Electroinc Supporting Information

Reactivity regulation for olefin metathesis-catalyzing ruthenium complexes with sulfur atoms at the terminal of 2-alkoxybenzylidene ligands

Tsubasa Kinugawa and Takashi Matsuo*

Division of Materials Science, Graduate School of Science and Technology, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama-cho, Ikoma, Nara 630-0192, Japan.

CONTENTS

Syntheses of ligands and ruthenium complexes

1-Bromo-2-(methylthio)ethane (12$_{-S}$).[1] In a 100-mL two-neck flask equipped with a dropping funnel, 2-(methylthio)ethanol (2.0 mL (d =1.06 g/mL), 23 mmol) was dissolved in anhydrous CH_2Cl_2 (30 mL), and stirred for 20 min in an ice bath. PBr_3 (2.4 g (d = 2.85 g/mL), 8.9 mmol) diluted with anhydrous CH_2Cl_2 (15 mL) was slowly added from a dropping funnel to the solution. After stirring for 1.5 h at room temperature, the reaction was quenched by adding 50 mL of water. The organic phase was separated and sat. $NaHCO_3$ aq. was added to adjust pH = 10. After washed with sat. $Na_2S_2O_3$ (50 mL), the solution was dried over Na_2SO_4. The solvent was evaporated to obtain **12$_{-S}$** as colorless oil (3.03 g, yield: 85%).^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 3.53–3.49 (m, 2H, -SCH$_2$C$\underline{H}_2$Br), 2.94–2.90 (m, 2H, -SC$\underline{H}_2$CH$_2$Br), 2.17 (s, 3H, C$\underline{H}_3$S-). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 36.1, 30.0, 15.4.

2-(2-Methylthioethoxy)benzaldehyde (13$_{-S}$). In a 100-mL two-neck flask, compound **12$_{-S}$** (2.5 g, 16 mmol) and salicylaldehyde (1.86 mL (d = 1.17 g/mL), 18 mmol) were dissolved in anhydrous DMF (35 mL), and K_2CO_3 (2.2 g, 16 mmol) was added to the solution. The reaction mixture was stirred at 70 ºC. After 17 h, the mixture was cooled to room temperature, and poured into water (100 mL). Organic substances were extracted with hexane/ethyl acetate = 1/1 (3 × 100 mL). After the organic phase was sequentially washed with water (2 × 100 mL) and brine (100 mL), the solution was dried over Na_2SO_4. After the solvent was evaporated, the residue was purified by silica gel chromatography (eluent: hexane/ethyl acetate = 6/1 (R_f = 0.31)) to obtain compound **13$_{-S}$** as light green transparent oil (2.20 g, yield: 70%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 10.51 (s, 1H, -CHO), 7.85 (dd, J = 7.6, 1.6 Hz, 1H, arom), 7.55 (ddd, J = 8.4, 7.6, 1.6 Hz, 1H, arom), 7.05 (t, J = 7.2 Hz, 1H, arom), 6.99 (d, 8.4 Hz, 1H, arom), 4.28 (t, J = 6.4 Hz, 2H, -SCH$_2$C$\underline{H}_2$O-), 2.96 (t, J = 6.4 Hz, 2H, -SC$\underline{H}_2$CH$_2$O-), 2.23 (s, 3H, C$\underline{H}_3$S-). ^{13}C-NMR (100 Hz, $CDCl_3$, ppm): δ 189.7, 160.8, 135.9, 128.5, 125.0, 121.1, 112.5, 67.9, 33.0, 16.3. MS (CI): Calcd. 197.0636 ($C_{10}H_{13}O_2S$ for $[M+H]^+$), found 197.0632.

2-(2-Methylthioethoxy)styrene (14$_{-S}$). In a flame-dried 100-mL two-neck flask, CH_3PPh_3Br (0.761 g, 2.13 mmol) was suspended in anhydrous THF (10 mL) under an N_2 atmosphere and cooled to –78 ºC. ^{n}BuLi solution in hexane (1.6 M, 1.9 mL, 3.04 mmol) was slowly dropwise added to the solution using a syringe, and the suspension was stirred for 1 h in an ice salt bath. The mixture turned to be orange in color. To the reaction mixture was added a solution of compound **13$_{-S}$** (0.322 g, 1.63 mmol) in anhydrous THF (5 mL) using a syringe. The reaction mixture was stirred for 2 h in an ice water bath. Afterward, the reaction mixture was transferred into a beaker, and treated with sat. NH_4Cl

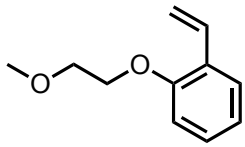
aq. (5 mL), hexane/ethyl acetate = 3/1 (60 mL) and water (100 mL) in an ice bath. After the mixture was stirred for 10 min, the organic phase was separated and sequentially washed with water (100 mL) and brine (100 mL). The solution was and dried over Na_2SO_4 and the solvent was evaporated. The residue was purified by silica gel chromatography (eluent: hexane/ethyl acetate = 6/1 (R_f = 0.28)) to obtain compound **14**$_{-S}$ as pale-yellow oil (263 mg, yield: 83%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.49 (dd, *J* = 7.8, 1.6 Hz, 1H, arom), 7.22 (ddd, *J* = 8.2, 7.8, 1.6 Hz, 1H, arom), 7.07 (dd, *J* = 17.8, 11.2 Hz, 1H, -C*H*=CH_2), 6.95 (t, *J* = 7.8 Hz, 1H, arom), 6.87 (d, *J* = 8.2 Hz, 1H, arom), 5.75 (dd, *J* = 17.8, 1.5 Hz, 1H, -CH=CH_{2a}), 5.26 (dd, *J* = 11.2, 1.5 Hz, 1H, -CH=CH_{2b}), 4.18 (t, *J* = 6.8 Hz, 2H, -SCH_2CH_2O-), 2.92 (t, *J* = 6.8 Hz, 2H, -SCH_2CH_2O-), 2.22 (s, 3H, CH_3S-). ^{13}C-NMR (100 Hz, $CDCl_3$, ppm): δ 155.8, 131.7, 129.0, 127.1, 126.7, 114.7, 112.2, 68.0, 33.3, 16.4. MS (EI): Calcd. 194.0756 ($C_{11}H_{14}OS$ for $[M]^+$), found 194.0762.

2-Methoxyethyl 4-methylbenzenesulfonate (12$_{-O}$**).**[2] In a 50-mL round-bottom flask equipped with a dropping funnel, 2-methoxyethanol (0.79 mL (*d* = 0.965 g/mL) 10 mmol) and tosyl chloride (2.12 g, 11 mmol) were dissolved in ethyl acetate (10 mL) and stirred for 10 min in an ice bath. Triethylamine diluted with ethyl acetate (5 mL) was slowly dropwise added from the dropping funnel to the abovementioned solution. After stirring for 16 h at room temperature, water (20 mL) was dropwise added from a dropping funnel to the solution in an ice bath and the mixture was stirred for 5 min. Organic substances were extracted with ethyl acetate (3 × 20 mL). The organic phase was washed with brine (30 mL) and dried over Na_2SO_4. After the solvent was evaporated, the residue was subjected to flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 6/1 (R_f = 0.47)) to obtain **12**$_{-O}$ as pale yellow oil (1.49 g, yield: 65%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.81 (d, *J* = 8.2 Hz, 2H, arom), 7.35 (d, *J* = 8.2 Hz, 2H, arom), 4.16 (t, *J* = 4.7 Hz, 2H, -CH_2CH_2-OTs), 3.58 (t = 4.7 Hz, 2H, -CH_2CH_2-OTs), 3.31 (s, 3H, $CH_3OCH_2CH_2$-), 2.45 (s, 3H, -OSO_2Phe-CH_3). ^{13}C-NMR (100 MHz, $CDCl_3$, ppm): δ 144.8, 132.9, 129.8, 127.98, 69.9, 69.1, 59.0, 22.7.

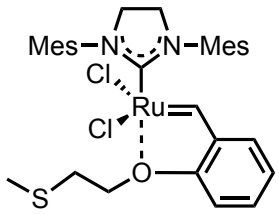
2-(2-Methoxyethoxy)benzaldehyde (13$_{-O}$**).** In a 100-mL two-neck flask, compound **11**$_{-O}$ (1.16 g, 5.0 mmol), salicylaldehyde (0.58 mL (*d* =1.17 g/mL), 5.5 mmol), and K_2CO_3 (0.766 g, 5.5 mmol) was added to the solution. The reaction mixture was stirred at 70 ºC. After 12 h, the reaction mixture was cooled to room temperature, and poured into water (100 mL). Organic substances were extracted with hexane/ethyl acetate = 2/1 (3 × 60 mL). The organic phase was sequentially washed with water (2 × 50 mL) and brine (100 mL). The solution was dried over Na_2SO_4. After the solvent was evaporated, the residue was subjected to flash column chromatography on silica gel (eluent: hexane/ethyl acetate = 6/1 (R_f = 0.09)) to obtain **13**$_{-O}$ as brown oil (0.790 g, yield: 88%). ^{1}H-NMR (400 MHz, $CDCl_3$,

ppm) : δ 10.54 (s, 1H, -CHO), 7.84 (dd, J = 7.6, 1.8 Hz, 1H, arom), 7.54 (ddd, J = 8.4, 7.6, 1.8 Hz, 1H, arom), 7.04 (t, J = 7.6 Hz, 1H, arom), 7.00 (d, 8.4 Hz, 1H, arom), 4.24 (t, J = 4.7 Hz, 2H, -$OCH_2C\underline{H_2}O$-), 3.82 (t, J = 4.7 Hz, 2H, $SC\underline{H_2}CH_2O$-), 3.47 (s, 3H, $C\underline{H_3}O$-). ^{13}C-NMR (100 Hz, $CDCl_3$, ppm): δ 189.6, 161.2, 135.9, 128.3, 125.1, 121.0, 112.7, 70.8, 68.2, 59.4. MS (EI): Calcd. 180.0786 ($C_{10}H_{12}O_3$ for $[M]^+$), found 180.0784.

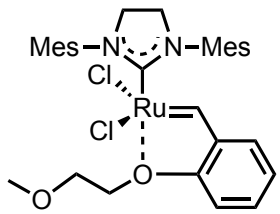
2-(2-Methoxythoxy)styrene (14-O). Compound **14-O** was synthesized in the same manner as the synthesis of compound **14-S** from compound **13-S**. Crude product was purified by silica gel chromatography (eluent: hexane/ethyl acetate = 6/1 (R_f = 0.39)) to obtain as pale yellow oil (yield: 61%). ^{1}H-NMR (400 MHz, $CDCl_3$, ppm): δ 7.48 (dd, J = 7.3, 1.7 Hz, 1H, arom), 7.19 (ddd, J = 8.3, 7.3, 1.7 Hz, 1H, arom), 7.08 (dd, J = 17.8, 11.2 Hz, 1H, -$C\underline{H}$=CH_2), 6.94 (t, J = 7.3 Hz, 1H, arom), 6.87 (d, J = 8.3 Hz, 1H, arom), 5.76 (dd, J = 17.8, 1.5 Hz, 1H, -CH=C$\underline{H_{2a}}$), 5.26 (dd, J = 11.2, 1.5 Hz, 1H, -CH=C$\underline{H_{2b}}$), 4.14 (t, J = 4.8 Hz, 2H $CH_3OCH_2C\underline{H_2}O$-), 3.78 (t, J = 4.8 Hz, 2H, $CH_3OC\underline{H_2}CH_2O$-), 3.46 (s, 3H, $C\underline{H_3}O$-). ^{13}C-NMR (100 Hz, $CDCl_3$, ppm): δ 156.0, 131.6, 128.8, 127.1, 126.5, 121.0, 114.4, 112.3, 71.1, 67.9, 59.3. MS (EI): Calcd. 178.0996 ($C_{11}H_{14}O_3$ for $[M]^+$), found 178.0994.



Complex 11-S. In a 100-mL two-neck flask with a condenser, Grubbs second generation complex (Grubbs-II, 54.5 mg, 0.064 mmol), compound **14-S** (12.2 mg, 0.063 mmol) and CuCl (8.5 mg, 0.086 mmol) were dissolved in anhydrous CH_2Cl_2 (10 mL) under an N_2 atmosphere. The mixture was refluxed for 1 h under N_2. The reaction mixture was concentrated under reduced pressure. The residue was purified by silica gel chromatography (eluent: ethyl acetate), and a green band was collected. Afterward, the solvent was evaporated followed by recrystallization (vapor diffusion of hexane into CH_2Cl_2 solution) at 5 ºC to obtain complex **11-S** as dark green solids (23.4 mg, yield: 56%). ^{1}H-NMR (400 MHz, CD_2Cl_2, ppm): δ 16.250 (s, 1H, benzylidene proton), 7.553 (dd, J = 7.6 Hz, 2.0 Hz, 1H, aromatic proton in ligand), 7.074 (s, 4H, aromatic proton in mesityl group), 6.967 (dd, J = 7.6 Hz, 7.6 Hz, 1H, aromatic proton in ligand), 6.903 (dd, J = 7.6 Hz, 2.0 Hz, 1H, aromatic proton in ligand), 6.903 (d, J = 7.6 Hz, 1H, aromatic proton in ligand), 4.141 (t, J = 7.6 Hz, 2H, -$SCH_2C\underline{H_2}O$-), 3.987 (s, 4H, NHC protons), 2.679 (t, J = 7.6 Hz, 2H, -$SC\underline{H_2}CH_2O$-), 2.442 (s, 12H, *o*-methyl group in mesityl group), 2.424 (s, 6H, *p*-methyl protons in mesityl group), 1.591 (s, 3H, $C\underline{H_3}SCH_2$-). ^{13}C-NMR (100 MHz, CD_2Cl_2, ppm): δ 304.71, 210.42, 153.50, 148.49, 139.40, 138.78, 138.55, 130.00, 129.19, 123.82, 122.48, 112.01, 62.27, 52.47, 36.67, 21.24, 19.21, 15.03. MS (ESI, positive): Calcd. 623.1434 ($C_{31}H_{38}ClN_2ORuS$ for $[M–Cl]^+$), found 623.1414.



Complex 11-O. The synthesis was conducted in the same manner as the synthesis of complex **11-S**. The product was recrystallized (vapor diffusion of hexane into CH_2Cl_2 solution) at 5 ºC to obtain complex **11-O** dark green solid (yield: 56%). δ 16.495 (s, 1H, benzylidene proton), 7.563 (dd, J = 7.6 Hz, 2.8 Hz, 1H, aromatic proton in ligand), 7.084 (s, 4H, aromatic proton in mesityl group), 6.945 (m, 3H, aromatic proton in ligand), 4.238 (t, J = 7.6 Hz, 2H, -MeOCH$_2$C<u>*H*</u>$_2$O-), 4.133 (s, 4H, NHC protons), 3.501 (t, J = 7.6 Hz, 2H, MeOC<u>*H*</u>$_2$CH$_2$O-), 3.113 (s, 3H, <u>Me</u>OCH$_2$CH$_2$O-), 2.443 (s, 12H, *o*-methyl group in mesityl group), 2.407 (s, 6H, *p*-methyl protons in mesityl group). ^{13}C-NMR (150 MHz, CD_2Cl_2, ppm): δ 293.38, 210.19, 153.42, 144.95, 139.20, 136.71 129.94 129.83 129.61, 123.83, 122.24 113.07, 69.51, 68.51, 58.91, 52.08, 21.28, 19.45.



MS (ESI, positive): Calcd. 571.1907 ($C_{31}H_{37}N_2O_2Ru$ for $[M–Cl_2–H]^+$), found 571.1852.

References

1. G. Ye, S. Li, Y. Feng, and C. Wang, China Patent, CN201811591908, 2018.

2. Y. Matsui, K. Soranaka, and Y. Sakamoto, World Intellectual Property Organization, WO2011152066A1, 2011.

Table S1. Quantification of components contained in the reaction mixture of the ligand exchange between complex **1** and ligand **14**$_{\text{-S}}$.[a]

ruthenium complexes					
time (h)	complex **1** (starting material)		complex **11**$_{\text{-S}}$ (product)		complex **1** + complex **11**$_{\text{-S}}$
	relative intensity[b] (^{i}Pr-methine proton) 4.87 ppm	concentration (mM)	relative intensity[b] (-$SCH_2C\underline{H_2}O$-) 2.67 ppm	concentration (mM)	concentration (mM)
0.5	0.5224	47.0	0.0657	2.96	50.0
1	0.4378	39.4	0.2404	10.8	50.2
2	0.368	33.1	0.3612	16.3	49.4
3	0.3129	28.2	0.4990	22.5	50.6
6	0.2183	19.6	0.6540	29.4	49.1
12	0.1474	13.3	0.8461	38.1	51.3
24	0.0944	8.50	0.9659	43.5	52.0
48	0.0820	7.38	0.9717	43.7	51.1
ligands					
time (h)	ligand **14**$_{\text{-S}}$ (starting material)		ligand **15** (product)		ligand **14**$_{\text{-S}}$ + ligand **15**
	relative intensity[b] (-SCH_2CH_2O-) 2.90 ppm	Concentration (mM)	relative intensity[b] (^{i}Pr-methine proton) 4.55 ppm	Concentration (mM)	Concentration (mM)
0.5	1.046	47.1	0.0300	2.70	49.8
1	0.8524	38.4	0.1085	9.77	48.1
2	0.7109	32.0	0.1717	15.5	47.4
3	0.6166	27.7	0.2205	19.8	47.6
6	0.4634	20.9	0.3137	28.2	49.1
12	0.2717	12.2	0.3967	35.7	47.9
24	0.1706	7.68	0.4581	41.2	48.9
48	0.1200	5.40	0.5030	45.3	50.7

[a]Reacion conditions: [HG-II (**1**)] = [**14**$_{\text{-S}}$] = 50 mM in CD_2Cl_2 at 25 ˚C. The reaction was conducted in an NMR tube with a J-young cap. Hexamethyl disiloxane (HMDSO; 5 mM) was added as an internal standard. [b]Relative intensity with reference to the signal of HMDSO (δ_H: 0.066 ppm).

Table S2. Quantification of components contained in the reaction mixture of the ligand exchange between complex **1** and ligand **14**$_{\text{-O}}$.[a]

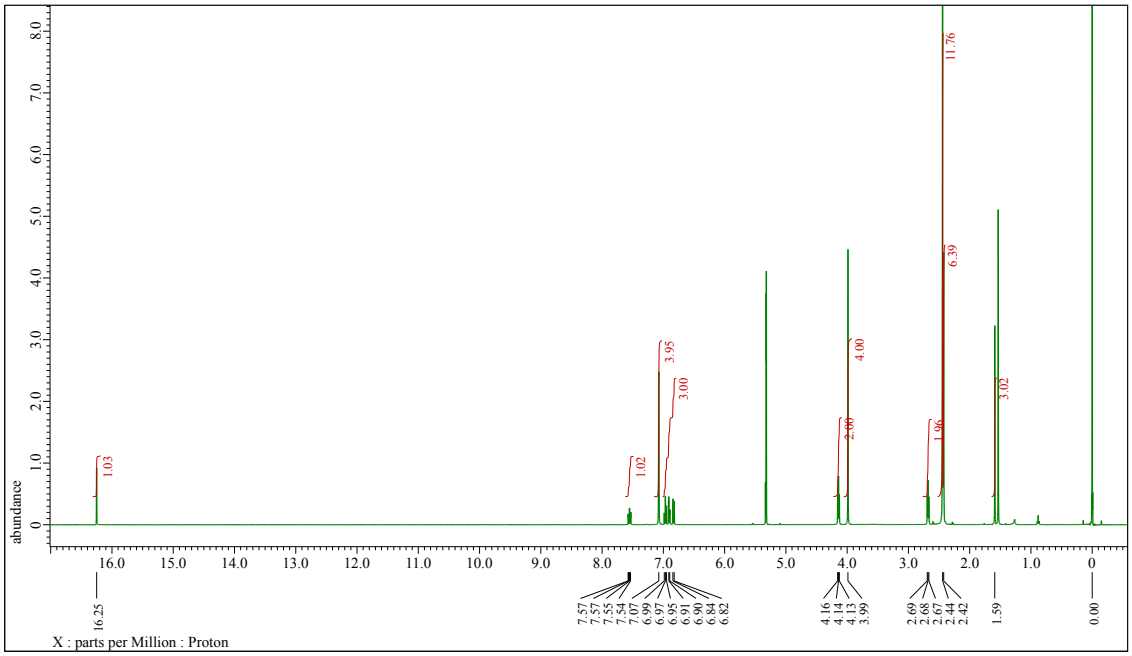
ruthenium complexes					
time (h)	complex **1** (starting material)		complex **11**$_{\text{-O}}$ (product)		complex **1** + complex **11**$_{\text{-O}}$
	relative intensity[b] (^{i}Pr-methine proton) 4.87 ppm	concentration (mM)	relative intensity[b] (MeOC$\underline{H}_2$CH$_2$-) 3.50 ppm	concentration (mM)	concentration (mM)
0.5	0.5246	47.2	0.0588	2.65	49.9
2	0.3958	35.6	0.2850	12.8	48.4
3	0.3649	32.8	0.3285	14.8	47.6
6	0.3625	32.6	0.3541	15.9	48.6
12	0.3520	31.7	0.3686	16.6	48.3
24	0.3548	31.9	0.3511	15.8	47.7
ligands					
time (h)	ligand **14**$_{\text{-O}}$ (starting material)		ligand **15** (product)		ligand **14**$_{\text{-O}}$ + ligand **15**
	relative intensity[b] (MeOC$\underline{H}_2$CH$_2$-) 3.75 ppm	Concentration (mM)	relative intensity[b] (^{i}Pr-methine proton) 4.55 ppm	Concentration (mM)	Concentration (mM)
0.5	1.0487	47.2	0.0270	2.43	49.6
2	0.8080	36.4	0.1497	13.5	49.8
3	0.7834	35.3	0.1497	13.5	48.7
6	0.6968	31.4	0.1654	14.9	46.2
12	0.6545	29.5	0.1535	13.8	43.3
24	0.5904	26.6	0.1667	15.0	41.6

[a]Reacion conditions: [HG-II (**1**)] = [**14**$_{\text{-O}}$] = 50 mM in CD_2Cl_2 at 25 ˚C. The reaction was conducted in an NMR tube with a J-young cap. Hexamethyl disiloxane (HMDSO; 5 mM) was added as an internal standard. [b]Relative intensity with reference to the signal of HMDSO (δ_H: 0.066 ppm).

Table S3. Crystal data, diffraction collection details, and structure refinement.

Compound		**11**-S	**11**-O
CCDC deposition number		2262936	2262938
Molecular formula		$C_{31}H_{38}Cl_2N_2OruS$	$C_{31}H_{38}Cl_2N_2O_2Ru$
Formula wight / g mol^{-1}		658.66	642.60
Crystal system		monoclinic	monoclinic
Space group		$P2_1/n$	$P2_1/n$
Cell metric	*a* / Å	13.1608 (2)	13.2694 (2)
	b / Å	10.8969 (2)	10.71431 (19)
	c / Å	21.8863 (4)	21.4432 (4)
	b / deg	103.350 (7)	101.277 (7)
Cell volume / Å^3		3053.95 (13)	2989.77 (12)
Z		4	4
Electrons per cell F_{000}		1360.0	1328.0
Calcd. Density / g cm^{-3}		1.433	1.428
m(Mo-*K*α) / cm^{-1}		7.831	7.331
Crystal shape and color		prism, green	prism, green
Crystal size / mm		0.24 × 0.22 × 0.12	0.19 × 0.06× 0.05
Radiation		Mo*K*α (λ = 0.71075)	Mo*K*α (λ = 0.71075)
Temperature / K		103.15	103.15
w oscillation Range		130.0 – 190.0˚	130.0 – 190.0˚
(c = 45.0, f = 0.0)		(80 sec /degree)	(130 sec /degree)
w oscillation Range		0.0 – 160.0˚	0.0 – 160.0˚
(c = 45.0, f = 180.0)		(80 sec /degree)	(80 sec /degree)
w oscillation Range		0.0 – 160.0˚	0.0 – 160.0˚
(c = 45.0, f = 90.0)		(80 sec /degree)	(80 sec /degree)
No. of Reflections Measured		Total: 49969	Total: 48620
		Unique: 3991	Unique: 6848
		(R_{int} = 0.0182)	(R_{int} = 0.0273)
Residuals: R_1 ($I > 2\sigma(I)$)		0.0327	0.0316
Residuals: R_1 (All reflections)		0.0335	0.0356
Residuals: wR_2 (All reflections)		0.0876	0.0761
Goodness of Fit Indicator		2.632	2.288

^{1}H-NMR (400 MHz, CD_2Cl_2)



^{13}C-NMR (100 MHz, CD_2Cl_2)

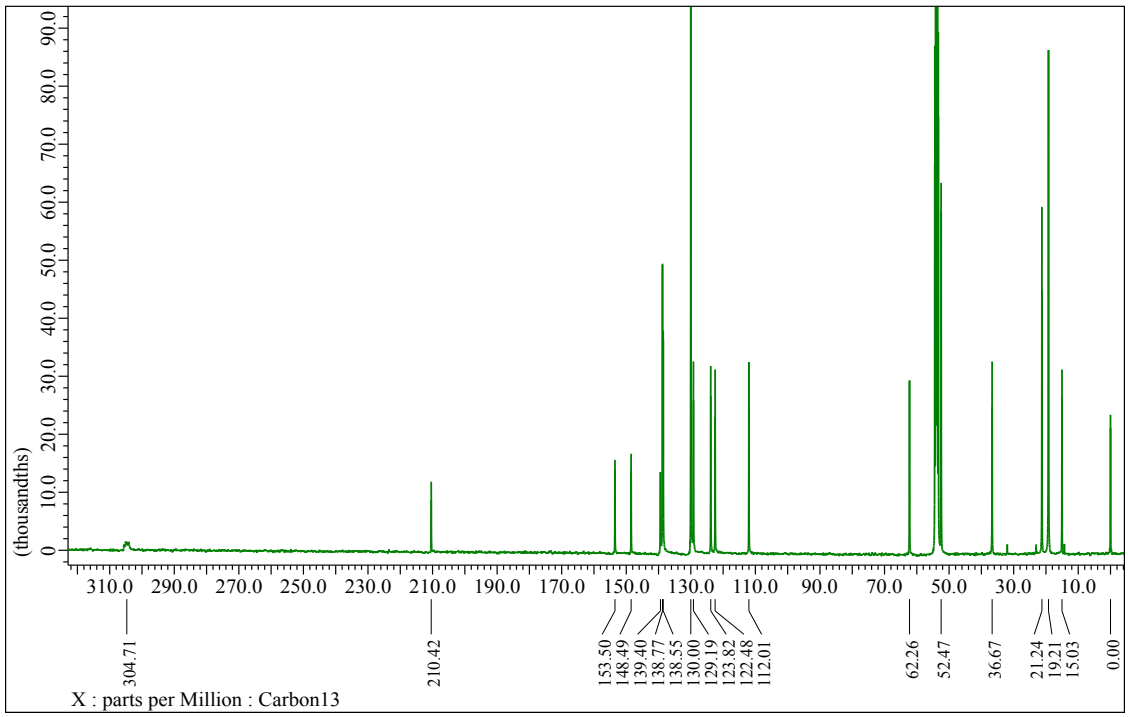
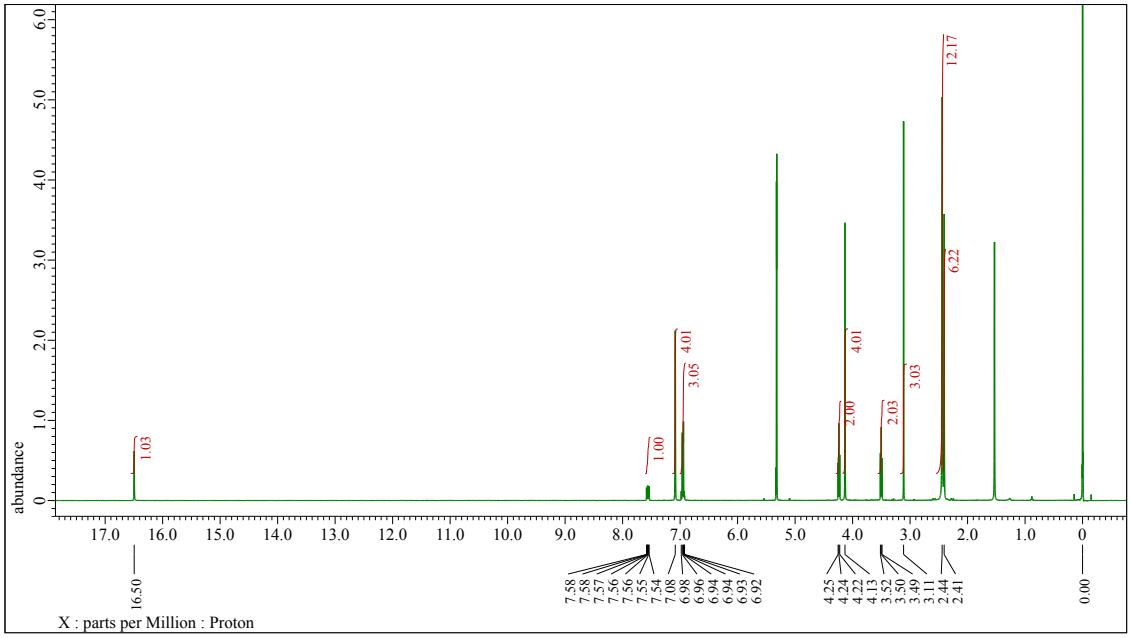


Fig. S1 NMR spectra of ruthenium complex **11**$_{\text{-S}}$.

^{1}H-NMR (400 MHz, CD_2Cl_2)



^{13}C-NMR (150 MHz, CD_2Cl_2)

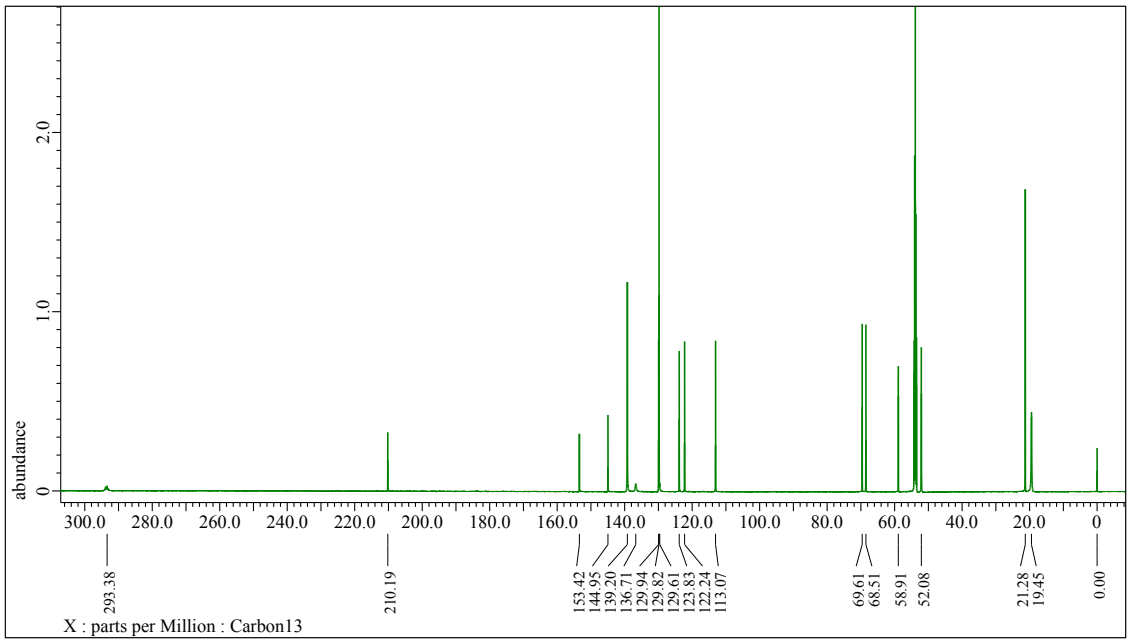
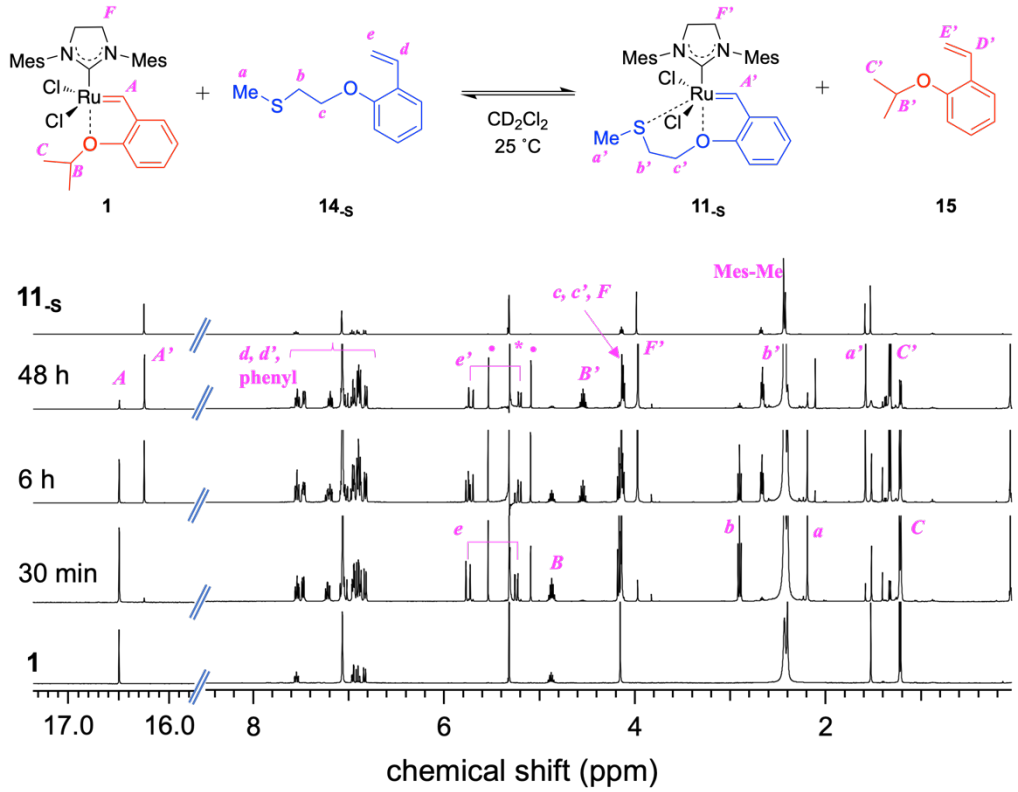


Fig. S2 NMR spectra of ruthenium complex **11**$_{\text{-O}}$.

(a)



(b)

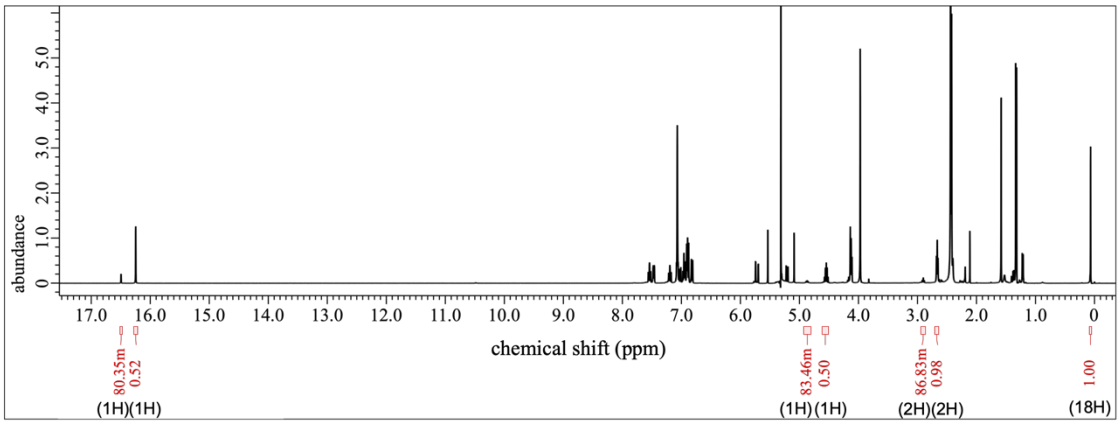
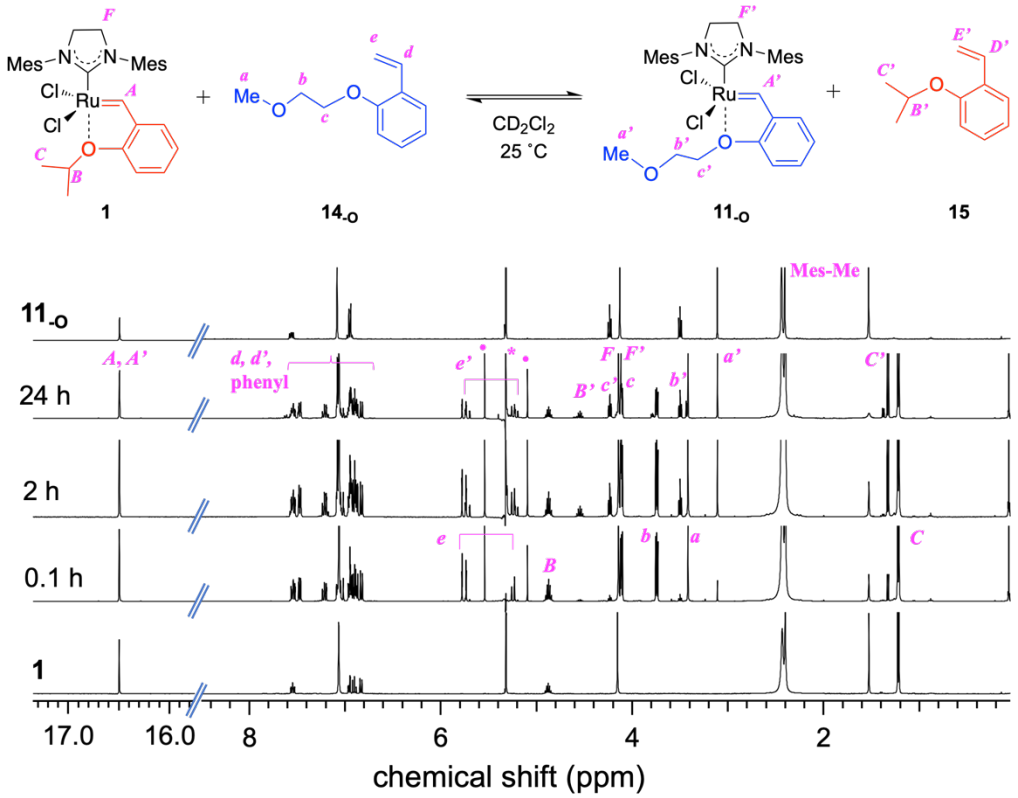


Fig. S3 ^{1}H-NMR spectral change during the ligand exchange between **1** and ligand **14**$_{\text{-S}}$ in CD_2Cl_2 at 25 ˚C; (a) NMR spectral change; (b) The quantification of reaction compoments at 24 h using hexamethyldisiloxane (HMDSO) as an internal standard. The measurements were carried out with presaturation technique for the undeuterated protons in solvent (peak with asterisk(*)). The peaks with a dot (•) are due to spinning side band. Chemical shifts were referenced to the peak of HMDSO (δ_H: 0.066 ppm).

(a)



(b)

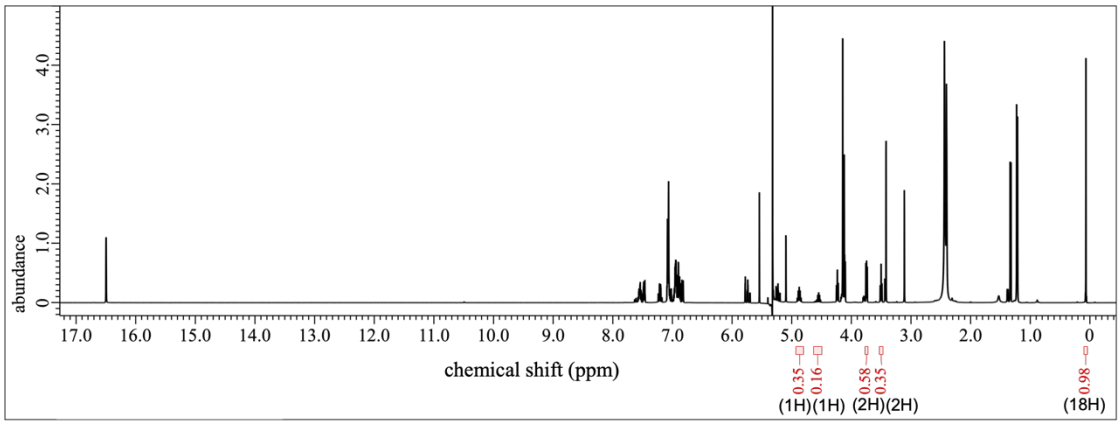


Fig. S4 ^{1}H-NMR spectral change during the ligand exchange between **1** and ligand **14-O** in CD_2Cl_2 at 25 ˚C; (a) NMR spectral change; (b) The quantification of reaction compoments was conducted using hexamethyldisiloxane (HMDSO) as an internal standard. The measurements were carried out with presaturation technique for the undeuterated protons in solvent (peak with asterisk(*)). The peaks with a dot (•) are due to spinning side band. Chemical shifts were referenced to the peak of HMDSO (δ_H: 0.066 ppm).

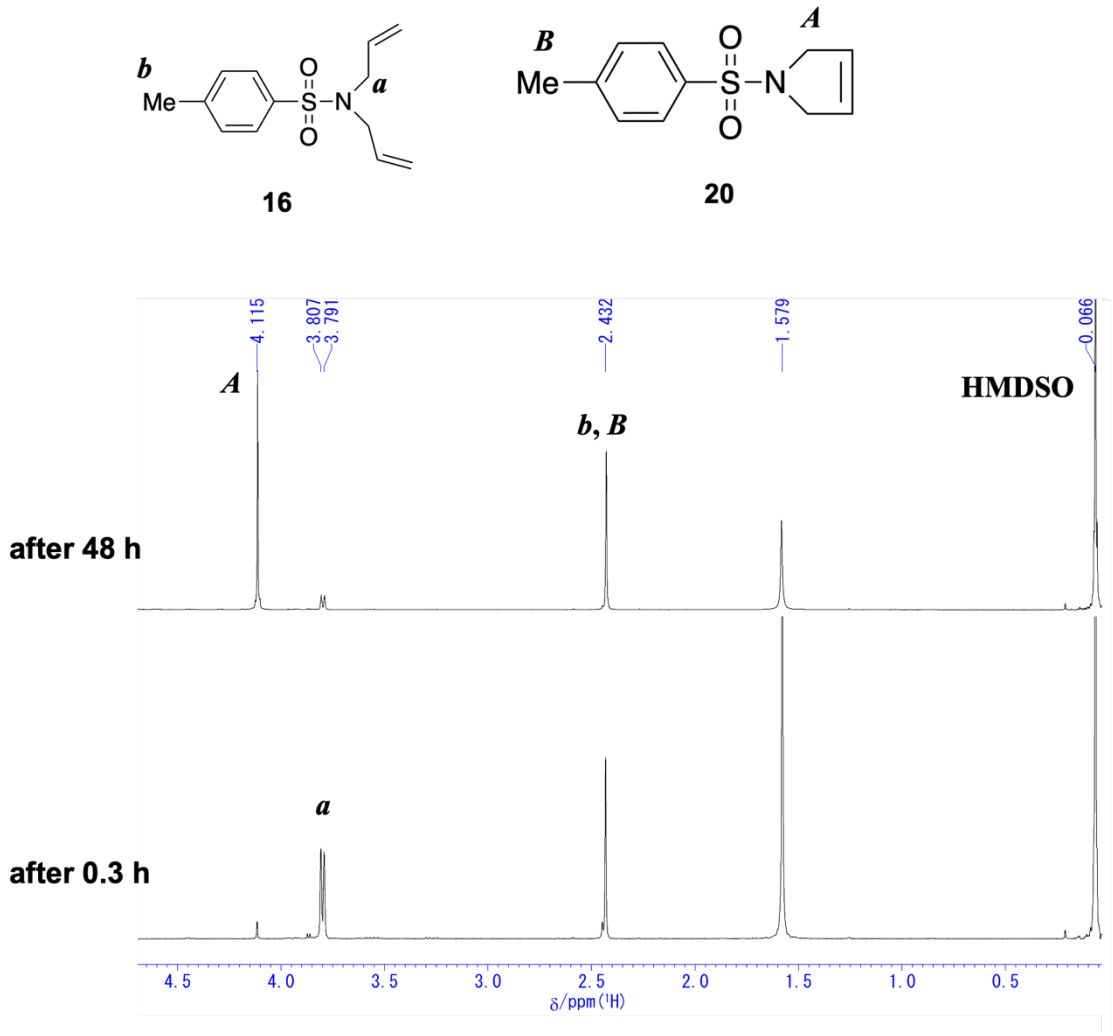


Fig. S5 ^{1}H-NMR spectral change in the **11**$_{-s}$-catalyzed RCM reaction of TDA (**16**) in CH_2Cl_2 at 25 ˚C in the presence of HMDSO (internal standard). At defined time, a sampled solution (100 μL) was diluted with $CDCl_3$ for an NMR measurement (see the details in Experimental section). The quantification of reaction compoments was carried out using hexamethyldisiloxane (HMDSO) as an internal standard. The NMR measurements were carried out with presaturation technique for the undeuterated protons of solvent. [**16**] = 42 mM, [Ru complex] = 0.042 mM (0.1 mol% catalyst load).

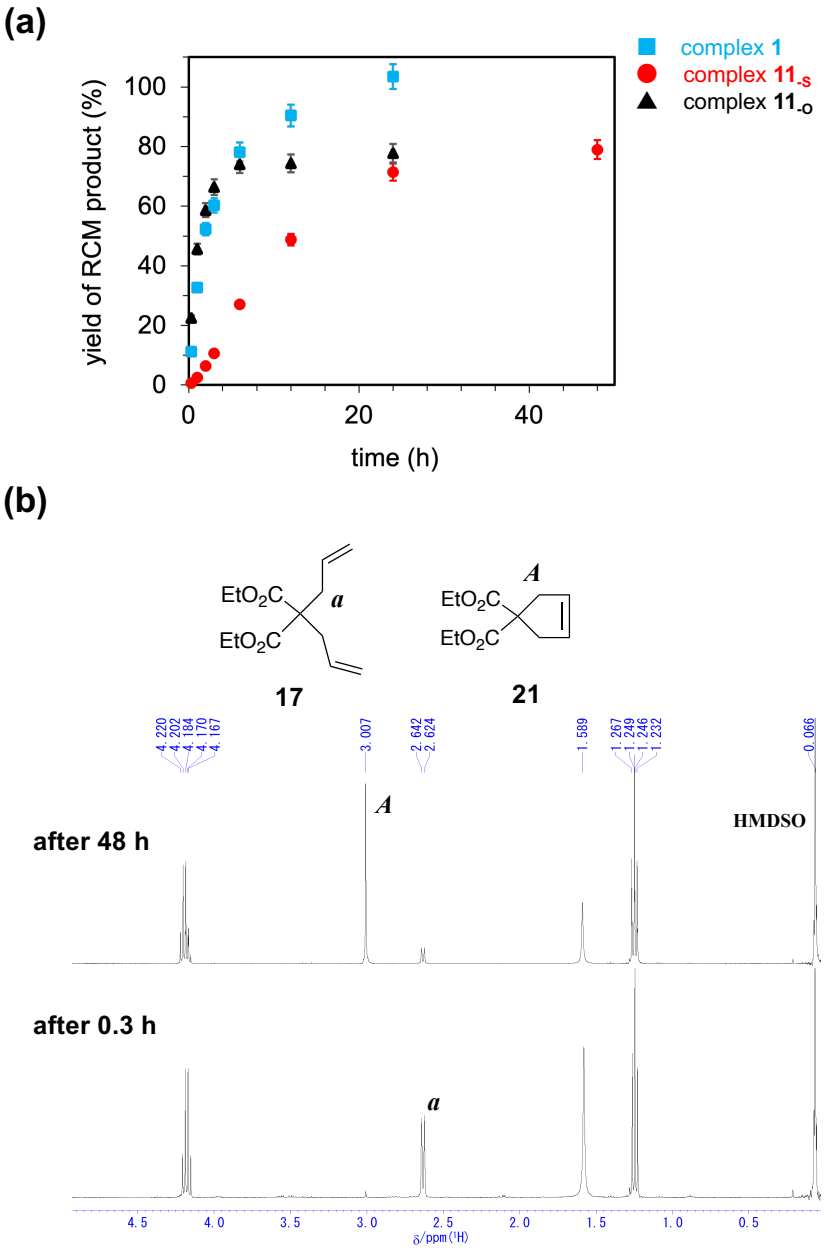


Fig. S6 Time-courses and ^{1}H-NMR spectral change of RCM reactions of diallyl malonate ester (**17**) in CH_2Cl_2 at 25 ˚C in the presence of HMDSO (internal standard); (a) time-courses of RCM product **21**; (b) ^{1}H-NMR spectral change during the **11**$_S$-catalyzed reaction. At defined time, a sampled solution (100 μL) was diluted with $CDCl_3$ for an NMR measurement (see the details in Experimental section). The quantification of reaction compoments was carried out using hexamethyldisiloxane (HMDSO) as an internal standard. The NMR measurements were carried out with presaturation technique for the undeuterated protons of solvent.The RCM produc was quantified with reference to the peak intensity of HMDSO (δ_H: 0.066 ppm). [**17**] = 42 mM, [Ru complex] = 0.042 mM (0.1 mol% catalyst load).

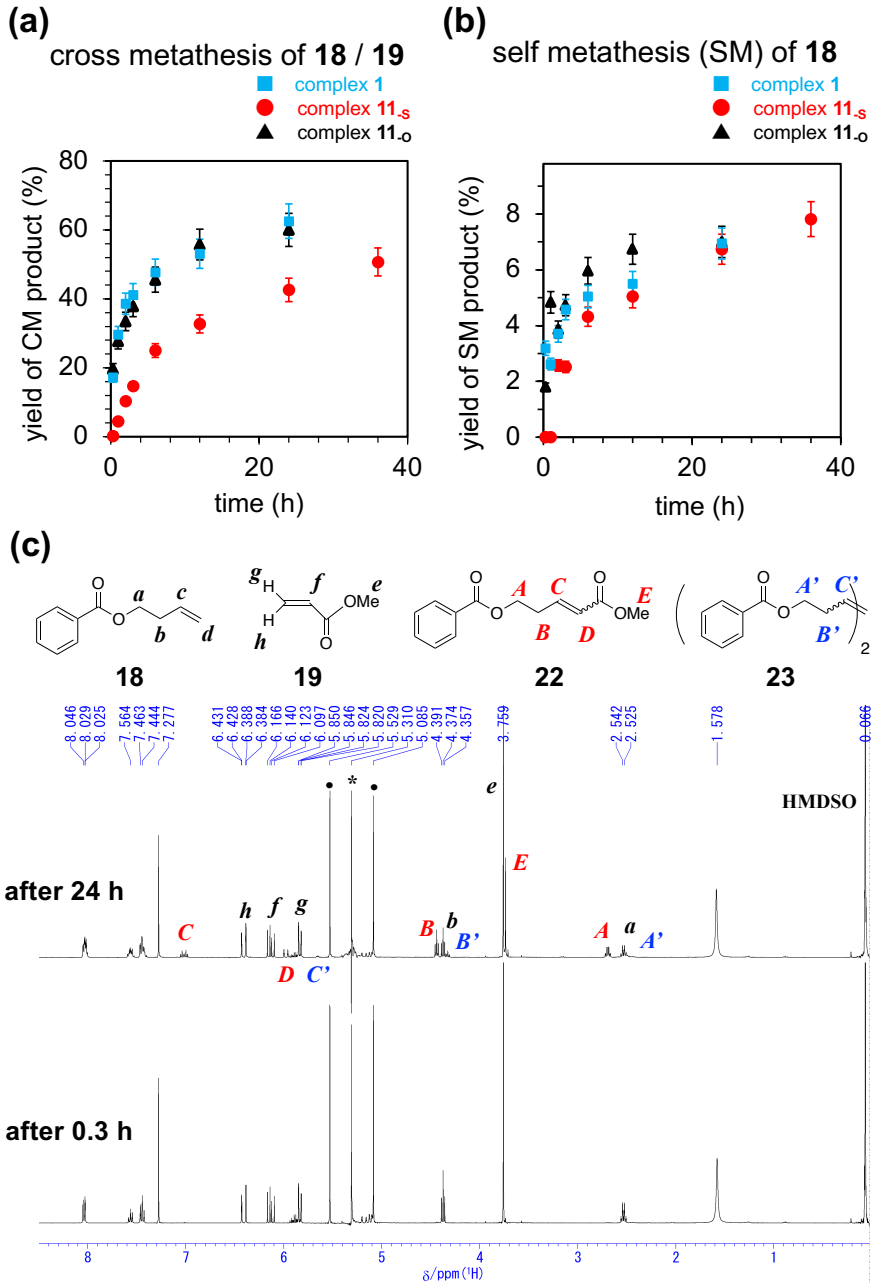
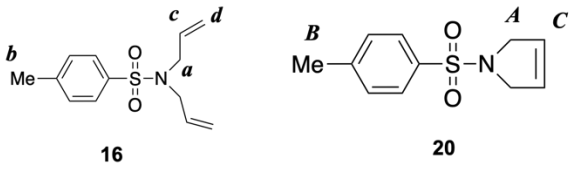


Fig. S7 Time-courses and ^{1}H-NMR spectral change of metathesis reactions of compounds **18** and methyl acrylate (**19**) in CH_2Cl_2 at 25 ˚C in the presence of HMDSO (internal standard); (a) time-courses of cross metathesis product **22**; (b) time-courses of self metathesis product **23**; (c) ^{1}H-NMR spectral change during the **11**$_{-S}$-catalyzed reaction. At defined time, a sampled solution (100 μL) was diluted with $CDCl_3$ for an NMR measurement (see the details in Experimental section). The quantification of reaction compoments was carried out using hexamethyldisiloxane (HMDSO) as an internal standard. The NMR measurements were carried out with presaturation technique for the undeuterated protons in solvent.The RCM product was quantified with reference to the peak intensity of HMDSO (δ_H: 0.066 ppm). [**18**] = 42 mM, [**19**] = 84 mM, [Ru complex] = 0.042 mM (0.1 mol% catalyst load).



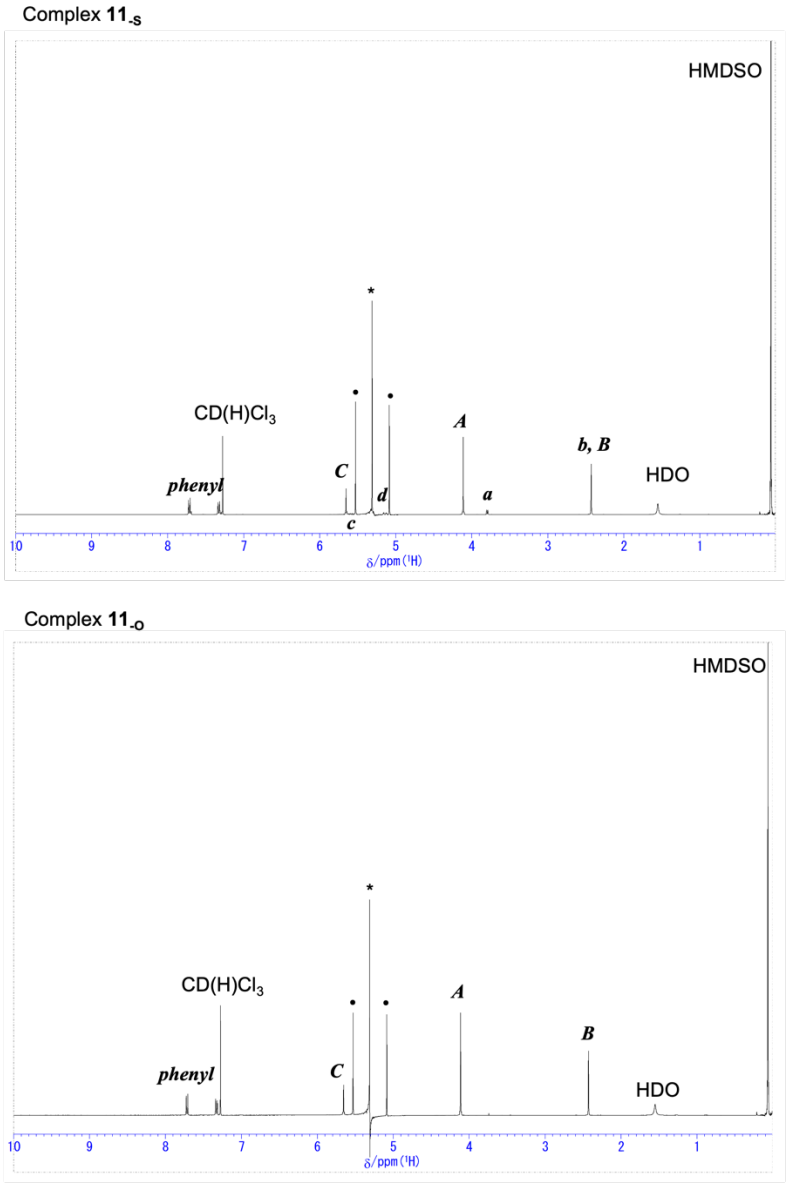


Fig. S8 ^{1}H-NMR spectra measured at the end of the RCM reaction of TDA (**16**) in CH_2Cl_2 at 25 ˚C in the presence of 1 mol% catalyst and HMDSO (internal standard). A sampled solution (100 μL) was diluted with $CDCl_3$ for an NMR measurement (see the details in Experimental section). The quantification of reaction compoments was carried out using hexamethyldisiloxane (HMDSO) as an internal standard. The measurements were carried out with presaturation technique for the undeuterated protons in solvent (peak with asterisk(*)). The peaks with a dot (•) are due to spinning side band. [**16**] = 42 mM, [Ru complex] = 0.42 mM (1 mol% catalyst load).

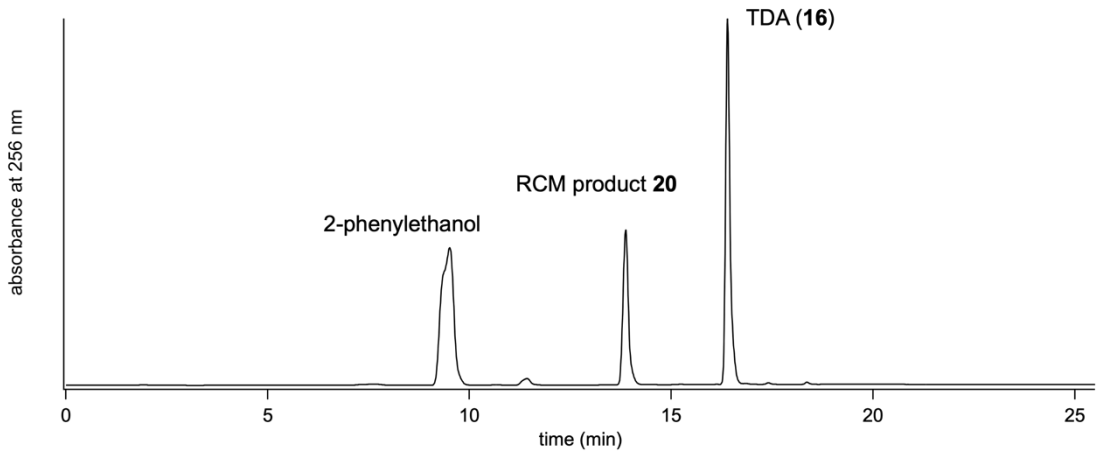


Fig. S9 HPLC chromatogram of a solution sampled from the reaction mixture (40 min) of the **10**$_S$-catalyzed RCM reaction of TDA (**15**) in 1,2-dichloroethane (1,2-DCE) that contains methanol (1%(v/v)) at 40 ˚C. 2-Phenylethanol was used as an internal standard.

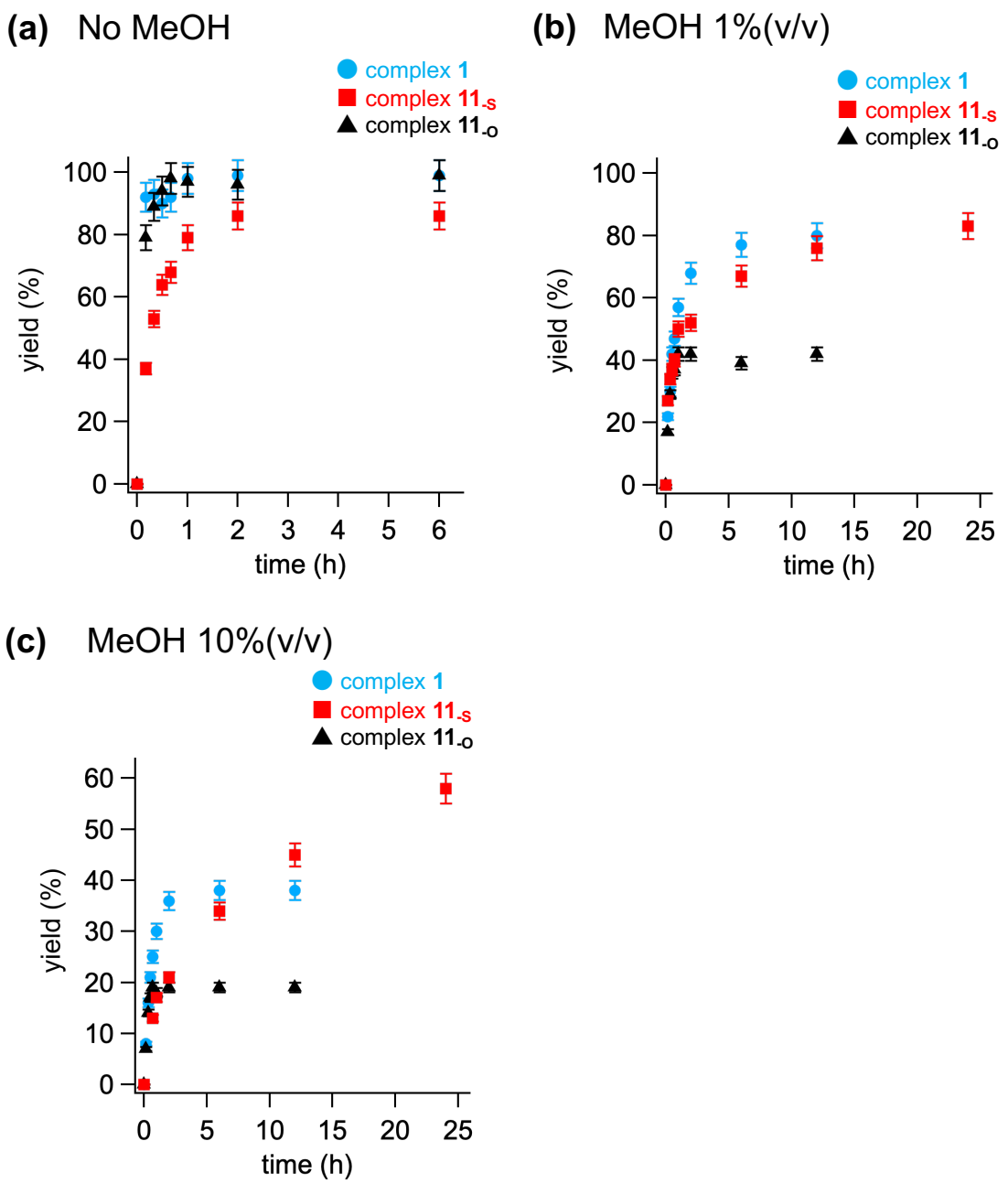


Fig. S10 Effect of MeOH on the RCM reactions of TDA (**16**) in 1,2-dichloroethane (1,2-DCE) at 40 ˚C; (a) without MeOH; (b) with MeOH (1%(v/v)); (c) with MeOH (10%(v/v)). [TDA (**16**)]) = 42 mM; [Ru complex] = 0.042 mM (0.1 mol%). 2-Phenylethanol was used as an internal standard.

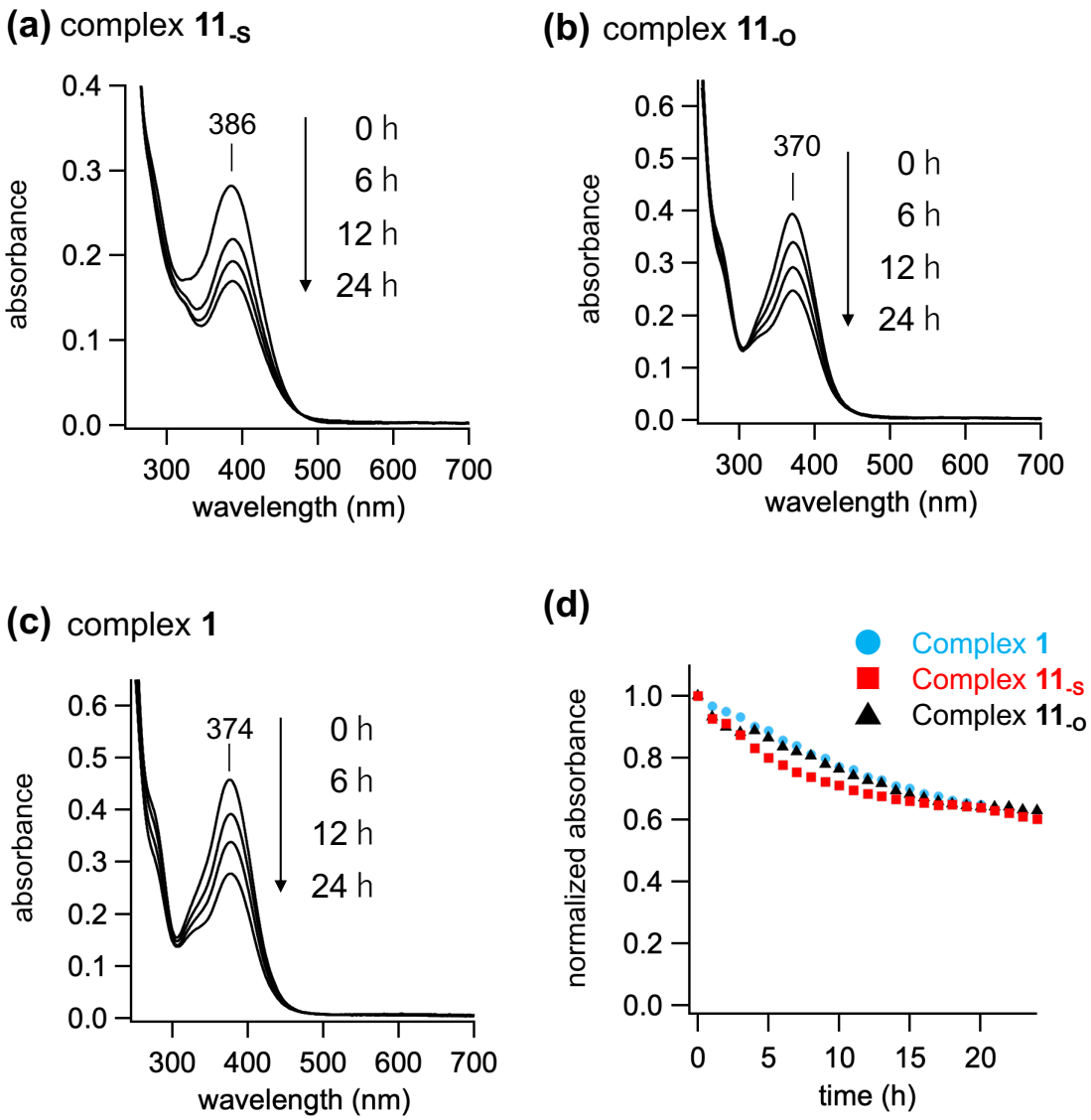
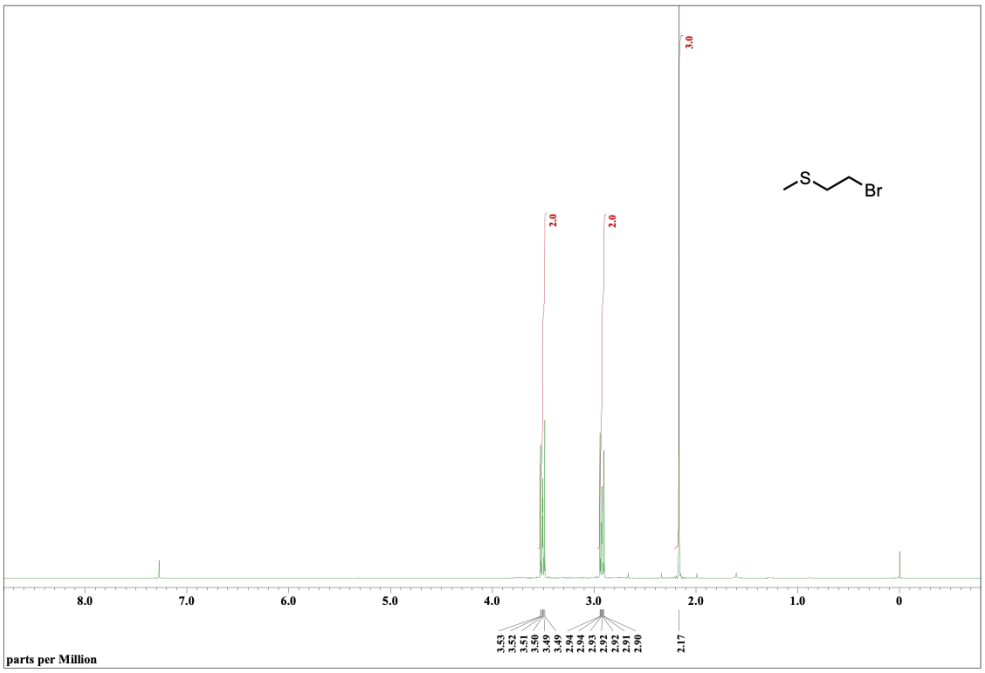


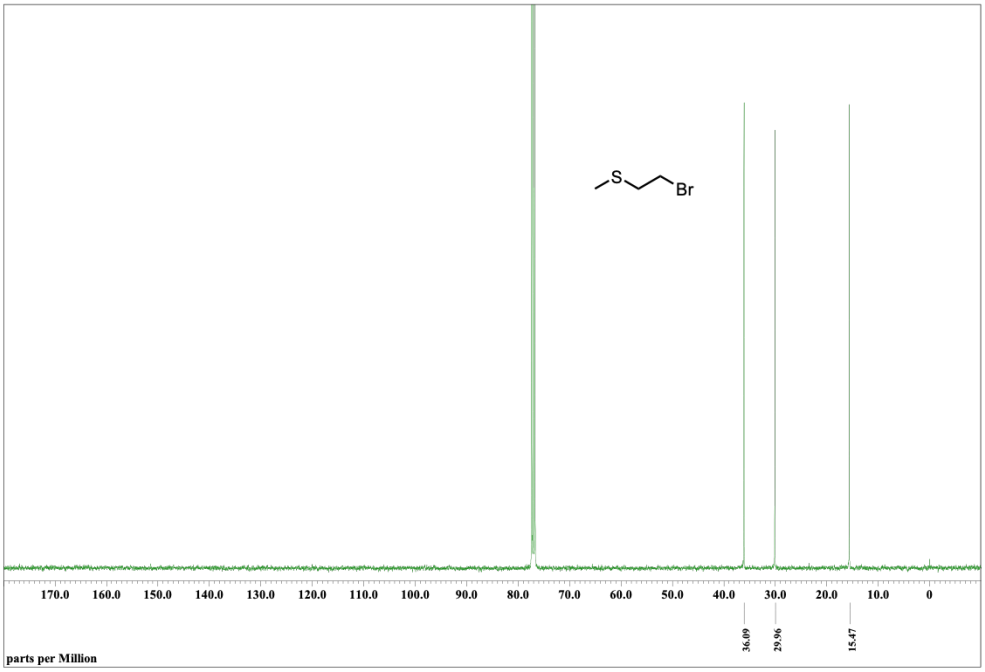
Fig. S11 UV-vis spectral changes of ruthenim complexes without an olefinic substrate and in the presence of MeOH (10%(v/v)) in 1,2-dichloroethane (1,2-DCE) at 40 ˚C; (a) complex **11**$_{-S}$; (b) with complex **11**$_{-O}$; (c) complex **1**; (d) time-courses of absorbances at maximum wavelength of MLCT band. [complex] = 50 μM.

NMR spectra of compound **12**$_{-S}$:

^{1}H-NMR (400 MHz, $CDCl_3$)

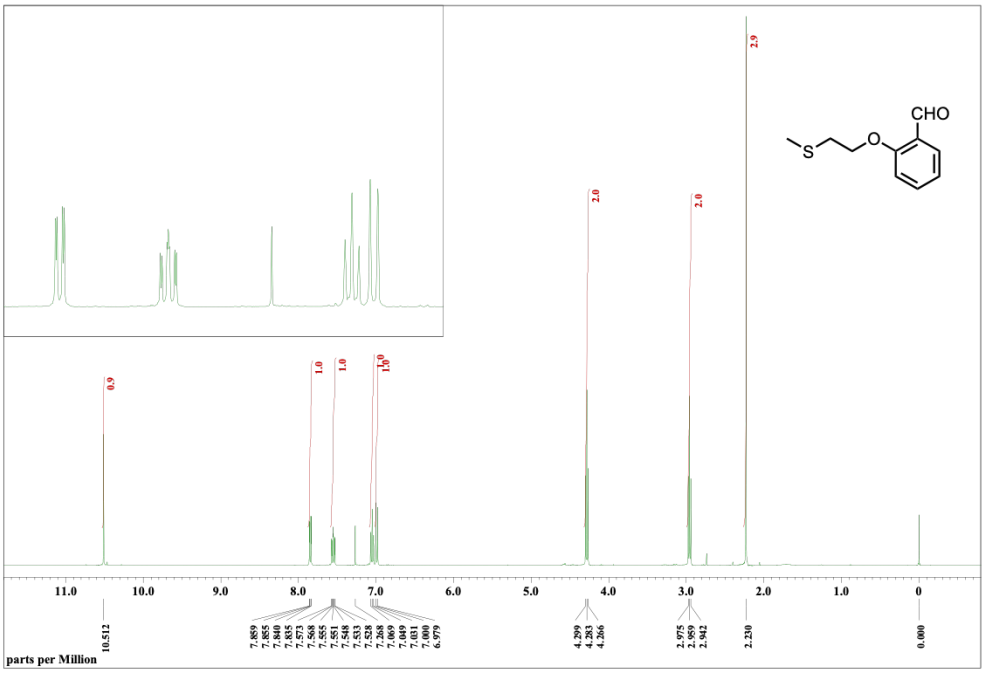


^{13}C-NMR (100 MHz, $CDCl_3$)

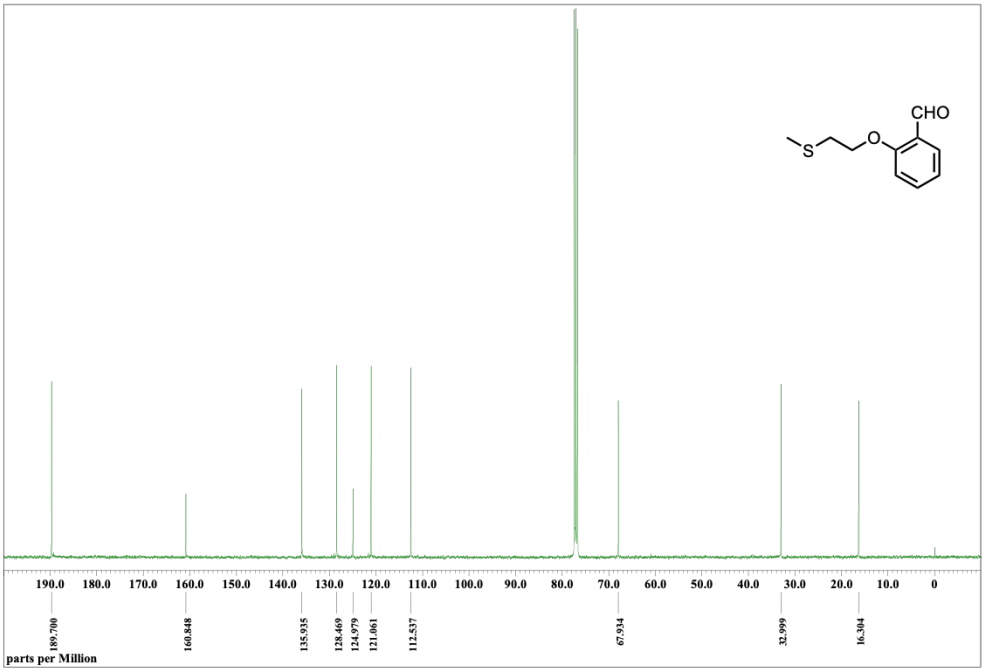


NMR spectra of compound **13**$_S$:

^{1}H-NMR (400 MHz, $CDCl_3$)

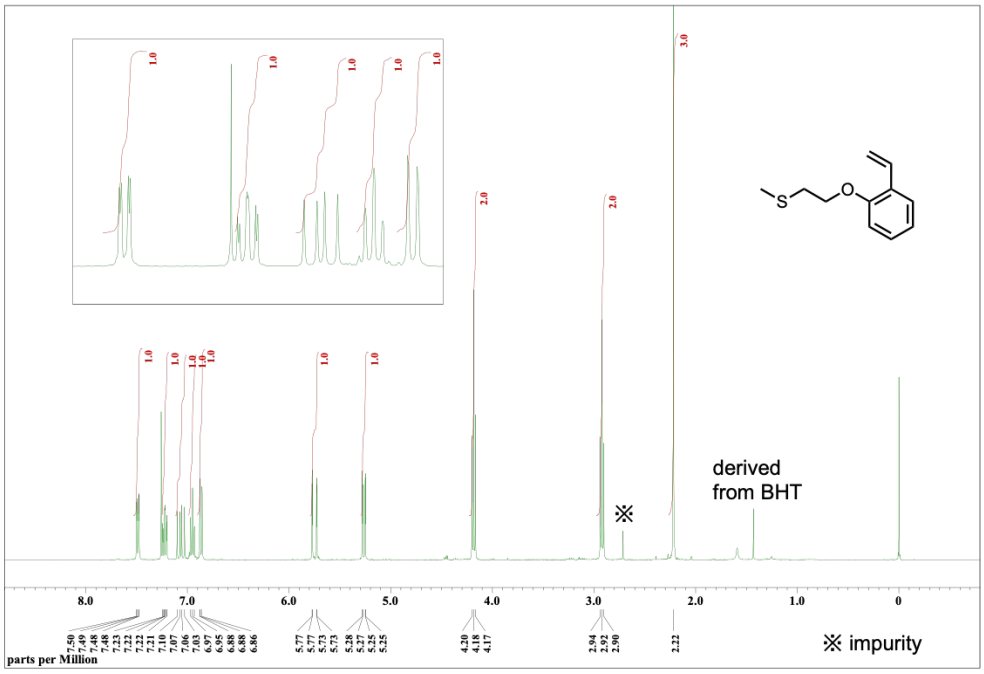


^{13}C-NMR (100 MHz, $CDCl_3$)

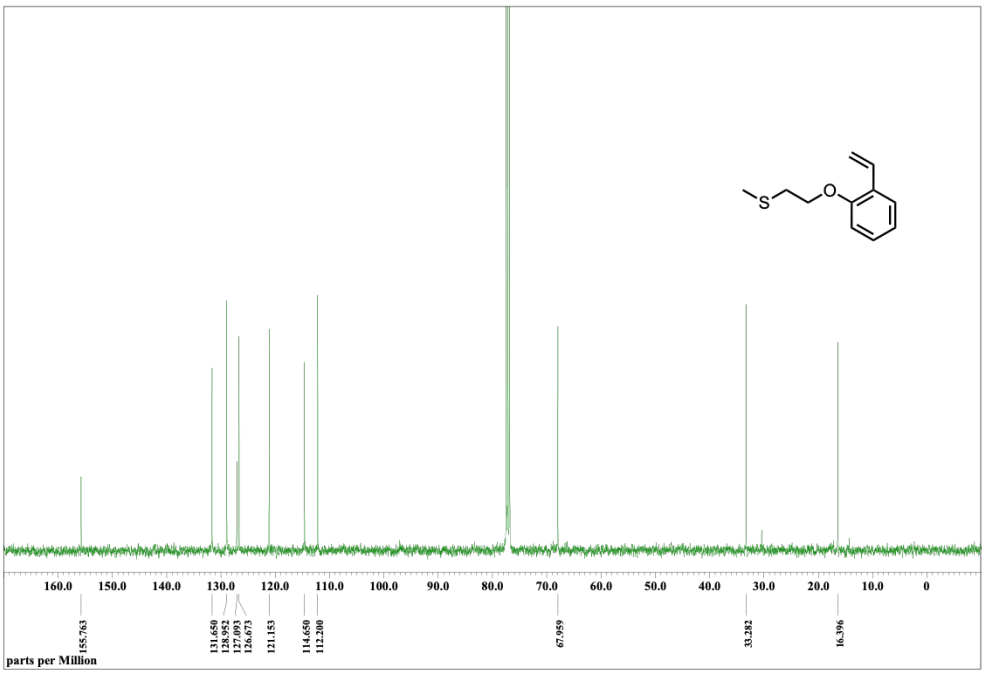


NMR spectra of compound **14**$_{-S}$:

^{1}H-NMR (400 MHz, $CDCl_3$)

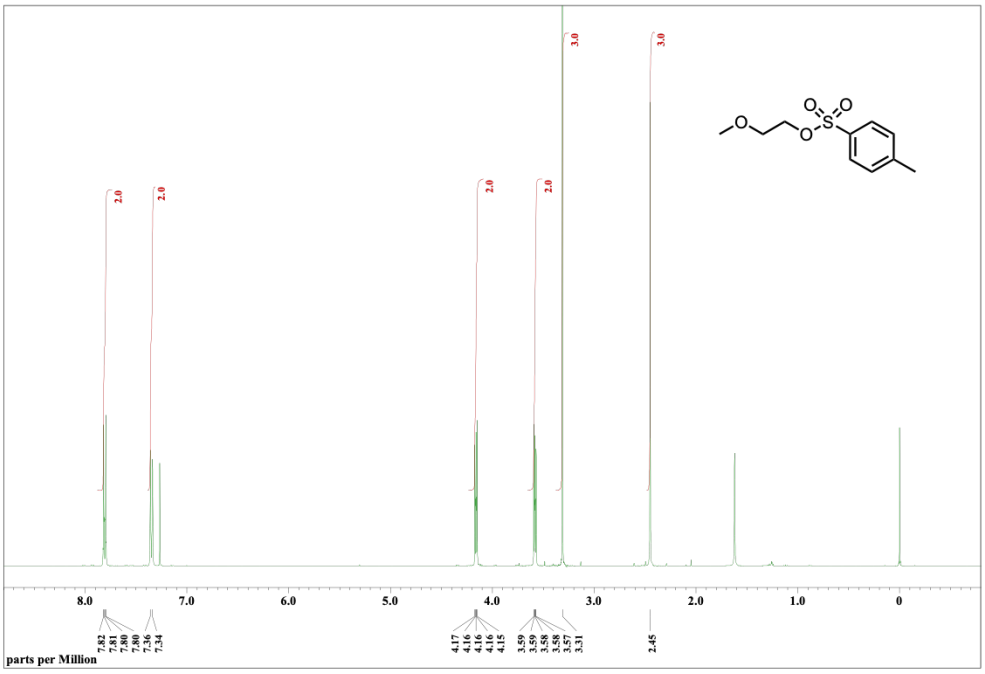


^{13}C-NMR (100 MHz, $CDCl_3$)

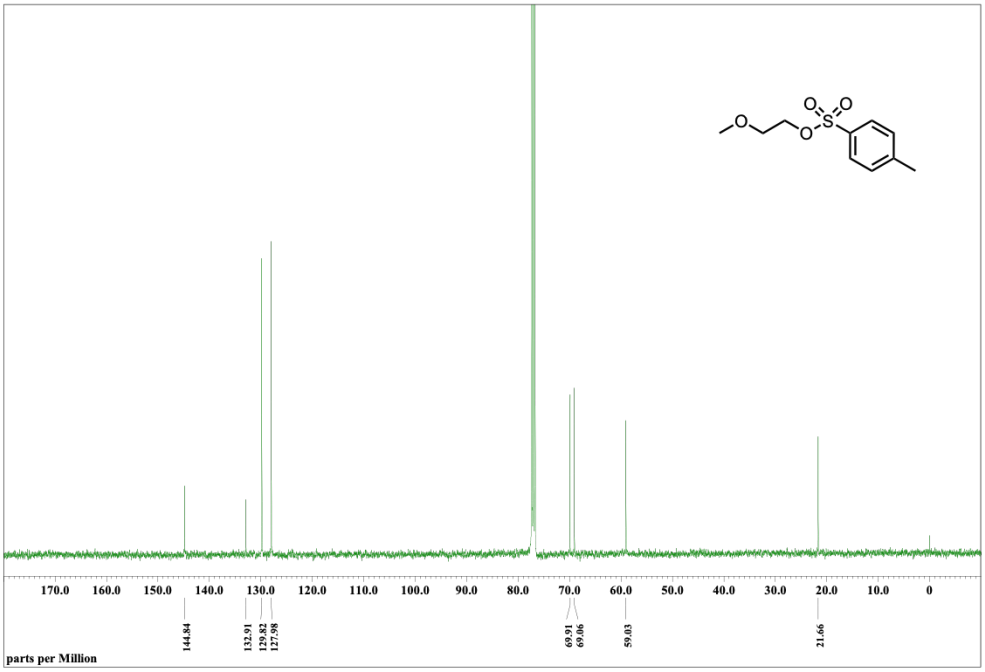


NMR spectra of compound **12**$_{\text{-O}}$:

^{1}H-NMR (400 MHz, $CDCl_3$)

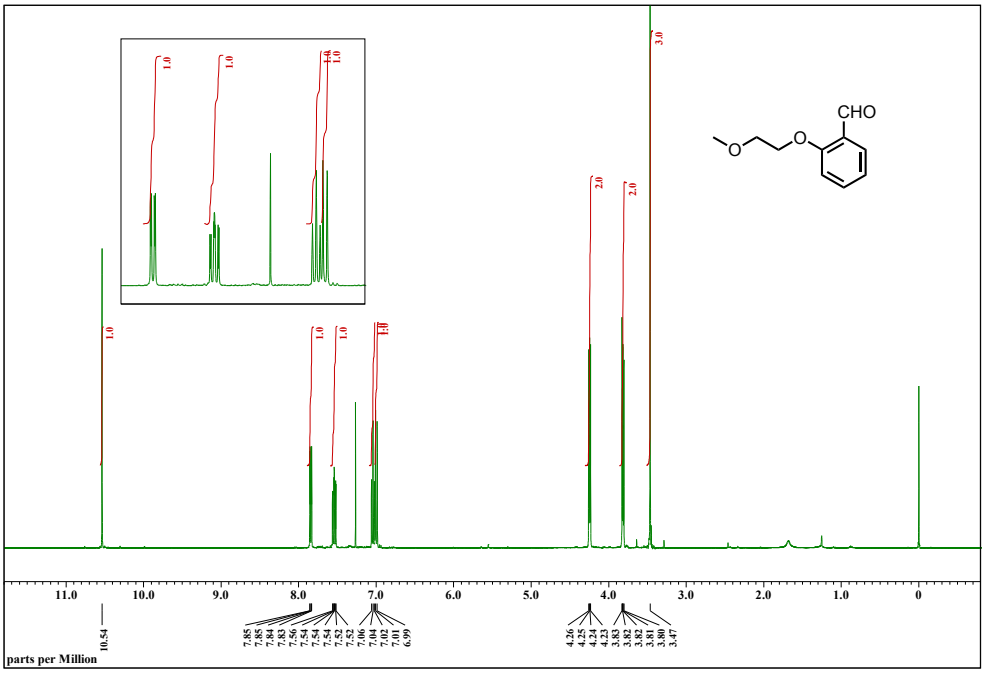


^{13}C-NMR (100 MHz, $CDCl_3$)

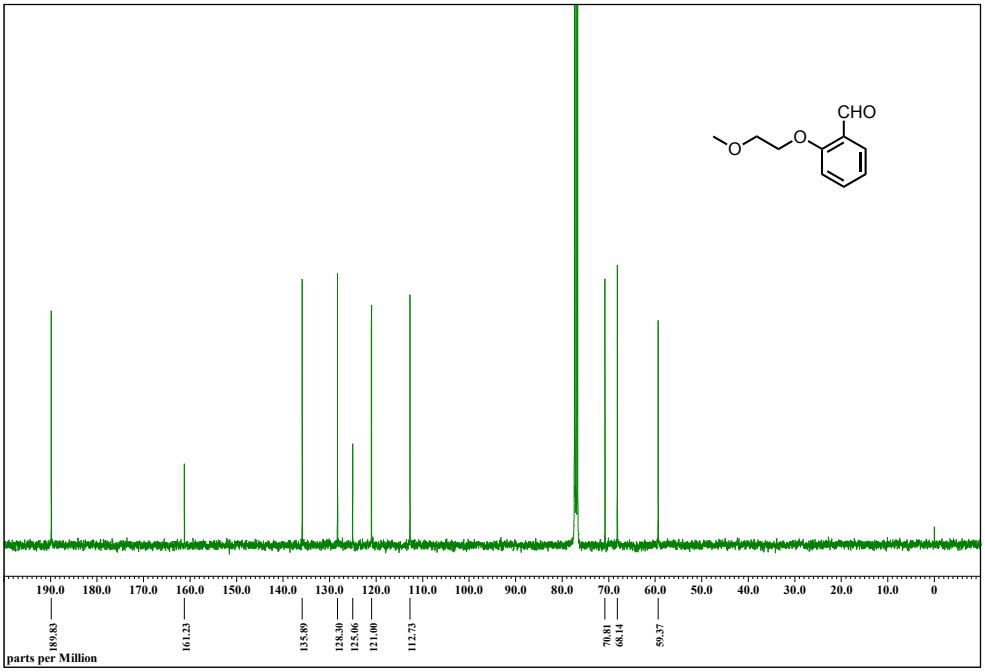


NMR spectra of compound **13**$_{\mathbf{-O}}$:

^{1}H-NMR (400 MHz, $CDCl_3$)

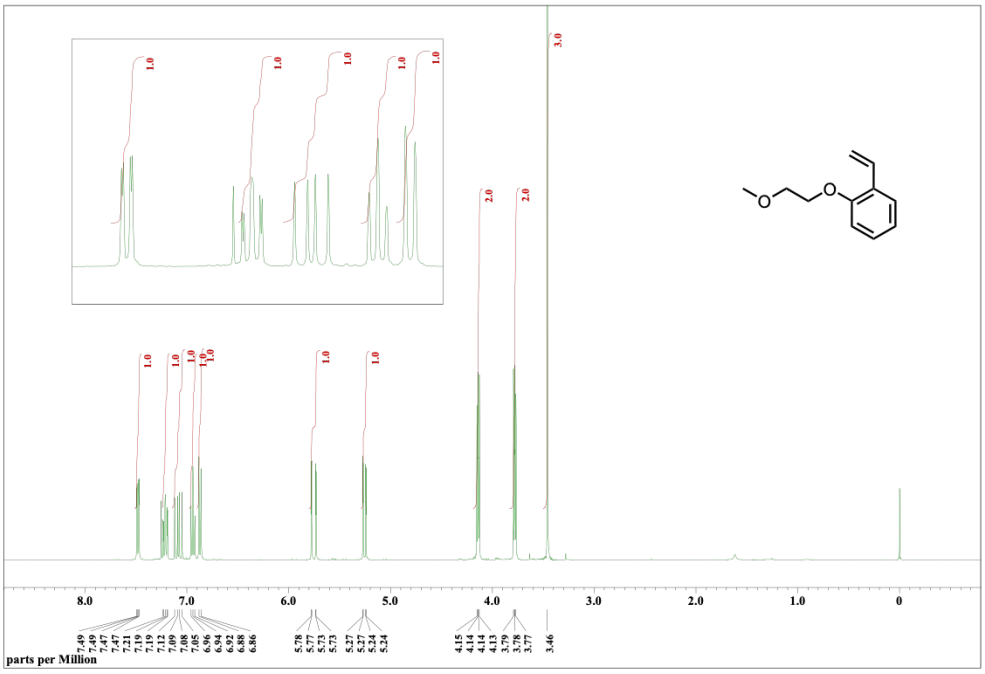


^{13}C-NMR (100 MHz, $CDCl_3$)



NMR spectra of compound **14**$_{\text{-O}}$:

^{1}H-NMR (400 MHz, $CDCl_3$)



^{13}C-NMR (100 MHz, $CDCl_3$)