Mechanochemistry Enabled Highly Efficient Solvent-Free Deoxygenation of Phosphine Oxides in Air

Koji Kubota,*^[a,b] Reon Hisazumi,^[a] Tamae Seo^[a] and Hajime Ito*^[a,b]

^aDivision of Applied Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo, Hokkaido, 060-8628, Japan. ^bInstitute for Chemical Reaction Design and Discovery (WPI-ICRD), Hokkaido University, Sapporo, Hokkaido 001-0021, Japan. e-mail: hajito@eng.hokudai.ac.jp, kbt@eng.hokudai.ac.jp

Table of Contents

- 1. Chemicals and Instrumentation
- 2. General Procedure for Deoxygenation of Phosphine Oxide in Air
- 3. General Procedure for Catalytic Wittig Reaction Using Mechanochemistry
- 4. Optimization Study on Mechanochemical Catalytic Wittig Reaction
- 5. Characterization of Obtained Products
- 6. References
- 7. NMR Spectra

1. Chemicals and Instrumentation

The starting materials were obtained from commercial suppliers and used as received. Solvents were purchased from commercial suppliers, and further dried over molecular sieve (MS 4Å). All mechanochemical reactions were carried out using grinding vessels in a Retsch MM400 mill (Figure S1). Both jars (5 mL) and balls (10 mm) are made of stainless (Figure S2). The heat gun with temperature control function HG-1450B was used (Figure S3). NMR spectra were recorded on JEOL JNM-ECX400P and JNM-ECS400 spectrometers (¹H: 392 MHz, ¹³C: 99 MHz, ³¹P: 159 MHz). CD₂Cl₂ (¹H, ¹³C, ³¹P) and CDCl₃ (¹H, ¹³C) was employed as external standards, respectively. Multiplicity was recorded as follows: s = singlet, brs = broad singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sept = septet, o = octet, m = multiplet. 1,1,2,2-Tetrachloroethane was used as an internal standard to determine NMR yields. Recycle preparative gel permeation chromatography (GPC) was conducted with a JAI LC-9101 using CHCl₃ as an eluent with JAIGEL-1H. The internal temperature of the jar after ball milling was confirmed by thermography was recorded with an NEC Avio Thermo GEAR G120. High-resolution mass spectra were recorded at the Global Facility Center, Hokkaido University.



Figure S1. Retsch MM400 used in this study.



Figure S2. Stainless jar and ball used in this study.



Figure S3. The temperature controllable heat-gun used in this study.

2. General Procedure for Deoxygenation of Phosphine Oxide in Air



Phosphine Oxide 1 (0.3 mmol), PhSiH₃ (2a) (0.75 mmol, 2.5 equiv) and 3c (0.03 mmol, 10 mol %) were placed in a ball milling vessel (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 10 mm). After the vessel was closed in air without purging with inert gas, the vessel was placed in the ball mill (Retch MM400, 30 min at 20 Hz) and heat gun (pre-set temperature at 250 °C). After 30 min, the mixture was filtrated with CH₂Cl₂. The crude mixture was then purified by flash column chromatography (SiO₂, CH₂Cl₂/hexane, typically 0:100 \rightarrow 10:90) to give the corresponding reduced product **4**.

Caution: Phenylsilane (2a) is potentially hazardous as the flash point of 2a is 7 °C. Although we did not experience any accidents during this study, but pay attention to its handling.

Reactions at higher frequencies



The reactions at higher frequencies also gave the desired product in excellent yield (99%).

Procedure for scaled-up reaction



Phosphine oxide **1a** (556.5 mg, 2.0 mmol), PhSiH₃ (**2a**) (615 μ L, 5.0 mmol, 2.5 equiv) and **3c** (69.1 mg, 0.20 mmol, 10 mol %) were placed in a ball milling vessel (stainless, 10 mL) loaded with one grinding ball (stainless, diameter: 10 mm). After the vessel was closed in air without purging with inert gas, the vessel was placed in the ball mill (Retch MM400, 30 min at 20 Hz) and a heat gun (pre-

set temperature at 250 °C). After 30 min, the mixture was filtrated with CH_2Cl_2 . The crude mixture was then purified by flash column chromatography (SiO₂, CH_2Cl_2 /hexane, 0:100 \rightarrow 10:90) to give the corresponding reduced product **4a** (99%).

3. General Procedure for Catalytic Wittig Reaction Using Mechanochemistry



Ethyl 2-bromoacetate (**5**) (0.3 mmol), aldehyde (0.39 mmol, 1.3 equiv), phosphine oxide **1m** (0.06 mmol, 20 mol%), PhSiH₃ (**2a**) (0.3 mmol, 1.0 equiv), ${}^{i}Pr_{2}EtN$ (0.45 mmol, 1.5 equiv) and **3c** (0.03 mmol, 10 mol%) were placed in a ball milling vessel (stainless, 5 mL) loaded with one grinding ball (stainless, diameter: 10 mm). After the vessel was closed in air without purging with inert gas, the vessel was placed in the ball mill (Retch MM400, 60 min at 20 Hz) and heat gun (pre-set temperature at 250 °C). After 60 min, the mixture was filtration with CH₂Cl₂. The crude mixture was then purified by flash column chromatography (SiO₂, typically CH₂Cl₂/hexane, typically 0-10:90) to give the corresponding reduced product **7**.

4. Optimization Study on Mechanochemical Catalytic Wittig Reaction



Mechanochemical deoxygenation of 1m



We have investigated the reaction of **1m** under the optimized conditions, providing the desired reduction product **4m** in moderate yield (50%). Although the mechanochemical reduction of **1m** was less efficient compared to the reaction of **1a**, the catalytic reaction using **1m** was much better than using **1a**. These conflicting results emphasize the need for further mechanistic studies to guide for improving reaction efficiency in mechanochemical conditions.

5. Characterization of Obtained Products.

Triphenylphosphine (4a).



The reaction was carried out with 83.4 mg (0.3 mmol) of **1a**. The product **4a** was obtained as a white powder (74.8 mg, 0.285 mmol, 95% yield) after pulification by silica-gel column chromatography (SiO₂, CH₂Cl₂/hexane, 0:100 \rightarrow 10:90). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.¹ ¹H NMR (392 MHz, CD₂Cl₂, δ): 7.26–7.38 (m, 15H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 128.9 (d, *J* = 7.5 Hz, CH), 129.1 (CH₃), 134.1 (d, *J* = 19.7 Hz, CH), 137.7 (d, *J* = 11.3 Hz, C). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -5.5. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₁₈H₁₅P, 262.0911; found, 262.0914.

Tri-*p*-tolylphosphine (4b).



The reaction was carried out with 96.1 mg (0.3 mmol) of **1b**. The product **4b** was obtained as a white powder (70.6 mg, 0.232 mmol, 77% yield) after pulification by silica-gel column chromatography (SiO₂, CH₂Cl₂/hexane, 0:100 \rightarrow 10:90). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.² ¹H NMR (392 MHz, CD₂Cl₂, δ): 2.34 (s, 9H), 7.12–7.21 (m, 12H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 21.4 (*C*H₃), 129.6 (d, *J* = 7.6 Hz, *C*H), 133.9 (d, *J* = 19.7 Hz, *C*H), 134.7 (d, *J* = 10.3Hz, *C*), 139.1 (*C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -8.0. HRMS-ESI (*m*/*z*): [M+H]⁺ calcd for C₂₁H₂₂P, 305.1454; found, 305.1447.

Tris(4-methoxyphenyl)phosphine (4c).



The reaction was carried out with 110.5 mg (0.3 mmol) of **1c**. The product **4c** was obtained as a white powder (79.7 mg, 0.226 mmol, 75% yield) after pulification by flash column chromatography with

CH₂Cl₂/hexane (0:100 \rightarrow 10:90 \rightarrow 20:80 \rightarrow 40:60). ¹H and ¹³C NMR were in agreement with the literature.¹

¹H NMR (392 MHz, CD₂Cl₂, δ): 3.79 (s, 9H), 6.84–6.91 (m, 6H), 7.17–7.25 (m, 6H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 55.5 (*C*H₃), 114.4 (d, *J* = 7.5 Hz, *C*H), 129.5 (d, *J* = 8.5 Hz, *C*), 135.3 (d, *J* = 20.7 Hz, *C*H), 160.6 (*C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): –10.3. HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₂₁H₂₂O₃P, 353.1301; found, 353.1298.

Methyl 4-(diphenylphosphaneyl)benzoate (4d).



4d

The reaction was carried out with 96.6 mg (0.30 mmol) of **1d**. The product **4d** was obtained as a brown oil (91.0 mg, 0.297 mmol, 99% yield) after pulification by flash column chromatography with EtOAc/Hexane (0:100 \rightarrow 3:97). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.² ¹H NMR (392 MHz, CD₂Cl₂, δ): 3.88 (s, 3H), 7.29–7.41 (m, 12H), 7.95 (dd, *J* = 1.4, 8.0 Hz, 2H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 52.4 (*C*H₃), 129.1 (d, *J* = 7.5 Hz, *C*H), 129.6 (d, *J* = 4.7 Hz, *C*H), 130.6 (*C*), 133.5 (d, *J* = 18.7 Hz, *C*H), 134.3 (d, *J* = 19.8 Hz, *C*H), 136.7 (d, *J* = 10.3 Hz, *C*), 144.5 (d, *J* = 15.0 Hz, *C*), 167.0 (*C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -5.0. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₂₀H₁₇O₂P, 320.0966; found, 320.0959.

Tris(4-chlorophenyl)phosphine (4e).



The reaction was carried out with 114.6 mg (0.30 mmol) of **1e**. The product **4e** was obtained as a white powder (101.3 mg, 0.277 mmol, 92% yield) after pulification by flash column chromatography with CH₂Cl₂/hexane (0:100 \rightarrow 10:90). ¹H and ¹³C NMR were in agreement with the literature.³ ¹H NMR (392 MHz, CD₂Cl₂, δ): 7.18–7.25 (m, 6H), 7.31–7.38 (m, 6H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 129.3 (d, *J* = 7.5 Hz, *C*H), 135.3 (d, *J* = 20.7 Hz, *C*H), 135.5 (*C*), 135.8 (*C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -8.4. HRMS-APCI (*m*/*z*): [M+H]⁺ calcd for C₁₈H₁₃Cl₃P, 364.9815; found, 364.9816. Tris(4-fluorophenyl)phosphine (4f).



The reaction was carried out with 99.6 mg (0.30 mmol) of **1f**. The product **4f** was obtained as a white powder (80.4 mg, 0.254 mmol, 85% yield) after pulification by reprecipitation from CH₂Cl₂/Hexane (0:100 \rightarrow 10:90). ¹H and ¹³C NMR were in agreement with the literature.⁴

¹H NMR (392 MHz, CD₂Cl₂, δ): 7.02–7.11 (m, 6H), 7.22–7.32 (m, 6H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 116.2 (dd, *J* = 7.5, 20.6 Hz, *C*H), 133.1 (dd, *J* = 2.8, 11.3 Hz, *C*), 135.9 (dd, *J* = 8.0, 21.1 Hz, *C*H), 163.9 (d, *J* = 248.9 Hz, *C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): –9.0. HRMS-APCI (*m*/*z*): [M+H]⁺ calcd for C₁₈H₁₃F₃P, 317.0702; found, 317.0698.

Tri(furan-2-yl)phosphine (4g).





The reaction was carried out with 74.5 mg (0.30 mmol) of **1g**. The product **4g** was obtained as a white powder (32.4 mg, 0.140 mmol, 46% yield) after pulification by silica-gel column chromatography (CH₂Cl₂/hexane, 0:100 \rightarrow 10:90). ¹H and ¹³C NMR were in agreement with the literature.¹ ¹H NMR (392 MHz, CD₂Cl₂, δ): 6.42–6.47 (m, 3H), 6.80 (dd, *J* = 2.0, 3.1 Hz, 3H), 7.67 (d, *J* = 1.6 Hz, 3H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 111.2 (d, *J* = 6.6 Hz, *C*H), 121.6 (d, *J* = 24.4 Hz, *C*H), 147.9 (d, *J* = 2.8 Hz, *C*H), 149.3 (d, *J* = 2.9 Hz, *C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -77.0. HRMS-EI (*m/z*): [M]⁺ calcd for C₁₂H₉O₃P, 232.0289; found, 232.0288.

2-Diphenylphosphino-6-methylpyridine (4h).



The reaction was carried out with 88.0 mg (0.30 mmol) of **1h**. The product **4h** was obtained as a white powder (73.5 mg, 0.265 mmol, 88% yield) after pulification by silica-gel column chromatography (CH₂Cl₂/hexane, $0:100 \rightarrow 10:90 \rightarrow 20:80 \rightarrow 40:60 \rightarrow 60:40 \rightarrow 100:0$). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.²

¹H NMR (392 MHz, CD₂Cl₂, δ): 2.53 (s, 3H), 6.85 (d, J = 7.8 Hz, 1H), 7.06 (d, J = 7.8 Hz, 1H), 7.32– 7.41 (m, 10H), 7.45 (td, J = 2.1, 7.7 Hz, 1H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 24.7 (CH₃), 122.3 (CH), 125.2 (d, J = 15.1 Hz, CH), 128.9 (d, J = 7.5 Hz, CH), 129.3 (CH), 134.5 (d, J = 19.7 Hz, CH), 136.2 (CH), 137.1 (d, J = 11.3 Hz, C), 159.4 (d, J = 13.1 Hz, C), 163.1 (d, J = 6.5 Hz, C). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -5.0. HRMS-ESI (m/z): [M+Na]⁺ calcd for C₁₈H₁₆NNaP, 300.0913; found, 300.0907.

Cyclohexyldiphenylphosphine (4i).



4i

The reaction was carried out with 85.1 mg (0.30 mmol) of **1i**. The product **4i** was obtained as a white powder (75.4 mg, 0.281 mmol, 94% yield) after pulification by flash column chromatography with CH₂Cl₂/Hexane (0:100 \rightarrow 10:90). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.² ¹H NMR (392 MHz, CD₂Cl₂, δ): 1.12–1.38 (m, 5H), 1.60–1.81 (m, 5H), 2.17–2.29 (m, 1H), 7.28–7.36 (m, 6H), 7.43–7.54 (m, 4H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 26.8 (*C*H₂), 27.2 (d, *J* = 11.2 Hz, *C*H₂), 30.0 (d, *J* = 16.0 Hz, *C*H₂), 35.7 (d, *J* = 9.5 Hz, *C*H), 128.6 (d, *J* = 7.5 Hz, *C*H), 128.9 (*C*H), 134.0 (d, *J* = 18.8 Hz, *C*H), 137.9 (d, *J* = 15.0 Hz, *C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -4.1. HRMS-ESI (*m/z*): [M+H]⁺ calcd for C₁₈H₂₂P, 269.1454; found, 269.1449.

1,2-Bis(diphenylphosphino)ethane (4j).



The reaction was carried out with 129.0 mg (0.3 mmol) of **1j**. The product **4j** was obtained as a white powder (66.7 mg, 0.167 mmol, 56% yield) after pulification by silica-gel column chromatography (SiO₂, CH₂Cl₂/hexane, 0:100 \rightarrow 10:90 \rightarrow 20:80). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.²

¹H NMR (392 MHz, CD₂Cl₂, δ): 2.08 (t, *J* = 4.2 Hz, 4H), 7.26–7.36 (m, 20H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 24.1 (*C*H₂), 128.8 (t, *J* = 2.9 Hz, *C*H), 129.0 (*C*H), 133.0 (t, *J* = 9.5 Hz, *C*H), 138.8 (t, *J* = 7.2 Hz, *C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): –12.8. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₂₆H₂₄P₂, 398.1353; found, 398.1342.

1,3-Bis(diphenylphosphino)propane (4k).



The reaction was carried out with 133.4 mg (0.3 mmol) of **1k**. The product **4k** was obtained as a yellow oil (85.4 mg, 0.207 mmol, 69% yield) after pulification by silica-gel column chromatography (SiO₂, CH₂Cl₂/hexane, 0:100 \rightarrow 10:90 \rightarrow 20:80). ¹H, ¹³C and ³¹P NMR were in agreement with the literature.² ¹H NMR (392 MHz, CD₂Cl₂, δ): 1.50–1.64 (m, 2H), 2.20 (t, *J* = 7.8 Hz, 4H), 7.27–7.41 (m, 20H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 22.9 (t, *J* = 17.4 Hz, CH₂), 29.8 (t, *J* = 12.7 Hz, CH₂), 128.8 (d, *J* = 6.5 Hz, CH), 128.9 (CH), 133.0 (d, *J* = 18.8 Hz, CH), 139.2 (d, *J* = 14.1 Hz, C). ³¹P NMR (159 MHz, CD₂Cl₂, δ): –17.5. HRMS-EI (*m*/*z*): [M]⁺ calcd for C₂₇H₂₆P₂, 412.1510; found, 412.1501.

Diphenyl(pyren-1-yl)phosphine (4l).



The reaction was carried out with 120.7 mg (0.30 mmol) of **11**. The product **41** was obtained as a yellow powder (99.4 mg, 0.257 mmol, 86% yield) after pulification by silica-gel column chromatography (CH₂Cl₂/hexane, 0:100 \rightarrow 10:90). ¹H and ¹³C NMR were in agreement with the literature.⁵ ¹H NMR (392 MHz, CD₂Cl₂, δ): 7.30–7.42 (m, 10H), 7.54–7.59 (m, 1H), 8.00–8.15 (m, 5H), 8.22 (t, J = 6.4 Hz, 2H), 8.72–8.80 (m, 1H). ¹³C NMR (99 MHz, CD₂Cl₂, δ): 124.8 (*C*), 125.0 (d, J = 4.7 Hz, *C*), 125.2 (*C*H), 125.5 (*C*H), 125.8 (*C*H), 125.9 (d, J = 6.6 Hz, *C*H), 126.5 (*C*H), 128.1 (d, J = 77.0 Hz, *C*H), 128.1 (d, J = 1.9 Hz, *C*H), 129.0 (d, J = 6.5 Hz, *C*H), 129.3 (*C*H), 131.2 (*C*), 131.3 (*C*H), 131.7 (*C*), 132.0 (d, J = 15.0 Hz, *C*), 132.2 (*C*), 134.4 (d, J = 22.6 Hz, *C*), 134.5 (d, J = 19.8 Hz, *C*H), 137.2 (d, J = 10.3 Hz, *C*). ³¹P NMR (159 MHz, CD₂Cl₂, δ): -14.1. HRMS-EI (m/z): [M]⁺ calcd for C₂₈H₁₉P, 386.1224; found, 386.1214.

6. References.

- 1. C. Laye, J. Lusseau, F. Robert, Y. Landais, Adv. Synth. Catal. 2021, 363, 3035–3043.
- Y. Li, L. Lu, S. Das, S. Pisiewicz, K. Junge, M. Beller, J. Am. Chem. Soc. 2012, 134, 18325– 18329.
- 3. J. Jeschke, M. Korb, T. Ruffer, C. Gabler, H. Lang, Adv. Synth. Catal. 2015, 357, 4069–4081.
- 4. J. Xiao, J. Wang, H. Zhang, J. Zhang, L. Han, J. Org. Chem. 2023, 88, 3909–3915.
- 5. C. Sire, H. Cattey, A. Tsivery, J. Hierso, J. Roger, Adv. Synth. Catal. 2022, 364, 440–452.





.







-







.











.

S26

---- PROCESSING PARAMETERS ---dc balance(0, FALSE) sexp(2.0[Hz], 0.0[s]) trapezoid3(0[%], 80[%], 100[%]) zerofill(1) fft(1, TRUE, TRUE) machinephase ppmDerived from: REO-056-pure-internal-31P-1.jdf 30.0 Filename = REO-056-pure-internal-31P Author = element Experiment = single pulse dec Sample Id = 1 Solvent = METHYLENE-CHLORI Actual Start Time = 30-AUG-2022 16:30:12 Revision Time = 2-SEP-2022 19:13:53 Comment = single pulse decoupled ga = 1D COMPLEX Data Format Dim Size = 26214 X Domain = 31P20.0 Dim Title = 31P Dim Units = [ppm] Dimensions = X Site = ECS 400 = JNM-ECS400 Spectrometer Field Strength = 9.20197068[T] (390[MHz])X Acq Duration = 0.2359296[s]X Domain = 31P X Freq = 158.59799923[MHz] X Offset = 0[ppm]X Points = 32768 X Prescans = 4 X Resolution = 4.23855252[Hz] X Sweep = 138.88888889[kHz]Irr Domain = 1H10.0 Irr Freq = 391.78655441[MHz] Irr Offset = 5[ppm] Clipped = FALSE = 30 Scans = 30 Total Scans Relaxation_Delay = 2[s]Recvr Gain = 50 Temp Get = 21.1[dC]X 90 Width = 13.25[us]X Acq Time = 0.2359296[s]X Angle = 30[deg] X Atn = 5.5[dB]abundance X Pulse = 4.41666667[us]Irr Atn Dec = 22.05[dB]Irr Atn Noe = 22.05[dB]Irr Noise = WALTZ 0 Decoupling = TRUE Initial Wait = 1[s]-8.0 -10.0 -12.0 -14.0 -16.0 -18.0 -20.0 -22.0 = TRUE 10.0 8.0 6.0 4.0 2.0 0 -2.0 -4.0 -6.0 Noe Noe Time = 2[s]Repetition Time = 2.2359296[s] 0.000 -9.033 X : parts per Million : 31P

---- PROCESSING PARAMETERS ----28.0 dc balance(0, FALSE) sexp(2.0[Hz], 0.0[s]) trapezoid3(0[%], 80[%], 100[%]) zerofill(1) 26.0 fft(1, TRUE, TRUE) machinephase ppm0 Derived from: REO-077-pure-internal-31P-1.jdf 24. 0 22. Filename = REO-077-pure-internal-31P Author = element Experiment = single pulse dec 0 Sample Id = 1 20. Solvent = METHYLENE-CHLORI Actual Start Time = 31-AUG-2022 00:33:41 Revision Time = 6-SEP-2022 11:17:49 0 = single pulse decoupled ga 18. Comment Data Format = 1D COMPLEX Dim Size = 26214 X Domain = 31P 16.0Dim Title = 31P Dim Units = [ppm] Dimensions = X Site = ECS 4000 = JNM-ECS400 Spectrometer 4 Field Strength = 9.20197068[T] (390[MHz]) X_Acq Duration = 0.2359296[s]0 X Domain = 31P 2 X Freq = 158.59799923[MHz] X Offset = 0[ppm] X Points = 32768 0 X Prescans = 4 10. X Resolution = 4.23855252[Hz] X Sweep = 138.88888889[kHz]Irr Domain = 1H0 = 391.78655441[MHz] Irr Freq ∞. Irr Offset = 5[ppm]= FALSE Clipped = 22 Scans 0 = 22 Total Scans 6 Relaxation Delay = 2[s]= 50 Recvr Gain 4.0 Temp Get = 21[dC]X 90 Width = 13.25[us]X Acq Time = 0.2359296[s]X Angle = 30[deg] X_Atn X_Pulse 0 = 5.5[dB]abundance i, = 4.41666667[us]= 22.05[dB]Irr Atn Dec Irr Atn Noe = 22.05[dB]Irr Noise = WALTZ 0 Decoupling = TRUE Initial Wait = 1[s]100.0 -100.0 -200.0 -300.0 Noe = TRUE 200.0 0 300.0 Noe Time = 2[s]= 2.2359296[s] Repetition Time 0.000 -4.998 X : parts per Million : 31P

.

6.0				PROCESSING PARAMETERS dc_balance(0, FALSE) sexp(2.0[Hz], 0.0[s]) trapezoid(0[%], 0[%], 80[%], 100[%]) zerofill(1) fft(1, TRUE, TRUE) machinephase ppm
			ILP PPD	Derived from: REO-088-pure-internal-31P_Carbo
5.0			白白	Filename= REO-088-pure-internal-311Author= elementExperiment= carbon.jxpSample_Id= REO-088-pure-internal-311Solvent= METHYLENE-CHLORIDE-D2Actual_Start_Time= 16-SEP-2022 11:12:00Revision_Time= 16-SEP-2022 19:56:09
4.0				Comment= single pulse decoupled gaData_Format= 1D COMPLEXDim_Size= 26214X_Domain= PhosphDim_Title= Phosphorus31Dim_Units= [ppm]Dimensions= XSite= JNM-ECS400Spectrometer= DELTA2_NMR
3.0				Field_Strength = 9.37221[T] (400[MHz]) X_Acq_Duration = 0.229376[s] X_Domain = 31P X_Freq = 161:53211155[MHz] X_Offset = 0[ppm]
2.0				X Points = 32768 X Prescans = 4 X Resolution = 4.35965402[Hz] X Sweep = 142.85714286[kHz] X Sweep_Clipped = 114.28571429[kHz] Irr Domain = Proton
-				Irr_Freq = 399.03472754[MHz] Irr_Offset = 5.0[ppm] Clipped = FALSE Scans = 100 Total_Scans = 100
1.0				Relaxation_Delay = 2[s] Recvr_Gain = 50 Temp_Get = 19.7[dC] x_{90} width = 16.75[us] x_{Acq} Time = 0.229376[s] x_{Acq} Lime = 30[deq]
	n frans de la grafia que fina que a se contra de se de se de de la contra de se de se de se de se de se de se In francé de la grafia que fina que de se de s			X_Angle = 5.0003 X_An = 4.7[dB] X_Pulse = 5.58333333[us] Irr_Atn_Bec = 25.823[dB] Irr_Atn_Noe = 25.823[dB] Irr_Noise = WALTZ
-4 _T	300.0 200.0	100.0 0	-100.0 -200.0	$-300.0 \begin{array}{rcl} Irr_Pwidth &= 0.115[ms]\\ Decoupling &= TRUE\\ Initial_Wait &= 1[s]\\ Noe &= TRUE \end{array}$
			- 220	Noe Time = 2[s] Repetition_Time = 2.229376[s]

