Electronic Supplementary Material (ESI) for Chemical Communications.

Diastereoselective Additions of H-Phosphinates to Alkenyl Ketones Under Phase-Transfer Conditions

Krishna P. Yadavalli, Johannah E. Cummines, Chace J. Carlisle, and Salvatore D. Lepore*

Department of Chemistry and Biochemistry, Florida Atlantic University, Boca Raton, FL 33431-0991
Fax: +1(561)297-2759; Email: slepore@fau.edu

Table of Contents

1. General Information

Reactions were performed in oven-dried glassware with magnetic stirring under an argon atmosphere (unless otherwise stated). Column chromatographic purification of products was carried out using silica gel 60 (200-300 mesh). Visualization of TLC plates was accomplished with UV light (254 nm), followed by staining with vanillin and drying with a heat gun. The NMR spectra were recorded on a Bruker spectrometer using tetramethylsilane (TMS) in $CDCl_3$ as internal standard for ^{1}H and ^{13}C NMR (^{1}H NMR: TMS at 0.00 ppm, $CHCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.16 ppm) and 85% H_3PO_4 as standard for ^{31}P NMR. Data are represented as follows: chemical shift, multiplicity (s= singlet, d=doublet, t=triplet, m=multiple) coupling constant in Hertz (Hz). High-resolution mass spectra were recorded using electro spray ionization (ESI) analyzed in positive mode. All reagents were purchased from commercially available sources and were used without further purification. Solvents were purified and dried on a solvent system or purchased anhydrous where required.

2. Representative procedure for phosphinate addition reaction

In a scintillation vial (6 dram) containing adamantyl phosphinate (100 mg, 0.36 mmol, 1.0 equiv) in toluene (1.80 mL) was added the di-substituted alkenyl phenyl ketone (118 mg, 0.43 mmol, 1.2 equiv), 18-crown-6 (19 mg, 0.072 mmol, 0.2 equiv) and K_2CO_3 (0500 mg, 3.62 mmol, 10 equiv). The reaction was stirred at room temperature for 4 d. Following its completion, the reaction mixture was quenched by adding water (10 mL) and extracted with ethyl acetate (3 × 10 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo to yield crude product, which was purified by flash chromatography to remove the excess alkenyl phenyl ketone and obtain the desired product at 25-30% EtOAc in hexanes. All spectral data are reported for the isolated major diastereomer of purified products.

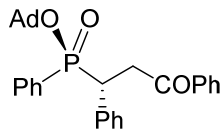
All the mono and disubstituted alkenyl phenyl ketones were synthesized according to literature reports.[1] Menthol phosphinate used for the synthesis of compound **5** was prepared and isolated as diastereopure material according to a reported procedure.[2]

[1] (a) Ding, B.; Zhang, Z.; Liu, Y.; Sugiya, M.; Imamoto, T.; Zhang, W., Chemoselective Transfer Hydrogenation of α,β-Unsaturated Ketones Catalyzed by Pincer-Pd Complexes Using Alcohol as a Hydrogen Source. *Org. Lett.* **2013,** *15*, 3690; (b) Tsuchiya, Y.; Hamashima, Y.; Sodeoka, M., A New Entry to Pd−H Chemistry: Catalytic Asymmetric Conjugate Reduction of Enones with EtOH and a Highly Enantioselective Synthesis of Warfarin. *Org. Lett.* **2006,** *8*, 4851; (c) Zhao, D.; Mao, L.; Wang, L.; Yang, D.; Wang, R., Catalytic asymmetric construction of tetrasubstituted carbon stereocenters by conjugate addition of dialkyl phosphine oxides to β,β-disubstituted α,β-unsaturated carbonyl compounds. *Chem. Commun.* **2012,** *48*, 889.

[2] Handoko; Benslimane, Z.; Arora, P. S., Diselenide-Mediated Catalytic Functionalization of Hydrophosphoryl Compounds. *Org. Lett.* **2020,** *22*, 5811.

3. Characterization data

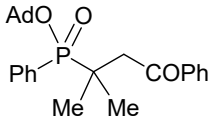
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-3-oxo-1,3-diphenylpropyl)(phenyl)phosphinate (**3a**)*
Yield: 126 mg, 72%; white solid (5:1 dr)
General procedure **A** was followed



3a

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.96 (m, 2H), 7.59 – 7.51 (m, 3H), 7.44 (ddd, *J* = 20.5, 7.6, 1.4 Hz, 3H), 7.31 (dd, *J* = 7.6, 3.4 Hz, 2H), 7.15 – 7.05 (m, 5H), 3.96 (ddd, *J* = 16.4, 9.3, 4.1 Hz, 1H), 3.88 – 3.74 (m, 2H), 2.10 (s, 3H), 2.01 (d, *J* = 2.3 Hz, 6H), 1.57 (t, *J* = 2.9 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 (d, *J* = 13.0 Hz), 136.9, 135.9 (d, *J* = 2.9 Hz), 133.2, 133.18, 131.9 (d, *J* = 9.3 Hz), 131.6 (d, *J* = 2.7 Hz), 129.5 (d, *J* = 6.2 Hz), 128.6, 128.2, 127.9 (d, *J* = 2.5 Hz), 127.8 (d, *J* = 12.6 Hz), 126.6(d, *J* = 3.1 Hz), 82.9 (d, *J* = 9.7 Hz), 44.5 (d, *J* = 3.8 Hz), 43.3 (d, *J* = 100.0 Hz), 37.8,35.7, 31.14. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.4. HRMS-ESI (m/z) calc for $C_{31}H_{33}O_3P$[M+ H] $^+$:485.2240 found 485.2250 and $C_{31}H_{33}O_3PNa^+$ [M+ Na] $^+$:507.2060 found 507.2070.

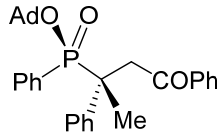
*(3s,5s,7s)-Adamantan-1-yl (2-methyl-4-oxo-4-phenylbutan-2-yl)(phenyl)phosphinate (**3b**)*
Yield: 127 mg, 85% gummy liquid
General procedure **A** was followed.



3b

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.4 Hz, 2H), 7.85 (dd, *J* = 9.4, 7.9 Hz, 2H), 7.58 – 7.53 (m, 2H), 7.50 (dd, *J* = 7.5, 3.1 Hz, 2H), 7.45 (t, *J* = 7.6 Hz, 2H), 3.19 (d, *J* = 7.9 Hz, 2H), 2.13 (s, 3H), 2.08 (s, 6H), 1.61 (s, 6H), 1.23 (dd, *J* = 30.9, 16.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.2 (d, *J* = 17.0 Hz), 138.4, 133.3 (d, *J* = 8.7 Hz), 132.9, 131.8 (d, *J* = 1.9 Hz), 130.6, 128.6, 128.3, 128.0 (d, *J* = 11.8 Hz), 82.6 (d, *J* = 10.1 Hz), 44.4(d, *J* = 3.4 Hz), 40.6, 36.8, 35.8, 31.2, 20.6 (d, *J* = 10.3 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 43.9. HRMS-ESI (m/z) calc for $C_{27}H_{33}O_3P$ [M+ H] $^+$:437.2240, found 437.2257 and $C_{27}H_{33}O_3PNa^+$ [M+ Na] $^+$:459.2060 found 459.2077.

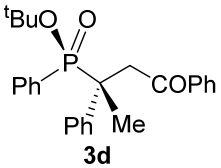
*(3S,5S,7S)-Adamantan-1-yl (R)-((R)-4-oxo-2,4-diphenylbutan-2-yl)(phenyl)phosphinate (**3c**)*
Yield: 126 mg, 70%; white solid (50:1 dr)
General procedure **A** was followed.



3c

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.86 (m, 2H), 7.58 – 7.52 (m, 1H), 7.50 – 7.41 (m, 3H), 7.35 – 7.23 (m, 4H), 7.14 (t, *J* = 2.1 Hz, 5H), 4.32 (dd, *J* = 18.1, 8.6 Hz, 1H), 3.56 (dd, *J* = 18.0, 5.4 Hz, 1H), 2.15 (s, 3H), 2.10 (s, 6H), 1.85 (d, *J* = 15.9 Hz, 3H), 1.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6 (d, *J* = 17.6 Hz), 138.8 (d, *J* = 4.1 Hz), 137.8 (d, *J* = 2.4 Hz), 133.2 (d, *J* = 8.6 Hz), 132.9, 131.6 (d, *J* = 2.7 Hz), 130.5 (d, *J* = 122.5 Hz), 128.5, 127.9 (d, *J* = 5.1 Hz), 127.8, 127.5 (d, *J* = 6.1 Hz), 127.4 (d, *J* = 2.8 Hz), 126.1 (d, *J* = 3.6 Hz), 83.1 (d, *J* = 10.4 Hz), 44.4 (d, *J* = 3.5 Hz), 43.5, 41.4, 35.8, 31.2, 19.4 (d, *J* = 4.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.8. HRMS-ESI (m/z) calc for $C_{32}H_{35}O_3P$ [M+ H] $^+$:499.2397, found 499.2400 and $C_{32}H_{35}O_3PNa^+$ [M+ Na] $^+$:521.2216 found 521.2230.

(*tert-Butyl (R)-((R)-4-oxo-2,4-diphenylbutan-2-yl) (phenyl)phosphinate (**3d**)*
Yield: 157 mg, 74%; gummy liquid (35:1 dr)
General procedure **A** was followed.

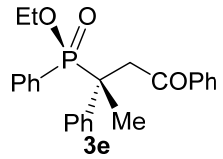


3d

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.44 (dtd, *J* = 4.4, 3.4, 1.5 Hz, 3H), 7.35 – 7.25 (m, 4H), 7.20 – 7.11 (m, 5H), 4.33 (dd, *J* = 18.1, 8.5 Hz, 1H), 3.54 (dd, *J* = 18.0, 5.4 Hz, 1H), 1.86 (d, *J* = 15.9 Hz, 3H), 1.50 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.5 (d, *J* = 17.5 Hz), 138.7 (d, *J* = 4.3 Hz), 137.7 (d, *J* = 2.4 Hz), 133.1 (d, *J* = 8.5 Hz), 132.9, 131.7 (d, *J* = 2.7 Hz), 130.3 (d, *J* = 122.6 Hz), 128.6, 127.9 (d, *J* = 5.2 Hz), 127.8 , 127.6, 127.5 (d, *J* = 2.0 Hz), 126.2 (d, *J* = 3.6 Hz), 83.5 (d, *J* = 9.9 Hz), 43.9 (d, *J* = 93.9 Hz), 41.4, 30.7 (d, *J* =

3.7 Hz), 19.3 (d, *J* = 4.1 Hz).[31]P NMR (162 MHz, $CDCl_3$) δ 40.8 HRMS-ESI (m/z) calc for $C_{26}H_{29}O_3P$ [M+ H] $^+$:421.1927 found 421.1915 and $C_{26}H_{29}O_3PNa^+$ [M+ Na] $^+$:443.1747 found 443.1728.

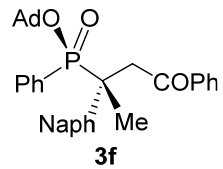
*(Ethyl (R)-((R)-4-oxo-2,4-diphenylbutan-2-yl) (phenyl)phosphinate (**3e**)*
Yield: 68 mg, 30%; white solid (3:1 dr) (inseparable diastereomers)
General procedure **A** was followed



3e

[1]H NMR (400 MHz, $CDCl_3$) δ 7.96-7.92 (m, 2H), 7.60 – 7.53 (m, 1H), 7.50 – 7.41 (m, 3H), 7.35 – 7.29 (m, 3H), 7.28 – 7.15 (m, 6H), 4.35 (dd, *J* = 18.0, 8.7 Hz, 1H), 4.24 – 4.16 (m, 1H), 4.02 – 3.95 (m, 1H), 3.61 (dd, *J* = 17.9, 5.3 Hz, 1H), 1.89 (d, *J* = 16.2 Hz, 3H), 1.40 (t, *J* = 7.0 Hz, 3H). [13]C NMR (101 MHz, $CDCl_3$) δ 196.3 (d, *J* = 17.0 Hz), 138.5 (d, *J* = 4.0 Hz), 137.6 (d, *J* = 2.3 Hz), 133.2 (d, *J* = 8.6 Hz), 133.0, 132.1(d, *J* = 2.7 Hz), 128.6, 128.5, 127.93, 127.9, 127.8(d, *J* = 4.9 Hz), 127.7(d, *J* = 3.1 Hz), 126.4 (d, *J* = 3.6 Hz), 61.6 (d, *J* = 7.3 Hz), 43.5 (d, *J* = 92.3 Hz), 41.4, 19.2 (d, *J* = 3.6 Hz), 16.5 (d, *J* = 6.1 Hz). [31]P NMR (162 MHz, $CDCl_3$) δ 46.2 HRMS-ESI (m/z) calc for $C_{24}H_{25}O_3P$ [M+ H] $^+$:393.1614, found 393.1614 and $C_{24}H_{25}O_3PNa^+$ [M+ Na] $^+$:415.1434 found 415.1415.

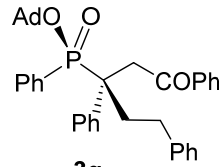
*(3S,5S,7S)-Adamantan-1-yl(R)-((R)-2-(naphthalen-1-yl)-4-oxo-4-phenylbutan-2-yl)(phenyl)phosphinate (**3f**)*
(E-chalcone) Yield: 158 mg, 80%; light yellow solid (single diastereomer).
(Z-chalcone) Yield: 135 mg, 68%; yellow solid (7:1 dr)
General procedure **A** was followed; reported data for E-chalcone ((2*E*)-1,3-diphenylprop-2-en-1-one) addition



3f

[1]H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.78 – 7.73 (m, 1H), 7.61 (dd, *J* = 12.1, 5.2 Hz, 2H), 7.58-7.52 (m, 2H), 7.41 (ddd, *J* = 16.0, 14.3, 8.3 Hz, 6H), 7.28 (t, *J* = 8.7 Hz, 2H), 7.20 (td, *J* = 7.6, 3.5 Hz, 2H), 4.43 (dd, *J* = 18.1, 8.6 Hz, 1H), 3.67 (dd, *J* = 18.0, 5.3 Hz, 1H), 2.16 (s, 3H), 2.12 (s, 6H), 1.97 (d, *J* = 15.8 Hz, 3H), 1.63 (s, 6H). [13]C NMR (101 MHz, $CDCl_3$) δ 196.5 (d, *J* = 17.5 Hz), 137.8, 136.5 (d, *J* = 4.3 Hz), 133.2 (d, *J* = 8.5 Hz), 132.95, 132.9,132.89, 131.9 (d, *J* = 2.6 Hz), 131.7 (d, *J* = 2.8 Hz), 130.4 (d, *J* = 122.6 Hz), 128.6, 128.1, 127.9, 127.4 (d, *J* = 12.1 Hz), 127.25, 127.2, 126.7, 126.1 (d, *J* = 3.5 Hz), 125.5 (d, *J* = 5.7 Hz), 83.2 (d, *J* = 10.4 Hz), 44.5 (d, *J* = 3.2 Hz), 43.7, 41.6, 35.8, 31.2, 19.6 (d, *J* = 3.7 Hz).[31]P NMR (162 MHz, $CDCl_3$) δ 40.7 HRMS-ESI (m/z) calc for $C_{36}H_{37}O_3P$ [M+ H] $^+$:549.2553, found 549.2552 and $C_{36}H_{37}O_3PNa^+$ [M+ Na] $^+$:571.2373 found 57Z1.2353.

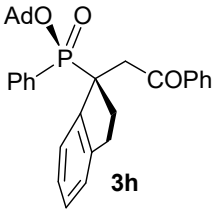
*(3S,5S,7S)-Adamantan-1-yl (R)-((R)-1-oxo-1,3,5-triphenylpentan-3-yl)(phenyl)phosphinate (**3g**)*
Yield: 75 mg, 47%; white solid (50:1 dr)
General procedure **A** was followed.



3g

[1]H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.00 (m, 2H), 7.60 (ddd, *J* = 6.7, 3.9, 1.2 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.46 – 7.39 (m, 1H), 7.34 – 7.18 (m, 9H), 7.15 – 7.03 (m, 5H), 4.13 (dd, *J* = 18.6, 9.7 Hz, 1H), 4.00 (dd, *J* = 18.7, 6.3 Hz, 1H), 3.37 – 3.26 (m, 1H), 2.91 – 2.78 (m, 2H), 2.66 – 2.54 (m, 1H), 2.15 (s, 3H), 2.11 (d, *J* = 2.5 Hz, 6H), 1.62 (s, 6H). [13]C NMR (101 MHz, $CDCl_3$) δ 196.7 (d, *J* = 17.7 Hz), 142.9, 139.7(d, *J* = 4.5 Hz), 137.6, 133.2, 133.1, 133.0, 131.6 (d, *J* = 16.9 Hz), 130.3, 128.6 (d, *J* = 4.9 Hz), 128.4, 128.1(d, *J* = 4.8 Hz), 127.9, 127.5, 127.3 (d, *J* = 2.8 Hz), 126.3 (d, *J* = 3.5 Hz), 125.8, 83.6 (d, *J* = 10.6 Hz), 47.4 (d, *J* = 92.4 Hz), 44.5 (d, *J* = 3.6 Hz), 36.3 (d, *J* = 32.2 Hz), 35.8, 35.4 (d, *J* = 3.4 Hz), 32.1, 31.2. [31]P NMR (162 MHz, $CDCl_3$) δ 41.0 HRMS-ESI (m/z) calc for $C_{39}H_{41}O_3P$ [M+ H] $^+$:589.2866 found 589.2844.

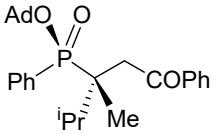
*(3S,5S,7S)-Adamantan-1-yl(R)-((R)-1-(2-oxo-2-phenylethyl)-2,3-dihydro-1H-inden-1-yl)(phenyl)phosphinate (**3h**)*
Yield: 19 mg, 30%; brown gummy liquid (11:1 dr)
General procedure **A** was followed on (0.12 mmol scale) at 35 °C for 4 d, purified by prep TLC after aqueous workup.



3h

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.3 Hz, 2H), 7.57 – 7.40 (m, 6H), 7.30 (dt, *J* = 10.6, 5.5 Hz, 2H), 7.17 (d, *J* = 6.8 Hz, 1H), 7.07 (p, *J* = 7.2 Hz, 2H), 6.97 (d, *J* = 7.0 Hz, 1H), 4.02 (dd, *J* = 17.1, 9.1 Hz, 1H), 3.72 (dd, *J* = 17.2, 6.1 Hz, 1H), 2.91 – 2.79 (m, 1H), 2.72 – 2.44 (m, 2H), 2.36 (dt, *J* = 16.3, 8.3 Hz, 1H), 2.16 (s, 3H), 2.13 (s, 6H), 1.63 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5 (d, *J* = 15.3 Hz), 145.4 (d, *J* = 6.8 Hz), 140.9, 138.1, 133.1 (d, *J* = 8.7 Hz), 132.8, 132.0, 131.7, 130.9, 128.2 (d, *J* = 47.8 Hz), 127.5 (d, *J* = 11.9 Hz), 127.1(d, *J* = 3.4 Hz), 125.6(d, *J* = 3.1 Hz), 125.1, 124.0, 83.1 (d, *J* = 10.2 Hz), 53.2 (d, *J* = 98.8 Hz), 44.5 (d, *J* = 3.6 Hz), 40.1, 35.8, 31.3, 31.0 , 30.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 40.0 HRMS-ESI (m/z) calc for $C_{33}H_{35}O_3P$ [M+ H] $^+$:511.2397 found 511.2398.

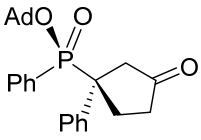
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-3,4-dimethyl-1-oxo-1-phenylpentan-3-yl)(phenyl)phosphinate (**3i**)*
Yield: 85 mg, 51%; gummy liquid (single diastereomer)
General procedure **A** was followed.



3i

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.84 (dd, *J* = 18.9, 10.4 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.50 – 7.41 (m, 4H), 3.41 (dd, *J* = 16.1, 11.0 Hz, 1H), 3.27 (dd, *J* = 16.0, 12.9 Hz, 1H), 2.23 – 2.13 (m, 1H), 2.07 (s, 3H), 1.98 (s, 6H), 1.55 (s, 6H), 1.36 (d, *J* = 16.6 Hz, 3H), 1.02 (dd, *J* = 6.9, 3.2 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.4 (d, *J* = 11.5 Hz), 138.6, 133.7 (d, *J* = 69.0 Hz), 133.2 (d, *J* = 9.0 Hz), 132.7, 131.6 (d, *J* = 2.6 Hz), 128.4 (d, *J* = 21.7 Hz), 128.1, 127.9 (d, *J* = 11.8 Hz), 83.1(d, *J* = 10.4 Hz), 44.4 (d, *J* = 3.3 Hz), 43.8 (d, *J* = 98.1 Hz), 38.6, 35.8, 31.5, 31.2, 19.0 (d, *J* = 2.1 Hz), 18.9.^{31}P NMR (162 MHz, $CDCl_3$) δ 43.9 HRMS-ESI (m/z) calc for $C_{29}H_{37}O_3P$ [M+ H] $^+$:465.2553, found 465.2548 and $C_{29}H_{37}O_3PNa^+$ [M+ Na] $^+$:487.2373 found 487.2350.

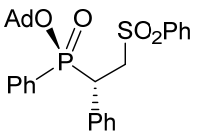
*(3S,5S,7S)-Adamantan-1-yl (R)-((R)-3-oxo-1-phenylcyclopentyl)(phenyl)phosphinate (**3j**)*
Yield:72 mg, 46%; white solid (1:1 dr) (Inseparable diastereomers)
General procedure **A** was followed.



3j

^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.50 – 7.41 (m, 1H), 7.32 – 7.24 (m, 4H), 7.24 – 7.14 (m, 3H), 7.05 – 6.95 (m, 2H), 3.29 – 3.15 (m, 1H), 3.14 – 2.92 (m, 1H), 2.81 – 2.56 (m, 2H), 2.47 – 2.21 (m, 2H), 2.11 (s, 3H), 2.02 (s, 6H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 216.1, 140.1, 132.8(d, *J* = 8.7 Hz), 131.9, 130.5 (d, *J* = 124.0 Hz), 128.6 (d, *J* = 4.2 Hz), 127.7 (d, *J* = 2.2 Hz), 127.6 (d, *J* = 3.7 Hz), 126.9 (d, *J* = 3.2 Hz), 84.0 (d, *J* = 9.9 Hz), 50.3 (d, *J* = 97.2 Hz), 46.2, 44.3 (d, *J* = 3.6 Hz), 36.7, 35.7, 31.2, 30.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 39.3 HRMS-ESI (m/z) calc for $C_{27}H_{31}O_3P$ [M+ H] $^+$:435.2084, found 435.2072 and $C_{27}H_{31}O_3PNa^+$ [M+ Na] $^+$:457.1894 found 457.1903.

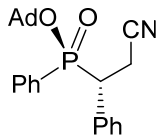
*(3R,5R,7R)-Adamantan-1-yl(S)-phenyl((S)-1-phenyl-2-(phenylsulfonyl)ethyl)phosphinate (**3k**)*
Yield: 112 mg, 59%; white solid (2:1 dr)
General procedure **A** was followed.



3k

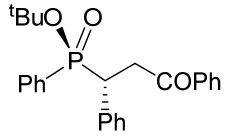
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.43 – 7.36 (m, 4H), 7.23 (ddd, *J* = 12.5, 7.9, 5.5 Hz, 4H), 6.95 – 6.90 (m, 1H), 6.84 (t, *J* = 7.7 Hz, 2H), 6.76 (dd, *J* = 7.4, 1.7 Hz, 2H), 3.99 (ddd, *J* = 8.0, 6.4, 4.1 Hz, 2H), 3.65 (ddd, *J* = 17.6, 10.7, 3.6 Hz, 1H), 2.13 (s, 3H), 2.03 (s, 6H), 1.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.8, 133.0, 132.1, 131.9 (d, *J* = 2.8 Hz), 131.8 (d, *J* = 9.5 Hz), 130.8, 129.5 (d, *J* = 6.0 Hz), 128.7, 128.0, 127.9 (d, *J* = 1.8 Hz), 127.7, 127.0 (d, *J* = 3.3 Hz), 84.0 (d, *J* = 9.7 Hz), 55.4 (d, *J* = 1.4 Hz), 44.5 (d, *J* = 3.8 Hz), 44.2, 35.6, 31.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 35.5 HRMS-ESI (m/z) calc for $C_{30}H_{33}NO_4PS$ [M+ H] $^+$:521.1915, found 521.1915 and $C_{30}H_{33}NO_4PS$ Na^+ [M+ Na] $^+$:543.1729 found 543.1729.

*(3R,5R,7R)-Adamantan-1-yl(S)-((R)-2-cyano-1-phenylethyl) (phenyl)phosphinate (**3l**)*
Yield: 69 mg, 47% white solid (4:1 dr)
General procedure **A** was followed.


3l

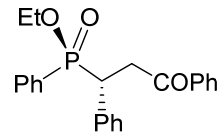
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.40 (m, 3H), 7.34 – 7.27 (m, 2H), 7.16 (dd, *J* = 3.6, 3.0 Hz, 3H), 7.08 – 7.03 (m, 2H), 3.37 (ddd, *J* = 15.8, 10.6, 5.0 Hz, 1H), 3.26 (ddd, *J* = 17.1, 7.8, 5.0 Hz, 1H), 3.02 (dt, *J* = 17.1, 10.4 Hz, 1H), 2.13 (s, 3H), 2.05 (s, 6H), 1.59 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.3 (d, *J* = 3.0 Hz), 132.2 (d, *J* = 2.8 Hz), 131.8, 130.6, 128.9 (d, *J* = 5.8 Hz), 128.5 (d, *J* = 2.3 Hz), 128.1 (d, *J* = 12.9 Hz), 127.7 (d, *J* = 3.0 Hz), 118.1(d, *J* = 17.3 Hz), 84.2 (d, *J* = 9.5 Hz), 44.7, 44.4 (d, *J* = 3.8 Hz), , 35.6, 31.2, 18.3.^{31}P NMR (162 MHz, $CDCl_3$) δ 35.2 HRMS-ESI (m/z) calc for $C_{25}H_{28}NO_2P$ [M+ H] $^+$:406.1930, found 406.1938 and $C_{25}H_{28}NO_2PNa^+$ [M+ Na] $^+$:428.1750 found 428.1767.

*tert-Butyl (S)-((R)-3-oxo-1,3-diphenylpropyl)(phenyl)phosphinate (**3m**)*
Yield:143 mg, 70% white solid (5:1 dr)
General procedure **A** was followed.


3m

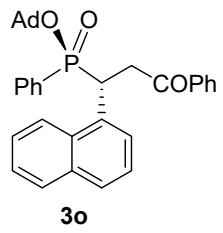
^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.99 – 7.95 (m, 2H), 7.58 – 7.49 (m, 3H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.42 – 7.37 (m, 1H), 7.31 – 7.28 (m, 2H), 7.12 – 7.04 (m, 5H), 3.96 (ddd, *J* = 16.5, 9.2, 4.1 Hz, 1H), 3.87 – 3.70 (m, 2H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.1 (d, *J* = 12.7 Hz), 136.8, 135.9, 133.2, 132.9, 131.9 (d, *J* = 9.3 Hz), 131.6, 129.5 (d, *J* = 6.1 Hz), 128.6, 128.1, 127.9 (d, *J* = 2.7 Hz), 127.8, 126.7 (d, *J* = 3.1 Hz), 83.3 (d, *J* = 9.3 Hz), 43.2 (d, *J* = 100.1 Hz), 37.8, 30.8 (d, *J* = 3.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.4 HRMS-ESI (m/z) calc for $C_{25}H_{27}O_3PNa^+$ [M+ Na] $^+$:429.1590 found 429.1604.

*Ethyl (S)-((R)-3-oxo-1,3-diphenylpropyl)(phenyl)phosphinate (**3n**)*
Yield:166 mg, 75**%;** white solid (3:1 dr) (Inseparable diastereomers)
General procedure **A** was followed.


3n

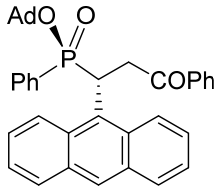
^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 7.99 (d, *J* = 7.5 Hz, 2H),7.66 (dd, *J* = 10.5, 8.1 Hz, 1H), 7.60 – 7.50 (m, 3H), 7.44 (dt, *J* = 19.7, 7.6 Hz, 3H), 7.38 – 7.33 (m, 2H), 7.30 – 7.20 (m, 1H), 7.16 (s, 1H), 7.11 (d, *J* = 7.1 Hz, 2H), 4.20 – 4.05 (m, 2H), 3.99 – 3.78 (m, 3H), 1.29 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8 (d, *J* = 12.9 Hz), 136.7, 135.5 (d, *J* = 3.3 Hz), 133.2, 132.2 (d, *J* = 3.1 Hz), 132.1 (d, *J* = 3.5 Hz), 129.7, 129.4 (d, *J* = 6.2 Hz), 128.6, 128.2 (d, *J* = 2.5 Hz), 128.1, 128.0, 126.9 (d, *J* = 3.2 Hz), 61.2 (d, *J* = 6.8 Hz), 42.1 (d, *J* = 98.2 Hz), 37.8 (d, *J* = 1.8 Hz), 16.4 (d, *J* = 6.3 Hz).^{31}P NMR (162 MHz, $CDCl_3$) δ 43.7 HRMS-ESI (m/z) calc for $C_{23}H_{23}O_3P$ [M+ H] $^+$:379.1458 found 379.1453 and $C_{23}H_{23}O_3P$ Na^+ [M+ Na] $^+$:401.1277 found 401.1259.

*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-1-(naphthalen-1-yl)-3-oxo-3-phenylpropyl) (phenyl)phosphinate (**3o**)*
Yield: 141 mg, 73%; white solid (10:1 dr)
General procedure **A** was followed.


3o

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.0 Hz, 1H), 8.01 – 7.97 (m, 2H), 7.69 – 7.64 (m, 2H), 7.60 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.53 (m, 1H), 7.45 (t, *J* = 7.9 Hz, 4H), 7.34 (t, *J* = 7.3 Hz, 3H), 7.21 (t, *J* = 6.9 Hz, 1H), 7.10 (td, *J* = 7.5, 3.5 Hz, 2H), 4.98 (ddd, *J* = 17.5, 8.8, 4.2 Hz, 1H), 4.08 (ddd, *J* = 17.6, 11.1, 4.2 Hz, 1H), 3.85 (dt, *J* = 17.7, 8.8 Hz, 1H), 2.09 (s, 3H), 2.00 (s, 6H), 1.56 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 (d, *J* = 11.9 Hz), 136.8, 133.5, 133.1, 133.0, 132.2 (d, *J* = 6.7 Hz), 131.9 (d, *J* = 9.4 Hz), 131.7, 131.4 (d, *J* = 2.8 Hz), 128.6, 128.3, 128.2, 127.5 (d, *J* = 12.5 Hz),127.4, 126.3 (d, *J* = 5.9 Hz), 125.3, 125.1, 124.9 (d, *J* = 3.6 Hz), 123.6, 83.1 (d, *J* = 9.8 Hz), 44.4 (d, *J* = 3.8 Hz), 39.3, 36.7 (d, *J* = 100.5 Hz), 35.7, 31.1.^{31}P NMR (162 MHz, $CDCl_3$) δ 38.7 HRMS-ESI (m/z) calc for $C_{35}H_{35}O_3P$ [M+ H] $^+$:535.2397 found 535.2414 and $C_{35}H_{35}O_3P$ Na^+ [M+ Na] $^+$:557.2216 found 557.2232.

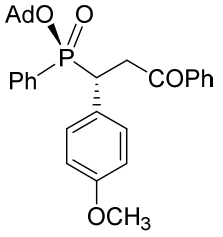
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-1-(anthracen-9-yl)-3-oxo-3-phenylpropyl)(phenyl)phosphinate (**3p**)*
Yield: 137 mg, 65%; yellow solid (6:1 dr)
General procedure **A** was followed.



3p

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (d, *J* = 9.0 Hz, 1H), 8.46 (d, *J* = 9.1 Hz, 1H), 8.19 (d, *J* = 2.6 Hz, 1H), 7.99 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.67 – 7.58 (m, 1H), 7.58 – 7.50 (m, 1H), 7.50 – 7.30 (m, 7H), 7.03 (td, *J* = 7.4, 1.3 Hz, 1H), 6.88 (td, *J* = 7.7, 3.5 Hz, 2H), 5.96 (dt, *J* = 22.6, 5.2 Hz, 1H), 4.62 (ddd, *J* = 18.4, 15.6, 4.6 Hz, 1H), 3.98 (ddd, *J* = 18.3, 9.2, 5.8 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 6H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2 (d, *J* = 7.8 Hz), 136.7, 133.1, 131.9, 131.7 (d, *J* = 3.7 Hz), 131.3 (d, *J* = 9.7 Hz), 131.2 (d, *J* = 2.8 Hz), 131.0 (d, *J* = 8.9 Hz), 130.5 (d, *J* = 4.8 Hz), 130.1 (d, *J* = 1.9 Hz), 128.9 (d, *J* = 3.0 Hz), 128.4 (d, *J* = 36.8 Hz), 127.72, 127.2 (d, *J* = 12.7 Hz), 125.5 (d, *J* = 52.1 Hz), 124.7, 124.4, 83.0 (d, *J* = 9.6 Hz), 44.5 (d, *J* = 3.8 Hz), 39.8 (d, *J* = 2.7 Hz), 36.7 (d, *J* = 99.7 Hz), 35.8, 31.2.^{31}P NMR (162 MHz, $CDCl_3$) δ 40.4 HRMS-ESI (m/z) calc for $C_{39}H_{37}O_3P$ [M+ H] $^+$:585.2553 found 585.2547 and $C_{35}H_{37}O_3P$ Na^+ [M+ Na] $^+$:607.2373 found 607.2387.

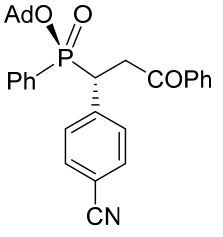
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)(phenyl)phosphinate (**3q**)*
Yield: 109 mg, 59%; gummy liquid (3:1 dr) (Inseparable diastereomers)
General procedure **A** was followed.



3q

^{1}H NMR (400 MHz, $CDCl_3$) major diastereomer δ 8.00 – 7.97 (m, 2H), 7.58 (s, 1H), 7.57 – 7.53 (m, 2H), 7.49 – 7.40 (m, 4H), 7.35 – 7.31 (m, 1H), 7.04 (dd, *J* = 8.8, 2.3 Hz, 2H), 6.63 (d, *J* = 8.4 Hz, 2H), 3.90 (ddd, *J* = 16.1, 9.5, 3.9 Hz, 1H), 3.86 – 3.80 (m, 1H), 3.78 (t, *J* = 2.0 Hz, 1H), 3.69 (s, 3H), 2.09 (s, 3H), 2.01 (s, 6H), 1.56 (t, *J* = 2.9 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.3 (d, *J* = 13.2 Hz), 158.3 (d, *J* = 2.9 Hz), 136.9, 133.1, 131.9 (d, *J* = 9.3 Hz), 131.6 (d, *J* = 2.5 Hz), 130.5 (d, *J* = 6.2 Hz), 128.6, 128.5, 128.2, 127.9 (d, *J* = 11.8 Hz), 127.8, 113.5, 82.8 (d, *J* = 10.0 Hz), 55.0, 44.5 (d, *J* = 3.7 Hz), 42.4 (d, *J* = 101.2 Hz), 37.9, 35.7, 31.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.5 HRMS-ESI (m/z) calc for $C_{32}H_{35}O_4P$ [M+ H] $^+$:515.2346 found 515.2335 and $C_{32}H_{35}O_4P$ Na^+ [M+ Na] $^+$:537.2165 found 537.2139.

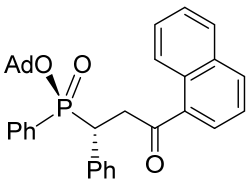
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-1-(4-cyanophenyl)-3-oxo-3-phenylpropyl)(phenyl)phosphinate (**3r**)*
Yield: 112 mg, 61% gummy liquid (2:1 dr)
General procedure **A** was followed.



3r

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.4, 1.3 Hz, 2H), 7.63 – 7.58 (m, 1H), 7.56 – 7.44 (m, 5H), 7.40 – 7.31 (m, 4H), 7.24 (dd, *J* = 8.4, 2.1 Hz, 2H), 3.98 (ddd, *J* = 16.3, 9.5, 4.1 Hz, 1H), 3.88 – 3.79 (m, 2H), 2.12 (s, 3H), 2.02 (s, 6H), 1.58 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6 (d, *J* = 13.1 Hz), 142.06 (d, *J* = 2.7 Hz), 136.5, 133.5, 132.7 (d, *J* = 25.7 Hz), 132.1 (d, *J* = 3.0 Hz), 131.8, 131.7 (d, *J* = 2.6 Hz), 130.2 (d, *J* = 6.0 Hz), 128.7, 128.5 (d, *J* = 12.6 Hz), 128.1, 118.8 (d, *J* = 2.0 Hz), 110.5 (d, *J* = 3.4 Hz), 83.8 (d, *J* = 9.6 Hz), 44.5 (d, *J* = 3.8 Hz), 43.4 (d, *J* = 4.5 Hz), 37.6 (d, *J* = 2.3 Hz), 35.6, 31.2. ^{31}P NMR (162 MHz, $CDCl_3$) δ 36.7 HRMS-ESI (m/z) calc for $C_{32}H_{32}NO_3P$ [M+ H] $^+$:510.2193 found 510.2181 and $C_{32}H_{32}NO_3PNa^+$ [M+ Na] $^+$:532.2012 found 532.2013.

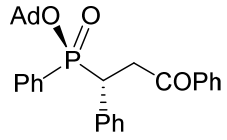
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-3-(naphthalen-1-yl)-3-oxo-1-phenylpropyl)(phenyl)phosphinate (**3s**)*
Yield:140 mg, 73% white solid, 5:1 dr)
General procedure **A** was followed.



3s

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H), 8.04 – 8.00 (m, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.65 – 7.54 (m, 4H), 7.46 – 7.40 (m, 1H), 7.35 – 7.31 (m, 2H), 7.19 – 7.14 (m, 2H), 7.08 (ddd, *J* = 10.7, 3.1, 1.8 Hz, 3H), 4.07 – 4.00 (m, 1H), 3.97 (dt, *J* = 7.5, 4.4 Hz, 2H), 2.10 (s, 3H), 2.04 (s, 6H), 1.57 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.4 (d, *J* = 13.1 Hz), 135.9 (d, *J* = 2.7 Hz), 135.6, 134.2, 133.2, 132.5, 132.0, 131.97,131.92, 131.6 (d, *J* = 2.8 Hz), 129.8 (d, *J* = 36.4 Hz), 129.5 (d, *J* = 6.2 Hz), 128.5 (d, *J* = 12.2 Hz), 128.0 (d, *J* = 2.5 Hz), 127.9, 127.8 (d, *J* = 5.2 Hz), 126.8, 126.7 (d, *J* = 3.2 Hz), 123.9, 83.0 (d, *J* = 9.8 Hz), 44.5 (d, *J* = 3.8 Hz), 43.4 (d, *J* = 100.2 Hz), 37.9 (d, *J* = 2.1 Hz), 35.7, 31.1 (d, *J* = 7.1 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.6 HRMS-ESI (m/z) calc for $C_{35}H_{35}O_3P$ [M+ H] $^{+}$:535.2397 found 535.2395 and $C_{35}H_{35}O_3P$ Na^{+} [M+ Na] $^{+}$:557.2216 found 557.2200.

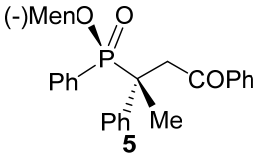
*(3R,5R,7R)-Adamantan-1-yl (S)-((R)-3-oxo-1-phenylbutyl)(phenyl)phosphinate (**3t**)*
Yield:78 mg, 51%; gummy liquid (5:1 dr)
General procedure **A** was followed.



3t

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.44 – 7.37 (m, 1H), 7.28 (td, *J* = 7.8, 3.4 Hz, 2H), 7.09 (dd, *J* = 5.2, 1.4 Hz, 3H), 7.03 (dd, *J* = 7.1, 2.4 Hz, 2H), 3.73 (ddd, *J* = 17.3, 9.8, 4.2 Hz, 1H), 3.29 (ddd, *J* = 17.3, 10.4, 4.2 Hz, 1H), 3.23 – 3.09 (m, 1H), 2.10 (s, 6H), 2.01 (s, 6H), 1.58 (s, 6H.^{13}C NMR (101 MHz, $CDCl_3$) δ 205.7 (d, *J* = 13.0 Hz), 135.6 (d, *J* = 3.2 Hz), 132.8, 131.9(d, *J* = 9.4 Hz), 131.7 (d, *J* = 2.8 Hz), 129.3 (d, *J* = 6.0 Hz), 128.0 (d, *J* = 2.6 Hz), 127.8 (d, *J* = 12.6 Hz), 126.7 (d, *J* = 3.2 Hz), 83.1 (d, *J* = 9.8 Hz), 44.5 (d, *J* = 3.7 Hz), 43.4 (d, *J* = 99.6 Hz), 42.5 (d, *J* = 2.1 Hz), 35.7, 31.1, 30.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 38.0 HRMS-ESI (m/z) calc for $C_{26}H_{31}O_3P$ [M+ H] $^{+}$:423.2084 found 423.2097 and $C_{26}H_{31}O_3P$ Na^{+} [M+ Na] $^{+}$:445.1903 found 445.1922.

*(1S,2R,5S)-2-Isopropyl-5-methylcyclohexyl ((R)-4-oxo-2,4-diphenylbutan-2-yl)(phenyl)phosphinate (**5**)*
Yield: 114 mg, 64%; gummy liquid (8:1 dr)
General procedure **A** was followed using **4.**



5

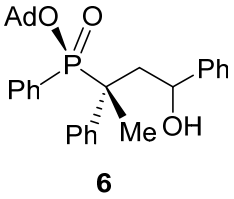
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.85 (m, 2H), 7.56 (ddd, *J* = 6.8, 4.0, 1.2 Hz, 1H), 7.48 – 7.39 (m, 3H), 7.33 – 7.29 (m, 1H), 7.27 (d, *J* = 1.8 Hz, 1H), 7.26 – 7.21 (m, 2H), 7.20 – 7.15 (m, 2H), 7.13 (dd, *J* = 4.6, 2.3 Hz, 3H), 4.57 – 4.36 (m, 2H), 3.56 (dd, *J* = 18.1, 5.0 Hz, 1H), 2.55 – 2.40 (m, 1H), 1.86 (d, *J* = 16.0 Hz, 4H), 1.78 – 1.70 (m, 1H), 1.70 – 1.61 (m, 1H), 1.54 (dd, *J* = 15.3, 7.6 Hz, 1H), 1.42 – 1.30 (m, 1H), 1.15 – 1.06 (m, 1H), 1.02 (dd, *J* = 7.0, 3.1 Hz, 6H), 0.97 – 0.78 (m, 2H), 0.75 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.2 (d, *J* = 17.1 Hz), 138.6 (d, *J* = 3.6 Hz), 137.6 (d, *J* = 2.4 Hz), 133.2 (d, *J* = 8.5 Hz), 133.0, 131.7 (d, *J* = 2.8 Hz), 129.5 (d, *J* = 122.0 Hz), 128.5, 127.85 , 127.8, 127.6 (d, *J* = 3.1 Hz), 127.3 (d, *J* = 12.1 Hz), 126.3 (d, *J* = 3.6 Hz), 49.0 (d, *J* = 6.0 Hz), 44.1 (d, *J* = 92.0 Hz), 43.3, 41.4, 34.0, 31.5, 25.7, 22.6, 21.9, 21.3, 19.2(d, *J* = 3.8 Hz), 15.6.^{31}P NMR (162 MHz, $CDCl_3$) δ 43.2 HRMS-ESI (m/z) calc for $C_{32}H_{39}O_3P$ [M+ H] $^{+}$:503.2710 found 503.2700 and $C_{32}H_{39}O_3P$ Na^{+} [M+ Na] $^{+}$:525.2529

Procedure for 6

In a flame dried reaction vial under argon, to compound **3c** (0.140 g, 0.28 mmol, 1.0 equiv) dissolved in methanol (1.40 mL) was added sodium borohydride (0.106 g, 2.81 mmol, 10.0 equiv) followed by stirring at room temperature

for 5 days. Solvents were evaporated, crude was diluted with EtOAc (10 mL) and water (5 mL). Separated organic layer was dried over Na_2SO_4 , solvents were removed under vacuum, residue was purified using column chromatography and the pure diastereomer (petroleum ether/EtOAc=1:1) was isolated as a white solid.

*(3S,5S,7S)-Adamantan-1-yl (R)-((2R,4R)-4-hydroxy-2,4-diphenylbutan-2-yl)(phenyl)phosphinate (**6**)*
Yield: 39 mg, 80 % white solid (4:1 dr)



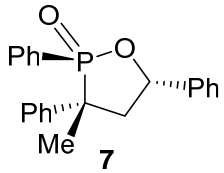
6

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.46 (m, 2H), 7.44 – 7.32 (m, 5H), 7.30 (d, *J* = 2.2 Hz, 3H), 7.27 – 7.20 (m, 5H), 4.84 (d, *J* = 8.4 Hz, 1H), 3.27 (d, *J* = 2.1 Hz, 1H), 2.90 (dt, *J* = 14.9, 8.9 Hz, 1H), 2.28 – 2.17 (m, 1H), 2.14 (s, 3H), 2.08 (s, 6H), 1.61 (s, 6H), 1.54 (d, *J* = 15.4 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.3, 138.8, 133.1 (d, *J* = 8.7 Hz), 131.6, 130.4, 128.7 (d, *J* = 5.6 Hz), 128.4, 127.9 (d, *J* = 2.1 Hz), 127.5, 127.3 (d, *J* = 7.8 Hz), 126.8 (d, *J* = 2.7 Hz), 126.1 83.5 (d, *J* = 10.3 Hz), 71.2 (d, *J* = 10.2 Hz), 45.7, 45.3, 44.4 (d, *J* = 3.5 Hz), 35.8, 31.2, 20.8. ^{31}P NMR (162 MHz, $CDCl_3$) δ 42.2 HRMS-ESI (m/z) calc for $C_{32}H_{37}O_3P$ [M+ H] $^+$:501.2553 found 501.2556 and $C_{32}H_{37}O_3P$ Na^+ [M+ Na] $^+$:523.2373 found 523.2354.

Procedure for 7

In a flame dried reaction vial under argon, compound **5** (0.075 g, 0.15 mmol, 1.0 equiv) was dissolved in 1,4-dioxane (1.50 mL); to it was added camphor sulfonic acid (0.035 g, 0.15 mmol, 1.0 equiv). The reaction was stirred at 70 °C for 4 days. The reaction mixture was diluted with EtOAc (15 mL) and washed the organic layer with Saturated $NaHCO_3$ (2 X 5 mL). The organic layer was dried over Na_2SO_4, and solvents were evaporated under vacuum. The crude was purified using column chromatography (petroleum ether/EtOAc=2:1) and further purified by prep TLC using 5% methanol/CH_2Cl_2 to obtain the pure cyclized product as white solids.

*(2R,3R,5S)-3-Methyl-2,3,5-triphenyl-1,2-oxaphospholane 2-oxide (**7**)*
Yield: 25 mg, 49%; white solid

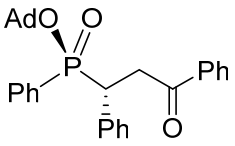


7

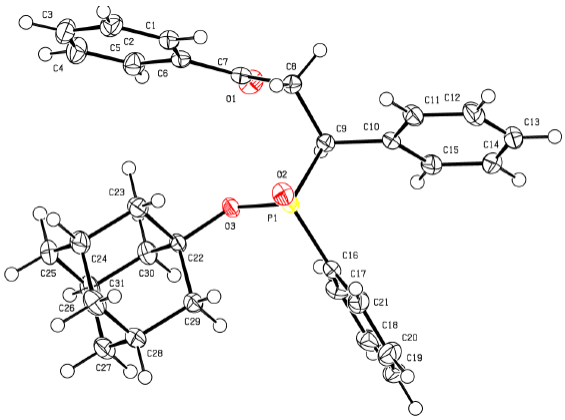
^{1}H NMR (400 MHz, $CDCl_3$) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 6H), 7.45 – 7.39 (m, 1H), 7.37 – 7.31 (m, 1H), 7.25 – 7.18 (m, 4H), 7.14 (t, *J* = 7.7 Hz, 2H), 7.09 – 7.04 (m, 1H), 5.97 (dd, *J* = 11.4, 4.1 Hz, 1H), 2.96 (t, *J* = 12.2 Hz, 1H), 2.74 (ddd, *J* = 28.0, 13.1, 4.2 Hz, 1H), 1.99 (d, *J* = 13.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 139.5 (d, *J* = 7.5 Hz), 132.5 (d, *J* = 9.8 Hz), 132.1 (d, *J* = 2.8 Hz), 130.1, 128.9, 128.4 (d, *J* = 1.5 Hz), 128.3, 127.9 (d, *J* = 13.0 Hz), 126.7, 126.1 (d, *J* = 6.4 Hz), 125.2, 78.8 (d, *J* = 4.0 Hz), 46.2 (d, *J* = 78.7 Hz), 44.4 (d, *J* = 6.2 Hz), 24.8 (d, *J* = 3.8 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 60.0 HRMS-ESI (m/z) calc for $C_{22}H_{21}O_2P$ [M+ H] $^+$:349.1352 found 349.1340 and $C_{22}H_{21}O_2P$ Na^+ [M+ Na] $^+$:371.1171 found 371.1155.

4. X-Ray Crystallographic data for **3a**

General procedure for crystal culture of **3a**: In a small test tube **3a** (10 mg) was dissolved in dichloromethane (0.5 mL). This solution was placed in a jar filled with n-hexane (5.0 mL); the jar was then capped. This vial-within-jar set up was stored in a dry and ventilated place for three days to allow for crystal growth. One of the crystals produced was placed onto the tip of a MiTeGen loop and mounted on a Bruker Venture D8 diffractometer equipped with a Photon III detector at 123 (2) K for analysis.

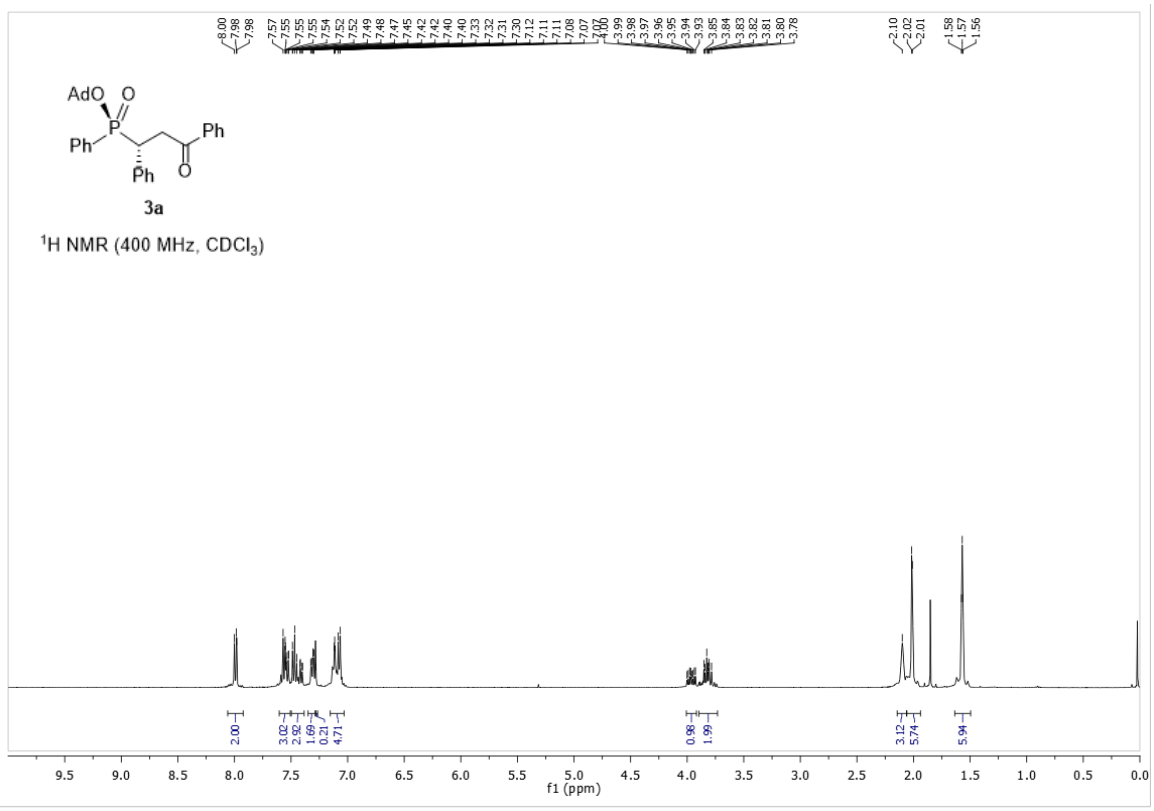


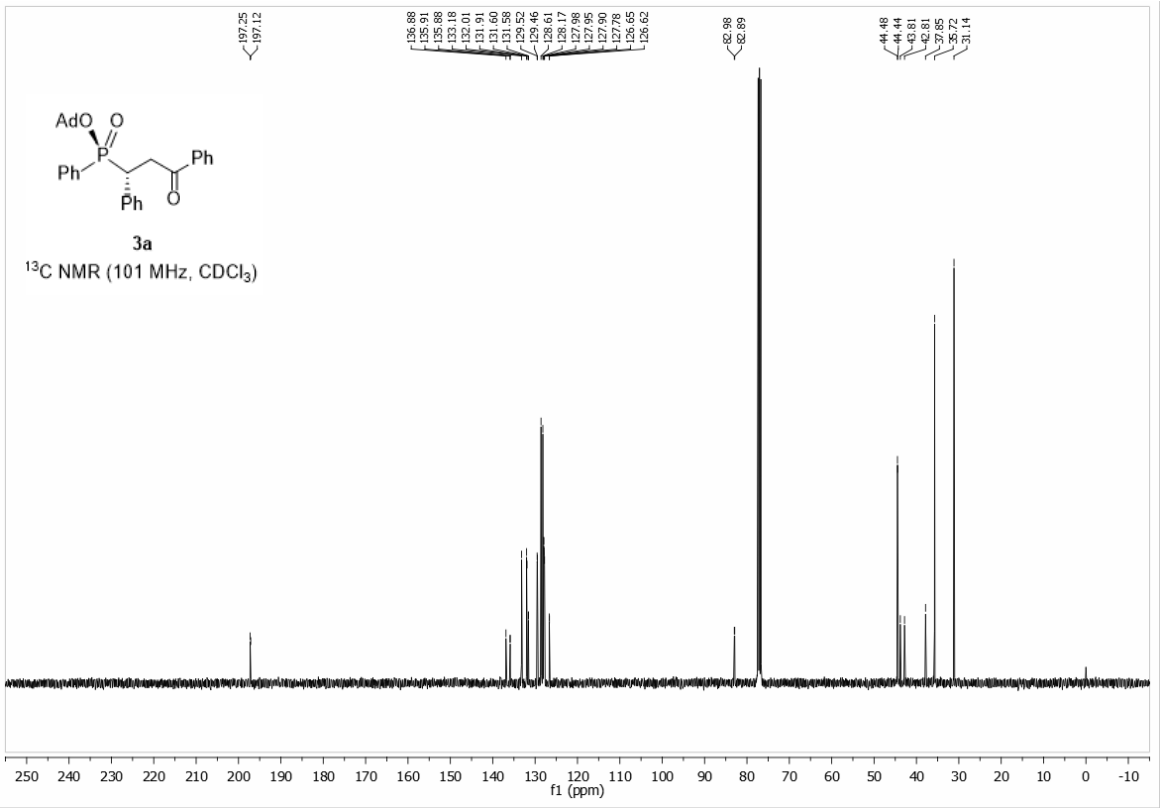
3a

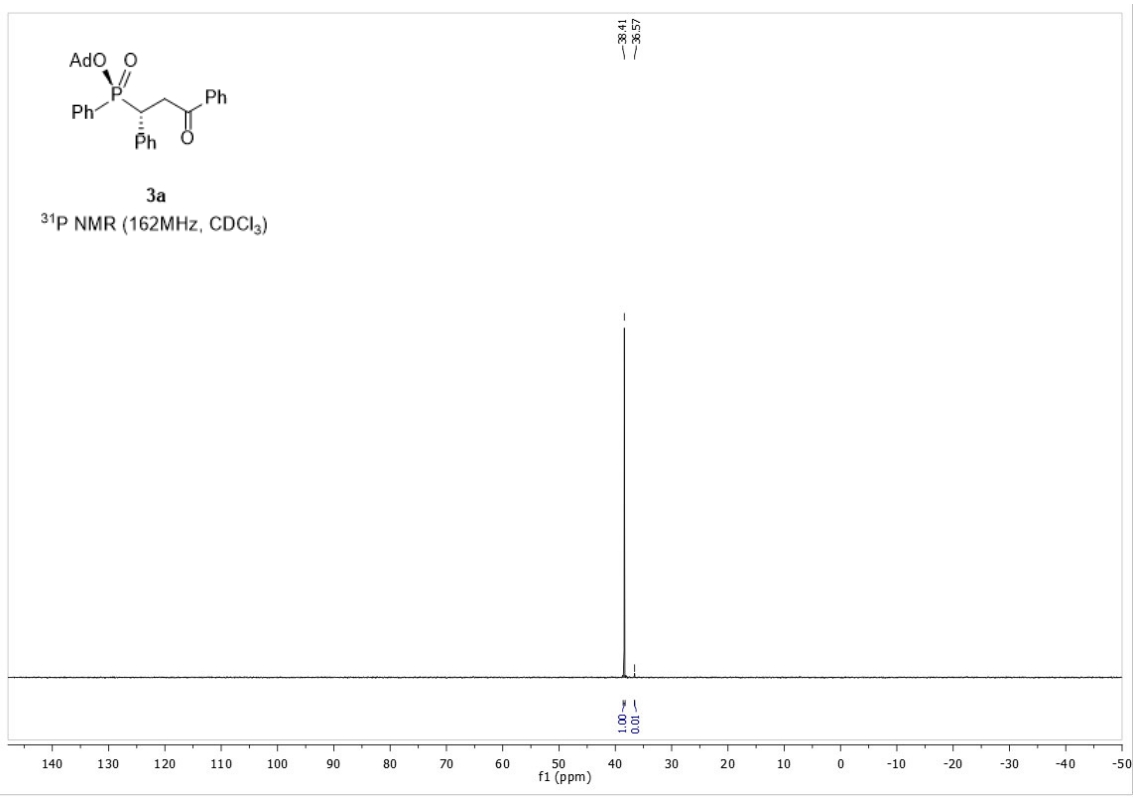


```
Bond precision:  C-C = 0.0021 A          Wavelength=0.71073

Cell:            a=12.9448(4)    b=16.4183(5)        c=13.3984(4)
                 alpha=90        beta=118.182(1)     gamma=90
Temperature:     123 K

                 Calculated                Reported
Volume           2510.01(13)               2510.01(13)
Space group      P 21/c                    P 21/c
Hall group       -P 2ybc                   -P 2ybc
Moiety formula   C31 H33 O3 P              ?
Sum formula      C31 H33 O3 P              C31 H33 O3 P
Mr               484.54                    484.54
Dx,g cm-3        1.282                     1.282
Z                4                         4
Mu (mm-1)        0.141                     0.141
F000             1032.0                    1032.0
F000'            1032.83
h,k,lmax         17,21,17                  17,21,17
Nref             6245                      6236
Tmin,Tmax        0.968,0.980               0.726,0.744
Tmin'            0.963

Correction method= # Reported T Limits: Tmin=0.726 Tmax=0.744
AbsCorr = MULTI-SCAN

Data completeness= 0.999          Theta(max)= 28.320

R(reflections)= 0.0367( 5155)     wR2(reflections)= 0.0935( 6236)

S = 1.035                 Npar= 316
```

5. Copies of ^{1}H, ^{13}C and ^{31}P NMR spectra

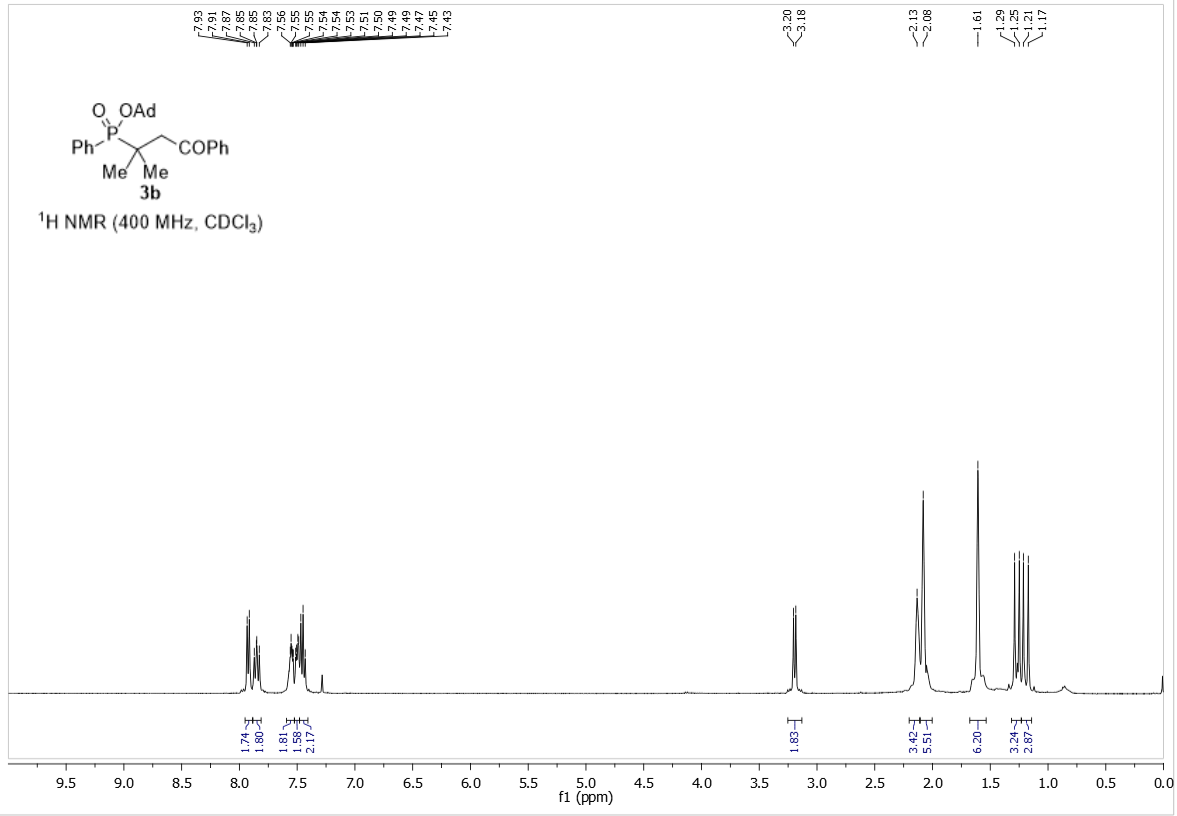






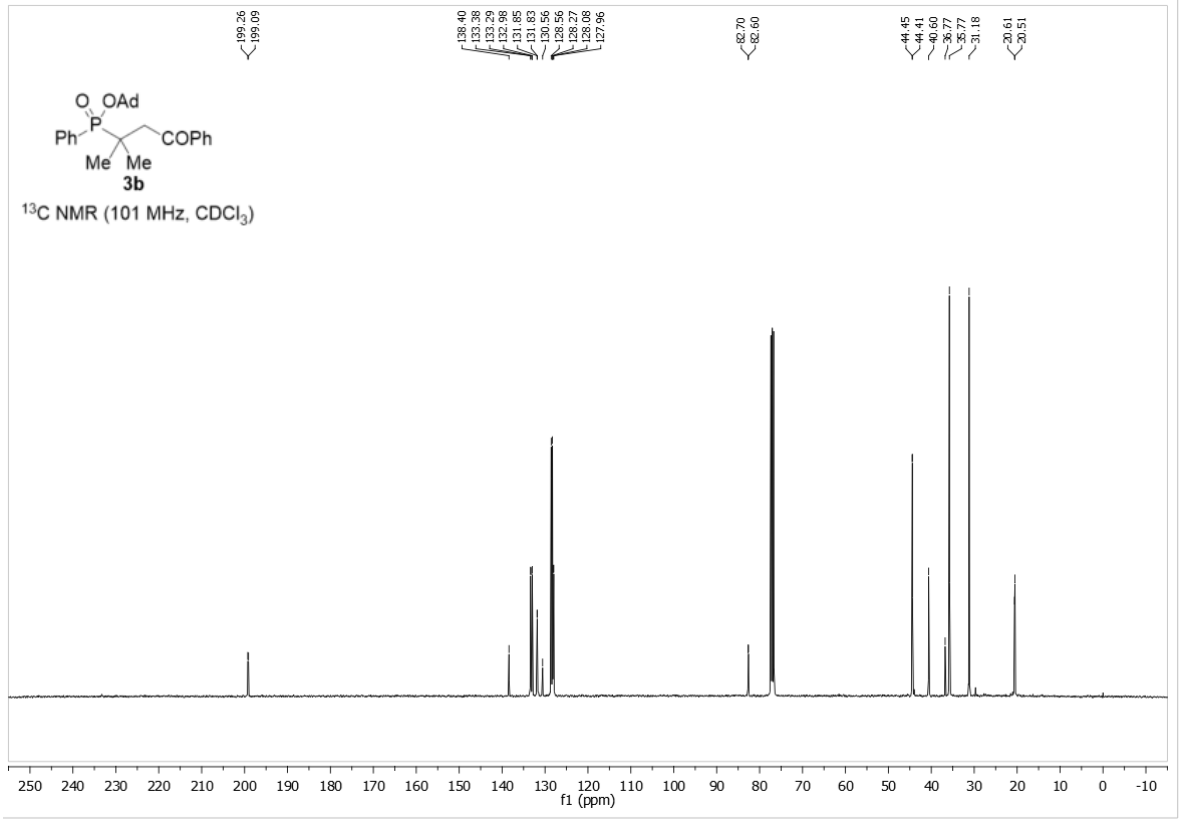
3a

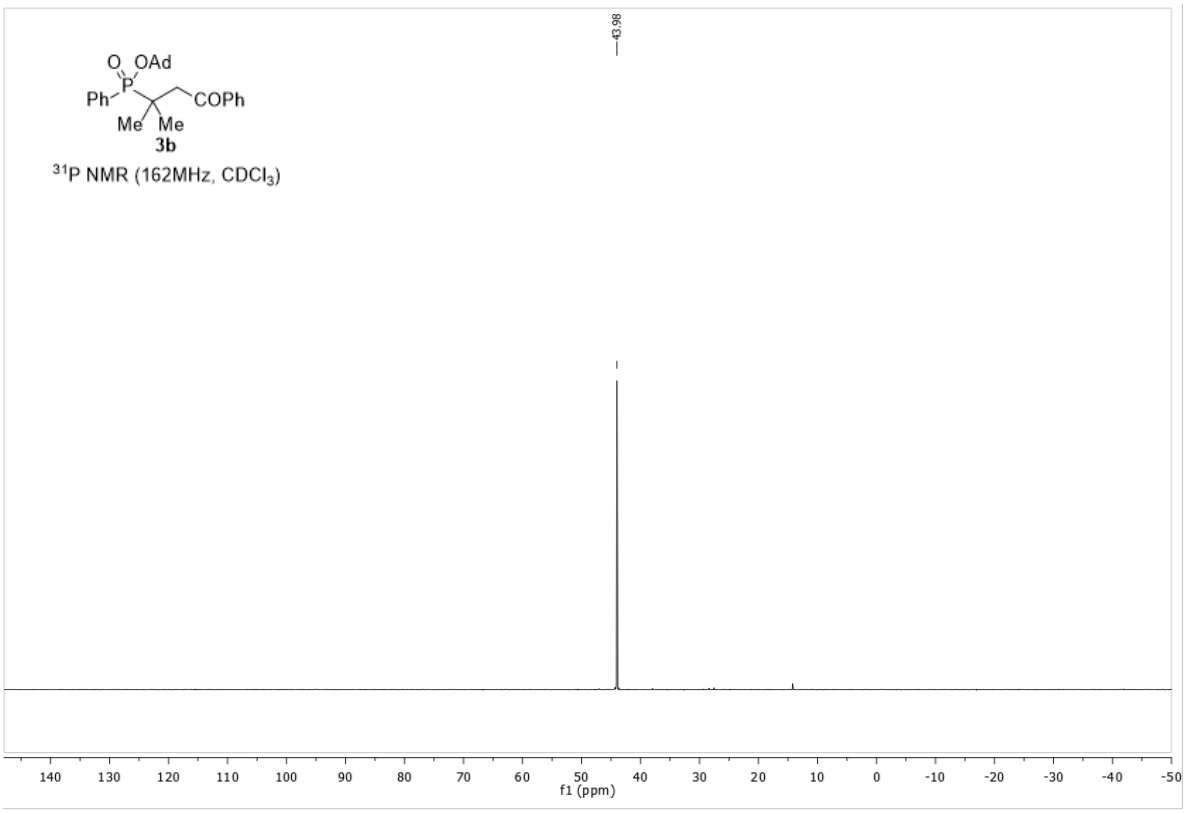
^{31}P NMR (162MHz, $CDCl_3$)

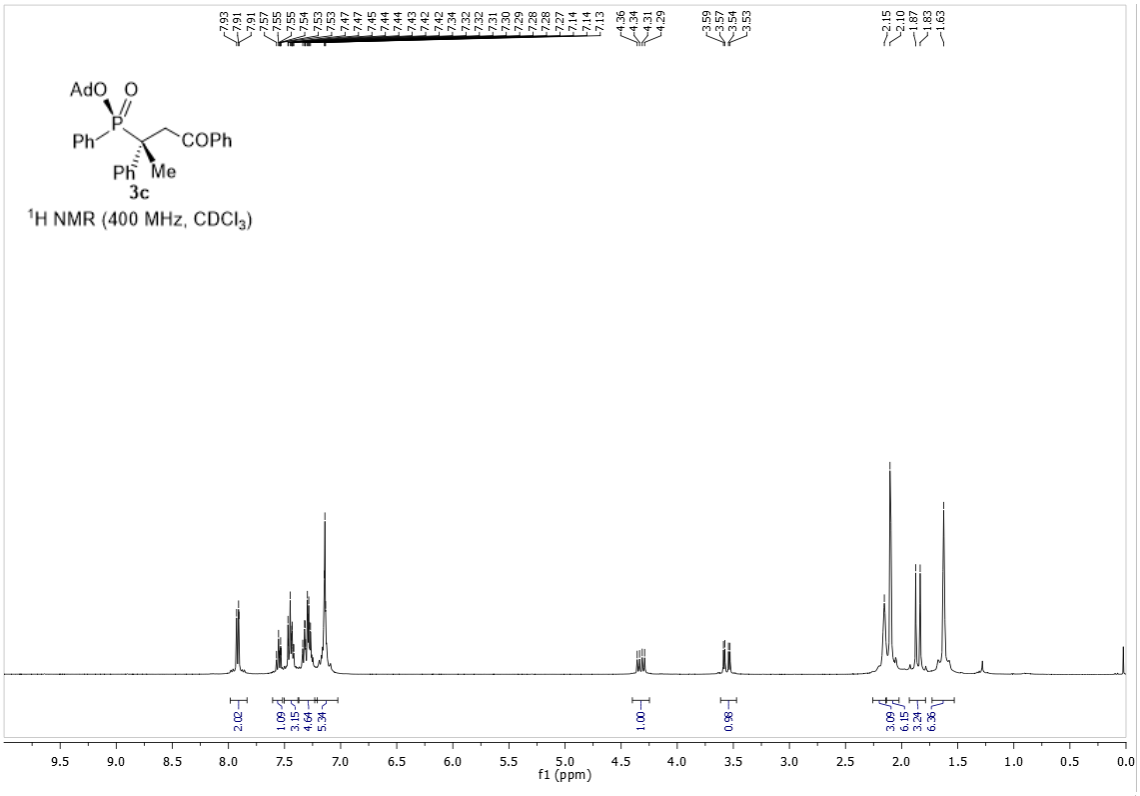


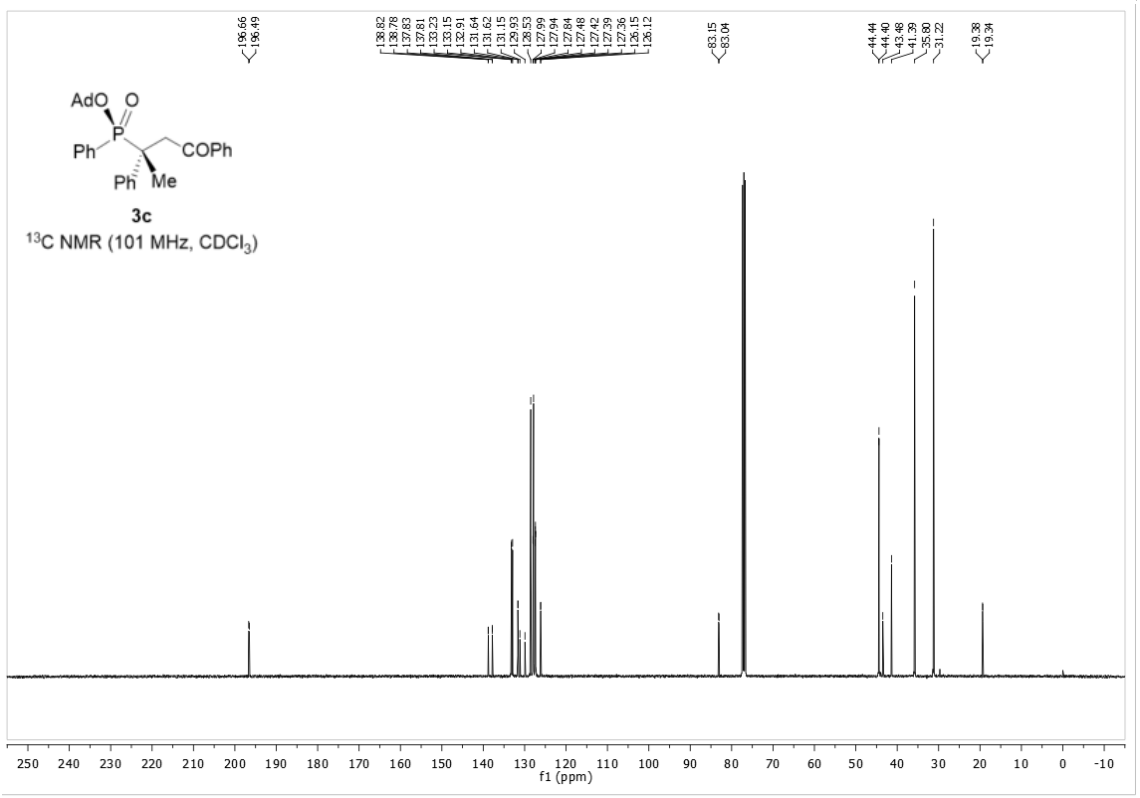
3b

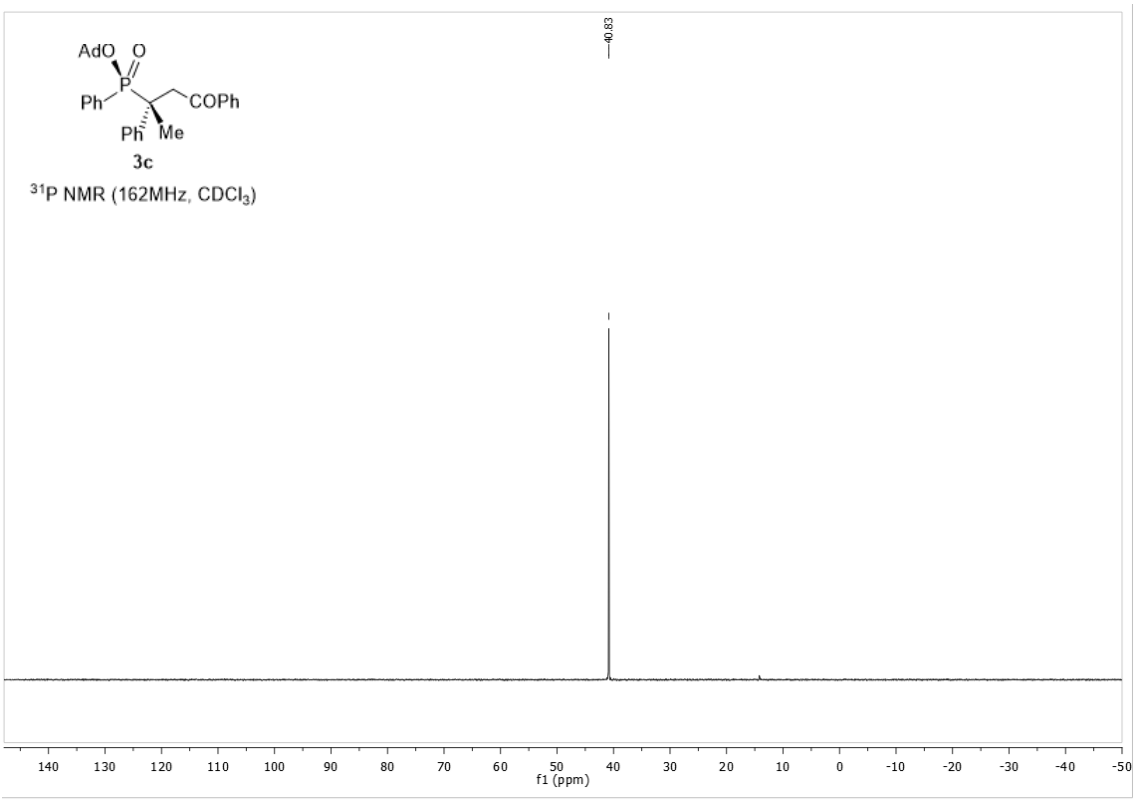
^{1}H NMR (400 MHz, $CDCl_3$)

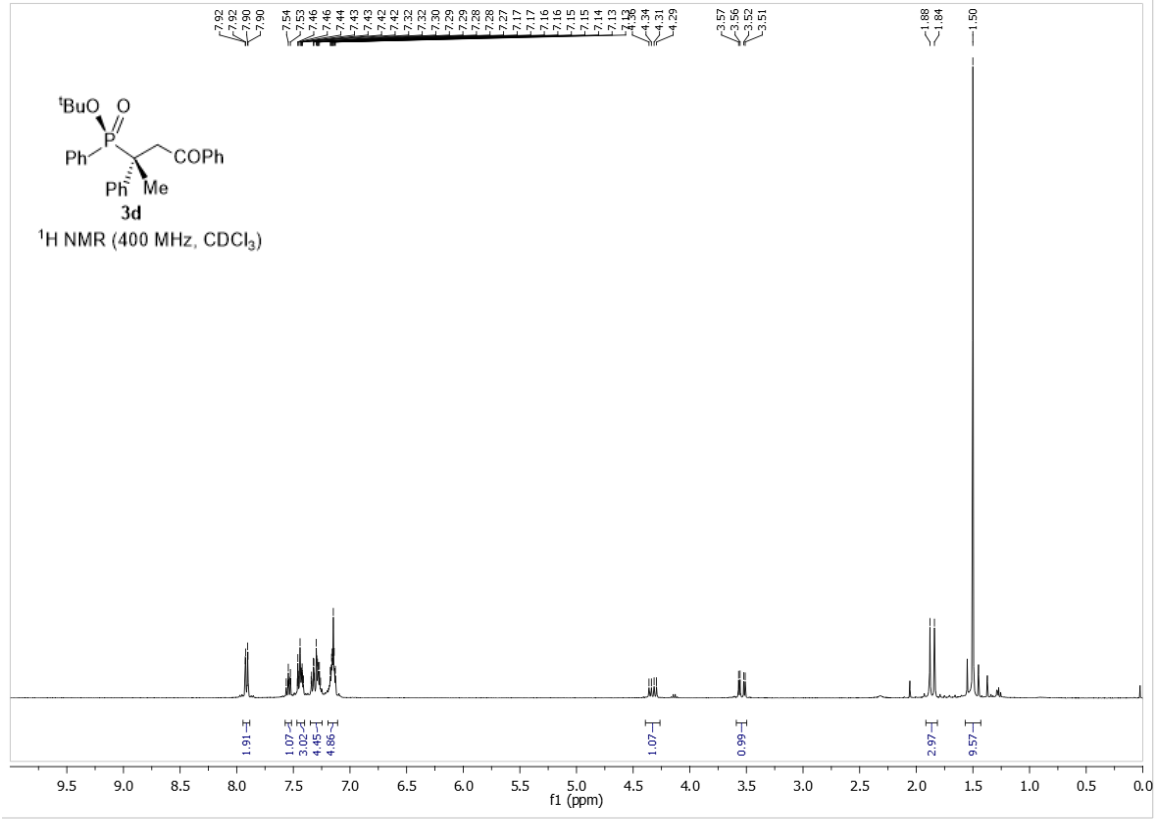

199.26
199.09
138.40
133.38
133.29
132.98
131.85
131.83
130.56
128.56
128.27
128.08
127.96
82.70
82.60
44.45
44.41
40.60
36.77
35.77
31.18
20.61
20.51
O OAd
Ph P
COPh
Me Me
3b
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

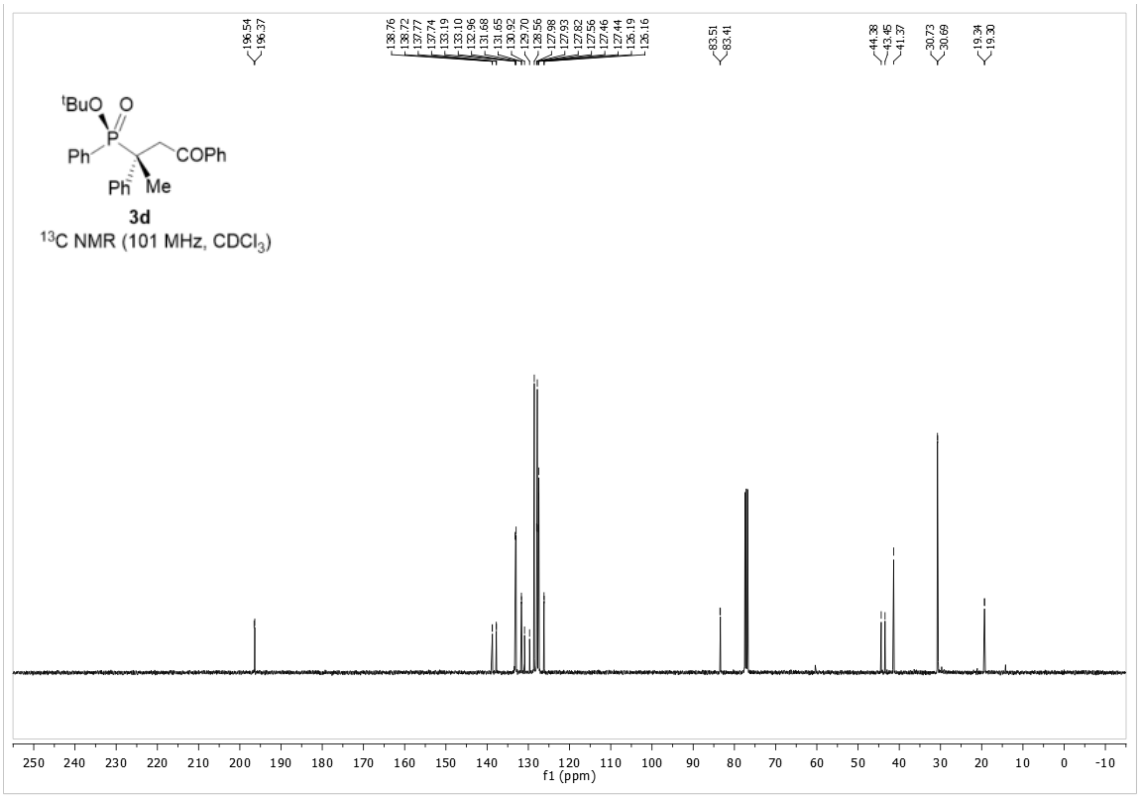

43.98
O OAd
Ph P
COPh
Me Me
3b
31P NMR (162MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

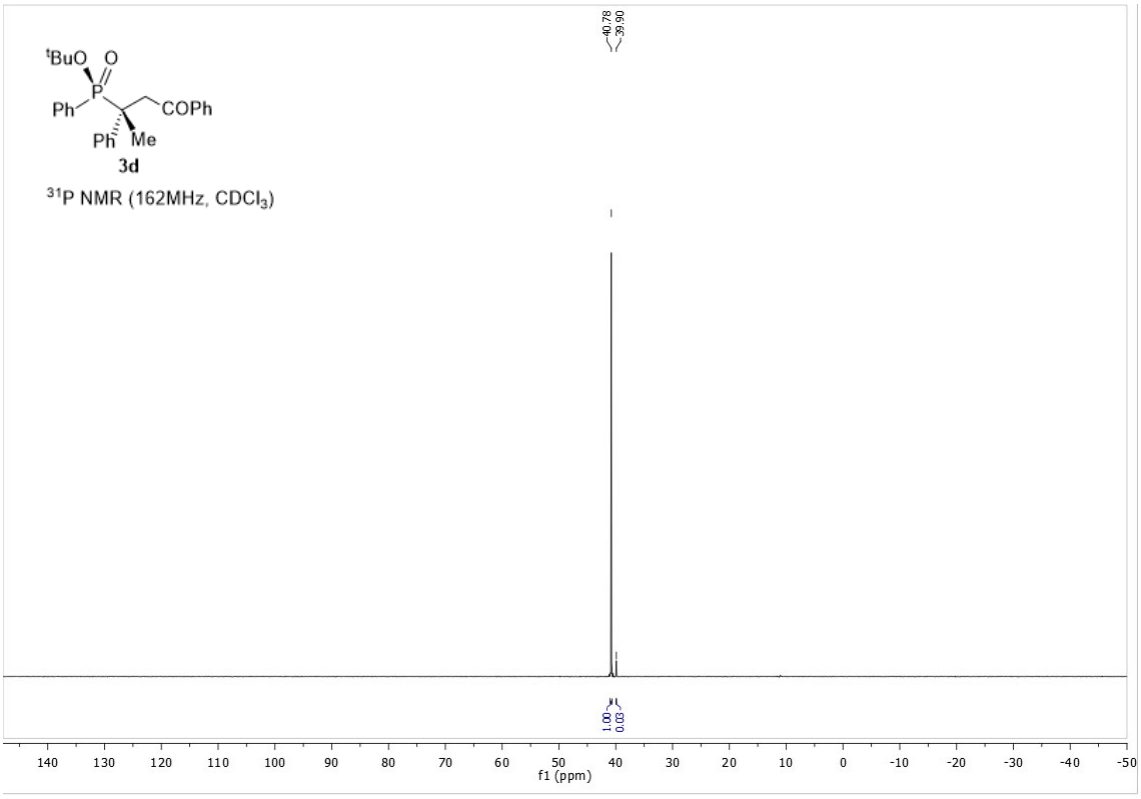

AdO
O
P
Ph
COPh
Ph
Me
3c
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

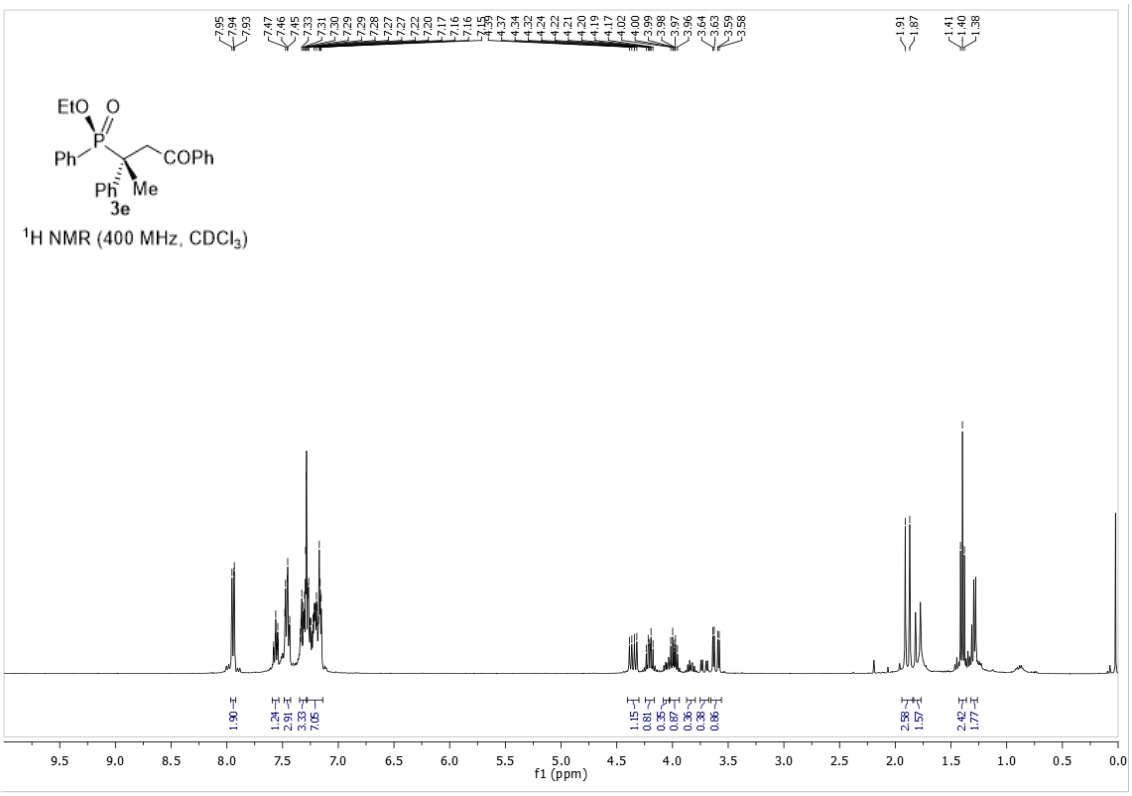

AdO
O
P
Ph
COPh
Ph
Me
3c
^{13}C NMR (101 MHz, $CDCl_3$)
f1 (ppm)

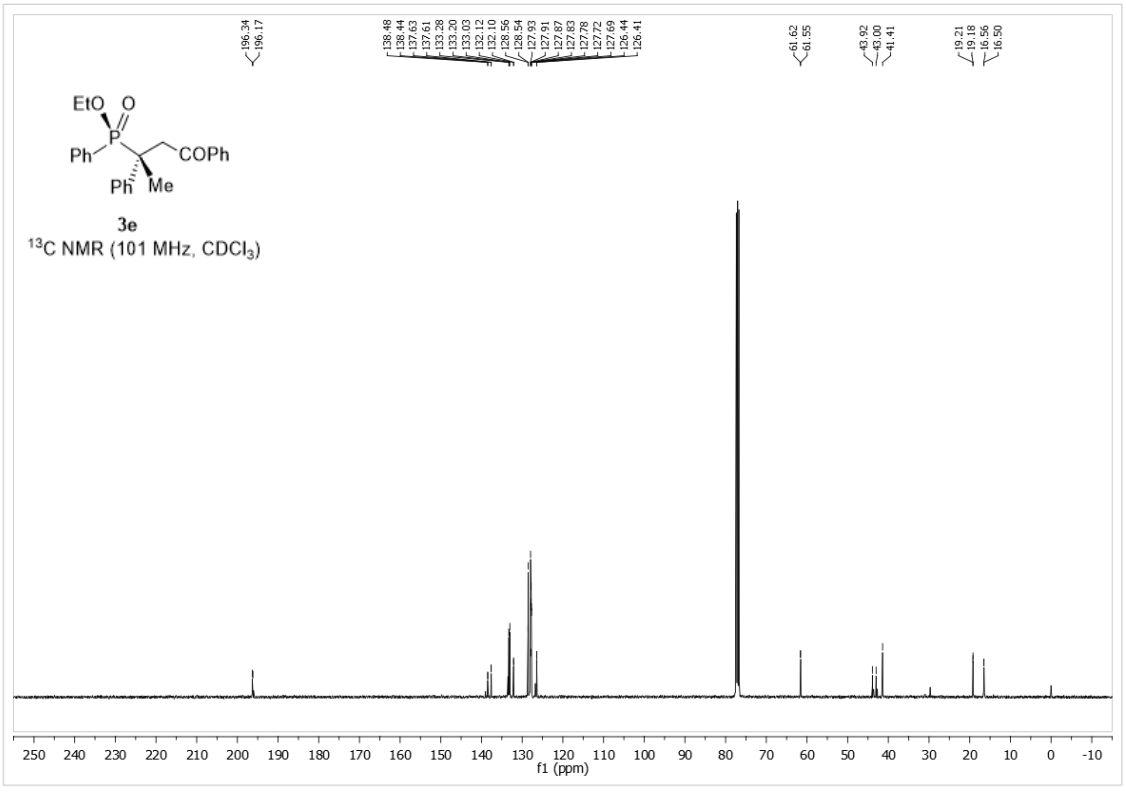

AdO
O
P
Ph
COPh
Ph
Me
3c
^{31}P NMR (162MHz, $CDCl_3$)
40.83
f1 (ppm)

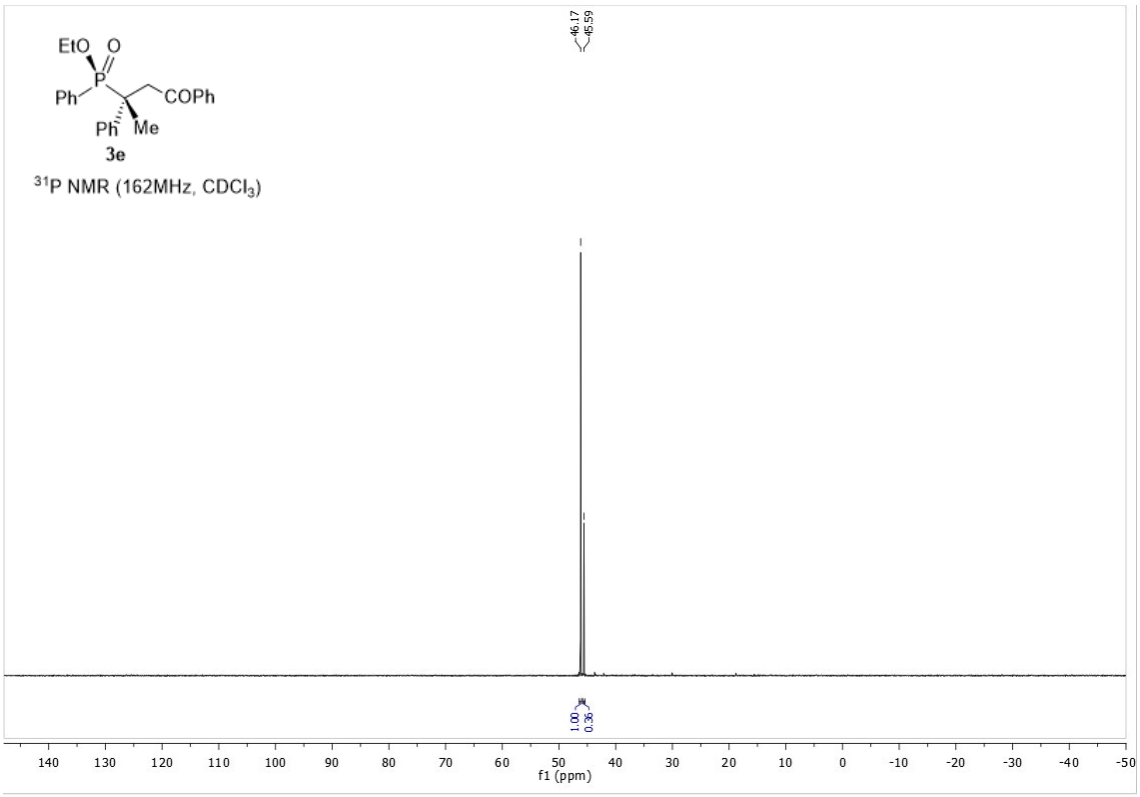

^{t}BuO
O
P
Ph
COPh
Ph
Me
3d
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

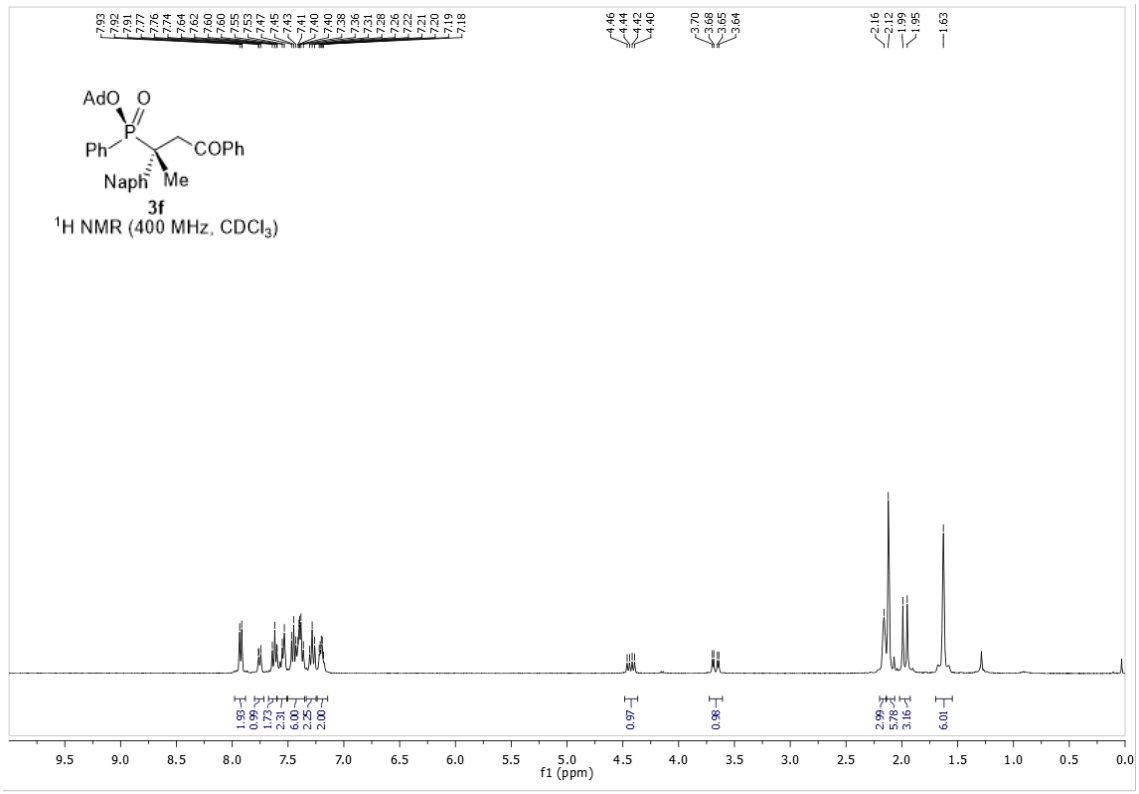

196.54
196.37
138.76
138.72
137.77
137.74
133.19
133.10
132.96
131.68
131.65
130.92
129.70
128.56
127.98
127.93
127.82
127.56
127.46
127.44
126.19
126.16
83.51
83.41
44.38
43.45
41.37
30.73
30.69
19.34
19.30
tBuO
O
P
Ph
COPh
Ph
Me
3d
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

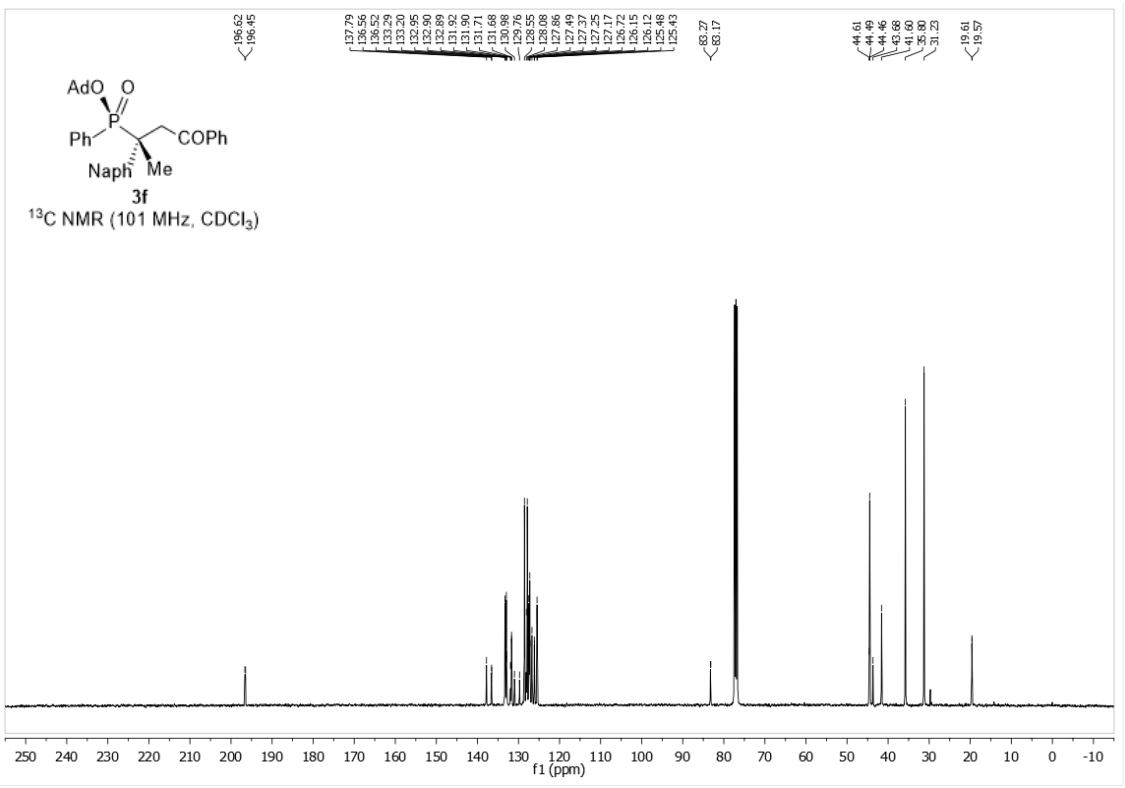

40.78
39.90
tBuO
O
P
Ph
COPh
Ph
Me
3d
31P NMR (162MHz, CDCl3)
1.00
0.03
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

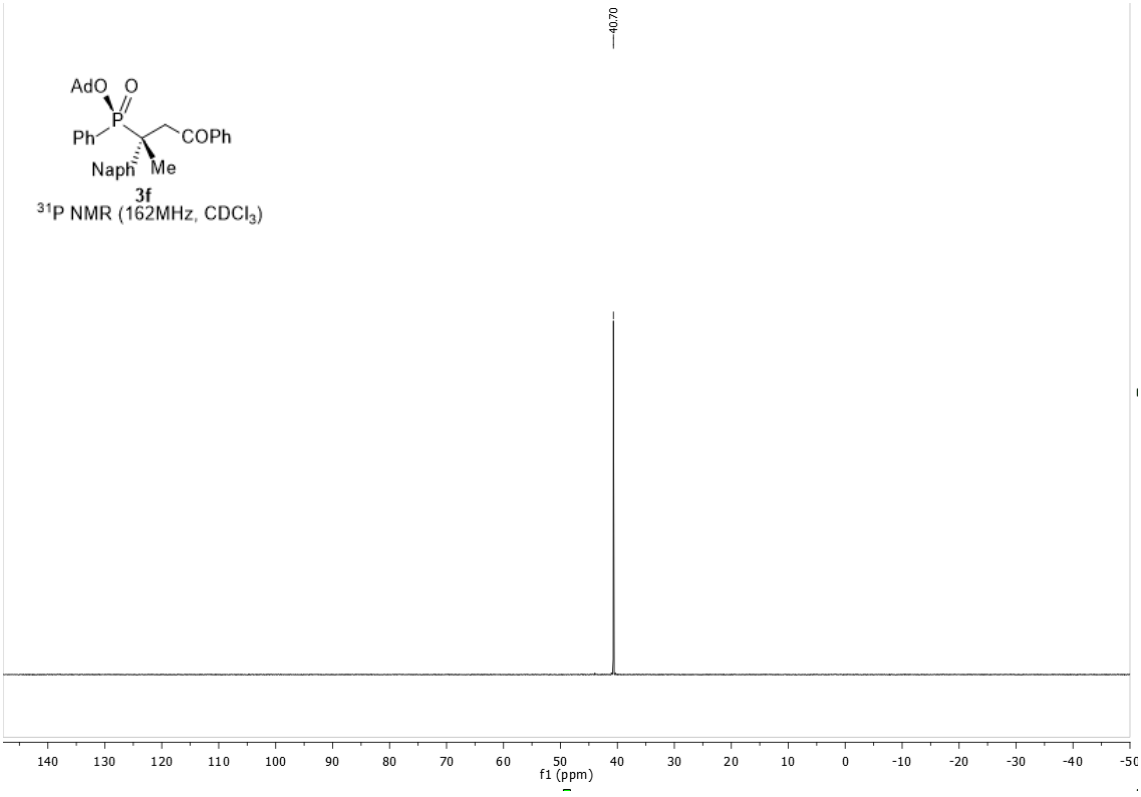

EtO
O
P
Ph
COPh
Ph
Me
3e
1H NMR (400 MHz, CDCl3)
f1 (ppm)

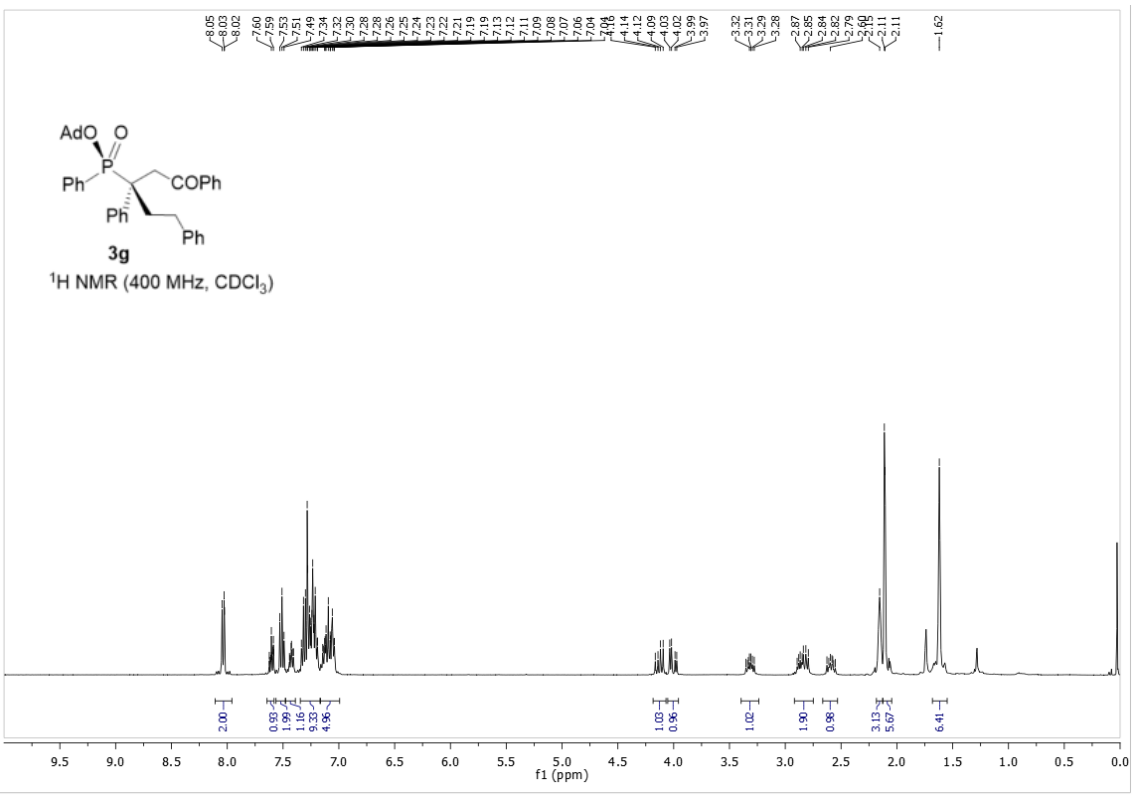

EtO
O
P
Ph
COPh
Ph
Me
3e
13C NMR (101 MHz, CDCl3)
f1 (ppm)

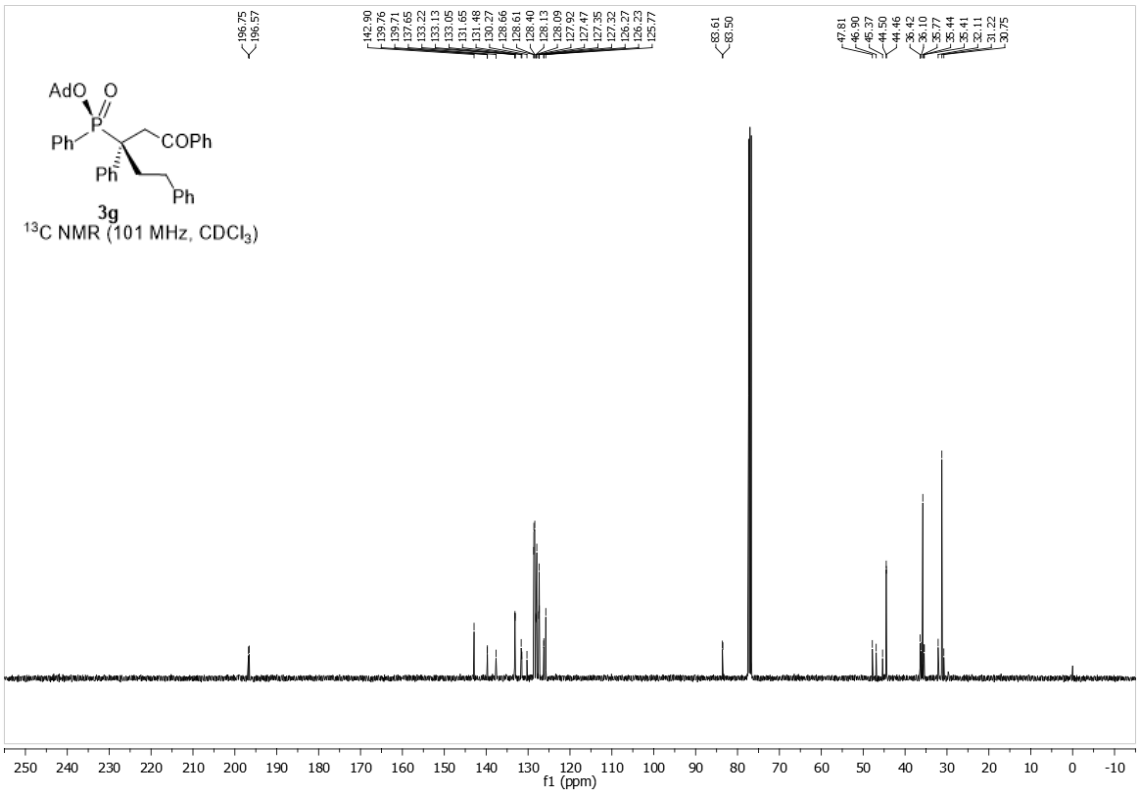

EtO O
Ph
P
COPh
Ph Me
3e
31P NMR (162MHz, CDCl3)
46.17
45.59
1.00
0.36
f1 (ppm)

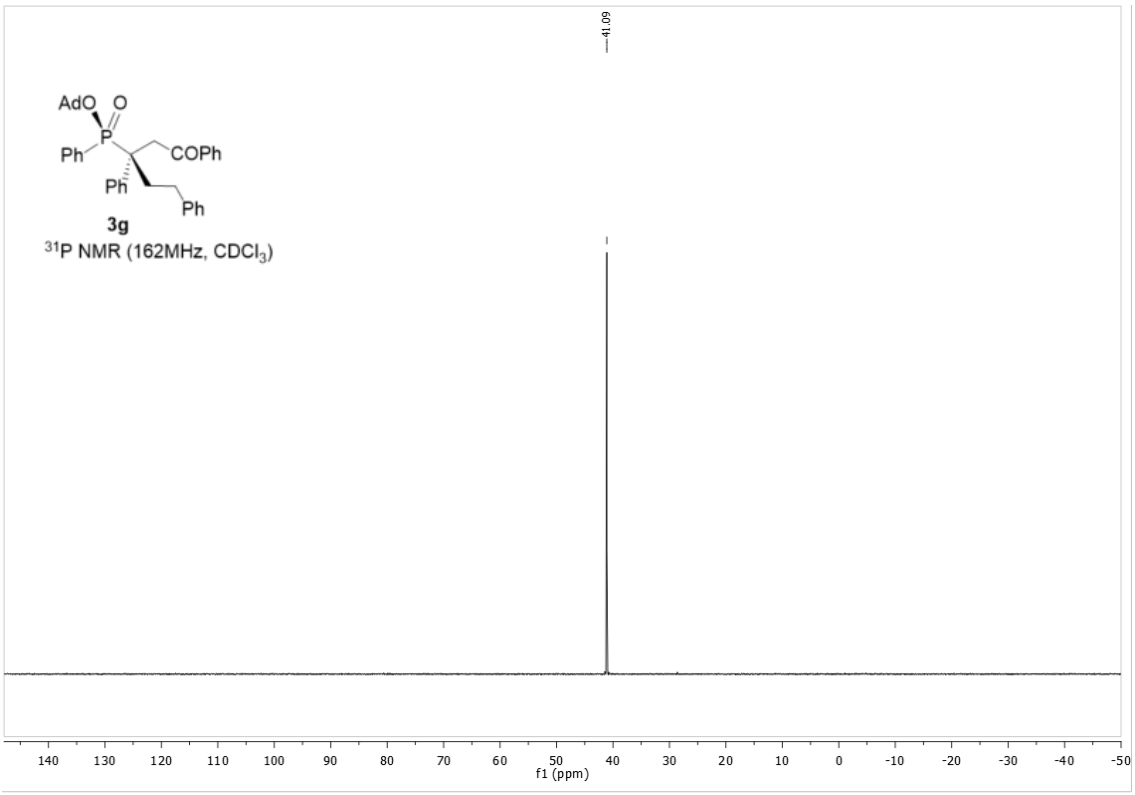

AdO O
Ph
P
COPh
Naph Me
3f
1H NMR (400 MHz, CDCl3)
f1 (ppm)

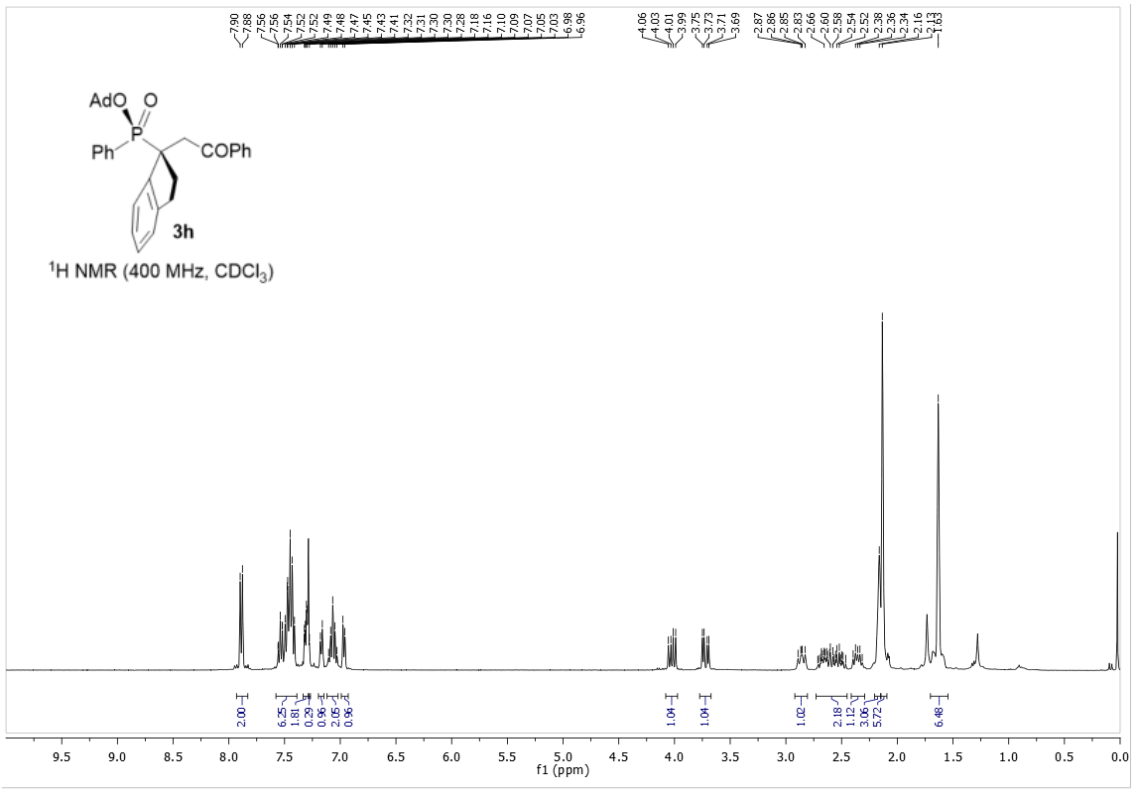

196.62
196.45
137.79
136.56
136.52
133.29
133.20
132.95
132.90
132.89
131.92
131.90
131.71
131.68
130.98
129.76
128.55
128.08
127.86
127.49
127.37
127.25
127.17
126.72
126.15
126.12
125.48
125.43
83.27
83.17
44.61
44.49
44.46
43.68
41.60
35.80
31.23
19.61
19.57
AdO
O
P
Ph
COPh
Naph
Me
3f
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

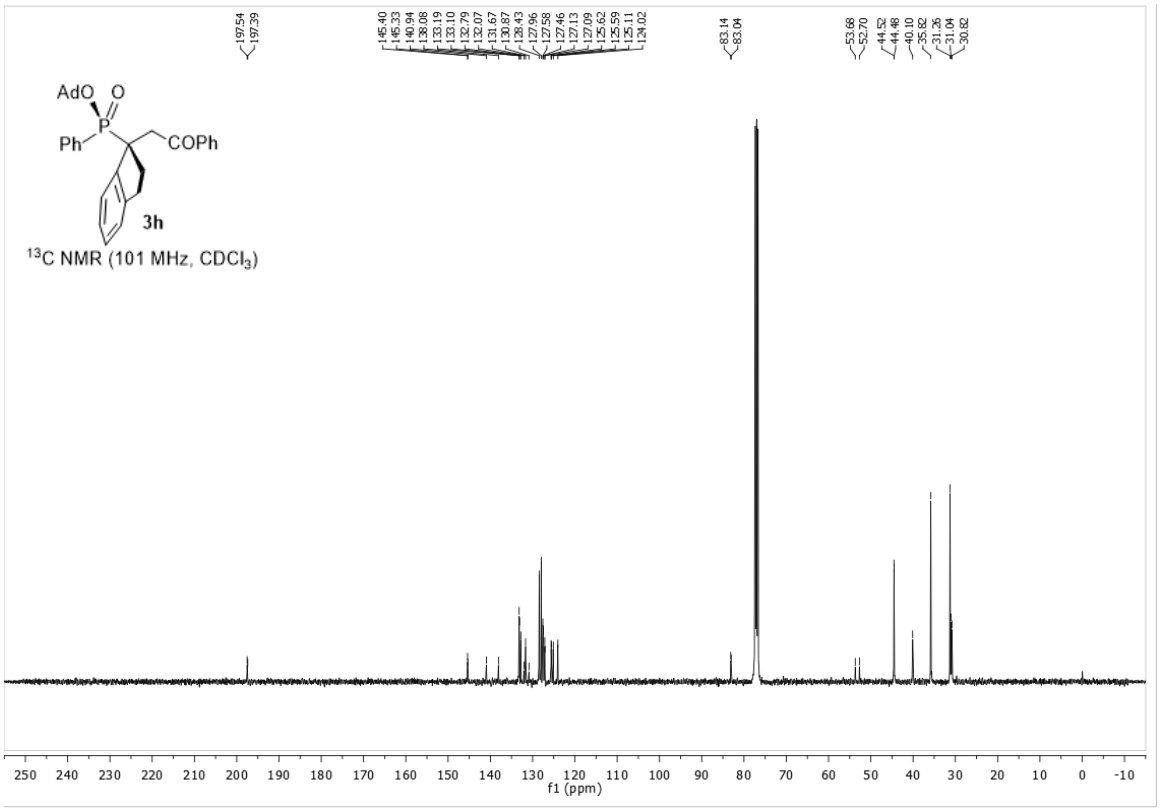

40.70
AdO
O
P
Ph
COPh
Naph
Me
3f
31P NMR (162MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

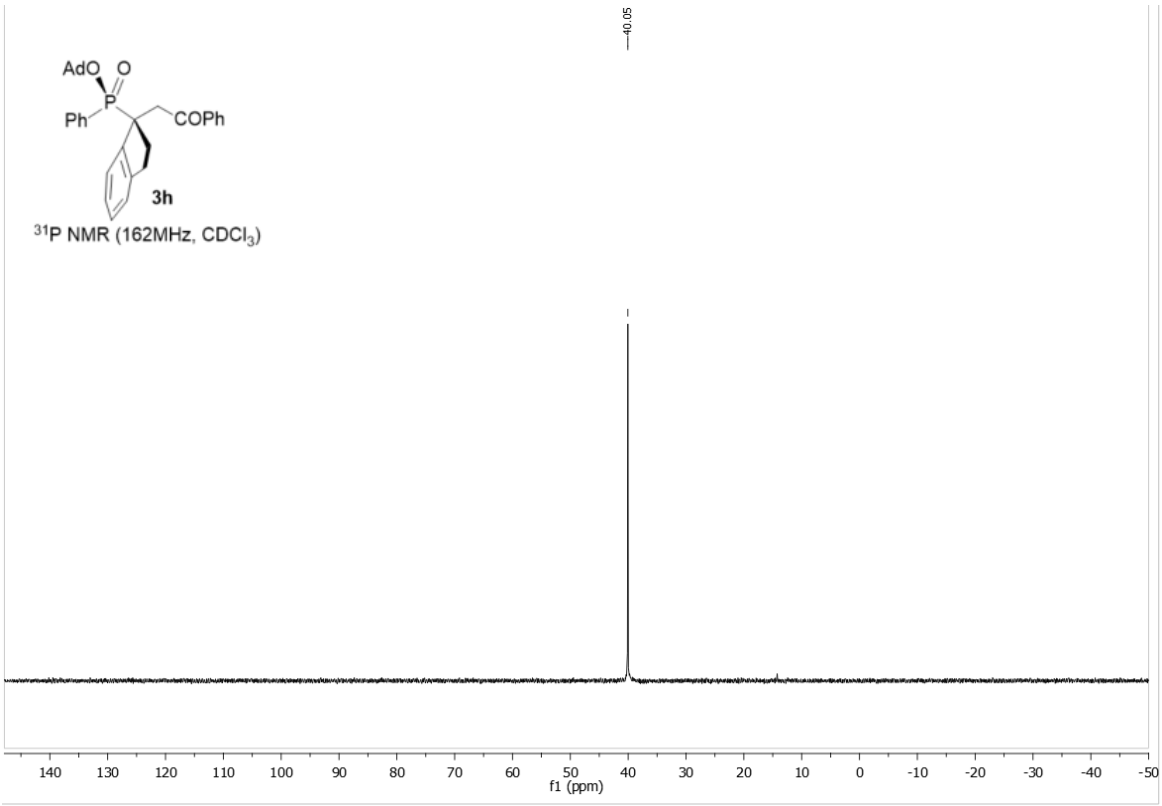

AdO
O
P
Ph
COPh
Ph
Ph
3g
1H NMR (400 MHz, CDCl3)
f1 (ppm)

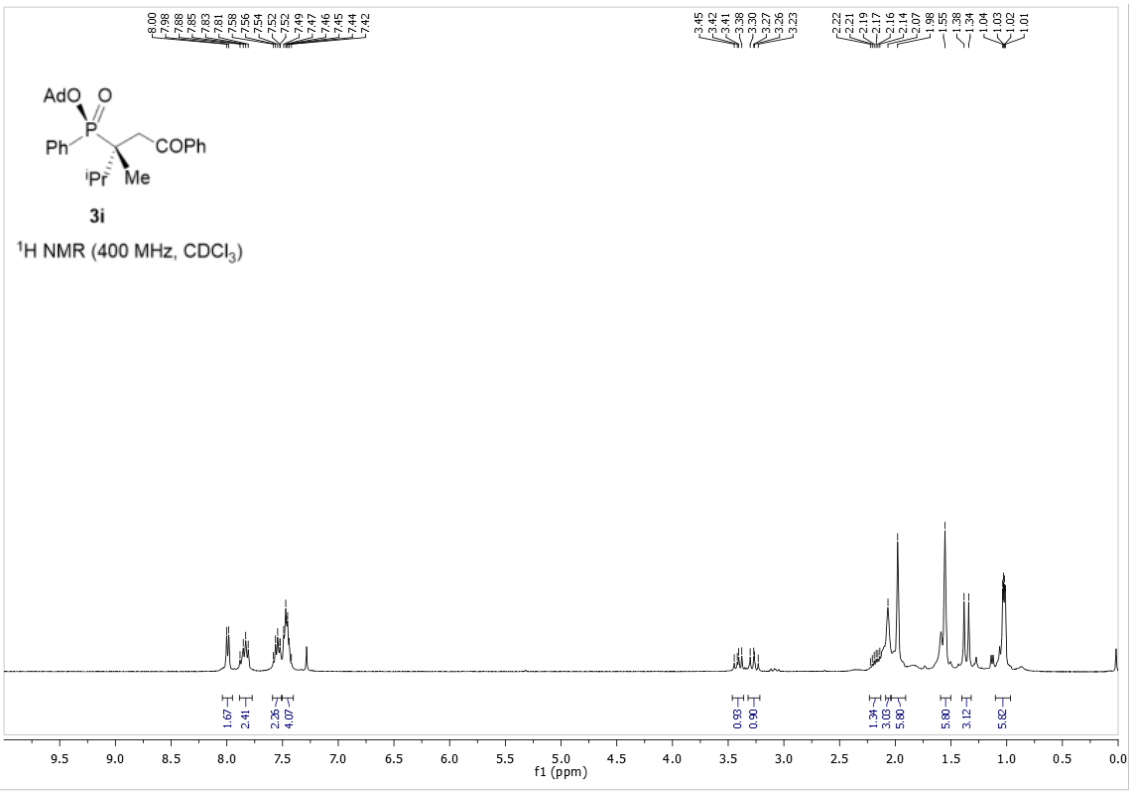

AdO
O
P
Ph
COPh
Ph
Ph
3g
13C NMR (101 MHz, CDCl3)
f1 (ppm)

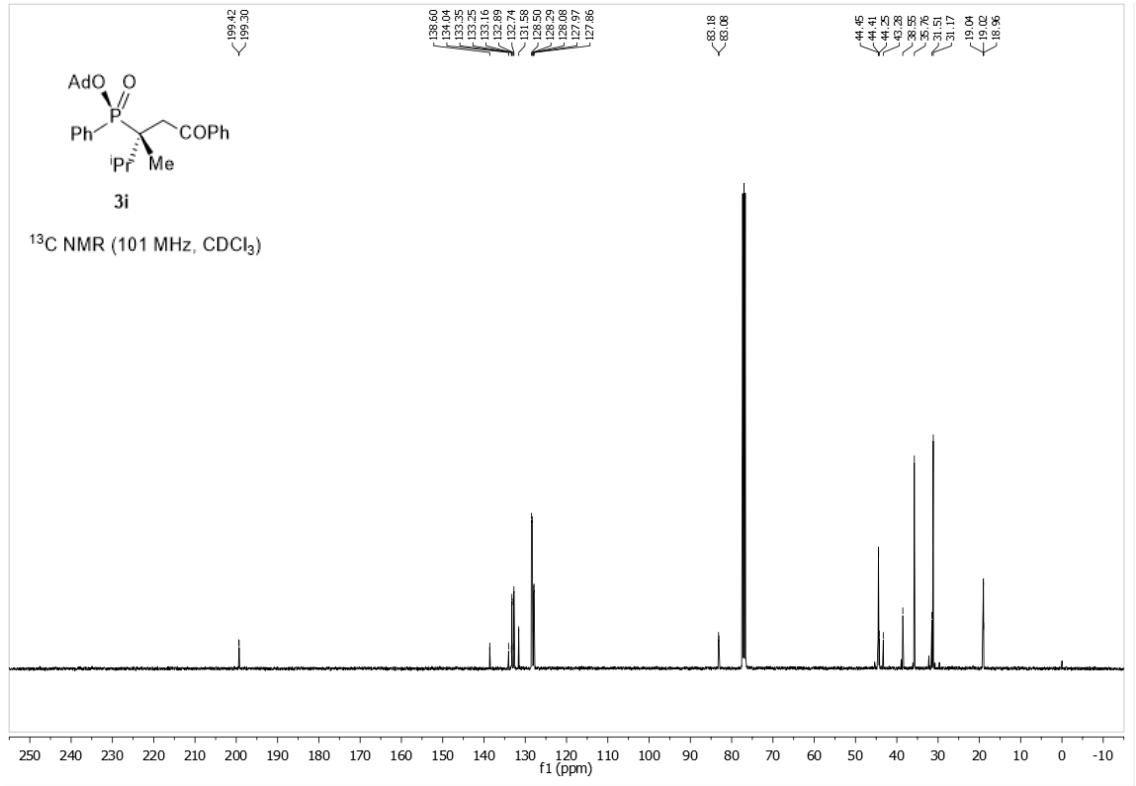

41.09
AdO
O
P
Ph
COPh
Ph
Ph
3g
31P NMR (162MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

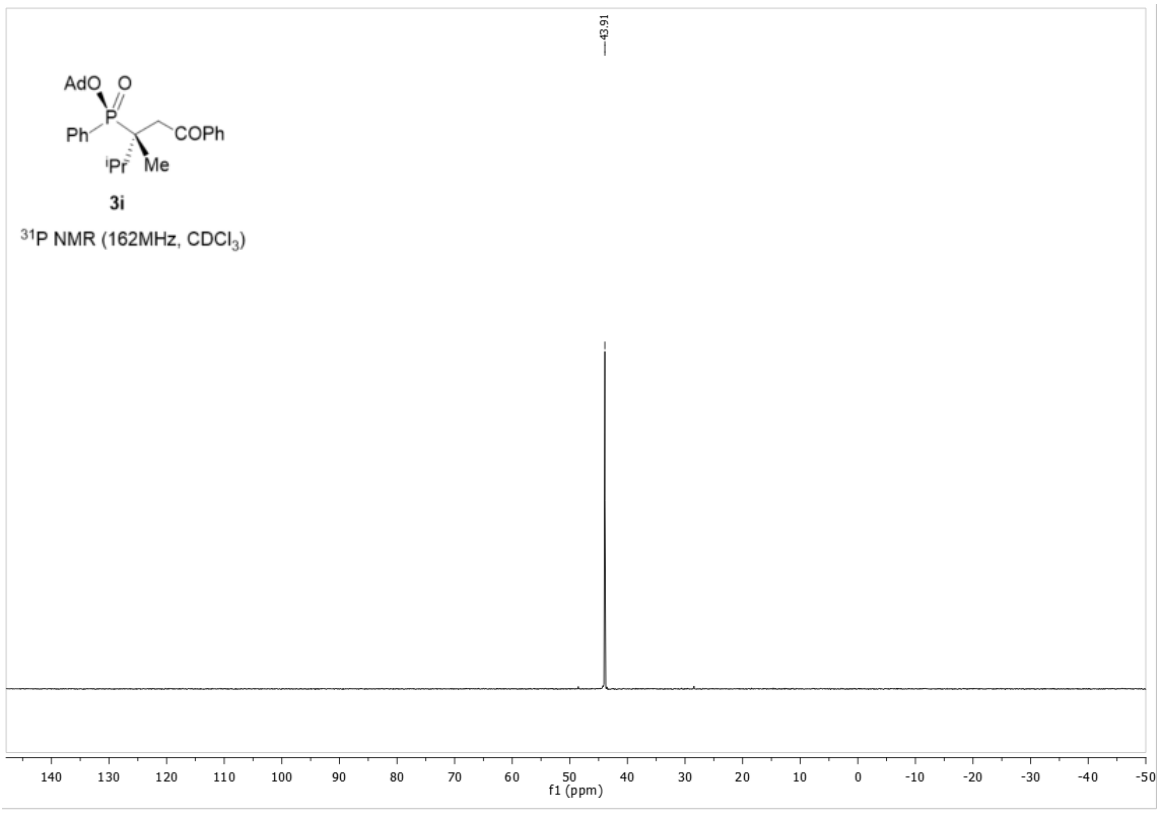

7.90 7.88 7.56 7.56 7.54 7.52 7.52 7.49 7.48 7.47 7.45 7.43 7.41 7.32 7.31 7.30 7.30 7.28 7.18 7.16 7.10 7.09 7.07 7.05 7.03 6.98 6.96
4.06 4.03 4.01 3.99 3.75 3.73 3.71 3.69
2.87 2.86 2.85 2.83 2.66 2.60 2.58 2.54 2.52 2.38 2.36 2.34 2.16 2.13 1.63
AdO
O
P
Ph
COPh
3h
1H NMR (400 MHz, CDCl3)
2.00 6.25 1.81 0.29 0.96 2.05 0.96 1.04 1.04 1.02 2.18 1.12 3.06 5.72 6.48
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 0.0
f1 (ppm)

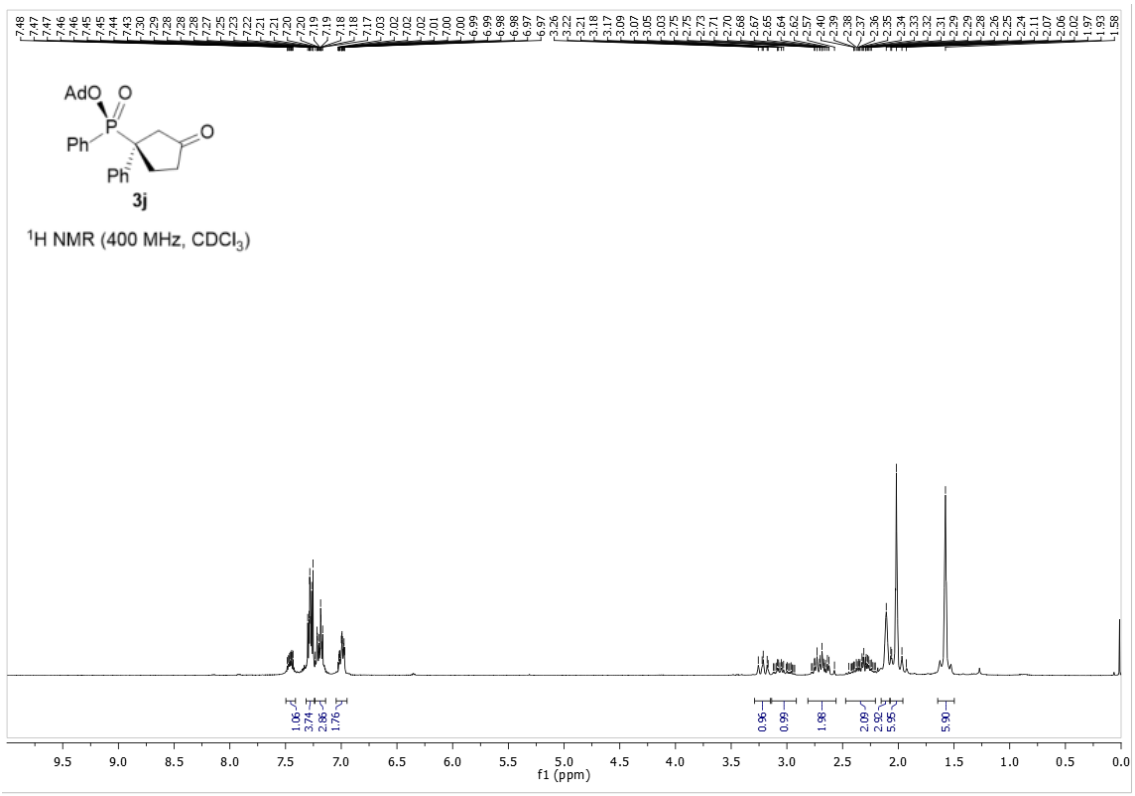

197.54
197.39
145.40
145.33
140.94
138.08
133.19
133.10
132.79
132.07
131.67
130.87
128.43
127.96
127.58
127.46
127.13
127.09
125.62
125.59
125.11
124.02
83.14
83.04
53.68
52.70
44.52
44.48
40.10
35.82
31.26
31.04
30.82
AdO
O
P
Ph
COPh
3h
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

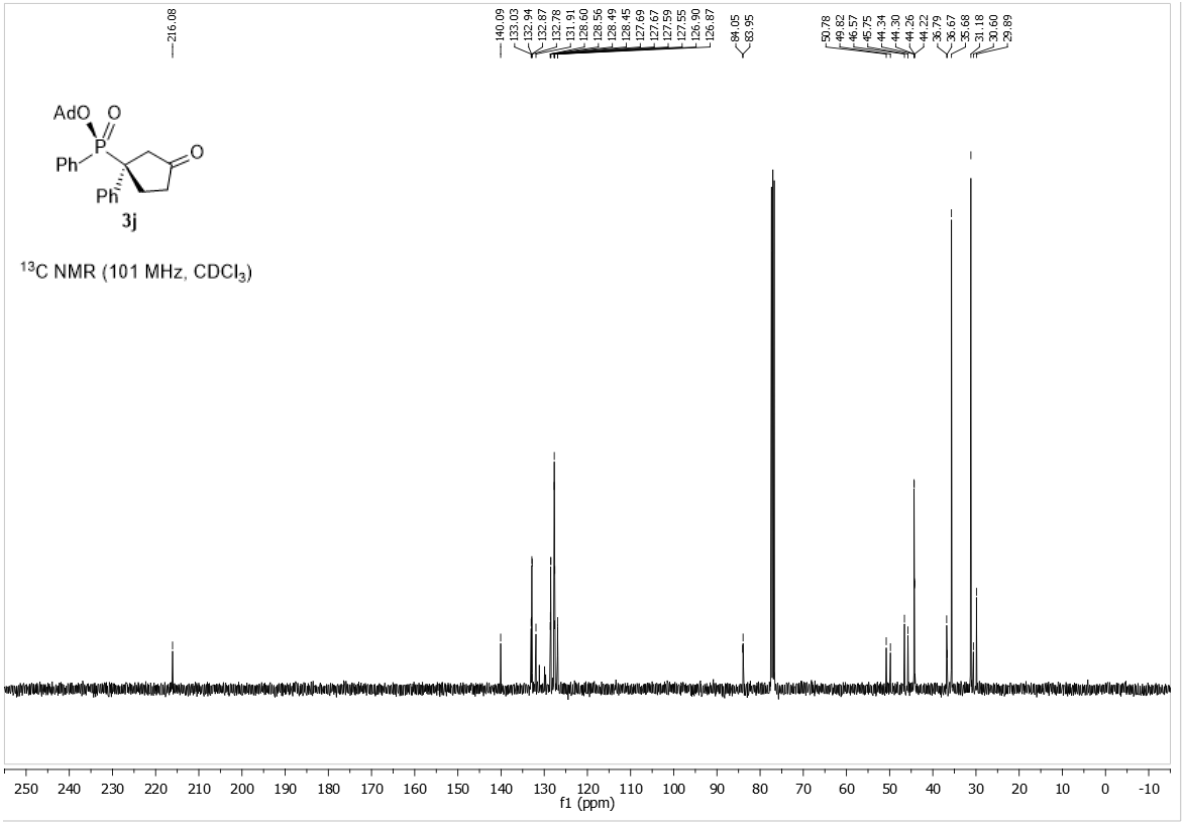

40.05
AdO
O
P
Ph
COPh
3h
31P NMR (162MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

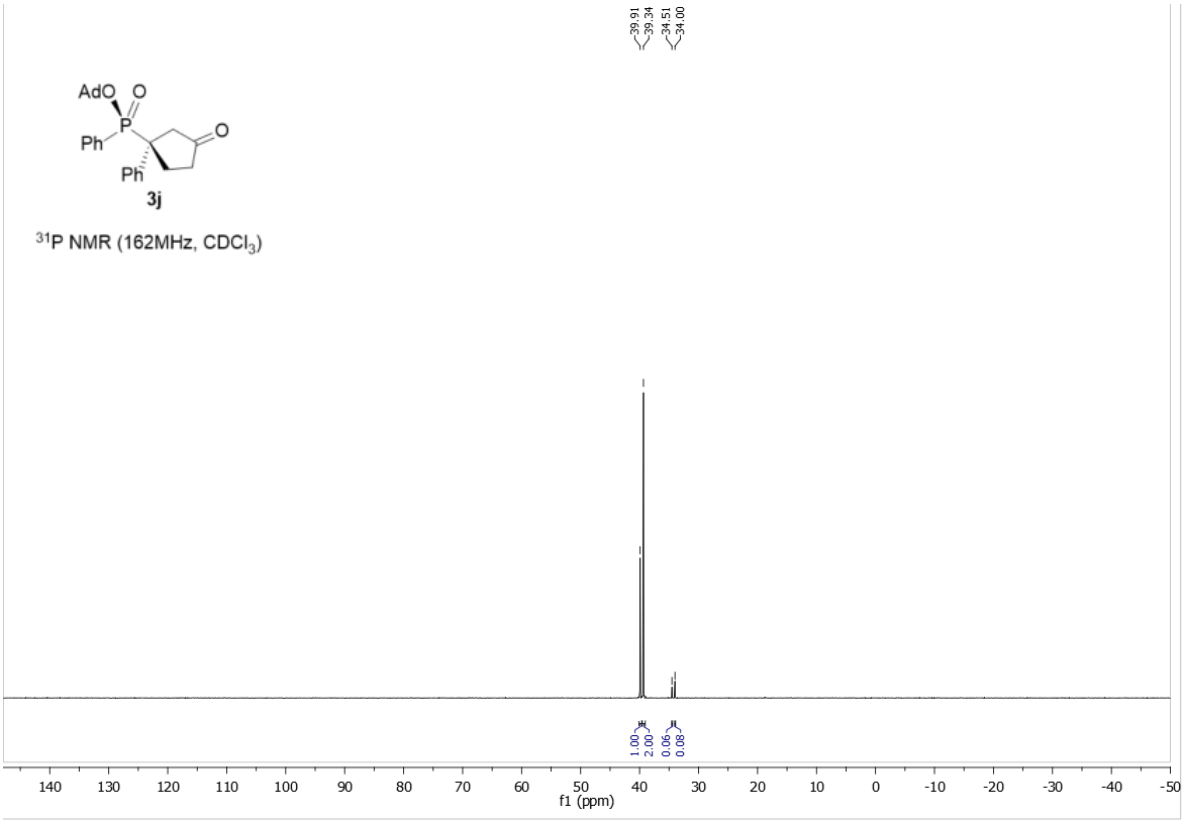

AdO
O
P
Ph
COPh
iPr
Me
3i
1H NMR (400 MHz, CDCl3)
f1 (ppm)

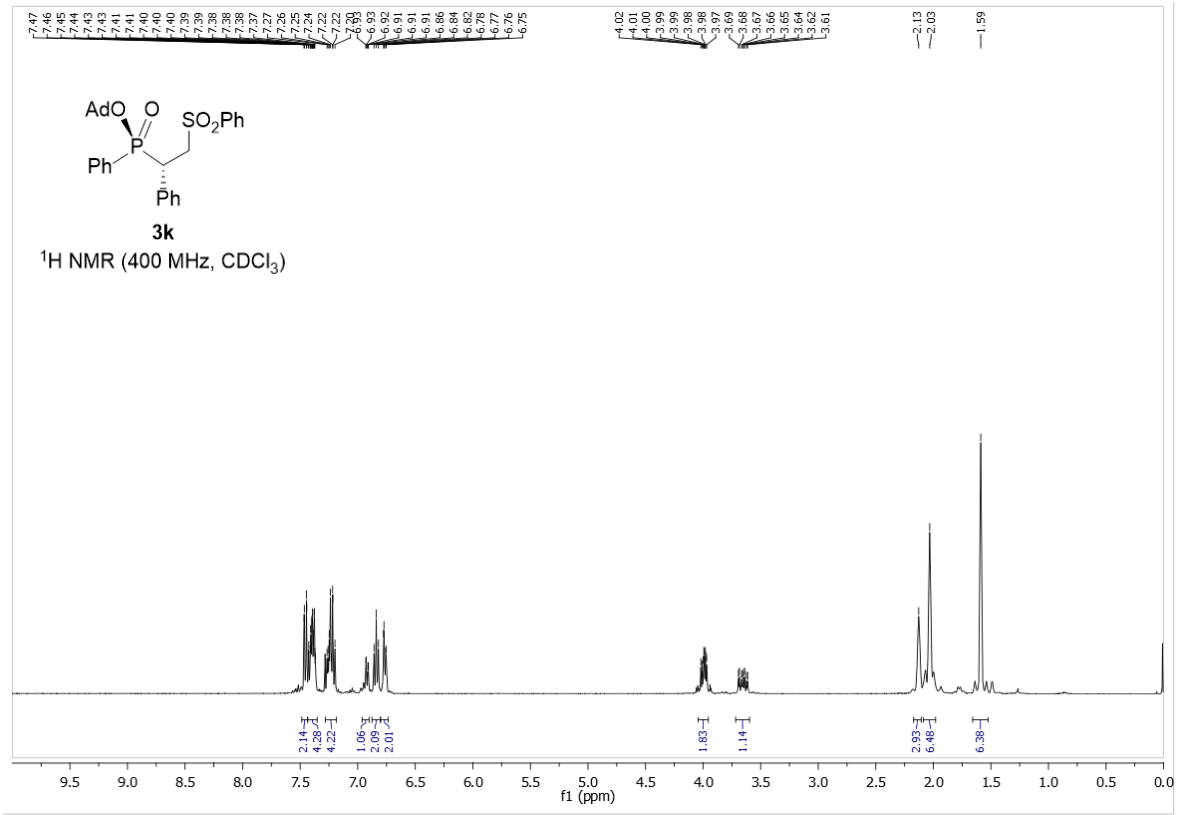

AdO
O
P
Ph
COPh
iPr
Me
3i
13C NMR (101 MHz, CDCl3)
f1 (ppm)

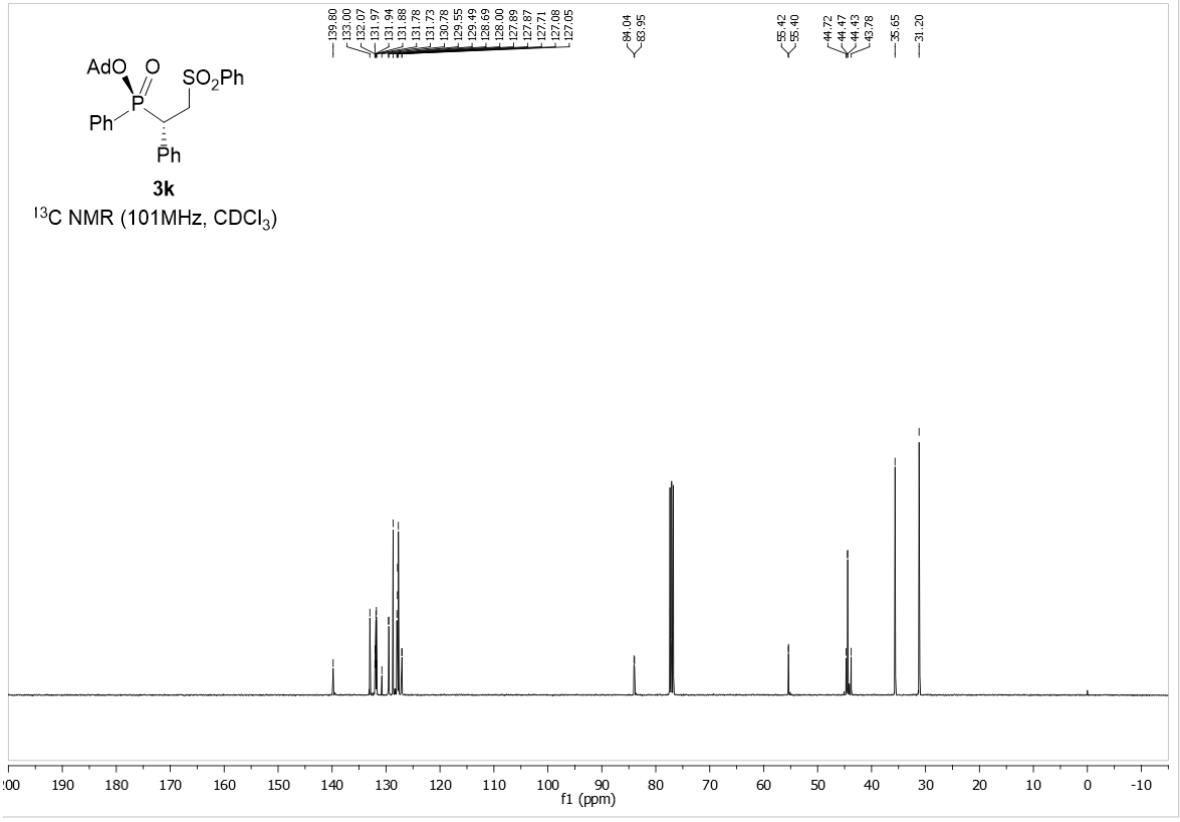

43.91
AdO
O
P
Ph
COPh
iPr
Me
3i
31P NMR (162MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

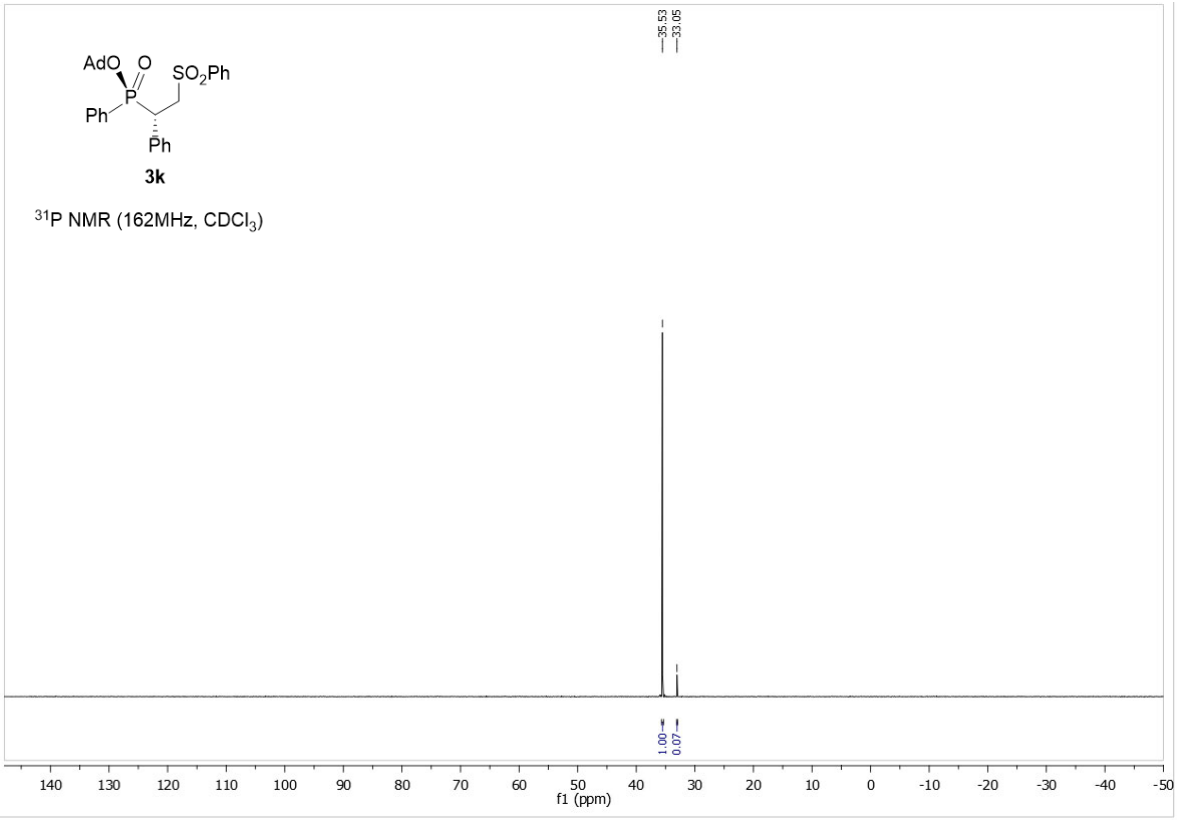

AdO
O
P
Ph
O
Ph
3j
1H NMR (400 MHz, CDCl3)
1.06
3.74
2.86
1.76
0.96
0.99
1.98
2.09
2.92
5.95
5.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


216.08
140.09
133.03
132.94
132.87
132.78
131.91
128.60
128.56
128.49
128.45
127.69
127.67
127.59
127.55
126.90
126.87
84.05
83.95
50.78
49.82
45.57
45.75
44.34
44.30
44.26
44.22
36.79
36.67
35.68
31.18
30.60
29.89
AdO
O
P
Ph
Ph
O
3j
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


39.91
39.34
34.51
34.00
AdO
O
P
Ph
Ph
O
3j
31P NMR (162MHz, CDCl3)
1.00
2.00
0.06
0.08
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

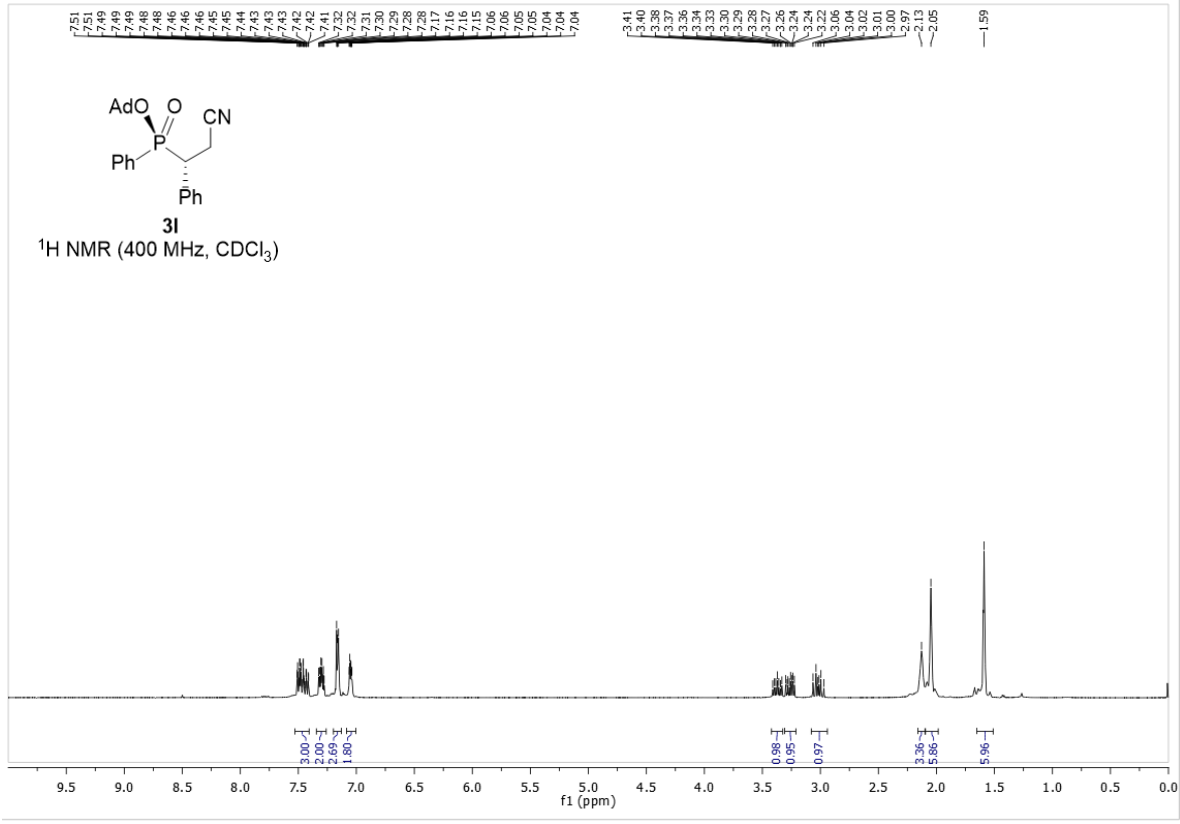

AdO
O
SO2Ph
Ph
Ph
3k
1H NMR (400 MHz, CDCl3)
f1 (ppm)


AdO
O
SO2Ph
Ph
Ph
3k
13C NMR (101MHz, CDCl3)
f1 (ppm)



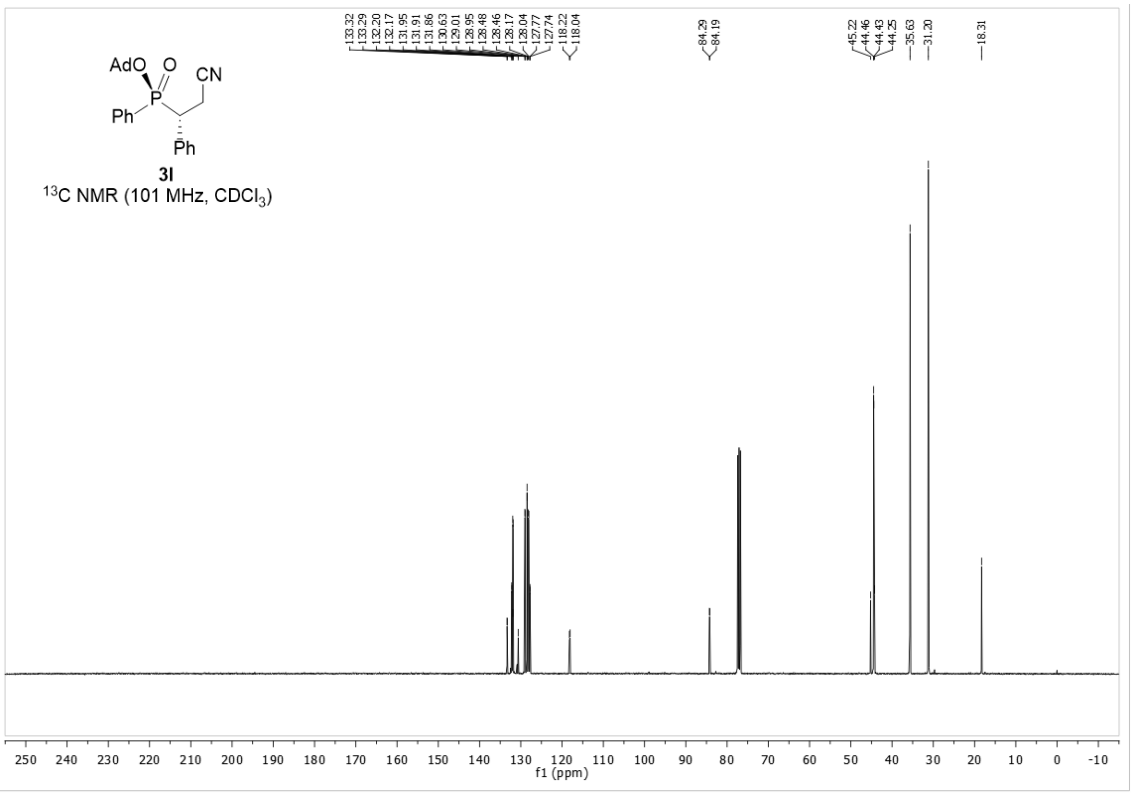
3k

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



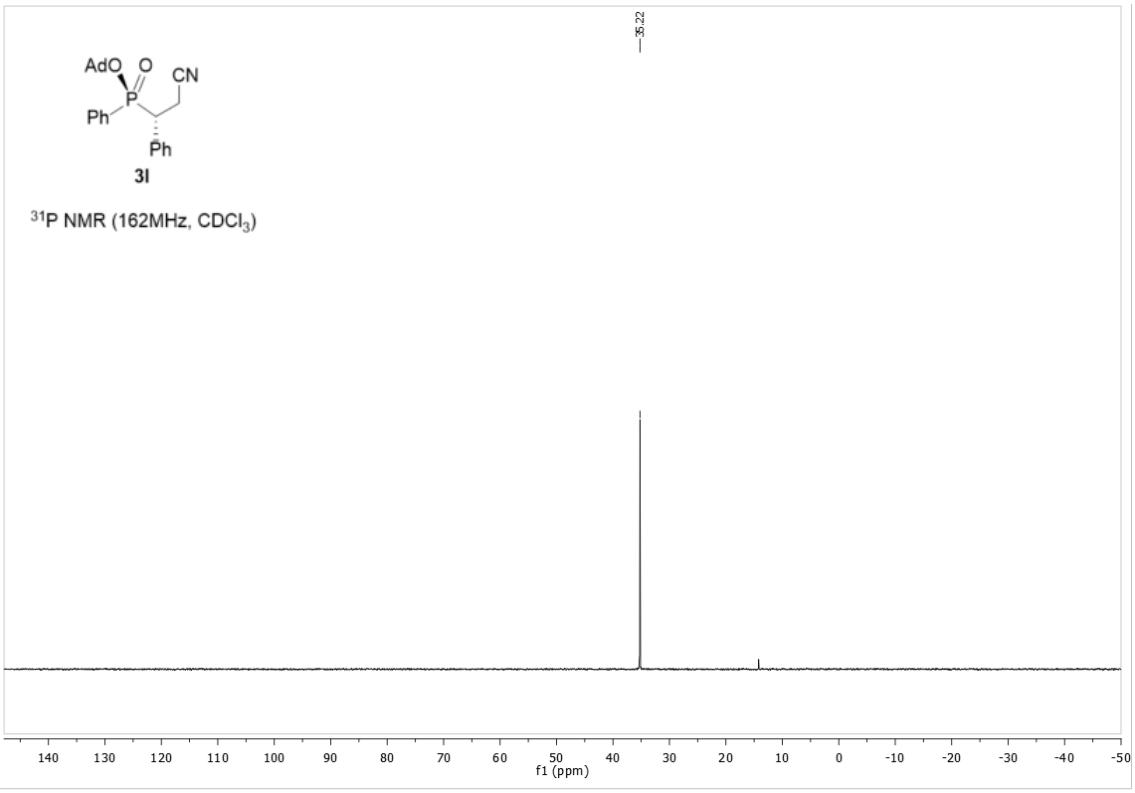
3l

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



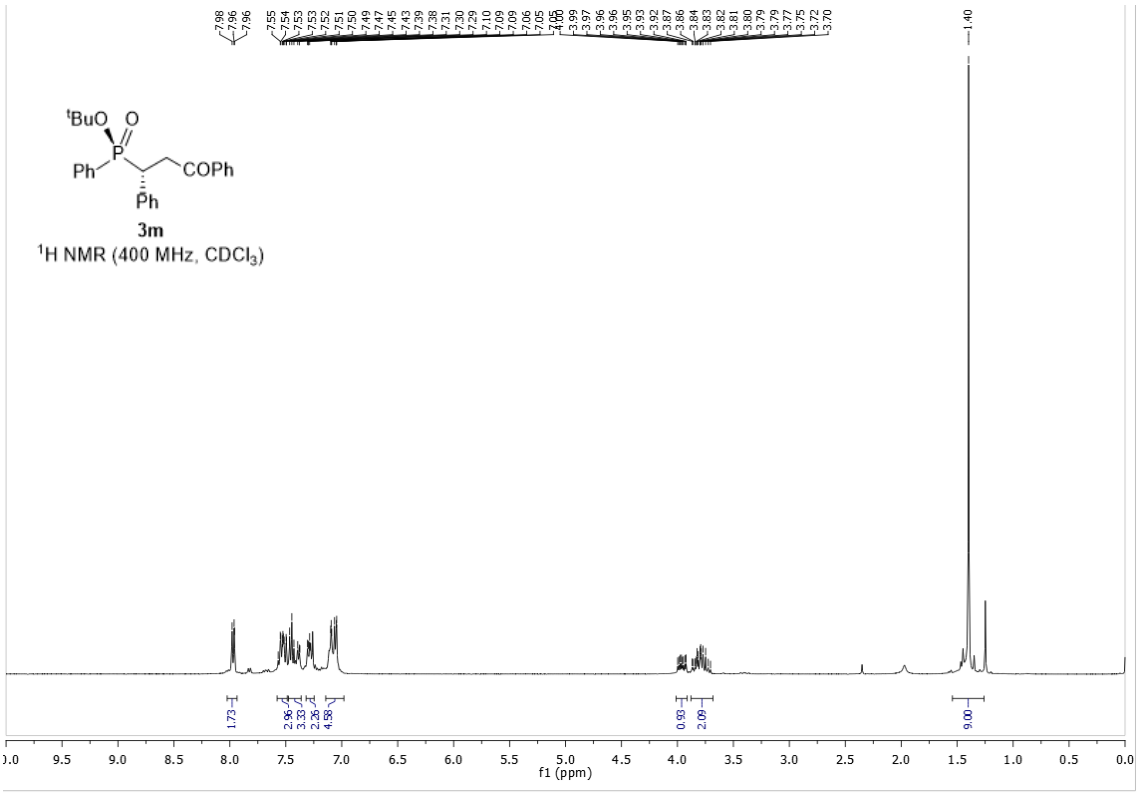
3l

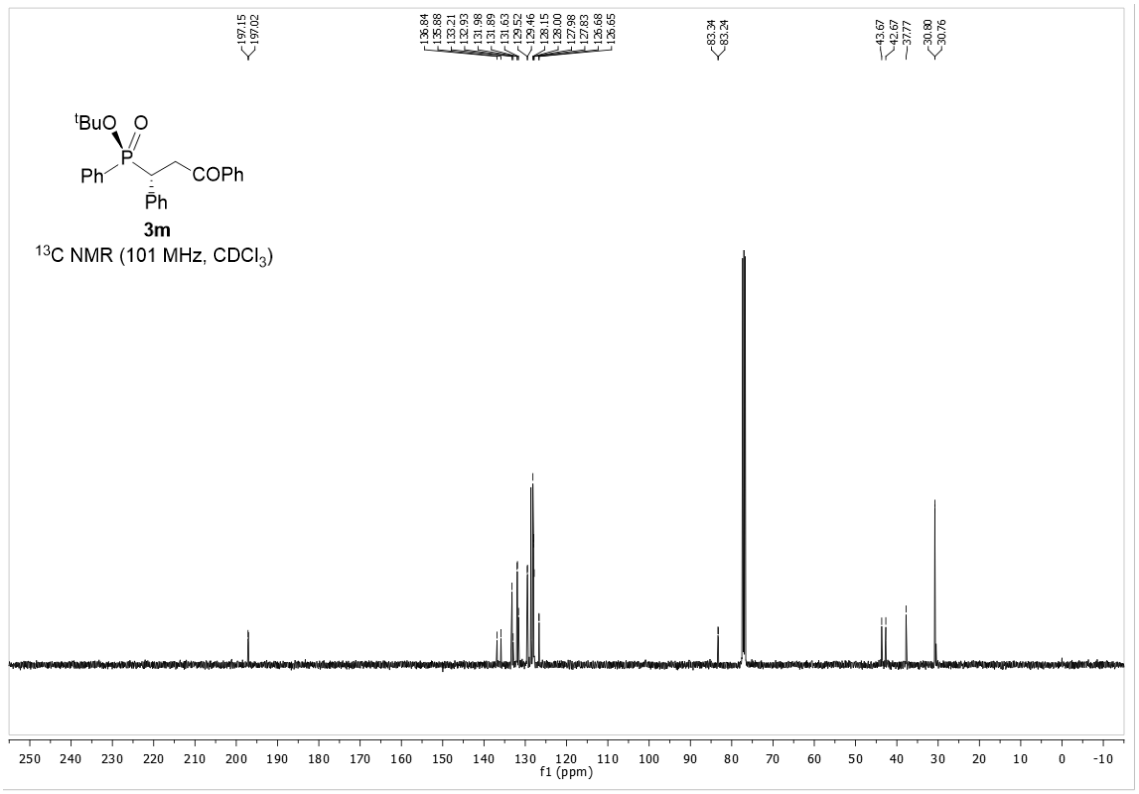
^{13}C NMR (101 MHz, $CDCl_3$)

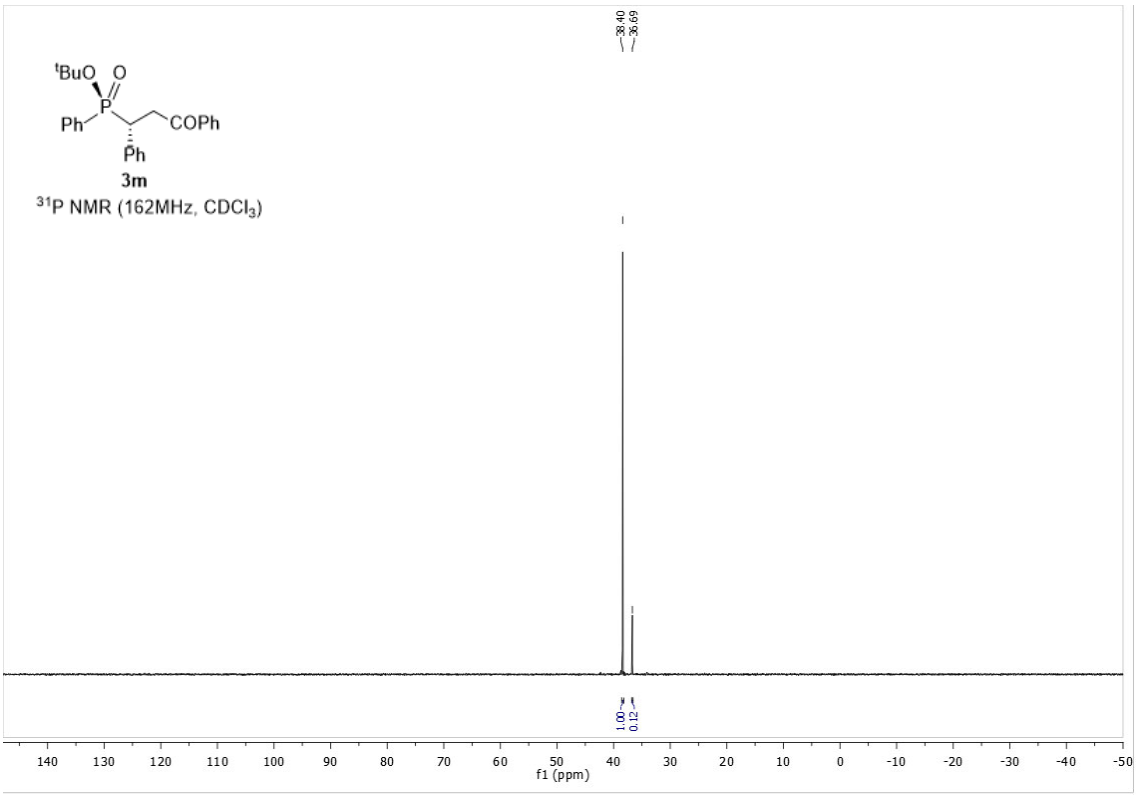


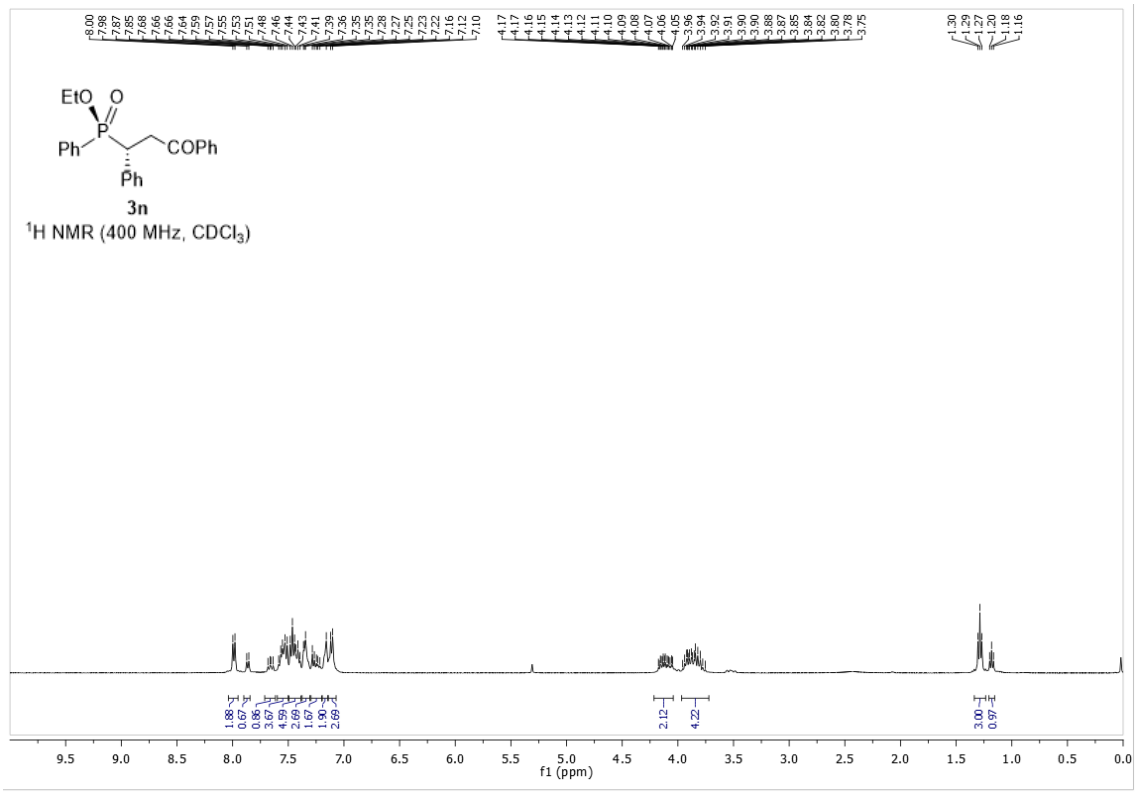
3l

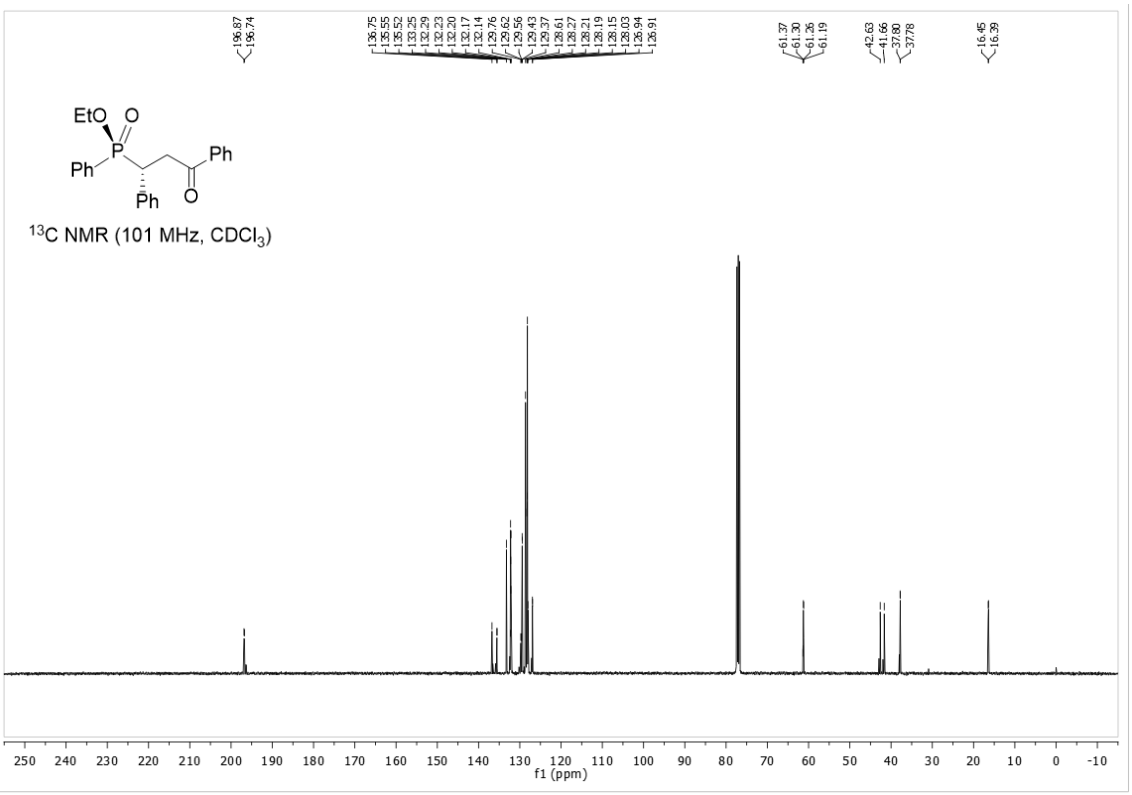
^{31}P NMR (162MHz, $CDCl_3$)

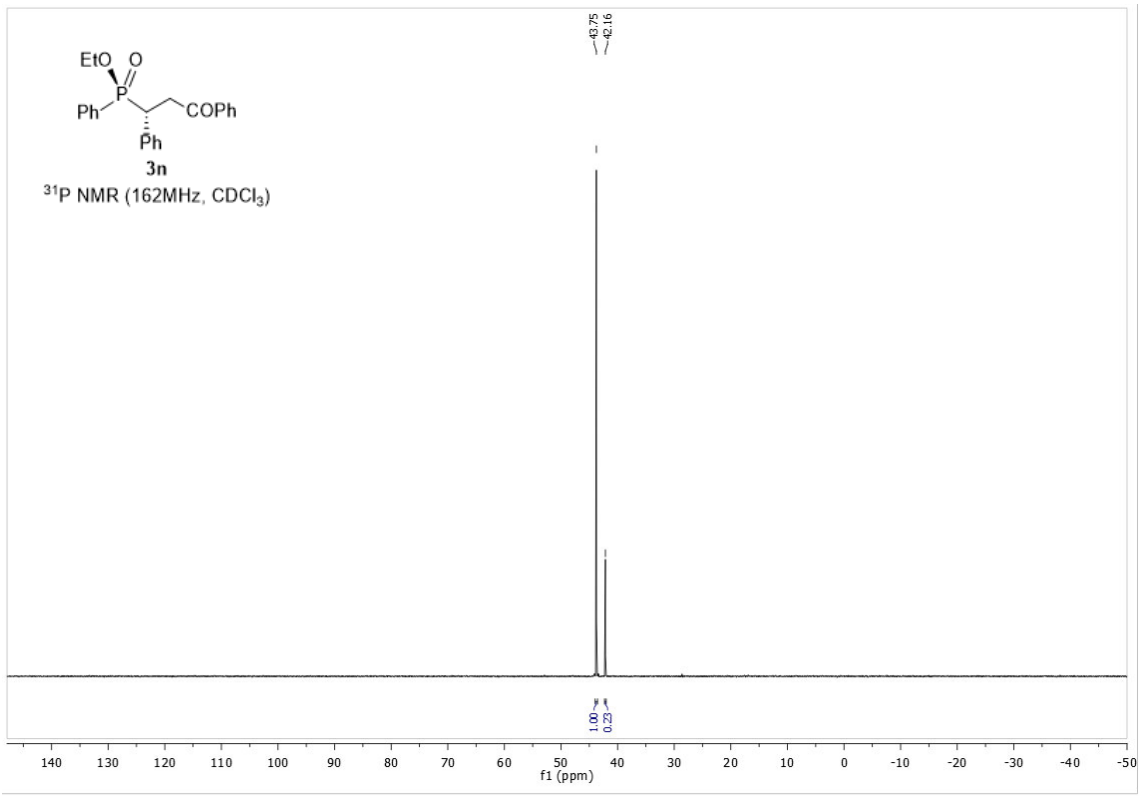

tBuO
O
P
Ph
COPh
Ph
3m
1H NMR (400 MHz, CDCl3)
f1 (ppm)

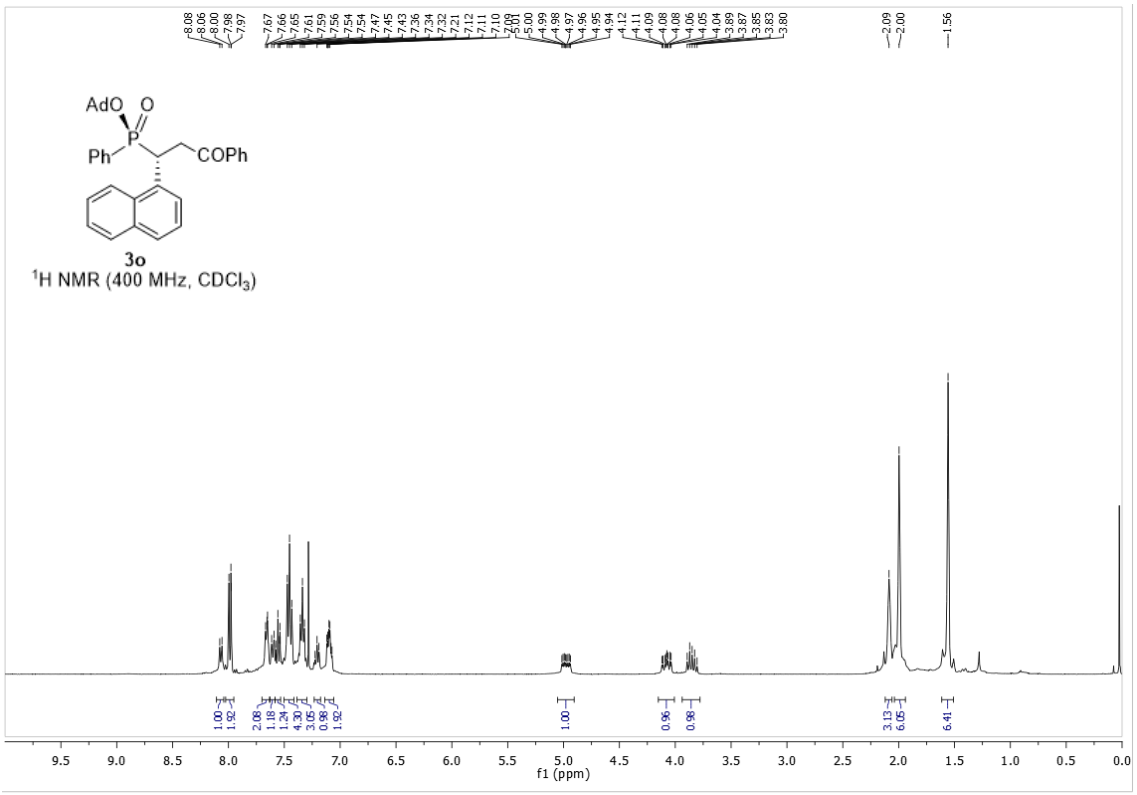

tBuO
O
P
Ph
COPh
Ph
3m
13C NMR (101 MHz, CDCl3)
f1 (ppm)

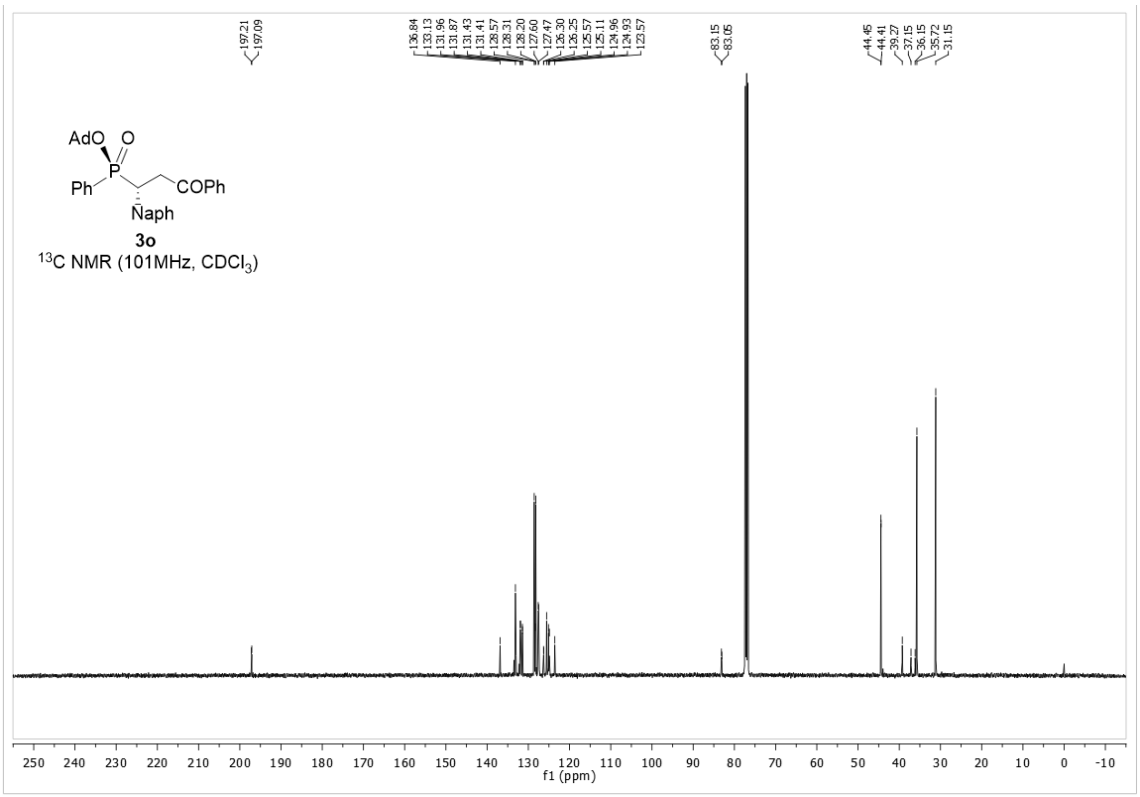

38.40
36.69
tBuO O
Ph
COPh
Ph
3m
31P NMR (162MHz, CDCl3)
1.00
0.12
f1 (ppm)

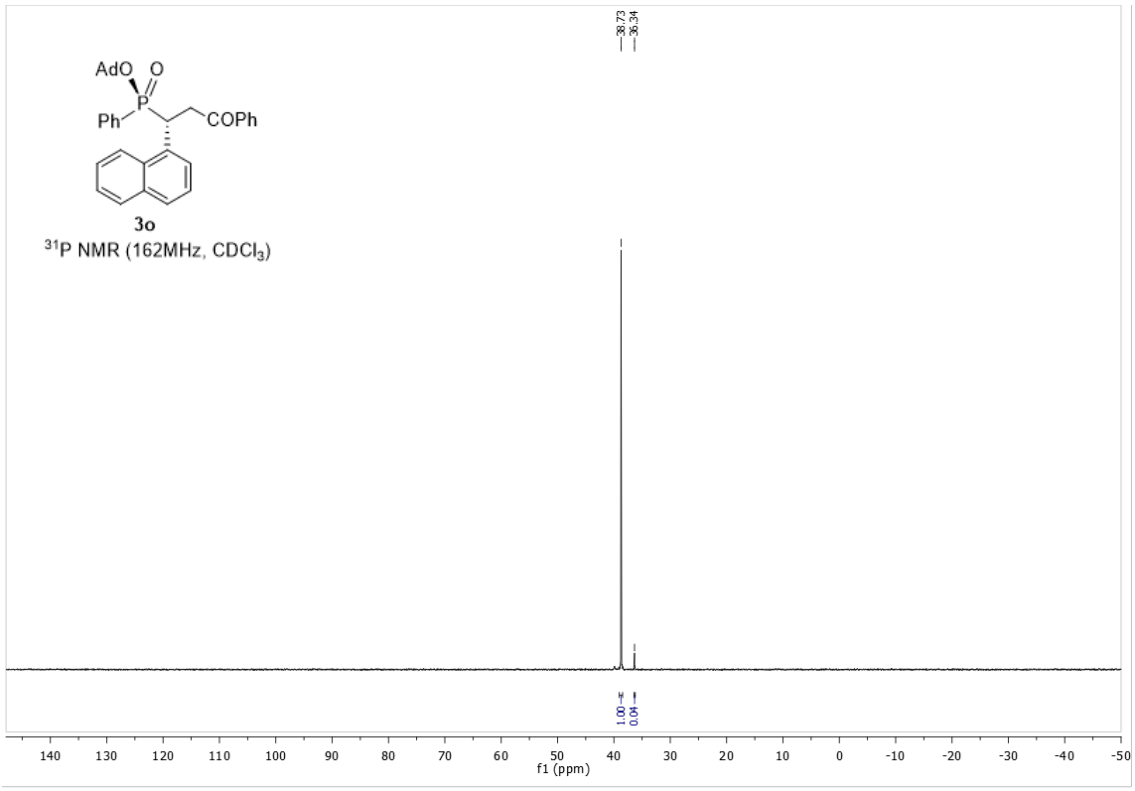

EtO O
Ph
COPh
Ph
3n
1H NMR (400 MHz, CDCl3)
f1 (ppm)

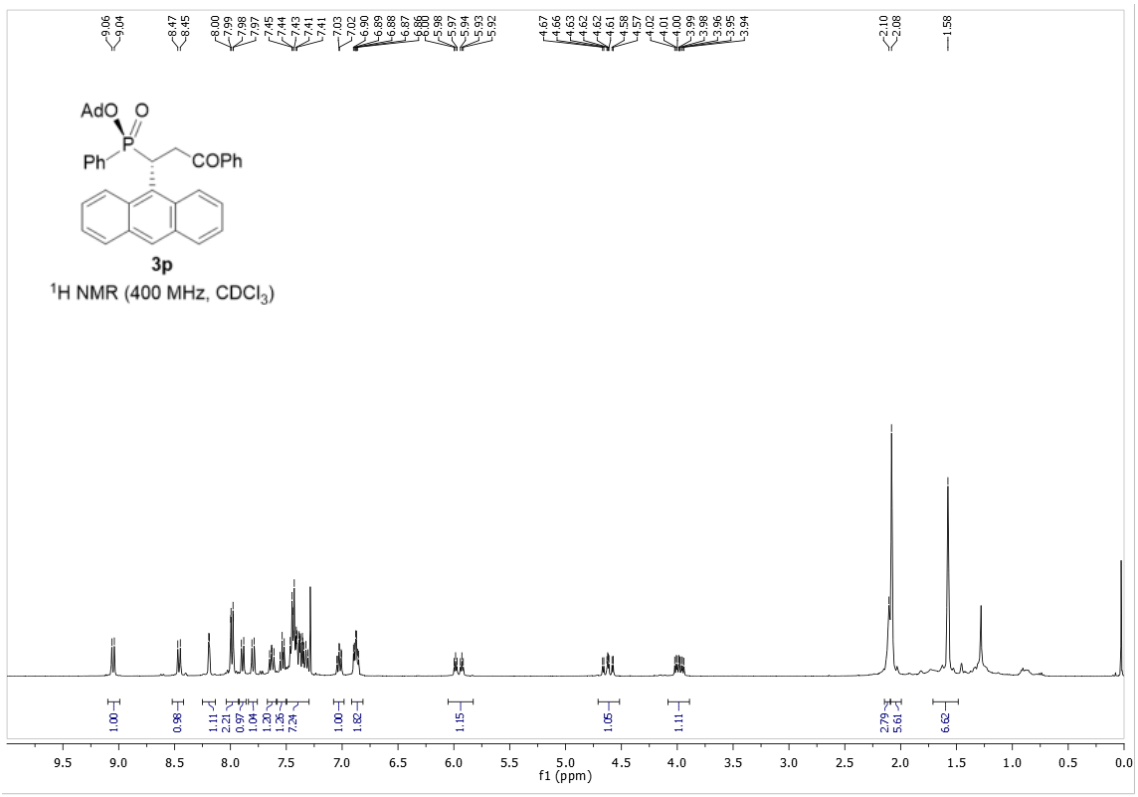

196.87
196.74
136.75
135.55
135.52
133.25
132.29
132.23
132.20
132.17
132.14
129.76
129.62
129.55
129.43
129.37
128.61
128.27
128.21
128.19
128.15
128.03
126.94
126.91
61.37
61.30
61.26
61.19
42.63
41.66
37.80
37.78
16.45
16.39
EtO
O
P
Ph
Ph
Ph
O
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

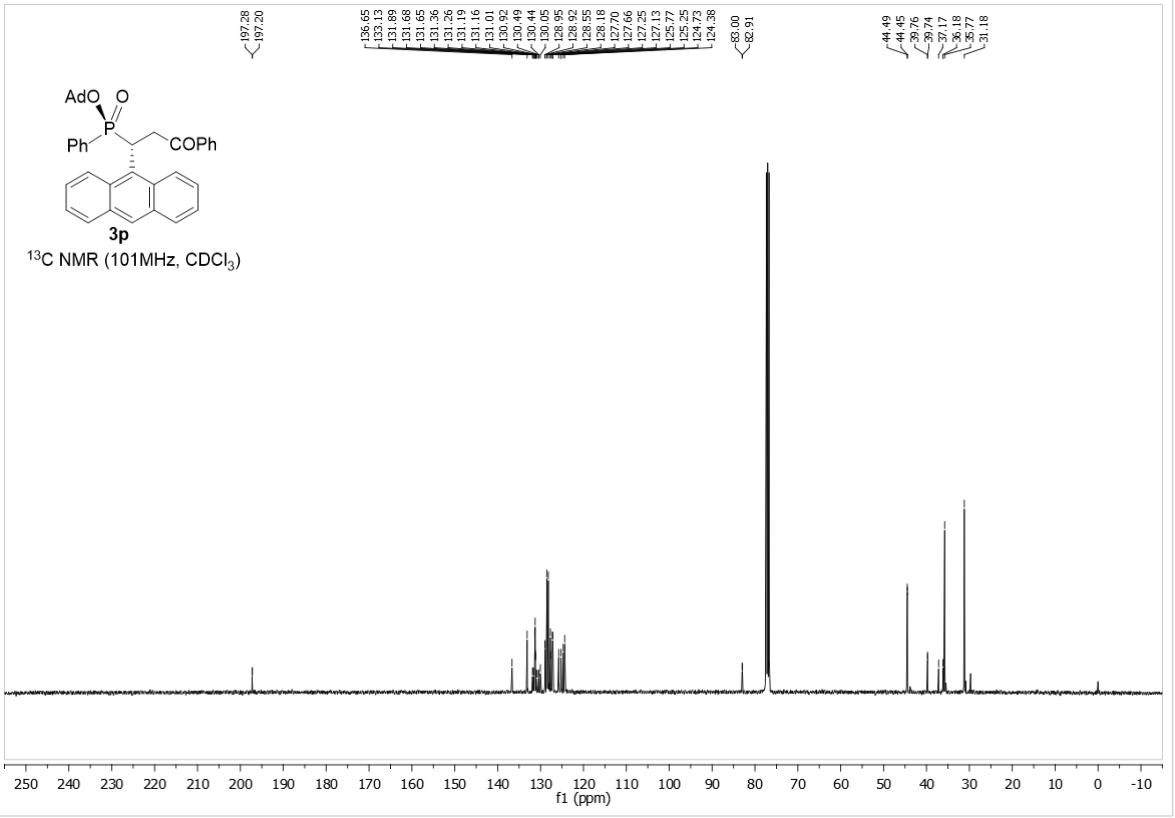

43.75
42.16
EtO
O
P
Ph
COPh
Ph
3n
31P NMR (162MHz, CDCl3)
1.00
0.23
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

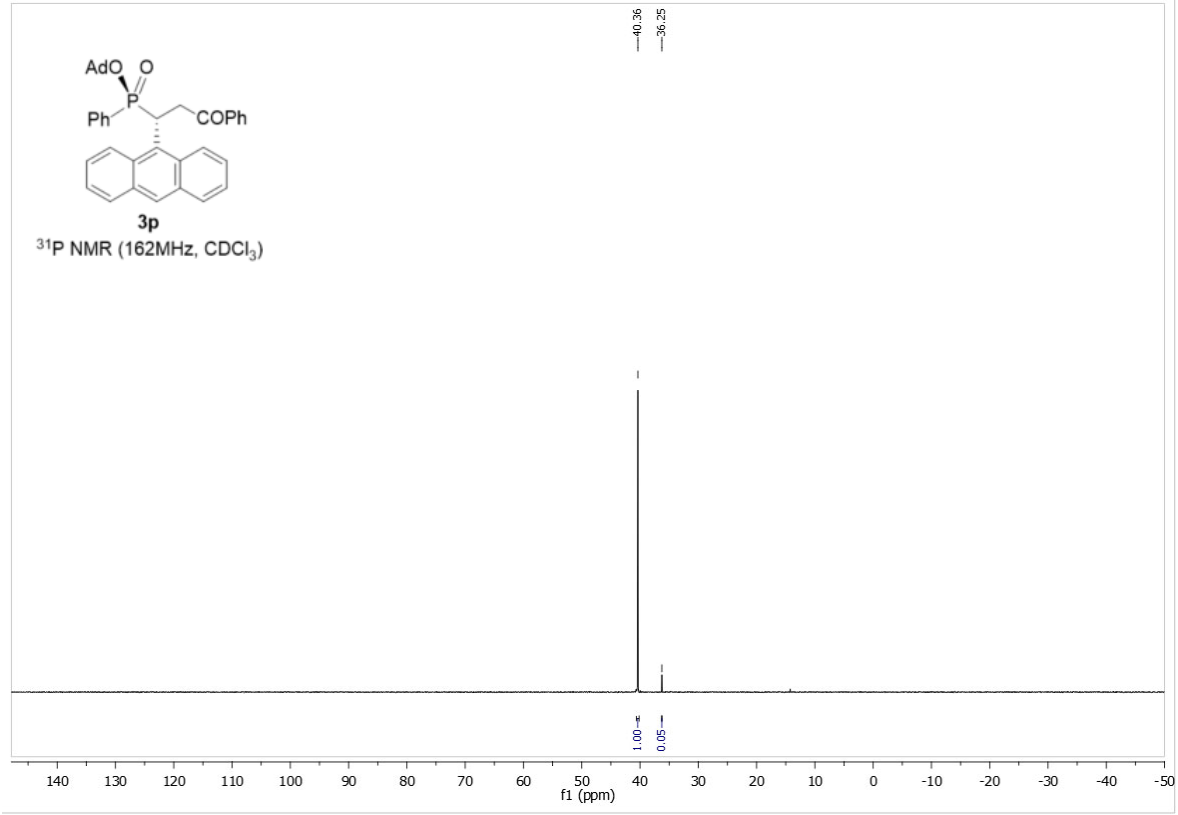

AdO
O
P
Ph
COPh
3o
1H NMR (400 MHz, CDCl3)
f1 (ppm)

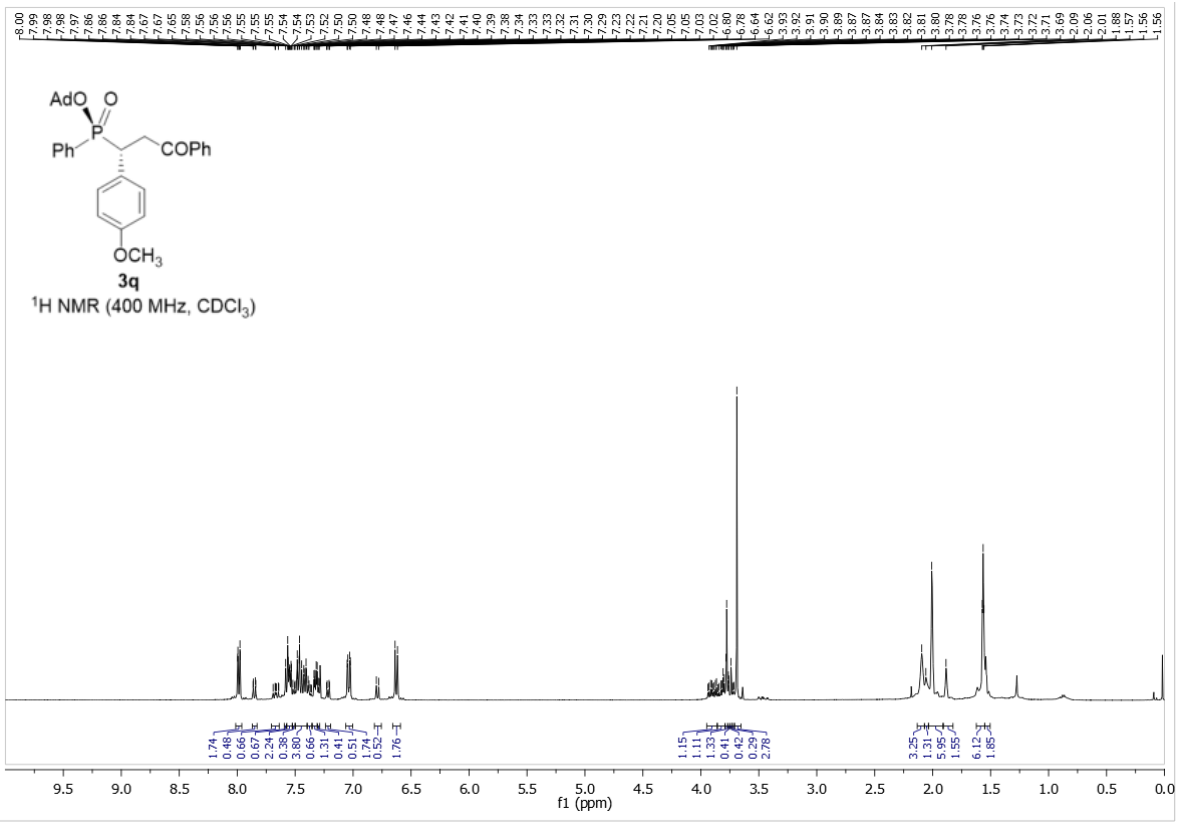

AdO
O
P
Ph
COPh
Naph
3o
13C NMR (101MHz, CDCl3)
f1 (ppm)

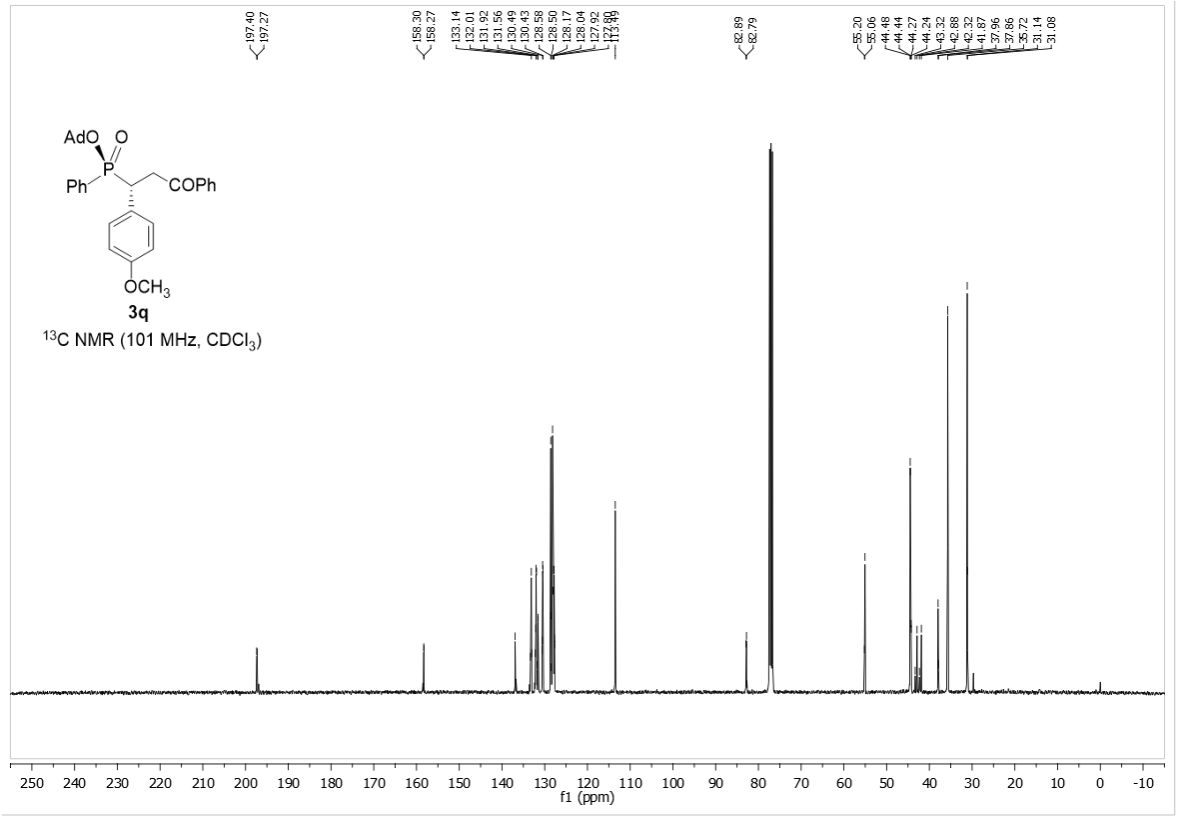

AdO
O
Ph
P
COPh
3o
31P NMR (162MHz, CDCl3)
38.73
36.34
1.00
0.04
f1 (ppm)

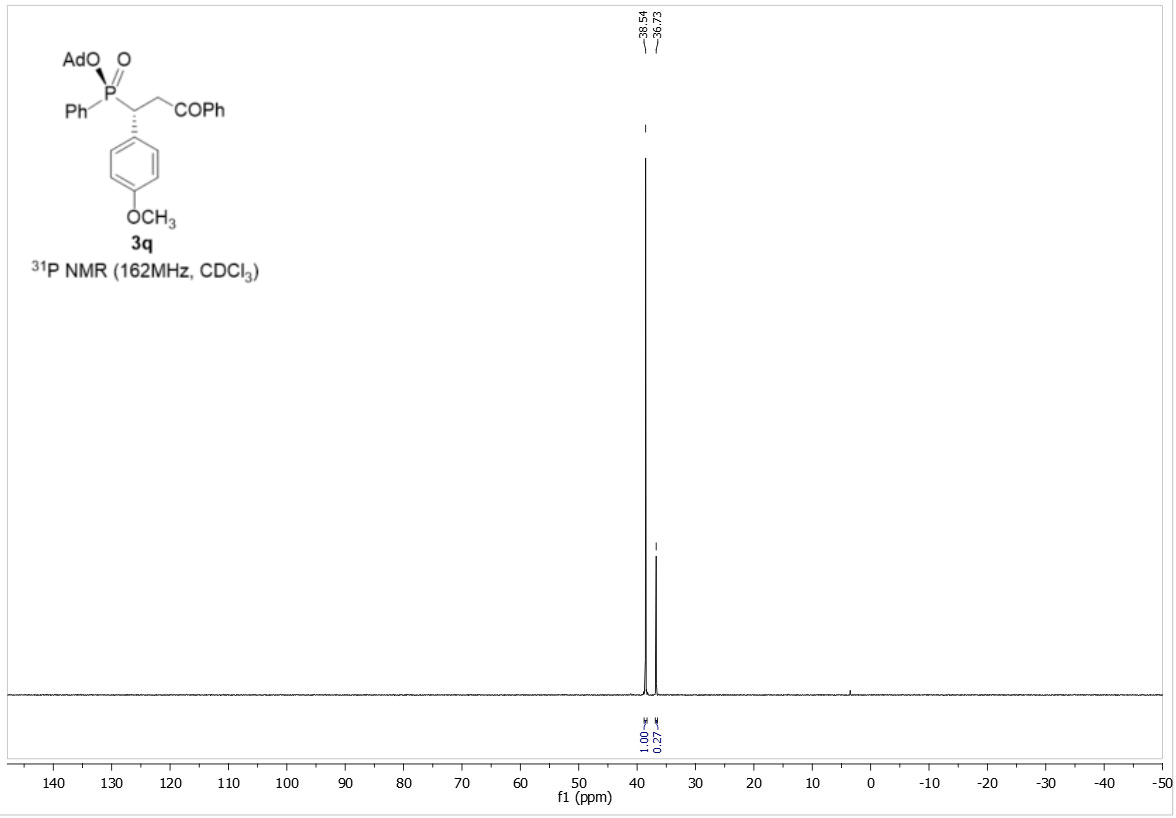

AdO
O
Ph
P
COPh
3p
1H NMR (400 MHz, CDCl3)
f1 (ppm)


AdO
O
P
Ph
COPh
3p
^{13}C NMR (101MHz, CDCl$_3$)
f1 (ppm)


AdO
O
P
Ph
COPh
3p
^{31}P NMR (162MHz, CDCl$_3$)
40.36
36.25
1.00
0.05
f1 (ppm)

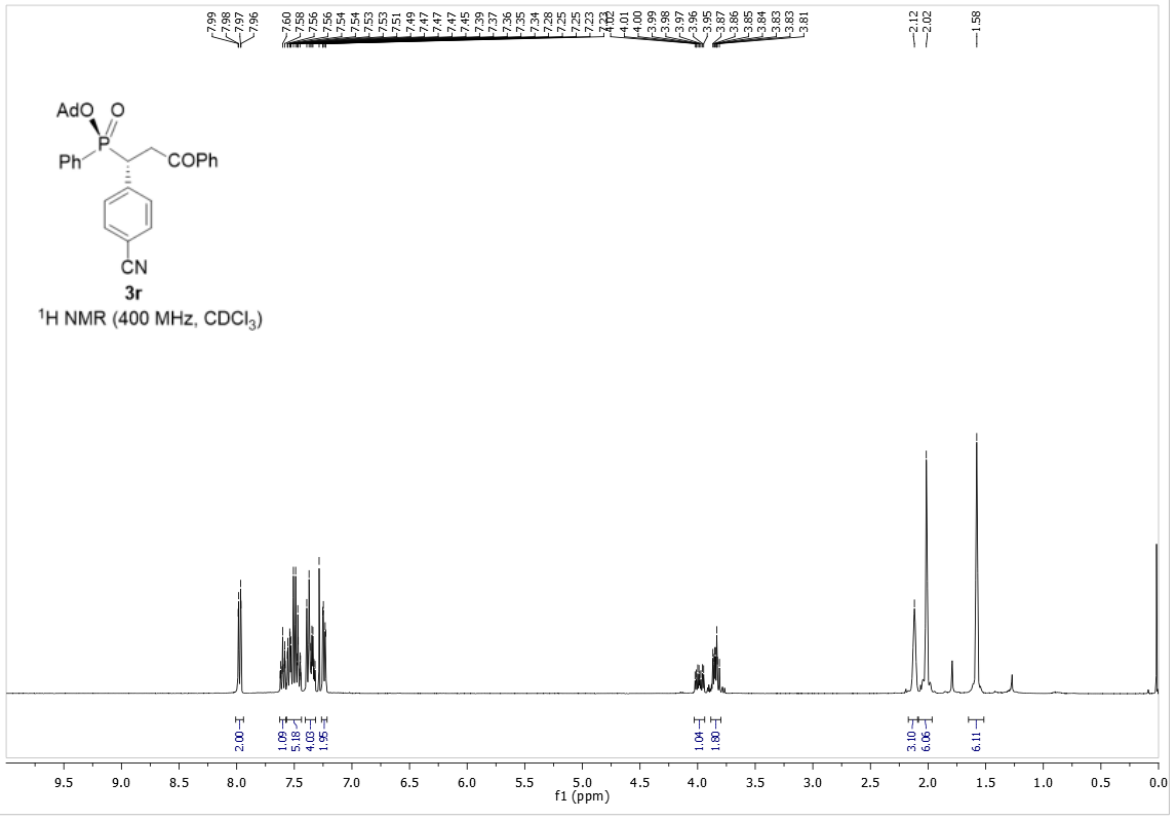

AdO
O
P
Ph
COPh
OCH3
3q
1H NMR (400 MHz, CDCl3)
f1 (ppm)


AdO
O
P
Ph
COPh
OCH3
3q
13C NMR (101 MHz, CDCl3)
f1 (ppm)



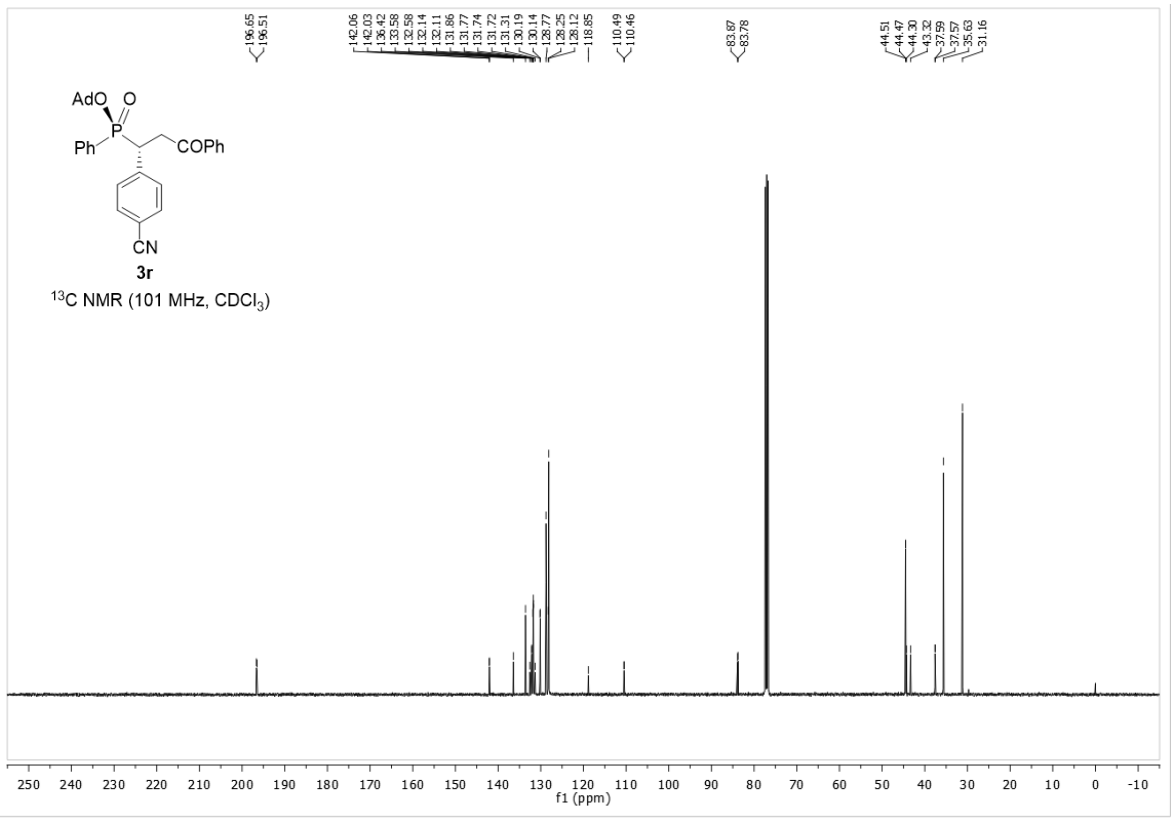
3q

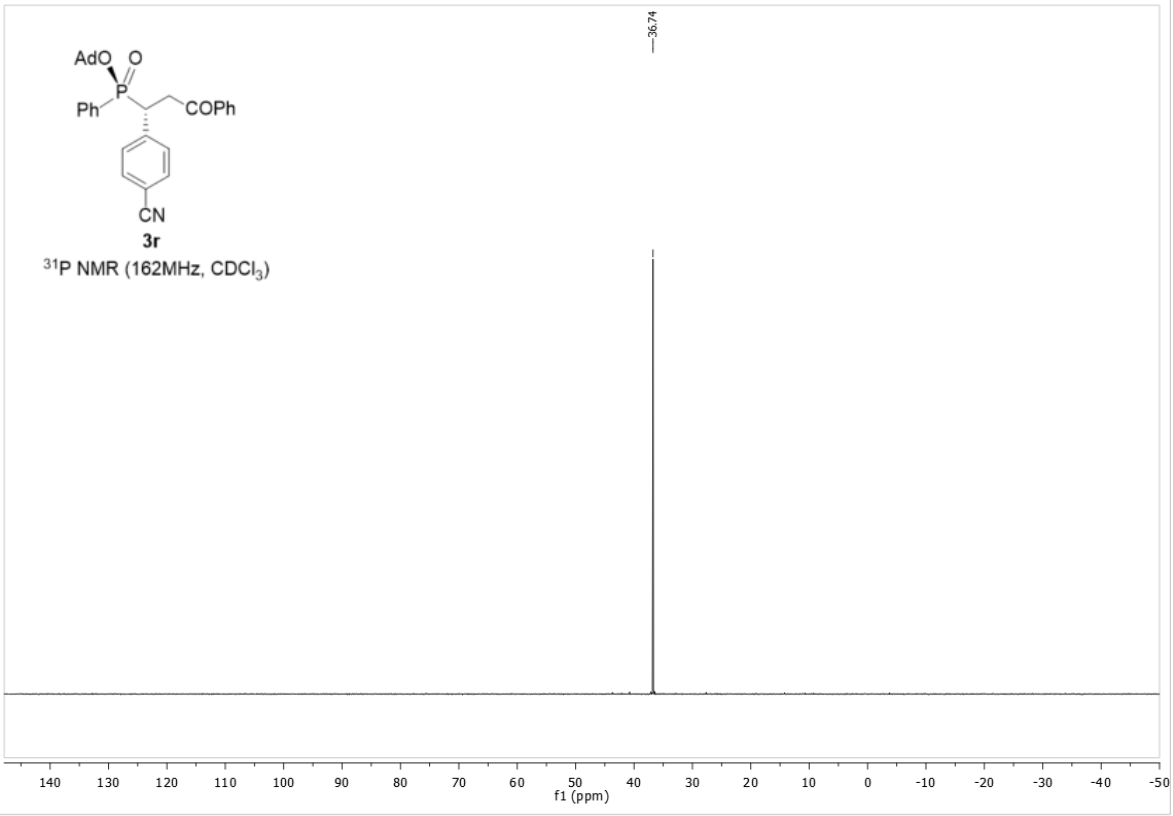
^{31}P NMR (162MHz, $CDCl_3$)

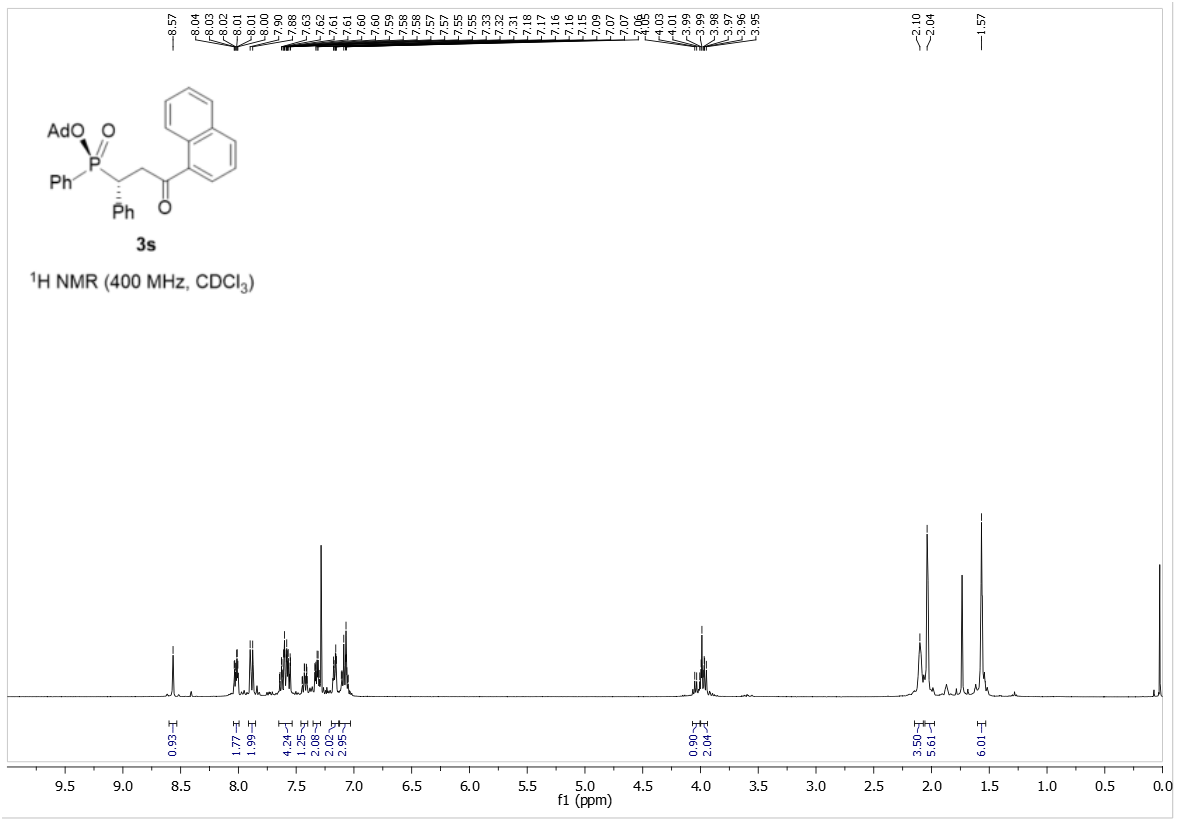


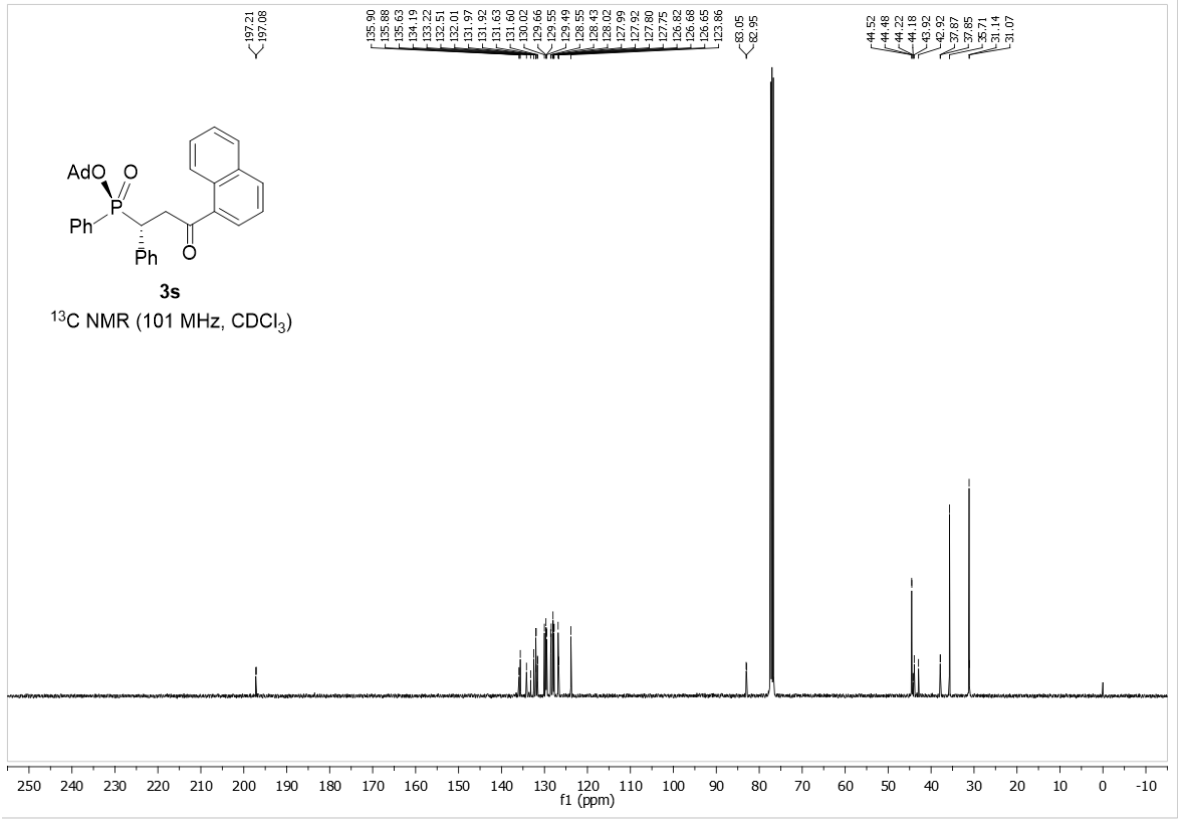
3r

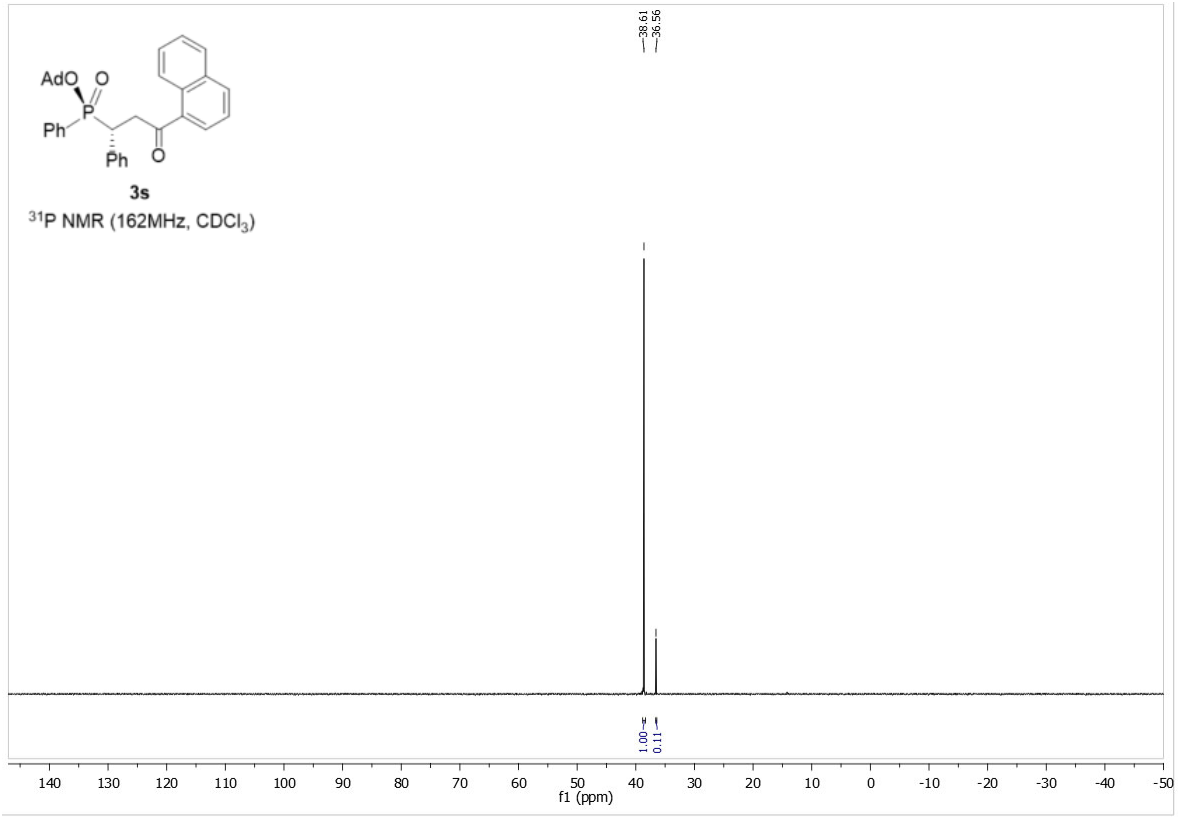
^{1}H NMR (400 MHz, $CDCl_3$)

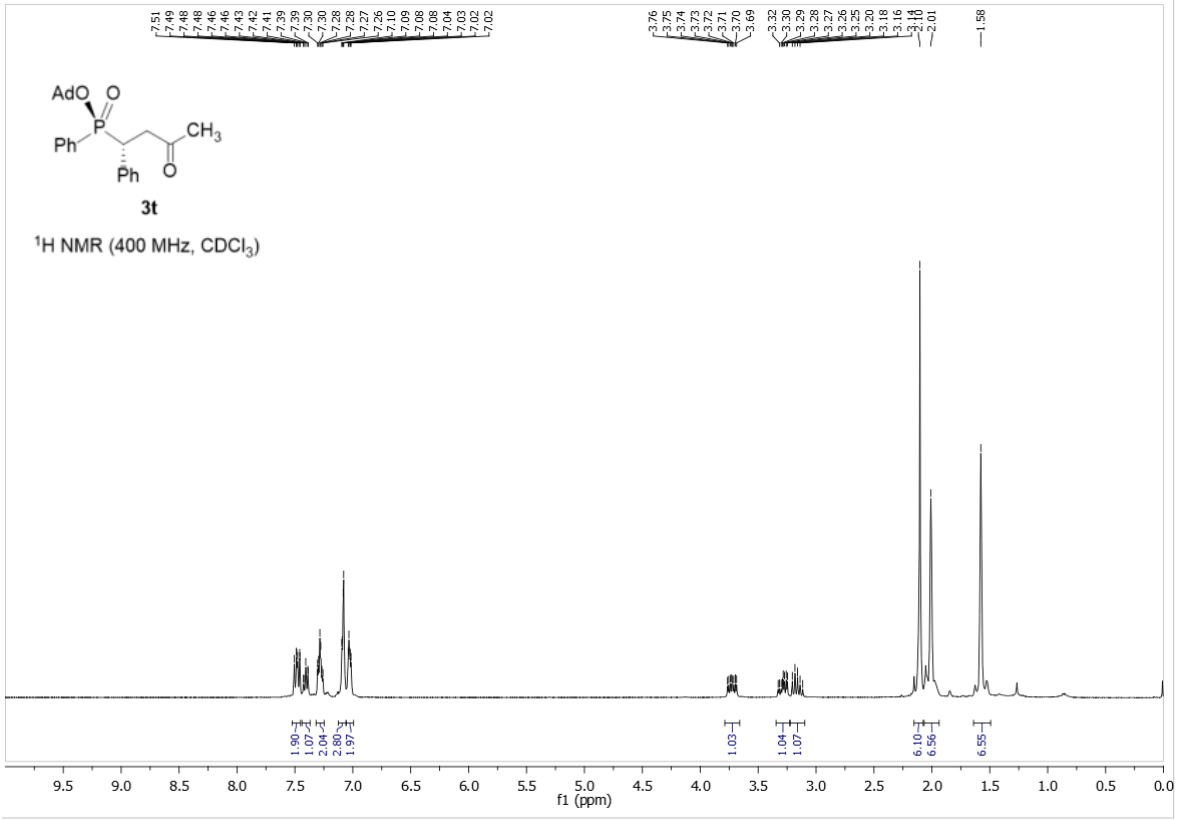

196.65
196.51
142.06
142.03
136.42
133.58
132.58
132.14
132.11
131.86
131.77
131.74
131.72
131.31
130.19
130.14
128.77
128.25
128.12
118.85
110.49
110.46
83.87
83.78
44.51
44.47
44.30
43.32
37.99
37.57
35.63
31.16
AdO
O
P
Ph
COPh
CN
3r
13C NMR (101 MHz, CDCl3)
250 240 230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

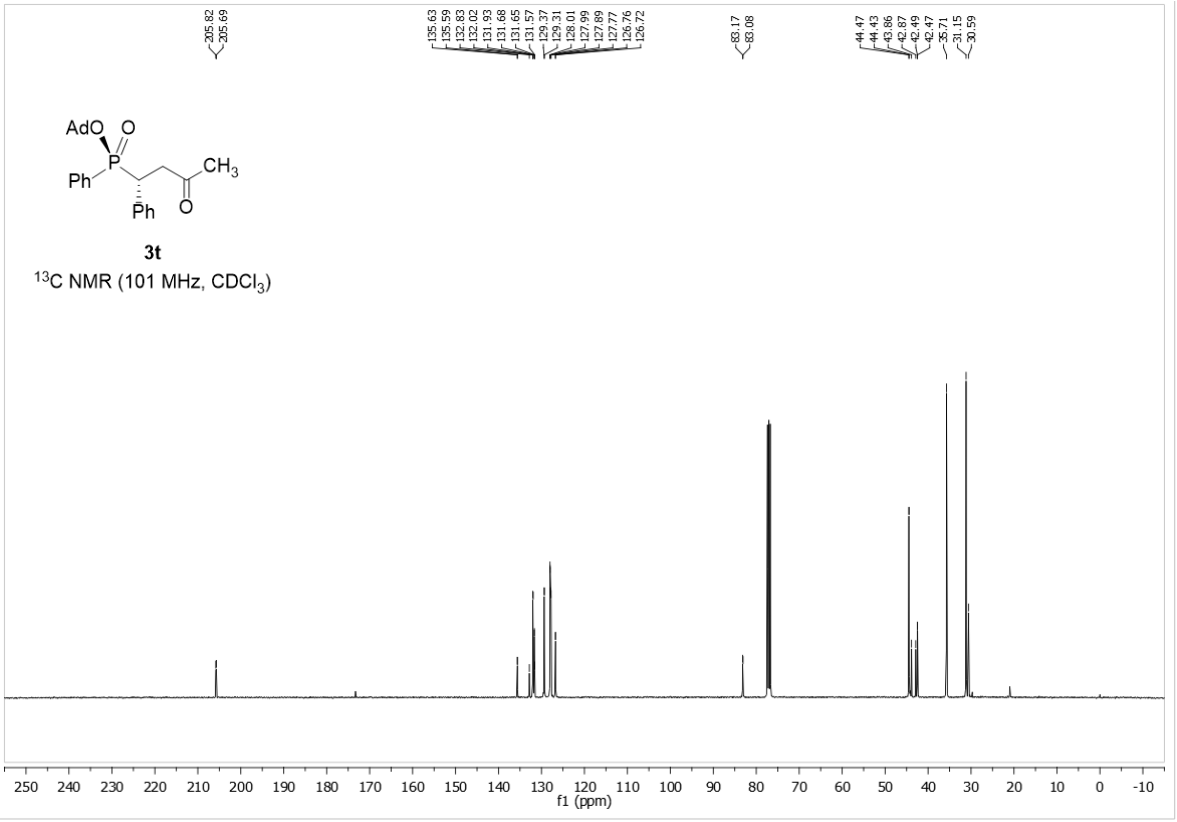

36.74
AdO
O
P
Ph
COPh
CN
3r
31P NMR (162MHz, CDCl3)
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)


AdO
O
P
Ph
Ph
O
3s
1H NMR (400 MHz, CDCl3)
f1 (ppm)


AdO
O
P
Ph
Ph
O
3s
13C NMR (101 MHz, CDCl3)
f1 (ppm)

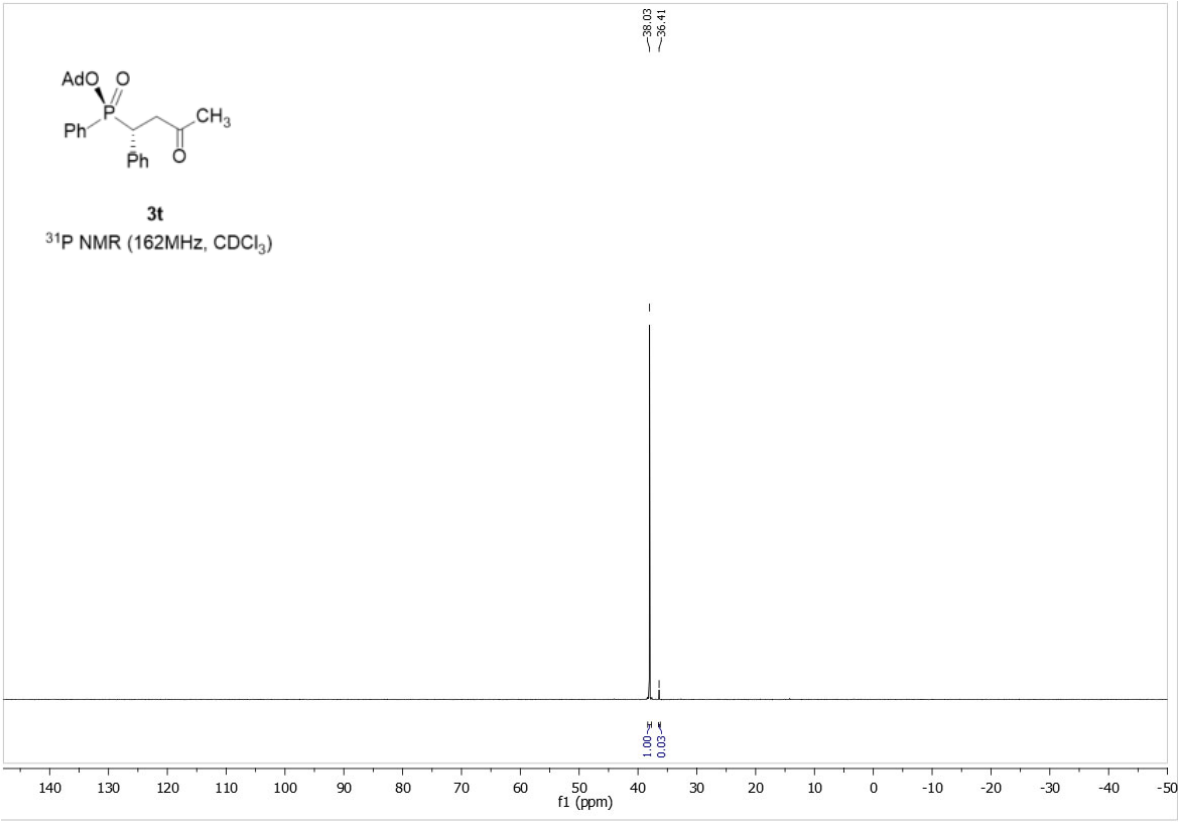

AdO
O
P
Ph
Ph
O
3s
31P NMR (162MHz, CDCl3)
38.61
36.56
1.00
0.11
f1 (ppm)


AdO
O
P
Ph
Ph
CH3
O
3t
1H NMR (400 MHz, CDCl3)
f1 (ppm)



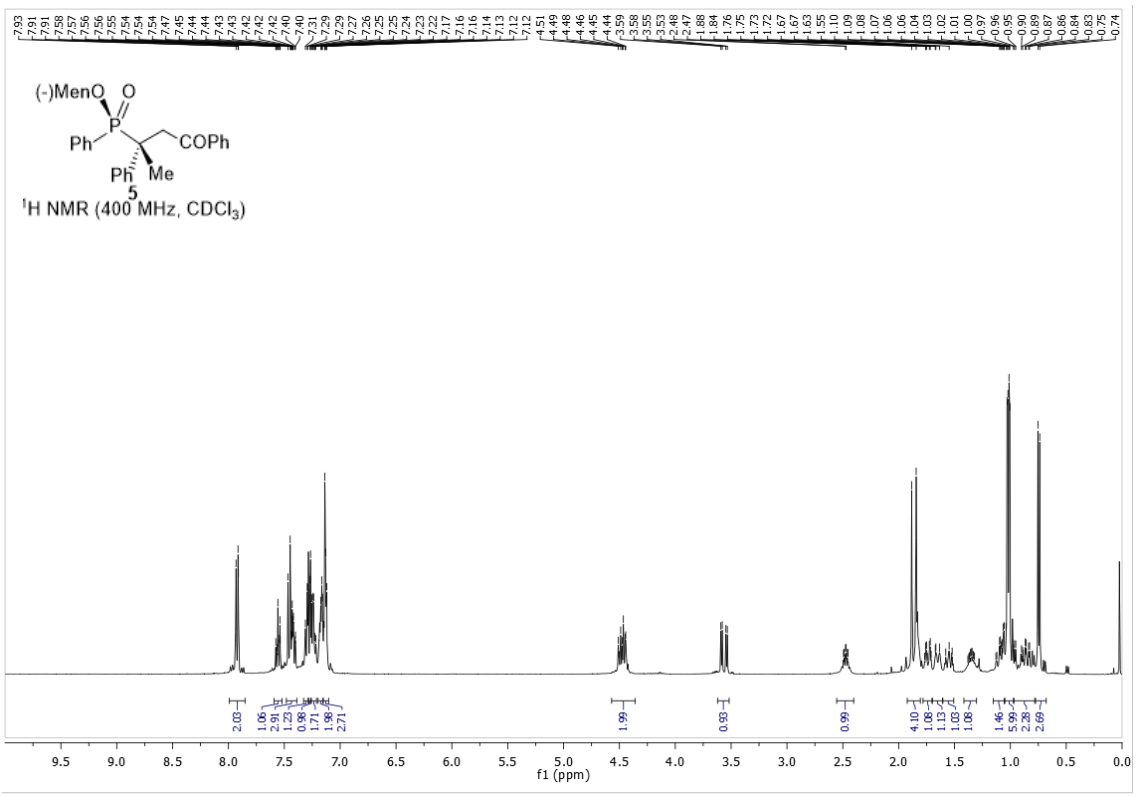
3t

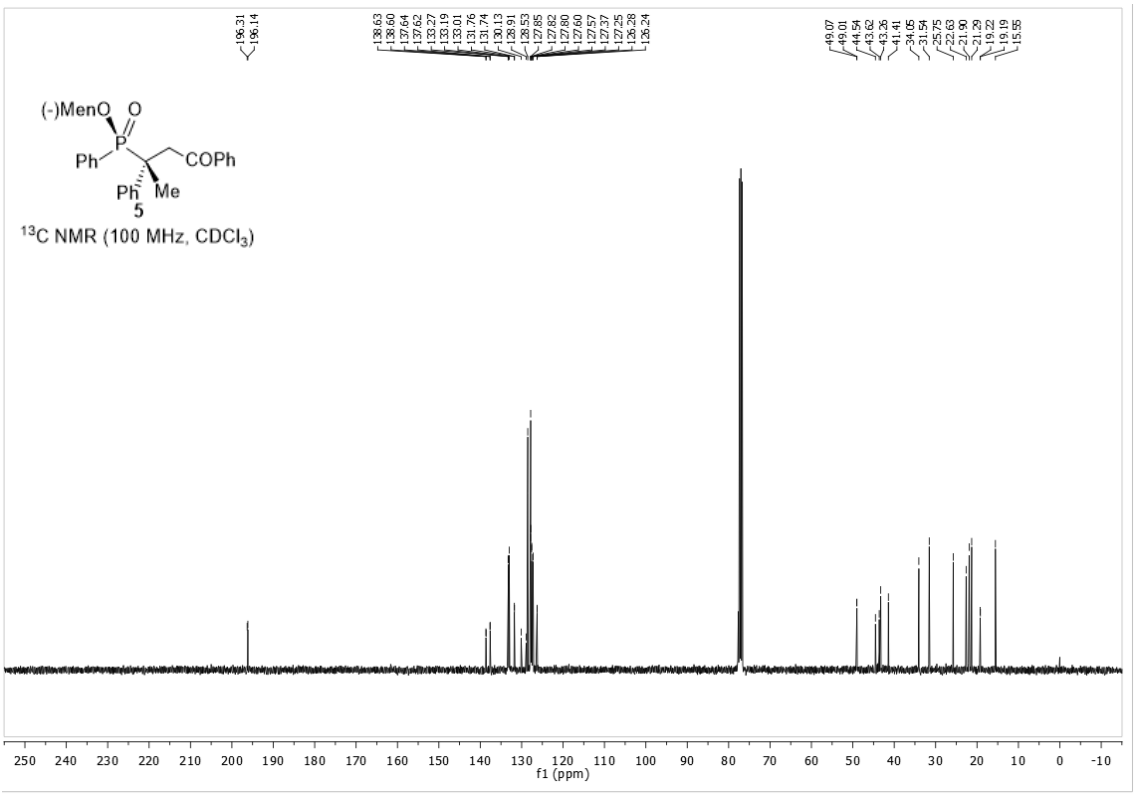
^{13}C NMR (101 MHz, $CDCl_3$)

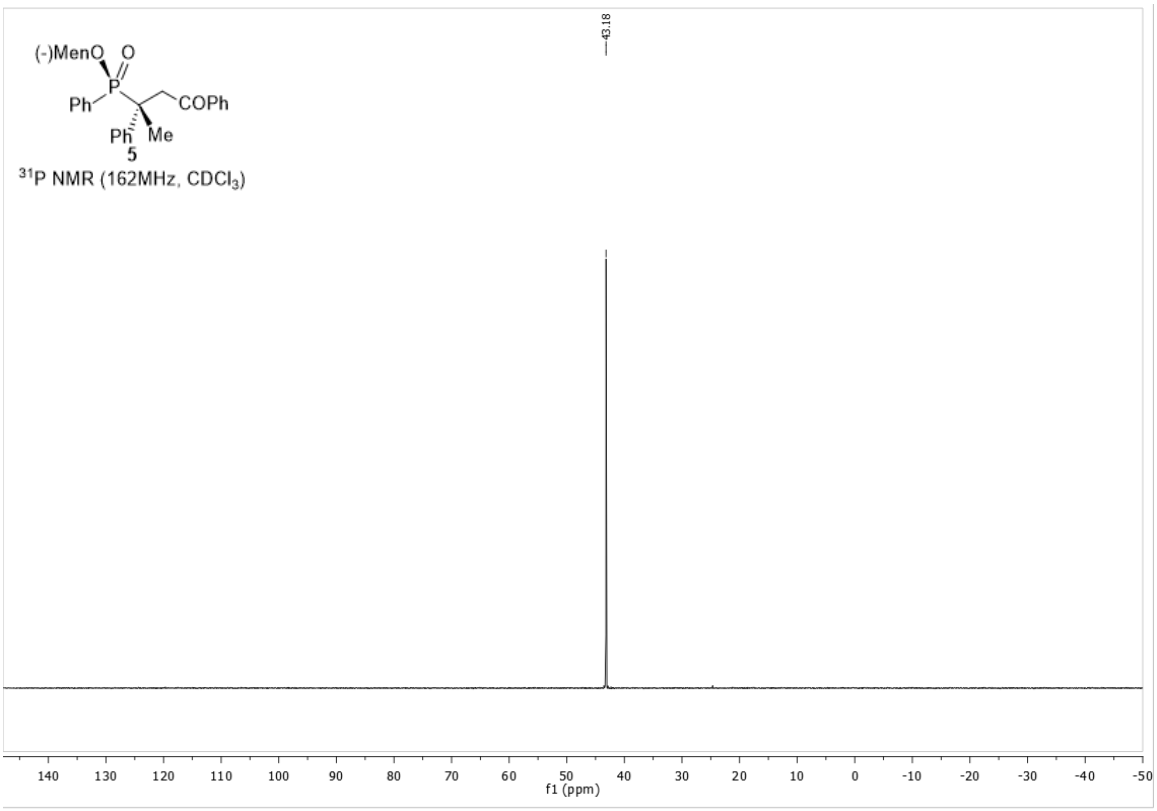


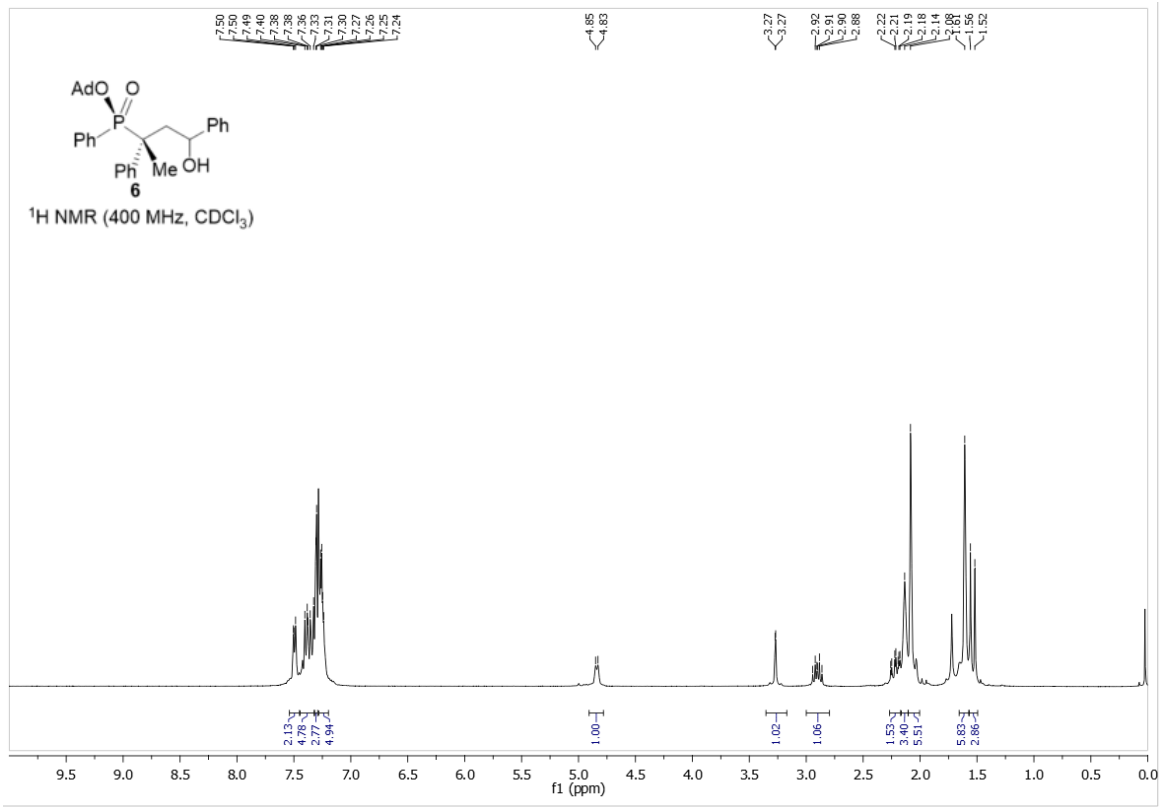
3t

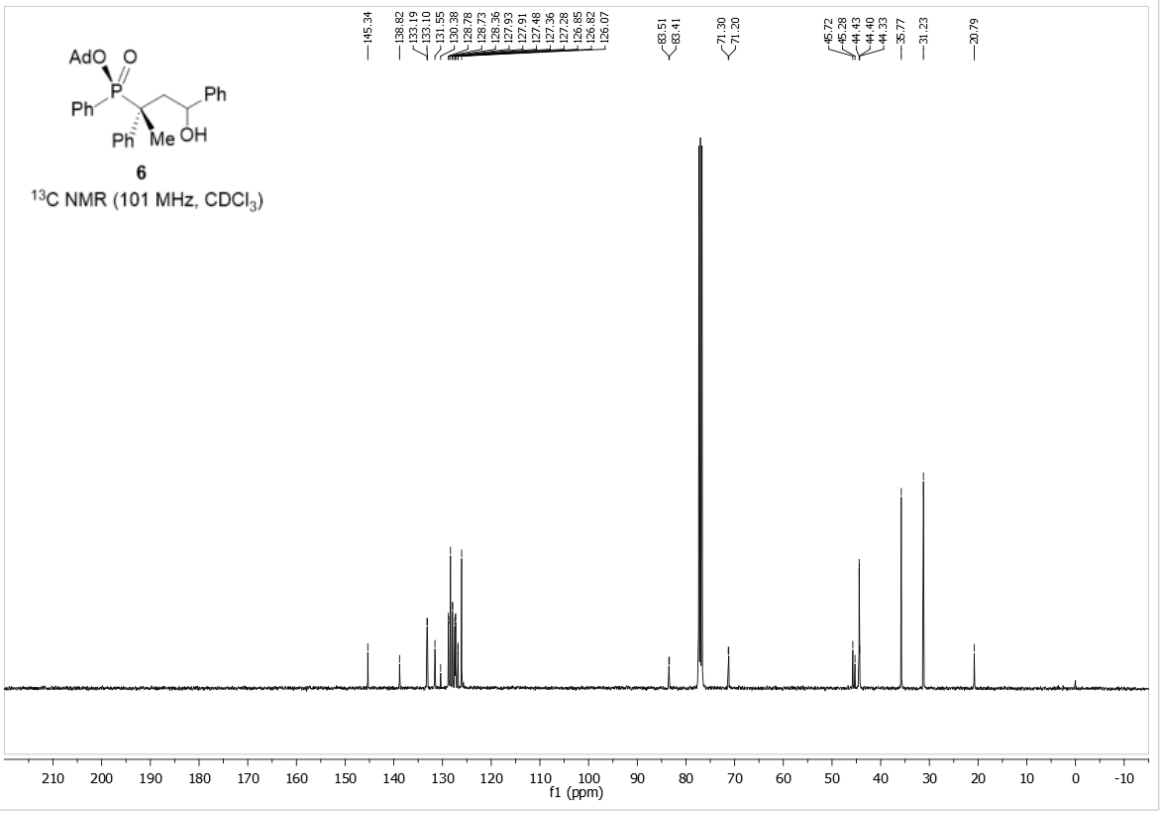
^{31}P NMR (162MHz, $CDCl_3$)

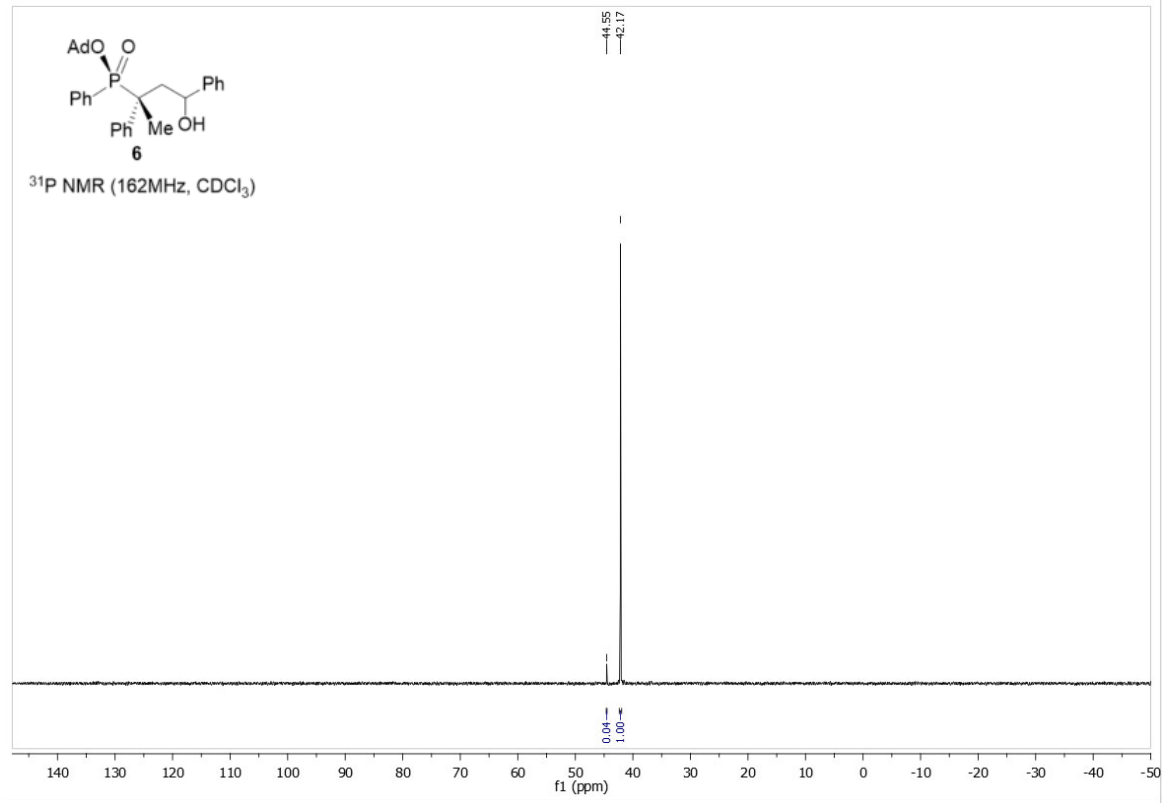

(-)MenO
O
P
Ph
COPh
Ph
Me
5
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

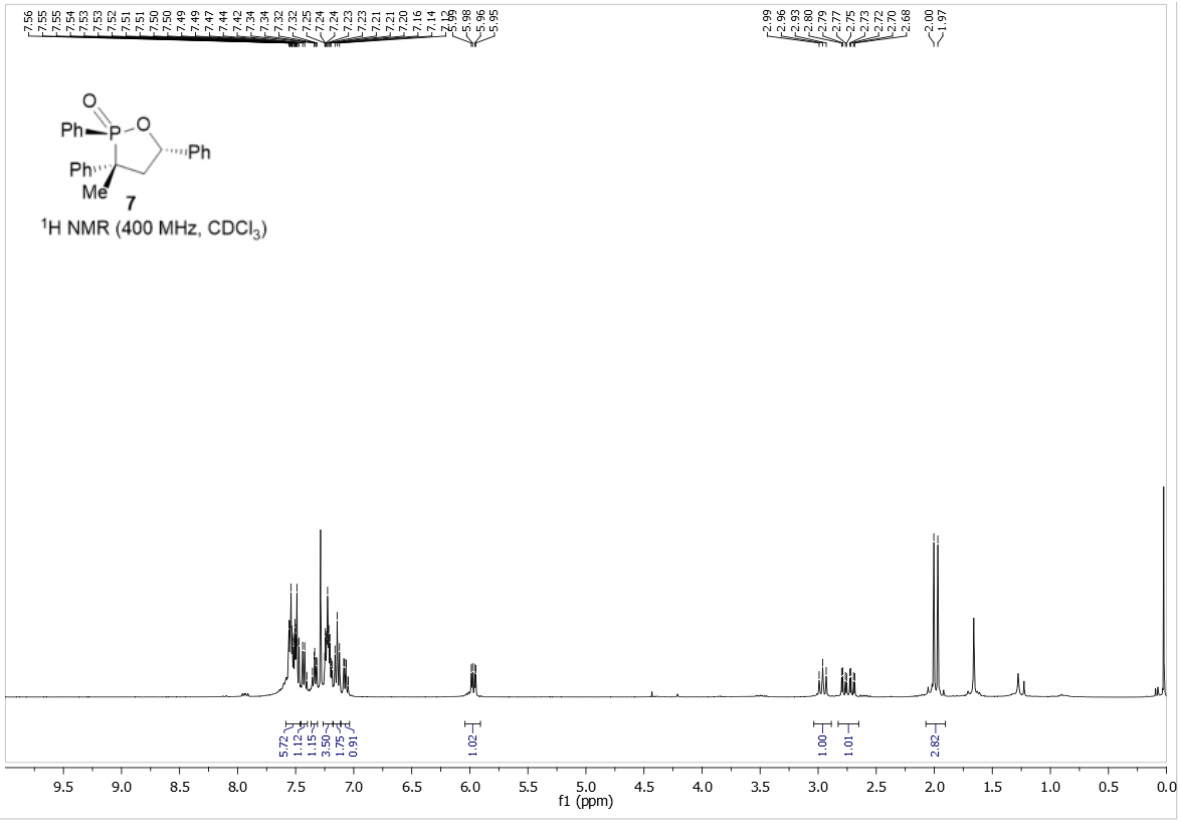

(-)MenO
O
P
Ph
COPh
Ph
Me
5
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)

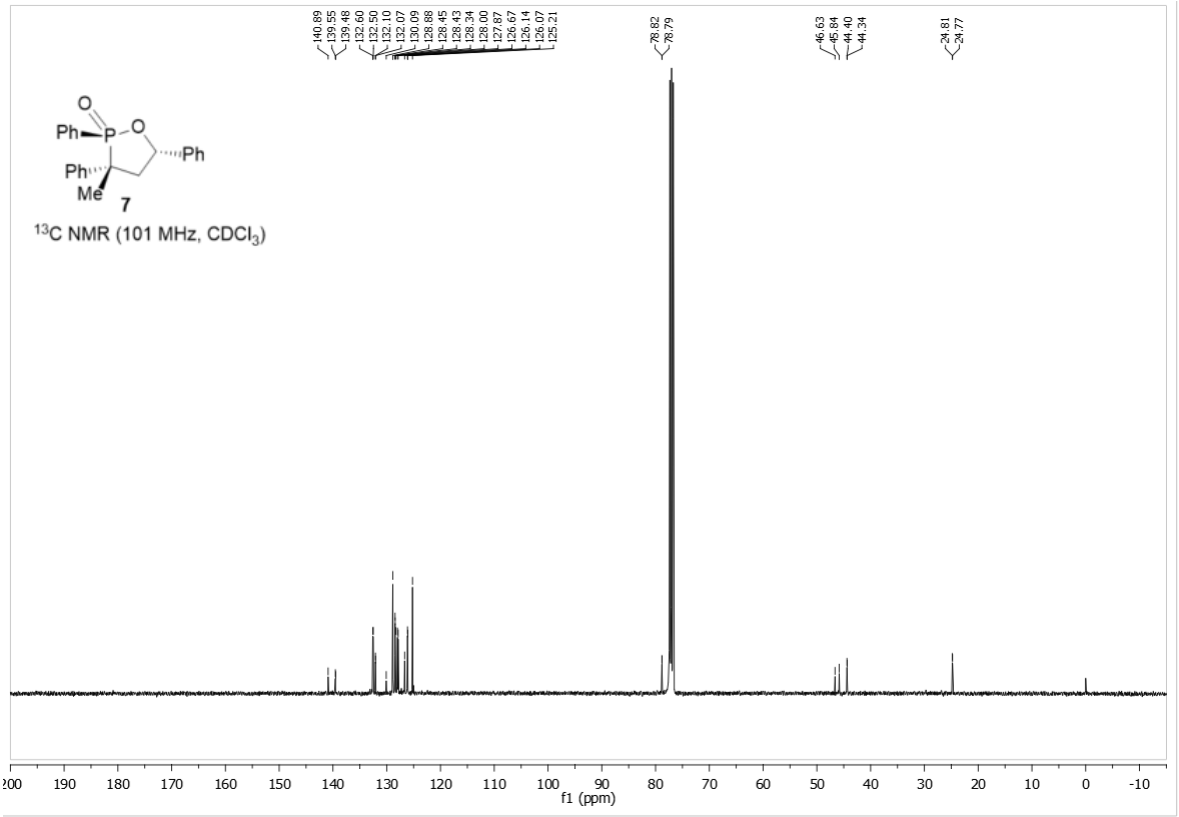

(-)MenO
O
P
Ph
COPh
Ph
Me
5
^{31}P NMR (162MHz, $CDCl_3$)
43.18
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

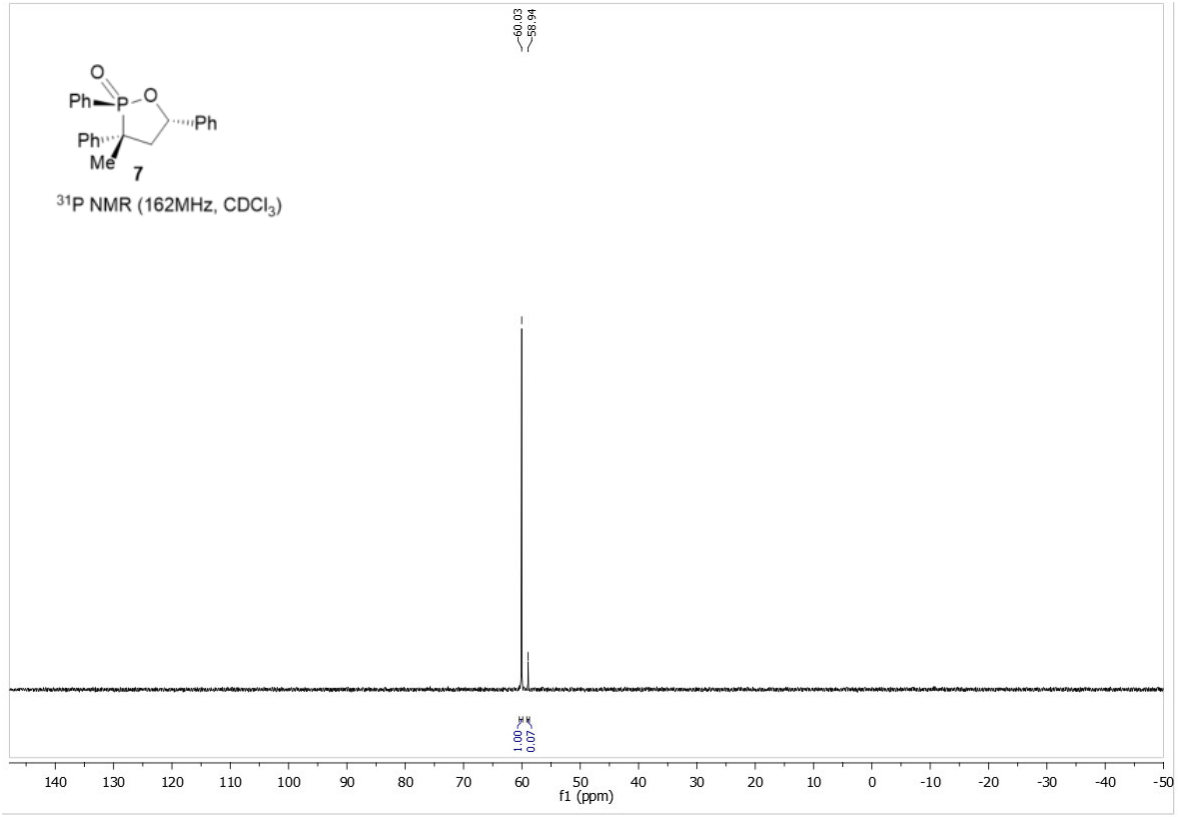

7.50 7.50 7.49 7.40 7.38 7.38 7.36 7.33 7.31 7.30 7.27 7.26 7.25 7.24
4.85 4.83
3.27 3.27
2.92 2.91 2.90 2.88
2.22 2.21 2.19 2.18 2.14 2.08 2.01 1.56 1.52
AdO
O
P
Ph
Ph
Ph
Me
OH
6
^{1}H NMR (400 MHz, $CDCl_3$)
2.13 4.78 2.77 4.94
1.00
1.02
1.06
1.53 3.40 5.51
5.83 2.86
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

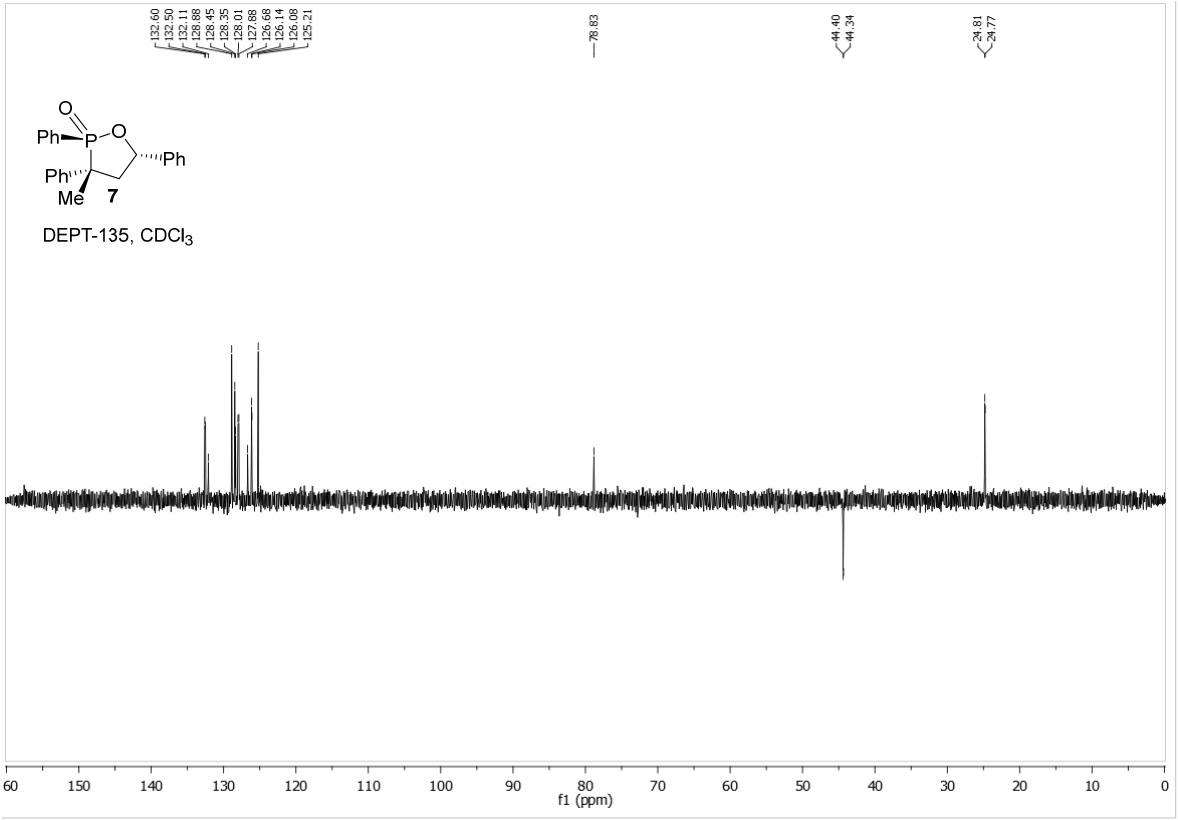

AdO
O
P
Ph
Ph
Ph
Me
OH
Ph
6
^{13}C NMR (101 MHz, CDCl$_3$)
145.34
138.82
133.19
133.10
131.55
130.38
128.78
128.73
128.36
127.93
127.91
127.48
127.36
127.28
126.85
126.82
126.07
83.51
83.41
71.30
71.20
45.72
45.28
44.43
44.40
44.33
35.77
31.23
20.79
f1 (ppm)

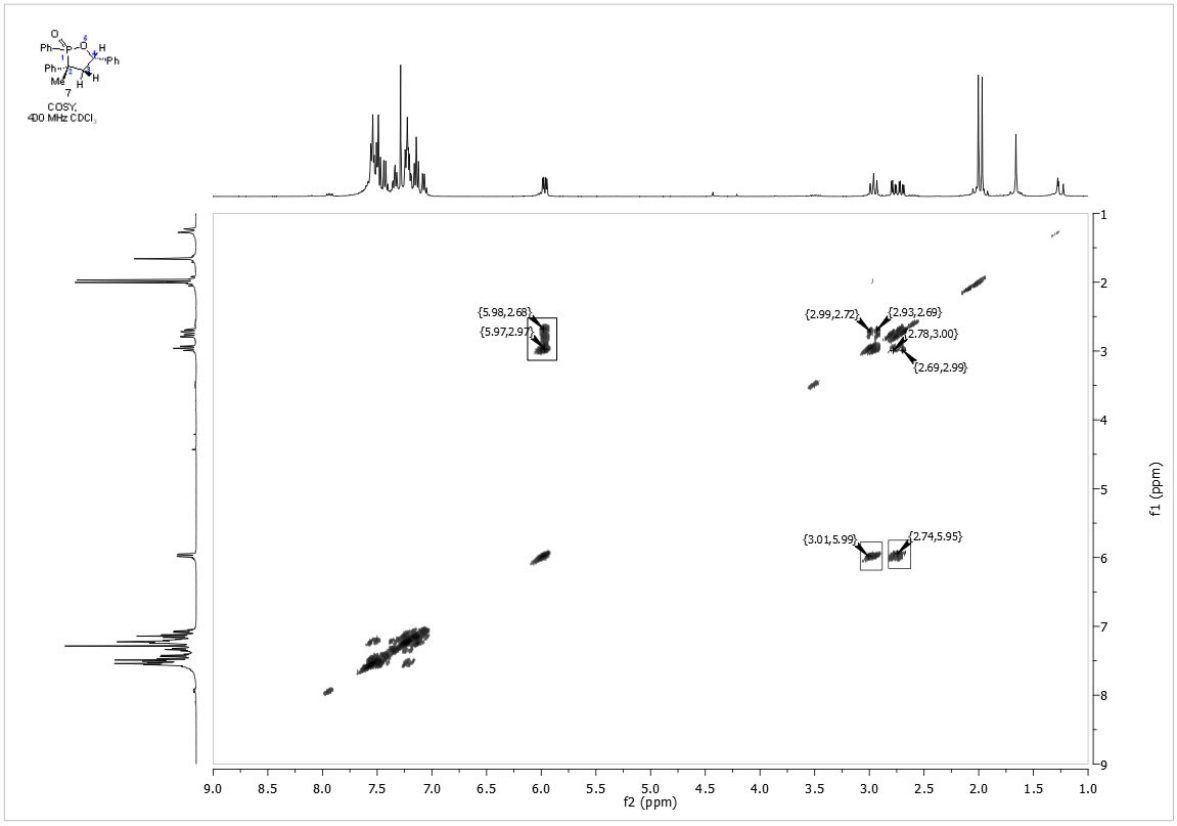

AdO
O
P
Ph
Ph
Ph
Me
OH
Ph
6
^{31}P NMR (162MHz, CDCl$_3$)
44.55
42.17
0.04
1.00
f1 (ppm)

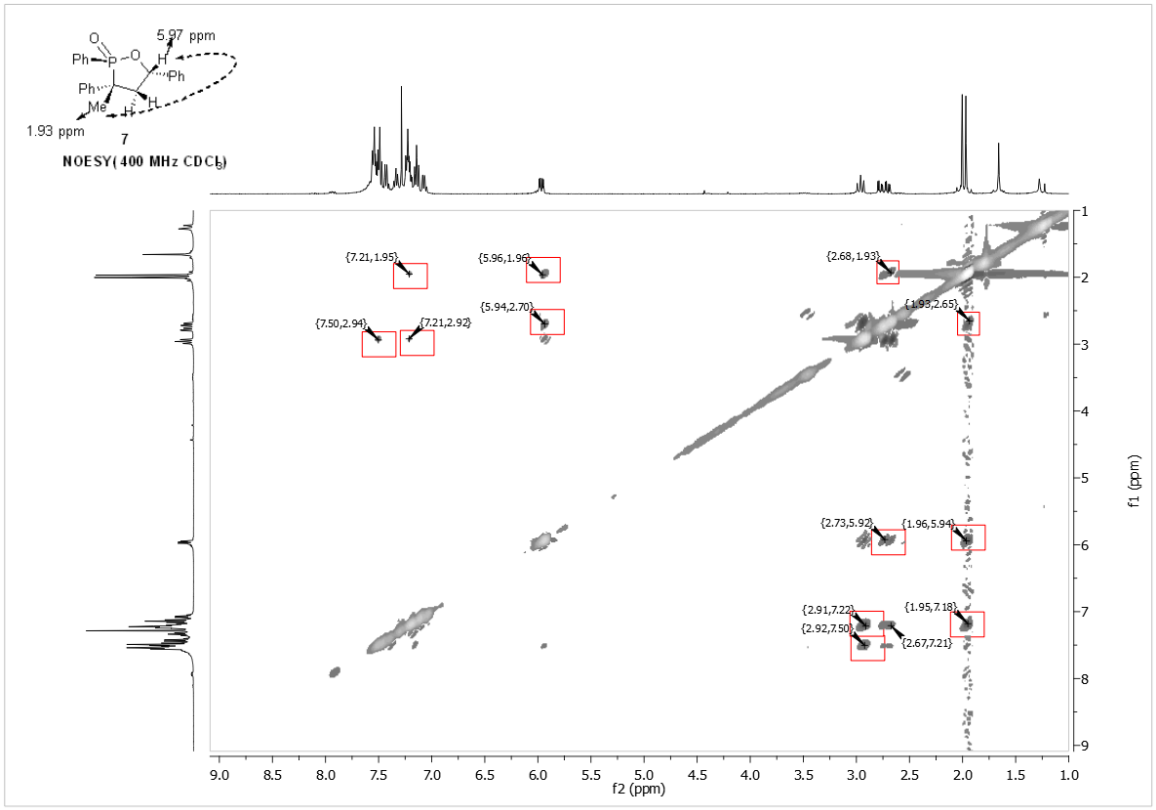

7.56 7.55 7.55 7.54 7.53 7.53 7.52 7.51 7.51 7.50 7.50 7.49 7.49 7.47 7.44 7.42 7.34 7.34 7.32 7.32 7.25 7.24 7.24 7.23 7.23 7.21 7.21 7.20 7.16 7.14 7.12 5.99 5.98 5.96 5.95
2.99 2.96 2.93 2.80 2.79 2.77 2.75 2.73 2.72 2.70 2.68 2.00 1.97
Ph P O Ph Ph Me 7
^{1}H NMR (400 MHz, $CDCl_3$)
5.72 1.12 1.15 3.50 1.75 0.91 1.02 1.00 1.01 2.82
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 0.0
f1 (ppm)


140.89 139.55 139.48 132.60 132.50 132.10 132.07 130.09 128.88 128.45 128.43 128.34 128.00 127.87 126.67 126.14 126.07 125.21
78.82 78.79
46.63 46.54 44.40 44.34
24.81 24.77
Ph P O Ph Ph Me 7
^{13}C NMR (101 MHz, $CDCl_3$)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


60.03
58.94
Ph
P
O
Ph
Ph
Me
7
31P NMR (162MHz, CDCl3)
1.00
0.07
140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50
f1 (ppm)

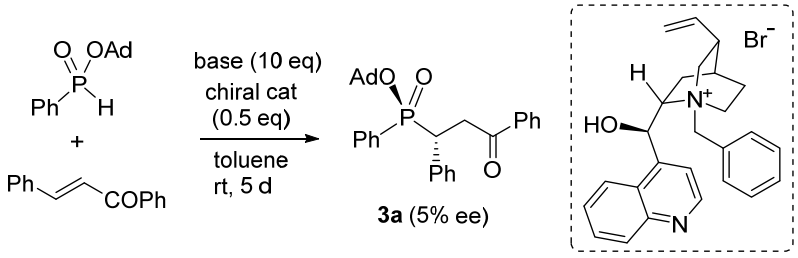

132.60
132.50
132.11
128.88
128.45
128.35
128.01
127.88
126.68
126.14
126.08
125.21
78.83
44.40
44.34
24.81
24.77
Ph
P
O
Ph
Ph
Me
7
DEPT-135, CDCl3
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7
COSY
400 MHz CDCl3
{5.98,2.68}
{5.97,2.97}
{2.99,2.72}
{2.93,2.69}
{2.78,3.00}
{2.69,2.99}
{3.01,5.99}
{2.74,5.95}
f1 (ppm)
f2 (ppm)

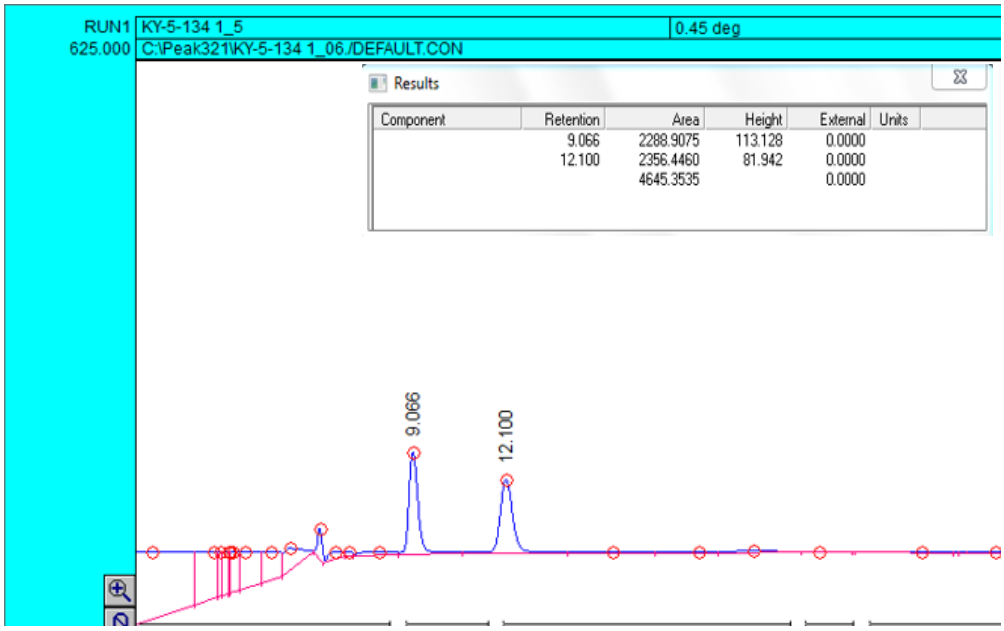

5.97 ppm
1.93 ppm
7
NOESY (400 MHz CDCl3)
{7.21,1.95}
{5.96,1.96}
{7.50,2.94}
{7.21,2.92}
{5.94,2.70}
{2.68,1.93}
{1.93,2.65}
{2.73,5.92}
{1.96,5.94}
{2.91,7.22}
{2.92,7.50}
{1.95,7.18}
{2.67,7.21}
f1 (ppm)
f2 (ppm)

6. Synthesis of Enantiopure compound **3a** with HPLC data

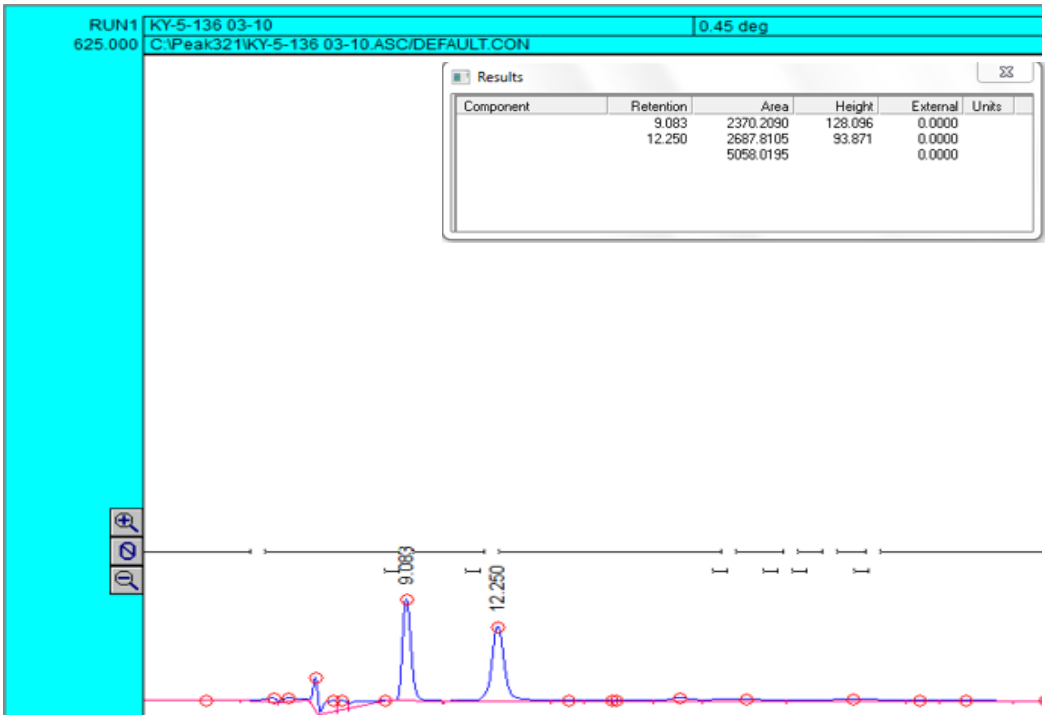
In a scintillation vial (6 dram) containing adamantyl phosphinate (25 mg, 0.091 mmol, 1.0 equiv) in toluene (0.36 mL) was added (2*E*)-1,3-diphenylprop-2-en-1-one (chalcone) (23 mg, 0.10 mmol, 1.2 equiv), N-benzylcinchonidinium bromide (20 mg, 0.045 mmol, 0.5 equiv) and K_2CO_3 (125 mg, 0.90 mmol, 10 equiv). The reaction was stirred at room temperature for 5 d. The reaction mixture was then quenched by adding water (5 mL) and extracted with ethyl acetate (3 × 5 mL). The combined organic extracts were dried (Na_2SO_4), filtered, and concentrated in vacuo to yield crude product, which was purified by pipette silica gel column to remove the excess chalcone and further purified by preparative TLC eluting with 25-30% EtOAc/hexanes to obtain the major diastereomer (35% yield). NMR data are consistent with racemic compound **3a**. The pure major diastereomer was then analyzed by chiral HPLC (equipped with a chiral Pak IC-3 column) and an ee of 5% was measured (see data below).



HPLC chromatograph of racemic compound **3a**:



HPLC chromatograph of chiral compound **3a**:



HPLC chromatograph was performed using chiral Pak IC-3 column (70:30 hexanes/isopropanol) as eluents with flowrate of 0.5 mL/min at 254 nm wavelength. Data were collected in triplicate and final %ee was calculated (see below).

Data for HPLC (triplicate study):

	Racemic sample			
	rt-1	**rt2**		
area 1	2594.017	2553.649		
area 2	2137.424	2195.808	Avg %ee = **0.6**	
area 3	2288.908	2356.446		
avg	2340.116	2368.634		
sd	189.9	189.9		
%rsd	8.1	8.1		
	Chiral Sample			
	rt-1	**rt2**		
area 1	2370.209	2687.811		
area 2	2386.619	2616.303		
area 3	2340.68	2654.524	Avg %ee = **5.7**	
avg	2365.836	2652.879		
sd	23.3	35.8		
%rsd	1.0	1.3		