

Supporting Information for

Cationic Ruthenium Alkylidene Catalysts Bearing Phosphine Ligands

Koji Endo and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

List of Figures and Tables

Figure S1. ^1H NMR spectrum of 8a	S2
Figure S2. ^{13}C NMR spectrum of 8a	S2
Figure S3. ^{31}P NMR spectrum of 8a	S3
Figure S4. ^1H NMR spectrum of 8b	S3
Figure S5. ^{13}C NMR spectrum of 8b	S4
Figure S6. ^{31}P NMR spectrum of 8b	S8
Figure S7. ^1H NMR spectrum of 8c	S5
Figure S8. ^{13}C NMR spectrum of 8c	S5
Figure S9. ^{31}P NMR spectrum of 8c	S6
Figure S10. ^1H NMR spectrum of 8d	S6
Figure S11. ^{13}C NMR spectrum of 8d	S7
Figure S12. ^{31}P NMR spectrum of 8d	S7
Figure S13. ^1H NMR spectrum of 11a	S8
Figure S14. ^{13}C NMR spectrum of 11a	S8
Figure S15. ^{31}P NMR spectrum of 11a	S9
Figure S16. ^1H NMR spectrum of 11b	S9
Figure S17. ^{13}C NMR spectrum of 11b	S10
Figure S18. ^{31}P NMR spectrum of 11b	S10
Table S1. Data for RCM of 12 by 7	S11
Table S2. Data for RCM of 12 by 8a	S11
Table S3. Data for RCM of 12 by 8b	S12
Table S4. Data for RCM of 12 by 8c	S13
Table S5. Data for RCM of 12 by 11a	S14
Table S6. GC response factors and retention times	S15
Table S7. Data for CM of 14 and 15 by 7	S16
Table S8. Data for CM of 14 and 15 by 8a	S16
Table S9. Data for CM of 14 and 15 by 8b	S17
Table S10. Data for CM of 14 and 15 by 11a	S17
Table S11. Data for CM of 14 and 15 by 11b	S18

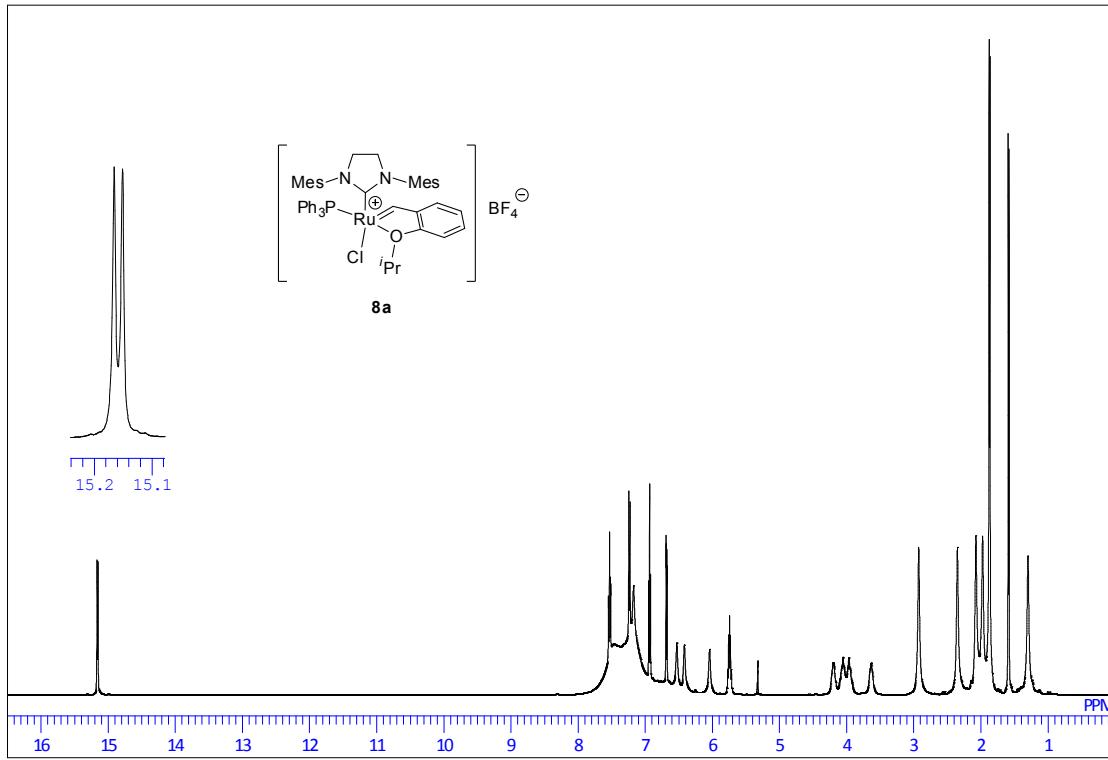


Figure S1. ^1H NMR spectrum of **8a** (CD_2Cl_2 , 500 MHz).

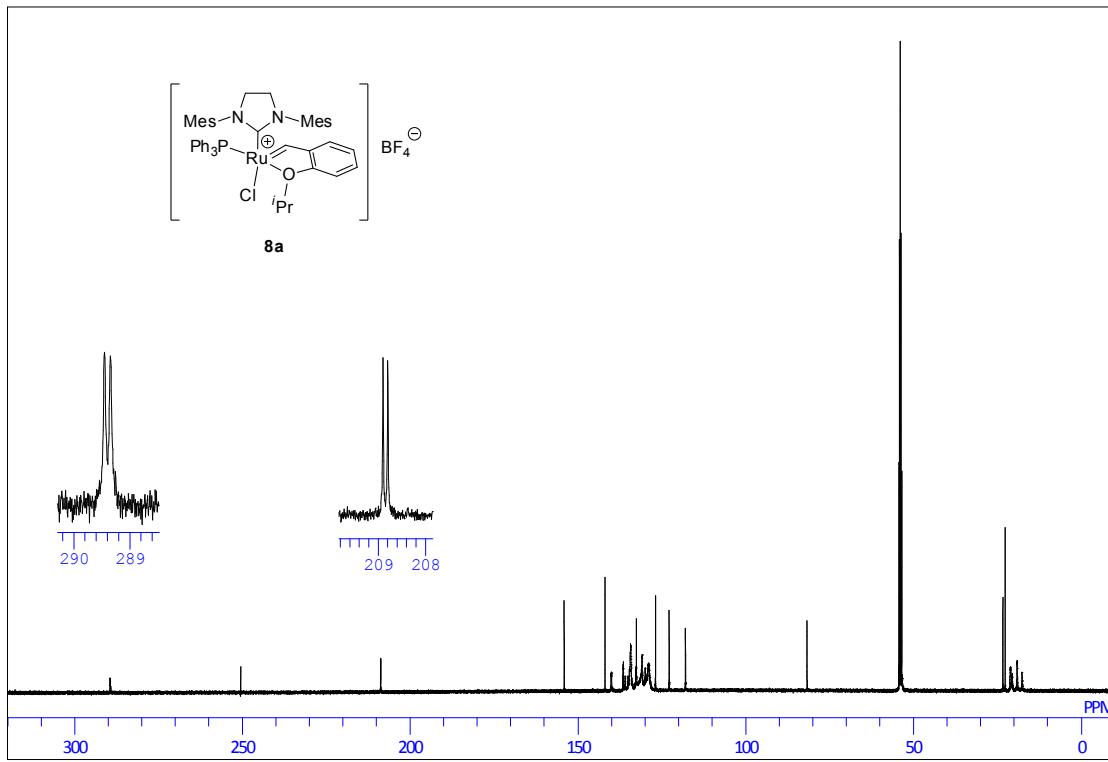


Figure S2. ^{13}C NMR spectrum of **8a** (CD_2Cl_2 , 125.7 MHz).

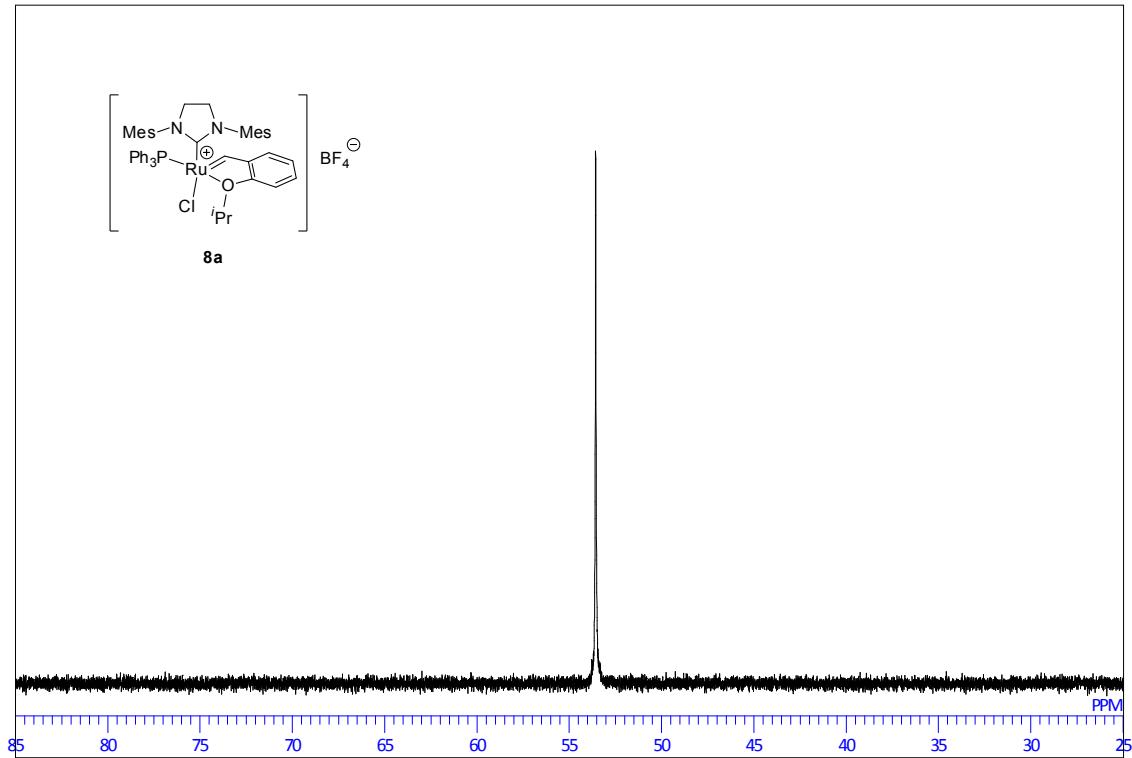


Figure S3. ^{31}P NMR spectrum of **8a** (CD_2Cl_2 , 121.4 MHz).

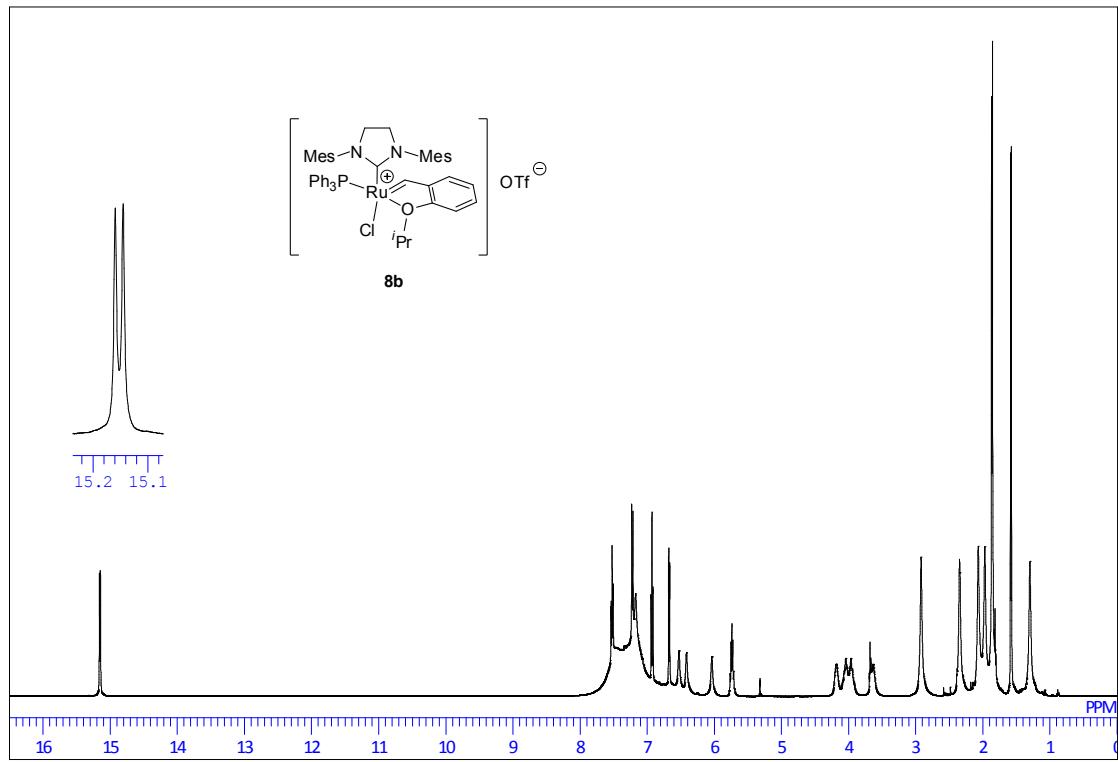


Figure S4. ^1H NMR spectrum of **8b** (CD_2Cl_2 , 500 MHz).

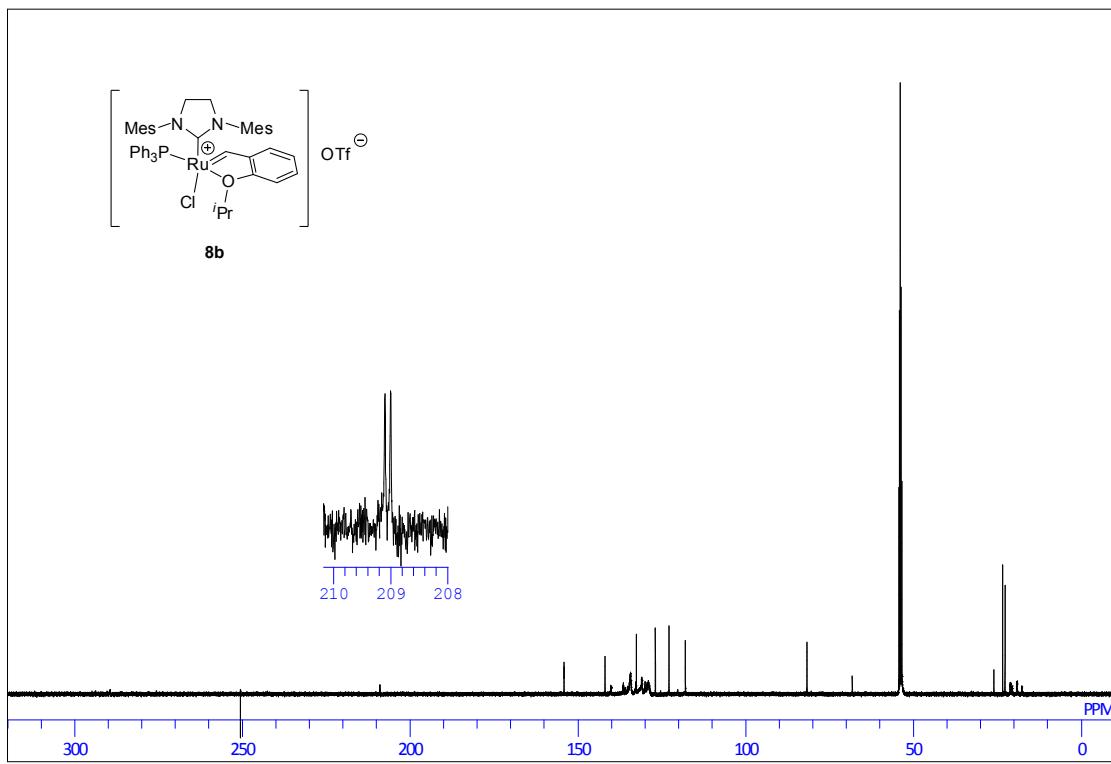


Figure S5. ^{13}C NMR spectrum of **8b** (CD_2Cl_2 , 125.7 MHz).

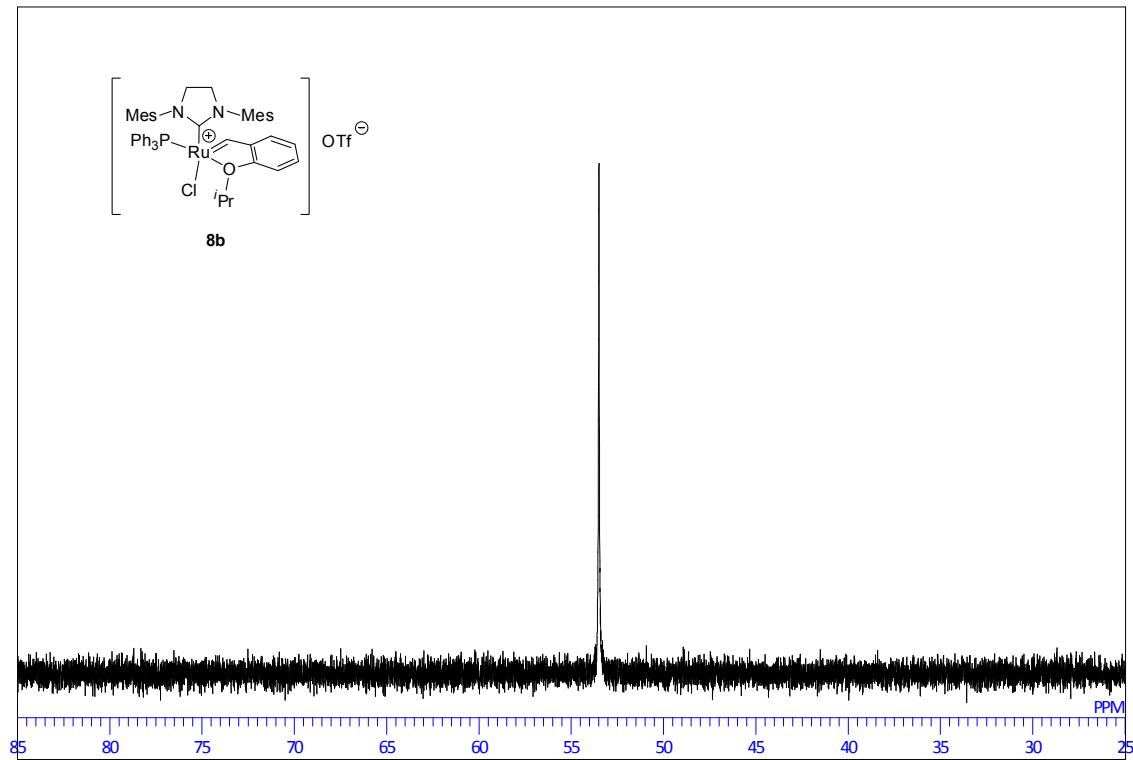


Figure S6. ^{31}P NMR spectrum of **8b** (CD_2Cl_2 , 121.4 MHz).

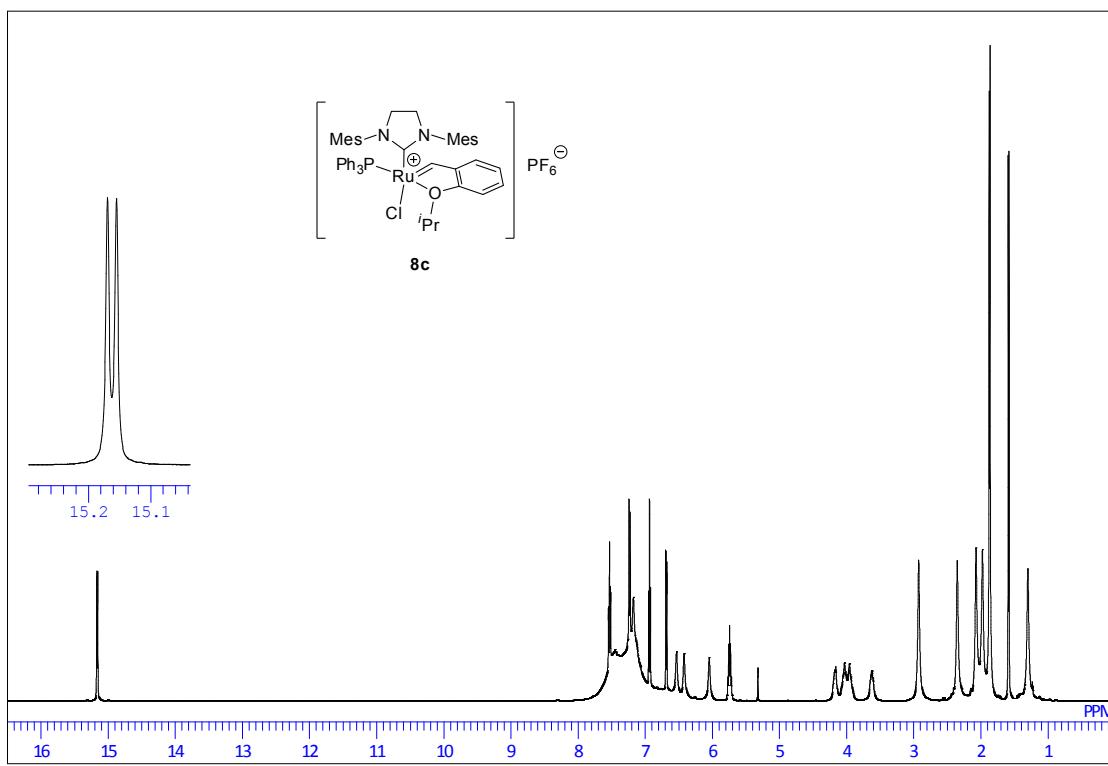


Figure S7. ^1H NMR spectrum of **8c** (CD_2Cl_2 , 500 MHz).

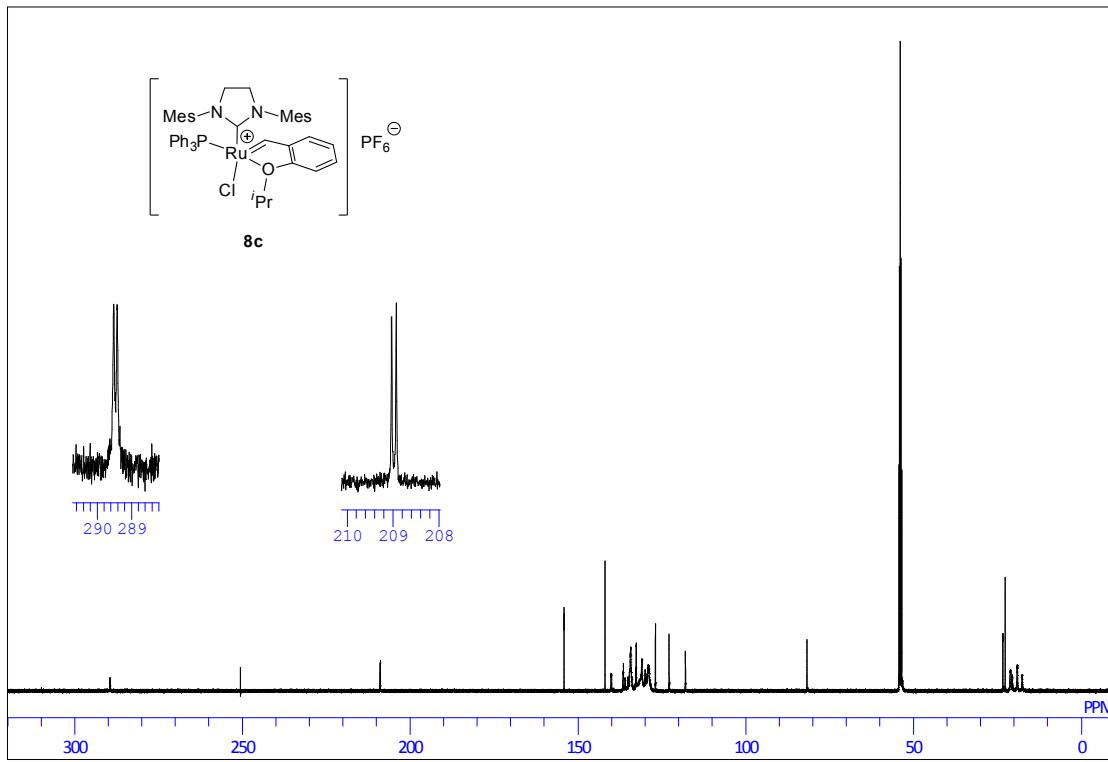


Figure S8. ^{13}C NMR spectrum of **8c** (CD_2Cl_2 , 125.7 MHz).

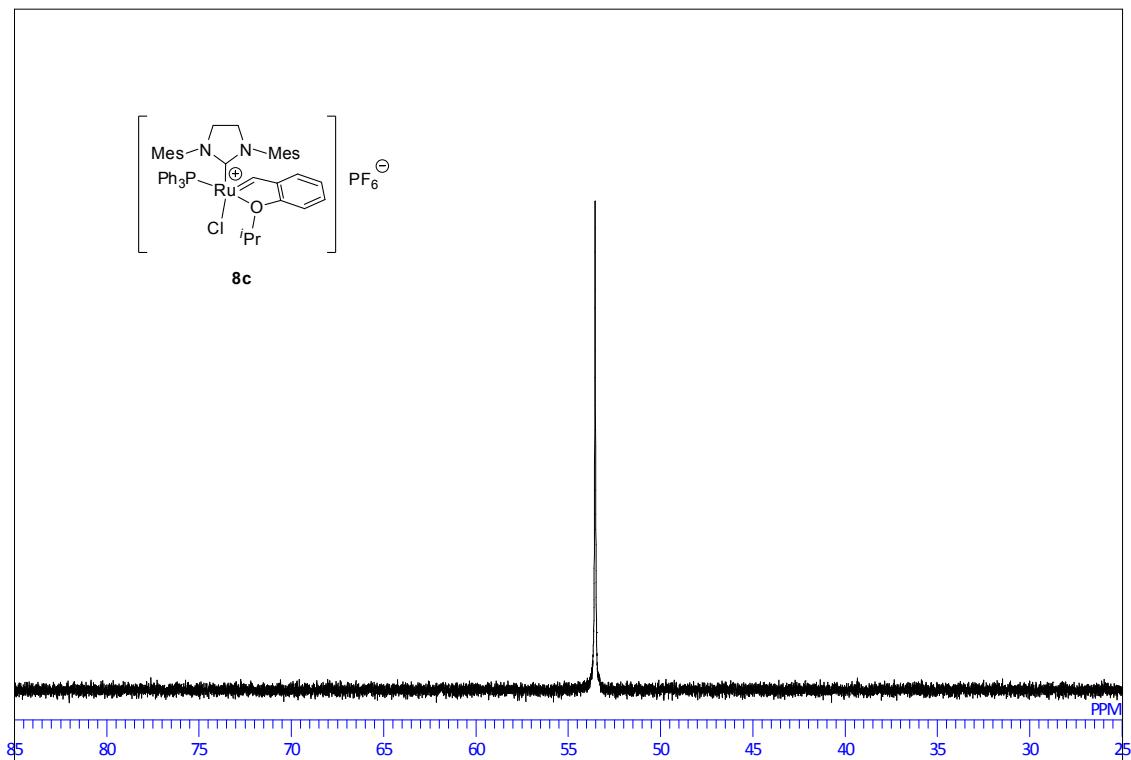


Figure S9. ^{31}P NMR spectrum of **8c** (CD_2Cl_2 , 121.4 MHz).

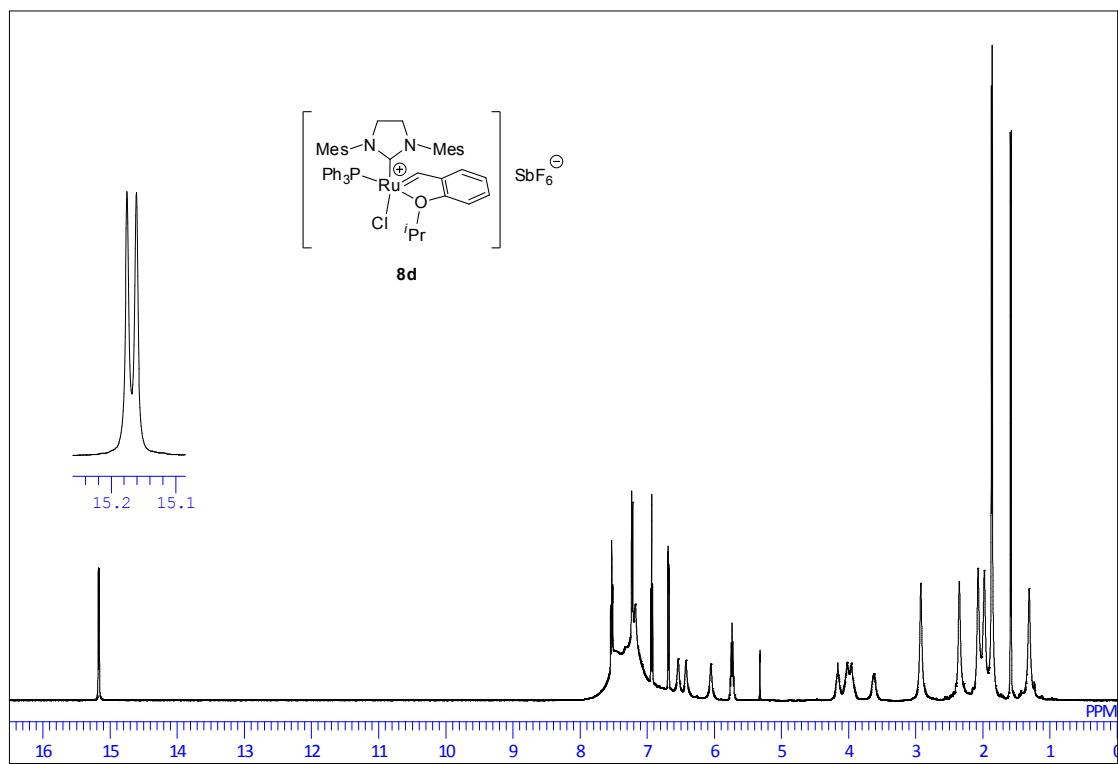


Figure S10. ^1H NMR spectrum of **8d** (CD_2Cl_2 , 500 MHz).

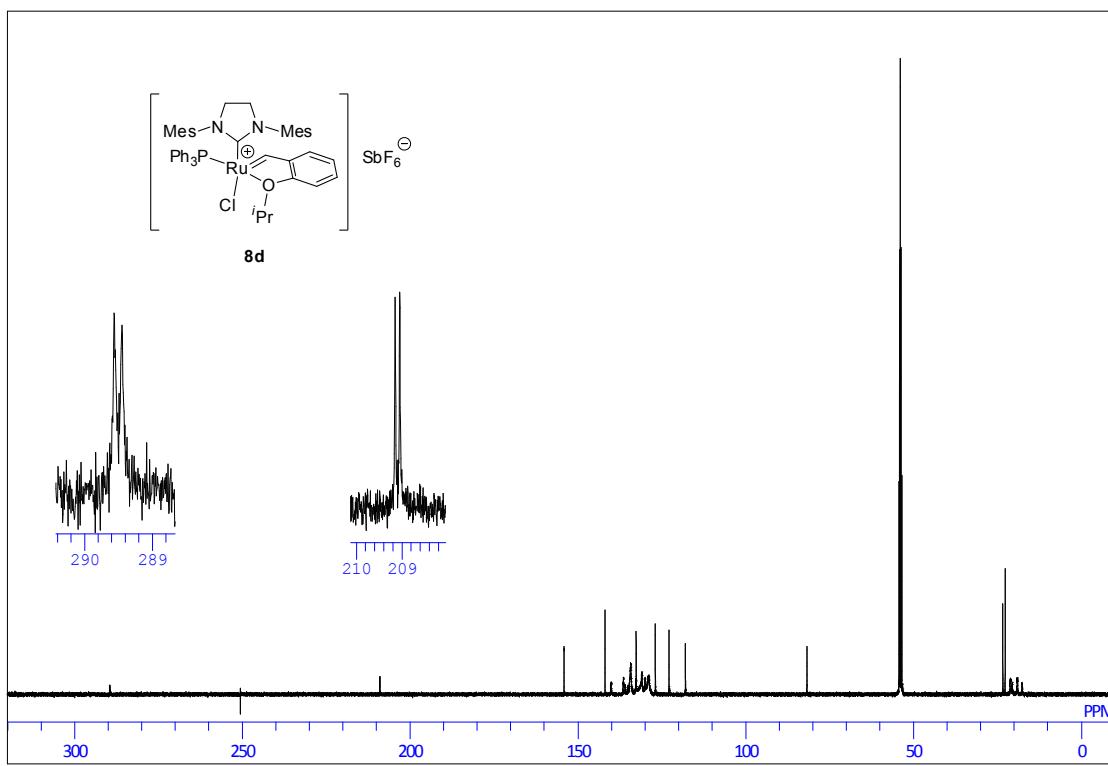


Figure S11. ^{13}C NMR spectrum of **8d** (CD_2Cl_2 , 125.7 MHz).

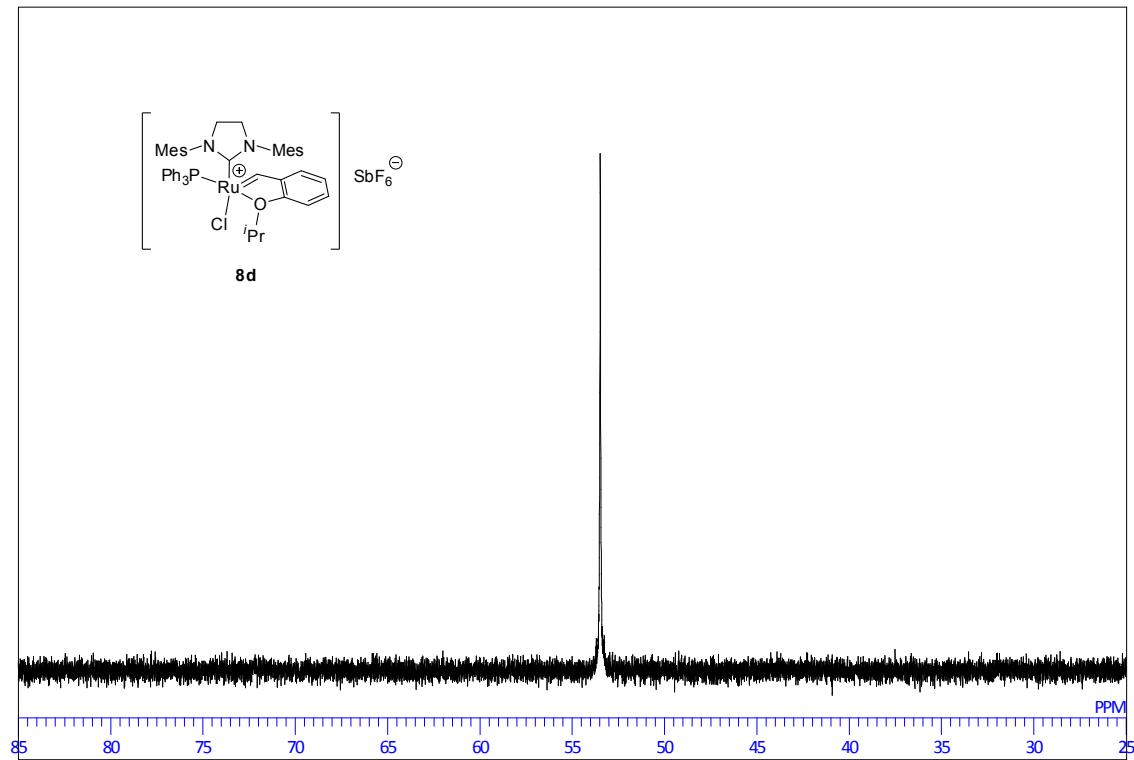


Figure S12. ^{31}P NMR spectrum of **8d** (CD_2Cl_2 , 121.4 MHz).

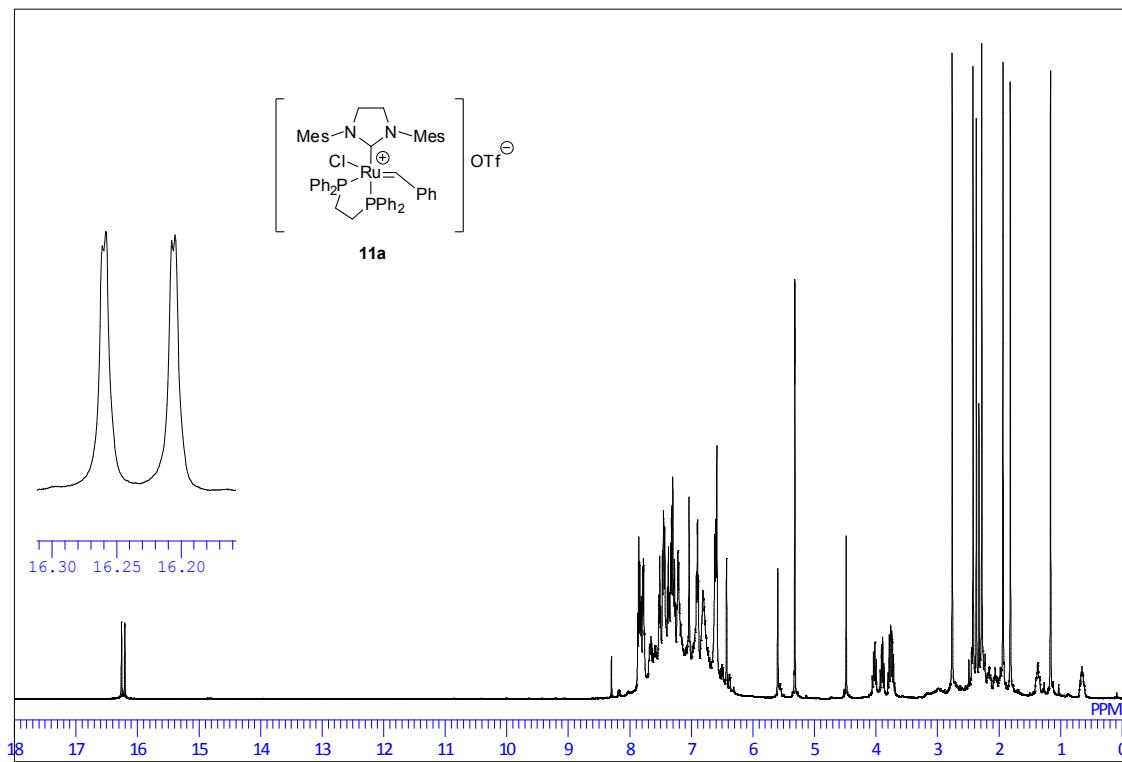


Figure S13. ^1H NMR spectrum of **11a** (CD_2Cl_2 , 500 MHz).

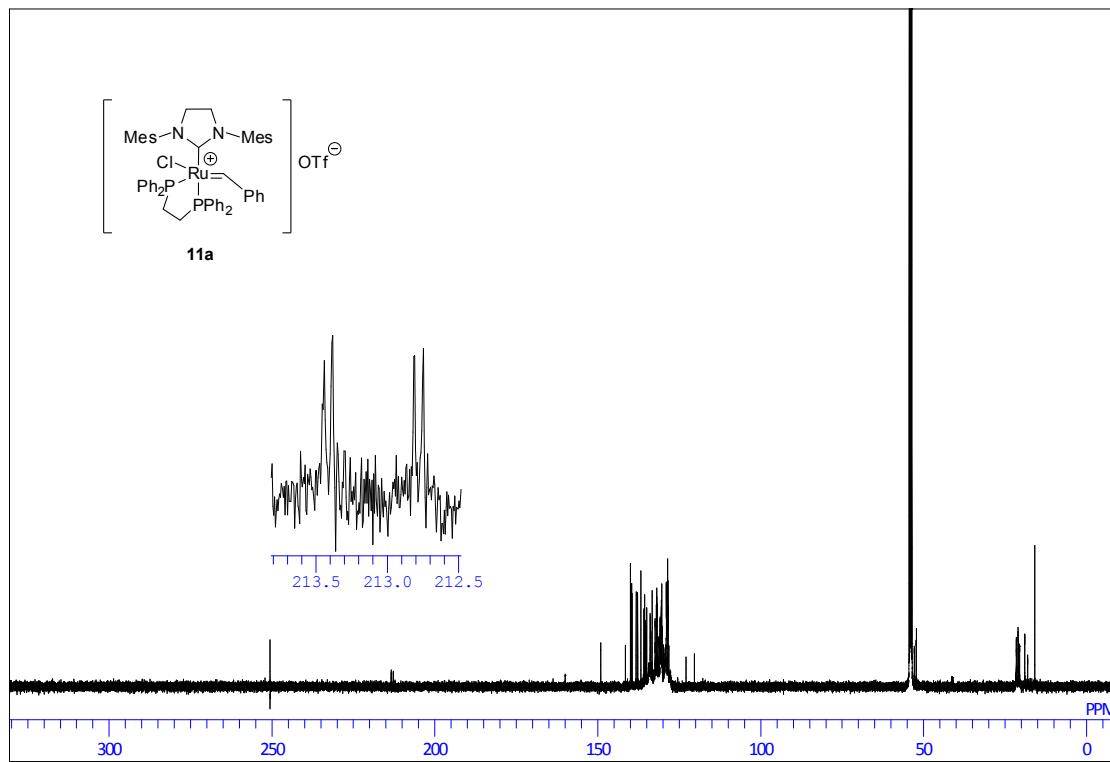


Figure S14. ^{13}C NMR spectrum of **11a** (CD_2Cl_2 , 125.7 MHz).

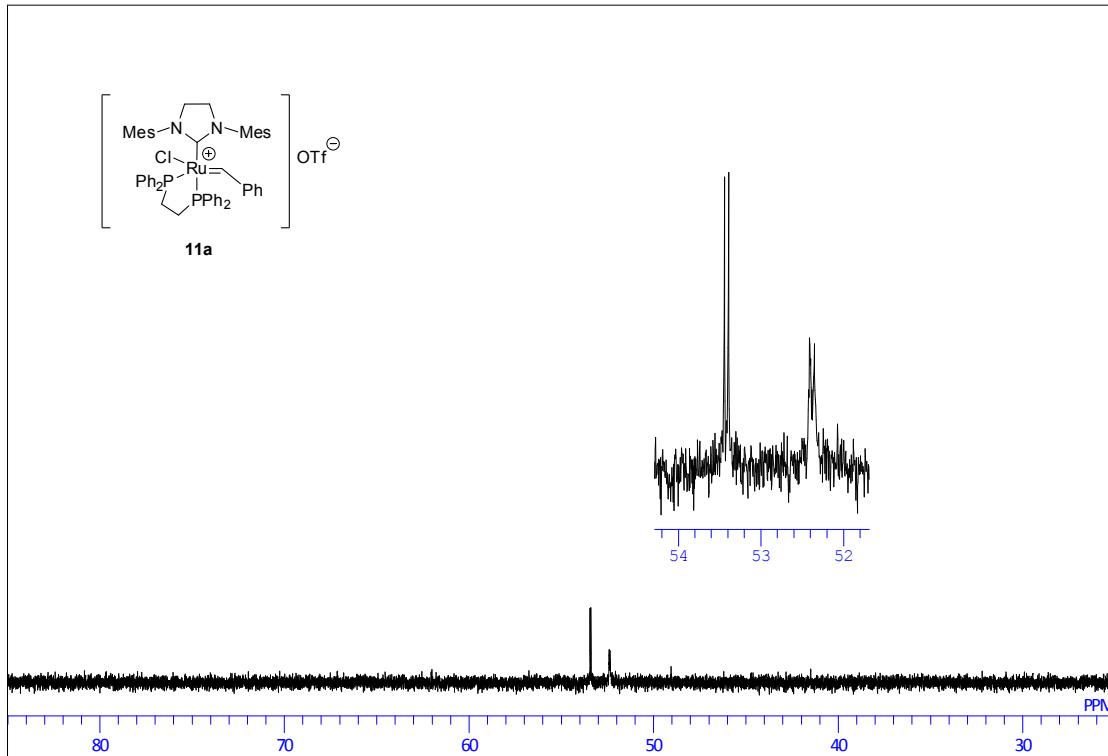


Figure S15. ^{31}P NMR spectrum of **11a** (CD_2Cl_2 , 121.4 MHz).

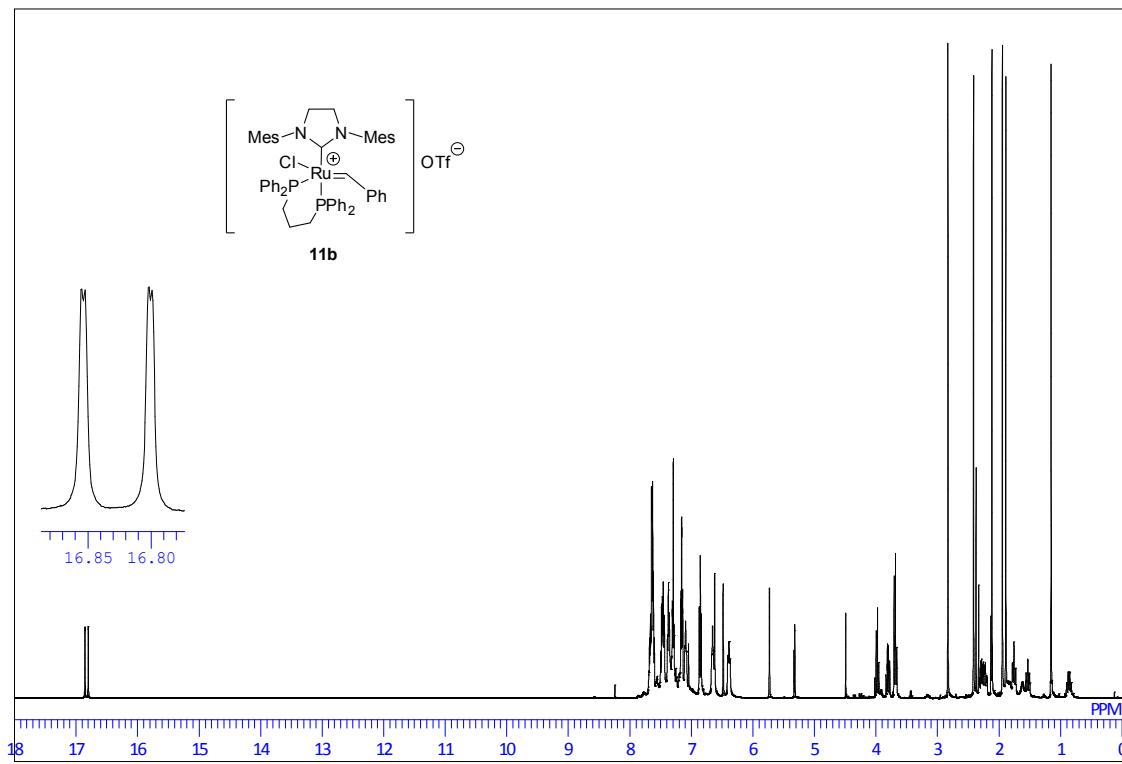


Figure S16. ^1H NMR spectrum of **11b** (CD_2Cl_2 , 500 MHz).

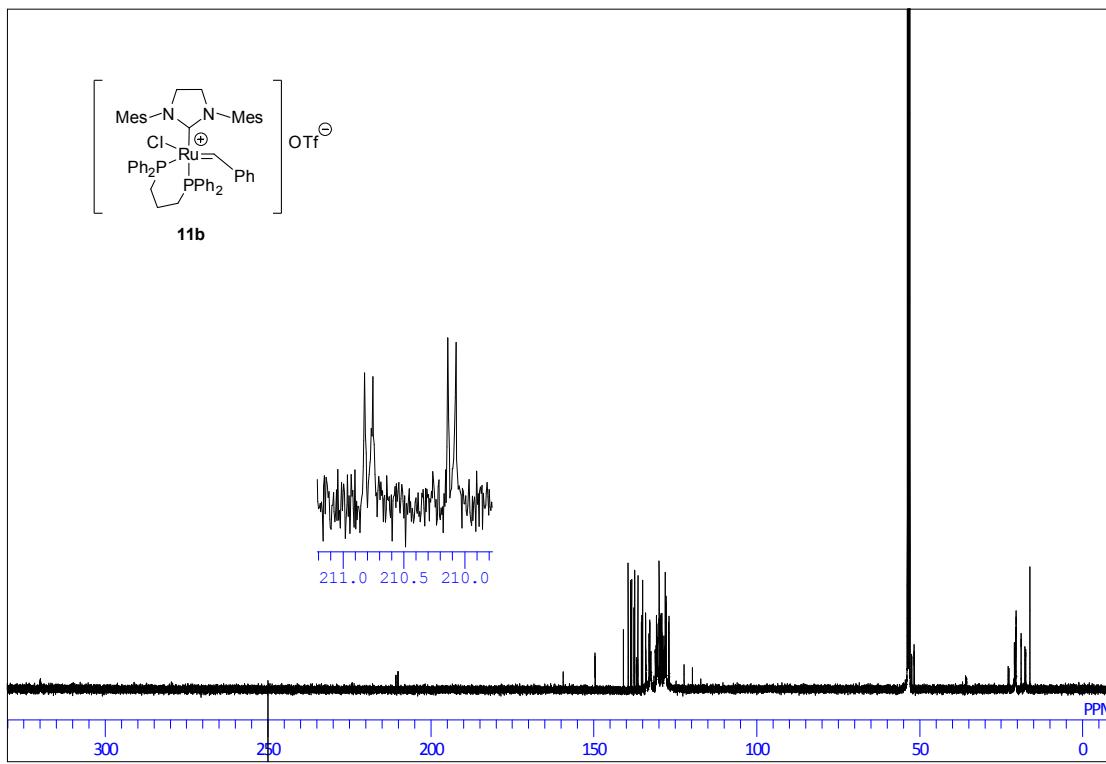


Figure S17. ^{13}C NMR spectrum of **11b** (CD_2Cl_2 , 125.7 MHz).

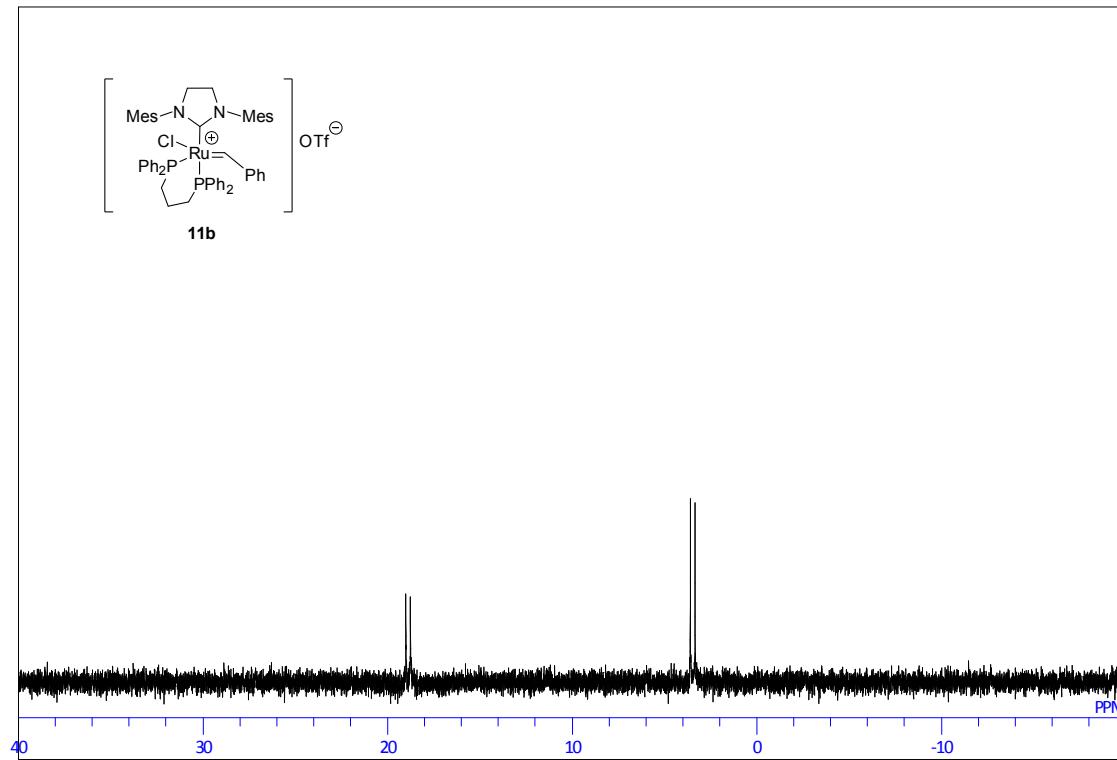


Figure S18. ^{31}P NMR spectrum of **11b** (CD_2Cl_2 , 121.4 MHz).

Table S1. Data for RCM of 12 by 7^a

time, min	conv, % ^b								
1.4	7.6	7.4	64.5	16.3	93.8	28.0	98.9	42.5	99.7
1.7	11.4	8.0	68.2	17.1	94.4	29.0	99.2	43.8	99.8
2.1	15.9	8.6	71.5	17.9	95.3	30.1	99.5	45.0	99.6
2.5	20.0	9.2	74.6	18.8	96.1	31.1	99.4	46.3	99.7
2.9	24.9	9.9	77.5	19.6	96.6	32.2	99.3	47.6	99.8
3.4	29.4	10.5	80.1	20.5	97.1	33.3	99.3	48.9	99.7
3.8	34.3	11.2	82.5	21.4	97.4	34.4	99.4	50.2	99.7
4.3	38.8	11.9	84.8	22.3	97.9	35.5	99.6	51.5	99.6
4.8	43.7	12.6	86.7	23.2	98.1	36.6	99.7	52.9	99.6
5.3	48.1	13.3	88.3	24.1	98.3	37.8	99.5		
5.8	52.6	14.0	89.9	25.1	98.5	38.9	99.6		
6.3	56.6	14.8	91.5	26.0	98.8	40.1	99.6		
6.9	60.6	15.5	92.4	27.0	98.9	41.3	99.5		

^a The reaction was carried out using **7** (0.80 µmol) and **12** (19.3 µl, 19.2 mg, 80 µmol) in CD₂Cl₂ (800 µl) at 30 °C. ^b Conversion of **12** to **13** calculated from the ratio of integrals of the methylene protons of **12** and **13** in ¹H NMR spectrum.

Table S2. Data for RCM of 12 by 8a^a

time, min	conv, % ^b								
0.7	0.2	11.1	1.0	38.5	6.4	83.1	19.3	144.7	44.3
0.7	-0.6	11.7	1.3	39.7	6.4	84.7	19.4	146.9	45.5
0.8	-0.3	12.3	1.9	40.8	7.1	86.4	20.5	149.1	46.4
0.9	-0.2	12.9	1.9	42.0	6.6	88.1	21.1	151.3	47.4
1.0	-0.1	13.6	2.1	43.2	7.3	89.8	21.3	153.6	47.9
1.2	-0.3	14.2	1.8	44.4	7.4	91.6	22.1	155.8	49.0
1.3	-0.4	14.9	2.3	45.6	7.3	93.3	23.2	158.1	50.0
1.5	-0.3	15.6	2.4	46.8	8.4	95.1	23.6	160.4	50.7
1.7	-0.4	16.3	1.9	48.1	8.2	96.9	24.0	162.7	51.6
1.9	-0.2	17.1	2.8	49.3	8.9	98.7	25.0	165.1	52.3
2.1	-0.1	17.8	2.4	50.6	8.8	100.5	26.0	167.4	52.5
2.3	0.1	18.6	2.2	51.9	9.4	102.3	26.3	169.8	53.2
2.6	0.5	19.4	3.0	53.2	9.3	104.2	27.2	172.2	53.4
2.8	0.5	20.2	2.8	54.6	10.4	106.0	28.3	174.6	54.2
3.1	0.2	21.0	3.4	55.9	10.0	107.9	29.0	177.0	54.7
3.4	0.0	21.8	3.2	57.3	11.0	109.8	29.5	179.4	55.6
3.7	0.4	22.7	3.6	58.7	11.6	111.7	30.2	181.9	55.9
4.1	0.5	23.5	3.1	60.1	11.8	113.7	31.1	184.3	56.8
4.4	0.0	24.4	4.0	61.5	11.6	115.6	31.8	186.8	57.6
4.8	0.4	25.3	3.6	62.9	12.5	117.6	33.1	189.4	59.8
5.2	0.4	26.2	3.9	64.4	13.0	119.6	34.0	191.9	60.3
5.6	0.9	27.2	3.8	65.8	13.1	121.6	34.8	194.4	61.0
6.0	0.9	28.1	4.1	67.3	14.1	123.6	35.3	197.0	61.8
6.4	0.6	29.1	4.1	68.8	14.4	125.6	36.2	199.6	62.3
6.9	0.2	30.1	4.9	70.3	14.6	127.7	37.2	202.1	63.1
7.3	0.6	31.1	4.9	71.9	15.4	129.7	38.3	204.7	63.6
7.8	1.2	32.1	4.8	73.4	16.0	131.8	39.1	207.4	64.4
8.3	0.7	33.1	4.8	75.0	15.9	133.9	39.8	210.0	65.0
8.8	1.2	34.2	5.1	76.6	16.6	136.0	41.0	212.6	65.5
9.4	1.3	35.2	6.0	78.2	17.3	138.2	41.8	215.3	66.1
9.9	0.9	36.3	5.9	79.8	18.0	140.3	42.8	218.0	66.8
10.5	1.0	37.4	6.0	81.4	18.0	142.5	43.6	220.7	67.3

Table S2. (Continued)

time, min	conv, % ^b								
223.4	68.0	319.1	83.5	431.9	92.1	561.8	96.4	708.7	98.3
226.1	68.5	322.4	84.0	435.7	92.4	566.1	96.3	713.6	98.4
228.9	69.2	325.7	84.3	439.6	92.7	570.5	96.4	718.5	98.3
231.7	69.6	329.0	84.6	443.4	93.0	574.9	96.5	723.4	98.3
234.4	70.3	332.3	84.9	447.2	92.9	579.2	96.6	728.3	98.6
237.2	70.8	335.6	85.2	451.1	93.0	583.6	96.6	733.2	98.6
240.1	71.4	339.0	85.6	455.0	93.3	588.1	96.7	738.2	98.6
242.9	72.0	342.4	85.9	458.9	93.4	592.5	96.9	743.2	98.7
245.7	72.5	345.7	86.3	462.8	93.7	596.9	97.0	748.1	98.8
248.6	73.0	349.1	86.6	466.7	93.7	601.4	96.9	753.1	98.7
251.5	73.6	352.6	87.0	470.7	93.9	605.9	97.0	758.2	98.6
254.4	74.2	356.0	87.4	474.7	94.1	610.4	97.1	763.2	98.7
257.3	74.7	359.4	87.5	478.6	94.0	614.9	97.2	768.2	98.9
260.2	75.2	362.9	87.8	482.6	94.3	619.4	97.4	773.3	98.8
263.2	75.6	366.4	88.0	486.7	94.3	624.0	97.2	778.4	98.8
266.2	76.2	369.9	88.2	490.7	94.4	628.6	97.3	783.5	98.9
269.1	76.6	373.4	88.7	494.7	94.5	633.1	97.4	788.6	98.9
272.1	77.2	376.9	88.8	498.8	94.7	637.7	105.7	793.7	98.9
275.2	77.5	380.5	89.1	502.9	94.8	642.4	97.3	798.9	99.0
278.2	78.1	384.1	89.3	507.0	94.9	647.0	97.6	804.1	98.9
281.2	78.6	387.6	89.6	511.1	95.1	651.6	97.7	809.2	99.1
284.3	79.0	391.2	90.0	515.2	95.1	656.3	97.7	814.4	99.1
287.4	79.5	394.9	90.2	519.4	95.3	661.0	98.0	819.7	99.1
290.5	79.9	398.5	90.3	523.6	95.4	665.7	97.9	824.9	99.0
293.6	80.3	402.1	90.6	527.7	95.3	670.4	98.1	830.1	99.1
296.7	80.8	405.8	90.9	531.9	95.6	675.1	98.1	835.4	99.0
299.9	81.2	409.5	91.0	536.2	95.7	679.9	98.0	840.7	99.2
303.1	81.6	413.2	91.2	540.4	95.8	684.7	98.1	846.0	99.2
306.2	82.0	416.9	91.5	544.6	96.0	689.4	98.2	851.3	99.2
309.4	82.4	420.6	91.5	548.9	96.1	694.2	98.2	856.6	99.2
312.7	82.8	424.4	91.8	553.2	96.1	699.1	98.3	862.0	99.2
315.9	83.1	428.2	92.0	557.5	96.3	703.9	98.2		

^a The reaction was carried out using **8a** (0.80 µmol) and **12** (19.3 µl, 19.2 mg, 80 µmol) in CD₂Cl₂ (800 µl) at 30 °C. ^b Conversion of **12** to **13** calculated from the ratio of integrals of the methylene protons of **12** and **13** in ¹H NMR spectrum.

Table S3. Data for RCM of 12 by 8b^a

time, min	conv, % ^b								
0.9	0.0	3.1	-0.1	8.0	0.3	15.8	0.8	26.5	2.6
1.0	-0.4	3.3	-0.2	8.5	0.4	16.6	0.9	27.4	2.7
1.0	-0.2	3.6	0.1	9.1	0.7	17.3	0.9	28.3	2.4
1.1	-0.5	4.0	0.0	9.6	0.8	18.0	1.0	29.3	3.2
1.3	-0.1	4.3	-0.2	10.1	1.1	18.8	1.2	30.3	2.9
1.4	-0.1	4.6	0.2	10.7	0.4	19.6	1.4	31.3	2.9
1.5	-0.3	5.0	0.5	11.3	0.6	20.4	2.0	32.3	2.9
1.7	-0.3	5.4	0.4	11.9	0.6	21.2	2.2	33.3	3.0
1.9	-0.3	5.8	0.0	12.5	0.6	22.0	1.9	34.4	3.2
2.1	0.3	6.2	0.8	13.1	1.3	22.9	2.1	35.5	3.7
2.3	0.0	6.6	0.6	13.8	0.6	23.8	1.9	36.5	3.9
2.5	-0.5	7.1	0.2	14.5	0.6	24.6	1.9	37.6	4.3
2.8	0.1	7.6	0.3	15.1	0.8	25.5	2.0	38.8	4.3

Table S3. (Continued)

time, min	conv, % ^b								
39.9	4.2	61.7	9.3	88.3	18.4	119.8	33.4	156.1	52.3
41.0	4.3	63.1	9.9	90.1	19.3	121.8	34.5	158.3	53.4
42.2	4.5	64.6	10.1	91.8	19.9	123.8	35.4	160.6	54.4
43.4	4.6	66.1	10.2	93.5	20.8	125.8	36.5	163.0	55.3
44.6	5.2	67.5	10.8	95.3	21.4	127.9	37.5	165.3	56.4
45.8	5.3	69.0	11.3	97.1	22.3	130.0	38.6	167.6	57.7
47.0	5.4	70.6	12.1	98.9	23.3	132.0	39.9	170.0	58.5
48.3	5.8	72.1	12.2	100.7	23.9	134.1	41.0	172.4	59.8
49.6	6.4	73.6	12.8	102.5	24.6	136.3	42.3	174.8	60.5
50.8	6.7	75.2	13.4	104.4	25.6	138.4	43.2	177.2	61.9
52.1	6.7	76.8	13.9	106.3	26.5	140.5	44.4	179.6	62.7
53.5	7.4	78.4	14.6	108.1	27.2	142.7	45.4	182.1	63.9
54.8	7.4	80.0	15.1	110.0	28.4	144.9	46.8	184.6	64.7
56.1	7.6	81.6	15.7	112.0	29.6	147.1	47.7	187.0	65.9
57.5	7.9	83.3	16.1	113.9	30.5	149.3	48.9	189.5	66.6
58.9	8.2	85.0	16.9	115.8	31.4	151.5	49.8		
60.3	9.2	86.6	17.6	117.8	32.5	153.8	51.2		

^a The reaction was carried out using **8b** (0.80 µmol) and **12** (19.3 µl, 19.2 mg, 80 µmol) in CD₂Cl₂ (800 µl) at 30 °C. ^b Conversion of **12** to **13** calculated from the ratio of integrals of the methylene protons of **12** and **13** in ¹H NMR spectrum.

Table S4. Data for RCM of **12 by **8c**^a**

time, min	conv, % ^b								
0.7	1.0	8.8	2.1	30.1	7.5	64.4	20.1	111.7	39.2
0.7	0.8	9.4	2.3	31.1	7.7	65.8	20.8	113.7	40.0
0.8	1.0	9.9	2.3	32.1	8.1	67.3	21.2	115.6	40.8
0.9	1.3	10.5	2.2	33.1	8.4	68.8	22.0	117.6	41.6
1.0	0.8	11.1	2.7	34.2	8.6	70.3	22.6	119.6	42.3
1.2	1.0	11.7	2.4	35.2	9.0	71.9	23.2	121.6	43.0
1.3	0.8	12.3	2.7	36.3	9.7	73.4	23.9	123.6	43.8
1.5	0.8	12.9	2.7	37.4	10.0	75.0	24.6	125.6	44.6
1.7	0.8	13.6	3.3	38.5	10.4	76.6	25.1	127.7	45.3
1.9	1.1	14.2	3.1	39.7	10.8	78.2	25.6	129.7	46.1
2.1	1.2	14.9	3.6	40.8	11.3	79.8	26.4	131.8	47.0
2.3	1.0	15.6	3.3	42.0	11.3	81.4	27.2	133.9	47.6
2.6	1.2	16.3	3.5	43.2	11.9	83.1	27.9	136.0	48.3
2.8	1.2	17.1	3.7	44.4	12.3	84.7	28.4	138.2	49.1
3.1	1.2	17.8	3.8	45.6	12.8	86.4	29.2	140.3	49.9
3.4	1.5	18.6	3.9	46.8	13.5	88.1	30.0	142.5	50.7
3.7	1.5	19.4	4.6	48.1	14.0	89.8	30.6	144.7	51.5
4.1	1.5	20.2	4.7	49.3	14.4	91.6	31.3	146.9	52.1
4.4	1.3	21.0	4.6	50.6	14.7	93.3	31.8	149.1	52.9
4.8	1.3	21.8	5.0	51.9	15.2	95.1	32.6	151.3	53.8
5.2	1.7	22.7	5.0	53.2	15.7	96.9	33.3	153.6	54.5
5.6	1.7	23.5	5.5	54.6	16.3	98.7	34.1	155.8	55.3
6.0	1.5	24.4	5.5	55.9	16.7	100.5	34.8	158.1	55.9
6.4	1.6	25.3	5.8	57.3	17.2	102.3	35.6	160.4	56.7
6.9	1.4	26.2	6.4	58.7	17.8	104.2	36.4	162.7	57.4
7.3	1.6	27.2	6.5	60.1	18.4	106.0	37.0	165.1	58.0
7.8	1.9	28.1	7.0	61.5	19.0	107.9	37.9	167.4	58.7
8.3	1.9	29.1	7.3	62.9	19.5	109.8	38.6	169.8	59.6

Table S4. (Continued)

time, min	conv, % ^b								
172.2	60.3	266.1	81.0	380.4	91.5	515.2	96.0	670.3	97.4
174.6	61.0	269.1	81.4	384.0	92.0	519.3	96.1	675.1	97.4
177.0	61.6	272.1	81.8	387.6	92.0	523.5	96.3	679.8	97.7
179.4	62.5	275.1	82.3	391.2	92.2	527.7	96.1	684.6	97.7
181.9	63.0	278.1	82.7	394.8	92.4	531.9	96.4	689.4	97.6
184.3	63.9	281.2	83.0	398.4	92.6	536.1	96.2	694.2	97.7
186.8	64.4	284.2	83.3	402.1	92.7	540.3	96.4	699.0	97.7
189.3	65.2	287.3	84.0	405.7	92.9	544.6	96.5	703.8	97.6
191.8	65.8	290.4	84.1	409.4	92.9	548.8	96.5	708.7	97.9
194.4	66.4	293.5	84.6	413.1	93.2	553.1	96.7	713.5	98.0
196.9	67.0	296.7	85.0	416.8	93.3	557.4	96.6	718.4	97.8
199.5	67.8	299.8	85.3	420.6	93.4	561.7	97.0	723.3	97.9
202.1	68.4	303.0	85.5	424.3	93.8	566.1	96.6	728.2	97.9
204.7	69.0	306.2	86.1	428.1	93.8	570.4	96.9	733.2	97.7
207.3	69.8	309.4	86.2	431.9	94.0	574.8	96.7	738.1	97.8
209.9	70.3	312.6	86.5	435.7	94.1	579.2	96.7	743.1	97.9
212.6	71.0	315.8	86.9	439.5	94.2	583.6	97.0	748.1	97.7
215.2	71.6	319.1	87.2	443.3	94.2	588.0	96.9	753.1	98.1
217.9	72.1	322.3	87.6	447.2	94.5	592.4	97.2	758.1	98.1
220.6	72.6	325.6	87.8	451.0	94.7	596.9	97.0	763.1	98.0
223.3	73.2	328.9	88.2	454.9	94.7	601.3	97.0	768.2	97.9
226.1	73.7	332.2	88.3	458.8	95.0	605.8	97.0	773.2	97.9
228.8	74.4	335.6	88.6	462.7	95.0	610.3	97.1	778.3	98.1
231.6	74.9	338.9	88.9	466.7	94.7	614.8	97.4	783.4	98.1
234.4	75.4	342.3	89.3	470.6	95.2	619.4	97.1	788.5	98.1
237.2	76.0	345.7	89.3	474.6	95.3	623.9	97.3	793.7	98.1
240.0	76.6	349.1	89.6	478.6	95.4	628.5	97.4	798.8	98.0
242.8	77.1	352.5	90.0	482.6	95.2	633.1	97.3	804.0	98.4
245.7	77.5	355.9	90.1	486.6	95.5	637.7	96.9	809.2	98.1
248.5	78.0	359.4	90.4	490.6	95.9	642.3	97.4	814.4	98.2
251.4	78.6	362.8	90.7	494.7	95.6	646.9	97.4	819.6	97.9
254.3	79.2	366.3	90.8	498.7	95.7	651.6	97.4	824.8	98.2
257.2	79.5	369.8	91.1	502.8	95.9	656.2	97.5	830.1	98.0
260.2	80.0	373.3	91.4	506.9	96.1	660.9	97.5	835.3	98.1
263.1	80.5	376.9	91.3	511.0	95.7	665.6	97.3		

^a The reaction was carried out using **8c** (0.80 µmol) and **12** (19.3 µL, 19.2 mg, 80 µmol) in CD₂Cl₂ (800 µL) at 30 °C. ^b Conversion of **12** to **13** calculated from the ratio of integrals of the methylene protons of **12** and **13** in ¹H NMR spectrum.

Table S5. Data for RCM of **12 by **11a**^a**

time, min	conv, % ^b								
0.8	-0.1	2.2	-0.2	5.3	0.4	10.0	0.7	16.4	1.2
0.8	-0.1	2.4	0.2	5.7	0.5	10.6	0.7	17.2	1.6
0.9	-0.4	2.7	-0.2	6.1	0.5	11.2	0.7	17.9	1.5
1.0	-0.3	2.9	0.2	6.5	0.3	11.8	1.0	18.7	1.8
1.1	-0.2	3.2	0.0	7.0	0.4	12.4	0.9	19.5	1.8
1.3	-0.1	3.5	0.0	7.4	0.6	13.0	0.8	20.3	1.7
1.4	0.0	3.8	0.0	7.9	0.7	13.7	0.9	21.1	1.9
1.6	-0.2	4.2	0.0	8.4	0.4	14.3	0.9	21.9	2.0
1.8	-0.2	4.5	0.0	8.9	0.5	15.0	1.2	22.8	2.0
2.0	-0.2	4.9	0.1	9.5	0.6	15.7	1.3	23.6	1.9

Table S5. (Continued)

time, min	conv, % ^b								
24.5	2.3	42.1	3.9	64.5	5.9	91.7	7.9	123.7	9.8
25.4	2.1	43.3	4.0	65.9	6.0	93.4	8.1	125.7	9.8
26.3	2.5	44.5	4.1	67.4	6.3	95.2	8.0	127.8	9.9
27.3	2.6	45.7	4.3	68.9	6.2	97.0	8.3	129.8	10.2
28.2	2.4	46.9	4.5	70.4	6.5	98.8	8.3	131.9	10.0
29.2	2.8	48.2	4.3	72.0	6.5	100.6	8.6	134.0	10.2
30.2	2.9	49.4	4.5	73.5	6.6	102.4	8.6	136.1	10.3
31.2	2.7	50.7	4.8	75.1	6.6	104.3	8.7	138.3	10.4
32.2	3.0	52.0	4.9	76.7	7.0	106.1	9.0	140.4	10.3
33.2	3.2	53.3	5.0	78.3	7.0	108.0	9.0	142.6	10.5
34.3	3.1	54.7	5.2	79.9	7.2	109.9	9.1	144.8	10.6
35.3	3.3	56.0	5.3	81.5	7.2	111.8	9.1	147.0	10.6
36.4	3.3	57.4	5.2	83.2	7.3	113.8	9.3	149.2	10.7
37.5	3.4	58.8	5.6	84.8	7.4	115.7	9.4		
38.6	3.7	60.2	5.7	86.5	7.5	117.7	9.4		
39.8	3.9	61.6	5.6	88.2	7.7	119.7	9.8		
40.9	3.7	63.0	5.9	89.9	7.9	121.7	9.7		

^a The reaction was carried out using **11a** (0.80 µmol) and **12** (19.3 µl, 19.2 mg, 80 µmol) in CD₂Cl₂ (800 µl) at 30 °C. ^b Conversion of **12** to **13** calculated from the ratio of integrals of the methylene protons of **12** and **13** in ¹H NMR spectrum.

Table S6. GC response factors and retention times^a

compound	response factor ^b	retention time, min
tridecane	--	11.7
14	1.20	10.9
Z-15	2.48	18.3
E-15	2.48	18.6
Z-16	1.30	21.4
E-16	1.30	21.7
Z-17	1.03	24.5
E-17	1.03	24.3

^a Instrument conditions were as follows; Inlet temperature: 250 °C, detector temperature: 250 °C, hydrogen flow: 32 ml/min, air flow: 400 ml/min, constant col + makeup flow: 30 ml/min. GC Method was as follows; 50 °C for 5 min, followed by a temperature increase of 10 °C/min to 240 °C and a subsequent isothermal period at 240 °C for 5 min (total run time = 29 min). Response factors and retention times are instrument dependent; values may vary on alternate machines. ^b Determined by reported method.^{S3}

Table S7. Data for CM of 14 and 15 by 7^a

time min	16		17	
	conversion ^b %	E/Z ^c	conversion ^b %	E/Z ^c
1	70	6.2	2	3.6
2	75	8.4	4	4.4
5	75	10.0	6	4.9
8	74	10.1	4	5.3
10	73	10.1	4	5.6
15	72	10.1	5	5.9
20	72	10.0	5	5.8
30	72	10.1	5	5.9

^a The reaction was carried out using **7** (3.1 mg, 5.0 μ mol), **14** (0.20 mmol), **15** (0.40 mmol) and tridecane (0.10 mmol) in 1.0 ml of CH₂Cl₂ at 23 °C. ^b Conversion of **14** to the product determined by GC analysis. ^c Molar ratio of *E* isomer and *Z* isomer of the product determined by GC analysis.

Table S8. Data for CM of 14 and 15 by 8a^a

time min	16		17	
	conversion ^b %	E/Z ^c	conversion ^b %	E/Z ^c
5	6.6	2.67	0.0	(NA) ^d
10	11.0	2.99	0.0	(NA) ^d
15	17.2	2.98	0.0	(NA) ^d
30	33.8	3.27	0.0	(NA) ^d
45	46.9	3.76	0.0	(NA) ^d
60	56.6	4.34	0.0	(NA) ^d
90	66.7	5.27	2.9	(NA) ^d
120	73.9	6.14	2.5	(NA) ^d
240	80.9	8.79	4.9	(NA) ^d
480	78.8	10.6	8.9	6.97

^a The reaction was carried out using **8a** (4.7 mg, 5.0 μ mol), **14** (0.20 mmol), **15** (0.40 mmol) and tridecane (0.10 mmol) in 1.0 ml of CH₂Cl₂ at 23 °C. ^b Conversion of **14** to the product determined by GC analysis. ^c Molar ratio of *E* isomer and *Z* isomer of the product determined by GC analysis. ^d GC signal of the product was too small to quantify.

Table S9. Data for CM of 14 and 15 by 8b^a

time min	16		17	
	conversion ^b %	E/Z ^c	conversion ^b %	E/Z ^c
5	2.2	NA	0.0	(NA) ^d
10	7.4	2.62	0.0	(NA) ^d
15	11.9	2.82	0.0	(NA) ^d
30	28.4	3.16	0.0	(NA) ^d
45	41.9	3.46	0.0	(NA) ^d
60	51.5	3.84	1.5	(NA) ^d
90	64.6	4.77	2.2	(NA) ^d
120	73.1	5.70	2.8	(NA) ^d
240	81.1	8.41	4.9	(NA) ^d
480	79.1	9.95	9.4	5.18

^a The reaction was carried out using **8b** (5.0 mg, 5.0 μ mol), **14** (0.20 mmol), **15** (0.40 mmol) and tridecane (0.10 mmol) in 1.0 ml of CH₂Cl₂ at 23 °C. ^b Conversion of **14** to the product determined by GC analysis. ^c Molar ratio of *E* isomer and *Z* isomer of the product determined by GC analysis. ^d GC signal of the product was too small to quantify.

Table S10. Data for CM of 14 and 15 by 11a^a

time min	16		17	
	conversion ^b %	E/Z ^c	conversion ^b %	E/Z ^c
5	0.0	NA	0.0	(NA) ^d
10	1.1	NA	0.0	(NA) ^d
15	1.9	NA	0.0	(NA) ^d
30	6.2	2.22	0.0	(NA) ^d
45	9.7	2.70	0.0	(NA) ^d
60	13.8	2.95	0.0	(NA) ^d
90	24.4	2.88	0.0	(NA) ^d
120	33.7	3.20	0.0	(NA) ^d
240	46.2	3.57	0.0	(NA) ^d
480	46.9	3.59	0.0	(NA) ^d

^a The reaction was carried out using **11a** (10.8 mg, 10.0 μ mol), **14** (0.20 mmol), **15** (0.40 mmol) and tridecane (0.10 mmol) in 1.0 ml of CH₂Cl₂ at 23 °C. ^b Conversion of **14** to the product determined by GC analysis. ^c Molar ratio of *E* isomer and *Z* isomer of the product determined by GC analysis. ^d GC signal of the product was too small to quantify.

Table S11. Data for CM of 14 and 15 by 11b^a

time min	16		17	
	conversion ^b %	E/Z ^c	conversion ^b %	E/Z ^c
5	0.0	(NA) ^d	0.0	(NA) ^d
10	0.0	(NA) ^d	0.0	(NA) ^d
15	0.0	(NA) ^d	0.0	(NA) ^d
30	0.0	(NA) ^d	0.0	(NA) ^d
45	0.0	(NA) ^d	0.0	(NA) ^d
60	0.0	(NA) ^d	0.0	(NA) ^d
90	0.0	(NA) ^d	0.0	(NA) ^d
120	0.0	(NA) ^d	0.0	(NA) ^d
240	0.0	(NA) ^d	0.0	(NA) ^d
480	0.0	(NA) ^d	0.0	(NA) ^d

^a The reaction was carried out using **11b** (10.9 mg, 10.0 µmol), **14** (0.20 mmol), **15** (0.40 mmol) and tridecane (0.10 mmol) in 1.0 ml of CH₂Cl₂ at 23 °C. ^b Conversion of **14** to the product determined by GC analysis. ^c Molar ratio of *E* isomer and *Z* isomer of the product determined by GC analysis. ^d GC signal of the product was too small to quantify.