Supporting Information

Ruthenium-Catalyzed Olefin Cross-Metathesis with Tetrafluoroethylene and Analogous Fluoroolefins

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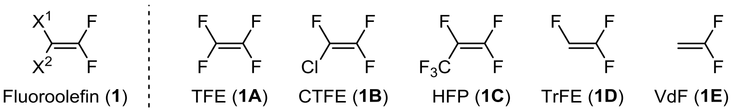
I. General

CAUTION! The International Agency for Research on Cancer (IARC) classifies tetrafluoroethylene (TFE) into “Group 2A: Probably carcinogenic to humans”,[S1] and hence all manipulations using TFE must be carried out with care.

CAUTION! Under the representative reaction conditions described below, TFE and analogous fluoroolefins (Chart S1) may ignite in the presence of oxygen and hence air must be completely removed from the operating system (e.g. NMR tube and autoclave).

Chart S1. Fluoroolefin (**1**). Tetrafluoroethylene (TFE, **1A**); chlorotrifluoroethylene (CTFE, **1B**); hexafluoropropylene (HFP, **1C**); trifluoroethylene (TrFE, **1D**); vinylidene fluoride (VdF, **1E**).

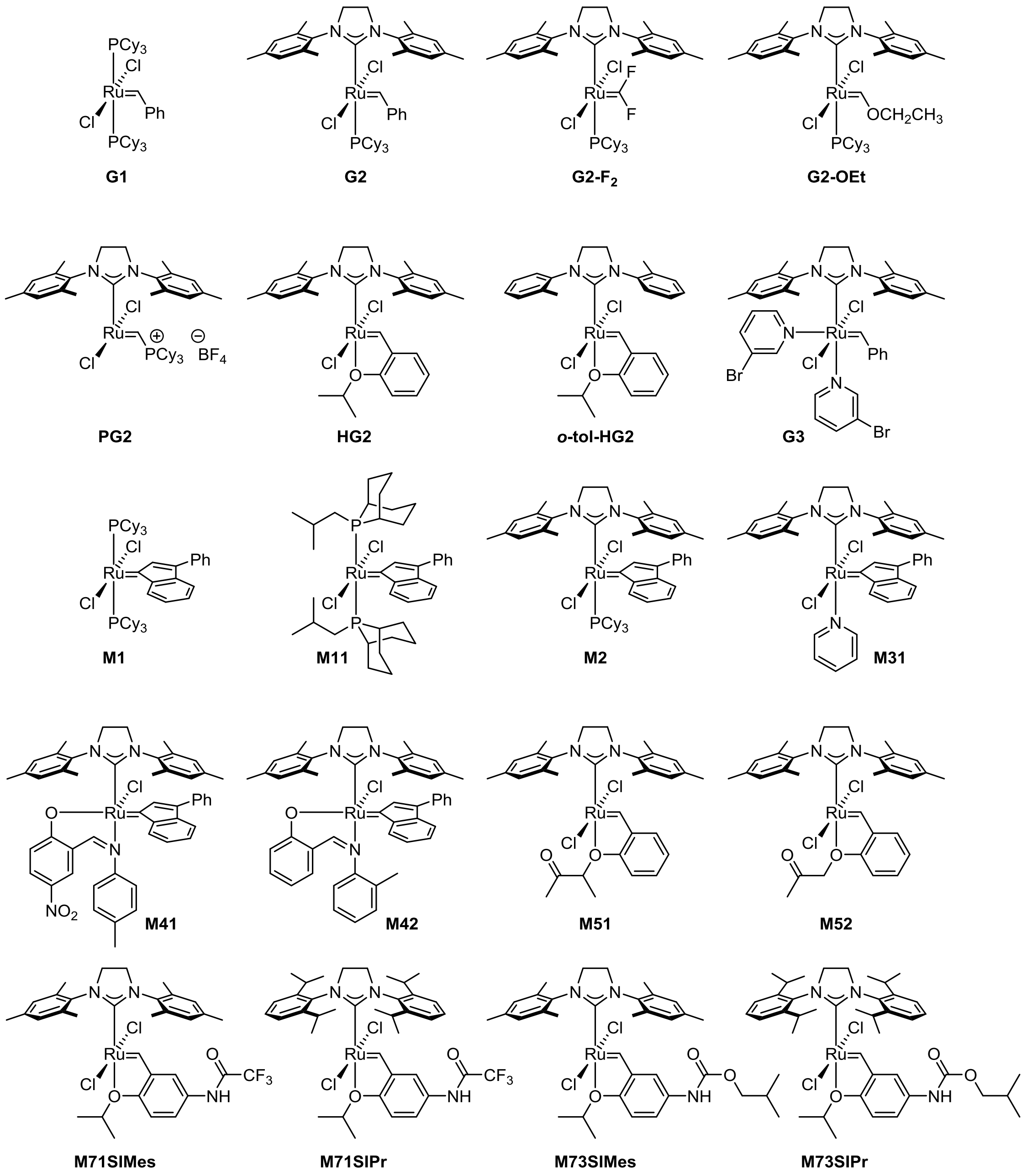


Precatalysts used in this work are listed in Chart S2. Grubbs series precatalysts (**G1**, **G2**, **PG2**, **HG2**, and ***o*-tol-HG2**) and Umicore M series precatalysts (**M1**, **M11**, **M2**, **M31**, **M41**, **M42**, **M51**, **M52**, **M71SIMes**, **M71SIPr**, **M73SIMes**, and **M73SIPr**) were purchased from Sigma-Aldrich and Wako Pure Chemical Industries, respectively. **G2-F$_2$** was prepared from **G2** and TFE as starting materials (see below for experimental procedures). **G2-OEt**[S2] and **G3**[S3] were prepared according to the literature procedures. Fluoroolefins (**1A−E**) were obtained from Asahi Glass and used considering ideal gas behavior. C_6H_6 and C_6D_6 were purchased from Kanto Chemical, degassed by freeze-pump-thaw cycle for a total of three times, and stored over 4Å molecular sieves under nitrogen. Dodecyl vinyl ether (**2a**) and ethyl vinyl ether (**2b**) was purchased (Tokyo Chemical Industry and Kanto Chemical, respectively), degassed by freeze-pump-thaw cycle for a total of three times, and stored over potassium hydroxide under nitrogen. 1-Ethoxyprop-1-ene (**2c**, *E*/*Z* mixture) was purchased from Wako Pure Chemical Industries and used as received. ASAHIKLIN AC-2000 was obtained from Asahi Glass and used as an eluent for column chromatography. Other solvents were purchased and used as received.

Unless otherwise noted, all reactions were set up in a nitrogen-filled glovebox, and all work-up procedures were manipulated under usual bench-top conditions using reagent-grade solvents. NMR-scale experiments were carried out in screw cap NMR tubes (Norell S-5-300-SC-7, purchased from Tokyo Chemical Industry). Analytical thin-layer chromatography were performed using TLC silica gel 60 F_{254} (Merck Millipore). The developed chromatogram were visualized with I_2 or *p*-anisaldehyde stain. Column chromatography were performed using M.S.GEL D-75-60A(N) (AGC Si-Tech). Recycling preparative HPLC was performed on an LC-9210NEXT (Japan Analytical Industry) equipped with JAIGEL-1H/JAIGEL-2H columns.

All new compounds were characterized by NMR spectroscopy and high-resolution mass spectrometry (HRMS). ^{1}H and ^{19}F NMR spectra were recorded on a JEOL JNM-AL300 spectrometer, and chemical shifts were reported in ppm relative to $Si(CH_3)_4$ (0.00 ppm) and CCl_3F (0.0 ppm), respectively. ^{1}H and ^{19}F NMR yields were determined using 1,4-bis(trifluoromethyl)-benzene as an internal standard. Long pulsing delay (60 s) gave practically accurate NMR yields due to long T_1 relaxation time (ca. 11 s) of protons and fluorines at vinylic positions on starting materials (e.g. **2a**) and products (e.g. **3Aa**). ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 spectrometer or a JNM-ECP400 FT-NMR spectrometer, and chemical shifts are reported in ppm relative to solvent signal (C_6D_6, 128.06 ppm; $CDCl_3$, 77.16 ppm). Quantitative ^{13}C NMR spectra were recorded on a JNM-ECP400 FT-NMR spectrometer. NMR data were reported as follows: Chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dq = doublet of quartets, qd = quartet of doublets, ddt = doublet of doublet of triplets, ddq = doublet of doublet of quartets, br = broad, m = multiplet), and coupling constants. The signal marked with a black square (■) corresponds to the solvent signal in NMR spectra. HRMS spectra were recorded on a JEOL JMS-T100GC gas chromatograph/time-of-flight mass spectrometer.

Chart S2. Ruthenium precatalysts.[a]



G1 **G2** **G2-F$_2$** **G2-OEt**

PG2 **HG2** ***o*-tol-HG2** **G3**

M1 **M11** **M2** **M31**

M41 **M42** **M51** **M52**

M71SIMes **M71SIPr** **M73SIMes** **M73SIPr**

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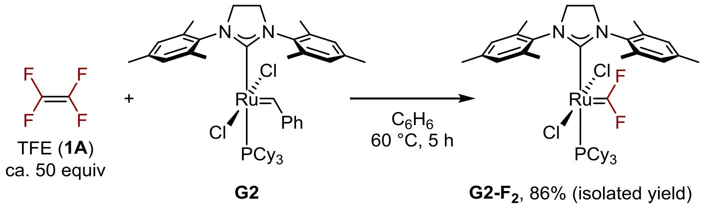
[a] Cy = cyclohexyl.

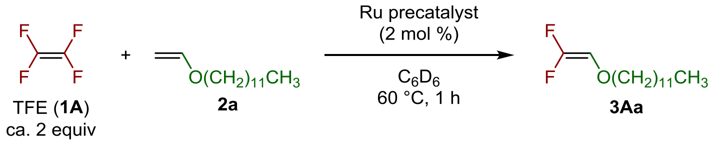
II. Experimental procedures

Stoichiometric metathesis of **G2** with TFE, Scheme 2.



An autoclave (volume of the headspace is ca. 0.125 L) equipped with a mechanical overhead stirrer was charged with **G2** (0.2 mmol, 170.0 mg) and C_6H_6 (10 mL). The mixture was frozen in acetone/dry ice bath for more than 30 min, evacuated using a oil rotary pump for 1 min, thawed, and refilled with **1A** (2 atm, ca. 10 mmol, ca. 50 equiv). The mixture was heated at 60 °C for 5 h under mechanical stirring at a rate of 600 rpm. After cooling to room temperature, the gaseous materials were purged with nitrogen, and then the autoclave was released. The resulting mixture was transferred to a round-bottom flask with C_6H_6, concentrated to ca. 1 mL, passed through a column of silica gel (hexane/ethyl acetate = 9/1, v/v), and an orange fraction was collected. After removal of solvents, sonication in hexane yielded an orange precipitate. **G2-F$_2$** (139.4 mg, 0.172 mmol, 86%) was isolated by filtration and dried under reduced pressure. The NMR data for **G2-F$_2$** were practically identical to those reported in the literature.[S4]

Screening of precatalysts, Table 1.



A stock solution containing dodecyl vinyl ether (**2a**) and 1,4-bis(trifluoromethyl)benzene (as an internal standard for determination of ^{19}F NMR yield) in C_6D_6 was prepared and stored in a nitrogen-filled glovebox (Solution A, Table S1). 0.3 mL of solution A (as 0.06 mmol of **2a**) was used for each experiment.

Table S1. Solution A.

	amount/mmol	weight/mg	volume/mL
dodecyl vinyl ether (**2a**)	2.4	509.7	0.624
1,4-bis(trifluoromethyl)benzene	0.4	85.6	0.062
C_6D_6	–	–	11.314
total	–	–	12.000

Four precatalysts were examined at once according to the following procedures: A screw cap NMR tube was charged with solution A (0.3 mL, 0.06 mmol of **2a**) and 0.3 mL of solution B (a precatalyst, 2 mol % relative to **2a**, 0.0012 mmol), capped, and removed from the glovebox. The headspace (ca. 2.7 mL, ca. 0.12 mmol, ca. 2 equiv) of the NMR tube was replaced with an atmospheric pressure of **1A** using a gastight syringe. The resulting mixture was shaken, and then heated at 60 °C. After 1 h, ^{19}F NMR spectrum was recorded and determined the yield of **3Aa**. All NMR tubes containing the reaction mixture were cooled around 0 °C using iced water bath until the NMR measurement. Table S3 summarized the results.

Table S2. Solution B.

	amount/mmol	weight/mg	volume/mL
precatalyst	0.012	ca. 7−11 mg	−
C_6D_6	−	−	3.000
total	−	−	3.000

Table S3. Screening of precatalysts.[a]

entry	precatalyst	yield of **3Aa**/%[b]	TON	entry	precatalyst	yield of **3Aa**/%[b]	TON
1	none[c]	n.d.	−	11	**M2**	5	2.4
2	**G1**	trace	0.1	12	**M31**	11	5.5
3	**G2**	6	3.2	13	**M41**	n.d.	−
4	**G2-F$_2$**	3	1.6	14	**M42**	n.d.	−
5	**PG2**[d]	15	7.7	15	**M51**	27	13.4
6	**HG2**	25	12.5	16	**M52**	24	12.2
7	***o*-tol-HG2**[d]	2	0.8	17	**M71SIMes**[d]	28	14.2
8	**G3**	2	1.1	18	**M71SIPr**[d]	21	10.7
9	**M1**	n.d.	−	19	**M73SIMes**[d]	27	13.7
10	**M11**	trace	0.2	20	**M73SIPr**	23	11.7

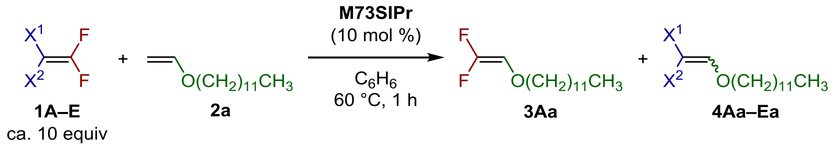
[a] n.d., not detected; TON, turnover number, **3Aa** (*x* mmol)/loading of precatalyst (0.0012 mmol).

[b] ^{19}F NMR yield.

[c] 0.3 mL of C_6D_6 was added instead of solution B.

[d] The precatalysts were partially soluble in C_6D_6.

Catalytic cross-metathesis with fluoroolefins, Table 2.



An autoclave (volume of the headspace is ca. 0.125 L) equipped with a mechanical overhead stirrer was charged with C_6H_6 (10 mL), **2a** (1.0 mmol, 212.4 mg) and **M73SIPr** precatalyst (10 mol %, 0.10 mmol, 82.6 mg). The mixture was frozen in acetone/dry ice bath for more than 30 min, evacuated using an oil rotary pump for 1 min, thawed, and refilled with a gaseous fluoroolefin (**1A−E**, 2 atm, ca. 10 mmol, ca. 10 equiv). The mixture was heated at 60 °C for 1 h under mechanical stirring at a rate of 600 rpm. After cooling to room temperature, the gaseous materials were purged with nitrogen then the autoclave was released, and 1,4-bis(trifluoromethyl)benzene (1.0 mmol, 214.1 mg, 154 μL, as internal standard for determination of ^{19}F NMR yield) was added to the reaction mixture. A 0.1 mL of the resulting mixture was sampled, diluted with C_6D_6, recorded ^{19}F NMR spectra, and determined yields of **3Aa** and **4Aa−Ea** (Table S4). The reaction mixture was then filtered through a short plug of silica gel (C_6H_6), concentrated under reduced pressure. Residual ruthenium species were completely removed by an additional silica gel column chromatography (for entries 1−3 and 5, hexane; for entry 4, hexane/C_6H_6 = 9/1, v/v).

Table S4. Catalytic cross-metathesis with fluoroolefins.[a-c]

				yield/%[d]			
entry	fluoroolefin	X^1	X^2	**3Aa**	**4Aa−Ea**		TON
1	TFE (**1A**)	F	F	69[e] (64)			6.9
2	CTFE (**1B**)	F	Cl	11	51	[39/61]	6.2
3	HFP (**1C**)	F	CF_3	n.d.	22	[25/75]	2.2
4	TrFE (**1D**)	F	H	n.d.	72	[20/80]	7.2
5	VdF (**1E**)	H	H	n.d.	–[f]		–

[a] n.d., not detected; TON, turnover number, products (*x* mmol)/loading of **M73SIPr** (0.1 mmol).

[b] Isolated yields are given in the parentheses.

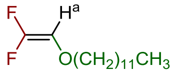
[c] *E*/*Z* ratios are given in the square brackets.

[d] ^{19}F NMR yield.

[e] **4Aa** is identical to **3Aa**.

[f] **4Ea** is identical to **2a**.

1-(2,2-Difluorovinyloxy)dodecane, **3Aa**.



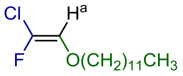
3Aa

^{1}H NMR (300 MHz, C_6D_6)
H^a: 5.19 ppm (1H, dd, $^3J_{HF\ (trans)}$ = 16.7 Hz, $^3J_{HF\ (cis)}$ = 3.0 Hz)

3Aa was obtained in 69% ^{19}F NMR yield according to the procedures described above, following which silica gel column chromatography (AC-2000) gave **3Aa** (159.2 mg, 0.641 mmol, 64%) as colorless oil. Although the preparation of **3Aa** has been reported previously, the NMR data are not available.[S5]

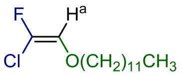
^{1}H NMR (300 MHz, C_6D_6) δ: 0.92 (3H, t, *J* = 6.6 Hz), 1.15−1.40 (20H, br m), 3.22 (2H, t, *J* = 6.6 Hz), 5.19 (1H, dd, *J* = 16.7, 3.0 Hz); ^{19}F NMR (283 MHz, C_6D_6) δ: −122.6 (1F, dd, *J* = 82.4, 3.0 Hz), −102.2 (1F, dd, *J* = 82.4, 16.7 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ: 14.4, 23.2, 26.0, 29.69, 29.74, 29.9, 30.0, 30.1, 30.2 (overlapped, 2C), 32.4, 73.5, 108.6 (dd, *J* = 51.8, 14.6 Hz), 155.8 (dd, *J* = 288, 274 Hz); HRMS (EI) calcd for $C_{14}H_{26}F_2O$: 248.1952, found: 248.1978.

(*E*)- and (*Z*)-1-(2-Chloro-2-fluorovinyloxy)dodecane, (*E*)- and (*Z*)-**4Ba**.



(*E*)-**4Ba** (minor isomer)

^{1}H NMR (300 MHz, C_6D_6)
H^a: 5.27 ppm (1H, d, $^3J_{HF\ (trans)}$ = 17.9 Hz)



(*Z*)-**4Ba** (major isomer)

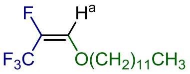
^{1}H NMR (300 MHz, C_6D_6)
H^a: 6.08 ppm (1H, d, $^3J_{HF\ (cis)}$ = 1.7 Hz)

(*E*)- and (*Z*)-**4Ba** were inseparable by both recycling preparative HPLC ($CHCl_3$) and careful silica gel column chromatography, which got us to record NMR spectra using a mixture of two stereoisomers (minor/major = ca. 40/60). In the ^{1}H NMR spectrum, the coupling constants of the vinylic proton signals at 5.27 ppm (minor isomer, $^3J_{HF}$ = 17.9 Hz) and 6.08 ppm (major isomer, $^3J_{HF}$ = 1.7 Hz) are indicative of (*E*)- and (*Z*)-**4Ba**, respectively. In the ^{19}F NMR spectrum, the coupling constants of the vinylic fluorine signals at −107.4 ppm (minor isomer, $^3J_{HF}$ = 17.9 Hz) and −128.3 ppm (major isomer, $^3J_{HF}$ = not resolved) are also indicative of (*E*)- and (*Z*)-**4Ba**, and we assigned the major product to (*Z*)-**4Ba**.[S6] Quantitative ^{13}C NMR (100 MHz, C_6D_6) spectrum was obtained independently using inverse gated decoupling technique, and we assigned the signals. HRMS (EI) data was recorded using a mixture containing at least **2a**, **3Aa**, (*E*)-**4Ba**, and (*Z*)-**4Ba**.

^{1}H NMR (300 MHz, C_6D_6) δ: 0.92 (3H, t, *J* = 6.6 Hz), 1.12−1.36 (20H, br m), 3.19 and 3.22 (2H in all; t, *J* = 6.6 Hz), 5.27 and 6.08 (1H in all; d, *J* = 17.9 Hz and d, *J* = 1.7 Hz, respectively); ^{19}F NMR (283 MHz, C_6D_6) δ: −128.3 and −107.4 (1F in all; not resolved and d, *J* = 17.9 Hz, respectively); ^{13}C

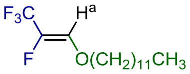
NMR (75 MHz, C_6D_6) δ: 14.4, 23.2, 25.89 (*E*), 25.94 (*Z*), 29.6, 29.7 (*Z*), 29.8 (*E*), 29.9, 30.0, 30.1, 30.2 (overlapped, 2C), 32.4, 73.3 (*Z*), 73.6 (*E*), 127.3 (*E*, d, *J* = 11.7 Hz), 130.4 (*Z*, d, *J* = 50.8 Hz), 135.3 (*E*, d, *J* = 295.0 Hz), 137.5 (*Z*, d, *J* = 280.0 Hz); HRMS (EI) calcd for $C_{14}H_{26}ClFO$: 264.1656, found: 264.1659 for (*E*)-**4Ba** and 264.1663 for (*Z*)-**4Ba**.

(*E*)- and (*Z*)-1-(2,3,3,3-Tetrafluoroprop-1-enyloxy)dodecane, (*E*)- and (*Z*)-**4Ca**.



(*E*)-**4Ca** (minor isomer)

^{1}H NMR (300 MHz, C_6D_6)
H^a: 6.04 ppm (1H, d, $^3J_{HF\ (cis)}$ = 9.0 Hz)



(*Z*)-**4Ca** (major isomer)

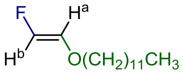
^{1}H NMR (300 MHz, C_6D_6)
H^a: 5.87 ppm (1H, dd, $^3J_{HF\ (trans)}$ = 19.9 Hz)

(*E*)- and (*Z*)-**4Ca** were partially isolated using a combination of recycling preparative HPLC ($CHCl_3$) and careful silica gel column chromatography (AC-2000). Comparing the coupling constants of the vinylic proton signals at 6.04 ppm (minor isomer, $^3J_{HF}$ = 9.0 Hz) and 5.87 ppm (major isomer, $^3J_{HF}$ = 19.9 Hz) in the ^{1}H NMR spectra, we assigned the major isomer to (*Z*)-**4Ca**.[S7]

(*E*)-**4Ca**: ^{1}H NMR (300 MHz, C_6D_6) δ: 0.93 (3H, t, *J* = 6.5 Hz), 1.02−1.38 (20H, br m), 3.07 (2H, t, *J* = 6.5 Hz), 6.04 (1H, d, *J* = 9.0 Hz); ^{19}F NMR (283 MHz, C_6D_6) δ: −181.7 (1F, dq, *J* = 12.2, 9.0 Hz), −67.6 (3F, d, *J* = 12.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 22.8, 25.6, 29.3, 29.5, 29.59, 29.61, 29.7, 29.8 (overlapped, 2C), 32.1, 75.4, 119.8 (qd, *J* = 270.6, 36.9 Hz), 136.9 (dq, *J* = 228.5, 40.1 Hz), 139.3 (apparent dd, *J* = 45.4, 2.3 Hz); HRMS (CI) calcd for $C_{15}H_{25}F_4O$, $[M - H]^+$: 297.1842, found: 297.1748.

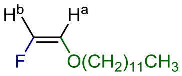
(*Z*)-**4Ca**: ^{1}H NMR (300 MHz, C_6D_6) δ: 0.92 (3H, t, *J* = 6.5 Hz), 1.05−1.36 (20H, br m), 3.15 (2H, t, *J* = 6.5 Hz), 5.87 (1H, dd, *J* = 19.9, 1.1 Hz); ^{19}F NMR (283 MHz, C_6D_6) δ: −165.5 (1F, dq, *J* = 19.9, 15.3 Hz), −70.3 (3F, d, *J* = 15.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.3, 22.9, 25.6, 29.4, 29.5, 29.6, 29.70, 29.72, 29.8 (overlapped, 2C), 32.1, 75.3, 120.3 (qd, *J* = 268.3, 35.4 Hz), 133.1 (dq, *J* = 249.0, 39.0 Hz), 134.0−134.1 (m); HRMS (CI) calcd for $C_{15}H_{25}F_4O$, $[M - H]^+$: 297.1842, found: 297.1812.

(*E*)- and (*Z*)-1-(2-Fluorovinyloxy)dodecane, (*E*)- and (*Z*)-**4Da**.



(*E*)-**4Da** (minor isomer)

^{1}H NMR (300 MHz, C_6D_6)
H^a: 6.65 ppm (1H, dd, $^3J_{HH\ (trans)}$ = 9.8 Hz)
H^b: 6.63 ppm (1H, dd, $^3J_{HH\ (trans)}$ = 9.8 Hz)



(*Z*)-**4Da** (major isomer)

^{1}H NMR (300 MHz, C_6D_6)
H^a: 5.09 ppm (1H, dd, $^3J_{HH\ (cis)}$ = 3.0 Hz)
H^b: 5.76 ppm (1H, dd, $^3J_{HH\ (cis)}$ = 3.0 Hz)

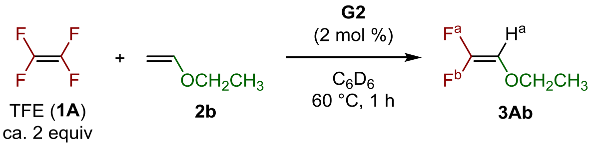
(*E*)- and (*Z*)-**4Da** were partially isolated by careful silica gel column chromatography (hexane). Comparing the coupling constants of the vinylic proton signals (H^a/H^b) at 6.65/6.63 ppm (minor isomer, $^3J_{HH}$ = 9.8 Hz) and 5.09/5.76 ppm (major isomer, $^3J_{HH}$ = 3.0 Hz) in the ^{1}H NMR spectra, we assigned the major product to (*Z*)-**4Da**.

(*E*)-**4Da**: ^{1}H NMR (300 MHz, C_6D_6) δ: 0.92 (3H, t, *J* = 6.5 Hz), 1.12−1.45 (20H, br m), 3.12 (2H, t, *J* = 6.5 Hz), 6.63 (1H, dd, *J* = 80.8, 9.8 Hz), 6.65 (1H, dd, *J* = 9.8, 7.6 Hz); ^{19}F NMR (283 MHz, C_6D_6) δ: −186.6 (1F, dd, *J* = 80.8, 7.6 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ: 14.4, 23.2, 26.2, 29.5, 29.7, 29.9, 30.0, 30.05, 30.13 (overlapped, 2C), 32.4, 70.8, 138.8 (d, *J* = 39.1 Hz), 139.7 (d, *J* = 230.0 Hz); HRMS (EI) calcd for $C_{14}H_{27}FO$: 230.2046, found: 230.2057.

(*Z*)-**4Da**: ^{1}H NMR (300 MHz, C_6D_6) δ: 0.92 (3H, t, *J* = 6.6 Hz), 1.12−1.47 (20H, br m), 3.41 (2H, t, *J* = 6.6 Hz), 5.09 (1H, dd, *J* = 27.5, 3.0 Hz), 5.76 (1H, dd, *J* = 76.2, 3.0 Hz); ^{19}F NMR (283 MHz, C_6D_6) δ: −163.0 (1F, dd, *J* = 76.2, 27.5 Hz); ^{13}C NMR (75 MHz, C_6D_6) δ: 14.4, 23.2, 26.1, 29.8, 29.9, 30.0 (overlapped, 2C), 30.1, 30.2 (overlapped, 2C), 32.4, 73.2, 131.7, 133.7 (d, *J* = 250.0 Hz); HRMS (EI) calcd for $C_{14}H_{27}FO$: 230.2046, found: 230.2065.

Mechanistic studies, Scheme 5.

As an authentic sample of the following experiments, **3Ab** was prepared from **1A** and **2b** according to the representative NMR-scale procedures described above, and assigned the ^{1}H and ^{19}F NMR data as shown below.



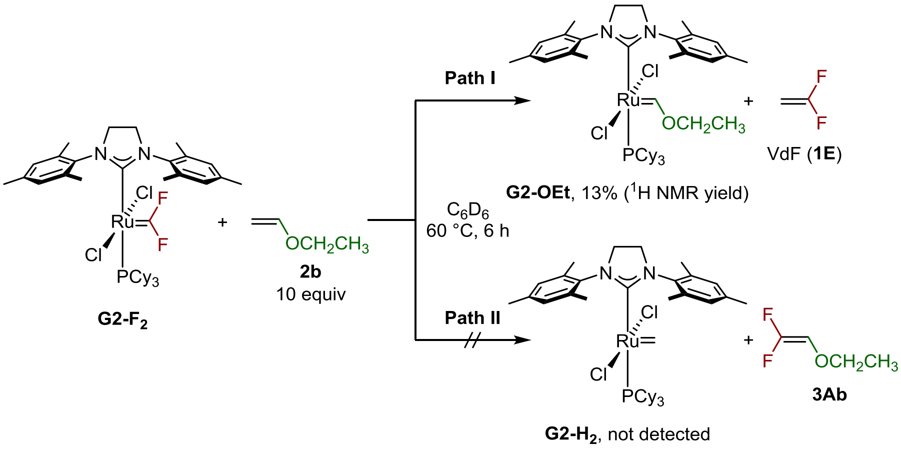
^{1}H NMR (300 MHz, C_6D_6) H^a: 5.10 ppm (1H, dd, *J* = 16.7, 2.6 Hz)
^{19}F NMR (283 MHz, C_6D_6) F^a: –122.4 ppm (1F, dd, *J* = 82.4, 2.6 Hz)
^{19}F NMR (283 MHz, C_6D_6) F^b: –102.2 ppm (1F, dd, *J* = 82.4, 16.7 Hz)

A 0.02 M C_6D_6 solution containing 1,4-bis(trifluoromethyl)benzene (as an internal standard for determination of ^{19}F NMR yield) was prepared and stored in a nitrogen-filled glovebox prior to the following experiments (Solution C, Table S5).

Table S5. Solution C.

	amount/mmol	weight/mg	volume/mL
1,4-bis(trifluoromethyl)benzene	0.2	42.8	0.031
C_6D_6	–	–	9.969
total	–	–	10.000

(a) Selective formation of **G2-OEt** over **G2-H$_2$**, Scheme 5a.

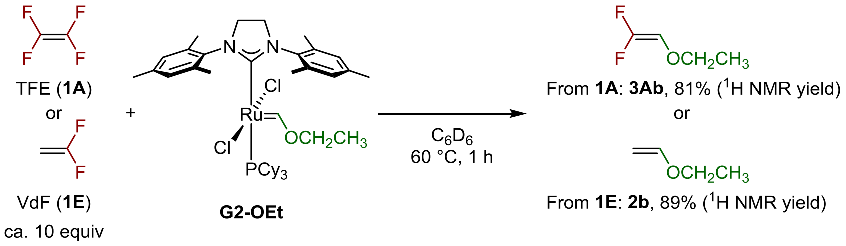


A screw cap NMR tube was charged with 0.1 mL of solution C (Table S5) and 0.5 mL of solution D (Table S6), capped, and removed from the glovebox. The resulting mixture containing 0.012 mmol of **G2-F$_2$**, 0.12 mmol of **2b** (10 equiv relative to **G2-F$_2$**), and 0.002 mmol of 1,4-bis(trifluoromethyl)benzene was shaken and then heated at 60 °C. After 1 h and 6 h, ^{1}H and ^{19}F NMR spectrum was recorded. Formation of **G2-OEt** and VdF were observed (^{1}H NMR yield of **G2-OEt**: 6% for 1 h and 13% for 6 h), whereas neither **G2-H$_2$** (lit.[S8] [Ru]=C$\underline{H}_2$; 18.41 ppm) nor **3Ab** was observed in both ^{1}H and ^{19}F NMR spectra.

Table S6. Solution D.

	amount/mmol	weight/mg	volume/mL
G2-F$_2$	0.0144	11.6	–
ethyl vinyl ether (**2b**)	0.1440	10.4	0.014
C$_6$D$_6$	–	–	0.586
total	–	–	0.600

(b) Nonproductive metathesis with VdF, Scheme 5b.

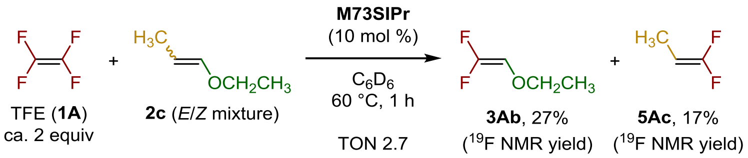


Two experiments were examined at once according to the following procedures: A screw cap NMR tube was charged with 0.1 mL of solution C (Table S5) and 0.5 mL of solution E (Table S7), capped, and removed from the glovebox. The headspace (ca. 2.7 mL, ca. 0.12 mmol, ca. 10 equiv) of the NMR tube was replaced with an atmospheric pressure of **1A** or **1E** using a gastight syringe. The resulting mixture containing 0.012 mmol of **G2-OEt**, ca. 0.12 mmol of **1A** or **1E** (ca. 10 equiv relative to **G2-OEt**), and 0.002 mmol of 1,4-bis(trifluoromethyl)benzene was shaken and then heated at 60 °C. After 1 h, ^{1}H NMR spectrum was recorded and determined the yield of products (**3Ab** in 81% from **1A**; **2b** in 89% from **1E**).

Table S7. Solution E.

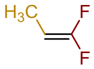
	amount/mmol	weight/mg	volume/mL
G2-OEt	0.0288	23.5	–
C_6D_6	–	–	1.2000
total	–	–	1.2000

“Tetrafluoroethenolysis”, Scheme 6.



A screw cap NMR tube was charged with 0.1 mL of solution C (Table S5), 0.2 mL of solution F (Table S8), and 0.3 mL of solution G (Table S9), capped, and removed from the glovebox. The headspace (ca. 2.7 mL, ca. 0.12 mmol, ca. 2 equiv) of the NMR tube was replaced with atmospheric pressure of **1A** using a gastight syringe. The resulting mixture containing 0.06 mmol of **2c**, ca. 0.12 mmol of **1A** (ca. 2 equiv relative to **2c**), 0.006 mmol of **M73SIPr** precatalyst (10 mol % relative to **2c**), and 0.002 mmol of 1,4-bis(trifluoromethyl)benzene was shaken and then heated at 60 °C. After 1 h, ^{19}F NMR spectrum was recorded and determined the turnover of 2.7 based on **3Ab**. Authentic NMR data for **5Ac** in C_6D_6 have not been reported previously, and we hence tentatively determined the formation of gaseous **5Ac** (lit.[S9] b.p. −29 °C) by ^{19}F NMR and HRMS analyses of the reaction mixture.

1,1-Difluoroprop-1-ene, **5Ac**.



5Ac

5Ac was obtained in 17% ^{19}F NMR yield; ^{19}F NMR (283 MHz, C_6D_6) δ: −93.5 (1F, apparent ddt, *J* = 50.9, 25.4, 2.8 Hz), −89.7 (1F, ddq, *J* = 50.9, 2.8, 2.8 Hz); HRMS (EI) calcd for $C_3H_4F_2$: 78.0281, found: 78.0280.

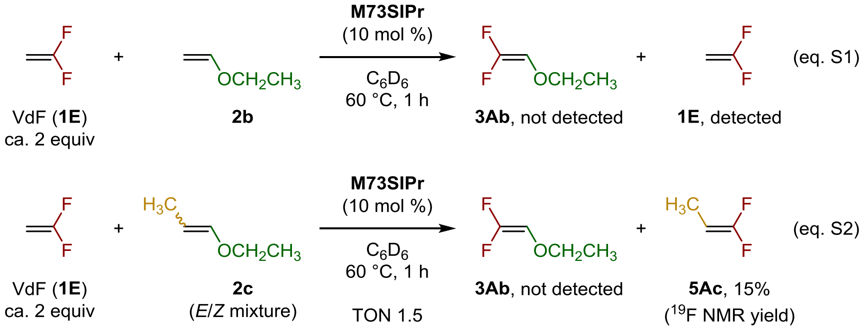
Table S8. Solution F.

	amount/mmol	weight/mg	volume/mL
1-ethoxyprop-1-ene (**2c**)	0.3	25.8	0.033
C_6D_6	–	–	0.967
total	–	–	1.000

Table S9. Solution G.

	amount/mmol	weight/mg	volume/mL
M73SIPr	0.012	9.9	–
C_6D_6	–	–	0.600
total	–	–	0.600

Catalytic cross-metathesis of enol ether (**2b** or **2c**) with VdF, eqs. S1 and S2.



A screw cap NMR tube was charged with 0.1 mL of solution C (Table S5), 0.2 mL of solution H (for eq. S1, Table S10) or solution F (for eq. S2, Table S8), and 0.3 mL of solution G (Table S9), capped, and removed from the glovebox. The headspace (ca. 2.7 mL, ca. 0.12 mmol, ca. 2 equiv) of the NMR tube was replaced with an atmospheric pressure of **1E** using a gastight syringe. The resulting mixture containing 0.06 mmol of **2b** (for eq. S1) or **2c** (for eq. S2), ca. 0.12 mmol of **1E** (ca. 2 equiv), 0.006 mmol of **M73SIPr** precatalyst (10 mol %), and 0.002 mmol of 1,4-bis(trifluoromethyl)-

benzene was shaken and then heated at 60 °C for 1 h, following which ^{19}F NMR spectrum was recorded. The comparison of these two experiments indicated that cross-metathesis between enol ether and VdF actually occurred: VdF reacted with **2c** to give **5Ac** in 15% ^{19}F NMR yield in an olefin metathesis manner (eq. S2), whereas a controlled experiment was useless for understanding if the cross-metathesis actually occur or not (eq. S1).

Table S10. Solution H.

	amount/mmol	weight/mg	volume/mL
ethyl vinyl ether (**2b**)	0.3	21.6	0.029
C_6D_6	–	–	0.971
total	–	–	1.000

III. NMR spectra of new compounds

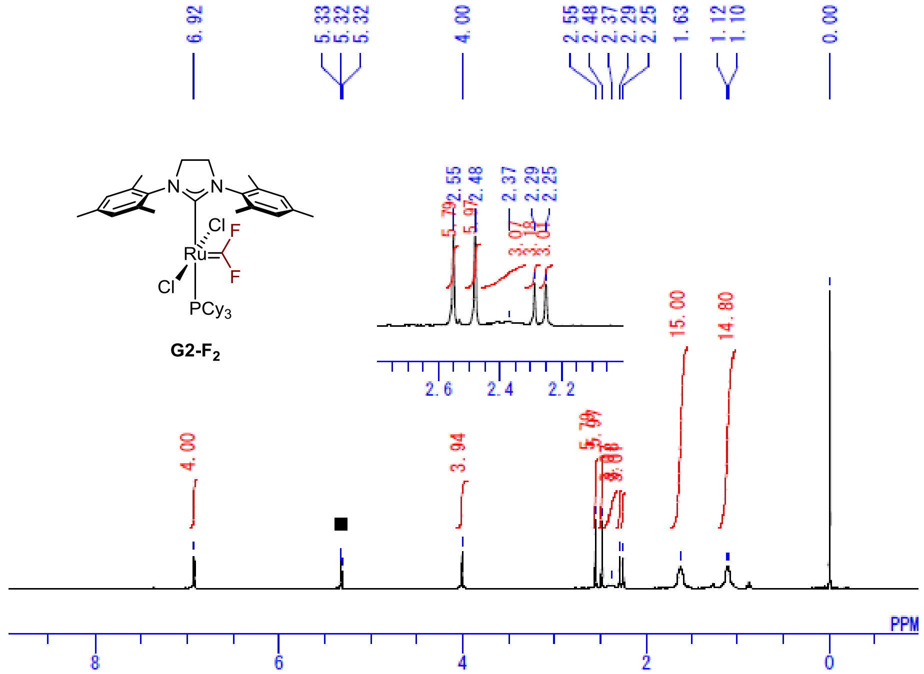


Figure S1. ^{1}H NMR (300 MHz, CD_2Cl_2) spectrum of **G2-F$_2$**.

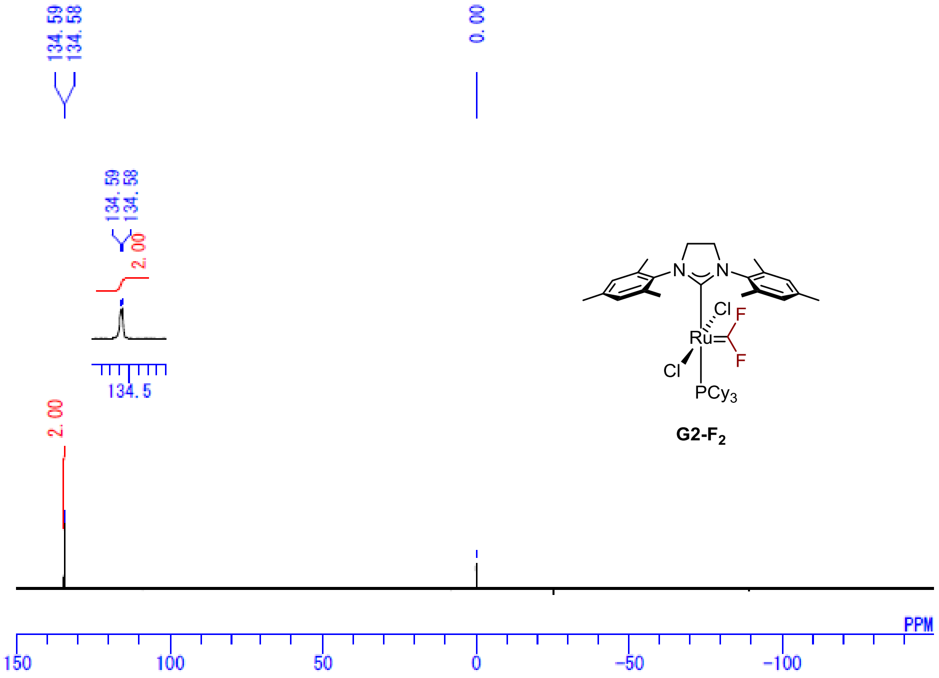


Figure S2. ^{19}F NMR (283 MHz, CD_2Cl_2) spectrum of **G2-F$_2$**.

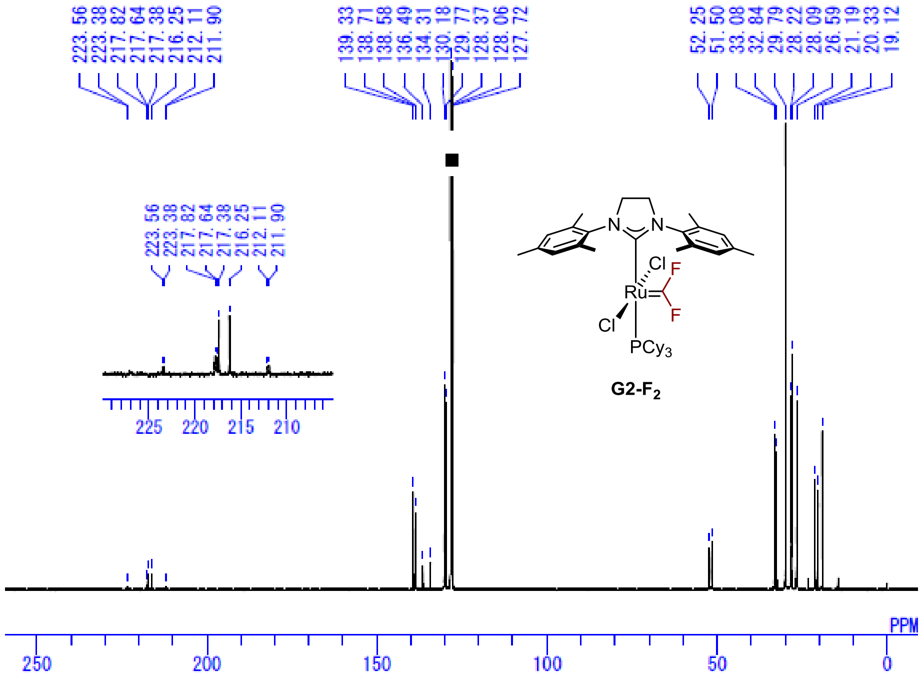


Figure S3. ^{13}C NMR (75 MHz, C_6D_6) spectrum of **G2-F$_2$**.

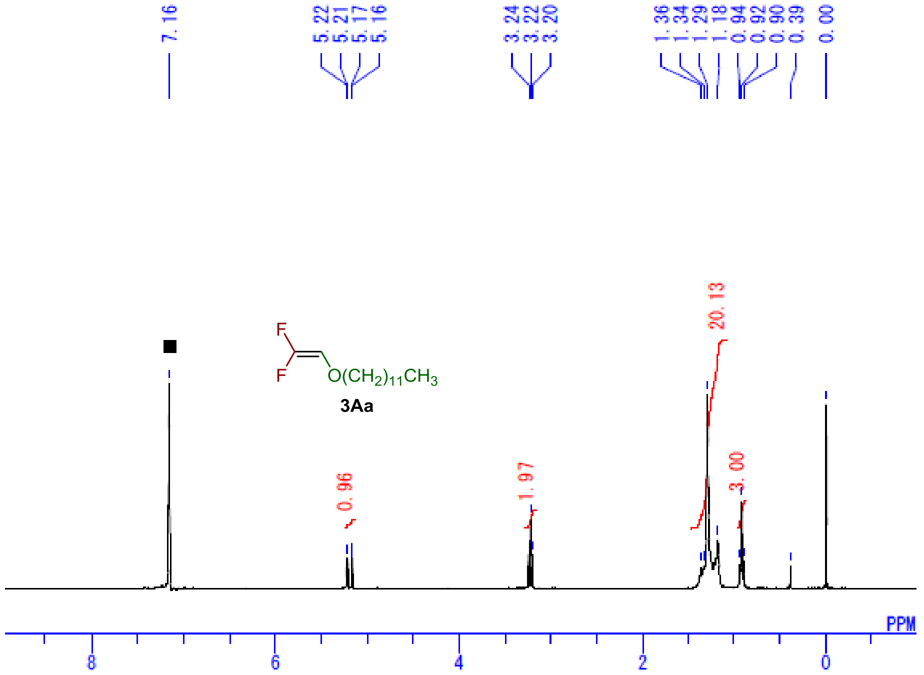


Figure S4. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **3Aa**.

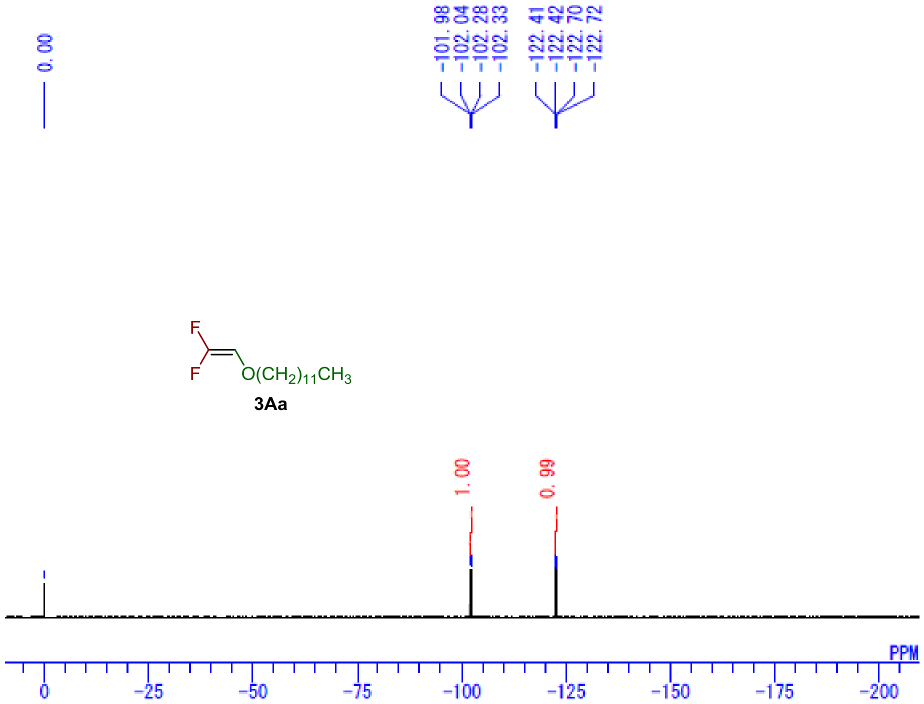


Figure S5. ^{19}F NMR (283 MHz, C_6D_6) spectrum of **3Aa**.

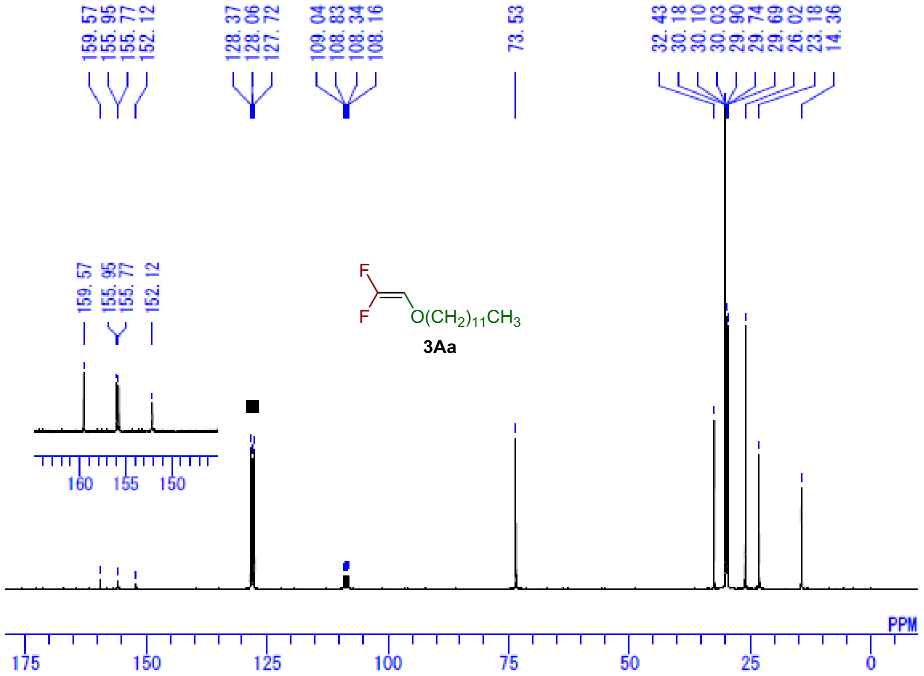


Figure S6. ^{13}C NMR (75 MHz, C_6D_6) spectrum of **3Aa**.

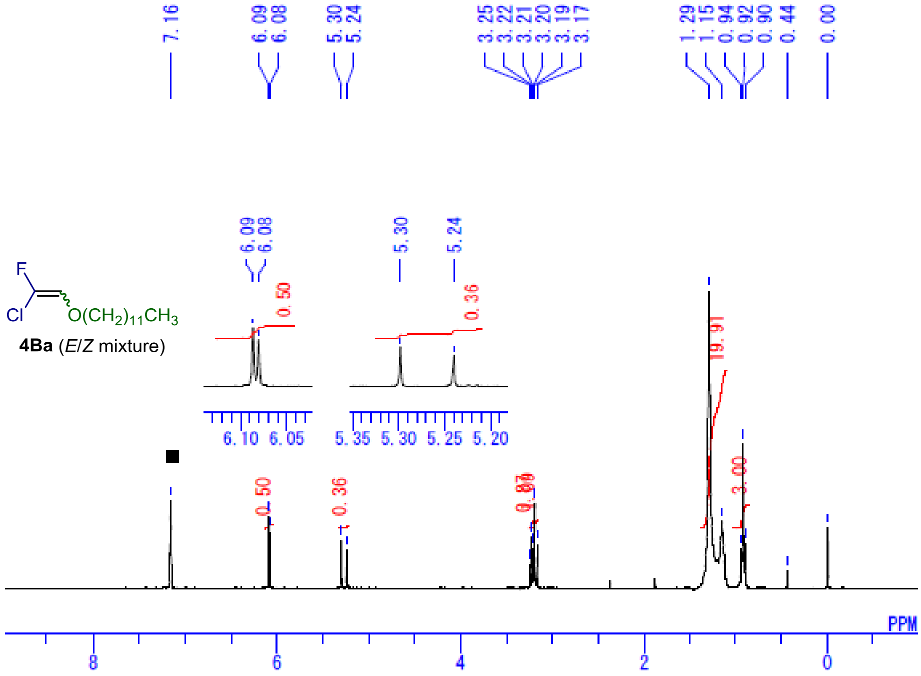


Figure S7. ^{1}H NMR (300 MHz, C_6D_6) spectrum of **4Ba** (*E*/*Z* mixture).

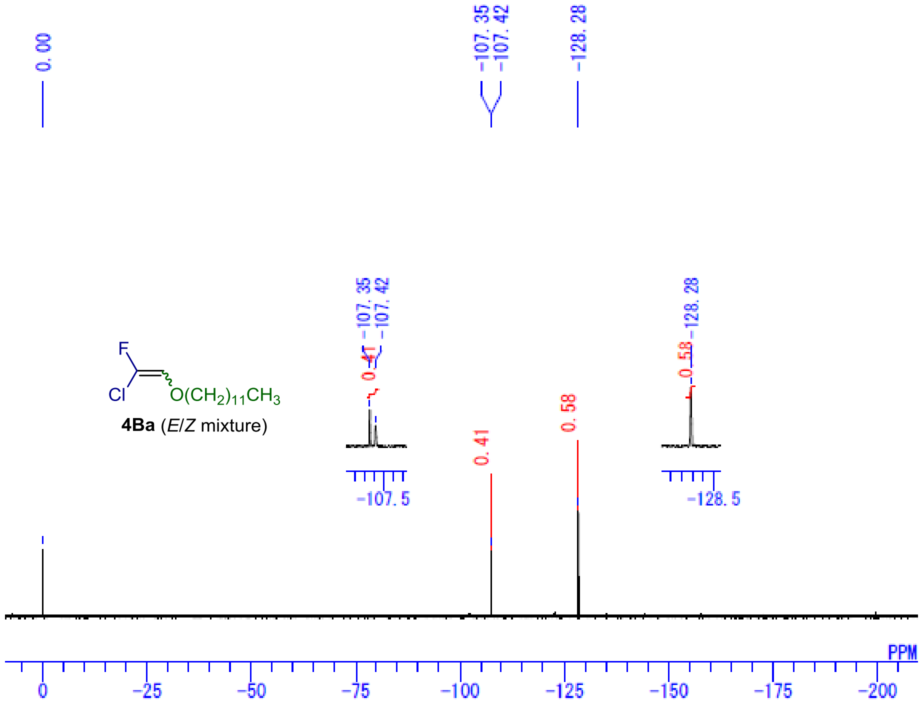


Figure S8. ^{19}F NMR (283 MHz, C_6D_6) spectrum of **4Ba** (*E*/*Z* mixture).

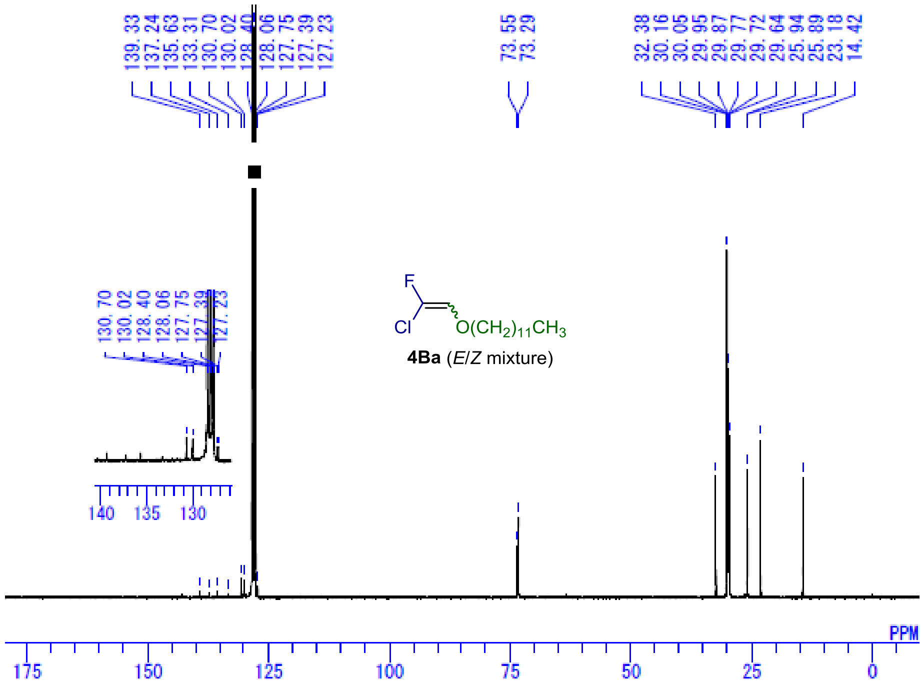


Figure S9. ^{13}C NMR (75 MHz, C_6D_6) spectrum of **4Ba** (*E*/*Z* mixture).

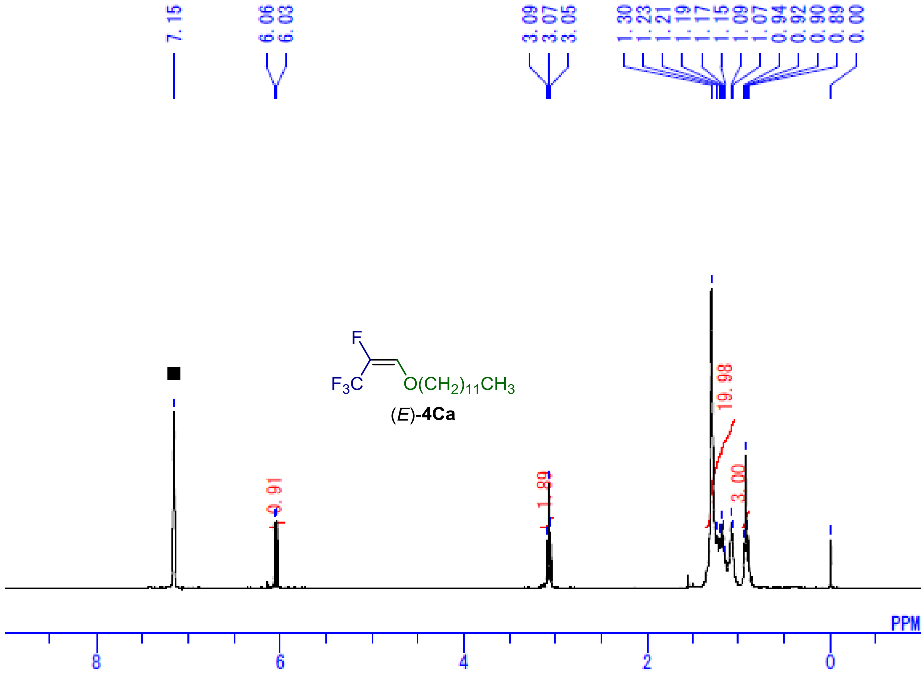


Figure S10. ^{1}H NMR (300 MHz, C_6D_6) spectrum of (*E*)**-4Ca**.

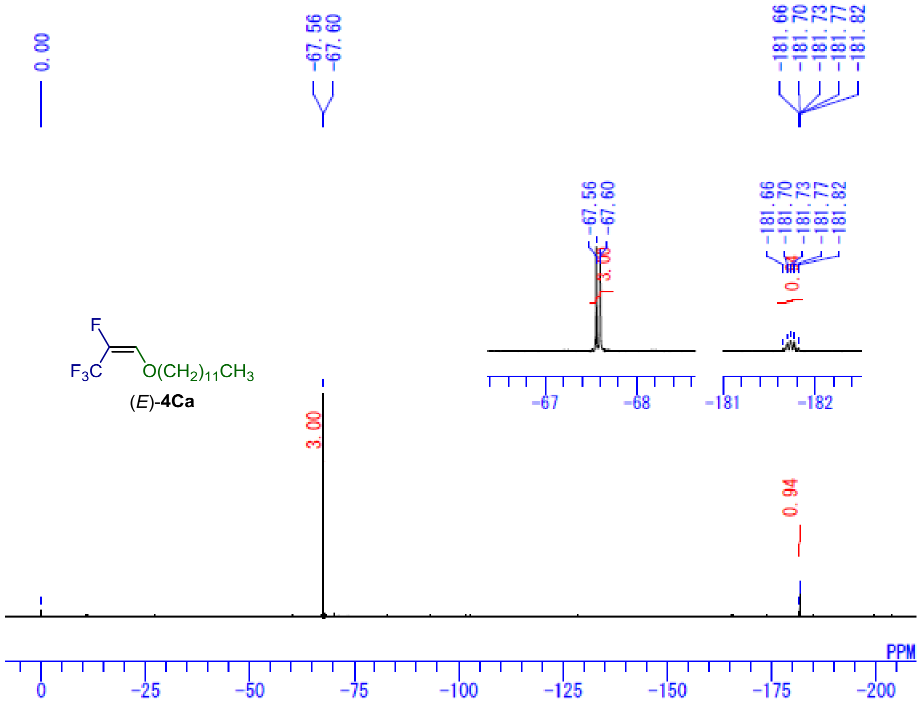


Figure S11. ^{19}F NMR (283 MHz, C_6D_6) spectrum of (*E*)-**4Ca**.

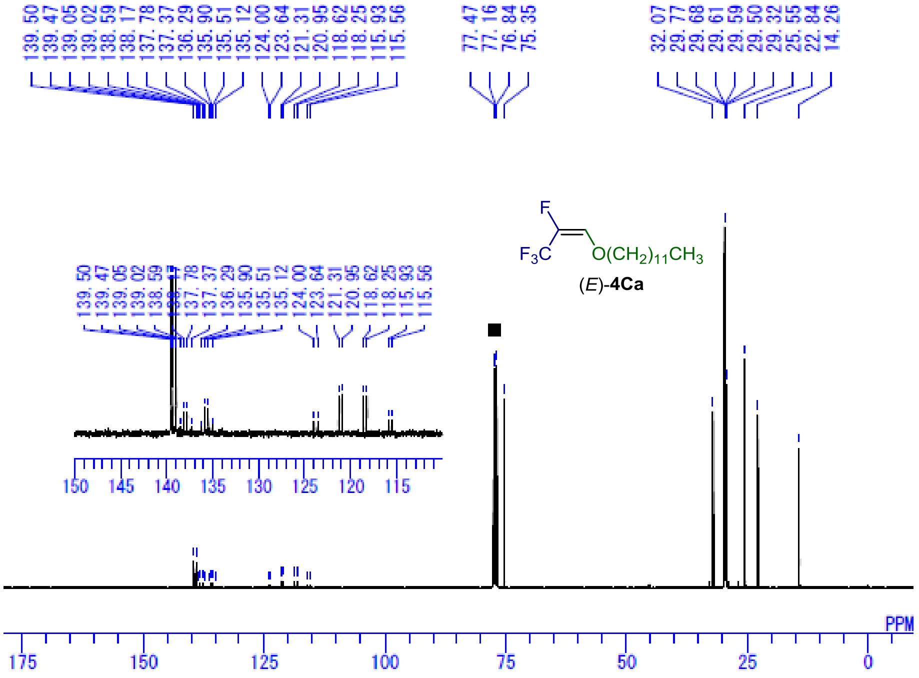


Figure S12. ^{13}C NMR (100 MHz, $CDCl_3$) spectrum of (*E*)-**4Ca**.

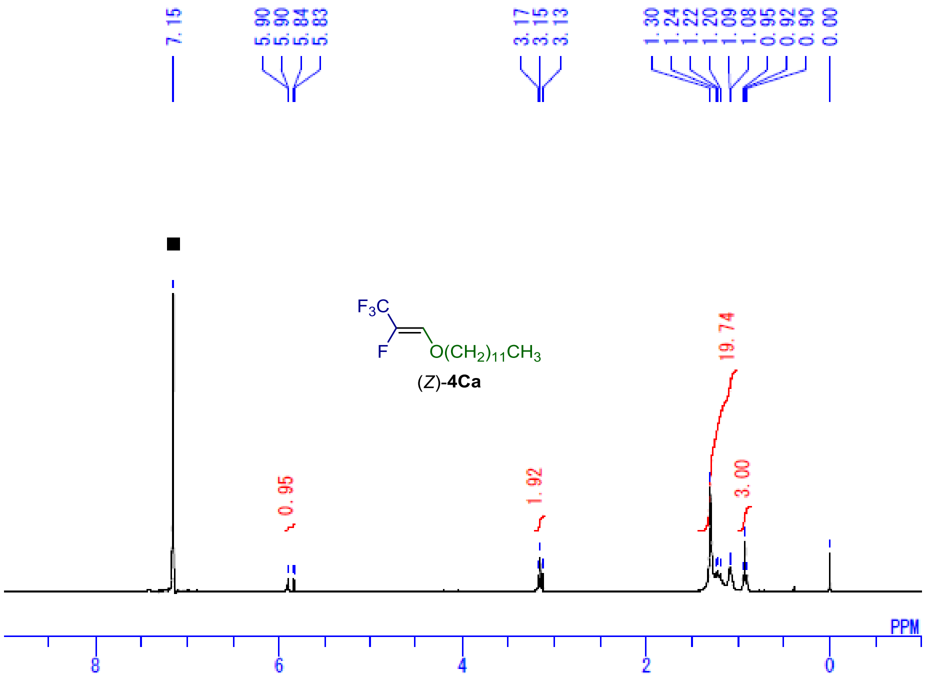


Figure S13. ^{1}H NMR (300 MHz, C_6D_6) spectrum of (*Z*)-**4Ca**.

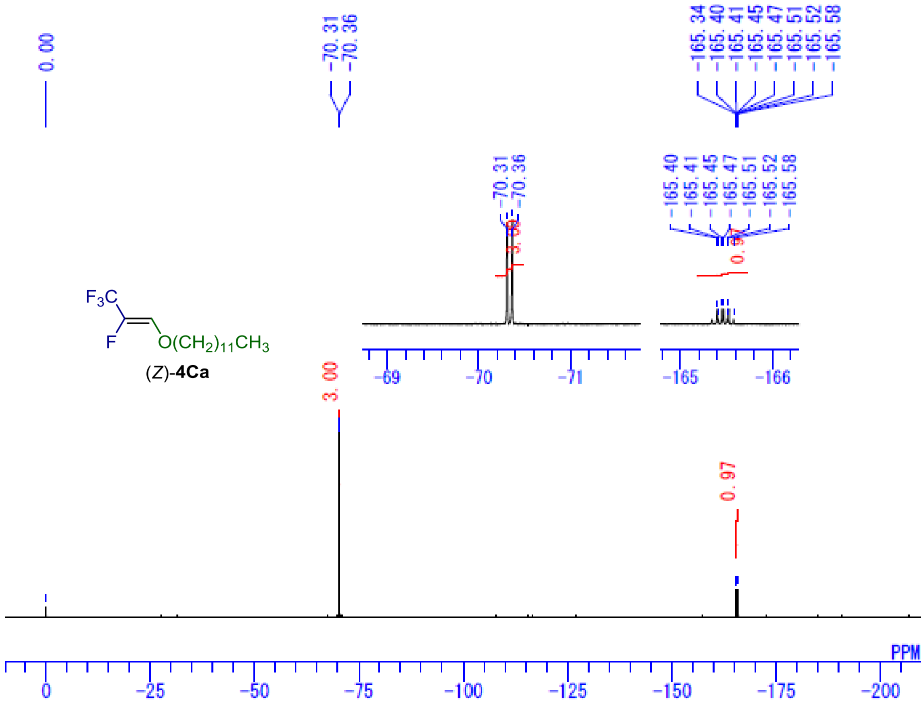


Figure S14. ^{19}F NMR (283 MHz, C_6D_6) spectrum of (*Z*)-**4Ca**.

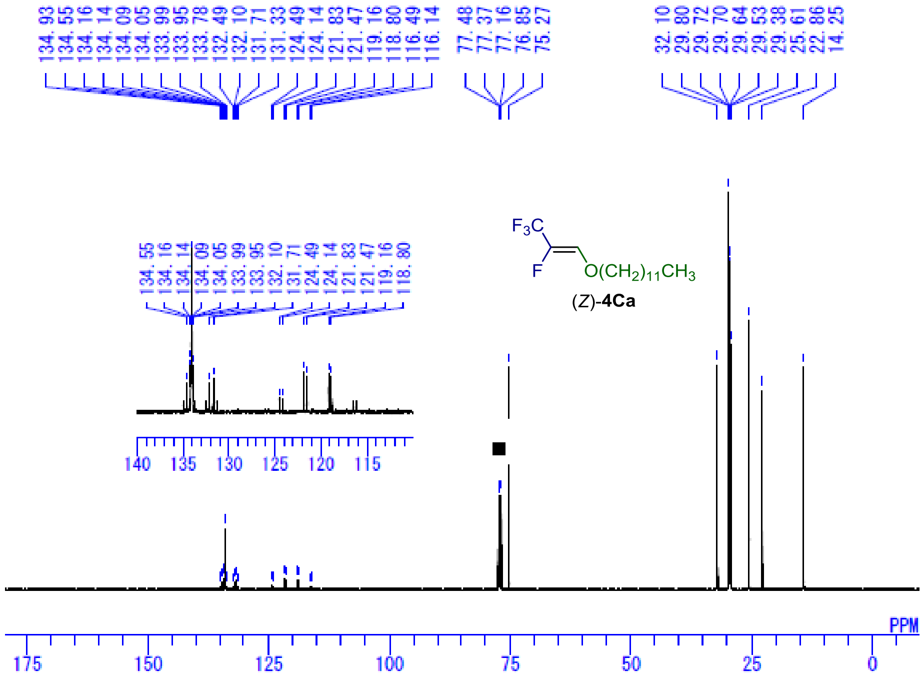


Figure S15. ^{13}C NMR (100 MHz, CDCl$_3$) spectrum of (*Z*)-**4Ca**.

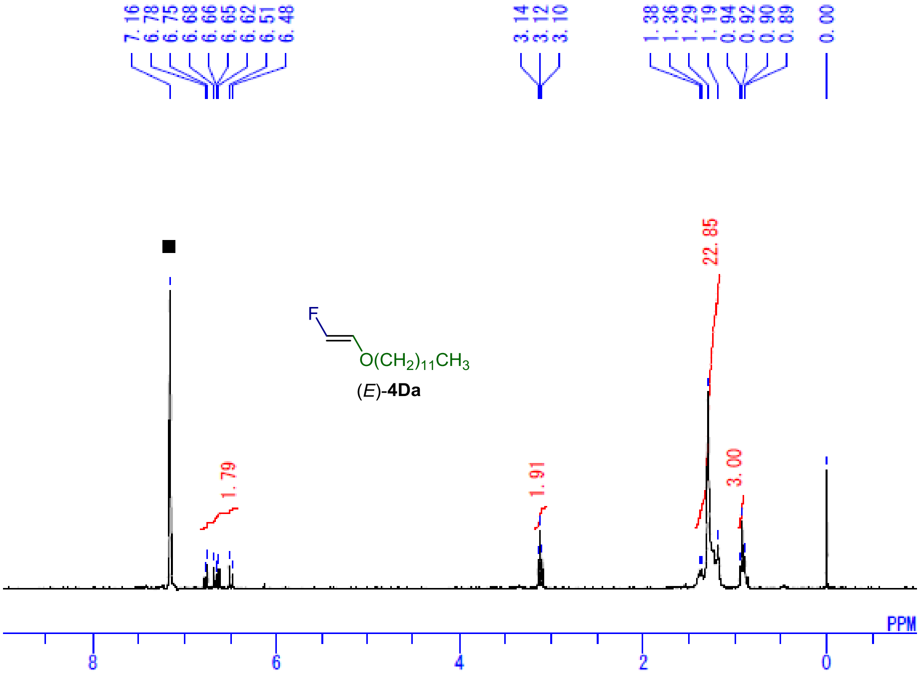


Figure S16. ^{1}H NMR (300 MHz, C$_6$D$_6$) spectrum of (*E*)-**4Da**.

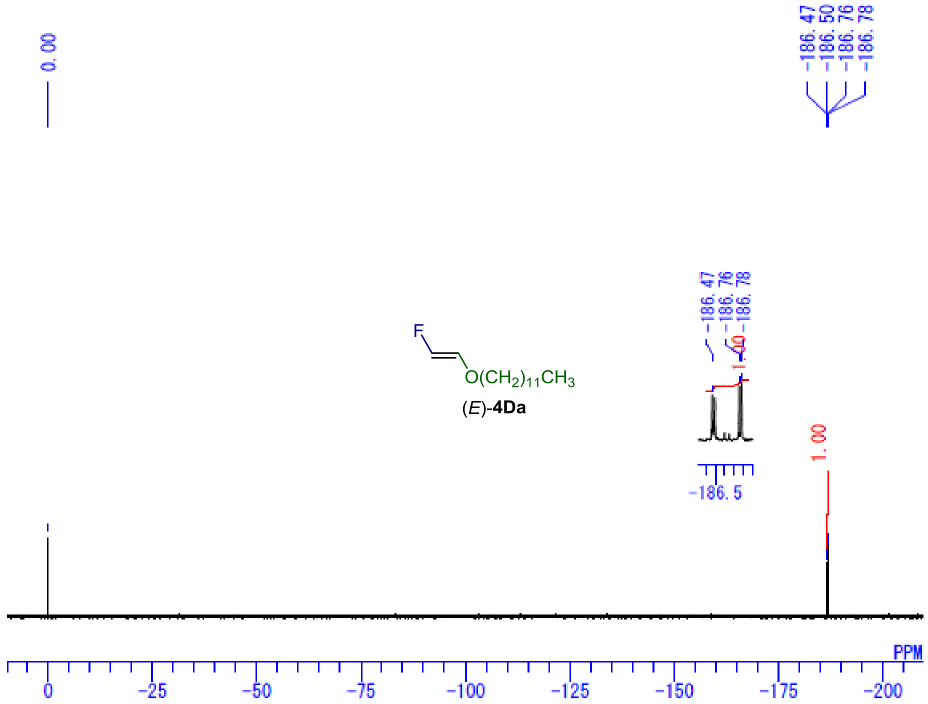


Figure S17. ^{19}F NMR (283 MHz, C_6D_6) spectrum of (*E*)-**4Da**.

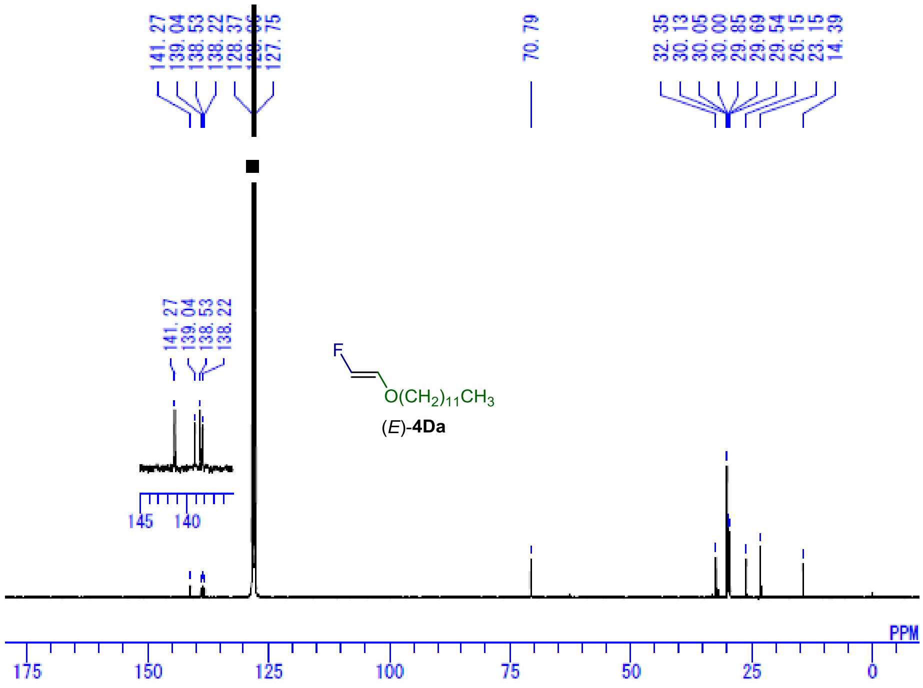


Figure S18. ^{13}C NMR (75 MHz, C_6D_6) spectrum of (*E*)-**4Da**.

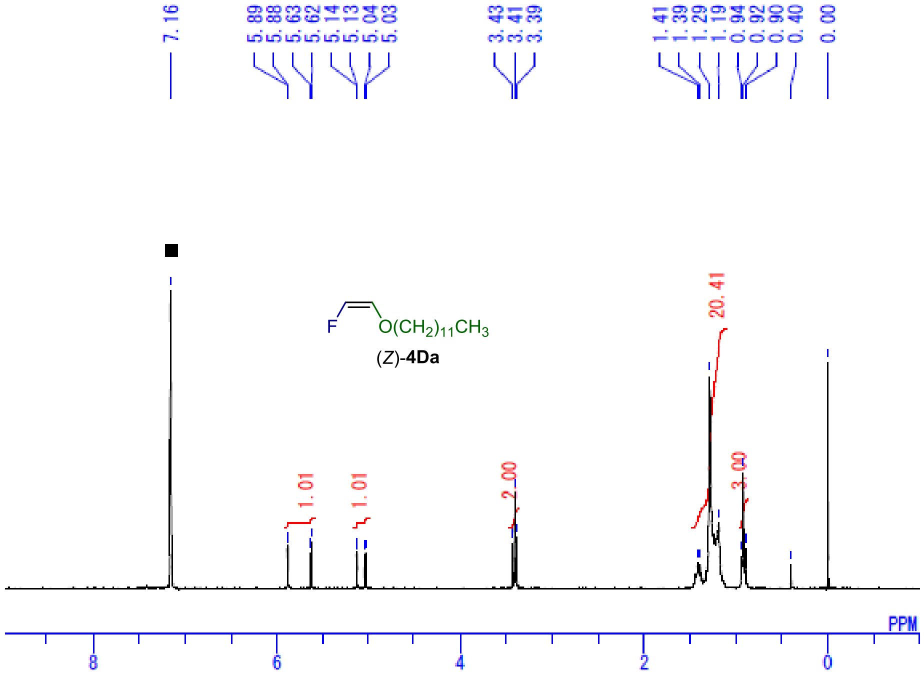


Figure S19. ^{1}H NMR (300 MHz, C_6D_6) spectrum of (*Z*)-**4Da**.

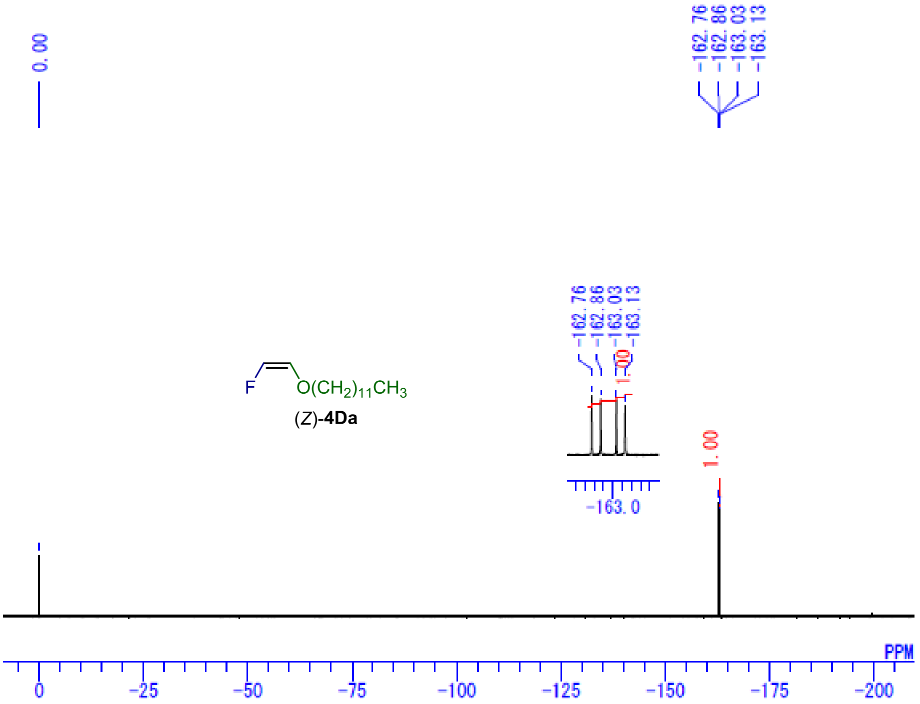


Figure S20. ^{19}F NMR (283 MHz, C_6D_6) spectrum of (*Z*)-**4Da**.

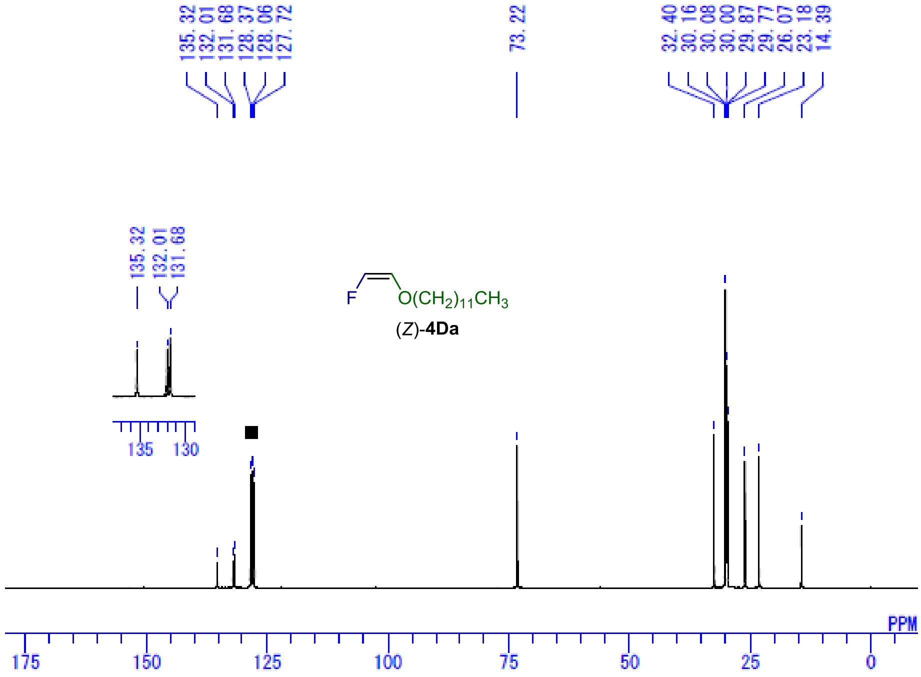


Figure S21. ^{13}C NMR (75 MHz, C_6D_6) spectrum of (*Z*)-**4Da**.

IV. References

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