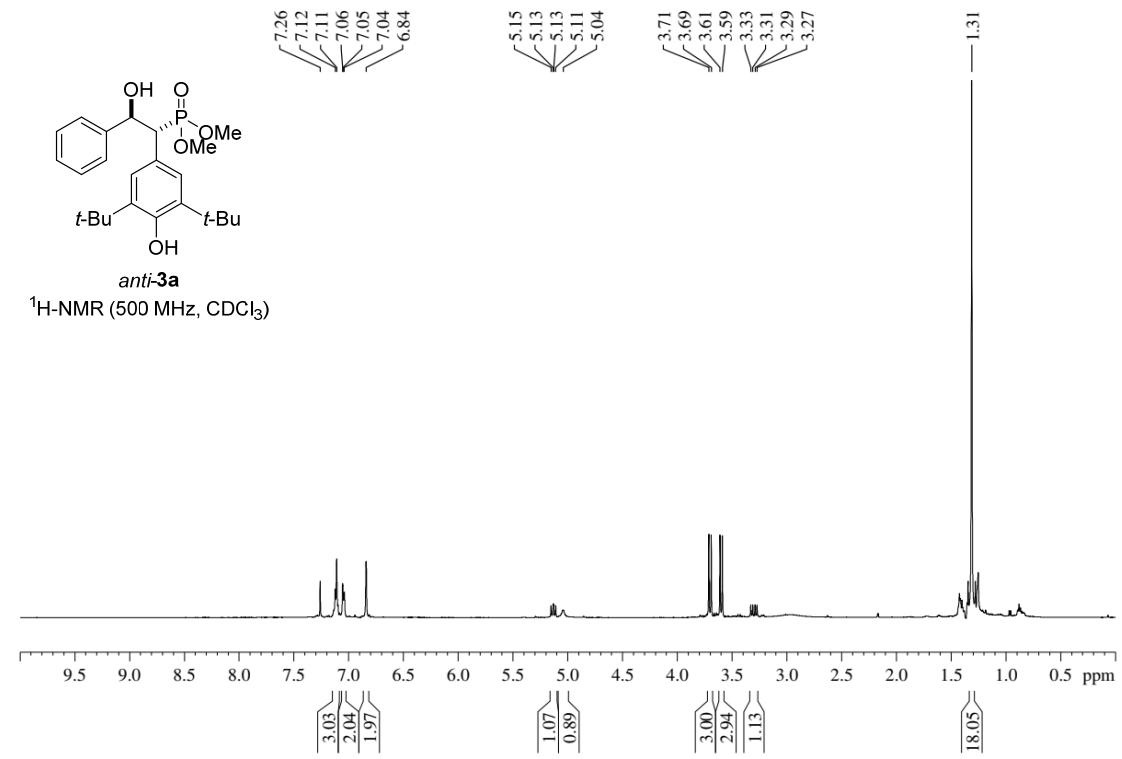
syn-**3a**
^{1}H-NMR (500 MHz, $CDCl_3$)



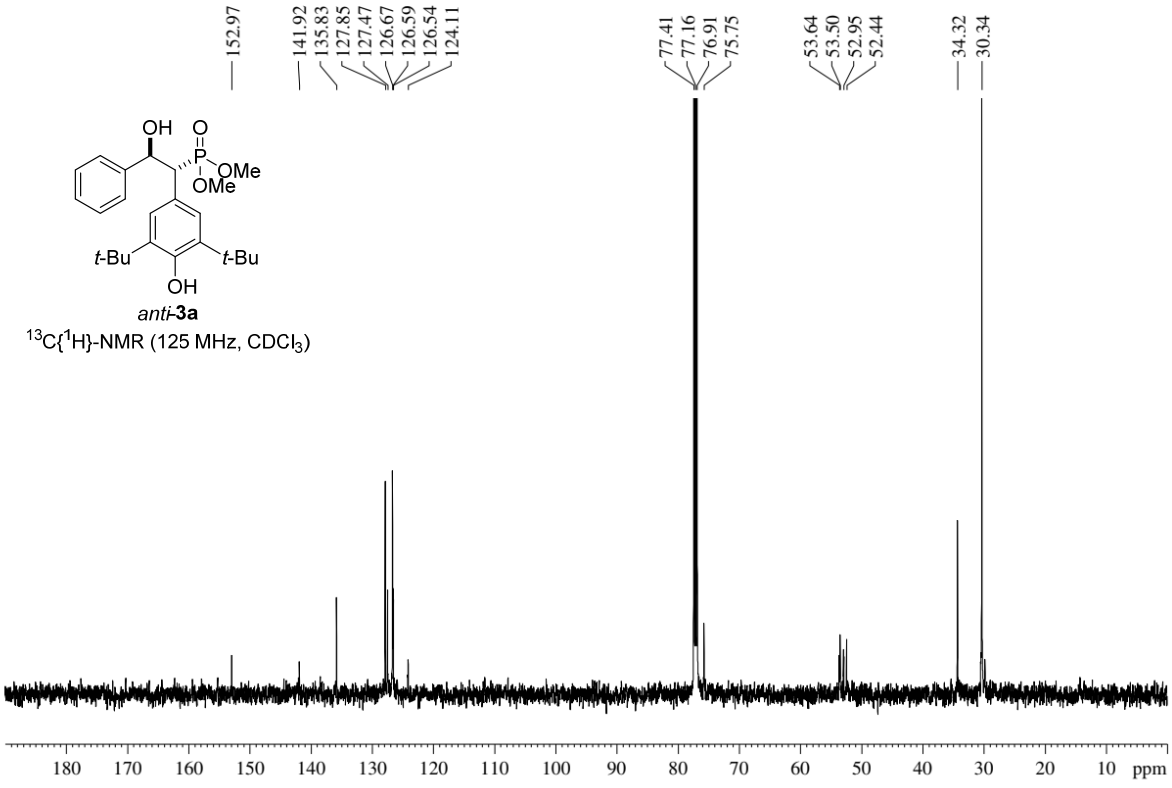
syn-**3a**
^{13}C-NMR (125 MHz, $CDCl_3$)



syn-**3a**
^{31}P-NMR (162 MHz, $CDCl_3$)

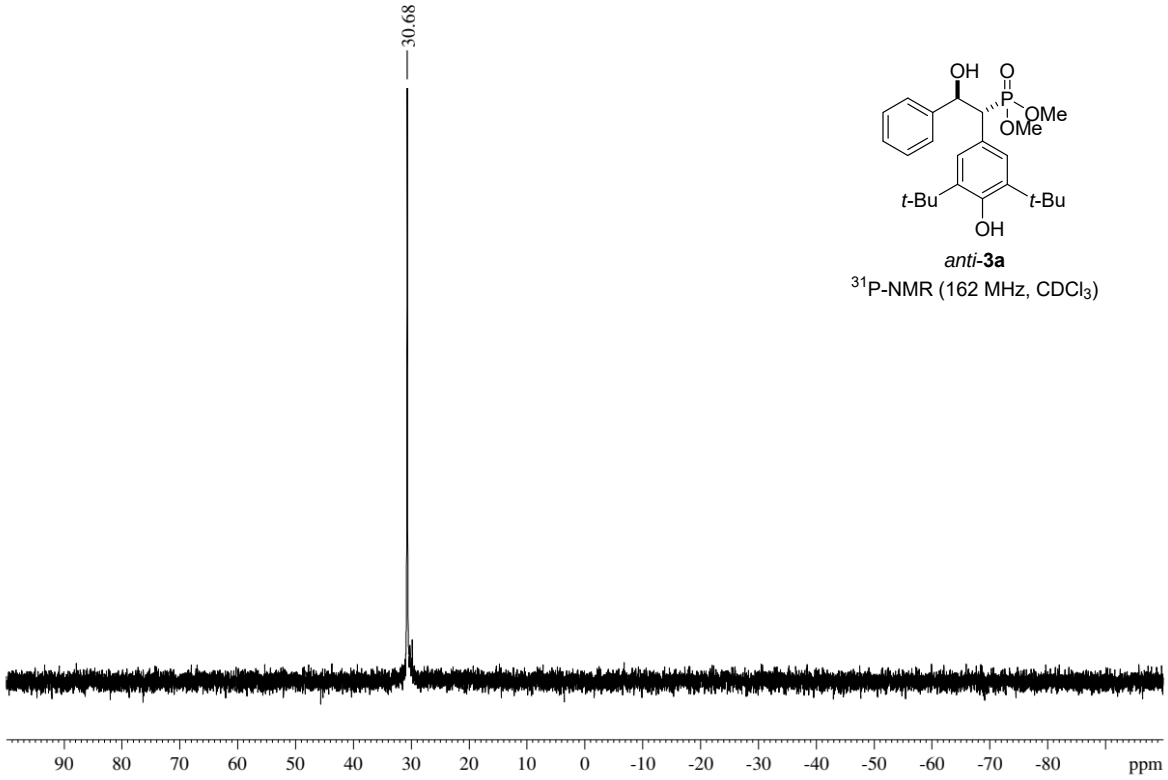


anti-**3a**
^{1}H-NMR (500 MHz, $CDCl_3$)



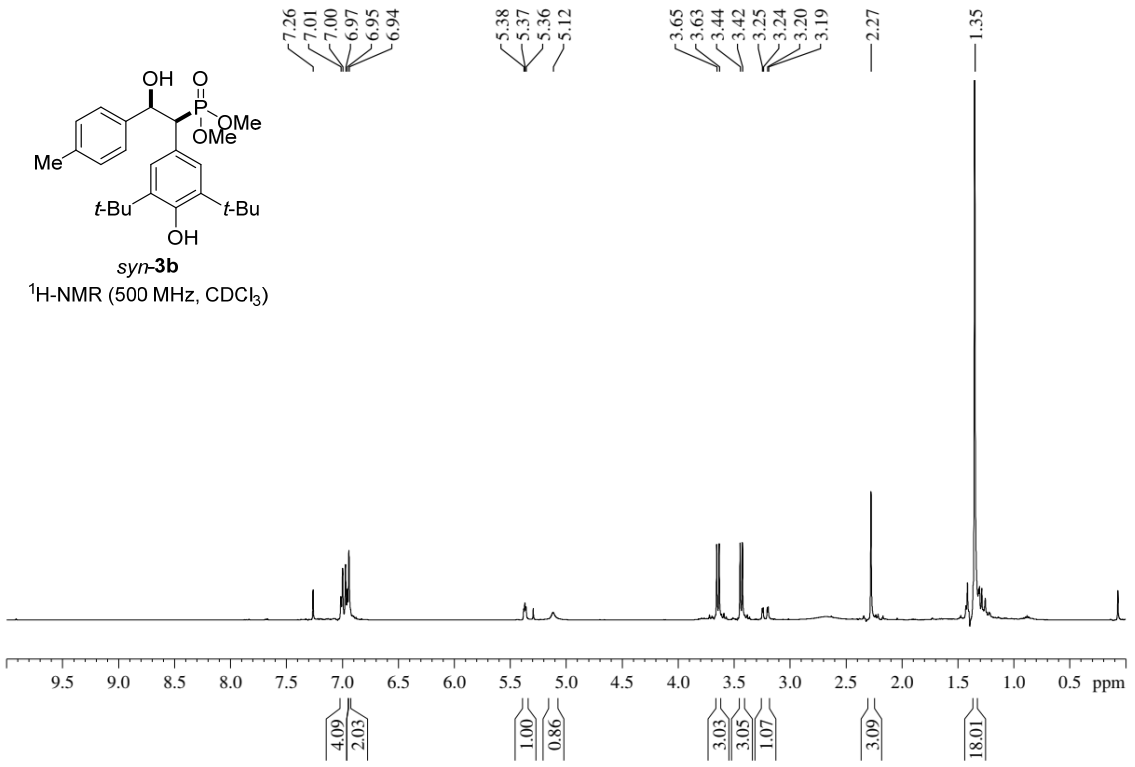
anti-**3a**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



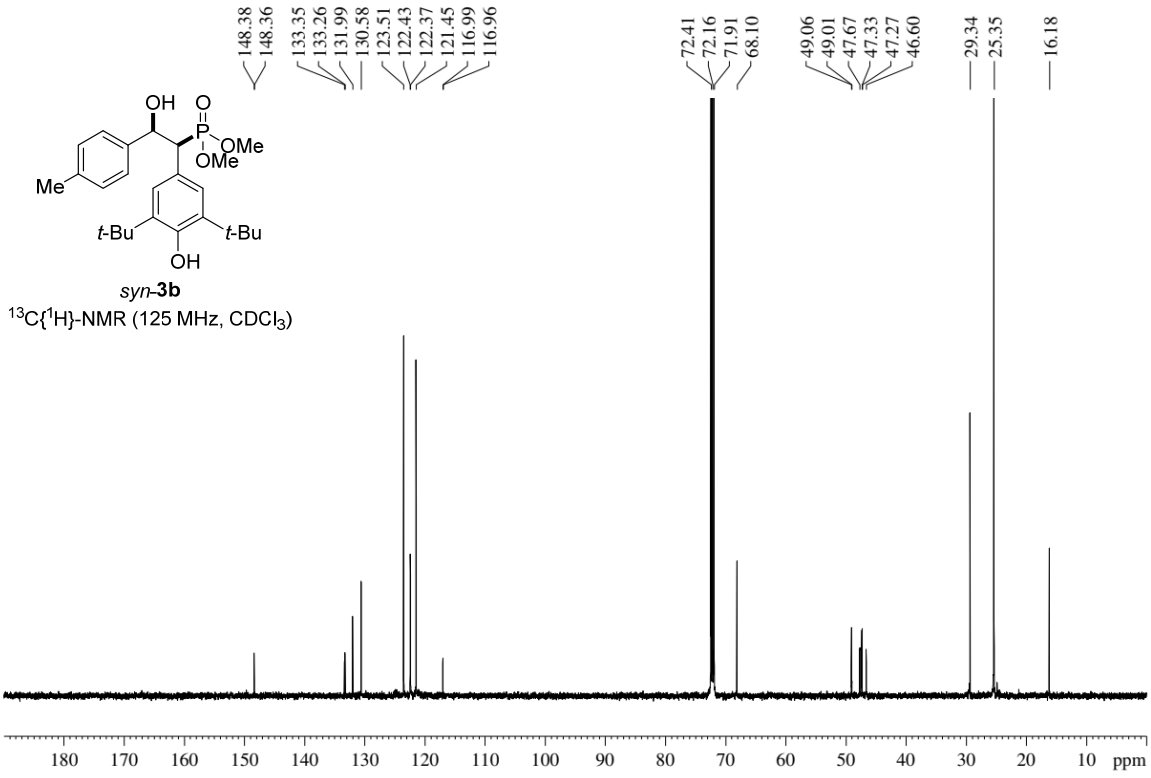
anti-**3a**

^{31}P-NMR (162 MHz, $CDCl_3$)



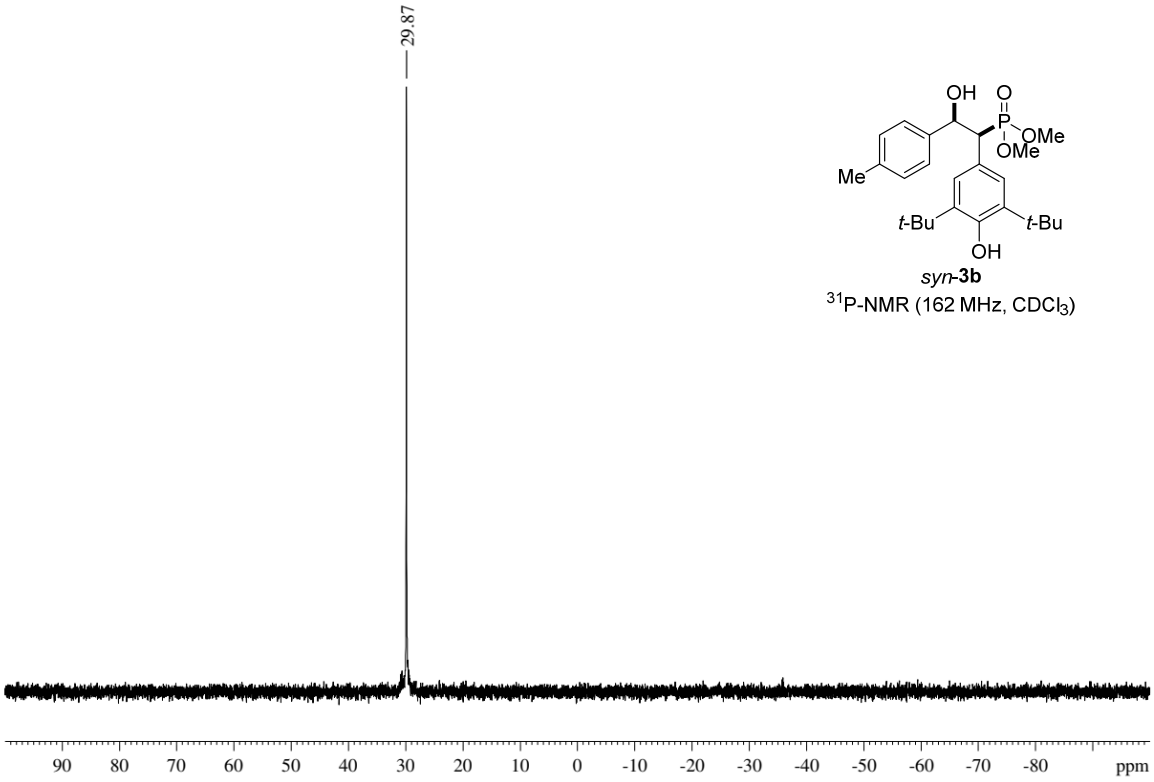
syn-**3b**

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



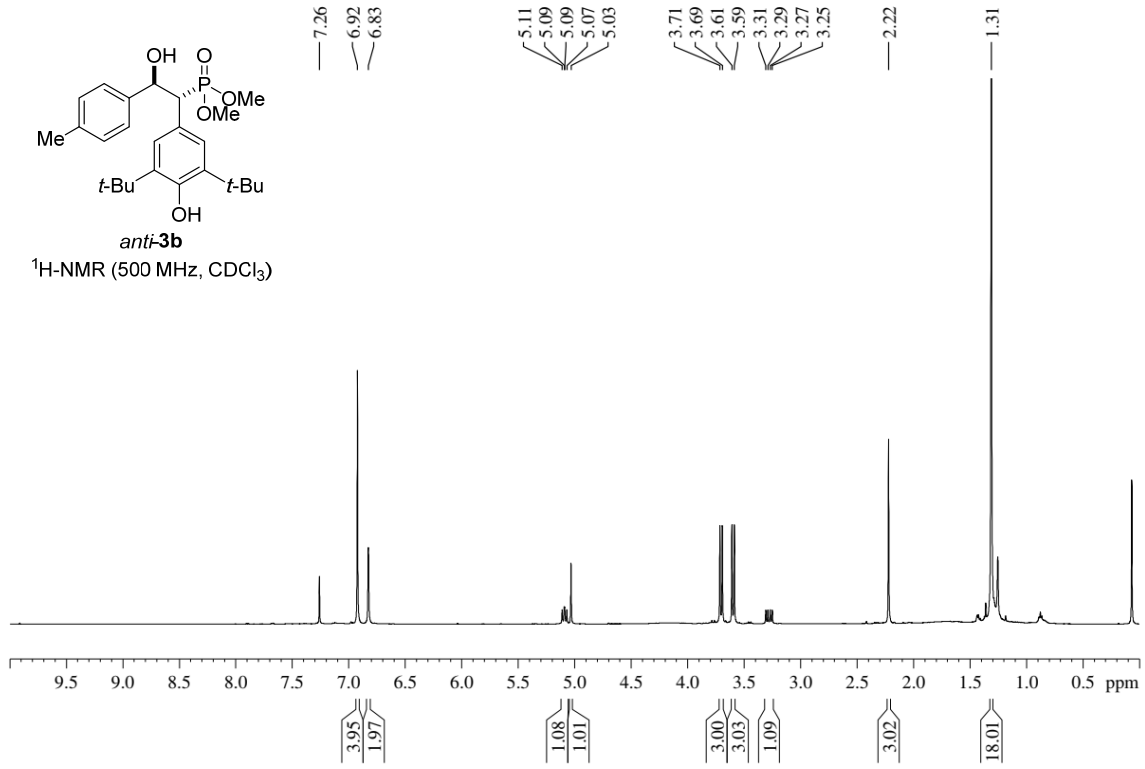
syn-**3b**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



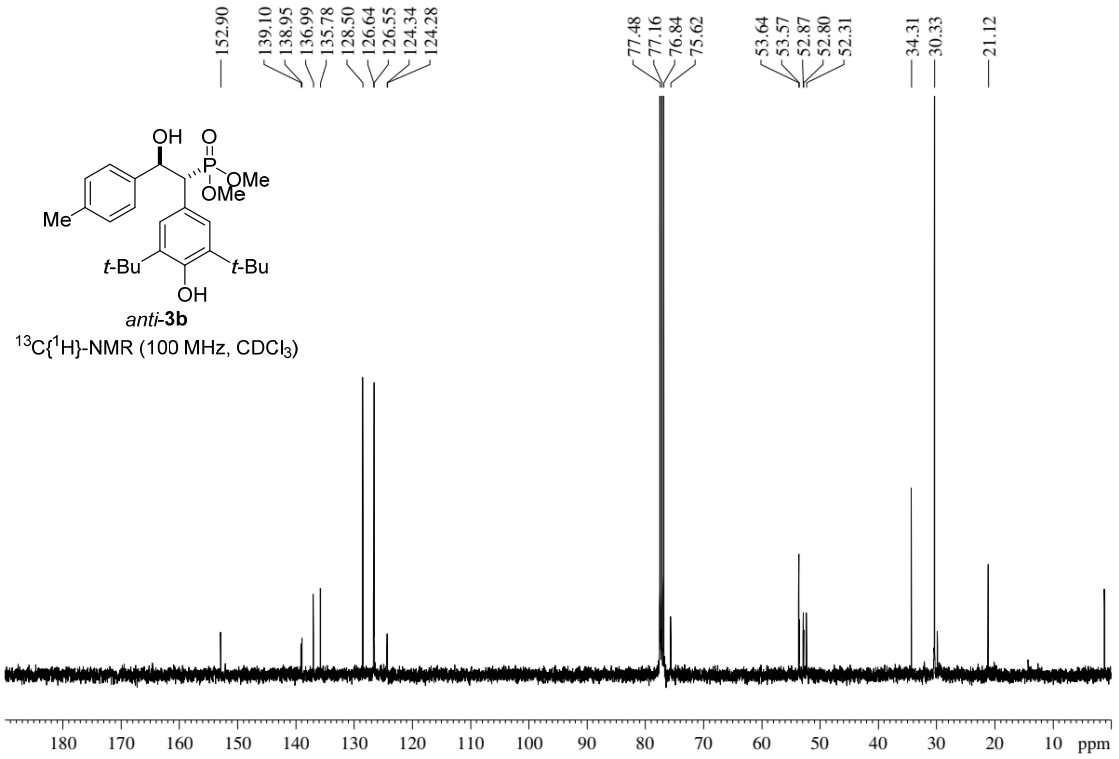
syn-**3b**

^{31}P-NMR (162 MHz, $CDCl_3$)



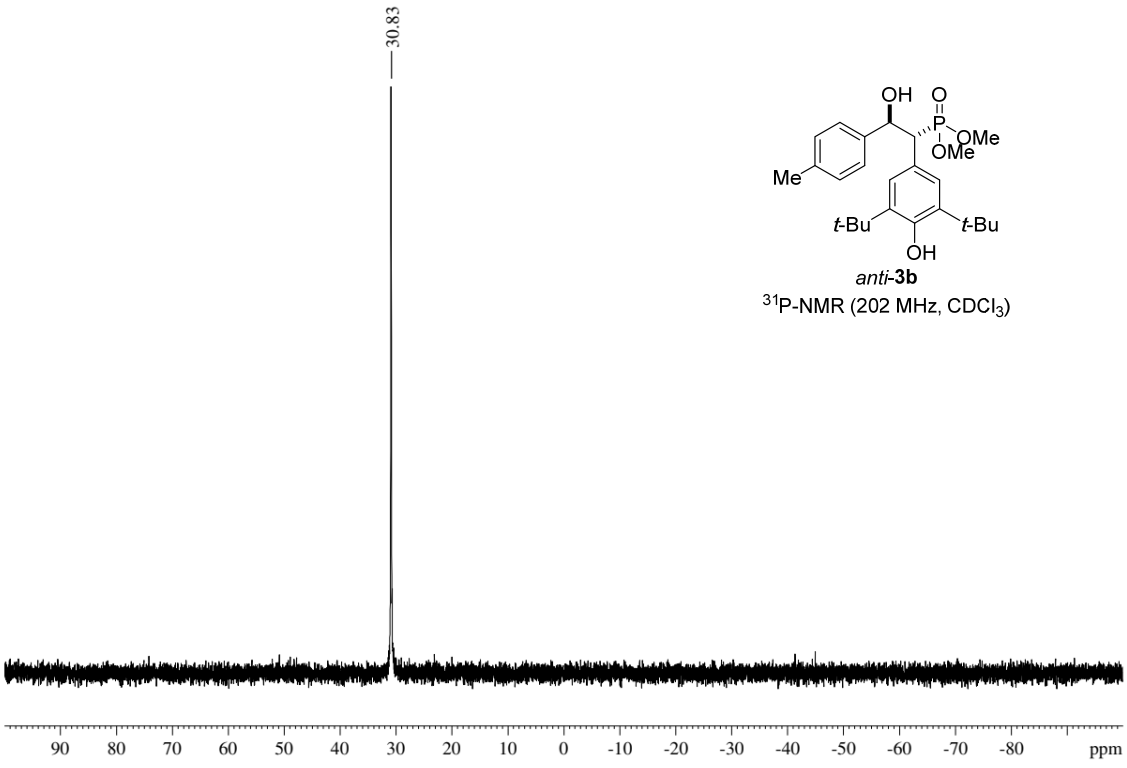
anti-**3b**

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



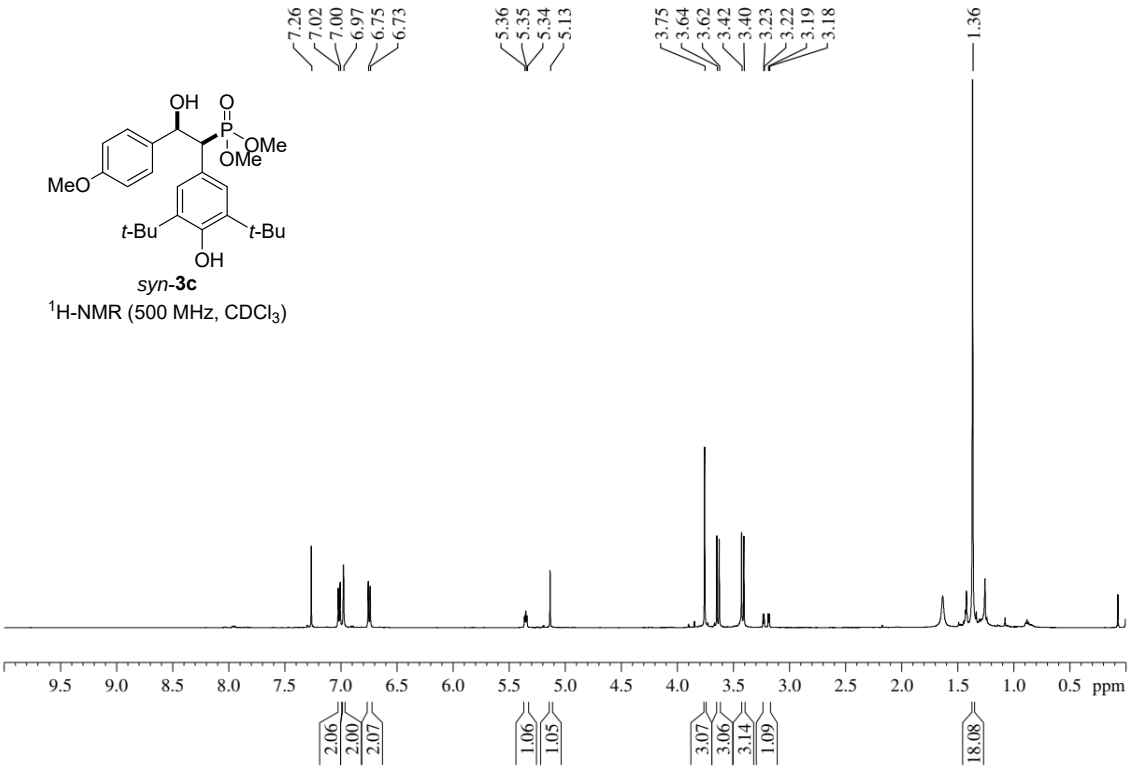
anti-**3b**

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)



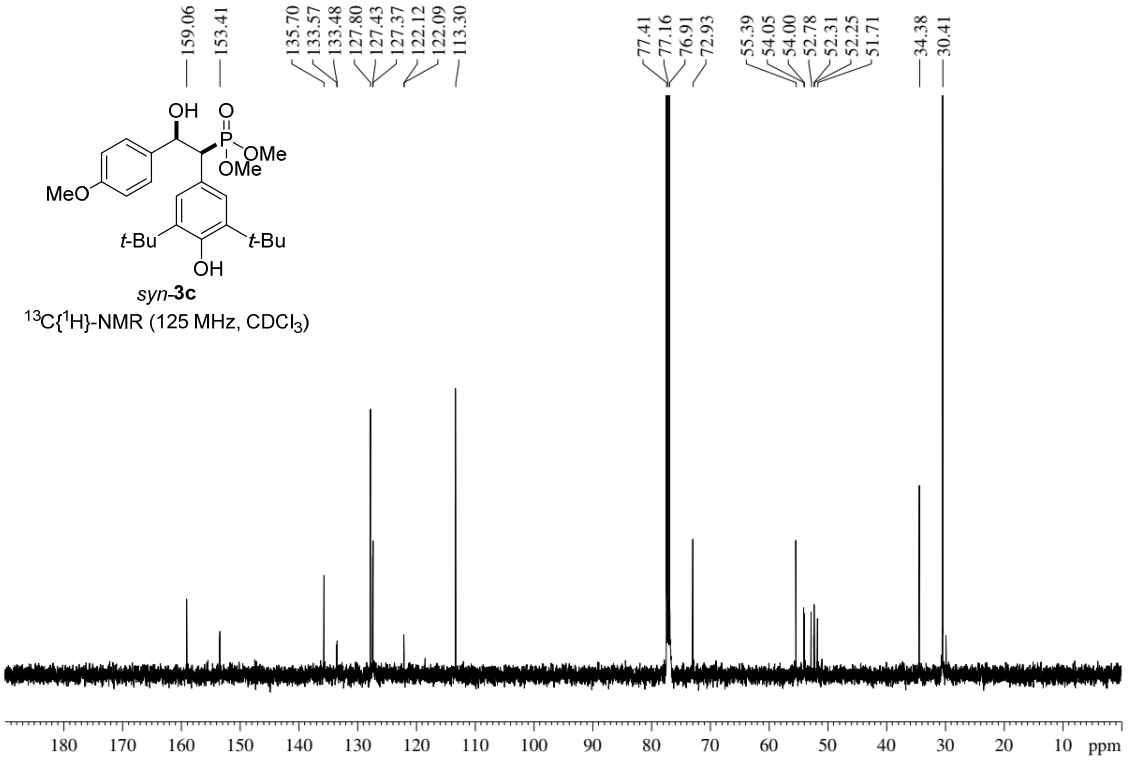
anti-**3b**

^{31}P-NMR (202 MHz, $CDCl_3$)



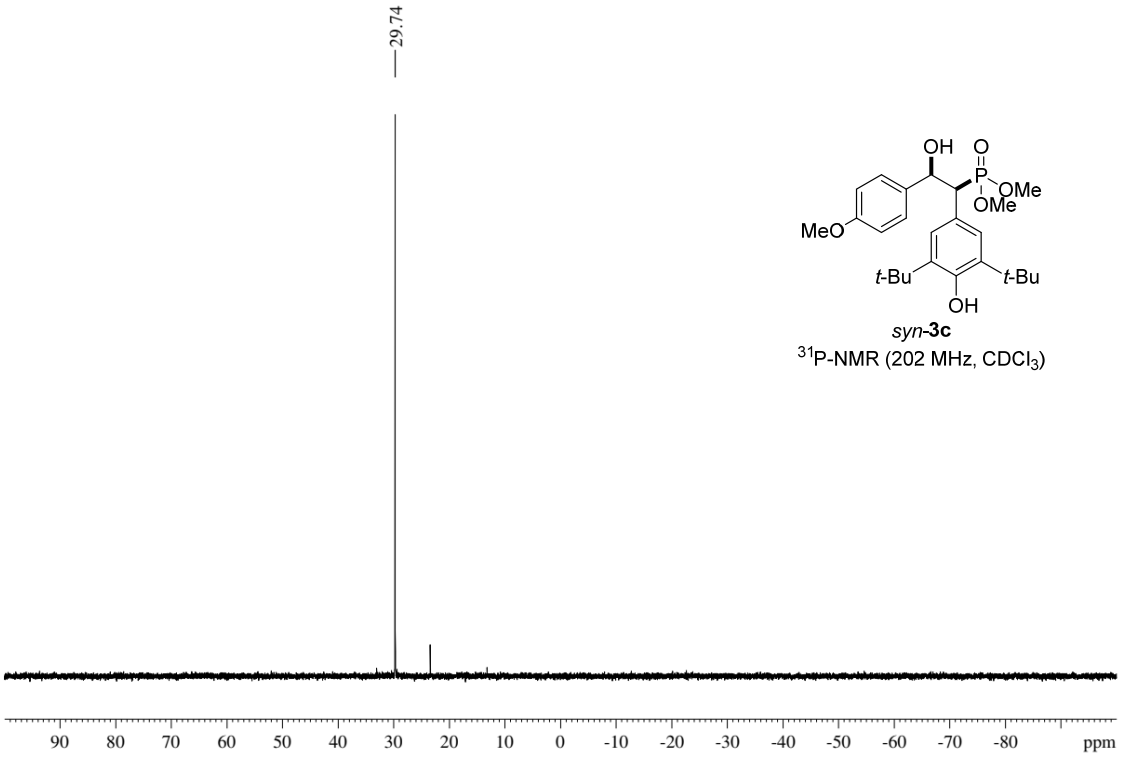
syn-**3c**

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



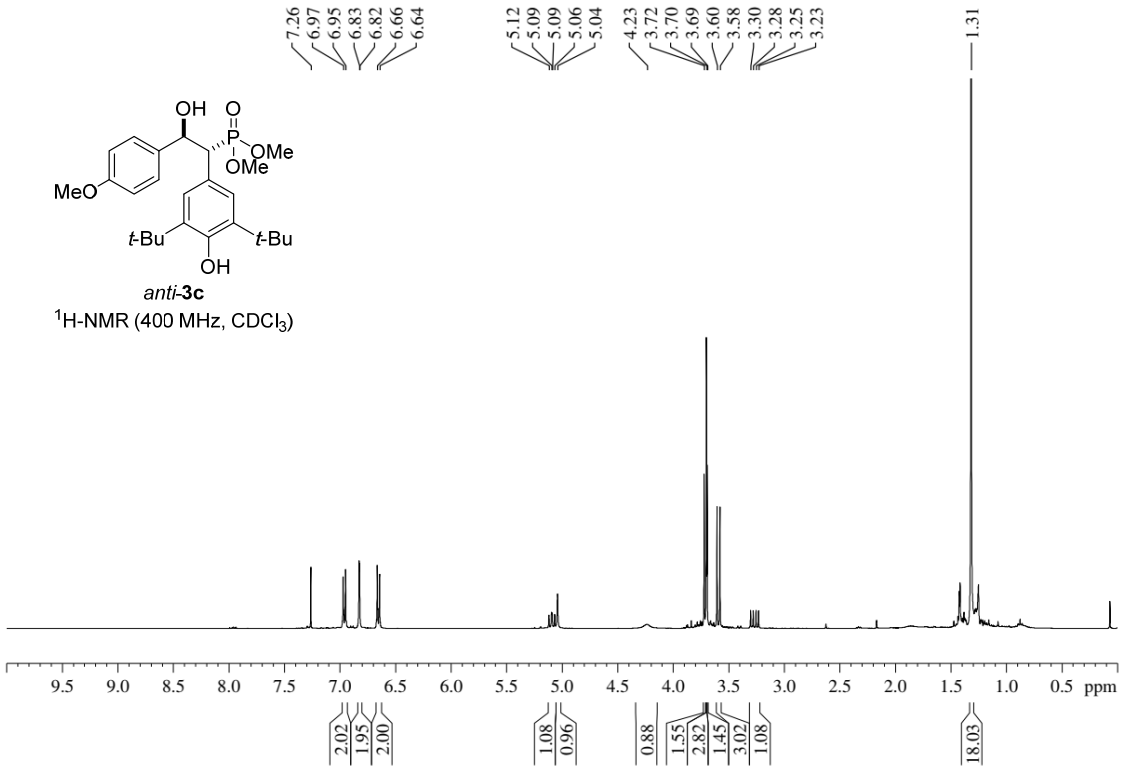
syn-**3c**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



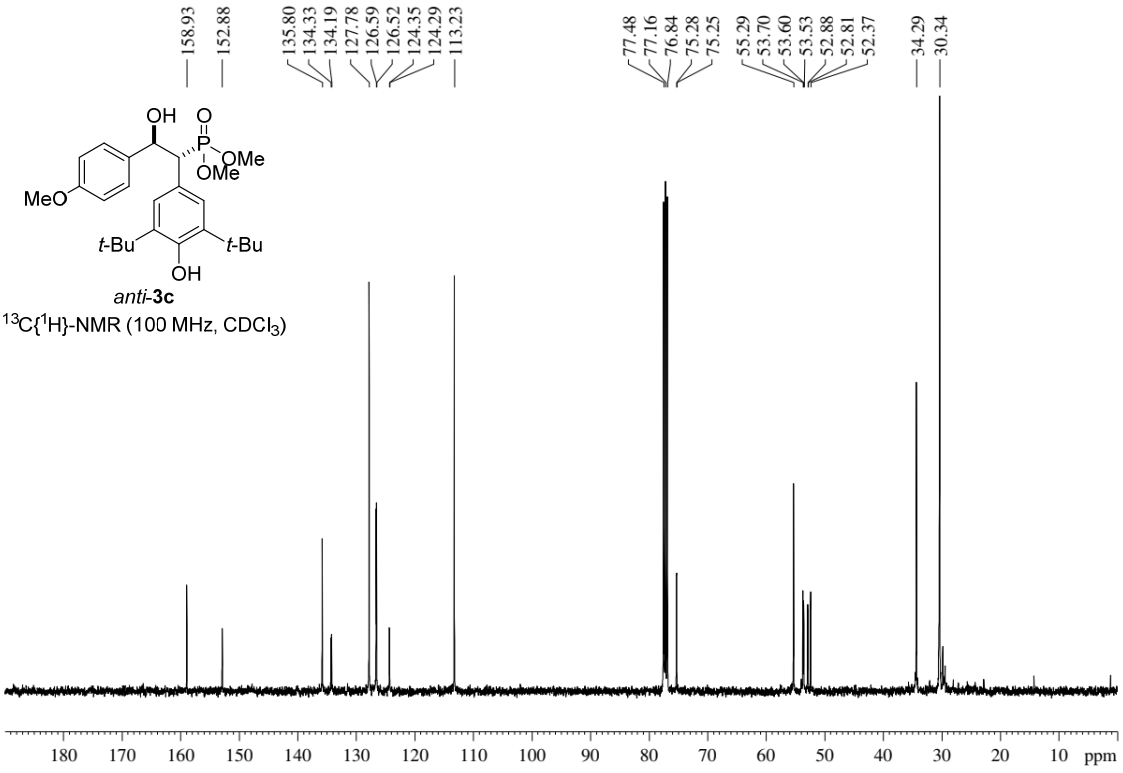
syn-**3c**

^{31}P-NMR (202 MHz, $CDCl_3$)



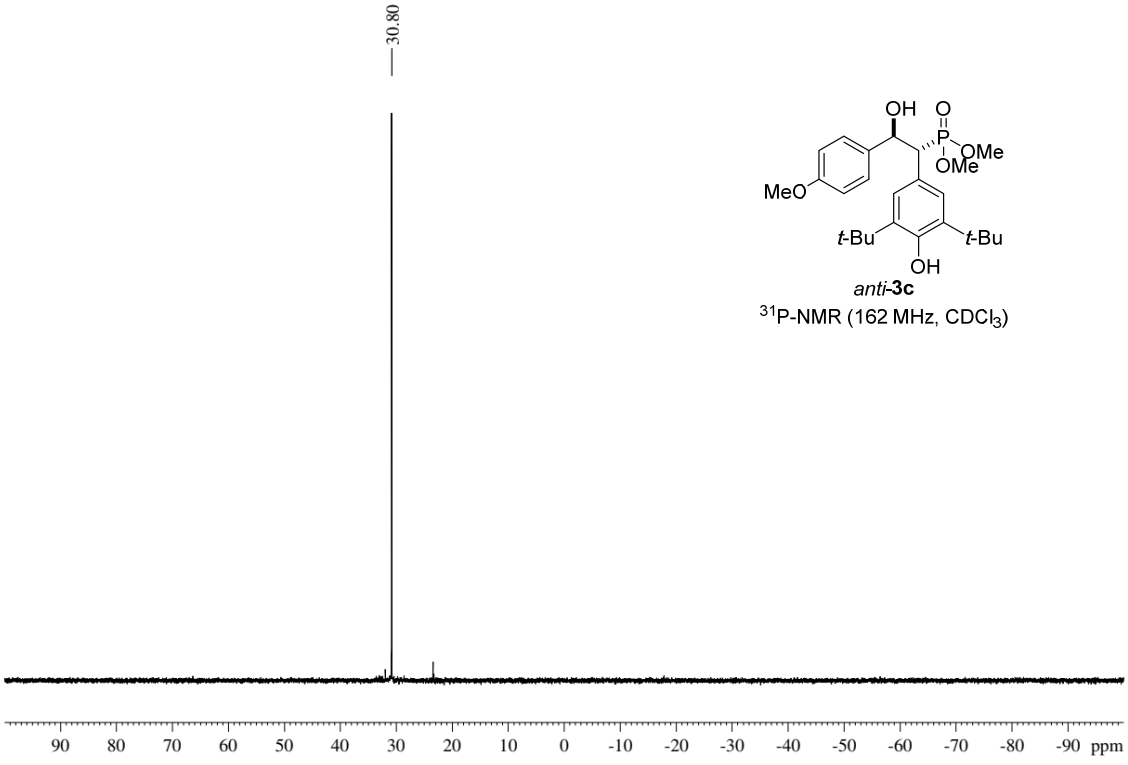
anti-**3c**

^{1}H-NMR (400 MHz, $CDCl_3$)



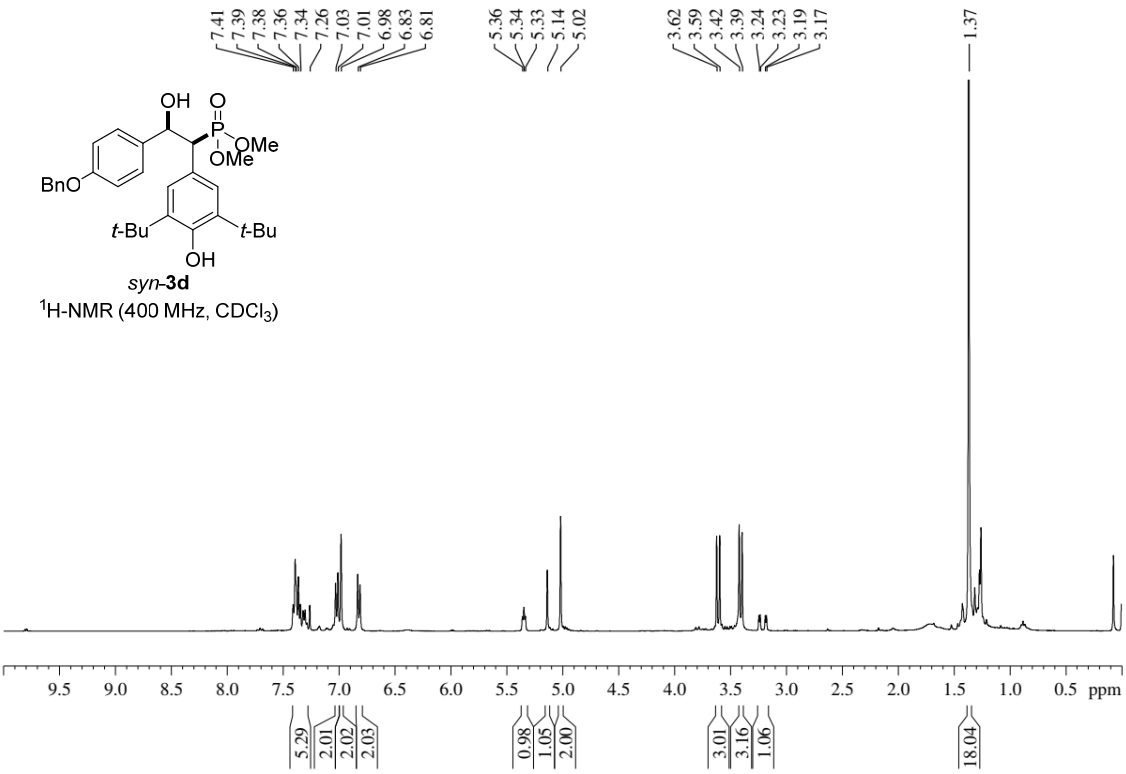
anti-**3c**

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)



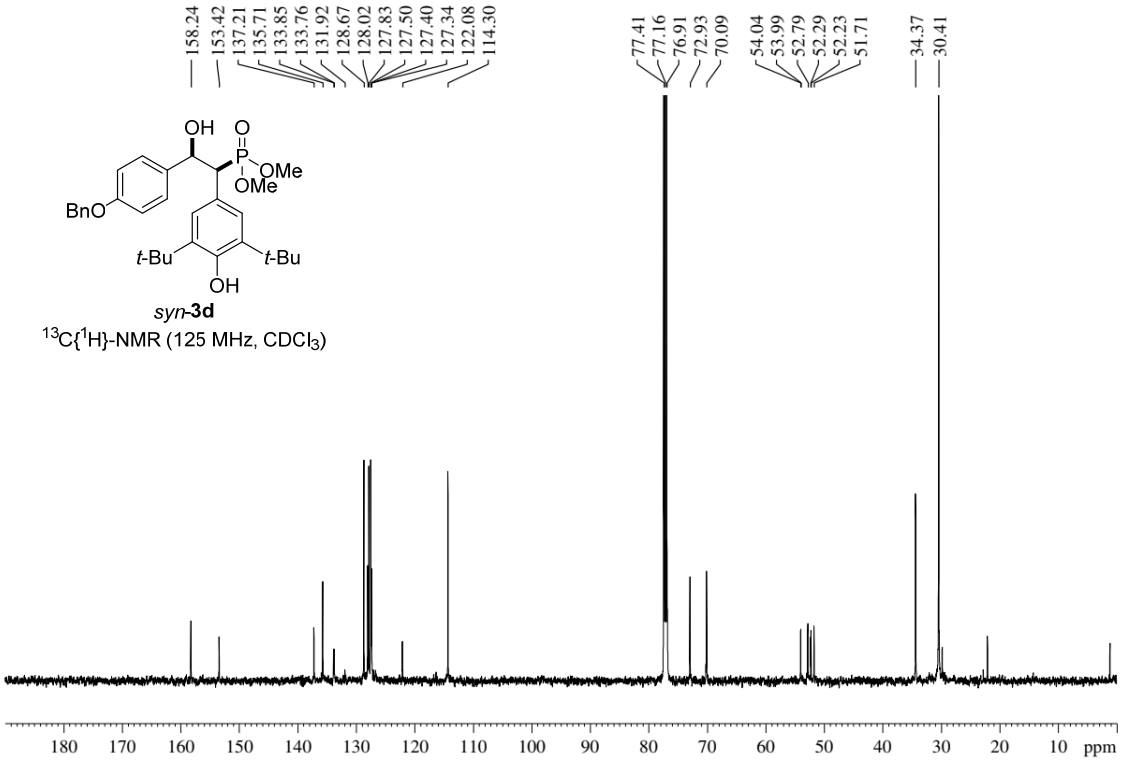
anti-**3c**

^{31}P-NMR (162 MHz, $CDCl_3$)



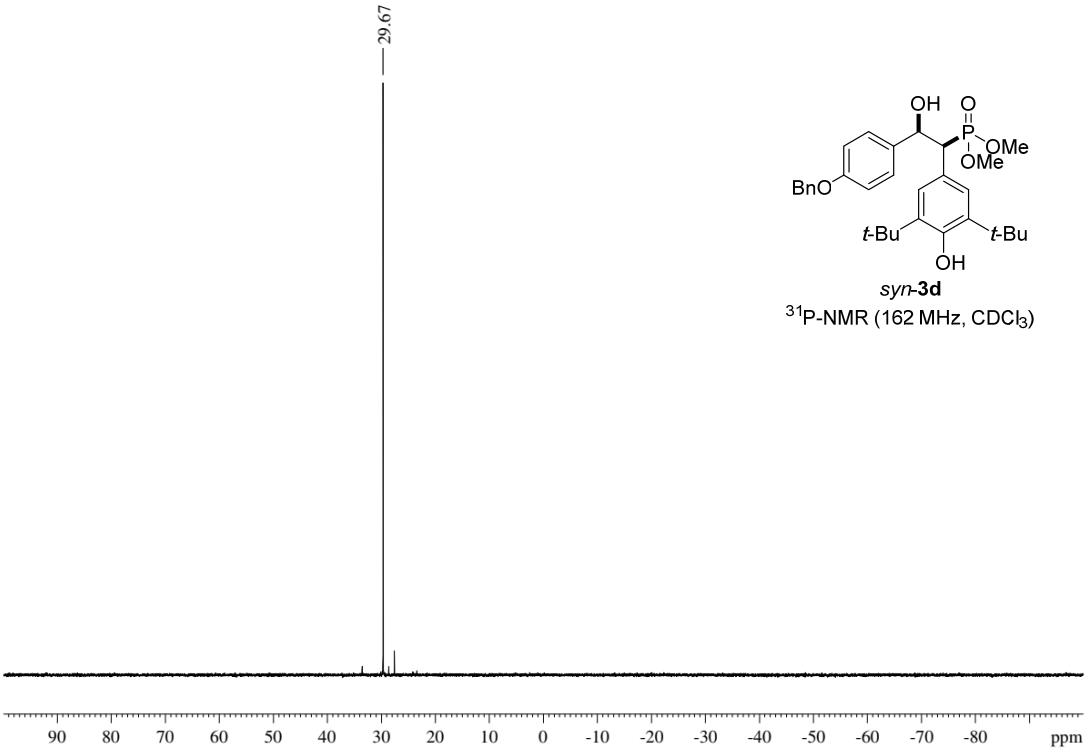
syn-**3d**

^{1}H-NMR (400 MHz, $CDCl_3$)

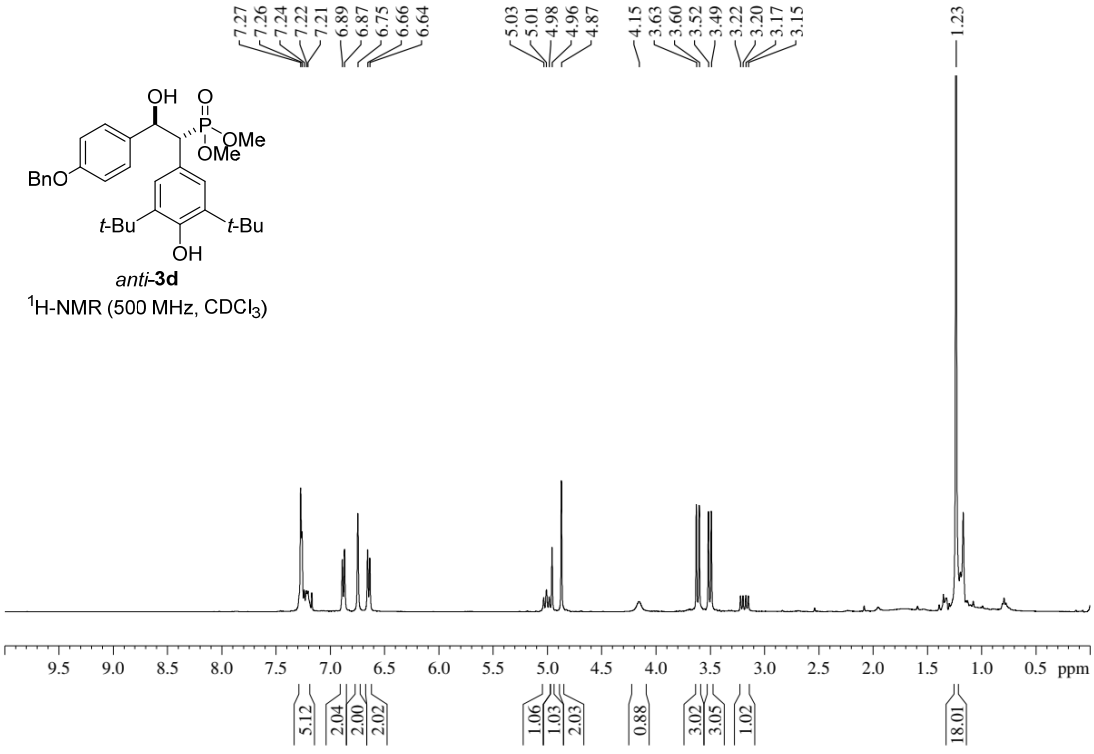


syn-**3d**

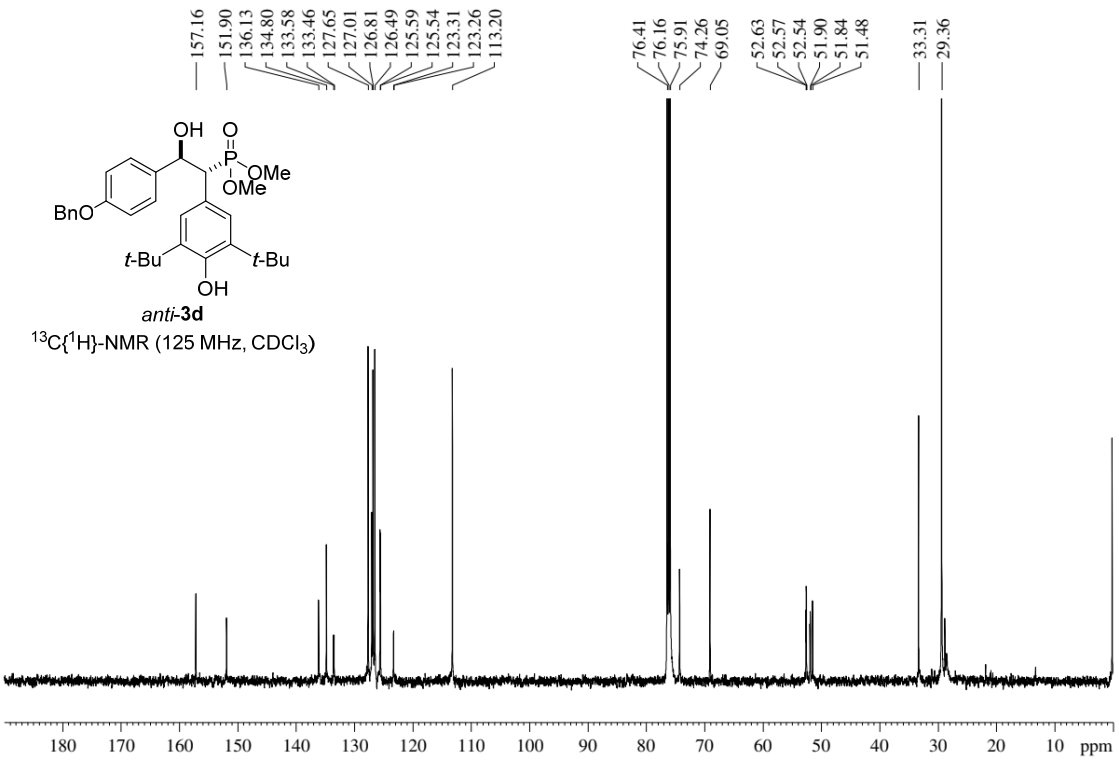
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



syn-**3d**
^{31}P-NMR (162 MHz, $CDCl_3$)

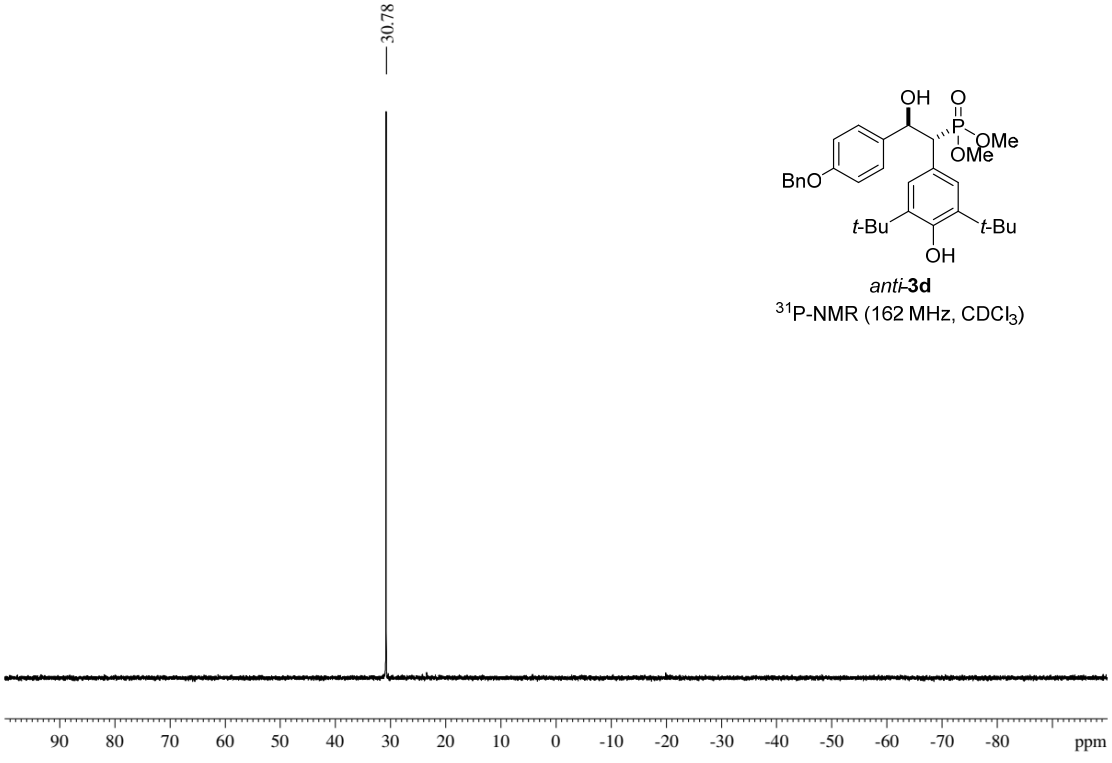


anti-**3d**
^{1}H-NMR (500 MHz, $CDCl_3$)



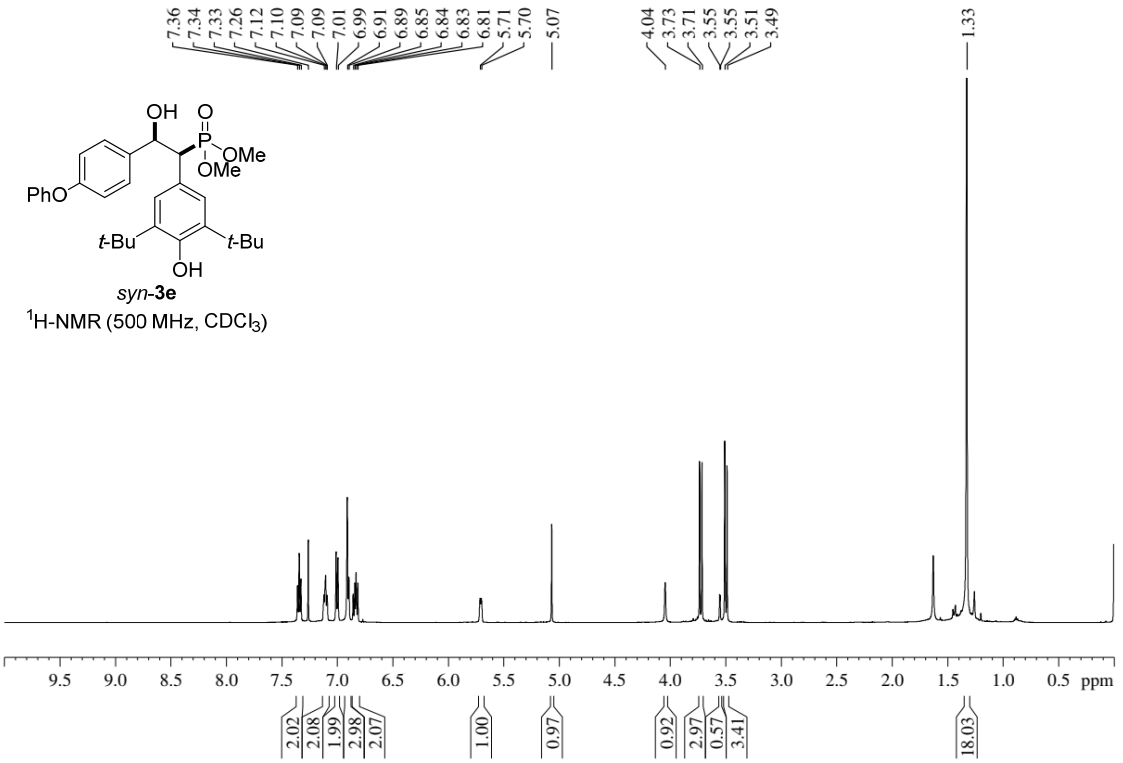
anti-**3d**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



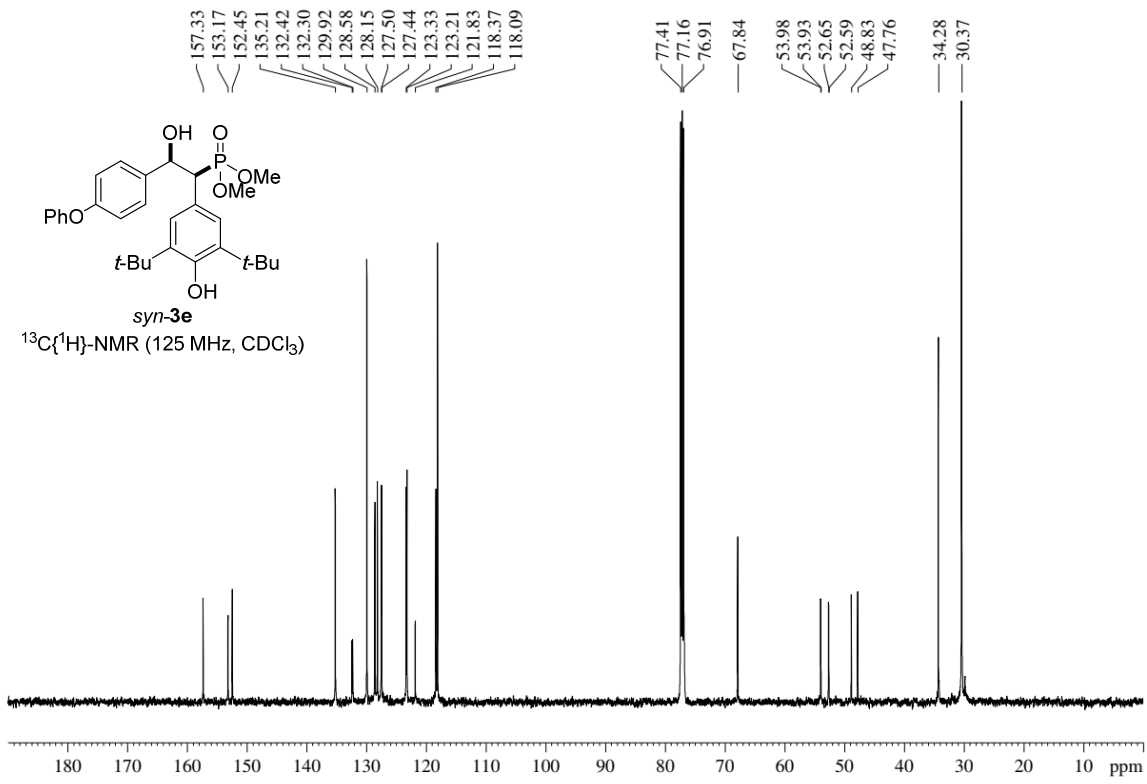
anti-**3d**

^{31}P-NMR (162 MHz, $CDCl_3$)



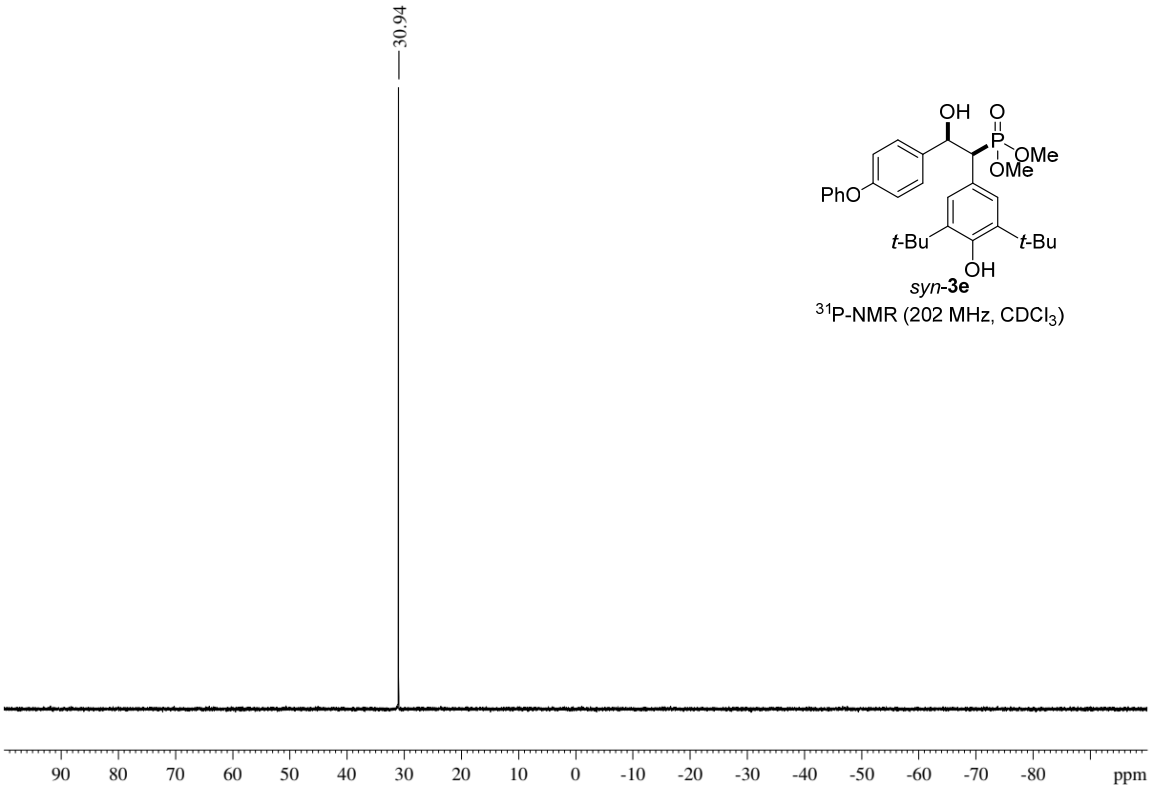
syn-**3e**

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



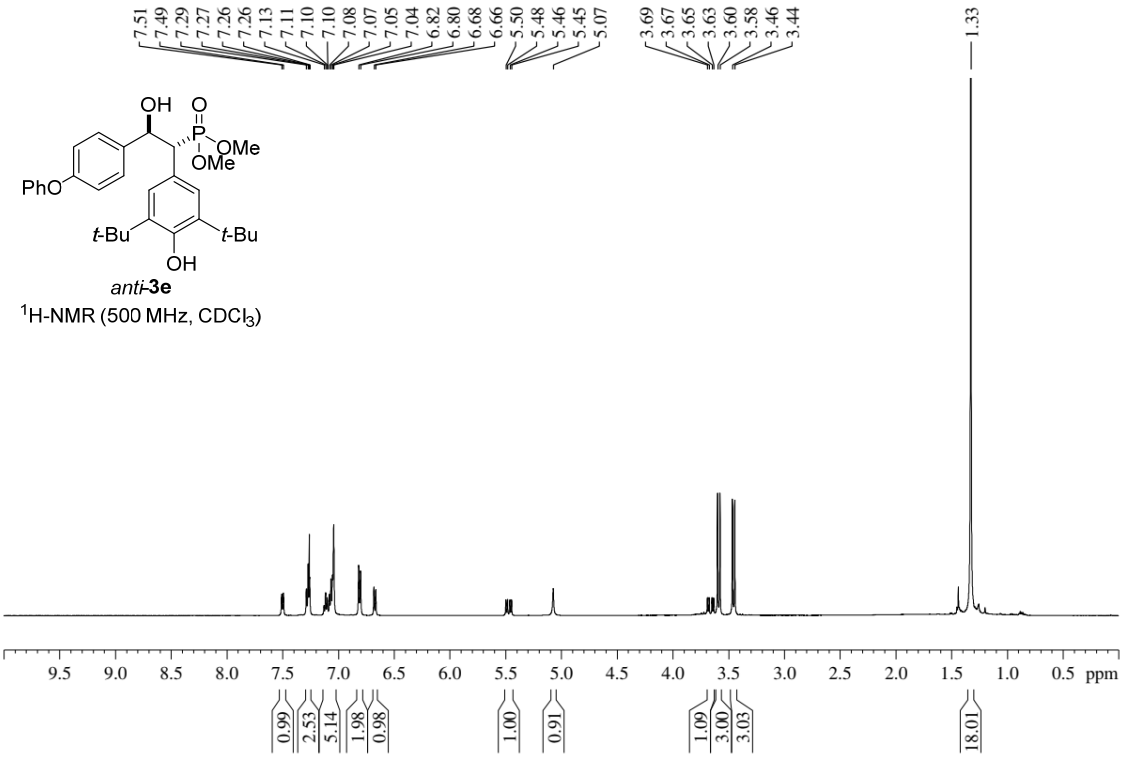
syn-**3e**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



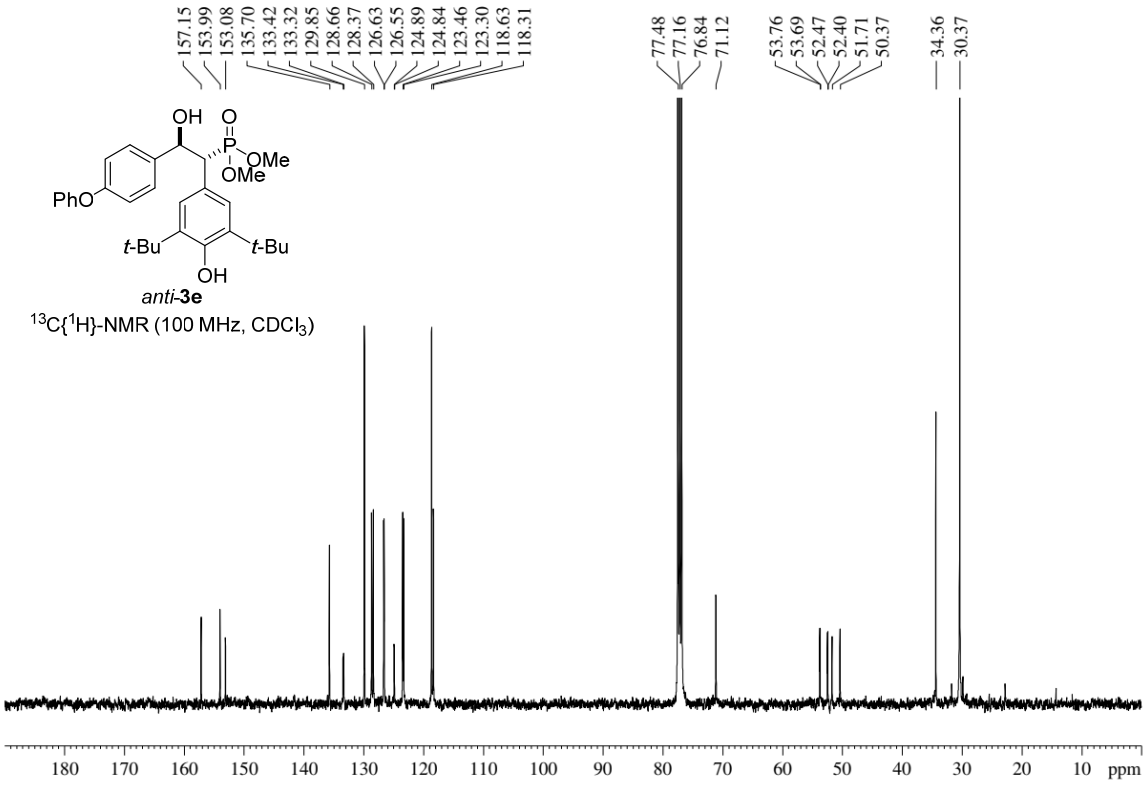
syn-**3e**

^{31}P-NMR (202 MHz, $CDCl_3$)



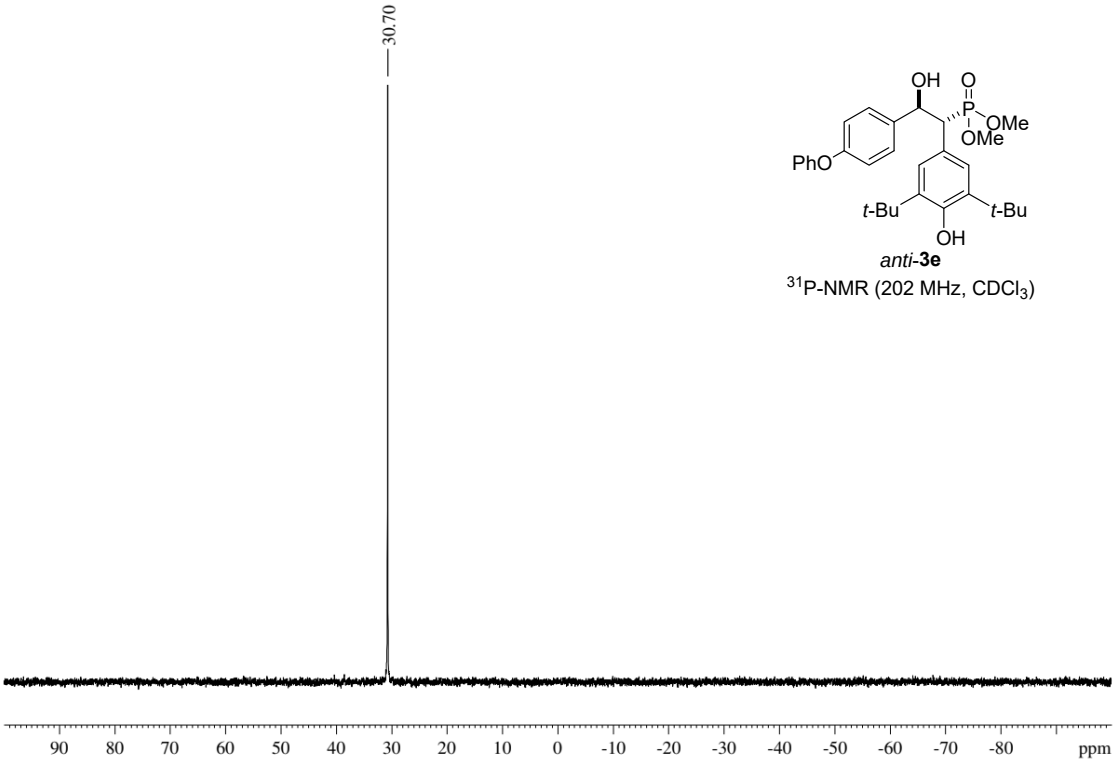
anti-**3e**

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



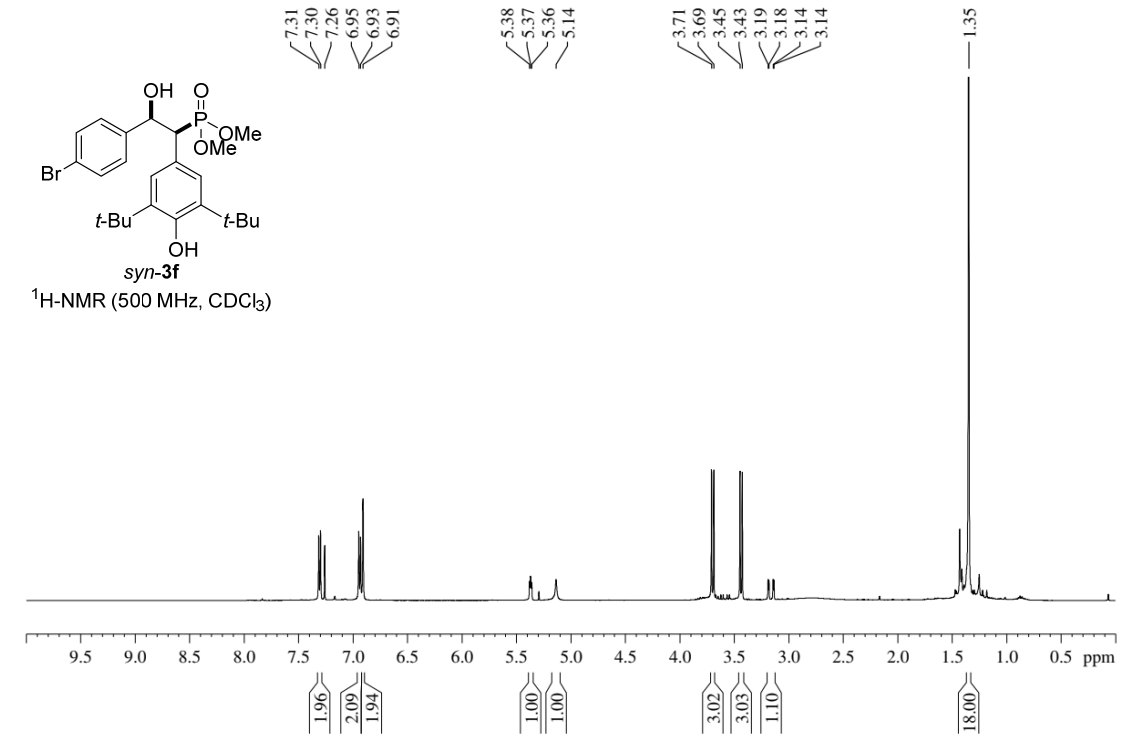
anti-**3e**

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)



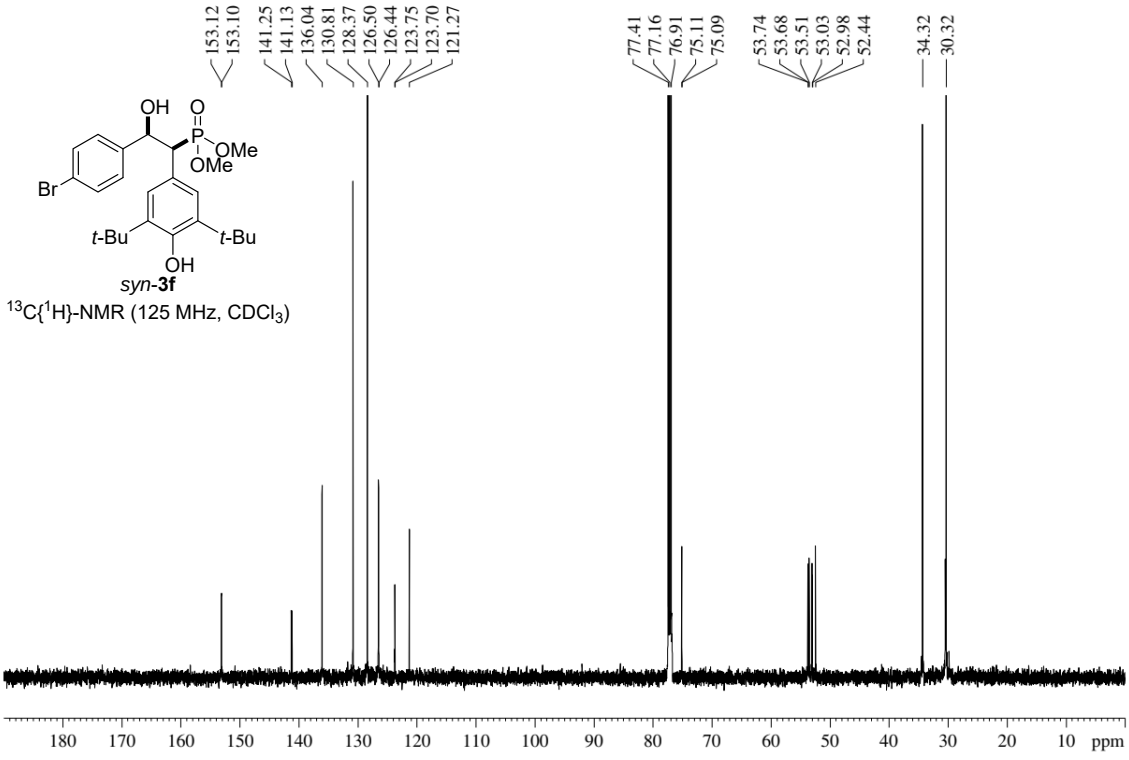
anti-**3e**

^{31}P-NMR (202 MHz, $CDCl_3$)



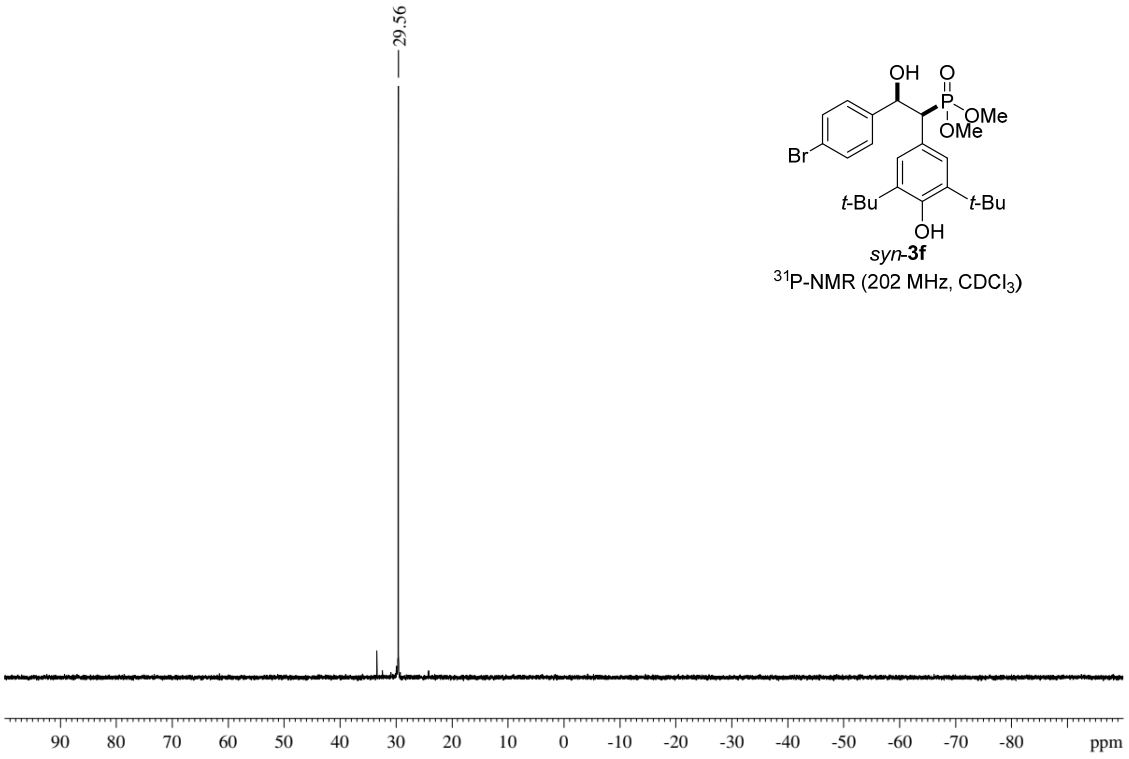
syn-**3f**

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



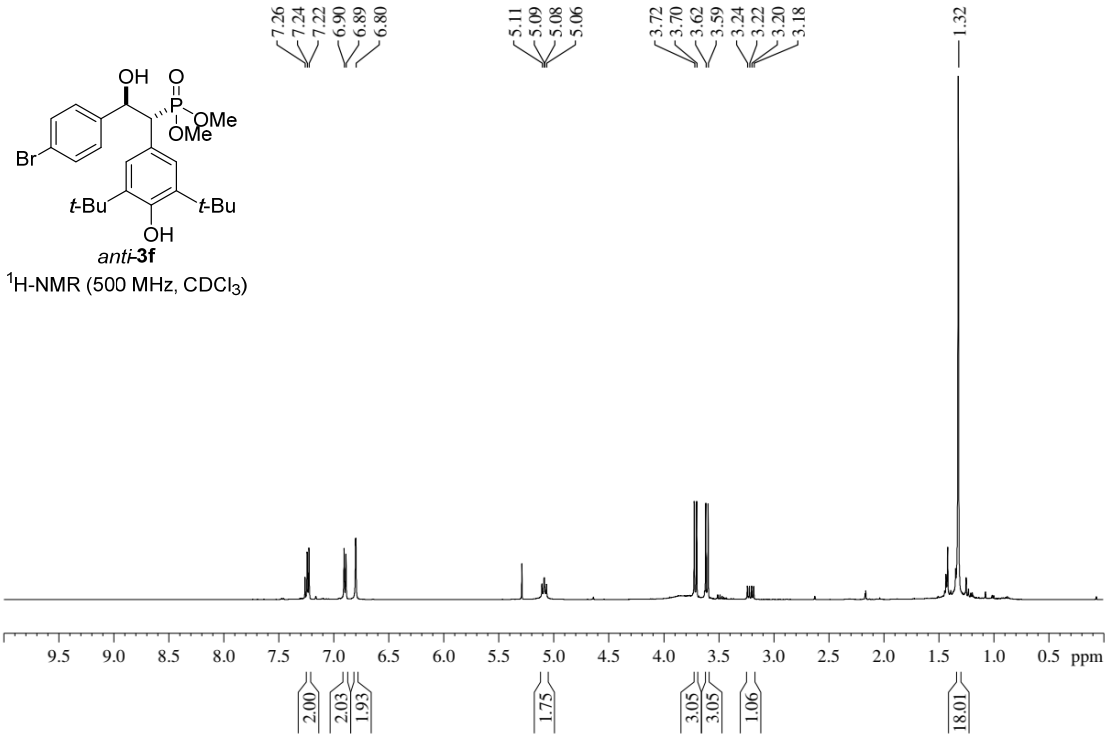
syn-**3f**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



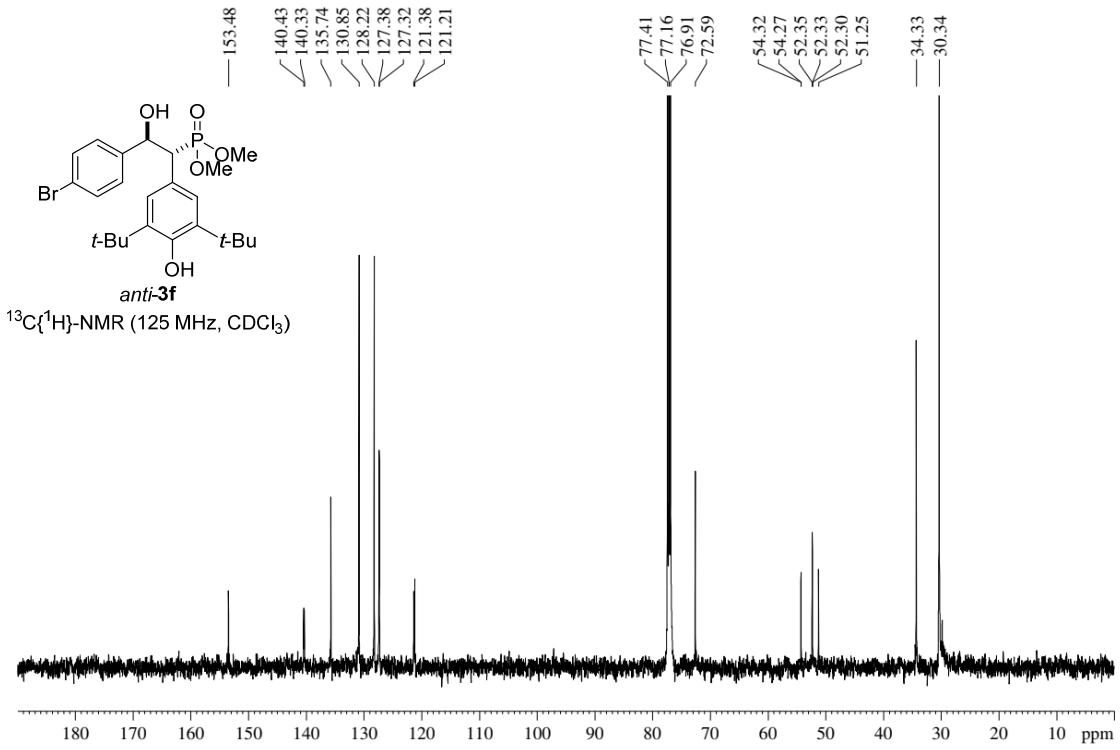
syn-**3f**

^{31}P-NMR (202 MHz, $CDCl_3$)



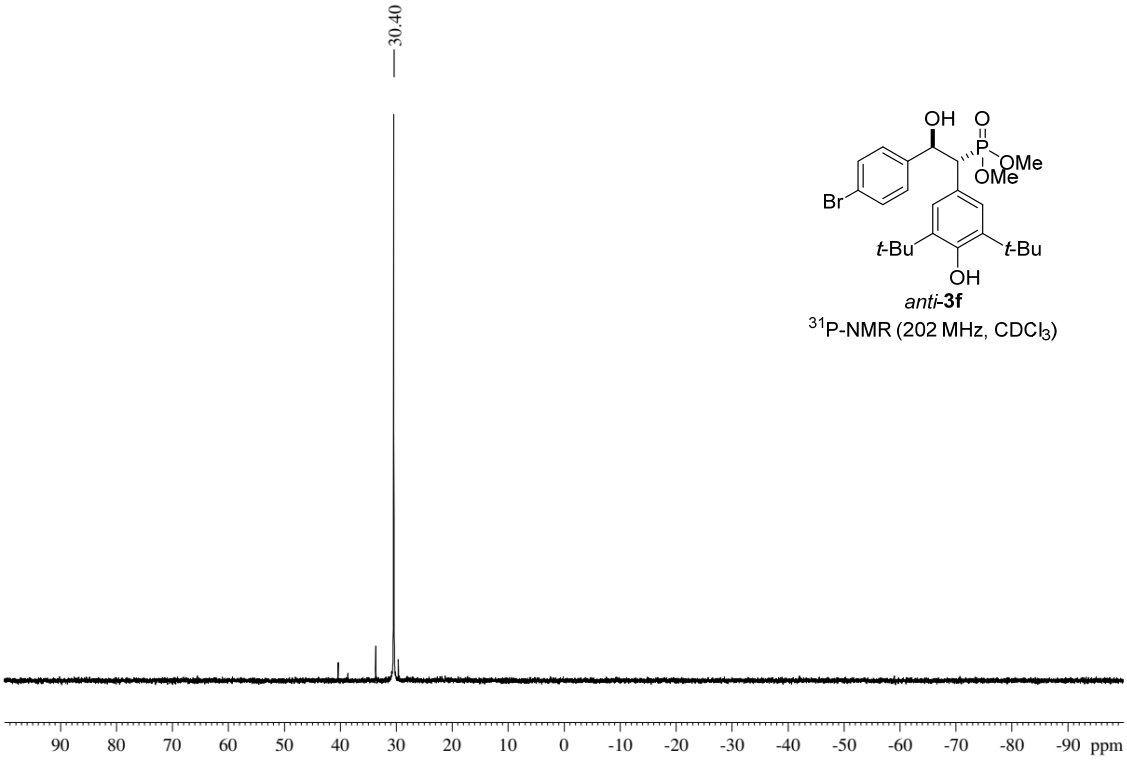
anti-**3f**

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



anti-**3f**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



anti-**3f**

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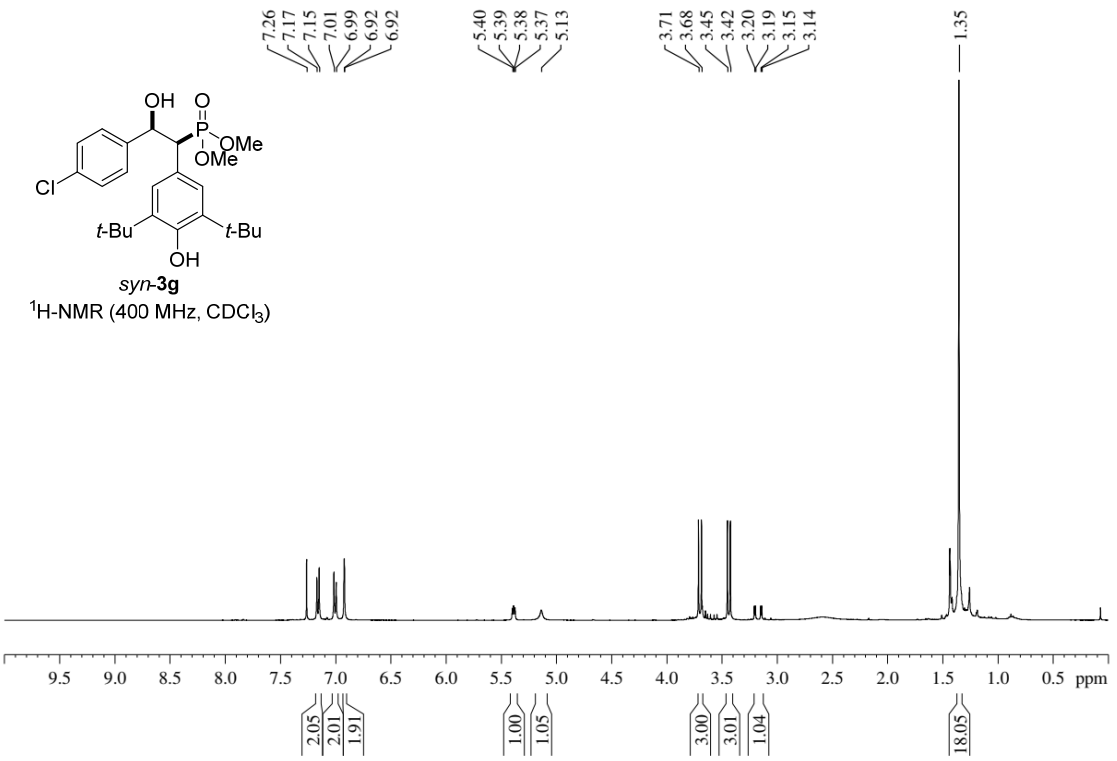
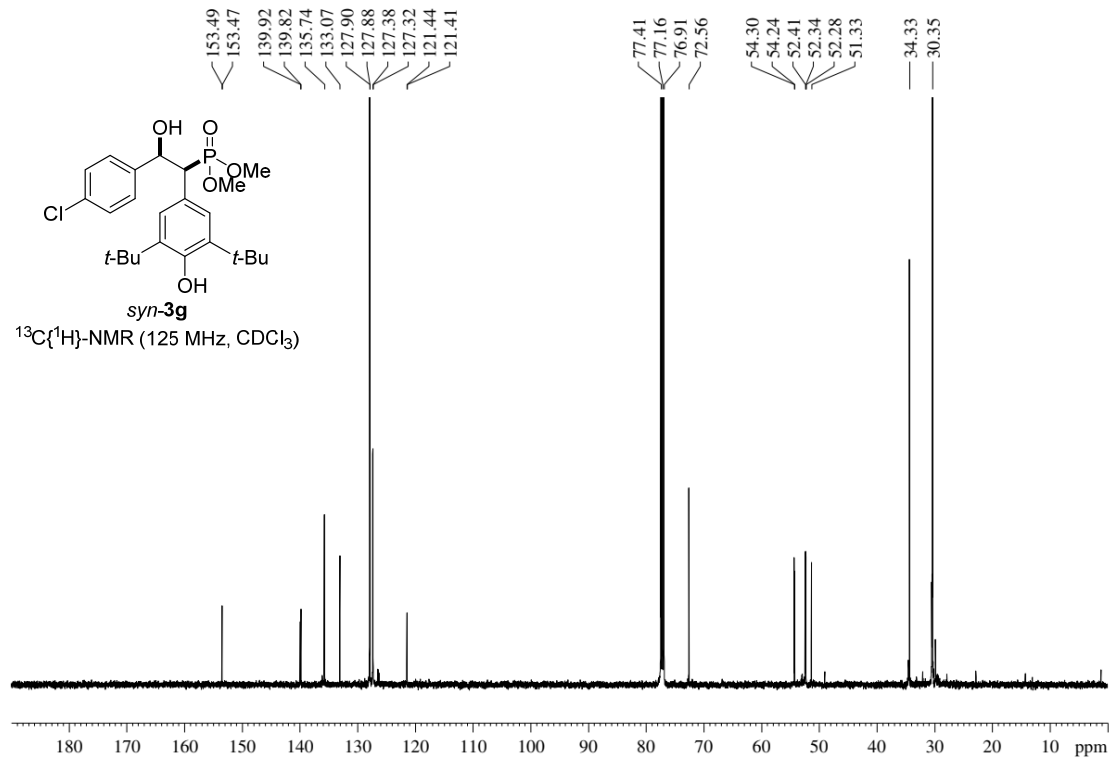


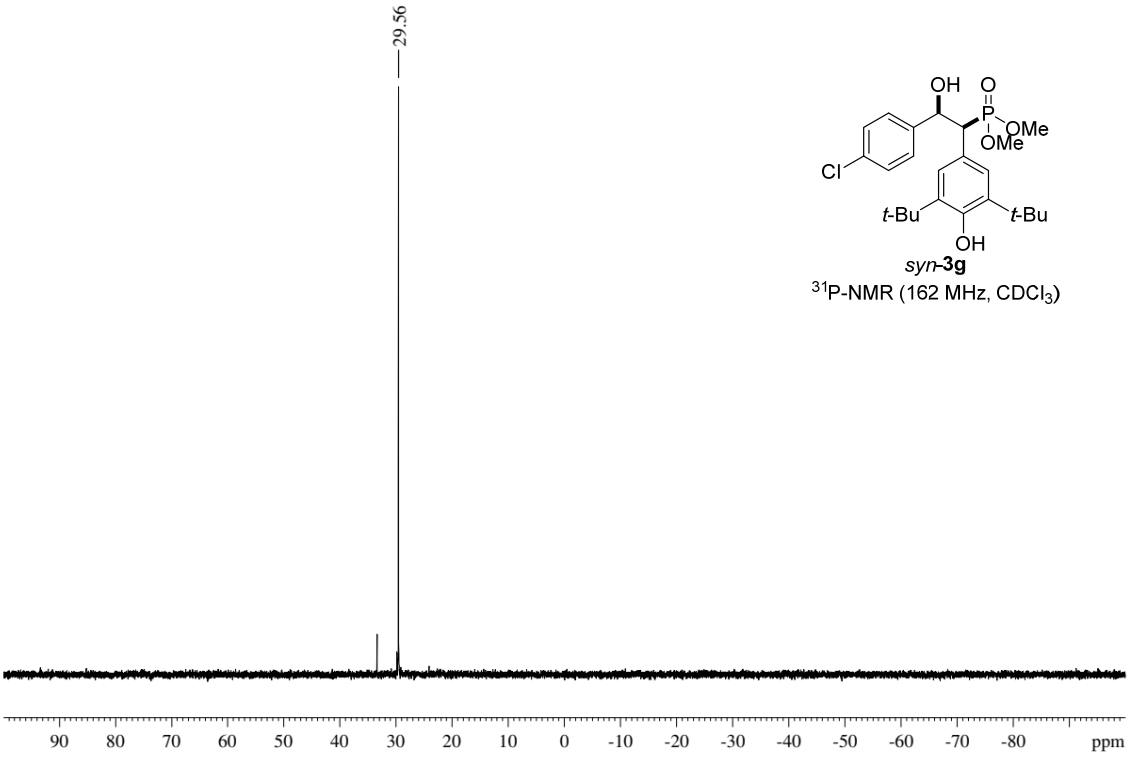
syn-**3g**

^{1}H-NMR (400 MHz, $CDCl_3$)



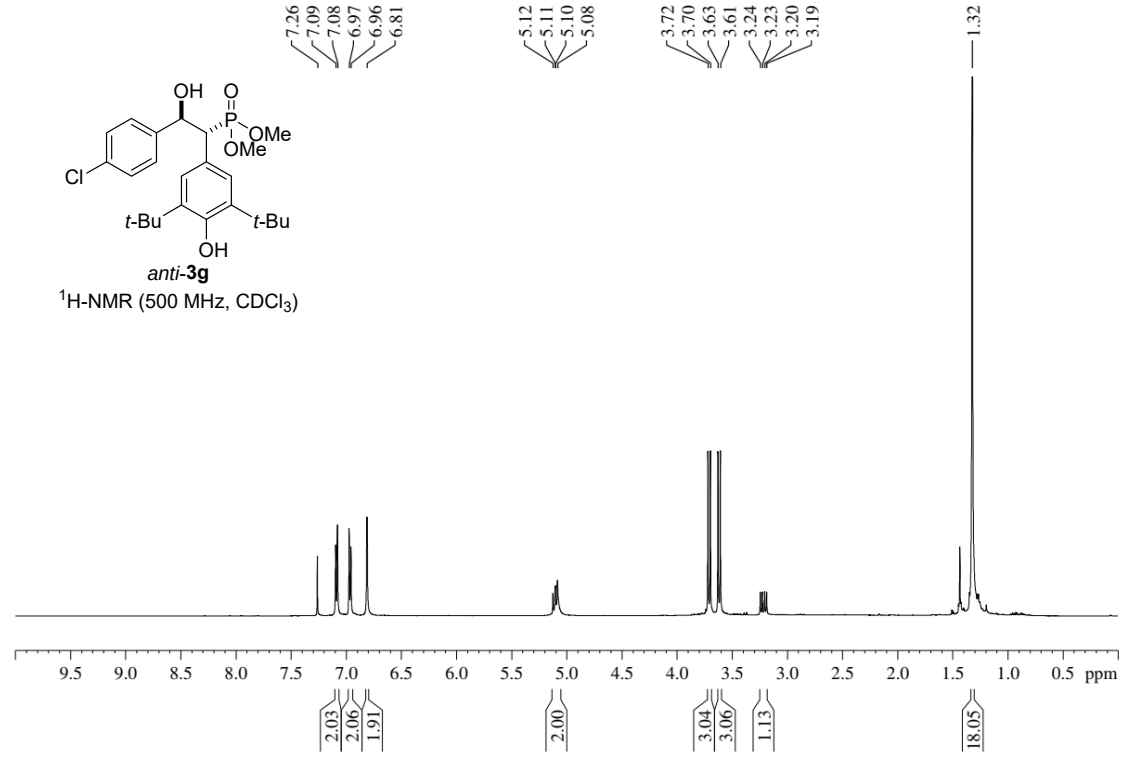
syn-**3g**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



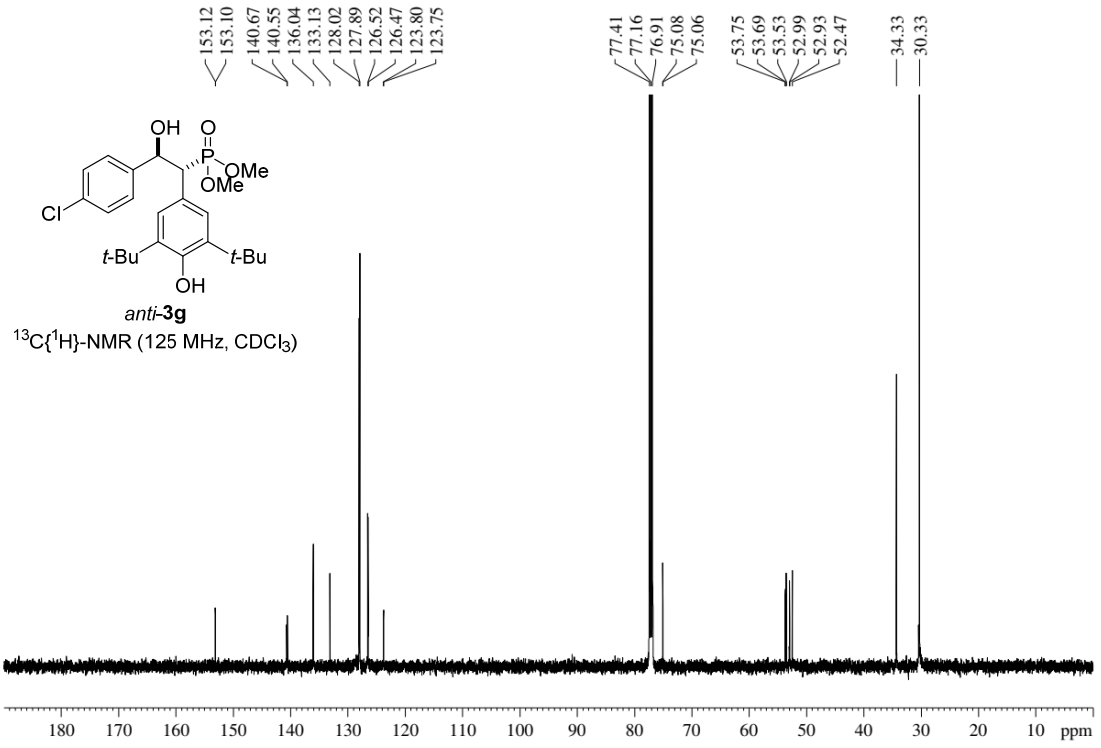
syn-**3g**

^{31}P-NMR (162 MHz, $CDCl_3$)



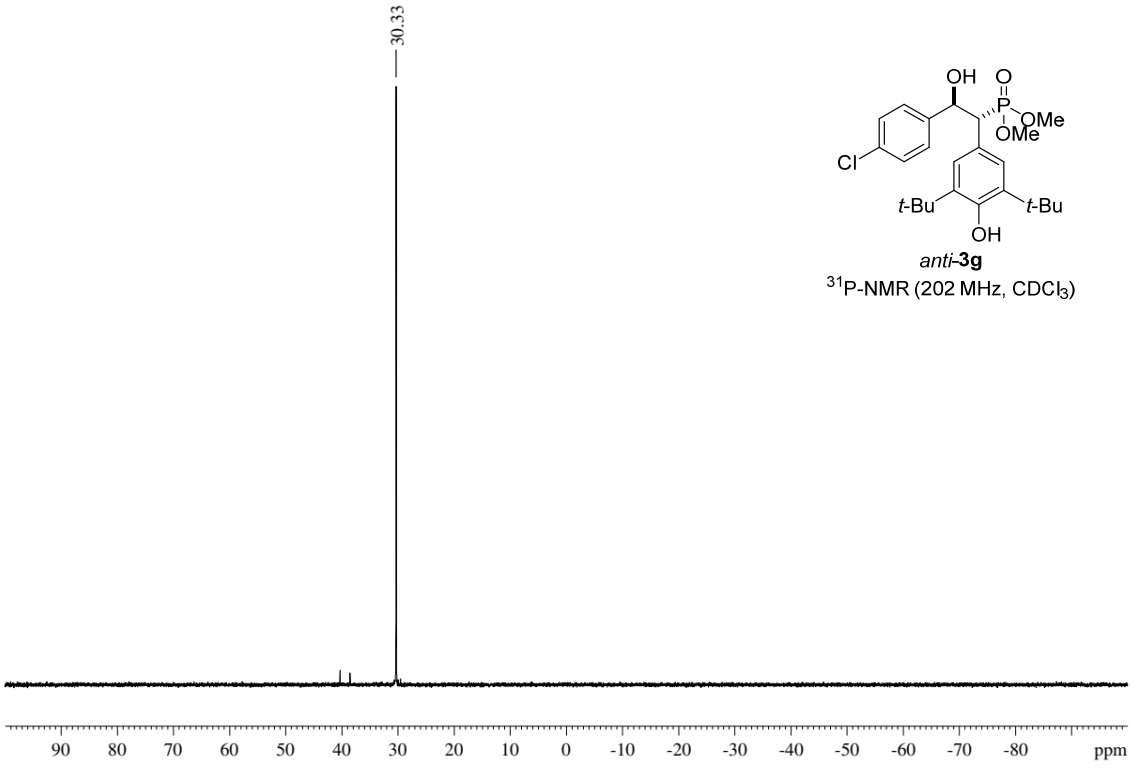
anti-**3g**

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



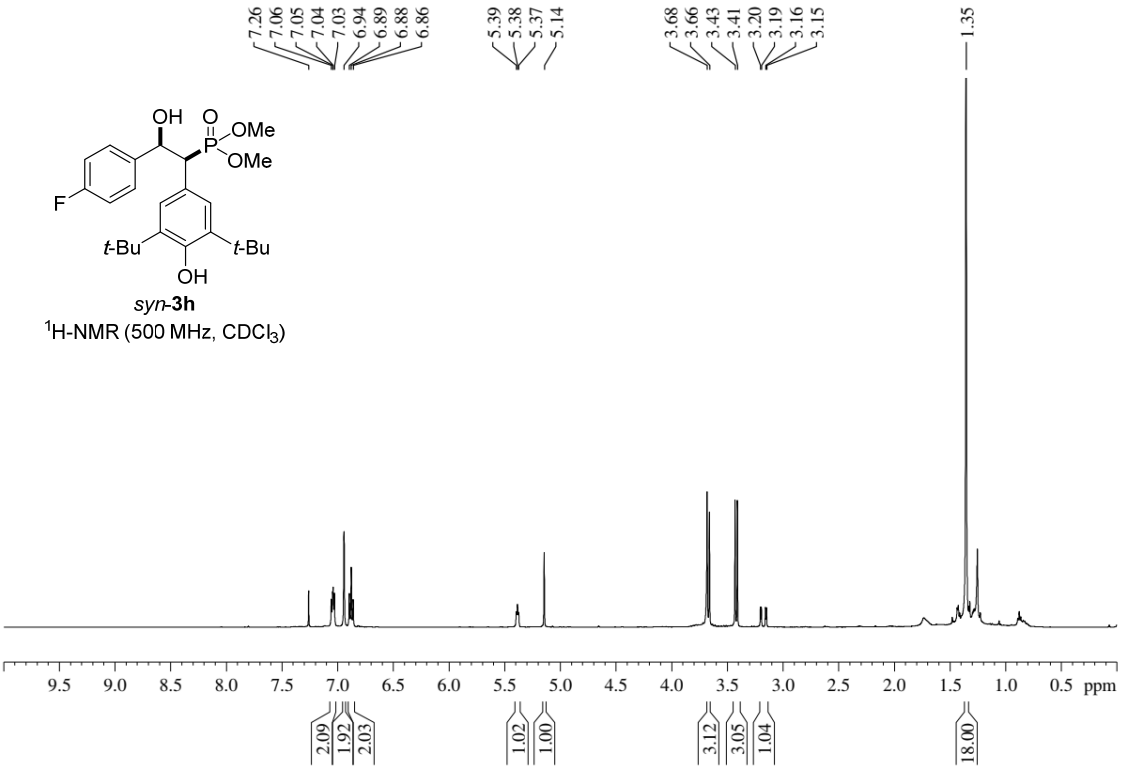
anti-**3g**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



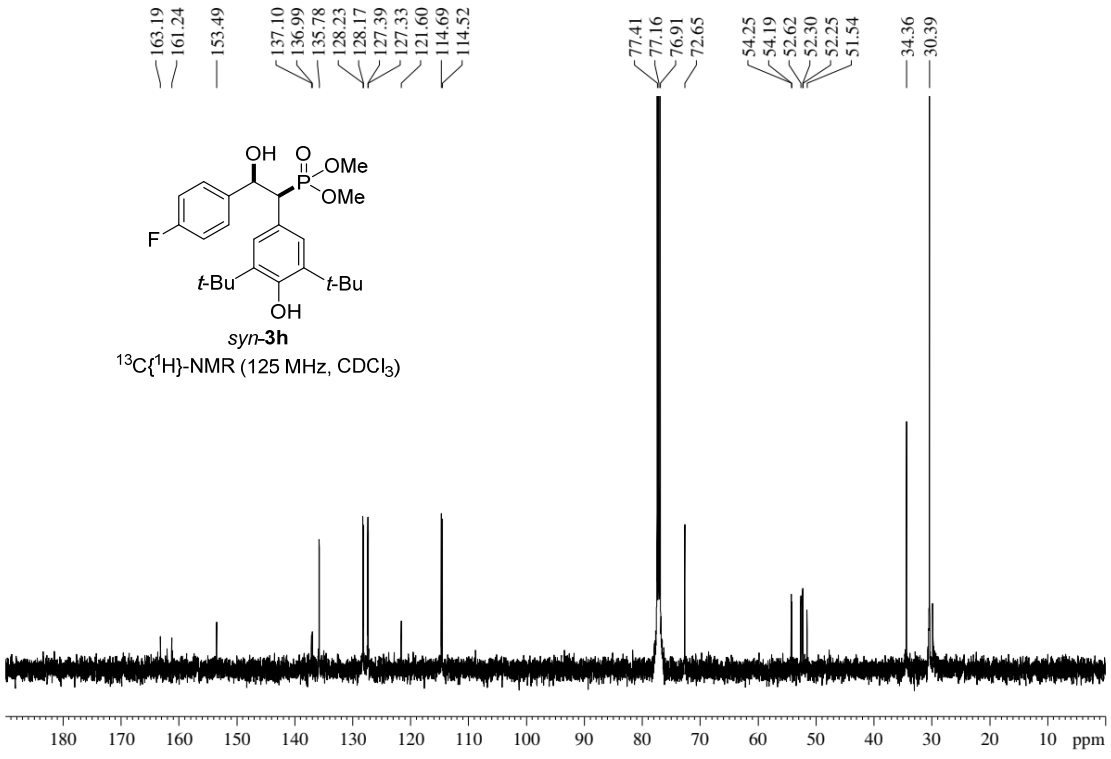
anti-**3g**

^{31}P-NMR (202 MHz, $CDCl_3$)



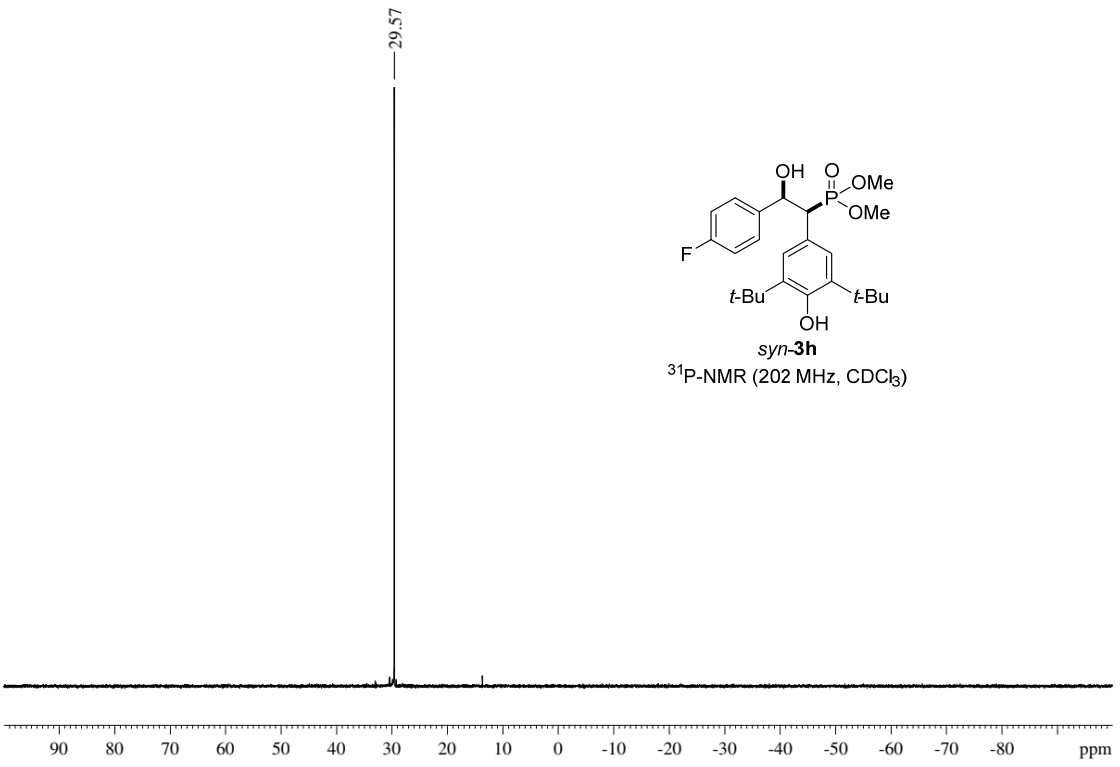
syn-**3h**

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

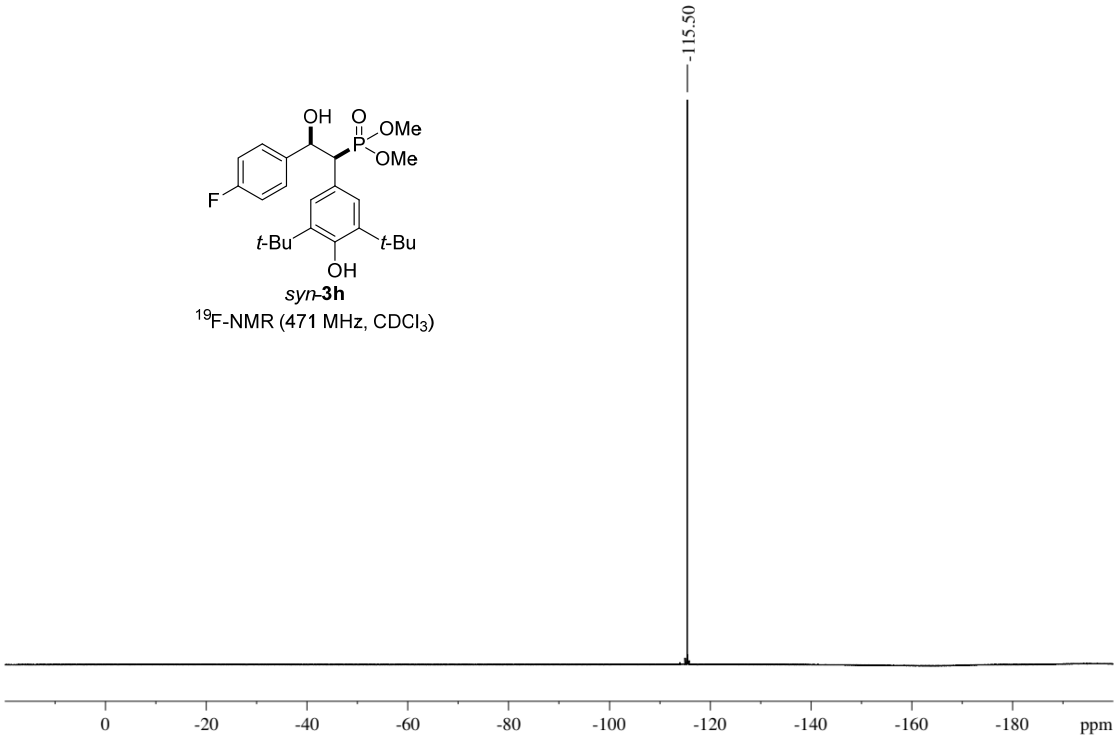


syn-**3h**

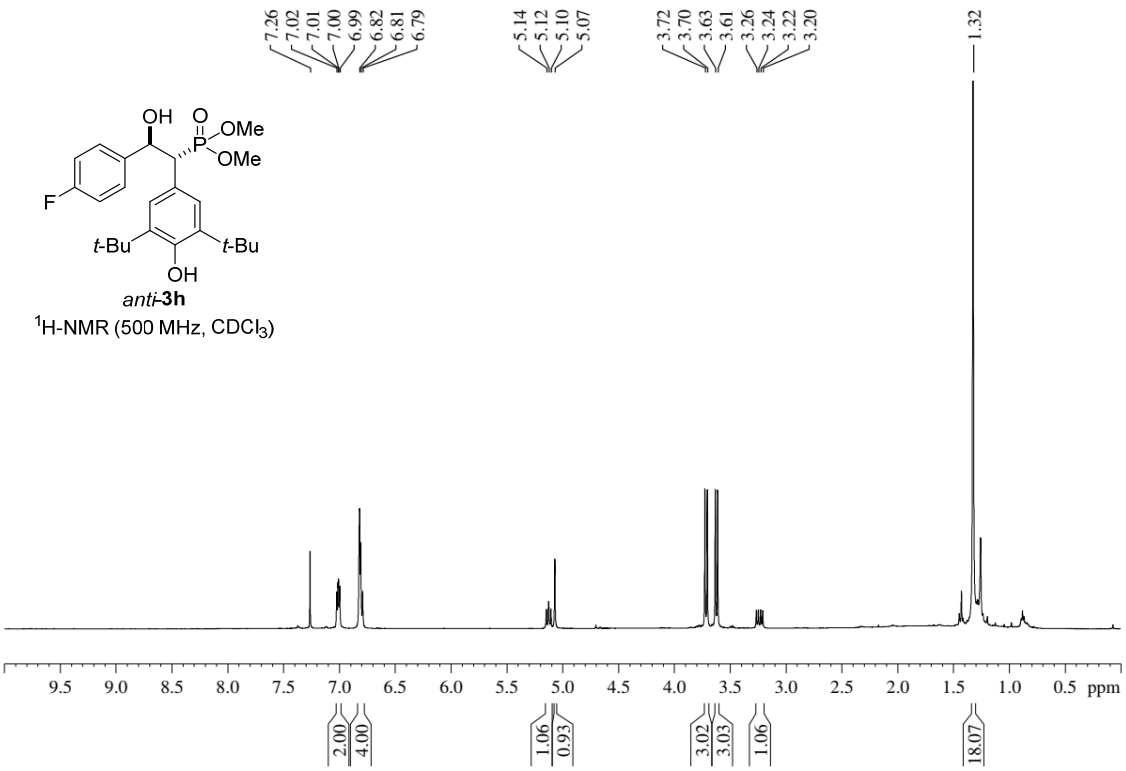
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



syn-**3h**
^{31}P-NMR (202 MHz, $CDCl_3$)

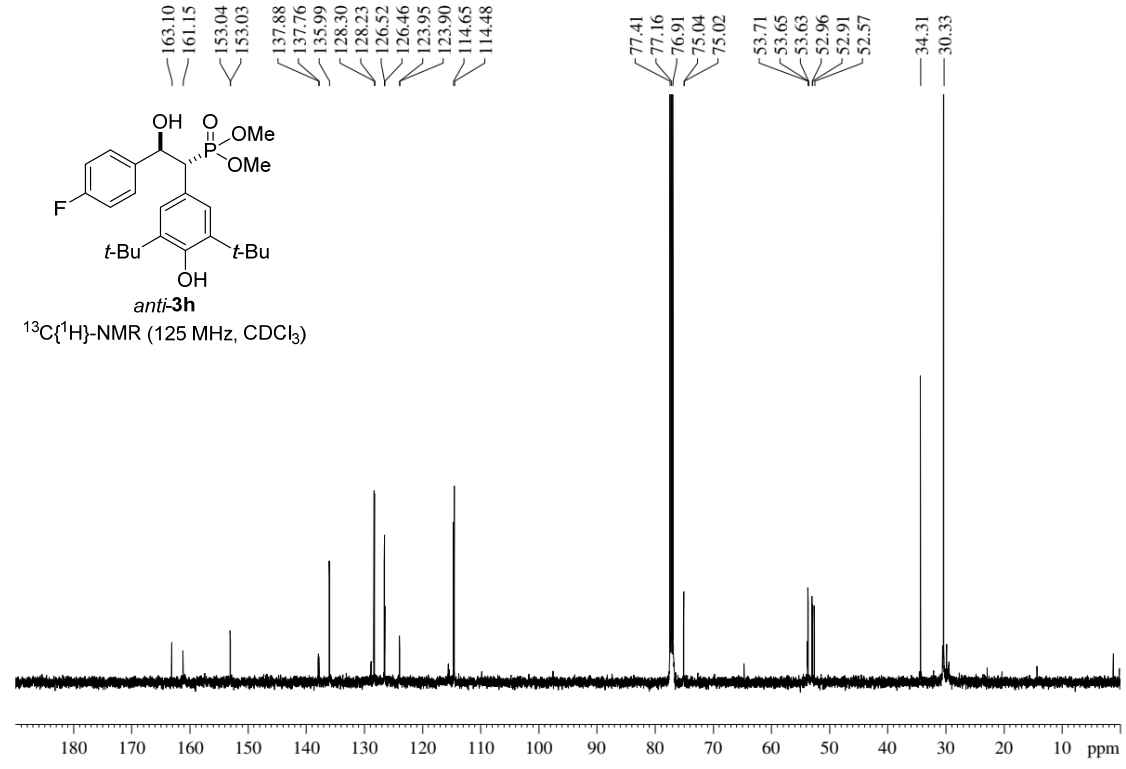


syn-**3h**
^{19}F-NMR (471 MHz, $CDCl_3$)



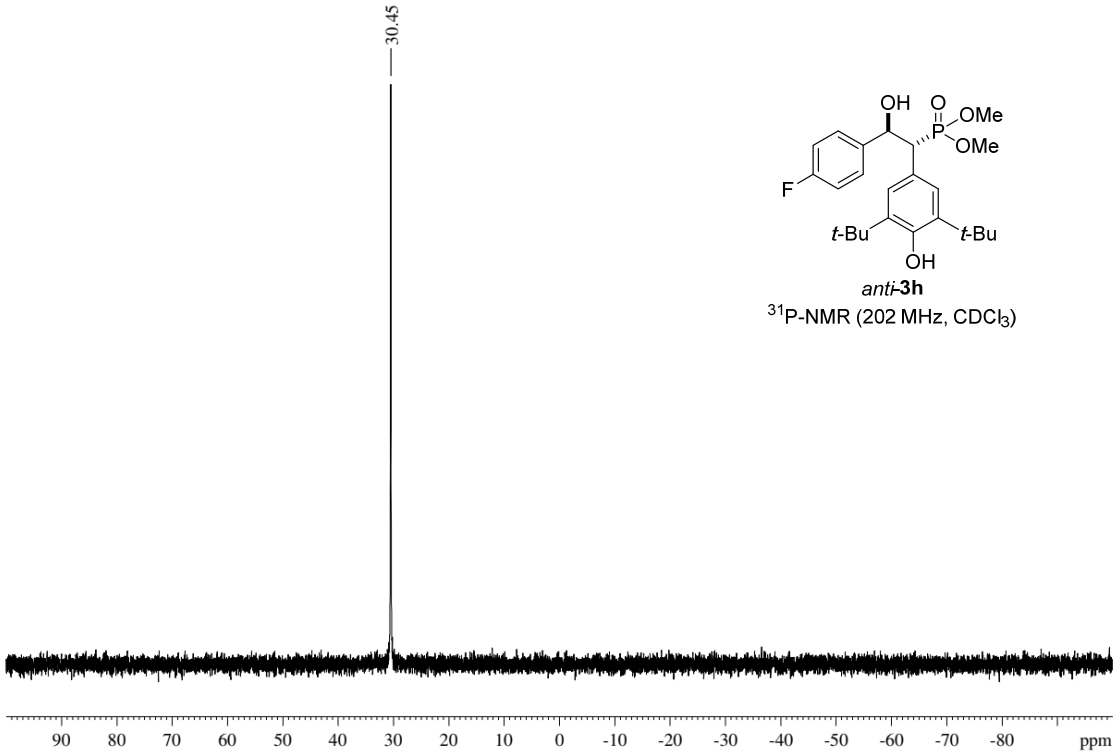
anti-**3h**

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

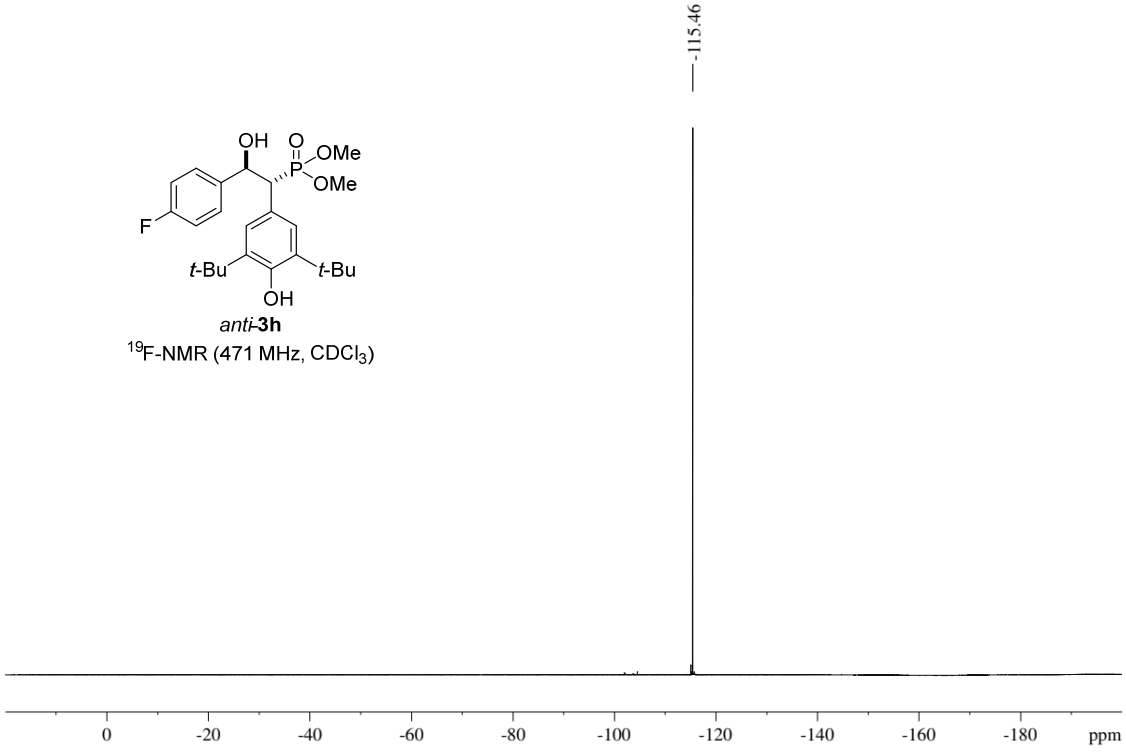


anti-**3h**

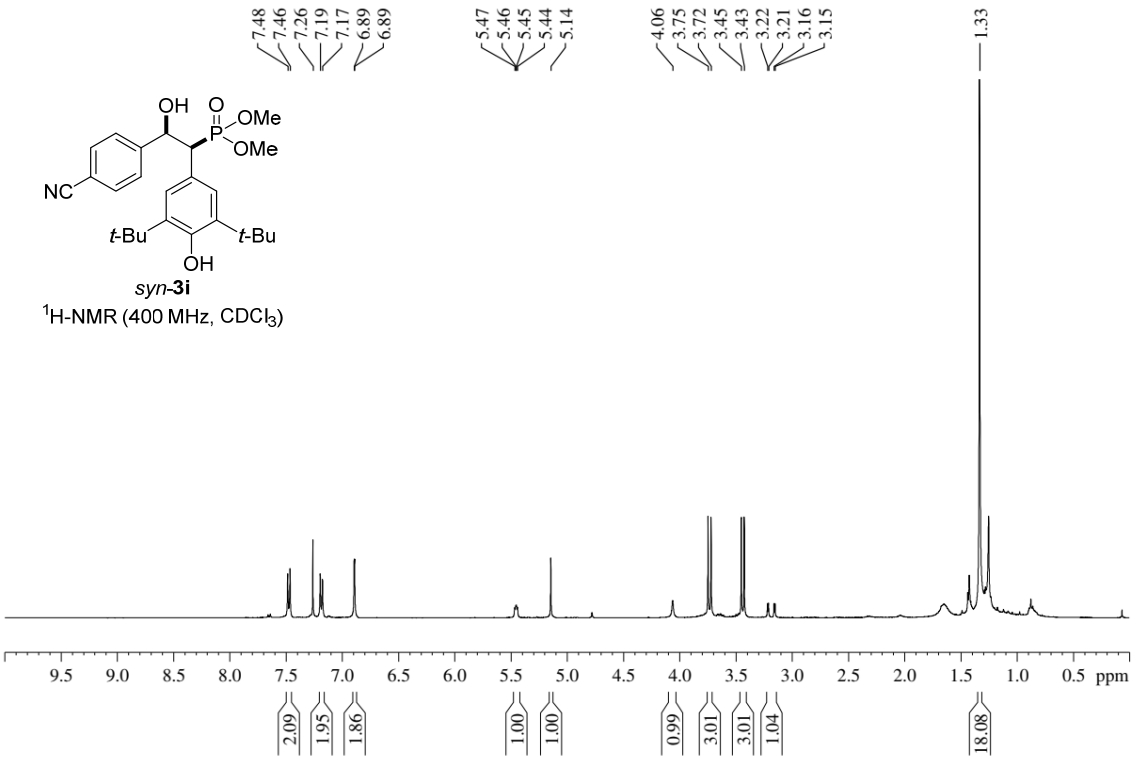
^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



anti-**3h**
^{31}P-NMR (202 MHz, $CDCl_3$)

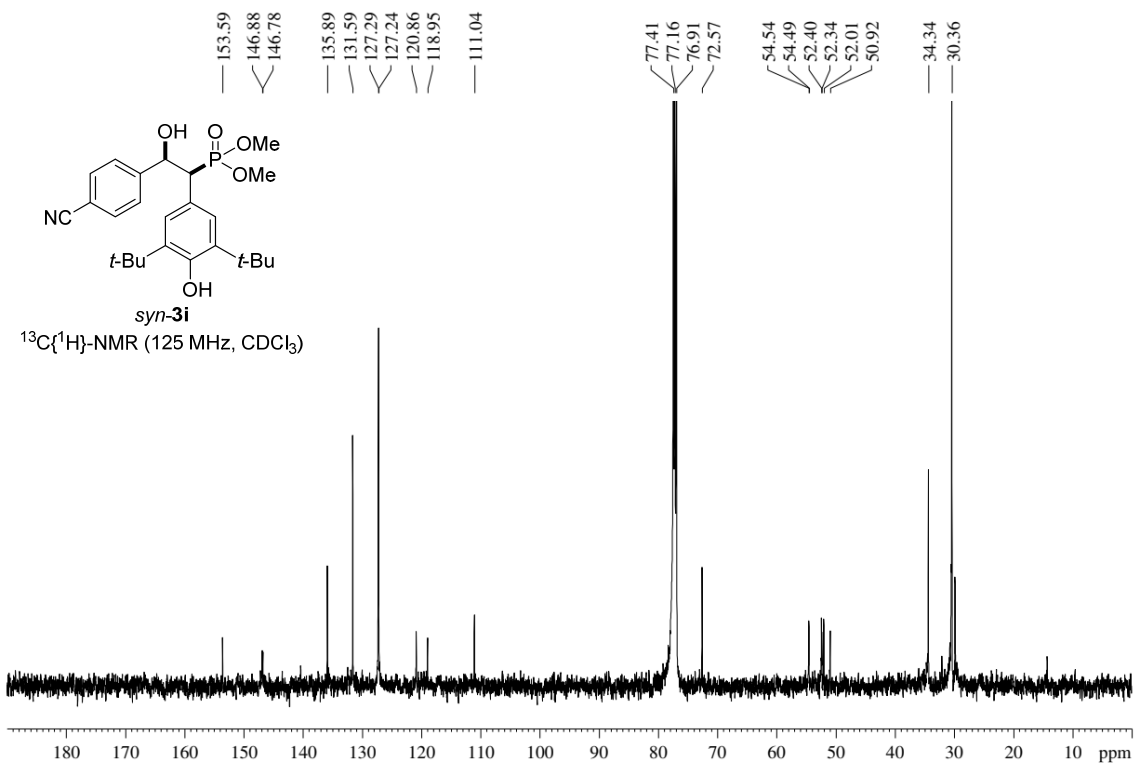


anti-**3h**
^{19}F-NMR (471 MHz, $CDCl_3$)



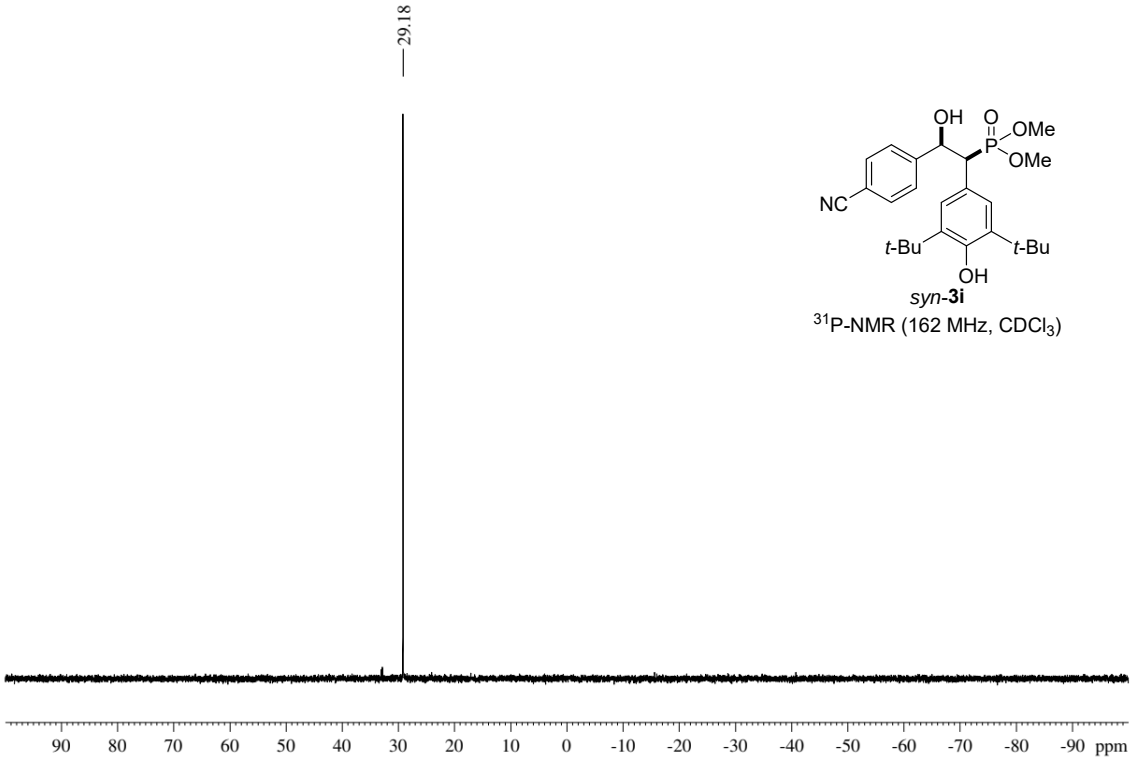
syn-**3i**

^{1}H-NMR (400 MHz, $CDCl_3$)



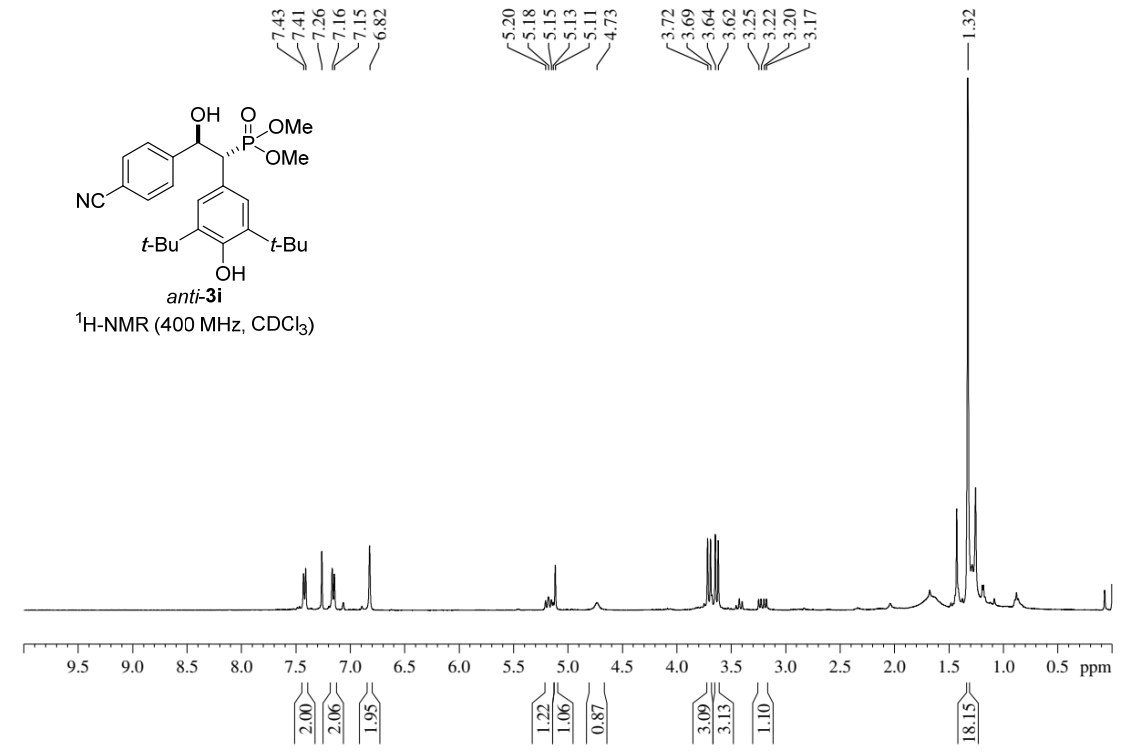
syn-**3i**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



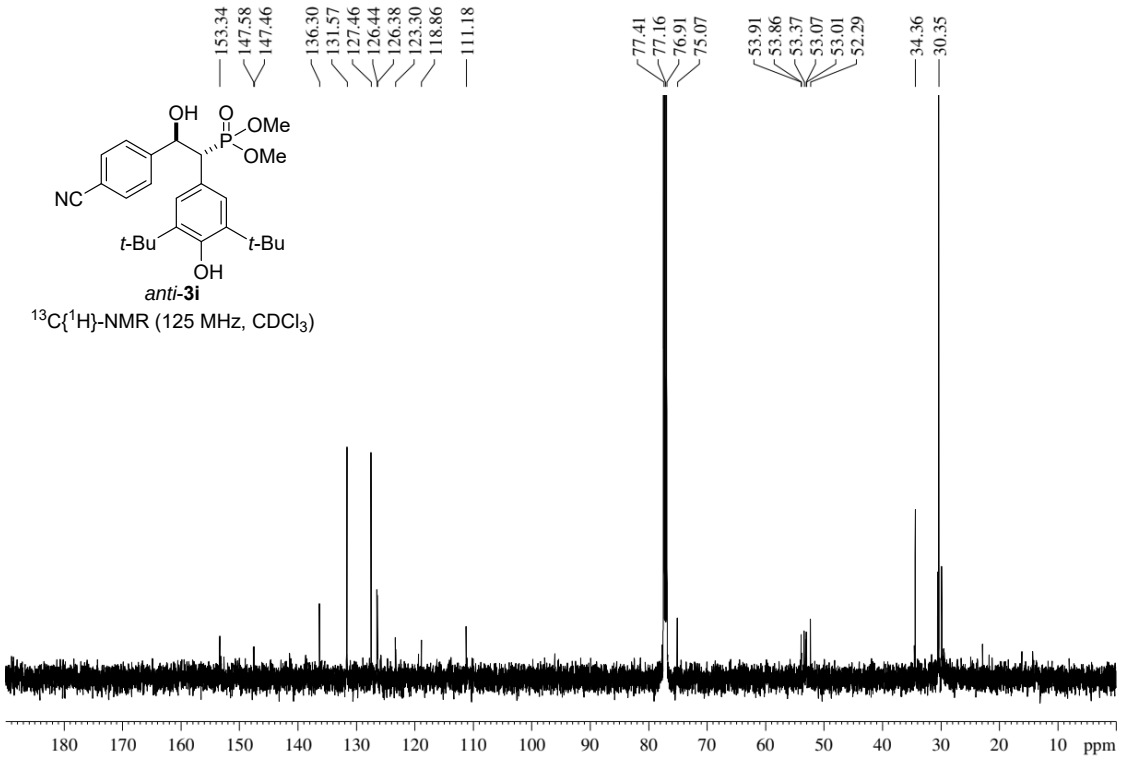
syn-**3i**

^{31}P-NMR (162 MHz, $CDCl_3$)



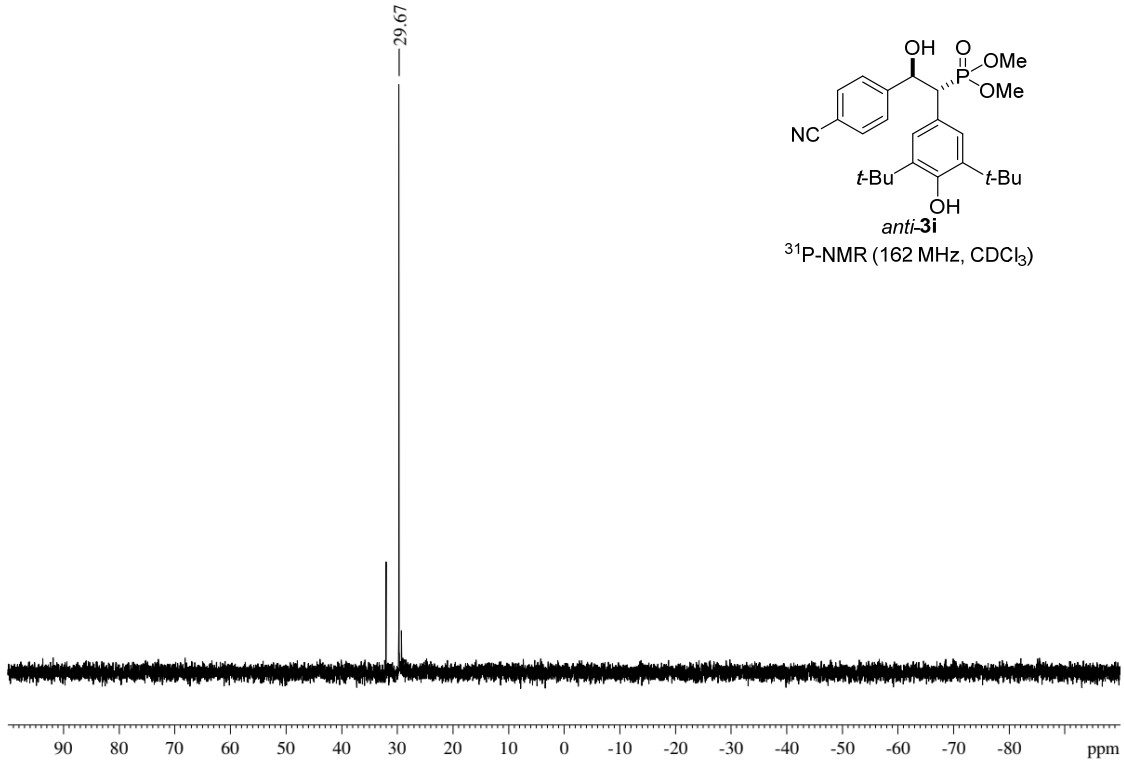
anti-**3i**

^{1}H-NMR (400 MHz, $CDCl_3$)



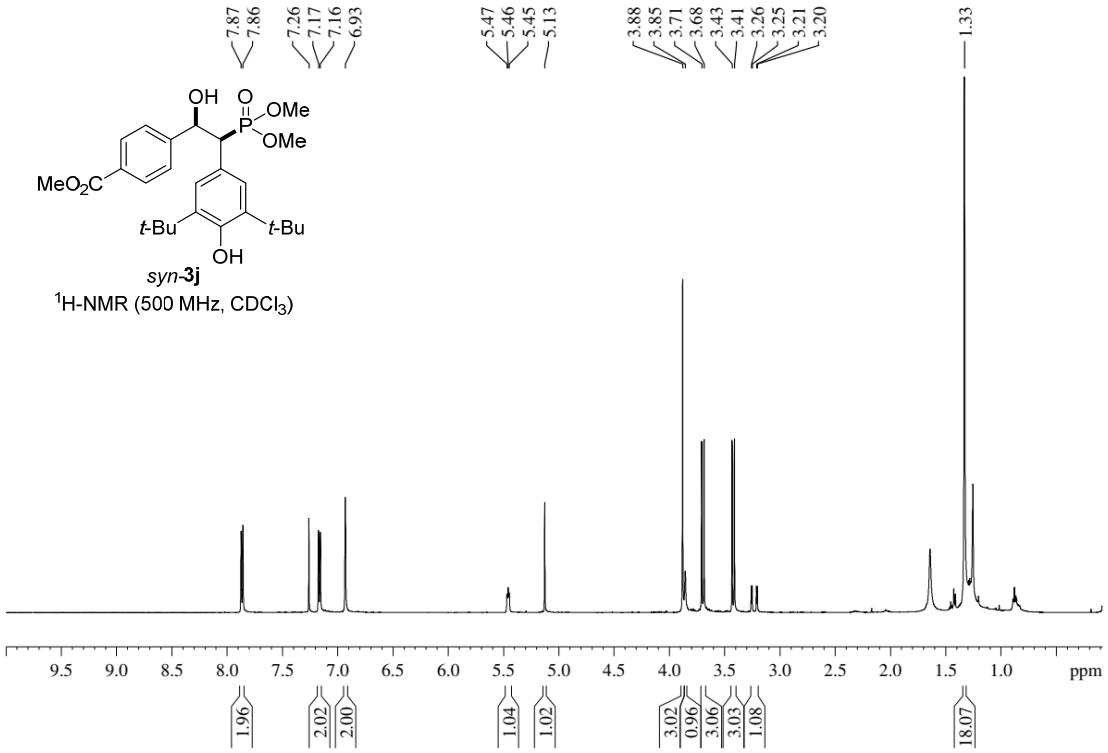
anti-**3i**

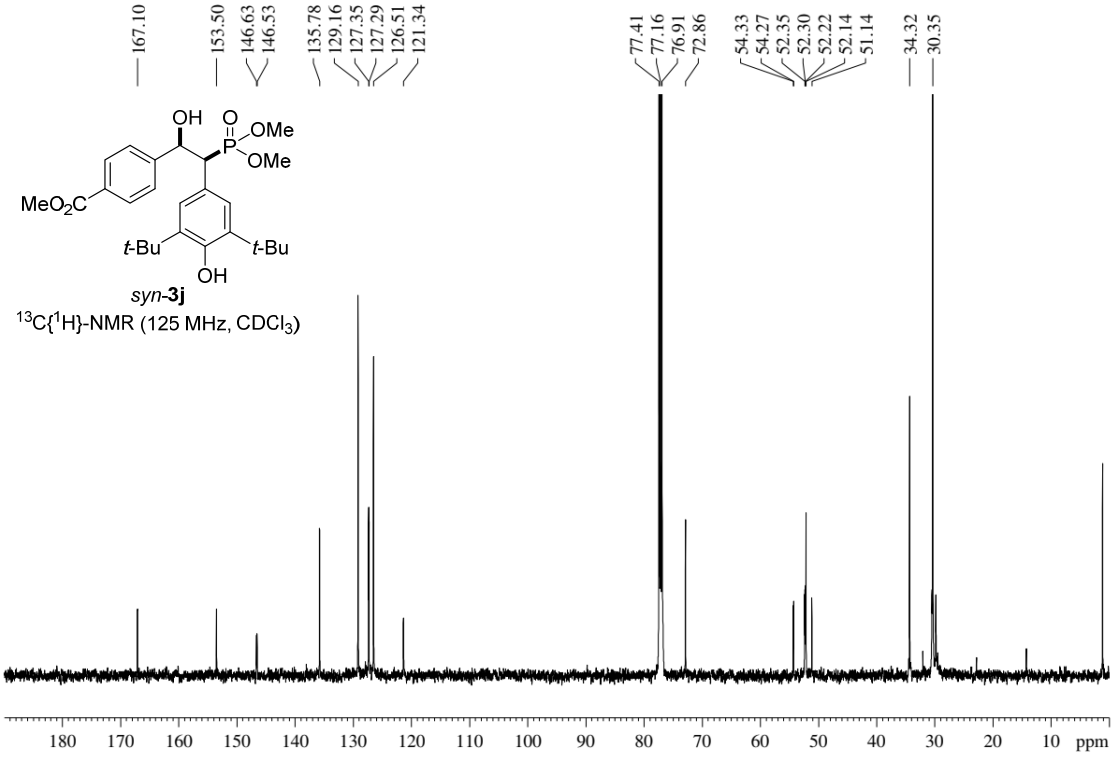
$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)

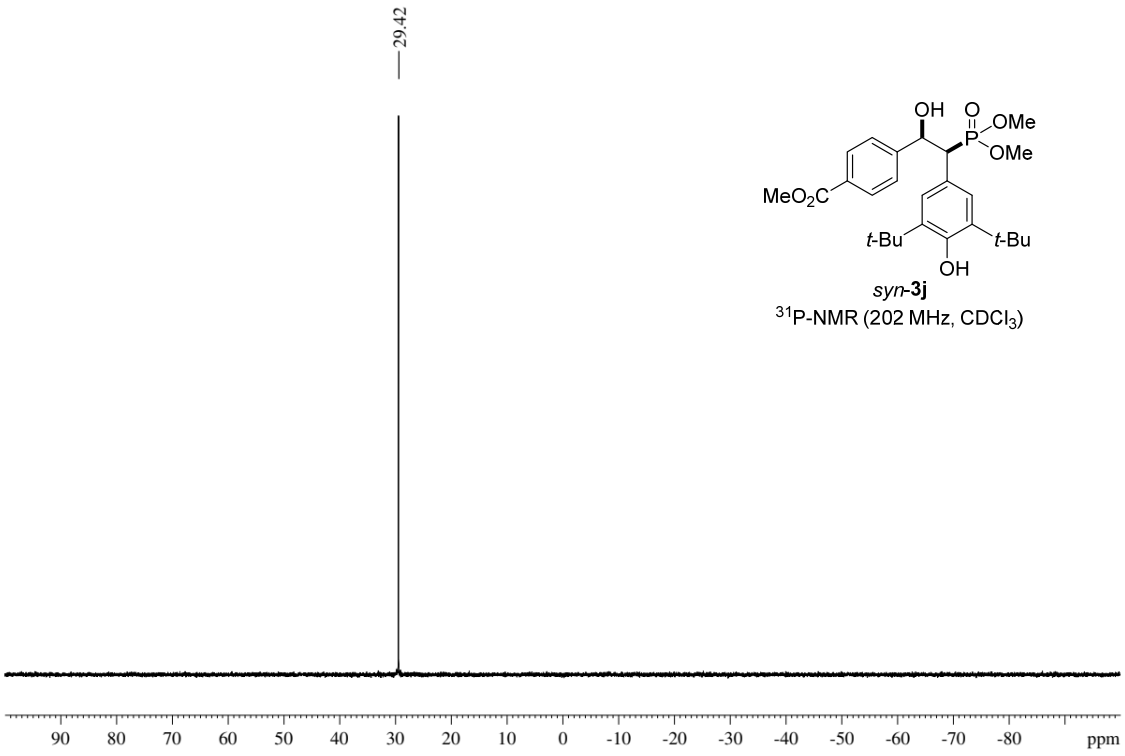


anti-**3i**

^{31}P-NMR (162 MHz, $CDCl_3$)

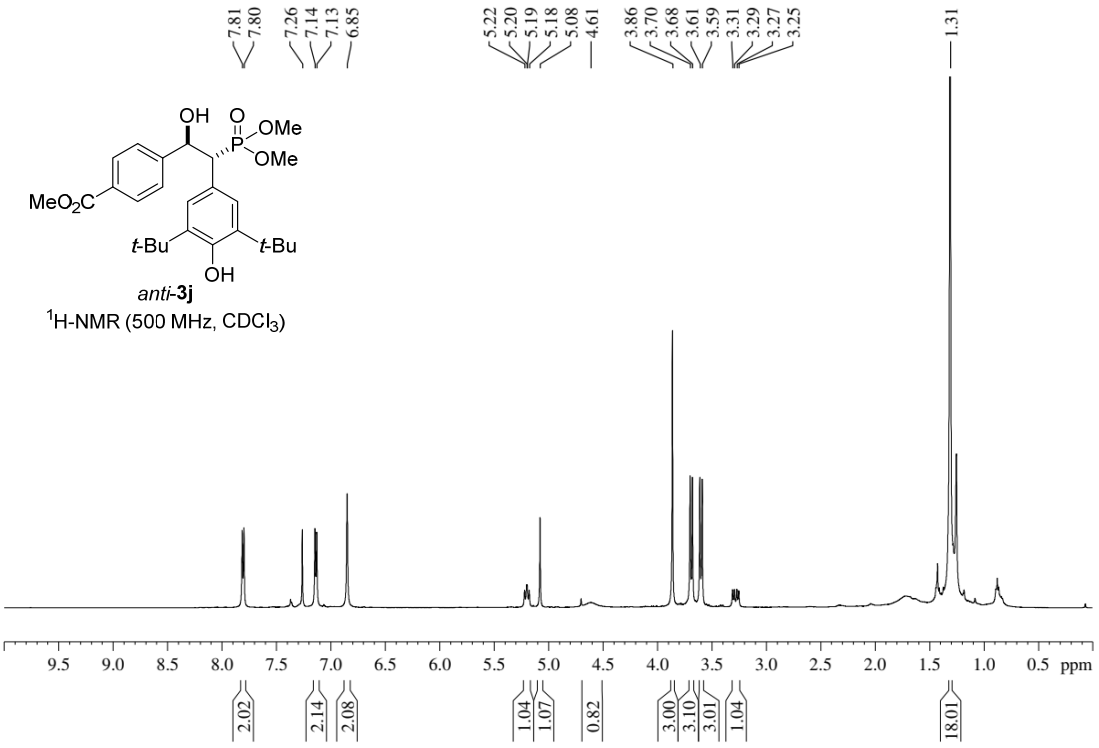

7.87
7.86
7.26
7.17
7.16
6.93
5.47
5.46
5.45
5.13
3.88
3.85
3.71
3.68
3.43
3.41
3.26
3.25
3.21
3.20
1.33
OH
O
OMe
P
OMe
MeO2C
t-Bu
t-Bu
OH
syn-3j
1H-NMR (500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 ppm
1.96
2.02
2.00
1.04
1.02
3.02
0.96
3.06
3.03
1.08
18.07


167.10
153.50
146.63
146.53
135.78
129.16
127.35
127.29
126.51
121.34
77.41
77.16
76.91
72.86
54.33
54.27
52.35
52.30
52.22
52.14
51.14
34.32
30.35
OH
O
OMe
P
OMe
MeO2C
t-Bu
t-Bu
OH
syn-3j
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



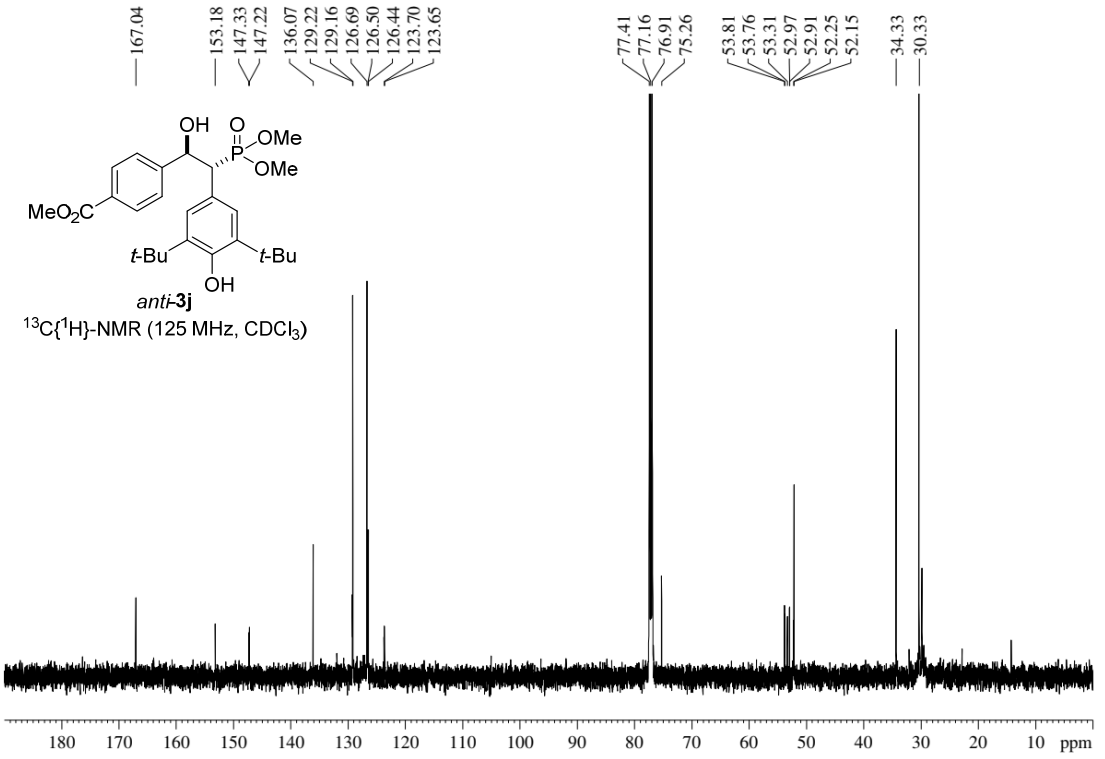
syn-**3j**

^{31}P-NMR (202 MHz, $CDCl_3$)



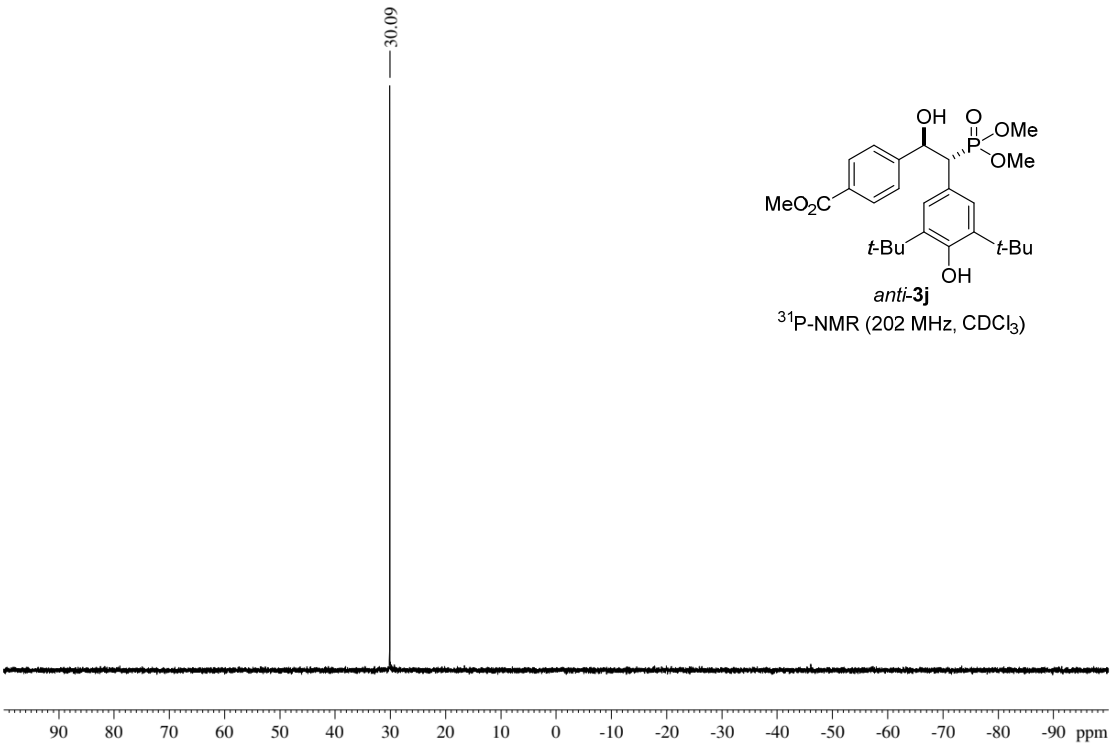
anti-**3j**

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



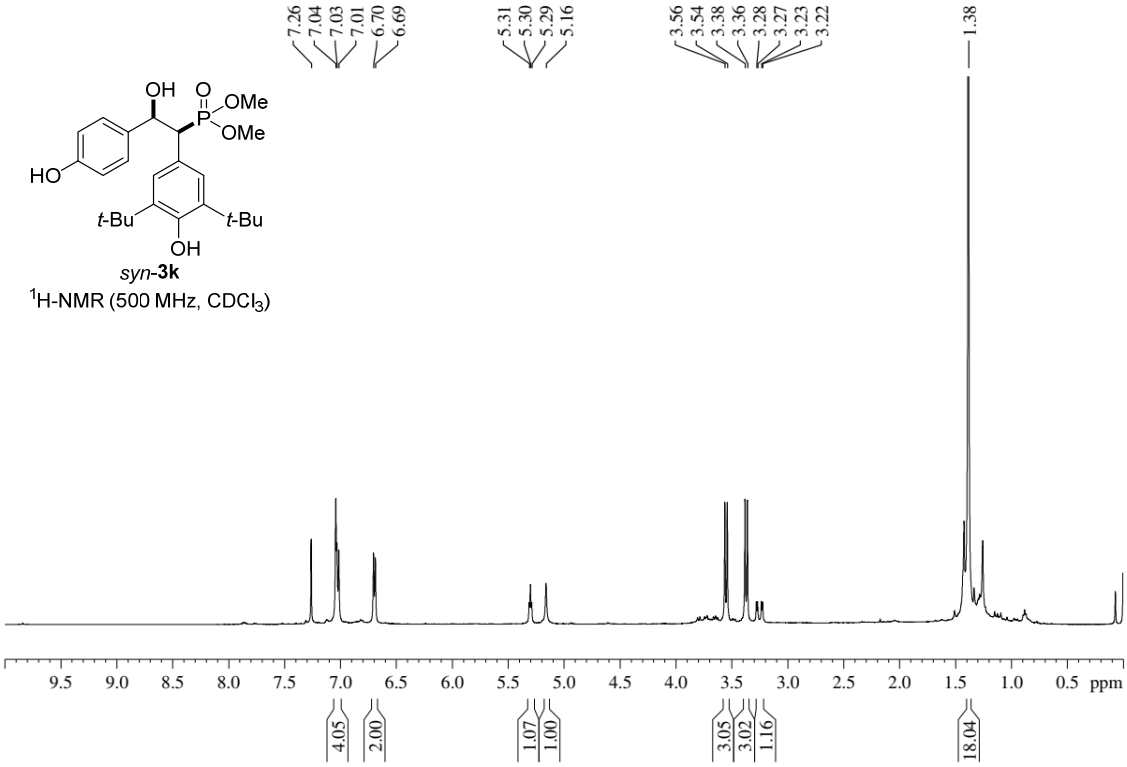
anti-**3j**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



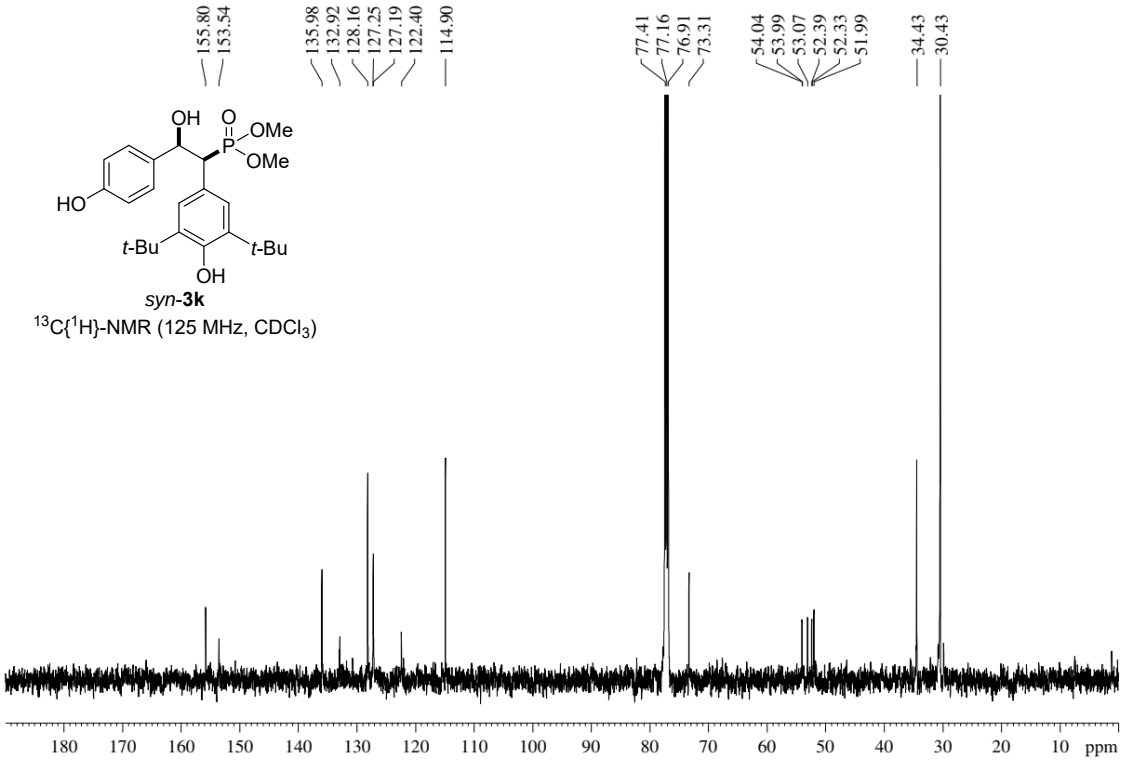
anti-**3j**

^{31}P-NMR (202 MHz, $CDCl_3$)



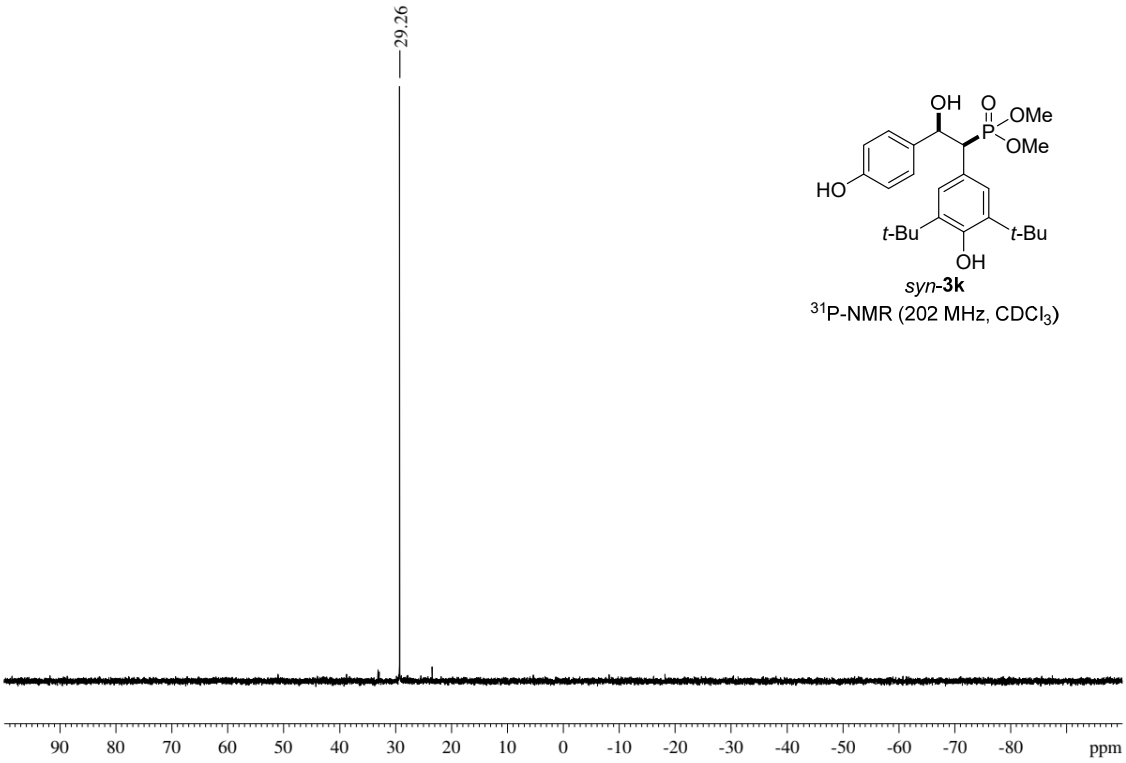
syn-**3k**

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



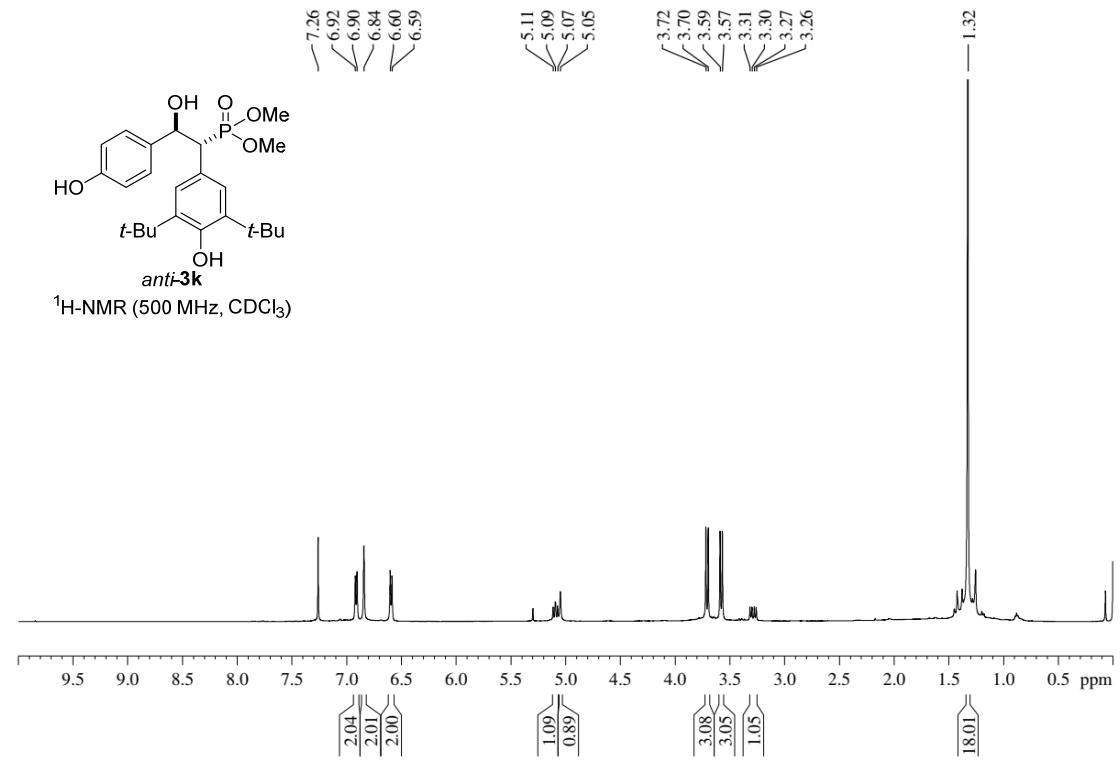
syn-**3k**

$^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$)



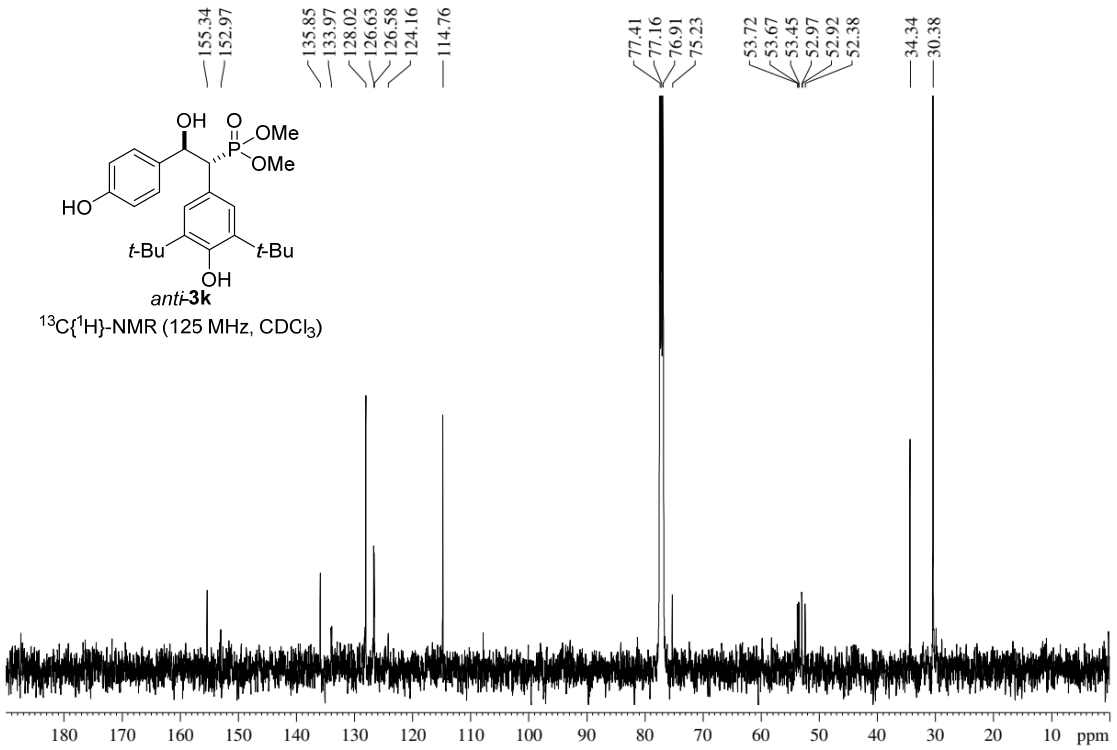
syn-**3k**

^{31}P-NMR (202 MHz, $CDCl_3$)



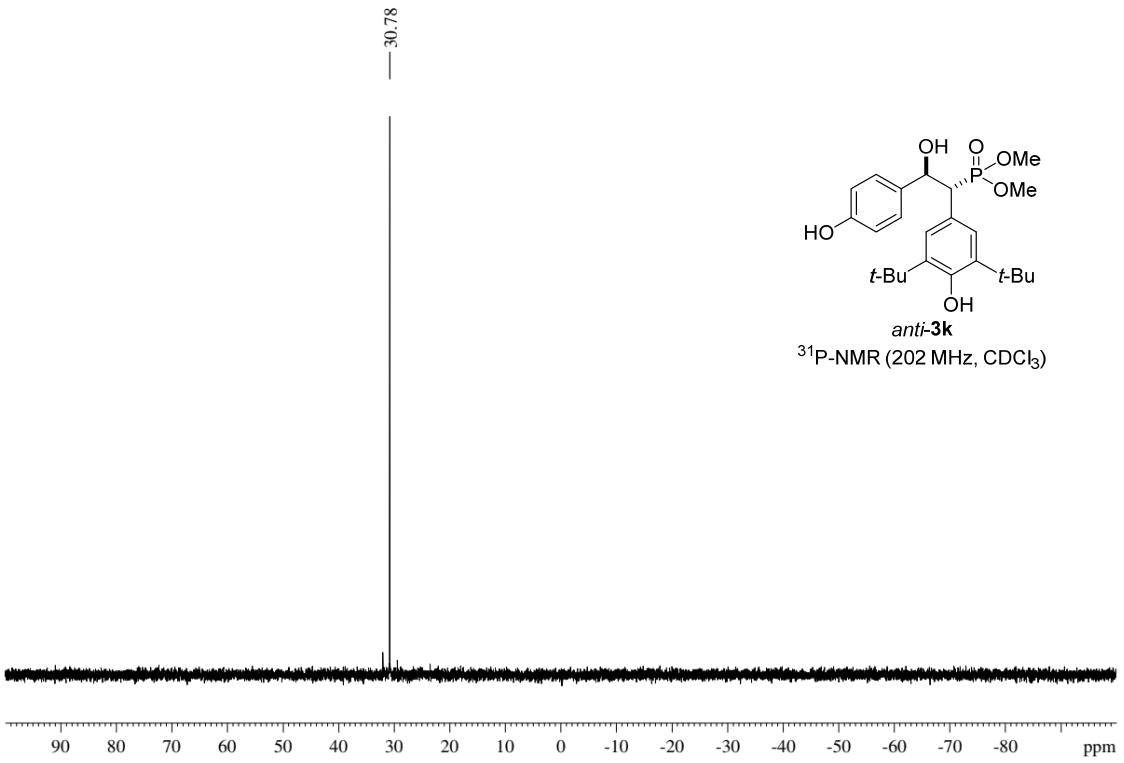
anti-**3k**

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



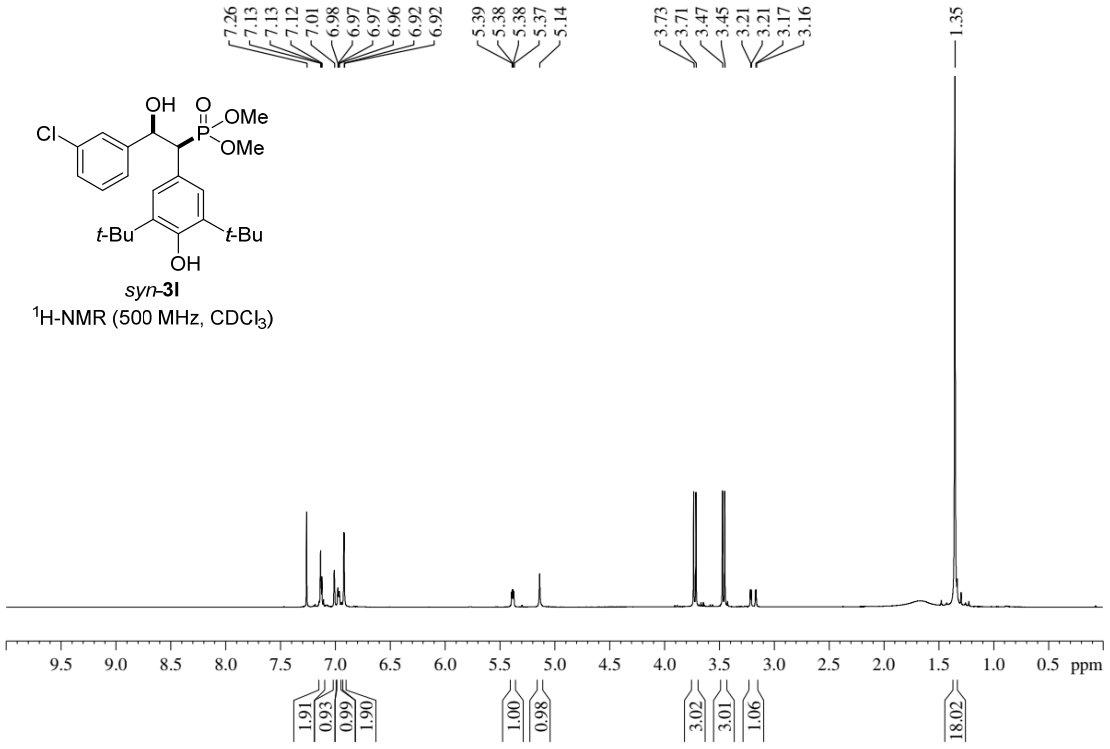
anti-**3k**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



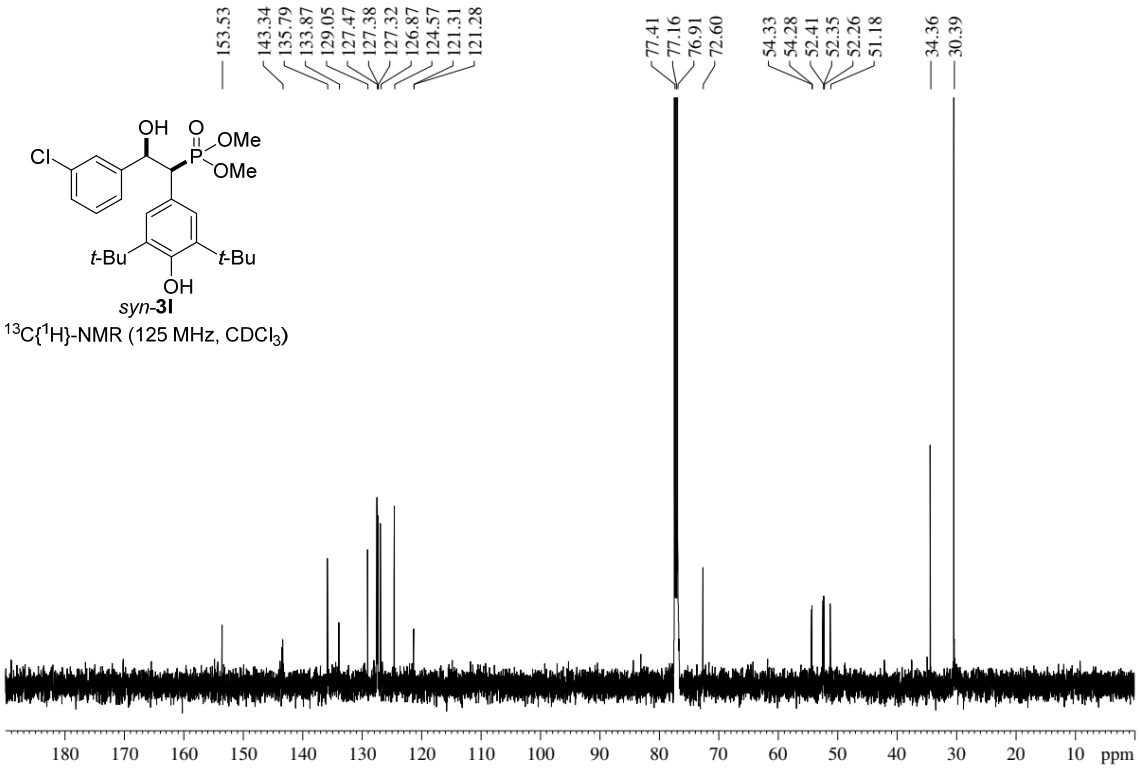
anti-**3k**

^{31}P-NMR (202 MHz, $CDCl_3$)



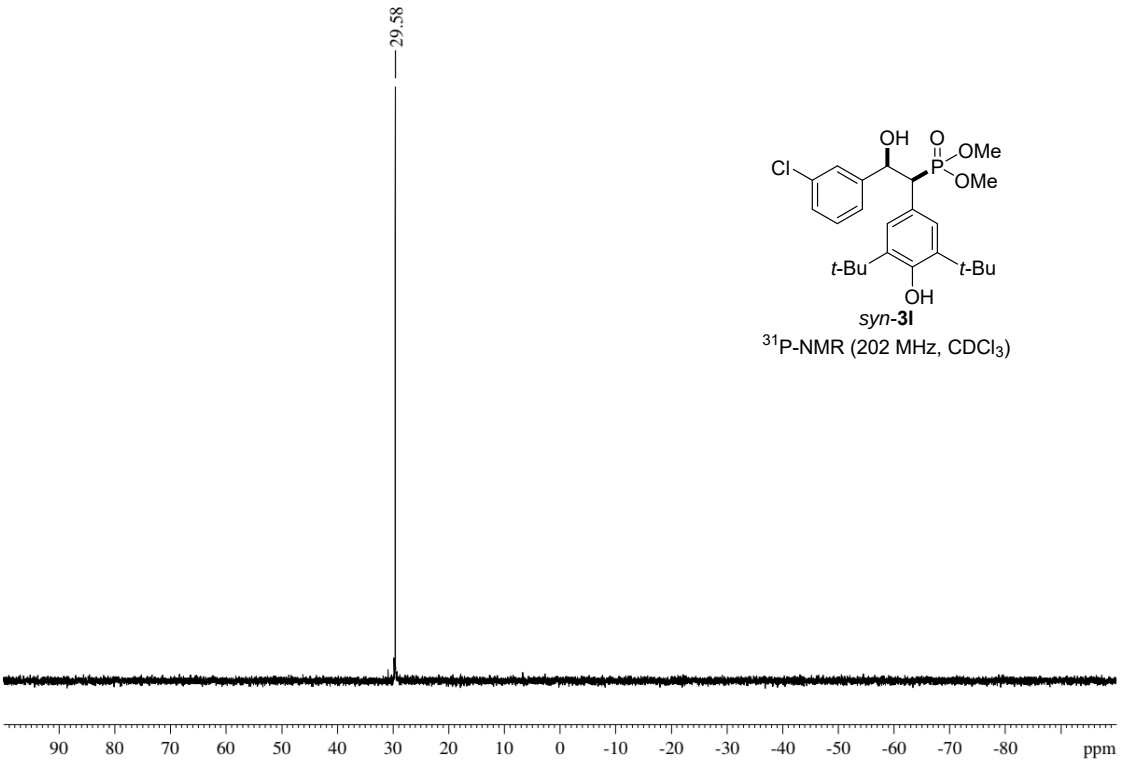
syn-**3l**

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



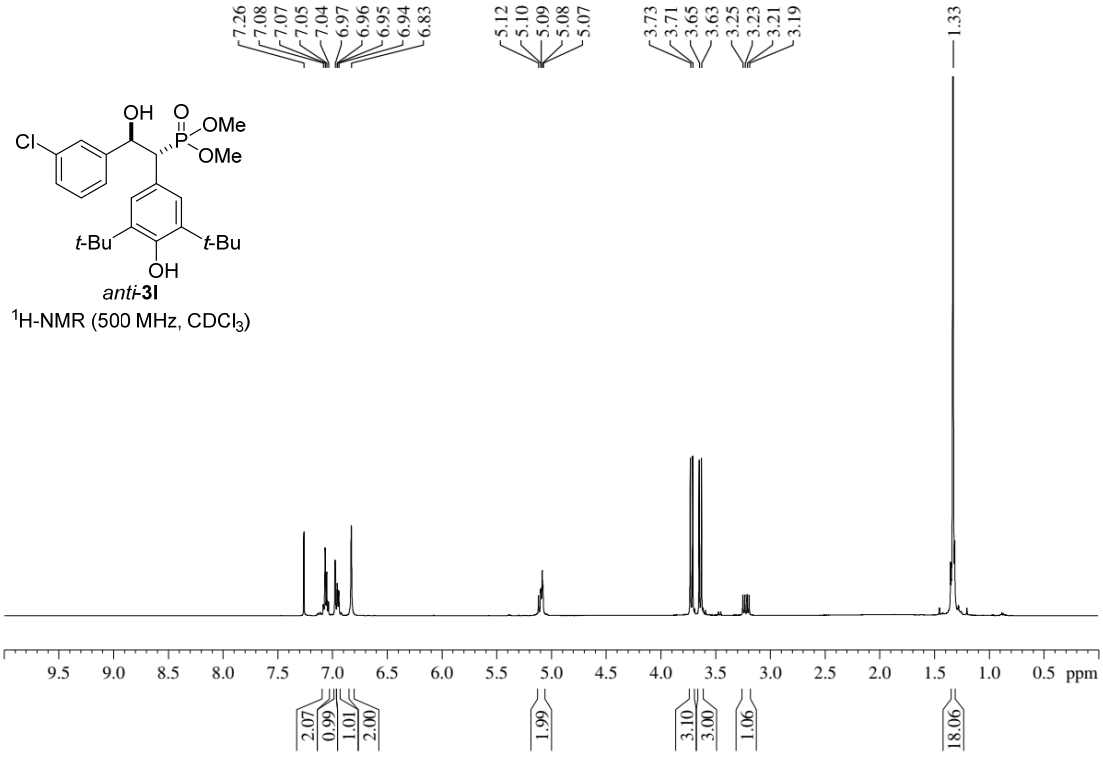
syn-**3l**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



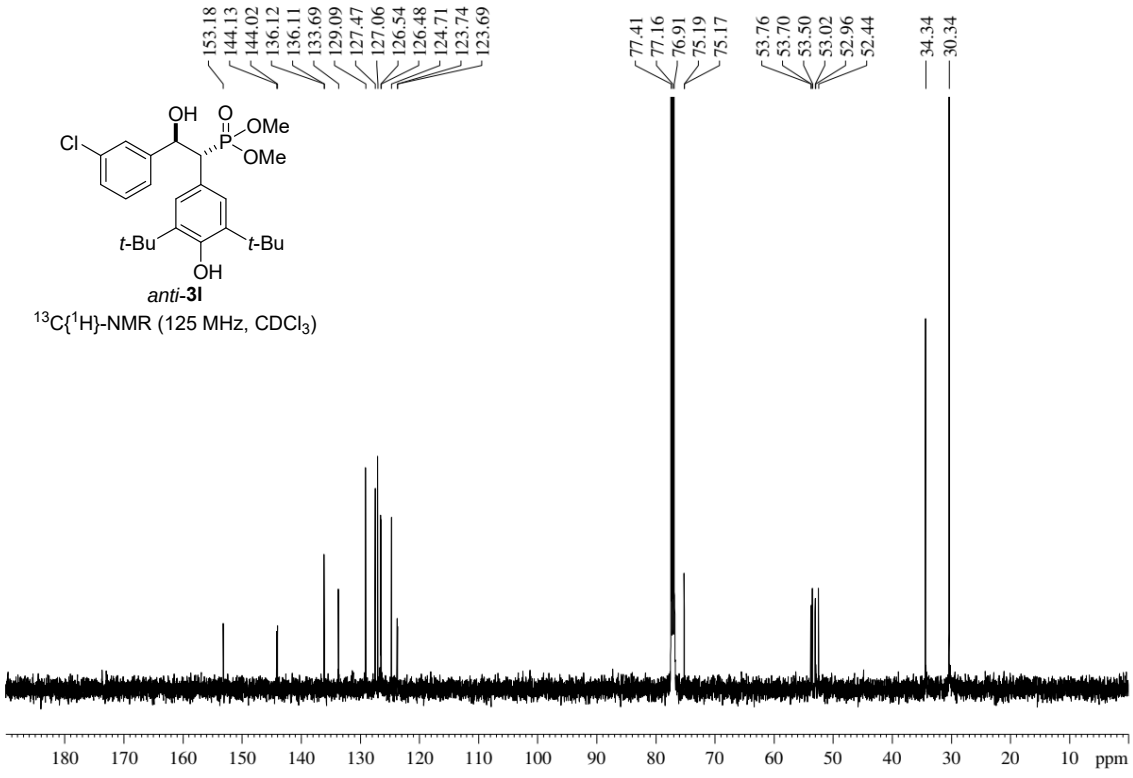
syn-**3l**

^{31}P-NMR (202 MHz, $CDCl_3$)



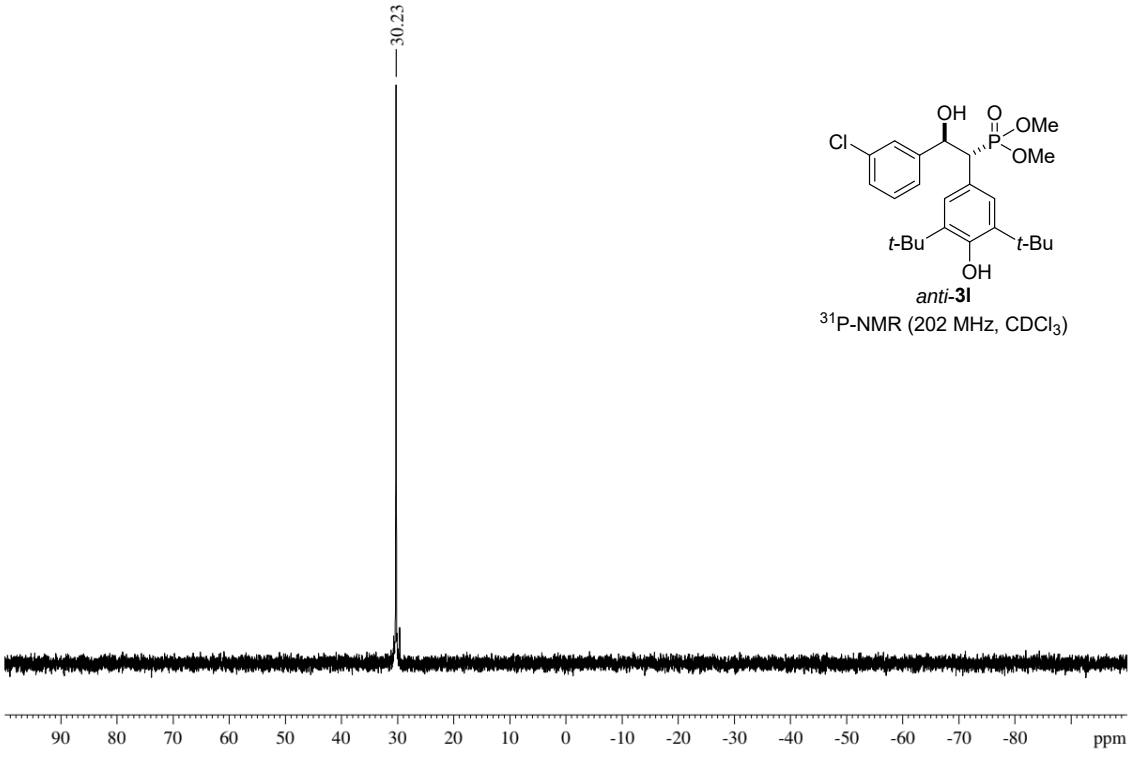
anti-**3l**

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



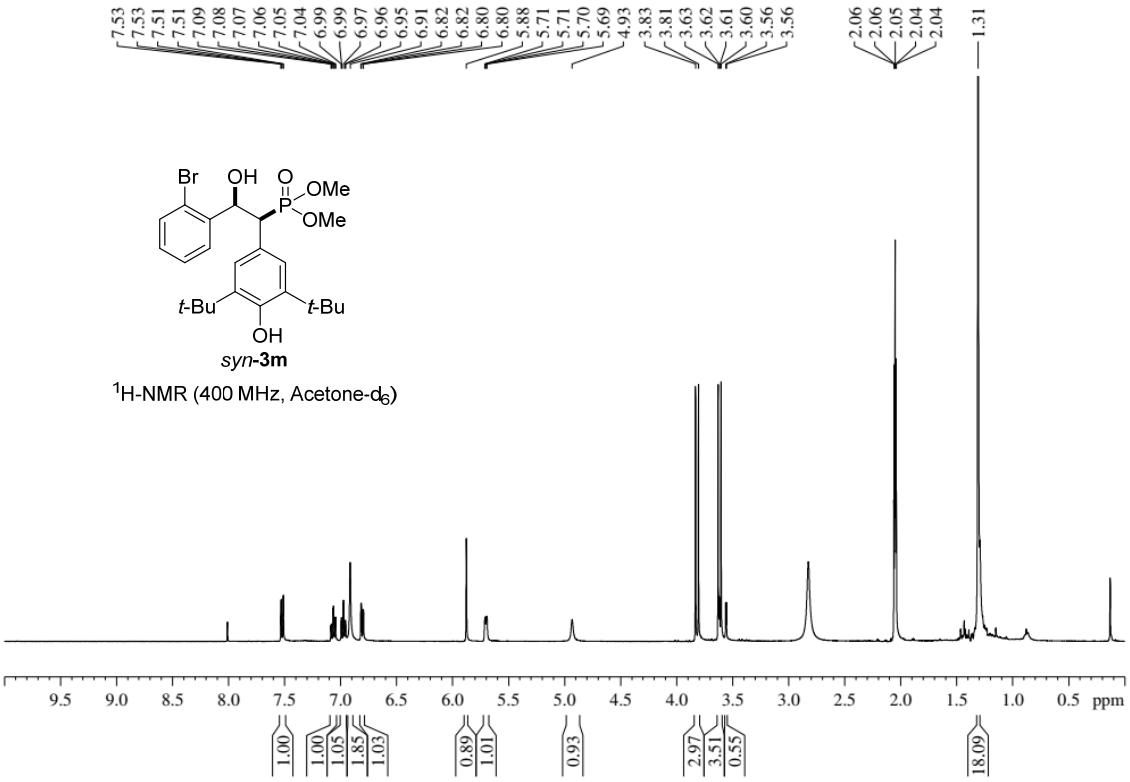
anti-**3l**

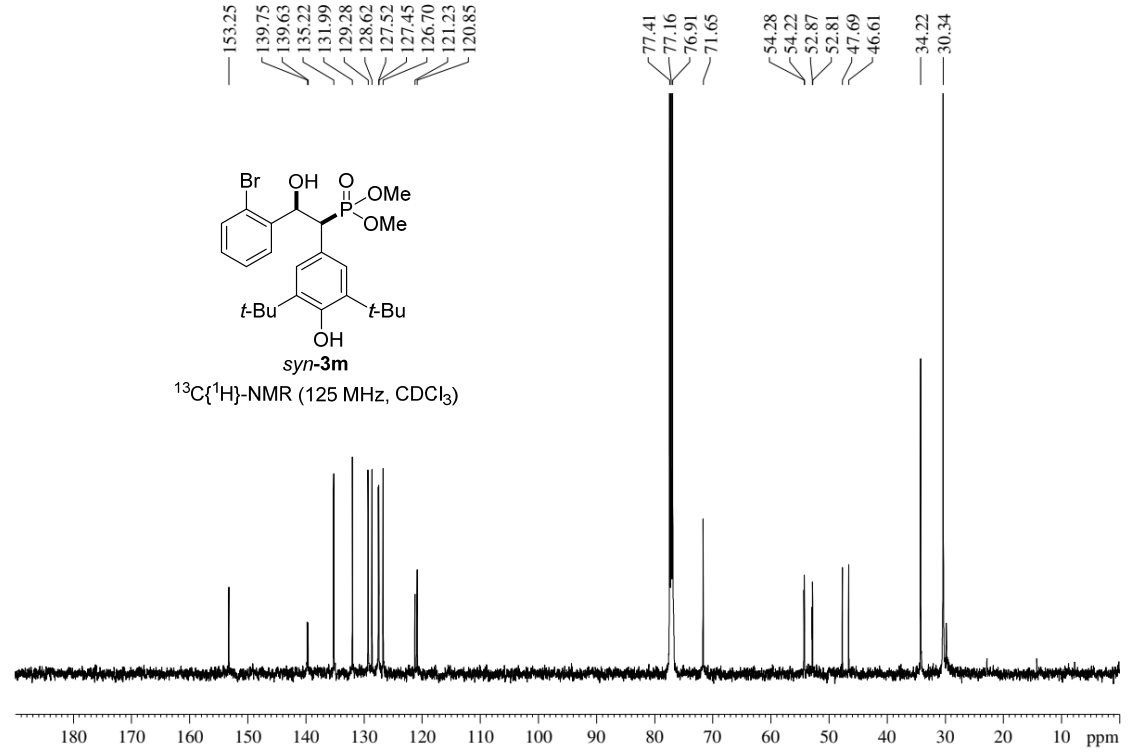
$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)

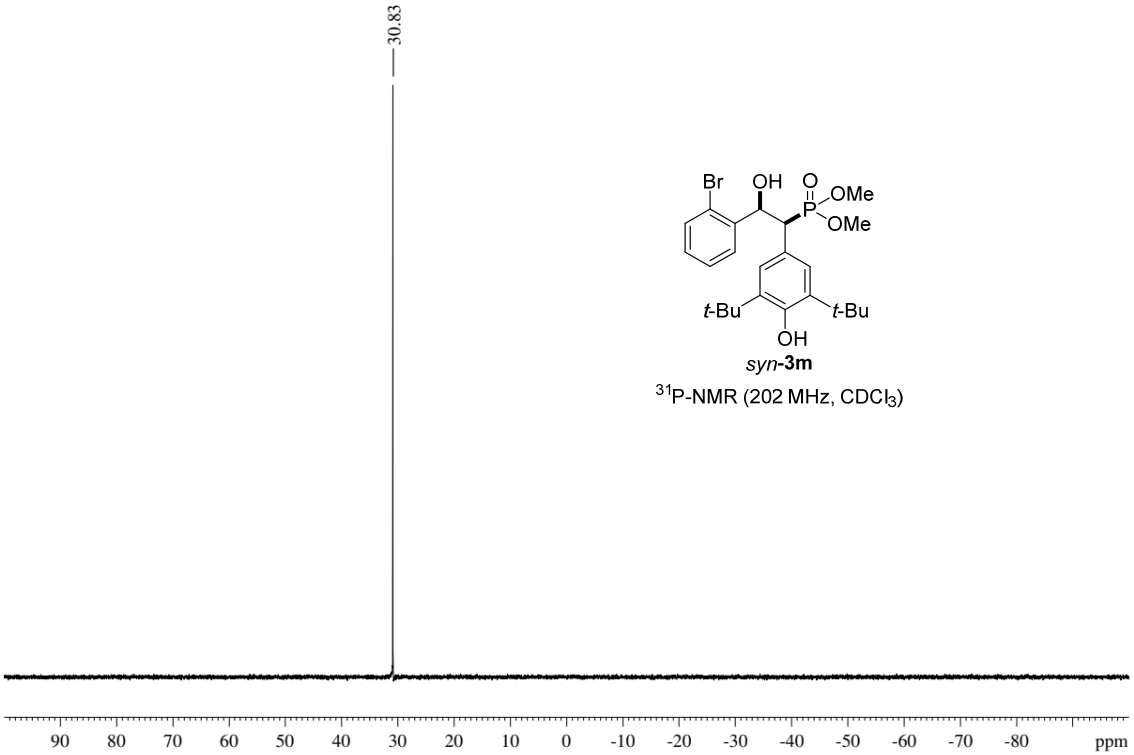


anti-**3l**

^{31}P-NMR (202 MHz, $CDCl_3$)

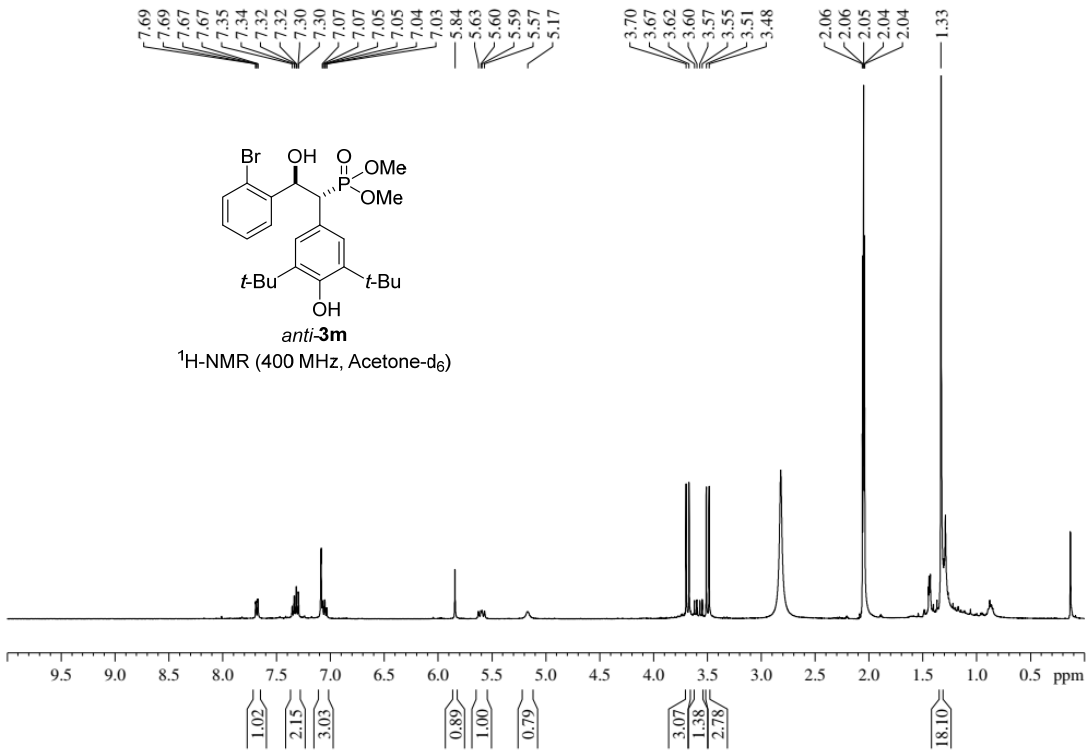

7.53
7.53
7.51
7.51
7.09
7.08
7.07
7.06
7.05
7.04
6.99
6.99
6.97
6.96
6.95
6.91
6.82
6.82
6.80
6.80
5.88
5.71
5.71
5.70
5.69
4.93
3.83
3.81
3.63
3.62
3.61
3.60
3.56
3.56
2.06
2.06
2.05
2.04
2.04
1.31
Br
OH
O
P
OMe
OMe
t-Bu
t-Bu
OH
syn-3m
1H-NMR (400 MHz, Acetone-d6)
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
1.00
1.00
1.05
1.85
1.03
0.89
1.01
0.93
2.97
3.51
0.55
18.09


153.25
139.75
139.63
135.22
131.99
129.28
128.62
127.52
127.45
126.70
121.23
120.85
77.41
77.16
76.91
71.65
54.28
54.22
52.87
52.81
47.69
46.61
34.22
30.34
Br
OH
O
P
OMe
OMe
t-Bu
t-Bu
OH
syn-3m
13C{1H}-NMR (125 MHz, CDCl3)
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm



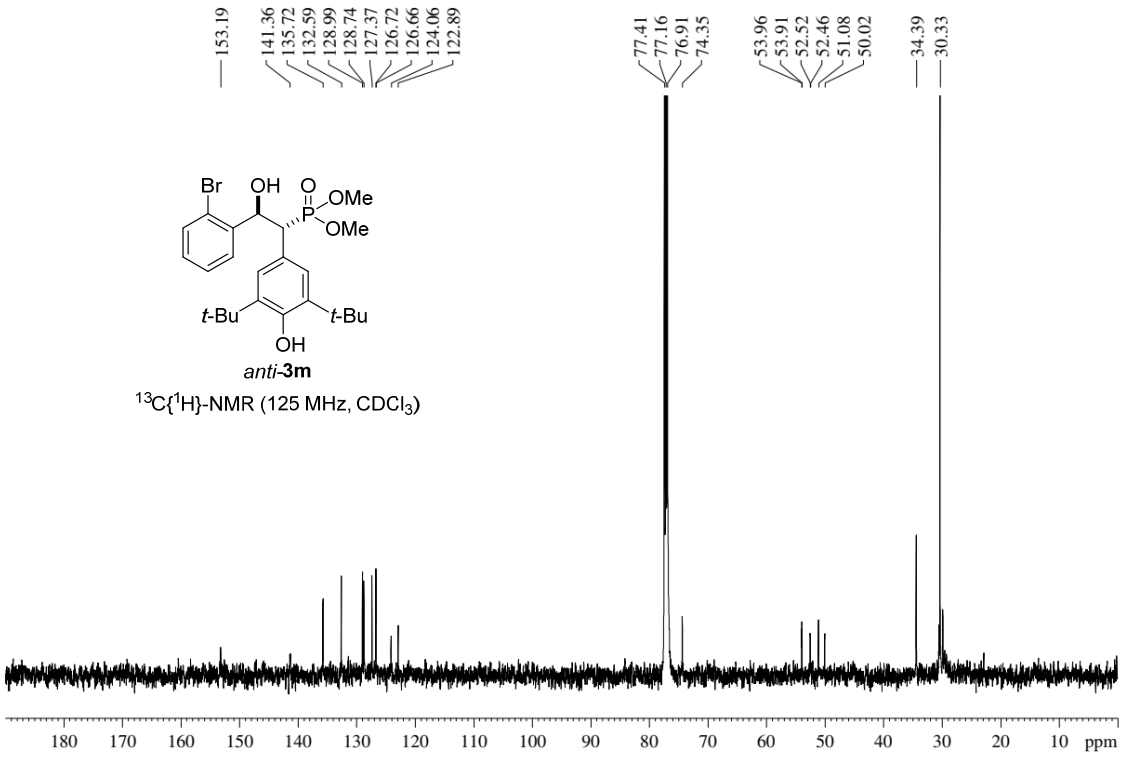
syn-**3m**

^{31}P-NMR (202 MHz, $CDCl_3$)



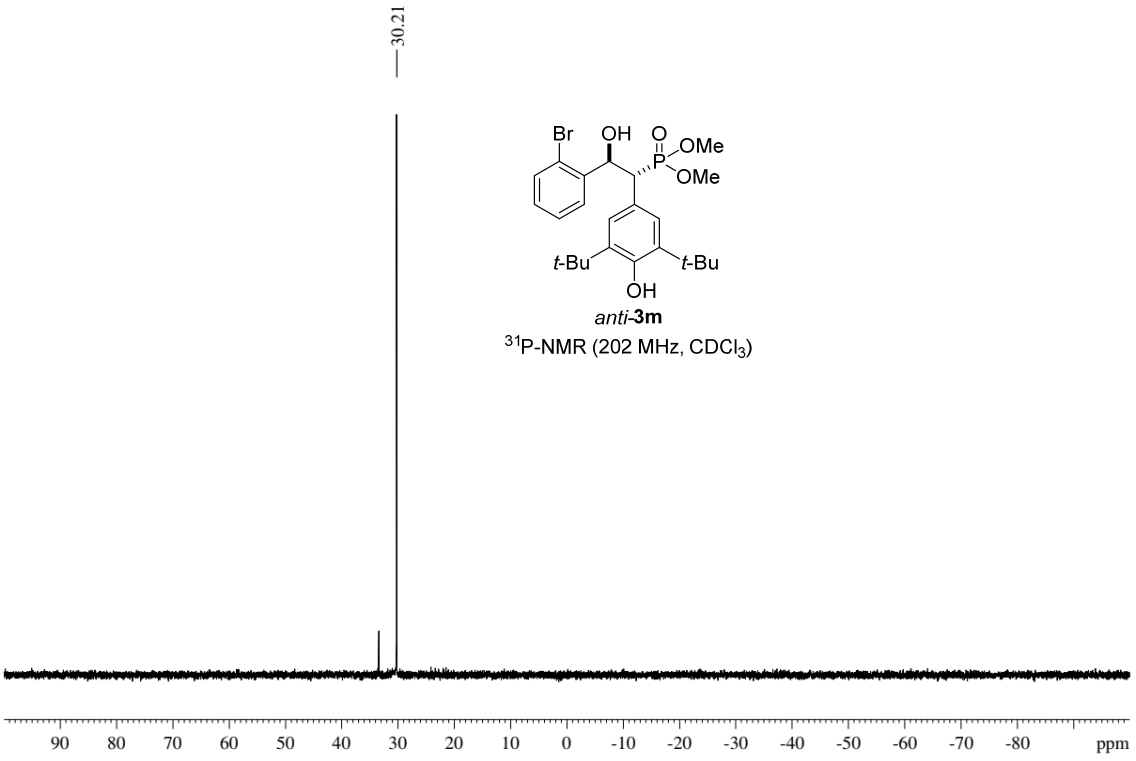
anti-**3m**

^{1}H-NMR (400 MHz, Acetone-d_6)



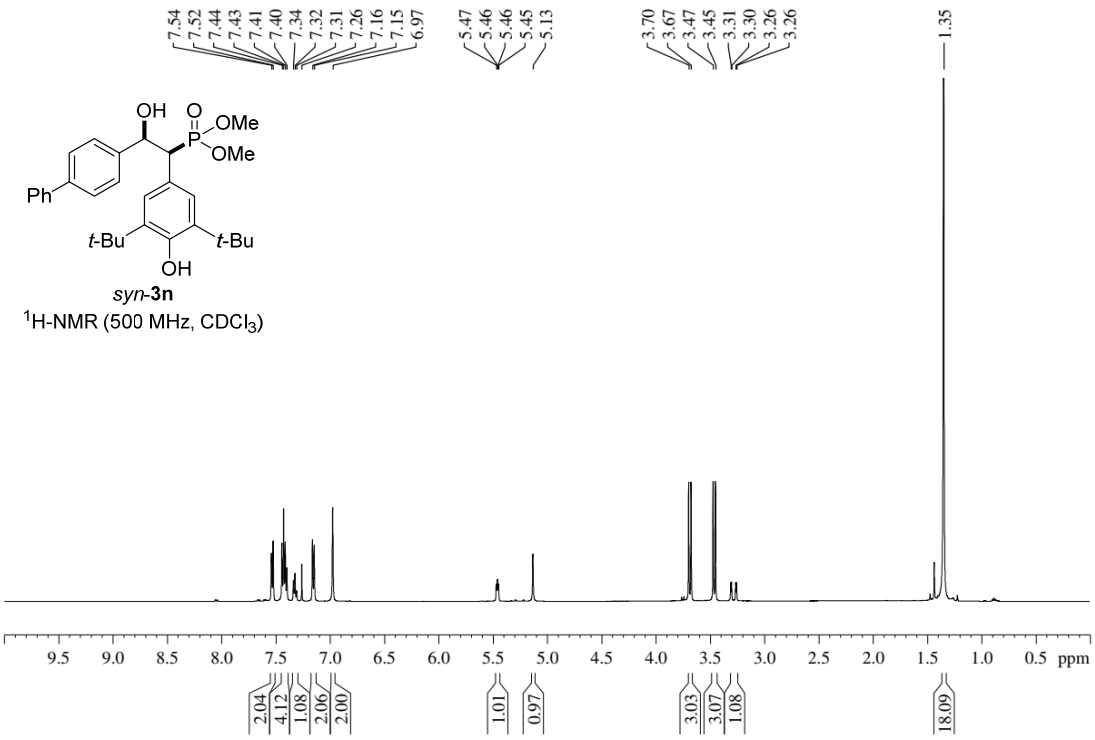
anti-**3m**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



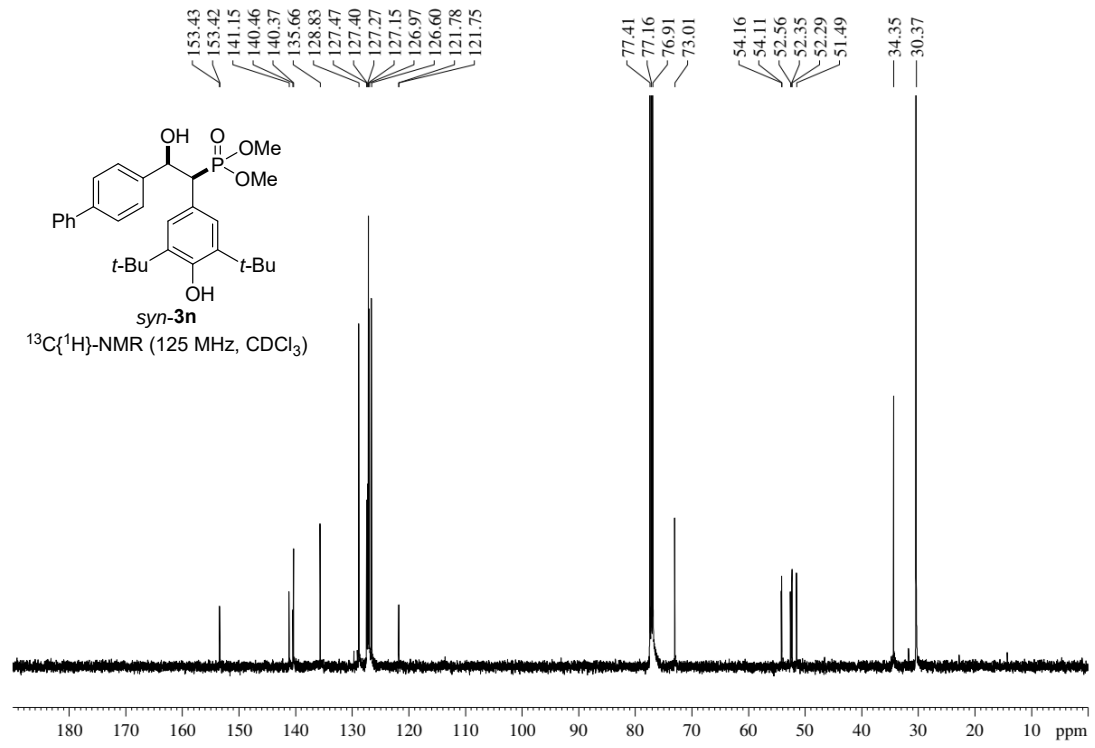
anti-**3m**

^{31}P-NMR (202 MHz, $CDCl_3$)



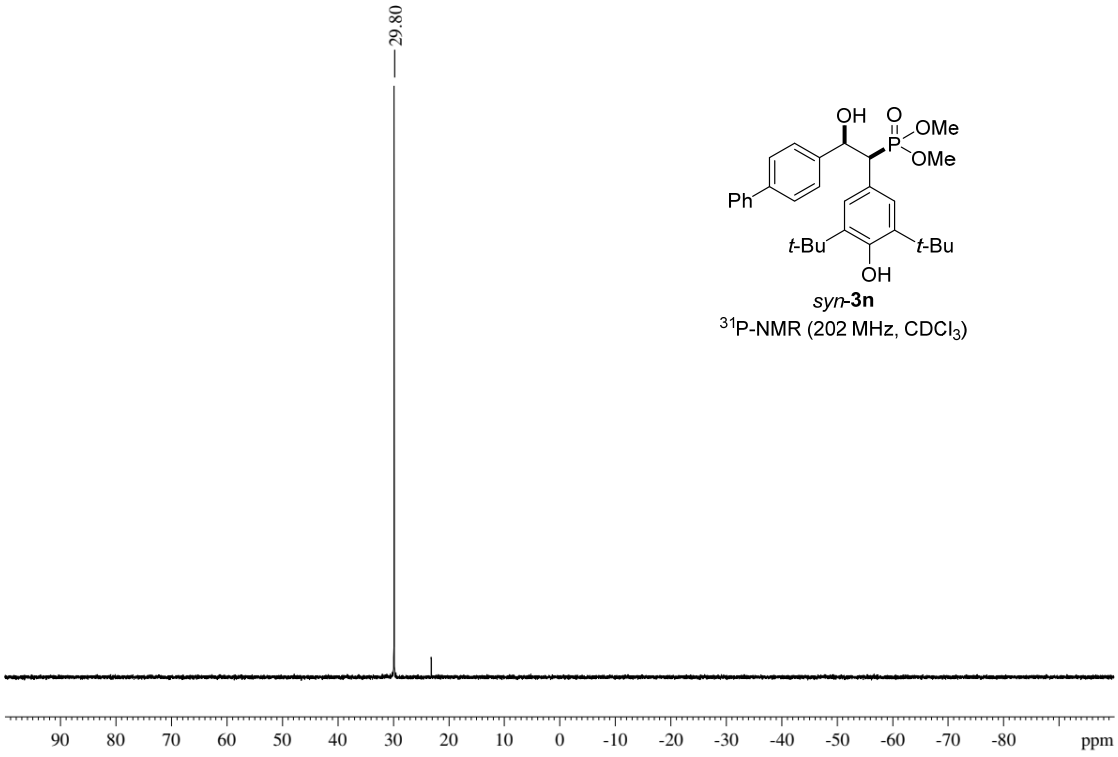
syn-**3n**

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



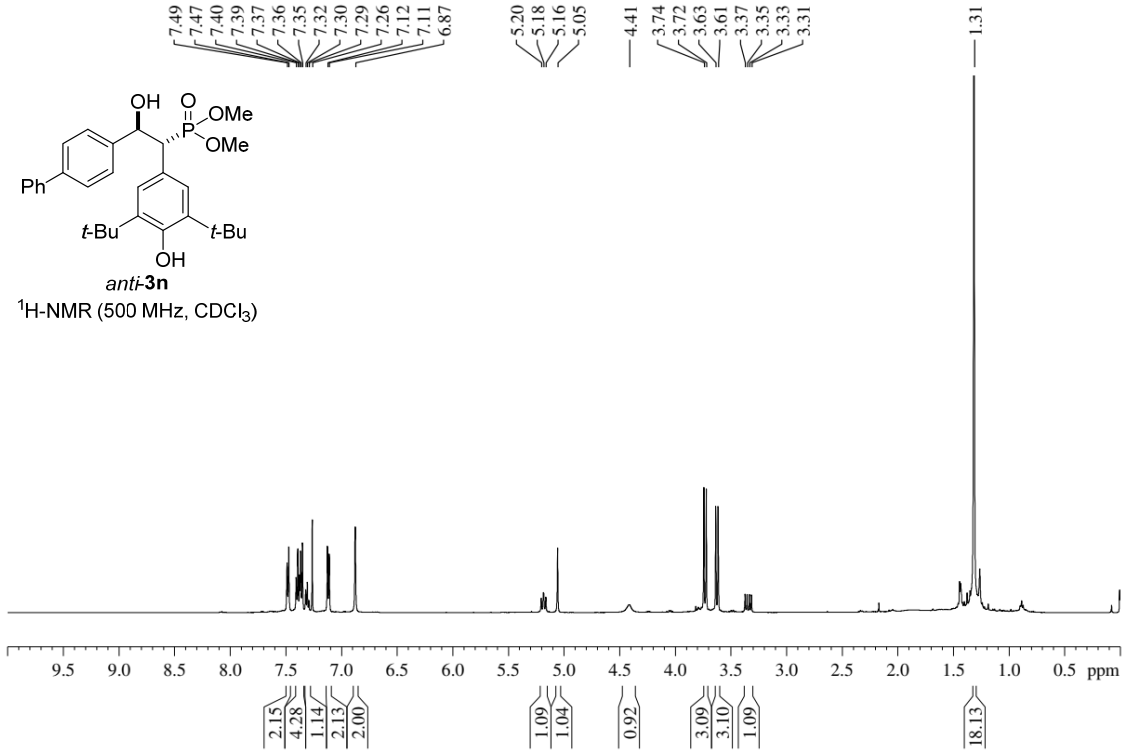
syn-**3n**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



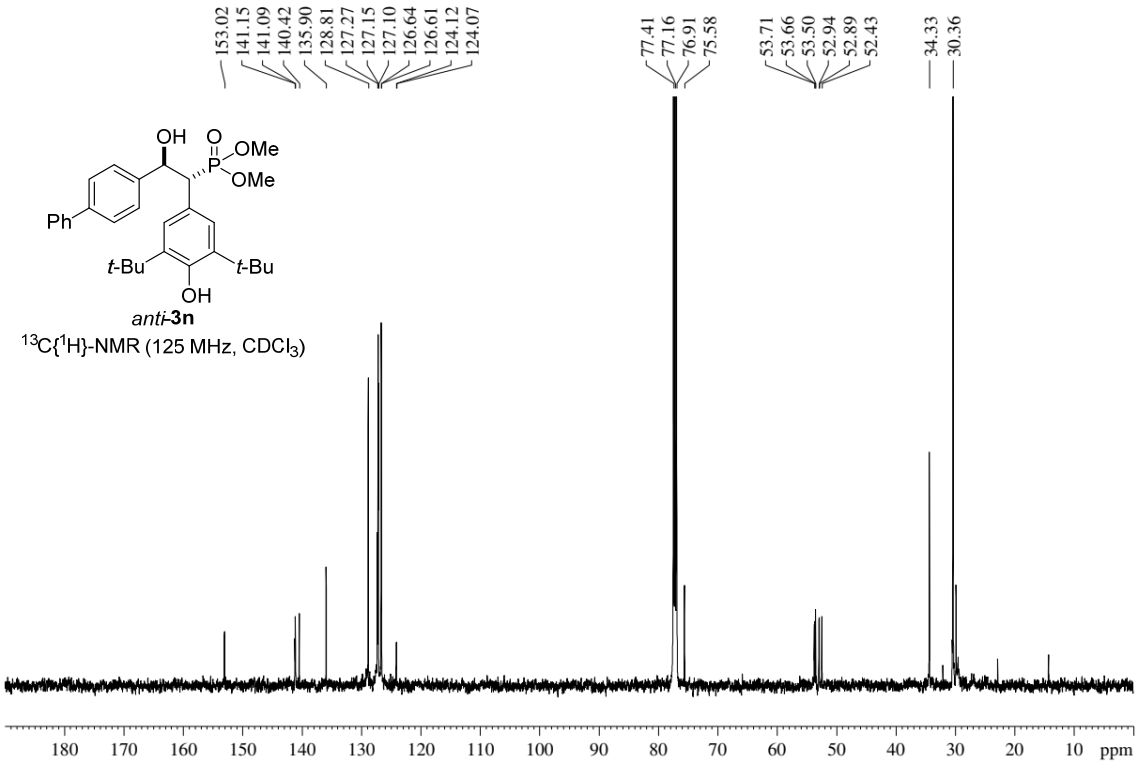
syn-**3n**

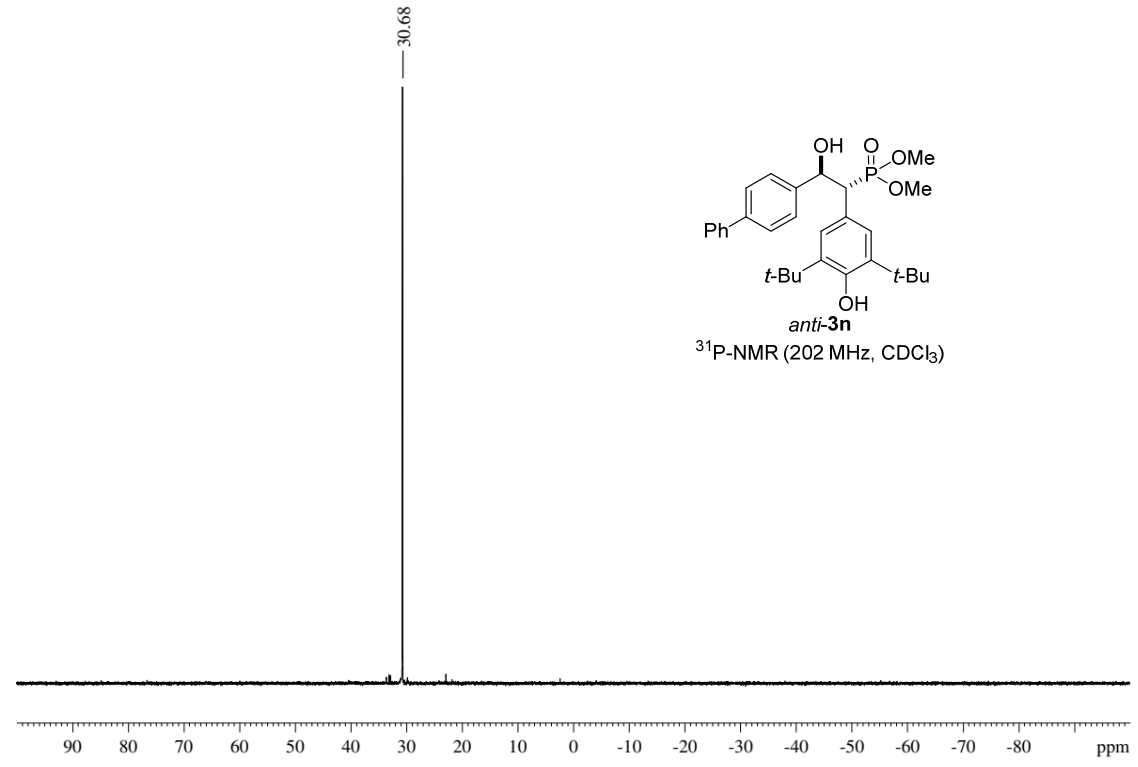
^{31}P-NMR (202 MHz, $CDCl_3$)

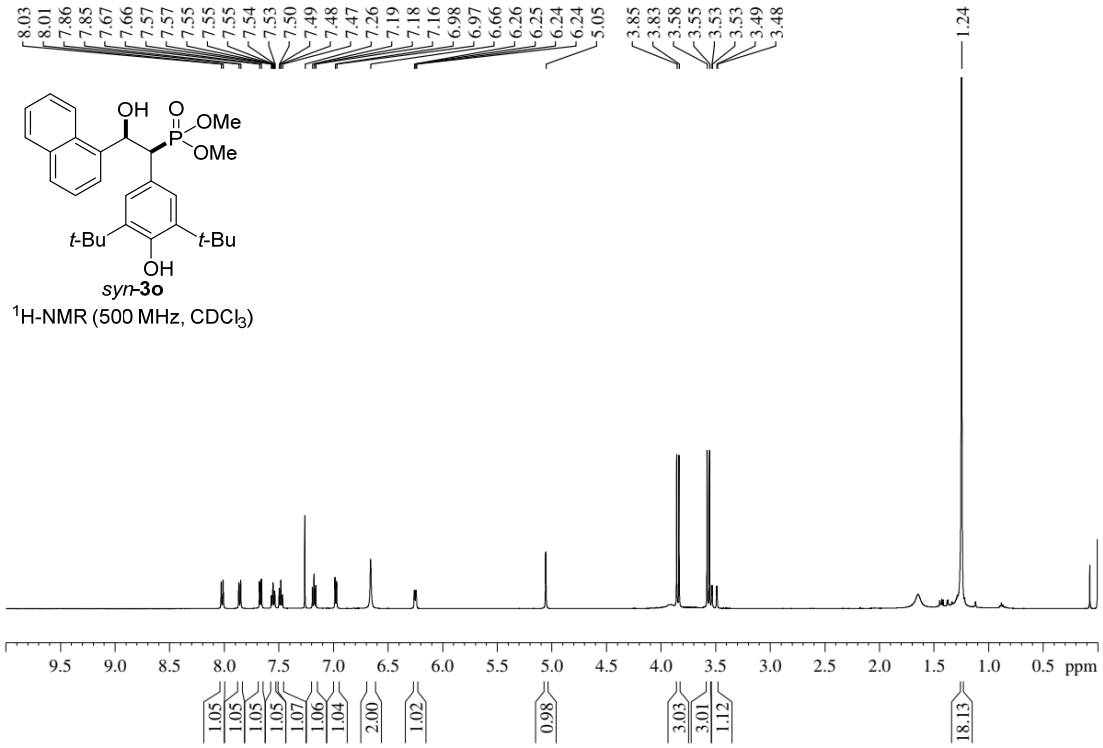


anti-**3n**

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

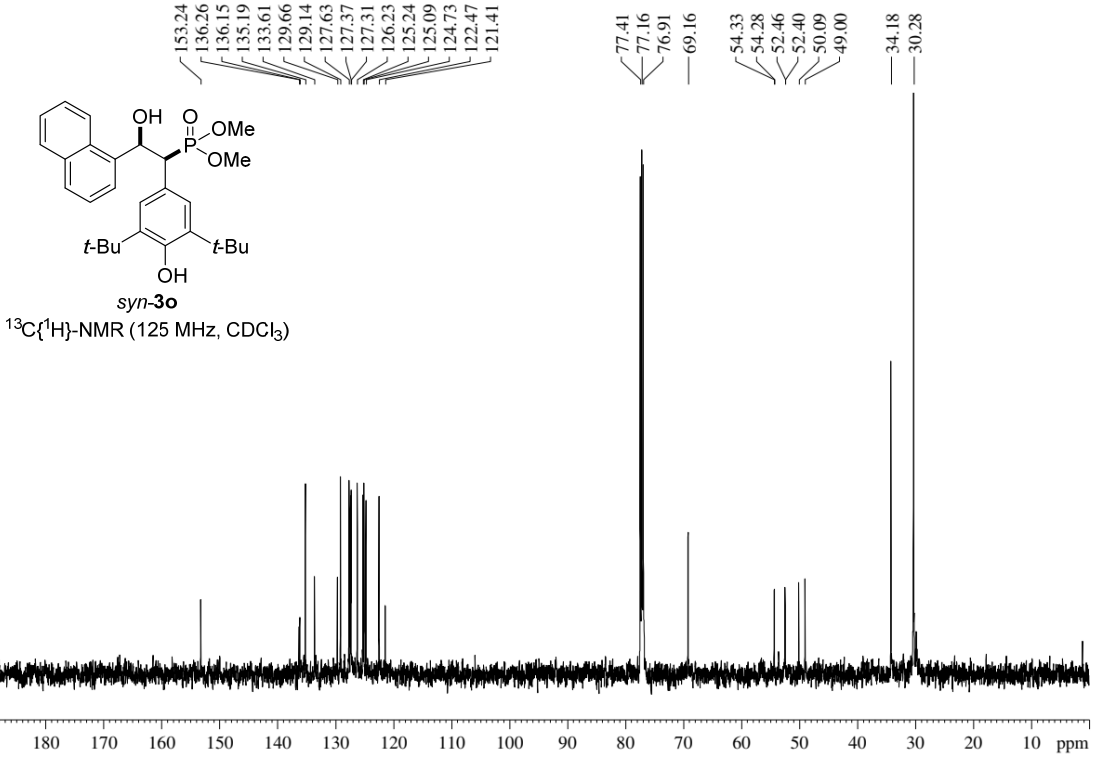

153.02
141.15
141.09
140.42
135.90
128.81
127.27
127.15
127.10
126.64
126.61
124.12
124.07
77.41
77.16
76.91
75.58
53.71
53.66
53.50
52.94
52.89
52.43
34.33
30.36
OH
O
OMe
P
OMe
Ph
t-Bu
t-Bu
OH
anti-3n
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


30.68
OH
O
OMe
P
OMe
Ph
t-Bu
t-Bu
OH
anti-3n
31P-NMR (202 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm



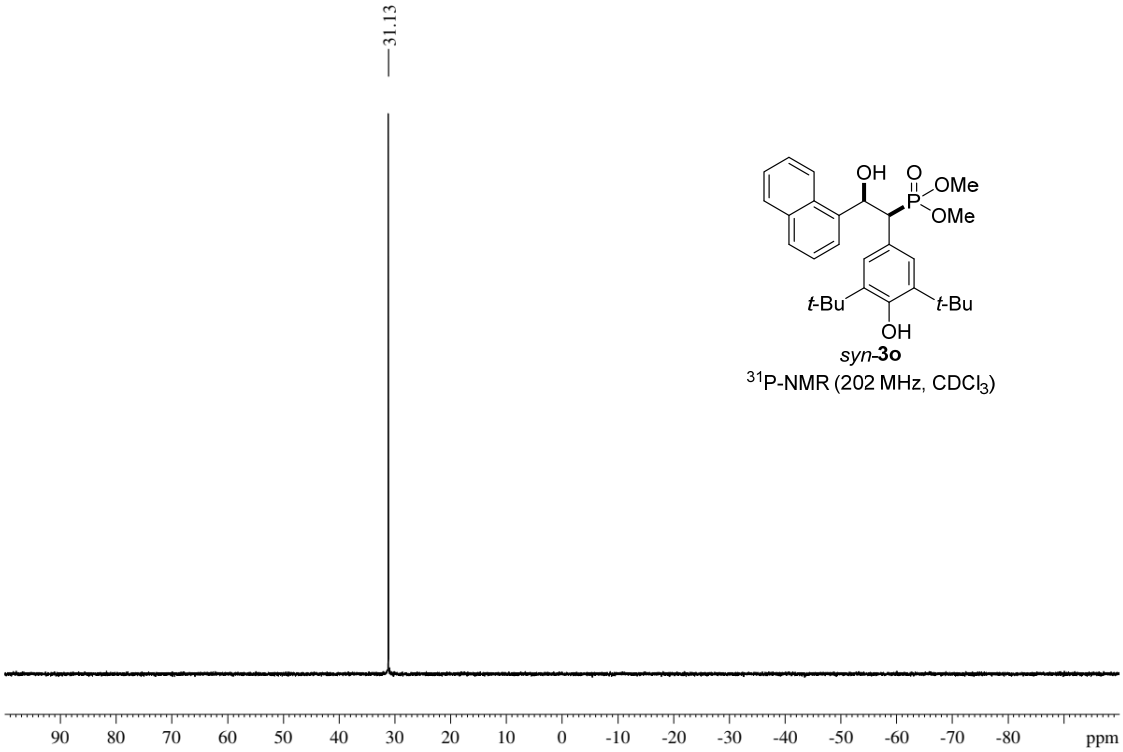
syn-**3o**

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



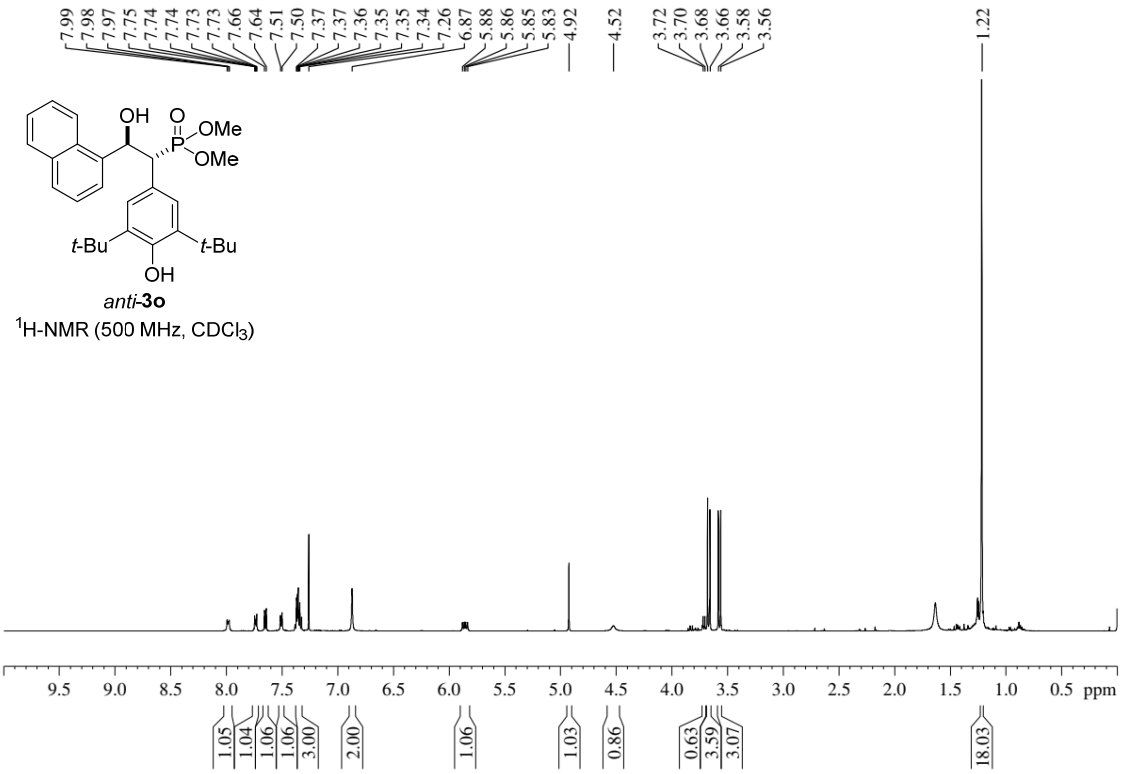
syn-**3o**

^{13}C{^{1}H}-NMR (125 MHz, $CDCl_3$)



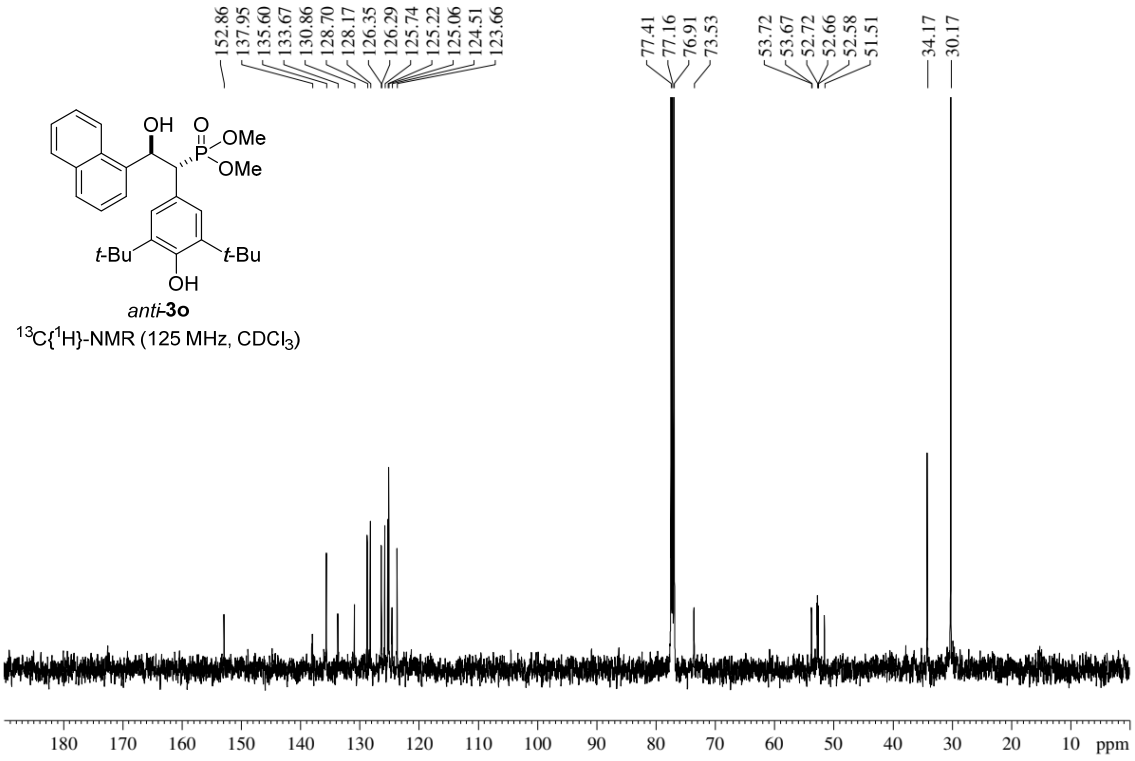
syn-**3o**

^{31}P-NMR (202 MHz, $CDCl_3$)



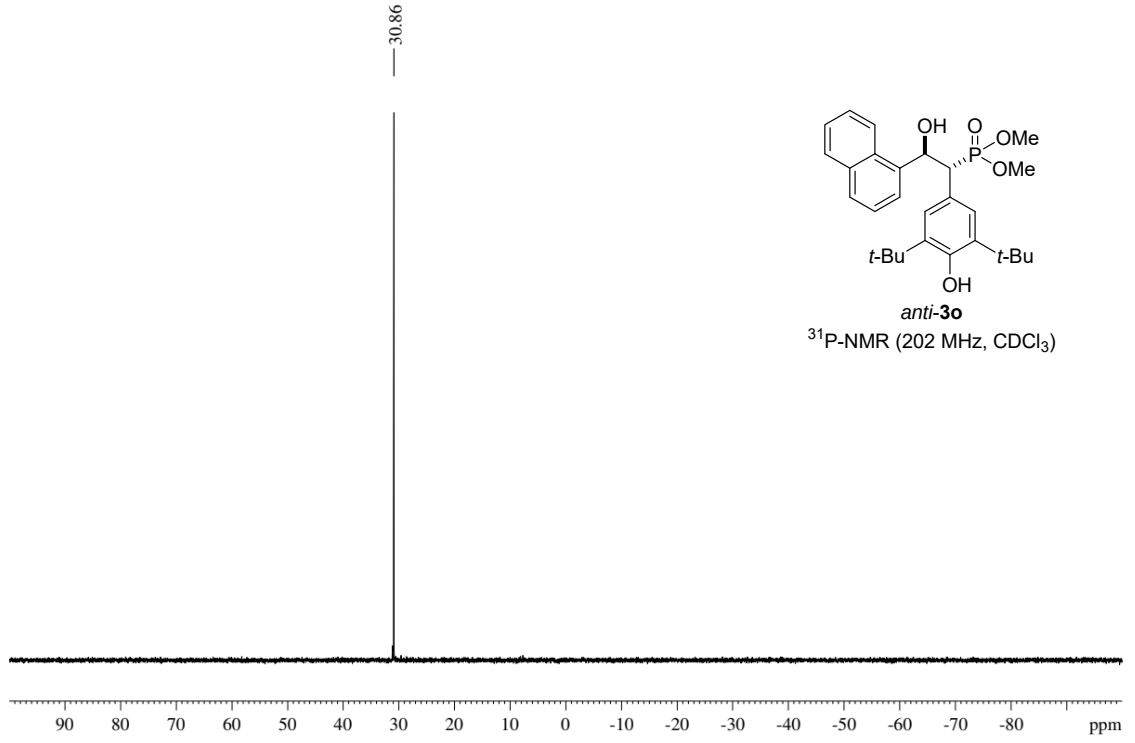
anti-**3o**

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



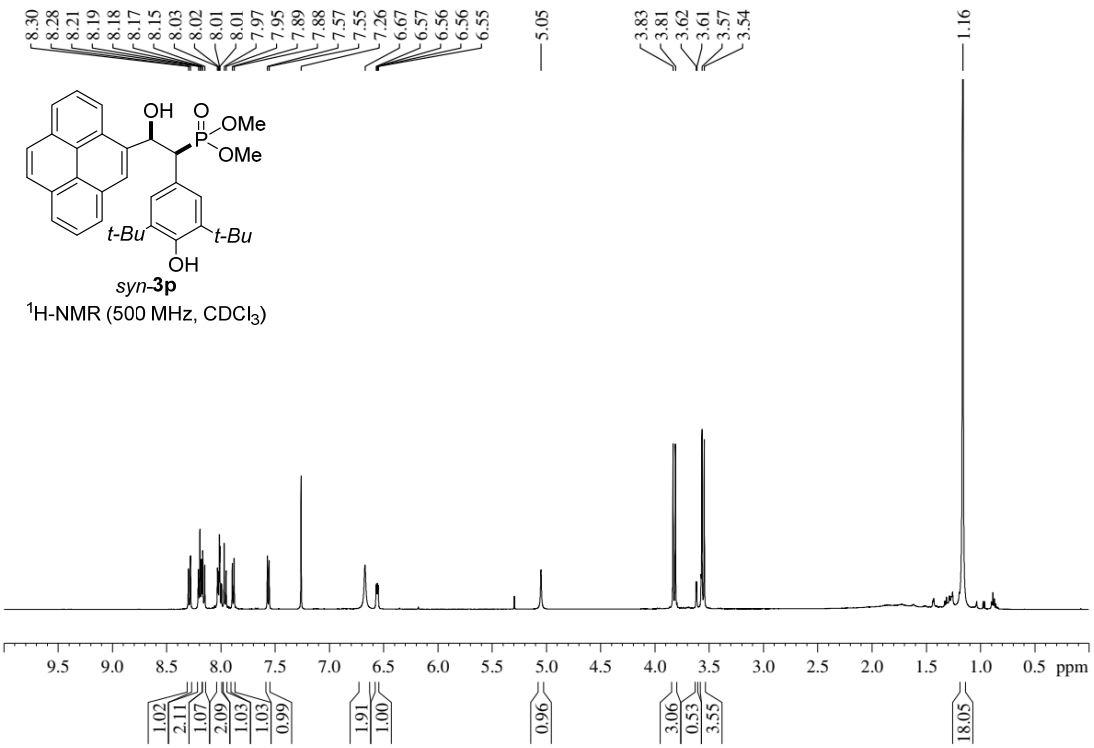
anti-**3o**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



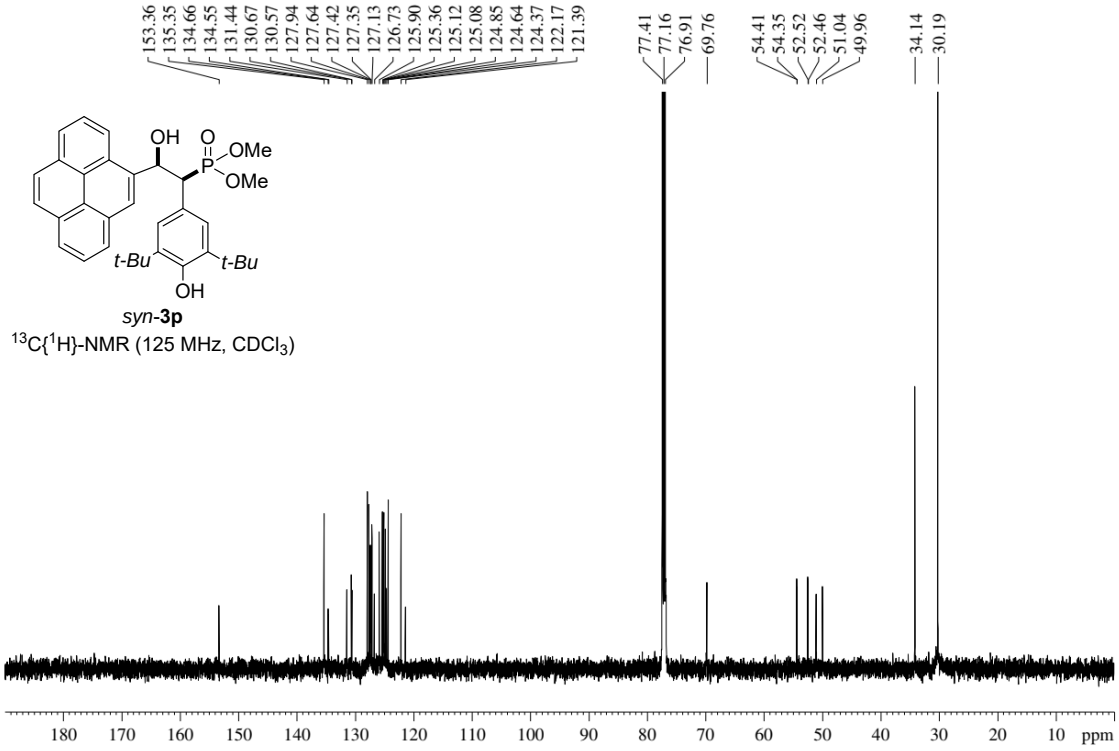
anti-**3o**

^{31}P-NMR (202 MHz, $CDCl_3$)



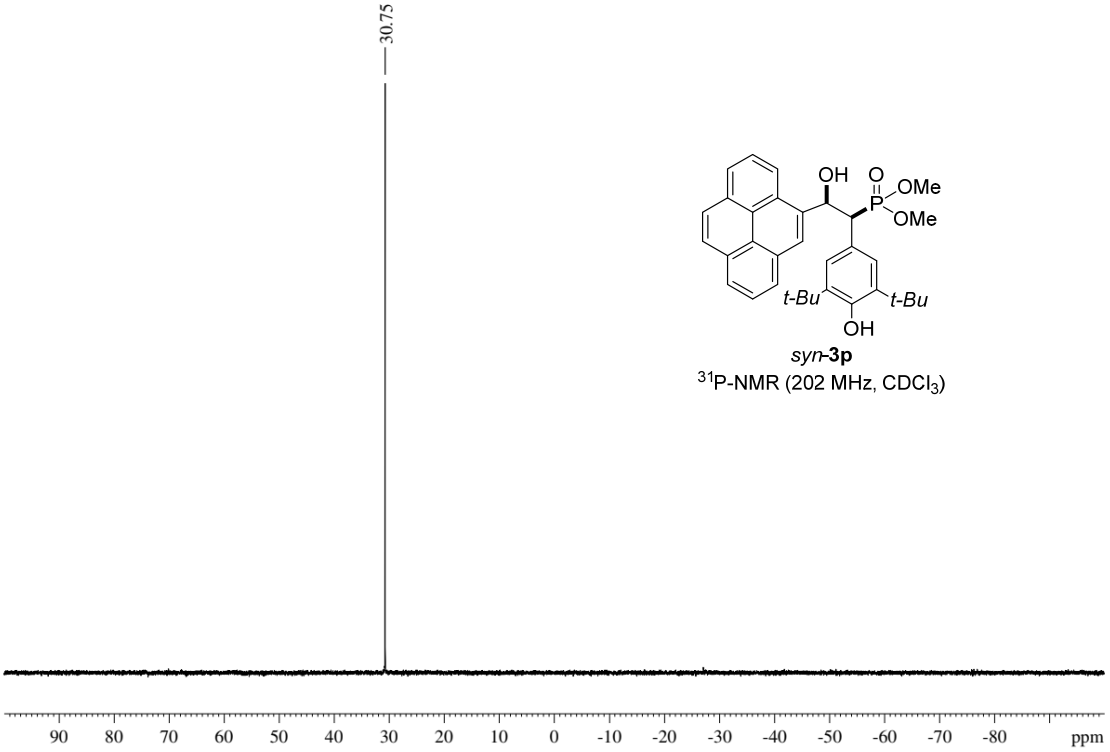
syn-**3p**

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

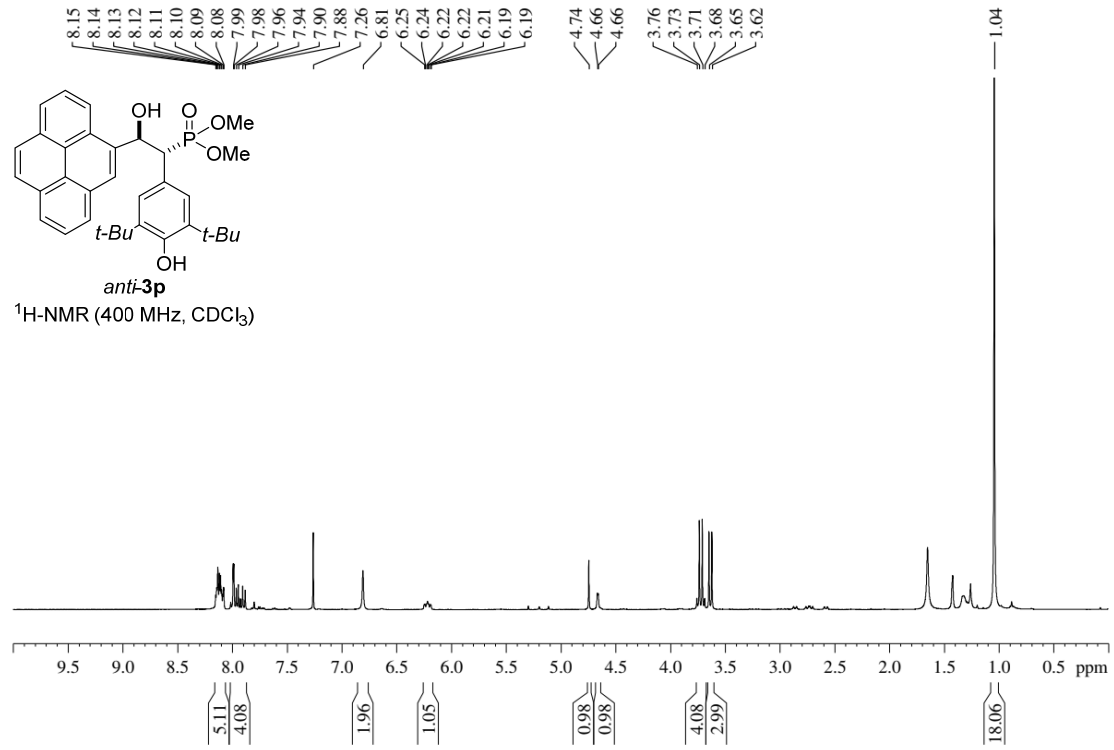


syn-**3p**

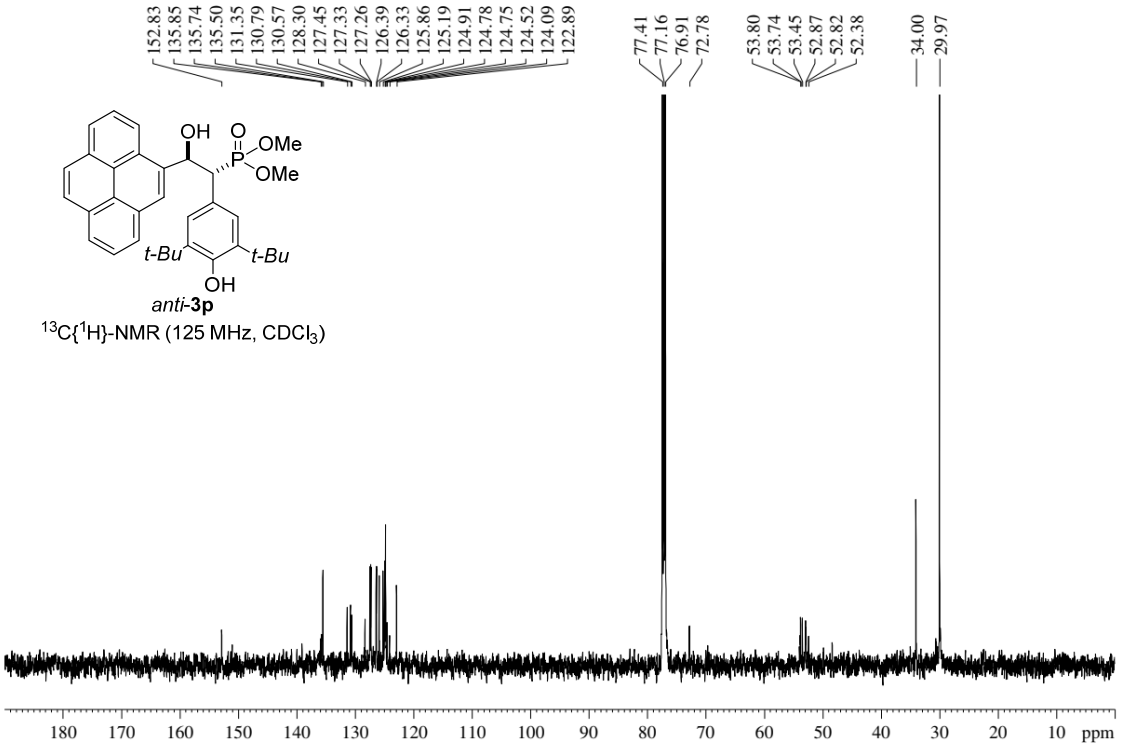
$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



syn-**3p**
^{31}P-NMR (202 MHz, $CDCl_3$)

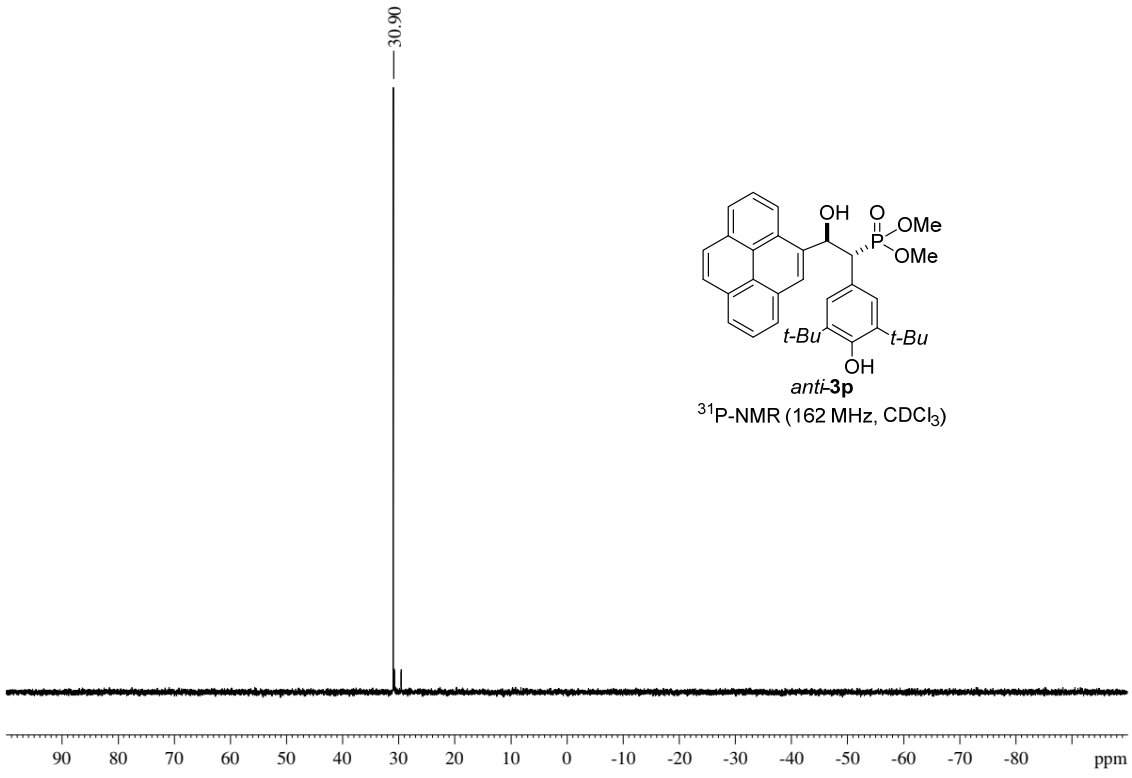


anti-**3p**
^{1}H-NMR (400 MHz, $CDCl_3$)



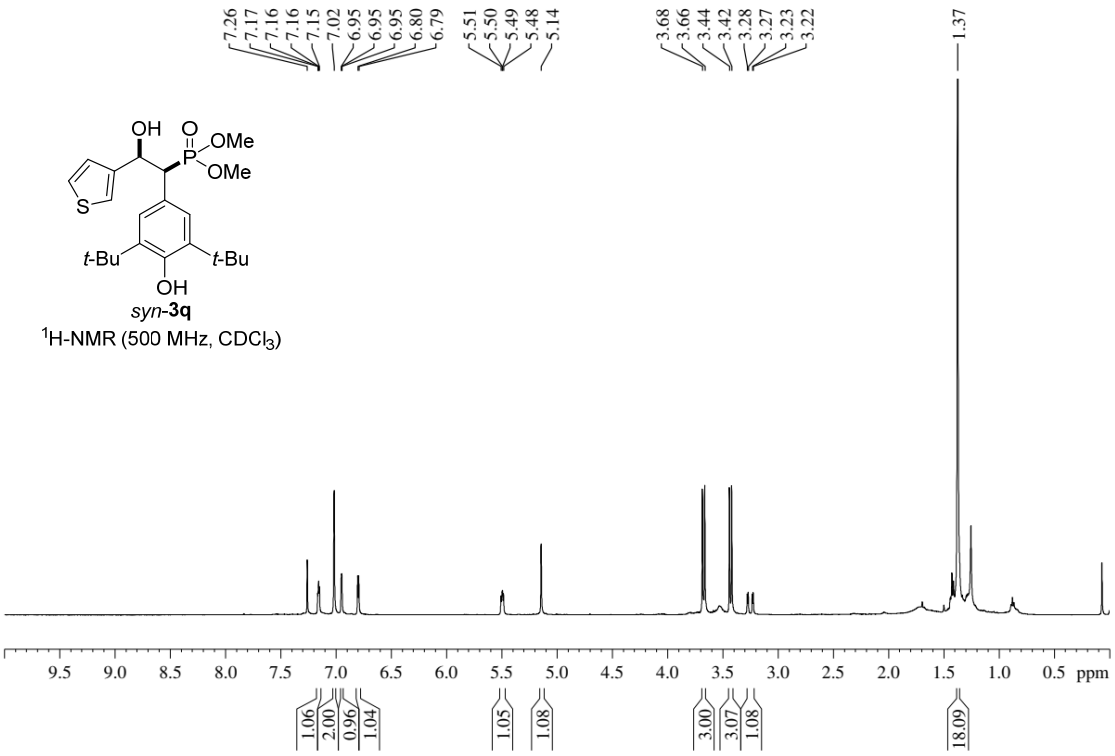
anti-**3p**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



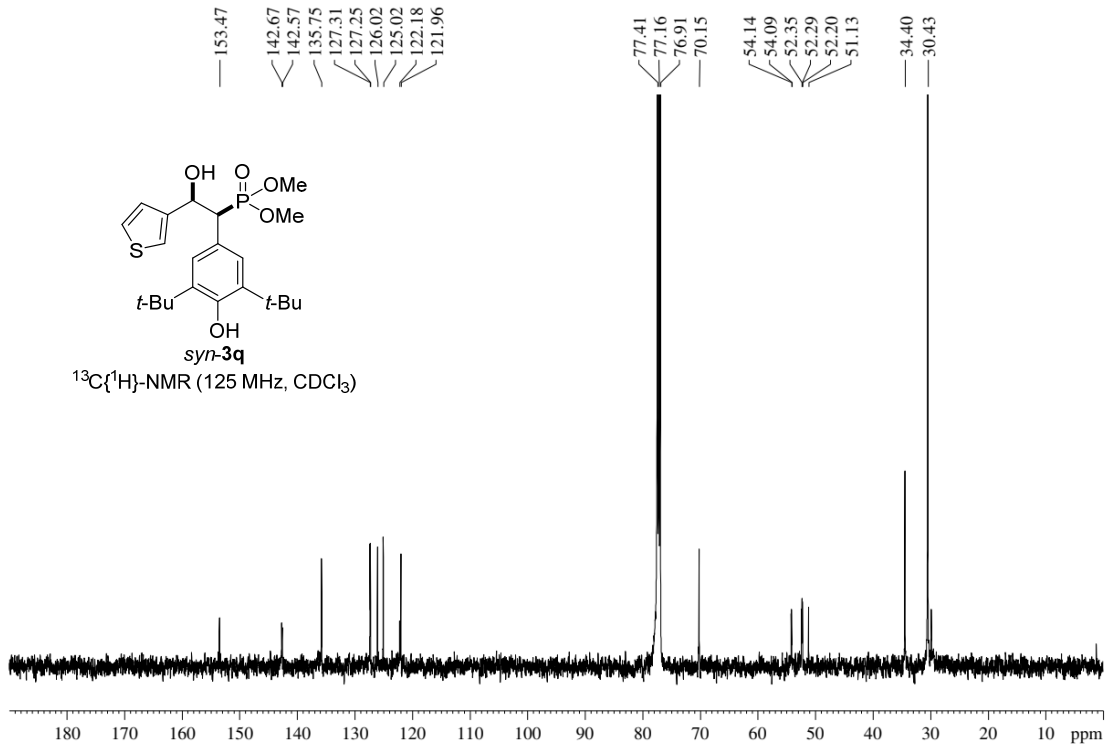
anti-**3p**

^{31}P-NMR (162 MHz, $CDCl_3$)



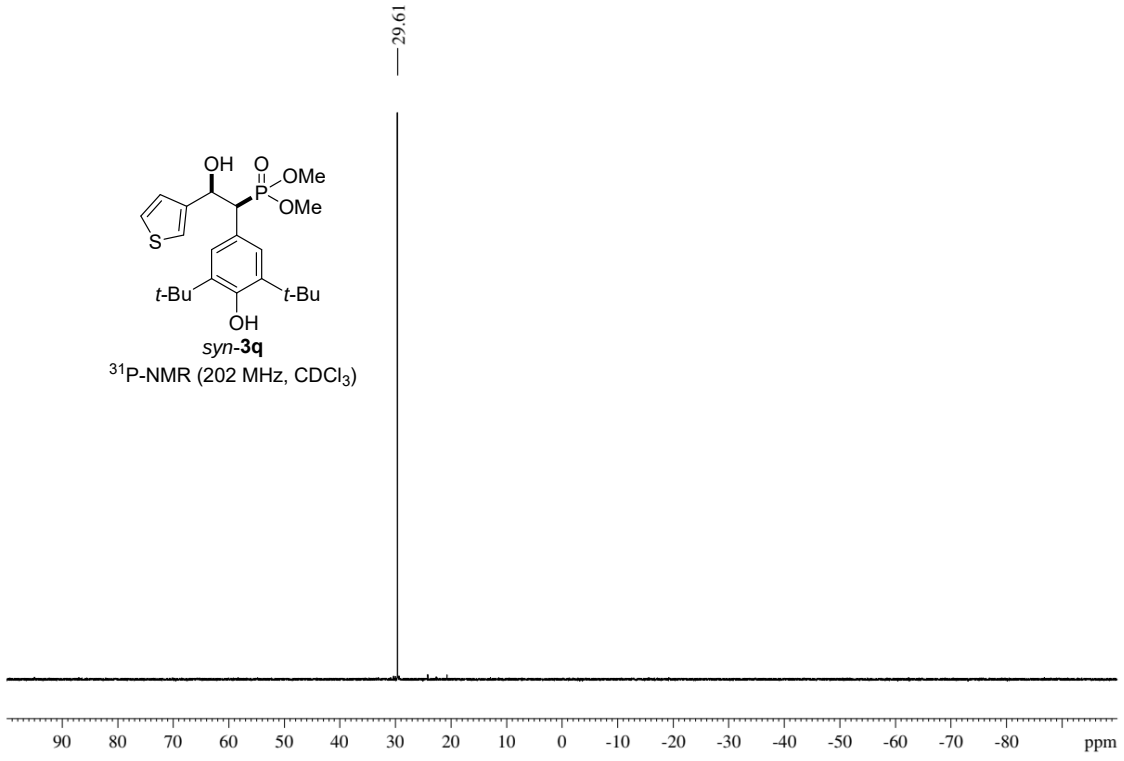
syn-**3q**

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



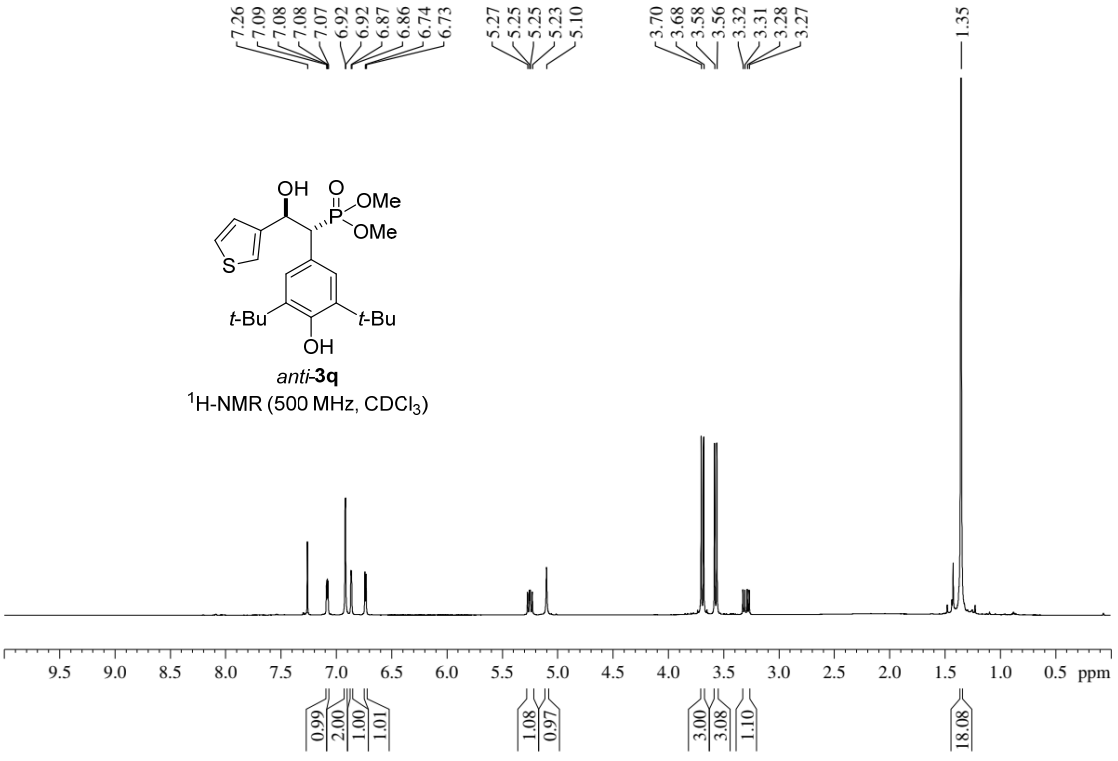
syn-**3q**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



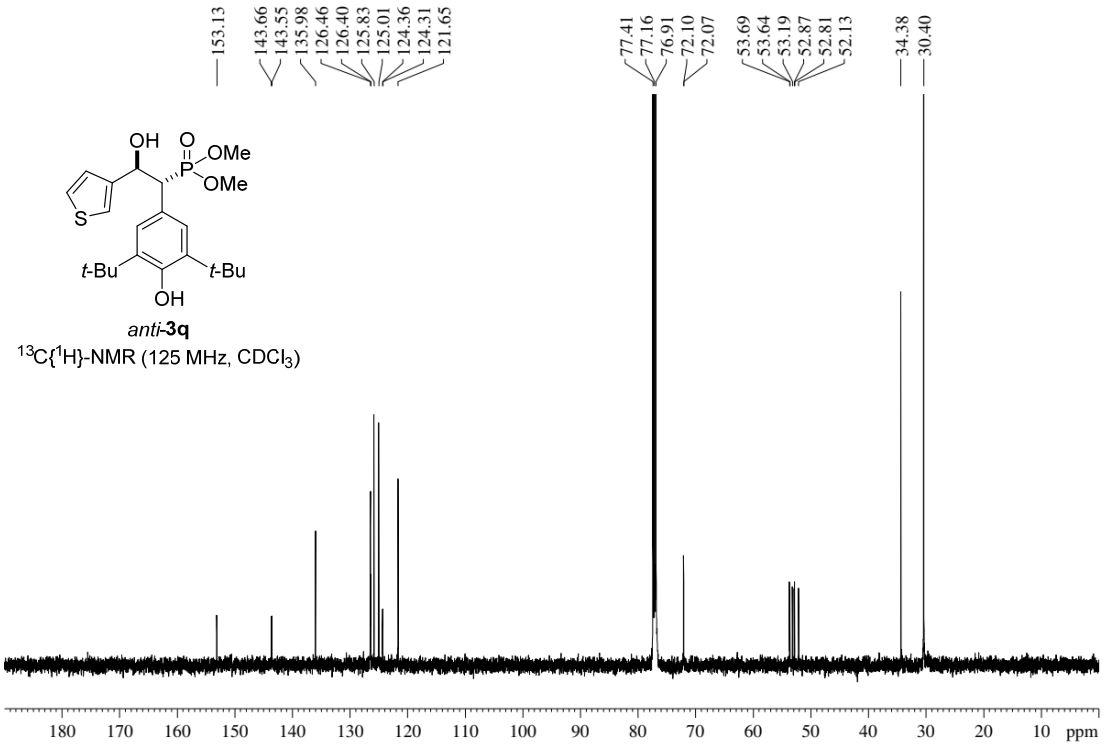
syn-**3q**

^{31}P-NMR (202 MHz, $CDCl_3$)



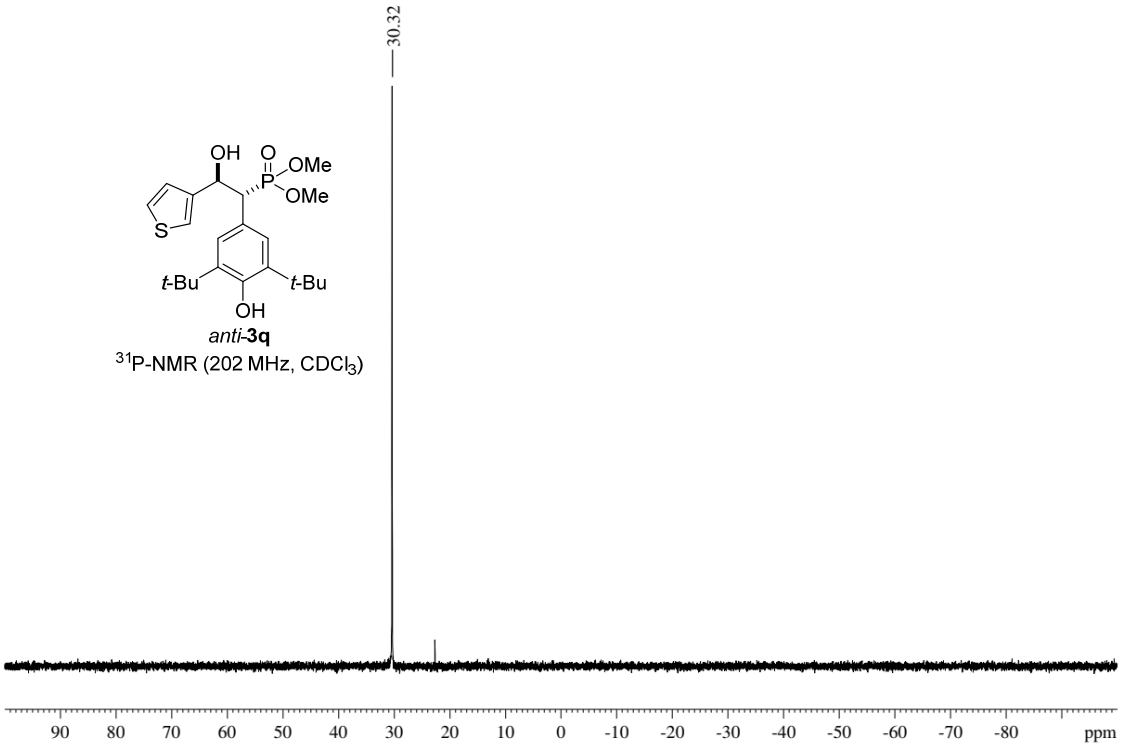
anti-**3q**

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



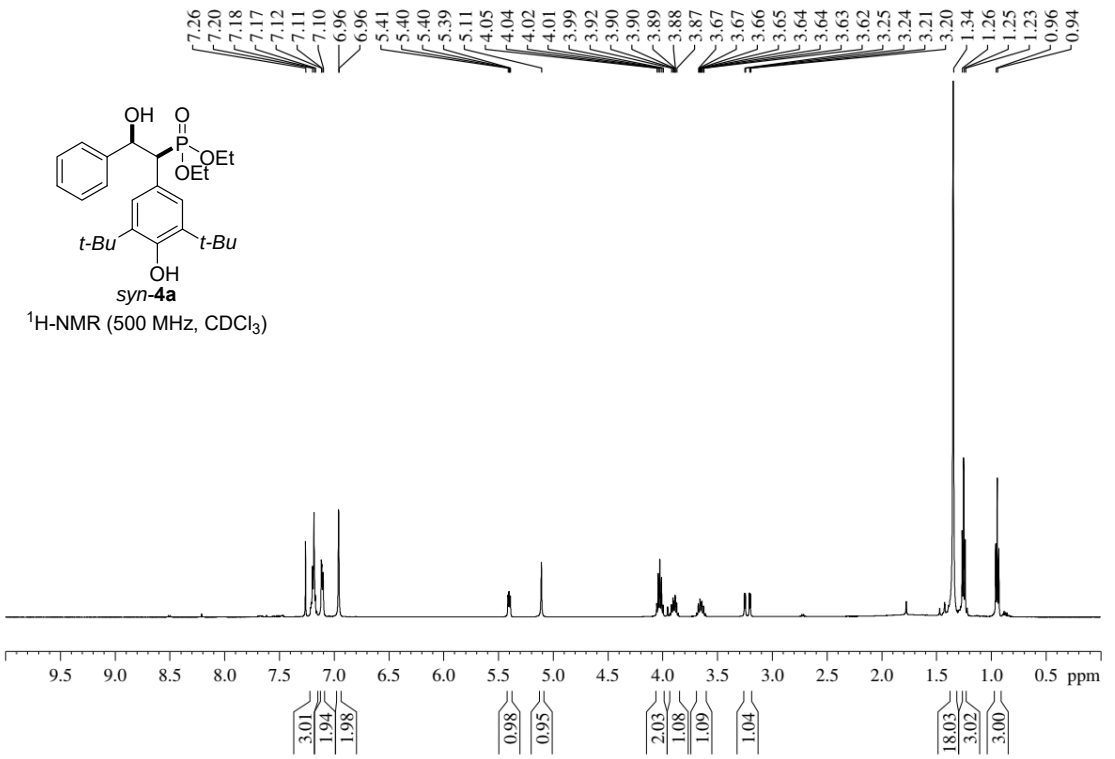
anti-**3q**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



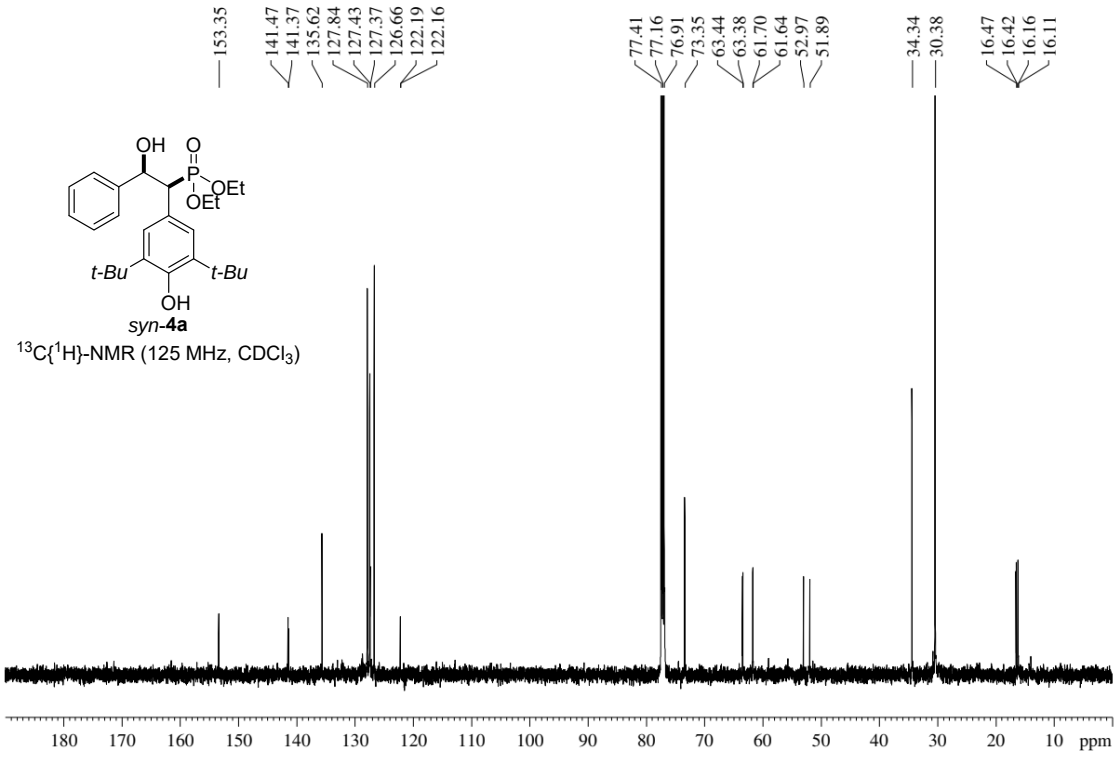
anti-**3q**

^{31}P-NMR (202 MHz, $CDCl_3$)



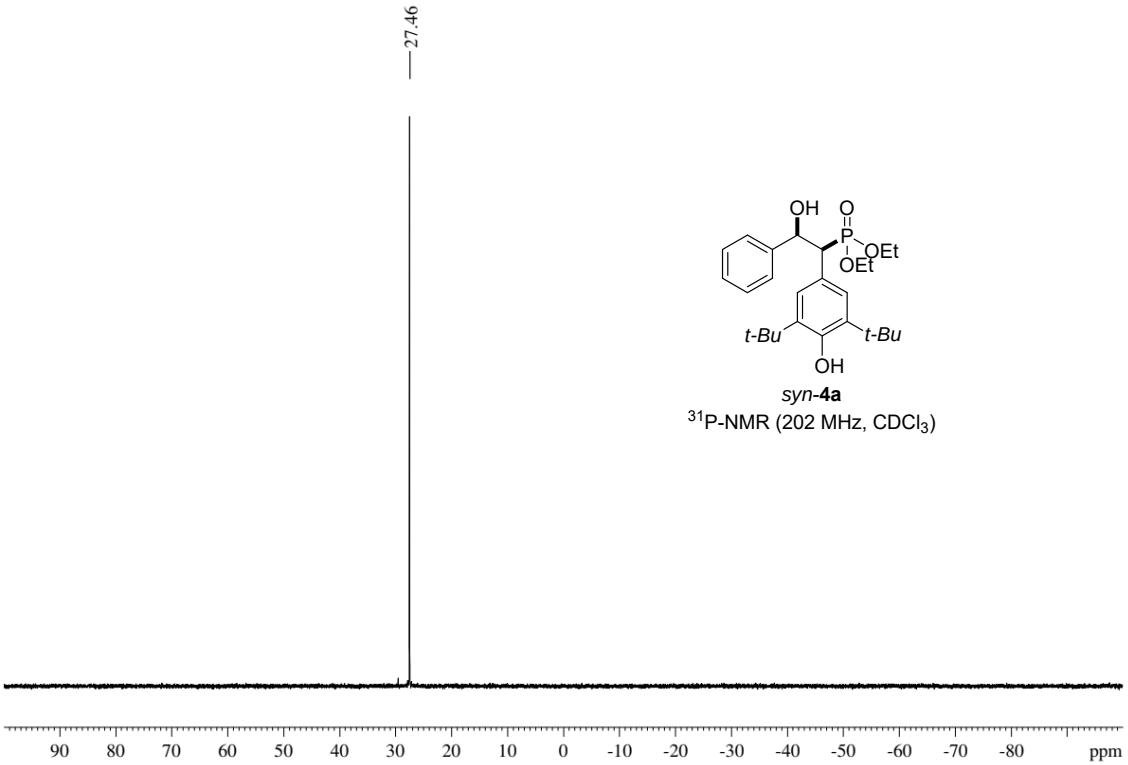
syn-**4a**

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



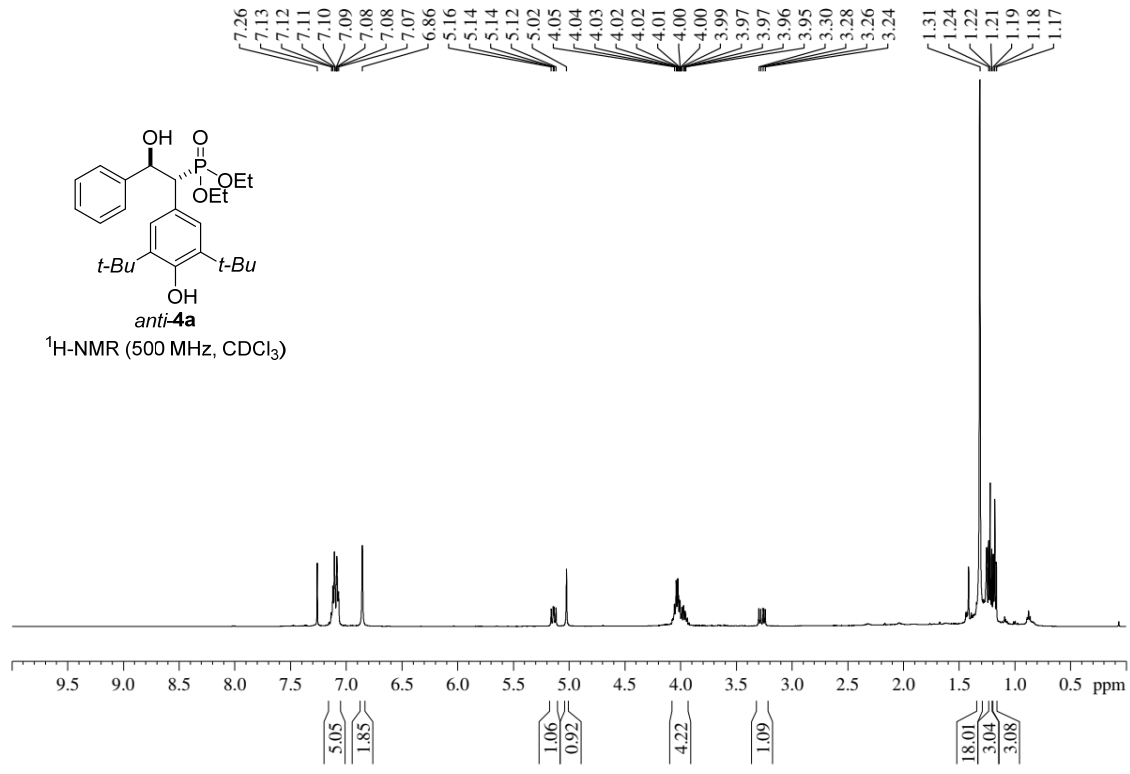
syn-**4a**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



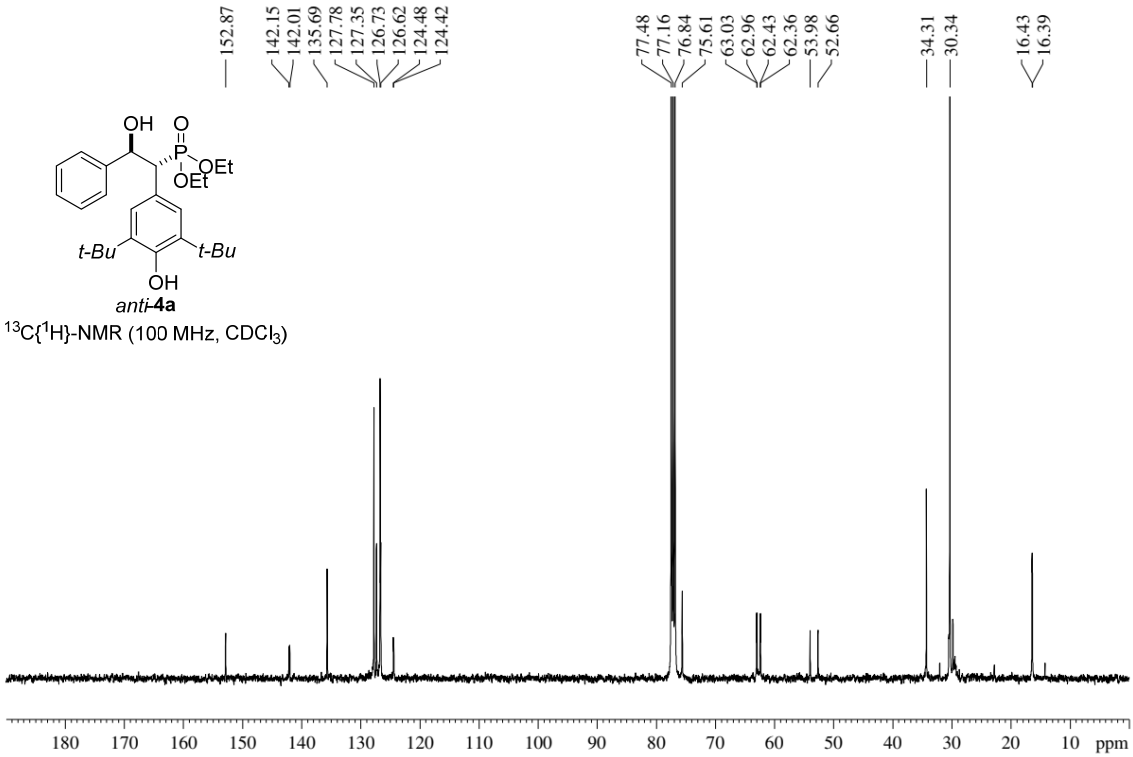
syn-**4a**

^{31}P-NMR (202 MHz, $CDCl_3$)



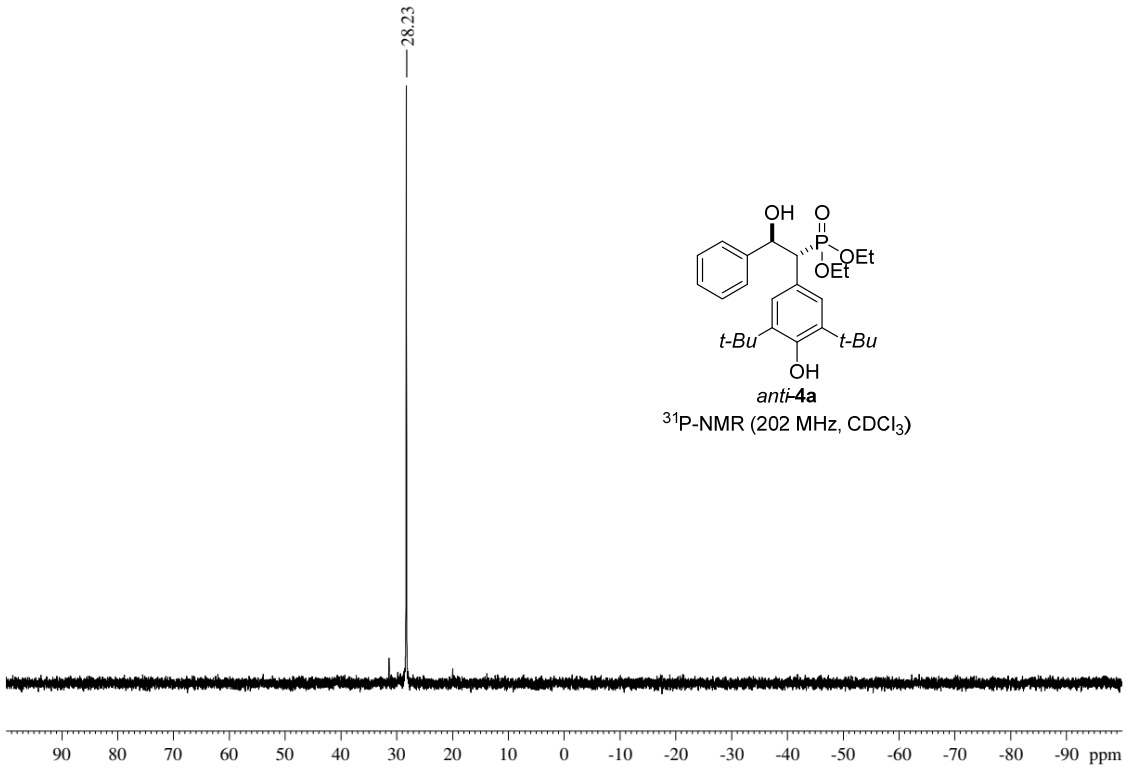
anti-**4a**

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



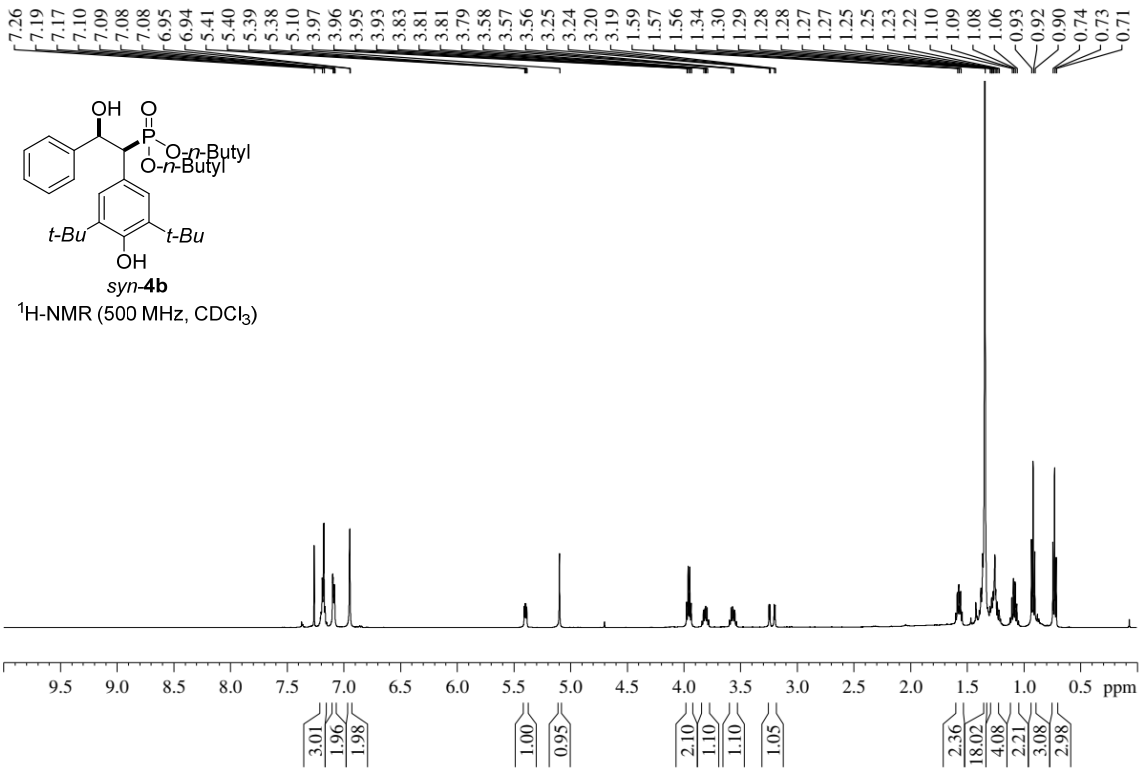
anti-**4a**

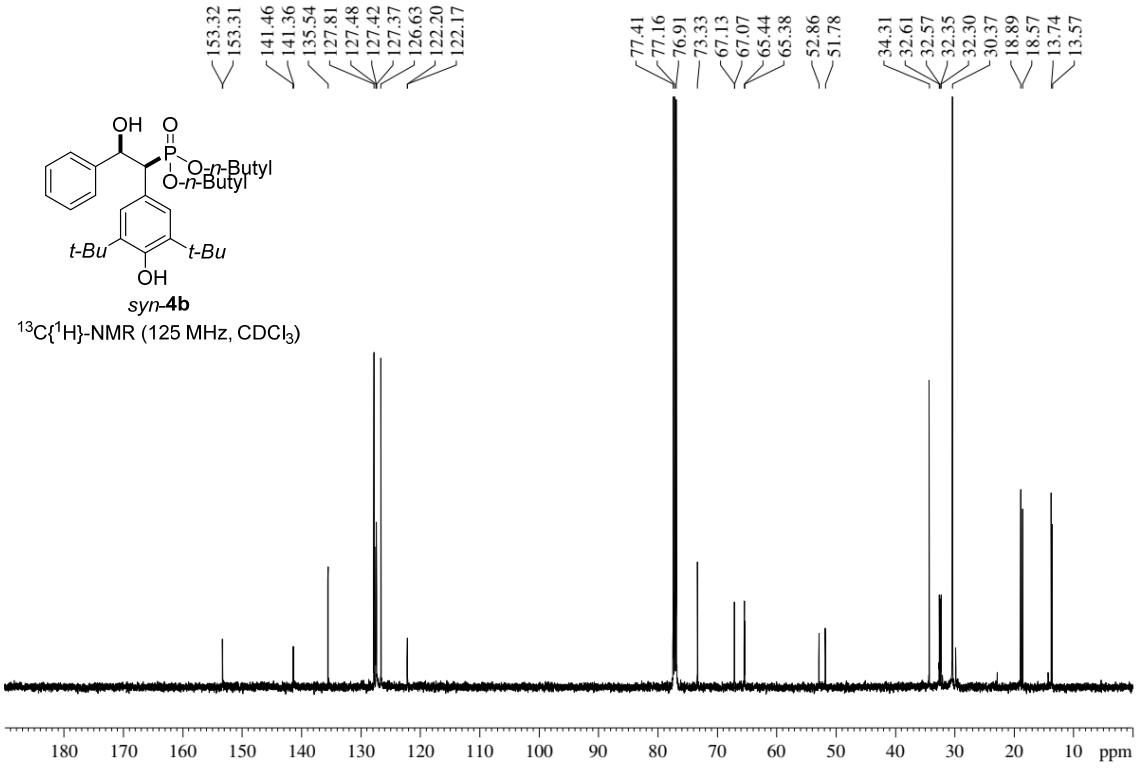
$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

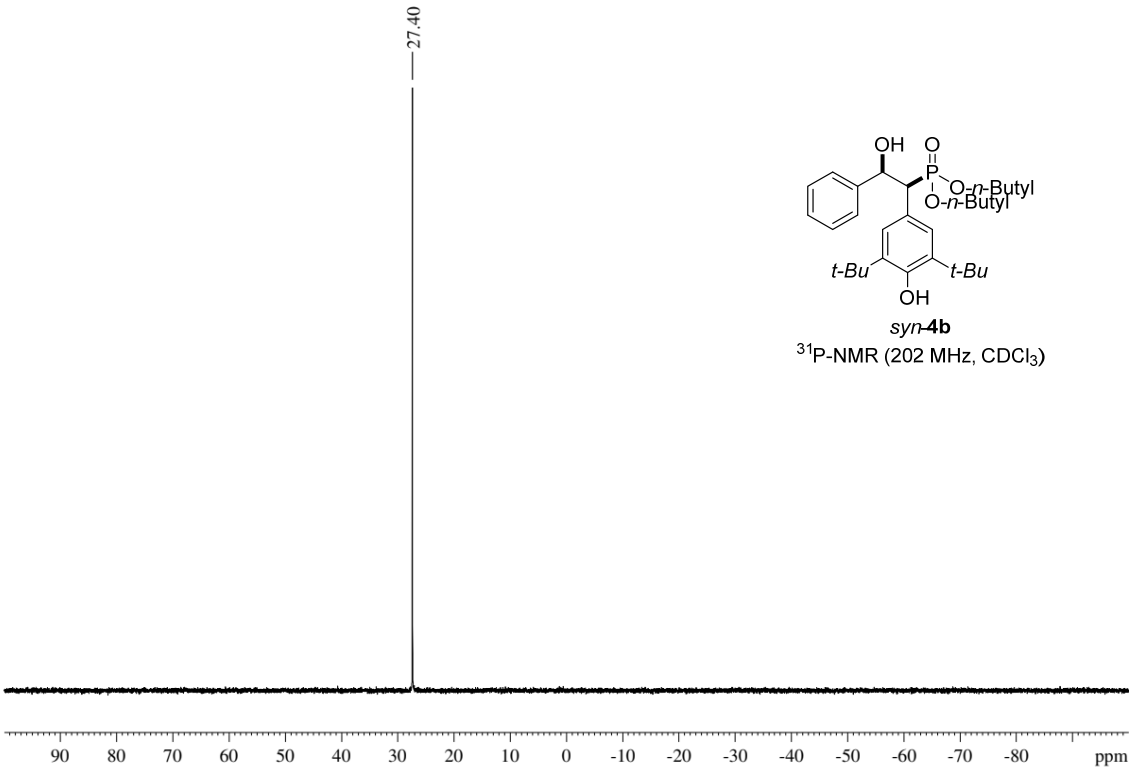


anti-**4a**

^{31}P-NMR (202 MHz, $CDCl_3$)

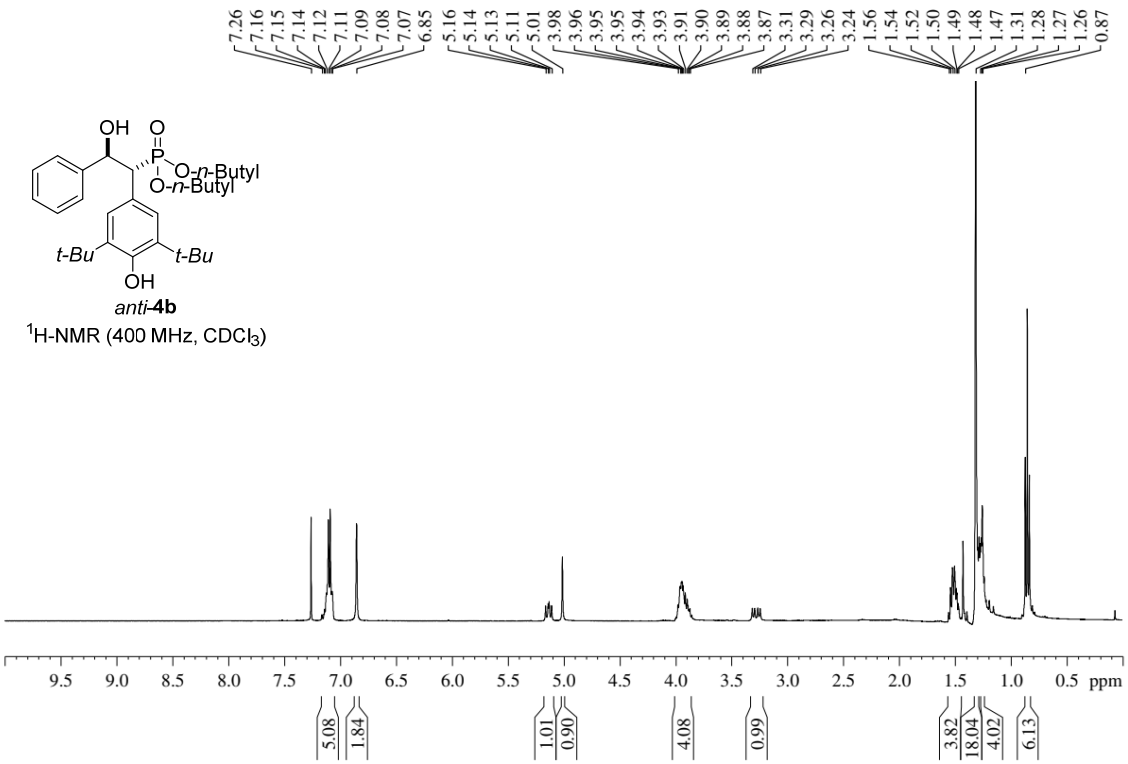

7.26 7.19 7.17 7.10 7.09 7.08 7.08 6.95 6.94 5.41 5.40 5.39 5.38 5.10 3.97 3.96 3.95 3.93 3.83 3.81 3.81 3.79 3.58 3.57 3.56 3.25 3.24 3.20 3.19 1.59 1.57 1.56 1.34 1.30 1.29 1.28 1.28 1.27 1.27 1.25 1.25 1.23 1.22 1.10 1.09 1.08 1.06 0.93 0.92 0.90 0.74 0.73 0.71
OH
O
P
O-n-Butyl
O-n-Butyl
t-Bu
t-Bu
OH
syn-4b
1H-NMR (500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.01 1.96 1.98 1.00 0.95 2.10 1.10 1.10 1.05 2.36 18.02 4.08 2.21 3.08 2.98


153.32 153.31 141.46 141.36 135.54 127.81 127.48 127.42 127.37 126.63 122.20 122.17
77.41 77.16 76.91 73.33 67.13 67.07 65.44 65.38 52.86 51.78
34.31 32.61 32.57 32.35 32.30 30.37 18.89 18.57 13.74 13.57
OH
O
P
O-n-Butyl
O-n-Butyl
t-Bu
t-Bu
OH
syn-4b
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



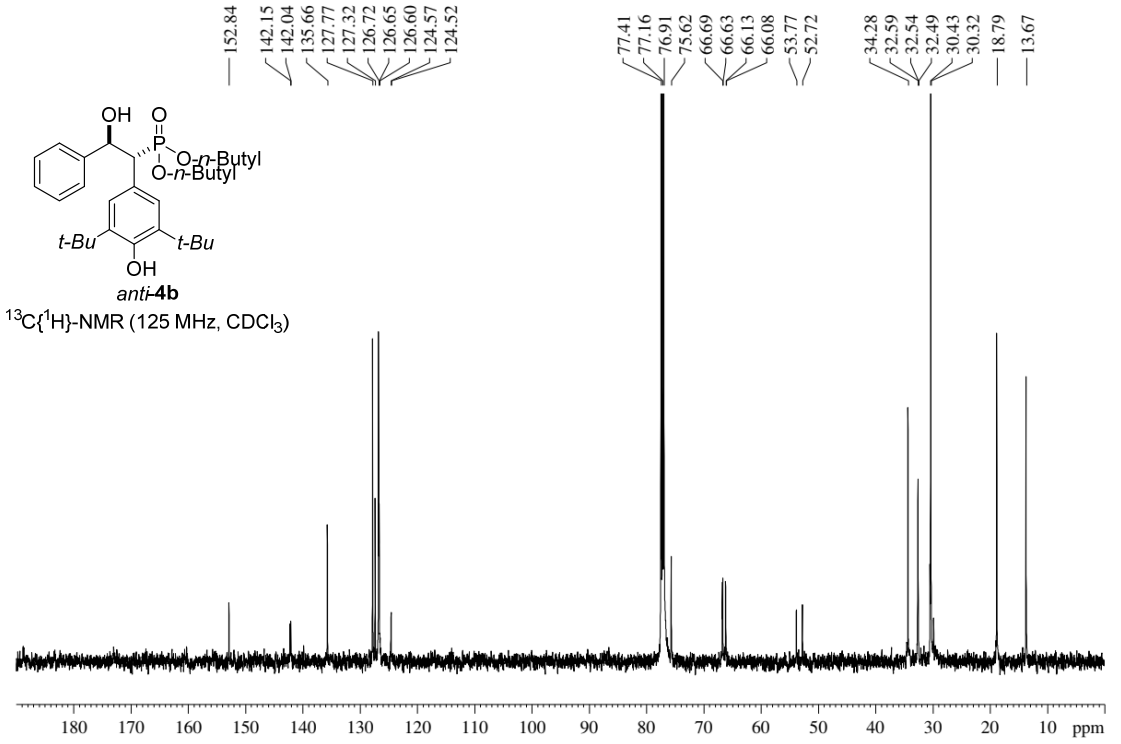
syn-**4b**

^{31}P-NMR (202 MHz, $CDCl_3$)



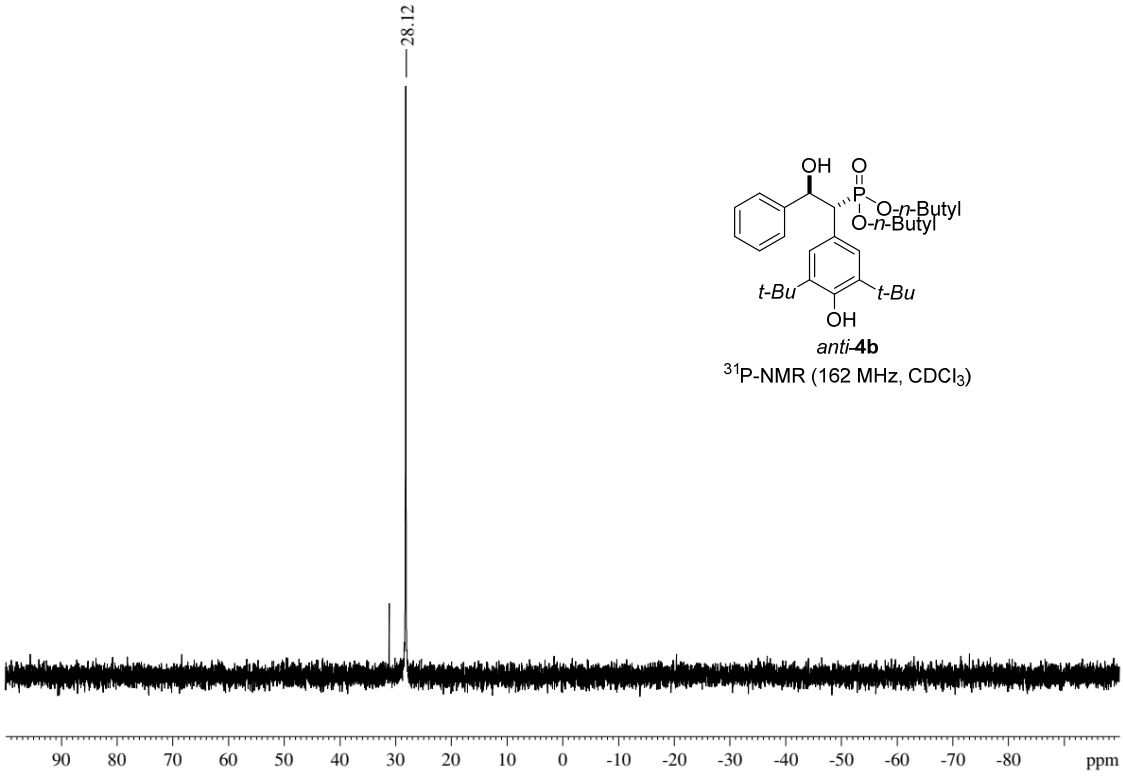
anti-**4b**

^{1}H-NMR (400 MHz, $CDCl_3$)



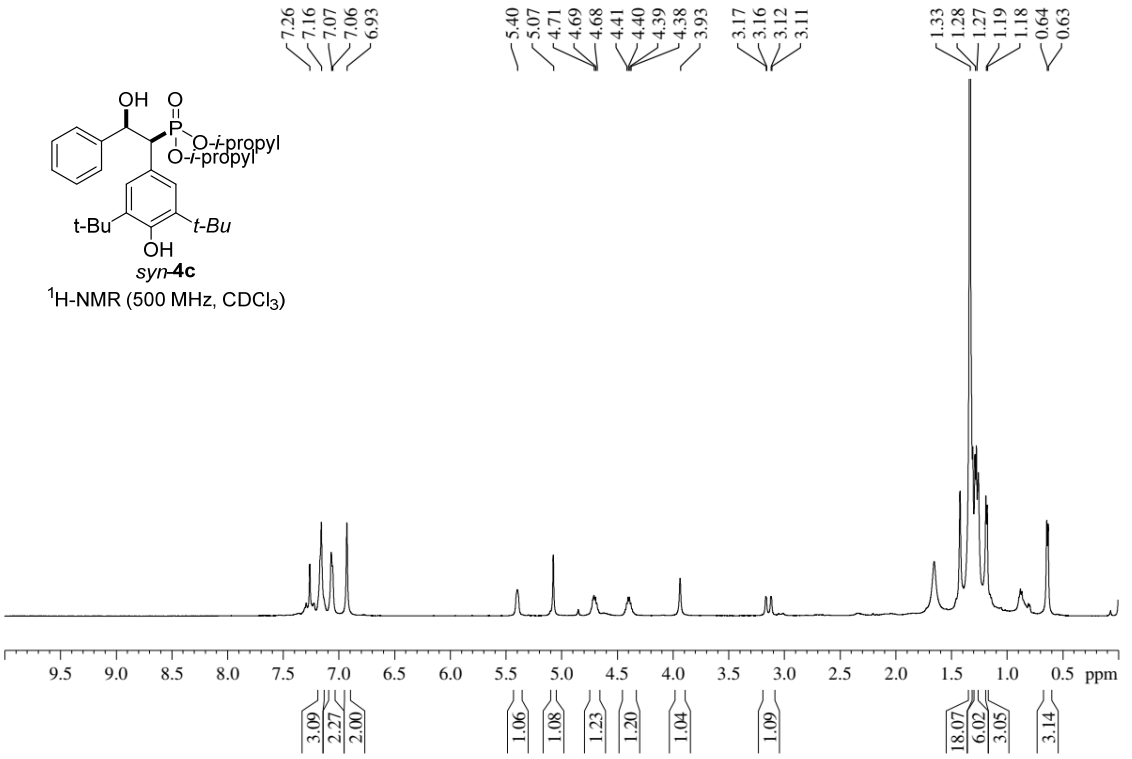
anti-**4b**

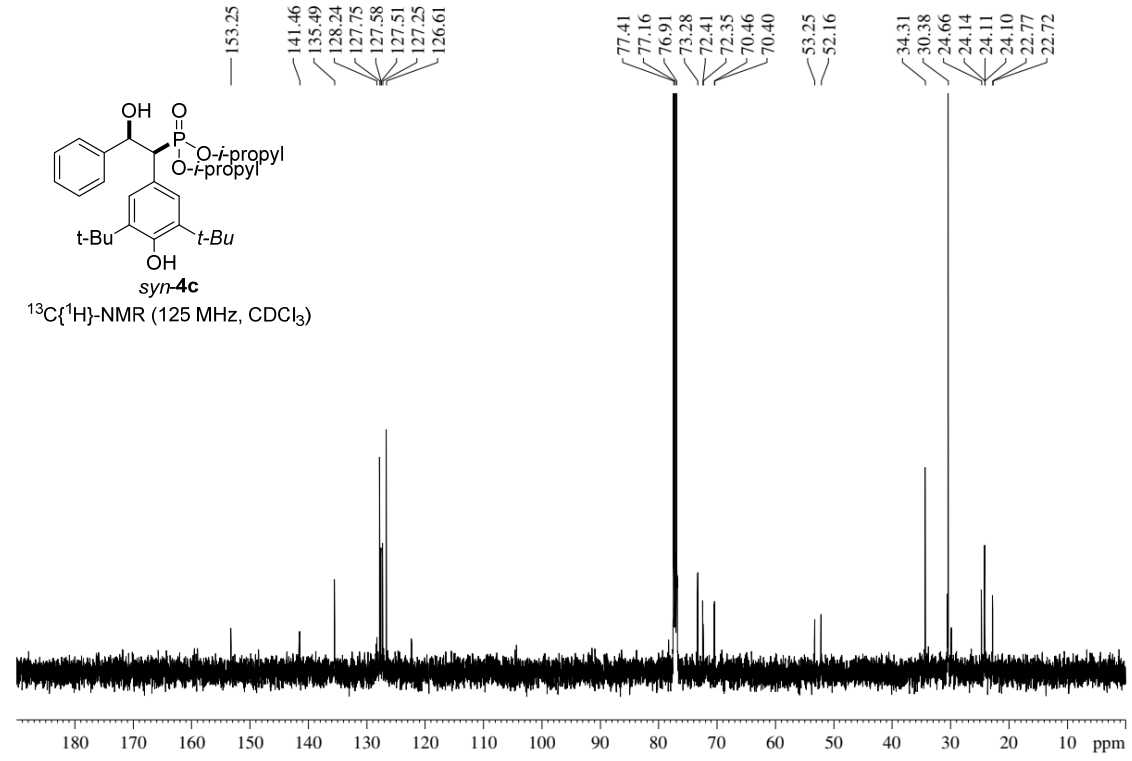
$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)

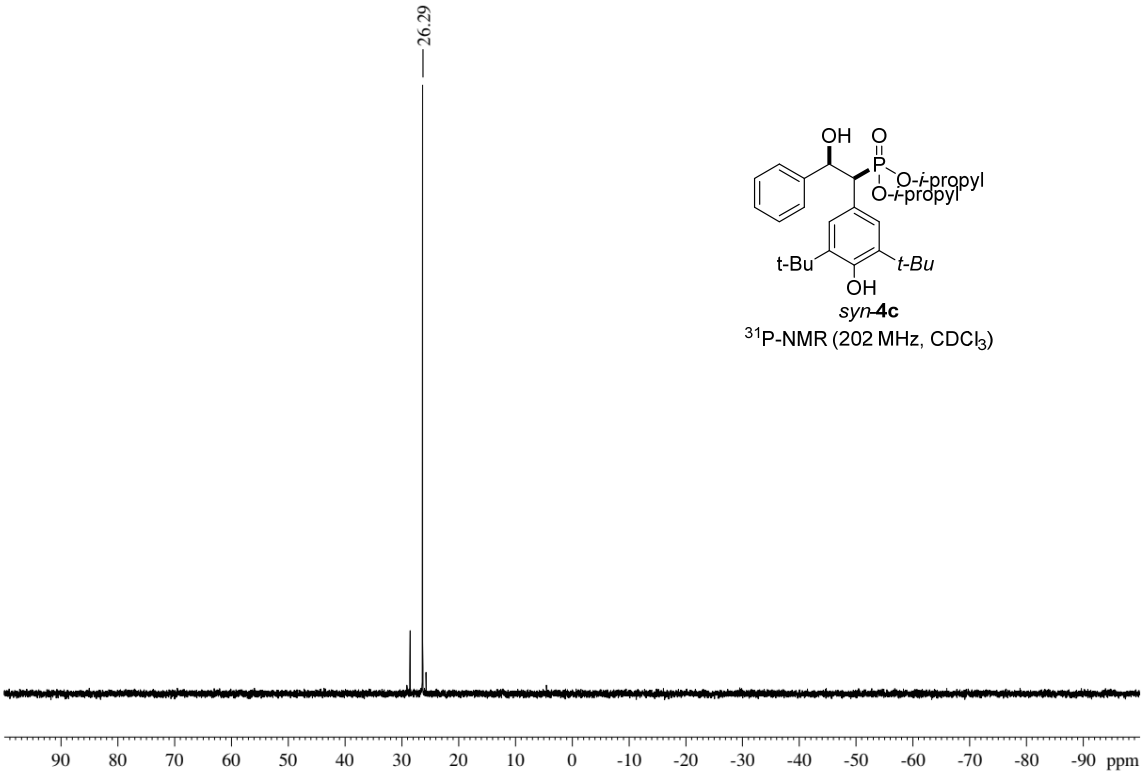


anti-**4b**

^{31}P-NMR (162 MHz, $CDCl_3$)

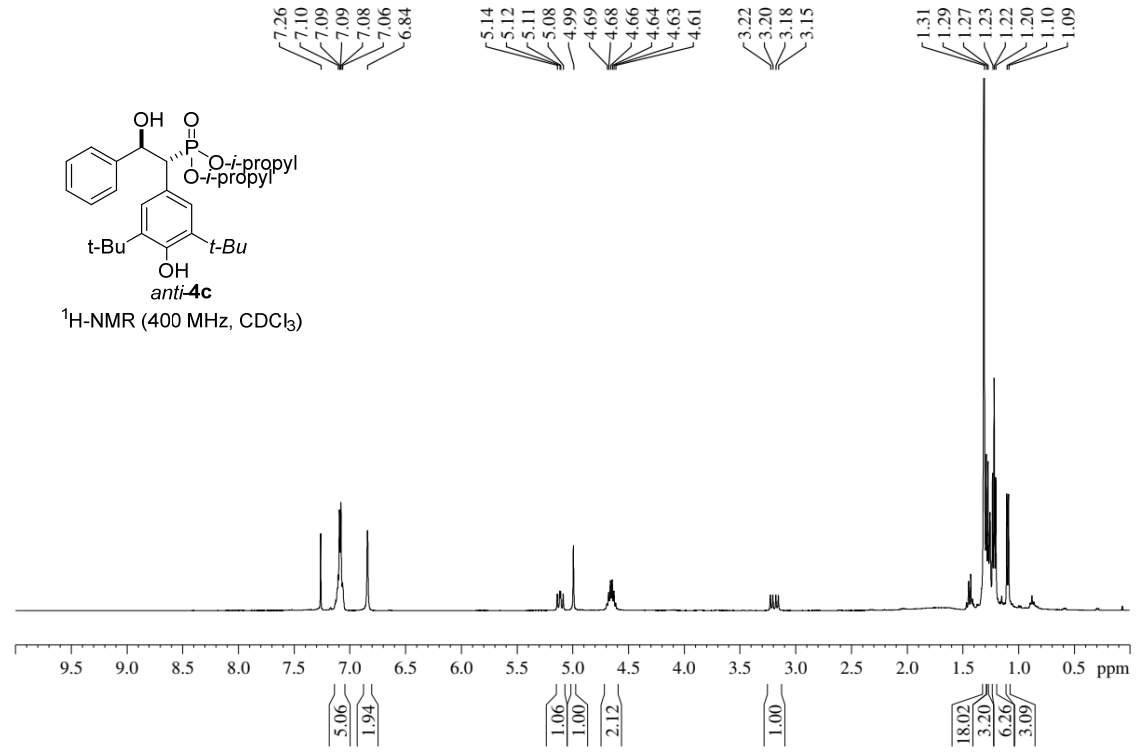

7.26
7.16
7.07
7.06
6.93
5.40
5.07
4.71
4.69
4.68
4.41
4.40
4.39
4.38
3.93
3.17
3.16
3.12
3.11
1.33
1.28
1.27
1.19
1.18
0.64
0.63
OH
O
P
O-i-propyl
O-i-propyl
t-Bu
t-Bu
OH
syn-4c
1H-NMR (500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.09
2.27
2.00
1.06
1.08
1.23
1.20
1.04
1.09
18.07
6.02
3.05
3.14


153.25
141.46
135.49
128.24
127.75
127.58
127.51
127.25
126.61
77.41
77.16
76.91
73.28
72.41
72.35
70.46
70.40
53.25
52.16
34.31
30.38
24.66
24.14
24.11
24.10
22.77
22.72
OH
O
P
O-i-propyl
O-i-propyl
t-Bu
t-Bu
OH
syn-4c
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



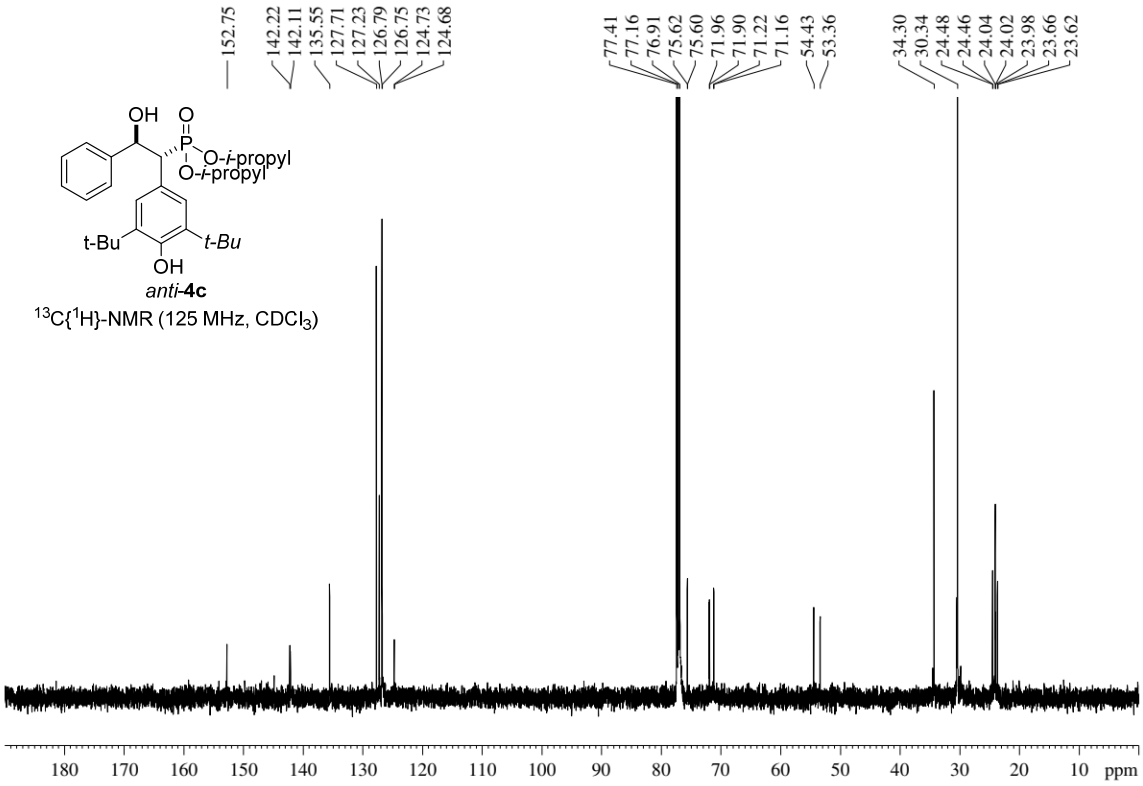
syn-**4c**

^{31}P-NMR (202 MHz, $CDCl_3$)



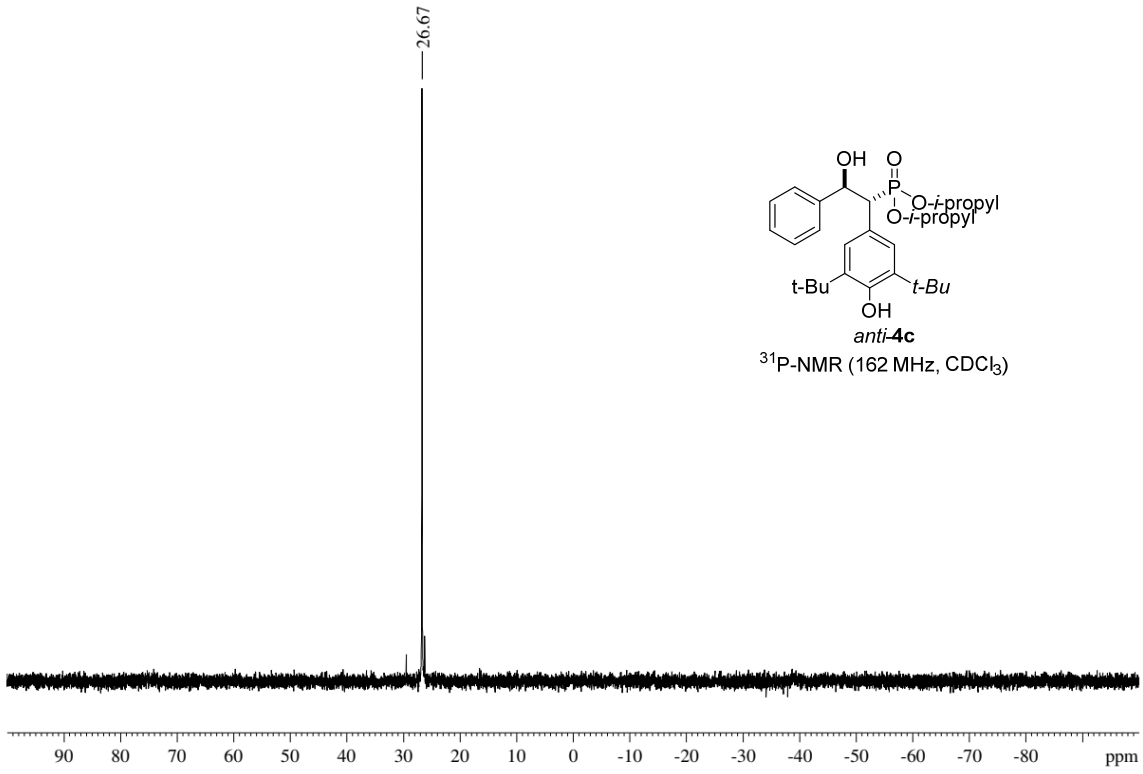
anti-**4c**

^{1}H-NMR (400 MHz, $CDCl_3$)



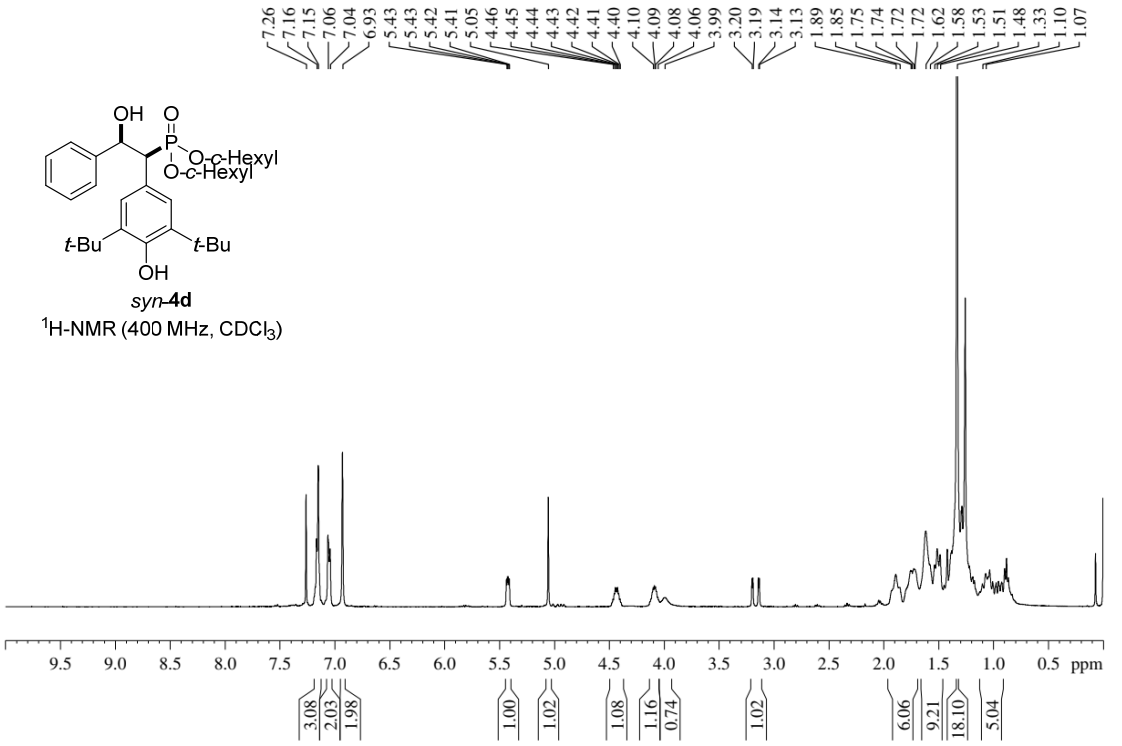
anti-**4c**

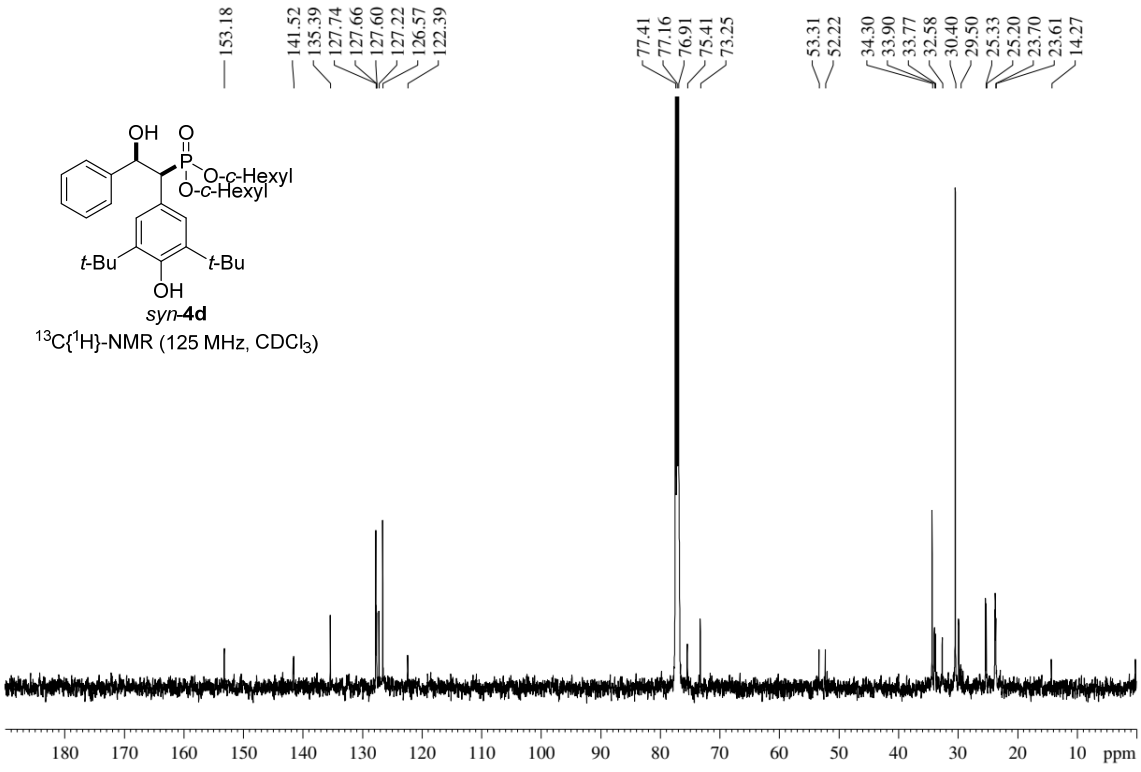
$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)

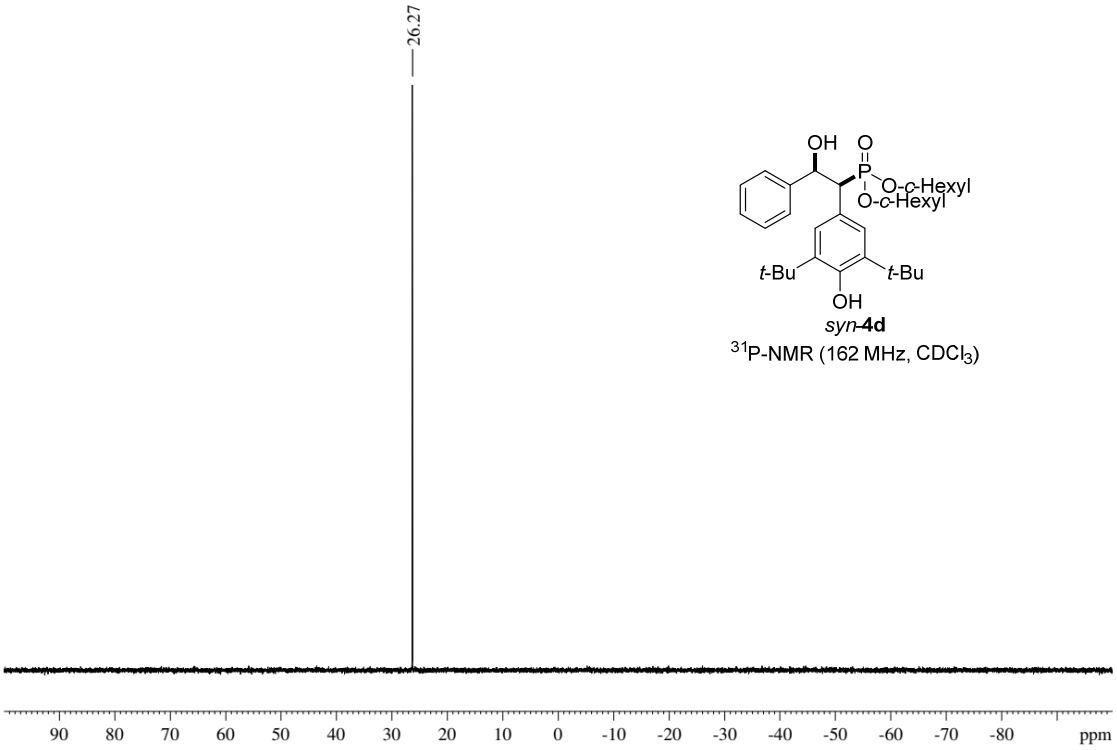


anti-**4c**

^{31}P-NMR (162 MHz, $CDCl_3$)

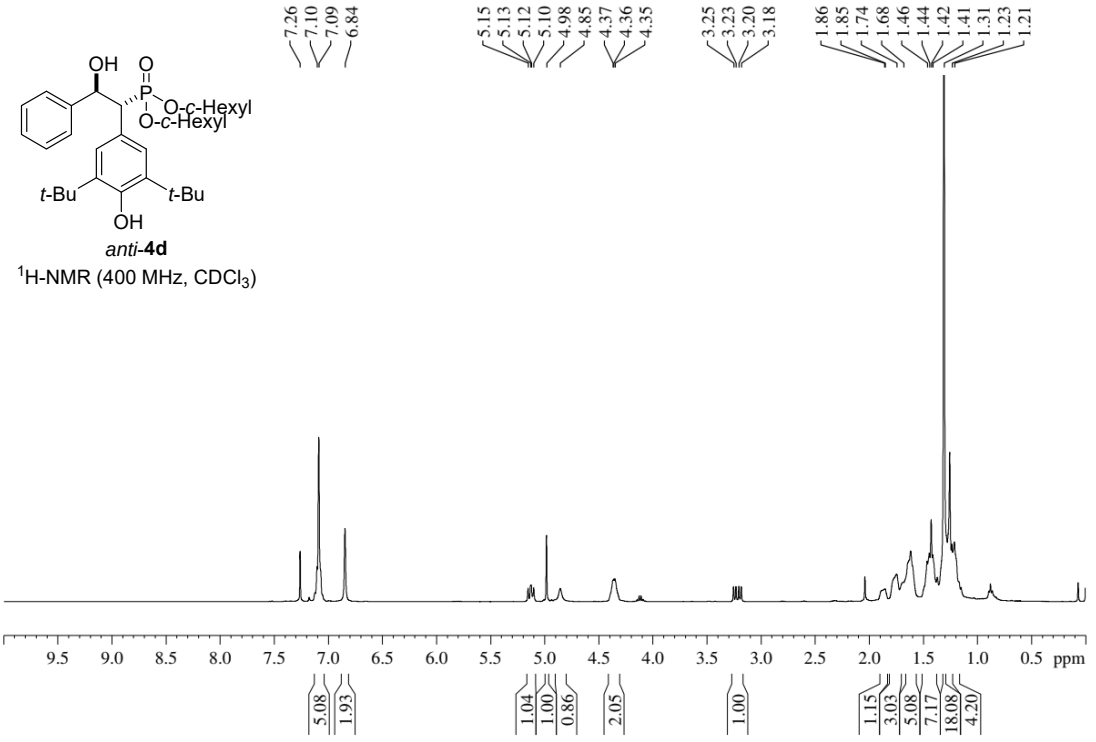

7.26
7.16
7.15
7.06
7.04
6.93
5.43
5.43
5.42
5.41
5.05
4.46
4.45
4.44
4.43
4.42
4.41
4.40
4.10
4.09
4.08
4.06
3.99
3.20
3.19
3.14
3.13
1.89
1.85
1.75
1.74
1.72
1.72
1.62
1.58
1.53
1.51
1.48
1.33
1.10
1.07
OH
O
P
O-c-Hexyl
O-c-Hexyl
t-Bu
t-Bu
OH
syn-4d
1H-NMR (400 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
3.08
2.03
1.98
1.00
1.02
1.08
1.16
0.74
1.02
6.06
9.21
18.10
5.04


153.18
141.52
135.39
127.74
127.66
127.60
127.22
126.57
122.39
77.41
77.16
76.91
75.41
73.25
53.31
52.22
34.30
33.90
33.77
32.58
30.40
29.50
25.33
25.20
23.70
23.61
14.27
OH
O
P
O-c-Hexyl
O-c-Hexyl
t-Bu
t-Bu
OH
syn-4d
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



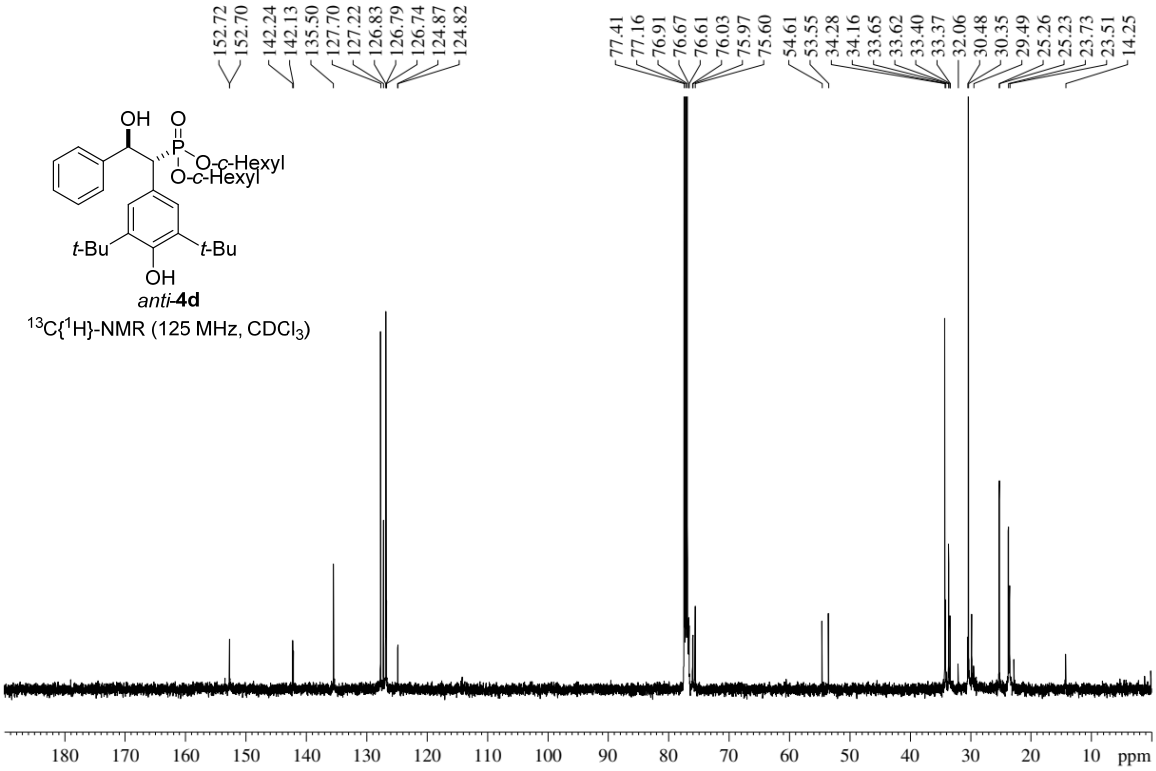
syn-**4d**

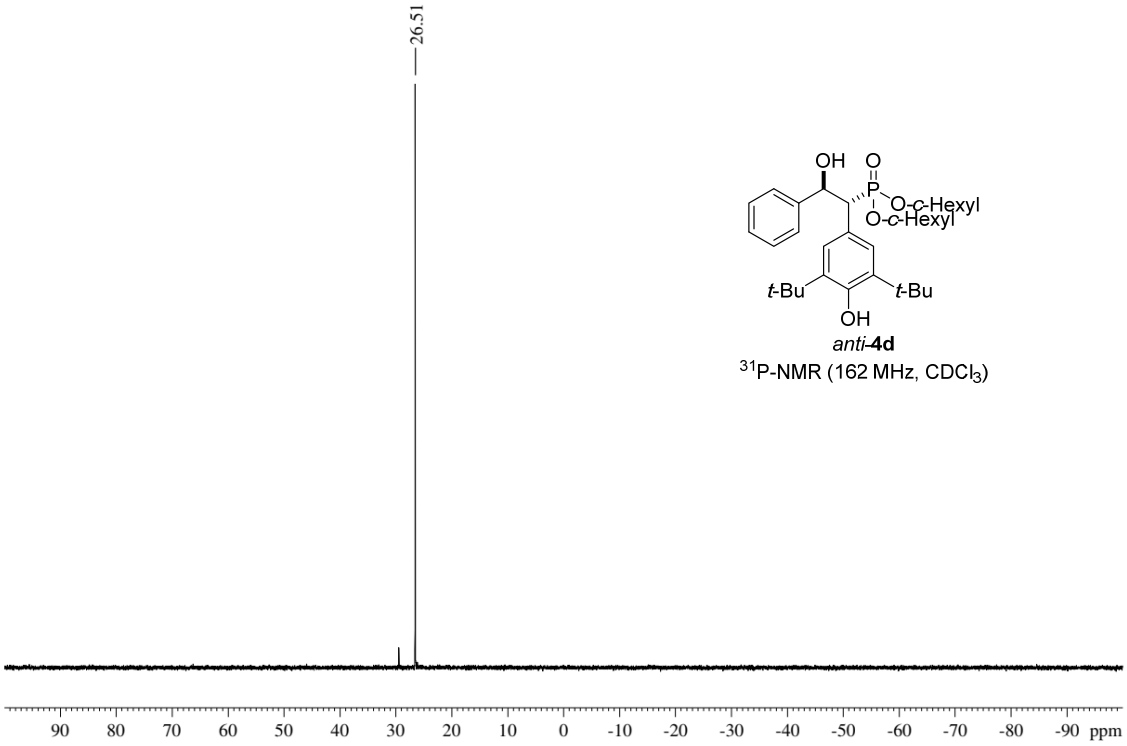
^{31}P-NMR (162 MHz, $CDCl_3$)

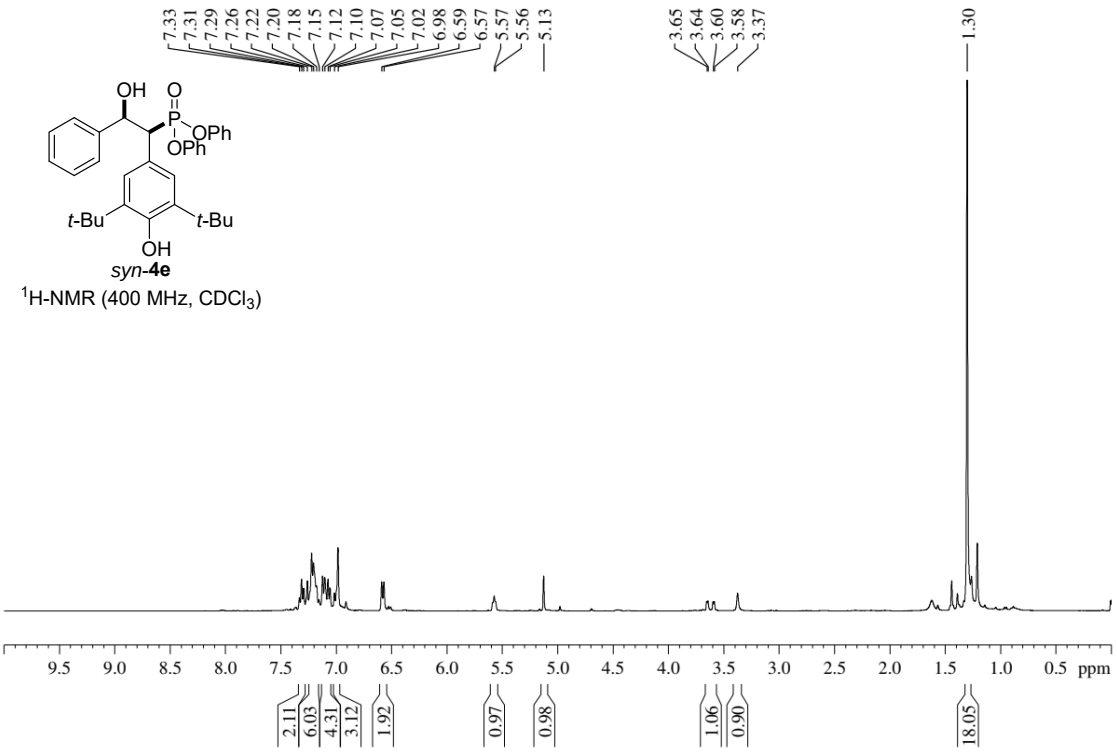


anti-**4d**

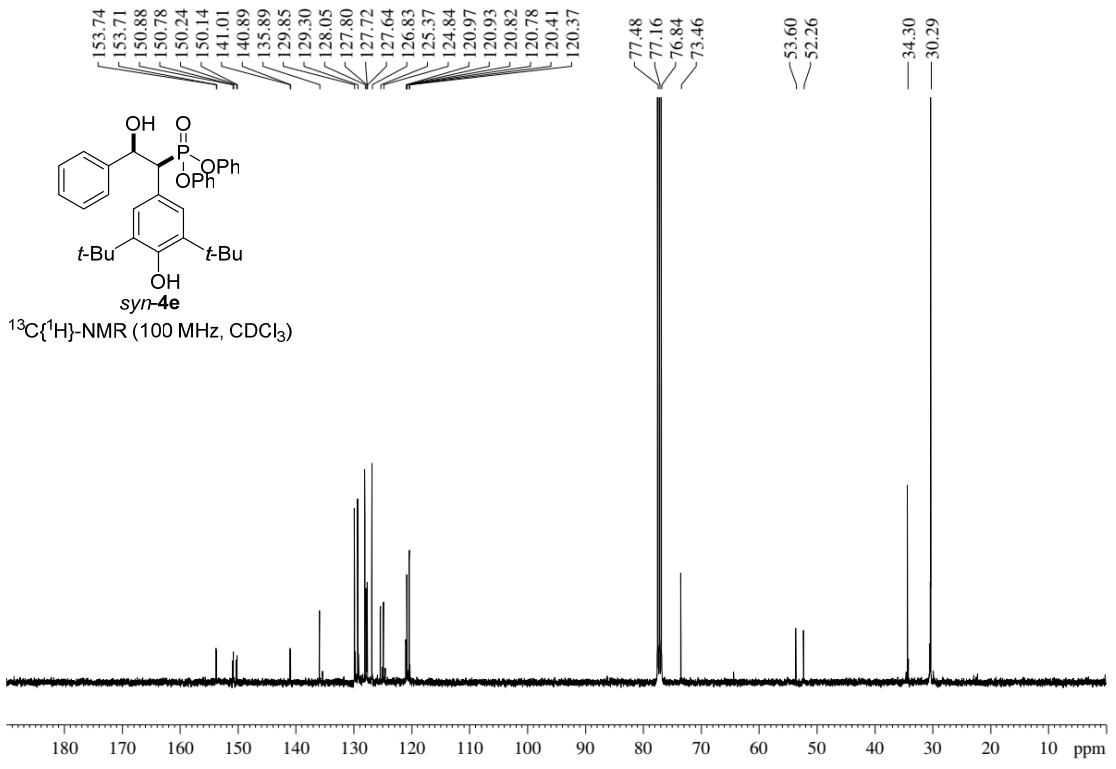
^{1}H-NMR (400 MHz, $CDCl_3$)


152.72
152.70
142.24
142.13
135.50
127.70
127.22
126.83
126.79
126.74
124.87
124.82
77.41
77.16
76.91
76.67
76.61
76.03
75.97
75.60
54.61
53.55
34.28
34.16
33.65
33.62
33.40
33.37
32.06
30.48
30.35
29.49
25.26
25.23
23.73
23.51
14.25
OH
O
P
O-c-Hexyl
O-c-Hexyl
t-Bu
t-Bu
OH
anti-4d
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

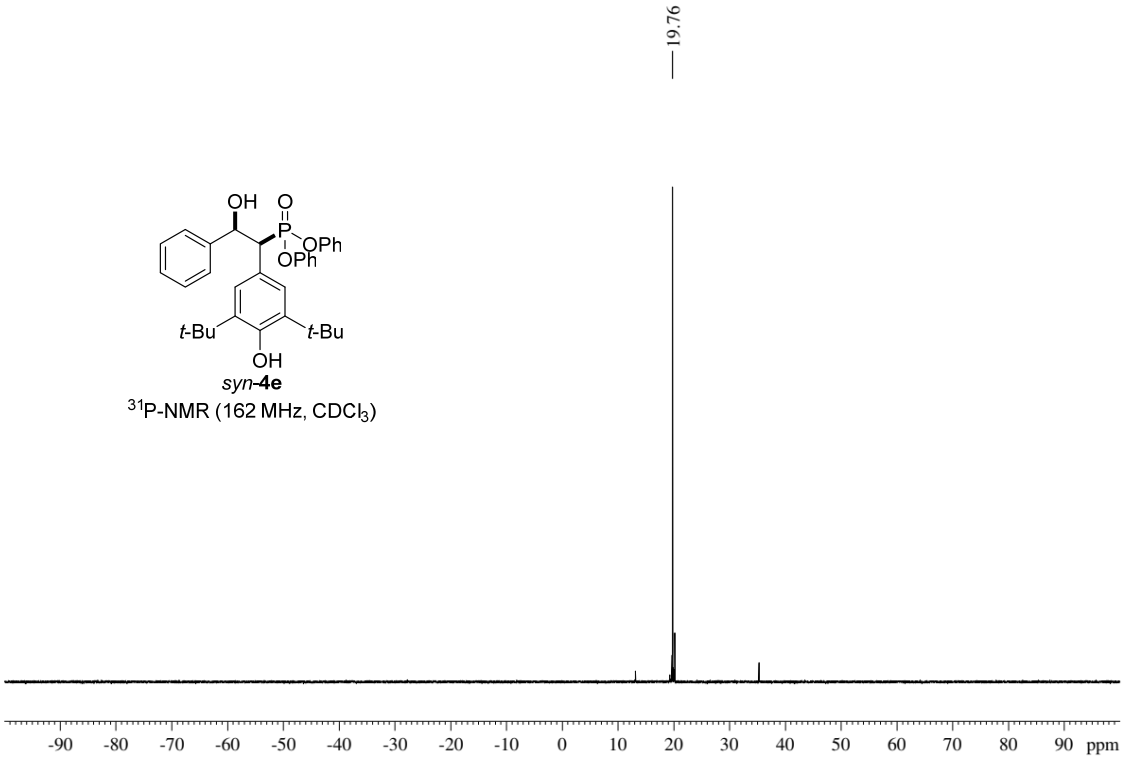

26.51
OH
O
P
O-c-Hexyl
O-c-Hexyl
t-Bu
t-Bu
OH
anti-4d
31P-NMR (162 MHz, CDCl3)
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 ppm



^{1}H-NMR (400 MHz, $CDCl_3$)

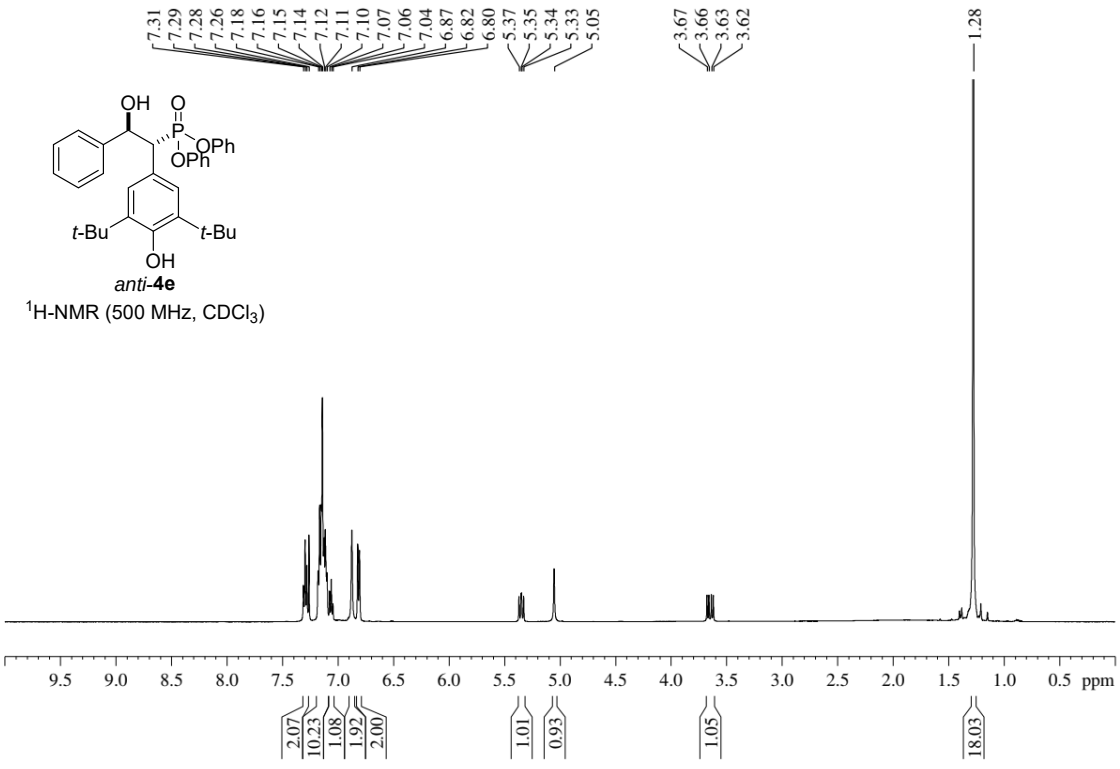


^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)



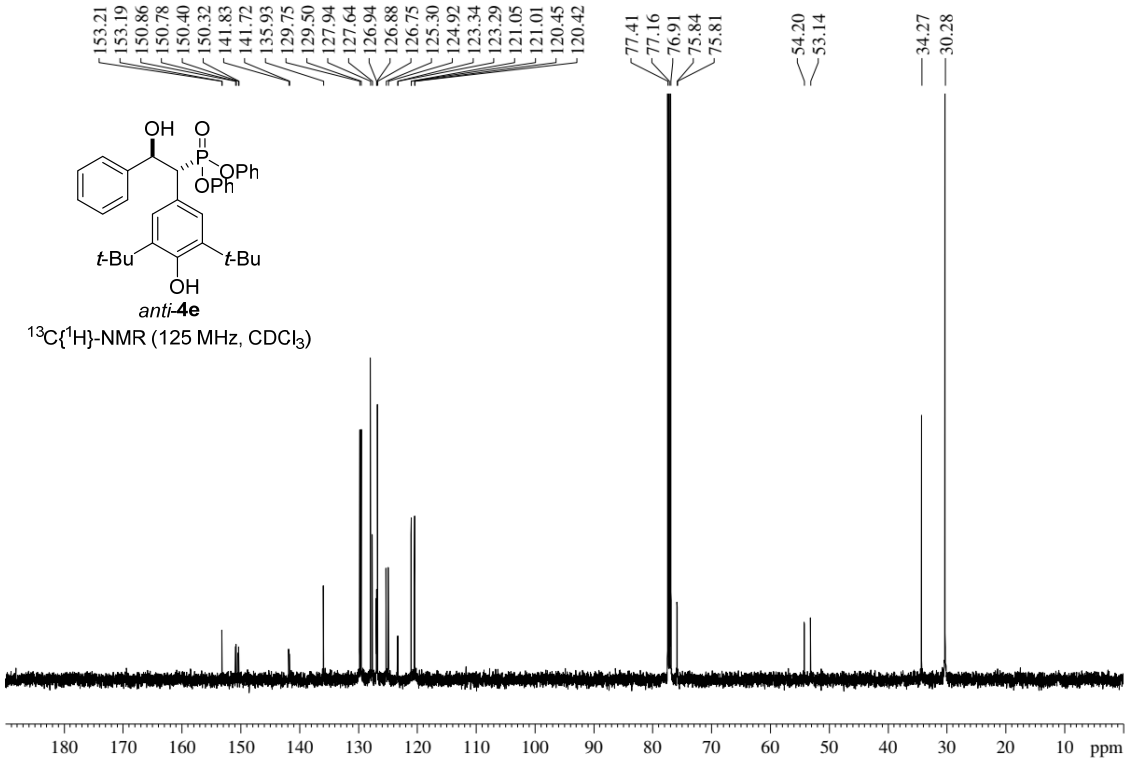
syn-**4e**

^{31}P-NMR (162 MHz, $CDCl_3$)



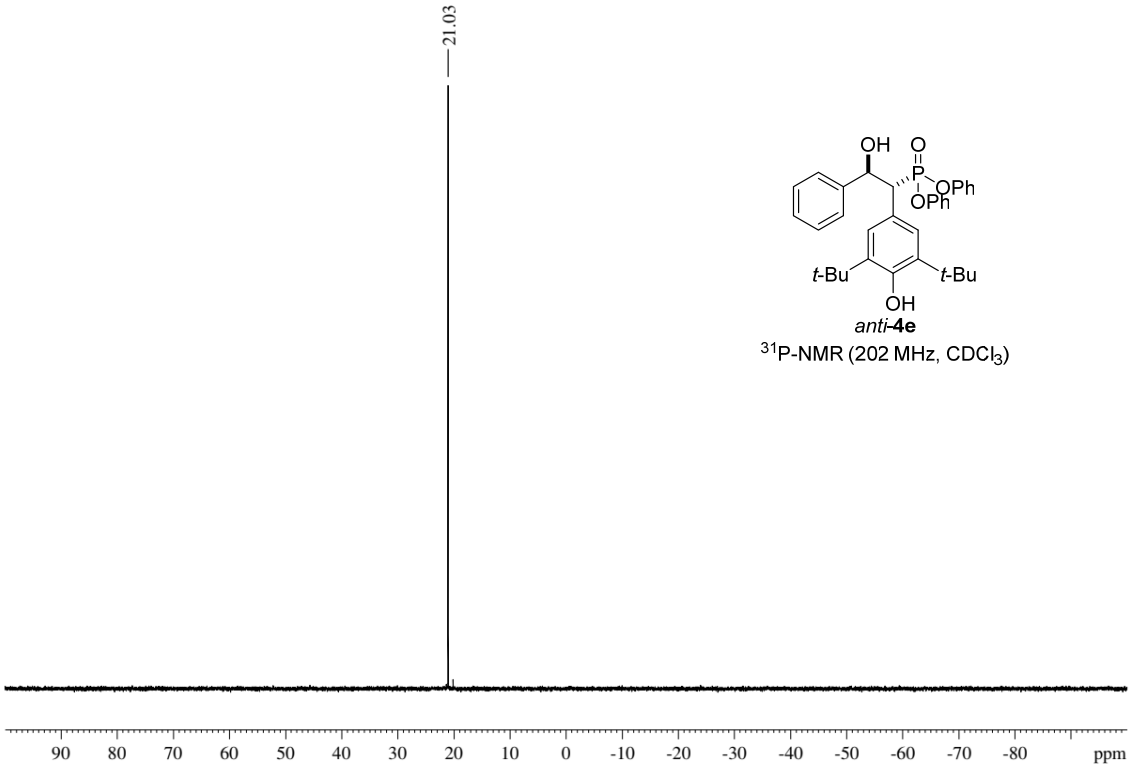
anti-**4e**

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



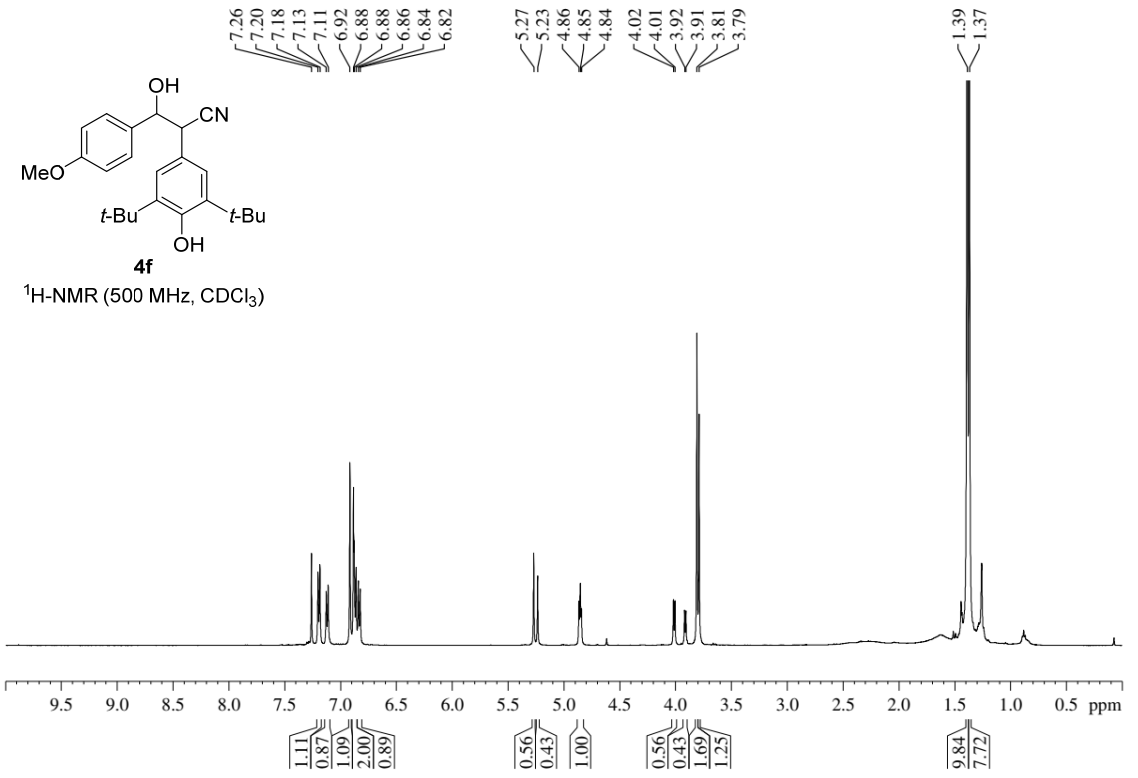
anti-**4e**

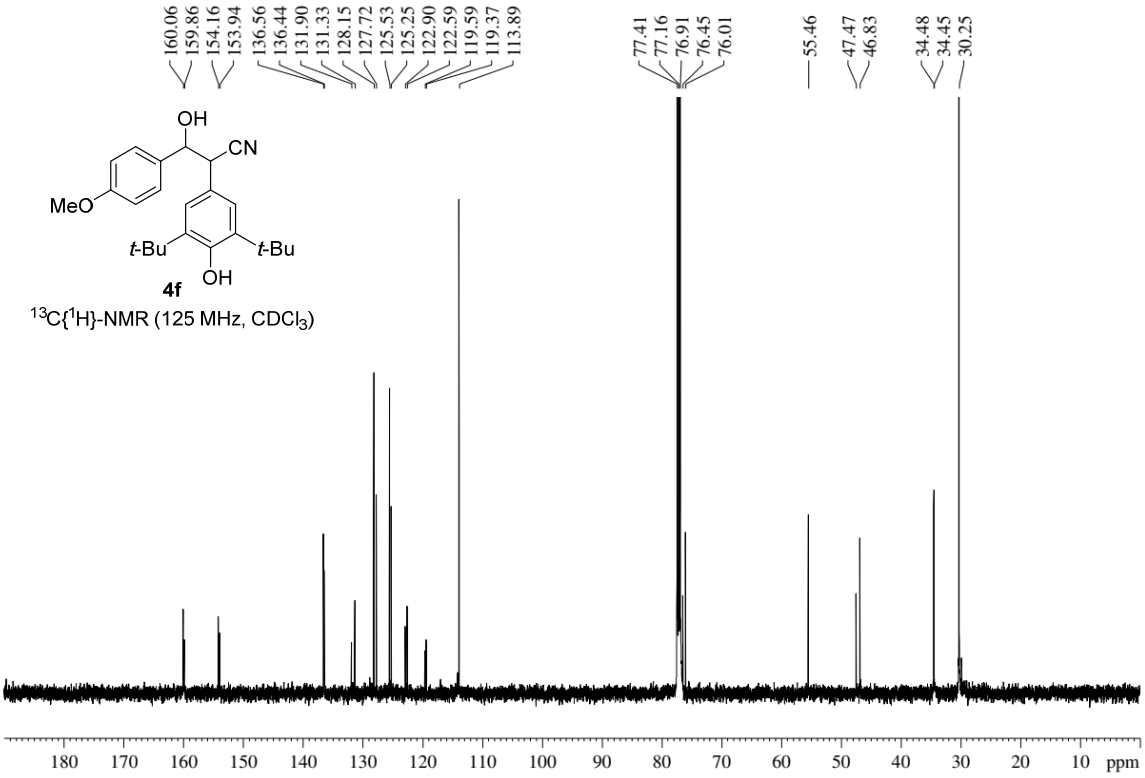
$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)

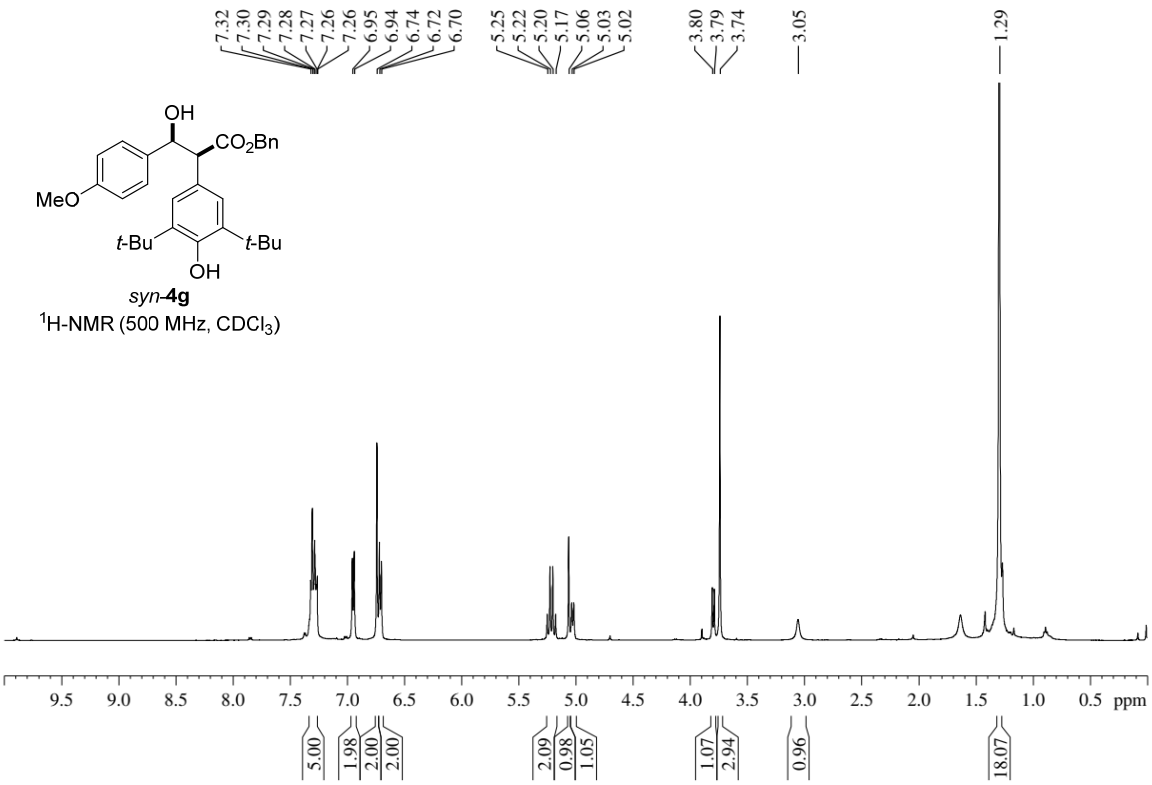


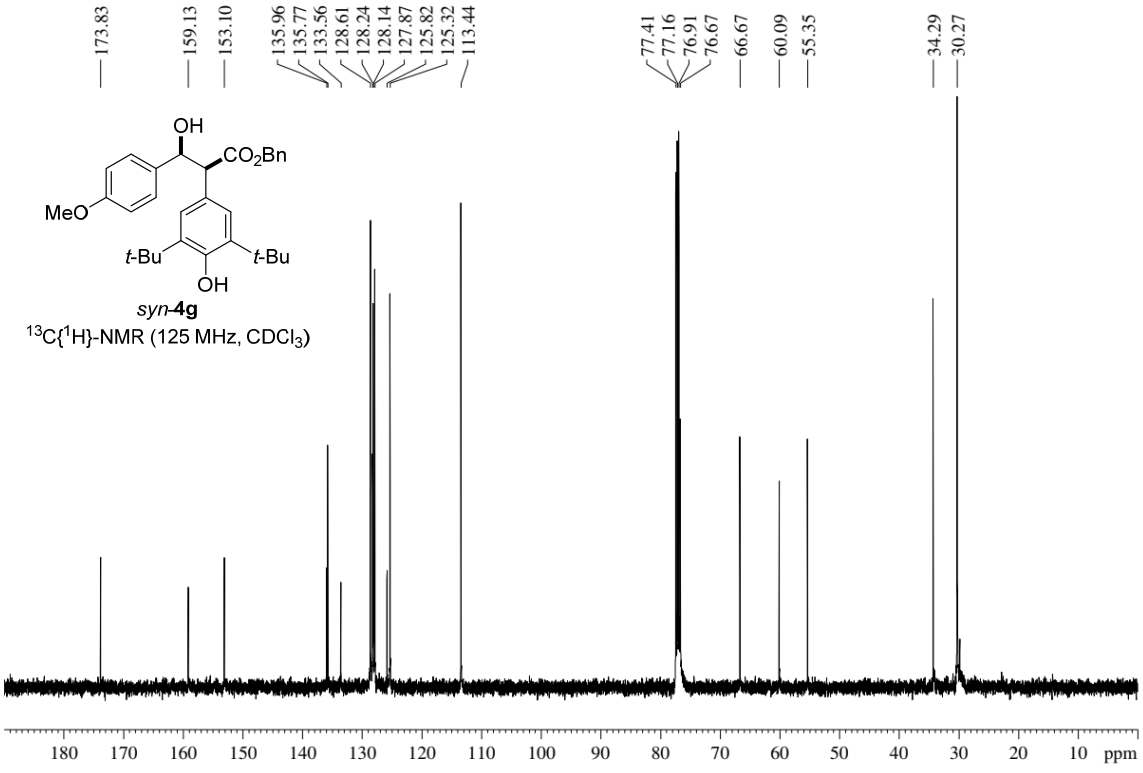
anti-**4e**

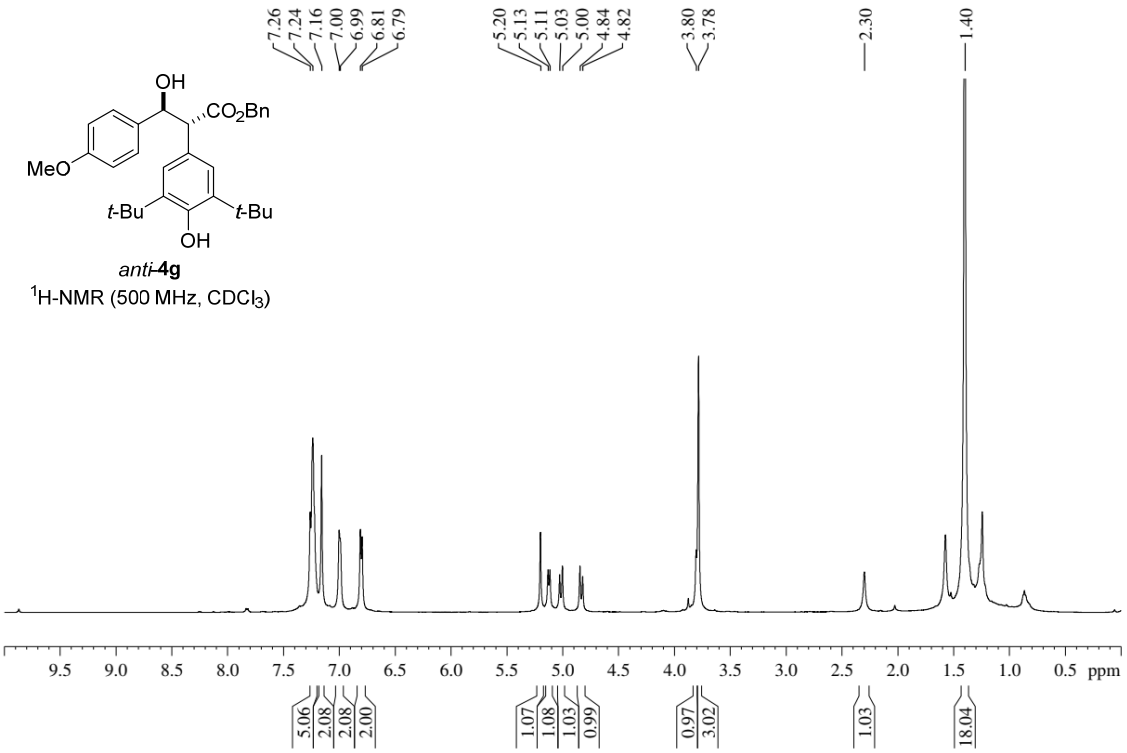
^{31}P-NMR (202 MHz, $CDCl_3$)


7.26
7.20
7.18
7.13
7.11
6.92
6.88
6.88
6.86
6.84
6.82
5.27
5.23
4.86
4.85
4.84
4.02
4.01
3.92
3.91
3.81
3.79
1.39
1.37
OH
CN
MeO
t-Bu
t-Bu
OH
4f
1H-NMR (500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
1.11
0.87
1.09
2.00
0.89
0.56
0.43
1.00
0.56
0.43
1.69
1.25
9.84
7.72


160.06
159.86
154.16
153.94
136.56
136.44
131.90
131.33
128.15
127.72
125.53
125.25
122.90
122.59
119.59
119.37
113.89
77.41
77.16
76.91
76.45
76.01
55.46
47.47
46.83
34.48
34.45
30.25
OH
CN
MeO
t-Bu
t-Bu
OH
4f
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

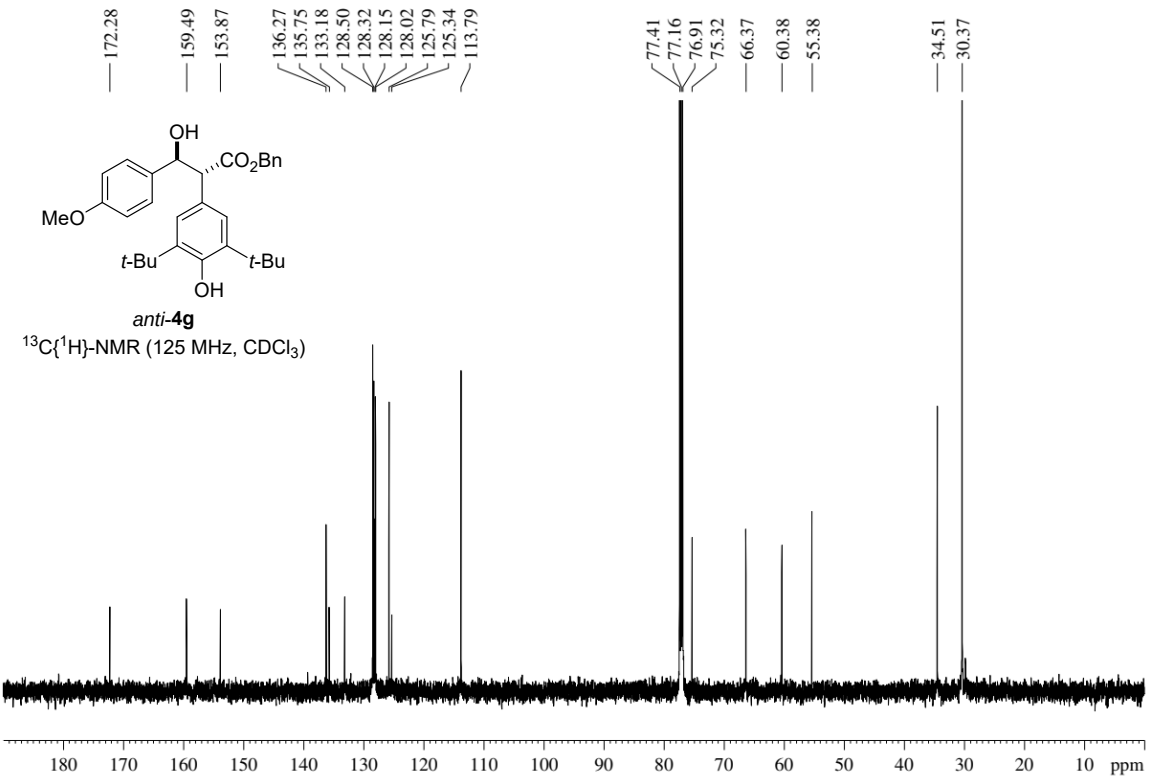

7.32
7.30
7.29
7.28
7.27
7.26
7.26
6.95
6.94
6.74
6.72
6.70
5.25
5.22
5.20
5.17
5.06
5.03
5.02
3.80
3.79
3.74
3.05
1.29
OH
CO2Bn
MeO
t-Bu
t-Bu
OH
syn-4g
1H-NMR (500 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
5.00
1.98
2.00
2.00
2.09
0.98
1.05
1.07
2.94
0.96
18.07


173.83
159.13
153.10
135.96
135.77
133.56
128.61
128.24
128.14
127.87
125.82
125.32
113.44
77.41
77.16
76.91
76.67
66.67
60.09
55.35
34.29
30.27
OH
CO2Bn
MeO
t-Bu
t-Bu
OH
syn-4g
13C{1H}-NMR (125 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



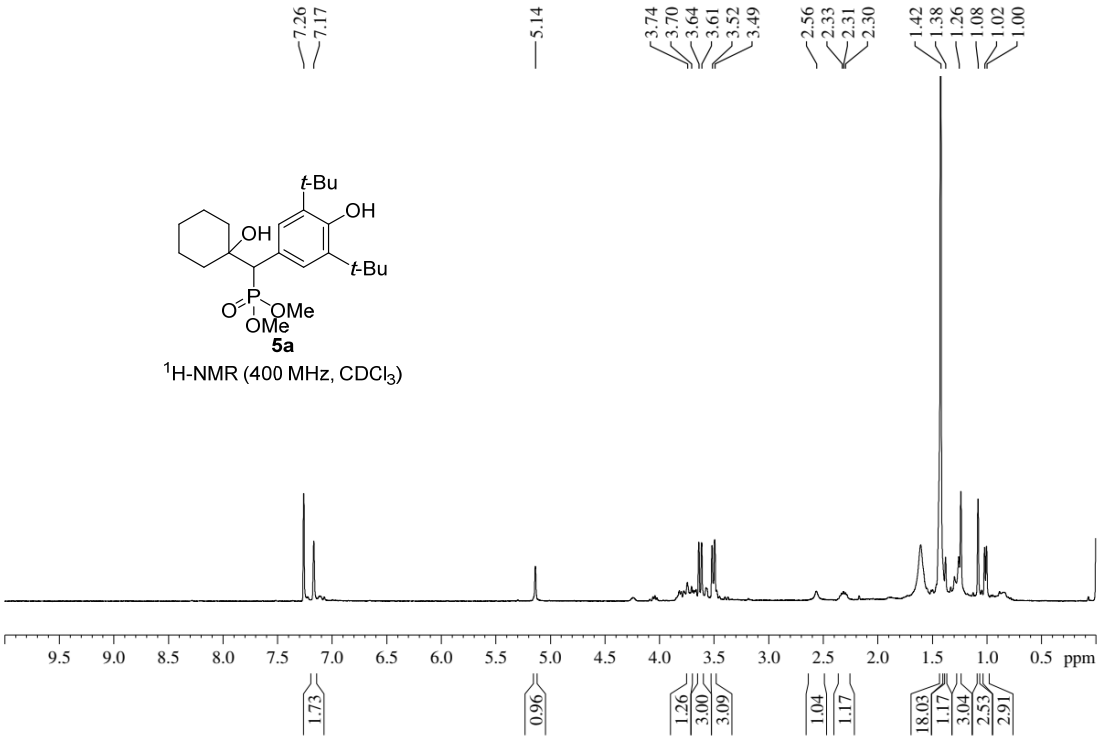
anti-**4g**

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



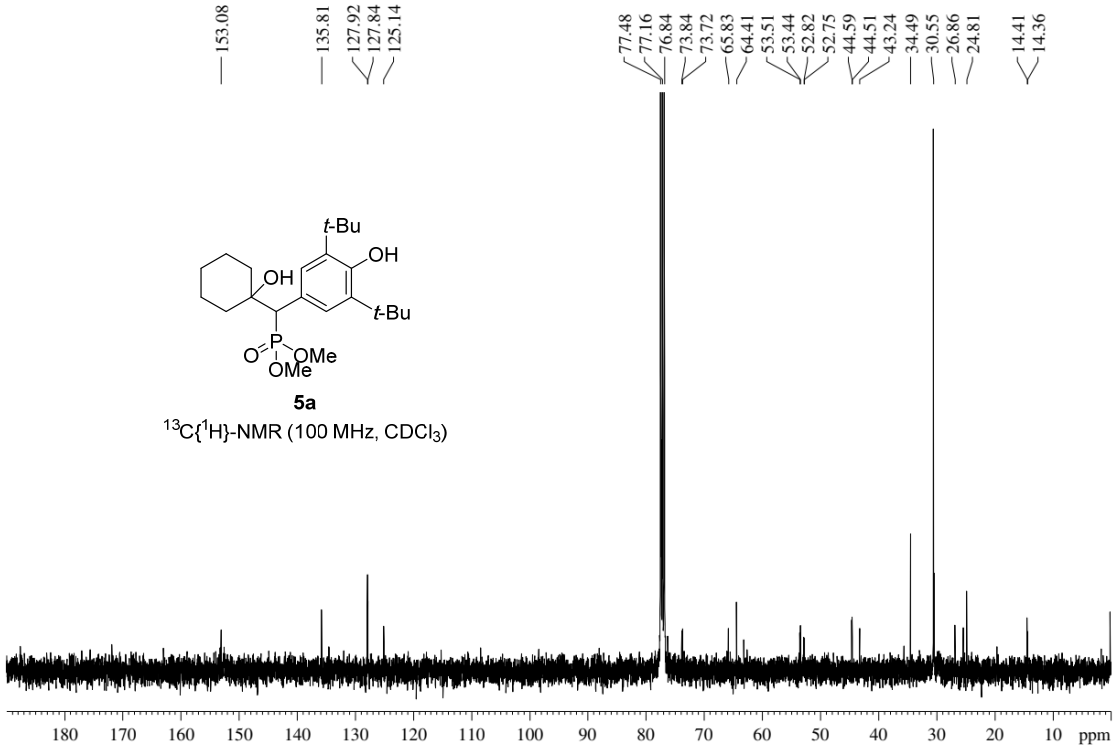
anti-**4g**

$^{13}C\{^1H\}$-NMR (125 MHz, $CDCl_3$)



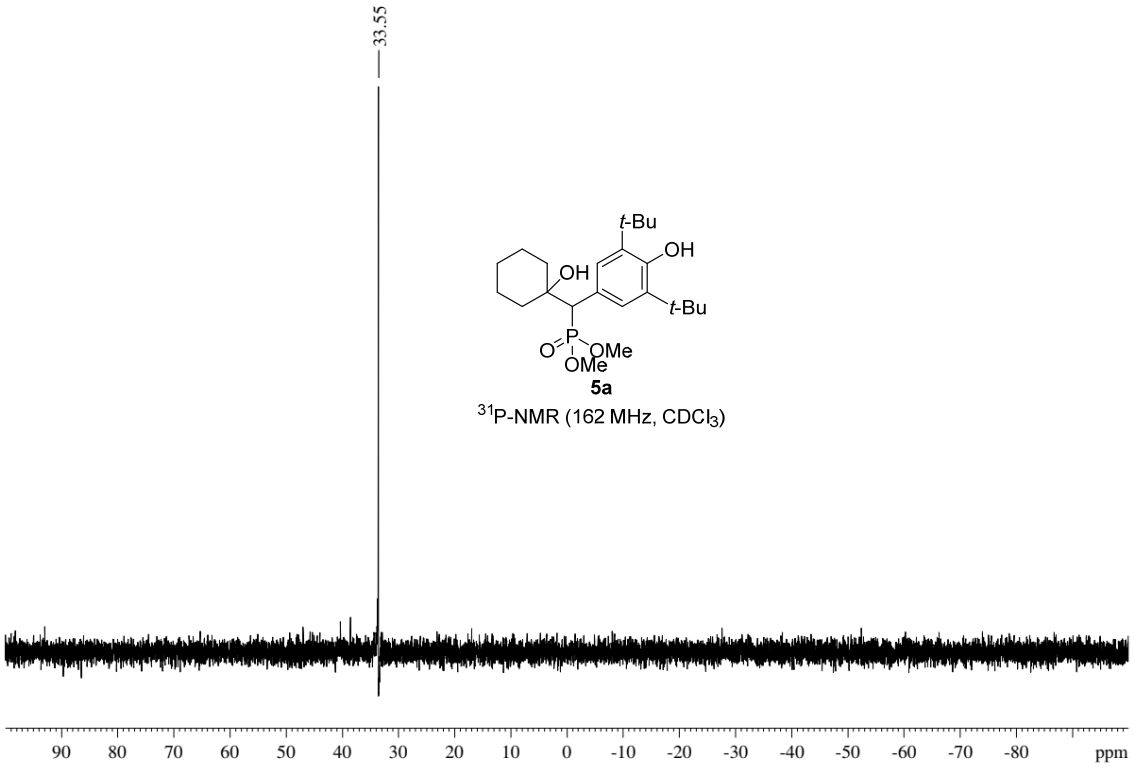
5a

^{1}H-NMR (400 MHz, $CDCl_3$)



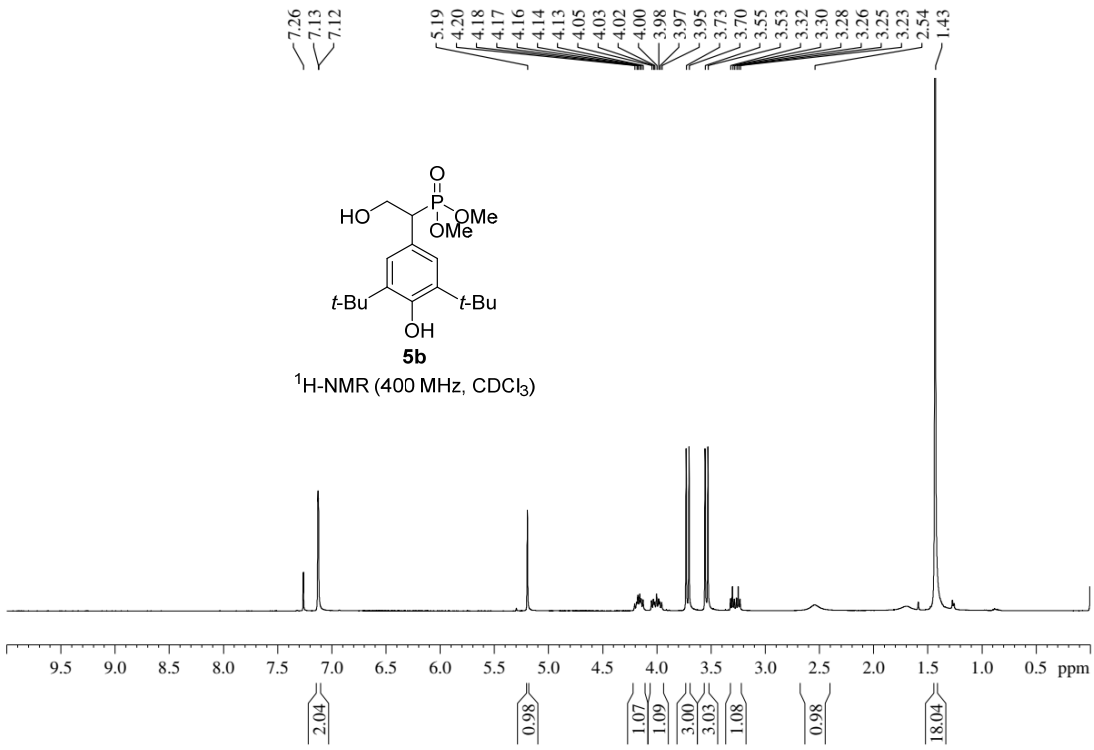
5a

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)



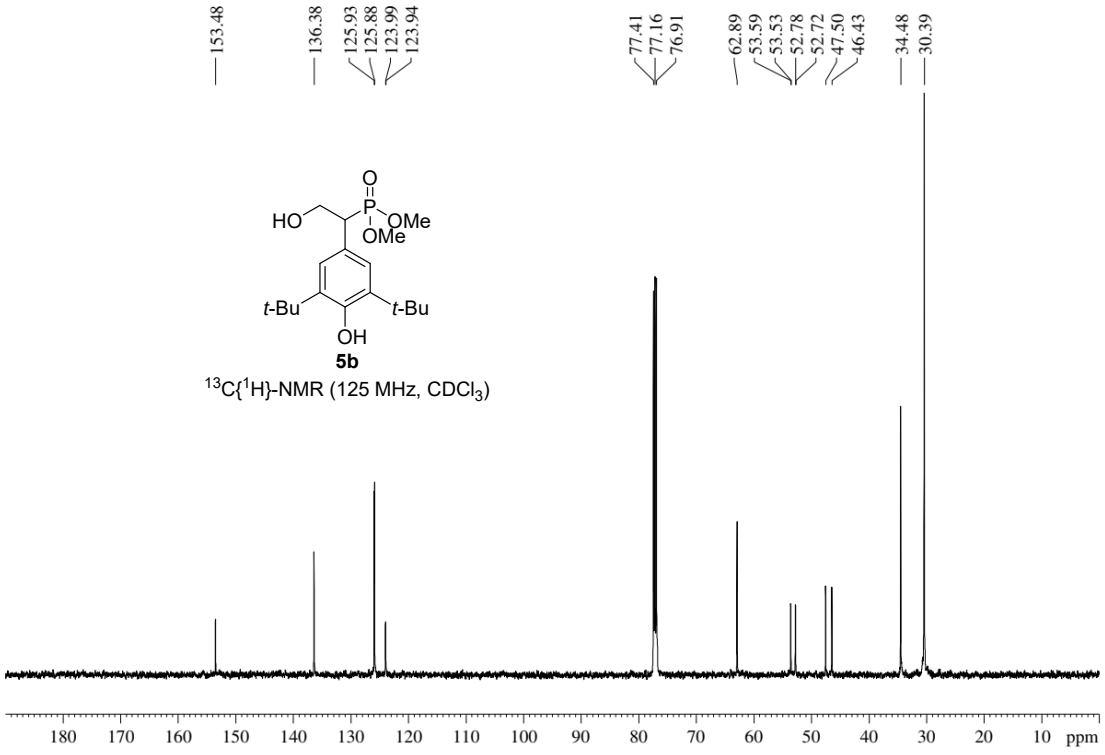
5a

^{31}P-NMR (162 MHz, $CDCl_3$)



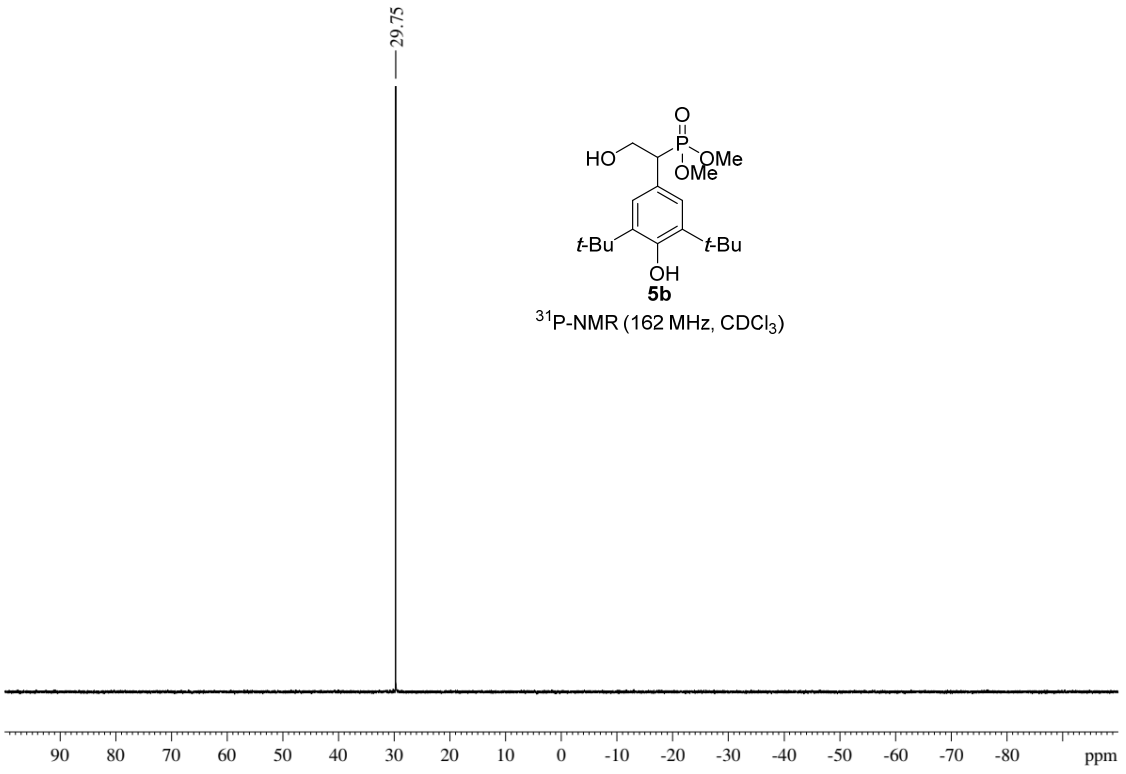
5b

^{1}H-NMR (400 MHz, $CDCl_3$)



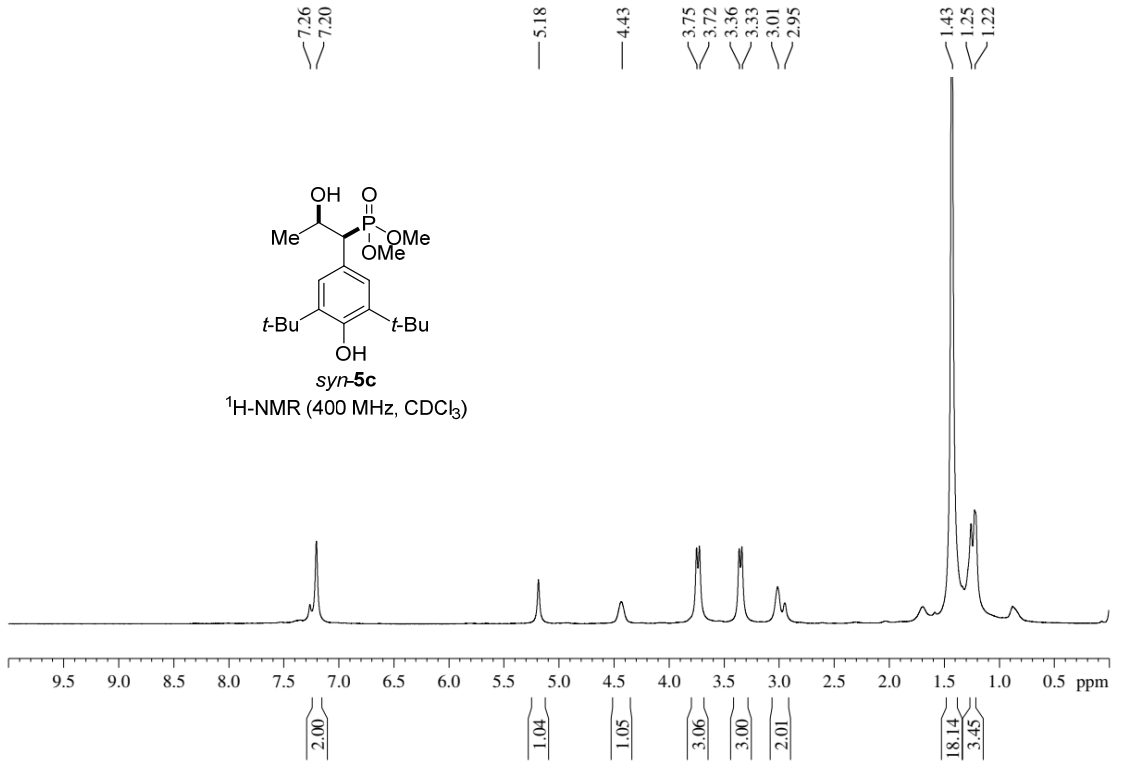
5b

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



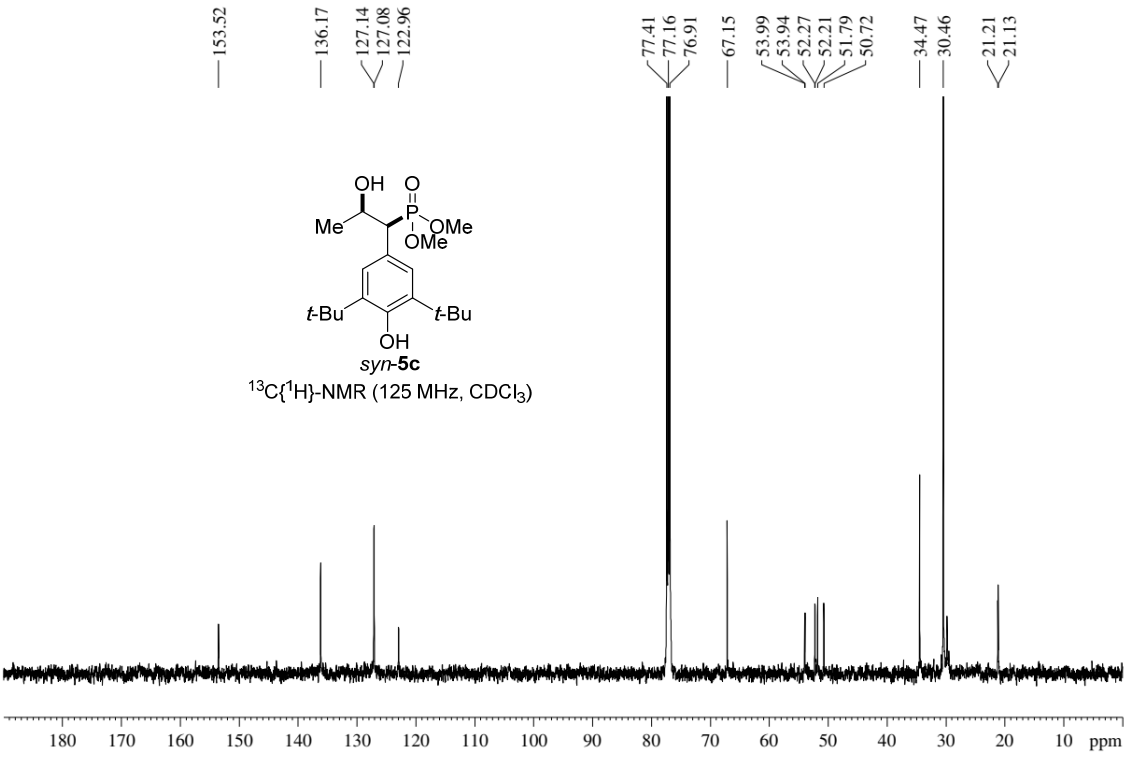
5b

^{31}P-NMR (162 MHz, $CDCl_3$)



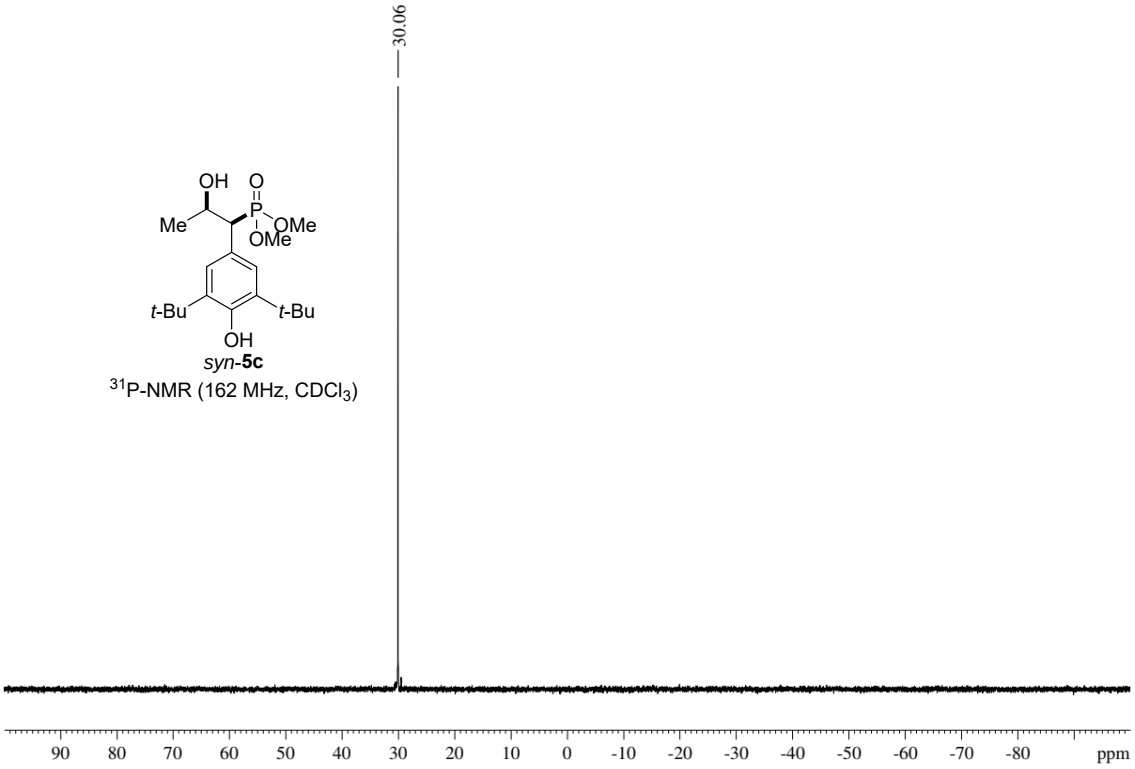
syn-**5c**

^{1}H-NMR (400 MHz, $CDCl_3$)



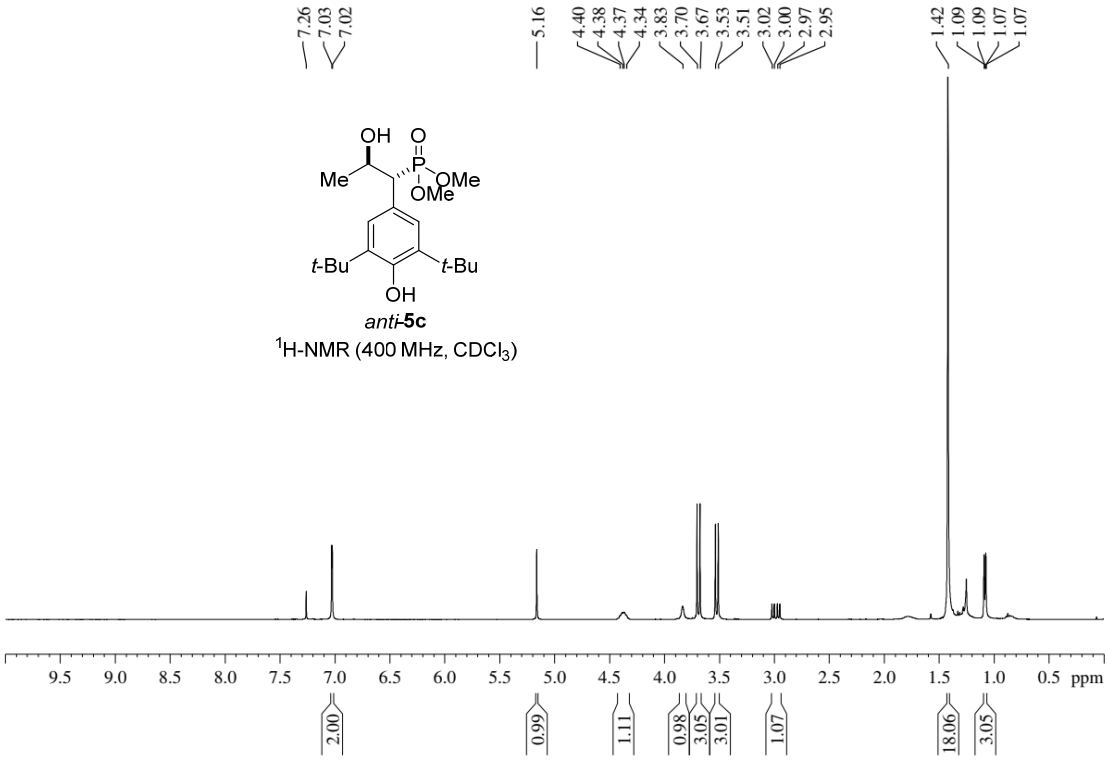
syn-**5c**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



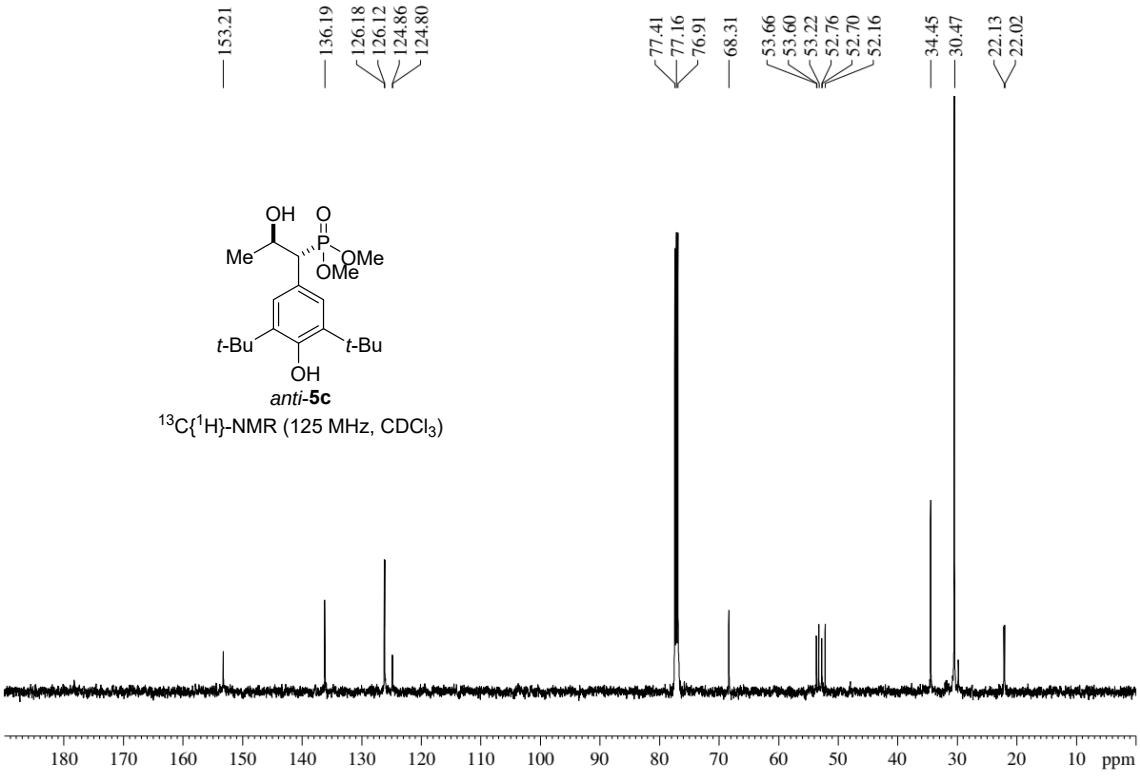
syn-**5c**

^{31}P-NMR (162 MHz, $CDCl_3$)



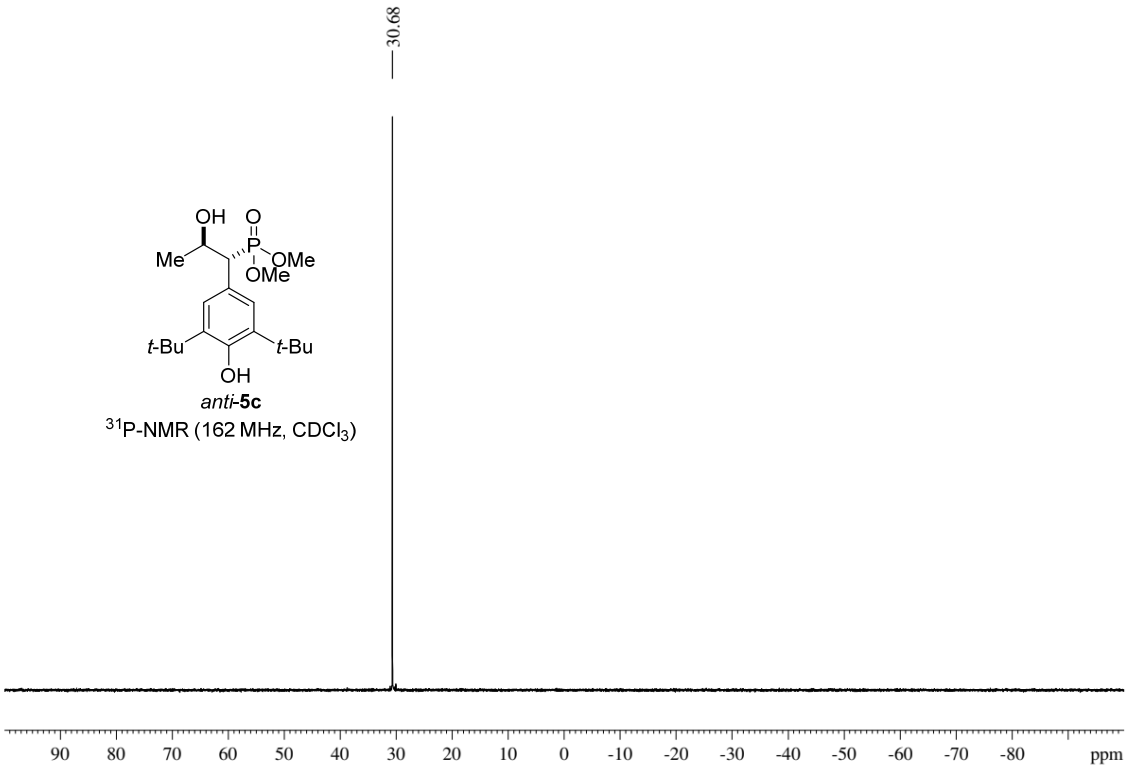
anti-**5c**

^{1}H-NMR (400 MHz, $CDCl_3$)



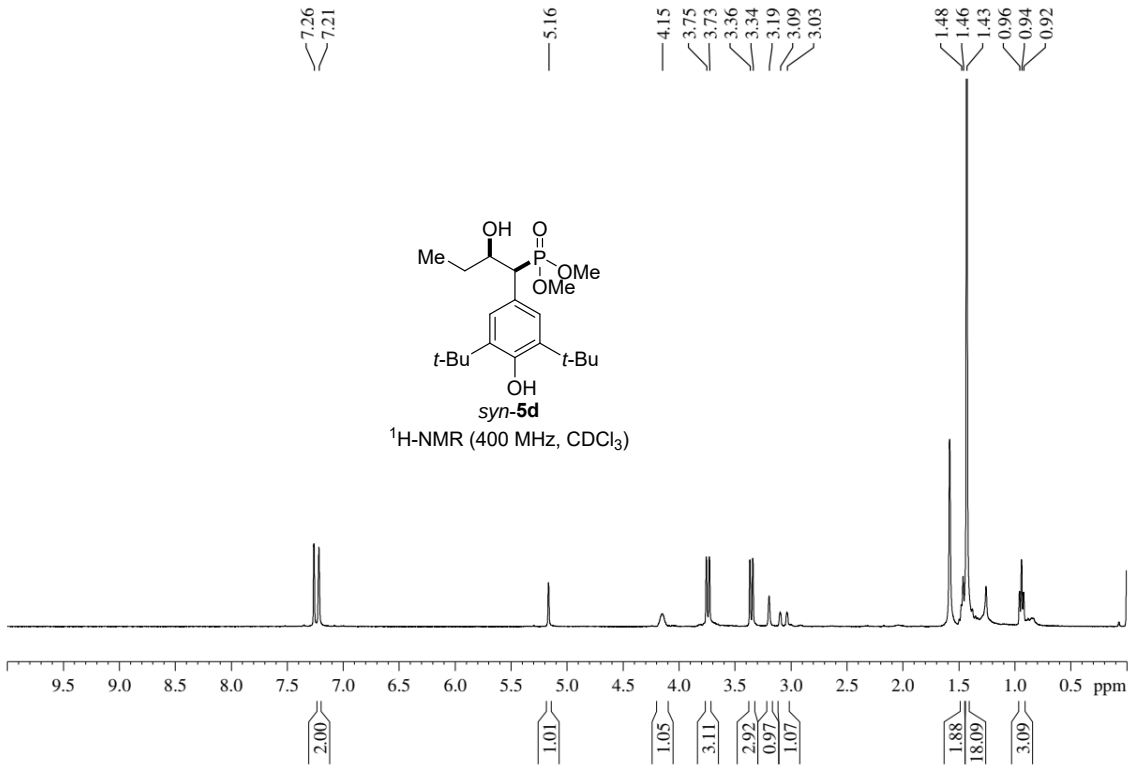
anti-**5c**

$^{13}C\{^{1}H\}$-NMR (125 MHz, $CDCl_3$)



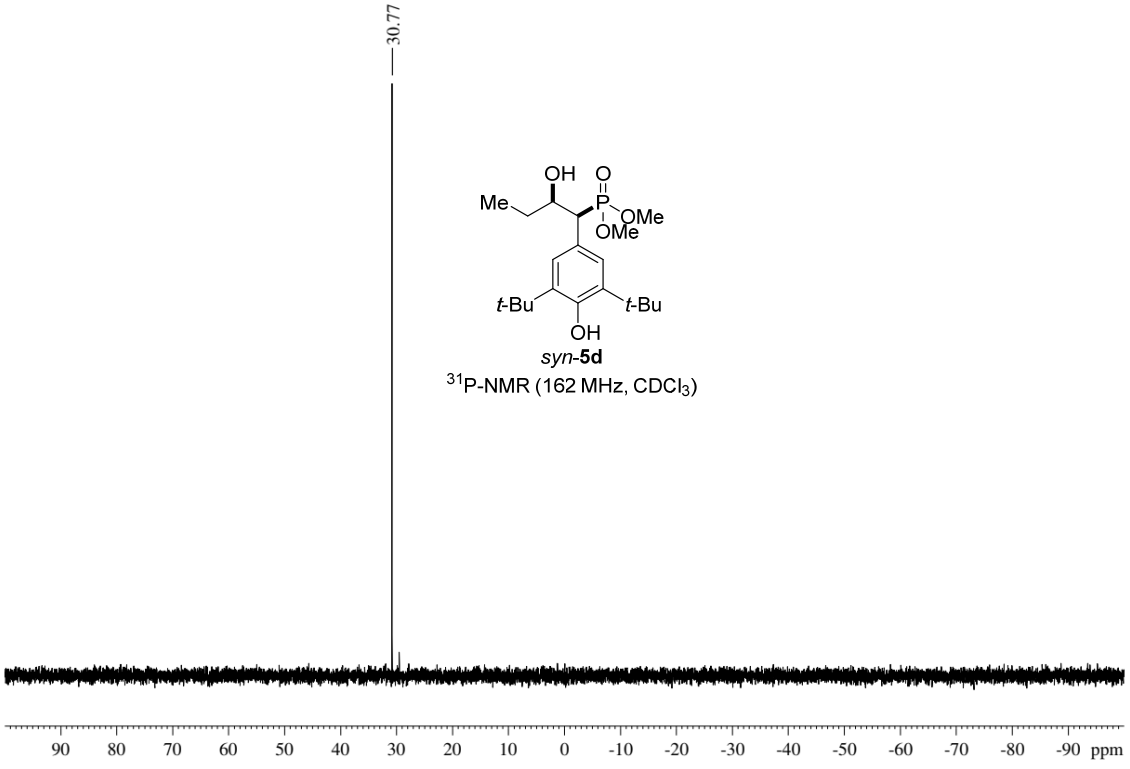
anti-**5c**

^{31}P-NMR (162 MHz, $CDCl_3$)



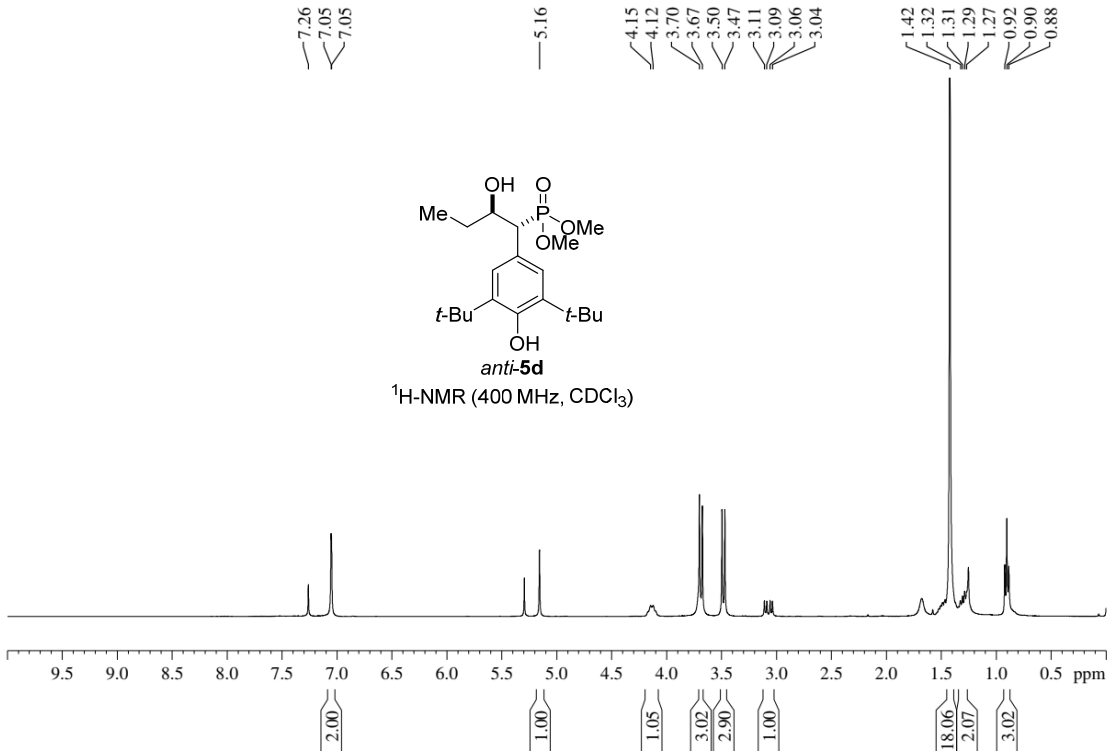
syn-**5d**

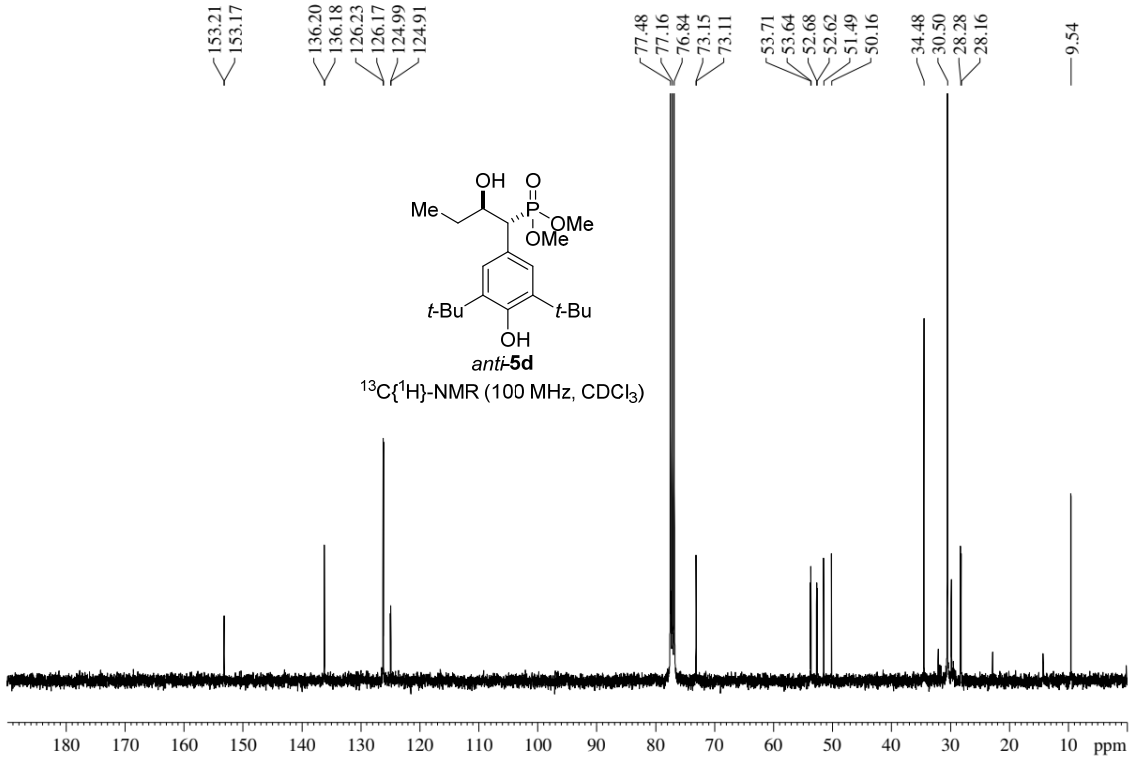
^{1}H-NMR (400 MHz, $CDCl_3$)

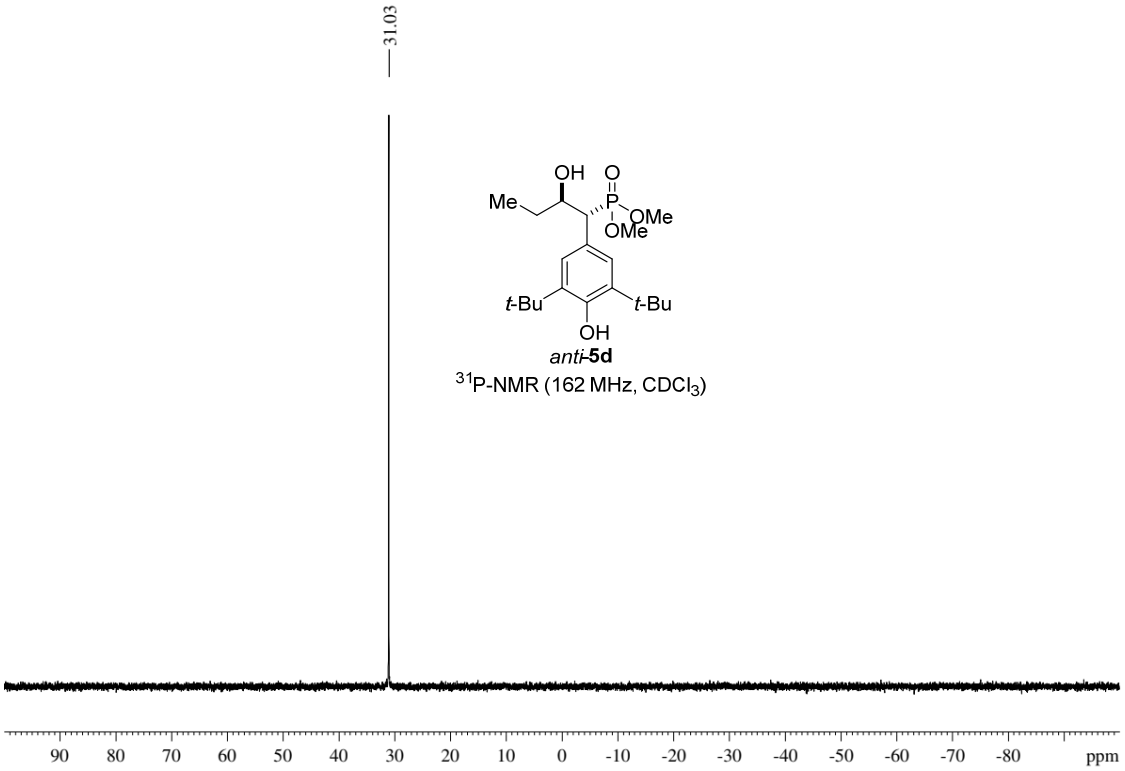


syn-**5d**

^{31}P-NMR (162 MHz, $CDCl_3$)

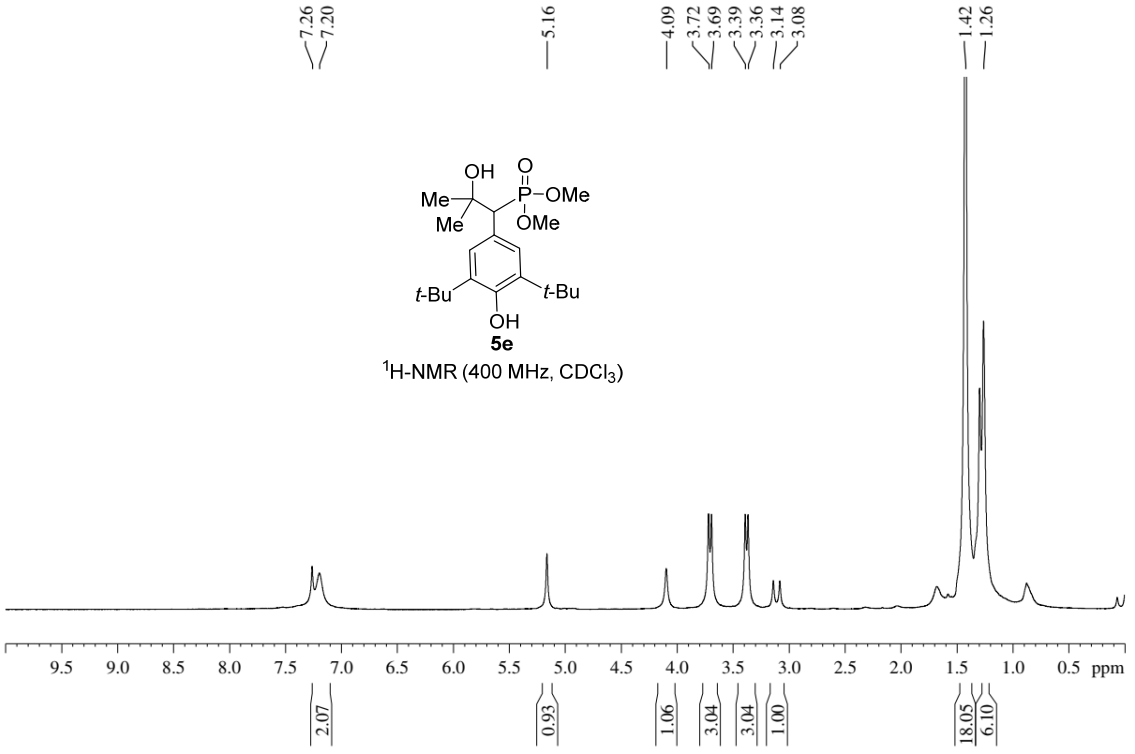

7.26
7.05
7.05
5.16
4.15
4.12
3.70
3.67
3.50
3.47
3.11
3.09
3.06
3.04
1.42
1.32
1.31
1.29
1.27
0.92
0.90
0.88
OH
O
Me
P
OMe
OMe
t-Bu
t-Bu
OH
anti-5d
1H-NMR (400 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
2.00
1.00
1.05
3.02
2.90
1.00
18.06
2.07
3.02


153.21
153.17
136.20
136.18
126.23
126.17
124.99
124.91
77.48
77.16
76.84
73.15
73.11
53.71
53.64
52.68
52.62
51.49
50.16
34.48
30.50
28.28
28.16
9.54
OH
O
Me
P
OMe
OMe
t-Bu
t-Bu
OH
anti-5d
13C{1H}-NMR (100 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm



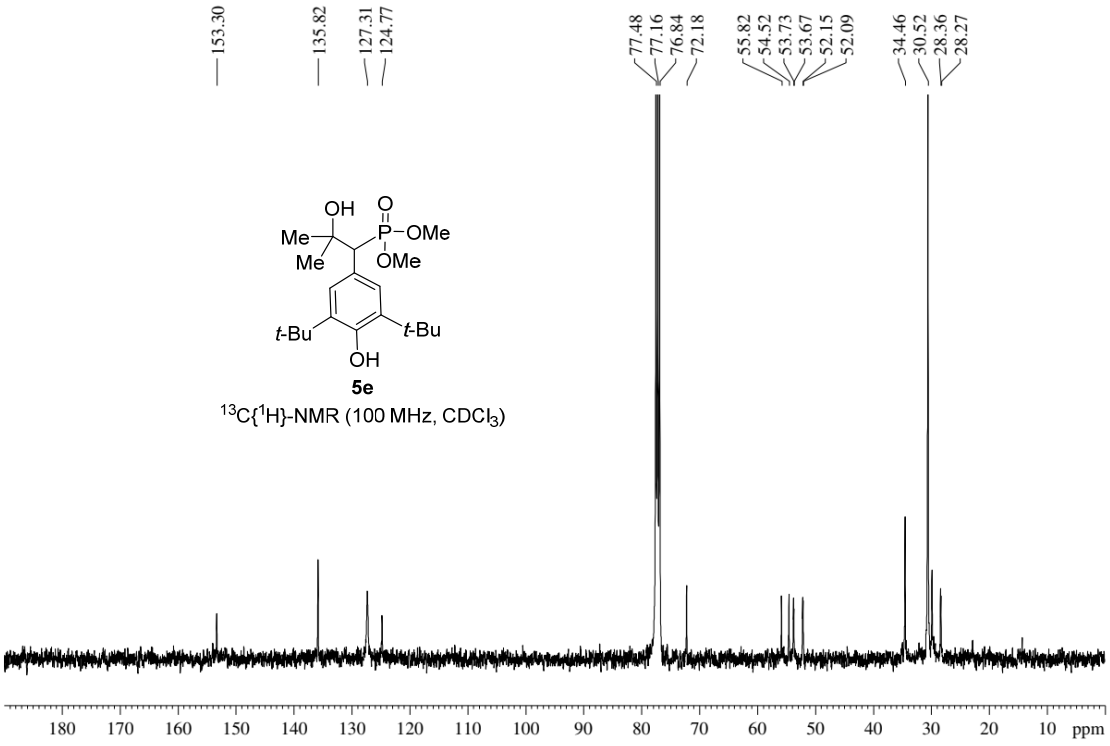
anti-**5d**

^{31}P-NMR (162 MHz, $CDCl_3$)



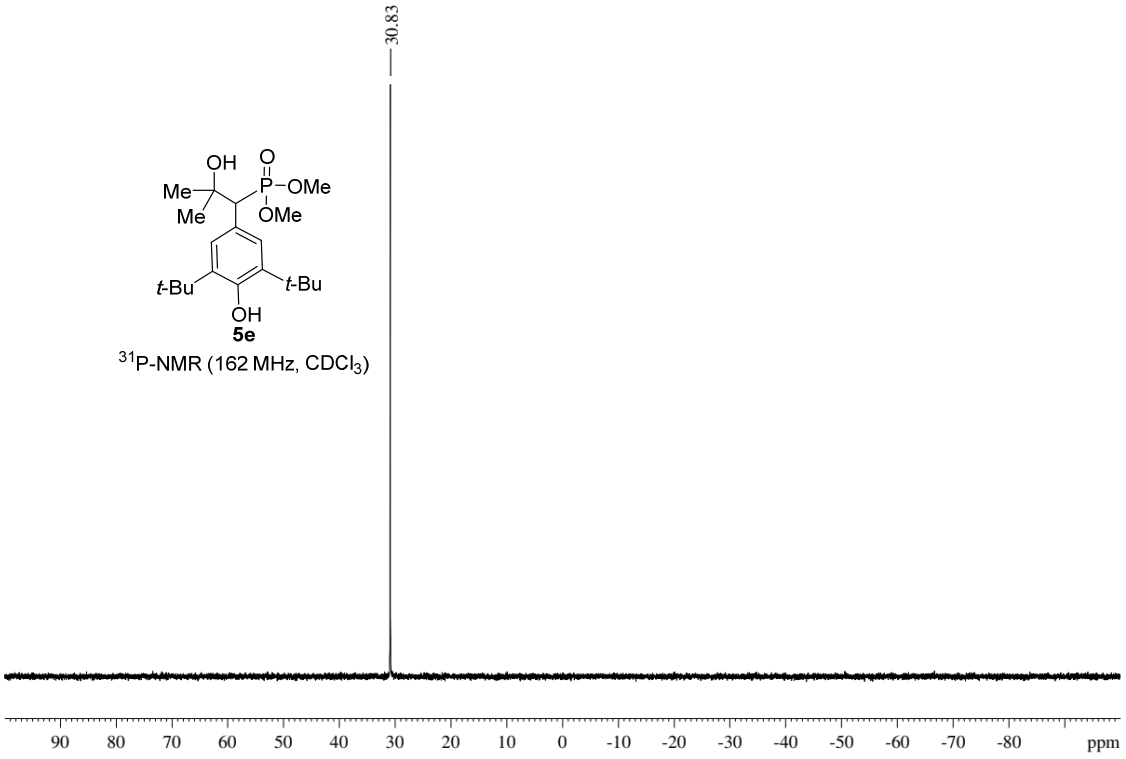
5e

^{1}H-NMR (400 MHz, $CDCl_3$)



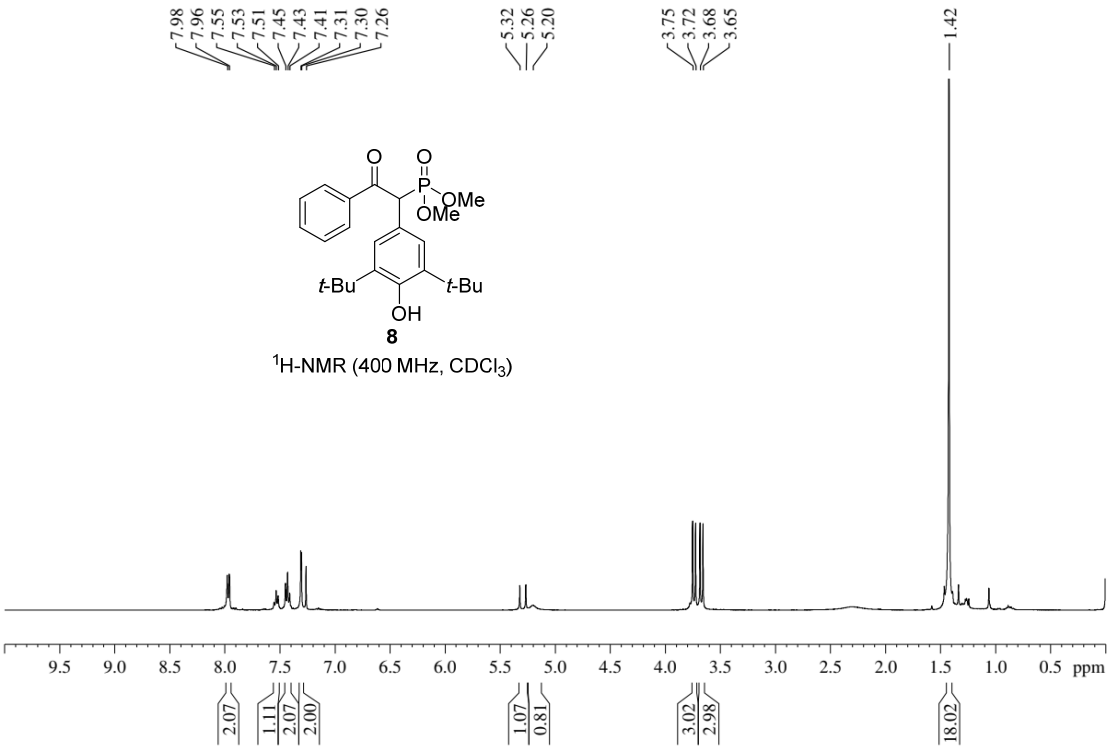
5e

$^{13}C\{^{1}H\}$-NMR (100 MHz, $CDCl_3$)

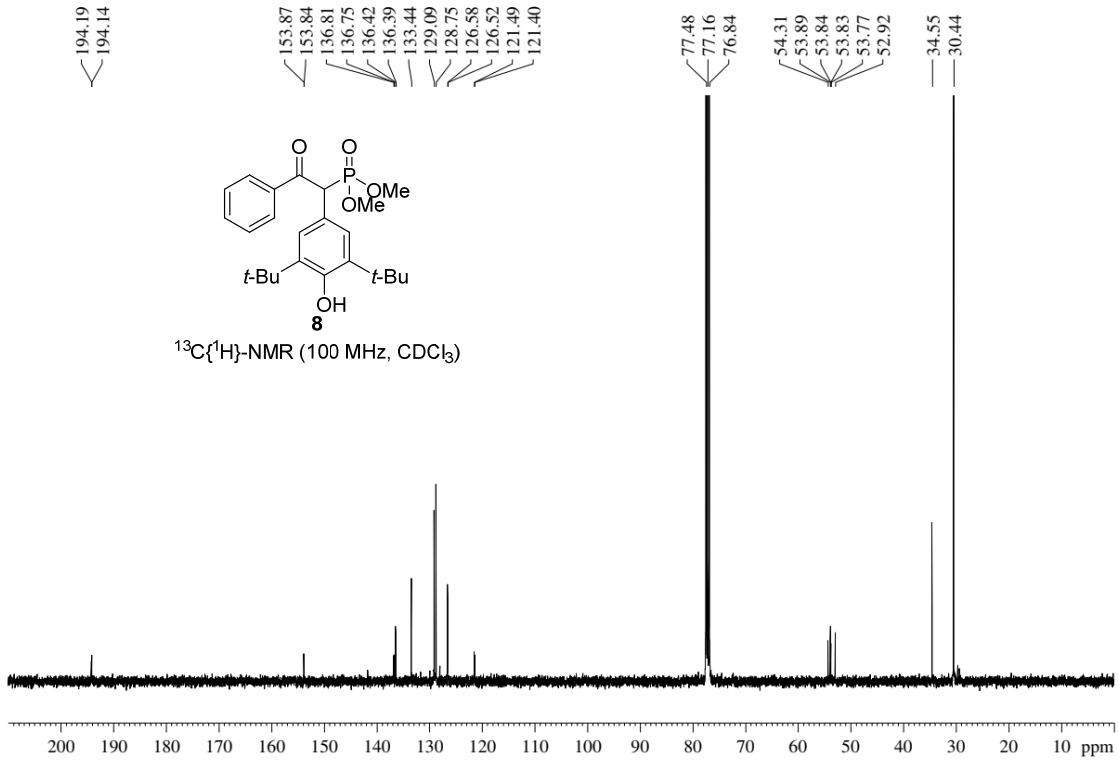


5e

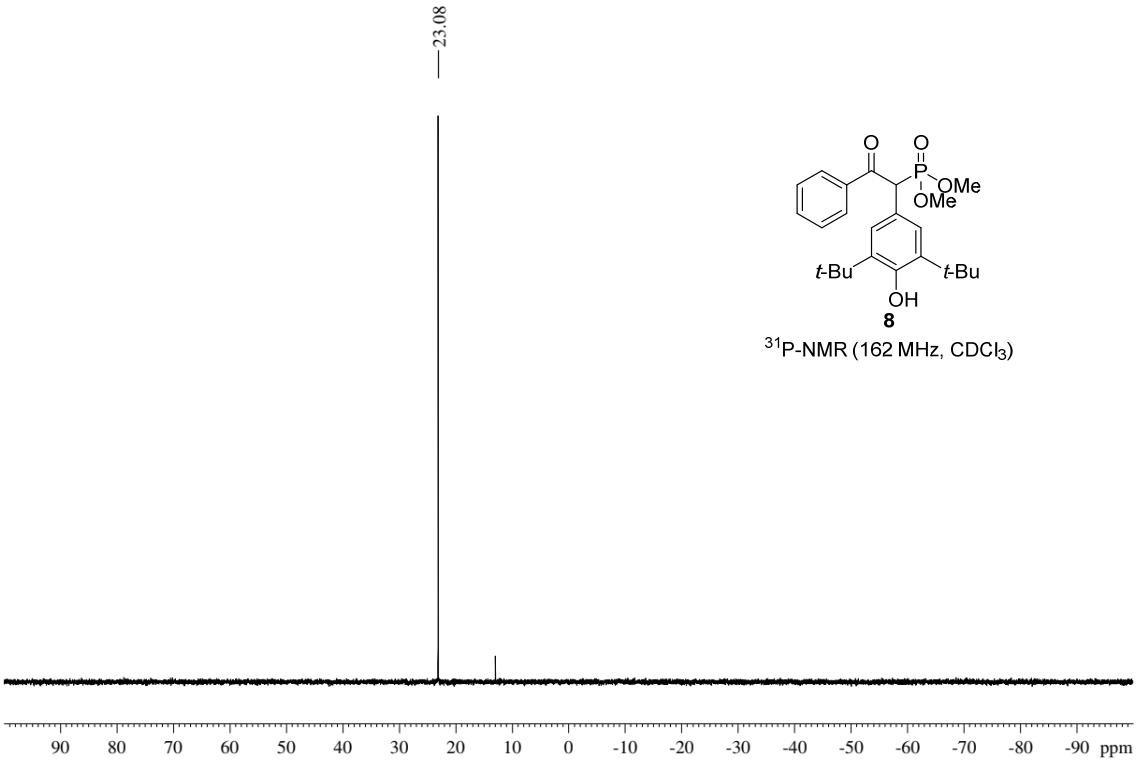
^{31}P-NMR (162 MHz, $CDCl_3$)



^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C{^{1}H}-NMR (100 MHz, $CDCl_3$)



8

^{31}P-NMR (162 MHz, $CDCl_3$)