Supplementary Information

Toward Autonomously Operating Molecular Machines Driven by Transition-metal Catalyst: Spectroscopic Observation of Ligand Motions

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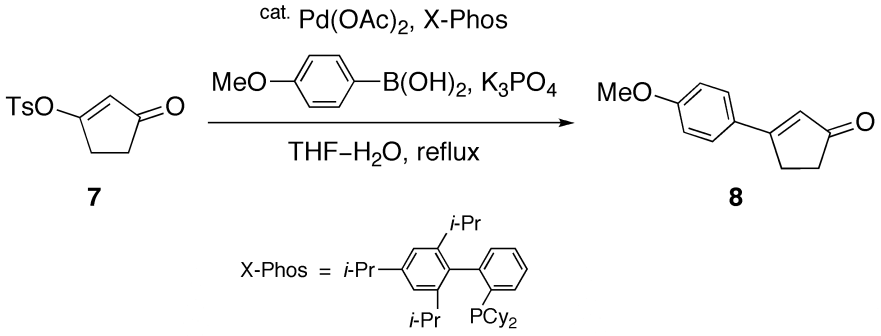
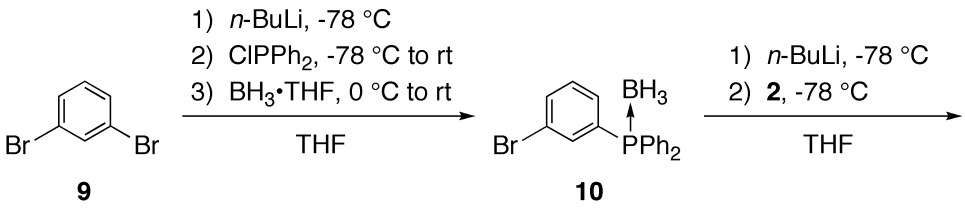
1. Materials and Methods

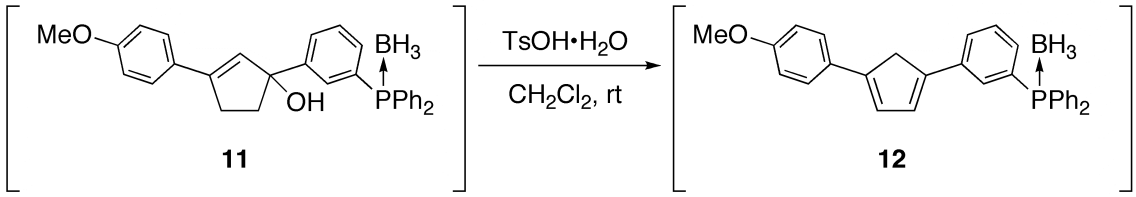
^{1}H NMR (500 MHz) and ^{31}P NMR (202 MHz) spectra were recorded in $CDCl_3$, CD_2Cl_2, toluene-d_8 or THF-d_8 on a JEOL type GSX-270 and GSX-500 spectrometers using a residual non–deuterated solvent as an internal reference. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry was performed with dithranol as a matrix on an Applied Biosystems BioSpectrometry Workstation^{TM} model Voyager-DE^{TM} STR spectrometer. Fast atom bombardment mass (FAB-MS) spectrometry was performed with 3-nitrobenzyl alcohol as a matrix on a JEOL type JMS-AX505H mass spectrometer. Electronic absorption, circular dichroism (CD) and infrared (IR) spectra were recorded on a JASCO type V-560 spectrometer, a JASCO type J-720 spectropolarimeter and a JASCO type FT/IR-610 spectrometer, respectively. Preparative high performance liquid chromatography (HPLC) was performed at room temperature using a 20 mm-ϕ × 250 mm long amylose column (DAICEL Chiralpak IA®) on a Japan Analytical Industry Model LC-918 recycling preparative HPLC system equipped with a JASCO type 875-UV variable-wavelength UV-Vis detector and a JASCO type CD-2095A variable-wavelength CD detector.

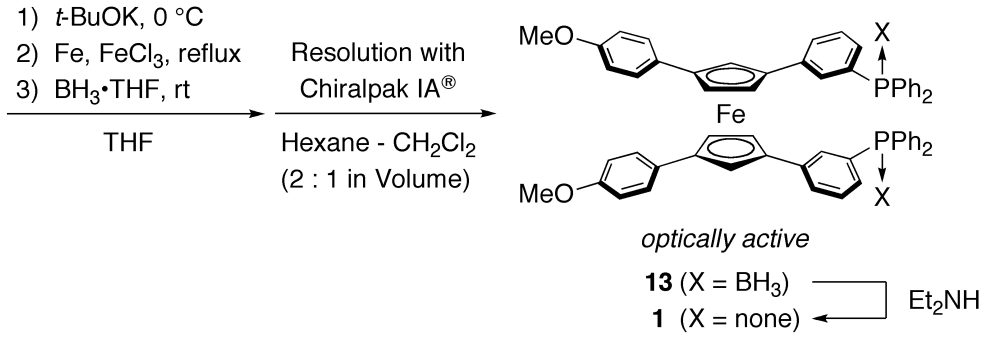
Tetrahydrofuran (THF) and CH_2Cl_2 for solvent were purchased from Kanto Chemical. CH_2Cl_2 and hexane for HPLC were purchased from Kanto Chemical. Diethylamine was distilled from potassium hydroxide before use. Other reagents were used as received.

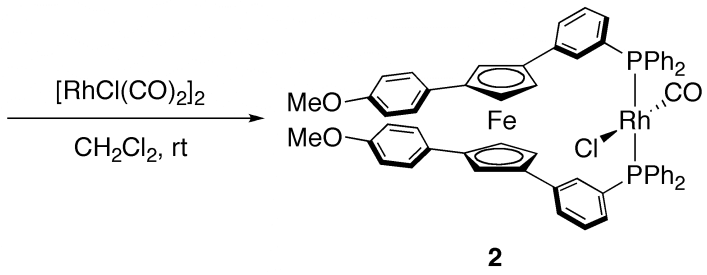
2. Synthesis of Rhodium(I) Complex 2







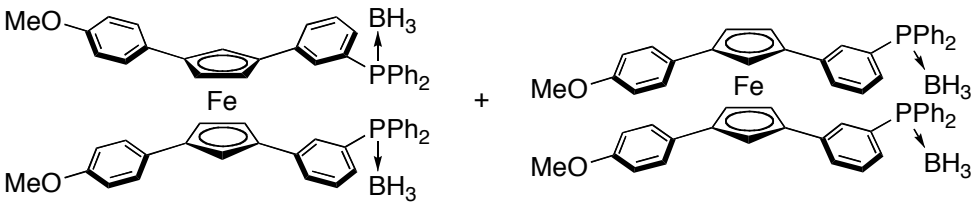




3-(4-Methoxyphenyl)-2-cyclopenten-1-one (8): 8 was prepared according to the procedure reported in the literature.[1] To a degassed THF/water (10 mL/0.27 mL) solution of 3-(*p*-toluenesulfonyloxy)-2-cyclopenten-1-one[2] (**7**) (1.27 g, 4.96 mmol), were subsequently added $Pd(OAc)_2$ (22.6 mg, 0.100 mmol, 2 mol%), 2-dicylohexylphosphino-2′,4′,6′-triisopropylbiphenyl (X-Phos) (118 mg, 0.248 mmol, 5 mol%), 4-methoxyphenylboronic acid (1.50 g, 9.87 mmol, 200 mol%), and potassium phosphate (3.15 g, 14.8 mmol, 300 mol%) at room temperature. The resulting mixture was heated to 80 °C, vigorously stirred for 12 h and then cooled down to room temperature. To the reaction mixture, were added H_2O (10 mL) and EtOAc (10 mL). The organic phase was separated, and the aqueous phase was extracted with EtOAc (20mL, 2 times). The combined organic extracts were washed twice with water (20 mL) and then with brine (20 mL). The organic extracts were dried over anhydrous Na_2SO_4, and filtered off from insoluble fractions. The filtrate was evaporated to dryness, and the residue was chromatographed on silica with hexane/ethyl acetate (3/1 to 1/1) as an eluent and then on GPC with $CHCl_3$ as an eluent to allow isolation of 3-(4-methoxyphenyl)-2-cyclopenten-1-one (**8**) as a white solid (554 mg, 2.94 mmol, 59% yield). ^{1}H NMR (500 MHz; $CDCl_3$; 20 °C; ppm) δ 2.54–2.56 (2H, m), 2.99–3.02 (2H, m), 3.85 (3H, s), 6.46 (1H, t, J = 1.8 Hz), 6.94 (2H, d, J = 8.8 Hz), 7.61 (2H, d, J = 8.8 Hz); Anal. Found: C, 76.43; H, 6.51%. Calcd. for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43%.

(3-Bromophenyl)diphenylphosphine-borane complex (10):[3] To a THF (16 mL) solution of 1,3-dibromobenzene (**9**) (3.77 g, 16.0 mmol) was added *n*-butyllithium in hexane (1.6 M, 10 mL, 16.0 mmol) at -78 °C and the resulting mixture was stirred for 1 h. Then, to the reaction mixture was slowly added chlorodiphenylphosphine (2.8 mL, 15.2 mmol), and the resulting mixture was stirred at 0 °C for 6 h. To the reaction mixture, was added Borane-THF complex in THF (1.0 M, 24 mL, 24.0 mmol), and the resulting mixture, allowed to warm up to room temperature, was further stirred for 14 h. The mixture was then diluted with Et_2O (30 mL), and poured into H_2O (30 mL). The organic phase was separated, and the aqueous layer was extracted with Et_2O (30 mL). The combined organic extracts were washed with brine (30 mL), dried over Na_2SO_4, and filtered off from insoluble fractions. The filtrate was evaporated to dryness and the residue was chromatographed on silica with hexane/EtOAc (19/1) as an eluent to allow isolation of (3-bromophenyl) diphenylphosphine/borane complex (**10**) as a white solid (4.24 g, 12.0 mmol, 79% yield). ^{1}H NMR (500 MHz; $CDCl_3$; 20 °C; ppm) δ 1.24 (3H, broad s), 7.29 (1H, td, J = 7.9, 2.4 Hz), 7.42-7.67 (13H, m); ^{13}C NMR (125.65 MHz; $CDCl_3$; 20 °C; ppm) δ 123.3 (d, $J_{P\text{-}C}$ = 12.4 Hz), 128.3 (d, $J_{P\text{-}C}$ = 57.0 Hz), 128.9 (d, $J_{P\text{-}C}$ = 10.4 Hz), 130.3 (broad s), 132.3 (d, $J_{P\text{-}C}$ = 54.9 Hz), 133.1 (d, $J_{P\text{-}C}$ = 9.3 Hz), 134.4 (broad s), 135.5 (d, $J_{P\text{-}C}$ = 11.4

Hz), 135.6 (d, $J_{P\text{-}C}$ = 10.3 Hz).

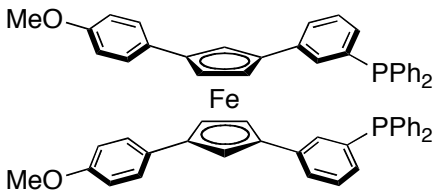


racemic *meso*

1,1´-Bis(3-diphenylphosphinophenyl)-3,3´-bis(4-methoxyphenyl)ferrocene/borane complex (13): To a THF (20 mL) solution of (3-bromophenyl)diphenylphosphine/borane complex (**10**) (1.59 g, 4.48 mmol) was slowly added *n*-butyllithium in hexane (1.60 M, 2.95 mL, 4.48 mmol) at -78 °C, and the resulting mixture was stirred for 1 h. To the reaction mixture, a solution of 3-(4-methoxyphenyl)-2-cyclopenten-1-one (**8**) (0.83 g, 4.42 mmol) in THF (30 mL) was transferred via cannula, and the resulting mixture was stirred at -78 °C for 1 h. Then the mixture was allowed to warm up to room temperature in 10 min, and poured into a mixture of water (30 mL) and Et_2O (30 mL). The organic phase was separated, and the aqueous phase was extracted with Et_2O (30 mL). The combined organic extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and filtered off from insoluble fractions. The filtrate was evaporated to dryness to afford 1-(3-diphenylphosphinophenyl)-3-(4-methoxyphenyl)-2-cyclopenten-1-ol/borane complex (**11**), which was immediately dissolved in CH_2Cl_2 (5 mL). To the resulting mixture was added *p*-toluenesulfonic acid hydrate. Disappearance of the spot corresponding to **11** was confirmed by thin layer chromatography (TLC), and the reaction mixture was subjected to silica gel column chromatography with hexane/EtOAc (9/1 to 4/1) as an eluent. Fluorescent fractions were collected, and the combined fractions were evaporated to dryness to afford 1-(3-diphenylphosphinophenyl)-4-(4-methoxyphenyl)-1,3-cyclopentadiene/borane complex (**12**) (1.13 g, 2.54 mmol, 57% yield) as yellow foam.

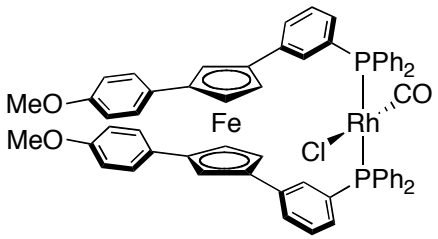
A THF (5 mL) suspension of a mixture of anhydrous $FeCl_3$ (150 mg, 0.927 mmol) and Fe powder (26.6 mg, 0.476 mmol) was refluxed for 3.5 h meanwhile the reaction mixture turned from yellow to colorless, and white precipitates (presumably $FeCl_2$) were formed. To a THF (10 mL) solution of crude **12** in another flask, was added potassium *tert*-butoxide (296 mg, 2.64 mmol) in one portion at 0 °C and the resulting mixture was stirred for 1 h. Then, the deep red reaction mixture was transferred into the suspension of $FeCl_2$ at 0 °C, and the resulting mixture was refluxed for 17 h. The reaction mixture was cooled down to 0 °C, and borane/THF complex in THF (1.0 M, 3 mL, 3.0 mmol) was added to the mixture. The resulting mixture was stirred for 3 h and then allowed to warm up to room temperature. The mixture was passed through short pad of silica gel to remove insoluble fractions,

and evaporated to dryness. The residue was chromatographed on silica gel with hexane/EtOAc (9/1 to 4/1) as an eluent to allow isolation of 1,1′-bis(3-diphenylphosphinophenyl)-3,3′-bis(4-methoxyphenyl)ferrocene/borane complex (**13**) (575 mg, 0.607 mmol, 27% yield) as a mixture of *racemic* and *meso* isomers. Resolution of the all stereoisomers was successfully performed by preparative HPLC using Chiralpak IA® column with hexane/CH_2Cl_2 (2/1) as an eluent. ^{1}H NMR (500 MHz; $CDCl_3$; 20 °C; ppm) *racemic* isomer: δ 1.40 (6H, broad), 3.76 (6H, s), 4.28–4.29 (2H, m), 4.32–4.33 (2H, m), 4.54–4.55 (2H, m), 6.61 (4H, d, J = 8.8 Hz), 6.97–7.04 (4H, m), 6.98 (4H, d, J = 8.8 Hz), 7.15–7.19 (2H, m), 7.44–7.48 (8H, m), 7.50–7.52 (4H, m), 7.59–7.67 (10H, m); *meso* isomer: δ 1.41 (6H, broad), 3.75 (6H, s), 4.29–4.30 (2H, m), 4.34–4.35 (2H, m), 4.58–4.59 (2H, m), 6.59 (4H, d, J = 8.5 Hz), 6.95–7.00 (4H, m), 6.96 (4H, d, J = 8.5 Hz), 7.15–7.19 (2H, m), 7.44–7.48 (8H, m), 7.50–7.54 (4H, m), 7.59–7.69 (10H, m).



optically active

Optically active 1,1′-bis(3-diphenylphosphinophenyl)-3,3′-bis(4-methoxyphenyl)ferrocene (1): Optically active stereoisomer of 1,1′-bis(3-diphenylphosphinophenyl)-3,3′-bis(4-methoxyphenyl) ferrocene/borane complex (**13**) (81.5 mg, 0.086 mmol) was dissolved in diethylamine (3 mL). The resulting mixture was stirred overnight at room temperature, and then evaporated to dryness. The residue was chromatographed on silica gel with CH_2Cl_2 as an eluent to allow isolation of optically active 1,1′-bis(3-diphenylphosphinophenyl)-3,3′-bis(4-methoxyphenyl)ferrocene (**1**) (67.3 mg, 0.073 mmol, 85% yield) as a reddish orange powder. ^{1}H NMR (500 MHz; THF-d_8; 20 °C; ppm) δ 3.74 (6H, s), 4.21 (2H, s), 4.31 (2H, s), 4.51–4.52 (2H, m), 6.62 (4H, d, $J_{H\text{-}H}$ = 8.8 Hz), 7.00 (2H, dd, $J_{H\text{-}H}$ = 7.3 Hz, $J_{H\text{-}P}$ = 7.3 Hz), 7.02 (4H, d, $J_{H\text{-}H}$ = 8.8 Hz), 7.09 (2H, ddd, $J_{H\text{-}H}$ = 7.3, 7.9 Hz, $J_{H\text{-}P}$ = 1.2 Hz), 7.14 (2H, d, $J_{H\text{-}H}$ = 7.9 Hz), 7.34–7.38 (20H, m), 7.42 (2H, d, $J_{H\text{-}P}$ = 8.5 Hz); ^{13}C NMR (125.65 MHz; THF-d_8; 20 °C; ppm) δ 55.3 (s), 70.4 (s), 87.3 (s), 89.4 (s), 96.0 (s), 114.5 (s), 127.5 (m), 129.3 (m), 129.6 (s), 134.6 (m), 138.1 (d, $J_{P\text{-}C}$ = 12.5 Hz), 138.7 (d, $J_{P\text{-}C}$ = 12.5 Hz), 139.4 (d, $J_{P\text{-}C}$ = 8.4 Hz), 159.4 (s); ^{31}P NMR (202.35 MHz; THF-d_8; 20 °C; ppm) δ -3.6 (s). MALDI-TOF-MS Found: m/z 918 Calcd. for $C_{60}H_{48}FeO_2P_2$: 918.



Rhodium complex 2: To a CH_2Cl_2 (6 mL) solution of optically active **1** (59.6 mg, 0.0649 mmol) was added di-μ-chlorobis(dicarbonylrhodium) (12.9 mg, 0.0330 mmol), and the resulting mixture was stirred for 5 h. The reaction mixture was filtered off from insoluble fractions, and the filtrate was evaporated to the minimum volume as possible. To the residue was slowly added hexane (10 mL) and the resulting mixture was stood overnight to allow precipitation of rhodium complex **2** (2.75 mg) as red crystalline solid. The resulting mixture was filtered off from crystals of **2**, and the filtrate was evaporated to dryness. The residue was recrystallized from CH_2Cl_2/EtOH (1/9, 20 mL) to allow isolation of additional **2** as red-orange solid (24.6 mg). The combined yield was 39% (0.0252 mmol). ^{1}H NMR (500 MHz; THF-d_8; 20 °C; ppm) δ 3.745 (3H, s), 3.748 (3H, s), 3.99 (1H, s), 4.12 (1H, s), 4.79 (1H, s), 4.94 (1H, s), 4.99–5.01 (2H, m), 6.60 (2H, d, J = 8.5 Hz), 6.63 (2H, d, J = 8.5 Hz), 7.03 (2H, d, J = 8.5 Hz), 7.05 (2H, d, J = 8.5 Hz), 7.09–7.31 (14H, m), 7.37–7.50 (8H, m), 7.99–8.03 (2H, m), 8.06–8.10 (2H, m), 9.36–9.39 (1H, broad), 9.56–9.58 (1H, broad); ^{13}C NMR (125.65 MHz; THF-d_8; 20 °C; ppm) δ 55.3 (s), 73.0 (s), 86.9 (s), 87.2 (s), 88.9 (s), 114.3 (d, $J_{P\text{-}C}$ = 8.4 Hz), 127.4 (m), 128.8 (m), 130.1 (d, $J_{P\text{-}C}$ = 8.4 Hz), 130.6 (s), 131.0 (s), 131.1 (d, $J_{P\text{-}C}$ = 12.5 Hz), 132.3 (s), 132.6 (s), 133.3 (m), 136.7 (m), 137.2–137.6 (m), 139.9 (m), 159.4 (s); ^{31}P NMR (202.35 MHz; THF-d_8; 20 °C; ppm) δ 31.0 (d, $J_{Rh\text{-}P}$ = 131 Hz); MALDI-TOF-MS Found: m/z 1084, Calcd. for $C_{61}H_{48}ClFeO_3P_2Rh$: 1084.

References

1. H. N. Nguyen, X. Huang and S. L. Buchwald, *J. Am. Chem. Soc.* 2003, **125**, 11818.
2. (a) T. Hayashi, N. Tokuyama and K. Inoue, *Org. Lett.* 2004, ***6***, 305. (b) X. Fu, S. Zhang, J. Yin and D. P. Schumacher, *Tetrahedron Lett.* 2002, **43**, 6673.
3. M. Reggelin, S. Dörr, M. Klussmann, M. Schultz and M. Holbach, *Proc. Nat. Acad. Sci.* 2004, **101**, 5461.

3. Optical Resolution of 13

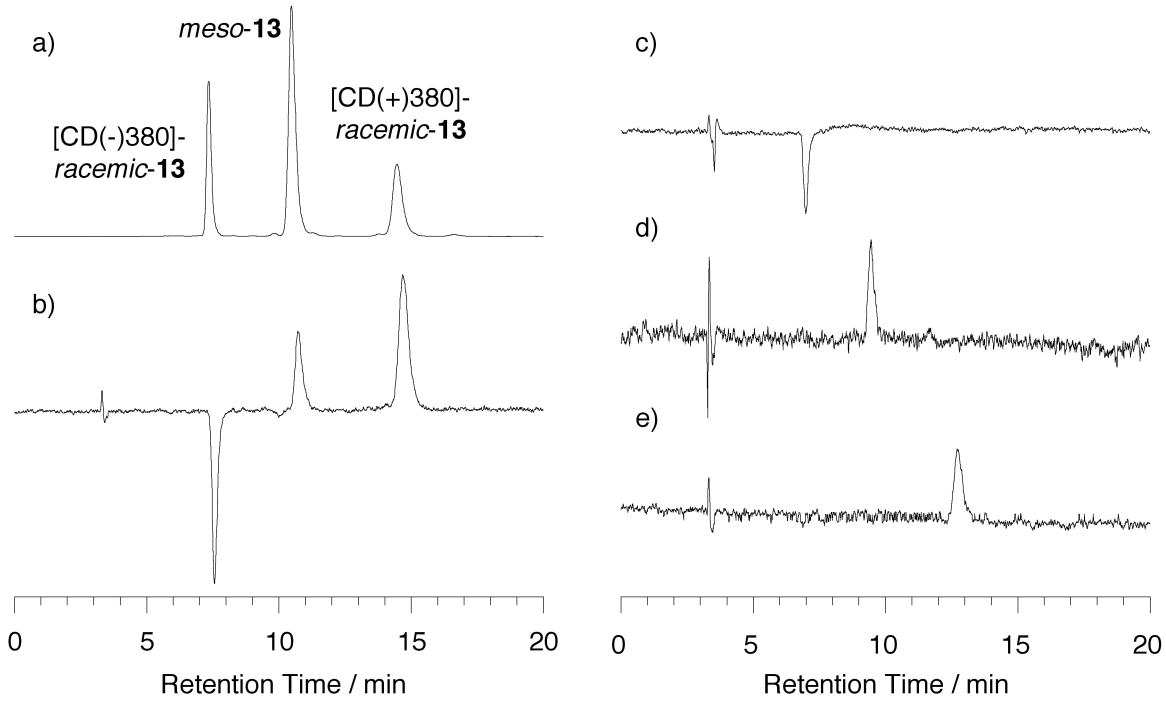


Figure S1. Analytical HPLC (DAICEL: Chiralpak IA®) chromatograms of **13** before and after separation of stereoisomers with hexane/CH_2Cl_2 (2/1) as an eluent at flow rate of 1.0 mL/min. The injection volume was 10 μL. (a) and (b): **13** before separation detected by UV and CD responses at 380 nm, respectively. (c) [CD(-)380]-**13** detected by CD responses at 380 nm. (d) *meso*-**13** detected by UV response at 380 nm. (e) [CD(+)380]-*racemic*-**13** detected by CD signals at 380 nm.

4. X-ray Crystallographic Analysis of Rhodium Complex 2

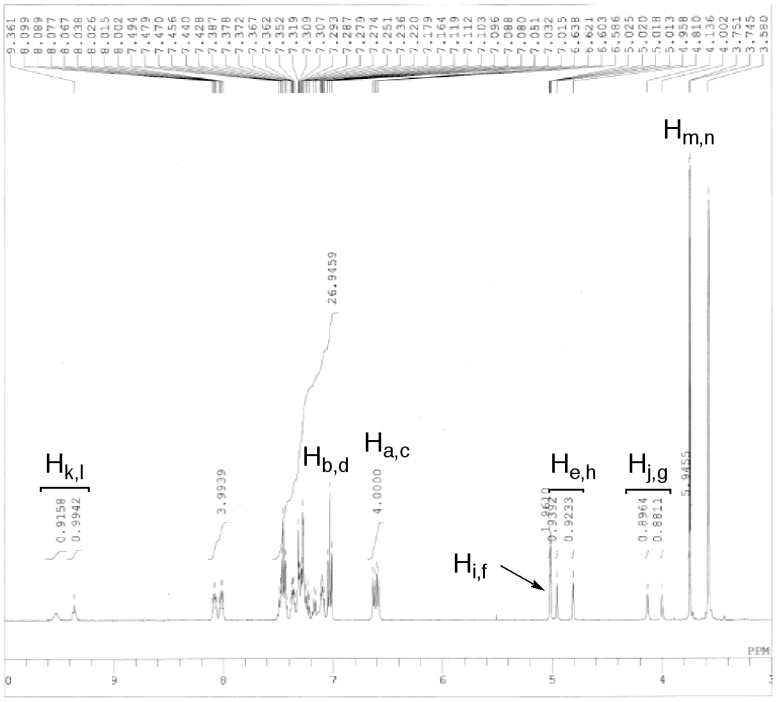
X-ray diffractions peaks were collected by a Rigaku Mercury CCD area detector with graphite monochromated Mo-Ka radiation at 123K. The structure was solved and refined by the program package Crystal Structure (RIGAKU).

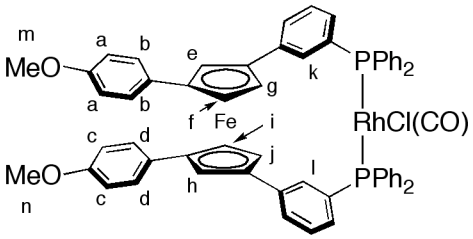
Table S1. Summary of crystallographic data for **2** (CCDC #675848)

Formula weight	1085.20
Empirical formula	$C_{61}H_{48}ClFeO_3P_2Rh$
Temperature	123K
Wavelength	0.71070 Å
Crystal system	Triclinic
Space group	*P*1
Unit cell dimensions	a = 9.356(2) Å b = 10.965(2) Å c = 12.863(3) Å
Volume	1221.6(5) $Å^3$
Z	1
Color of crystal	Colorless
Density (calculated)	1.475 g/cm^3
Absorption coefficient	0.802 mm^{-1}
F(000)	556.00
Crystal size	0.20 × 0.20 × 0.20 mm
Index ranges	-12 <= h <=12, -11 <= k <= 14, -16 <= l <= 16
Reflections collected	9438
Reflections used	7275
Absorption correction	None
Refinement method	Full-matrix least squares on F
Data / parameters	9081/671
Goodness-of-fit on F^2	1.254
Final R Indices [I>Iσ(I)]	0.026
.*R* Indices (all data)	0.026
Largest diff. peak and hole	-0.73, 1.22
Flack parameter	0.060(14)

5. NMR Spectroscopy of Complex 2

a)





b)

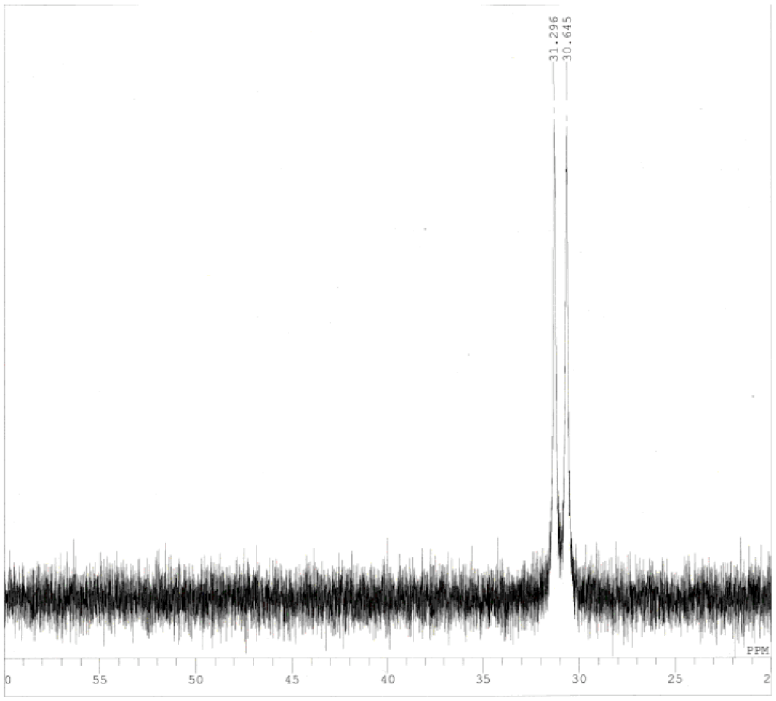


Figure S2. (a) ^{1}H NMR and (b) ^{31}P NMR spectra of rhodium complex **2** in THF-d_8 at room temperature.

6. 2D NMR Spectroscopy of Rhodium Complex 2

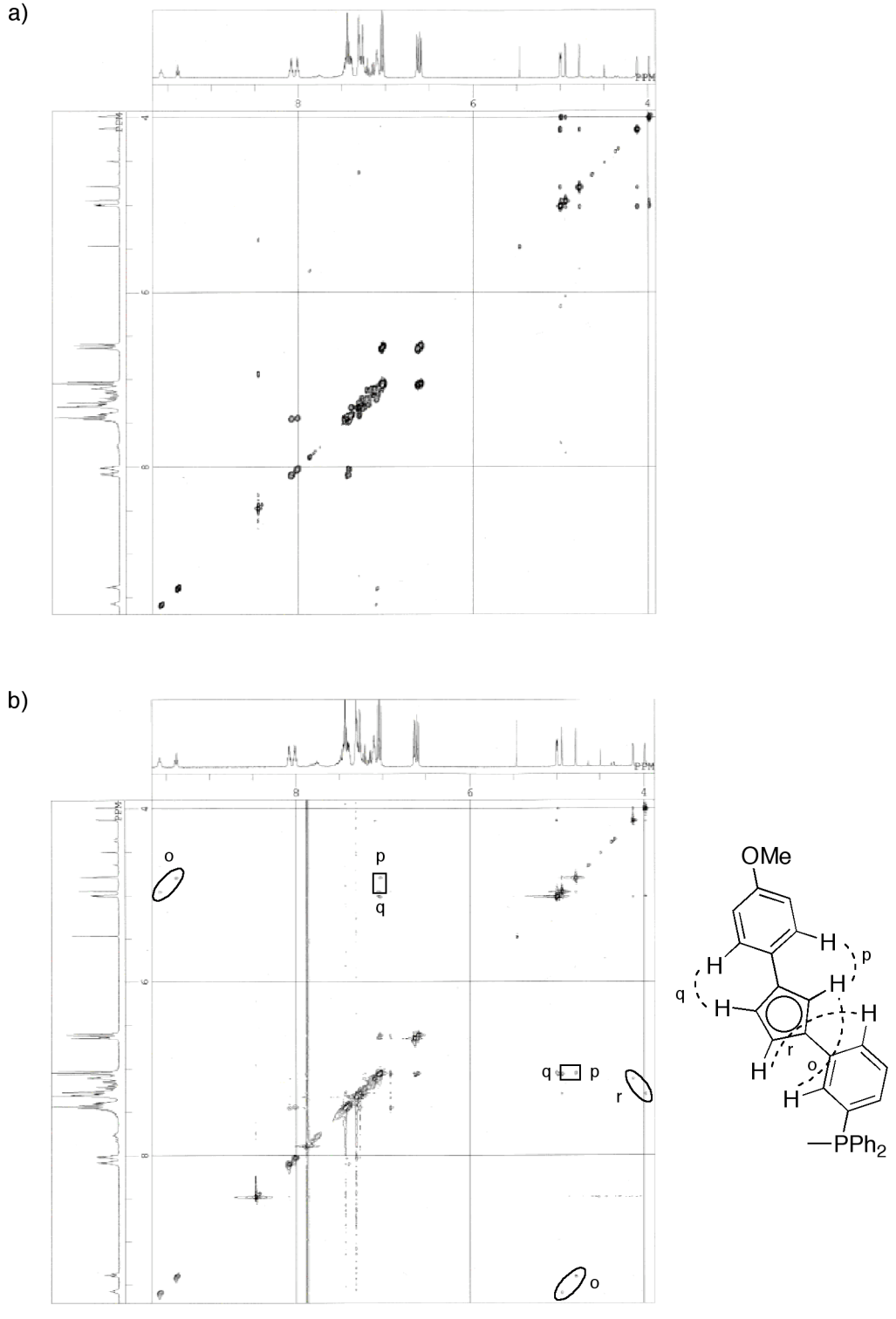
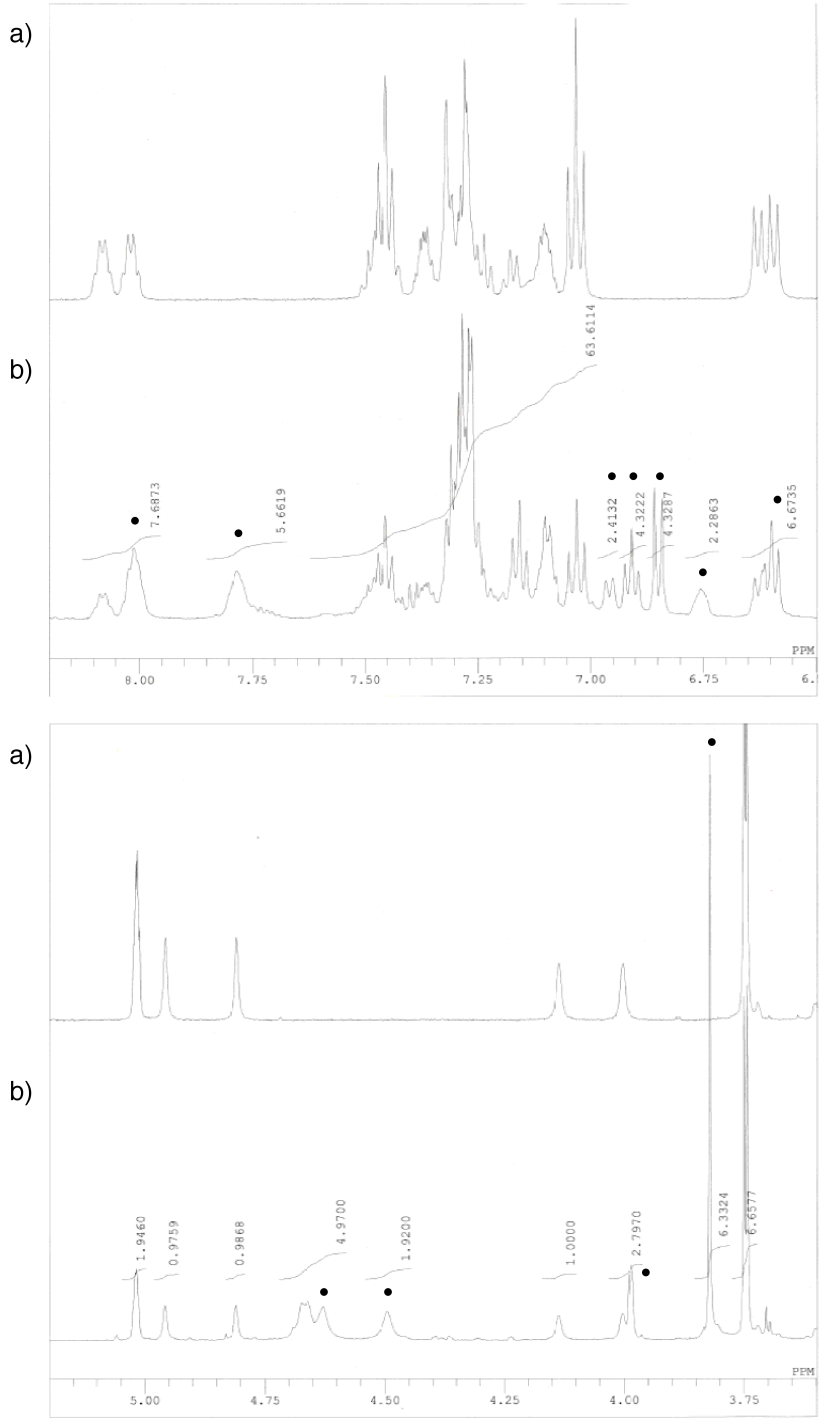


Figure S3. (a) ^{1}H-^{1}H COSY and (b) ^{1}H-^{1}H NOESY spectra of rhodium complex **2** in THF-d_8 at 323K.

7. NMR Spectroscopic Studies on Reaction of 2 with Diphenylphosphoryl Azide



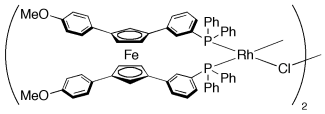


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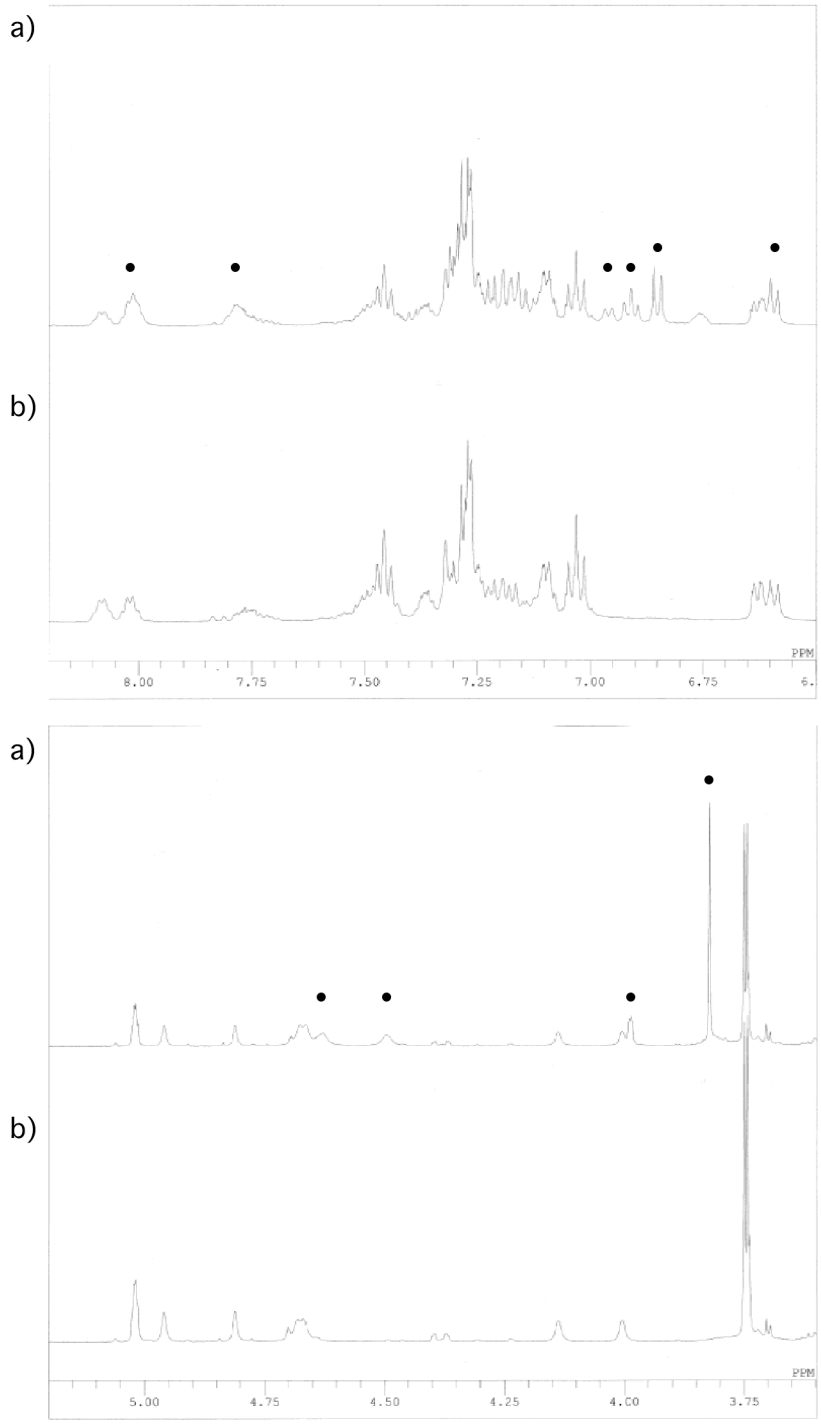
Figure S4. (a) ^{1}H NMR spectrum of rhodium complex **2** in THF-d_8 at room temperature. (b) ^{1}H-NMR spectrum of the mixture **2** (4.01×10^{-3} M) with diphenylphosphoryl azide (1.0 molar amount) in THF-d_8 at room temperature stood after 12.5 h. Selected signals due to dimeric rhodium complex **4** are marked by black dots.

8. NMR Spectroscopic Studies on Reaction of a Mixture of 2 and Diphenylphosphoryl Azide with 3-Phenylpropanal



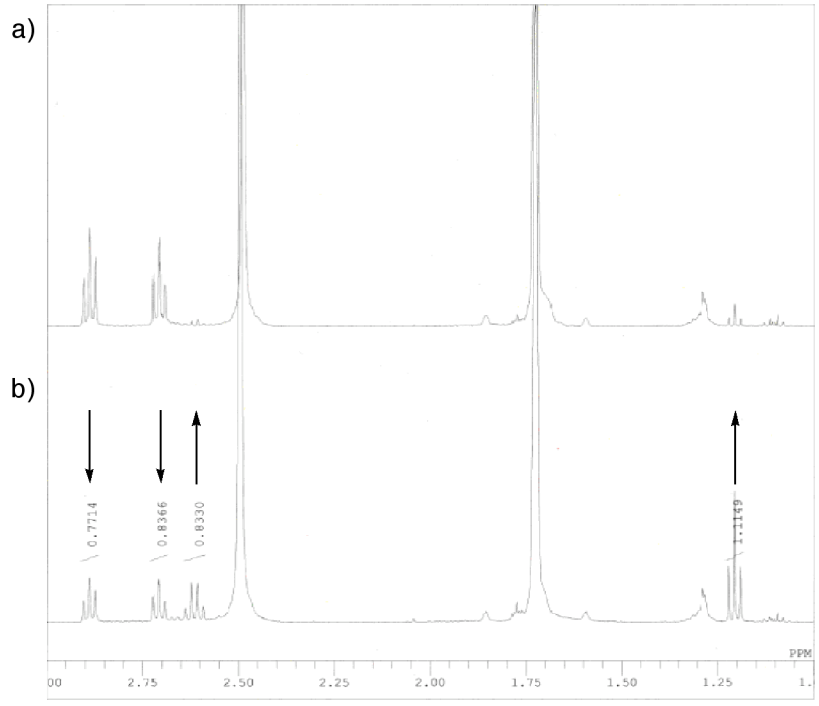


Figure S5. (a) ^{1}H-NMR spectrum of the mixture of **2** (4.01×10^{-3} M), diphenylphosphoryl azide (1.0 molar amount), and 3-phenylpropanal (1.0 molar amount) in THF-d_8 at room temperature stood for 1 h, after addition of 3-phenylpropanal to the mixture of **2** and diphenylphosphoryl azide. Selected signals corresponding to dimeric rhodium complex **4** are marked by black dots. (b) ^{1}H-NMR spectrum of the mixture in THF-d_8 at room temperature, obtained 30 h after addition of 3-phenylpropanal.

9. Decarbonylation of 3-Phenylpropanal by 2 in the Presence of Diphenylphosphoryl Azide

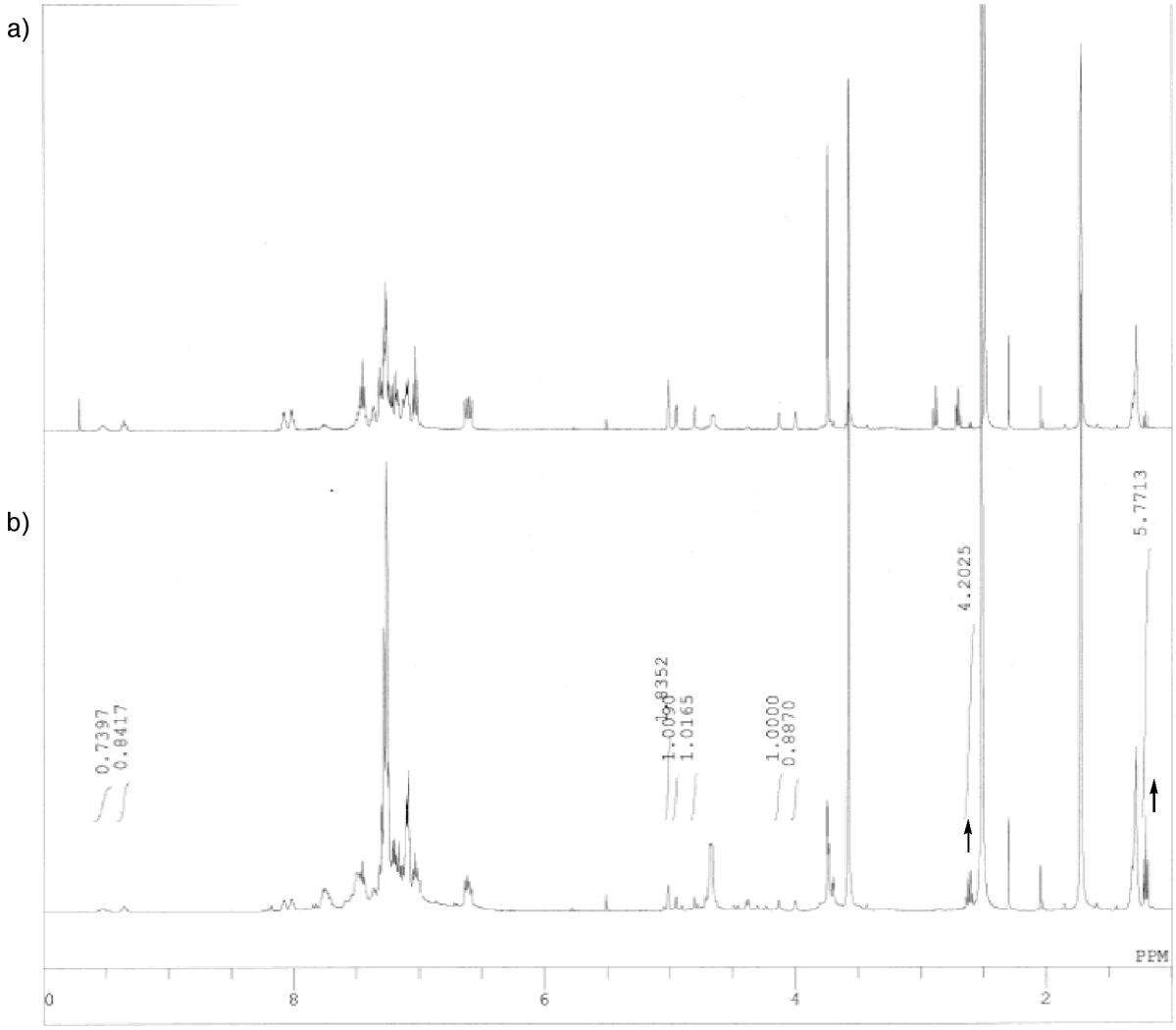


Figure S6. (a) ^{1}H-NMR spectrum of a mixture of **2** (5.00×10^{-3} M), diphenylphosphoryl azide (1.02 molar amount), and 3-phenylpropanal (1.27 molar amount) in THF-d_8 at room temperature measured 12.5 h after mixing. (b) ^{1}H-NMR spectrum of the mixture in THF-d_8 at room temperature, 5 days after further addition of diphenylphosphoryl azide (2.04 molar amount).

10. Reaction of 2 with Diphenylphosphoryl Azide in the Presence of Excess Pyridine

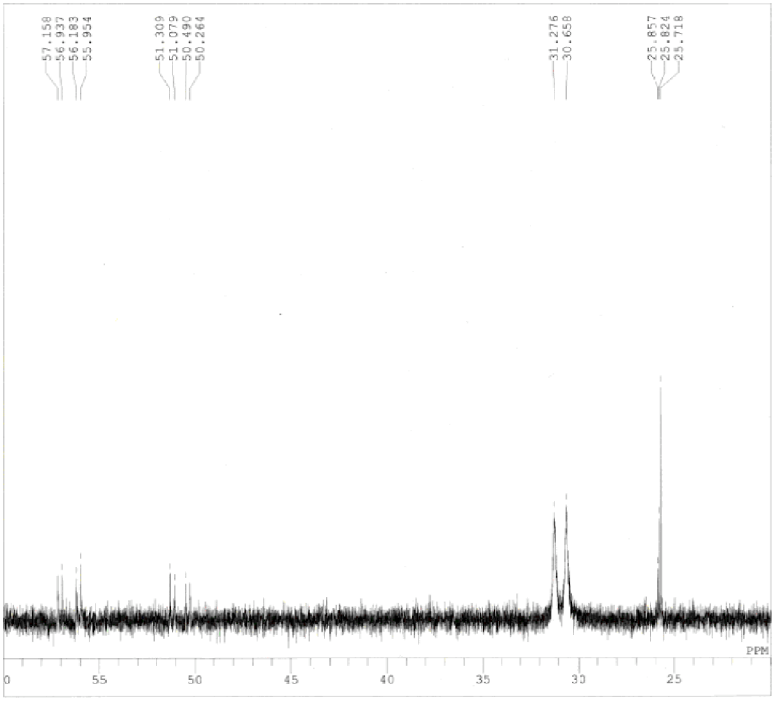


Figure S7. $^{31}P\{^{1}H\}$-NMR spectrum of a mixture of **2** with diphenylphosphoryl azide in THF-d_8 at room temperature, measured 22 h after addition of pyridine (3.0 molar amount).