Rhodium-Catalyzed Cross-Coupling of Vinylarenes with Arylaluminum Reagents in the Presence of Ketones

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SHORT COMMUNICATION

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Rhodium-Catalyzed Cross Coupling of Vinylarenes with Arylaluminum Reagents Promoted by the Addition of Ketone

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Keywords: Rhodium / Organoaluminum / Addition-elimination reaction/ Cross coupling / Stilbene

Rhodium-catalyzed addition-elimination reaction of arylaluminum reagents with vinylarenes is achieved to obtain stilbene derivatives. The reaction of diethyl(phenyl)aluminum with styrene in the presence of chloro(1,5-cyclooctadiene)rhodium(I) dimer [RhCl(cod)]2, and diisopropylketone (2,4-dimethyl-3-pentanone) as an additive occurs to give (*E*)-stilbene in quantitative yield The use of other arylaluminum reagents affords β-arylated products in good to excellent yields. This reaction is found to be promoted by ketone as an additive, which is reduced to give the corresponding alcohol to be confirmed by ^{1}H NMR analysis of crude reaction mixture.

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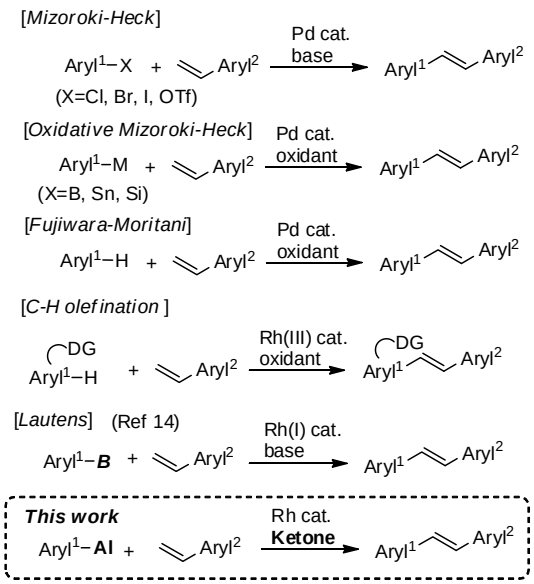
Introduction

Organoaluminum reagents have played a significant role in organic chemistry as Lewis acid, nucleophile or co-catalyst for olefin polymerization.[1] In particular, C-C bond formation reactions with organoaluminum reagents such as 1,2-addition to carbonyl compounds,[2] conjugate addition to enones[3] and cross coupling with organic halides[4] have been widely used in organic synthesis as functional-group-tolerant nucleophiles compared with organomagnesium or organolithium. Development of novel reactions with organoaluminum is thereby an important issue in organic synthesis. Although a number of C-C bond formation reactions with organoaluminum have been developed, addition-elimination type reactions with olefines have not been reported so far to the best of our knowledge. Accordingly, we envisaged that it is intriguing to develop additon-elimination-type reaction of arylaluminum with vinylarene to affford stilbene derivatives, which have attracted much attention as π-conjugated organic materials. Synthesis of stilbene derivatives using addition-elimination reaction can be categoryzed as summarized in Scheme 1. The palladium-catalyzed reaction of aryl halides with vinylarene is well-known as Mizoroki-Heck reaction,[5], [6] and has been widely used to synthesize biologically active molecules[7] and various π-conjugated materials[8] bearing an olefinic moiety. The reactions of main group organometallic species (boron, silicon or tin) with vinylic compounds have also been shown to proceed with palladium catalyst in the presence of an oxidant to afford stilbene, which are recognized as oxidative Mizoroki-Heck-type reactions.[9] Oxidative C-H coupling of arenes with vinylarenes is also shown to take place with palladium(II) catalyst (Fujiwara-Moritani reaction).[10] And the related addition-elimination reaction has recently been reported with Cp*Rh(III) complexes at the C-H bond although the reaction is required to possess a neighboring directing group.[11] On the other hand, cross-coupling reaction of several main group arylmetal species bearing no directing group with olefinic compounds catalyzed by rhodium(I) complex has also attracted much attention.[12] We have shown that several main-group reagents such as boron, silicon, and tin react with α,β-unsaturated carbonyl compounds,[13] however, few reaction has been shown to proceed with a simple olefin. The only successful example using rhodium(I) for the reaction of styrene was shown by Lautens and coworkers with phenylboronic acid.[14] Herein, we report that arylaluminum reagent effectively reacts with vinylarenes in the presence of a rhodium(I) catalyst to undergo Mizoroki-Heck-type addition-elimination reaction, where ketone as an additive plays a key role for the catalytic reaction.



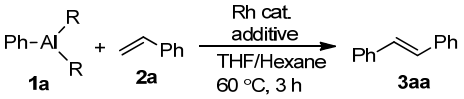
Scheme 1. Transition-metal-catalyzed cross coupling of arylhalide or arylmetal species with vinylarenes

Results and Discussion

We first investigated rhodium-catalyzed reaction of diethyl(phenyl)aluminum (**1a**) with styrene (**2a**). Preparation of **1a** was carried out with diethylaluminum chloride and

phenylmagnesium bromide.[15] As summarized in Table 1, the reaction of **1a** with **2a** in the presence of 2.5 mol % of chloro(1,5-cyclooctadiene)rhodium(I) dimer $[RhCl(cod)]_2$ at 60 ºC for 3 h took place to afford (*E*)-stilbene (**3aa**) in 43% yield. Longer reaction period for 24 h did not improve the yield (entry 2). Increased loading of $[RhCl(cod)]_2$ (5.0 mol%) slightly improved the yield of **3aa** to 61% (entry 3). By contrast, when 2.0 equivalent of diiropropylketone was employed as an additive, the reaction proceeded smoothly to give **3aa** in quantitative yield (entry 4). The reaction of **1a** with **2a** by lowering the reaction temperature to room temerature also proceeded, the yield was found to be slightly inferior (56%, entry 5). The use of toluene as a slovent also gave **3aa** in a quantitative yield at 60 ºC for 3 h (entry 6). Use of acetone or pinacolone (3,3-dimethyl-2-butanone) as an additive instead of diisopropylketone also underwent the reaction (entry 7, 8). The reaction with hydroxy(1,5-cyclooctadiene)rhodium(I) dimer $[Rh(OH)(cod)]_2$ was found to give **3aa** in an excellent yield (93%). Rhodium methoxide complex $[Rh(OMe)(cod)]_2$ also served as an effective catalyst to afford **3aa** in 62% yield whereas the reaction with norbornadiene rhodium(I) chloride dimer $[RhCl(nbd)]_2$ and Wilkinson's catalyst $RhCl(PPh_3)_3$ was found to be ineffective. When $[RhCp^*Cl_2]_2$ was used as a catalyst, the reaction did not occur at all (entry 13). The reaction of dimethyl(phenyl)aluminum with styrene in the presence of $[RhCl(cod)]_2$ took place to give **3aa** in quantitative yield (entry 14). Although the reaction of phenylaluminum dichloride occurred, the yield of **3aa** was found to be lower (38%, entry 15). In contrast with our previous reports, in which only hydroxy and methoxy rhodium complexes have been effective for the Mizoroki-Heck-type addition-elimination of α,β-unsaturated carbonyl compounds whereas chlororhodium showed little efficiency, it should be pointed out that the use of chlororhodium effectively induced the catalytic reaction with arylaluminum.

Table 1. The reaction of phenylaluminum reagent with stryrene catalyzed by a rhodium complex[a]



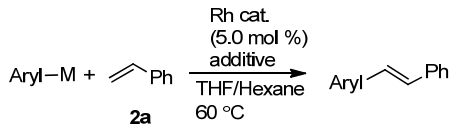
entry	R	catalyst (mol %)	additive	yield/%[b]
1	Et	$[RhCl(cod)]_2$ (2.5)	none	43
2[c]		$[RhCl(cod)]_2$ (2.5)	none	45
3		$[RhCl(cod)]_2$ (5.0)	none	61
4		$[RhCl(cod)]_2$ (2.5)	diisopropylketone	>99
5[d]		$[RhCl(cod)]_2$ (5.0)	diisopropylketone	56
6[e]		$[RhCl(cod)]_2$ (5.0)	diisopropylketone	>99
7		$[RhCl(cod)]_2$ (2.5)	acetone	72
8		$[RhCl(cod)]_2$ (2.5)	pinacolone	>99
9		$[Rh(OH)(cod)]_2$ (2.5)	diisopropylketone	93
10		$[Rh(OMe)(cod)]_2$ (2.5)	diisopropylketone	62
11		$[RhCl(nbd)]_2$ (5.0)	diisopropylketone	3[f]
12		$RhCl(PPh_3)_3$ (5.0)	diisopropylketone	3[f]
13		$[RhCp^*Cl_2]_2$ (2.5)	diisopropylketone	0
14	Me	$[RhCl(cod)]_2$ (2.5)	diisopropylketone	>99
15[g]	Cl	$[RhCl(cod)]_2$ (2.5)	diisopropylketone	38

[a] Unless otherwise noted, the reaction was performed with styrene (0.5 mmol), arylaluminum (1.0 mmol), and additive (1.0 mmol) in 1.0 mL of THF and 1.0 mL of hexane at 60 ºC for 3 h. [b] Isolated yield. [c] The reaction time: 24 h. [d] The reaction was carried out at room temperature. [e] Toluene was used as solvent. [f] The yield was determined by ^{1}H NMR analysis. [g] The reaction time: 20 h.

We next carried out the rhodium-catalyzed reaction of several arylalminum reagents with various vinylarens **2**. The results are summmerized in Scheme 2. The reaction of **1a** with 4-methylstyrene (**2b**) and 4-methoxystyrene (**2c**) at 60 ºC for 3 h proceeded to give β-phenylated products **3ab** and **3ac** in 96% and 95% yields, respectively. The reaction of 4-fluorostyrene (**2d**) also took place to give **3ad** in good yield (74%). Although the reaction of a more bulky styrene derivative, 1-vinylnaphthalene (**2e**), occurred, the yield of **3ae** was decreased to 19%. The reaction of electron deficient styrene, 4-trifluoromehtylstyrene (**2f**), with **1a** proceeded to afford **3af** in 30% yield. The reaction of various styrene derivatives with other arylaluminum reagents, 4-methylphenyl, 4-methoxyphenyl, 4-fluorophenyl, 3,5-dimethylphenyl, 2-methoxyphenyl, 1-naphthyl, and 4-dimethylaminophenyl aluminum species occurred to afford β-arylated products in good to excelent yields. The reaction of diethyl(2-methoxyphenyl)aluminum resulted in poor yield, which might be poisoned by a coordinating methoxy substituent, while the related non-coordinating methyl substituent to give **3ah** and distal methoxy and *N*,*N*-dimehtylamino groups (leading to **3ai** and **3bc**) did not decrease the yield.

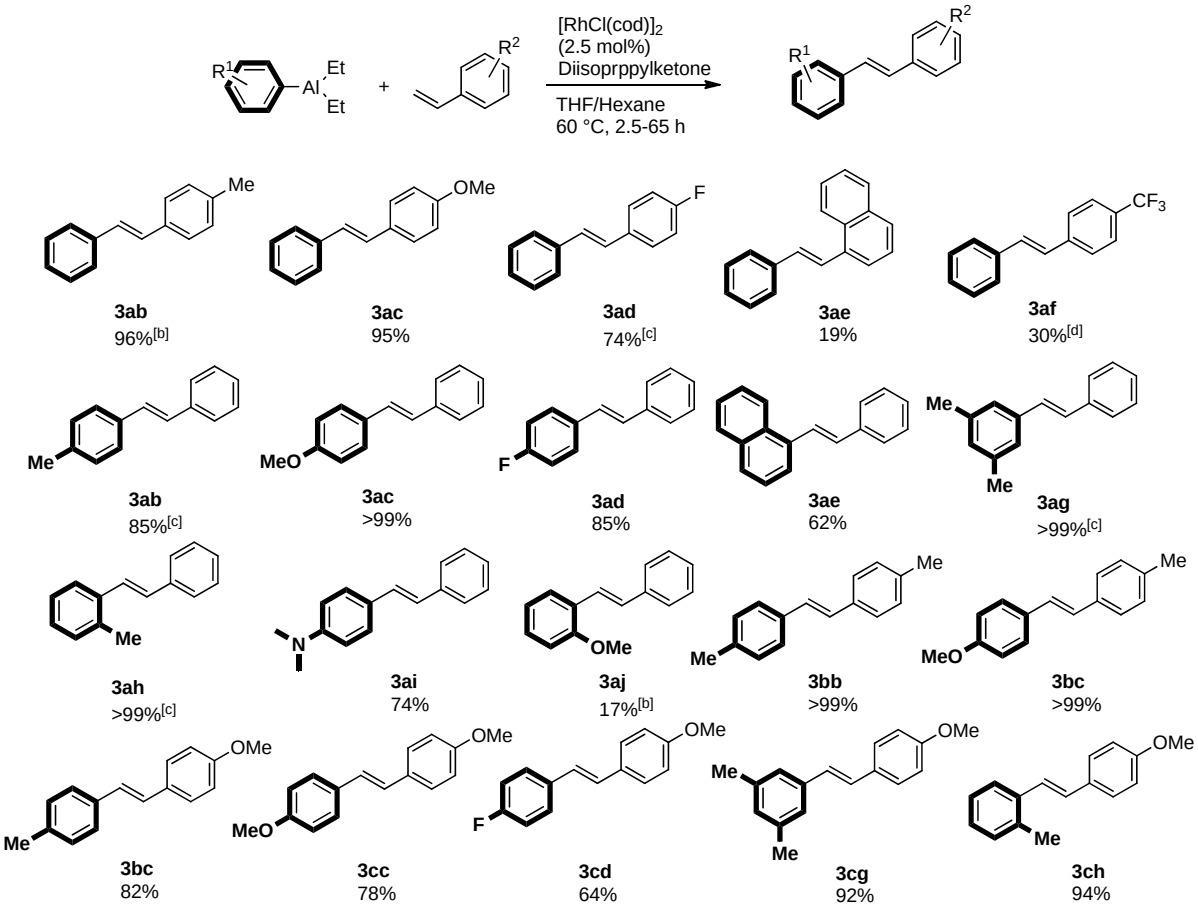
We then performed the reaction of other aryl metal species with styrene (**2a**). These results are summerized in Table 2. The reaction of aryllithium species with styrene in the presense of rhodium catalyst did not afford the desierd product **3ba** (entry 1). The reaction of aryl magnesium bromide with **2a** gave **3ba** in only 9% yield. In contrast with the reaction of arylaluminum, the use of diisopropylketone as an additive for Grignard reagent was found to be ineffective (entry 3). The reaction of arylzinc chloride, which was obtained from aryl Grignard reagent and $ZnCl_2$·(tmeda) complex (tmeda=*N*,*N*,*N'*,*N'*-tetramethylethylenediamine) with **2a** took place, however, the yield was inferior to afford **3ba** in 42% yield (entry 4). Addition of ketone to the reaction of an arylzinc reagent with styrene gave **3ba** in slightly higher yield (entry 5, 59%). The use of triarylaluminum as a nucleophile also proceeded in a lower yield (42%) to afford **3ba** (entry 6). The reaction of aluminum ate complex, Ar-Al(^{i}Bu)$_3$·MgBr, which was prepared from aryl Grignard reagent and triisobutylaluminum, proceeded to give 48% yield (entry 7). Phenyl boronic acid and phenyltrimethoxy silane also reacted with styrene in toluene at 100 ºC to afford corresponding stilbene in 35% and 41% yields, respectively (entry 8, 9). These results suggest that the reaction with stronger nucleophile such as magnesium and lithium induces direct nucleophilic attack to ketone, whereas insufficient reduction may result in inferior yields with zinc, boron, and silane reagents.

Table 2. The reaction of various aryl metal species with styrene.[a]



entry	Aryl-M	additive	time/h	yield/%[b]
1[c], [d]	*p*-Tol-Li	none	4	0
2	*p*-Tol-MgBr	none	3	9[e]
3	*p*-Tol-MgBr	diisopropylketone	3	11[e]
4	*p*-Tol-ZnCl·(tmeda)	none	17	49
5	*p*-Tol-ZnCl·(tmeda)	diisopropylketone	14	59
6	(*p*-Tol)$_3$-Al	diisopropylketone	14	42
7[d]	*p*-Tol-Al^{i}Bu$_3$·MgBr	diisopropylketone	18	48
8[f]	$PhB(OH)_2$	diisopropylketone	13	35
9[f]	$PhSi(OMe)_3$	diisopropylketone TBAF[g]	13	41

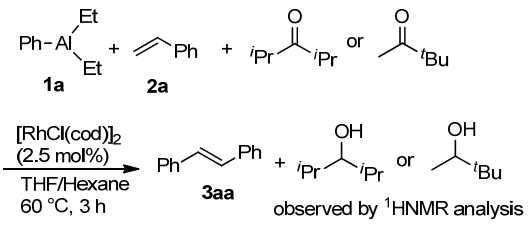
[a] Unless otherwise noted, the reaction performed with aryl metal species (0.6 mmol), styrene (0.3 mmol), $[RhCl(cod)]_2$ (0.015 mmol) and additive (0.6 mmol) in 1.2-2.8 mL of THF at 60 ºC. [b] Isolated yield. [c] The reaction was carried out in toluene at room temperature. [d] The reaction was performed with 0.5 mmol of **2a**. [e] The yield was estimated by ^{1}H NMR analysis. [f] The reaction was performed with 5.0 mol % of $[Rh(OH)(cod)]_2$ at 100 ºC in toluene. [g] TBAF = tetrabutylammonium fluoride.



[a] The reaction was carried out **1a** (1.0 mmol), vinylarene (0.5 mmol), diisopropylketone (1.0 mmol), and $[RhCl(cod)]_2$ (0.0125 mmol) in 2.0 mL of THF and hexane cosolvent at 60 ºC for 2.5-65 h. The yield was determined by isolated product. [b] The yield was estimated by ^{1}H NMR analysis. [c] The yield was estimated by GC analysis. [d] The reaction was performed with 0.3 mmol of styrene **2f**.

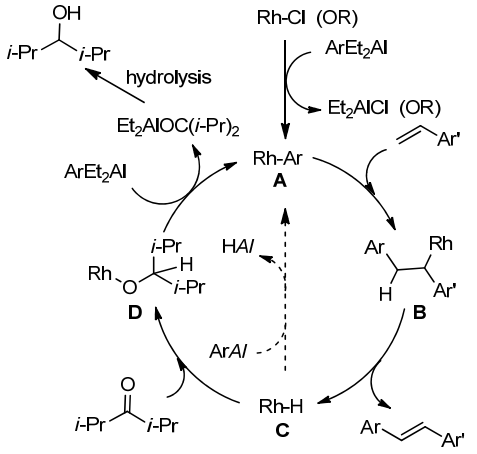
Scheme 2. The reaction of arylaluminum with vinylarenes.[a]

The effect of ketone in this addition-elimination reaction was investigated as shown in Scheme 3. The reaction of **1a** with **2a** was perfomed at 60 ºC for 3 h in the presence of diisopropylketone or pinacolone to observe the corresponding secondary alcohol by ^{1}H NMR analysis of the crude reaction mixture (See Supporting Information) showing that reduction of ketone was observed in the catalytic system.



Scheme 3. Studies on the effect of ketone in the reaction of arylaluminum with vinylarene.

Based on the above experiments a plausible reaction mechanism is shown in Scheme 4. Transmetalation of the aryl group in arylaluminum species to the rhodium chloride as well as hydroxy and alkoxy complexes occurs to afford arylrhodium species **A**. Insertion of styrene to the carbon-metal bond of **A** forms **B**, which undergoes β-hydride elimination to give stilbene along with hydridorhodium species **C**. The obtained complex **C** reacts with ketone to give rhodium alkoxide complex **D**, which is capable of inducing transmetalation with arylaluminum to regenerate arylrhodium complex **A** and the corresponding aluminum alkoxide. This aluminum alkoxide is transformed into alcohol by hydrolysis after quenching reaction mixture.[16] The hydridorohdium **C** may also undergo transmetalation with arylmetals leading to **A** thereby resulting in less efficient catalytic reaction in the absence of ketone with neutral aluminum, and zinc (entries 1-3 of Table 1, entry 4 of Table 2), however, formation of rhodium alkoxide by the reduction of ketone would facilitate more efficient transmetalation, which results in the catalytic reaction highly efficiently.



Scheme 4. Plausible mechanism of catalytic addition-elimination reaction of arylaluminum reagent with vinylarenes

Conclusions

In conclusion, a rhodium-catalyzed cross-coupling reaction of arylaluminum reagents with vinylarenes was shown to take place. The use of ketone as an additive, which behaves as a hydride acceptor of rhodium species, was found to drastically promote the catalytic reaction. Although such a rhodium-catalyzed addition-elimination reaction has only been shown to proceed with α,β-carbonyl compounds with main group reagents, boron, silicon, and tin, we have shown that a more organometallic aluminum species can also be an available reagents, with which scope of the reaction is enlarged.

Experimental Section

General: All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on Varian Gemini 300 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. Gas chromatography analyses were carried out with SHIMADZU GCMS-QP2010 Plus. Arylmagnesium bromide was prepared from arylbromide and magnesium turning. Rhodium catalysts, $[RhCl(cod)]_2$,[17] $[Rh(OH)(cod)]_2$,[18] $[Rh(OMe)(cod)]_2$,[18] $[RhCp^*Cl_2]_2$,[19] were prepared according to the literature procedures. $ZnCl_2$·(tmeda) complex was prepared according to the literature procedures.[20] Ketones (diisopropylketone, acetone and pinacolone) were dried over molecular sieves (3Å) and stored overnight prior to use. For the solvent of the rhodium-catalyzed reaction anhydrous THF and toluene were employed. Other chemicals were purchased and used without further purification.

General procedure for the reaction of arylaluminum reagent with vinylarene: To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added 1.05 M diethylaluminum chloride in hexane (1.0 mmol, 0.95 mL). To the solution was slowly added a THF solution of arylmagnesium bromide (1.0 M, 1.0 mmol, 1.0 mL) dropwise at 0 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. To the resulting white suspension were added styrene (0.5 mmol, 0.057 mL), diisopropylketone (1.0 mmol, 0.142 mL), and [RhCl(cod)]2 (0.0125 mmol, 6.1 mg) and stirred at 60 °C for 2.5-65 h. After cooling to room temperature the reaction mixture was quenched with water (CAUTION: Gas evolution occurs.). To the solution was added 1.0 M hydrochloric acid (1.0 mL) and the solution was poured into the mixture of diethyl ether/water to result in separation into two phases. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel and preparative SEC.

Supporting Information (see footnote on the first page of this article): … . Experimental detaols and characterization of new compounds.

Acknowledgments

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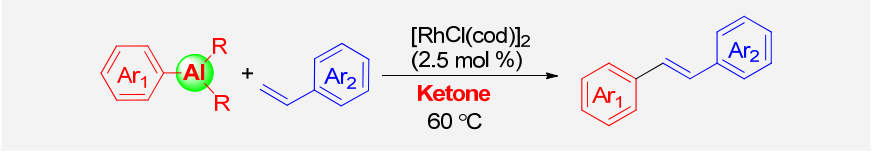
Entry for the Table of Contents ((Please choose one layout.))

Layout 2:

Transition metal catalysis



Ketone plays a key role for the rhodium-catalyzed addition-elimination reaction of arylaluminum reagents with vinylarenes leading to 1,2-diarylethenes in excellent yields, otherwise, the related reaction in the absence of ketone only gives the same product in a moderate yield. The reaction of phenyldiethyl aluminum and styrene with 2.5 mol % $[RhCl(cod)]_2$ in the presence of diisopropylketone gives stilbene in a quantitative yield after stirring at 60 °C for 3 h.

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Rhodium-Catalyzed Cross Coupling of Vinylarenes with Arylaluminum Reagents Promoted by the Addition of Ketone

Keywords: Rhodium / organoaluminum / Addition-elimination reaction/ Cross coupling / Stilbene

Supporting Information

Rhodium-Catalyzed Cross Coupling of Vinylarenes with Arylaluminum Reagents Promoted by the Addition of Ketone

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Experimental Section

General

All the reactions were carried out under nitrogen atmosphere. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were measured on Varian Gemini 300 as a $CDCl_3$ solution unless noted. The chemical shifts were expressed in ppm with $CHCl_3$ (7.26 ppm for ^{1}H) or $CDCl_3$ (77.0 ppm for ^{13}C) as internal standards. High resolution mass spectra (HRMS) were measured by JEOL JMS-T100LP AccuTOF LC-Plus (ESI) with a JEOL MS-5414DART attachment. For thin layer chromatography (TLC) analyses throughout this work, Merck precoated TLC plates (silica gel 60 F254) were used. Purification by HPLC with preparative SEC column (JAI-GEL-2H) was performed by JAI LC-9201. Gas chromatography analyses were carried out with SHIMADZU GCMS-QP2010 Plus. Arylmagnesium bromide was prepared from arylbromide and magnesium turning. Rhodium catalysts, $[RhCl(cod)]_2$,[1] $[Rh(OH)(cod)]_2$,[2] $[Rh(OMe)(cod)]_2$,[2] $[RhCp^*Cl_2]_2$,[3] were prepared according to the literature procedures. $ZnCl_2$·(tmeda) complex was prepared according to the literature procedures.[4] Ketones (diisopropyl ketone, acetone and pinacolone) were dried over molecular sieves (3Å) and stored overnight prior to use. For the solvent of the rhodium-catalyzed reaction anhydrous THF and toluene were employed. Other chemicals were purchased and used without further purification.

General procedure for the reaction of arylaluminum reagent with vinylarene: To a 20 mL Schlenk tube equipped with a magnetic stirring bar was added 1.05 M diethylaluminum chloride in hexane (1.0 mmol, 0.95 mL). To the solution was slowly added a THF solution of arylmagnesium bromide (1.0 M, 1.0 mmol, 1.0 mL) dropwise at 0 °C. The reaction was allowed to warm to room temperature and stirred for 3 h. To the resulting white suspension were added styrene (0.5 mmol, 0.057 mL), diisopropylketone (1.0 mmol, 0.142 mL), and $[RhCl(cod)]_2$ (0.0125 mmol, 6.1 mg) and stirred at 60 °C for 2.5-65 h. After cooling to room temperature the reaction mixture was quenched with water (CAUTION: Gas evolution occurs.). To the solution was added 1.0 M hydrochloric acid (1.0 mL) and the solution was poured into the mixture of diethyl ether/water to result in separation into two phases. Aqueous was extracted with diethyl ether twice and the combined organic layer was dried over anhydrous sodium sulfate and concentrated under reduced pressure to leave a crude oil, which was purified by column chromatography on silica gel and preparative SEC.

(*E*)-Stilbene (3aa)[5], colorless solid, m.p. 120.0-121.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (s, 2H), 7.23-7.30 (m, 2H), 7.32-7.43 (m, 4H), 7.49-7.56 (m, 4H); ^{13}C NMR δ 126.5, 127.6, 128.67, 128.74, 137.4; HRMS (DART-ESI+) Calcd for $C_{14}H_{13}$ $[M+H]^+$: 181.1017; found: m/z 181.1017.

(*E*)-1-(4-Methylphenyl)-2-phenylethene (3ab)[5], colorless solid, m.p. 114.0-115.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 3H), 7.08 (s, 2H), 7.17 (d, J = 8.0 Hz, 2H), 7.21-7.29 (m, 1H), 7.35 (t, J = 7.6 Hz, 2H), 7.42 (d, J = 8.0 Hz, 2H), 7.51 (d, J = 7.5 Hz, 2H); ^{13}C NMR δ 21.1, 126.38 (×2), 126.42 (×2), 127.4, 127.7, 128.6 (×3), 129.4 (×2), 134.6, 137.47, 137.53; HRMS (DART-ESI+) Calcd for $C_{15}H_{15}$ $[M+H]^+$: 195.1174; found: m/z 195.1175.

(*E*)-1-(4-Methoxyphenyl)-2-phenylethene (3ac)[5], pale yellow solid, m.p. 130.0-132.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.46 (s, 3H), 6.91 (d, J = 8.8 Hz, 2H), 6.98 (d, J = 16.3 Hz, 1H), 7.08 (d, J = 16.3 Hz, 1H), 7.20-7.26 (m, 1H), 7.30-7.39 (m, 2H), 7.46 (d, J = 8.8 Hz, 2H), 7.46-7.52 (m, 2H); ^{13}C NMR δ 55.2, 114.1, 126.2, 126.6, 127.2, 127.7, 128.2, 128.6, 130.1, 137.6, 159.3; HRMS (DART-ESI+) Calcd for $C_{15}H_{15}O$ $[M+H]^+$: 211.1123; found: m/z 211.1121.

(*E*)-1-(4-Fluorophenyl)-2-phenylethene (3ad)[5], colorless solid, m.p. 119.5-120.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.98-7.12 (m, 4H), 7.23-7.30 (m, 1H), 7.32-7.40 (m, 2H), 7.44-7.54 (m, 4H); ^{13}C NMR δ 115.6 (d, J_{C-F} = 21.6 Hz), 126.4, 127.5 (d, J_{C-F} = 0.9 Hz), 127.7, 128.0 (d, J_{C-F} = 8.0 Hz), 128.5 (d, J_{C-F} = 2.4 Hz), 128.7, 133.5 (d, J_{C-F} = 3.3 Hz), 137.2, 162.4 (d, J_{C-F} = 247.4 Hz); HRMS (DART-ESI+) Calcd for $C_{14}H_{12}F$ $[M+H]^+$: 199.0923; found: m/z 199.0927.

(*E*)-1-(1-Naphthyl)-2-phenylethene (3ae)[6], colorless solid, m.p. 65.5-66.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17 (d, *J* = 16.0 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.47-7.59 (m, 3H), 7.62 (d, *J* = 7.5 Hz, 2H), 7.76 (d, *J* = 7.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 7.2 Hz, 1H), 7.90 (d, *J* = 16.0 Hz, 1H); ^{13}C NMR δ 123.6, 123.8, 125.7, 125.80, 125.83, 126.1, 126.7 (×2), 127.7, 128.0, 128.6, 128.7 (×2), 131.4, 131.8, 133.8, 135.0, 137.6; HRMS (DART-ESI+) Calcd for $C_{18}H_{15}$ $[M+H]^+$: 231.1174; found: m/z 231.1172.

(*E*)-1-Phenyl-2-[4-(trifluoromethyl)phenyl]ethene (3af)[6], colorless solid, m.p. 126.4-127.5 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.12 (d, *J* = 16.3 Hz, 1H), 7.21 (d, *J* = 16.3 Hz, 1H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.39 (t, *J* = 7.3 Hz, 2H), 7.54 (d, *J* = 7.2 Hz, 2H), 7.61 (s, 4H); ^{13}C NMR δ 124.2 (q, J_{C-F} = 271 Hz), 125.6 (q, J_{C-F} = 3.9 Hz), 126.6, 126.8, 127.2, 128.3, 128.8, 129.3 (q, J_{C-F} = 32.4 Hz), 131.2, 136.7, 140.8 ; GCMS (EI) *m*/*z* (relative intensity): 249 (13), 248 (M^+, 100), 247 (16), 233 (9), 227 (8), 207 (3), 180 (9), 179 (57), 178 (36), 177, (3), 102 (1), 78 (4)

(*E*)-1-(-3,5-Dimethylphenyl)-2-phenylethene (3ag)[7], colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.34 (s, 6H), 6.92 (s, 1H), 7.07 (s, 1H), 7.08 (s, 1H), 7.15 (s, 2H), 7.21-7.29 (m, 1H), 7.36 (d, *J* = 7.5 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR δ 21.3, 124.4, 126.4, 127.4, 128.3, 128.6, 128.9, 129.4, 137.2, 137.5, 138.0; HRMS (DART-ESI+) Calcd for $C_{16}H_{17}$ $[M+H]^+$: 209.1330; found: m/z 209.1328.

(*E*)-1-(2-Methylphenyl)-2-phenylethene (3ah)[6], colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.01 (d, *J* = 16.2 Hz, 1H), 7.16-7.33 (m, 5H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.3. Hz, 2H), 7.60 (d, *J* = 7.2 Hz, 1H); ^{13}C NMR δ 19.9, 125.4, 126.2, 126.54, 126.56, 127.51, 127.55, 128.6, 130.0, 130.4, 135.8, 136.4, 137.7; HRMS (DART-ESI+) Calcd for $C_{15}H_{15}$ $[M+H]^+$: 195.1174; found: m/z 195.1173.

(*E*)-1-[4-*N*,*N*-(dimethylamino)phenyl]-2-phenylethene (3ai)[8], yellow solid, m.p. 143.0-145.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.99 (s, 6H), 6.75 (d, *J* = 8.8 Hz, 2H), 6.92 (d, *J* = 16.3 Hz, 1H), 7.05 (d, *J* = 16.3 Hz, 1H), 7.20 (t, *J* = 7.3 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 7.48 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR δ 40.5, 112.6, 124.6, 126.0, 126.1, 126.7, 127.6, 128.5, 128.8, 138.2, 150.0; HRMS (DART-ESI+) Calcd for $C_{16}H_{18}N$ $[M+H]^+$: 224.1439; found: m/z 224.1433.

(*E*)-1-(2-Methoxyphenyl)-2-phenylethene (3aj)[9], colorless oil, ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.90 (s, 3H), 6.91 (d, *J* = 8.2 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 7.12 (d, *J* = 16.5 Hz, 1H), 7.20-7.29 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.49 (d, *J* = 16.5 Hz, 1H), 7.54 (d, *J* = 7.1 Hz, 2H), 7.60 (dd, *J* = 7.7, 1.6 Hz, 1H); ^{13}C NMR δ 55.5, 111.0, 120.8, 123.6, 126.4, 126.5, 126.6, 127.3, 128.56, 128.62, 129.1, 138.0, 157.0; HRMS (DART-ESI+) Calcd for $C_{15}H_{15}O$ $[M+H]^+$: 211.1123; found: m/z 211.1122.

(*E*)-1,2-Bis(4-methylphenyl)ethene (3bb)[5], colorless solid, m.p. 177.0-179.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.36 (s, 6H), 7.04 (s, 2H), 7.16 (d, *J* = 8.0 Hz, 4H), 7.40 (d, *J* = 8.0 Hz, 4H); ^{13}C NMR δ 21.2, 126.3, 127.7, 129.3, 134.8, 137.2; HRMS (DART-ESI+) Calcd for $C_{16}H_{17}$ $[M+H]^+$: 209.1330; found: m/z 209.1327.

(*E*)-1-(4-Methoxyphenyl)-2-(4-methylphenyl)ethene (3bc)[5], colorless solid, m.p. 162.8-165.0 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.28 (s, 3H), 3.76 (s, 3H), 6.82 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 16.3 Hz, 1H), 6.95 (d, *J* = 16.3 Hz, 1H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR δ 21.2, 55.3, 114.1 (×2), 126.2 (×2), 126.6, 127.2, 127.6 (×2), 129.3 (×2), 130.4, 134.9, 137.0, 159.2; HRMS (DART-ESI+) Calcd for $C_{16}H_{17}O$ $[M+H]^+$: 225.1279; found: m/z 225.1279.

(*E*)-1,2-Bis(4-methoxylphenyl)ethene (3cc)[10], colorless solid, m.p. 207.5-209.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 6H), 6.89 (d, *J* = 8.7 Hz, 4H), 6.93 (s, 2H), 7.43 (d, *J* = 8.7 Hz, 4H); ^{13}C NMR δ 55.3, 114.1, 126.2, 127.4, 130.5, 159.0; HRMS (DART-ESI+) Calcd for $C_{16}H_{17}O_2$ $[M+H]^+$: 241.1229; found: m/z 241.1226.

(*E*)-1-(4-Fluorophenyl)-2-(4-methoxyphenyl)ethene (3cd)[11], colorless solid, m.p. 139.4-141.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.83 (s, 3H), 6.90 (d, J = 8.8 Hz, 2H), 6.92 (d, J = 16.0 Hz, 2H), 6.99 (d, J = 16.0 Hz, 2H), 7.03 (t, J = 8.7 Hz, 2H), 7.39-7.49 (m, 4H); ^{13}C NMR δ 55.3, 114.2, 115.5 (d, J_{C-F} = 21.6 Hz), 125.4, 127.64, 127.66 (d, J_{C-F} = 7.9 Hz), 128.0 (d, J_{C-F} = 2.2 Hz), 130.0, 133.9 (d, J_{C-F} = 3.6 Hz), 159.4, 162.1 (d, J_{C-F} = 246.3 Hz); HRMS (DART-ESI+) Calcd for $C_{15}H_{14}FO$ $[M+H]^+$: 229.1029; found: m/z 229.1027.

(*E*)-1-(-3,5-Dimethylphenyl)-2-(4-methoxyphenyl)ethene (3cg)[12], yellow solid, m.p. 53.9-54.9 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.33 (s, 6H), 3.83 (s, 3H), 6.89 (s, 1H), 6.90 (d, J = 8.7 Hz, 2H), 6.92 (d, J = 16.3 Hz, 1H), 7.05 (d, J = 16.3 Hz, 1H), 7.12 (s, 2H), 7.44 (d, J = 8.7 Hz, 2H),; ^{13}C NMR δ 21.3, 55.3, 114.1, 124.2, 126.8, 127.6, 127.8, 129.0, 130.4, 137.6, 138.0, 159.2; HRMS (DART-ESI+) Calcd for $C_{17}H_{19}O$ $[M+H]^+$: 239.1436; found: m/z 239.1436.

(*E*)-1-(4-Methoxyphenyl)-2-(2-methylphenyl)ethene (3ch)[6], colorless solid, m.p. 76.6-77.6 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.42 (s, 3H), 3.84 (s, 3H), 6.91 (d, J = 8.7 Hz, 2H), 6.95 (d, J = 16.3 Hz, 1H), 7.13-7.25 (m, 4H), 7.47 (d, J = 8.7 Hz, 2H), 7.58 (d, J = 7.1 Hz, 1H); ^{13}C NMR δ 19.9, 55.3, 114.1, 124.5, 125.1, 126.1, 127.1, 127.7, 129.5, 130.3, 130.5, 135.5, 136.7, 159.3; HRMS (DART-ESI+) Calcd for $C_{16}H_{17}O$ $[M+H]^+$: 225.1279; found: m/z 225.1275.

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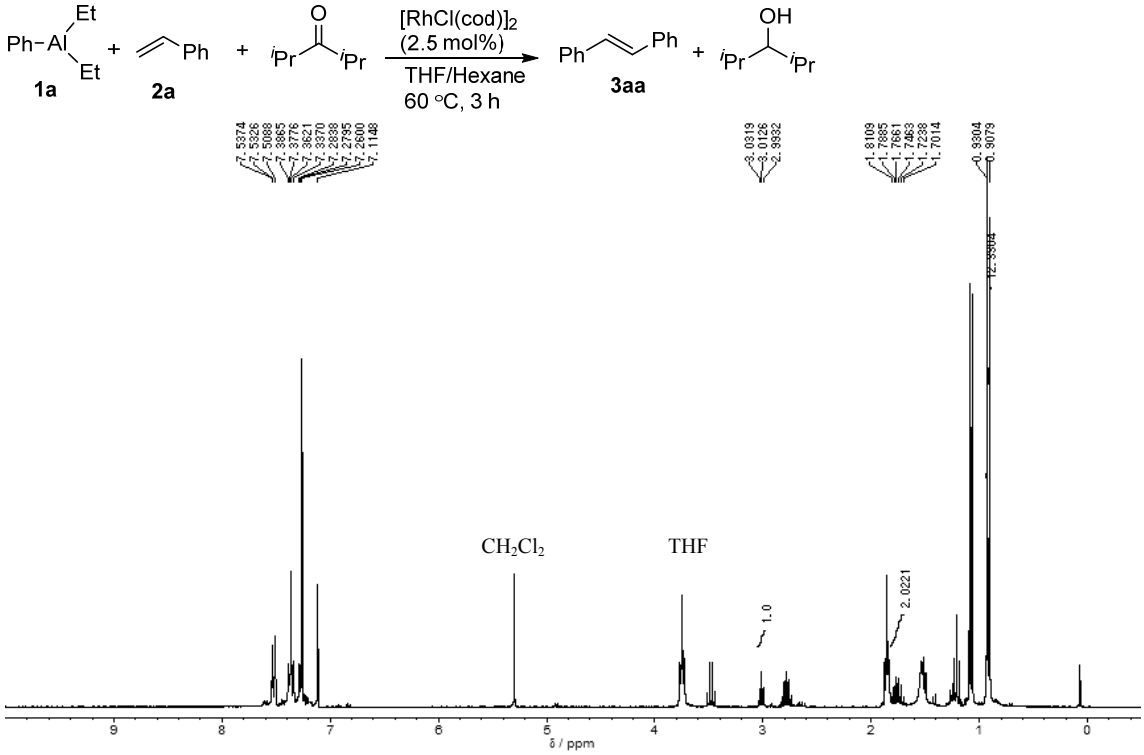
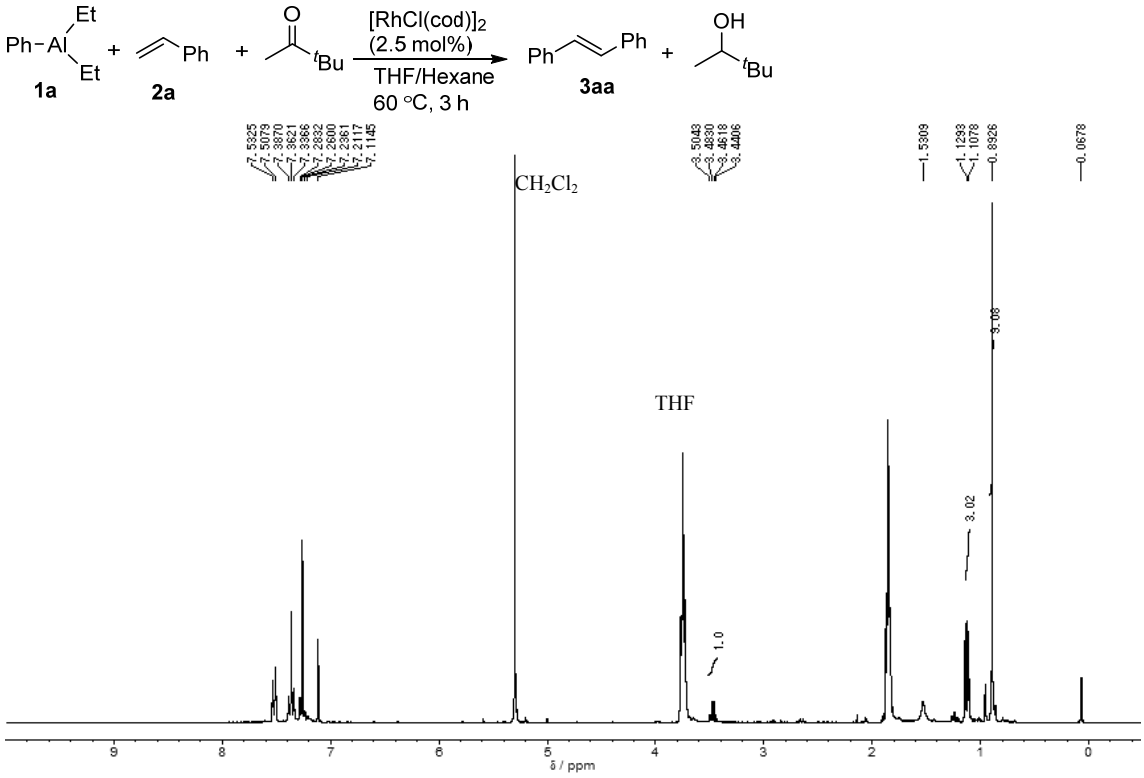
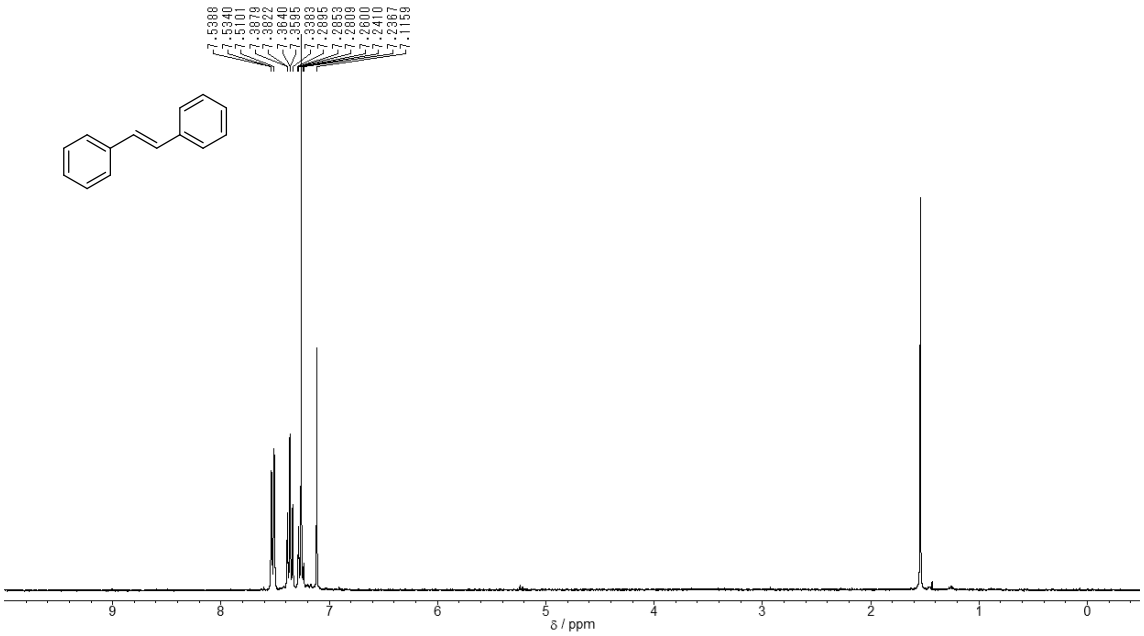
^{1}H NMR spectrum of the crude reaction mixture (Table 1, entry 4)



^{1}H NMR spectrum of the crude reaction mixture (Table 1, entry 8)



^{1}H NMR spectrum of **3aa**



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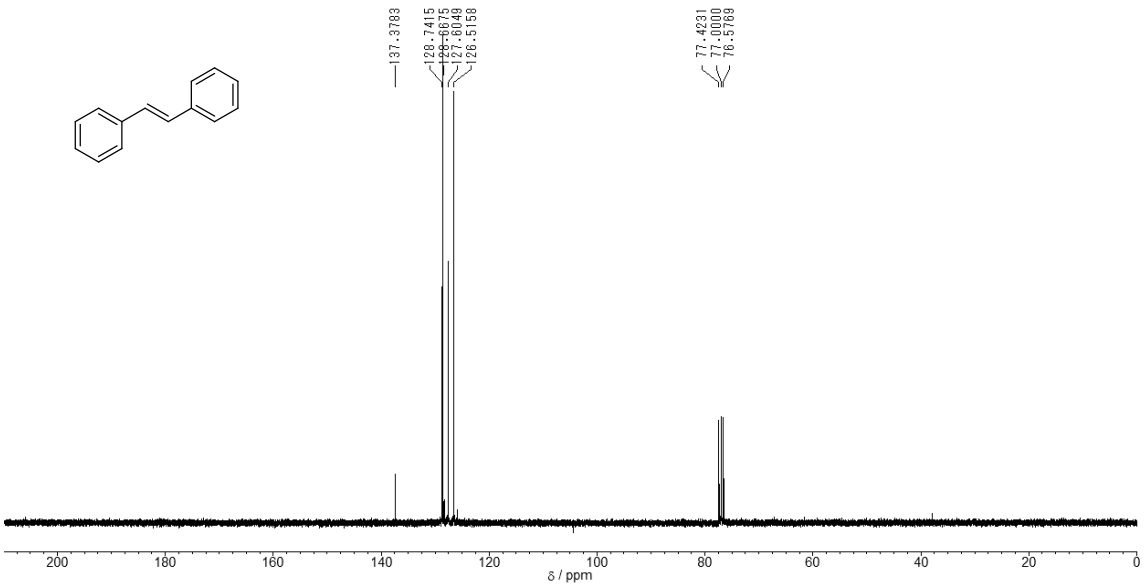

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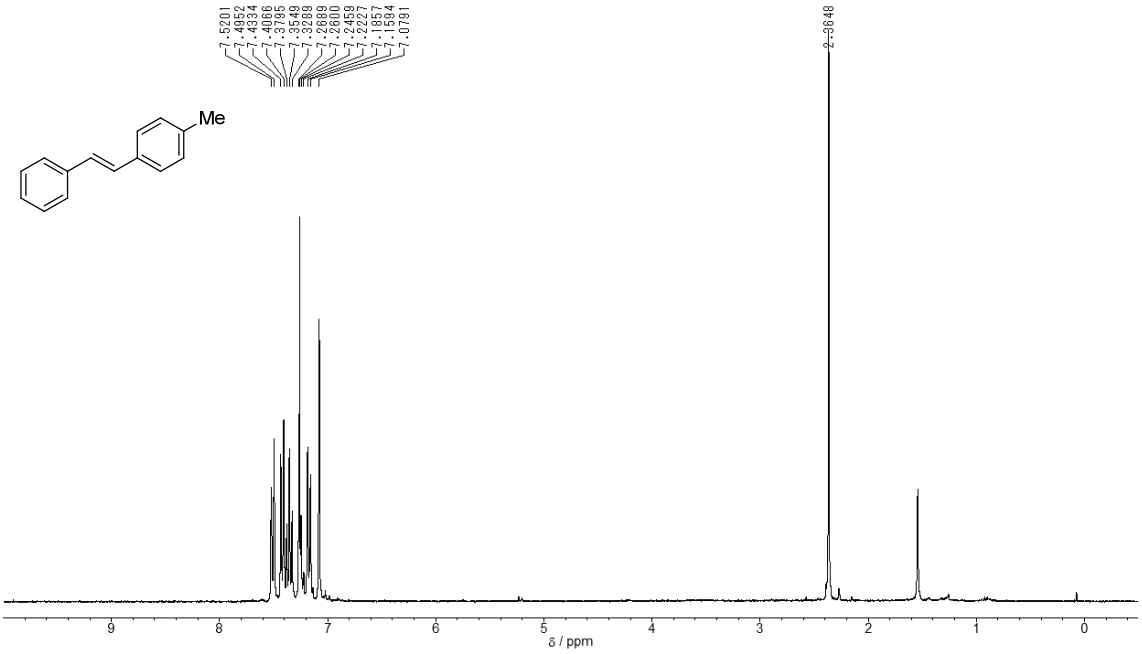
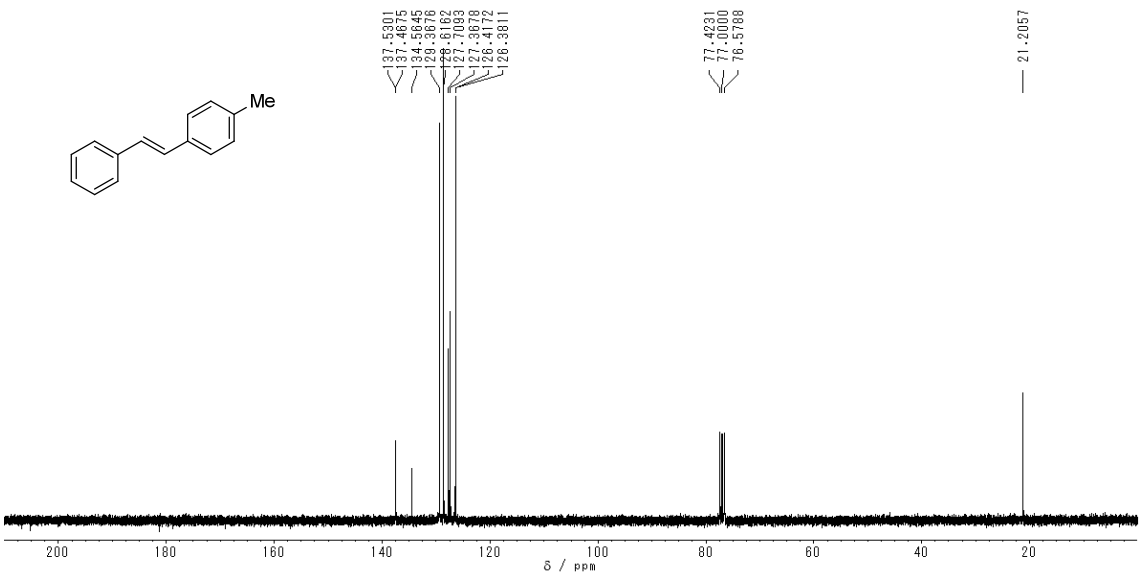


^{13}C NMR spectrum of **3ab**



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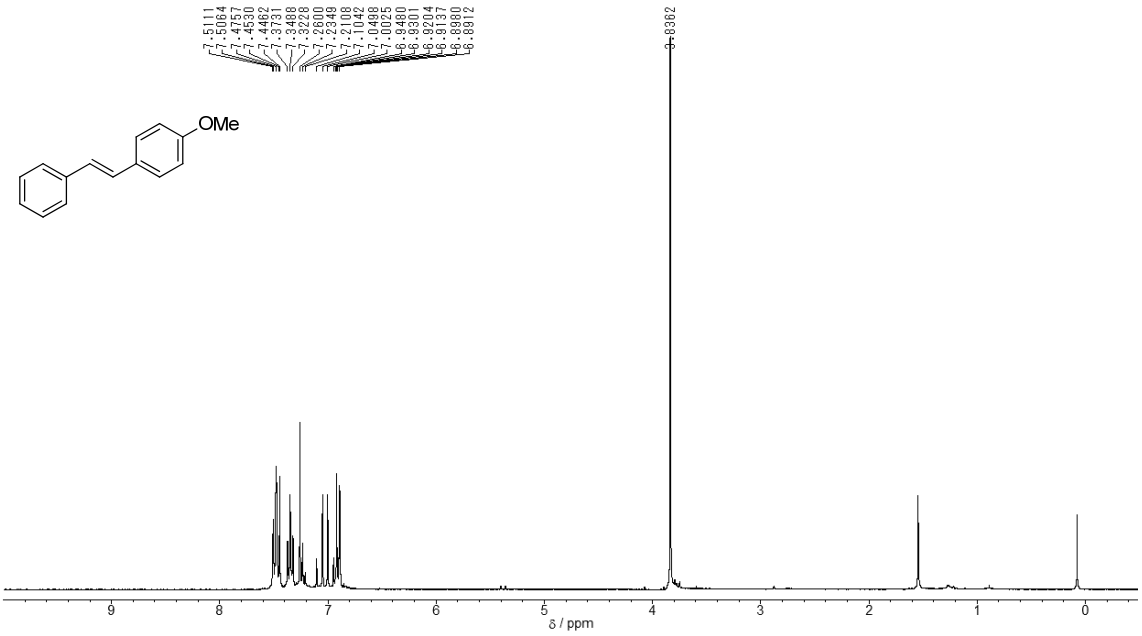
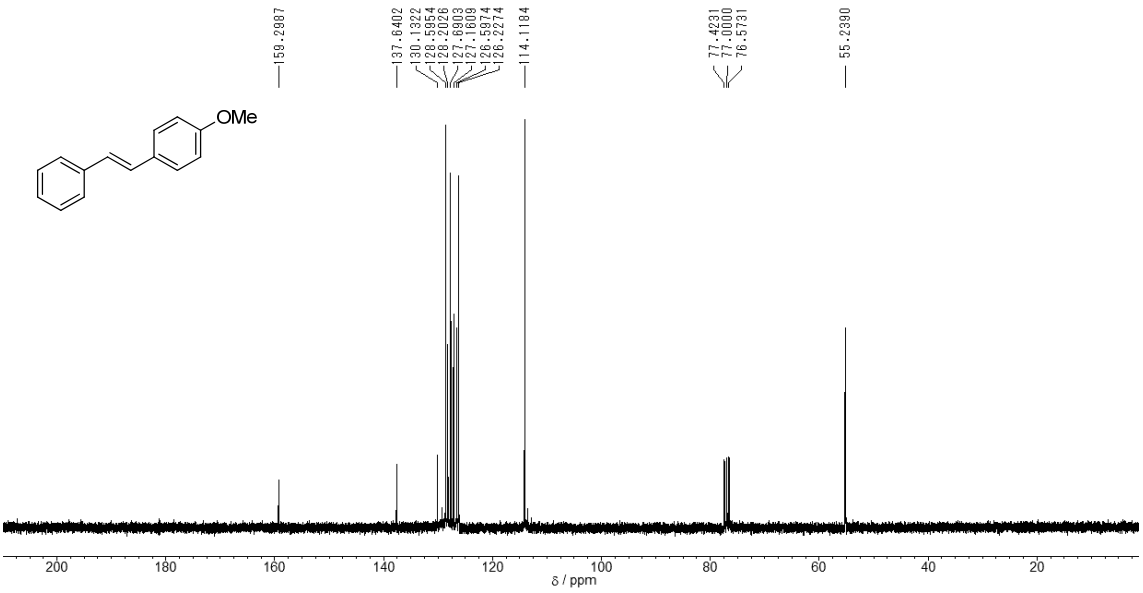


^{13}C NMR spectrum of **3ac**



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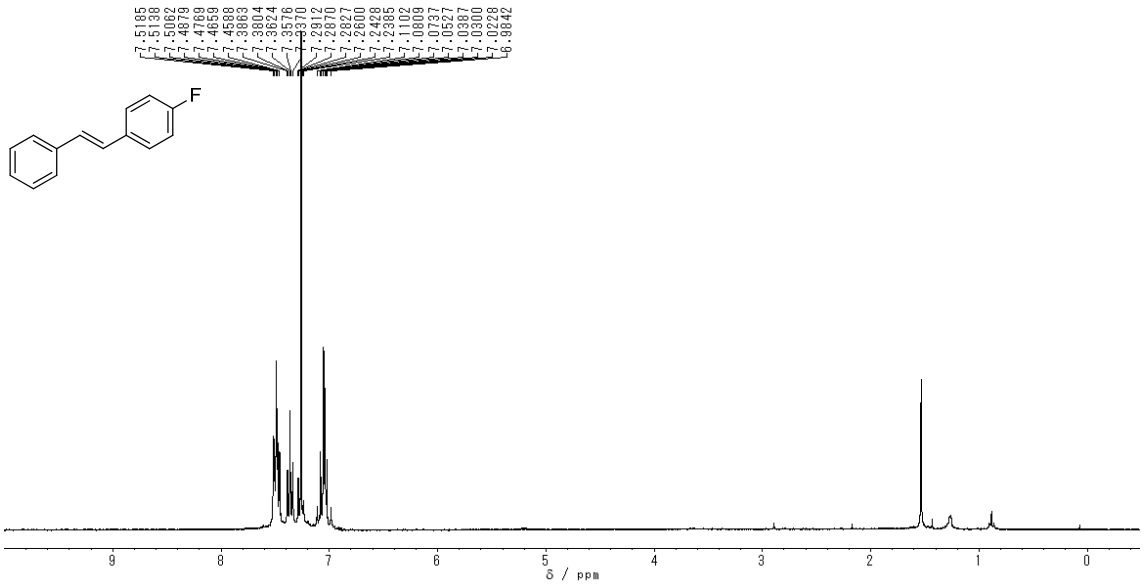

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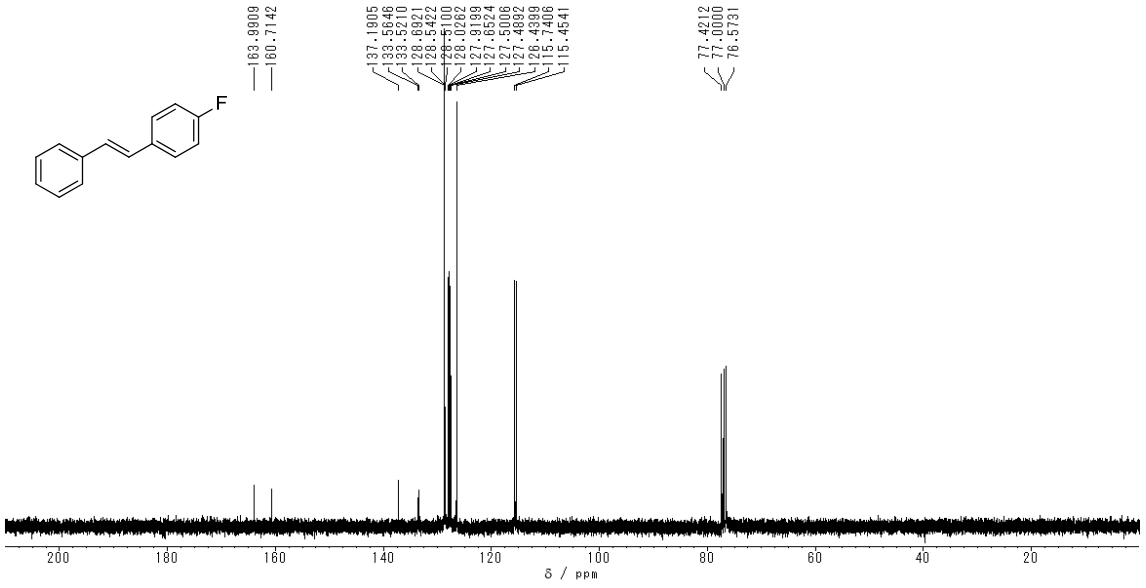

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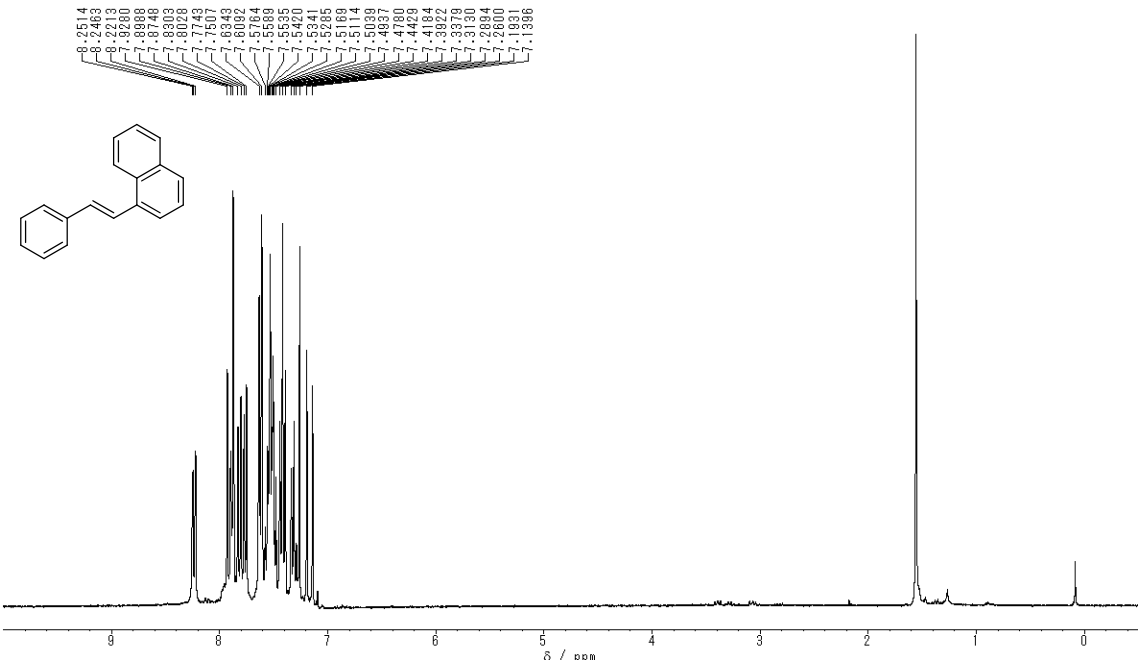

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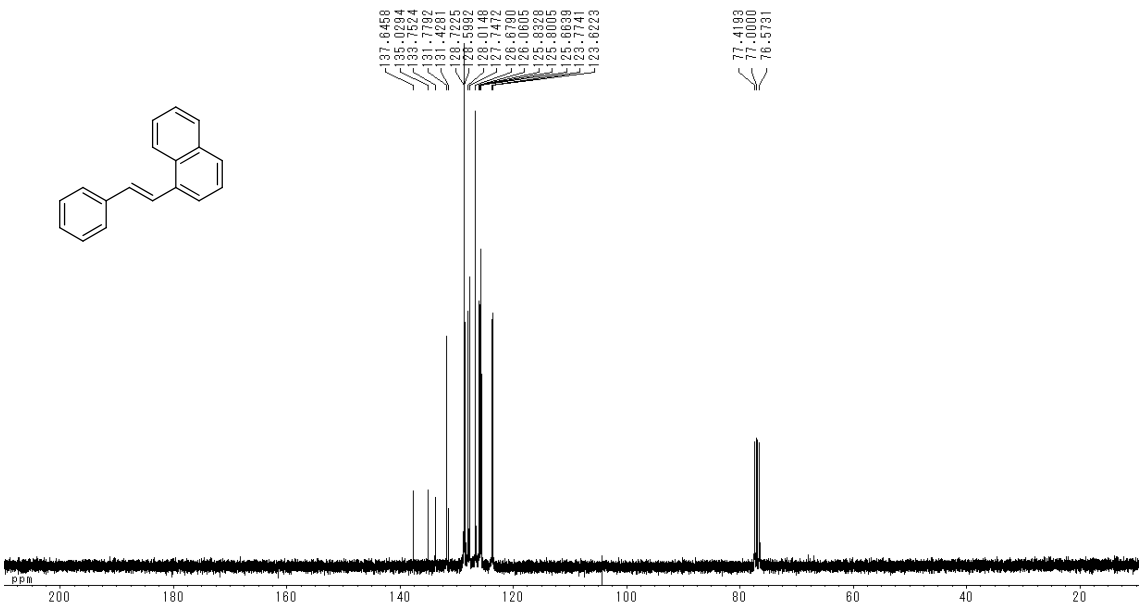

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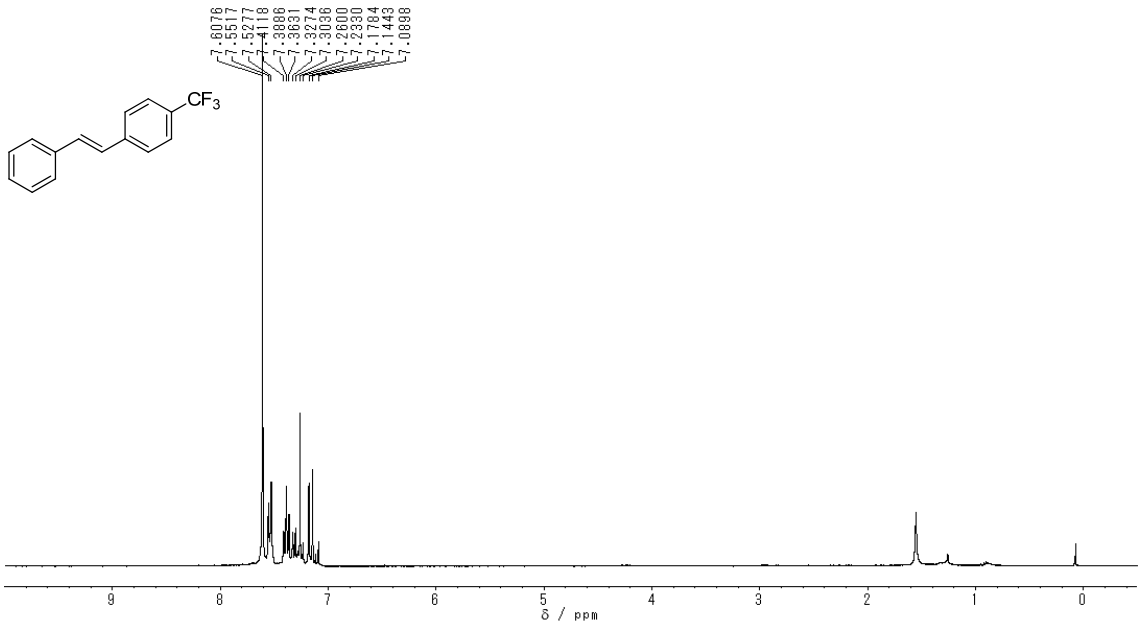
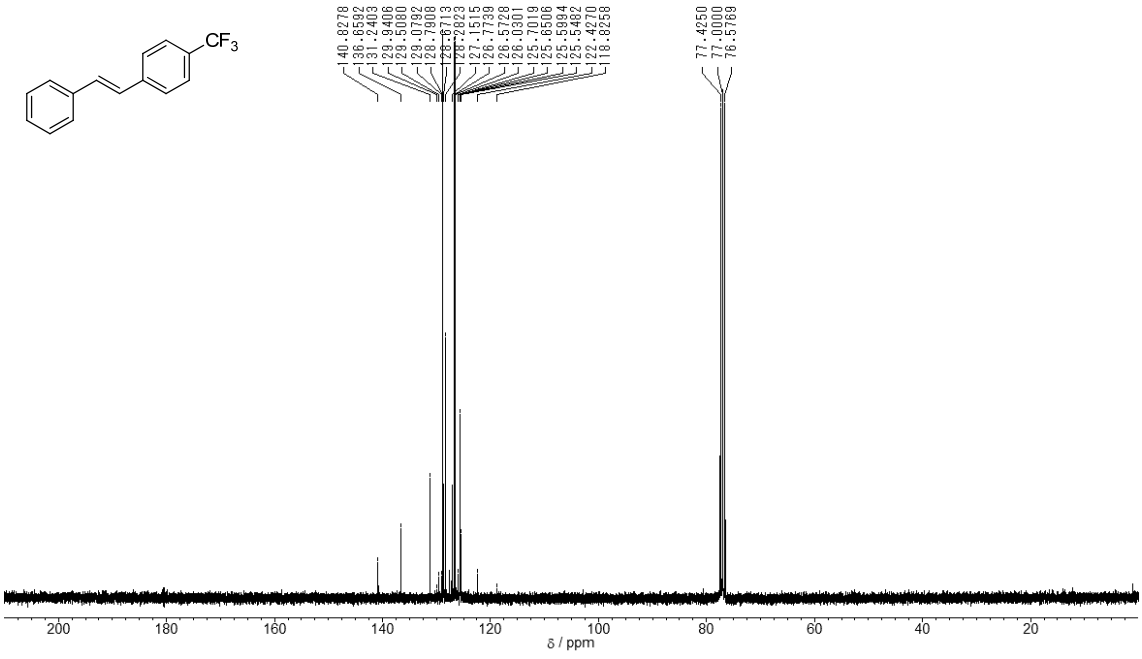
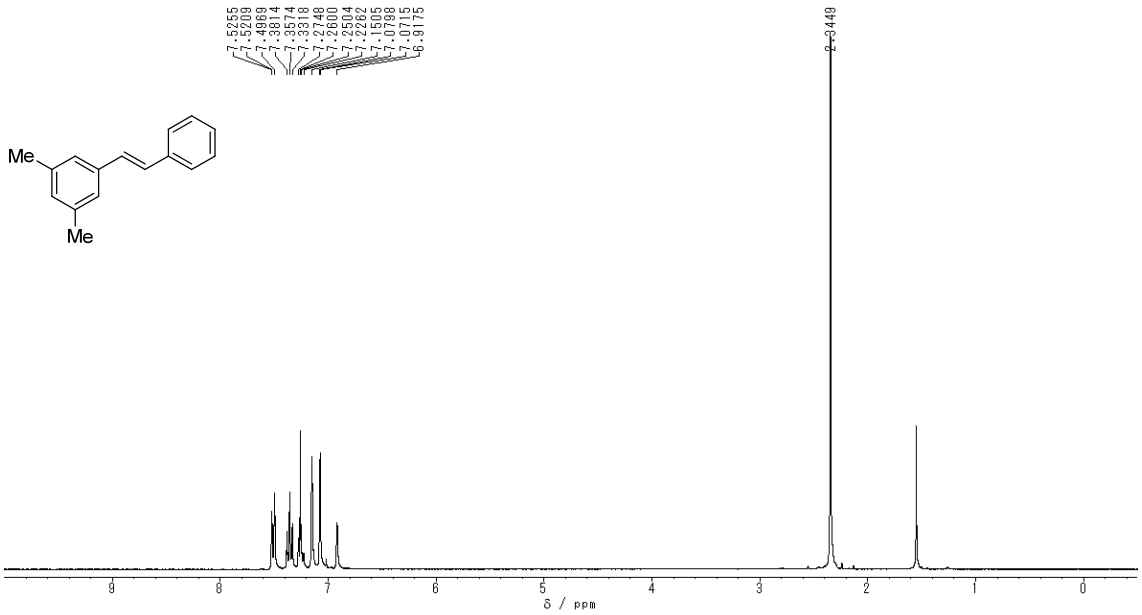


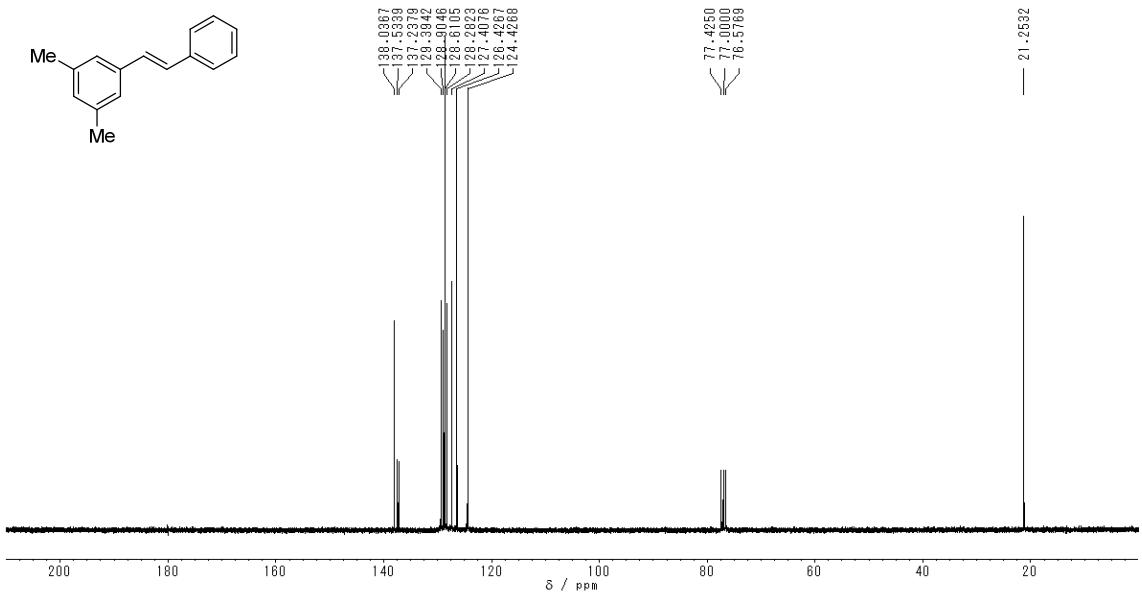
^{13}C NMR spectrum of **3af**



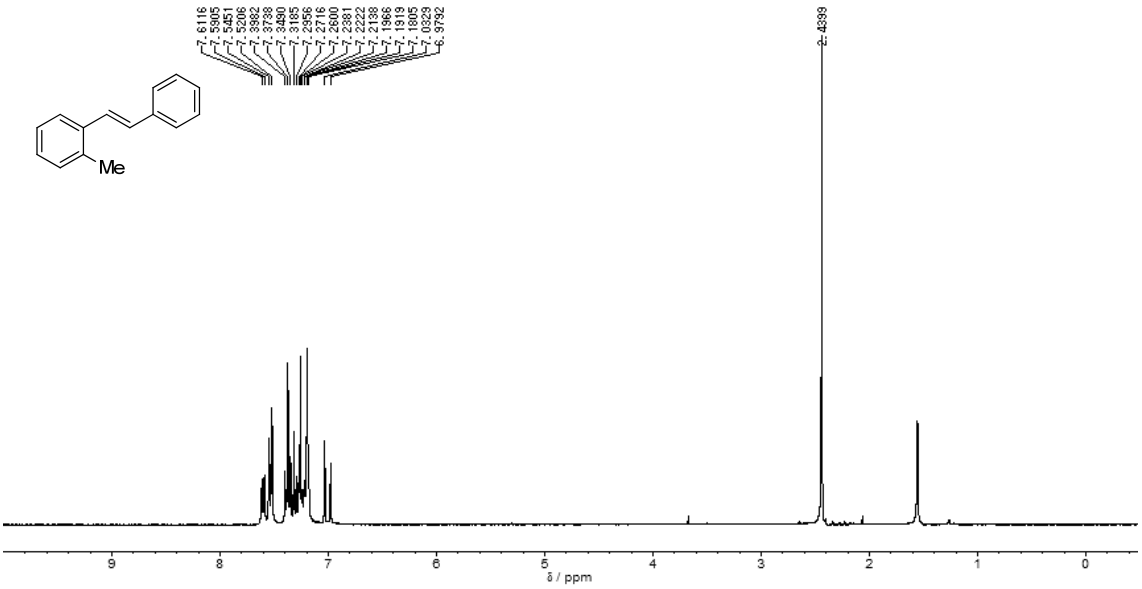
^{1}H NMR spectrum of **3ag**



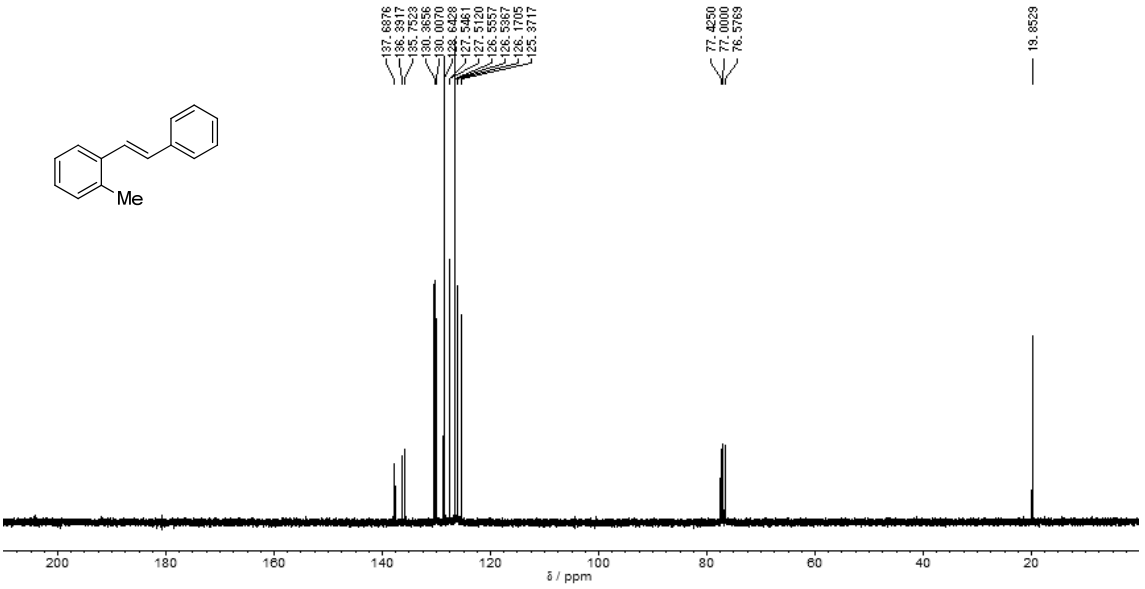
^{13}C NMR spectrum of **3ag**



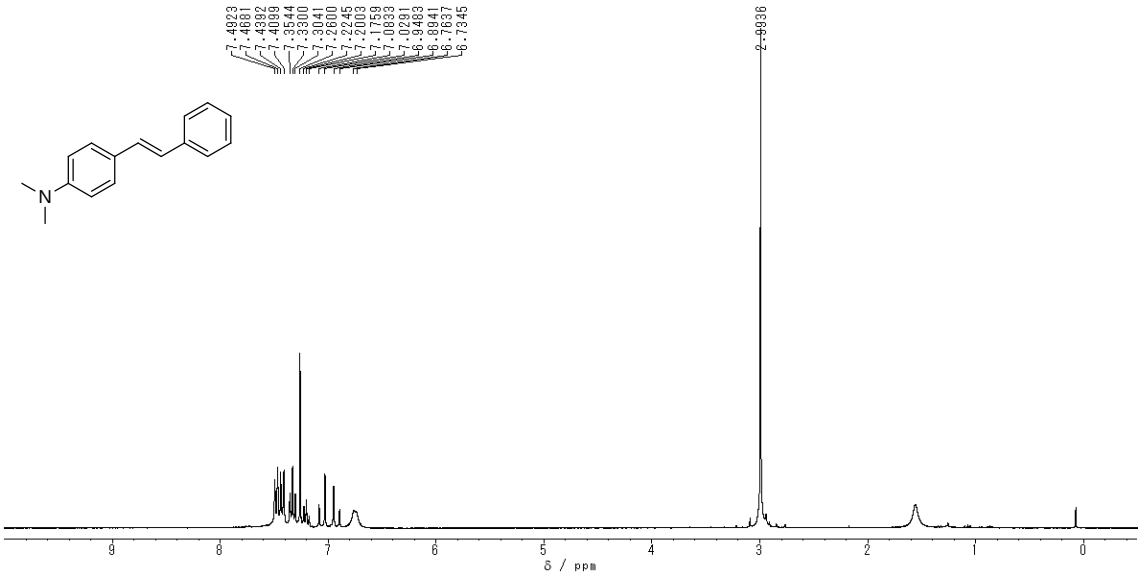
^{1}H NMR spectrum of **3ah**



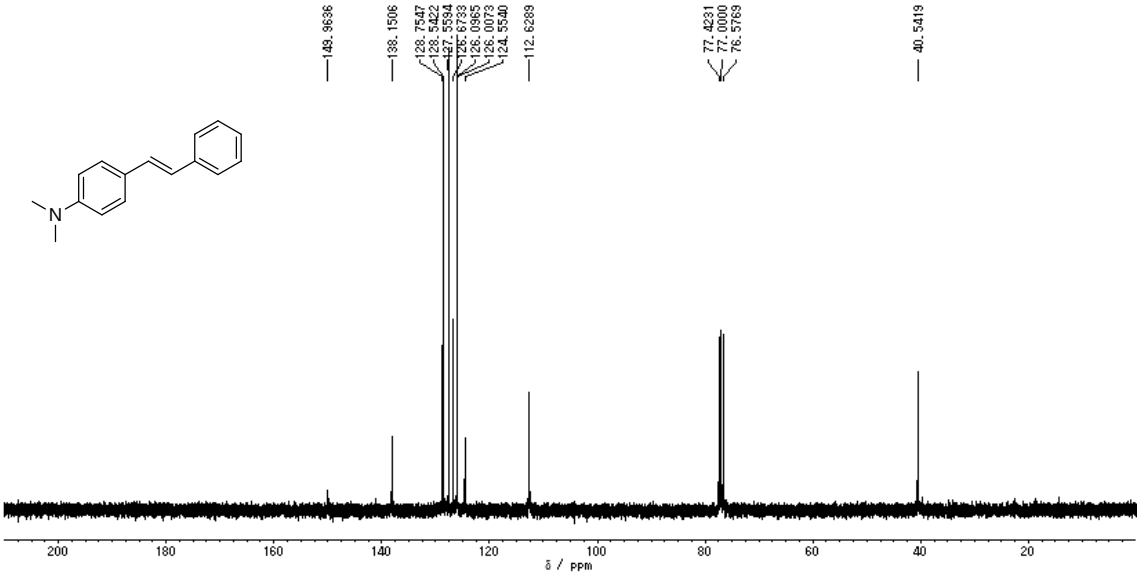
^{13}C NMR spectrum of **3ah**



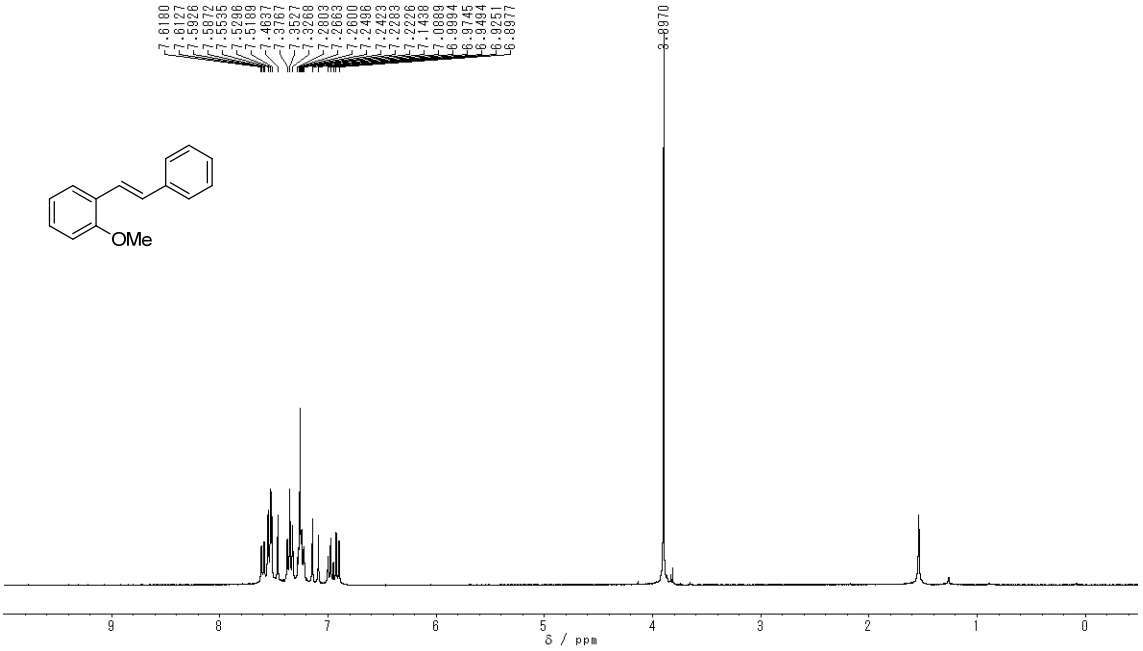
^{1}H NMR spectrum of **3ai**



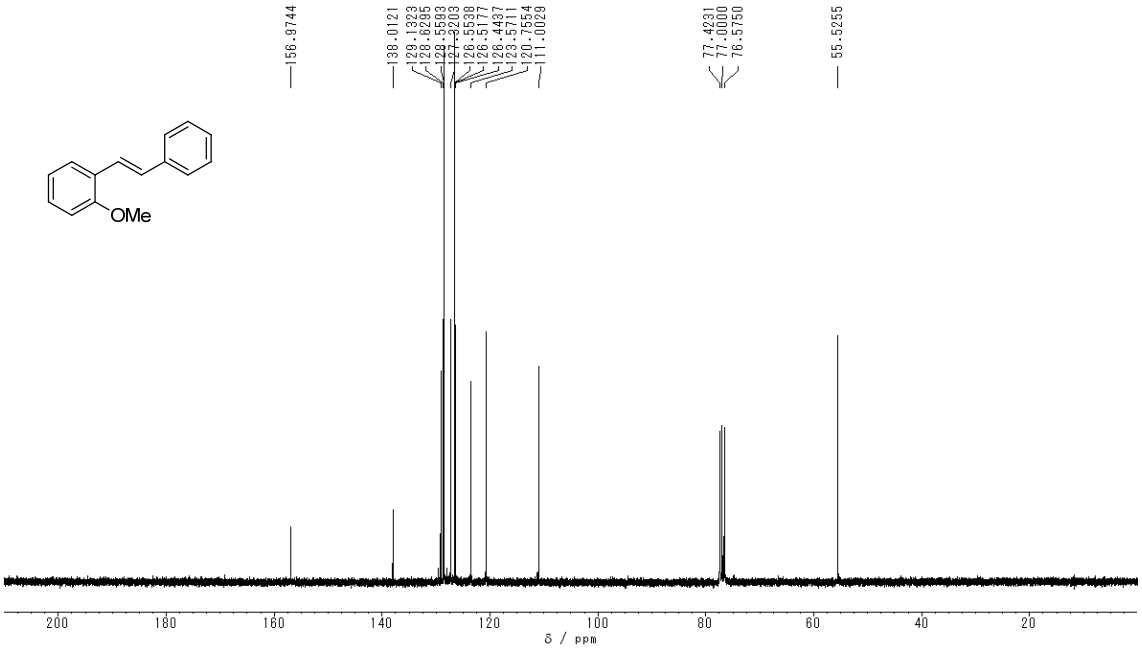
^{13}C NMR spectrum of **3ai**



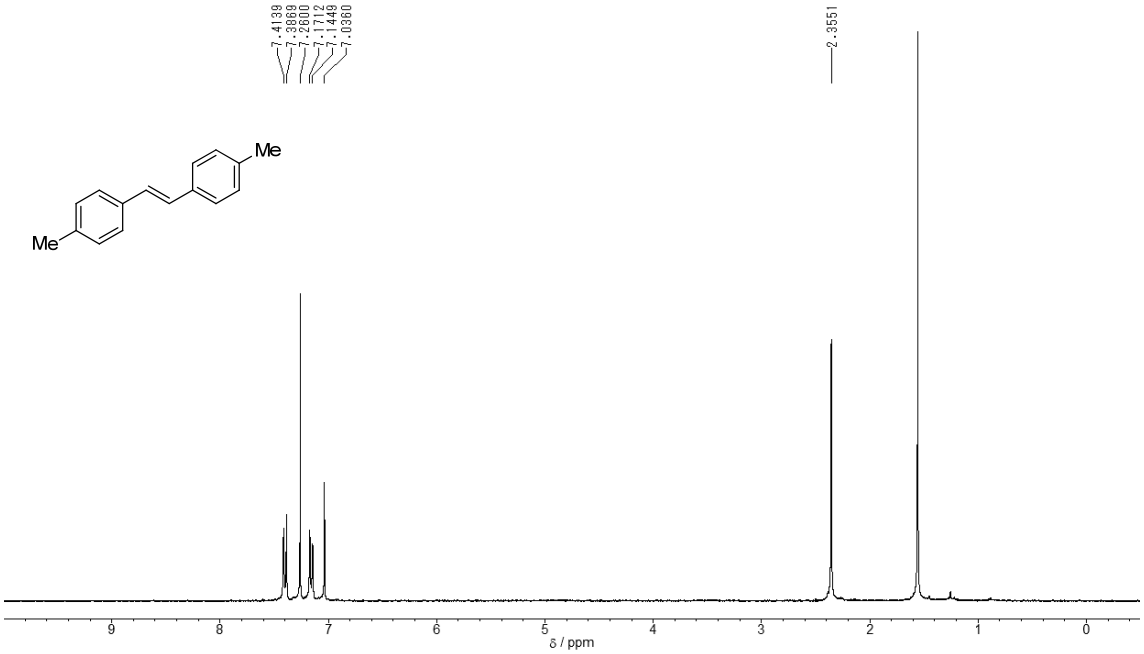
^{1}H NMR spectrum of **3aj**



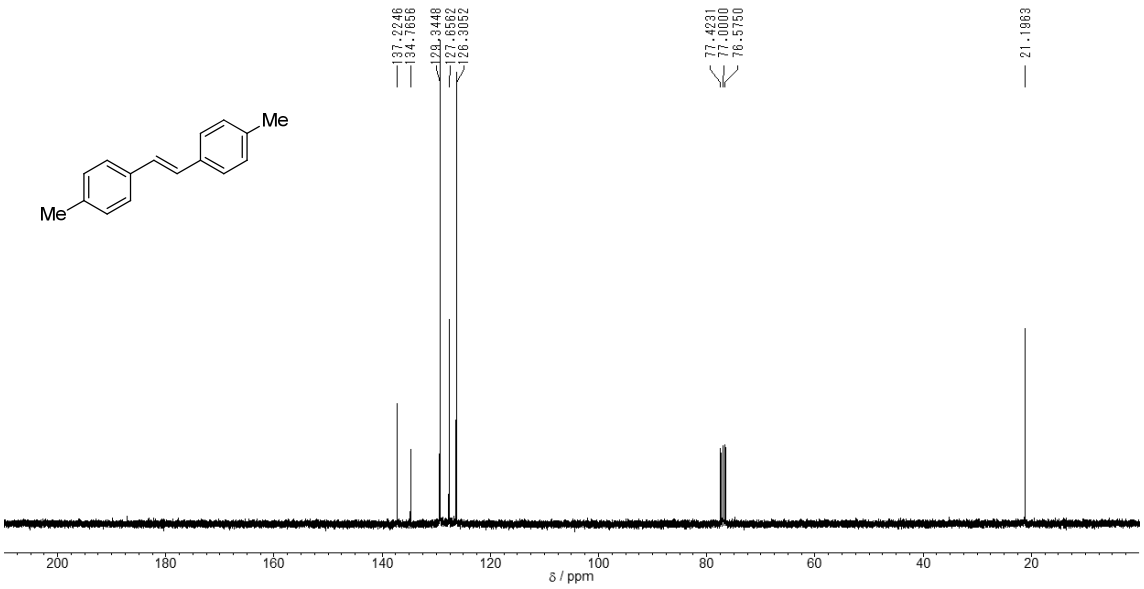
^{13}C NMR spectrum of **3aj**



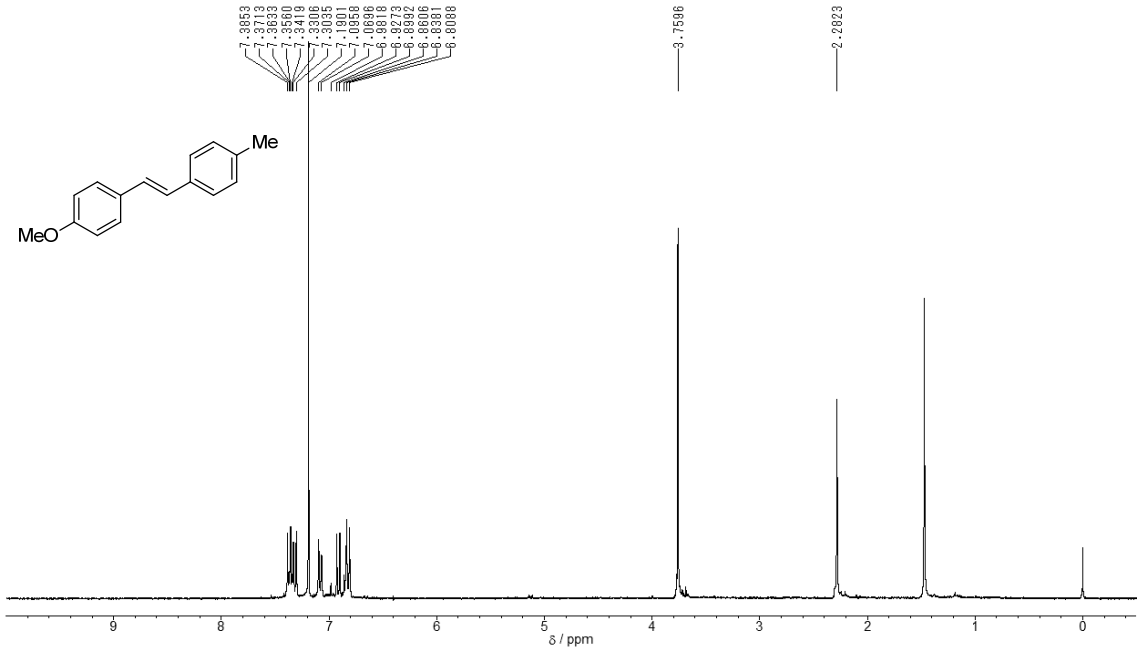
^{1}H NMR spectrum of **3bb**



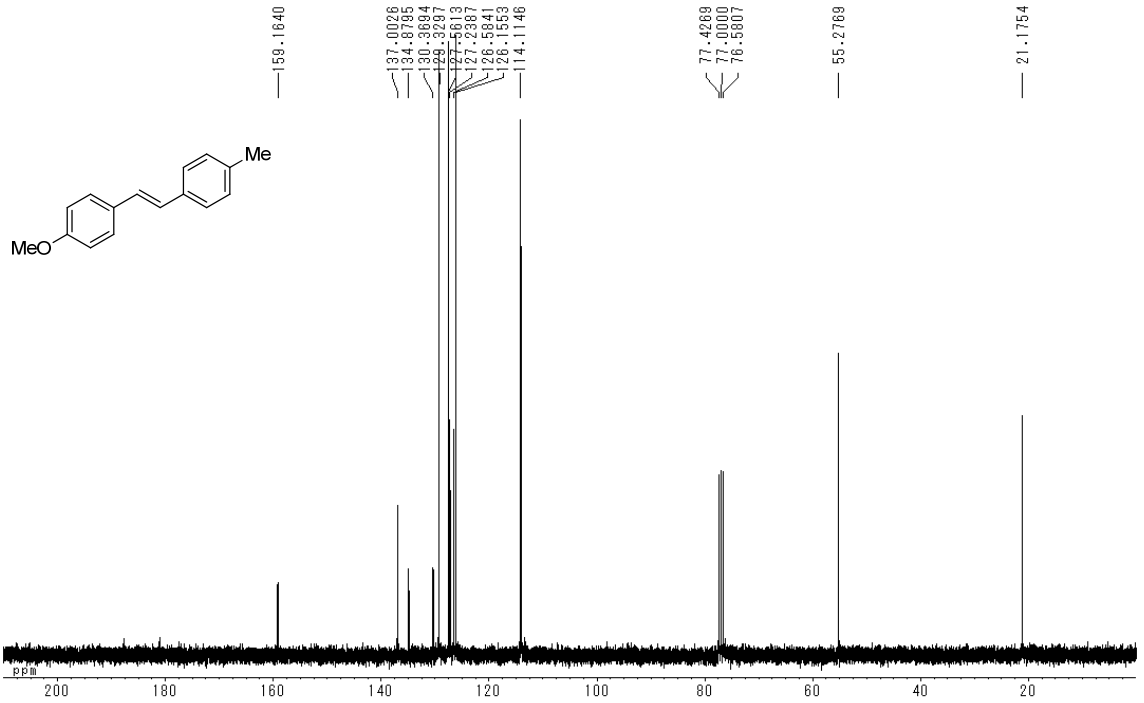
^{13}C NMR spectrum of **3bb**



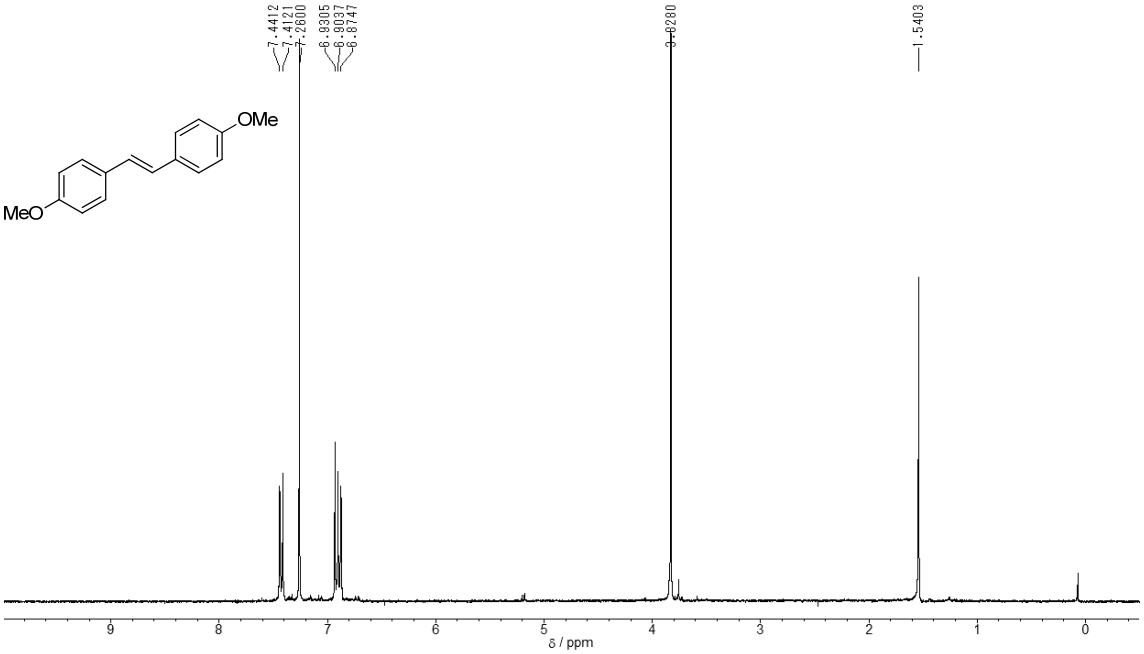
^{1}H NMR spectrum of **3bc**



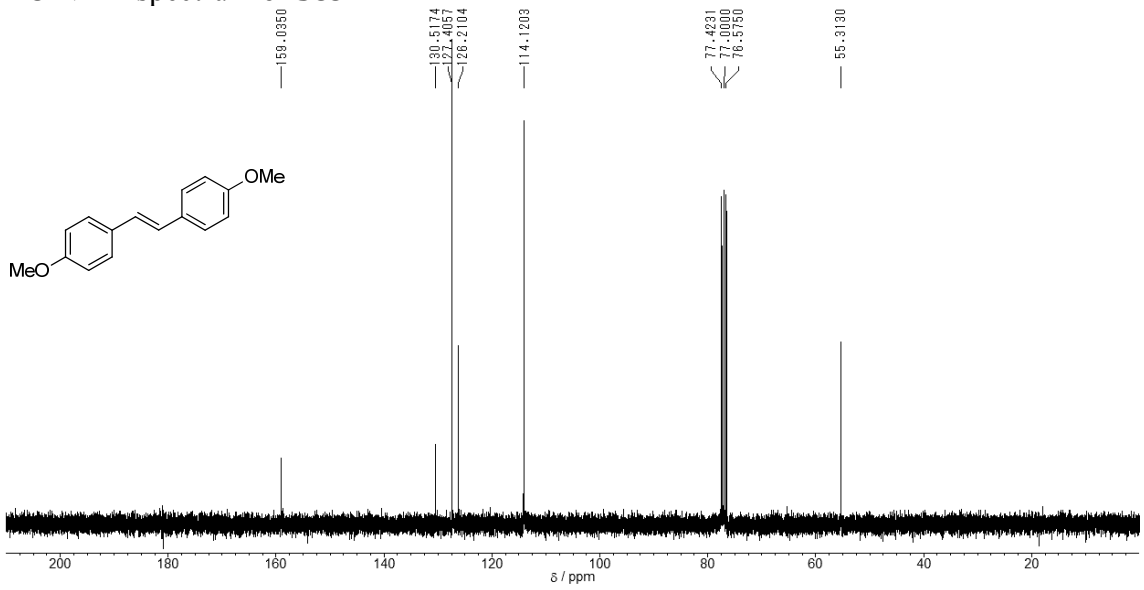
^{13}C NMR spectrum of **3bc**



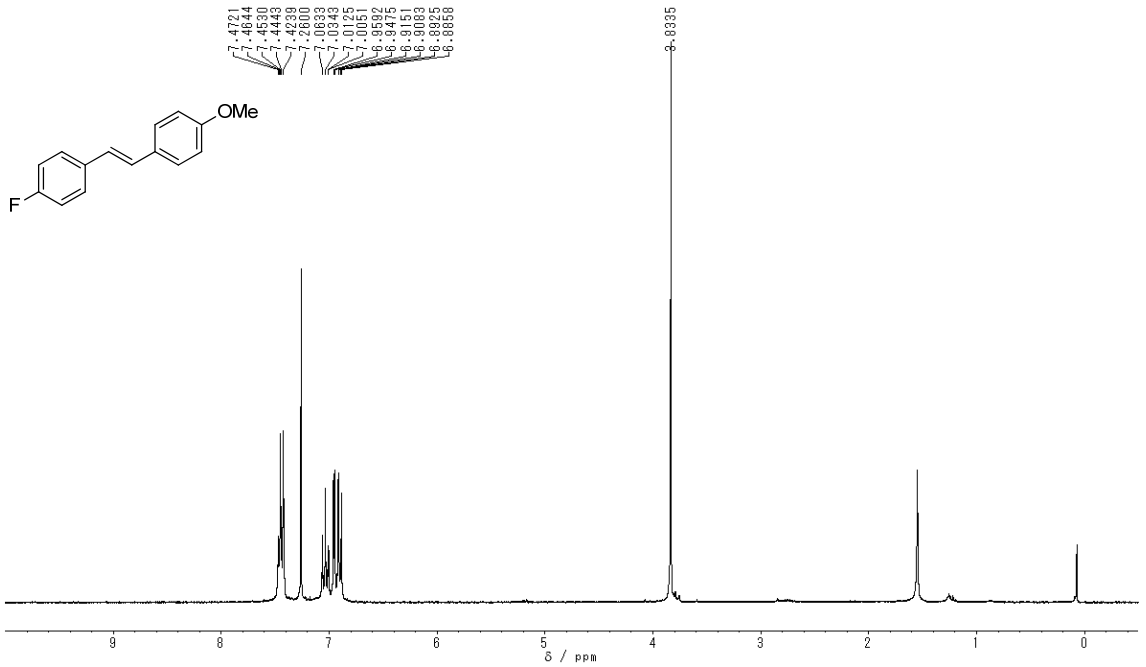
^{1}H NMR spectrum of **3cc**



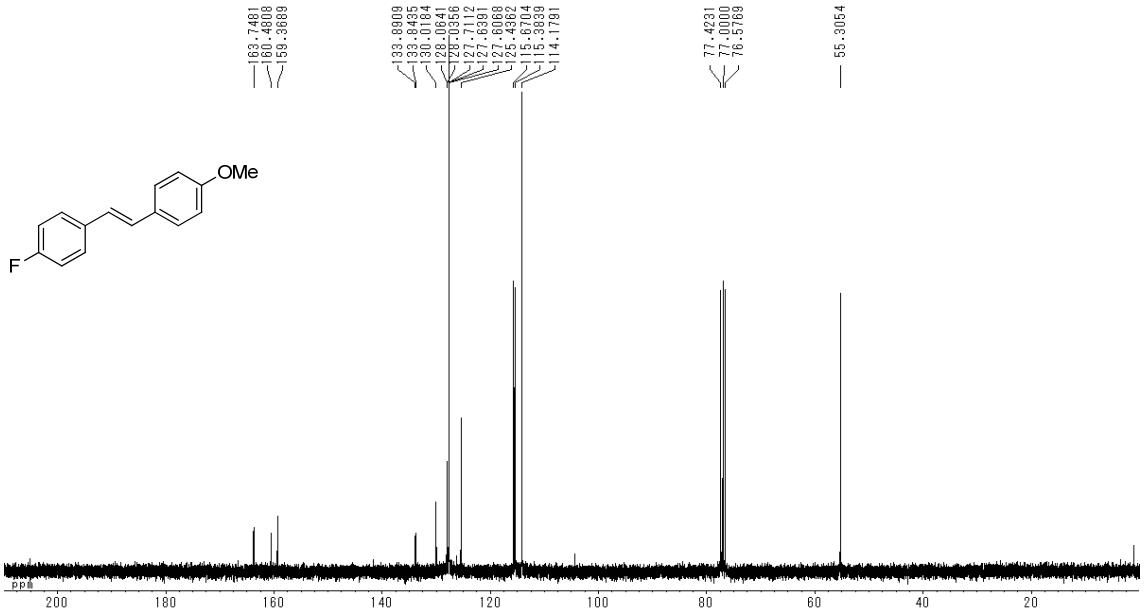
^{13}C NMR spectrum of **3cc**



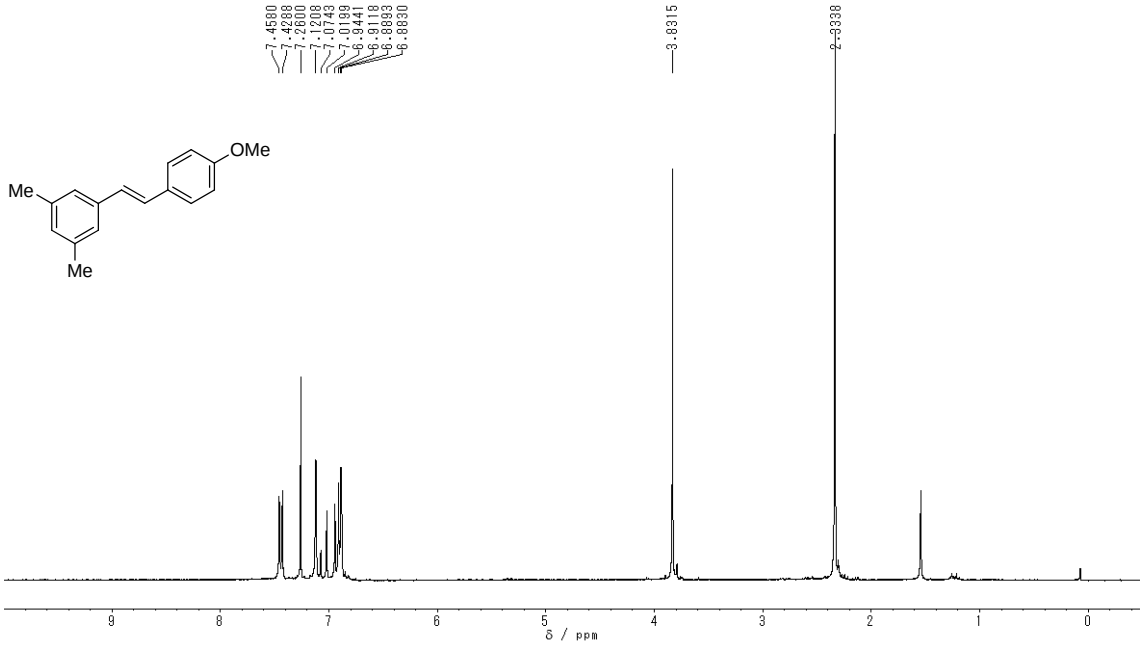
^{1}H NMR spectrum of **3cd**



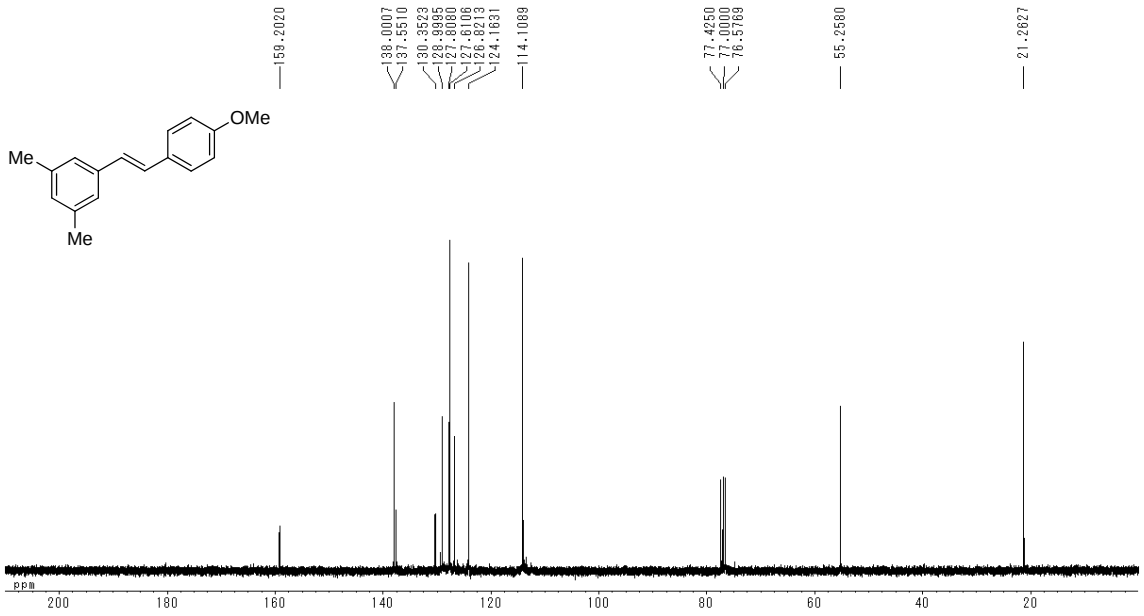
^{13}C NMR spectrum of **3cd**



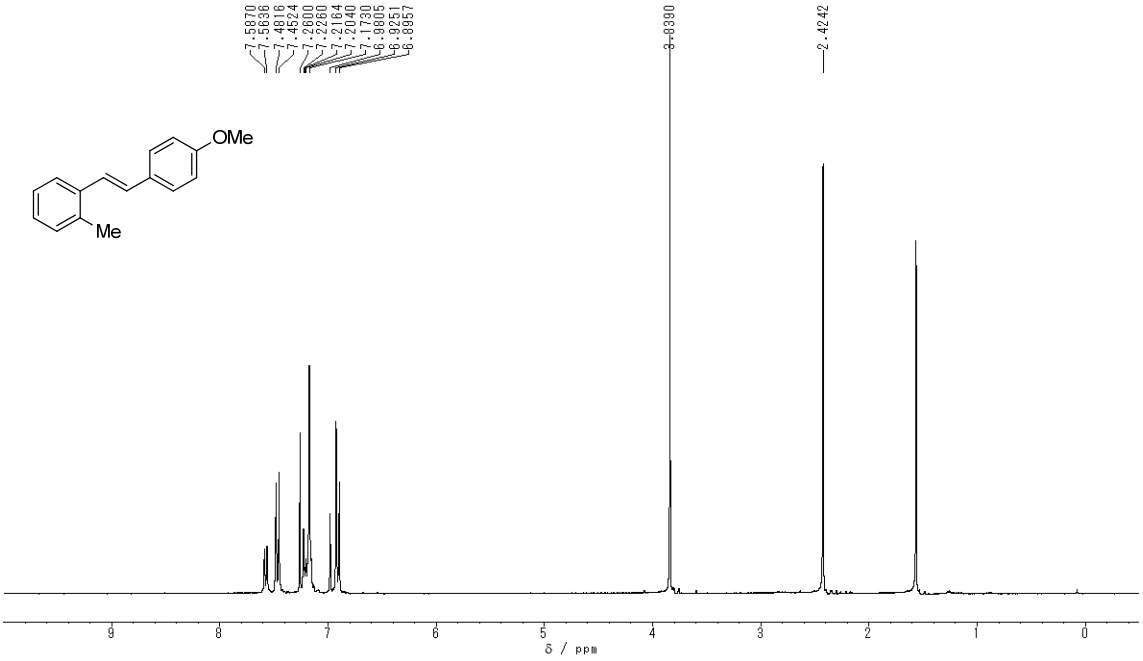
^{1}H NMR spectrum of **3cg**



^{13}C NMR spectrum of **3cg**



^{1}H NMR spectrum of **3ch**



^{13}C NMR spectrum of **3ch**