Supporting Information

Traditional Morita–Baylis–Hillman reaction of aldehydes with methyl vinyl ketone co-catalyzed by triphenylphosphine and nitrophenol

Min Shi* and Ying-Hao Liu

State Key Laboratory of Organometallic Chemistry,

Shanghai Institute of Organic Chemistry,

Chinese Academy of Sciences,354 Fenglin Lu, Shanghai 200032 China,

mshi@pub.sioc.ac.cn

Experimental Procedures

General Methods. ^{1}H NMR spectra were recorded on a Bruker AM-300 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; *J*-values are in Hz. Organic solvents were dried by standard methods when necessary. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} silica gel coated plates. Flash Column Chromatography was carried out using 300-400 mesh silica gel at increased pressure.

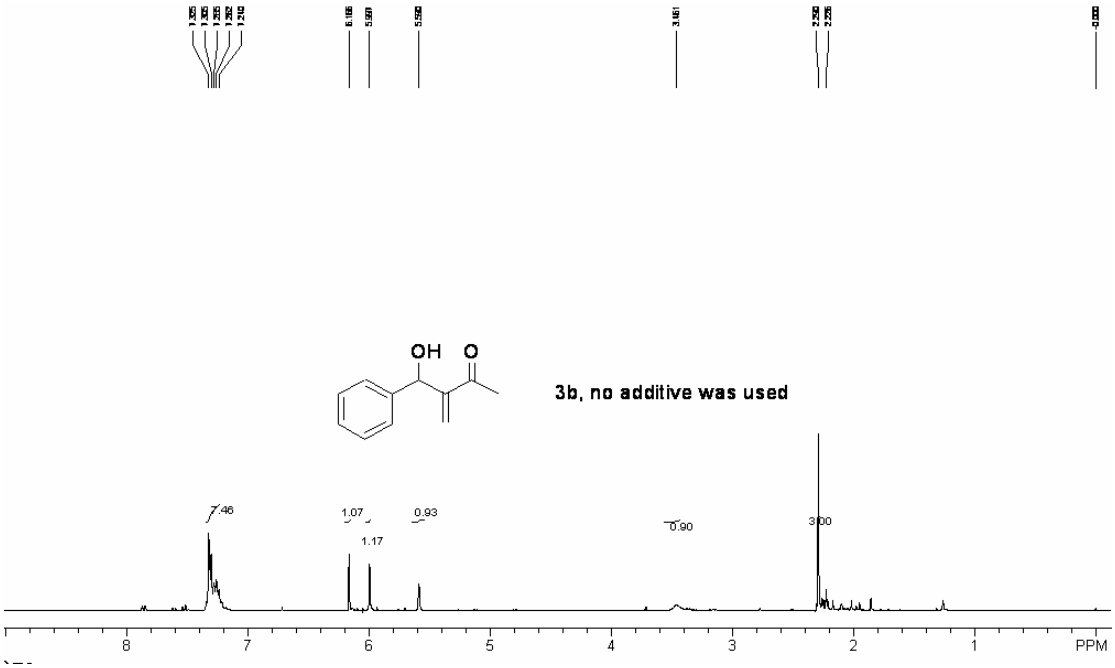
Typical reaction procedure for triphenylphosphine and nitrophenol co-catalyzed Morita-Baylis-Hillman reaction of arylaldehydes with methyl vinyl ketone (MVK).

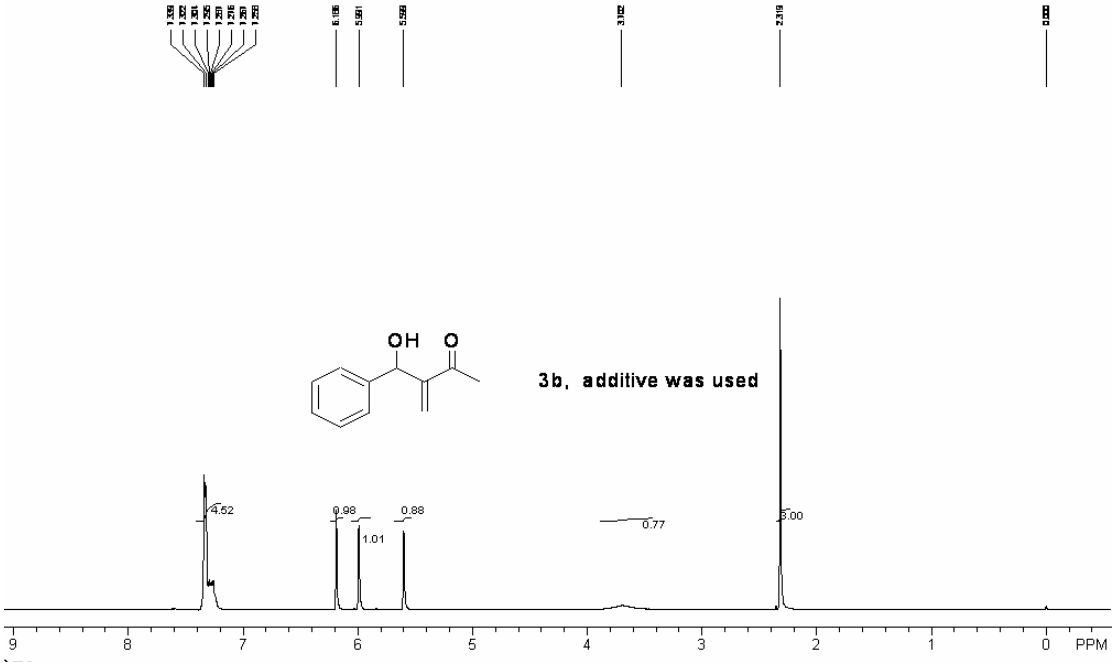
To a solution of PPh_3 (42 mg, 0.16 mmol), *p*-nitrophenol (34 mg, 0.24 mmol) and *p*-chlorobenzaldehyde **1b** (112 mg, 0.8 mmol) in THF (2.0 mL) was added methyl vinyl ketone

(MVK) **2** (199 μL, 2.4 mmol) and the reaction mixture was stirred at room temperature for 18 h. The solvent was removed under reduced pressure and the residue was purified by flash silica gel chromatography to give the compound **3b** (154 mg, 92%) as a colorless solid (eluent: ethyl acetate/petroleum ether = 1/10).

4-hydroxy-3-methylene-4-phenylbutan-2-one (3a):

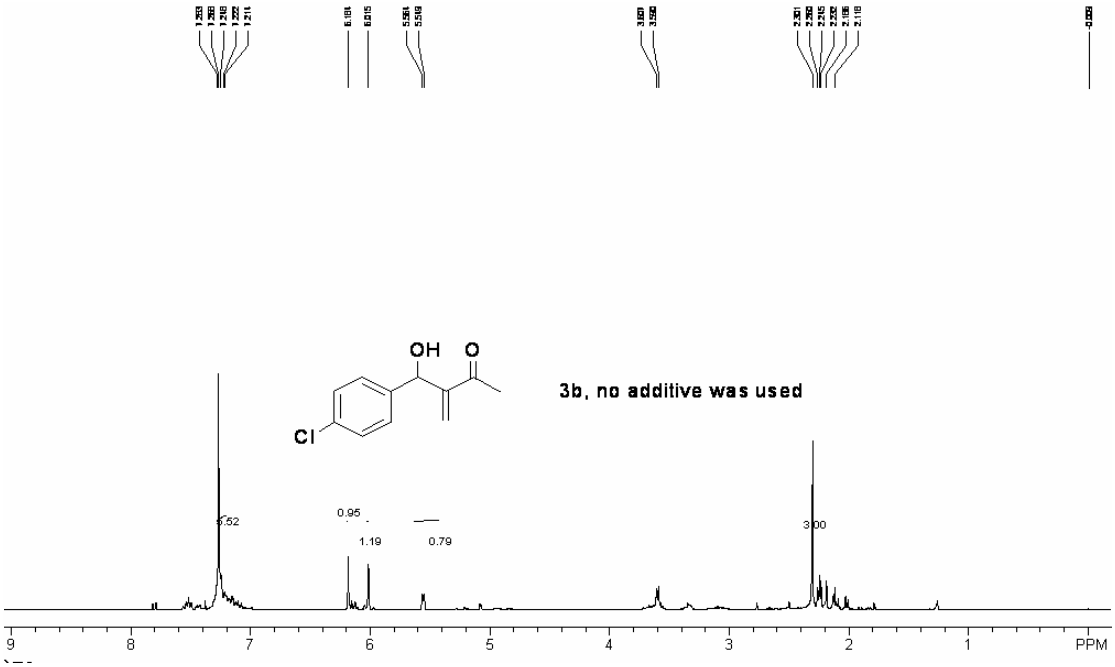
a colorless liquid, yield 52%. This is a known compound.[1] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.32 (3H, s, CH_3), 3.70 (1H, br, OH), 5.60 (1H, s, CH), 5.99 (1H, s, C=CH_2), 6.19 (1H, s, C=CH_2), 7.24-7.34 (5H, m, ArH).

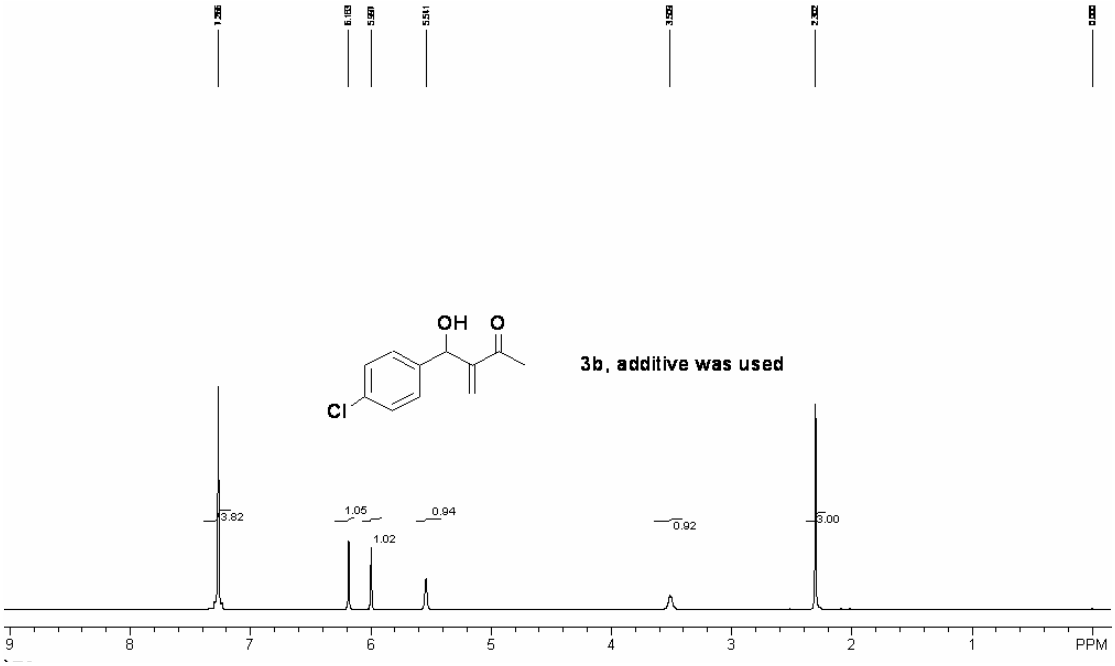




4-hydroxy-4-(4-chlorophenyl)-3-methylenebutan-2-one (3b):

a colorless liquid, yield 92%. This is a known compound.[2] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.30 (3H, s, CH_3), 3.51 (1H, br, OH), 5.54 (1H, s, CH), 5.99 (1H, s, C=CH_2), 6.19 (1H, s, C=CH_2), 7.25 (2H, d, J = 9.0 Hz, ArH), 7.28 (2H, d, J = 9.0 Hz, ArH).





4-hydroxy-4-(4-nitrophenyl)-3-methylenebutan-2-one (3c):

a colorless liquid, yield 98%; This is a known compound.[3] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.30 (3H, s, CH_3), 3.53 (1H, br, OH), 5.68 (s, 1H, CH), 6.05 (1H, s, C=CH_2), 6.28 (1H, s, C=CH_2), 7.56 (2H, d, J = 9.0 Hz, Ar), 8.20 (2H, d, J = 9.0 Hz, Ar).

4-hydroxy-4-(3-nitrophenyl)-3-methylenebutan-2-one (3d):

a colorless liquid, yield 90%; This is a known compound.[4] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.35 (3H, s, CH_3), 3.64 (1H, br, OH), 5.68 (1H, s, CH), 6.15 (1H, s, C=CH_2), 6.31 (1H, s, C=CH_2), 7.49 (1H, dd, J = 9.0 Hz, 9.0 Hz, Ar), 7.70 (1H, d, J = 8.4 Hz, Ar), 8.08 (1H, d, J = 8.4 Hz, Ar), 8.21 (1H, s, Ar).

4-hydroxy-4-(2-nitrophenyl)-3-methylenebutan-2-one (3e):

a colorless liquid, yield 98%. This is a known compound.[5] ^{1}H NMR ($CDCl_3$, 300 MHz, TMS):

δ 2.39 (3H, s, CH_3), 3.53 (1H, br, OH), 5.80 (1H, s,CH), 6.19 (1H, s, C=CH_2), 6.25 (1H, s, C=CH_2), 7.50 (1H, dd, *J* = 7.1 Hz, *J* = 7.1 Hz, Ar), 7.70 (1H, dd, *J* = 7.6 Hz, 7.6 Hz, Ar), 7.79 (1H, d, *J* = 7.6 Hz, Ar), 8.0 (1H, d, *J* = 8.2 Hz, Ar).

4-hydroxy-4-(4-methylphenyl)-3-methylenebutan-2-one (3f):

a colorless liquid, yield 42%. This is a known compound.[2] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.32 (3H, s, CH_3), 2.34 (3H, s, CH_3), 5.60 (1H, s, CH), 5.72 (1H, br, OH), 6.06 (1H, s, C=CH_2), 6.24 (1H, s, C=CH_2), 7.13 (2H, d, *J* = 8.1 Hz, ArH), 7.22 (2H, d, *J* = 8.1 Hz, ArH).

4-hydroxy-4-(4-methoxyphenyl)-3-methylenebutan-2-one (3g):

a colorless liquid, yield 35%; This is a known compound.[6] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.34 (3H, s, CH_3), 3.79 (3H, s, OCH_3), 5.58 (1H, d, *J* = 3.9 Hz, CH), 5.72 (1H, br, OH), 6.06 (1H, s, C=CH_2), 6.24 (1H, s, C=CH_2), 6.86 (2H, d, *J* = 9.0 Hz, ArH), 7.26 (2H, d, *J* = 9.0 Hz, ArH).

4-hydroxy-4-(2,4-dichlorophenyl)-3-methylenebutan-2-one (3h):

a colorless liquid, yield 95%. This is a known compound.[7] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.37 (3H, s, CH_3), 4.51 (1H, br, OH), 5.73 (1H, s, CH), 5.92 (1H, s, C=CH_2), 6.20 (1H, s, C=CH_2), 7.25 (1H, dd, *J* = 8.7 Hz, *J* = 1.8 Hz, ArH), 7.33 (1H, d, *J* = 1.8 Hz, ArH), 7.33 (1H, d, *J* = 8.7 Hz, ArH).

4-hydroxy-4-(4-fluorophenyl)-3-methylenebutan-2-one (3i):

a colorless liquid, yield 87%; This is a known compound.[2] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.32 (3H, s, CH_3), 4.84 (1H, br, OH), 5.59 (1H, s, CH), 6.04 (1H, s, C=CH_2), 6.22 (1H, s, C=CH_2), 6.99 (2H, dd, *J* = 9.0 Hz, *J* = 9.0 Hz, ArH), 7.29 (2H, dd, *J* = 9.0 Hz, *J* = 9.0 Hz, ArH).

4-hydroxy-4-(3-fluorophenyl)-3-methylenebutan-2-one (3j):

a colorless liquid, yield 93%. This is a known compound.[2] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.32 (3H, s, CH_3), 4.76 (1H, br, OH), 5.59 (1H, s, CH), 6.04 (1H, s, C=CH_2), 6.24 (1H, s, C=CH_2), 6.91-6.97 (1H, m, ArH), 7.04-7.11 (2H, m, ArH), 7.23-7.31 (1H, m, ArH).

4-hydroxy-4-(4-bromophenyl)-3-methylenebutan-2-one (3k):

a colorless liquid, yield 83%. This is a known compound.[8] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.32 (3H, s, CH_3), 4.88 (1H, br, OH), 5.54 (1H, s, CH), 6.04 (1H, s, C=CH_2), 6.22 (1H, s, C=CH_2), 7.19 (2H, d, *J* = 7.5 Hz, ArH), 7.41 (2H, d, *J* = 8.1 Hz, ArH).

4-hydroxy-6-phenyl-3-methylenehexan-2-one (3l):

a colorless liquid, yield 72%. This is a known compound.[9] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 1.91-1.98 (2H, m), 2.35 (3H, s, CH_3), 2.64- 2.83 (2H, m), 4.50 (1H, t, *J* = 6.6 Hz, CH), 5.49 (1H, br, OH), 6.05 (1H, s, C=CH_2), 6.15 (1H, s, C=CH_2), 7.14-7.19 (3H, m, ArH), 7.24-7.29 (2H, m, ArH).

4-hydroxy-4-(2-pyridyl)-3-methylenebutan-2-one (3m):

a colorless liquid, yield 80%; This is a known compound.[10] ^{1}H NMR ($CDCl_3$, TMS, 300 MHz): δ 2.33 (3H, s, CH_3), 4.84 (1H, br, OH), 5.72 (1H, s, CH), 6.17 (1H, s, C=CH_2), 6.23 (1H, s, C=CH_2), 7.16-7.20 (1H, m, ArH), 7.42 (1H, d, *J* = 6.0 Hz ArH), 7.62-7.68 (1H, m, ArH), 8.48-8.50 (1H, m, ArH).

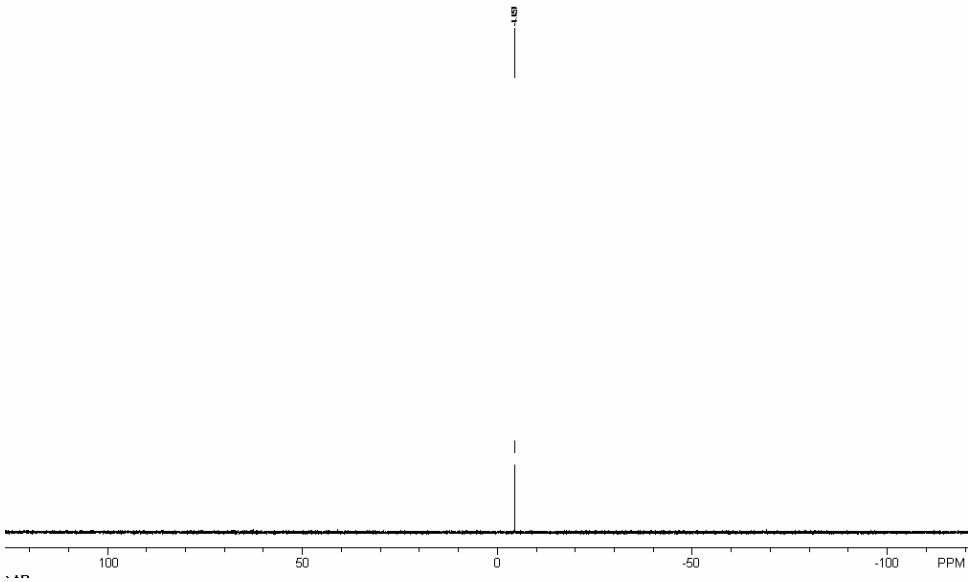


Figure 2. ^{31}P NMR spectrum of PPh_3 in $CDCl_3$.

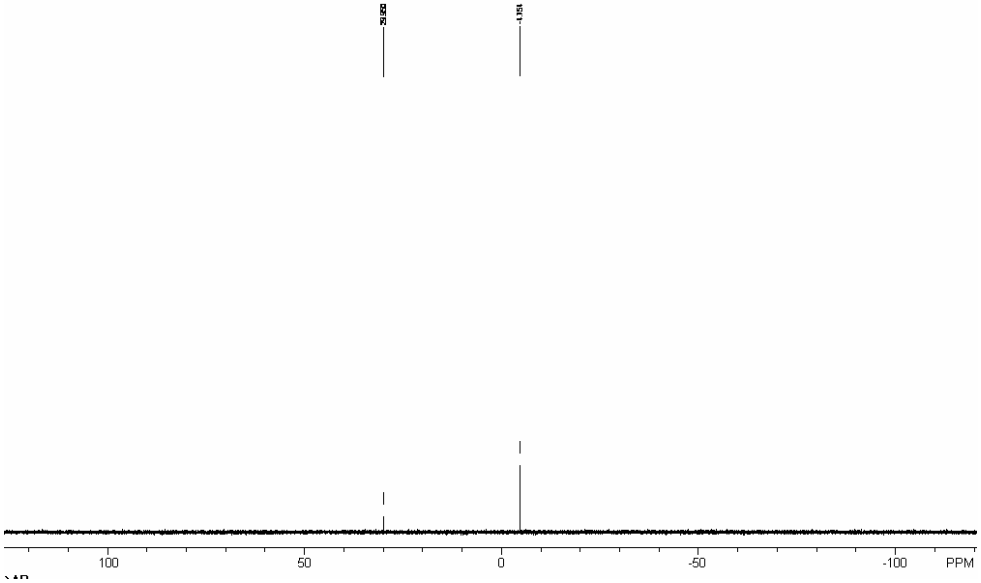


Figure 3. ^{31}P NMR spectrum of PPh_3 with MVK in $CDCl_3$.

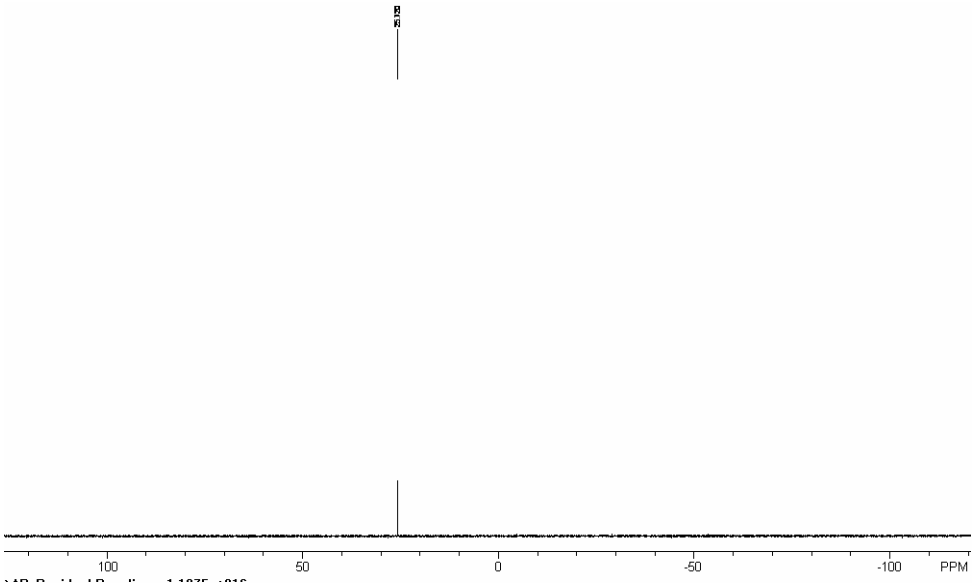


Figure 4. ^{31}P NMR spectrum of PPh_3 with MVK and *p*-nitrophenol in $CDCl_3$.

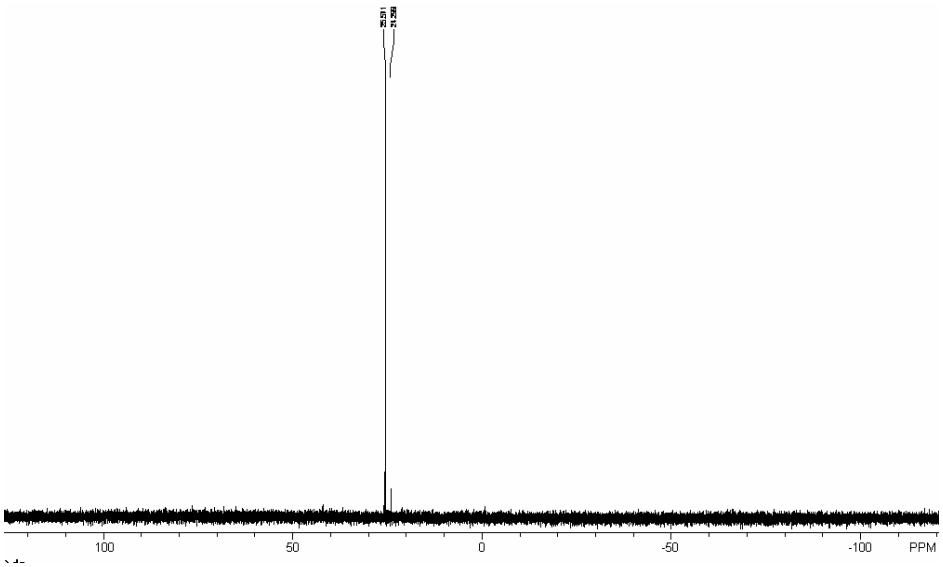


Figure 5. ^{31}P NMR spectrum of PPh_3 with MVK, *p*-nitrophenol and *p*-chlorobenzaldehyde in $CDCl_3$.

REFERENCE:

1. Sato, S.; Matsuda, I.; Shibata, M. *J. Organomet. Chem.* **1989**, *377*, 347-356.

2. Huang, J. W.; Shi, M. *Adv. Synth. Catal.* **2003**, *345*, 953-958.

3. Shi, M.; Li, C. Q.; Jiang, J. K. *Tetrahedron.* **2003**, *59*, 1181-1190.

4. Shi, M.; Jiang, Y. *J. Chem. Res. Synop.* **2003**, *9*, 564-566.

5. Krishna, P. R.; Sekhar, E. R.; Kannan, V. *Synthesis* **2004**, *6*, 857-860.

6. Matsumoto, S.i.; Okubo, Y.; Mikami, K. *J. Am. Chem. Soc.* **1998**, *120*, 4015-4016.

7. Hayashi, Y.; Tamura, T.; Shoji, M. *Adv. Synth. Catal.* **2004**, *346*, 1106-1110.

8. Shi, M.; Li, C. Q.; Jiang, J. K. *Chem. Commun.* **2001**, 833-834.

9. Iwama, T.; Kinoshita, H.; Kataoka, T. *Tetrahedron Lett.* **1999**, *40*, 3741-3744.

10. Bode, M. L.; Kaye, P. T. *J. Chem. Soc. Perkin Trans. 1*. **1993**, 1809-1814.

11. Reetz, M. T.; Merk, C.; Naberfeld, G.; Rudolph, J.; Griebenow, N.; Goddard, R. *Tetrahedron Lett.* **1997**, *38*, 5273-5276.

12. McDougal, N. T.; Schaus, S. E. *J. Am. Chem. Soc.* **2003**, *125,* 12094-12095.