Supporting Information

for

Cobalt-catalyzed nucleophilic addition of the allylic C(sp^3)–H bond of simple alkenes to ketones

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Experimental details and characterization data

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(A) General

All manipulations were carried out under an atmosphere of argon or nitrogen unless otherwise noted. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 Plus Fourier transform infrared spectrophotometer. NMR spectra were recorded on a JEOL ECA-500 spectrometer, operating at 500 MHz (^{1}H) or 125 MHz (^{13}C). Chemical shifts in $CDCl_3$ were reported in the scale relative to $CHCl_3$ (7.26 ppm) for ^{1}H NMR, and to $CDCl_3$ (77.0 ppm) for ^{13}C NMR as internal references, respectively. NMR data are reported as follows: chemical shifts, multiplicity (s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet, br: broad signal), coupling constant (Hz), and integration. EI-HRMS and ESI-HRMS spectra were measured on a JEOL JMS-T100GCv and Thermo Scientific Exactive, respectively. Gel permeation chromatography was performed on HPLC LC-9201 (Japan Analytical Industry Co., Ltd). Column chromatography was performed with Wakogel® FC-40 (20–40 μm, spherical, neutral). DMA was distilled from CaH_2. $AlMe_3$ (2.0 M in toluene) was purchased from Sigma-Aldrich Co. LLC. $Co(acac)_2$ and Xantphos were purchased from Tokyo Kasei, Co., Ltd.

(B) Materials and methods

(B-1) Availability of ketones

Acetophenone (**2a**) was purchased Nacalai Tesque. Inc. 4'-Methylacetophenone (**2b**) was purchased from Wako Pure Chemical Industries, Ltd. 4'-Methoxyacetophenone (**2c**) and 2-naphtophenone (**2f**) were purchased from Tokyo Kasei, Co., Ltd. 4'-Fluoroacetophenone (**2d**) was purchased from Sigma-Aldrich Co. LLC. Methyl 4-acetylbenzoate (**2e**) was purchased from Acros Organics Inc. Propiophenone (**2g**) was purchased from Kanto Chemical Co., Inc. All ketones except **2e** and **2f** were purified by distillation before use. **2e** and **2f** were used as received.

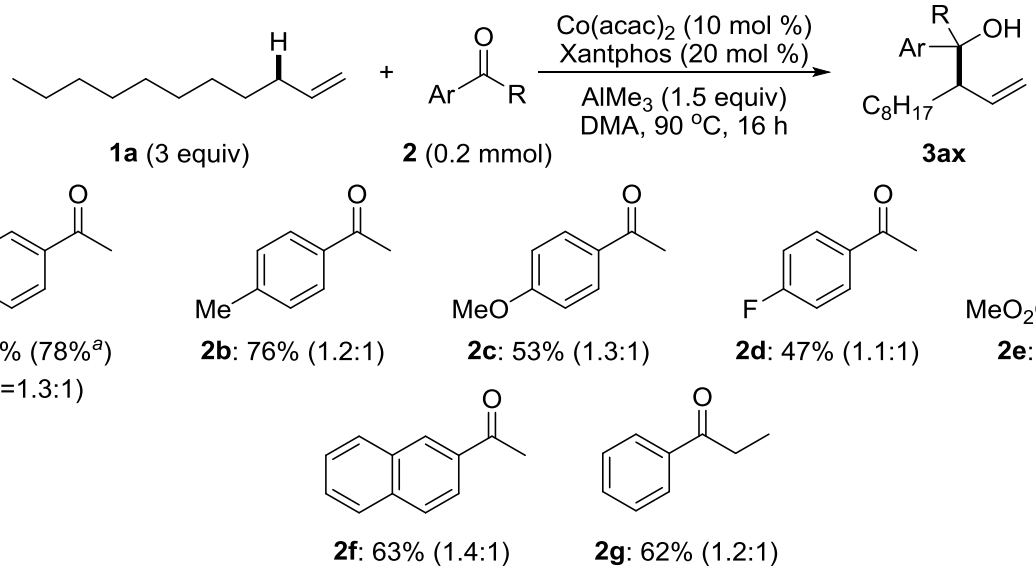
(B-2) Preparation of alkenes

1-Undecene (**1a**) and 1-octadecene (**1b**) were purchased from Tokyo Kasei, Co., Ltd and used after distillation. 6-Phenyl-1-hexene (**1c**) was prepared according to the reported procedure.[1]

[1] Krishna, P. R.; Srinivas, R. *Tetrahedron Lett.* **2007**, *48*, 2013.

(C) General procedure for allylic C(sp^3)–H addition to ketones

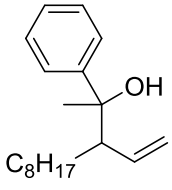
(C-1) Examination of ketone electrophiles



[a]With 1 mmol of **2a**.

To an oven-dried test tube was placed $Co(acac)_2$ (5.2 mg, 20 μmol, 10 mol %) and Xantphos (23.1 mg, 40 μmol, 20 mol %) in DMA (2 mL). The resulting mixture was stirred at room temperature until the materials had been completely dissolved. After the solution had been cooled to 0 °C, it was stirred for 1 minute, and then $AlMe_3$ (2 M in toluene, 0.15 mL, 0.3 mmol, 1.5 equiv) was added. The dark green solution was stirred for another 1 minute, and then 1-undecene (**1a**, 0.6 mmol, 120 μL, 3.0 equiv) was added followed by the addition of ketone **2** (0.2 mmol, 1.0 equiv). The resulting mixture was stirred at 90 °C for 16 h. After cooling the mixture to 0 °C, the reaction was quenched by 1 M HCl aq and extracted with ethyl acetate (3 times). The combined organic layer was washed with brine and dried over Na_2SO_4. After the solids had been filtered off, the solvent was removed under reduced pressure and the residue was dried under vacuum to afford the crude mixture. The approximate yield of **3ax** was determined at this stage using 1,1,2,2-tetrachloroethane (δ = 6.1 ppm in $CDCl_3$, 2H) as an internal standard. If ketone **2** remained, $NaBH_4$ was added to convert it into the corresponding alcohol, which could be easily separated from **3ax** by silica-gel column chromatography. It was then purified by silica-gel column chromatography to afford the product **3ax**.

2-Phenyl-3-vinylundecan-2-ol (3aa): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2a** (23 μL, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 20:1) afforded **3aa** as colorless oil (38.5 mg, 140 μmol, 70%, dr = 1.3:1). Preparative scale synthesis: **1a** (600 μL, 3 mmol, 3.0 equiv), **2a** (117 μL, 1 mmol, 1.0 equiv), $Co(acac)_2$ (25.7 mg, 0.1 mmol, 10 mol %), Xantphos (115.7 mg, 0.2 mmol, 20 mol %), and $AlMe_3$ (2 M in toluene, 0.75 mL, 1.5 mmol, 1.5 equiv) were used in DMA (10 mL). Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 20:1) afforded 3aa as colorless oil (215.1 mg, 0.784 mmol, 78%, dr = 1.3:1).

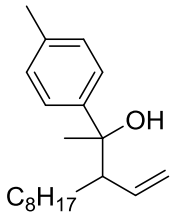


3aa

IR (neat): 3467, 2925, 2855, 1637, 1446, 1375, 1065, 913, 759, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.21 (m, 5H), 5.63-5.52 (m, 1H), 5.21-5.01 (m, 2H), 2.30-2.23 (m, 1H), 1.53/1.51 (s, 3H), 1.26-1.06

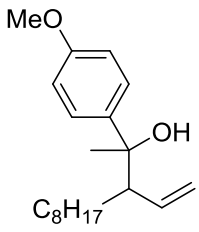
(m, 14H), 0.85 (t, J = 7.1 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 146.5, 138.9, 138.6, 127.84, 127.75, 126.6, 126.3, 125.9, 125.2, 118.8, 118.1, 76.0, 75.5, 56.6, 55.6, 31.8, 29.42, 29.41, 29.37, 29.2, 28.9, 28.6, 28.4, 27.8, 27.7, 25.4, 22.6, 14.1 ppm; HRMS (EI) *m/z* calcd. for $C_{19}H_{28}$ $[M\text{-}H_2O]^+$: 256.2191, found: 256.2191.

2-(*p*-Tolyl)-3-vinylundecan-2-ol (3ab): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2b** (27 μL, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 100:1 to 20:1) afforded **3ab** as colorless oil (44 mg, 153 μmol, 76%, dr = 1.2:1). IR (neat): 3466, 2925, 2855, 1637, 1512, 1457, 1374, 1078, 912, 817 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31/7.26 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H), 5.63-5.52 (m, 1H), 5.21-5.03 (m, 2H), 2.34 (s, 3H), 2.27-2.22 (m, 1H), 1.51/1.49 (s, 3H), 1.25-1.06 (m, 14H), 0.85 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.2, 143.6, 139.1, 138.7, 136.1, 135.8, 128.54, 128.46, 125.8, 125.1, 118.7, 117.9, 75.8, 75.3, 56.6, 55.6, 31.8, 29.45, 29.43, 29.42, 29.39, 29.2, 28.9, 28.7, 28.5, 27.8, 27.7, 25.4, 22.6, 20.94, 20.91, 14.1 ppm; HRMS (EI) *m/z* calcd. for $C_{20}H_{30}$ $[M\text{-}H_2O]^+$: 270.2348, found: 270.2349.



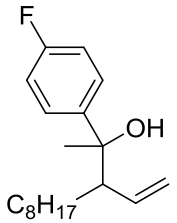
3ab

2-(4-Methoxyphenyl)-3-vinylundecan-2-ol (3ac): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2c** (27.5 mg, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 50:1) afforded **3ac** as colorless oil (29 mg, 96 μmol, 53%, dr = 1.3:1). IR (neat): 3466, 2925, 2854, 1611, 1510, 1248, 1179, 1036, 912, 832 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.35 (d, J = 8.5 Hz, 1H), 7.29 (d, J = 8.5 Hz, 1H), 6.86 (d, J = 8.5 Hz, 2H), 5.61-5.52 (m, 1H), 5.22-5.03 (m, 2H), 3.81 (s, 3H), 2.26-2.20 (m, 1H), 1.51/1.49 (s, 3H), 1.26-1.00 (m, 14H), 0.85 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 158.2, 158.0, 139.3, 139.1, 138.7, 127.1, 126.4, 118.8, 118.0, 113.1, 113.0, 75.7, 75.2, 56.8, 55.8, 55.2, 31.84, 31.82, 29.5, 29.4, 29.2, 28.82, 28.79, 28.5, 27.8, 27.7, 25.3, 22.6, 14.1 ppm; HRMS (EI) *m/z* calcd. for $C_{20}H_{30}O$ $[M\text{-}H_2O]^+$: 286.2297, found: 286.2292.



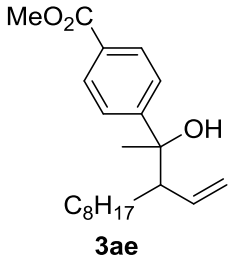
3ac

2-(4-Fluorophenyl)-3-vinylundecan-2-ol (3ad): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2d** (25.7 mg, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 20:1 to 10:1) afforded **3ad** as colorless oil (26 mg, 88 μmol, 47%, dr = 1.1:1). IR (neat): 3466, 2926, 2855, 1603, 1509, 1226, 1161, 1077, 915, 837 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41-7.31 (m, 2H), 7.04-6.98 (m, 2H), 5.60-5.50 (m, 1H), 5.23-5.03 (m, 2H), 2.25-2.18 (m, 1H), 1.56 (s, 1H), 1.52/1.50 (s, 3H), 1.29-1.00 (m, 14H), 0.86 (t, J = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 161.7 (d, J_{CF} = 248 Hz), 161.5 (d, J_{CF} = 249 Hz), 142.9 (d, J_{CF} = 2.8 Hz), 142.3 (d, J_{CF} = 2.9Hz), 138.8, 138.3, 127.6 (d, J_{CF} = 7.6 Hz), 126.9 (d, J_{CF} = 7.6 Hz), 119.2, 118.3, 114.52 (d, J_{CF} = 21 Hz), 114.46 (d, J_{CF} = 22 Hz), 75.7, 75.2, 56.8, 55.7, 31.8, 29.42, 29.40, 29.38, 29.2, 28.9, 28.7, 28.5, 27.7, 27.6, 25.3, 22.6, 14.0 ppm; HRMS (EI) *m/z* calcd. for $C_{19}H_{27}F$ $[M\text{-}H_2O]^+$: 274.2097, found: 274.2094.



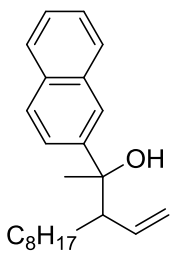
3ad

Methyl 4-(2-Hydroxy-3-vinylundecan-2-yl)benzoate (3ae): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2e** (36.9 mg, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 20:1 to 10:1) afforded **3ae** as colorless oil (46 mg, 139 μmol, 66%, dr = 1.4:1). IR (neat): 3500, 2926, 2855, 1726, 1609, 1437, 1281, 1191, 1115, 713 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.00 (dd, *J* = 8.6, 1.4 Hz, 2H), 7.51-7.45 (m, 2H), 5.63-5.49 (m, 1H), 5.23-5.06 (m, 2H), 3.91 (s, 3H), 2.30-2.22 (m, 1H), 1.51/1.52 (s, 3H), 1.36-1.03 (m, 14H), 0.85 (t, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.0, 152.6, 151.9, 138.4, 138.0, 129.2, 129.1, 128.5, 128.2, 126.0, 125.3, 119.2, 118.5, 76.1, 75.6, 56.5, 55.4, 52.0, 31.8, 29.38, 29.36, 29.31, 29.2, 28.9, 28.5, 28.4, 27.7, 27.6, 25.5, 22.6, 14.1 ppm; HRMS (EI) *m/z* calcd. for $C_{21}H_{33}O_3$ $[M]^+$: 333.2430, found: 333.2423.



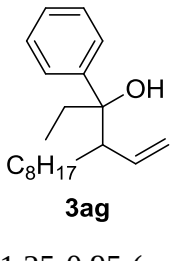
3ae

2-(Naphthalen-2-yl)-3-vinylundecan-2-ol (3af): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2f** (33.4 mg, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 50:1) afforded **3af** as colorless oil (40 mg, 123 μmol, 63%, dr = 1.4:1). IR (neat): 3466, 2925, 2854, 1636, 1464, 1375, 1127, 913, 817, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87-7.78 (m, 4H), 7.59-7.41 (m, 3H), 5.69-5.55 (m, 1H), 5.22-5.07 (m, 2H), 2.40-2.33 (m, 1H), 1.62/1.57 (s, 3H), 1.26-1.02 (m, 14H), 0.81 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 144.1, 138.9, 138.5, 133.0, 132.9, 132.3, 132.1, 128.2, 128.1, 127.5, 127.44, 127.41, 125.9, 125.8, 125.67, 125.58, 124.56, 124.54, 124.48, 123.8, 123.7, 119.0, 118.2, 76.3, 75.7, 56.4, 55.3, 31.79, 31.78, 29.44, 29.39, 29.3, 29.2, 29.1, 28.7, 28.5, 27.8, 27.7, 25.4, 22.6, 14.1 ppm; HRMS (EI) *m/z* calcd. for $C_{23}H_{30}$ $[M\text{-}H_2O]^+$: 306.2348, found: 306.2345.



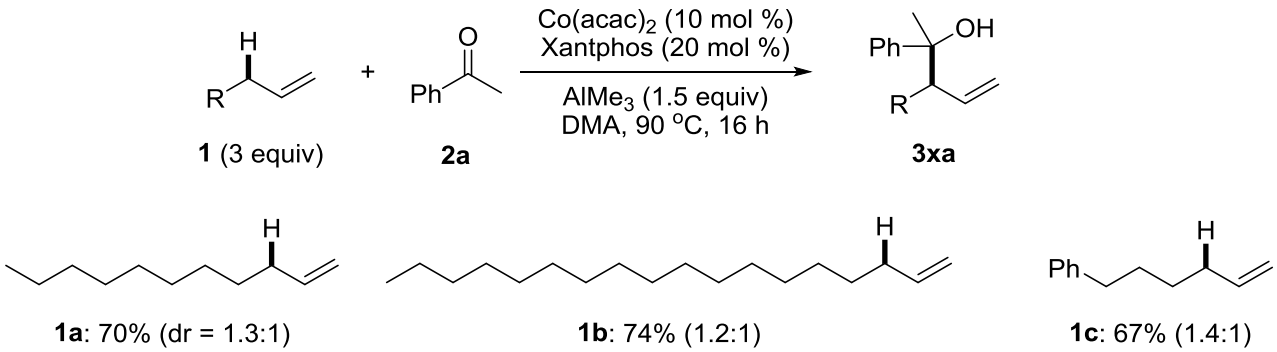
3af

3-Phenyl-4-vinyldodecan-3-ol (3ag): 1a (120 μL, 0.6 mmol, 3.0 equiv) and **2g** (27 μL, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 50:1) afforded **3ag** as colorless oil (36 mg, 125 μmol, 62%, dr = 1.2:1). IR (neat): 3495, 2925, 2855, 1637, 1463, 1376, 1002, 968, 913, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.38-7.30 (m, 4H), 7.25-7.20 (m, 1H), 5.64-5.43 (m, 1H), 5.21-5.02 (m, 2H), 2.33-2.23 (m, 1H), 2.10-2.02/1.87-1.74 (m, 2H), 1.25-0.95 (m, 14H), 0.88-0.83 (m, 3H), 0.77/0.66 (t, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 144.7, 144.1, 138.9, 138.7, 127.8, 127.6, 126.5, 126.3, 126.2, 125.8, 117.98, 117.96, 78.6, 78.1, 55.8, 54.8, 33.5, 31.8, 31.0, 29.6, 29.5, 29.4, 29.33, 29.26, 29.2, 28.3, 27.88, 27.78, 27.6, 22.64, 22.62, 14.1, 7.63, 7.58 ppm; HRMS (EI) *m/z* calcd. for $C_{20}H_{30}$ $[M\text{-}H_2O]^+$: 270.2348, found: 270.2347.



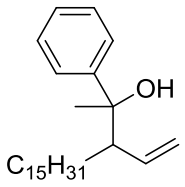
3ag

(C-2) Examination of alkenes



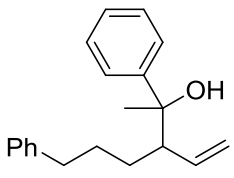
To an oven-dried test tube was placed $Co(acac)_2$ (5.2 mg, 20 μmol, 10 mol %) and Xantphos (23.1 mg, 40 μmol, 20 mol %) in DMA (2 mL). The resulting mixture was stirred at room temperature until the materials had been completely dissolved. After the solution had been cooled to 0 ºC, it was stirred for 1 minute, and then $AlMe_3$ (2 M in toluene, 0.15 mL, 0.3 mmol, 1.5 equiv) was added. The dark green solution was stirred for another 1 minute, and then alkene **1** (0.6 mmol, 3.0 equiv) was added followed by the addition of acetophenone (**2a**, 0.2 mmol, 23 μL, 1.0 equiv). The resulting mixture was stirred at 90 ºC for 16 h. After cooling the mixture to 0 ºC, the reaction was quenched by 1 M HCl aq and extracted with ethyl acetate (3 times). The combined organic layer was washed with brine and dried over Na_2SO_4. After the solids had been filtered off, the solvent was removed under reduced pressure and the residue was dried under vacuum to afford the crude mixture. The approximate yield of **3xa** was determined at this stage using 1,1,2,2-tetrachloroethane (δ = 6.1 ppm in $CDCl_3$, 2H) as an internal standard. If acetophenone (**2a**) remained, $NaBH_4$ was added to convert it into the corresponding 1-phenylethyl alcohol, which could be easily separated from **3xa** by silica-gel column chromatography. It was then purified by silica-gel column chromatography to afford the product **3xa**.

2-Phenyl-3-vinyloctadecan-2-ol (3ba): 1b (190 μL, 0.6 mmol, 3.0 equiv) and **2a** (24 μL, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 50:1) afforded **3ba** as colorless oil (58 mg, 155 μmol, 74%, dr = 1.2:1). IR (neat): 3467, 2924, 2853, 1637, 1465, 1375, 1065, 913, 759, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.21 (m, 5H), 5.64-5.52 (m, 1H), 5.21-5.05 (m, 2H), 2.29-2.23 (m, 1H), 1.54/1.51 (s, 3H), 1.34-1.02 (m, 28H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.2, 146.5, 138.9, 138.6, 127.84, 127.76, 126.6, 126.3, 126.0, 125.2, 118.8, 118.1, 76.0, 75.5, 56.6, 55.6, 31.9, 29.7, 29.64, 29.60, 29.57, 29.52, 29.49, 29.48, 29.41, 29.38, 29.35, 28.9, 28.6, 28.5, 27.8, 27.7, 25.4, 22.7, 14.1 ppm; HRMS (EI) *m/z* calcd. for $C_{26}H_{42}$ $[M-H_2O]^+$: 354.3287, found: 354.3282.



3ba

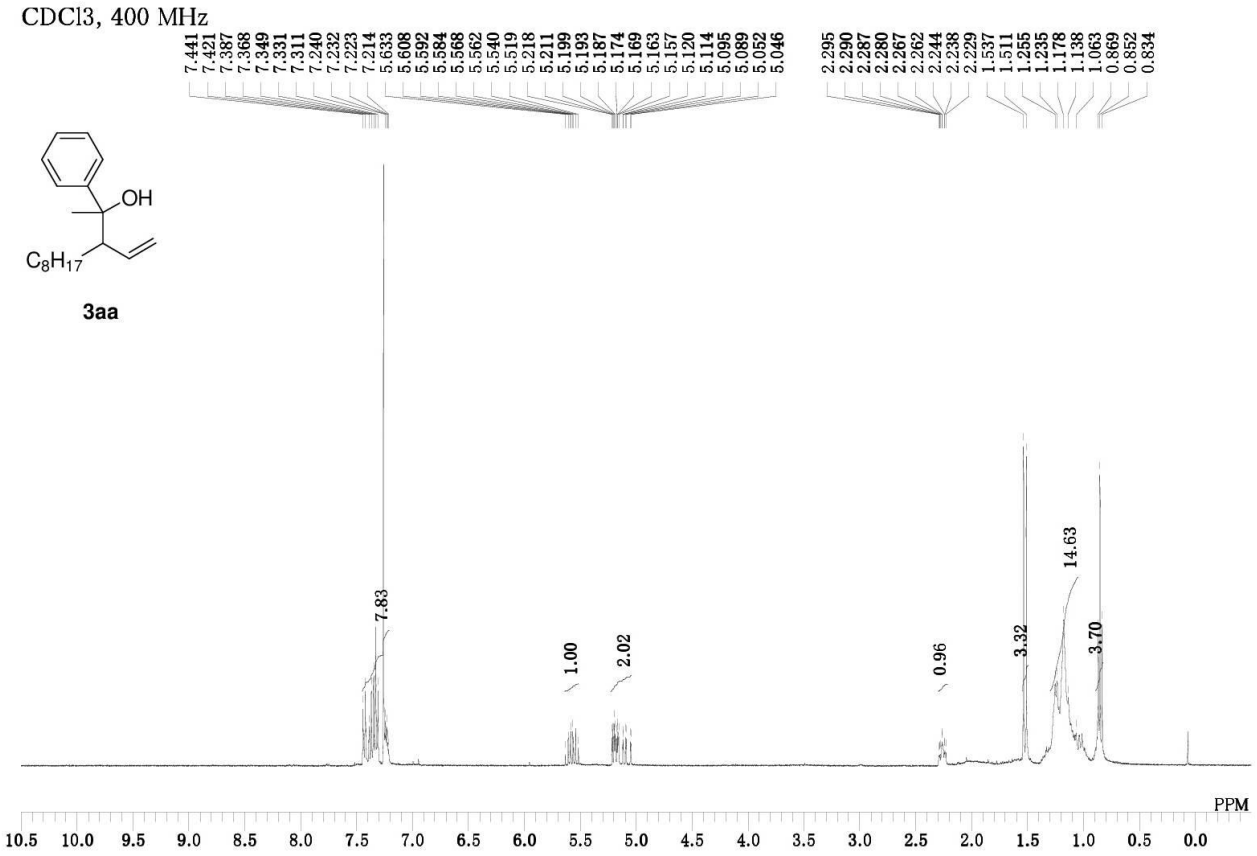
2,6-Diphenyl-3-vinylhexan-2-ol (3ca): 1c (96 mg, 0.6 mmol, 3.0 equiv) and **2a** (23 μL, 0.2 mmol, 1.0 equiv) were employed as starting materials. Purification of the crude product by silica-gel column chromatography (eluent: hexane/ethyl acetate, 40:1 to 10:1) afforded **3ca** as colorless oil (36 mg, 140 μmol, 67%, dr = 1.4:1). IR (neat): 3466, 3025, 2930, 2857, 1602, 1494, 1446, 914, 749, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ: 7.44-7.04 (m, 1H), 5.66-5.51 (m, 1H), 5.21-5.05 (m, 2H), 2.56-2.49 (m,

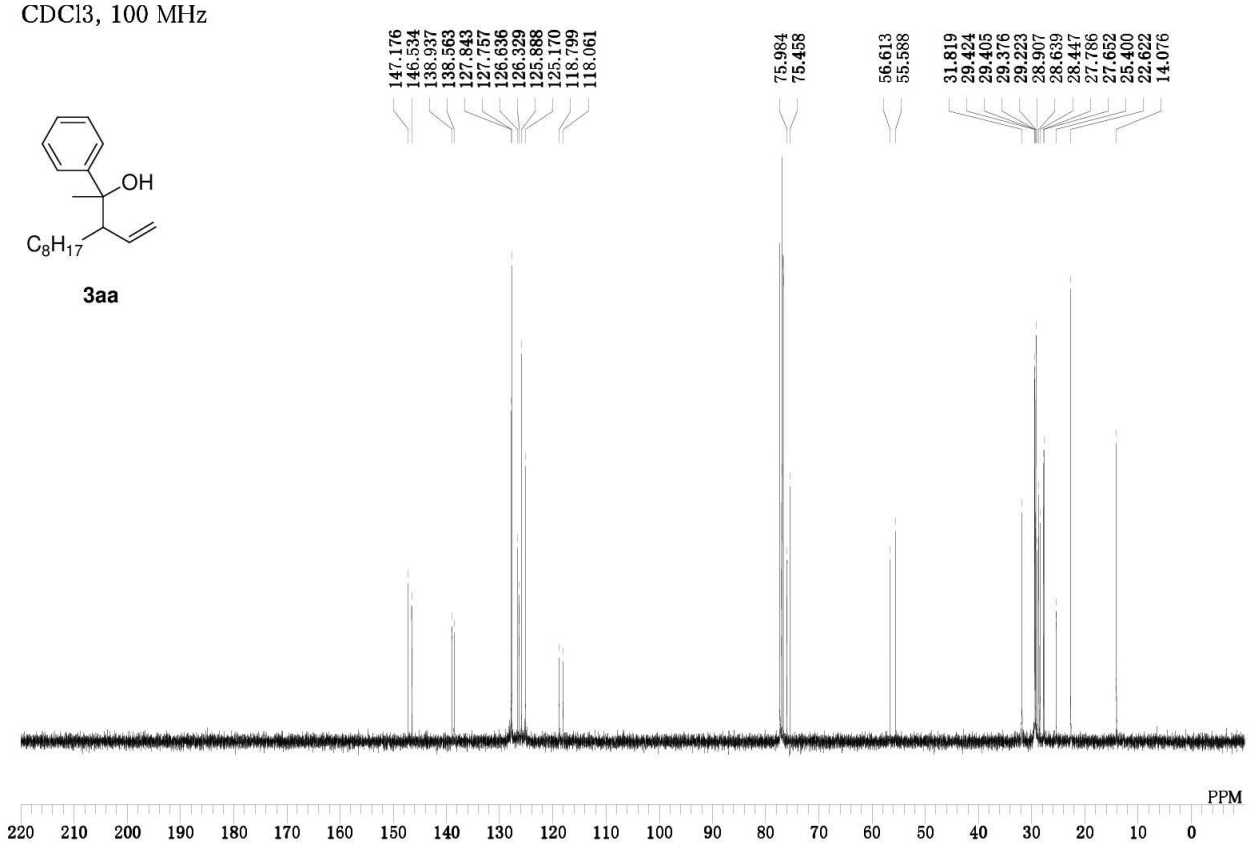


3ca

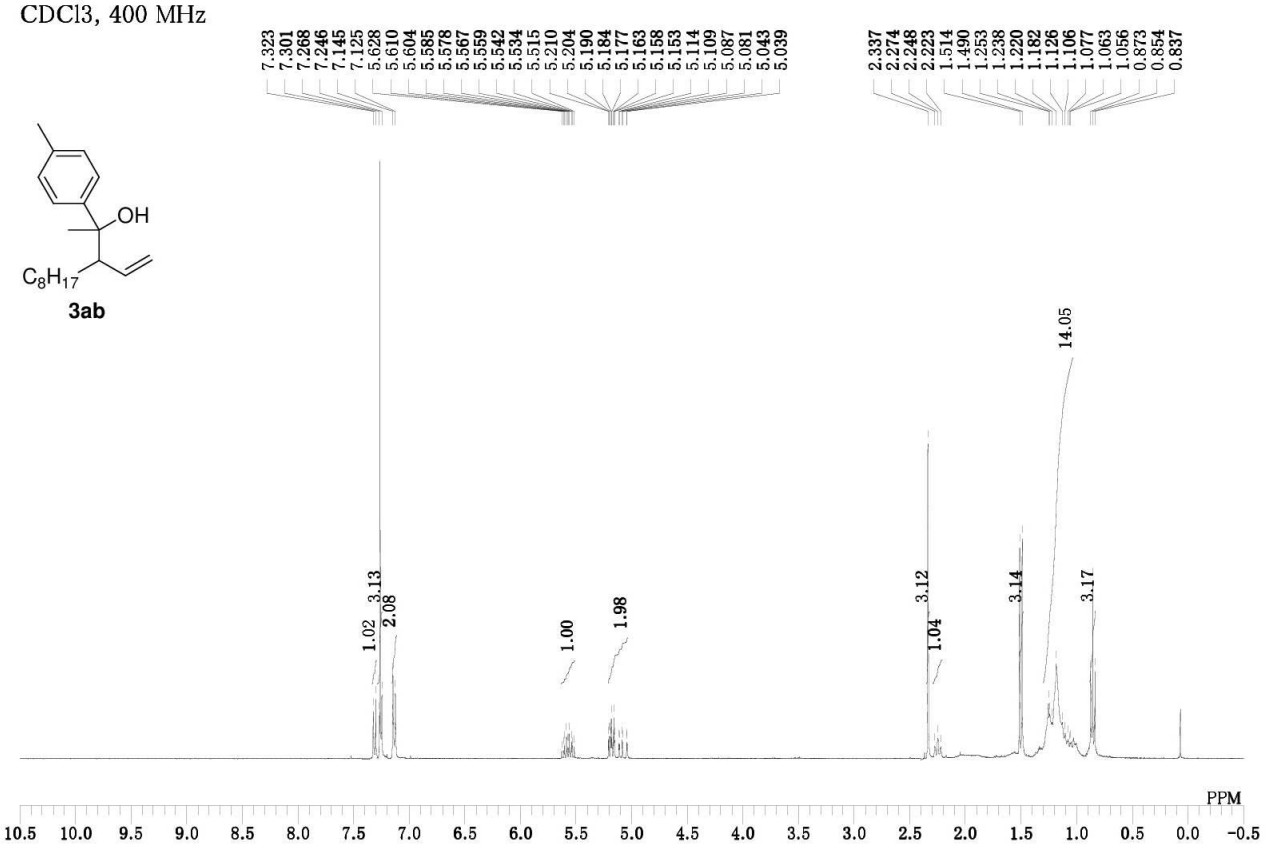
1H), 2.43-2.36 (m, 1H), 2.35-2.29 (m, 1H), 1.54/1.51 (s, 3H), 1.47-1.24 (m, 4H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$) δ: 147.0, 146.4, 142.6, 142.5, 138.6, 138.3, 128.3, 128.2, 127.9, 127.8, 126.7, 126.4, 125.9, 125.5, 125.2, 119.1, 118.3, 76.0, 75.5, 56.5, 55.5, 35.7, 35.6, 29.8, 29.7, 28.9, 28.4, 28.2, 25.5 ppm; HRMS (ESI) *m/z* calcd. for $C_{20}H_{24}ONa$ $[M+Na]^+$: 303.1719, found: 303.1727.

(D) Copies of ^{1}H NMR and ^{13}C NMR spectra

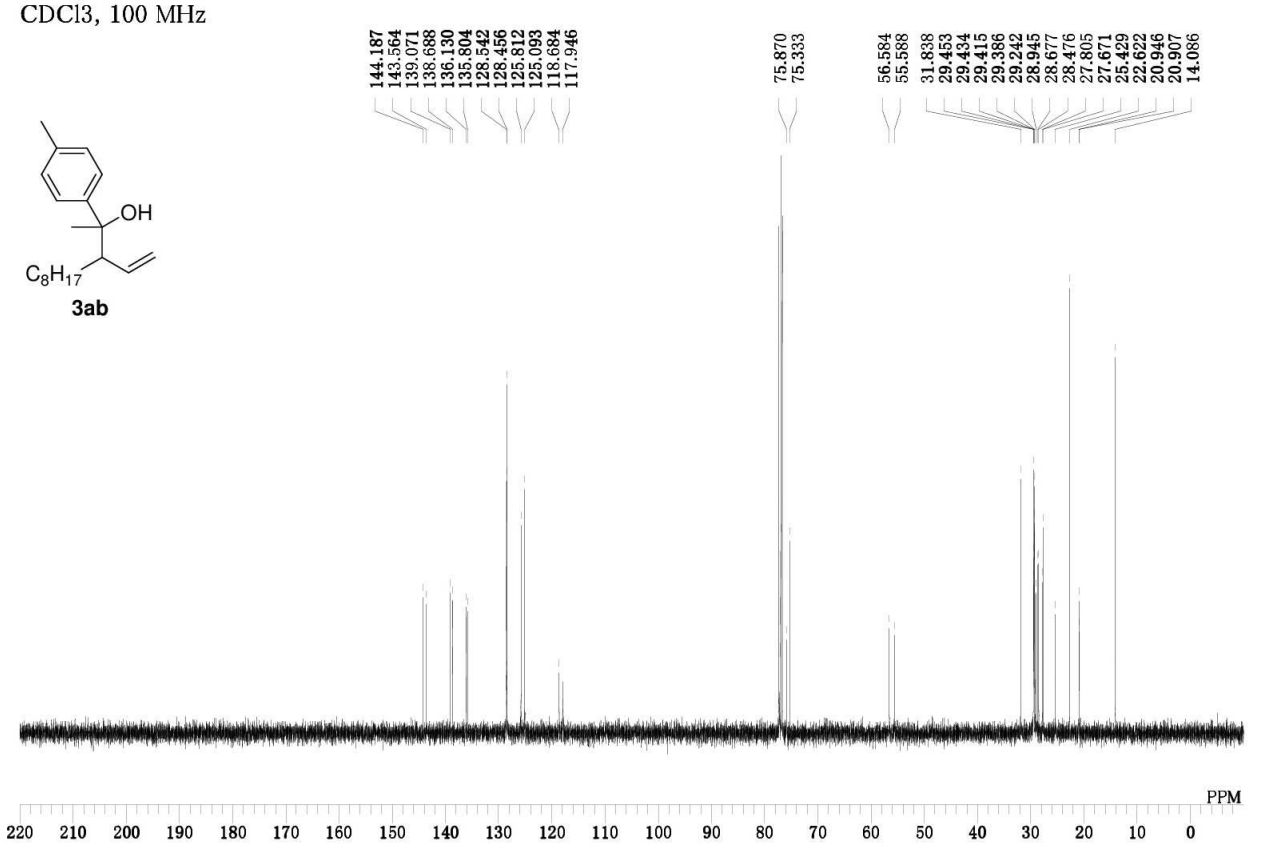




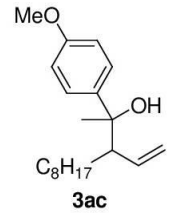
CDCl3, 400 MHz



CDCl3, 100 MHz

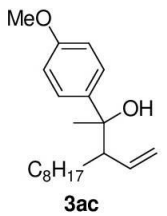


CDCl3, 400 MHz



3ac

CDCl3, 100 MHz



3ac

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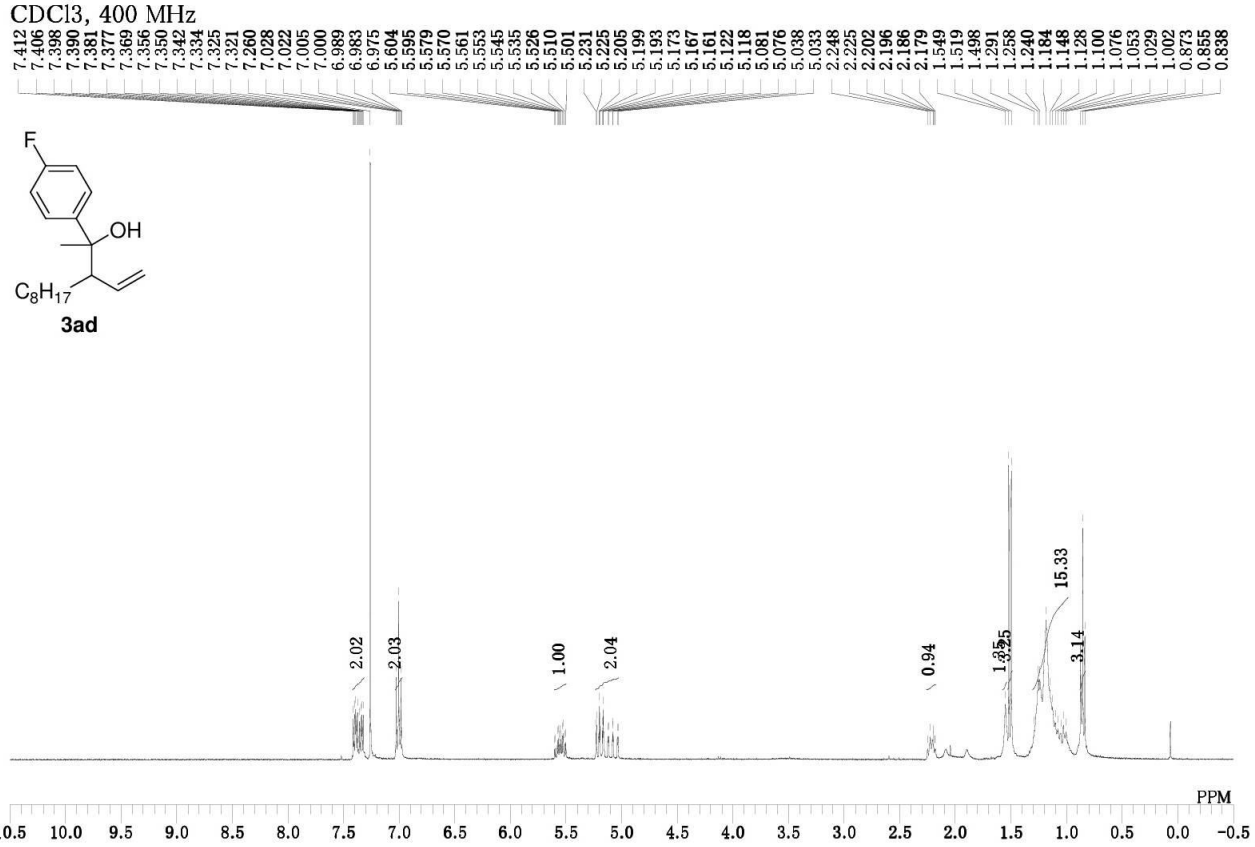

3ad

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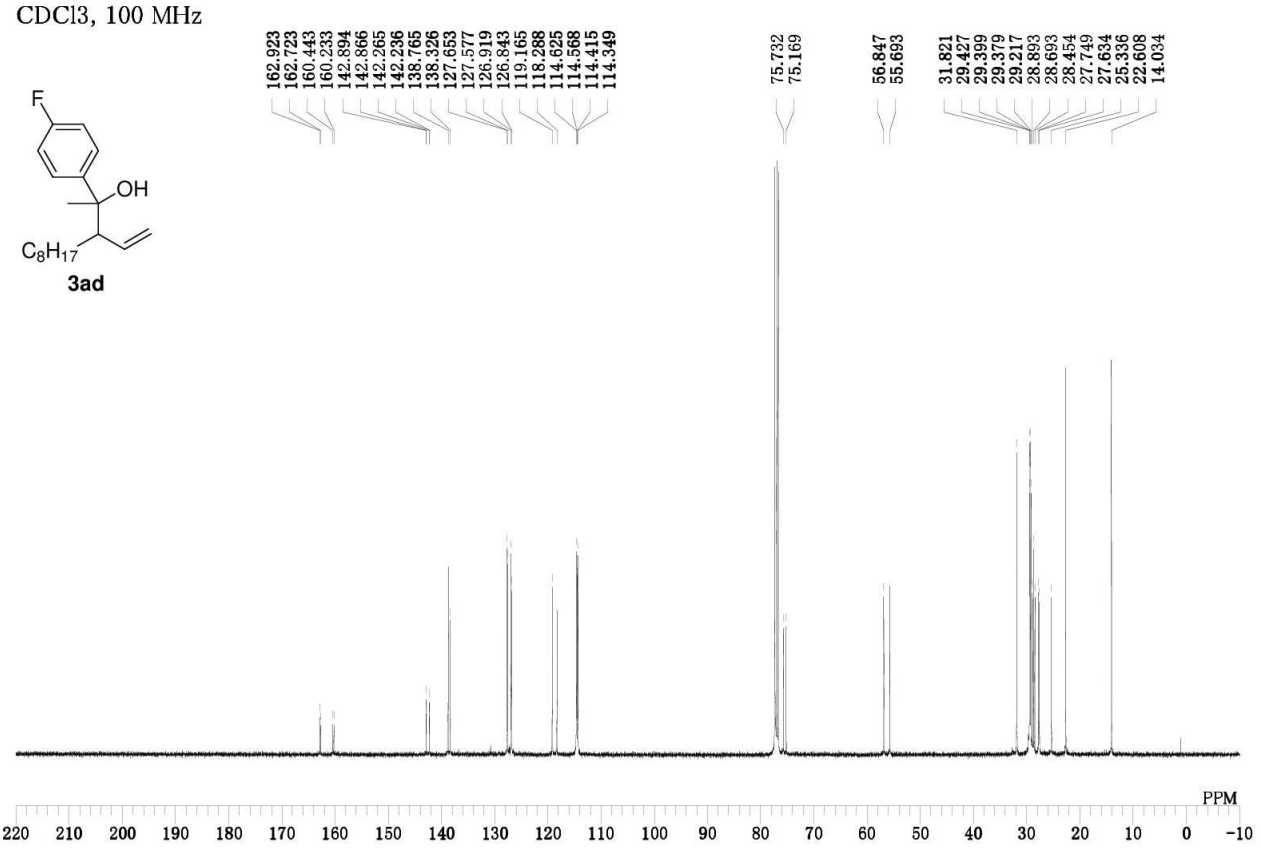
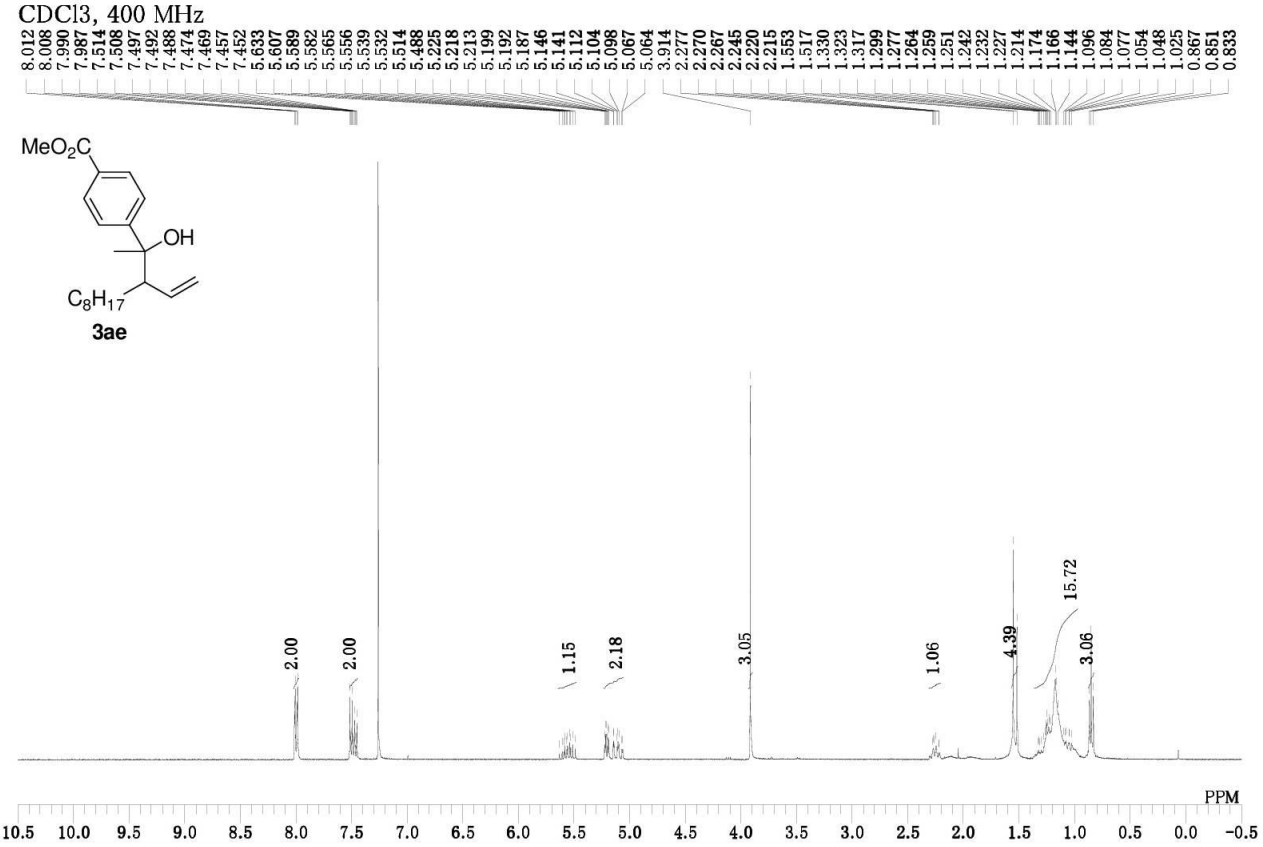
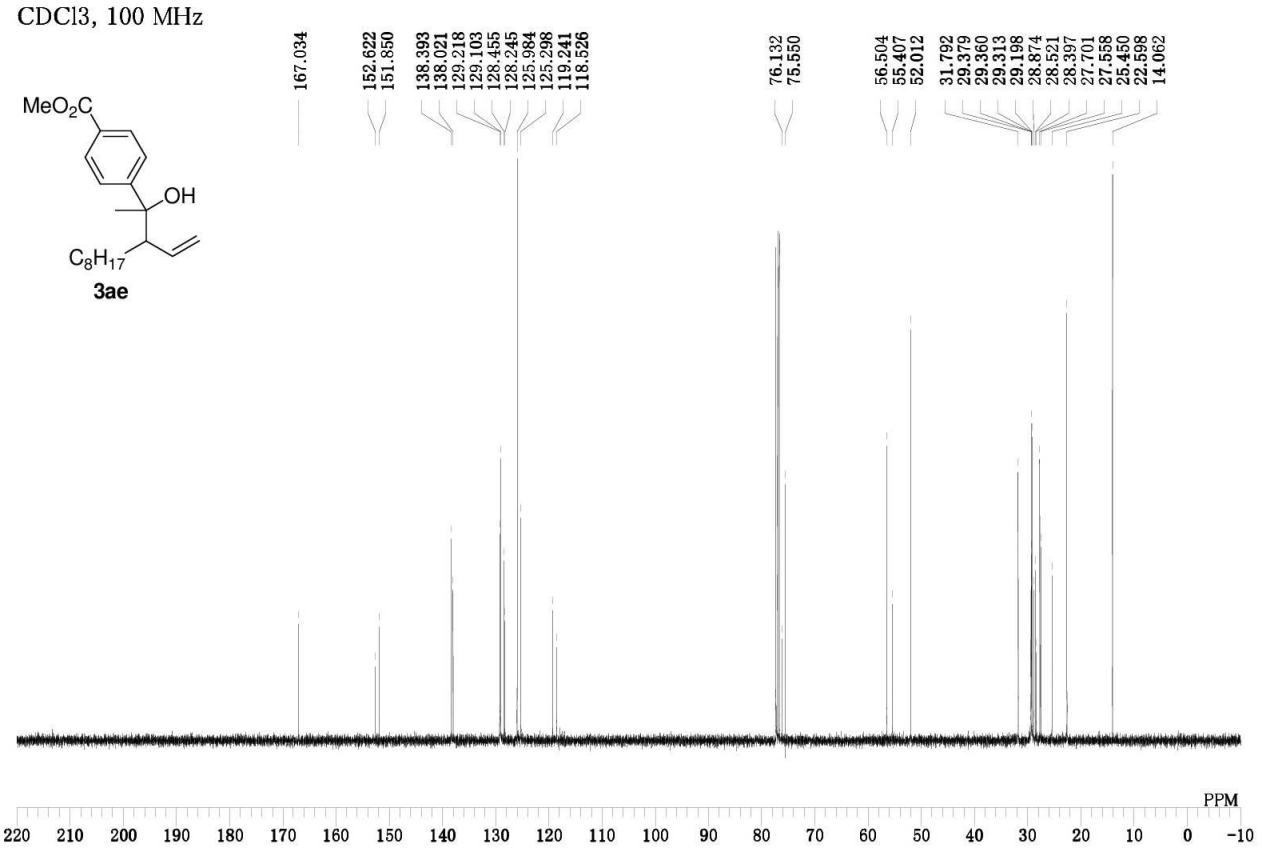


3ad

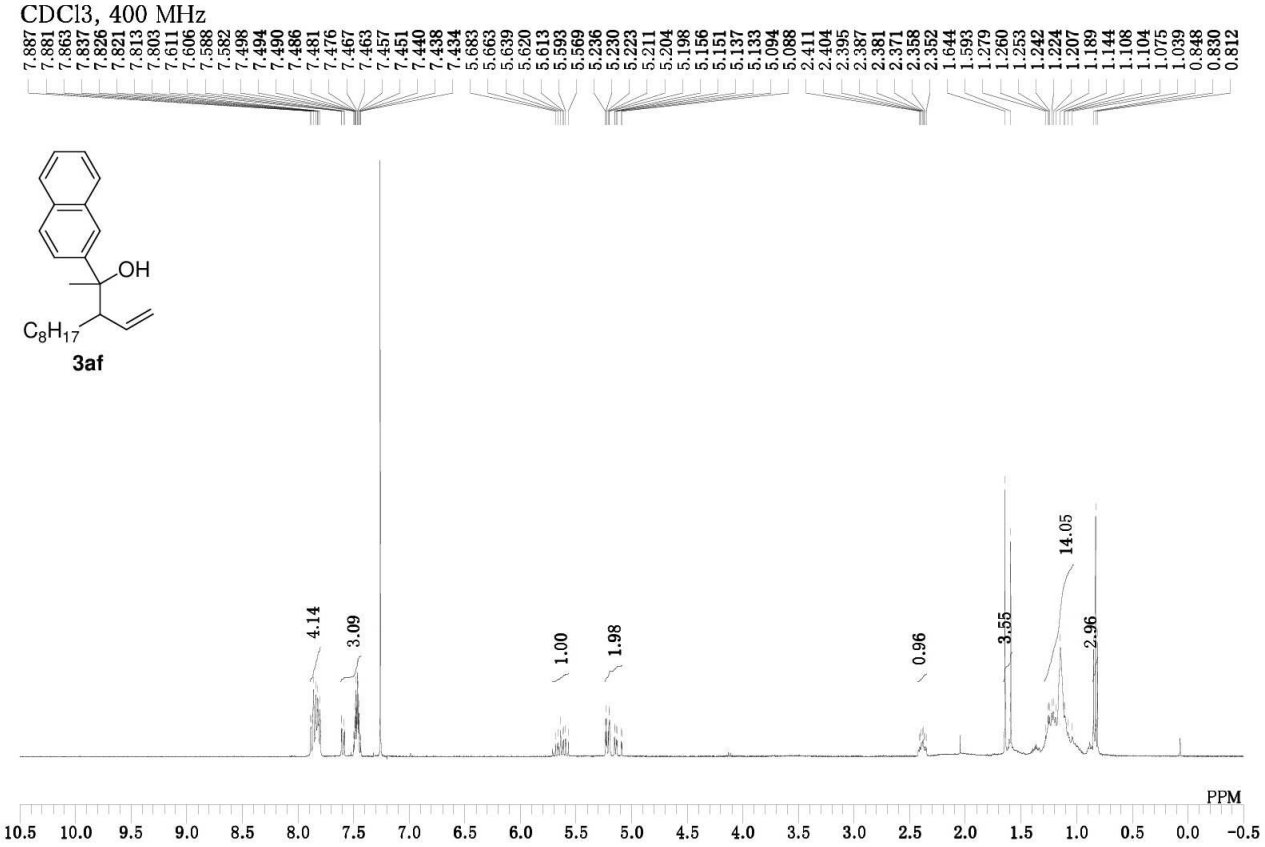
CDCl3, 400 MHz



CDCl3, 100 MHz

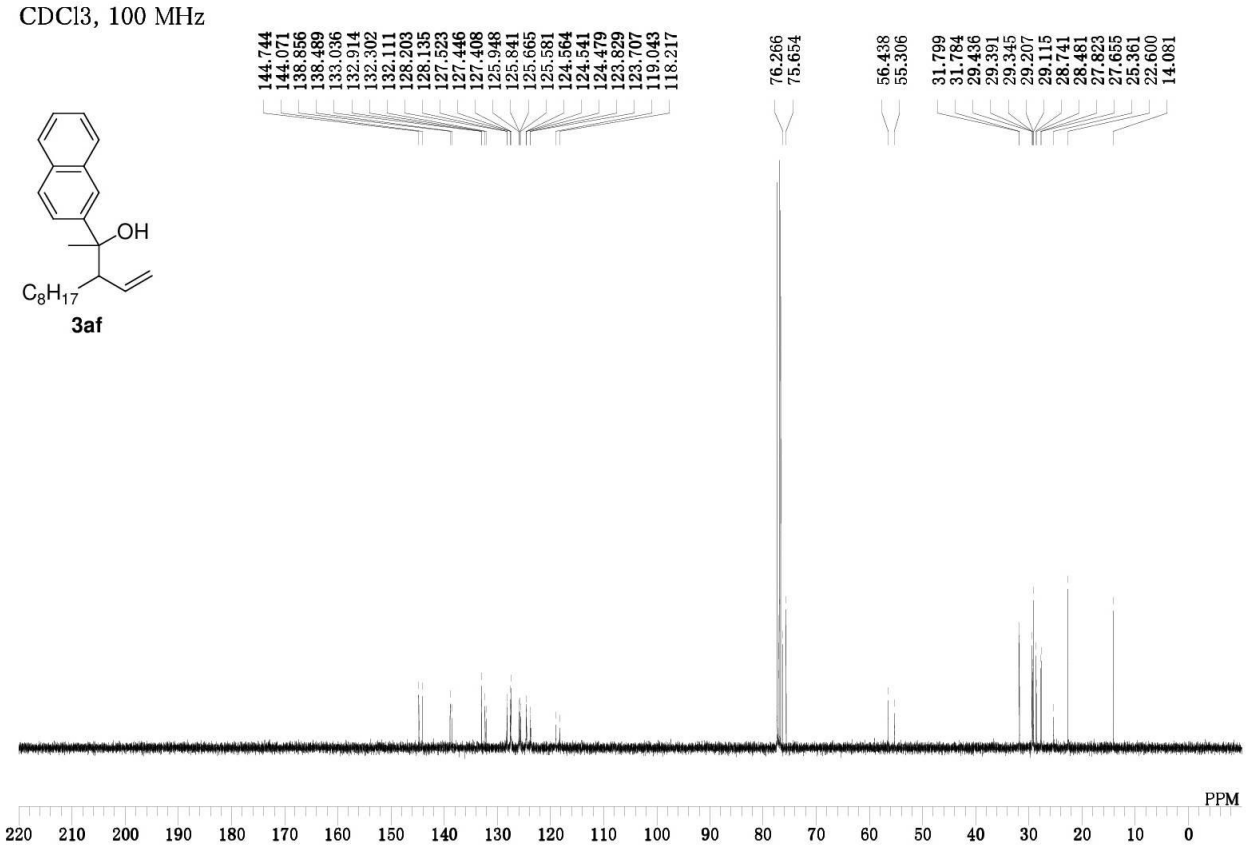


CDCl3, 400 MHz



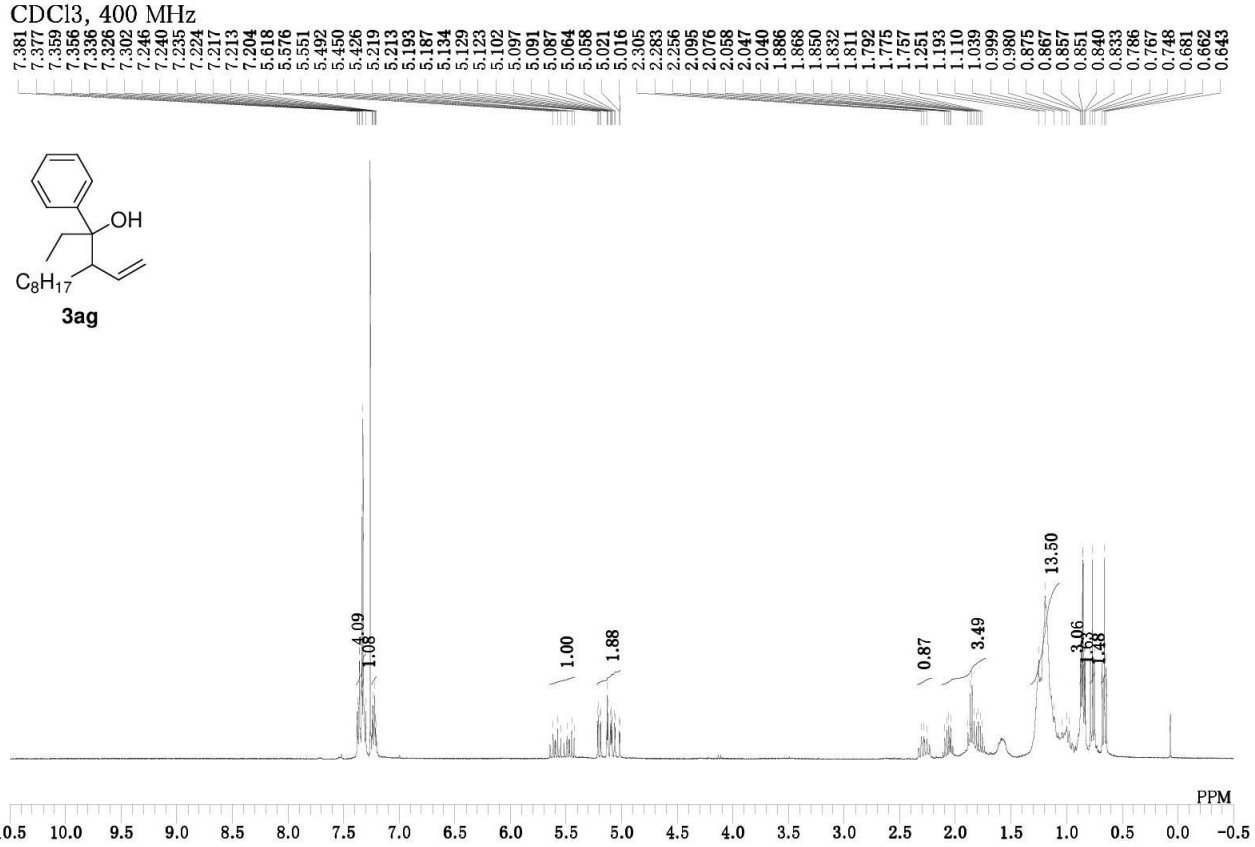
3af

CDCl3, 100 MHz



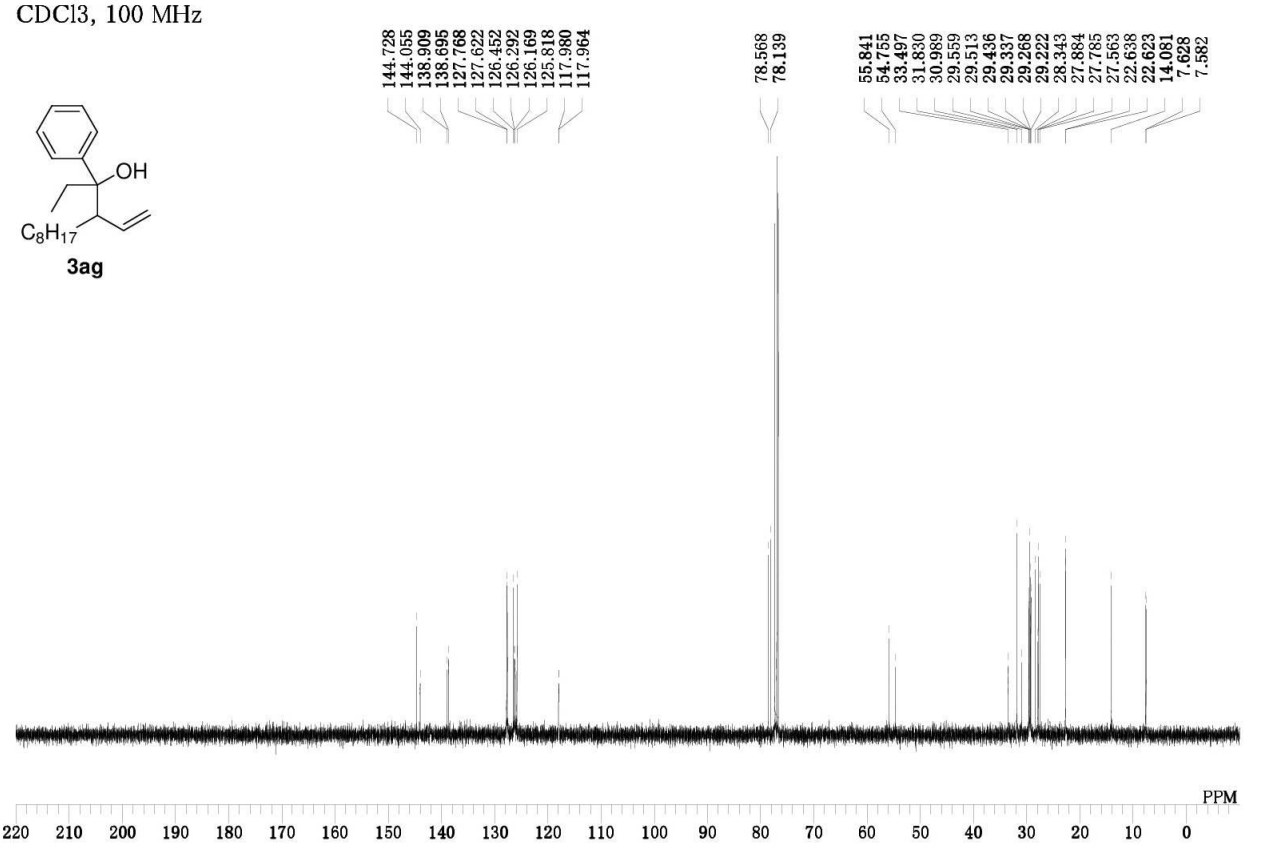
3af

CDCl3, 400 MHz



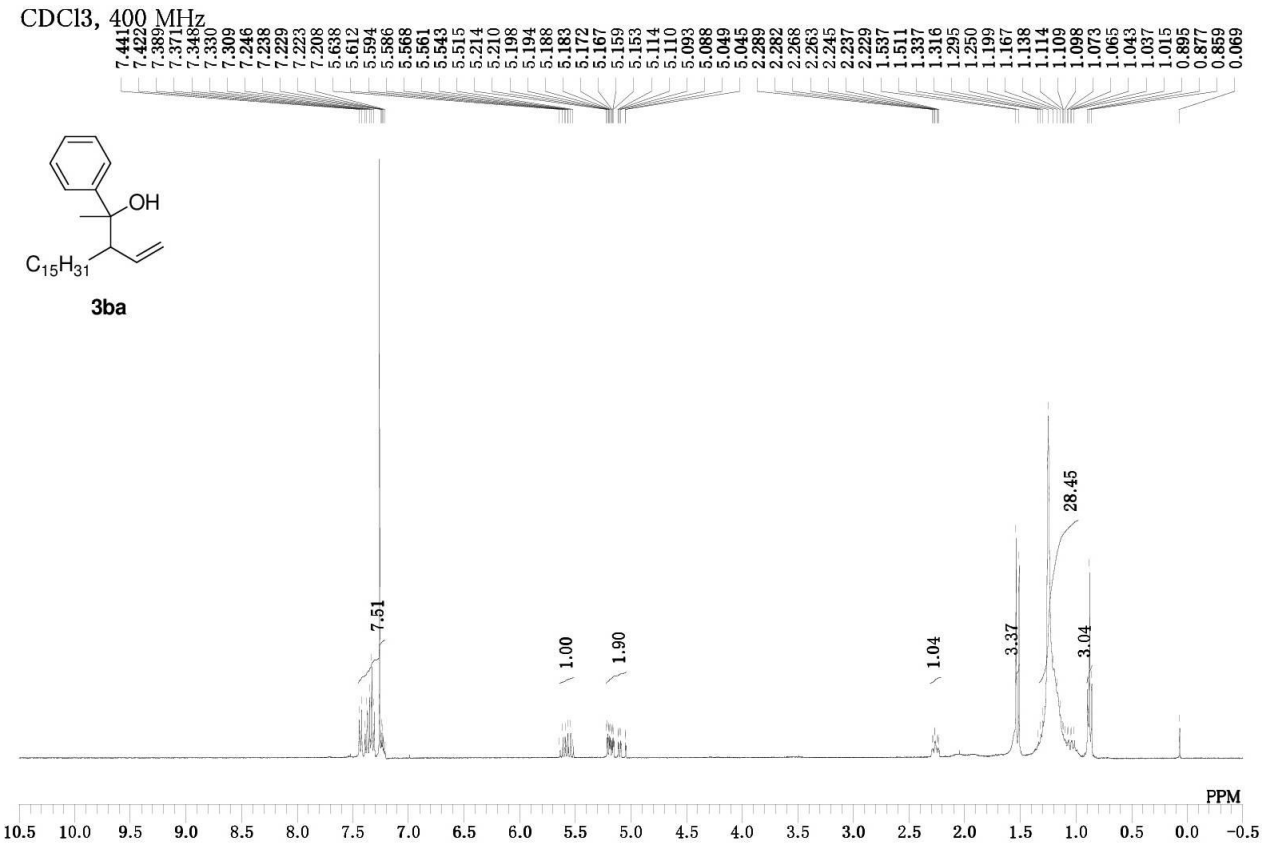
3ag

CDCl3, 100 MHz



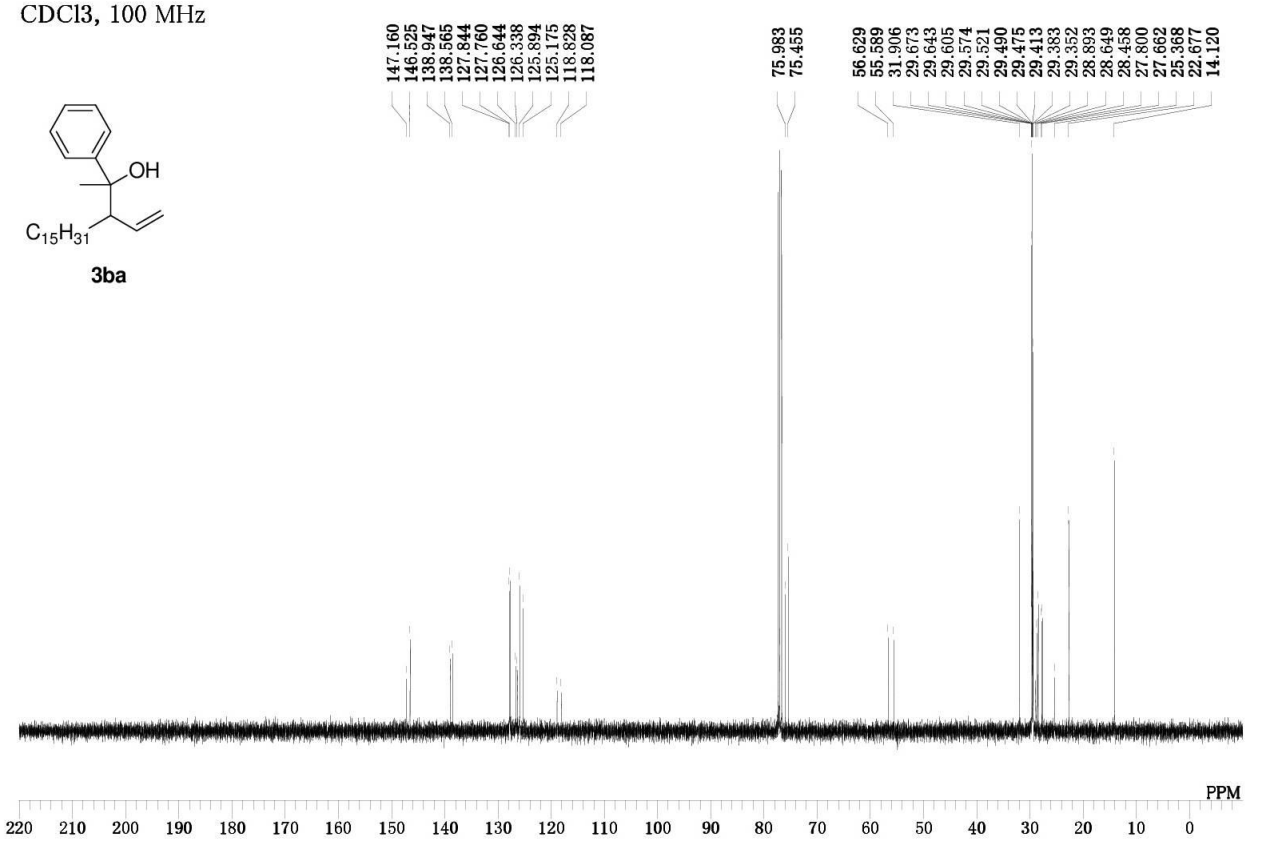
3ag

CDCl3, 400 MHz



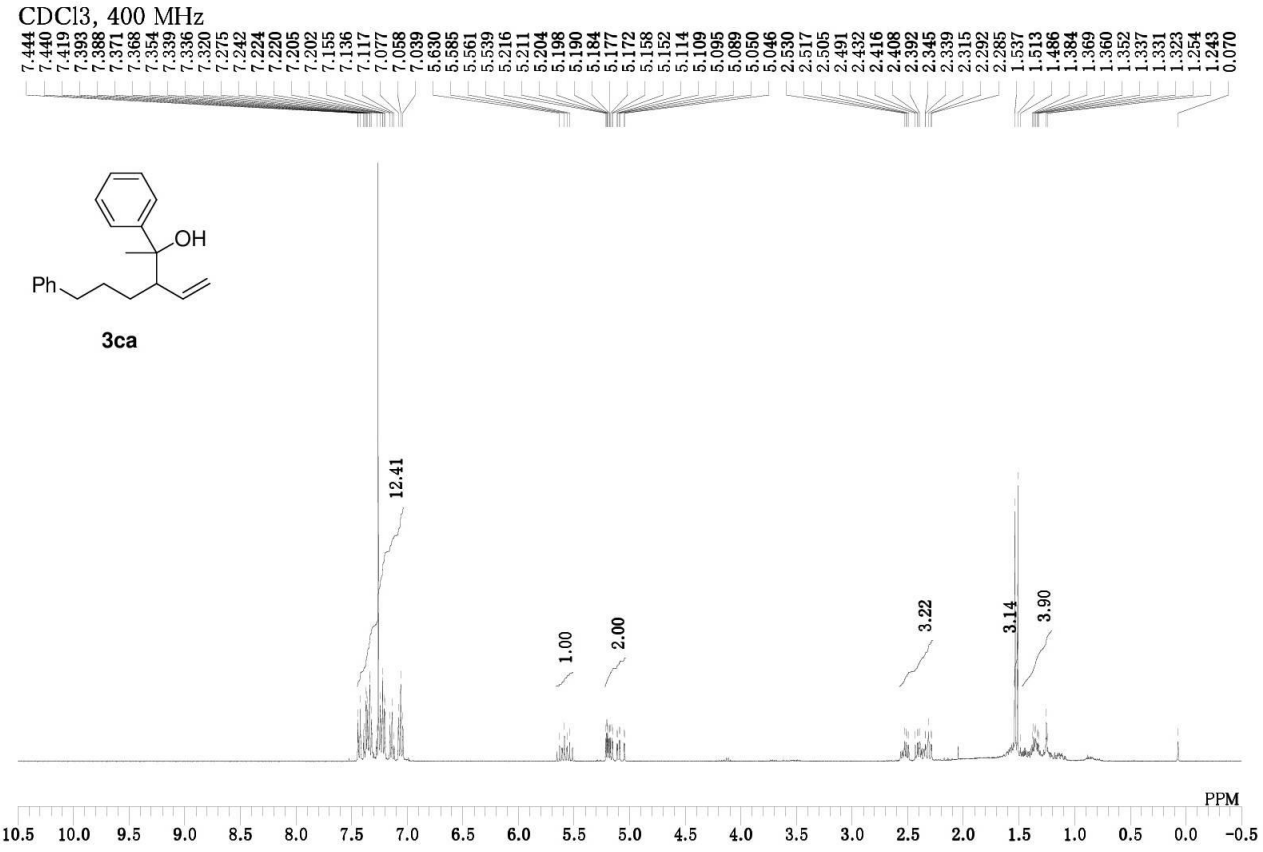
3ba

CDCl3, 100 MHz



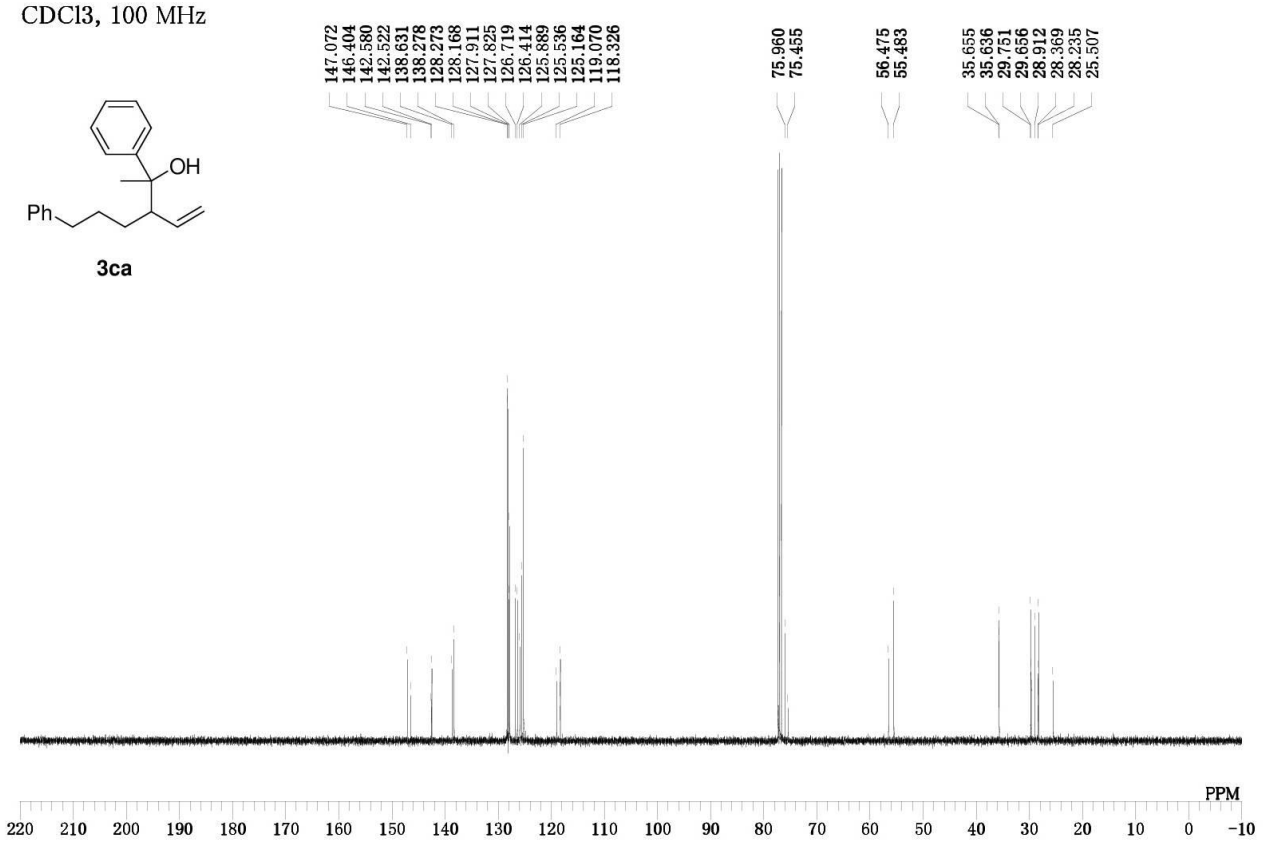
3ba

CDCl3, 400 MHz



3ca

CDCl3, 100 MHz



3ca