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Boraformylation and Silaformylation of Allenes

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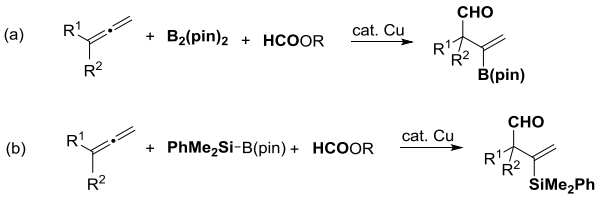
Abstract: Boraformylation of allenes proceeds using $B_2(pin)_2$ and a formate ester as boron and formyl sources, respectively, in the presence of a copper catalyst. The reaction selectively affords the corresponding β-boryl-β,γ-unsaturated aldehydes in good-to-high yields. In addition, silaformylation of allenes is achieved with a formate ester using $PhMe_2Si$–B(pin) as a silicon source.

Organoboronic acids and esters are versatile boryl functionalities in organic synthesis, especially for cross coupling reactions.[1] Thus, various preparation methods of organoboron compounds have been explored, typically hydroboration of carbon-carbon (C–C) unsaturated bonds[2] and reactions of boron electrophiles with organolithium or Grignard reagents.[1a] Being more common in organic synthesis, silyl functionalities achieve a variety of highly efficient transformations.[3]

Simultaneous incorporation of two different functionalities onto C–C unsaturated bonds is one of the most capable methodologies for the preparation of complex molecules. In particular, allenes (1,2-dienes) are valuable reaction platforms owing to their structurally diverse array of products.[4] However, this dual functionalization of allenes provides a range of regio- and stereoisomers. Thus, selective formation of desired products is a highly important task.

Herein, we report on boraformylation of allenes via simultaneous incorporation of boryl and formyl functionalities onto the C–C double bonds of allenes to afford β-boryl-β,γ-unsaturated aldehydes with high regioselectivity (Scheme 1a). The formyl moiety is a potent functionality, which can be further converted to useful compounds. It is frequently provided via oxidation of primary alcohols,[5] reduction of carboxylic acids,[5] and, in industry, via the hydroformylation of alkenes under CO/H_2 pressure.[6] We found that boraformylation of allenes was achieved by employing $B_2(pin)_2$ and a formate ester as boron and formyl sources, respectively, in the presence of a copper catalyst. Formate esters were used as a formyl source in Claisen-type condensation reactions.[7] To the best of our knowledge, this is the first report on the boraformylation of unsaturated substrates. Furthermore, silaformylation of allenes was achieved for the first time, by employing $PhMe_2Si$–B(pin) as a silicon source along with a formate ester (Scheme 1b).



Scheme 1. Boraformylation and Silaformylation of Allenes.

First, the reaction of 3-methyl-1,2-nonadiene (**1a**), $B_2(pin)_2$, and hexyl formate was conducted at 50 °C by employing 3.0 mol % of CuOAc and 4.0 mol % of a ligand in toluene (Table 1).[8] Impressively, the steric effect of the ligands strongly affected the reaction. PPh_3, dppe, xantphos, and dppbz[9] (Figure 1) were ineffective in the catalytic reaction, yielding the desired β-boryl-β,γ-unsaturated aldehyde (**2a**) in only trace amounts (entries 1–4). However, Xy-dppbz produced **2a** in 9% yield (entry 5). Finally, DTB-dppbz[10] and DTBM-dppbz ligands selectively afforded **2a** in 99% and 96% yields, respectively (entries 6 and 7). As for *N*-heterocyclic carbene (NHC) ligands, IPr gave **2a** in 32% yield (entry 8), whereas IMes did not produce this compound (entry 9). Benzyl formate (in place of hexyl formate) successfully afforded **2a** in 80%. yield (entry 10), although utilization of phenyl formate considerably decreased the yield (entry 11).

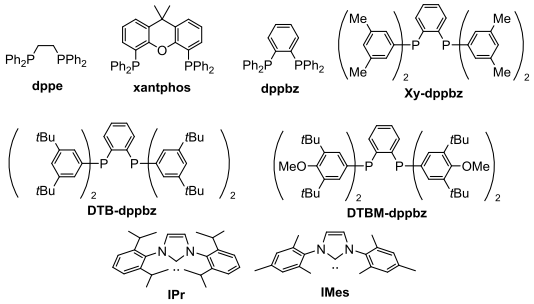
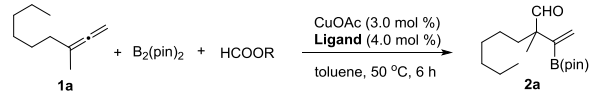


Figure 1. Structure of Ligands.

Table 1. Ligand Effect on the Cu-catalyzed boraformylation of **1a**[a]



Entry	Ligand	Formate R=	Yield [%][b]
1	PPh_3	C_6H_{13}	trace
2	dppe	C_6H_{13}	2
3	xantphos	C_6H_{13}	trace
4	dppbz	C_6H_{13}	trace
5	Xy-dppbz	C_6H_{13}	9
6	DTB-dppbz	C_6H_{13}	99
7	DTBM-dppbz	C_6H_{13}	96
8[c]	IPrCuCl/*t*BuOK	C_6H_{13}	32
9[d]	IMesCuCl/*t*BuOK	C_6H_{13}	0
10	DTBM-dppbz	$PhCH_2$	80
11	DTBM-dppbz	Ph	31

[a] Conditions: **1a** (0.30 mmol), $B_2(pin)_2$ (0.36 mmol, 1.2 equiv), formate (0.33 mmol, 1.1 equiv), CuOAc (3.0 mol %), ligand (4.0 mol %), in toluene (0.45 mL) at 50 °C for 6 h. [b] Determined by GC. [c] A mixture of IPrCuCl (3.0 mol %) and *t*BuOK (10 mol %) was used. [d] A mixture of IMesCuCl (3.0 mol %) and *t*BuOK (10 mol %) was used.

With DTBM-dppbz as the ligand, various allenes were employed as substrates under optimal reaction conditions (Table 2). Thus, 1,1-dialkyl-substituted allenes (**1a–d**) provided the corresponding β-boryl-β,γ-unsaturated aldehydes (**2a–d**) in good to high isolated yields (entries 1–4). In some cases, the addition of sodium laurate[11] (20 mol %) increased the catalytic activity. Actually, **1e** afforded the corresponding product (**2e**) in 78% isolated yield (entry 5) as compared to 65% GC yield in the absence of sodium laurate. With sodium laurate, allenes bearing several functionalities such as terminal olefins (**1e**), Cl-C(sp^2)(**1f**), I-C(sp^2)(**1g**), silyloxy (**1h**), acetal (**1i**), ester (**1j**), and carbamate (**1k**) provided the corresponding products (**2e–k**) in moderate-to-good yields (entries 5–11). As for mono-substituted allenes, 4,4-dimethyl-1,2-hexadiene (**1l**) did not afford the corresponding boraformylation products, even after full consumption.

The present procedure was amenable to a gram-scale reaction. Thus, starting from 0.83 g (6.0 mmol) of **1a**, 1.3 g of **2a** was obtained in 72% yield (Scheme 2a). Suzuki–Miyaura coupling[1a] of **2a** with 4-*tert*-butyliodobenzene smoothly afforded the product in 83% isolated yield (Scheme 2b). Coupling with β-bromostyrene also provided the corresponding diene in 58% yield (Scheme 2c). Horner-Wadsworth-Emmons reaction[12] of **2a** gave the olefinated product in a high isolated yield (Scheme 2d).

Formate esters, especially *aryl* formates, are known to decompose to CO,[13] thereby offering the opportunity to afford the boraformylation with the *in situ* CO evolved. However, hexyl formate did not convert upon removing both $B_2(pin)_2$ and **1a** from entry 1, Table 2. Furthermore, no boraformylation product (**2a**) was obtained (Eq 1) upon replacement of hexyl formate with a

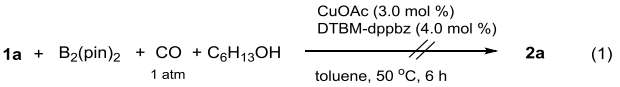
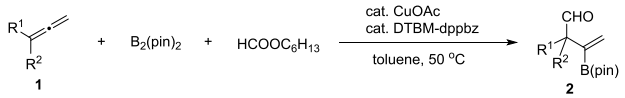
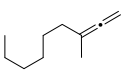
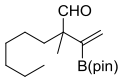
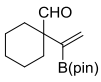
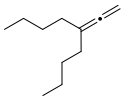
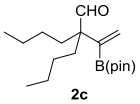
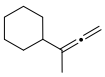
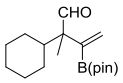
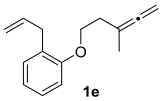
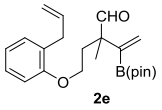
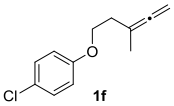
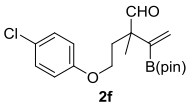
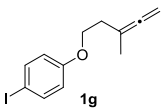
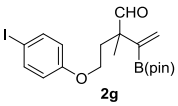
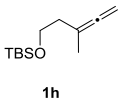
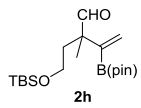
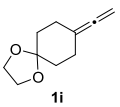
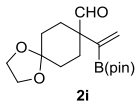
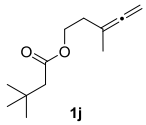
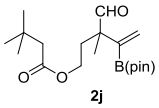
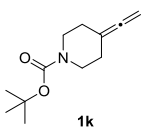
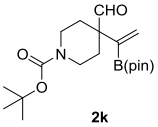
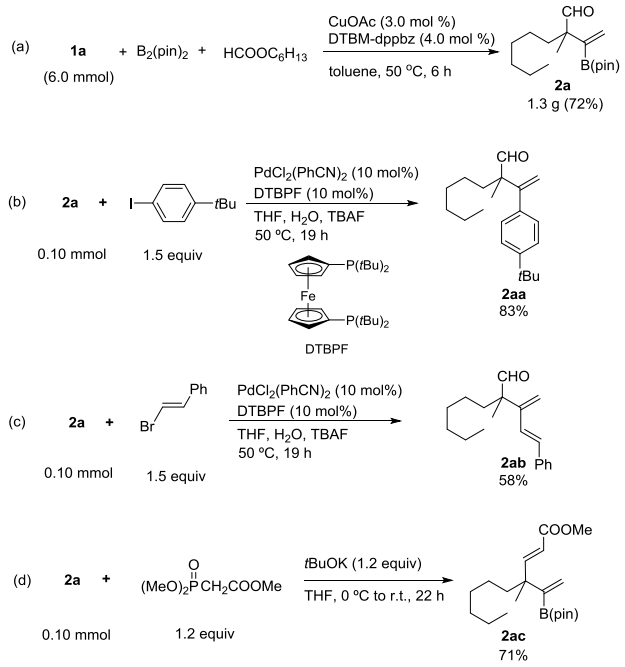


Table 2. Boraformylation of Various Allenes[a]



Entry	Allene **1**	Product **2**	Yield [%][b]
1	 **1a**	 **2a**	87
2	 **1b**	 **2b**	84
3[c]	 **1c**	 **2c**	64
4	 **1d**	 **2d**	46
5[d]	 **1e**	 **2e**	78
6[d]	 **1f**	 **2f**	74
7[d]	 **1g**	 **2g**	52
8[d]	 **1h**	 **2h**	73
9[d]	 **1i**	 **2i**	90
10[d]	 **1j**	 **2j**	56
11[d]	 **1k**	 **2k**	45

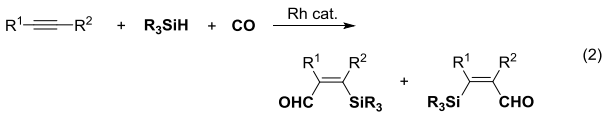
[a] Conditions of boraformylation: **1** (0.30 mmol), $B_2(pin)_2$ (0.36 mmol, 1.2 equiv), hexyl formate (0.33 mmol, 1.1 equiv), CuOAc (3.0 mol %), DTBM-dppbz (4.0 mol %), in toluene (0.45 mL) at 50 °C for 6 h. [b] Isolated yield of **2**. [c] For 16 h. [d] Sodium laurate (20 mol %) was added.



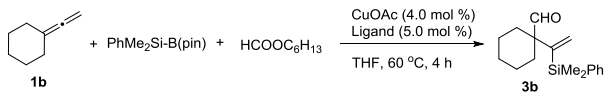
Scheme 2. Derivatization of Boraformylation Product

mixture of CO (1 atm) and hexanol. Thus, CO was not involved in the present boraformylation of allenes.

In the case of silaformylation (silylformylation)[14] of C–C unsaturated bonds, Matsuda et al. reported the Rh-catalyzed reaction of alkynes employing hydrosilanes under carbon monoxide (CO) pressure (Eq 2).[14a,b] Intramolecular silaformylation of alkenes also proceeded under CO (1,000

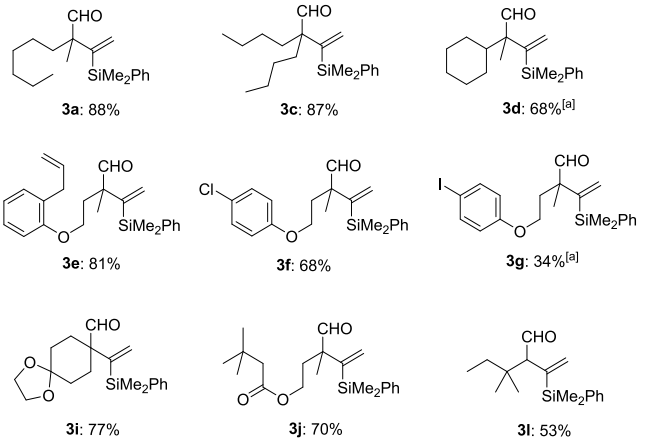


psi).[14h] However, there is no precedent for silaformylation of allenes. Silaformylation of allenes was found to proceed by employing a silylborane and a formate ester as silyl and formyl sources, respectively, in the presence of a copper catalyst (Scheme 1b). Note that toxic CO was not required in the present silaformylation. When the reaction of **1b** with $PhMe_2Si$–B(pin) and hexyl formate was conducted in THF at 60 °C, the silaformylation product (**3b**) was obtained in 91% GC and 86% isolated yields (Scheme 3a). Less bulky ligands such as Xy-dppbz and dppbz were not effective (Scheme 3b and c), which is in good agreement with the ligand effect observed in the boraformylation (Table 1).



	Ligand	Yield [%][a] of **3b**
(a)	DTBM-dppbz	91 (86)[b]
(b)	Xy-dppbz	25
(c)	dppbz	9

Scheme 3. Ligand Effect on Silaformylation. Reaction conditions: Reaction conditions, **1b** (0.20 mmol), $PhMe_2Si$–B(pin) (0.24 mmol, 1.2 equiv), hexyl formate (0.22 mmol, 1.1 equiv), CuOAc (4.0 mol %), ligand (5.0 mol %), in THF (0.20 mL) at 60 °C for 4 h. [a] By GC analysis. [b] Isolated yield.



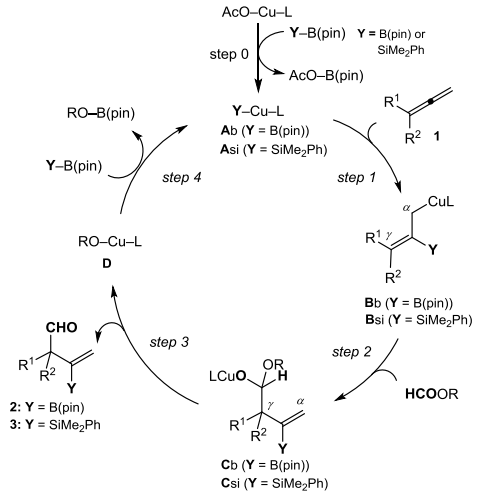
Scheme 4. Silaformylation of Various Allenes. Reaction conditions, **1a** (0.20 mmol), $PhMe_2Si$–B(pin) (0.24 mmol), hexyl formate (0.22 mmol), CuOAc (4.0 mol %), DTBM-dppbz (5.0 mol %), in THF (0.20 mL) at 60 °C for 4 h. Isolated yields of **3** were shown. [a] For 15 h.

Various allenes gave the corresponding β-silyl-β,γ-unsaturated aldehydes in good to high yields via the silaformylation reaction (Scheme 4). Functionalities such as terminal olefin (**3e**), Cl-C(sp^2) (**3f**), I-C(sp^2) (**3g**), acetal (**3i**), and ester (**3j**) were tolerated in the reaction. From the mono-substituted allene (**1l**), the corresponding silaformylation product (**3l**) was obtained in a moderate yield. Gram-scale silaformylation of **1b** (4.0 mmol) was also amenable and provided **3b** (1.0 g) in 95% yield.

Both the bora- and silaformylation proceeded following similar catalytic cycles (Scheme 5). It is known that boryl copper species (**A**b) is generated by the reaction of $B_2(pin)_2$ with Cu compounds.[15] Silyl copper species (**A**si) is also afforded upon reaction of $PhMe_2Si$–B(pin) with copper compounds.[16] Thus, **A**b and **A**si must be key catalyst species involved in the catalytic cycles (step 0). **A**b and **A**si subsequently add across a terminal double bond of an allene (**1**), generating β-boryl (**B**b)[17] and β-silyl (**B**si)[18] allylcopper intermediates (step 1). Next, **B**b and **B**si react with a formate ester at the γ-position to provide **C**b and **C**si via a six-membered ring transition state (step 2). β-Elimination from **C**b and **C**si produces **2** (Y = B(pin)) and **3** (Y = $SiMe_2Ph$) extruding alkoxycopper species **D** (step 3). It has been reported that ketones,[17e, 18b] aldehydes,[17e,18b,d] and imines[17f,g] react with **B**b and **B**si to give the corresponding allylated alcohols and amines. In the present reaction, the alkoxy moiety of a formate is efficiently removed as an alkoxy-Cu species (**D**) by copper species bearing significantly bulky ligands such as DTBM-dppbz and DTB-dppbz. Finally, σ-bond metathesis of **D** with $B_2(pin)_2$ and $PhMe_2Si$–B(pin) regenerates the active catalyst species **A**b and **A**si (step 4).

In conclusion, bora- and silaformylation of allenes were developed for the first time. In the case of boraformylation, $B_2(pin)_2$ was a good boron source, with formate ester as efficient formyl sources in the presence of a copper catalyst. The corresponding β-boryl-β,γ-unsaturated aldehydes were selectively obtained in good-to-high yields. In the case of

silaformylation, β-silyl-β,γ-unsaturated aldehydes were provided by employing $PhMe_2Si$–B(pin) as a silicon source with a formate ester. Further studies on the reaction mechanism and enantioselective reactions are now in progress.



Scheme 5. A Possible Catalytic Cycle.

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Keywords: Allene • Borylation • Copper •Formate Ester • Silylation

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[8] See Supporting Information for detail.

[9] Abbreviations: dppe = 1,2-bis(diphenylphosphino)ethane; xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; dppbz = 1,2-bis(diphenhylphosphino)benzene; Xy-dppbz = 1,2-bis(bis(3,5-dimethylphenyl)phosphino)benzene; DTB-dppbz = 1,2-bis(bis(3,5-di-*tert*-butylphenyl)phosphino)benzene; DTBM-dppbz = 1,2-bis(bis(3,5-di-*tert*-butyl-4-methoxyphenyl)phosphino)benzene; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazole-2-ylidene; IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazole-2-ylidene.

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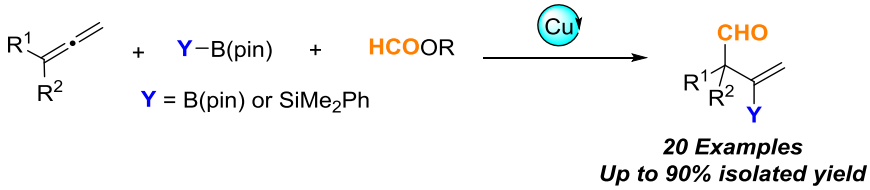
Entry for the Table of Contents



I

Boraformylation and silaformylation of allenes smoothly proceeds with a formate ester using $B_2(pin)_2$ and $PhMe_2Si–B(pin)$ as a boron and silicon sources, respectively, in the presence of a copper catalyst. The reaction selectively affords the corresponding β-boryl- or β-silyl-β,γ-unsaturated aldehydes in good-to-high yields with perfect regioselectivity.

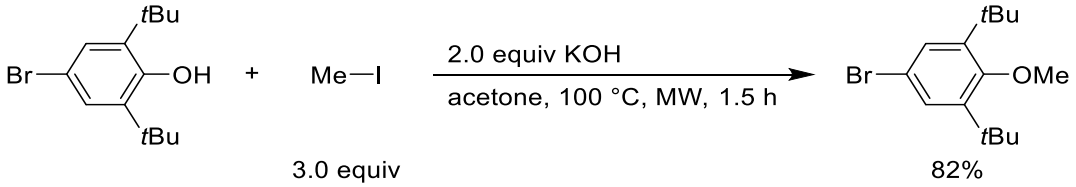
1. Instrumentation and Chemicals

Anhydrous THF and toluene were purchased from Kanto Chemical Co., Inc or Wako Pure Chemical Industries Ltd. and further purified by passage through activated alumina under positive argon pressure as described by Grubbs et al.[1] Unless otherwise noted, reactions were performed under an argon atmosphere using heat-gun-dried glassware on a dual-manifold Schlenk line. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL ECX-400P spectrometer or a Bruker AVANCE-500 spectrometer. Chemical shift values (δ) are reported in ppm and calibrated to tetramethylsilane (TMS, 0.00 ppm) residual protiated solvent (7.26 ppm in $CDCl_3$ or 7.16 ppm in C_6D_6-*d*$_6$) for ^{1}H and to $CDCl_3$ (77.0 ppm) or C_6D_6-*d*$_6$ (128.0 ppm) for ^{13}C. IR spectra were recorded on a Shimadzu IRTracer-100 FT-IR Spectrometer equipped with a Shimadzu MIRacle A (Ge) Single Reflection HATR. High-resolution mass spectra were obtained with a Thermo Fischer Scientific EXACTIVE spectrometer for ESI- and APCI-HRMS, a Thermo Fischer Scientific LTQ orbitrap XL spectrometer for MALDI-HRMS and a JEOL JMS-MS700 spectrometer for EI-HRMS. Elemental analysis was carried out at the Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. GC analysis was carried out using a Shimadzu GC-2014 equipped with a capillary column (GL Sciences InertCap 5, 0.25 mm × 30 m). TLC analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck Silica gel 60F_{254}. Column chromatography was carried out on silica-gel (Kanto N60, spherical, neutral, 63–210 μm or 40–50 μm). In the case of boron-containing products, a boronic-acid-doped silica-gel (B-silica-gel) was used.[2] Medium pressure liquid chromatography (MPLC) was performed on a Biotage Isorera One with a silica-gel column (Biotage SNAP Ultra 25 g or 10 g, HP-Sphere 25 μm). Microwave reaction was performed on a Biotage Initiator. .

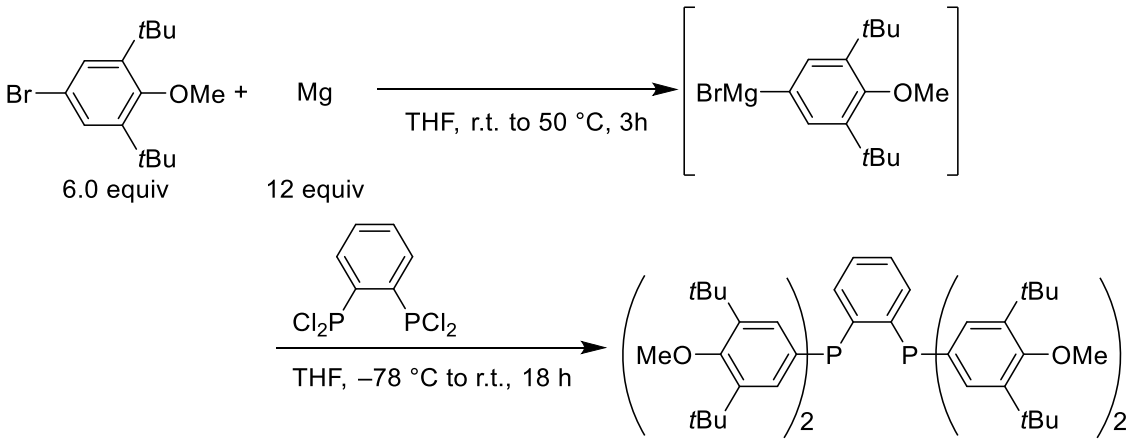
Hexyl formate was purified by distillation. $B_2(pin)_2$ were purified by recrystallization prior to use. Unless otherwise noted, chemicals obtained from commercial suppliers were used without further purification. 3,5-XydppBz,[3] allenes (**1a**–**d**, **1i**, **1k, 1h** and **1l**)[4] and $PhMe_2Si$–B(pin)[5] were synthesized according to the literatures.

2. Preparation of Materials

2-1. Preparation of 1,2-bis[bis(3,5-di-*tert*-buthylphenyl-4-methoxyphenyl)phosphino]benzene (DTBM-dppbz)



To a 20 mL vial were added 4-bromo-2,6-di-*tert*-butylphenol (8.6 g, 30 mmol), methyl iodide (5.6 mL, 90 mmol), KOH (3.4 g, 60 mmol), and acetone (6.0 mL). The vial was sealed and stirred at 100 °C for 1.5 h under microwave irradiation. After the reaction mixture was cooled to room temperature, CH_2Cl_2 (30 mL) and H_2O (30 mL) were added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (5 mL × 3). The combined organic layer was washed with H_2O (10 mL × 3), dried with Na_2SO_4, filtered, and then evaporated to dryness. The crude mixture was purified by silica-gel column chromatography (eluent: hexane) to give the product as slightly yellow crystals (7.3 g, 24 mmol, 82%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.33 (s, 2H), 3.67 (s, 3H), 1.40 (s, 18H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 158.8, 146.0, 129.5, 116.4, 64.4, 35.9, 31.9. All the resonances in ^{1}H and ^{13}C NMR spectra were in good agreement with literature values.[6]

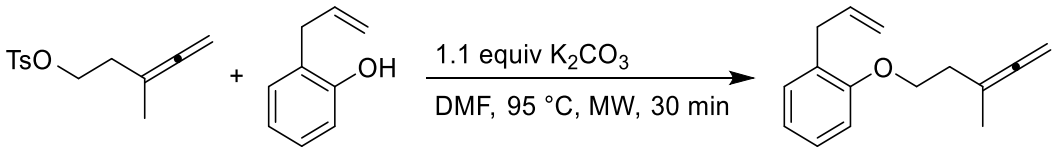


To a 200 mL 2-necked round flask with a dropping funnel was added Mg (1.7 g, 68 mmol) under Ar. The apparatus was dried, then evacuated and backfilled with Ar three times. 5-Bromo-1,3-di-*tert*-butyl-2-methoxybenzene (10 g, 34 mmol) was added into the dropping funnel. After THF (38 mL) was added into the dropping funnel, the THF solution was added dropwise for 15 min keeping the temperature around 35–50 °C. Then, the reaction mixture was stirred at 50 °C for 3 h to afford the corresponding Grignard reagent. To a dried 300 mL 2-necked round flask with a dropping funnel was added 1,2-bis(dichlorophosphino)benzene (1.6 g, 5.7 mmol) under Ar. Then, THF (7 mL) was added to the flask, the Grignard reagent was transferred to the dropping funnel. After the apparatus was cooled to –78 °C, the Grignard reagent was added dropwise for 15 min. The reaction mixture was stirred for 18 h from –78 °C to RT. After all volatile was removed *in vacuo*, CH_2Cl_2 (30 mL) and saturated $NaHCO_3$

aq. (15 mL) were added to the residue. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (10 mL × 3). The combined organic layer was washed with brine (10 mL × 3), dried with $MgSO_4$, filtered, evaporated, and then dried *in vacuo*. The residue was washed with MeOH under supersonic, and the solid was filtered and washed with MeOH. The solid was purified by silica-gel column chromatography (eluent: CH_2Cl_2) to give DTBM-dppbz as white solids (4.8 g, 4.7 mmol, 84%). **^{1}H NMR** (500 MHz, C_6D_6) δ: 7.50–7.42 (m, 10H), 7.00 (dd, *J* = 5.5, 3.4 Hz, 2H), 3.42 (s, 12H), 1.38 (s, 72H). **^{13}C NMR** (125 MHz, C_6D_6) δ: 160.3, 145.7 (t, *J* = 8.6 Hz), 143.7 (t, *J* = 3.8 Hz), 134.1 (t, *J* = 2.9 Hz), 133.1 (t, *J* = 11.0 Hz), 132.6 (t, *J* = 2.9 Hz), 129.0, 128.2 (t, *J* = 23.8 Hz,), 64.1, 36.1, 32.4. **^{31}P NMR** (202 MHz, C_6D_6) δ: –11.5. **Anal.** Calcd. for $C_{66}H_{96}O_4P$: C, 78.07; H, 9.53. Found: C, 77.49; H, 9.38.

2-2. Preparation of Allenes (1e-g, 1j)

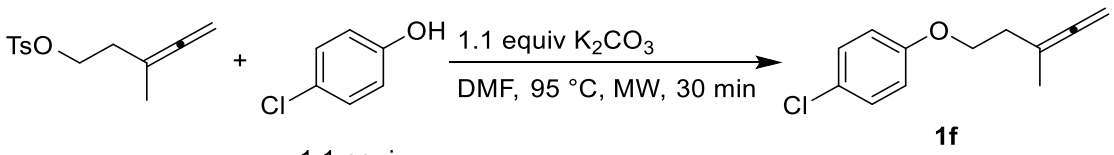
Preparation of allene 1e



1e
68%

To a 5 mL vial were added K_2CO_3 (0.15 g, 1.1 mmol), 2-allylphenol (0.15 g, 1.1 mmol), an allene[7,8] (0.25 g, 1.0 mmol), and DMF (0.75 mL). The vial was sealed and stirred at 95 °C for 30 min under microwave irradiation. After the mixture was cooled to room temperature, Et_2O (5 mL) and H_2O (5 mL) were added. The organic layer was separated and the aqueous layer was extracted with Et_2O (5 mL × 3). The combined organic layer was dried with Na_2SO_4, filtered, and then evaporated. The residue was dried with $MgSO_4$, filtered, evaporated, and then dried *in vacuo*. The crude mixture was purified by MPLC (eluent: hexane/ethyl acetate = 24:1) to give **1e** as a colorless liquid (145 mg, 0.68 mmol, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.20–7.13 (m, 2H), 6.92–6.84 (m, 2H), 6.05–5.96 (m, 1H), 5.10–5.02 (m, 2H), 4.66–4.62 (m, 2H), 4.08 (t, *J* = 6.7 Hz, 2H), 3.40 (d, *J* = 6.7 Hz, 2H), 2.47–2.43 (m, 2H), 1.78 (t, *J* = 3.1 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 206.42, 156.6, 137.1, 129.7, 128.9, 127.2, 120.5, 115.2, 111.3, 95.2, 74.5, 66.2, 34.4, 33.2, 19.0. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{19}O$, 215.1436; found, 215.1430. **Anal.** Calcd. for $C_{15}H_{18}O$: C, 84.07; H, 8.47. Found: C, 83.87; H, 8.32.

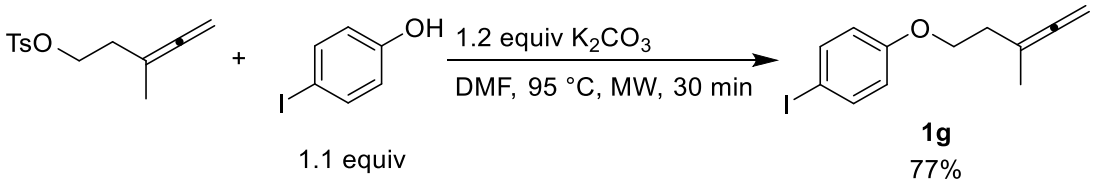
Preparation of allene 1f



1f
72%

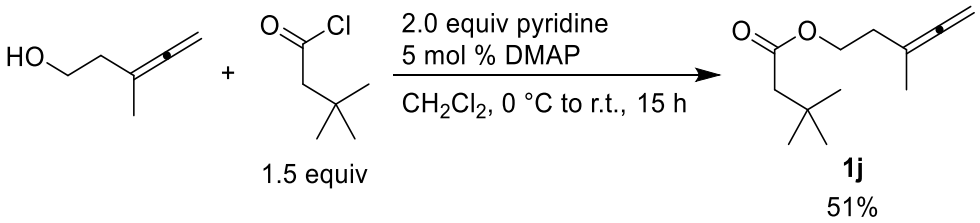
To a 5 mL vial were added K_2CO_3 (0.23 g, 1.6 mmol), 4-chlorophenol (0.21 g, 1.6 mmol), an allene (0.38 g, 1.5 mmol), and DMF (0.75 mL). The vial was sealed and the reaction mixture was stirred at 95 °C for 30 min under microwave irradiation. After the mixture was cooled to room temperature, Et_2O (5 mL) and H_2O (5 mL) were added. The organic layer was separated and the aqueous layer was extracted with Et_2O (5 mL × 4). The combined organic layer was dried with Na_2SO_4, filtered, and then evaporated. The residue was dried with $MgSO_4$, filtered, evaporated, and then dried *in vacuo*. The crude mixture was purified by MPLC (eluent: hexane/ethyl acetate = 49:1) to give **1f** as a colorless liquid (225 mg, 1.1 mmol, 72%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.22 (d, *J* = 8.9 Hz, 2H), 6.82 (d, *J* = 8.9 Hz, 2H), 4.66–4.61 (m, 2H), 4.03 (t, *J* = 6.9 Hz, 2H), 2.43–2.38 (m, 2H), 1.76 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 206.2, 157.6, 129.3, 125.5, 115.9, 95.0, 74.9, 66.6, 32.8, 19.1. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{14}ClO$, 209.0733; found, 209.0724. **Anal.** Calcd. for $C_{12}H_{13}ClO$: C, 69.07; H, 6.28. Found: C, 68.93; H, 6.37.

Preparation of allene 1g



To a 5 mL vial were added K_2CO_3 (0.25 g, 1.8 mmol), 4-iodophenol (0.36 g, 1.6 mmol), an allene (0.38 g, 1.5 mmol), and DMF (0.75 mL). The vial was sealed and the reaction mixture was stirred at 95 °C for 30 min under microwave irradiation. After the mixture was cooled to room temperature, Et_2O (5 mL) and H_2O (5 mL) were added. After the organic layer was separated and the aqueous layer was extracted with Et_2O (5 mL × 3). The combined organic layer was dried with $MgSO_4$, filtered, and then evaporated. The residue was dried with $MgSO_4$, filtered, evaporated, and then dried *in vacuo*. The crude mixture was purified by MPLC (eluent: hexane/ethyl acetate = 19:1) to give **1g** as a colorless liquid (346 mg, 1.2 mmol, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 7.54 (dt, *J* = 9.3, 2.6 Hz, 2H), 6.68 (dt, *J* = 9.3, 2.6 Hz, 2H), 4.66–4.62 (m, 2H), 4.03 (t, *J* = 6.9 Hz, 2H), 2.43–2.37 (m, 2H), 1.76 (t, *J* = 3.2 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 206.1, 158.8, 138.1, 117.0, 94.9, 82.6, 74.9, 66.3, 32.7, 19.1. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{14}IO$, 301.0089; found, 301.0076. **Anal.** Calcd. for $C_{12}H_{13}IO$: C, 48.02; H, 4.37. Found: C, 48.22; H, 4.41.

Preparation of allene 1j



To a 20 mL Schlenk tube were added CH_2Cl_2 solution (1 mL) of an allenol (0.29 g, 3.0 mmol), *N*,*N*-dimethylaminopyridine (DMAP, 18 mg, 0.15 mmol), pyridine (0.48 mL, 6.0 mmol), and CH_2Cl_2

(8 mL). After the mixture was cooled to 0 °C, 3,3-dimethylbutanoyl chloride (0.62 mL, 4.5 mmol) was added dropwise with syringe. The reaction mixture was stirred at 0 °C to room temperature for 15 h. The resulting solution was washed with 1 M HCl aq. (10 mL and 5 mL), saturated $NaHCO_3$ aq. (5mL × 2), and brine (5 mL). The organic layer was dried with Na_2SO_4, filtered, evaporated, and then dried *in vacuo*. The crude mixture was purified by MPLC twice (eluent: hexane/ethyl acetate =19:1 and 24:1) to give **1j** as colorless liquid (0.30 g, 1.5 mmol, 51%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 4.63–4.58 (m, 2H), 4.15 (t, *J* = 6.9 Hz, 2H), 2.28–2.23 (m, 2H), 2.18 (s, 2H), 1.70 (t, *J* = 3.1 Hz, 3H), 1.01 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 206.2, 172.3, 94.7, 74.8, 62.0, 48.0, 32.5, 30.6, 29.6, 18.7. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{12}H_{21}O_2$, 197.1536; found, 197.1535. **Anal.** Calcd. for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.20; H, 10.18.

3. Experimental Procedures

3.1. Optimization of Reaction Condition of Boraformylation of 1a (Table 1)

To a Schlenk tube filled with Ar was added CuOAc (1.1 mg, 9.0 μmol) and ligand (12 μmol). The tube was dried, then evacuated and backfilled with Ar three times. In the case of IPrCuCl or IMesCuCl, the complex (9.0 μmol) and *t*BuOK (1M THF solution, 30 μmol) was added. Toluene (0.25 mL), 3-methyl-1,2-nonadiene (**1a**, 55 μL, 0.30 mmol), and hexyl formate (49 μL, 0.33 mmol) were added to the Schlenk tube in this order. Then, a solution $B_2(pin)_2$ (91 mg, 0.36 mmol) in toluene (0.20 mL) in a Spitz tube was added to the Schlenk tube. The system was closed, and the mixture was stirred at 50 °C for 6 h. After tridecane (50 μL) was added as an internal standard, the resulting mixture was diluted with Et_2O (10 mL), and then an aliquot of the organic phase was filtered through a pad of Celite®. The filtrate was analyzed by GC.

3.2. A Procedure for Boraformylation of Allene (1) (Table 2)

To a Schlenk tube filled with Ar was added CuOAc (1.1 mg, 9.0 μmol) and DTBM-dppbz (12 mg, 12 μmol). In the case of entries 5–11, $C_{11}H_{23}CO_2K$ (14 mg, 60 μmol) was also added. The tube was dried, then evacuated and backfilled with Ar three times. Toluene (0.25 mL), allene (**1**, 0.30 mmol), and hexyl formate (49 μL, 0.33 mmol) were added to the Schlenk tube in this order. Then, a solution $B_2(pin)_2$ (91 mg, 0.36 mmol) in toluene (0.20 mL) in a Spitz tube was added to the Schlenk tube. The system was closed, and the mixture was stirred at 50 °C for 6 h. The resulting mixture was diluted with Et_2O (10 mL) and filtered through a pad of Celite®. The filtrate was evaporated and then dried *in vacuo*. The residue was purified by B-silica-gel column chromatography.

3.3. A Procedure of Pd-catalyzed Suzuki-Miyaura Coupling of 2a with an Aryl Iodide (Scheme 2b)

To a Schlenk tube filled with Ar was added $PdCl_2(PhCN)_2$ (3.8 mg, 10 μmol) and DTBPF (4.7 mg, 10 μmol). The tube was dried, then evacuated and backfilled with Ar three times. THF (0.40 mL) and **2a** (29 mg, 0.10 mmol) were added, then the mixture was stirred at room temperature for 30 min. TBAF (172 μL, 0.60 mmol), H_2O (40 μL), and 1-*tert*-butyl-4-iodobenzene (26 μL, 0.15 mmol) were added in this order. The system was closed, and the mixture was stirred at 50 °C for 19 h. The resulting mixture was diluted with Et_2O (10 mL) and filtered through a pad of Celite®. The filtrate was evaporated and dried *in vacuo*. The residue was purified by silica-gel column chromatography.

3.4. A Procedure of Pd-catalyzed Suzuki-Miyaura Coupling of 2a with an Alkenyl Bromide (Scheme 2c)

To a Schlenk tube filled with Ar was added $PdCl_2(PhCN)_2$ (3.8 mg, 10 μmol) and DTBPF (4.7 mg, 10 μmol). The tube was dried, then evacuated and backfilled with Ar three times. THF (0.40 mL) and **2a** (29 mg, 0.10 mmol) were added, then the mixture was stirred at room temperature for 30 min. TBAF (172 μL, 0.60 mmol), H_2O (40 μL), and *β*-bromostyrene (19 μL, 0.15 mmol) were added in this order. The system was closed, and the mixture was stirred at 50 °C for 19 h. The resulting mixture was

diluted with Et_2O (10 mL) and filtered through a pad of Celite®. The filtrate was evaporated and dried *in vacuo*. The residue was purified by silica-gel column chromatography.

3.5. Horner-Wadsworth-Emmons Olefination of 2a (Scheme 2d)

The Schlenk tube was dried, then evacuated and backfilled with Ar three times. After *t*BuOK (1.0 M in THF, 0.12 mL) was added, the solution was cooled to 0 ºC. Trimethyl phosphonoacetate (17 μL, 0.12 mmol) was added, and then stirred for 15 min at 0 ºC. After THF (0.18 mL) and **2a** (29 mg, 0.10 mmol) were added, then the system was closed, and the mixture was stirred at 0 ºC to RT for 22 h. The resulting mixture was diluted with Et_2O (10 mL) and filtered through a pad of Celite®. The filtrate was evaporated and then dried *in vacuo*. The residue was purified by B-silica-gel column chromatography.

3.6. A Procedure of the reaction for eq 1

To a Schlenk tube filled with Ar was added CuOAc (1.1 mg, 9.0 μmol) and DTBM-dppbz (12 mg, 12 μmol). The tube was dried, then evacuated and backfilled with CO. Toluene (0.25 mL), **1a** (0.30 mmol), and hexanol (41 μL, 0.33 mmol) were added to the Schlenk tube in this order. Then, a solution $B_2(pin)_2$ (91 mg, 0.36 mmol) in toluene (0.20 mL) in a Spitz tube was added to the Schlenk tube. The system was closed, and the mixture was stirred at 50 °C for 6 h. After tridecane (50 μL) was added as an internal standard, the resulting mixture was diluted with Et_2O (10 mL), and then an aliquot of the organic phase was filtered through a pad of Celite®. The filtrate was analyzed by GC.

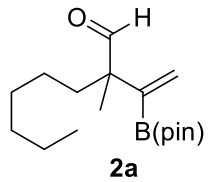
3.7. General Procedure for Silaformylation of 1b (Scheme 3)

To a Schlenk tube filled with Ar was added CuOAc (1.0 mg, 8.0 μmol) and ligand (10 μmol). The tube was dried, then evacuated and backfilled with Ar three times. THF (0.20 mL), 1,1-pentamethyleneallene (**1b**) (26 μL, 0.20 mmol), hexyl formate (32 μL, 0.22 mmol) and $PhMe_2Si$–B(pin) (66 μL, 0.24 mmol) were added in this order. The system was closed, and the mixture was stirred at 60 °C for 4 h. After tridecane (50 μL) was added as an internal standard, the resulting mixture was diluted with hexane (10 mL), and then an aliquot of the organic phase was filtered through a pad of Celite®. The filtrate was analyzed by GC.

3.8. A Procedure for the Cu-Catalyzed Silaformylation of allene (1) (Scheme 4)

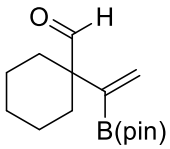
To a Schlenk tube filled with Ar were added CuOAc (1.0 mg, 8.0 μmol) and DTBM-dppbz (10 mg, 10 μmol). The tube was dried, then evacuated and backfilled with Ar three times. THF (0.20 mL), allene (**1**) (0.20 mmol), hexyl formate (32 μL, 0.22 mmol) and $PhMe_2Si$–B(pin) (66 μL, 0.24 mmol) were added in this order. The system was closed, and the mixture was stirred at 60 °C for 4 h. After tridecane (50 μL) was added as an internal standard, the resulting mixture was diluted with hexane (10 mL), and then an aliquot of the organic phase was filtered through a pad of Celite®. The residue was purified by silica-gel column chromatography.

4. Characterization of Products



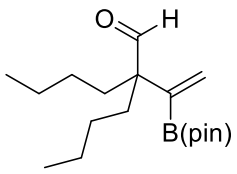
2a

Purified by B-silica-gel column chromatography (eluent: hexane/CH_2Cl_2/acetone = 150:10:1). Pale yellow oil (77 mg, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.55 (s, 1H), 6.02 (d, *J* = 2.1 Hz, 1H), 5.65 (d, *J* = 2.1 Hz, 1H), 1.85–1.79 (m, 1H), 1.64–1.58 (m, 1H), 1.29–1.24 (m, 18H), 1.17–1.11 (m, 5H), 0.86 (t, *J* = 6.9 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 204.8, 130.3, 83.6, 54.5, 34.5, 31.6, 29.9, 24.7, 24.6, 23.9, 22.6, 18.2, 14.0. **ESI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{17}H_{32}BO_3$, 295.2445; found, 295.2434.



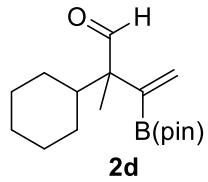
2b

Purified by B-silica-gel column chromatography (eluent: hexane/CH_2Cl_2/acetone = 150:10:1). Yellow oil (67 mg, 84%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.47 (s, 1H), 6.00 (s, 1H), 5.67 (s, 1H), 2.03–1.98 (m, 2H), 1.67–1.61 (m, 2H), 1.58–1.45 (m, 3H), 1.41–1.32 (m, 2H), 1.30–1.21 (m, 13H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 204.5, 130.7, 83.6, 54.9, 30.3, 25.7, 24.6, 22.6. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{15}H_{25}BO_3$, 265.1975; found, 265.1965.



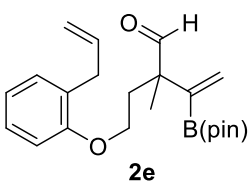
2c

Purified by B-silica-gel column chromatography (eluent: hexane/CH_2Cl_2/acetone = 150:10:1). Colorless oil (59 mg, 64%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.49 (s, 1H), 6.07 (d, *J* = 2.1 Hz, 1H), 5.66 (d, *J* = 2.1 Hz, 1H), 1.75–1.65 (m, 4H), 1.32–1.23 (m, 16H), 1.16–1.05 (m, 4H), 0.87 (t, *J* = 7.5 Hz, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 205.2, 130.7, 83.5, 57.4, 31.5, 26.0, 24.6, 23.4, 13.9. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{18}H_{34}BO_3$, 309.2601; found, 309.2586.



2d

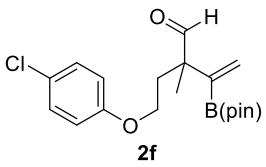
Purified by B-silica-gel column chromatography three times (eluent: hexane/CH_2Cl_2/acetone = 100:10:1, hexane/CH_2Cl_2 = 3:1, and hexane/CH_2Cl_2 = 5:1). White solid (41 mg, 46%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.73 (s, 1H), 6.03 (d, *J* = 1.5 Hz, 1H), 5.64 (d, *J* = 1.5 Hz, 1H), 2.22 (tt, *J* = 12.2, 3.1 Hz, 1H), 1.78–1.73 (m, 2H), 1.68–1.63 (m, 1H), 1.54–1.50 (m, 1H), 1.30–1.20 (m, 16H), 1.08 (s, 3H), 0.87 (dq, *J* = 12.5, 3.1 Hz, 1H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 205.4, 131.0, 83.7, 58.5, 41.1, 28.7, 27.3, 27.0, 27.0, 26.5, 24.8, 24.5, 13.2. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{17}H_{30}BO_3$, 293.2288; found, 293.2278.



2e

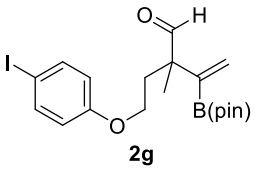
Purified by B-silica-gel column chromatography three times (eluent: hexane/CH_2Cl_2 = 6:1, hexane/CH_2Cl_2/acetone = 90:10:1, and hexane/CH_2Cl_2 = 3:1). Yellow oil (86 mg, 78%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.62 (s, 1H), 7.16–7.11 (m, 2H), 6.87 (dt, *J* = 7.3, 0.9 Hz, 1H), 6.79 (d, *J* = 8.2 Hz, 1H), 6.07 (d, *J* = 1.5 Hz, 1H), 5.98 (ddt, *J* = 16.8, 10.1, 6.7 Hz,1H), 5.73 (d, *J* = 1.5 Hz, 1H),

5.07–5.01 (m, 2H), 3.98–3.93 (m, 2H), 3.37–3.34 (m, 2H), 2.30 (t, *J* = 6.6 Hz, 2H), 1.30 (s, 3H), 1.25 (d, *J* = 1.5 Hz, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.5, 156.3, 137.0, 130.7, 129.7, 128.7, 127.2, 120.5, 115.3, 111.1, 83.8, 64.3, 53.2, 34.3, 34.3, 24.7, 24.6, 18.8. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{22}H_{32}BO_4$, 371.2394; found, 371.2379.



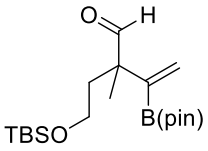
2f

Purified by B-silica-gel column chromatography (eluent: hexane/CH_2Cl_2/acetone = 90:10:1). White solid (80 mg, 74%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.58 (s, 1H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.77 (d, *J* = 8.9 Hz, 2H), 6.05 (s, 1H), 5.69 (s, 1H), 3.98–3.87 (m, 2H), 2.32–2.19 (m, 2H), 1.26 (s, 3H), 1.24 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.3, 157.2, 130.5, 129.2, 125.5, 115.8, 83.8, 64.6, 53.0, 34.0, 24.6, 24.6, 18.7. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{27}BClO_4$, 365.1691; found, 365.1680.



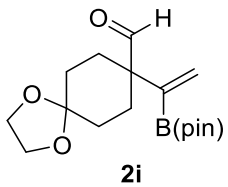
2g

Purified by B-silica-gel column chromatography twice (eluent: hexane/CH_2Cl_2/acetone = 90:10:1 and hexane/CH_2Cl_2 = 3:1).White solid (71 mg, 52%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.58 (s, 1H), 7.52 (d, *J* = 8.6 Hz, 2H), 6.63 (d, *J* = 8.6 Hz, 2H), 6.05 (d, *J* = 1.4 Hz, 1H), 5.70 (d, *J* = 1.4 Hz, 1H), 3.97–3.88 (m, 2H), 2.34–2.18 (m, 2H), 1.27 (s, 3H), 1.25 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.2, 158.5, 138.1, 130.5, 116.9, 83.8, 82.7, 64.4, 53.0, 33.9, 24.6, 24.6, 18.7. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{27}BIO_4$, 457.1047; found, 457.1033.



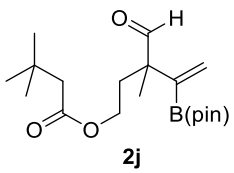
2h

Purified by B-silica-gel column chromatography three times (eluent: hexane/CH_2Cl_2/acetone = 100:10:1, hexane/CH_2Cl_2/acetone = 150:10:1, and hexane/CH_2Cl_2 = 6:1). Colorless oil (81 mg, 73%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.57 (s, 1H), 5.99 (d, *J* = 1.8 Hz, 1H), 5.65 (d, *J* = 1.8 Hz, 1H), 3.65-3.55 (m, 2H), 2.18-2.04 (m, 1H), 2.00-1.90 (m, 1H), 1.25 (s, 12H), 1.22 (s, 3H), 0.87 (s, 9H), 0.02 (s, 3H), 0.02 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 204.0, 129.8, 83.7, 59.4, 53.0, 37.9, 25.9, 24.7, 24.6, 18.4, 18.2, -5.4, -5.5. **ESI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{37}BO_4Si$, 391.2452; found, 391.2435.



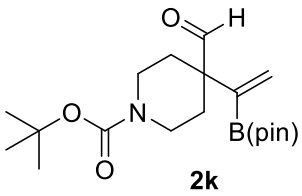
2i

Purified by B-silica-gel column chromatography (eluent: hexane/CH_2Cl_2/acetone = 60:10:1). Yellow oil (87 mg, 90%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.51 (s, 1H), 6.09 (s, 1H), 5.77 (s, 1H), 3.92 (s, 4H), 2.19–2.13 (m, 2H), 1.95–1.88 (m, 2H), 1.71–1.58 (m, 4H), 1.25 (s, 12H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.3, 131.8, 108.4, 83.7, 64.2, 64.2, 54.0, 31.3, 27.4, 24.6, 24.6. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{17}H_{28}BO_5$, 323.2030; found, 323.2018.



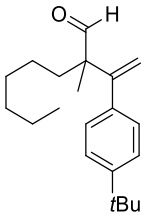
2j

Purified by B-silica-gel column chromatography twice (eluent: hexane/CH_2Cl_2/acetone = 30:10:1 and hexane/CH_2Cl_2/acetone = 80:10:1). Colorless oil (59 mg, 56%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.52 (s, 1H), 6.07 (s, 1H), 5.70 (s, 1H), 4.09–3.96 (m, 2H), 2.22–2.16 (m, 1H), 2.15 (s, 2H), 2.09–2.02 (m, 1H), 1.25 (s, 12H), 1.23 (s, 3H), 1.01 (s, 9H).**^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.2, 172.1, 131.1, 83.8, 60.5, 53.0, 47.8, 33.1, 30.7, 29.6, 24.7, 24.6, 18.3. **MALDI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{33}BNaO_5$, 375.23187; found, 375.23089.



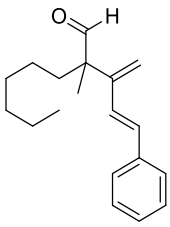
2k

Purified by B-silica-gel column chromatography (eluent: eluent: hexane/CH_2Cl_2/acetone = 60:10:1). Pale yellow solid (49 mg, 45%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.52 (s, 1H), 6.12 (d, *J* = 1.4 Hz, 1H), 5.73 (d, *J* = 1.4 Hz, 1H), 3.79–3.62 (m, 2H), 3.10 (t, *J* = 11.1 Hz, 2H), 2.12 (dt, *J* = 13.6, 3.6 Hz, 2H), 1.85–1.73 (m, 2H), 1.44 (s, 9H), 1.25 (s, 12H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 203.0, 154.8, 132.2, 83.9, 79.5, 77.2, 53.5, 29.5, 29.5, 28.4, 24.6. **EI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{32}BNO_5$, 365.2374; found, 365.2368.



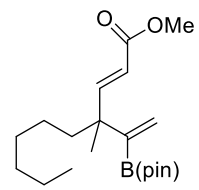
2aa

Purified by silica-gel column chromatography (eluent: hexane/Et_2O = 30:1). Pale yellow oil (23 mg, 83 μmol, 83%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.53 (s, 1H), 7.30 (d, *J* = 8.5 Hz ,2H), 7.03 (d, *J* = 8.5 Hz ,2H), 5.29 (s, 1H), 5.23 (s, 1H), 1.72–1.59 (m, 2H), 1.31 (s, 9H), 1.28–1.17 (m, 11H), 0.85 (t, *J* = 6.7 Hz ,3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.4, 150.1, 149.9, 138.4, 127.6, 124.8, 117.6, 55.6, 34.4, 34.0, 31.6, 31.3, 29.7, 23.8, 22.5, 18.9, 14.0. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{21}H_{33}O$, 301.2531; found, 301.2517.

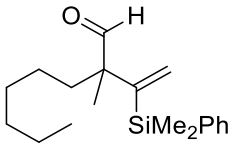


2ab

Purified by silica-gel column chromatography (eluent: hexane/Et_2O = 30:1). Yellow oil (16 mg, 58 μmol, 58%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.45 (s, 1H), 7.41–7.35 (m, 2H), 7.35–7.28 (m, 2H), 7.25–7.22 (m, 1H), 6.73 (d, *J* = 15.9 Hz, 1H), 6.57 (d, *J* = 15.9 Hz, 1H), 5.55 (s, 1H), 5.05 (s, 1H), 1.84–1.74 (m, 1H), 1.72–1.61 (m, 1H), 1.34–1.13 (m, 11H), 0.85 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.5, 146.1, 136.9, 130.8, 128.6, 127.8, 127.5, 126.6, 114.4, 54.6, 33.7, 31.6, 29.8, 23.6, 22.6, 18.3, 14.0. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{19}H_{27}O$, 271.2062; found, 271.2048.

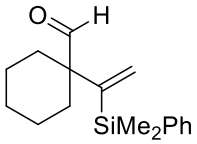


Purified by B-silica-gel column chromatography (eluent: hexane/CH_2Cl_2/acetone = 120:10:1).Colorless oil (25 mg, 71 μmol, 71%). **^{1}H NMR** (500 MHz, $CDCl_3$) *δ*: 7.15 (d, *J* = 15.9 Hz, 1H), 5.84 (d, *J* = 2.3 Hz, 1H), 5.72 (d, *J* = 15.9 Hz, 1H), 5.53 (d, *J* = 2.3 Hz, 1H), 3.72 (s, 3H), 1.75–1.64 (m, 1H), 1.62–1.52 (m, 1H), 1.24 (s, 20H), 1.20 (s, 3H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) *δ*: 167.6, 157.3, 128.1, 117.9, 83.3, 51.3, 44.8, 39.2, 31.7, 29.9, 29.6, 24.7, 24.6, 24.5, 22.8, 22.6, 14.1. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{20}H_{36}BO_4$, 351.2707; found, 351.2692.



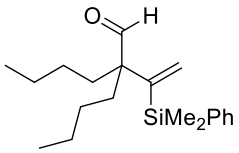
3a

Purified by column chromatography (eluent: hexane/CH_2Cl_2/acetone = 200:10:3). Colorless oil (54 mg, 88%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 9.28 (s, 1H), 7.51–7.50 (m, 2H), 7.36–7.34 (m, 3H), 5.81 (d, *J* = 1.4 Hz, 1H), 5.78 (d, *J* = 1.4 Hz, 1H), 1.64–1.55 (m, 2H), 1.31–0.97 (m, 11H), 0.86 (t, *J* = 7.0 Hz, 3H), 0.43 (s, 6H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ: 203.4, 150.4, 138.5, 133.8, 130.6, 129.0, 127.8, 56.5, 35.0, 31.6, 29.7, 23.9, 22.5, 19.1, 14.0, –0.7, –0.8. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.7. **IR** (ATR): 733.0, 775.4, 819.8, 835.2, 939.3, 1111.0, 1249.9, 1427.3, 1726.3, 2856.6, 2929.9, 2955.0. **MALDI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{30}OSiNa$, 325.1958; found, 325.1962.



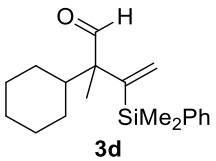
3b

Purified by column chromatography (eluent: hexane/CH_2Cl_2/acetone = 200:10:3). White opaque oil (47 mg, 86%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ:9.16 (s, 1H), 7.50–7.49 (m, 2H), 7.36–7.35 (m, 3H), 5.82 (s, 1H), 5.74 (s, 1H), 2.02–1.99 (m, 2H), 1.51–1.49 (m, 5H), 1.26–1.24 (m, 2H), 1.10–1.07 (m, 1H), 0.43 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.0, 150.2, 138.7, 133.8, 131.3, 129.0, 127.8, 57.2, 31.6, 25.4, 22.9, –0.5. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.3. **IR** (ATR): 733.0, 777.3, 817.8, 833.3, 906.5, 943.2, 1109.1, 1249.9, 1427.3, 1448.5, 1724.4, 2854.7, 2933.7. **ESI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{17}H_{24}OSiNa$, 295.1489; found, 295.1490.



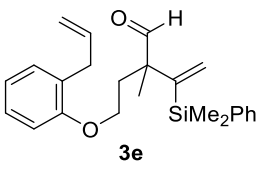
3c

Purified by column chromatography (eluent: hexane/CH_2Cl_2/acetone = 200:10:3). Colorless oil (54 mg, 87%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.24 (s, 1H), 7.53–7.49 (m, 2H), 7.37–7.32 (m, 3H), 5.85 (d, *J* = 1.2 Hz, 1H), 5.82 (d, *J* = 1.2 Hz, 1H), 1.65–1.57 (m, 4H), 1.22–0.87 (m, 8H), 0.82 (t, *J* = 7.3 Hz, 6H), 0.42 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.8, 149.5, 138.6, 133.8, 131.2, 129.0, 127.7, 59.8, 31.3, 25.9, 23.1, 13.9, –0.7. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.8. **IR** (ATR): 733.0, 775.4, 819.8, 835.2, 939.3, 1109.1, 1249.9, 1379.1, 1427.3, 1724.4, 2931.8, 2956.9. **ESI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{20}H_{32}OSiNa$, 339.2115; found, 339.2112.



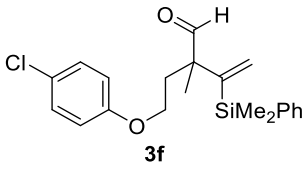
3d

Purified by column chromatography twice (eluent: hexane/CH_2Cl_2/acetone = 100:5:1, and hexane/CH_2Cl_2 = 5:1). Colorless oil (41 mg, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.33 (s, 1H), 7.51–7.44 (m, 2H), 7.38–7.31 (m, 3H), 5.91 (s, 1H), 5.85 (s, 1H), 1.95–1.86 (m, 1H), 1.76–1.55 (m, 4H), 1.45–1.38 (m, 1H), 1.28–0.96 (m, 7H), 0.89–0.79 (m, 1H), 0.43 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 203.6, 149.8, 138.7, 133.8, 131.2, 129.0, 127.8, 60.0, 42.0, 28.6, 26.8, 26.8, 26.7, 26.5, 14.3, –0.4, –0.6. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.4. **IR** (ATR): 702.1, 734.9, 777.3, 819.8, 835.2, 906.5, 937.4, 1109.1, 1249.9, 1427.3, 1450.5, 1722.4, 2852.7, 2927.9. **MALDI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{28}OSiNa$, 323.1802; found, 323.1808.



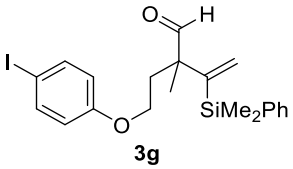
3e

Purified by column chromatography (eluent: hexane/CH_2Cl_2/acetone = 200:10:3). Colorless oil (61 mg, 81%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.33 (s, 1H), 7.51-7.49 (m, 2H), 7.35-7.32 (m, 3H), 7.15-7.09 (m, 2H), 6.87 (dd, *J* = 7.6, 7.6 Hz, 1H), 6.68 (d, *J* = 7.6 Hz, 1H), 5.98-5.89 (m, 1H), 5.87 (s, 1H), 5.84 (s, 1H), 5.04-5.02 (m, 1H), 5.00 (s, 1H), 3.80 (t, *J* = 6.6 Hz, 2H), 3.35-3.25 (m, 2H), 2.24-2.17 (m, 1H), 2.12-2.06 (m, 1H), 1.23 (s, 3H), 0.45 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 202.0, 156.2, 150.0, 138.1, 136.9, 133.8, 131.3, 129.7, 129.2, 128.6, 127.9, 127.1, 120.5, 115.3, 110.9, 64.0, 55.1, 34.8, 34.2, 19.6, -0.8, -0.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.4. **IR** (ATR): 702.1, 734.9, 750.3, 777.3, 817.8, 835.2, 912.3, 943.2, 997.2, 1022.3, 1047.4, 1109.1, 1240.2, 1427.3, 1454.3, 1475.5, 1492.9, 1600.9, 1724.4. **ESI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{24}H_{30}O_2SiNa$, 401.1907; found, 401.1902. **Anal.** Calcd. for $C_{24}H_{30}O_2Si$: C, 76.14; H, 7.99. Found: C, 76.23; H, 7.97.



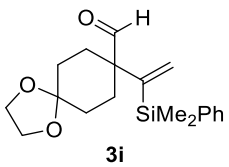
3f

Purified by column chromatography twice (eluent: hexane/CH_2Cl_2/acetone = 200:10:3). White solid (51 mg, 68%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.31 (s, 1H), 7.50–7.48 (m, 2H), 7.35–7.33 (m, 3H), 7.18 (d, *J* = 9.2 Hz, 2H), 6.69 (d, *J* = 9.2 Hz, 2H), 5.84 (s, 1H), 5.83 (s, 1H), 3.81–3.72 (m, 2H), 2.20–2.14 (m, 1H), 2.08–2.02 (m, 1H), 1.20 (s, 3H), 0.45 (s, 3H), 0.44 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 201.9, 157.1, 149.8, 138.1, 133.8, 131.3, 129.2, 129.2, 127.9, 125.5, 115.6, 64.4, 55.0, 34.4, 19.6, –0.8, –0.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.4. **IR** (ATR): 704.0, 733.0, 771.5, 785.0, 819.8, 827.5, 902.7, 950.9, 1018.4, 1030.0, 1087.9, 1109.1, 1246.0, 1290.4, 1469.8, 1494.8, 1712.8. **APCI-HRMS** (*m*/*z*): $[M+H]^+$ calcd for $C_{21}H_{26}ClO_2Si$, 373.1358; found, 373.1378.



3g

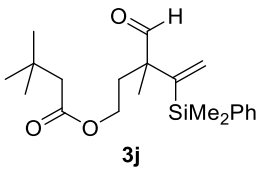
Purified by column chromatography three times (eluent: hexane/CH_2Cl_2/acetone = 200:10:3, hexane/CH_2Cl_2 = 5:1 to hexane/CH_2Cl_2/acetone = 50:10:3, and hexane/CH_2Cl_2 = 5:1). White solid (32 mg, 34%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.31 (s, 1H), 7.52–7.47 (m, 4H), 7.36–7.32 (m, 3H), 6.54 (d, *J* = 8.9 Hz, 2H), 5.84 (s, 1H), 5.83 (s, 1H), 3.80–3.70 (m, 2H), 2.19–2.13 (m, 1H), 2.08–2.02 (m, 1H), 1.19 (s, 3H), 0.45 (s, 3H), 0.44 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 201.9, 158.3, 149.8, 138.1, 138.1, 133.8, 131.3, 129.3, 127.9, 116.8, 82.7, 64.2, 55.0, 34.4, 19.6, –0.8, –0.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.4. **IR** (ATR): 702.1, 734.9, 777.3, 817.8, 835.2, 943.2, 999.1, 1020.3, 1058.9, 1111.0, 1174.7, 1242.2, 1280.7, 1400.3, 1427.3, 1475.5, 1485.2, 1585.5, 1722.4. **ESI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{25}IO_2SiNa$, 487.0561; found, 478.0554.



3i

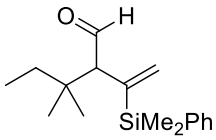
Purified by column chromatography (eluent: eluent: hexane/CH_2Cl_2/acetone = 100:10:3). Colorless oil (51.2 mg, 77%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.17 (s, 1H), 7.52–7.44 (m, 2H), 7.39–7.29 (m, 3H), 5.83 (s, 1H), 5.75 (s, 1H), 3.88 (s, 4H), 2.08–1.95 (m, 2H), 1.88–1.77 (m, 2H), 1.62–1.53 (m, 2H), 1.52–1.42 (m, 2H),

0.44 (s, 6H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 202.1, 148.9, 138.3, 133.8, 131.7, 129.1, 127.8, 108.0, 64.2, 64.2, 56.2, 31.5, 28.5, –0.7. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.1. **IR** (ATR): 731.0, 779.2, 821.7, 875.7, 945.1, 997.2, 1033.9, 1109.1, 1251.8, 1369.5, 1427.3, 1720.5, 2955.0. **ESI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{19}H_{26}O_3SiNa$, 353.1543; found, 353.1538.



3j

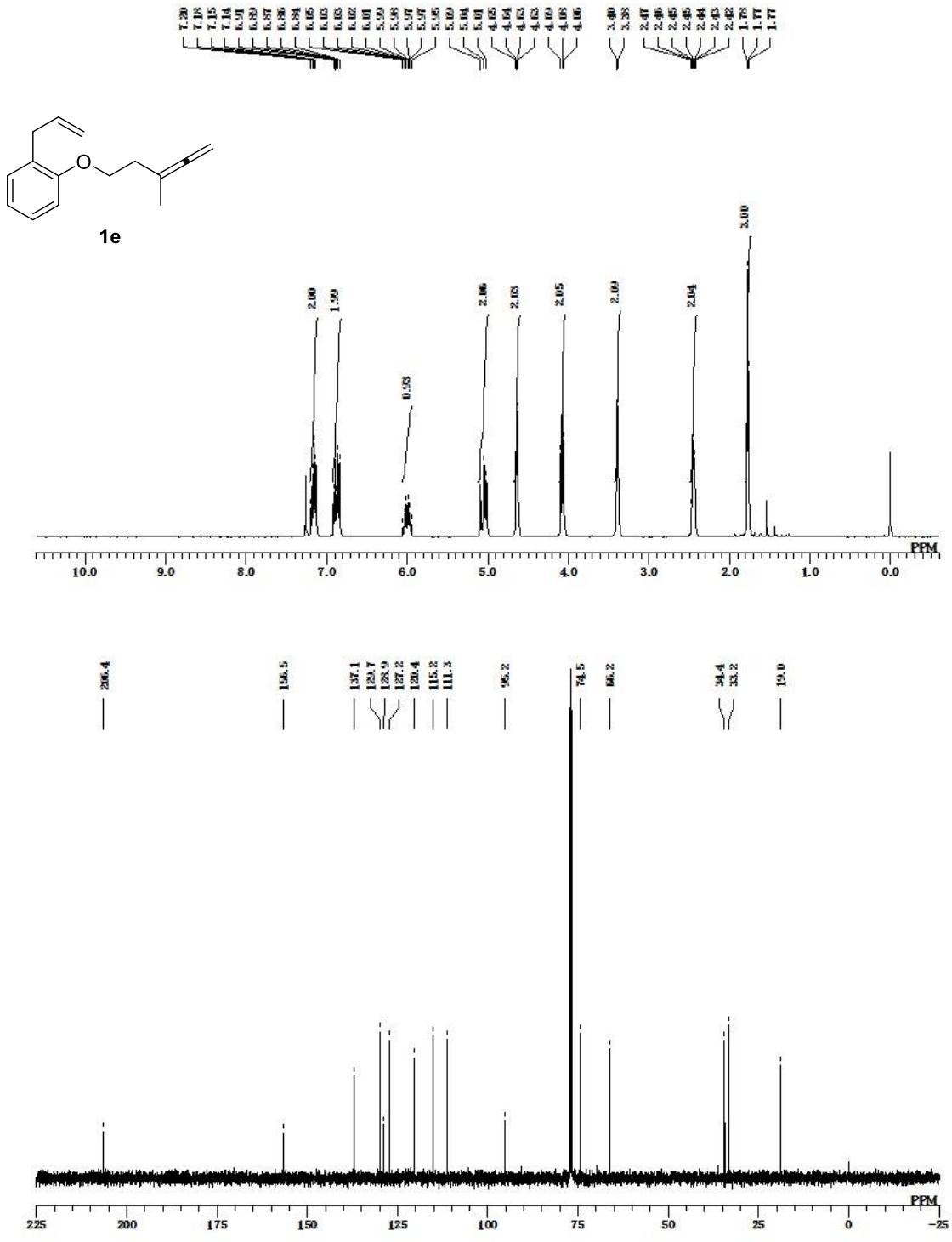
Purified by column chromatography twice (eluent: eluent: hexane/CH_2Cl_2/acetone = 60:10:3, and eluent: hexane/CH_2Cl_2/acetone = 100:10:3). Colorless oil (50.6 mg, 70%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.24 (s, 1H), 7.51–7.47 (m, 2H), 7.37–7.33 (m, 3H), 5.83 (s, 1H), 5.82 (s, 1H), 3.92 (t, *J* = 7.3 Hz, 2H), 2.12 (s, 2H), 2.01–1.91 (m, 2H), 1.17 (s, 3H), 0.99 (s, 9H), 0.44 (s, 3H), 0.43 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 201.7, 172.0, 149.4, 137.9, 133.8, 131.4, 129.2, 127.9, 60.3, 54.9, 47.8, 33.5, 30.6, 29.6, 19.3, –0.8, –0.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –7.4. **IR** (ATR): 702.1, 734.9, 777.3, 819.8, 835.2, 943.2, 999.1, 1111.0, 1130.3, 1228.7, 1249.9, 1323.2, 1367.5, 1429.3, 1465.9, 1728.2, 2958.8. **ESI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{21}H_{32}O_3SiNa$, 383.2013; found, 383.2005. **Anal.** Calcd. for $C_{21}H_{32}O_3Si$: C, 69.95; H, 8.95. Found: C, 70.00; H, 8.96.

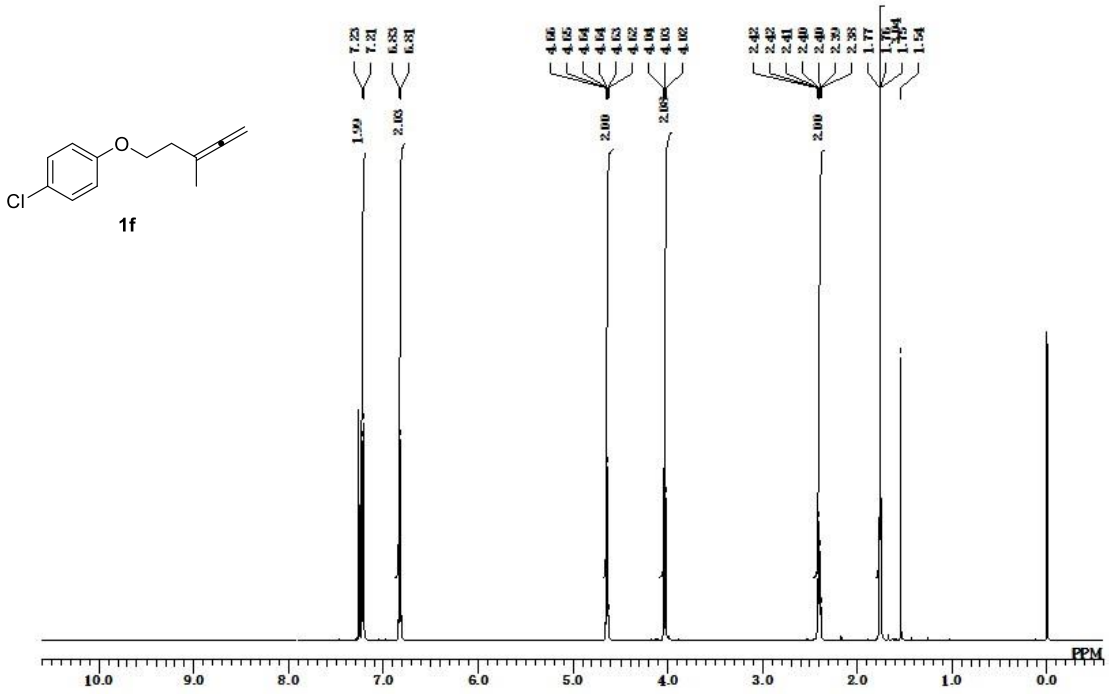


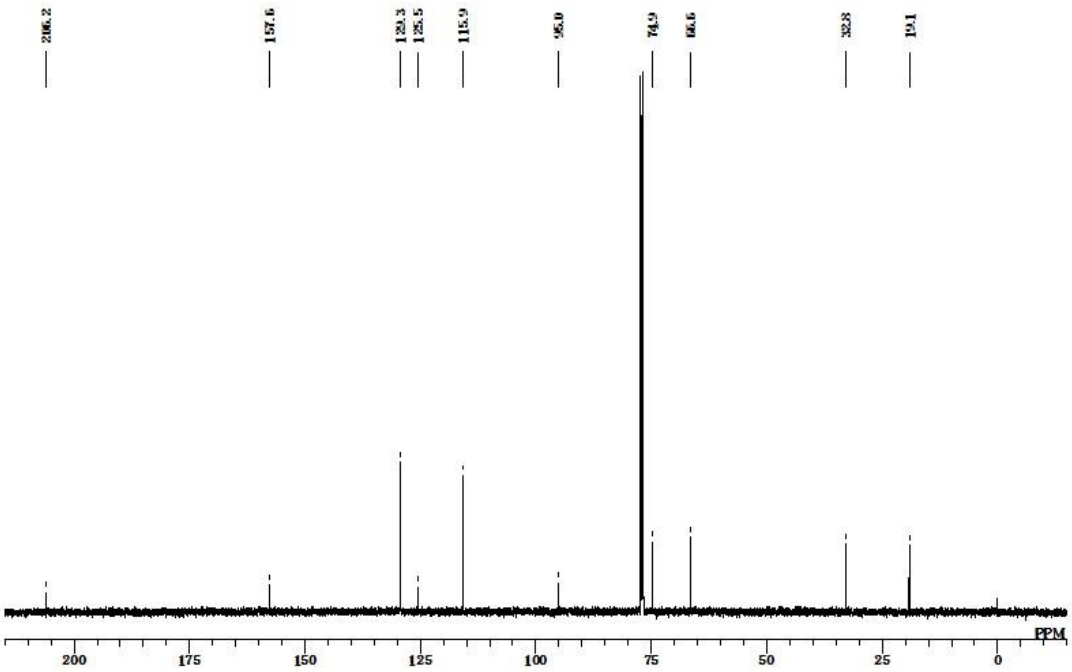
3l

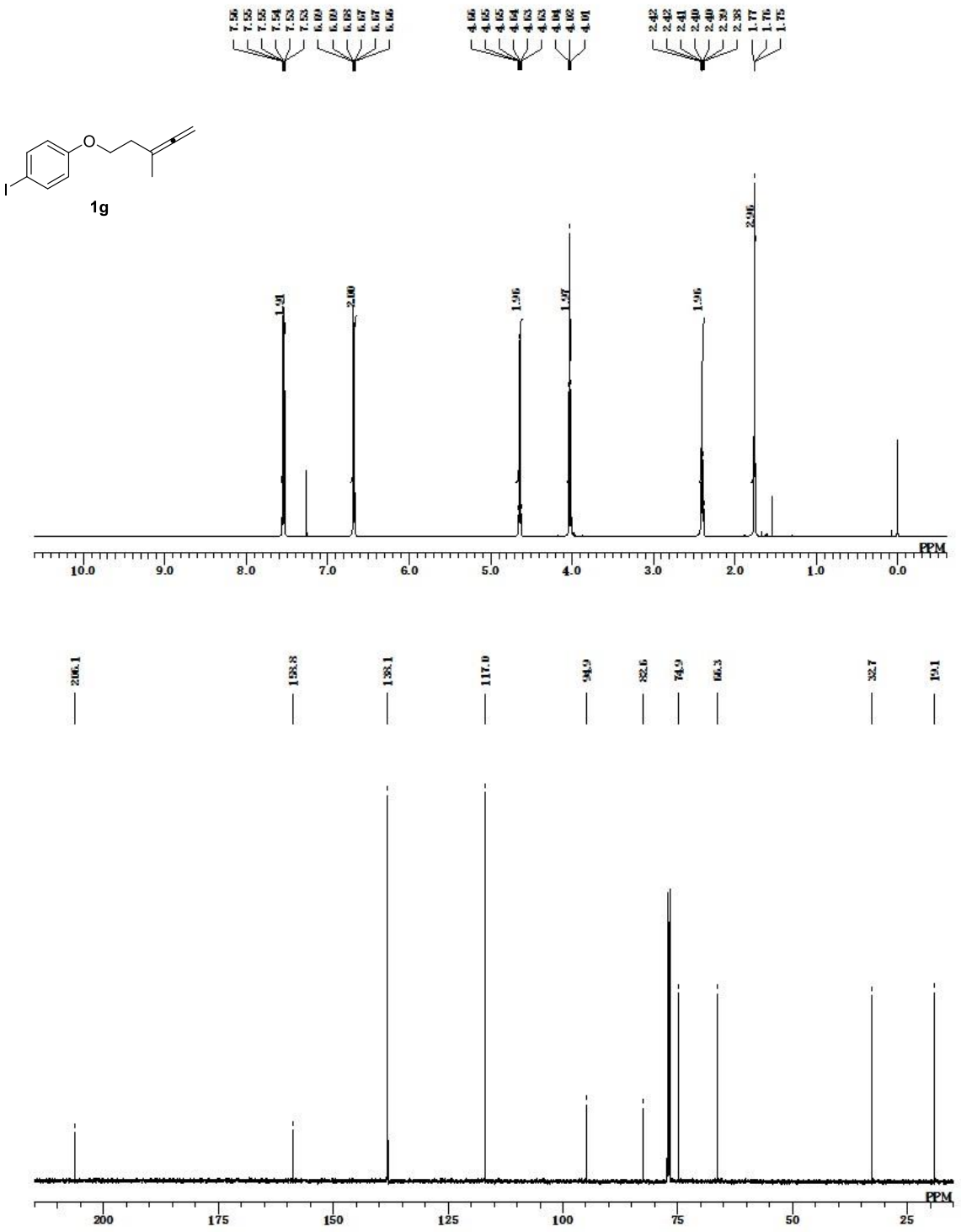
Purified by column chromatography three times (eluent: hexane/CH_2Cl_2/acetone = 200:10:3, hexane/acetone = 100:1, and hexane/CH_2Cl_2 = 5:1). Colorless oil (29 mg, 53%). **^{1}H NMR** (500 MHz, $CDCl_3$) δ: 9.58 (d, *J* = 4.7 Hz, 1H), 7.55–7.44 (m, 2H), 7.41–7.29 (m, 3H), 6.05 (s, 1H), 5.88 (s, 1H), 2.97 (d, *J* = 4.7 Hz, 1H), 1.42–1.30 (m, 1H), 1.29–1.18 (m, 1H), 0.96 (s, 3H), 0.82 (s, 3H), 0.75 (t, *J* = 7.5 Hz, 3H), 0.40 (s, 3H), 0.39 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ: 202.1, 144.8, 137.0, 134.1, 132.4, 129.3, 127.8, 63.0, 37.9, 33.6, 24.6, 8.0, –2.8, –2.9. **^{29}Si NMR** (99 MHz, $CDCl_3$) δ: –6.0. **IR** (ATR): 734.9, 777.3, 817.8, 833.3, 941.3, 1111.0, 1249.9, 1427.3, 1716.7, 2964.6. **APCI-HRMS** (*m*/*z*): $[M+Na]^+$ calcd for $C_{17}H_{26}OSiNa$, 297.1645; found, 297.1639.

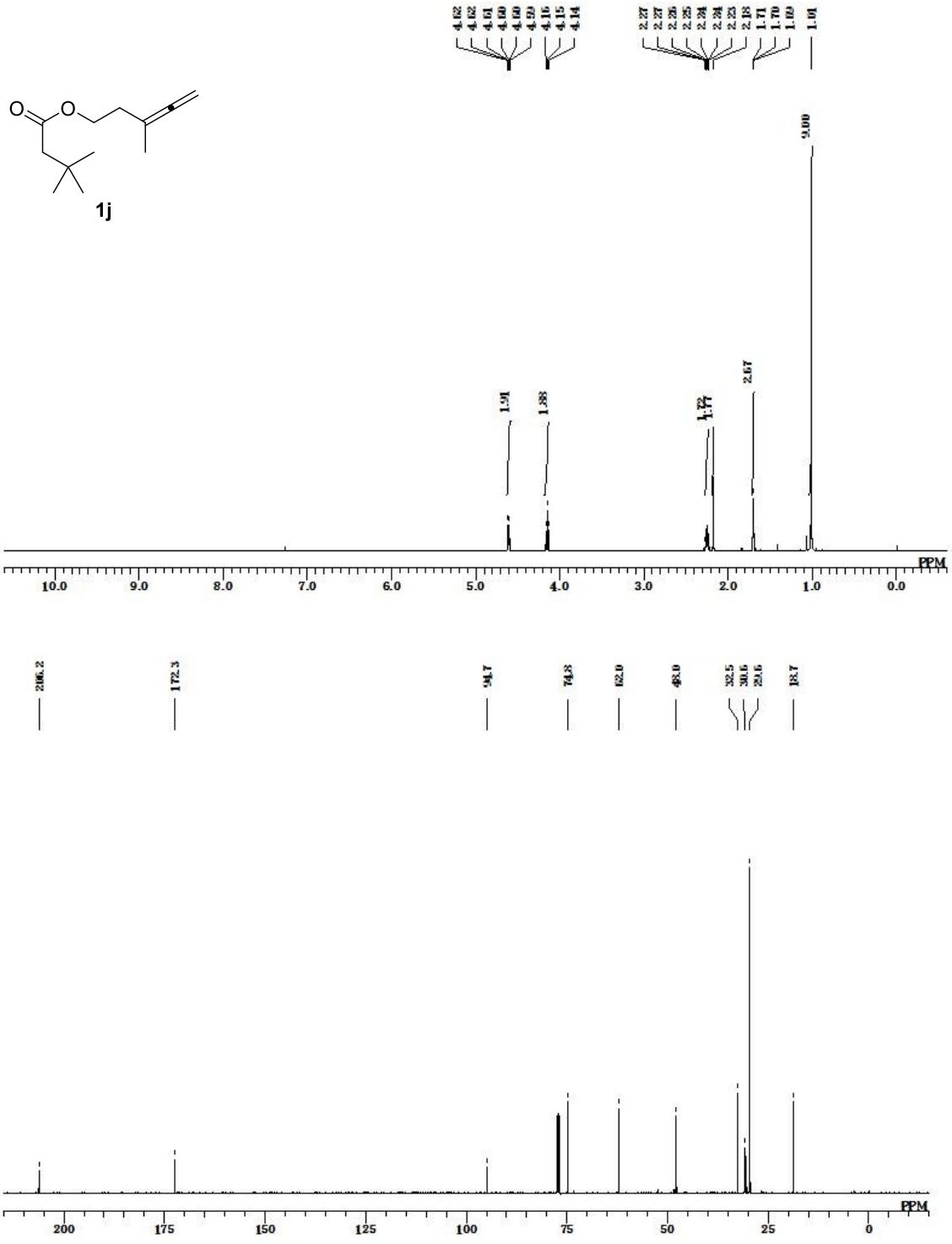
6. NMR Charts



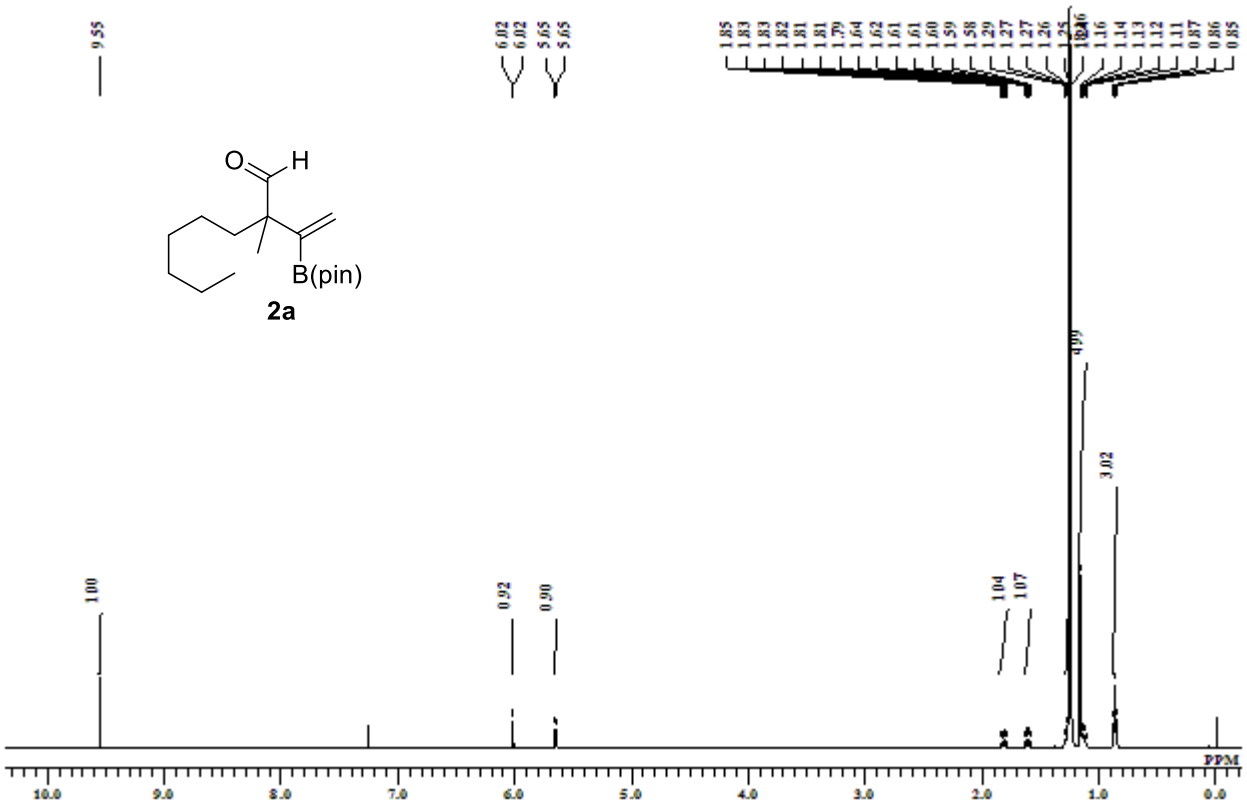


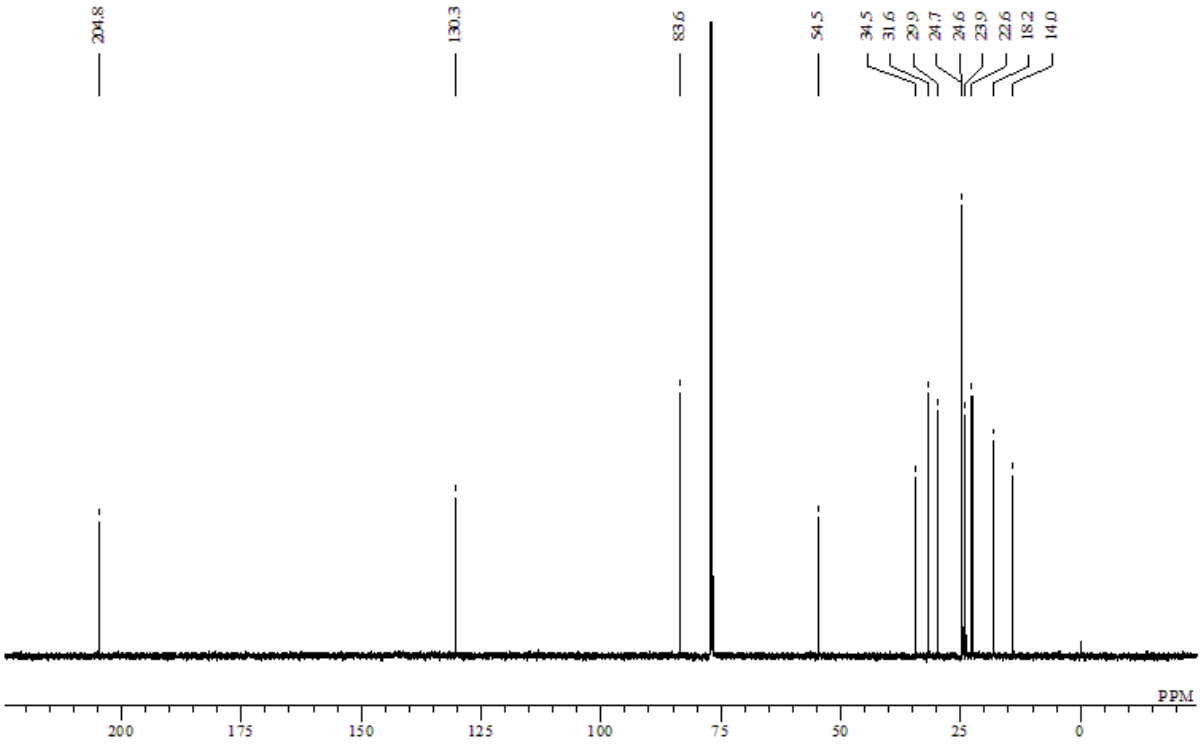


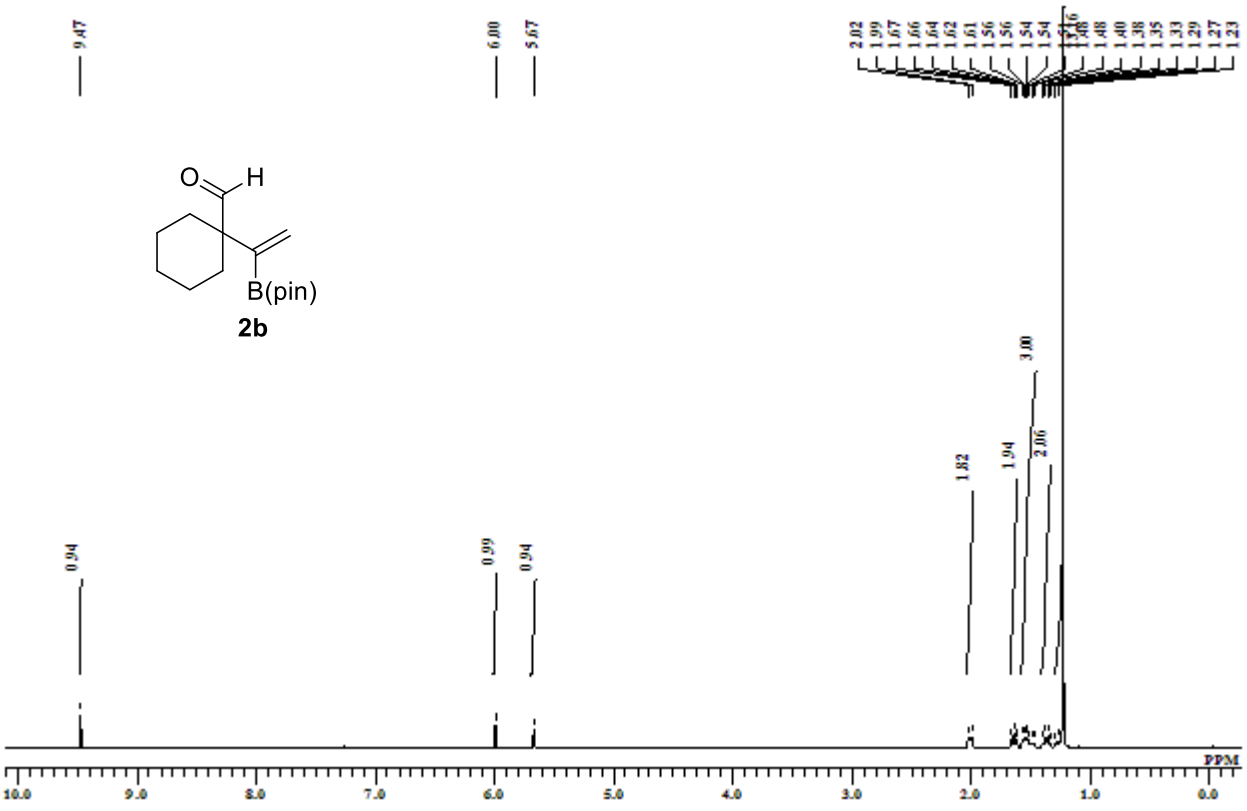


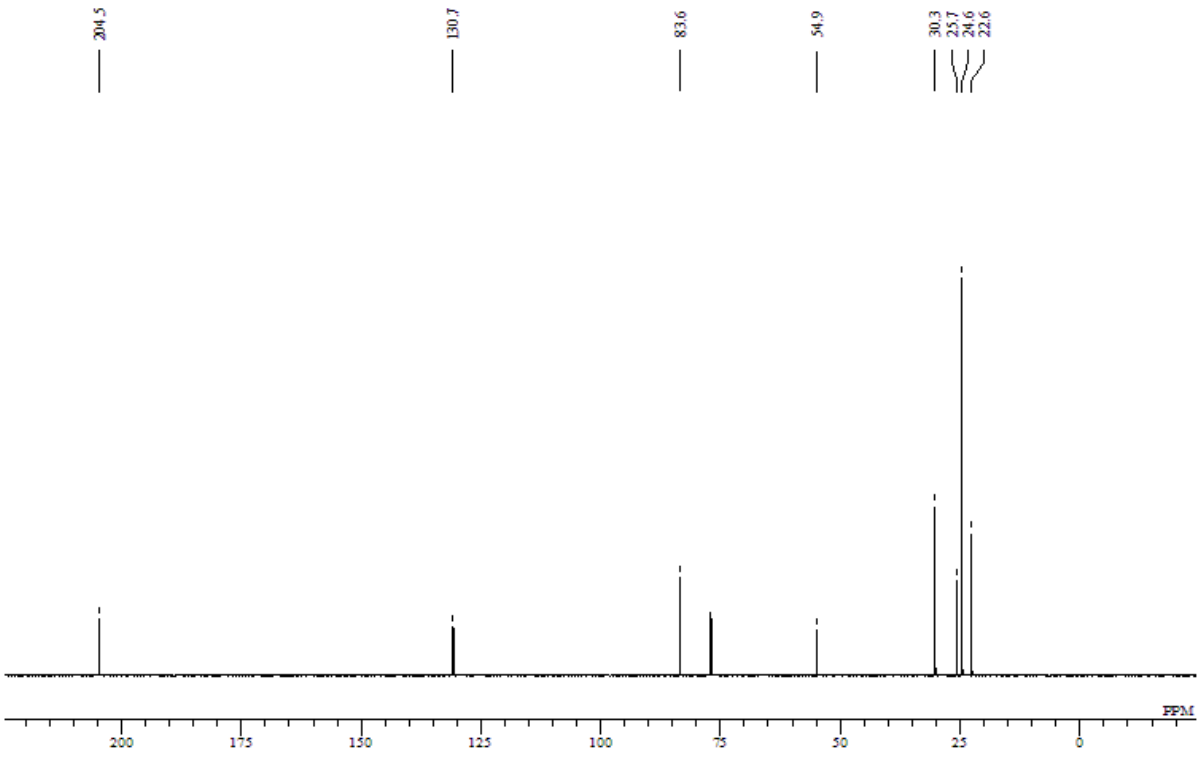


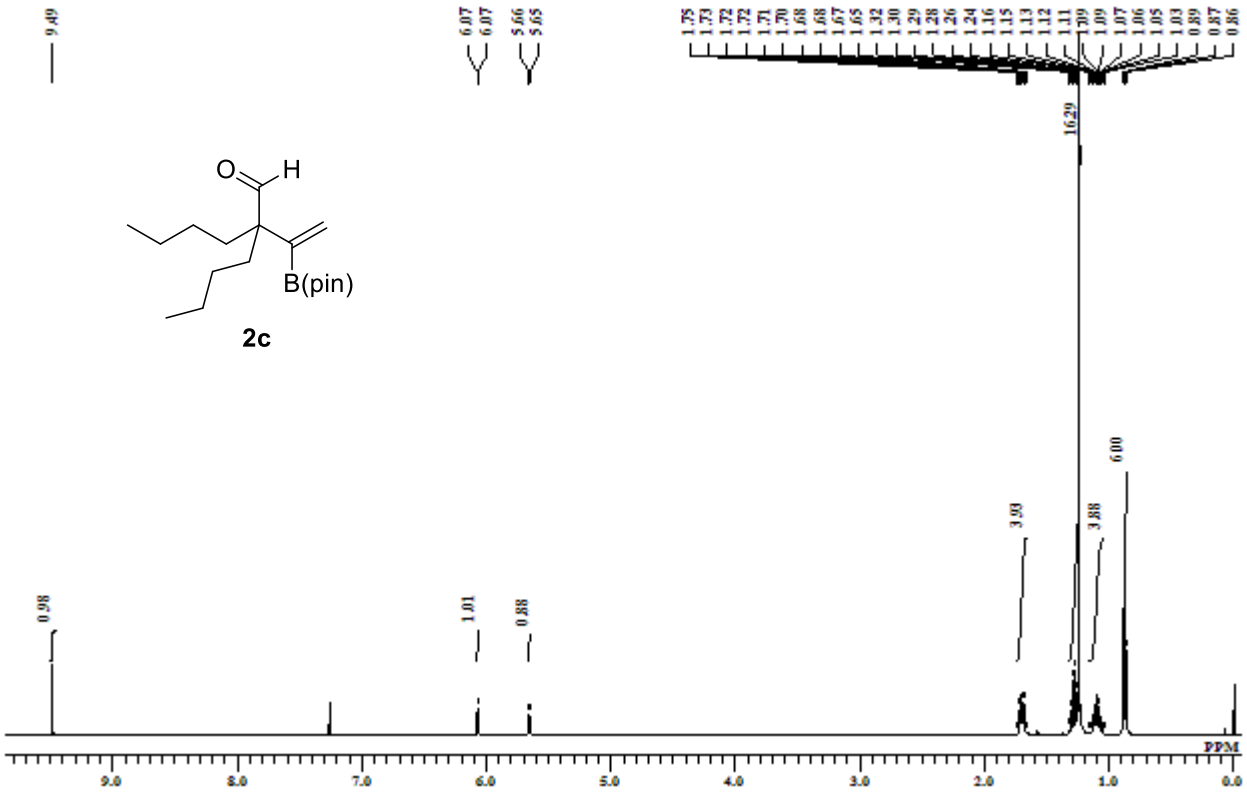
1j

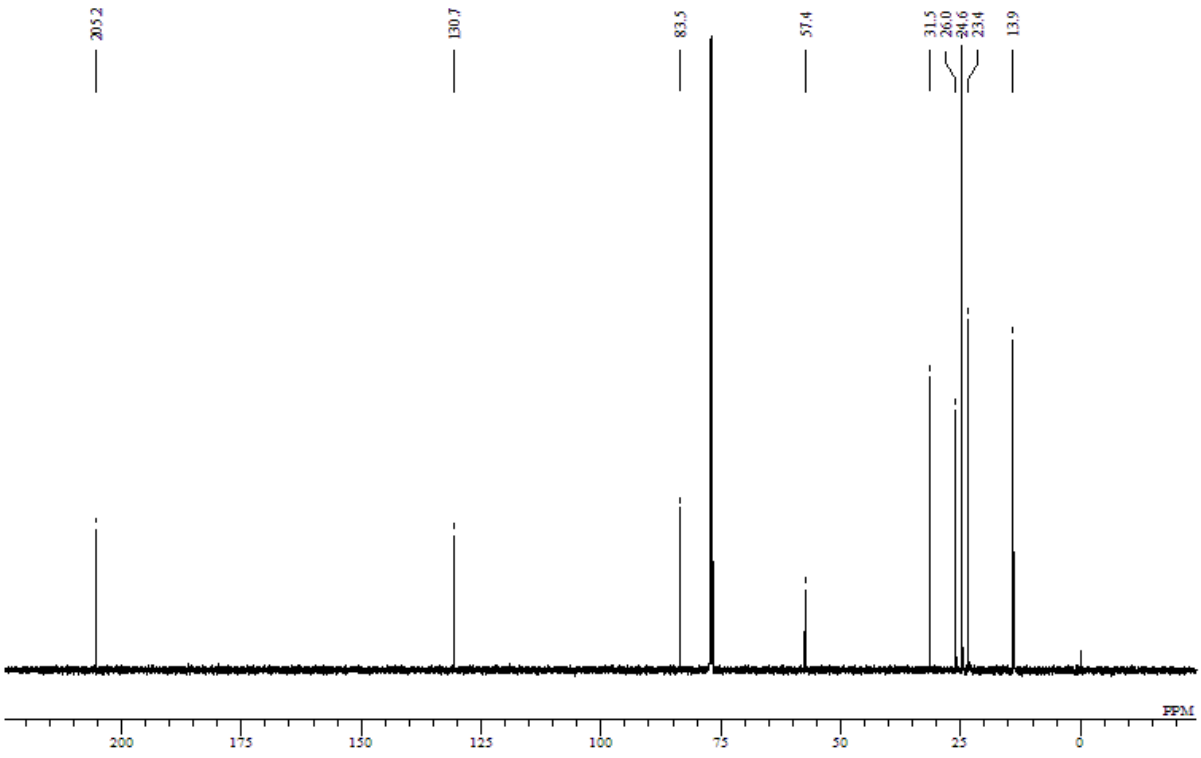


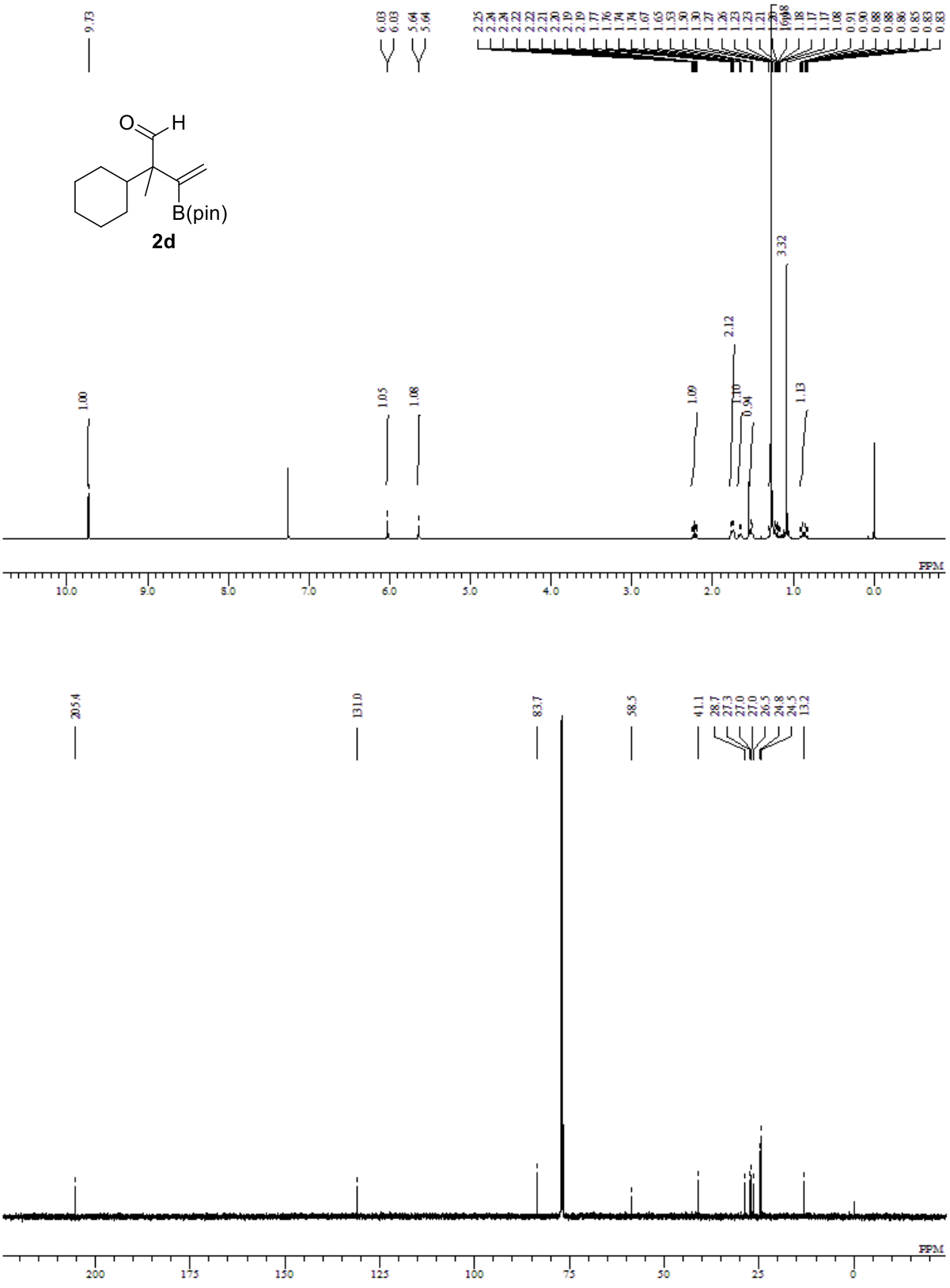


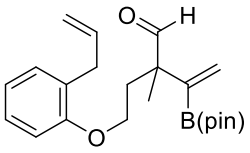












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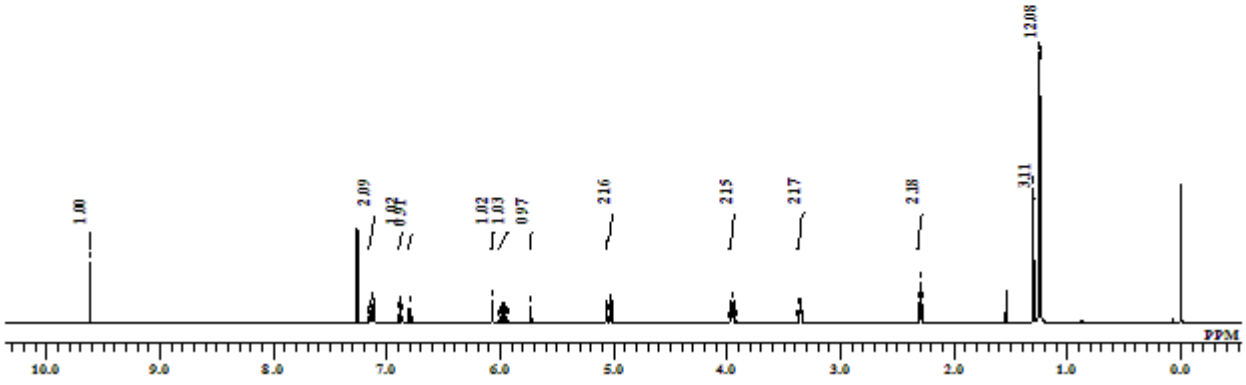

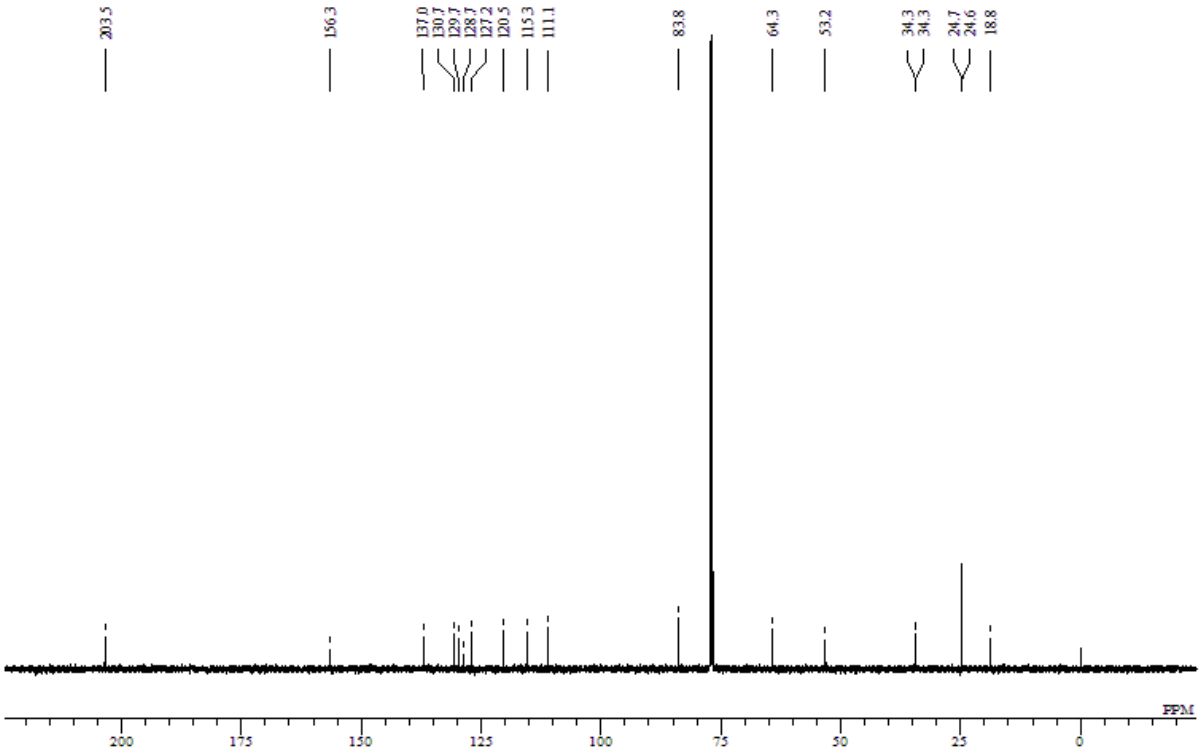

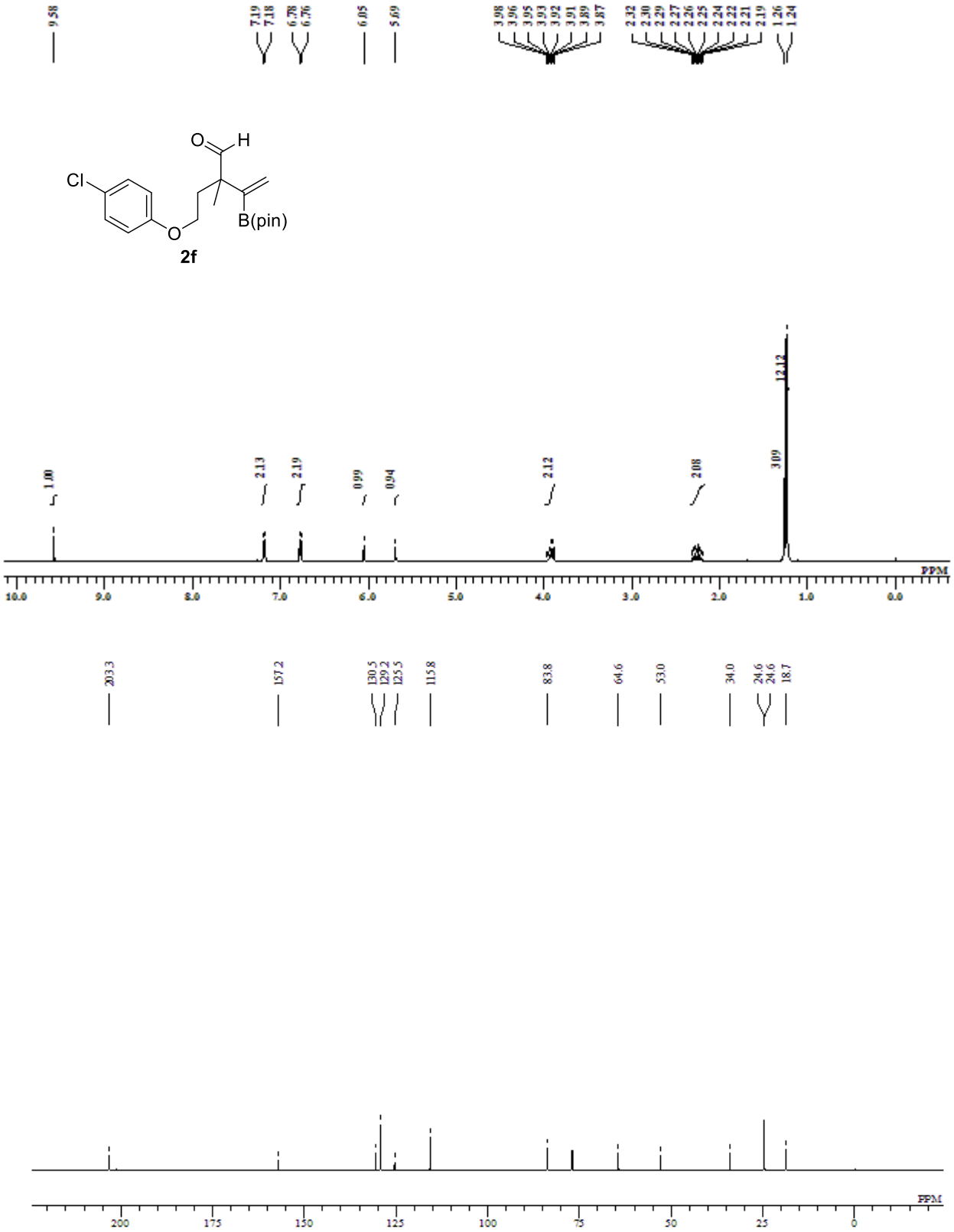

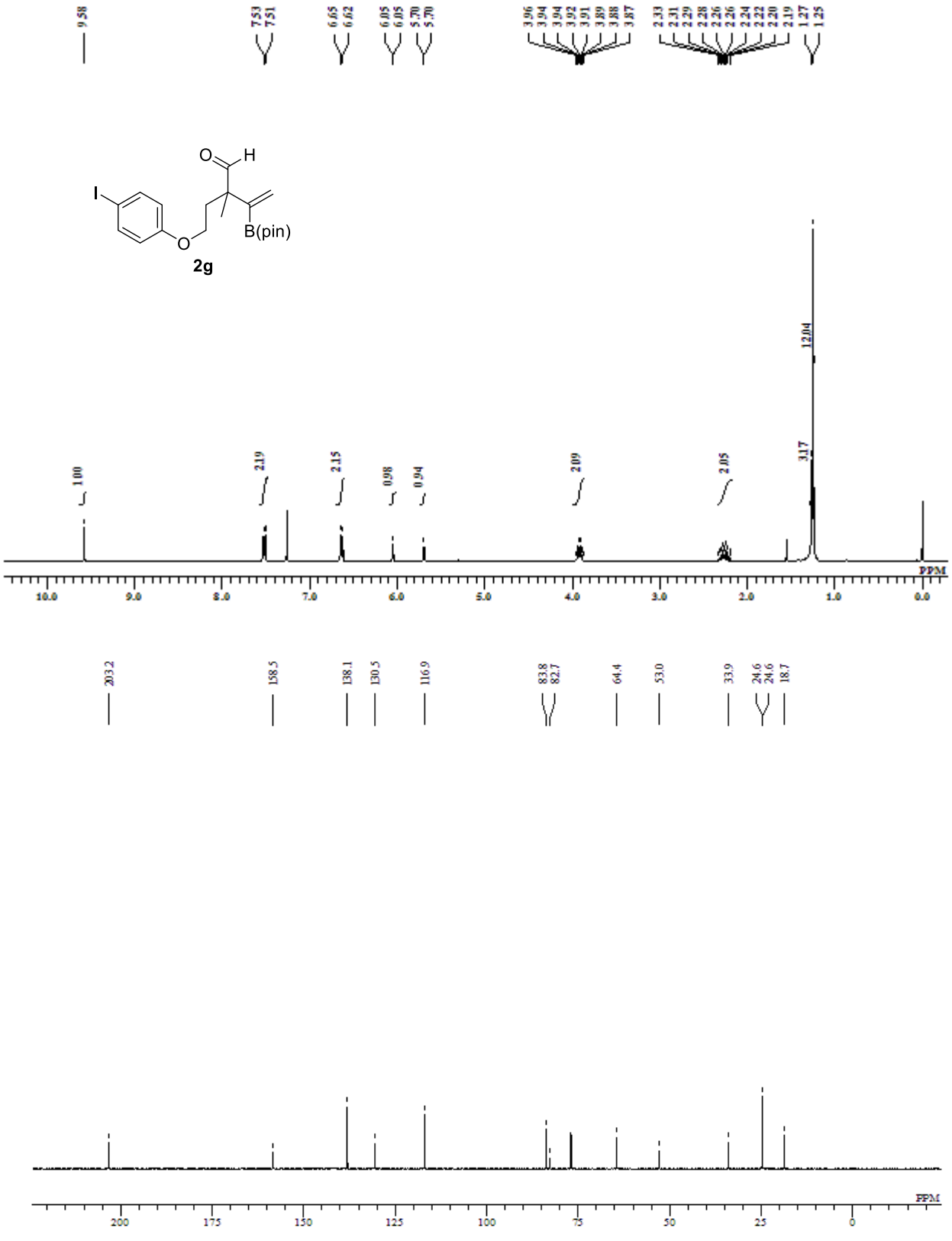

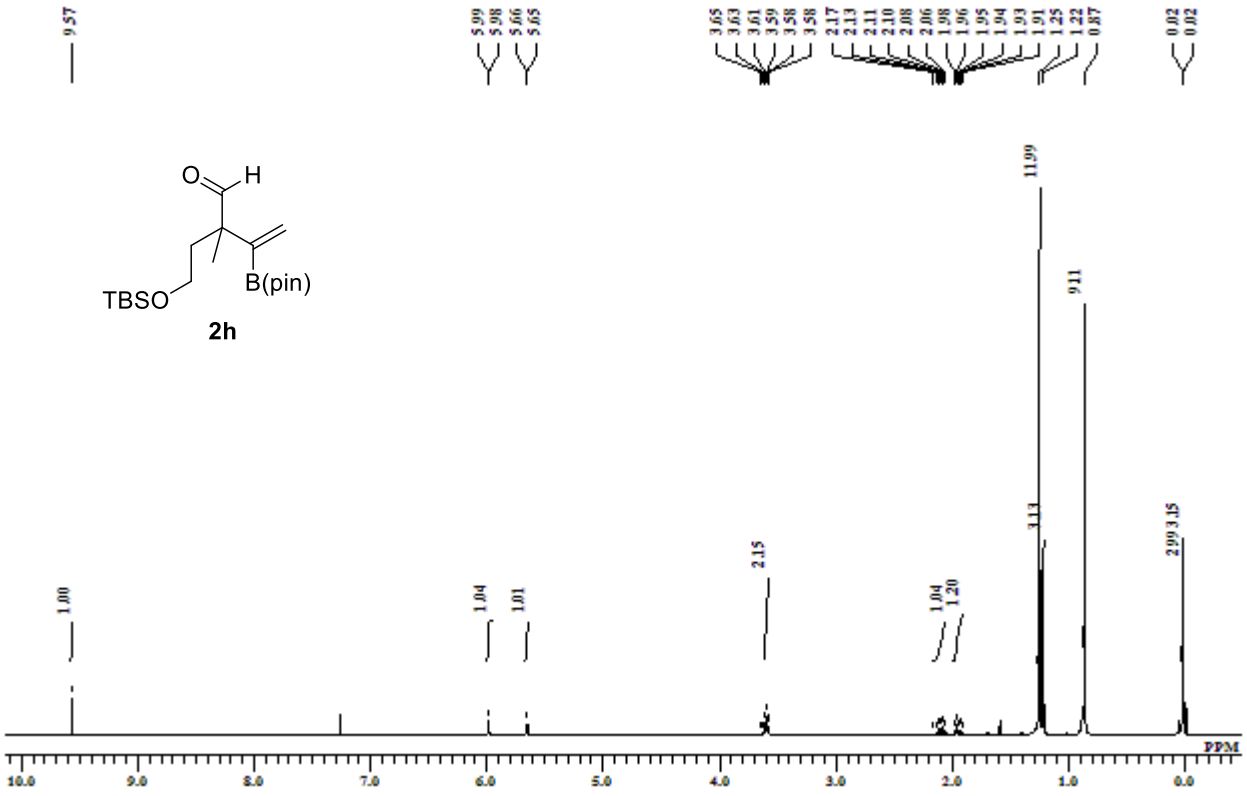

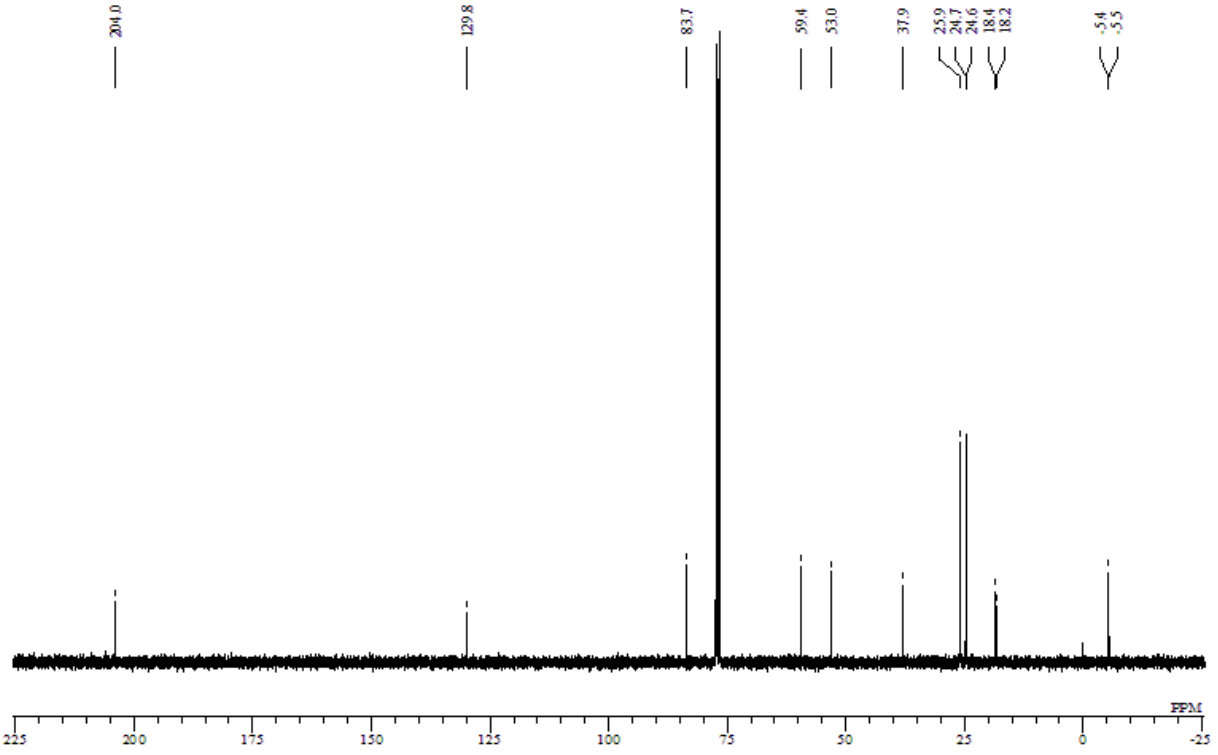

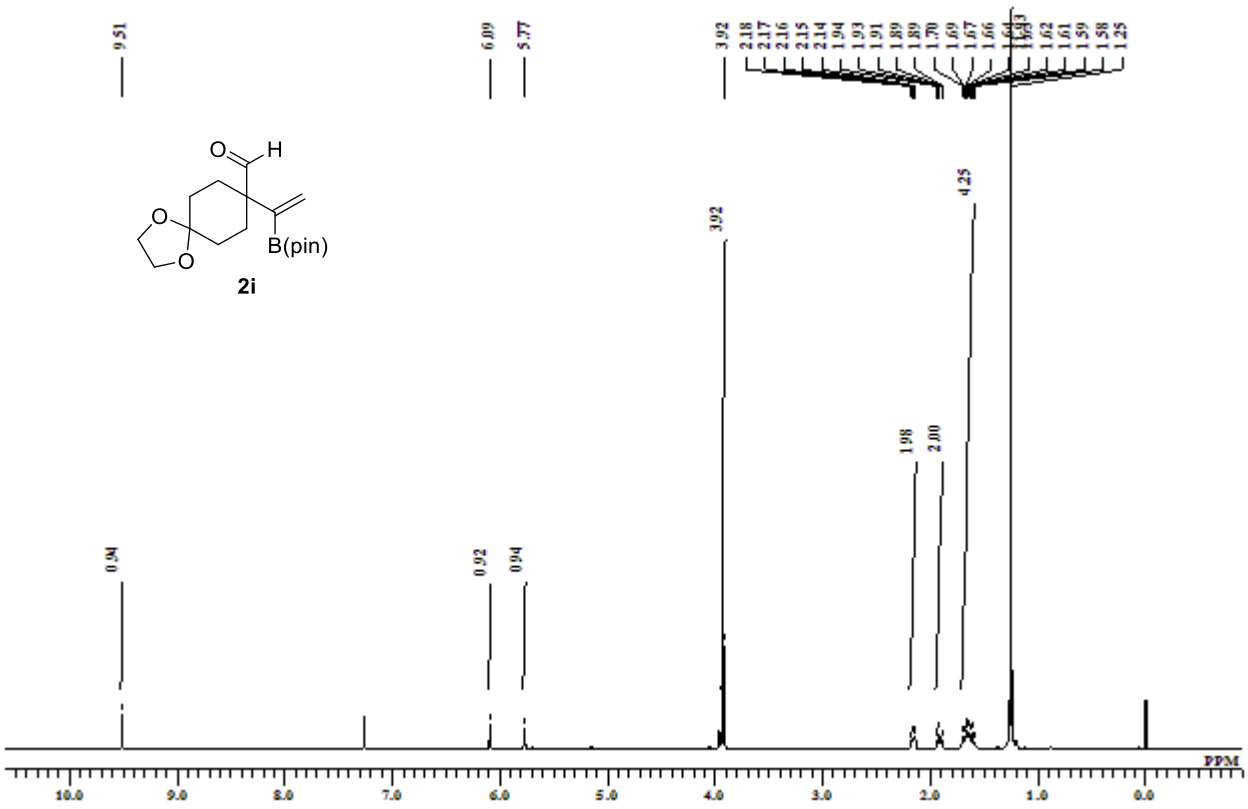

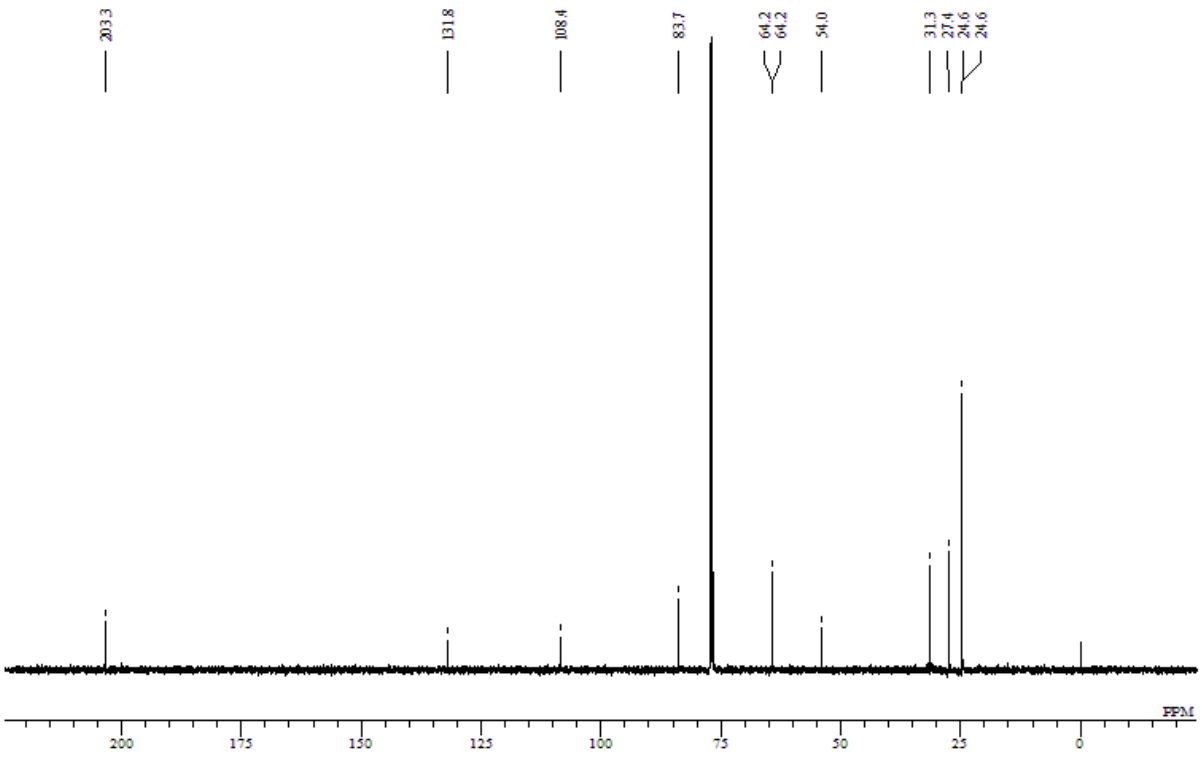

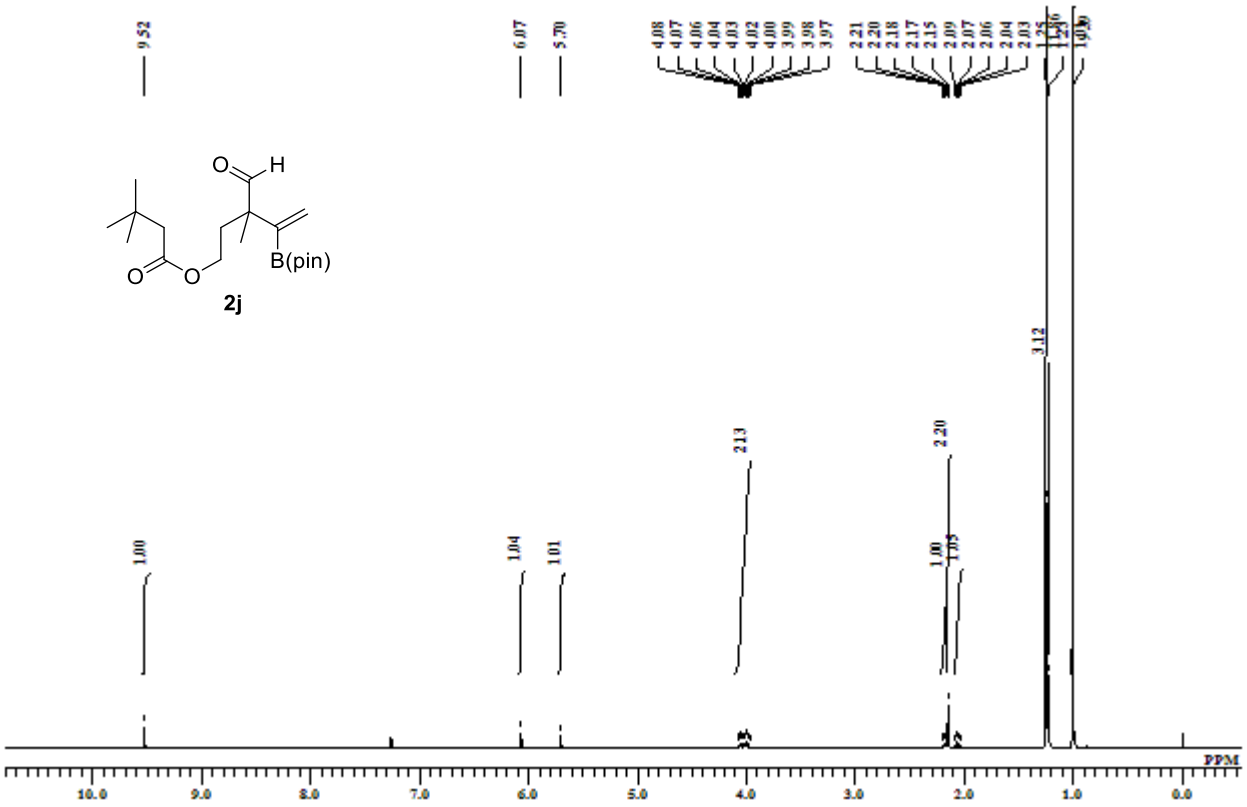

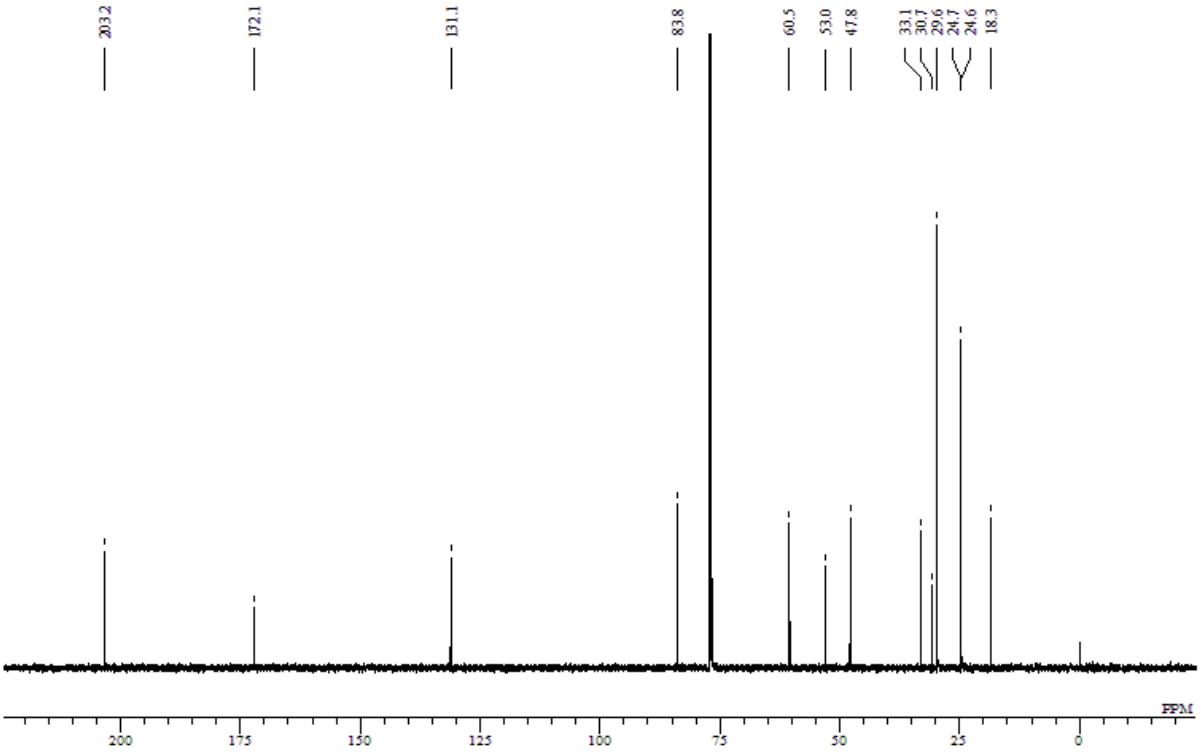

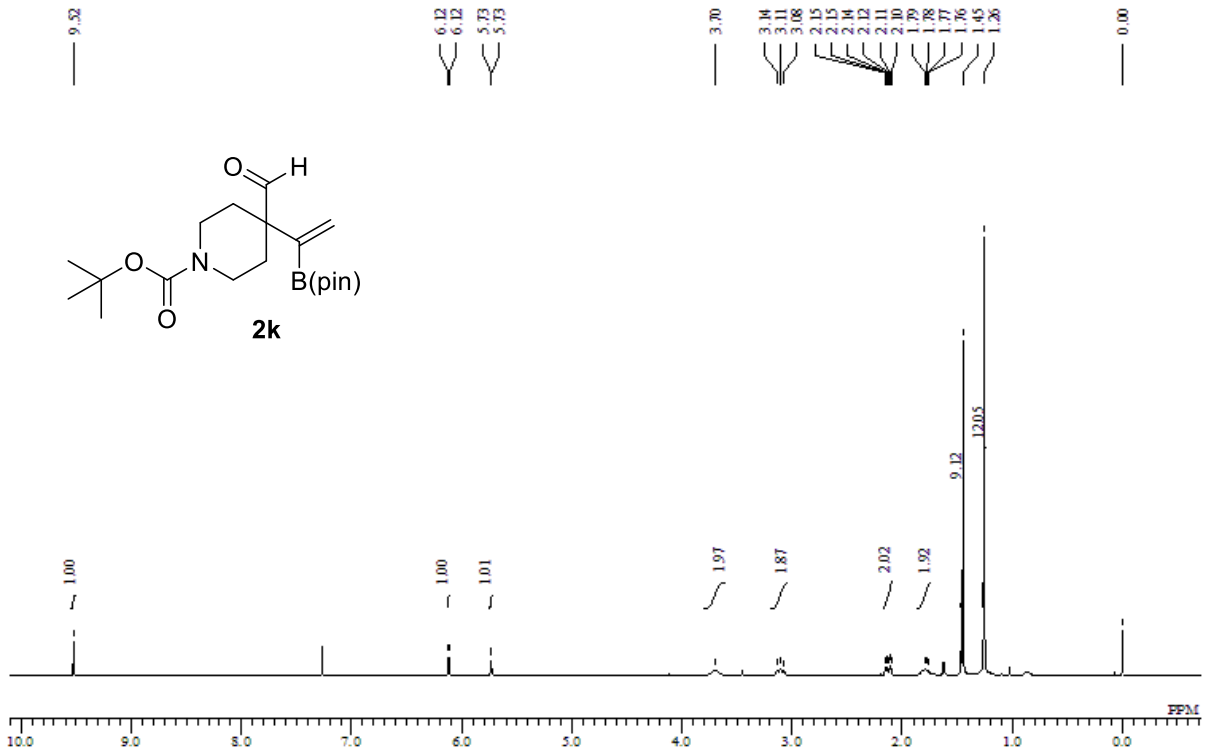

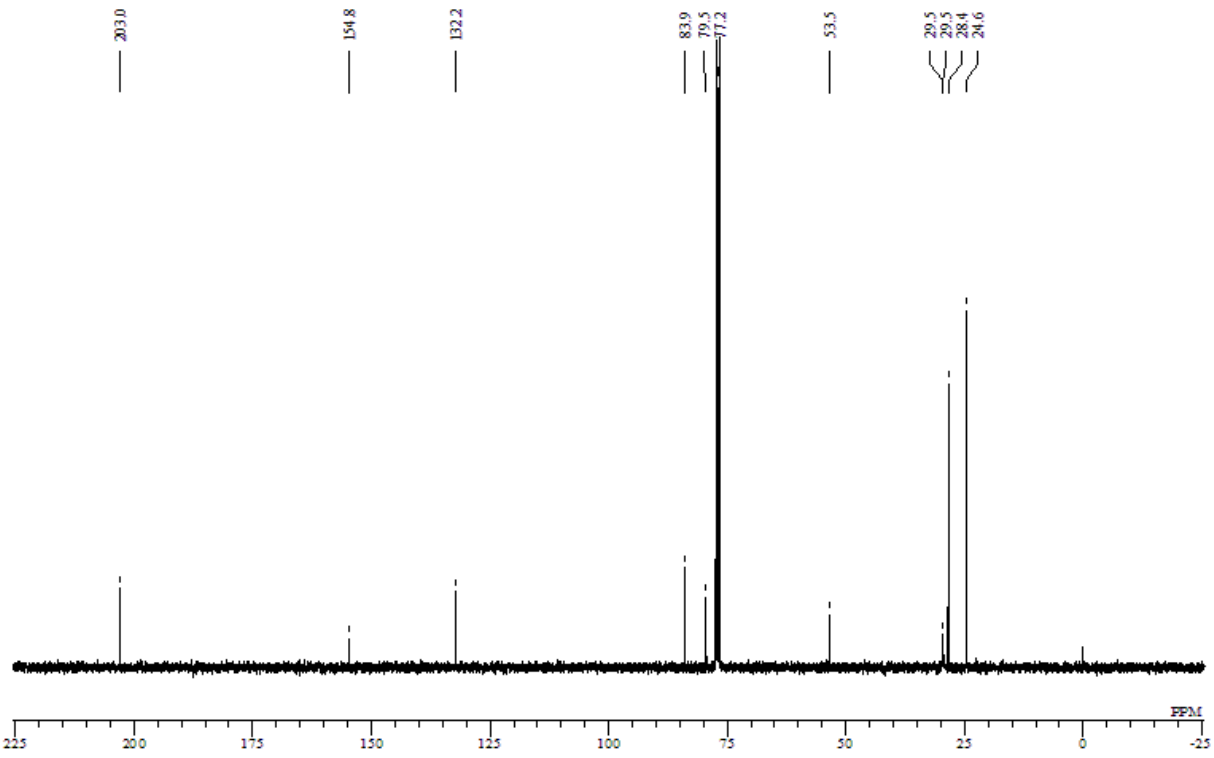

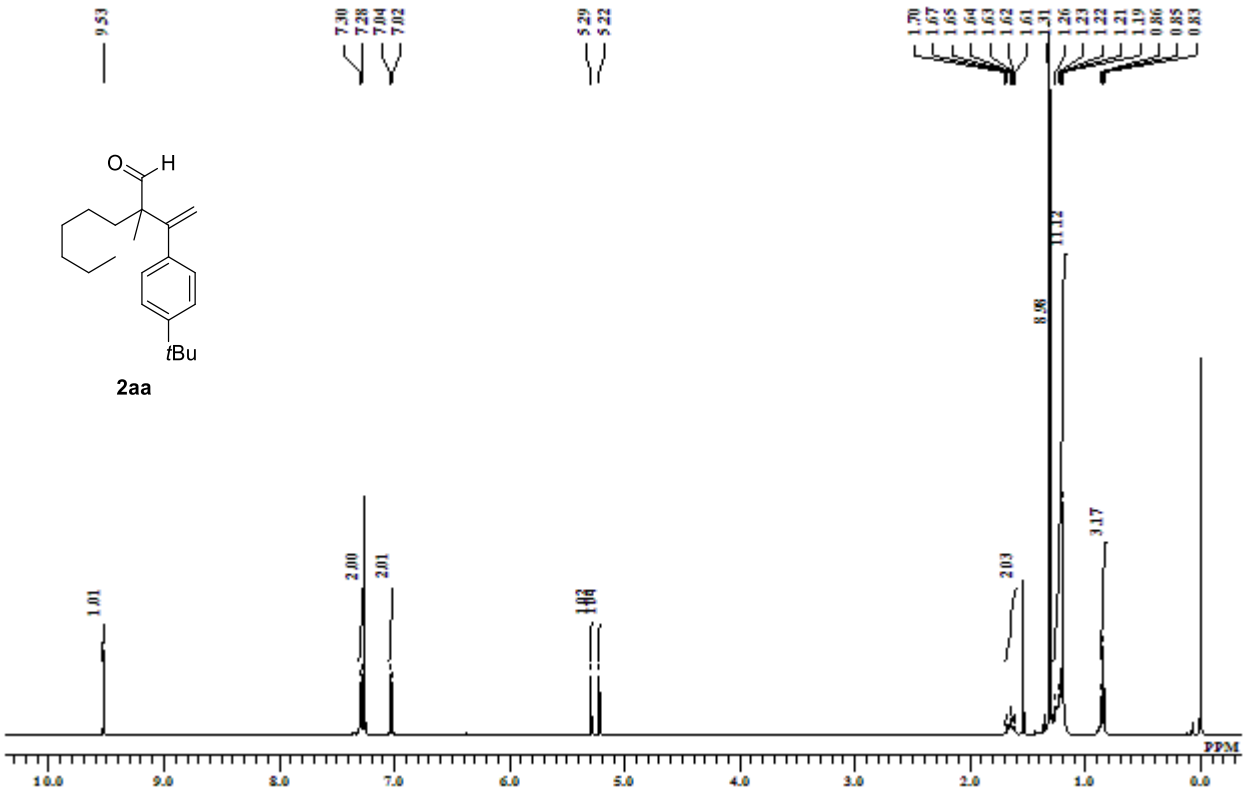

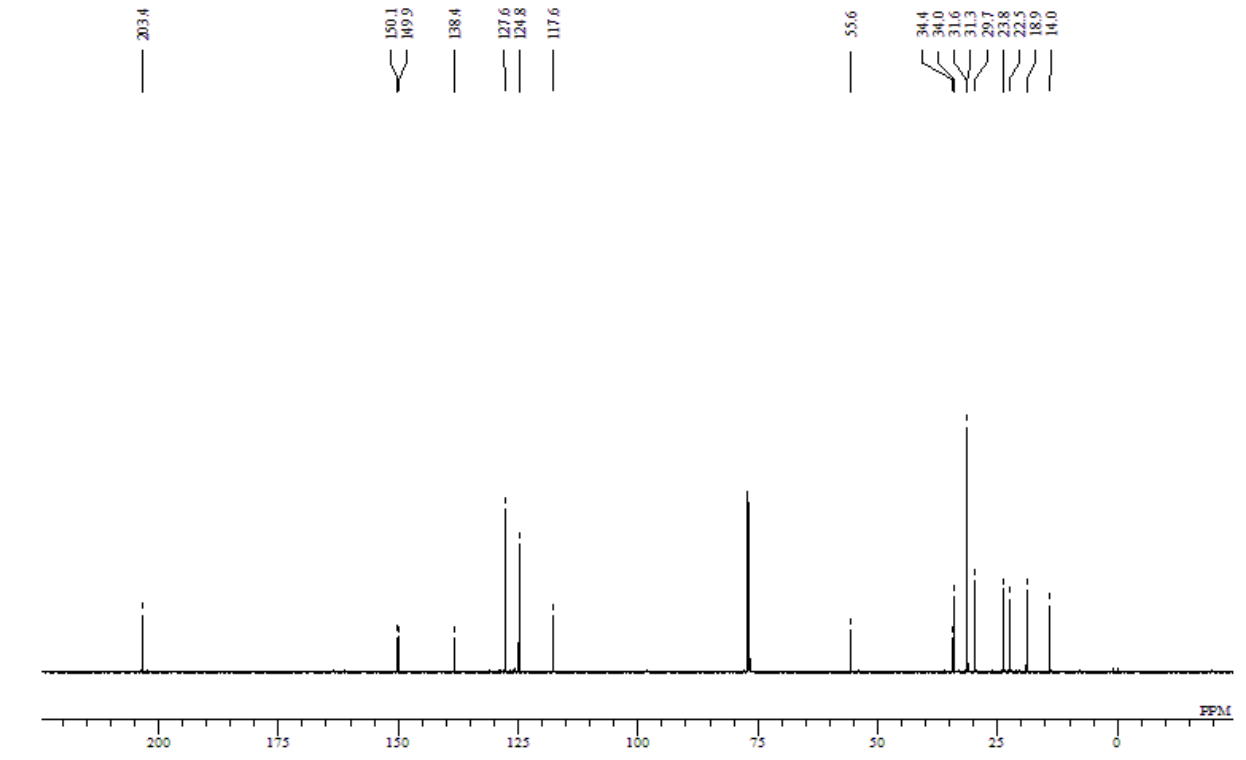

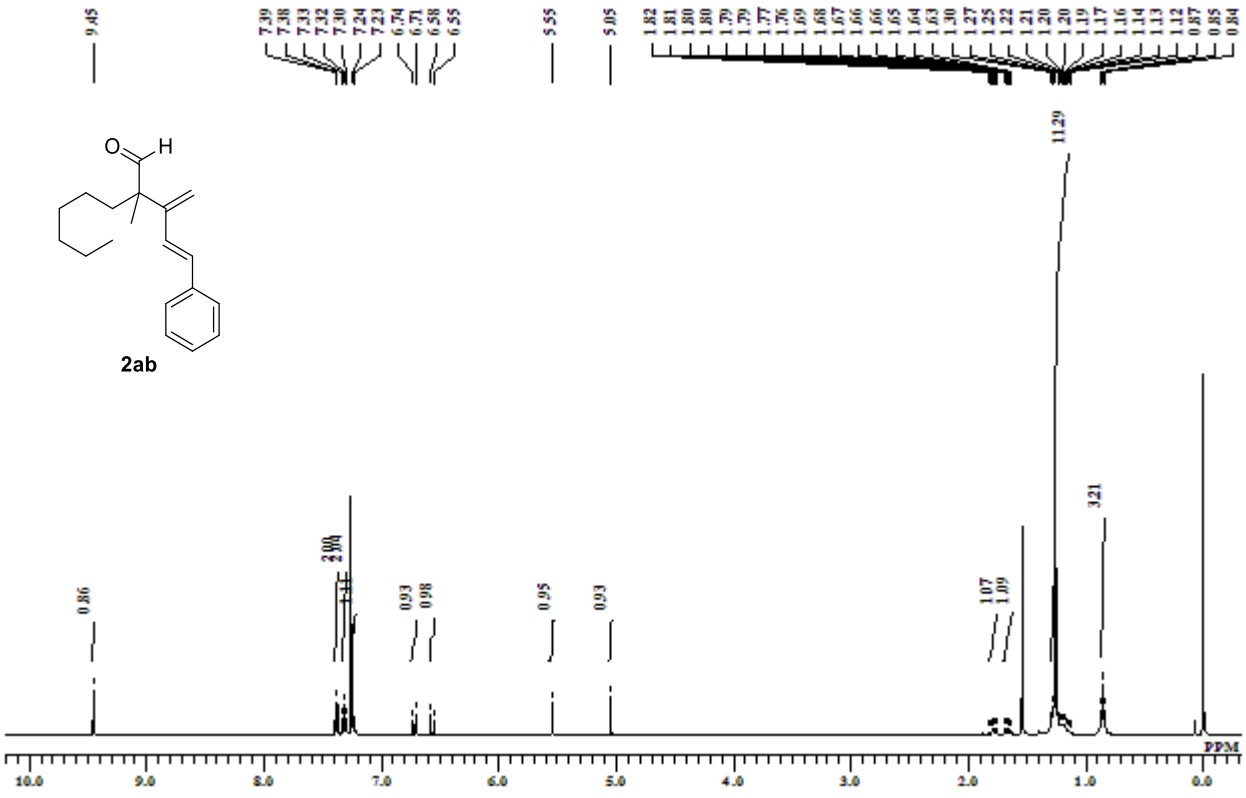

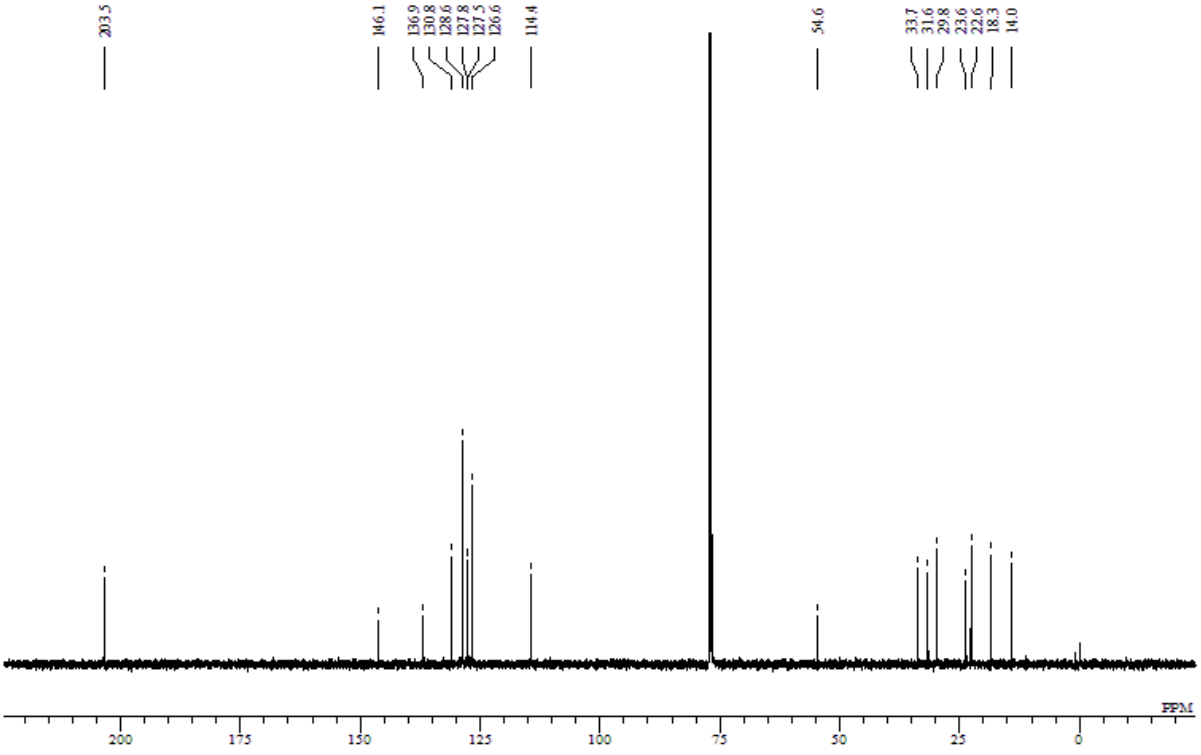

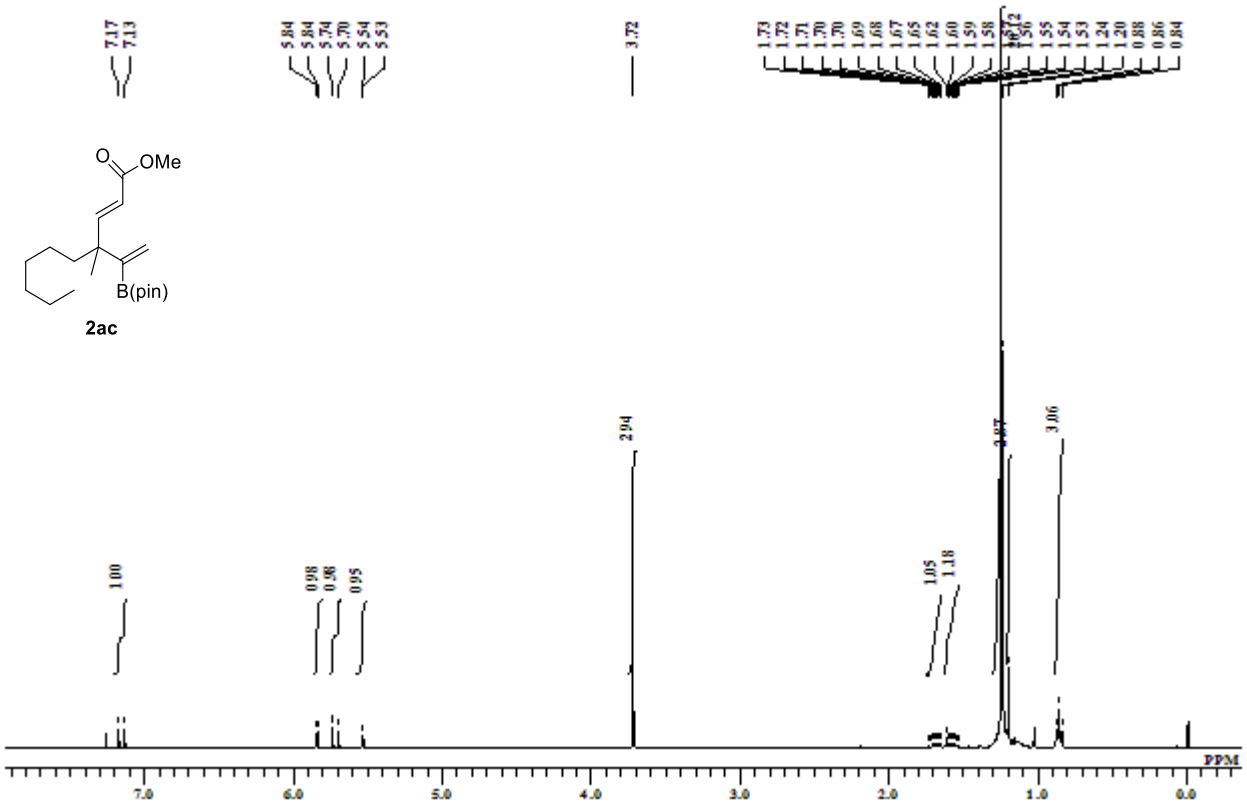

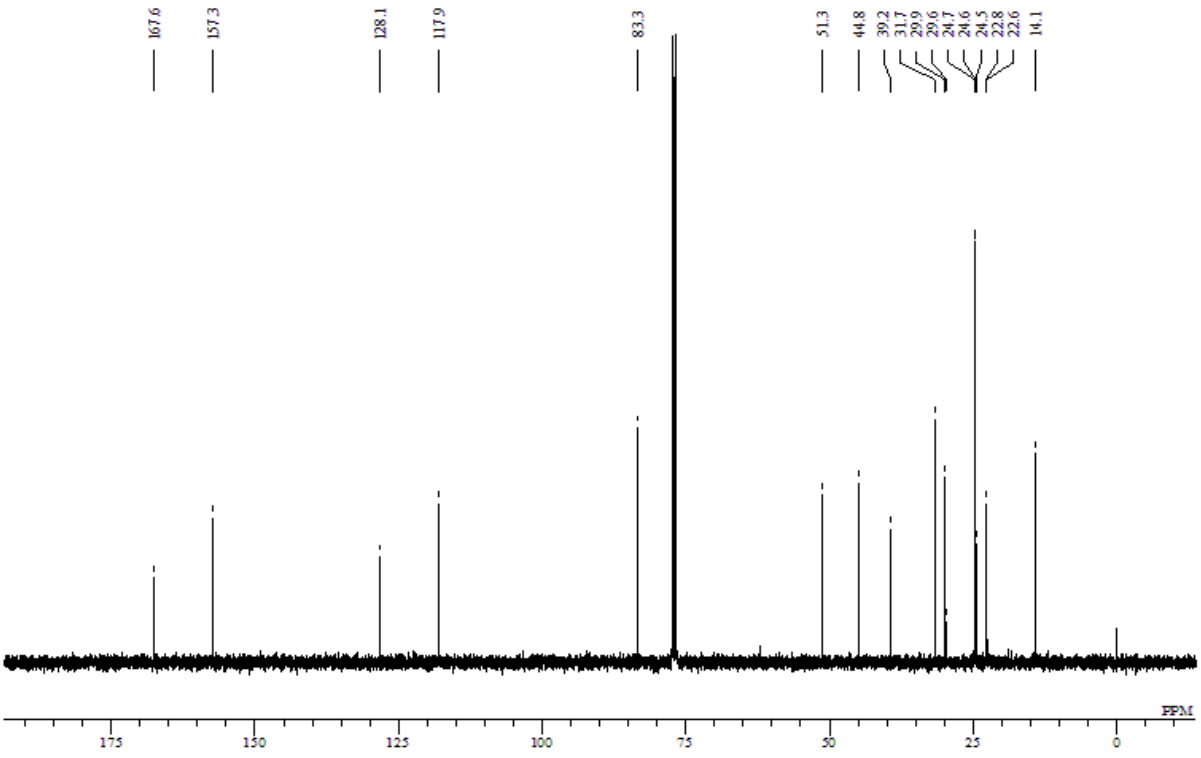

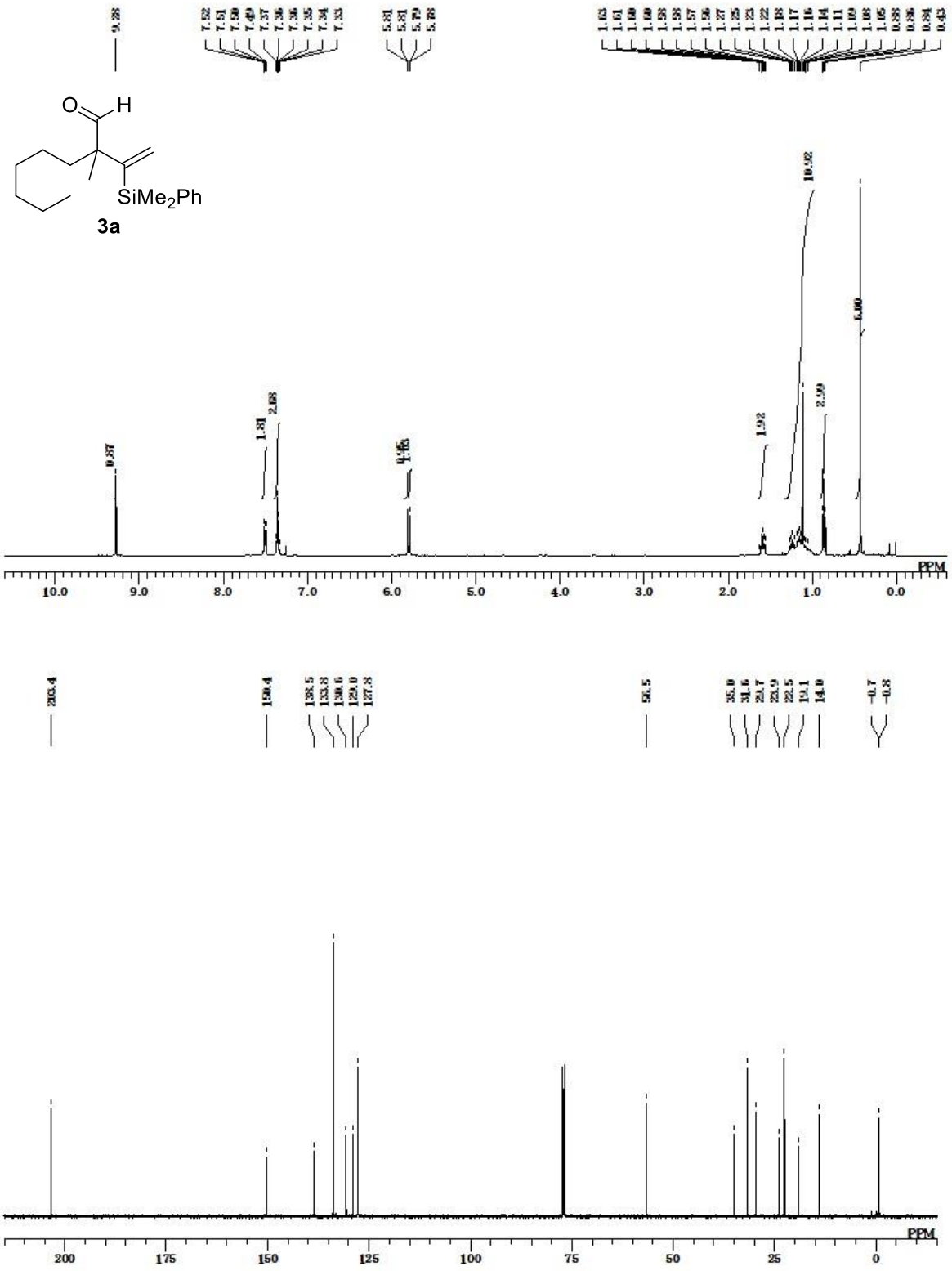

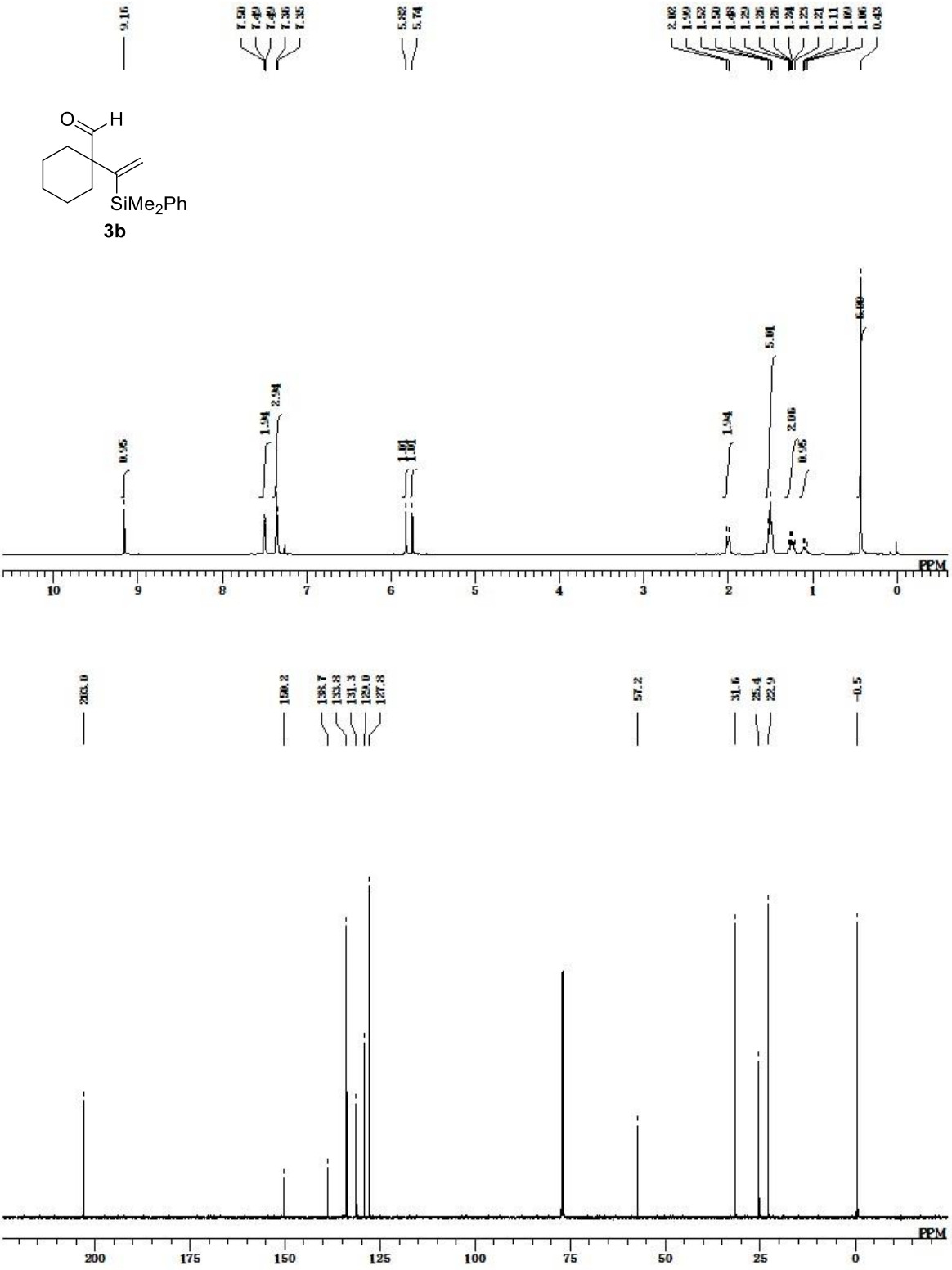

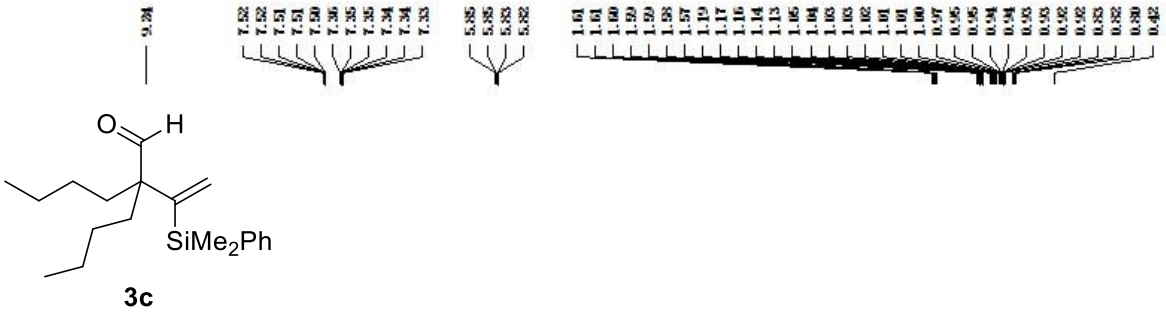

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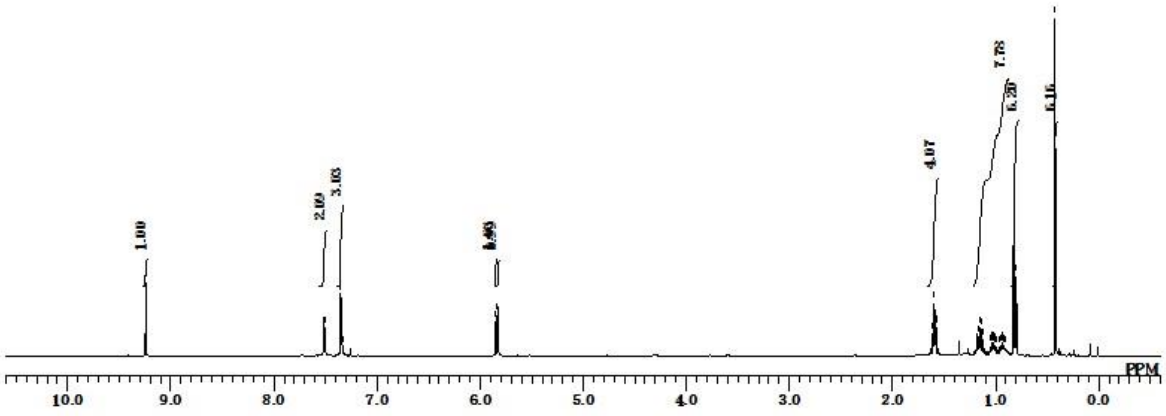

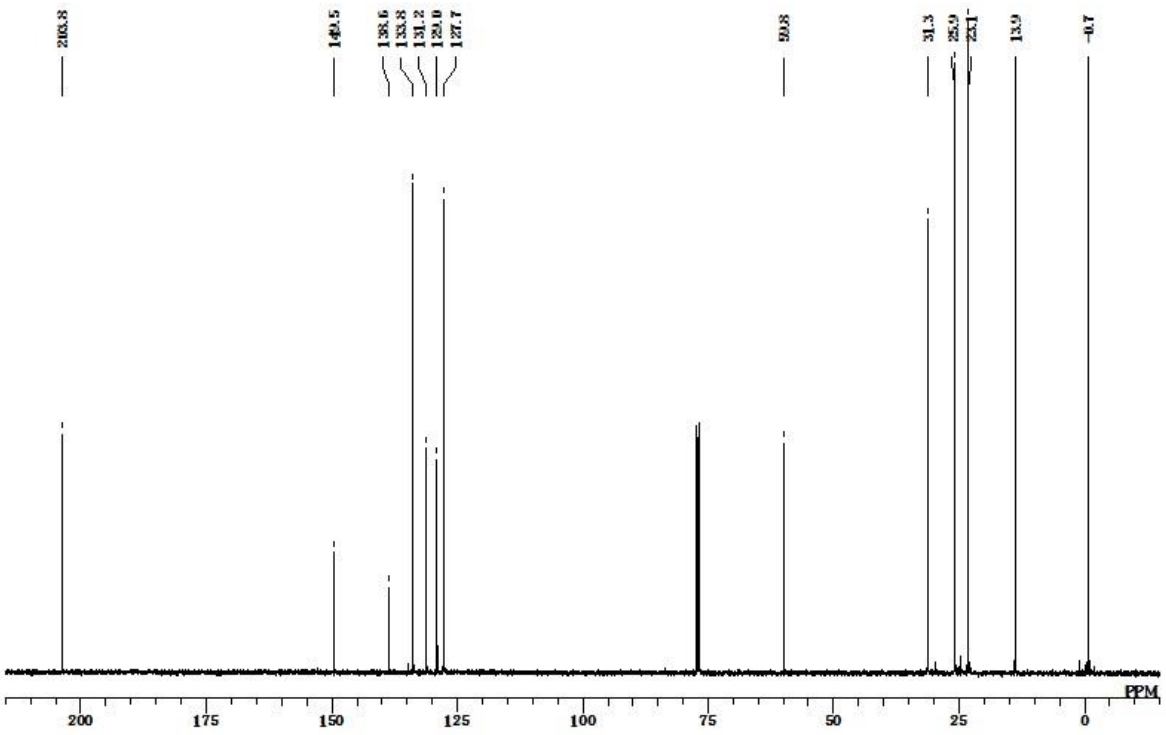

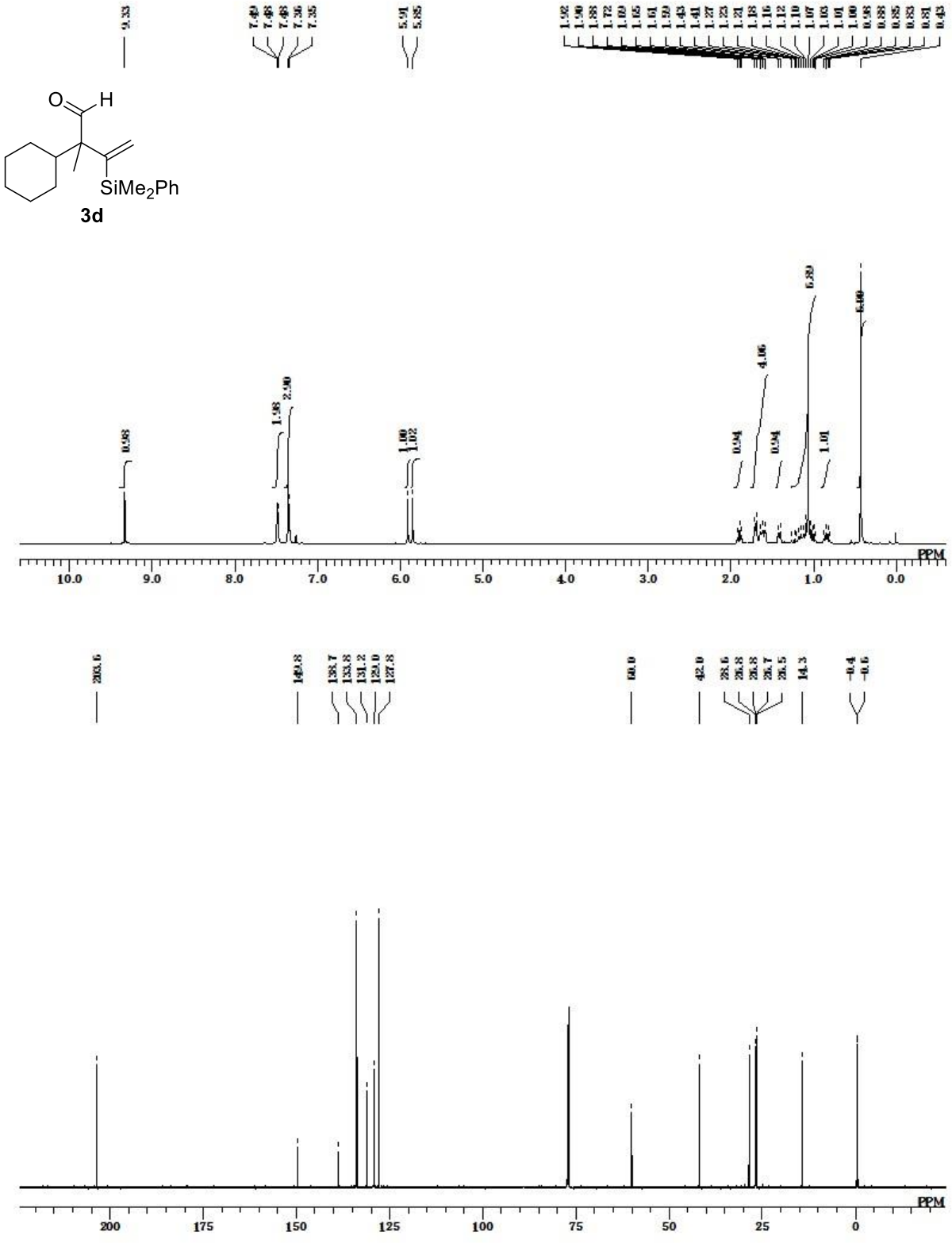

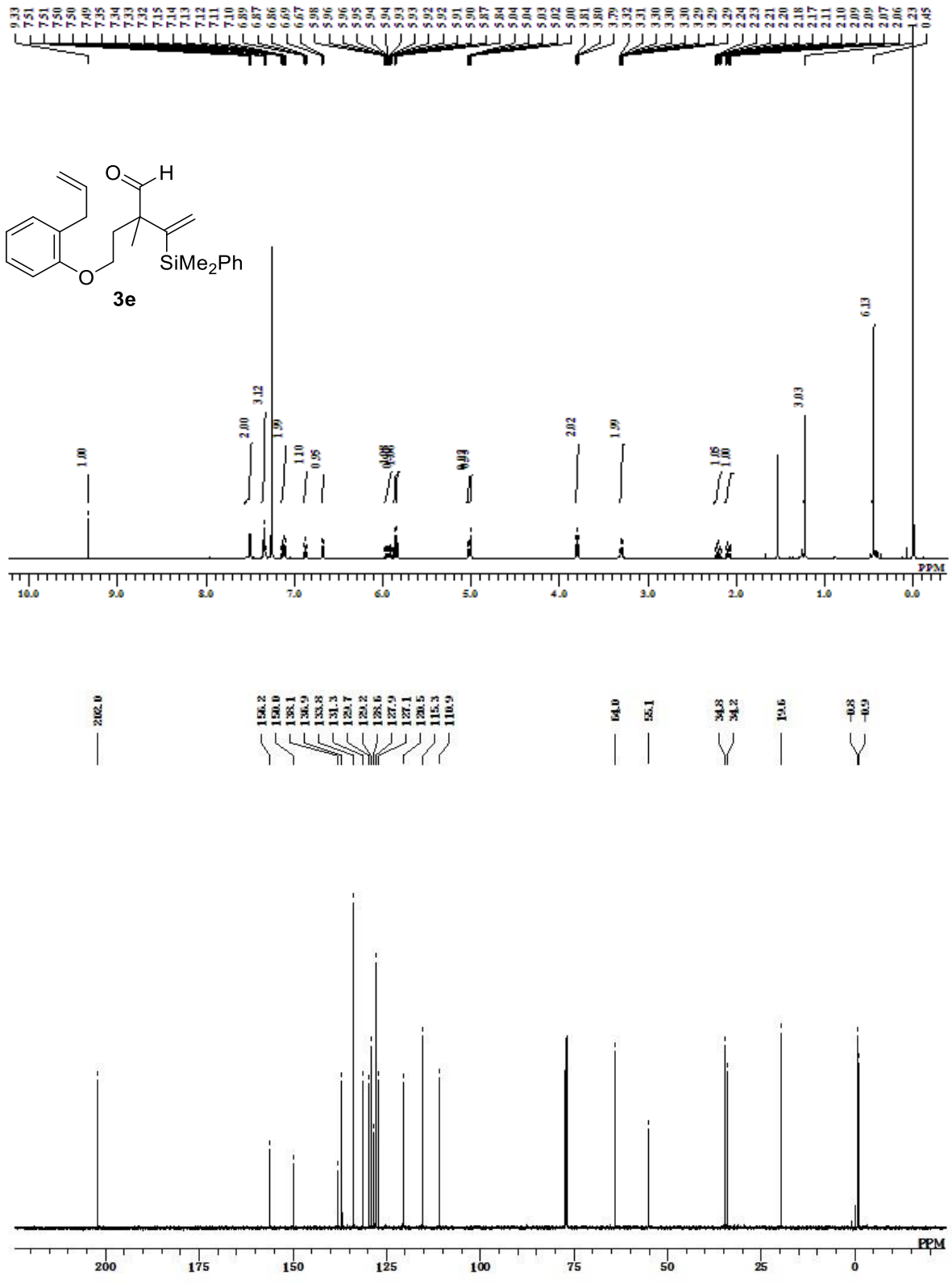

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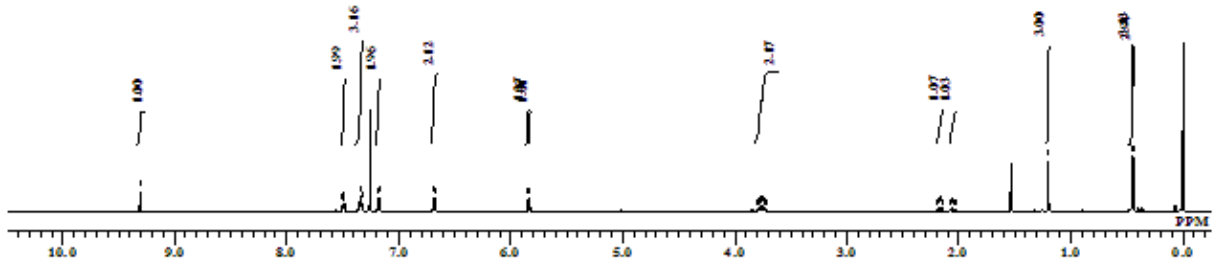

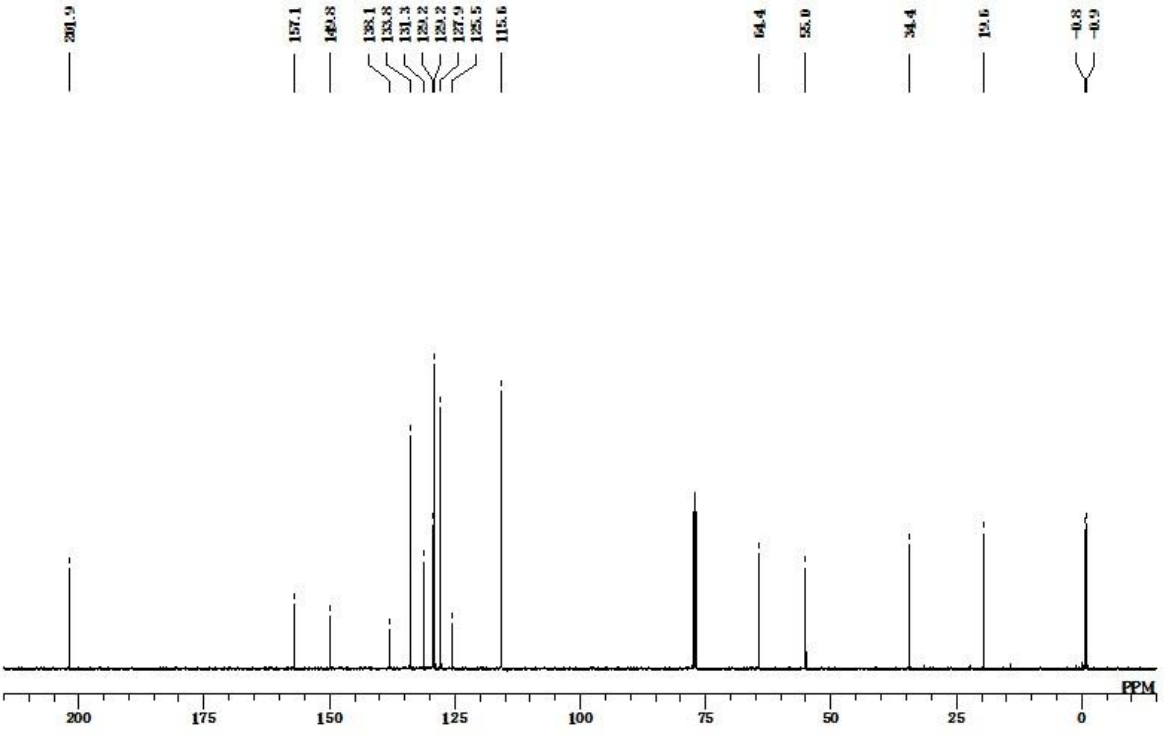

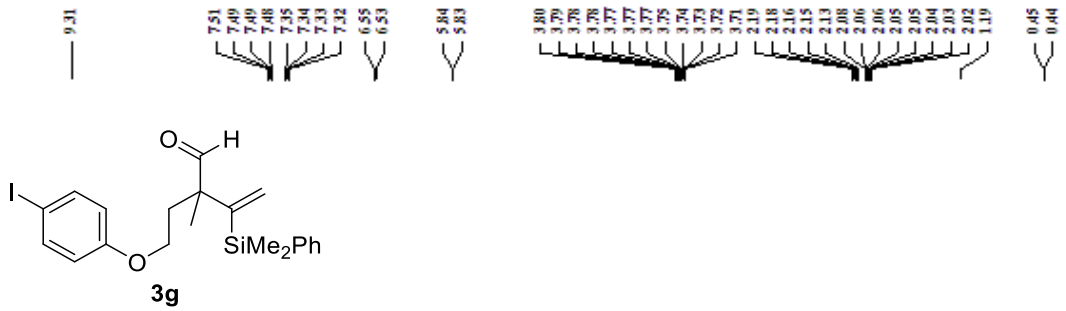

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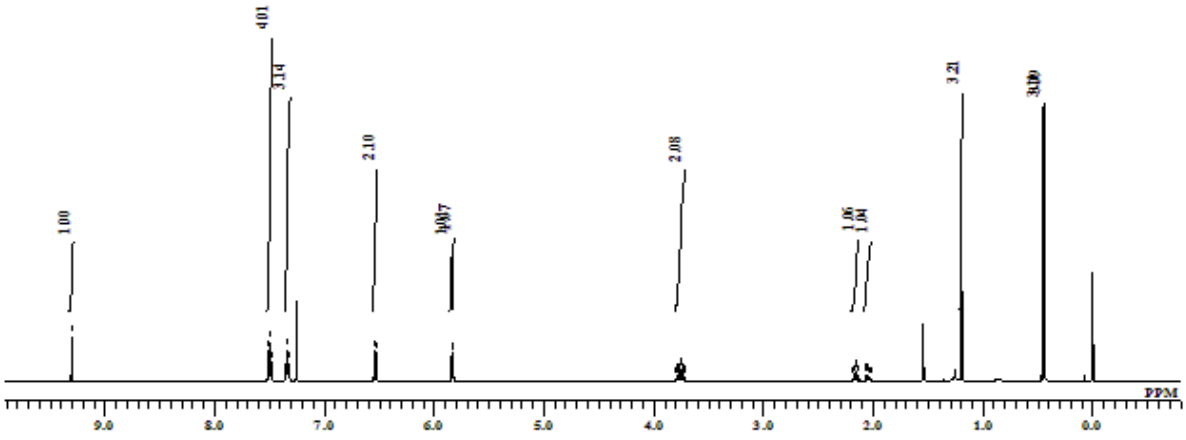

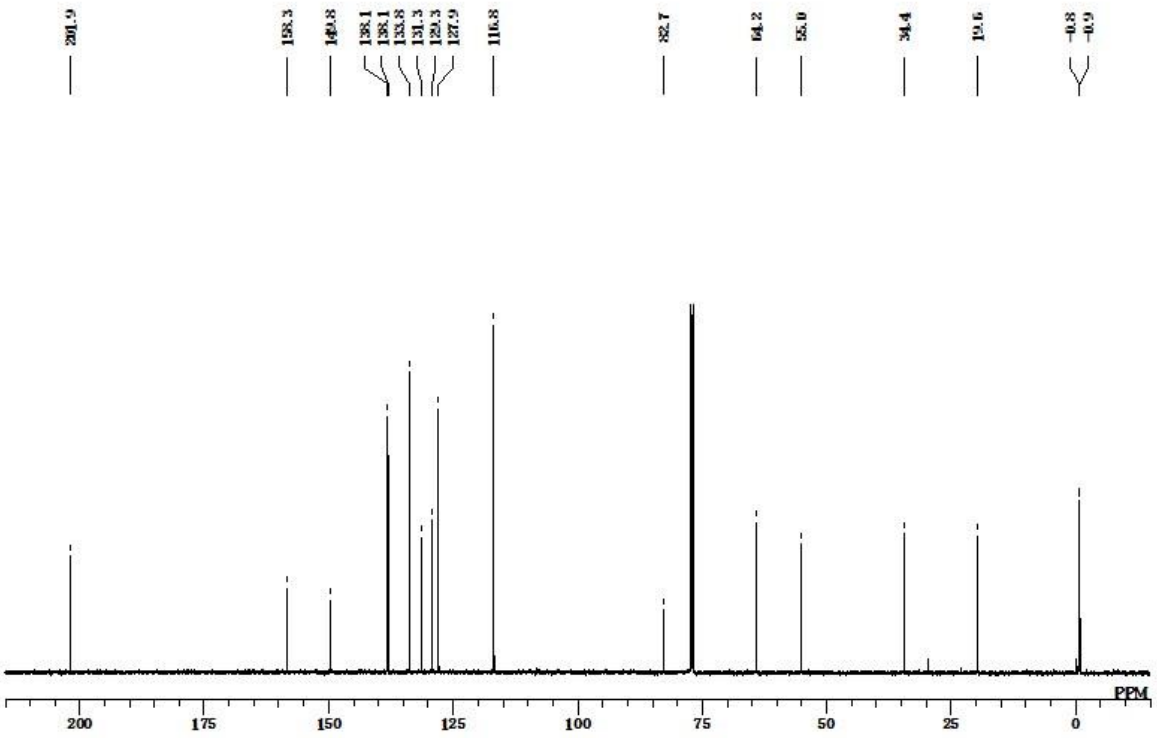

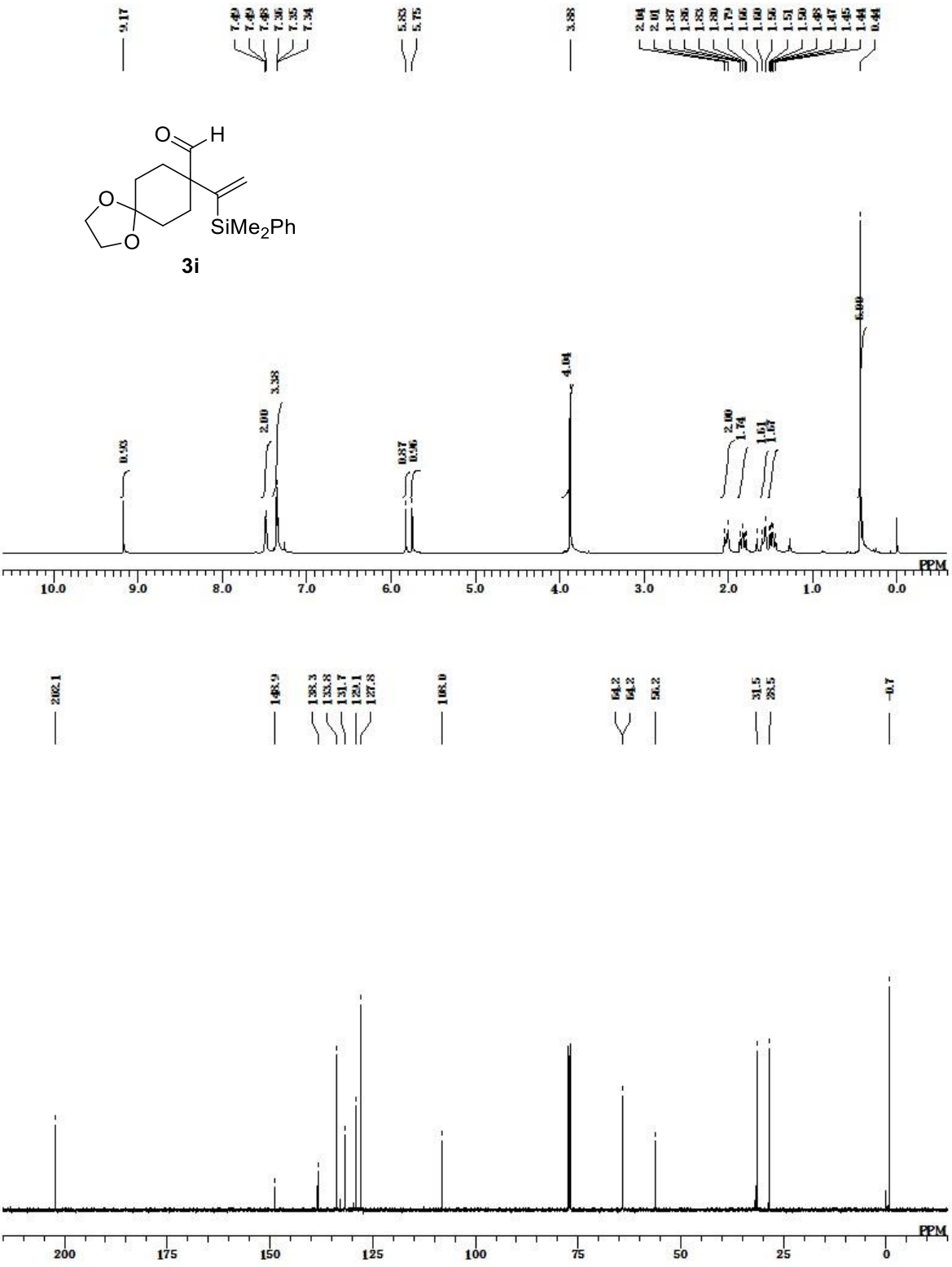

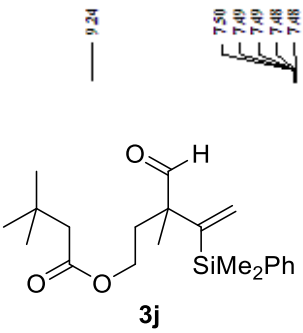

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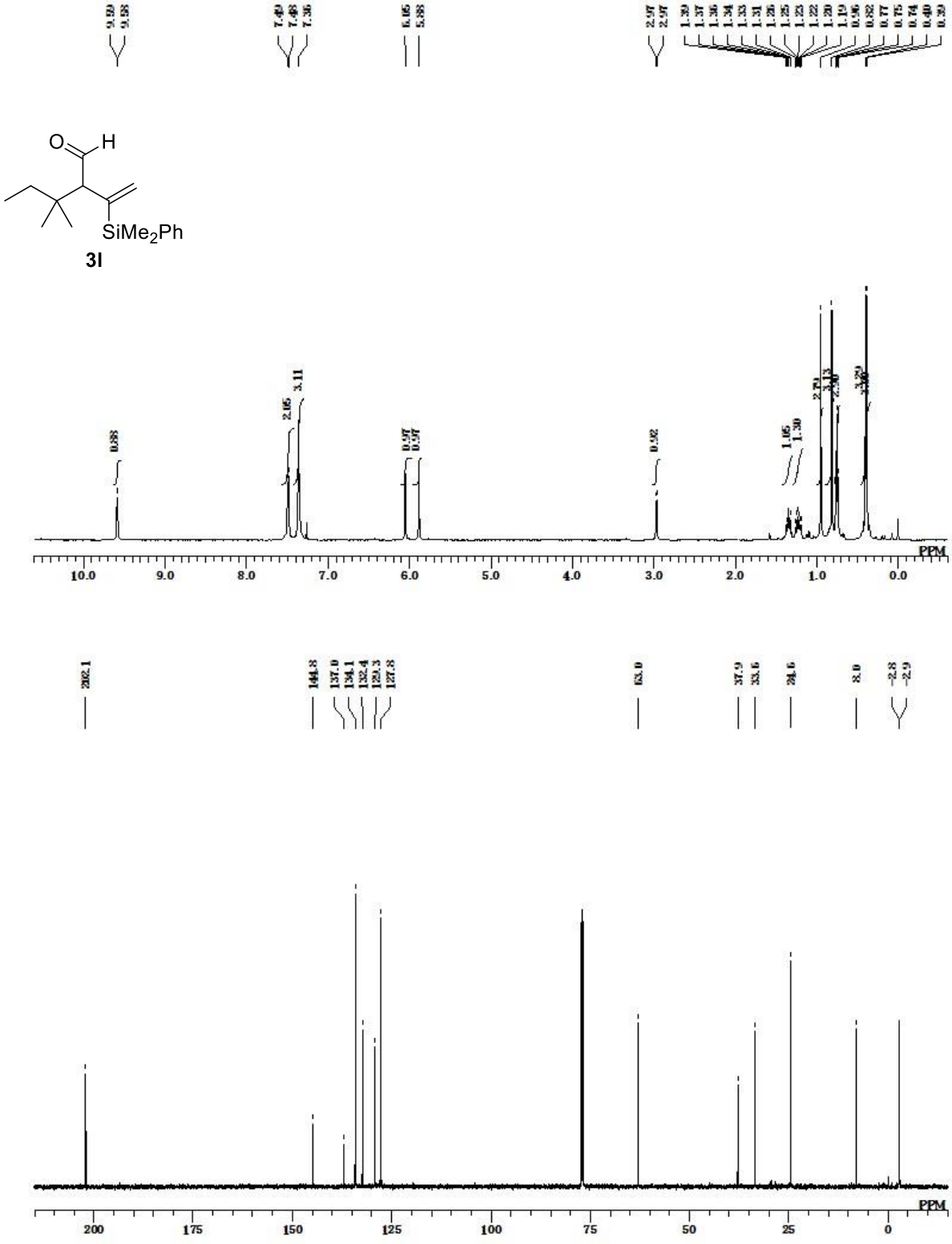

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