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Pallacycle Catalyzed Enantioselective Phospha-Michael Addition of Diarylphosphines to β,γ-unsaturated α-ketoesters and amides

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Supporting Information

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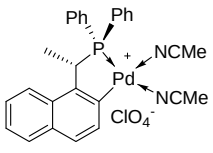
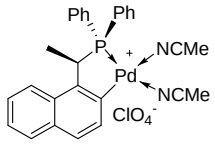
I. General Information

All air sensitive manipulations were performed under a positive pressure of nitrogen using Schlenk techniques. Solvents were degassed prior to use when necessary. Chloroform (AR) and dichloromethane (AR) were purchased from Merck Mililipore and Fischer Scientific; tetrahydrofuran (AR) and toluene from TEDIA Company, acetone from QREC (Asia) and 1,2-dichloroethane (DCE) from Alfa Aesar. Solvents were used directly without further purification. Low Temp PAIRSTIRRER PSL-1800 machine was used for controlling low temperatures for reactions. Silica plug filtration was conducted on Merck silica gel 60 (0.040-0.063mm).

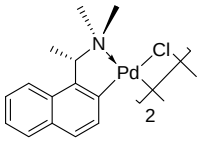
NMR spectra were recorded on Bruker ACF 400 spectrometers. ^{1}H NMR spectra chemical shifts were reported in δ ppm relative to tetramethylsilane (δ = 0.00 ppm) or chloroform (δ = 7.26 ppm). Multiplicities were given as: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The number of protons (n) for a given resonance was indicated by nH while coupling constants were reported as *J* value in Hertz (Hz). ^{13}C NMR spectra chemical shifts were recorded relative to solvent resonance ($CDCl_3$: δ = 77.23 ppm). $^{31}P\{^{1}H\}$ NMR spectra chemical shifts are referenced to an external standard of 85% H_3PO_4. Optical rotations of monophosphine products were measured as soon as possible without inert gas protection in the specified solution using a 0.1 dm cell at 23 ^{o}C with a Atago AP-300 polarimeter. Chiral palladacycles (*S*)-**3**, (*R*)-**3**[1], (*S*)-**4**, (*R*)-**4**[2] and β,γ-unsaturated α-ketoesters and amides **1**[3] were prepared according to literature methods.



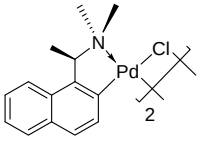
(*S*)-**4**



(*R*)-**4**



(*S*)-**6**

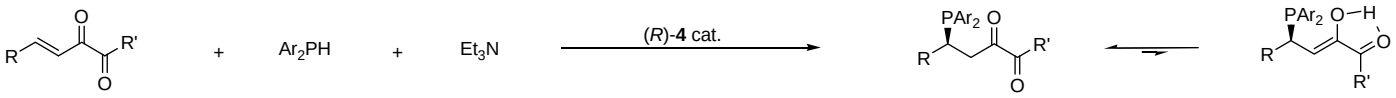


(*R*)-**6**

Caution! Perchlorate salts of metal complexes are potentially explosive and should be handled with care.

II. Experimental Section

(1) General procedure for the palladacycle (4) catalyzed asymmetric hydrophosphination of β,γ-unsaturated α-ketoesters and amides (1) with diarylphosphines

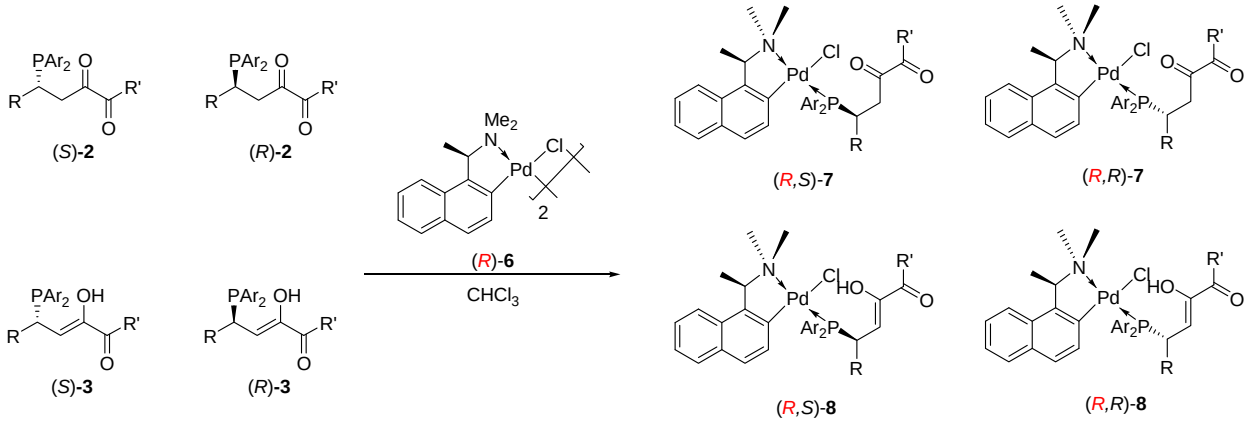


1 **2** **3**

To a degassed 2-neck round bottom flask at room temperature was charged with diarylphosphine (0.1 mmol, 1 equiv.), degassed chloroform (2.8 mL) and dichloromethane (0.4 mL). The solution was slightly agitated before introduction of (*R*)-**4** (0.005 mmol, 5mol%) with stirring to achieve complete dissolution. The setup was bought to -80 ^{o}C followed by addition of **1** (0.1 mmol, 1equiv.) and dropwise addition of triethylamine (0.02 mmol, 0.2 equiv) in chloroform (0.8 mL) over a period of 15 minutes. The reaction was stirred at -80 ^{o}C and its progress monitored by $^{31}P\{^{1}H\}$ NMR. Upon completion, the setup is bought to room temperature and the solvents removed via a vacuum pump. Degassed chloroform (10 mL) was then added to dissolve the solids which have precipitated, before passing it through a silica plug in a Pasteur pipette into a separate degassed 2-neck flask in order to remove (*R*)-**4** as well as phosphine oxides (if any). The filtrate is then subject to solvent strip under reduced pressure to afford the desired product. Enantiomeric excess (*ee*) is determined from the $^{31}P\{^{1}H\}$ NMR integration signals of diastereomers arising from the treatment of **2** and **3** with (*R*)-**6** and/or (*S*)-**6**.

(2) Determination of enantiomeric excess (*ee*)

The obtained adducts **2** and **3** were allowed to react with enantiopure dimeric complex (*R*)-**6** (0.51 equiv) in degassed chloroform to form derivatives **7** (keto) and **8**(enol). Enantiomeric excess (*ee* %) was then determined from the $^{31}P\{^{1}H\}$ NMR spectrum of the integral ratios of respective diastereomers.



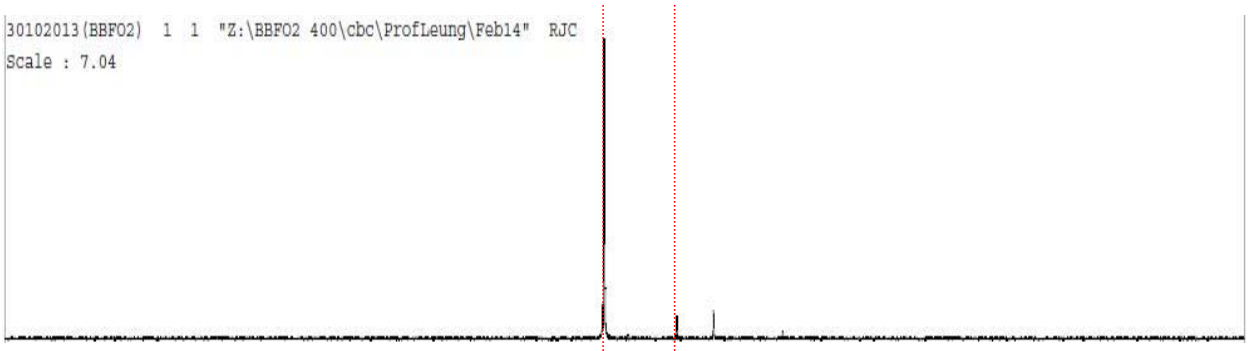
$$ee = \left| \frac{[(R,S)\textbf{-7} + (R,S)\textbf{-8}] - [(R,R)\textbf{-7} + (R,R)\textbf{-8}]}{[(R,S)\textbf{-7} + (R,S)\textbf{-8}] + [(R,R)\textbf{-7} + (R,R)\textbf{-8}]} \right|$$

In order to determine the absolute configuration, a mixture of **7** and **8** was purified by flash chromatography on silica gel to afford only 2 products. The major product was recrystallized from ethyl acetate/pentane to afford yellow prisms. Single crystal X-ray show that instead of the expected structure of either (*R*,*S*)-**7a** or (*R*,*S*)-**8a**, a phosphine-enolate chelate (*R*,*S*)-**9a** is formed instead.[4] Our studies revealed that the elimination of a molecule of HCl to give **9** occurs during silica gel purification.

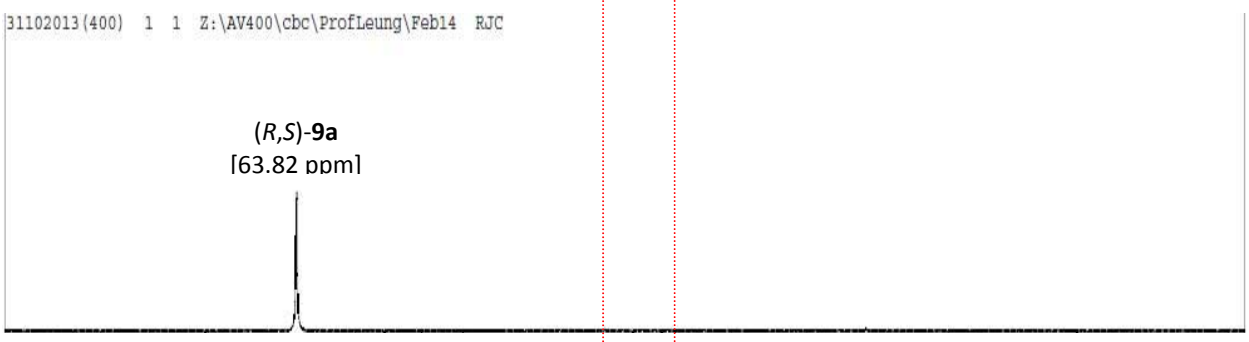
• **Re-coordination Experiment: Determination of positions of (*R*,*S*)-7a and (*R*,*S*)-8a**

To determine the chemical shifts of (*R*,*S*)-**7a** and (*R*,*S*)-**8a** on the $^{31}P\{^{1}H\}$ NMR spectrum, (*R*,*S*)-**9a** (δ = 63.82 ppm) was treated with aqueous KCN (in degassed water) and stirred vigourously at room temperature for 2.5 hours to give (*S*)-**2** and **3**. Solution is extracted trice with DCM before re-coordiation with (*R*)-**6**. Subsequent $^{31}P\{^{1}H\}$ NMR of the mixture confirms that the chemical shifts of (*R*,*S*)-**7a** and (*R*,*S*)-**8a** are 49.23ppm and 45.77ppm respectively.

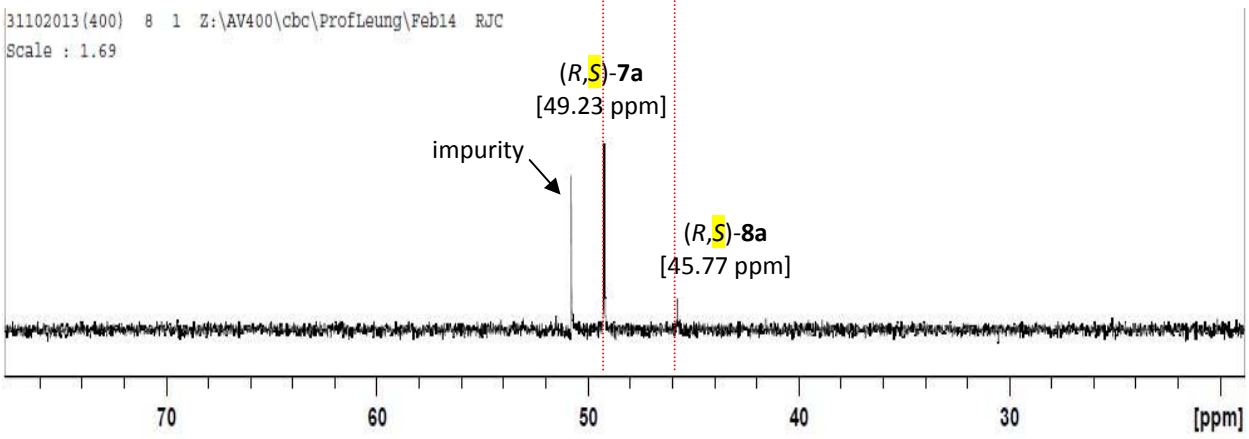
- After treatment of adducts 2 and 3 with (*R*)-6



- Major product (*R*,*S*)-9a from silica gel purification



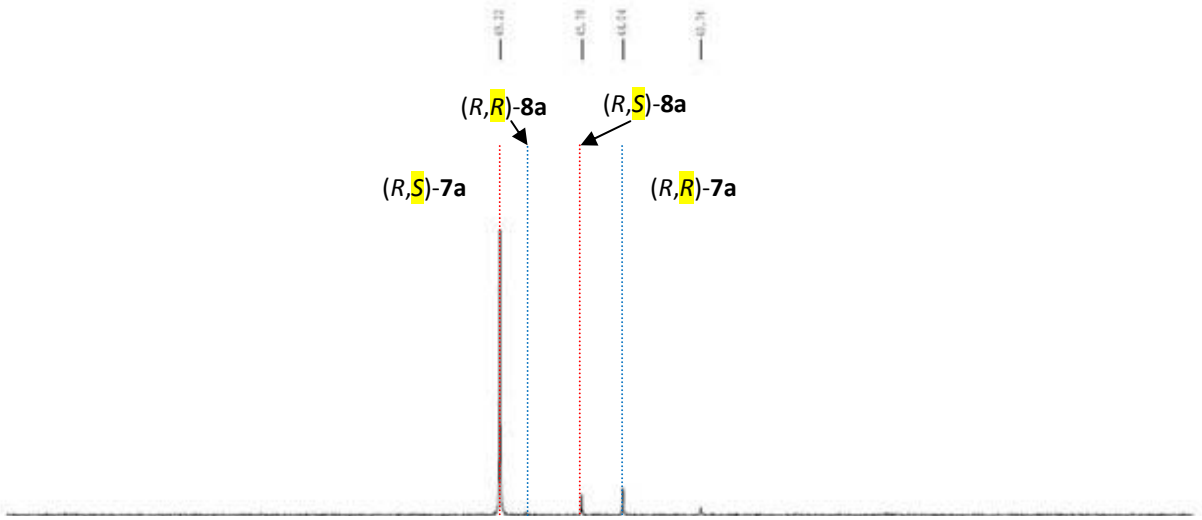
- Treatment of (*R*,*S*)-9a with KCN followed by reaction with (*R*)-6



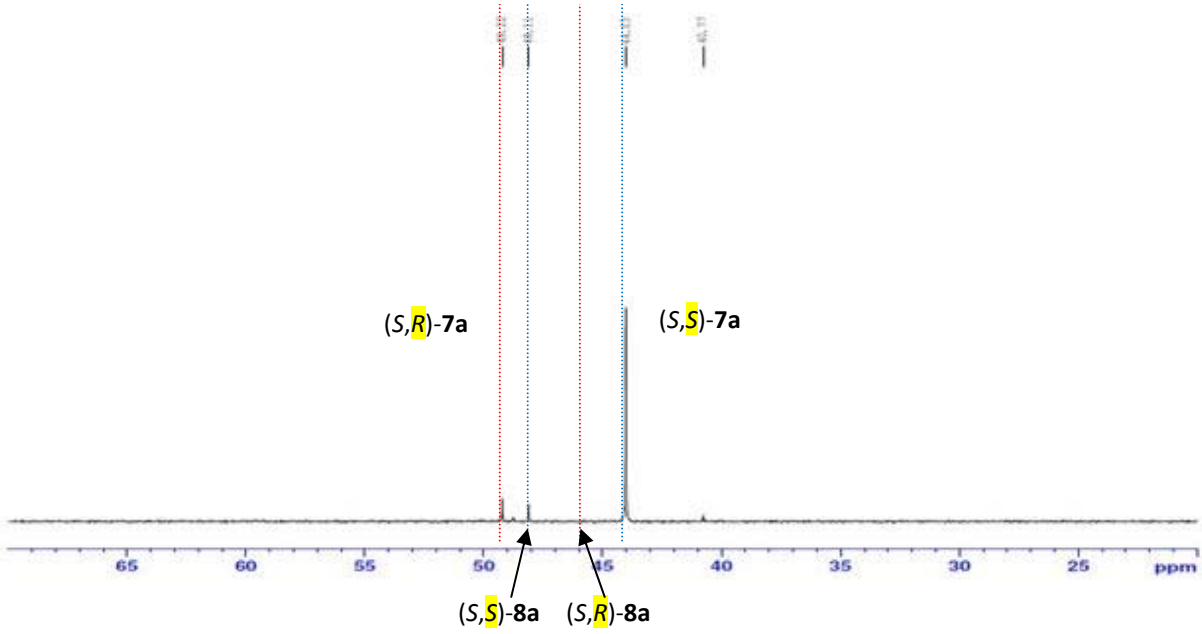
• Coordination of 2 and 3 with (*S*)-6: Determination of positions of *R*-stereoisomers

The re-coordination study allowed us to determine the positions of the *S* stereoisomers (major). By comparison of NMR spectra derived from the coordination **2** and **3** with (*S*)-**6** instead of (*R*)-**6**, we are able to confirm the positions of the *R* stereoisomers (minor).

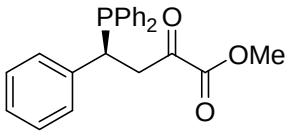
- After treatment of adducts 2 and 3 with (*R*)-6



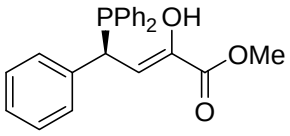
- After treatment of adducts 2 and 3 with (*S*)-6



(3) Synthesis and Characterization



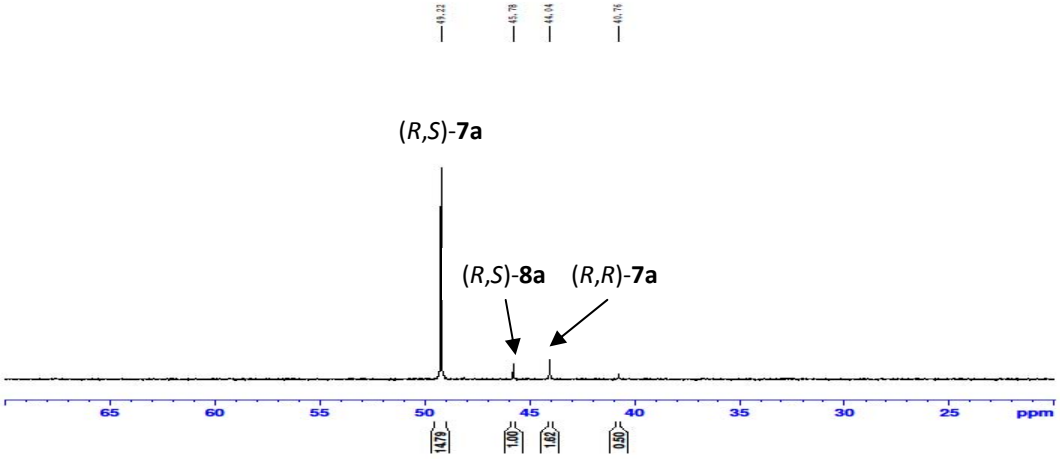
(*S*)-**2a**



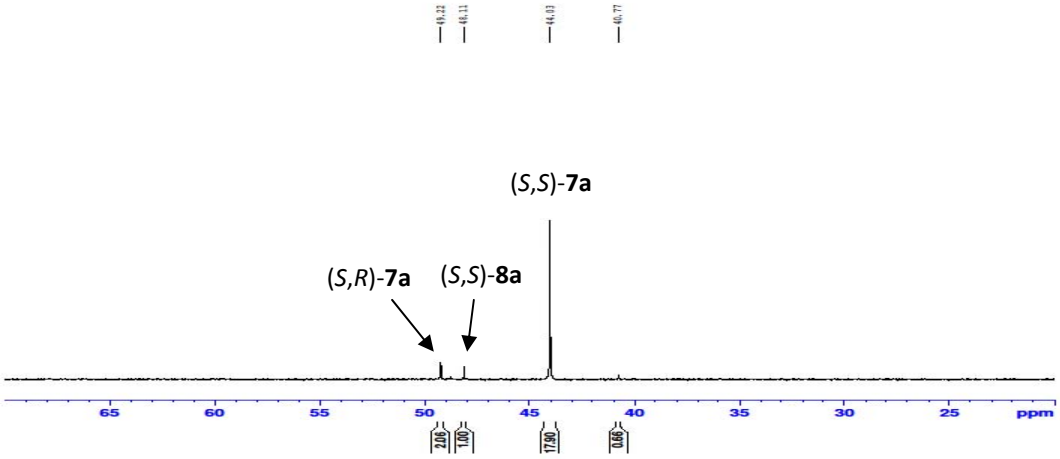
(*S*)-**3a**

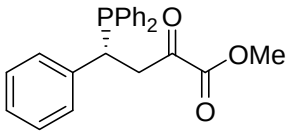
(*S*)-**2a** was prepared according to general procedure (36.9 mg, 98% yield [7% as (*S*)-**3a**], 81% *ee*): $[\alpha]_D^{23}$ = -155.6° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.12 [(*S*)-**2a**], 3.66 [(*S*)-**3a**]; ^1H ($CDCl_3$, 400 MHz): δ 2.92-2.99 (m, 1H), 3.42-3.51 (m, 1H), 3.64 (s, 3H), 4.05-4.10 (m, 1H), 7.03-7.59 (m, 15H); ^{13}C ($CDCl_3$, 101 MHz): δ 39.7 (d, 1C, $^2J_{CP}$ = 14 Hz), 43.4 (d, 1C, $^1J_{CP}$ = 22 Hz), 53.1 (s, 1C), 126.9-139.9 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.2 (d, 1C, $^3J_{CP}$ = 12 Hz).

- Treatment of (*S*)-2a and (*S*)-3a with (*R*)-6

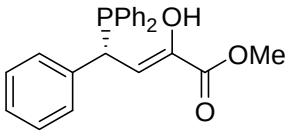


- Treatment of (*S*)-2a and (*S*)-3a with (*S*)-6





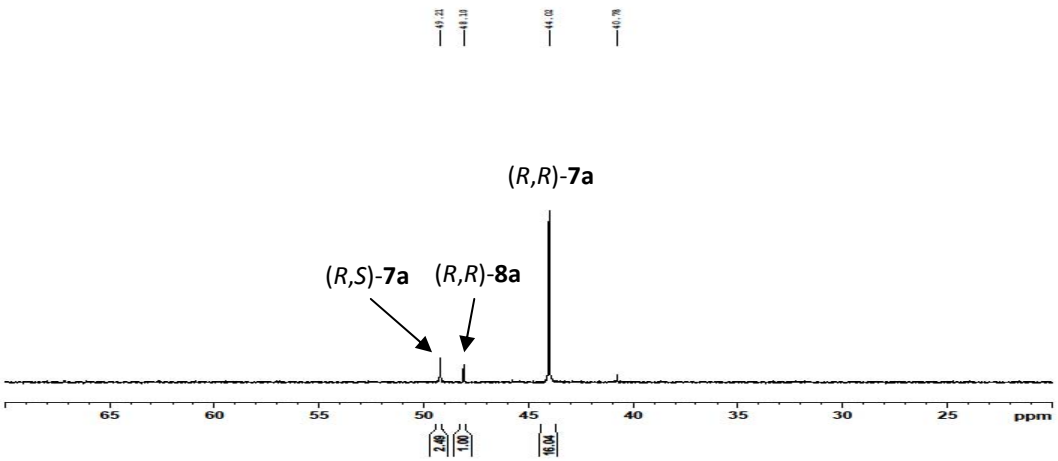
(*R*)-**2a**



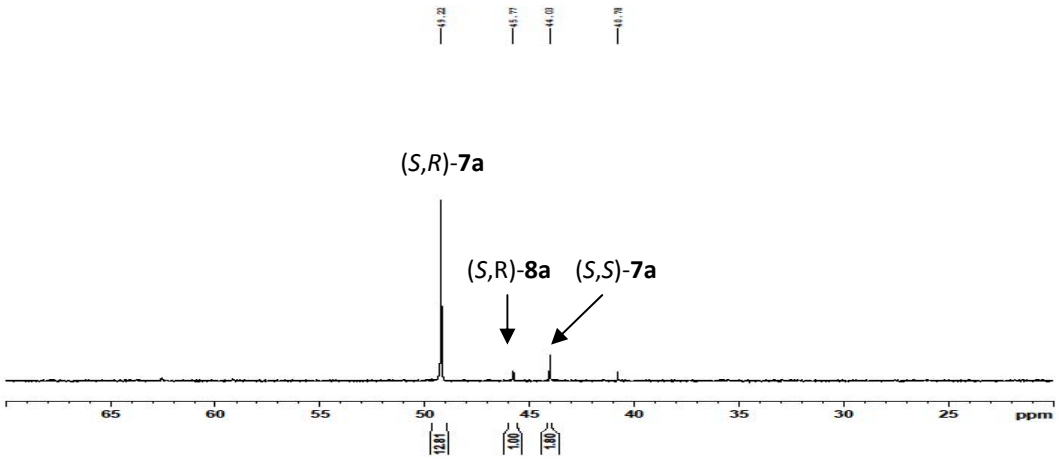
(*R*)-**3a**

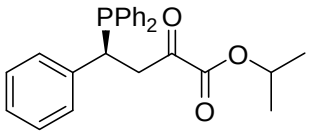
(*R*)-**2a** was prepared according to general procedure with the exception that (*S*)-**4** was employed (36.9 mg, 98% yield [9% as (*R*)-**3a**], 77% *ee*): $[\alpha]_D^{23}$ = +134.2° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.07 [(*R*)-**2a**], 3.63 [(*R*)-**3a**]; ^1H ($CDCl_3$, 400 MHz): δ 2.92-2.99 (m, 1H), 3.43-3.51 (m, 1H), 3.64 (s, 3H), 4.05-4.15 (m, 1H), 7.03-7.59 (m, 15H); ^{13}C ($CDCl_3$, 101 MHz): δ 39.7 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.4 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.1 (s, 1C), 126.9-139.9 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.2 (d, 1C, $^3J_{CP}$ = 13 Hz).

- Treatment of (*R*)-2a and (*R*)-3a with (*R*)-6

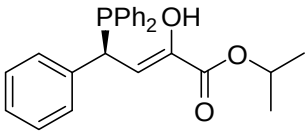


- Treatment of (*R*)-2a and (*R*)-3a with (*S*)-6



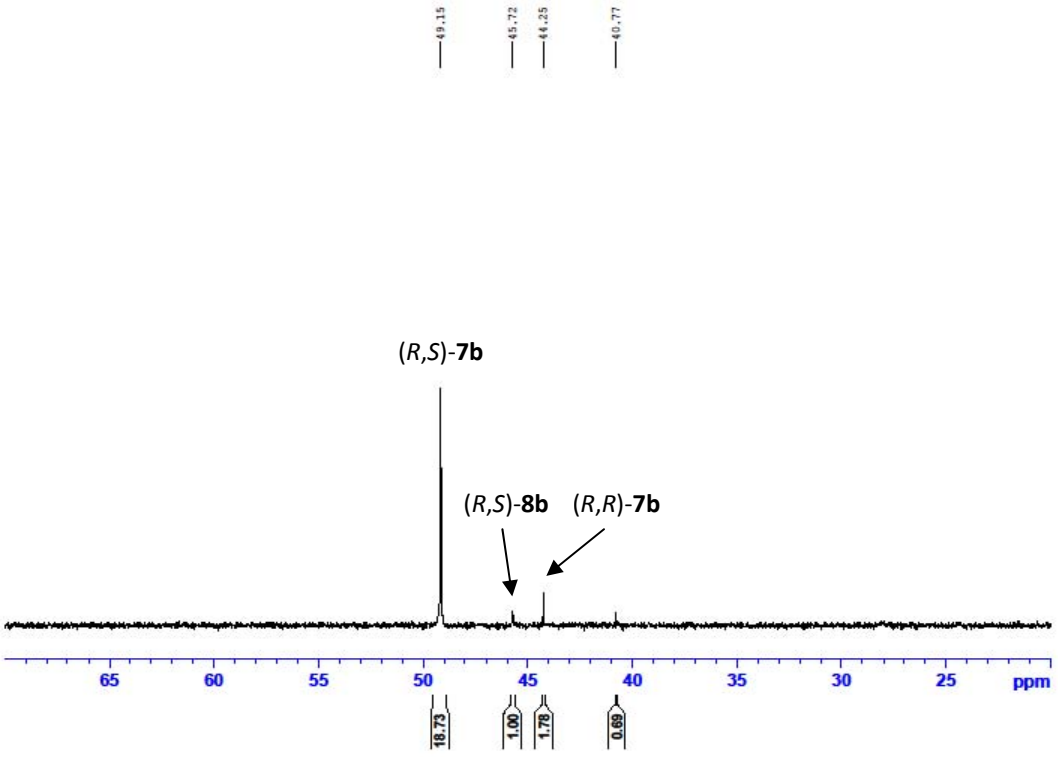


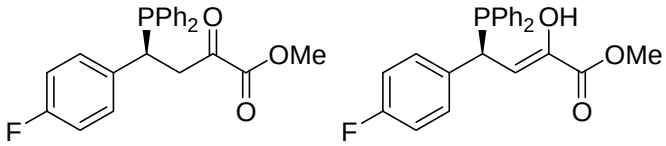
(*S*)-**2b**



(*S*)-**3b**

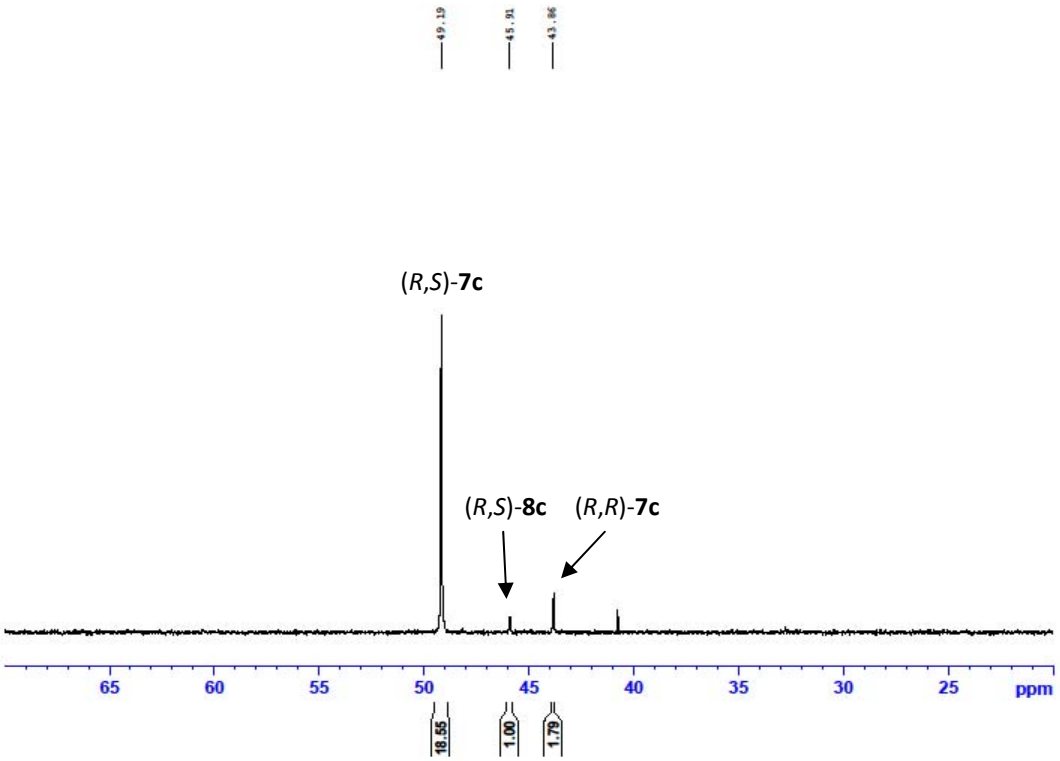
(*S*)-**2b** was prepared according to general procedure (39.9 mg, 98% yield [6% as (*S*)-**3a**], 83% *ee*): $[\alpha]_D^{23}$ = -137.9° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.29 [(*S*)-**2b**], 3.98 [(*S*)-**3b**]; ^1H ($CDCl_3$, 400 MHz): δ 1.14 (d, 3H, $^3J_{HH}$ = 4 Hz), 1.15 (d, 3H, $^3J_{HH}$ = 4 Hz), 2.91-2.96 (m, 1H), 3.41-3.48 (m, 1H), 4.05-4.09 (m, 1H), 4.86-4.93 (m, 1H), 7.03-7.58 (m, 15H); ^{13}C ($CDCl_3$, 101 MHz): δ 21.7 (s, 2C), 39.8 (d, 1C, $^2J_{CP}$ = 10 Hz), 43.2 (d, 1C, $^1J_{CP}$ = 18 Hz), 70.9 (s, 1C), 126.9-139.9 (m, 18C), 160.4 (d, 1C, $^4J_{CP}$ = 2 Hz), 193.1 (d, 1C, $^3J_{CP}$ = 10 Hz).

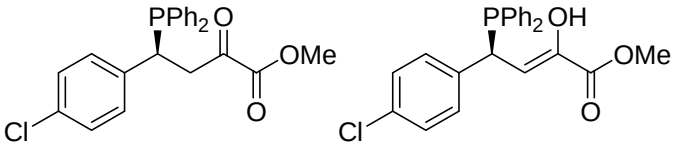




(*S*)-**2c** (*S*)-**3c**

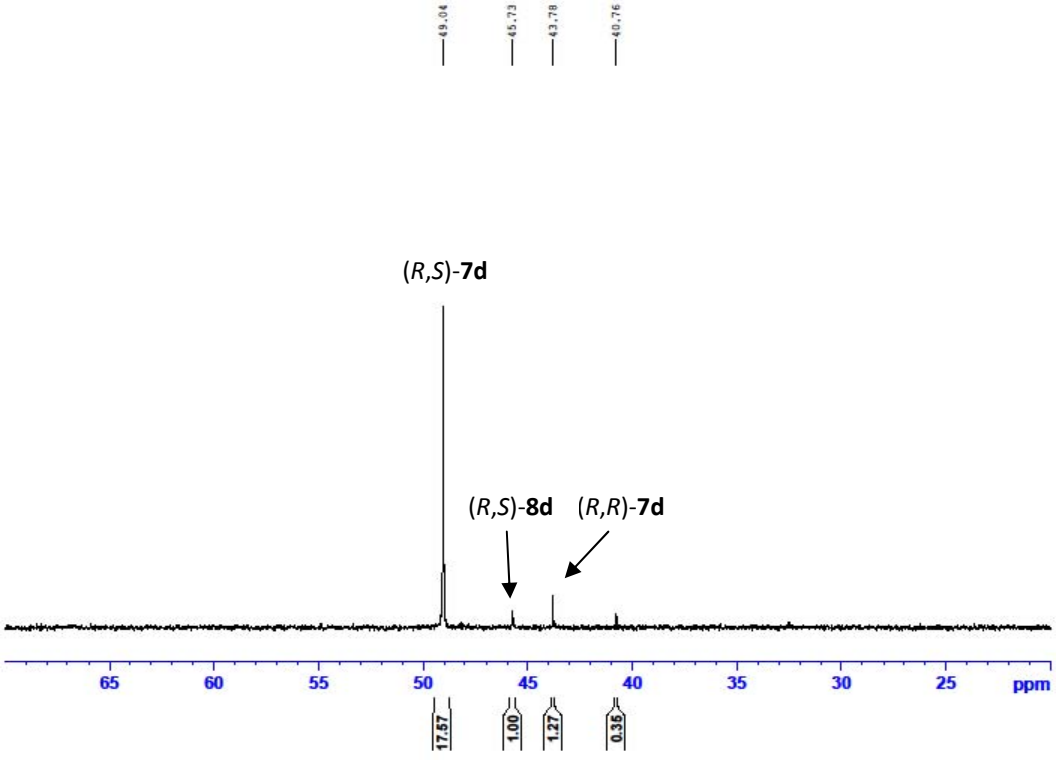
(*S*)-**2c** was prepared according to general procedure (38.6 mg, 98% yield [7% as (*S*)-**3c**], 83% *ee*): $[\alpha]_D^{23}$ = -140.4° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -0.17 [(*S*)-**2c**], 3.66 [(*S*)-**3c**]; ^1H ($CDCl_3$, 400 MHz): δ 2.91-2.98 (m, 1H), 3.39-3.47 (m, 1H), 3.65 (s, 3H), 4.04-4.07 (m, 1H), 6.75-7.58 (m, 14H); ^{19}F ($CDCl_3$, 377 MHz): δ -115.82 (d, 1F, $^6J_{FP}$ = 4 Hz) [(*S*)-**2c**], -116.3 (d, 1F, $^6J_{FP}$ = 4 Hz) [(*S*)-**3c**]; ^{13}C ($CDCl_3$, 101 MHz): δ 38.9 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.4 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.1 (s, 1C), 115.3-135.9 (m, 18C), 161.0 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.1 (d, 1C, $^3J_{CP}$ = 13 Hz).

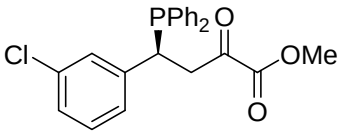




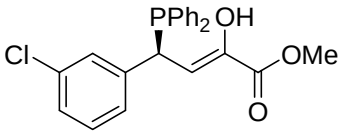
(*S*)-**2d** (*S*)-**3d**

(*S*)-**2d** was prepared according to general procedure (40.3 mg, 98% yield [6% as (*S*)-**3d**], 94% *ee*): $[\alpha]_D^{23}$ = -211.6° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.00 [(*S*)-**2d**], 3.83 [(*S*)-**3d**]; ^1H ($CDCl_3$, 400 MHz): δ 2.91-2.99 (m, 1H), 3.38-3.47 (m, 1H), 3.66 (s, 3H), 4.02-4.07 (m, 1H), 7.00-7.56 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 39.1 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.3 (d, 1C, $^1J_{CP}$ = 22 Hz), 53.2 (s, 1C), 128.3-138.6 (m, 18C), 161.0 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.0 (d, 1C, $^3J_{CP}$ = 13 Hz).



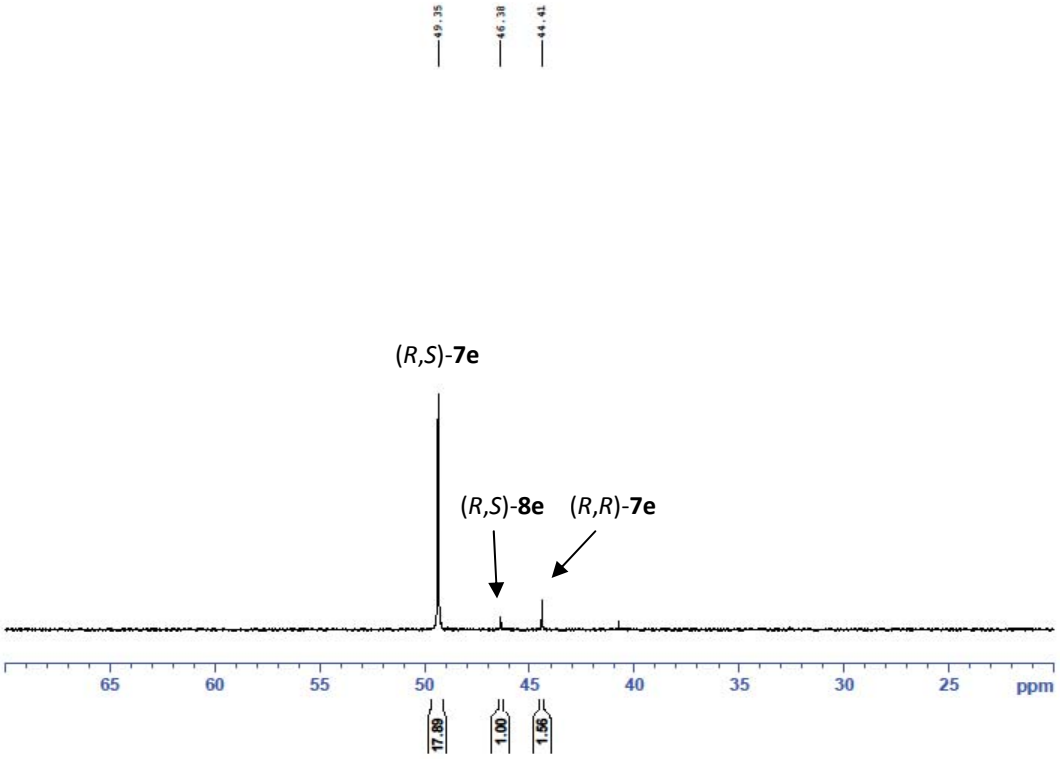


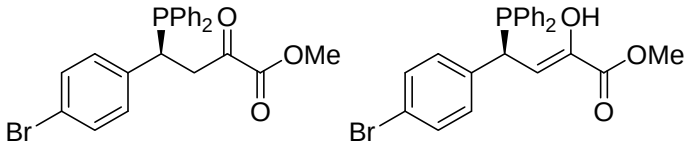
(*S*)-**2e**



(*S*)-**3e**

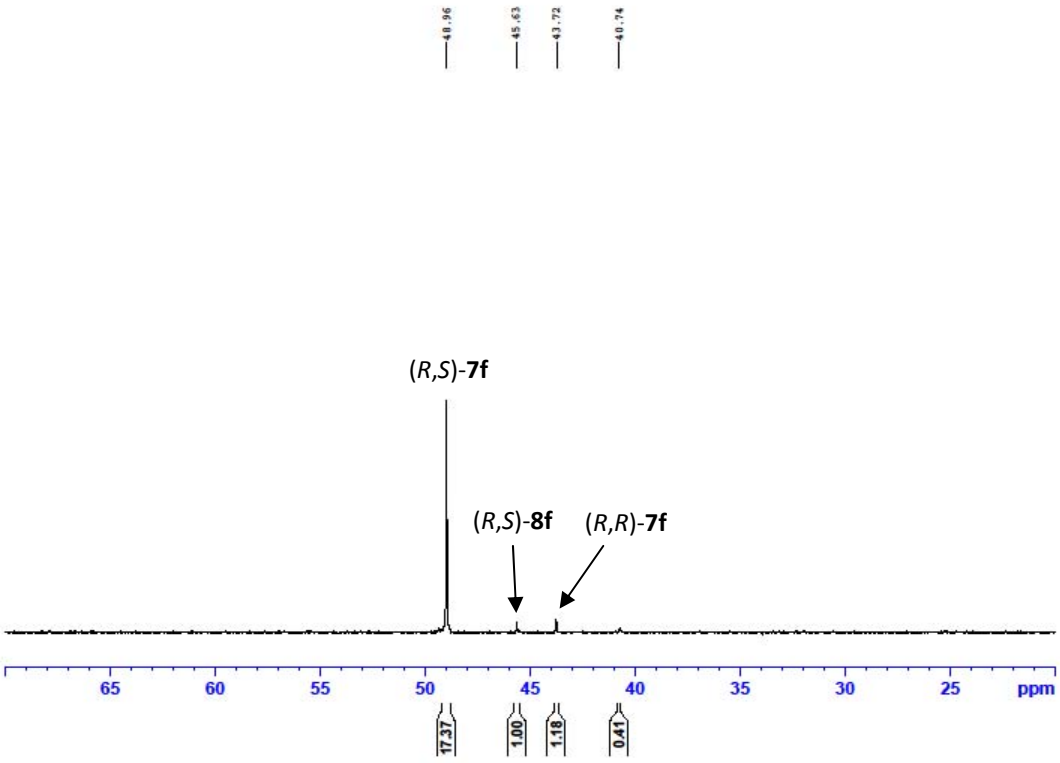
(*S*)-**2e** was prepared according to general procedure (40.3 mg, 98% yield [10% as (*S*)-**3e**], 85% *ee*): $[\alpha]_D^{23}$ = -258.8° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.45 [(*S*)-**2e**], 4.38 [(*S*)-**3e**]; ^1H ($CDCl_3$, 400 MHz): δ 2.94-3.00 (m, 1H), 3.39-3.48 (m, 1H), 4.02 (s, 3H), 4.01-4.05 (m, 1H), 6.96-7.57 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 39.4 (d, 1C, $^2J_{CP}$ = 14 Hz), 43.2 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.2 (s, 1C), 127.1-142.2 (m, 18C), 161.0 (d, 1C, $^4J_{CP}$ = 2 Hz), 191.9 (d, 1C, $^3J_{CP}$ = 12 Hz).

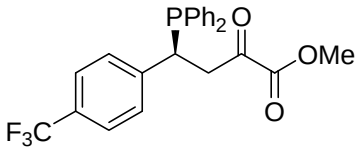




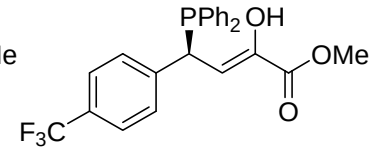
(*S*)-**2f** (*S*)-**3f**

(*S*)-**2f** was prepared according to general procedure (45.1 mg, 99% yield [5% as (*S*)-**3f**], 87% *ee*): $[\alpha]_D^{23}$ = -160.3° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.05 [(*S*)-**2f**], 3.82 [(*S*)-**3f**]; ^1H ($CDCl_3$, 400 MHz): δ 2.91-2.98 (m, 1H), 3.38-3.46 (m, 1H), 3.66 (s, 3H), 4.01-4.06 (m, 1H), 6.95-7.56 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 39.2 (d, 1C, $^2J_{CP}$ = 14 Hz), 43.2 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.2 (s, 1C), 120.7-139.2 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 2 Hz), 192.0 (d, 1C, $^3J_{CP}$ = 13 Hz).



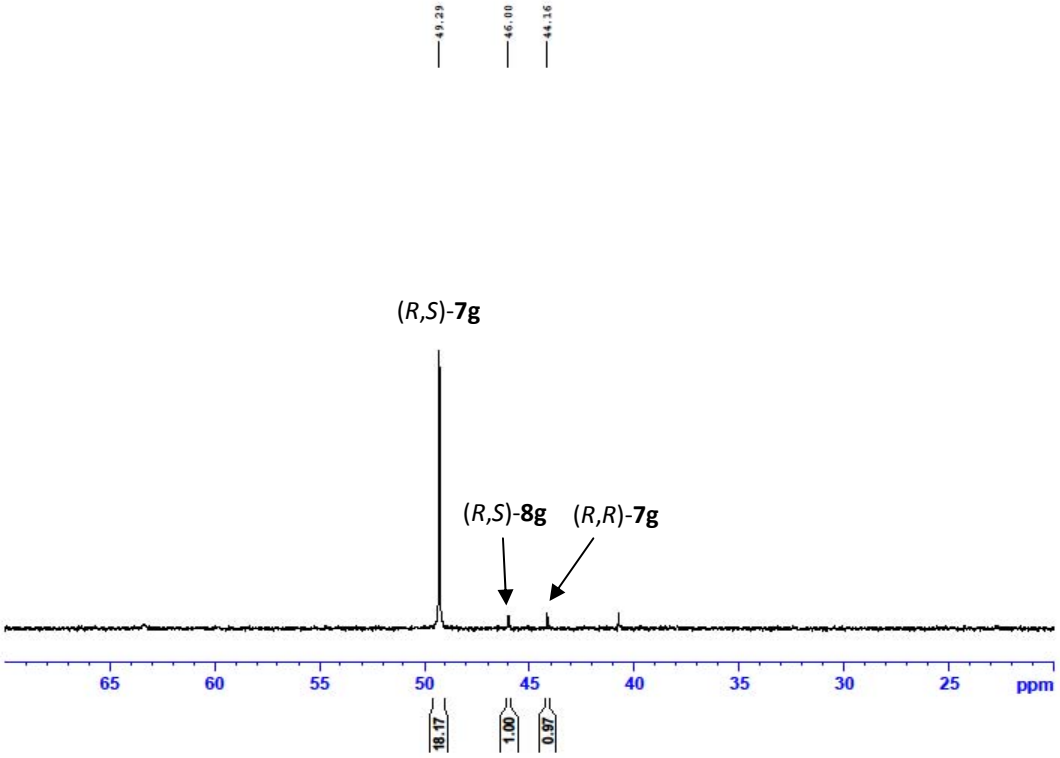


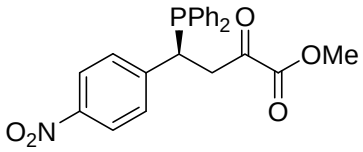
(*S*)-**2g**



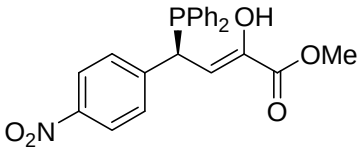
(*S*)-**3g**

(*S*)-**2g** was prepared according to general procedure (43.5 mg, 98% yield [10% as (*S*)-**3g**], 90% *ee*): $[\alpha]_D^{23}$ = -92.7° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.78 [(*S*)-**2g**], 4.33 [(*S*)-**3g**]; ^1H ($CDCl_3$, 400 MHz): δ 2.97-3.04 (m, 1H), 3.45-3.54 (m, 1H), 3.67 (s, 3H), 4.11-4.16 (m, 1H), 7.05-7.56 (m, 14H); ^{19}F ($CDCl_3$, 377 MHz): δ -62.49 [(*S*)-**2c**], -62.76 [(*S*)-**3c**]; ^{13}C ($CDCl_3$, 101 MHz): δ 39.5 (d, 1C, $^2J_{CP}$ = 15 Hz), 43.1 (d, 1C, $^1J_{CP}$ = 21 Hz), 53.2 (s, 1C), 125.5-135.4 (m, 19C), 161.0 (d, 1C, $^4J_{CP}$ = 3 Hz), 191.8 (d, 1C, $^3J_{CP}$ = 12 Hz).



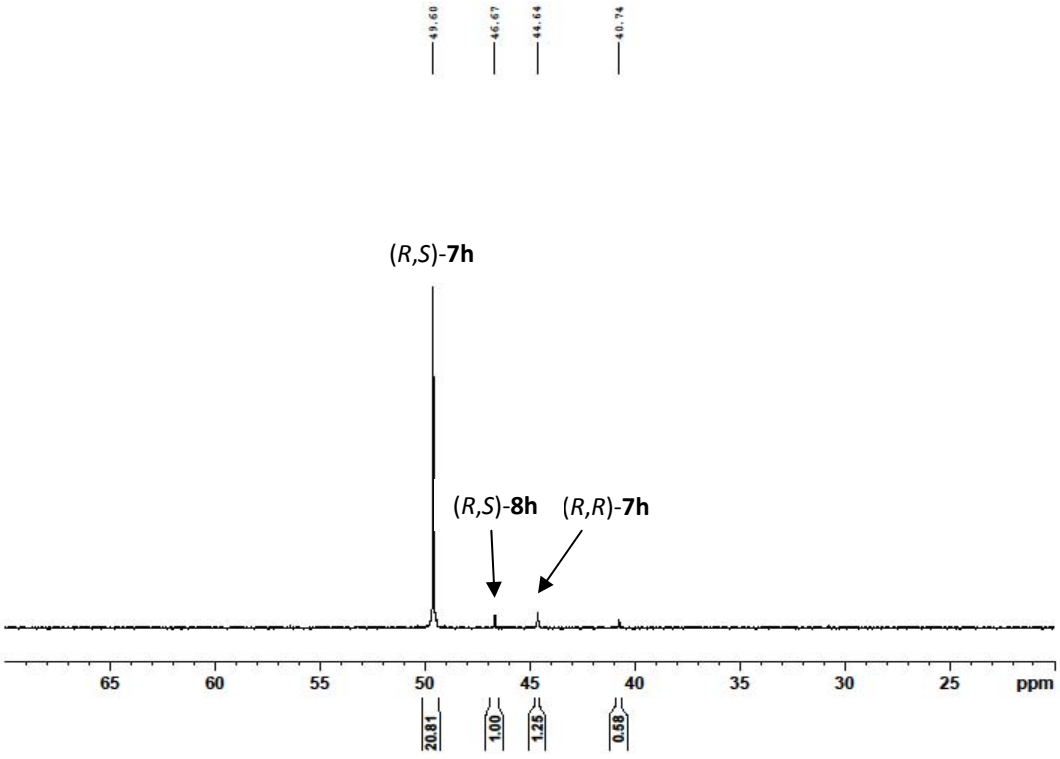


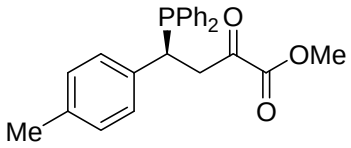
(*S*)-**2h**



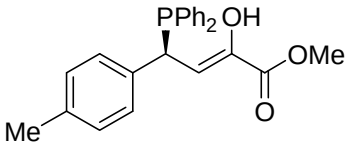
(*S*)-**3h**

(*S*)-**2h** was prepared according to general procedure (41.3 mg, 98% yield [6% as (*S*)-**3h**], 89% *ee*): $[\alpha]_D^{23}$ = -133.9^o [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 1.64 [(*S*)-**2h**], 6.07 [(*S*)-**3h**]; ^1H ($CDCl_3$, 400 MHz): δ 3.02-3.10 (m, 1H), 3.47-3.56 (m, 1H), 3.68 (s, 3H), 4.16-4.21 (m, 1H), 7.07-7.94 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 39.8 (d, 1C, $^2J_{CP}$ = 16 Hz), 42.9 (d, 1C, $^1J_{CP}$ = 21 Hz), 53.3 (s, 1C), 123.7-148.2 (m, 18C), 160.9 (d, 1C, $^4J_{CP}$ = 2 Hz), 191.6 (d, 1C, $^3J_{CP}$ = 13 Hz).



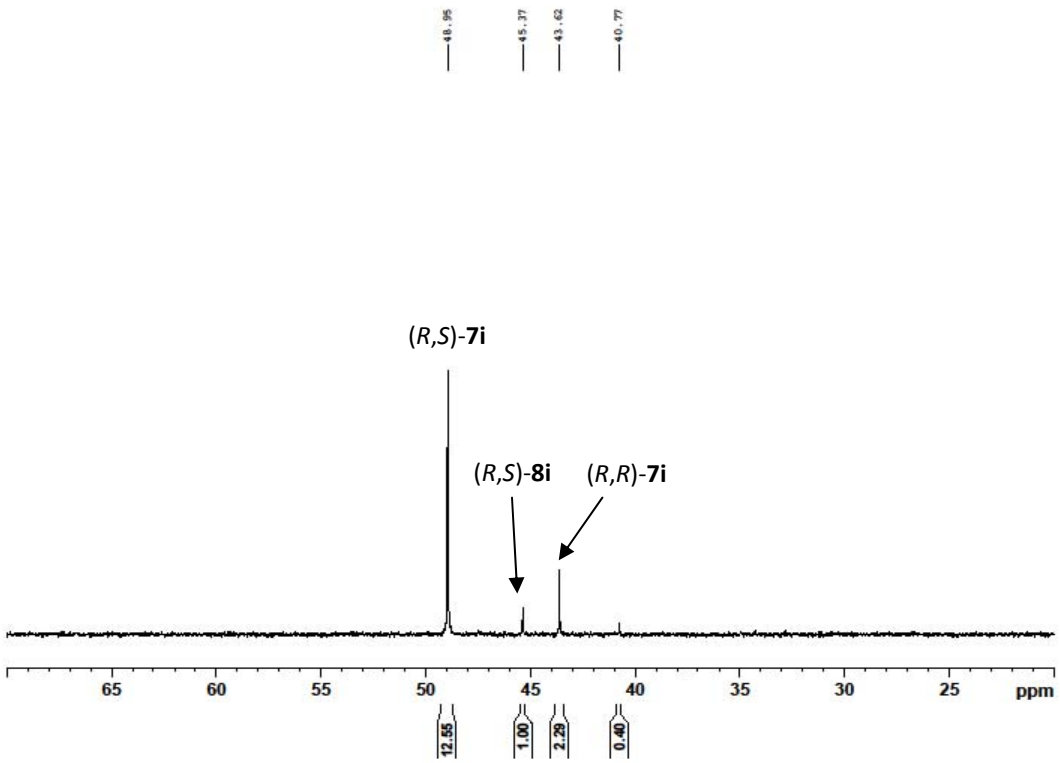


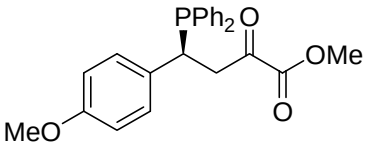
(*S*)-**2i**



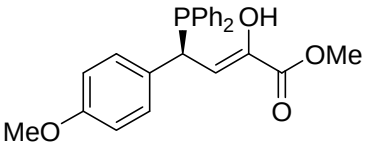
(*S*)-**3i**

(*S*)-**2i** was prepared according to general procedure (38.3 mg, 98% yield [9% as (*S*)-**3i**], 71% *ee*): $[\alpha]_D^{23}$ = -135.4° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -0.42 [(*S*)-**2i**], 2.65 [(*S*)-**3i**]; ^1H ($CDCl_3$, 400 MHz): δ 2.16 (s, 3H), 2.89-2.96 (m, 1H), 3.37-3.46 (m, 1H), 3.63 (s, 3H), 4.02-4.07 (m, 1H), 6.88-7.57 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 21.2 (s, 1C), 39.2 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.6 (d, 1C, $^1J_{CP}$ = 22 Hz), 53.0 (s, 1C), 128.2-136.7 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.3 (d, 1C, $^3J_{CP}$ = 13 Hz).



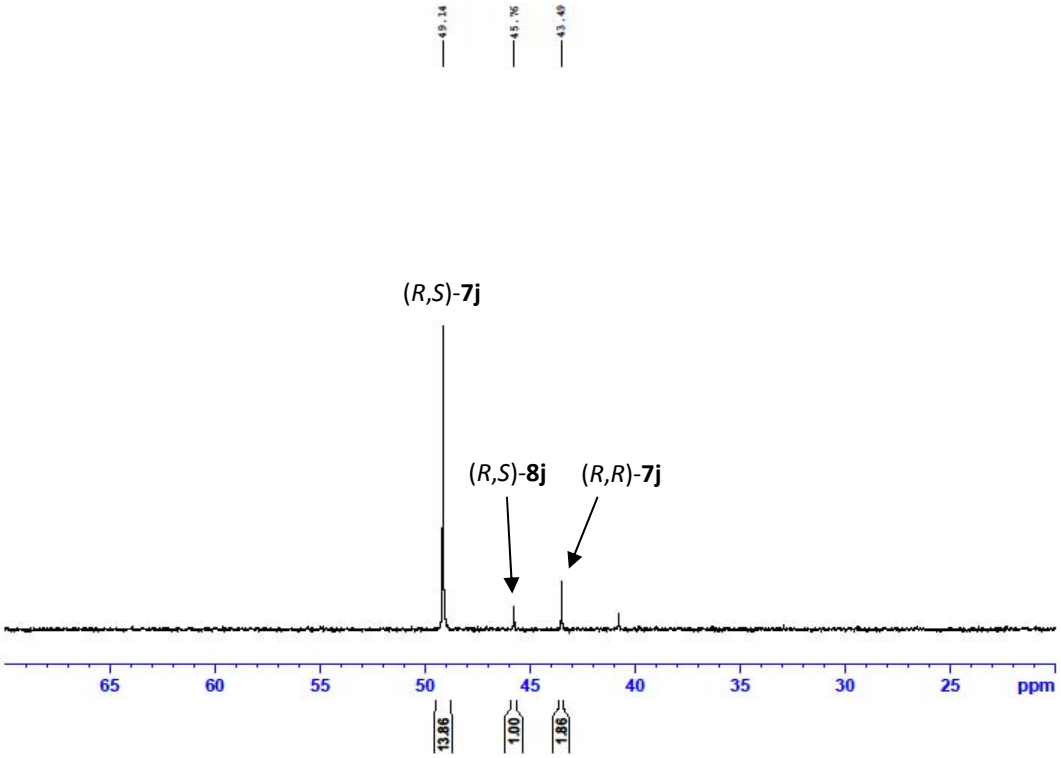


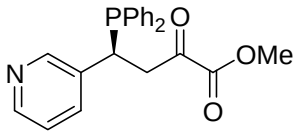
(*S*)-**2j**



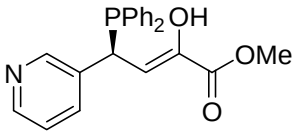
(*S*)-**3j**

(*S*)-**2j** was prepared according to general procedure (37.8 mg, 93% yield [5% as (*S*)-**3j**], 78% *ee*): $[\alpha]_D^{23}$ = -158.2° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -0.67 [(*S*)-**2j**], 2.56 [(*S*)-**3j**]; ^1H ($CDCl_3$, 400 MHz): δ 2.88-2.95 (m, 1H), 3.36-3.45 (m, 1H), 3.64 (s, 3H), 3.65 (s, 3H), 4.00-4.05 (m, 1H), 6.62-7.57 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 38.8 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.6 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.1 (s, 1C), 55.4 (s, 1C), 114.0-158.5 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.4 (d, 1C, $^3J_{CP}$ = 13 Hz).



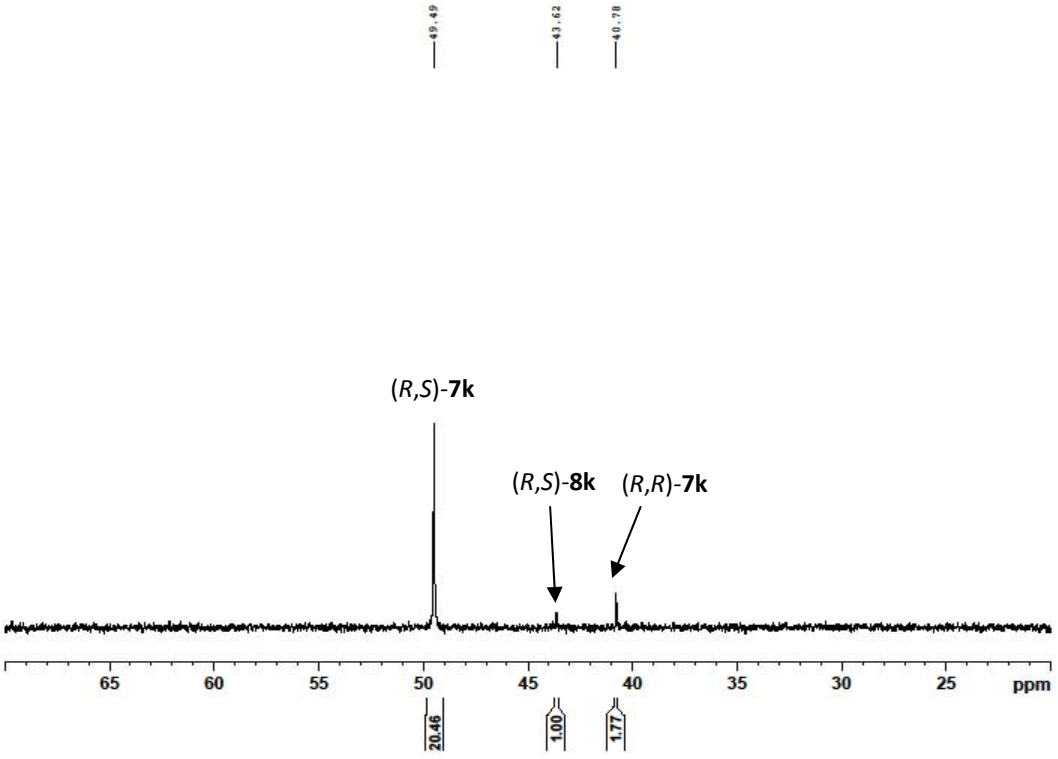


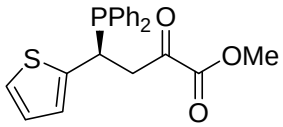
(*S*)-**2k**



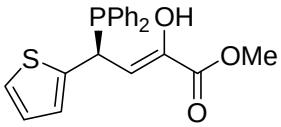
(*S*)-**3k**

(*S*)-**2k** was prepared according to general procedure (34.0 mg, 90% yield [7% as (*S*)-**3k**], 84% *ee*): $[\alpha]_D^{23}$ = -157.7° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.36 [(*S*)-**2k**], 4.45 [(*S*)-**3k**]; ^1H ($CDCl_3$, 400 MHz): δ 3.00-3.08 (m, 1H), 3.44-3.53 (m, 1H), 3.69 (s, 3H), 4.06-4.11 (m, 1H), 7.02-8.28 (m, 14H); ^{13}C ($CDCl_3$, 101 MHz): δ 36.9 (d, 1C, $^2J_{CP}$ = 15 Hz), 42.9 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.3 (s, 1C), 123.43-136.5 (m, 17C), 160.9 (d, 1C, $^4J_{CP}$ = 3 Hz), 191.7 (d, 1C, $^3J_{CP}$ = 13 Hz).



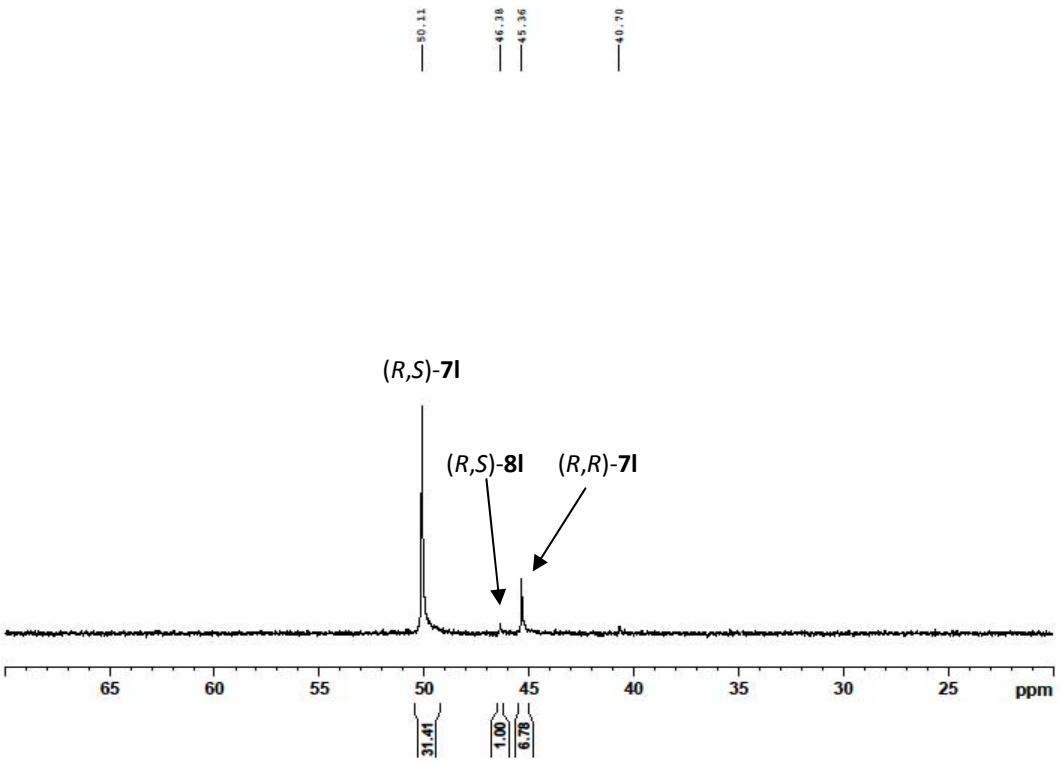


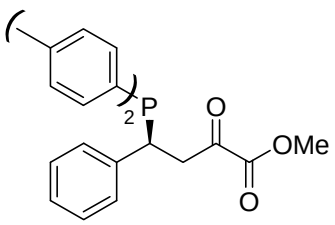
(*S*)-**2l**



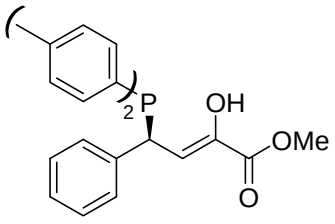
(*S*)-**3l**

(*S*)-**2l** was prepared according to general procedure (35.9 mg, 94% yield [5% as (*S*)-**3l**], 65% *ee*): $[\alpha]_D^{23}$ = -67.9° [c 0.4, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ 0.71 [(*S*)-**2l**], 4.32 [(*S*)-**3l**]; ^1H ($CDCl_3$, 400 MHz): δ 2.93-3.00 (m, 1H), 3.37-3.45 (m, 1H), 3.68 (s, 3H), 4.41-4.43 (m, 1H), 6.66-7.55 (m, 13H); ^{13}C ($CDCl_3$, 101 MHz): δ 34.8 (d, 1C, $^2J_{CP}$ = 14 Hz), 44.7 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.2 (s, 1C), 124.4-143.4 (m, 16C), 161.0 (d, 1C, $^4J_{CP}$ = 3 Hz), 191.8 (d, 1C, $^3J_{CP}$ = 12 Hz).



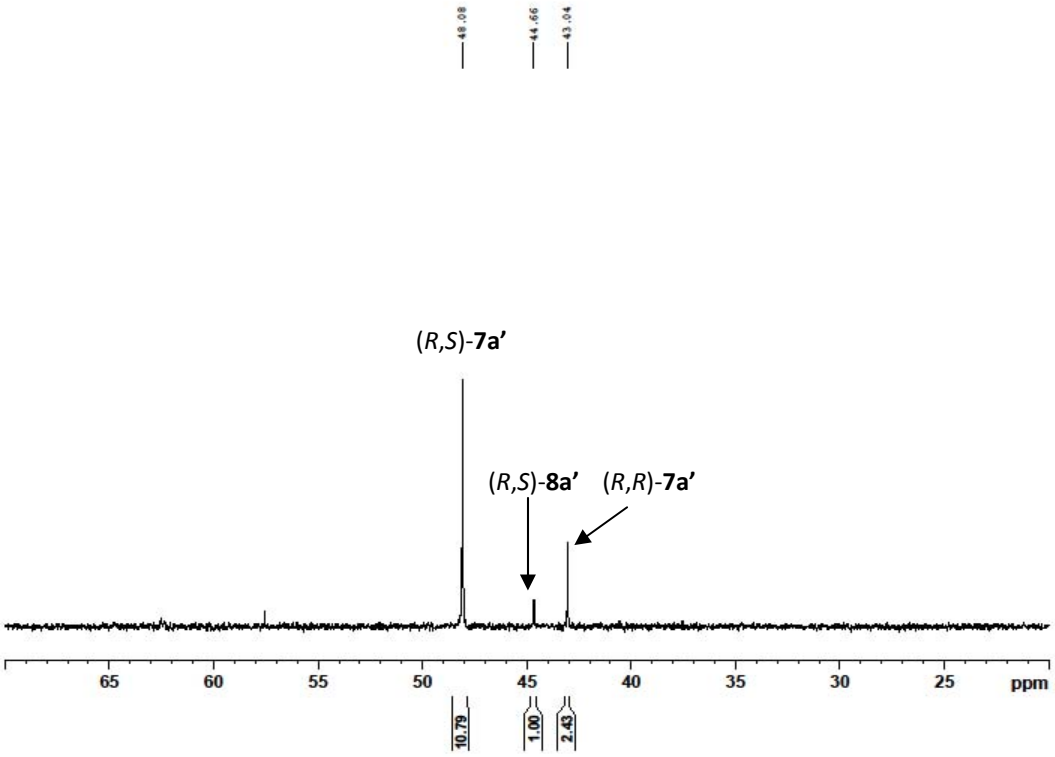


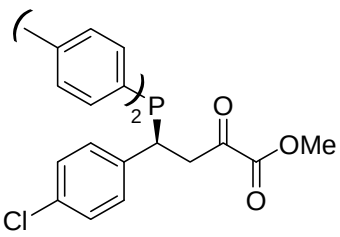
(*S*)-**2a'**



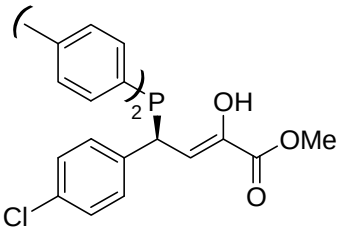
(*S*)-**3a'**

(*S*)-**2a'** was prepared according to general procedure (39.6 mg, 98% yield [4% as (*S*)-**3a'**], 66% *ee*): $[\alpha]_D^{23}$ = -194.6° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -0.44 [(*S*)-**2a'**], 2.20 [(*S*)-**3a'**]; ^1H ($CDCl_3$, 400 MHz): δ 2.16 (s, 3H), 2.29 (s, 3H), 2.89-2.96 (m, 1H), 3.39-3.47 (m, 1H), 3.63 (s, 3H), 4.01-4.06 (m, 1H), 6.85-7.46 (m, 13H); ^{13}C ($CDCl_3$, 101 MHz): δ 21.4 (s, 1C), 21.6 (s, 1C), 39.8 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.5 (d, 1C, $^1J_{CP}$ = 23 Hz), 53.0 (s, 1C), 126.8-140.2 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 2 Hz), 192.4 (d, 1C, $^3J_{CP}$ = 12 Hz).



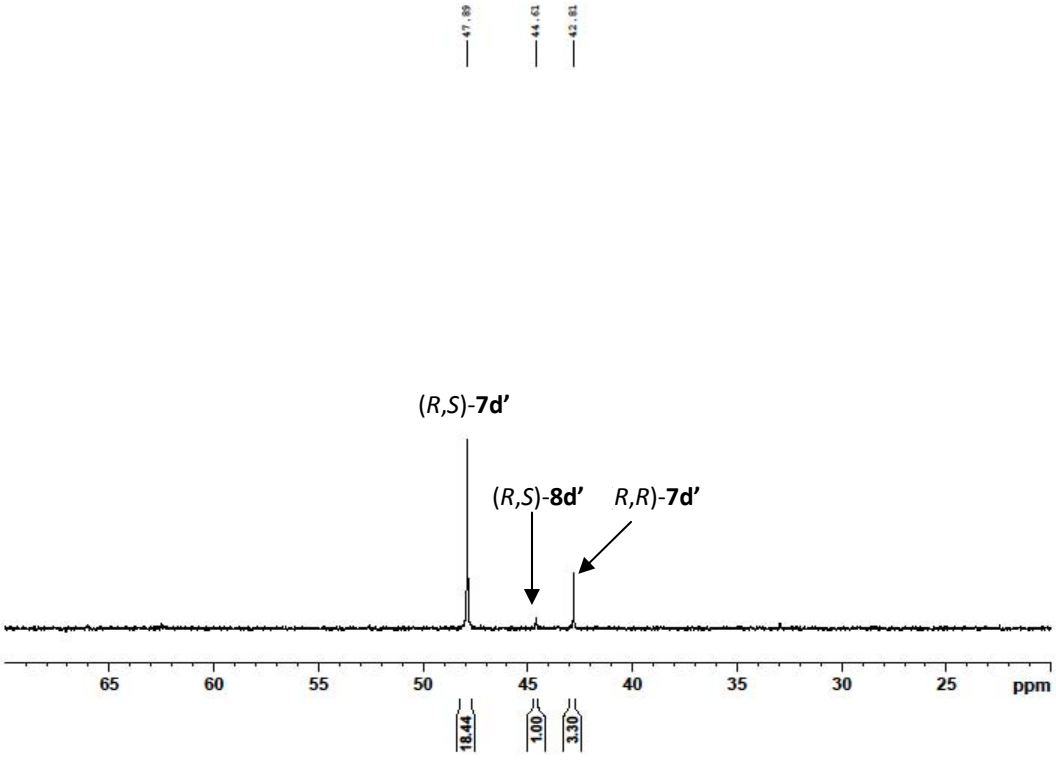


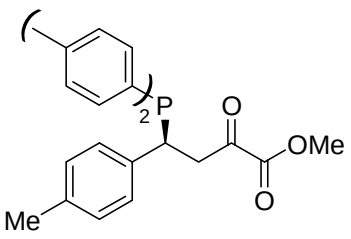
(*S*)-**2d'**



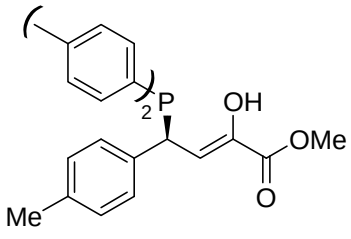
(*S*)-**3d'**

(*S*)-**2d'** was prepared according to general procedure (43.4 mg, >99% yield [4% as (*S*)-**3d'**], 71% *ee*): $[\alpha]_D^{23}$ = -150.0° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -1.53 [(*S*)-**2d'**], 2.39 [(*S*)-**3d'**]; ^1H ($CDCl_3$, 400 MHz): δ 2.17 (s, 3H), 2.29 (s, 3H), 2.89-2.95 (m, 1H), 3.34-3.43 (m, 1H), 3.65 (s, 3H), 3.98-4.03 (m, 1H), 6.89-7.45 (m, 12H); ^{13}C ($CDCl_3$, 101 MHz): δ 21.4 (s, 1C), 21.6 (s, 1C), 39.2 (d, 1C, $^2J_{CP}$ = 14 Hz), 43.3 (d, 1C, $^1J_{CP}$ = 22 Hz), 53.1 (s, 1C), 128.7-140.2 (m, 18C), 161.0 (d, 1C, $^4J_{CP}$ = 3 Hz), 192.2 (d, 1C, $^3J_{CP}$ = 13 Hz).



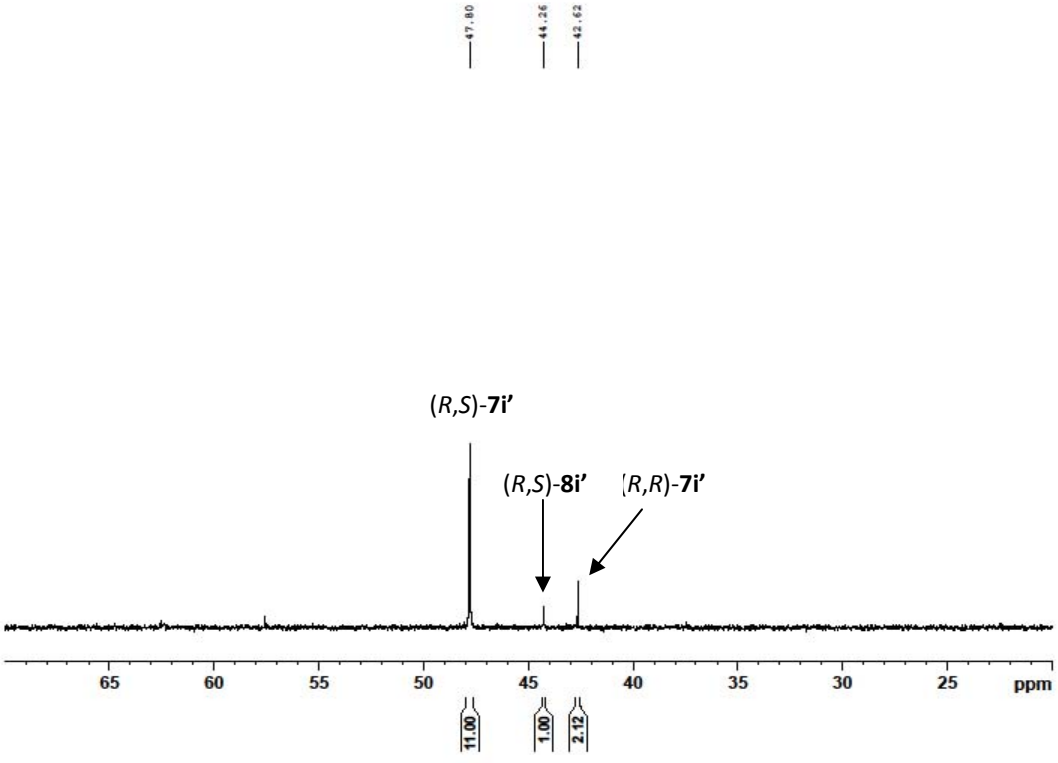


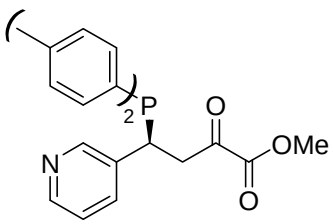
(*S*)-**2i'**



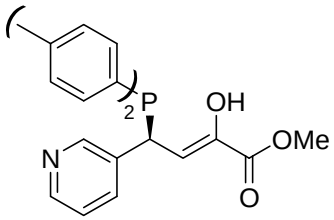
(*S*)-**3i'**

(*S*)-**2i'** was prepared according to general procedure (41.0 mg, 98% yield [6% as (*S*)-**3i'**], 70% *ee*): $[\alpha]_D^{23}$ = -107.1° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -2.00 [(*S*)-**2i'**], 1.11 [(*S*)-**3i'**]; ^1H ($CDCl_3$, 400 MHz): δ 2.16 (s, 6H), 2.29 (s, 3H), 2.87-2.93 (m, 1H), 3.33-3.41 (m, 1H), 3.63 (s, 3H), 3.99-4.04 (m, 1H), 6.87-7.45 (m, 12H); ^{13}C ($CDCl_3$, 101 MHz): δ 21.2 (s, 1C), 21.4 (s, 1C), 21.6 (s, 1C), 39.3 (d, 1C, $^2J_{CP}$ = 13 Hz), 43.7 (d, 1C, $^1J_{CP}$ = 22 Hz), 53.0 (s, 1C), 129.0-140.0 (m, 18C), 161.1 (d, 1C, $^4J_{CP}$ = 2 Hz), 192.5 (d, 1C, $^3J_{CP}$ = 12 Hz).



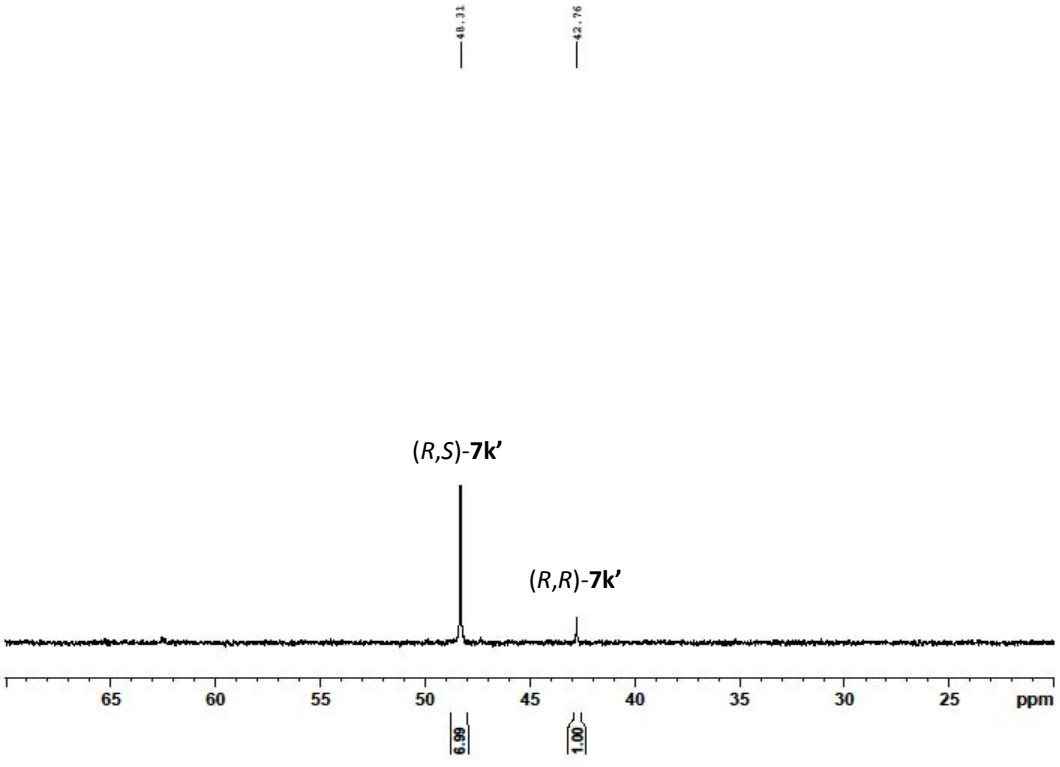


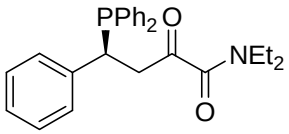
(*S*)-**2k'**



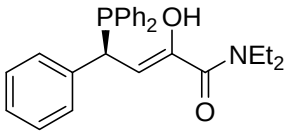
(*S*)-**3k'**

(*S*)-**2k'** was prepared according to general procedure (40.1 mg, >99% yield [10% as (*S*)-**3k'**], 75% *ee*): $[\alpha]_D^{23}$ = -84.4° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -1.07 [(*S*)-**2k'**], 3.09 [(*S*)-**3k'**]; ^1H ($CDCl_3$, 400 MHz): δ 2.17 (s, 3H), 2.30 (s, 3H), 2.97-3.05 (m, 1H), 3.40-3.49 (m, 1H), 3.67 (s, 3H), 4.01-4.06 (m, 1H), 6.89-8.27 (m, 12H); ^{13}C ($CDCl_3$, 101 MHz): δ 21.4 (s, 1C), 21.6 (s, 1C), 37.0 (d, 1C, $^2J_{CP}$ = 15 Hz), 43.0 (d, 1C, $^1J_{CP}$ = 22 Hz), 53.2 (s, 1C), 129.3-150.7 (m, 17C), 161.0 (d, 1C, $^4J_{CP}$ = 3 Hz), 191.9 (d, 1C, $^3J_{CP}$ = 12 Hz).



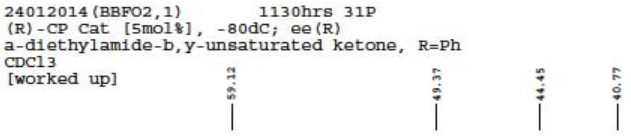


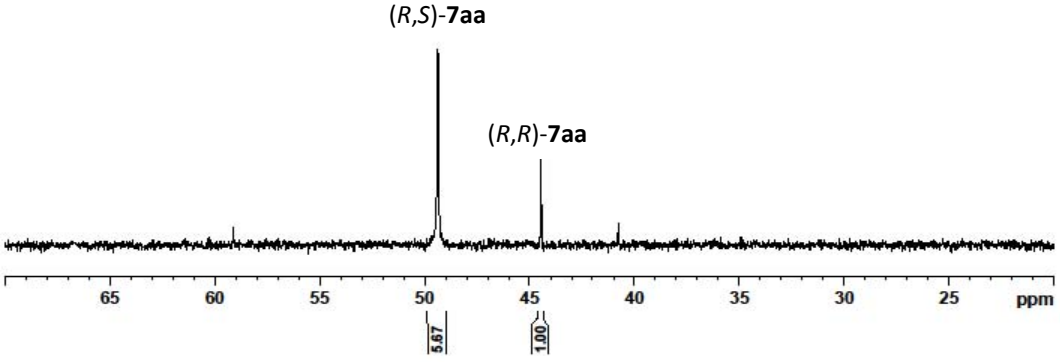
(*S*)-**2aa**



(*S*)-**3aa**

(*S*)-**2aa** was prepared according to general procedure (39.7 mg, 95% yield [<1% as (*S*)-**3aa**], 70% *ee*): $[\alpha]_D^{23}$ = -200.0° [c 0.5, $CHCl_3$]. $^{31}P\{^1H\}$ ($CDCl_3$, 162 MHz): δ -5.45 [(*S*)-**2aa**], 1.14 [(*S*)-**3aa**]; ^1H ($CDCl_3$, 400 MHz): δ 0.77 (t, 3H, $^3J_{HH}$ = 7Hz), 0.98 (t, 3H, $^3J_{HH}$ = 7Hz), 2.39-2.46 (m, 2H), 3.09-3.25 (m, 4H), 3.64 (s, 3H), 4.07-4.11 (m, 1), 7.00-7.62 (m, 15H); ^{13}C ($CDCl_3$, 101 MHz): δ 12.6 (s, 1C), 14.1 (s, 1C), 39.6 (d, 1C, $^2J_{CP}$ = 14 Hz), 39.6 (s, 1C), 41.5 (s, 1C), 43.8 (d, 1C, $^1J_{CP}$ = 22 Hz), 126.9-139.9 (m, 18C), 166.2 (d, 1C, $^4J_{CP}$ = 1 Hz), 199.8 (d, 1C, $^3J_{CP}$ = 13 Hz).





III. References

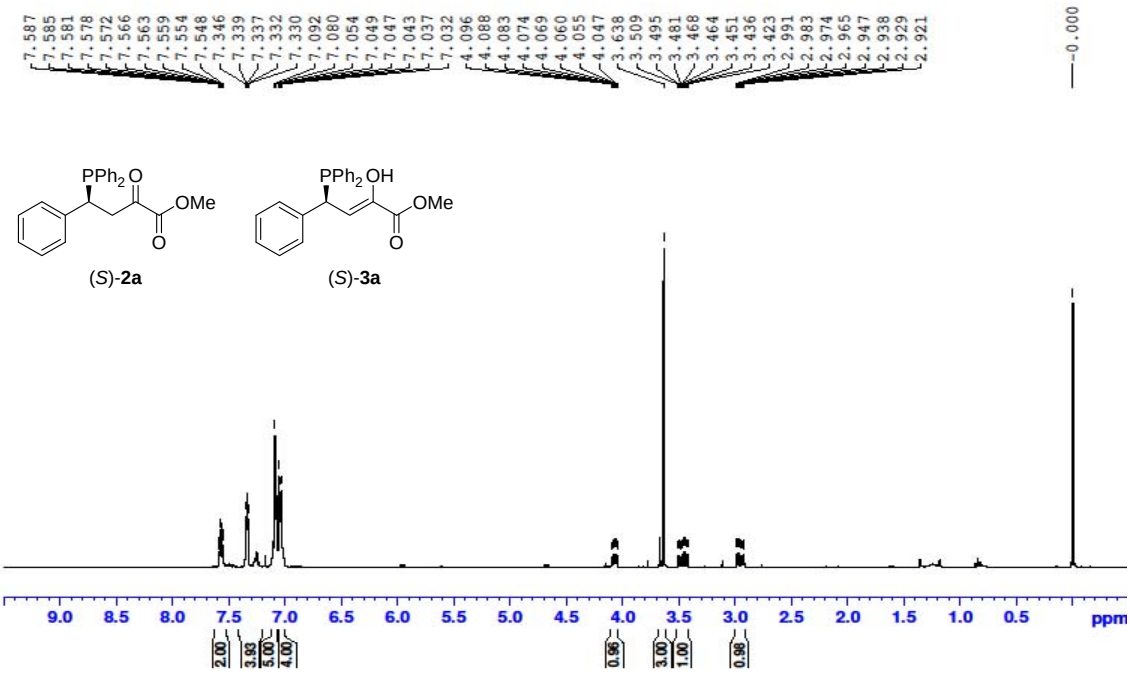
[1] J. K. Ng, G.-K. Tan, J. J. Vittal, P.-H. Leung, *Inorg. Chem*. **2003**, *42*, 7674-7682.

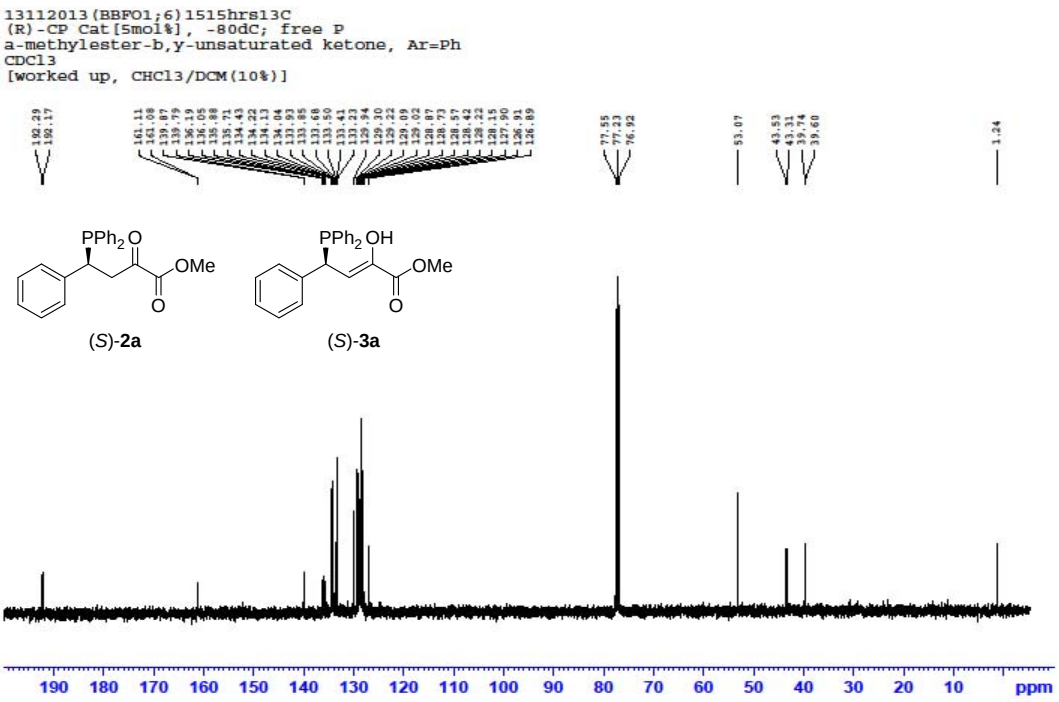
[2] S. Y. M. Chooi, P.-H. Leung, C. C. Lim, K. F. Mok, G. H. Quek, K. Y. Sim, M. K. Tan, *Tetrahedron: Asymmetry* **1992**, *3*, 529-532.

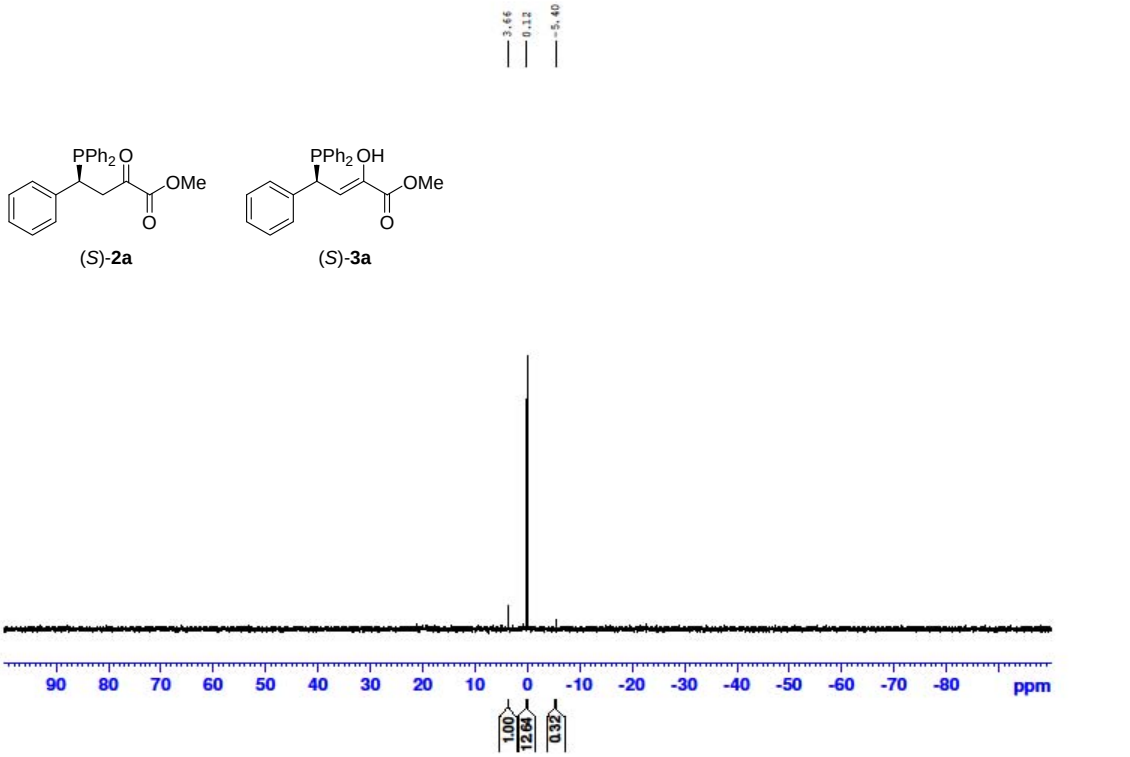
[3] a) L. Zhu, Q. Meng, W. Fan, X. Xie, Z. Zhang, *J. Org. Chem.* **2010**, *75*, 6027-6030; b) C. Allais, F. Liéby-Muller, T. Constantieux, J. Rodriguez, *Adv. Synth. Catal.* **2012**, *354*, 2537-2544.

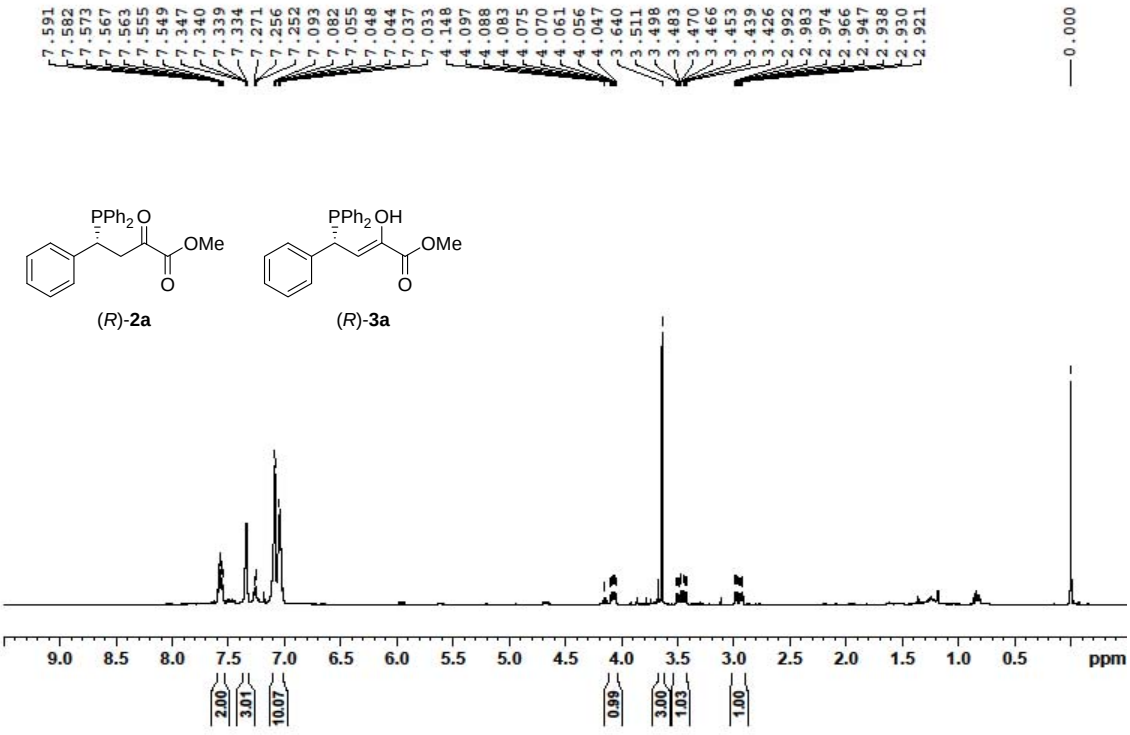
[4] a) See **V. Single Crystal X-Ray Diffraction Data**; b) CCDC 988281 contains the crystallographic data for compound (*R*,*S*)-**9a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

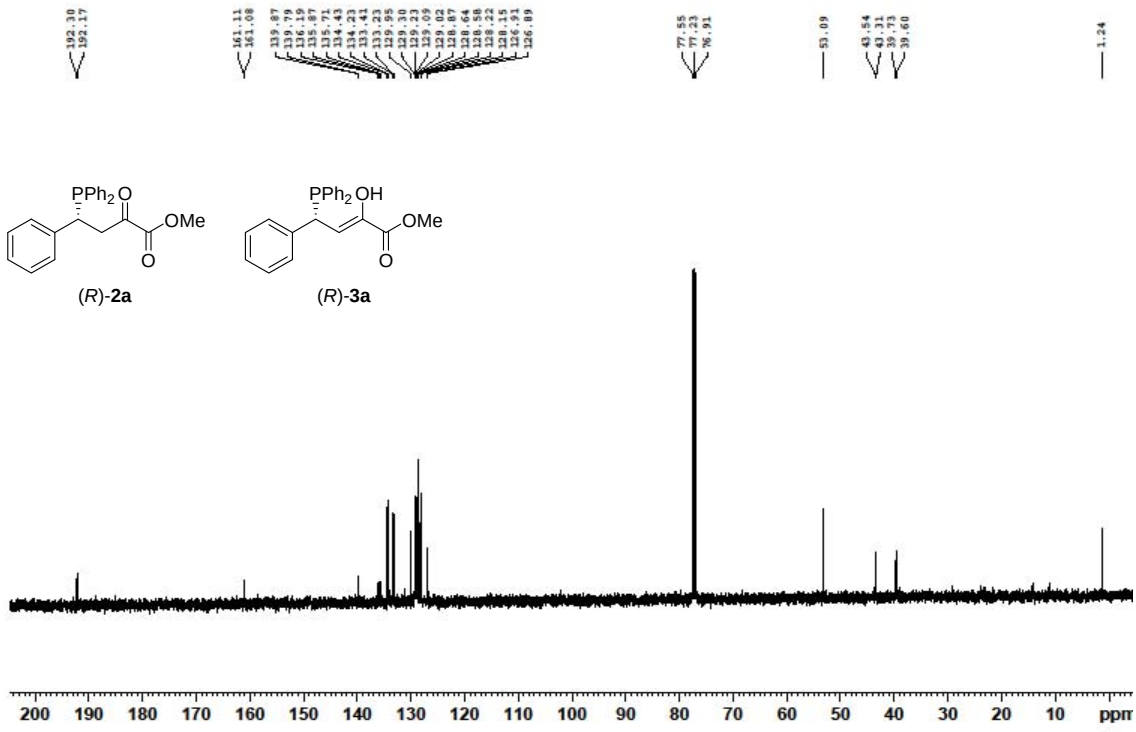
IV. NMR Spectra

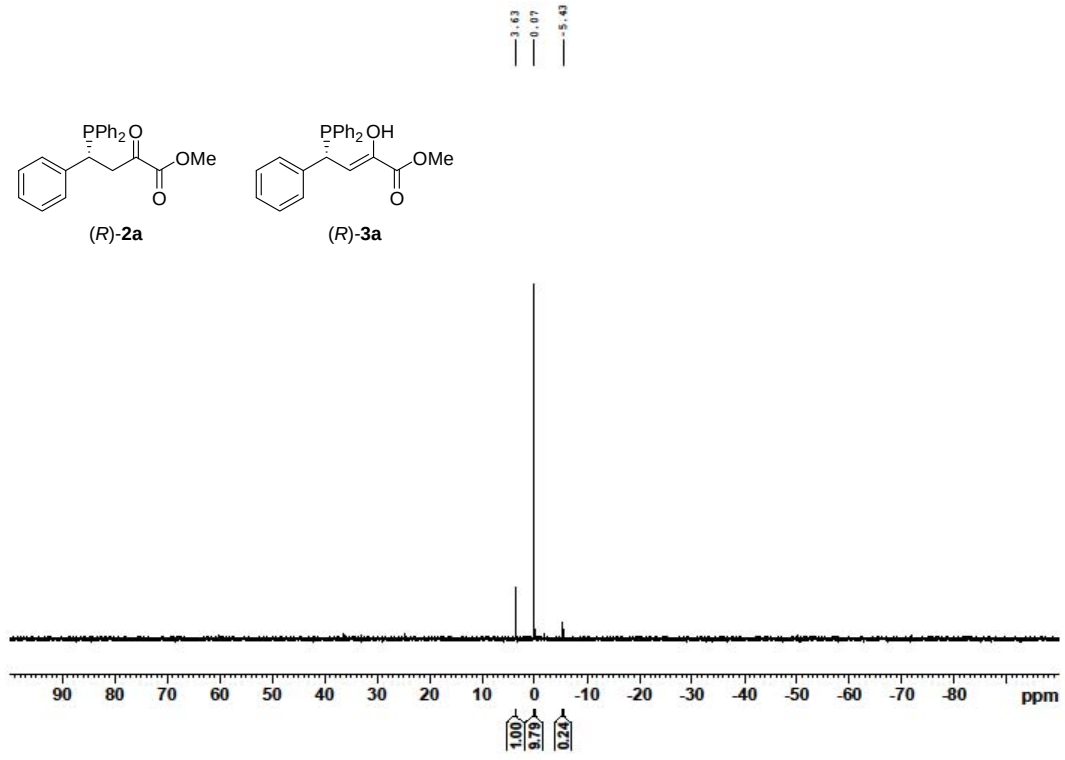


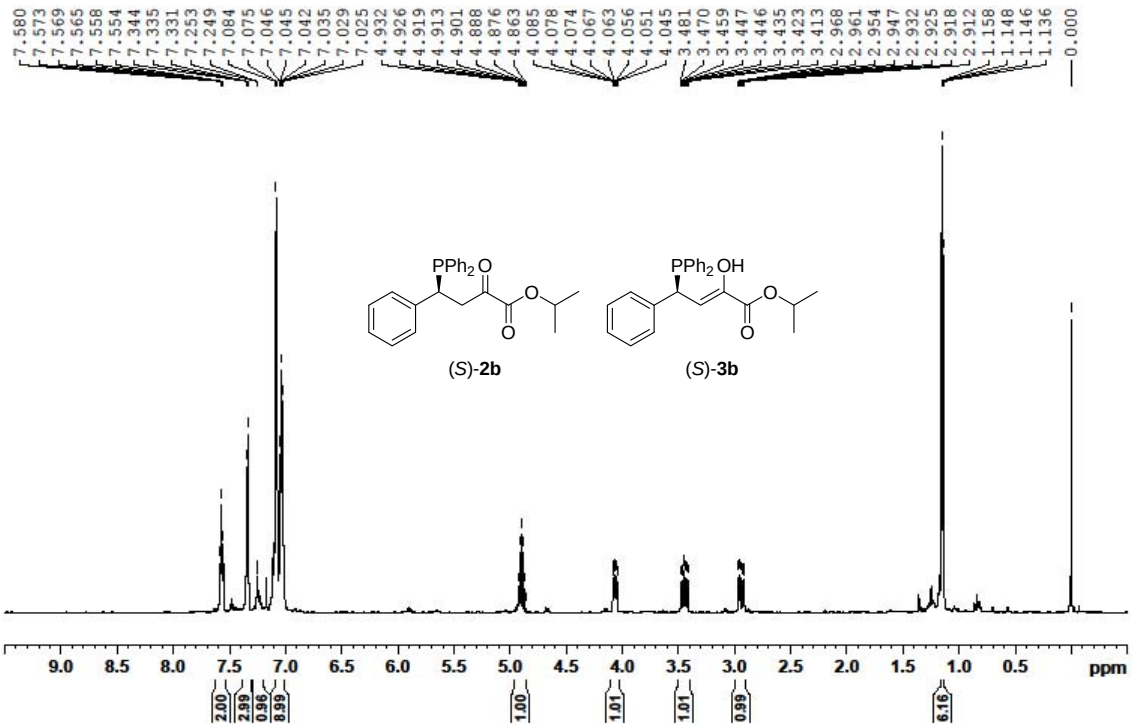



3.66
0.12
-5.40
PPh2 O
OMe
O
(S)-2a
PPh2 OH
OMe
O
(S)-3a
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm
1.00
12.64
0.32


7.591
7.582
7.573
7.567
7.563
7.555
7.549
7.347
7.340
7.339
7.334
7.271
7.256
7.252
7.093
7.082
7.055
7.048
7.044
7.037
7.033
4.148
4.097
4.088
4.083
4.075
4.070
4.061
4.056
4.047
3.640
3.511
3.498
3.483
3.470
3.466
3.453
3.439
3.426
2.992
2.983
2.974
2.966
2.947
2.938
2.930
2.921
0.000
PPh2 O
OMe
O
(R)-2a
PPh2 OH
OMe
O
(R)-3a
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
3.01
10.07
0.99
3.00
1.03
1.00


192.30
192.17
161.11
161.08
139.87
139.79
136.19
135.87
135.71
134.43
134.23
133.41
133.23
129.95
129.30
129.23
129.09
129.02
128.87
128.64
128.58
128.22
128.15
126.91
126.89
77.55
77.23
76.91
53.09
43.54
43.31
39.73
39.60
1.24
PPh2 O
OMe
O
(R)-2a
PPh2 OH
OMe
O
(R)-3a
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


3.63
0.07
-5.43
PPh2 O
OMe
O
(R)-2a
PPh2 OH
OMe
O
(R)-3a
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm
1.00
9.79
0.24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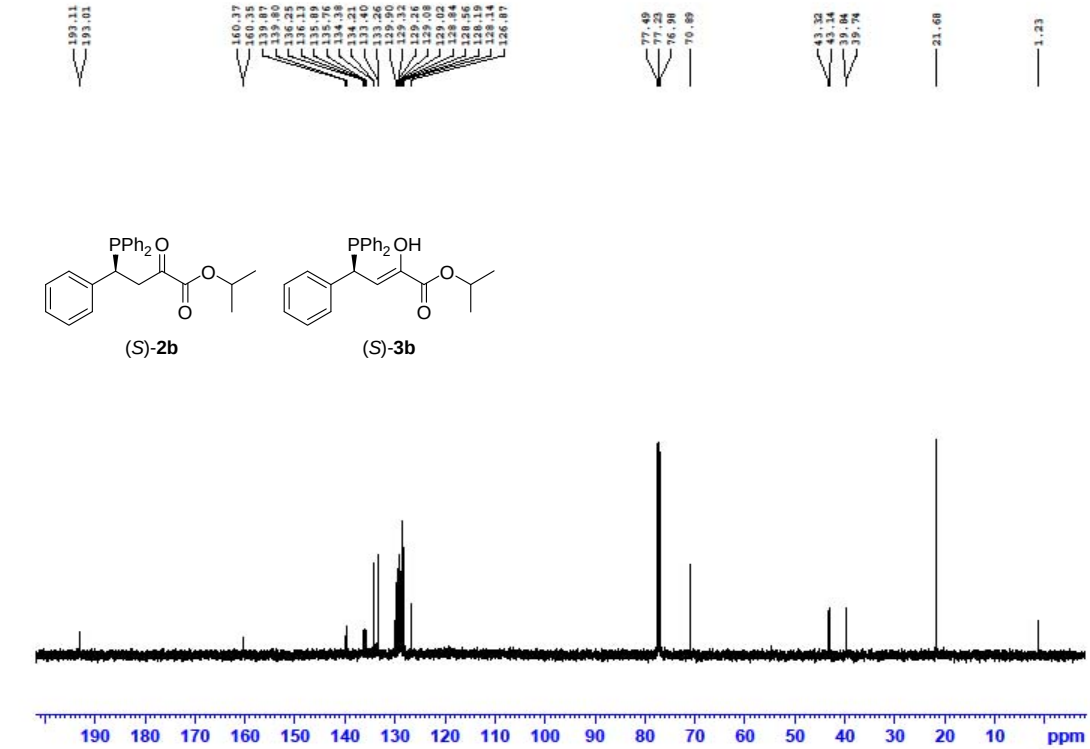
7.573
7.569
7.565
7.558
7.554
7.344
7.335
7.331
7.253
7.249
7.084
7.075
7.046
7.045
7.042
7.035
7.029
7.025
4.932
4.926
4.919
4.913
4.901
4.888
4.876
4.863
4.085
4.078
4.074
4.067
4.063
4.056
4.051
4.045
3.481
3.470
3.459
3.447
3.446
3.435
3.423
3.413
2.968
2.961
2.954
2.947
2.932
2.925
2.918
2.912
1.158
1.148
1.146
1.136
0.000
PPh2 O
O
O
(S)-2b
PPh2 OH
O
O
(S)-3b
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
2.99
0.96
8.99
1.00
1.01
1.01
0.98
6.16


193.11
193.01
160.37
160.35
139.87
139.80
136.25
136.13
135.89
135.76
134.38
134.21
133.40
133.26
129.90
129.32
129.26
129.08
129.02
128.84
128.56
128.19
128.14
126.97
77.49
77.23
76.98
70.89
43.32
43.14
39.84
39.74
21.68
1.23
PPh2 O
O
O
(S)-2b
PPh2 OH
O
O
(S)-3b
190
180
170
160
150
140
130
120
110
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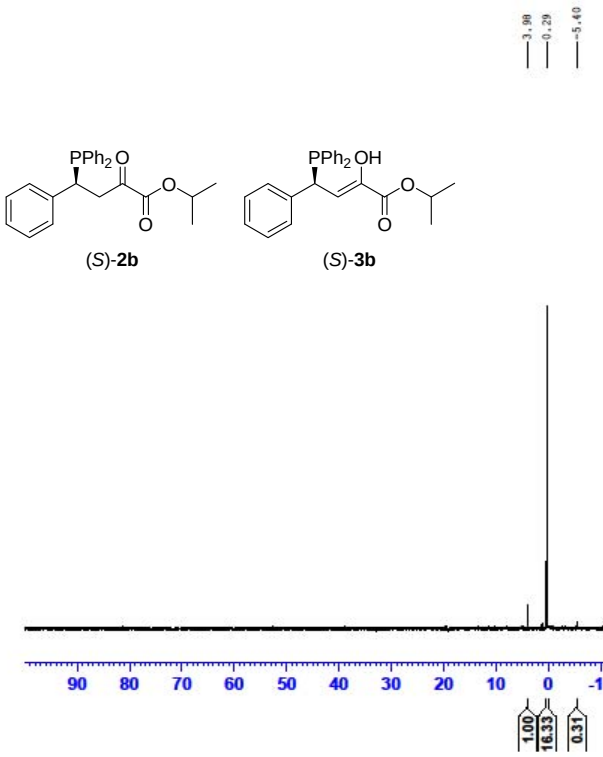
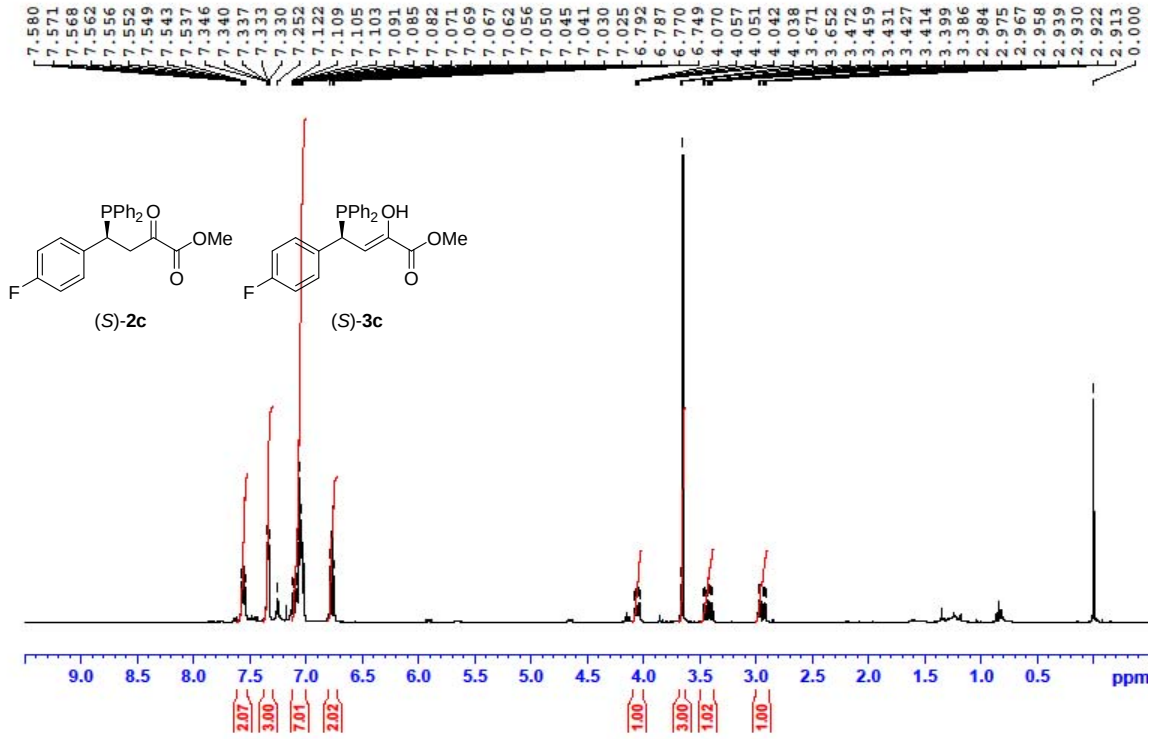
90
80
70
60
50
40
30
20
10
ppm


PPh2 O
O
O
(S)-2b
PPh2 OH
O
O
(S)-3b
3.98
0.29
5.40
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm
1.00
16.33
0.31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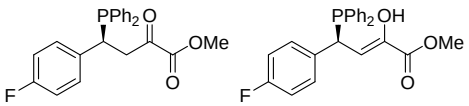
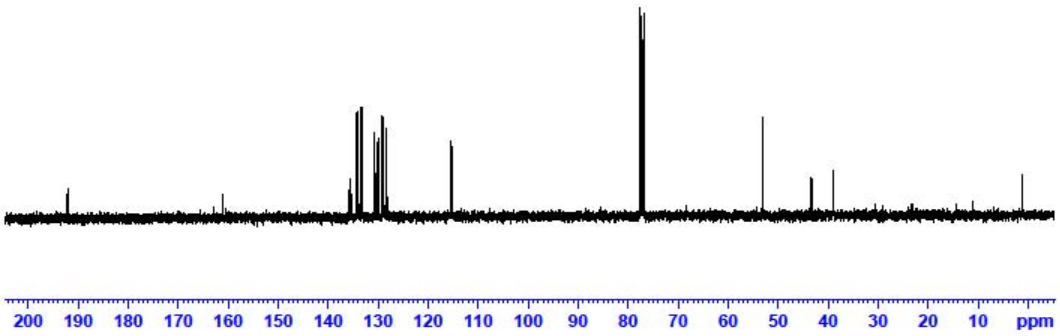
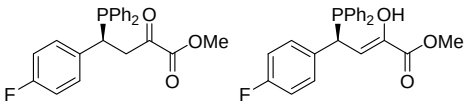
7.571
7.568
7.562
7.556
7.552
7.549
7.543
7.537
7.346
7.340
7.337
7.333
7.330
7.252
7.122
7.109
7.105
7.103
7.091
7.085
7.082
7.071
7.069
7.067
7.062
7.056
7.050
7.045
7.041
7.030
7.025
6.792
6.787
6.770
6.749
4.070
4.057
4.051
4.042
4.038
3.671
3.652
3.472
3.459
3.431
3.427
3.414
3.399
3.386
2.984
2.975
2.967
2.958
2.939
2.930
2.922
2.913
0.000
PPh2 O
OMe
O
F
(S)-2c
PPh2 OH
OMe
O
F
(S)-3c
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
2.07
3.00
7.01
2.02
1.00
3.00
1.02
1.00



(*S*)-**2c** (*S*)-**3c**





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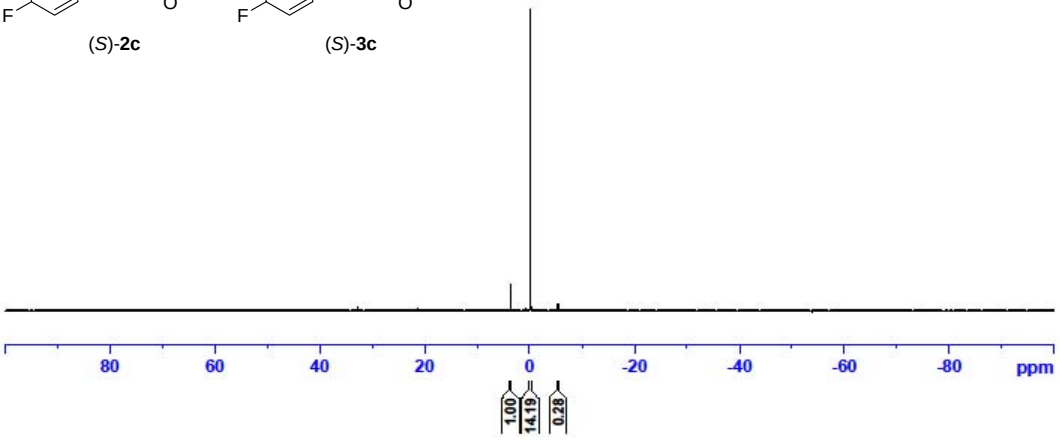

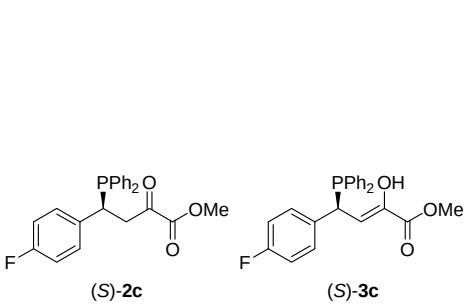

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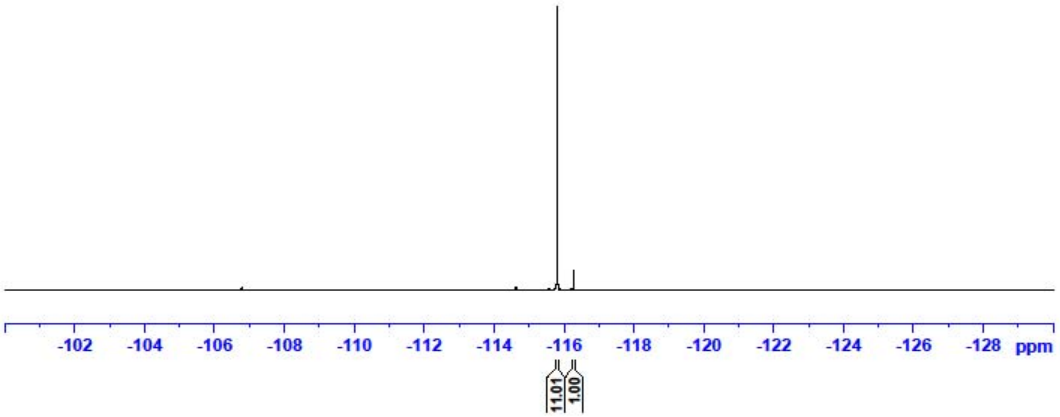

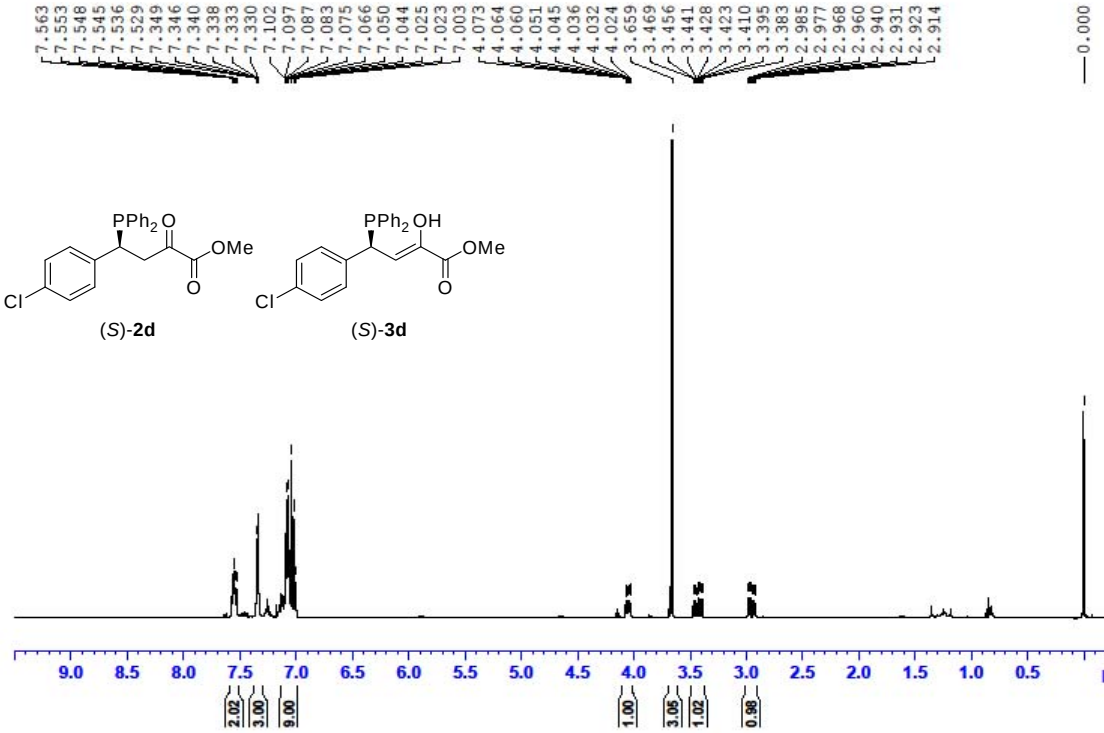

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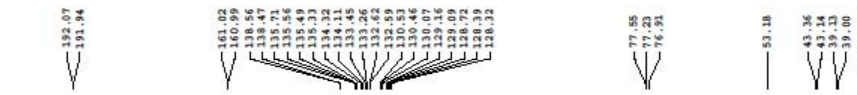

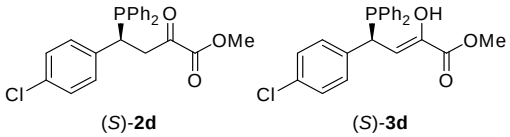

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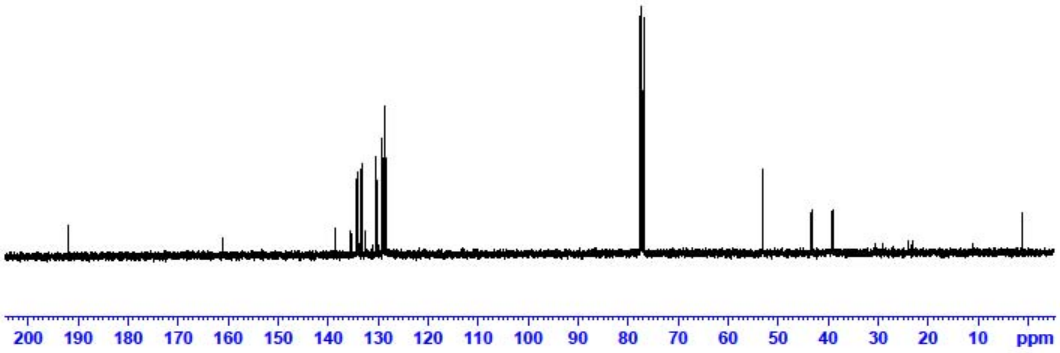
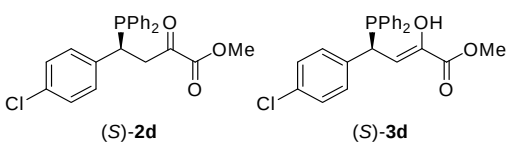
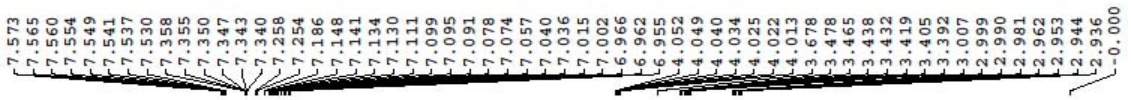
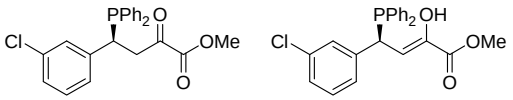




(*S*)-**2d** (*S*)-**3d**





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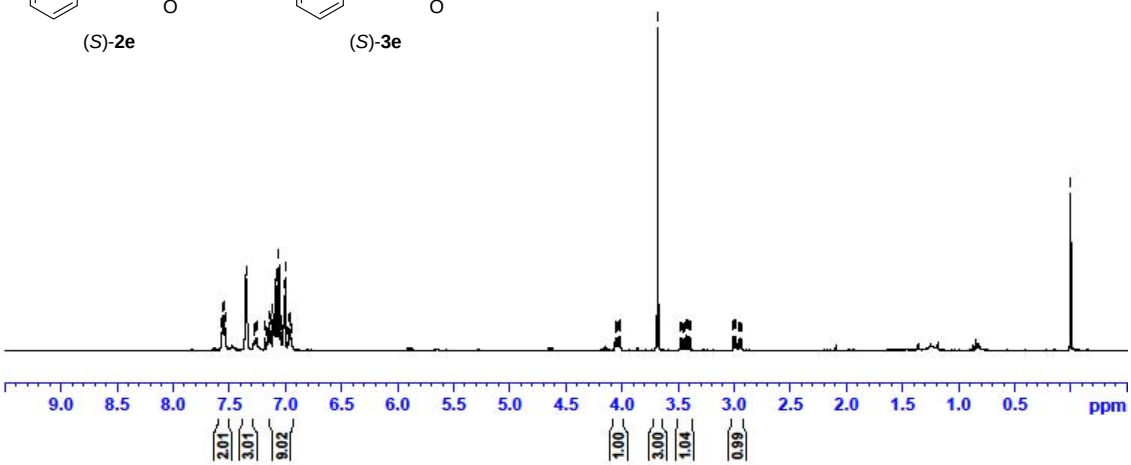

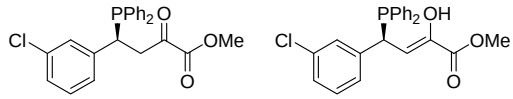

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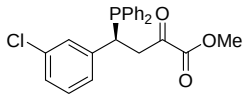

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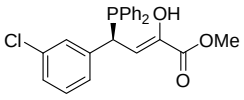

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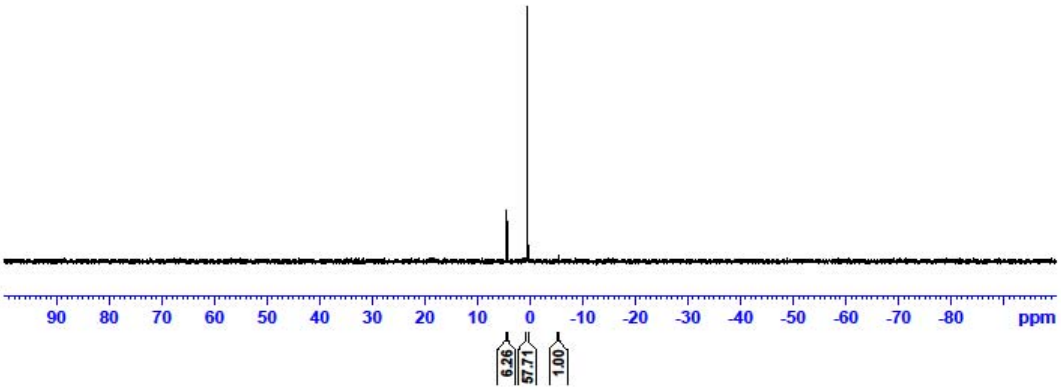

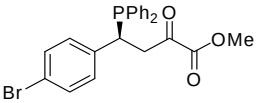

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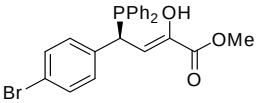

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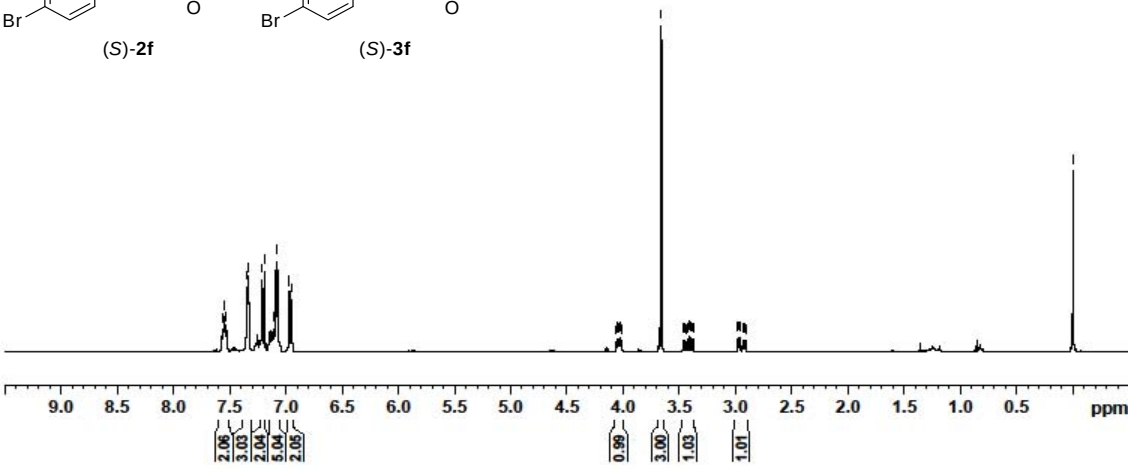

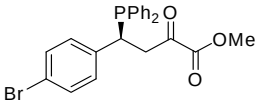

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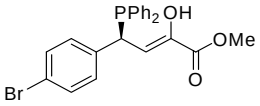

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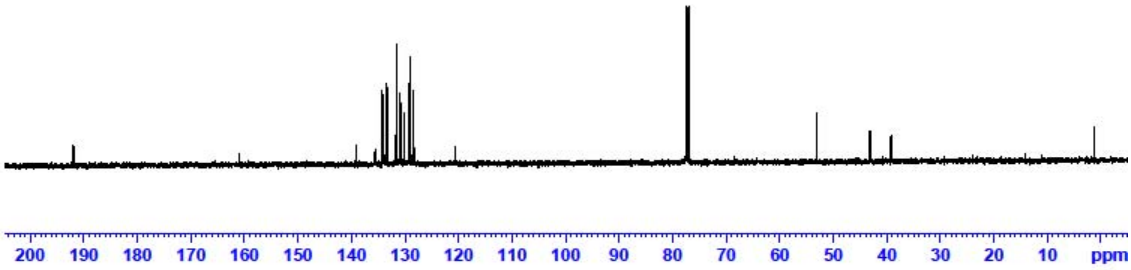
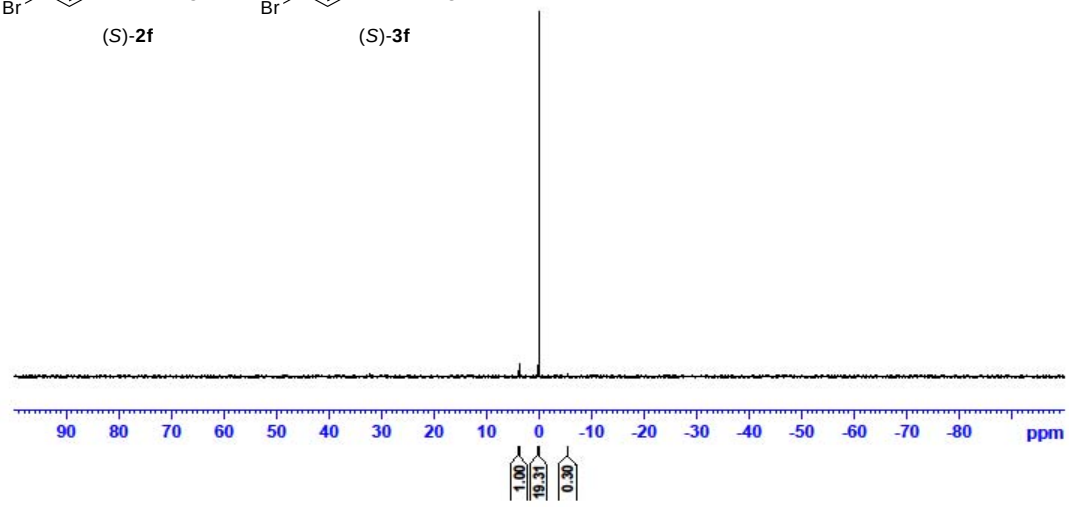
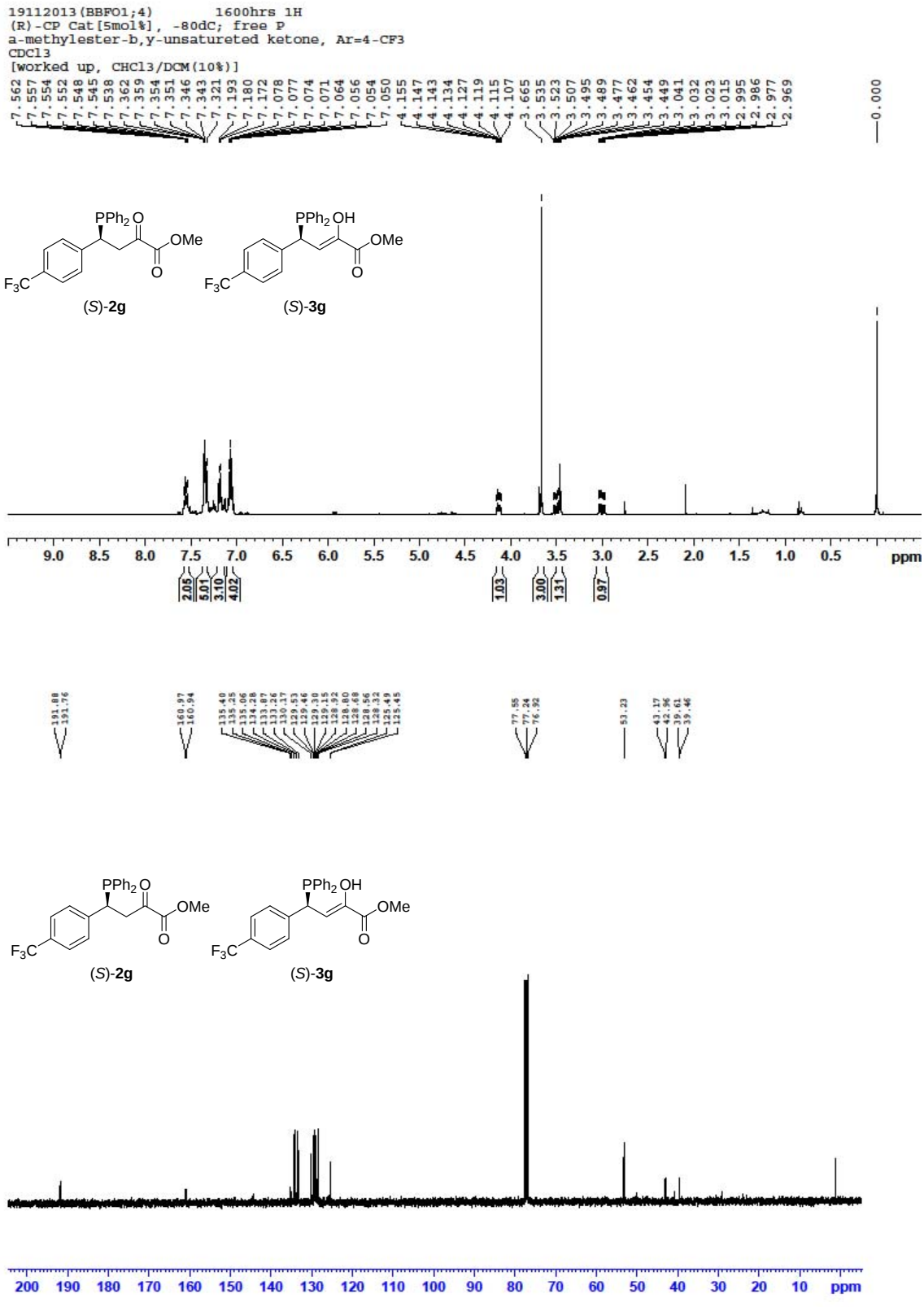
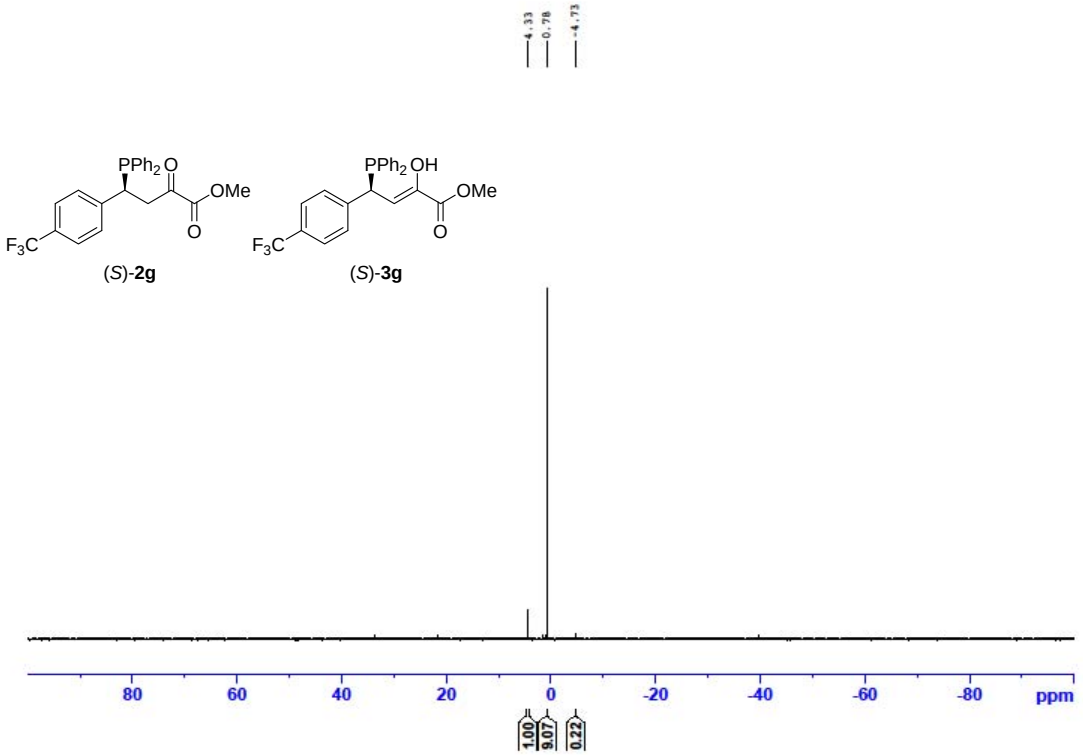


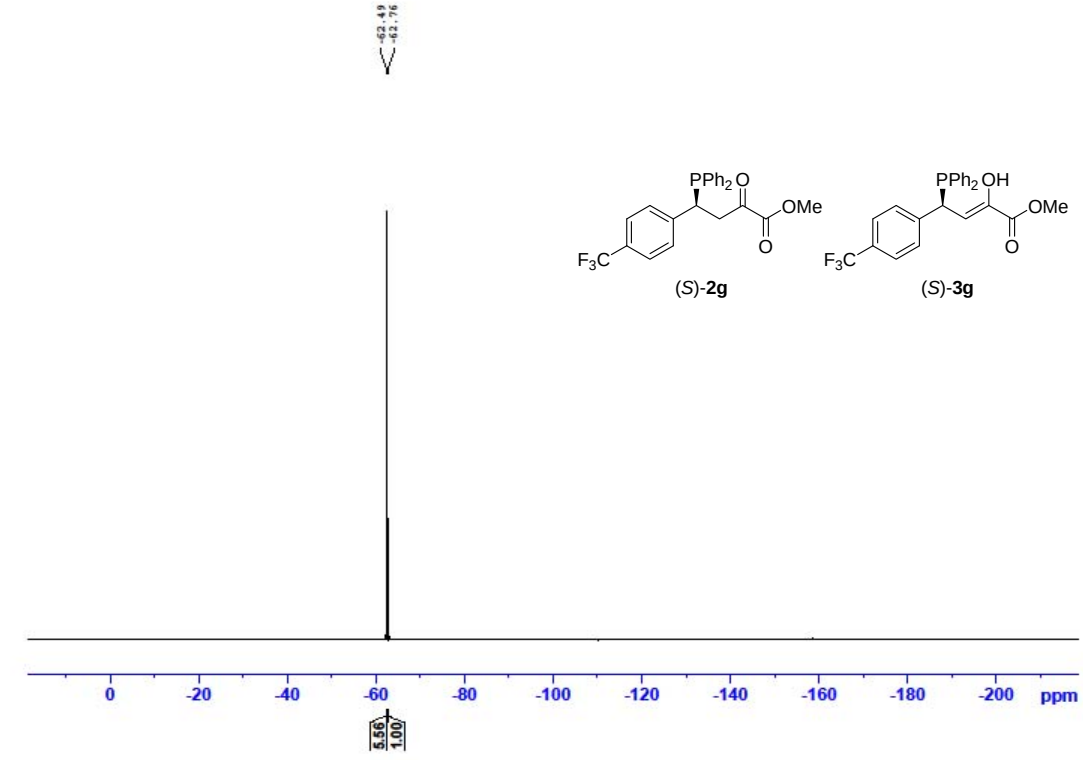
(*S*)-**2f**

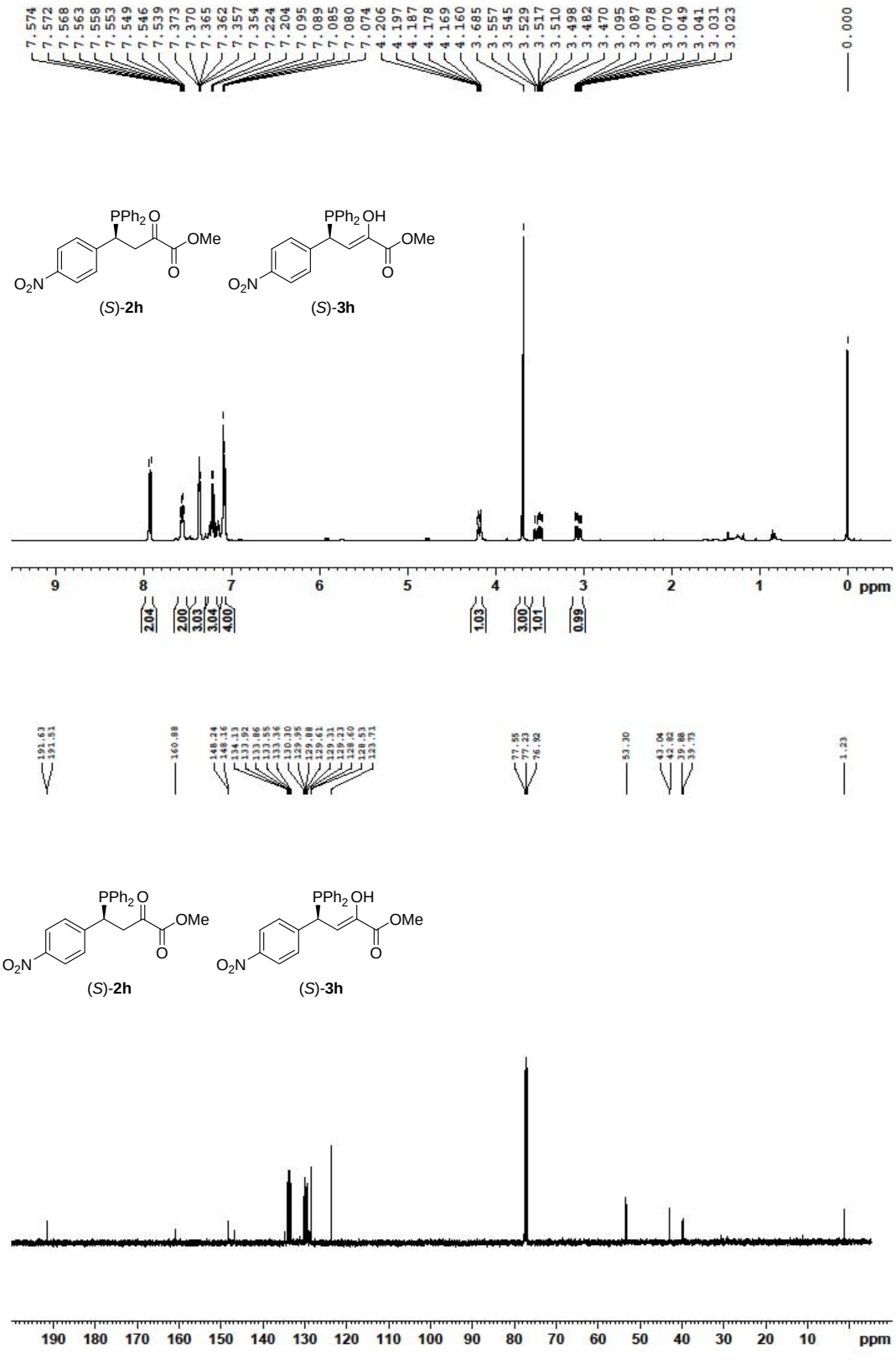
(*S*)-**3f**

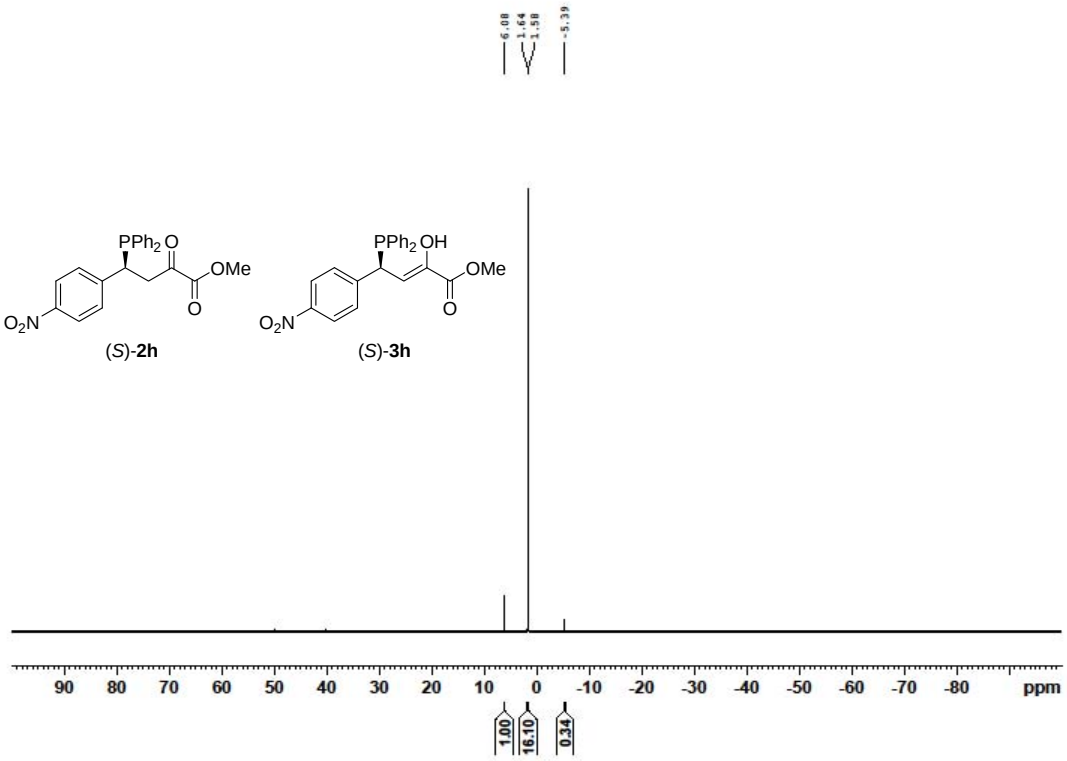


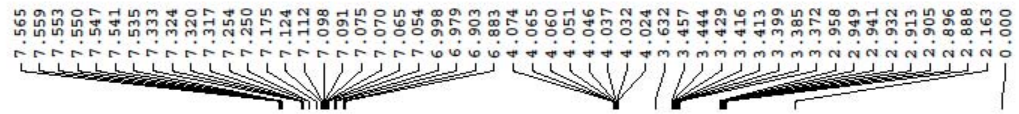

19112013(BBFO1;4) 1600hrs 1H
(R)-CP Cat[5mol%], -80dC; free P
a-methylester-b,y-unsatureted ketone, Ar=4-CF3
CDCl3
[worked up, CHCl3/DCM(10%)]
PPh2 O
OMe
O
F3C
(S)-2g
PPh2 OH
OMe
O
F3C
(S)-3g
ppm
ppm

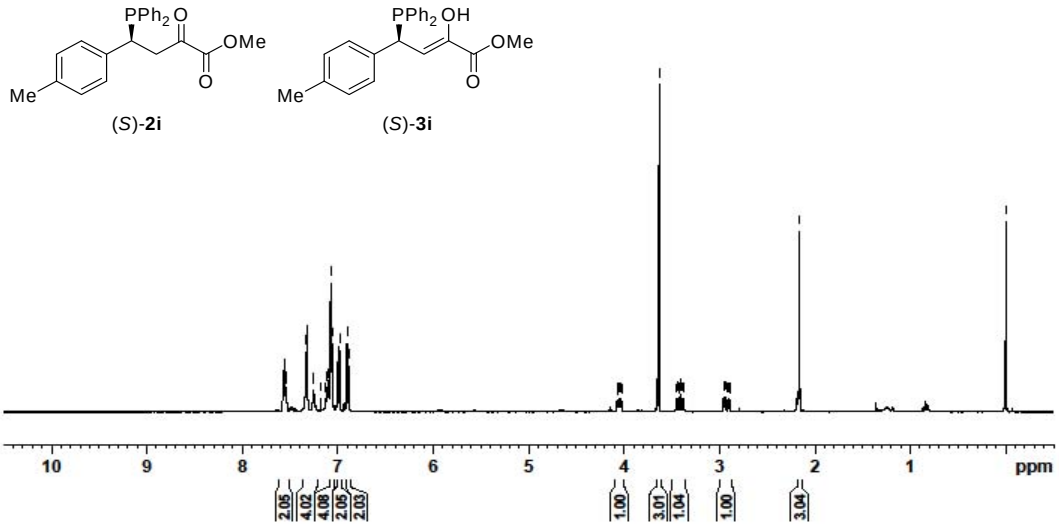

-4.33
-0.78
-4.73
PPh2 O
OMe
O
F3C
(S)-2g
PPh2 OH
OMe
O
F3C
(S)-3g
80
60
40
20
0
-20
-40
-60
-80
ppm
1.00
9.07
0.22

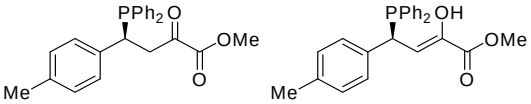

-62.49
-62.76
PPh2 O
OMe
O
F3C
(S)-2g
PPh2 OH
OMe
O
F3C
(S)-3g
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
-200
ppm
5.56
1.00


7.574
7.572
7.568
7.563
7.558
7.553
7.549
7.546
7.539
7.373
7.370
7.365
7.362
7.357
7.354
7.224
7.204
7.095
7.089
7.085
7.080
7.074
4.206
4.197
4.187
4.178
4.169
4.160
3.685
3.557
3.545
3.529
3.517
3.510
3.498
3.482
3.470
3.095
3.087
3.078
3.070
3.049
3.041
3.031
3.023
0.000
PPh2 O
OMe
O
O2N
(S)-2h
PPh2 OH
OMe
O
O2N
(S)-3h
9
8
7
6
5
4
3
2
1
0 ppm
2.04
2.00
3.03
3.04
4.00
1.03
3.00
1.01
0.99
191.63
191.51
160.88
148.24
148.16
134.13
133.92
133.86
133.55
133.36
130.10
130.05
129.88
129.61
129.31
129.23
128.60
128.53
123.71
77.55
77.23
76.92
53.30
43.04
42.82
39.88
39.73
1.23
PPh2 O
OMe
O
O2N
(S)-2h
PPh2 OH
OMe
O
O2N
(S)-3h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


6.08
1.64
1.58
-5.39
PPh2 O
OMe
O
O2N
(S)-2h
PPh2 OH
OMe
O
O2N
(S)-3h
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm
1.00
16.10
0.34

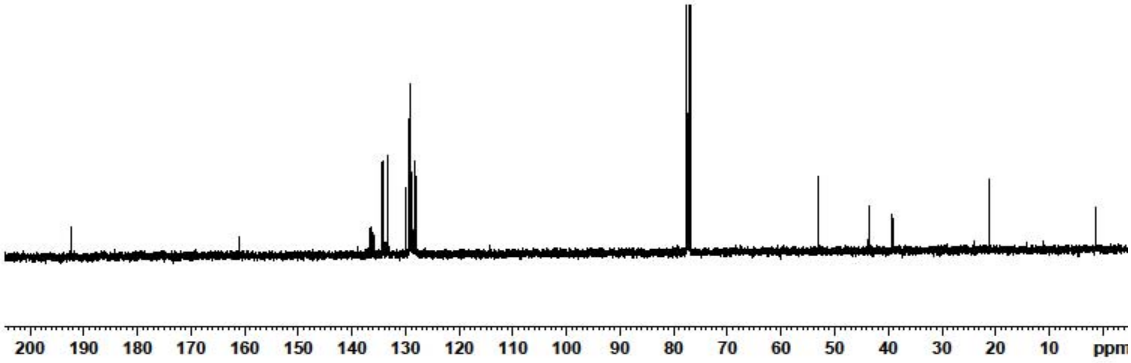

7.565
7.559
7.553
7.550
7.547
7.541
7.535
7.333
7.324
7.320
7.317
7.254
7.250
7.175
7.124
7.112
7.098
7.091
7.075
7.070
7.065
7.054
6.998
6.979
6.903
6.883
4.074
4.065
4.060
4.051
4.046
4.037
4.032
4.024
3.632
3.457
3.444
3.429
3.416
3.413
3.399
3.385
3.372
2.958
2.949
2.941
2.932
2.913
2.905
2.896
2.888
2.163
0.000

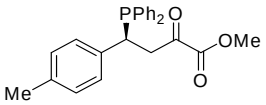

PPh2 O
OMe
O
Me
(S)-2i
PPh2 OH
OMe
O
Me
(S)-3i
10 9 8 7 6 5 4 3 2 1 ppm
2.05
4.02
4.08
2.05
2.03
1.00
3.01
1.04
1.00
3.04



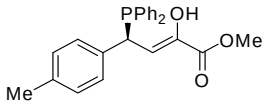
(*S*)-**2i**

(*S*)-**3i**

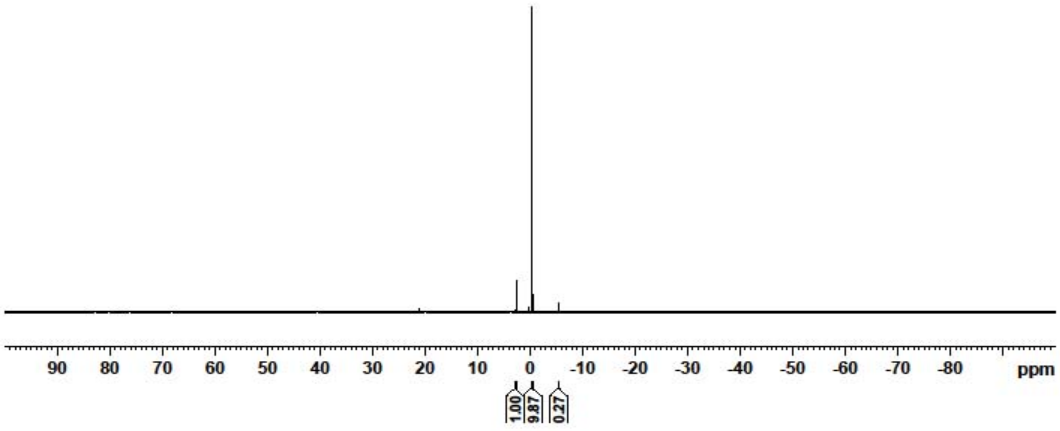


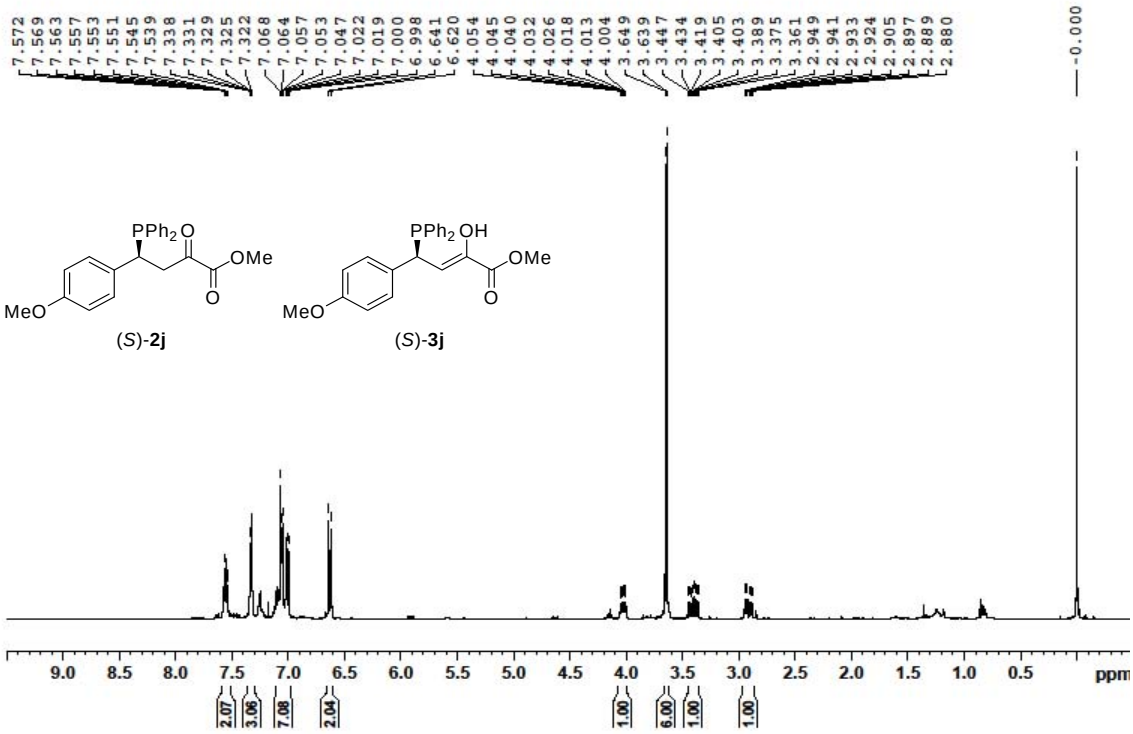


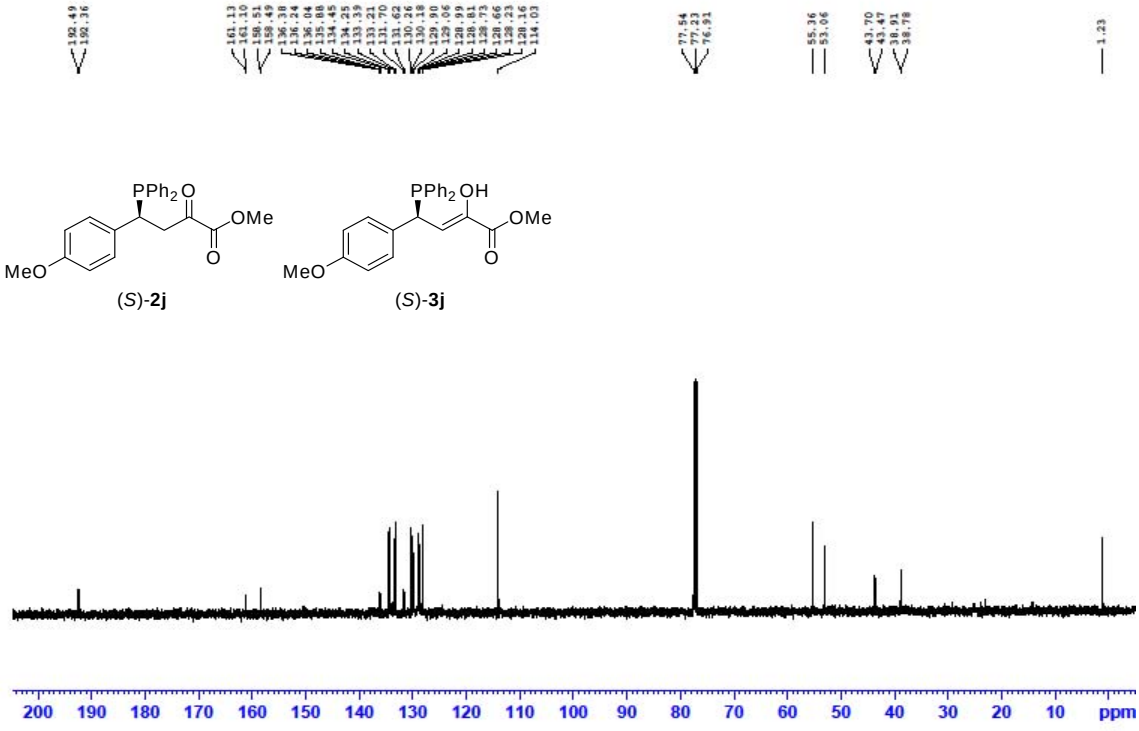
(*S*)-**2i**

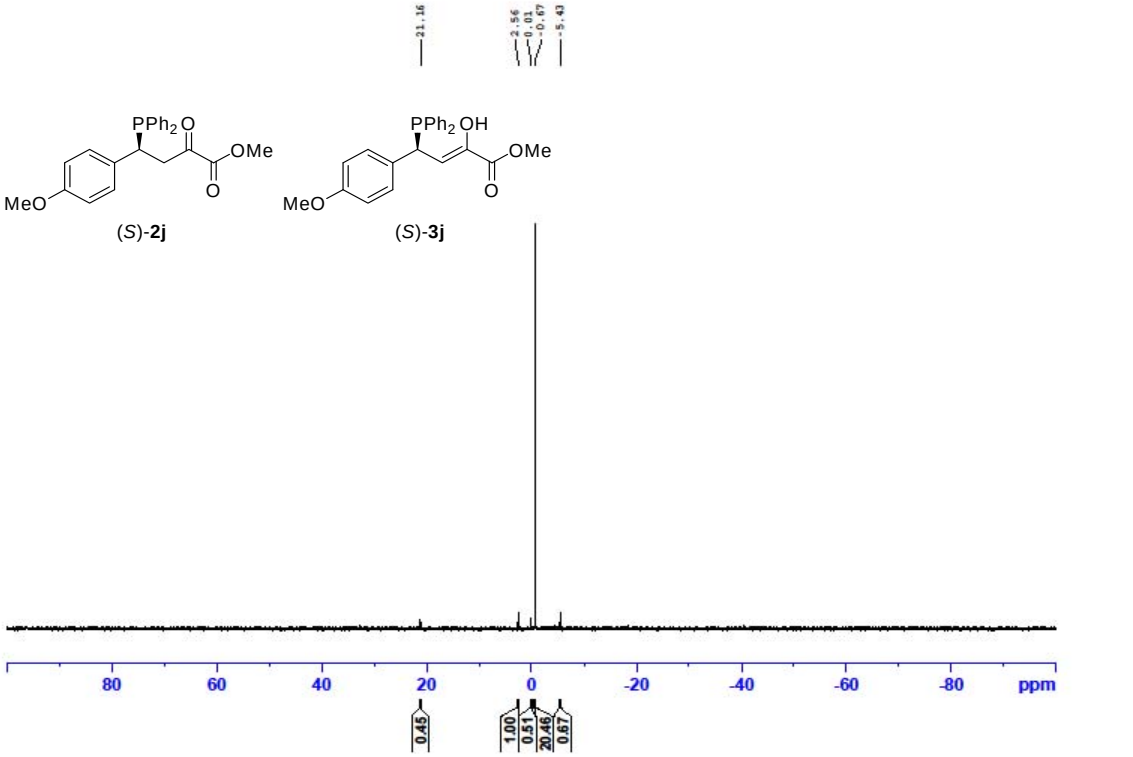


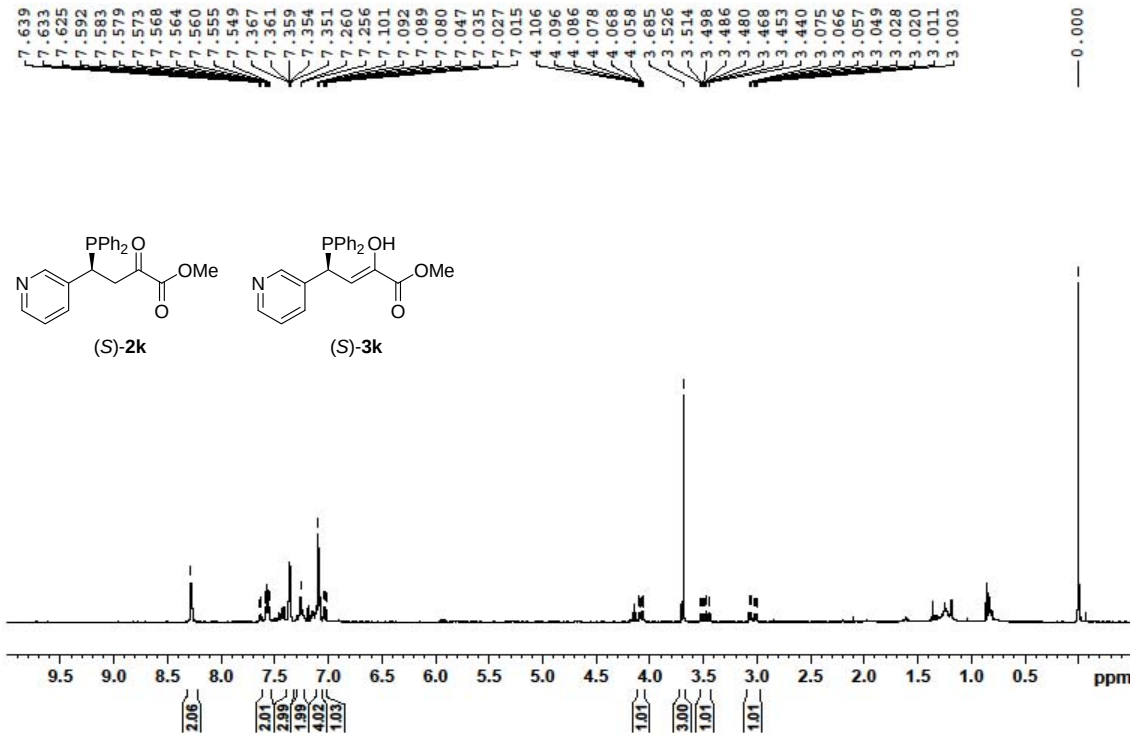
(*S*)-**3i**

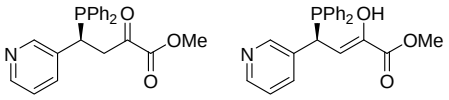



7.572
7.569
7.563
7.557
7.553
7.551
7.545
7.539
7.338
7.331
7.329
7.325
7.322
7.068
7.064
7.057
7.053
7.047
7.022
7.019
7.000
6.998
6.641
6.620
4.054
4.045
4.040
4.032
4.026
4.018
4.013
4.004
3.649
3.639
3.447
3.434
3.419
3.405
3.403
3.389
3.375
3.361
2.949
2.941
2.933
2.924
2.905
2.897
2.889
2.880
-0.000
PPh2 O
OMe
O
MeO
(S)-2j
PPh2 OH
OMe
O
MeO
(S)-3j
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
2.07
3.06
7.08
2.04
1.00
6.00
1.00
1.00


192.49
192.36
161.13
161.10
158.51
158.49
136.38
136.24
136.04
135.88
134.45
134.25
133.39
133.21
131.70
131.62
130.26
130.18
129.90
129.06
128.99
128.81
128.73
128.66
128.23
128.16
114.03
77.54
77.23
76.91
55.36
53.06
43.70
43.47
38.91
38.78
1.23
PPh2 O
OMe
O
MeO
(S)-2j
PPh2 OH
OMe
O
MeO
(S)-3j
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

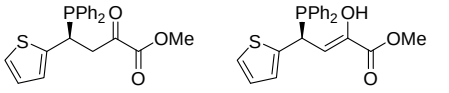

21.16
2.56
0.01
0.67
5.43
PPh2 O
OMe
MeO
O
(S)-2j
PPh2 OH
OMe
MeO
O
(S)-3j
80
60
40
20
0
-20
-40
-60
-80
ppm
0.45
1.00
0.51
20.46
0.67


7.639
7.633
7.625
7.592
7.583
7.579
7.573
7.568
7.564
7.560
7.555
7.549
7.367
7.361
7.359
7.354
7.351
7.260
7.256
7.101
7.092
7.089
7.080
7.047
7.035
7.027
7.015
4.106
4.096
4.086
4.078
4.068
4.058
3.685
3.526
3.514
3.498
3.486
3.480
3.468
3.453
3.440
3.075
3.066
3.057
3.049
3.028
3.020
3.011
3.003
0.000
PPh2 O
OMe
N
O
(S)-2k
PPh2 OH
OMe
N
O
(S)-3k
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
2.06
2.01
2.99
1.99
4.02
1.03
1.01
3.00
1.01
1.01



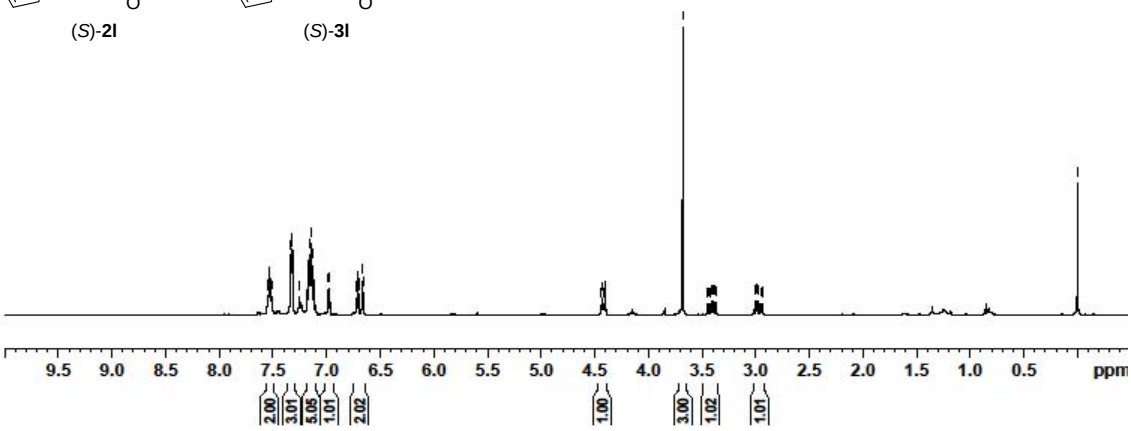
(*S*)-**2k**

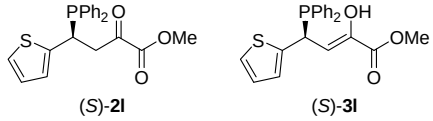
(*S*)-**3k**



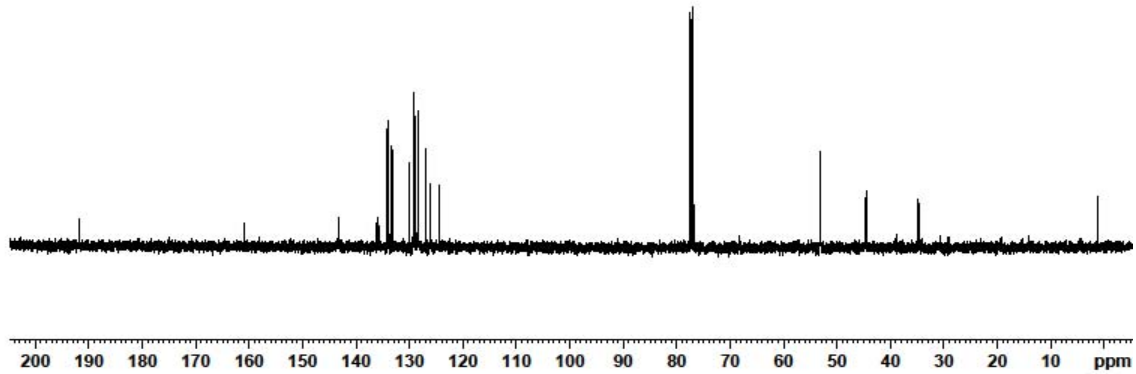
(*S*)-**2l**

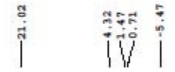
(*S*)-**3l**

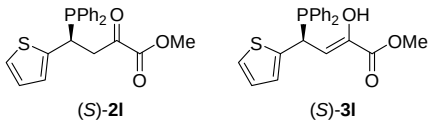




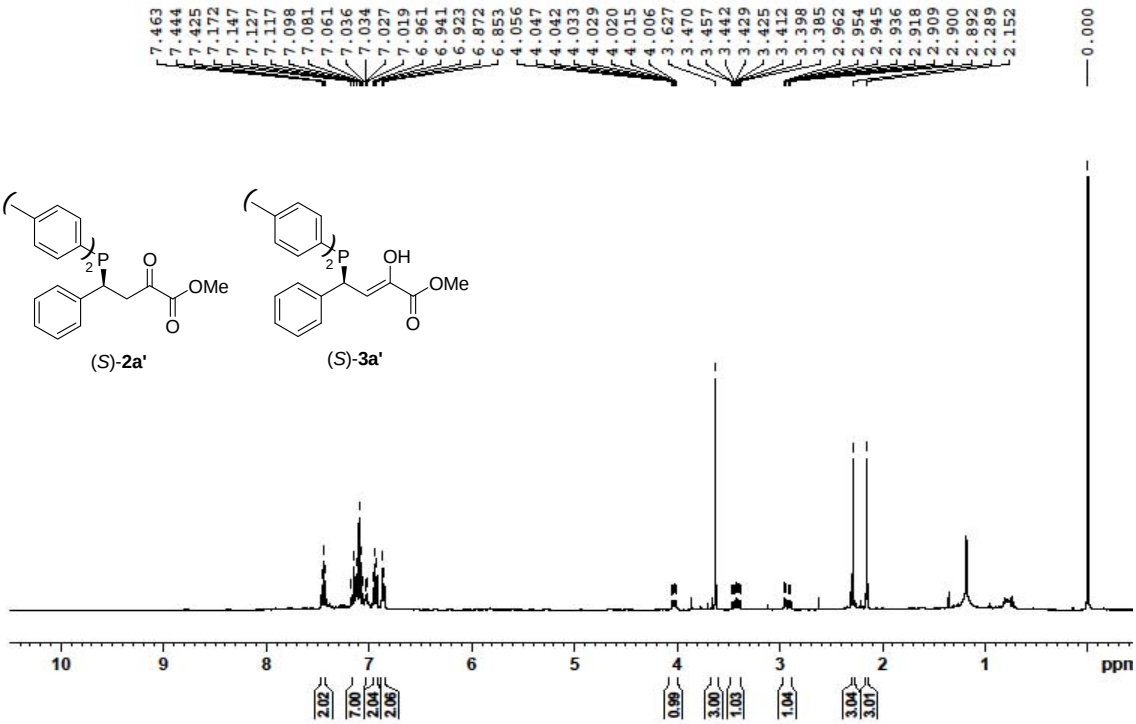
(*S*)-**2l** (*S*)-**3l**

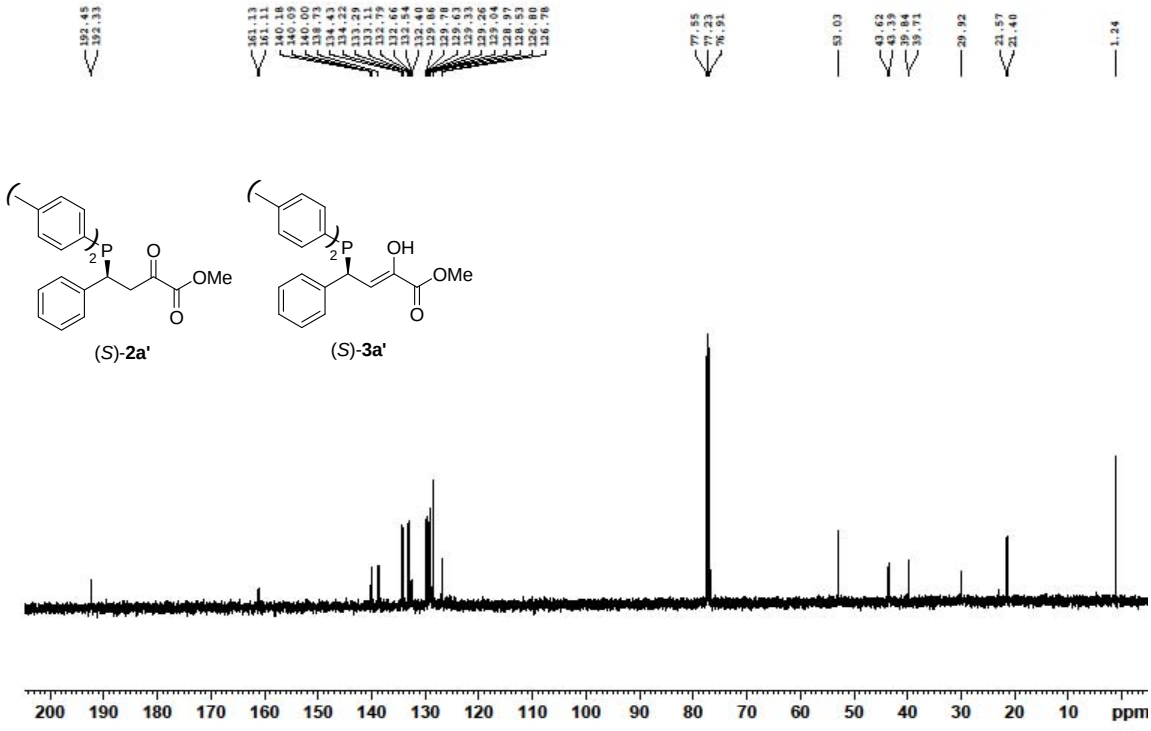


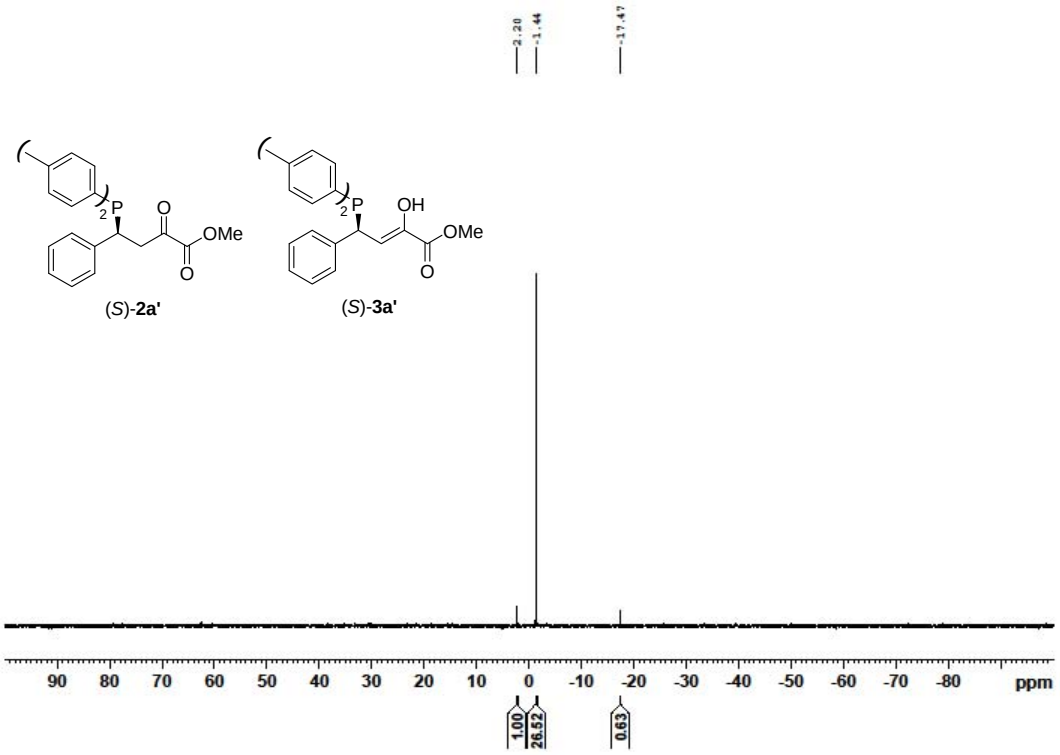


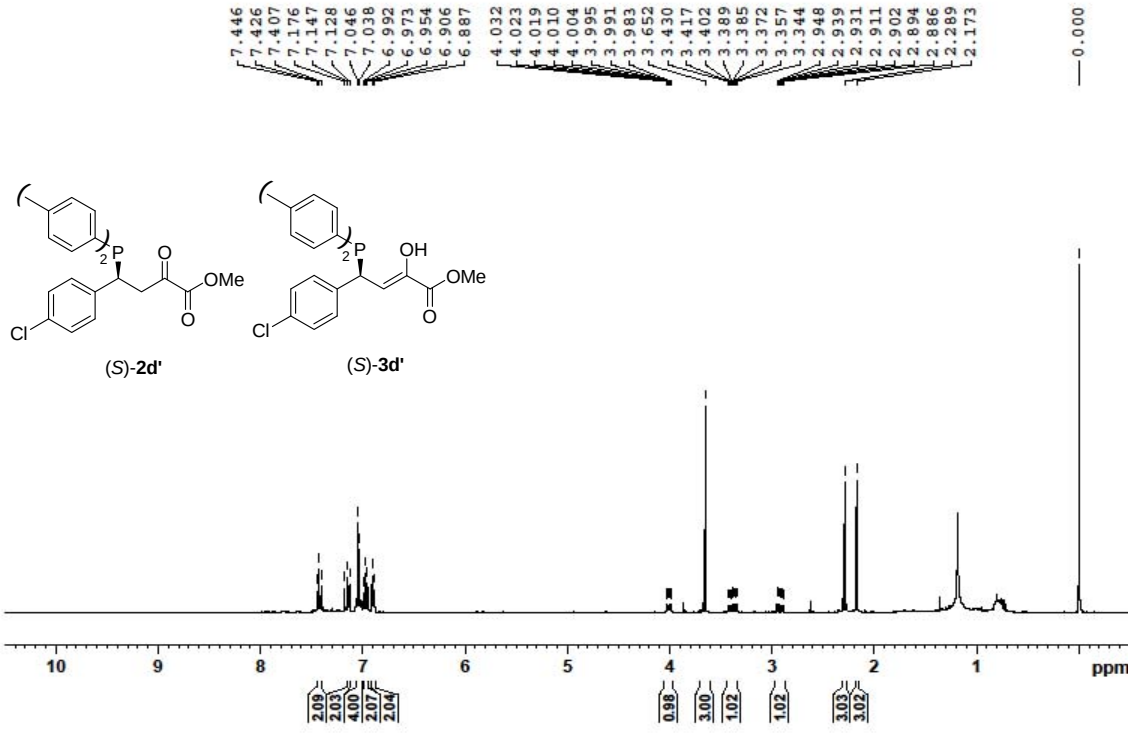


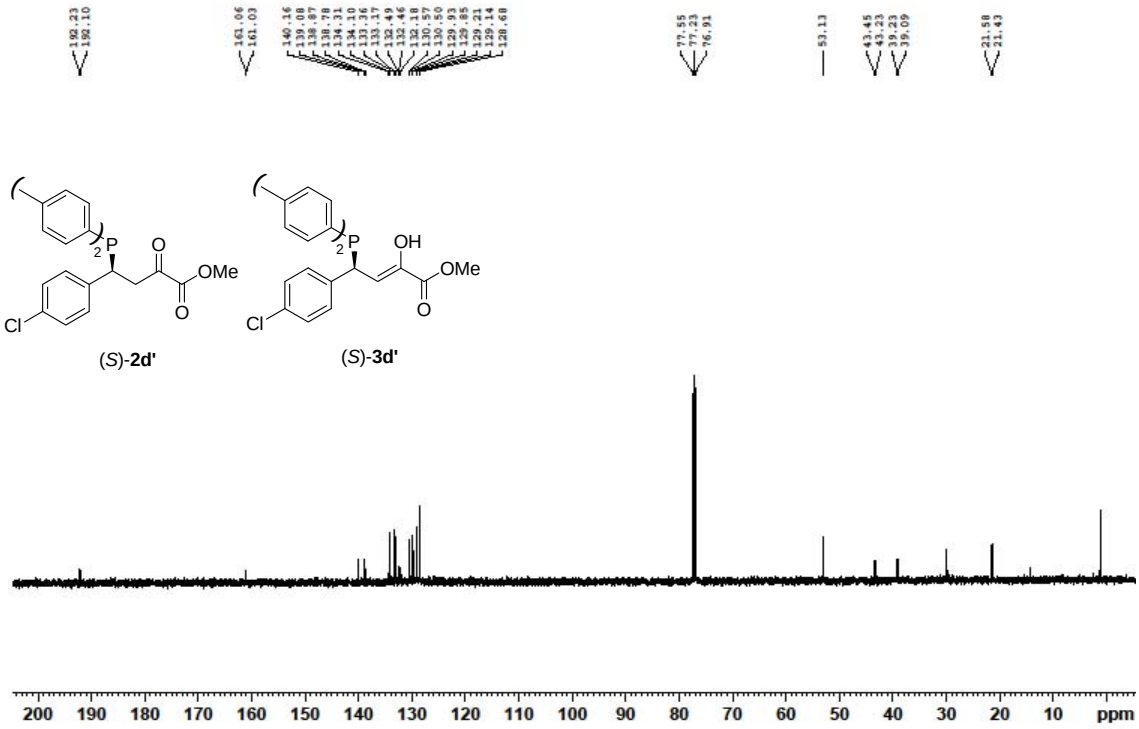
(*S*)-**2l** (*S*)-**3l**

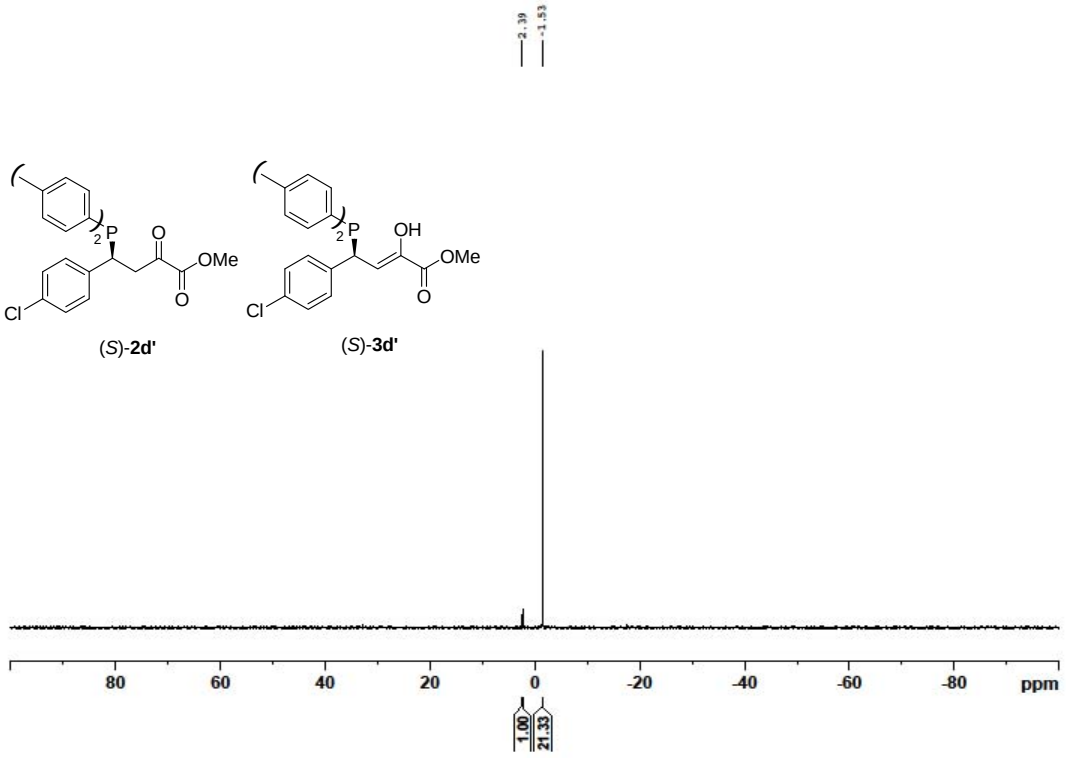

7.463
7.444
7.425
7.172
7.147
7.127
7.117
7.098
7.081
7.061
7.036
7.034
7.027
7.019
6.961
6.941
6.923
6.872
6.853
4.056
4.047
4.042
4.033
4.029
4.020
4.015
4.006
3.627
3.470
3.457
3.442
3.429
3.425
3.412
3.398
3.385
2.962
2.954
2.945
2.936
2.918
2.909
2.900
2.892
2.289
2.152
0.000
OMe
OH
(S)-2a'
(S)-3a'
10
9
8
7
6
5
4
3
2
1
ppm
2.02
7.00
2.04
2.06
0.98
3.00
1.03
1.04
3.04
3.01

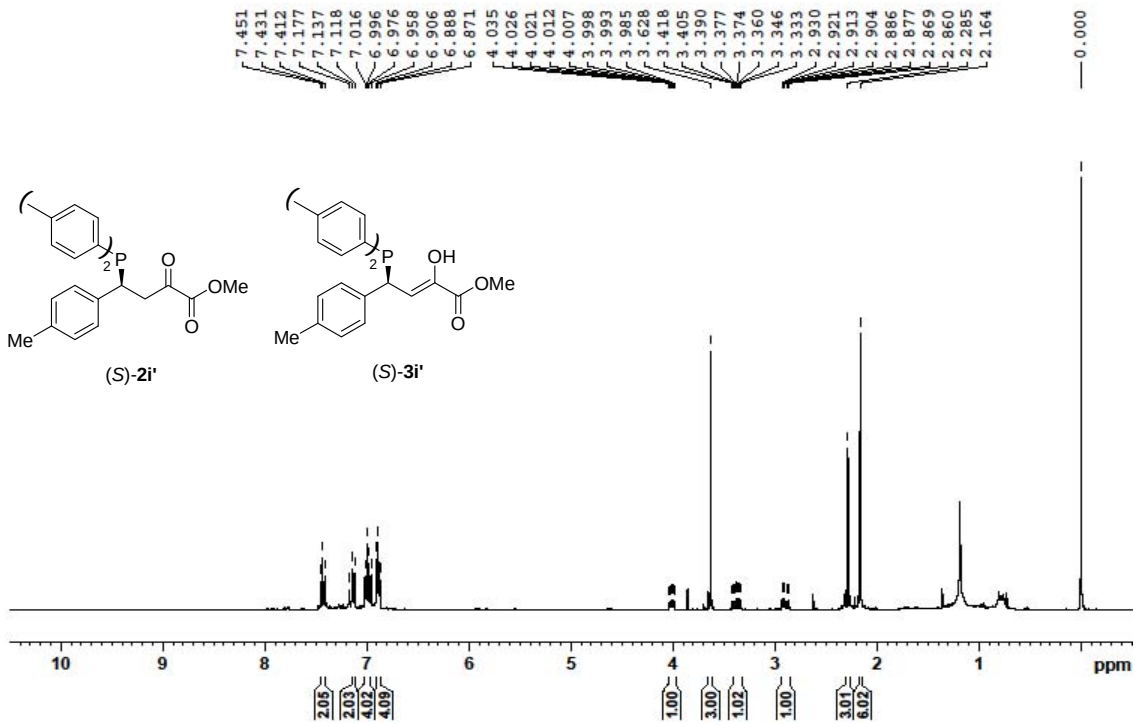

192.45
192.33
161.13
161.11
140.18
140.09
140.00
138.73
134.43
134.22
133.29
133.11
132.75
132.66
132.54
132.40
129.86
129.78
129.63
129.33
129.26
129.04
128.57
128.53
126.80
126.78
77.55
77.23
76.91
53.03
43.62
43.39
39.84
39.71
29.92
21.57
21.40
1.24
OMe
OH
(S)-2a'
(S)-3a'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

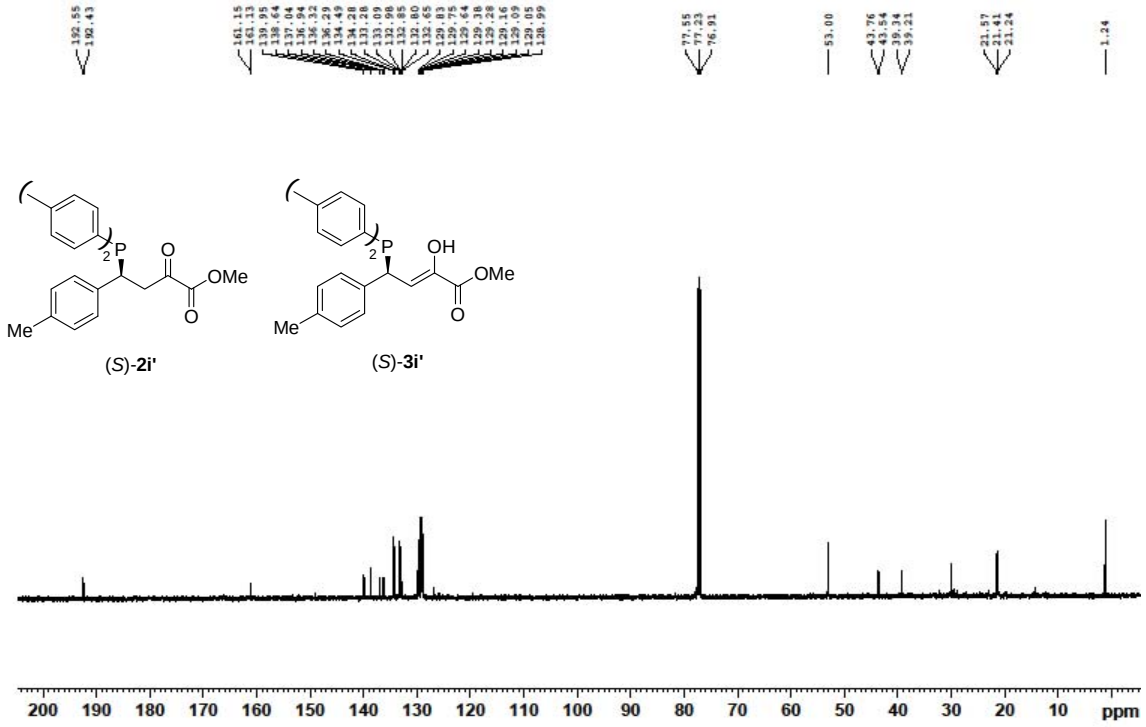

2.20
1.44
17.47
OMe
OH
(S)-2a'
(S)-3a'
90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 ppm
1.00
26.52
0.63

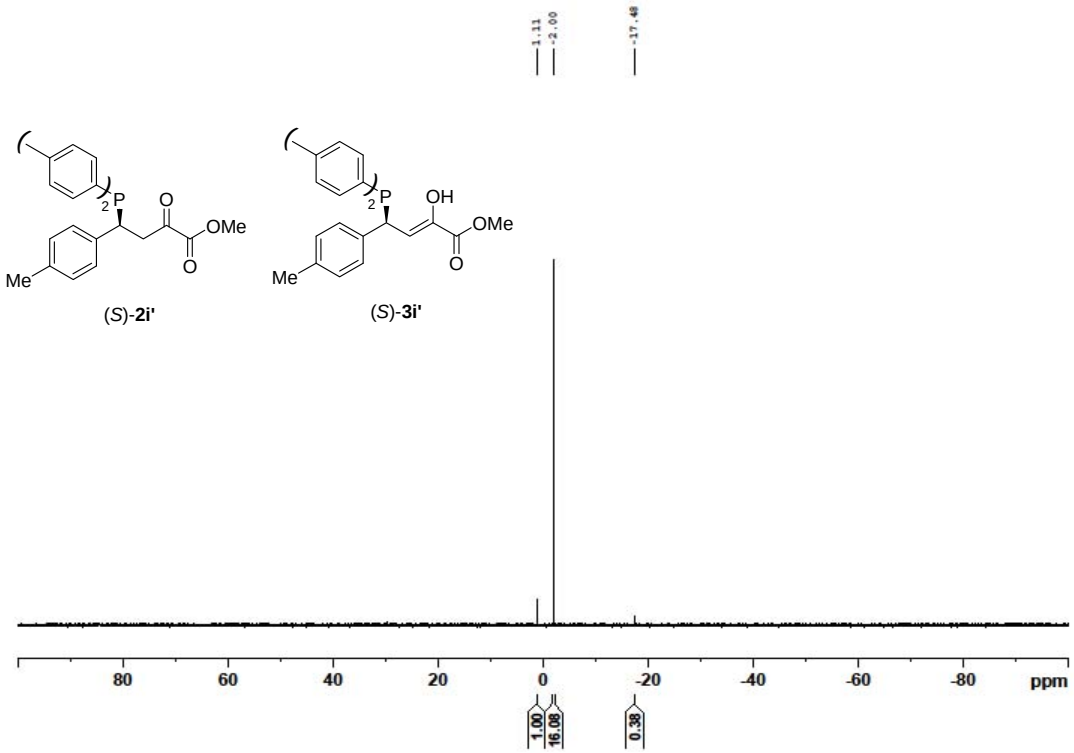

7.446
7.426
7.407
7.176
7.147
7.128
7.046
7.038
6.992
6.973
6.954
6.906
6.887
4.032
4.023
4.019
4.010
4.004
3.995
3.991
3.983
3.652
3.430
3.417
3.402
3.389
3.385
3.372
3.357
3.344
2.948
2.939
2.931
2.911
2.902
2.894
2.886
2.289
2.173
0.000
OMe
OH
Cl
(S)-2d'
(S)-3d'
10 9 8 7 6 5 4 3 2 1 ppm
2.09
2.03
4.00
2.07
2.04
0.98
3.00
1.02
1.02
3.03
3.02

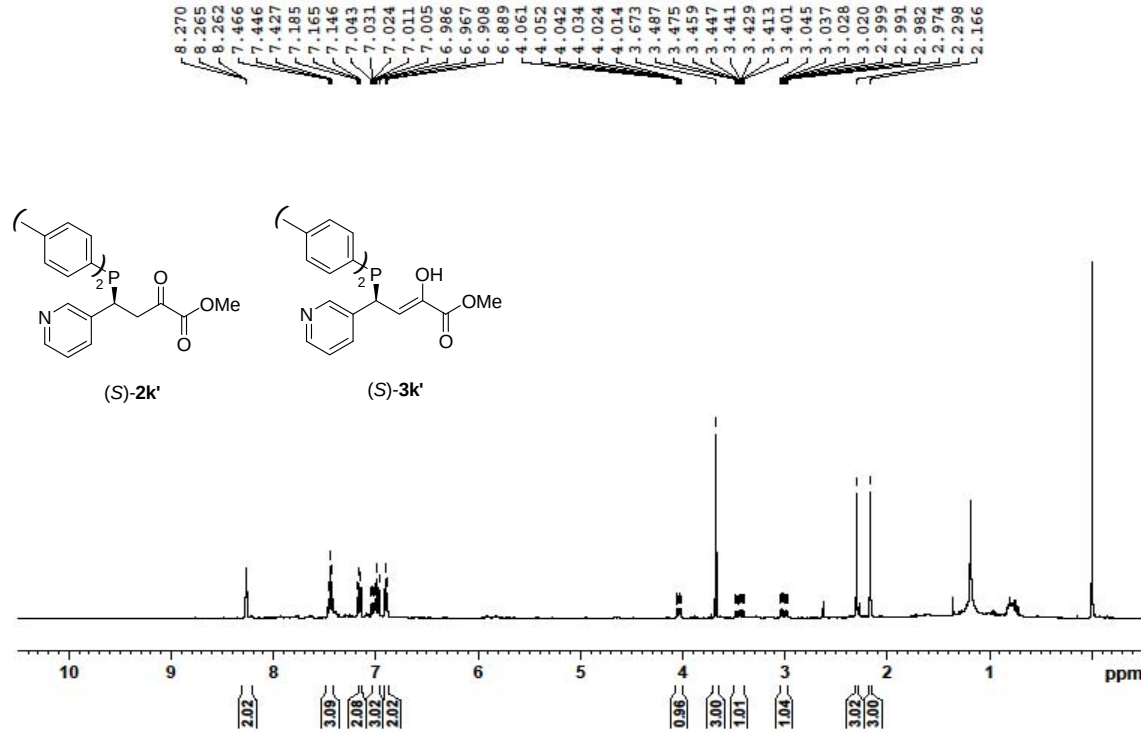

192.23
192.10
161.06
161.03
140.16
139.09
138.87
138.78
134.31
134.10
133.36
133.17
132.49
132.46
132.18
131.57
130.50
129.93
129.85
129.21
129.14
128.60
77.55
77.23
76.91
53.13
43.45
43.23
39.23
39.09
21.58
21.43
P
O
OMe
O
Cl
(S)-2d'
P
OH
OMe
O
Cl
(S)-3d'
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

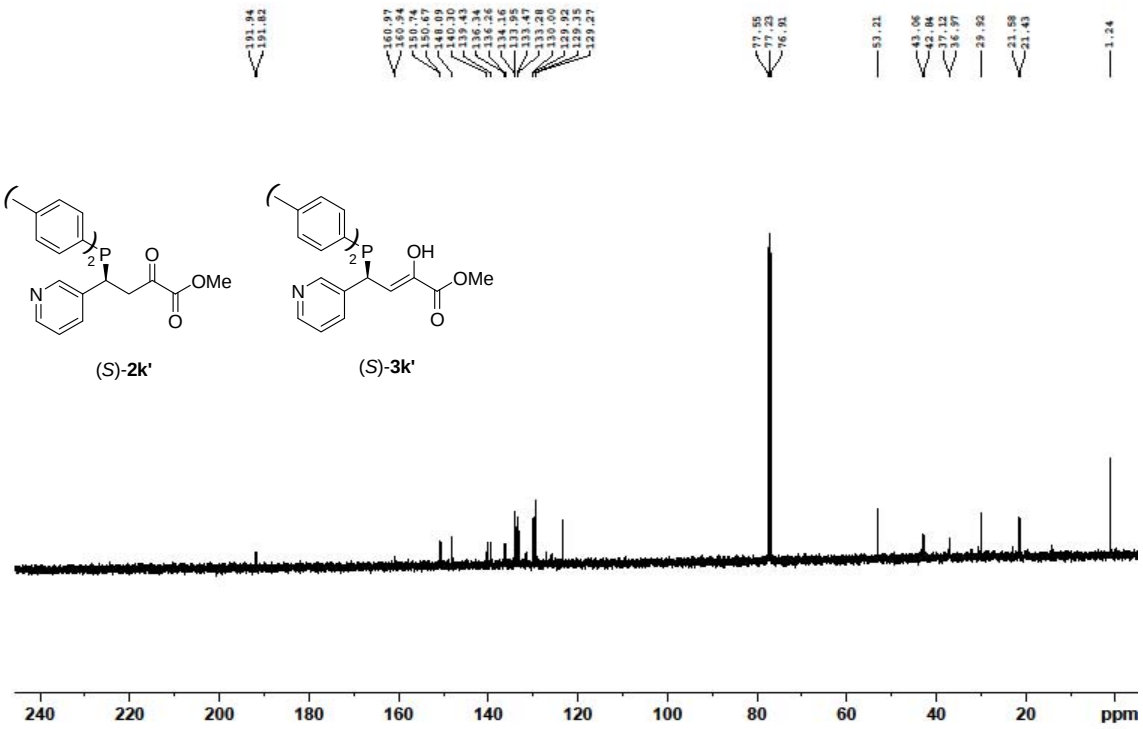

2.39
-1.53
P
O
OMe
O
Cl
(S)-2d'
P
OH
OMe
O
Cl
(S)-3d'
80
60
40
20
0
-20
-40
-60
-80
ppm
1.00
21.33

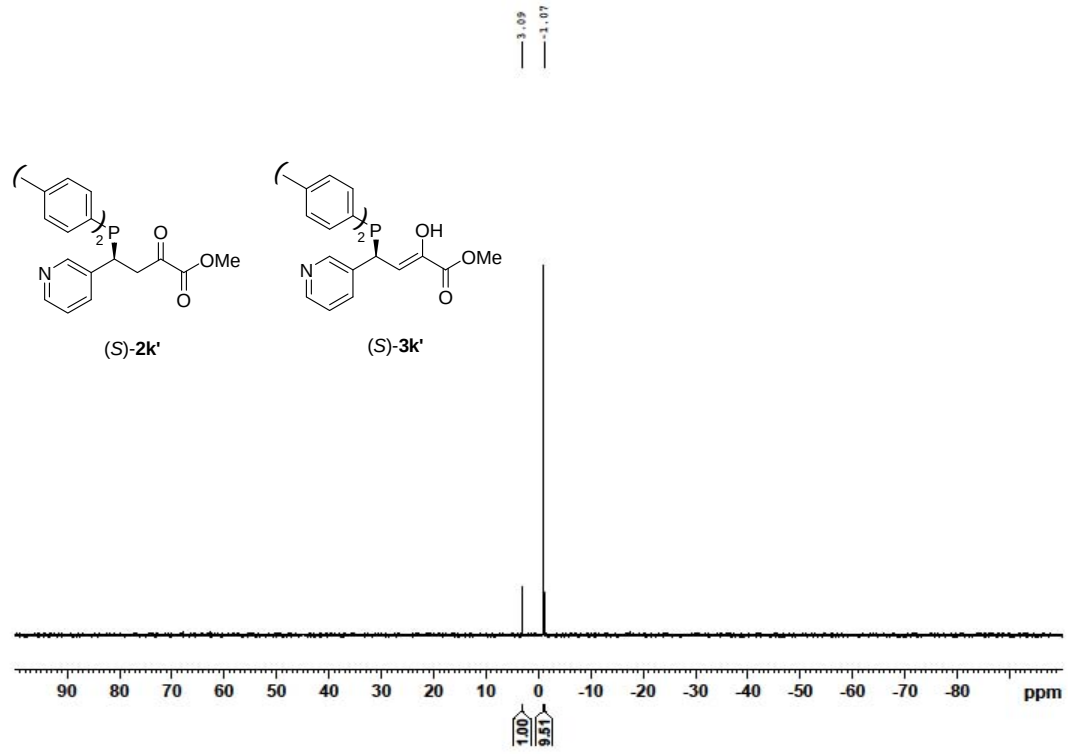

(S)-2i'
(S)-3i'
ppm


(S)-2i'
(S)-3i'
ppm


(S)-2i'
(S)-3i'
ppm


(S)-2k'
(S)-3k'
ppm


191.94
191.82
160.97
160.54
160.34
150.67
148.09
140.30
139.43
136.34
136.26
134.16
133.95
133.47
133.18
130.00
129.92
129.35
129.27
77.55
77.23
76.91
53.21
43.06
42.84
37.12
36.97
29.92
21.58
21.43
1.24
P
O
OMe
N
OH
(S)-2k'
(S)-3k'
240
220
200
180
160
140
120
100
80
60
40
20
ppm


3.09
1.07
P
O
OMe
N
OH
(S)-2k'
(S)-3k'
90
80
70
60
50
40
30
20
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0
-10
-20
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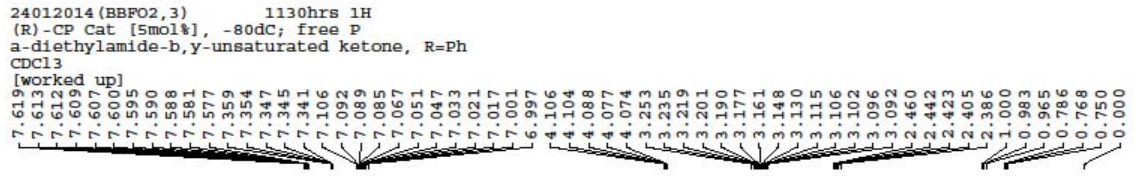
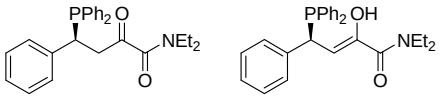
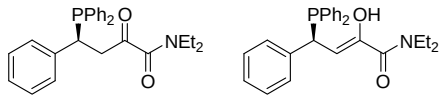
-40
-50
-60
-70
-80
ppm
1.00
9.51





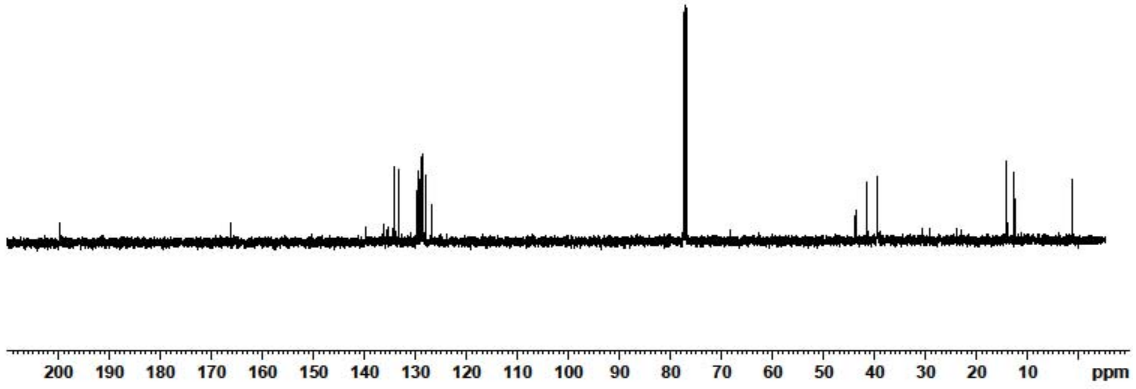
(*S*)-**2aa**

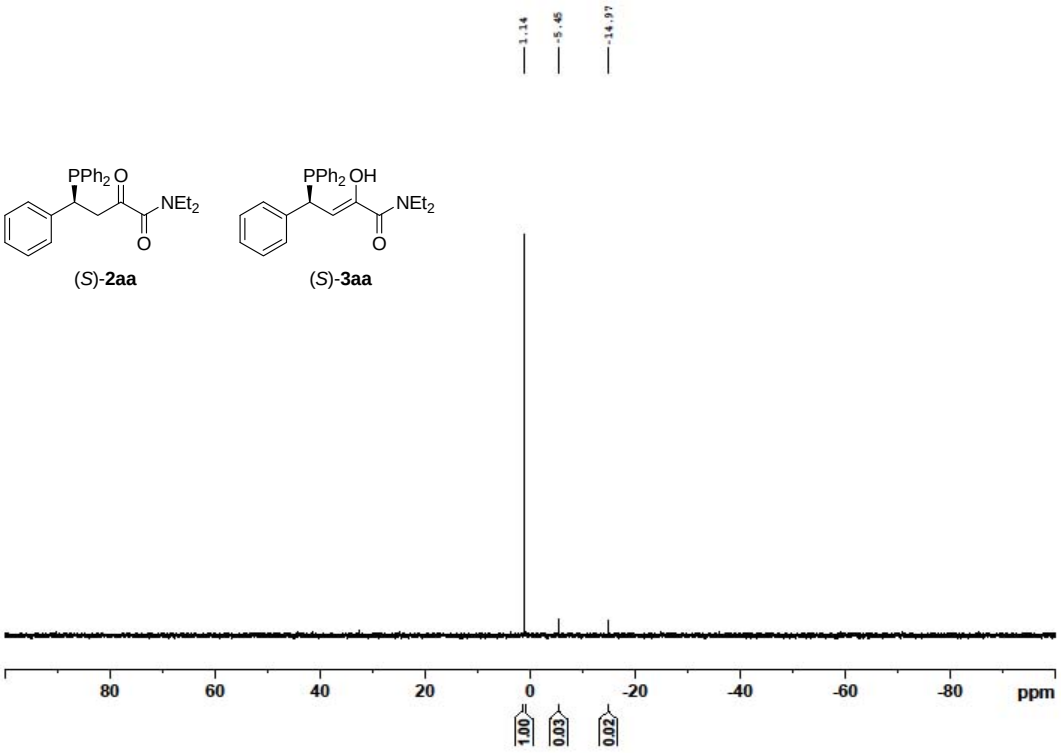
(*S*)-**3aa**



(*S*)-**2aa**

(*S*)-**3aa**





V. Single crystal X-Ray diffraction data

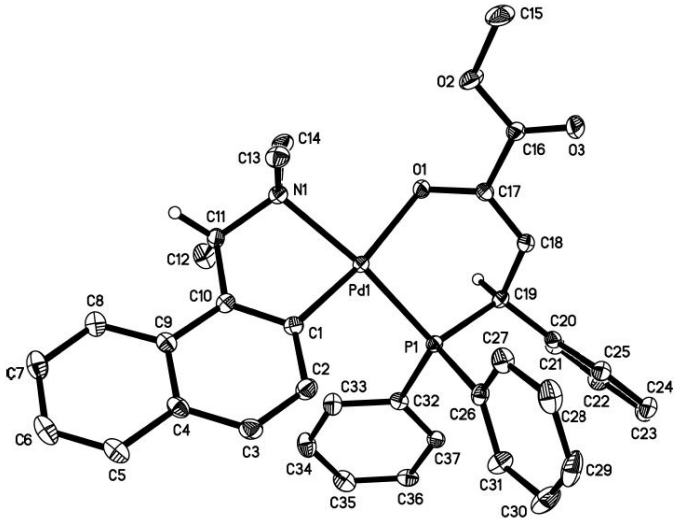


Figure 1. Molecular structure and absolute stereochemistry of adduct (*R*,*S*)-**9a** with 50% thermal ellipsoids shown. Hydrogen atoms except those on the chiral centre are omitted for clarity.[4]

Table 1. Crystal data and structure refinement for (*R*,*S*)-**9a**

Identification code	leung765s	
Chemical formula	$C_{37}H_{36}NO_3PPd$	
Formula weight	680.04	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.160 x 0.240 x 0.400 mm	
Crystal habit	yellow block	
Crystal system	orthorhombic	
Space group	P 21 21 21	
Unit cell dimensions	a = 10.06410(10) Å	α = 90°
	b = 11.7975(2) Å	β = 90°
	c = 26.1920(4) Å	γ = 90°
Volume	3109.81(8) $Å^3$	
Z	4	
Density (calculated)	1.452 g/cm^3	
Absorption coefficient	0.686 mm^{-1}	
F(000)	1400	
Theta range for data collection	3.45 to 31.03°	
Index ranges	-14<=h<=10, -17<=k<=17, -37<=l<=37	
Reflections collected	29841	
Independent reflections	9892 [R(int) = 0.0362]	
Coverage of independent reflections	99.3%	
Absorption correction	multi-scan	
Max. and min. transmission	0.8980 and 0.7710	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL-2013 (Sheldrick, 2013)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	9892 / 0 / 392	
Goodness-of-fit on F2	1.026	
Δ/σmax	0.001	
Final R indices	9465 data; I>2σ(I)	R1 = 0.0260, wR2 = 0.0573
	all data	R1 = 0.0278, wR2 = 0.0583

Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0241P)^2+0.8635P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.455 and -0.728 $eÅ^{-3}$
R.M.S. deviation from mean	0.064 $eÅ^{-3}$