*Electronic Supplementary Information (ESI)*

# Oxovanadium(V)-catalyzed oxidative cross-coupling of enolates using $O_2$ as a terminal oxidant

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## 1. Figs. S1-S2 and Tables S1

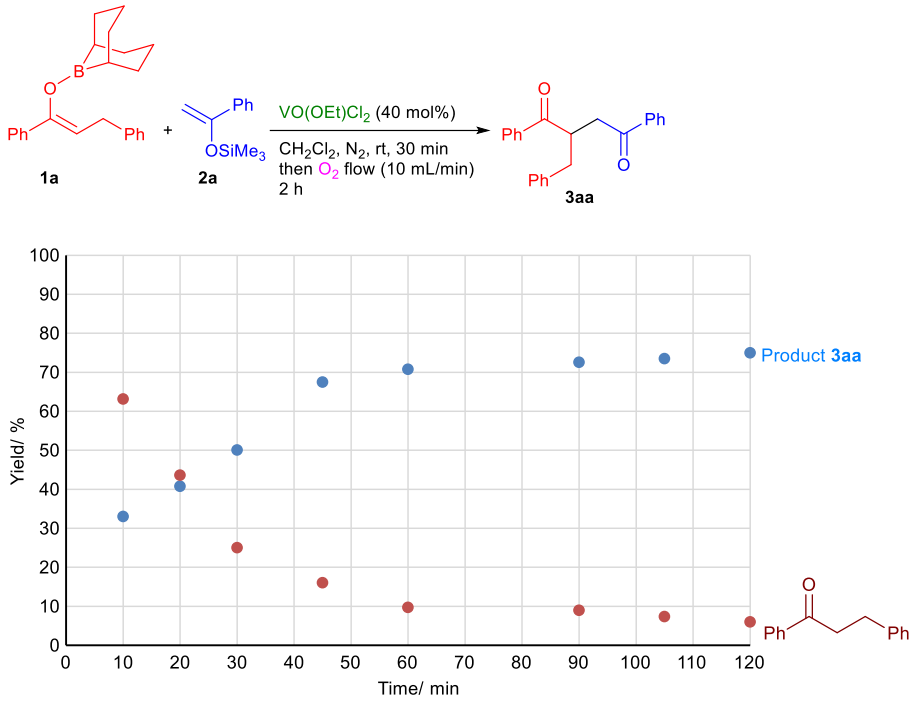



**Fig. S1** Time dependence of the yield. The experiments were carried out by repeating the sampling from the reaction mixture. Each yield was calculated based on the integral ratio compared to an internal standard (1,3,5-trimethoxybenzene) in the crude $^{1}$H NMR spectrum.

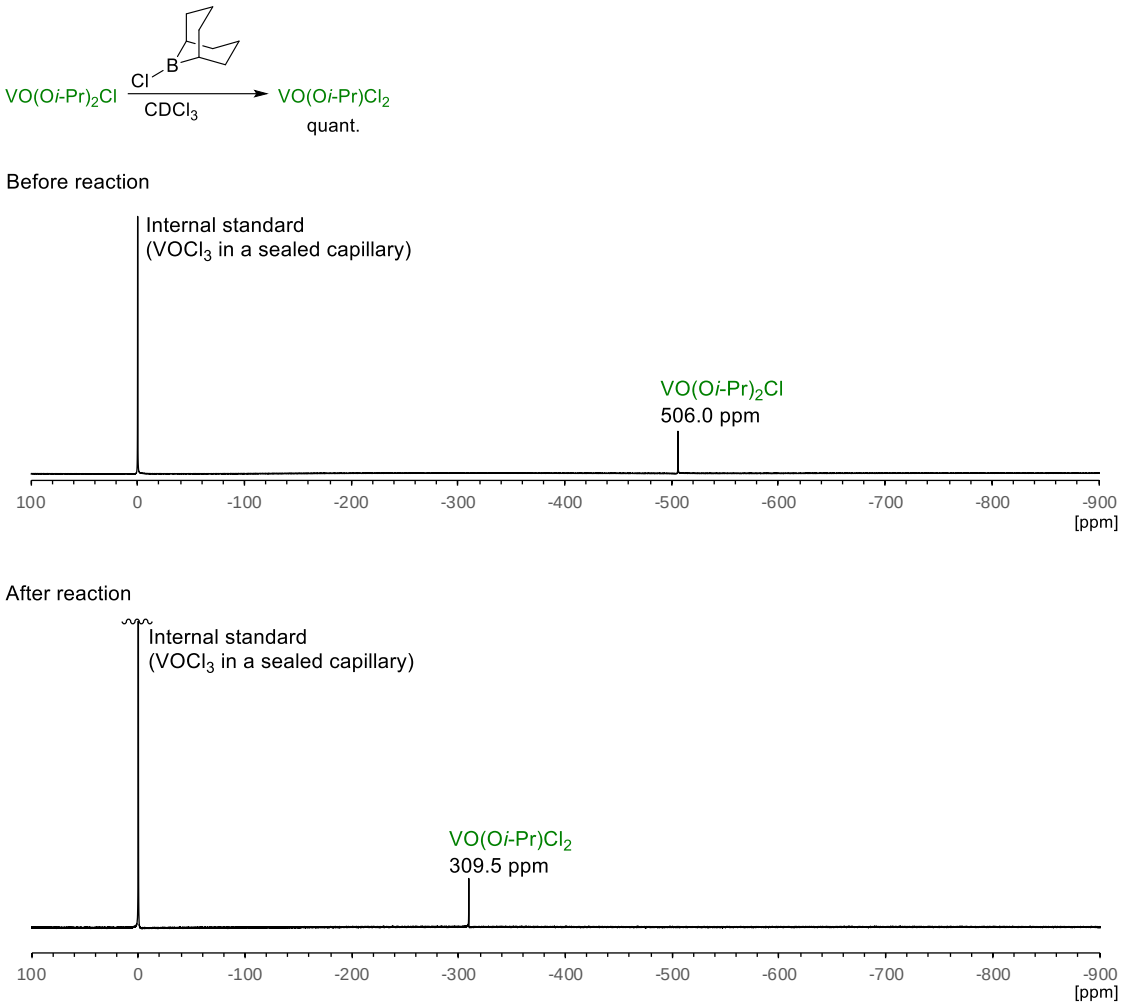
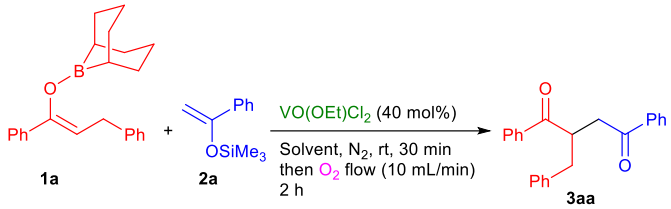



**Fig. S2** $^{51}$V NMR spectra before and after reaction for the ligand exchange of VO(O*i*-Pr)$_2$Cl in the presence of *B*-Cl-9-BBN.

**Table S1.** Screening of solvents




| Entry | Solvent | Yield (%)[a] |
|---|---|---|
| 1 (same as entry 3 in Table 1 in the main text) | $CH_2Cl_2$ | 87 |
| 2 | 1,2-Dichloroethane | 78 |
| 3 | Toluene | 69 |
| 4 | Benzene | 72 |
| 5 | 1,2-Dichlorobenzene | 70 |
| 6 | THF | 33 |
| 7 | MeCN | 33 |

[a] Calculated based on the integral ratio toward the internal standard (1,3,5-trimethoxybenzene) in the crude $^1$H NMR spectrum.

## 2. General and Materials

### General

$^{1}H$ (400 MHz), $^{13}C$ (100 MHz), and $^{51}V$ (105 MHz) NMR spectra were measured on a JEOL ECS400 spectrometer. $CDCl_3$ was used as a solvent and the corresponding solvent peak ($^{1}H$, $\delta$ = 7.26 ppm for residual $CHCl_3$; $^{13}C$, $\delta$ = 77.0 ppm for $CDCl_3$) or internal standard ($^{51}V$, $\delta$ = 0 ppm for $VOCl_3$ in a sealed capillary) was used as a reference. Recycling preparative HPLC was performed on Japan Analytical Industry LC-9225NEXT with tandemly arranged GPC columns (JAIGEL-1H + JAIGEL-2H) using $CHCl_3$ as a solvent. Infrared spectra were recorded on a JASCO FT/IR-480plus. High resolution mass spectra (HRMS) were obtained on a JEOL JMS-T100LP AccuTOF LC-plus in direct analysis real time (DART) method using PEG as the internal standard. ESR spectra were taken on a Bruker EMX micro spectrometer (modulation amplitude: 1.0 G, modulation frequency: 100.0 KHz, conversion: 30.00 ms, time constant: 10.24 ms).

### Materials

$VO(OEt)Cl_2$, donated from Nichia corporation, was bacically used after distillation (new bottle opened in the $N_2$-filled glove box is not a problem for use of the reaction. To keep the quality, it was stored in -30 °C freezer in the glove box.). Dry $CH_2Cl_2$, toluene, THF, and MeCN were prepared using a Glass Contour Solvent Dispensing System. Dry 1,2-dichloroethane was prepared by distillation after refluxing with $CaH_2$. Boron enolates **1a-h** were prepared via 1,4-hydroboration of the corresponding enones with 9-borabicyclo[3.3.1]nonane (9-BBN) dimer in $CH_2Cl_2$ (see experimental section for the typical procedure.). Boron enolates **1a** used for entry 4 in Table 1 was prepared from 3-phenylpropiophenone with $N(i\text{-}Pr)_2Et$.[S1] Boron enolates **1i-j** were prepared from ethyl 3-phenylpropanoate or *N*,*N*-diethyl-3-phenylpropanamide with $Cy_2BOTf$ and $NEt_3$.[S2-3] Silyl enol ether **2a**, **2c**, and **2d** were purchased from Aldrich, and used without further purification. Silyl enol ether **2b** was prepared from 4'-fluoroacetophenone with $Me_3SiCl$ in the presence of $NEt_3$ and NaI,[S4] and used after distillation. Ketene silyl acetal **2e**[S5] was prepared by trapping the lithium enolate generated by $LiN(i\text{-}Pr)_2$ with $t\text{-}BuMe_2SiCl$. Methallyltrimethylsilane **2f** was purchased from TCI, and used without further purification. *B*-Cl-9-BBN was prepared from the reaction of *B*-MeO-9-BBN and $PCl_5$ according to the literature procedure.[S6]

## 3. Experimental Procedure

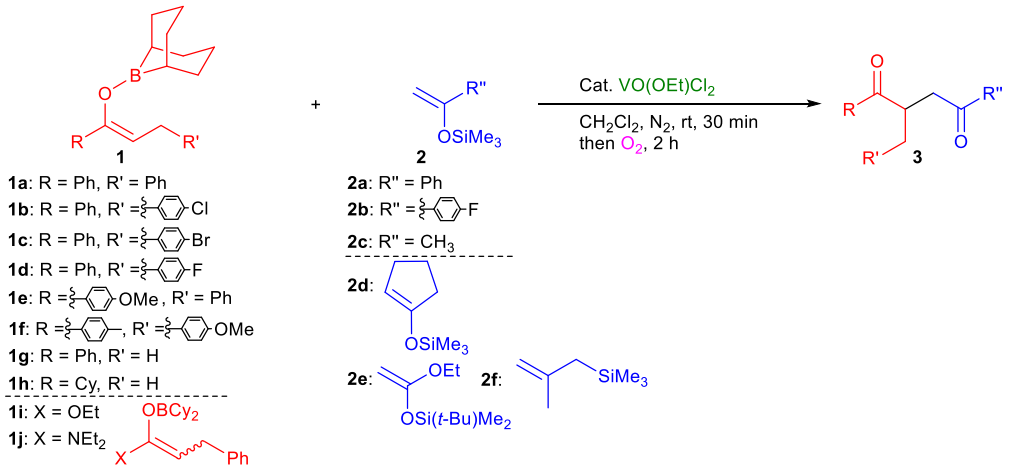
### A procedure for the preparation of boron enolates 1

The experiment was conducted in the $N_2$-filled glove box. Chalcone (6.25 g, 30 mmol), 9-BBN dimer (4.0 g, 23 mmol), and anhydrous $CH_2Cl_2$ (48 mL) were added to the dried 100 mL round bottomed flask at room temperature. The mixture was stirred at room temperature for 24 h. To check the completion of the reaction, a sample (ca. 300 μL) was taken from the reaction mixture. The sample was transferred to the J-Young valve attached NMR tube. The solvent was removed *in vacuo* and dry $CDCl_3$ was added, and $^1$H NMR spectrum was measured. The concentration of boron enolate **1a** was determined from the integral ratio to the internal standard (1,3,5-trimethoxybenzene) in the $^1$H NMR spectrum. The boron enolate **1a** was cleanly obtained as (*Z*)-form in a quantitative conversion. Other boron enolates **1b-h** were prepared in a small scale manner as compared to the above example.

Boron enolates **1i-j** were prepared from ethyl 3-phenylpropanoate or *N*,*N*-diethyl-3-phenylpropanamide with $Cy_2BOTf$ and $NEt_3$.[S2-3]

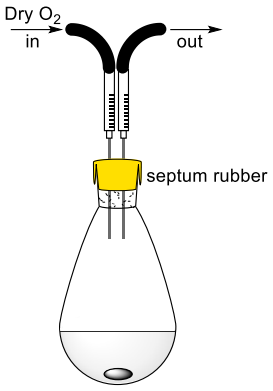
The $^1$H NMR data for boron enolates **1a**,[S1] **1b-c**,[S2] **1f-h,** [S1] and **1i-j**[S2] are reported. The $^1$H NMR data for boron enolates **1d** and **1e** are described below.

### A procedure for the oxidative cross-coupling




This is the procedure for entry 3 in Table 1, which is a typical one. The experiment was conducted in the $N_2$-filled glove box. 0.649 M $CH_2Cl_2$ solution of boron enolate **1a** (1.54 mL, 1.0 mmol), silyl enolate **2a** (410 μL, 2.0 mmol), and dry $CH_2Cl_2$ (10.0 mL) were added to a 50 mL round-bottomed flask. To the mixture was added $VO(OEt)Cl_2$ (48.9 μL, 0.4 mmol) at room temperature. After the reaction mixture was stirred at the same temperature for 30 min, the flask was taken out of the glove box. Dry $O_2$ passed through conc. $H_2SO_4$ was flowed into flask (10 mL/min) for 2 h, see the Figure for the equipments. The reaction mixture was then quenched with

aqueous saturated $NaHCO_3$ and $Na_2S_2O_3$ solution (1: 1 v/v, 20 mL in total). The aqueous layer was extracted with $Et_2O$ twice. The combined organic layer was washed with water and brine, and dried with $Na_2SO_4$. 1,3,5-Trimethoxybenzene was added to the mixture as an internal standard. After filtration, the filtrate was concentrated *in vacuo*. The yield was calculated by the integral ratio of the peaks for **3aa** and internal standard in the $^1$H NMR spectrum (87% yield). The crude mixture was purified by silica-gel column chromatography, which was performed on Yamazen EPCLC-W-Prep 2XY A-Type with a UNIVERSAL™ COLUMN PREMIUM cartridge. The product **3aa** was eluted with $CH_2Cl_2$/hexane = 75/25 to 100/0. Some by-products were still observed. So, silica-gel column chromatography was repeated again, which was performed on Yamazen EPCLC-W-Prep 2XY A-Type with a UNIVERSAL™ COLUMN PREMIUM cartridge. The product **3aa** was eluted with $CH_2Cl_2$ to give the desired product **3aa** (232.1 mg, 0.71 mmol, 72% yield). The scale-up was possible. A gram-scale reaction was performed 7 times (7 mmol of **1a**) as compared to the above-described reaction (Entry 7 in Table 1). The crude product was first purified by manually-operated silica-gel column chromatography (eluted with 45% ethyl acetate in hexane. Silica-gel: silicagel 60N, spherical, neutral, Kanto chemical). In order to remove volatile impurity such as acetophenone, the obtained products were heated at 100 °C under reduced pressure using glass tube oven to give the product (including a little impurity) in 72% yield. Further purification by recycle preparative GPC gave a completely pure product **1a** in 57% yield.

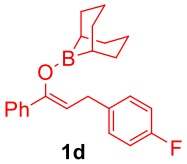



The experiments for other entries in Table 2 were performed similarly. In case the impurity was observed after silica-gel column chromatography, it was purified with recycle preparative GPC.

Identification of the products **3aa**[S1], **3fa**[S1], **3ga**[S1], **3ab**[S1], and **3ac**[S7] was conducted by comparison with the $^1$H NMR data reported previously after isolation of the product. Identification of the products **3ad**[S1], **3ae**[S1], **3ha**[S1], **3ia**[S2], and **3ja**[S2] was conducted by comparison with the previously reported $^1$H NMR data. The data of **3ba**, **3ca**, **3da**, **3ea**, and **3af** are described below.

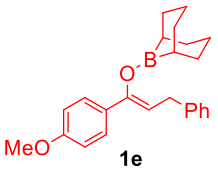
**Spectral data for 1d**, **1e**, **3ba**, **3ca**, **3da 3ea**, and **3af**

Boron enolate **1d**: $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.49-7.52 (m, 2H), 7.19-7.36 (m, 5H), 6.95-7.02 (m, 2H, 5.70 (t, $J$ = 7.3 Hz, 1H), 3.52 (d, $J$ = 7.3 Hz, 2H), 1.60-1.88 (m,10H), 1.27-1.35 (m, 4H) ppm.



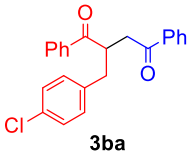
1d

Boron enolate **1e**: $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.45-7.50 (m, 2H), 7.20-7.36 (m, 5H), 6.85-6.92 (m, 2H), 5.64 (t, $J$ = 7.3 Hz, 1H), 3.82 (s, 3H), 3.56 (d, $J$ = 7.3 Hz, 2H), 1.66-1.91 (m, 10H), 1.31-1.40 (m, 4H) ppm.



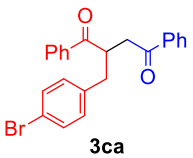
**1e**

2-(4-chlorobenzyl)-1,4-diphenylbutane-1,4-dione (**3ba**): $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.01-8.03 (m, 2H), 7.89-7.92 (m, 2H), 7.53-7.59 (m, 2H), 7.41-7.49 (m, 4H), 7.21-7.26 (m, 2H), 7.12-7.16 (m, 2H), 4.36-4.43 (m, 1H), 3.66 (dd, $J$ = 8.9, 18.1 Hz, 1H), 3.06-3.13 (m, 2H), 2.73 (dd, $J$ = 8.2, 13.7 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 202.55, 198.32, 137.24, 136.56, 136.51, 133.47, 133.28, 132.56, 130.53, 128.85, 128.83, 128.71, 128.61, 128.19, 43.29, 40.37, 37.55 ppm; IR (ATR) 1772, 1678, 1597, 1580, 1558, 1541, 1519, 1507, 1492, 1447, 1400, 1329, 1249, 1220, 1179, 1092, 1002, 770, 705, 687,666, 654, 612 cm$^{-1}$; HRMS: $[M+H]^+$ calcd for $C_{23}H_{20}O_2Cl$ 363.1146; found, 363.1135.



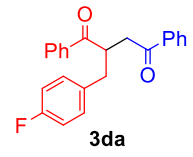
**3ba**

2-(4-bromobenzyl)-1,4-diphenylbutane-1,4-dione (**3ca**): $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.01-8.03 (m, 2H), 7.90-7.92 (m, 2H), 7.53-7.59 (m, 2H), 7.36-7.50 (m, 6H), 7.07-7.10 (m, 2H), 4.36-4.43 (m, 1H), 3.66 (dd, $J$ =18.3, 8.2 Hz, 1H), 3.06-3.12 (m, 2H), 2.71 (dd, $J$ =13.7, 8.2 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 202.32, 198.13, 137.59, 136.35, 136.32, 133.30, 133.12, 132.84, 131.61, 130.93, 130.75, 128.69, 128.54, 128.44, 128.02, 120.45, 43.06, 40.18, 37.41 ppm; IR (ATR) 1778, 1728, 1679, 1596, 1580, 1510, 1488, 1447, 1400, 1332, 1248, 1221, 1179, 1072, 774, 702, 688, 487, 441, 416, 406 cm$^{-1}$; HRMS: $[M+H]^+$ calcd for $C_{23}H_{20}O_2Br$ 407.0641; found, 407.0638.



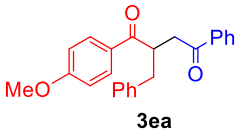
**3ca**

2-(4-fluorobenzyl)-1,4-diphenylbutane-1,4-dione (**3da**): $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.00-8.02 (m, 2H), 7.90-7.9 (d, $J$ = 7.3Hz, 2H), 7.53-7.58 (m, 2H), 7.41-7.49 (m, 4H), 7.14-7.18 (m, 2H), 6.92-6.97(m, 2H), 4.36-4.43 (m, 1H), 3.67 (dd, $J$ = 18.3, 8.7 Hz), 3.07-3.13 (m, 2H), 2.74 (dd, 13.7, 8.2 Hz) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 202.59, 198.24, 161.61 (d, $J_{C\text{-}F}$ = 244.4 Hz), 136.44 (d, $J_{C\text{-}F}$ = 11.5 Hz), 134.25, 133.29, 133.07, 130.46 (d, $J_{C\text{-}F}$ = 7.7 Hz), 128.66, 128.55, 128.45, 128.04, 115.37 (d, $J_{C\text{-}F}$ = 21.0 Hz), 43.32, 40.27, 37.35 ppm; IR (ATR) 1776, 1679, 1509, 1448, 1398, 1326, 1249, 1221, 1180, 1158, 771, 756, 687, 668, 635, 625 cm$^{-1}$; HRMS: $[M+H]^+$ calcd for $C_{23}H_{20}O_2F$ 347.1442; found, 347.1447.



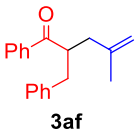
**3da**

2-Benzyl-1-(4-methoxyphenyl)-4-phenylbutane-1,4-dione (**3ea**): $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.03-8.05 (m, 2H), 7.89-7.92 (m, 2H), 7.51-7.55 (m, 1H), 7.40-7.44 (m, 2H), 7.17-7.29 (m, 5H), 6.94-6.97 (m, 2H), 4.34-4.41(m, 1H), 3.88 (s, 3H), 3.70 (dd, *J* = 9.4, 18.1 Hz, 1H), 3.04-3.16 (m, 2H), 2.72 (dd, *J* = 8.7, 13.5 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 201.09, 198.56, 163.44. 138.83, 136.52, 133.15, 130.81, 129.45, 129.02, 128.57, 128.49, 128.06, 126.56, 113.81, 55.47, 42.90, 40.22, 38.39 ppm; IR (ATR) 1778, 1678, 1599, 1509, 1333, 1313, 1246, 1220, 1171, 751, 698, 688, 667, 517, 507, 498, 487, 468, 442, 426, 414, 403 $cm^{-1}$; HRMS: $[M+H]^+$ calcd for $C_{24}H_{24}O_3$ 359.1642; found, 359.1631.



**3ea**

2-benzyl-4-methyl-1-phenylpent-4-en-1-one (**3af**): $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.82-7.84 (m, 2H), 7.49-7.53 (m, 1H), 7.38-7.42 (m, 2H), 7.12-7.24 (m, 5H), 4.73 (d, *J* = 19.7 Hz, 2H), 3.89-3.96 (m, 1H), 3.10 (dd, *J* = 8.2, 13.7 Hz, 1H), 2.78 (dd, *J* = 5.7, 13.5 Hz, 1H), 2.55 (dd, *J* = 7.6, 14.4 Hz, 1H), 2.21 (dd, *J* = 6.6, 14.4 Hz, 1H), 1.72 (s, 3H) ppm; $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 203.26, 142.77, 139.74, 137.24, 132.84, 128.96, 128.53, 128.36, 128.10,126.18, 112.50, 46.48, 40.24, 37.98, 22.67 ppm; IR (ATR) 3082, 3061, 3026, 2929, 1795, 1681, 1649, 1596, 1580, 1495, 1446, 1374, 1363, 1229, 1179, 1076, 1029, 1002, 946, 773, 748, 741, 698, 490, 469 $cm^{-1}$; HRMS: $[M+H]^+$ calcd for $C_{19}H_{20}O$ 265.1598; found 265.1593.



**3af**

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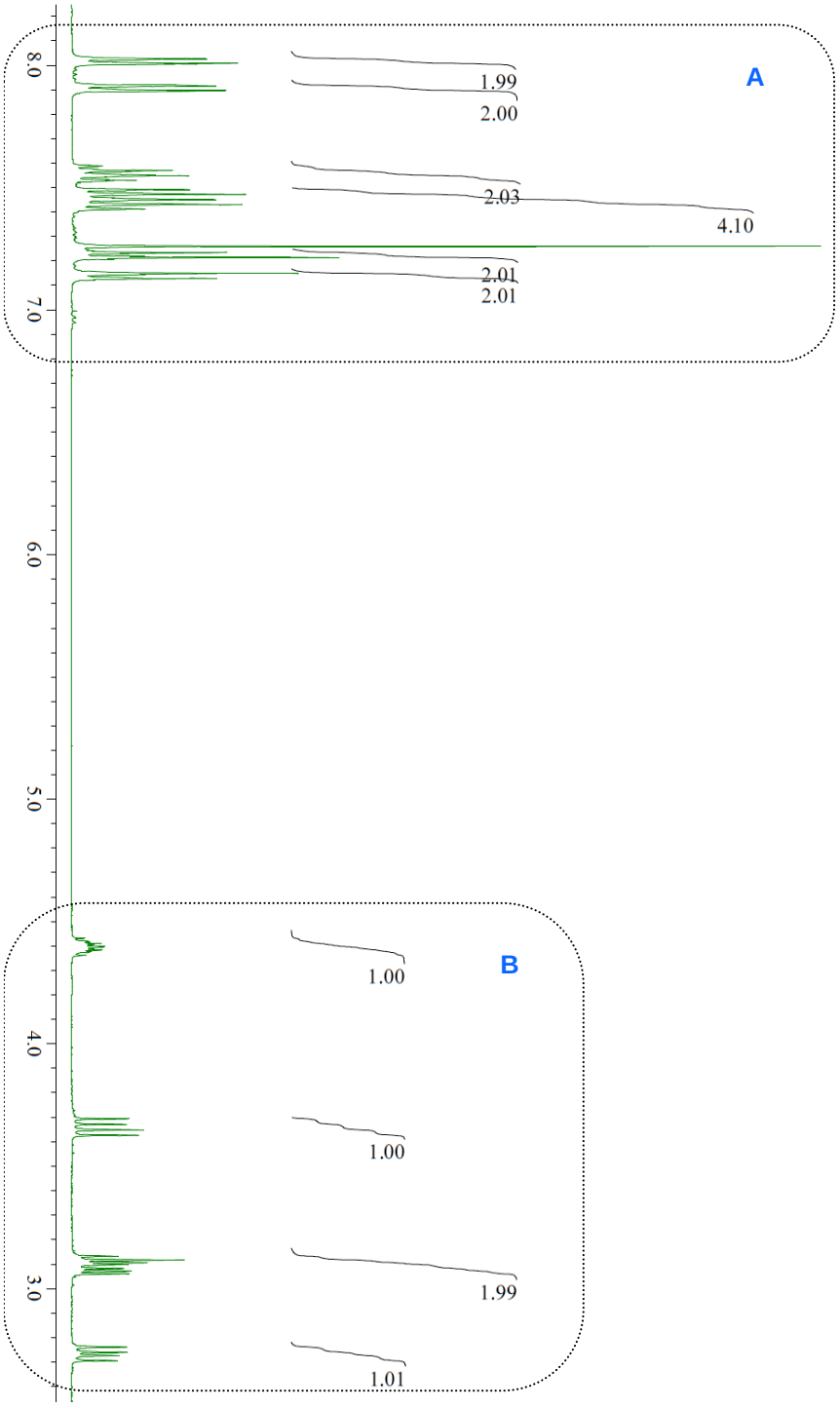
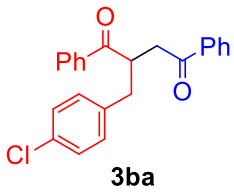
## 4. NMR Spectra

$^{1}H$ and $^{13}C$ NMR spectra of new compounds (**3ba**, **3ca**, **3da**, **3ea**, and **3af**) in the oxidative cross-coupling products.

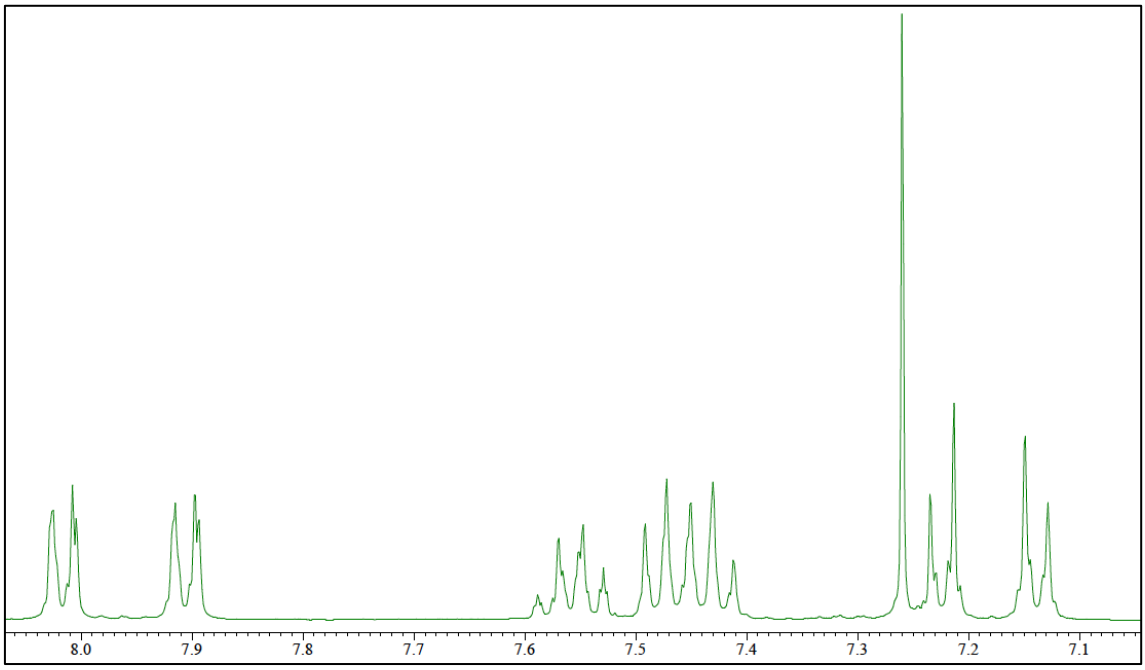
$^{1}H$ NMR spectrum of **3ba** (400 MHz, $CDCl_3$)



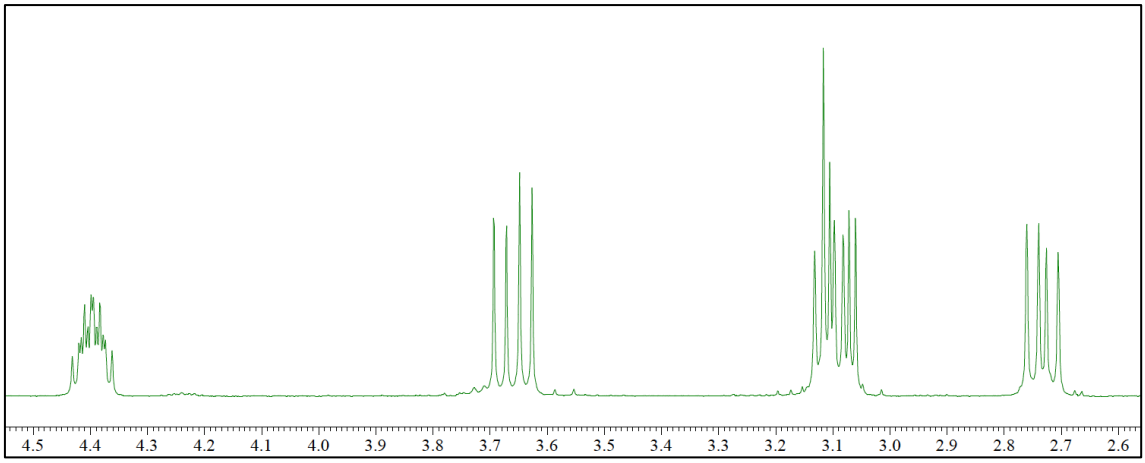




**3ba**

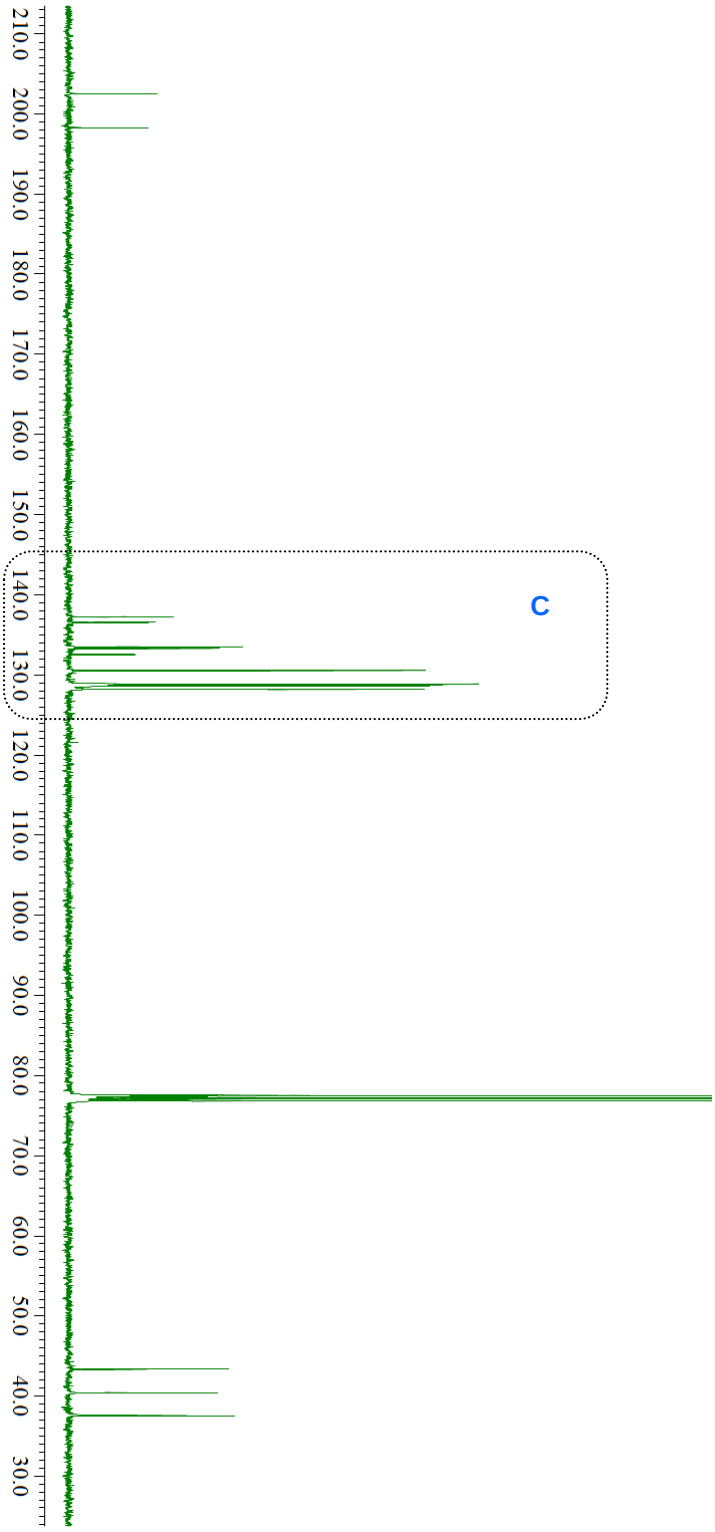
**Enlarged view A**

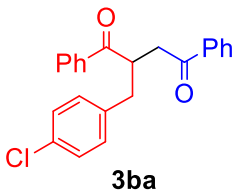



**Enlarged view B**



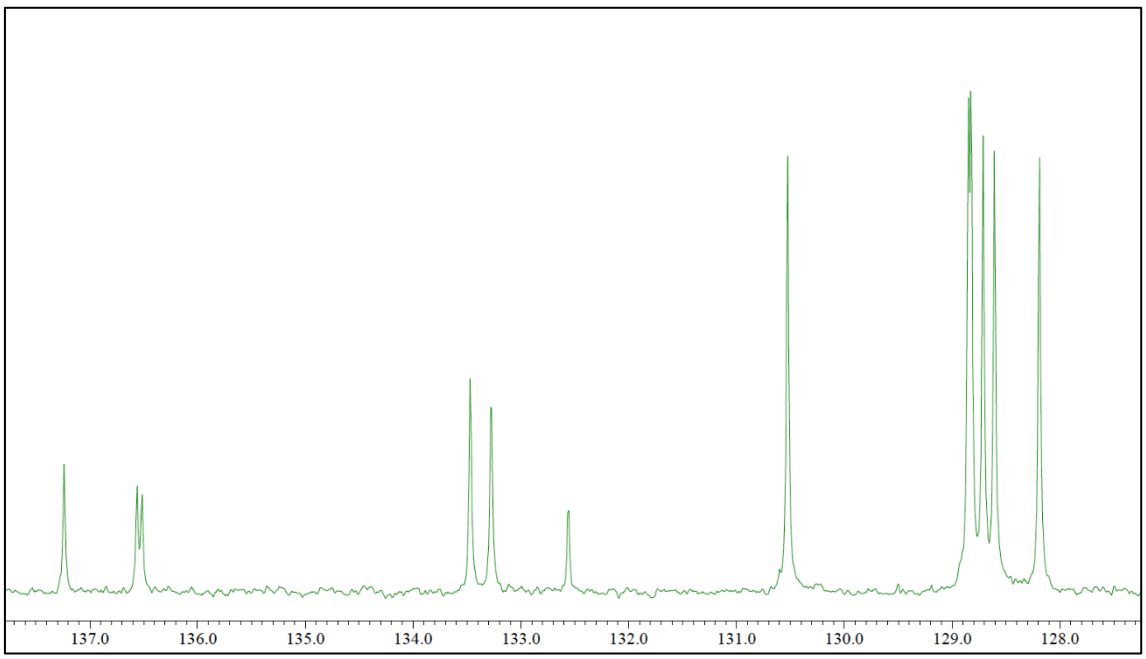
$^{13}C$ NMR spectrum of **3ba** ($100$ MHz, $CDCl_3$)



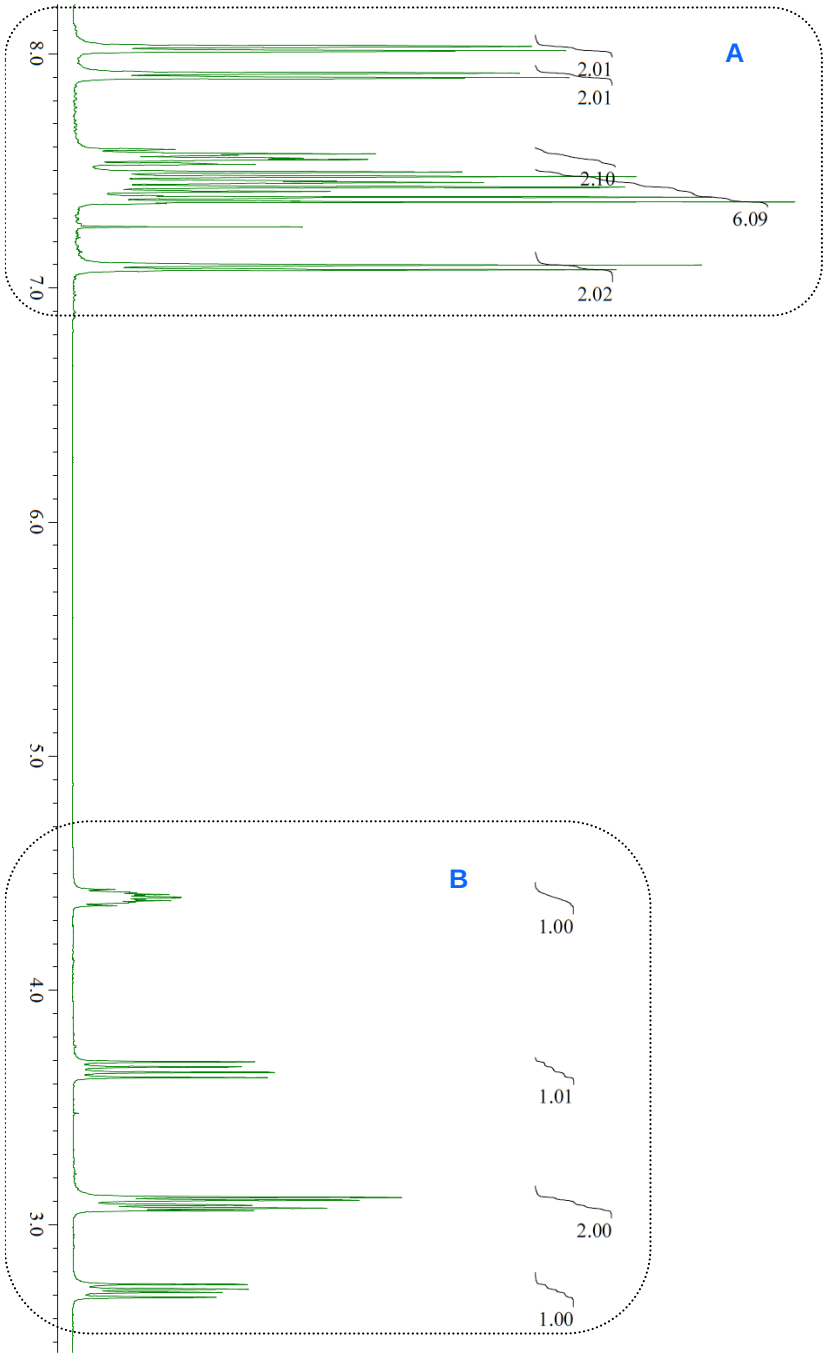



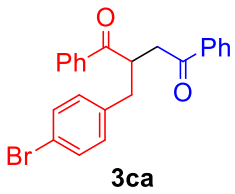

**3ba**

**Enlarged view C**



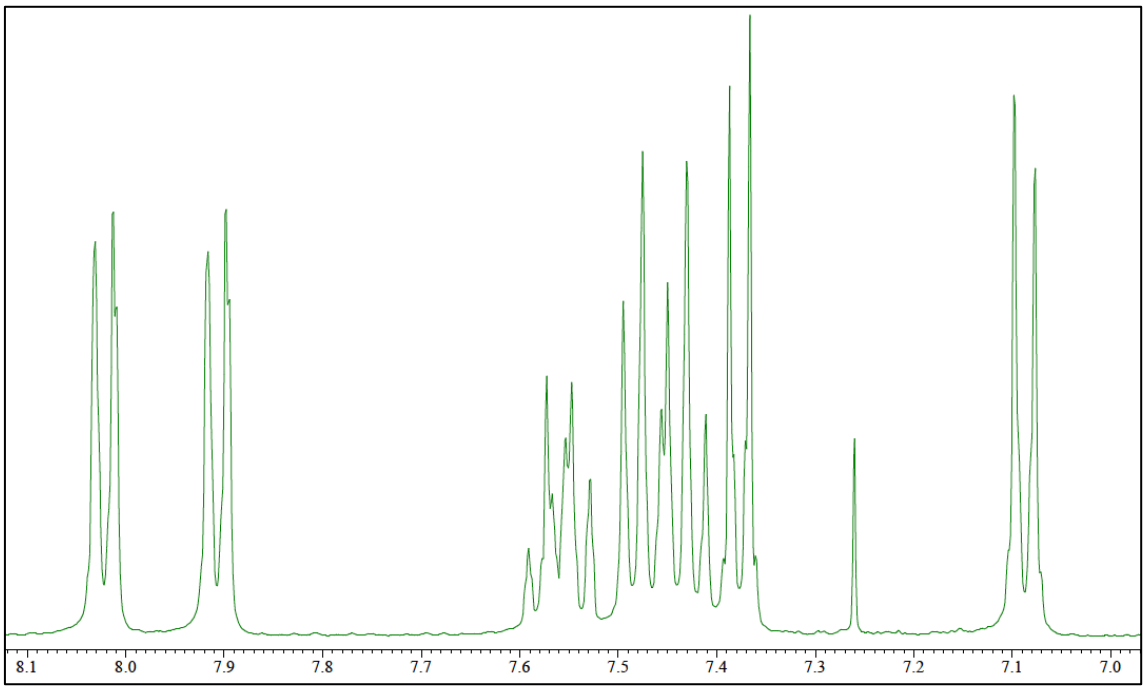
$^{1}$H NMR spectrum of **3ca** (400 MHz, $CDCl_3$)



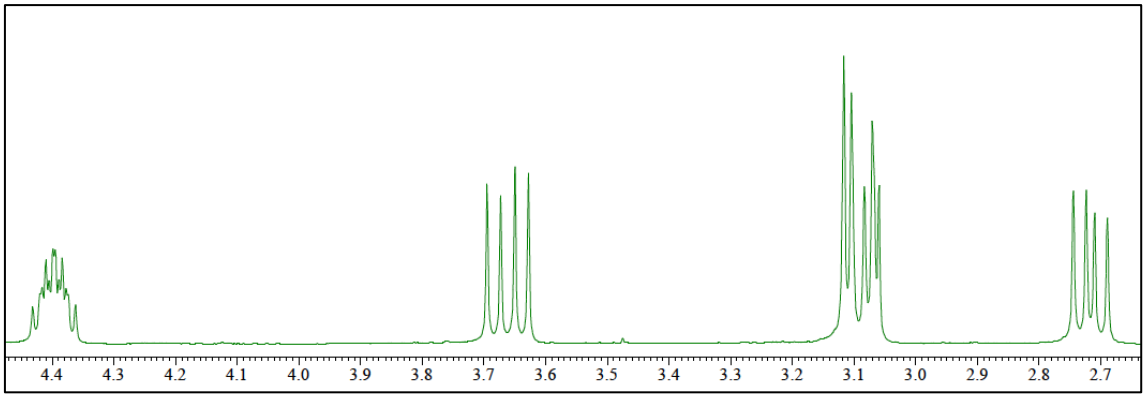




**3ca**

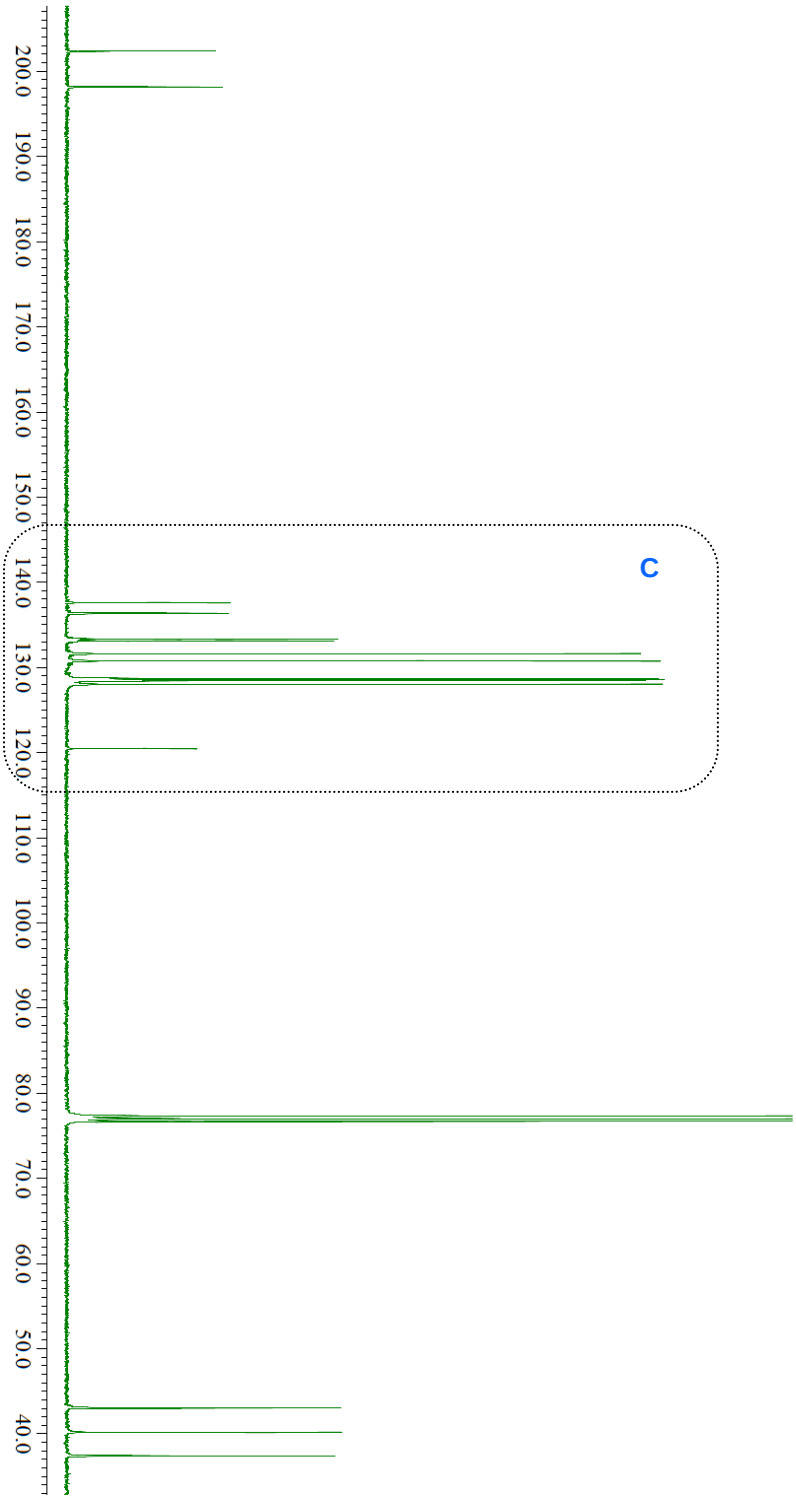
**Enlarged view A**

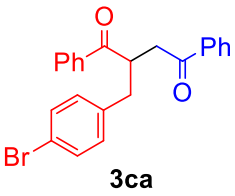



**Enlarged view B**



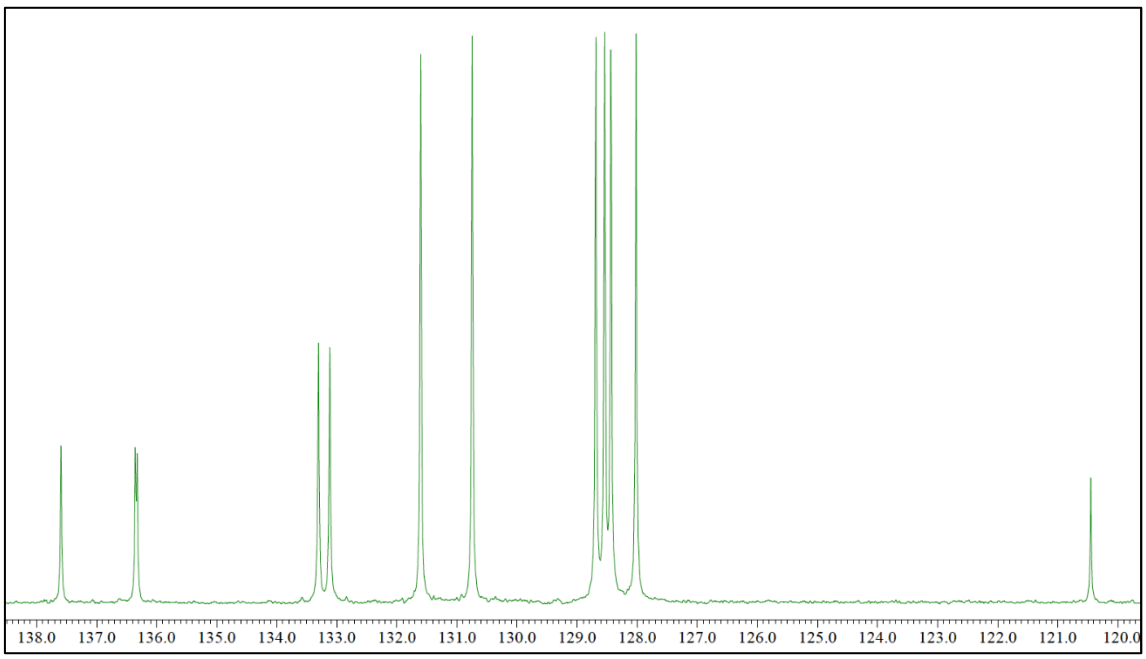
$^{13}C$ NMR spectrum of **3ca** ($100$ MHz, $CDCl_3$)



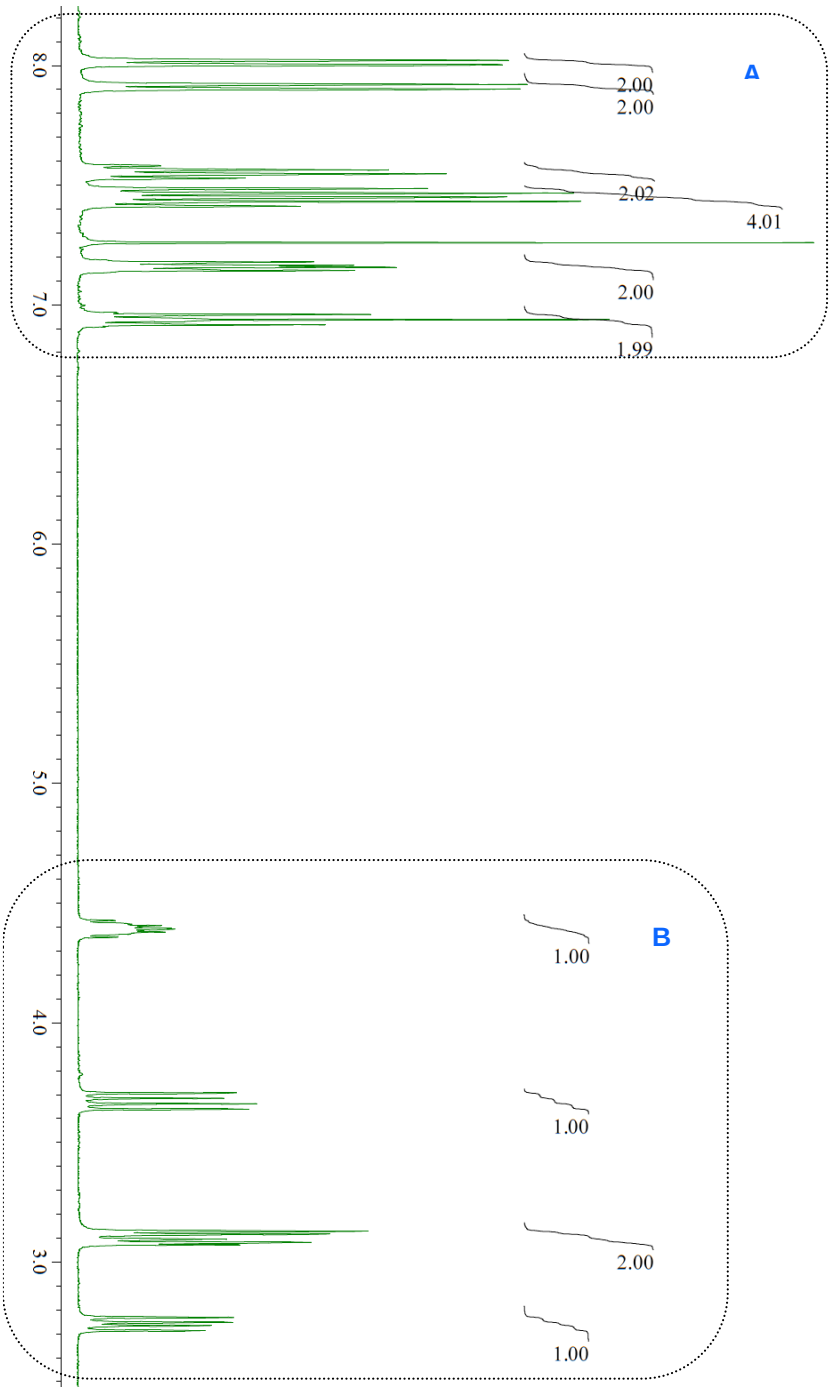



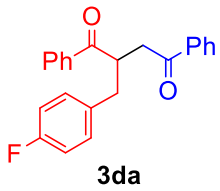

**3ca**

**Enlarged view C**



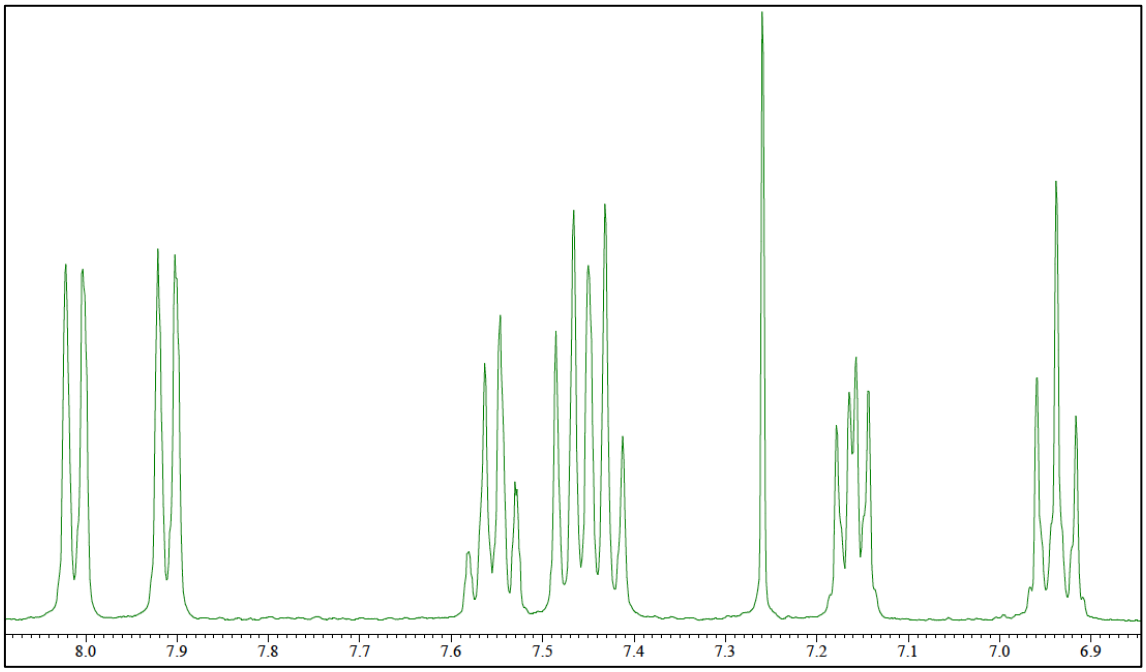
$^{1}$H NMR spectrum of **3da** (400 MHz, $CDCl_3$)



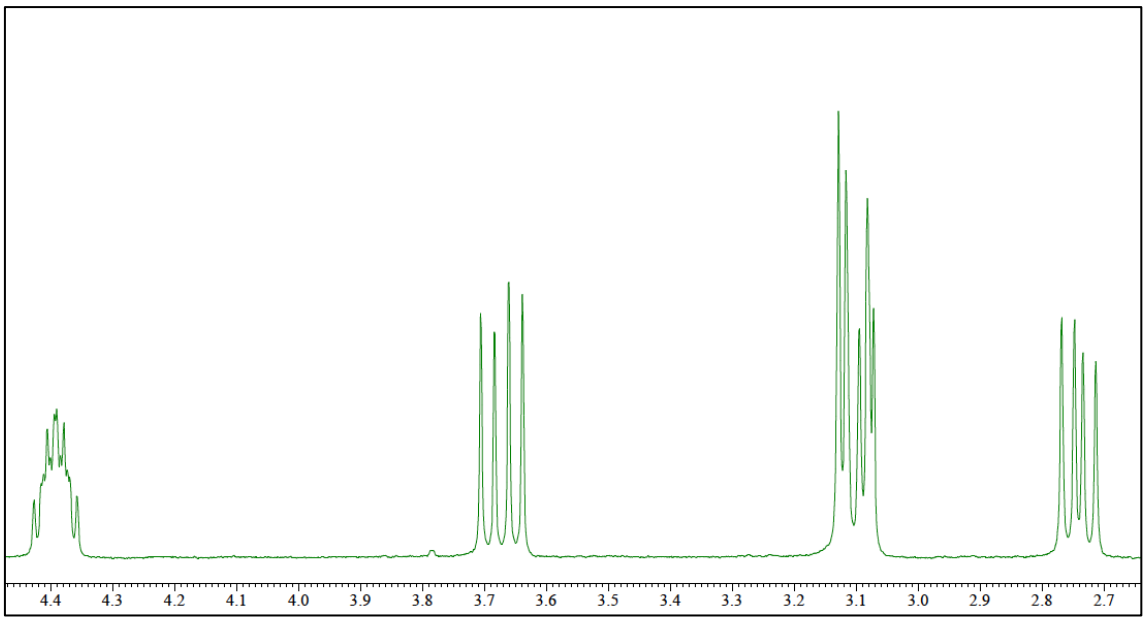




**3da**

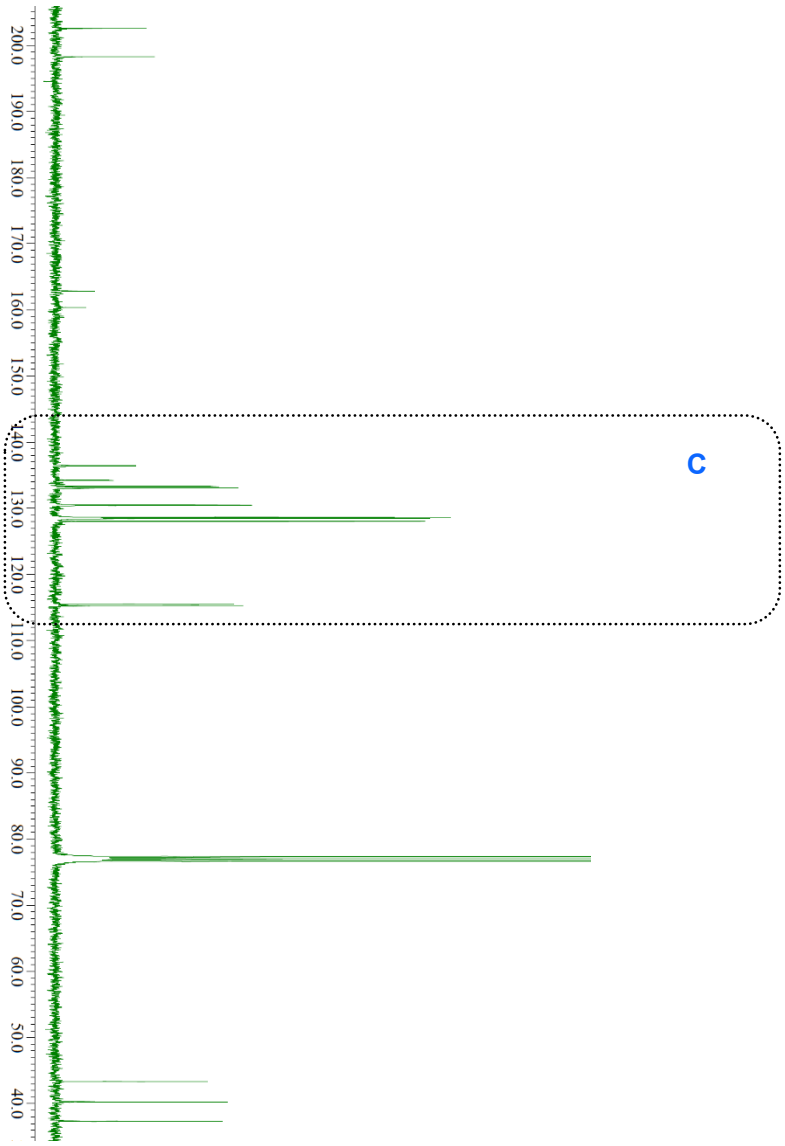
**Enlarged view A**

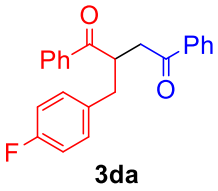



**Enlarged view B**



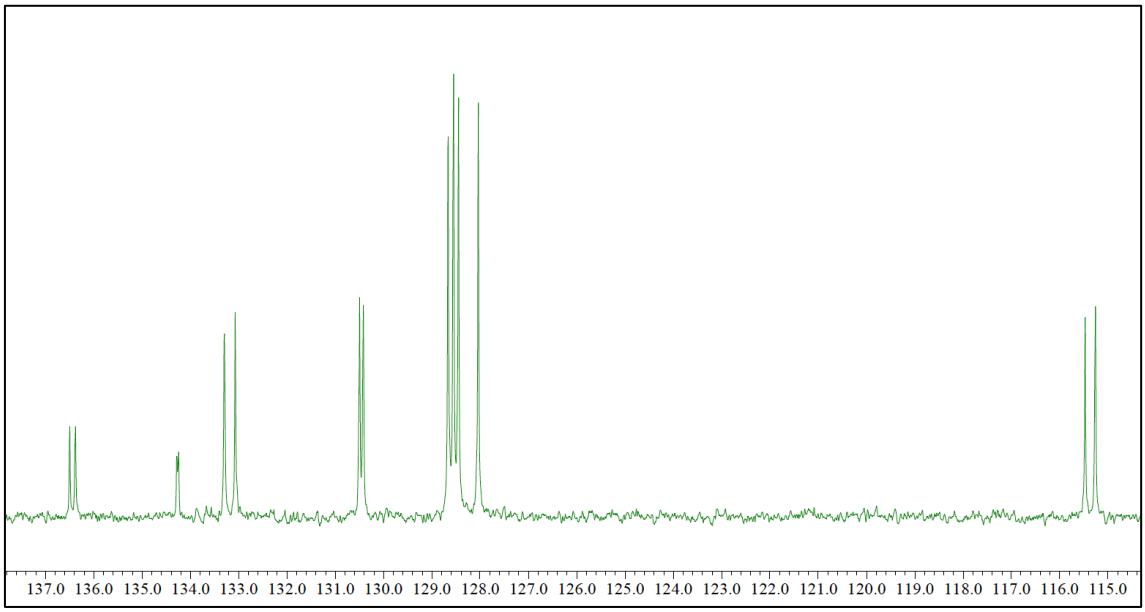
$^{13}$C NMR spectrum of **3da** (100 MHz, $CDCl_3$)



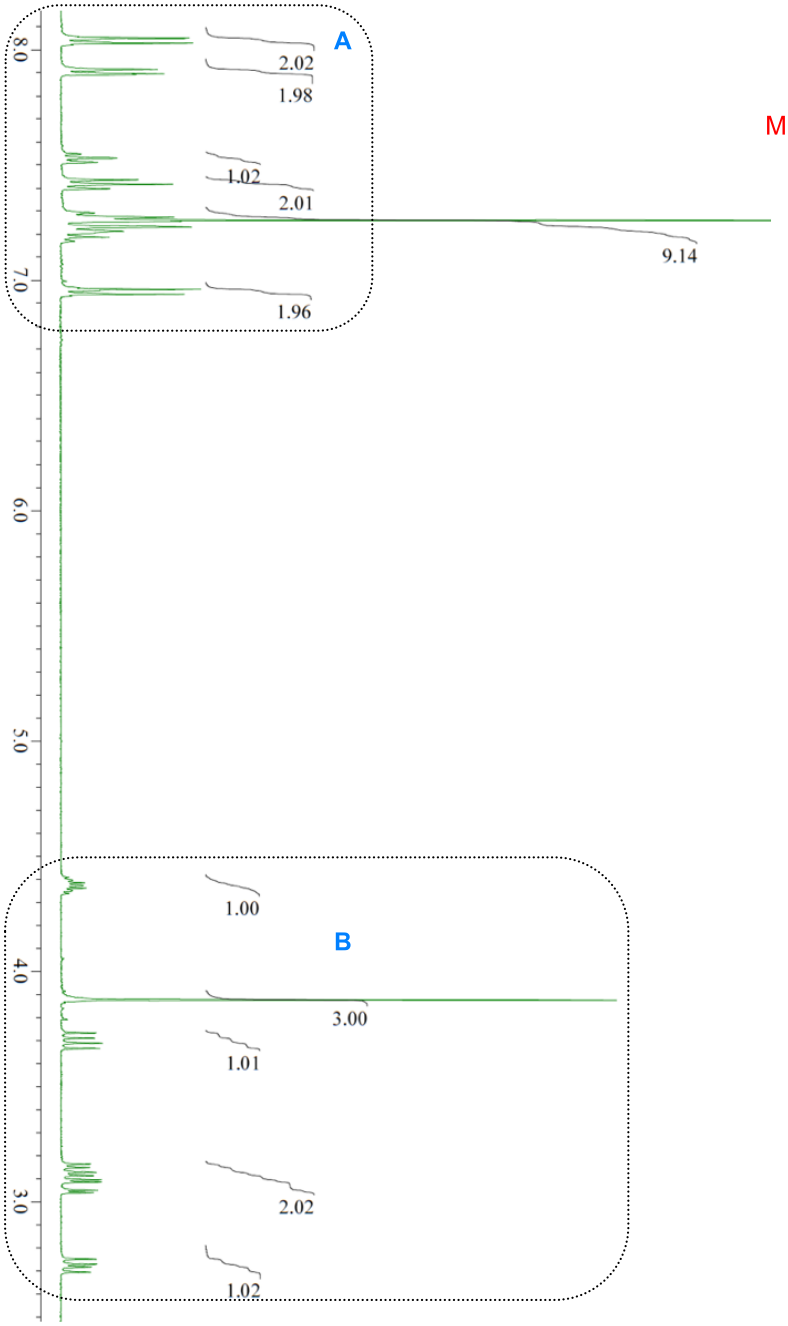



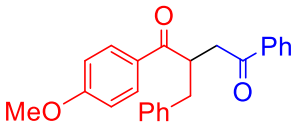

**3da**

**Enlarged view C**



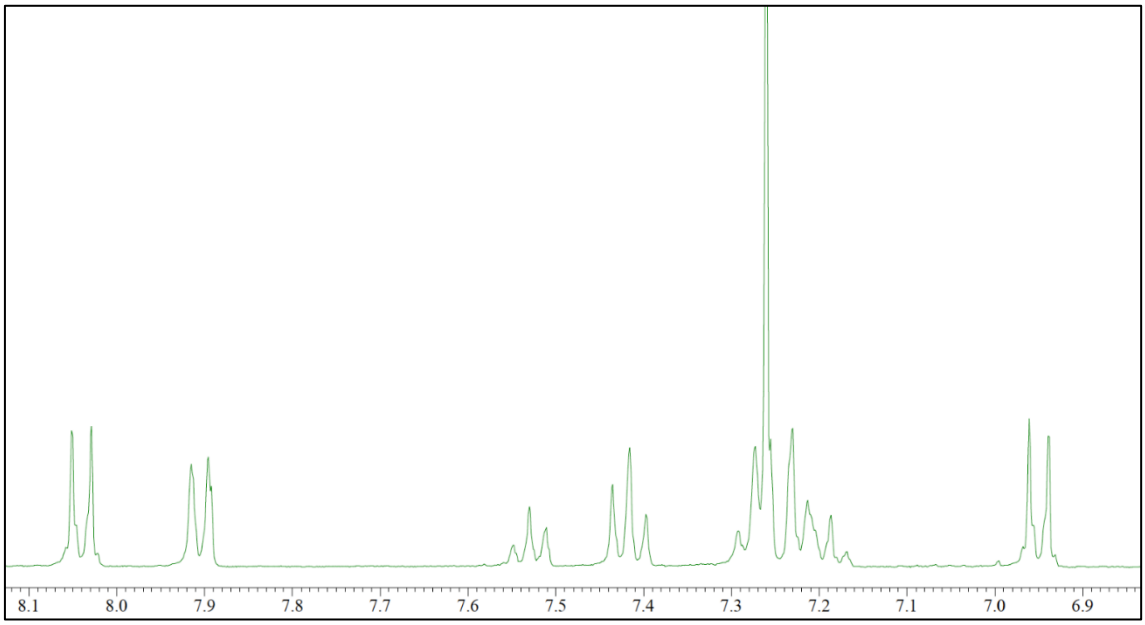
$^{1}$H NMR spectrum of **3ea** (400 MHz, $CDCl_3$)



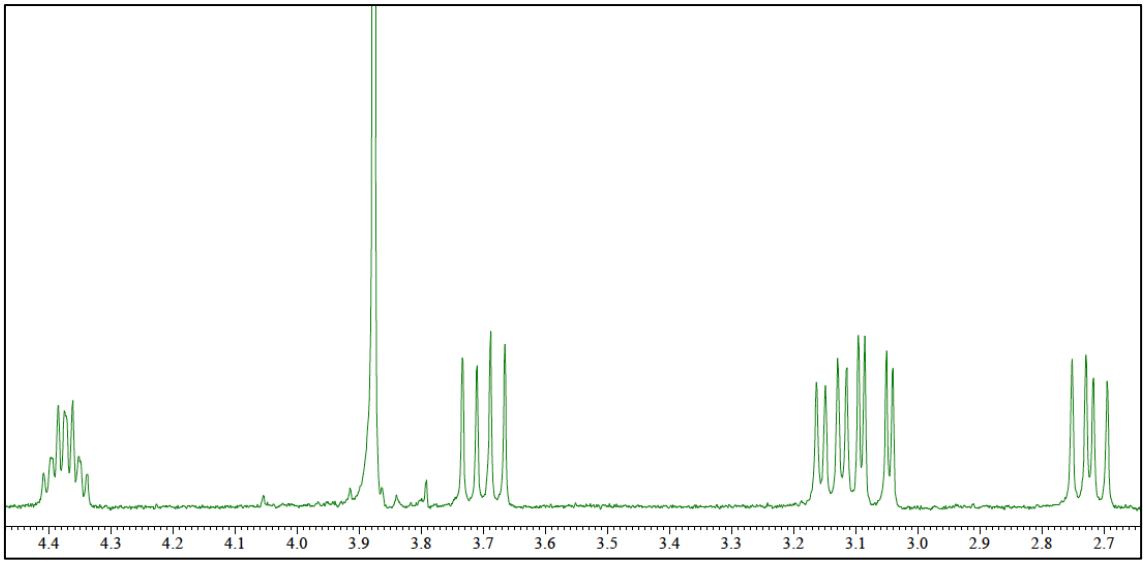




**3ea**

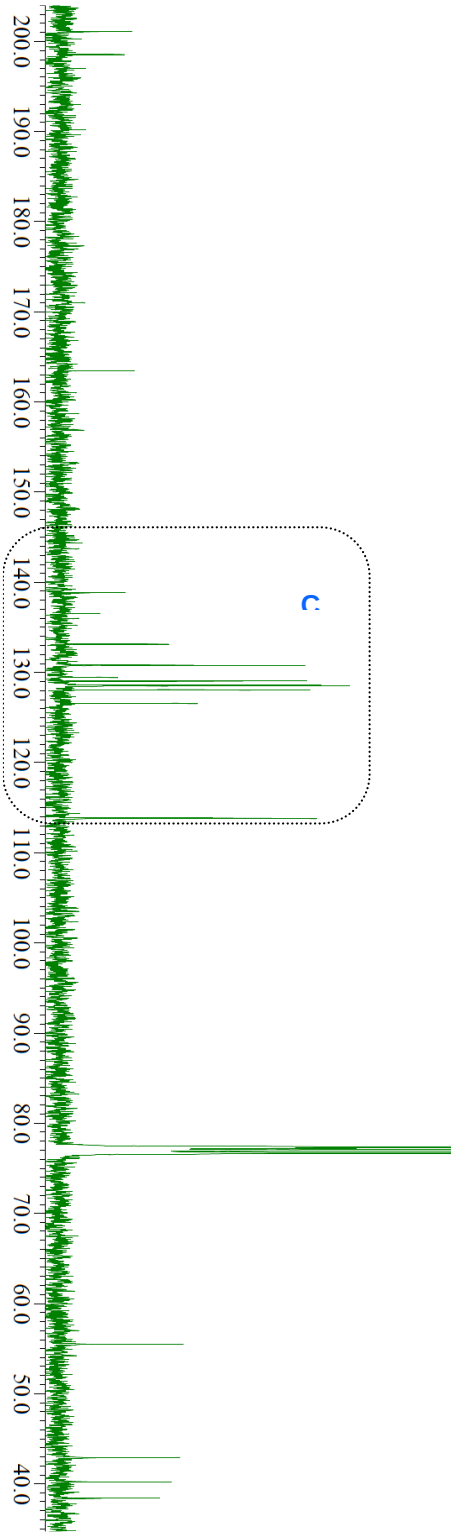
**Enlarged view A**

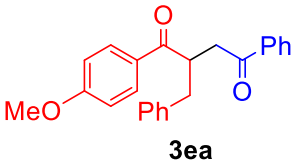



**Enlarged view B**



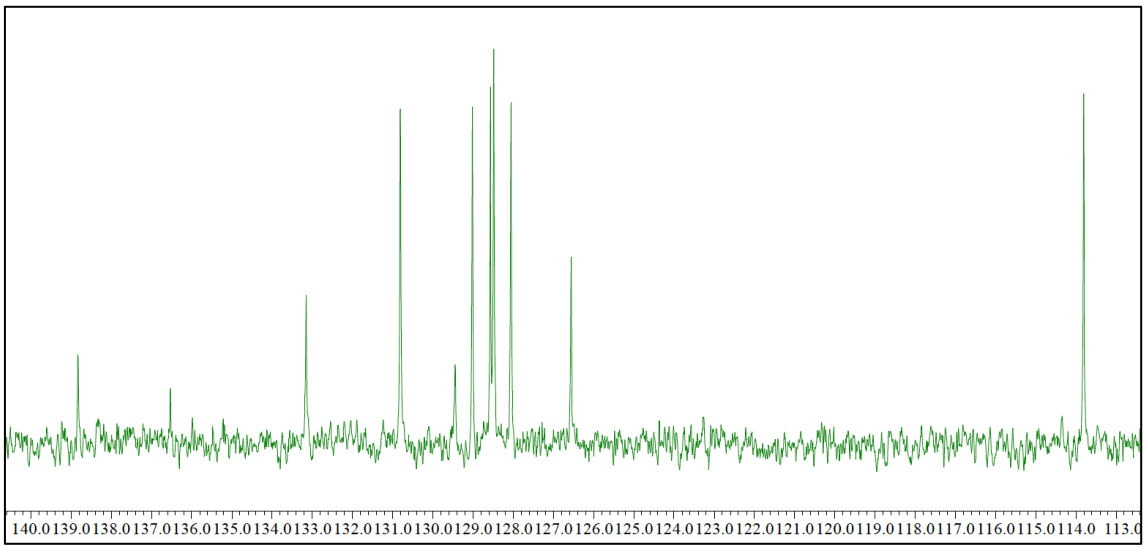
$^{13}$C NMR spectrum of **3ea** (100 MHz, $CDCl_3$)



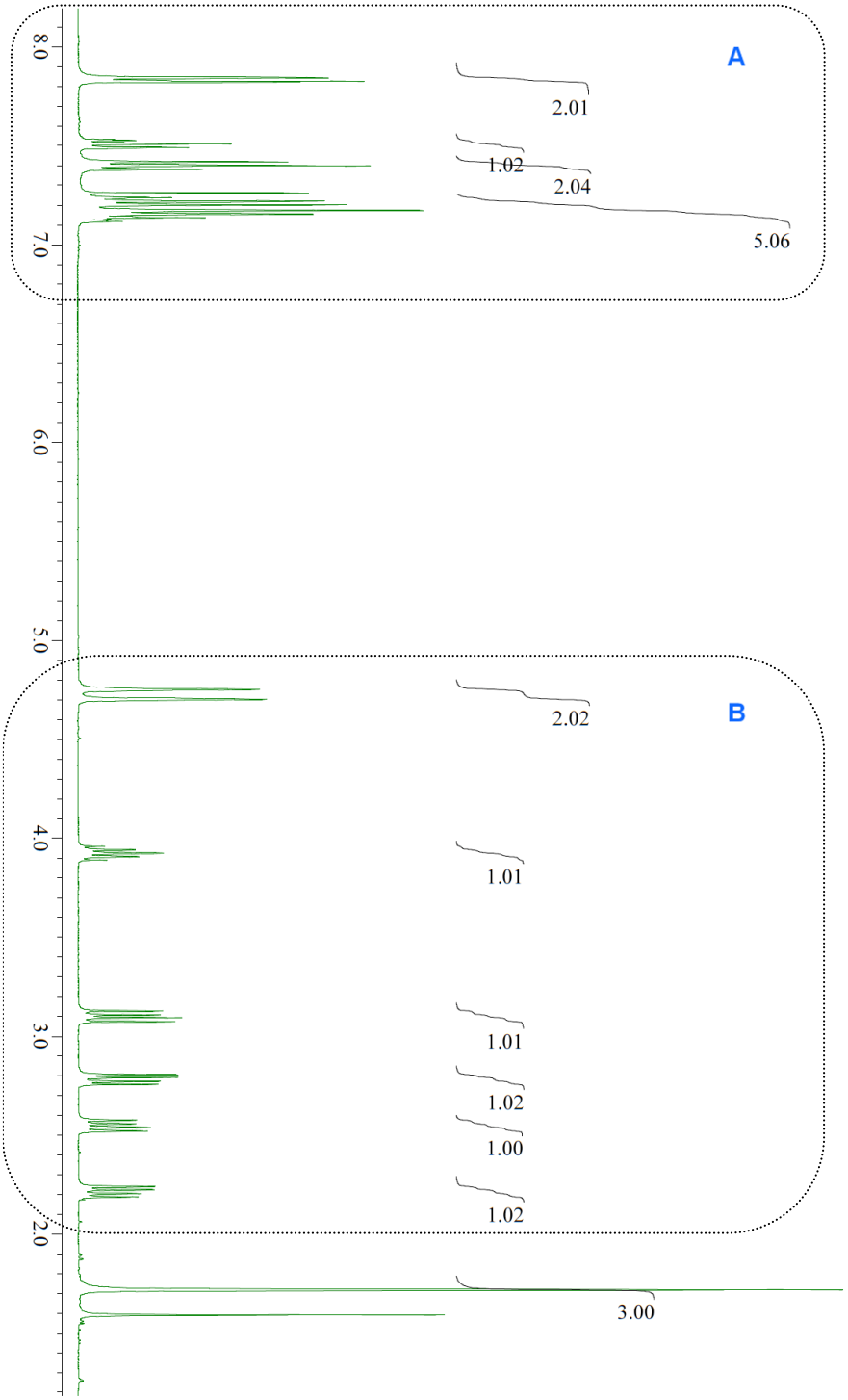




**3ea**

**Enlarged view C**



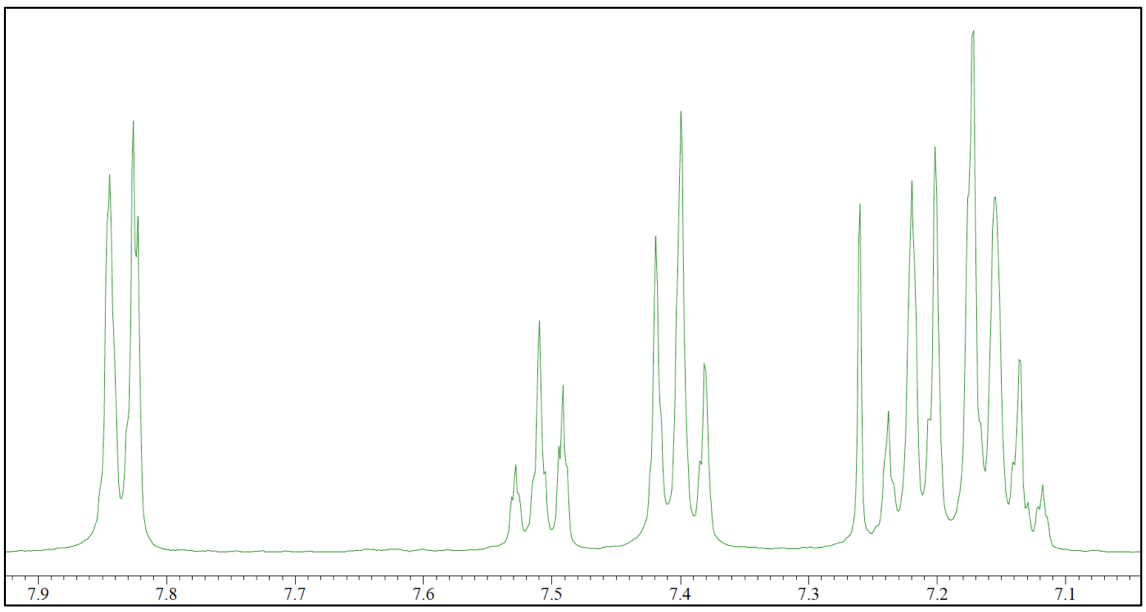
$^{1}$H NMR spectrum of **3af** (400 MHz, $CDCl_3$)



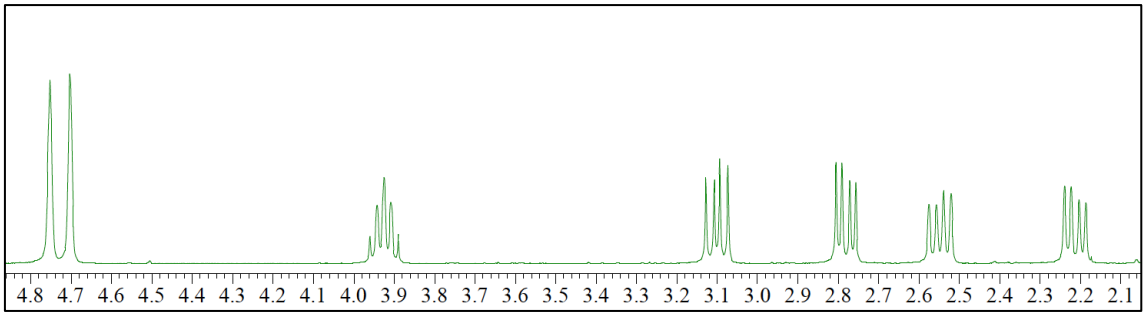


**3af**

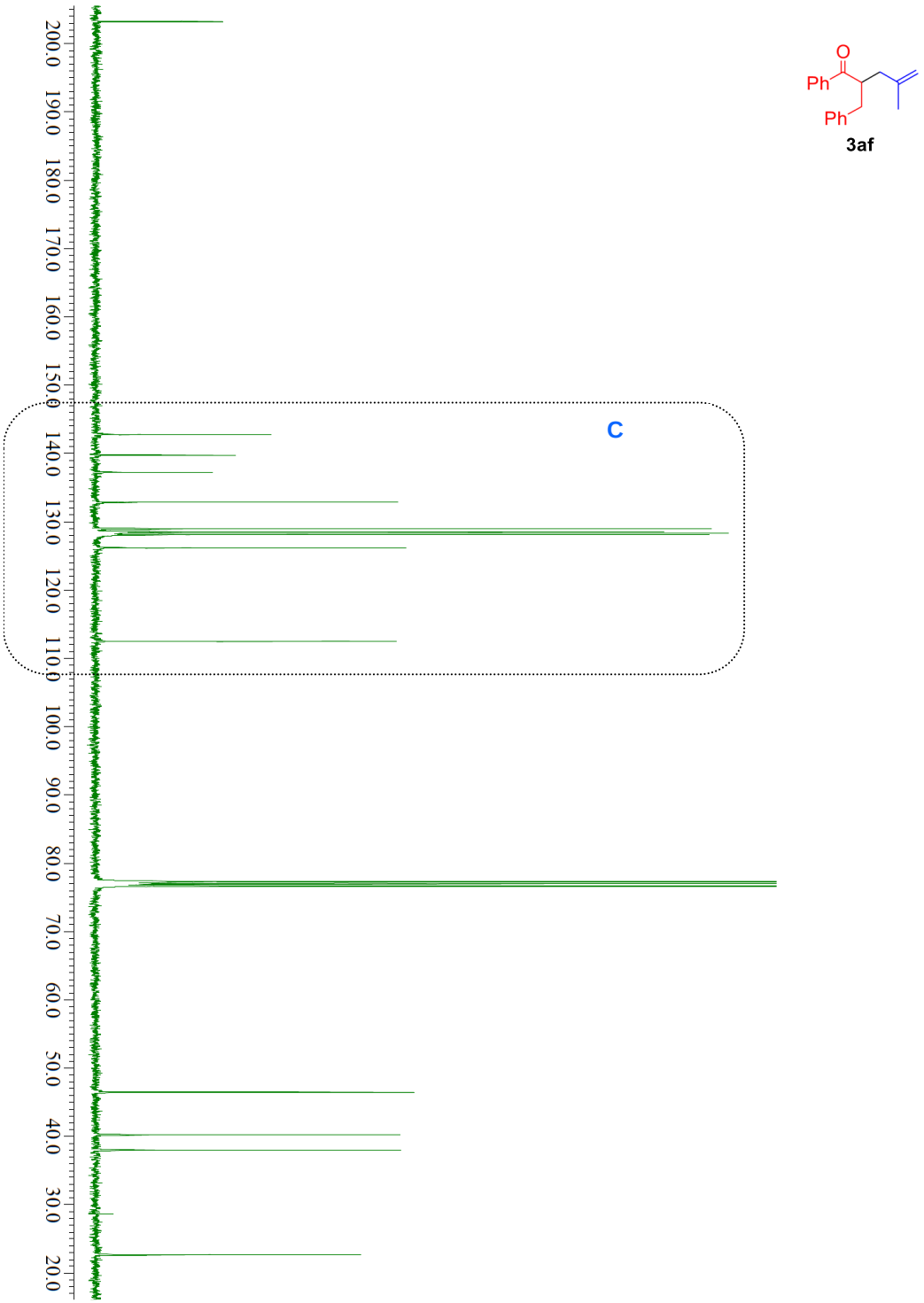
**Enlarged view A**




**Enlarged view B**



$^{13}$C NMR spectrum of **3af** (100 MHz, $CDCl_3$)



**Enlarged view C**