Supporting Information

Photoinduced Decarbonylative Borylation of Alkyl Aldehyde through 4-Alkyl-1,4-Dihydropyridines

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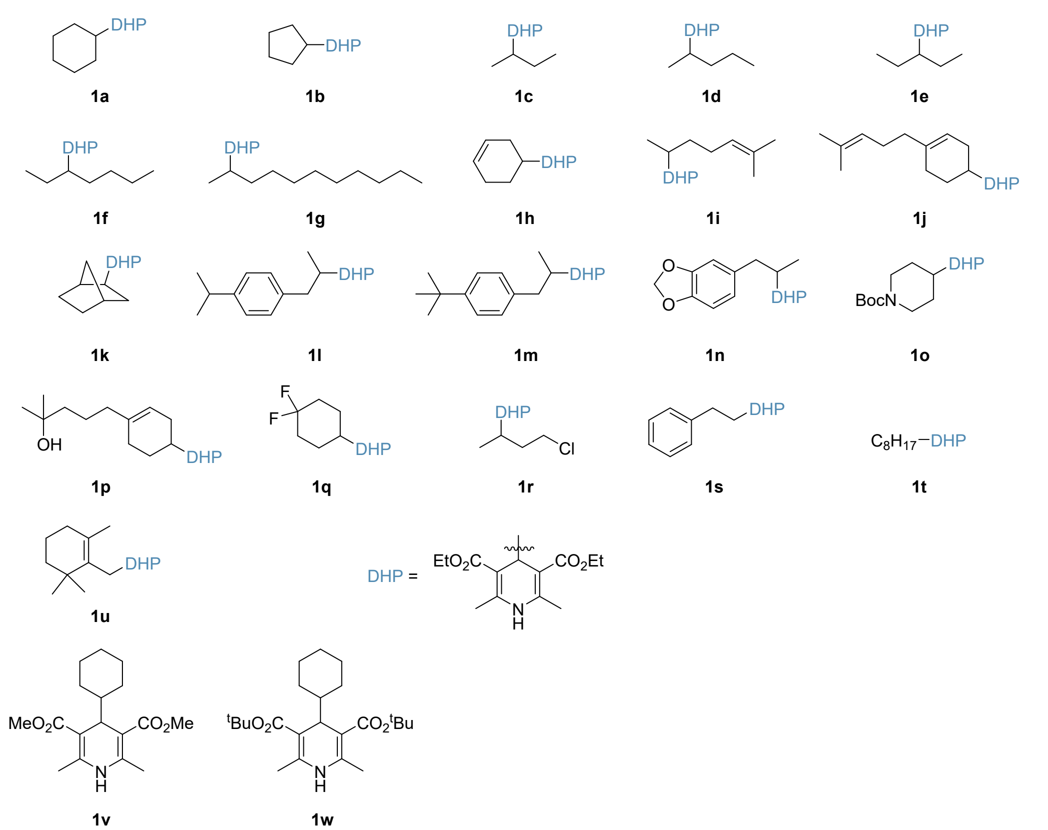
Content

1 General procedures

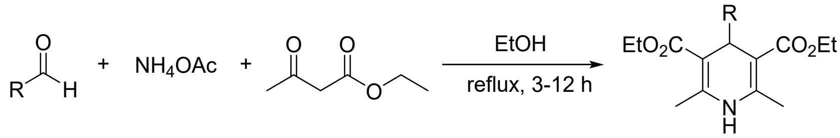
B_2cat_2 and *fac*-Ir(ppy)$_3$ were purchased from Energy Chemical. Hantzsch esters were prepared from corresponding alkyl aldehydes. All solvents were purchased from J&K Scientific and stored in a nitrogen-filled glovebox. The 200-300 mesh silica gels for the chromatography (from Qingdao, China) were used to purified organic compouds. ^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were measured on Bruker-400 spectrometer. Chemical shifts were reported in ppm using tetramethylsilane (TMS) as the internal standard. Infrared spectra were recorded on a Thermal Fisher Nicolet iS50 Fourier transform infrared spectrometer (FT-IR) and reported in wave numbers, cm^{-1}. For HRMS data, Fourier transform ion cyclotron resonance mass spectrometer was used. GC-MS and FID data were measured using the Agilent Technologies 7890B GC and the Agilent Technologies 5977B MSD.

1.1 General procedure for the preparation of Hantzsch esters

Synthesized Hantzcsh esters **1**:



Preparation of Hantzsch esters from corresponding alkyl aldehydes (**1a-1j, 1l-1p, 1s-1u**).[1]



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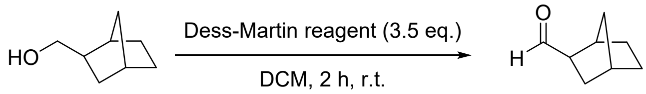
General procedure I: In a round-bottom flask, ammonium acetate (10 mmol, 1.0 equiv., 0.77 g) and ethanol (2.5 M) was added. Next, ethyl acetoacete (20 mmol, 2.0 equiv., 2.60 g) was added followed by alkyl aldehyde (10 mmol, 1.0 equiv.) in one portion. The reaction system was refluxed at 80 °C for 3-12 hours. When reaction was accomplished, the mixture of brine and dichloromethane were added and the layers were separated. The aqueous layer was extracted with dichloromethane for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (15:1-3:1) to obtain the corresponding alkyl substituted Hantzsch esters.

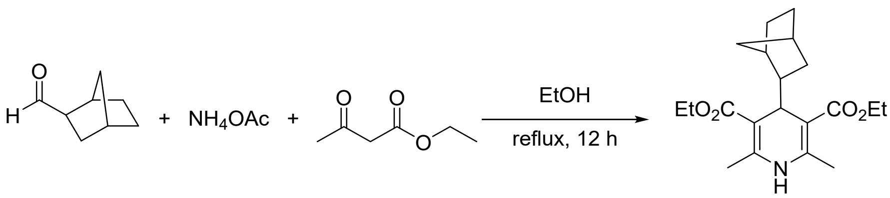
Synthesis of Hantzsch ester 1k



S1 S2

Bicyclo[2.2.1]heptane-2-carbaldehyde (**S2**)

In a round-bottom flask, bicyclo[2.2.1]heptan-2-ylmethanol (**S1**, 4 mmol, 1.0 equiv., 0.5 g) and Dess-Martin periodinane (35 mmol, 3.5 equiv., 5.9 g) were added. Next, dichloromethane (DCM, 0.1 M) was added in one portion. The reaction system was stirred at room temperature for 2 hours. When reaction was accomplished, the reaction was quenched with saturated $NaHCO_3$ aqueous solution. Then, the mixture of brine and dichloromethane were added and the layers were separated. The combined organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (30:1-10:1) to obtain aldehyde **S2** (0.40 g, 60%) as colorless oil.[2]

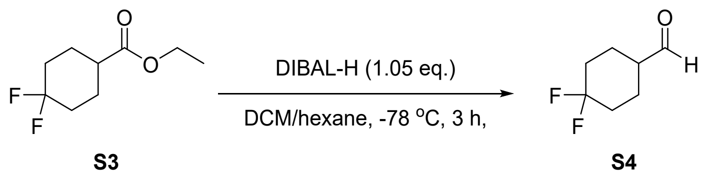


S2 1k

Diethyl 4-(bicyclo[2.2.1]heptan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1k**)

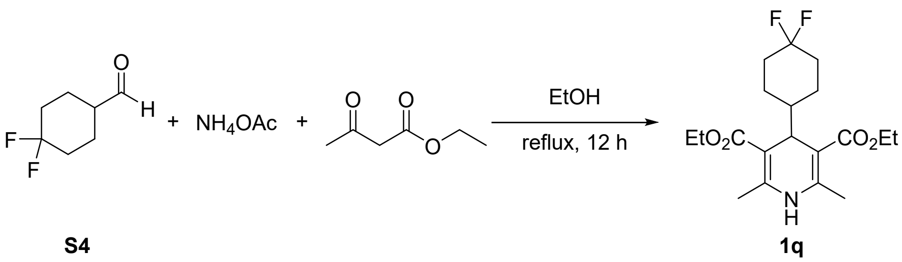
1k was synthesized according to General Procedure I using **S2** (2.4 mmol, 1.0 equiv., 0.30 g), ammonium acetate (2.4 mmol, 1.0 equiv., 0.18 g), ethanol (2.5 M) and ethyl acetoacete (4.8 mmol, 2.0 equiv., 0.62 g), with a stirring at 80 °C for 12 hours. The crude product was purified by column chromatography with PE/EA (15:1-3:1) to obtain Hantzsch ester **1k** (0.26 g, 31%) as white solid.

Synthesis of Hantzsch ester 1q



4,4-Difluorocyclohexane-1-carbaldehyde (**S4**)

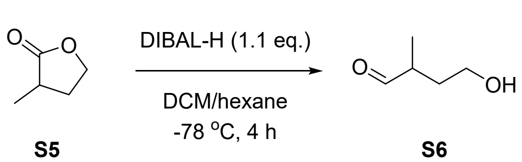
DIBAL-H (5.3 mL, 1 mol/L in hexane) was slowly added to the solution of ethyl 4,4-difluorocyclohexane-1-carboxylate (**S3**, 5 mmol, 1.0 equiv., 0.96 g) in a mixture of dichloromethane (12 mL) and hexane (12 mL) at -78 °C. The reaction system was stirred at the same temperature for 3 hours. Then, Et_2O (10 mL) and water (6 mL) were added to the reaction at 0 °C. The mixture was stirred for 30 minutes at room temperature, and then filtered through Celite. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product **S4** could be used in next step without further purification.[3]



Diethyl 4-(4,4-difluorocyclohexyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1q**)

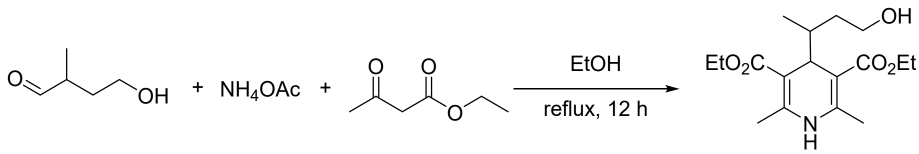
1q was synthesized according to General Procedure I using **S4** (5 mmol, 1.0 equiv., 0.74 g), ammonium acetate (5 mmol, 1.0 equiv., 0.39 g), ethanol (2.5 M) and ethyl acetoacete (10 mmol, 2.0 equiv., 1.30 g), with a stirring at 80 °C for 12 hours. The crude product was purified by column chromatography with PE/EA (15:1-3:1) to obtain Hantzsch ester **1k** (0.22 g, 12%) as white solid.

Synthesis of Hantzsch ester 1r



4-Hydroxy-2-methylbutanal (**S6**)

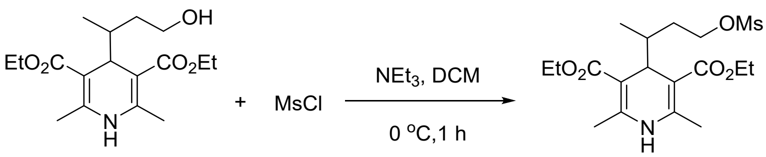
DIBAL-H (21 mL, 1 mol/L in hexane) was slowly added to the solution of 3-methyldihydrofuran-2(*3H*)-one (**S5**, 20 mmol, 1.0 equiv., 2.0 g) in a mixture of dichloromethane (50 mL) and hexane (50 mL) at -78 °C. The reaction system was stirred at the same temperature for 3 hours. Then, Et_2O (40 mL) and water (20 mL) were added to the reaction at 0 °C. The mixture was stirred for 30 minutes at room temperature, and then filtered through Celite. The organic layer was dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product **S6** could be used in next step without further purification.[4]



S6 **S7**

Diethyl 4-(4-hydroxybutan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**S7**)

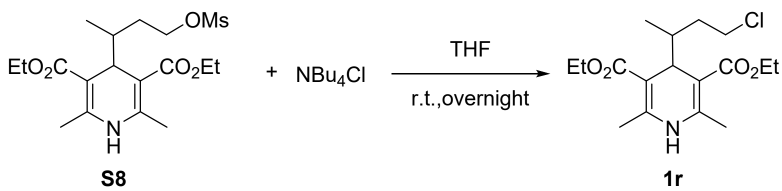
S7 was synthesized according to General Procedure I using **S6** (20 mmol, 1.0 equiv., 2.04 g), ammonium acetate (20 mmol, 1.0 equiv., 1.54 g), ethanol (2.5 M) and ethyl acetoacete (40 mmol, 2.0 equiv., 5.2 g), with a stirring at 80 °C for 12 hours. The crude product was purified by column chromatography with PE/EA (15:1-3:1) to obtain Hantzsch ester **S7** (1.47 g, 23%) as yellow oil.[4]



S7 **S8**

Diethyl 2,6-dimethyl-4-(4-((methylsulfonyl)oxy)butan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (**S8**)

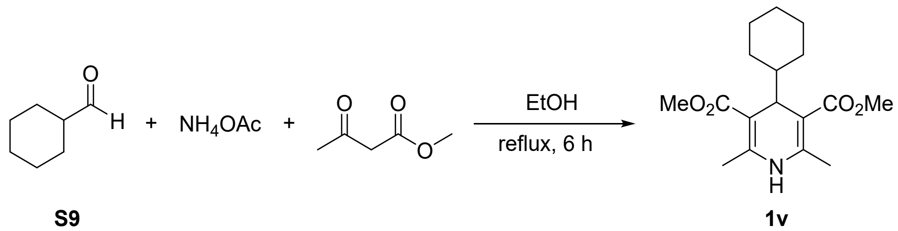
In a 100 mL Schlenk tube, **S7** (8 mmol, 1.0 equiv., 816 mg), triethylamine (10.4 mmol, 1.3 equiv., 1.5 mL) and dichloromethane (20 mL) were added in one portion under N_2 atmosphere. In the ice bath, reaction mixture was added methanesulfonyl chloride (10.4 mmol, 1.3 equiv., 0.8 mL) dropwise and stirred at 0 °C for 1 hour. Then 2 M NH_4Cl aqueous solution (20 mL) was added and the mixture was extracted with dichloromethane. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product **S8** could be used in next step without further purification.[4]



Diethyl 4-(4-chlorobutan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1r**)

In a round-bottom flask, **S8** (1 mmol, 1.0 equiv., 403 mg) and NBu_4Cl (1.5 mmol, 1.5 equiv., 417 mg) were stirred in tetrahydrofuran (THF, 5 mL) at room temperature overnight. The reaction mixture was directly purified by column chromatography with PE/EA (20:1-1:1) to obtain Hantzsch eater **1r** (0.21 g, 60%) as yellow oil.

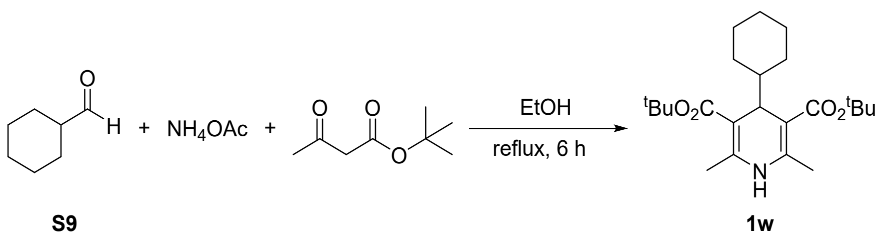
Synthesis of Hantzsch ester 1v



Dimethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1v**)

In a round-bottom flask, ammonium acetate (10 mmol, 1.0 equiv., 0.77 g) and ethanol (2.5 M) was added. Next, methyl acetoacetate (20 mmol, 2.0 equiv., 2.32 g) was added followed by cyclohexanecarboxaldehyde (**S9**, 10 mmol, 1.0 equiv., 1.12 g) in one portion. The reaction system was refluxed at 80 ^{o}C for 6 hours. When reaction was accomplished, the mixture of brine and dichloromethane were added and the layers were separated. The aqueous layer was extracted with dichloromethane for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (15:1-3:1) to obtain Hantzsch ester **1v** (1.81 g, 59%) as white solid.

Synthesis of Hantzsch ester 1w

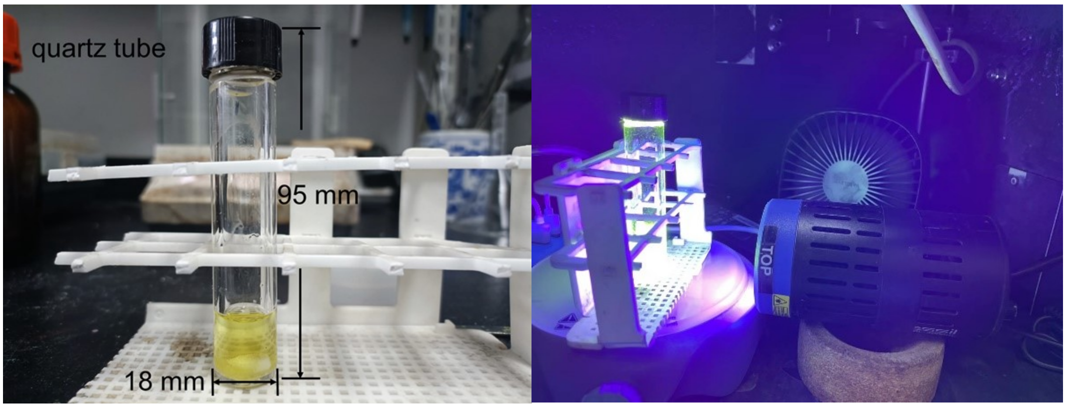


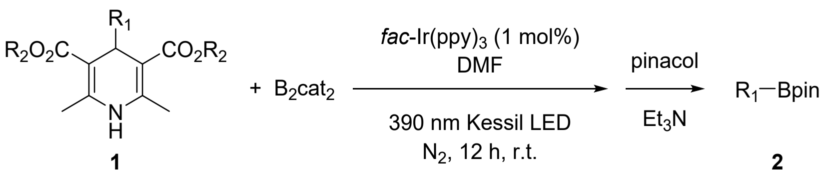
Di-tert-butyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1w**)

In a round-bottom flask, ammonium acetate (10 mmol, 1.0 equiv., 0.77 g) and ethanol (2.5 M) was added. Next, *tert*-butyl acetoacetate (20 mmol, 2.0 equiv., 3.16 g) was added followed by cyclohexanecarboxaldehyde (**S9**, 10 mmol, 1.0 equiv., 1.12 g) in one portion. The reaction system was refluxed at 80 °C for 6 hours. When reaction was accomplished, the mixture of brine and dichloromethane were added and the layers were separated. The aqueous layer was extracted with dichloromethane for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (15:1-3:1) to obtain Hantzsch ester **1w** (0.56 g, 14%) as white solid.

1.2 General procedure for alkyl borylation reactions

Reaction equipment:

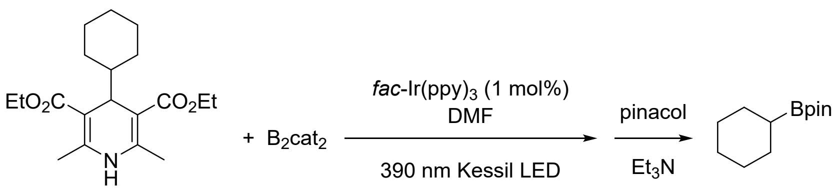




In glove box, alkyl-substituted Hantzcsh esters (**1**, 0.3 mmol, 1.0 equiv.), B_2cat_2 (1.2 mmol, 4.0 equiv., 286 mg) and *fac*-Ir(ppy)$_3$ (0.003 mmol, 1 mol %, 2 mg) were weighed in a 10 mL quartz reaction tube. *N*,*N*-Dimethylformamide (DMF, 0.1 M, 3 mL) was added in succession. The reaction system was stirred under N_2 atmosphere and irradiated with Kessil 390 nm LED (40 W, 3 cm away from the vial) 12 hours at room temperature. When reaction was accomplished, pinacol (2.4 mmol, 8.0

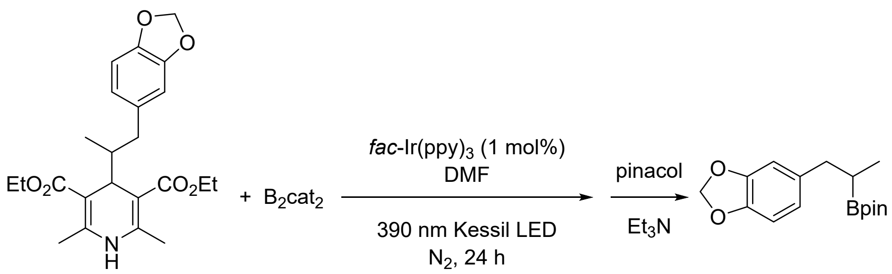
equiv., 283 mg) and 1.0 mL triethylamine were added, and the mixture was stirred at room temperature for 1 hour. The mixture of brine and ethyl acetate (20 mL) were added to the reaction system and the layers were separated. The aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (100:1-10:1) to obtain borylated products **2** as colorless oil.

1.3 General procedure for gram-scale borylation reactions



1a **2a**

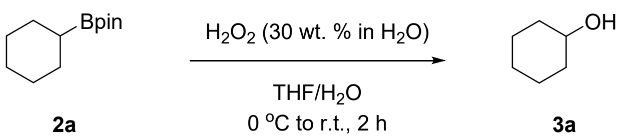
In glove box, diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1a**, 8 mmol, 1.0 equiv., 2.68 g), B_2cat_2 (32 mmol, 4.0 equiv., 7.62 g) and *fac*-Ir(ppy)$_3$ (0.08 mmol, 1 mol %, 52 mg) were weighed in a 50 mL quartz reaction tube. *N*,*N*-Dimethylformamide (0.27 M, 30 mL) was added in succession. The reaction system was stirred under N_2 atmosphere and irradiated with two Kessil 390 nm LEDs (40 W, 5 cm away from the vial) 24 hours at room temperature. When reaction was accomplished, pinacol (64 mmol, 8.0 equiv., 7.55 g) and 30 mL triethylamine were added, and the mixture was stirred at room temperature for 3 hours. The mixture of brine and ethyl acetate (80 mL) were added and the layers were separated. The aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (100:1-10:1) to obtain borylated products **2a** in 65% isolated yield (1.09 g) as colorless oil.



1n **2n**

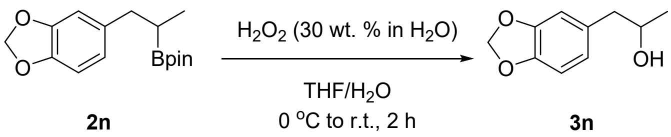
In glove box, diethyl 4-(1-(benzo[d][1,3]dioxol-5-yl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (**1n**, 5 mmol, 1.0 equiv., 2.08 g), B_2cat_2 (20 mmol, 4.0 equiv., 4.76 g) and *fac*-Ir(ppy)$_3$ (0.05 mmol, 1 mol %, 33 mg) were weighed in a 50 mL quartz reaction tube. *N*,*N*-Dimethylformamide (0.25 M, 20 mL) was added in succession. The reaction system was stirred under N_2 atmosphere and irradiated with two Kessil 390 nm LEDs (40 W, 5 cm away from the vial) 24 hours at room temperature. When reaction was accomplished, pinacol (40 mmol, 8.0 equiv, 4.72 g) and 20 mL triethylamine were added, and the mixture was stirred at room temperature for 3 hours. The mixture of brine and ethyl acetate (50 mL) were added and the layers were separated. The aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (50:1-10:1) to obtain borylated products **2n** in 52% isolated yield (0.73 g) as colorless oil.

1.4 General procedure for oxidation of borylation products



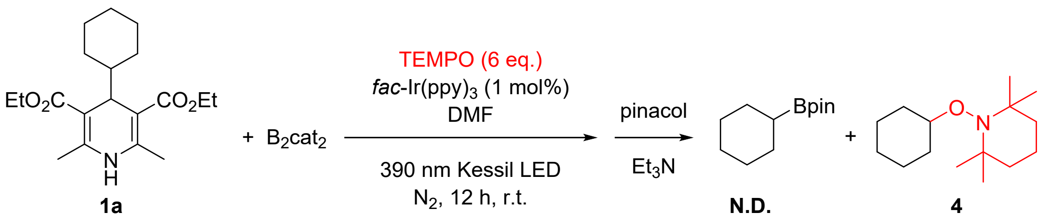
2a **3a**

In a round-bottom flask, 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2a**, 1 mmol, 210 mg), tetrahydrofuran (8 mL) and 3 M NaOH aqueous solution (5 mL) were added in on portion. In the ice bath, H_2O_2 (30 wt. % in H_2O, 5 mL) was added dropwise. Then the mixture warmed up to room temperature and reacted for 2 hours. $Na_2S_2O_3$ saturated aqueous solution (20 mL) was added to the reaction system dropwise at 0 ^oC, and the mixture heated up to room temperature and reacted for 30 minutes. When reaction was accomplished, ethyl acetate (20 mL) was added and the layers were separated. The organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (10:1-3:1) to obtain cyclohexanol **3** in 58% isolated yield as colorless oil.



In a round-bottom flask, 2-(1-(benzo[*d*][1,3]dioxol-5-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2n**, 1 mmol, 290 mg), tetrahydrofuran (8 mL) and 3 M NaOH aqueous solution (5 mL) were added in on portion. In the ice bath, H_2O_2 (30 wt. % in H_2O, 5 mL) was added dropwise. Then the mixture warmed up to room temperature and reacted for 2 hours. $Na_2S_2O_3$ saturated aqueous solution (20 mL) was added to the reaction system dropwise at 0 °C, and the mixture heated up to room temperature and reacted for 30 minutes. When reaction was accomplished, ethyl acetate (20 mL) was added and the layers were separated. The organic layers were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by column chromatography with PE/EA (10:1-1:1) to obtain 1-(benzo[*d*][1,3]dioxol-5-yl)propan-2-ol **4** in 74% isolated yield as colorless oil.

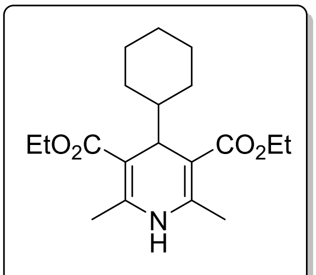
1.5 General procedure for gram-scale borylation reactions



In glove box, Hantzcsh esters **1a** (0.3 mmol, 1.0 equiv.), B_2cat_2 (1.2 mmol, 4.0 equiv., 286 mg), *fac*-Ir(ppy)$_3$ (0.003 mmol, 1 mol %, 2 mg) and TEMPO (1.8 mmol, 6.0 equiv., 281 mg) were weighed in a 10 mL quartz reaction tube. Then *N*,*N*-dimethylformamide (0.1 M, 3 mL) was added in succession. The reaction system was stirred under N_2 atmosphere and irradiated with Kessil 390 nm LED (40 W, 3 cm away from the vial) 12 hours at room temperature. When reaction was accomplished, pinacol (2.4 mmol, 8.0 equiv., 283 mg) and 1.0 mL triethylamine were added, and the mixture was stirred at room temperature for 1 hour. The mixture of brine and ethyl acetate (20 mL) were added to the reaction system and the layers were separated. The aqueous layer was extracted with ethyl acetate for 3 times. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated *in vacuo*. The reaction system was detected by GC-MS. The result shown that no borylation product was formed and radical trapping product **4** was observed. The crude product was purified by column chromatography with PE/EA (30:1-3:1) to obtain 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine **5** in 28% isolated yield (20 mg) as colorless oil.

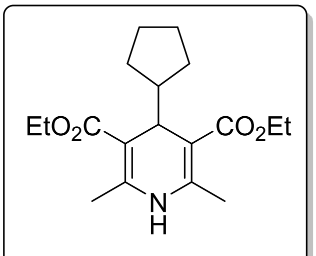
Spectra data for Hantzsch esters and borylation products

Diethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1a)[5]



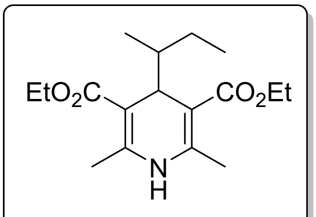
white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.53 (s, 1H), 4.26-4.10 (m, 4H), 3.92 (d, *J* = 5.7 Hz, 1H), 2.30 (s, 6H), 1.65 (d, *J* = 6.2 Hz, 2H), 1.54 (d, *J* = 12.3 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.08 (t, *J* = 8.9 Hz, 3H), 0.93 (t, *J* = 13.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 144.4, 101.9, 59.6, 45.8, 38.4, 28.8, 26.7, 26.6, 19.4, 14.4.

Diethyl 4-cyclopentyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1b)[6]



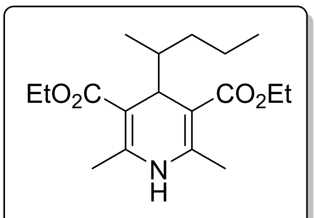
white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.67 (br, 1H), 4.26-4.11 (m, 4H), 4.00 (d, *J* = 7.2 Hz, 1H), 2.30 (s, 6H), 1.78-1.68 (m, 1H), 1.66-1.54 (m, 2H), 1.52-1.45 (m, 2H), 1.43-1.37 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.21-1.11 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 144.5, 102.9, 59.6, 48.2, 35.8, 28.4, 24.0, 19.5, 14.4.

Diethyl 4-(sec-butyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1c)[5]



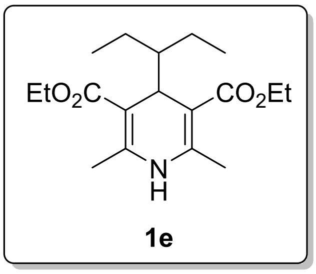
white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.61 (br, 1H), 4.26-4.09 (m, 4H), 4.02 (d, *J* = 4.3 Hz, 1H), 2.29 (d, *J* = 2.4 Hz, 6H), 1.36-1.27 (m, 8H), 1.00-0.93 (m, 1H), 0.85 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.0, 168.6, 144.8, 144.6, 102.2, 101.2, 59.6, 43.1, 37.5, 25.2, 19.3, 19.3, 14.7, 14.3, 14.3, 12.2.

Diethyl 2,6-dimethyl-4-(pentan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1d)[6]



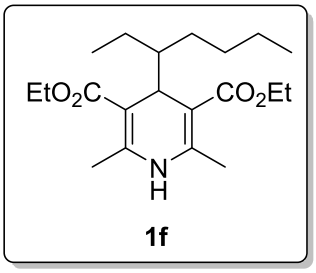
white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.88 (br, 1H), 4.26-4.11 (m, 4H), 4.01 (d, *J* = 4.5 Hz, 1H), 2.29 (d, *J* = 3.7 Hz, 6H), 1.47-1.34 (m, 2H), 1.30 (t, J = 7.1 Hz, 6H), 1.26-1.14 (m, 2H), 0.99-0.91 (m, 2H), 0.83 (t, J = 6.9 Hz, 3H), 0.71 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.9, 162.2, 141.0, 123.1, 81.3, 61.4, 36.2, 24.8, 18.7, 18.2, 14.3, 14.1.

Diethyl 2,6-dimethyl-4-(pentan-3-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1e)[5]



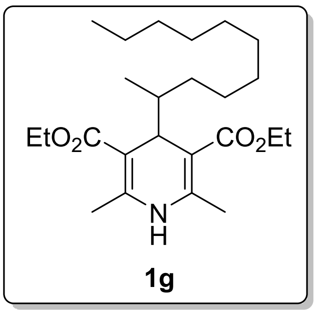
white solid. ^{1}H NMR (400 MHz, Chloroform-d): δ 5.88 (br, 1H), 4.26-4.11 (m, 4H), 4.01 (d, J = 4.5 Hz, 1H), 2.29 (d, J = 3.7 Hz, 6H), 1.47-1.34 (m, 2H), 1.30 (t, J = 7.1 Hz, 6H), 1.26-1.14 (m, 2H), 0.99-0.91 (m, 2H), 0.83 (t, J = 6.9 Hz, 3H), 0.71 (t, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.9, 162.2, 141.0, 123.1, 81.3, 61.4, 36.2, 24.8, 18.7, 18.2, 14.3, 14.1.

Diethyl 4-(hexan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1f)[5]



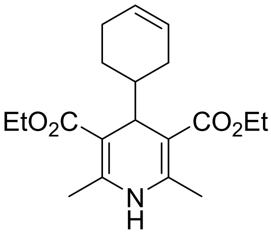
white solid. ^{1}H NMR (400 MHz, Chloroform-d): δ 5.74 (br, 1H), 4.19-4.13 (m, 5H), 2.28 (d, J = 2.1 Hz, 6H), 1.30 (t, J = 7.1 Hz, 6H), 1.26-1.08 (m, 9H), 0.86 (t, J = 6.8 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.8, 144.6, 144.5, 102.3, 102.2, 59.6, 48.1, 35.0, 29.5, 28.4, 23.2, 21.8, 19.4, 19.3, 14.3, 14.1, 11.8.

Diethyl 2,6-dimethyl-4-(undecan-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1g)



white solid. ^{1}H NMR (400 MHz, Chloroform-d): δ 5.55 (s, 1H), 4.26-4.09 (m, 4H), 4.00 (d, J = 4.5 Hz, 1H), 2.29 (d, J = 3.8 Hz, 6H), 1.43-1.35 (m, 1H), 1.30 (t, J = 7.1 Hz, 9H), 1.26-1.16 (m, 12H), 0.95-0.93 (m, 1H), 0.88 (t, J = 6.8 Hz, 3H), 0.71 (d, J = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 165.8, 162.2, 141.1, 123.2, 81.3, 61.5, 34.1, 31.9, 29.7, 29.5, 29.3, 25.4, 24.6, 22.6, 18.3, 14.2, 14.1. HRMS (ESI) calcd. for $C_{24}H_{42}NO_4^+$ [M+H]$^+$: 408.3108, found: 408.3107. IR (film, υ cm^{-1}): 2926, 2854, 1720, 1443, 1367, 1285, 1222, 1104, 1043.

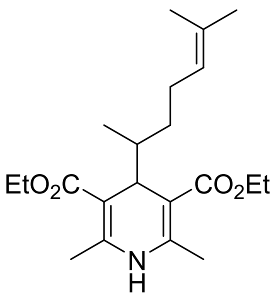
Diethyl 4-(cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1h)[5]



1h

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.62-5.55 (m, 3H), 4.27-4.10 (m, 4H), 4.02 (d, *J* = 5.8 Hz, 1H), 2.31 (d, *J* = 1.7 Hz, 6H), 2.04-1.77 (m, 4H), 1.65-1.60 (m, 4H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.19 (qd, *J* = 12.3, 6.1 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.9, 162.2, 141.1, 126.9, 123.6, 80.1, 61.5, 29.2, 25.9, 24.8, 23.3, 14.3.

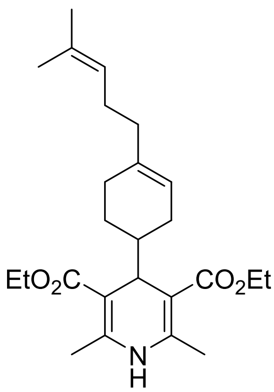
Diethyl 2,6-dimethyl-4-(6-methylhept-5-en-2-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1i)[5]



1i

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.66 (d, *J* = 21.5 Hz, 1H), 5.03 (tdd, *J* = 6.8, 2.8, 1.4 Hz, 1H), 4.26-4.09 (m, 4H), 4.01 (d, *J* = 4.3 Hz, 1H), 2.29 (d, *J* = 2.9 Hz, 6H), 1.99 (td, *J* = 15.2, 6.4 Hz, 1H), 1.87 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.65 (s, 3H), 1.57 (s, 3H), 1.50-1.34 (m, 2H), 1.29 (td, *J* = 7.1, 1.5 Hz, 6H), 1.03-0.94 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.9, 168.5, 144.7, 144.5, 130.8, 125.2, 102.1, 101.3, 59.6, 59.5, 40.9, 38.0, 32.7, 26.1, 25.7, 19.3, 19.3, 17.7, 14.9, 14.3, 14.3.

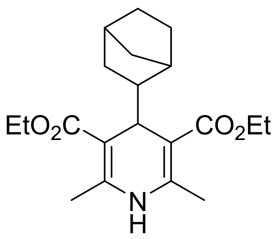
Diethyl 2,6-dimethyl-4-(4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)-1,4-dihydropyridine-3,5-dicarboxylate (1j)[7]



1j

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.66 (d, *J* = 21.5 Hz, 1H), 5.03 (tdd, *J* = 6.8, 2.8, 1.4 Hz, 1H), 4.26-4.09 (m, 4H), 4.01 (d, *J* = 4.3 Hz, 1H), 2.29 (d, *J* = 2.9 Hz, 6H), 1.99 (td, *J* = 15.2, 6.4 Hz, 1H), 1.87 (dq, *J* = 14.7, 7.3 Hz, 1H), 1.65 (s, 3H), 1.57 (s, 3H), 1.50-1.34 (m, 2H), 1.29 (td, *J* = 7.1, 1.5 Hz, 6H), 1.03-0.94 (m, 1H), 0.73 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.6, 168.5, 144.8, 144.6, 137.4, 131.3, 124.5, 120.6, 101.8, 59.6, 41.7, 37.6, 37.6, 29.2, 27.5, 26.5, 25.7, 25.4, 19.5, 19.5, 17.7, 17.6, 14.4.

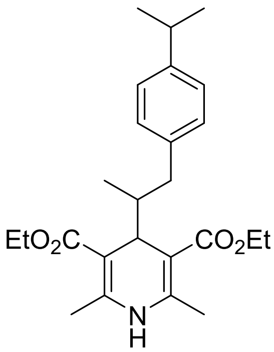
Diethyl 4-(bicyclo[2.2.1]heptan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1k)[5]



1k

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.64 (d, *J* = 101.1 Hz, 1H), 4.32-4.07 (m, 4H), 3.90 (dd, *J* = 65.8, 10.1 Hz, 1H), 2.30 (dd, *J* = 15.3, 12.8 Hz, 6H), 2.18-2.04 (m, 1H), 1.99-1.85 (m, 1H), 1.73-1.49 (m, 1H), 1.47-1.32 (m, 4H), 1.32-1.25 (m, 6H), 1.17 (q, *J* = 9.3 Hz, 1H), 1.03 (ddd, *J* = 30.3, 12.5, 8.4 Hz, 2H), 0.96-0.74 (m, 1H). ^{13}C NMR NMR for the major diastereoisomer (101 MHz, Chloroform-*d*) δ 168.8, 168.6, 145.0, 148.8, 103.8, 102.6, 59.7, 59.6, 48.5, 38.2, 36.6, 35.6, 34.0, 30.3, 29.2, 22.6, 19.4, 19.4, 14.3. ^{13}C NMR NMR for the minor diastereoisomer (101 MHz, Chloroform-*d*) δ 168.6, 168.5, 144.7, 144.0, 102.5, 102.5, 59.6, 59.6, 47.4, 39.4, 37.9, 36.6, 33.2, 31.6, 30.9, 22.2, 19.5, 19.2, 14.4.

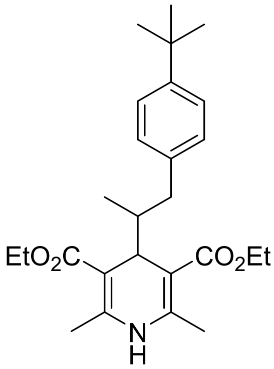
Diethyl 4-(1-(4-isopropylphenyl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1l)[5]



1l

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.09 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 5.63 (br, 1H), 4.27-4.12 (m, 5H), 2.88-2.81 (m, 1H), 2.76 (dd, *J* = 13.3, 3.6 Hz, 1H), 2.31 (d, *J* = 1.7 Hz, 6H), 2.08 (dd, *J* = 13.3, 11.2 Hz, 1H), 1.78-1.68 (m, 1H), 1.30 (dt, *J* = 12.4, 7.1 Hz, 6H), 1.22 (d, *J* = 6.9 Hz, 6H), 0.64 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.8, 168.5, 145.9, 144.9, 139.4, 128.9, 126.0, 101.8, 59.7, 43.1, 38.8, 38.7, 33.7, 26.9, 24.1, 19.4, 14.5, 14.5, 14.4.

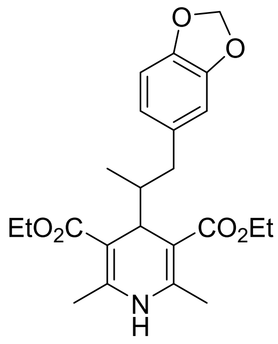
Diethyl 4-(1-(4-(tert-butyl)phenyl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1m)[4]



1m

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.26-7.24 (m, 2H), 7.01 (d, *J* = 8.3 Hz, 2H), 5.64 (br, 1H), 4.28-4.13 (m, 5H), 2.76 (dd, *J* = 13.3, 3.6 Hz, 1H), 2.31 (d, *J* = 1.6 Hz, 6H), 2.09 (dd, *J* = 13.3, 11.1 Hz, 1H), 1.78-1.69 (m, 1H), 1.32 (d, *J* = 7.1 Hz, 3H), 1.28 (d, *J* = 1.7 Hz, 12H), 0.64 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 168.4, 148.1, 144.8, 144.7, 139.0, 128.7, 124.9, 102.0, 101.5, 59.7, 43.1, 38.7, 34.3, 31.4, 19.5, 19.4, 14.5, 14.5, 14.4.

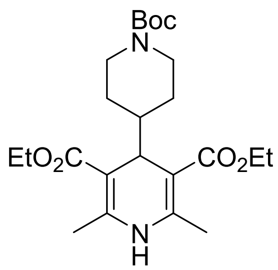
Diethyl 4-(1-(benzo[*d*][1,3]dioxol-5-yl)propan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1n)[4]



1n

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 6.68 (d, *J* = 7.9 Hz, 1H), 6.57 (d, *J* = 1.7 Hz, 1H), 6.52 (dd, *J* = 7.8, 1.7 Hz, 1H), 5.89 (q, *J* = 1.5 Hz, 2H), 5.72 (br, 1H), 4.28-4.12 (m, 4H), 4.10 (d, *J* = 4.8 Hz, 1H), 2.72 (dd, *J* = 13.4, 3.5 Hz, 1H), 2.32 (d, *J* = 1.2 Hz, 6H), 2.02 (dd, *J* = 13.3, 11.3 Hz, 1H), 1.72-1.64 (m, 1H), 1.31 (dt, *J* = 9.1, 7.1 Hz, 6H), 0.63 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.7, 168.5, 147.3, 145.3, 145.0, 136.0, 121.7, 109.3, 107.8, 101.8, 101.3, 100.6, 59.7, 43.3, 39.0, 38.6, 19.4, 19.4, 14.5, 14.4.

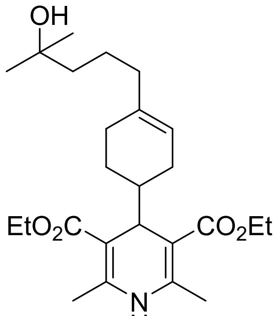
Diethyl 4-(1-(*tert*-butoxycarbonyl)piperidin-4-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1o)[4]



1o

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.84 (br, 1H), 4.25-4.05 (m, 6H), 4.00 (d, *J* = 5.6 Hz, 1H), 2.50 (t, *J* = 11.7 Hz, 2H), 2.31 (s, 6H), 1.49-1.37 (m, 12H), 1.30 (t, *J* = 7.1 Hz, 6H), 1.13 (qd, *J* = 12.5, 4.3 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.4, 154.9, 145.5, 100.9, 79.2, 59.7, 44.0, 37.5, 28.5, 26.9, 22.6, 19.4, 14.4.

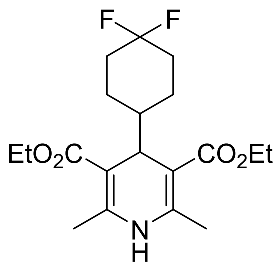
Diethyl 4-(4-(4-hydroxy-4-methylpentyl)cyclohex-3-en-1-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1p)



1p

yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.80 (d, *J* = 7.2 Hz, 1H), 5.31 (d, *J* = 13.8 Hz, 1H), 4.26-4.11 (m, 4H), 4.02 (t, *J* = 5.6 Hz, 1H), 2.31 (d, *J* = 2.2 Hz, 6H), 1.89-1.84 (m, 4H), 1.78-1.63 (m, 3H), 1.4-1.43 (m, 6H), 1.30 (td, J = 7.1, 1.7 Hz, 6H), 1.20 (s, 6H), 0.88-0.83 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-d) δ 168.7, 168.6, 137.6, 137.2, 120.9, 120.3, 101.5, 71.0, 59.6, 43.6, 43.5, 42.0, 41.6, 38.2, 37.8, 37.7, 37.5, 29.1, 28.9, 27.5, 25.3, 22.5, 19.4, 19.3, 14.4, 14.4. HRMS (ESI) calcd. for $C_{25}H_{40}NO_5^+$ [M+H]$^+$: 434.2901, found: 434.2903. IR (film, υ cm^{-1}): 3337, 2936, 1673, 1486, 1369, 1210, 1096, 1046.

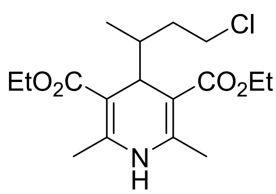
Diethyl 4-(4,4-difluorocyclohexyl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1q)



1q

white solid. ^{1}H NMR (400 MHz, Chloroform-d): δ 5.83 (br, 1H), 4.26-4.12 (m, 4H), 4.01 (d, J = 2.6 Hz, 1H), 2.32 (s, 6H), 2.08-1.98 (m, 2H), 1.65-1.47 (m, 4H), 1.30 (t, J = 7.1 Hz, 9H). ^{13}C NMR (101 MHz, Chloroform-d) δ (101 MHz, Chloroform-d) δ 168.3, 145.1, 126.3, 101.4, 59.8, 43.4, 37.0, 33.8 (J = 20.2 Hz), 24.8 (J = 9.7 Hz), 19.6, 14.4. HRMS (ESI) calcd. for $C_{18}H_{28}F_2NO_4^+$ [M+H]$^+$: 372.1981, found: 372.1977. IR (film, υ cm^{-1}): 2948, 2159, 2029, 1694, 1651, 1484, 1371, 1294, 1208, 1094, 1047.

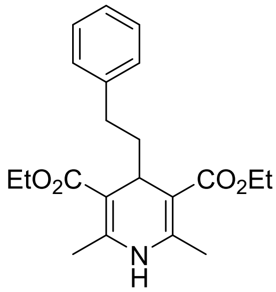
Diethyl 4-(4-chlorobutan-2-yl)-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1r)



1r

white solid. ^{1}H NMR (400 MHz, Chloroform-d): δ 5.56 (br, 1H), 4.27-4.11 (m, 4H), 4.03 (d, J = 4.2 Hz, 1H), 3.63-3.51 (m, 2H), 2.31 (s, 6H), 1.68-1.42 (m, 3H), 1.31 (t, J = 7.1 Hz, 9H), 0.75 (t, J = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ (101 MHz, Chloroform-d) δ 168.6, 168.2, 145.5, 145.3, 101.6, 100.3, 59.8, 59.8, 43.8, 38.6, 37.0, 35.8, 19.5, 19.3, 14.8, 14.4, 14.3. HRMS (ESI) calcd. for $C_{17}H_{27}ClNO_4^+$ [M+H]$^+$: 344.1623, found: 344.1620. IR (film, υ cm^{-1}): 2977, 1692, 1486, 1368, 1209, 1097, 1047, 773.

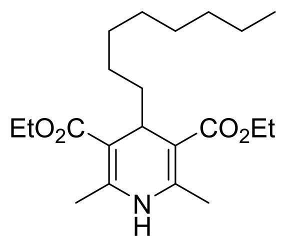
Diethyl 2,6-dimethyl-4-phenethyl-1,4-dihydropyridine-3,5-dicarboxylate (1s)[7]



1s

white solid. ^{1}H NMR (400 MHz, Chloroform-d): δ 7.23 (dd, J = 8.0, 6.9 Hz, 2H), 7.13 (d, J = 7.4, 6.9 Hz, 3H), 5.62 (br, 1H), 4.26-4.12 (m, 4H), 4.06 (t, J = 5.7 Hz, 1H), 2.56-2.52 (m, 2H), 2.30 (s, 6H), 1.69-1.63 (m, 3H), 1.29 (t, *J* = 7.1 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 144.9, 143.1, 128.2, 128.1, 125.4, 103.0, 59.7, 38.4, 33.2, 31.4, 19.6, 14.4.

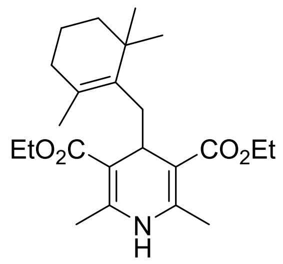
Diethyl 2,6-dimethyl-4-phenethyl-1,4-dihydropyridine-3,5-dicarboxylate (1t)[7]



1t

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.66 (br, 1H), 4.26-4.11 (m, 4H), 3.92 (t, *J* = 5.8 Hz, 1H), 2.28 (s, 6H), 1.29 (t, *J* = 7.1 Hz, 9H), 1.23-1.15 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 144.7, 103.3, 59.6, 36.9, 32.9, 31.9, 29.9, 29.7, 29.4, 24.9, 22.7, 19.4, 14.4, 14.1.

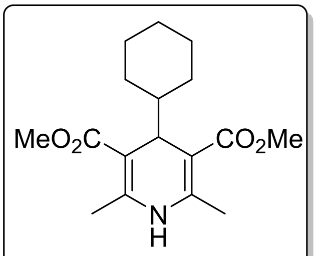
Diethyl 2,6-dimethyl-4-((2,6,6-trimethylcyclohex-1-en-1-yl)methyl)-1,4-dihydropyridine-3,5-dicarboxylate (1u)



1u

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.68 (br, 1H), 4.23-4.09 (m, 5H), 2.27 (s, 6H), 2.11-1.82 (m, 4H), 1.59 (s, 3H), 1.55-1.37 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.02-0.83 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.2, 144.5, 133.0, 129.7, 103.9, 59.7, 40.1, 35.2, 33.6, 33.5, 33.1, 30.3, 20.6, 19.5, 19.4, 14.5. HRMS (ESI) calcd. for $C_{23}H_{36}ClNO_4^+$ $[M+H]^+$: 390.2639, found: 390.2638. IR (film, υ cm^{-1}): 2929, 1720, 1600, 1444, 1285, 1223, 1105, 1004.

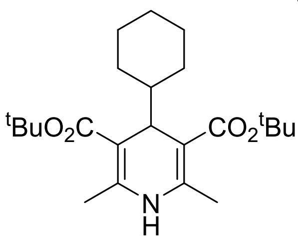
Dimethyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1v)[6]



1v

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.68 (br, 1H), 4.23-4.09 (m, 5H), 2.27 (s, 6H), 2.11-1.82 (m, 4H), 1.59 (s, 3H), 1.55-1.37 (m, 4H), 1.31 (t, *J* = 7.1 Hz, 6H), 1.02-0.83 (m, 6H). ^{13}C NMR(101 MHz, Chloroform-*d*) δ 169.1, 144.8, 101.6, 50.9, 45.6, 38.4, 28.6, 26.7, 26.6, 19.4.

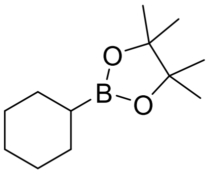
Di-*tert*-butyl 4-cyclohexyl-2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate (1w)[6]



1w

white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.53-5.42 (m, 1H), 3.84 (dd, *J* = 6.1, 1.7 Hz, 1H), 2.26 (s, 6H), 1.66-1.65 (m, 2H), 1.59-1.56 (m, 3H), 1.49 (s, 18H), 1.16-1.08 (s, 4H), 0.98-0.88 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 143.3, 103.3, 79.3, 45.8, 39.0, 29.2, 28.3, 26.8, 26.7, 19.3.

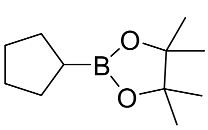
2-Cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[8]



2a

53 mg, 84% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.67-1.58 (m, 5H), 1.38 1.27 (m, 5H), 1.23 (s, 12H), 1.00-0.97 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.7, 27.9, 27.1, 26.7, 24.7.

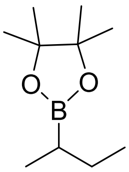
2-Cyclopentyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)[8]



2b

35 mg, 60% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.74 (dd, *J* = 12.0, 7.5 Hz, 2H), 1.61-1.57 (m, 2H), 1.54-1.39 (m, 4H), 1.24 (s, 12H), 1.19-1.15 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.8, 28.5, 26.8, 24.7.

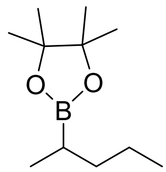
2-(*sec*-Butyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2c)[8]



2c

86% GC-FID yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.24 (s, 12H), 0.96 (s, 3H), 0.92-0.90 (m, 2H), 0.89-0.83 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.7, 26.1, 24.7, 24.7, 15.2, 13.4.

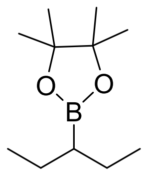
4,4,5,5-Tetramethyl-2-(pentan-2-yl)-1,3,2-dioxaborolane (2d)[9]



2d

38 mg, 64% isolated yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.45-1.39 (m, 1H), 1.35-1.29 (m, 4H), 1.24 (s, 12H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.8, 35.5, 24.7 (d, *J* = 3.0 Hz), 22.2, 15.5, 14.3.

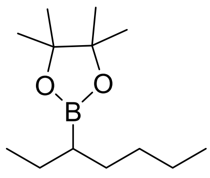
4,4,5,5-Tetramethyl-2-(pentan-3-yl)-1,3,2-dioxaborolane (**2e**)[9]



2e

40 mg, 68% isolated yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.42 (dq, *J* = 13.5, 6.9, 6.3 Hz, 4H), 1.25 (s, 12H), 0.90 (t, *J* = 7.4 Hz, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.8, 24.8, 24.0, 13.7.

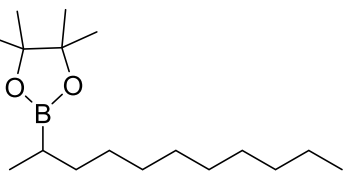
2-(Heptan-3-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2f**)[10]



2f

57 mg, 90% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.46-1.27 (m, 8H), 1.25 (s, 12H), 0.91-0.86 (m, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.8, 31.5, 30.8, 24.8 (d, *J* = 1.6 Hz), 24.3, 23.0, 14.1, 13.0.

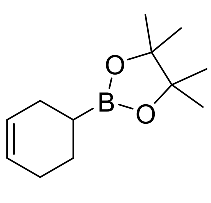
4,4,5,5-Tetramethyl-2-(undecan-2-yl)-1,3,2-dioxaborolane (**2g**)[11]



2g

76 mg, 90% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.46-1.39 (m, 1H), 1.26 (s, 15H), 1.24 (s, 12H), 0.95 (d, *J* = 5.2 Hz, 3H), 0.88 (t, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.7, 33.3, 31.9, 29.9, 29.6 (d, *J* = 4.0 Hz), 29.3, 29.0, 26.9, 24.7 (d, *J* = 3.3 Hz), 22.7, 15.5, 14.1.

2-(Cyclohex-3-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**2h**)[12]

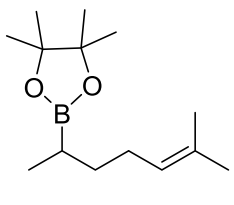


2h

22 mg, 35% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-

d): δ 5.73-5.65 (m, 2H), 2.06-1.98 (m, 4H), 1.79 (dq, *J* = 12.7, 4.5 Hz, 1H), 1.59-1.49 (m, 2H), 1.24 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 127.6, 127.0, 82.9, 26.3, 25.3, 24.8 (d, *J* = 4.4 Hz), 23.9.

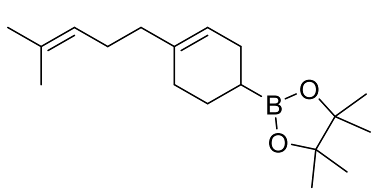
4,4,5,5-Tetramethyl-2-(6-methylhept-5-en-2-yl)-1,3,2-dioxaborolane (2i)[13]



2i

44 mg, 62% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.12 (ddd, *J* = 7.2, 5.7, 1.5 Hz, 1H), 1.98 (q, *J* = 7.7 Hz, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.53-1.44 (m, 1H), 1.31 (dd, *J* = 13.5, 7.4 Hz, 1H), 1.24 (s, 12H), 1.08-1.00 (m, 1H), 0.97 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.1, 125.0, 82.8, 33.4, 27.4, 25.7, 24.7 (d, *J* = 6.1 Hz), 17.6, 15.5.

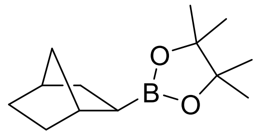
4,4,5,5-Tetramethyl-2-(4-(4-methylpent-3-en-1-yl)cyclohex-3-en-1-yl)-1,3,2-dioxaborolane (2j)[14]



2j

44 mg, 62% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 5.12 (ddd, *J* = 7.2, 5.7, 1.5 Hz, 1H), 1.98 (q, *J* = 7.7 Hz, 2H), 1.67 (s, 3H), 1.60 (s, 3H), 1.53-1.44 (m, 1H), 1.31 (dd, *J* = 13.5, 7.4 Hz, 1H), 1.24 (s, 12H), 1.08-1.00 (m, 1H), 0.97 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 131.1, 125.0, 82.8, 33.4, 27.4, 25.7, 24.7 (d, *J* = 6.1 Hz), 17.6, 15.5.

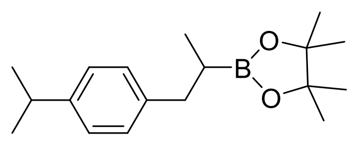
2-((1*R*,2*R*,4*R*)-Bicyclo[2.2.1]heptan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2k)[8]



2k

44 mg, 66% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.29-2.28 (m, 1H), 2.22 (s, 1H), 1.57-1.43 (m, 3H), 1.38-1.31 (m, 1H), 1.26-1.25 (m, 1H), 1.23 (s, 12H), 1.15 (dt, *J* = 9.4, 1.9 Hz, 1H), 0.88 (dd, *J* = 9.4, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.8, 38.7, 38.1, 36.6, 32.2, 32.2, 29.3, 24.7.

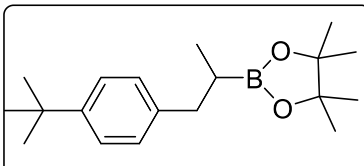
2-(1-(4-Isopropylphenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2l)



2l

74 mg, 86% isolated yield, colorless oil. [1]H NMR (400 MHz, Chloroform-*d*): δ 7.11 (d, *J* = 1.5 Hz, 4H), 2.85 (p, *J* = 6.9 Hz, 1H), 2.76 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.51 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.36 (q, *J* = 7.6 Hz, 1H), 1.22 (d, *J* = 7.0 Hz, 6H), 1.17 (d, *J* = 8.0 Hz, 12H), 0.96 (dd, *J* = 7.4, 1.0 Hz, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 146.0, 139.6, 128.8, 126.0, 82.9, 38.6, 33.7, 24.7 (d, *J* = 3.7 Hz), 24.1 (d, *J* = 1.4 Hz), 15.3. HRMS (ESI) calcd. for $C_{18}H_{30}BO_2^+$ $[M+H]^+$: 289.2339, found: 289.2330. IR (film, υ cm^{-1}): 2958, 1459, 1370, 1316, 1231, 1142, 857, 804.

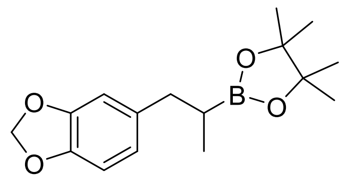
2-(1-(4-(*tert*-Butyl)phenyl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2m)[15]



2m

80 mg, 88% isolated yield, colorless oil. [1]H NMR (400 MHz, Chloroform-*d*): δ 7.26 (d, *J* = 8.3 Hz, 2H), 7.12 (d, *J* = 8.3 Hz, 2H), 2.76 (dd, *J* = 13.6, 7.5 Hz, 1H), 2.52 (dd, *J* = 13.6, 8.4 Hz, 1H), 1.36 (q, *J* = 7.6 Hz, 1H), 1.29 (s, 9H), 1.17 (d, *J* = 9.0 Hz, 12H), 0.97 (d, *J* = 7.4 Hz, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 148.3, 139.2, 128.6, 124.9, 82.9, 38.5, 34.3, 31.5, 24.7 (d, *J* = 5.0 Hz), 15.3.

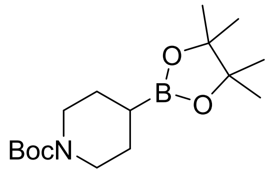
2-(1-(Benzo[*d*][1,3]dioxol-5-yl)propan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)[16]



2n

78 mg, 90% isolated yield, yellow oil. [1]H NMR (400 MHz, Chloroform-*d*): δ 6.69 (d, *J* = 7.8 Hz, 2H), 6.64 (dd, *J* = 7.9, 1.7 Hz, 1H), 5.89 (s, 2H), 2.72 (dd, *J* = 13.6, 7.6 Hz, 1H), 2.46 (dd, *J* = 13.6, 8.2 Hz, 1H), 1.30 (q, *J* = 7.6 Hz, 1H), 1.20 (d, *J* = 3.4 Hz, 12H), 0.95 (d, *J* = 7.4 Hz, 3H). [13]C NMR (101 MHz, Chloroform-*d*) δ 147.3, 145.4, 136.2, 121.6, 109.4, 107.8, 100.6, 83.0, 38.7, 24.7 (d, *J* = 3.4 Hz), 15.1.

***tert*-Butyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)piperidine-1-carboxylate (2o)**[10]

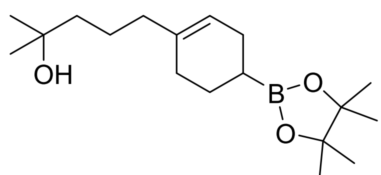


2o

65 mg, 70% isolated yield, colorless oil. [1]H NMR (400 MHz, Chloroform-*d*): δ 3.78 (d, *J* = 13.3 Hz, 2H), 2.96-2.89 (m, 2H), 1.63-

1.61 (m, 2H), 1.46 (s, 1H), 1.44 (s, 9H), 1.27-1.25 (m, 2H), 1.23 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 154. 9, 83.1， 79.0, 29.7, 28.5, 27.0, 24.8.

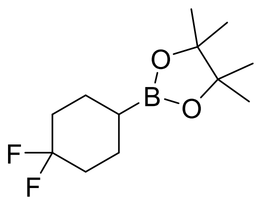
2-Methyl-5-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)cyclohex-1-en-1-yl)pentan-2-ol (2p)



2p

19 mg, 21% isolated yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.29-2.28 (m, 1H), 2.22 (s, 1H), 1.57-1.43 (m, 3H), 1.38-1.31 (m, 1H), 1.26-1.25 (m, 1H), 1.23 (s, 12H), 1.15 (dt, *J* = 9.4, 1.9 Hz, 1H), 0.88 (dd, *J* = 9.4, 6.8 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 138.13, 137.46 (d, *J* = 4.8 Hz), 124.59 (d, *J* = 9.3 Hz), 120.96 (dd, *J* = 52.4, 14.0 Hz), 109.61 (d, *J* = 2.9 Hz), 82.86, 38.13, 37.71 (d, *J* = 5.7 Hz), 37.51 (d, *J* = 9.8 Hz), 28.94 (dd, *J* = 105.7, 10.8 Hz), 26.17 (dd, *J* = 81.1, 11.8 Hz), 24.75 (d, *J* = 2.7 Hz), 22.47 (d, *J* = 4.0 Hz), 17.70 (d, *J* = 3.3 Hz). HRMS (ESI) calcd. for $C_{18}H_{34}BO_3^+$ $[M+H]^+$: 309.2596, found: 309.2595. IR (film, υ cm^{-1}): 2922, 2852, 1729, 1457, 1377, 1072, 720.

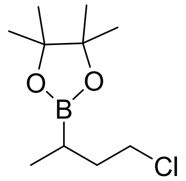
2-(4,4-Difluorocyclohexyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)[10]



2q

52 mg, 71% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.05-1.93 (m, 2H), 1.84-1.58 (m, 6H), 1.24 (s, 12H), 1.04-0.93 (m, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 123.7 (t, *J* = 240.6 Hz), 83.2, 34.4 (t, *J* = 23.4 Hz), 24.7, 24.3.

2-(4-Chlorobutan-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)

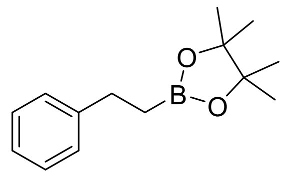


2r

51 mg, 76% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 3.51 (t, *J* = 7.1 Hz, 2H), 1.93-1.81 (m, 1H), 1.67 (dq, *J* = 14.0, 7.0 Hz, 1H), 1.17 (s, 12H), 0.93 (d, *J* = 7.5 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 83.1, 44.5, 35.9, 24.8 (d, *J* = 8.2 Hz), 15.0. HRMS (ESI) calcd. for $C_{10}H_{21}BclO_2^+$ $[M+H]^+$: 219.1319, found: 219.1317. IR (film, υ

cm^{-1}): 2922, 2853, 1727, 1464, 1259, 1093, 1023, 798.

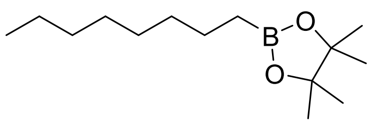
4,4,5,5-Tetramethyl-2-phenethyl-1,3,2-dioxaborolane (2s)[8]



2s

19 mg, 27% isolated yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 7.23 (dd, *J* = 14.6, 7.2 Hz, 4H), 7.17-7.13 (m, 1H), 2.77-2.73 (m, 2H), 1.22 (s, 12H), 1.16-1.12 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.4, 128.2, 128.0, 125.5, 83.1, 30.0, 24.8.

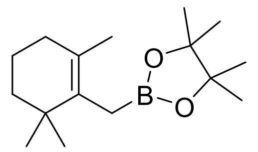
4,4,5,5-Tetramethyl-2-octyl-1,3,2-dioxaborolane (2t)[8]



2t

31% GC-FID yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.41-1.26 (m, 12H), 1.24 (s, 12H), 0.87 (t, *J* = 6.3 Hz, 3H), 0.76 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 82.8, 32.4, 31.9, 29.4, 29.3, 24.8, 24.0, 22.7, 14.1.

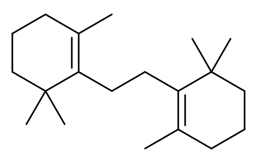
4,4,5,5-Tetramethyl-2-((2,6,6-trimethylcyclohex-1-en-1-yl)methyl)-1,3,2-dioxaborolane (2u)[17]



2u

20 mg, 25% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 1.94 (t, *J* = 6.2 Hz, 2H), 1.59-1.56 (m, 4H), 1.54 (s, 3H), 1.44-1.41 (m, 2H), 1.22 (s, 12H), 0.96 (s, 6H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 133.7, 124.6, 82.8, 39.6, 34.8, 32.7, 28.2, 24.7, 20.3, 19.7.

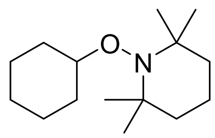
1,2-Bis(2,6,6-trimethylcyclohex-1-en-1-yl)ethane (2u')[18]



2u'

25 mg, 61% isolated yield, white solid. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.06 (s, 4H), 1.94 (t, *J* = 6.3 Hz, 4H), 1.71 (s, 6H), 1.57 (tq, *J* = 6.3, 2.8 Hz, 4H), 1.43-1.40 (m, 4H), 1.05 (s, 12H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.9, 127.3, 40.4, 35.0, 33.3, 29.1, 29.0, 20.6, 19.6.

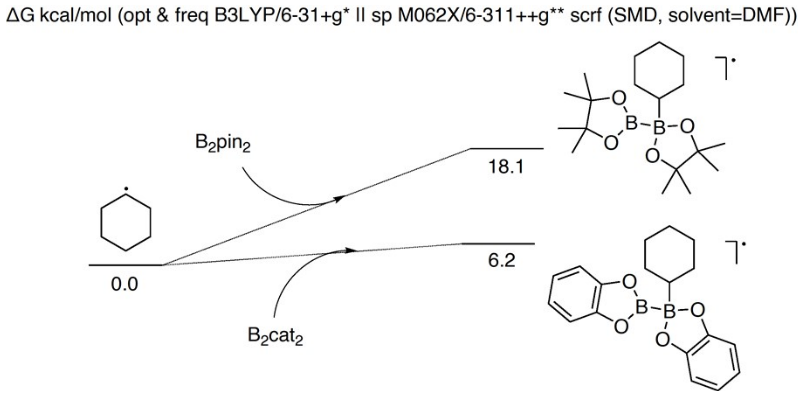
1,2-Bis(2,6,6-trimethylcyclohex-1-en-1-yl)ethane (4)[19]



4

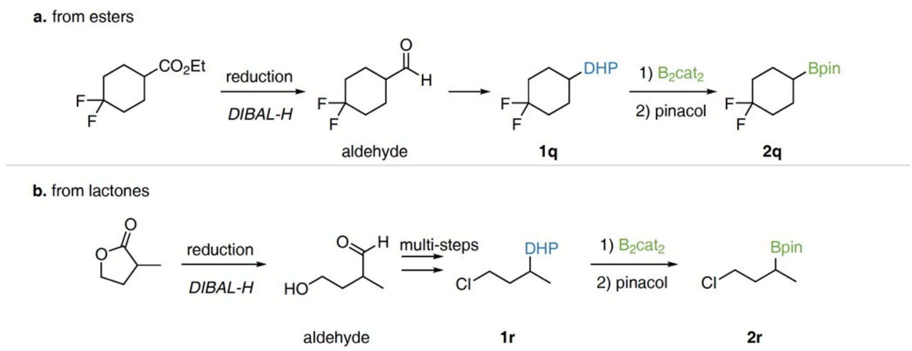
20 mg, 28% isolated yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*): δ 2.05-1.93 (m, 2H), 1.84-1.58 (m, 6H), 1.24 (s, 12H), 1.04-0.93 (m, 1H).

2 Additional mechanism explorations

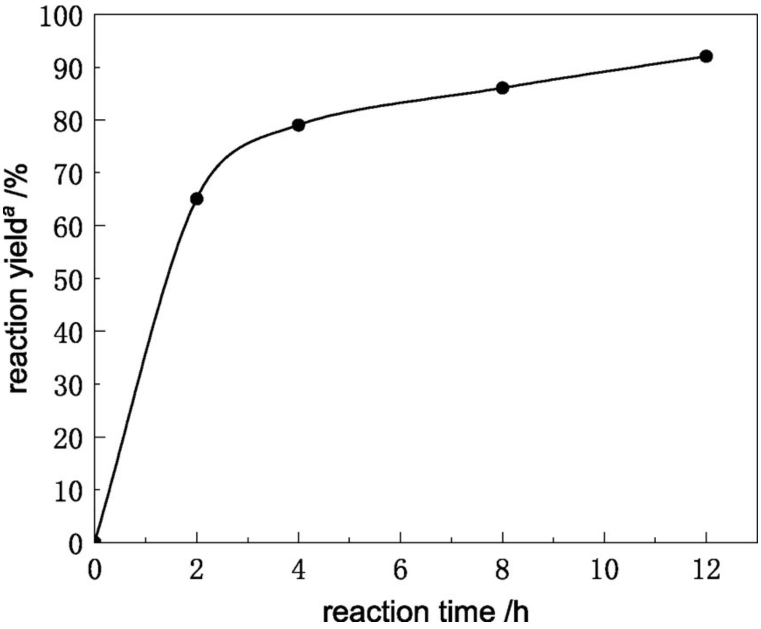


Scheme S1. DFT calculated Gibbs energy change of the reaction between cyclohexyl radical and different diboron reagents.

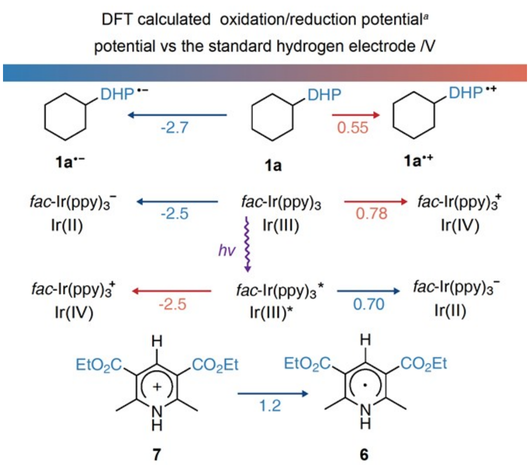
[a] Conditions: the Gibbs free energies were calculated under B3LYP/6-31+g* level for optimization and frequency analysis and M062x/6-311++g** level with an implicit solvation model SMD (solvent = DMF) for single point calculations.



Scheme S2. The pre-conversion of this borylation reaction from (a) esters and (b) lactones.



Scheme S3. The control experiment of reaction time.



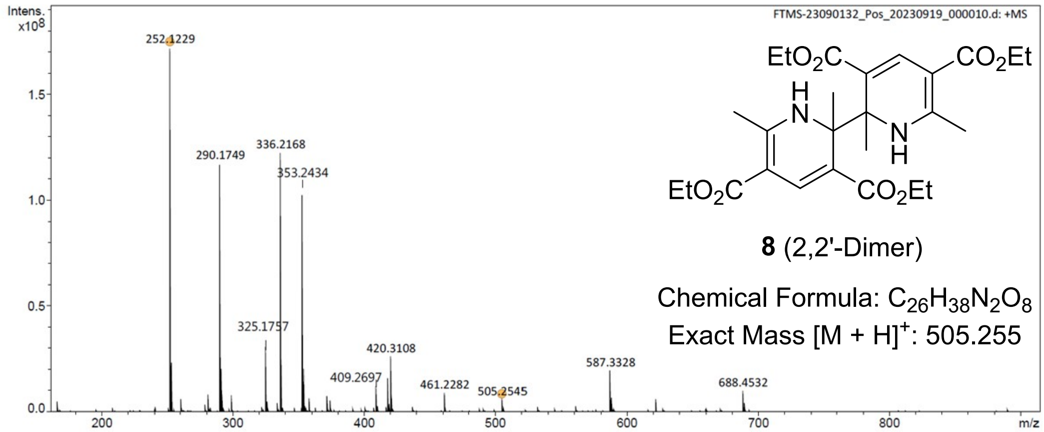
Scheme S4. DFT calculated redox potentials.

[a] Conditions: the Gibbs free energies were calculated under B3LYP/6-31+g* level for optimization and frequency analysis and M062x/6-311++g** level with an implicit solvation model SMD (solvent = DMF) for single point calculations.

Peking University Mass Spectrometry Sample Analysis Report

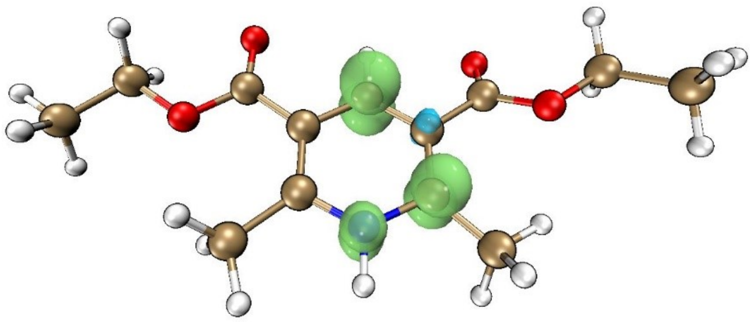
Analysis Info

Analysis Name	FTMS-23090132_Pos_20230919_000010.d	Acquisition Date	9/19/2023 2:32:50 PM
Sample	lc-730	Instrument	Bruker Solarix XR FTMS
Comment		Operator	Peking University



Meas. m/z	#	Ion Formula	Score	m/z	err [ppm]	Mean err [ppm]	mSigma	rdb	e⁻ Conf	N-Rule
252.1229	1	C13H18NO4	100.00	252.1230	0.4	0.2	2.3	6.0	even	ok
505.2545	1	C26H37N2O8	100.00	505.2544	-0.0	-0.2	15.5	10.0	even	ok

Scheme S5. Mass spectrometry of the reaction systems.



Scheme S6. The spin density of **6**.

3 DFT calculations

All density functional theory (DFT) calculations were performed with Gaussian 09w[20] and supported by National Supercomputing Center in Shenzhen. All geometry optimizations and vibrational frequency analysis were computed at the B3LYP level of theory with 6-31+G* basis set.

On the basis of the gas phase optimized structures, the single point (SP) energies were calculated with the M062X functional and basis set of 6-311++G** basis set, and solvent energy corrections were calculated using the SMD model with DMF as the solvent. All time dependent DFT (TD-DFT) calculations were completed at the B3LYP /6-311+G** level with a SMD solvation model. For iridium atoms, a basis set of SDD potential function was applied.

Table S1. Energies and lowest frequencies.

species	TCG	sp	G	lowest Freq/nm
1a	0.403875	-1097.011032	-1096.607157	20.19
1a$^{\cdot +}$	0.401816	-1096.825547	-1096.423731	16.78
cyclohexyl radical	0.124925	-235.149328	-235.024403	73.34
7	0.250578	-861.658481	-861.407903	17.37
B2cat2	0.146094	-812.80245	-812.656356	23.17
cyclohexyl B_2CAT_2 radical	0.294709	-1047.965446	-1047.670737	14.79
cyclohexyl Bcat	0.214056	-641.629342	-641.415286	22.36
BcatDMF radical	0.156213	-654.859956	-654.703743	29.03
DMF	0.07346	-248.482303	-248.408843	106.86
6	0.244092	-861.771323	-861.527231	19.22
8	0.525904	-1723.610699	-1723.084795	13.76
Ir(III)	0.422268	-1540.370405	-1539.948137	33.38
Ir(III)*	0.420909	-1540.249792	-1539.828883	19.74
Ir(II)	0.414269	-1540.432067	-1540.017798	27.74
TS_B2cat2cyDMF_rad	0.390785	-1296.474188	-1296.083403	-390.05
B_2pin_2	0.316703	-822.44382	-822.127117	12.50
cyclohexyl B_2pin_2 radical	0.467012	-1057.589652	-1057.12264	13.80

Table S2. Energies and lowest frequencies (Scheme S4).

species	TCG	sp	G	lowest Freq
Ir(IV)	0.421076	-1540.177123	-1539.756047	23.97
1a$^{\cdot -}$	0.397795	-1097.068934	-1096.671139	27.38

Table S3. TD-DFT energies (Scheme 6b).

species	T1/eV	S1/eV
Ir(III)	2.7205	3.0167
1a	3.1446	4.1939

Cartesian coordinates of the structures

1a

C	-1.91354500	-1.48864600	-0.95118900
C	-1.31186000	-0.35566900	-0.47251500
C	0.16278900	-0.23941500	-0.88639500
H	0.12573900	-0.35215000	-1.98551600
C	0.84510900	-1.54224500	-0.43817900
C	0.22467800	-2.66065500	-0.90098000
N	-1.05396100	-2.47212200	-1.45494400
H	-1.50202500	-3.30793900	-1.80945900
C	-1.95171000	0.57983900	0.46679200
C	2.00102600	-1.65360900	0.47884100
O	-1.35011500	1.33554900	1.21416300
O	2.88985600	-2.49197500	0.41906600
O	-3.31646400	0.53039400	0.45756200
O	1.95586700	-0.71675800	1.45548800
C	-3.98600100	1.40465000	1.39492200
H	-3.65111800	1.15834200	2.40792500
H	-3.68805200	2.43769300	1.18857800

C	-5.48158800	1.20354700	1.22646500
H	-5.76946100	0.16816400	1.44020200
H	-6.02137500	1.85844600	1.92067300
H	-5.80083200	1.44859300	0.20736800
C	3.03634300	-0.73202200	2.41727700
H	3.98282300	-0.58855400	1.88430800
H	3.06824100	-1.71756200	2.89324600
C	2.77119500	0.37627100	3.42011000
H	3.56796700	0.38853300	4.17343000
H	2.74455300	1.35497300	2.92966200
H	1.81412500	0.22338900	3.92984800
C	0.90545200	1.10144700	-0.69165500
H	0.93953700	1.35094100	0.37064400
C	2.35884800	1.00793400	-1.24601400
H	3.02145800	0.61161300	-0.46901400
H	2.39494600	0.28921200	-2.07739800
C	0.18313000	2.24637200	-1.43226000
H	0.25340000	2.06237300	-2.51547600
H	-0.88422000	2.27008100	-1.19565500
C	2.91726800	2.36937900	-1.72962700
H	2.66374900	2.52866500	-2.78734300
H	4.01362100	2.35800300	-1.67865900
C	0.80913300	3.61667900	-1.08915400
H	0.57102600	4.33000500	-1.88998700
H	0.34782600	4.00935800	-0.17412300
C	2.34342200	3.52645600	-0.90203400
H	2.81959400	4.47654200	-1.17632000
H	2.58188100	3.35760300	0.15764400
C	0.66649800	-4.09539900	-0.82214100

H	1.67991500	-4.16839600	-0.42986200
H	-0.01139100	-4.68566600	-0.18972400
H	0.65651500	-4.54447700	-1.82557900
C	-3.36957400	-1.88069900	-0.94962400
H	-3.67645400	-2.26036900	0.03332500
H	-4.01617400	-1.03797600	-1.19088300
H	-3.54490700	-2.67755100	-1.68331800

1a$^{\cdot+}$

C	0.92646400	2.07529100	1.28484800
C	1.24326200	1.14986700	0.30554400
C	0.20628700	0.19288200	-0.16053600
H	0.39871400	-0.14183300	-1.18133500
C	-1.18445900	0.71159100	-0.03206300
C	-1.47630100	1.64241700	0.94593300
N	-0.40242700	2.18463200	1.61935700
H	-0.62397200	2.85714100	2.34888700
C	2.63170500	1.10774700	-0.25418400
C	-2.17703100	0.20265000	-1.03388900
O	3.59064500	1.63674900	0.27910600
O	-1.81189900	-0.24864500	-2.10337900
O	2.67015500	0.44949800	-1.41606400
O	-3.45158000	0.30965500	-0.64697400
C	3.97015600	0.37538200	-2.08967800
H	4.33002700	1.39832700	-2.23061600
H	4.66240800	-0.14312600	-1.41998000
C	3.76575800	-0.35533100	-3.40030800
H	3.05868400	0.17602300	-4.04536500

H	4.72443600	-0.42176700	-3.92638800
H	3.39635600	-1.37300800	-3.23709200
C	-4.46476000	-0.15338800	-1.60454100
H	-4.24933800	-1.20031600	-1.83433600
H	-4.34675000	0.43145500	-2.52086000
C	-5.82388300	0.03296200	-0.96314500
H	-6.59716600	-0.31154600	-1.65843600
H	-5.91325300	-0.55058900	-0.04097700
H	-6.01926000	1.08621500	-0.73618500
C	0.30943300	-1.19456900	0.76333000
H	0.05110900	-0.85214900	1.77424500
C	-0.72066000	-2.24123500	0.28137700
H	-1.70671700	-1.99460900	0.69588400
H	-0.81733000	-2.20243900	-0.80892300
C	1.71544800	-1.80277300	0.79758100
H	1.95661400	-2.20951800	-0.19203000
H	2.48569200	-1.06243400	1.03155500
C	-0.32733000	-3.68386500	0.69510000
H	0.29314400	-4.13720700	-0.08878300
H	-1.23460100	-4.29550300	0.75824700
C	1.77384200	-2.92412600	1.87497100
H	2.58206300	-3.61150300	1.59818500
H	2.05746500	-2.48655400	2.83997900
C	0.44283500	-3.69613800	2.01854100
H	0.63725900	-4.72445800	2.34244500
H	-0.17799000	-3.24207600	2.80370700
C	-2.82259400	2.18393100	1.34413200
H	-3.32008600	2.65465700	0.49126400
H	-3.47941500	1.38453600	1.69525300

H	-2.72596400	2.93218700	2.13746800
C	1.85949500	3.01152900	1.99964000
H	2.64843100	2.46002500	2.51663500
H	2.36454900	3.67349300	1.28938200
H	1.31730500	3.62715400	2.72524200

cyclohexyl radical

C	0.39025100	-1.37807200	0.26930000
H	0.61683000	-2.36233900	0.67288900
C	1.48849500	-0.36824700	0.11714300
H	1.98161600	-0.19792200	1.09024400
H	2.28900400	-0.74770200	-0.54417600
C	-0.95696200	-1.08422900	-0.31011200
H	-0.90090400	-1.13541000	-1.41495700
H	-1.68467400	-1.85126300	-0.02009200
C	0.94791200	0.97095000	-0.42093400
H	0.74457600	0.88738100	-1.49840700
H	1.70608600	1.75611900	-0.30825700
C	-1.48153100	0.33025900	0.07868000
H	-2.14723300	0.68964000	-0.71710000
H	-2.09605700	0.25278900	0.98409100
C	-0.34202200	1.35372000	0.32107200
H	-0.67201800	2.35880200	0.02945500
H	-0.11407800	1.40361600	1.39541200

7

C	1.22492800	1.35515600	0.00016300
C	1.23010900	-0.04415100	0.00026200

C	-0.00001000	-0.71140200	0.00023900
H	-0.00003000	-1.79789200	0.00021800
C	-1.23011100	-0.04416700	0.00021300
C	-1.22492900	1.35514300	0.00021100
N	-0.00000200	1.95442200	0.00020100
H	0.00000200	2.97186600	0.00020100
C	2.45964200	-0.92775100	0.00024700
C	-2.45963700	-0.92776300	0.00019100
O	2.36149300	-2.13520400	-0.00003500
O	-2.36147800	-2.13521500	0.00061000
O	3.60497500	-0.24443900	0.00056700
O	-3.60496200	-0.24444600	-0.00040200
C	4.83956700	-1.04733000	0.00028100
H	4.81581000	-1.68462500	0.88793600
H	4.81460800	-1.68607100	-0.88628100
C	6.01161900	-0.08935600	-0.00124000
H	6.01020000	0.54741100	0.88962000
H	6.94261800	-0.66659800	-0.00130300
H	6.00911100	0.54587100	-0.89319800
C	-4.83956600	-1.04732300	-0.00054800
H	-4.81529700	-1.68540200	0.88652000
H	-4.81512300	-1.68528900	-0.88769500
C	-6.01160700	-0.08934200	-0.00059600
H	-6.94260900	-0.66658100	-0.00073500
H	-6.00973100	0.54658000	0.89086800
H	-6.00955600	0.54673300	-0.89194900
C	-2.40538900	2.27969700	0.00041600
H	-3.03322900	2.10203600	-0.87703600
H	-3.03383600	2.10087200	0.87716700

H	-2.08838600	3.32730300	0.00119000
C	2.40536600	2.27974000	-0.00016900
H	3.03353400	2.10186900	0.87697500
H	3.03349700	2.10115800	-0.87722800
H	2.08833200	3.32733500	-0.00061400

B_2cat_2

C	-2.94143900	0.69761900	-0.00047100
C	-2.94143800	-0.69761900	-0.00052500
C	-4.11511900	-1.43445900	-0.00074600
C	-5.31160500	-0.70157500	-0.00091200
C	-5.31160600	0.70157300	-0.00085800
C	-4.11512000	1.43445900	-0.00063400
H	-4.10272600	-2.51972500	-0.00078600
H	-6.25829000	-1.23447700	-0.00108800
H	-6.25829200	1.23447300	-0.00099300
H	-4.10272900	2.51972400	-0.00059100
C	2.94143900	-0.69761900	0.00046900
C	2.94143800	0.69761900	0.00052300
C	4.11512000	-1.43445900	0.00064000
C	4.11511900	1.43445900	0.00075000
C	5.31160600	-0.70157300	0.00086900
H	4.10272900	-2.51972400	0.00059700
C	5.31160500	0.70157500	0.00092300
H	4.10272600	2.51972500	0.00079000
H	6.25829200	-1.23447300	0.00100900
H	6.25829000	1.23447700	0.00110400
B	-0.84340400	0.00000300	-0.00014900
B	0.84340400	-0.00000300	0.00012700

O	1.63583300	-1.14455800	0.00023200
O	1.63583200	1.14455500	0.00032100
O	-1.63583200	-1.14455500	-0.00032700
O	-1.63583300	1.14455800	-0.00023800

cyclohexyl B_2cat_2 radical

C	3.15697100	-0.57863500	0.67275200
C	3.30922500	-0.12132100	-0.63644000
C	4.55367800	-0.00121900	-1.23317500
C	5.66202500	-0.36310700	-0.45045300
C	5.50911200	-0.82108100	0.86580500
C	4.24075100	-0.93818500	1.45705400
H	4.66056300	0.35482400	-2.25302700
H	6.65865800	-0.28532000	-0.87610400
H	6.38919800	-1.09215400	1.44240600
H	4.11024700	-1.29183900	2.47499500
C	-1.96092300	-1.70420000	-0.76649700
C	-2.08022500	-1.39189900	0.62079100
C	-2.69512000	-2.75061000	-1.34269500
C	-2.93809700	-2.11807200	1.45895400
C	-3.54327700	-3.46341100	-0.50259700
H	-2.59539600	-2.98149100	-2.39835300
C	-3.66250900	-3.15227500	0.87683400
H	-3.02002500	-1.87415300	2.51318800
H	-4.13119400	-4.28185600	-0.90851900
H	-4.33813000	-3.74112000	1.49086800
B	1.14547900	-0.13611700	-0.14927200
B	-0.57040700	0.06460900	-0.30812700

O	-1.09587300	-0.89243600	-1.35068700
O	-1.29284600	-0.37753600	0.93567400
O	2.06314800	0.16033300	-1.15970600
O	1.81262000	-0.59389700	0.98839500
C	-0.93822300	1.63364200	-0.70634500
H	-0.48578300	1.77099000	-1.69877200
C	-0.27773400	2.64033500	0.26547400
H	-0.36757500	2.29349000	1.30504300
H	0.79752500	2.70569300	0.05473000
C	-2.47174700	1.87496900	-0.82246800
H	-2.67376800	2.48669200	-1.71503100
H	-3.01456100	0.93498600	-0.98901800
C	-3.03812100	2.59330700	0.41132500
H	-4.13056500	2.67396800	0.33698100
H	-2.83520000	1.98164800	1.30025800
C	-0.92795300	4.02865300	0.14554600
H	-0.85491000	4.35850400	-0.90053600
H	-0.37030100	4.76523500	0.73833700
C	-2.41265000	3.99566100	0.58805900
H	-2.98360200	4.73361200	0.00849300
H	-2.49804100	4.29879900	1.64010000

cyclohexyl Bcat

B	-0.05805300	-0.12804300	-0.24115300
C	3.09556800	1.38500700	0.50534000
C	4.34297700	0.75295900	0.37408100
C	4.44789100	-0.56982900	-0.07725300
C	3.31013100	-1.31976700	-0.41749100

C	2.08719800	-0.68408300	-0.28223500
C	1.98297800	0.63316600	0.16696400
H	3.00273900	2.40894500	0.85335800
H	5.24439300	1.30345300	0.62847000
H	5.42932000	-1.02708000	-0.16690900
H	3.37966600	-2.34445800	-0.76874300
O	0.82179800	-1.17023100	-0.54319200
O	0.65032900	0.99305500	0.19566200
C	-1.61644300	-0.23144900	-0.33859200
H	-1.83863900	-1.00004100	-1.09451900
C	-2.29977800	1.10317200	-0.76102600
H	-1.74102800	1.95641300	-0.35700600
H	-2.24879900	1.19320100	-1.85459200
C	-2.22931900	-0.73462800	0.99838600
H	-1.68773000	-1.61214300	1.37347200
H	-2.10591700	0.05015100	1.75729600
C	-3.73012600	-1.07919700	0.83058800
H	-3.83763900	-2.13691300	0.55604700
H	-4.23437600	-0.95888200	1.79895200
C	-3.77559200	1.19264300	-0.29981000
H	-3.82867500	1.65604800	0.69574500
H	-4.33704500	1.85274700	-0.97300100
C	-4.42274100	-0.19695800	-0.23542100
H	-5.49572900	-0.11788800	-0.02008400
H	-4.34374700	-0.67215000	-1.22367600

BcatDMF radical

C	-2.87676600	1.52563300	-0.10991900

C	-1.81154000	0.64563900	-0.04322900
C	-1.99453500	-0.73649100	0.05434200
C	-3.25508100	-1.30671100	0.09000300
C	-4.34748800	-0.42497200	0.02334500
C	-4.16294800	0.95970500	-0.07439800
H	-2.72137700	2.59718400	-0.18581800
H	-3.38647000	-2.38146400	0.16541000
H	-5.35547100	-0.82945300	0.04804400
H	-5.02958700	1.61290700	-0.12405800
O	-0.76372600	-1.36074500	0.10226400
O	-0.45637200	0.92530400	-0.05780600
B	0.16481100	-0.32245600	0.03506700
O	1.49469400	-0.54165400	0.06845900
C	2.43141400	0.47289200	-0.10568600
N	3.72718000	0.08656900	0.22259100
C	4.71126700	1.15834200	0.15138000
H	5.62123000	0.84475100	0.67248200
H	4.97281500	1.41899300	-0.88846100
H	4.32183300	2.05285100	0.64756900
C	4.19964400	-1.19069600	-0.30693800
H	3.44137500	-1.95789000	-0.14483300
H	4.41913400	-1.12906800	-1.38719900
H	5.11282700	-1.47789100	0.22354800
H	2.12880100	1.45208200	0.26310500

DMF

O	1.95781700	-0.09395200	0.00001100
C	0.86558600	-0.64685800	0.00001300

N	-0.34550600	-0.01996800	-0.00019100
C	-1.59158100	-0.76503000	0.00002700
H	-2.18889500	-0.52809200	0.89070700
H	-2.18929700	-0.52803700	-0.89036800
H	-1.37962300	-1.83823200	-0.00008400
C	-0.42702700	1.43269600	0.00004600
H	0.58674100	1.83568300	0.00097200
H	-0.96033100	1.78726700	-0.89177400
H	-0.96191600	1.78678100	0.89110500
H	0.76745900	-1.74882600	0.00018300

6

C	-1.23994600	1.37317300	-0.22133300
C	-1.24774700	-0.01695700	-0.24036200
C	-0.04577600	-0.74107100	-0.17174800
H	-0.05788900	-1.82114500	-0.20773400
C	1.22749400	-0.05736200	-0.05019800
C	1.23955400	1.32206500	-0.01828900
N	0.03408600	1.98144700	-0.11049700
H	0.05527000	2.99160400	-0.09239000
C	-2.49320900	-0.84496300	-0.34253900
C	2.42204500	-0.91979500	0.03526300
O	-2.52623000	-1.95299000	-0.84097700
O	2.36880800	-2.14024900	0.03908700
O	-3.58154800	-0.26444000	0.21832900
O	3.60912900	-0.25099800	0.10666500
C	-4.80460600	-1.04307600	0.18364700
H	-5.05567400	-1.25314800	-0.86111100

H	-4.61958300	-1.99963000	0.68204100
C	-5.88367600	-0.23571900	0.88156500
H	-6.06252500	0.71623600	0.36951800
H	-6.82175100	-0.80310400	0.88481800
H	-5.60688500	-0.02380800	1.91995400
C	4.79140000	-1.08000000	0.18856000
H	4.81840100	-1.74075000	-0.68380400
H	4.71792300	-1.71016300	1.08088200
C	5.99753400	-0.15927200	0.24126900
H	6.91440000	-0.75709900	0.30462200
H	6.05817700	0.46498000	-0.65717800
H	5.95702100	0.49741600	1.11752300
C	2.43232900	2.23471800	0.10542000
H	3.00712500	2.01536600	1.00856900
H	3.11429200	2.11082900	-0.74040000
H	2.11391100	3.28279200	0.14308700
C	-2.35906600	2.35856200	-0.34805800
H	-3.30757600	1.86634600	-0.55138500
H	-2.48453300	2.94801000	0.57498800
H	-2.15796300	3.07273900	-1.16252700

8

C	-0.24711600	1.70167400	-1.38407700
C	-0.98112300	0.65130700	-1.93382800
C	-0.27553100	-0.57756100	-2.14322500
H	-0.77622800	-1.34105800	-2.73045600
C	0.97590300	-0.84128200	-1.67097300
C	1.72414700	0.18905200	-0.81711700

N	1.02316800	1.47490200	-0.99836000
H	1.52922600	2.26117900	-0.60782100
C	-2.38109600	0.69006300	-2.37674000
C	1.53741400	-2.15209500	-2.04771000
O	-2.95804500	-0.26052600	-2.88680000
O	1.11462200	-2.87977600	-2.93038600
O	-3.00914500	1.87827200	-2.15897400
O	2.60179200	-2.53981000	-1.26298800
C	-4.40065100	1.94068600	-2.54998800
H	-4.47304500	1.74598500	-3.62502100
H	-4.94695400	1.14778000	-2.02956900
C	-4.91961300	3.32005100	-2.18509400
H	-4.36428300	4.10469500	-2.71108200
H	-5.97595400	3.40197100	-2.46725500
H	-4.83827200	3.49989400	-1.10755000
C	3.23084300	-3.79349400	-1.63309300
H	3.54594600	-3.72625700	-2.67892800
H	2.48805500	-4.59434600	-1.56277800
C	4.40601900	-4.02302100	-0.69973300
H	4.90243100	-4.96433400	-0.96289100
H	5.14271700	-3.21621900	-0.78050700
H	4.08233800	-4.09342300	0.34499600
C	3.15109200	0.43081600	-1.36353900
H	3.62160700	1.28232700	-0.86294900
H	3.79116200	-0.44128000	-1.23763800
H	3.08427300	0.65624500	-2.43276200
C	-0.71785800	3.12111100	-1.20458900
H	-1.15516300	3.51331800	-2.12467100
H	-1.49633900	3.16630900	-0.43656600

H	0.10953900	3.76885900	-0.89661000
C	1.72370000	-0.18913100	0.81731500
C	0.97525100	0.84135400	1.67081400
C	-0.27630000	0.57773600	2.14283500
H	-0.77707600	1.34130600	2.72990100
C	-0.98192100	-0.65111400	1.93345900
C	-0.24794900	-1.70151800	1.38374200
N	1.02236700	-1.47485100	0.99810800
H	1.52842300	-2.26119700	0.60770400
C	1.53676000	2.15214400	2.04764100
C	-2.38188000	-0.68987600	2.37641200
O	1.11353200	2.88009500	2.92988700
O	-2.95882800	0.26064900	2.88657700
O	2.60178300	2.53945700	1.26359300
O	-3.00995200	-1.87805400	2.15847400
C	3.23089100	3.79304500	1.63393800
H	2.48826600	4.59402400	1.56335400
H	3.54558100	3.72574300	2.67989400
C	4.40647700	4.02238200	0.70104600
H	4.08321500	4.09286100	-0.34380700
H	4.90295400	4.96360200	0.96441200
H	5.14300000	3.21544700	0.78208900
C	-4.40144700	-1.94047600	2.54953200
H	-4.94779200	-1.14765100	2.02903500
H	-4.47381700	-1.74566700	3.62454900
C	-4.92035500	-3.31990200	2.18479200
H	-5.97670100	-3.40181700	2.46693800
H	-4.83898100	-3.49987100	1.10727300
H	-4.36501300	-4.10446300	2.71089200

C	-0.71886800	-3.12087300	1.20405400
H	-1.15605900	-3.51320500	2.12414500
H	-1.49750200	-3.16583300	0.43617400
H	0.10839300	-3.76865900	0.89580100
C	3.15033200	-0.43116700	1.36443500
H	3.62100900	-1.28264500	0.86393500
H	3.79056300	0.44088200	1.23902800
H	3.08293800	-0.65678100	2.43358300

Ir(III)

Ir	0.00000000	0.00000000	0.02331900
C	-0.87359000	2.81896200	-0.59332000
C	0.00000000	2.89924300	0.58252800
C	0.52569200	1.66503500	1.07082500
C	-1.51551200	3.90988800	-1.21005900
N	-1.05300600	1.56163100	-1.09388700
C	0.29972800	4.12379200	1.21271300
C	1.35465900	1.74157900	2.20907900
C	1.12162600	4.15797300	2.33390800
C	-3.38429000	-0.05141400	2.83069800
C	-2.51081800	-1.44962100	0.58252800
C	-2.18558100	0.30237900	2.20907900
C	-1.70480900	-0.37725500	1.07082500
N	1.87891500	0.13111400	-1.09388700
C	2.87808700	-0.65293000	-0.59332000
C	0.83092200	-2.04395900	2.20907900
C	1.17911600	-1.28778000	1.07082500
C	2.51081800	-1.44962100	0.58252800

C	-3.72117200	-1.80232400	1.21271300
C	-4.16172300	-1.10762900	2.33390800
C	1.73667100	-2.90517400	2.83069800
C	3.42144400	-2.32146800	1.21271300
C	3.04009700	-3.05034300	2.33390800
C	1.64761900	2.95658800	2.83069800
C	-2.32782800	3.70908000	-2.31881700
C	-1.84609000	1.37199000	-2.16322200
C	-2.00449800	-2.16603200	-0.59332000
C	2.11122300	0.91276600	-2.16322200
C	4.14381800	-0.64247300	-1.21005900
C	-2.50143200	2.41111700	-2.81281200
C	-2.62830700	-3.26741600	-1.21005900
N	-0.82590900	-1.69274500	-1.09388700
C	3.33880500	0.96074500	-2.81281200
C	4.37607100	0.16141800	-2.31881700
C	-2.04824300	-3.87049800	-2.31881700
C	-0.26513300	-2.28475600	-2.16322200
C	-0.83737300	-3.37186200	-2.81281200
H	-1.37900700	4.90948900	-0.81315000
H	-0.10759800	5.05720700	0.83159500
H	1.77361700	0.82872400	2.62266700
H	1.34975400	5.10441400	2.81738500
H	-3.71726600	0.49798400	3.70946000
H	-1.60450400	1.12163500	2.62266700
H	-0.16911300	-1.95035900	2.62266700
H	-4.32587100	-2.62178600	0.83159500
H	-5.09542900	-1.38328600	2.81738500
H	1.42736600	-3.46823900	3.70946000

H	4.43346900	-2.43542100	0.83159500
H	3.74567500	-3.72112800	2.81738500
H	2.28990000	2.97025500	3.70946000
H	-2.82456300	4.55231700	-2.79170200
H	-1.95138400	0.34391900	-2.49491900
H	1.27353500	1.51798800	-2.49491900
H	4.94124600	-1.26049000	-0.81315000
H	-3.13208700	2.20508800	-3.67178600
H	-3.56223900	-3.64900000	-0.81315000
H	3.47570500	1.60992300	-3.67178600
H	5.35470300	0.16998500	-2.79170200
H	-2.53014000	-4.72230200	-2.79170200
H	0.67784900	-1.86190800	-2.49491900
H	-0.34361900	-3.81501000	-3.67178600

Ir(III)*

Ir	-0.00873400	-0.00553800	-0.09791200
C	2.89893900	-0.43704300	0.58424600
C	2.87179200	0.41050500	-0.59857100
C	1.57849900	0.79033000	-1.09400700
C	4.06249700	-0.86975300	1.25801800
N	1.66116600	-0.81574300	1.06219300
C	4.04081200	0.88949800	-1.23604300
C	1.52600800	1.67287900	-2.18878000
C	3.94912800	1.73801200	-2.33585600
C	0.48206600	-3.39664900	-2.83734000
C	-1.09073000	-2.70289800	-0.60969800
C	0.67063400	-2.16277200	-2.20283600

C	-0.11302800	-1.77176600	-1.10111700
N	-0.12831500	1.85207700	1.05359100
C	-1.06245700	2.74150400	0.56569600
C	-2.22827200	0.48927100	-2.19059800
C	-1.48250400	0.97548600	-1.10046300
C	-1.78071200	2.29544800	-0.61826800
C	-1.27199700	-3.94720700	-1.25755200
C	-0.49664300	-4.28707600	-2.36254800
C	-3.19663800	1.27556700	-2.82656100
C	-2.75964300	3.08157400	-1.26991500
C	-3.45579600	2.57788500	-2.36508000
C	2.68958400	2.13713600	-2.81455900
C	3.96267700	-1.68979800	2.37004000
C	1.57341600	-1.62022900	2.13884400
C	-1.83165600	-2.31016200	0.57829900
C	0.60896400	2.17734100	2.13247500
C	-1.26192200	3.97184900	1.22973400
C	2.68622200	-2.08543100	2.82337000
C	-2.77014000	-3.11318000	1.26306500
N	-1.55040400	-1.04533400	1.05059800
C	0.46565800	3.38122500	2.80668700
C	-0.50325900	4.29580600	2.34265300
C	-3.42537600	-2.62281400	2.38078800
C	-2.19733800	-0.57334300	2.13356000
C	-3.14224000	-1.31441000	2.82771700
H	5.03887400	-0.55880700	0.90204200
H	5.02383300	0.59922500	-0.87531800
H	0.56131400	1.98484100	-2.57968300
H	4.85576600	2.09399200	-2.81975500

H	1.08950500	-3.66253000	-3.69980400
H	1.42176400	-1.48217700	-2.59398200
H	-2.03102200	-0.50906000	-2.57137300
H	-2.02097600	-4.64890600	-0.90016000
H	-0.64934500	-5.24450100	-2.85547400
H	-3.74353400	0.87973800	-3.67962200
H	-2.97651100	4.08800500	-0.92206700
H	-4.20335000	3.19427600	-2.85909700
H	2.61675200	2.80296500	-3.67186700
H	4.85934400	-2.02330200	2.88541300
H	0.56952600	-1.88746700	2.45273000
H	1.33119600	1.43557200	2.45761500
H	-2.01381600	4.66397100	0.86564300
H	2.56154000	-2.73484900	3.68382700
H	-2.97332500	-4.11956100	0.91250900
H	1.08838100	3.59733400	3.66883900
H	-0.65540600	5.24381900	2.85160800
H	-4.14787400	-3.24137000	2.90635800
H	-1.93384800	0.43262100	2.44413800
H	-3.63904700	-0.88607600	3.69229900

Ir(II)

Ir	0.00101400	-0.00199400	-0.05256600
C	0.90588800	-2.79943600	0.60528300
C	1.62184400	-2.40456100	-0.59893100
C	1.35440500	-1.08831000	-1.10148200
C	1.05813400	-4.01846900	1.29625500
N	0.01702100	-1.85826500	1.08871600

C	2.53485200	-3.25845100	-1.25638800
C	2.06002700	-0.70328800	-2.25761600
C	3.20345600	-2.83954300	-2.39893900
C	-2.83557700	-1.76744500	-2.90433800
C	-2.89251600	-0.19151700	-0.59389100
C	-1.64570100	-1.41824500	-2.26076100
C	-1.62125200	-0.62115600	-1.10013900
N	1.59754500	0.93845800	1.09339900
C	1.97088800	2.17916400	0.61318300
C	-0.41668300	2.13906600	-2.25335500
C	0.26844100	1.71671600	-1.09808500
C	1.27531500	2.60395100	-0.59256000
C	-4.09055900	-0.54287100	-1.25438200
C	-4.06681600	-1.32340200	-2.40256500
C	-0.13252000	3.34880600	-2.89201400
C	1.56122900	3.82221700	-1.24759900
C	0.86581800	4.19511600	-2.39015100
C	2.96635100	-1.55147300	-2.89861300
C	0.31184600	-4.29163700	2.43069400
C	-0.71142900	-2.13706200	2.18412800
C	-2.87193200	0.61432000	0.61808500
C	2.19716200	0.44635800	2.19204100
C	2.94747000	2.91976600	1.30936000
C	-0.61051900	-3.32635900	2.88900300
C	-4.00101000	1.08449600	1.31879000
N	-1.61056700	0.90775000	1.09939200
C	3.17246300	1.12805500	2.90291200
C	3.55050200	2.40959200	2.44710600
C	-3.85930200	1.85492400	2.46106700

C	-1.48264000	1.66685300	2.20199800
C	-2.56006800	2.16657900	2.91675200
H	1.77174800	-4.74983800	0.92999000
H	2.71715400	-4.26250100	-0.87772000
H	1.88555000	0.28638100	-2.66988500
H	3.90348700	-3.50733800	-2.89795400
H	-2.80542600	-2.38525100	-3.80102800
H	-0.70388900	-1.76696100	-2.67483800
H	-1.18874500	1.49646600	-2.66651300
H	-5.04905900	-0.19427700	-0.87407400
H	-4.99671800	-1.58559200	-2.90411600
H	-0.68816000	3.63400100	-3.78452400
H	2.34018700	4.48022400	-0.86668800
H	1.09632600	5.13579600	-2.88716100
H	3.48875300	-1.21076300	-3.79172500
H	0.43646000	-5.23545000	2.95624000
H	-1.40036500	-1.35644700	2.49258600
H	1.86426000	-0.54087500	2.49820700
H	3.22553900	3.90365800	0.94485200
H	-1.23277600	-3.49690700	3.76201200
H	-4.99252300	0.83489700	0.95430400
H	3.62617100	0.67404900	3.77841200
H	4.30270600	2.98895900	2.97722800
H	-4.73653500	2.21286800	2.99478300
H	-0.46071400	1.87037500	2.50799000
H	-2.39301800	2.78155200	3.79559900

TS1

C	-2.49747900	-1.78458200	1.01321500
C	-2.58036000	-1.72627100	-0.38525400
C	-3.78046600	-1.89586100	-1.05481400
C	-4.92188100	-2.13477600	-0.26808400
C	-4.84098700	-2.19256000	1.12773700
C	-3.61709200	-2.01493200	1.79704100
H	-3.83154800	-1.84514700	-2.13822300
H	-5.88264300	-2.27339200	-0.75641100
H	-5.74044200	-2.37608200	1.70926800
H	-3.54371200	-2.05573600	2.87946900
C	2.17599100	0.99586500	1.26777600
C	2.35255500	1.01567200	-0.12415900
C	3.25899300	1.00170300	2.13652100
C	3.61440100	1.05807700	-0.69967000
C	4.54220300	1.04024800	1.56311900
H	3.11230700	0.98925000	3.21228200
C	4.71804100	1.07200200	0.17336300
H	3.73769100	1.10165200	-1.77832400
H	5.41314100	1.05912800	2.21307800
H	5.72246900	1.12406800	-0.23911600
B	-0.48247000	-1.31347500	0.22270400
B	0.14814800	0.95809700	0.31061700
O	0.84856400	0.99194100	1.56284300
O	1.13317700	1.00146000	-0.74070900
O	-1.33178700	-1.48825000	-0.91356300
O	-1.20266600	-1.58436200	1.41777400
C	-1.27695500	1.65084900	0.14746900
H	-2.02745800	1.07995300	0.71005100
C	-1.76284000	1.75743800	-1.33286200

H	-1.29639900	0.98261800	-1.94979800
H	-2.84483300	1.56837900	-1.37857300
C	-1.22521100	3.06250700	0.82047500
H	-1.25455500	2.94407900	1.90963800
H	-0.27454700	3.56864600	0.59635900
C	-2.38359400	3.94256200	0.33061200
H	-3.32891300	3.41444900	0.52071300
H	-2.43144100	4.87470700	0.90923600
C	-1.48141700	3.14326700	-1.93319600
H	-1.74988100	3.15715200	-2.99797400
H	-0.40105900	3.33560200	-1.88947000
C	-2.24669700	4.25594700	-1.18035300
H	-3.24568500	4.38444700	-1.61914800
H	-1.72552200	5.21318700	-1.31832800
O	0.84553500	-1.84230400	0.13334000
C	1.44754100	-2.10047300	-0.98744800
H	0.91750400	-1.99083400	-1.92794000
N	2.74353800	-2.42653200	-1.00278500
C	3.45170200	-2.57008200	-2.26708900
H	3.86288000	-3.58285900	-2.35752100
H	2.76898000	-2.38894100	-3.10033500
H	4.27486900	-1.84780400	-2.32193900
C	3.51428500	-2.62282000	0.22237400
H	4.20506000	-1.78520600	0.37454900
H	2.83780600	-2.68451600	1.07429400
H	4.08579700	-3.55474300	0.13893200

B_2pin_2

B	0.85207300	-0.00000800	-0.00021100
B	-0.85205500	0.00006500	-0.00024100
O	-1.61787000	-1.00570600	-0.54397400
O	-1.61776800	1.00581700	0.54362400
O	1.61774400	-0.54496600	1.00501400
O	1.61793500	0.54503100	-1.00522600
C	3.01113400	0.55154300	-0.56389600
C	3.29709500	1.96643900	-0.04169400
H	4.34368800	2.07949500	0.26272400
H	3.09131300	2.68669900	-0.84024900
H	2.65711200	2.21762400	0.81029700
C	3.89983800	0.25006700	-1.76946100
H	3.80311900	1.05521700	-2.50551200
H	4.95348100	0.18791800	-1.47114400
H	3.61912000	-0.68649200	-2.25719800
C	3.01101600	-0.55156800	0.56393100
C	3.29698300	-1.96645600	0.04172000
H	4.34358800	-2.07953900	-0.26267500
H	3.09118500	-2.68671900	0.84026300
H	2.65701500	-2.21762200	-0.81028400
C	3.89951600	-0.25017300	1.76967900
H	3.61881600	0.68643500	2.25732600
H	3.80253000	-1.05527900	2.50574500
H	4.95323700	-0.18817700	1.47159400
C	-3.01099700	0.56456300	0.55094500
C	-3.89968200	1.76983300	0.24824600
H	-4.95329600	1.47138800	0.18626800
H	-3.80309300	2.50667900	1.05268100
H	-3.61888700	2.25670400	-0.68874400

C	-3.29679700	0.04385200	1.96647300
H	-2.65686000	-0.80795300	2.21837800
H	-3.09082700	0.84307700	2.68592200
H	-4.34340200	-0.26037200	2.08002700
C	-3.01114600	-0.56448600	-0.55090100
C	-3.29736300	-0.04391600	-1.96640900
H	-4.34402800	0.26024800	-2.07973500
H	-2.65752600	0.80788900	-2.21853800
H	-3.09152100	-0.84318800	-2.68584000
C	-3.89964100	-1.76983800	-0.24790000
H	-4.95326100	-1.47155900	-0.18546900
H	-3.80328300	-2.50660900	-1.05244300
H	-3.61838100	-2.25671900	0.68895800

cyclohexyl B_2pin_2 radical

B	-1.06518500	0.10799000	0.08598100
B	0.77673700	-0.08372300	0.25392600
O	0.94483500	-1.08387200	1.25847500
O	1.33522500	-0.55515800	-0.96182500
O	-1.82910700	0.77865900	0.99633700
O	-1.78053900	-0.46916400	-0.92447300
C	1.11844800	1.50551200	0.69300000
H	0.49063400	1.72899200	1.56231500
C	0.80470000	2.52204400	-0.42795500
H	1.04302900	2.09156600	-1.41031700
H	-0.26994100	2.74472600	-0.43732400
C	2.61426800	1.59759300	1.13446600
H	2.67574600	2.28497800	1.99302600

H	2.97392300	0.63220000	1.50598300
C	3.51524500	2.12599800	0.01066100
H	4.56922900	2.08809900	0.31714200
H	3.42223600	1.46306200	-0.85835200
C	1.60736000	3.82105300	-0.24276000
H	1.38836100	4.23078500	0.75366600
H	1.27804500	4.58029600	-0.96424900
C	3.12861000	3.56946800	-0.38821100
H	3.67871200	4.28984300	0.23243900
H	3.44129100	3.75481800	-1.42459300
C	-3.23287400	0.46317900	0.70732600
C	-3.16755900	0.00168600	-0.80267400
C	-4.06735100	1.71483300	0.96859200
H	-5.11908600	1.54035200	0.71113300
H	-4.01713800	1.97255900	2.03162800
H	-3.70600000	2.57253500	0.39645900
C	-3.63743700	-0.65327500	1.67800600
H	-3.03549600	-1.55517900	1.52950000
H	-3.47449900	-0.30713600	2.70364900
H	-4.69513600	-0.91683900	1.56671600
C	-3.32721000	1.14850500	-1.80816200
H	-4.35575700	1.52597900	-1.82446700
H	-2.65456200	1.98152100	-1.58132100
H	-3.07938200	0.78002300	-2.80873700
C	-4.09714400	-1.15224900	-1.17047900
H	-3.90592800	-2.04004200	-0.56304400
H	-5.14653000	-0.86053100	-1.04174700
H	-3.94741700	-1.42226800	-2.22109400
C	1.33997700	-2.32636600	0.63457000

C	1.92319900	-1.86075800	-0.76867700
C	2.35131800	-3.01629000	1.55606600
H	1.86558400	-3.26352900	2.50614500
H	2.71794400	-3.94835800	1.10899600
H	3.20784300	-2.37425000	1.77518800
C	0.08563700	-3.21040100	0.52090900
H	-0.67616000	-2.75357700	-0.11623600
H	0.32806100	-4.19973600	0.11620800
H	-0.33980300	-3.34576800	1.52142000
C	1.52673300	-2.74605900	-1.95490800
H	1.91493000	-3.76491700	-1.83388500
H	0.44236600	-2.79415000	-2.07801000
H	1.95026300	-2.32911000	-2.87504400
C	3.44963000	-1.67277500	-0.77066000
H	3.74774800	-1.20957900	-1.71701900
H	3.78115300	-1.02009800	0.04128300
H	3.97136100	-2.63250100	-0.67977000

Ir(IV)

Ir	0.00000000	0.00000000	0.06276100
C	-0.88630200	2.80704700	-0.59098200
C	0.00000000	2.89838200	0.57498100
C	0.56518100	1.67561500	1.05211200
C	-1.53828000	3.89290600	-1.20189700
N	-1.06564300	1.54736200	-1.08565500
C	0.31567900	4.11920700	1.19561300
C	1.46060600	1.74433300	2.13752100
C	1.18486300	4.15162500	2.28350600

C	-3.44181300	0.04046700	2.75368500
C	-2.51007200	-1.44919100	0.57498100
C	-2.24094000	0.39275600	2.13752100
C	-1.73371500	-0.34834700	1.05211200
N	1.87287600	0.14919300	-1.08565500
C	2.87412500	-0.63596400	-0.59098200
C	0.78033400	-2.13708900	2.13752100
C	1.16853500	-1.32726800	1.05211200
C	2.51007200	-1.44919100	0.57498100
C	-3.72517800	-1.78621700	1.19561300
C	-4.18784400	-1.04969100	2.28350600
C	1.68586100	-3.00093100	2.75368500
C	3.40949900	-2.33299000	1.19561300
C	3.00298100	-3.10193400	2.28350600
C	1.75595200	2.96046400	2.75368500
C	-2.36807900	3.68073300	-2.29540300
C	-1.87754600	1.34416300	-2.14033700
C	-1.98782300	-2.17108400	-0.59098200
C	2.10285300	0.95392100	-2.14033700
C	4.14049500	-0.61426300	-1.20189700
C	-2.54621100	2.37926100	-2.77940700
C	-2.60221500	-3.27864300	-1.20189700
N	-0.80723300	-1.69655500	-1.08565500
C	3.33360600	1.01545300	-2.77940700
C	4.37164800	0.21045000	-2.29540300
C	-2.00356900	-3.89118300	-2.29540300
C	-0.22530600	-2.29808400	-2.14033700
C	-0.78739500	-3.39471400	-2.77940700
H	-1.39622900	4.89587500	-0.81671900

H	-0.11029900	5.05143200	0.83651300
H	1.90690900	0.83399700	2.52473200
H	1.41939300	5.09806700	2.76189400
H	-3.79930400	0.61379700	3.60531900
H	-1.67571700	1.23443400	2.52473200
H	-0.23119200	-2.06843000	2.52473200
H	-4.31951900	-2.62123800	0.83651300
H	-5.12475200	-1.31980300	2.76189400
H	1.36808800	-3.59719300	3.60531900
H	4.42981800	-2.43019500	0.83651300
H	3.70535900	-3.77826400	2.76189400
H	2.43121600	2.98339600	3.60531900
H	-2.87519600	4.51829600	-2.76570300
H	-1.98500300	0.31525000	-2.46706800
H	1.26551600	1.56143800	-2.46706800
H	4.93806700	-1.23876800	-0.81671900
H	-3.19055000	2.16943800	-3.62659400
H	-3.54183800	-3.65710700	-0.81671900
H	3.47406300	1.67837900	-3.62659400
H	5.35055700	0.23084500	-2.76570300
H	-2.47536100	-4.74914100	-2.76570300
H	0.71948700	-1.87668800	-2.46706800
H	-0.28351300	-3.84781700	-3.62659400

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C	2.10782600	1.08174500	-1.13272900
C	1.34871500	0.05162800	-0.52863800
C	-0.14866800	0.20364200	-0.87554600

H	-0.14775600	0.31764800	-1.97644600
C	-0.59094800	1.60090300	-0.38843900
C	0.18273800	2.61335400	-0.99246200
N	1.41565500	2.23405900	-1.47810000
H	1.92906600	2.92997600	-2.00547200
C	1.86230200	-0.89710400	0.39607900
C	-1.51855000	1.95926500	0.63785500
O	1.26276200	-1.81833000	0.98313300
O	-1.87741600	3.10935600	0.95964600
O	3.24331400	-0.72062100	0.66919600
O	-2.02155000	0.87402200	1.35660000
C	3.80811000	-1.65845400	1.57541100
H	3.27810900	-1.62189800	2.53631400
H	3.69172400	-2.68011400	1.18774300
C	5.28050000	-1.30613100	1.74945700
H	5.39418500	-0.28895700	2.14341500
H	5.75852200	-2.00422200	2.45044600
H	5.81305500	-1.36003000	0.79208900
C	-2.91234800	1.19205400	2.42165000
H	-3.81749100	1.67264200	2.02413200
H	-2.43925200	1.91315400	3.09976000
C	-3.24791700	-0.10611500	3.14389500
H	-3.92317200	0.09461000	3.98705000
H	-3.73949300	-0.81741600	2.46984000
H	-2.33873500	-0.58077800	3.52981400
C	-1.08554500	-1.01081400	-0.67912300
H	-1.14471400	-1.25906900	0.38297400
C	-2.51384900	-0.70496000	-1.22148400
H	-3.08314000	-0.18007300	-0.44978200

H	-2.43729400	-0.01455400	-2.07472000
C	-0.55855500	-2.25146700	-1.43029800
H	-0.62748900	-2.06145600	-2.51450900
H	0.49405400	-2.42506500	-1.20273800
C	-3.28986700	-1.97221500	-1.66480700
H	-3.09557800	-2.18820800	-2.72674000
H	-4.37278100	-1.79704900	-1.58404700
C	-1.37463500	-3.51222600	-1.06551200
H	-1.27343100	-4.25897100	-1.86830500
H	-0.94910500	-3.96388700	-0.16003600
C	-2.87260800	-3.19386600	-0.83501700
H	-3.49654400	-4.06712000	-1.07694800
H	-3.04726300	-2.97339800	0.22770200
C	-0.13017800	4.08131100	-1.08837800
H	-1.18853200	4.25444900	-1.30369800
H	0.08219100	4.61207200	-0.14872000
H	0.47095400	4.55127500	-1.88423400
C	3.57577600	1.10630800	-1.45618400
H	4.19592700	1.47878200	-0.62518700
H	3.94588800	0.10564900	-1.69962300
H	3.76782600	1.75703400	-2.32635400

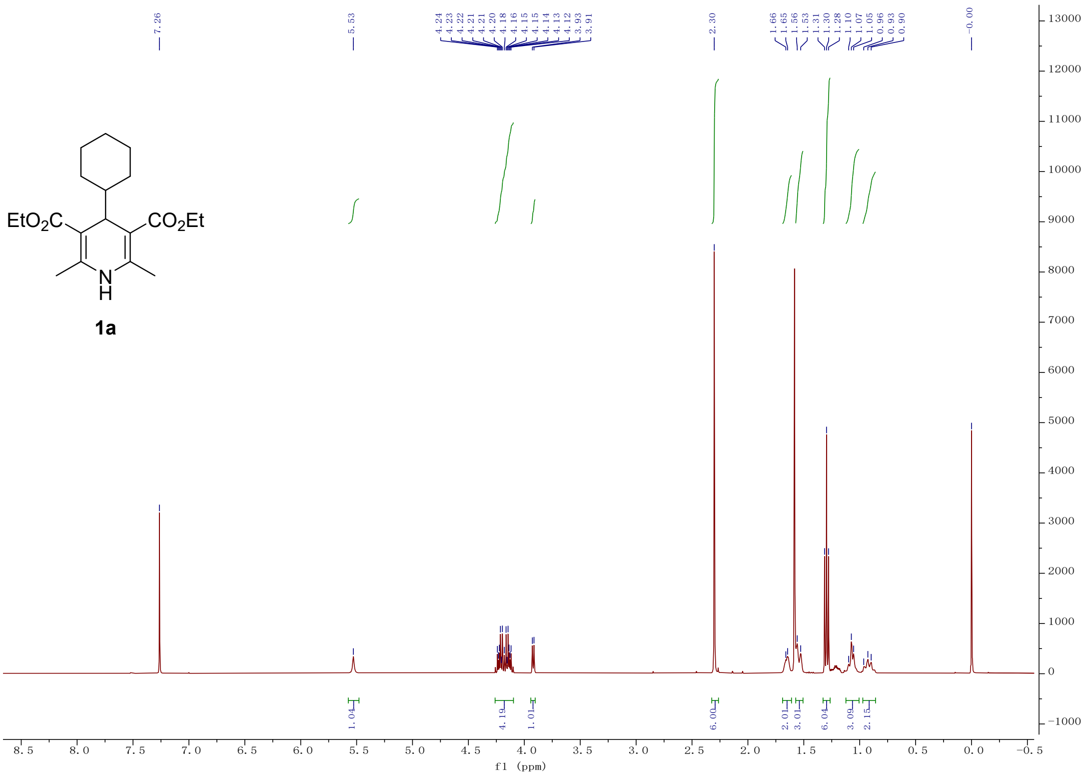
4 References

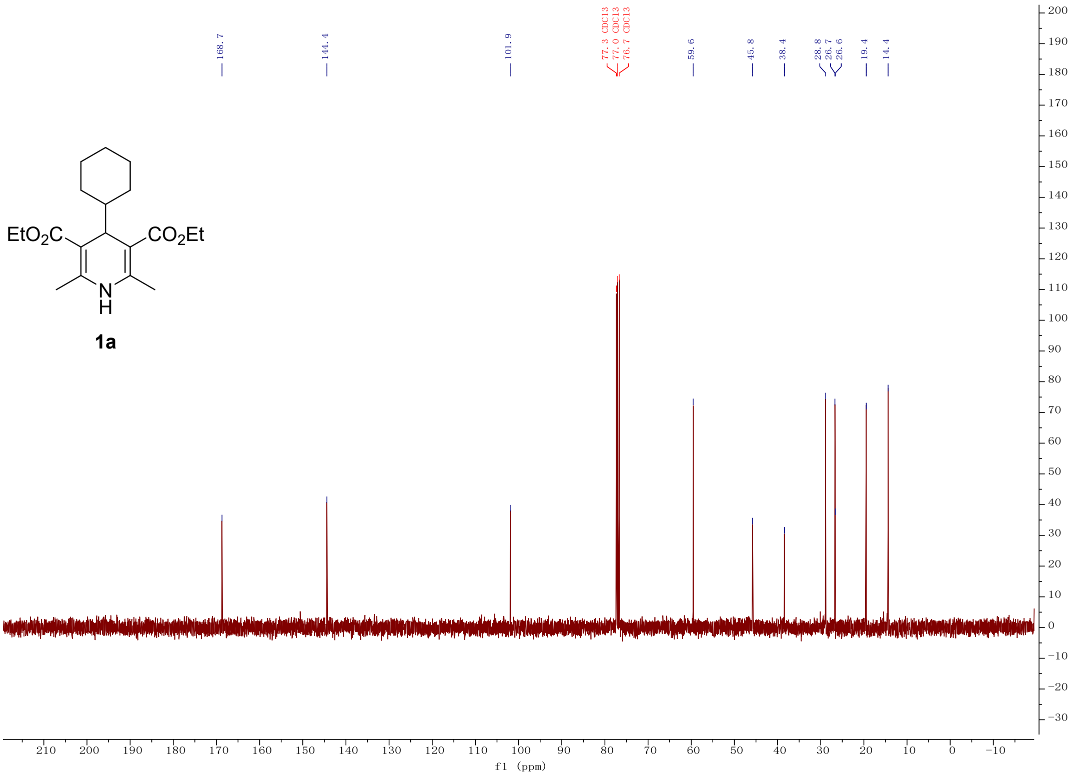
1. X. Wang, R. Liu, Q. Ding, W. Xiao and J. Wu, *Synergistic Photoredox and Tertiary Amine Catalysis: Generation of Allylic Sulfones from Morita–Baylis–Hillman Acetates and Sulfur Dioxide*, *Organic Chemistry Frontiers*, 2021, **8**, 3308-3313.
2. D. B. Dess and J. C. Martin, *Readily Accessible 12-I-5 Oxidant for the Conversion of Primary and Secondary Alcohols to Aldehydes and Ketones*, *The Journal of Organic Chemistry*, 1983, **48**, 4155-4156.
3. Y. Hu, C. F. Zorumski and D. F. Covey, *Neurosteroid Analogs: Structure-Activity Studies of Benz[E]Indene Modulators of Gabaa Receptor Function. 1. The Effect of 6-Methyl Substitution on the Electrophysiological Activity of 7-Substituted Benz[E]Indene-3-Carbonitriles*, *Journal of Medicinal Chemistry*, 1993, **36**, 3956-3967.
4. S. Liang, T. Kumon, R. A. Angnes, M. Sanchez, B. Xu and G. B. Hammond, *Synthesis of Alkyl Halides from Aldehydes Via Deformylative Halogenation*, *Organic Letters*, 2019, **21**, 3848-3854.
5. Á. Gutiérrez-Bonet, C. Remeur, J. K. Matsui and G. A. Molander, *Late-Stage C–H Alkylation of Heterocycles and 1,4-Quinones Via Oxidative Homolysis of 1,4-Dihydropyridines*, *Journal of the American Chemical Society*, 2017, **139**, 12251-12258.
6. L. Li, S.-q. Zhang, Y. Chen, X. Cui, G. Zhao, Z. Tang and G.-x. Li, *Photoredox Alkylation of Sulfinylamine Enables the Synthesis of Highly Functionalized Sulfinamides and S(Vi) Derivatives*, *ACS Catalysis*, 2022, **12**, 15334-15340.
7. B. Chen, C. S. Kuai, J. X. Xu and X. F. Wu, *Manganese(Iii)‐Promoted Double Carbonylation of Anilines toward Α‐Ketoamides Synthesis*, *Advanced Synthesis and Catalysis*, 2022, **364**, 487-492.
8. M. L. Shegavi, A. Agarwal and S. K. Bose, *Efficient Synthesis of Alkylboronic Esters Via Magnetically Recoverable Copper Nanoparticle-Catalyzed Borylation of Alkyl Chlorides and Bromides*, *Green Chemistry*, 2020, **22**, 2799-2803.
9. C. Shu, A. Noble and V. K. Aggarwal, *Metal-Free Photoinduced C(Sp3)–H Borylation of Alkanes*, *Nature*, 2020, **586**, 714-719.
10. J. Wang, M. Shang, H. Lundberg, K. S. Feu, S. J. Hecker, T. Qin, D. G. Blackmond and P. S. Baran, *Cu-Catalyzed Decarboxylative Borylation*, *ACS catalysis*, 2018, **8**, 9537-9542.
11. A. S. Dudnik and G. C. Fu, *Nickel-Catalyzed Coupling Reactions of Alkyl Electrophiles, Including Unactivated Tertiary Halides, to Generate Carbon–Boron Bonds*, *Journal of the American Chemical Society*, 2012, **134**, 10693-10697.
12. W. Chen, Y. Chen, X. Gu, Z. Chen and C.-Y. Ho, *(Nhc)Pd(Ii) Hydride-Catalyzed Dehydroaromatization by Olefin Chain-Walking Isomerization and Transfer-Dehydrogenation*, *Nature Communications*, 2022, **13**, 5507.
13. Y. Cheng, C. Mück-Lichtenfeld and A. Studer, *Metal-Free Radical Borylation of Alkyl and Aryl Iodides*, *Angewandte Chemie International Edition*, 2018, **57**, 16832-16836.
14. A. M. Sarotti, P. L. Pisano and S. C. Pellegrinet, *A Facile Microwave-Assisted Diels–Alder Reaction of Vinylboronates*, *Organic & Biomolecular Chemistry*, 2010, **8**, 5069-5073.
15. X. Chen, Z. Cheng and Z. Lu, *Cobalt-Catalyzed Asymmetric Markovnikov Hydroboration of Styrenes*, *ACS Catalysis*, 2019, **9**, 4025-4029.
16. Y. Wen, J. Xie, C. Deng and C. Li, *Selective Synthesis of Alkylboronates by Copper(I)-Catalyzed*

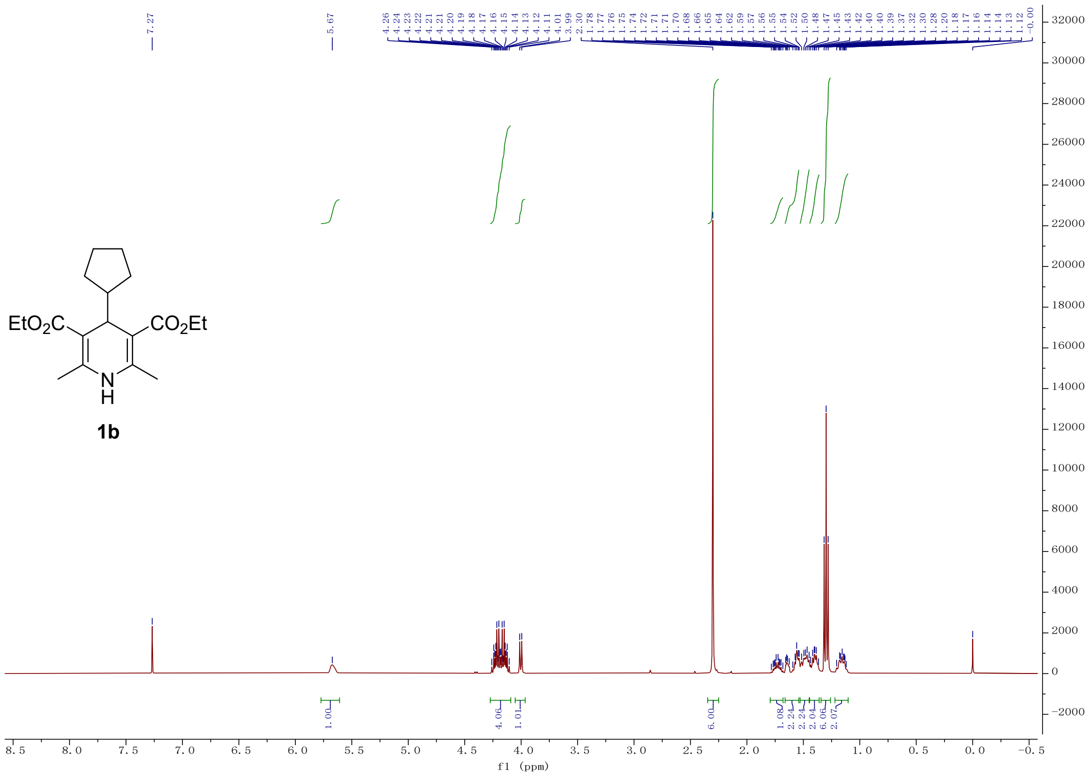
Borylation of Allyl or Vinyl Arenes, *The Journal of Organic Chemistry*, 2015, **80**, 4142-4147.

17. P. J. Chirik, T. Diao and R. Yu, *Hydroboration and Borylation with Cobalt Catalysts*, *Journal*, 2018.
18. A. R. Araujo, D. K. Ohira and P. M. Imamura, *Lda Promoted Coupling Reactions of B-Cyclogeranyl Bromide*, *Synthetic Communications*, 1992, **22**, 1409-1416.
19. F.-T. Xiong, B.-H. He, Y. Liu, Q. Zhou and J.-H. Fan, *Iron-Promoted Oxidative Alkylation/Cyclization of Ynones with 4-Alkyl-1,4-Dihydropyridines: Access to 2-Alkylated Indenones*, *The Journal of Organic Chemistry*, 2022, **87**, 8599-8610.
20. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, Williams, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman and D. J. Fox, *Gaussian 09 Rev. D.01*, *Journal*, 2016.

^1H, ^{13}C and ^{19}F NMR spectra of the prepared compounds







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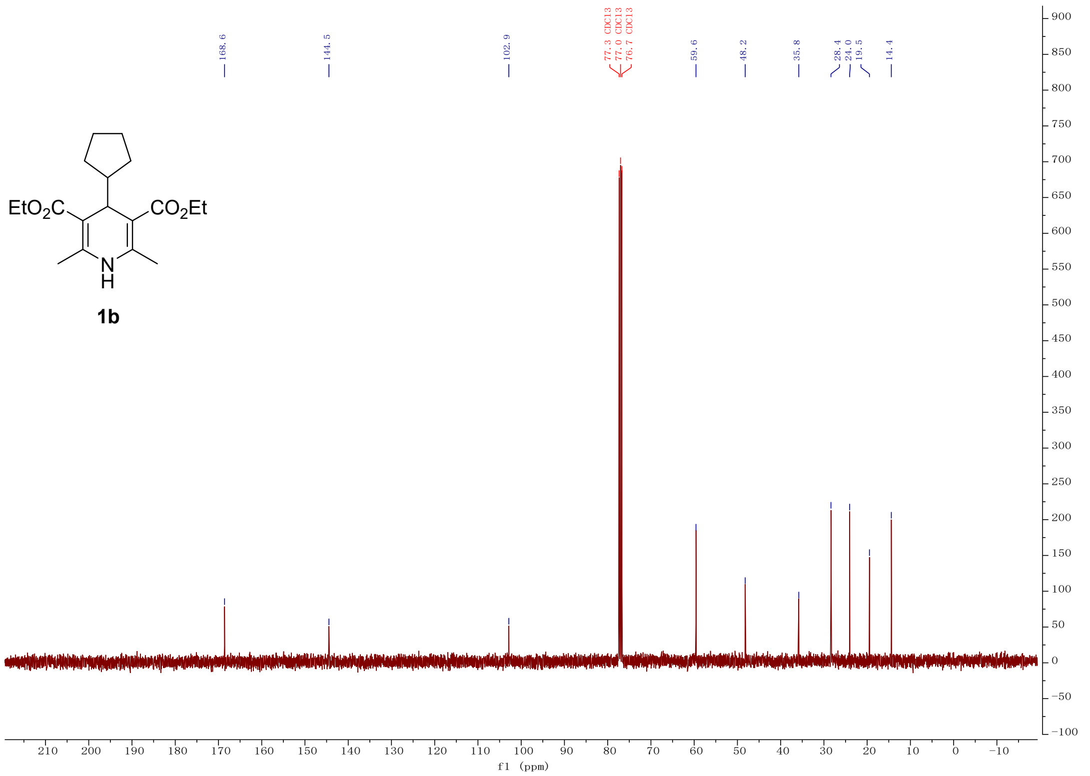

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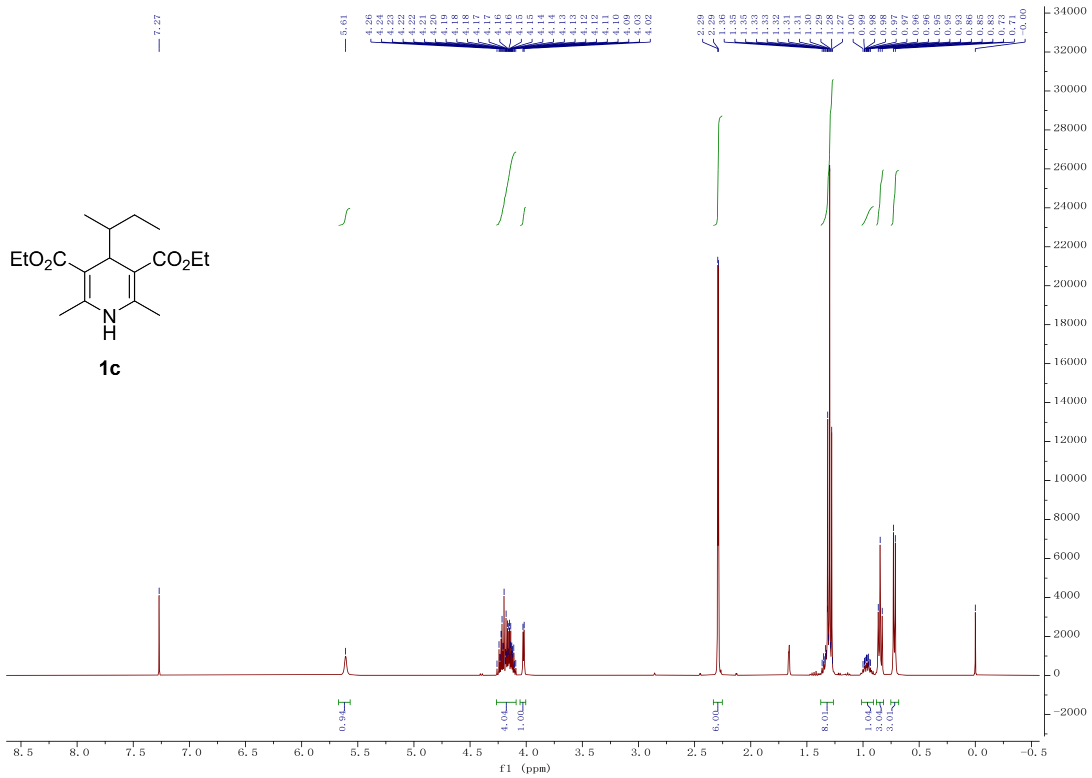

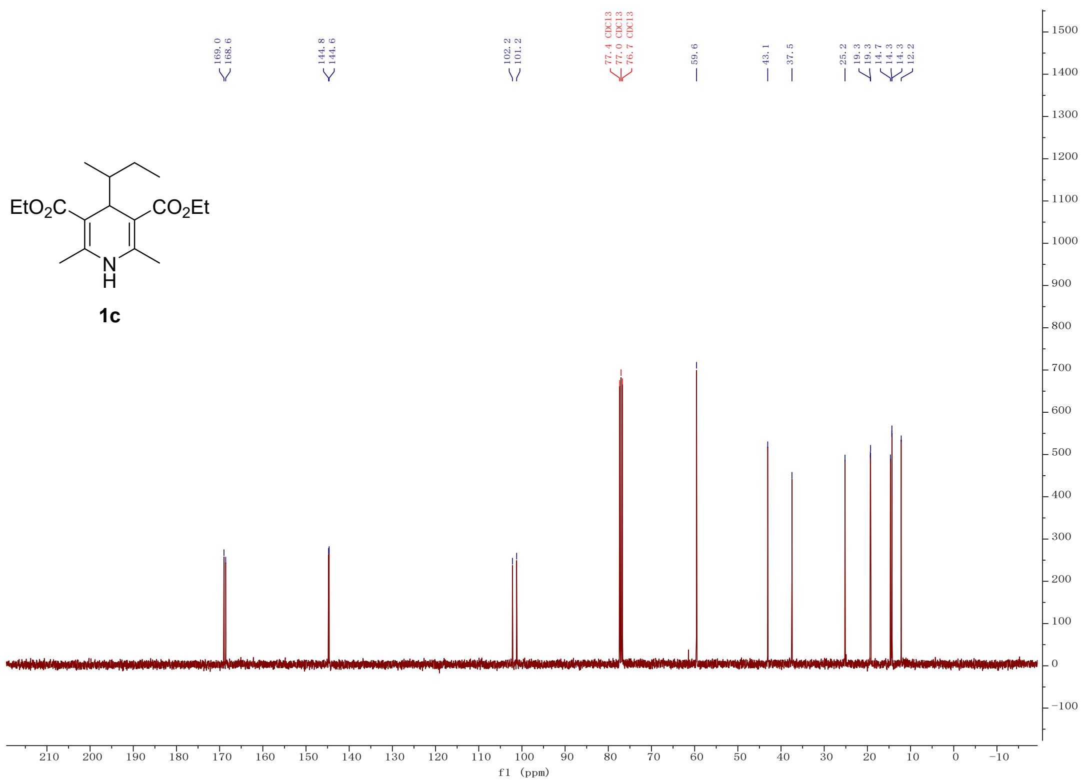

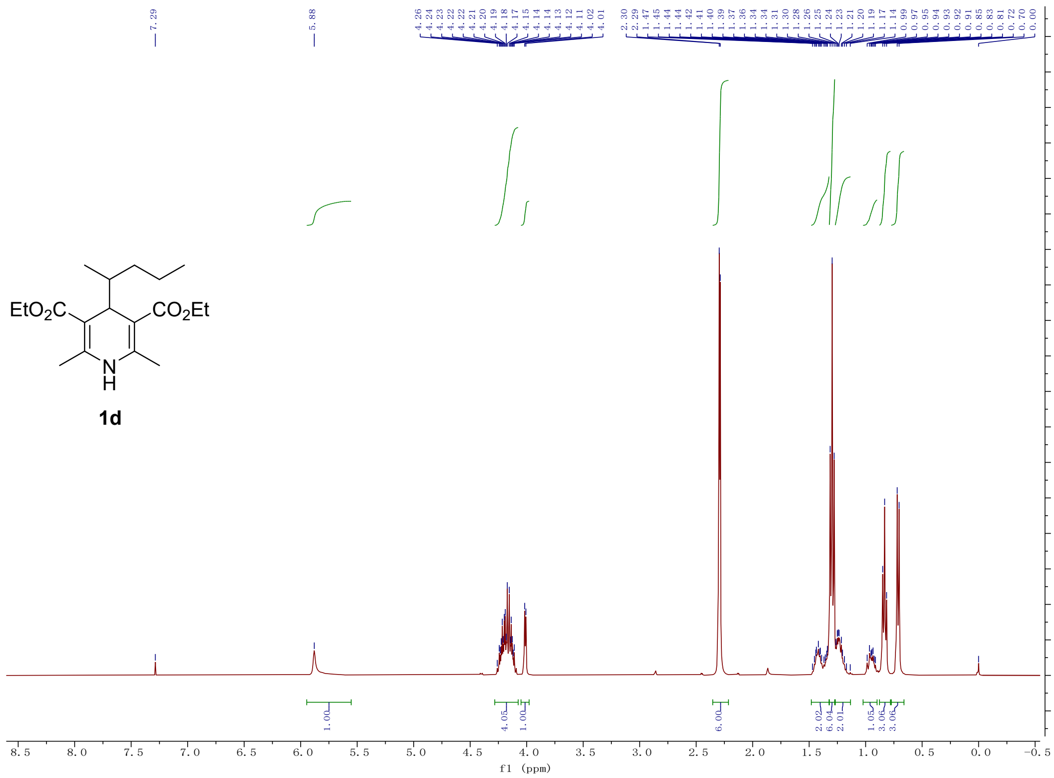

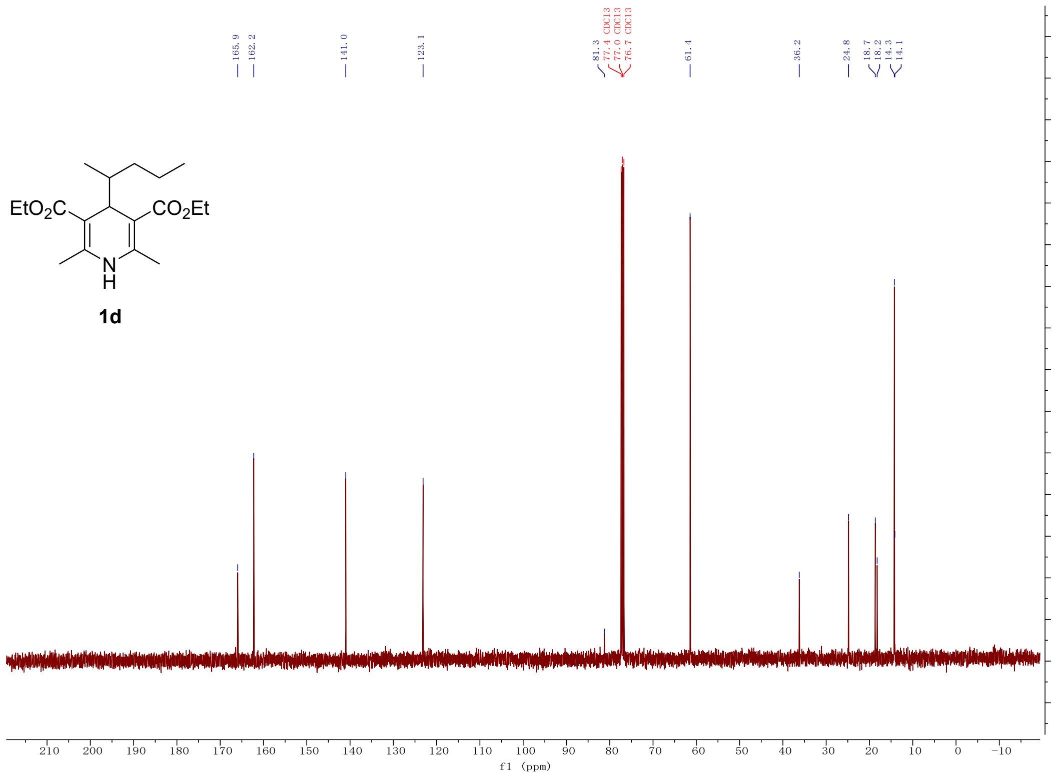

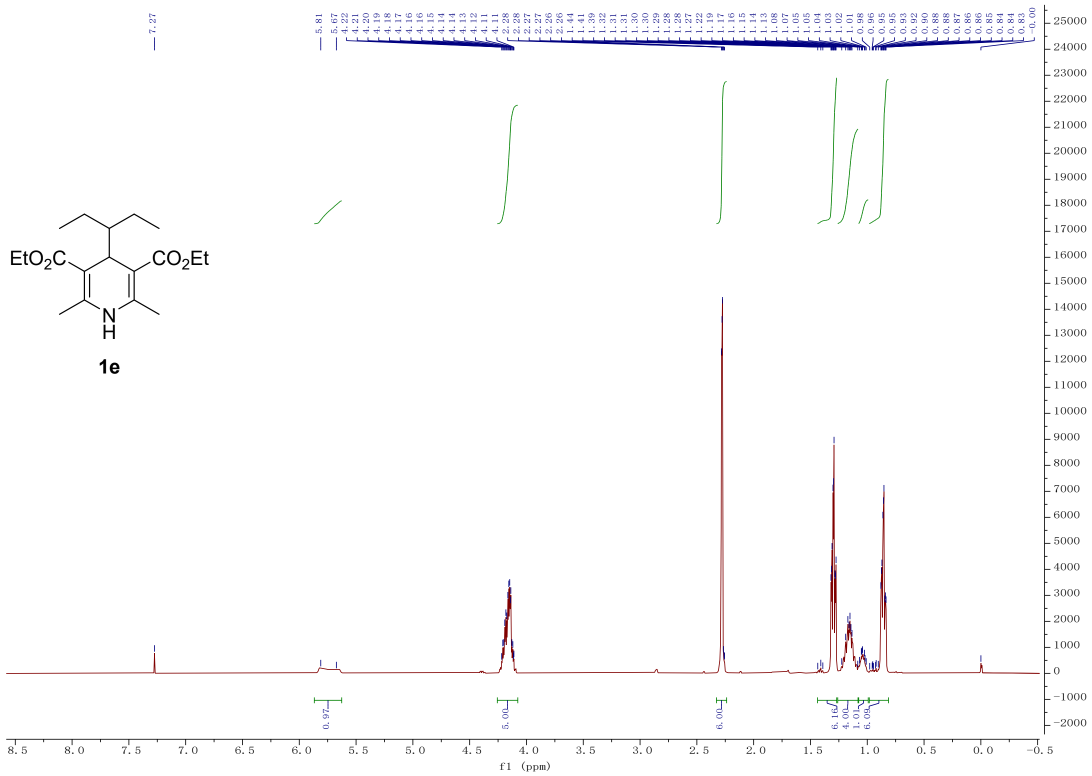

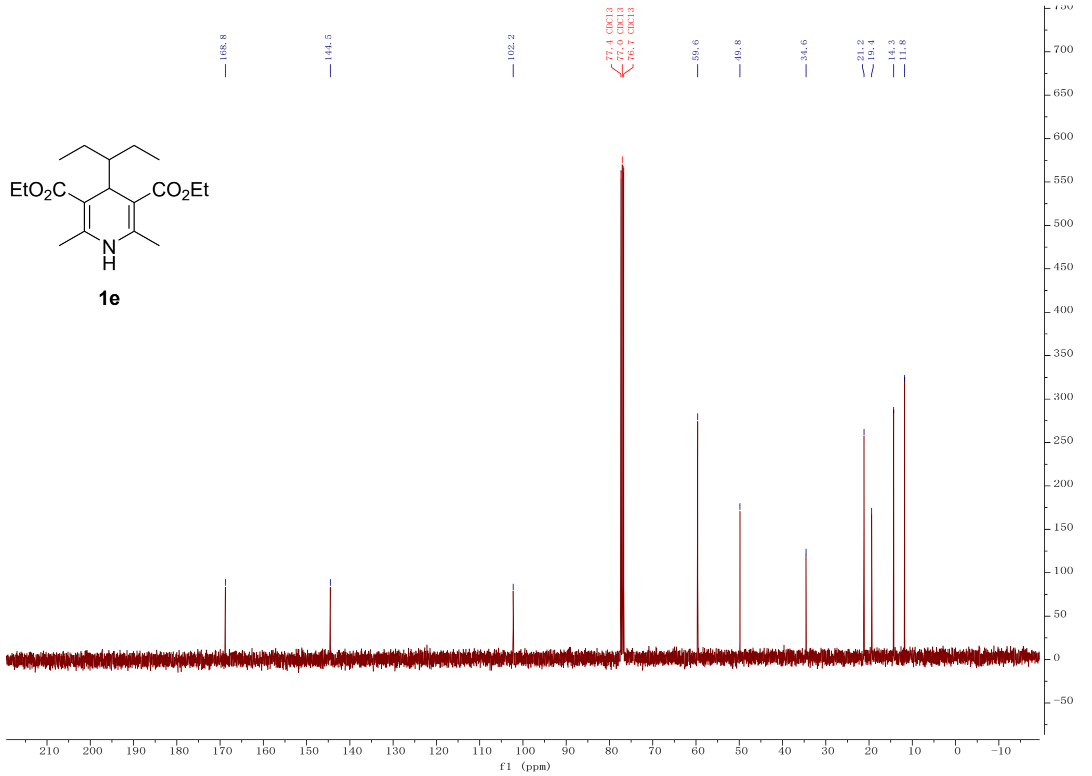

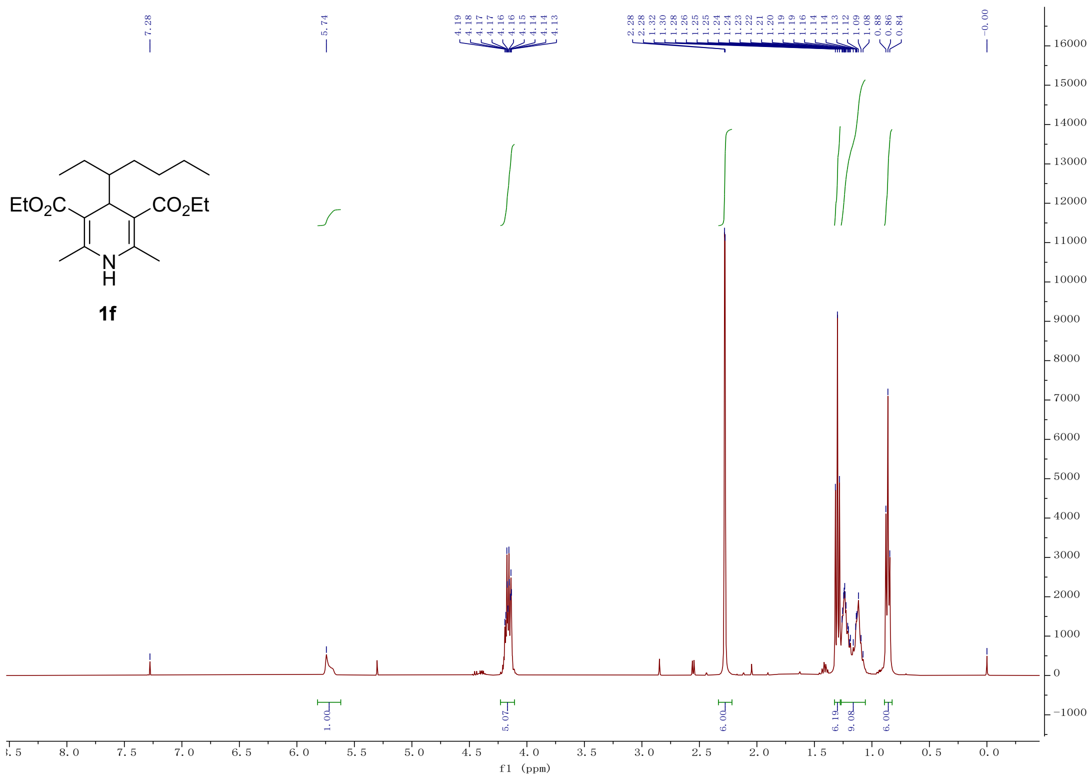

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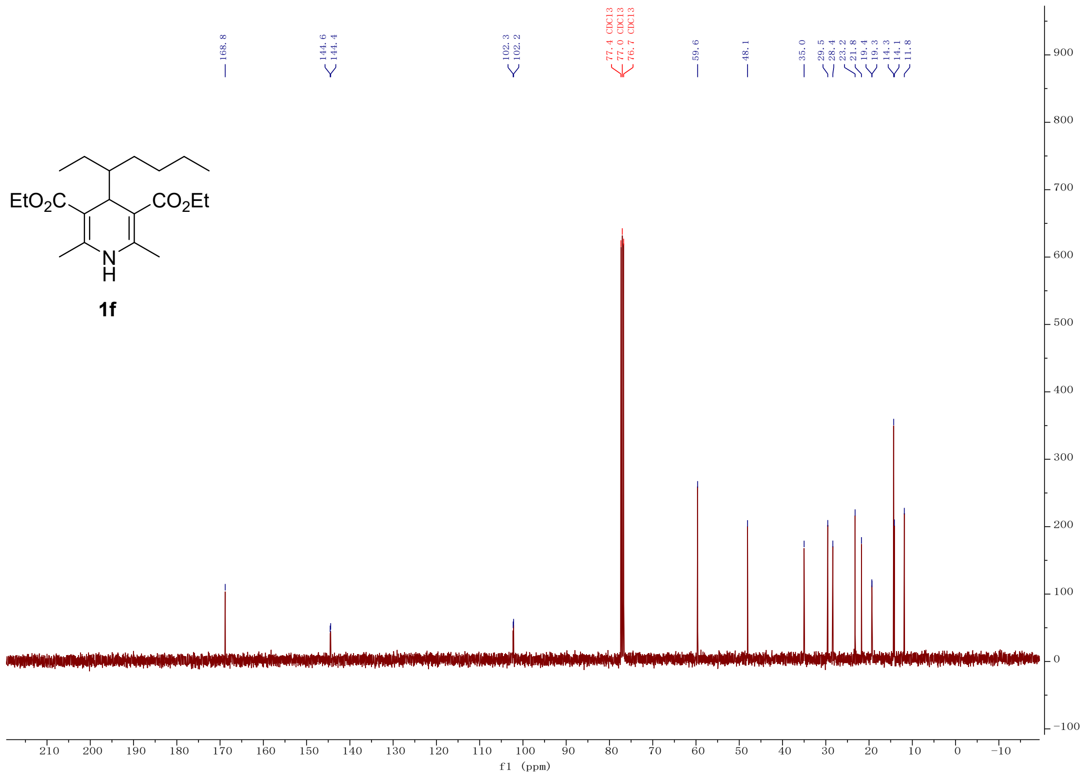

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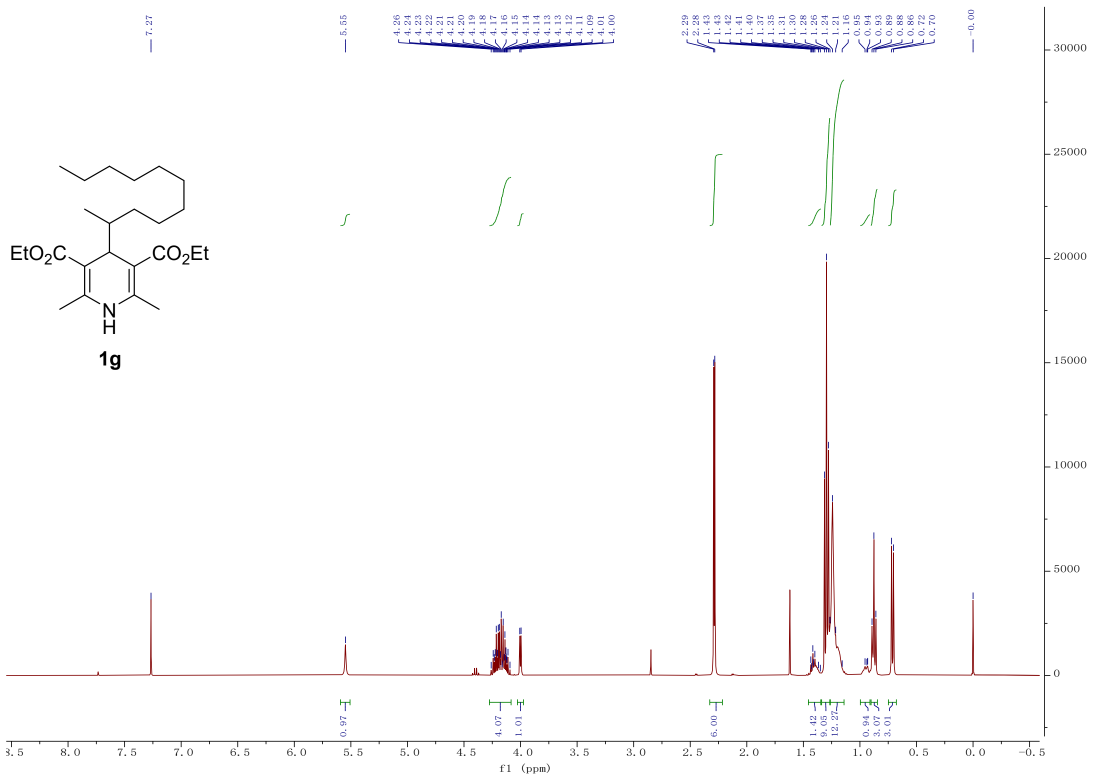

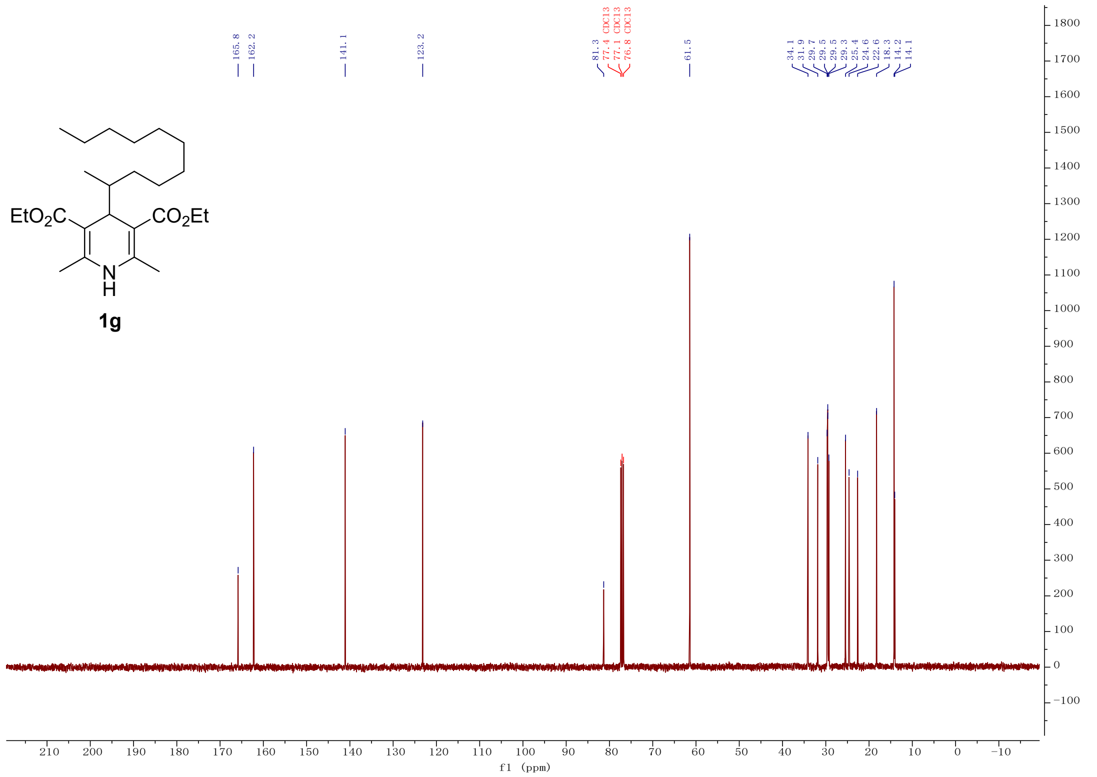

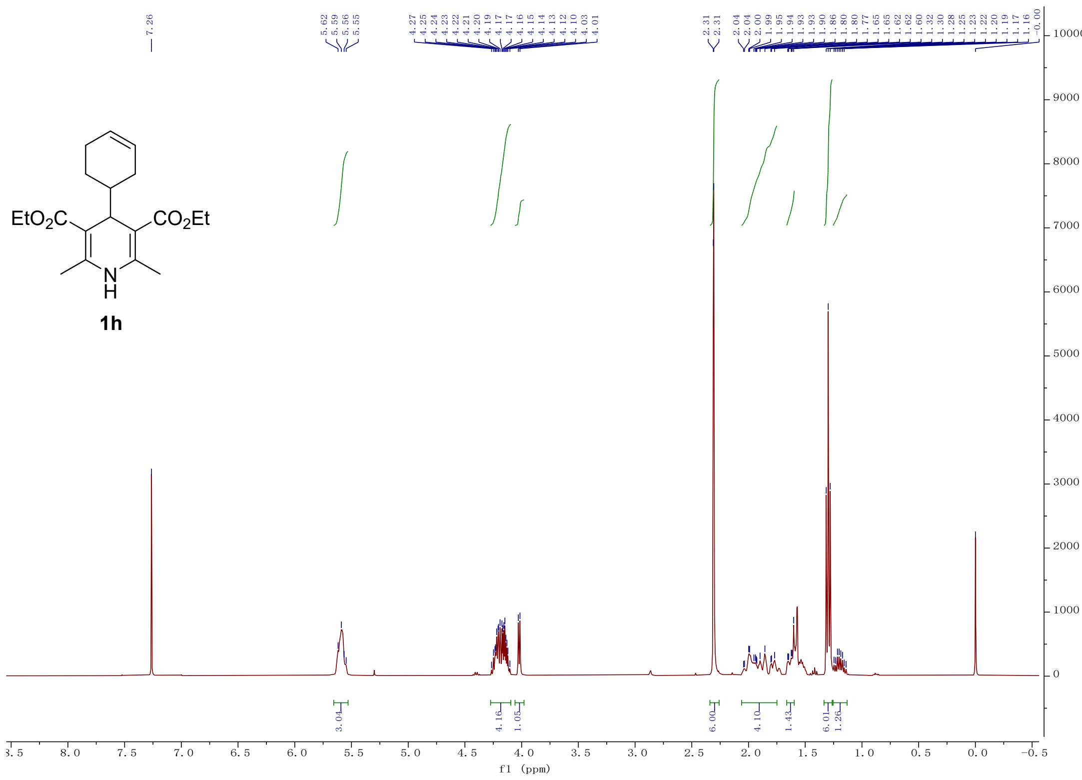

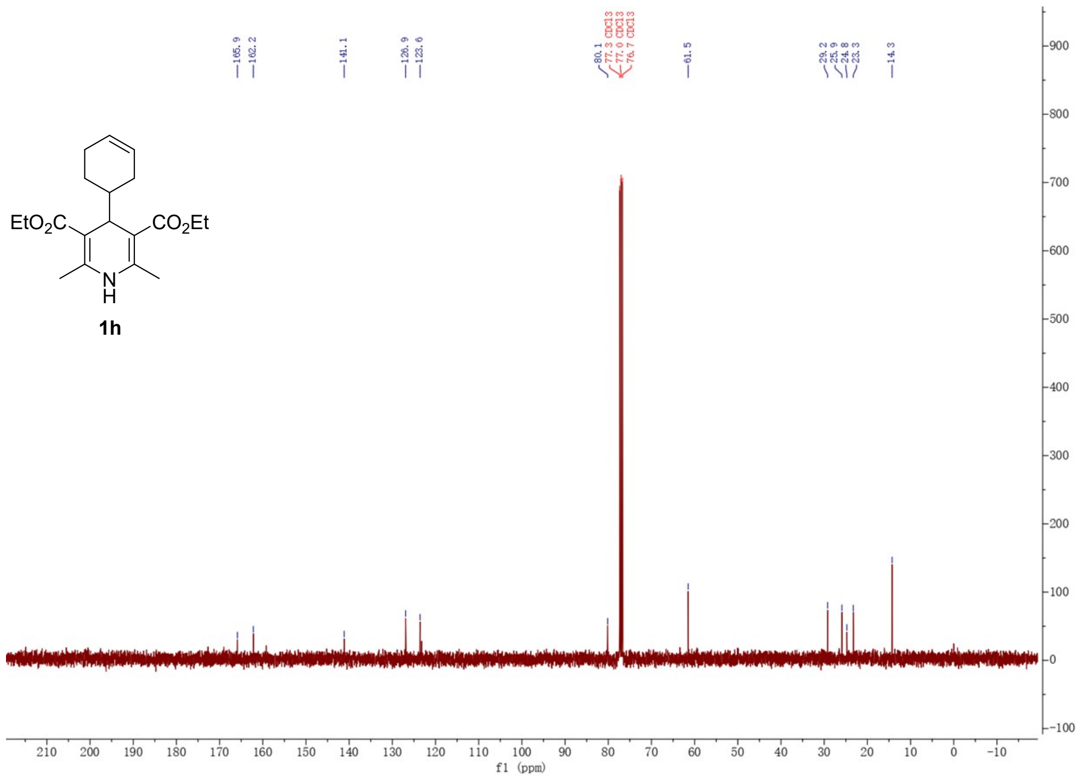

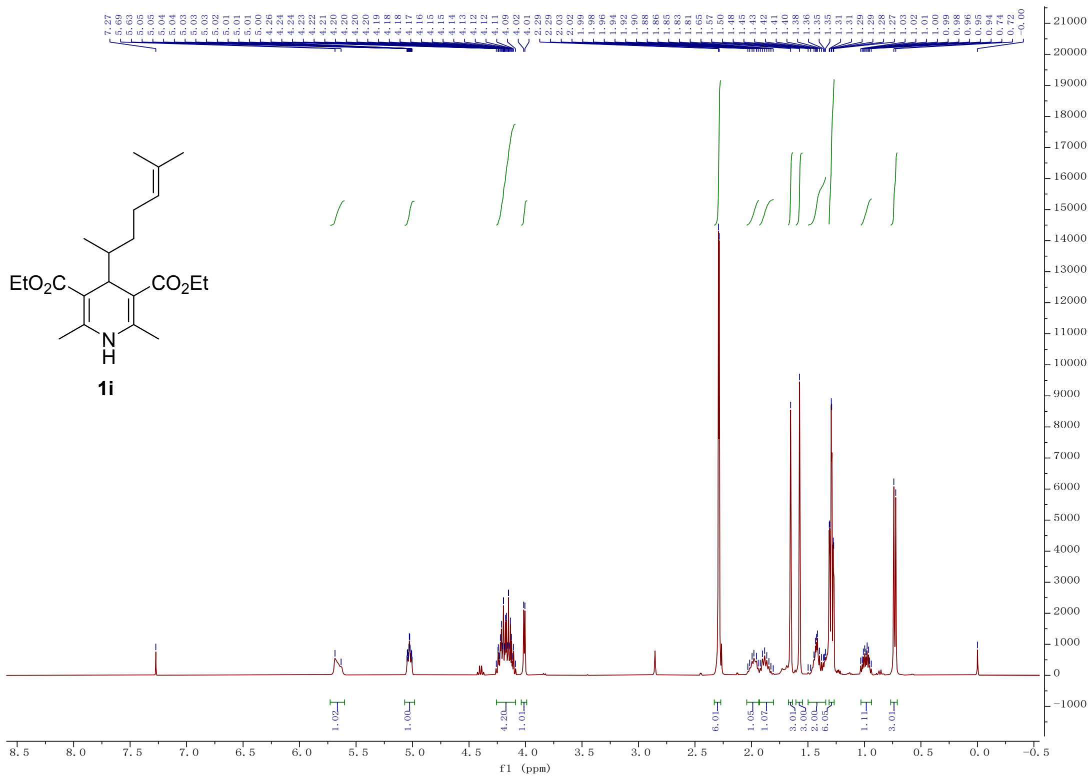

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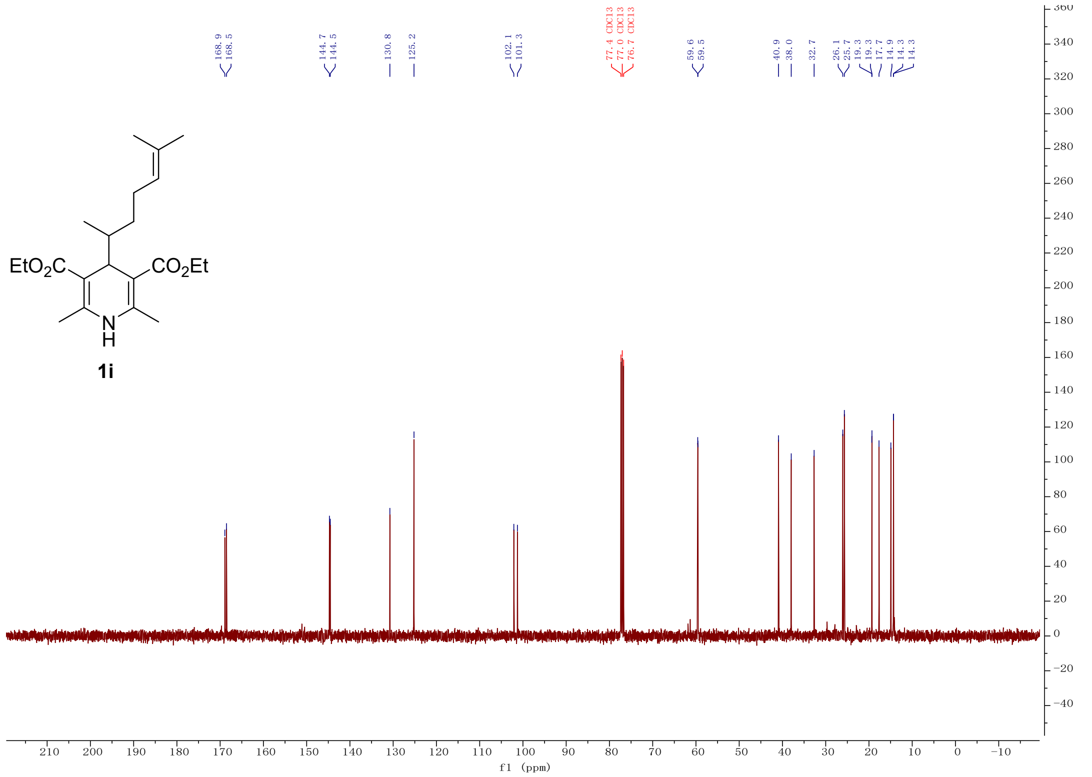

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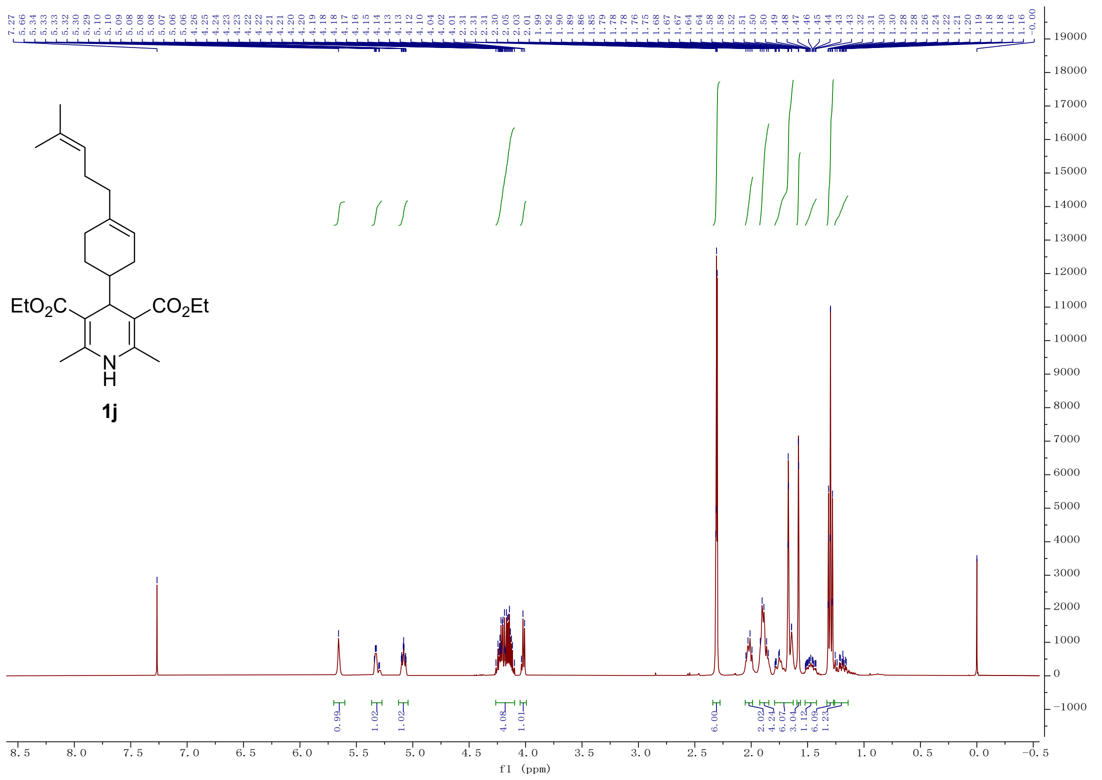

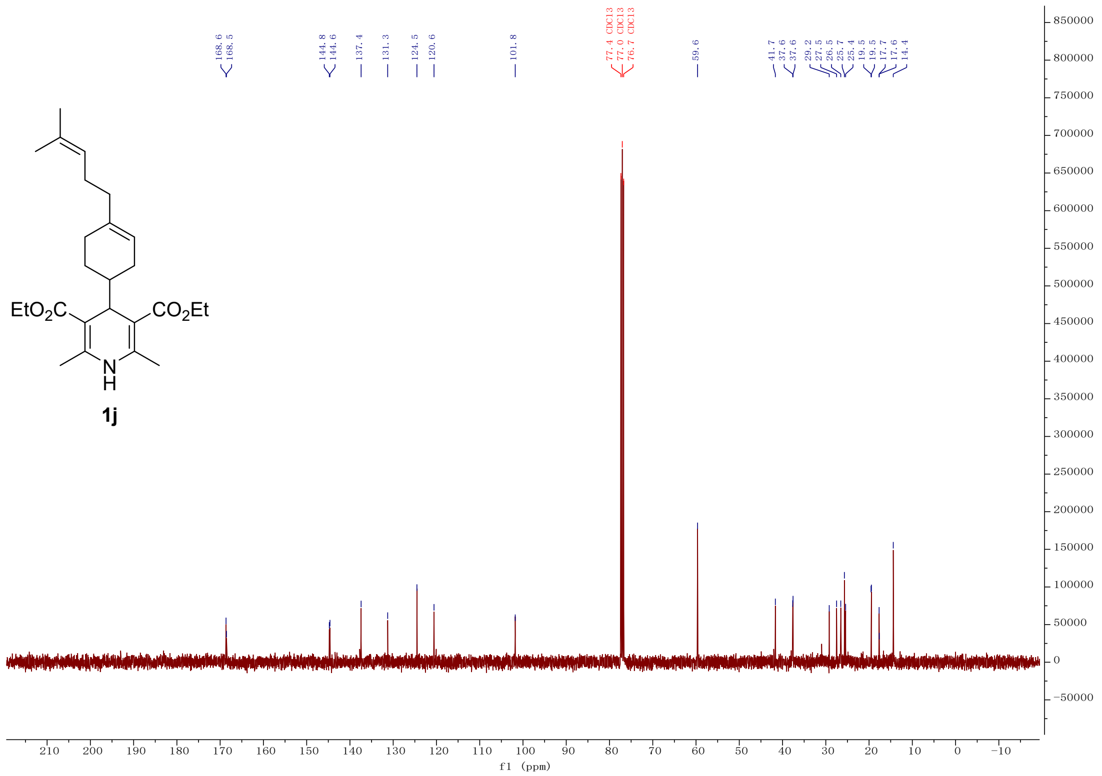

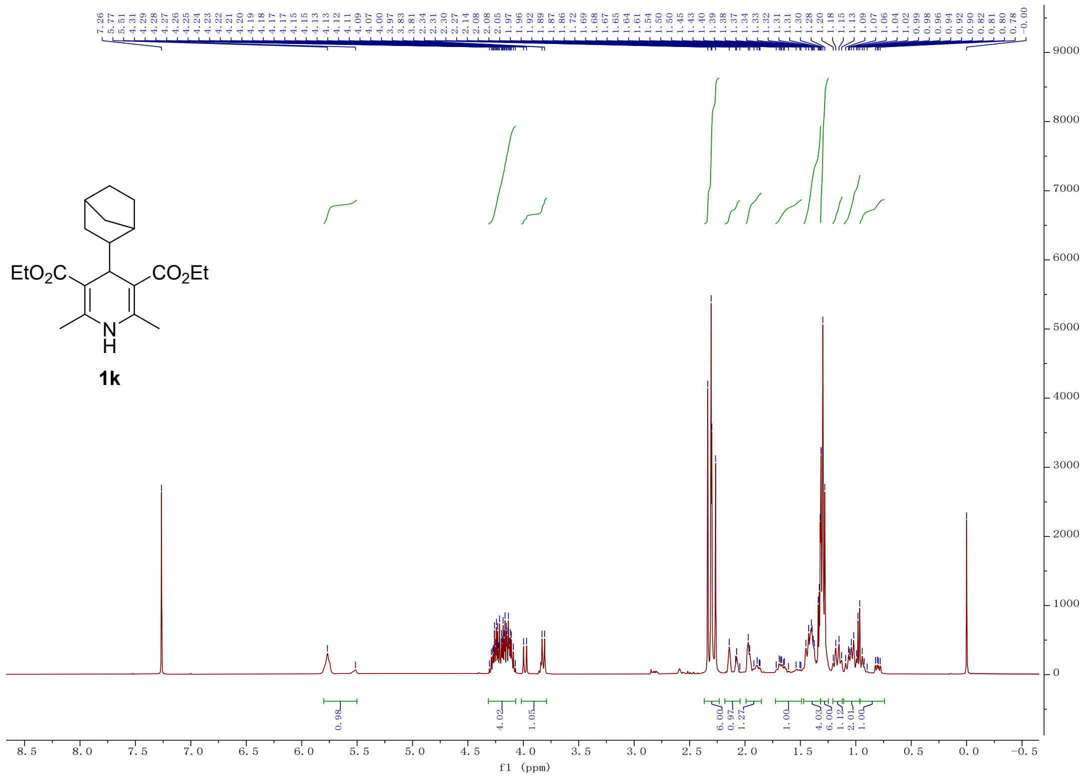
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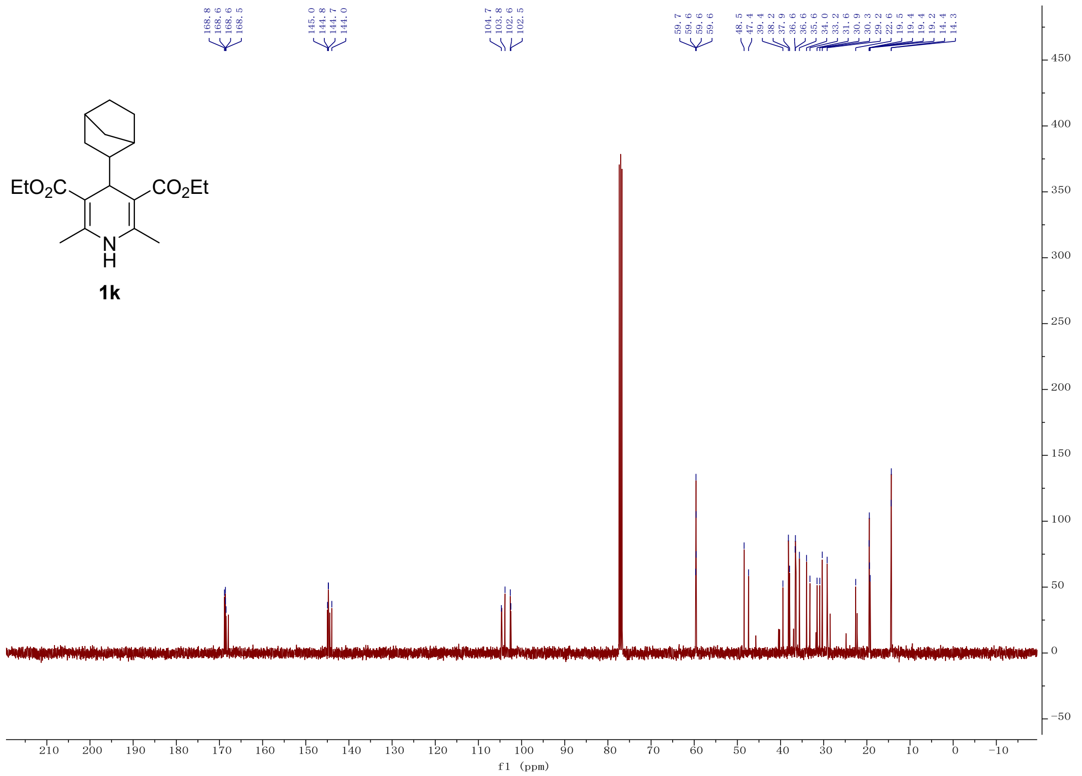
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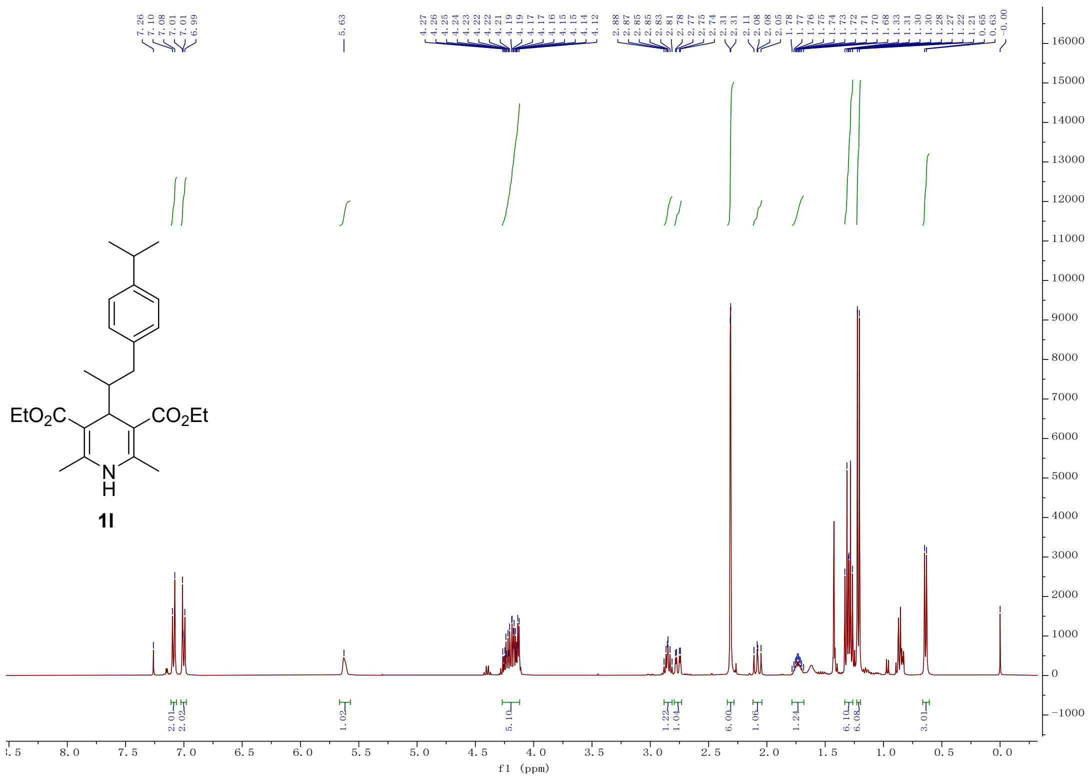

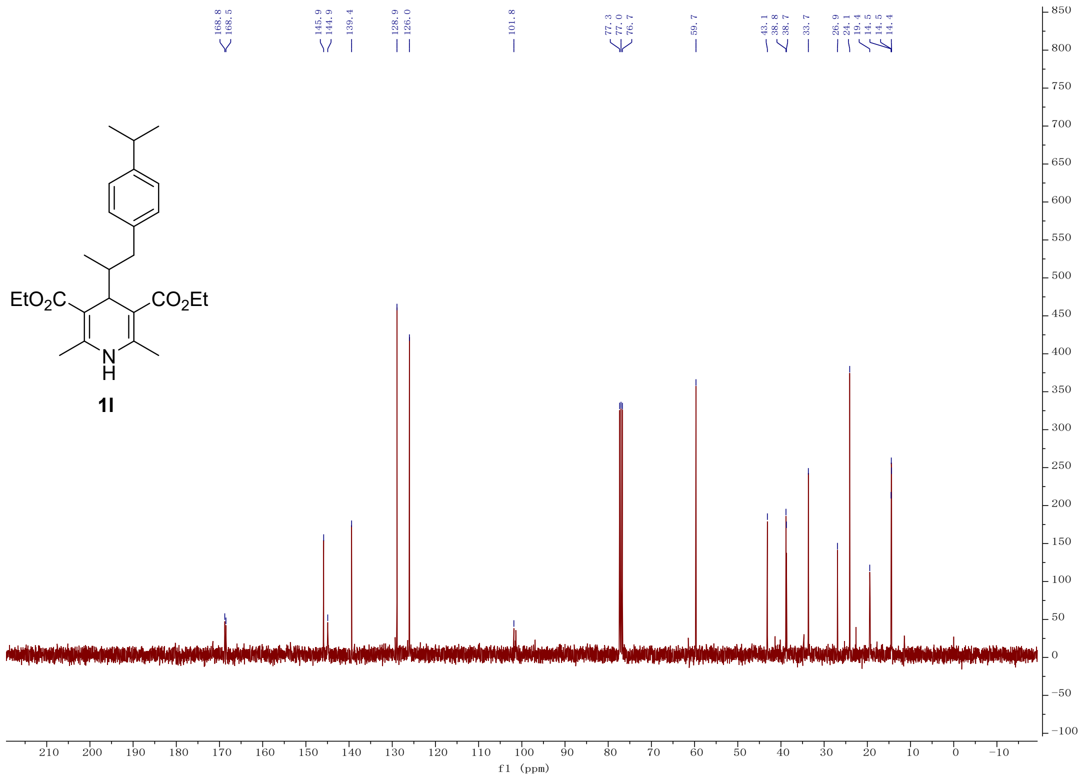

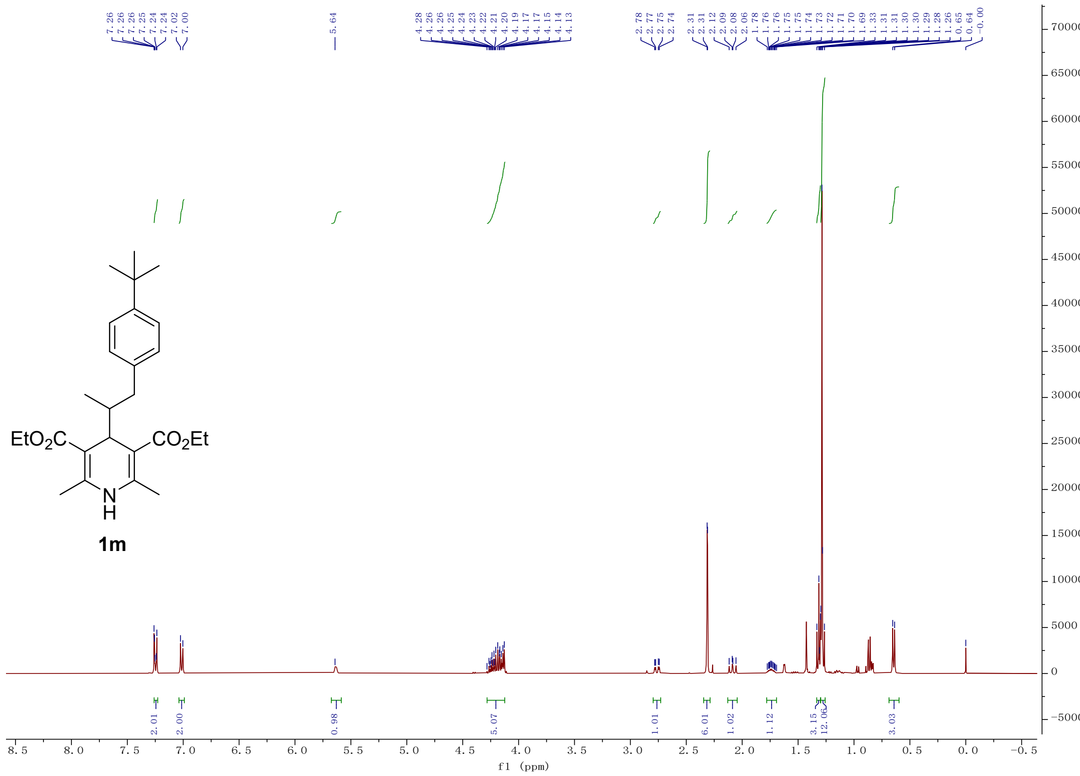
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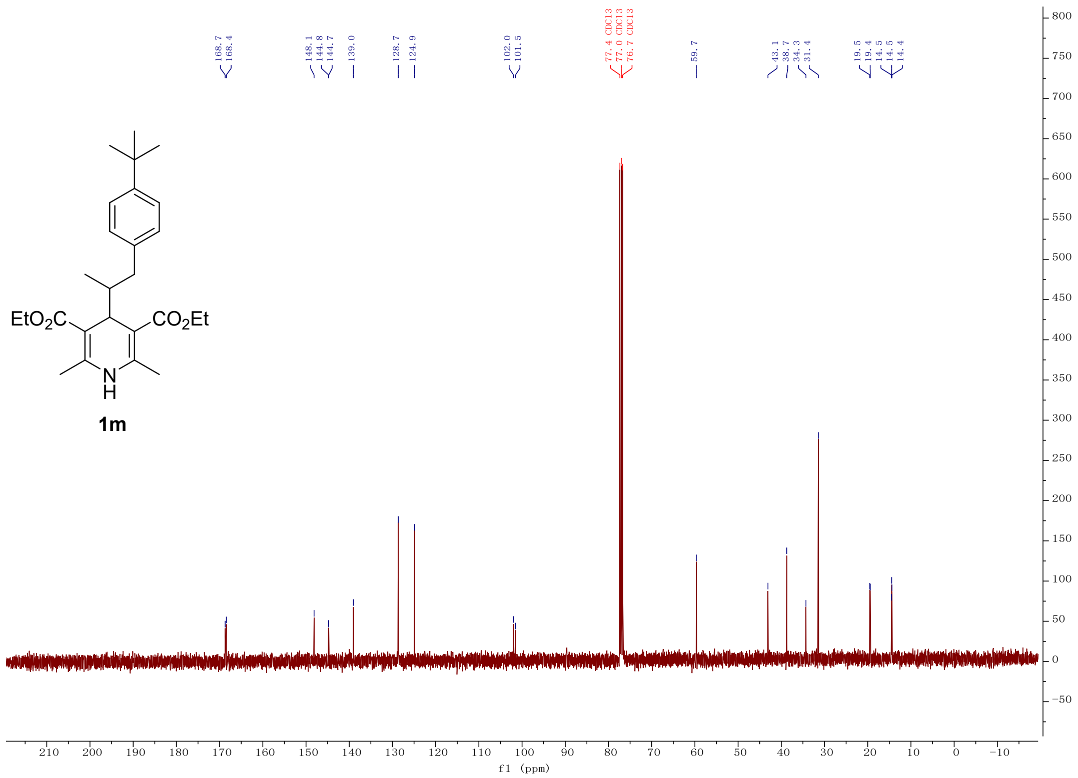
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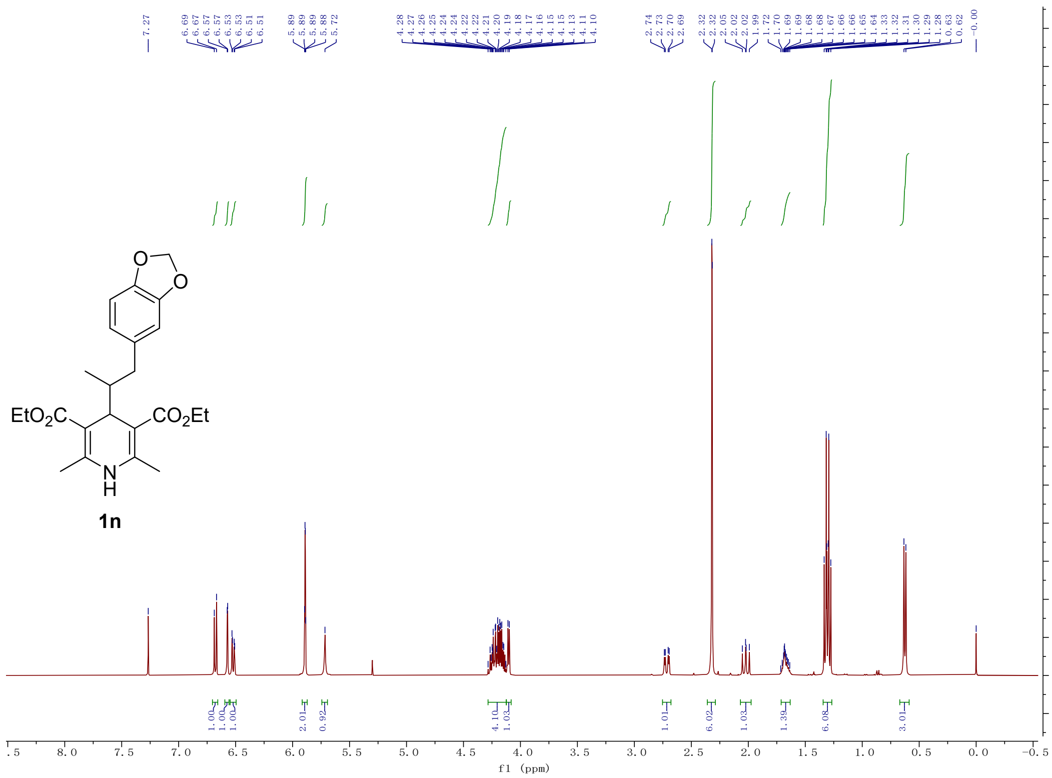

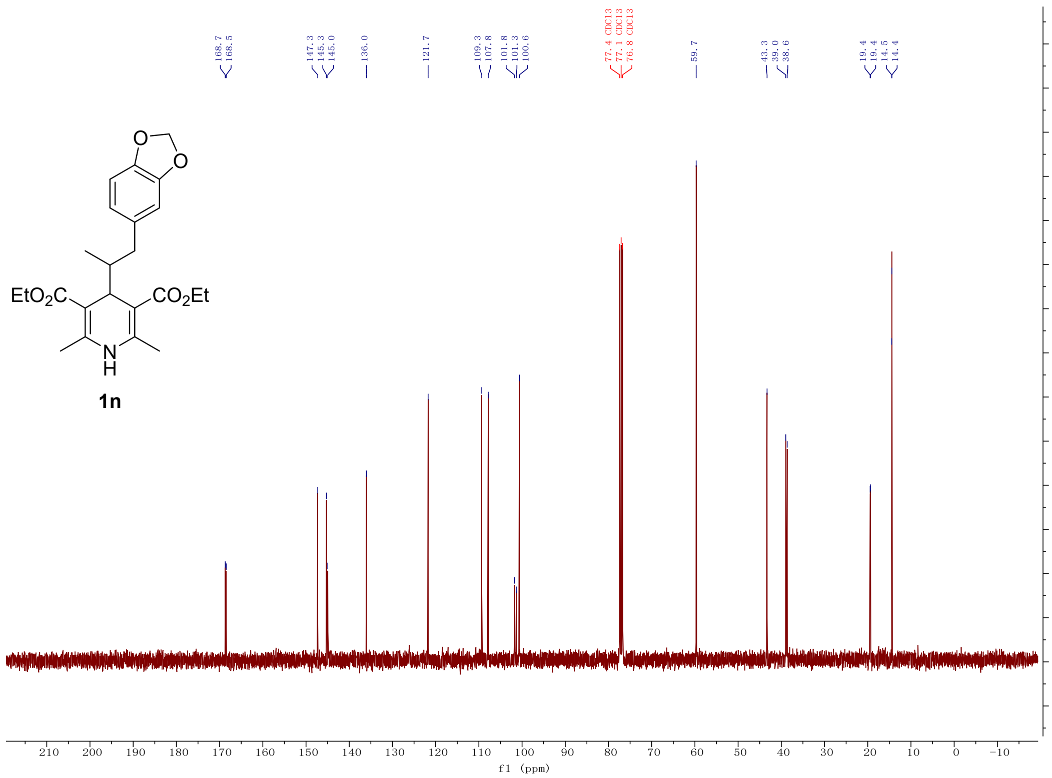

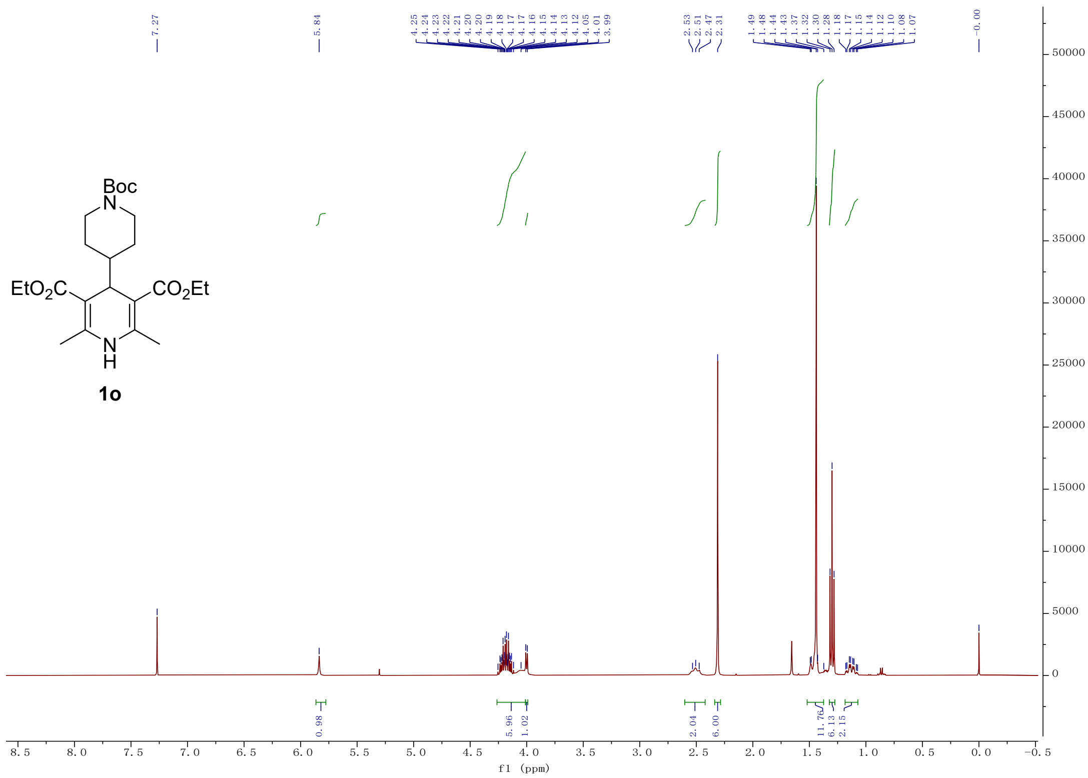
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H
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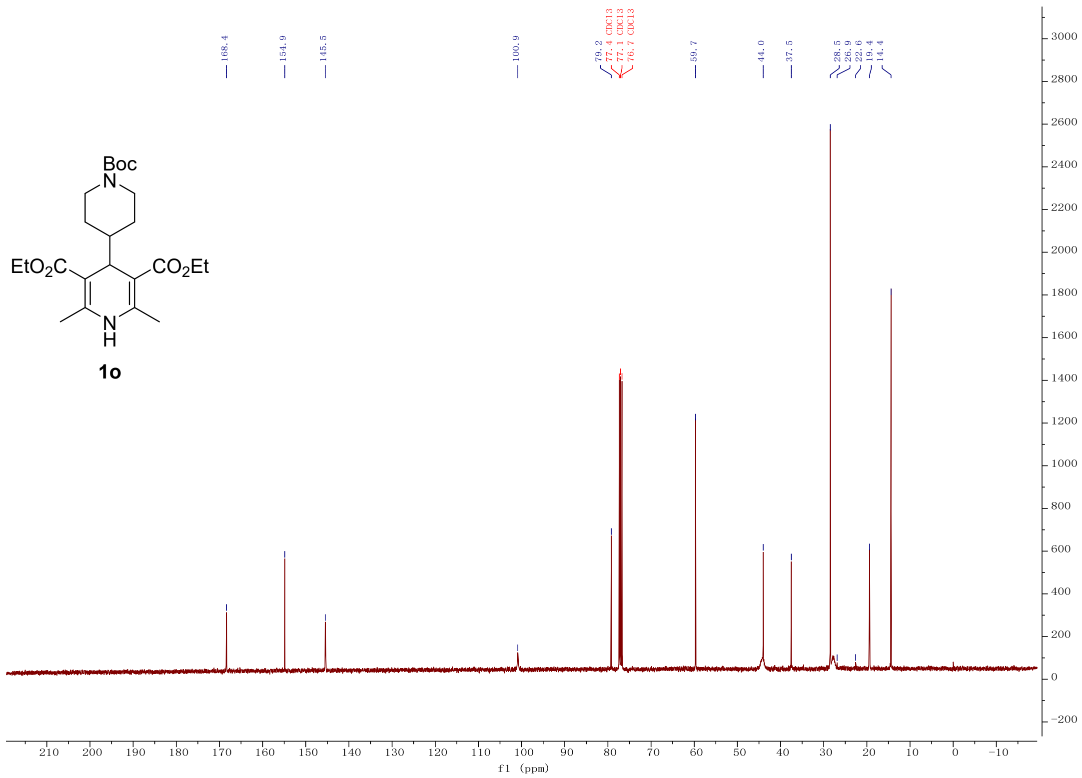
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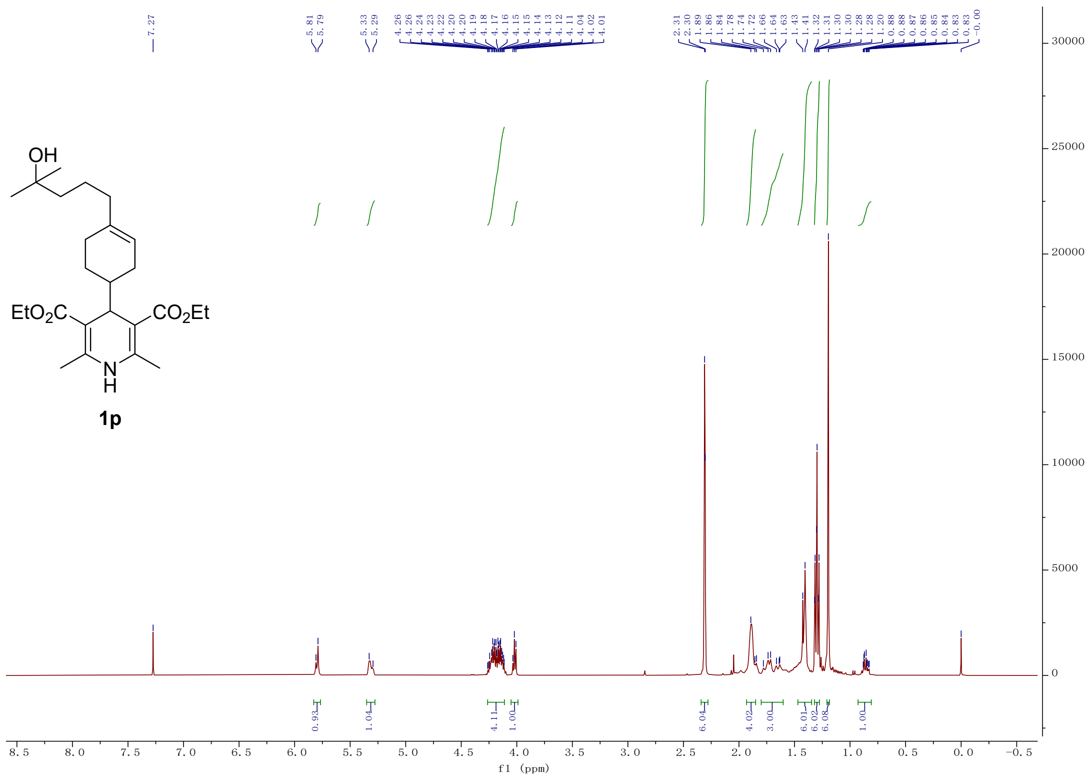

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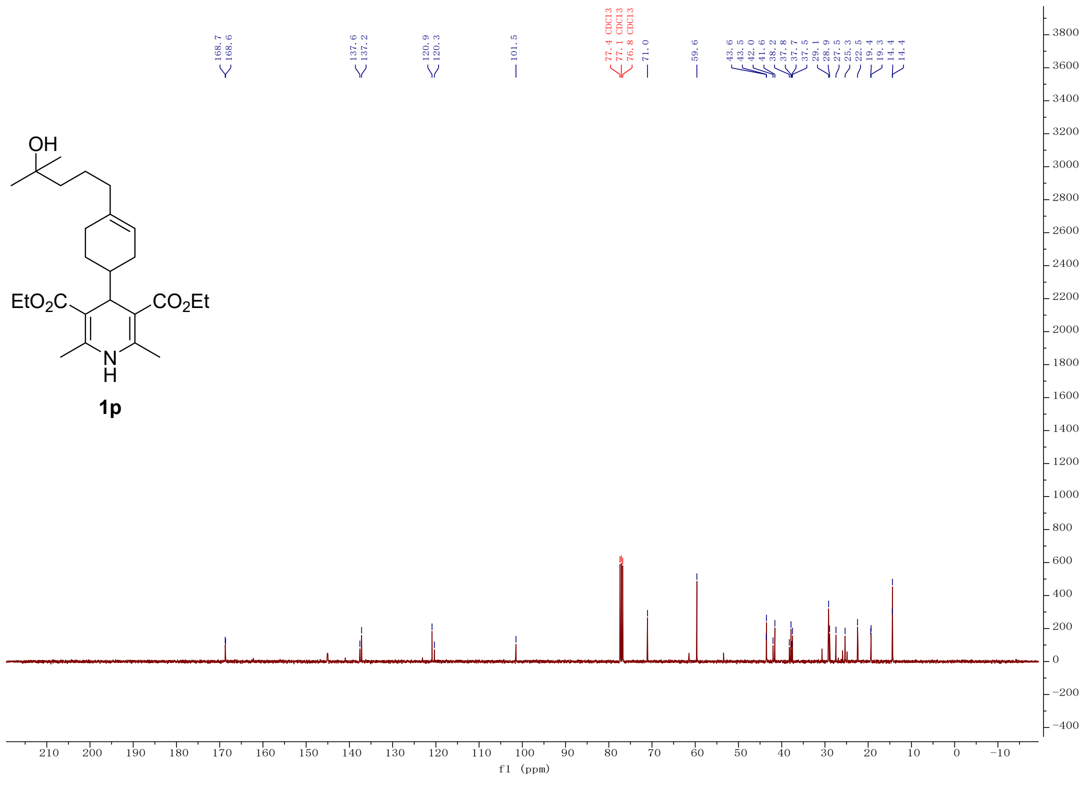

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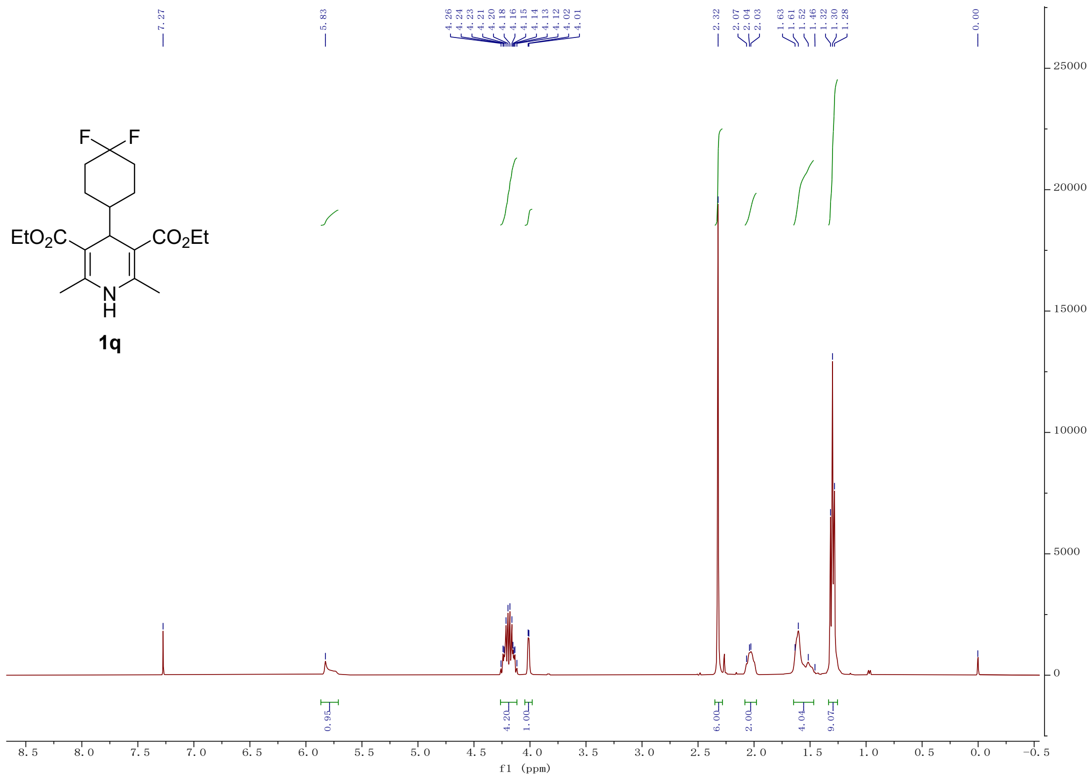
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2.32
2.07 2.04 2.03
1.63 1.61 1.52 1.46 1.32 1.30 1.28
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0.95
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1.00
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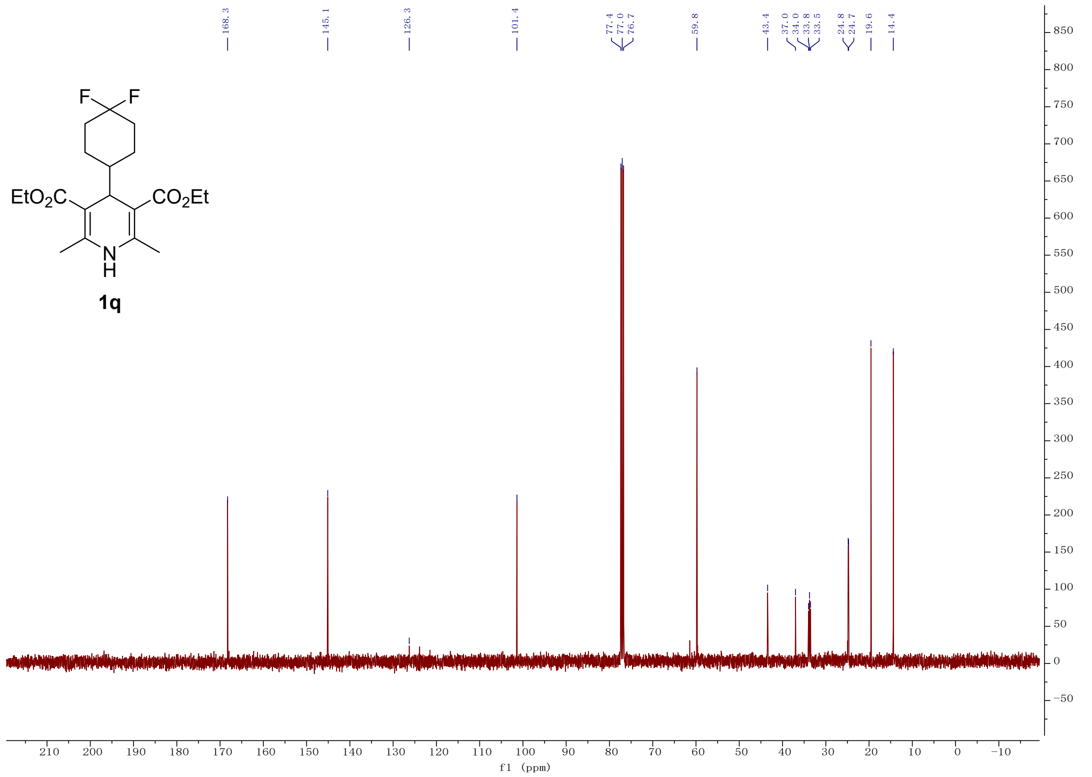
2.00
4.04
9.07
f1 (ppm)

1q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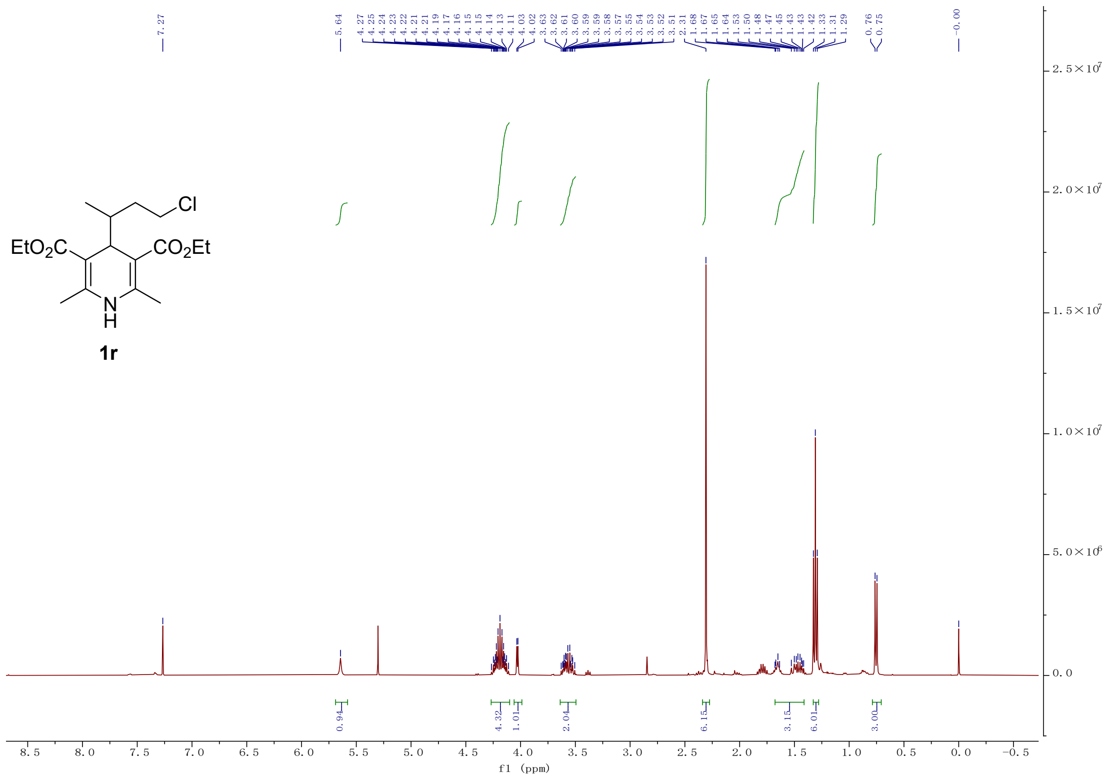
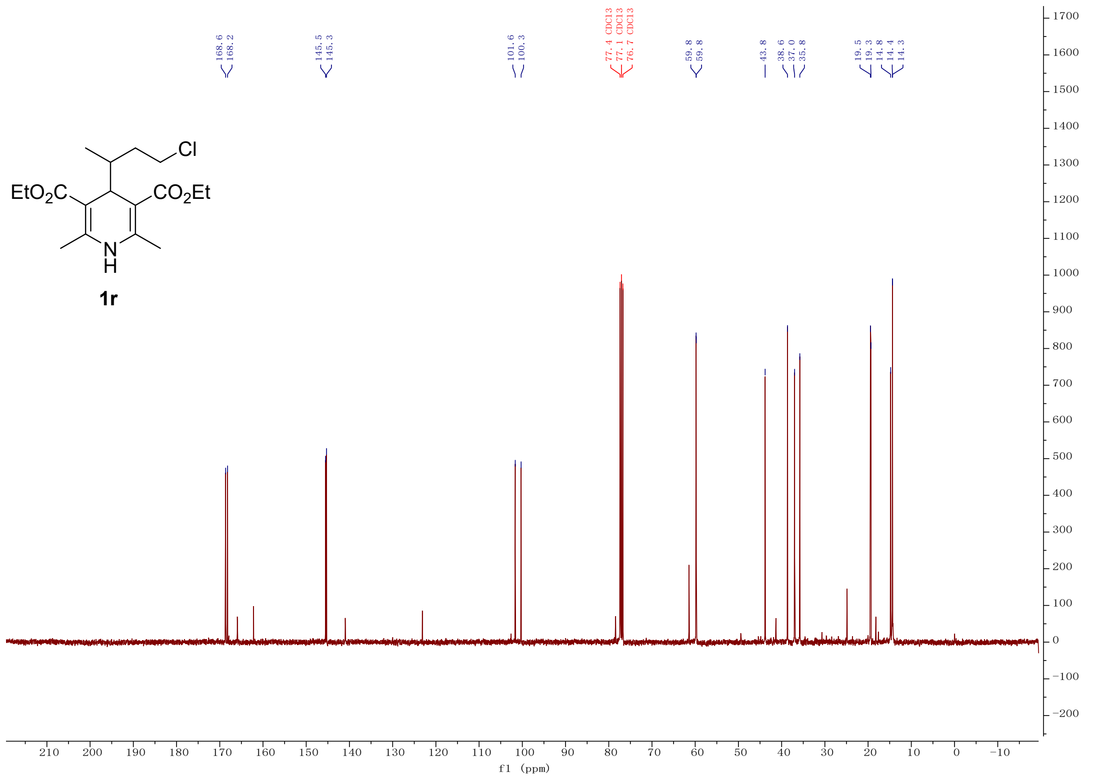
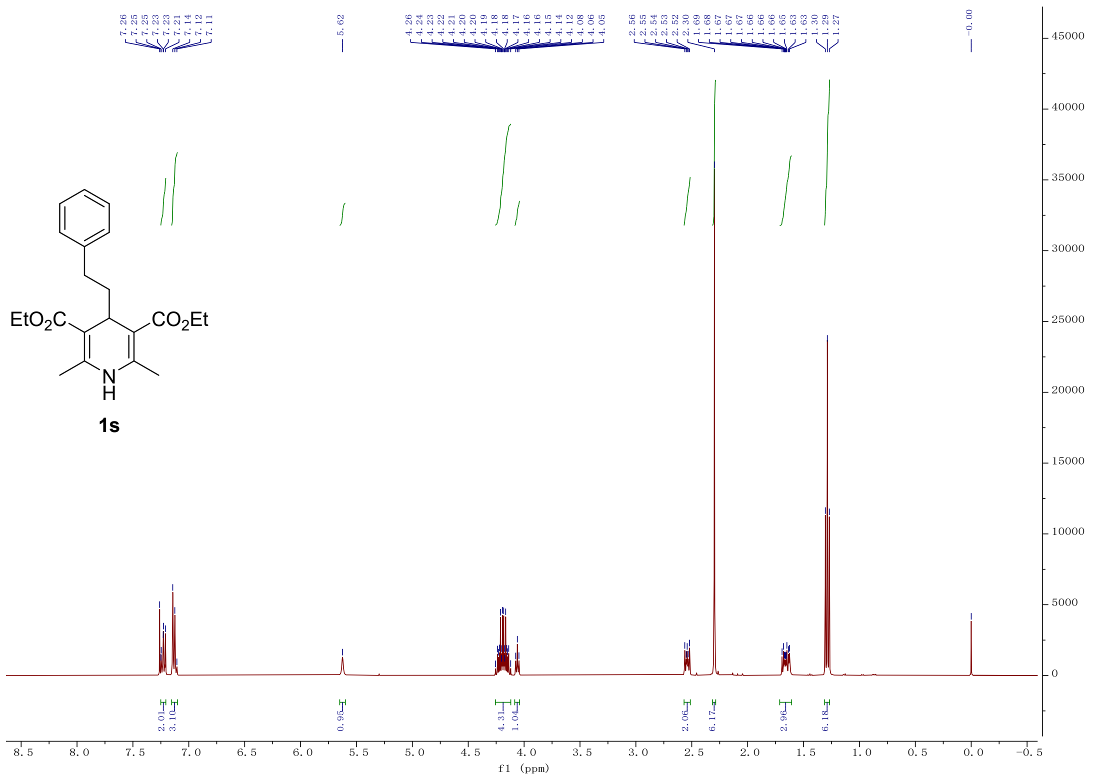
19.6
14.4
f1 (ppm)

1q



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2.56 2.55 2.54 2.53 2.52 2.30 1.69 1.68 1.67 1.67 1.67 1.66 1.66 1.65 1.63 1.63 1.30 1.29 1.27
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CO2Et
N
H
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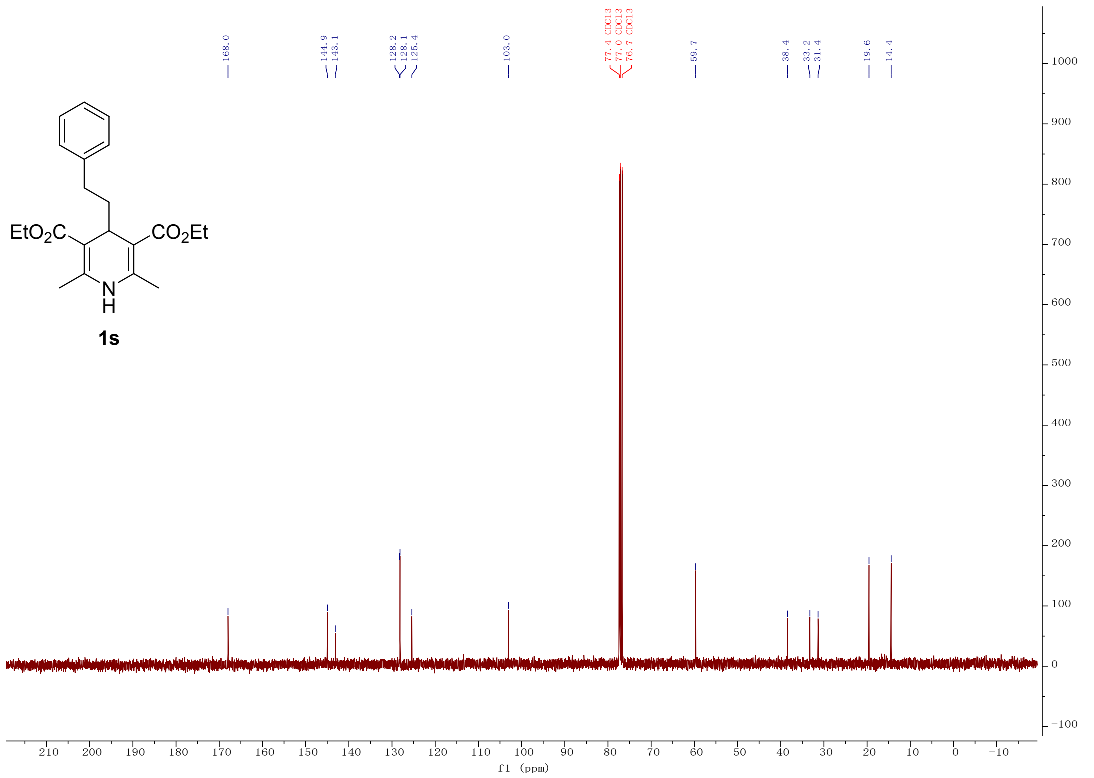
f1 (ppm)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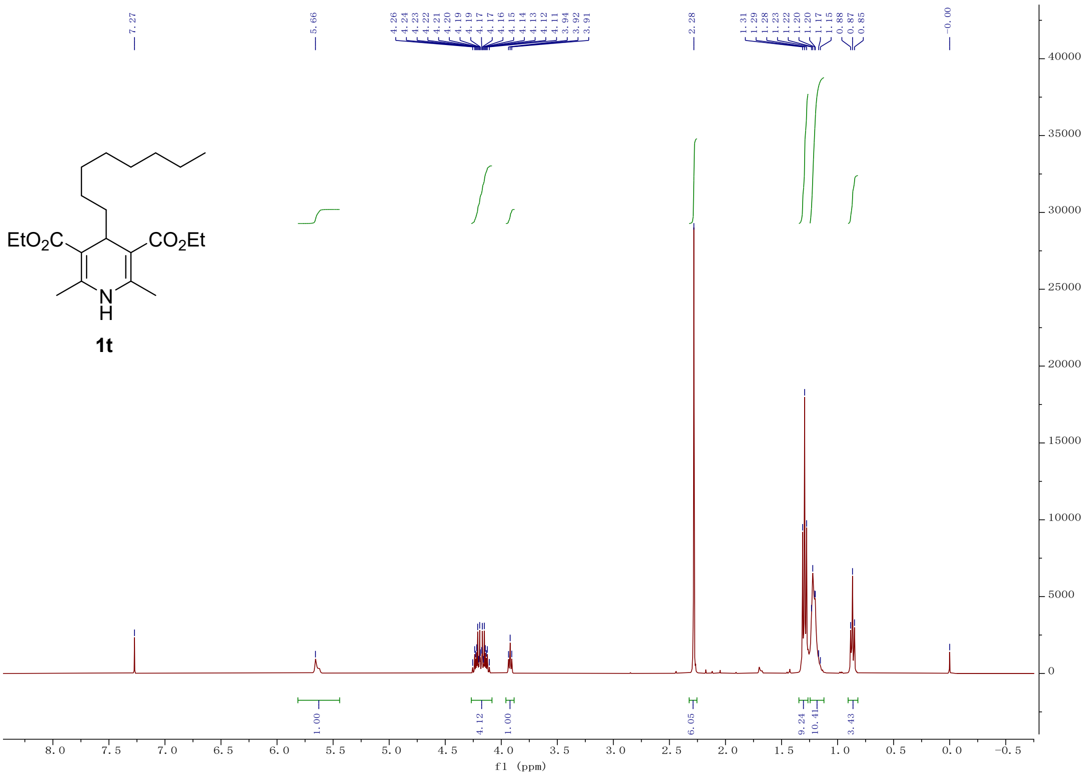
H
1s
f1 (ppm)



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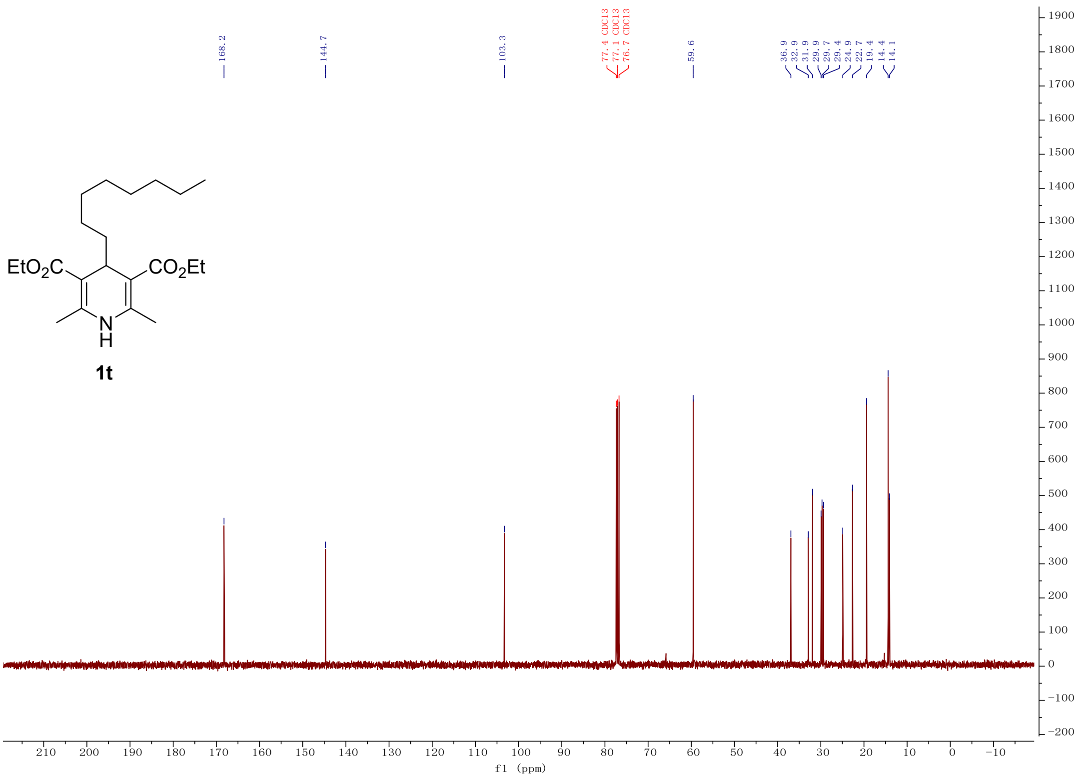

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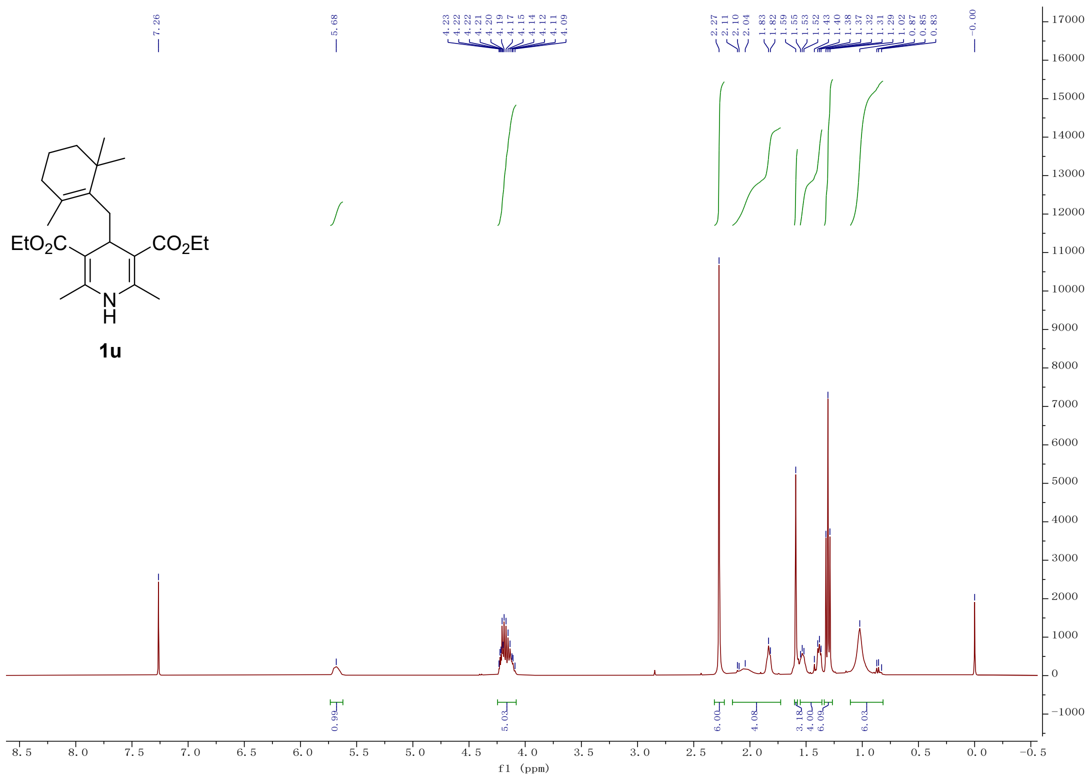

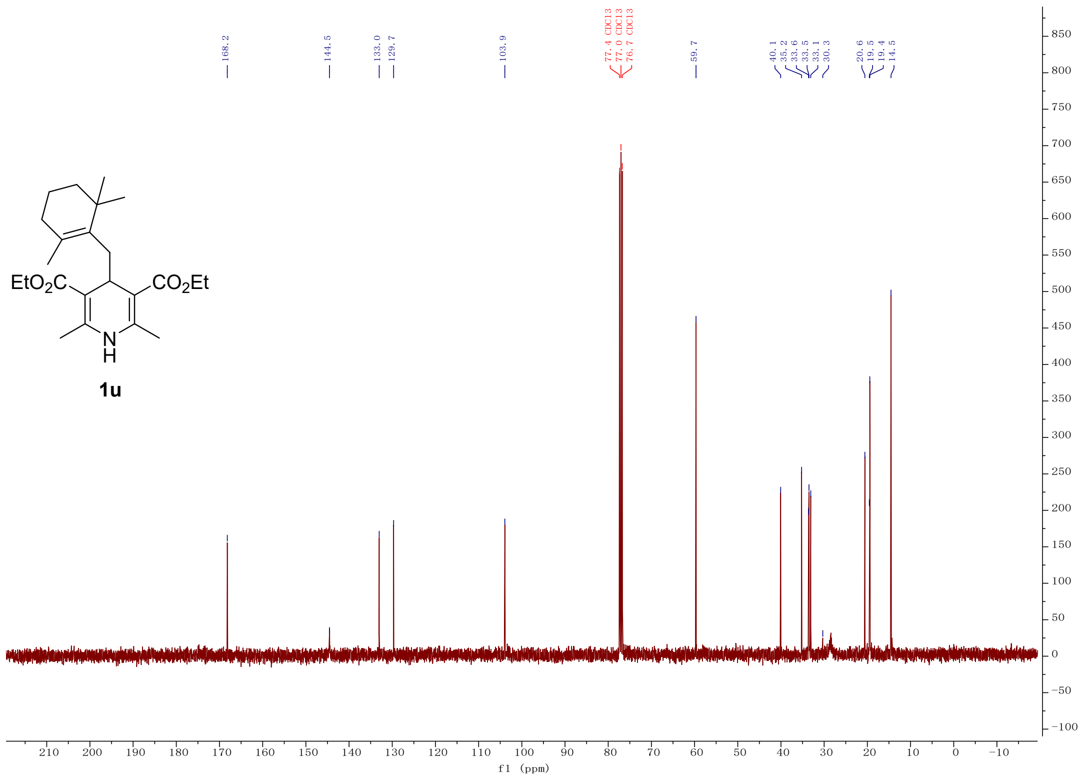

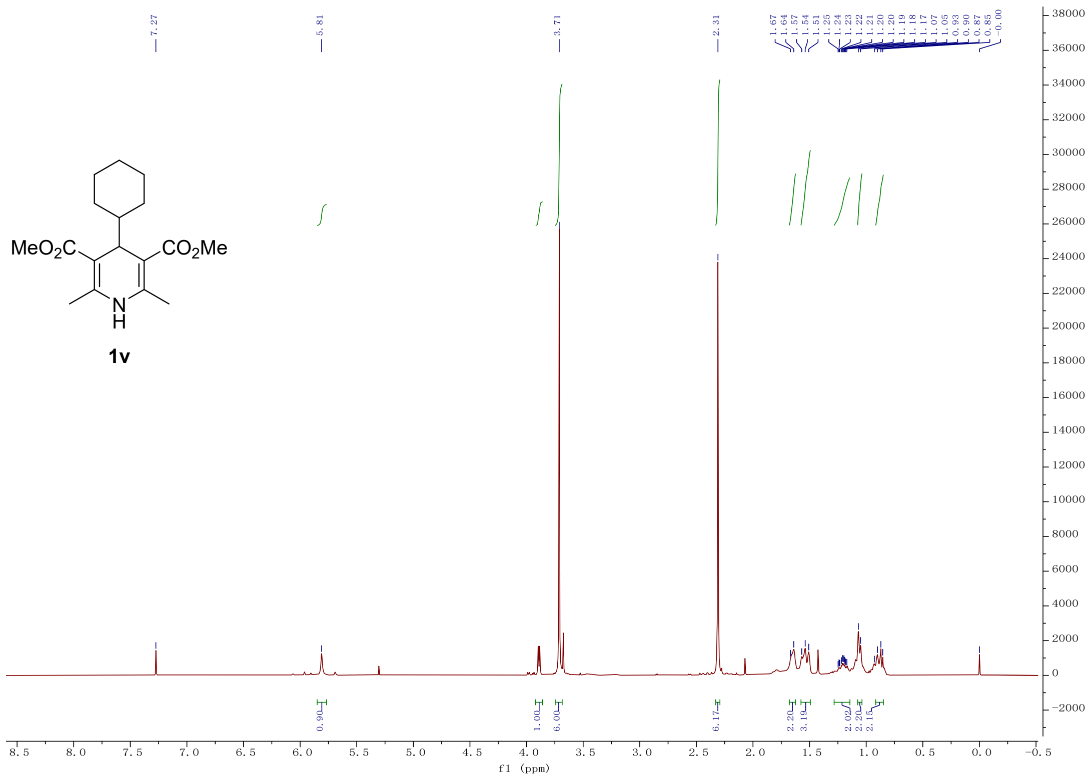
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MeO2C
CO2Me
N
H
1v
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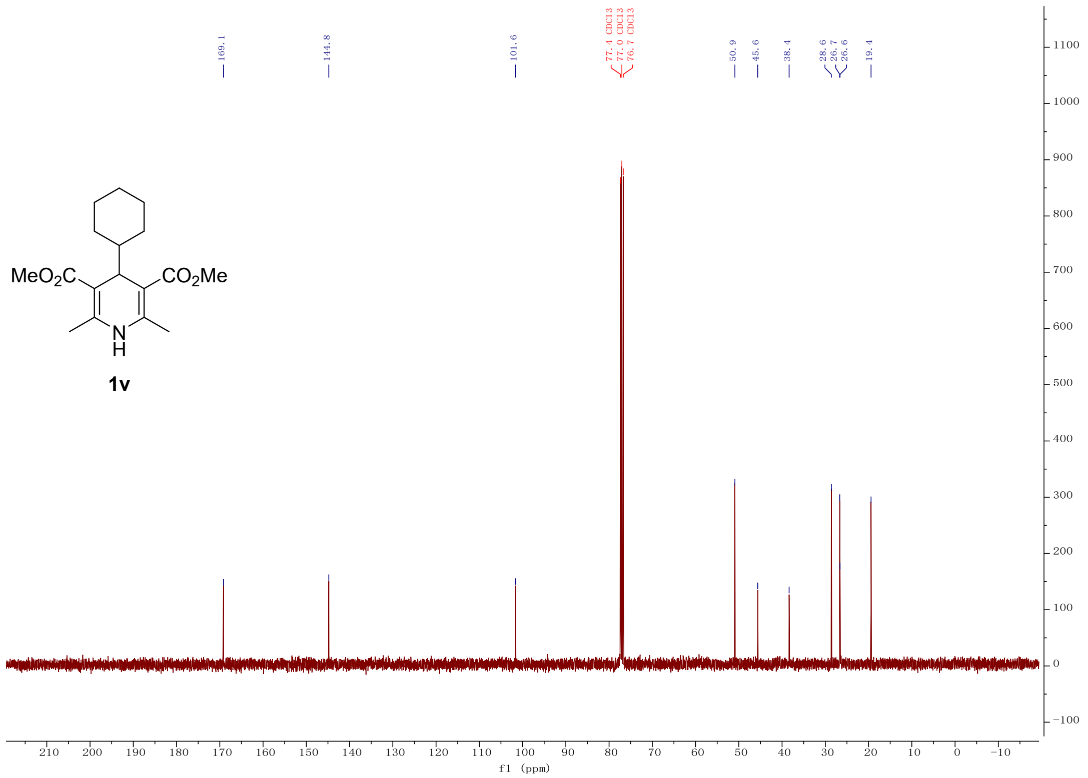
6.00
6.17
2.20
3.19
2.02
2.20
2.15
f1 (ppm)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101.6
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77.0 CDCl3
76.7 CDCl3
50.9
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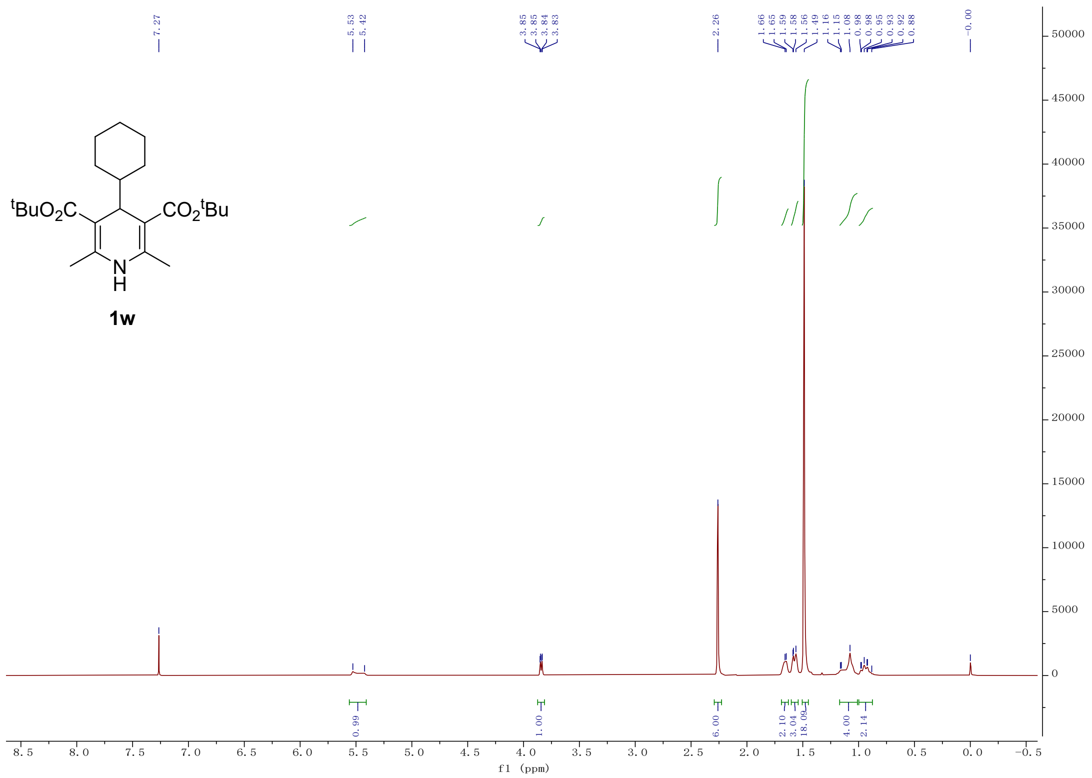
28.6
26.7
26.6
19.4
MeO2C
CO2Me
N
H
1v
f1 (ppm)



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3.83
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1.58
1.56
1.49
1.16
1.15
1.08
0.98
0.98
0.95
0.93
0.92
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18.09
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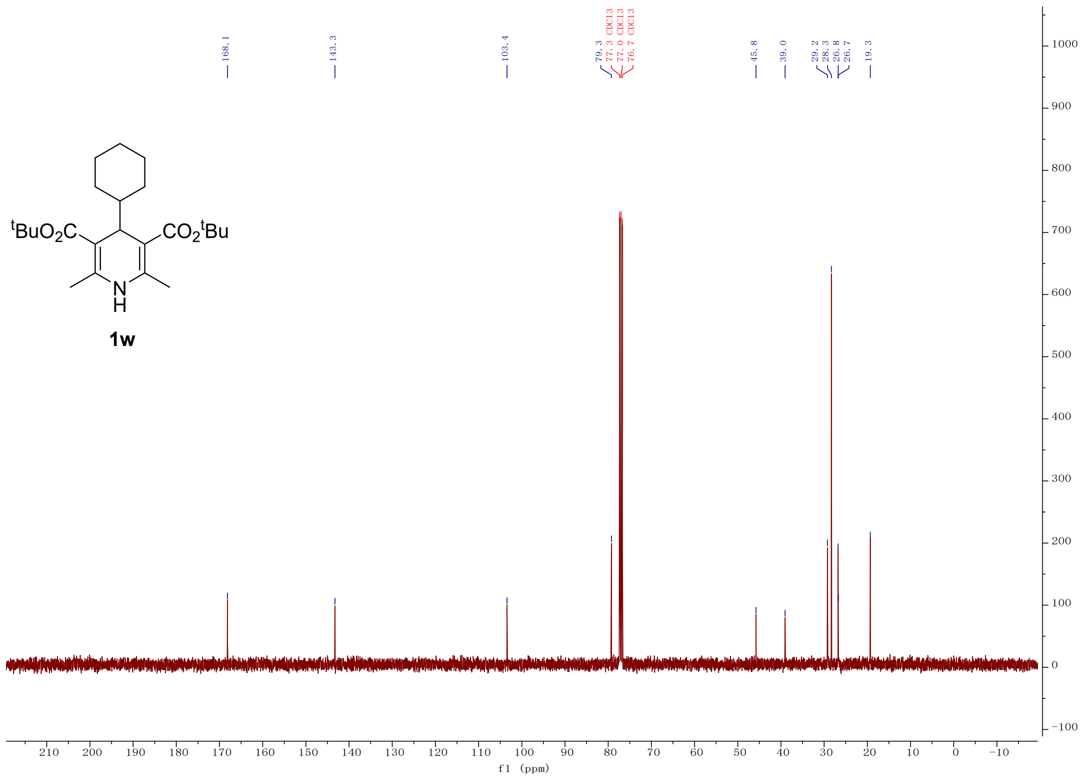
2.14
f1 (ppm)



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39.0
29.2
28.3
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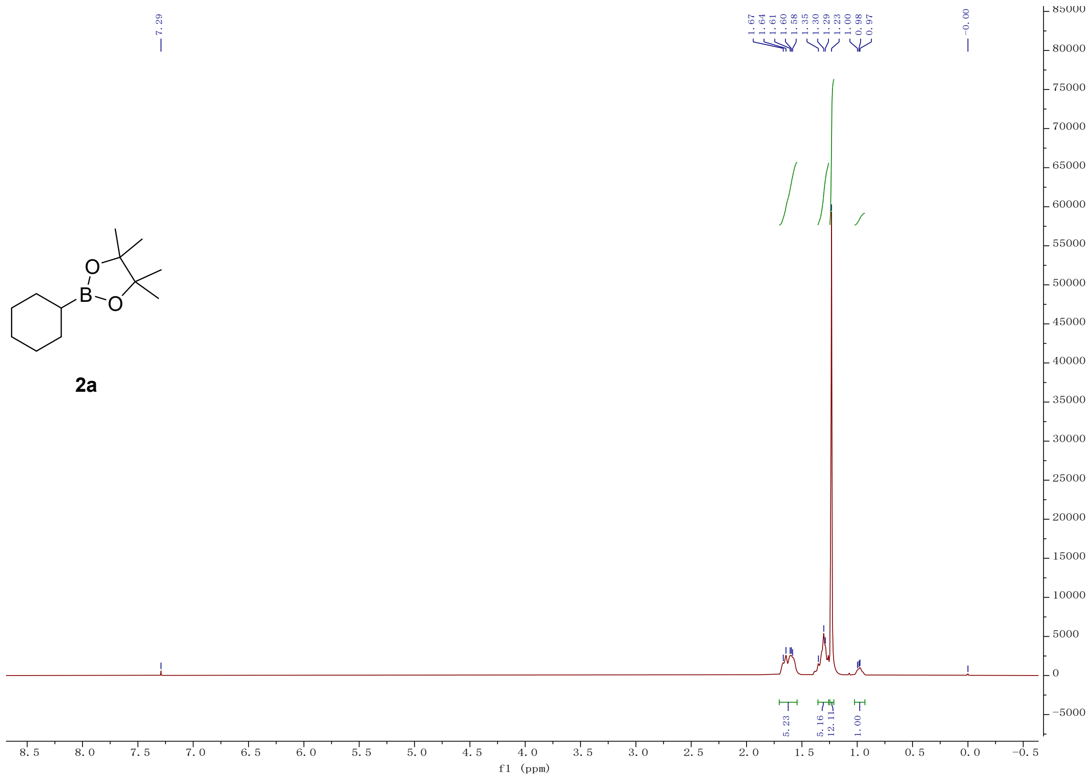
26.7
19.3
f1 (ppm)



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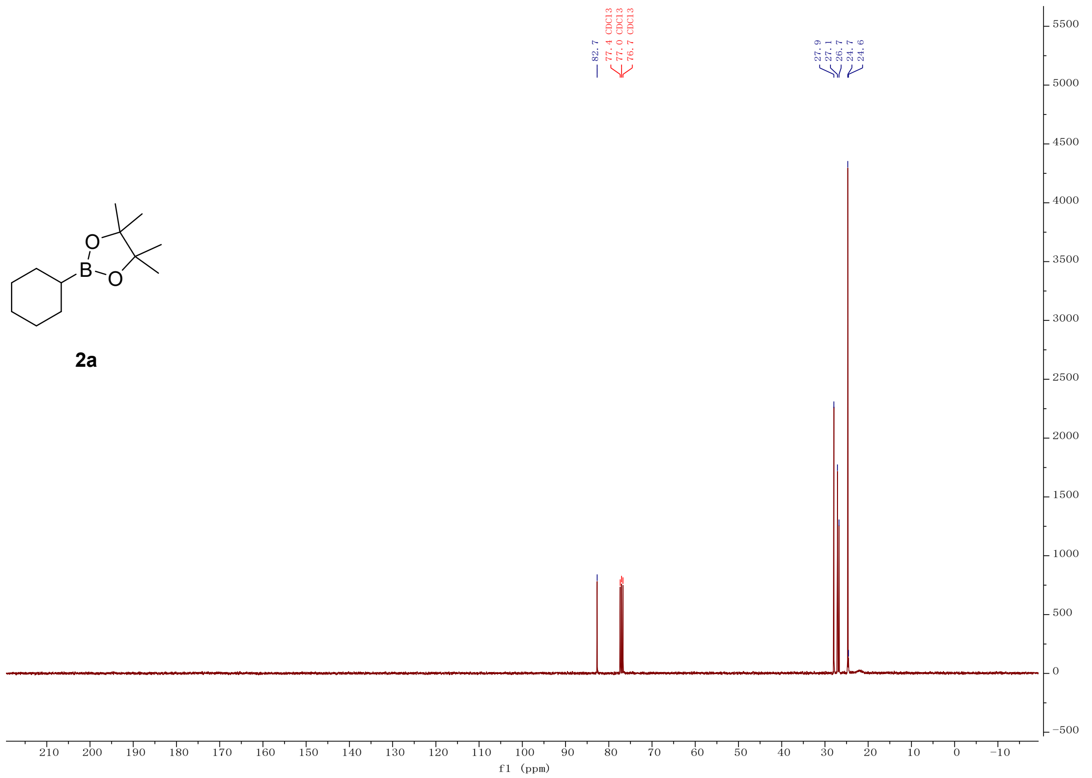

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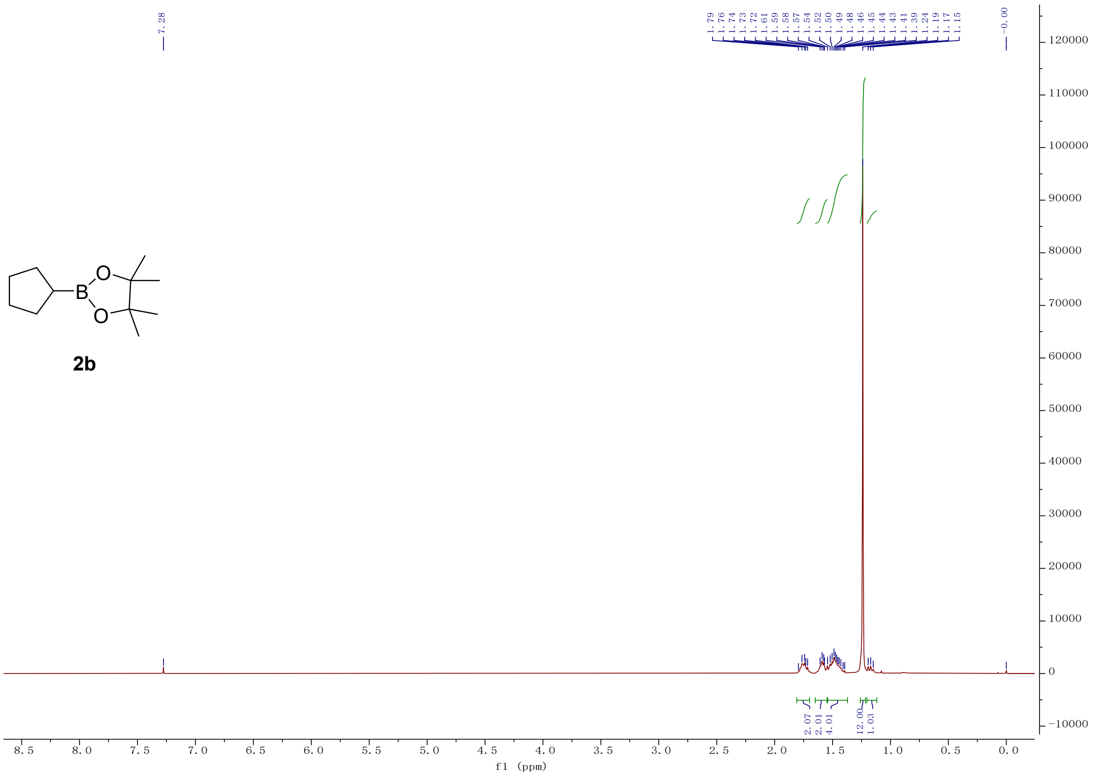
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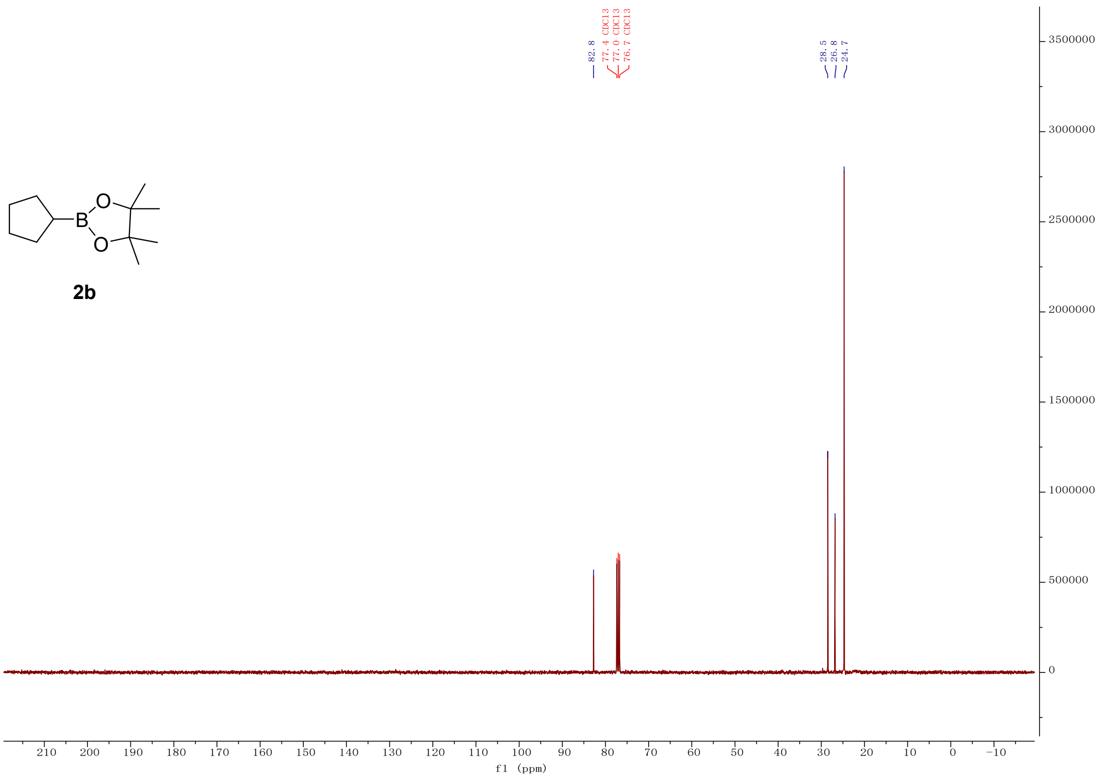
2.07 2.01 4.01 12.00 1.03
f1 (ppm)

2b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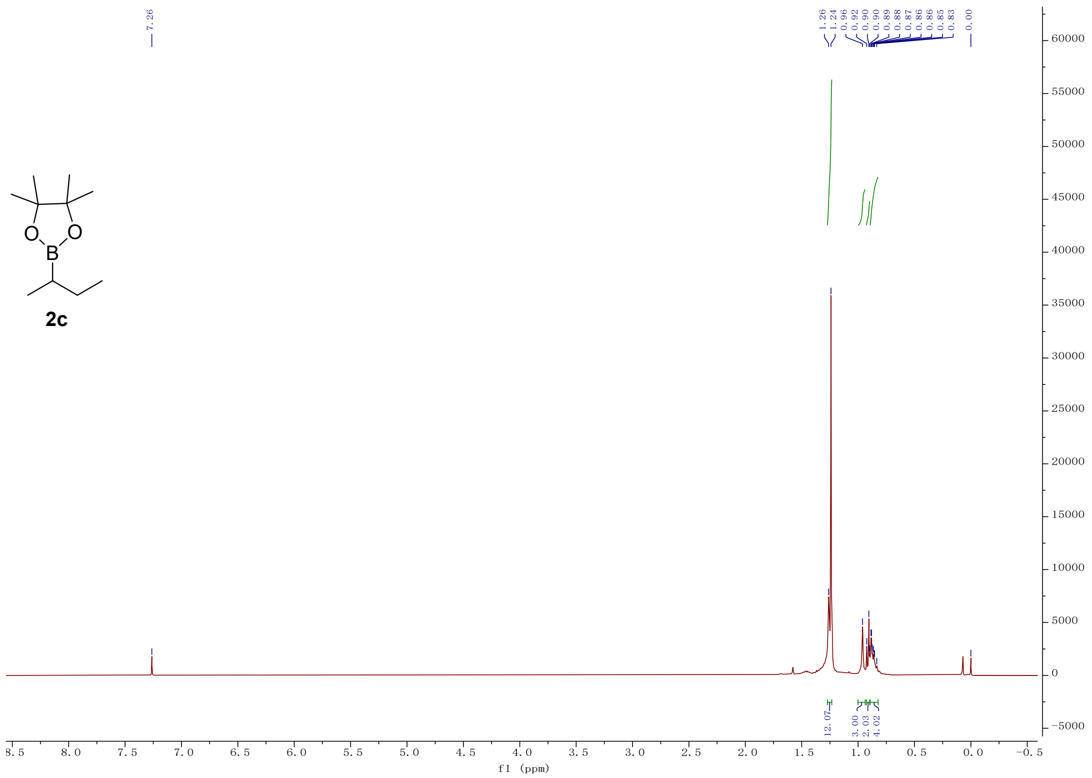
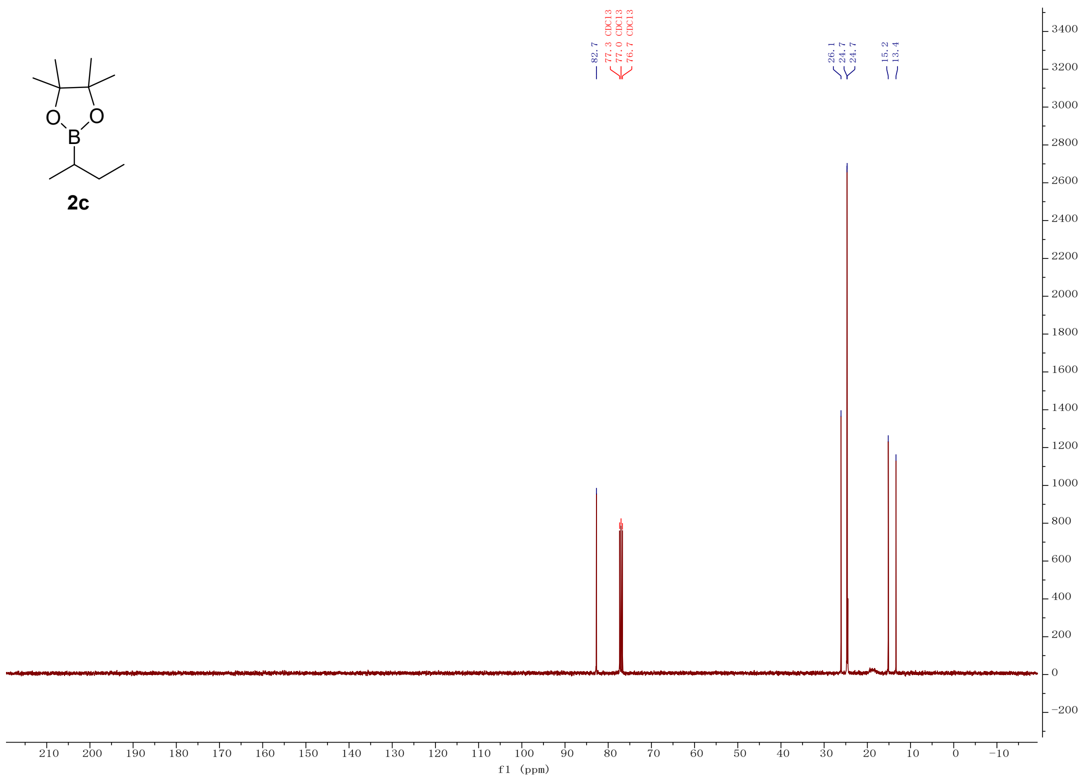
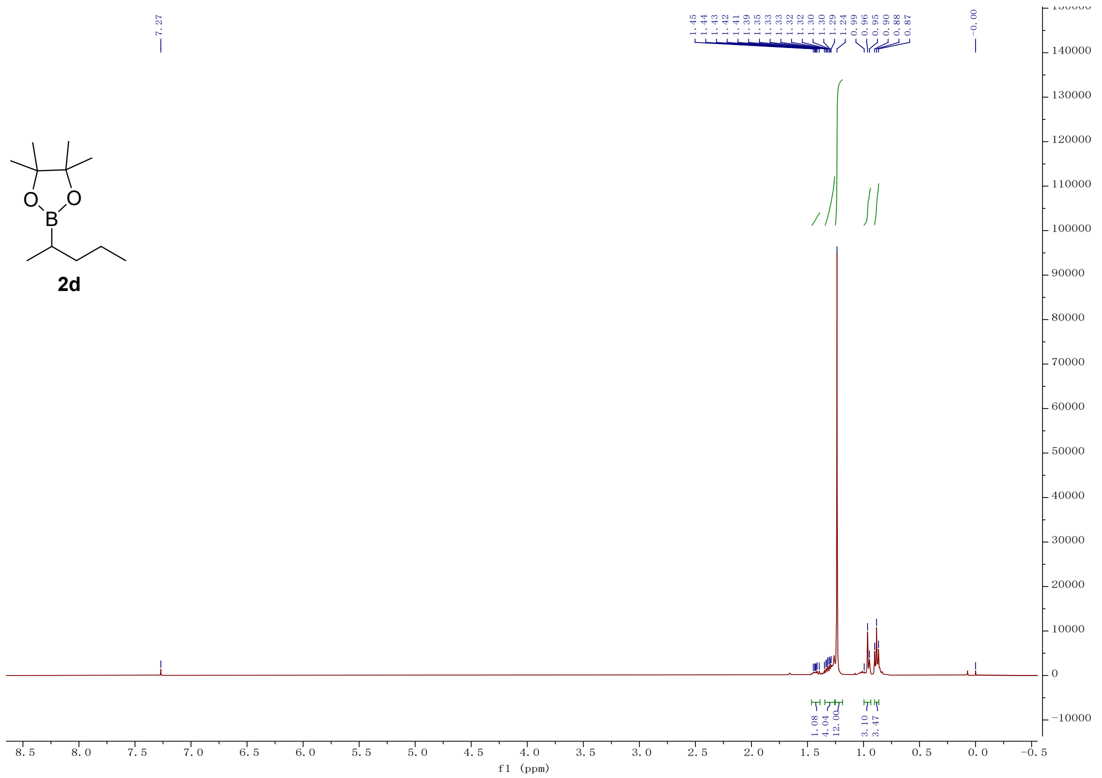
24.7
f1 (ppm)

2b



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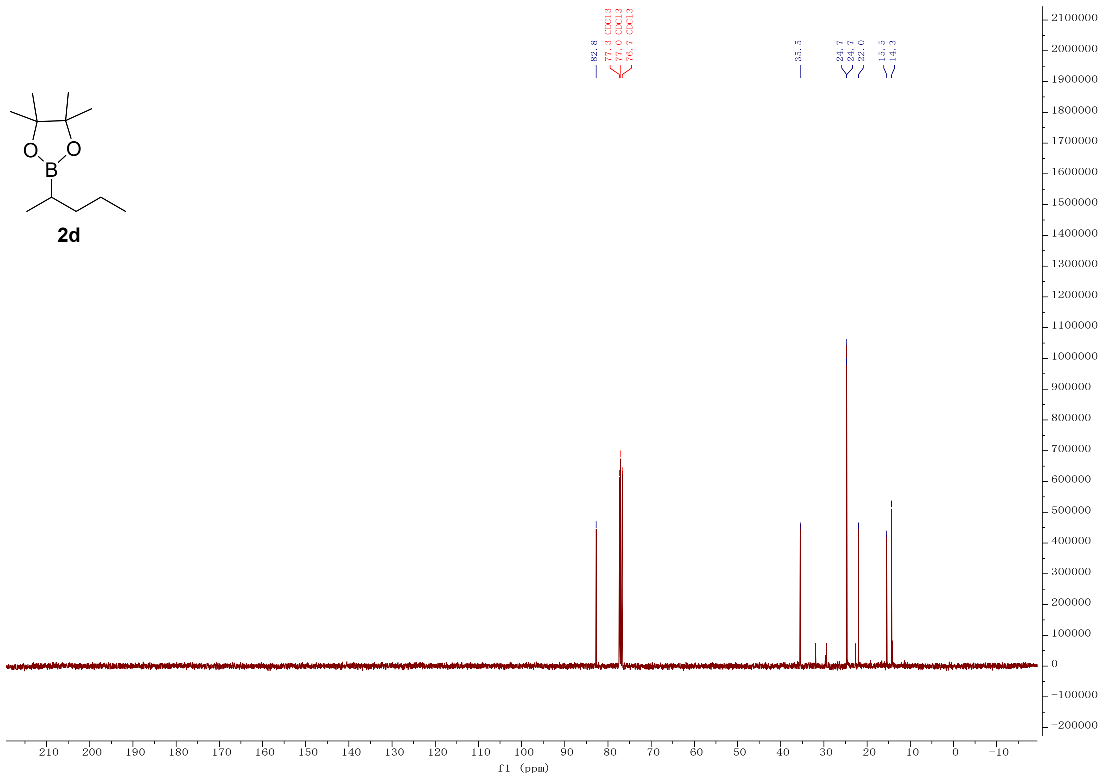
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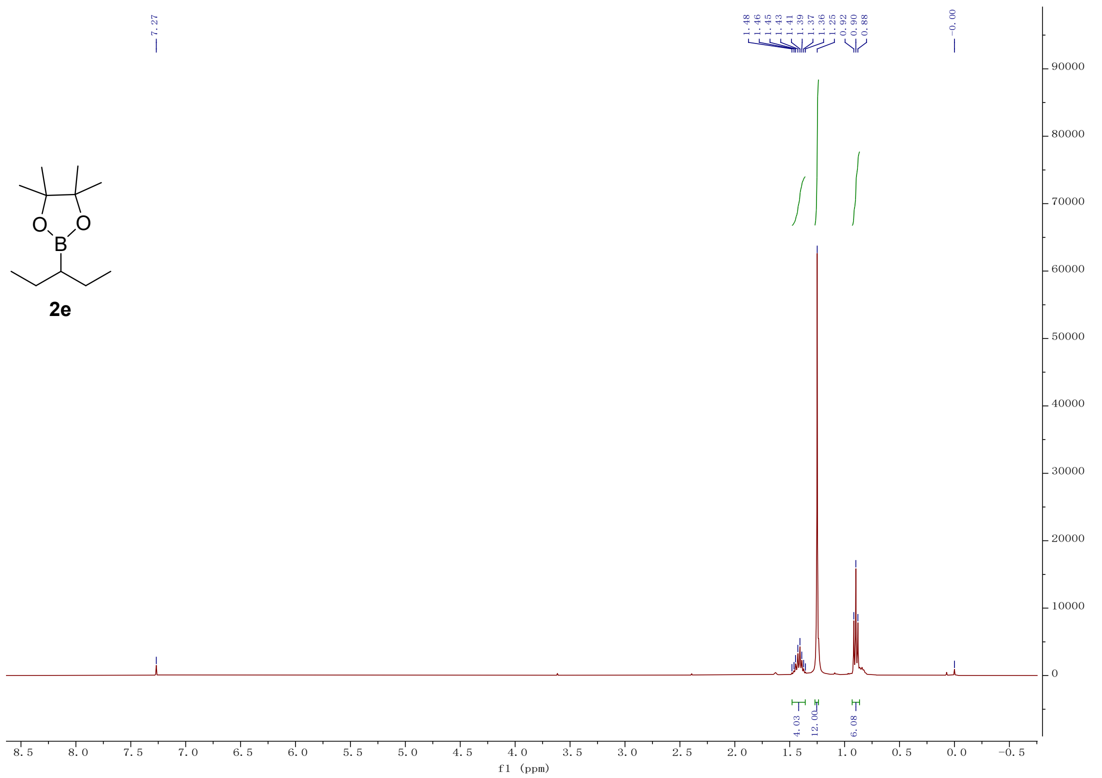
2d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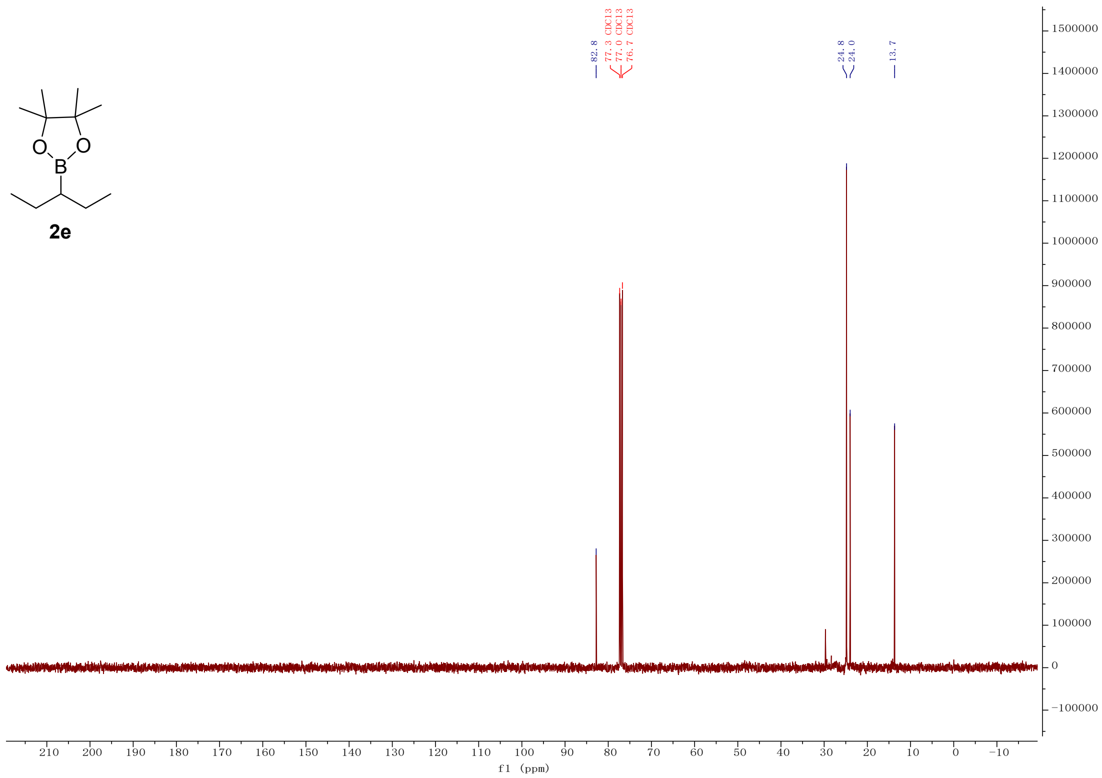
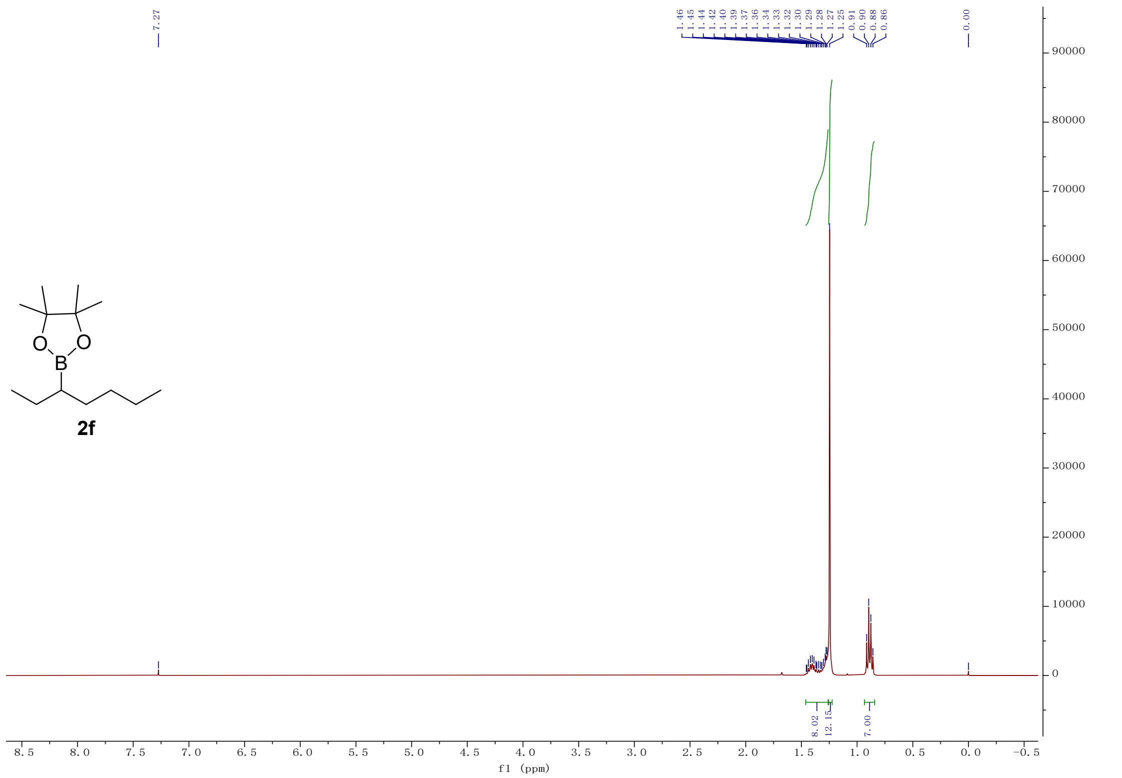
6.08
f1 (ppm)


82.8
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
24.8
24.0
13.7
2e
f1 (ppm)



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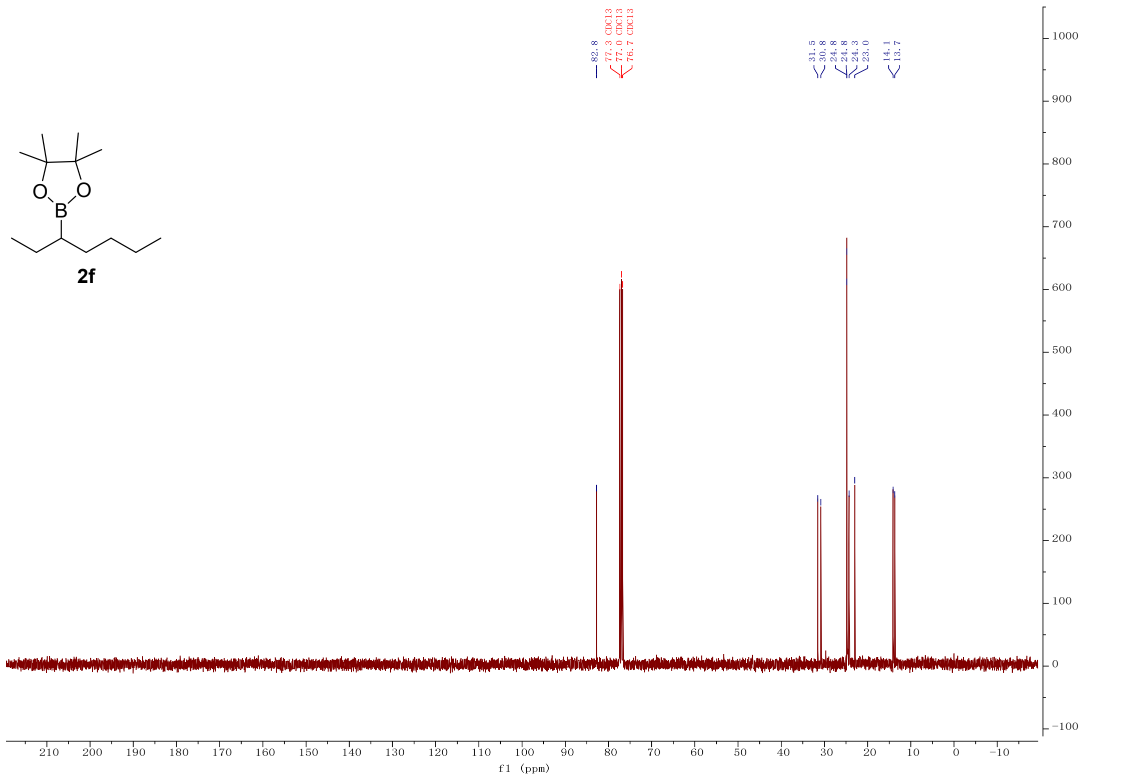

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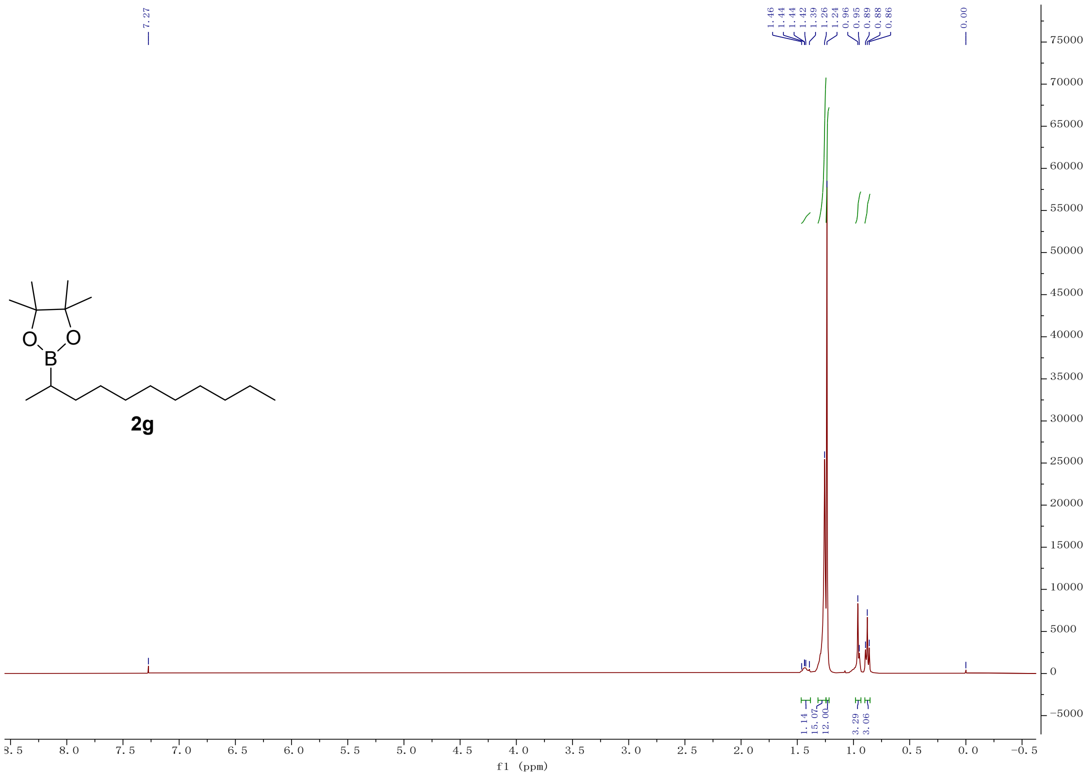
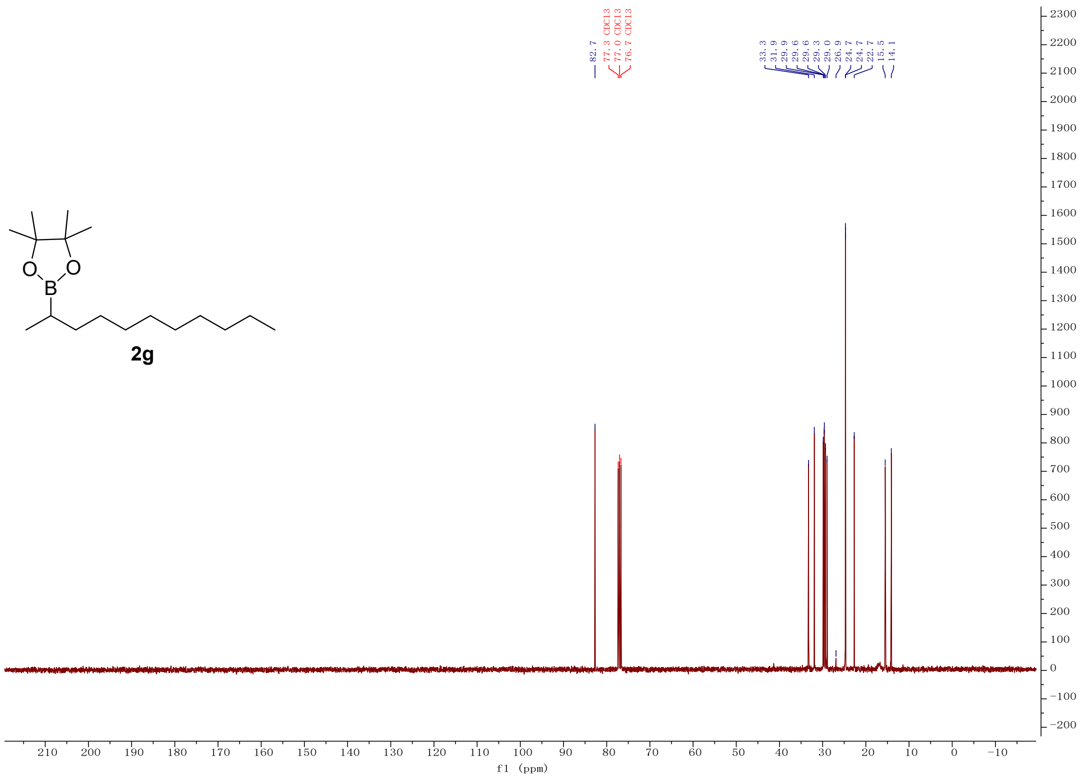


2g



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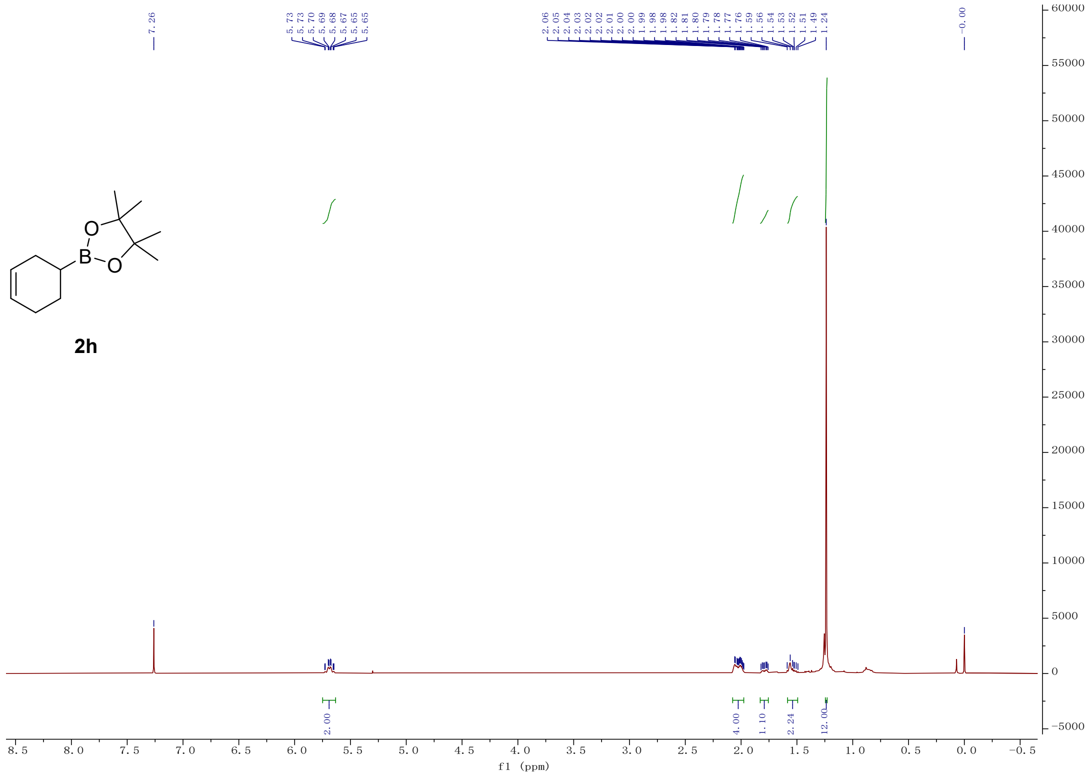
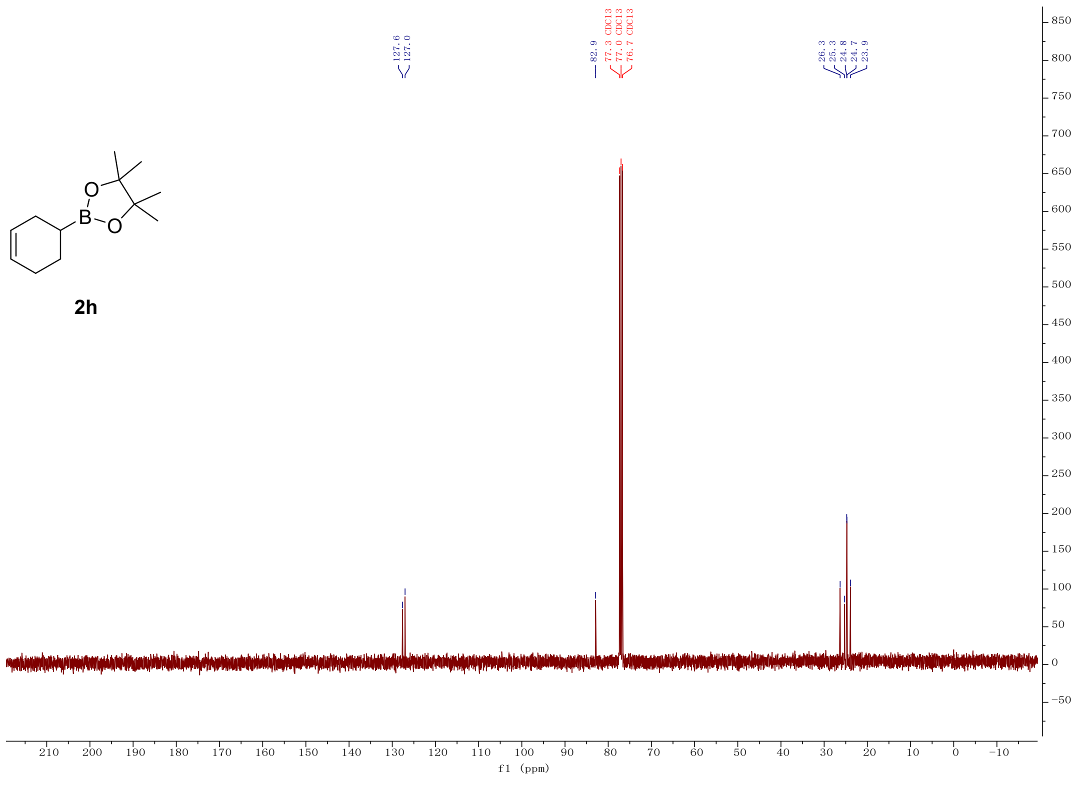
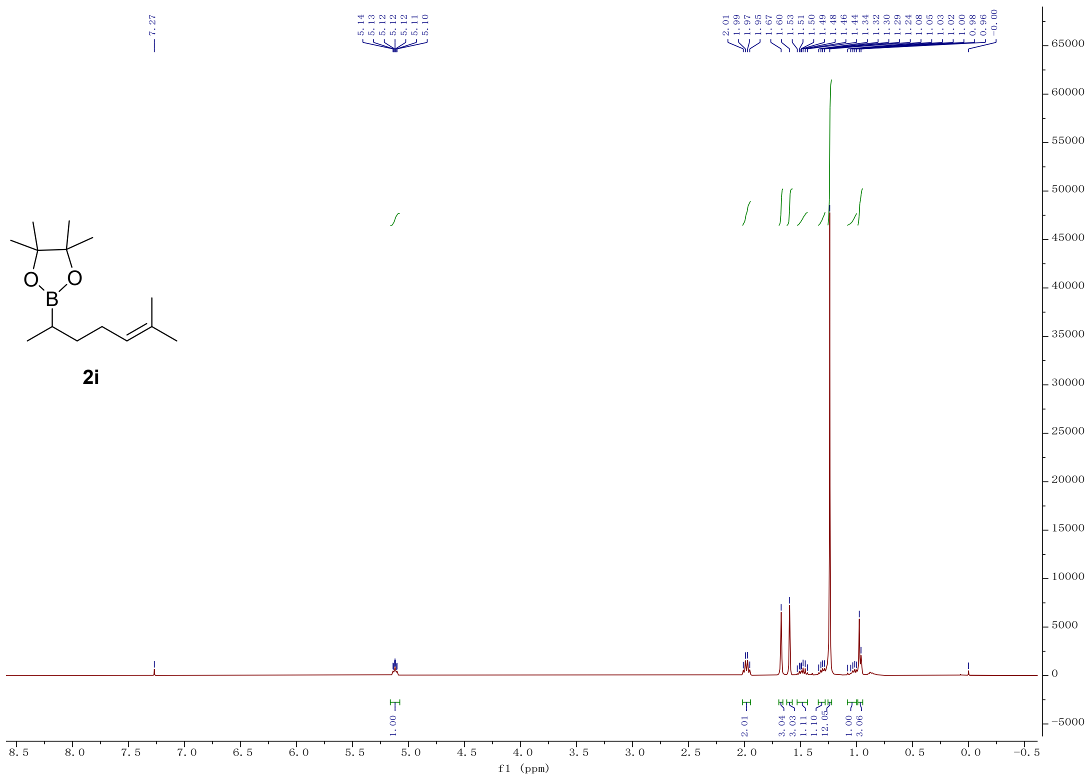
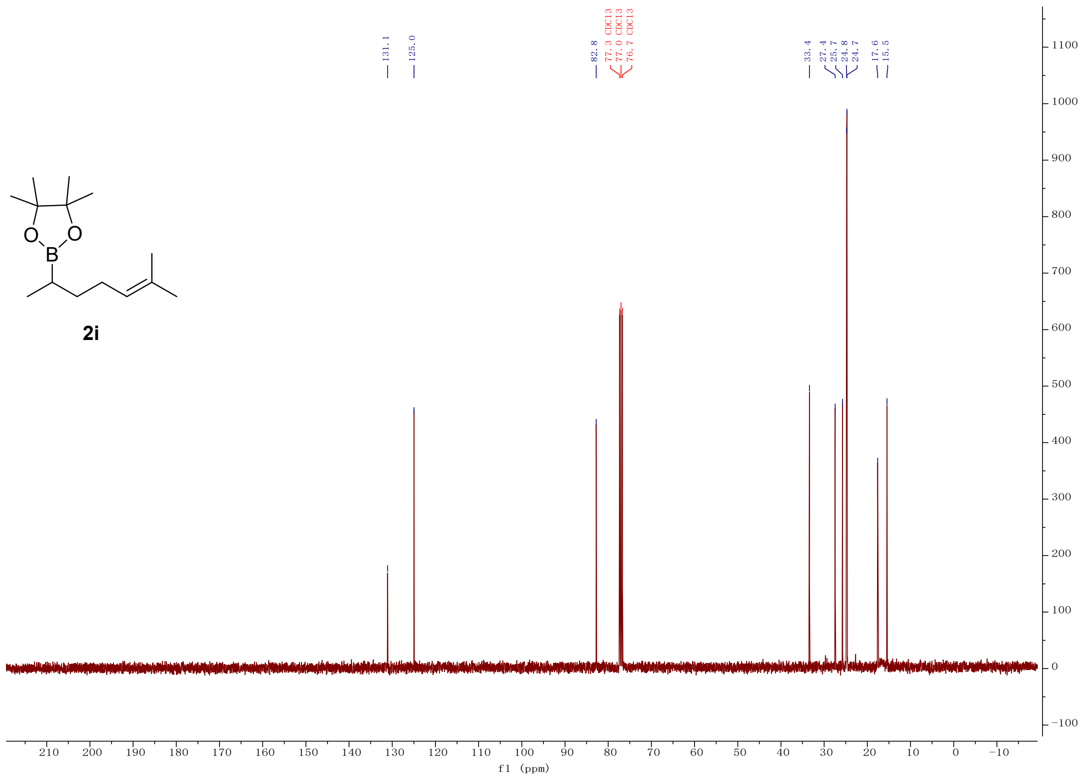
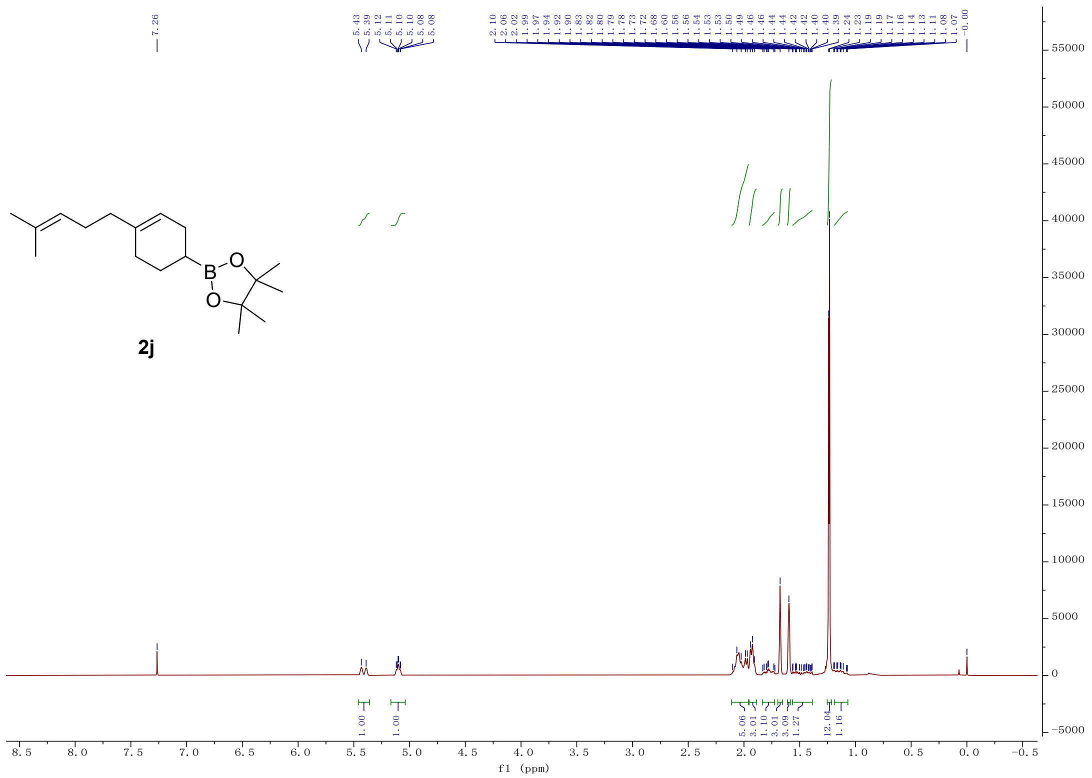

O
B
O
2h
7.26
5.73
5.73
5.70
5.69
5.68
5.67
5.65
5.65
2.06
2.05
2.04
2.03
2.02
2.02
2.01
2.00
2.00
1.99
1.98
1.98
1.82
1.81
1.80
1.79
1.78
1.77
1.76
1.59
1.56
1.54
1.53
1.52
1.51
1.49
1.24
-0.00
2.00
4.00
1.10
2.24
12.00
f1 (ppm)

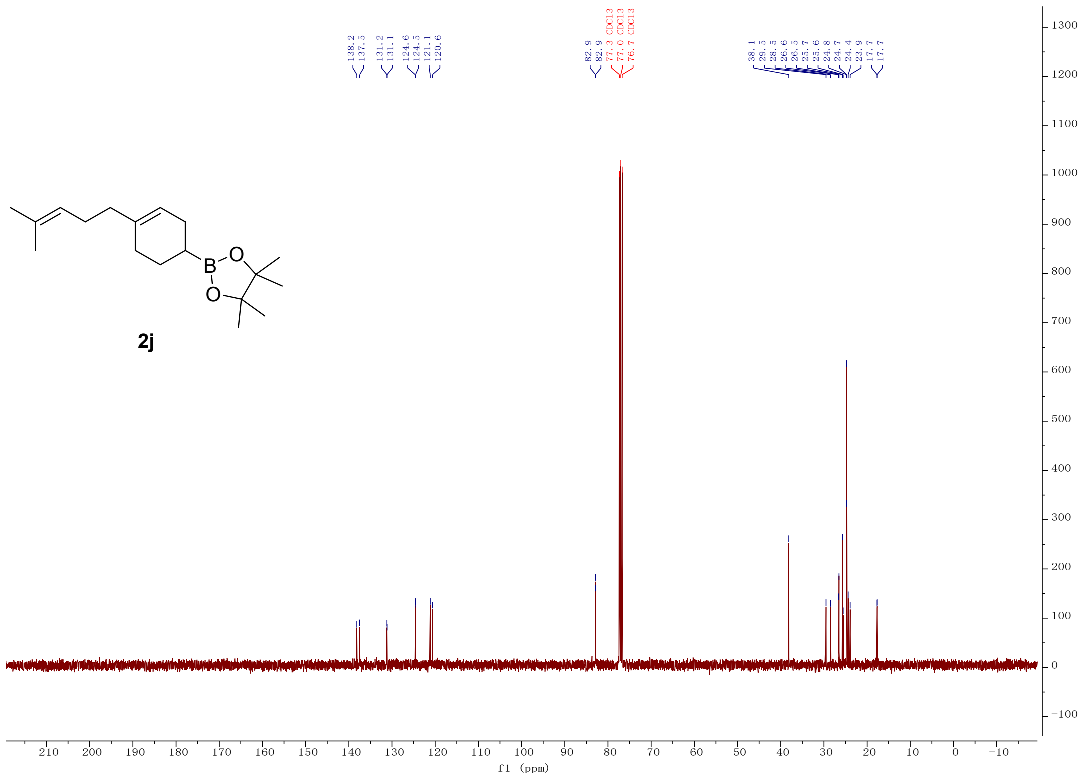

O
B
O
2h
127.6
127.0
82.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
26.3
25.3
24.8
24.7
23.9
f1 (ppm)


7.27
5.14 5.13 5.12 5.12 5.12 5.11 5.10
2.01 1.99 1.97 1.95 1.67 1.60 1.53 1.51 1.50 1.49 1.48 1.46 1.44 1.34 1.32 1.30 1.29 1.24 1.08 1.05 1.03 1.02 1.00 0.98 0.96 -0.00
O B O
2i
1.00
2.01
3.04 3.03 1.11 1.10 12.05
1.00 3.06
f1 (ppm)


131.1
125.0
82.8
77.3 CDCl3 77.0 CDCl3 76.7 CDCl3
33.4
27.4 25.7 24.8 24.7
17.6 15.5
O B O
2i
f1 (ppm)



2j



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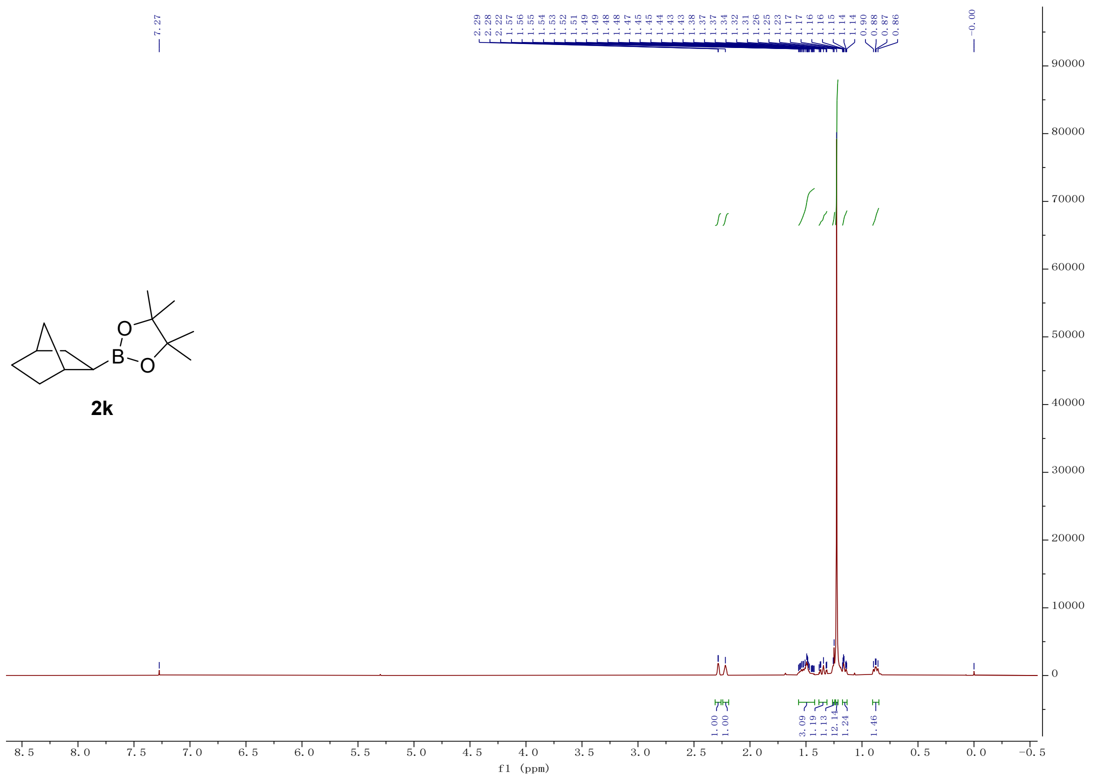

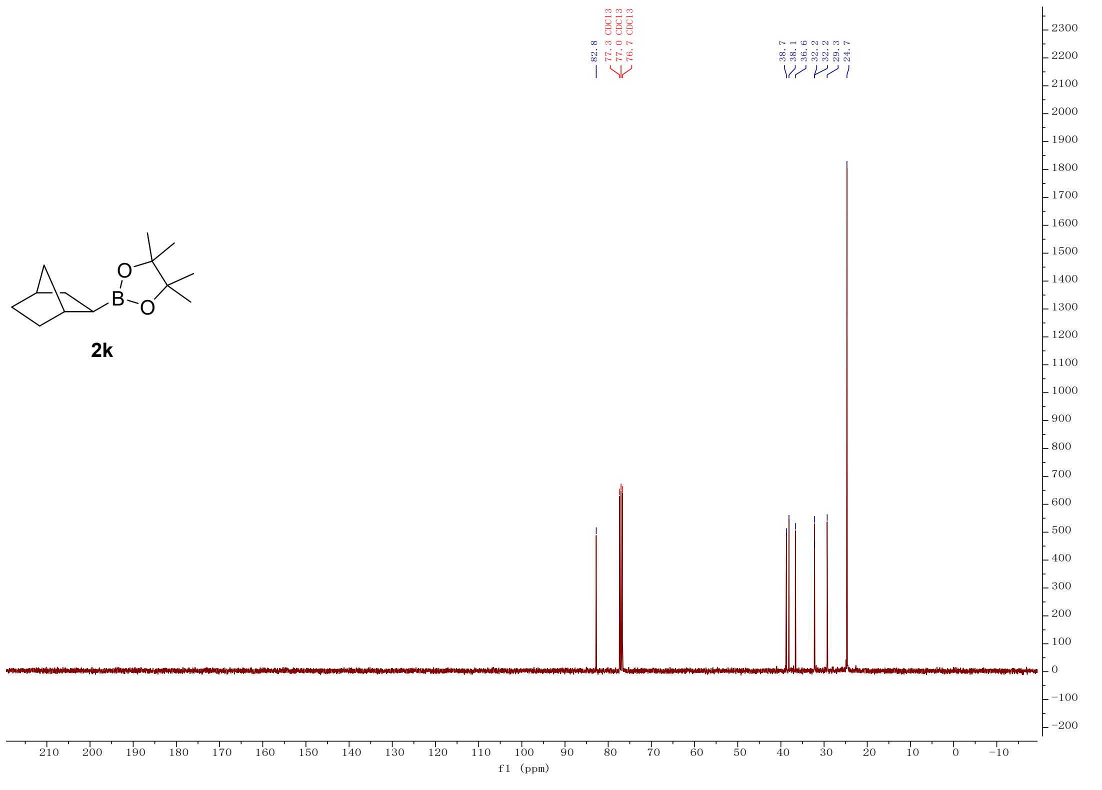

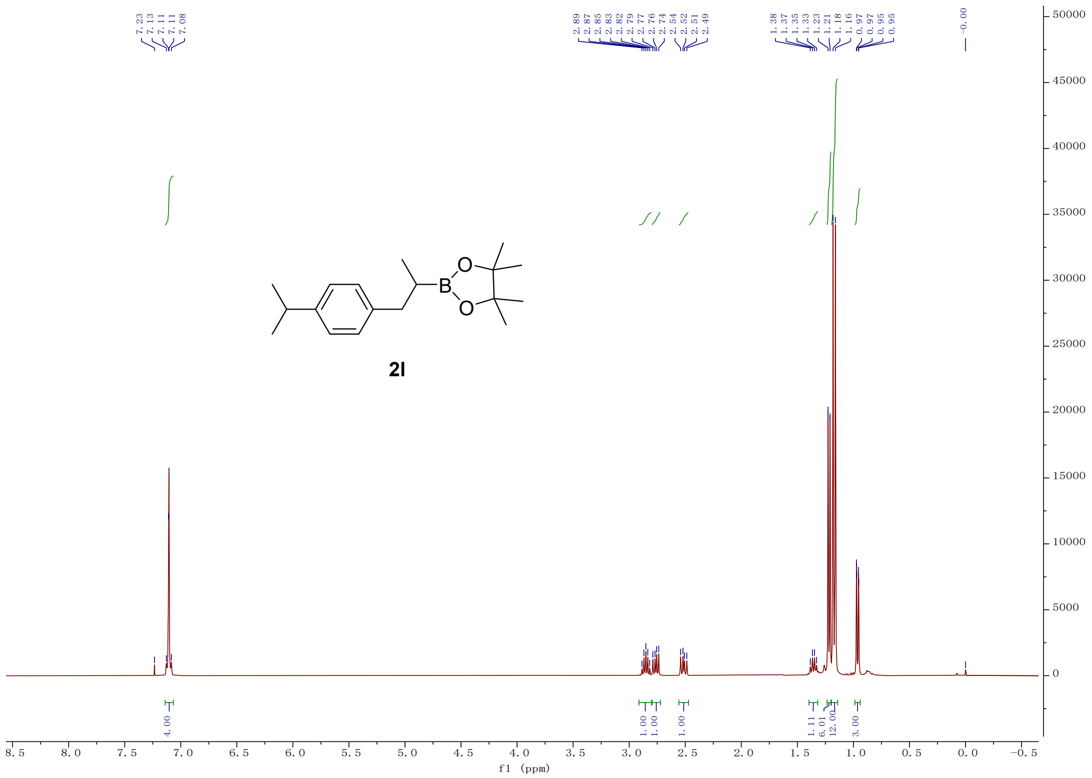
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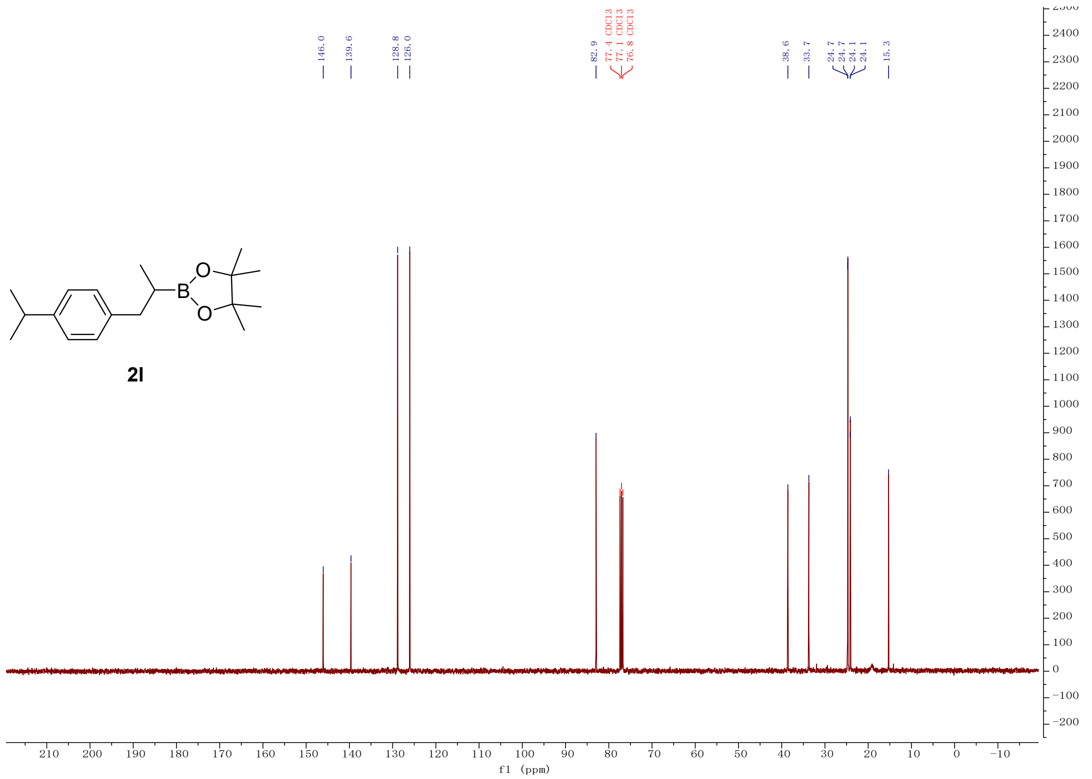
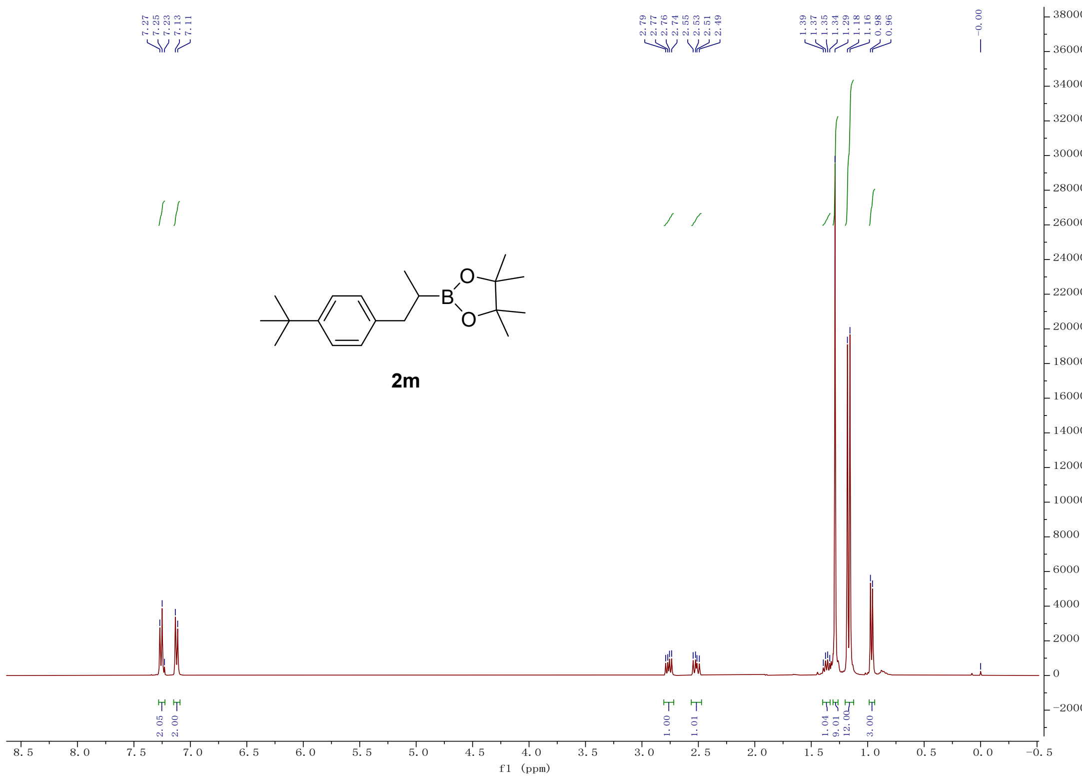
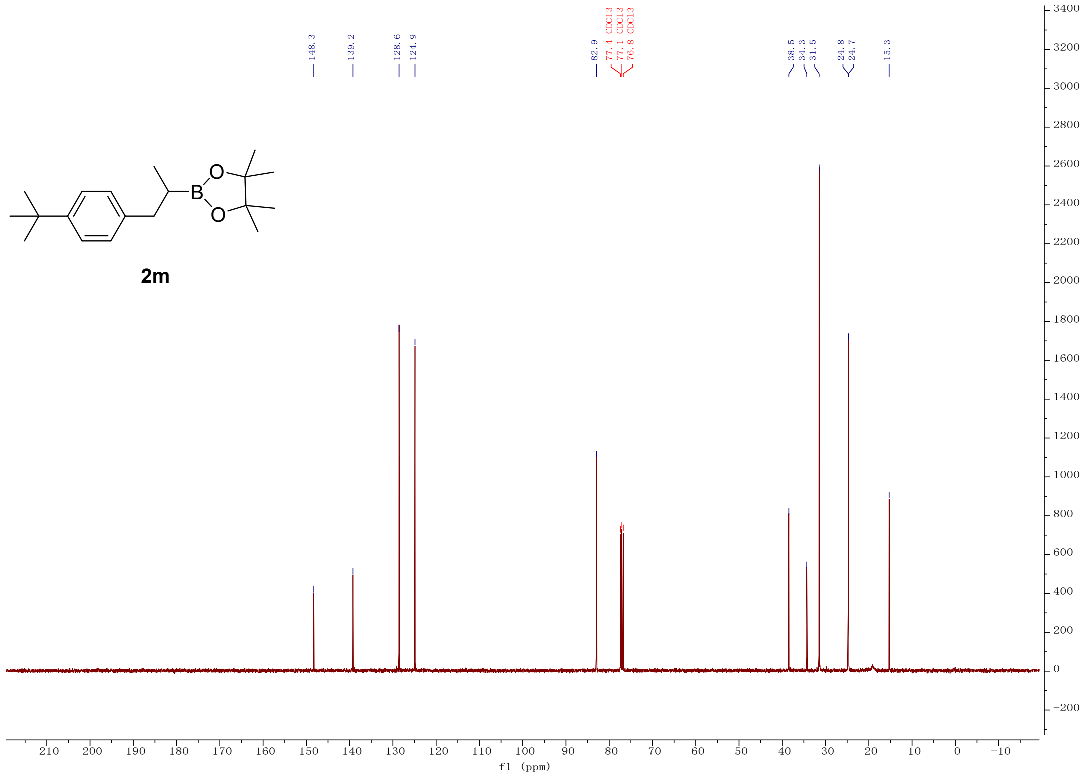
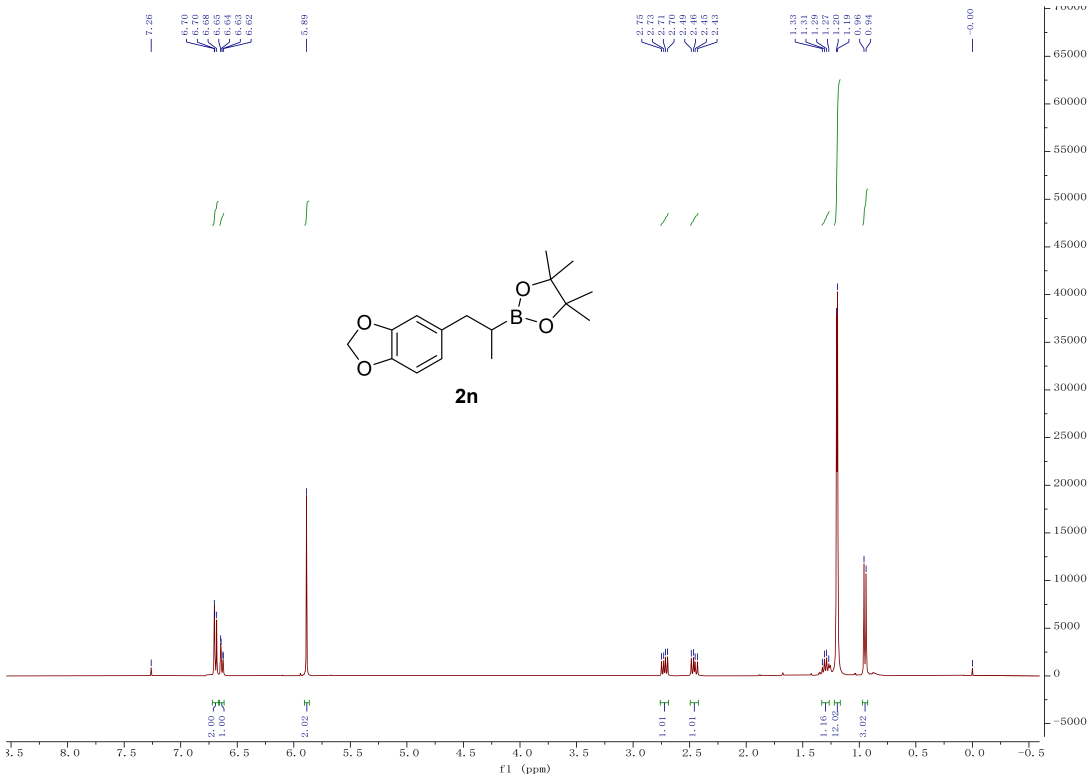
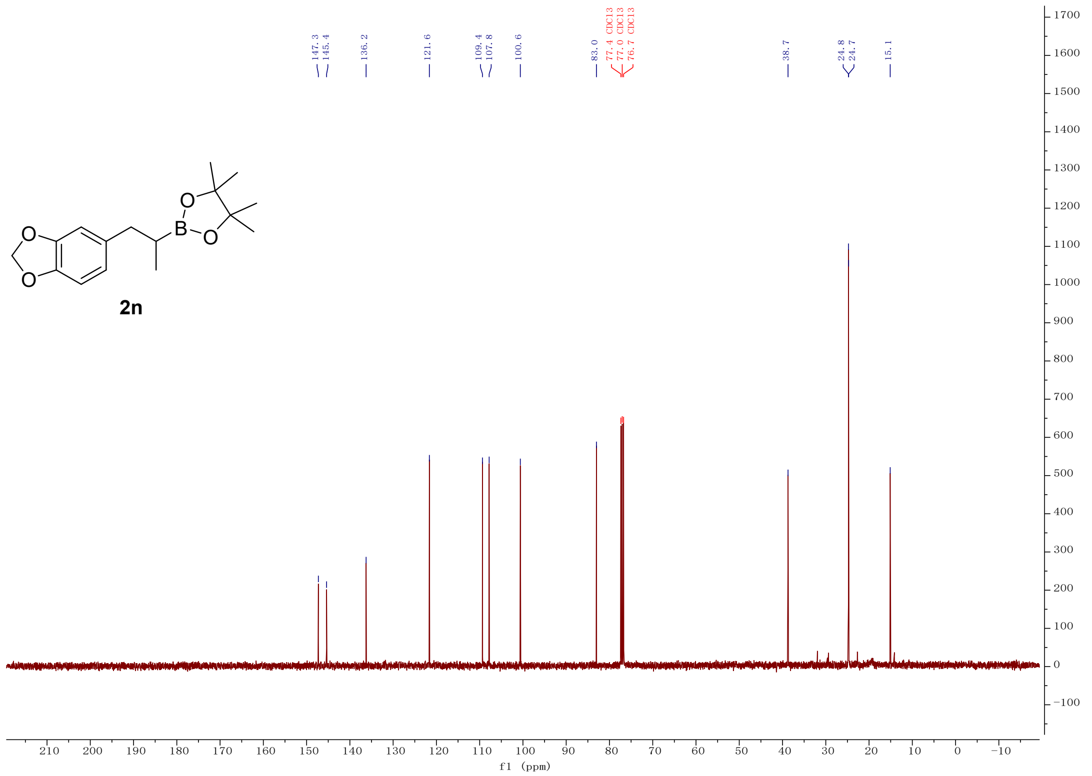
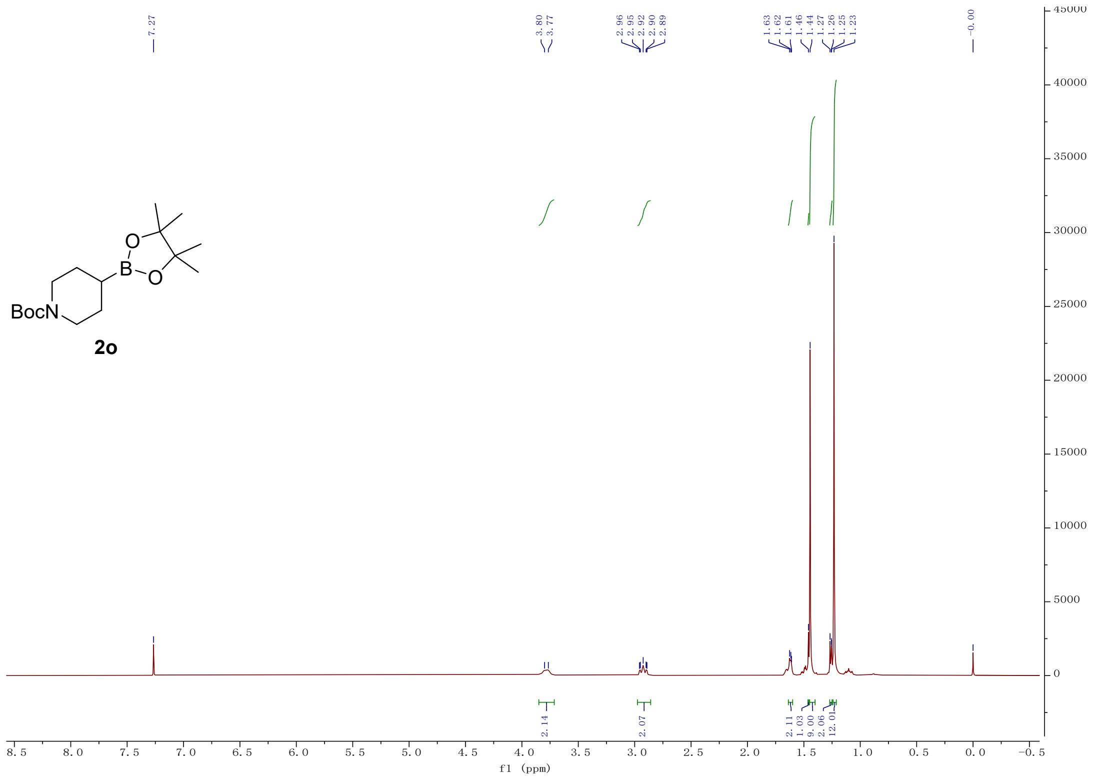

2l


7.27 7.25 7.23 7.13 7.11
2.79 2.77 2.76 2.74 2.55 2.53 2.51 2.49
1.39 1.37 1.35 1.34 1.29 1.18 1.16 0.98 0.96
-0.00
2m
2.05 2.00 1.00 1.01 1.04 9.01 12.06 3.00
f1 (ppm)

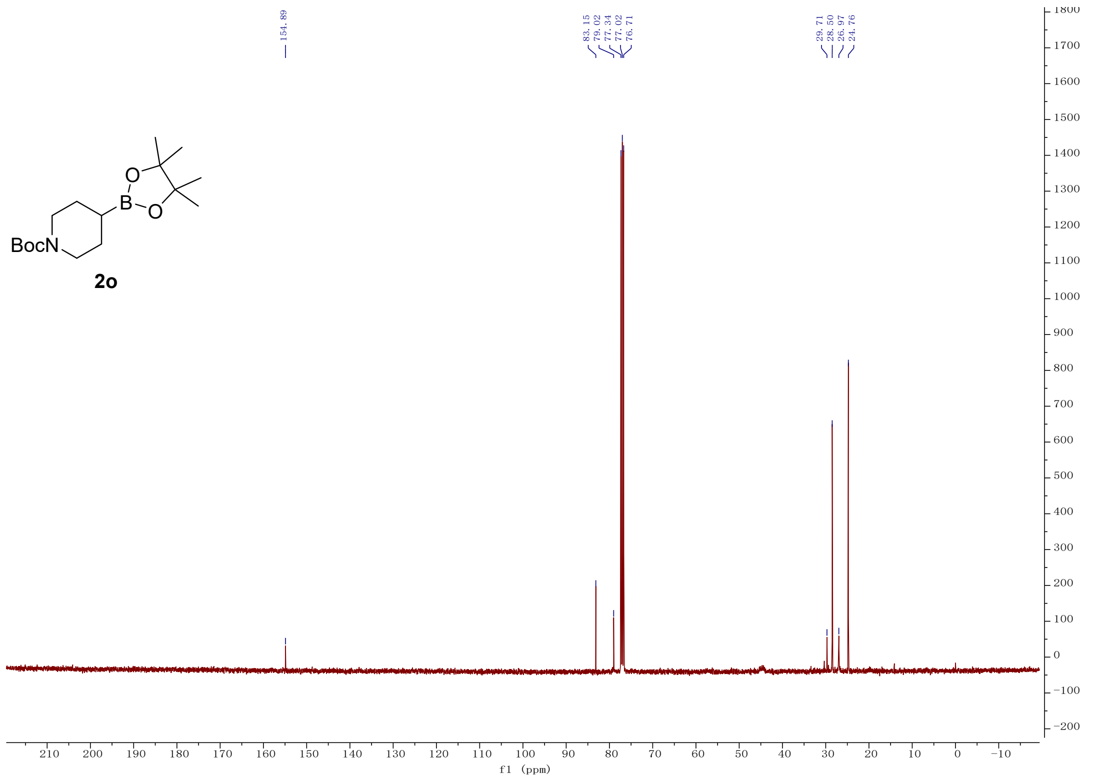

148.3 139.2 128.6 124.9
82.9 77.4 CDCl3 77.1 CDCl3 76.8 CDCl3
38.5 34.3 31.5 24.8 24.7 15.3
2m
f1 (ppm)


2n
f1 (ppm)

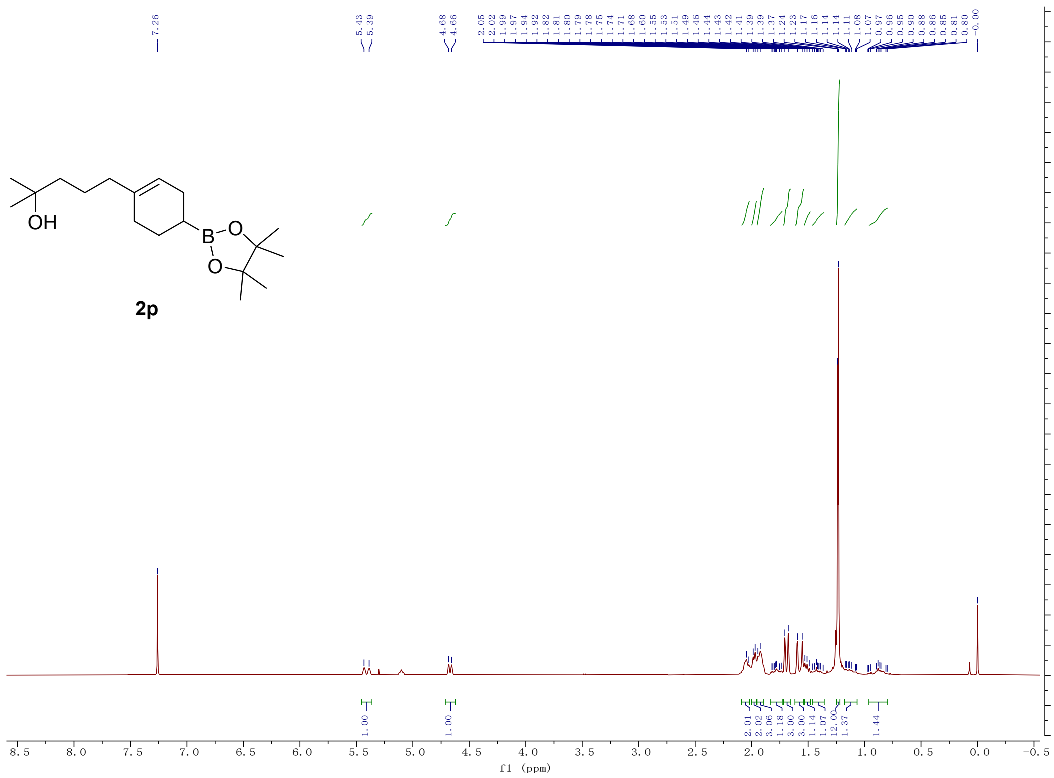

2n
f1 (ppm)

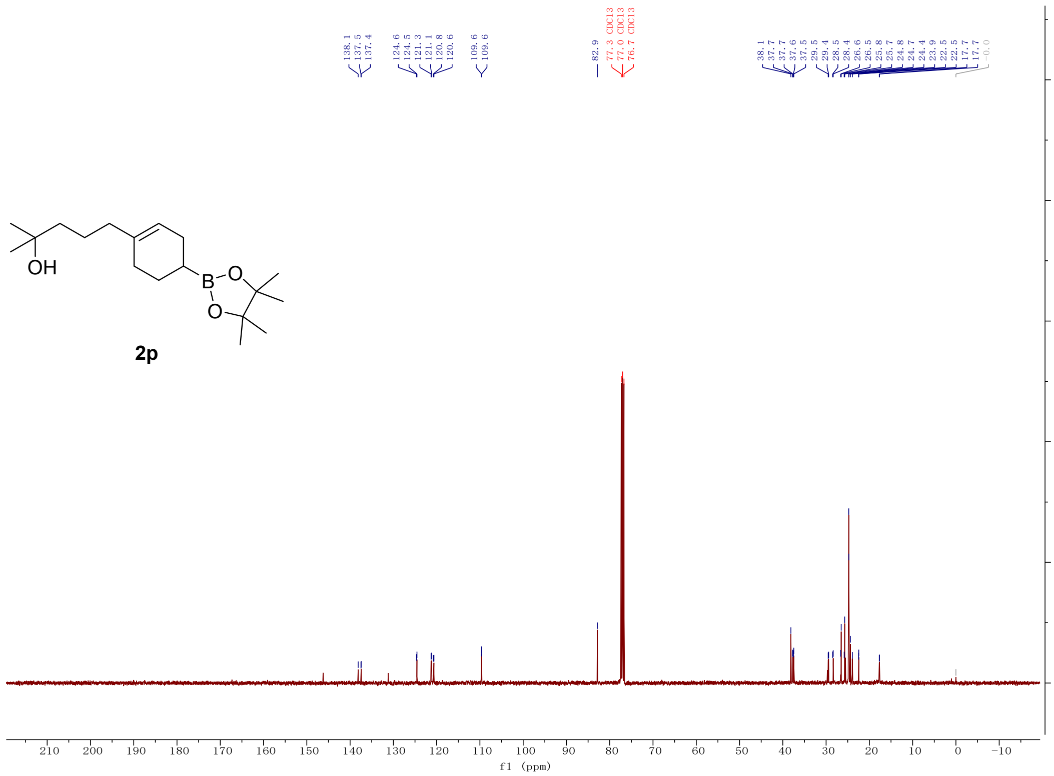

7.27
3.80
3.77
2.96
2.95
2.92
2.90
2.89
1.63
1.62
1.61
1.46
1.44
1.27
1.26
1.25
1.23
-0.00
2.14
2.07
2.11
1.03
9.00
2.06
12.01
f1 (ppm)

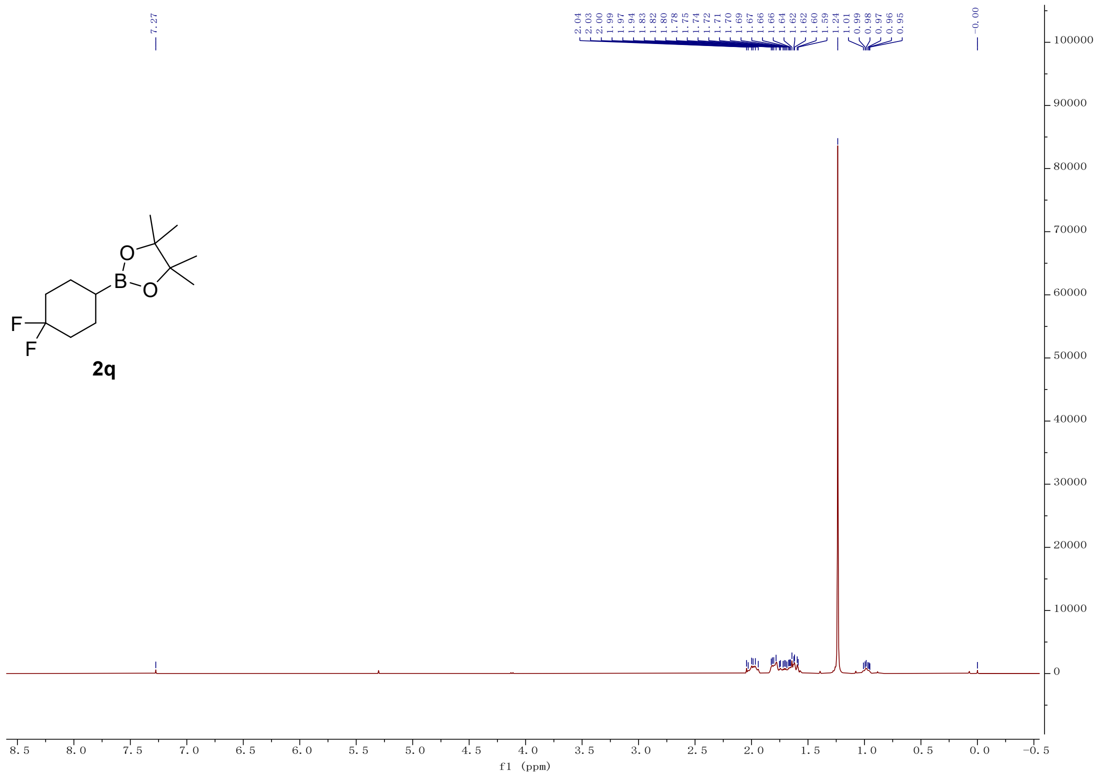
2o


154.89
83.15
79.02
77.34
77.02
76.71
29.71
28.50
26.97
24.76
f1 (ppm)

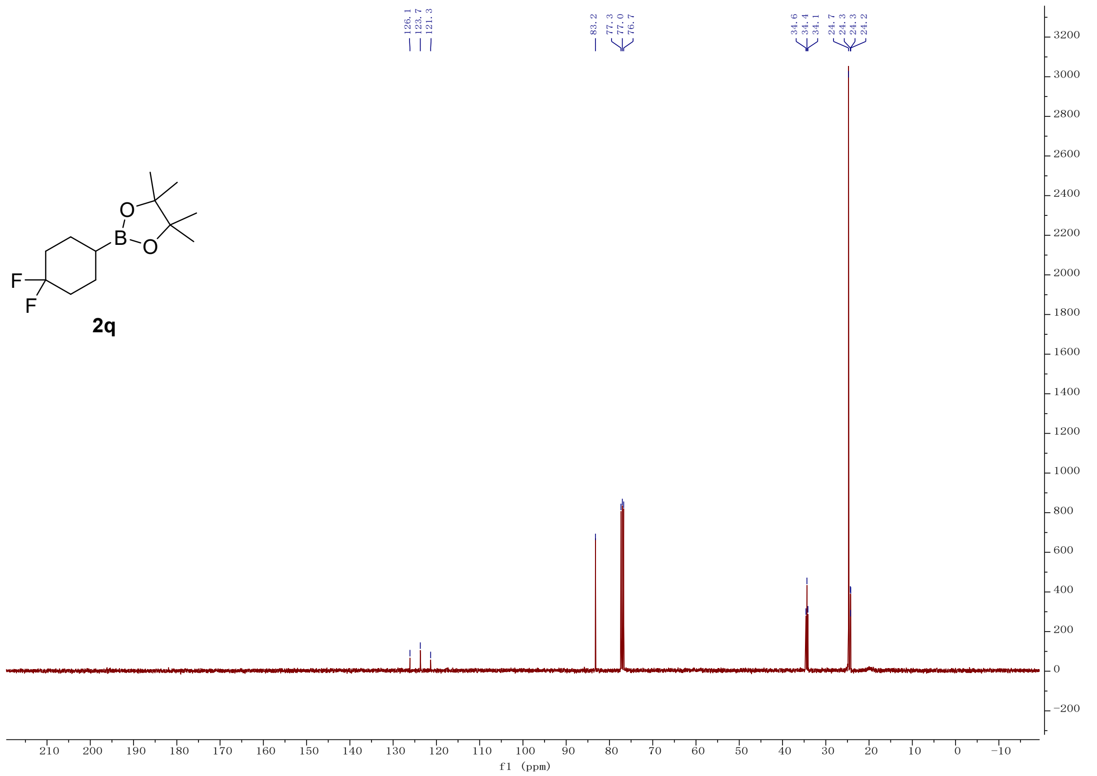
2o


7.26
5.43
5.39
4.68
4.66
2.05
2.02
1.99
1.97
1.94
1.92
1.82
1.81
1.80
1.79
1.78
1.75
1.74
1.71
1.68
1.60
1.55
1.53
1.51
1.49
1.46
1.44
1.43
1.42
1.41
1.39
1.39
1.37
1.24
1.23
1.17
1.16
1.14
1.14
1.11
1.08
1.07
0.97
0.97
0.96
0.95
0.90
0.88
0.86
0.85
0.81
0.80
-0.00
OH
B
O
O
2p
1.00
1.00
2.01
2.02
3.06
1.18
3.00
3.00
1.14
1.07
12.00
1.37
1.44
f1 (ppm)

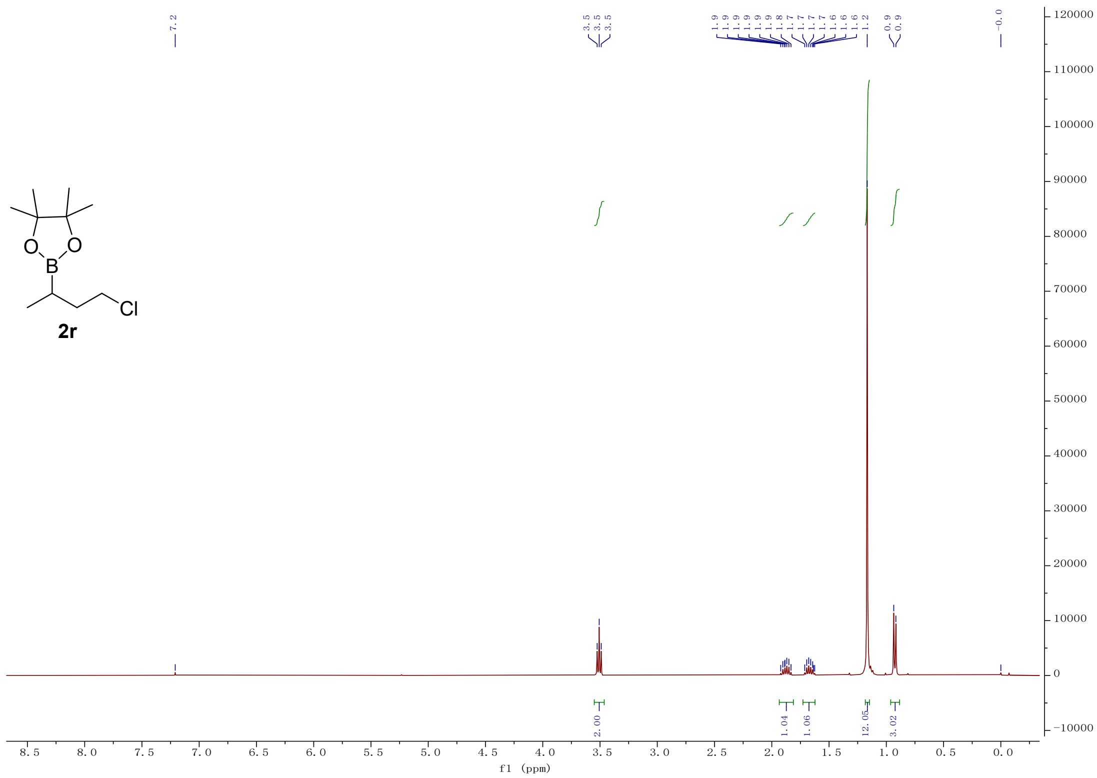

138.1
137.5
137.4
124.6
124.5
121.3
121.1
120.8
120.6
109.6
109.6
82.9
77.3 CDCl3
77.0 CDCl3
76.7 CDCl3
38.1
37.7
37.6
37.5
29.5
29.4
28.5
28.4
26.6
26.5
25.8
25.7
24.8
24.7
24.4
23.9
22.5
17.7
17.7
-0.0
OH
B
O
O
2p
f1 (ppm)

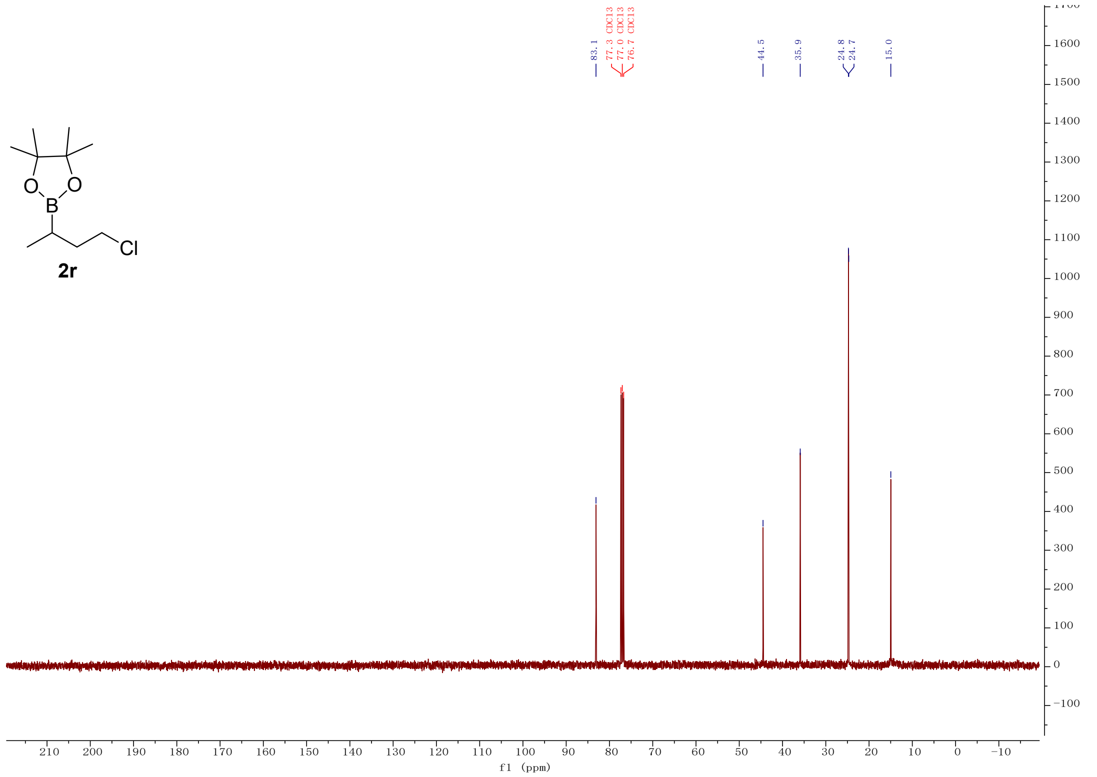

7.27
2.04 2.03 2.00 1.99 1.97 1.94 1.83 1.82 1.80 1.78 1.75 1.74 1.72 1.71 1.70 1.69 1.67 1.66 1.66 1.64 1.62 1.62 1.60 1.59 1.24 1.01 0.99 0.98 0.97 0.96 0.95
-0.00
f1 (ppm)

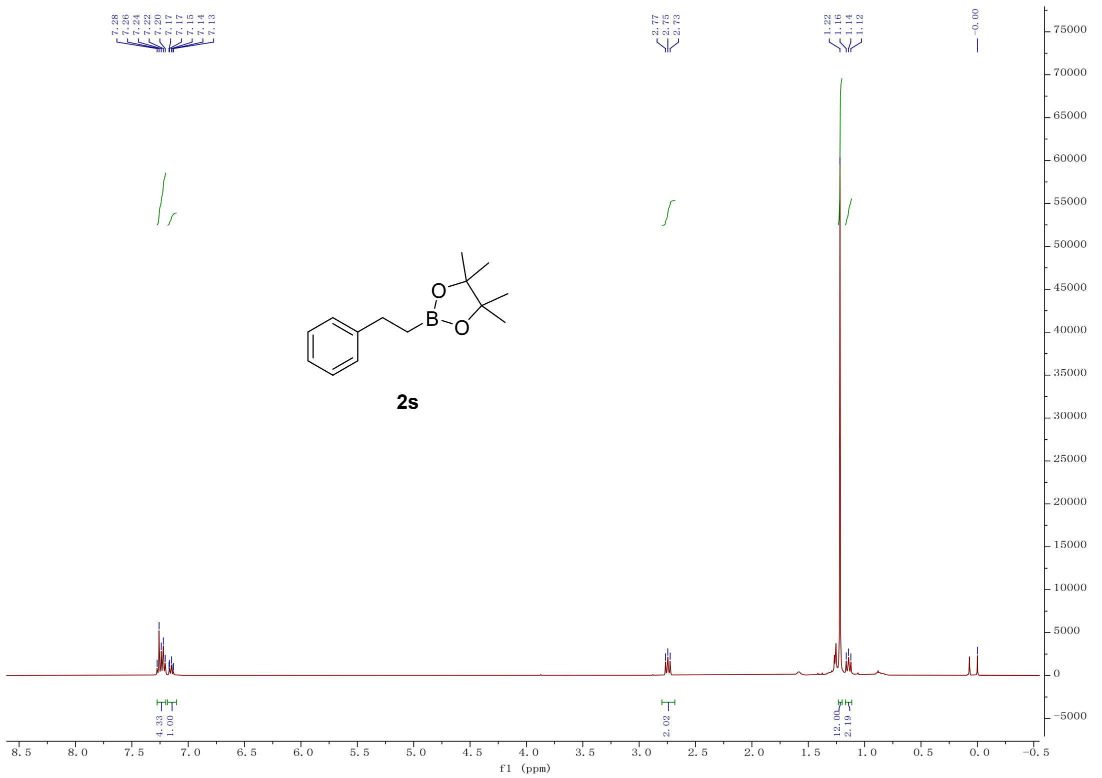
2q


126.1 123.7 121.3
83.2 77.3 77.0 76.7
34.6 34.4 34.1 24.7 24.3 24.3 24.2
f1 (ppm)

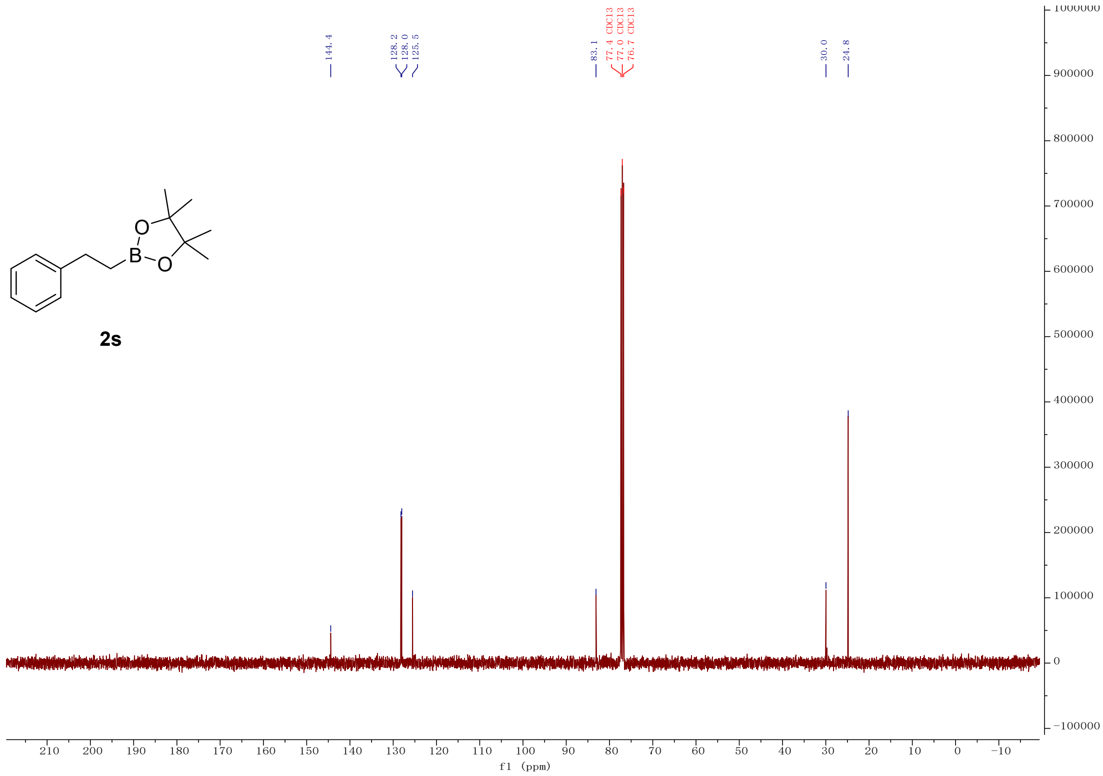
2q



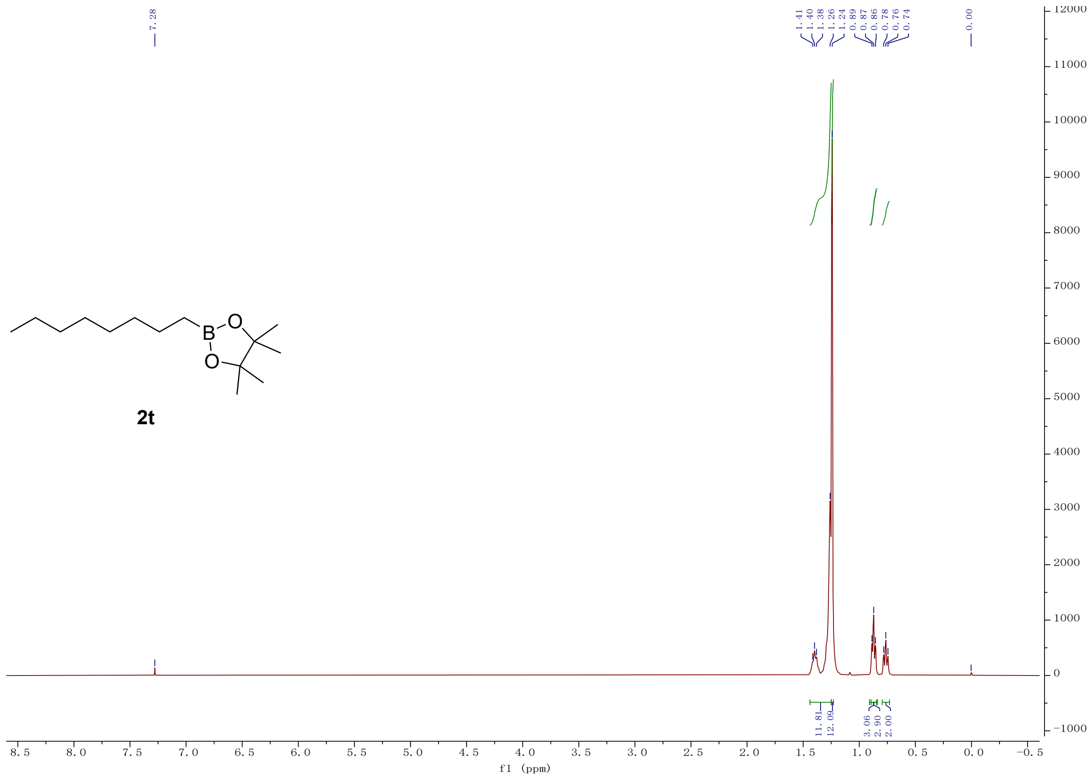


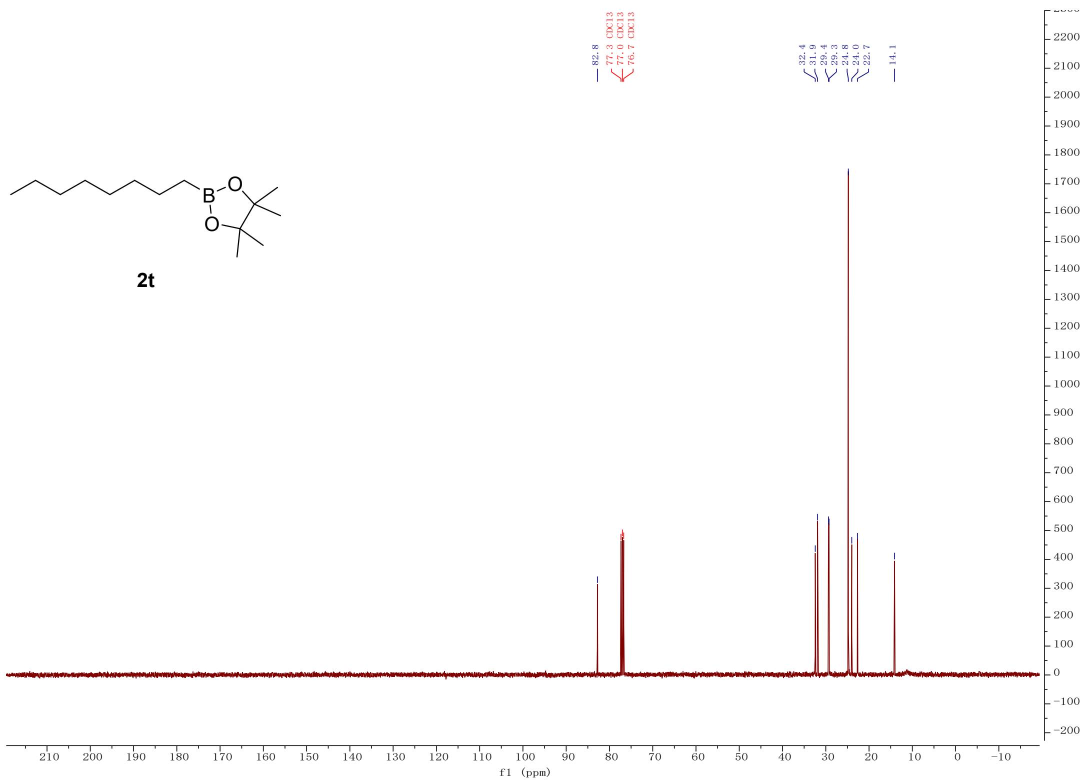

7.28
7.26
7.24
7.22
7.20
7.17
7.17
7.15
7.14
7.13
2.77
2.75
2.73
1.22
1.16
1.14
1.12
-0.00
4.33
1.00
2.02
12.00
2.19
f1 (ppm)

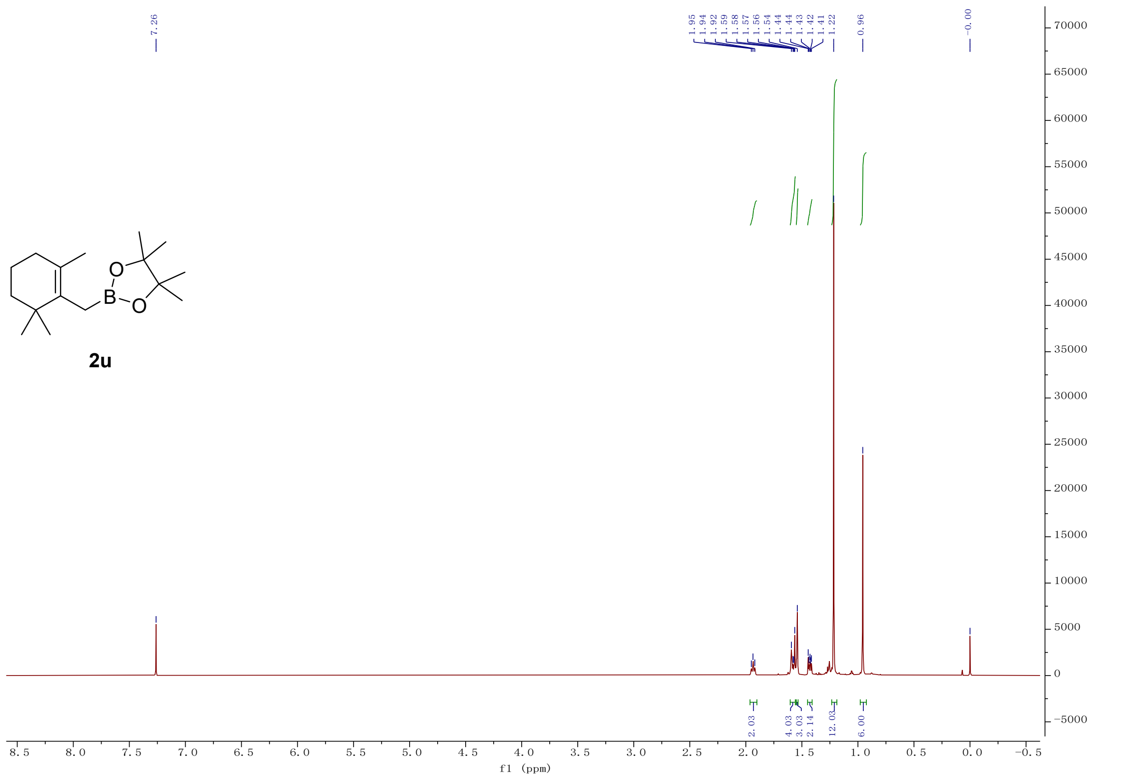
2s


144.4
128.2
128.0
125.5
83.1
77.4 CDCl3
77.0 CDCl3
76.7 CDCl3
30.0
24.8
f1 (ppm)

2s


2t
f1 (ppm)


2t
f1 (ppm)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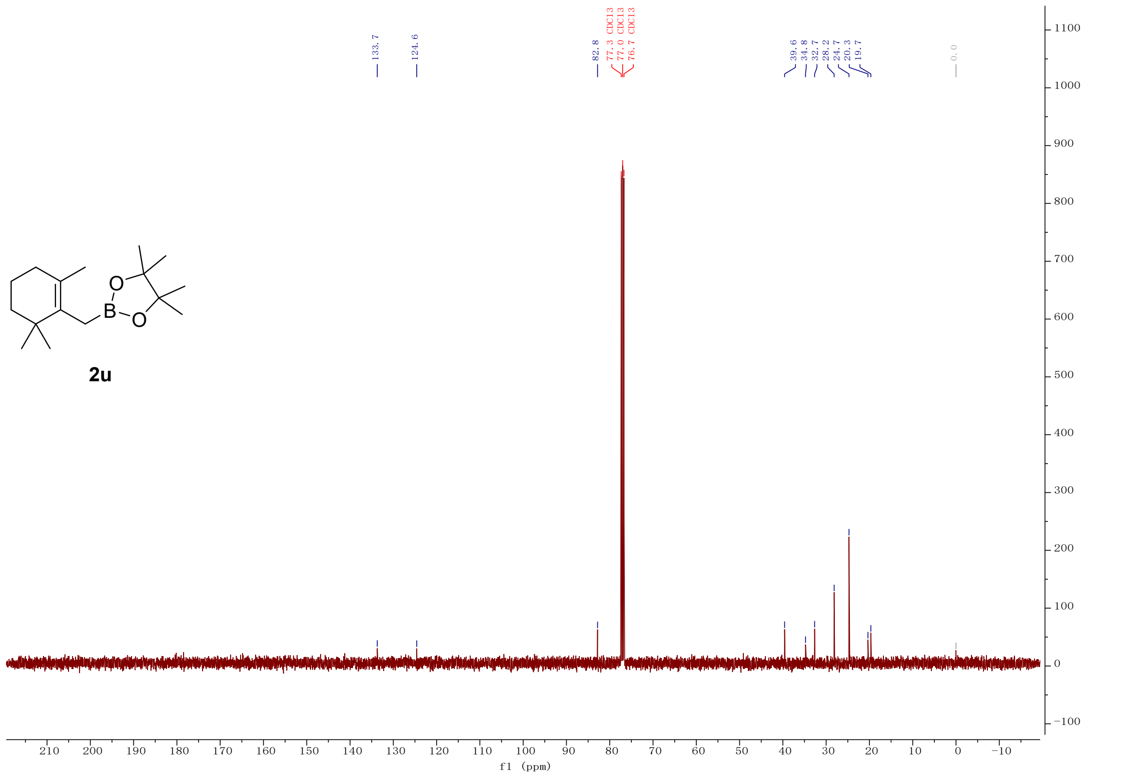
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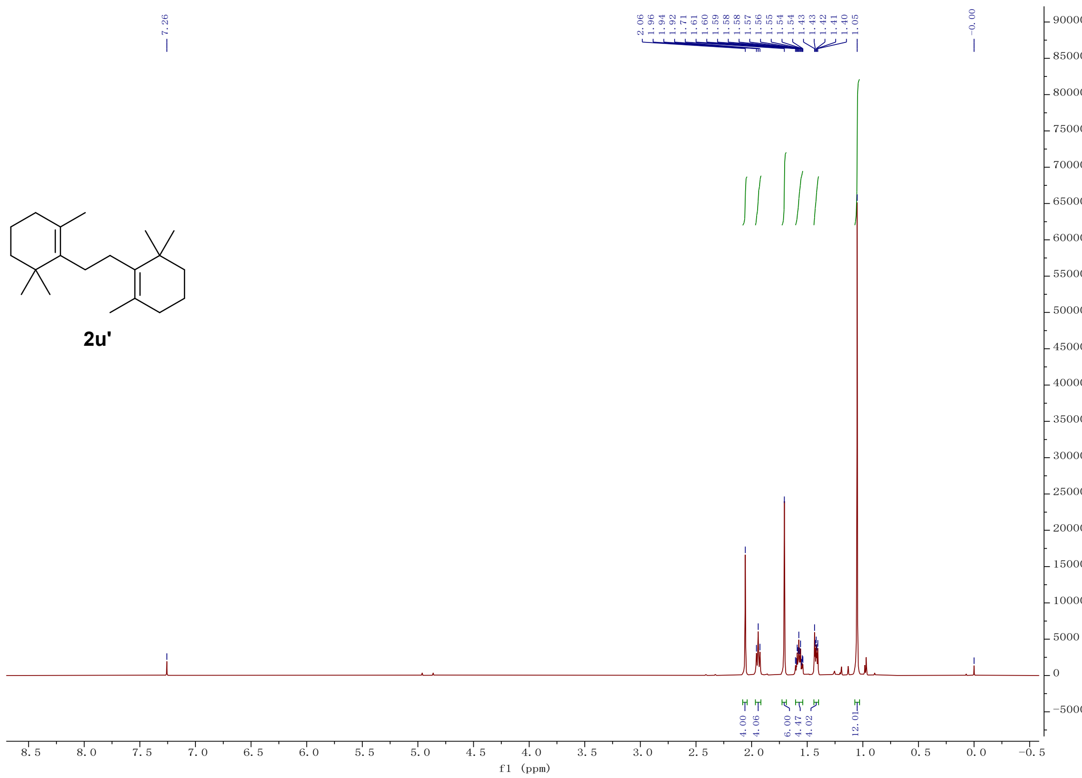
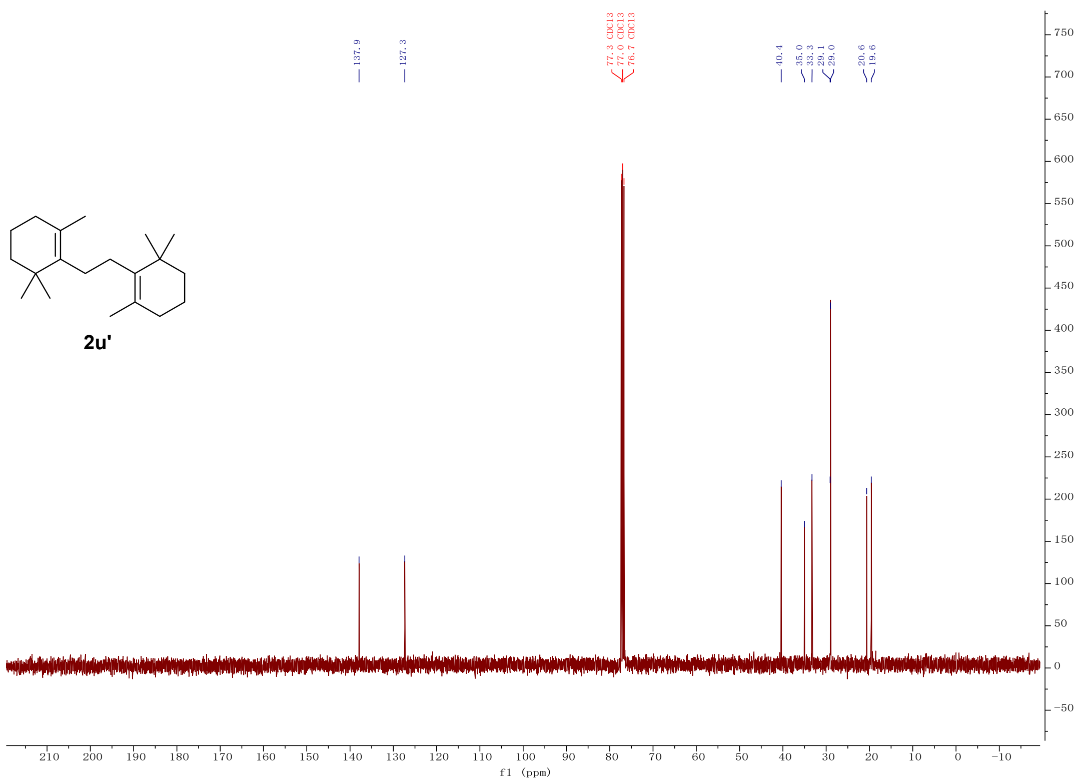


2u'



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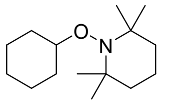

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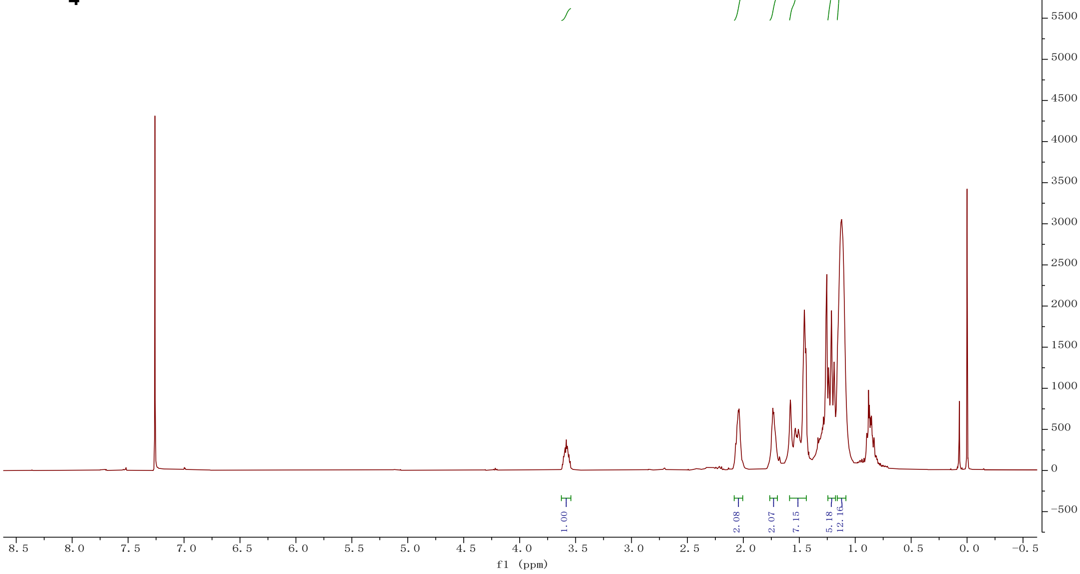
8000
7500
7000
6500
6000
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
−500
1.00
2.08
2.07
7.15
5.18
12.16
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
−0.5
f1 (ppm)