Supplementary Information

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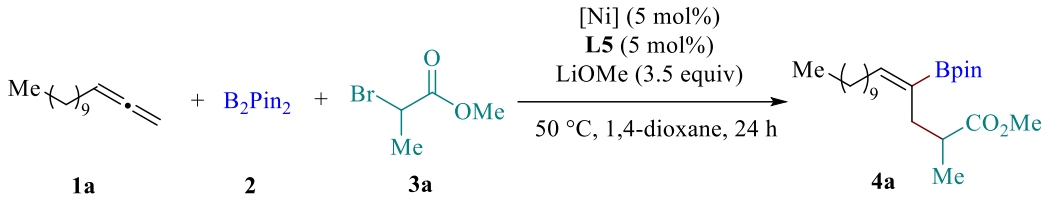
Table S1. Effects of Nickel catalysts on the reaction of trideca-1,2-diene **1a**, B_2Pin_2 **2** and methyl 2-bromopropanoate **3a**.[a]

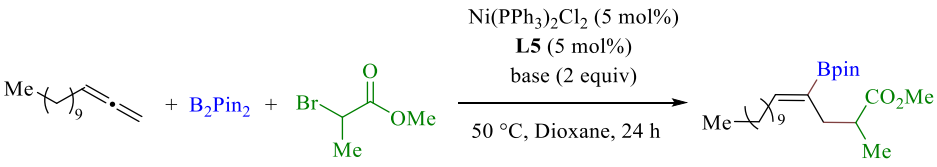


1a **2** **3a** **4a**

entry	[Ni]	Yield % (**4a**) [b]
1	$NiBr_2$·diglyme	56
2	$Ni(dppf)_2Cl_2$	trace
3	$Ni(PPh_3)_2Cl_2$	65
4	$Ni(acac)_2$	43
5	$NiCl_2$·DME	50

[a] Reaction procedure: The trideca-1,2-diene **1a** (36 mg, 0.2 mmol), B_2Pin_2 **2** (56 mg, 0.22 mmol, 1.1equiv), bromoester **3a** (50 mg, 0.3 mmol, 1.5 equiv), $Ni(PPh_3)_2Cl_2$ (6.54 mg, 0.005 mmol, 0.05 equiv), **L5** (2.68 mg, 0.005 mmol, 0.05 equiv) and 1,4-dioxane (2 mL) were sequentially added into a sealed tube and the mixture was stirred at 50 ºC for 24 h under an argon atmosphere. [b] Yields were determined by ^{1}H NMR spectroscopy of crude product using 4-bromobenzaldehyde as an internal standard sample.

Table S2. Effects of base on the reaction of trideca-1,2-diene **1a**, B_2Pin_2 **2** and methyl 2-bromopropanoate **3a**.[a]



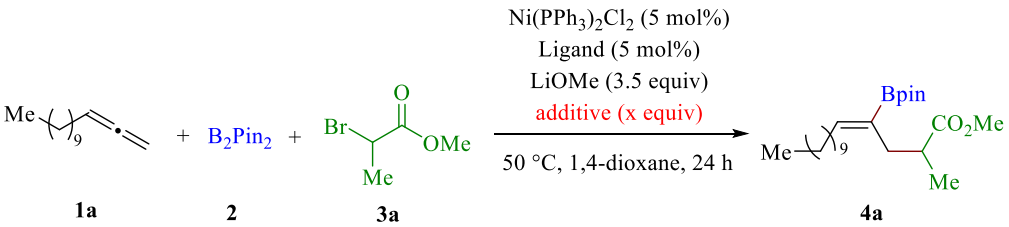
1a **2** **3a** **4a**

entry	base	Yield of % **4a** [b]
1	KO*t*Bu	24
2	NaO*t*Bu	13
3	LiO*t*Bu	44

4	LiOMe	65
5	LiOH	10
6	Li_2CO_3	n.r.
7	$LiOAc·H_2O$	15
8	MeONa	trace
9	MeOK	trace
10[c]	LiOMe	46
11[d]	LiOMe	58
12[e]	LiOMe	72

[a] Reaction procedure: The trideca-1,2-diene **1a** (36 mg, 0.2 mmol), B_2Pin_2 **2** (56 mg, 0.22 mmol, 1.1 equiv), bromo ester **3a** (50 mg, 0.3 mmol, 1.5 equiv), $Ni(PPh_3)_2Cl_2$ (6.54 mg, 0.005 mmol, 0.05 equiv), **L5** (2.68 mg, 0.005 mmol, 0.05 equiv) and 1,4-dioxane (2 mL) were sequentially added into a sealed tube and the mixture was stirred at 50 ºC for 24 h under an argon atmosphere. [b] Yields were determined by ^{1}H NMR spectroscopy of crude product using 4-bromobenzaldehyde as an internal standard sample. [c] 1.0 equiv LiOMe. [d] 2.0 equiv LiOMe. [e] 3.0 equiv LiOMe.

Table S3. Effects of additive on the reaction of trideca-1,2-diene **1a**, B_2Pin_2 **2** and methyl 2-bromopropanoate **3a**.[a]



1a **2** **3a** **4a**

entry	Additive (1.0 eq.)	Yield of **4a**%[b]
1	^{n}Bu$_4$NBr	60
2	Et$_4$NBr	65
3	Me$_4$NBr	67
4	Octyl$_4$NBr	59
5	KBr	61
6	LiBr	80
7	$ZnBr_2$	10

8	CsBr	65
9	$MnBr_2$	5
10	LiCl	86
11[c]	LiCl	75
12[d]	LiCl	69
13[e]	LiCl	64

[a] Reaction procedure: The trideca-1,2-diene **1a** (36 mg, 0.2 mmol), B_2Pin_2 **2** (56 mg, 0.22 mmol, 1.1 equiv), bromo ester **3a** (50 mg, 0.3 mmol, 1.5 equiv), $Ni(PPh_3)_2Cl_2$ (6.54 mg, 0.005 mmol, 0.05 equiv), **L5** (2.68 mg, 0.005 mmol, 0.05 equiv) and 1,4-dioxane (2 mL) were sequentially added into a sealed tube and the mixture was stirred at 50 ºC for 24 h under an argon atmosphere. [b] Yields were determined by ^{1}H NMR spectroscopy of crude product using 4-bromobenzaldehyde as an internal standard sample. [c] 0.5 equiv LiCl. [d] 2.0 equiv LiCl. [e] 3.0 equiv LiCl.

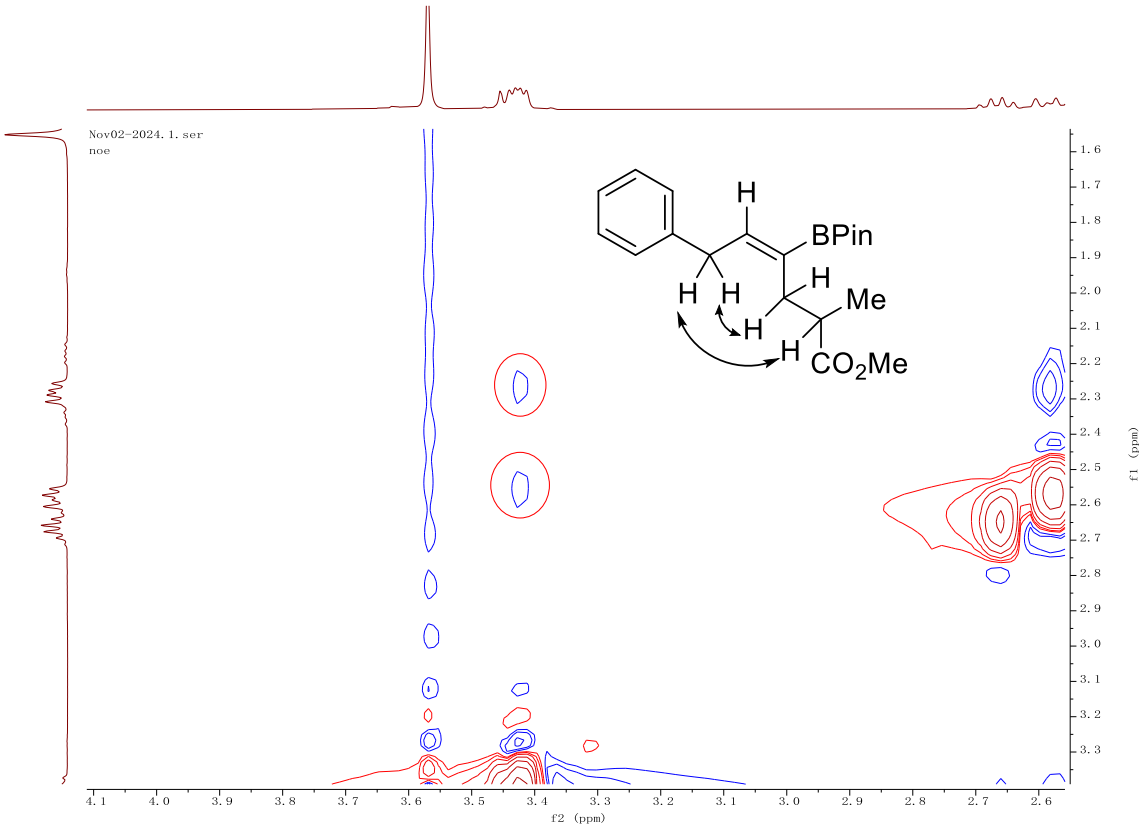


Figure S1. 2D NMR for the structural confirmation of product **4a**

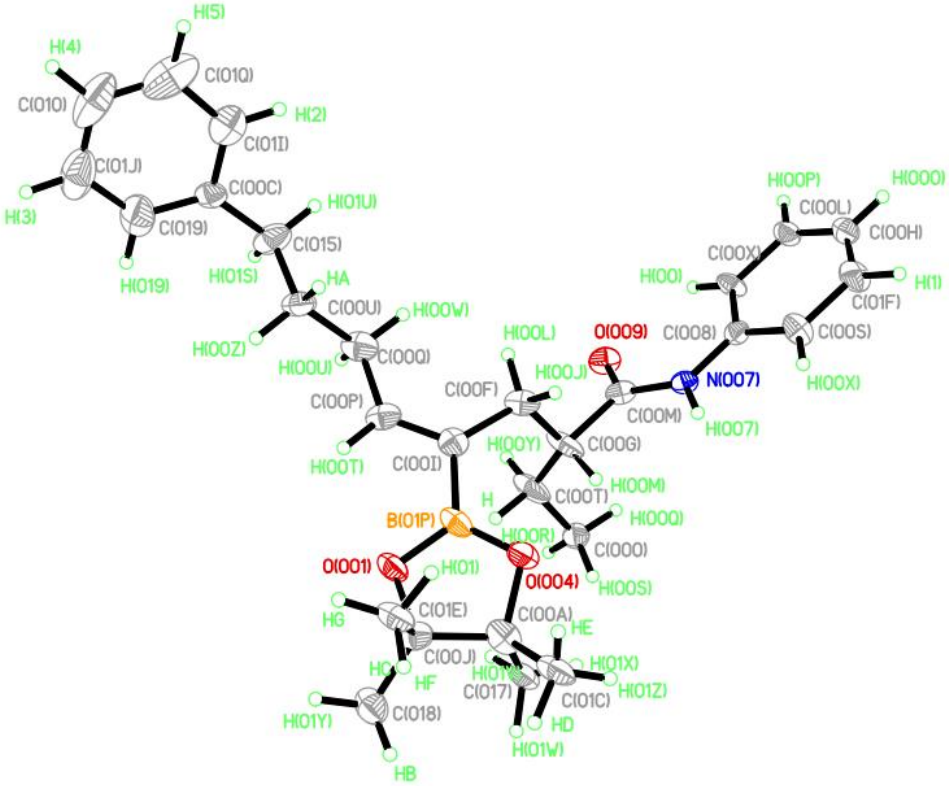
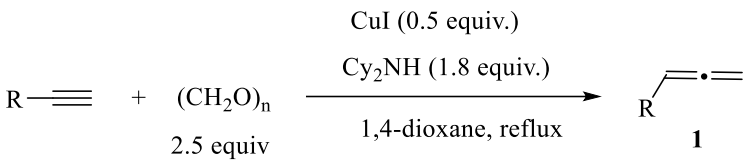


Figure S2. The ORTEP image of **4cc** (30% probility)

1. General Information

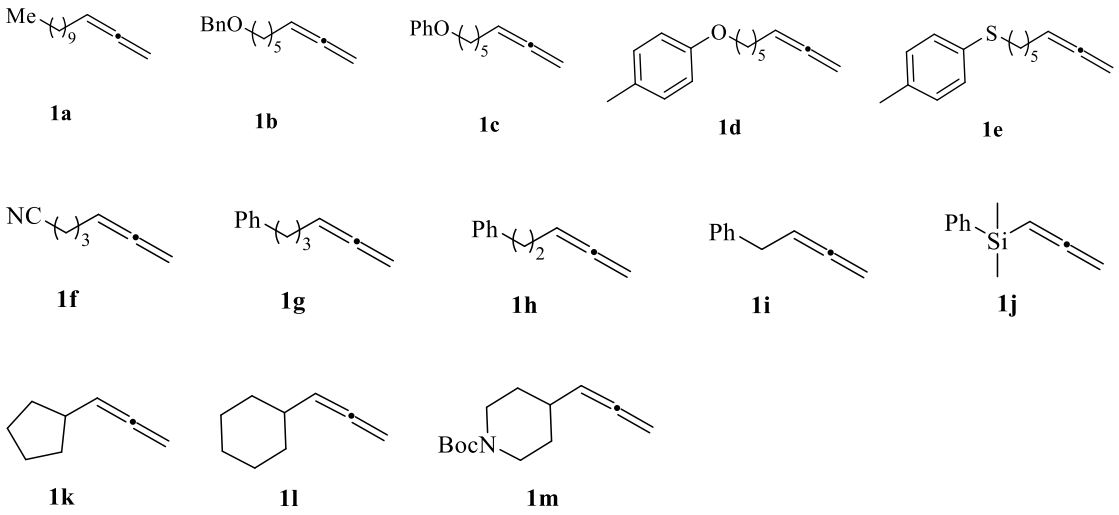
Unless otherwise noted, all manipulations were carried out using standard Schlenk line. Allenes were synthesized according to relative literatures[1-4]. Organozinc reagents were synthesized according to relative literatures. TLC analysis was performed on pre-coated, glass-backed silica gel plates and visualized with UV light. Flash column chromatography was performed on silica gel (200-300 mesh). The NMR spectra were recorded on Bruker 400 AV spectrometers at 400 MHz (^{1}H NMR), 101 MHz (^{13}C NMR) and Bruker 600 AV spectrometers at 600 MHz (^{1}H NMR), 151 MHz (^{13}C NMR). Abbreviations are used in the description of NMR data as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qui = quintet, hept = heptet, m = multiplet, br =broad, dd = doublet of doublets, dt = doublet of triplets), coupling constant (*J*, Hz). High resolution mass spectrometric (HRMS) analyses spectrum was determined on the Varian 7.0T FTMS instrument.

2. Preparation of allenes[1-4]:



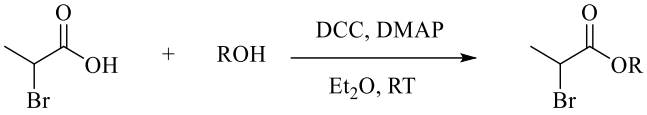
CuI (0.95 g, 5.0 mmol, 0.5 equiv), $(CH_2O)_n$ (0.75 g, 25 mmol, 2.5 equiv), 1,4-dioxane (20 mL), alkyne (10 mmol), and amine (3.3 g, 18 mmol, 1.8 equiv) were sequentially added into a dried reaction tube equipped with a reflux condenser under an argon atmosphere. The mixture was stirred under reflux. After the reaction was complete as monitored by TLC, then cooled it to room temperature. Water (10 mL) and ethyl ether (20 mL) were added and then the aqueous solution was separated and extracted with dichloromethane (DCM) (3 × 10 mL). The organic layer was then washed with brine and dried over anhydrous Na_2SO_4, followed by the filtration and concentration. The obtained residue was purified by the column chromatography on silica gel (eluent: petroleum ether or petroleum ether/Et_2O) afforded the terminal allenes **1**.

The list of allenes **1**



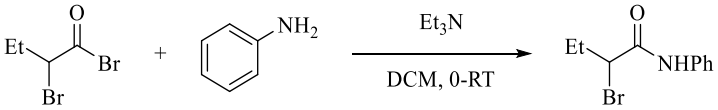
3. Preparation of α-bromoesters and 2-bromoamides 3

Procedure A



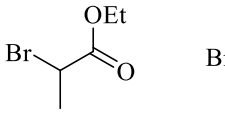
Adding α-bromopropionic acid (3.0 g, 20 mmol) to a stirred solution of dicyclohexylcarbodiimide (DCC) (5.0 g, 24 mmol) in ether (60 mL) in a tube, then adding a solution of the corresponding ROH (24 mmol) and 4-dimethylaminopyridine (DMAP) (147 mg, 1.2 mmol) in ether (12 mL) to this tube. The mixture was stirred at room temperature for 3 hours. After the reaction is completed, dilute it with hexane, filter, concentrate, and separate by column chromatography.

Procedure B

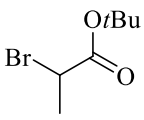


Triethylamine (30.0 mmol) and aniline (20.0 mmol) were stirred in dichloromethane (50.0 mL) at 0 °C. 2-Bromobutyric acid bromide (20.0 mmol) was added dropwise, and the mixture was stirred for 0.5 hour. After removing the cooling bath, the mixture was stirred for overnight. The mixture was washed with water and then extracted with dichloromethane. The solvents were evaporated, and the product was purified by recrystallization.

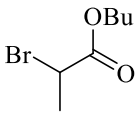
The list of esters **2**



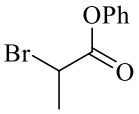
2a



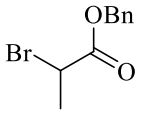
2b



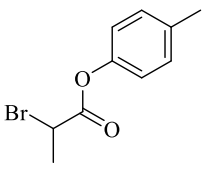
2c



2d



2e



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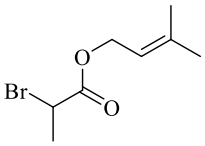
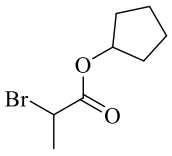
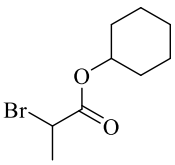


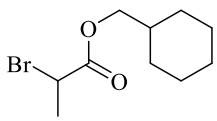
2g



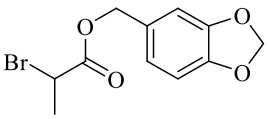
2h



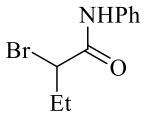
2i



2j

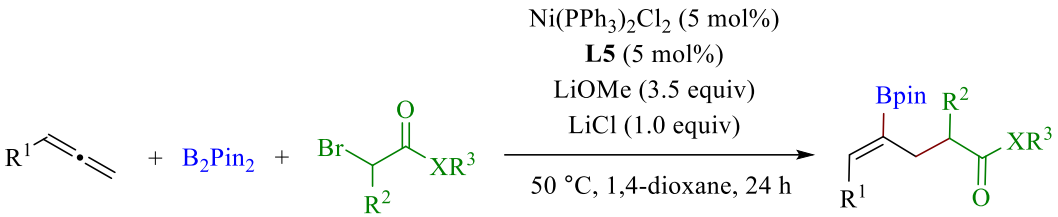


2k



2l

4. General procedure for carboborylation reaction of allenes

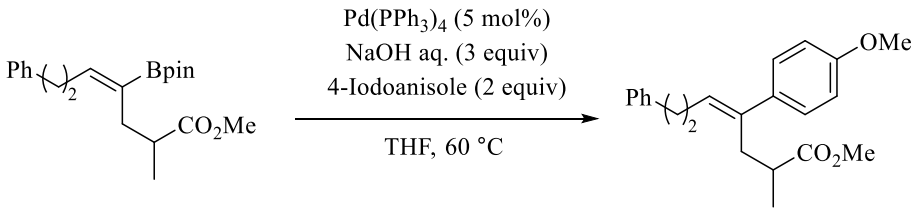


1 **2** **3** **4**

In the glovebox, the allenes **1** (0.2 mmol), **2** (0.22 mmol, 56 mg), **3** (0.3 mmol), $Ni(PPh)_3Cl_2$ (6.54 mg, 0.01 mmol), **L5** (2.68 mg, 0.01 mmol), LiCl (0.2 mmol, 8.4 mg), 1,4-dioxane (2.0 mL) were sequentially added into a Sealed tube, the mixture was stirred at 50 ºC under an argon atmosphere for 24 h. After the reaction is completed, the residue concentrated under vacuum. The desired product **4** was separated by a flash silica gel column (petroleum ether: ethyl acetate = 120:1-50:1).

5. Transformations of products

Methyl (*E*)-4-(4-methoxyphenyl)-2-methyl-7-phenylhept-4-enoate (7)



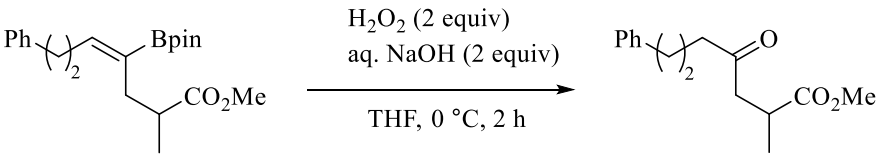
4h **7**

According to a literature procedure[1]. Under an argon atmosphere, $Pd(PPh_3)_4$ (5.8 mg, 0.005 mmol) dissolved in tetrahydrofuran (0.5 mL), **4h** (35.8 mg, 0.1 mmol) dissolved in tetrahydrofuran (0.25 mL), 4-Iodoanisole (46.8 mg, 0.2 mmol) dissolved in tetrahydrofuran (0.25 mL), and an aqueous solution of sodium hydroxide (120 μL, 2.5 M, 0.3 mmol) were added successively to a flame-dried Schlenk tube. The mixture was stirred at 60 °C, and after 14 hours, the reaction was completed as monitored by thin-

layer chromatography (TLC). Subsequently, the reaction mixture was evaporated, and then purified by column chromatography on silica gel (eluent: n-pentane/ethyl ether = 150/1) to obtain the desired product **7** (22 mg, 52% yield): Colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.24 (m, 3H), 7.23 – 7.16 (m, 5H), 6.87 – 6.80 (m, 2H), 5.66 (t, *J* = 7.22 Hz, 1H), 3.79 (s, 3H), 3.59 (d, *J* = 22.99 Hz, 3H), 2.82 (dd, *J* = 14.00, 6.33 Hz, 1H), 2.73 (t, *J* = 7.72 Hz, 2H), 2.59 – 2.47 (m, 3H), 2.45 – 2.34 (m, 1H), 1.25 (s, 2H), 1.01 (d, *J* = 6.93 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.7, 137.4, 129.2, 128.5, 128.4, 127.6, 125.9, 113.7, 55.3, 51.5, 38.0, 36.1, 33.3, 30.7, 16.2. **HRMS (ESI)** calcd. for $C_{23}H_{28}BNaO_3^+$ $(M + Na)^+$: 375.1931, Found: 375.1938.

Methyl 2-methyl-4-oxo-7-phenylheptanoate (8)

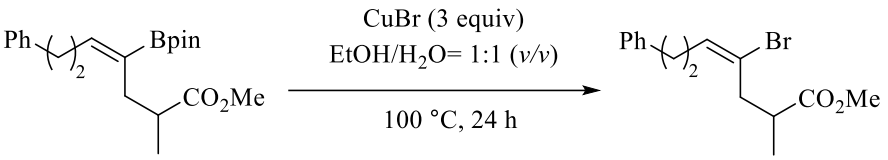


4h **8**

According to a literature procedure[1], **4h** (35.8 mg, 0.1 mmol), tetrahydrofuran (1 mL), an aqueous solution of sodium hydroxide (80 μL, 2.5 M, 0.2 mmol), and 30% aqueous hydrogen peroxide (20 μL, 0.2 mmol) were added successively to a Schlenk tube. The mixture was stirred at 0 °C, and after 2 hours, the reaction was completed as monitored by thin-layer chromatography (TLC). Subsequently, the reaction mixture was evaporated and then purified by column chromatography on silica gel (eluent: n-pentane/ethyl ether = 100/1) to obtain the target product **8** as a colorless oil (25 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.26 (m, 2H), 7.23 – 7.13 (m, 3H), 3.67 (s, 3H), 2.95 – 2.82 (m, 2H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.52 – 2.32 (m, 3H), 1.97 – 1.80 (m, 2H), 1.17 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 207.6, 175.3, 140.5, 127.4, 127.4, 124.9, 50.8, 44.8, 41.0, 34.0, 33.5, 24.1, 16.1. **HRMS (ESI)** calcd. for $C_{15}H_{20}BNaO_3^+$ $(M + Na)^+$: 271.1305, Found: 271.1310.

Methyl (*Z*)-2,4-dimethyl-7-phenylhept-4-enoate (9)

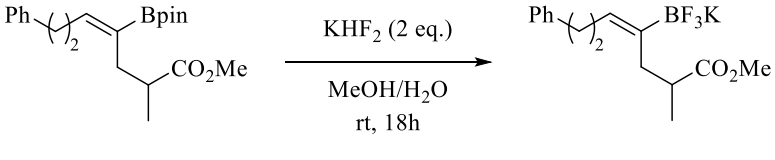


4h **9**

According to a literature procedure[2], a 25 mL Schlenk tube was loaded with **4h** (35.8 mg, 0.1 mmol), $CuBr_2$ (68 mg, 0.3 mmol, 3 equiv), ethanol (1 mL) and water (1 mL). The mixture was heated at 100 °C and monitored by thin-layer chromatography (TLC). After 24 hours, the heating was stopped and the reaction was cooled to room temperature. The reaction mixture was diluted with water and then extracted with petroleum ether/ethyl acetate (volume ratio of 10:1). The organic phase was washed with brine and dried over anhydrous magnesium sulfate. The mixture was filtered, and the filtrate was concentrated by rotary evaporation and then purified by flash column chromatography (eluent: n-pentane/ethyl ether = 30/1) to obtain the target product **9** (25 mg, 80% yield): colorless oil.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 (tt, *J* = 8.06, 1.46 Hz, 2H), 7.24 – 7.15 (m, 3H), 5.98 (t, *J* = 7.58 Hz, 1H), 4.13 (q, *J* = 7.15 Hz, 2H), 2.91 – 2.79 (m, 1H), 2.77 – 2.63 (m, 3H), 2.53 – 2.45 (m, 1H), 2.44 – 2.32 (m, 2H), 1.26 (t, *J* = 7.14 Hz, 3H), 1.11 (d, *J* = 7.01 Hz, 3H).. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 174.6, 139.9, 132.7, 127.4, 127.4, 127.4, 127.4, 125.1, 122.2, 59.5, 37.8, 37.0, 34.3, 30.6, 15.1, 13.2. **HRMS (ESI)** calcd. for $C_{16}H_{21}BNaO_3^+$ $(M + Na)^+$: 347.0617, Found: 347.0625.

(*Z*)-trifluoro (7-methoxy-6-methyl-7-oxo-1-phenylhept-3-en-4-yl) borate (10)



4h **10**

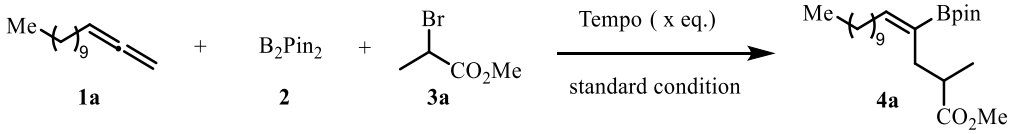
According to a literature procedure[3], **4h** (143.2 mg, 0.4 mmol), methanol (5 mL), and a solution of potassium hydrogen difluoride (KHF_2, 625 mg, 0.8 mmol) in water (2 mL) were added sequentially to a flask. After being stirred at room temperature for 18 h, the resulting mixture was concentrated under reduced pressure. The residue was dissolved

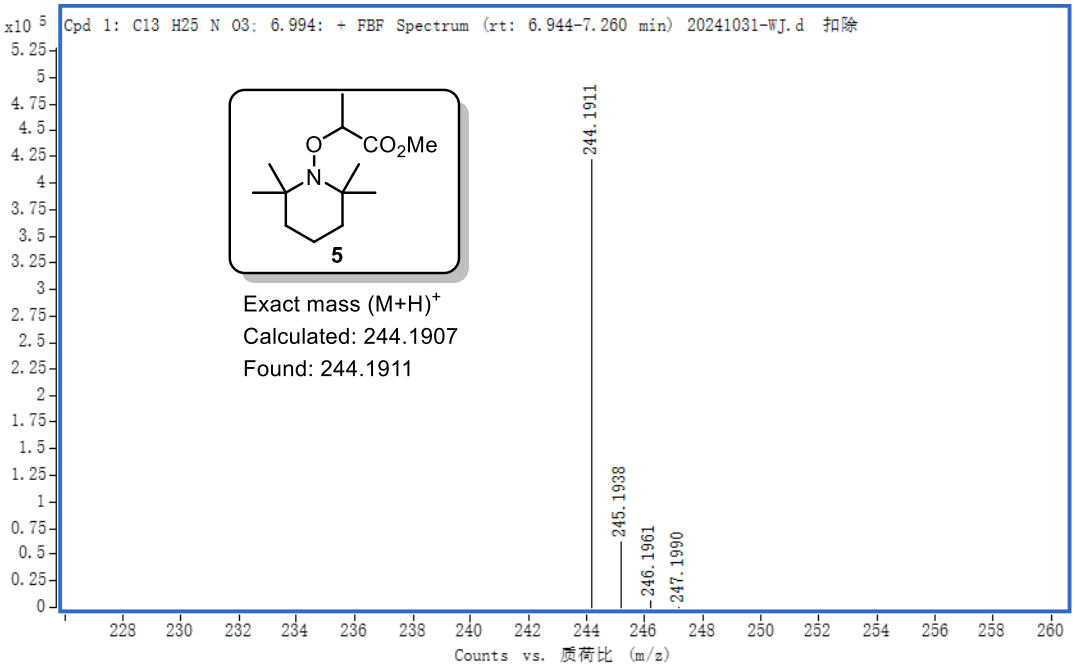
in 100 mL of hot acetone (at 50 °C), and then the resulting mixture was filtered through a short silica gel column (3 cm) which was eluted with hot acetone (at 50 °C, 100 mL × 2). The filtrate was concentrated in vacuo to obtain the crude product **10** (74 mg, 55% yield): white solid.

^{1}H NMR (400 MHz, Methanol-d_4) δ 7.12 (t, J = 7.5 Hz, 3H), 7.02 (dd, J = 15.4, 8.2 Hz, 2H), 5.66 (t, J = 6.9 Hz, 1H), 3.50 (s, 3H), 2.64 (hept, J = 6.9 Hz, 1H), 2.49 (s, 1H), 2.35 – 2.30 (m, 1H), 2.21 (d, J = 7.6 Hz, 1H), 2.13 – 1.96 (m, 1H), 1.20 – 1.11 (m, 1H), 0.97 (d, J = 7.0 Hz, 4H). **^{13}C NMR** (101 MHz, Methanol-d_4) δ 180.4, 144.1, 132.6, 129.4, 129.3, 126.6, 126.4, 52.1, 44.2, 41.2, 41.0, 38.35, 37.6, 34.9, 33.7, 31.5, 25.2, 17.7, 17.4. **^{19}F NMR** (376 MHz, DMSO-d_6) δ -134.86 (dd, J = 36.30, 17.80 Hz), -135.38, -143.62 (d, J = 21.68 Hz).

6. Control experiments

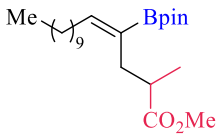
Radical trap experiment





7. Characterization of Products

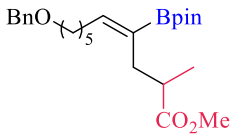
Methyl (*Z*)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) pentadec-4-enoate (4a)



Follow the general procedure, 65 mg, 83% yield of **4a** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 150:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.37 (t, *J* = 7.13 Hz, 1H), 3.63 (d, *J* = 1.30 Hz, 3H), 2.65 (p, *J* = 7.23 Hz, 1H), 2.50 (dd, *J* = 13.24, 6.93 Hz, 1H), 2.23 (dd, *J* = 13.15, 8.13 Hz, 1H), 2.12 (q, *J* = 7.48 Hz, 2H), 1.27 – 1.24 (m, 28H), 1.10 (d, *J* = 6.95 Hz, 3H), 0.88 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.2, 147.4, 82.1, 50.3, 38.6, 31.4, 30.9, 28.7, 28.6, 28.6, 28.6, 28.5, 28.3, 28.3, 28.1, 27.7, 25.7, 23.7, 23.7, 21.8, 15.7, 13.1. **HRMS (ESI)** calcd. for $C_{23}H_{43}BNaO_4^+$ (M + Na)$^+$: 417.3147, Found: 417.3154.

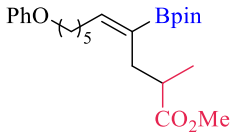
Methyl (*Z*)-10-(benzyloxy)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) dec-4-enoate (4b)



Follow the general procedure, 73 mg, 83% yield of **4b** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 140:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 4.38 Hz, 4H), 7.31 – 7.26 (m, 1H), 6.37 (t, *J* = 7.10 Hz, 1H), 4.50 (s, 2H), 3.63 (s, 3H), 3.46 (t, *J* = 6.61 Hz, 2H), 2.66 (dt, *J* = 7.96, 6.85 Hz, 1H), 2.54 – 2.46 (m, 1H), 2.23 (dd, *J* = 13.10, 8.11 Hz, 1H), 2.14 (qt, *J* = 6.84, 4.85, 3.63 Hz, 2H), 1.66 – 1.56 (m, 2H), 1.39 (p, *J* = 3.56 Hz, 4H), 1.25 (s, 12H), 1.10 (d, *J* = 6.92 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) 176.2, 147.0, 137.7, 127.3, 126.6, 126.4, 82.1, 76.3, 76.0, 75.7, 71.9, 69.4, 50.3, 38.6, 31.47, 28.7, 28.7, 28.0, 27.6, 25.1, 23.8, 23.7, 23.7, 15.7. **HRMS (ESI)** calcd. for $C_{25}H_{39}BNaO_5^+$ (M + Na)$^+$: 453.2783, Found: 453.2792.

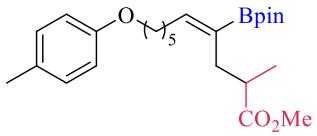
Methyl (*Z*)-2-methyl-10-phenoxy-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) dec-4-enoate (4c)



Follow the general procedure, 73 mg, 88% yield of **4c** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 140:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.30 – 7.24 (m, 2H), 6.94 – 6.87 (m, 3H), 6.38 (t, *J* = 7.09 Hz, 1H), 3.95 (t, *J* = 6.54 Hz, 2H), 3.63 (s, 3H), 2.67 (h, *J* = 7.29 Hz, 1H), 2.51 (dd, *J* = 13.15, 7.08 Hz, 1H), 2.20 (dq, *J* = 26.14, 7.36, 6.67 Hz, 3H), 1.78 (p, *J* = 6.67 Hz, 2H), 1.47 (dt, *J* = 6.41, 3.61 Hz, 4H), 1.25 (s, 12H), 1.11 (d, *J* = 6.93 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.1, 158.1, 146.8, 128.4, 119.4, 113.5, 82.1, 66.7, 50.3, 38.5, 31.5, 28.2, 27.8, 27.6, 24.9, 23.7, 23.7, 15.7. **HRMS (ESI)** calcd. for $C_{24}H_{37}BNaO_5^+$ $(M+Na)^+$: 439.2626, Found: 439.2633.

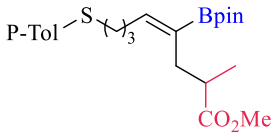
Methyl (*Z*)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-10-(p-tolyloxy) dec-4-enoate (4d)



Follow the general procedure, 72 mg, 84% yield of **4d** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 140:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.11 – 7.04 (m, 2H), 6.83 – 6.76 (m, 2H), 6.37 (t, *J* = 7.09 Hz, 1H), 3.92 (t, *J* = 6.54 Hz, 2H), 3.63 (s, 3H), 2.65 (p, *J* = 7.18 Hz, 1H), 2.51 (dd, *J* = 13.07, 7.14 Hz, 1H), 2.29 – 2.12 (m, 6H), 1.77 (t, *J* = 6.94 Hz, 2H), 1.46 (p, *J* = 3.37 Hz, 4H), 1.25 (s, 12H), 1.10 (d, *J* = 6.96 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.2, 155.9, 146.8, 128.8, 128.8, 113.3, 82.1, 66.9, 50.3, 38.5, 31.5, 28.2, 27.8, 27.6, 24.9, 23.7, 23.7, 19.4, 15.7. **HRMS (ESI)** calcd. for $C_{25}H_{39}BNaO_5^+$ $(M + Na)^+$: 453.2783, Found: 453.2788.

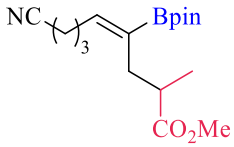
Methyl (*Z*)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-8-(p-tolylthio)oct-4-enoate (4e)



Follow the general procedure, 71 mg, 85% yield of **4e** was obtained. Yellow oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 – 7.22 (m, 2H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.34 (t, *J* = 7.1 Hz, 1H), 3.63 (s, 3H), 2.90 – 2.82 (m, 2H), 2.72 – 2.59 (m, 1H), 2.54 – 2.42 (m, 1H), 2.31 (s, 3H), 2.22 (dd, *J* = 13.1, 8.1 Hz, 1H), 2.12 (q, *J* = 7.1 Hz, 2H), 1.60 (d, *J* = 7.4 Hz, 2H), 1.40 (q, *J* = 7.2, 6.3 Hz, 5H), 1.25 (s, 12H), 1.10 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 228.0, 177.2, 147.8, 135.9, 133.0, 129.9, 129.6, 83.1, 51.3, 39.6, 34.3, 32.5, 29.2, 28.6, 28.5, 24.7, 24.7, 21.0, 16.7. **HRMS (ESI)** calcd. for $C_{25}H_{39}BNaO_4S^+$ $(M + Na)^+$: 469.2554, Found: 469.2564.

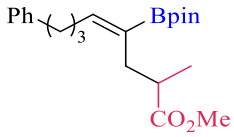
Methyl (*Z*)-8-cyano-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-enoate (4f)



Follow the general procedure, 51 mg, 80% yield of **4f** was obtained. Yellow oil. The flash chromatography was performed with PE: EA= 40:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.96 (s, 1H), 3.63 (s, 5H), 2.69 – 2.60 (m, 1H), 2.51 – 2.43 (m, 3H), 2.39 (s, 0H), 2.31 (t, *J* = 7.3 Hz, 4H), 2.23 (dd, *J* = 13.1, 7.0 Hz, 2H), 1.74 – 1.69 (m, 4H), 1.27 (s, 23H), 1.10 (d, *J* = 7.0 Hz, 6H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.9, 145.9, 120.0, 83.2, 51.3, 41.1, 39.8, 29.8, 25.6, 24.8, 24.8, 16.9, 16.3. **HRMS (ESI)** calcd. for $C_{17}H_{28}BNNaO_4^+$ $(M + Na)^+$: 344.2004, Found: 344.2010.

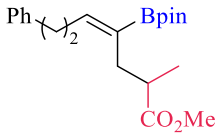
Methyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-enoate (4g)



Follow the general procedure, 61 mg, 82% yield of **4g** was obtained. Yellow oil. The flash chromatography was performed with PE: EA= 100:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 – 7.24 (m, 2H), 7.20 – 7.13 (m, 3H), 6.39 (dd, *J* = 7.7, 6.5 Hz, 1H), 3.62 (s, 3H), 2.70 – 2.55 (m, 3H), 2.52 – 2.46 (m, 1H), 2.26 – 2.14 (m, 2H), 1.72 (p, *J* = 7.7 Hz, 2H), 1.25 (s, 14H), 1.09 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.2, 146.6, 141.3, 127.34, 127.2, 124.7, 82.1, 50.3, 38.5, 34.6, 31.5, 29.7, 27.3, 23.72, 23.7, 15.7. **HRMS (ESI)** calcd. for $C_{23}H_{33}BNaO_4^+$ $(M + Na)^+$: 395.2364, Found: 395.2373.

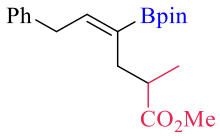
Methyl (*Z*)-2-methyl-7-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hept-4-enoate (4h)



Follow the general procedure, 57 mg, 80% yield of **4h** was obtained. Yellow oil. The flash chromatography was performed with PE: EA= 100:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (dd, *J* = 6.6, 1.6 Hz, 2H), 7.11 (d, *J* = 7.4 Hz, 3H), 6.37 (t, *J* = 7.0 Hz, 1H), 3.54 (s, 3H), 2.65 – 2.51 (m, 4H), 2.47 – 2.28 (m, 3H), 2.17 – 2.10 (m, 1H), 1.17 (s, 15H), 1.01 (d, *J* = 6.9 Hz, 3H).^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.1, 146.8, 141.9, 128.3, 125.9, 125.6, 83.2, 51.3, 39.5, 35.4, 32.5, 30.8, 29.7, 24.7, 16.8. **HRMS (ESI)** calcd. for $C_{21}H_{31}BNaO_4^+$ $(M + Na)^+$: 381.2208, Found: 381.2214.

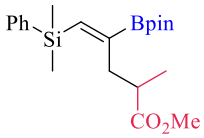
Methyl (*Z*)-2-methyl-6-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)hex-4-enoate (4i)



Follow the general procedure, 53 mg, 77% yield of **4i** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 80:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.29 – 7.25 (m, 2H), 7.18 (d, J = 4.72 Hz, 3H), 6.51 (t, J = 7.18 Hz, 1H), 3.64 (d, J = 1.22 Hz, 3H), 3.55 – 3.47 (m, 2H), 2.75 (dt, J = 14.24, 7.22 Hz, 1H), 2.65 (dd, J = 12.88, 7.34 Hz, 1H), 2.35 (dd, J = 13.05, 7.73 Hz, 1H), 1.24 (d, J = 1.20 Hz, 12H), 1.16 (d, J = 6.85 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.1, 144.8, 139.2, 127.7, 127.3, 124.9, 82.2, 50.4, 38.6, 33.9, 31.6, 23.7, 23.6, 15.9. **HRMS (ESI)** calcd. for $C_{20}H_{29}BNaO_4^+$ $(M + Na)^+$: 367.2051, Found: 367.2060.

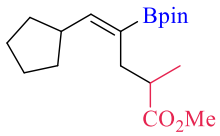
Methyl (*Z*)-5-(dimethyl(phenyl)silyl)-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (4j)



Follow the general procedure, 61 mg, 78% yield of **4j** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (ddt, *J* = 5.4, 3.7, 2.2 Hz, 1H), 7.33 (dd, *J* = 4.1, 2.3 Hz, 1H), 6.68 (s, 0H), 3.59 (s, 2H), 2.76 – 2.67 (m, 0H), 2.54 (d, *J* = 1.1 Hz, 0H), 2.36 – 2.26 (m, 0H), 1.24 (d, *J* = 16.1 Hz, 8H), 0.97 (d, *J* = 7.0 Hz, 2H), 0.47 – 0.37 (m, 4H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.5, 147.0, 139.9, 134.7, 133.9, 129.6, 128.5, 84.4, 52.0, 40.1, 39.6, 25.5, 25.4, 17.3. **HRMS (ESI)** calcd. for $C_{21}H_{33}BNaO_4Si^+$ $(M + Na)^+$: 411.2133, Found: 411.2140.

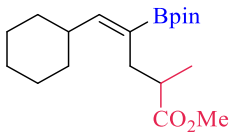
Methyl (*Z*)-5-cyclopentyl-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (4k)



Follow the general procedure, 52 mg, 81% yield of **4k** was obtained. Yellow oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.27 (d, *J* = 9.7 Hz, 1H), 3.64 (d, *J* = 3.0 Hz, 4H), 2.87 – 2.75 (m, 1H), 2.69 – 2.62 (m, 1H), 2.52 (ddd, *J* = 13.1, 7.0, 1.2 Hz, 1H), 1.81 – 1.71 (m, 2H), 1.70 – 1.61 (m, 1H), 1.61 – 1.51 (m, 1H), 1.26 (d, *J* = 2.8 Hz, 12H), 1.11 (dd, *J* = 6.9, 3.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.3, 153.1, 83.1, 51.3, 39.7, 39.1, 33.5, 33.3, 32.7, 25.7, 25.7, 24.7, 24.7, 16.7. **HRMS (ESI)** calcd. for $C_{18}H_{31}BNaO_4^+$ $(M + Na)^+$: 345.2208, Found: 345.2215.

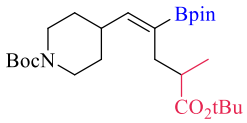
Methyl (*Z*)-5-cyclohexyl-2-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-4-enoate (4l)



Follow the general procedure, 51 mg, 76% yield of **4l** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.11 (d, *J* = 9.7 Hz, 1H), 3.59 (s, 3H), 2.70 – 2.51 (m, 1H), 2.51 – 2.08 (m, 3H), 1.70 – 1.56 (m, 4H), 1.55 – 1.44 (m, 2H), 1.21 (d, *J* = 3.4 Hz, 15H), 1.06 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 176.3, 152.3, 82.1, 50.3, 38.6, 36.4, 31.6, 31.6, 31.5, 30.9, 28.7, 25.0, 24.8, 24.8, 23.7, 23.7, 15.7, 13.1. **HRMS (ESI)** calcd. for $C_{19}H_{33}BNaO_4^+$ $(M + Na)^+$: 359.2364, Found: 359.2370.

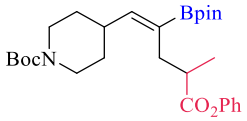
***Tert*-butyl (*Z*)-4-(5-(tert-butoxy)-4-methyl-5-oxo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)piperidine-1-carboxylate (4m)**



Follow the general procedure, 74.7 mg, 79% yield of **4m** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 50:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.09 (d, *J* = 9.26 Hz, 1H), 4.06 (s, 2H), 2.84 – 2.69 (m, 2H), 2.62 – 2.42 (m, 3H), 2.15 (dd, *J* = 12.57, 7.13 Hz, 1H), 1.44 (dd, *J* = 12.97, 1.73 Hz, 16H), 1.26 (d, *J* = 1.83 Hz, 12H), 1.09 – 1.02 (m, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 179.1, 153.2, 149.2, .2, 40.2, 39.3, 34.4, 32.0, 30.3, 27.5, 27.1, 23.9, 23.8, 23.6, 16.0. **HRMS (ESI)** calcd. for $C_{26}H_{46}BNNaO_6^+$ $(M + Na)^+$: 502.3310, Found: 502.3315.

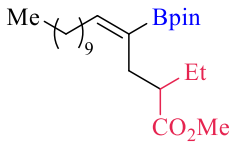
***Tert*-butyl (*Z*)-4-(4-methyl-5-oxo-5-phenoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pent-1-en-1-yl)piperidine-1-carboxylate (4n)**



Follow the general procedure, 71.8 mg, 72% yield of **4n** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 40:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.11 (m, 2H), 7.00 – 6.70 (m, 3H), 6.11 (dd, *J* = 9.71, 3.65 Hz, 1H), 4.14 – 4.00 (m, 2H), 3.73 – 3.55 (m, 2H), 2.72 (dt, *J* = 14.67, 5.93 Hz, 2H), 2.52 (dd, *J* = 13.23, 7.73 Hz, 1H), 2.23 (ddt, *J* = 12.35, 7.49, 2.88 Hz, 1H), 1.80 (d, *J* = 7.08 Hz, 1H), 1.45 (s, 10H), 1.26 (s, 15H), 1.12 (d, *J* = 6.96 Hz, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.4, 155.1, 149.6, 128.5, 119.2, 114.3, 82.3, 78.6, 59.2, 50.4, 38.5, 34.4, 31.8, 30.4, 27.5, 23.7, 15.9, 13.2. **HRMS (ESI)** calcd. for $C_{28}H_{42}BNNaO_6^+$ $(M + Na)^+$: 522.2997, Found: 522.3005.

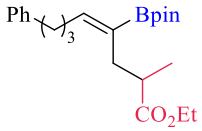
Methyl (*Z*)-2-ethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentadec-4-enoate (4o)



Follow the general procedure, 64.5 mg, 79% yield of **4o** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 100:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.34 (t, *J* = 7.1 Hz, 1H), 4.30 – 3.86 (m, 3H), 2.55 – 2.42 (m, 2H), 2.20 (ddt, *J* = 58.4, 15.2, 7.7 Hz, 3H), 1.74 (s, 1H), 1.56 (dtdd, *J* = 15.9, 13.1, 8.1, 6.0 Hz, 2H), 1.32 – 1.27 (m, 23H), 0.89 (t, *J* = 7.1 Hz, 9H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.2, 148.0, 83.0, 59.8, 47.4, 31.9, 31.2, 29.7, 29.6, 29.6, 29.5, 29.3, 29.1, 28.7, 25.2, 24.8, 24.8, 24.7, 24.6, 22.7, 14.3, 14.1, 11.9, 1.0. **HRMS (ESI)** calcd. for $C_{24}H_{45}BNaO_4^+$ $(M + Na)^+$: 431.3303, Found: 431.3310.

Ethyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-enoate (4p)

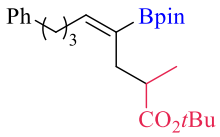


Follow the general procedure, 64.8 mg, 84% yield of **4p** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.24 (m, 2H), 7.17 (d, *J* = 6.9 Hz, 3H), 6.38 (t, *J* = 7.1 Hz, 1H), 4.07 (qd, *J* = 7.2, 1.6 Hz, 2H), 2.66 – 2.59 (m, 3H), 2.54 – 2.46 (m, 1H), 2.20 (ddd, *J* = 14.6, 9.6, 6.8 Hz, 3H), 1.76 – 1.67 (m, 2H), 1.24 (d, *J* = 6.9 Hz, 15H), 1.09 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.8, 146.4, 141.3, 127.4, 127.2, 124.6, 82.1, 58.9, 38.5, 34.6, 31.6, 29.7, 27.3, 23.7, 23.6, 15.8, 13.2. **HRMS (ESI)** calcd. for $C_{23}H_{35}BNaO_4^+$ $(M + Na)^+$: 409.2521, Found: 409.2529.

***Tert*-butyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-**

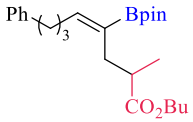
yl)oct-4-enoate (4q)



Follow the general procedure, 66 mg, 80% yield of **4q** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.25 (d, *J* = 7.0 Hz, 2H), 7.16 (s, 3H), 6.37 (t, *J* = 7.0 Hz, 1H), 2.61 (q, *J* = 8.8, 8.4 Hz, 2H), 2.56 – 2.46 (m, 2H), 2.26 – 2.11 (m, 3H), 1.75 – 1.68 (m, 2H), 1.41 (s, 11H), 1.25 (s, 12H), 1.05 (d, *J* = 6.6 Hz, 4H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.3, 146.1, 141.4, 127.4, 127.2, 124.6, 82.0, 78.5, 39.3, 34.6, 31.8, 29.7, 27.3, 27.1, 27.0, 23.8, 23.6, 15.9. **HRMS (ESI)** calcd. for $C_{25}H_{39}BNaO_4^+$ $(M + Na)^+$: 437.2834, Found: 437.2841.

Butyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-enoate (4r)

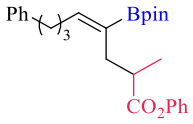


Follow the general procedure, 70 mg, 85% yield of **4r** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 (t, *J* = 7.45 Hz, 2H), 7.18 (d, *J* = 6.94 Hz, 3H), 6.39 (t, *J* = 7.08 Hz, 1H), 4.02 (dd, *J* = 6.56, 3.35 Hz, 2H), 2.64 (q, *J* = 8.00, 7.50 Hz, 4H), 2.52 (dd, *J* = 13.05, 7.11 Hz, 1H), 2.20 (ddt, *J* = 11.82, 7.39, 4.27 Hz, 3H), 1.75 – 1.69 (m, 2H), 1.61 – 1.56 (m, 2H), 1.38 (dd, *J* = 7.51, 2.29 Hz, 2H), 1.26 (s, 12H), 1.10 (dd, *J* = 6.89, 2.32 Hz, 3H), 0.92 (d, *J* = 7.28 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.8, 146.4, 141.3, 127.4, 127.2, 124.6, 82.1, 62.9, 38.6, 34.6, 31.6, 29.7, 27.3, 23.7, 23.6, 18.1, 15.8, 12.7. **HRMS (ESI)** calcd. for $C_{25}H_{39}BNaO_4^+$ $(M + Na)^+$: 437.2834, Found: 437.2840.

Phenyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-

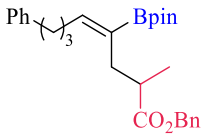
4-enoate (4s)



Follow the general procedure, 68 mg, 78% yield of **4s** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 100:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.26 (m, 2H), 7.16 (s, 4H), 6.39 (t, *J* = 7.1 Hz, 1H), 3.62 (s, 3H), 2.63 (q, *J* = 7.9, 7.5 Hz, 3H), 2.54 – 2.42 (m, 1H), 2.27 – 2.13 (m, 3H), 1.69 (dp, *J* = 19.7, 7.2, 6.6 Hz, 4H), 1.25 (s, 14H), 1.09 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.2, 175.8, 146.6, 141.3, 127.4, 127.2, 127.2, 124.7, 82.1, 82.1, 50.3, 38.5, 34.6, 31.5, 29.7, 27.3, 23.7, 15.7. **HRMS (ESI)** calcd. for $C_{27}H_{35}BNaO_4^+$ $(M + Na)^+$: 457.2521, Found: 457.2530.

Benzyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-4-enoate (4t)

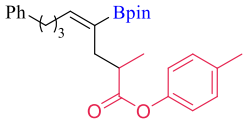


Follow the general procedure, 74 mg, 82% yield of **4t** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 100:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 (d, *J* = 3.86 Hz, 5H), 7.24 (d, *J* = 7.25 Hz, 2H), 7.18 – 7.13 (m, 3H), 6.39 (t, *J* = 7.10 Hz, 1H), 5.07 (s, 2H), 2.73 (p, *J* = 7.19 Hz, 1H), 2.63 – 2.53 (m, 3H), 2.27 – 2.12 (m, 3H), 1.76 – 1.62 (m, 3H), 1.24 (d, *J* = 9.25 Hz, 14H), 1.12 (d, *J* = 6.95 Hz, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.5, 146.7, 141.3, 135.3, 127.4, 124.6, 82.1, 64.8, 50.3, 38.6, 34.6, 31.6, 29.7, 27.3, 23.7, 23.6, 15.8, 15.7. **HRMS (ESI)** calcd. for $C_{28}H_{39}BNaO_4^+$ $(M + Na)^+$: 471.2677, Found: 471.2683.

***p*-tolyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)oct-**

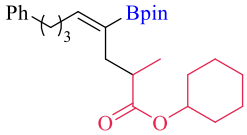
4-enoate (4u)



Follow the general procedure, 65 mg, 73% yield of **4u** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 90:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.21 (m, 3H), 7.21 – 7.12 (m, 4H), 7.09 (d, *J* = 8.14 Hz, 1H), 6.98 (d, *J* = 8.32 Hz, 1H), 6.39 (t, *J* = 7.12 Hz, 1H), 3.62 (d, *J* = 1.22 Hz, 3H), 2.64 (dt, *J* = 15.29, 7.53 Hz, 4H), 2.49 (dd, *J* = 13.18, 7.11 Hz, 1H), 2.19 (p, *J* = 7.34, 6.59 Hz, 3H), 1.75 – 1.69 (m, 2H), 1.25 (d, *J* = 1.23 Hz, 12H), 1.09 (dd, *J* = 6.95, 1.15 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 176.2, 146.6, 141.3, 128.9, 127.4, 127.2, 124.7, 115.4, 92.8, 82.1, 67.8, 50.3, 38.5, 34.6, 31.5, 29.7, 27.3, 23.6, 15.7. **HRMS (ESI)** calcd. for $C_{28}H_{39}BNaO_4^+$ $(M + Na)^+$: 471.2677, Found: 471.2683.

Cyclohexyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oct-4-enoate (4v)

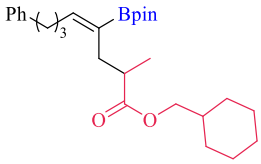


Follow the general procedure, 71 mg, 81% yield of **4v** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 – 7.25 (m, 2H), 7.17 (d, *J* = 6.94 Hz, 3H), 6.37 (t, *J* = 7.06 Hz, 1H), 4.71 (dt, *J* = 8.73, 4.48 Hz, 1H), 2.62 (dd, *J* = 8.77, 7.09 Hz, 3H), 2.54 – 2.48 (m, 1H), 2.23 – 2.16 (m, 3H), 1.83 – 1.75 (m, 3H), 1.73 – 1.65 (m, 5H), 1.42 – 1.35 (m, 4H), 1.26 (s, 12H), 1.09 (d, *J* = 6.89 Hz, 3H).. **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.2, 146.3, 141.4, 127.4, 127.2, 124.6, 82.09, 38.7, 34.6, 31.7, 30.6, 30.6, 29.7, 27.3, 24.5, 23.8, 23.6, 22.6, 15.8. **HRMS (ESI)** calcd. for $C_{27}H_{41}BNaO_4^+$ $(M + Na)^+$: 463.2990, Found: 463.2995.

Cyclohexylmethyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2- dioxabor

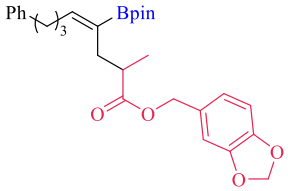
olan-2-yl) oct-4-enoate (4w)



Follow the general procedure, 73 mg, 80% yield of **4w** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 120:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.26 (m, 2H), 7.18 (dd, *J* = 6.89, 1.75 Hz, 3H), 6.40 (t, *J* = 7.10 Hz, 1H), 3.89 – 3.81 (m, 2H), 2.68 – 2.60 (m, 3H), 2.53 (dd, *J* = 13.08, 7.04 Hz, 1H), 2.21 (ddd, *J* = 14.39, 10.01, 6.88 Hz, 3H), 1.80 – 1.55 (m, 11H), 1.27 – 1.23 (m, 12H), 1.11 (dd, *J* = 6.98, 1.83 Hz, 3H), 0.99 – 0.91 (m, 2H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.8, 146.4, 141.3, 127.4, 127.4, 127.2, 127.2, 124.6, 124.5, 68.2, 38.8, 36.1, 36.1, 34.6, 34.5, 29.7, 28.7, 27.3, 25.4, 24.7, 23.8, 23.6, 15.8. **HRMS (ESI)** calcd. for $C_{28}H_{43}BNaO_4^+$ (M + Na)$^+$: 477.3147, Found: 477.3153.

Benzo[d][1,3]dioxol-5-ylmethyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oct-4-enoate (4x)

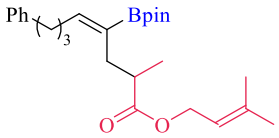


Follow the general procedure, 71 mg, 72% yield of **4x** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 80:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 3H), 6.86 – 6.75 (m, 3H), 6.40 (t, *J* = 7.08 Hz, 1H), 5.95 (s, 2H), 4.97 (s, 2H), 2.70 (q, *J* = 7.20 Hz, 1H), 2.61 (dd, *J* = 8.90, 6.69 Hz, 2H), 2.56 – 2.50 (m, 1H), 2.20 (dp, *J* = 21.57, 7.55 Hz, 3H), 1.71 (dd, *J* = 8.68, 6.82 Hz, 2H), 1.24 (s, 12H), 1.11 (d, *J* = 6.97 Hz, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.5, 146.6, 146.4, 141.3, 129.1, 127.4, 127.2, 124.6, 120.9, 107.9, 107.1, 100.0, 82.1, 64.8, 38.6, 34.6, 31.6, 29.7, 27.3, 23.7, 23.6, 15.7. **HRMS (ESI)** calcd. for $C_{29}H_{37}BNaO_4^+$ (M + Na)$^+$: 515.2575, Found: 515.2580.

3-methylbut-2-en-1-yl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2 dioxab

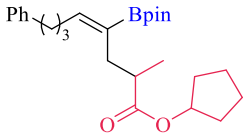
orolan-2-yl) oct-4-enoate (4y)



Follow the general procedure, 38 mg, 45% yield of **4y** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 130:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.36 (m, 2H), 7.29 (d, *J* = 6.79 Hz, 3H), 6.50 (t, *J* = 7.07 Hz, 1H), 5.43 (ddt, *J* = 7.09, 4.23, 1.48 Hz, 1H), 4.64 (d, *J* = 7.13 Hz, 2H), 2.80 – 2.68 (m, 4H), 2.62 (dd, *J* = 13.12, 7.03 Hz, 1H), 2.36 – 2.27 (m, 3H), 1.82 – 1.71 (m, 7H), 1.36 (s, 12H), 1.20 (d, *J* = 6.95 Hz, 3H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 175.8, 146.5, 141.3, 137.2, 127.4, 127.2, 124.6, 118.0, 82.1, 60.1, 38.6, 34.6, 31.5, 29.7, 27.3, 24.7, 23.7, 23.6, 17.0, 15.8. **HRMS (ESI)** calcd. for $C_{26}H_{39}BNaO_4^+$ $(M + Na)^+$: 449.2834, Found: 449.2849.

Cyclopentyl (*Z*)-2-methyl-8-phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oct-4-enoate (4z)

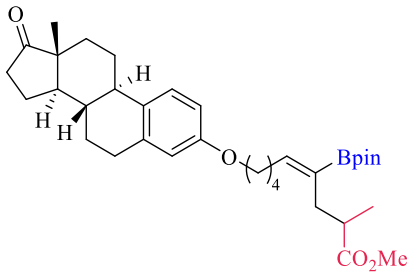


Follow the general procedure, 74 mg, 87% yield of **4z** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 130:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.27 – 7.24 (m, 2H), 7.20 – 7.14 (m, 3H), 6.37 (t, *J* = 7.1 Hz, 1H), 5.10 (tt, *J* = 5.5, 2.6 Hz, 1H), 2.61 (d, *J* = 8.0 Hz, 2H), 2.53 – 2.44 (m, 1H), 2.25 – 2.12 (m, 3H), 1.87 – 1.76 (m, 2H), 1.76 – 1.62 (m, 3H), 1.61 – 1.52 (m, 2H), 1.25 (s, 12H), 1.07 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.6, 146.3, 141.3, 127.4, 127.2, 124.64, 82.1, 38.6, 34.6, 31.7, 31.6, 29.7, 27.3, 23.8, 23.6, 22.8, 22.7, 15.8. **HRMS (ESI)** calcd. for $C_{26}H_{39}BNaO_4^+$ $(M + Na)^+$: 449.2834, Found: 449.2841.

Methyl (*E*)-2-methyl-9-(((8S,9R,13R,14R)-13-methyl-17-oxo 7,8,9,11,12,13,14,15,

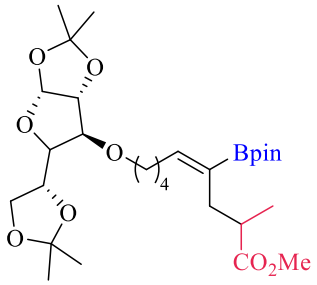
16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl) oxy)-4-(4,4,5,5-tetramethyl -1,3,2-dioxaborolan-2-yl)non-4-enoate (4aa)



Follow the general procedure, 75 mg, 65% yield of **4aa** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 30:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.61 Hz, 1H), 6.73 – 6.67 (m, 1H), 6.62 (s, 1H), 6.37 (t, *J* = 7.06 Hz, 1H), 3.92 (t, *J* = 6.40 Hz, 2H), 3.62 (d, *J* = 3.73 Hz, 3H), 2.91 – 2.85 (m, 2H), 2.67 (q, *J* = 7.23 Hz, 1H), 2.54 – 2.46 (m, 2H), 2.38 (t, *J* = 6.22 Hz, 2H), 2.29 – 2.12 (m, 6H), 2.03 – 1.93 (m, 3H), 1.77 (dd, *J* = 9.29, 6.08 Hz, 2H), 1.57 (ddd, *J* = 18.33, 11.42, 7.49 Hz, 6H), 1.44 (dd, *J* = 17.76, 2.99 Hz, 2H), 1.25 (s, 12H), 1.10 (d, *J* = 6.78 Hz, 3H), 0.90 (s, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 221.0, 177.2, 157.1, 147.5, 137.7, 131.8, 126.3, 114.5, 114.5, 112.1, 112.1, 83.2, 67.7, 51.4, 51.3, 50.4, 48.0, 44.0, 41.2, 39.9, 39.5, 38.4, 35.9, 32.6, 31.6, 29.7, 29.1, 28.3, 26.6, 25.9, 25.6, 24.8, 24.7, 21.6, 16.8, 13.9. **HRMS (ESI)** calcd. for $C_{35}H_{51}BNaO_6^+$ $(M + Na)^+$: 601.3671, Found: 601.3680.

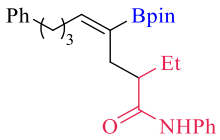
Methyl (Z)-9-(((3aR,6S,6aR)-5-((R)-2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl tetrahydrofuro[2,3-d][1,3]dioxol-6-yl)oxy)-2-methyl-4-(4,4,5,5-tetra- methyl-1,3, 2-dioxaborolan-2-yl)non-4-enoate (4bb)



Follow the general procedure, 86 mg, 76% yield of **4bb** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 10:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.32 (t, *J* = 7.05 Hz, 1H), 5.85 (d, *J* = 3.67 Hz, 1H), 4.50 (d, *J* = 3.57 Hz, 1H), 4.28 (q, *J* = 6.47 Hz, 1H), 4.08 (ddt, *J* = 17.66, 8.70, 4.93 Hz, 3H), 3.96 (dd, *J* = 8.54, 5.92 Hz, 1H), 3.82 (d, *J* = 3.02 Hz, 1H), 3.60 (d, *J* = 5.51 Hz, 4H), 3.52 – 3.46 (m, 1H), 2.70 – 2.56 (m, 1H), 2.48 (dd, *J* = 13.19, 7.15 Hz, 1H), 2.25 – 2.18 (m, 1H), 2.13 (q, *J* = 7.27 Hz, 2H), 1.56 (dq, *J* = 11.80, 6.47 Hz, 3H), 1.47 (s, 3H), 1.40 (s, 3H), 1.32 (s, 3H), 1.30 (s, 3H), 1.23 (d, *J* = 4.36 Hz, 12H), 1.08 (d, *J* = 6.87 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 177.1, 147.5, 111.7, 108.9, 108.8, 105.3, 83.1, 82.5, 82.1, 81.2, 72.5, 72.5, 70.52, 70.5, 67.2, 67.2, 51.3, 51.2, 39.5, 32.5, 29.5, 28.3, 26.8, 26.8, 26.2, 25.6, 25.4, 24.7, 24.7, 16.8. **HRMS (ESI)** calcd. for $C_{29}H_{49}BNaO_{10}^{+}$ $(M+Na)^{+}$: 591.3311, Found: 591.3317.

(*Z*)-2-ethyl-N,8-diphenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) oct-4-enamide (4cc)

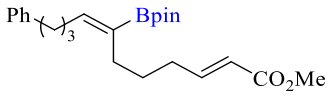


Follow the general procedure, 49 mg, 55% yield of **4cc** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 30:1 as the eluent.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.49 – 7.43 (m, 2H), 7.21 (d, *J* = 6.06 Hz, 4H), 7.13 – 7.08 (m, 3H), 7.05 – 7.00 (m, 1H), 6.35 (t, *J* = 7.10 Hz, 1H), 2.58 – 2.53 (m, 2H), 2.42 (dd, *J* = 13.15, 6.84 Hz, 1H), 2.32 – 2.22 (m, 2H), 2.14 (qd, *J* = 7.21, 1.68 Hz, 2H), 1.72 – 1.63 (m, 4H), 1.45 – 1.37 (m, 1H), 1.22 (d, *J* = 4.83 Hz, 12H), 0.88 (t, *J* = 7.32 Hz, 3H). **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 173.0, 146.9, 141.3, 137.3, 127.9, 127.4, 127.2, 124.6, 122.8, 118.5, 82.4, 49.3, 34.5, 31.6, 29.6, 27.3, 23.8, 23.8, 23.7, 11.4. **HRMS (ESI)** calcd. for $C_{28}H_{38}BNaO_{4}^{+}$ $(M + Na)^{+}$: 470.2837, Found: 470.2842.

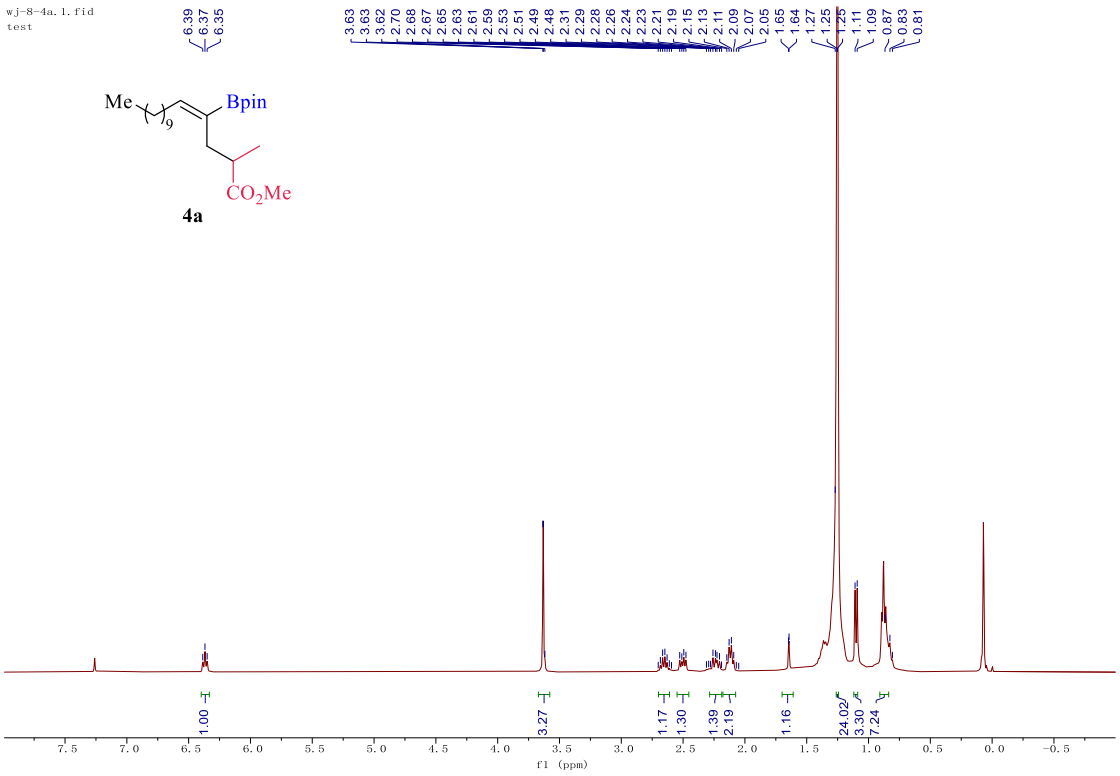
Methyl (2*E*,7*Z*)-11-phenyl-7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)undeca-

2,7-dienoate (6)

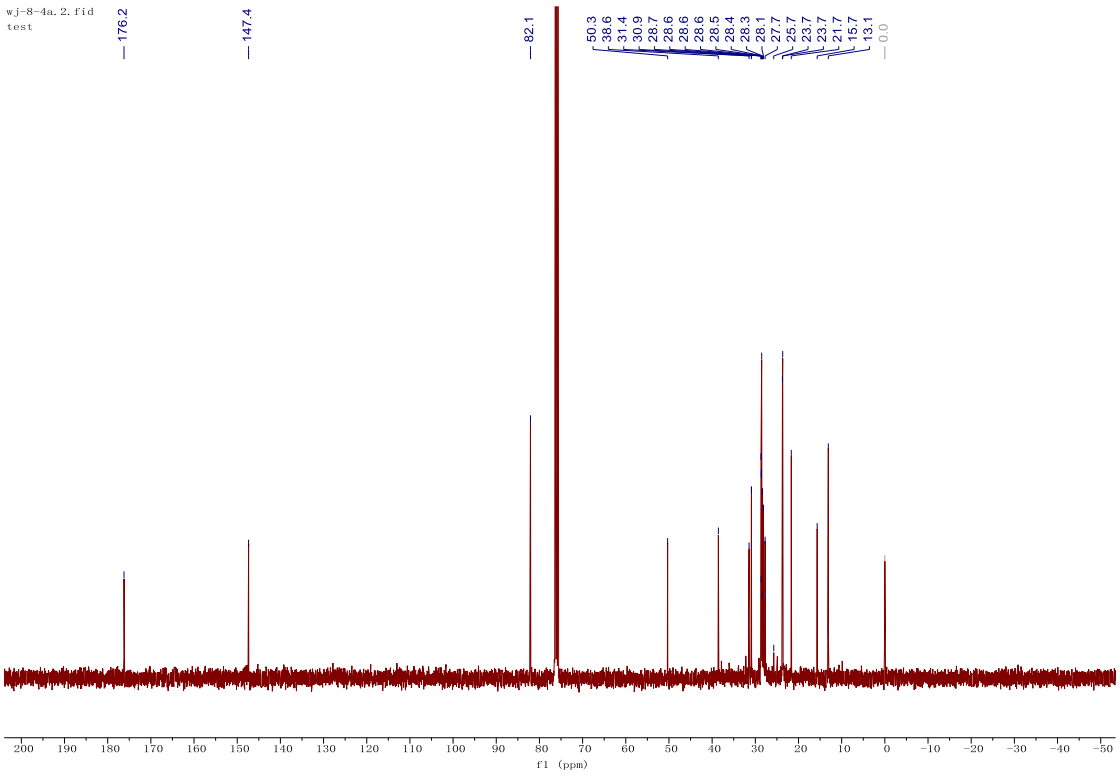


Follow the general procedure, 29 mg, 36% yield of **6** was obtained. Colorless oil. The flash chromatography was performed with PE: EA= 150:1 as the eluent.

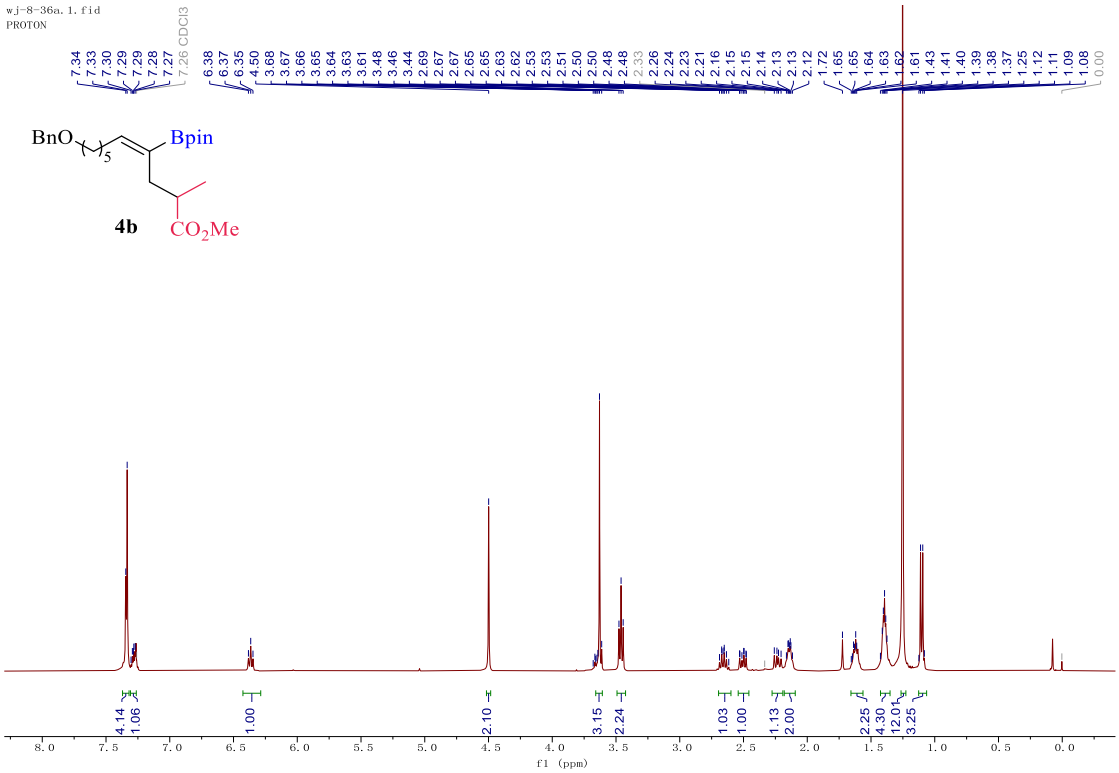
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 (d, *J* = 6.91 Hz, 3H), 7.02 – 6.93 (m, 1H), 6.34 (t, *J* = 7.07 Hz, 1H), 5.83 (dt, *J* = 15.64, 1.55 Hz, 1H), 3.73 (s, 3H), 2.62 (d, *J* = 7.66 Hz, 2H), 2.16 – 2.13 (m, 3H), 1.76 – 1.70 (m, 2H), 1.50 – 1.45 (m, 2H), 1.25 (s, 14H), 0.96 – 0.86 (m, 1H).**^{13}C NMR** (101 MHz, Chloroform-*d*) δ 166.3, 148.9, 145.1, 141.3, 127.4, 127.2, 124.7, 119.7, 82.1, 50.3, 34.6, 31.0, 29.7, 27.3, 27.1, 27.0, 23.7, 23.7. **HRMS (ESI)** calcd. for $C_{24}H_{35}BNaO_3^+$ $(M+Na)^+$: 405.2571, Found: 405.2579.



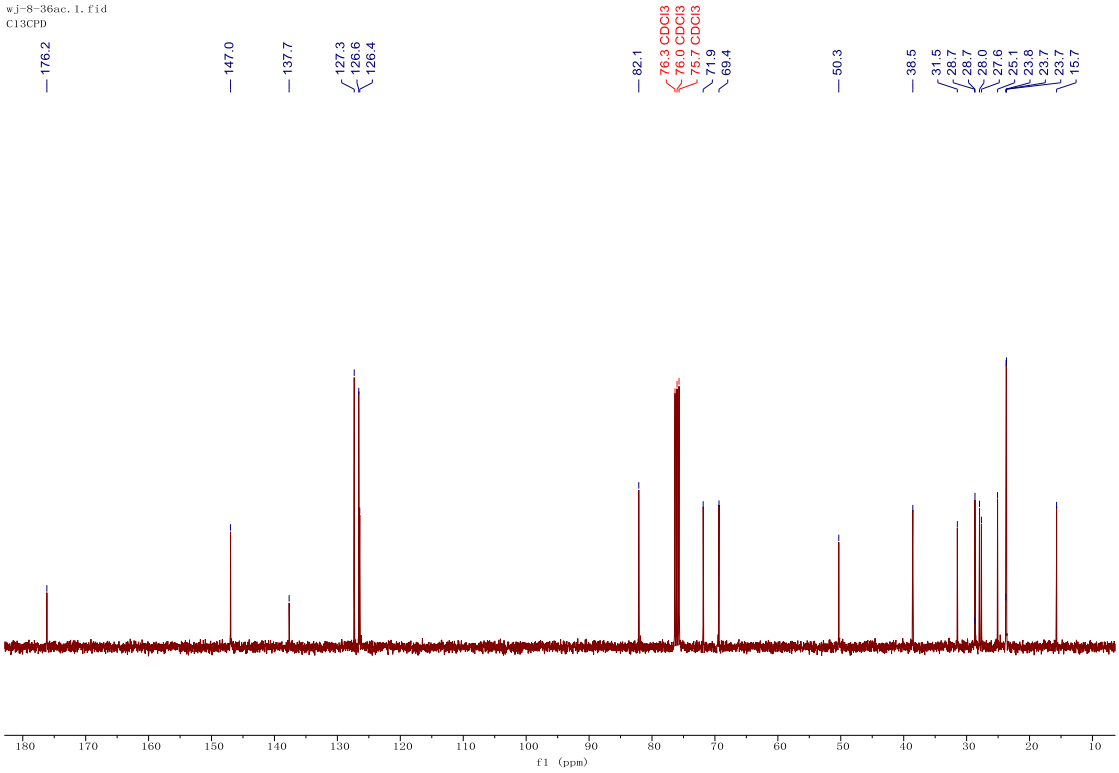
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4a**



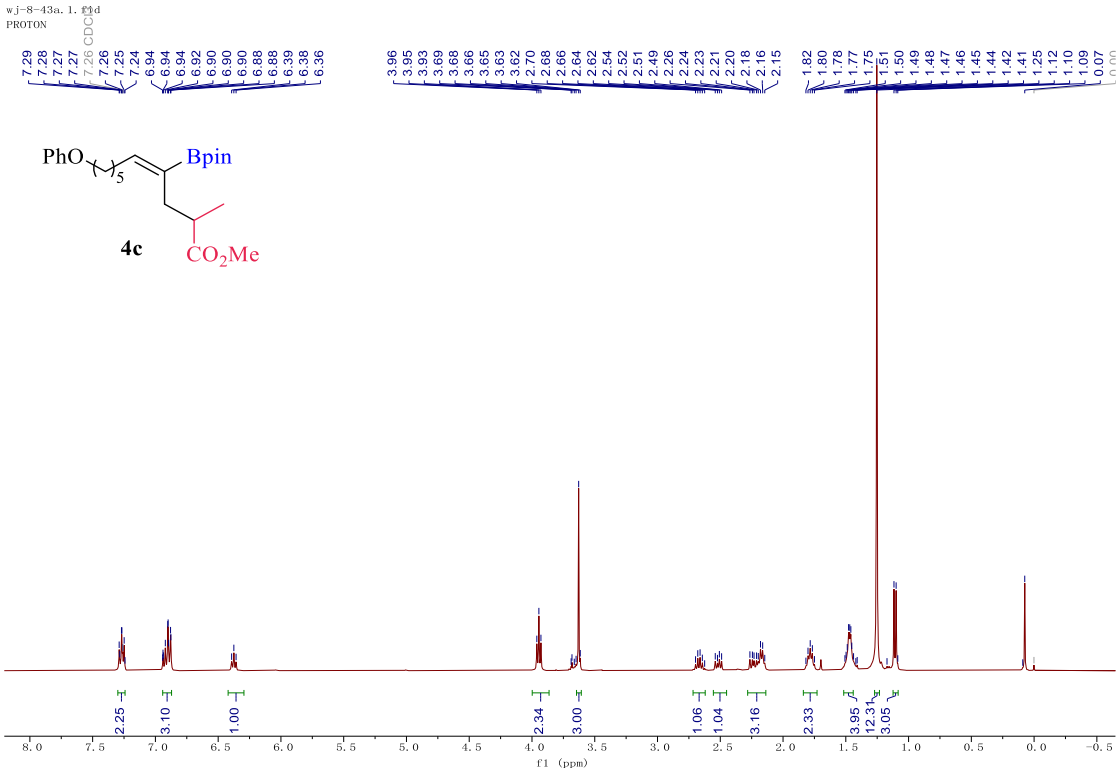
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4a**



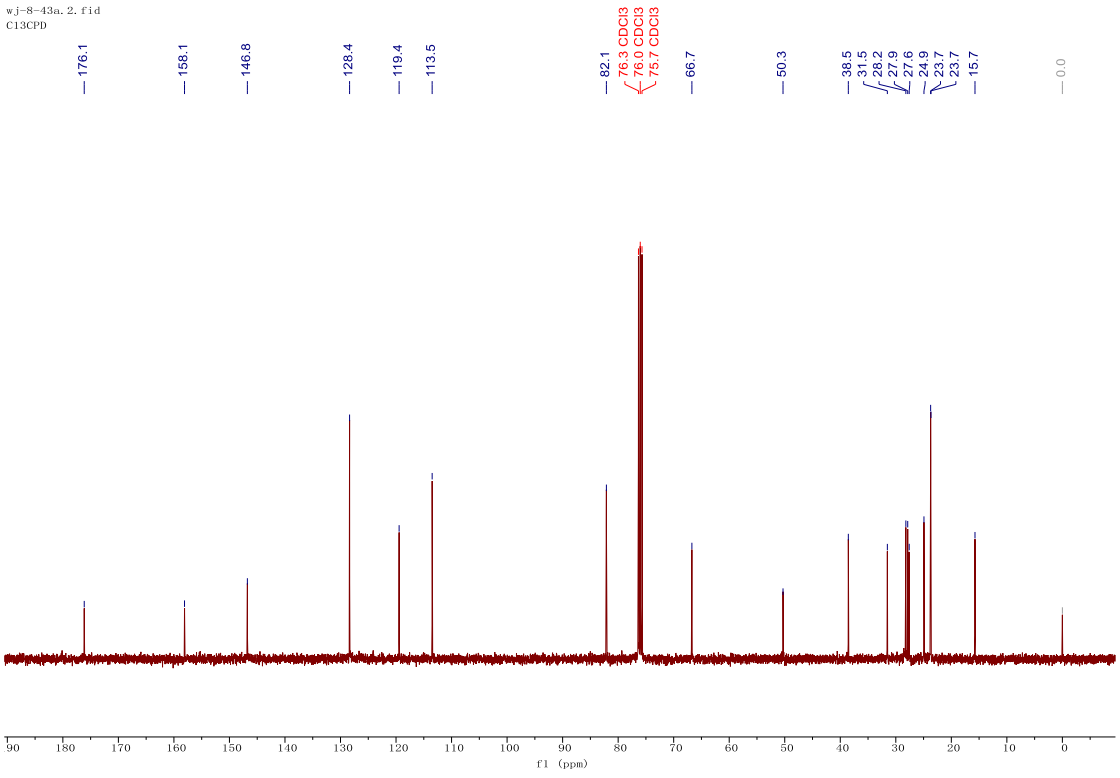
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4b**



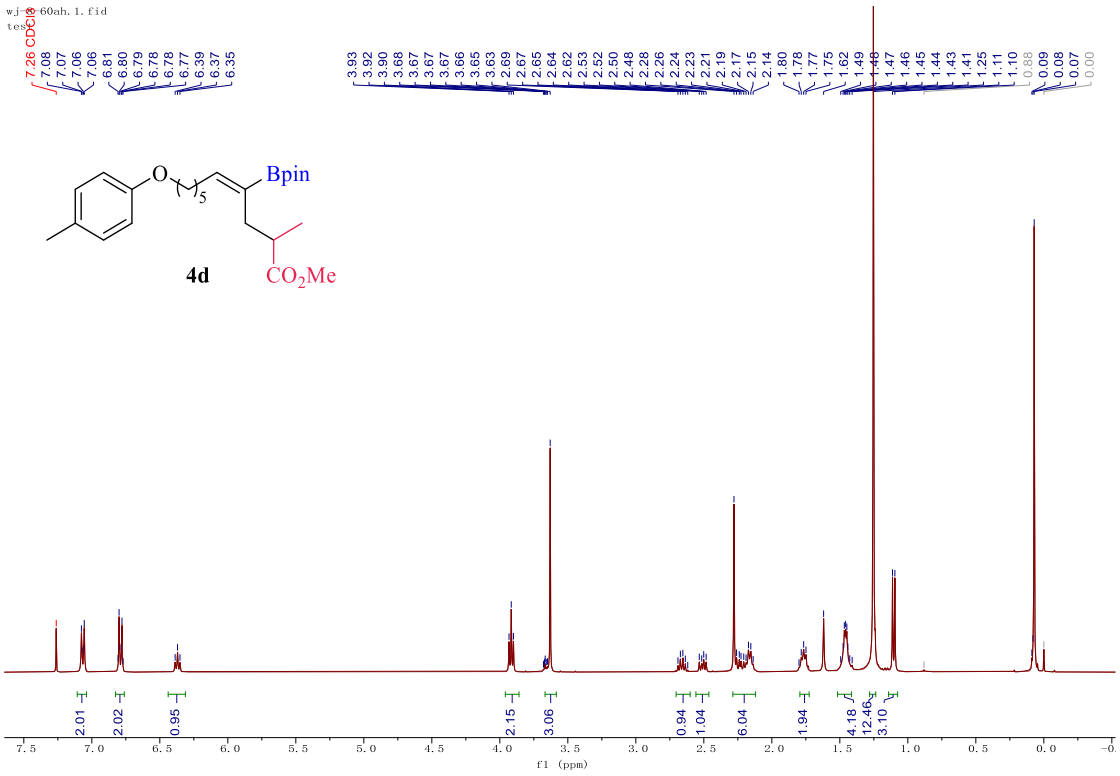
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4b**



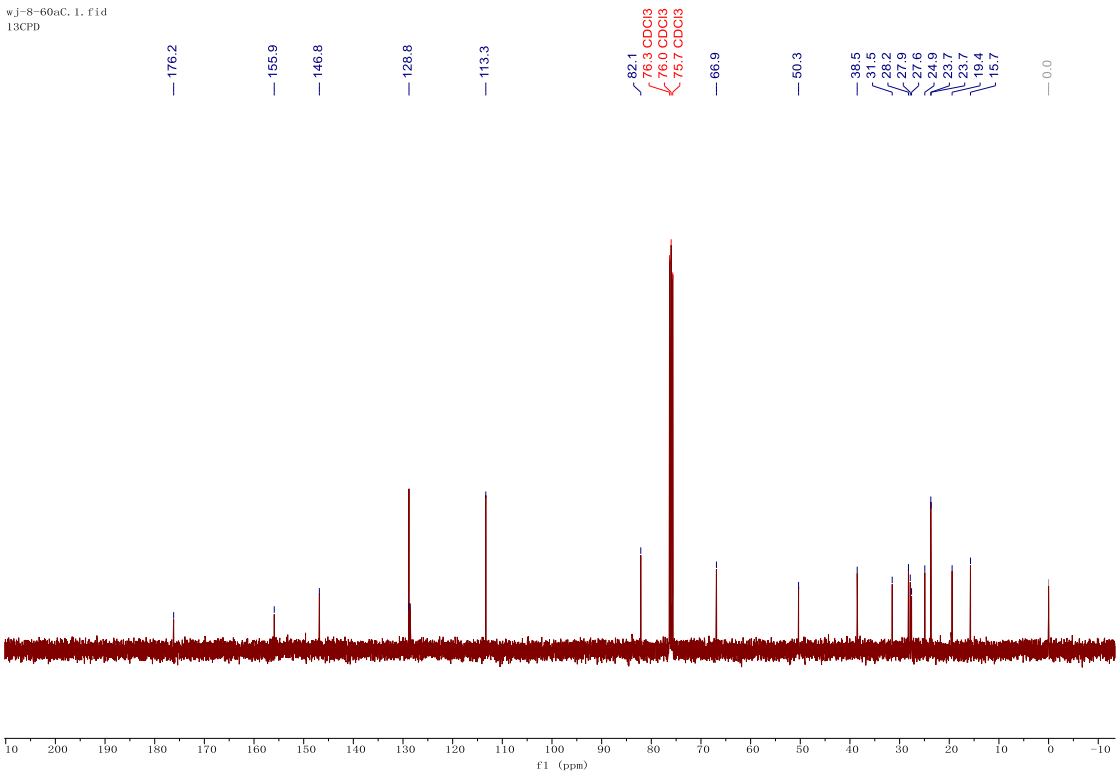
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4c**



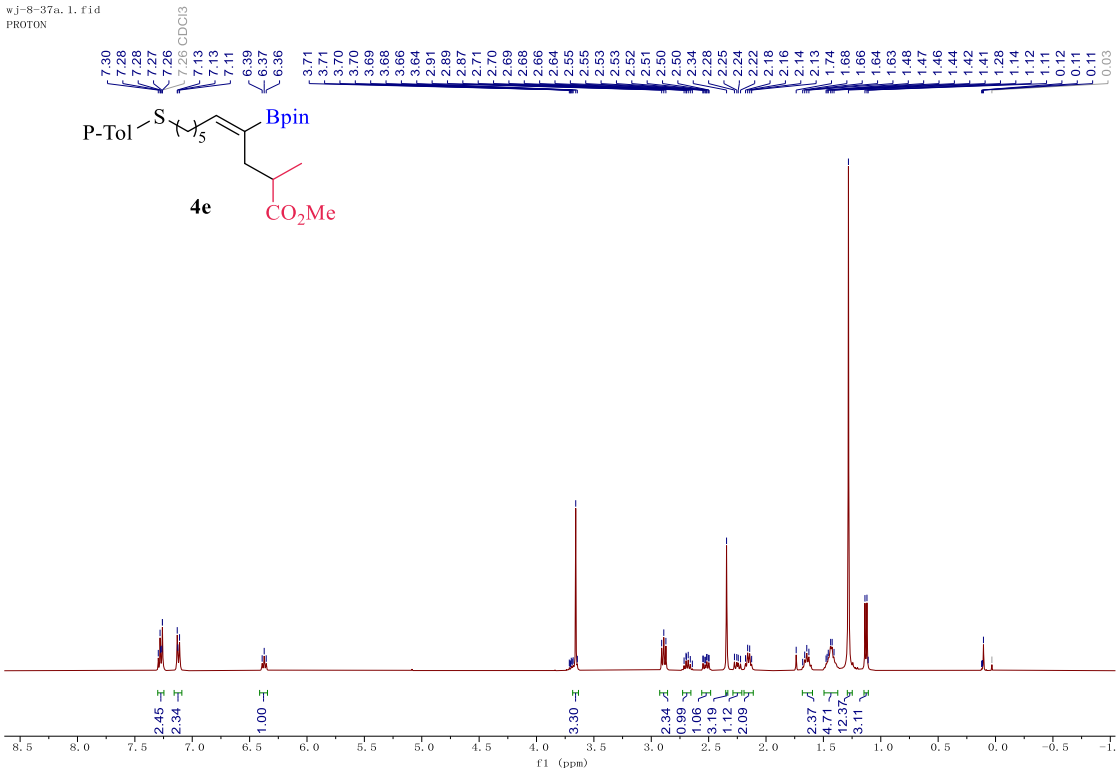
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4c**



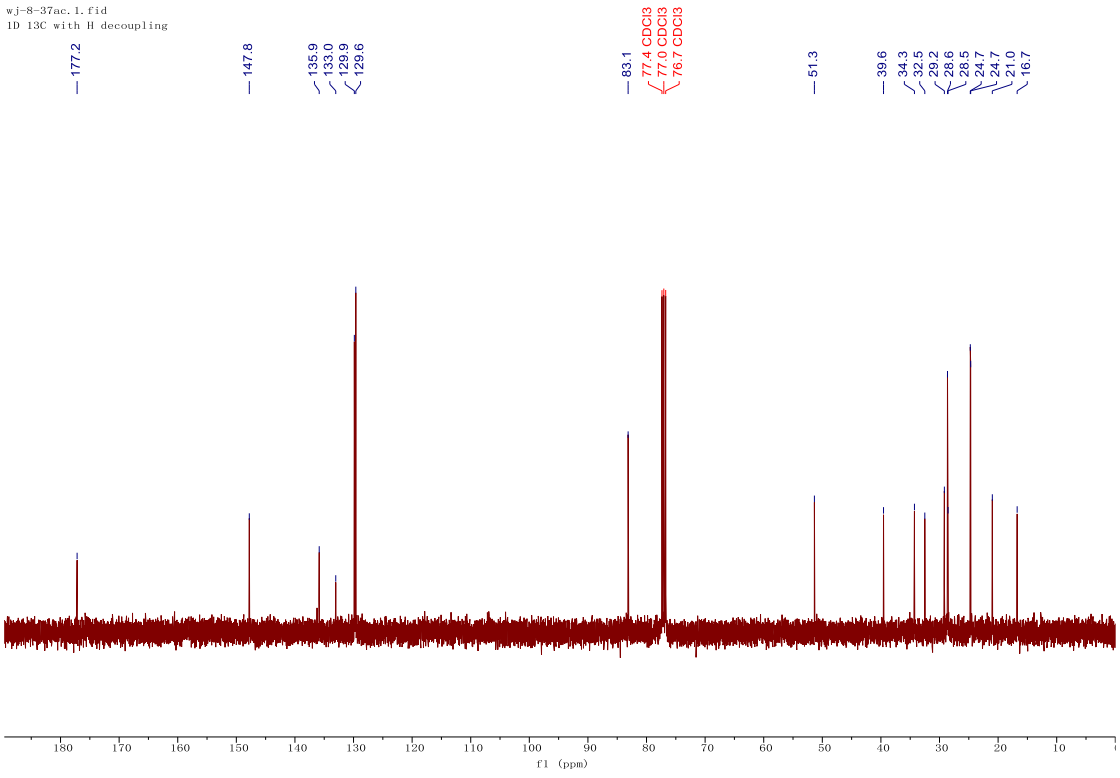
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4d**



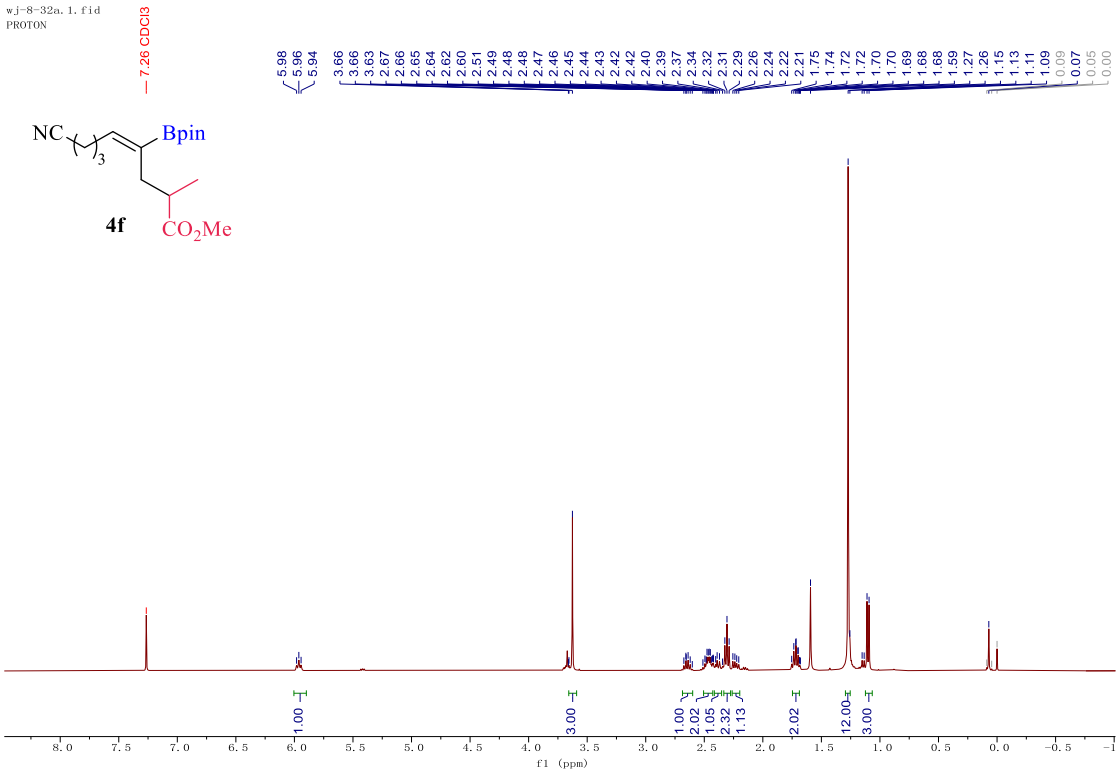
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4d**



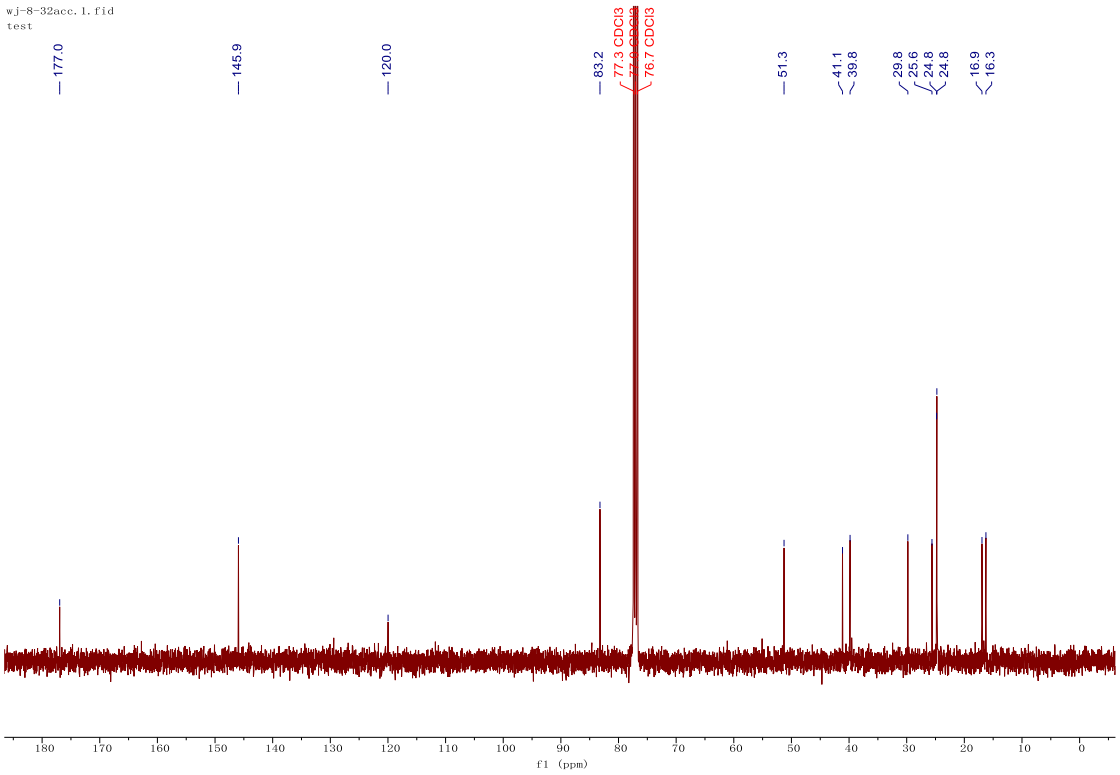
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4e**



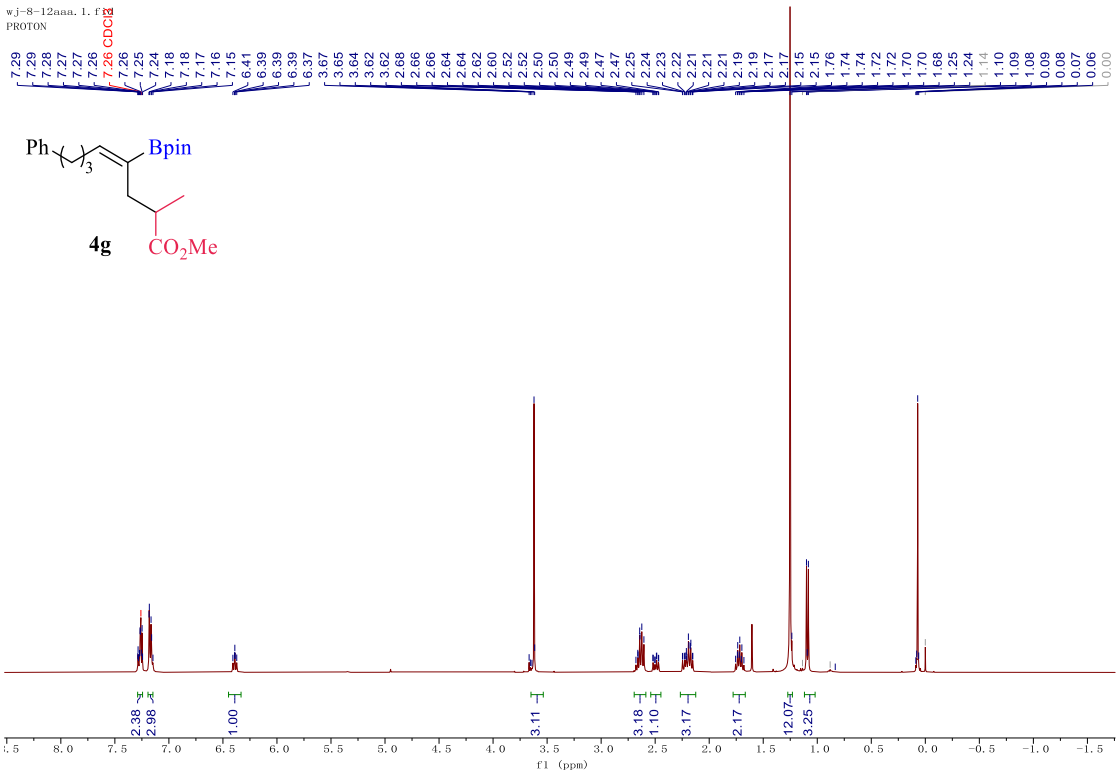
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4e**



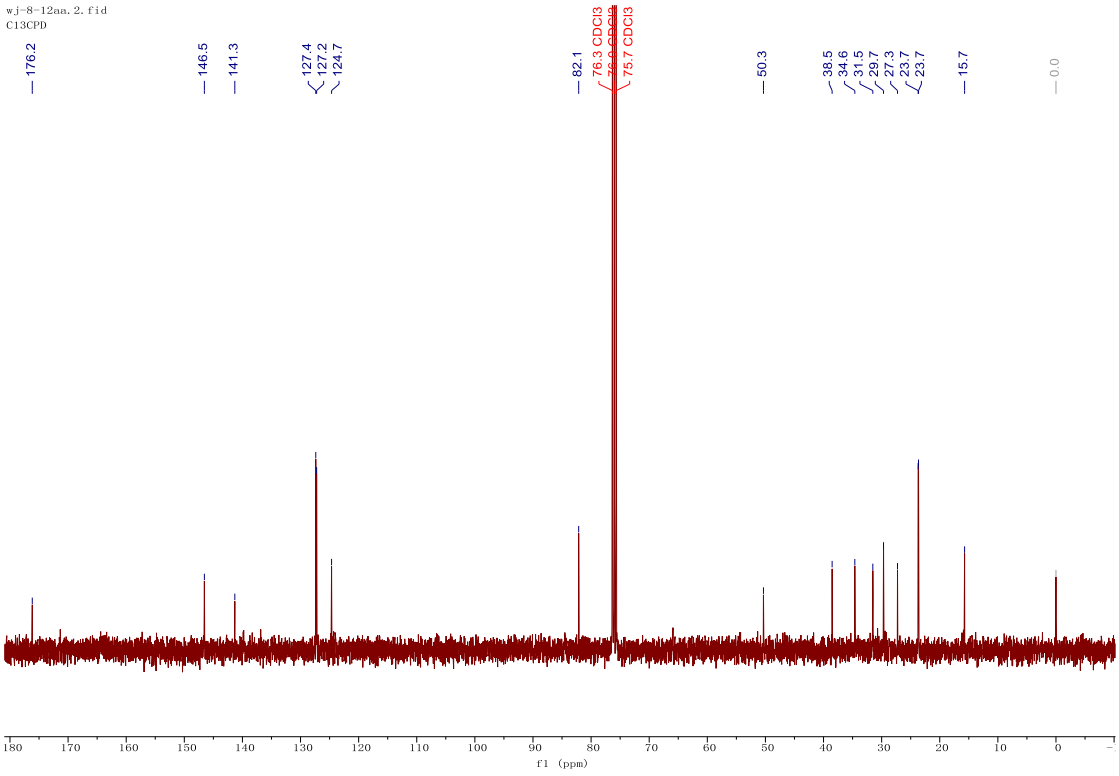
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4f**



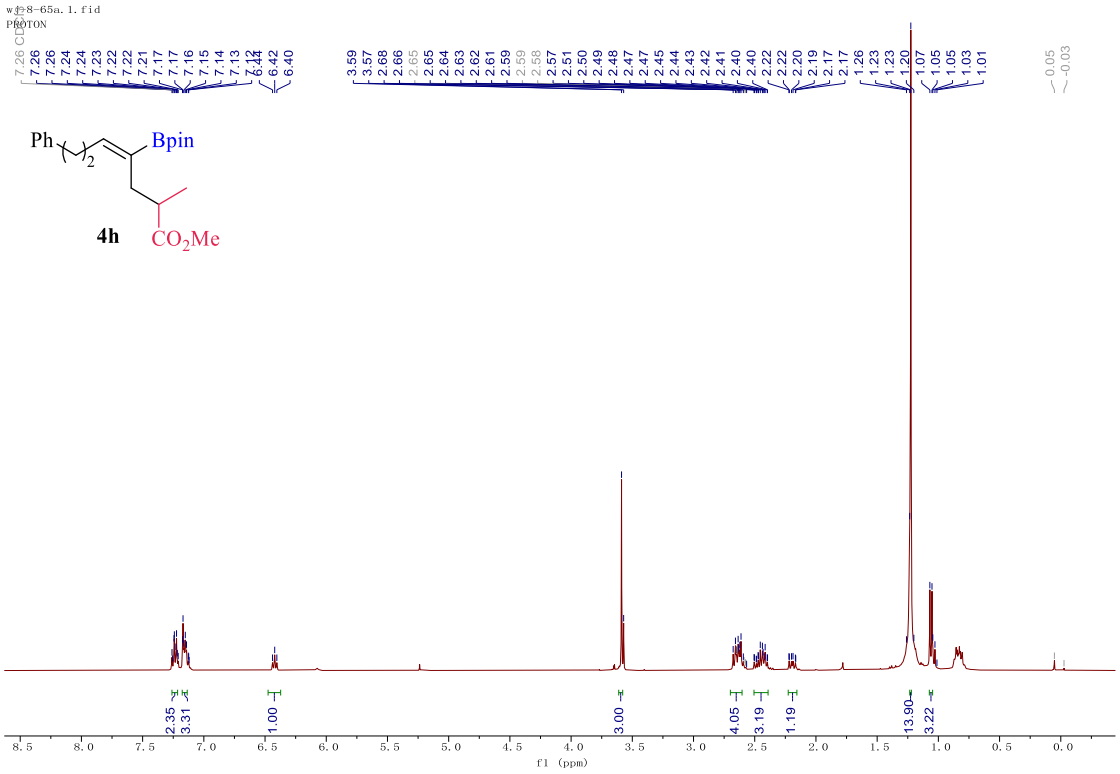
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4f**



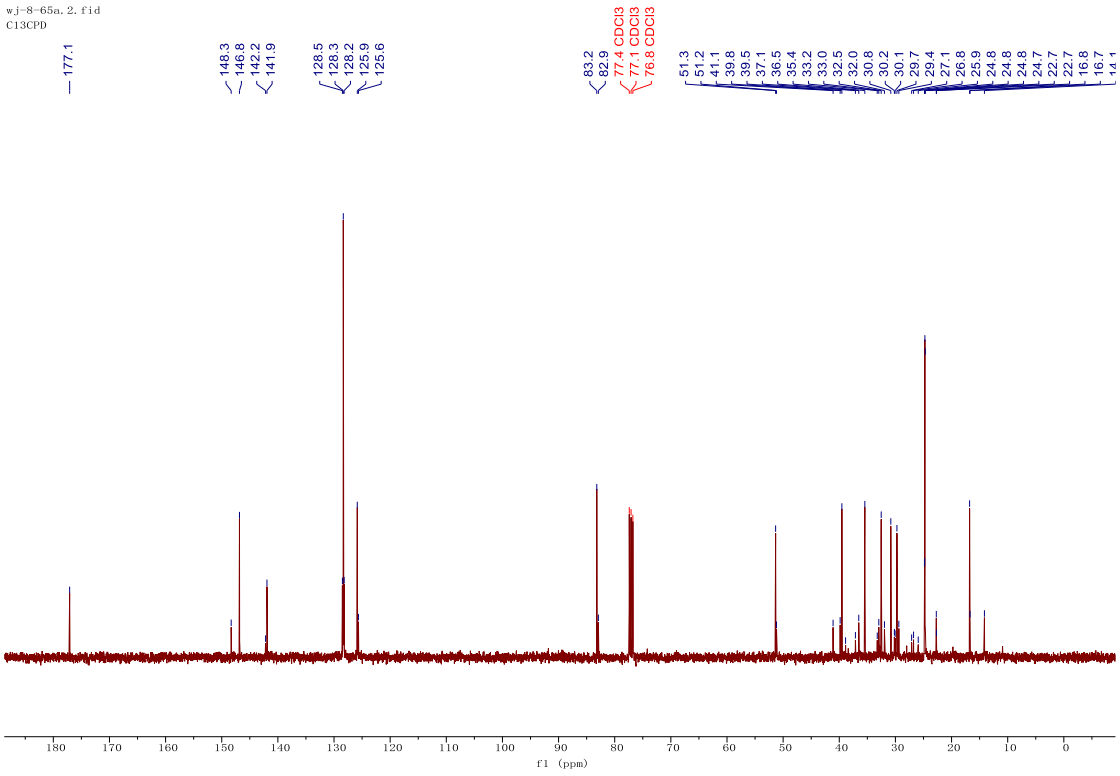
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4g**



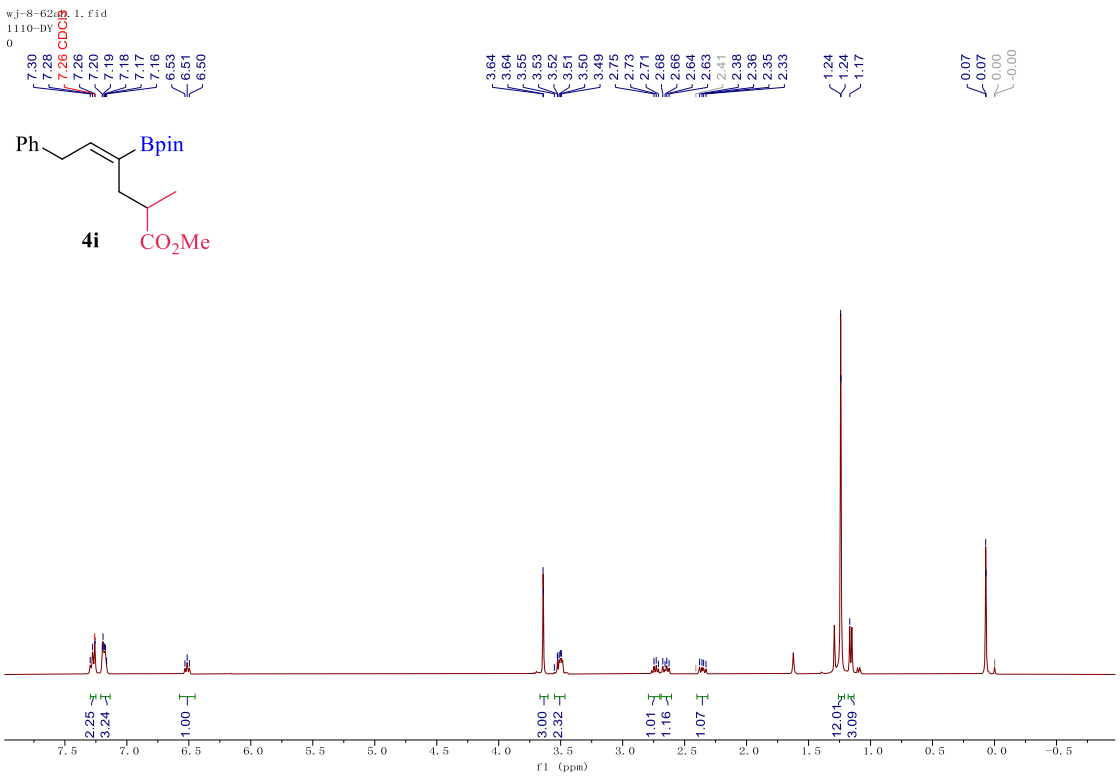
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4g**



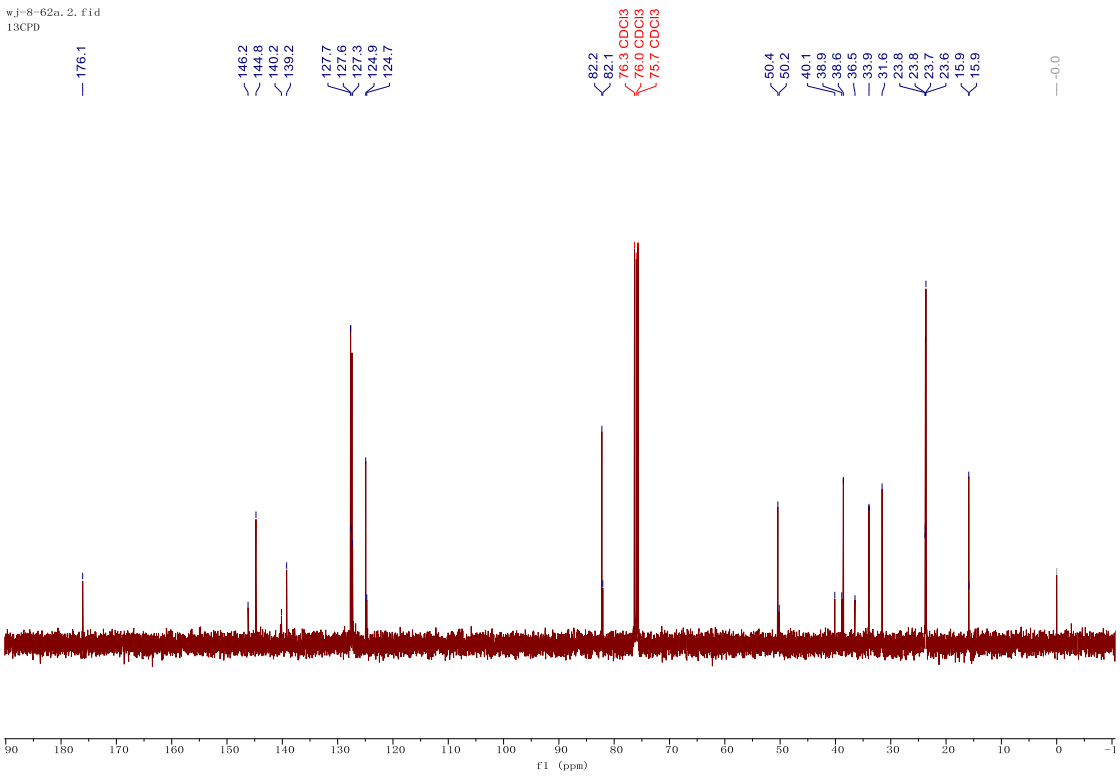
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4h**



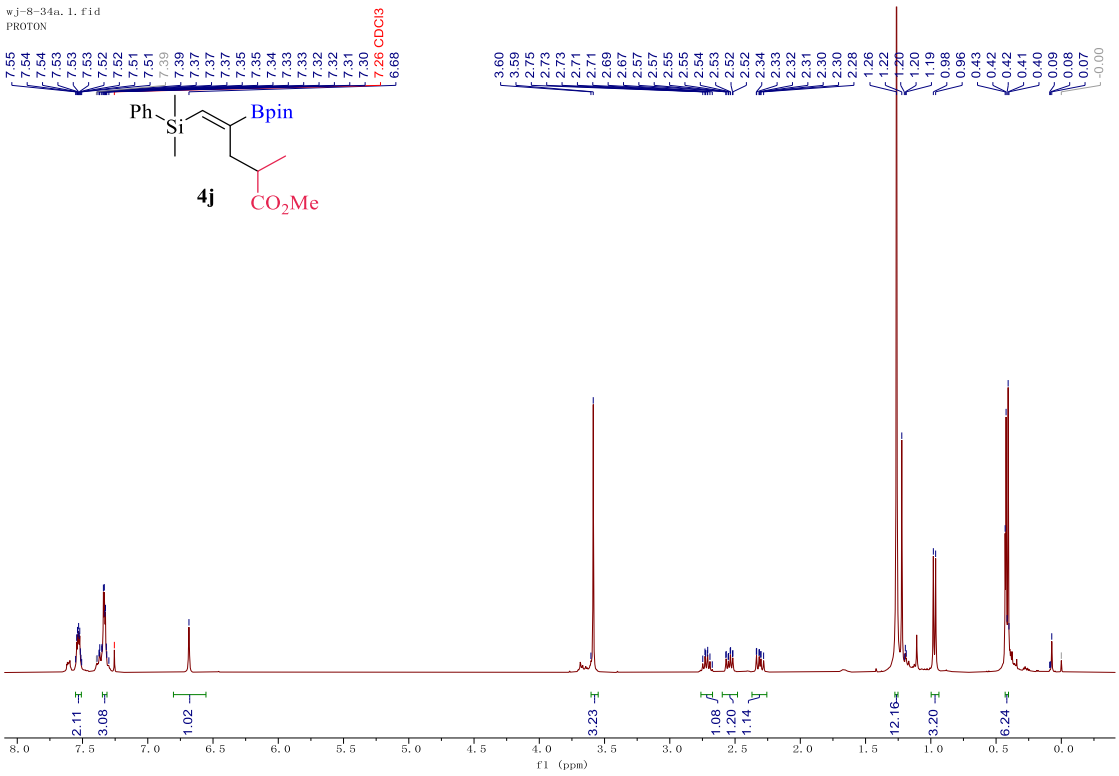
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4h**



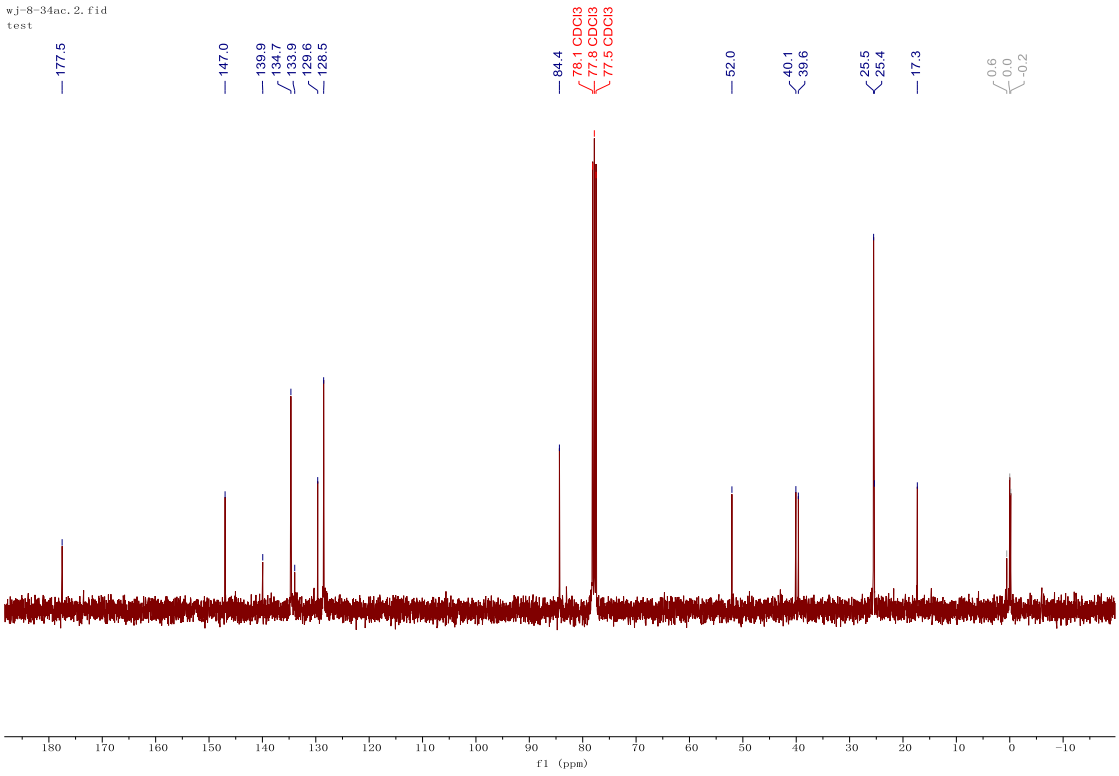
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4i**



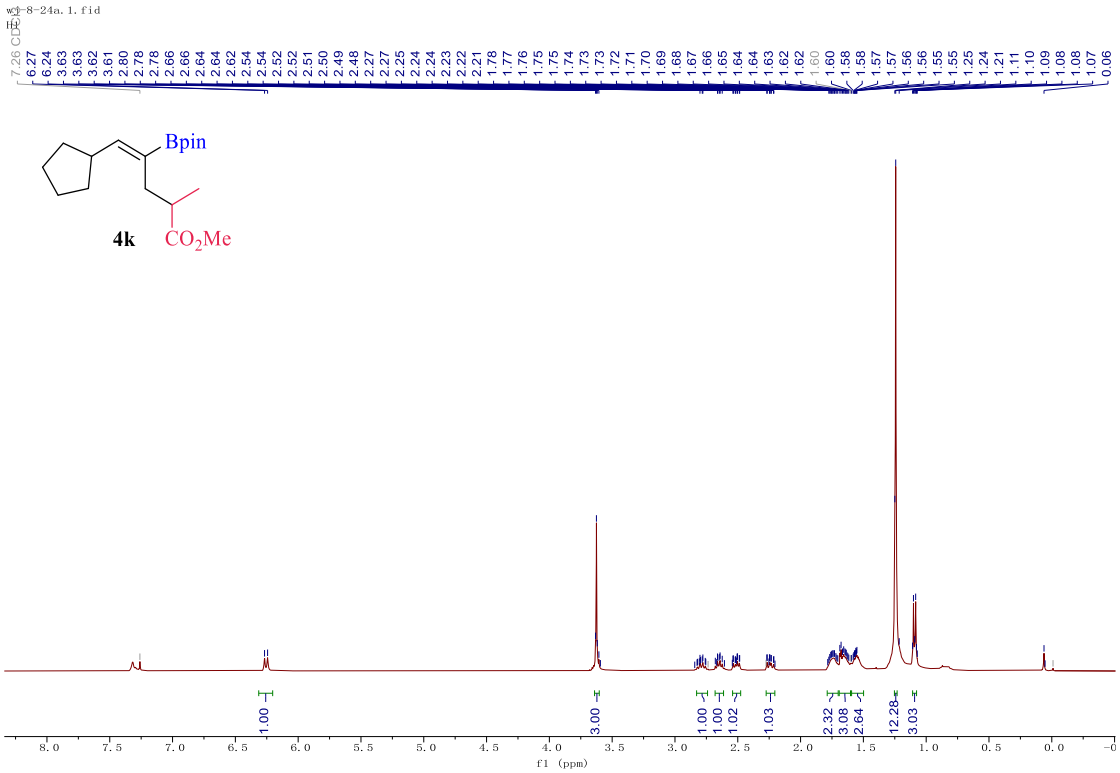
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4i**



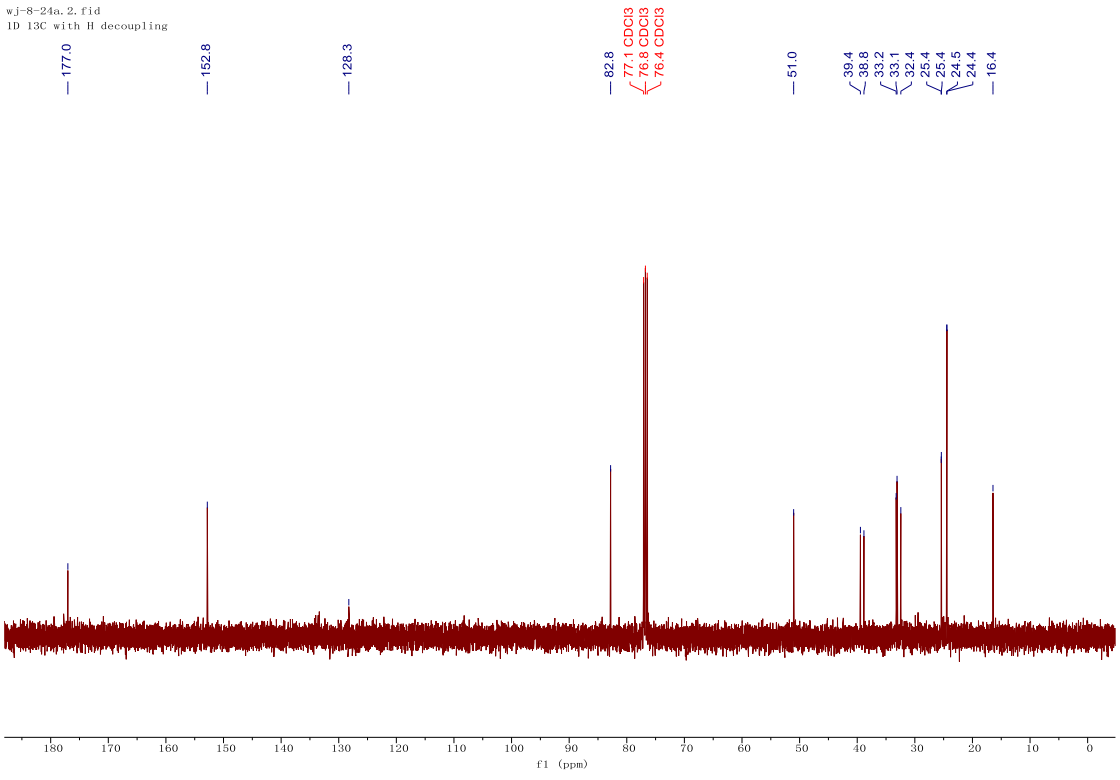
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4j**



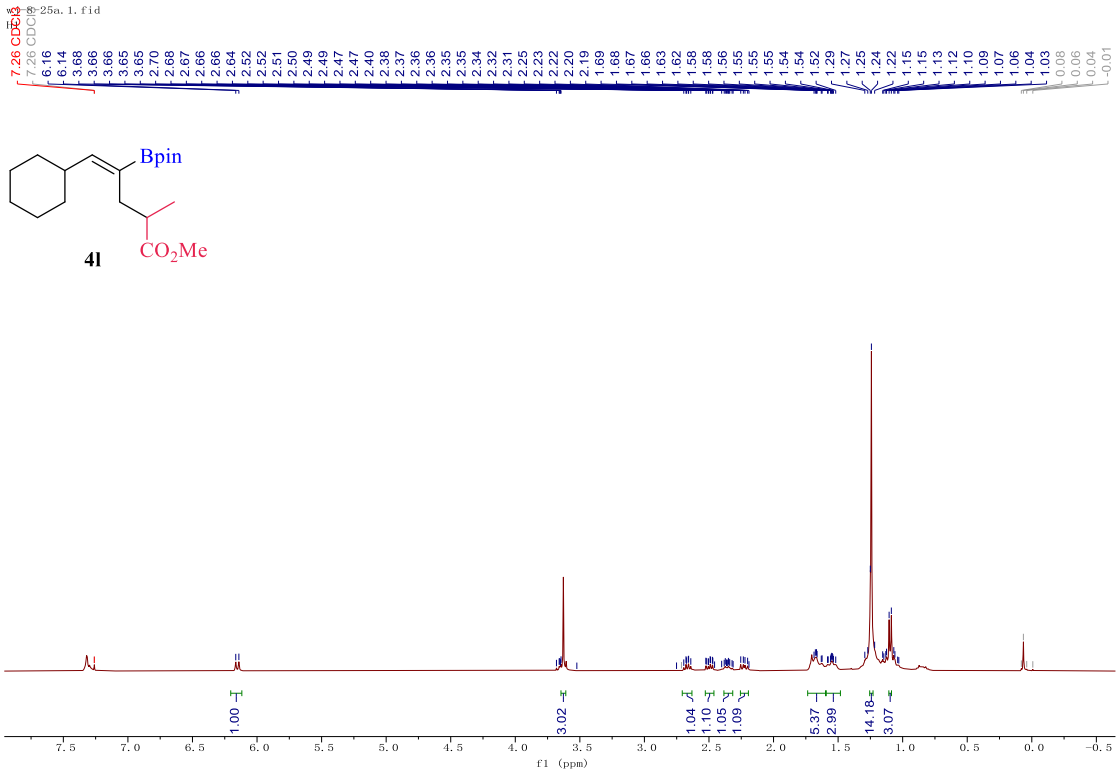
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4j**



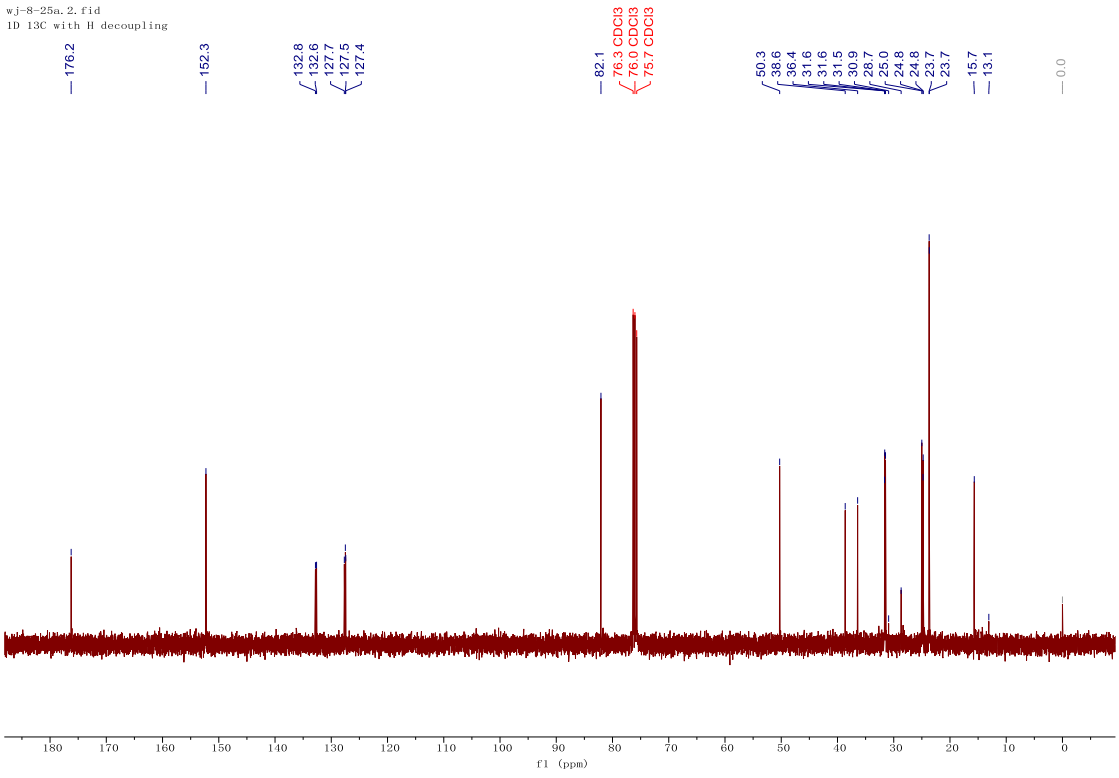
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4k**



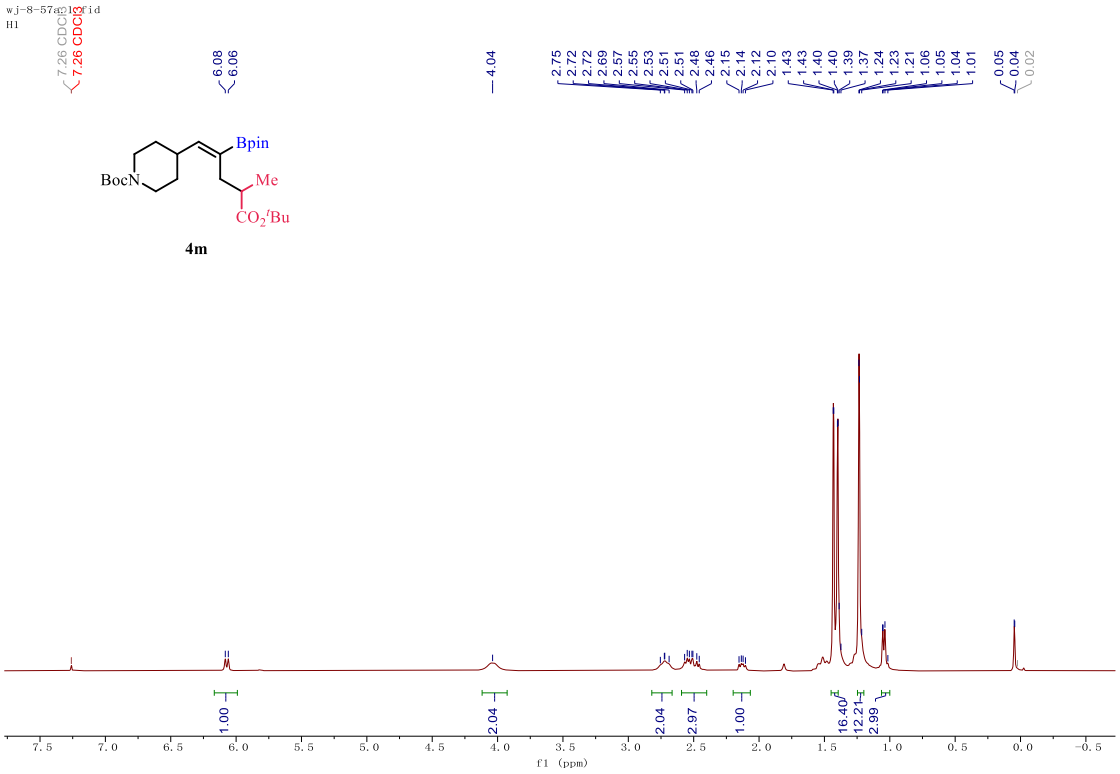
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4k**



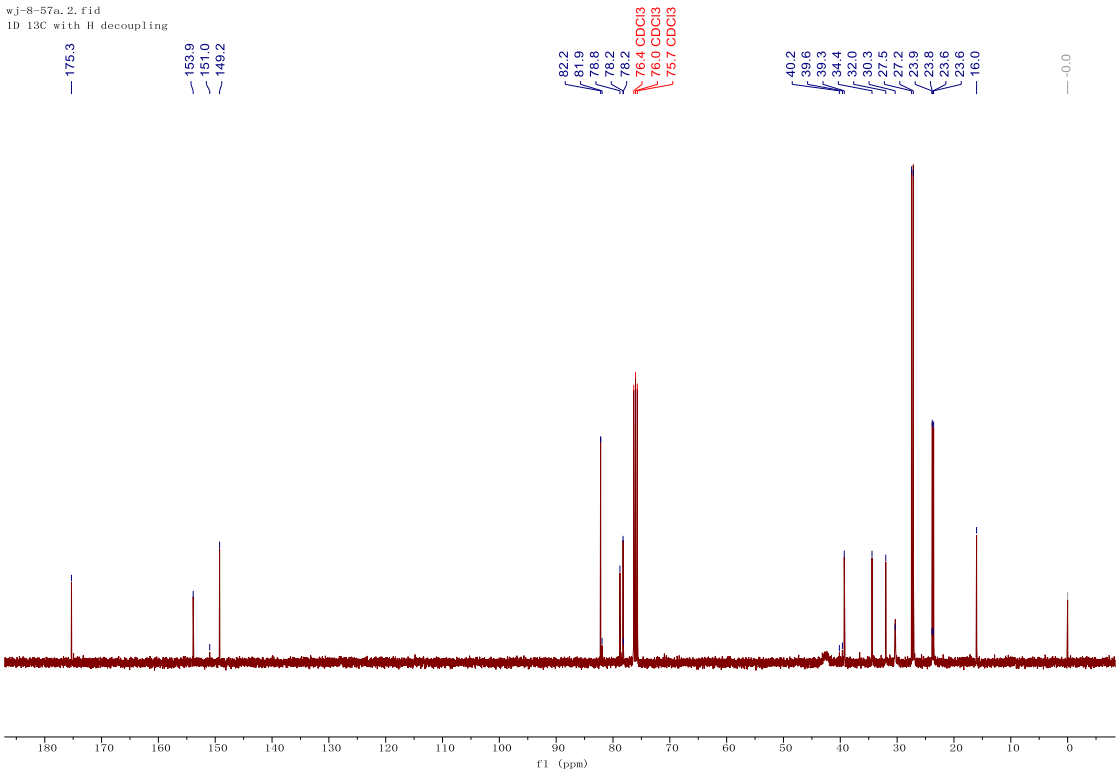
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4l**



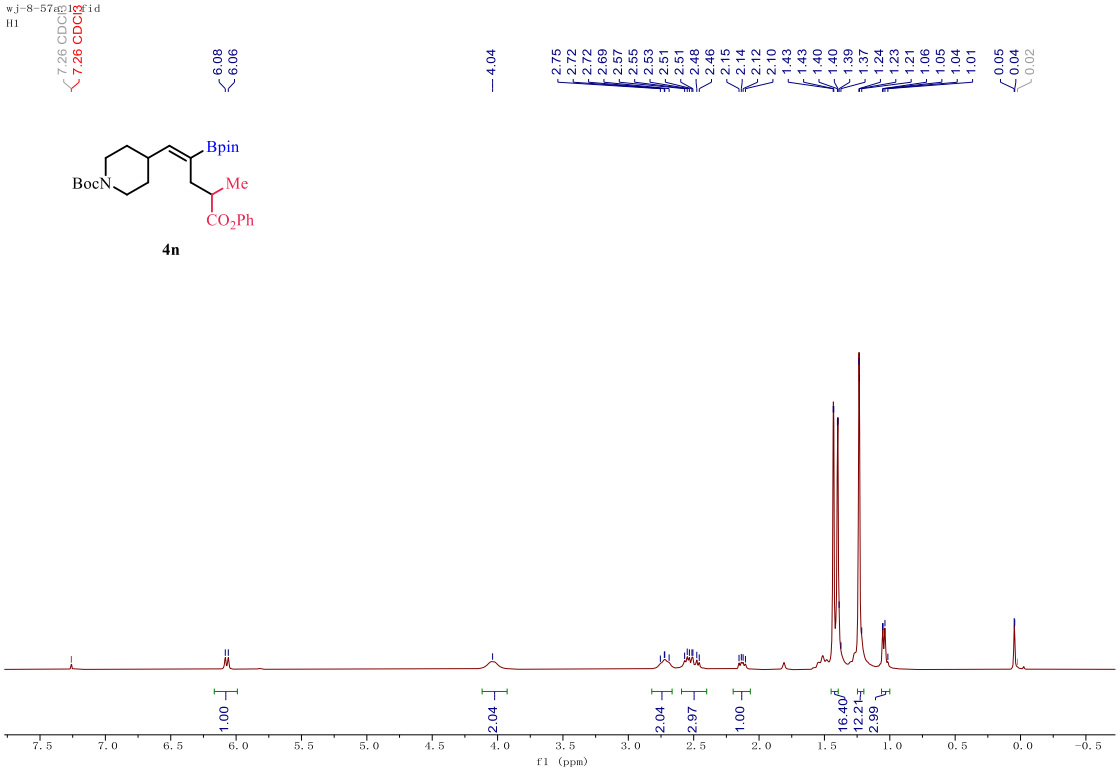
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4l**



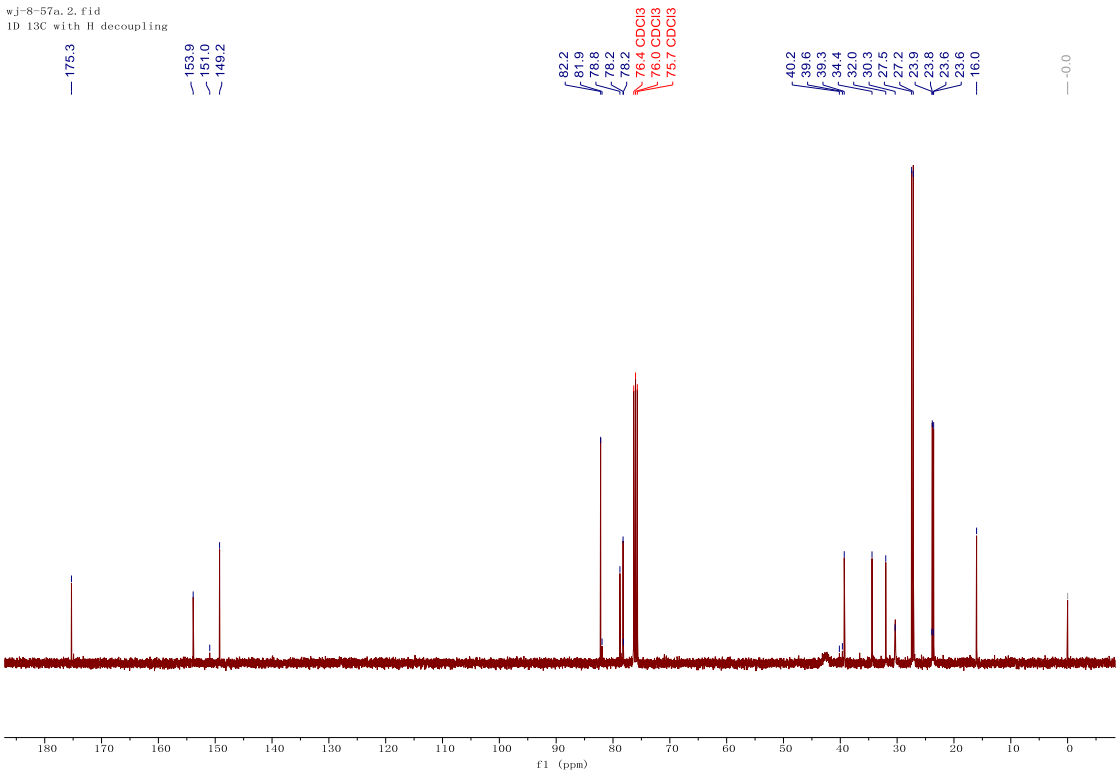
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4m**



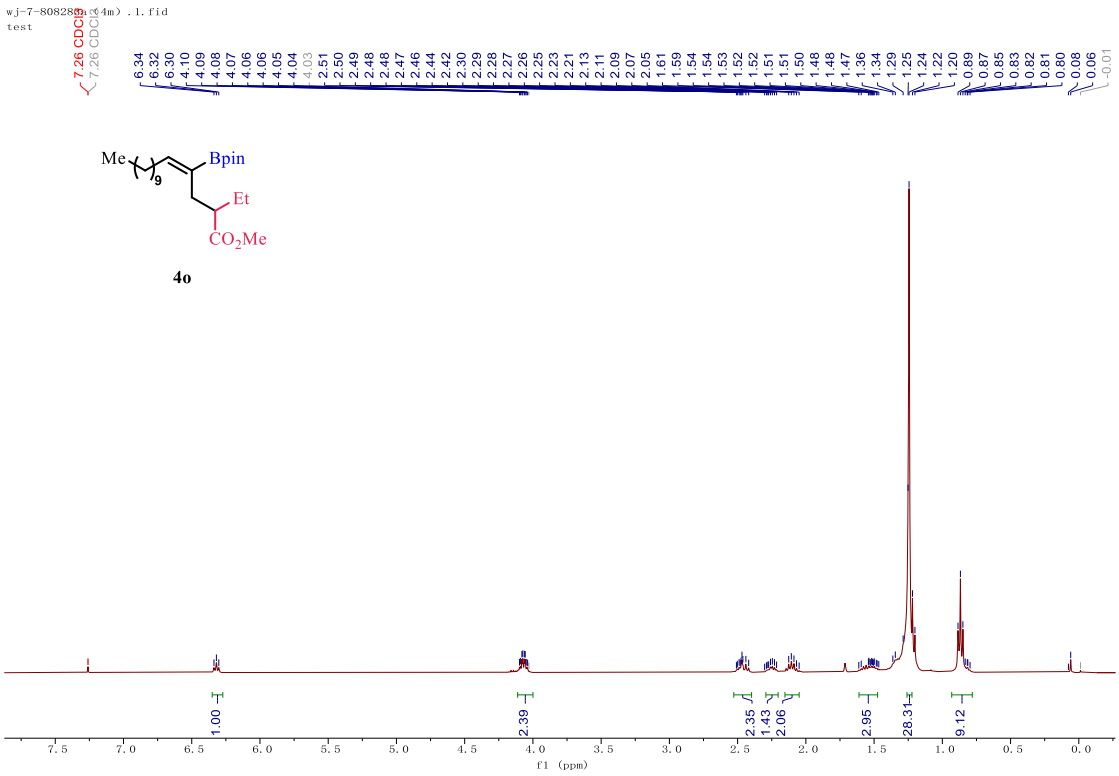
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4m**



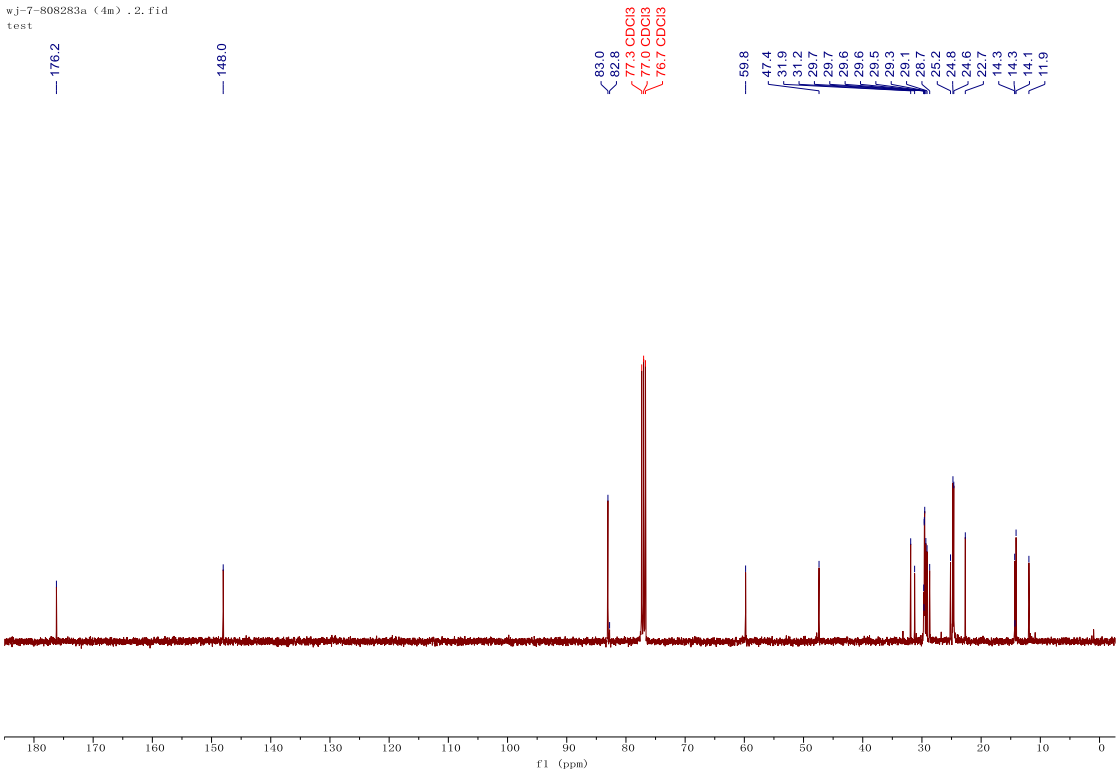
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4n**



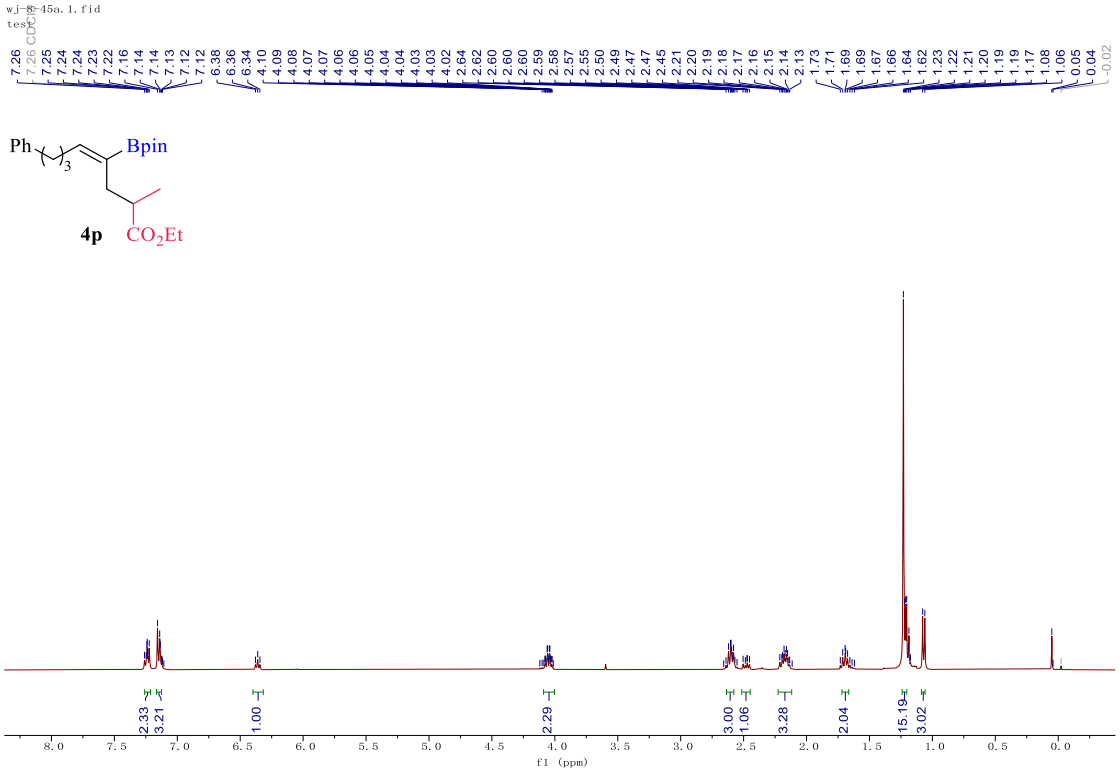
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4n**



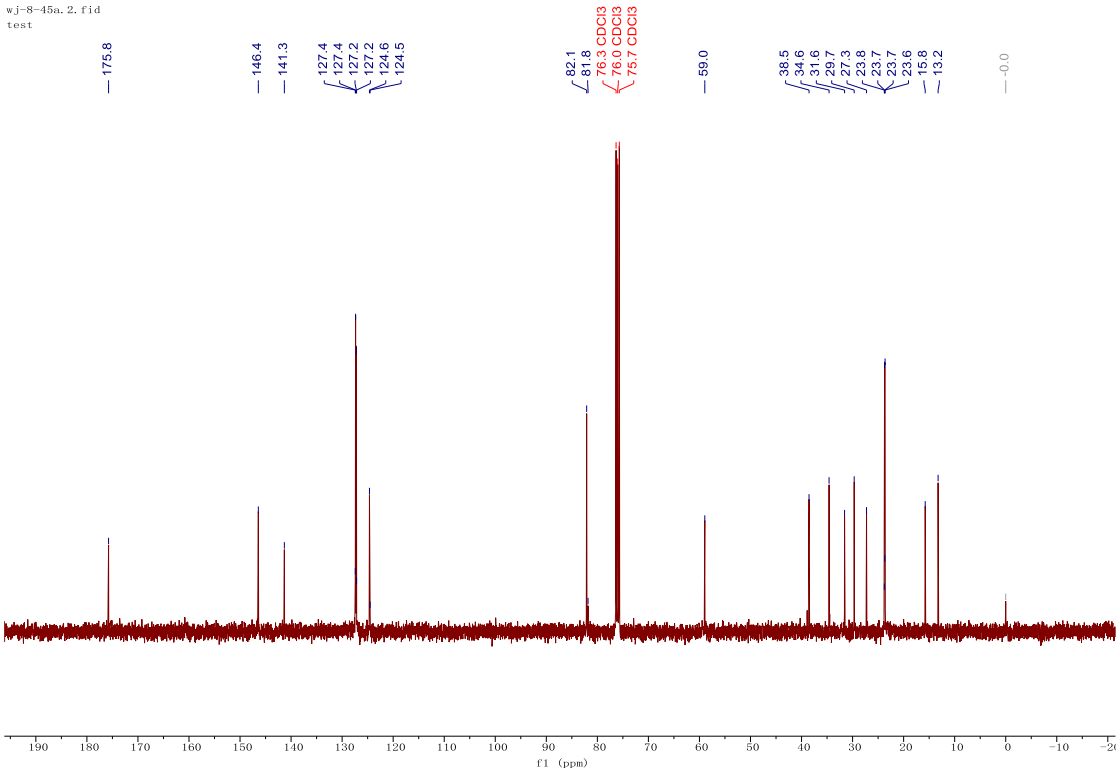
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4o**



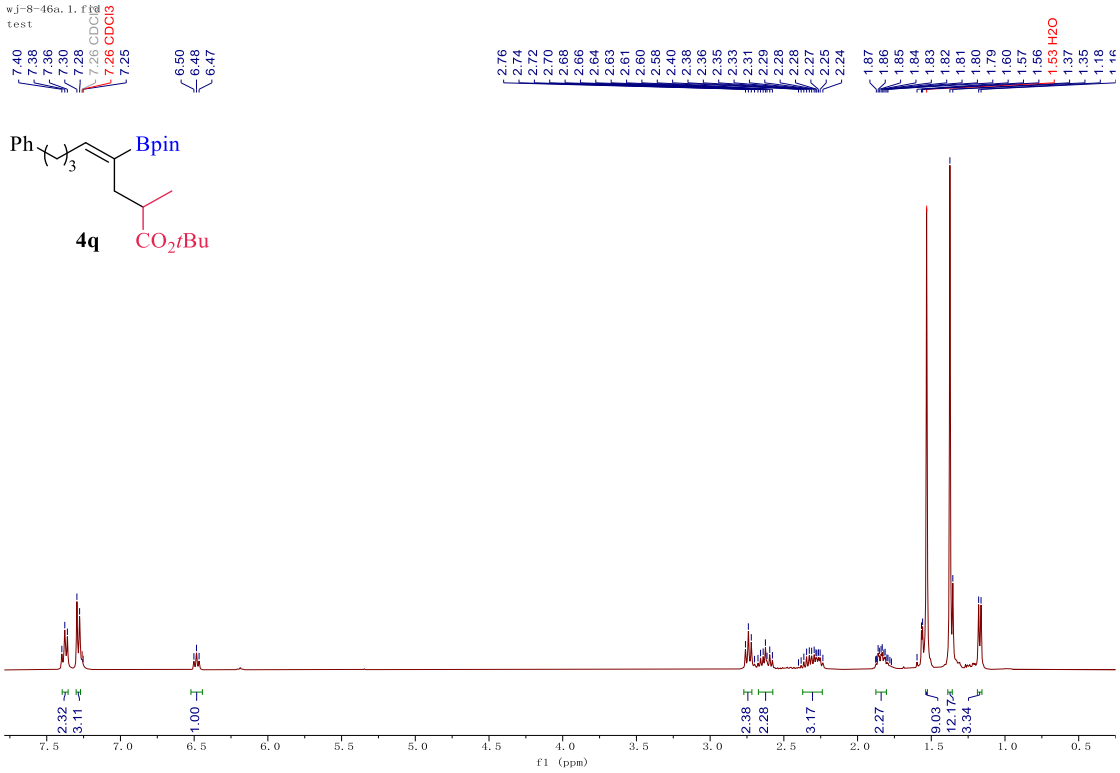
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4o**



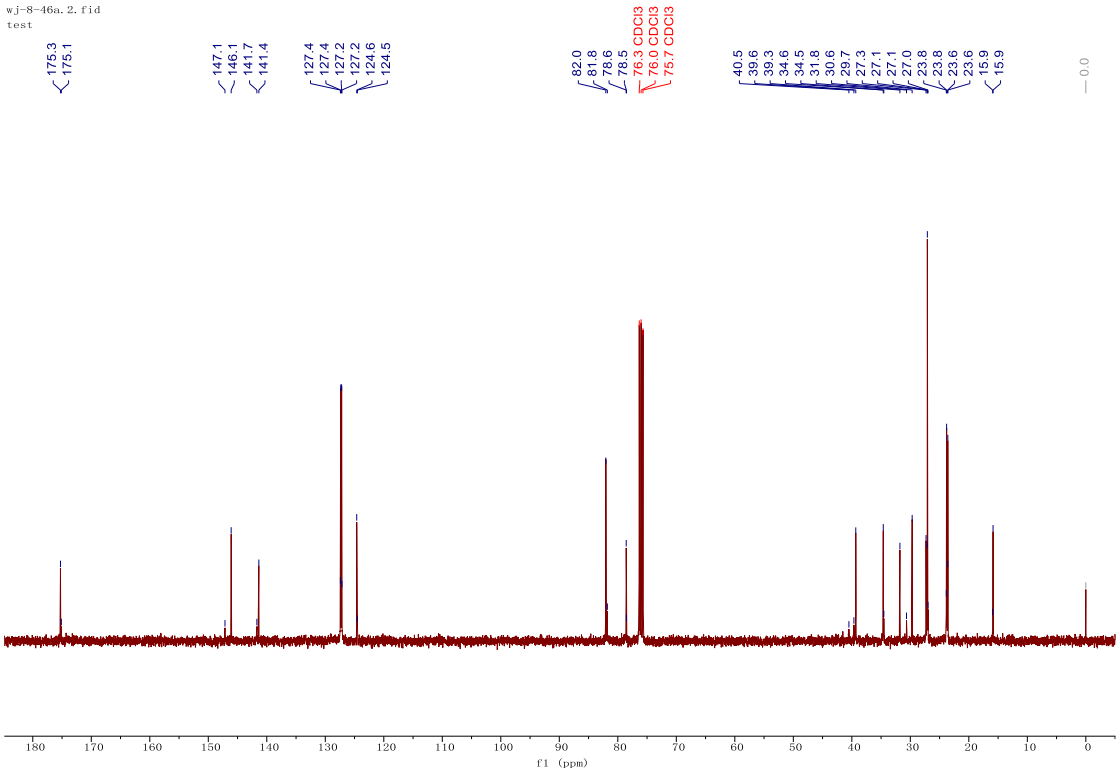
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4p**



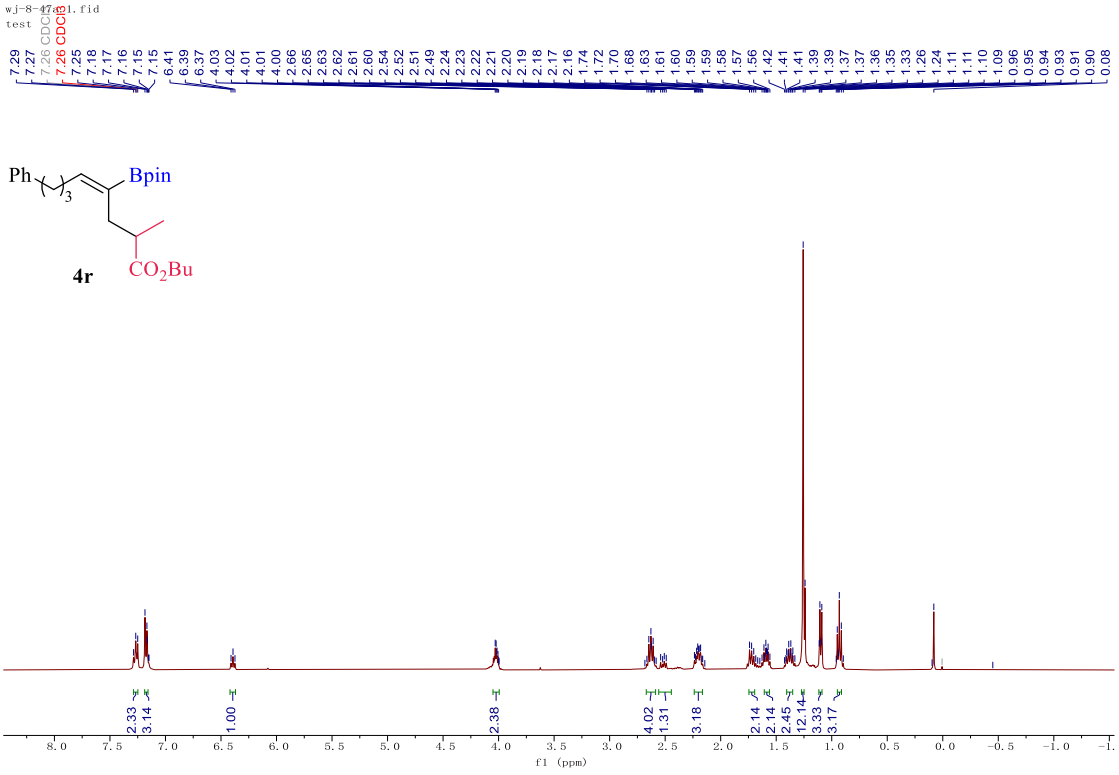
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4p**



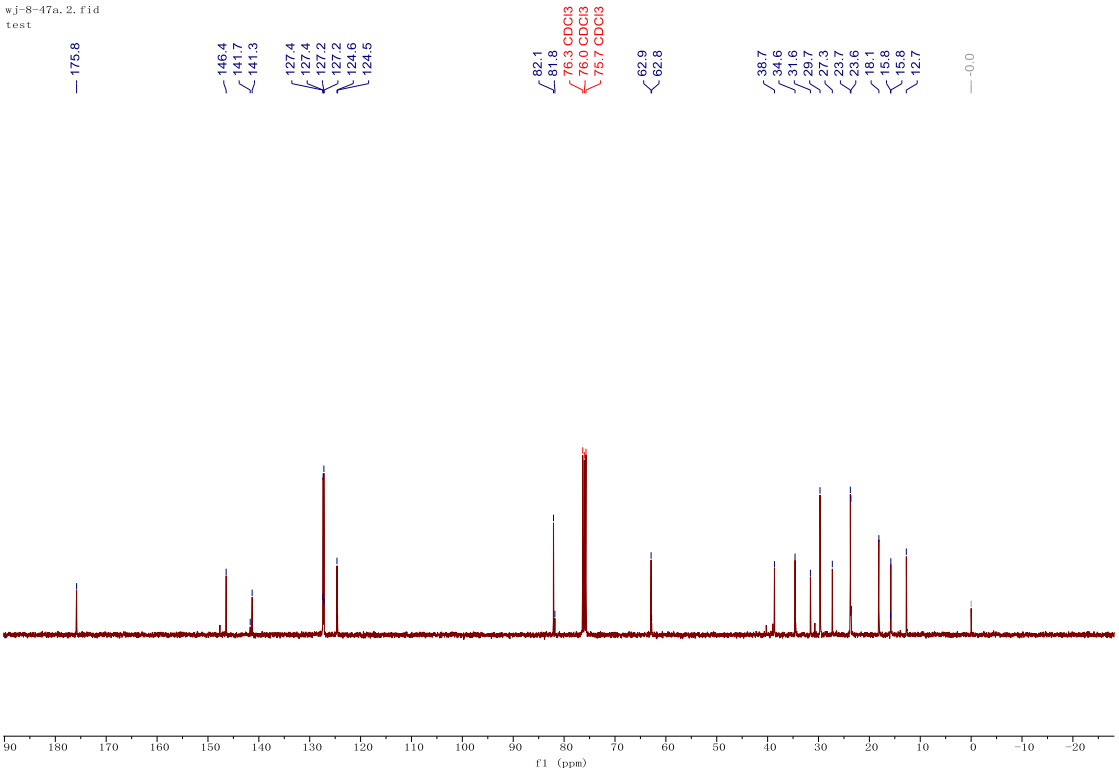
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4q**



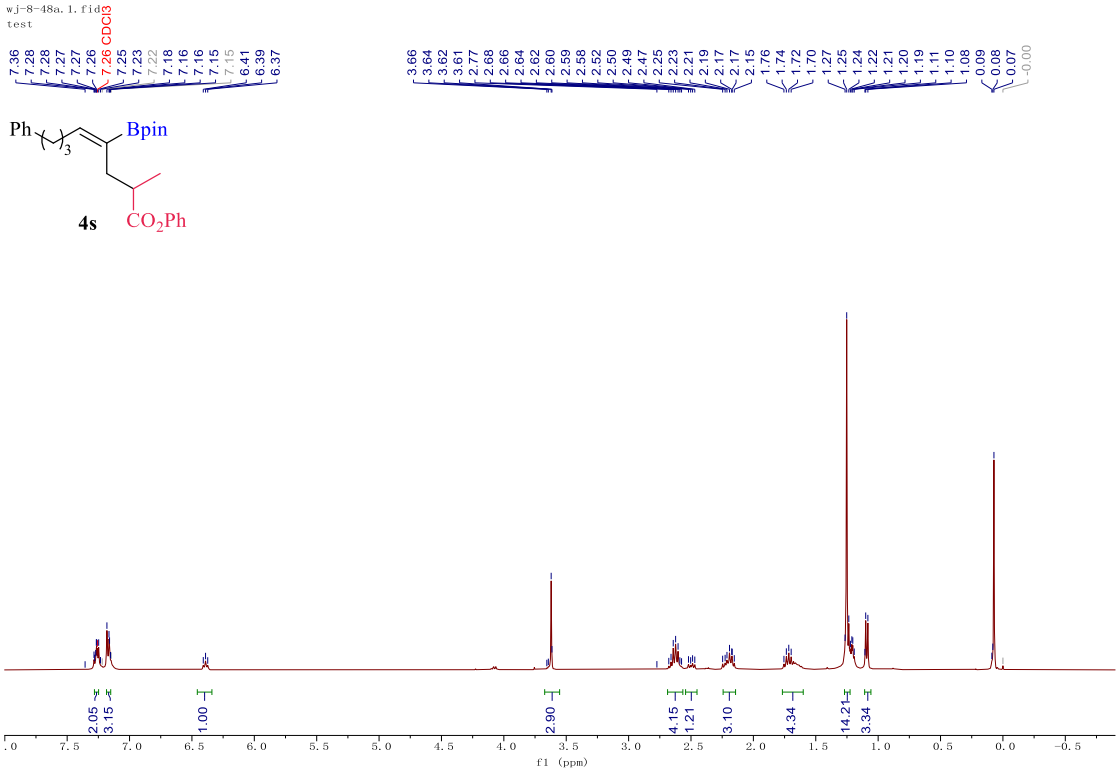
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4q**



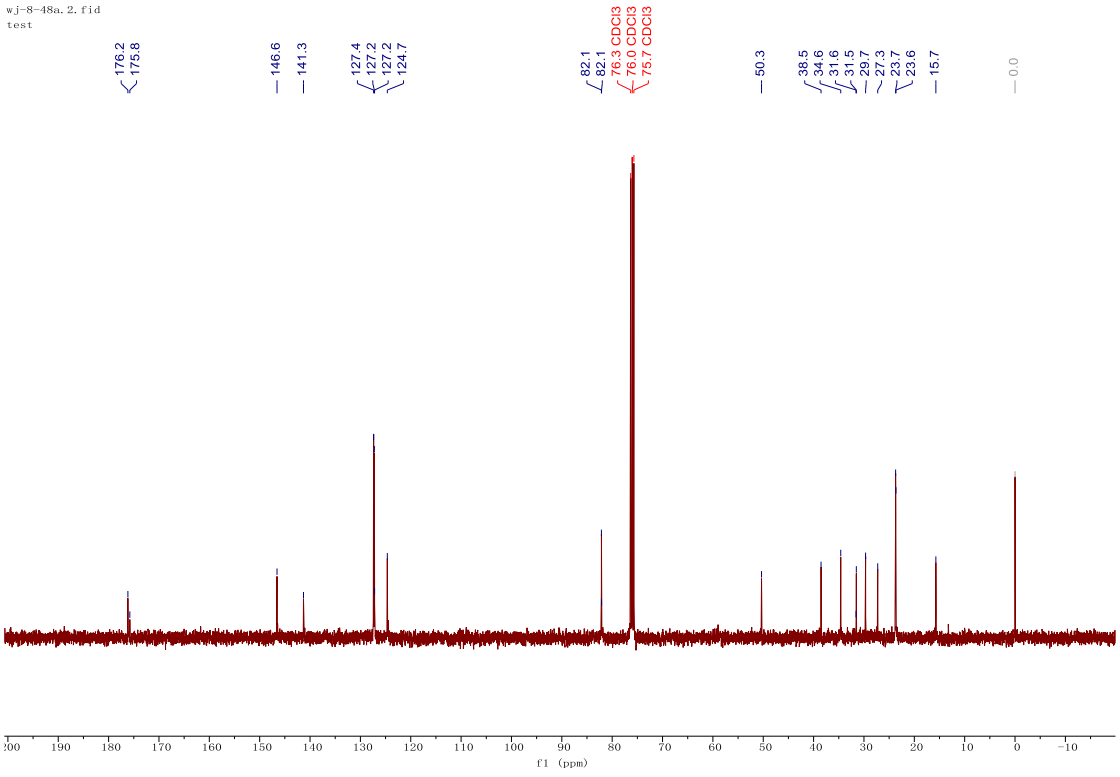
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4r**



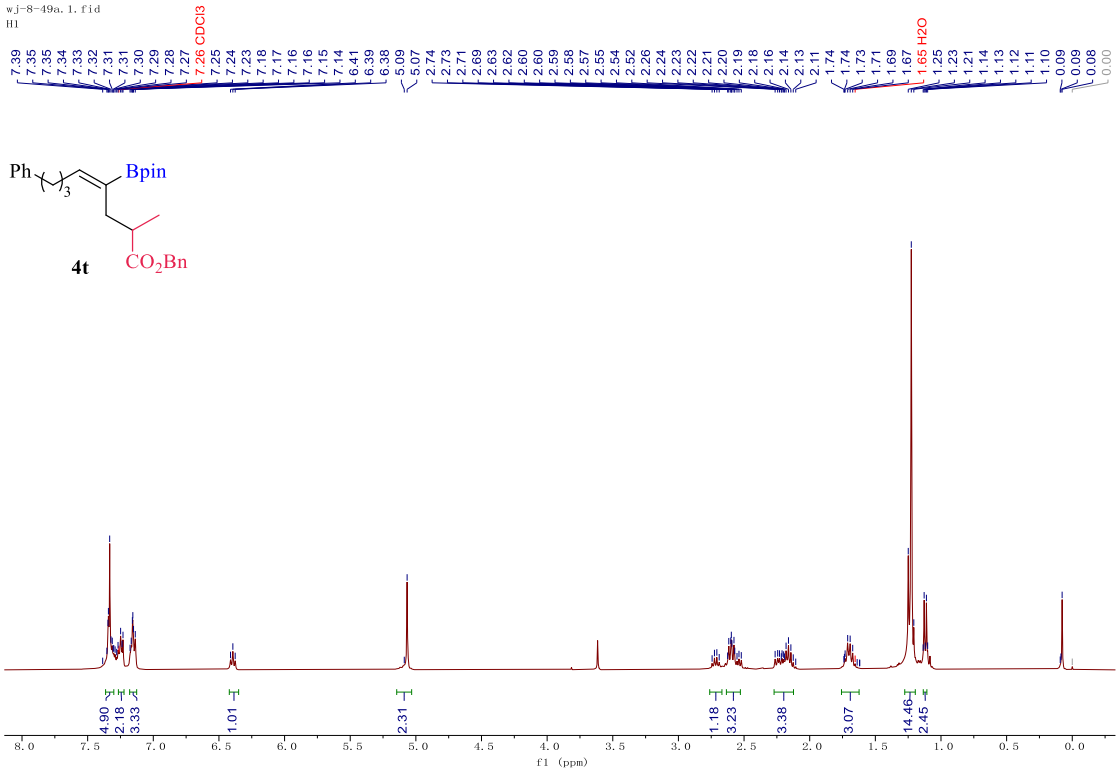
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4r**



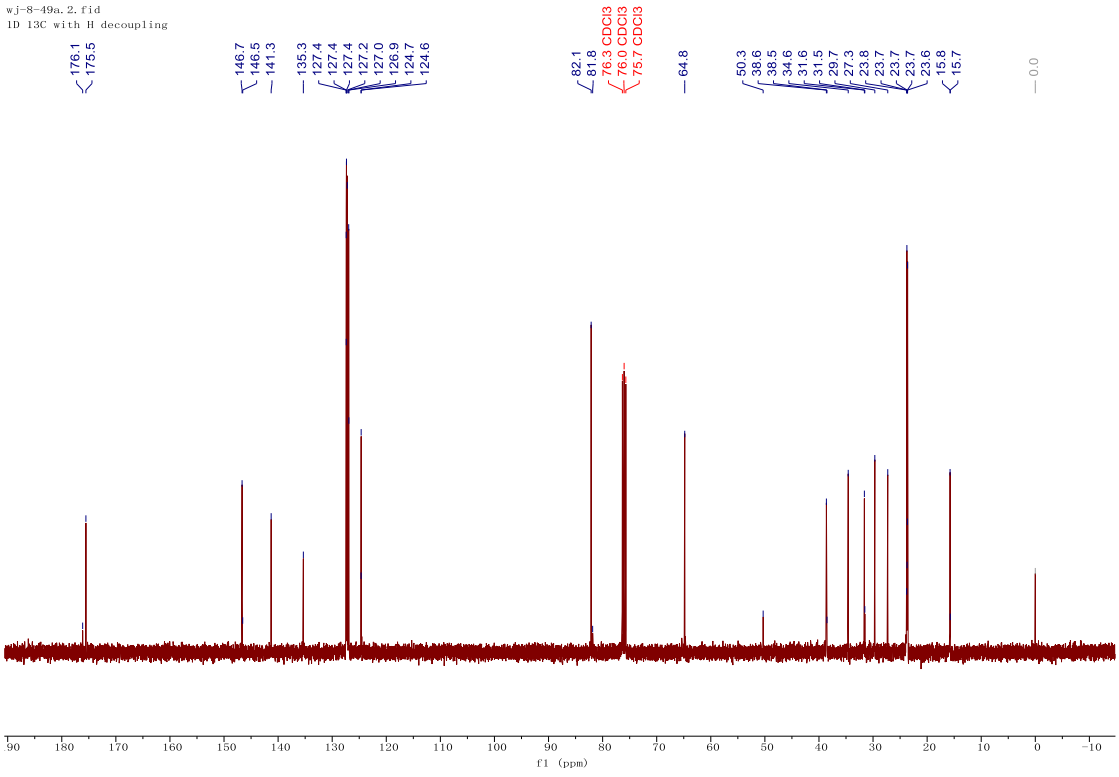
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4s**



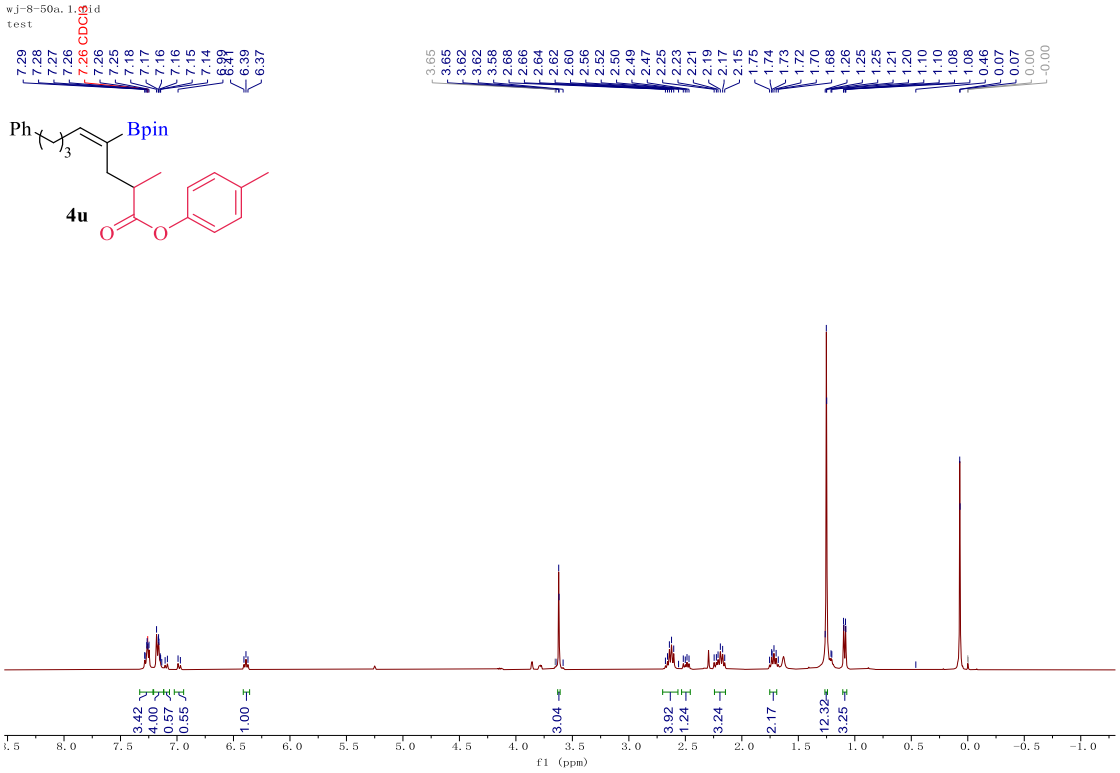
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4s**



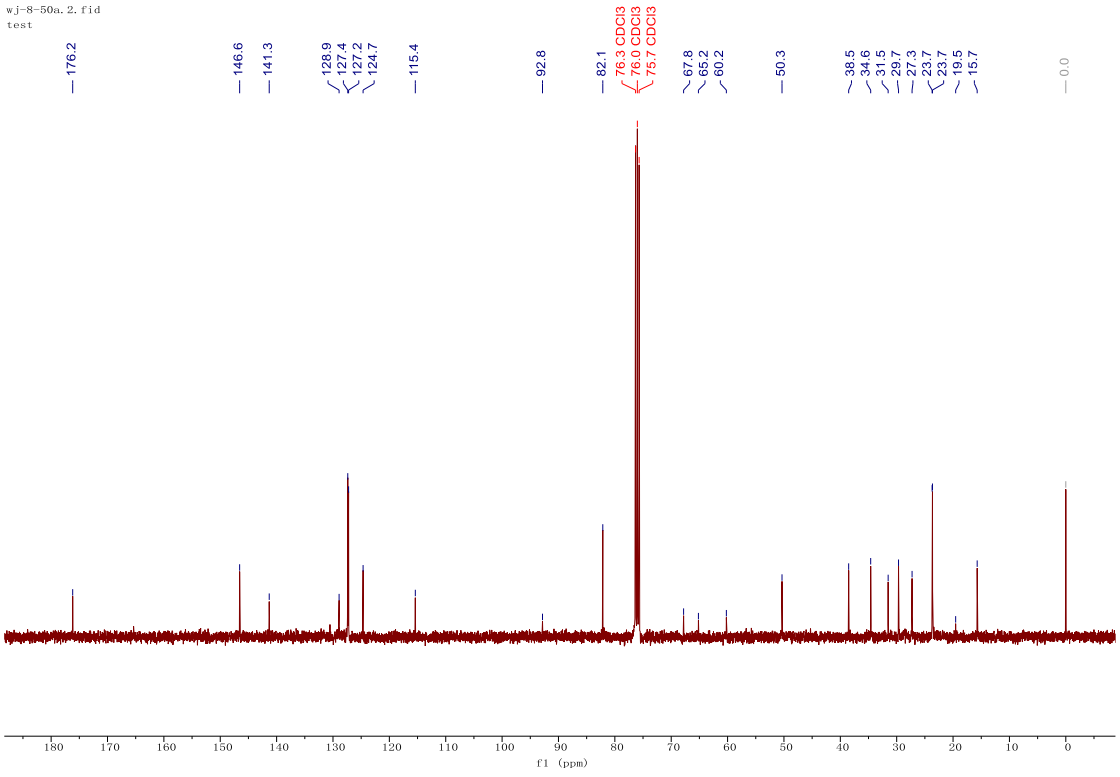
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4t**



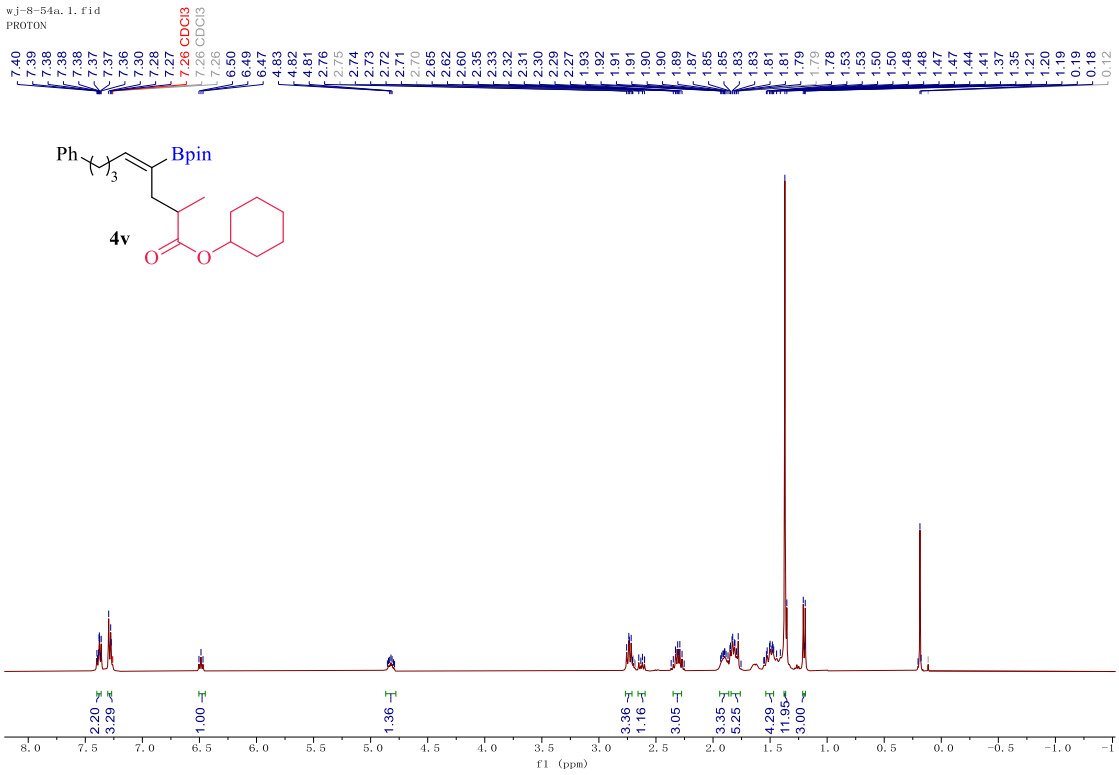
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4t**



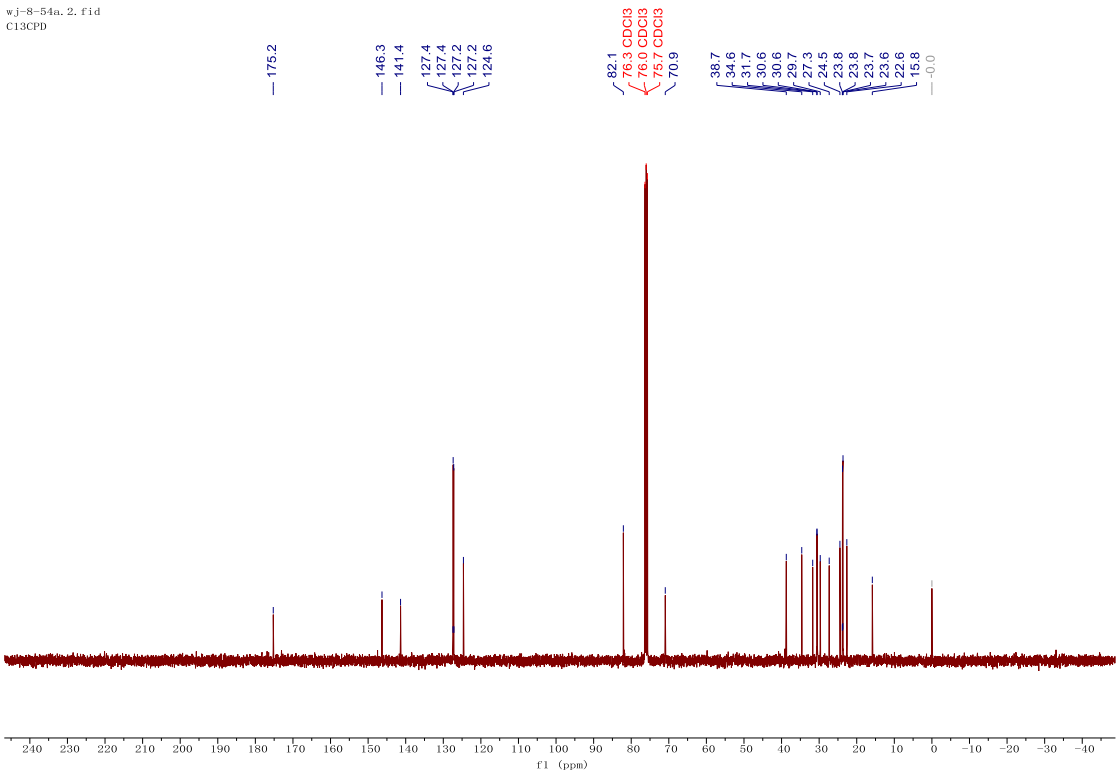
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4u**



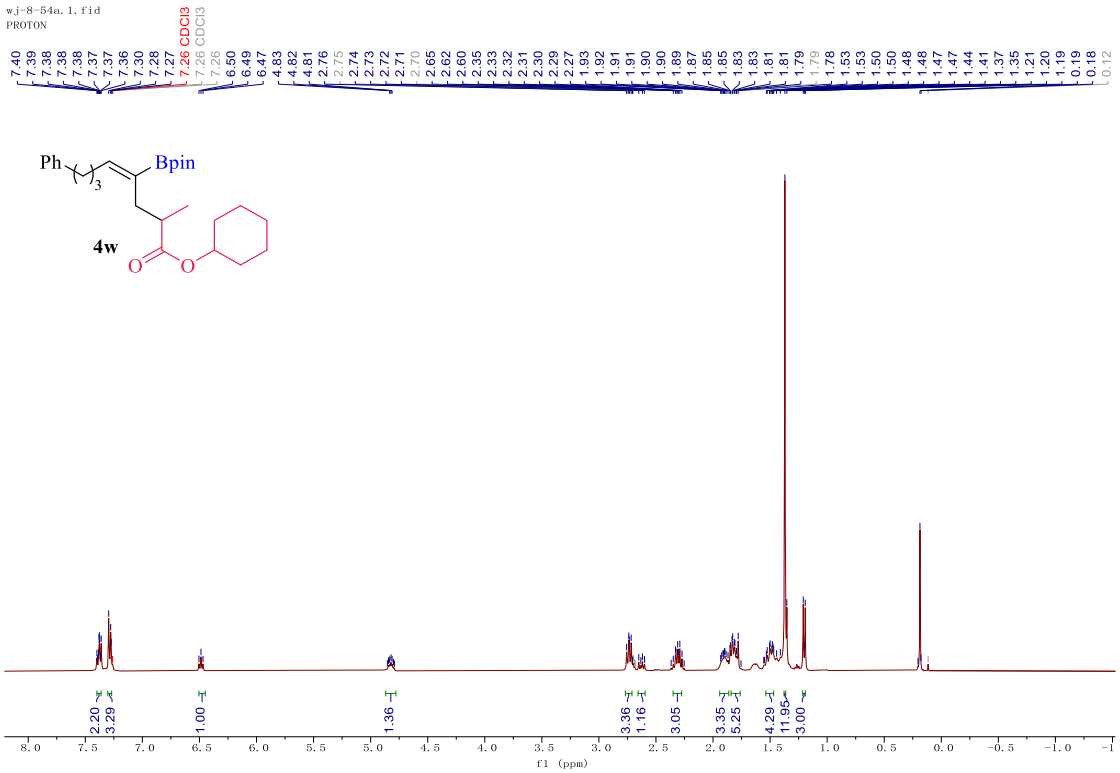
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4u**



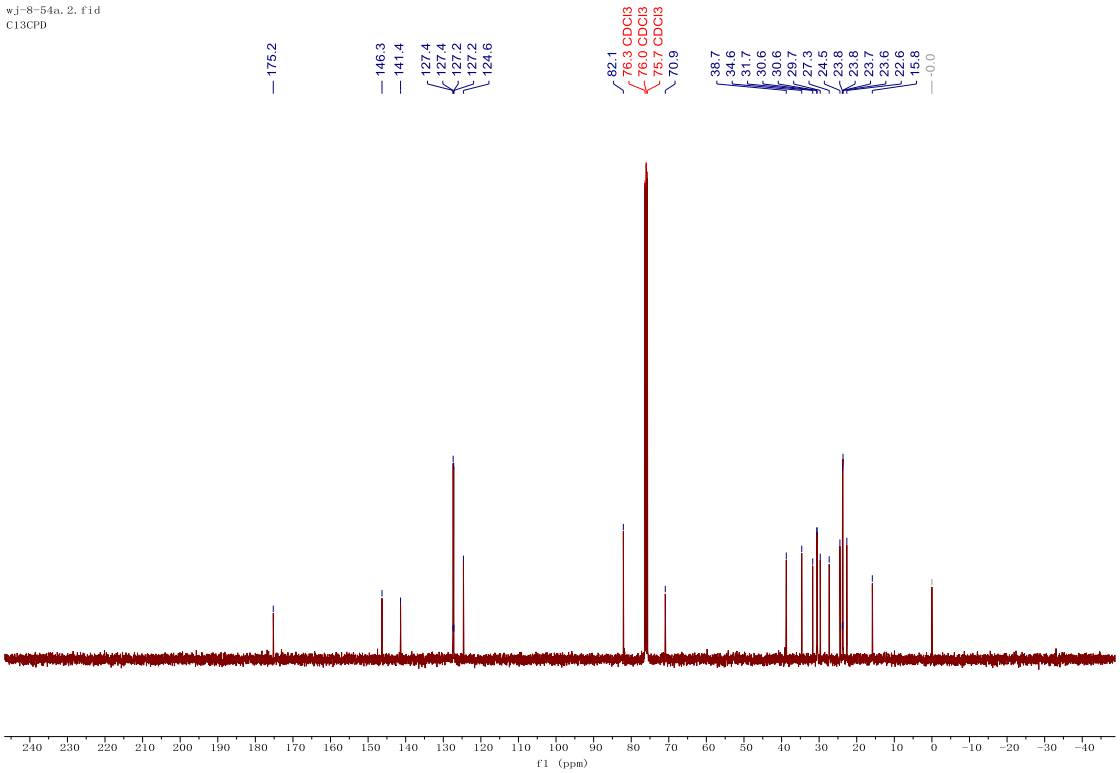
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4v**



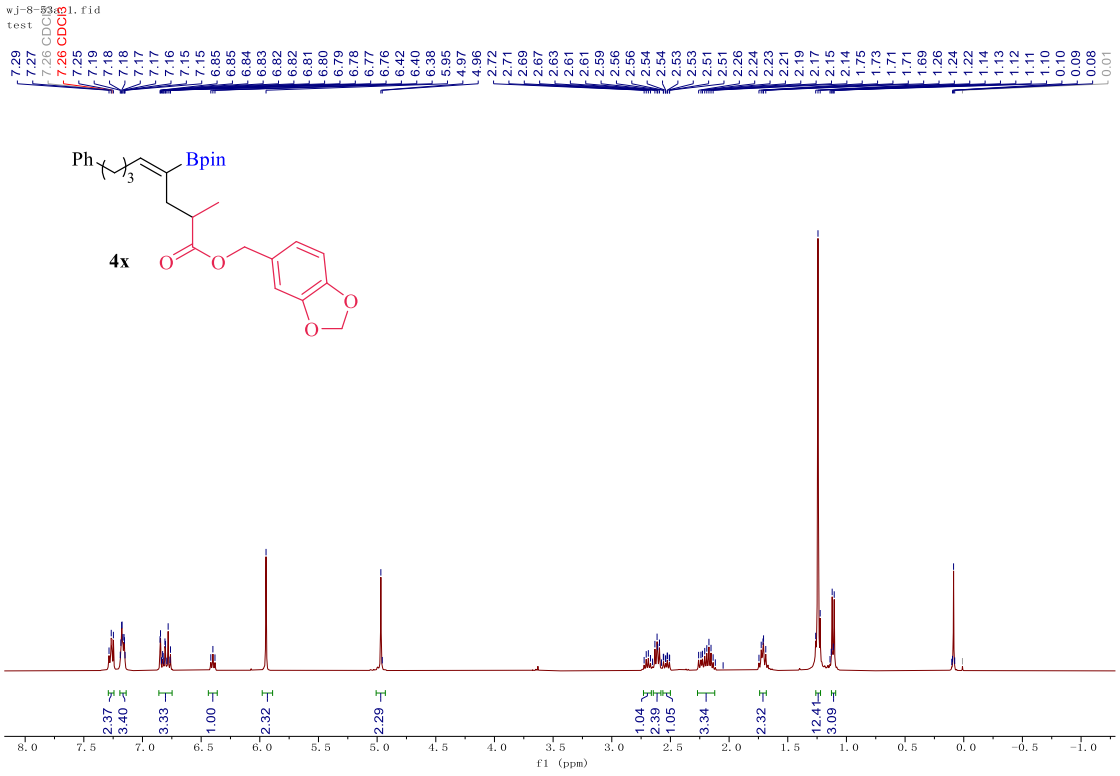
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4v**



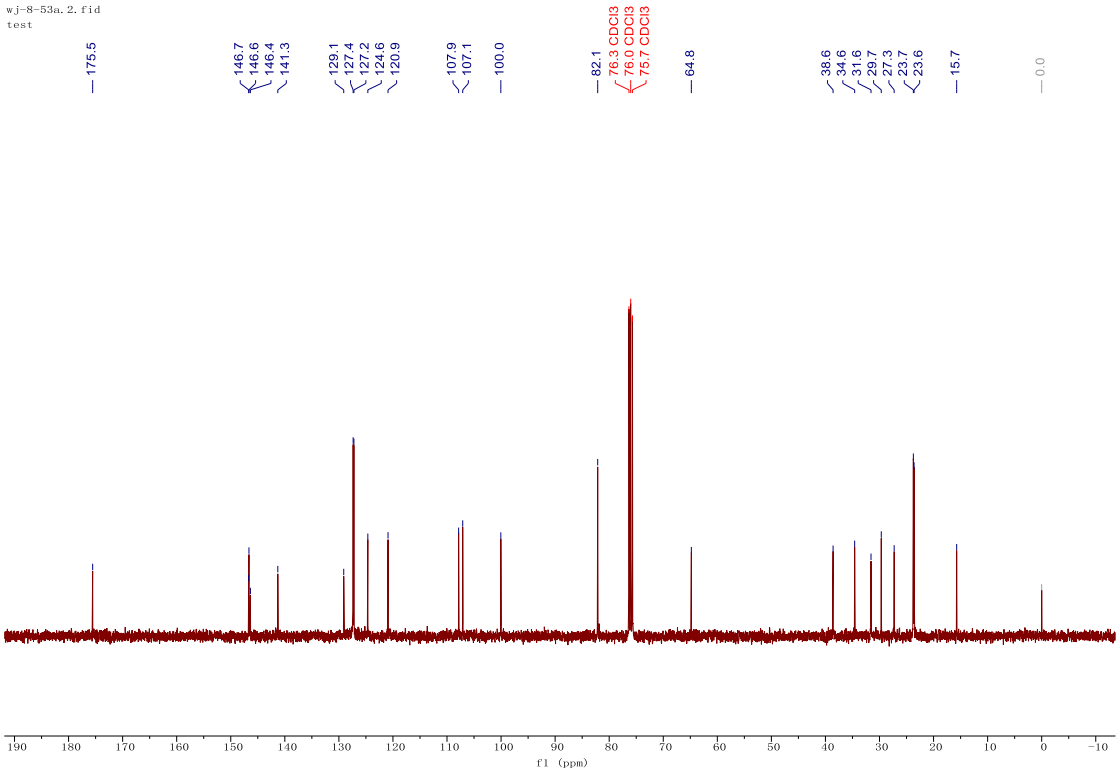
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4w**



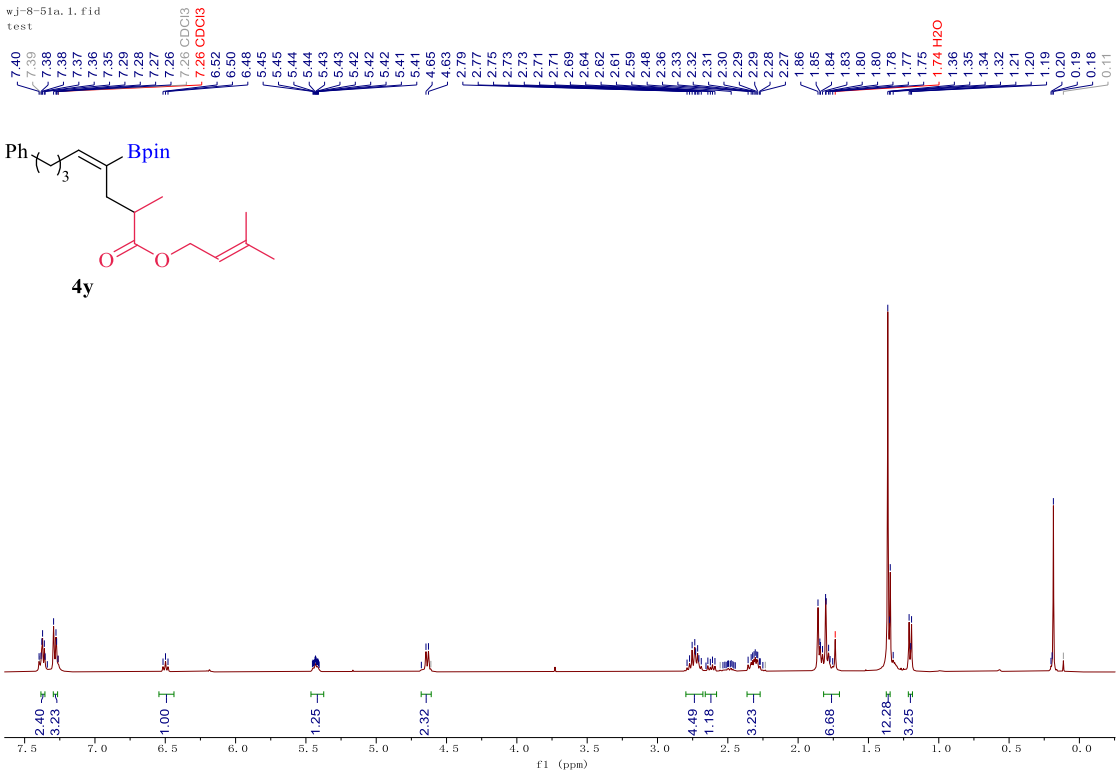
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4w**



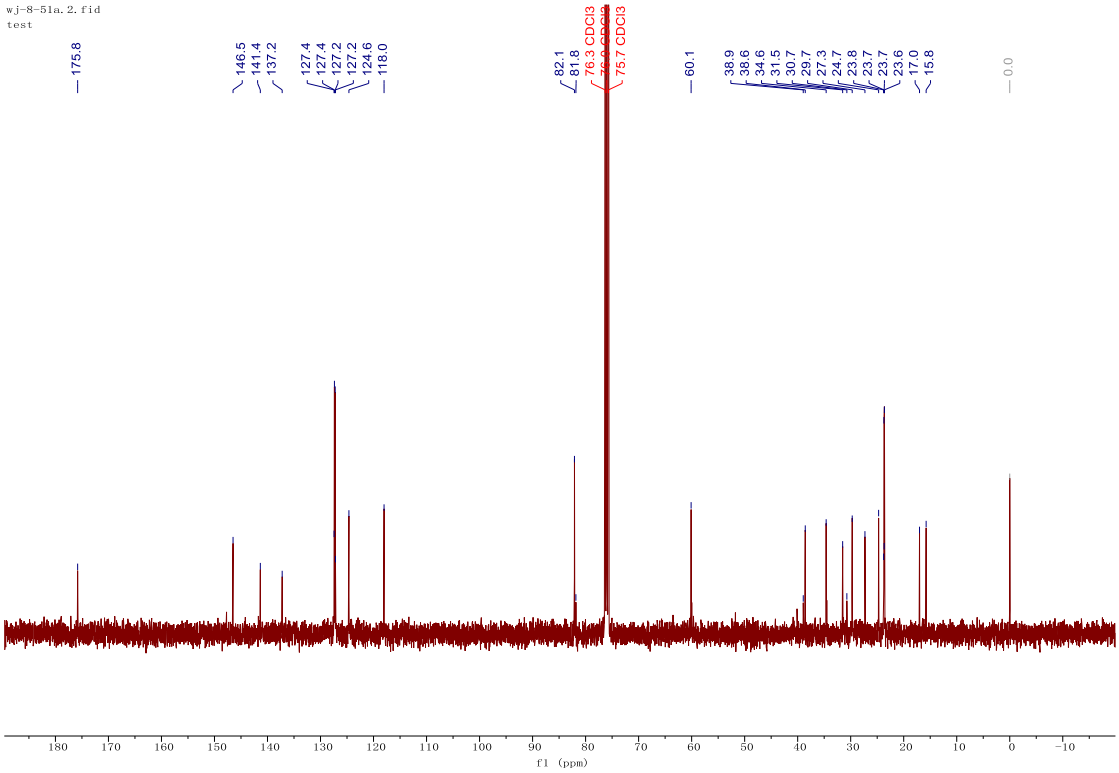
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4**



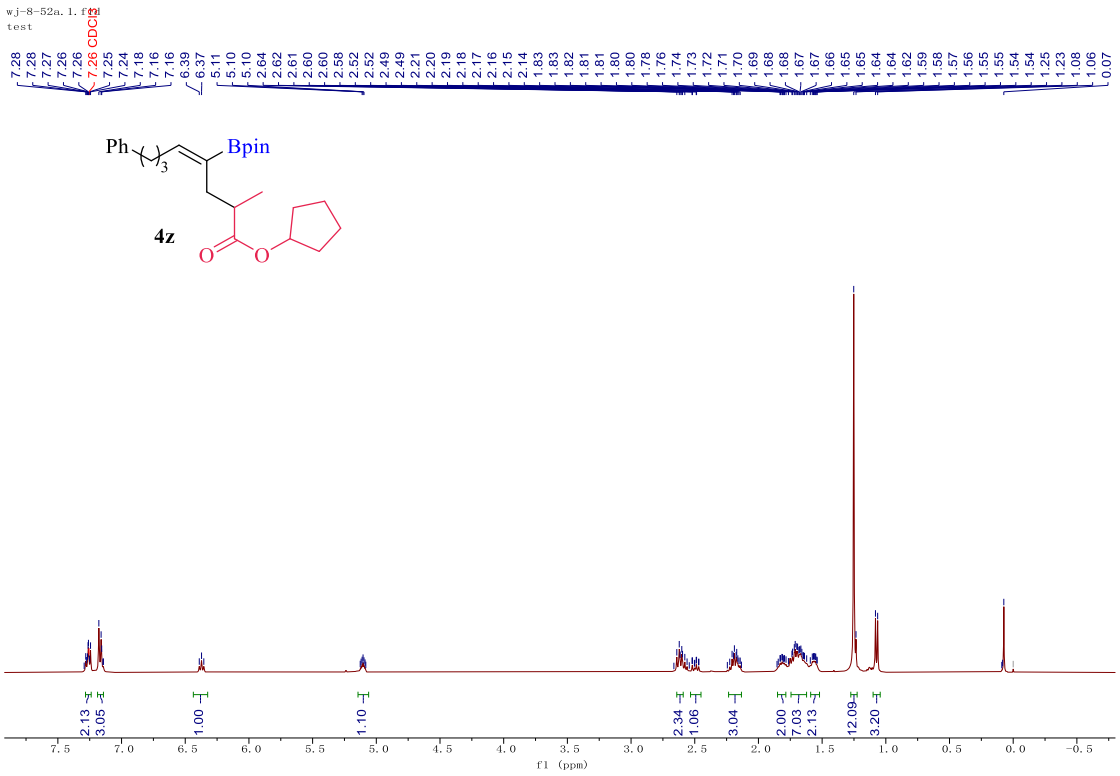
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4x**



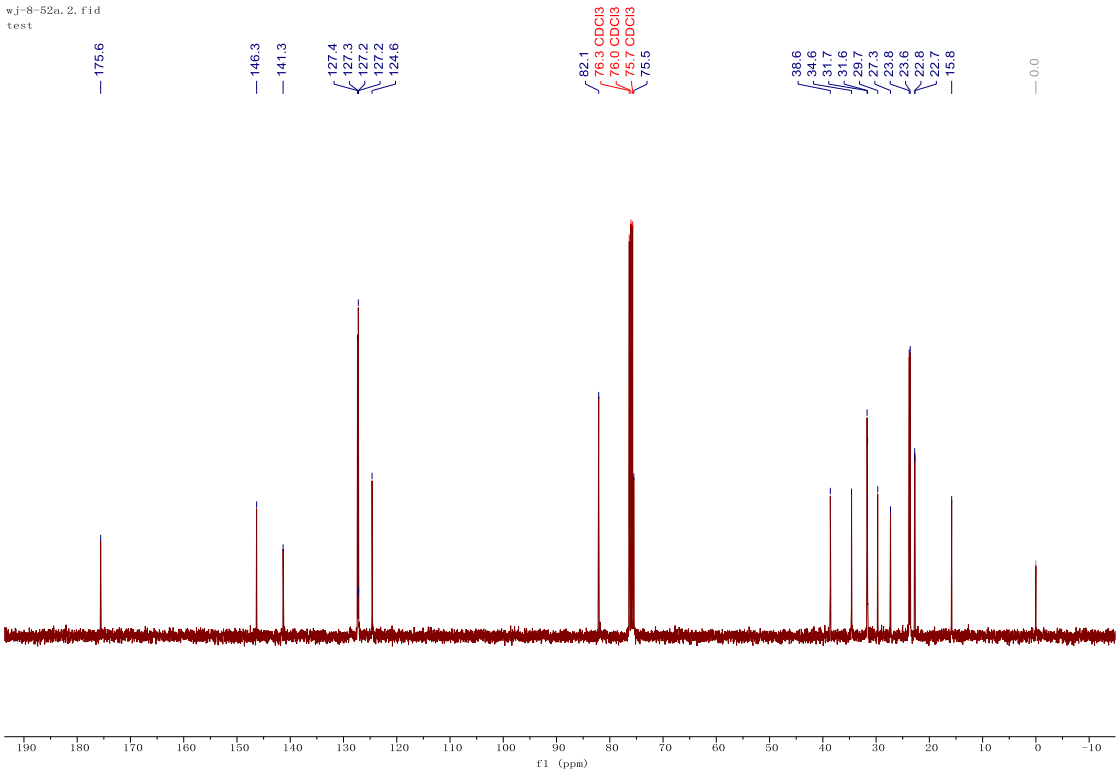
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4y**



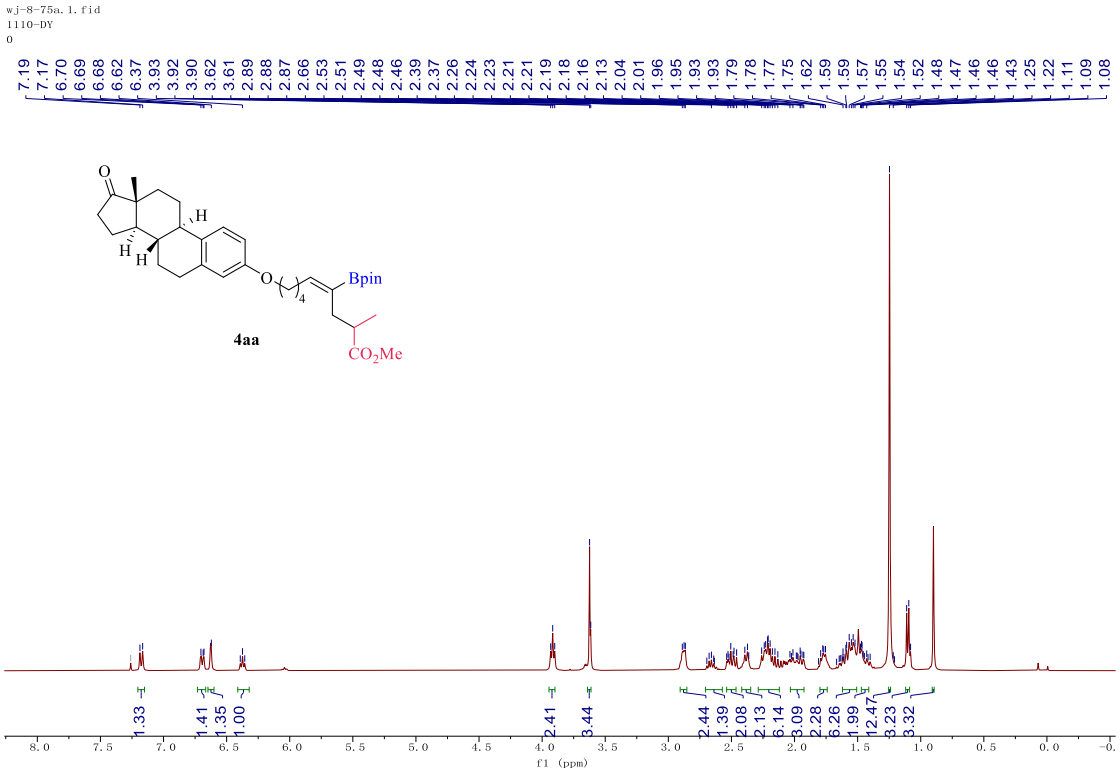
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4y**



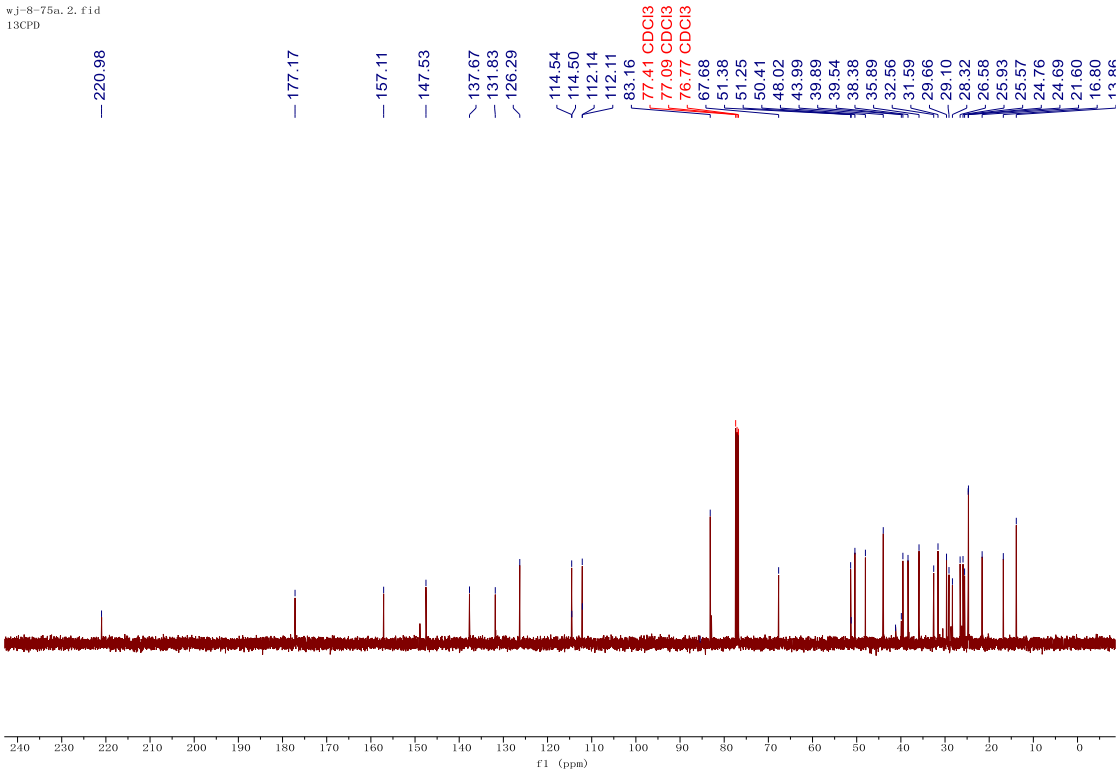
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4z**



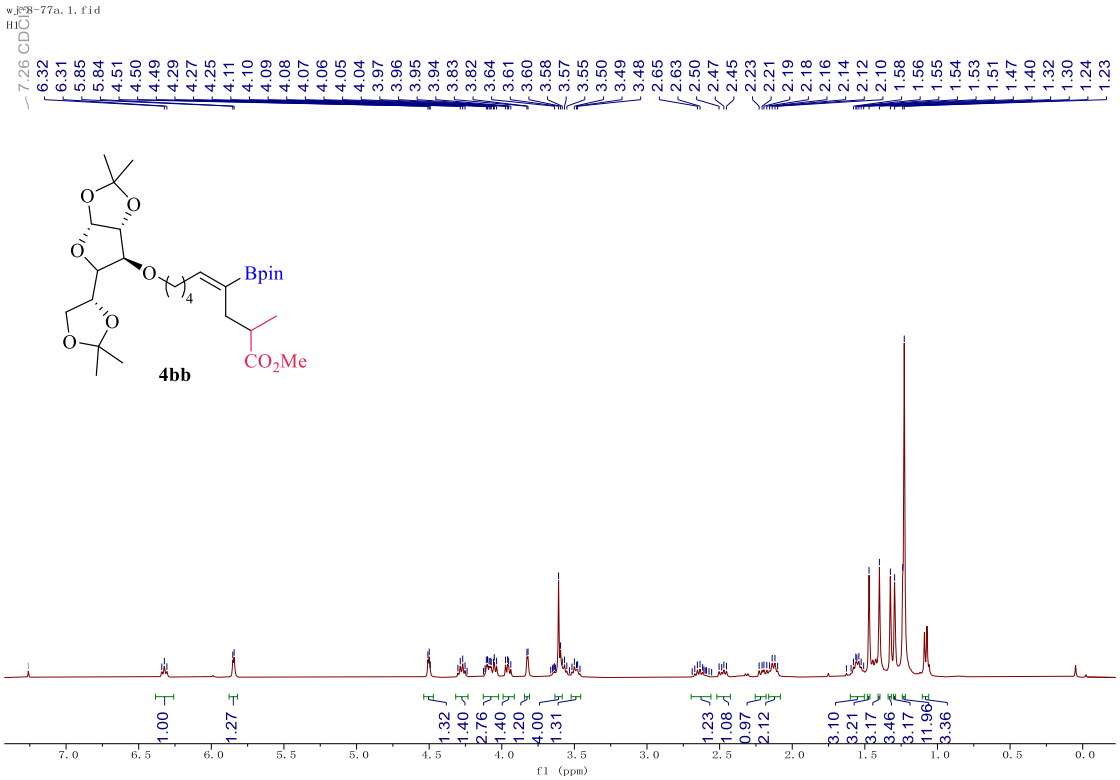
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **4z**



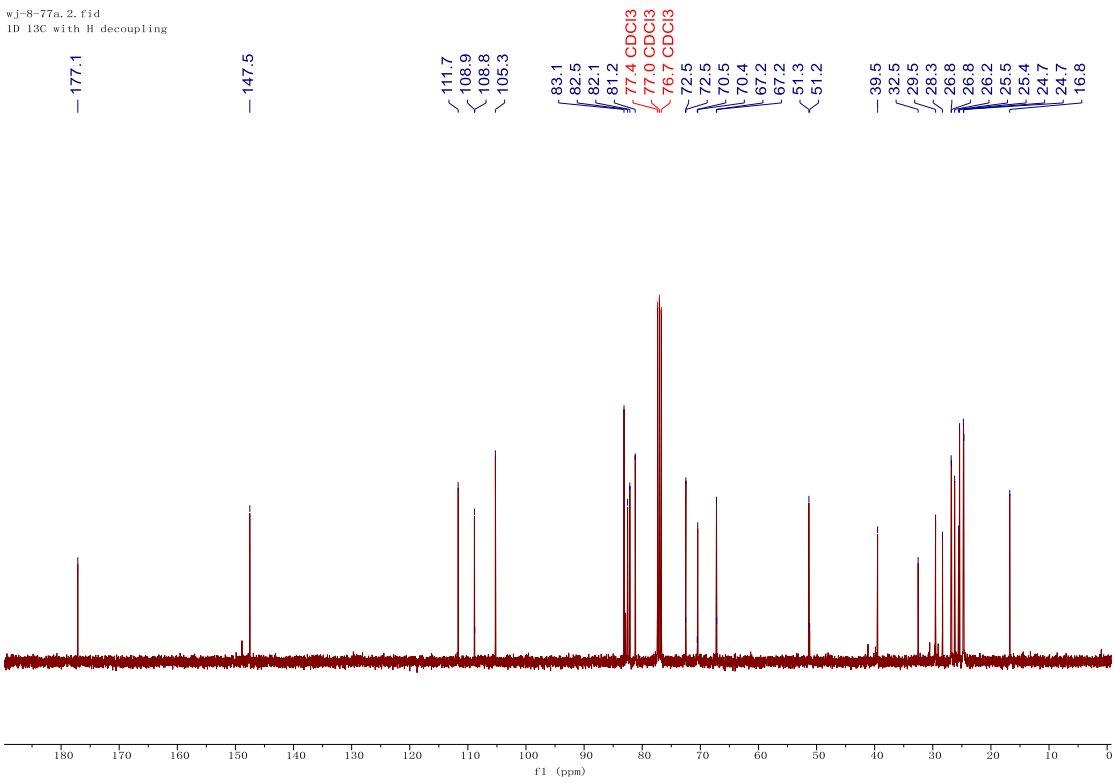
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4aa**



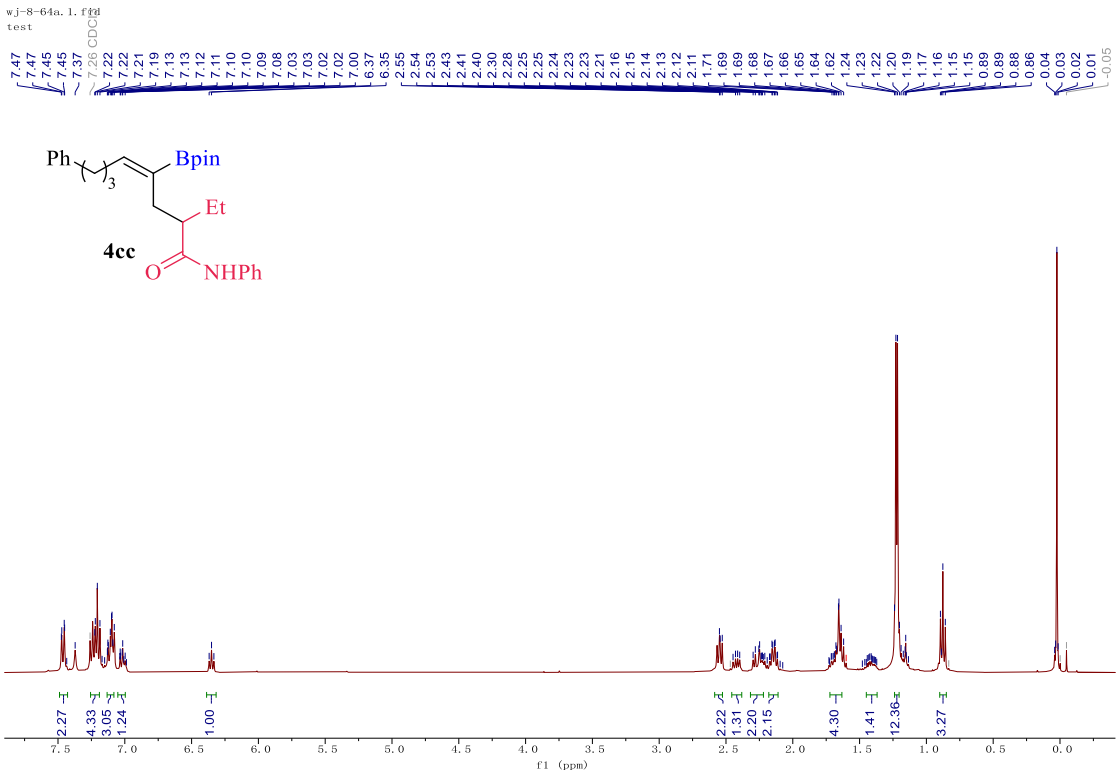
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4aa**



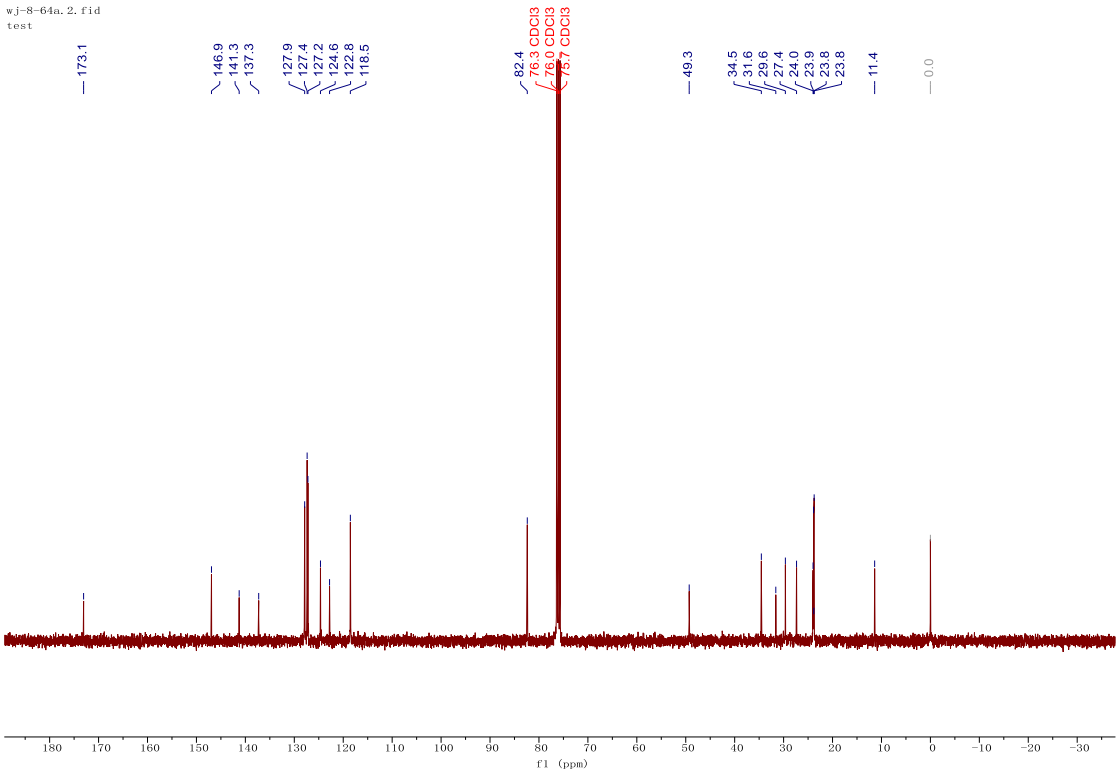
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4bb**



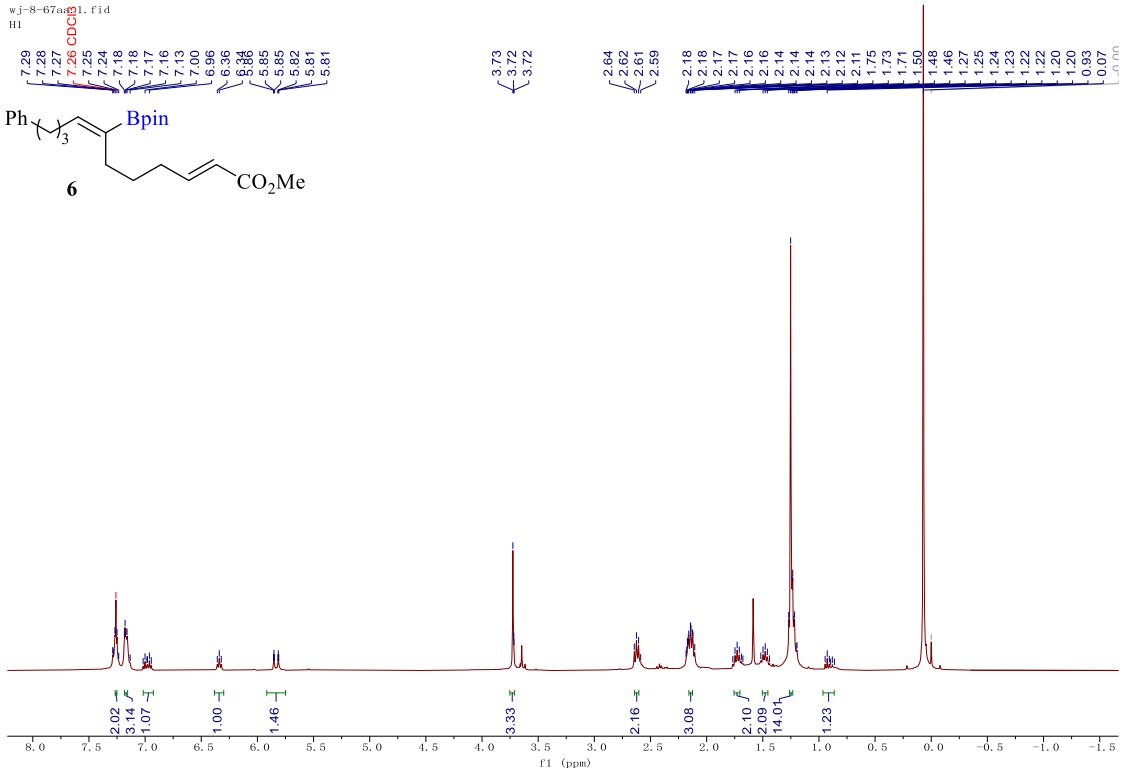
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4bb**



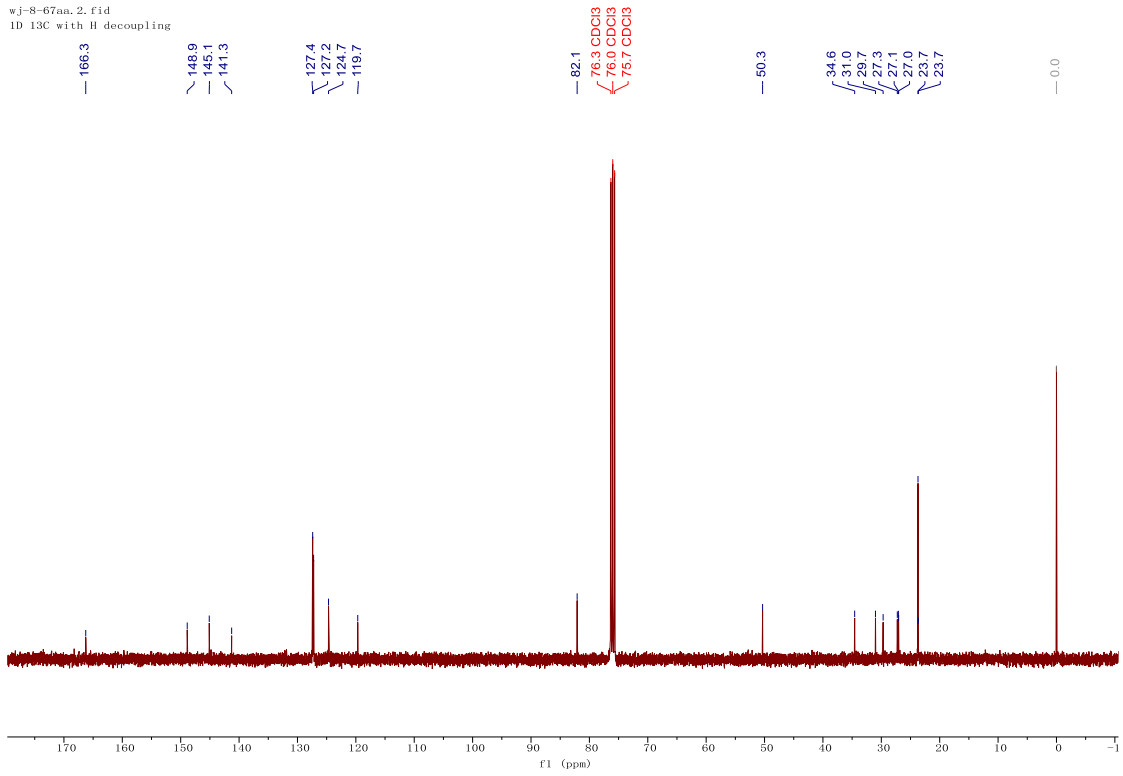
The ^{1}H NMR (400 MHz, chloroform-*d*) of **4cc**



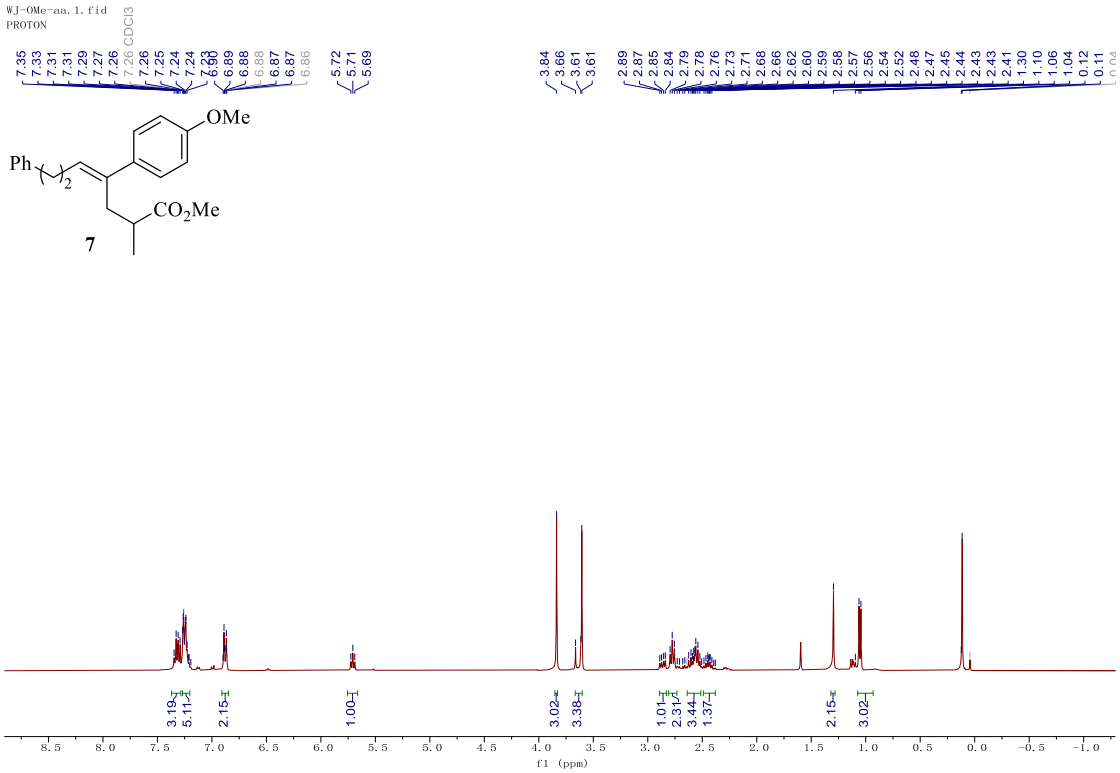
The $^{13}C\{^{1}H\}$ NMR (101 MHz, chloroform-*d*) of **4cc**



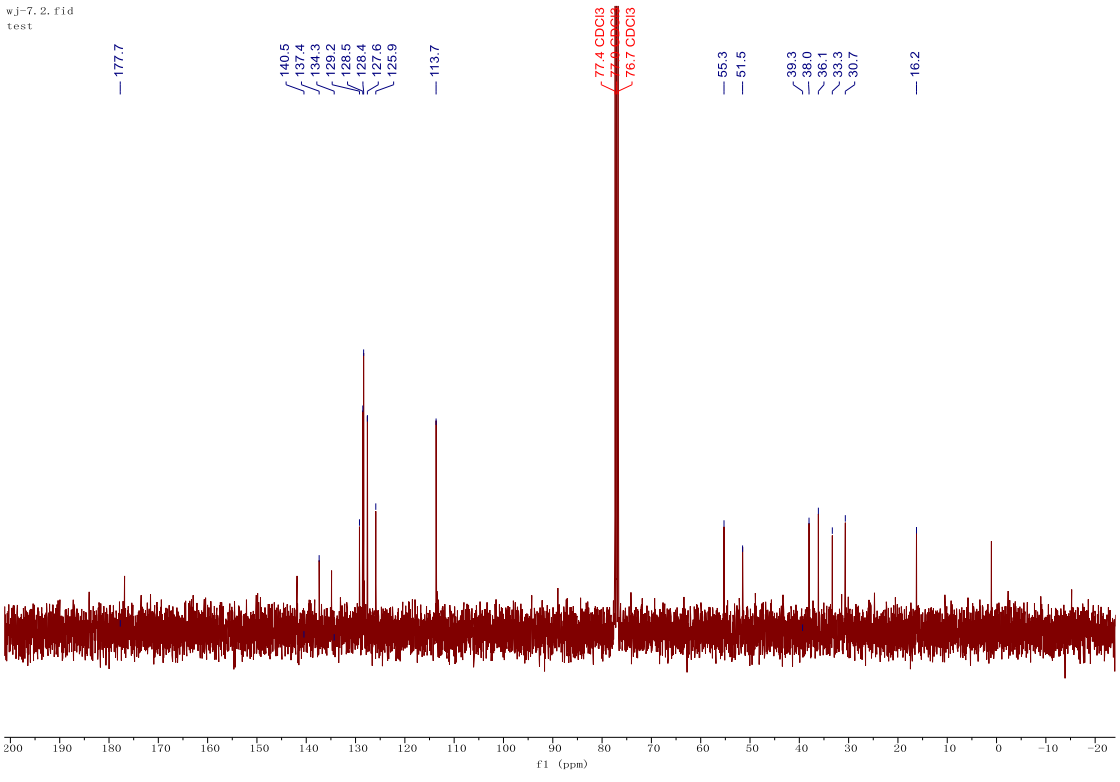
The ^{1}H NMR (400 MHz, chloroform-*d*) of **6**



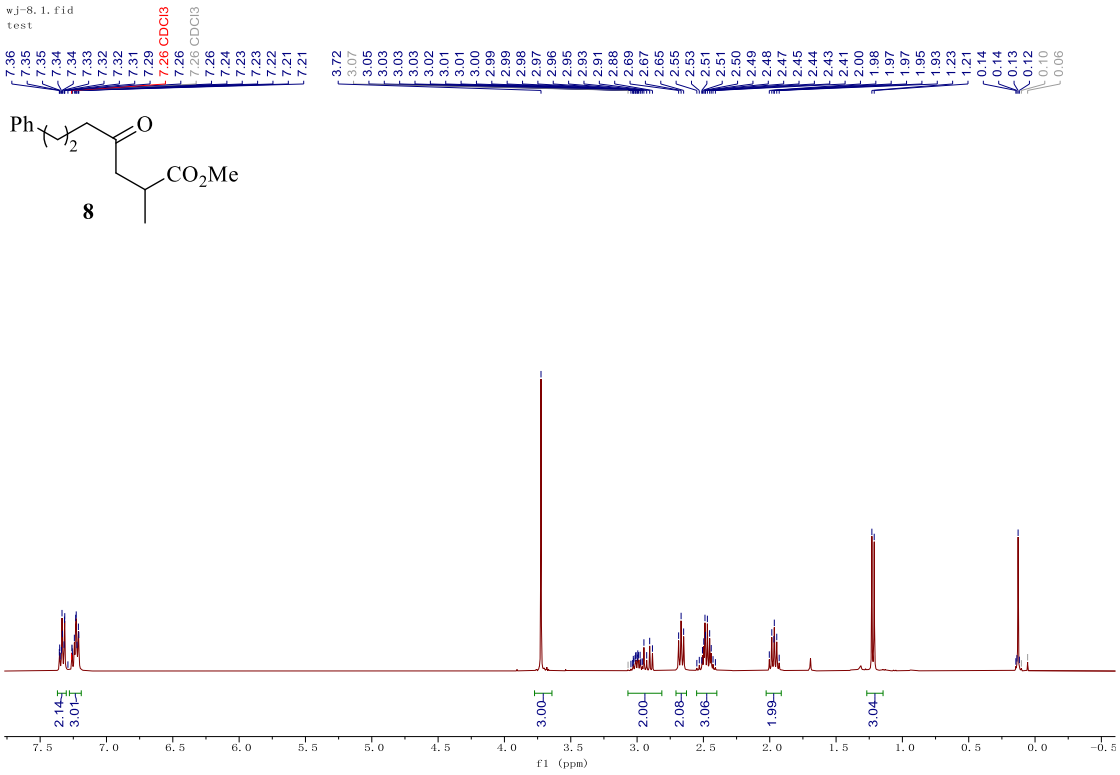
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **6**



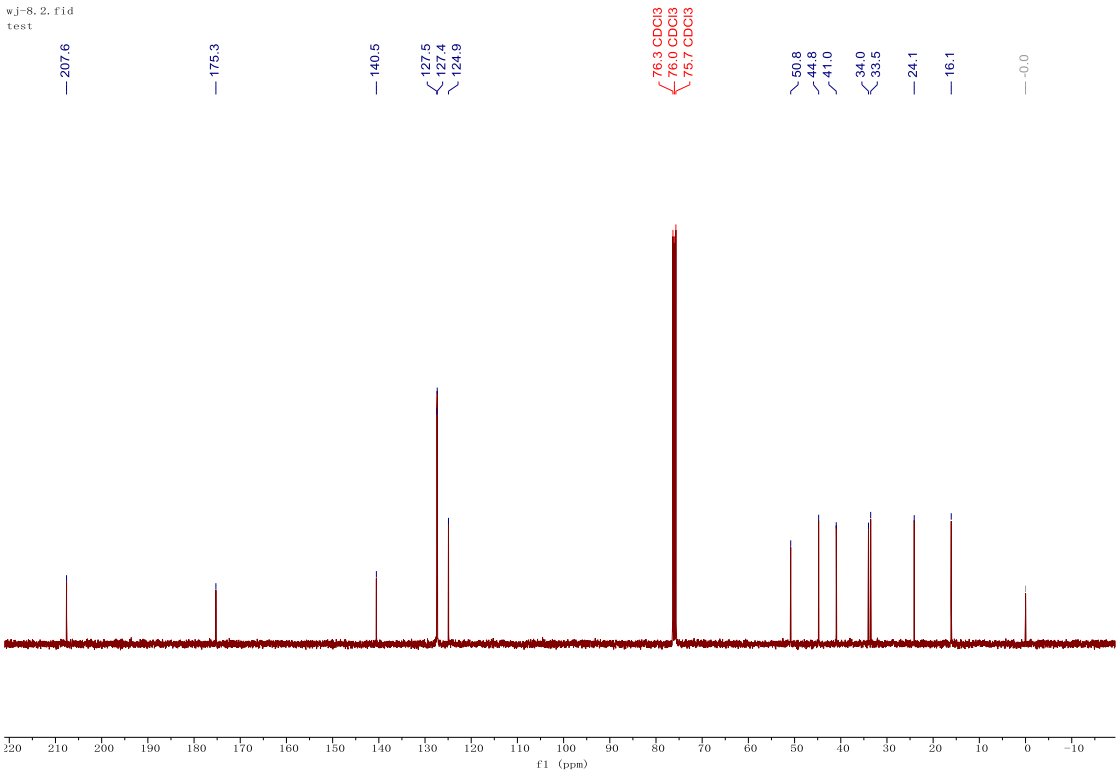
The ^{1}H NMR (400 MHz, chloroform-*d*) of **7**



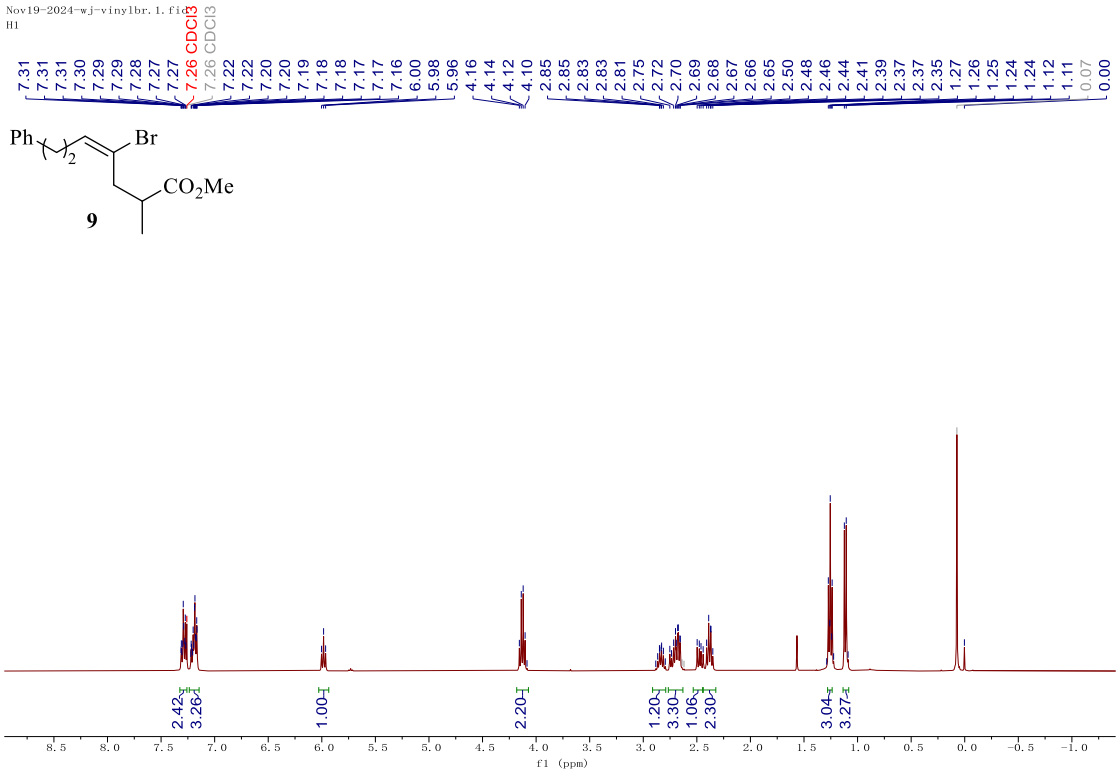
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **7**



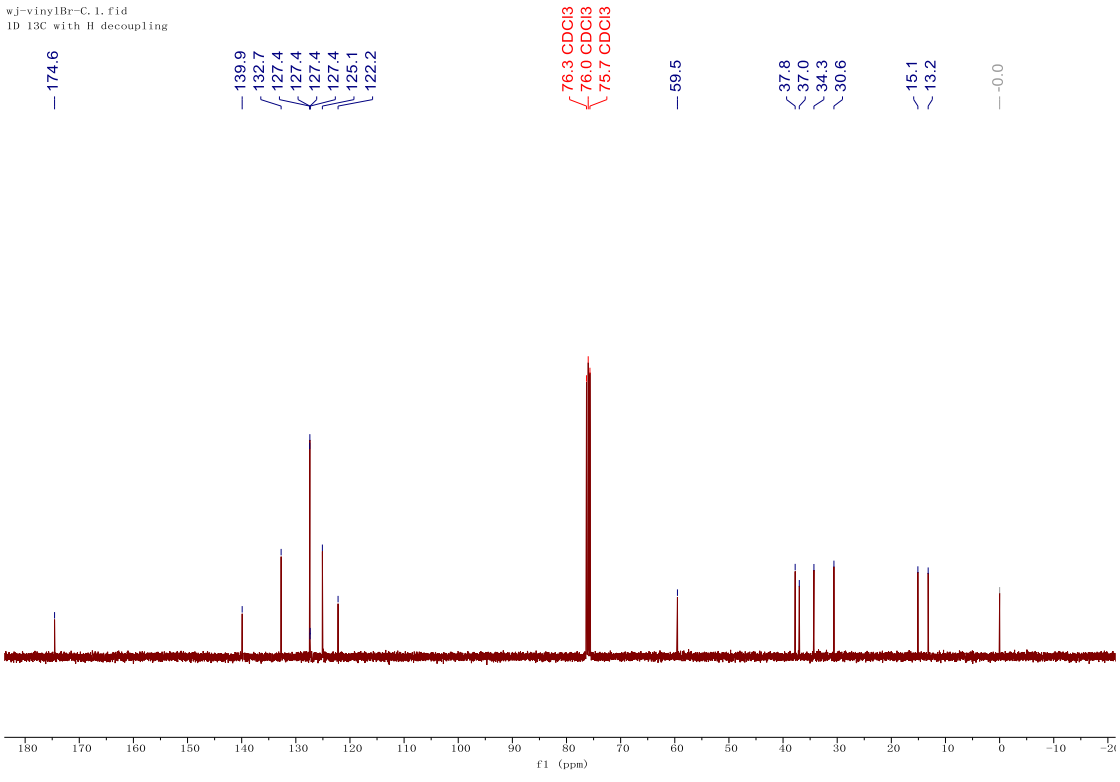
The ^{1}H NMR (400 MHz, chloroform-*d*) of **8**



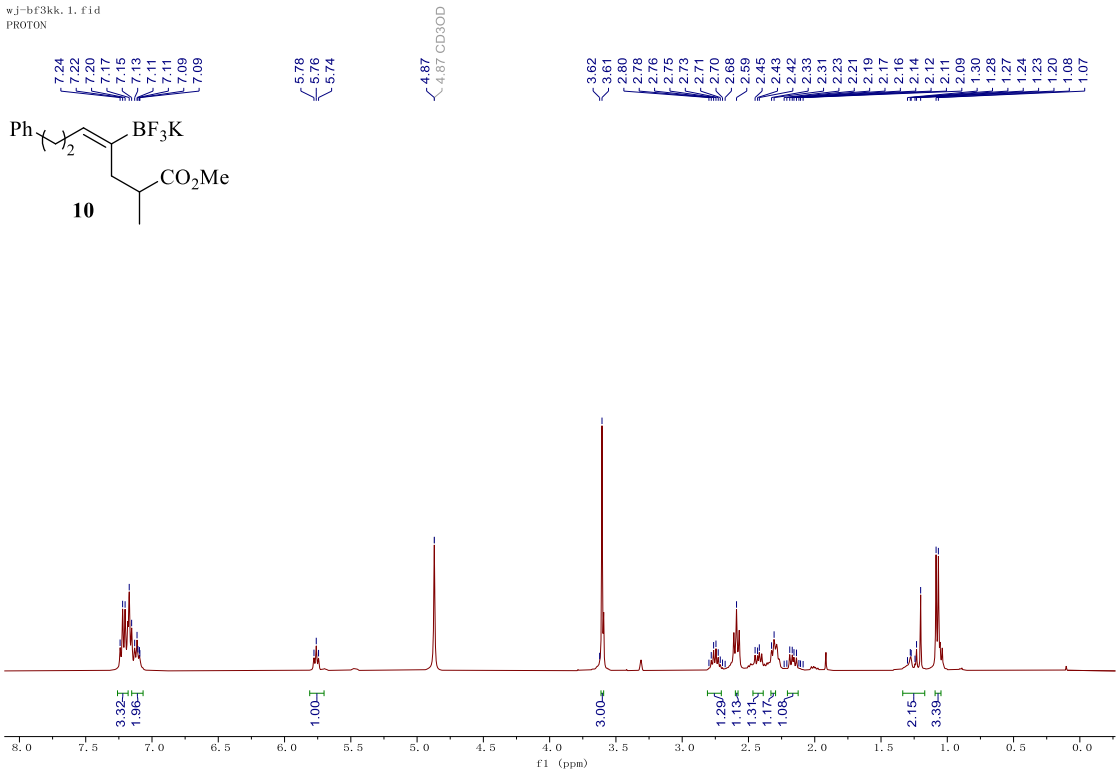
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **8**



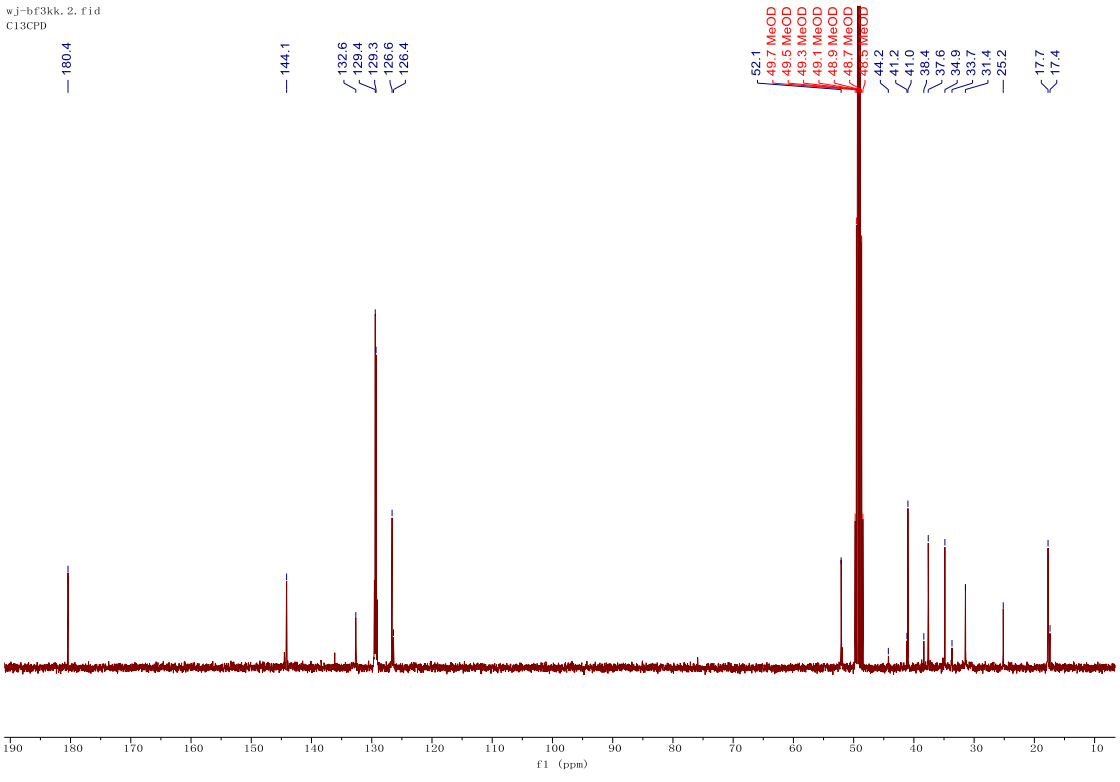
The ^{1}H NMR (400 MHz, chloroform-*d*) of **9**



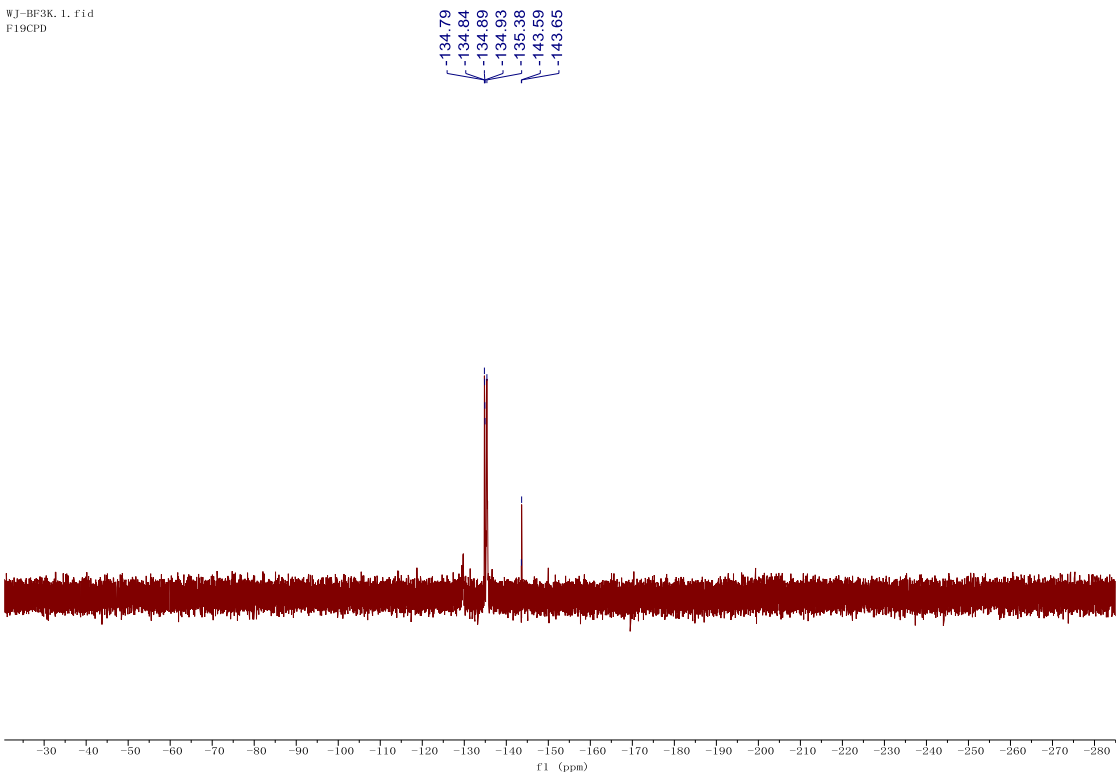
The ^{13}C{^{1}H} NMR (101 MHz, chloroform-*d*) of **9**



The ^{1}H NMR (400 MHz, Methanol-d_4) of **10**



The ^{13}C{^{1}H} NMR (101 MHz, Methanol-d_4) of **10**



The ^{19}F NMR (376 MHz, DMSO-d_6) of **10**

12. References

1. Zhu, C.; Yang, B.; Qiu, Y.; Bäckvall, J.-E. Olefin-Directed Palladium-Catalyzed Regio- and Stereoselective Hydroboration of Allenes. *Chem. Eur. J*. **2016**, *22*, 2939−2943.

2. Yan, D, Z; Xiao, Y, L; Qian. K. M; Wen. B. S; Jia. B. Z;, Shou. F. Zhu, Highly regioselective cobalt-catalyzed hydroboration of internal alkynes. *Angew. Chem. Int. Ed.* **2022**, *61*, e202208473.

3. Wei, Y, W; Yi, B, Y; Bao, C; Hua, Y, F; Xue, Z; Hui, Q; Sheng, M, M, Stereodefined rhodium-catalysed 1,4-H/D delivery for modular syntheses and deuterium integration, *Na. Catal*. **2021,** *4*, 586–594.