

Supporting Information for

A Rh-Catalyzed Isomerization of 1-Alkenes to (*E*)-2-Alkenes: from Homogeneous Rh/PPh₃ Catalyst to Heterogeneous Rh/POP-PPh₃-SO₃Na Catalyst

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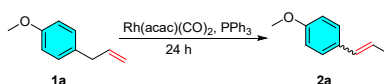
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1. General methods.

Unless otherwise noted, all manipulations involving air- or moisture-sensitive compounds were performed in a nitrogen-filled glovebox or using standard Schlenk techniques. Solvents were dried according to standard procedures. ^1H NMR spectra were recorded on 400 MHz by using a Bruker Avance 400 spectrometer. Chemical shifts (δ values) were reported in ppm with internal TMS (^1H NMR) as the standard. The SEM and TEM spectra were obtained on a Zeiss sigma 500 and JEOL-2100F spectrometers, respectively. N_2 sorption isotherm was obtained on a Micromeritics ASAP 2460. Thermogravimetric analysis was determined on NETZSCH TG 209 F1. X-ray photoelectron spectroscopy (XPS) was performed on a ThermoScientific ESCALAB 250Xi with the Al $\text{K}\alpha$ radiation as X-ray source ($h\nu=1486.6$ eV). The binding energies were referenced to the C1s line at 284.8 eV from adventitious carbon.

2. Studies of the isomerization reaction conditions.

Table S1. Studies of the isomerization reaction conditions^a

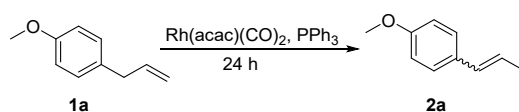


entry	PPh_3/Rh	solvent	T (°C)	yield ^b (%)	<i>E/Z</i> ^b
1	0:1	EtOH	100	46	6
2	1:1	EtOH	100	52	7
3	2:1	EtOH	100	79	10
4	3:1	EtOH	100	98	14
5	4:1	EtOH	100	97	12
6	5:1	EtOH	100	70	11
7	3:1	EtOH	90	37	8
8	3:1	EtOH	110	97	11
9	3:1	Toluene	100	63	8
10	3:1	1,4-Dioxane	100	81	11
11	3:1	THF	100	10	8
12	3:1	CH_2Cl_2	100	48	9
13	3:1	MeOH	100	92	11
14	3:1	<i>n</i> -Propanol	100	30	9

15	3:1	<i>i</i> -Propanol	100	98	13
16	3:1	Glycol	100	85	6
17	3:1	Glycerol	100	48	9
18 ^c	3:1	EtOH	100	66	12
19 ^d	3:1	EtOH	100	73	11
20 ^e	3:1	EtOH	100	55	10

^aReaction conditions: **1a** (2.0 mmol), Rh(acac)(CO)₂ (0.002 mmol), reaction solvent (2 mL), H₂O (10 μL), 24 h. ^bYields and *E/Z* ratios were determined by GC analysis, decane as the internal standard. ^cWithout H₂O as the additive. ^dH₂O (5 μL), ^eH₂O (20 μL).

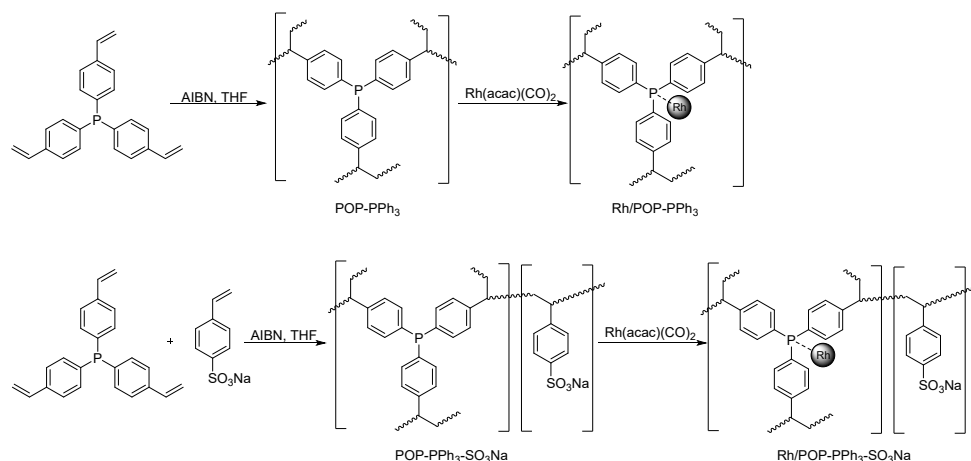
Table S2. Screening of phosphine ligands in isomerization reaction of **1a**.



entry	Ligand	solvent	temp (°C)	yield (%)	<i>E/Z</i>
1	PPh ₃	EtOH	100	98	14
2	DPPB	EtOH	100	76	11
3	DPPE	EtOH	100	79	12
4	DPPF	EtOH	100	62	10
5	Xantphos	EtOH	100	80	9
6	BINAP	EtOH	100	64	6
7	Tris(4-methoxyphenyl)phosphane	EtOH	100	98	12
8	Tri- <i>o</i> -tolylphosphane	EtOH	100	87	11

Reaction conditions: **1a** (2.0 mmol), Rh(acac)(CO)₂ (0.002 mmol), Rh:Ligand = 1:3, EtOH (2 mL), H₂O (10 μL), 100 °C, 24 h. Yields and *E/Z* ratios were determined by GC analysis, decane as the internal standard.

3. Synthesis of Rh/POP-PPh₃ and Rh/POP-PPh₃-SO₃Na.



Synthesis of Rh/POP-PPh₃.

Tris(4-vinylphenyl)phosphine was prepared by following the reported literature procedure^[1]. Under nitrogen, the obtained tris(4-vinylphenyl) phosphine (1.0 g, 2.95 mmol), AIBN (24.0 mg, 0.15 mmol) and THF (20 mL) were added into Schlenk flask. After stirring for 30 minutes at room temperature, the mixture was heated to 100 °C for 24 h. The white solid was formed. After evaporation of THF at 40 °C under vacuum, the crude product was washed by THF (3 × 8 mL) and separated by centrifugation. The white solid POP-PPh₃ (956 mg) was obtained.

A mixture of POP-PPh₃ (200.0 mg) in toluene (10 mL) was added in Rh(acac)(CO)₂ (12.0 mg) in Schlenk flask. After stirring for 24 h under N₂ at room temperature, the crude product was separated by using centrifuge and further washed by toluene. After removing the residual solvent under reduced pressure, the Rh/POP-PPh₃ (194.0 mg) was obtained.

Synthesis of Rh/POP-PPh₃-SO₃Na.

In glove box, tris(4-vinylphenyl)phosphine (100.0 mg), sodium-4-vinylbenzenesulfonate (20.2 mg), AIBN(4.0 mg) and THF (2 mL) were added into a Schlenk flask. The mixture was heated to 100 °C for 24 h. The resulting product was separated by centrifugation. The crude product was washed by Toluene (4 × 2 mL) and dried under vacuum. The catalyst POP-PPh₃-SO₃Na (106.5 mg) was obtained.

A mixture of POP-PPh₃-SO₃Na (100.0 mg) in toluene (5 mL) was added into Rh(acac)(CO)₂ (3.65 mg) in Schlenk flask. After stirring for 24 h under N₂ at room temperature, the crude product was separated by using centrifuge and further washed

by toluene. After removing the residual solvent under reduced pressure, the Rh/POP-PPh₃-SO₃Na (98.2 mg) was obtained.

4. XPS spectra of Rh/POP-PPh₃-SO₃Na

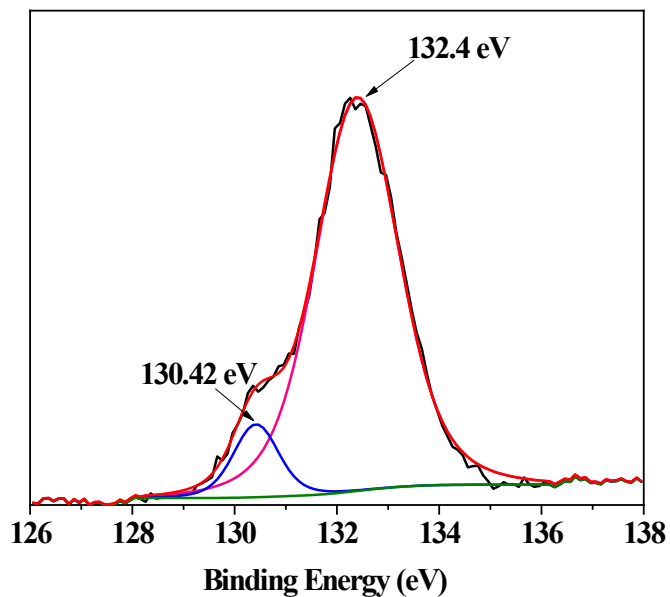


Figure S1. P 2p XPS spectra of POP-PPh₃-SO₃Na

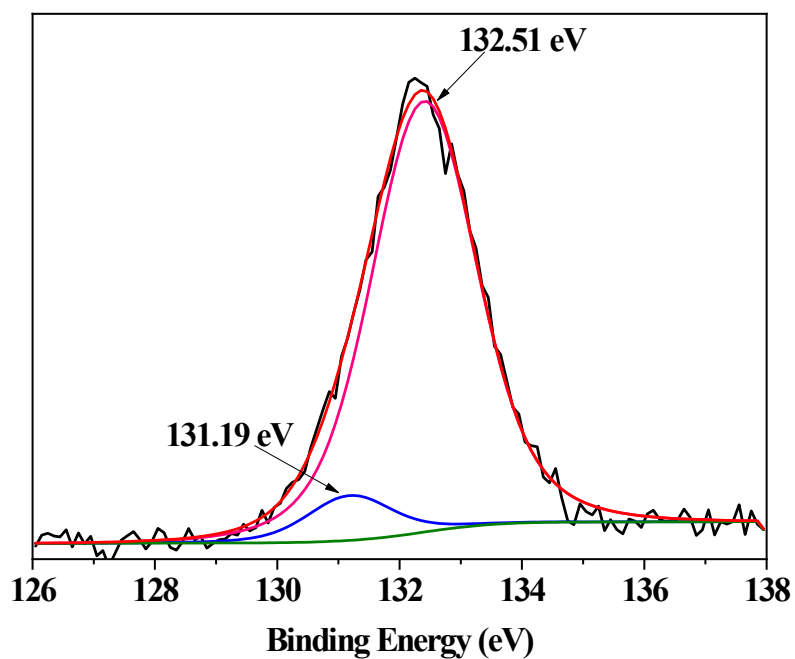


Figure S2. P 2p XPS spectra of recovered Rh/POP-PPh₃-SO₃Na

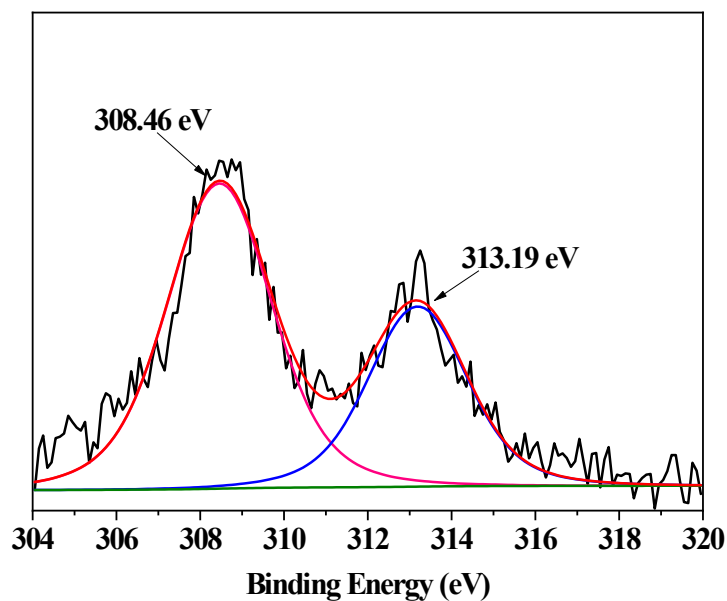


Figure S3. Rh 3d XPS spectra of recovered Rh/POP-PPh₃-SO₃Na

5. TGA curve of Rh/POP-PPh₃-SO₃Na.

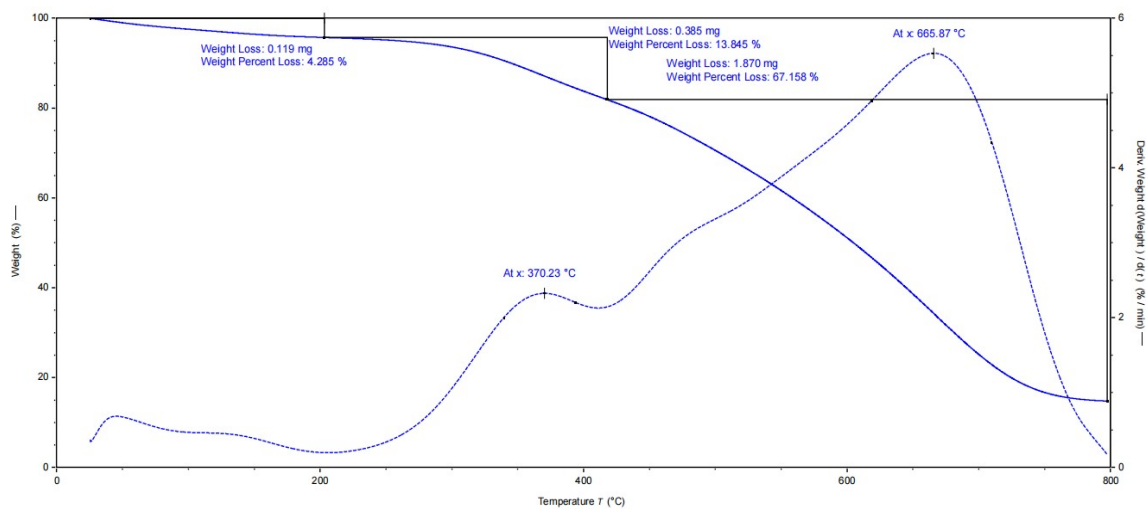


Figure S4. TGA curve of Rh/POP-PPh₃-SO₃Na

6. General procedure for Rh-catalyzed isomerization of 1-alkenes.

1. General procedure for homogeneous Rh/PPh₃-catalyzed isomerization of 1-alkenes.

In a glove box, an Schlenk flask with a magnetic stirring bar was charged with 1-alkenes **1** (2 mmol), Rh(acac)(CO)₂ (0.5 mg, 0.002 mmol), PPh₃ (1.5 mg, 0.006 mmol), EtOH(2 mL), H₂O (10 μL). The mixture was then heated to 100 °C (oil bath)

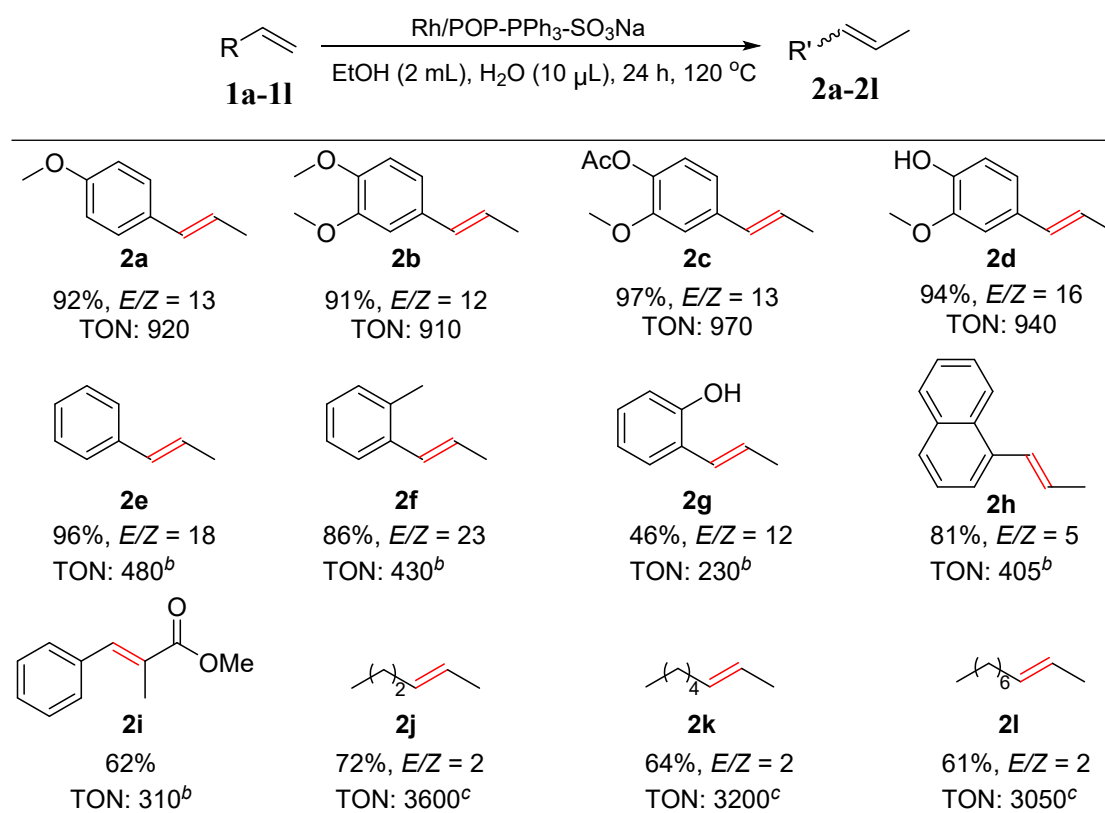
for 24 h.

2. General procedure for heterogeneous Rh-catalyzed isomerization of 1-alkenes.

In a glove box, an Schlenk flask with a magnetic stirring bar was charged with **1** (1.26 mmol), Rh/POP-PPh₃-SO₃Na (8.9 mg), EtOH (2 mL), H₂O (10 μL). The mixture was then heated to 120 °C (oil bath) for 24 h.

7. Study scope for isomerization of 1-alkenes catalyzed by Rh/POP-PPh₃-SO₃Na.

Table S3. Study scope for isomerization of 1-alkenes catalyzed by Rh/POP-PPh₃-SO₃Na^a



^a1-alkenes (1.26 mmol), Rh/POP-PPh₃-SO₃Na (8.9 mg), S/C = 1000. Yields and *E/Z* ratios were determined by GC analysis or ¹H NMR. ^b1-alkenes (0.63 mmol), Rh/POP-PPh₃-SO₃Na (8.9 mg), S/C = 500. ^c1-alkenes (6.3 mmol), Rh/POP-PPh₃-SO₃Na (8.9 mg), S/C = 5000.

8. Recycling tests of the Rh/POP-PPh₃-SO₃Na in the isomerization of **1a**

A Schlenk flask with a magnetic stirring bar was successively charged with **1a** (1.26 mmol), Rh/POP-PPh₃-SO₃Na (8.9 mg), EtOH (2 mL) and H₂O (10 μL). The Schlenk flask was purged with N₂ for three times. The mixture was stirred under a

nitrogen (balloon) atmosphere at 120 °C for 10 h. After the reaction, the mixture was diluted with EtOH (3×2 mL). The catalyst of Rh/POP-PPh₃-SO₃Na was recovered by centrifugation. Then the recovered catalyst used to test next recycling reaction with the same condition and procedure. Yields of **2a** were determined on the basis of GC analysis. GC analysis condition: SE-54, 30 m×0.32 mm×0.33 mm, flow rate 2.0 mL min⁻¹, method: 50 °C was maintained for 5 min, and then ramped from 50 °C to 250 °C at a rate of 20 °C min⁻¹, 250 °C was maintained for 5 min.

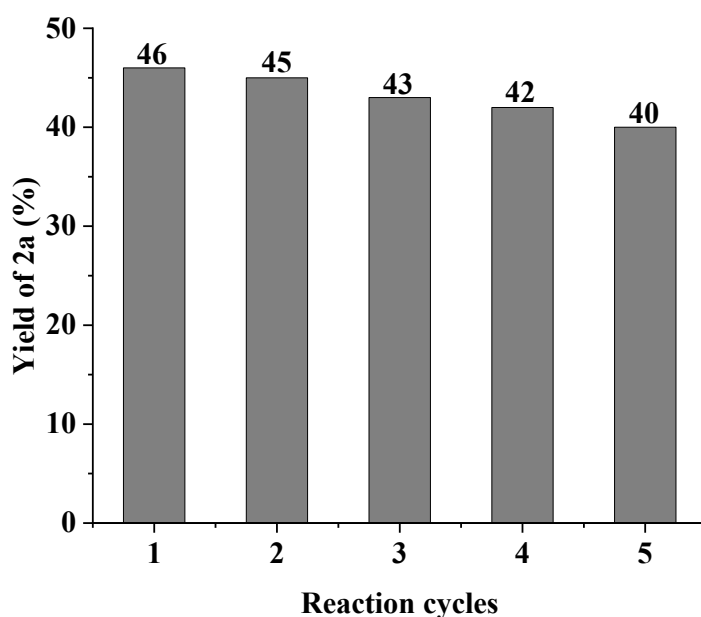
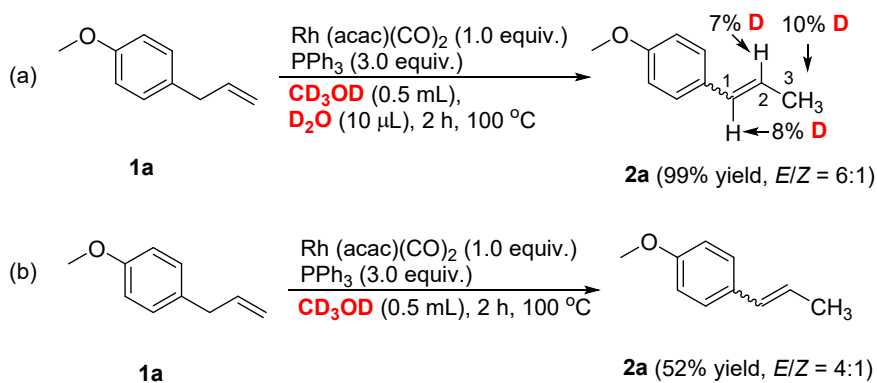


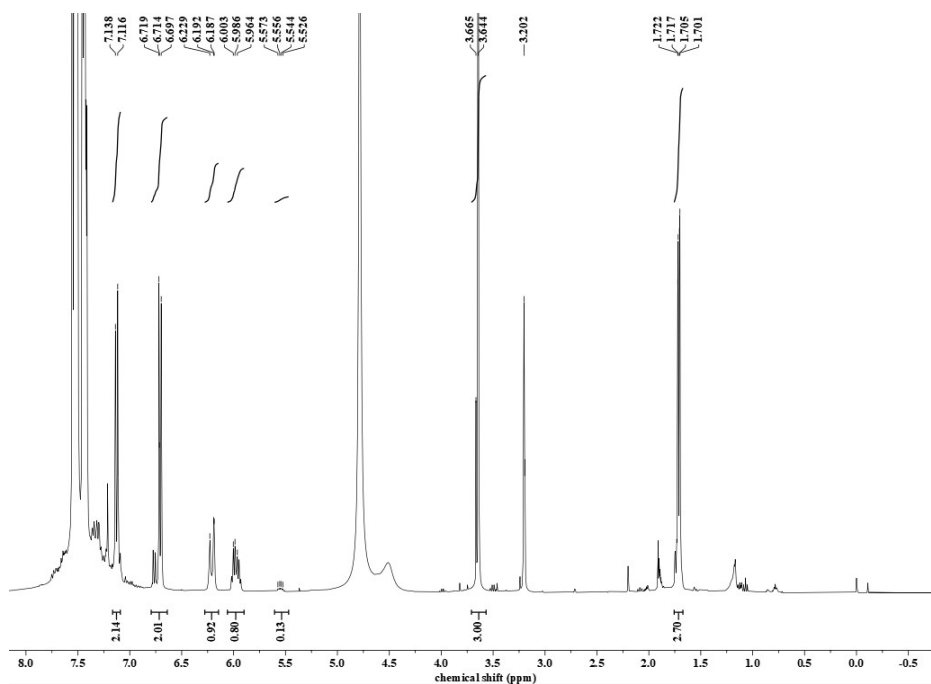
Figure S5. Reusability studies of the Rh/POP-PPh₃-SO₃Na in the isomerization of **1a**

9. Deuterium-labelling experiments

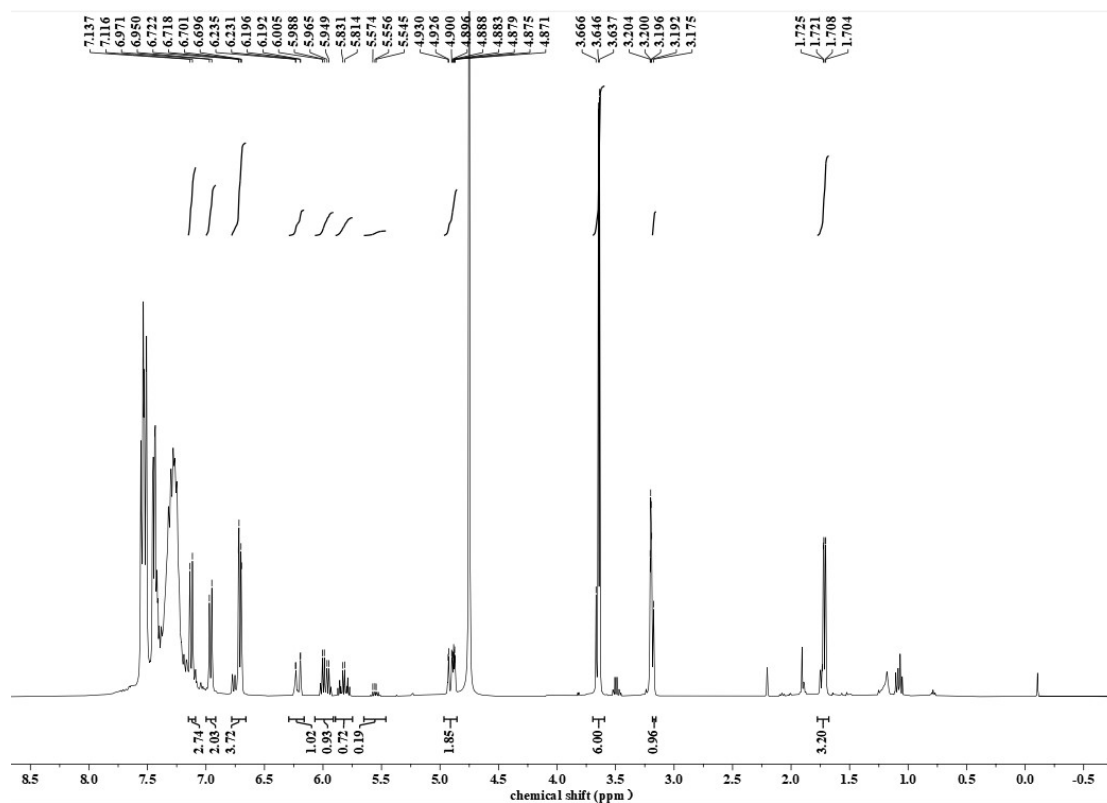


(a): In glove box, **1a** (3 μL, 1 eq), Rh(acac)(CO)₂ (5.0 mg, 1 eq), PPh₃ (15.0 mg, 3 eq), CD₃OD (0.5 mL), D₂O (10 μL) were added into a Schlenk flask. The mixture

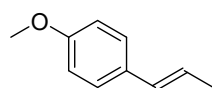
was heated to 100 °C for 2 h, then the mixture was directly characterized by ^1H NMR.



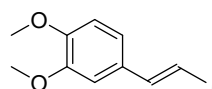
(b): In glove box, 1a (3 μL , 1 eq), $\text{Rh}(\text{acac})(\text{CO})_2$ (5.0 mg, 1 eq) PPh_3 (15.0 mg, 3 eq), CD_3OD (0.5 mL) were added into a Schlenk flask. The mixture was heated to 100 °C for 2 h, then the mixture was directly characterized by ^1H NMR.



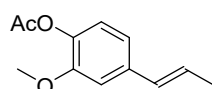
10. Characterization data for the products *trans*-2-alkenes.



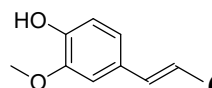
1-(4-Methoxyphenyl)propene (2a)^[2]: colorless oil, 293.0 mg, 99% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.22 (d, *J* = 7.2 Hz, 2H), 6.80 (d, *J* = 7.2 Hz, 2H), 6.32 (d, *J* = 12.8 Hz, 1H), 6.09-6.02 (m, 1H), 3.76 (s, 3H), 1.82 (dd, *J* = 5.2, 1.6 Hz, 3H) ppm.



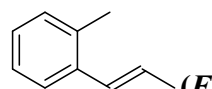
(E)-1,2-dimethoxy-4-(prop-1-en-1-yl)benzene (2b)^[2]: colorless oil, 331.5 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 6.89-6.78 (m, 3H), 6.34 (dd, *J* = 15.6, 2.0 Hz, 1H), 6.13-6.07 (m, 1H), 3.88 (s, 3H), 3.86 (s, 3H), 1.86 (dd, *J* = 6.4, 1.6 Hz, 3H) ppm.



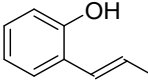
(E)-2-methoxy-4-(prop-1-en-1-yl)phenyl acetate (2c)^[2]: colorless oil, 408.4 mg, 99% yield. ¹H NMR (400 MHz, CDCl₃): δ 6.97-6.89 (m, 3H), 6.38 (d, *J* = 15.6 Hz, 1H), 6.22-6.17 (m, 1H), 3.83 (s, 3H), 2.31 (s, 3H), 1.88 (d, *J* = 6.0 Hz, 3H) ppm.

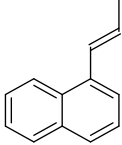


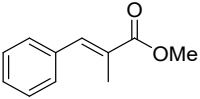
(E)-2-methoxy-4-(prop-1-en-1-yl)phenol (2d)^[2]: light yellow oil, 305.4 mg, 93% yield. ¹H NMR (400 MHz, CDCl₃): δ 6.89-6.85 (m, 3H), 6.35 (d, *J* = 12.8 Hz, 1H), 6.13-6.08 (m, 1H), 5.73-5.71 (m, 1H), 3.89 (s, 3H), 1.89 (d, *J* = 5.2 Hz, 3H).



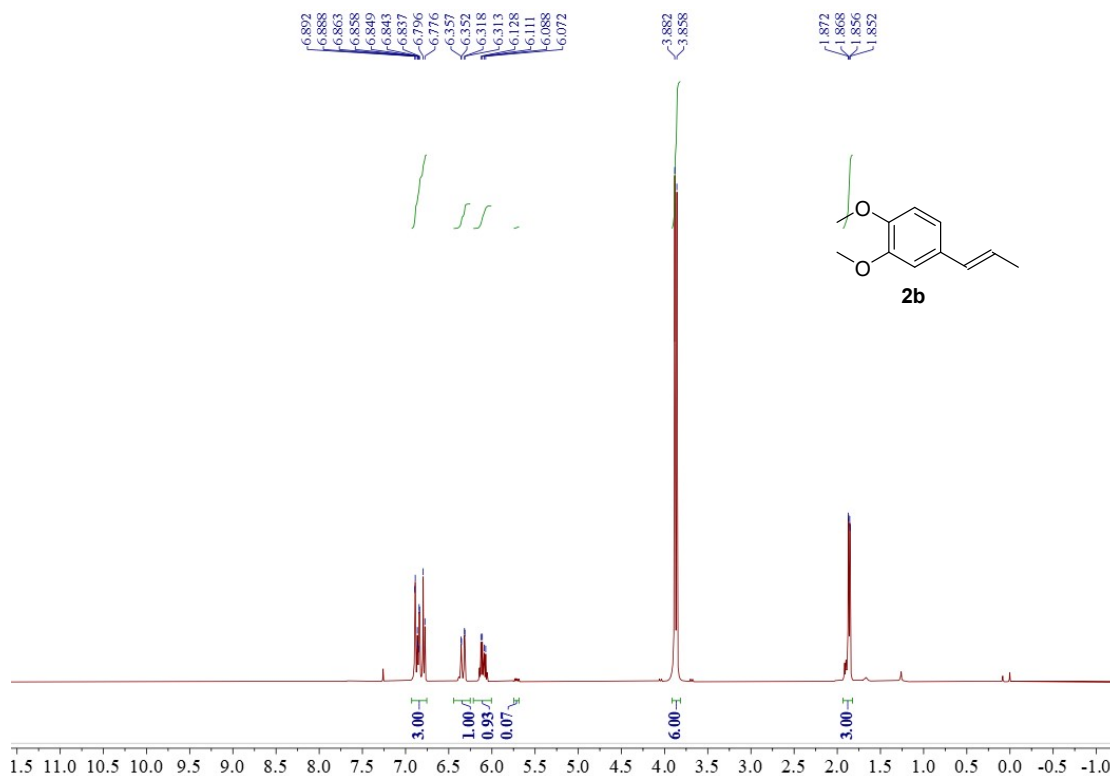
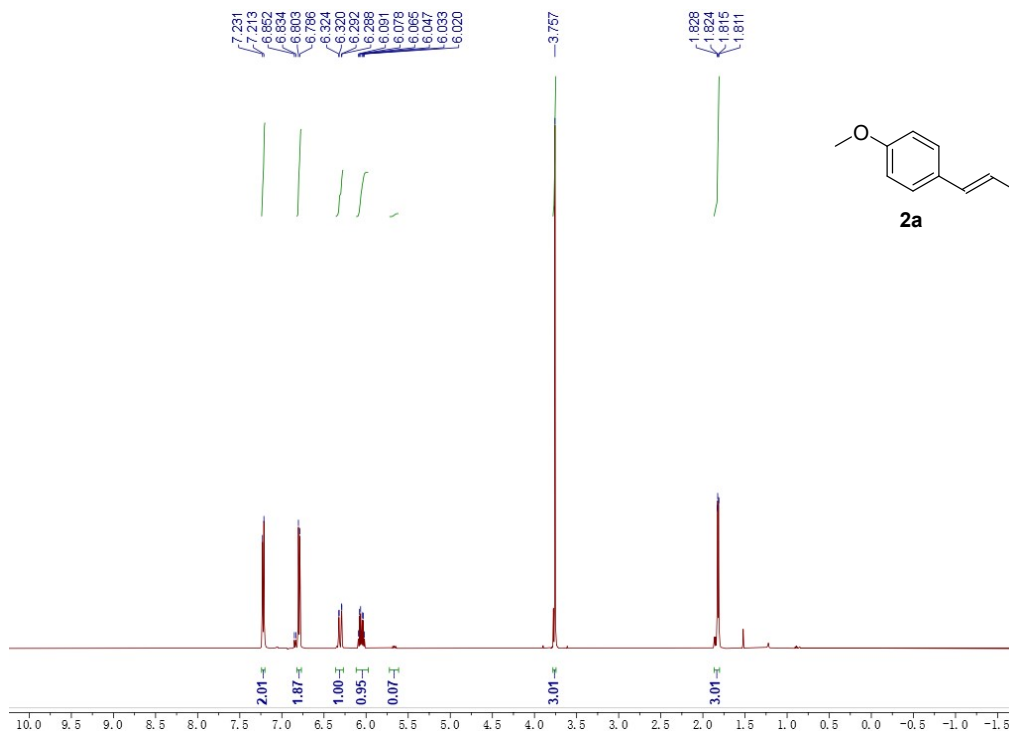
(E)-1-methyl-2-(prop-1-en-1-yl)benzene (2f)^[3]: colorless oil, 238.0 mg, 90% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.38 (d, *J* = 15.6 Hz, 1H), 7.14-7.09 (m, 3H), 6.58 (dd, *J* = 15.6, 2.0 Hz, 1H), 6.14-6.05 (m, 1H), 2.32 (s, 3H), 1.89 (dd, *J* = 6.4, 1.6 Hz, 3H) ppm.

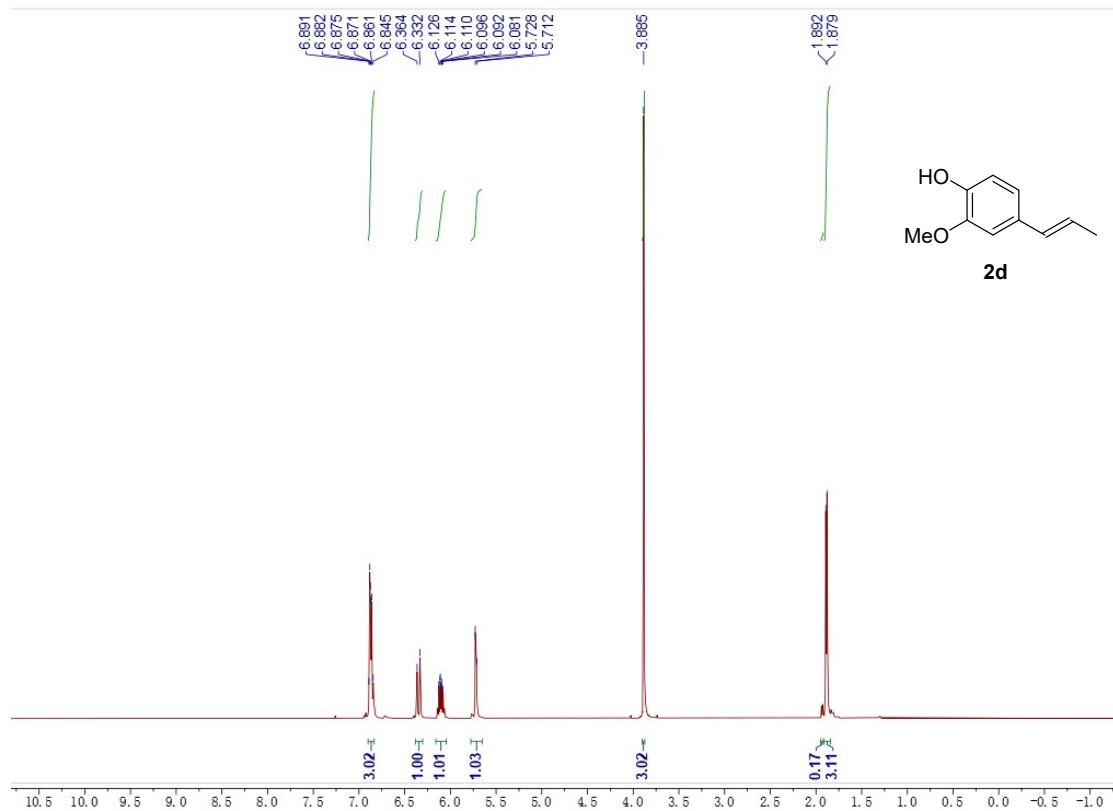
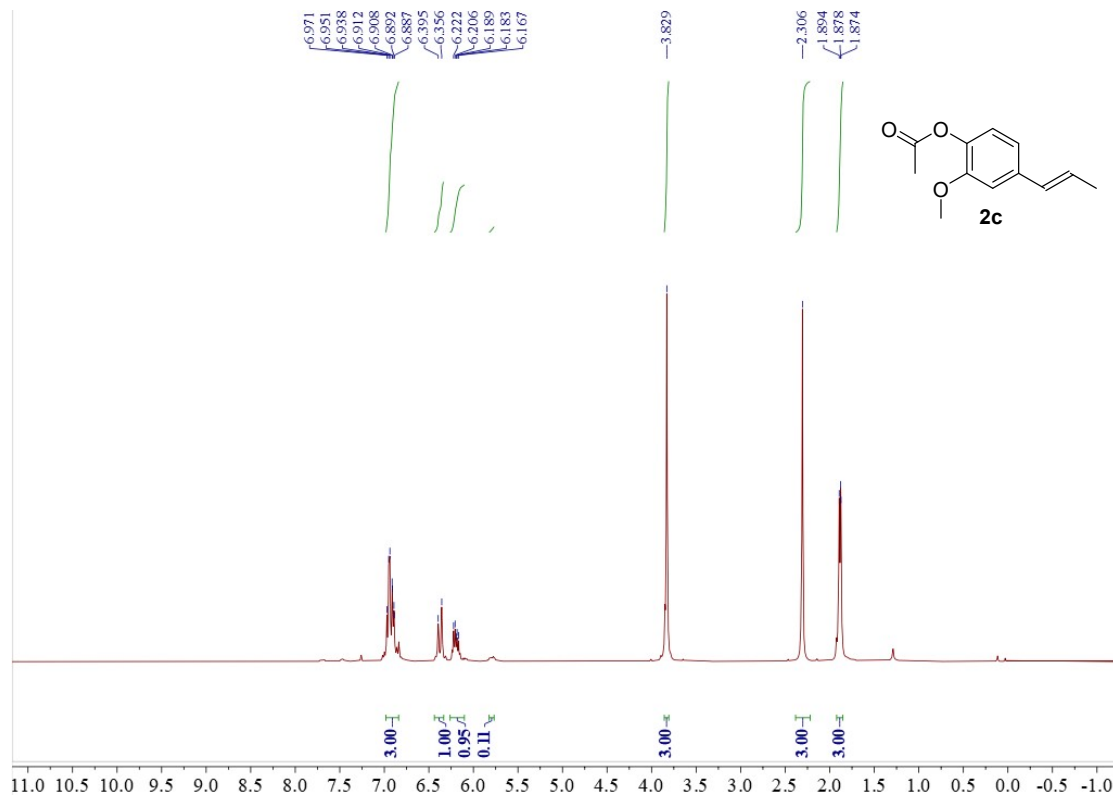
 **(E)-2-(prop-1-en-1-yl)phenol (2g)** ^[4]: light yellow oil, 139.5 mg, 52% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.30-6.56 (m, 4H), 6.58 (dd, *J* = 16.0, 2.0 Hz, 1H), 6.21-6.15 (m, 1H), 1.87 (dd, *J* = 6.8, 2.0 Hz, 3H) ppm.

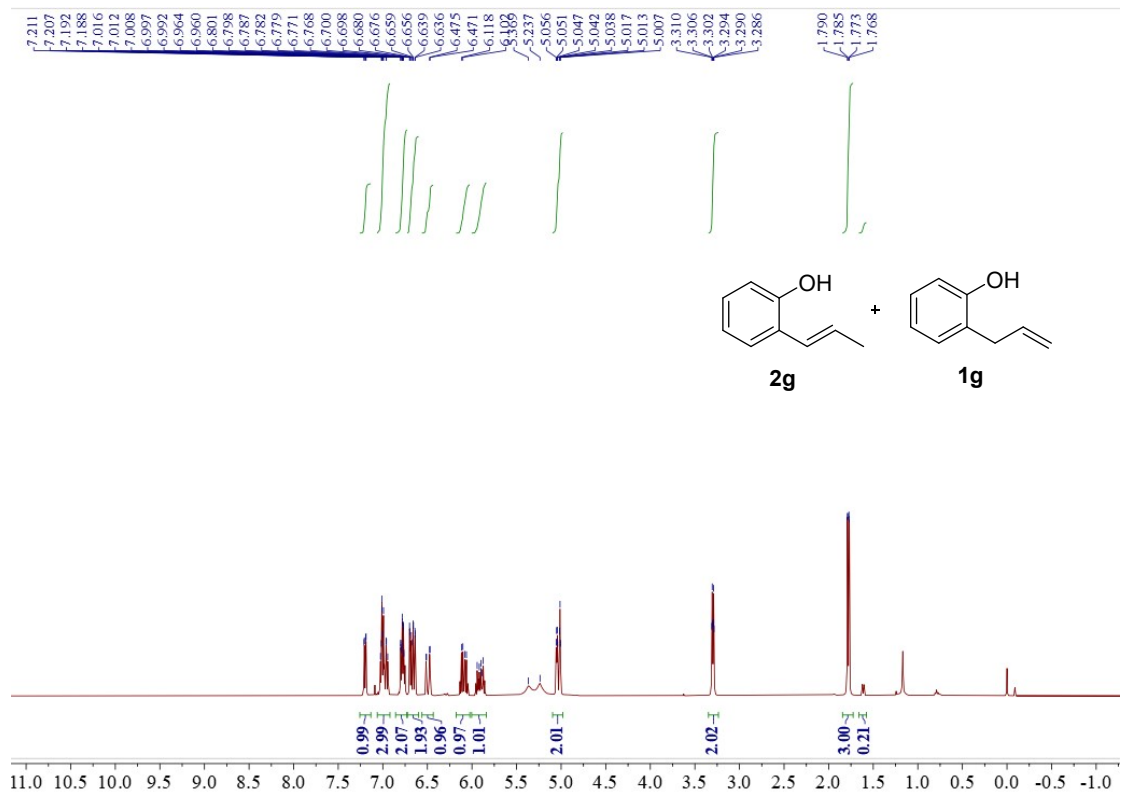
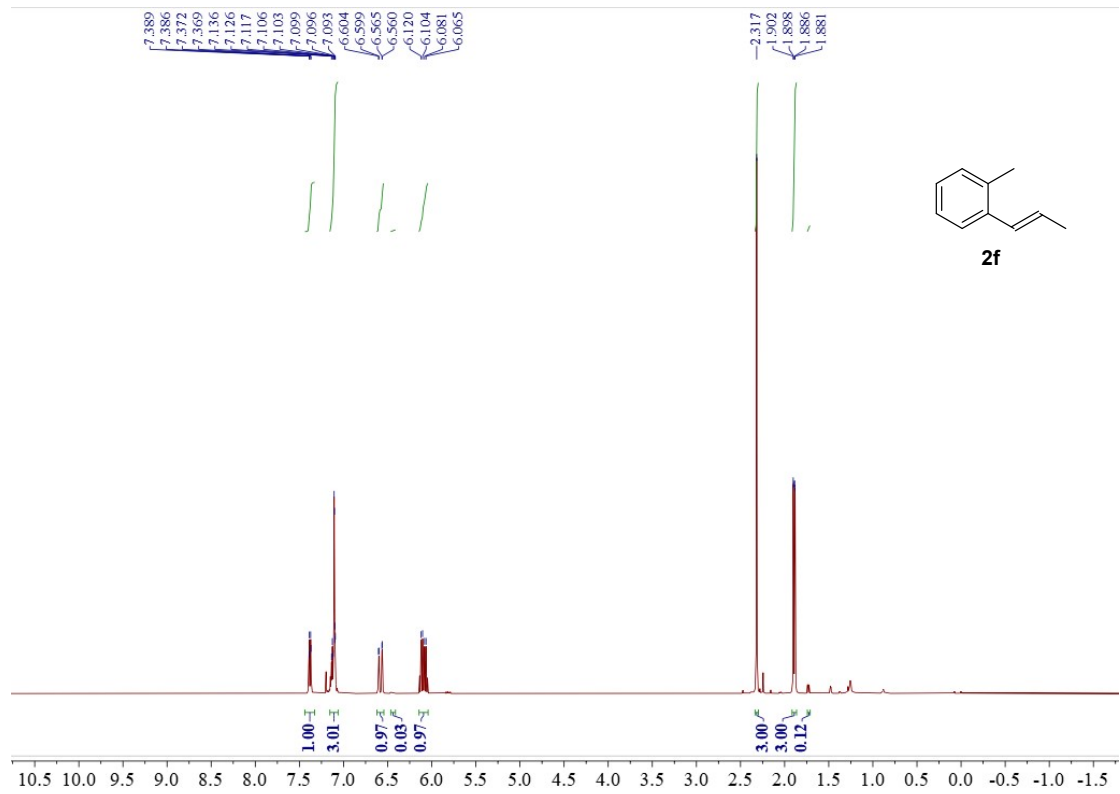
 **(E)-1-(prop-1-en-1-yl)naphthalene (2h)** ^{[5],[6]}: colorless oil, 299.4 mg, 89% yield. ¹H NMR (400 MHz, CDCl₃): δ 8.15 (d, *J* = 7.6 Hz, 1H), 7.88-7.85 (m, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.57-7.43 (m, 4H), 7.16 (dd, *J* = 15.6, 2.0 Hz, 1H), 6.32-6.23 (m, 1H), 2.03 (dd, *J* = 6.8, 2.0 Hz, 3H) ppm.

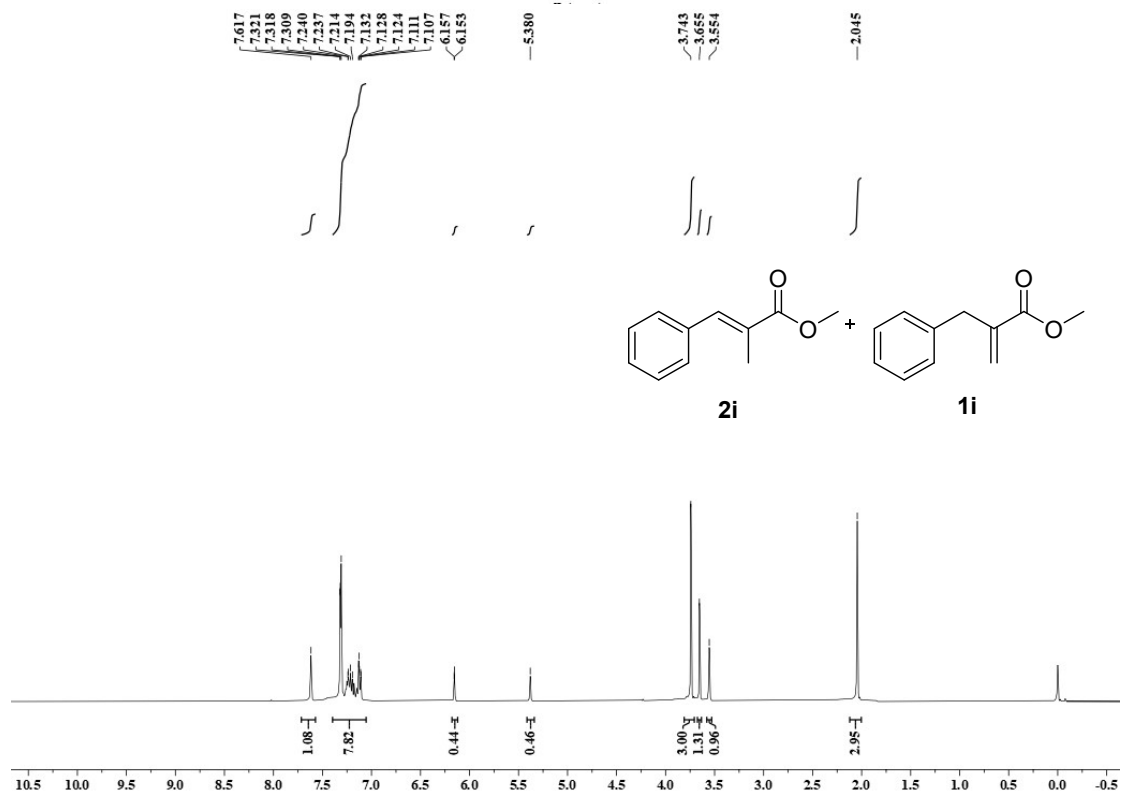
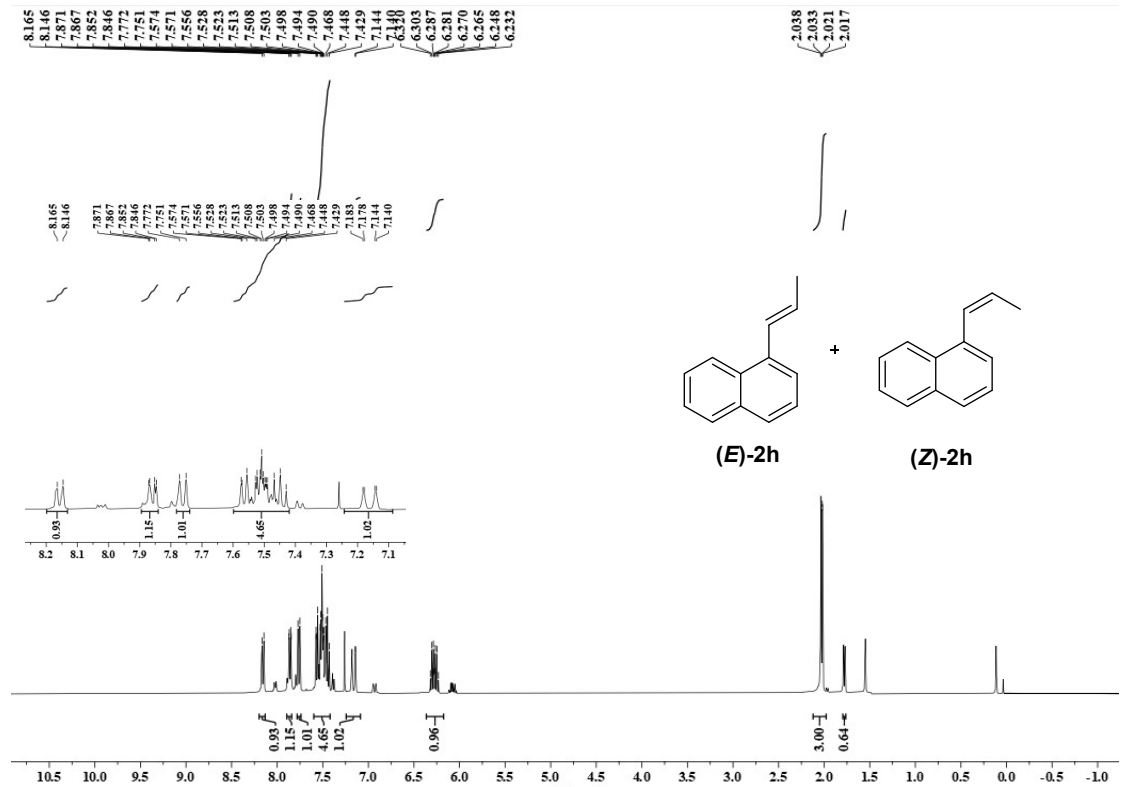
 **methyl (E)-2-methyl-3-phenylacrylate (2i)** ^[7]: colorless oil, 246.7 mg, 70% yield. ¹H NMR (400 MHz, CDCl₃): δ 7.62 (s, 1H), 7.32-7.11 (m, 5H), 3.74 (s, 3H), 2.05 (s, 3H) ppm.

11. NMR spectra of internal alkenes.



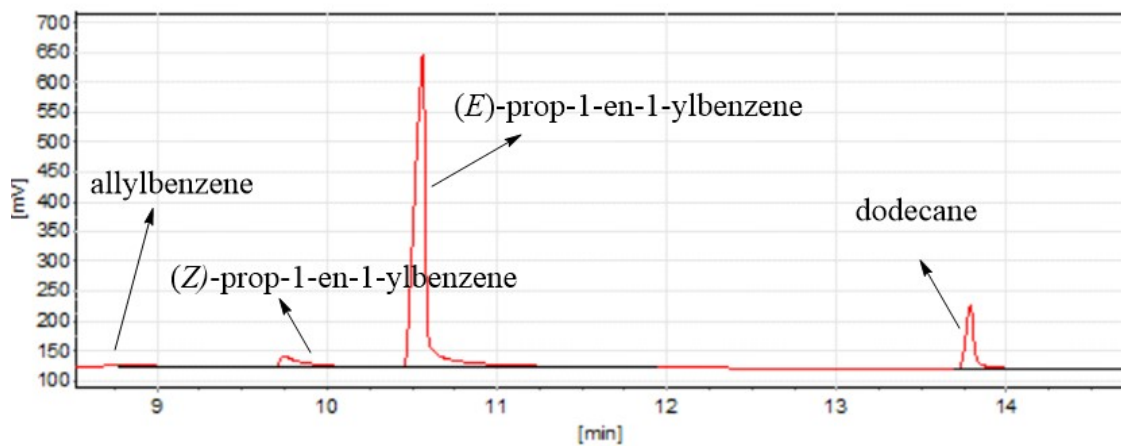




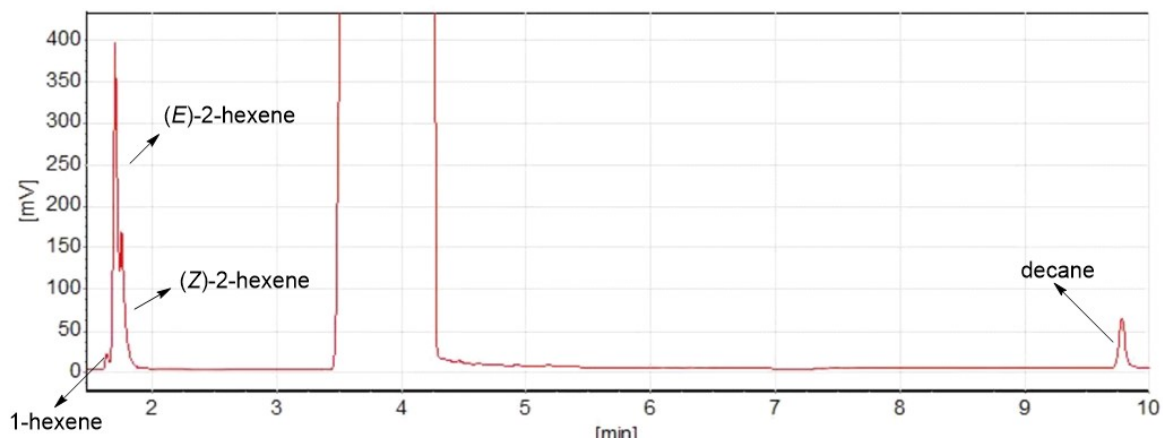


12. GC data for entries 5, 10-12.

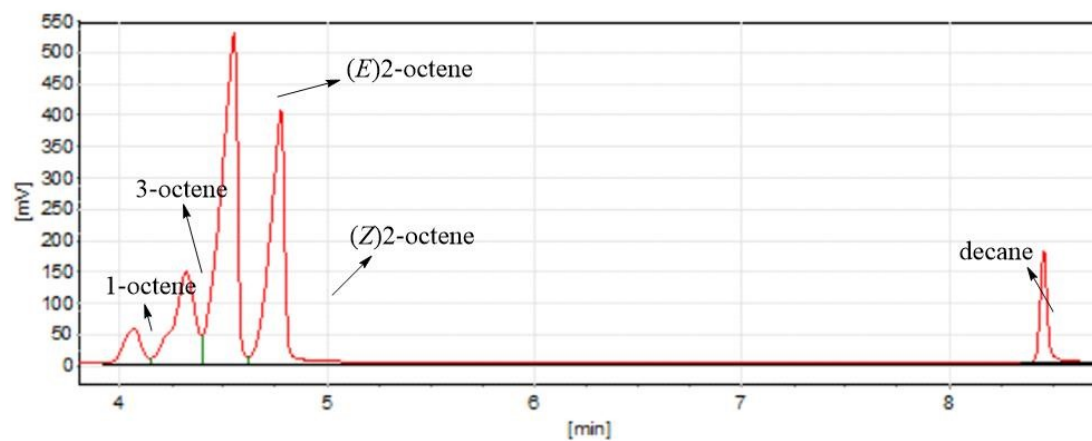
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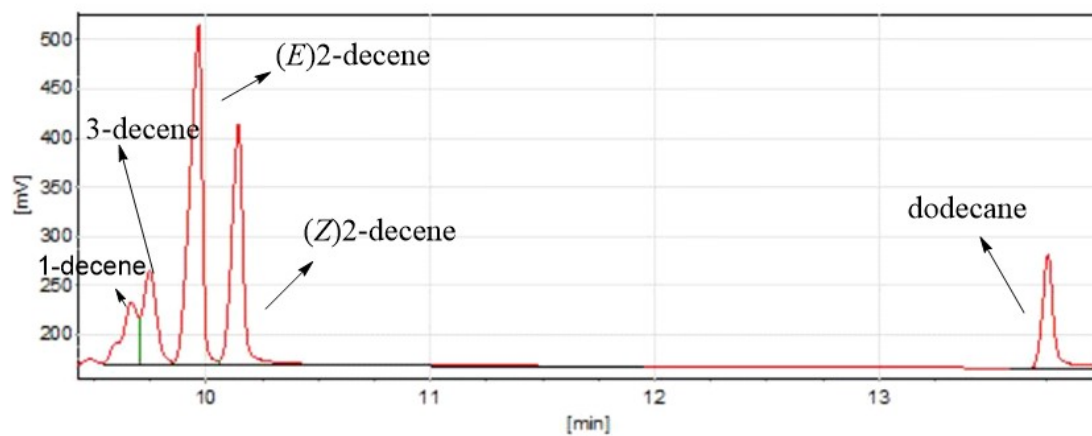
entry 10:



entry 11:



entry 12:



References:

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