Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Enantioselective Hydrovinylation via Asymmetric Counteranion-Directed Ruthenium Catalysis

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General: All reactions were carried out under argon atmosphere in oven-dried and/or flame-dried glassware with magnetic stirring. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. All solvents employed in the reactions were distilled from appropriate drying agent prior to use. Organic solutions were concentrated under reduced pressure on a Büchi rotary evaporator. Reactions were monitored by thin layer chromatography using 0.25 mm E. Merck silica gel precoated glass plates (0.25 mm thickness, 60F-254, E. Merck) using UV light to visualize the course of reaction. Flash column chromatography was performed using E. Merck siliga gel 60 (particle size 0.040–0.063 mm). Chemical yields refer to pure isolated substances. ^{1}H and ^{13}C NMR spectra were obtained using either a Bruker DPX-300, DPX-500 or AV-400 spectrometer. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. The following abbreviations were used to designate chemical shift mutiplicities: s = singlet, d = doublet, t = triplet, q = quartet, h = heptet, m = multiplet. MS (EI): Finnigan MAT 8200 (70 eV), ESI-MS: Finnigan MAT 95, accurate mass determinations: Bruker APEX III FT-MS (7 T magnet). The enantiomeric excesses were determined by GC or HPLC analysis employing a chiral stationary phase column specified in the individual experiment, by comparing the samples with the appropriate racemic mixtures.

Experimental Section:

Preparation of Ru complexes:[1]

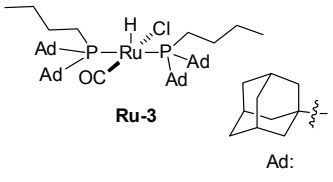
For RuHCl(CO)(PCy_3)$_2$, Ru-1 : The ruthenium complex $[RuCl_2(COD)]_2$ (500 mg, 1.78 mmol) and PCy_3 (1.00 g, 3.56 mmol) were charged in a 50 mL Schlenck tube equipped with a Teflon valve in a glove box. 20 mL of anhydrous ethanol was added to the reaction tube via syringe. The Teflon valve was closed, and the reaction tube was heated for 2 d at 93ºC. A yellowish microcrystalline solid precipitated during the reaction. After cooling the reaction mixture to room temperature, the solid was filtered by cannula under argon, and washed with anhydrous ethanol and anhydrous ether. Recrystallization from methanol/CH_2Cl_2 at -20°C followed by drying under vacuum led to a bright yellow microcrystalline solid.

With phosphines, such as triphenylphosphine, tri-*tert*-butylphosphine, trimesitylphosphine, dppe, di-adamantan-1-yl)(benzyl)phosphine, tributylphosphine, and 1-(dicyclohexylphosphino)-2-(*o*-tolyl)-1H-indole, only Ru black observed at 5-60 min under the same reaction condition.

With phosphines, such as tribenzylphosphine, dicyclohexyl(2,6-diisopropylphenyl)phosphine, dicyclohexyl(2',6'-dimethoxy-[1,1'-biphenyl]-2-yl)phosphine, and dicyclohexyl(1-methyl-2,2 diphenylcyclopropyl)phosphine, microcrystalline solids can be isolated under the same reaction condition. But these complexes are completely inactive for the hydrovinylation.

With triisopropylphosphine and di-adamantan-1-yl)(butyl)phosphine, a microcrystalline solid can be isolated under the same reaction condition. Both are active for the hydrovinylation.

Ru-1[1] and **Ru-2**[2] have previously been reported and their structure is confirmed by comparison with the published spectral data. The characterization data for the newly synthesized compound **Ru-3** and its ^{1}H NMR and ^{31}P NMR spectra are given below.



Ru-3

Ad:

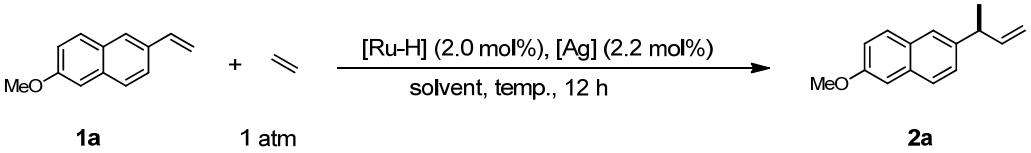
Ru-3: pale-green microcrystalline solid.

^{1}H-NMR (500 MHz, CD_2Cl_2): δ = -24.99 (t, J_{PH} = 17 Hz, Ru-H), 0.83-0.86 (m, 6H), 1-51-1.91 (m, 52H), 2.11-2.21 (m, 20H); **^{31}P-NMR** (200 MHz, CD_2Cl_2): δ = 50.46 (s).

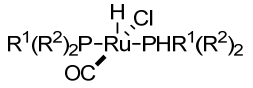
Typical Reaction Procedure for the hydrovinylation: To a flame-dried Schlenck tube charged with magnetic stir bar, was added **Ru-1** (2.9 mg, 0.004 mmol, 2.0 mol%), and **Ag-1** (3.8 mg, 0.0044 mol, 2.2 mol%) in 1.0 mL of dried benzene. The resulting suspension was stirred at room temperature under argon for 1 h, followed by the addition of 1.0 mL dried benzene solution containing **1a** (36.8 mg, 0.2 mmol). Ethylene was bubbled into the reaction flask, and a balloon was filled to maintain an atmosphere of ethylene. The reaction mixture was stirred for 12 h and then opened to air and filtered through a small pipette packed with silica gel to remove the metal catalyst. The product was then passed through another silica-packed pipette column, washed with hexane or CH_2Cl_2 or EA, and the solvent was removed via evaporation.

Ag-1 was dried at 60°C under $1.2x10^{-1}$ mbar for overnight before use.

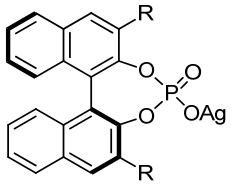
The effects of Ru-catalysts and Ag-salts:



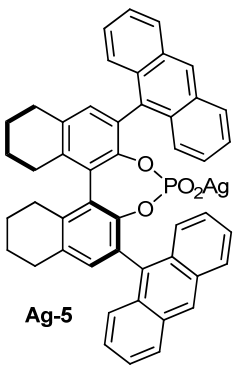
1a 1 atm **2a**



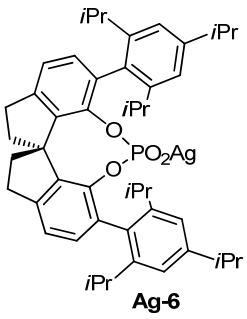
Ru-1: $R^1 = R^2$ = Cy
Ru-2: $R^1 = R^2 = {}^i$Pr
Ru-3: R^1 = *n*-Butyl, R^2 = 1-adamantyl



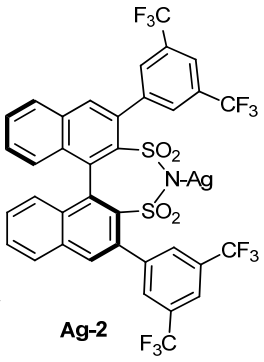
Ag-1: R = 2,4,6-(*i*Pr)$_3$C$_6$H$_2$
Ag-3: R = Anthr-9-yl
Ag-4: R = 4-Anthr-9-yl-2,6-(*i*Pr)$_2$C$_6$H$_2$



Ag-5



Ag-6



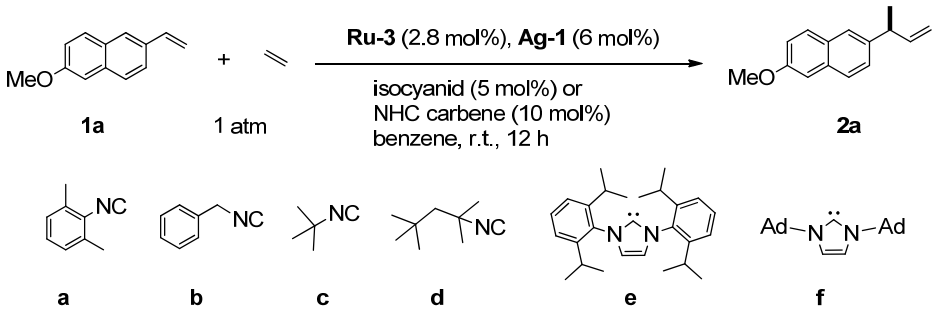
Ag-2

entry[a]	Ru-cat.	Ag salt	conv. (%)[b]	selectivity (%)[b]	er[c]
1	**Ru-1**	**Ag-1**	> 99	> 99	73:27
2		**Ag-2**	n.r.	-	-
3		**Ag-3**	> 99	> 99	75:25
4		**Ag-4**	97	98	74:26
5		**Ag-5**	95	96	74:26
6		**Ag-6**	97	97	74:26
7	**Ru-2**	**Ag-1**	> 99	> 99	70:30
8	**Ru-3**	**Ag-1**	> 99	> 99	77:23

[a] Reaction conditions: **1a** (0.2 mmol), ethylene (1 atm), [**Ru**] (2.0 mol%), [**Ag**] (2.2 mol%), benzene (1 mL), 22 °C, 12 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by HPLC.

The effects of isocyanide and NHC carbene:

Reaction Procedure: In a nitrogen-filled glovebox, to a flame-dried Schlenck tube charged with magnetic stir bar was added **Ru-3** (5.0 mg, 0.0063 mmol, 2.8 mol%), and isocyanid (5.0 mol%) or NHC carbene (10 mol%) in 1.0 mL of dried benzene. The resulting suspension was stirred at room temperature under argon for 1 h. The color of the reaction mixture changed from pale-green to white. Then **Ag-1** (10.4 mg, 0.024 mol, 6.0 mol%) was added and the mixture was stirred at room temperature for another 1 h to result in a suspension, followed by the addition of 0.5 mL dried benzene solution containing **1a** (36.8 mg, 0.2 mmol). Then the Schlenck tube as removed from the glove box and Ethylene was bubbled into the reaction flask, and a balloon was filled to maintain an atmosphere of ethylene. The suspension was stirred for 12 h and then opened to air and filtered through a small pipette packed with silica gel to remove the metal catalyst. The product was then passed through another silica-packed pipette column (hexane), and the solvent was removed via rotary evaporator.



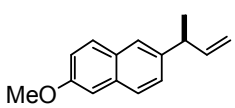
entry[a]	additive	conv.(%)[b]	select. (%)[b]	e.r.[c]
1	**-**	> 99	> 99	77:23
2	**a**	15	> 99	73:27
3	**b**	12	> 99	72:28
4	**c**	16	> 99	75:25
5	**d**	19	> 99	72:28
6	**e**	15	> 99	71:29
7	**f**	14	> 99	72:28

[a] Reaction conditions: **1a** (0.2 mmol), ethylene (1 atm), **Ru-3** (2.8 mol%), **Ag-1** (6 mol%), benzene (1.5 mL), 22 °C, 12 h. [b] Determined by ^{1}H NMR analysis of the crude reaction mixture. [c] Determined by HPLC.

Preparation of racemic products: In a nitrogen-filled glovebox, a 10 mL reaction flask equipped with a stir bar was charged with **Ru-1** (0.004 mmol) and AgOTf (0.006 mmol). The reaction mixture was removed from the glovebox, purged with argon, and charged with CH_2Cl_2. The reaction mixture was stirred for 1 h at room temperature followed by the addition of olefin (0.2 mmol) under a stream of argon. Ethylene was bubbled into the reaction flask, and a balloon was filled to maintain an atmosphere of ethylene. The reaction mixture was stirred for 6 h and then opened to air and filtered through a small pipette packed with silica gel (silicycle 60 Å ultrapure) to remove the metal catalyst. The product was then passed through another silica-packed pipette column (hexane), and the solvent was removed via rotary evaporator. **NMR** results showed the conversions and selectivity were in 55-80% and 90-98%, respectively.

Substrates, hydrovinylation product, and isomerized product are inseparable.

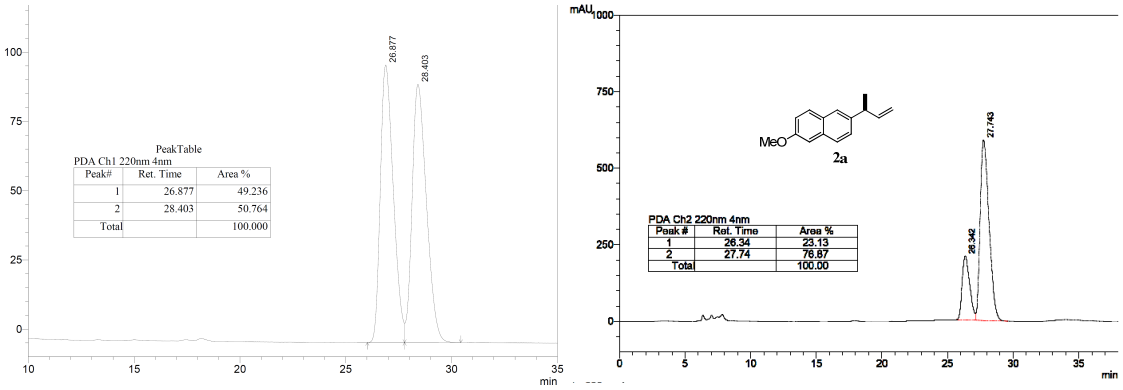
Compounds **2a**,[3] **2b**,[3] **2c**,[4] **2d**,[5] **2e**,[3] and **2f**[6] have previously been reported and their structure is confirmed by comparison with the published spectral data. ^{1}H NMR data and spectra are given below.

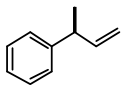


2a

(*S*)-2-(but-3-en-2-yl)-6-methoxynaphthalene (2a): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.43 (d, *J* = 7.0 Hz, 3H), 3.60 (m, 1H), 3.91 (s, 3H), 5.05-5.11 (m, 1H), 6.04-6.11 (m, 1H), 7.13 (t, 2H), 7.33 (m, 1H), 7.57 (s, 1H), 7.67-7.70 (m, 2H). The enantiomeric ratio was determined to be 23:77 by

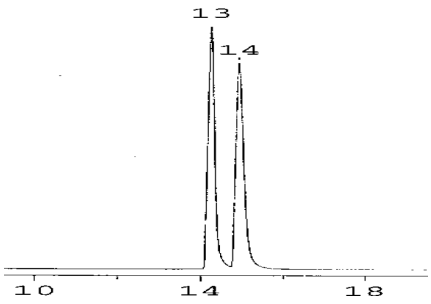
HPLC using chiral Chiralcel OJ-H column 250 mm, 4.6 mm i.D. (96:4 *n*-heptane / *i*-PrOH, 0.5 ml/min). Major enantiomer: t_R= 27.74 min, minor enantiomer: t_R = 26.34 min.



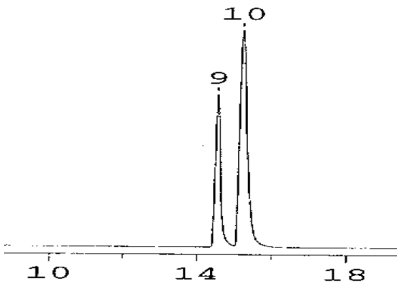


2b

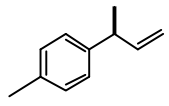
(*S*)-but-3-en-2-ylbenzene (2b): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.37 (d, *J* = 7.0 Hz, 3H), 3.46-3.49 (m, 1H), 5.02-5.07 (m, 2H), 5.98-6.05 (m, 1H), 7.20-7.24 (m, 2H), 7.29-7.32 (m, 3H). The enantiomeric ratio was determined to be 32:68 by GC using chiral BGB-178/BGB-15 0.25/0.25df G/481 column 30m. Major enantiomer: t_R = 15.11 min, minor enantiomer: t_R = 14.48 min.



No.	min.	area-%
13	14.15	49.4
14	14.83	50.6



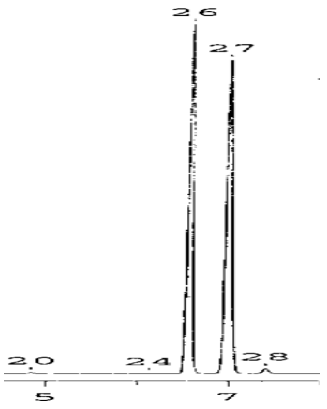
No.	min.	area-%
9	14.48	31.7
10	15.11	68.3

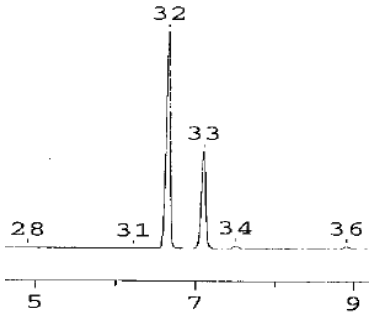


2c

(*S*)-1-(but-3-en-2-yl)-4-methylbenzene (2c): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 7.0 Hz, 3H), 2.32 (s, 3H), 3.40-3.46 (m, 1H), 5.00-5.06 (m, 2H), 5.96-6.03 (m, 1H), 7.09-7.13 (m, 4H). The enantiomeric

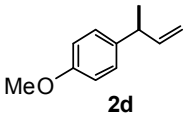
ratio was determined to be 32:68 by GC using chiral Lipodex G 0.25/df G/566 column 25m. Major enantiomer: t_R = 6.63 min, minor enantiomer: t_R = 7.09 min.





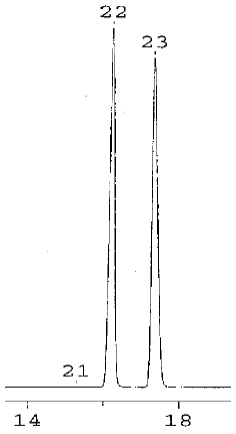
No.	min.	area-%
26	6.55	48.4
27	6.96	51.6

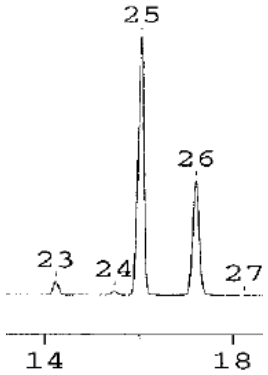
No.	min.	area-%
32	6.63	67.1
33	7.09	32.9



2d

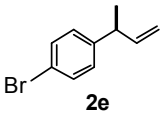
(*S*)-1-(but-3-en-2-yl)-4-methoxybenzene (2d): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.33 (d, *J* = 7.0 Hz, 3H), 3.40-3.45 (m, 1H), 3.79 (s, 3H), 5.00-5.05 (m, 2H), 5.95-6.02 (m, 1H), 6.84-6.86 (dd, *J* = 2.5 Hz, 6.5 Hz, 2H), 7.12-7.14 (dd, *J* = 2.0 Hz, 6.5 Hz, 2H). The enantiomeric ratio was determined to be 32:68 by GC using chiral Lipodex G 0.25/df G/566 column 25m. Major enantiomer: t_R = 16.02 min, minor enantiomer: t_R = 17.20 min.





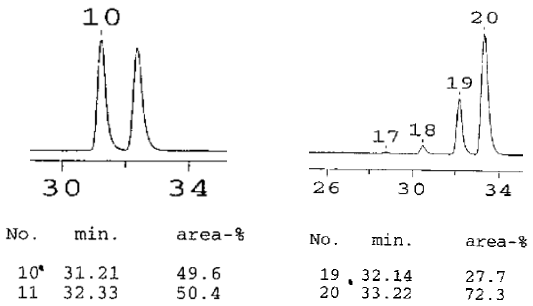
No.	min.	area-%
22	16.22	49.9
23	17.32	50.1

No.	min.	area-%
25	16.02	67.2
26	17.20	32.8



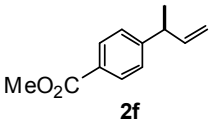
2e

(*S*)-1-bromo-4-(but-3-en-2-yl)benzene (2e): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.34 (d, *J* = 7.5 Hz, 3H), 3.40-3.46 (m, 1H), 5.02-5.06 (m, 2H), 5.92-5.99 (m, 1H), 7.08 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H). The enantiomeric ratio was determined to be 28:72 by GC using chiral BGB-178/BGB-15 0.25/0.25df G/481 column 30m. Major enantiomer: t_R = 33.22 min, minor enantiomer: t_R = 32.14 min.



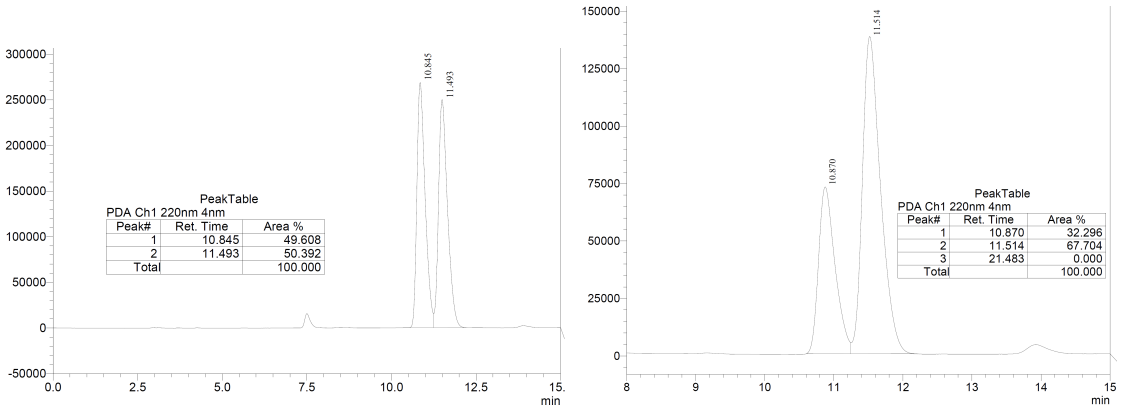
No.	min.	area-%
10	31.21	49.6
11	32.33	50.4

No.	min.	area-%
19	32.14	27.7
20	33.22	72.3



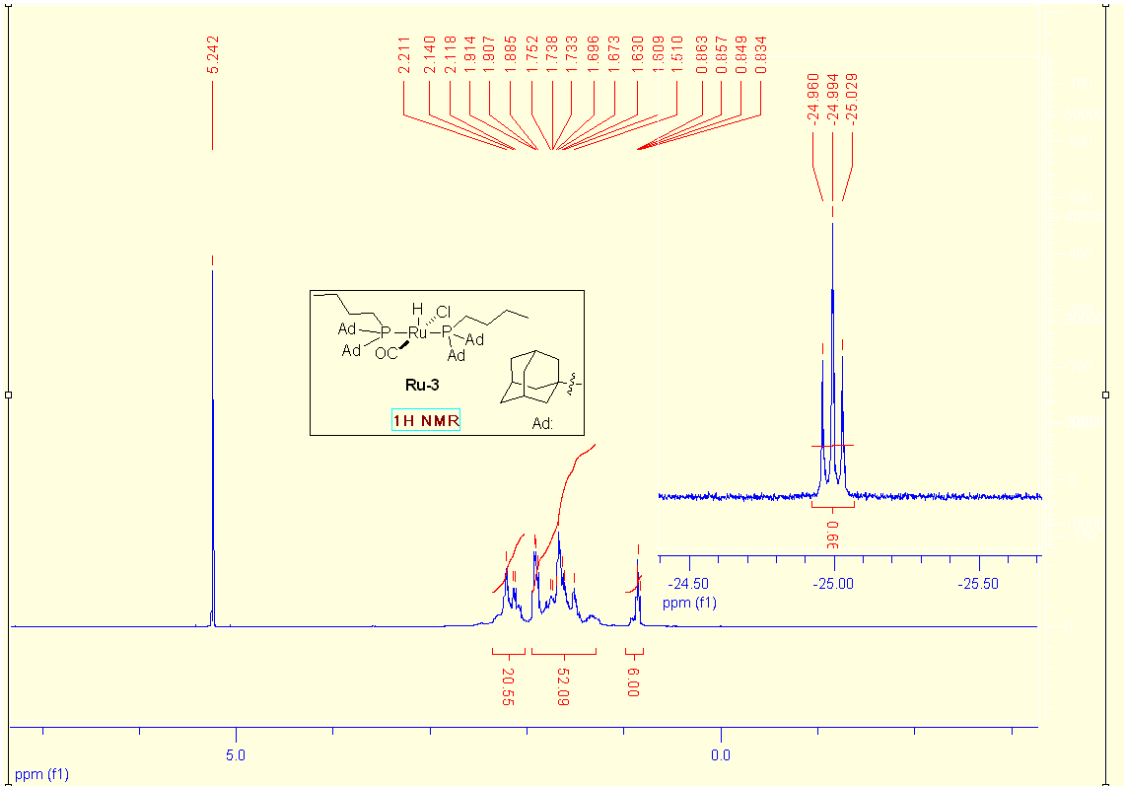
2f

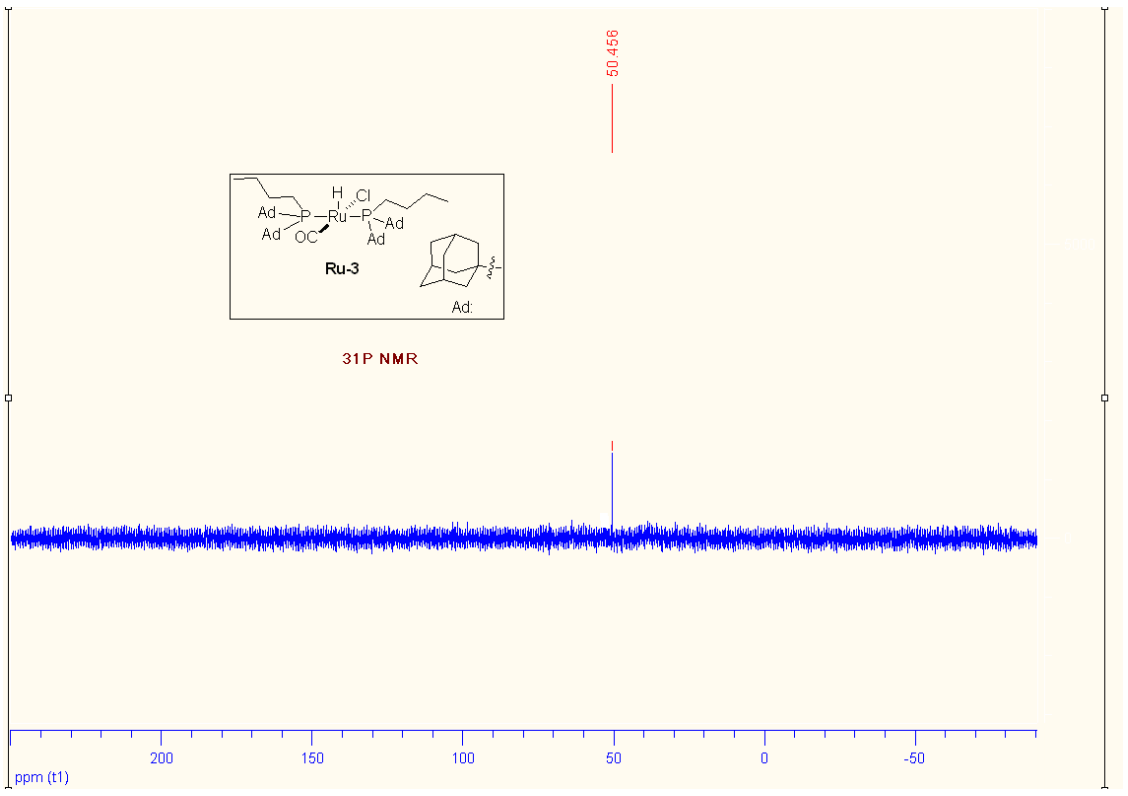
(*S*)-methyl 4-(but-3-en-2-yl)benzoate (2f): ^{1}H-NMR (500 MHz, $CDCl_3$): δ = 1.35 (d, *J* = 7.0 Hz, 3H), 2.29 (s, 3H), 3.45-3.48 (m, 1H), 5.02-5.07 (m, 2H), 5.95-6.01 (m, 1H), 7.01 (d, *J* = 8.5 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H). The enantiomeric ratio was determined to be 23:77 by HPLC using chiral Chiralcel OJ-H column 250 mm, 4.6 mm i.D. (98:2 *n*-heptane / *i*-PrOH, 1.0 ml/min). Major enantiomer: t_R= 11.51 min, minor enantiomer: t_R = 10.87 min.

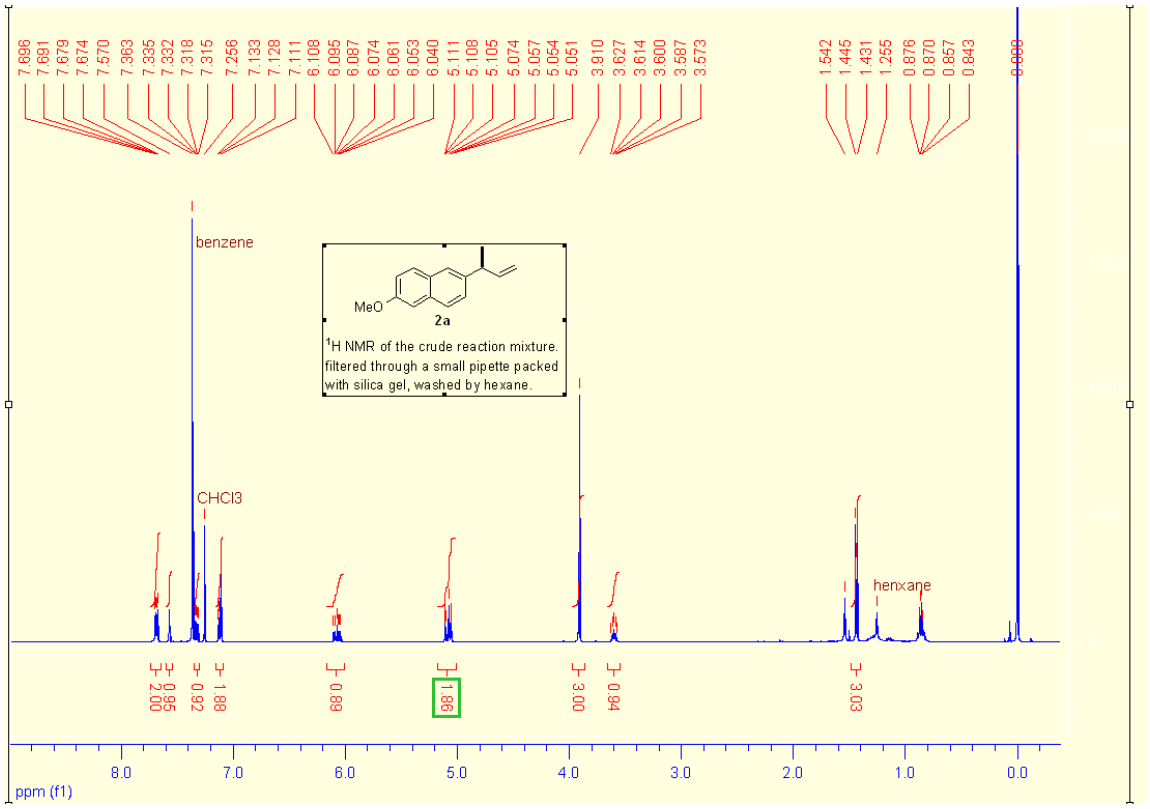


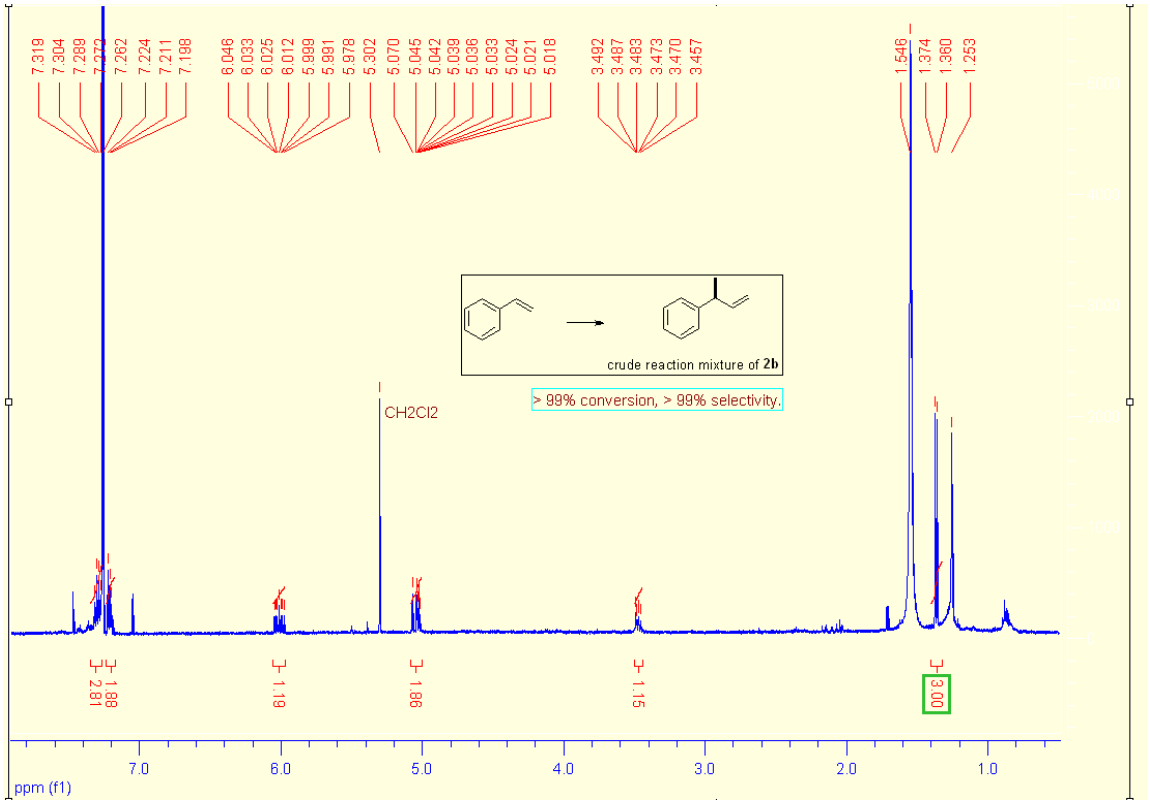
(1) C. S. Yi, D. W. Lee, Y. Chen, *Organometallics* 1999, **18**, 2043-2045.
(2) M. A. Esteruelas, H. Werner, *J. Organomet. Chem.* 1986, **303**, 221-231.
(3) N. Lassauque, G. Franciò, W. Leitner, *Adv. Synth. Catal.* 2009, **351**, 3133-3138.
(4) B. Saha, T. V. RajanBabu, *J. Org. Chem.* 2007, **72**, 2357-2363.
(5) C. R. Smith, T. V. RajanBabu, *Org. Lett.*, 2008, **10**, 1657-1659.
(6) Y. Yamamoto, S. Takada, N. Miyaura, *Organometallics*, 2009, **28**, 152-160.

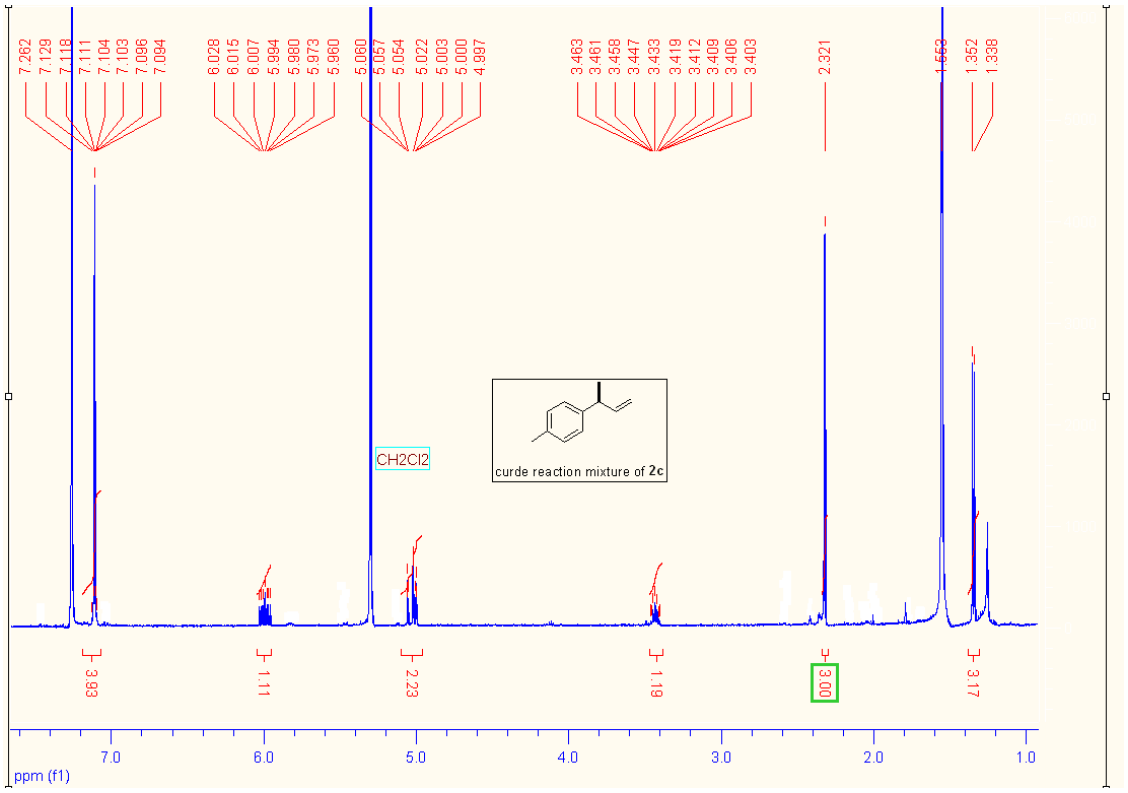
NMR-Spectra:

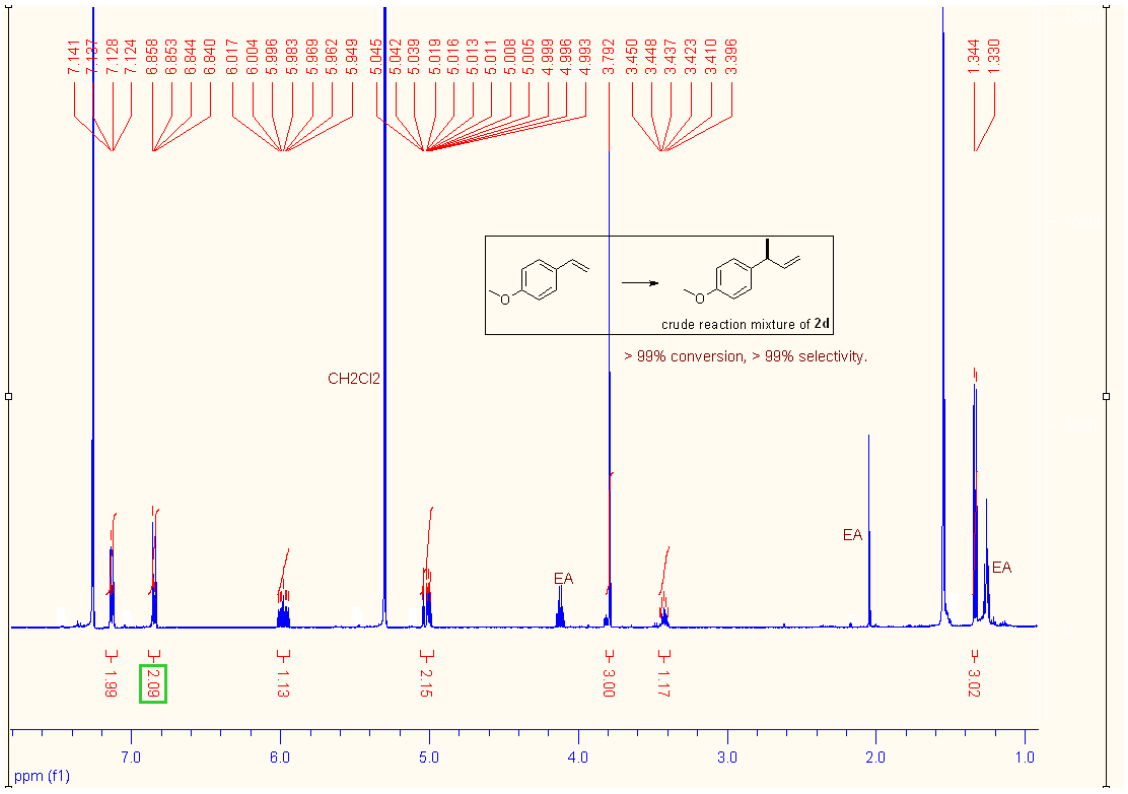

5.242
2.211
2.140
2.118
1.914
1.907
1.885
1.752
1.738
1.733
1.696
1.673
1.630
1.609
1.510
0.863
0.857
0.849
0.834
-24.960
-24.994
-25.029
Ru-3
1H NMR
Ad:
20.55
52.09
6.00
39.0
-24.50
-25.00
-25.50
ppm (f1)
5.0
0.0
ppm (f1)

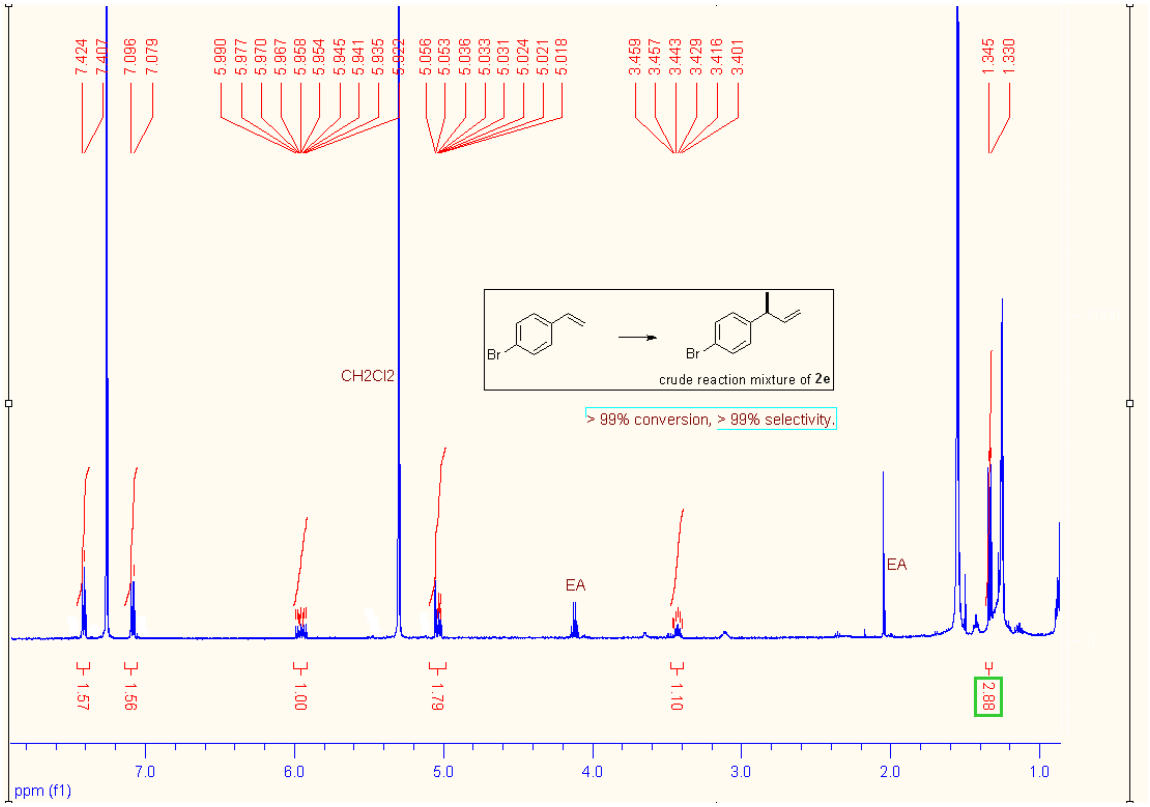

50.456
Ru-3
Ad:
31P NMR
200
150
100
50
0
-50
ppm (t1)

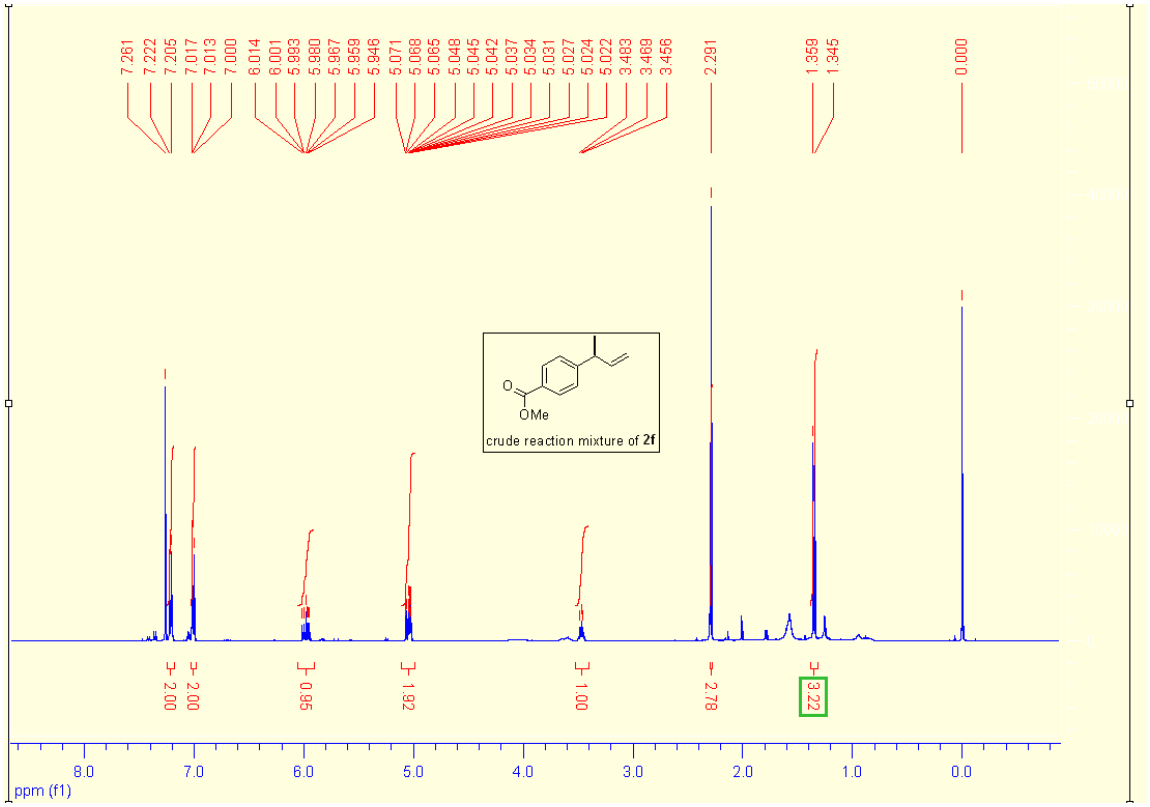

benzene
MeO
2a
^{1}H NMR of the crude reaction mixture. filtered through a small pipette packed with silica gel, washed by hexane.
CHCl3
henxane
ppm (f1)


crude reaction mixture of 2b
> 99% conversion, > 99% selectivity.
CH2Cl2
ppm (f1)

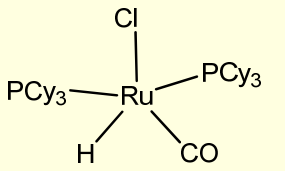

7.262
7.129
7.118
7.111
7.104
7.103
7.096
7.094
6.028
6.015
6.007
5.994
5.980
5.973
5.960
5.060
5.057
5.054
5.022
5.003
5.000
4.997
3.463
3.461
3.458
3.447
3.433
3.419
3.412
3.409
3.406
3.403
2.321
1.563
1.352
1.338
CH2Cl2
curde reaction mixture of 2c
3.83
1.11
2.23
1.18
3.00
3.17
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


7.141
7.137
7.128
7.124
6.858
6.853
6.844
6.840
6.017
6.004
5.986
5.983
5.969
5.962
5.949
5.045
5.042
5.038
5.019
5.016
5.013
5.011
5.008
5.005
4.999
4.996
4.993
3.792
3.450
3.448
3.437
3.423
3.410
3.396
1.344
1.330
crude reaction mixture of 2d
> 99% conversion, > 99% selectivity.
CH2Cl2
EA
EA
EA
1.99
2.00
1.13
2.15
3.00
1.17
3.02
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


7.424
7.407
7.096
7.079
5.990
5.977
5.970
5.967
5.958
5.954
5.945
5.941
5.935
5.922
5.056
5.053
5.036
5.033
5.031
5.024
5.021
5.018
3.459
3.457
3.443
3.428
3.416
3.401
1.345
1.330
CH2Cl2
EA
EA
Br
Br
crude reaction mixture of 2e
> 99% conversion, > 99% selectivity.
1.57
1.56
1.00
1.79
1.10
2.88
7.0
6.0
5.0
4.0
3.0
2.0
1.0
ppm (f1)


7.261
7.222
7.205
7.017
7.013
7.000
6.014
6.001
5.993
5.980
5.967
5.959
5.946
5.071
5.068
5.065
5.048
5.045
5.042
5.037
5.034
5.031
5.027
5.024
5.022
3.483
3.469
3.456
2.291
1.359
1.345
0.000
O
OMe
crude reaction mixture of 2f
2.00
2.00
0.95
1.82
1.00
7.78
3.22
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

^{31}P-NMR:



Before recrystallization

^{31}P-NMR:

After one recrystalization from $MeOH/CH_2Cl_2$