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Electronic Supplementary Information (ESI)

Cross Metathesis of Methyl Oleate (MO) with Terminal, Internal Olefins by Ruthenium Catalysts: Factors Affecting the Efficient MO Conversion and the Selectivity

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(i) General procedure and analysis data for their identifications and metathesis experiment.

1-1. General procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade dichloromethane (DCM) and *n*-hexane (Kanto Chemical Co., Inc.) were transferred into a bottle containing molecular sieves (mixture of 3A 1/16, 4A 1/8 and 13X 1/16) in the drybox. Methyl oleate (≥ 99%), *cis*-stilbene, β-pinene *cis*-4-octene, *cis*-1,4-diacetoxy-2-butene, vanillideneacetone, allyl trimethylsilane and allyl glycidal ether were used in the drybox as received (Aldrich Chemical Co. or Tokyo Chemical Industry Co., lLtd.) without purification. Grubbs catalyst 1st generation $RuCl_2(PCy_3)_2(CHPh)$ (**1**), 2nd generation $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**) and Hoveyda-Grubbs catalyst 2nd generation $RuCl_2(IMesH_2)(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)$ (**3**) were used in the drybox as received [Cy = cyclohexyl, $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene] (Aldrich Chemical Co.). Nonane and dodecane purchased from Tokyo Chemical Industry Co., Ltd were used as the internal standard (IS) for GC analyses.

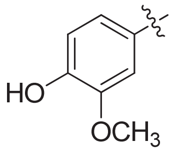
The gas chromatograph mass spectrometer (GC/MS) analyses were performed on Shimadzu GC-17A gas chromatograph directly coupled to the mass spectrometer system (MS) of Shimadzu GCMS QP5050. Agilent column model DB-1 30m length, 0.25mm in diameter and film thickness and polyethylene glycol stationary phase was used throughout the experiment. Helium was used as the carrier gas at a flow rate of 1.7 mL/min. The oven temperature was programmed from 50°C for 10 min at a rate of 15°C/min with a final hold 200°C for 55 min (the total analysis time was 75 min).

Shimadzu GC-2025 gas chromatograph with FID detector (GC-FID) was employed for quantitative analysis of the starting materials and products using a (0.25 µm x 0.25 mm x 30m) DB-1 column. Nitrogen gas was used as the carrier gas at a flow rate of 2.0 mL/min. The oven temperature was programmed from 50°C for 10 min at a rate of 15°C/min with a final hold 200°C for 45 min (the total analysis time was 65 min). The quantitative analyses were performed by comparing the peak area of the products with known amount of nonane or dodecane as an internal standard. Calibration coefficient was determined by analyzing the mixtures of MO and the internal standard with different ratios. The amount of MO was calculated by normalization using the internal standard method with the calibration coefficient. The conversion of MO was obtained from the comparison of peak areas before and after reactions.

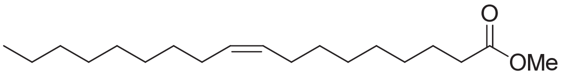
1-2. The effective carbon number (ECN) of materials.

The effective carbon number (ECN) concept for GC-FID analyses was used to calculate the yields of products.[1] The ECN contributions of some functional groups (CH_2SiMe_3, $C_6H_3(3\text{-}OCH_3)(4\text{-}OH)$) were calculated from the GC-FID data of the related compounds containing similar moiety (allyltrimethylsilane (ATMS), vanillylidenacetone (VA)). Nonane was used as the internal standard. Contributions to the effective carbon number were summarized in Table S1. ECNs of starting materials and products for both self- and cross-metathesis reactions were shown in Figure S1-S4.

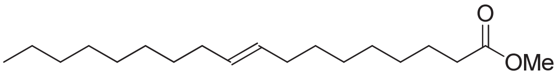
Table S1. ECN contributions of atoms or groups.

type	atom	ECN contribution[a]
Aliphatic	C	1
Aromatic	C	1
Olefinic	C	0.95
Carbonyl	C	0
Ester group	-	-1.49
Ether	O	-1.0
$-CH_2SiMe_3$	-	4.01[b]
	-	5.2[c]

[a] Ref X. [b] Calculated from GC-FID response of allyltrimethylsilane (ATMS) relative to nonane. [c] Calculated from GC-FID response of vanillylidenacetone (VA) relative to nonane.

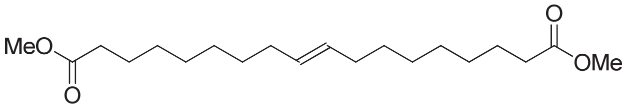


methyl oleate (**MO**)
ECN = 17.41



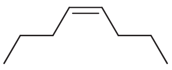
(*E*)-methyl octadec-9-enoate (**SM3**)
ECN = 17.41

(*E*)-octadec-9-ene (**SM1**)
ECN = 17.9

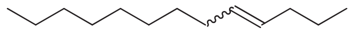


(*E*)-dimethyl octadec-9-enedioate (**SM2)**
ECN = 16.92

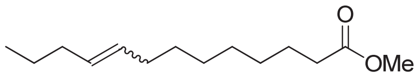
Figure S1. ECN of the starting material and products for self metathesis of methyl oleate (MO).



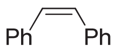
cis-4-octene (**CO**)
ECN = 7.9



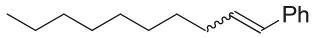
tridec-4-ene (**CM1**)
ECN = 12.9



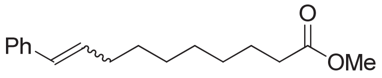
methyl tridec-9-enoate (**CM2**)
ECN = 12.41



cis-stilbene (**CS**)
ECN = 13.9

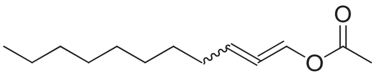


dec-1-en-1-ylbenzene (**CM1**)
ECN = 15.9

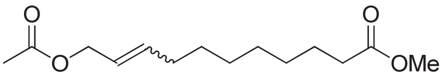


methyl 10-phenyldec-9-enoate (**CM2**)
ECN = 15.41

cis-1,4-diacetoxy
-2-butene (**DAB**)
ECN = 4.92

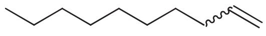


undec-2-en-1-yl acetate (**CM1**)
ECN = 11.41

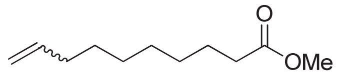


methyl 11-acetoxyundec-9-enoate (**CM2**)
ECN = 10.92

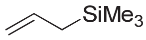
Figure S2. ECN of the starting material and products for cross-metathesis of methyl oleate (MO) with symmetric internal olefins.



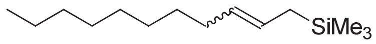
dec-1-ene (**CM1**)
ECN = 9.9



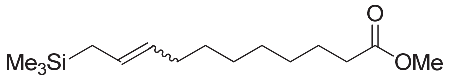
methyl dec-9-enoate (**CM2**)
ECN = 9.41



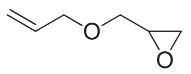
allyltrimethylsilane
(**ATMS**)
ECN = 5.91



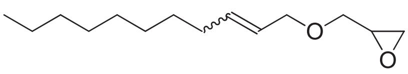
trimethyl(undec-2-en-1-yl)silane (**CM3**)
ECN = 13.91



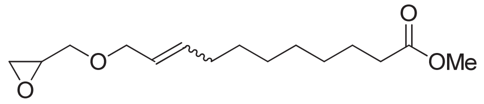
methyl 11-(trimethylsilyl)undec-9-enoate (**CM4**)
ECN = 13.42



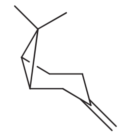
allyl glycidal ether
(**AGE**)
ECN = 3.9



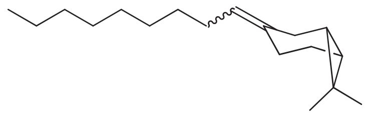
((undec-2-en-1-yloxy)methyl)
oxirane (**CM3**)
ECN = 11.9



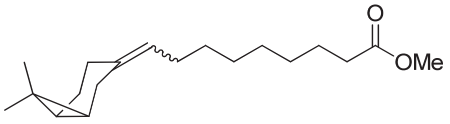
methyl 11-(oxiran-2-ylmethoxy)undec
-9-enoate (**CM4**)
ECN = 11.41



β-pinene (**PN**)
ECN = 9.9

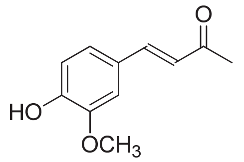


7,7-dimethyl-3-nonylidenebicyclo
[4.1.0]heptane (**CM3**)
ECN = 17.9

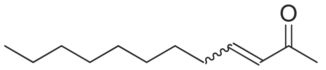


methyl 9-((1*R*,6*S*)-7,7-dimethylbicyclo
[4.1.0]heptan-3-ylidene)nonanoate (**CM4**)
ECN = 17.41

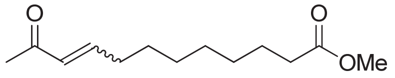
Figure S3. ECN of the starting material and products for cross-metathesis of methyl oleate (MO) with terminal olefins.



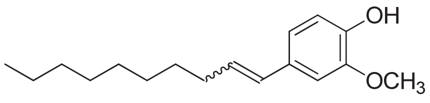
vanillylidenacetone (**VA**)
ECN = 8.1



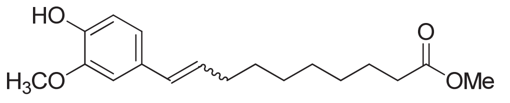
dodec-3-en-2-one (**CM1**)
ECN = 10.9



methyl 11-oxododec-9-enoate (**CM2**)
ECN = 10.41



4-(dec-1-en-1-yl)-2-methoxyphenol (**CM3**)
ECN = 15.1



methyl 10-(4-hydroxy-3-methoxyphenyl)dec-9-enoate (**CM4**)
ECN = 16.61

Figure S4. ECN of the starting material and products for cross-metathesis of methyl oleate (MO) with an asymmetric internal olefin.

(ii) Calculation of yield, conversion and selectivity.

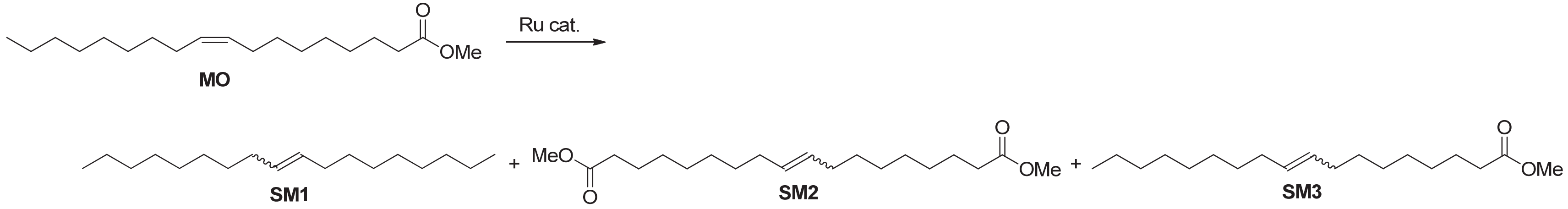
2-1. Self-metathesis reaction of methyl oleate (MO).

Typical procedure (run 2, Table 2, S2) is as follows. Methyl oleate (MO, 0.593 g, 2.00 mmol) and dodecane (0.100 g) as an internal standard for GC analyses were dissolved in 1.0 mL of CH_2Cl_2 (DCM). Grubbs catalyst 2nd generation $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**) (0.0085 g, 0.5 mol%, 0.010 mmol) was added into the solution. The mixture was stirred at 50 ºC for 1 hour, and then the resulting mixture was filtered through a Celite pad. The obtained filtrate was analyzed using the gas chromatograph with FID detector (GC-FID) and the gas chromatograph mass spectrometer (GC/MS). The results of self-metathesis reactions are summarized in Table 2, S2. GC-FID and GC/MS spectra are shown in Figure S5-S6.

2-2. Cross-metathesis reaction of methyl oleate (MO) with olefins.

Typical procedure (run 11, Table 2, S3) is as follows. Methyl oleate (MO, 0.593 g, 2.00 mmol), *cis*-4-octene (CO, 0.224g, 2.00 mmol) and nonane (0.100 g) as an internal standard for GC analyses were dissolved in 1.0 mL of CH_2Cl_2 (DCM). Grubbs catalyst 2nd generation $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**) (0.0085 g, 0.5 mol%, 0.010 mmol) was added into the solution. The mixture was stirred at 50 ºC for 1 hour, and then the resulting mixture was filtered through a Celite pad. The obtained filtrate was analyzed using the gas chromatograph with FID detector (GC-FID) and the gas chromatograph mass spectrometer (GC/MS). The results of cross-metathesis reactions are summarized in Table 2-3, S3-S9. GC-FID and GC/MS spectra are shown in Figure S7-S20.

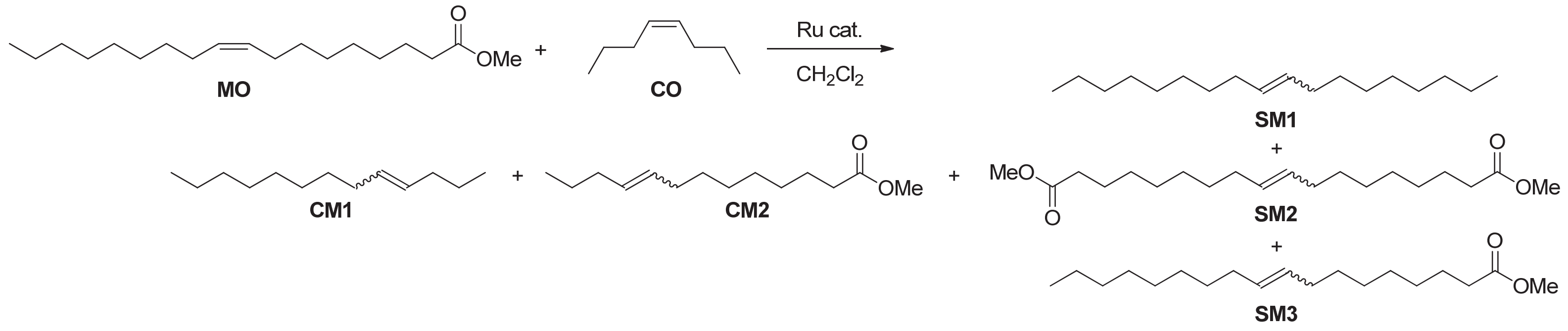
Table S2. Self metathesis of methyl oleate (MO) by $RuCl_2(PCy_3)_2(CHPh)$ (**1**) or $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



run[a]	catalyst (mol%)	solvent	temp (°C)	Time (h)	Conv. of MO (%)[b]	SM1 *trans* (%)[c]	SM1 *cis* (%)[c]	SM2 *trans* (%)[c]	SM2 *cis* (%)[c]	SM3 *trans* (%)[c]	SM3 *cis* (%)[c]	Select. (1) (%)[d]	Select. (2) (%)[e]
1	**2** (0.1)	CH_2Cl_2	50	1	62	23	6	15	4	29	8	77	56
2	**2** (0.5)	CH_2Cl_2	50	1	75	18	5	10	3	19	5	48	60
3	**2** (1.0)	CH_2Cl_2	50	1	77	17	4	8	3	18	5	42	58
4	**1** (0.5)	CH_2Cl_2	50	1	66	7	2	9	3	20	15	32	38
5	**2** (0.5)	CH_2Cl_2	50	0.33	80	25	7	7	3	16	5	53	67
6	**2** (0.5)	CH_2Cl_2	50	24	65	19	4	14	4	28	8	64	53
7	**2** (0.5)	hexane	50	0.33	79	25	7	7	3	16	5	53	67
8	**2** (0.1)	CH_2Cl_2	23	1	55	24	6	19	5	36	9	98	55
9	**2** (0.5)	CH_2Cl_2	23	1	76	17	5	11	4	19	5	49	61

[a] Conditions: methyl oleate 2.00 mmol, solvent 1.0 mL. [b] Conversion of MO estimated by GC using international standard. [c] GC yield estimated according to the effect of carbon number (ECN) rule. [d] Selectivity of SM1,2 based on the conversion of MO. [e] Selectivity of self metathesis products (%) = (SM1+SM2)/(SM1+SM2+SM3). SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate.

Table S3. Cross metathesis of methyl oleate (**MO**) with *cis*-4-octene (**CO**) by $RuCl_2(PCy_3)_2(CHPh)$ (**1**), $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**) or $RuCl_2(IMesH_2)(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)$ (**3**).[a]

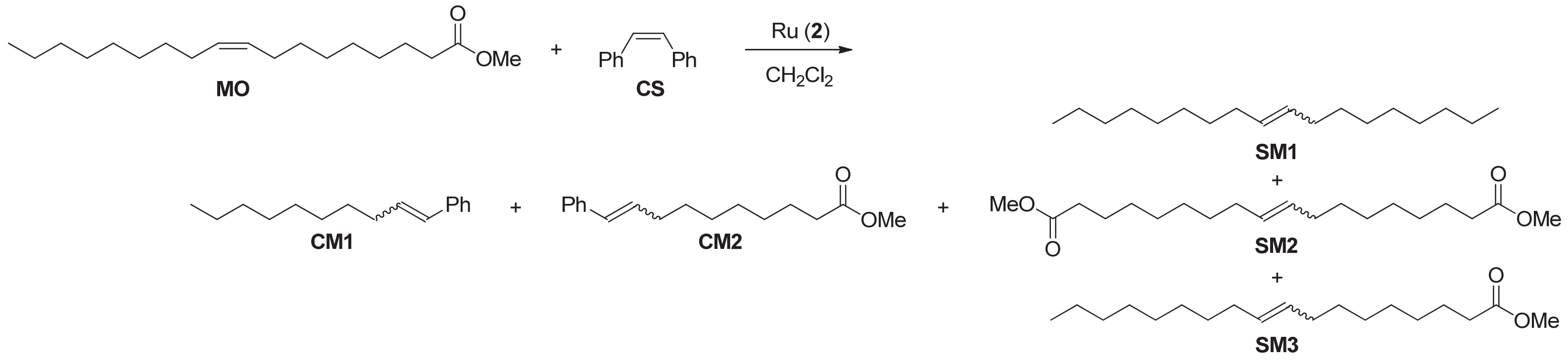


run[a]	CO (eq.)[b]	Time (h)	Ru cat.[c]	Conv. of MO (%)[d]	CM1 (%)[e]	CM2 (%)[e]	SM1 *trans* (%)[e]	SM1 *cis* (%)[e]	SM2 *trans* (%)[e]	SM2 *cis* (%)[e]	SM3 *trans* (%)[e]	SM3 *cis* (%)[e]	Select. (1) (%)[f]	Select. (2) (%)[g]
10	1.0	17	**1**	17	2	2	0	0	1	0	8	75	18	80
11	1.0	1	**2**	81	43	41	9	2	8	2	17	3	78	80
12	1.0	1	**3**	82	32	31	8	1	7	1	16	3	61	79
13	5.0	1	**2**	93	88	86	3	0	3	0	6	1	>99	97
14	10	1	**2**	94	93	90	1	0	1	0	4	2	>99	99
15[h]	10	1	**2**	80	44	50	2	0	2	0	6	14	64	96
21	1.0	8	**2**	82	43	40	10	2	8	1	16	3	76	80

[a] Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C. [b] Based on MO. [c] $RuCl_2(CHPh)(PCy_3)_2$ [Ru(**1**)], Cy = cyclohexyl, $RuCl_2(PCy_3)(IMesH_2)(CHPh)$ [Ru(**2**), $IMesH_2$ = 1,3-bis(2,4,6-trimethylphenyl)imidazolin-2-ylidene], $RuCl_2(CH\text{-}2\text{-}O^iPr\text{-}C_6H_4)(IMesH_2)$ [Ru(**3**)].

[d]Conversion of MO estimated by GC using international standard. [e]GC yield estimated according to the effect of carbon number (ECN) rule. [f]Selectivity of CM1,2 and SM1,2 based on the conversion of MO. [g]Selectivity of cross metathesis products (%) = (CM1+CM2)/(CM1+CM2+SM1+SM2). CM1: tridec-4-ene, CM2: methyl tridec-9-enoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate. [h]Reaction without solvent (CH_2Cl_2).

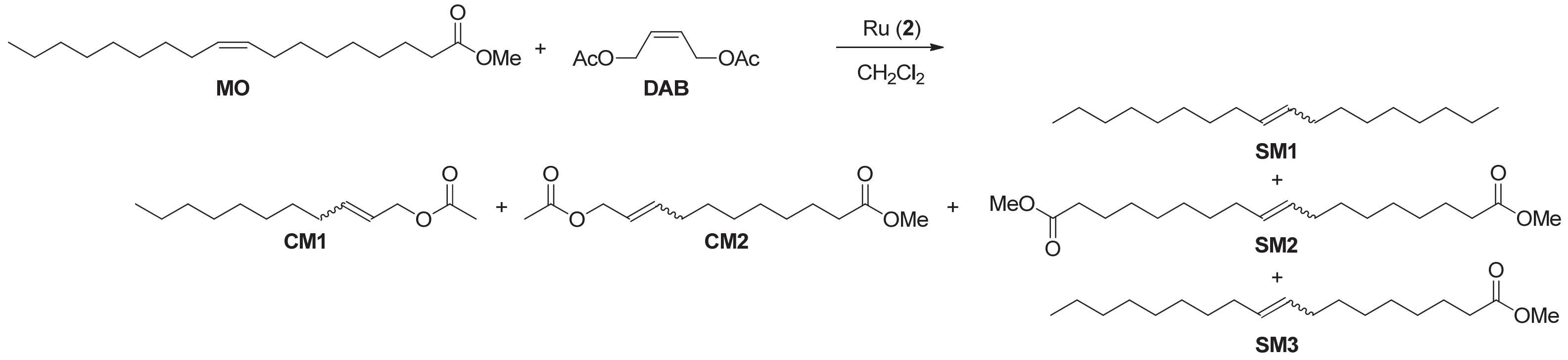
Table S4. Cross metathesis of methyl oleate (**MO**) with *cis*-stilbene (**CS**) by $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



run[a]	CS (eq.)[b]	Time (h)	Conv. of MO (%)[c]	CM1 (%)[d]	CM2 (%)[d]	SM1 *trans* (%)[d]	SM1 *cis* (%)[d]	SM2 *trans* (%)[d]	SM2 *cis* (%)[d]	SM3 *trans* (%)[d]	SM3 *cis* (%)[d]	Select. (1) (%)[e]	Select. (2) (%)[f]
16	1.0	1	92	45	34	8	2	9	3	6	2	67	78
17	5.0	1	97	88	76	2	0	3	1	2	1	91	96

[a]Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C. [b]Based on MO. [c]Conversion of MO estimated by GC using international standard. [d]GC yield estimated according to the effect of carbon number (ECN) rule. [e]Selectivity of CM1,2 and SM1,2 based on the conversion of MO. [f]Selectivity of cross metathesis products (%) = (CM1+CM2)/(CM1+CM2+SM1+SM2). CM1: dec-1-en-1-ylbenzene, CM2: methyl 10-phenyldec-9-enoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate.

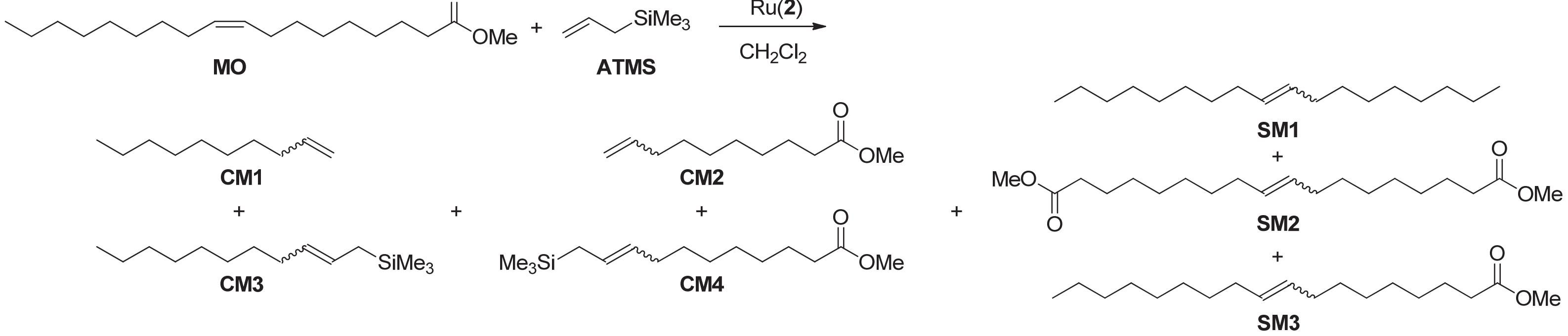
Table S5. Cross metathesis of methyl oleate (**MO**) with *cis*-1,4-diacetoxy-2-butene (**DAB**) by $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



run[a]	DAB (eq.)[b]	Time (h)	Conv. of MO (%)[c]	CM1 *trans* (%)[d]	CM1 *cis* (%)[d]	CM2 *trans* (%)[d]	CM2 *cis* (%)[d]	SM1 *trans* (%)[d]	SM1 *cis* (%)[d]	SM2 *trans* (%)[d]	SM2 *cis* (%)[d]	SM3 *trans* (%)[d]	SM3 *cis* (%)[d]	Select. (1) (%)[e]	Select. (2) (%)[f]
18	1.0	1	87	59	6	56	5	5	1	87	65	11	2	86	91
19	5.0	1	80	19	8	22	2	1	1	80	27	13	6	41	88
20	10	1	67	4	2	4	2	0	0	67	6	1	33	10	92
22	1.0	3	90	48	6	44	3	7	1	5	1	10	2	72	88

[a] Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C. [b] Based on MO. [c] Conversion of MO estimated by GC using international standard. [d] GC yield estimated according to the effect of carbon number (ECN) rule. [e] Selectivity of CM1,2 and SM1,2 based on the conversion of MO. [f] Selectivity of cross metathesis products (%) = (CM1+CM2)/(CM1+CM2+SM1+SM2). CM1: undec-2-en-1-yl acetate, CM2: methyl 11-acetoxyundec-9-enoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate.

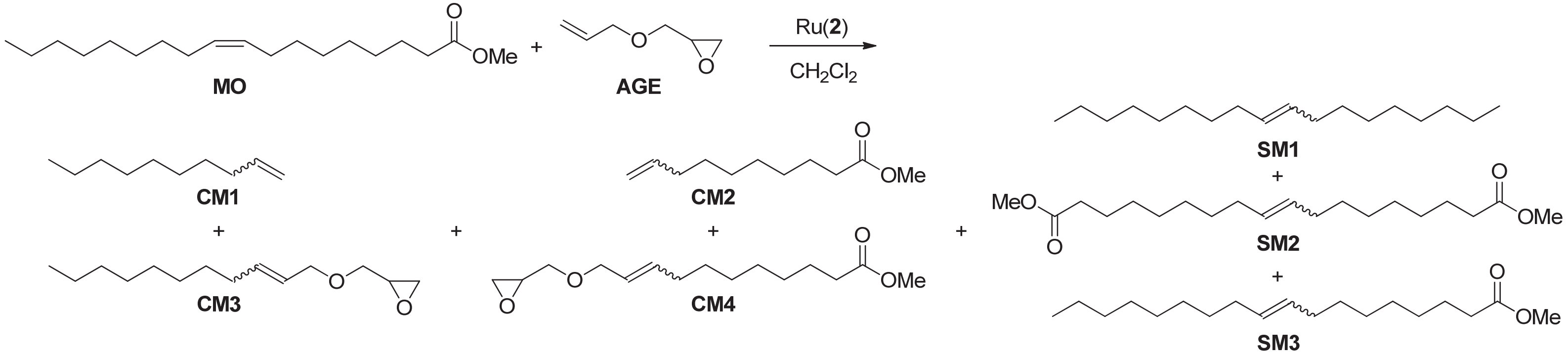
Table S6. Cross metathesis of methyl oleate (**MO**) with allyltrimethylsilane (**ATMS**) by $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



run[a]	ATMS (eq.)[b]	Conv. of MO (%)[c]	CM1 (%)[d]	CM2 (%)[d]	CM3 *trans* (%)[d]	CM3 *cis* (%)[d]	CM4 *trans* (%)[d]	CM4 *cis* (%)[d]	SM1 *trans* (%)[d]	SM1 *cis* (%)[d]	SM2 *trans* (%)[d]	SM2 *cis* (%)[d]	SM3 *trans* (%)[d]	SM3 *cis* (%)[d]	Select. (1) (%)[e]	Select. (2) (%)[f]
23	1.0	80	10	10	21	7	19	7	9	2	8	2	17.0	3.2	71.5	78.7
24	5.0	94	36	39	37	13	36	13	2	1	3	1	4.9	1.3	>99	96.4
25	10	96	46	47	35	13	33	12	1	0	1	0	2.9	1.0	>99	98.4
26[g]	10	96	27	37	22	8	25	9	1	1	2	0	2	1	71	97

[a] Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C, time 1 h. [b] Based on MO. [c] Conversion of MO estimated by GC using international standard. [d] GC yield estimated according to the effect of carbon number (ECN) rule. [e] Selectivity of CM1-4 and SM1,2 based on the conversion of MO. [f] Selectivity of cross metathesis products (%) = (CM1+CM2+CM3+CM4)/(CM1+CM2+CM3+CM4+SM1+SM2). CM1: dec-1-ene, CM2: methyl dec-9-enoate, CM3: trimethyl(undec-2-en-1-yl)silane, CM4: methyl 11-(trimethylsilyl)undec-9-enoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate. [g] Reaction without solvent (CH_2Cl_2).

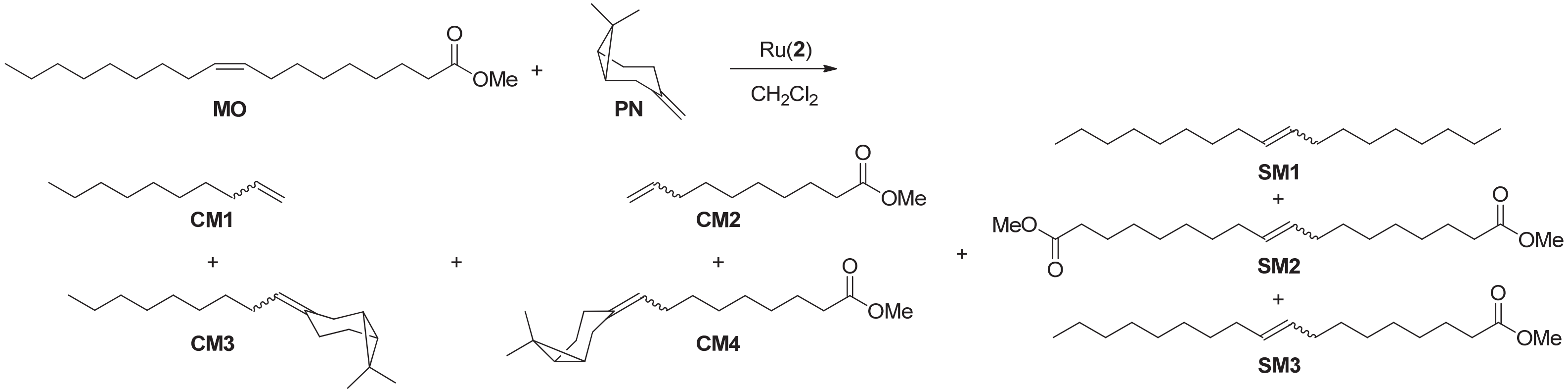
Table S7. Cross metathesis of methyl oleate (**MO**) with allyl glycidal ether (**AGE**) by $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



run[a]	AGE (eq.)[b]	Conv. of MO (%)[c]	CM1 (%)[d]	CM2 (%)[d]	CM3 (%)[d]	CM4 (%)[d]	SM1 *trans* (%)[d]	SM1 *cis* (%)[d]	SM2 *trans* (%)[d]	SM2 *cis* (%)[d]	SM3 *trans* (%)[d]	SM3 *cis* (%)[d]	Select. (1) (%)[e]	Select. (2) (%)[f]
27	1.0	38	1	1	1	1	1	1	1	1	15	47	16	50
28	5.0	55	1	1	1	1	0	0	0	0	7	36	4	>99
29	10	46	1	1	v	1	0	0	0	0	4	50	4	>99

[a] Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C, time 1 h. [b] Based on MO. [c] Conversion of MO estimated by GC using international standard. [d] GC yield estimated according to the effect of carbon number (ECN) rule. [e] Selectivity of CM1-4 and SM1,2 based on the conversion of MO. [f] Selectivity of cross metathesis products (%) = (CM1+CM2+CM3+CM4)/(CM1+CM2+CM3+CM4+SM1+SM2). CM1: dec-1-ene, CM2: methyl dec-9-enoate, CM3: 2-((undec-2-en-1-yloxy)methyl)oxirane, CM4: methyl 11-(oxiran-2-ylmethoxy)undec-9-enoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate.

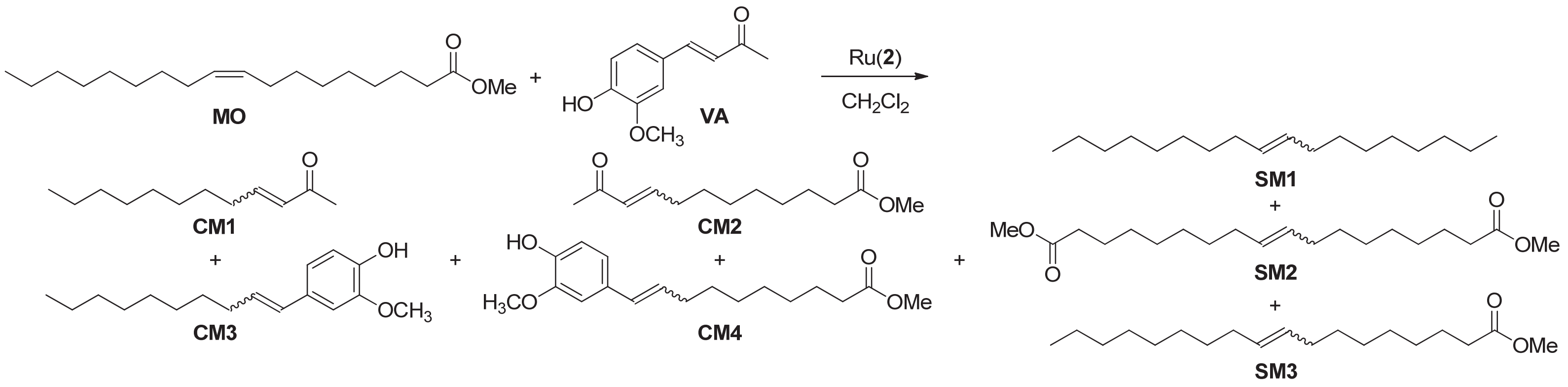
Table S8. Cross metathesis of methyl oleate (**MO**) with β-pinene (**PN**) by $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



run[a]	PN (eq.)[b]	Conv. of MO (%)[c]	CM1 (%)[d]	CM2 (%)[d]	CM3 (%)[d]	CM4 (%)[d]	SM1 *trans* (%)[d]	SM1 *cis* (%)[d]	SM2 *trans* (%)[d]	SM2 *cis* (%)[d]	SM3 *trans* (%)[d]	SM3 *cis* (%)[d]	Select. (1) (%)[e]	Select. (2) (%)[f]
30	1.0	77	1	2	0	1	19	3	14	4	17	4	55	9
31	5.0	80	5	2	0	1	17	4	13	4	15	4	53	17

[a] Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C, time 1 h. [b] Based on MO. [c] Conversion of MO estimated by GC using international standard. [d] GC yield estimated according to the effect of carbon number (ECN) rule. [e] Selectivity of CM1-4 and SM1,2 based on the conversion of MO. [f] Selectivity of cross metathesis products (%) = (CM1+CM2+CM3+CM4)/(CM1+CM2+CM3+CM4+SM1+SM2). CM1: dec-1-ene, CM2: methyl dec-9-enoate, CM3: 7,7-dimethyl-3-nonylidenebicyclo[4.1.0]heptane, CM4: methyl 9-(7,7-dimethylbicyclo[4.1.0]heptan-3-ylidene)nonanoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate.

Table S9. Cross metathesis of methyl oleate (**MO**) with vanillylidenacetone (**VA**) by $RuCl_2(PCy_3)(H_2IMes)(CHPh)$ (**2**).[a]



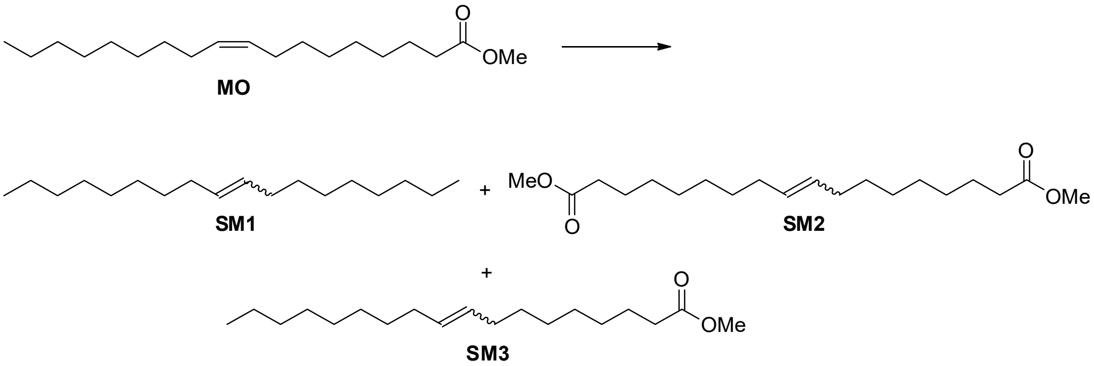
run[a]	VA (eq.)[b]	Conv. of MO (%)[c]	CM1 (%)[d]	CM2 (%)[d]	CM3 (%)[d]	CM4 (%)[d]	SM1 *trans* (%)[d]	SM1 *cis* (%)[d]	SM2 *trans* (%)[d]	SM2 *cis* (%)[d]	SM3 *trans* (%)[d]	SM3 *cis* (%)[d]	Select. (1) (%)[e]	Select. (2) (%)[f]
32	1.0	67	4	4	3	2	17	3	15	4	30	7	68	25
33	5.0	74	17	16	13	10	13	3	11	4	19	5	80	64

[a] Conditions: methyl oleate 2.00 mmol, CH_2Cl_2 1.0 mL, catalyst (**2**) 0.010 mmol, temperature 50 °C, time 1 h. [b] Based on MO. [c] Conversion of MO estimated by GC using international standard. [d] GC yield estimated according to the effect of carbon number (ECN) rule. [e] Selectivity of CM1-4 and SM1,2 based on the conversion of MO. [f] Selectivity of cross metathesis products (%) = (CM1+CM2+CM3+CM4)/(CM1+CM2+CM3+CM4+SM1+SM2). CM1: dodec-3-en-2-one, CM2: methyl 11-oxododec-9-enoate, CM3: 4-(dec-1-en-1-yl)-2-methoxyphenol, CM4: methyl 10-(4-hydroxy-3-methoxyphenyl)dec-9-enoate, SM1: octadec-9-ene, SM2: dimethyl octadec-9-enedioate, SM3: methyl octadec-9-enoate.

(iii) GC-FID and GC-MS chromatograms.

3-1. Self-metathesis of methyl oleate (MO).

9-Octadecene (**SM1**, m/z 252) and 9-octadecene-1,18-dioate (**SM2**, m/z 341) appears at 22.3 (*cis*-**SM1**), 22.4 (*trans*-**SM1**) and 45.6 (*cis*-**SM2**), 46.2 (*trans*-**SM2**) min, respectively, while (**MO**, **SM3**, m/z 296) which is also the starting material methyl oleate appeared at 28.6 (*cis*), 28.8 (*trans*) min on GC chromatogram (Figure S5). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S6.



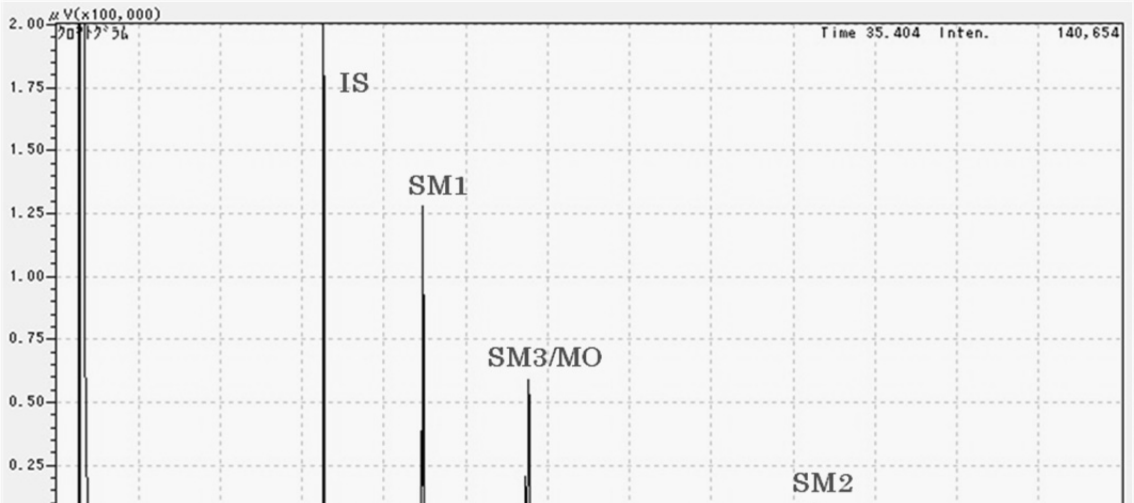


Figure S5. GC-FID chromatogram for the self-metathesis reaction of methyl oleate.

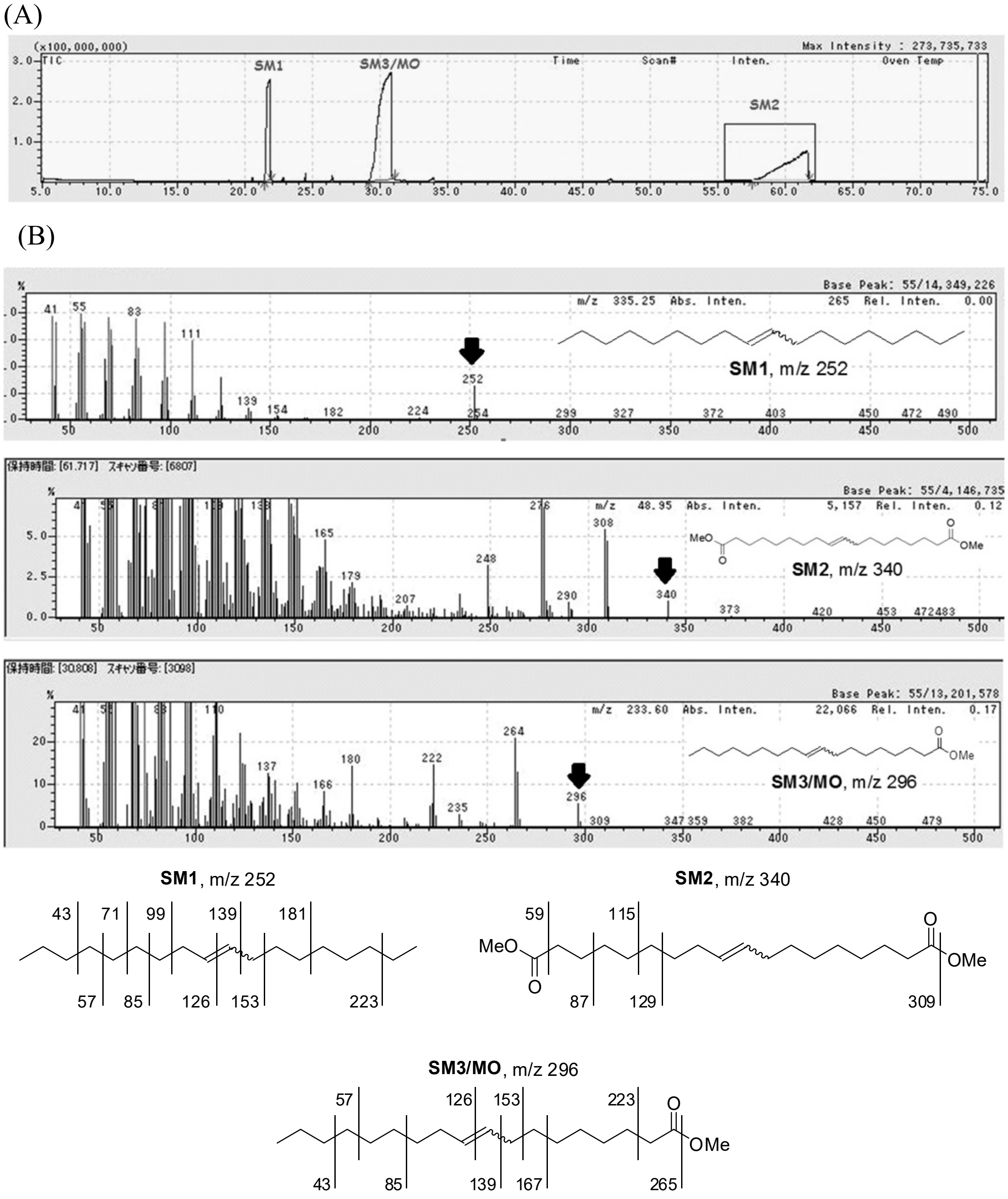
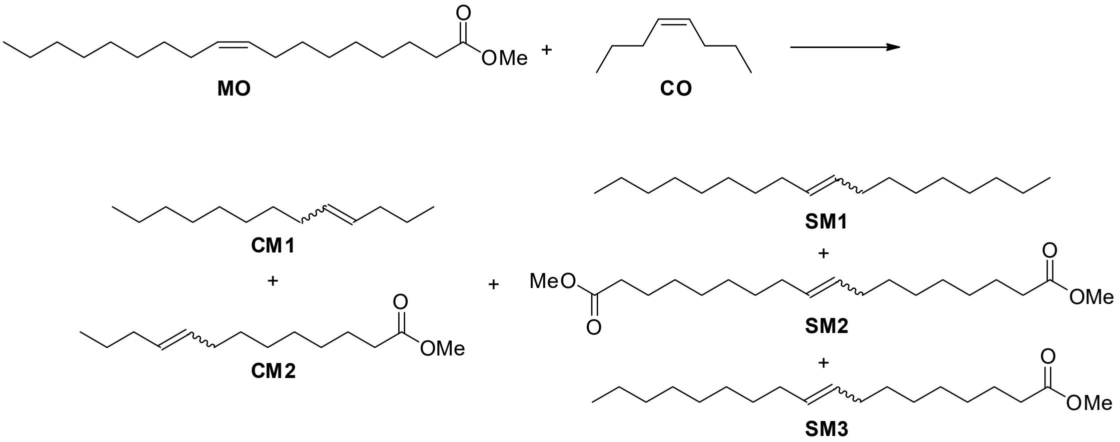


Figure S6. GC-MS chromatogram for the self-metathesis reaction of methyl oleate (A), and MS fragmentation patterns of the self-metathesis products (B).

3-2. Cross-metathesis of methyl oleate (MO) with *cis*-4-octene (CO).

Tridec-4-ene (**CM1**, m/z 182), methyl tridec-9-enoate (**CM2**, m/z 226), 9-octadecene (**SM1**, m/z 252) and 9-octadecene-1,18-dioate (**SM2**, m/z 341) appears at 17.4 (**CM1**), 20.4 (**CM2**), 22.3 (*cis*-**SM1**), 22.4 (*trans*-**SM1**), 45.6 (*cis*-**SM2**), and 46.2 (*trans*-**SM2**) min, respectively, while (**MO**, **SM3**, m/z 296) which is also the starting material methyl oleate appeared at 28.6 (*cis*), 28.8 (*trans*) min (Figure S7). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S8.



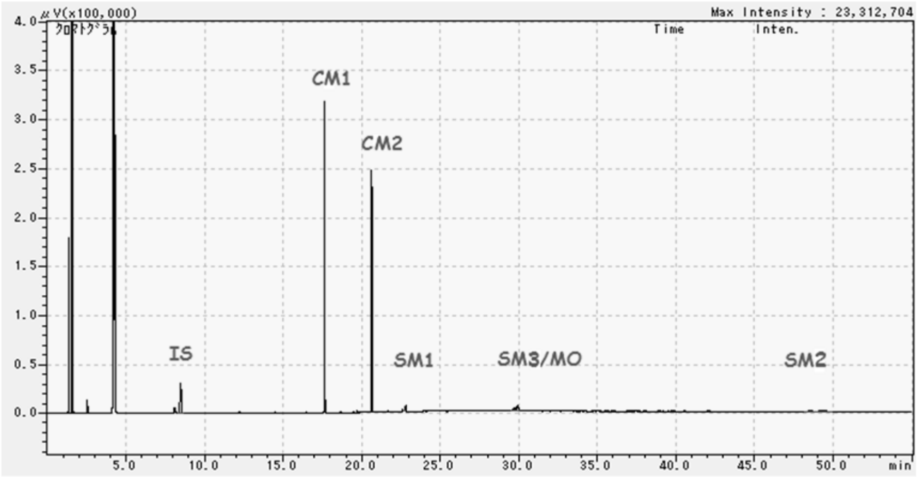


Figure S7. GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) with *cis*-4-octene (**CO**).

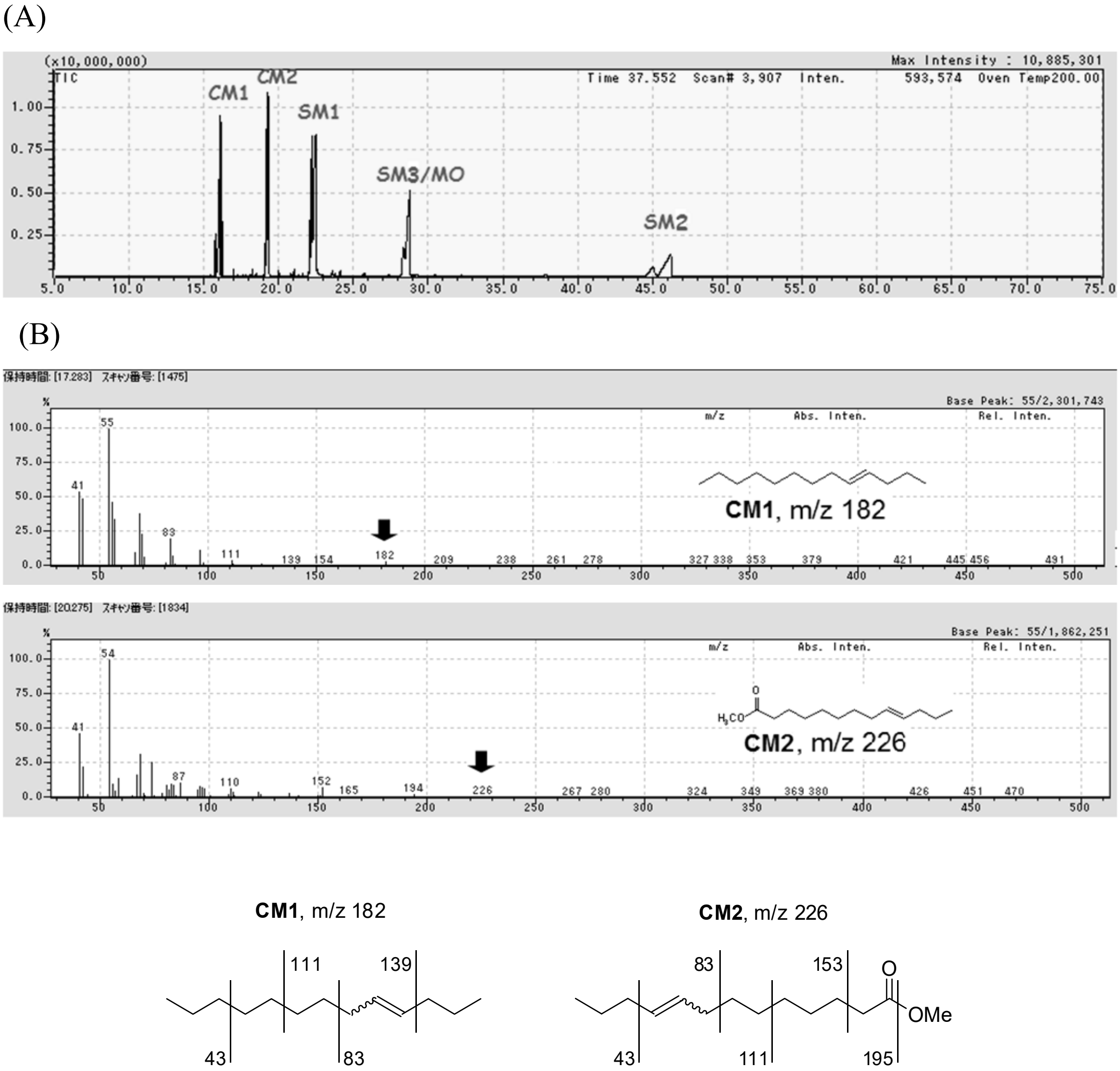
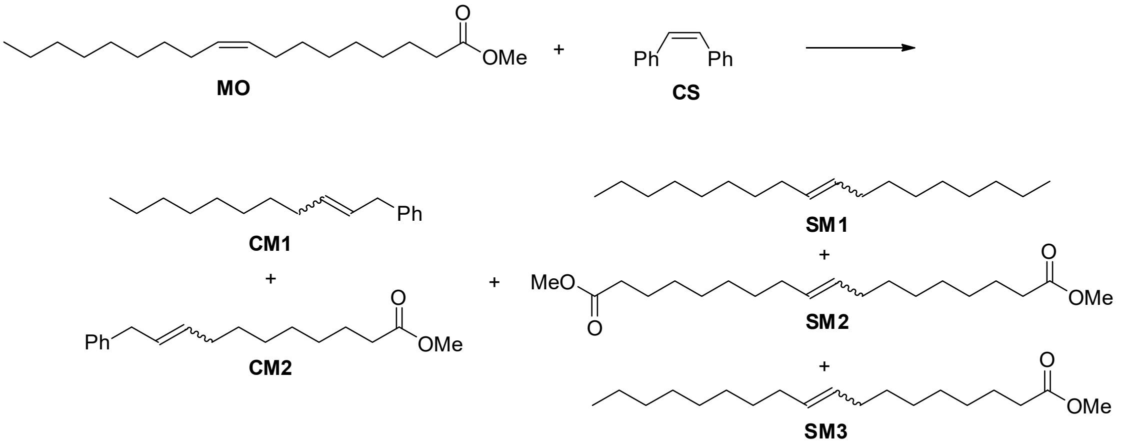


Figure S8. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) with *cis*-4-octene (**CO**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

3-3. Cross metathesis methyl oleate (MO) with *cis*-stilbene (CS).

Two targeted products dec-1-en-1-ylbenzene (**CM1**, m/z 216) and methyl 10-phenyldec-9-enoate (**CM2**, m/z 260) were observed at retention time of 21.7 (**CM1**) and 28.7 (**CM2**) min, respectively (Figure S9). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S10.



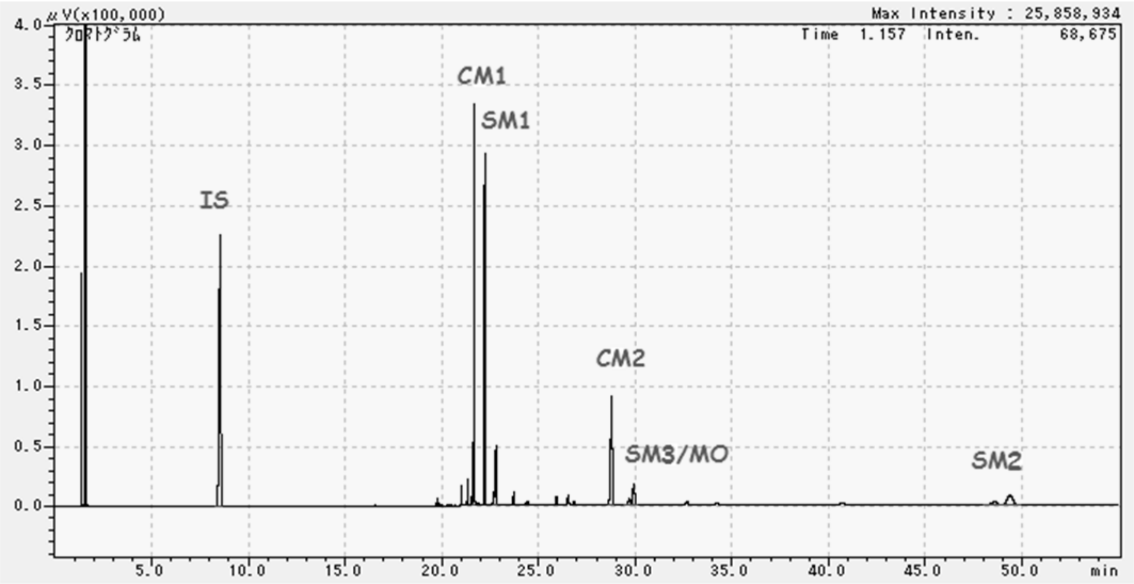


Figure S9. GC-FID chromatograms for the cross-metathesis reaction of methyl oleate (**MO**) and *cis*-stilbene (**CS**).

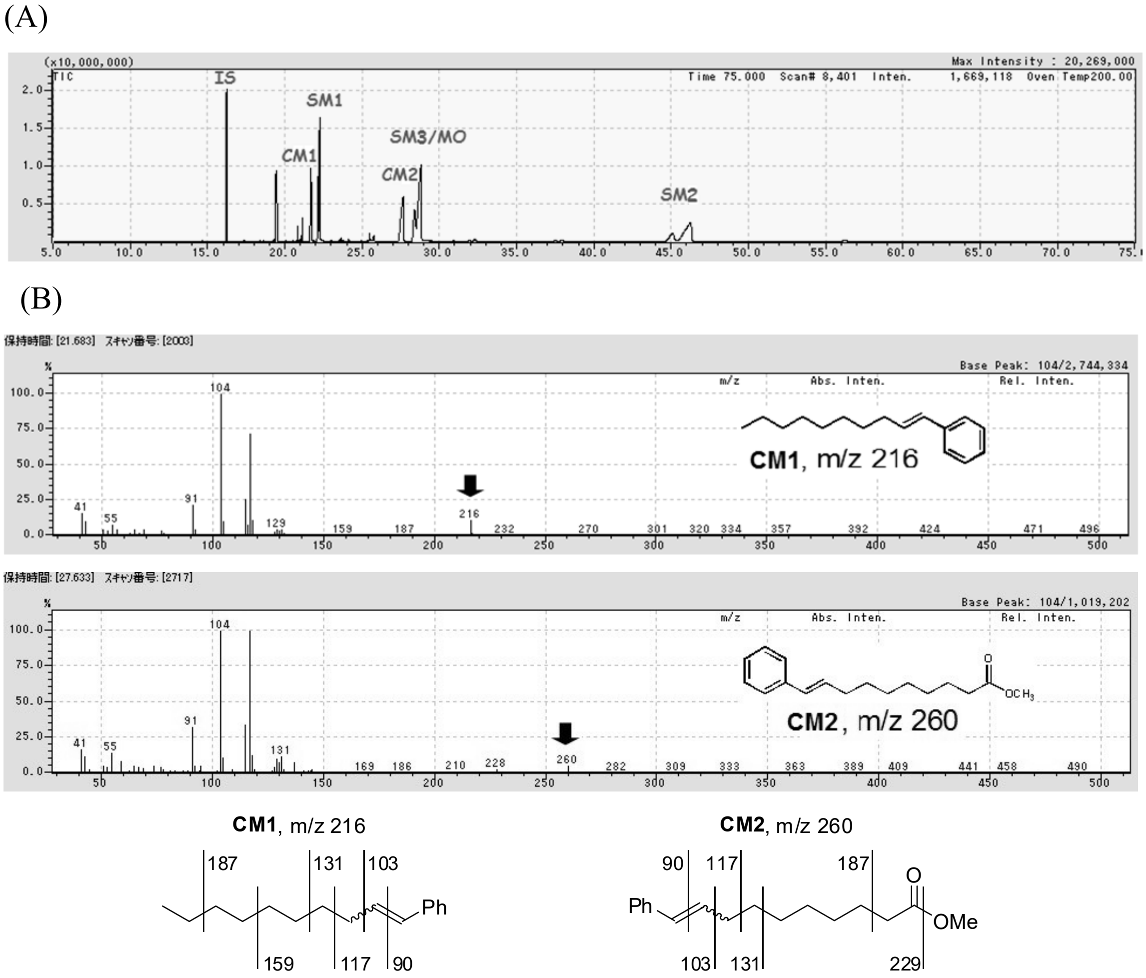
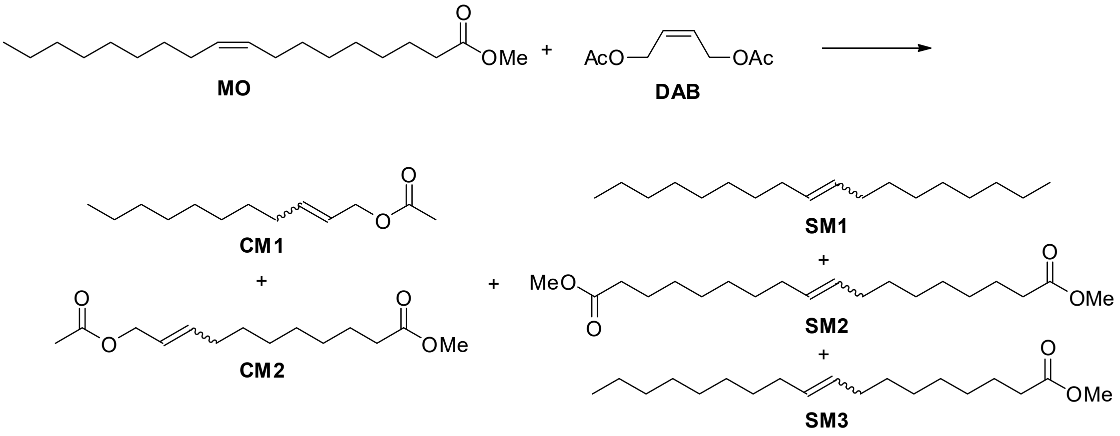


Figure S10. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and *cis*-stilbene (**CS**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

3-4. Cross metathesis methyl oleate (MO) with *cis*-1,4-diacetoxy-2-butene (DAB).

Two targeted products undec-2-en-1-yl acetate (**CM1**, m/z 212) and methyl 11-acetoxyundec-9-enoate (**CM2**, m/z 256) were observed at retention time of 19.3 (*cis*-**CM1**), 19.4 (*trans*-**CM1**) and 22.5 (*cis*-**CM2**), 22.6 (*trans*-**CM2**) min, respectively (Figure S11). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S12.



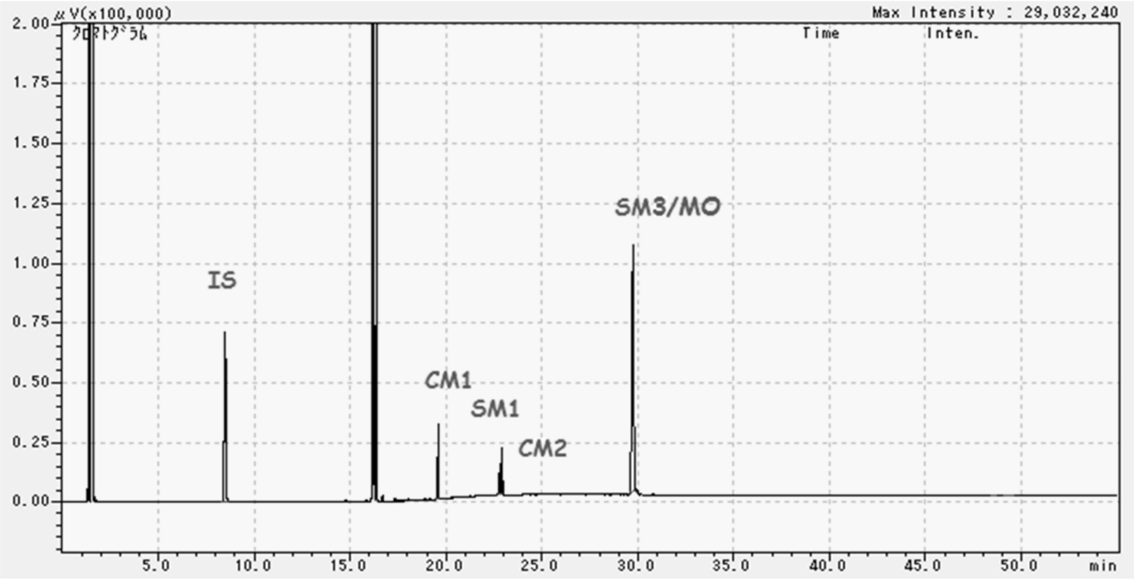
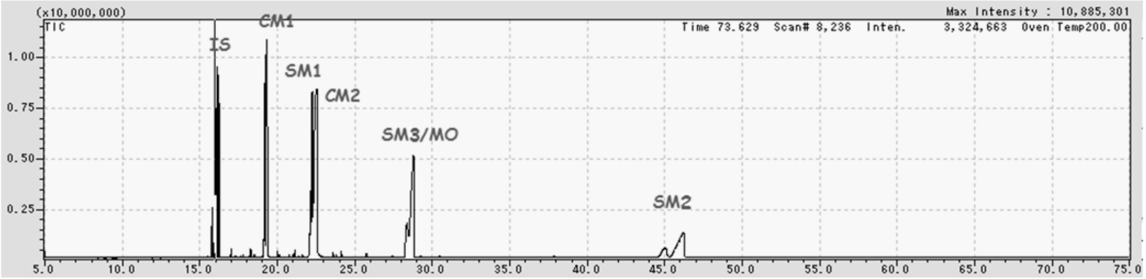


Figure S11. GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and *cis*-1,4-diacetoxy-2-butene (**DAB**).

(A)



(B)

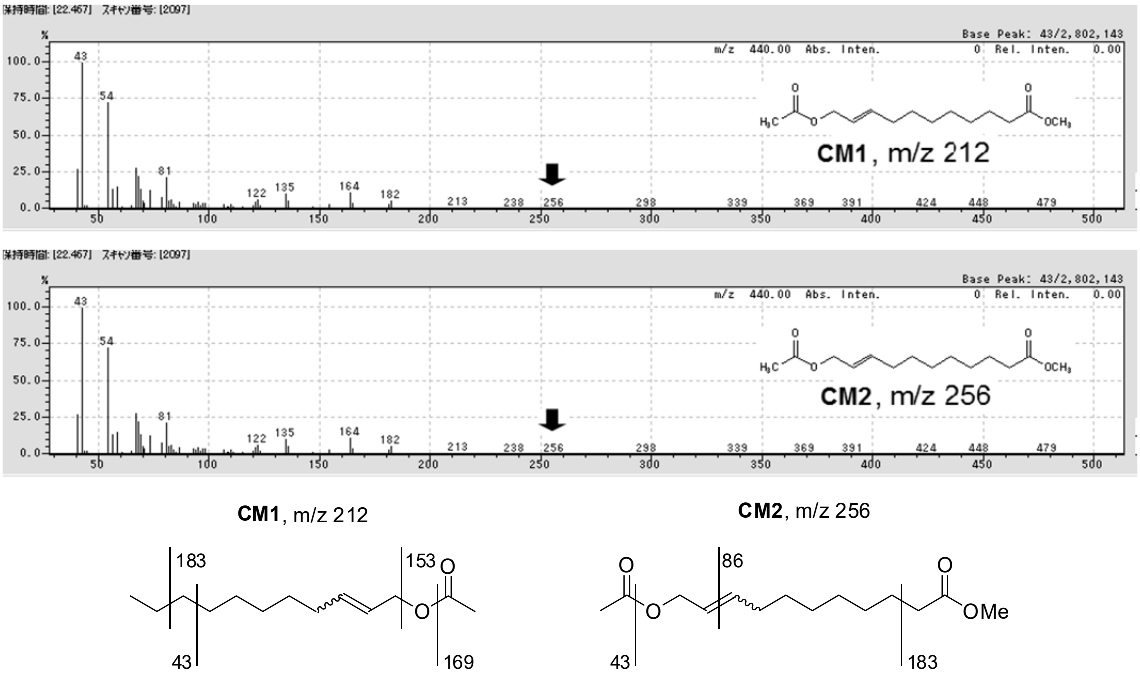
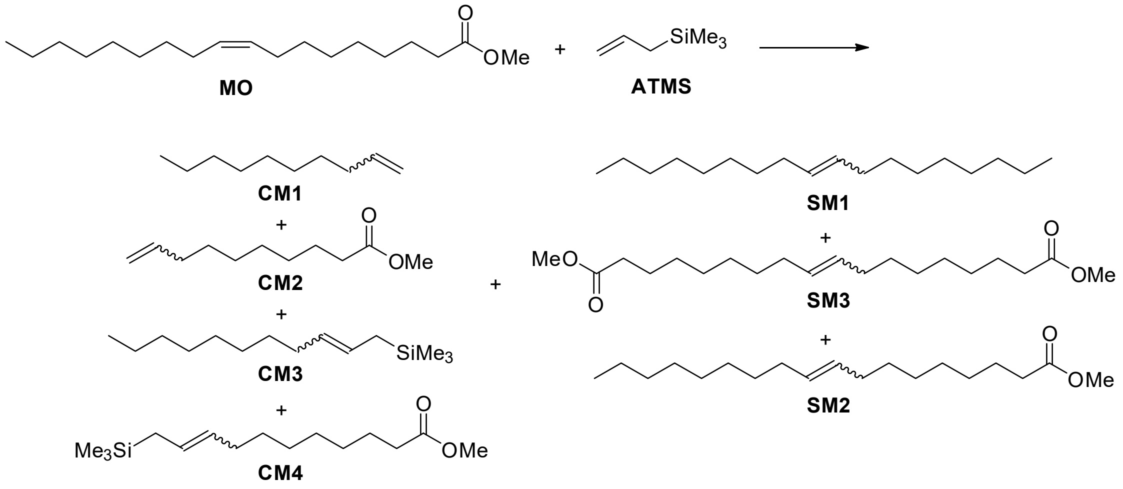


Figure S12. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) with *cis*-1,4-diacetoxy-2-butene (**DAB**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

3-5. Cross metathesis of methyl oleate (MO) with Allyltrimethylsilane (ATMS).

Four targeted products dec-1-ene (**CM1**, m/z 140), methyl dec-9-enoate (**CM2**, m/z 184), trimethyl(undec-2-en-1-yl)silane (**CM3**, m/z 226), and methyl 11-(trimethylsilyl)undec-9-enoate (**CM4**, m/z 270) were observed at retention time of 12.3 (**CM1**), 17.8 (**CM2**), 18.9 (*cis*-**CM3**), 18.8 (*trans*-**CM3**), 21.8 (*cis*-**CM4**), and 21.9 (*trans*-**CM4**) min, respectively (Figure S13). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S14.



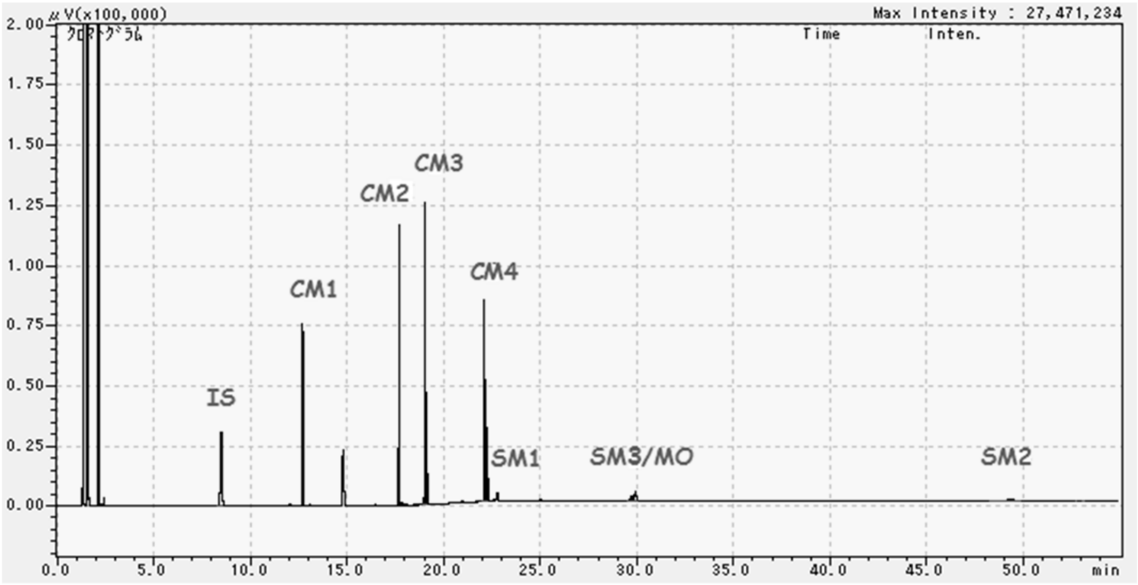
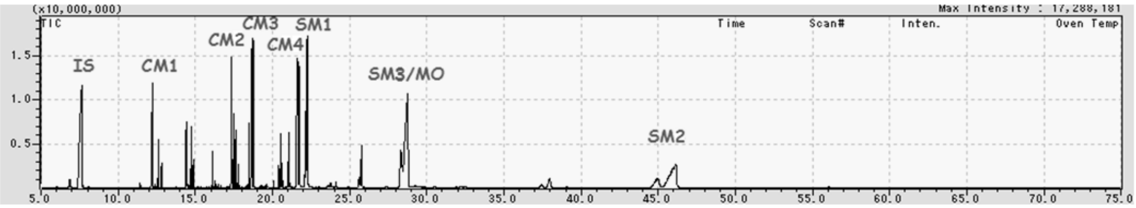


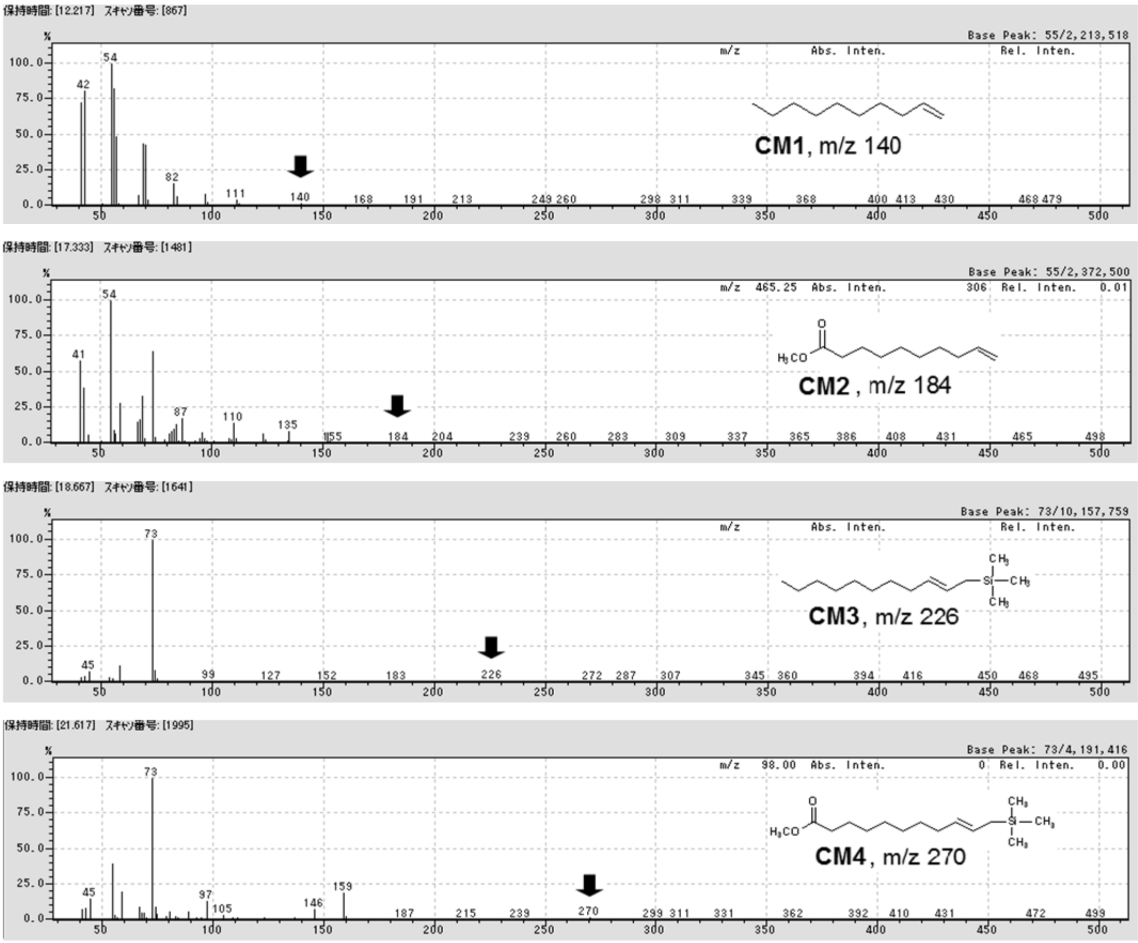
Figure S13. GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and allyltrimethylsilane (**ATMS**).

(A)



(x10,000,000)
Max Intensity : 17,288,181
TIC
Time
Scan#
Inten.
Oven Temp
IS
CM1
CM2
CM3
CM4
SM1
SM3/MO
SM2
1.5
1.0
0.5
5.0
10.0
15.0
20.0
25.0
30.0
35.0
40.0
45.0
50.0
55.0
60.0
65.0
70.0
75.0

(B)



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Base Peak: 55/2,213,518
42
54
82
111
140
CM1, m/z 140
保持時間: [17.333] スキャン番号: [1481]
Base Peak: 55/2,372,500
41
54
87
110
135
184
H3CO
O
CM2, m/z 184
保持時間: [18.667] スキャン番号: [1641]
Base Peak: 73/10,157,759
45
73
226
Si
CH3
CM3, m/z 226
保持時間: [21.617] スキャン番号: [1995]
Base Peak: 73/4,191,416
45
73
97
105
146
159
270
H3CO
O
Si
CH3
CM4, m/z 270
m/z
Abs. Inten.
Rel. Inten.
%
100.0
75.0
50.0
25.0
0.0
50
100
150
200
250
300
350
400
450
500

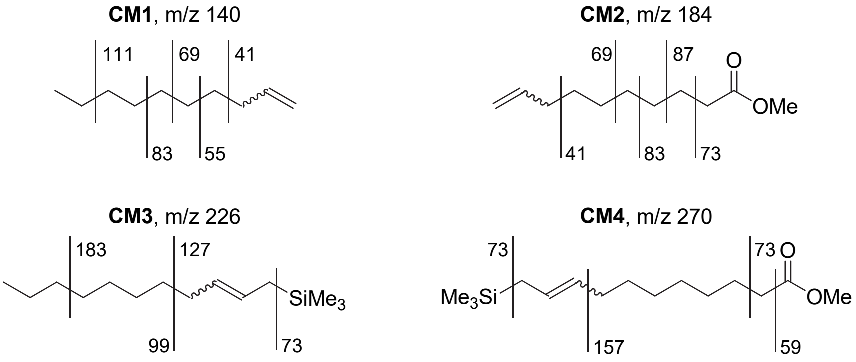


Figure S14. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and allyltrimethylsilane (**ATMS**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

3-6. Cross metathesis of methyl oleate (MO) with allyl glycidal ether (AGE).

Four targeted products dec-1-ene (**CM1**, m/z 140), methyl dec-9-enoate (**CM2**, m/z 184), 2-((undec-2-en-1-yloxy)methyl)oxirane (**CM3**, m/z 226), and methyl 11-(oxiran-2-ylmethoxy)undec-9-enoate (**CM4**, m/z 270) were observed at retention time of 12.7 (**CM1**), 17.7 (**CM2**), 21.6 (**CM3**), and 27.1 (**CM4**) min, respectively (Figure S15). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S16.

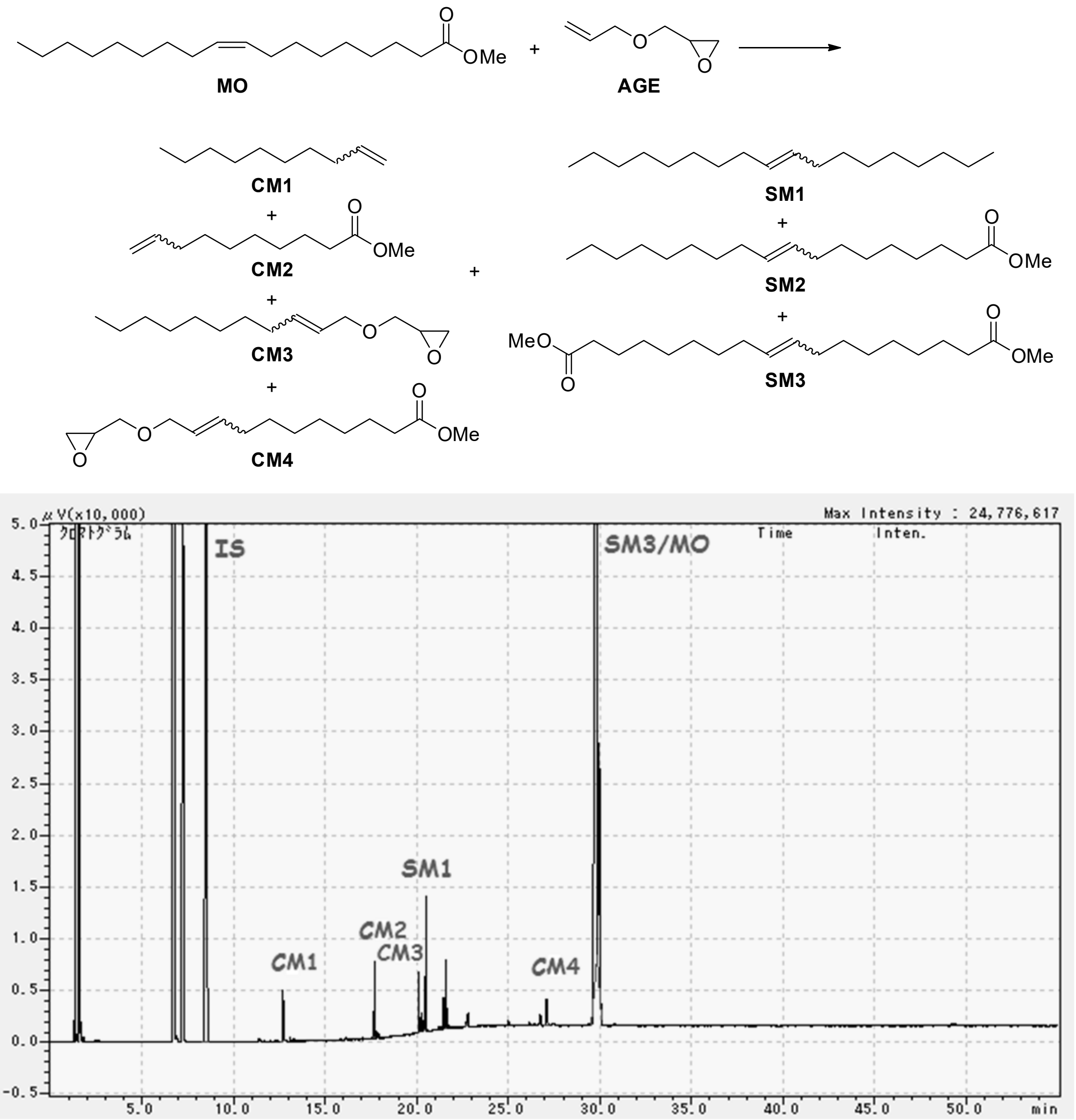


Figure S15. GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and allyl glycidal ether (**AGE**).

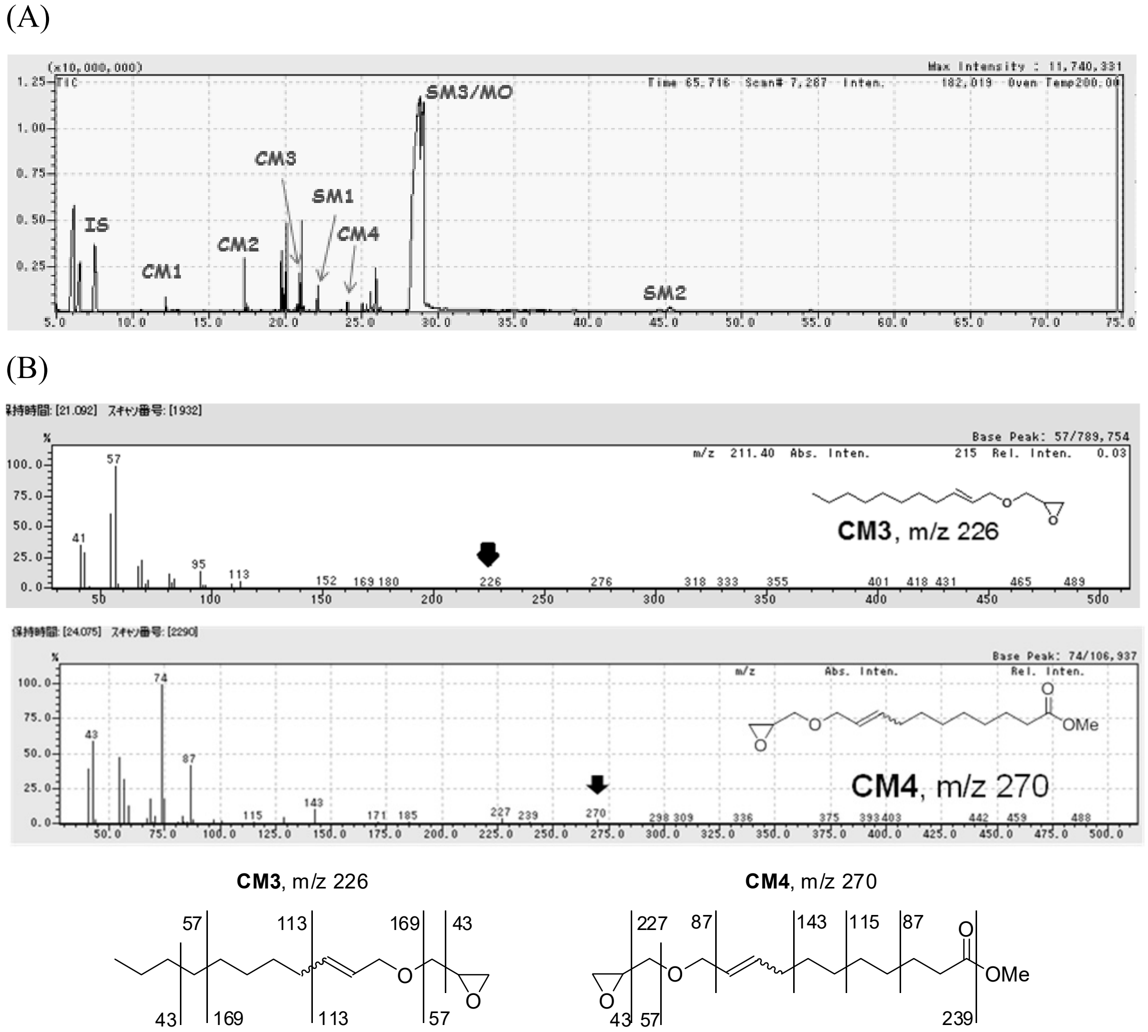
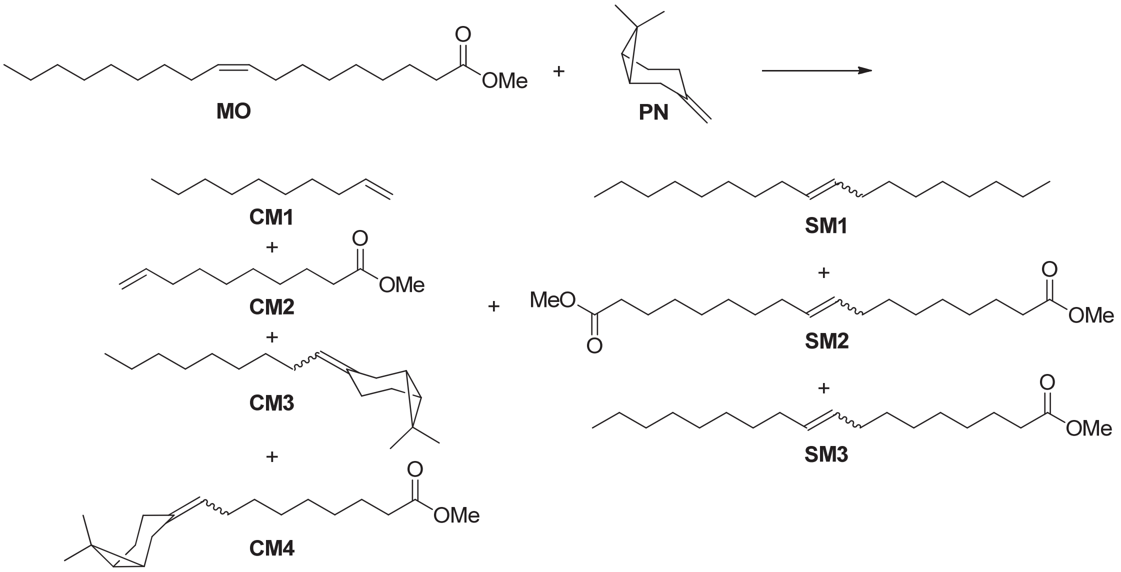


Figure S16. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and allyl glycidal ether (**AGE**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

3-7. Cross metathesis of methyl oleate (MO) with β-pinene (PN).

Four targeted products dec-1-ene (**CM1**, m/z 140), methyl dec-9-enoate (**CM2**, m/z 184), 7,7-dimethyl-3-nonylidenebicyclo[4.1.0]heptane (**CM3**, m/z 248), and methyl 9-(7,7-dimethylbicyclo[4.1.0]heptan-3-ylidene)nonanoate (**CM4**, m/z 292) were observed at retention time of 12.7 (**CM1**), 17.7 (**CM2**), 22.3 (**CM3**), and 30.3 (**CM4**) min, respectively (Figure S17). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S18.



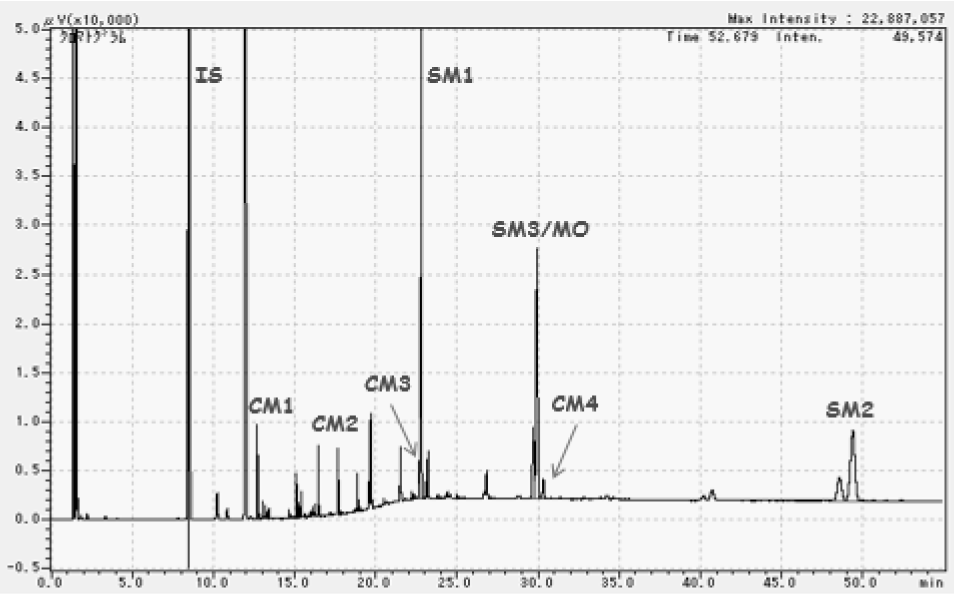


Figure S17. GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and β-pinene (**PN**).

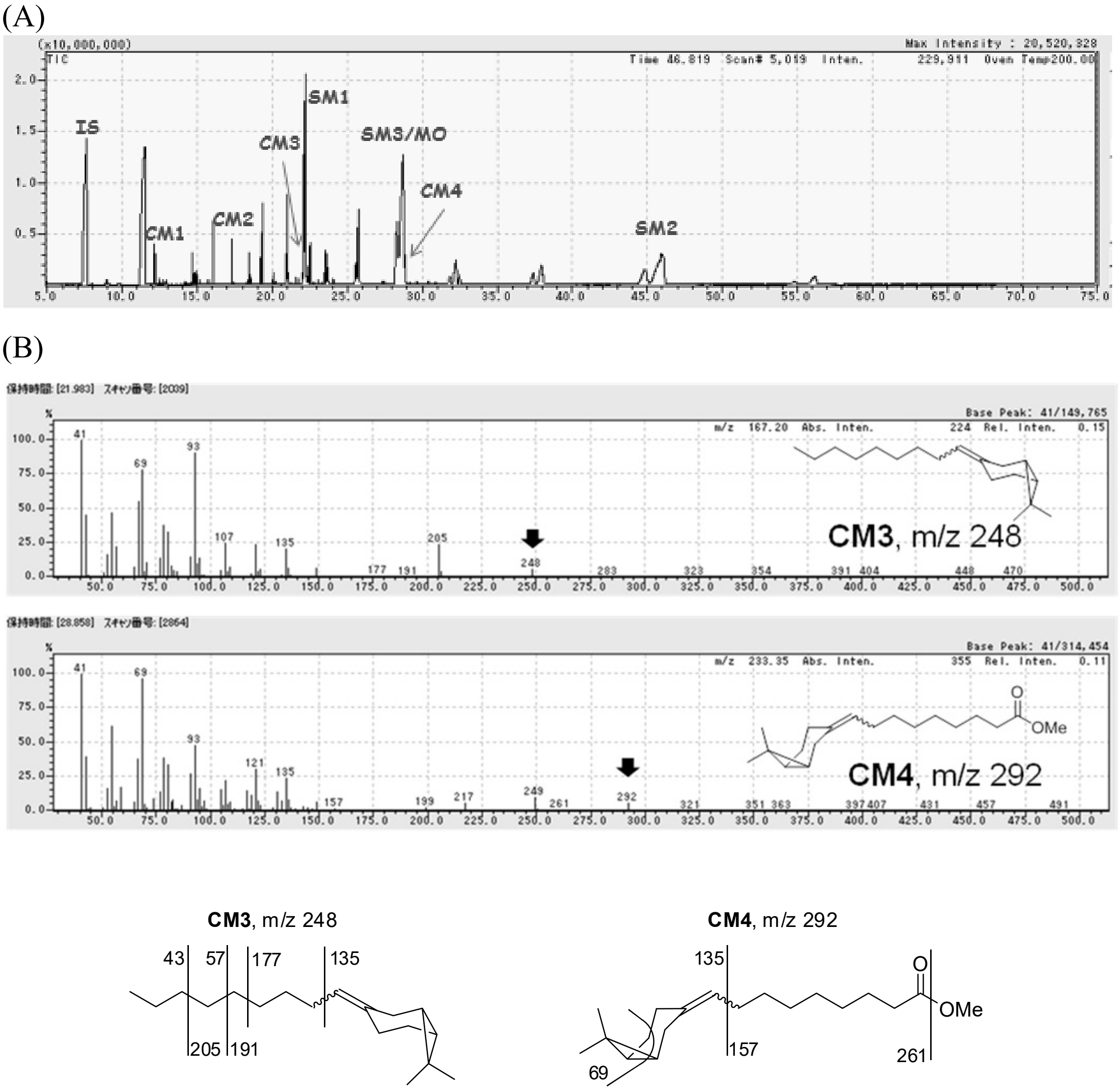


Figure S18. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and β-pinene (**PN**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

3-8. Cross metathesis of methyl oleate (MO) with vanillidenacetone (VA).

Four targeted products dodec-3-en-2-one (**CM1**, m/z 182), methyl 11-oxododec-9-enoate (**CM2**, m/z 226), 4-(dec-1-en-1-yl)-2-methoxyphenol (**CM3** m/z 262), and methyl 10-(4-hydroxy-3-methoxyphenyl)dec-9-enoate (**CM4**, m/z 306) were observed at retention time of 18.9 (**CM1**), 22.1 (**CM2**), 32.1 (**CM3**), and 56.0 (**CM4**) min, respectively (Figure S19). GC–MS chromatogram and the mass fragmentation patterns of each peak are shown in Figure S20.

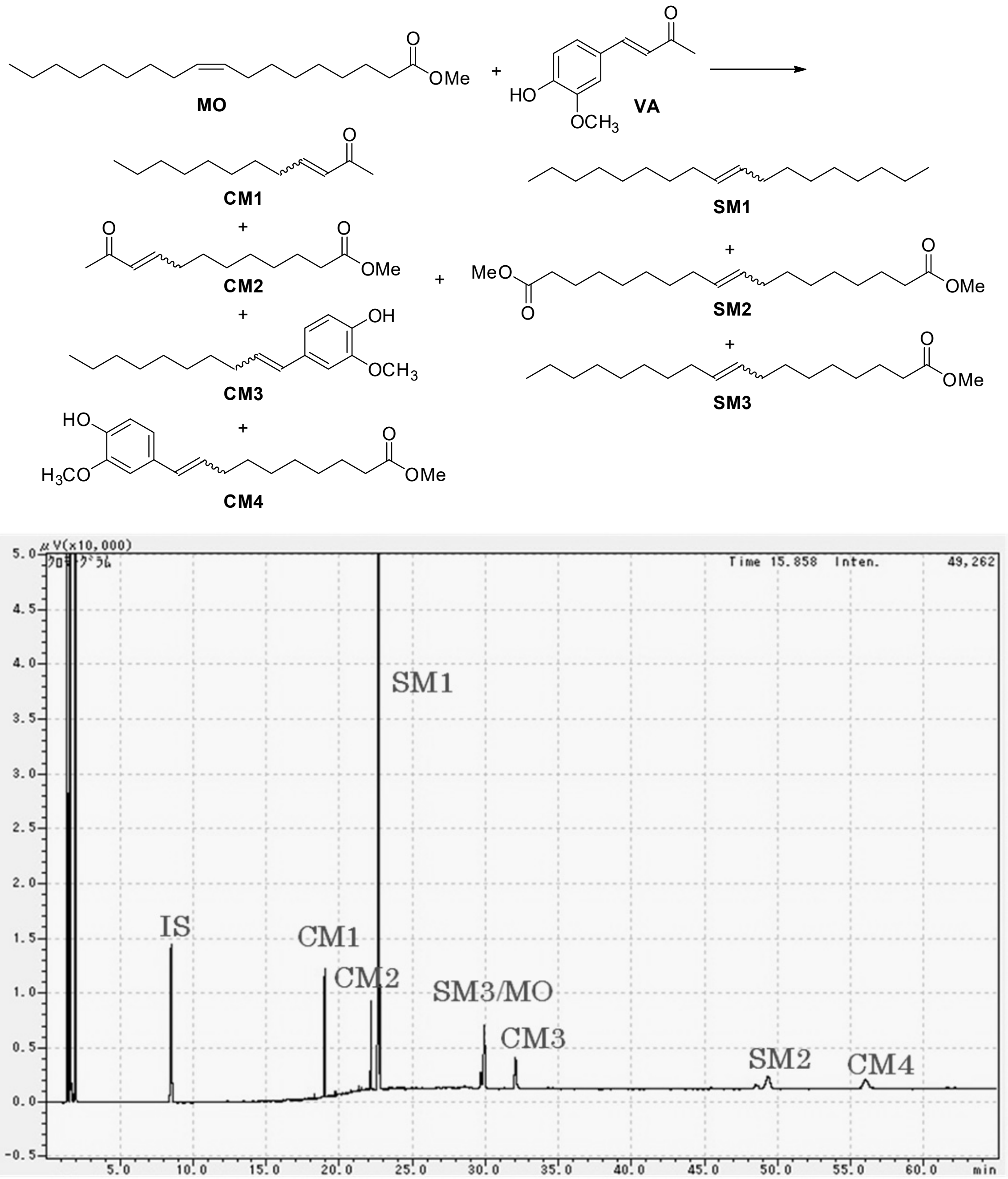
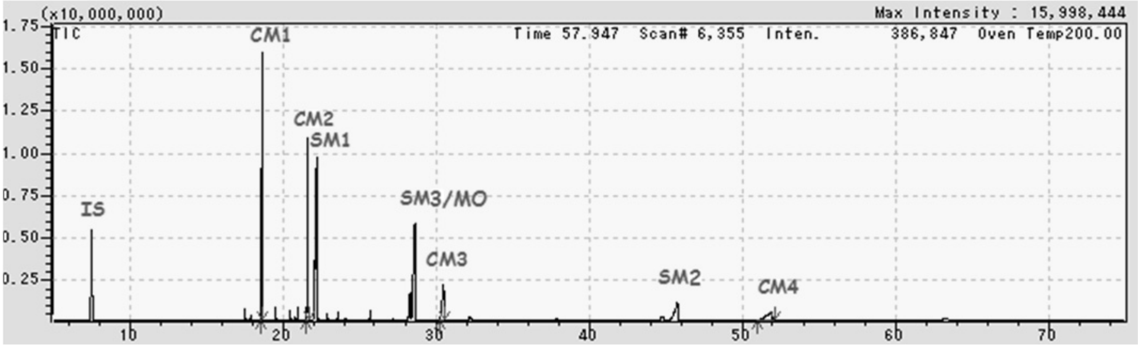
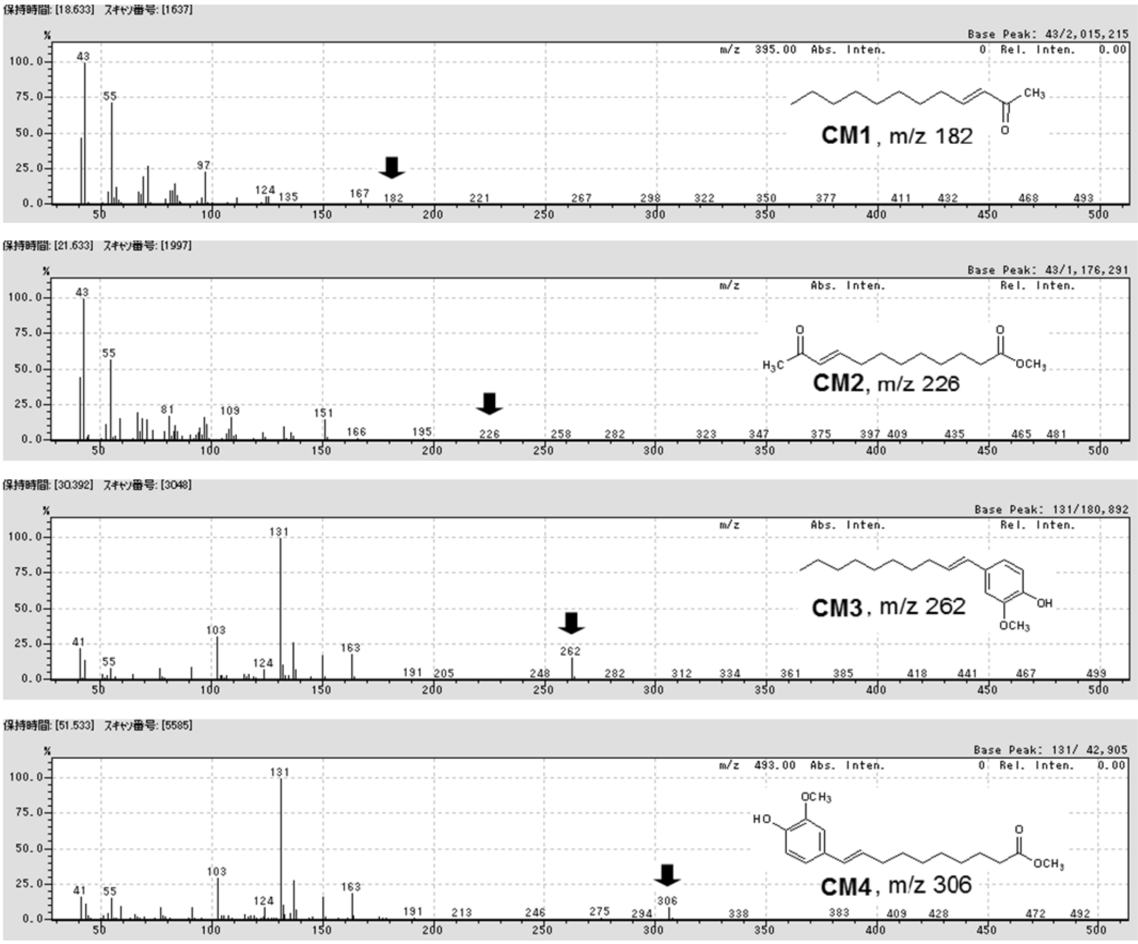


Figure S19. GC-FID chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and vanillidenacetone (**VA**).

(A)


(x10,000,000)
Max Intensity : 15,998,444
TIC
Time 57.947 Scan# 6,355 Inten. 386,847 Oven Temp200.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
IS
CM1
CM2
SM1
SM3/MO
CM3
SM2
CM4
10
20
30
40
50
60
70

(B)


保持時間: [18.633] スキャン番号: [1637]
Base Peak: 43/2,015,215
m/z 395.00 Abs. Inten. 0 Rel. Inten. 0.00
43
55
97
124
135
167
182
CM1, m/z 182
保持時間: [21.633] スキャン番号: [1997]
Base Peak: 43/1,176,291
43
55
81
109
151
166
195
226
CM2, m/z 226
保持時間: [30.392] スキャン番号: [3048]
Base Peak: 131/180,892
41
55
103
124
131
163
191
262
CM3, m/z 262
保持時間: [51.533] スキャン番号: [5585]
Base Peak: 131/ 42,905
m/z 493.00 Abs. Inten. 0 Rel. Inten. 0.00
41
55
103
124
131
163
306
CM4, m/z 306
%
50
100
150
200
250
300
350
400
450
500

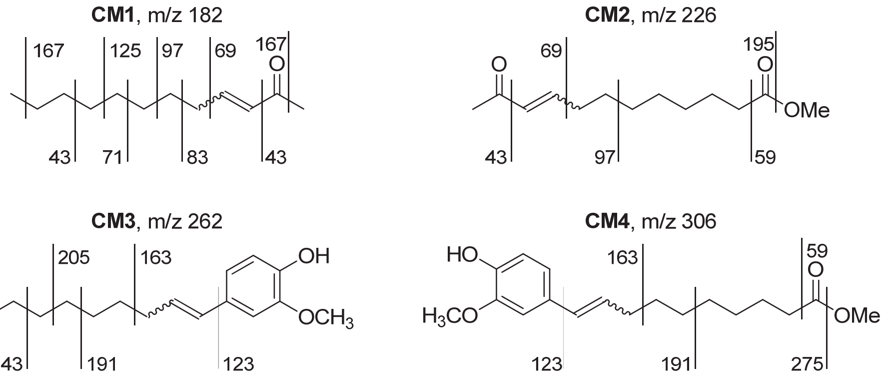


Figure S20. GC-MS chromatogram for the cross-metathesis reaction of methyl oleate (**MO**) and vanillideneacetone (**VA**) (A), and MS fragmentation patterns of the cross-metathesis products (B).

References

(1) (a) Kállai, M.; Balla, J. *Chromatographia* **2002**, *54*, 511-517. (b) R. L. Grob, E. F. Barry (Eds.), Modern Practice of Gas Chromatography, Wiley-Interscience, New York (2004), pp. 302-305. (c) Kállai, M.; Veres, Z., Balla, J. *Chromatographia* **2001**, *54*, 511-517. (d) Scanlon, J. T.; Willis, D. E. *J. Chromatogr. Sci.* **1985**, *23*, 333-340.