Supporting Information

Palladium (II)-Catalyzed Asymmetric Hydrophosphination of Enones: Efficient Access to Chiral Tertiary Phosphines

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General information:

All air-sensitive manipulations were performed under a positive pressure of nitrogen or argon using standard Schlenk line. Solvents were degassed prior to use when necessary. THF was used without being dried. Column chromatography was conducted on Silica gel 60 (Merck). NMR spectra were recorded on Bruker ACF 300, 400 and 500 spectrometers. Chemical shifts are reported in δ ppm referenced to an internal SiMe4 standard (δ = 0 ppm) for 1H NMR, chloroform-d (δ = 77.23 ppm) for 13C NMR. Optical rotations were measured on the specified solution in a 0.1 dm cell at 20 ºC with a Perkin-Elmer 341 polarimeter. Elemental analyses were performed by the Elemental Analysis Laboratory of the Division of Chemistry and Biological Chemistry at Nanyang Technological University. Melting points were measured using the SRS Optimelt Automated Melting Point System, SRS MPA100. Infrared spectra were recorded on a SHIMADZU IR Prestige-21 FT-IR Spectrometer.

The catalyst and (*R*)-{[Pd[$Me_2NCH(Me)C_{10}H_6$](μ-Cl)}$_2$[1] and enones[2] were prepared according to literatures. The enatiomeric excess of hydrophosphination products was determined by reaction with (*R*)-{[Pd[$Me_2NCH(Me)C_{10}H_6$](μ-Cl)}$_2$ (0.5 equiv.) using $^{31}P\{^1H\}$ NMR spectroscopy.[3]

Experimental Sections

General Procedures and Compound Characterization

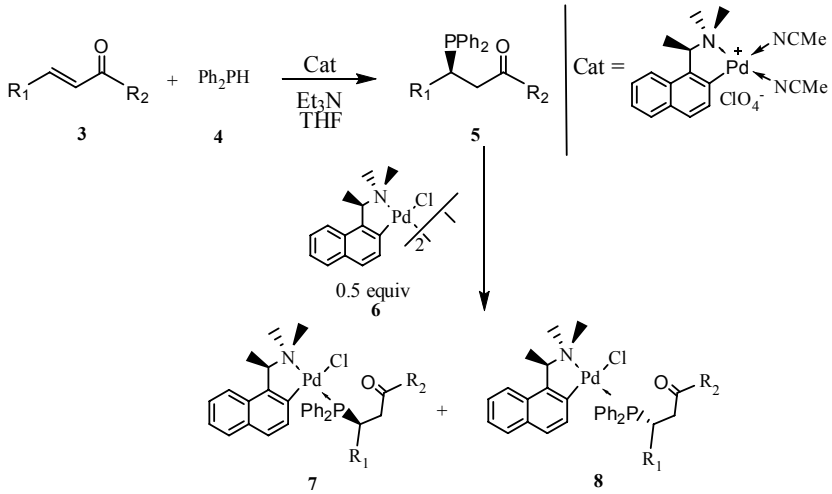


Table 2 (*R*)-1a-Catalyzed asymmetric hydrophosphination of various aromatic enones with Ph_2PH [a]

Entry	R_1	R_2	Temp °C	Time	Product	Yield[b] (%)	ee[c] (%)
1	Ph	Ph	−80	23 h	5a	65 (99)	98 (77)
2	Ph	2-Naph	−80	50 h	5b	53 (99)	94 (74)
3	2-Naph	Ph	−80	60 h	5c	(99)	(86)
4	2-Naph	1-Naph	−80	6 d	5d	48 (97)	96 (57)
5	4-ClPh	Ph	−80	40 h	5e	70 (99)	98 (77)
6	Ph	4-ClPh	−80[d]	6 d	5f	(96)	(57)
7	4-BrPh	Ph	−80[d]	7 d	5g	(92)	(51)
8	4-NO_2Ph	Ph	−80	6 d	5h	67 (99)	88 (70)
9	3-NO_2Ph	Ph	−80	4 d	5i	41 (99)	85 (55)
10	4-OHPh	Ph	−80	7 d	5j	40 (98)	99 (73)
11	4-MeOPh	Ph	20	40 h	5k	(97)	(33)

[a] THF was used without being dried [b] Yields of isolated products after a recrystalization. In parentheses are yields of isolated products before recrystalization. [c] ee after a recrystalization determined from $^{31}P\{^1H\}$ NMR integration of the signals. In the parentheses are the ee's before recrystalization. [d] Temperature raised gradually to 0 °C for another day after indicated time.

To a solution of Ph_2PH **4** (65.2 mg, 0.35 mmol, 1.0 equiv) in THF (5 mL) is added Cat (0.0175 mmol, 5 mol %) and the solution was cooled to －80 ℃. Subsequently, aromatic enones **3** (0.39 mmol, 1.1 equiv) was added. Et_3N (17.7 mg, 0.18 mmol, 0.5 equiv) in THF (0.5 mL) was added drop wise. The solution was subsequently stirred at －80 ℃. The reaction was monitored by $^{31}P\{^1H\}$ NMR. After the reaction is completed, the mixture was warmed to room temperature and the solution was evaporated by vacuum pump to give crude **5** (air sensitive) as solids. Compound **5** was dissolved in 8 ml DCM, and filtered by a short silica gel column using a pipette fixed on a two-neck Schlenk flask protected by nitrogen or argon. The solvent was removed by vacuum pump to give (±)**5** (enantio-rich). In order to check ee value, the obtained **5** was allowed to react with 0.5 equiv of enantiopure (2-naphthyl)ethylamine palladium chloride dimmer, (*R*)-$\{[Pd[Me_2NCH(Me)C_{10}H_6](\mu\text{-}Cl)\}_2$ (**6**) to form two diastereomers **7** and **8**. The enatiomeric excess (ee %) was determined by integration of the $^{31}P\{^1H\}$ NMR spectra of the resulting diastereomers **7** and **8** which corresponds to the ratio of enantiomers formed.

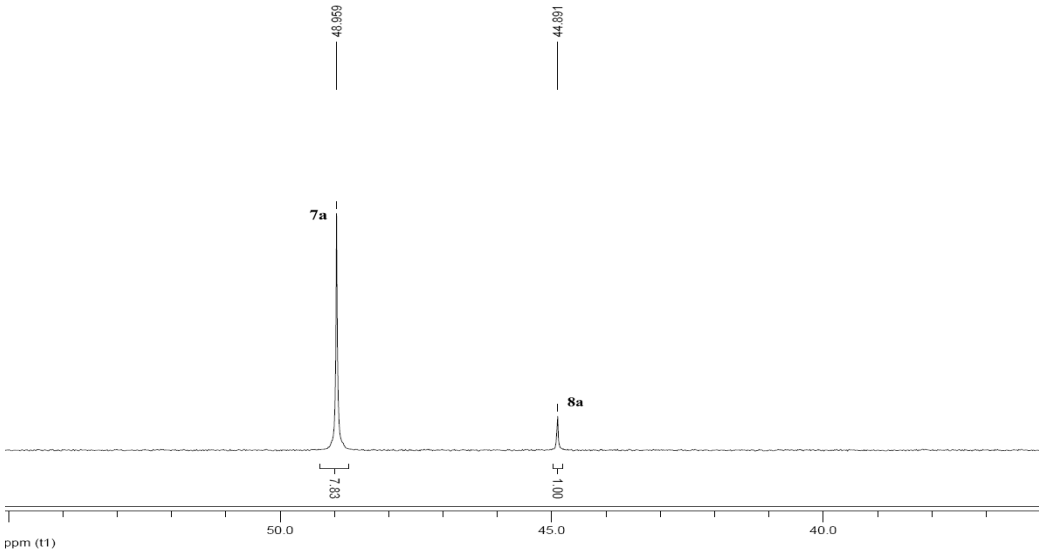
In some instances, nearly enantiopure **5** could be obtained by a single recrystalization of the crude product **5** from DCM/Aceotne.

Synthesis of $Ph_2PCH(Ph)CH_2COPh$ (5a)

Compound **3a** (81.2 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 23 h according to the general procedure to provide (±)**5a** (136.7 mg, 99 % yield, 77 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 121 MHz): δ 0.1; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.07 (ddd, 1H, *J* = 17.3 Hz, 8.3 Hz, 2.8 Hz, C*H*HCOPh),

3.58－3.69 (m, 1H, CH*H*COPh), 4.23－4.29 (m, 1H, PC*H*CH_2), 6.98－7.68 (m, 20H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.0 (d, 1C, $^1J_{PC}$ = 11.4 Hz, P*C*H), 42.6 (d, 1C, $^2J_{PC}$ = 22.1 Hz, *C*H_2COPh), 126.5－141.0 (m, 24C, Ar), 198.1 (d, 1C, $^3J_{PC}$ = 12.8 Hz, *C*OPh).

Determination of ee: Compound **5a** was dissolve in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the ^{31}P{^{1}H} NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 77 % evaluated by integration of **7a** and **8a** signals.



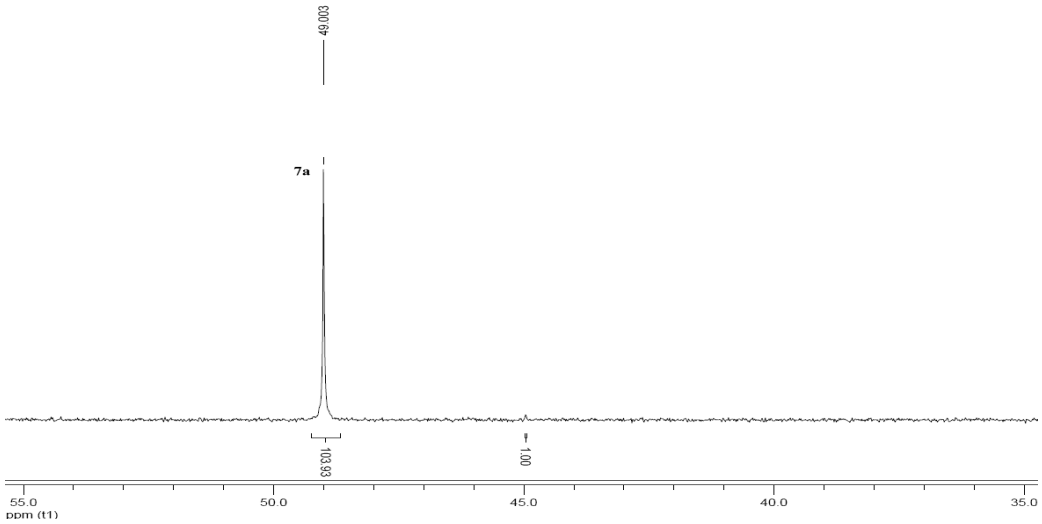
7a and **8a** were isolated by silica gel column (EA/Hexane = 1/4) and crystallized from benzene/pentane system. Absolute configurations of **7a** (Fig 1) and **8a** (Fig 2) were confirmed by X-ray crystal diffraction analysis.

7a (major): $[\alpha]_D$ = －129.3 (*c* 1.0, CH_2Cl_2). Mp: 180－182 ℃. Anal. Calcd for $C_{41}H_{39}ClNOPPd$: C, 67.0; H, 5.4; N, 1.9. Found: C, 67.3: H, 5.3; N, 1.7. ^{31}P{^{1}H} NMR($CDCl_3$, 161 MHz): δ 49.1 Hz; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.98 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.66 (s, 3H, N*Me*Me), 3.05 (d, 3H, $^4J_{PH}$ = 2.1 Hz, NMe*Me*), 3.83－

3.90 (m, 1H, CH*H*COPh), 4.26－4.29 (m, 1H, C*H*Me), 4.54－4.61 (m, 1H, C*H*HCOPh), 4.76－4.81 (m, 1H, PC*H*CH_2), 6.38－8.39 (m, 26H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.0 (s, 1C, CH*Me*), 43.5 (d, 1C, $^2J_{PC}$ = 6.7 Hz, *C*H_2COPh), 43.8 (d, 1C, $^1J_{PC}$ = 28.5 Hz, P*C*H), 48.0 (s, 1C, N*Me*Me), 50.6 (s, 1C, NMe*Me*), 72.9 (d, 1C, $^3J_{PC}$ = 2.6 Hz, *C*HCH_3), 123.0－151.2 (m, 34C, Ar), 197.7 (d, 1C, $^3J_{PC}$ = 13.5 Hz, *C*OPh).

8a (minor): $[\alpha]_D$ = +181.6 (*c* 1.0, CH_2Cl_2). Mp: 188－190 ℃ (dec). Anal. Calcd for $C_{41}H_{39}ClNOPPd$: C, 67.0; H, 5.4; N, 1.9. Found: C, 66.9; H, 5.0; N, 1.8. $^{31}P\{^1H\}$ NMR($CDCl_3$, 161 MHz): δ 44.9 Hz; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 1.88 (d, 3H, $^3J_{HH}$ = 6.3 Hz, CH*Me*), 2.60 (s, 3H, N*Me*Me), 3.00 (d, 3H, $^4J_{PH}$ = 2.9 Hz, NMe*Me*), 3.54－3.60 (m, 1H, CH*H*COPh), 3.88－3.95 (m, 1H, C*H*HCOPh), 4.20－4.26 (m, 1H, C*H*Me), 5.60－5.65 (m, 1H, PC*H*CH_2), 6.02－7.91 (m, 26H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.1 (s, 1C, CH*Me*), 38.0 (d, 1C, $^1J_{PC}$ = 24.6 Hz, P*C*H), 41.0 (s, 1C, *C*H_2COPh), 48.4 (s, 1C, N*Me*Me), 51.0 (s, 1C, NMe*Me*), 73.1 (d, 1C, $^3J_{PC}$ = 2.9 Hz, *C*HCH_3), 123.1－151.5 (m, 34C, Ar), 197.2 (d, 1C, $^3J_{PC}$ = 11.4 Hz, *C*OPh).

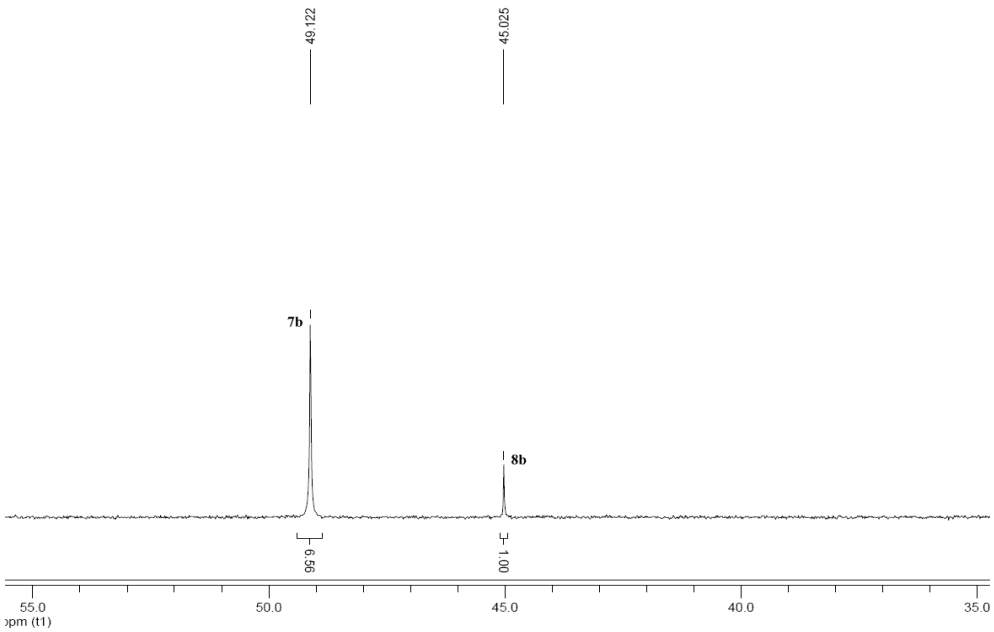
Purification by recrystalization: The obtained (±)**5a** (136.7 mg) was dissolved in DCM/Aceotne (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum pump to provide nearly optical pure (*S*)-**5a** (89.7 mg, 65 % yield, based on Ph_2PH, 98 % ee). $[\alpha]_D^{20}$ = －141.1 (*c* 0.9, CH_2Cl_2), $^{31}P\{^1H\}$, ^{1}H, ^{13}C NMR spectra were identical with those of (±)**5a**.



Synthesis of $Ph_2PCH(Ph)CH_2CO(2\text{-}Naph)$ (5b)

Compound **3b** (100.7 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 50 h according to the general procedure to provide (±)**5b** (154.1 mg, 99 % yield, 74 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 121 MHz): δ 0.1; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.21 (ddd, 1H, J = 16.9 Hz, 8.2 Hz, 2.8 Hz, C*H*HCOPh), 3.70－3.81 (m, 1H, CH*H*COPh), 4.27－4.33 (m, 1H, PC*H*CH_2), 6.97－8.15 (m, 22H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.3 (d, 1C, $^1J_{PC}$ = 11.4 Hz, P*C*H), 42.7 (d, 1C, $^2J_{PC}$ = 22.2 Hz, *C*H_2COPh), 124.0－140.8 (m, 28C, Ar), 198.1 (d, 1C, $^3J_{PC}$ = 13.2 Hz, *C*OPh).

Determination of ee: Compound **5b** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 77 % evaluated by intergration of **7b** and **8b** signals.



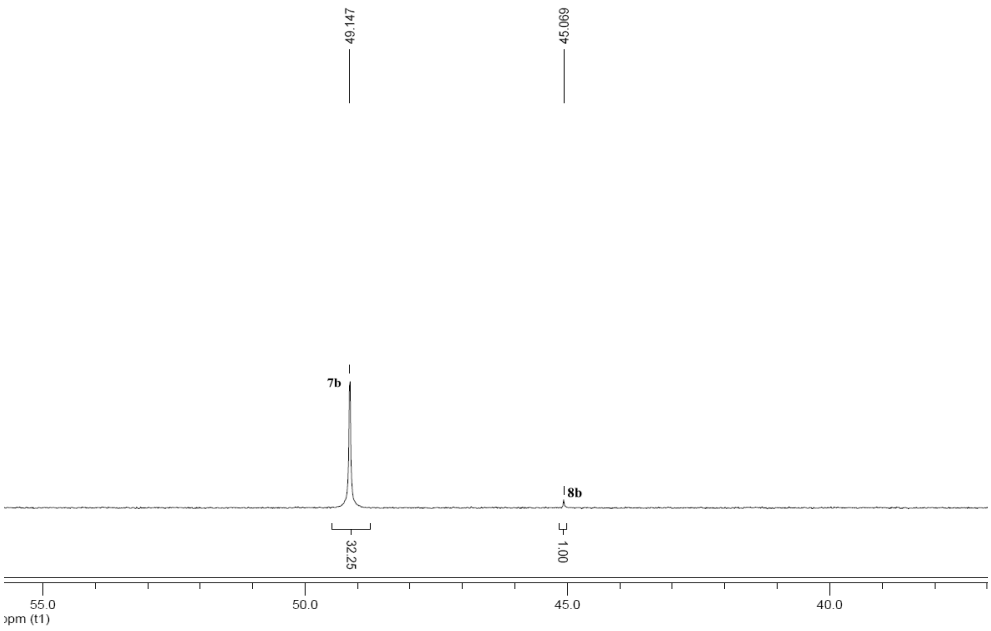
7b and **8b** were isolated by silica gel column (EA/Hexane = 1/4).

7b (major): $[\alpha]_D$ = －167.6 (*c* 1.0, CH_2Cl_2). Mp: 200－202 ℃ (dec). Anal. Calcd for $C_{45}H_{41}ClNOPPd$: C, 68.9; H, 5.3; N, 1.8. Found: C, 69.2; H, 5.3; N, 2.0. $^{31}P\{^1H\}$ NMR($CDCl_3$, 161 MHz): δ 49.2 Hz; ^1H NMR ($CDCl_3$, 400 MHz): δ 2.00 (d, 3H, $^3J_{HH}$ = 6.2 Hz, CH*Me*), 2.71 (s, 3H, N*Me*Me), 3.08 (d, 3H, $^4J_{PH}$ = 2.5 Hz, NMe*Me*), 3.99－4.07 (m, 1H, CH*H*COPh), 4.29－4.36 (m, 1H, C*H*Me), 4.58－4.64 (m, 1H, C*H*HCOPh), 4.80－4.86 (m, 1H, PC*H*CH_2), 6.37－8.62 (m, 28H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.2 (s, 1C, CH*Me*), 43.8 (d, 1C, $^2J_{PC}$ = 6.8 Hz, *C*H_2COPh), 44.4 (d, 1C, $^1J_{PC}$ = 28.1 Hz, P*C*H), 48.3 (s, 1C, N*Me*Me), 50.8 (s, 1C, NMe*Me*), 73.2 (d, 1C, $^3J_{PC}$ = 2.8 Hz, *C*HCH_3), 123.2－151.5 (m, 38C, Ar), 198.2 (d, 1C, $^3J_{PC}$ = 13.8 Hz, *C*OPh).

8b (minor): $[\alpha]_D$ = +201.0 (*c* 1.0, CH_2Cl_2). Mp: 187－189 ℃ (dec). Anal. Calcd for $C_{45}H_{41}ClNOPPd$: C, 68.9; H, 5.3; N, 1.8. Found: C, 68.9; H, 5.0; N, 1.7. $^{31}P\{^1H\}$ NMR($CDCl_3$, 161 MHz): δ 45.1 Hz; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.89 (d, 3H, $^3J_{HH}$

= 6.3 Hz, CH*Me*), 2.61 (s, 3H, N*Me*Me), 3.01 (d, 3H, $^{4}J_{PH}$ = 2.9 Hz, NMe*Me*), 3.69－3.75 (m, 1H, CH*H*COPh), 3.99－4.07 (m, 1H, C*H*HCOPh), 4.20－4.26 (m, 1H, C*H*Me), 5.66－5.72 (m, 1H, PC*H*CH_2), 6.05－8.31 (m, 28H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 23.2 (s, 1C, CH*Me*), 38.4 (d, 1C, $^{1}J_{PC}$ = 24.5 Hz, P*C*H), 41.2 (s, 1C, *C*H_2COPh), 48.4 (s, 1C, N*Me*Me), 51.1 (s, 1C, NMe*Me*), 73.2 (d, 1C, $^{3}J_{PC}$ = 3.1 Hz, *C*HCH_3), 123.2－151.6 (m, 38C, Ar), 197.3 (d, 1C, $^{3}J_{PC}$ = 11.3 Hz, *C*OPh).

Purification by recrystalization: The obtained (±)**5b** (155.6 mg) was dissolved in DCM/Acetone (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum pump to provide product (*S*)-**5b** (82.5 mg, 53 % yield, based on Ph_2PH, 94 % ee). $[\alpha]_D^{20}$ = －147.8 (*c* 0.9, CH_2Cl_2), ^{31}P{^{1}H}, ^{1}H, ^{13}C NMR spectra were identical with those of (±)**5b**.

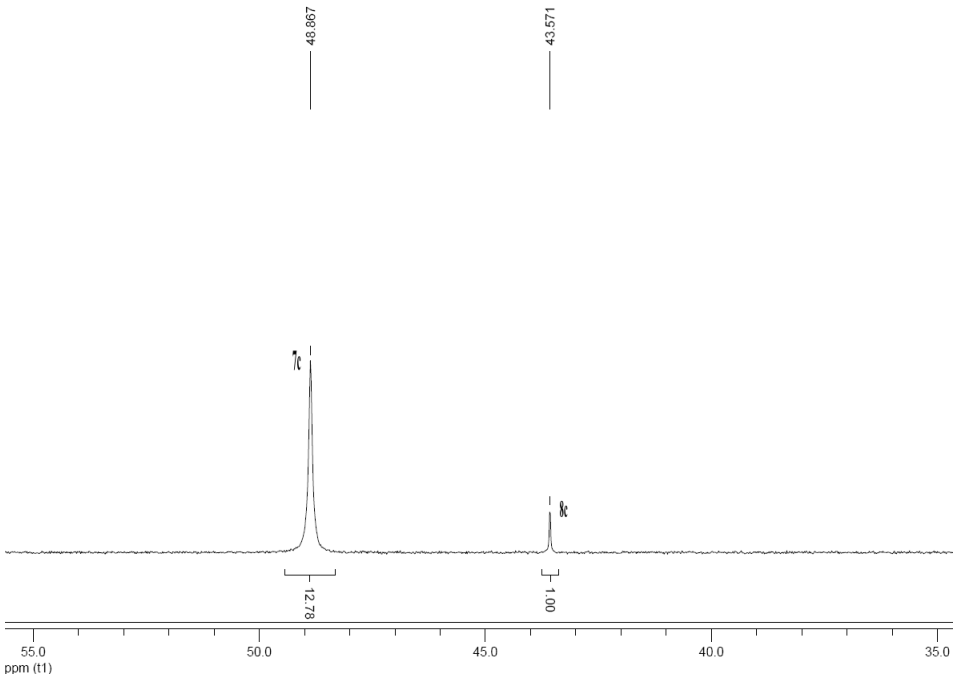


Synthesis of Ph_2PCH(2-Naph)CH_2CO(Ph) (5c)

Compound **3c** (100.7 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 60 h according to the general procedure to provide

(±)**5c** (154.0 mg, 99 % yield, 86 % ee). $^{31}P\{^{1}H\}$ NMR($CDCl_3$, 161 MHz): δ−0.7; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.15 (ddd, 1H, J = 17.4 Hz, 8.2 Hz, 2.7 Hz, C*H*HCOPh), 3.70−3.78 (m, 1H, CH*H*COPh), 4.42−4.47 (m, 1H, PC*H*CH_2), 6.99−7.68 (m, 22H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.0 (d, 1C, $^{1}J_{PC}$ = 11.7 Hz, P*C*H), 42.6 (d, 1C, $^{2}J_{PC}$ = 22.4 Hz, *C*H_2COPh), 125.5−138.7 (m, 28C, Ar), 197.9 (d, 1C, $^{3}J_{PC}$ = 12.3 Hz, *C*OPh).

Determination of ee: Compound **5c** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 86 % evaluated by integration of **7c** and **8c** signals.



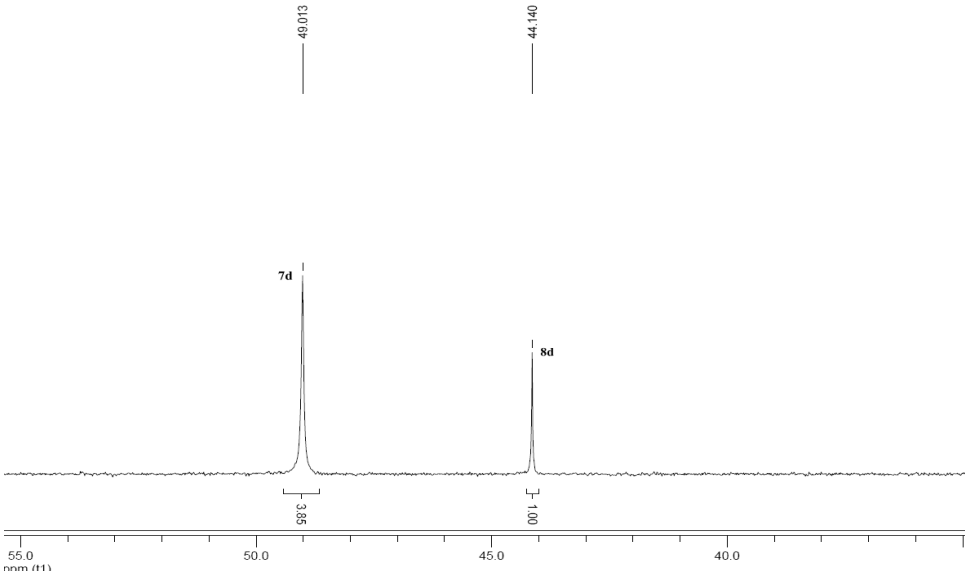
This compound can not be purified by the recrystalization mentioned above.

Synthesis of Ph_2PCH(2-Naph)CH_2CO(1-Naph) (5d)

Compound **3d** (120.3 mg, 0.39 mmol, 1.1 equiv) reacted with **4** (65.2 mg, 0.35

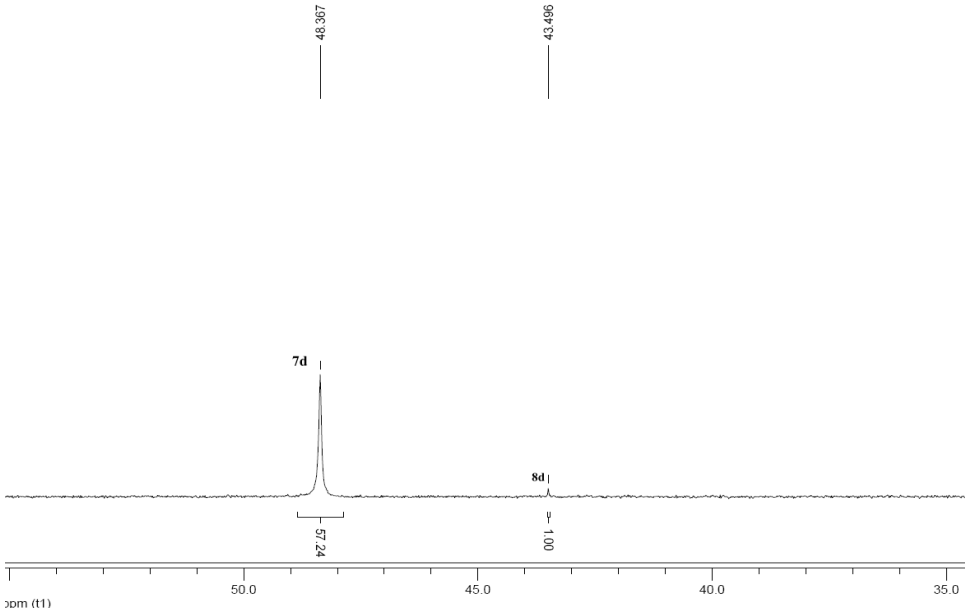
mmol, 1.0 equiv) at －80 ℃ for 6 d according to the general procedure to provide (±)**5d** (167.9 mg, 97 % yield, 57 % ee). $^{31}P\{^{1}H\}$ NMR($CDCl_3$, 161 MHz): δ－0.6; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.27 (ddd, 1H, *J* = 16.6 Hz, 7.5 Hz, 3.0 Hz, C*H*HCOPh), 3.61－3.69 (m, 1H, CH*H*COPh), 4.39－4.44 (m, 1H, PC*H*CH_2), 6.96－7.88 (m, 24H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 41.0 (d, 1C, $^{1}J_{PC}$ = 12.8 Hz, P*C*H), 46.5 (d, 1C, $^{2}J_{PC}$ = 20.9 Hz, *C*H_2COPh), 124.4－138.3 (m, 32C, Ar), 202.8 (d, 1C, $^{3}J_{PC}$ = 12.7 Hz, *C*OPh).

Determination of ee: Compound **5d** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 121 MHz) spectrum recorded ee = 57 % evaluated by integration of **7d** and **8d** signals.



Purification by recrystalization: The obtained (±)**5d** (167.9 mg) was dissolved in appropriate DCM/Acetone (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum

pump to provide product (*S*)-**5d** (80.6 mg, 48 % yield, based on Ph_2PH, 96 % ee). $[\alpha]_D^{20}$ = －147.8 (*c* 0.9, CH_2Cl_2), $^{31}P\{^1H\}$, ^1H, ^{13}C NMR spectra were identical with those of (±)**5d**.

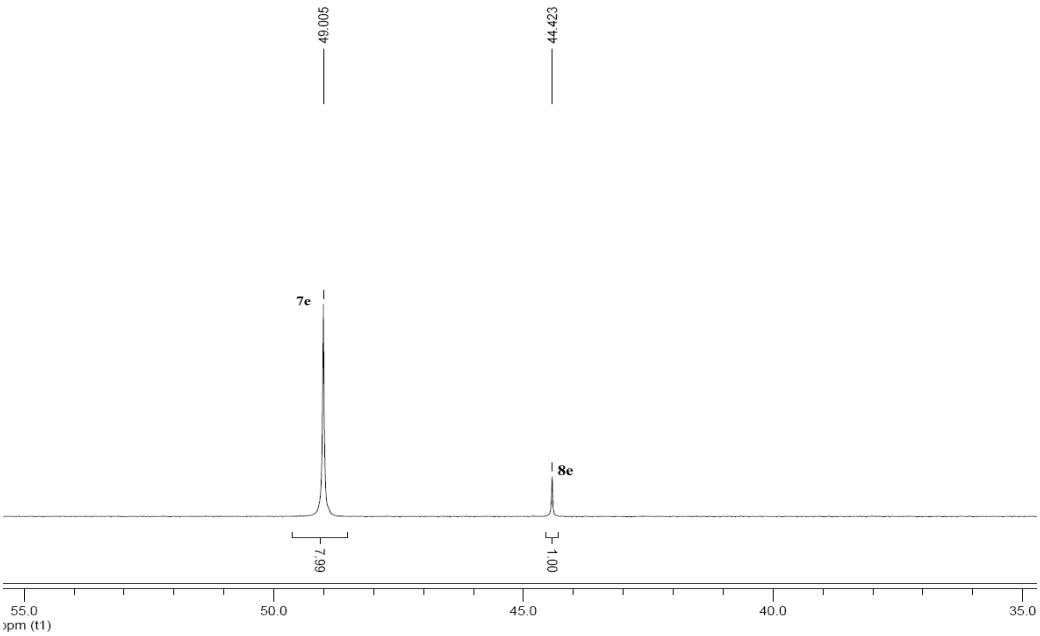


Synthesis of $Ph_2PCH(4\text{-}Cl\text{-}Ph)CH_2CO(Ph)$ (5e)

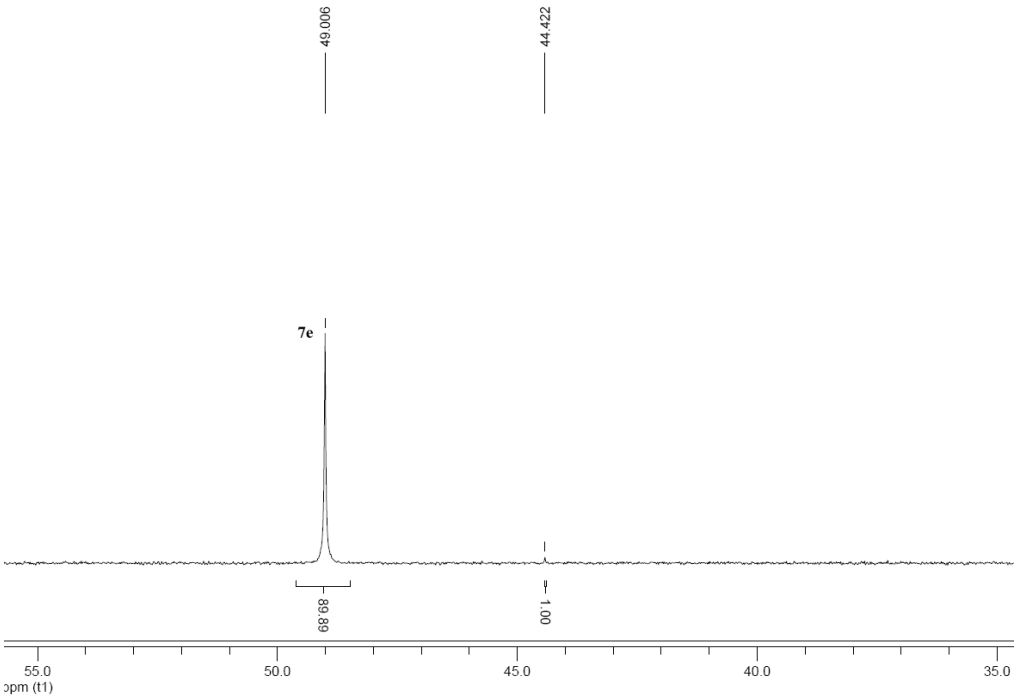
Compound **3e** (94.6 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 40 h according to the general procedure to provide (±)**5e** (148.6 mg, 99 % yield, 77 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 121 MHz): δ 0.0; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.07 (ddd, 1H, *J* = 17.4 Hz, 7.9 Hz, 2.8 Hz, C*H*HCOPh), 3.52－3.63 (m, 1H, CH*H*COPh), 4.20－4.27 (m, 1H, PC*H*CH_2), 7.02－7.68 (m, 19H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.8 Hz, P*C*H), 42.4 (d, 1C, $^2J_{PC}$ = 22.0 Hz, *C*H_2COPh), 128.1－139.6 (m, 24C, Ar), 197.8 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

Determination of ee: Compound **5e** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 77 %

evaluated by integration of **7e** and **8e** signals.



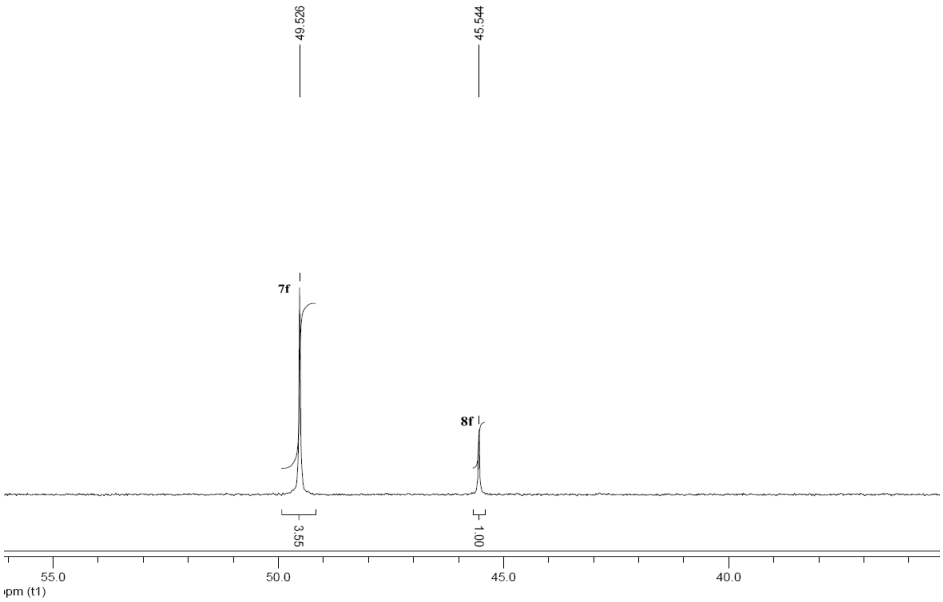
Purification by recrystalization: The obtained (±)**5e** (148.6 mg) was dissolved in appropriate DCM/Acetone (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum pump to provide product (*S*)-**5b** (105.0 mg, 70 % yield, based on Ph_2PH, 98 % ee). $[\alpha]_D^{20}$ = −162.7 (*c* 1.1, CH_2Cl_2), $^{31}P\{^1H\}$, ^1H, ^{13}C NMR spectra were identical with those of (±)**5e**.



Synthesis of $Ph_2PCH(Ph)CH_2CO(4\text{-}Cl\text{-}Ph)$ (5f)

Compound **3f** (94.6 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 6 d, then raise temperature to 0 ℃ gradually and stir at 0 ℃ for another day to provide (±)**5f** (144.1 mg, 96 % yield, 57 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 121 MHz): δ 0.0; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.02 (ddd, 1H, J = 17.1 Hz, 8.6 Hz, 2.9 Hz, C*H*HCOPh), 3.50－3.61 (m, 1H, CH*H*COPh), 4.18－4.25 (m, 1H, PC*H*CH_2), 6.97－7.60 (m, 19H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 40.1 (d, 1C, $^1J_{PC}$ = 11.7 Hz, P*C*H), 42.4 (d, 1C, $^2J_{PC}$ = 22.3 Hz, *C*H_2COPh), 126.6－140.8 (m, 24C, Ar), 196.9 (d, 1C, $^3J_{PC}$ = 12.7 Hz, *C*OPh).

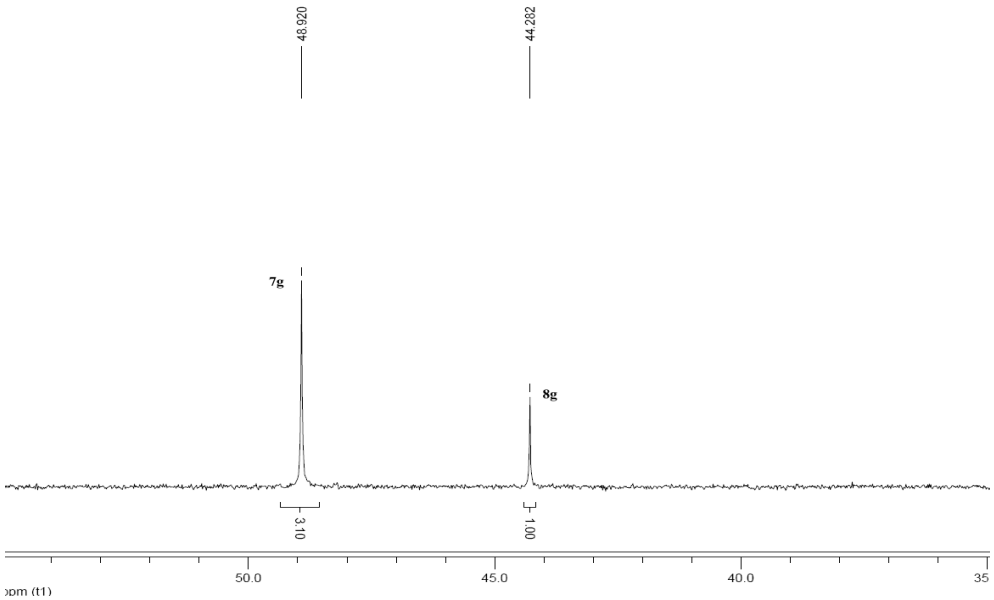
Determination of ee: Compound **5f** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) spectrum recorded ee = 57 % evaluated by integration of **7f** and **8f** signals.



Synthesis of $Ph_2PCH(4\text{-}Br\text{-}Ph)CH_2CO(Ph)$ (5g)

Compound **3g** (112.1 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 7 d, then raise temperature to 0 ℃ gradually and stir at 0 ℃ for another day to provide (±)**5f** (152.4 mg, 92 % yield, 51 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 161 MHz): δ－0.7; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.07 (ddd, 1H, J = 17.2 Hz, 7.6 Hz, 2.4 Hz, C*H*HCOPh), 3.53－3.61 (m, 1H, CH*H*COPh), 4.20－4.25 (m, 1H, PC*H*CH_2), 7.00－7.68 (m, 19H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.8 Hz, P*C*H), 42.3 (d, 1C, $^2J_{PC}$ = 21.2 Hz, *C*H_2COPh), 120.3－140.2 (m, 24C, Ar), 197.8 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

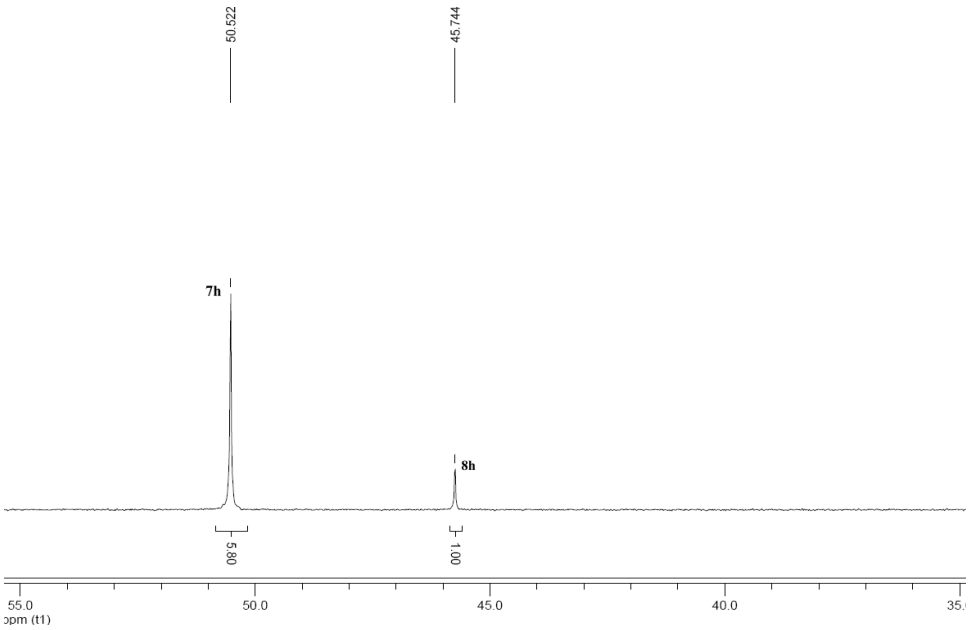
Determination of ee: Compound **5g** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz) spectrum recorded ee = 51 % evaluated by integration of **7e** and **8e** signals.



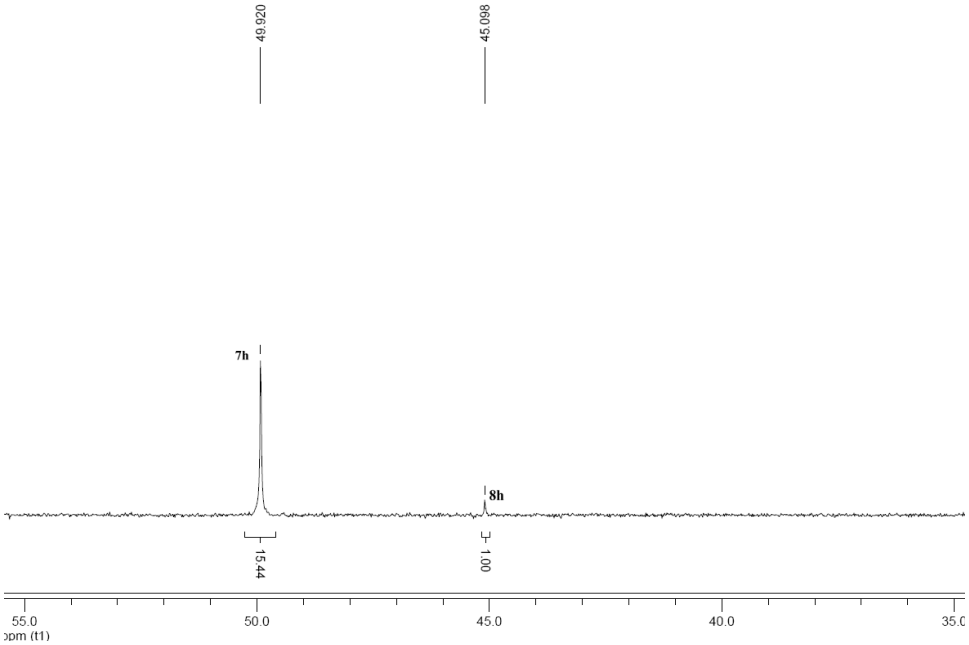
Synthesis of $Ph_2PCH(4\text{-}NO_2\text{-}Ph)CH_2CO(Ph)$ (5h)

Compound **3h** (98.8 mg, 0.39 mmol, 1.1 equiv) reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 6 d according to the general procedure to provide (±)**5h** (152.3 mg, 99 % yield, 70 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 121 MHz): δ 1.5; ^1H NMR ($CDCl_3$, 300 MHz): δ 3.19 (ddd, 1H, J = 17.8 Hz, 7.7 Hz, 2.8 Hz, C*H*HCOPh), 3.60－3.71 (m, 1H, CH*H*COPh), 4.34－4.40 (m, 1H, PC*H*CH_2), 7.07－7.91 (m, 19H, Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 39.4 (d, 1C, $^1J_{PC}$ = 11.8 Hz, P*C*H), 42.4 (d, 1C, $^2J_{PC}$ = 22.0 Hz, *C*H_2COPh), 123.6－149.4 (m, 24C, Ar), 197.3 (d, 1C, $^3J_{PC}$ = 12.6 Hz, *C*OPh).

Determination of ee: Compound **5h** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz) spectrum recorded ee = 70 % evaluated by integration of **7h** and **8h** signals.



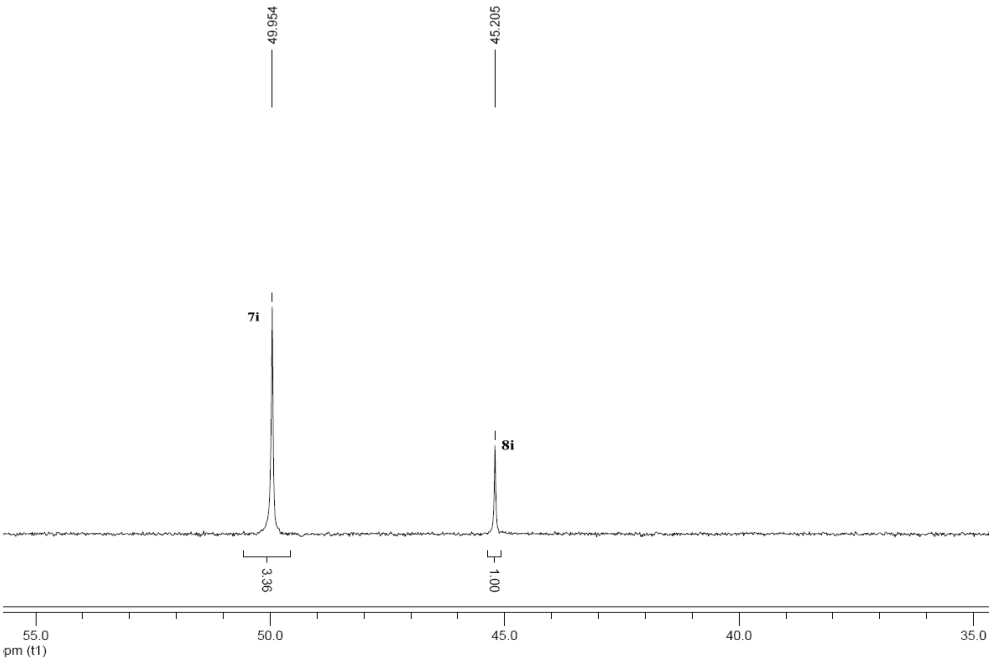
Purification by recrystalization: The obtained (±)**5h** (152.3 mg) was dissolved in appropriate DCM/Acetone (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum pump to provide product (*S*)-**5h** (103.1 mg, 67 % yield, based on Ph_2PH, 88 % ee). $[\alpha]_D^{20}$ = −241.3 (*c* 0.9, CH_2Cl_2), $^{31}P\{^1H\}$, ^1H, ^{13}C NMR spectra were identical with those of (±)**5h**.



Synthesis of $Ph_2PCH(3\text{-}NO_2\text{-}Ph)CH_2CO(Ph)$ (5i)

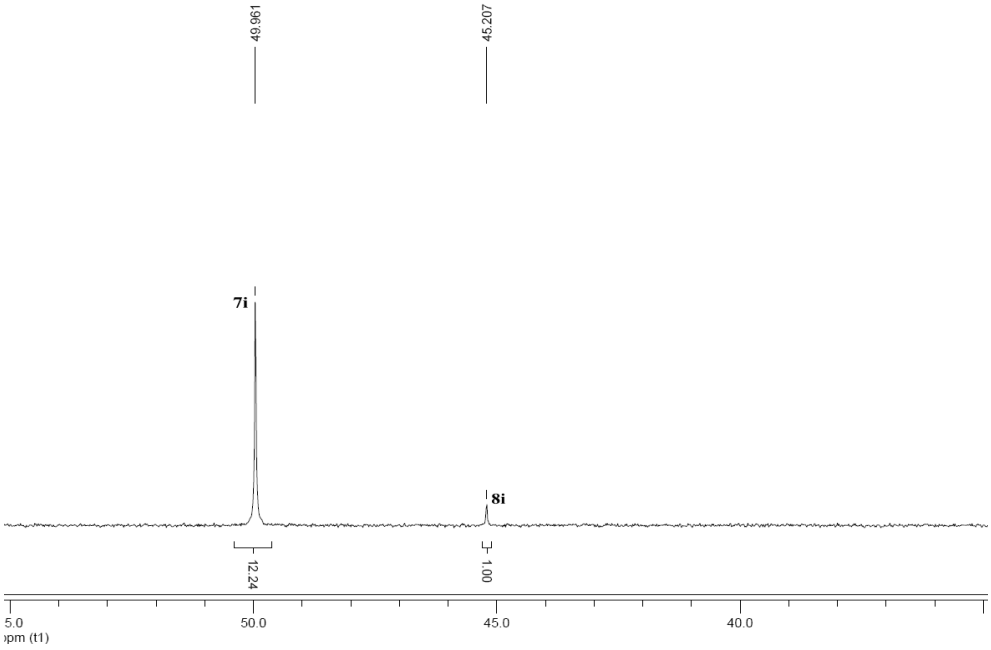
Compound **3i** (98.8 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at －80 ℃ for 4 d according to the general procedure to provide (±)**5i** (152.3 mg, 99 % yield, 55 % ee). $^{31}P\{^{1}H\}$ NMR($CDCl_3$, 161 MHz): δ 0.3; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 3.20 (ddd, 1H, J = 17.8 Hz, 7.8 Hz, 2.7 Hz, C*H*HCOPh), 3.63－3.71 (m, 1H, CH*H*COPh), 4.35－4.39 (m, 1H, PC*H*CH_2), 7.07－7.97 (m, 19H, Ar); ^{13}C NMR ($CDCl_3$, 125 MHz): δ 39.8 (d, 1C, $^{1}J_{PC}$ = 13.0 Hz, P*C*H), 41.9 (d, 1C, $^{2}J_{PC}$ = 21.8 Hz, *C*H_2COPh), 121.6－148.2 (m, 24C, Ar), 197.3 (d, 1C, $^{3}J_{PC}$ = 12.6 Hz, *C*OPh).

Determination of ee: Compound **5i** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^{1}H\}$ NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 55 % evaluated by integration of **7i** and **8i** signals.



Purification by recrystalization: The obtained (±)**5i** (152.3 mg) was dissolved in

appropriate DCM/Acetone (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum pump to provide product (*S*)-**5i** (63.1 mg, 41 % yield, based on Ph_2PH, 85 % ee). $[\alpha]_D^{20}$ = −241.3 (*c* 0.9, CH_2Cl_2), $^{31}P\{^1H\}$, ^1H, ^{13}C NMR spectra were identical with those of (±)**5i**.

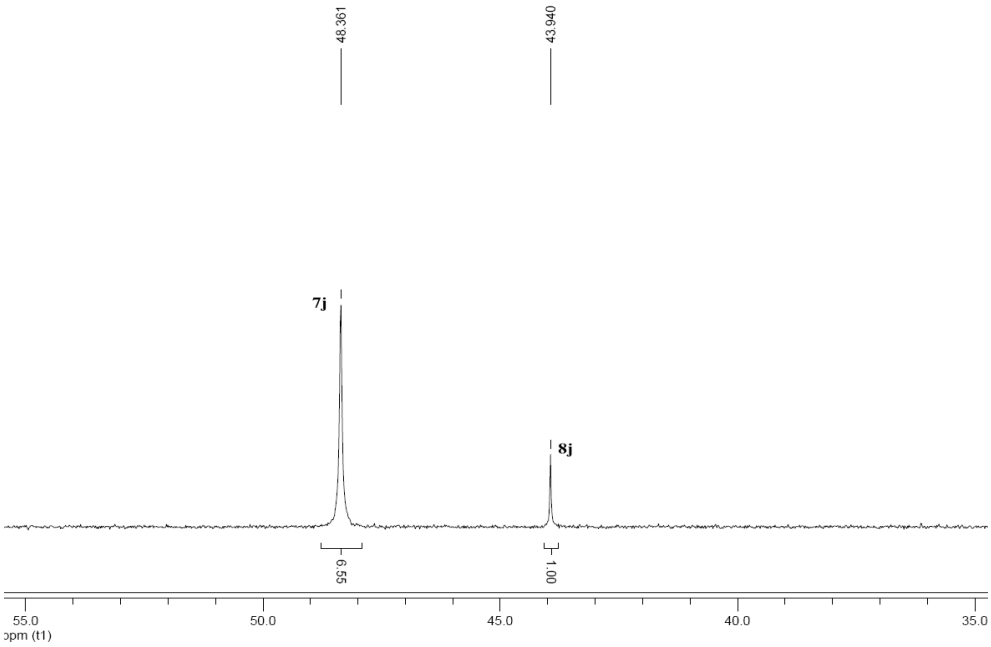


Synthesis of Ph_2PCH(4-OH-Ph)CH_2CO(Ph) (5j)

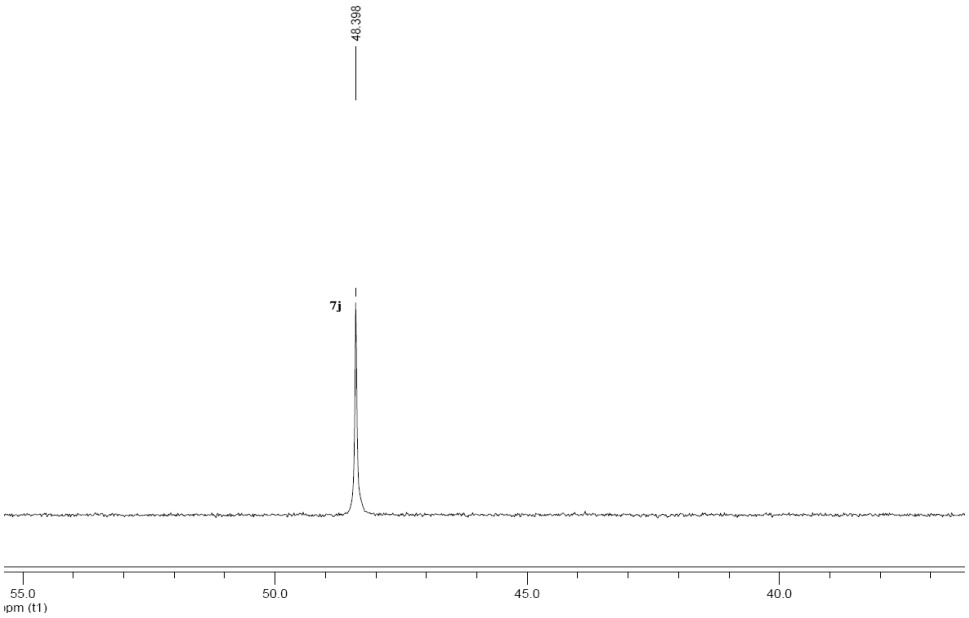
Compound **3j** (87.5 mg, 0.39 mmol, 1.1 equiv) was reacted with **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at −80 ℃ for 7 d according to the general procedure to provide (±)**5i** (140.8 mg, 98 % yield, 73 % ee). $^{31}P\{^1H\}$ NMR(DMSO-d_6, 161 MHz): δ−2.9; ^1H NMR (DMSO-d_6, 400 MHz): δ 2.73 (ddd, 1H, J = 20.0 Hz, 8.1 Hz, 2.5 Hz, C*H*HCOPh), 3.67−3.76 (m, 1H, CH*H*COPh), 4.20−4.26 (m, 1H, PC*H*CH_2), 6.51−7.75 (m, 19H, Ar), 9.14 (s, 1H, O*H*); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 38.4 (d, 1C, $^1J_{PC}$ = 10.4 Hz, P*C*H), 41.8 (d, 1C, $^2J_{PC}$ = 23.2 Hz, *C*H_2COPh), 114.8−155.5 (m, 24C,

Ar), 197.8 (d, 1C, $^{3}J_{PC}$ = 13.4 Hz, *C*OPh).

Determination of ee: Compound **5j** was dissolved in DCM (with small mount of THF, due to its poor solubility) followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{H\}$ NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 73 % evaluated by integration of **7j** and **8j** signals.



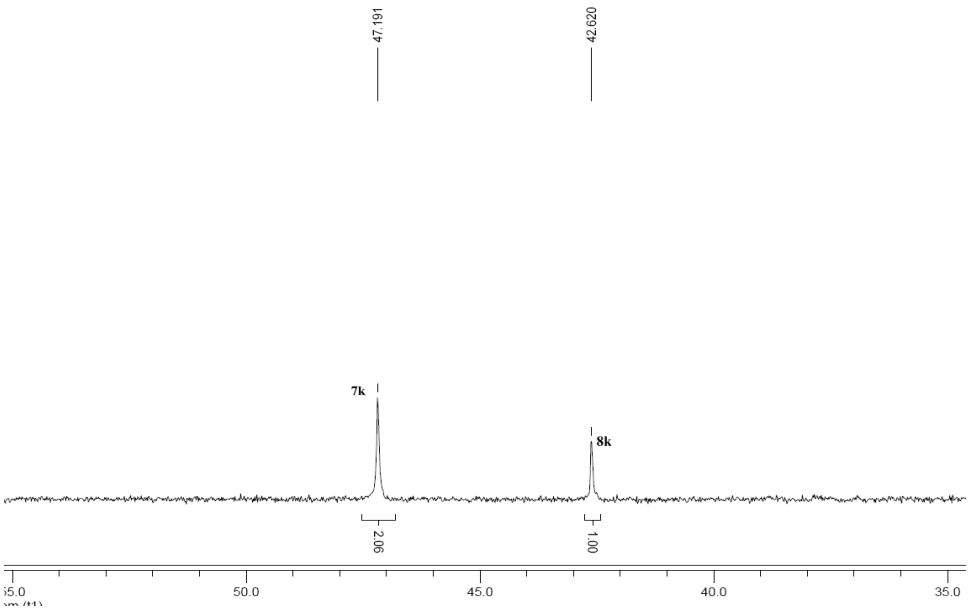
Purification by recrystalization: The obtained (±)**5j** (140.8 mg) was dissolved in appropriate DCM/Acetone (1:1) (heating needed), then cooled to 0 ℃, precipitation occurred. The solution was transferred out and the precipitate was dried by vacuum pump to provide product (*S*)-**5j** (57.5 mg, 40 % yield, based on Ph_2PH, 99 % ee). $[\alpha]_D^{20}$ = −102.0 (*c* 1.0, acetone), $^{31}P\{^{1}H\}$, ^{1}H, ^{13}C NMR spectra were identical with those of (±)**5j**.



Synthesis of $Ph_2PCH(4\text{-}MeO\text{-}Ph)CH_2CO(Ph)$ (5k)

3k (92.9 mg, 0.39 mmol, 1.1 equiv) was added to **4** (65.2 mg, 0.35 mmol, 1.0 equiv) at 0 ℃, followed by Et_3N (17.7 mg, 0.17 mmol), then warm to 20 ℃ gradually and stirr for 40 h to provide (±)**5k** (144.1 mg, 97 % yield, 73 % ee). $^{31}P\{^1H\}$ NMR($CDCl_3$, 161 MHz): δ−1.4; ^1H NMR ($CDCl_3$, 400 MHz): δ 3.03 (ddd, 1H, J = 17.1 Hz, 7.9 Hz, 2.6 Hz, C*H*HCOPh), 3.53−3.62 (m, 1H, CH*H*COPh), 3,63 (s, 3H, CH_3O), 4.18−4.23 (m, 1H, PC*H*CH_2), 6.60−7.68 (m, 19H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 39.1 (d, 1C, $^1J_{PC}$ = 11.0 Hz, P*C*H), 42.7 (d, 1C, $^2J_{PC}$ = 22.4 Hz, *C*H_2COPh), 55.3 (s, 1C, *C*H_3O), 113.9−158.2 (m, 24C, Ar), 198.3 (d, 1C, $^3J_{PC}$ = 13.0 Hz, *C*OPh).

Determination of ee: Compound **5k** was dissolved in DCM followed by addition of 0.5 equiv Pd dimmer complex **6**. After stirring for 20 min at RT, the solvent was evaporated and the $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz) spectrum recorded ee = 33 % evaluated by integration of **7k** and **8k** signals.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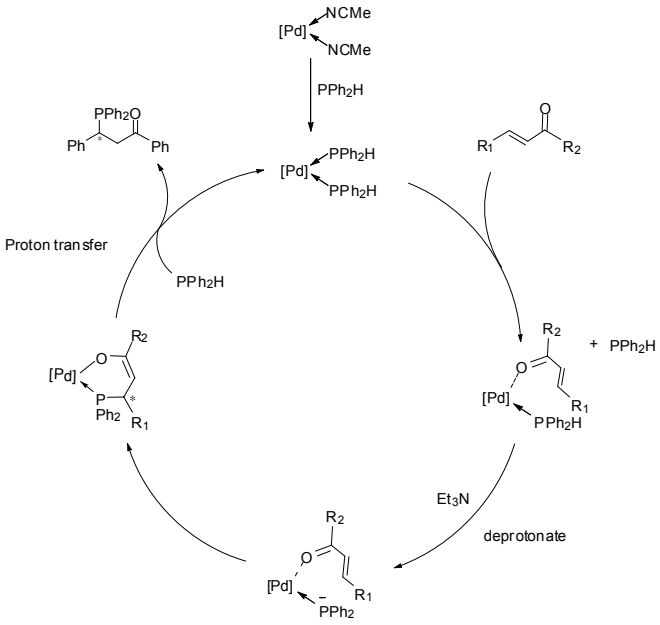
42.620
7k
8k
2.06
1.00
50.0
45.0
40.0
35.0

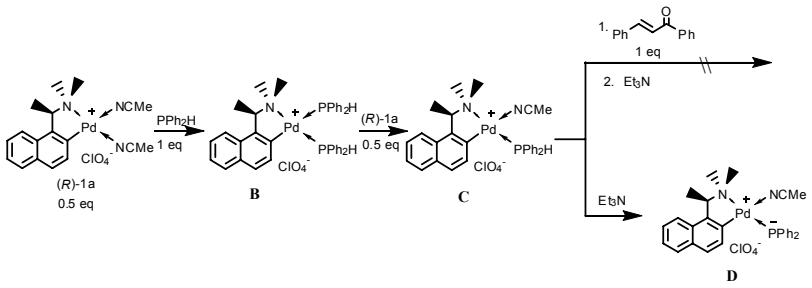
Mechanism Studies



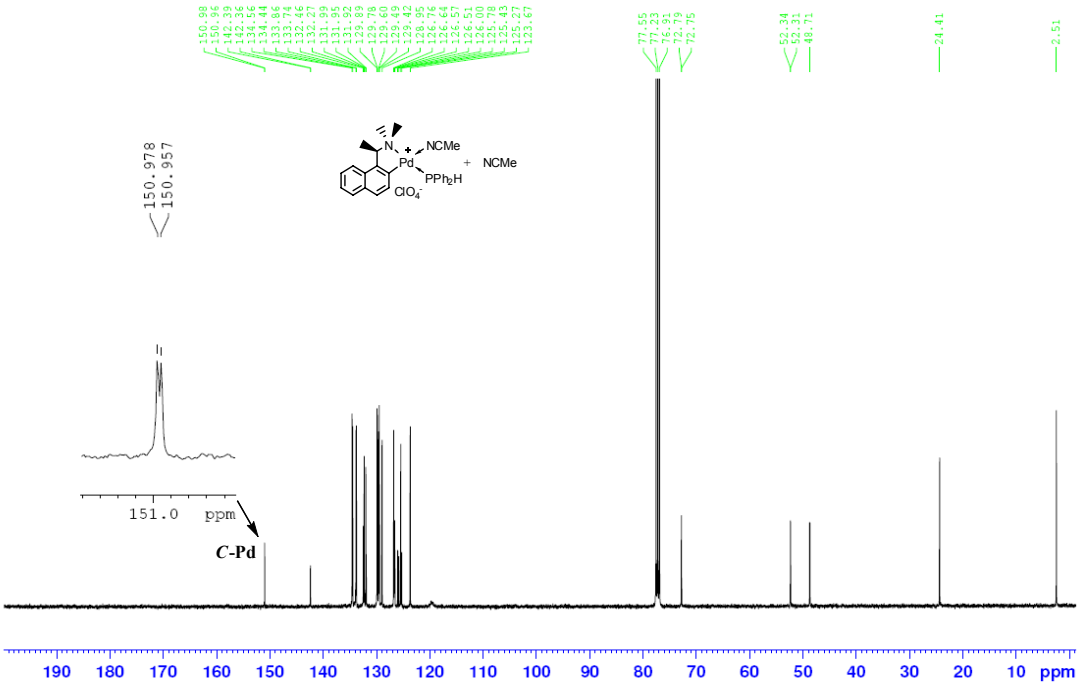
Scheme 1 Proposed catalytic cycle

Regarding the addition of nucleophiles to enones catalyzed by palladium, the mechanism involving C=C bond coordination with palladium leading to formation of *C*-bound palladium enolate in equilibrium with *O*-enolate or oxa-π-ally species has been proposed.[4] However, in our case, we propose that the carbonyl oxygen coordinates to palladium rather than the C=C moiety leading to formation of *O*-enolate intermediate followed by proton transfer to generate the product (Scheme 1) We propose it based on the following experimental observations.

(1) Stoichiometric model:



Complex (*R*)-1a (48.6 mg, 0.1 mmol, 0.5 eqiv) was treated with PPh_2H (37.2 mg, 0.2 mmol, 1 eqiv) in dichloromethane (10 mL) for 10 min at 0 ℃ to form the bisdiphenylphosphine complex B ($^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ−9.4 (d, J = 39.0 Hz), 10.8 (d, J = 39.0 Hz)) followed by addition of another 0.5 eqiv of complex (*R*)-1a (48.6 mg, 0.1 mmol) to give complex **C** which indicates that the $HPPh_2$ *trans* to carbon is more labile and could dissociate easily. Alternatively, complex **C** could be obtained directly by treatment of equal amount (mol) of complex (*R*)-1a and PPh_2H. The ^{13}C NMR of complex **C** showed a small coupling of the Pd-C carbon with ^{31}P (J_{CP} = 2.04 Hz) which indicates the *cis* coordination of diphenylphosphine. Complex C: $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ 12.7; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.97 (d, 3H, $^4J_{HP}$ = 6.4 Hz, CHCH_3), 2.84 (d, 3H, $^4J_{HP}$ = 1.0 Hz, NCH_3CH_3), 2.97 (d, 3H, $^4J_{HP}$ = 3.8 Hz, NCH_3CH_3), 4.40 (m, 1H, CHCH_3), 6.42 (d, 1H, $^1J_{HP}$ = 383.7 Hz, Ph_2PH), 6.89−7.85 (m, 16H, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): 24.4 (s, 1C, CHCH$_3$), 48.7 (s, 1C, NCH$_3$CH$_3$), 52.3 (d, 1C, $^3J_{CP}$ = 2.7 Hz, NCH$_3$CH$_3$), 72.8 (d, 1C, $^3J_{CP}$ = 3.4 Hz, CHCH$_3$), 123.7−142.4 (m, 21C, Ar), 150.9 (d, 1C, $^2J_{CP}$ = 2.04 Hz, C−Pd)).

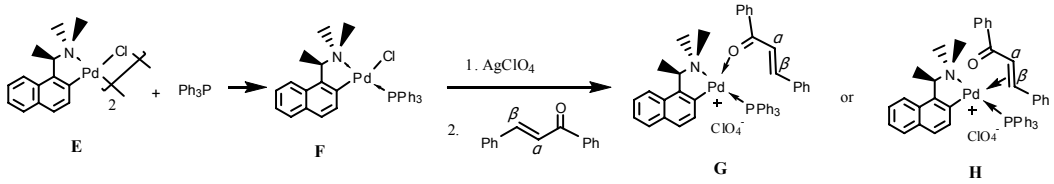


The phosphido intermediate D ($^{31}P\{^1H\}$ NMR ($CDCl_3$, 121 MHz): δ−69.7) can be

detected immediately by treatment of complex C with Et_3N. However, it is difficult to isolate due to its ready dimerization. Treatment of stoichiometric amount of complex **C** and *trans* chalcone under the same conditions described in the manuscript lead to the phosphido intermediate **D** and its dimerization compound instead of the expected addition product. However, if more free phosphine such as PPh_3 was added, the phosphido intermediate **D** disappeared and the expected addition product can be detected from $^{31}P\{^1H\}$ NMR which indicates that the free phosphines play an important role in driving the catalytic cycle.

(2) Coordination experiment:

We did the following experiment using PPh_3 as the equivalent of $HPPh_2$ to check whether coordination occurs between palladium and ketone oxygen or C=C bonds.



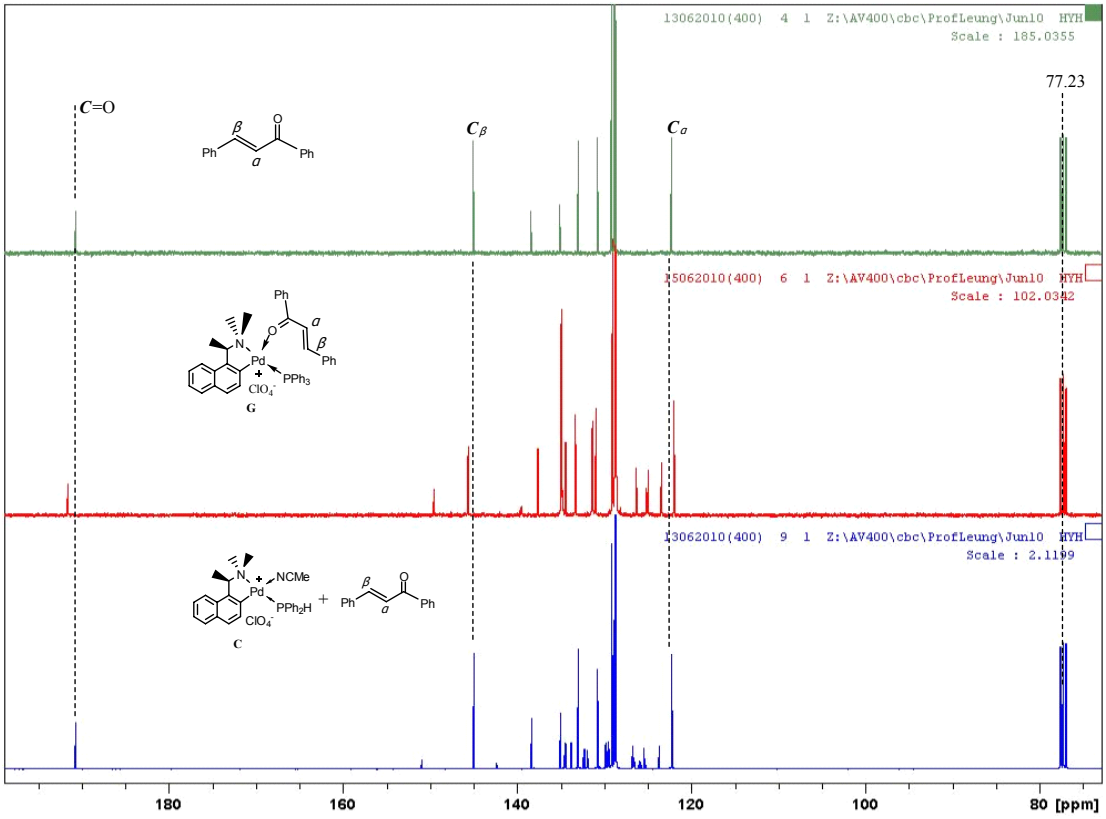
The dimeric complex **E** (68.0 mg, 0.1 mmol, 0.5 equiv) was treated with PPh_3 (52.5 mg, 0.2 mmol, 1.0 equiv) in dichloromethane (15 mL) for 20 min at RT to form complex F ($^{31}P\{^1H\}$ NMR ($CDCl_3$, 202 MHz): δ 40.3). Subsequently $AgClO_4$ (62.1 mg, 0.3 mmol, 1.5 equiv) was added and after stirring for 30 min, the mixture was filtered through celite and dried by $MgSO_4$. Subsequently, *trans*-chalcone (41.7 mg, 0.2 mmol, 1.0 equiv) was added and after stirring for 20 min in CH_2Cl_2, the solvent was evaporated by vacuum pump to obtain the species as solids. $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161 MHz): δ 38.6; ^1H NMR ($CDCl_3$, 400 MHz): δ 1.95 (d, 3H, $^4J_{PH}$ = 6.4 Hz, CHCH_3), 2.63 (d, 3H, $^4J_{PH}$ = 2.4 Hz, NCH_3CH$_3$), 2.69 (s, 3H, NCH$_3$CH_3), 4.27 (m,

1H, C*H*CH_3), 6.40－7.83 (m, 33H, C*H*=C*H*, Ar); ^{13}C NMR ($CDCl_3$, 100 MHz): 23.76 (s, 1C, CH*C*H_3), 46.90 (s, 1C, N*C*H_3CH_3), 51.31 (s, 1C, N*C*H_3CH_3), 71.65 (d, 1C, $^3J_{CP}$= 2.6 Hz, *C*HCH_3), 121.94 (s, 1C, PhCH=*C*H), 123.39－145.59 (m, 39C, Ar), 149.47 (d, 1C, $^2J_{CP}$ = 1.30 Hz, *C*－Pd)), 191.55 (s, 1C, *C*=O). IR (KBr, ν(C=O)/cm^{-1}, 1660.7; ν(C=C)/cm^{-1}, 1602.8).

trans-chalcone: ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.24－8.03 (m, 12H, C*H*=C*H*, Ar), ^{13}C NMR ($CDCl_3$, 100 MHz): 122.25 (s, 1C, PhCH=*C*H), 128.62－138.37 (m, 12C, Ar), 144.99 (s, 1C, Ph*C*H=CH), 190.68 (s, 1C, *C*=O). IR (KBr, ν(C=O)/cm^{-1}, 1664.6; ν(C=C)/cm^{-1}, 1606.7)

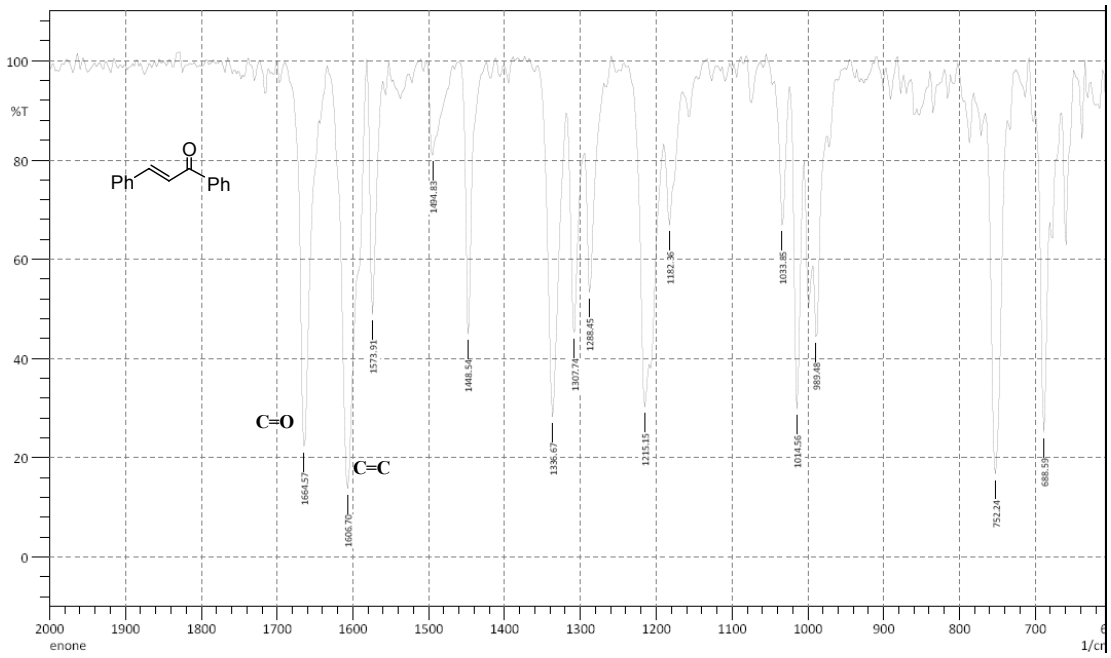
If coordination occurs through oxygen of the ketone meoity, then complex **G** could be expected, alternatively if coordination occurs through C=C bonds, then complex **H** could be expected. We then analysed the product by ^{13}C NMR (100 MHz, $CDCl_3$) and compared it with *trans* chalcone to find that the carbonyl C shifted Δδ= 0.87 ppm (toward low field); *α*-C: Δδ= －0.31 ppm (toward high field) and *β*-C: Δδ= 0.60 ppm (toward low field). This indicates that complex **G** is most likely formed since when C=O oxygen is coordinated to Pd, carbonyl C becomes more electron deficient, so it

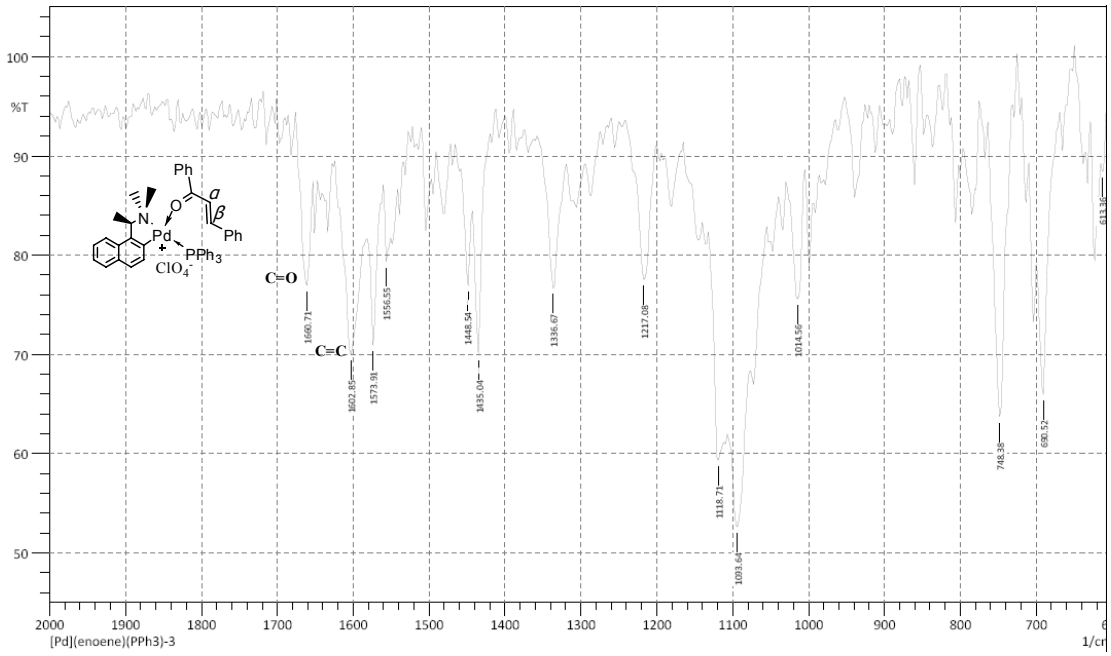
shifts toward low field as seen in our experiments. Due to the electron inducing effect, α-C becomes more electron rich and β-C becomes electron deficient and their resonances shift towards high field and low field respectively. However, if the C=C double bonds are coordinated to Pd as in complex **H**, then α-C and β-C should both become significantly electron deficient, and consequently both should shift towards the low field region. We also compared the ^{13}C NMR spectrum of *trans* chalcone with the mixture of equal mount (mol) of [Pd](NCMe)($HPPh_2$) and *trans* chalcone. No chemical shift can be detected in this instance which indicates that the enone itself can not replace NCMe and coordinate to Pd.



IR analysis was also conducted by comparing *trans* chalcone (KBr, ν(C=O)/cm^{-1},

1664.6; ν(C=C)/cm^{-1}, 1606.7) with the species [Pd](enone)(PPh_3) (KBr, ν(C=O)/cm^{-1}, 1660.7; ν(C=C)/cm^{-1}, 1602.8). The IR shifts are also consistent with the formation of complex **G** though the shifts are quite small in magnitude.





Therefore, we believe that it most likely to undergo ketone complexation followed by 1,4-addition to generate *O*-enolate (as shown in the proposed catalytic cycle).

Reference

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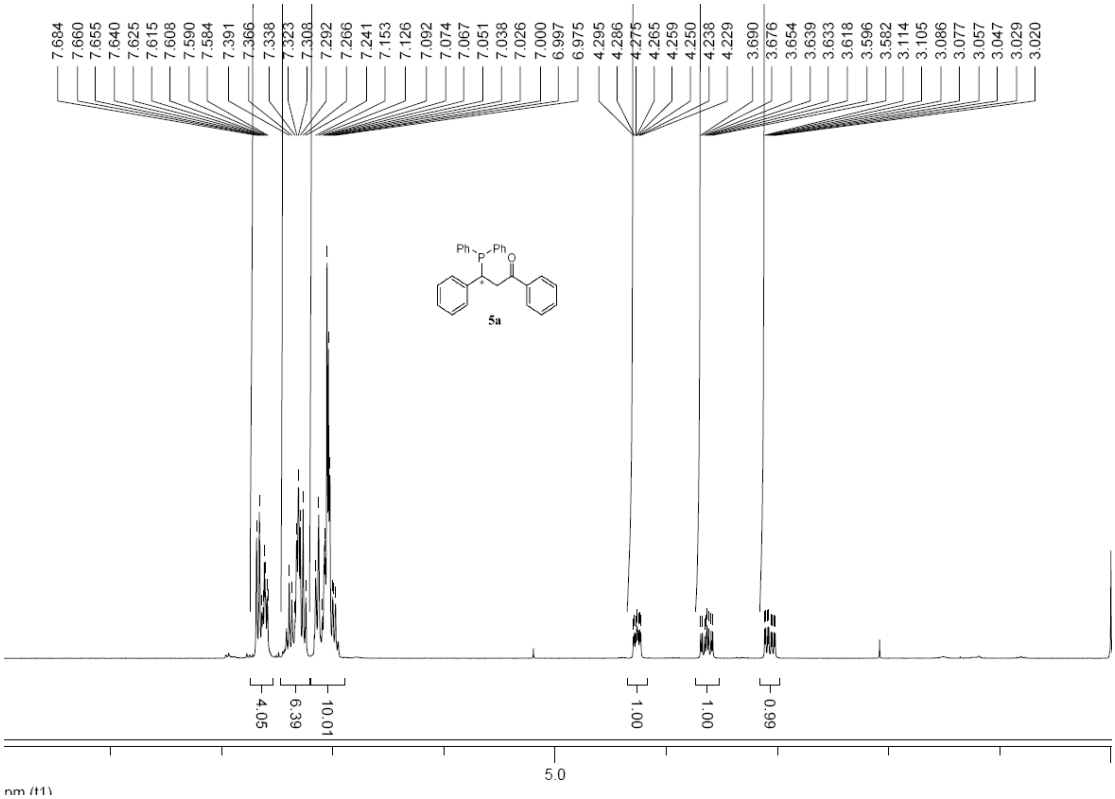
(2) T. P. Robinson,; R. B. Hubbard Iv, T. J. Ehlers, J. L. Arbiser, D. J. Goldsmith, J. P. Bowen, *Bioorg. Med. Chem*. 2005, **13**, 4007.

(3) A. D. Sadow, I. Haller, L. Fadini, A. Togni, *J. Am. Chem. Soc*., 2004, **126**, 14704.

(4) For recent selected examples, see: (a) T. Nishikata, Y. Yamamoto, I. D. Gridnev, N. Miyaura, Organometallics, 2005, 24, 5025. (b) T. Nishikata, Y. Yamamoto, N. Miyaura, Organometallics, 2004, 23, 4317.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4.250
4.238
4.229
3.690
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3.654
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3.633
3.618
3.596
3.582
3.114
3.105
3.086
3.077
3.057
3.047
3.029
3.020
Ph
P
Ph
O
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1.00
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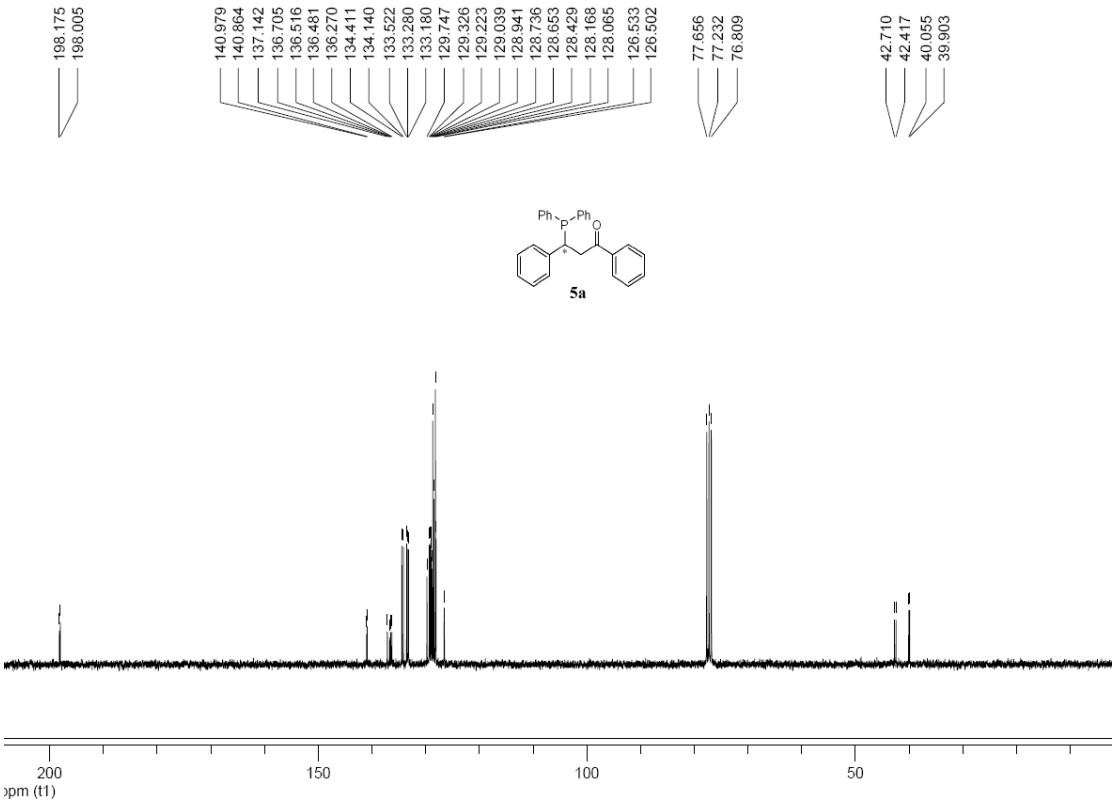
ppm (t1)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128.653
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126.533
126.502
77.656
77.232
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P
Ph
O
5a
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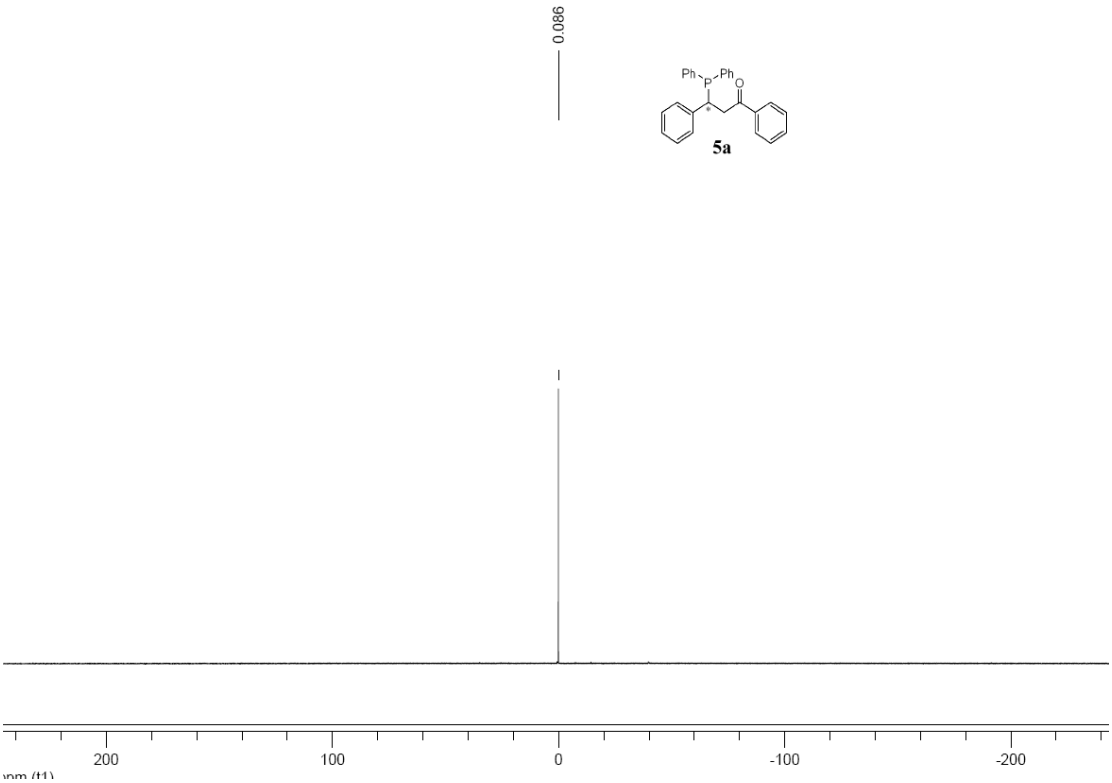
100
50
ppm (t1)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P
Ph
O
5a
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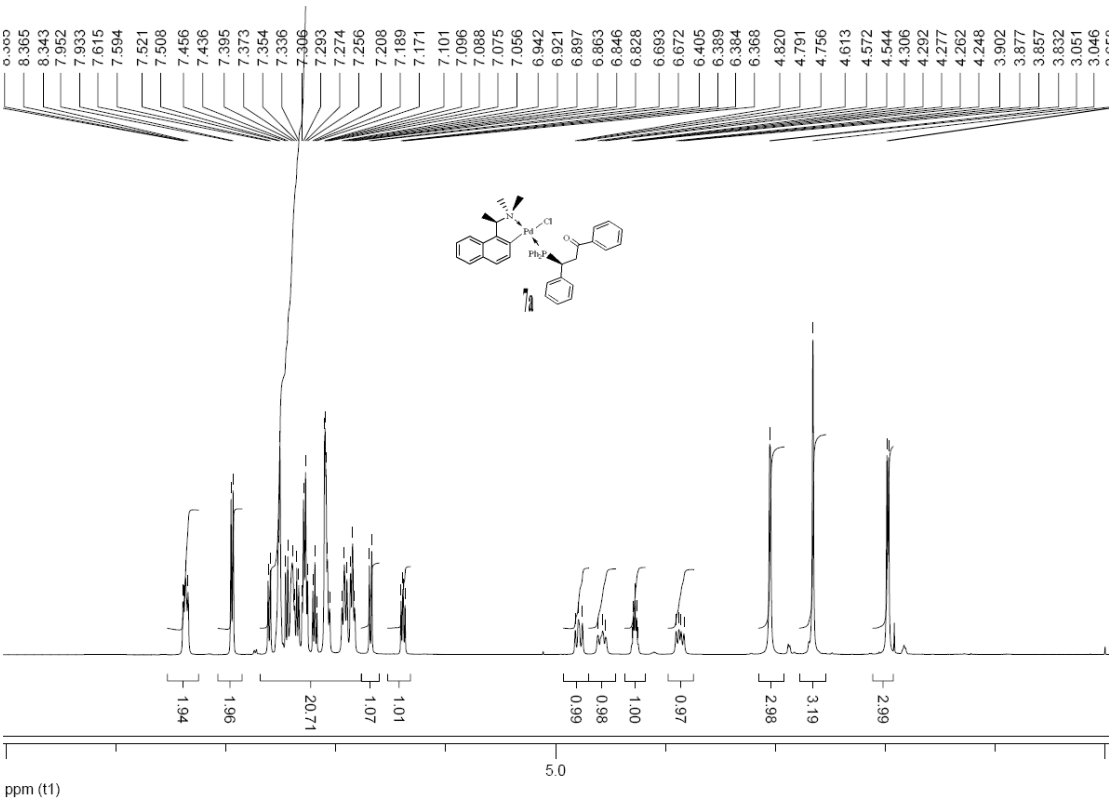
ppm (t1)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7.293
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7.189
7.171
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7.096
7.088
7.075
7.056
6.942
6.921
6.897
6.863
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6.384
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4.756
4.613
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4.262
4.248
3.902
3.877
3.857
3.832
3.051
3.046
1.94
1.96
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3.19
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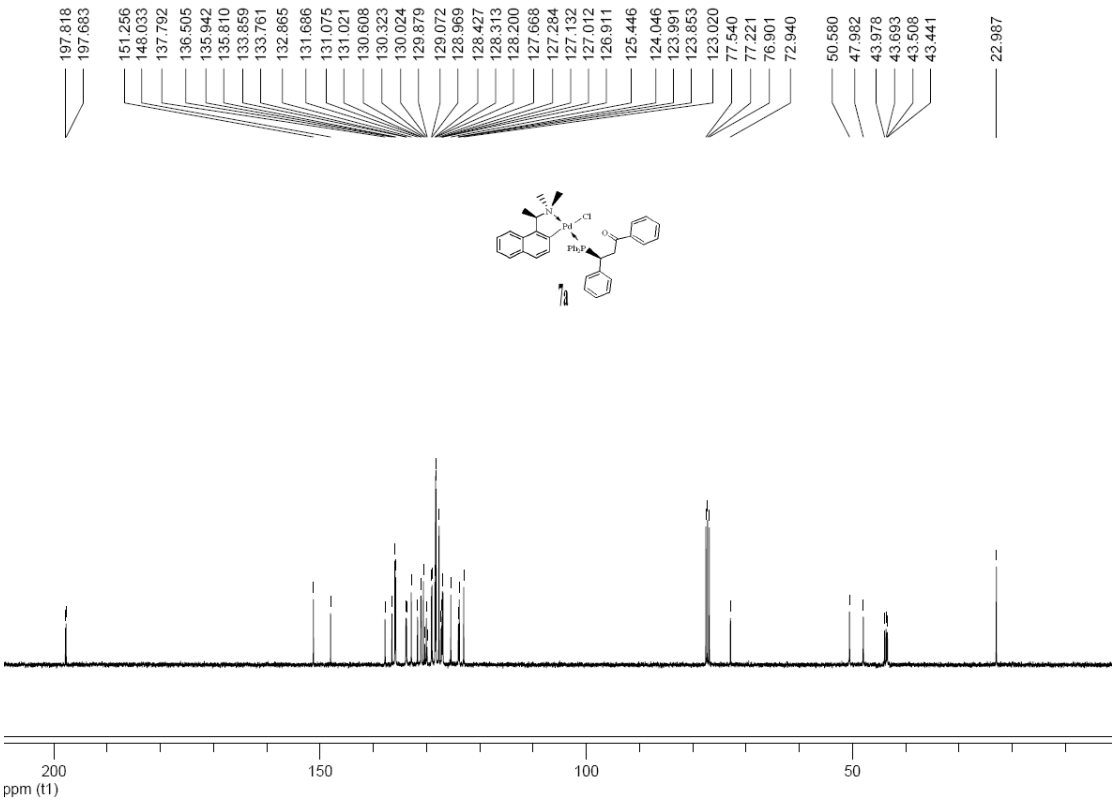
ppm (t1)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127.132
127.012
126.911
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77.221
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72.940
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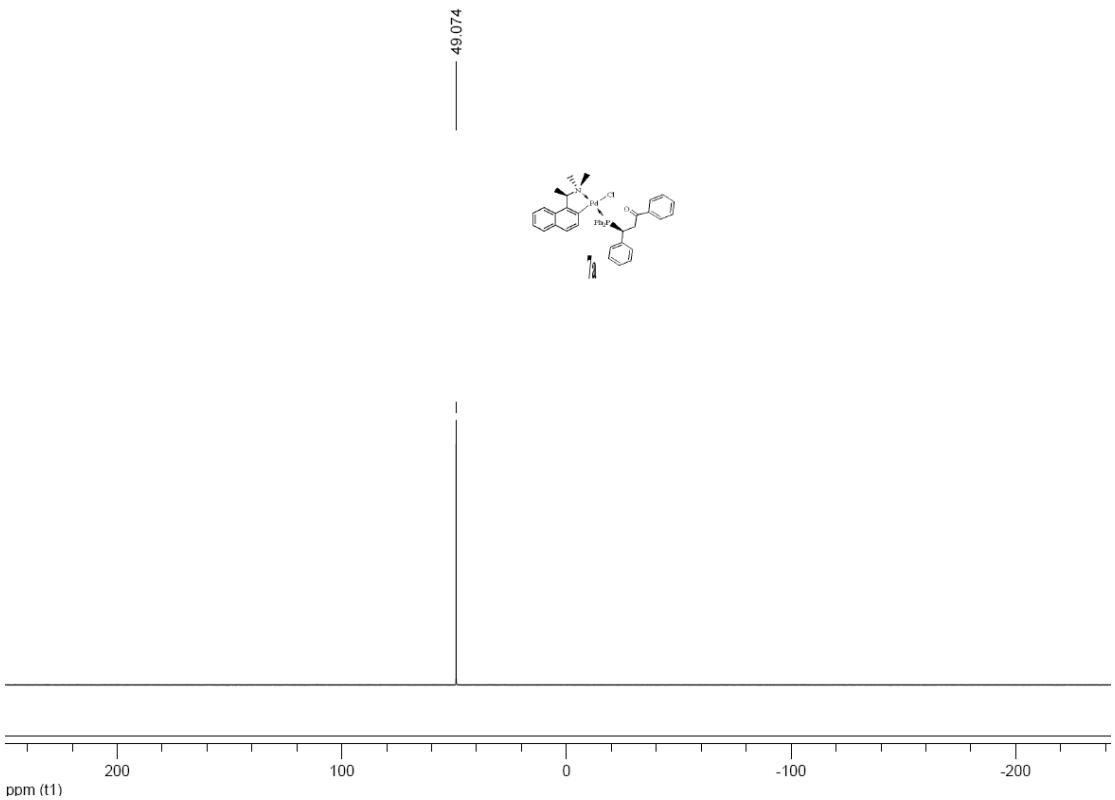
50
ppm (t1)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100
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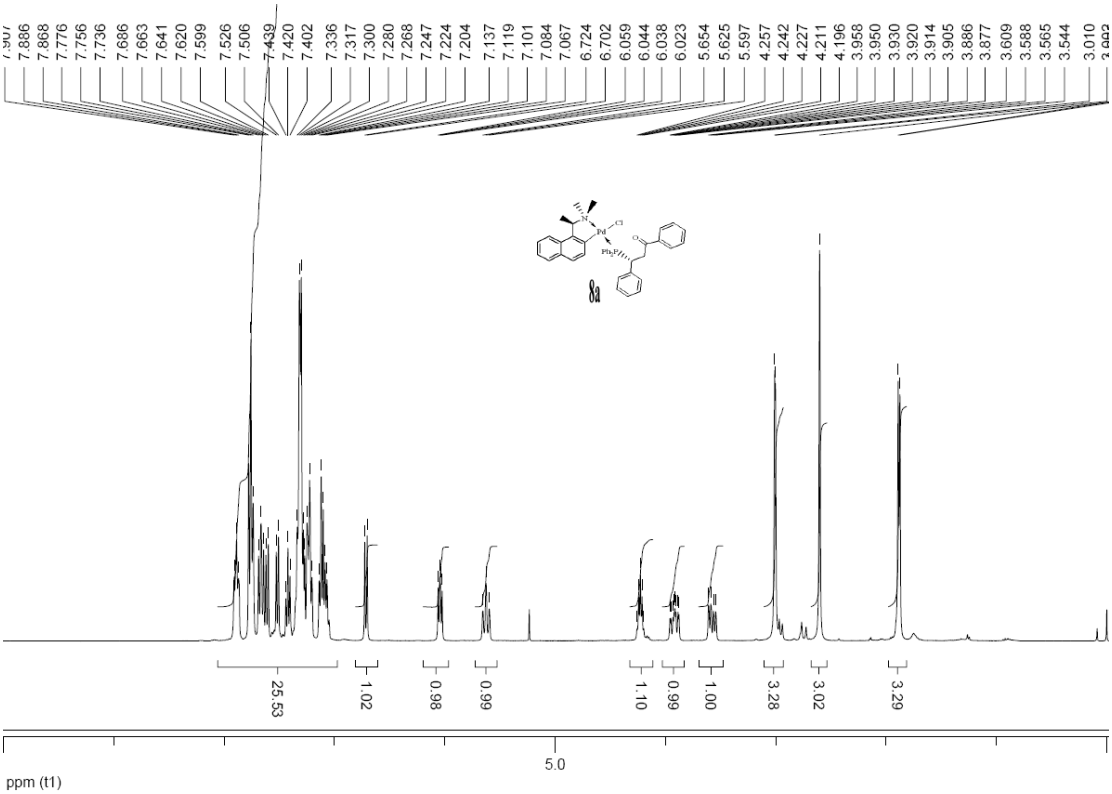
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7.439
7.420
7.402
7.336
7.317
7.300
7.280
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7.247
7.224
7.204
7.137
7.119
7.101
7.084
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6.038
6.023
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5.597
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4.227
4.211
4.196
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3.930
3.920
3.914
3.905
3.886
3.877
3.609
3.588
3.565
3.544
3.010
25.53
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0.98
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1.10
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1.00
3.28
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3.29
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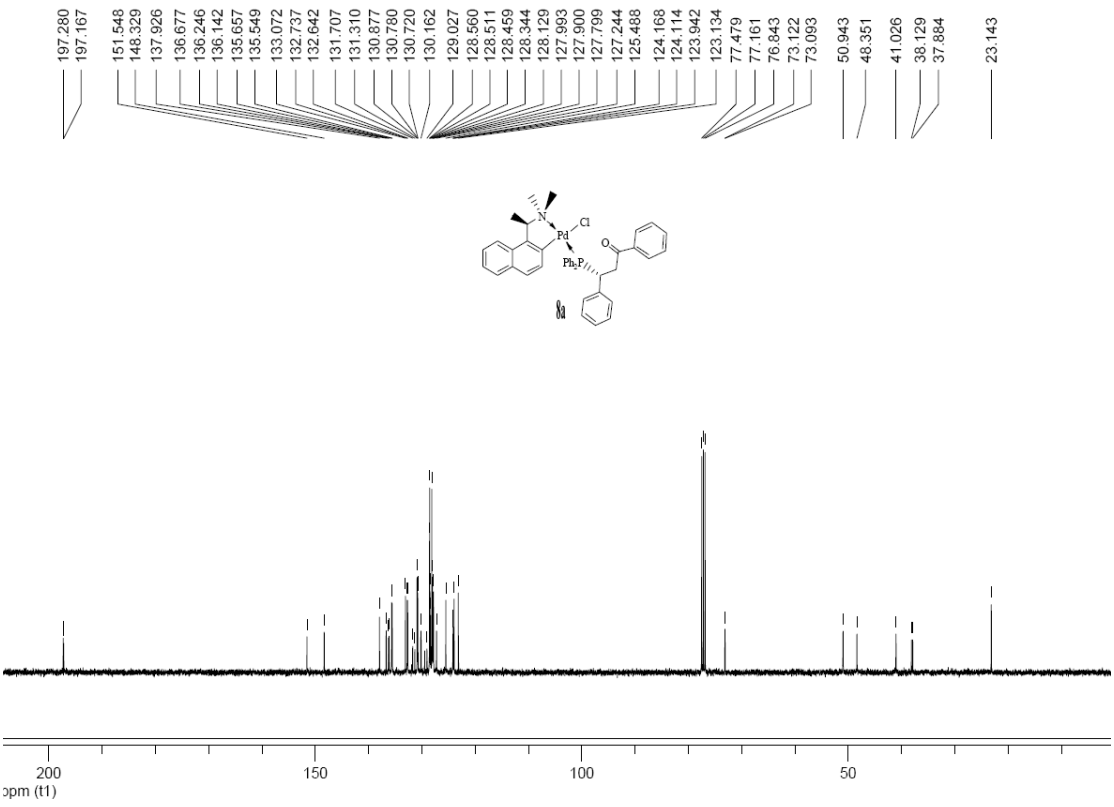
ppm (t1)

8a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132.642
131.707
131.310
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130.162
129.027
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128.511
128.459
128.344
128.129
127.993
127.900
127.799
127.244
125.488
124.168
124.114
123.942
123.134
77.479
77.161
76.843
73.122
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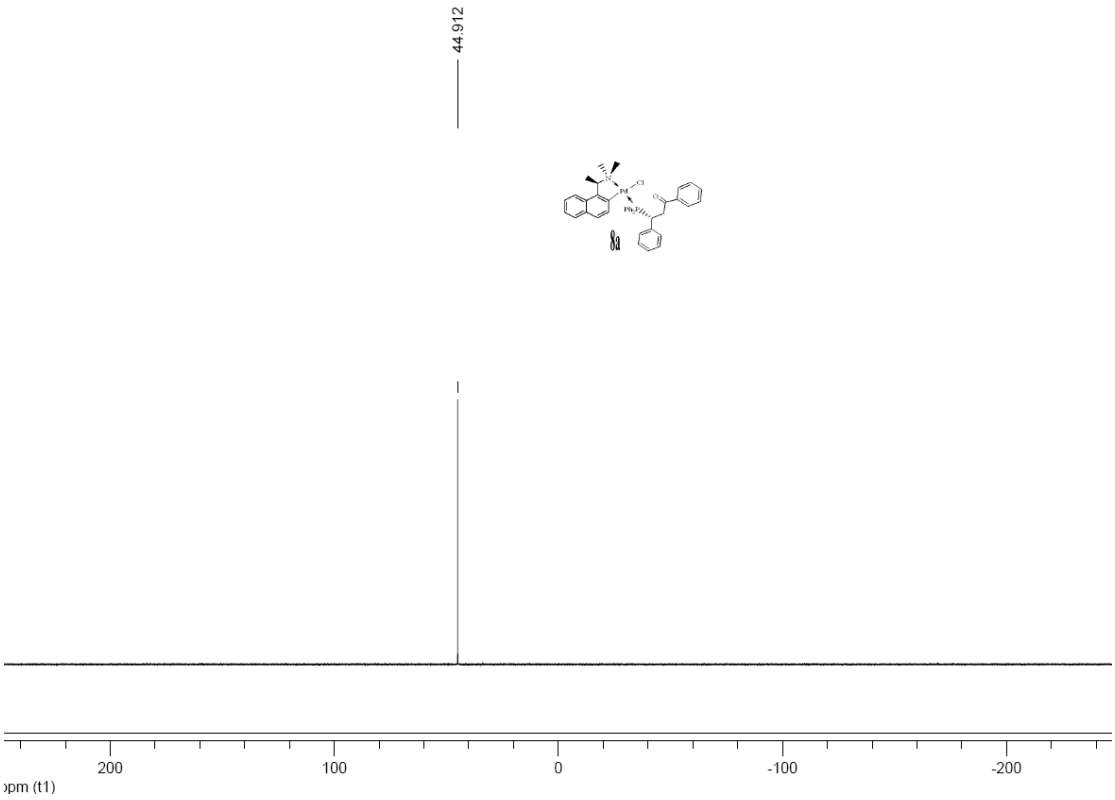
48.351
41.026
38.129
37.884
23.143
200
150
100
50
ppm (t1)

8a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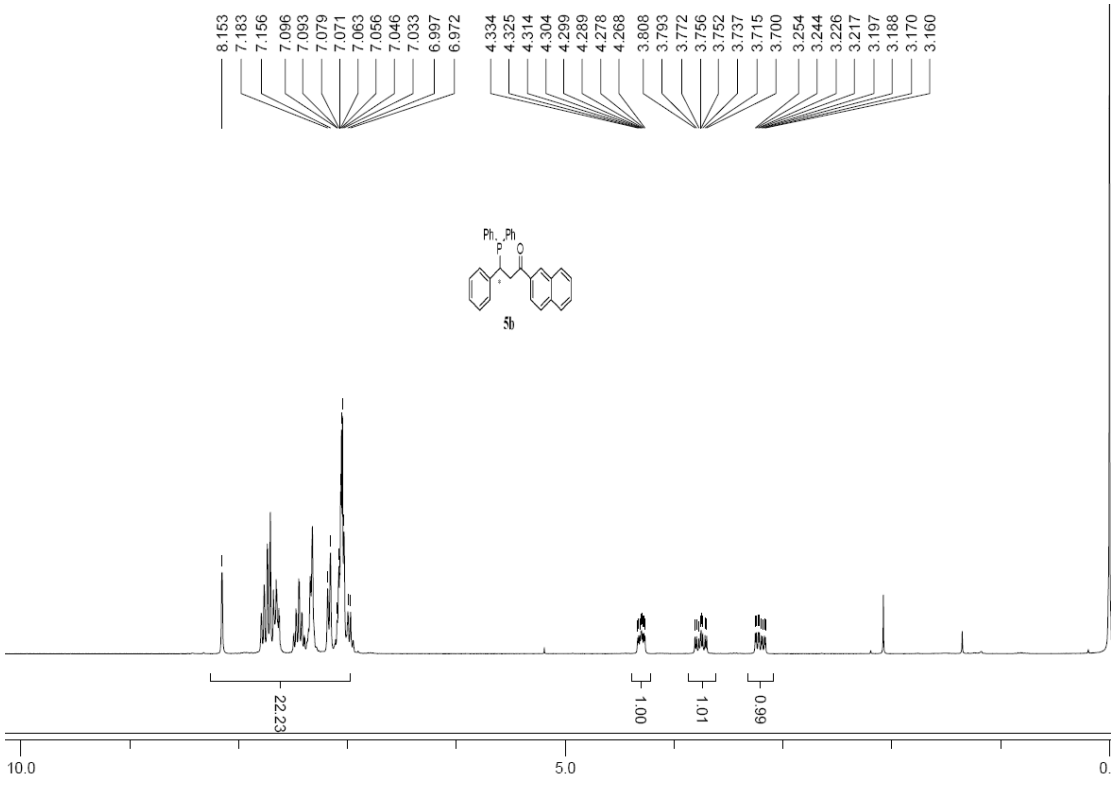
8a
200
100
0
-100
-200
ppm (t1)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7.079
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7.063
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7.033
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6.972
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4.325
4.314
4.304
4.299
4.289
4.278
4.268
3.808
3.793
3.772
3.756
3.752
3.737
3.715
3.700
3.254
3.244
3.226
3.217
3.197
3.188
3.170
3.160
Ph
Ph
P
O
5b
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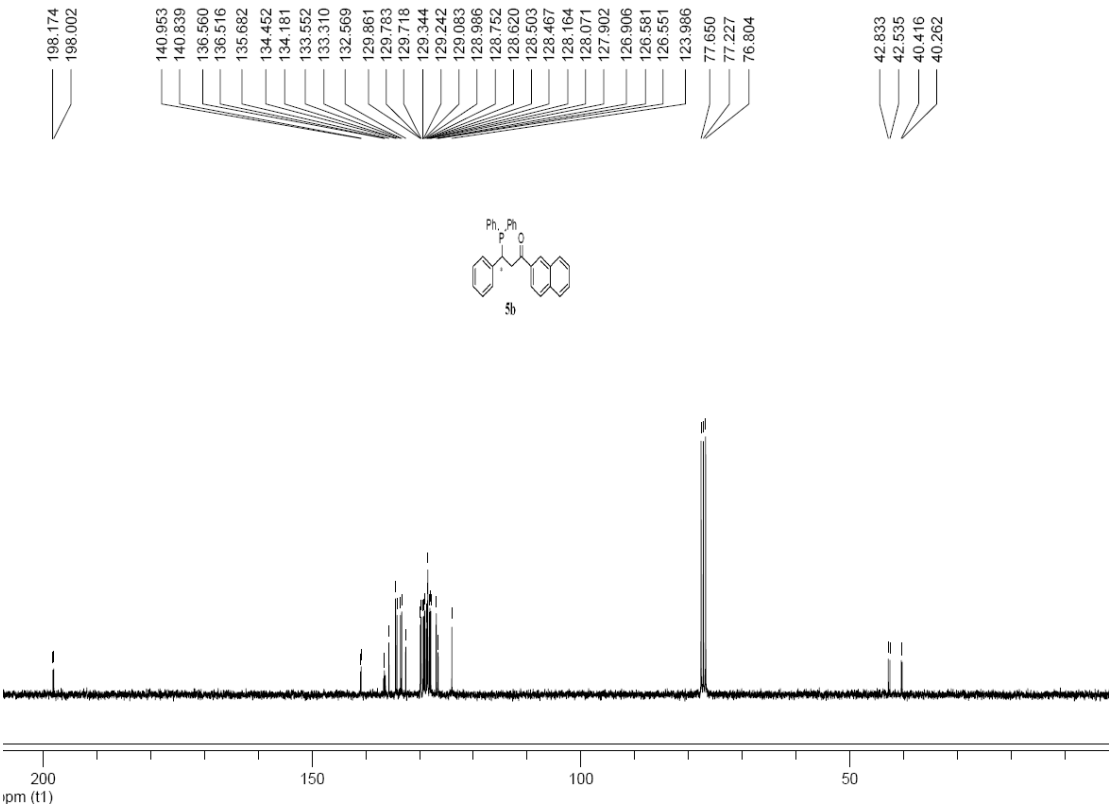
1.01
0.99
10.0
5.0
0.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129.783
129.718
129.344
129.242
129.083
128.986
128.752
128.620
128.503
128.467
128.164
128.071
127.902
126.906
126.581
126.551
123.986
77.650
77.227
76.804
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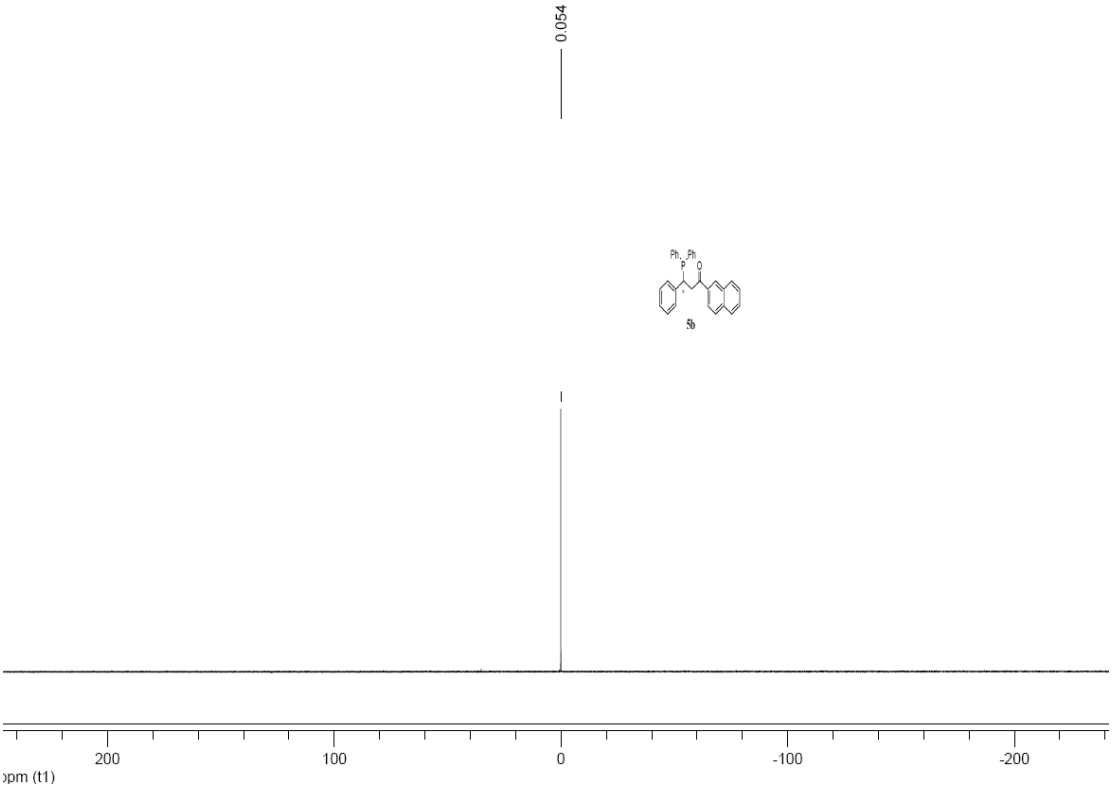
42.535
40.416
40.262
Ph
Ph
P
O
5b
200
150
100
50
ppm (t1)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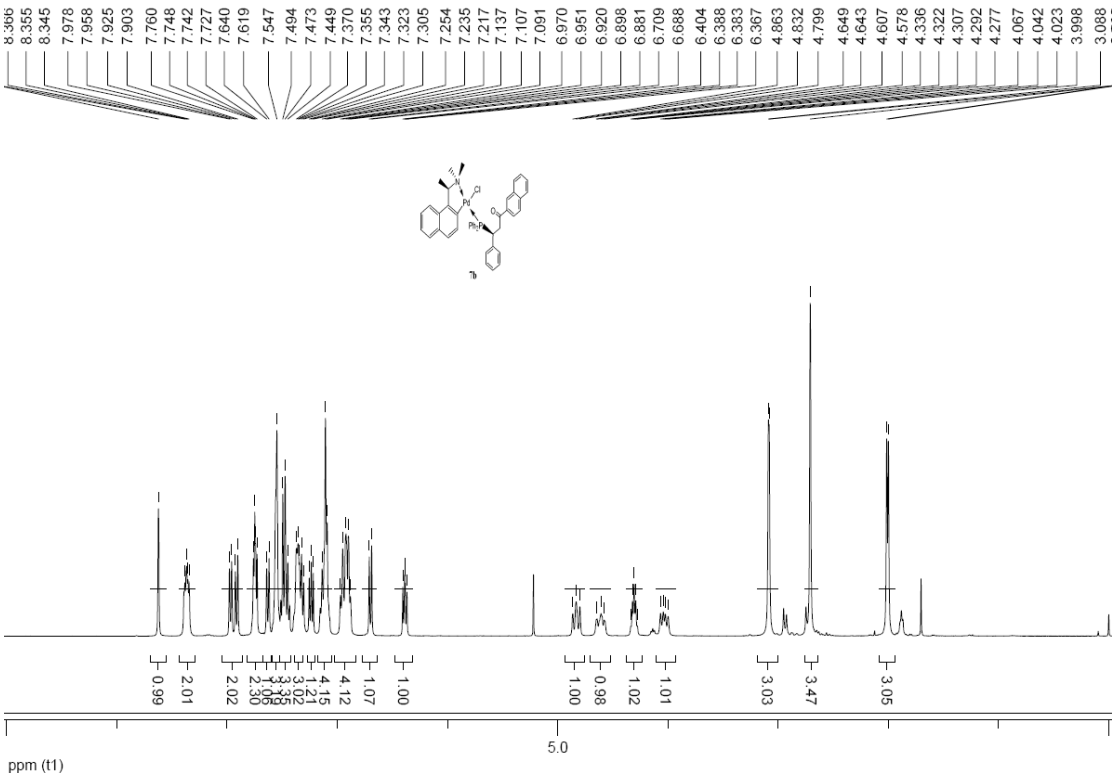
Ph
Ph
P
O
5b
200
100
0
-100
-200
ppm (t1)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7.305
7.254
7.235
7.217
7.137
7.107
7.091
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6.951
6.920
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6.881
6.709
6.688
6.404
6.388
6.383
6.367
4.863
4.832
4.799
4.649
4.643
4.607
4.578
4.336
4.322
4.307
4.292
4.277
4.067
4.042
4.023
3.998
0.99
2.01
2.02
2.30
3.02
1.21
4.15
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1.00
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1.02
1.01
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3.47
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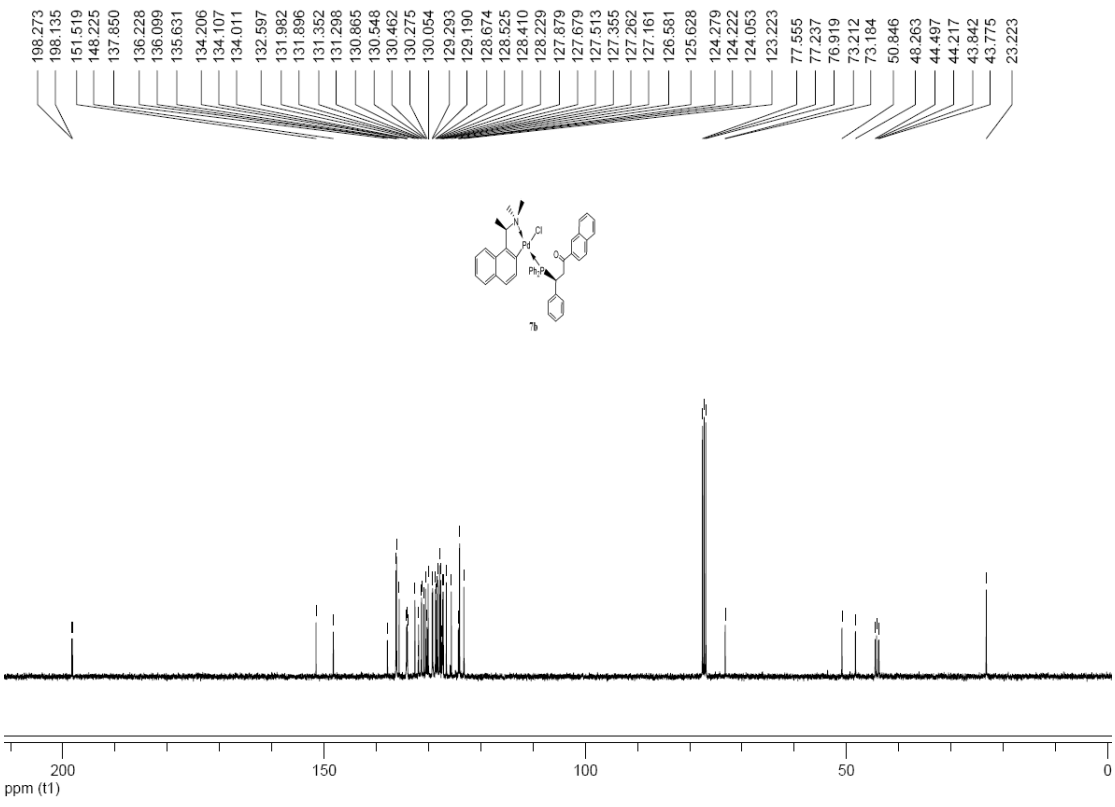
ppm (t1)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131.352
131.298
130.865
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129.190
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128.229
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127.513
127.355
127.262
127.161
126.581
125.628
124.279
124.222
124.053
123.223
77.555
77.237
76.919
73.212
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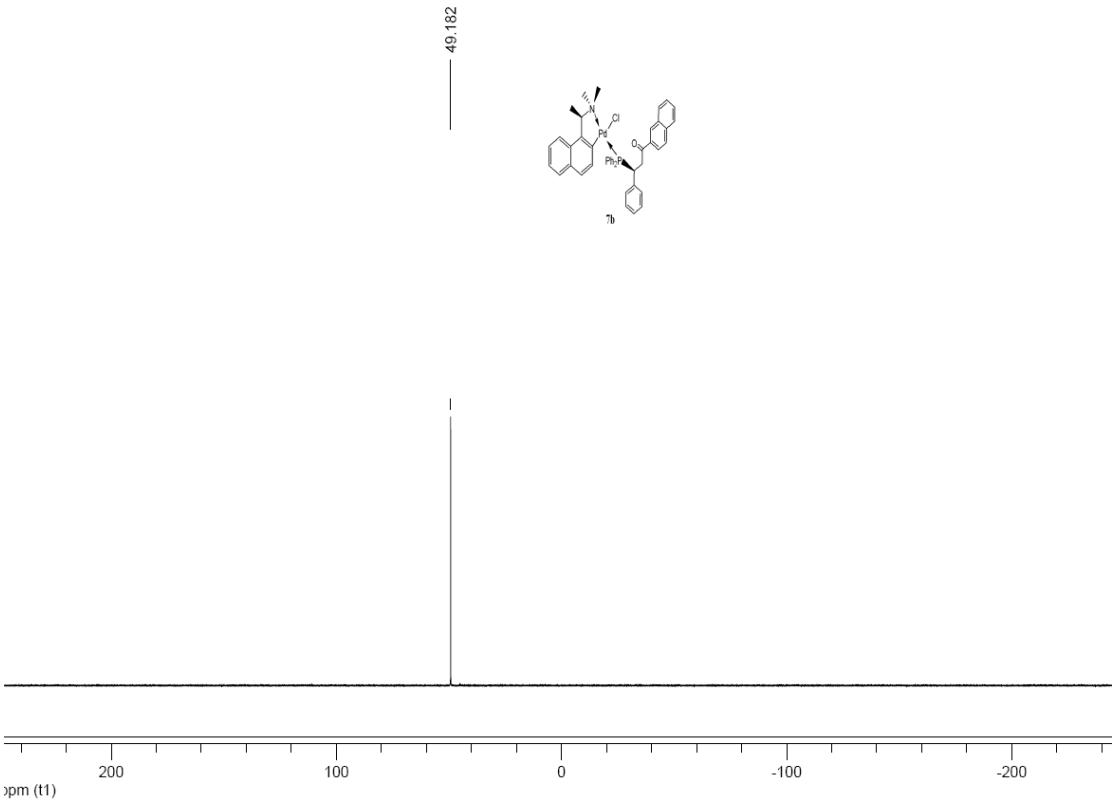
100
50
0
ppm (t1)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7b
200
100
0
-100
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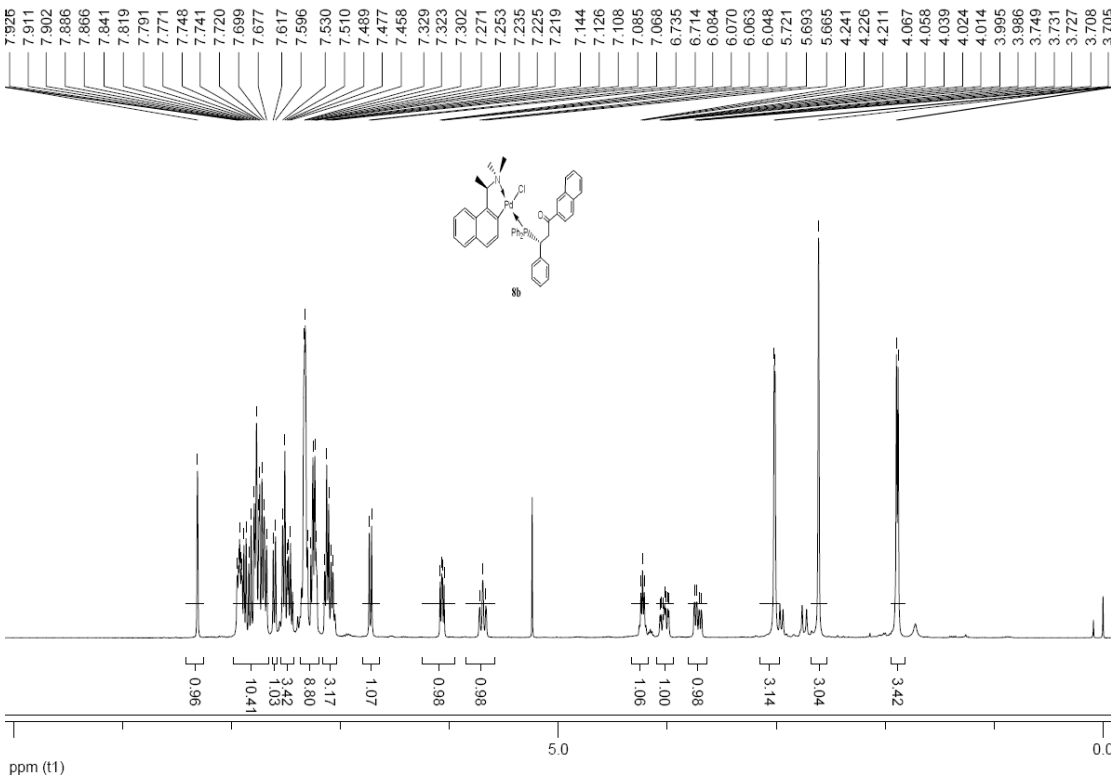
ppm (t1)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7.720
7.699
7.677
7.617
7.596
7.530
7.510
7.489
7.477
7.458
7.329
7.323
7.302
7.271
7.253
7.235
7.225
7.219
7.144
7.126
7.108
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7.068
6.735
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6.084
6.070
6.063
6.048
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5.693
5.665
4.241
4.226
4.211
4.067
4.058
4.039
4.024
4.014
3.995
3.986
3.749
3.731
3.727
3.708
8b
0.96
10.41
1.03
3.42
8.80
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0.98
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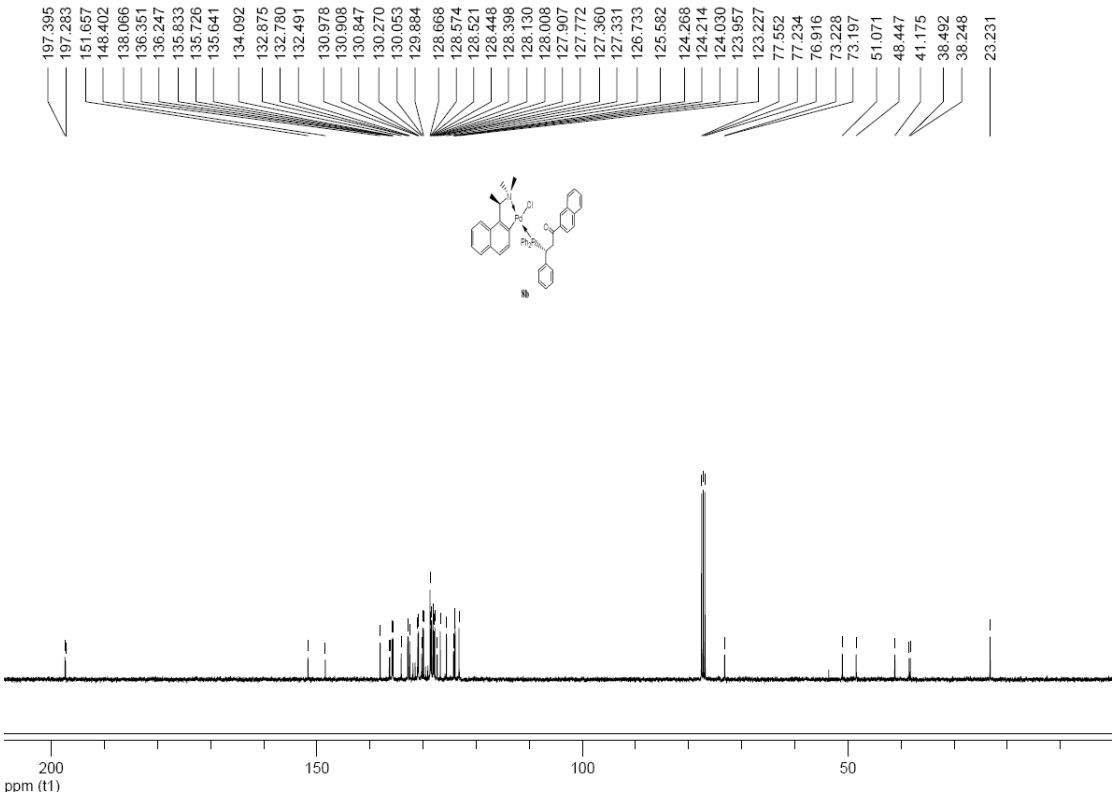
ppm (t1)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130.847
130.270
130.053
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128.521
128.448
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128.130
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127.331
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125.582
124.268
124.214
124.030
123.957
123.227
77.552
77.234
76.916
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23.231
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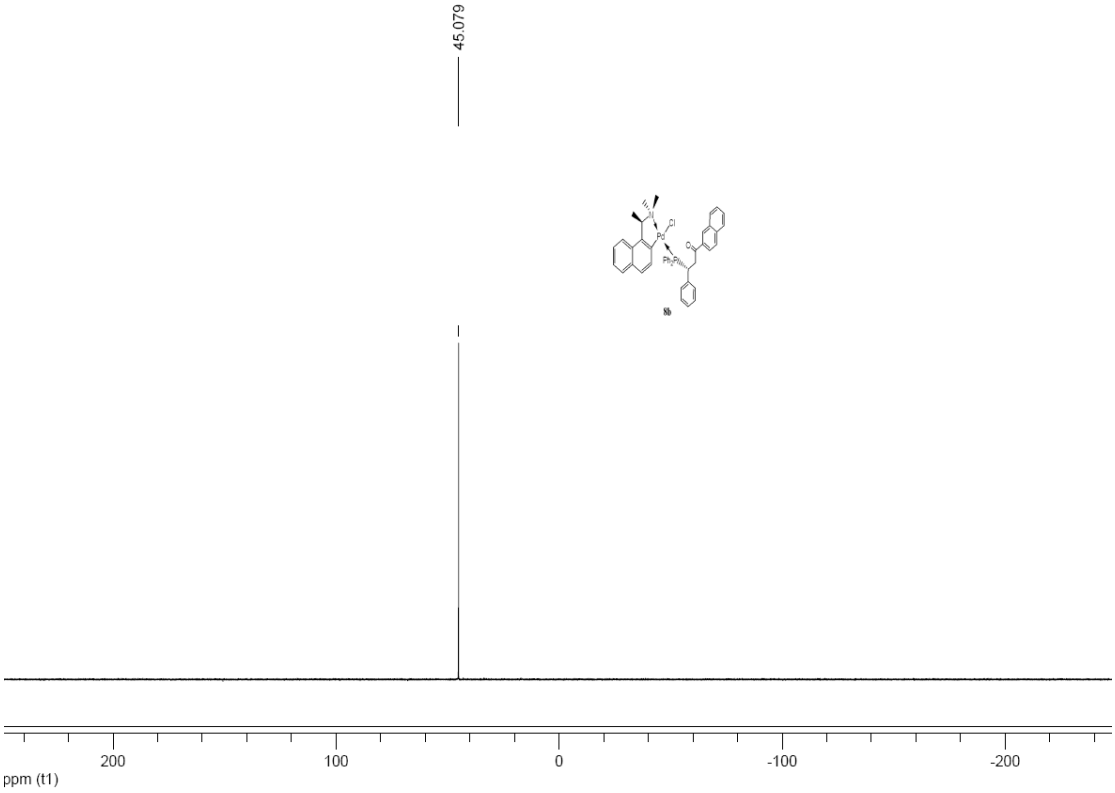
150
100
50
ppm (t1)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100
0
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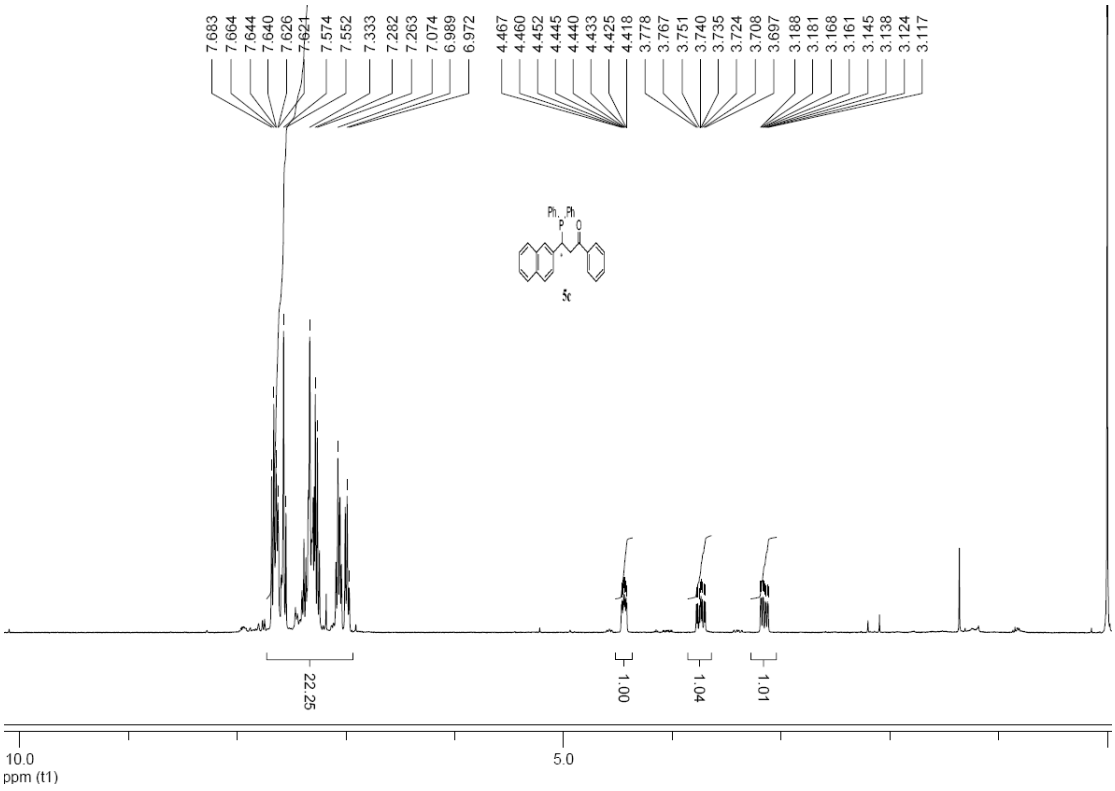
-200
ppm (t1)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7.621
7.574
7.552
7.333
7.282
7.263
7.074
6.989
6.972
4.467
4.460
4.452
4.445
4.440
4.433
4.425
4.418
3.778
3.767
3.751
3.740
3.735
3.724
3.708
3.697
3.188
3.181
3.168
3.161
3.145
3.138
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Ph Ph
P
O
5c
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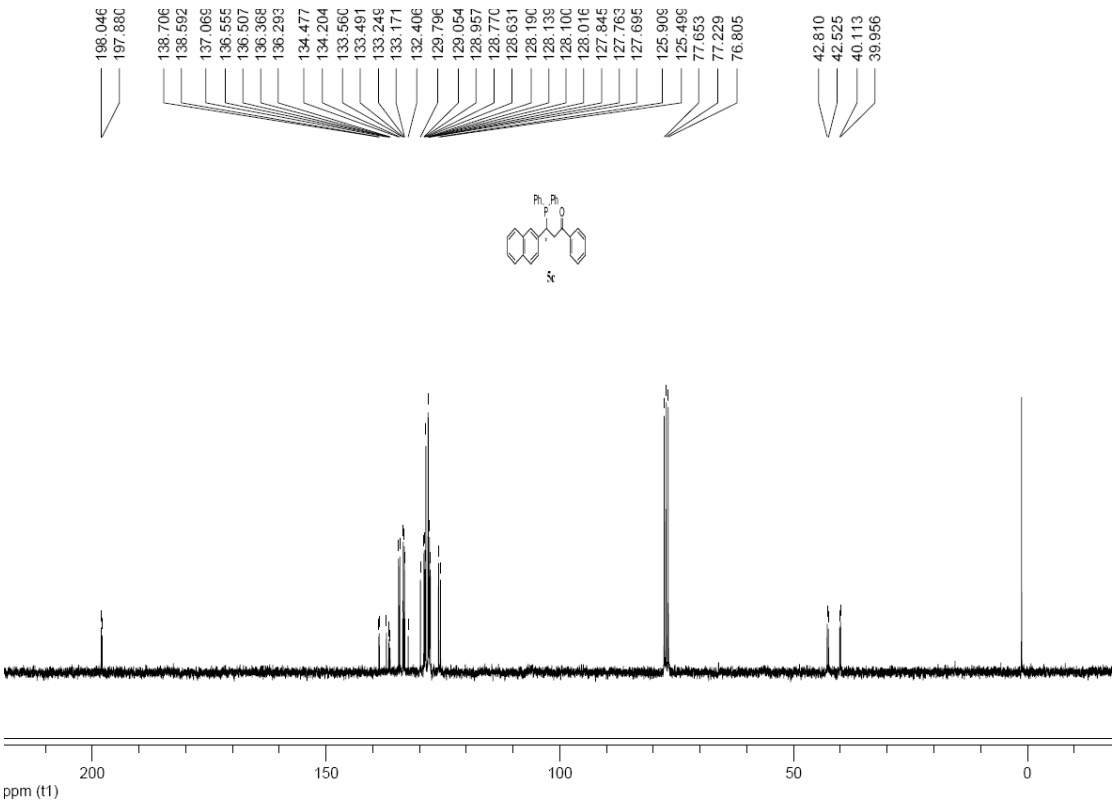
5.0
ppm (t1)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128.770
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128.016
127.845
127.763
127.695
125.908
125.496
77.653
77.229
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40.113
39.956
Ph Ph
P
O
5c
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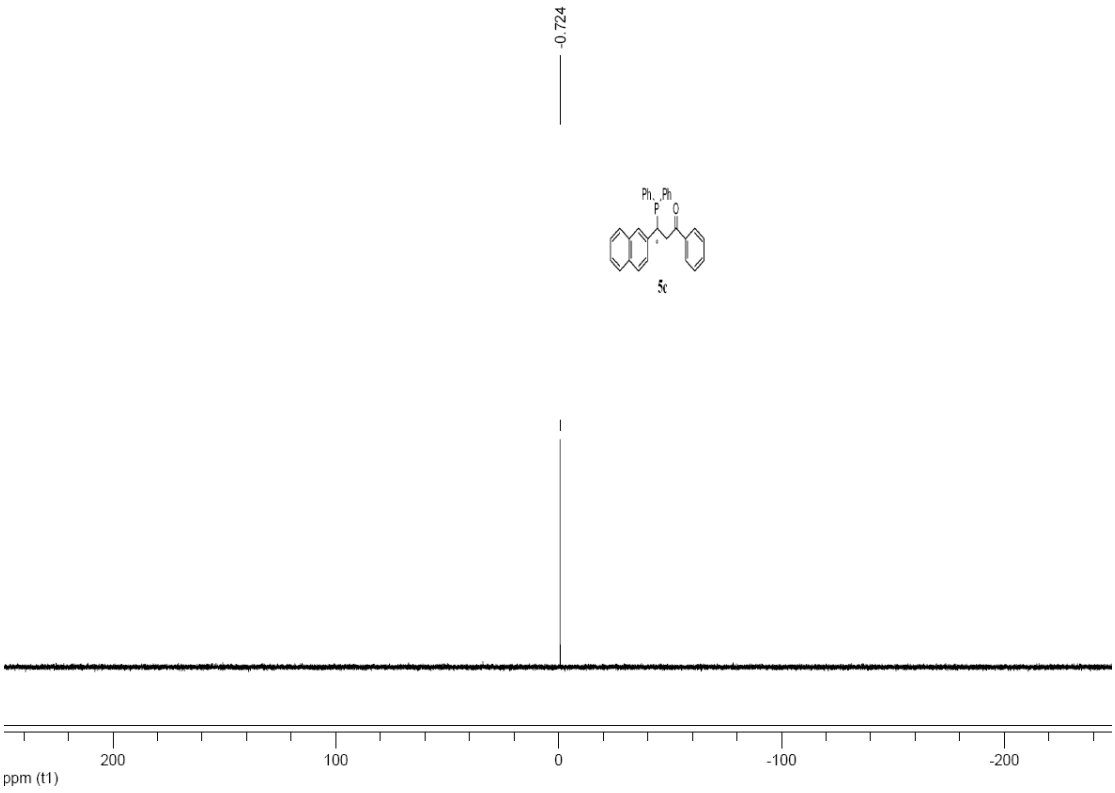
150
100
50
0
ppm (t1)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P
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-100
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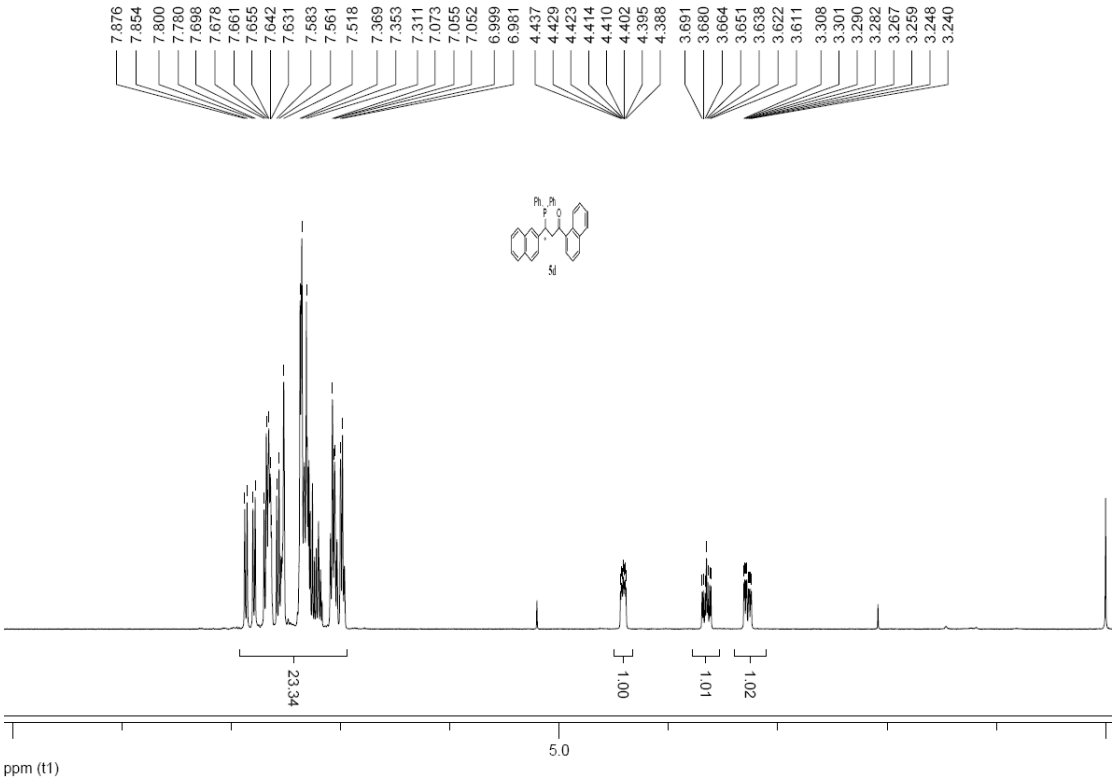
ppm (t1)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7.518
7.369
7.353
7.311
7.073
7.055
7.052
6.999
6.981
4.437
4.429
4.423
4.414
4.410
4.402
4.395
4.388
3.691
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3.664
3.651
3.638
3.622
3.611
3.308
3.301
3.290
3.282
3.267
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Ph
Ph
P
O
5d
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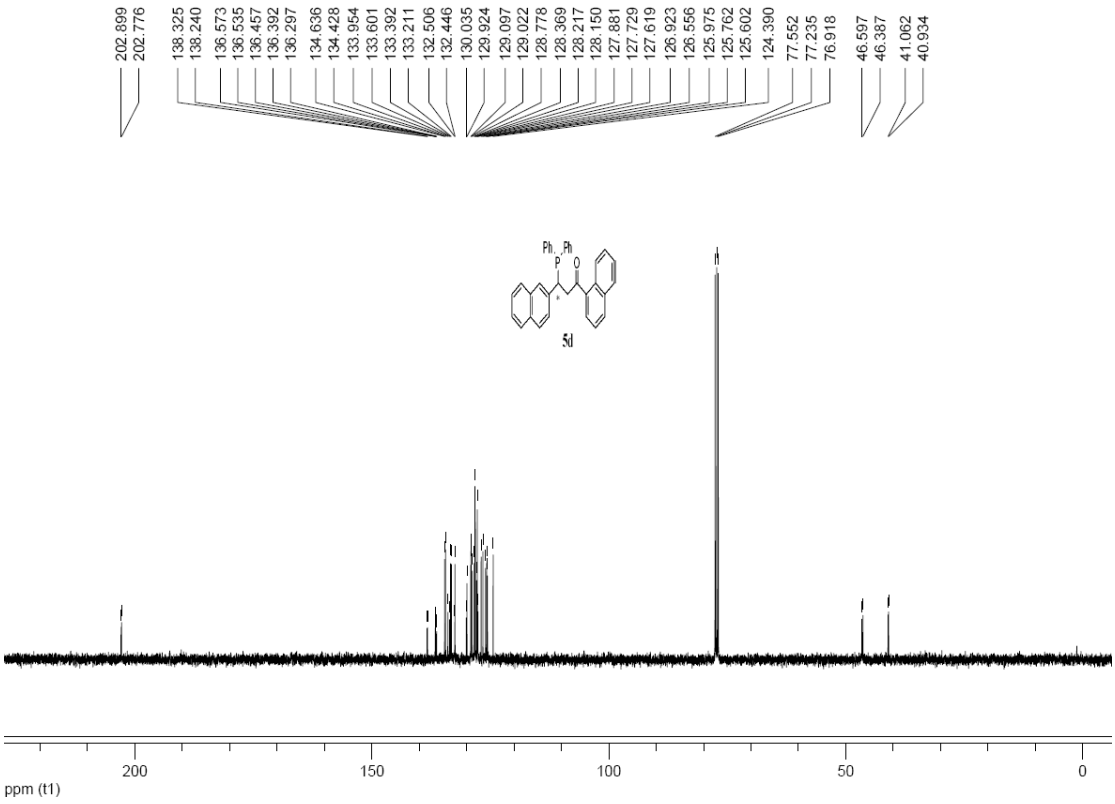
ppm (t1)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133.392
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125.975
125.762
125.602
124.390
77.552
77.235
76.918
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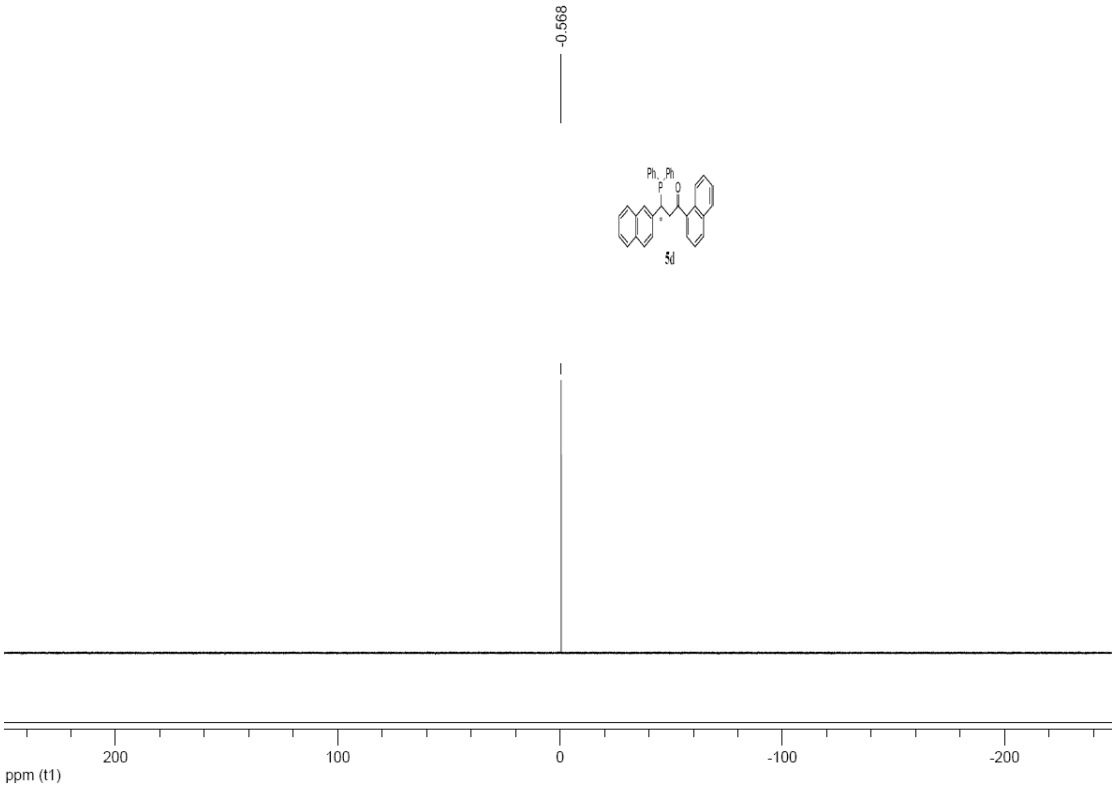
40.934
Ph
Ph
P
O
5d
200
150
100
50
0
ppm (t1)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P
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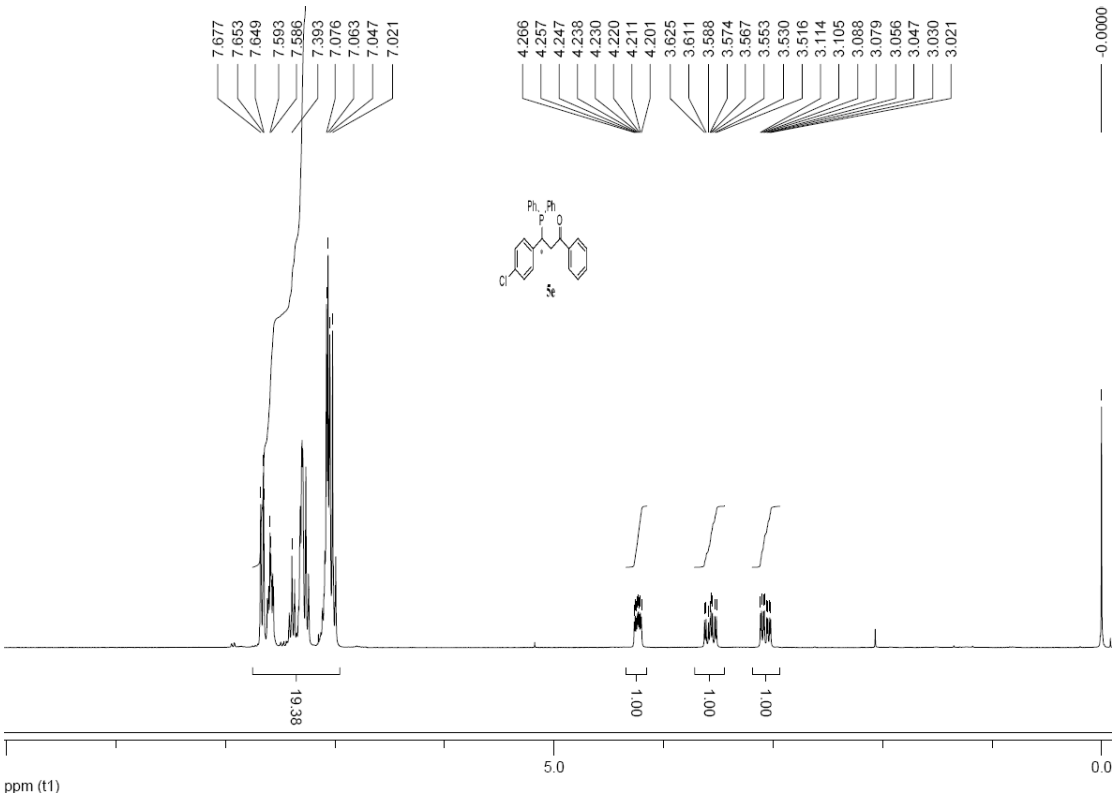
ppm (t1)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7.063
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7.021
4.266
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4.238
4.230
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3.625
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3.588
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3.516
3.114
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O
Cl
5e
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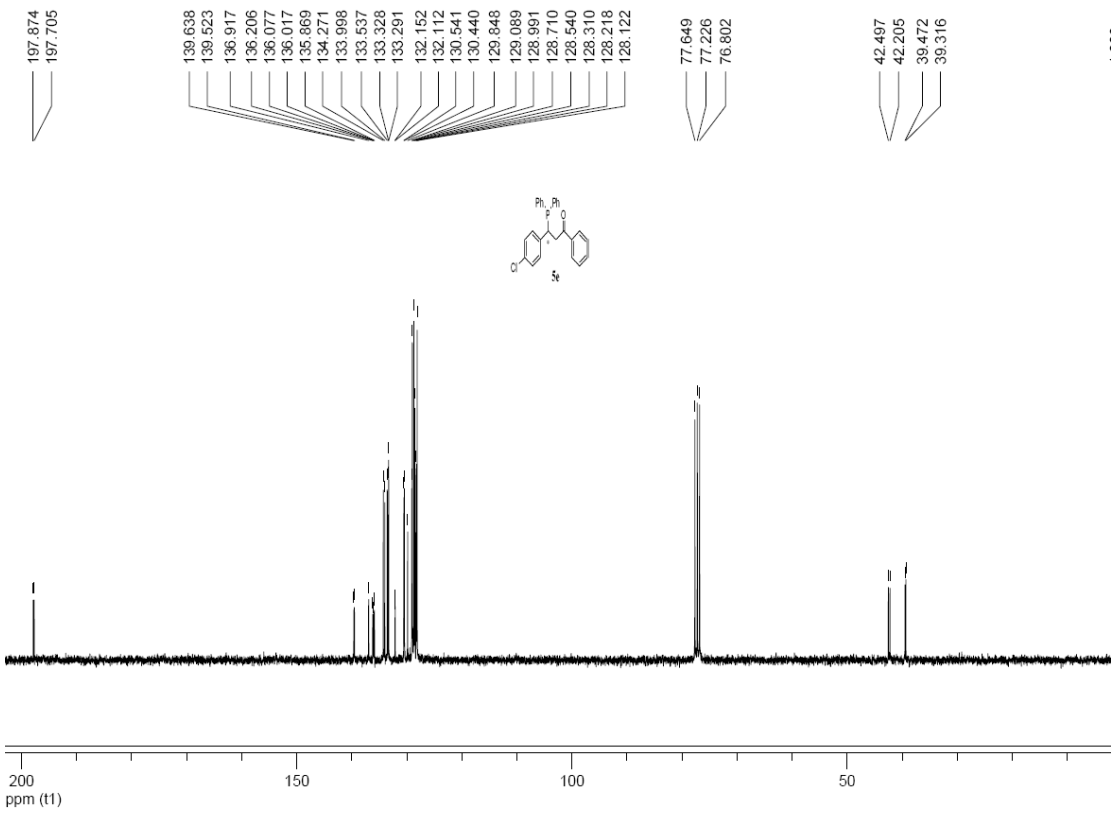
ppm (t1)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130.440
129.848
129.089
128.991
128.710
128.540
128.310
128.218
128.122
77.649
77.226
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Ph
P
O
Cl
5e
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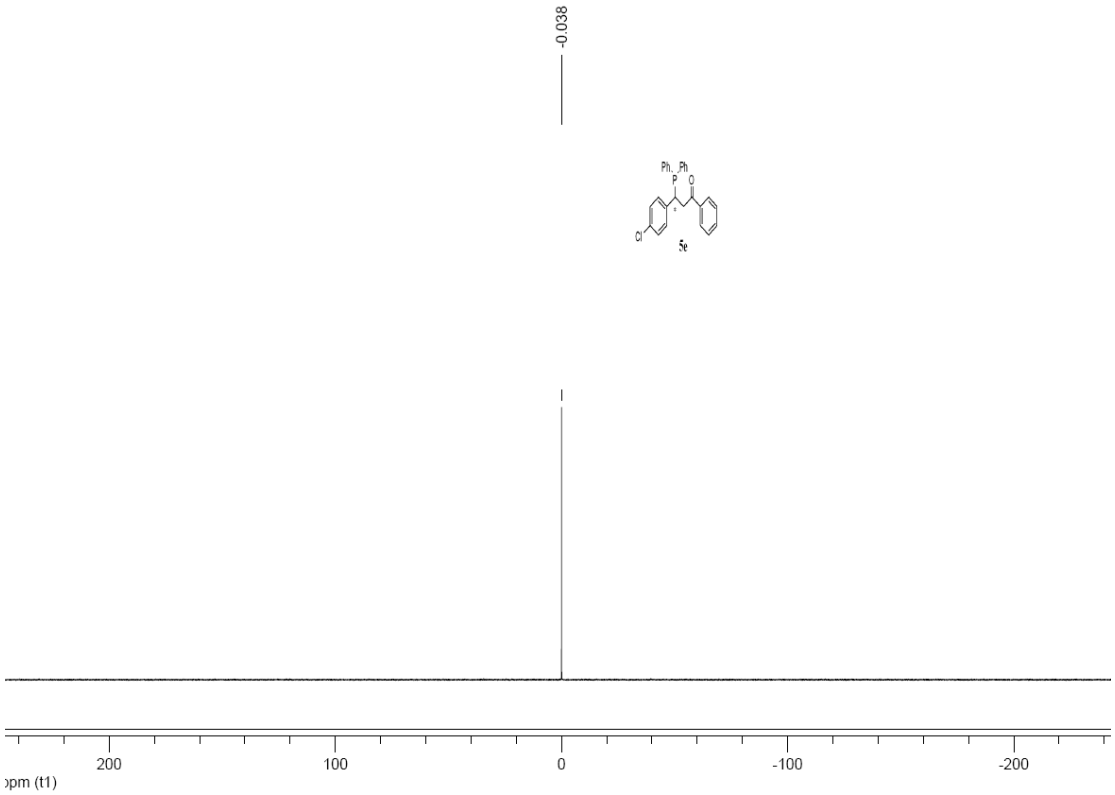
100
50
ppm (t1)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Ph
P
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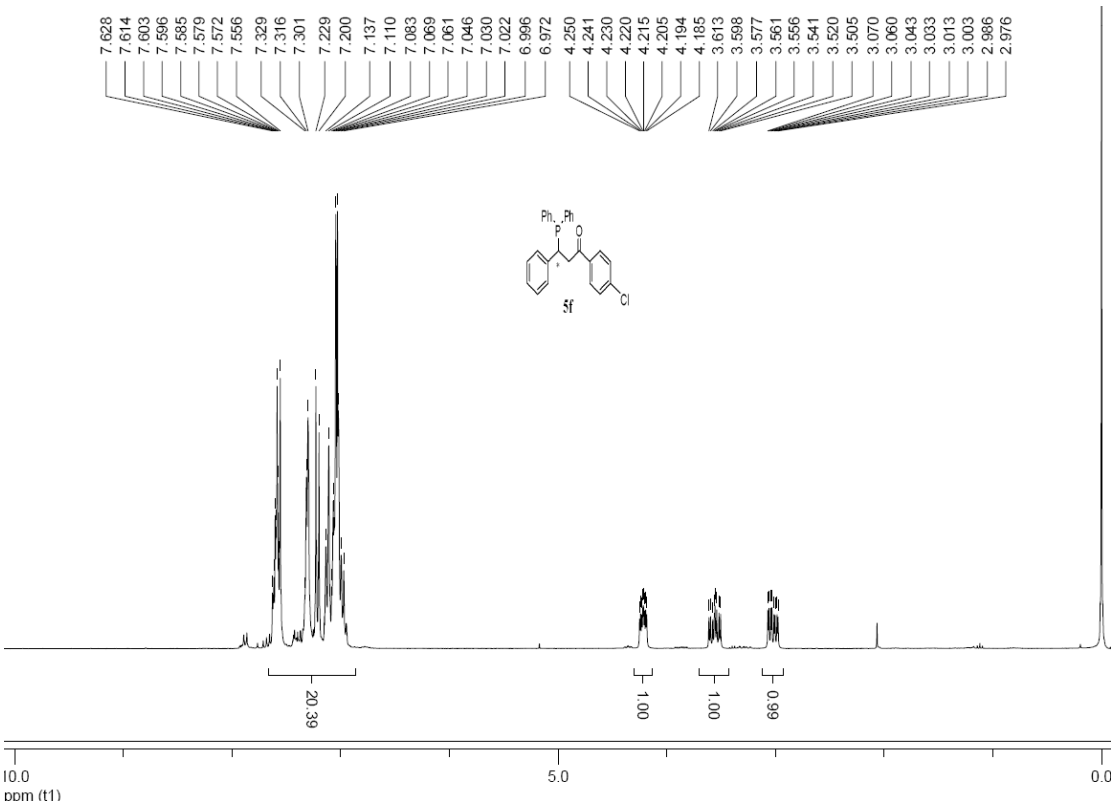
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7.556
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7.301
7.229
7.200
7.137
7.110
7.083
7.069
7.061
7.046
7.030
7.022
6.996
6.972
4.250
4.241
4.230
4.220
4.215
4.205
4.194
4.185
3.613
3.598
3.577
3.561
3.556
3.541
3.520
3.505
3.070
3.060
3.043
3.033
3.013
3.003
2.986
2.976
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Ph
P
O
Cl
5f
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1.00
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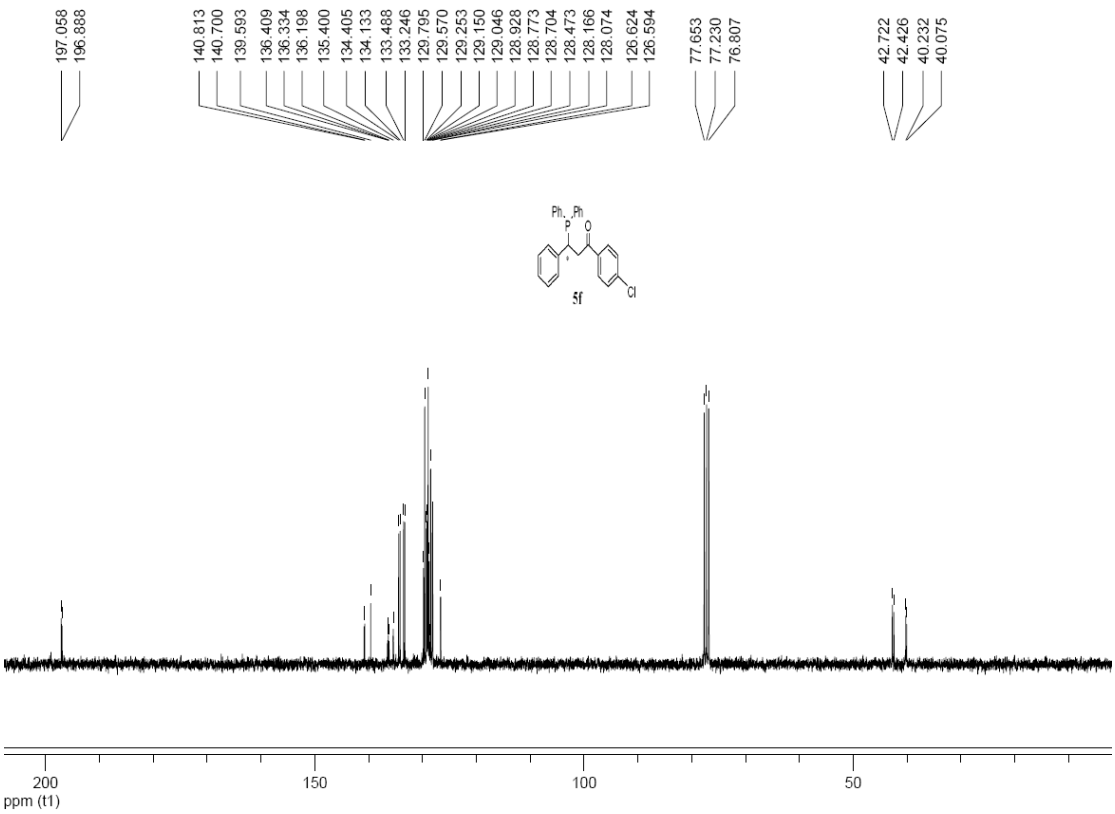
0.0
ppm (t1)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140.813
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129.570
129.253
129.150
129.046
128.928
128.773
128.704
128.473
128.166
128.074
126.624
126.594
77.653
77.230
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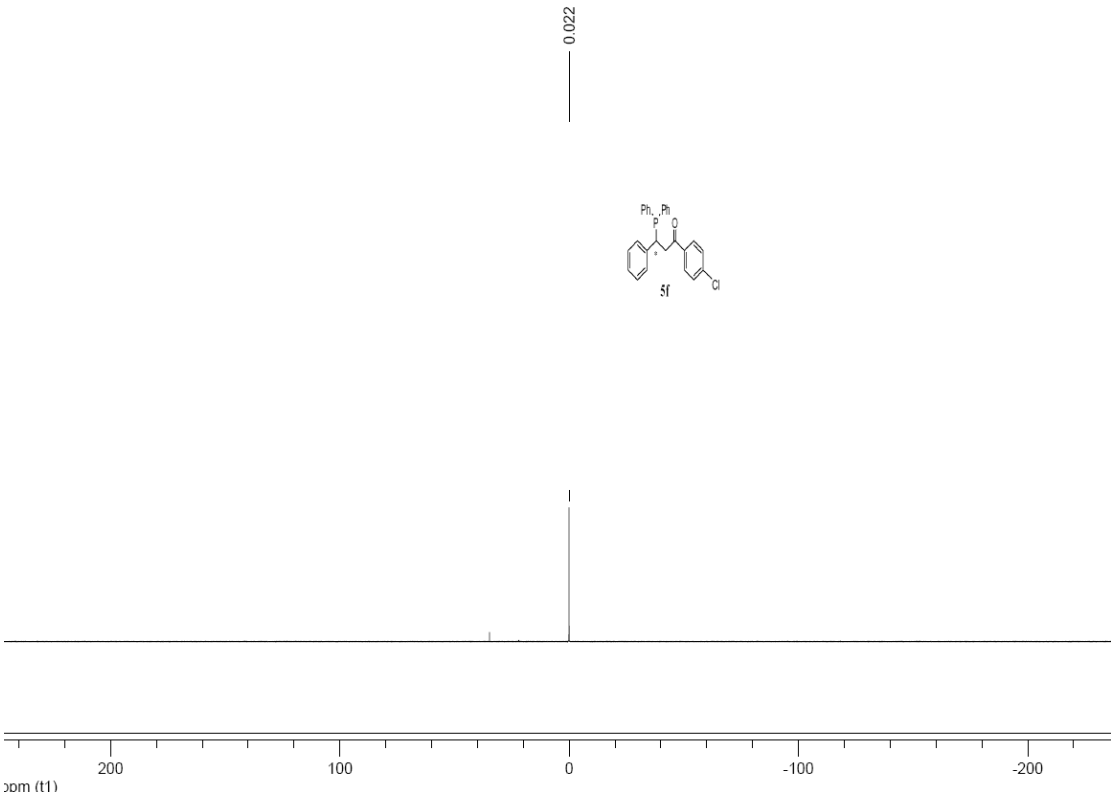
O
Cl
5f
200
150
100
50
ppm (t1)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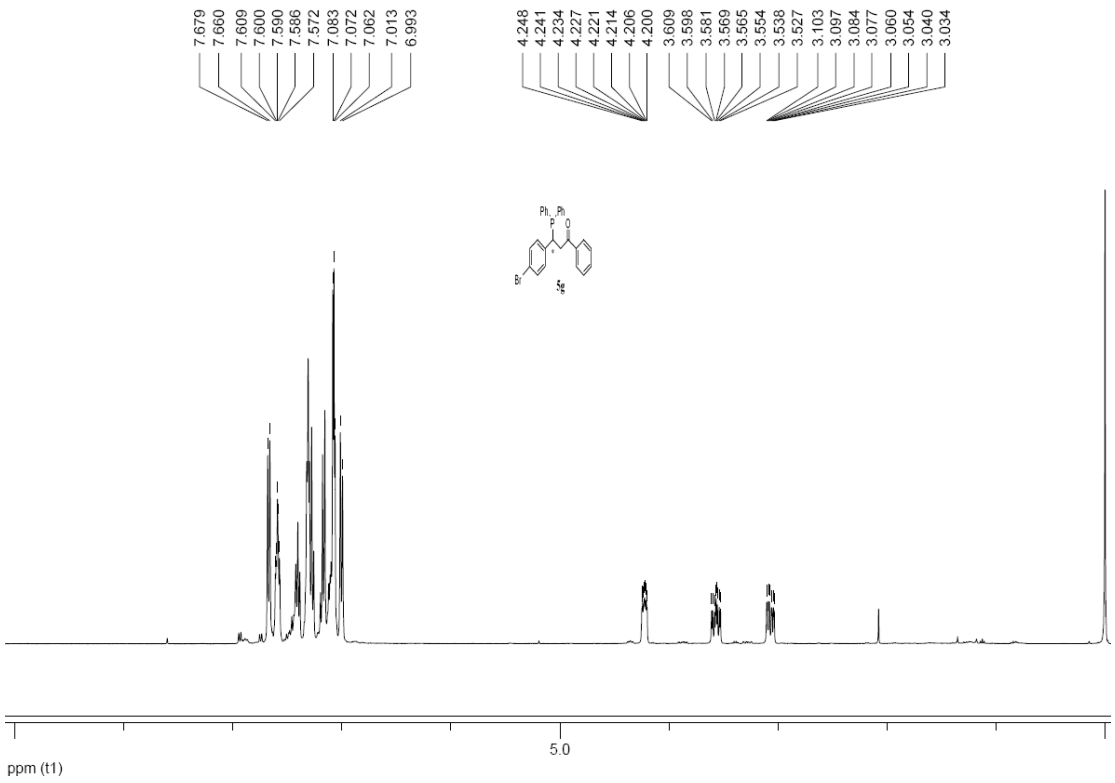
P
O
Cl
5f
200
100
0
-100
-200
ppm (t1)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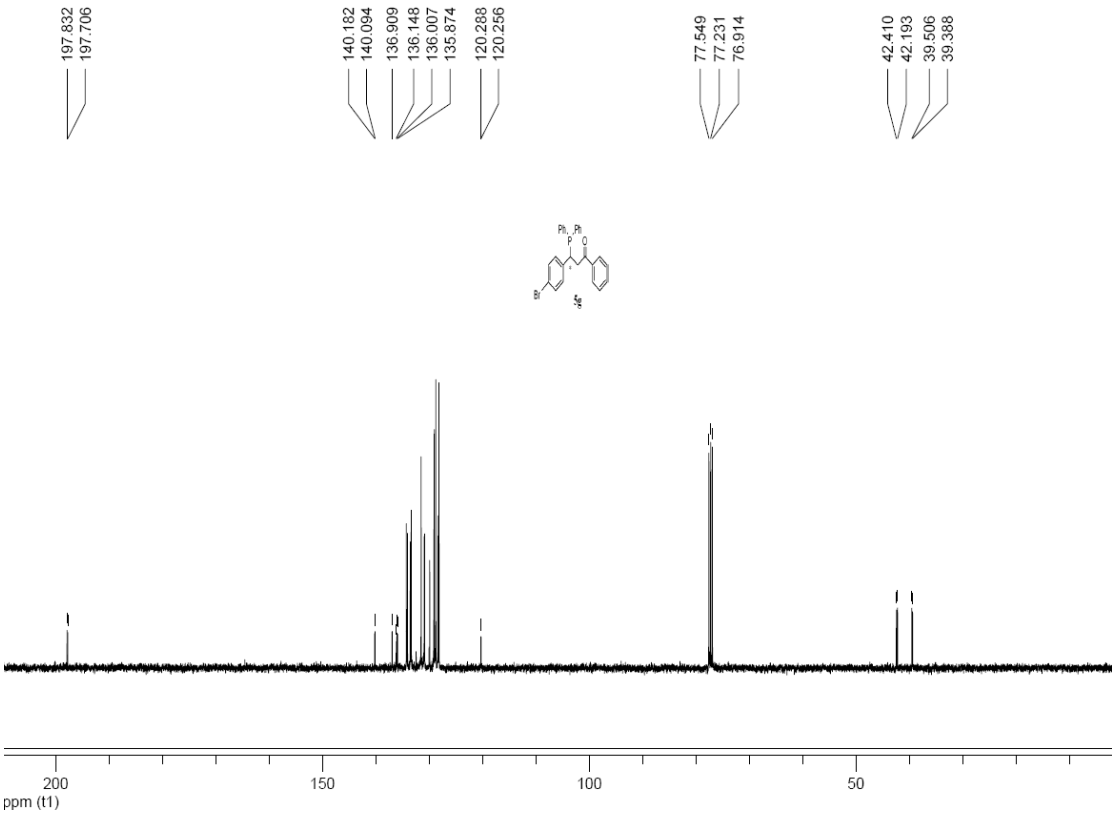
7.609
7.600
7.590
7.586
7.572
7.083
7.072
7.062
7.013
6.993
4.248
4.241
4.234
4.227
4.221
4.214
4.206
4.200
3.609
3.598
3.581
3.569
3.565
3.554
3.538
3.527
3.103
3.097
3.084
3.077
3.060
3.054
3.040
3.034
Ph
Ph
P
O
Br
5g
5.0
ppm (t1)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140.182
140.094
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136.007
135.874
120.288
120.256
77.549
77.231
76.914
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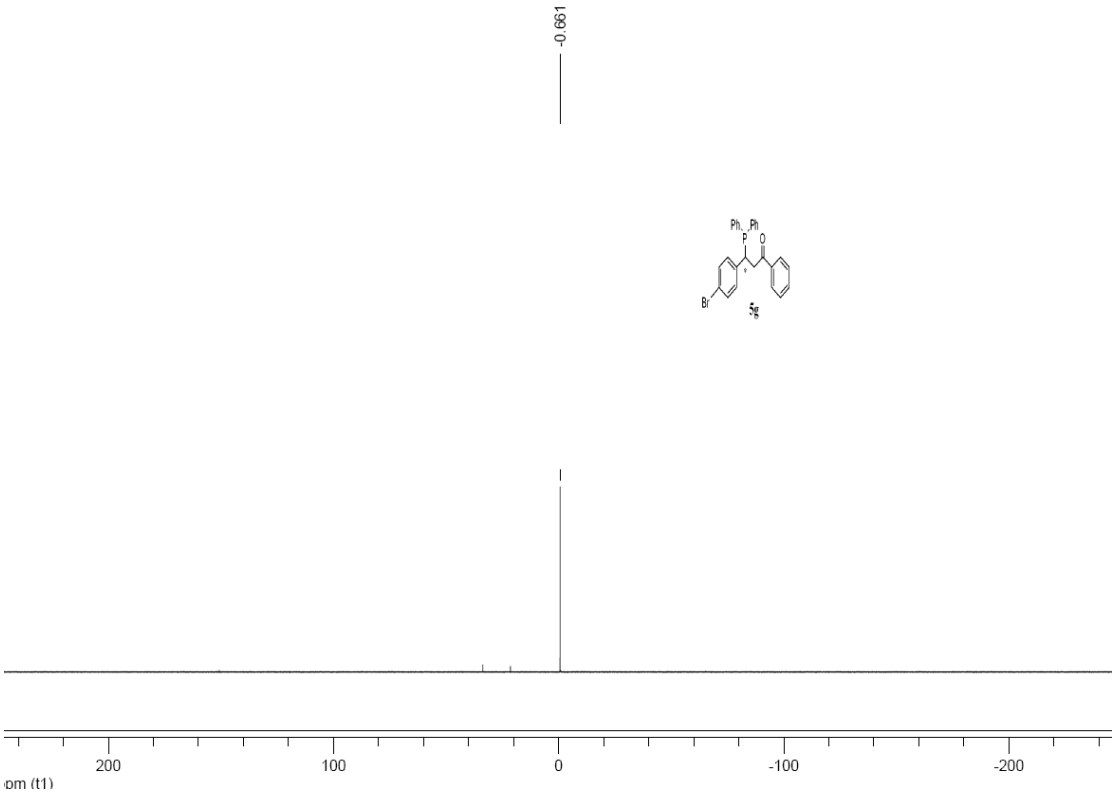
42.193
39.506
39.388
Ph
Ph
P
O
Br
5g
200
150
100
50
ppm (t1)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P
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Br
5g
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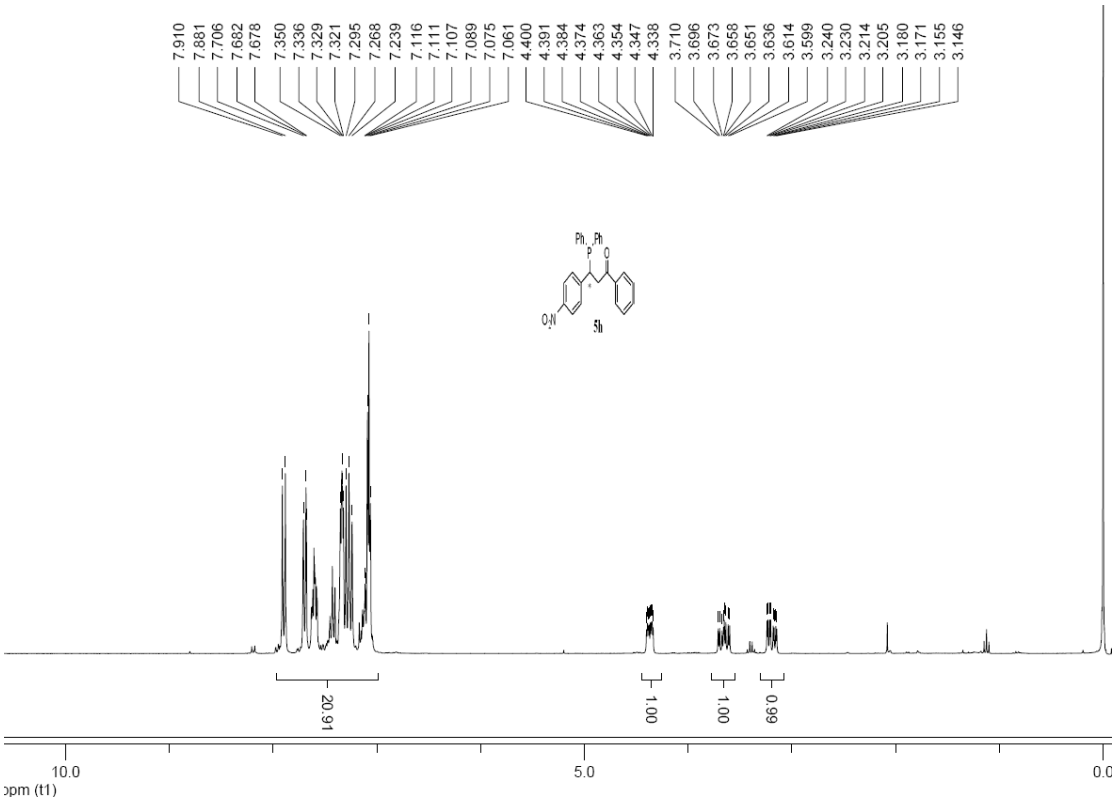
0
-100
-200
ppm (t1)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7.336
7.329
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7.239
7.116
7.111
7.107
7.089
7.075
7.061
4.400
4.391
4.384
4.374
4.363
4.354
4.347
4.338
3.710
3.696
3.673
3.658
3.651
3.636
3.614
3.599
3.240
3.230
3.214
3.205
3.180
3.171
3.155
3.146
Ph
Ph
P
O
O2N
5h
20.91
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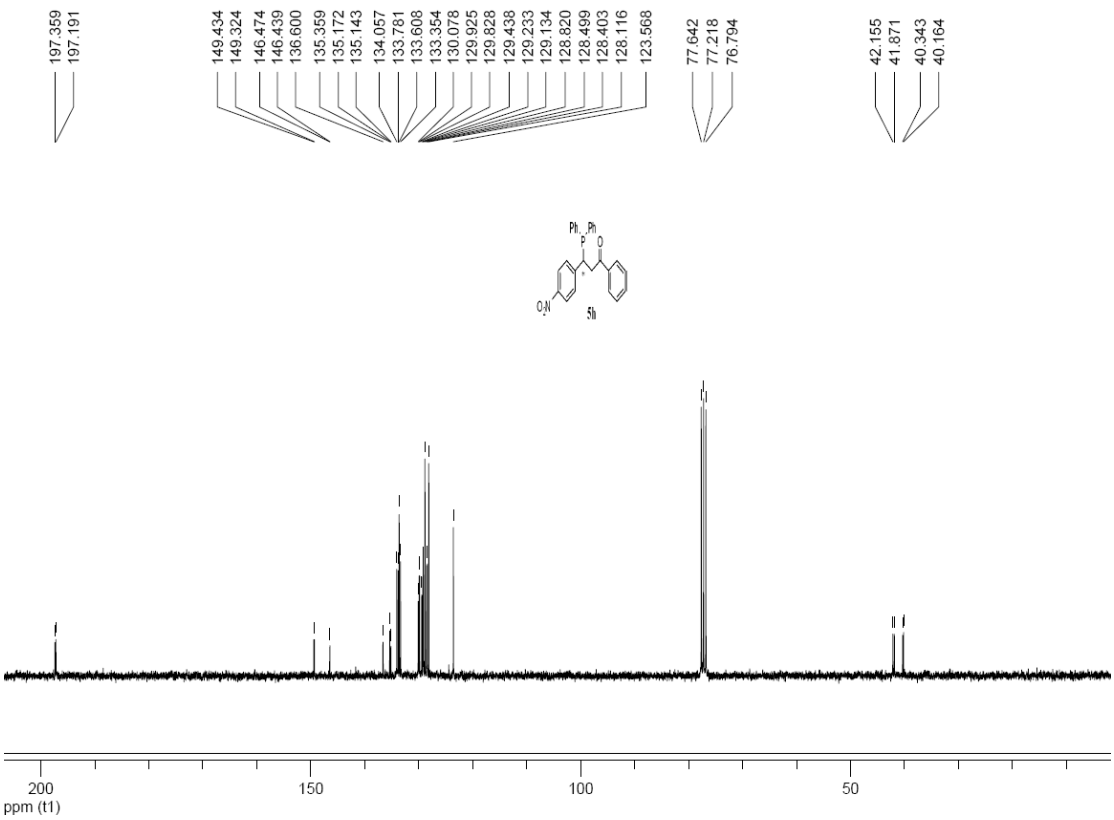
1.00
0.99
10.0
5.0
0.0
ppm (t1)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146.439
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135.359
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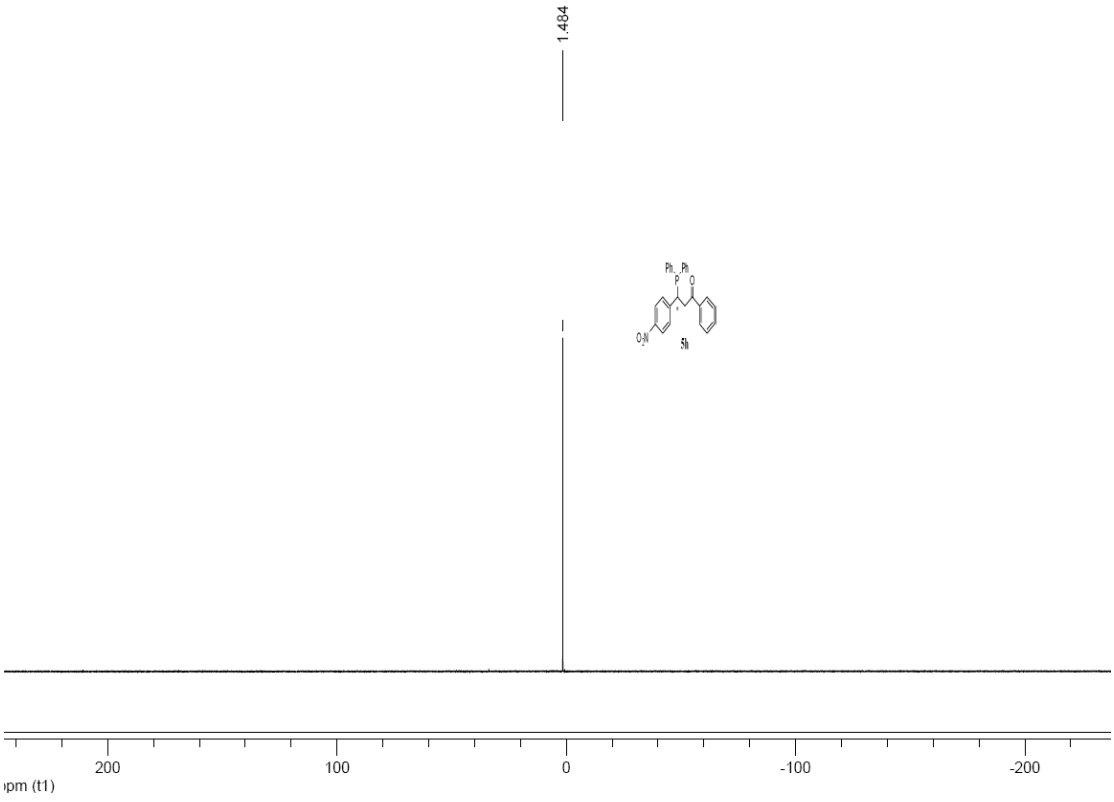
135.143
134.057
133.781
133.608
133.354
130.078
129.925
129.828
129.438
129.233
129.134
128.820
128.499
128.403
128.116
123.568
77.642
77.218
76.794
42.155
41.871
40.343
40.164
Ph
Ph
P
O
O2N
5h
200
150
100
50
ppm (t1)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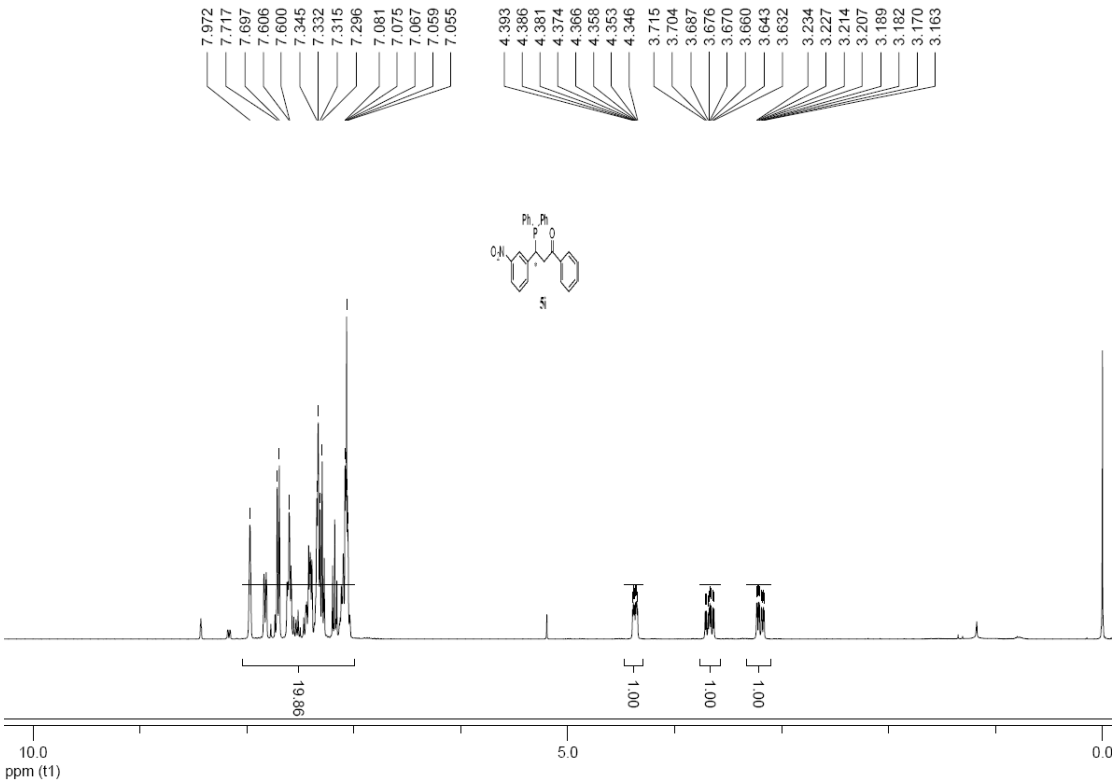
Ph
Ph
P
O
O2N
5h
200
100
0
-100
-200
ppm (t1)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7.081
7.075
7.067
7.059
7.055
4.393
4.386
4.381
4.374
4.366
4.358
4.353
4.346
3.715
3.704
3.687
3.676
3.670
3.660
3.643
3.632
3.234
3.227
3.214
3.207
3.189
3.182
3.170
3.163
Ph
Ph
P
O
O2N
5i
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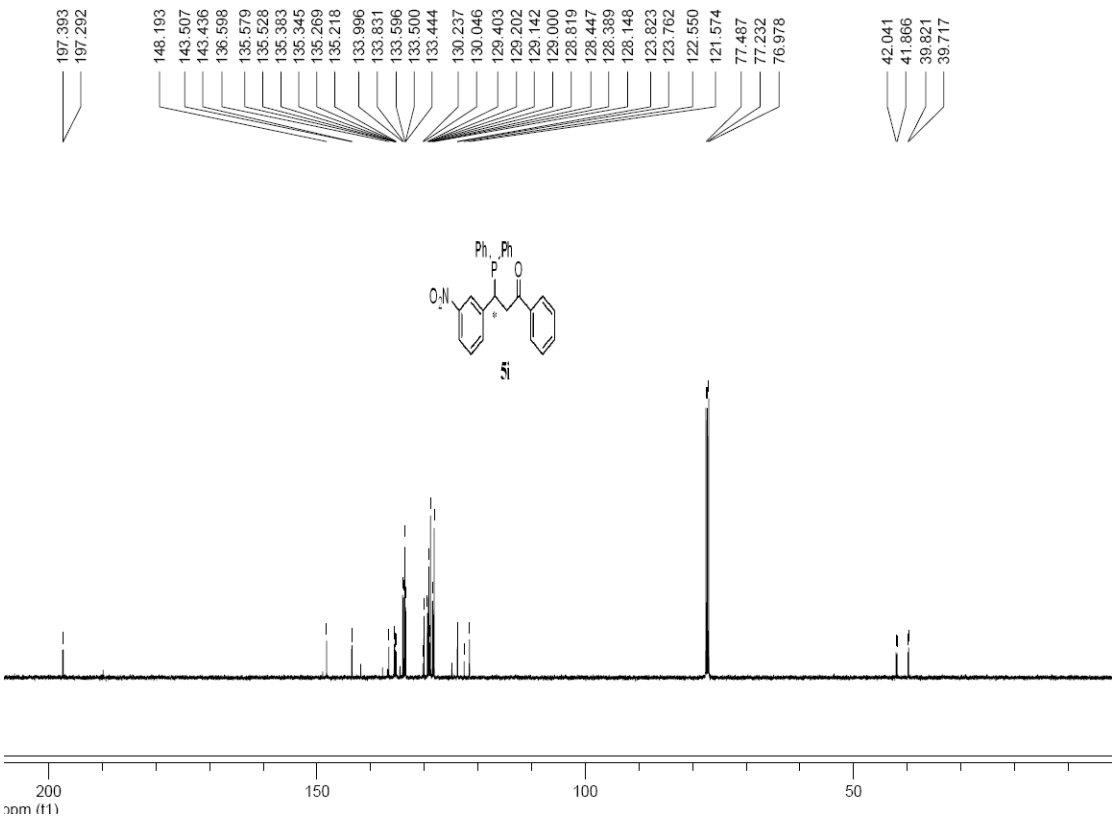
ppm (t1)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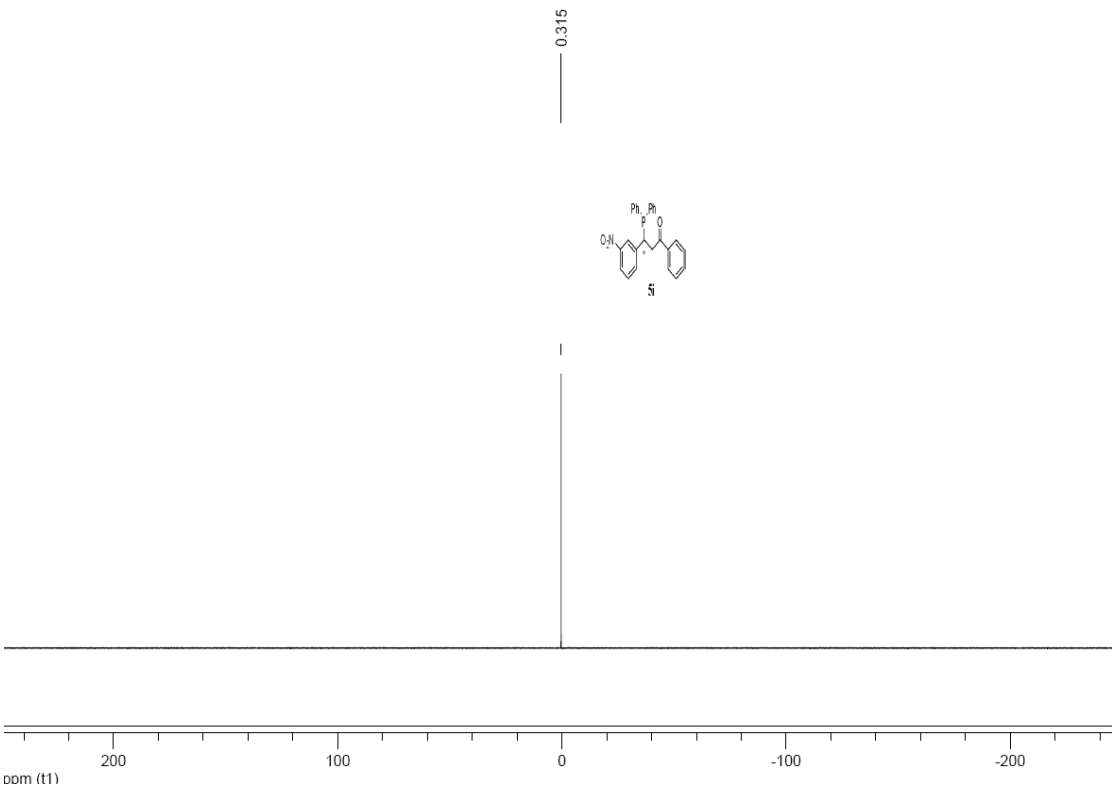
133.831
133.596
133.500
133.444
130.237
130.046
129.403
129.202
129.142
129.000
128.819
128.447
128.389
128.148
123.823
123.762
122.550
121.574
77.487
77.232
76.978
42.041
41.866
39.821
39.717
Ph
Ph
P
O
O2N
5i
200
150
100
50
ppm (t1)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P
O
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5i
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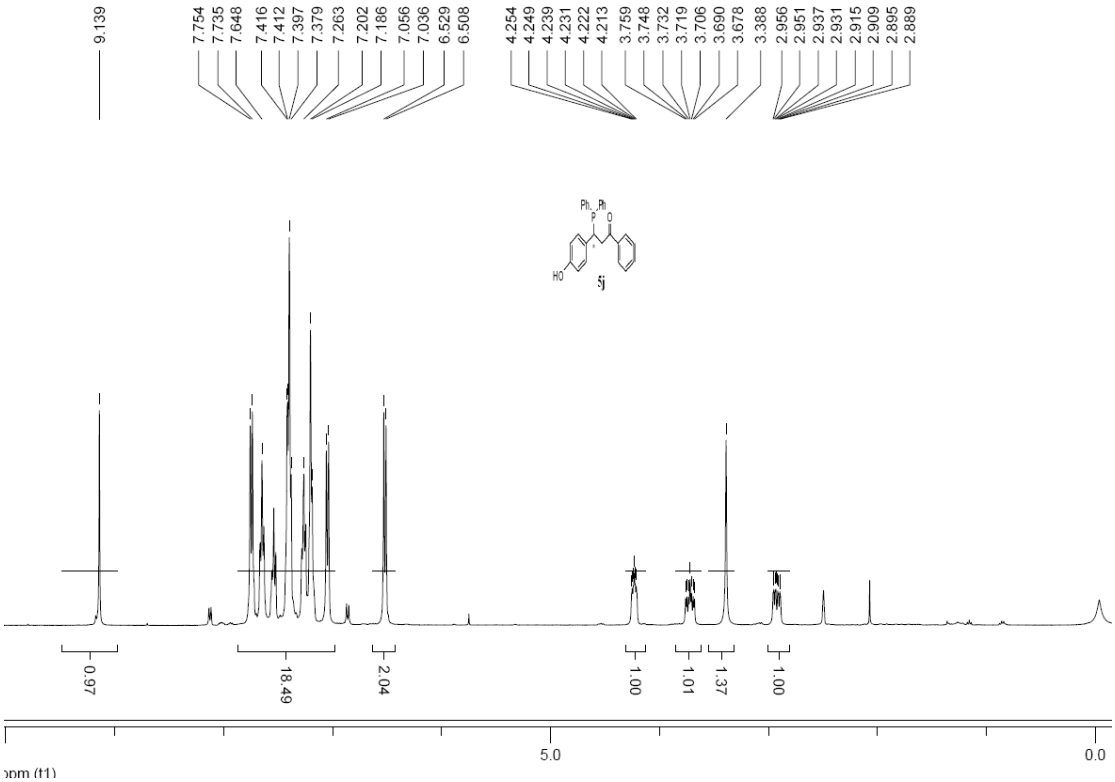
0
-100
-200
ppm (t1)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7.202
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7.036
6.529
6.508
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4.249
4.239
4.231
4.222
4.213
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3.748
3.732
3.719
3.706
3.690
3.678
3.388
2.956
2.951
2.937
2.931
2.915
2.909
2.895
2.889
Ph Ph
P
O
HO
5j
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1.01
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1.00
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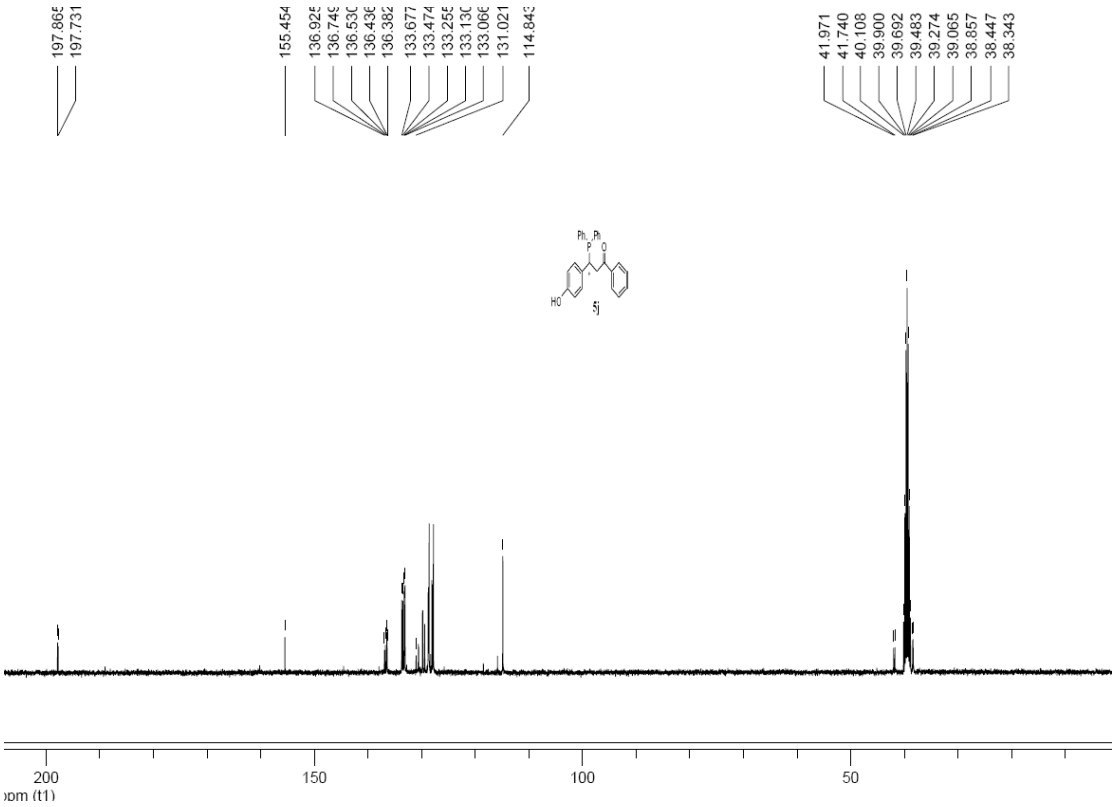
ppm (t1)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133.474
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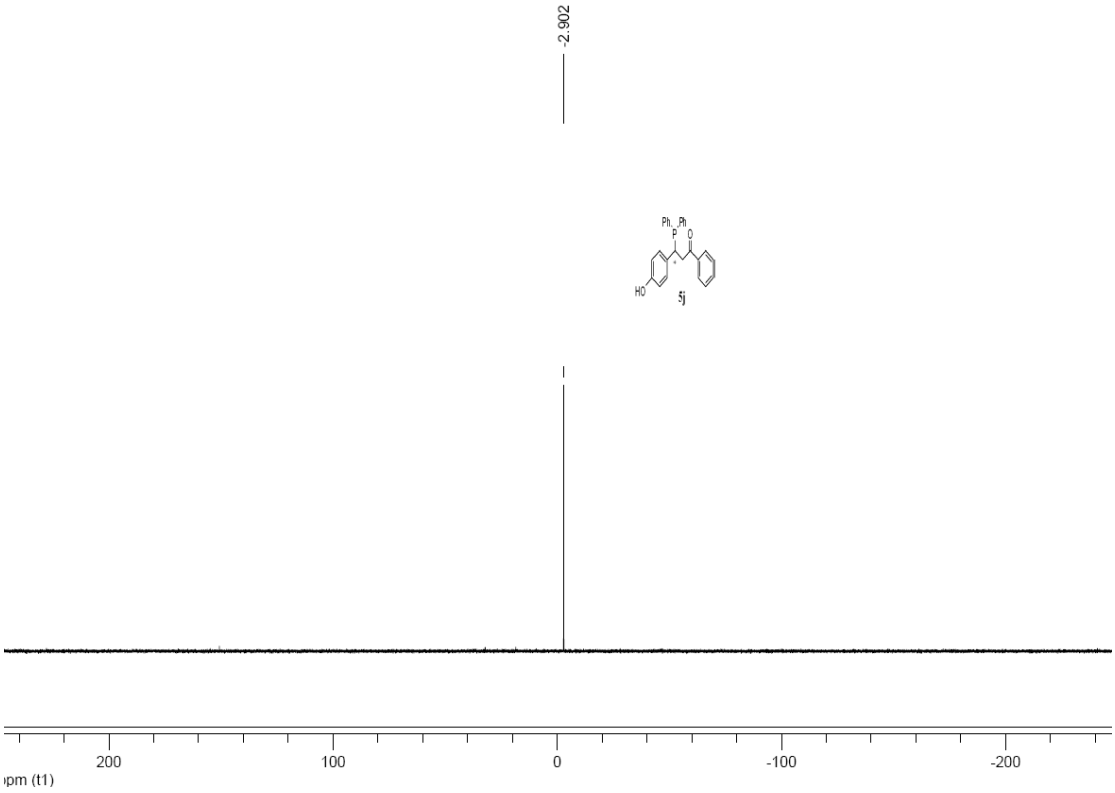
131.021
114.842
41.971
41.740
40.108
39.900
39.692
39.483
39.274
39.065
38.857
38.447
38.343
Ph Ph
P
O
HO
5j
200
150
100
50
ppm (t1)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P
O
HO
5j
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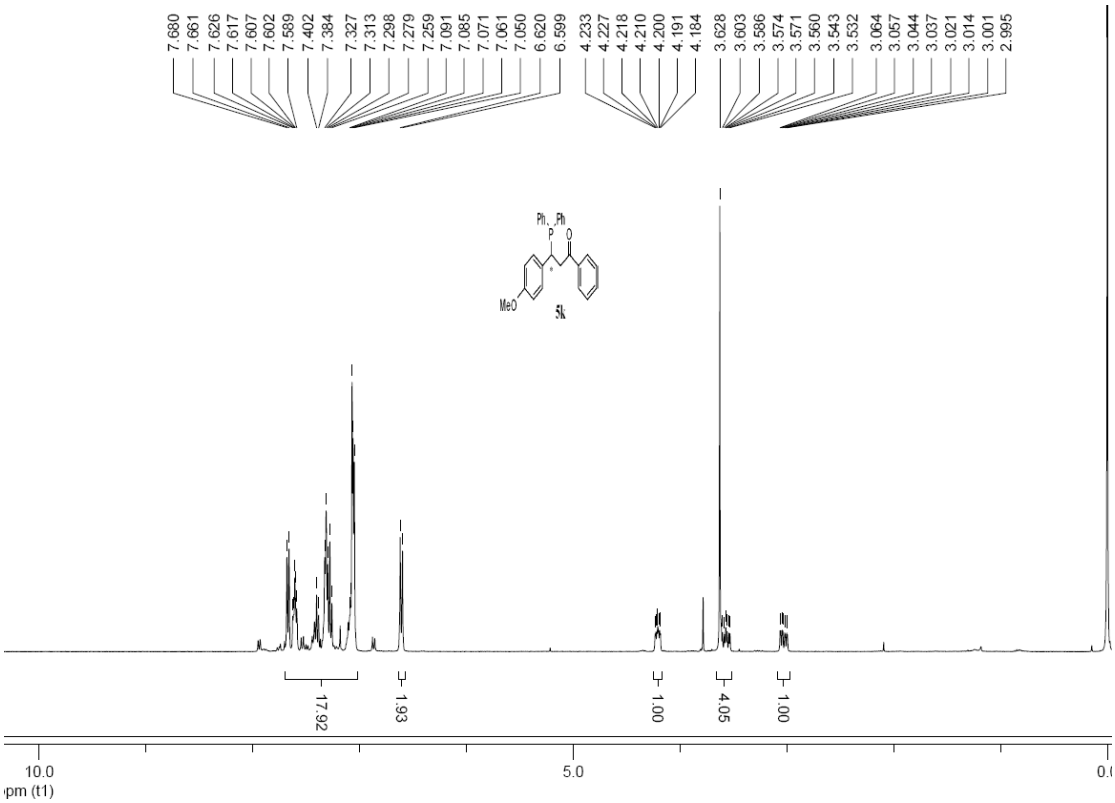
0
-100
-200
ppm (t1)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7.327
7.313
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7.279
7.259
7.091
7.085
7.071
7.061
7.050
6.620
6.599
4.233
4.227
4.218
4.210
4.200
4.191
4.184
3.628
3.603
3.586
3.574
3.571
3.560
3.543
3.532
3.064
3.057
3.044
3.037
3.021
3.014
3.001
2.995
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P
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1.00
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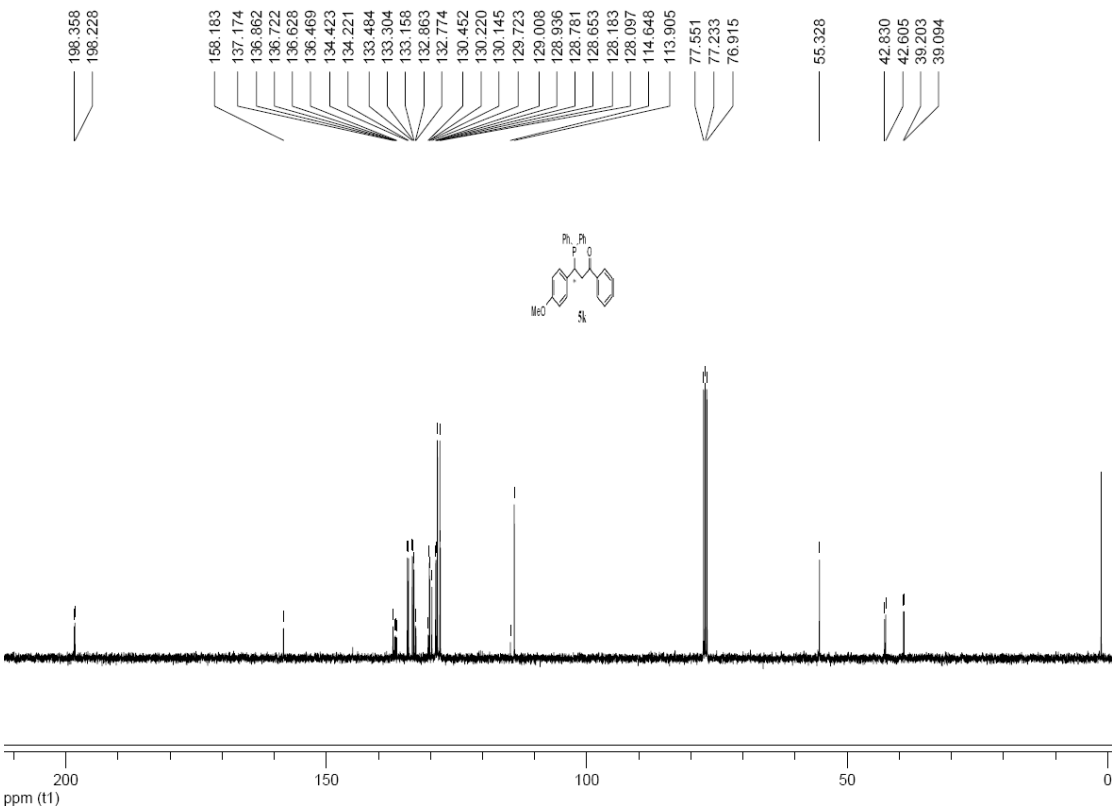
ppm (t1)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136.469
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134.221
133.484
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133.158
132.863
132.774
130.452
130.220
130.145
129.723
129.008
128.936
128.781
128.653
128.183
128.097
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77.233
76.915
55.328
42.830
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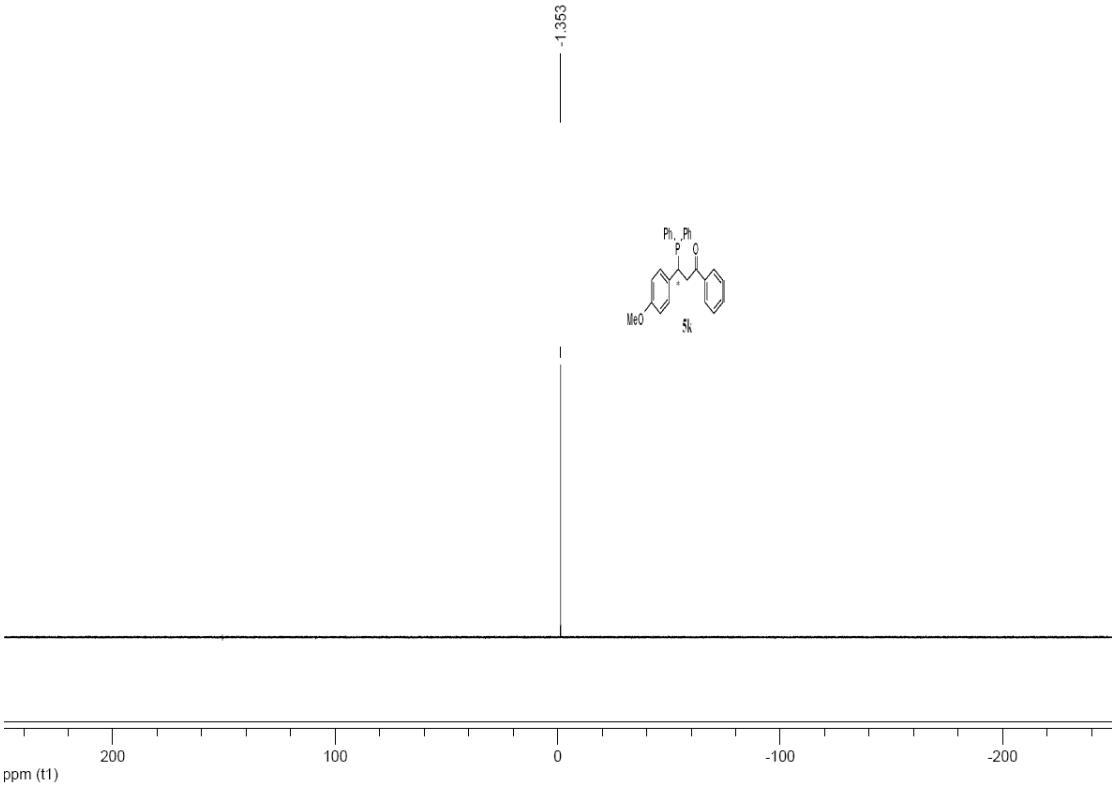
39.203
39.094
Ph Ph
P
O
MeO
5k
200
150
100
50
0
ppm (t1)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Ph
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O
MeO
200
100
0
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ppm (t1)

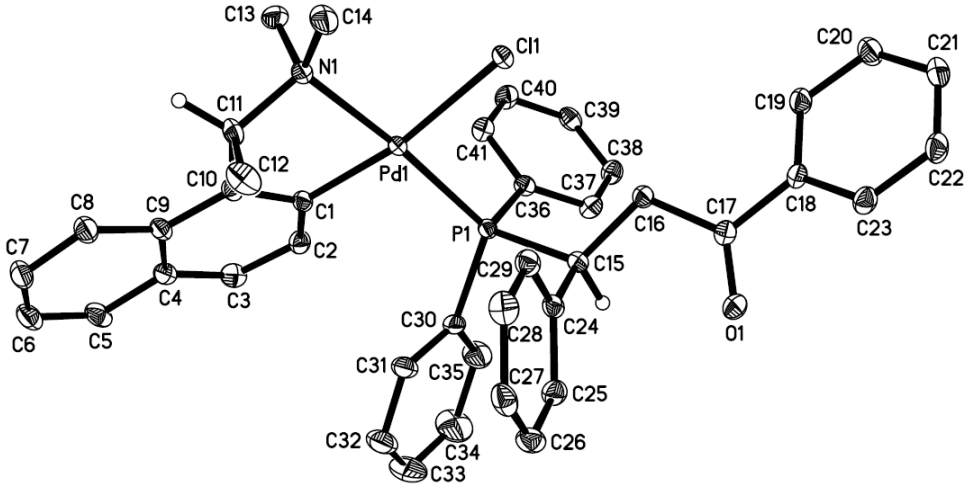

Fig. 1 Molecular structure and absolute stereochemistry of complex 7a with 50% probability thermal ellipsoids shown

Table 1. Crystal data and structure refinement for leung466s.

Identification code	leung466s	
Empirical formula	C47 H45 Cl N O P Pd	
Formula weight	812.66	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 11.9358(3) Å	α= 90°.
	b = 10.0903(3) Å	β= 105.1340(10)°.
	c = 17.0594(4) Å	γ = 90°.
Volume	1983.31(9) $Å^3$	
Z	2	
Density (calculated)	1.361 Mg/m^3	
Absorption coefficient	0.612 mm^{-1}	
F(000)	840	
Crystal size	0.40 x 0.08 x 0.02 mm^3	
Theta range for data collection	1.77 to 33.07°.	
Index ranges	-17<=h<=17, -8<=k<=15, -25<=l<=25	
Reflections collected	34075	

Independent reflections	12613 [R(int) = 0.0393]
Completeness to theta = 33.07°	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9879 and 0.7919
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	12613 / 1 / 472
Goodness-of-fit on F^2	1.083
Final R indices [I>2sigma(I)]	R1 = 0.0331, wR2 = 0.0722
R indices (all data)	R1 = 0.0446, wR2 = 0.0882
Absolute structure parameter	-0.023(16)
Largest diff. peak and hole	0.796 and -1.073 e.$Å^{-3}$

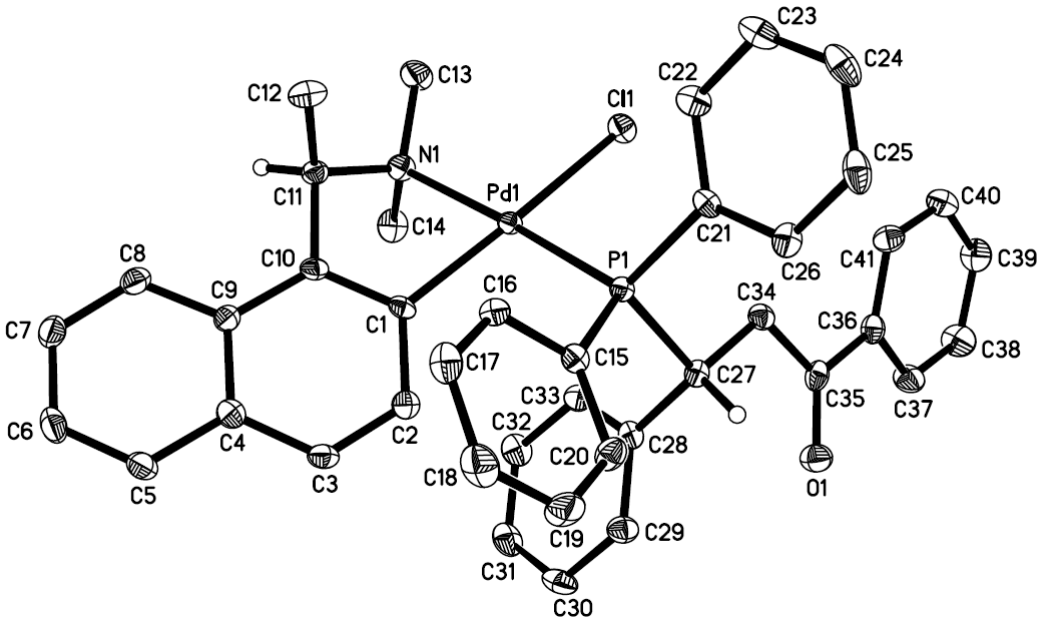

Fig. 2 Molecular structure and absolute stereochemistry of complex 8a with 50% probability thermal ellipsoids shown

Table 1. Crystal data and structure refinement for leung478s.

Identification code	leung478s	
Empirical formula	C41 H39 Cl N O P Pd	
Formula weight	734.55	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 15.6428(8) Å	α= 90°.
	b = 17.0104(11) Å	β= 90°.
	c = 25.5760(16) Å	γ = 90°.
Volume	6805.5(7) Å^3	
Z	8	
Density (calculated)	1.434 Mg/m^3	
Absorption coefficient	0.705 mm^{-1}	
F(000)	3024	
Crystal size	0.34 x 0.14 x 0.02 mm^3	
Theta range for data collection	1.59 to 31.05°.	

Index ranges	-18<=h<=22, -22<=k<=24, -37<=l<=33
Reflections collected	63762
Independent reflections	21013 [R(int) = 0.0455]
Completeness to theta = 31.05°	98.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9860 and 0.7956
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	21013 / 0 / 835
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0362, wR2 = 0.0781
R indices (all data)	R1 = 0.0522, wR2 = 0.0962
Absolute structure parameter	-0.008(14)
Largest diff. peak and hole	1.839 and -0.844 e.$Å^{-3}$