

Supplementary Information

β -Boron or β -silicon effect enables a regioselective Ni-catalyzed hydrocyanation of internal alkynes

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1. General Information

Unless otherwise noted, all commercially available materials were used without further purification. All reactions were performed in glassware under argon. Anhydrous DCM, CH₃CN, DMF and DMSO were purchased from Enezy Organics and stored under argon.

NMR-spectra were recorded on Bruker AvanceIII-400M and AscendTM 500M in solvents as indicate. Chemical shifts (δ) are given in ppm relative to tetramethylsilane ($\delta = 0$). The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (Acetone-*d*₆: $\delta_{\text{H}} = 2.05$ ppm, $\delta_{\text{C}} = 29.84$ ppm). The following abbreviations were used to describe peak splitting patterns: s (singlet), bs (broad singlet), d (doublet), t (triplet), q (quartet), m (multiplet), dd (doublet of doublets), dt (doublet of triplets). Coupling constants (J) were reported in hertz unit (Hz). High-resolution mass spectra (HRMS, LCMS-IT-TOF) were recorded on a Bruker VPXII spectrometer with EI and ESI mode unless otherwise stated. Analytical thin layer chromatography was performed on Polygram SIL G/UV254 plates. Visualization was accomplished by UV light (254 nm), or KMnO₄ staining solutions followed by heating, also by Gas chromatograph-Mass spectrometer analysis (GC-MS) on Agilent Technologies 5977A MSD. Flash column chromatography was performed using silica gel (200–300 mesh). Reactions that require heating were heated in oil bath unless otherwise noted.

No attempts were made to optimize yields for substrate synthesis.

2. Reaction Development and Optimization.

Table S1. Screening of hydrocyanation reaction of propargylic B(MIDA).

The reaction scheme shows the hydrocyanation of propargylic B(MIDA) boronate **S-1** to products **1** and **1'**. The starting material **S-1** is a propargylic boronate with a methyl group on the nitrogen of the MIDA group. The reaction conditions are [Ni] (10 mol%), ligand (12 mol%), AIBN, solvent, and TEMP. The products are **1** (the terminal alkene) and **1'** (the internal alkene).

entry	AIBN (equiv)	[Ni] (10 mol%)	ligand (12 mol%)	solvent	Temp. (°C)	1/1' (isolated yield of 1)
1	2.0	Ni(COD) ₂	Xantphos	iPrOH	90	NR
2	2.0	Ni(COD) ₂	Xantphos	THF	90	trace
3	2.0	Ni(COD) ₂	Xantphos	MeCN	90	76%/20% (73%)
4	2.0	Ni(COD) ₂	Xantphos	MeCN	70	trace
5	2.0	Ni(COD) ₂	Xantphos	MeCN	110	62%/34%
6	2.0	Ni(PPh ₃)Cl ₂	Xantphos	MeCN	90	trace
7	2.0	NiCl ₂	Xantphos	MeCN	90	NR
8	2.0	Ni(CF ₃ SO ₃) ₂	Xantphos	MeCN	90	trace
9	2.0	Ni(acac) ₂	Xantphos	MeCN	90	trace
10	2.0	Ni(PCy ₃) ₂ Cl ₂	Xantphos	MeCN	90	NR
11	2.0	Ni(dppp)Cl ₂	Xantphos	MeCN	90	73%/25%
12	2.0	Ni(COD) ₂	BINAP	MeCN	90	trace
13	2.0	Ni(COD) ₂	DPEPhos	MeCN	90	trace
14	2.0	Ni(COD) ₂	DPPE	MeCN	90	trace
15	2.0	Ni(COD) ₂	DPPM	MeCN	90	trace
16	2.0	Ni(COD) ₂	1,10-Phen.	MeCN	90	NR
17	2.0	Ni(COD) ₂	Xantphos	DMSO	90	73%/22%
18	2.0	Ni(COD) ₂	Xantphos	acetone	90	69%/24%
19	2.0	Ni(COD) ₂	Xantphos	DCM	90	trace
20	2.0	Ni(COD) ₂	Xantphos	1, 4-dioxane	90	50/0
21	2.0	Ni(COD) ₂	Xantphos	1, 4-dioxane	110	74%/21%
22	4.0	Ni(COD)₂	Xantphos	1, 4-dioxane	90	75%/0% (79%)
23	4.0	Ni(COD) ₂	Xantphos	anisole	90	NR
24	4.0	Ni(COD) ₂	Xantphos	sulfolane	90	NR
25	4.0	Ni(COD) ₂	Xantphos	EtOAc	90	46%/11%

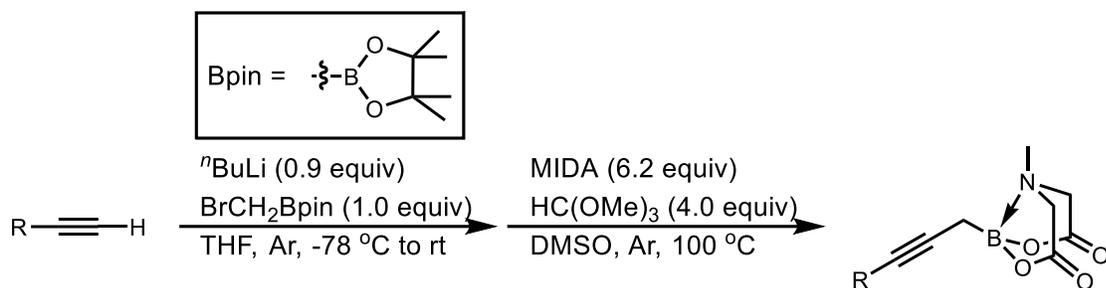
1,10-Phen.: 1,10-Phenanthroline; THF: tetrahydrofuran; DMSO: Dimethylsulfoxide; NR: No reaction;

3. General Procedure and Characterization of reagent and starting materials

Starting material AIBN are purchased from commercial sources and used without further purification unless otherwise indicated. The propargyl MIDA boronates were synthesized according to general procedure (see below) and spectroscopic data of known compounds were consistent with the reported values¹.

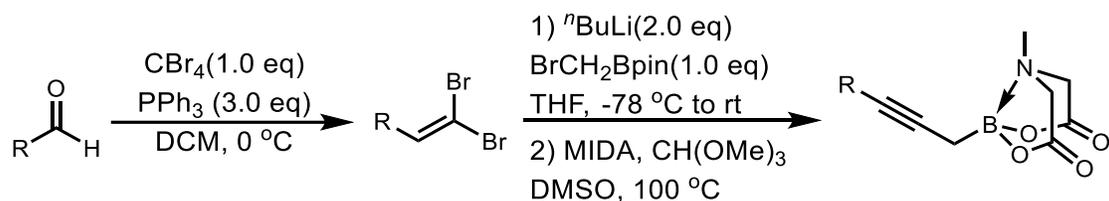
General procedure for Synthesis of propargylic MIDA boronates or propargylic TMSs

General procedure A^{1b, 1d}:



To a stirred solution of THF (10 mL) containing terminal alkynes (5 mmol, 1.0 eq), *n*-butyl lithium in hexane (2.5 M, 1.8 mL, 4.5 mmol) was added dropwise at -78°C . The resulting solution was stirred at the same temperature for 1 h, and then (bromomethyl)pinacolborane (BrCH_2Bpin , 1.1 g, 5 mmol, 1.0 eq) was added dropwise and the mixture was stirred at room temperature for 2 h. After the reaction, Saturated NH_4Cl (aq., 5 mL) was added to the reaction mixture at 0°C and the solution was stirred for 20 min. The reaction mixture was mixed with water and the product was extracted repeatedly with dichloromethane (DCM). The organic phase was separated and the aqueous layer was extracted with DCM (30 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Anhydrous DMSO (5 mL) was added to dissolve the solid (or viscous oil) which was then added via syringe to a suspension of *N*-methyliminodiacetic acid (MIDA, 6.2 equiv.) and $\text{CH}(\text{OMe})_3$ (4.0 equiv.) in DMSO (20 mL). The resulting mixture was stirred at 100°C in an oil bath until the propargyl boronic esters was used up by GC-MS monitoring. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (10 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure B^{1b-d, 2}:

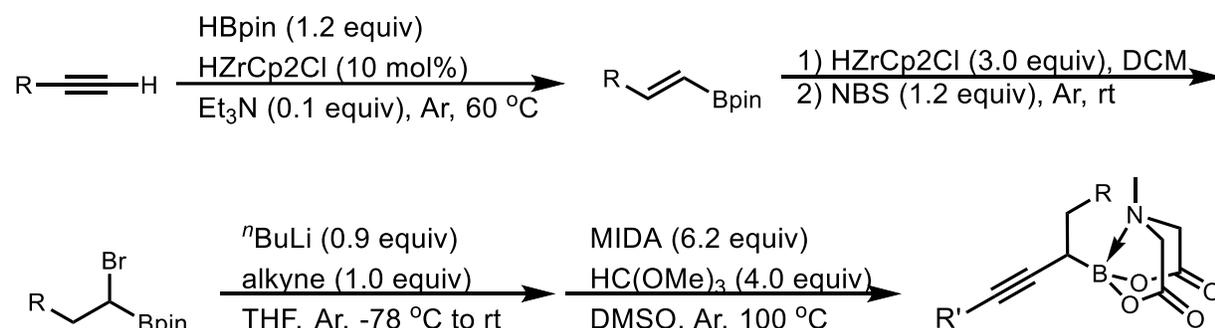


CBr_4 (10 mmol, 1.0 eq) was added to a dry, cooled sealed bottle. The bottle was pumped under high vacuum and then backfilled with argon, and this cycle repeated two times more. DCM (20 mL) was added, followed by PPh_3 (30 mmol, 3.0 eq) in DCM (20 mL) in an ice bath. The resulting mixture was allowed to react for 15 min under 0°C before the aldehyde (10 mmol) in DCM (15 mL) was added via syringe. The resulting slurry stirred vigorously for 4 h monitoring by GC-MS. After the CBr_4 was used up, solvent was removed under reduced pressure and the crude reaction mixture was filtered through a short pad of SiO_2 (100% hexane) and concentrated in vacuo to obtain dibromoolefin as a colorless oil (~80% yield).

To a stirred solution of THF (10 mL) containing dibromoolefin (5 mmol, 1.0 eq), *n*-butyl lithium in hexane (2.5 M, 4.0 mL, 10 mmol) was added dropwise at -78°C . The resulting solution

was stirred at the same temperature for 1 h, and then α -bromo boronic esters (5 mmol, 1.0 eq) was added dropwise and the mixture was stirred at room temperature for 2 h. After the reaction, Saturated $\text{NH}_4\text{Cl}(\text{aq.})$ was added to the reaction mixture at 0°C and the solution was stirred for 20 min. The reaction mixture was mixed with water and the product was extracted repeatedly with DCM. The organic phase was separated and the aqueous layer was extracted with DCM (30 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Anhydrous DMSO (5 mL) was added to dissolve the solid (or viscous oil) which was then added via syringe to a suspension of *N*-methyliminodiacetic acid (MIDA, 6.2 equiv.) and $\text{CH}(\text{OMe})_3$ (4.0 equiv) in DMSO. The resulting mixture was stirred at 100°C in an oil bath until the propargyl boronic esters was used up by GC-MS monitoring. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (10 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure C^{1d}:



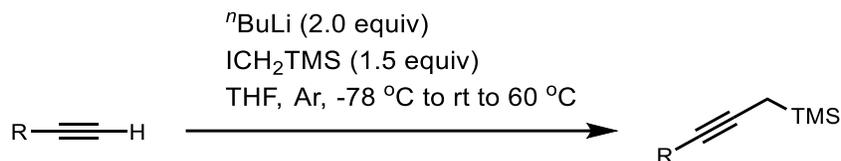
Alkynes (10 mmol) was added to a dry, cooled sealed tube. The tube was pumped under high vacuum and then backfilled with argon, and this cycle repeated two times more. Pinacolborane (HBpin, 1.8 mL, 12 mmol) was added, followed by Et_3N (140 μL , 1.0 mmol) and Schwartz's reagent (258 mg, 1.0 mmol). The resulting beige slurry was heated to 60°C and stirred vigorously for 24 h. while protected from light. On heating, the solid dissolves to afford a clear orange solution. After cooling, the crude reaction mixture was filtered through a short pad of SiO_2 (100% DCM) and concentrated in vacuo to a yellow heavy oil.

The resulting oil was added via syringe to a suspension of Schwartz's reagent (7.8 g, 30 mmol) in DCM (30 mL) and afforded a clear yellow solution. *N*-Bromosuccinimide (NBS, 10.7 g, 12 mmol) was added slowly at 0°C and stirred for 20 min. After the reaction, the crude reaction mixture was filtered through a short pad of SiO_2 (100% hexane) and the solvent was removed under reduced pressure. The afforded crude was extracted with hexane provided the crude oil α -bromo boronic esters.

To a stirred solution of THF (10 mL) containing 1-Hexyne (0.6 mL, 5 mmol), *n*-butyl lithium in hexane (2.5M, 1.8 mL, 4.5 mmol) was added dropwise at -78°C . The resulting solution was stirred at the same temperature for 1 h, and then α -bromo boronic esters (5 mmol) was added dropwise and the mixture was stirred at room temperature for 2 h. After the reaction, Saturated $\text{NH}_4\text{Cl}(\text{aq.})$ was added to the reaction mixture at 0°C and the solution was stirred for 20 min. The

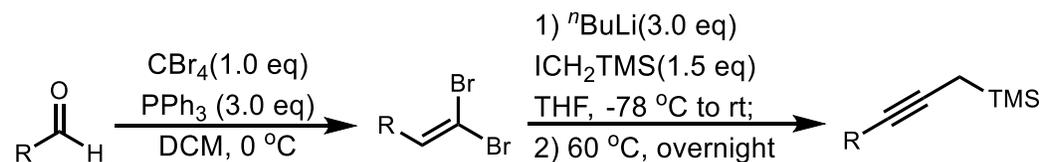
reaction mixture was mixed with water and the product was extracted repeatedly with DCM. The organic phase was separated and the aqueous layer was extracted with DCM (30 mL) for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Anhydrous DMSO (5 mL) was added to dissolve the solid (or viscous oil) which was then added via syringe to a suspension of *N*-methyliminodiacetic acid (MIDA, 6.2 equiv) and CH(OMe)₃ (4.0 equiv) in DMSO. The resulting mixture was stirred at 100 °C until the propargyl boronic esters was used up by GC-MS monitoring. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (10 mL) and water (10 mL). The organic phase was separated and the aqueous layer was extracted with ethyl acetate (10 mL) for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent to afford the pure product.

General procedure D:



To a stirred solution of THF (5.0 mL) containing terminal alkynes (5 mmol, 1.0 eq), *n*-butyl lithium in hexane (2.5 M, 4 mL, 10 mmol) was added dropwise at -78 °C. The resulting solution was stirred at the same temperature for 0.5 h and the mixture was stirred at room temperature for 15 min. Then ICH₂TMS (7.5 mmol, 1.5 eq) was added dropwise before the mixture was heated to 60 °C and stirred overnight. After the reaction, Saturated NH₄Cl (aq.) was added to the reaction mixture at 0 °C and the solution was stirred for 20 min. The reaction mixture was mixed with water and the product was extracted repeatedly with PE. The organic phase was separated and the aqueous layer was extracted with PE (5 mL) for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent (most time are PE) to afford the pure product.

General procedure E:²



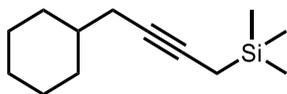
CBr₄ (10 mmol, 1.0 eq) was added to a dry, cooled sealed bottle. The bottle was pumped under high vacuum and then backfilled with argon, and this cycle repeated two times more. DCM (20 mL) was added, followed by PPh₃ (30 mmol, 3.0 eq) in DCM (20 mL) in an ice bath. The resulting mixture was allowed to react for 15 min under 0 °C before the aldehyde (10 mmol) in DCM (15 mL) was added via syringe. The resulting slurry stirred vigorously for 4 h monitoring by GC-MS. After the CBr₄ was used up, solvent was removed under reduced pressure and the

crude reaction mixture was filtered through a short pad of SiO₂ (100% hexane) and concentrated in vacuo to obtain dibromoolefin as a colorless oil (~80% yield).

To a stirred solution of THF (5 mL) containing dibromoolefin (5 mmol, 1.0 eq), *n*-butyl lithium in hexane (2.5 M, 6 mL, 15 mmol) was added dropwise at -78 °C. The resulting solution was stirred at the same temperature for 0.5 h and the mixture was stirred at room temperature for 15 min. Then ICH₂TMS (7.5 mmol, 1.5 eq) was added dropwise before the mixture was heated to 60 °C and stirred overnight. After the reaction, Saturated NH₄Cl(aq.) was added to the reaction mixture at 0 °C and the solution was stirred for 20 min. The reaction mixture was mixed with water and the product was extracted repeatedly with PE. The organic phase was separated and the aqueous layer was extracted with PE (5.0 mL) for three times. The combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The resulting crude product was purified by flash chromatography on silica gel with an appropriate solvent as eluent (most time are PE) to afford the pure product.

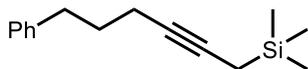
Characterization for Starting materials

(4-cyclohexylbut-2-yn-1-yl)trimethylsilane (**S-47**)



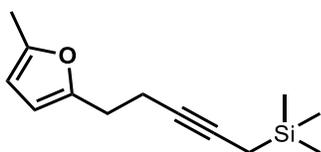
Following the general procedure D, the product **S-47** was obtained in 45% yield as colorless oil after column chromatography (eluent: Petroleum); *R_F* (Petroleum): 0.72; ¹H NMR (500 MHz, Chloroform-*d*) δ 2.03 (dt, *J* = 6.2, 2.7 Hz, 2H), 1.82 – 1.74 (m, 2H), 1.70 (dt, *J* = 12.5, 3.1 Hz, 2H), 1.64 (ddt, *J* = 12.3, 3.3, 1.7 Hz, 1H), 1.42 (t, *J* = 2.7 Hz, 2H), 1.29 – 1.08 (m, 4H), 0.98 (qd, *J* = 12.4, 3.2 Hz, 2H), 0.09 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 78.2, 77.8, 38.0, 32.8, 27.0, 26.5, 26.3, 7.1, -1.9; GC-MS (EI) *m/z*: [*M* - e]⁺ Calcd for C₁₃H₂₄Si 208.1642; Found 208.1642.

trimethyl(6-phenylhex-2-yn-1-yl)silane (**S-48**)



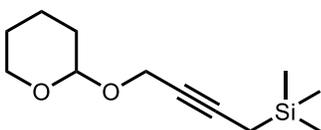
Following the general procedure D, the product **S-48** was obtained in 87% yield as colorless oil after column chromatography (eluent: Petroleum); *R_F* (Petroleum): 0.72; ¹H NMR (500 MHz, Chloroform-*d*) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.22 – 7.15 (m, 3H), 2.75 – 2.68 (m, 2H), 2.21 – 2.15 (m, 2H), 1.79 (p, *J* = 7.1 Hz, 2H), 1.45 (t, *J* = 2.7 Hz, 2H), 0.12 (s, 9H); ¹³C NMR (126 MHz, CDCl₃) δ 142.2, 128.7, 128.4, 125.9, 78.5, 78.1, 35.0, 31.3, 18.6, 7.1, -1.9; HRMS (ESI) *m/z*: [*M* + Na]⁺ Calcd for C₁₅H₂₂SiNa 253.1383; Found 253.1388.

trimethyl(5-(5-methylfuran-2-yl)pent-2-yn-1-yl)silane (**S-49**)



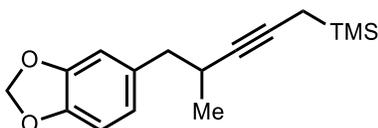
Following the general procedure D, the product **S-49** was obtained in 16% yield as colorless oil after column chromatography (eluent: Petroleum); R_f (Petroleum): 0.65; ^1H NMR (500 MHz, Chloroform-*d*) δ 5.91 (d, $J = 3.0$ Hz, 1H), 5.84 (d, $J = 2.9$ Hz, 1H), 2.76 (t, $J = 7.5$ Hz, 2H), 2.50 – 2.42 (m, 2H), 2.25 (s, 3H), 1.41 (t, $J = 2.7$ Hz, 2H), 0.07 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 153.1, 150.5, 106.0, 106.0, 78.2, 77.9, 28.6, 18.5, 13.6, 7.1, 7.0, -2.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{20}\text{OSiNa}$ 243.1175; Found 243.1176.

trimethyl(4-((tetrahydro-2H-pyran-2-yl)oxy)but-2-yn-1-yl)silane (**S-50**)



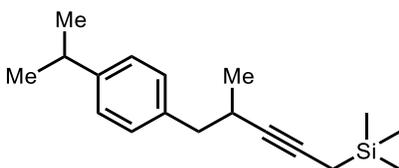
Following the general procedure D, the product **S-50** was obtained in 30% yield as colorless oil after column chromatography (eluent: Petroleum/DCM = 3:1); R_f (Petroleum/DCM = 3:1): 0.52; ^1H NMR (400 MHz, Chloroform-*d*) δ 6.38 – 6.17 (m, 1H), 4.61 (t, $J = 3.4$ Hz, 1H), 4.34 – 4.20 (m, 1H), 4.06 (dd, $J = 14.1, 6.6$ Hz, 1H), 3.83 (ddd, $J = 11.2, 8.4, 3.1$ Hz, 1H), 3.56 – 3.48 (m, 1H), 1.86 – 1.73 (m, 2H), 1.71 (s, 2H), 1.64 – 1.49 (m, 4H), 0.12 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 140.2, 120.5, 114.3, 98.5, 63.1, 62.3, 30.6, 25.5, 21.3, 19.3, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_2\text{SiNa}$ 249.1281; Found 249.1285.

(5-(benzo[*d*][1,3]dioxol-5-yl)-4-methylpent-2-yn-1-yl)trimethylsilane (**S-51**)



Following the general procedure E, the product **S-51** was obtained in 40% yield as colorless oil after column chromatography (eluent: Petroleum/DCM = 10:1); R_f (Petroleum/DCM = 10:1): 0.48; ^1H NMR (400 MHz, Chloroform-*d*) δ 6.74 – 6.69 (m, 2H), 6.65 (dd, $J = 8.0, 1.6$ Hz, 1H), 5.91 (s, 2H), 2.74 – 2.51 (m, 3H), 1.41 (d, $J = 2.2$ Hz, 2H), 1.12 (d, $J = 6.3$ Hz, 3H), 0.05 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 147.4, 145.9, 134.2, 122.2, 109.8, 108.0, 100.8, 83.2, 78.6, 43.6, 28.4, 21.4, 7.1, -2.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2\text{SiNa}$ 297.1281; Found 297.1278.

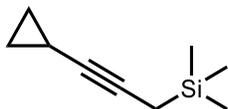
(5-(4-isopropylphenyl)-4-methylpent-2-yn-1-yl)trimethylsilane (**S-52**)



Following the general procedure E, the product **S-52** was obtained in 71% yield as colorless oil

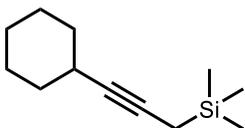
after column chromatography (eluent: Petroleum); R_f (Petroleum): 0.68; ^1H NMR (500 MHz, Chloroform- d) δ 7.15 (s, 4H), 2.89 (p, J = 6.9 Hz, 1H), 2.76 (dd, J = 12.4, 6.9 Hz, 1H), 2.68 (ddt, J = 13.3, 4.7, 2.3 Hz, 1H), 2.62 (dd, J = 12.4, 6.6 Hz, 1H), 1.42 (d, J = 2.4 Hz, 2H), 1.25 (d, J = 6.9 Hz, 6H), 1.15 (d, J = 6.6 Hz, 3H), 0.05 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 146.6, 137.6, 129.2, 126.2, 83.4, 78.4, 43.5, 33.9, 28.2, 24.2, 21.5, 7.1, -2.0; GC-MS (EI) m/z : $[\text{M} - \text{e}]^+$ Calcd for $\text{C}_{18}\text{H}_{28}\text{Si}$ 295.1955; Found 272.1955.

(3-cyclopropylprop-2-yn-1-yl)trimethylsilane (**S-53**)



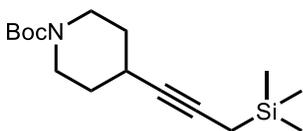
Following the general procedure D, the product **S-53** was obtained in 10% yield as colorless oil after column chromatography (eluent: Petroleum); R_f (Petroleum): 0.85; ^1H NMR (500 MHz, Chloroform- d) δ 1.39 (d, J = 2.0 Hz, 2H), 1.18 (ddt, J = 8.5, 5.4, 1.9 Hz, 1H), 0.70 – 0.64 (m, 2H), 0.55 (pd, J = 4.1, 1.5 Hz, 2H), 0.07 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 82.2, 73.0, 8.2, 7.1, -0.1, -2.0; GC-MS (EI) m/z : $[\text{M} - \text{e}]^+$ Calcd for $\text{C}_9\text{H}_{16}\text{Si}$ 152.1016; Found 152.1016.

(3-cyclohexylprop-2-yn-1-yl)trimethylsilane (**S-54**)



Following the general procedure D, the product **S-54** was obtained in 52% yield as colorless oil after column chromatography (eluent: Petroleum); R_f (Petroleum): 0.64; ^1H NMR (500 MHz, Chloroform- d) δ 2.37 – 2.25 (m, 1H), 1.75 (dd, J = 13.0, 6.6 Hz, 2H), 1.67 (dtd, J = 12.8, 6.6, 3.3 Hz, 2H), 1.52 – 1.20 (m, 8H), 0.07 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 83.7, 77.3, 33.6, 29.5, 26.2, 25.1, 7.0, -2.0; GC-MS (EI) m/z : $[\text{M} - \text{H}]^+$ Calcd for $\text{C}_{12}\text{H}_{22}\text{Si}$ 194.1485; Found 194.1485.

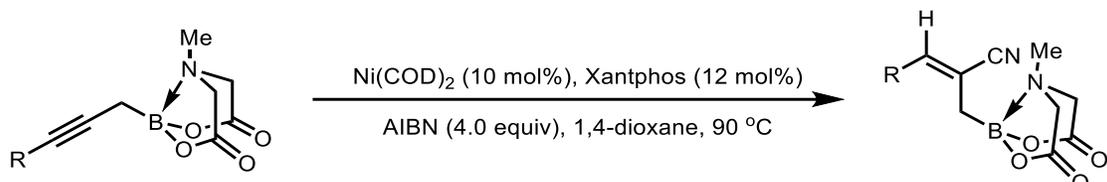
tert-butyl 4-(3-(trimethylsilyl)prop-1-yn-1-yl)piperidine-1-carboxylate (**S-55**)



Following the general procedure D, the product **S-55** was obtained in 26% yield as colorless oil after column chromatography (eluent: Petroleum/DCM = 3:1); R_f (Petroleum/DCM = 3:1): 0.54; ^1H NMR (400 MHz, Chloroform- d) δ 3.64 (ddd, J = 13.3, 6.9, 3.6 Hz, 2H), 3.18 (ddd, J = 13.4, 8.3, 3.4 Hz, 2H), 2.60 – 2.47 (m, 1H), 1.72 (ddt, J = 13.9, 7.2, 3.7 Hz, 2H), 1.55 – 1.47 (m, 2H), 1.44 (s, 9H), 1.42 (d, J = 2.5 Hz, 2H), 0.08 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 154.9, 81.1, 79.4, 79.2, 42.3, 32.2, 28.6, 27.3, 7.0, -1.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{29}\text{NO}_2\text{SiNa}$ 318.1860; Found 318.1862.

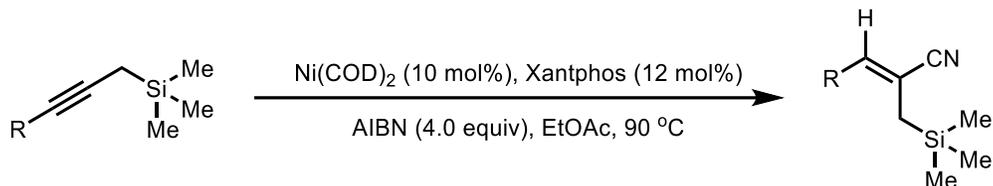
4. General Procedure and Characterization for Products

General procedure F:



The propargylic MIDA boronates (0.1 mmol, 1.0 equiv), AIBN (0.4 mmol, 4.0 equiv), Ni(COD)₂ (2.8 mg, 0.01 mmol, 10 mol%) and Xantphos (6.9 mg, 0.012 mmol, 12 mol%) were added to a 15 mL oven-dried pressure tube equipped with a stir bar under nitrogen atmosphere in glove box. 1,4-dioxane (1.0 mL) was added to the tube followed by sealed with a thread plug and then stirred at 90 °C. After the reaction finished, solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent (eluent = Petroleum ether/EtOAc from 1:1 to 1:3 v/v) to afford the pure product as semi solid.

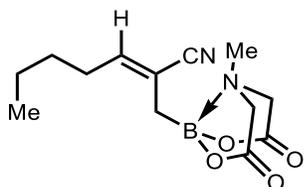
General procedure G:



AIBN (0.4 mmol, 4.0 equiv), Ni(COD)₂ (2.8 mg, 0.01 mmol, 10 mol%) and Xantphos (6.9 mg, 0.012 mmol, 12 mol%) were added to a 15 mL oven-dried pressure tube equipped with a stir bar under nitrogen atmosphere in glove box. The propargylic TMS (0.2 mmol, 1.0 equiv) dissolved in EtOAc (2.0 mL) was added to the tube followed by sealed with a thread plug and then stirred at 90 °C. After the reaction finished (2~18 h), solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent (eluent = Petroleum ether/DCM from 10:1 to 4:1 v/v) to afford the pure product as colorless oil.

Characterization for Products

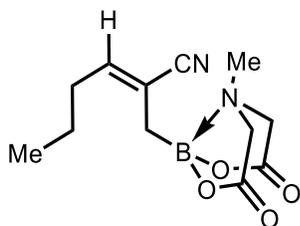
(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hept-2-enitrile (**1**)



Following the general procedure F, the product **1** was obtained in 79% yield as a semi solid (22.1 mg, 79%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to

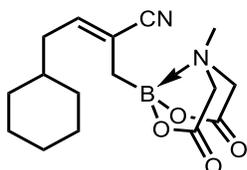
Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.62; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 6.28 (t, $J = 7.4$ Hz, 1H), 4.23 (d, $J = 17.0$ Hz, 2H), 4.05 (d, $J = 17.0$ Hz, 2H), 2.91 (s, 3H), 2.14 (q, $J = 7.3$ Hz, 2H), 1.68 (s, 2H), 1.43 – 1.25 (m, 4H), 0.87 (t, $J = 7.1$ Hz, 4H); $^{13}\text{C NMR}$ (126 MHz, $\text{Acetone-}d_6$) δ 168.4, 147.8, 121.9, 112.7, 62.9, 46.6, 31.2, 29.1, 23.0, 14.3, 14.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{19}\text{BN}_2\text{O}_4\text{Na}$ 301.1330; Found 301.1326.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hex-2-enenitrile (**2**)



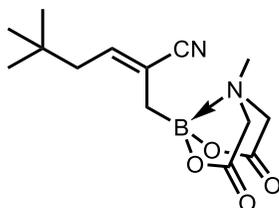
Following the general procedure F, the product **2** was obtained in 94% yield as a semi solid (24.8 mg, 94%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.63; $^1\text{H NMR}$ (400 MHz, $\text{Acetone-}d_6$) δ 6.27 (t, $J = 7.4$ Hz, 1H), 4.27 (d, $J = 16.9$ Hz, 2H), 4.12 (d, $J = 16.9$ Hz, 2H), 3.22 (s, 2H), 2.20 (q, $J = 7.4$ Hz, 2H), 1.83 (s, 2H), 1.47 (h, $J = 7.4$ Hz, 2H), 0.93 (t, $J = 7.4$ Hz, 2H); $^{13}\text{C NMR}$ (126 MHz, $\text{Acetone-}d_6$) δ 167.5, 146.7, 121.0, 112.0, 62.0, 45.7, 30.4, 21.4, 13.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{17}\text{BN}_2\text{O}_4\text{Na}$ 287.1173; Found 287.1174.

(*E*)-4-cyclohexyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)but-2-enenitrile (**3**)



Following the general procedure F, the product **3** was obtained in 66% yield as a semi solid (21.0 mg, 66%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.62; $^1\text{H NMR}$ (500 MHz, $\text{Acetone-}d_6$) δ 6.32 (t, $J = 7.5$ Hz, 1H), 4.27 (dd, $J = 16.9, 1.4$ Hz, 2H), 4.12 (dd, $J = 16.9, 1.4$ Hz, 2H), 3.21 (s, 3H), 2.12 (t, $J = 7.2$ Hz, 2H), 1.82 (s, 2H), 1.77 – 1.56 (m, 4H), 1.44 (dt, $J = 7.3, 3.8$ Hz, 1H), 1.33 – 1.09 (m, 4H), 1.04 – 0.91 (m, 2H); $^{13}\text{C NMR}$ (126 MHz, $\text{Acetone-}d_6$) δ 168.4, 146.7, 113.3, 62.9, 46.6, 38.4, 37.0, 33.8, 27.1, 27.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{23}\text{BN}_2\text{O}_4\text{Na}$ 341.1643; Found 341.1644.

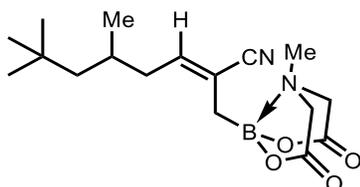
(*E*)-5,5-dimethyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hex-2-enenitrile (**4**)



Following the general procedure F, the product **4** was obtained in 88% yield as a semi solid (25.7 mg, 88%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.64; $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 6.37 (t, $J = 7.5$ Hz, 1H), 4.27 (d, $J = 17.0$ Hz, 2H), 4.12 (d, $J = 16.9$ Hz, 2H), 3.21 (s, 3H), 2.16 (d, $J = 7.5$ Hz, 2H), 1.84 (s, 2H), 0.95 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ 168.4, 145.1, 122.0, 114.0, 63.0, 46.6, 42.9, 31.9, 29.6; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{BN}_2\text{O}_4\text{Na}$ 315.1486; Found 315.1490.

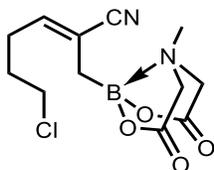
(E)-5,7,7-trimethyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)oct-2-enenitrile

(5)



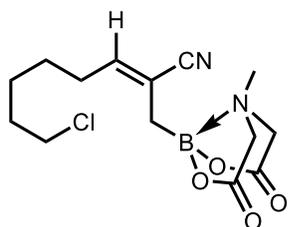
Following the general procedure F, the product **5** was obtained in 46% yield as a semi solid (30.8 mg, 46%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.67; $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 6.31 (t, $J = 7.3$ Hz, 1H), 4.27 (d, $J = 17.0$ Hz, 2H), 4.12 (d, $J = 16.9$ Hz, 2H), 3.21 (s, 3H), 2.16 (ddq, $J = 30.2, 15.2, 6.9$ Hz, 2H), 1.82 (s, 2H), 1.80 – 1.66 (m, 1H), 1.29 (dd, $J = 13.9, 3.5$ Hz, 1H), 1.10 (dd, $J = 14.0, 6.6$ Hz, 1H), 0.96 (d, $J = 6.7$ Hz, 3H), 0.91 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ 168.3, 146.9, 121.9, 113.3, 62.8, 51.2, 46.5, 38.6, 31.5, 30.2, 29.9, 22.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{27}\text{BN}_2\text{O}_4\text{Na}$ 357.1956; Found 357.1959.

(E)-6-chloro-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hex-2-enenitrile (**6**)



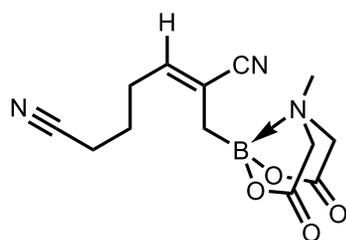
Following the general procedure F, the product **6** was obtained in 66% yield as a semi solid (19.7 mg, 66%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.59; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.30 (t, $J = 7.5$ Hz, 1H), 4.29 (d, $J = 17.0$ Hz, 2H), 4.14 (d, $J = 16.9$ Hz, 2H), 3.64 (t, $J = 6.7$ Hz, 2H), 3.23 (s, 3H), 2.38 (q, $J = 7.4$ Hz, 2H), 1.94 (p, $J = 7.0$ Hz, 2H), 1.86 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.4, 146.0, 121.8, 113.9, 63.0, 46.7, 45.3, 32.1, 26.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{16}\text{BClN}_2\text{O}_4\text{Na}$ 321.0784; Found 321.0783.

(*E*)-8-chloro-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)oct-2-enenitrile (**7**)



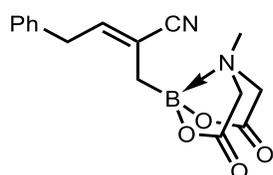
Following the general procedure F, the product **7** was obtained in 80% yield as a semi solid (26.1 mg, 80%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.61; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.28 (t, $J = 7.4$ Hz, 1H), 4.28 (d, $J = 17.0$ Hz, 2H), 4.13 (d, $J = 17.0$ Hz, 2H), 3.61 (t, $J = 6.7$ Hz, 2H), 3.22 (s, 3H), 2.24 (q, $J = 6.6$ Hz, 2H), 1.83 (s, 2H), 1.78 (p, $J = 6.8$ Hz, 2H), 1.51 – 1.45 (m, 4H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.4, 147.5, 121.9, 113.0, 63.0, 46.6, 45.7, 33.2, 29.3, 28.3, 27.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{20}\text{BClN}_2\text{O}_4\text{Na}$ 349.1097; Found 349.1101.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hept-2-enedinitrile (**8**)



Following the general procedure F, the product **8** was obtained in 57% yield as a semi solid (16.5 mg, 57%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.55; $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 6.30 (t, $J = 7.5$ Hz, 1H), 4.30 (d, $J = 16.9$ Hz, 2H), 4.14 (d, $J = 16.9$ Hz, 2H), 3.22 (s, 3H), 2.52 (t, $J = 7.3$ Hz, 2H), 2.37 (q, $J = 7.5$ Hz, 2H), 1.93 – 1.73 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ 167.5, 144.5, 120.7, 119.6, 113.4, 62.1, 45.8, 27.5, 24.1, 15.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{16}\text{BN}_3\text{O}_4\text{Na}$ 312.1126; Found 312.1130.

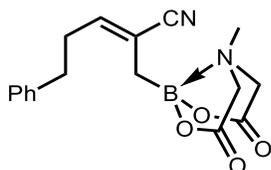
(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-4-phenylbut-2-enenitrile (**9**)



Following the general procedure F, the product **9** was obtained in 54% yield as a semi solid (16.9 mg, 54%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.54; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 7.39 – 7.16 (m, 5H), 6.38 (t, $J = 7.5$ Hz, 1H), 4.32 (d, $J = 17.0$ Hz, 2H), 4.17 (d, $J = 17.0$ Hz, 2H), 3.59 (d, $J = 7.5$

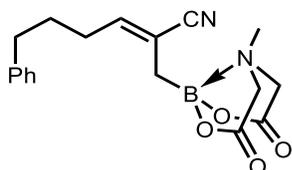
Hz, 2H), 1.98 (s, 2H).; ^{13}C NMR (126 MHz, Acetone) δ 168.5, 145.9, 139.8, 129.6, 129.5, 127.3, 121.7, 113.5, 63.1, 46.8, 35.5; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{BN}_2\text{O}_4\text{Na}$ 335.1173; Found 335.1176.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-5-phenylpent-2-enenitrile (**10**)



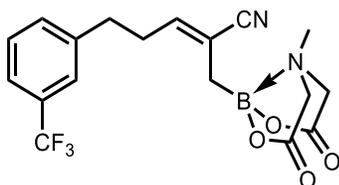
Following the general procedure F, the product **10** was obtained in 78% yield as a semi solid (25.4 mg, 78%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.54; ^1H NMR (500 MHz, Acetone- d_6) δ 7.39 – 7.16 (m, 5H), 6.38 (t, $J = 7.5$ Hz, 1H), 4.32 (d, $J = 17.0$ Hz, 2H), 4.17 (d, $J = 17.0$ Hz, 2H), 3.59 (d, $J = 7.5$ Hz, 2H), 1.98 (s, 2H).; ^{13}C NMR (126 MHz, Acetone) δ 168.5, 145.9, 139.8, 129.6, 129.5, 127.3, 121.7, 113.5, 63.1, 46.8, 35.5; ^{11}B NMR (160 MHz, Acetone) δ 11.8; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{17}\text{BN}_2\text{O}_4\text{Na}$ 335.1173; Found 335.1176.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-6-phenylhex-2-enenitrile (**11**)



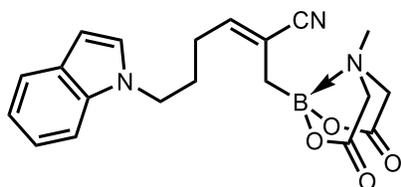
Following the general procedure F, the product **11** was obtained in 92% yield as a semi solid (31.3 mg, 92%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.61; ^1H NMR (400 MHz, Acetone- d_6) δ 7.33 – 7.10 (m, 5H), 6.33 (t, $J = 7.4$ Hz, 1H), 4.28 (dd, $J = 16.9, 0.9$ Hz, 2H), 4.12 (dd, $J = 16.8, 1.0$ Hz, 2H), 3.19 (d, $J = 1.0$ Hz, 3H), 2.68 – 2.61 (m, 2H), 2.31 – 2.23 (m, 2H), 1.86 – 1.72 (m, 4H); ^{13}C NMR (101 MHz, Acetone- d_6) δ 168.4, 147.4, 143.0, 129.3, 129.1, 126.6, 121.9, 113.0, 62.9, 46.6, 36.1, 31.0, 29.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{BN}_2\text{O}_4\text{Na}$ 363.1486; Found 363.1491.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-5-(3-(trifluoromethyl)phenyl)pent-2-enenitrile (**12**)



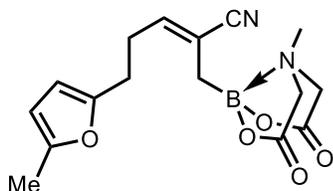
Following the general procedure F, the product **12** was obtained in 96% yield as a semi solid (38.2 mg, 97%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.56; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 7.75 – 7.39 (m, 4H), 6.33 (t, $J = 7.4$ Hz, 1H), 4.30 (d, $J = 16.9$ Hz, 2H), 4.14 (d, $J = 17.0$ Hz, 2H), 3.21 (s, 3H), 2.57 (q, $J = 7.7$ Hz, 2H), 1.82 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.4, 146.1, 143.7, 133.4, 131.4 – 123.7 (m), 130.0, 126.0 (q, $J = 3.8$ Hz), 123.6 (q, $J = 3.9$ Hz), 121.7, 113.6, 62.9, 46.6, 34.6, 31.3; $^{19}\text{F NMR}$ (376 MHz, Acetone- d_6) δ -63.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{18}\text{BF}_3\text{N}_2\text{O}_4\text{Na}$ 417.1204; Found 417.1200.

(*E*)-6-(1H-indol-1-yl)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)methyl)hex-2-enenitrile (**13**)



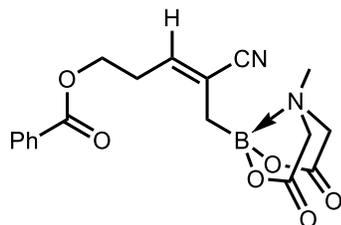
Following the general procedure F, the product **13** was obtained in 84% yield as a semi solid (31.9 mg, 84%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.50; $^1\text{H NMR}$ (400 MHz, Acetone- d_6) δ 7.55 (d, $J = 7.9$ Hz, 1H), 7.50 – 7.43 (m, 1H), 7.31 (d, $J = 3.1$ Hz, 1H), 7.16 – 7.10 (m, 1H), 7.01 (ddd, $J = 7.9, 7.0, 1.0$ Hz, 1H), 6.43 (dd, $J = 3.1, 0.7$ Hz, 1H), 6.32 (t, $J = 7.5$ Hz, 1H), 4.32 – 4.22 (m, 4H), 4.07 (d, $J = 16.9$ Hz, 2H), 3.11 (s, 3H), 2.25 (q, $J = 7.5$ Hz, 2H), 2.04 – 1.97 (m, 2H), 1.72 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, Acetone- d_6) δ 168.5, 146.4, 137.1, 129.7, 129.1, 122.0, 121.8, 121.5, 119.9, 113.5, 110.6, 101.7, 63.0, 46.6, 46.3, 29.3, 26.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{22}\text{BN}_3\text{O}_4\text{Na}$ 402.1595; Found 402.1599.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxaborocan-2-yl)methyl)-5-(5-methylfuran-2-yl)pent-2-enenitrile (**14**)



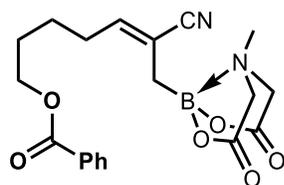
Following the general procedure F, the product **14** was obtained in 91% yield as a semi solid (30.1 mg, 91%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.56; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.29 (t, $J = 7.3$ Hz, 1H), 5.92 (dd, $J = 39.2, 2.9$ Hz, 2H), 4.29 (d, $J = 16.9$ Hz, 2H), 4.14 (d, $J = 17.0$ Hz, 2H), 3.23 (s, 3H), 2.73 (t, $J = 7.5$ Hz, 2H), 2.53 (q, $J = 7.4$ Hz, 2H), 2.21 (s, 3H), 1.84 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.4, 153.8, 151.1, 146.3, 121.8, 113.6, 107.1, 106.9, 63.0, 46.6, 28.2, 27.2, 13.5; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{19}\text{BN}_2\text{O}_5\text{Na}$ 353.1279; Found 353.1280.

(E)-4-cyano-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-3-en-1-yl benzoate (**15**)



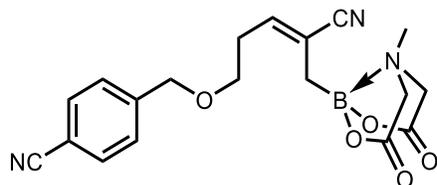
Following the general procedure F, the product **15** was obtained in 70% yield as a semi solid (25.9 mg, 70%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.45; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 8.02 – 7.95 (m, 2H), 7.71 – 7.62 (m, 1H), 7.53 (t, $J = 7.7$ Hz, 2H), 6.42 (t, $J = 7.2$ Hz, 1H), 4.35 (t, $J = 6.5$ Hz, 2H), 4.25 (d, $J = 17.0$ Hz, 2H), 4.06 (d, $J = 17.0$ Hz, 2H), 2.92 (s, 3H), 2.65 (q, $J = 6.7$ Hz, 2H), 1.77 (s, 2H); $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 168.7, 165.7, 142.5, 133.4, 129.6, 129.2, 128.8, 120.9, 113.9, 63.1, 61.9, 45.7, 28.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{19}\text{BN}_2\text{O}_6\text{Na}$ 393.1228; Found 393.1235.

(E)-6-cyano-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-en-1-yl benzoate (**16**)



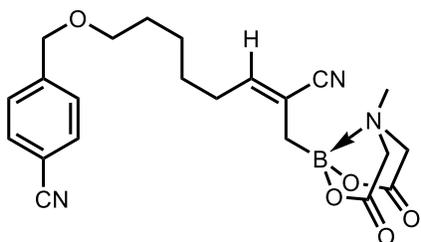
Following the general procedure F, the product **16** was obtained in 56% yield as a semi solid (22.3 mg, 56%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.48; $^1\text{H NMR}$ (500 MHz, $\text{Acetone-}d_6$) δ 8.06 – 8.01 (m, 2H), 7.69 – 7.58 (m, 1H), 7.51 (t, $J = 7.9$ Hz, 2H), 6.33 (t, $J = 7.4$ Hz, 1H), 4.33 (t, $J = 6.6$ Hz, 2H), 4.29 (d, $J = 16.8$ Hz, 2H), 4.13 (d, $J = 16.9$ Hz, 2H), 3.22 (s, 3H), 2.33 (q, $J = 7.5$ Hz, 2H), 1.88 – 1.78 (m, 4H), 1.65 (p, $J = 7.7$ Hz, 2H); $^{13}\text{C NMR}$ (126 MHz, $\text{Acetone-}d_6$) δ 168.5, 166.8, 147.4, 133.9, 131.5, 130.2, 129.5, 121.9, 113.2, 65.3, 63.0, 46.7, 29.2, 29.1, 25.7; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{23}\text{BN}_2\text{O}_6\text{Na}$ 421.1541; Found 421.1549.

(E)-4-(((4-cyano-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)pent-3-en-1-yl)oxy)methyl)benzonitrile (**17**)



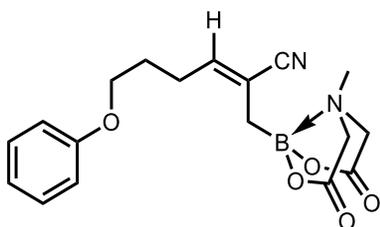
Following the general procedure F, the product **17** was obtained in 71% yield as a semi solid (27.1 mg, 71%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.52; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 7.82 (d, $J = 7.8$ Hz, 2H), 7.52 (d, $J = 7.8$ Hz, 2H), 6.33 (t, $J = 7.3$ Hz, 1H), 4.58 (s, 2H), 4.25 (d, $J = 16.9$ Hz, 2H), 4.06 (d, $J = 16.9$ Hz, 2H), 3.56 (t, $J = 6.6$ Hz, 2H), 2.91 (s, 3H), 2.50 – 2.44 (m, 2H), 1.72 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ 168.7, 144.4, 143.6, 132.3, 127.8, 121.0, 118.9, 113.1, 110.0, 70.9, 68.4, 61.8, 45.7, 28.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{BN}_3\text{O}_5\text{Na}$ 404.1388; Found 404.1388.

(*E*)-4-(((7-cyano-8-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)oct-6-en-1-yl)oxy)methyl)benzonitrile (**18**)



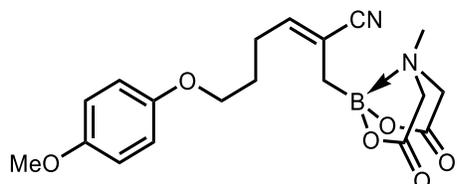
Following the general procedure F, the product **18** was obtained in 68% yield as a semi solid (28.8 mg, 68%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.56; $^1\text{H NMR}$ (400 MHz, $\text{DMSO-}d_6$) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 2H), 6.29 (t, $J = 7.3$ Hz, 1H), 4.55 (s, 2H), 4.24 (d, $J = 17.0$ Hz, 2H), 4.06 (d, $J = 17.0$ Hz, 2H), 3.46 (t, $J = 6.4$ Hz, 2H), 2.91 (s, 3H), 2.15 (q, $J = 7.1$ Hz, 2H), 1.69 (s, 2H), 1.57 (p, $J = 6.6$ Hz, 2H), 1.47 – 1.29 (m, 4H); $^{13}\text{C NMR}$ (101 MHz, $\text{DMSO-}d_6$) δ 168.6, 147.1, 144.8, 132.2, 127.8, 121.2, 118.9, 111.5, 110.0, 70.9, 70.0, 61.7, 45.6, 29.0, 28.2, 27.6, 25.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{26}\text{BN}_3\text{O}_5\text{Na}$ 446.1858; Found 446.1859.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-6-phenoxyhex-2-enenitrile (**19**)



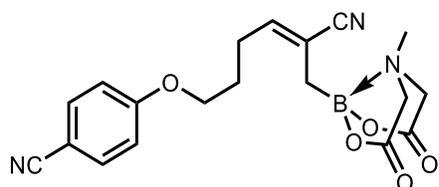
Following the general procedure F, the product **19** was obtained in 68% yield as a semi solid (24.2 mg, 68%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.56; $^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 7.27 (t, $J = 7.7$ Hz, 2H), 6.93 (d, $J = 8.1$ Hz, 3H), 6.38 (t, $J = 7.5$ Hz, 1H), 4.25 (d, $J = 17.0$ Hz, 2H), 4.05 (d, $J = 17.0$ Hz, 2H), 3.96 (t, $J = 6.5$ Hz, 2H), 2.90 (s, 3H), 2.31 (d, $J = 7.4$ Hz, 2H), 1.84 (p, $J = 6.5$ Hz, 2H), 1.69 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, $\text{DMSO-}d_6$) δ 169.1, 159.0, 146.7, 129.9, 121.6, 121.0, 120.9, 114.9, 112.5, 67.1, 62.2, 46.1, 27.9, 25.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{BN}_2\text{O}_5\text{Na}$ 379.1436; Found 379.1429.

(*E*)-6-(4-methoxyphenoxy)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hex-2-enenitrile (**20**)



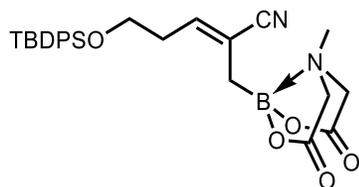
Following the general procedure F, the product **20** was obtained in 82% yield as a semi solid (31.7 mg, 82%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.56; ^1H NMR (500 MHz, Acetone- d_6) δ 6.88 (d, J = 9.0 Hz, 2H), 6.83 (d, J = 9.2 Hz, 2H), 6.36 (t, J = 7.5 Hz, 1H), 4.29 (d, J = 17.0 Hz, 2H), 4.12 (d, J = 17.0 Hz, 2H), 3.95 (t, J = 6.3 Hz, 2H), 3.73 (s, 3H), 3.20 (s, 3H), 2.41 (q, J = 7.5 Hz, 2H), 1.90 (p, J = 6.9 Hz, 2H), 1.84 (s, 2H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.5, 154.9, 154.1, 147.0, 121.9, 116.3, 115.4, 113.4, 68.3, 63.0, 55.9, 46.7, 28.9, 26.2; ^{11}B NMR (128 MHz, Acetone) δ 11.5; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{23}\text{BN}_2\text{O}_6\text{Na}$ 409.1541; Found 409.1543.

(*E*)-4-((5-cyano-6-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hex-4-en-1-yl)oxy)benzonitrile (**21**)



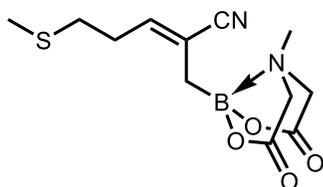
Following the general procedure F, the product **21** was obtained in 40% yield as a semi solid (15.2 mg, 40%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.51; ^1H NMR (500 MHz, DMSO- d_6) δ 7.75 (d, J = 8.3 Hz, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.37 (t, J = 7.5 Hz, 1H), 4.25 (d, J = 17.1 Hz, 2H), 4.12 – 3.98 (m, 4H), 2.90 (s, 3H), 2.36 – 2.25 (m, 2H), 1.91 – 1.82 (m, 2H), 1.68 (s, 2H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 168.7, 162.0, 146.0, 134.2, 121.1, 119.2, 115.6, 112.2, 102.7, 67.4, 61.8, 45.7, 27.1, 24.8; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{20}\text{BN}_3\text{O}_5\text{Na}$ 404.1388; Found 404.1384.

(*E*)-5-((*tert*-butyldiphenylsilyl)oxy)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pent-2-enenitrile (**22**)



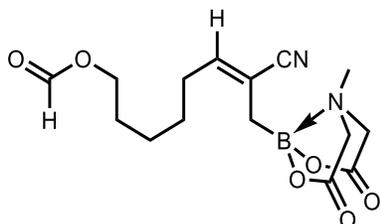
Following the general procedure F, the product **22** was obtained in 74% yield as a semi solid (37.3 mg, 74%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.67; ^1H NMR (500 MHz, Chloroform- d) δ 7.64 (d, J = 7.1 Hz, 4H), 7.40 (dt, J = 14.2, 6.5 Hz, 6H), 6.43 (t, J = 7.2 Hz, 1H), 4.03 (d, J = 16.8 Hz, 2H), 3.79 (d, J = 16.9 Hz, 2H), 3.74 (t, J = 6.1 Hz, 2H), 2.95 (s, 3H), 2.43 (q, J = 6.6 Hz, 2H), 1.73 (s, 2H), 1.04 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.5, 146.4, 135.7, 133.6, 129.9, 127.9, 121.7, 111.6, 62.4, 62.1, 46.3, 32.4, 27.0, 19.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{27}\text{H}_{33}\text{BN}_2\text{O}_5\text{SiNa}$ 527.2144; Found 527.2149.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-5-(methylthio)pent-2-enenitrile (**23**)



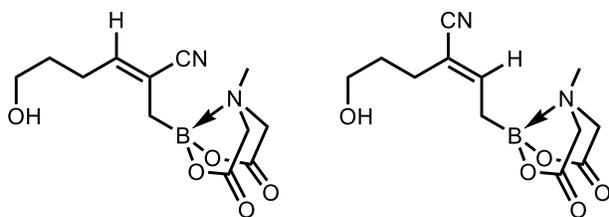
Following the general procedure F, the product **23** was obtained in 58% yield as a semi solid (17.2 mg, 58%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.60; ^1H NMR (500 MHz, Acetone- d_6) δ 6.33 (t, J = 7.2 Hz, 1H), 4.30 (d, J = 16.9 Hz, 2H), 4.15 (d, J = 17.0 Hz, 2H), 3.24 (s, 3H), 2.62 (t, J = 7.3 Hz, 2H), 2.51 (q, J = 7.3 Hz, 2H), 2.10 (s, 3H), 1.86 (s, 2H); ^{13}C NMR (126 MHz, Acetone) δ 167.5, 144.7, 120.8, 113.0, 62.1, 45.7, 32.0, 28.3, 14.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{17}\text{BN}_2\text{O}_4\text{SNa}$ 319.0894; Found 319.0886.

(*E*)-7-cyano-8-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)oct-6-en-1-yl) formate (**24**)



Following the general procedure F, the product **24** was obtained in 50% yield as a semi solid (16.8 mg, 50%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.56; ^1H NMR (400 MHz, Acetone- d_6) δ 8.11 (s, 1H), 6.28 (t, J = 7.4 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.17 – 4.08 (m, 4H), 3.22 (s, 3H), 2.24 (q, J = 7.3 Hz, 2H), 1.83 (s, 2H), 1.67 (p, J = 6.8 Hz, 2H), 1.56 – 1.34 (m, 4H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.4, 162.0, 147.6, 121.9, 112.9, 64.1, 62.9, 46.6, 29.3, 29.1, 28.6, 26.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{21}\text{BN}_2\text{O}_6\text{Na}$ 359.1385; Found 359.1384.

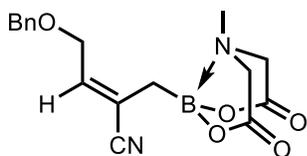
(*E*)-6-hydroxy-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hex-2-enenitrile (**25**)



4.5:1

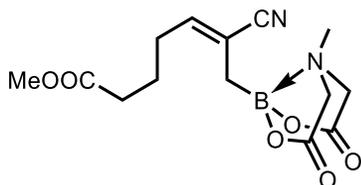
Following the general procedure F, the product **25** was obtained in 57% yield as a mixture (16.0 mg, 57%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.40; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.31 (t, J = 7.5 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.14 (d, J = 17.0 Hz, 2H), 3.56 (t, J = 6.4 Hz, 2H), 3.22 (s, 3H), 2.29 (q, J = 7.6 Hz, 2H), 1.83 (s, 2H), 1.65 – 1.55 (m, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.0, 147.2, 121.4, 112.3, 62.4, 61.2, 46.1, 31.7, 25.5, 13.9.; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{17}\text{BN}_2\text{O}_5\text{Na}$ 303.1123; Found 303.1129.

(*E*)-5-(benzyloxy)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pent-2-enitrile
(26)



Following the general procedure F, the product **26** was obtained in 69% yield as a semi solid (24.6 mg, 69%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.52; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 7.46 – 7.19 (m, 5H), 6.42 (d, J = 6.2 Hz, 1H), 4.54 (s, 2H), 4.32 – 4.23 (m, 4H), 4.12 (d, J = 16.9 Hz, 2H), 3.20 (s, 3H), 1.86 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.3, 143.8, 139.4, 129.1, 128.5, 128.3, 121.1, 114.9, 73.1, 67.2, 63.0, 46.8, 46.6; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{18}\text{H}_{21}\text{BN}_2\text{O}_5\text{Na}$ 379.1436; Found 379.1437.

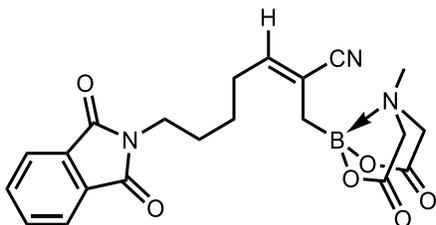
methyl (*E*)-6-cyano-7-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)hept-5-enoate **(27)**



Following the general procedure F, the product **27** was obtained in 93% yield as a semi solid (30.0 mg, 93%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.48; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.29 (t, J = 7.5 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.13 (d, J = 17.0 Hz, 2H), 3.62 (s, 4H), 3.22 (s, 3H), 2.35 (t, J = 7.4 Hz, 2H), 2.26 (q, J = 7.5 Hz, 2H), 1.83 (s, 2H), 1.74 (p, J = 7.5 Hz, 2H); $^{13}\text{C NMR}$ (126 MHz,

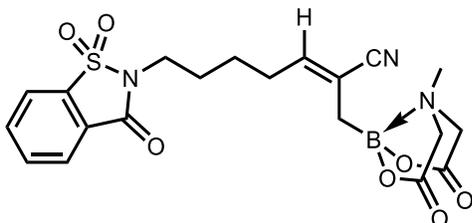
Acetone- d_6) δ 173.9, 168.4, 146.7, 121.8, 113.6, 62.9, 51.6, 46.6, 33.7, 28.6, 24.3; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{14}H_{19}BN_2O_6Na$ 345.1228; Found 345.1235.

(*E*)-7-(1,3-dioxoisindolin-2-yl)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hept-2-enenitrile (**28**)



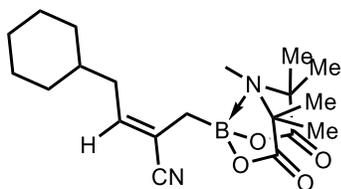
Following the general procedure F, the product **28** was obtained in 76% yield as a semi solid (32.2 mg, 76%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.46; 1H NMR (400 MHz, Acetone- d_6) δ 7.92 – 7.73 (m, 4H), 6.28 (t, J = 7.5 Hz, 1H), 4.27 (d, J = 16.9 Hz, 2H), 4.13 (d, J = 16.9 Hz, 2H), 3.67 (t, J = 7.0 Hz, 2H), 3.23 (s, 3H), 2.29 (q, J = 7.5 Hz, 2H), 1.84 (s, 2H), 1.72 (p, J = 7.1 Hz, 2H), 1.51 (q, J = 7.8 Hz, 2H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.9, 168.4, 147.2, 134.9, 133.1, 123.7, 121.8, 113.1, 62.9, 46.6, 38.1, 28.9, 26.1; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{21}H_{22}BN_3O_6Na$ 446.1494; Found 446.1499.

(*E*)-7-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hept-2-enenitrile (**29**)



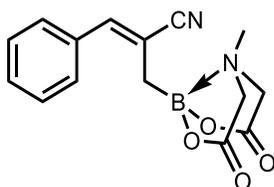
Following the general procedure F, the product **29** was obtained in 64% yield as a semi solid (29.4 mg, 64%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.45; 1H NMR (400 MHz, Chloroform- d) δ 8.02 (dd, J = 7.0, 1.6 Hz, 1H), 7.94 – 7.90 (m, 1H), 7.89 – 7.78 (m, 2H), 6.31 (t, J = 7.4 Hz, 1H), 4.10 (d, J = 17.0 Hz, 2H), 3.90 (d, J = 17.0 Hz, 2H), 3.76 (t, J = 7.1 Hz, 2H), 3.04 (s, 3H), 2.25 (q, J = 7.5 Hz, 2H), 1.85 (dt, J = 14.7, 7.1 Hz, 2H), 1.76 (s, 2H), 1.53 (p, J = 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.1, 159.2, 148.1, 137.6, 135.0, 134.6, 127.4, 125.3, 121.7, 121.1, 111.3, 62.5, 46.5, 39.0, 28.2, 28.0, 25.3; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{20}H_{22}BN_3O_7SNa$ 482.1164; Found 482.1158.

(*E*)-4-cyclohexyl-2-((5,5,6,7,7-pentamethyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)but-2-enenitrile (**30**)



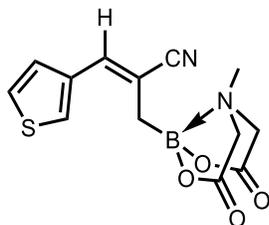
Following the general procedure F, the product **30** was obtained in 99% yield as a semi solid (37.0 mg, 99%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.75; $^1\text{H NMR}$ (500 MHz, Chloroform- d) δ 6.37 (t, J = 7.4 Hz, 1H), 2.66 (s, 3H), 2.13 – 2.03 (m, 2H), 1.76 (s, 2H), 1.72 (s, 6H), 1.71 – 1.69 (m, 4H), 1.62 (s, 6H), 1.44 – 1.36 (m, 1H), 1.27 – 1.07 (m, 4H), 0.99 – 0.89 (m, 2H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 173.3, 147.5, 121.7, 111.3, 63.1, 39.6, 37.6, 36.6, 36.3, 33.1, 26.3, 26.2; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{31}\text{BN}_2\text{O}_4\text{Na}$ 397.2269; Found 397.2266.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-3-phenylacrylonitrile (**31**)



Following the general procedure F, the product **31** was obtained in 67% yield as a semi solid (20.0 mg, 67%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.62; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 7.55 – 7.50 (m, 2H), 7.44 – 7.33 (m, 3H), 7.25 (s, 1H), 4.32 (d, J = 17.0 Hz, 2H), 4.15 (d, J = 17.0 Hz, 2H), 3.20 (s, 3H), 2.11 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.4, 143.7, 130.1, 129.7, 129.6, 129.4, 129.3, 122.3, 114.5, 63.0, 46.7.; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{15}\text{BN}_2\text{O}_4\text{Na}$ 321.1017; Found 321.1020.

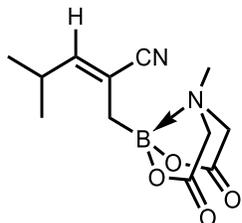
(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-3-(thiophen-3-yl)acrylonitrile (**32**)



Following the general procedure F, the product **32** was obtained in 51% yield as a semi solid (15.4 mg, 51%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.60; $^1\text{H NMR}$ (500 MHz, DMSO- d_6) δ 7.82 (s, 1H), 7.65 – 7.55 (m, 1H), 7.33 (d, J = 5.0 Hz, 1H), 7.23 (s, 1H), 4.28 (d, J = 17.0 Hz, 2H), 4.10 (d, J = 17.1 Hz, 2H), 2.98 (s, 3H), 2.00 (s, 2H); $^{13}\text{C NMR}$ (126 MHz, DMSO- d_6) δ 168.6, 136.6, 135.9, 128.8,

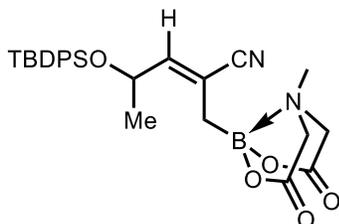
128.3, 126.5, 122.0, 110.6, 61.9, 45.8 ; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{13}H_{13}BN_2O_4SNa$ 327.0581; Found 327.0591.

(*E*)-4-methyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pent-2-enitrile (**33**)



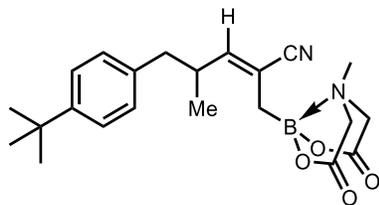
Following the general procedure F, the product **33** was obtained in 99% yield as a semi solid (26.0 mg, 99%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.67; 1H NMR (500 MHz, Acetone- d_6) δ 6.05 (d, J = 10.2 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.13 (d, J = 16.9 Hz, 2H), 3.22 (d, J = 1.6 Hz, 3H), 2.81 – 2.67 (m, 1H), 1.82 (s, 2H), 1.00 (d, J = 6.7 Hz, 6H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.4, 153.9, 122.0, 110.6, 63.0, 46.6, 28.7, 21.9; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{12}H_{17}BN_2O_4Na$ 287.1173; Found 287.1171.

(*E*)-4-((tert-butyldiphenylsilyloxy)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pent-2-enitrile (**34**)



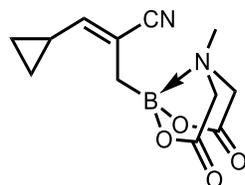
Following the general procedure F, the product **34** was obtained in 72% yield as a semi solid (36.3 mg, 72%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.70; 1H NMR (400 MHz, Chloroform- d) δ 7.65 (ddd, J = 7.6, 5.8, 1.7 Hz, 4H), 7.40 (ddd, J = 12.3, 7.2, 5.3 Hz, 6H), 6.27 (d, J = 8.8 Hz, 1H), 4.52 – 4.31 (m, 1H), 3.90 (dd, J = 16.9, 6.0 Hz, 2H), 3.66 (d, J = 16.9 Hz, 1H), 3.48 (d, J = 17.0 Hz, 1H), 2.64 (d, J = 2.6 Hz, 3H), 1.31 (d, J = 6.2 Hz, 3H), 1.04 (s, 9H), 0.98 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.8, 167.4, 150.6, 136.0, 135.9, 133.9, 133.7, 130.0, 130.0, 127.9, 127.8, 121.1, 109.6, 65.8, 62.3, 62.0, 46.1, 26.9, 23.1, 19.3; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{27}H_{33}BN_2O_5SiNa$ 527.2144; Found 527.2150.

(*E*)-5-(4-(tert-butyl)phenyl)-4-methyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pent-2-enitrile (**35**)



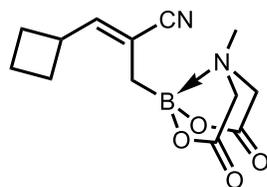
Following the general procedure F, the product **35** was obtained in 72% yield as a semi solid (28.5 mg, 72%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.68; ^1H NMR (500 MHz, Chloroform- d) δ 7.29 (d, J = 7.8 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.21 (d, J = 10.4 Hz, 1H), 3.95 (d, J = 16.7 Hz, 2H), 3.78 (dd, J = 16.7, 6.9 Hz, 2H), 2.93 (s, 3H), 2.85 – 2.74 (m, 1H), 2.69 – 2.50 (m, 2H), 1.30 (s, 12H), 1.03 (d, J = 6.5 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.7, 154.4, 149.0, 136.0, 128.8, 125.1, 121.7, 108.4, 99.9, 62.3, 62.1, 46.0, 41.6, 35.6, 34.3, 31.3, 29.6, 18.9; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{22}\text{H}_{29}\text{BN}_2\text{O}_4\text{Na}$ 419.2112; Found 419.2117.

(*E*)-3-cyclopropyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)acrylonitrile (**36**)



Following the general procedure F, the product **36** was obtained in 65% yield as a semi solid (17.0 mg, 65%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.65; ^1H NMR (400 MHz, Acetone- d_6) δ 5.67 (d, J = 10.4 Hz, 1H), 4.27 (d, J = 16.9 Hz, 2H), 4.12 (d, J = 16.9 Hz, 2H), 3.23 (s, 3H), 1.92 (s, 2H), 1.87 – 1.70 (m, 1H), 0.96 – 0.85 (m, 2H), 0.65 – 0.54 (m, 2H); ^{13}C NMR (101 MHz, Acetone- d_6) δ 168.5, 152.1, 122.1, 109.6, 63.0, 46.6, 12.6, 8.6; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{12}\text{H}_{15}\text{BN}_2\text{O}_4\text{Na}$ 285.1017; Found 285.1014.

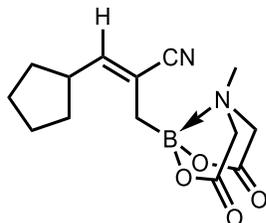
(*E*)-3-cyclobutyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)acrylonitrile (**37**)



Following the general procedure F, the product **37** was obtained in 37% yield as a semi solid (10.2 mg, 37%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.66; ^1H NMR (400 MHz, Acetone- d_6) δ 6.37 (d, J = 9.6 Hz, 1H), 4.26 (d, J = 16.9 Hz, 2H), 4.12 (d, J = 16.9 Hz, 2H), 3.48 – 3.27 (m, 1H), 3.20 (s, 3H), 2.29 – 2.14 (m, 2H), 2.00 – 1.79 (m, 4H), 1.79 (s, 2H); ^{13}C NMR (101 MHz, Acetone- d_6) δ 168.4,

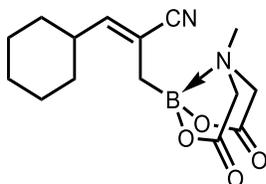
151.8, 122.0, 111.0, 63.0, 46.6, 35.4, 29.3, 19.4; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{13}H_{17}BN_2O_4Na$ 299.1173; Found 299.1180.

(*E*)-3-cyclopentyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)acrylonitrile (**38**)



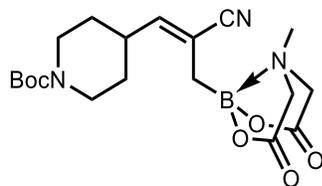
Following the general procedure F, the product **38** was obtained in 50% yield as a semi solid (14.5 mg, 50%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.65; 1H NMR (400 MHz, Acetone- d_6) δ 6.17 (d, J = 10.2 Hz, 1H), 4.27 (d, J = 16.9 Hz, 2H), 4.12 (d, J = 16.9 Hz, 2H), 3.22 (s, 3H), 2.93 – 2.81 (m, 1H), 1.90 (ddd, J = 17.0, 7.4, 2.6 Hz, 2H), 1.84 (s, 2H), 1.69 (tt, J = 9.0, 5.0 Hz, 2H), 1.57 (qt, J = 6.9, 2.9 Hz, 2H), 1.36 – 1.25 (m, 2H); ^{13}C NMR (101 MHz, Acetone- d_6) δ 168.5, 152.6, 122.2, 111.1, 63.1, 46.7, 40.3, 33.4, 26.2; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{14}H_{19}BN_2O_4Na$ 313.1330; Found 313.1339.

(*E*)-3-cyclohexyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)acrylonitrile (**39**)



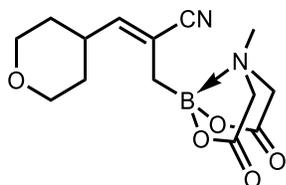
Following the general procedure F, the product **39** was obtained in 92% yield as a semi solid (28.0 mg, 92%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.66; 1H NMR (500 MHz, Acetone- d_6) δ 6.07 (d, J = 10.2 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H), 4.13 (d, J = 16.9 Hz, 2H), 3.21 (s, 3H), 2.45 (dt, J = 10.7, 3.6 Hz, 1H), 1.83 (s, 2H), 1.75 – 1.56 (m, 5H), 1.36 – 1.17 (m, 4H), 1.16 – 1.06 (m, 2H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.4, 152.5, 122.1, 110.8, 62.9, 46.5, 38.4, 32.1, 26.4, 26.1; HRMS (ESI) m/z : $[M + Na]^+$ Calcd for $C_{15}H_{21}BN_2O_4Na$ 327.1486; Found 327.1493.

tert-butyl (*E*)-4-(2-cyano-3-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)prop-1-en-1-yl)piperidine-1-carboxylate (**40**)



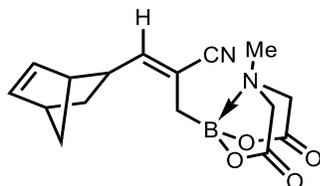
Following the general procedure F, the product **40** was obtained in 81% yield as a semi solid (32.8 mg, 81%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.46; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.10 (d, J = 10.2 Hz, 1H), 4.30 (d, J = 16.9 Hz, 2H), 4.14 (d, J = 16.9 Hz, 2H), 4.09 – 3.98 (m, 2H), 3.21 (s, 3H), 2.78 – 2.60 (m, 3H), 1.89 (s, 2H), 1.69 (d, J = 13.2 Hz, 2H), 1.33 – 1.21 (m, 2H); $^{13}\text{C NMR}$ (126 MHz, Acetone- d_6) δ 168.4, 155.0, 150.6, 121.9, 112.0, 79.4, 62.9, 46.6, 36.8, 31.2, 28.6; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{28}\text{BN}_3\text{O}_6\text{Na}$ 428.1963; Found 428.1955.

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-3-(tetrahydro-2H-pyran-4-yl)acrylonitrile (**41**)



Following the general procedure F, the product **41** was obtained in 71% yield as a semi solid (21.7 mg, 71%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.38; $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 6.13 (d, J = 10.1 Hz, 1H), 4.25 (d, J = 17.0 Hz, 2H), 4.07 (d, J = 17.0 Hz, 2H), 3.88 – 3.78 (m, 2H), 3.34 – 3.25 (m, 2H), 2.92 (s, 3H), 2.73 – 2.58 (m, 1H), 1.73 (s, 2H), 1.57 – 1.44 (m, 2H), 1.44 – 1.30 (m, 2H); $^{13}\text{C NMR}$ (126 MHz, DMSO- d_6) δ 169.1, 150.5, 111.0, 66.6, 62.2, 46.1, 34.7, 31.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{19}\text{BN}_2\text{O}_5\text{Na}$ 329.1279; Found 329.1288.

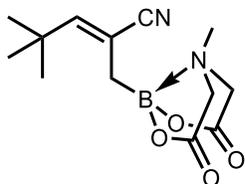
(*E*)-3-(bicyclo[2.2.1]hept-5-en-2-yl)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)acrylonitrile (**42**)



Following the general procedure F, the product **42** was obtained in 30% yield as a semi solid (9.6 mg, 30%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_F (EtOAc): 0.56; $^1\text{H NMR}$ (500 MHz, Acetone- d_6) δ 6.24 (dd, J = 5.8, 3.1 Hz, 1H), 6.03 (dd, J = 5.8, 2.9 Hz, 1H), 5.77 (d, J = 10.6 Hz, 1H), 4.28 (d, J = 16.9 Hz, 2H),

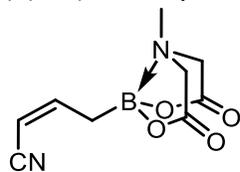
4.13 (dd, $J = 16.9, 2.0$ Hz, 2H), 3.22 (s, 3H), 3.15 – 3.06 (m, 1H), 2.97 (s, 1H), 2.85 (s, 1H), 2.11 – 2.06 (m, 1H), 1.89 (s, 2H), 1.40 – 1.35 (m, 1H), 1.28 (t, $J = 7.4$ Hz, 1H), 0.78 – 0.70 (m, 1H); ^{13}C NMR (101 MHz, Acetone- d_6) δ 168.4, 168.4, 152.7, 138.7, 133.3, 122.0, 111.4, 62.9, 50.1, 47.9, 46.5, 43.5, 38.8, 33.7; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{16}\text{H}_{19}\text{BN}_2\text{O}_4\text{Na}$ 337.1330; Found 337.1329.

(*E*)-4,4-dimethyl-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)pent-2-enenitrile
(**43**)



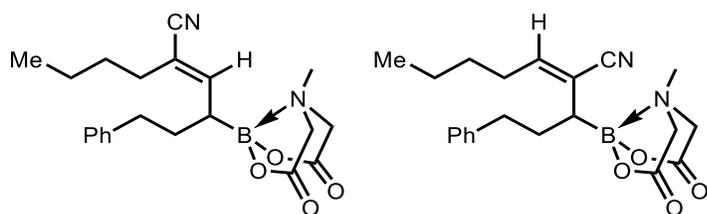
Following the general procedure F, the product **43** was obtained in 77% yield as a semi solid (21.4 mg, 77%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.75; ^1H NMR (500 MHz, Acetone- d_6) δ 6.18 (s, 1H), 4.29 (d, $J = 16.9$ Hz, 2H), 4.13 (d, $J = 16.9$ Hz, 2H), 3.23 (s, 3H), 1.96 (s, 2H), 1.18 (s, 9H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.4, 155.9, 122.9, 112.4, 63.0, 46.7, 35.4, 30.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{19}\text{BN}_2\text{O}_4\text{Na}$ 301.1330; Found 301.1326.

(*Z*)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)but-2-enenitrile (**44**)



Following the general procedure F, the product **44** was obtained in 27% yield as a semi solid (6.0 mg, 27%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.4; ^1H NMR (500 MHz, Acetone- d_6) δ 6.70 (dt, $J = 10.8, 8.4$ Hz, 1H), 5.43 (d, $J = 10.8$ Hz, 1H), 4.30 (d, $J = 16.9$ Hz, 2H), 4.15 (d, $J = 16.8$ Hz, 2H), 3.21 (s, 3H), 2.02 (d, $J = 9.5$ Hz, 2H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.1, 154.4, 117.0, 98.8, 62.7, 46.4.

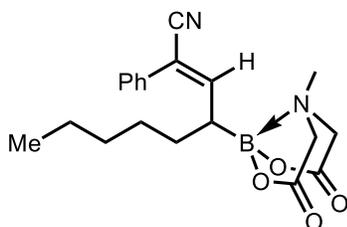
(*E*)-2-(1-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylethyl)hept-2-enenitrile(**45**)



4:1

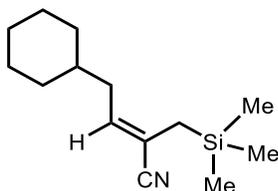
Following the general procedure F, the product **45** was obtained in 99% yield as a semi solid (37.8 mg, 99%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.73; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.26 (t, J = 7.4 Hz, 3H), 7.19 – 7.10 (m, 4H), 6.33 (d, J = 11.5 Hz, 1H), 3.98 (dd, J = 16.9, 5.0 Hz, 2H), 3.67 (dd, J = 19.7, 16.7 Hz, 2H), 2.80 (s, 3H), 2.66 (ddd, J = 14.3, 10.0, 4.9 Hz, 1H), 2.41 (dt, J = 15.2, 7.9 Hz, 1H), 2.20 (ddd, J = 15.6, 9.8, 6.3 Hz, 1H), 2.07 (dddd, J = 18.5, 14.7, 10.6, 6.4 Hz, 3H), 1.97 – 1.86 (m, 1H), 1.84 – 1.67 (m, 2H), 1.60 – 1.48 (m, 1H), 1.45 – 1.25 (m, 3H), 0.93 (t, J = 7.5 Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 167.6, 150.0, 141.6, 128.6, 128.6, 128.5, 126.2, 120.3, 115.5, 62.7, 62.7, 45.9, 35.3, 31.9, 30.1, 28.6, 22.5, 14.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{21}\text{H}_{27}\text{BN}_2\text{O}_4\text{Na}$ 405.1956; Found 405.1959.

(*E*)-4-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-phenylnon-2-enenitrile (**46**)



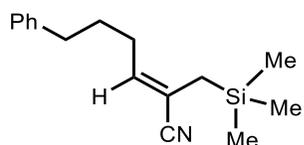
Following the general procedure F, the product **46** was obtained in 24% yield as a semi solid (8.8 mg, 24%) after column chromatography (eluent: from Petroleum ether/EtOAc 1:1 v/v to Petroleum ether/EtOAc 1:3 v/v); R_f (EtOAc): 0.76; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.45 – 7.34 (m, 5H), 6.64 (d, J = 12.2 Hz, 1H), 3.85 (dd, J = 16.5, 7.8 Hz, 2H), 3.60 (t, J = 17.3 Hz, 2H), 2.56 (s, 3H), 2.28 (ddd, J = 12.4, 9.1, 3.5 Hz, 1H), 1.30 – 1.17 (m, 8H), 0.88 (t, J = 7.0 Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 166.4, 166.3, 152.9, 132.4, 129.0, 129.0, 128.3, 119.7, 114.5, 62.4, 62.3, 45.3, 31.9, 30.3, 28.9, 22.5, 22.4, 14.0, 14.0; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{20}\text{H}_{25}\text{BN}_2\text{O}_4\text{Na}$ 391.1799; Found 391.1800.

(*Z*)-4-cyclohexyl-2-((trimethylsilyl)methyl)but-2-enenitrile (**47**)



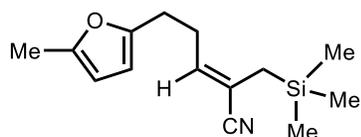
Following the general procedure G, the product **47** was obtained in 43% yield as colorless oil (20.4 mg, 43%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.48; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.22 (t, J = 7.4 Hz, 1H), 1.97 (t, J = 7.1 Hz, 2H), 1.74 – 1.67 (m, 4H), 1.66 (s, 2H), 1.44 – 1.31 (m, 1H), 1.31 – 1.08 (m, 4H), 0.99 – 0.85 (m, 2H), 0.11 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 143.9, 121.5, 112.2, 37.9, 36.5, 33.3, 26.4, 26.3, 20.4, -1.3; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{25}\text{NSiNa}$ 258.1648; Found 258.1654.

(*Z*)-6-phenyl-2-((trimethylsilyl)methyl)hex-2-enenitrile (**48**)



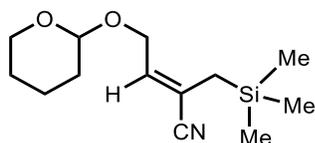
Following the general procedure G, the product **48** was obtained in 71% yield as colorless oil (36.3 mg, 71%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.48; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.19 (dt, $J = 7.8, 3.7$ Hz, 2H), 7.12 – 7.05 (m, 3H), 6.11 (t, $J = 6.8$ Hz, 1H), 2.54 (t, $J = 6.6$ Hz, 2H), 2.04 – 1.97 (m, 2H), 1.64 (dt, $J = 15.8, 7.9$ Hz, 2H), 1.53 (s, 2H), -0.01 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.2, 141.5, 133.5, 128.5, 128.5, 126.1, 121.3, 112.3, 35.4, 30.1, 28.2, 20.4, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NSi Na}$ 280.1492; Found 280.1492.

(*Z*)-5-(5-methylfuran-2-yl)-2-((trimethylsilyl)methyl)pent-2-enitrile (**49**)



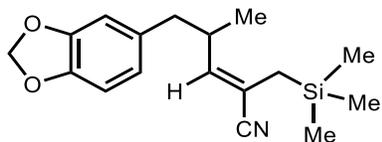
Following the general procedure G, the product **49** was obtained in 43% yield as colorless oil (32.2 mg, 65%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.48; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.19 (t, $J = 7.2$ Hz, 1H), 5.87 (s, 1H), 5.85 (s, 1H), 2.67 (t, $J = 7.3$ Hz, 2H), 2.41 (q, $J = 7.2$ Hz, 2H), 2.25 (s, 3H), 1.66 (s, 2H), 0.11 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 152.3, 151.0, 143.2, 121.2, 112.7, 106.5, 106.1, 27.6, 26.9, 20.5, 13.6, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{21}\text{NOSiNa}$ 270.1284; Found 270.1281.

(*Z*)-4-((tetrahydro-2H-pyran-2-yl)oxy)-2-((trimethylsilyl)methyl)but-2-enitrile (**50**)



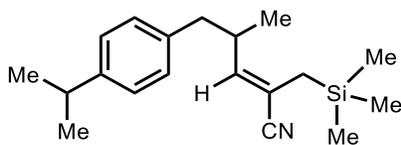
Following the general procedure G, the product **50** was obtained in 35% yield as colorless oil (17.5 mg, 35%) after column chromatography (eluent: from Petroleum ether/DCM 3:1 v/v to Petroleum ether/DCM 2:1 v/v); R_f (PE/DCM = 1:1): 0.56; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.38 – 6.17 (m, 1H), 4.61 (t, $J = 3.4$ Hz, 1H), 4.34 – 4.20 (m, 1H), 4.06 (dd, $J = 14.1, 6.6$ Hz, 1H), 3.83 (ddd, $J = 11.2, 8.4, 3.1$ Hz, 1H), 3.56 – 3.48 (m, 1H), 1.86 – 1.73 (m, 2H), 1.71 (s, 2H), 1.64 – 1.49 (m, 4H), 0.12 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 140.2, 120.5, 114.3, 98.5, 63.1, 62.3, 30.6, 25.5, 21.3, 19.3, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{23}\text{NO}_2\text{SiNa}$ 276.1390; Found 276.1388.

(*Z*)-5-(benzo[d][1,3]dioxol-5-yl)-4-methyl-2-((trimethylsilyl)methyl)pent-2-enitrile (**51**)



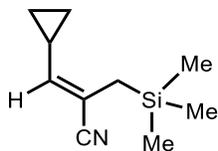
Following the general procedure G, the product **51** was obtained in 48% yield as colorless oil (29.1 mg, 48%) after column chromatography (eluent: from Petroleum ether/DCM 5:1 v/v to Petroleum ether/DCM 2:1 v/v); R_f (PE/DCM = 1:1): 0.58; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.19 (dt, J = 7.8, 3.7 Hz, 2H), 7.12 – 7.05 (m, 3H), 6.11 (t, J = 6.8 Hz, 1H), 2.54 (t, J = 6.6 Hz, 2H), 2.04 – 1.97 (m, 2H), 1.64 (dt, J = 15.8, 7.9 Hz, 2H), 1.53 (s, 2H), -0.01 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.2, 141.5, 133.5, 128.5, 128.5, 126.1, 121.3, 112.3, 35.4, 30.1, 28.2, 20.4, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}_2\text{SiNa}$ 324.1390; Found 324.1388.

(*Z*)-5-(4-isopropylphenyl)-4-methyl-2-((trimethylsilyl)methyl)pent-2-enitrile (**52**)



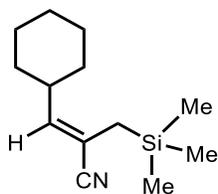
Following the general procedure G, the product **52** was obtained in 75% yield as colorless oil (45.0 mg, 75%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.50; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.14 (d, J = 7.8 Hz, 2H), 7.03 (d, J = 7.8 Hz, 2H), 6.05 (d, J = 9.6 Hz, 1H), 2.88 (hept, J = 7.0 Hz, 1H), 2.68 – 2.51 (m, 3H), 1.60 (s, 2H), 1.23 (d, J = 6.9 Hz, 6H), 1.00 (d, J = 6.3 Hz, 3H), 0.06 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 149.6, 147.1, 136.6, 129.2, 126.5, 121.4, 111.0, 42.3, 35.6, 33.9, 29.8, 24.2, 24.2, 20.0, 19.5, 1.2, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{19}\text{H}_{29}\text{NSiNa}$ 322.1961; Found 322.1963.

(*Z*)-3-cyclopropyl-2-((trimethylsilyl)methyl)acrylonitrile (**53**)



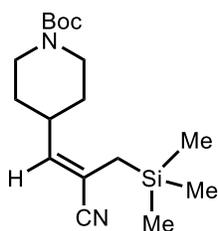
Following the general procedure G, the product **53** was obtained in 79% yield as colorless oil (28.4 mg, 79%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.62; ^1H NMR (400 MHz, Chloroform-*d*) δ 5.54 (d, J = 10.4 Hz, 1H), 1.76 (s, 2H), 1.55 – 1.44 (m, 1H), 0.99 – 0.90 (m, 2H), 0.61 – 0.53 (m, 2H), 0.13 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 148.9, 121.7, 108.8, 20.2, 12.2, 8.7, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{10}\text{H}_{17}\text{NSiNa}$ 202.1022; Found 202.1026.

(*Z*)-3-cyclohexyl-2-((trimethylsilyl)methyl)acrylonitrile (**54**)



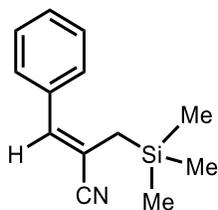
Following the general procedure G, the product **54** was obtained in 25% yield as colorless oil (11.1 mg, 25%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.51; $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 6.01 (d, $J = 10.0$ Hz, 1H), 2.19 (dddt, $J = 14.2, 10.6, 7.3, 3.6$ Hz, 1H), 1.74 (d, $J = 9.7$ Hz, 2H), 1.60 (d, $J = 8.4$ Hz, 2H), 1.33 – 1.20 (m, 3H), 1.18 – 1.07 (m, 3H), 0.12 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 149.9, 121.6, 109.9, 37.8, 31.9, 25.8, 25.5, 20.2, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{23}\text{NSiNa}$ 244.1492; Found 244.1495.

tert-butyl (Z)-4-(2-cyano-3-(trimethylsilyl)prop-1-en-1-yl)piperidine-1-carboxylate (**55**)



Following the general procedure G, the product **55** was obtained in 66% yield as colorless oil (42.8 mg, 66%) after column chromatography (eluent: from Petroleum ether/DCM 5:1 v/v to Petroleum ether/DCM 2:1 v/v); R_f (PE/DCM = 1:1): 0.40; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 5.98 (d, $J = 9.9$ Hz, 1H), 4.23 – 3.94 (m, 2H), 2.77 – 2.69 (m, 2H), 2.37 – 2.31 (m, 1H), 2.06 – 1.92 (m, 1H), 1.69 (s, 2H), 1.59 – 1.56 (m, 1H), 1.46 (s, 9H), 1.34 – 1.27 (m, 2H), 0.13 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 154.8, 147.3, 121.1, 111.5, 79.9, 36.0, 30.8, 29.8, 28.6, 20.5, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{17}\text{H}_{30}\text{N}_2\text{O}_2\text{SiNa}$ 345.1969; Found 345.1967.

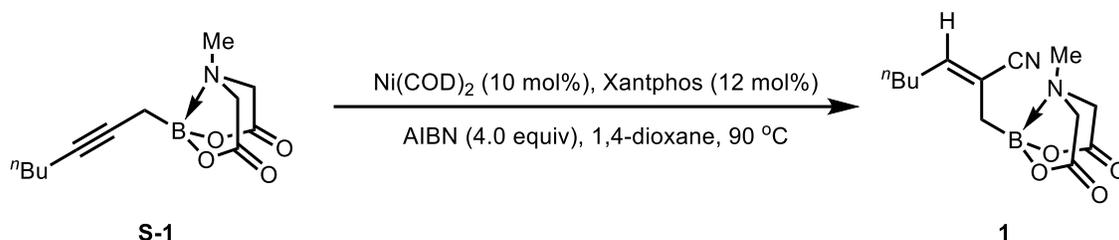
(Z)-3-phenyl-2-((trimethylsilyl)methyl)acrylonitrile (**56**)



Following the general procedure G, the product **56** was obtained in 65% yield as colorless oil (27.8 mg, 65%) after column chromatography (eluent: from Petroleum ether/DCM 10:1 v/v to Petroleum ether/DCM 4:1 v/v); R_f (PE/DCM = 3:1): 0.53; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 7.19 (dt, $J = 7.8, 3.7$ Hz, 2H), 7.12 – 7.05 (m, 3H), 6.11 (t, $J = 6.8$ Hz, 1H), 2.54 (t, $J = 6.6$ Hz, 2H), 2.04 – 1.97 (m, 2H), 1.64 (dt, $J = 15.8, 7.9$ Hz, 2H), 1.53 (s, 2H), -0.01 (s, 9H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 144.2, 141.5, 133.5, 128.5, 128.5, 126.1, 121.3, 112.3, 35.4, 30.1, 28.2, 20.4, -1.4; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{17}\text{NSiNa}$ 238.1022; Found 238.1020.

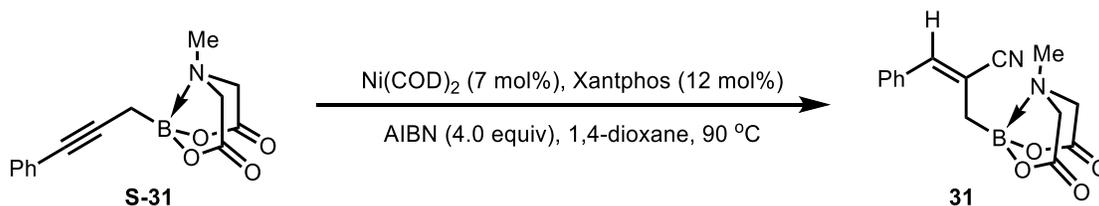
5. Synthetic application

Large-scale preparation of **1**:



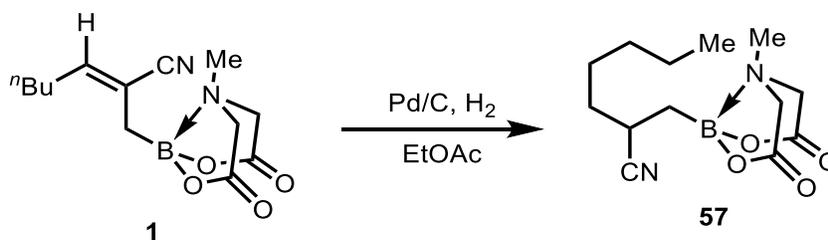
The propargylic MIDA boronates **S-1** (3.0 mmol, 1.0 equiv), AIBN (12.0 mmol, 4.0 equiv), Ni(COD)₂ (0.3 mmol, 10 mol%) and Xantphos (0.36 mmol, 12 mol%) were added to a 75 mL oven-dried pressure tube equipped with a stir bar under nitrogen atmosphere. 1,4-dioxane (30 mL) was added to the tube followed by sealed with a thread plug and then stirred at 90 °C. After the reaction finished, solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent (eluent = Petroleum ether/EtOAc from 1:1 to 1:3 v/v) to afford the pure product **1** as white solid (451 mg, 54%).

Gram-scale preparation of **31**:



The propargylic MIDA boronates **S-31** (5.0 mmol, 1.0 equiv), AIBN (20.0 mmol, 4.0 equiv), Ni(COD)₂ (0.35 mmol, 7 mol%) and Xantphos (0.36 mmol, 12 mol%) were added to a 75 mL oven-dried pressure tube equipped with a stir bar under nitrogen atmosphere. 1,4-dioxane (30 mL) was added to the tube followed by sealed with a thread plug and then stirred at 90 °C. After the reaction finished, solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent (eluent = Petroleum ether/EtOAc from 1:1 to 1:3 v/v) to afford the pure product **31** as white solid. (1.11 g, 74%).

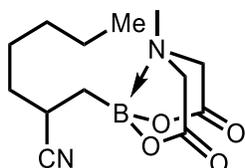
Synthesis of compound **57**:



In a Schlenk tube, MIDA boronate **1** (27.8 mg, 0.1 mmol), Pd/C (10%, w.t, 20 mg) were added. The tube was evacuated and filled with H₂ (three cycles). Then EtOAc (1.0 mL) was added into

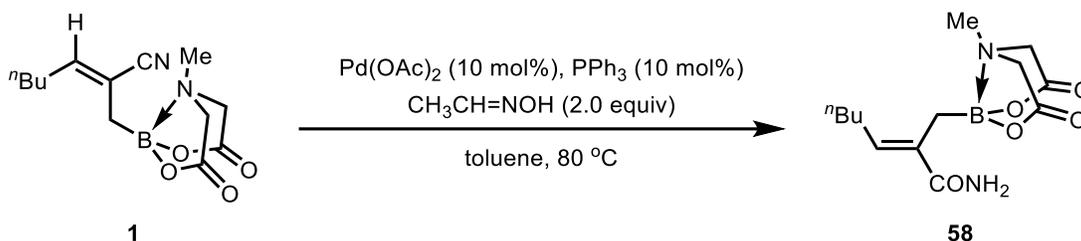
the tube via syringe and the mixture was stirred under balloon pressure of H₂ for 24 h. After the reaction was complete, the mixture was filtered through a short pad of celite and the solvent was removed under reduced pressure. Then the residue was purified by silica gel flash column chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 1:3 v/v) to afford **57** as a white solid (27.9 mg, 99%).

2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)heptanenitrile (**57**)



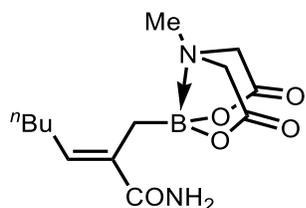
Compound **57** was prepared via above procedure, after purification by silica gel column chromatograph (PE/EA = 1/3 v/v), it obtained as a white solid (27.9 mg, 99%). *R_F* (EtOAc): 0.61; ¹H NMR (500 MHz, Acetone-*d*₆) δ 4.24 (d, *J* = 17.0 Hz, 2H), 4.08 (dd, *J* = 16.7, 11.8 Hz, 2H), 3.15 (s, 2H), 2.74 – 2.64 (m, 1H), 1.76 – 1.65 (m, 1H), 1.63 – 1.50 (m, 2H), 1.49 – 1.39 (m, 1H), 1.39 – 1.27 (m, 4H), 1.08 (ddd, *J* = 87.3, 14.6, 7.4 Hz, 2H), 0.90 (t, 3H); ¹³C NMR (126 MHz, Acetone-*d*₆) δ 168.6, 124.5, 62.7, 46.5, 46.5, 35.0, 32.1, 27.8, 27.6, 23.1, 14.3; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₃H₂₁BN₂O₄Na 303.1486; Found 303.1490.

Synthesis of compound **58**:



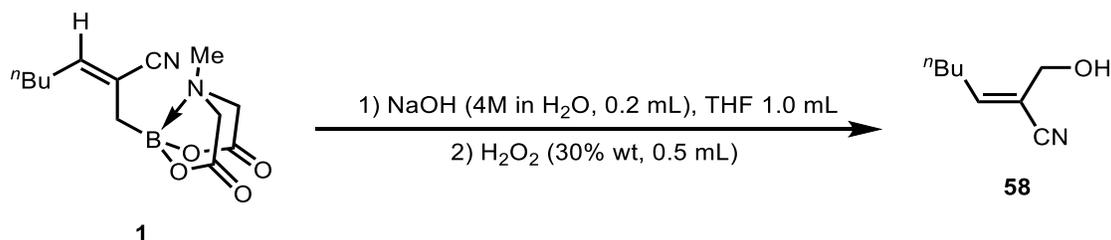
To a mixture of Pd(OAc)₂ (2.0 mg, 0.01 mmol, 10 mol%), PPh₃ (3.6 mg, 0.01 mmol, 10 mol%) in toluene (1.0 mL) was added MIDA boronate **1** (27.8 mg, 0.1 mmol) and CH₃CH=NOH (12 μL, 0.2 mmol, 2.0 equiv). The reaction mixture was stirred at 80 °C until the complete consumption of boronates as monitored by TLC analysis (12 h). The mixture was directly purified by flash chromatography on silica gel with a mixture of MeCN and EtOAc as eluent (eluent = MeCN/EtOAc 1:5 v/v) to afford the pure product **58** (18.6 mg, 63%).

(*E*)-2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)hept-2-enamide (**58**)



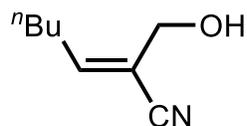
Compound **58** was prepared via above procedure, after purification by silica gel column chromatography (from EA to MeCN/EA = 1/5 v/v), it obtained as a white solid (18.6 mg, 63%). R_F (MeCN/EA = 1/5 v/v): 0.28; $^1\text{H NMR}$ (400 MHz, DMSO- d_6) δ 6.13 (t, J = 7.1 Hz, 1H), 4.14 (d, J = 16.9 Hz, 2H), 3.96 (d, J = 16.9 Hz, 2H), 2.94 (s, 3H), 2.08 (q, J = 7.1 Hz, 2H), 1.70 (s, 2H), 0.89 (t, J = 7.0 Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, DMSO- d_6) δ 171.3, 168.7, 133.6, 133.4, 61.7, 45.6, 30.8, 27.8, 22.0, 13.9; HRMS (ESI) m/z : $[M + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{21}\text{BN}_2\text{O}_5\text{Na}$ 319.1436; Found 319.1434.

Synthesis of compound 59:



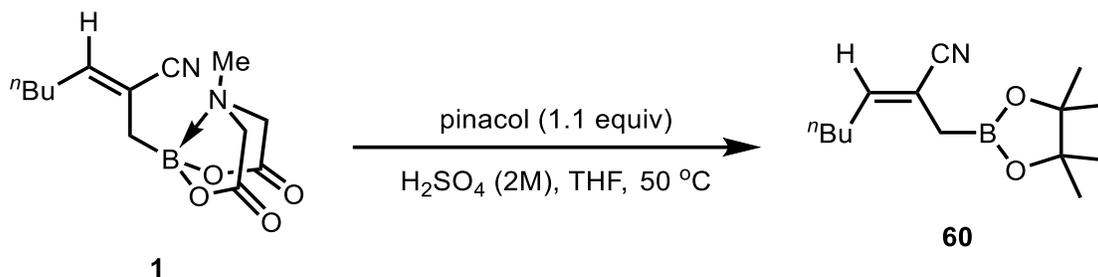
In a Schlenk tube, MIDA boronate **1** (27.8 mg, 0.1 mmol) was added. The tube was evacuated and filled with N_2 (three cycles) and then THF (1.0 mL) was added into the tube via syringe at 0 °C. 4M NaOH aqueous (0.2 mL) was added via syringe at 0 °C monitored by TLC. After the reaction was complete, H_2O_2 (30% wt, 0.5 mL) was added at 0 °C and then stirred at 30 °C for 3 h. Dilute the reaction with water and extracted with DCM for three times. Combine the organic layers and removed the solvent under reduced pressure. Then the residue was purified by silica gel flash column chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 3:1 v/v) to afford **59** as colorless liquid (14.0 mg, 99%).

(*Z*)-2-(hydroxymethyl)hept-2-enitrile (**59**)



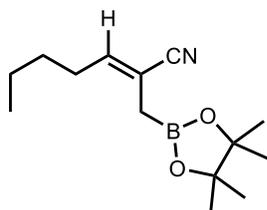
Compound **59** was prepared via above procedure, after purification by silica gel column chromatography (from PE/EA = 5/1 v/v to PE/EA = 3/1 v/v), it was obtained as colorless liquid (14.0 mg, 99%). R_F (PE/EA = 1/1 v/v): 0.48; $^1\text{H NMR}$ (400 MHz, Chloroform- d) δ 6.48 (t, J = 7.8 Hz, 1H), 4.26 (s, 2H), 2.29 – 2.19 (m, 2H), 1.46 – 1.37 (m, 2H), 1.36 – 1.28 (m, 2H), 0.90 (t, J = 7.2 Hz, 3H); $^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 150.8, 119.1, 115.1, 58.0, 30.6, 28.5, 22.4, 13.8; HRMS (ESI) m/z : $[M+\text{Na}]^+$ Calcd for $\text{C}_8\text{H}_{13}\text{NONa}$ 162.0889; Found 162.0890.

Synthesis of compound 60:



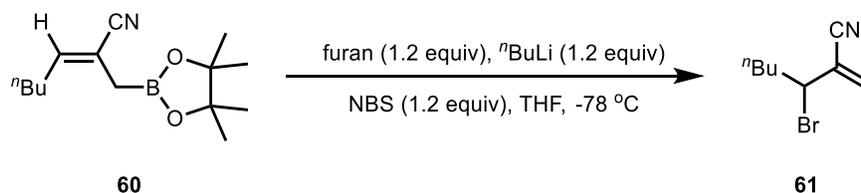
To a stirred solution of **1** (27.8 mg, 0.1 mmol) in THF (1.0 mL) was added 2 M H₂SO₄ (0.1 mL, 2.0 equiv) and pinacol (13 mg, 1.1 equiv) sequentially. The reaction mixture was stirred for 12 h at 50 °C before being quenched by the addition of water (1.0 mL). The mixture was then extracted by diethyl ether (1.0 mL × 3), dried over anhydrous MgSO₄, filtered, and concentrated in vacuo. Then the residue was purified by silica gel flash column chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 5:1 v/v) to afford **60** as colorless liquid (19.1 mg, 77%).

(*E*)-2-((4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)hept-2-enenitrile (**60**)



Compound **60** was prepared via above procedure, after purification by silica gel column chromatography (PE/EA = 5/1 v/v), it was obtained as colorless liquid (19.1 mg, 77%). *R*_F (PE/EA = 5/1 v/v): 0.50; ¹H NMR (400 MHz, Chloroform-*d*) δ 6.28 (t, *J* = 7.5 Hz, 1H), 2.11 (q, *J* = 7.3 Hz, 2H), 1.84 (s, 2H), 1.43 – 1.28 (m, 4H), 1.25 (s, 12H), 0.89 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 147.4, 120.9, 110.4, 84.2, 30.4, 28.5, 24.8, 22.4, 13.9; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₄H₂₄BNO₂Na 272.1792; Found 272.1293.

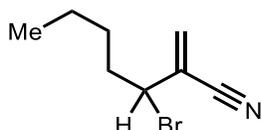
Synthesis of compound 61:



*n*BuLi (2.5 M in hexanes, 0.24 mmol, 1.2 equiv) was added dropwise at –78 °C to a solution of furan (0.24 mmol, 1.2 equiv) in THF (1.0 mL). The cooling bath was removed and the mixture was stirred at room temperature for 1 h. The mixture was cooled to –80 °C and **60** (0.2 mmol, 1.0

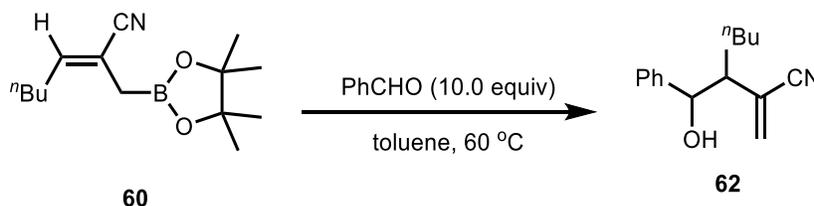
equiv.) was added dropwise as a solution in THF (1.0 mL). The mixture was stirred for 1 hour at $-78\text{ }^{\circ}\text{C}$ and a solution of NBS (0.24 mmol, 1.2 equiv.) in THF (1.0 mL) was added dropwise. After 12 h at $-80\text{ }^{\circ}\text{C}$, a saturated aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ was added and the reaction mixture was allowed to warm to room temperature. After addition of Et_2O and water, the layers were separated and the aqueous layer was extracted with Et_2O (3 \times 5 mL). The combined organic layers were dried over MgSO_4 and concentrated in vacuo. The residue was purified by silica gel flash column chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 50:1 v/v) to afford **61** as colorless liquid (33.1 mg, 82%).

3-bromo-2-methyleneheptanenitrile (**61**)



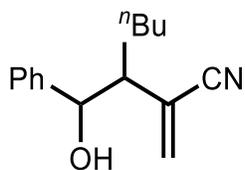
Compound **61** was prepared via above procedure, after purification by silica gel column chromatography (PE/EA = 50/1 v/v), it was obtained as pale yellow liquid (33.1 mg, 82%). R_F (PE/EA = 50/1 v/v): 0.40; $^1\text{H NMR}$ (500 MHz, Chloroform- d) δ 5.87 (d, J = 14.6 Hz, 2H), 4.37 (t, J = 7.5 Hz, 1H), 2.06 – 1.90 (m, 2H), 1.38 – 1.29 (m, 2H), 1.26 – 1.18 (m, 2H), 0.86 (t, J = 6.7 Hz, 3H); $^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 130.8, 125.8, 116.0, 77.4, 50.6, 37.2, 29.8, 21.9, 13.9; GC-MS (EI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_8\text{H}_{13}\text{BrN}$ 202.0226; Found 202.0226.

Synthesis of compound **62**:



To a stirred solution of **60** (49.8 mg, 0.2 mmol) in toluene (2.0 mL) was added PhCHO (212 mg, 10.0 equiv). The reaction mixture was stirred for 12 h at $60\text{ }^{\circ}\text{C}$. Then the mixture was purified by silica gel flash column chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 10:1 v/v) to afford **62** as colorless liquid (21.5 mg, 47%).

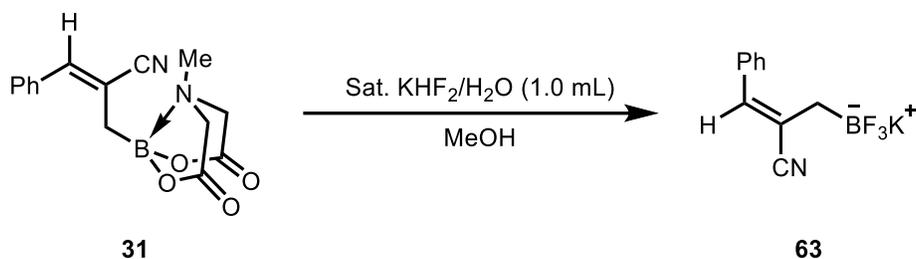
3-(hydroxy(phenyl)methyl)-2-methyleneheptanenitrile (**62**)



Compound **62** was prepared via above procedure, after purification by silica gel column chromatography (PE/EA = 10/1 v/v), it was obtained as colorless liquid (21.5 mg, 47%). R_F (PE/EA

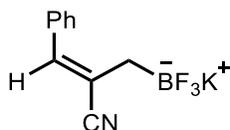
= 10/1 v/v): 0.48; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.35 – 7.25 (m, 3H), 7.24 – 7.13 (m, 2H), 5.65 (s, 1H), 5.36 (s, 1H), 4.61 (d, J = 7.9 Hz, 1H), 2.52 – 2.34 (m, 1H), 2.12 (s, 1H), 1.95 – 1.84 (m, 1H), 1.52 (m, 1H), 1.30 – 1.23 (m, 2H), 1.13 – 1.04 (m, 2H), 0.83 (t, J = 6.8 Hz, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 142.2, 133.0, 128.6, 128.3, 126.6, 123.9, 117.8, 76.5, 53.4, 29.5, 28.5, 22.6, 14.1; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{19}\text{NONa}$ 252.1359; Found 252.1355.

Synthesis of compound 63:



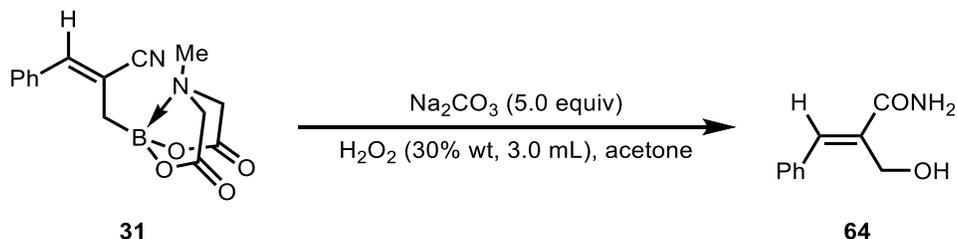
To a stirred solution of **31** (49.6 mg, 0.2 mmol) in MeOH (2.0 mL) was added saturated $\text{KHF}_2/\text{H}_2\text{O}$ (1.0 mL). The reaction was allowed to stirred at 60 °C overnight. After the reaction was completed, solvent was removed under reduced pressure. The crude was resolved in acetone and filtered. Solution was collected and removed solvent under reduced pressure. Product was recrystallization in acetone/ Et_2O to afford **63** as white solid (36.5 mg, 73%).

potassium (*E*)-(2-cyano-3-phenylallyl)trifluoroborate (**63**)



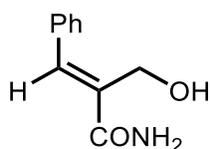
Compound **63** was prepared via above procedure and obtained as white solid (36.5 mg, 73%); ^1H NMR (400 MHz, Acetone- d_6) δ 7.62 (d, J = 7.4 Hz, 2H), 7.41 – 7.17 (m, 3H), 6.88 (s, 1H), 1.55 (s, 2H); ^{13}C NMR (101 MHz, Acetone) δ 138.3, 136.7, 130.1, 128.7, 128.4, 123.8, 120.3; ^{11}B NMR (128 MHz, Acetone- d_6) δ 3.81 (q, J = 61.5, 59.7 Hz); ^{19}F NMR (376 MHz, Acetone- d_6) δ -134.28 – -142.65 (m); HRMS (ESI) m/z : $[\text{M}-\text{K}]^-$ Calcd for $\text{C}_{10}\text{H}_8\text{BF}_3\text{N}$ 210.0707; Found 210.0703.

Synthesis of compound 64:



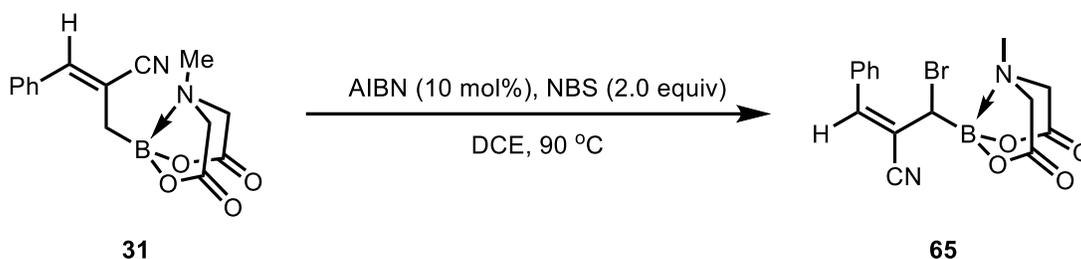
To a stirred solution of **31** (49.6 mg, 0.2 mmol) in acetone (1.5 mL) was added NaCO₃ (106 mg, 5.0 equiv). The reaction mixture was stirred at 0 °C and then H₂O₂ (30% wt, 0.5 mL) was added. The reaction was monitored by TLC and after the reaction was completed, the mixture was quenched with NH₄Cl and extracted with EtOAc for three times. The organic layers were combined and solvent was removed under reduced pressure. The crude was purified by chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 1:3 v/v) to afford **64** as colorless liquid (14.3 mg, 40%).

(*E*)-2-(hydroxymethyl)-3-phenylacrylamide (**64**)



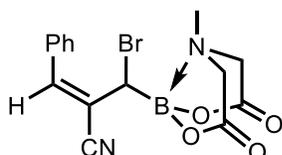
Compound **64** was prepared via above procedure and obtained as semi solid (14.0 mg, 40%); ¹H NMR (400 MHz, DMSO-*d*₆) δ 7.40 (ddd, *J* = 33.0, 18.7, 7.1 Hz, 7H), 7.13 (s, 1H), 4.25 (s, 2H); ¹³C NMR (101 MHz, DMSO) δ 169.8, 135.8, 135.7, 135.4, 129.3, 128.4, 128.3, 56.0; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₀H₁₁NO₂Na 200.0682; Found 200.0679.

Synthesis of compound **65**:



To a stirred solution of **31** (29.8 mg, 0.1 mmol) and AIBN (1.6 mg, 10 mol%) in DCE (0.5 mL) was added solution of NBS (37.8 mg, 2.0 equiv) in DCE (0.5 mL). The reaction was stirred at 90 °C for 8h. After the reaction was completed, solvent was removed under reduced pressure. The crude was purified by chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 1:3 v/v) to afford **65** as white solid (28.9 mg, 77%).

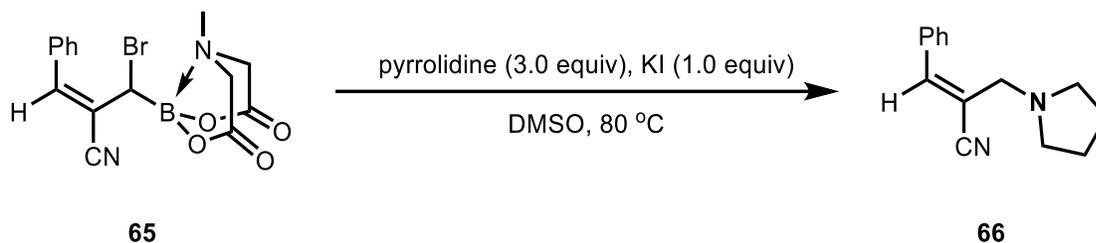
2-(bromo(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)methyl)-3-phenylacrylonitrile (**65**)



Compound **65** was prepared via above procedure and obtained as white solid (28.9 mg, 77%); ¹H NMR (500 MHz, DMSO-*d*₆) δ 7.78 (dd, *J* = 7.1, 2.3 Hz, 2H), 7.54 – 7.48 (m, 4H), 4.72 (s, 1H), 4.49

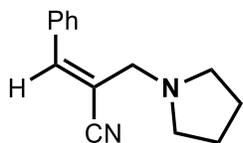
(d, $J = 17.4$ Hz, 1H), 4.31 (d, $J = 17.1$ Hz, 1H), 4.12 (dd, $J = 17.2, 5.3$ Hz, 2H), 3.10 (s, 3H); ^{13}C NMR (126 MHz, DMSO- d_6) δ 168.3, 168.2, 145.7, 132.9, 131.0, 129.2, 128.9, 117.3, 111.6, 63.2, 62.9, 46.2, 39.5; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{15}\text{H}_{14}\text{BBrN}_2\text{O}_4\text{Na}$ 399.0122; Found 399.0123.

Synthesis of compound 66:



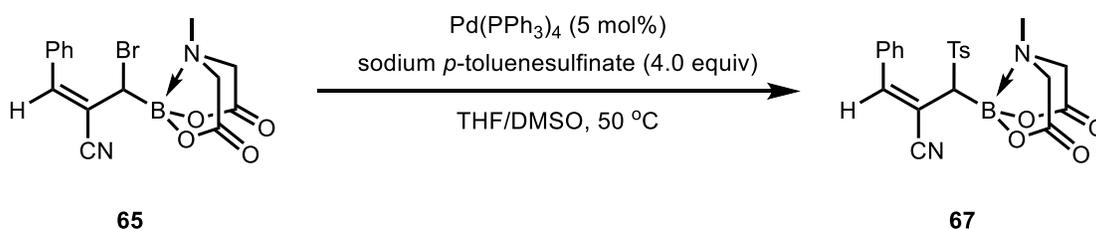
To a stirred solution of **65** (37.6 mg, 0.1 mmol) and KI (16.6 mg, 1.0 equiv) in DMSO (1.0 mL) was added pyrrolidine (24.5 μL , 3.0 equiv). The reaction was stirred at 80 $^\circ\text{C}$ for 12h. After the reaction was completed, the mixture was quenched with NaCl (aq.) then extracted with EtOAc for three time. Solvent was removed under reduced pressure and the giving crude was purified by chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 1:3 v/v) to afford **66** as white solid (12.6 mg, 59%).

3-phenyl-2-(pyrrolidin-1-ylmethyl)acrylonitrile (**66**)



Compound **66** was prepared via above procedure and obtained as colorless liquid (12.6 mg, 59%); ^1H NMR (400 MHz, Chloroform- d) δ 7.80 – 7.70 (m, 2H), 7.52 – 7.38 (m, 3H), 7.27 – 7.24 (m, 1H), 3.48 (s, 2H), 2.89 – 2.51 (m, 4H), 1.99 – 1.76 (m, 4H); ^{13}C NMR (101 MHz, CDCl_3) δ 133.3, 130.7, 129.2, 129.0, 118.9, 59.7, 53.8, 23.7; HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{17}\text{N}_2$ 213.1386; Found 213.1390.

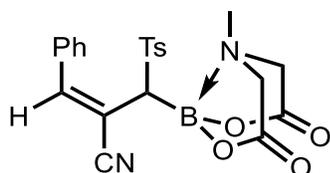
Synthesis of compound 67:



In a Schlenk tube, MIDA boronate **65** (27.0 mg), Pd (PPh_3) $_4$ (8.3 mg, 5 mol%) and sodium *p*-toluenesulfonate (71.3 mg, 5.5 equiv) was added. The tube was evacuated and filled with N_2

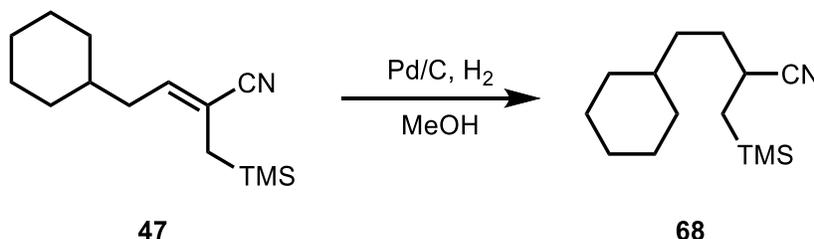
(three cycles) and then THF (2.0 mL) and DMSO (0.3 mL) were added into the tube. The reaction was stirred at 50 °C and monitored by TLC. After the reaction was complete, solvent was removed under reduced pressure. Then the residue was purified by silica gel flash column chromatography with a mixture of Petroleum ether and EtOAc as eluent (eluent = Petroleum ether/EtOAc 1:3 v/v) to afford **67** as white solid (18.2 mg, 56%).

2-((6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)(tosyl)methyl)-3-phenylacrylonitrile (**67**)



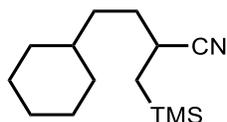
Compound **67** was prepared via above procedure and obtained as white solid (18.3 mg, 56%); ¹H NMR (400 MHz, Acetone-*d*₆) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.61 (dd, *J* = 6.3, 3.0 Hz, 2H), 7.48 – 7.36 (m, 5H), 7.08 (s, 1H), 4.53 (d, *J* = 17.4 Hz, 1H), 4.37 (s, 2H), 4.26 (d, *J* = 17.3 Hz, 2H), 3.60 (s, 3H), 2.43 (s, 3H); ¹³C NMR (101 MHz, Acetone-*d*₆) δ 168.3, 167.6, 150.7, 145.7, 137.2, 134.4, 131.3, 130.4, 129.6, 129.5, 118.2, 105.6, 64.7, 63.5, 47.8, 21.4; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₂₂H₂₁BN₂O₆SNa 475.1106; Found 475.1102.

Synthesis of compound 68:



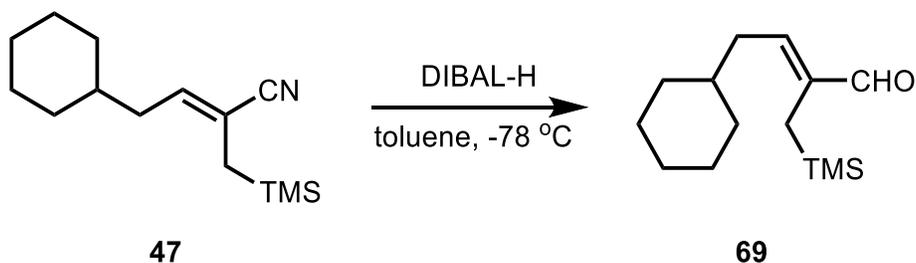
In a Schlenk tube, **47** (23.5 mg, 0.1 mmol), Pd/C (10%, w.t, 20 mg) were added. The tube was evacuated and filled with H₂ (three cycles). Then MeOH (1.0 mL) was added into the tube via syringe and the mixture was stirred under balloon pressure of H₂ for 24 h. After the reaction was complete, the mixture was filtered through a short pad of celite and the solvent was removed under reduced pressure. Then the residue was purified by silica gel flash column chromatography with a mixture of Petroleum ether and DCM as eluent (eluent = Petroleum ether/DCM 5:1 v/v) to afford **68** as colorless oil (21.7 mg, 92%).

4-cyclohexyl-2-((trimethylsilyl)methyl)butanenitrile (**68**)



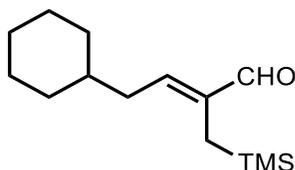
Compound **68** was prepared via above procedure and obtained as colorless oil (21.7 mg, 92%); ^1H NMR (500 MHz, Chloroform-*d*) δ 2.61 – 2.44 (m, 1H), 1.69 (d, J = 11.9 Hz, 2H), 1.63 – 1.52 (m, 2H), 1.23 – 1.10 (m, 4H), 1.03 – 0.75 (m, 6H), 0.10 (s, 9H); ^{13}C NMR (126 MHz, CDCl_3) δ 123.7, 37.5, 34.8, 33.5, 33.5, 33.2, 27.5, 26.7, 26.4, 20.6, -1.1; GC-MS (EI) m/z : $[\text{M} - \text{H}]^+$ Calcd for $\text{C}_{14}\text{H}_{26}\text{NSi}$ 236.1829; Found 236.1829.

Synthesis of compound 69:



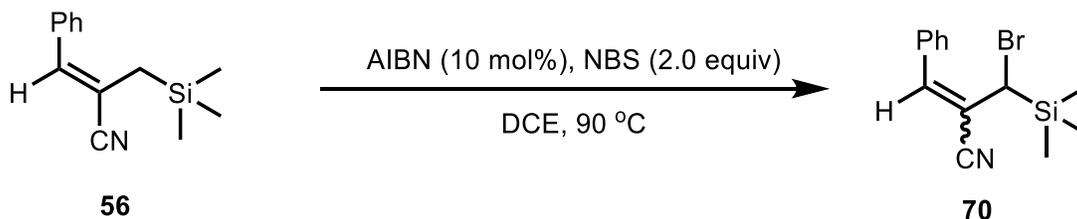
In a Schlenk tube, **47** (47 mg, 0.2 mmol), toluene was added under Ar atmosphere. The tube was cooled to $-78\text{ }^\circ\text{C}$ and then DIBAL-H (1 M, 0.4 mL) was added into the tube dropwise via syringe. After the reaction was complete, the mixture was quenched with water under $-78\text{ }^\circ\text{C}$ and extract with EtOAc for three times. Organic layers were combined and dry with Solvent was removed under reduced pressure and the giving crude was purified by silica gel flash column chromatography with a mixture of Petroleum ether and DCM as eluent (eluent = Petroleum ether/DCM 5:1 v/v) to afford **69** as colorless oil (32.9 mg, 69%).

(*Z*)-4-cyclohexyl-2-((trimethylsilyl)methyl)but-2-enal (**69**)



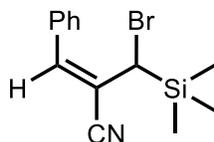
Compound **69** was prepared via above procedure and obtained as colorless oil (32.9 mg, 69%); ^1H NMR (400 MHz, Chloroform-*d*) δ 9.33 (s, 1H), 6.36 (t, J = 7.3 Hz, 1H), 2.17 (t, J = 7.1 Hz, 2H), 1.76 – 1.70 (m, 6H), 1.28 – 1.25 (s, 4H), 1.07 – 0.80 (m, 3H), -0.03 (s, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.2, 150.9, 142.6, 38.1, 37.3, 33.4, 29.8, 26.5, 26.4, 14.9, -0.8; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{14}\text{H}_{26}\text{OSiNa}$ 261.1645; Found 261.1648.

Synthesis of compound 70:



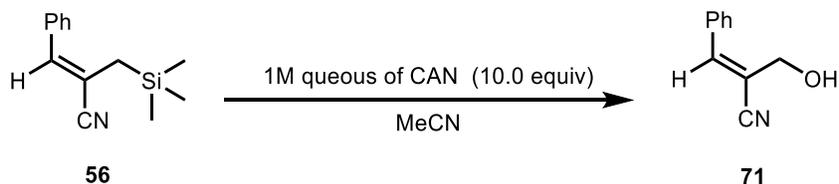
To a tube with NBS (37.8 mg, 2.0 equiv) AIBN (16.4 mg, 1.0 equiv) inside was added **56** (21.5 mg, 0.1 mmol) in DCE (1.0 mL). The reaction was stirred at 90 °C for 16h. After the reaction was completed, solvent was removed under reduced pressure. The crude was purified by chromatography with a mixture of Petroleum ether and DCM as eluent (eluent = Petroleum ether/DCM 5:1 v/v) to afford **70** as semi solid (15.2 mg, 52%).

2-(bromo(trimethylsilyl)methyl)-3-phenylacrylonitrile (**70**)



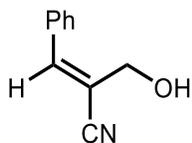
Compound **70** was prepared via above procedure and obtained as colorless oil (15.2 mg, 52%); ^1H NMR (500 MHz, Chloroform-*d*) δ 7.78 – 7.72 (m, 2H), 7.43 (dtd, $J = 6.8, 5.2, 2.7$ Hz, 3H), 7.13 (d, $J = 4.6$ Hz, 1H), 3.99 (d, $J = 14.6$ Hz, 1H), 0.28 (d, $J = 11.4$ Hz, 9H); ^{13}C NMR (101 MHz, CDCl_3) δ 144.3, 143.6, 133.1, 130.8, 130.7, 129.4, 129.1, 129.1, 128.9, 128.3, 117.5, 51.9, 42.2, -2.4, -3.0; GC-MS (EI) m/z : $[\text{M} - \text{e}]^+$ Calcd for $\text{C}_{13}\text{H}_{16}\text{BrNSi}$ 293.0230; Found 293.0230.

Synthesis of compound **71**:



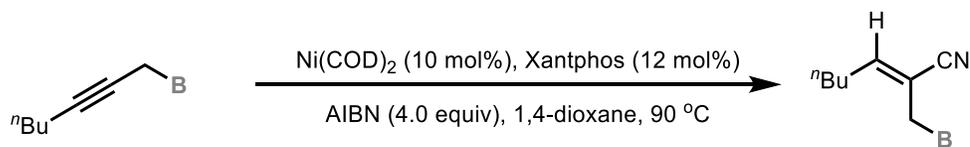
To a solution of **56** (21.5 mg, 0.1 mmol) in MeCN (1.0 mL) was added aqueous CAN (1M, 1.0 mL). The reaction was stirred at room temperature for 18h. After the reaction was completed, solution was diluted with EA. The organic layer was separated and the aqueous layer was extracted with EtOAc for three time. The organic layers was combined and solvent was removed under reduced pressure. The crude was purified by chromatography with a mixture of Petroleum ether and DCM as eluent (eluent = Petroleum ether/DCM 3:1 v/v) to afford **71** as yellow oil (10.2 mg, 64%).

(Z)-2-(hydroxymethyl)-3-phenylacrylonitrile (**71**)



Compound **71** was prepared via above procedure and obtained as colorless oil (10.2 mg, 64%), the spectra data was consistent with reported literature;

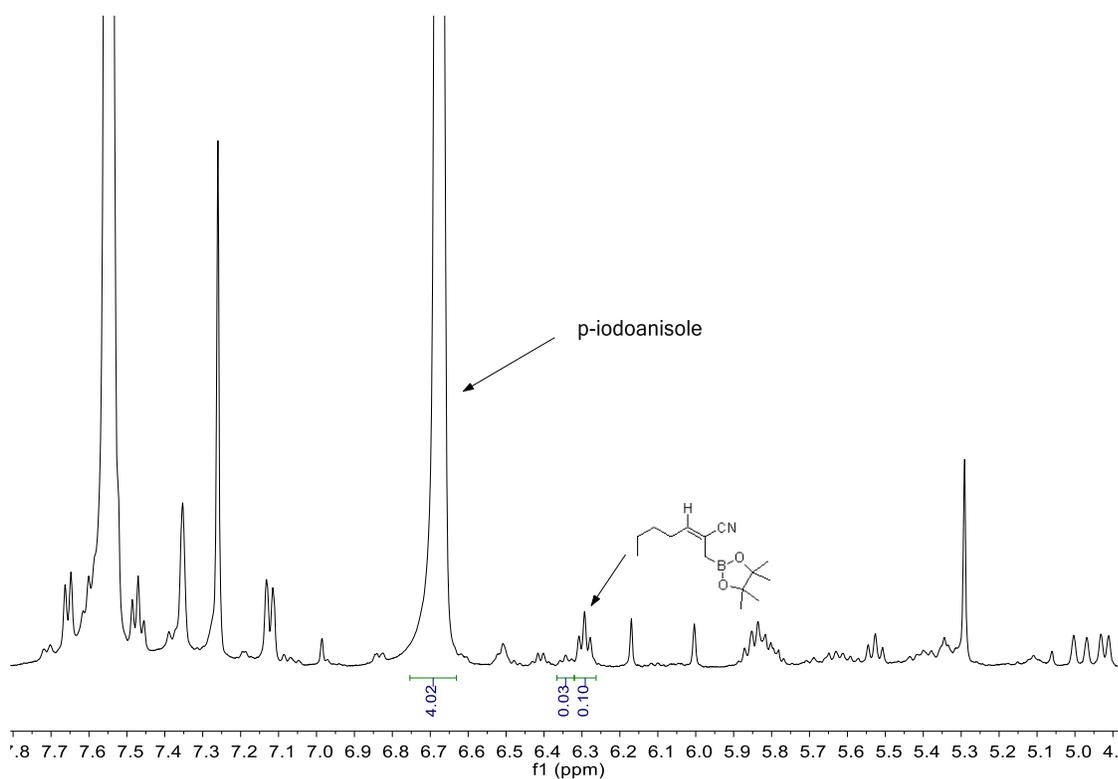
6. Control experiment

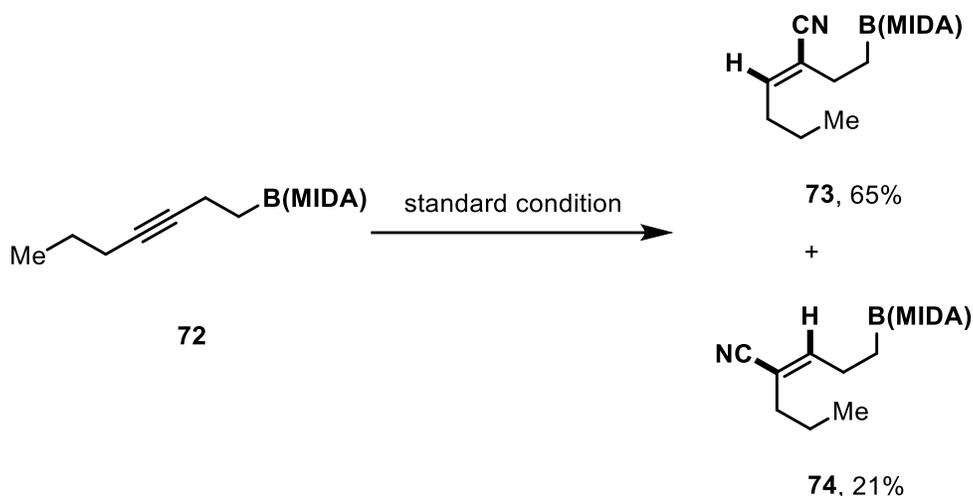


B = Bpin, BF_3K

B = Bpin, 10%, r.r. = 3.3 :1
B = BF_3K , NR

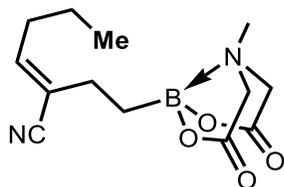
The propargylic boron substrates (0.1 mmol, 1.0 equiv), AIBN (0.4 mmol, 4.0 equiv), Ni(COD)_2 (0.01 mmol, 10 mol%) and Xantphos (0.012 mmol, 12 mol%) were added to a 15 mL oven-dried pressure tube equipped with a stir bar under nitrogen atmosphere. 1,4-dioxane (1.0 mL) was added to the tube followed by sealed with a thread plug and then stirred at 90 °C. After the reaction finished, solvent was removed under reduced pressure. *p*-iodoanisole (46.8 mg, 0.2 mmol) was added as internal standard was yields were determined by $^1\text{H NMR}$.





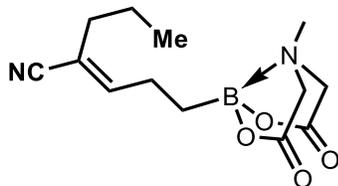
The homo-propargylic boronates **72** (0.1 mmol, 1.0 equiv), AIBN (0.4 mmol, 4.0 equiv), Ni(COD)₂ (0.01 mmol, 10 mol%) and Xantphos (0.012 mmol, 12 mol%) were added to a 15 mL oven-dried pressure tube equipped with a stir bar under nitrogen atmosphere. 1,4-dioxane (1.0 mL) was added to the tube followed by sealed with a thread plug and then stirred at 90 °C. After the reaction finished, solvent was removed under reduced pressure. The residues were purified by flash column chromatography on silica with an appropriate solvent (eluent = Petroleum ether/EtOAc from 1:1 to 1:3 v/v) to afford the pure product as semi solid. **73** and **74** was respectively obtained in 65% and 21% yields.

(*E*)-2-(2-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)ethyl)hex-2-enenitrile (**73**)



Compound **73** was prepared via above procedure and obtained as white solid (18.2 mg, 65%); ¹H NMR (400 MHz, Acetone-*d*₆) δ 6.30 (t, *J* = 7.5 Hz, 1H), 4.23 (d, *J* = 16.9 Hz, 2H), 4.09 (d, *J* = 16.9 Hz, 2H), 3.15 (s, 3H), 2.32 – 2.25 (m, 3H), 2.22 (q, *J* = 7.5 Hz, 2H), 1.47 (h, *J* = 7.3 Hz, 2H), 0.93 (t, *J* = 7.4 Hz, 3H), 0.89 – 0.81 (m, 3H).; ¹³C NMR (126 MHz, Acetone-*d*₆) δ 168.7, 146.9, 120.7, 118.7, 62.8, 46.3, 30.7, 24.2, 22.3, 13.9; HRMS (ESI) *m/z*: [M + Na]⁺ Calcd for C₁₃H₁₉BN₂O₄Na 301.1330; Found 301.1332.

(*E*)-5-(6-methyl-4,8-dioxo-1,3,6,2-dioxazaborocan-2-yl)-2-propylpent-2-enenitrile (**74**)



Compound **74** was prepared via above procedure and obtained as white solid (5.9 mg, 21%); ^1H NMR (400 MHz, Acetone- d_6) δ 6.46 (t, J = 7.6 Hz, 1H), 4.21 (d, J = 16.9 Hz, 2H), 4.05 (d, J = 16.9 Hz, 2H), 3.12 (s, 3H), 2.25 (dt, J = 10.0, 8.0 Hz, 4H), 1.55 (h, J = 7.4 Hz, 3H), 0.94 (t, J = 7.4 Hz, 3H), 0.80 – 0.73 (m, 2H); ^{13}C NMR (126 MHz, Acetone- d_6) δ 168.7, 151.6, 120.7, 114.0, 62.7, 46.3, 30.7, 24.0, 22.0, 13.5; HRMS (ESI) m/z : $[\text{M} + \text{Na}]^+$ Calcd for $\text{C}_{13}\text{H}_{19}\text{BN}_2\text{O}_4\text{Na}$ 301.1330; Found 301.1333.

7. Computational Studies

The DFT calculations were performed by Gaussian 09 programs³. Geometry optimizations and frequency analyses were performed at the level of the B3LYP functional⁴ and a standard 6-31G(d) basis set (Lanl2dz⁵ for Ni) in gas phase. Single point energies were further refined at the M06 functional⁶ and a standard 6-311++G(d,p) basis set (SDD⁷ for Ni) level using SMD⁸ solvation model (solvent = 1,4-dioxane). Throughout the paper, the energies presented are the M06-calculated Gibbs free energies in the 1,4-dioxane solvent with B3LYP-calculated thermodynamic corrections.

Cartesian Coordinates and Energies of the Optimized Structures

alkyne

Zero-point correction = 0.299056 (Hartree/Particle)
 Thermal correction to Energy = 0.317552
 Thermal correction to Enthalpy = 0.318496
 Thermal correction to Gibbs Free Energy = 0.249463
 Sum of electronic and zero-point Energies = -848.393514
 Sum of electronic and thermal Energies = -848.375018
 Sum of electronic and thermal Enthalpies = -848.374073
 Sum of electronic and thermal Free Energies = -848.443106

SCF Done: E(RM06) = -848.405688679

O	1.89091800	-1.88098700	-7.96107900
O	1.72237600	-3.83379800	-9.09529600
O	-1.59596200	0.95236700	-8.66132500
O	0.42414000	0.06151300	-8.15932900
N	-0.32864000	-1.87408100	-6.92479300
C	1.24327400	-2.94739400	-8.43610800

C	1.76296800	-0.28398600	-5.97159000
C	-0.23574600	-2.88761300	-8.02389300
C	-0.90368900	0.15494400	-8.08085600
C	-0.33407900	-2.53153300	-5.58976300
C	-1.44862500	-0.91029300	-7.11596000
B	1.03917000	-0.92691000	-7.25709000
H	2.24786500	-1.06681100	-5.37115400
H	2.58312800	0.33692900	-6.36069100
H	-0.82454400	-2.55613800	-8.88372700
H	-0.60429300	-3.86427600	-7.70415400
H	-1.24016400	-3.13427600	-5.47448600
H	-0.29208600	-1.76138200	-4.81860500
H	0.54400500	-3.17628300	-5.50864000
H	-1.66579400	-0.43135300	-6.15856800
H	-2.35161900	-1.39040700	-7.49988700
C	0.88790200	0.53475000	-5.13068800
C	0.16192200	1.21782500	-4.43942400
C	-0.69867400	2.08933200	-3.63320900
H	-0.12051900	2.49723800	-2.79143300
H	-1.50875600	1.49945400	-3.17916500
C	-1.31123100	3.25530400	-4.43921500
H	-0.49934500	3.84974600	-4.87719000
H	-1.88225300	2.84877200	-5.28437000
C	-2.21283900	4.15230200	-3.58326100
H	-1.63315900	4.54787400	-2.73696000
H	-3.01740800	3.54513100	-3.14355400
C	-2.82308400	5.31452100	-4.37325700
H	-3.46520100	5.93475500	-3.73774600
H	-2.04296600	5.96146200	-4.79209800
H	-3.43207500	4.94889400	-5.20877500

L*Ni_HCN

Zero-point correction = 0.615292 (Hartree/Particle)

Thermal correction to Energy = 0.655166

Thermal correction to Enthalpy = 0.656110

Thermal correction to Gibbs Free Energy = 0.540550

Sum of electronic and zero-point Energies = -2525.485266

Sum of electronic and thermal Energies = -2525.445391

Sum of electronic and thermal Enthalpies = -2525.444447

Sum of electronic and thermal Free Energies = -2525.560008

SCF Done: E(RM06) = -2526.95225183

C	-2.81790300	0.63413000	1.68803200
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C	-1.68437400	-0.11669200	1.33775800
C	-0.46497300	0.23278200	1.94152600
C	-0.35458400	1.27054400	2.87986900
C	-1.50797000	1.99282100	3.19420200
C	-2.73283800	1.68011600	2.60268900
H	-3.77106500	0.40463700	1.22201200
H	-1.45793900	2.80884000	3.90687800
H	-3.61945800	2.25477200	2.85458800
C	1.02049700	1.50303800	3.51532900
C	2.05438600	1.32109800	2.39865700
C	1.83804100	0.28108800	1.48140200
C	3.21031700	2.09129700	2.25325500
C	2.74562300	-0.02387500	0.45309200
C	4.12662900	1.82296100	1.23529000
H	3.40426000	2.90984400	2.93778800
C	3.89621300	0.77425500	0.34922300
H	5.01871000	2.43411500	1.13310000
H	4.60639000	0.58010200	-0.44834200
O	0.67779400	-0.46818500	1.59133500
C	1.12552000	2.88233500	4.18578200
H	0.96518900	3.69893500	3.47352900
H	0.39075500	2.97658900	4.99131100
H	2.10954200	3.01302200	4.64637000
C	1.25958600	0.41004200	4.59788100
H	2.25298000	0.53170100	5.04457700
H	0.50850900	0.49444400	5.39153500
H	1.19643200	-0.59550000	4.17268900
P	2.42173100	-1.39934400	-0.74322500
P	-1.78832900	-1.48846200	0.09877700
C	0.36344900	-3.72318800	-0.32912900
N	0.40552900	-4.89018000	-0.24135000
Ni	0.26508900	-1.85988100	-0.62627600
C	-2.67712600	-2.83596700	0.99120700
C	-2.80279900	-4.07556100	0.34190000
C	-3.22579900	-2.68144400	2.27294300
C	-3.48389300	-5.12651100	0.95360100
H	-2.34086100	-4.23107800	-0.62666800
C	-3.89863100	-3.74090200	2.88654800
H	-3.13108200	-1.73821100	2.80005000
C	-4.03379500	-4.96252400	2.22694800
H	-3.56464900	-6.08080300	0.44101800
H	-4.31390400	-3.60755100	3.88215200
H	-4.55488200	-5.78689600	2.70664500
C	-3.04275000	-0.87915800	-1.11375600

C	-4.40280900	-1.21365800	-1.01769800
C	-2.62059500	-0.05257400	-2.16738100
C	-5.32014400	-0.72069200	-1.94848200
H	-4.74612100	-1.86568900	-0.22110200
C	-3.54005700	0.44276500	-3.09157700
H	-1.56743900	0.19417200	-2.25835700
C	-4.89238800	0.10992300	-2.98497800
H	-6.36935500	-0.99091300	-1.86285800
H	-3.19773400	1.08145700	-3.90157600
H	-5.60707100	0.48960700	-3.71033600
C	3.63867400	-2.70356500	-0.27449900
C	3.55616200	-3.93923800	-0.93800500
C	4.62760100	-2.52154500	0.70334900
C	4.45942100	-4.95913700	-0.64469700
H	2.76701200	-4.11680600	-1.66001700
C	5.52490100	-3.55016300	1.00117800
H	4.70219200	-1.58097100	1.23819300
C	5.44612800	-4.76778300	0.32519600
H	4.37618600	-5.91133300	-1.16077800
H	6.28294500	-3.39625800	1.76481300
H	6.14254900	-5.56834300	0.56042500
C	3.08689800	-0.75323900	-2.34184800
C	2.24391700	0.00306000	-3.17153900
C	4.40588100	-0.99748400	-2.75676800
C	2.71503400	0.51860600	-4.37889900
H	1.21723600	0.17755600	-2.86554900
C	4.87285100	-0.48432700	-3.96869300
H	5.06740900	-1.59563300	-2.13829000
C	4.03040500	0.27625100	-4.78088200
H	2.05016600	1.10137800	-5.01097300
H	5.89527100	-0.68438800	-4.27823500
H	4.39404400	0.67106500	-5.72585700
H	0.15710600	-0.40301700	-1.01563100

Ni_Xantphos

Zero-point correction = 0.598004 (Hartree/Particle)

Thermal correction to Energy = 0.635532

Thermal correction to Enthalpy = 0.636476

Thermal correction to Gibbs Free Energy = 0.524828

Sum of electronic and zero-point Energies = -2432.044976

Sum of electronic and thermal Energies = -2432.007448

Sum of electronic and thermal Enthalpies = -2432.006504

Sum of electronic and thermal Free Energies = -2432.118152

SCF Done: E(RM06) = -2433.52017227

C	-3.44047800	0.84844800	0.73280300
C	-2.21999400	0.15759300	0.68470200
C	-1.17119800	0.65850600	1.47676200
C	-1.29531600	1.79275400	2.28991100
C	-2.52694800	2.45509600	2.29430700
C	-3.59224300	1.98601600	1.52486400
H	-4.27210900	0.50122000	0.12843200
H	-2.66386700	3.34232800	2.90324800
H	-4.54339000	2.51095100	1.54120400
C	-0.08724600	2.18431200	3.15127200
C	1.17204500	1.91437400	2.31684400
C	1.17690600	0.77584100	1.49955300
C	2.33182600	2.69487200	2.34782800
C	2.28373200	0.38773100	0.72345700
C	3.45336400	2.33679600	1.59889900
H	2.36909800	3.58907200	2.96124000
C	3.42890900	1.19555300	0.79837600
H	4.34774600	2.95257300	1.63649100
H	4.30120900	0.93746500	0.20684600
O	0.03958200	-0.00651000	1.44079600
C	-0.16434900	3.64543600	3.62379000
H	-0.18838300	4.34633800	2.78244000
H	-1.05761300	3.80805100	4.23478900
H	0.69411400	3.89306800	4.25571100
C	-0.05592000	1.26098200	4.40388600
H	0.81824800	1.49239600	5.02349900
H	-0.95951500	1.40937500	5.00645000
H	-0.00388200	0.20620700	4.11880400
P	2.15421200	-1.08994900	-0.40412000
P	-1.92133900	-1.31365900	-0.41723100
Ni	0.12692500	-1.35385900	-1.01296500
C	-2.41809100	-2.74316900	0.65372900
C	-1.98406200	-4.02218100	0.26699600
C	-3.18893800	-2.61834700	1.81922900
C	-2.32689800	-5.14839600	1.01479700
H	-1.36542400	-4.12582400	-0.62102000
C	-3.52354800	-3.74570300	2.57397000
H	-3.52747300	-1.63851900	2.14285600
C	-3.09700700	-5.01249300	2.17258000
H	-1.98386100	-6.13058700	0.69985700
H	-4.11838000	-3.63156600	3.47680300
H	-3.35707100	-5.88824100	2.76147500

C	-3.33294200	-1.19331200	-1.61707500
C	-4.59359800	-1.77692000	-1.41944600
C	-3.09200100	-0.49835000	-2.81384700
C	-5.59100100	-1.65764400	-2.39069100
H	-4.79665000	-2.33174000	-0.50822800
C	-4.09124900	-0.36928700	-3.77828700
H	-2.10790400	-0.06839500	-2.98643300
C	-5.34419400	-0.95119700	-3.56922300
H	-6.56132300	-2.11933300	-2.22544800
H	-3.88824900	0.17393600	-4.69770200
H	-6.12073700	-0.86163300	-4.32444000
C	2.81105900	-2.47392900	0.63876600
C	2.51187900	-3.78568700	0.23434500
C	3.57482200	-2.28547800	1.80025300
C	2.97905700	-4.88046700	0.96121500
H	1.89957700	-3.94017500	-0.65070700
C	4.03404300	-3.38222800	2.53415400
H	3.80961100	-1.27990300	2.13625800
C	3.74064200	-4.68093900	2.11539100
H	2.73962200	-5.88864900	0.63291700
H	4.62137000	-3.21960600	3.43446800
H	4.09759000	-5.53286100	2.68827200
C	3.54175900	-0.78001700	-1.59813500
C	3.22892600	-0.05684700	-2.76124400
C	4.85374900	-1.24746500	-1.42824500
C	4.20665900	0.21374800	-3.71810600
H	2.20721500	0.28379400	-2.91372100
C	5.83054600	-0.98678600	-2.39302100
H	5.11425200	-1.82140800	-0.54382500
C	5.51127500	-0.25274800	-3.53655300
H	3.94803300	0.77750400	-4.61082300
H	6.84173600	-1.35946300	-2.24953700
H	6.27208600	-0.05227300	-4.28647000

INT-1

Zero-point correction = 0.916378 (Hartree/Particle)

Thermal correction to Energy = 0.976389

Thermal correction to Enthalpy = 0.977333

Thermal correction to Gibbs Free Energy = 0.817895

Sum of electronic and zero-point Energies = -3373.871647

Sum of electronic and thermal Energies = -3373.811636

Sum of electronic and thermal Enthalpies = -3373.810692

Sum of electronic and thermal Free Energies = -3373.970130

SCF Done: E(RM06) = -3375.37687045

C	-3.45145300	1.23305400	0.65226300
C	-2.27132800	0.48289600	0.57484400
C	-1.20975600	0.86607600	1.40785200
C	-1.27604100	1.93246400	2.30907200
C	-2.46864600	2.66459900	2.34487800
C	-3.54338400	2.31992100	1.52396600
H	-4.29443600	0.97518900	0.02035200
H	-2.56829700	3.50904400	3.01893200
H	-4.46093300	2.89995600	1.56607600
C	-0.06301600	2.16701000	3.21927000
C	1.19371400	1.87505200	2.38661800
C	1.13153000	0.83517900	1.44917700
C	2.41289100	2.54531400	2.52501200
C	2.20826300	0.47141000	0.62533100
C	3.52051800	2.17819600	1.75999300
H	2.50820800	3.35779700	3.23761400
C	3.41850400	1.15522900	0.81839000
H	4.46411700	2.70067700	1.88921100
H	4.27945100	0.90059400	0.21012900
O	-0.04558300	0.12862200	1.30872700
C	-0.04962100	3.58957800	3.80272000
H	-0.00398200	4.35166500	3.01745900
H	-0.94553200	3.76714300	4.40546900
H	0.80683000	3.72808300	4.46949100
C	-0.12597600	1.14853800	4.39429400
H	0.74635300	1.26845900	5.04711500
H	-1.03162300	1.31213200	4.98974800
H	-0.13889100	0.11795800	4.02726400
P	1.96734900	-0.78063700	-0.72601900
P	-1.96620100	-0.90587000	-0.60347000
C	-0.15722200	-2.31719700	-2.77296700
N	-0.23064300	-3.30977300	-3.39502000
Ni	-0.06161200	-0.62041600	-1.87654800
C	-2.00791700	-2.38722200	0.51350300
C	-1.64832100	-3.63900800	-0.01159500
C	-2.42790700	-2.31001300	1.85047300
C	-1.71304300	-4.78317700	0.78421200
H	-1.31531800	-3.72099900	-1.04042600
C	-2.48616400	-3.45742200	2.64468100
H	-2.71554800	-1.35507400	2.27819800
C	-2.12938700	-4.69734000	2.11400400
H	-1.43071500	-5.74365700	0.36136000

H	-2.81307200	-3.37844000	3.67848200
H	-2.17419900	-5.58993400	2.73262900
C	-3.55849400	-1.08522000	-1.52321300
C	-4.75219500	-1.48452500	-0.89699300
C	-3.56305200	-0.85275900	-2.90571600
C	-5.92553700	-1.62017100	-1.63838200
H	-4.76148900	-1.70174100	0.16744400
C	-4.73757900	-0.99235200	-3.65012600
H	-2.63914500	-0.57874600	-3.40473800
C	-5.92008400	-1.37164600	-3.01451900
H	-6.84278600	-1.92876800	-1.14327300
H	-4.70784500	-0.81376600	-4.72075600
H	-6.83567400	-1.48407100	-3.58957900
C	2.38817800	-2.37783000	0.10981600
C	2.11587200	-3.58383000	-0.55753800
C	2.98982200	-2.42631600	1.37735100
C	2.45199400	-4.80583200	0.02688000
H	1.63049300	-3.57130400	-1.52767400
C	3.31251200	-3.65172700	1.96355000
H	3.21077100	-1.50716000	1.91008800
C	3.04836200	-4.84437800	1.28876000
H	2.23618100	-5.72914900	-0.50428800
H	3.77331400	-3.67111700	2.94785800
H	3.30133200	-5.79768300	1.74551600
C	3.44910200	-0.45078100	-1.78503900
C	3.43240600	0.70182200	-2.59028200
C	4.56715600	-1.29498000	-1.83605600
C	4.51468700	1.00768700	-3.41441900
H	2.56300400	1.35323900	-2.57670400
C	5.64439500	-0.99393900	-2.67485800
H	4.60101000	-2.18878400	-1.22179200
C	5.62333100	0.15723300	-3.46229500
H	4.48852900	1.90505300	-4.02708400
H	6.50203300	-1.66101100	-2.70631100
H	6.46218300	0.39046200	-4.11255200
H	-0.01790400	0.69846200	-1.22926100
O	1.44678800	-0.35256100	-7.63605200
O	1.78952700	-0.94876600	-9.79430600
O	-2.98104900	-0.35906800	-6.47031200
O	-0.77129500	0.04228000	-6.70123200
N	0.00850800	-2.20735700	-6.97090900
C	1.22465100	-1.07715400	-8.73792400
C	1.21050100	-0.48245900	-5.08127100
C	0.12523700	-2.11245500	-8.46219300

C	-1.83584700	-0.74242200	-6.55119500
C	0.81930000	-3.35024700	-6.45913900
C	-1.40348100	-2.21293800	-6.49100800
B	0.52474100	-0.65619500	-6.54486100
H	1.53763700	-1.43858100	-4.66176800
H	2.12926300	0.10270800	-5.22139000
H	-0.81411400	-1.74816100	-8.88754900
H	0.36070100	-3.07975100	-8.90967600
H	0.47856900	-4.27558200	-6.93418000
H	0.69240800	-3.43135900	-5.37827800
H	1.86760200	-3.17585200	-6.71496000
H	-1.41376700	-2.56161100	-5.45226700
H	-2.04866000	-2.85478700	-7.09599800
C	0.35178600	0.22429900	-4.11930900
C	-0.43073100	0.97516100	-3.54194100
C	-1.33127300	2.10252100	-3.22923300
H	-0.83461100	2.77084800	-2.51243900
H	-2.22919800	1.73438900	-2.71885000
C	-1.74102600	2.88541400	-4.49408800
H	-0.83710000	3.25705800	-4.99473000
H	-2.22595500	2.19986300	-5.19950300
C	-2.67628900	4.05789100	-4.17267200
H	-2.18802900	4.72935300	-3.45126800
H	-3.57809000	3.67607200	-3.67301200
C	-3.08140100	4.85294000	-5.41851100
H	-3.75118000	5.68237100	-5.16310200
H	-2.20261200	5.27557200	-5.92099100
H	-3.59998300	4.21354700	-6.14283600

INT-1a

Zero-point correction = 0.915565 (Hartree/Particle)

Thermal correction to Energy = 0.976146

Thermal correction to Enthalpy = 0.977090

Thermal correction to Gibbs Free Energy = 0.813843

Sum of electronic and zero-point Energies = -3373.859189

Sum of electronic and thermal Energies = -3373.798608

Sum of electronic and thermal Enthalpies = -3373.797664

Sum of electronic and thermal Free Energies = -3373.960911

SCF Done: E(RM06) = -3375.37098659

C	-2.60869900	1.49659400	0.92808600
C	-1.55977800	0.58271400	0.76103400
C	-0.40782300	0.77161200	1.54543600

C	-0.26606500	1.80343400	2.47960800
C	-1.33451600	2.70075300	2.60567000
C	-2.49210800	2.55220600	1.83738300
H	-3.51809700	1.38180200	0.34703900
H	-1.27527600	3.51562000	3.31930900
H	-3.31745900	3.24797400	1.96576600
C	1.00287600	1.82246500	3.34395300
C	2.16776800	1.32010500	2.47842500
C	1.90235500	0.36418000	1.49095400
C	3.49262800	1.73886400	2.62919600
C	2.87610600	-0.11767800	0.60252100
C	4.50267200	1.22237900	1.81890200
H	3.74622700	2.47727900	3.38164000
C	4.19516900	0.31528500	0.80761000
H	5.52863300	1.55105000	1.95724000
H	4.98047700	-0.03881100	0.14848900
O	0.61582400	-0.12800500	1.36068900
C	1.28651200	3.22967200	3.90017700
H	1.46702200	3.94382700	3.09030300
H	0.45080500	3.58429500	4.51180400
H	2.16267400	3.21851100	4.55524500
C	0.79726100	0.83559400	4.52832000
H	1.69911100	0.79893200	5.15012500
H	-0.04382700	1.15635400	5.15441000
H	0.59033800	-0.17712700	4.16863200
P	2.41225300	-1.16024200	-0.86301500
P	-1.51430000	-0.78396500	-0.48566400
C	0.01562200	-2.30946000	-2.78401500
N	-0.21397200	-3.26059100	-3.42958100
Ni	0.37606000	-0.70498200	-1.79153000
C	-1.69912000	-2.29226300	0.57628500
C	-1.47454900	-3.55257700	-0.00131100
C	-2.08670600	-2.22064200	1.92355200
C	-1.64520500	-4.71236900	0.75603700
H	-1.16154500	-3.62866200	-1.03747000
C	-2.24960200	-3.38441800	2.67787800
H	-2.26209800	-1.25687700	2.39160900
C	-2.03072900	-4.63349200	2.09550600
H	-1.46722600	-5.67995400	0.29465100
H	-2.54787000	-3.31153000	3.72081700
H	-2.15661000	-5.53928100	2.68307100
C	-3.16284000	-0.69376100	-1.31741000
C	-4.37277500	-0.92513900	-0.64064500
C	-3.19273900	-0.43475000	-2.69545100

C	-5.58717500	-0.86823700	-1.32405700
H	-4.36382700	-1.16689500	0.41851000
C	-4.41035500	-0.38312500	-3.37902300
H	-2.25846100	-0.30057100	-3.23237700
C	-5.60770600	-0.59404700	-2.69485300
H	-6.51634000	-1.05088700	-0.79034200
H	-4.41860500	-0.19312100	-4.44905700
H	-6.55424500	-0.56053500	-3.22818400
C	2.77224000	-2.88194000	-0.28838800
C	2.38114800	-3.96554500	-1.09348800
C	3.43600800	-3.14183900	0.92158600
C	2.66659300	-5.27440900	-0.70128700
H	1.83674100	-3.79205500	-2.01544700
C	3.70819400	-4.45355600	1.31444900
H	3.74289000	-2.32154400	1.56170500
C	3.32859900	-5.52324300	0.50243700
H	2.35826800	-6.09955200	-1.33781000
H	4.21922000	-4.63620100	2.25638200
H	3.54237200	-6.54408500	0.80878600
C	3.79967500	-0.76930200	-2.02177300
C	3.84610200	0.52781600	-2.56504200
C	4.76395400	-1.70700500	-2.41544600
C	4.84566400	0.87643800	-3.47203400
H	3.09723600	1.26186000	-2.28123300
C	5.75667600	-1.35592700	-3.33550400
H	4.74337800	-2.71306300	-2.00925400
C	5.80213400	-0.06570200	-3.86355400
H	4.87129300	1.88351900	-3.87978100
H	6.49557600	-2.09502700	-3.63430300
H	6.57558600	0.20573000	-4.57725300
H	0.66996300	0.54692800	-1.07280000
O	0.52407700	4.22917100	-3.97977100
O	0.79597300	6.26947900	-4.92451500
O	2.01802300	4.07350600	0.29119600
O	1.34402400	3.51826800	-1.79832900
N	-0.61536000	4.93223800	-1.92356400
C	0.48949100	5.56242200	-3.99896100
C	-0.73705300	2.31484300	-2.80848500
C	-0.00315400	6.09530600	-2.64375800
C	1.21125900	4.09650700	-0.60604900
C	-2.09685300	4.94801800	-2.04937700
C	-0.14557600	4.80968100	-0.51595000
B	0.17563900	3.63340400	-2.69557500
H	-1.14823700	2.05219000	-1.82744300

H	-1.59664800	2.51394800	-3.46541100
H	0.85624500	6.46924900	-2.08049500
H	-0.71733200	6.91145500	-2.77020800
H	-2.50422700	5.83310400	-1.55089300
H	-2.50717200	4.04724600	-1.59177200
H	-2.36554200	4.96940600	-3.10778700
H	-0.84217800	4.18037900	0.04721000
H	-0.06509000	5.77894800	-0.01844700
C	0.00360600	1.16931600	-3.36097200
C	0.63195400	0.36333900	-4.03336500
C	1.34457700	-0.44006800	-5.03633400
H	0.84904300	-1.41263100	-5.13456300
H	2.36105900	-0.64832600	-4.68061400
C	1.41308300	0.27028400	-6.40481200
H	0.39289100	0.45764300	-6.76623800
H	1.88538300	1.25388800	-6.28222800
C	2.18752600	-0.55245500	-7.44214700
H	1.71843200	-1.54105500	-7.54352600
H	3.20561500	-0.73429900	-7.06980300
C	2.25673600	0.12687300	-8.81387100
H	2.81946600	-0.48060100	-9.53220900
H	1.25353800	0.28780100	-9.22766600
H	2.74722900	1.10598800	-8.74759500

INT-2

Zero-point correction = 0.918297 (Hartree/Particle)

Thermal correction to Energy = 0.978334

Thermal correction to Enthalpy = 0.979278

Thermal correction to Gibbs Free Energy = 0.816508

Sum of electronic and zero-point Energies = -3373.893670

Sum of electronic and thermal Energies = -3373.833633

Sum of electronic and thermal Enthalpies = -3373.832689

Sum of electronic and thermal Free Energies = -3373.995459

SCF Done: E(RM06) = -3375.39480235

C	-3.81345700	0.56197800	0.66702500
C	-2.52441500	0.02873900	0.53270500
C	-1.48451200	0.64244800	1.25551600
C	-1.69948900	1.71493300	2.13187200
C	-2.99957900	2.22645800	2.21771200
C	-4.04565900	1.66423400	1.48807900
H	-4.63635500	0.11450100	0.12105200
H	-3.20612700	3.06679900	2.87125600

H	-5.04761700	2.07492100	1.57202400
C	-0.53568900	2.18332300	3.01205000
C	0.76060100	2.01808800	2.21199800
C	0.86398400	0.95270500	1.30854400
C	1.88968700	2.82720100	2.38547400
C	2.03880000	0.66129500	0.59234100
C	3.07351300	2.56677200	1.69734600
H	1.85171400	3.66660800	3.07095700
C	3.14755900	1.49058500	0.81455100
H	3.94062300	3.20279900	1.85189000
H	4.07005100	1.29802000	0.27716400
O	-0.22022900	0.11882600	1.08728900
C	-0.73013000	3.62984500	3.50151500
H	-0.78483100	4.33736500	2.66735300
H	-1.64538500	3.72123000	4.09372400
H	0.09115000	3.93187300	4.15774800
C	-0.46379700	1.24550200	4.25278300
H	0.37599600	1.53144000	4.89660600
H	-1.38978600	1.31209900	4.83583000
H	-0.32205700	0.20237700	3.95273100
P	2.00180800	-0.69617300	-0.67201400
P	-2.15428100	-1.39241000	-0.59186900
C	-0.52199000	-2.56900900	-3.10241500
N	-0.36204700	-3.63968500	-3.55517900
Ni	-0.77668600	-0.88620200	-2.41168400
C	-1.76183800	-2.77993900	0.55830800
C	-1.27057700	-3.97700600	0.01303000
C	-1.99499500	-2.70266900	1.93960000
C	-1.02635200	-5.07487600	0.83870100
H	-1.07581300	-4.05187400	-1.05199800
C	-1.74092600	-3.80230100	2.76153600
H	-2.38137000	-1.78759000	2.37711000
C	-1.25817200	-4.99114100	2.21267100
H	-0.64572100	-5.99504000	0.40413300
H	-1.92396300	-3.72812300	3.83041300
H	-1.06146400	-5.84687100	2.85316900
C	-3.81547300	-1.85792800	-1.24619900
C	-4.71764200	-2.65629400	-0.52439000
C	-4.18073700	-1.40234700	-2.52183100
C	-5.95895800	-2.98423600	-1.07068100
H	-4.44783800	-3.02795500	0.45947000
C	-5.42262400	-1.73109300	-3.06842100
H	-3.49245300	-0.79482200	-3.10155900
C	-6.31290700	-2.52336100	-2.34187000

H	-6.64799000	-3.60572200	-0.50457000
H	-5.66843800	-1.37466400	-4.06384500
H	-7.27830100	-2.78773300	-2.76574500
C	2.49737600	-2.19185700	0.29467900
C	2.33583500	-3.43529200	-0.34084100
C	3.02470200	-2.15996100	1.59444800
C	2.71797500	-4.61397100	0.30026600
H	1.90300600	-3.48076600	-1.33732400
C	3.39106900	-3.34296000	2.24046100
H	3.15474400	-1.20887700	2.10242300
C	3.24526800	-4.57116400	1.59290300
H	2.59394100	-5.56666200	-0.20803500
H	3.79641100	-3.30282100	3.24853500
H	3.53603200	-5.49033800	2.09505400
C	3.54602700	-0.33405700	-1.63438100
C	3.43923900	0.57762800	-2.69965100
C	4.78993000	-0.93704400	-1.39065100
C	4.54820600	0.89138400	-3.48586400
H	2.47798500	1.03527900	-2.91803800
C	5.89738400	-0.63031400	-2.18527100
H	4.89460000	-1.65087300	-0.57956000
C	5.78121000	0.28604800	-3.23170000
H	4.44697200	1.59973300	-4.30421300
H	6.85254200	-1.10874200	-1.98349100
H	6.64364100	0.52263700	-3.84937700
H	-0.94493000	0.86722300	-2.16745000
O	0.17461100	0.19198200	-7.69799300
O	0.10137500	-0.14395400	-9.93628500
O	-3.90370400	-0.33046000	-5.72627600
O	-1.79681500	0.28141100	-6.26412700
N	-0.95419100	-1.85069700	-6.98232100
C	-0.21511000	-0.43591300	-8.81069800
C	0.54098100	-0.21000000	-5.20696500
C	-1.14640200	-1.59939800	-8.44789100
C	-2.76909500	-0.60189100	-6.04700700
C	0.01422400	-2.96528400	-6.77016100
C	-2.24351100	-2.02753100	-6.25542500
B	-0.45729600	-0.31542500	-6.47854200
H	1.18465700	-1.09472500	-5.13545500
H	1.21552700	0.62278400	-5.44930400
H	-2.17884200	-1.29472600	-8.64151300
H	-0.92871100	-2.49036600	-9.03972900
H	-0.36544500	-3.87139100	-7.25239200
H	0.13535200	-3.15047800	-5.70232900

H	0.96930000	-2.68601500	-7.22201500
H	-2.03810100	-2.48920500	-5.28470000
H	-2.95198600	-2.64915500	-6.80815400
C	-0.09759200	0.05013800	-3.88626900
C	-0.51046400	1.10555800	-3.20840100
C	-0.61072200	2.60535900	-3.40758000
H	-0.12638400	3.10640400	-2.55561200
H	-1.67308800	2.88631900	-3.34997700
C	-0.01771400	3.13151400	-4.71957700
H	1.05083100	2.88005400	-4.76856300
H	-0.50101300	2.62753700	-5.56476900
C	-0.18440800	4.65009800	-4.86690500
H	0.28625300	5.15451200	-4.01050300
H	-1.25349800	4.90174800	-4.81998600
C	0.41083700	5.19115500	-6.17110800
H	0.27003500	6.27497100	-6.25422400
H	1.48747600	4.98915800	-6.22942200
H	-0.05997600	4.72379200	-7.04412700

INT-2a

Zero-point correction = 0.919323 (Hartree/Particle)

Thermal correction to Energy = 0.979106

Thermal correction to Enthalpy = 0.980050

Thermal correction to Gibbs Free Energy = 0.818975

Sum of electronic and zero-point Energies = -3373.888909

Sum of electronic and thermal Energies = -3373.829126

Sum of electronic and thermal Enthalpies = -3373.828182

Sum of electronic and thermal Free Energies = -3373.989257

SCF Done: E(RM06) = -3375.39293806

C	-2.72086800	0.07375400	2.74822400
C	-1.57604400	-0.36698400	2.06510600
C	-0.34576800	-0.19357900	2.70478300
C	-0.19920700	0.41180500	3.96074700
C	-1.36289200	0.85172100	4.59628800
C	-2.61373500	0.67768000	3.99888700
H	-3.69574300	-0.04049900	2.28690200
H	-1.30243200	1.33245400	5.56690900
H	-3.50826600	1.02146100	4.51035800
C	1.21487300	0.49850400	4.54994400
C	2.16904400	0.77443500	3.38100500
C	1.89373500	0.15116400	2.15885200
C	3.31904100	1.56666300	3.44756900

C	2.68851100	0.28677900	1.01599900
C	4.15299200	1.70646600	2.33717800
H	3.57425900	2.07728100	4.37013600
C	3.84577900	1.07151700	1.13370000
H	5.04726700	2.31902000	2.40790100
H	4.49802200	1.20246900	0.27859000
O	0.77424400	-0.64534600	2.03621400
C	1.31891100	1.57354800	5.64447300
H	1.07176200	2.56945300	5.26162500
H	0.64556200	1.34623100	6.47674200
H	2.33042000	1.60463000	6.06111600
C	1.57872000	-0.88160200	5.17010900
H	2.59775200	-0.85981600	5.57339800
H	0.88708400	-1.12596500	5.98461800
H	1.52429800	-1.67964700	4.42370300
P	2.13733000	-0.54878400	-0.55075500
P	-1.64537300	-1.12937200	0.37190000
C	-1.31215400	-1.55554700	-2.57209700
N	-2.05639600	-2.17403600	-3.23380000
Ni	-0.07104300	-0.72166200	-1.47902700
C	-2.03523300	-2.89767500	0.76757500
C	-2.40704200	-3.78153700	-0.26324900
C	-1.90963300	-3.40023300	2.07277600
C	-2.65786300	-5.12531700	0.01853400
H	-2.49798200	-3.42375400	-1.28327000
C	-2.15135300	-4.74828700	2.34472200
H	-1.62696400	-2.74212800	2.88713100
C	-2.52980000	-5.61518900	1.31978600
H	-2.95207800	-5.79001700	-0.78957300
H	-2.04728300	-5.11576500	3.36247700
H	-2.72326000	-6.66343500	1.53274100
C	-3.22048100	-0.37578500	-0.23449200
C	-4.45597600	-1.03268600	-0.26020600
C	-3.14542800	0.95046800	-0.69166200
C	-5.59228400	-0.37375900	-0.73937200
H	-4.53529900	-2.05974400	0.08165300
C	-4.27881800	1.61021900	-1.16303600
H	-2.19289900	1.47442400	-0.68326500
C	-5.50736300	0.94406600	-1.19007600
H	-6.54461000	-0.89729800	-0.76208600
H	-4.19348300	2.63425700	-1.51815900
H	-6.39328200	1.44973100	-1.56519600
C	2.61306500	-2.30988200	-0.24551700
C	1.90390200	-3.31680800	-0.91985100

C	3.64886300	-2.67716500	0.62811600
C	2.22775700	-4.66152700	-0.72836200
H	1.08907900	-3.04803300	-1.58813800
C	3.96949900	-4.02176300	0.81906700
H	4.20425400	-1.91219800	1.16268700
C	3.26006000	-5.01625100	0.14121200
H	1.66483500	-5.42847700	-1.25301600
H	4.77269900	-4.29222800	1.49973300
H	3.50855200	-6.06312500	0.29478100
C	3.42919900	0.08210900	-1.71105000
C	3.32804400	1.41814500	-2.13505500
C	4.49699700	-0.69845200	-2.17391700
C	4.28778200	1.96843400	-2.98446700
H	2.49822200	2.03609100	-1.80835200
C	5.44746700	-0.15141200	-3.04016600
H	4.59021000	-1.73326600	-1.86083700
C	5.34879000	1.18165300	-3.44161400
H	4.19709800	3.00924600	-3.28171100
H	6.26830800	-0.76941000	-3.39500200
H	6.09550300	1.60645100	-4.10773200
H	-0.85395500	1.54422300	-2.59510400
O	1.52220100	4.06343200	-3.35936100
O	2.94982000	5.81547900	-3.29416200
O	-2.91016000	5.07938400	-2.93489900
O	-0.88442600	4.07056300	-2.94527000
N	-0.03781000	4.94692500	-5.02906100
C	1.90776100	5.30899400	-3.63018500
C	0.09044000	2.21680500	-4.45909100
C	0.82433500	6.02569200	-4.45157300
C	-1.86570200	4.79609700	-3.47018600
C	0.38668500	4.61259600	-6.41360100
C	-1.49359500	5.22791100	-4.90022100
B	0.20334300	3.70110100	-3.88609600
H	-0.77904100	2.14452800	-5.13911800
H	0.96981100	1.94872000	-5.05800600
H	0.23198500	6.65212800	-3.77868200
H	1.25807400	6.65863200	-5.22837800
H	0.21260900	5.46480100	-7.07802700
H	-0.17666500	3.74661100	-6.76181000
H	1.45018900	4.36394300	-6.40796700
H	-2.04208000	4.60617200	-5.61387200
H	-1.73805500	6.27604700	-5.08844000
C	-0.11928000	1.21857500	-3.33133500
C	0.44842900	0.01395500	-3.17559200

C	1.34271200	-0.67627300	-4.18140000
H	1.87713700	-1.50806200	-3.70729300
H	2.12440400	0.02303700	-4.51661900
C	0.59677100	-1.21736900	-5.41863800
H	-0.20871200	-1.88313200	-5.09109700
H	0.10868700	-0.38249000	-5.94108100
C	1.52519100	-1.95519700	-6.39197900
H	2.01094400	-2.78963700	-5.86531600
H	2.33791700	-1.28442200	-6.70919000
C	0.79469100	-2.49298100	-7.62749700
H	1.47878800	-3.02168200	-8.30237900
H	-0.00085600	-3.19130600	-7.34102800
H	0.32750400	-1.67944100	-8.19712400

INT-3

Zero-point correction = 0.918965 (Hartree/Particle)

Thermal correction to Energy = 0.978774

Thermal correction to Enthalpy = 0.979718

Thermal correction to Gibbs Free Energy = 0.819106

Sum of electronic and zero-point Energies = -3373.897440

Sum of electronic and thermal Energies = -3373.837631

Sum of electronic and thermal Enthalpies = -3373.836687

Sum of electronic and thermal Free Energies = -3373.997298

SCF Done: E(RM06) = -3375.39991080

C	-3.69930400	0.24771700	1.21242200
C	-2.39225000	-0.15612400	0.90019600
C	-1.34423100	0.55366700	1.50110300
C	-1.53330200	1.62985700	2.37761800
C	-2.85252300	2.00543000	2.64840800
C	-3.92459900	1.31950300	2.07467500
H	-4.54105100	-0.26671800	0.76298500
H	-3.05371100	2.83777800	3.31439900
H	-4.94242900	1.62532400	2.29893400
C	-0.29029500	2.26712000	3.01448500
C	0.82695200	2.24179700	1.96301900
C	0.88786500	1.14169600	1.10233900
C	1.83010700	3.20848800	1.83142200
C	1.87745700	0.96872500	0.12529200
C	2.84940600	3.05789000	0.89021100
H	1.82649400	4.08490900	2.47075300
C	2.87776600	1.94700700	0.04632000
H	3.62662800	3.81274700	0.81230100

H	3.67005000	1.84871900	-0.68688300
O	-0.06340200	0.14555400	1.19120400
C	-0.56928900	3.69234800	3.52106300
H	-0.88904400	4.35692900	2.71148000
H	-1.34683900	3.68547900	4.29098000
H	0.32454000	4.11915800	3.98597800
C	0.15039200	1.38648000	4.21954800
H	1.05598600	1.79820700	4.67977800
H	-0.64167100	1.35514700	4.97650200
H	0.36447300	0.36058900	3.90443000
P	1.71106500	-0.48818700	-1.00513400
P	-2.00146000	-1.50013300	-0.31714600
C	-0.97716000	-2.55847500	-3.04094900
N	-1.26906000	-3.55855900	-3.58173800
Ni	-0.33499200	-1.10786700	-2.06837200
C	-1.83609400	-3.01801900	0.72105300
C	-1.75465400	-4.25999300	0.06457200
C	-1.75310400	-2.98060200	2.11921800
C	-1.60783400	-5.43503100	0.80087700
H	-1.80977500	-4.30774700	-1.01936200
C	-1.59428900	-4.16041000	2.85083700
H	-1.82076200	-2.03296600	2.64422400
C	-1.52470600	-5.38959700	2.19540000
H	-1.55818300	-6.38856800	0.28140300
H	-1.53281500	-4.11489900	3.93508700
H	-1.40841100	-6.30714900	2.76626000
C	-3.62543000	-1.73214700	-1.16211300
C	-4.64979200	-2.53310700	-0.63293400
C	-3.83841100	-1.07210600	-2.38240100
C	-5.86326600	-2.66364300	-1.31085200
H	-4.49781600	-3.06377300	0.30227000
C	-5.05074100	-1.20518200	-3.06114600
H	-3.04641200	-0.47247900	-2.82192000
C	-6.06441600	-2.00129700	-2.52412800
H	-6.64748800	-3.29009200	-0.89343800
H	-5.17780700	-0.71225100	-4.01999800
H	-7.00603000	-2.11430000	-3.05524800
C	2.22070800	-1.90196700	0.06812000
C	1.76485700	-3.18744500	-0.26136300
C	3.06449800	-1.74065500	1.17804900
C	2.14932800	-4.29092100	0.50313600
H	1.10263400	-3.32348000	-1.11219900
C	3.44365400	-2.84440100	1.94243600
H	3.42693400	-0.75214700	1.44429000

C	2.98787800	-4.12139700	1.60553400
H	1.77965400	-5.27833000	0.24265700
H	4.09618700	-2.70675000	2.80078900
H	3.28264000	-4.97976500	2.20350800
C	3.16006800	-0.28372500	-2.13807300
C	3.18691300	0.80210600	-3.03174300
C	4.21418400	-1.20860700	-2.17405500
C	4.24721100	0.96471100	-3.92304200
H	2.36906100	1.51494500	-3.03930900
C	5.26858600	-1.05032100	-3.07724000
H	4.21728000	-2.05632700	-1.49760400
C	5.29095500	0.03644600	-3.95101300
H	4.25128100	1.81194600	-4.60354000
H	6.07468400	-1.77923300	-3.09135500
H	6.11239600	0.15915100	-4.65171300
H	-0.80444600	1.24664300	-2.49345500
O	0.59508000	-0.23765000	-7.47027500
O	0.82764100	-0.54078000	-9.70057900
O	-3.71767700	-0.47568200	-6.09842500
O	-1.50567100	-0.05166600	-6.25309000
N	-0.75051200	-2.22534700	-6.96469000
C	0.34100500	-0.83034300	-8.63490700
C	0.69689300	-0.74349500	-4.98029300
C	-0.68361200	-1.95199600	-8.43619400
C	-2.57565300	-0.84342600	-6.25411600
C	0.06030900	-3.42560800	-6.61566900
C	-2.15623300	-2.29912900	-6.46868100
B	-0.19935800	-0.73408900	-6.33545000
H	1.12351700	-1.73456400	-4.79326000
H	1.56498000	-0.11121900	-5.22020100
H	-1.65600100	-1.60064500	-8.79294900
H	-0.41187700	-2.84753300	-8.99867600
H	-0.32269100	-4.29511100	-7.15949300
H	-0.01402200	-3.60645000	-5.54343800
H	1.09866100	-3.24429700	-6.90436800
H	-2.16500700	-2.82153300	-5.50670400
H	-2.81509800	-2.81479700	-7.17145300
C	0.07394000	-0.21494100	-3.71422800
C	-0.39020600	1.02022600	-3.48783700
C	-0.42573900	2.20178500	-4.44165400
H	-1.43099600	2.28494500	-4.87855900
H	0.25002600	2.02146700	-5.28694200
C	-0.06477300	3.53165300	-3.75906700
H	-0.74276500	3.69690200	-2.90787300

H	0.94677300	3.46888200	-3.32981700
C	-0.13964100	4.73708800	-4.70533900
H	-1.14894600	4.79313100	-5.13668900
H	0.54266900	4.57610200	-5.55184600
C	0.19863200	6.06557400	-4.02027500
H	0.13607300	6.90562500	-4.72180600
H	-0.49122200	6.27097400	-3.19211500
H	1.21512100	6.05211800	-3.60692700

TS-1

Zero-point correction = 0.914582 (Hartree/Particle)

Thermal correction to Energy = 0.974289

Thermal correction to Enthalpy = 0.975233

Thermal correction to Gibbs Free Energy = 0.815489

Sum of electronic and zero-point Energies = -3373.870211

Sum of electronic and thermal Energies = -3373.810505

Sum of electronic and thermal Enthalpies = -3373.809561

Sum of electronic and thermal Free Energies = -3373.969304

SCF Done: E(RM06) = -3375.37363433

C	-3.63425000	0.81200000	0.77973300
C	-2.37719700	0.21219400	0.63065500
C	-1.31695000	0.73747900	1.38459000
C	-1.45662600	1.81006400	2.27255600
C	-2.72542000	2.39139800	2.37628100
C	-3.80242500	1.89893700	1.63844600
H	-4.47913500	0.43787600	0.21206200
H	-2.88327200	3.23232200	3.04314300
H	-4.78004000	2.36230300	1.73605500
C	-0.23661500	2.21009800	3.11239900
C	1.01075200	2.01514700	2.24005600
C	1.02342500	0.94689500	1.33514700
C	2.16847000	2.79601300	2.32511200
C	2.11724700	0.63764000	0.51171900
C	3.28812800	2.50231300	1.54612200
H	2.20623100	3.63729300	3.00901100
C	3.26424500	1.43303800	0.65094000
H	4.18286800	3.11203900	1.63540100
H	4.13549700	1.22645400	0.03896800
O	-0.08784400	0.13388500	1.22268800
C	-0.34934300	3.65041700	3.64071400
H	-0.41201200	4.37901200	2.82543500
H	-1.23405200	3.76358100	4.27456100

H	0.51321600	3.90305500	4.26462200
C	-0.14191500	1.24066700	4.32645900
H	0.73836100	1.47885300	4.93460400
H	-1.03503300	1.33000900	4.95580800
H	-0.05704100	0.20034600	3.99761400
P	1.92332900	-0.71763600	-0.74092700
P	-2.01616300	-1.15388800	-0.56169400
C	-0.32891300	-2.44326900	-2.86810500
N	-0.31485100	-3.48525300	-3.40821700
Ni	-0.37309200	-0.71023100	-2.07041600
C	-1.90459700	-2.64903700	0.52419800
C	-1.67899300	-3.89828700	-0.07874100
C	-2.07691200	-2.58811100	1.91473900
C	-1.63623300	-5.05659600	0.69664200
H	-1.52842500	-3.96624100	-1.15108300
C	-2.02318900	-3.75050900	2.68769100
H	-2.26291300	-1.63649700	2.40160000
C	-1.80556900	-4.98742600	2.08135900
H	-1.46509500	-6.01547300	0.21443800
H	-2.15674600	-3.68505300	3.76446300
H	-1.76722000	-5.89164700	2.68324100
C	-3.62797400	-1.41398000	-1.42179500
C	-4.71606900	-2.04583300	-0.79611300
C	-3.76352500	-0.97872900	-2.74757700
C	-5.91725800	-2.22236400	-1.48309900
H	-4.62080800	-2.40733500	0.22373600
C	-4.96493200	-1.15976100	-3.43692400
H	-2.91918000	-0.51439500	-3.24832200
C	-6.04283400	-1.77920500	-2.80290400
H	-6.75230100	-2.71354700	-0.99011500
H	-5.03451200	-0.83285600	-4.46954900
H	-6.97751700	-1.92643600	-3.33801300
C	2.38204900	-2.22809300	0.22385600
C	1.97908700	-3.47580400	-0.27961000
C	3.11986600	-2.18459700	1.41797700
C	2.32119300	-4.65219700	0.39037200
H	1.39366300	-3.52817400	-1.19252300
C	3.44913600	-3.36185900	2.09123300
H	3.43915900	-1.22987500	1.82483600
C	3.05341800	-4.59871300	1.57733600
H	2.00236400	-5.60965800	-0.01276100
H	4.01801400	-3.31171900	3.01631500
H	3.31129100	-5.51497800	2.10226500
C	3.41015500	-0.44471800	-1.81105500

C	3.44810900	0.71225200	-2.61132000
C	4.45791600	-1.37023100	-1.92339800
C	4.51102000	0.94287200	-3.48382200
H	2.63913200	1.43495600	-2.55200400
C	5.51554700	-1.14446800	-2.80898100
H	4.45103100	-2.27110200	-1.31882400
C	5.54824500	0.01164100	-3.58863000
H	4.52565800	1.84638500	-4.08800100
H	6.31759500	-1.87459600	-2.88223400
H	6.37251200	0.18671400	-4.27483200
H	-0.51198100	0.65514700	-1.52664100
O	1.06925800	-0.17546600	-7.55463400
O	1.30153900	-0.62675900	-9.76180700
O	-3.27751500	-0.40586000	-6.19984100
O	-1.08628500	0.07955400	-6.44296300
N	-0.25985100	-2.12211000	-6.92088900
C	0.80911600	-0.84206100	-8.68325700
C	1.03860800	-0.47429000	-5.01451400
C	-0.22895400	-1.93781900	-8.40814300
C	-2.12453400	-0.74786600	-6.32711300
C	0.61064800	-3.26618600	-6.52171100
C	-1.64546600	-2.20337900	-6.37623100
B	0.23673500	-0.58426000	-6.42325300
H	1.46797700	-1.43129600	-4.70540700
H	1.90003900	0.18047800	-5.20465700
H	-1.20475800	-1.59237000	-8.76120900
H	0.01970200	-2.86761900	-8.92298200
H	0.26464000	-4.17537500	-7.02325400
H	0.55531500	-3.40660400	-5.44119700
H	1.63570700	-3.04789800	-6.83193800
H	-1.59684300	-2.61196600	-5.36107600
H	-2.29887900	-2.82891300	-6.98916400
C	0.26381800	0.12912800	-3.90549600
C	-0.39869600	1.02840200	-3.34624300
C	-1.09561500	2.33303200	-3.22903600
H	-0.66772900	2.90640000	-2.39492200
H	-2.14664900	2.15678800	-2.96302300
C	-1.01890100	3.15192700	-4.53141300
H	0.03541100	3.34156900	-4.77544000
H	-1.42658200	2.55341600	-5.35417400
C	-1.77153400	4.48422100	-4.42432700
H	-1.36426100	5.06941400	-3.58692600
H	-2.82380400	4.28580500	-4.17565100
C	-1.69912400	5.31356500	-5.71095400

H	-2.24845900	6.25664300	-5.60908700
H	-0.66087900	5.55785900	-5.96724500
H	-2.12828200	4.76548900	-6.55816300

TS-1a

Zero-point correction = 0.914228 (Hartree/Particle)

Thermal correction to Energy = 0.974132

Thermal correction to Enthalpy = 0.975076

Thermal correction to Gibbs Free Energy = 0.814454

Sum of electronic and zero-point Energies = -3373.856229

Sum of electronic and thermal Energies = -3373.796325

Sum of electronic and thermal Enthalpies = -3373.795381

Sum of electronic and thermal Free Energies = -3373.956003

SCF Done: E(RM06) = -3375.36646354

C	-2.90857800	1.01359600	1.31523000
C	-1.76295100	0.27458500	0.99453200
C	-0.57830100	0.58558200	1.67993900
C	-0.49381100	1.56953100	2.67064000
C	-1.65689800	2.29738500	2.94563600
C	-2.85022600	2.02586300	2.27485600
H	-3.84448100	0.80246400	0.80913700
H	-1.63820500	3.08129200	3.69496000
H	-3.74361600	2.59801900	2.51024400
C	0.83123400	1.71449900	3.42996200
C	1.97021400	1.43448400	2.44076700
C	1.75827200	0.48787200	1.43158400
C	3.23589000	2.02477800	2.50823000
C	2.72778600	0.13610200	0.48037900
C	4.24140000	1.66977000	1.60862200
H	3.44634300	2.76744300	3.27019800
C	3.98954400	0.73703400	0.60379500
H	5.22280900	2.12969300	1.68591700
H	4.76925300	0.49014100	-0.10878800
O	0.53415700	-0.14875500	1.33832600
C	0.96744200	3.10202800	4.08078900
H	0.94903700	3.89385300	3.32687200
H	0.15876600	3.27434700	4.79839000
H	1.90094700	3.17367700	4.64765800
C	0.87103400	0.62748600	4.54290800
H	1.81948600	0.68073000	5.08993700
H	0.05019800	0.77868300	5.25398700
H	0.77790500	-0.37805900	4.12072000

P	2.24965300	-0.99196800	-0.91231100
P	-1.67930200	-1.02605100	-0.31601200
C	-0.40005700	-2.29958900	-2.85062300
N	-0.53459400	-3.31771900	-3.41520400
Ni	-0.17100200	-0.62150400	-1.95952800
C	-1.62152800	-2.59496100	0.66590800
C	-1.44293900	-3.81184600	-0.01273800
C	-1.78841100	-2.61070400	2.05947900
C	-1.43997100	-5.01501200	0.69375200
H	-1.29850100	-3.81988400	-1.08796500
C	-1.77794700	-3.81806600	2.76119500
H	-1.92932800	-1.68213500	2.60308900
C	-1.60549600	-5.02338900	2.08007100
H	-1.30015600	-5.94801100	0.15444500
H	-1.90562200	-3.81272800	3.84079500
H	-1.59695400	-5.96294200	2.62668500
C	-3.39301400	-1.04904500	-1.00794700
C	-4.48690100	-1.55932000	-0.28969400
C	-3.60016100	-0.55408800	-2.30332700
C	-5.76428500	-1.55485800	-0.85064500
H	-4.33765000	-1.96988000	0.70491700
C	-4.87957600	-0.55050400	-2.86302000
H	-2.74755300	-0.20046700	-2.87644400
C	-5.96307100	-1.04781100	-2.13756400
H	-6.60260100	-1.95538900	-0.28653600
H	-5.02523500	-0.17465400	-3.87245900
H	-6.95740600	-1.05312700	-2.57664300
C	2.72835700	-2.66350000	-0.27853200
C	2.19941600	-3.78941700	-0.93247700
C	3.59526900	-2.85563600	0.80905600
C	2.54847600	-5.07599600	-0.51608400
H	1.50988400	-3.66323100	-1.76195800
C	3.93006700	-4.14338300	1.23043000
H	4.01068200	-1.99844000	1.32980500
C	3.41100000	-5.25685500	0.56639600
H	2.13427300	-5.93590500	-1.03592500
H	4.59959700	-4.27541400	2.07688800
H	3.67443700	-6.25932100	0.89437600
C	3.57333900	-0.61854200	-2.15308100
C	3.61707200	0.67887500	-2.69606700
C	4.45512000	-1.58597500	-2.65737400
C	4.52496000	1.00531100	-3.70270000
H	2.93907500	1.44265100	-2.33119800
C	5.35789500	-1.26126400	-3.67447700

H	4.43844900	-2.59585100	-2.26018800
C	5.39800900	0.03186700	-4.19831300
H	4.53681300	2.01708300	-4.10035100
H	6.03399400	-2.02411200	-4.05260900
H	6.10338100	0.28040000	-4.98716500
H	-0.07476400	0.70886400	-1.31516700
O	1.73690100	3.49042100	-3.38606300
O	3.35308500	4.86453900	-4.17022500
O	0.64126000	4.50816400	0.88091100
O	0.93329300	3.42596500	-1.08866700
N	0.16768600	5.18402000	-2.56387300
C	2.32578000	4.67177500	-3.57085700
C	-0.61514700	2.53895600	-2.99256000
C	1.50477900	5.78018700	-2.89368400
C	0.49731800	4.41478100	-0.31272600
C	-0.85253800	5.57475800	-3.57159300
C	-0.25032600	5.45581600	-1.16200800
B	0.56608700	3.52022000	-2.51562800
H	-1.46324000	2.57482500	-2.29704200
H	-0.99459200	2.85810100	-3.97448600
H	2.01495500	6.07969800	-1.97405800
H	1.40587200	6.65674900	-3.53706300
H	-1.01875300	6.65593500	-3.53769700
H	-1.78625500	5.05179600	-3.36147600
H	-0.49991700	5.29054700	-4.56541200
H	-1.32726400	5.28407400	-1.07059400
H	-0.02882800	6.47807600	-0.84730300
C	-0.14105200	1.14108500	-3.15771800
C	0.38473600	0.20686900	-3.79800200
C	1.00575700	-0.48336700	-4.94652100
H	0.35789400	-1.31178700	-5.25552600
H	1.94432300	-0.94614300	-4.61858200
C	1.27976700	0.47009900	-6.12566700
H	0.32860200	0.89587300	-6.47650700
H	1.89186700	1.31035000	-5.77340500
C	1.98844300	-0.23636800	-7.28833500
H	1.38492700	-1.09516900	-7.61411600
H	2.94018300	-0.64952900	-6.92699500
C	2.25119900	0.68838500	-8.48162000
H	2.76336800	0.15804700	-9.29287600
H	1.31369800	1.08974500	-8.88704600
H	2.87839300	1.54059600	-8.19185300

TS-2

Zero-point correction = 0.918818 (Hartree/Particle)
 Thermal correction to Energy = 0.977740
 Thermal correction to Enthalpy = 0.978684
 Thermal correction to Gibbs Free Energy = 0.821068
 Sum of electronic and zero-point Energies = -3373.889489
 Sum of electronic and thermal Energies = -3373.830567
 Sum of electronic and thermal Enthalpies = -3373.829622
 Sum of electronic and thermal Free Energies = -3373.987238

SCF Done: E(RM06) = -3375.39892007

C	-3.67943800	0.44536800	1.77261200
C	-2.43348800	0.02677500	1.28087700
C	-1.29596800	0.51163600	1.93710100
C	-1.33618800	1.38761300	3.02882200
C	-2.59853200	1.79236900	3.47285200
C	-3.75815600	1.32157600	2.85422300
H	-4.58917900	0.09634100	1.29807900
H	-2.68622900	2.47592900	4.31064000
H	-4.73055400	1.64228500	3.21694300
C	-0.00351600	1.78473900	3.67851900
C	1.03110100	1.90808900	2.55183300
C	0.94093800	1.01081200	1.48216100
C	2.09245700	2.81846700	2.53078000
C	1.83048800	0.98956700	0.40183200
C	3.02045200	2.80888000	1.48819200
H	2.20570900	3.53848200	3.33412000
C	2.89427400	1.90360200	0.43426000
H	3.84571000	3.51525600	1.49466800
H	3.61468700	1.92016800	-0.37545900
O	-0.07729700	0.08049200	1.45515200
C	-0.12496200	3.08420900	4.49227400
H	-0.44090400	3.92705400	3.86843200
H	-0.84712200	2.96621200	5.30598700
H	0.83101800	3.33953700	4.95962900
C	0.44109700	0.63852100	4.63243200
H	1.40651500	0.87980600	5.09191500
H	-0.29859300	0.49888400	5.42920800
H	0.54731700	-0.30792800	4.09365300
P	1.49087700	-0.19044600	-0.99311900
P	-2.22116800	-1.04273100	-0.22292200
C	-1.59218800	-1.55890800	-3.18987800
N	-2.20392100	-2.42429400	-3.71681500
Ni	-0.68176500	-0.60794500	-1.93277700

C	-1.98379200	-2.74071800	0.47667700
C	-2.00766200	-3.83057500	-0.41334200
C	-1.75210600	-2.98121300	1.83732200
C	-1.81249000	-5.12843100	0.05872700
H	-2.18917700	-3.66179100	-1.47120700
C	-1.54454300	-4.28241600	2.30256100
H	-1.74008300	-2.15698300	2.54287700
C	-1.57584500	-5.35902400	1.41670400
H	-1.84778000	-5.96216000	-0.63814900
H	-1.36542400	-4.45110900	3.36130500
H	-1.42136500	-6.37126300	1.78122800
C	-3.96042500	-1.09477900	-0.84969300
C	-4.90949000	-2.01710700	-0.38468100
C	-4.35262400	-0.14436300	-1.80340400
C	-6.21995700	-1.98876600	-0.86669300
H	-4.62616000	-2.76337100	0.35094800
C	-5.66334900	-0.11030100	-2.27856300
H	-3.62429900	0.56412000	-2.18702300
C	-6.59987000	-1.03546400	-1.81287600
H	-6.94243800	-2.71470300	-0.50277500
H	-5.94770500	0.62841600	-3.02292200
H	-7.61869100	-1.01745100	-2.19066800
C	2.16931100	-1.78088500	-0.33814600
C	1.62857100	-2.98209200	-0.82081100
C	3.20178600	-1.83513000	0.61170000
C	2.11438300	-4.21128900	-0.37102900
H	0.81261000	-2.95235100	-1.53812600
C	3.68470900	-3.06422000	1.06238800
H	3.62794100	-0.91564900	1.00214600
C	3.14310400	-4.25450400	0.57090500
H	1.67689400	-5.13222500	-0.74606100
H	4.48338500	-3.09182000	1.79915600
H	3.51770100	-5.21081200	0.92636400
C	2.77166800	0.36480300	-2.20568700
C	2.55565400	1.58637100	-2.86718200
C	3.90923700	-0.38575800	-2.53096400
C	3.45962900	2.04805000	-3.82286200
H	1.67080900	2.17435000	-2.63971400
C	4.80754800	0.07166600	-3.49921800
H	4.09631400	-1.33232700	-2.03463300
C	4.58682600	1.28711400	-4.14657500
H	3.27727200	2.99477500	-4.32434200
H	5.67951500	-0.52738600	-3.74762200
H	5.28355000	1.63787100	-4.90275600

H	-1.79754700	1.17114300	-3.52900900
O	1.88515400	-1.53270600	-6.84378600
O	2.87213700	-2.75665200	-8.47176900
O	-2.40968200	-0.39018400	-7.82144000
O	-0.31291700	-0.47964900	-6.98514500
N	-0.16273200	-2.84478000	-6.59107100
C	1.92478600	-2.48268700	-7.77602200
C	0.77579100	-0.94608600	-4.65305200
C	0.56761300	-3.19147100	-7.85173400
C	-1.50965900	-0.99158000	-7.28642800
C	-0.01023300	-3.93258600	-5.58650900
C	-1.58148300	-2.45503200	-6.84232500
B	0.57087100	-1.36106200	-6.20226400
H	1.18745100	-1.79200700	-4.08897500
H	1.60396500	-0.22535100	-4.70541200
H	0.01990500	-2.80385400	-8.71542800
H	0.68100100	-4.27129700	-7.96749800
H	-0.43574700	-4.86003500	-5.98351000
H	-0.53607300	-3.64666500	-4.67643400
H	1.05449600	-4.07786500	-5.38665700
H	-2.13047100	-2.51799100	-5.89545600
H	-2.05779100	-3.08924000	-7.59394500
C	-0.34313000	-0.29637800	-3.86601600
C	-0.92385900	0.89686600	-4.12441300
C	-0.51459000	1.93649600	-5.14137900
H	-1.14838600	1.83487400	-6.03443700
H	0.51113000	1.75937100	-5.48516800
C	-0.64714400	3.37144800	-4.60208100
H	-1.68072100	3.53719300	-4.26233500
H	-0.01412400	3.49415300	-3.71035400
C	-0.27897100	4.44094200	-5.63841500
H	-0.91340800	4.31379700	-6.52641100
H	0.75330800	4.27524000	-5.97886500
C	-0.41920200	5.87165200	-5.10761000
H	-0.14843400	6.61043000	-5.87087100
H	-1.45017700	6.07892900	-4.79473400
H	0.22886200	6.03860000	-4.23783800

TS-2a

Zero-point correction = 0.918738 (Hartree/Particle)

Thermal correction to Energy = 0.977876

Thermal correction to Enthalpy = 0.978821

Thermal correction to Gibbs Free Energy = 0.819845

Sum of electronic and zero-point Energies = -3373.883012

Sum of electronic and thermal Energies = -3373.823873
Sum of electronic and thermal Enthalpies = -3373.822929
Sum of electronic and thermal Free Energies = -3373.981904

SCF Done: E(RM06) = -3375.38723087

C	-2.65500200	0.48015300	2.61381000
C	-1.54314300	-0.10268700	1.98558300
C	-0.31699200	-0.01851400	2.65452500
C	-0.14519700	0.62389200	3.88833300
C	-1.27504900	1.20919200	4.46615000
C	-2.51997700	1.13314900	3.83753700
H	-3.62570100	0.43416200	2.13240400
H	-1.19331100	1.72528900	5.41693400
H	-3.38886800	1.58766900	4.30509100
C	1.25088100	0.58278700	4.52431000
C	2.26756100	0.70583100	3.38200000
C	1.96391500	0.07135600	2.17155300
C	3.49410400	1.37138200	3.46507000
C	2.79983200	0.09160900	1.04921200
C	4.37156400	1.38590700	2.37962300
H	3.77481700	1.88166100	4.38044400
C	4.02956600	0.75492200	1.18387200
H	5.32438500	1.90110300	2.46288000
H	4.71274800	0.79729400	0.34323100
O	0.77041700	-0.60846900	2.04307600
C	1.43621600	1.68471100	5.58067900
H	1.31494900	2.68499400	5.15146100
H	0.71311100	1.56704600	6.39364100
H	2.42964500	1.62178400	6.03544300
C	1.44075000	-0.80115700	5.20991300
H	2.44494600	-0.87531700	5.64312100
H	0.70508600	-0.93146800	6.01207600
H	1.31628200	-1.61937500	4.49454400
P	2.19673100	-0.68468400	-0.52999500
P	-1.63135000	-0.94868100	0.33445100
C	-0.97660500	-1.55794300	-2.67523000
N	-1.57574300	-2.37547800	-3.28151600
Ni	-0.02511700	-0.70875400	-1.35659300
C	-2.04326300	-2.69156800	0.81684600
C	-2.23511500	-3.65245800	-0.19336300
C	-2.13978200	-3.09486800	2.15786200
C	-2.52696600	-4.97596600	0.13991900
H	-2.16137200	-3.37089700	-1.23914200

C	-2.41956000	-4.42361000	2.48427500
H	-2.00034800	-2.37377000	2.95590000
C	-2.61662200	-5.36826400	1.47709500
H	-2.67972300	-5.70195700	-0.65452300
H	-2.48690300	-4.71559300	3.52931300
H	-2.83828900	-6.40157700	1.73172500
C	-3.21994500	-0.24246900	-0.30330000
C	-4.42133100	-0.95755400	-0.37681000
C	-3.19666400	1.09128600	-0.74792300
C	-5.57239400	-0.35176600	-0.89047700
H	-4.46292500	-1.98840700	-0.04041000
C	-4.34623100	1.69927200	-1.25028100
H	-2.27353300	1.66401300	-0.70279500
C	-5.53876400	0.97313600	-1.32576900
H	-6.49618300	-0.92186500	-0.94843000
H	-4.29998400	2.73088700	-1.58961800
H	-6.43619600	1.43910000	-1.72459300
C	2.68671700	-2.45686700	-0.31159200
C	1.96463400	-3.43535400	-1.01403900
C	3.74229100	-2.86152200	0.52104600
C	2.29875700	-4.78580900	-0.89485500
H	1.13101200	-3.14066800	-1.64629400
C	4.07195700	-4.21235200	0.64176100
H	4.30605200	-2.12095300	1.08045000
C	3.35218900	-5.17704300	-0.06708500
H	1.72679700	-5.52973700	-1.44266200
H	4.89014600	-4.51073900	1.29237400
H	3.60792300	-6.22890000	0.03104000
C	3.45982100	-0.00818200	-1.70059600
C	3.31801300	1.33624300	-2.08523000
C	4.52853100	-0.75158400	-2.21956900
C	4.23900800	1.93155700	-2.94673900
H	2.48412900	1.92628600	-1.71693900
C	5.43911900	-0.16025000	-3.10025300
H	4.65426400	-1.79228000	-1.93810600
C	5.30150300	1.18143100	-3.45953700
H	4.12051100	2.97977400	-3.20711600
H	6.26064800	-0.75039400	-3.49862800
H	6.01853700	1.64076400	-4.13537100
H	-1.29214300	1.16078000	-2.75892500
O	1.20425500	3.79039000	-3.11778800
O	2.66548100	5.50120200	-2.89119700
O	-3.21543900	4.86363500	-2.84672500
O	-1.22286600	3.79099600	-2.83963700

N	-0.25162800	4.80225600	-4.81032400
C	1.62954400	5.03907300	-3.30122500
C	-0.16305800	2.03900000	-4.42587200
C	0.60208600	5.82593700	-4.12871300
C	-2.15513900	4.58613100	-3.35346400
C	0.22840700	4.55107800	-6.19494300
C	-1.70582400	5.10678600	-4.72953000
B	-0.08452600	3.47967600	-3.73800400
H	-0.98962100	2.02543200	-5.16135700
H	0.75377900	1.82442400	-4.98745500
H	-0.00959500	6.42625100	-3.44915500
H	1.08607500	6.49289300	-4.84494200
H	0.09487900	5.44762900	-6.80824700
H	-0.33146300	3.71969400	-6.62370400
H	1.28715800	4.28519000	-6.16108300
H	-2.23242400	4.54838000	-5.50917500
H	-1.92040100	6.17056300	-4.85564800
C	-0.44118700	0.95775700	-3.40467900
C	0.21065400	-0.21661600	-3.24199800
C	1.25960200	-0.76902600	-4.18666400
H	1.77150800	-1.61621300	-3.71804500
H	2.03174800	-0.00387200	-4.34676400
C	0.70390400	-1.22691600	-5.55022200
H	-0.08507400	-1.96767800	-5.37770500
H	0.22484700	-0.37648900	-6.05599100
C	1.78737800	-1.81575300	-6.46273200
H	2.25932200	-2.67078300	-5.95764400
H	2.58668800	-1.07468500	-6.61293400
C	1.24593100	-2.26640300	-7.82397300
H	2.03853200	-2.68975600	-8.45257900
H	0.46823400	-3.03053900	-7.70553300
H	0.80000400	-1.42607700	-8.37143300

TS-rot

Zero-point correction = 0.918195 (Hartree/Particle)

Thermal correction to Energy = 0.977358

Thermal correction to Enthalpy = 0.978303

Thermal correction to Gibbs Free Energy = 0.819592

Sum of electronic and zero-point Energies = -3373.892330

Sum of electronic and thermal Energies = -3373.833166

Sum of electronic and thermal Enthalpies = -3373.832222

Sum of electronic and thermal Free Energies = -3373.990933

SCF Done: E(RM06) = -3375.39380049

C	-3.81105300	0.43934800	0.91497800
C	-2.50926200	-0.05168000	0.74418000
C	-1.48089300	0.58104200	1.46010100
C	-1.69766300	1.64165600	2.34831900
C	-3.01032100	2.11004100	2.47381000
C	-4.05539700	1.51976900	1.76234800
H	-4.63211000	-0.01969400	0.37565200
H	-3.22755800	2.93863100	3.13920000
H	-5.06727600	1.89777600	1.87620000
C	-0.50874300	2.14651900	3.17667700
C	0.74517000	2.05025000	2.29882600
C	0.83501500	0.99482800	1.38485100
C	1.84245800	2.91465800	2.38464200
C	1.94217200	0.78022900	0.54969000
C	2.97622100	2.71490400	1.59616500
H	1.82040800	3.74923700	3.07698300
C	3.02691800	1.65839200	0.68704800
H	3.82226700	3.39026600	1.68720800
H	3.90447800	1.52574400	0.06347800
O	-0.20613900	0.09355500	1.26416100
C	-0.73644900	3.57628900	3.69792300
H	-0.86943000	4.29086100	2.87873900
H	-1.62001000	3.61949700	4.34183300
H	0.10842700	3.90581000	4.30993900
C	-0.32866800	1.19408400	4.39453900
H	0.53103400	1.50695300	4.99840600
H	-1.22359000	1.21072200	5.02751700
H	-0.15885500	0.16289200	4.06925200
P	1.80807900	-0.53926200	-0.74445900
P	-2.08070000	-1.43436000	-0.40925000
C	-0.56168800	-2.56895000	-2.98085100
N	-0.57560700	-3.61821600	-3.50757700
Ni	-0.52180200	-0.92972000	-2.13494700
C	-1.79333600	-2.87257700	0.71186400
C	-1.37220700	-4.08244400	0.13457700
C	-2.01016600	-2.81595000	2.09615800
C	-1.18359400	-5.21175800	0.93110100
H	-1.19227300	-4.14189700	-0.93452100
C	-1.81009700	-3.94767100	2.88992100
H	-2.34205700	-1.89214400	2.55920700
C	-1.39920500	-5.14804400	2.30938600
H	-0.86091400	-6.14196700	0.47129300
H	-1.98057900	-3.88889400	3.96184600

H	-1.24647300	-6.02874400	2.92772100
C	-3.70601400	-1.83361600	-1.18523500
C	-4.66075300	-2.65389800	-0.56284100
C	-3.99238600	-1.29228600	-2.44724800
C	-5.87816100	-2.91872200	-1.19186400
H	-4.45049800	-3.09113500	0.40861700
C	-5.21087800	-1.55619100	-3.07577400
H	-3.25719300	-0.67111900	-2.95016700
C	-6.15456500	-2.37053500	-2.44709000
H	-6.60834200	-3.55811800	-0.70239800
H	-5.39668100	-1.13640700	-4.05930300
H	-7.10144100	-2.58438900	-2.93630600
C	2.33500200	-2.07173300	0.14160200
C	2.12380900	-3.30122200	-0.50548600
C	2.94769300	-2.06600800	1.40378700
C	2.53565100	-4.49378600	0.09104600
H	1.63238200	-3.32879100	-1.47410600
C	3.34375100	-3.26245700	2.00461900
H	3.12152500	-1.12531900	1.91748900
C	3.14399100	-4.47815600	1.34776000
H	2.37006300	-5.43585800	-0.42484300
H	3.81452900	-3.24242700	2.98430800
H	3.45714500	-5.40832000	1.81479500
C	3.28193800	-0.16124500	-1.80156100
C	3.20863500	0.95374300	-2.65600900
C	4.44314700	-0.94794900	-1.82620100
C	4.27098400	1.27952500	-3.49855800
H	2.31082600	1.56432900	-2.66643900
C	5.50196600	-0.62735800	-2.68016800
H	4.52519500	-1.81508400	-1.17941300
C	5.42152700	0.48673100	-3.51591300
H	4.19588100	2.14730000	-4.14882800
H	6.39262900	-1.25054400	-2.68618500
H	6.24626300	0.73489300	-4.17866300
H	-0.93049100	0.96810900	-2.15475800
O	0.42697500	0.12622600	-7.49979900
O	0.40983000	-0.12992300	-9.74972200
O	-3.75435100	-0.18744800	-5.72075400
O	-1.59134900	0.29857500	-6.14619600
N	-0.85535600	-1.86157700	-6.89241600
C	0.03776000	-0.43879100	-8.64559800
C	0.66528100	-0.37738400	-5.00512500
C	-0.97391900	-1.55475900	-8.35487800
C	-2.62562500	-0.52562900	-5.99630700

C	0.03044000	-3.04235900	-6.67952600
C	-2.18058600	-1.97579600	-6.21906800
B	-0.28223400	-0.37590100	-6.31937100
H	1.20023200	-1.32755600	-4.90047500
H	1.44799600	0.36590900	-5.21071400
H	-1.97826800	-1.18356400	-8.57806500
H	-0.78549500	-2.43857800	-8.96723400
H	-0.38253500	-3.90540200	-7.21111000
H	0.08794000	-3.26855500	-5.61416000
H	1.02116100	-2.80982500	-7.07805600
H	-2.04026700	-2.46962700	-5.25212300
H	-2.90304200	-2.54027100	-6.81348500
C	0.00850300	-0.02357900	-3.70968700
C	-0.52398400	1.08106000	-3.20621900
C	-0.78486400	2.49116600	-3.71575900
H	-0.78560000	3.17620100	-2.85607500
H	-1.80457500	2.52074100	-4.12737500
C	0.19579400	3.01798900	-4.77243200
H	1.22249800	2.96482100	-4.38235400
H	0.16415900	2.38127900	-5.66298100
C	-0.11414500	4.46386700	-5.18494000
H	-0.09352800	5.11101100	-4.29592300
H	-1.14010400	4.51342300	-5.57573400
C	0.85951500	5.00599600	-6.23675900
H	0.60970800	6.03510000	-6.51985800
H	1.89038900	5.00530500	-5.86056700
H	0.83935400	4.39393100	-7.14633000

PC1

Zero-point correction = 0.321390 (Hartree/Particle)
 Thermal correction to Energy = 0.341653
 Thermal correction to Enthalpy = 0.342597
 Thermal correction to Gibbs Free Energy = 0.270382
 Sum of electronic and zero-point Energies = -941.862270
 Sum of electronic and thermal Energies = -941.842007
 Sum of electronic and thermal Enthalpies = -941.841063
 Sum of electronic and thermal Free Energies = -941.913278

SCF Done: E(RM06) = -941.858155771

C	-0.87823900	-2.18202100	-3.70550500
N	-0.99597800	-3.27616100	-3.31900100
H	-2.55028900	-0.28494000	-3.55304700
O	1.76731300	-0.54927500	-7.29442000

O	3.05449200	-1.10934000	-9.07160100
O	-2.67004300	-1.34013300	-7.98422200
O	-0.67696200	-0.54793700	-7.26262100
N	0.50925800	-2.63818100	-7.08544300
C	2.14185900	-1.32421200	-8.31698800
C	0.62065100	-0.67936200	-5.02915900
C	1.22256200	-2.55021600	-8.40264900
C	-1.55839600	-1.50909400	-7.55171100
C	1.19302400	-3.61226600	-6.18929100
C	-0.95178600	-2.88755000	-7.24313700
B	0.56345700	-1.00798600	-6.60864700
H	1.43244200	-1.22879900	-4.53666000
H	0.91189500	0.37661400	-4.97558400
H	0.49847100	-2.38834600	-9.20593500
H	1.78393200	-3.46162400	-8.61658000
H	1.16508400	-4.60939800	-6.63893700
H	0.69425500	-3.63497300	-5.22082400
H	2.23237300	-3.30116800	-6.06094300
H	-1.35518000	-3.26103100	-6.29729200
H	-1.16843000	-3.61326800	-8.03036000
C	-0.67424400	-0.87339600	-4.26213000
C	-1.66858000	0.02889200	-4.11159900
C	-1.70774600	1.43016200	-4.64049800
H	-2.41476800	1.45421800	-5.48434200
H	-0.73834300	1.72286000	-5.05742400
C	-2.15859500	2.45332100	-3.58036600
H	-3.13361600	2.14894300	-3.17281400
H	-1.45531900	2.43716500	-2.73600200
C	-2.26155800	3.87927000	-4.13584400
H	-2.95999000	3.88620000	-4.98443500
H	-1.28610900	4.18098300	-4.54237400
C	-2.71673400	4.89956200	-3.08789500
H	-2.77955800	5.90678700	-3.51468400
H	-3.70611300	4.64442300	-2.68890300
H	-2.01901000	4.93902600	-2.24238500

PC2

Zero-point correction = 0.321451 (Hartree/Particle)
 Thermal correction to Energy = 0.341746
 Thermal correction to Enthalpy = 0.342691
 Thermal correction to Gibbs Free Energy = 0.270683
 Sum of electronic and zero-point Energies = -941.858313
 Sum of electronic and thermal Energies = -941.838018
 Sum of electronic and thermal Enthalpies = -941.837074

Sum of electronic and thermal Free Energies = -941.909081

SCF Done: E(RM06) = -941.856228972

O	0.99358000	3.51578900	-3.53985400
O	2.26340000	2.69523300	-5.22633800
O	-3.47280800	3.37977700	-4.40951600
O	-1.41938300	3.88489200	-3.60181600
N	-0.57202400	1.64391200	-3.32491000
C	1.29568800	2.65092100	-4.51271000
C	-0.24489900	3.61127000	-1.31408300
C	0.21006300	1.56802000	-4.60298000
C	-2.42047700	3.06031300	-3.91916400
C	-0.09343700	0.62172800	-2.35742200
C	-2.04488000	1.61644400	-3.54909800
B	-0.28727000	3.26428100	-2.89037400
H	0.62958700	3.13735500	-0.85062900
H	-0.05041600	4.69155400	-1.28303800
H	-0.44290600	1.79679500	-5.44972300
H	0.64116600	0.57628600	-4.75294200
H	-0.27713600	-0.38262100	-2.75064700
H	-0.61921900	0.74516900	-1.41095100
H	0.97792200	0.75952000	-2.19551400
H	-2.54498300	1.35134300	-2.61346100
H	-2.33705900	0.90404700	-4.32384400
C	-1.47416800	3.27288700	-0.52505200
C	-2.60602000	4.00250800	-0.39854100
C	-2.87234000	5.37412800	-0.98844500
H	-3.75231000	5.31086500	-1.64314000
H	-2.03704300	5.65919100	-1.63365900
C	-3.11126200	6.45677400	0.08111200
H	-3.94091500	6.15059200	0.73272700
H	-2.22403100	6.52988000	0.72564500
C	-3.42042200	7.83009600	-0.52833400
H	-4.30655200	7.74764300	-1.17304700
H	-2.59269300	8.13163900	-1.18566800
C	-3.65505200	8.91261000	0.53004600
H	-3.87566900	9.88094200	0.06697200
H	-4.49899500	8.65362100	1.18084200
H	-2.77222300	9.04145300	1.16816600
C	-3.66827200	3.43751000	0.39067700
N	-4.54279100	2.98922500	1.01567200
H	-1.45938200	2.31750200	0.00046700

8. X-ray crystal structure data

Crystal structure data for 1:

Experimental

Single crystals of $C_{13}H_{19}BN_2O_4$ **1** were colorless crystal. A suitable crystal was selected on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [1], the structure was solved with the SHELXT [2] structure solution program using Intrinsic Phasing and refined with the SHELXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J., Howard, J.A.K. & Puschmann, H. (2009), *J. Appl. Cryst.* 42, 339-341.
2. Sheldrick, G.M. (2015). *Acta Cryst.* A71, 3-8.
3. Sheldrick, G.M. (2015). *Acta Cryst.* C71, 3-8.

Crystal structure determination of 1

Crystal Data for $C_{13}H_{19}BN_2O_4$ ($M = 278.11$ g/mol): monoclinic, space group $P2_1/c$ (no. 14), $a = 7.1742(2)$ Å, $b = 20.2220(4)$ Å, $c = 10.1873(2)$ Å, $\beta = 100.812(2)^\circ$, $V = 1451.70(6)$ Å³, $Z = 4$, $T = 100.01(10)$ K, $\mu(\text{Cu K}\alpha) = 0.767$ mm⁻¹, $D_{\text{calc}} = 1.272$ g/cm³, 9189 reflections measured ($8.746^\circ \leq 2\theta \leq 151.094^\circ$), 2863 unique ($R_{\text{int}} = 0.0435$, $R_{\text{sigma}} = 0.0454$) which were used in all calculations. The final R_1 was 0.0451 ($I > 2\sigma(I)$) and wR_2 was 0.1254 (all data).

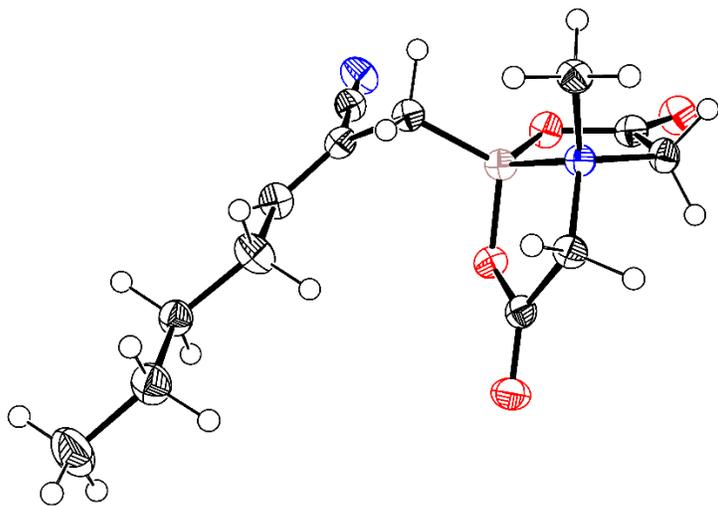


Fig. S1. Absolute configuration of **1** (CCDC 2375222).

Table S2 Crystal data and structure refinement for **1**.

Identification code	chenzh_230522_auto
Empirical formula	$C_{13}H_{19}BN_2O_4$
Formula weight	278.11
Temperature/K	100.01(10)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	7.1742(2)
$b/\text{\AA}$	20.2220(4)
$c/\text{\AA}$	10.1873(2)
$\alpha/^\circ$	90
$\beta/^\circ$	100.812(2)
$\gamma/^\circ$	90
Volume/ \AA^3	1451.70(6)

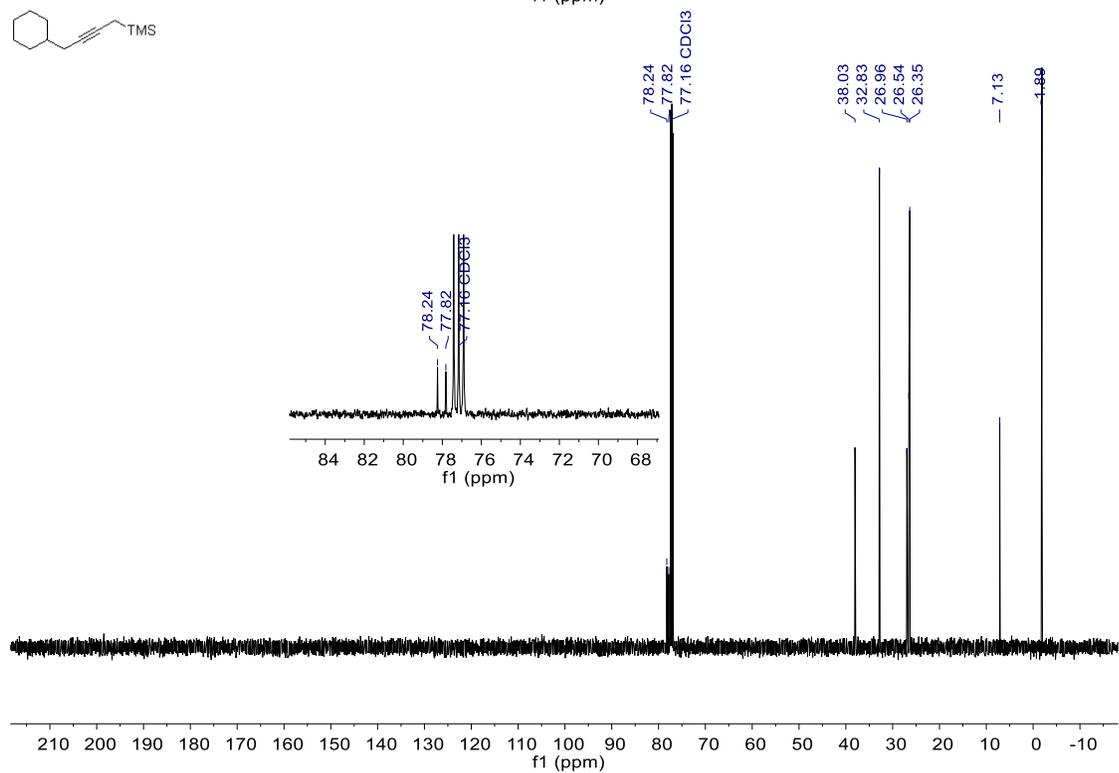
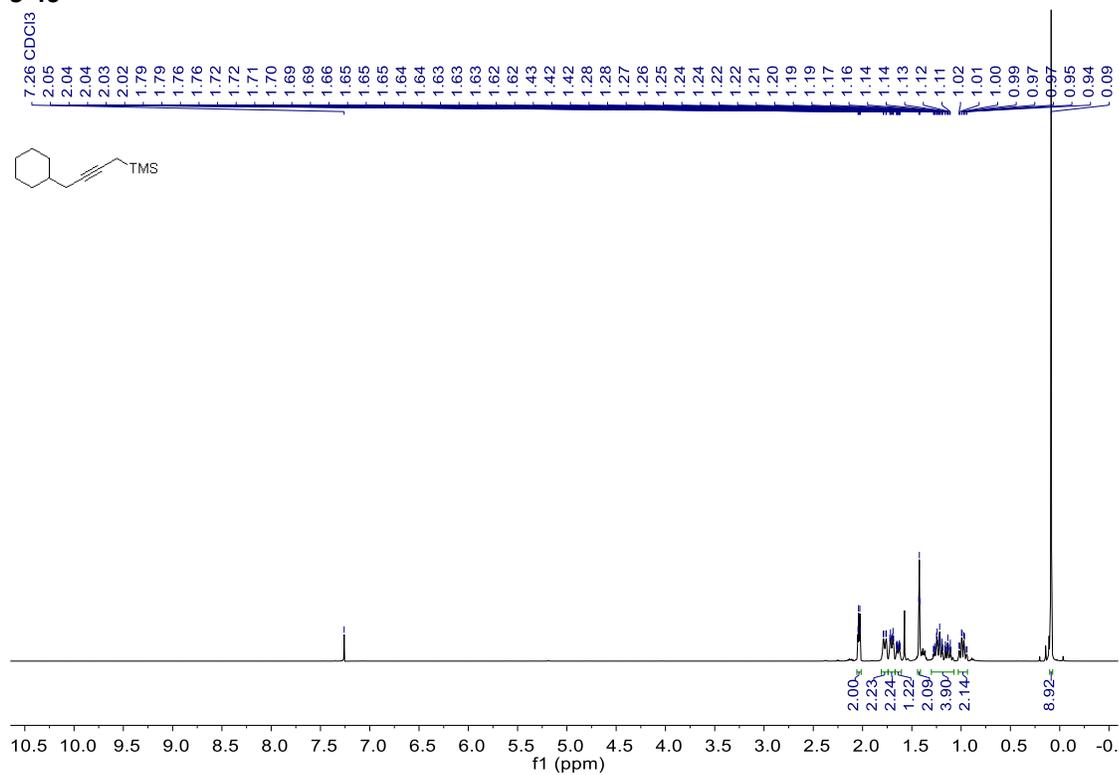
Z	4
ρ_{calc}mg/mm³	1.272
μ/mm⁻¹	0.767
F(000)	592.0
Crystal size/mm³	0.2 × 0.1 × 0.05
2θ range for data collection	8.746 to 151.094
Index ranges	-8 ≤ h ≤ 9, -9 ≤ k ≤ 25, -12 ≤ l ≤ 12
Reflections collected	9189
Independent reflections	2863 [R _{int} = 0.0435, R _{sigma} = 0.0454]
Data/restraints/parameters	2863/0/183
Goodness-of-fit on F²	1.066
Final R indexes [I ≥ 2σ (I)]	R ₁ = 0.0451, wR ₂ = 0.1204
Final R indexes [all data]	R ₁ = 0.0506, wR ₂ = 0.1254
Largest diff. peak/hole / e Å⁻³	0.29/-0.27

9. Reference

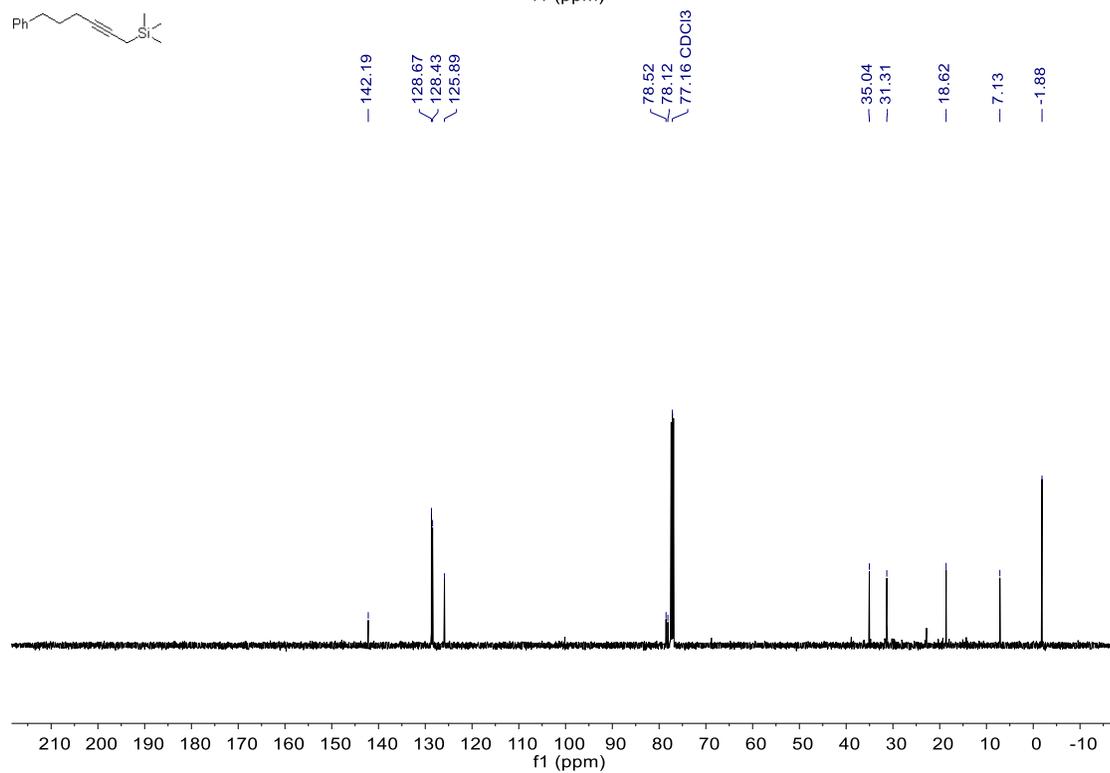
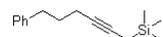
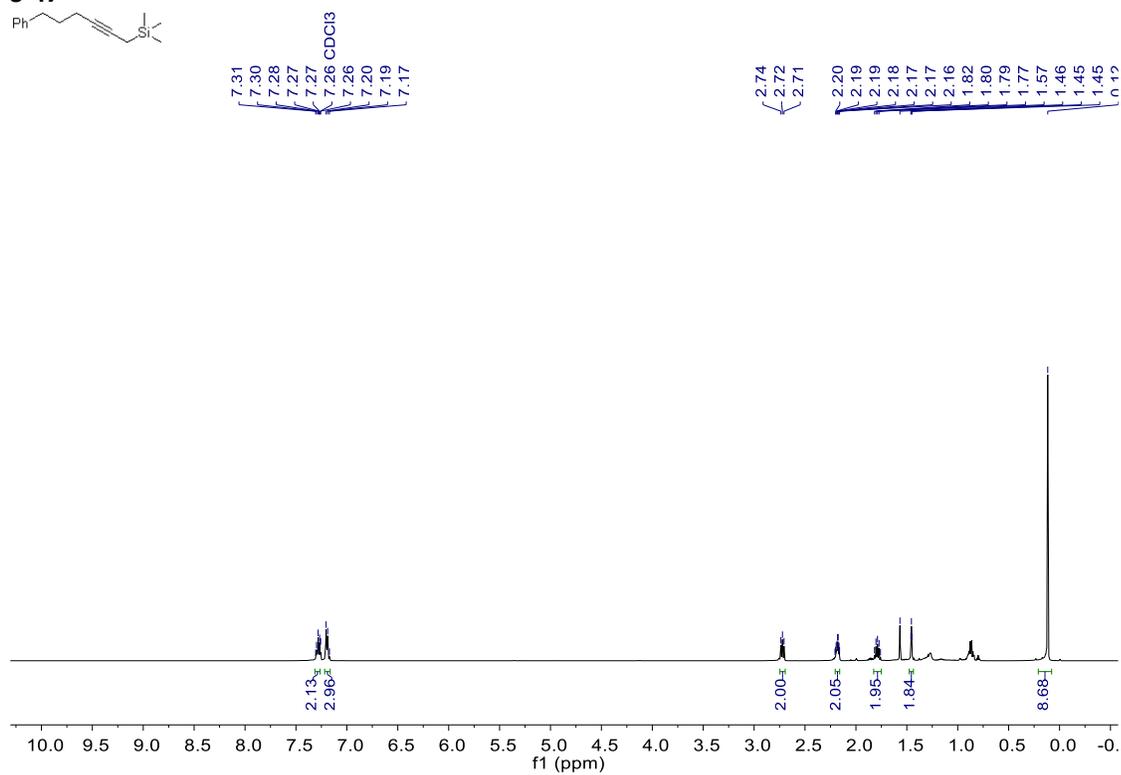
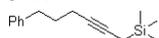
- [1] (a) Liu, L.-C.; Lin, S.; Xu, K.; Qian, J.; Wu, R.; Li, Q.; Wang, H., NHC-Au-Catalyzed Isomerization of Propargylic B(MIDA)s to Allenes and Double Isomerization of Alkynes to 1,3-Dienes. *Adv. Sci.* **2024**, *11* (21), 2308710; (b) Li, Y.; Chen, Z.-H.; Lin, S.; Liu, Y.; Qian, J.; Li, Q.; Huang, Z.-S.; Wang, H., Regioselective Electrophilic Addition to Propargylic B(MIDA)s Enabled by β -Boron Effect. *Adv. Sci.* **2023**, *10* (30), 2304282; (c) Chen, Z.-H.; Su, X.-X.; Li, Q.; Wu, J.-Q.; Ou, T.-M.; Wang, H., Synthesis of α -Boryl Ketones via Hydration or Oxidation of B(MIDA)-Decorated Alkynes. *Org. Lett.* **2023**, *25* (7), 1099-1103; (d) Liu, Y.; Chen, Z.-H.; Li, Y.; Qian, J.; Li, Q.; Wang, H., Boryl-Dictated Site-Selective Intermolecular Allylic and Propargylic C-H Amination. *J. Am. Chem. Soc.* **2022**, *144* (31), 14380-14387.
- [2] Corey, E. J.; Fuchs, P. L., A synthetic method for formyl \rightarrow ethynyl conversion (RCHO \rightarrow RC CH or RC CR'). *Tetrahedron Lett.* **1972**, *13* (36), 3769-3772.
- [3] Frisch, M. J. T., G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. Gaussian 09 Rev. D.01, Wallingford, CT, **2013**.
- [4] Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J., Ab Initio Calculation of Vibrational Absorption and Circular Dichroism Spectra Using Density Functional Force Fields. *J. Phys. Chem.* **1994**, *98* (45), 11623-11627.
- [5] Hay, P. J.; Wadt, W. R., Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. *J. Phys. Chem.* **1985**, *82* (1), 270-283.
- [6] Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120* (1), 215-241.
- [7] Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H., Energy-adjusted ab initio pseudopotentials for the first row transition elements. *J. Phys. Chem.* **1987**, *86* (2), 866-872.
- [8] Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113* (18), 6378-6396.

10. NMR spectrum of starting materials and products

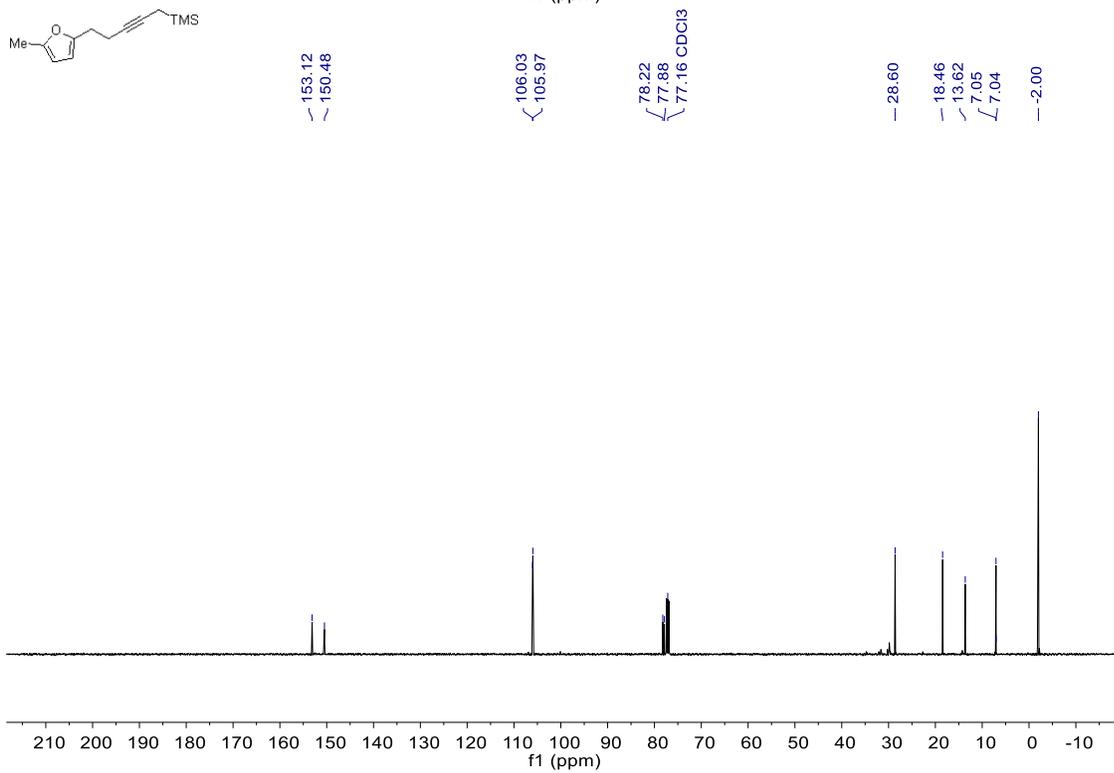
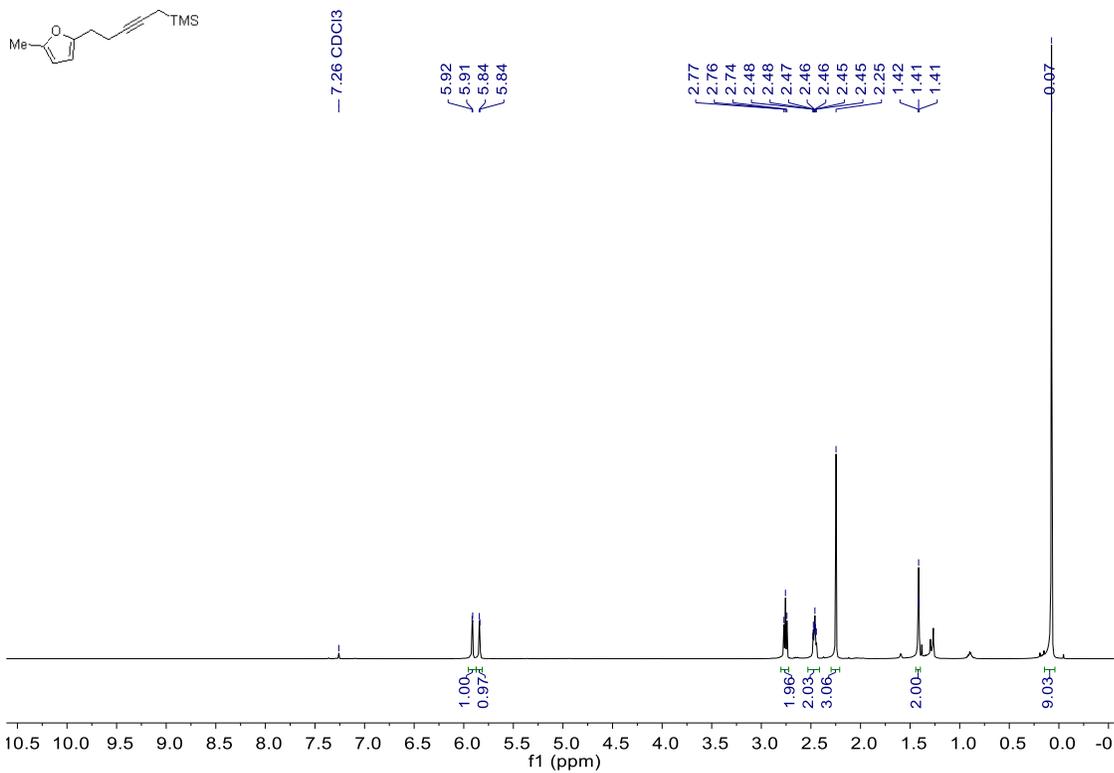
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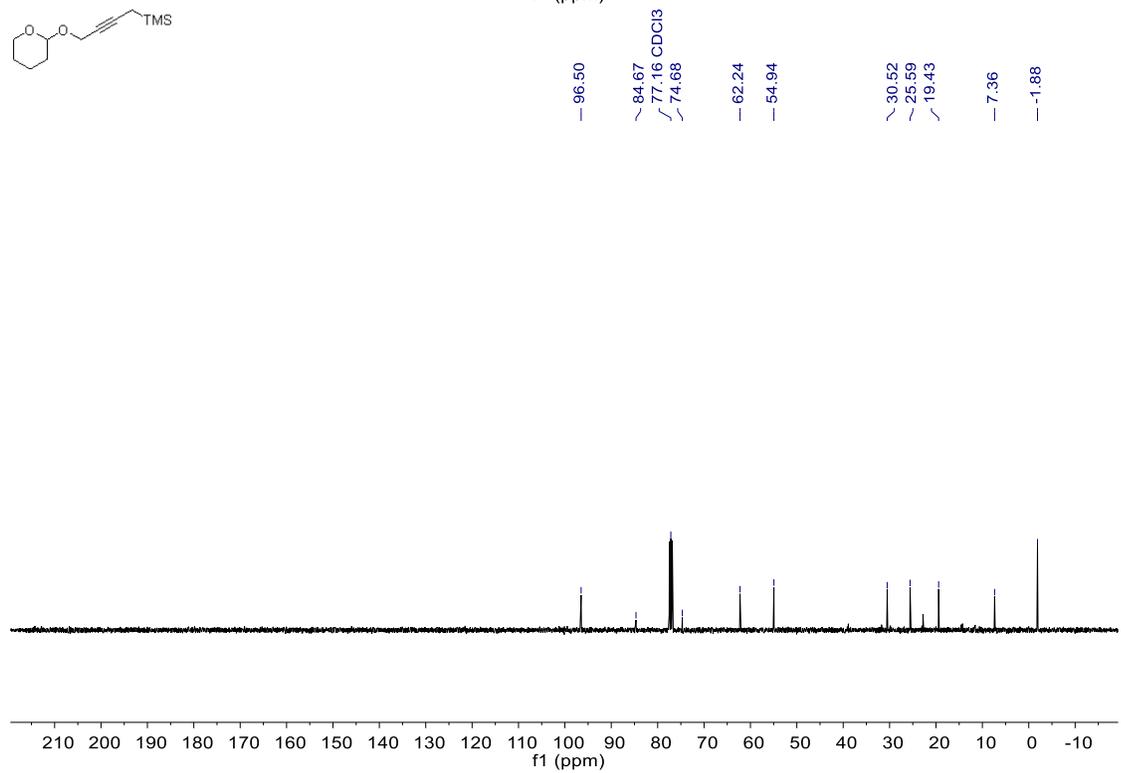
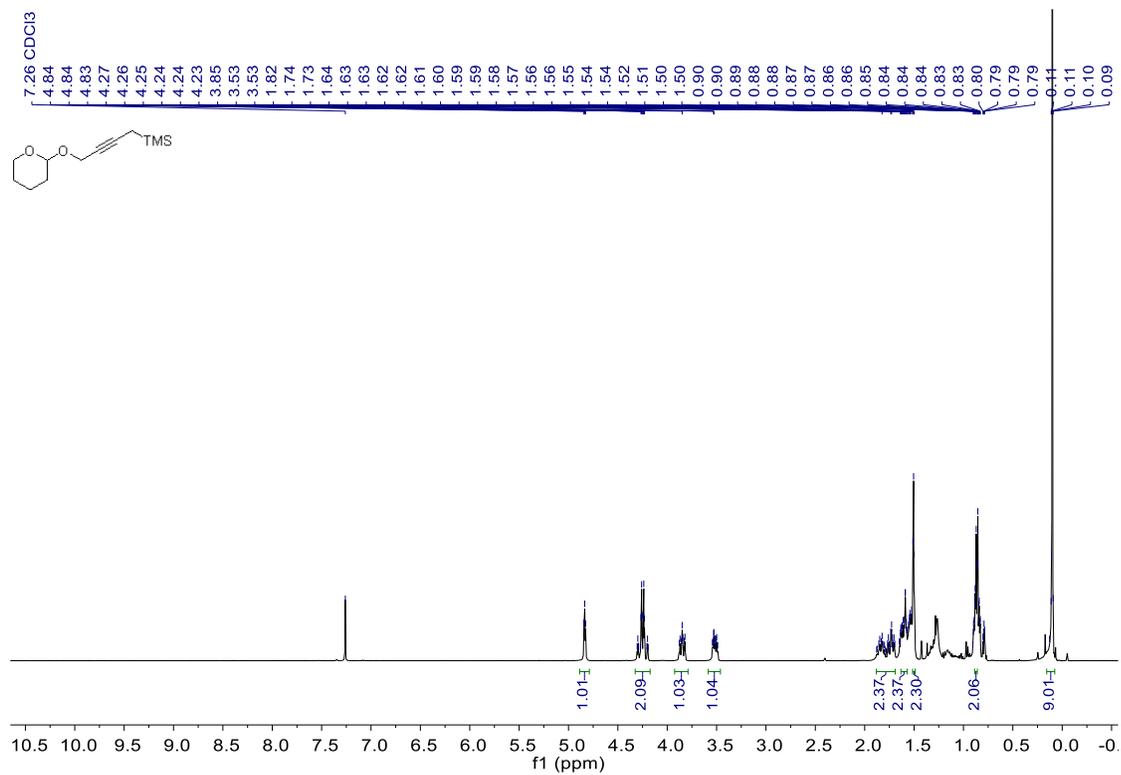
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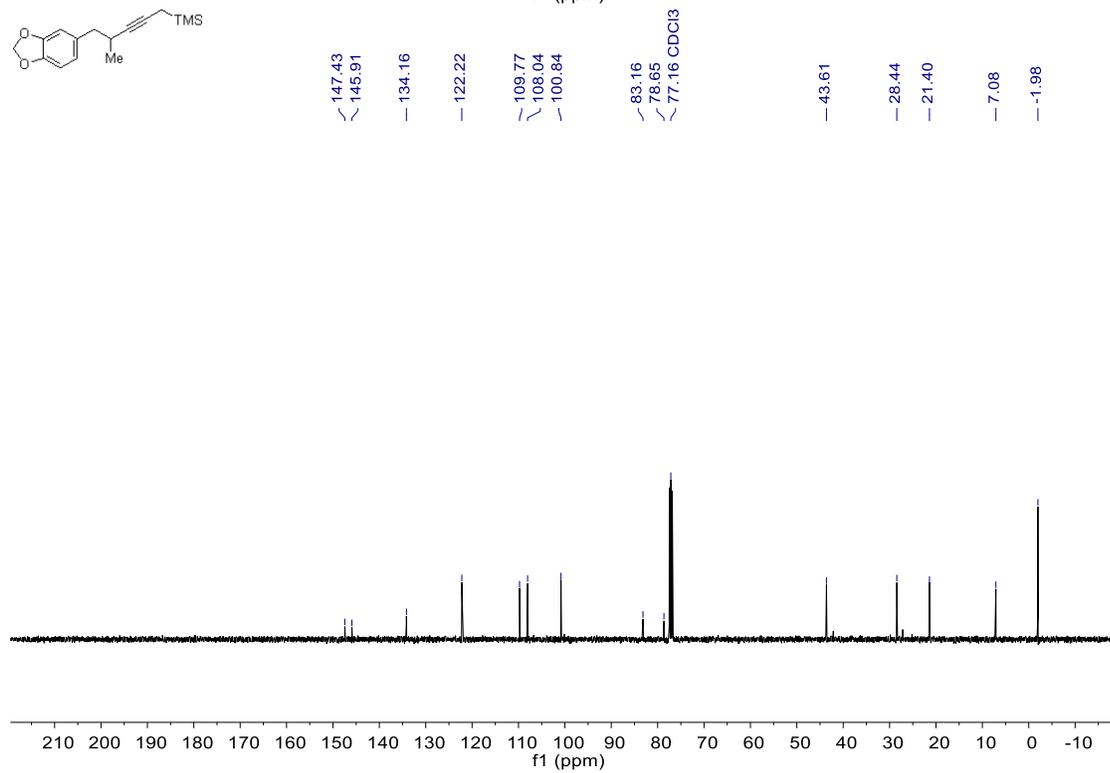
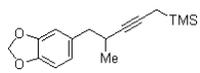
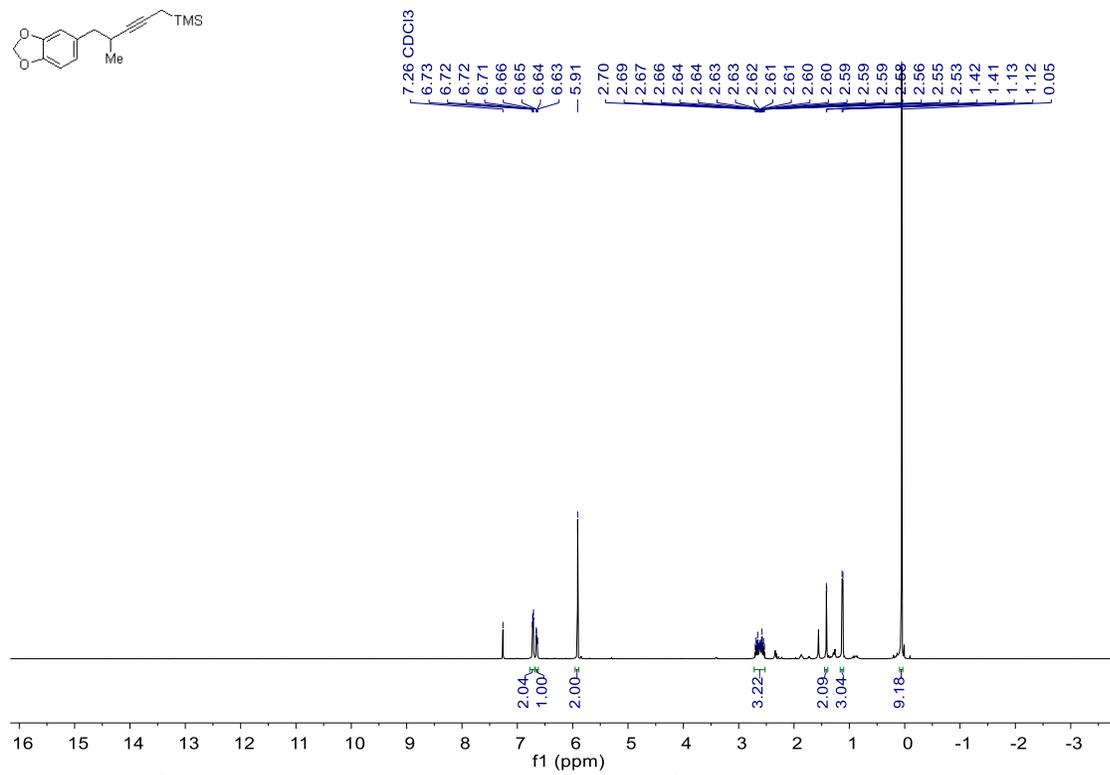
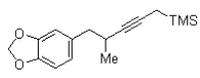
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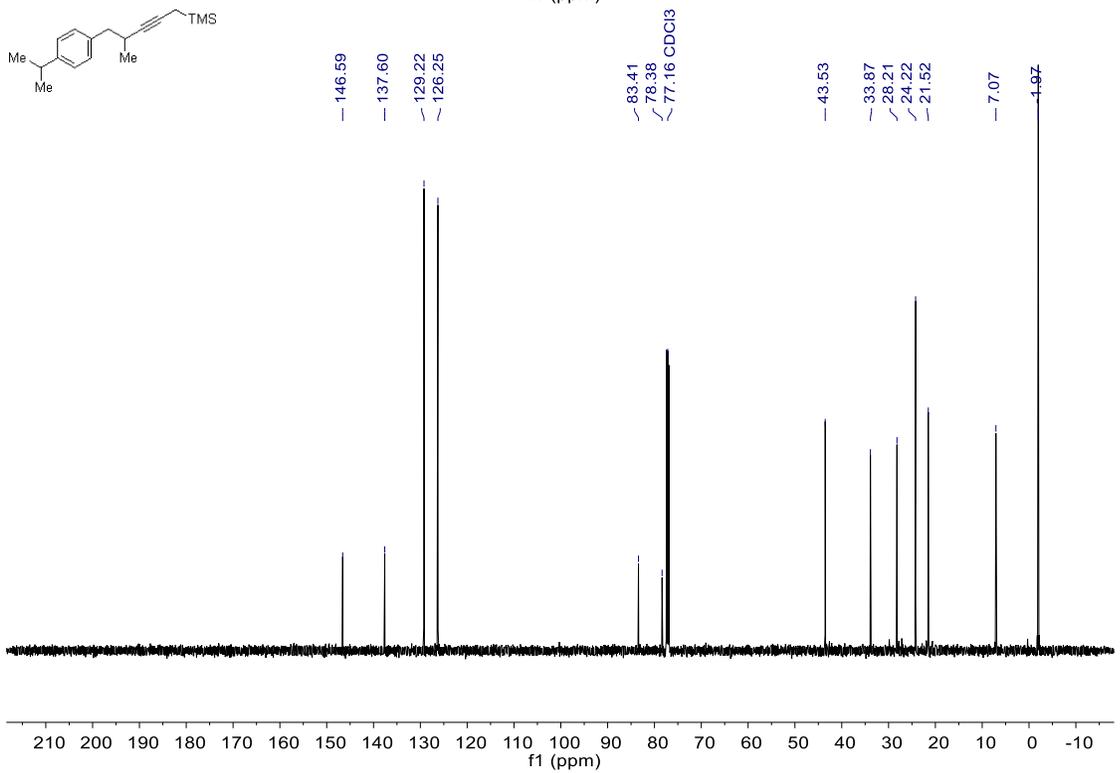
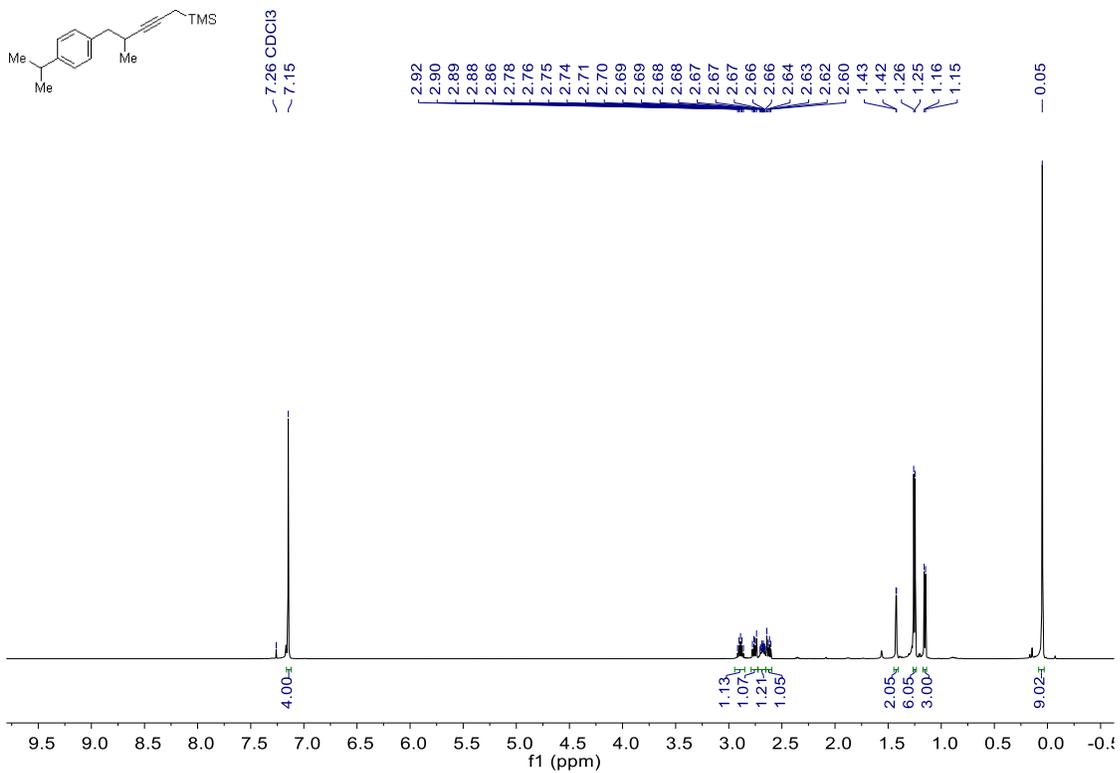
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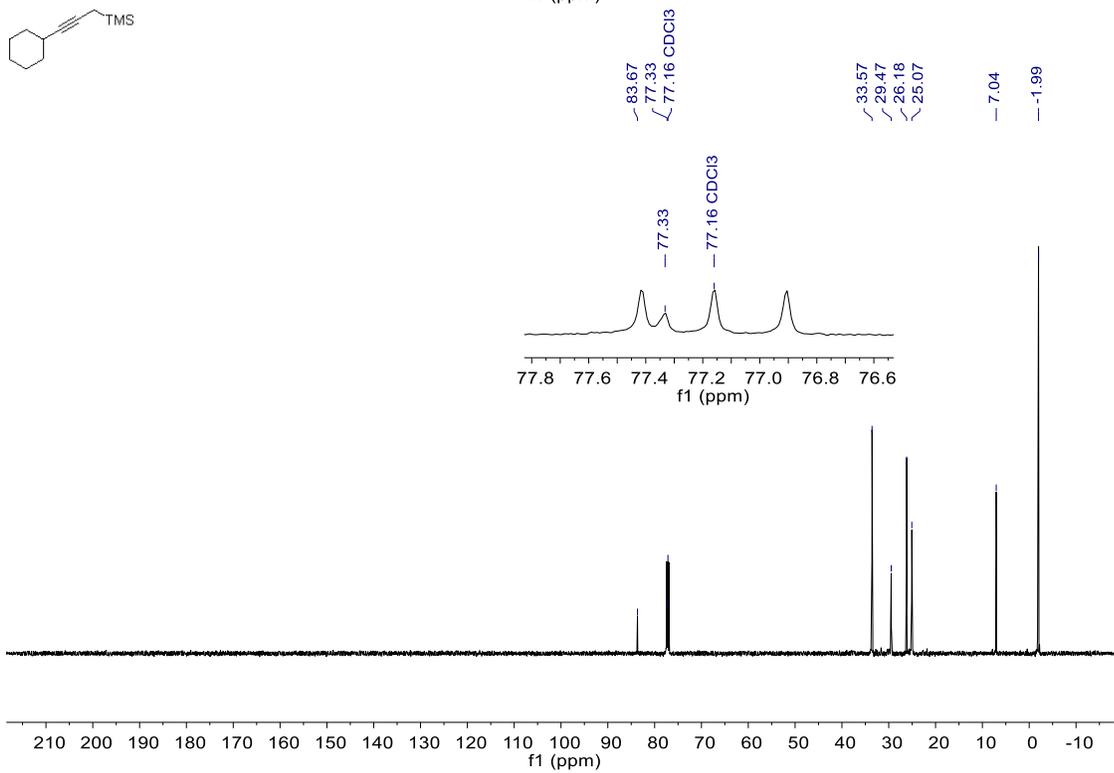
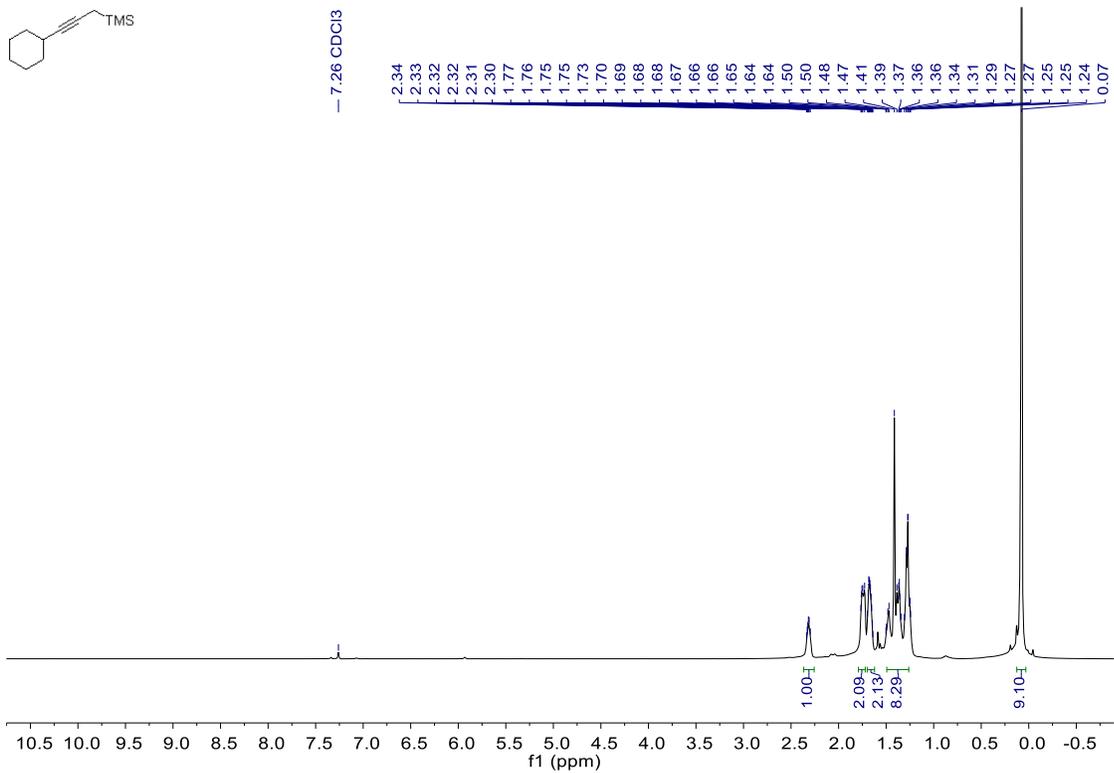
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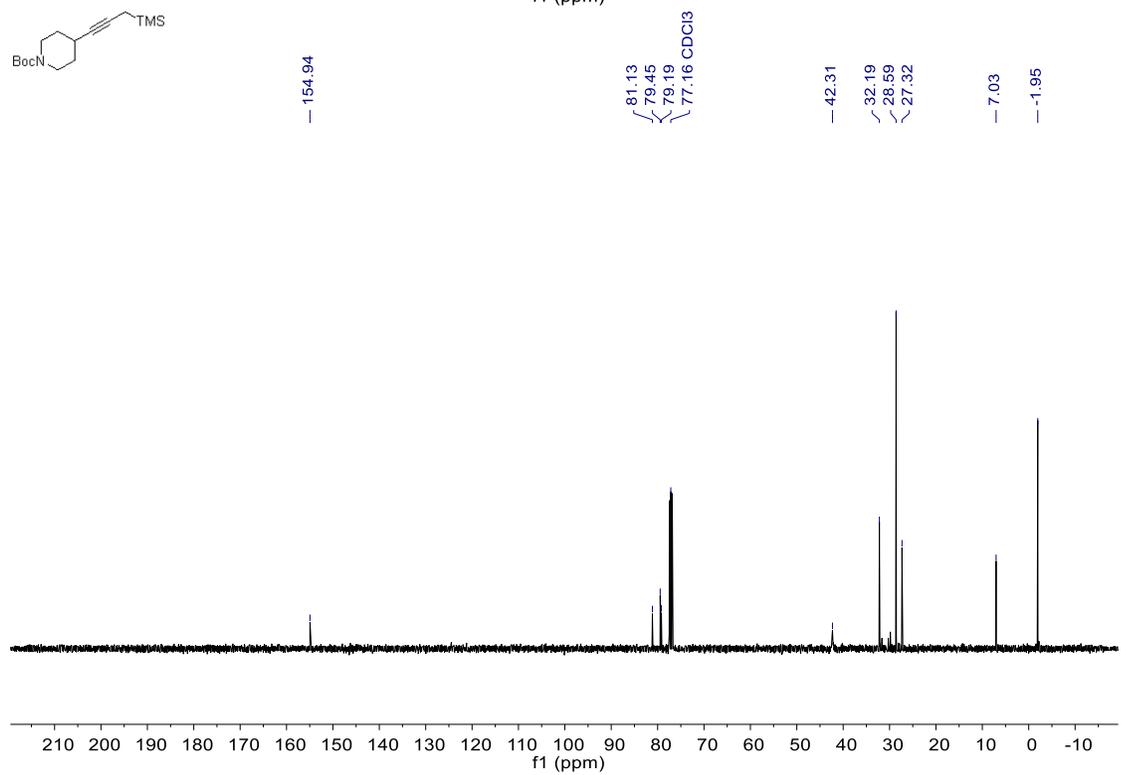
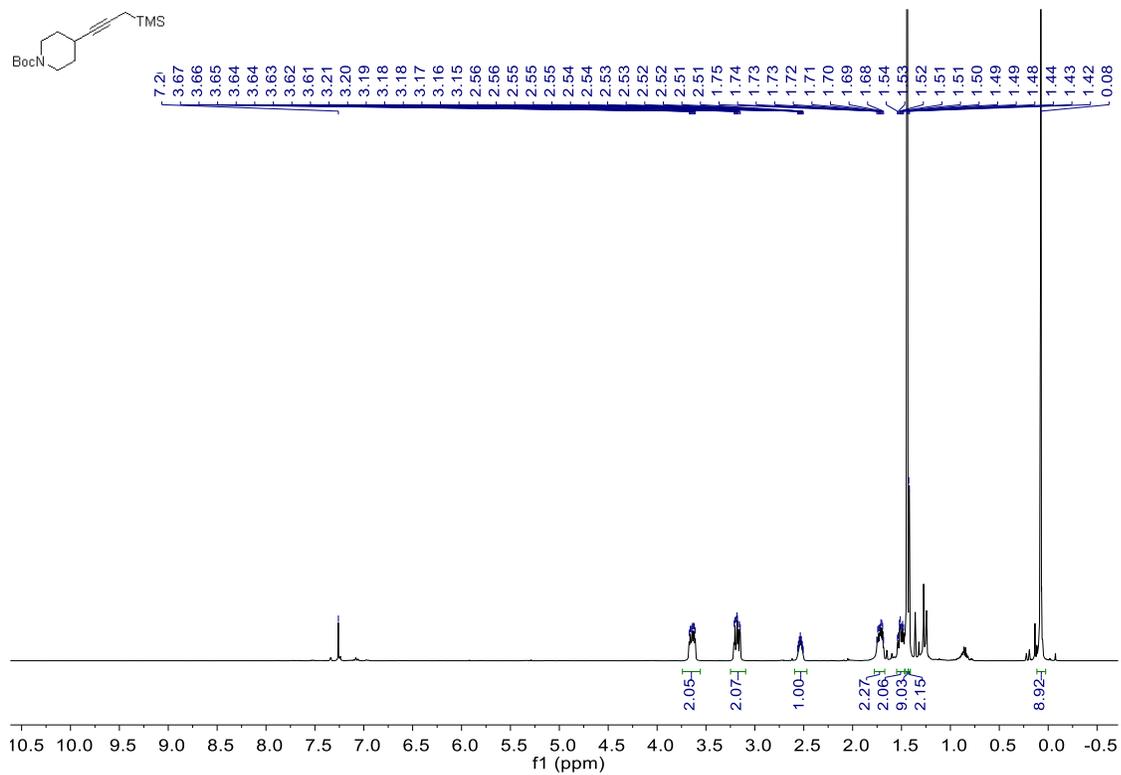
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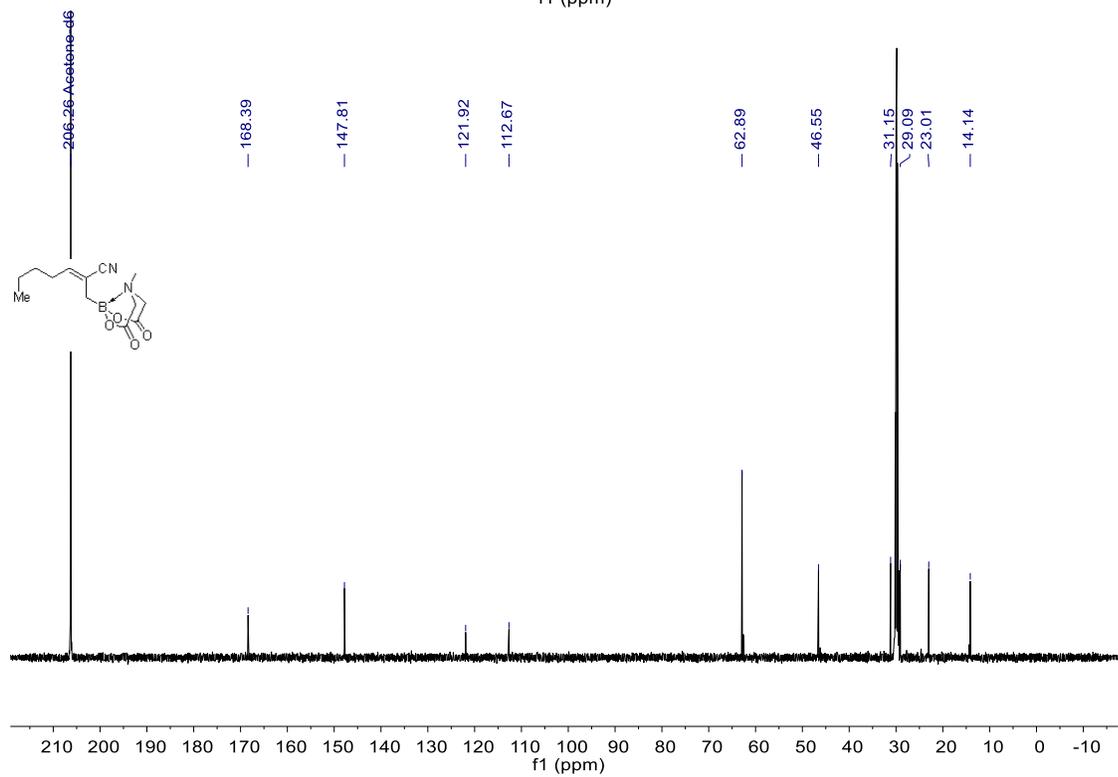
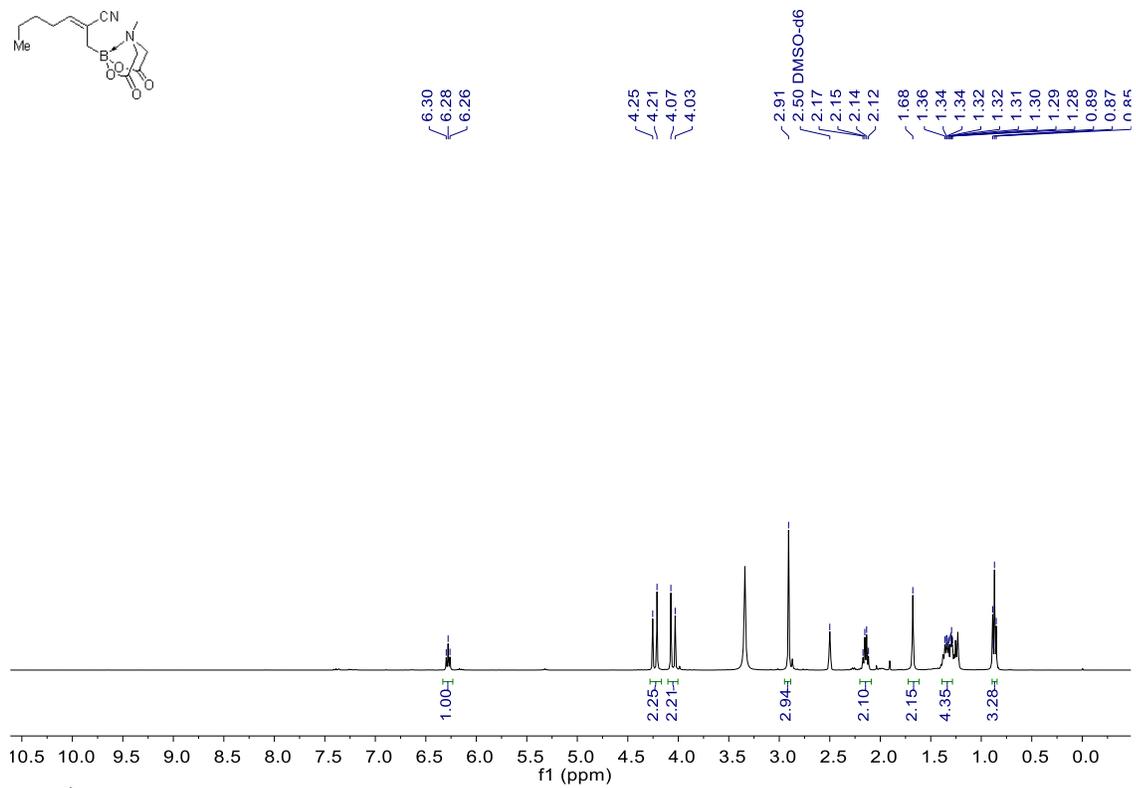
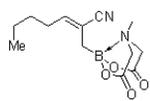
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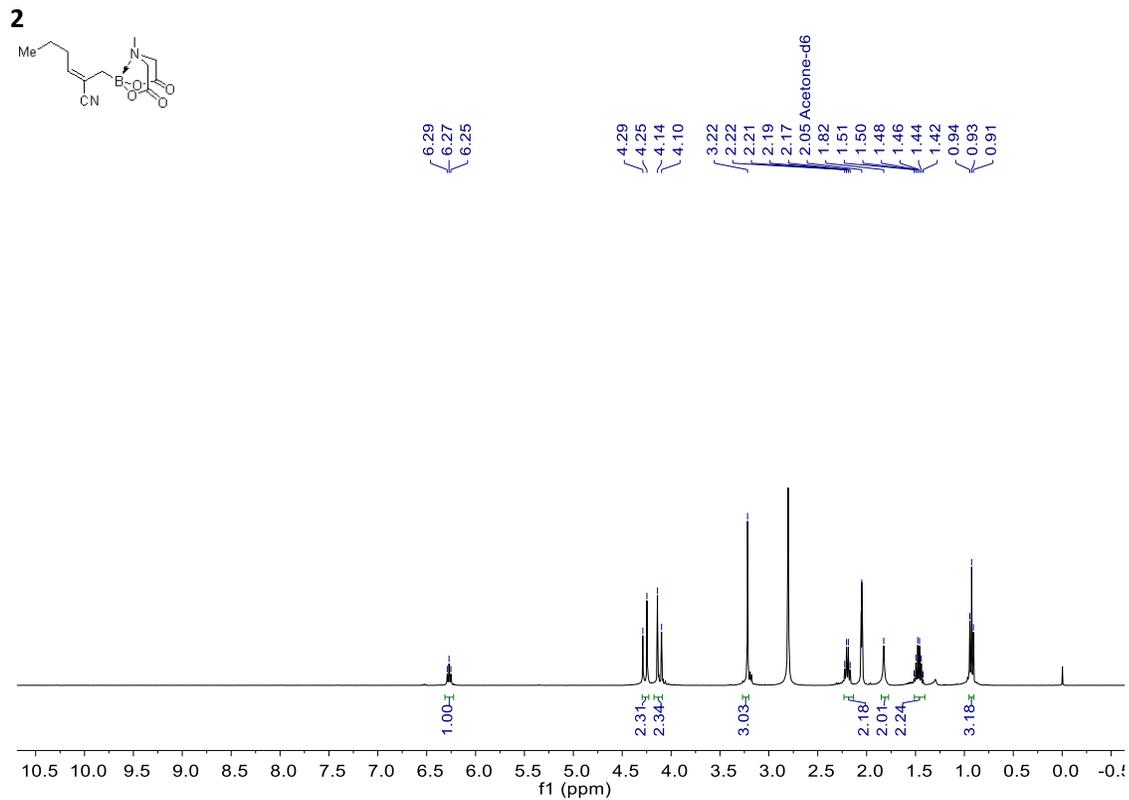
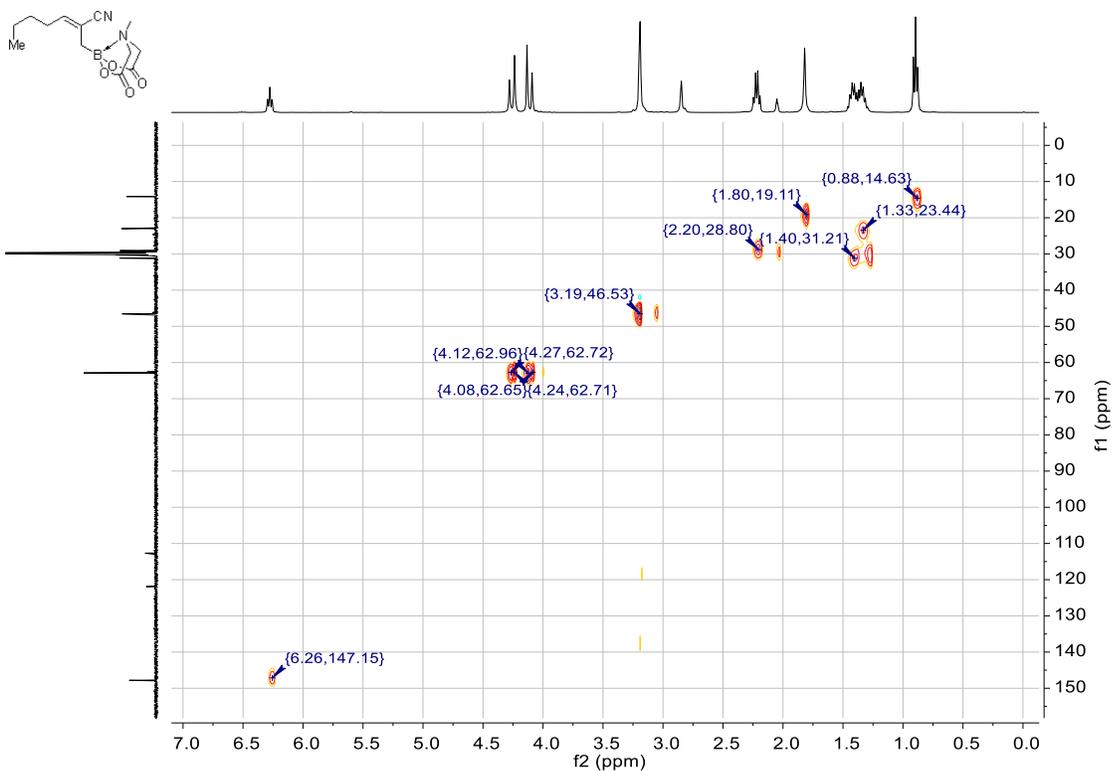


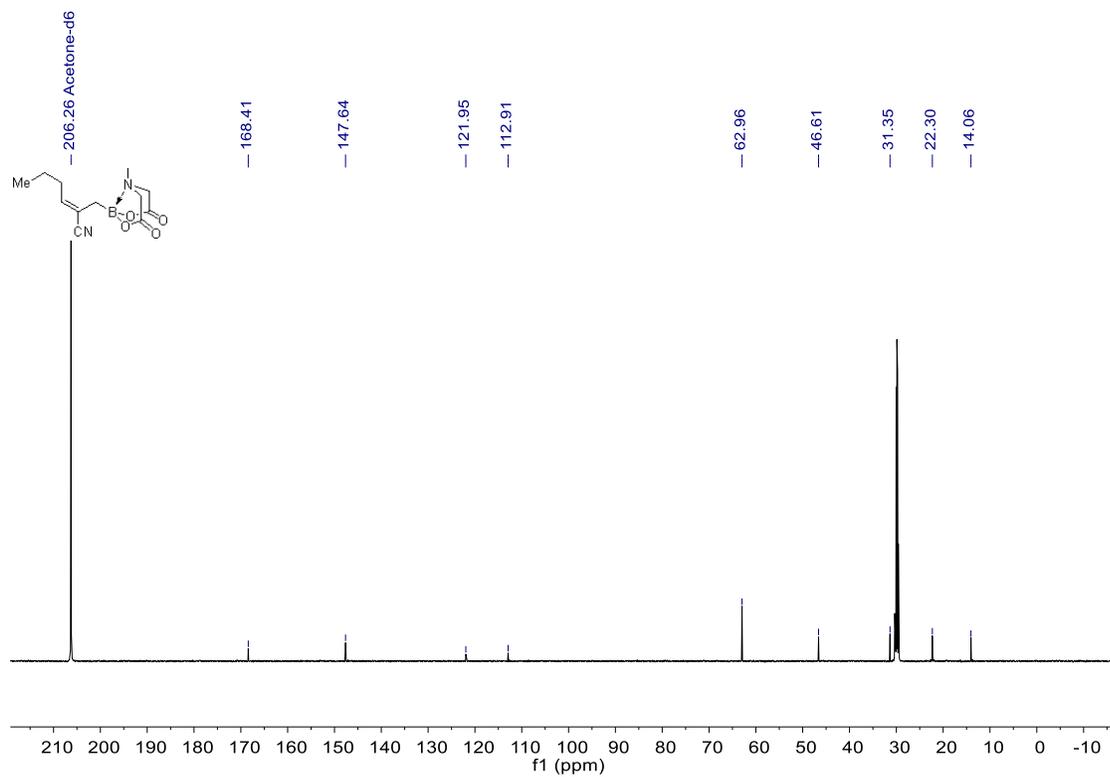
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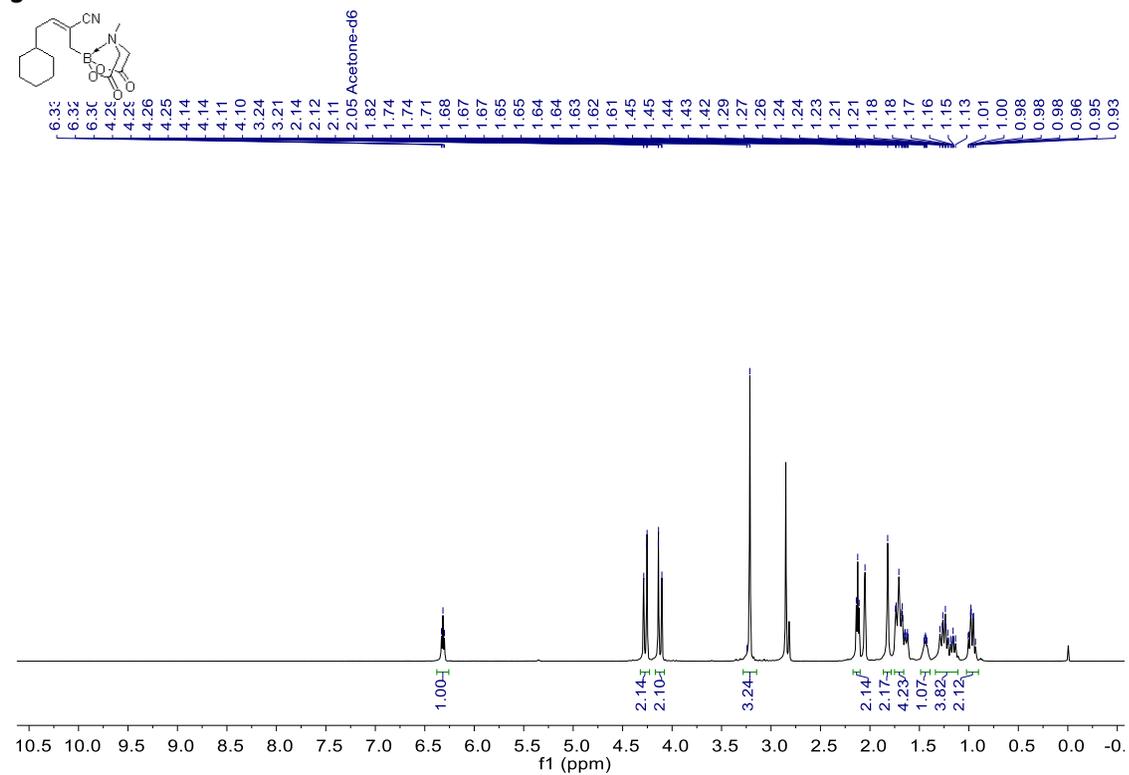
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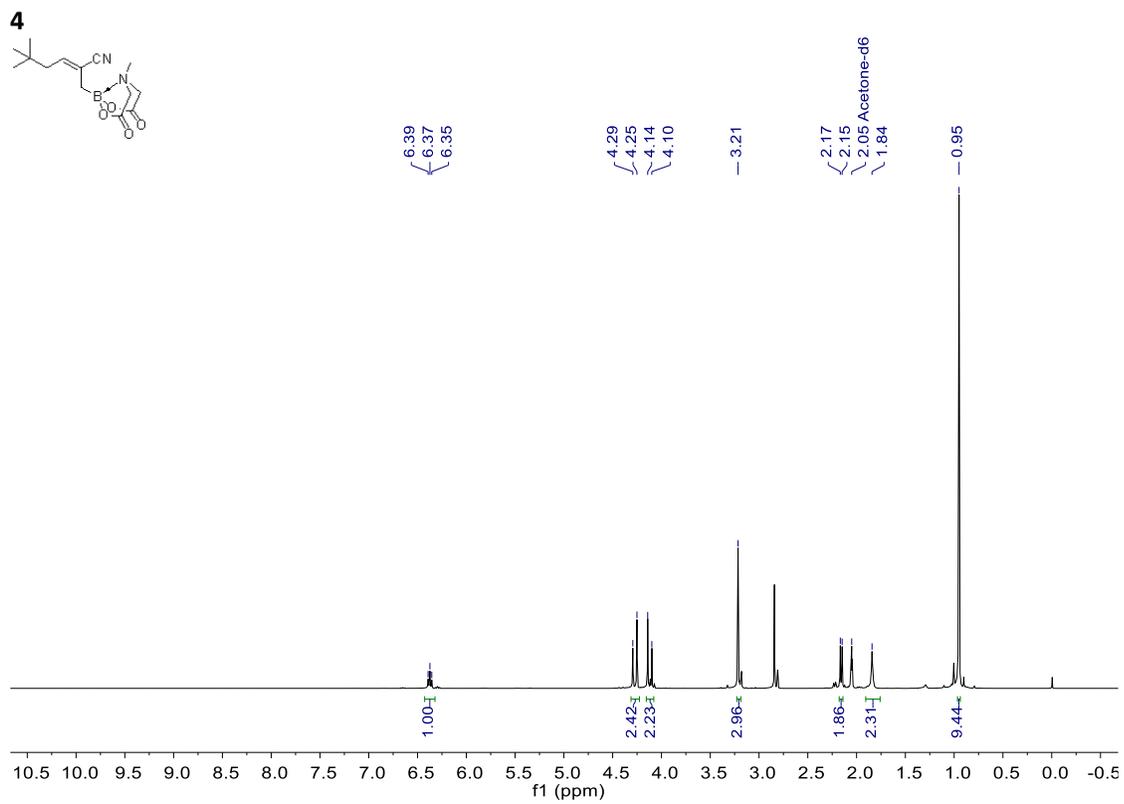
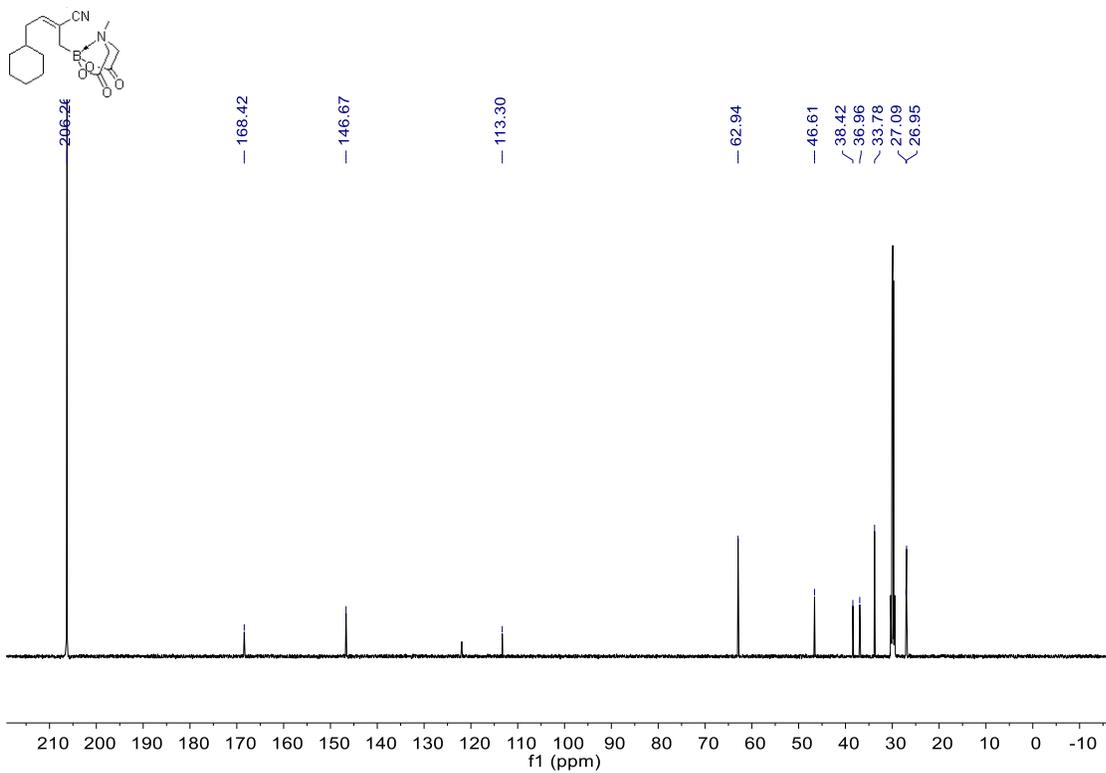


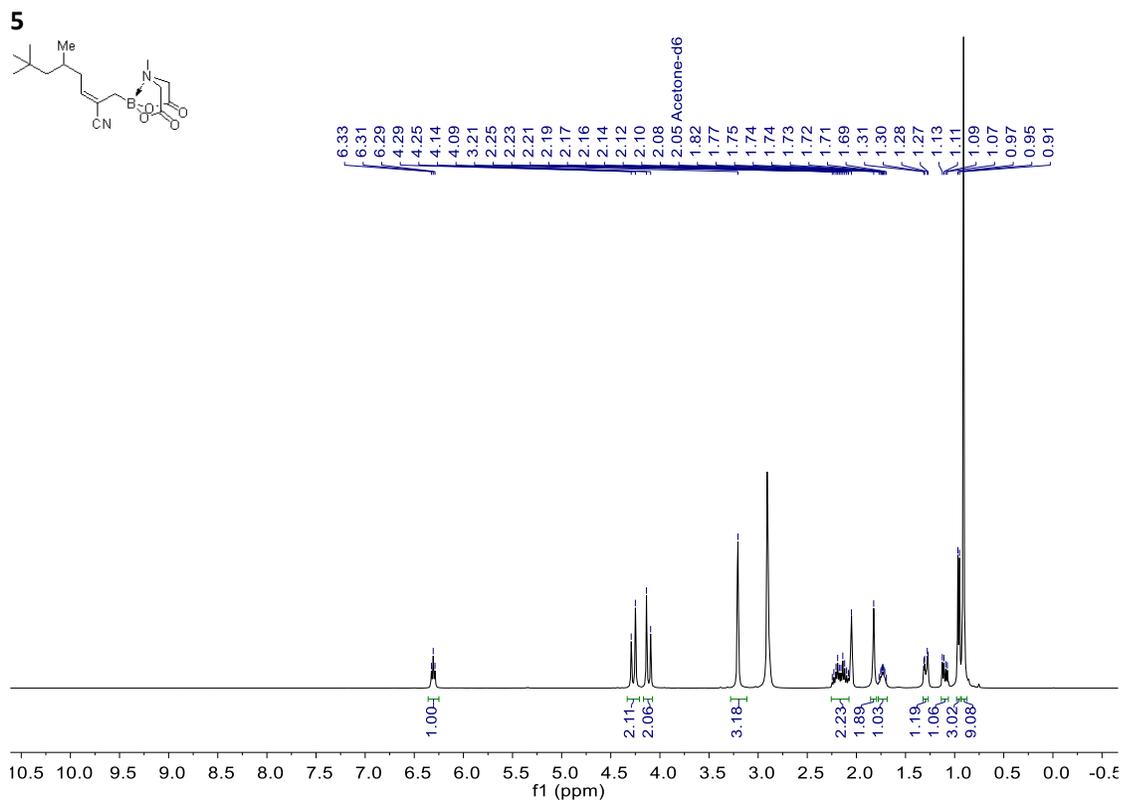
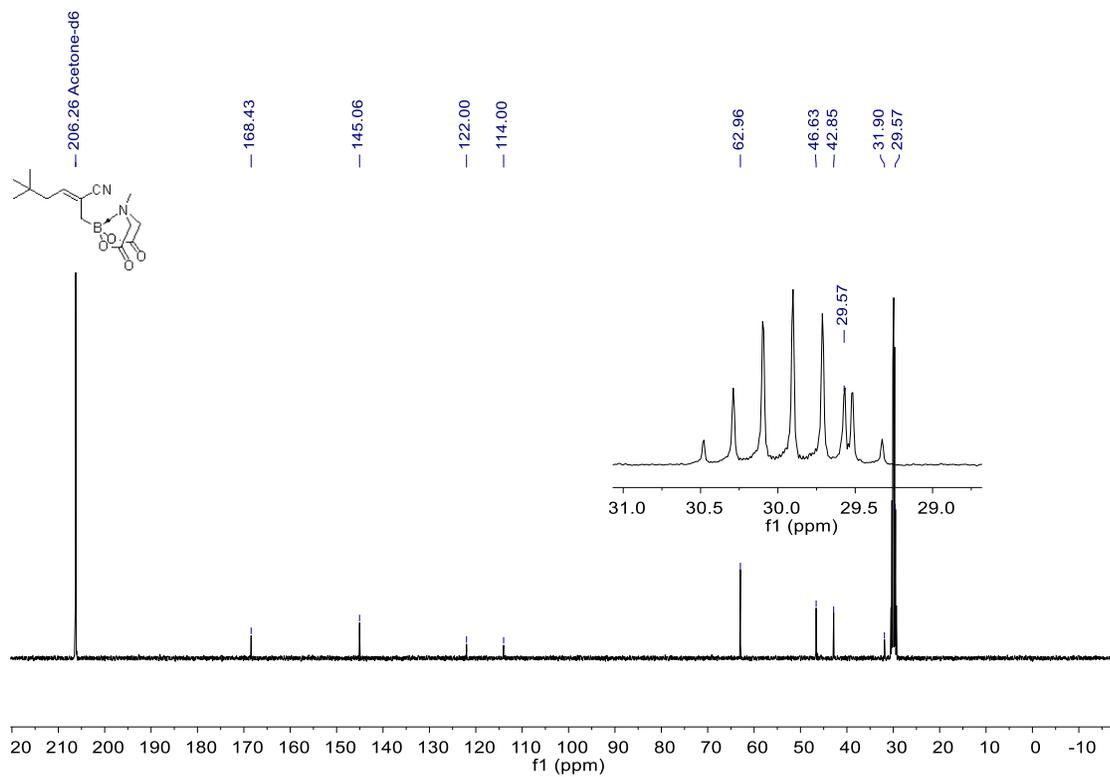


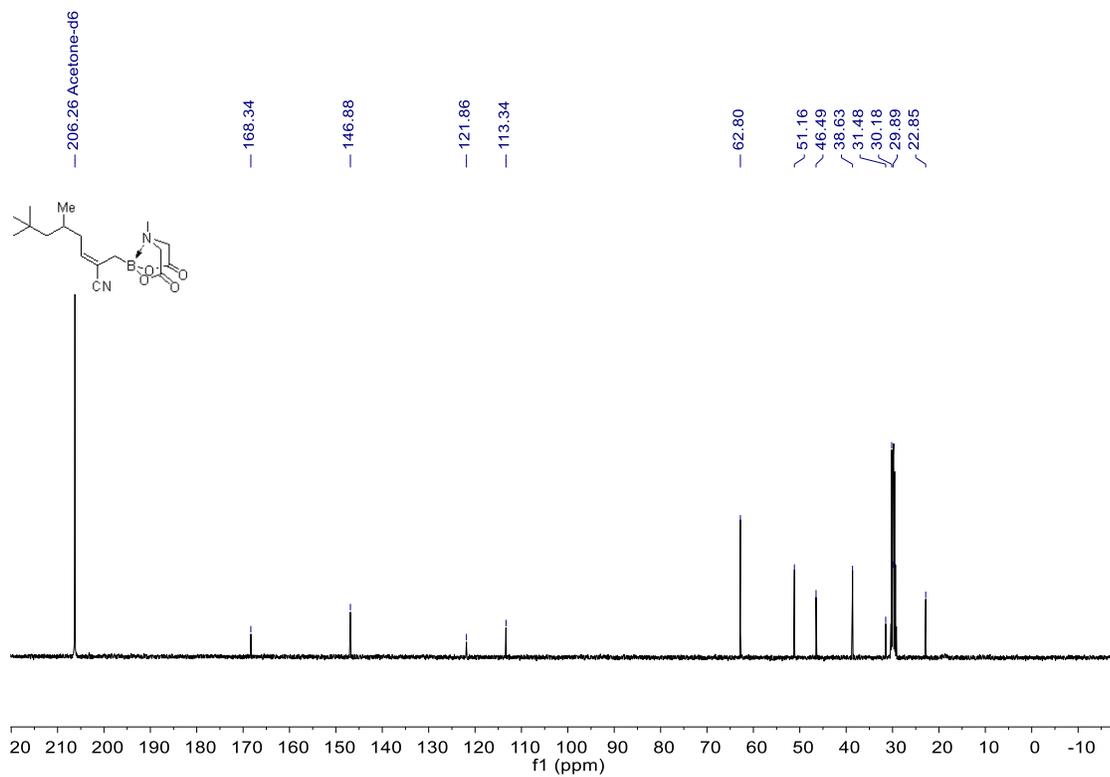


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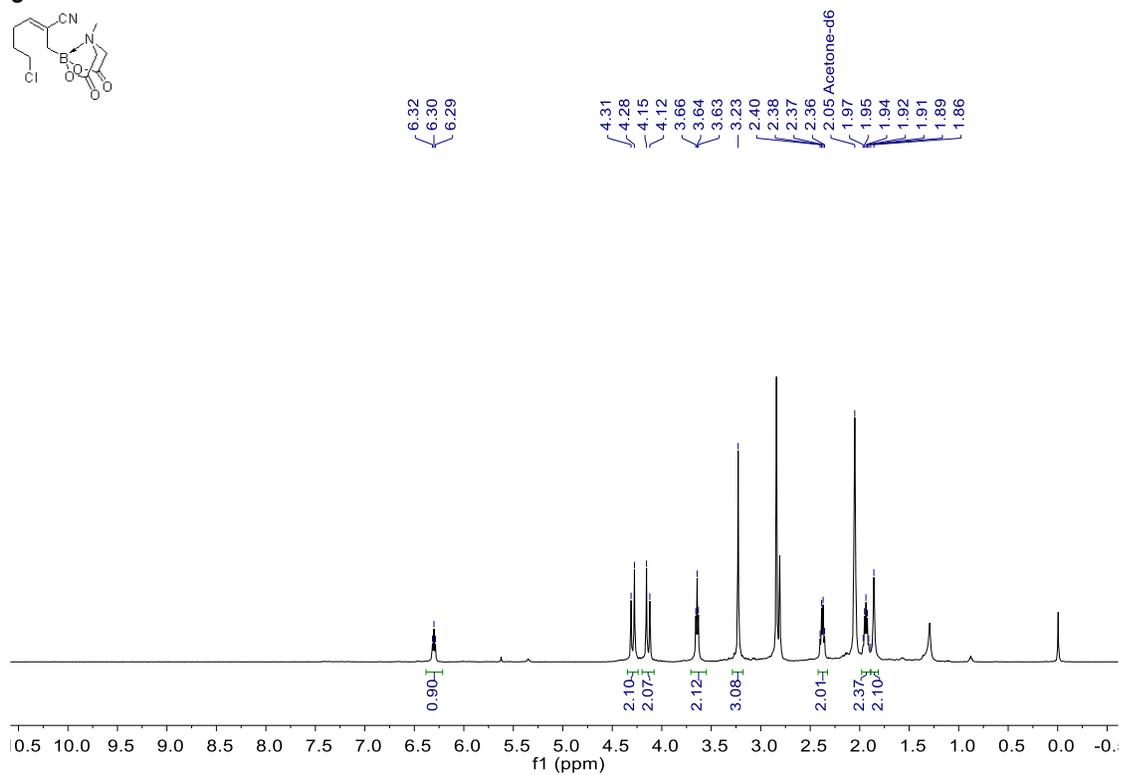


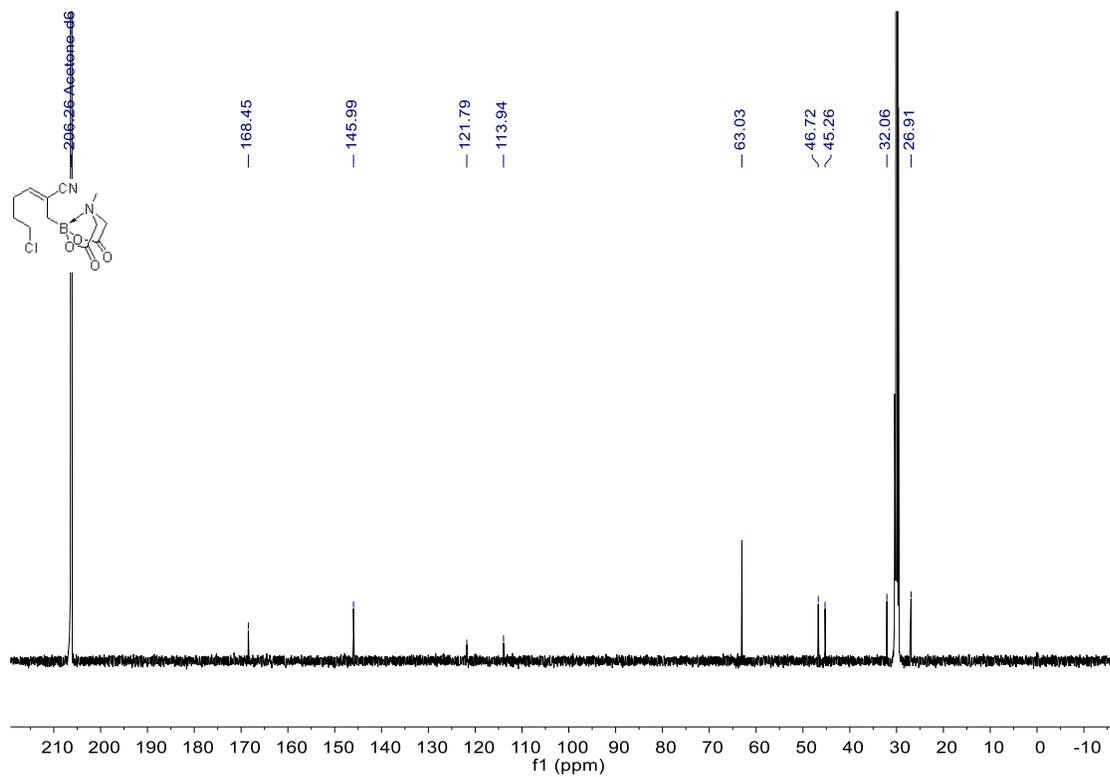




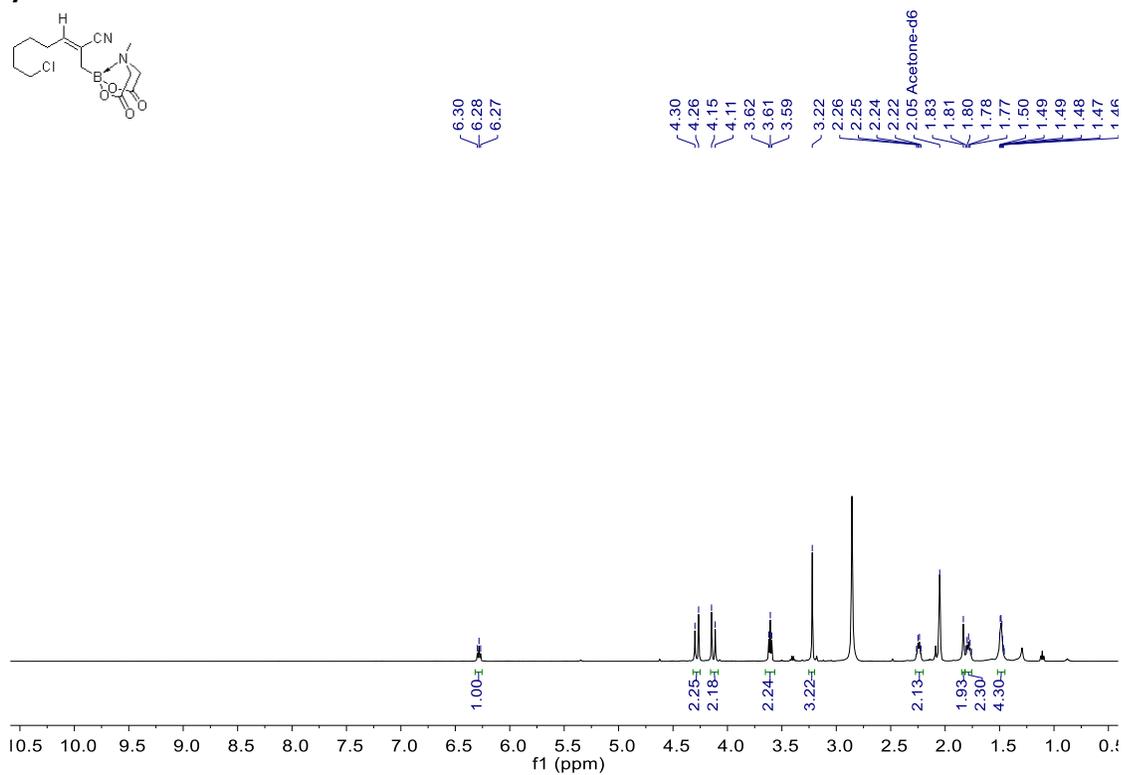


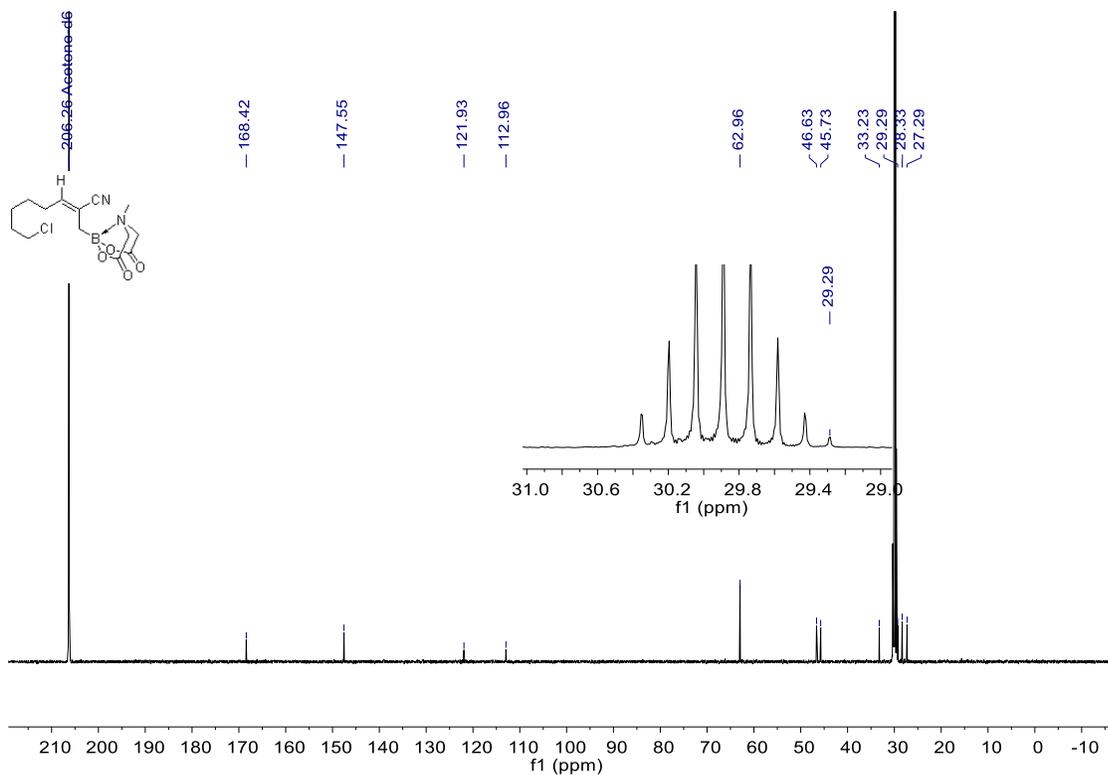
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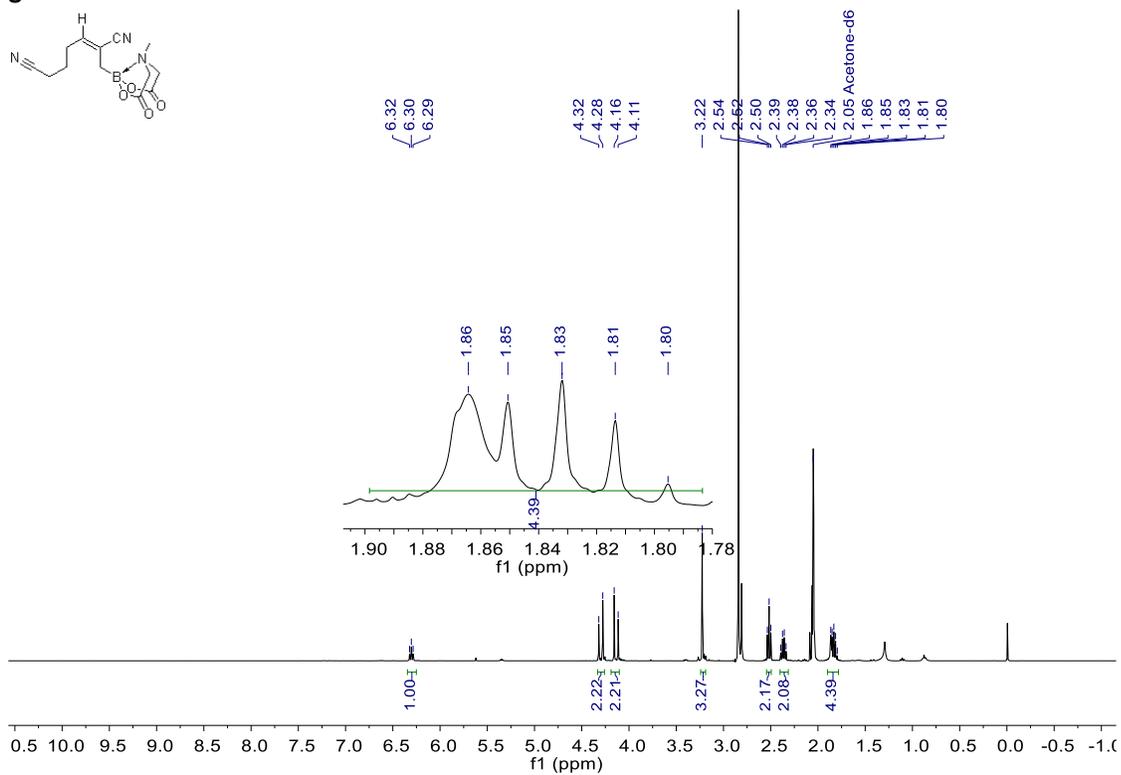


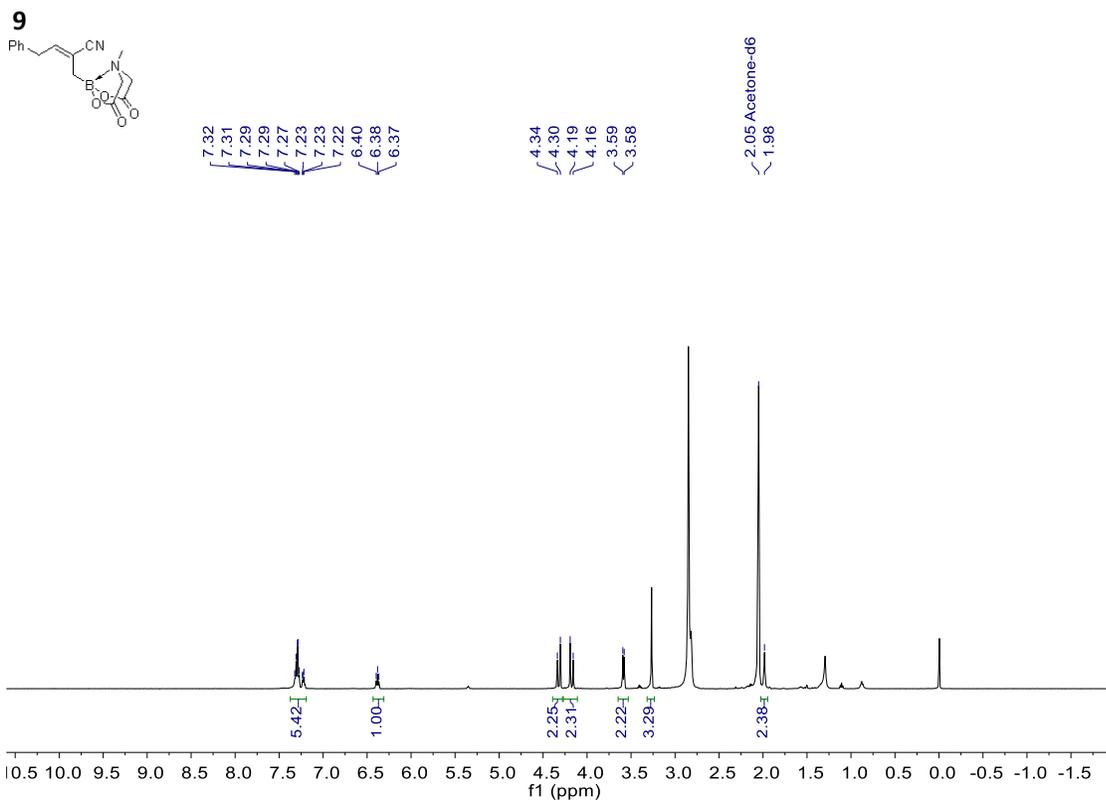
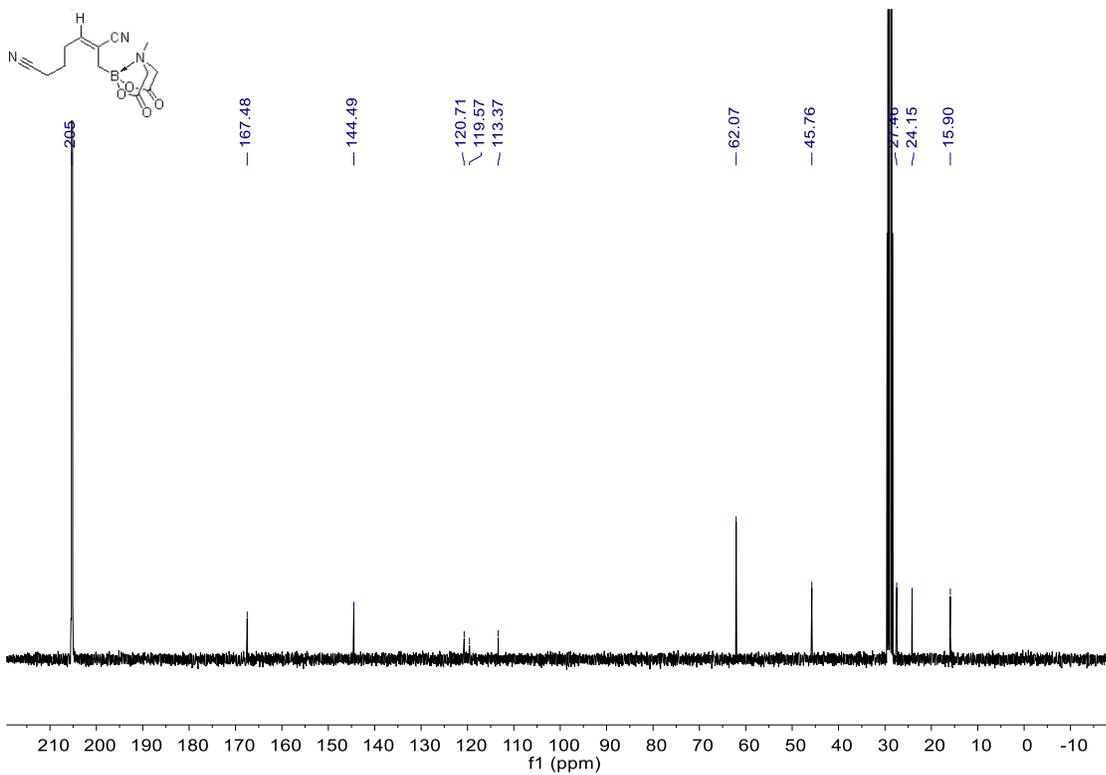
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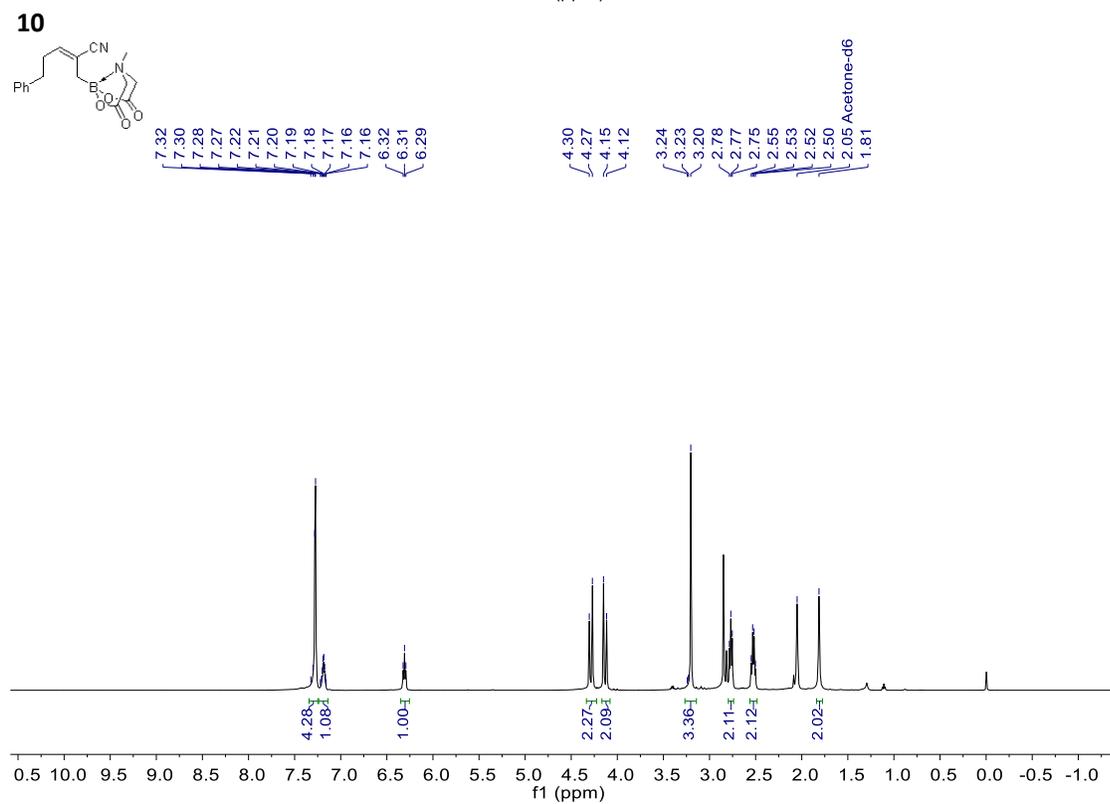
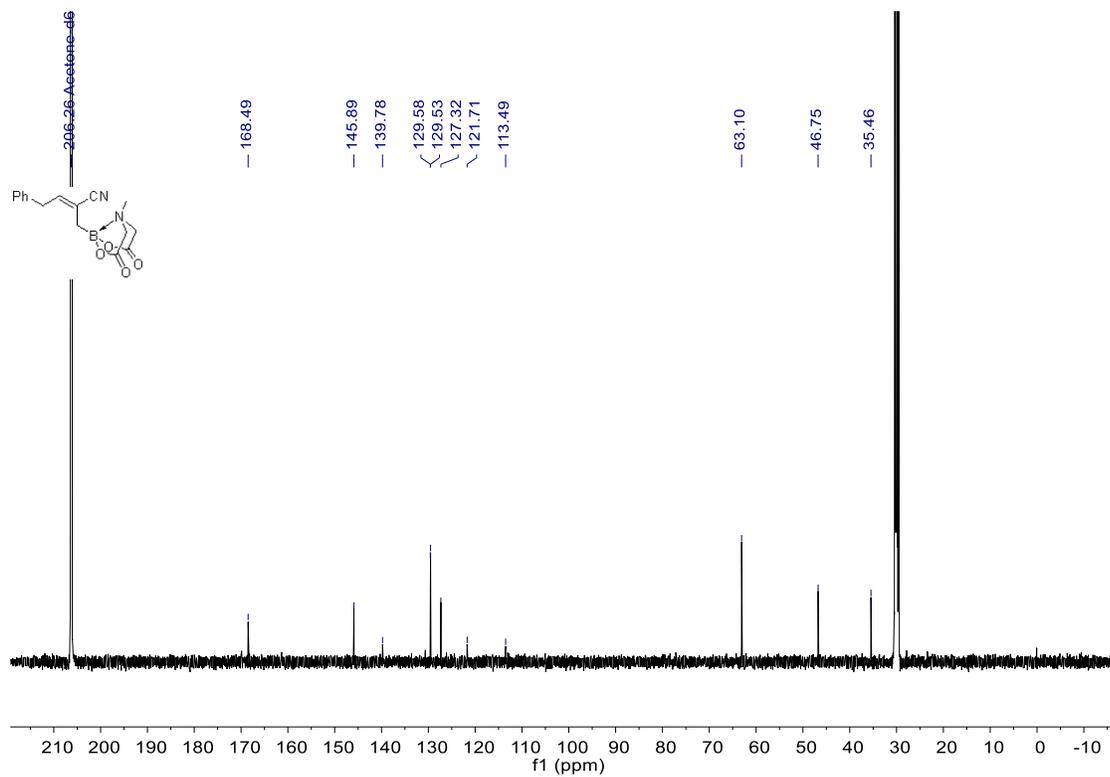


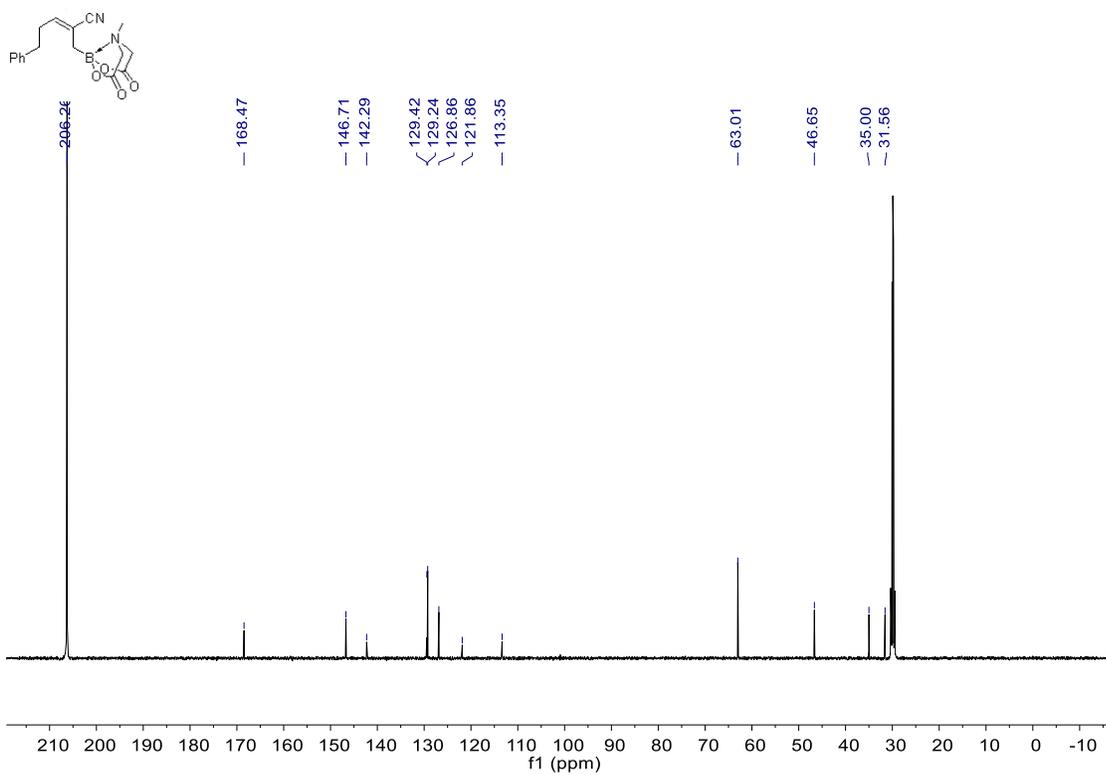


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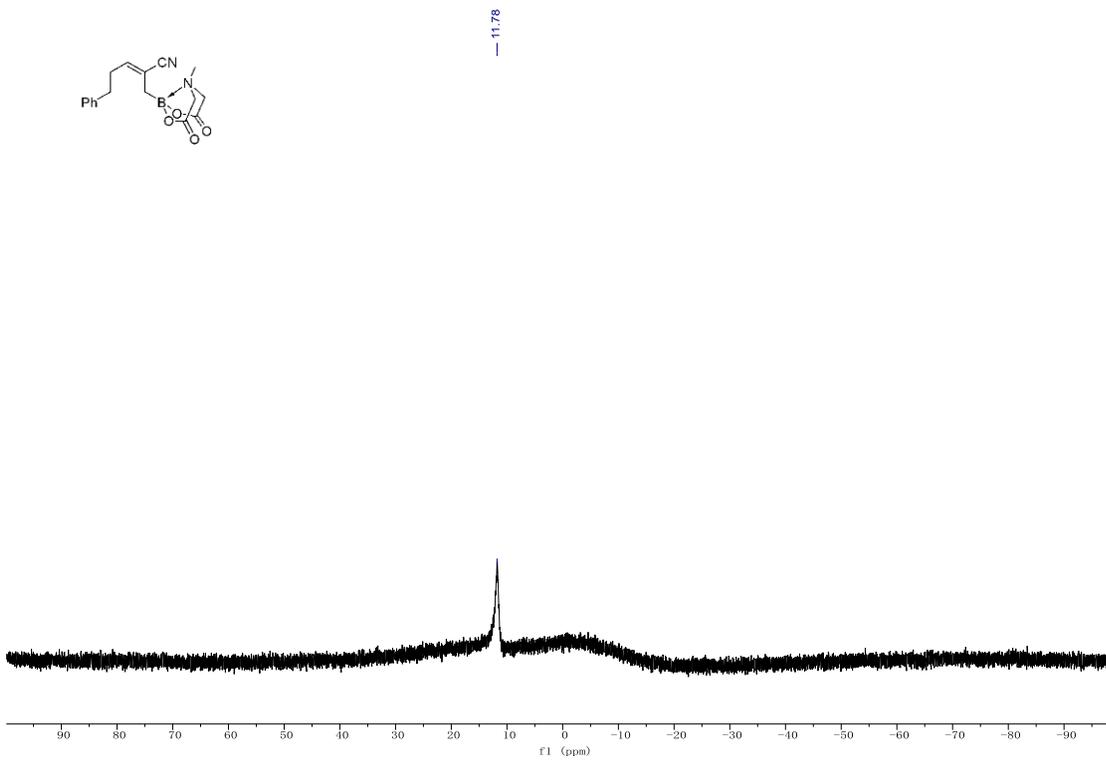




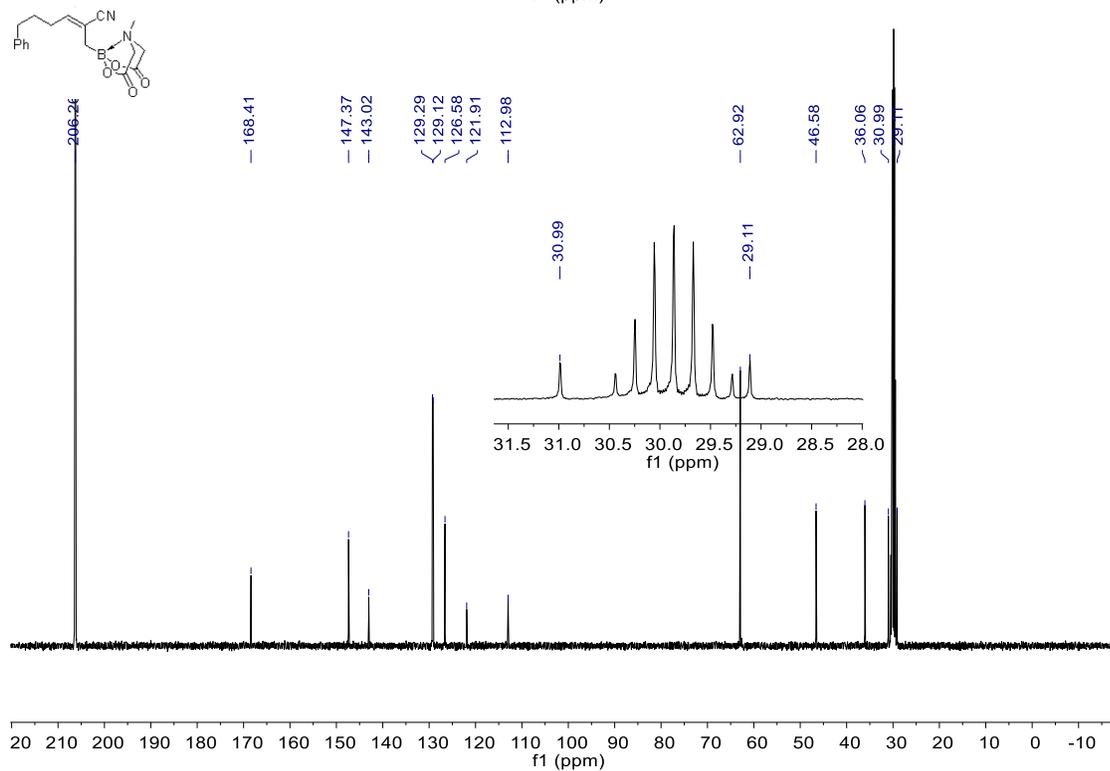
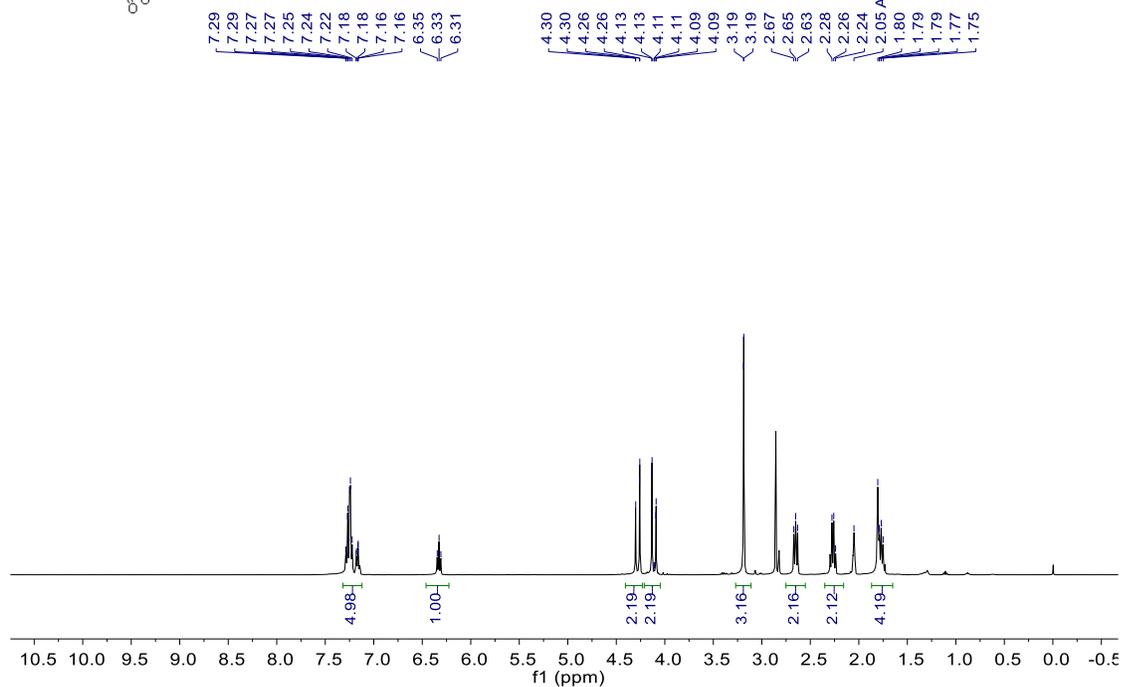
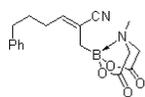




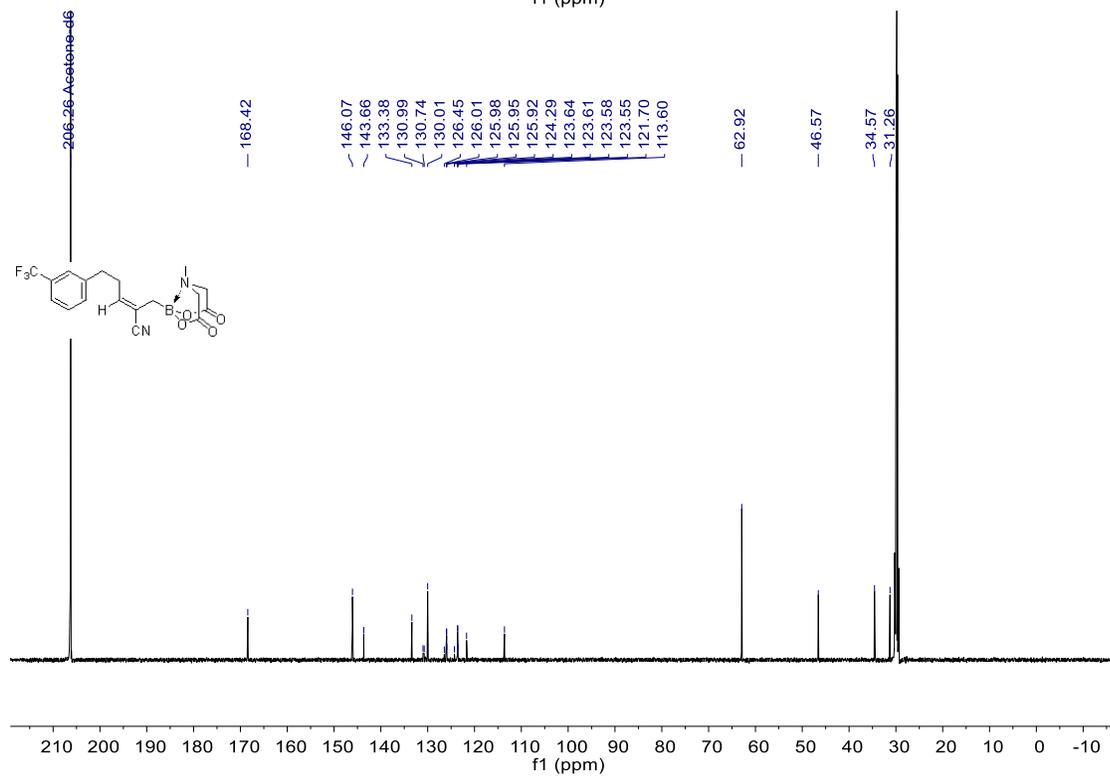
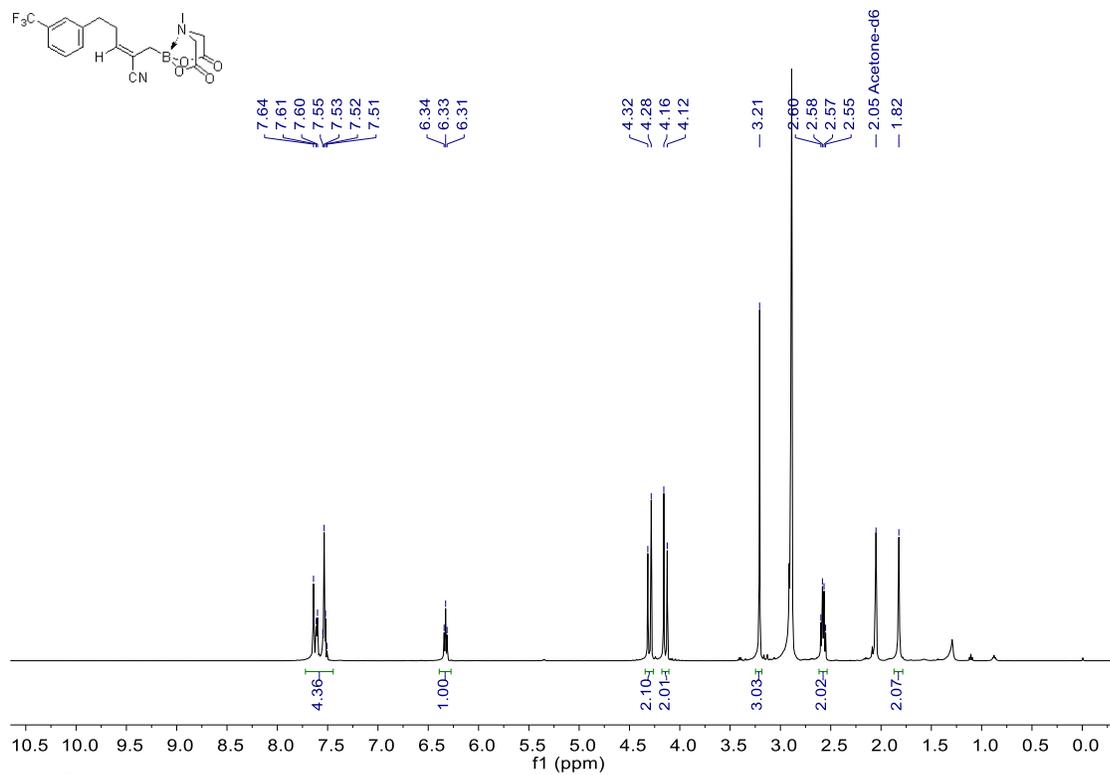
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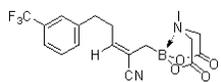


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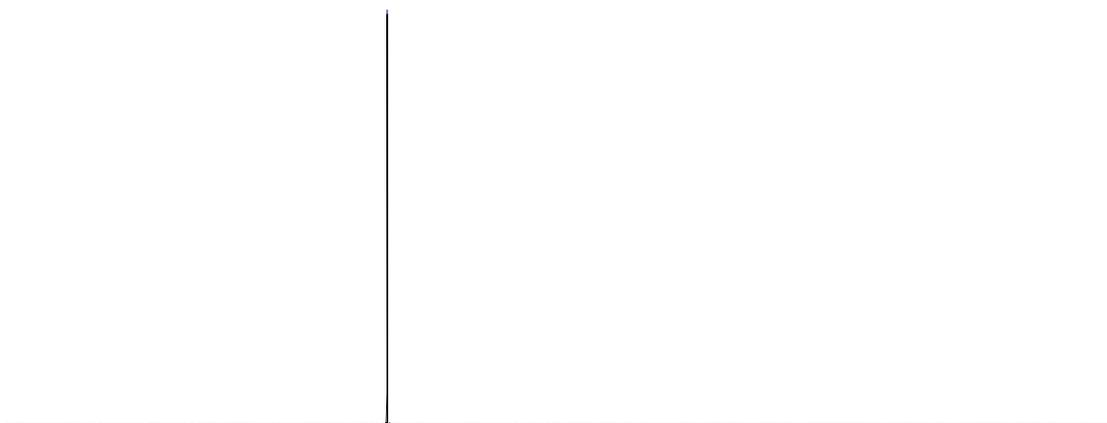


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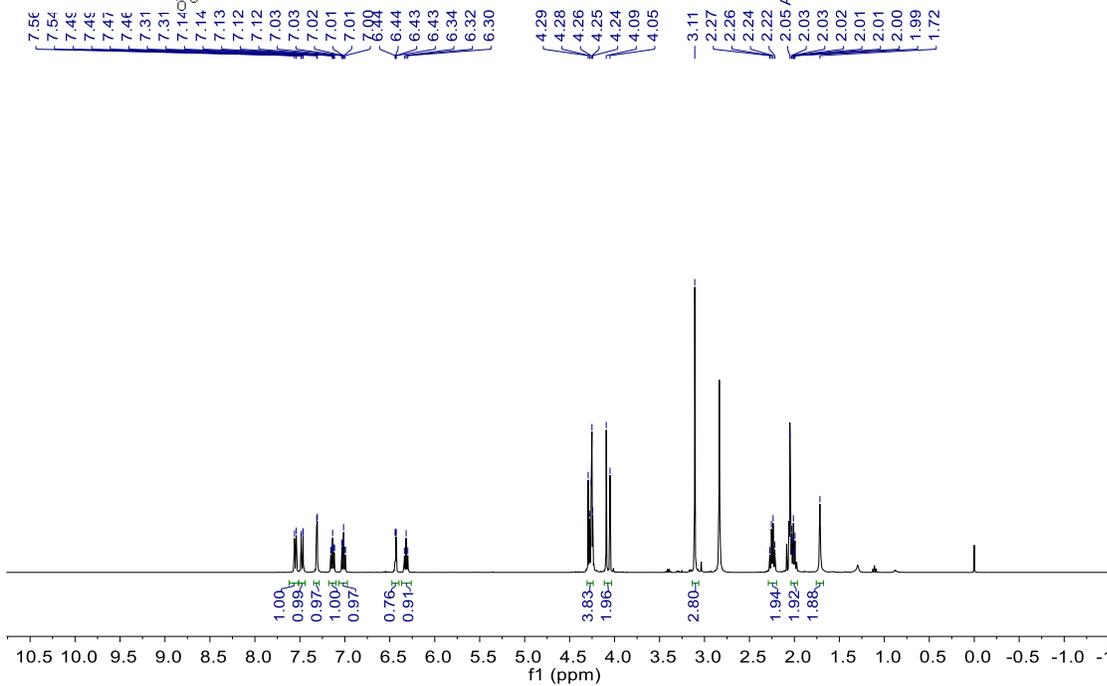
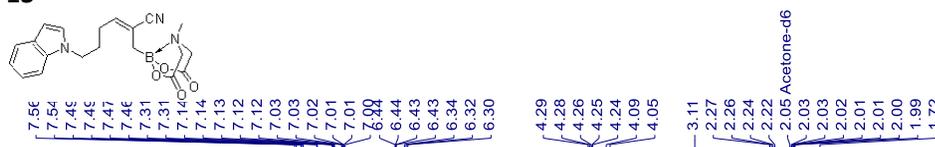


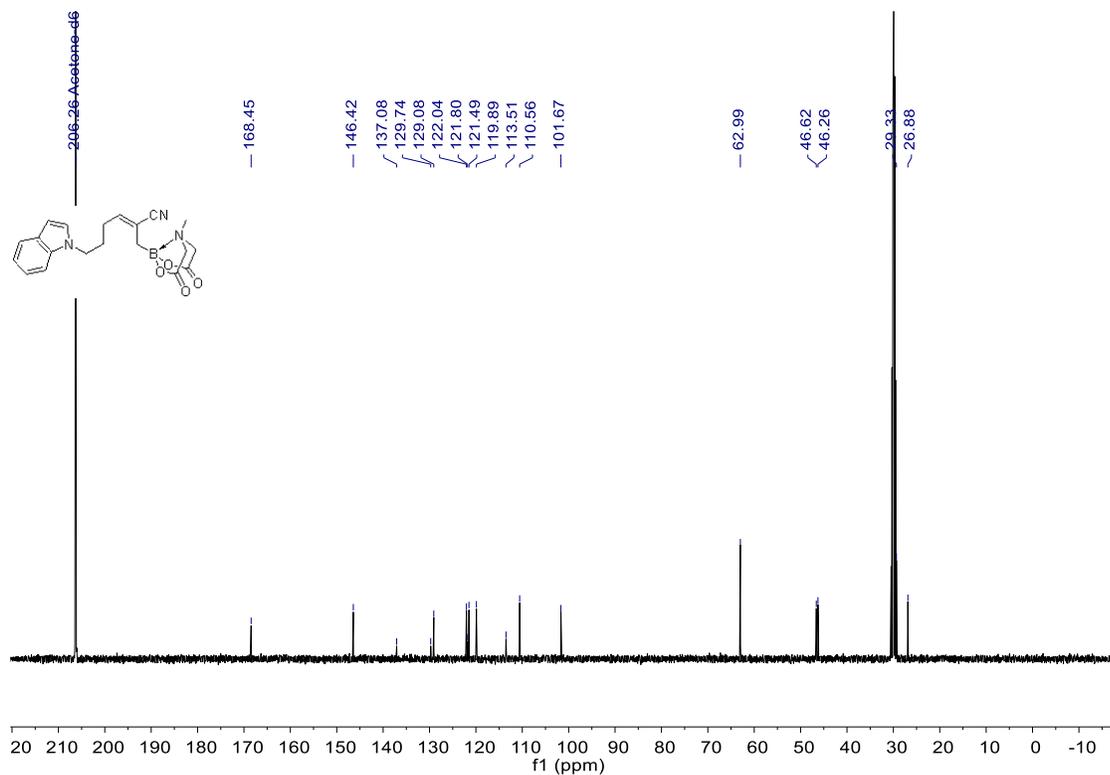
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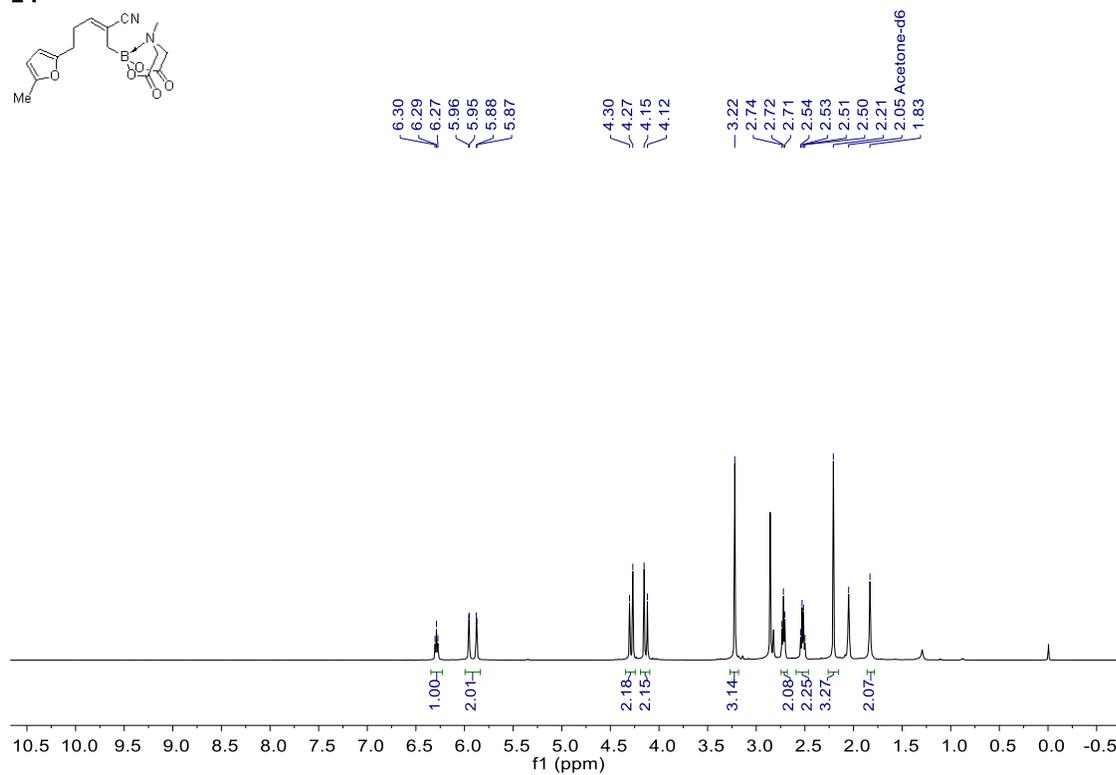
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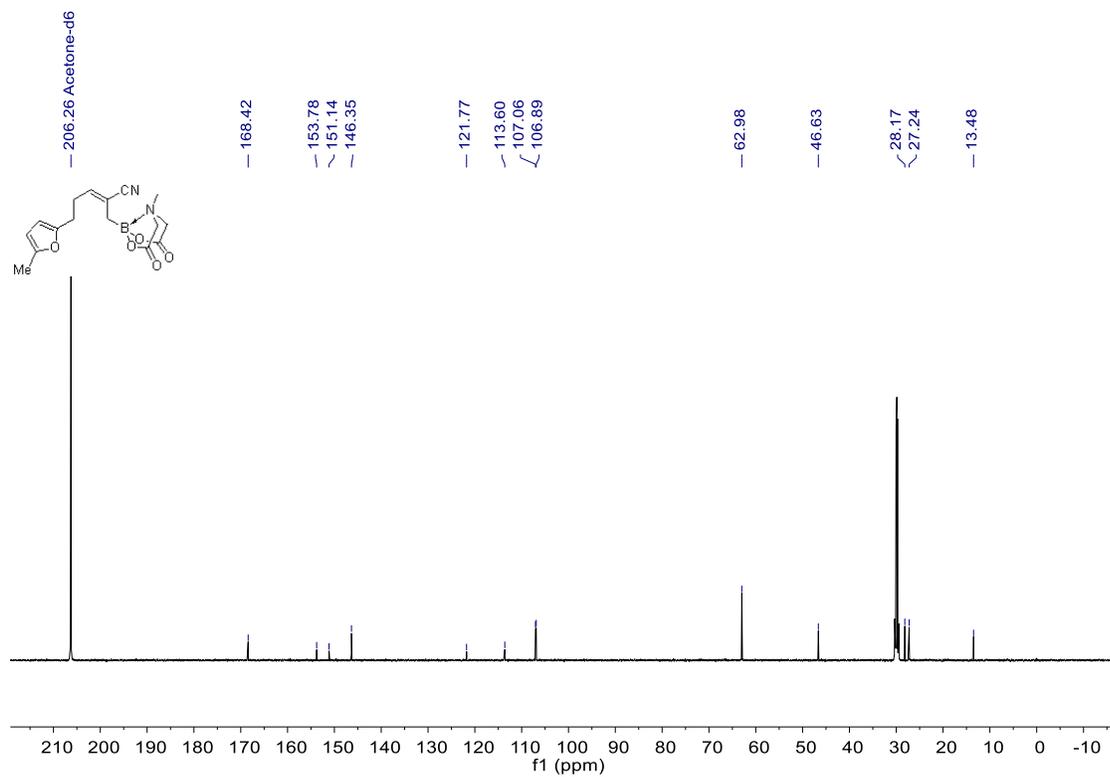
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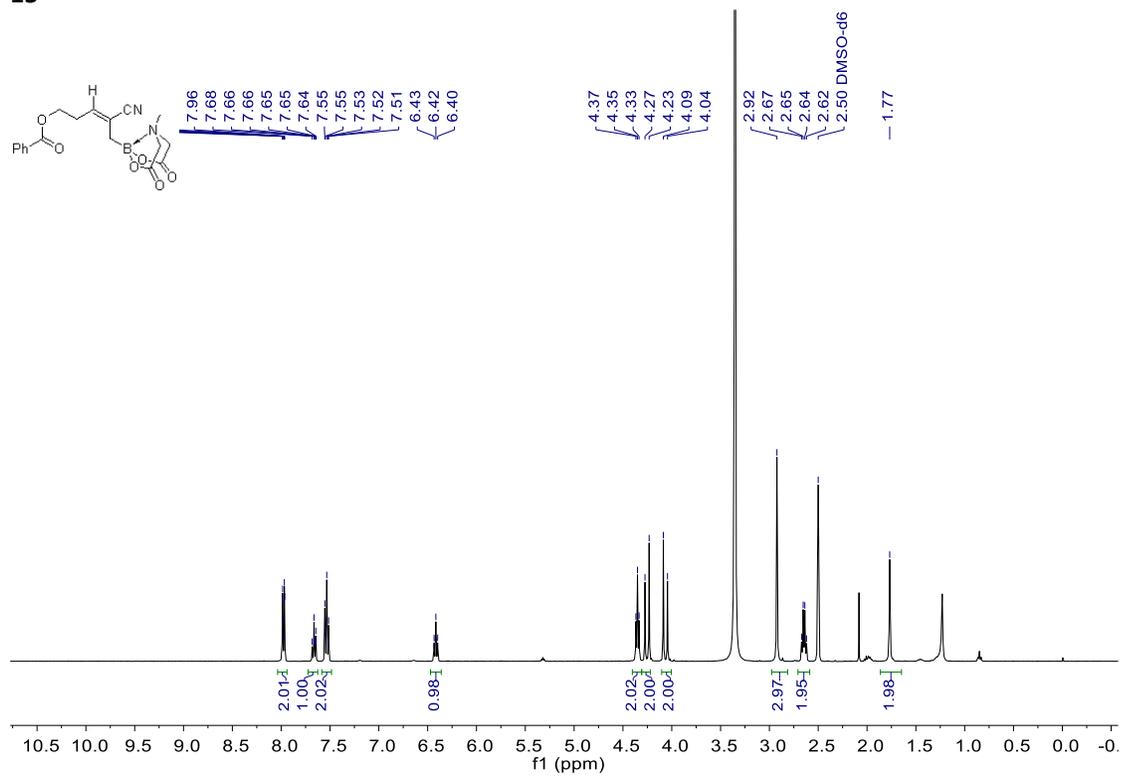


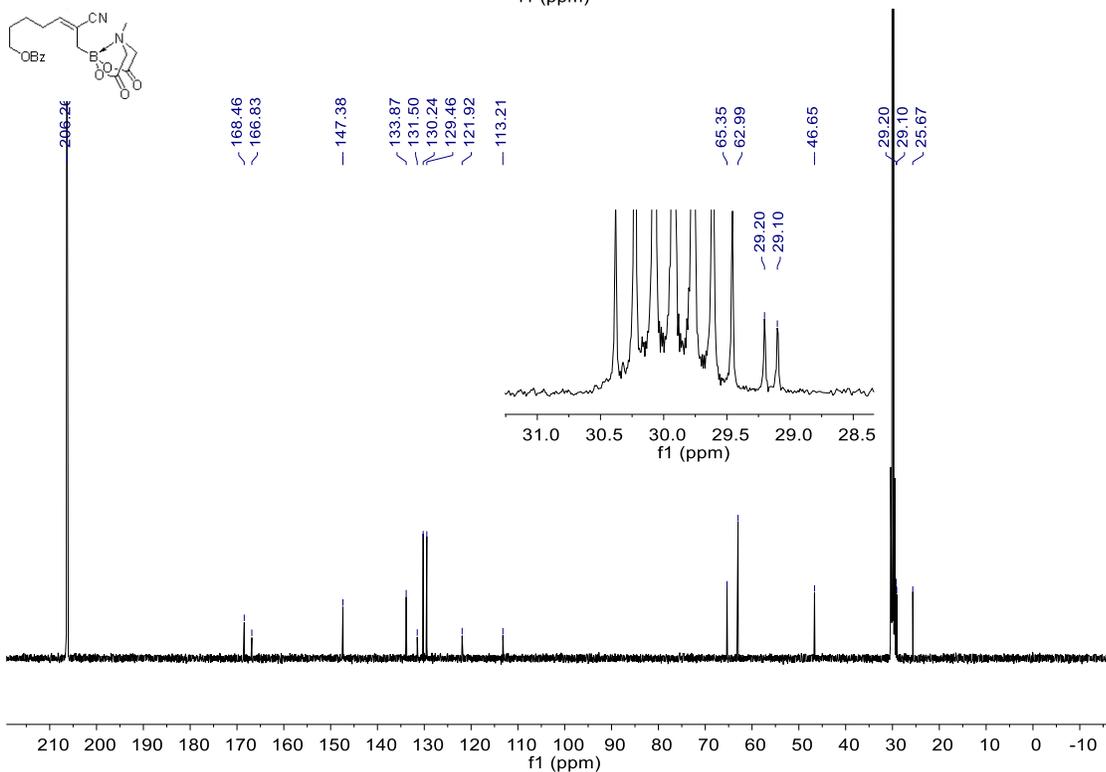
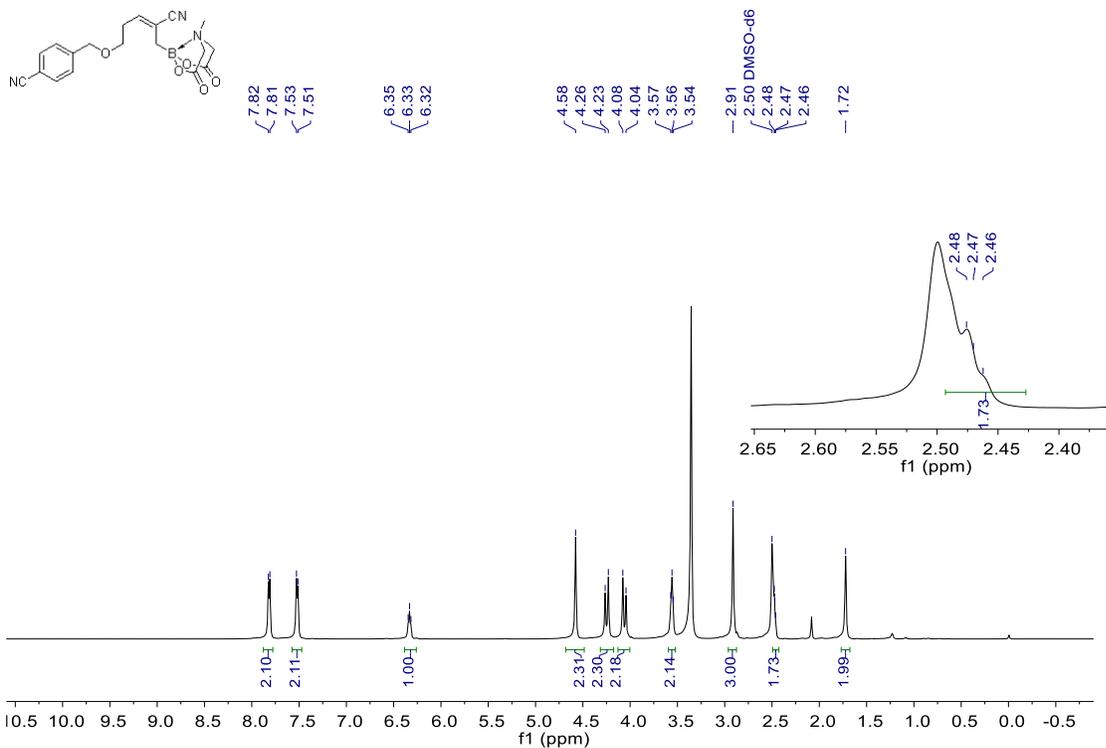
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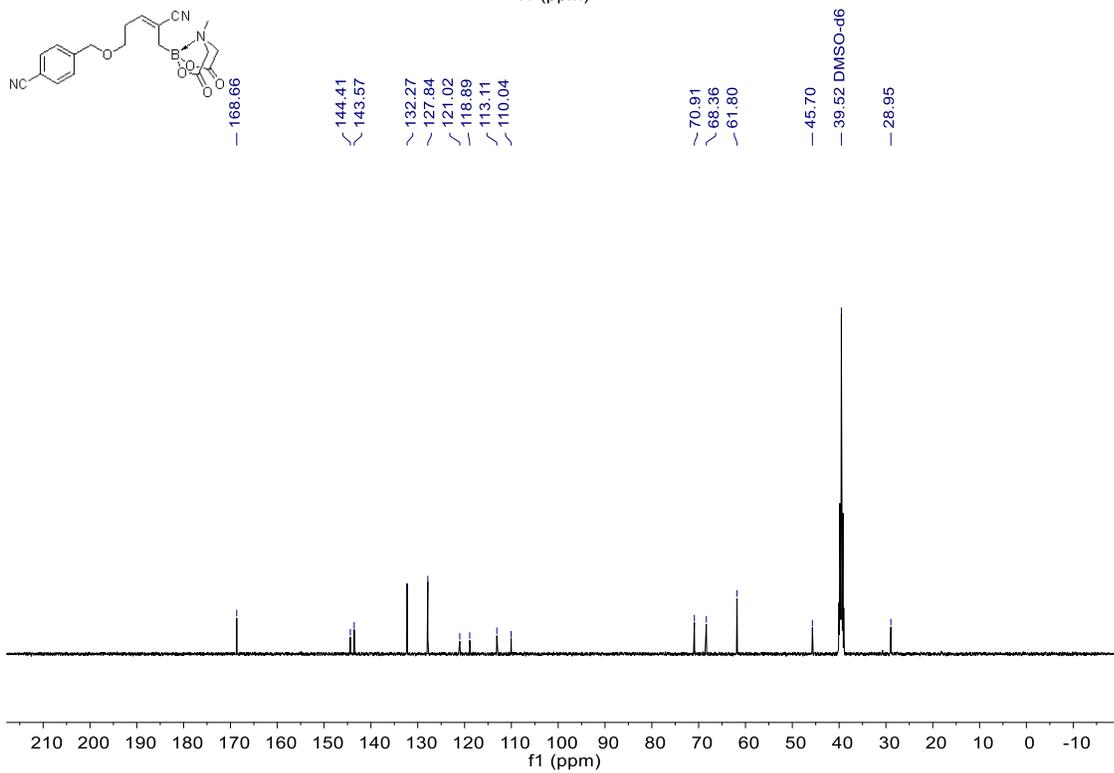
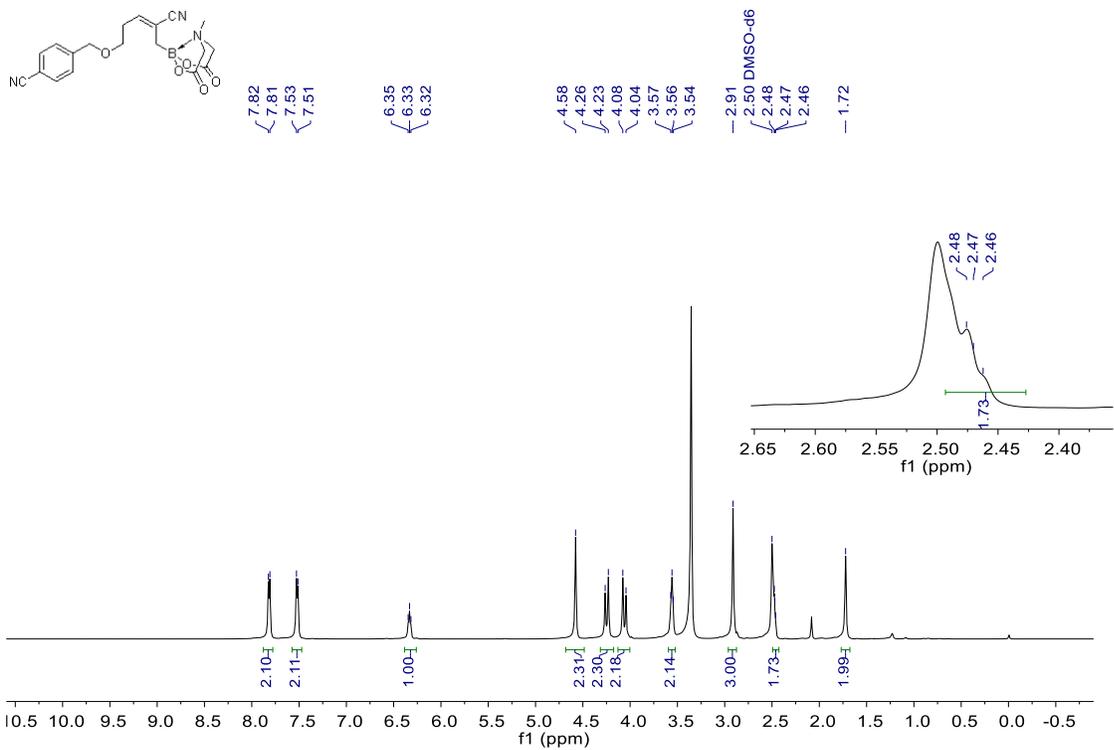


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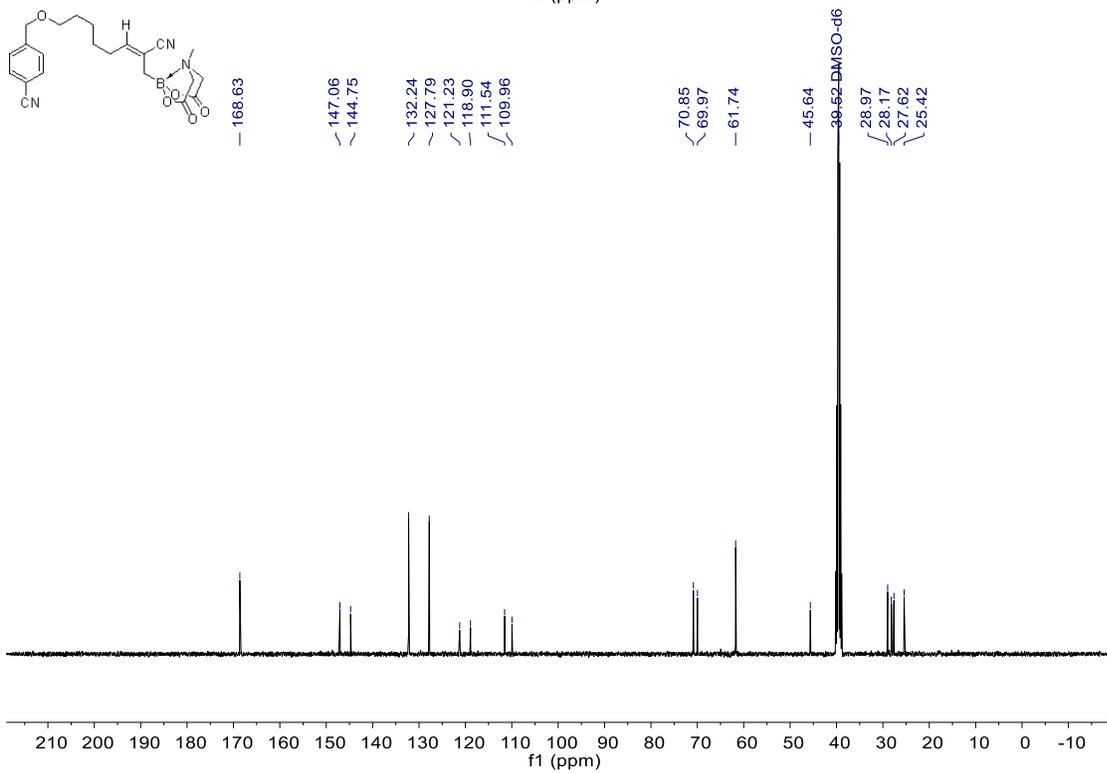
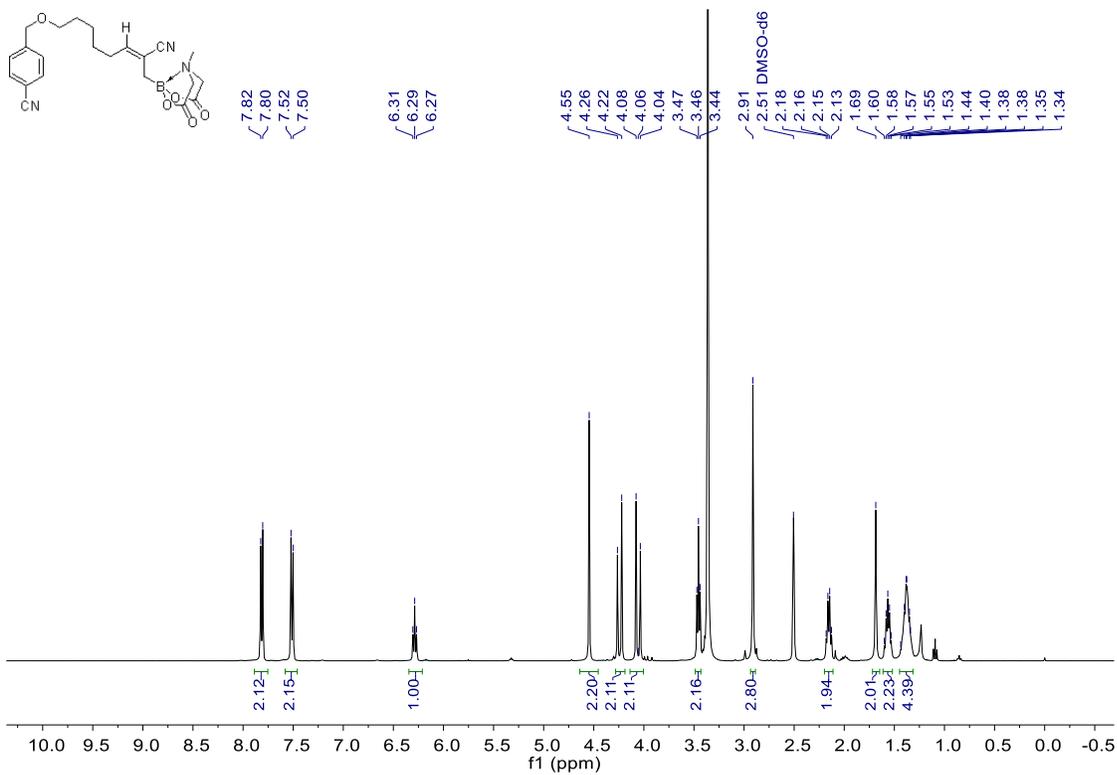




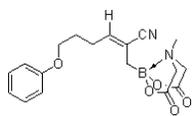
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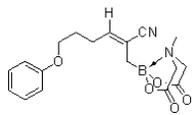
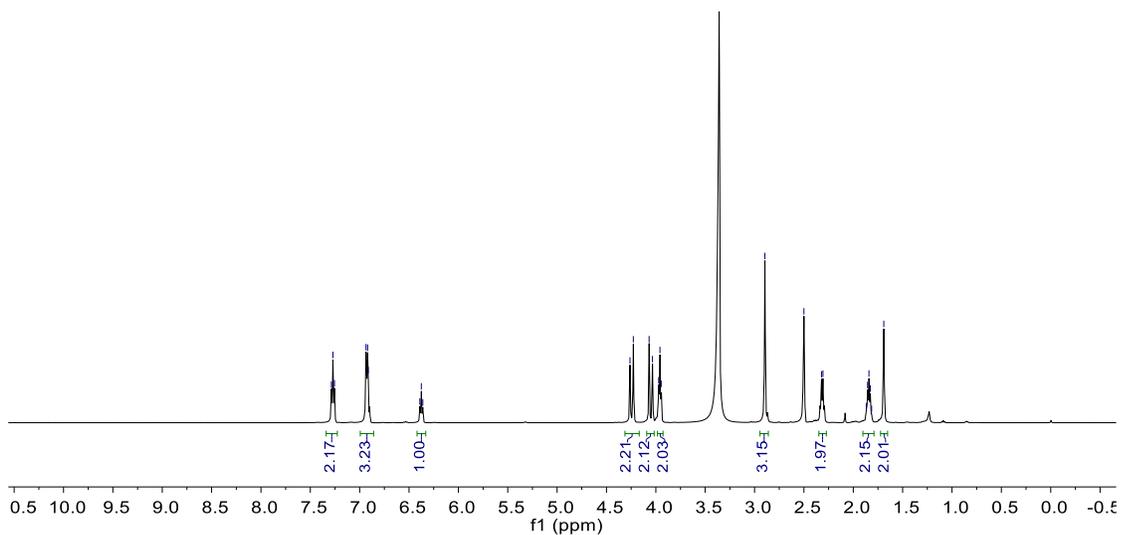
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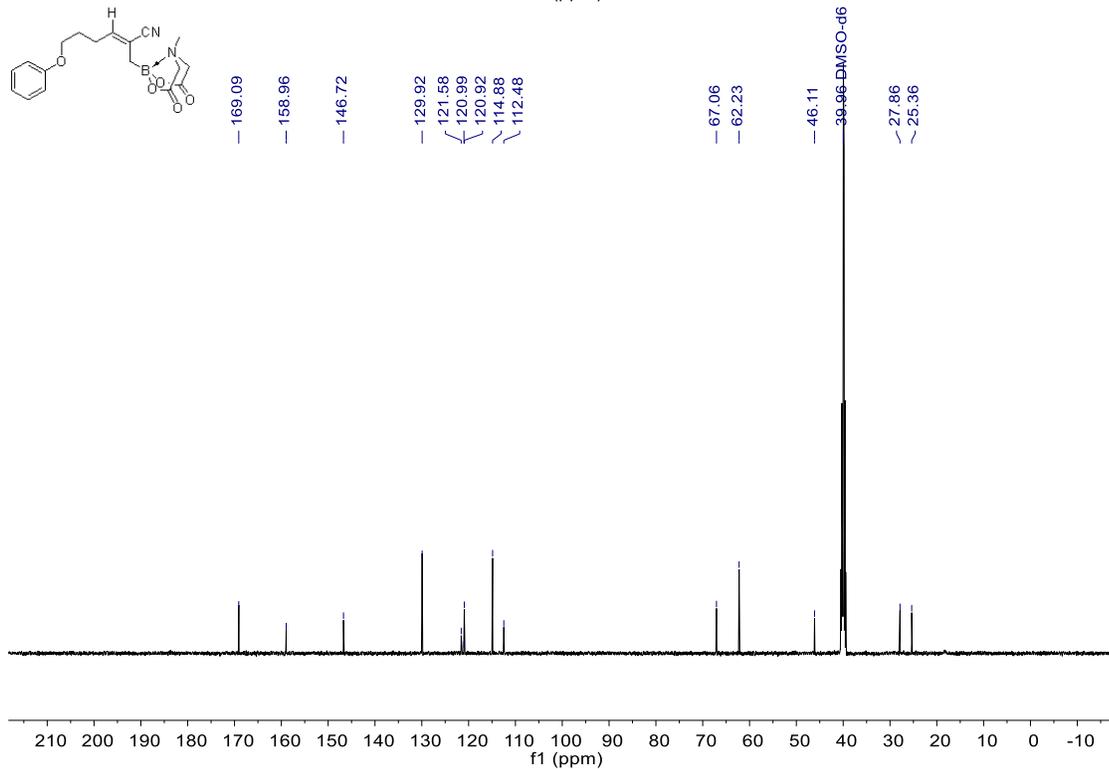
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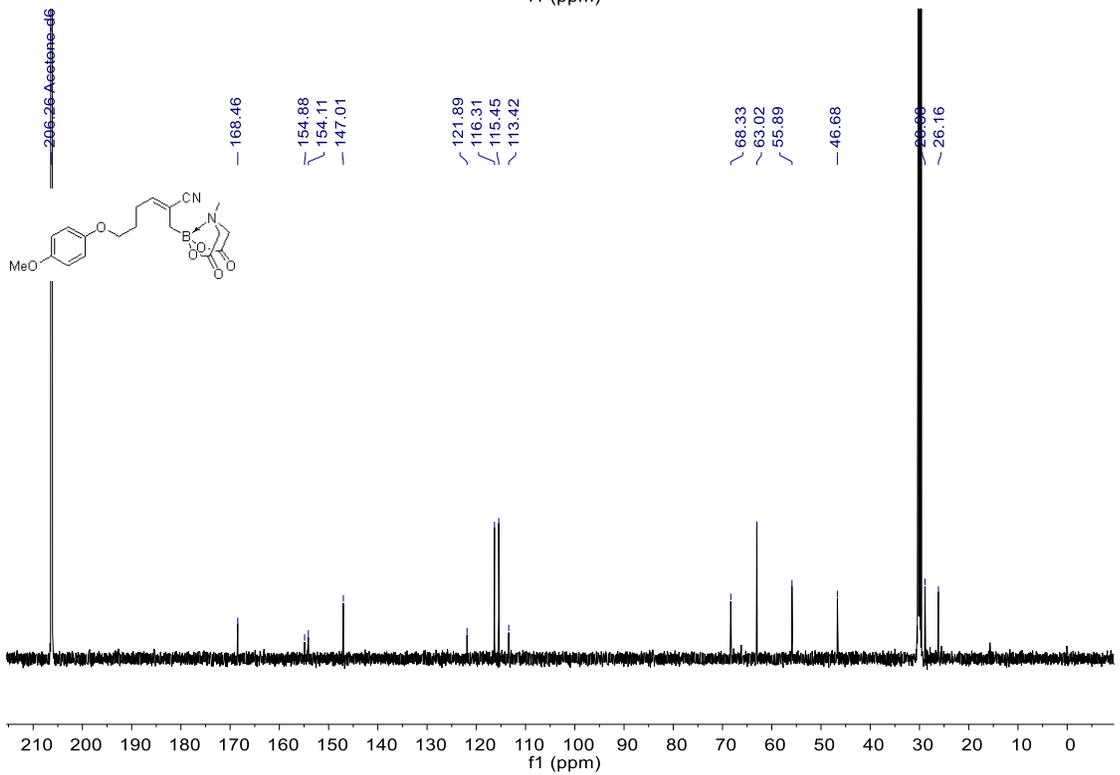
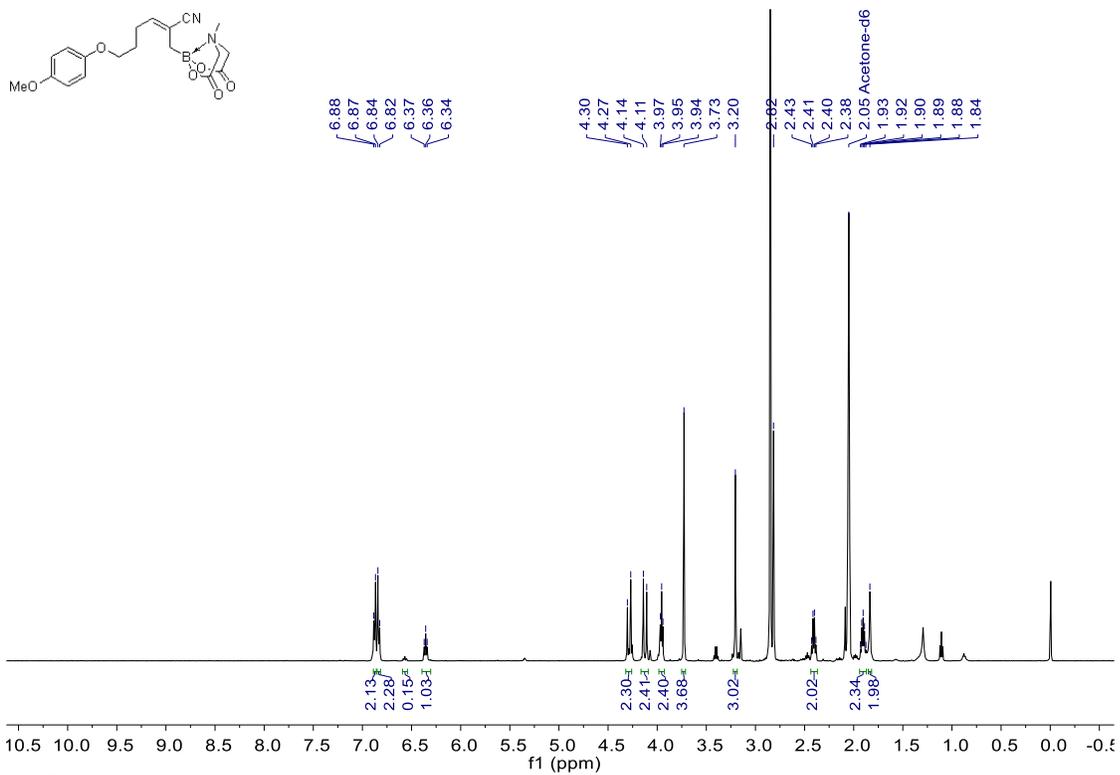


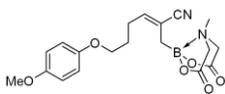
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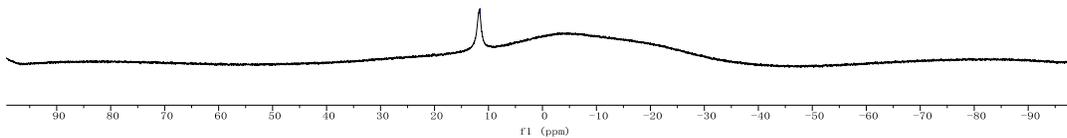


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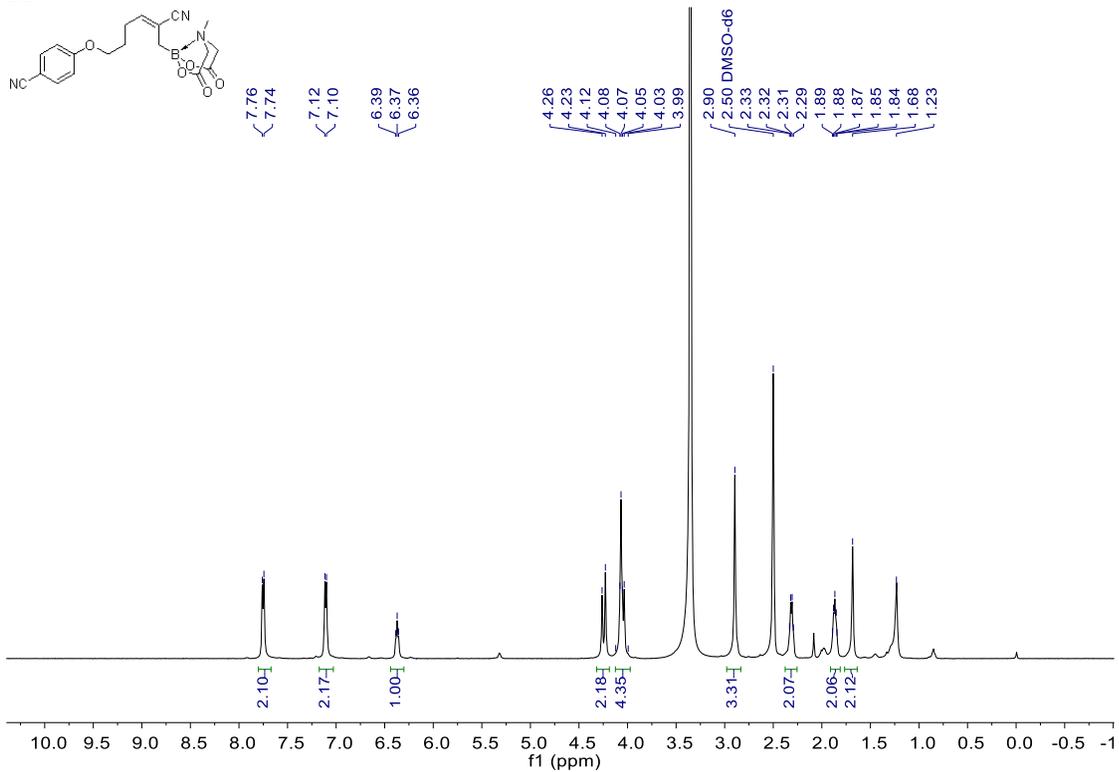
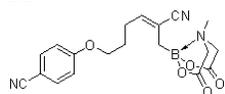


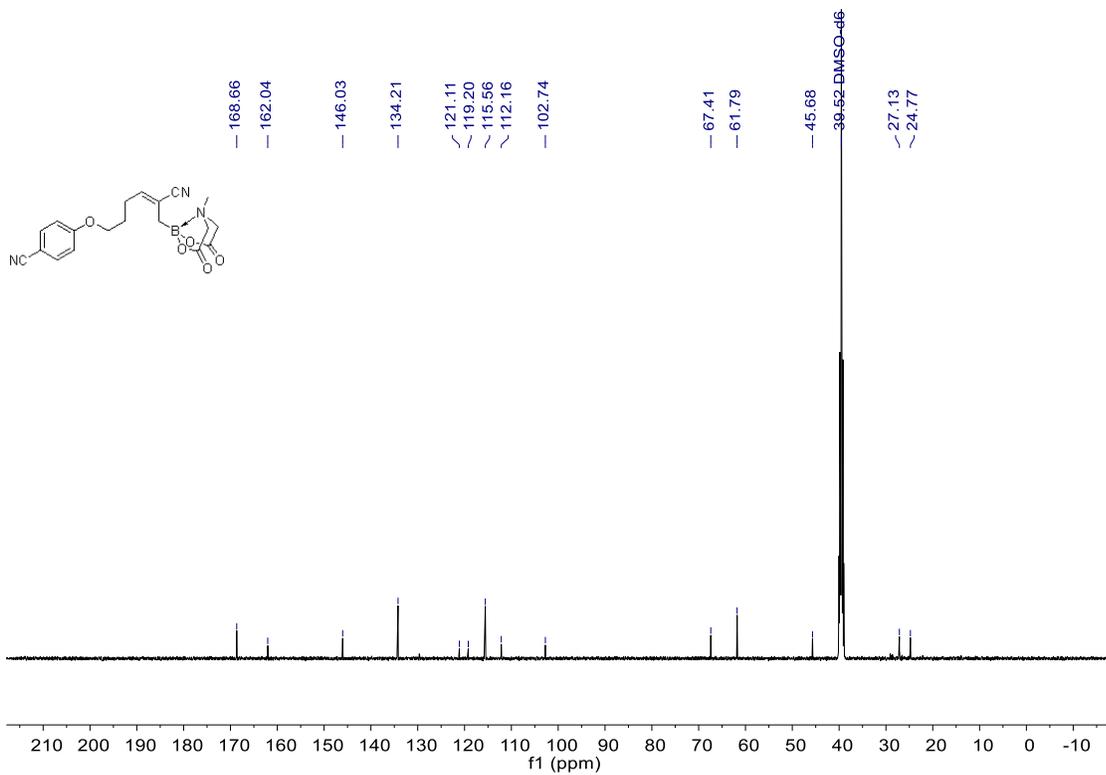


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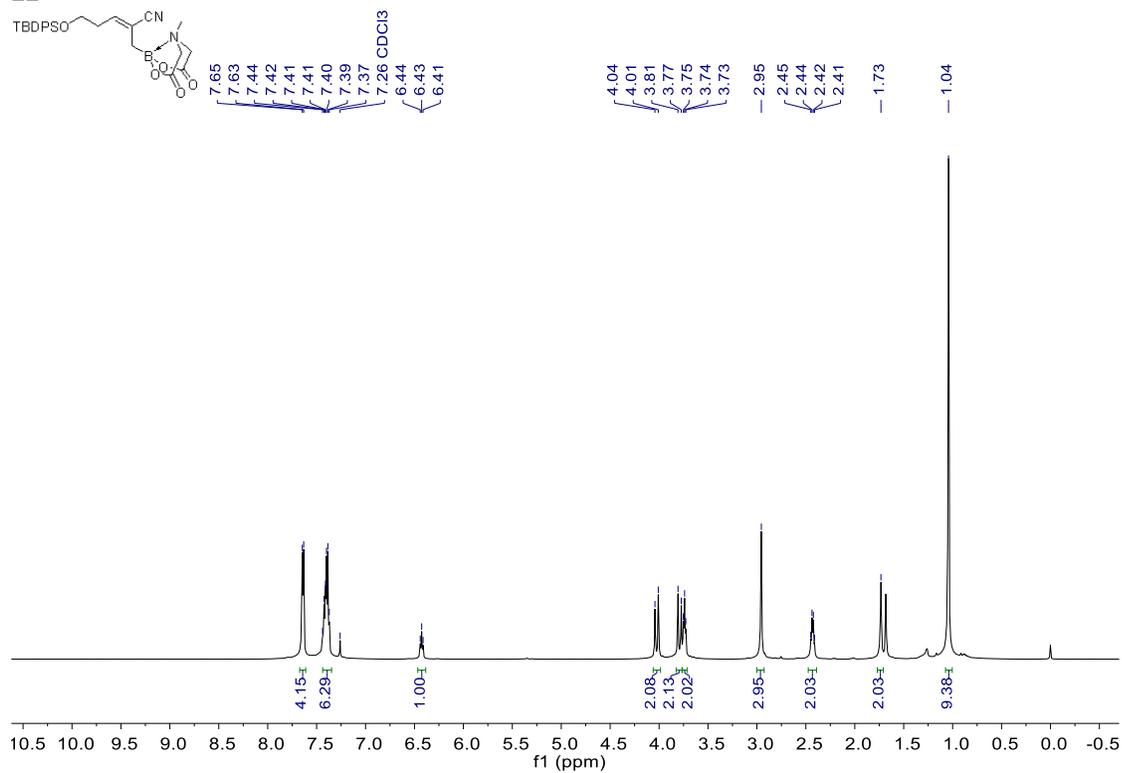


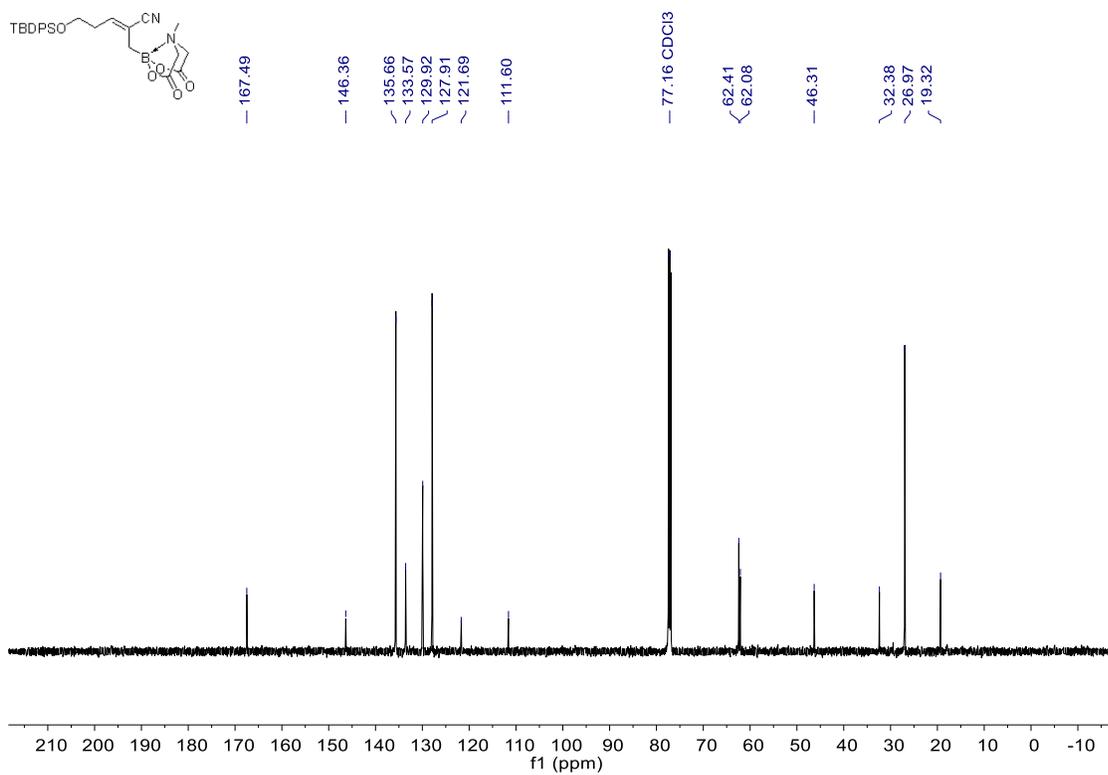
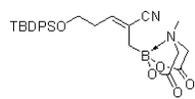
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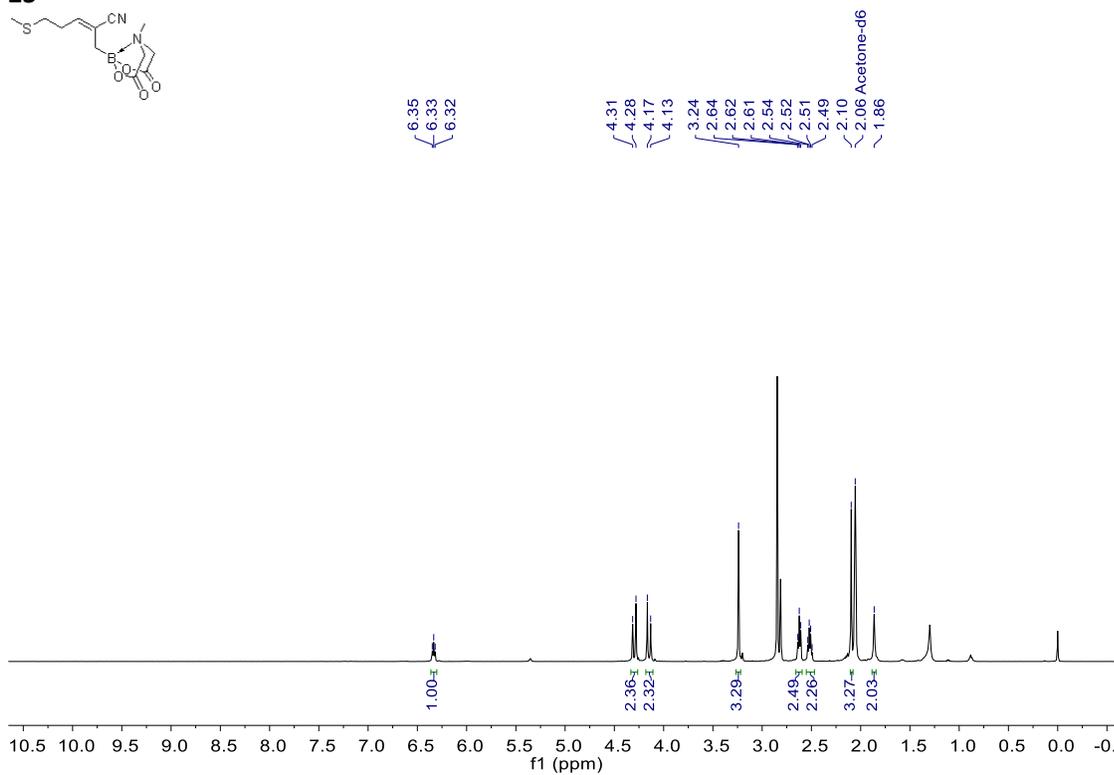
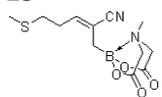


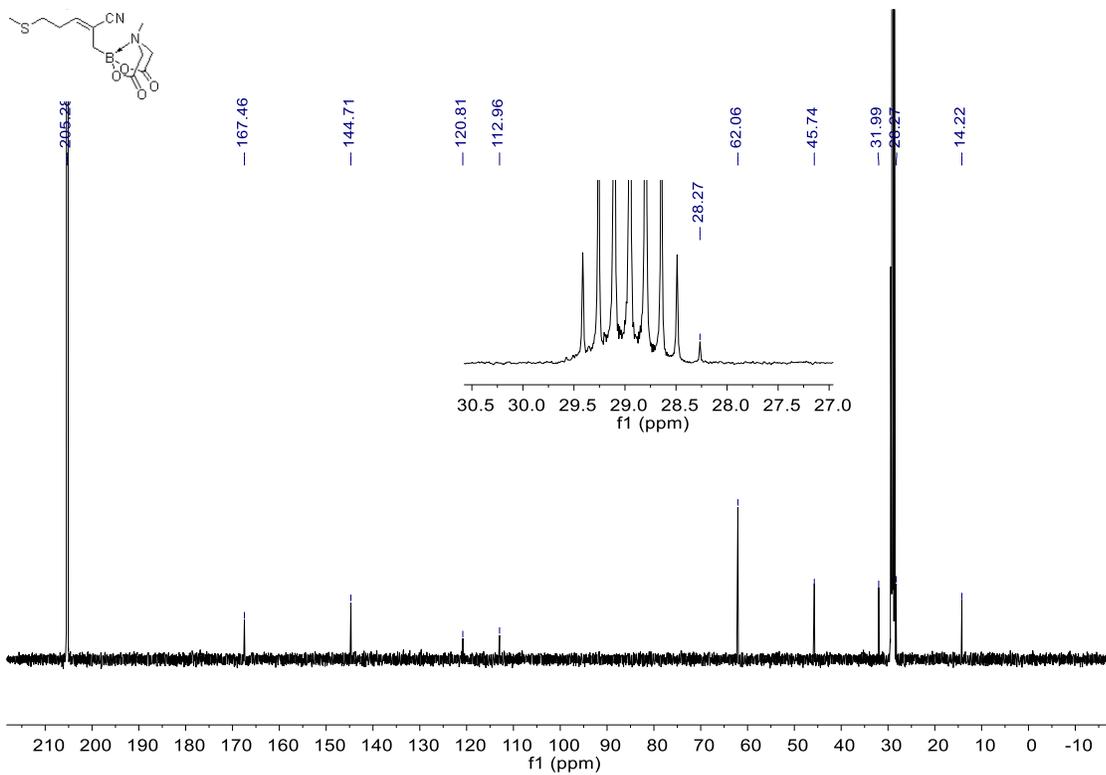
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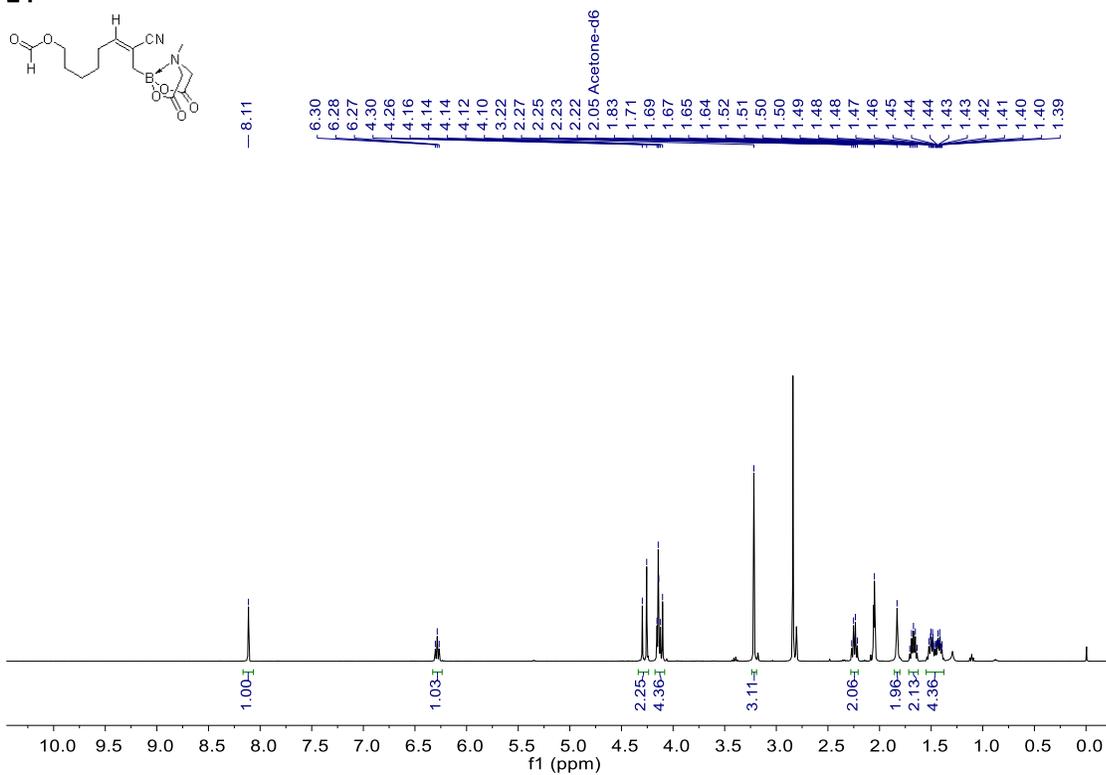


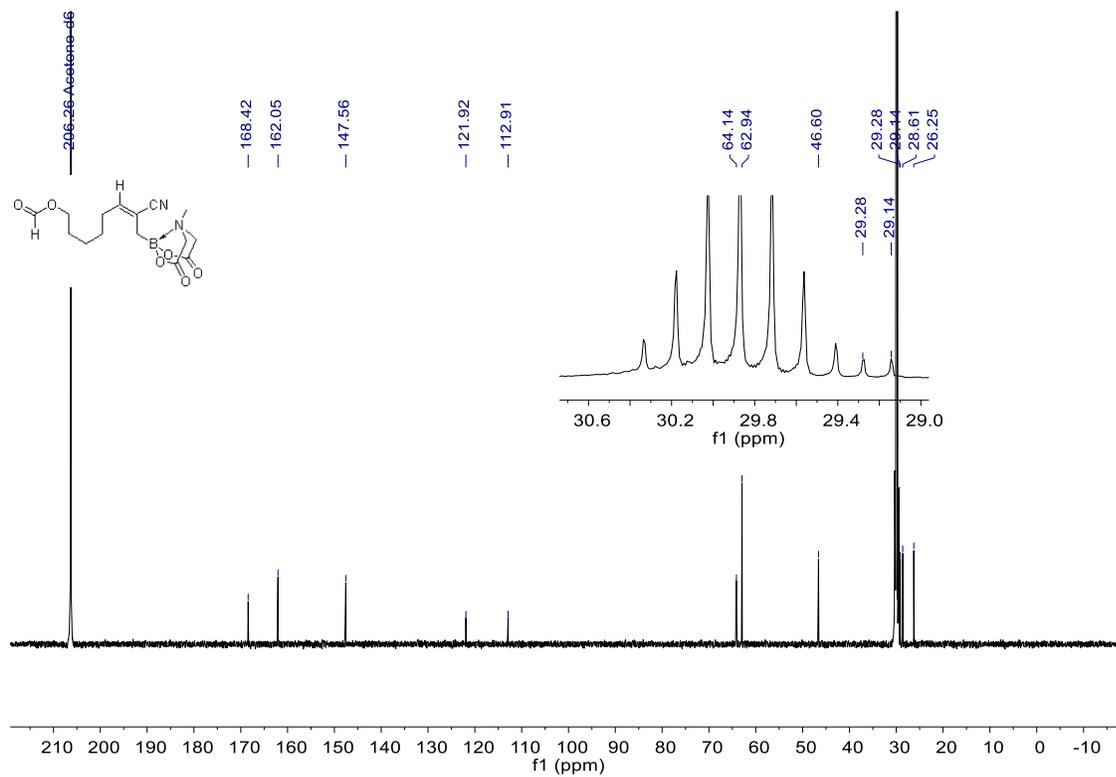
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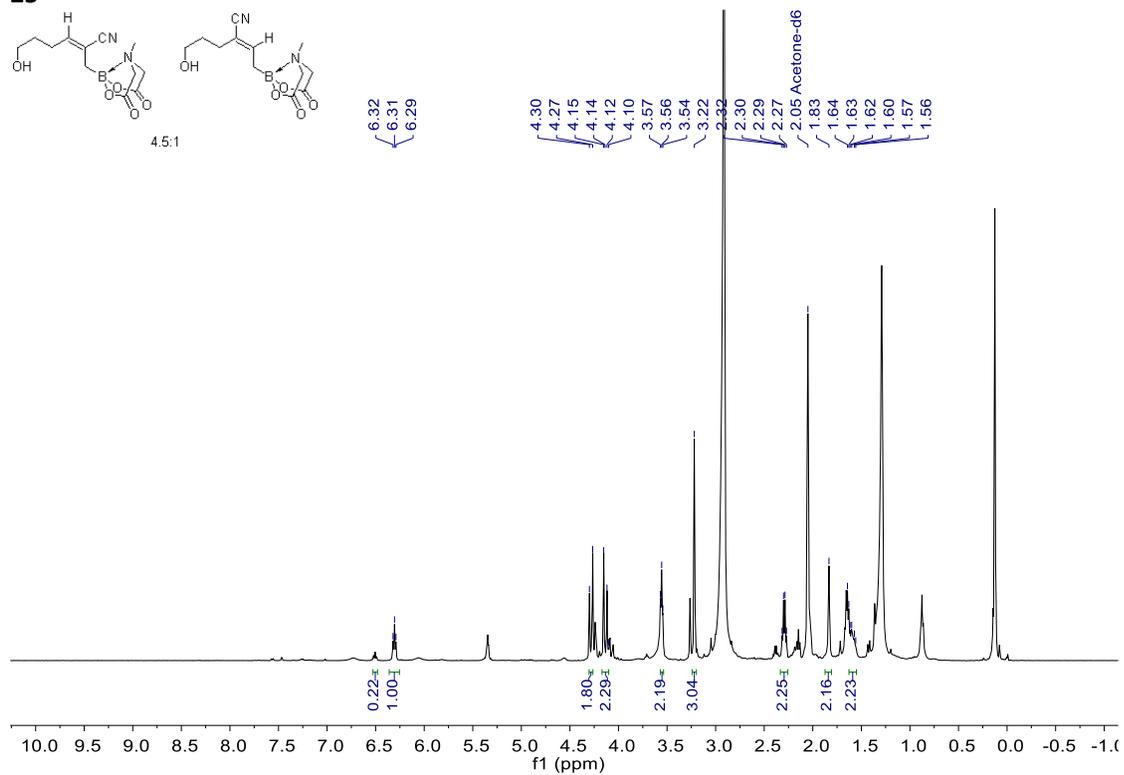


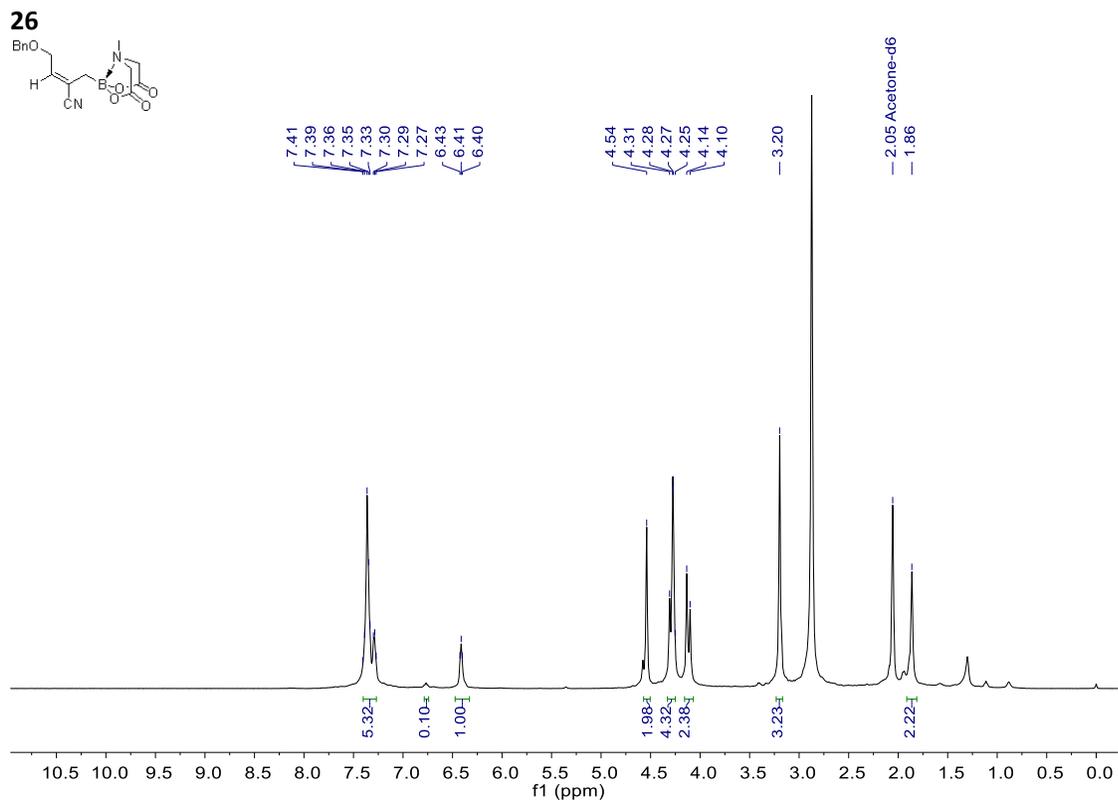
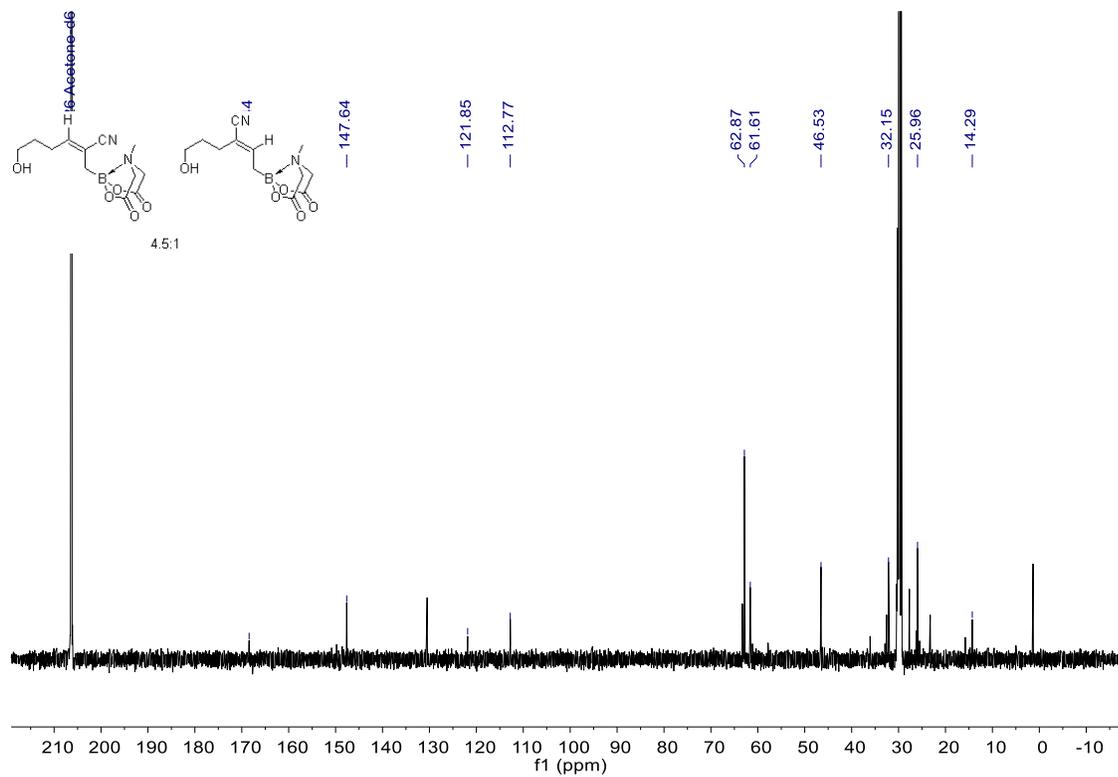
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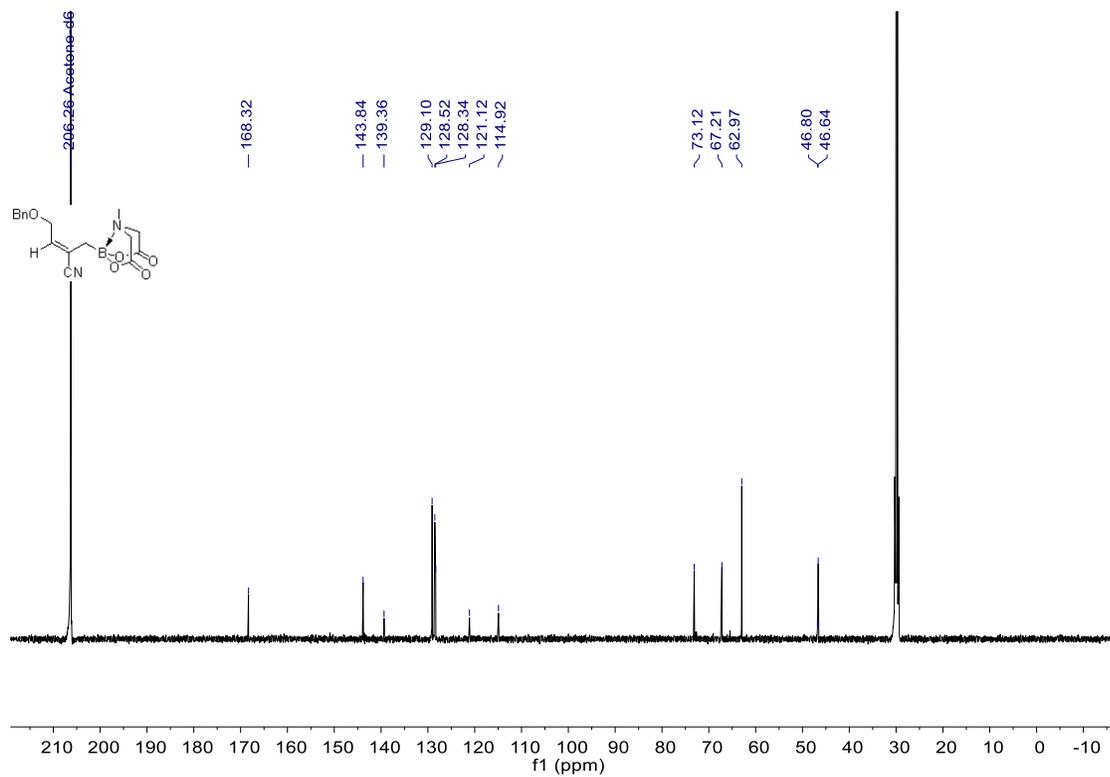




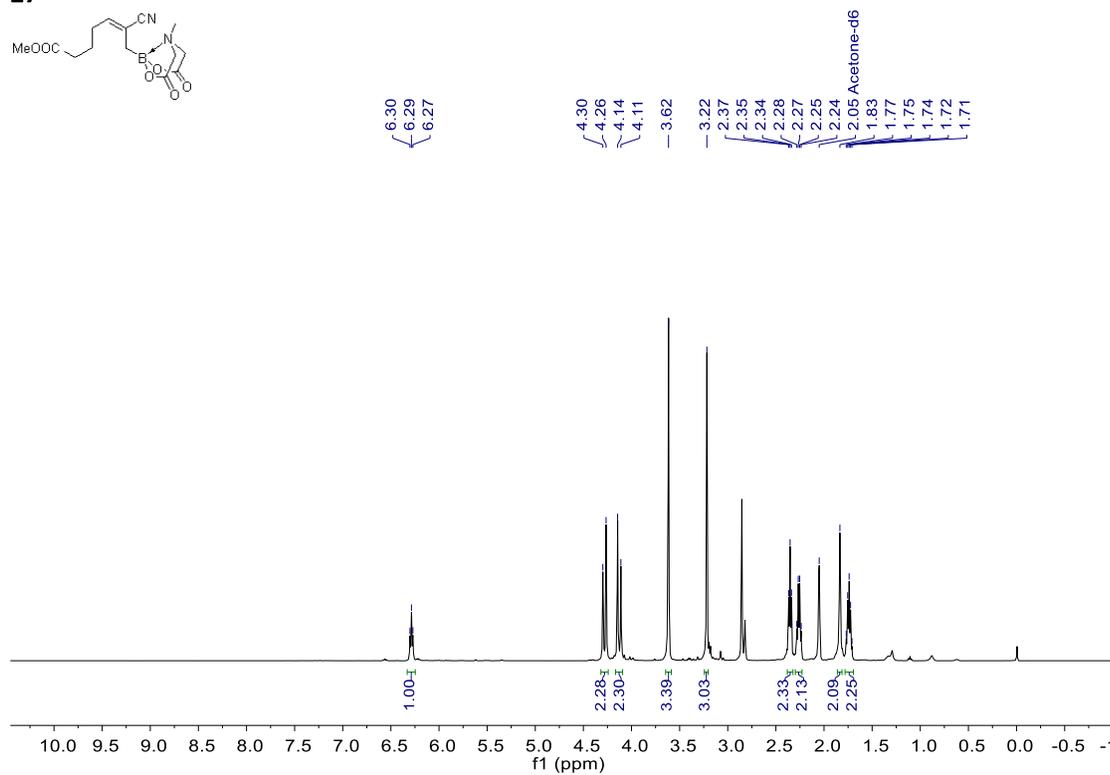
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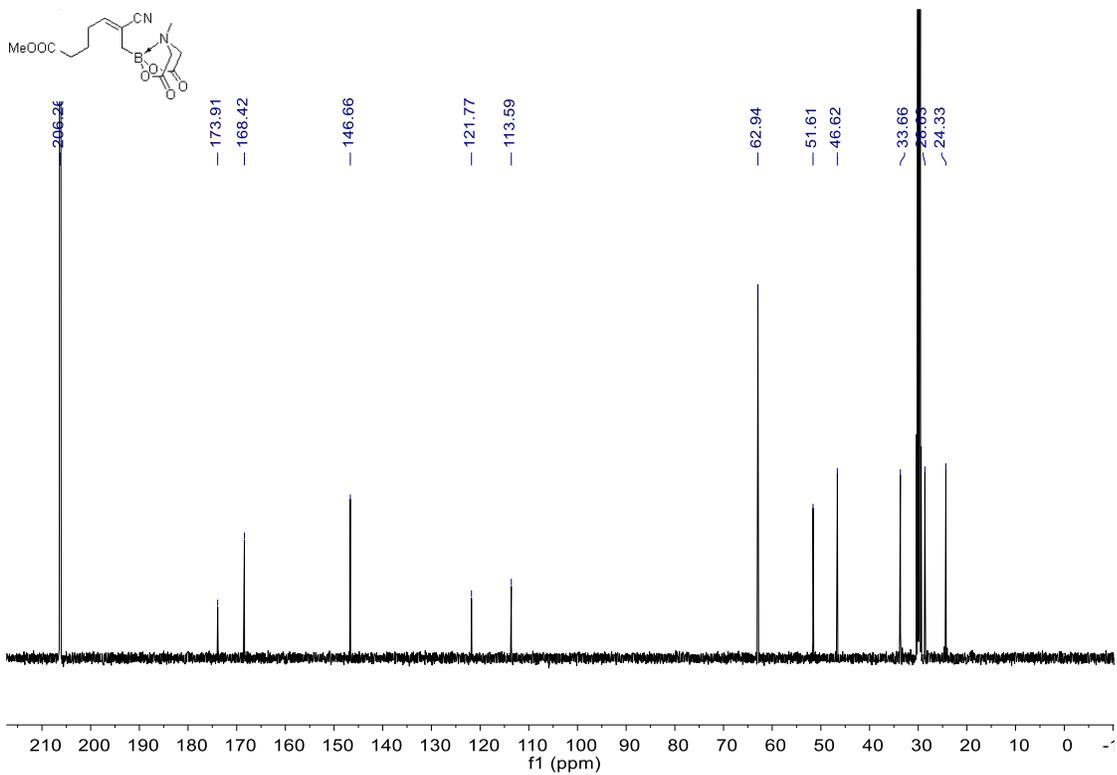




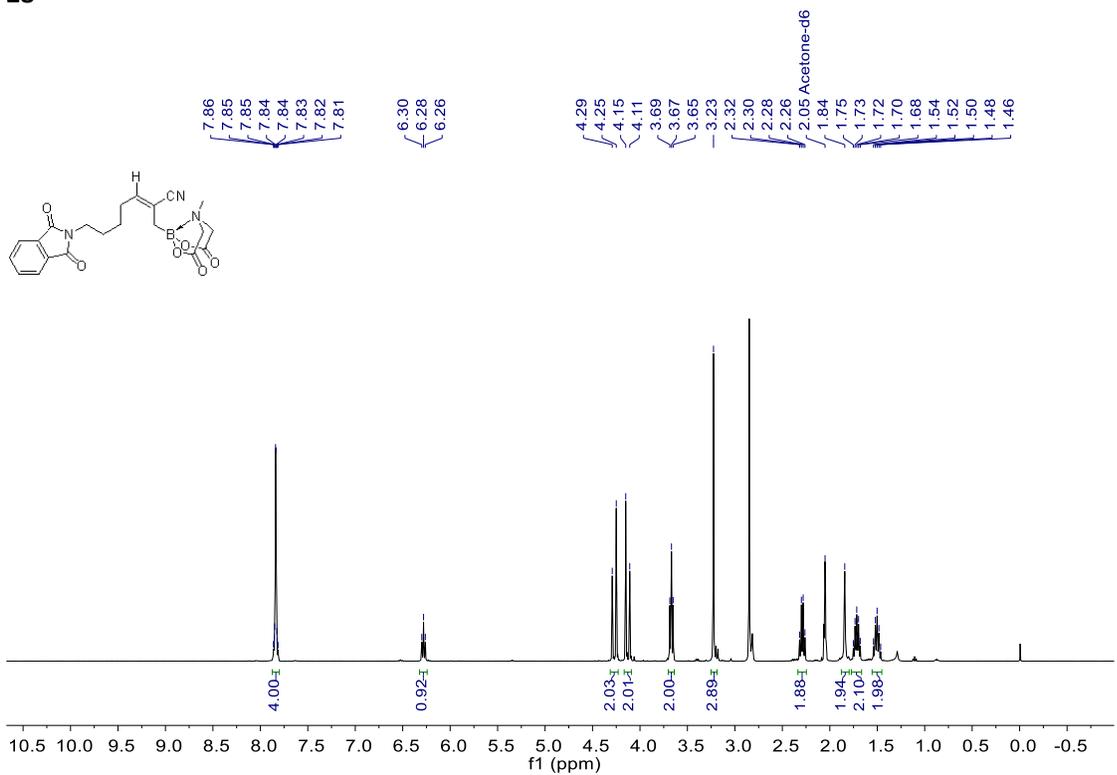


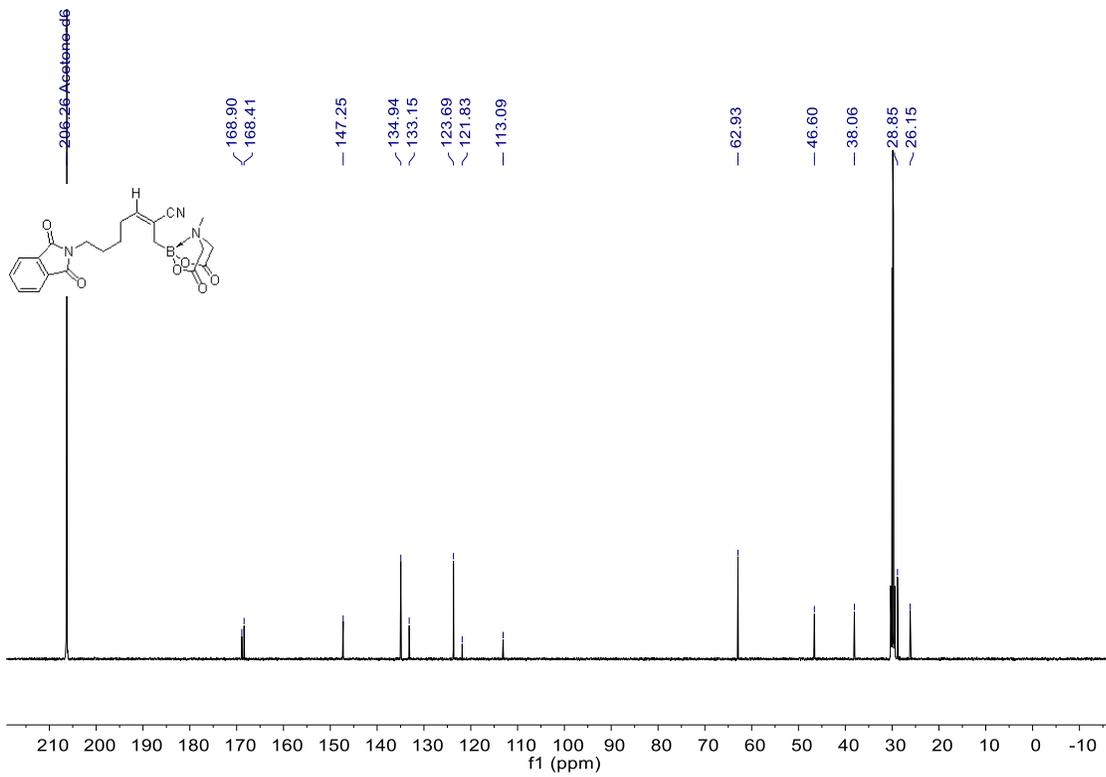
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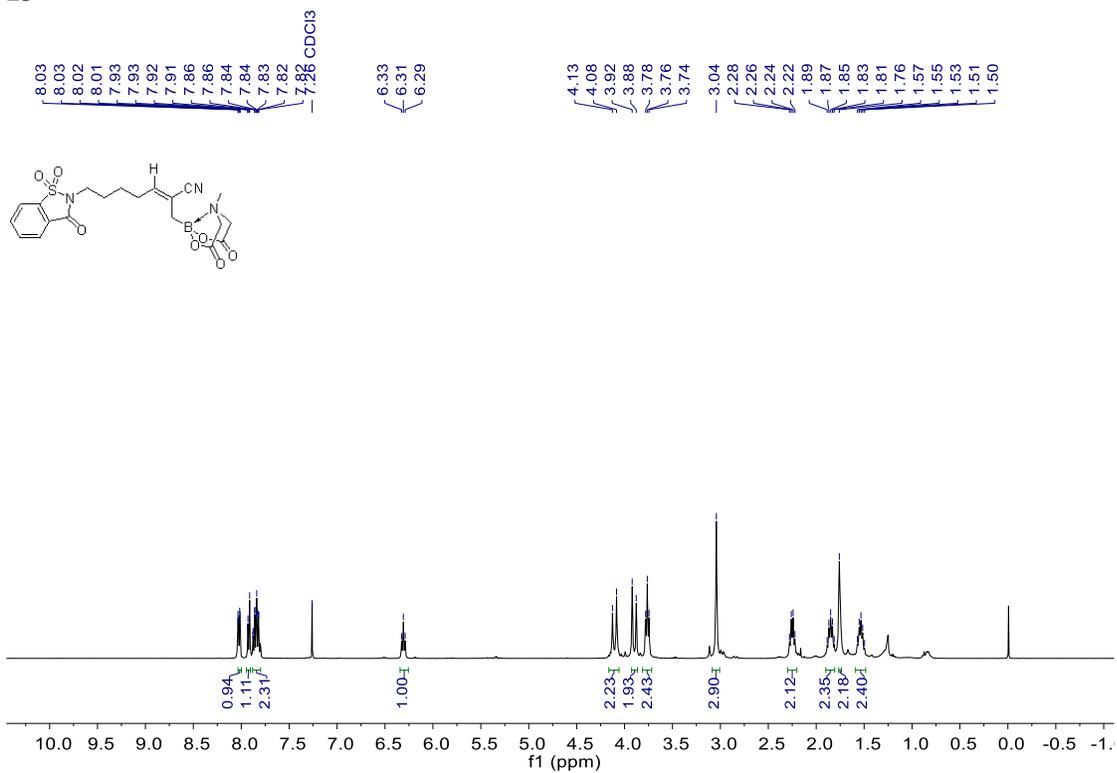


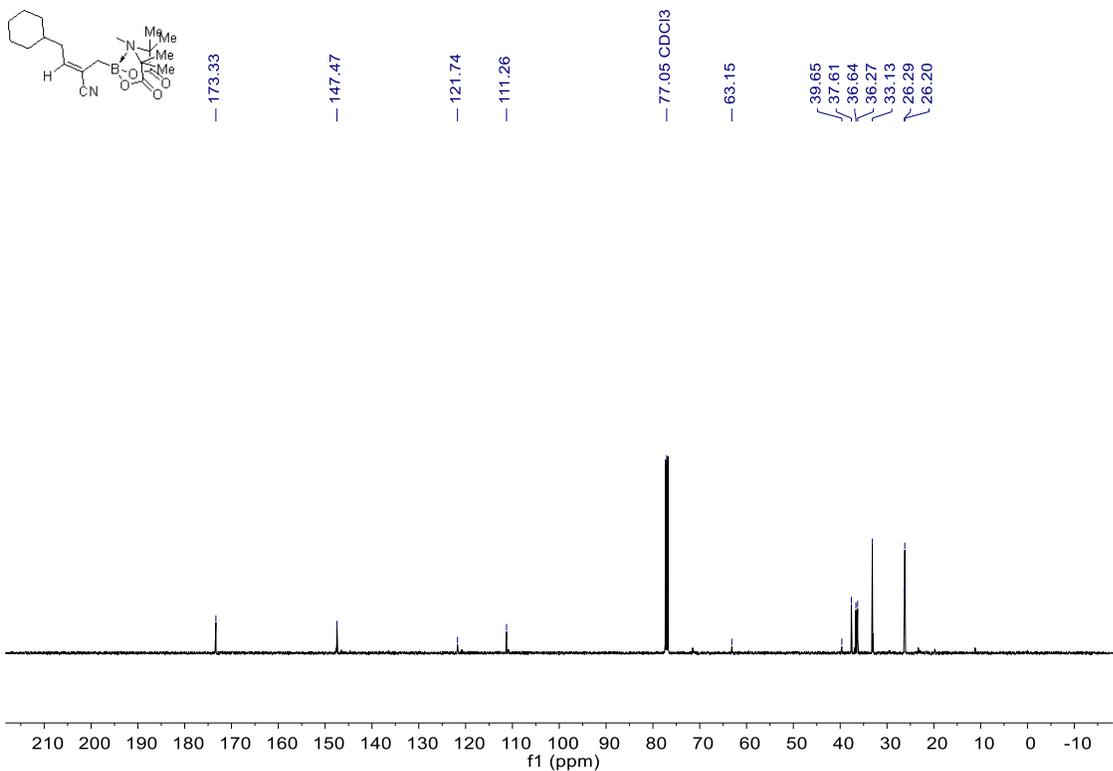
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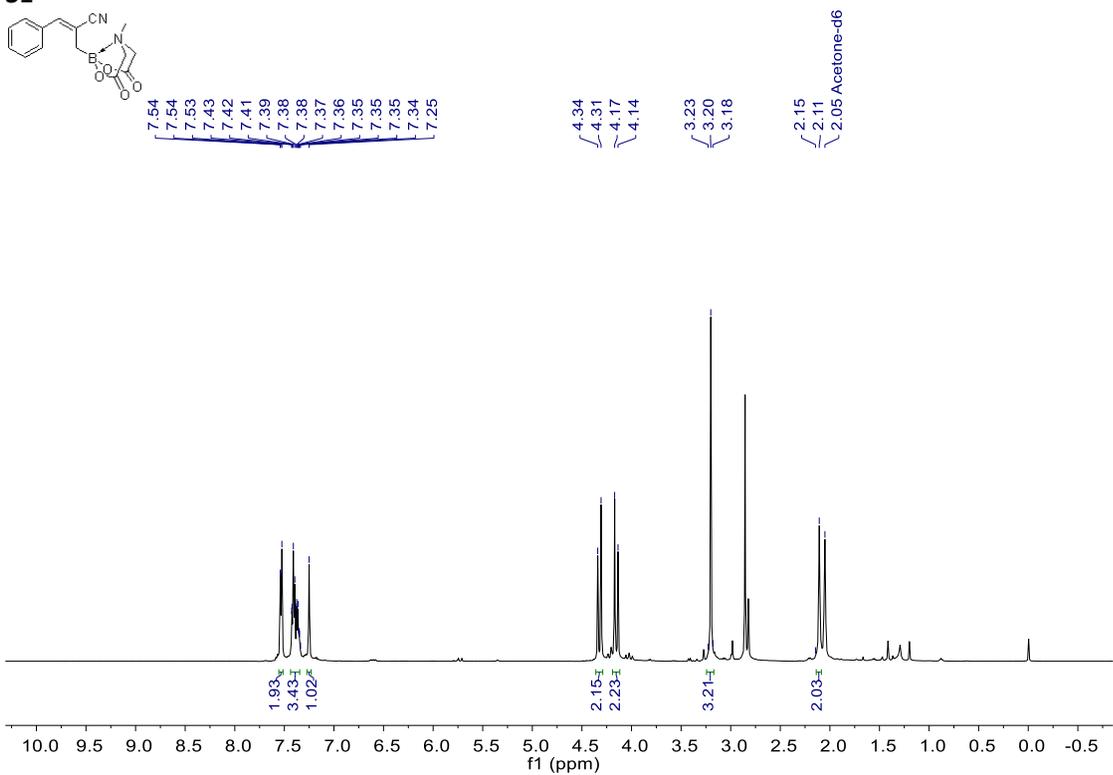


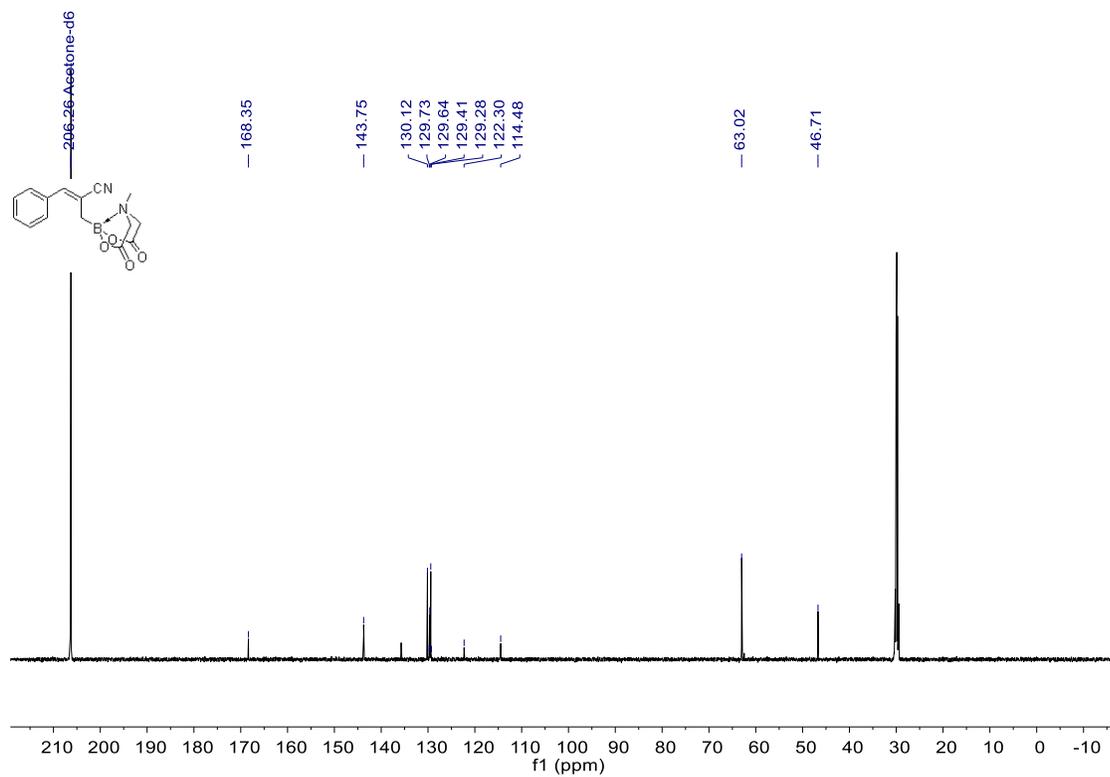
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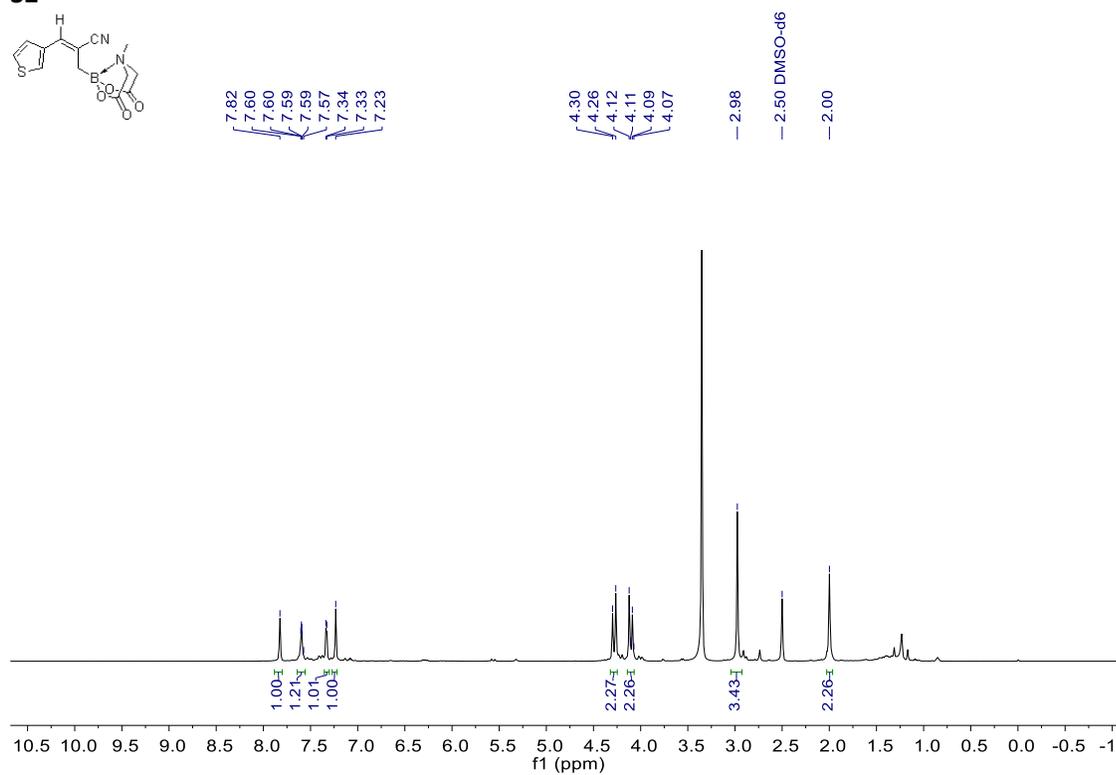


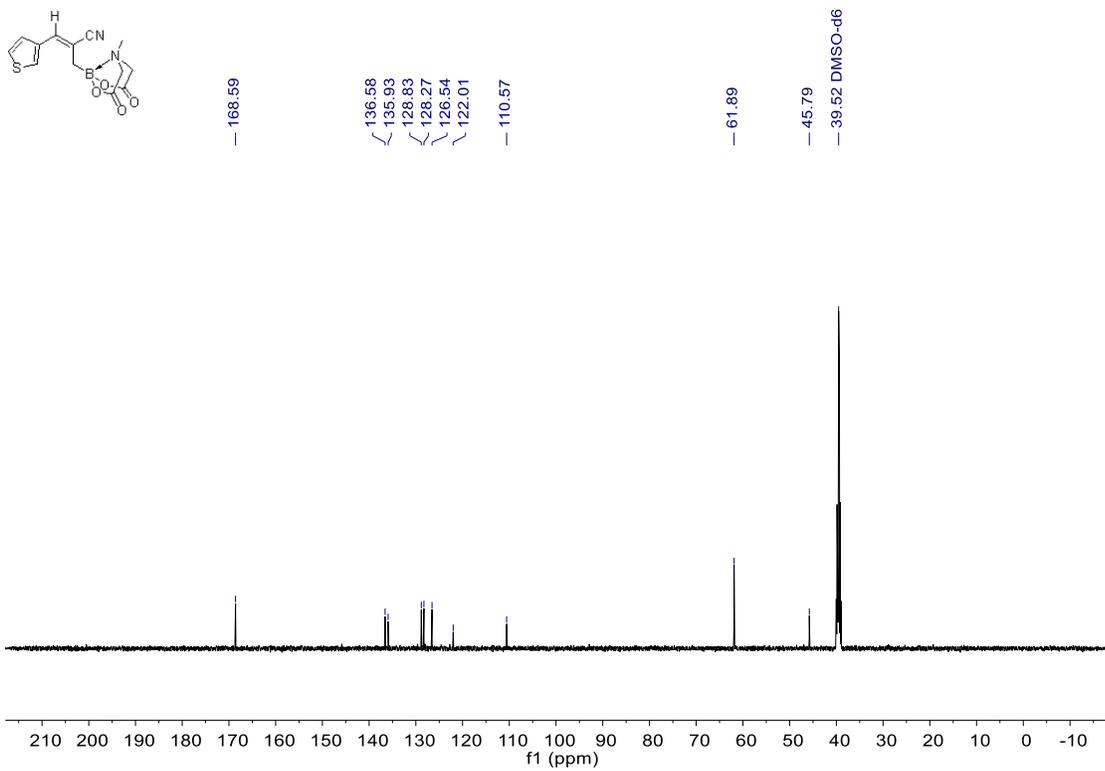
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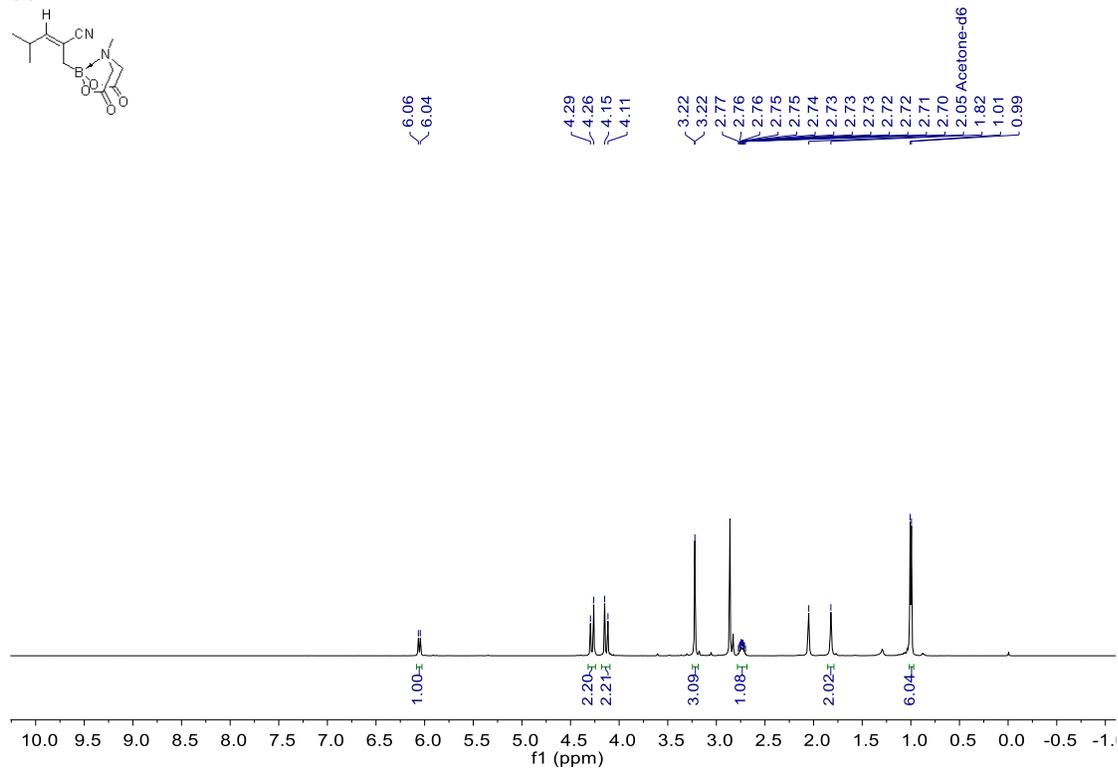


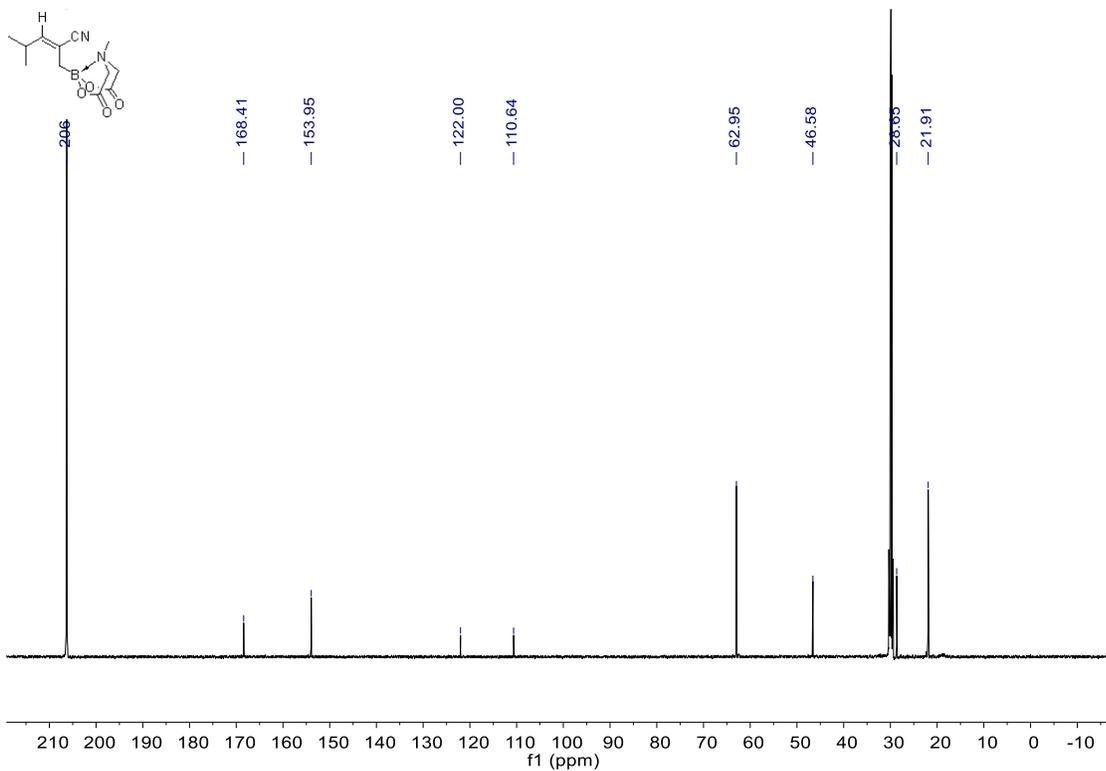
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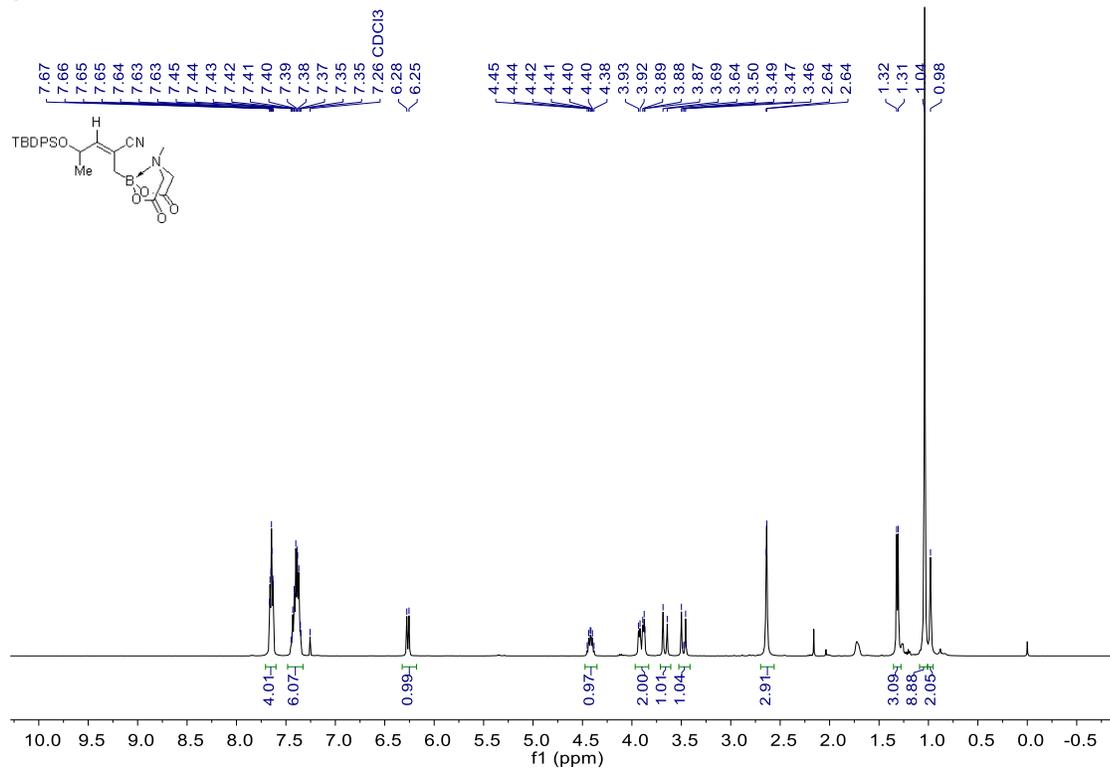


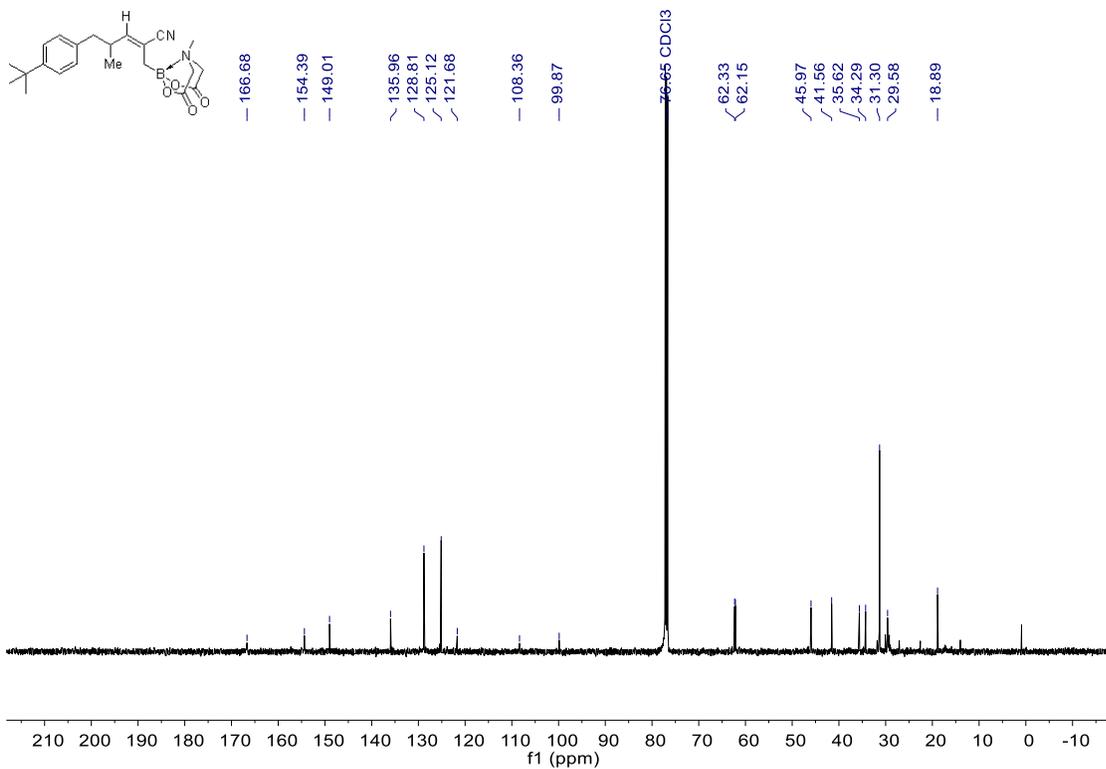
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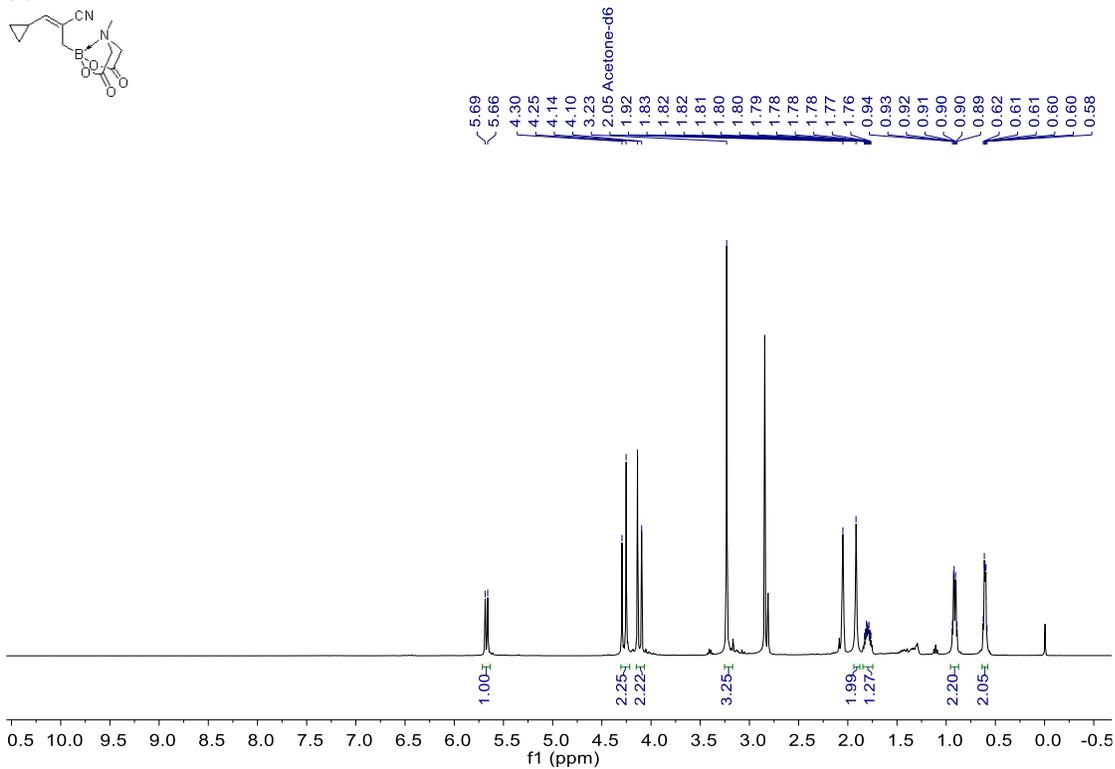


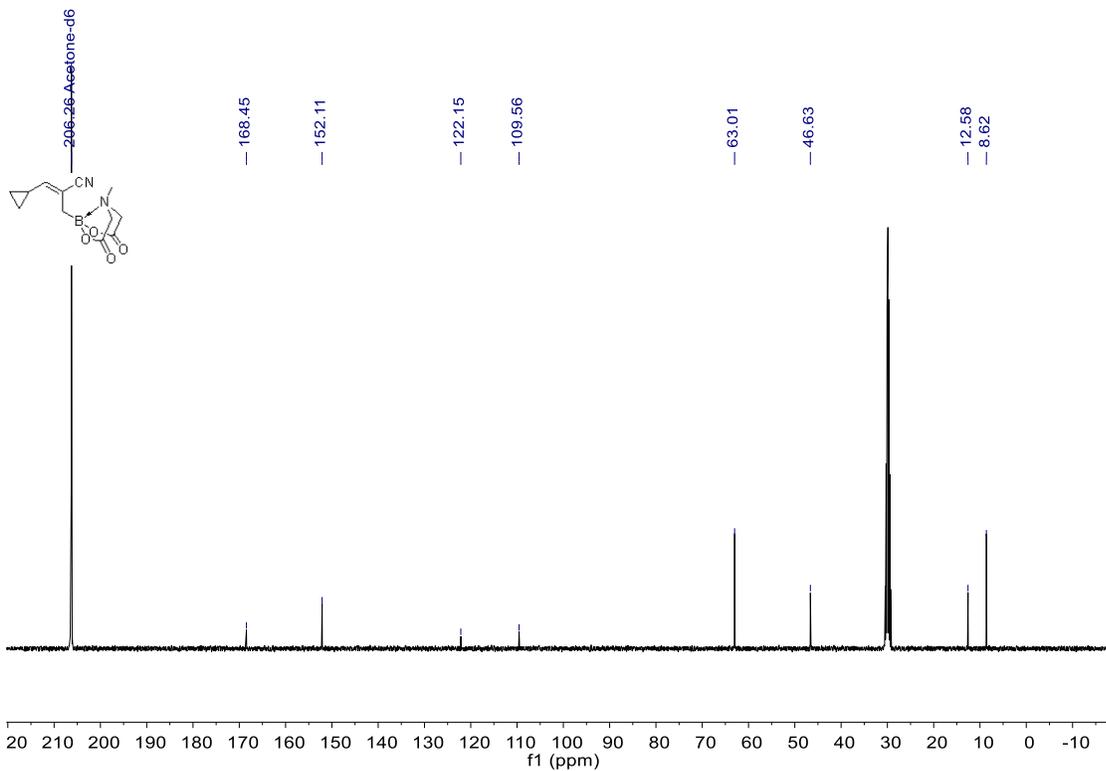
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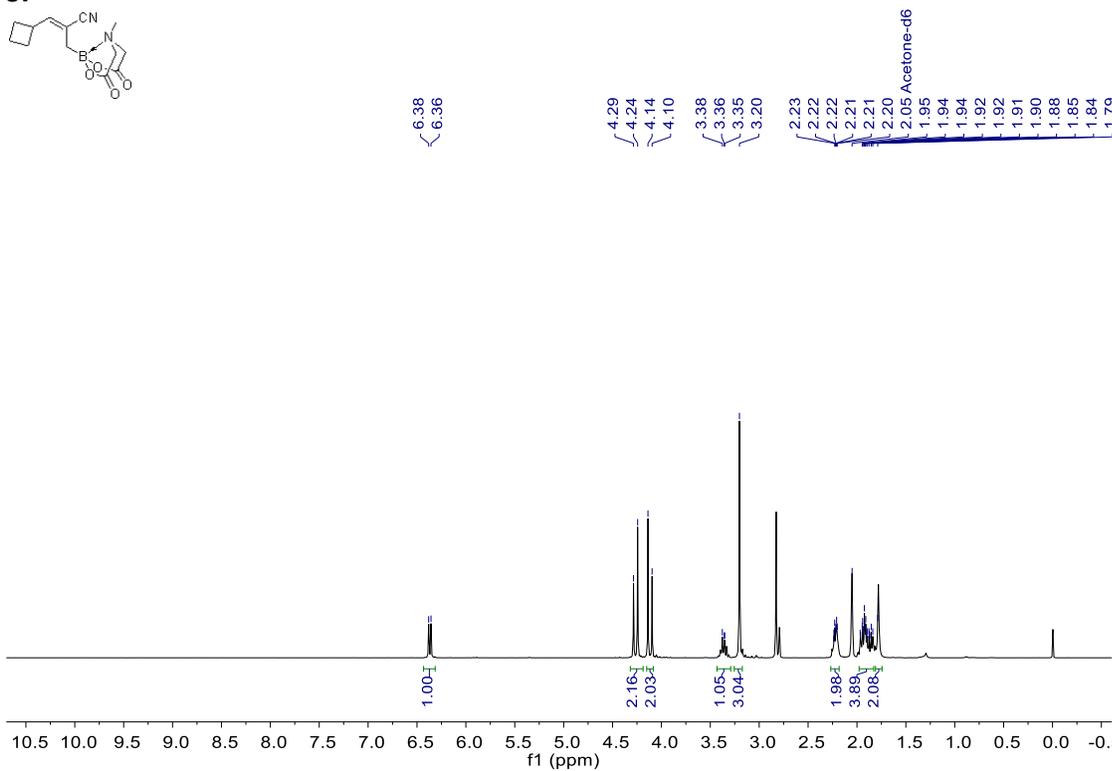


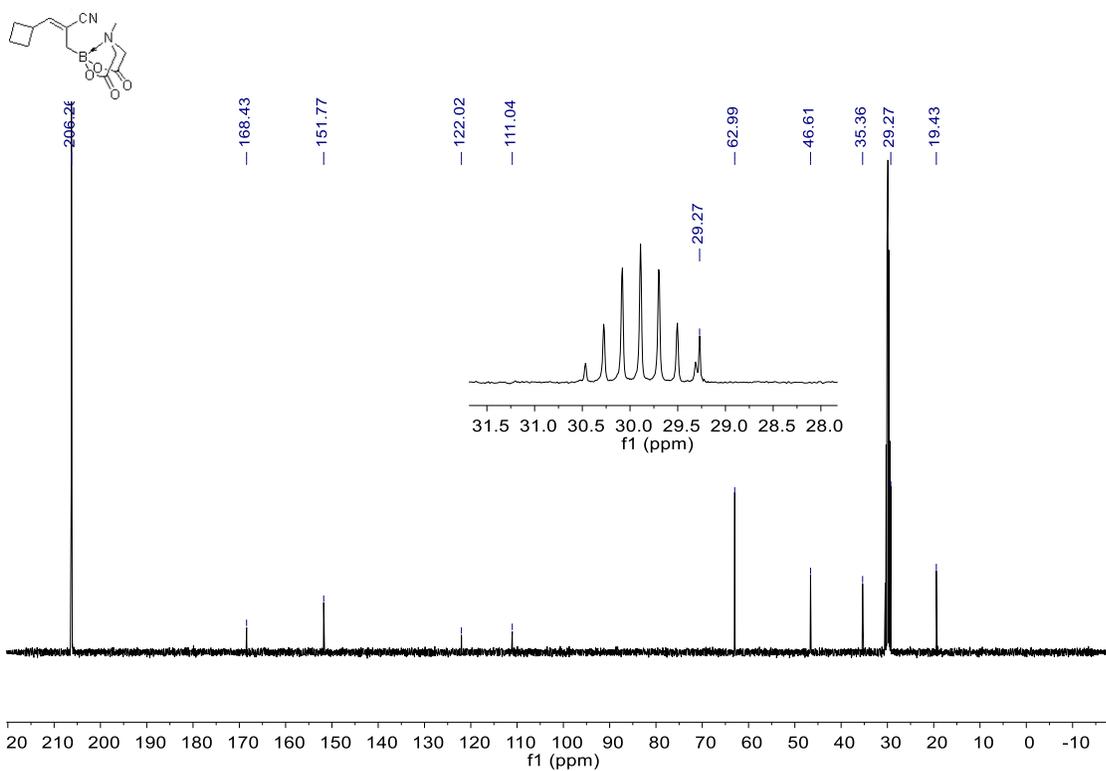
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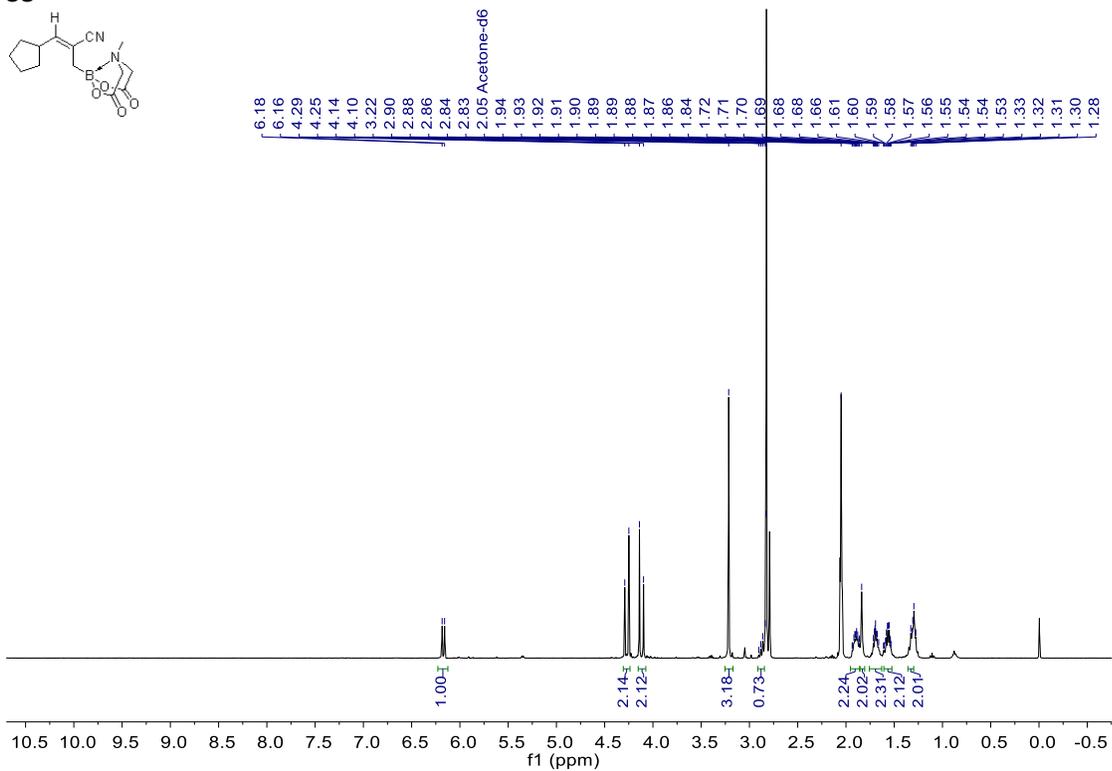


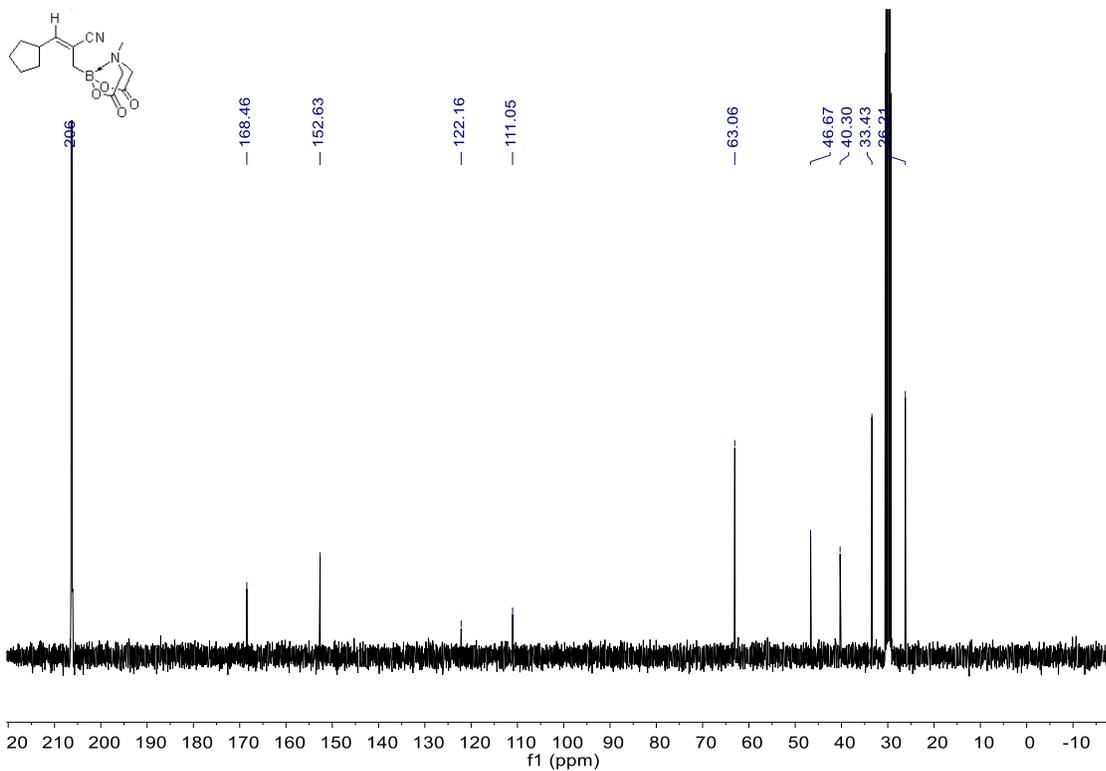
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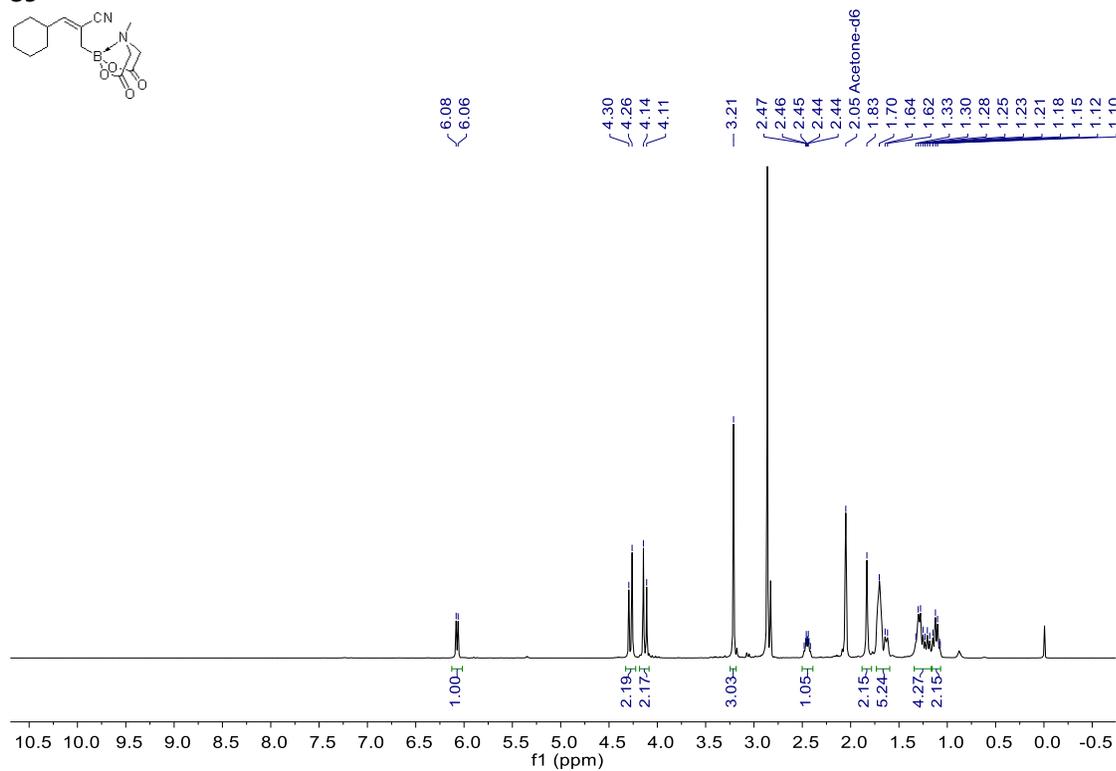


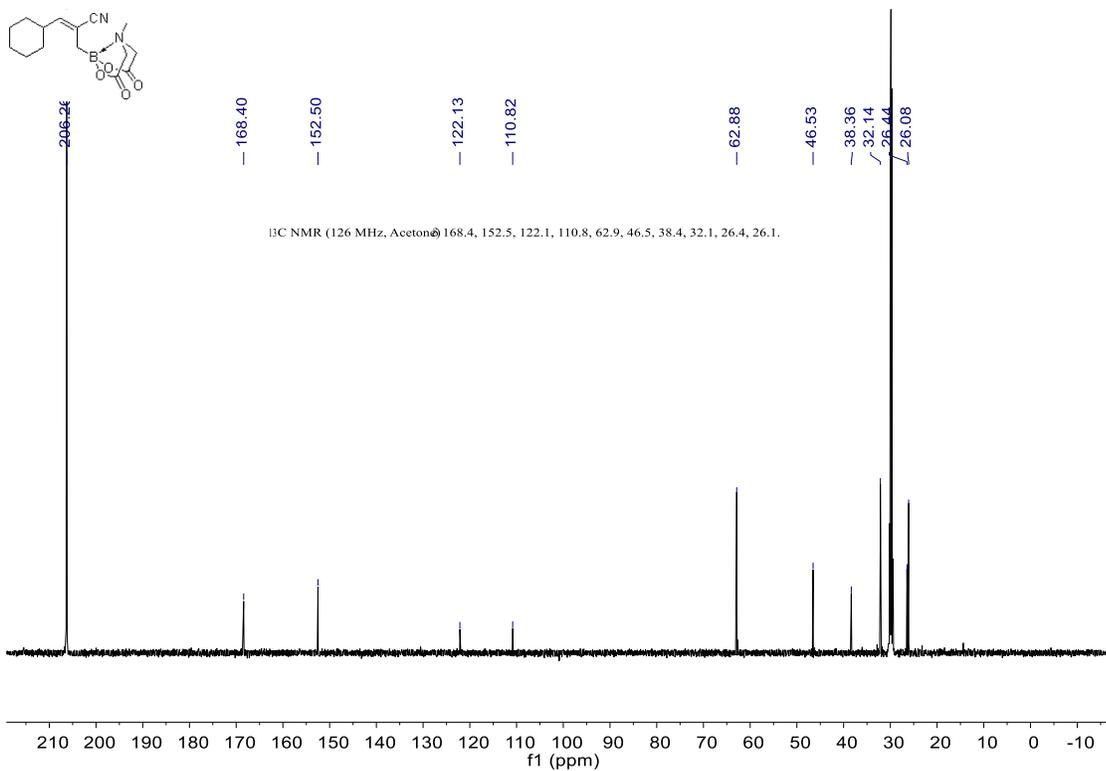
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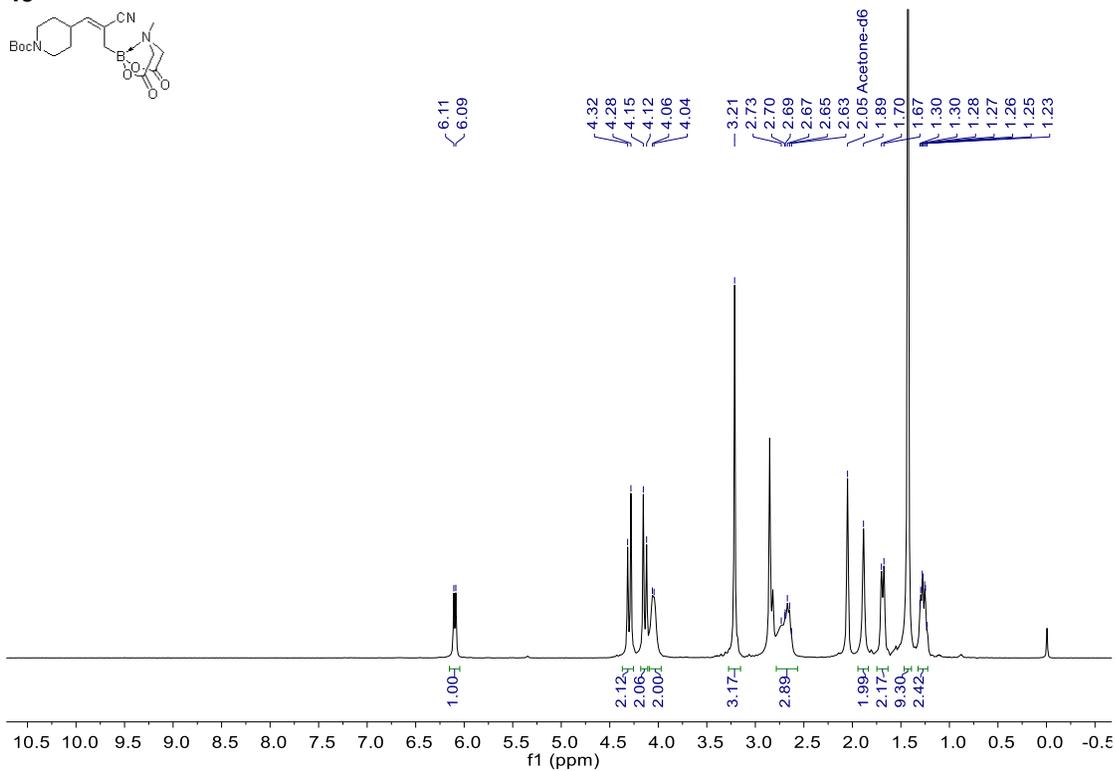


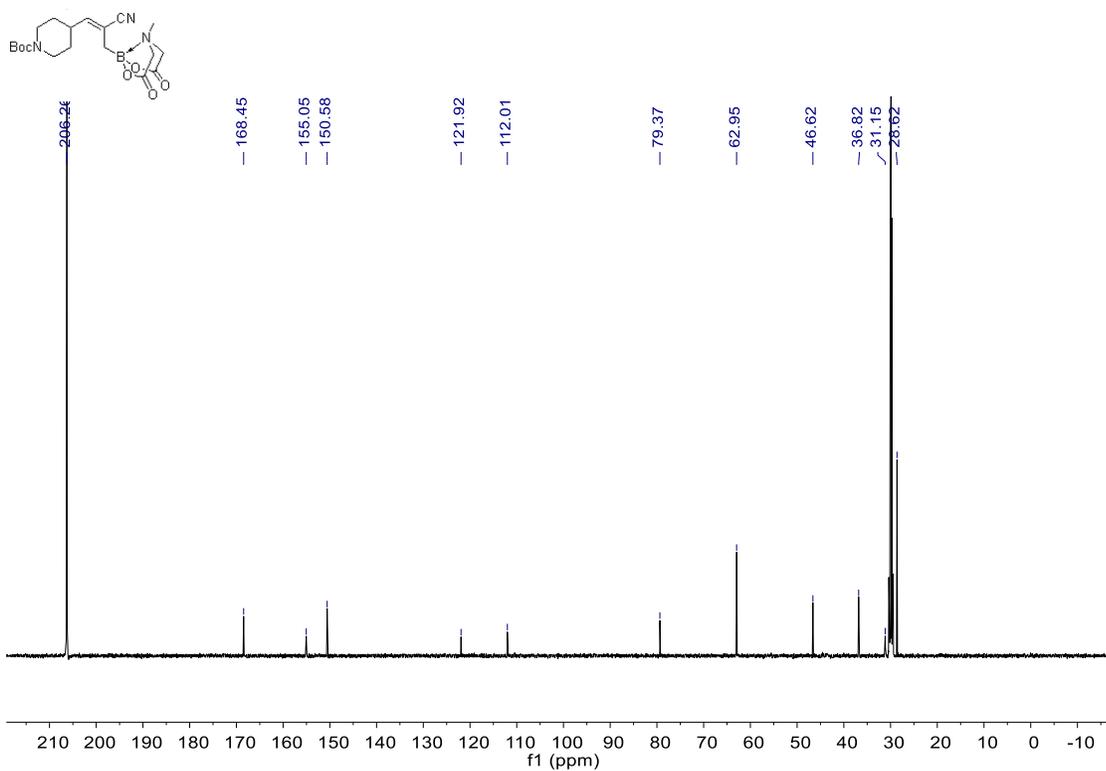
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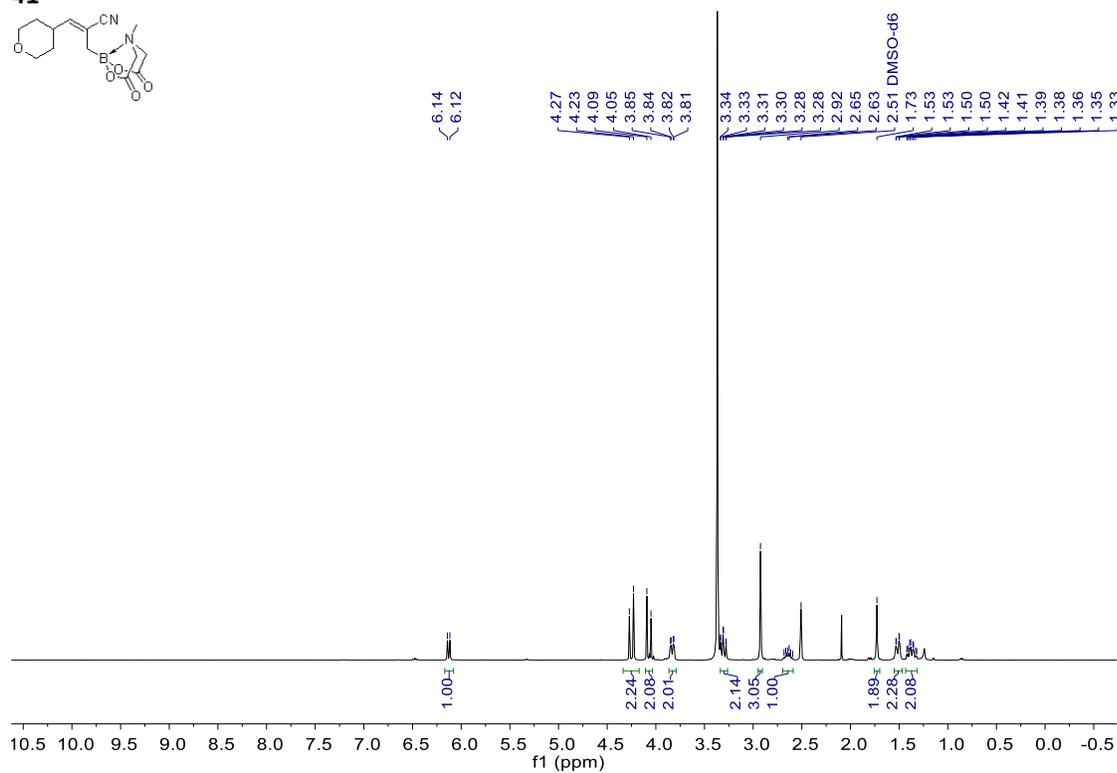


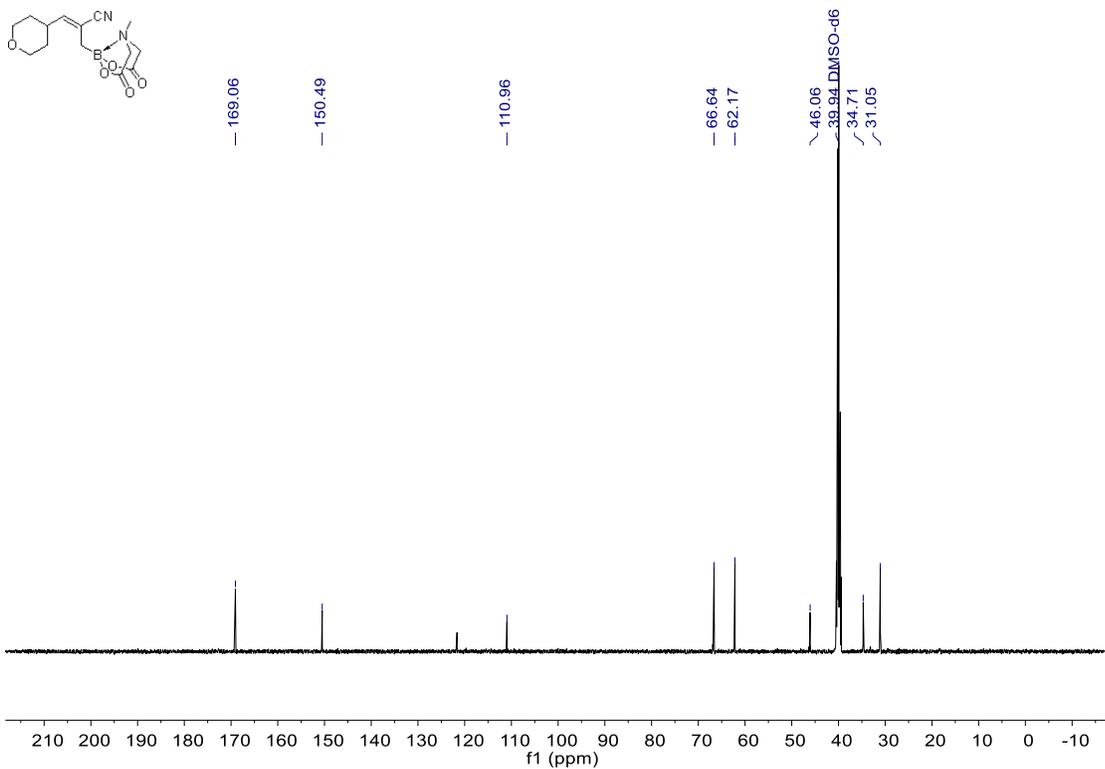
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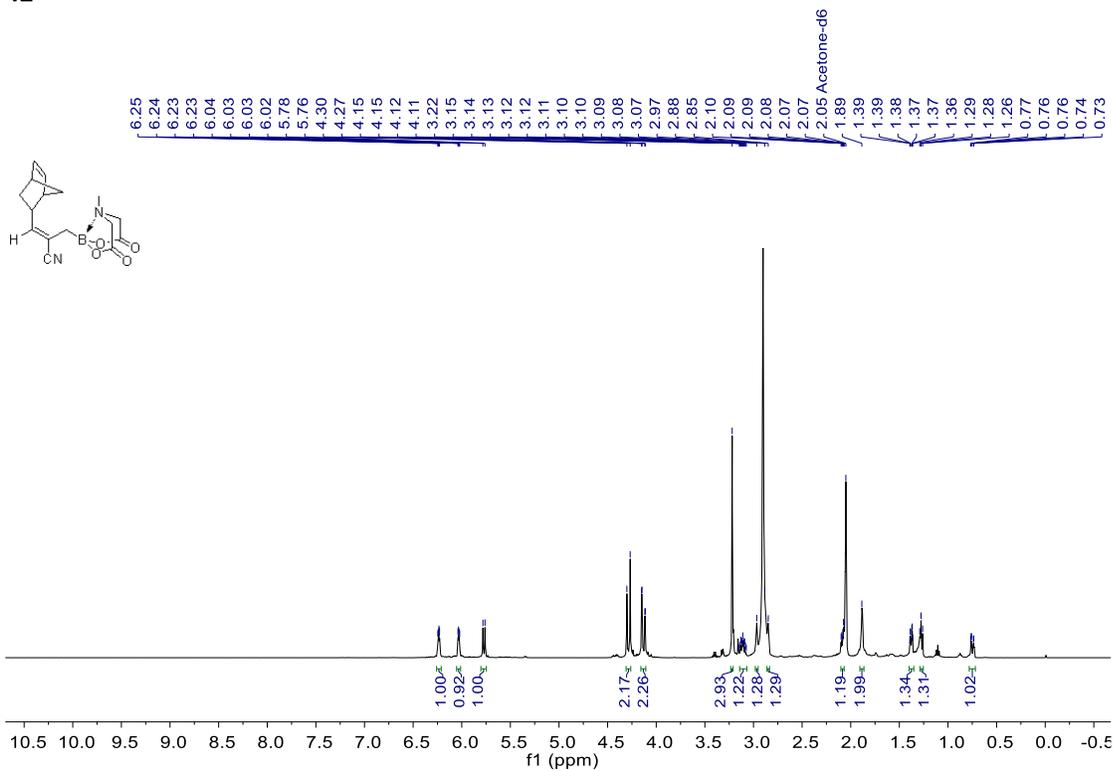


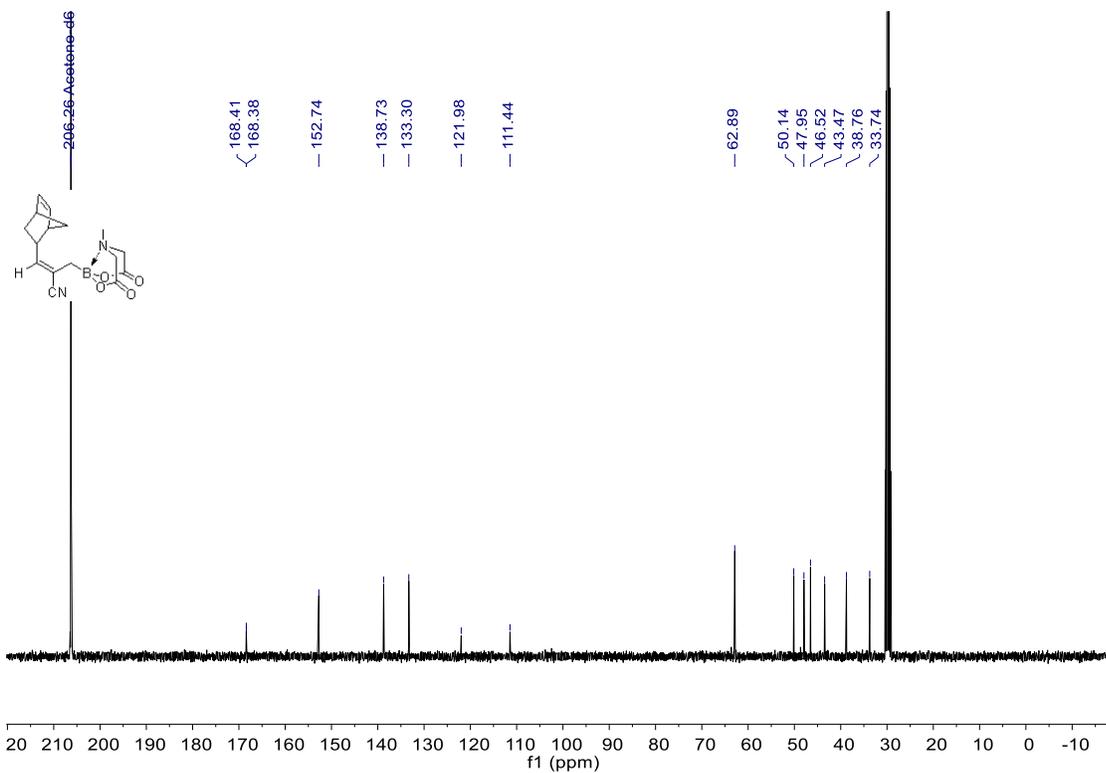
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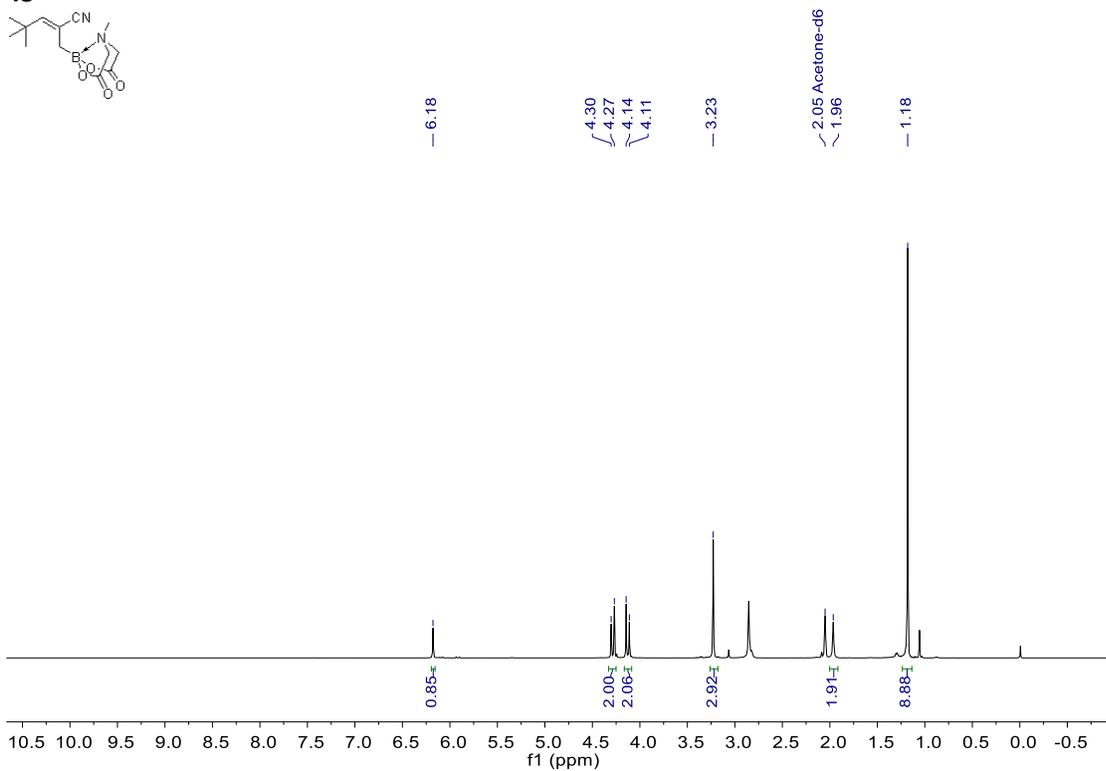


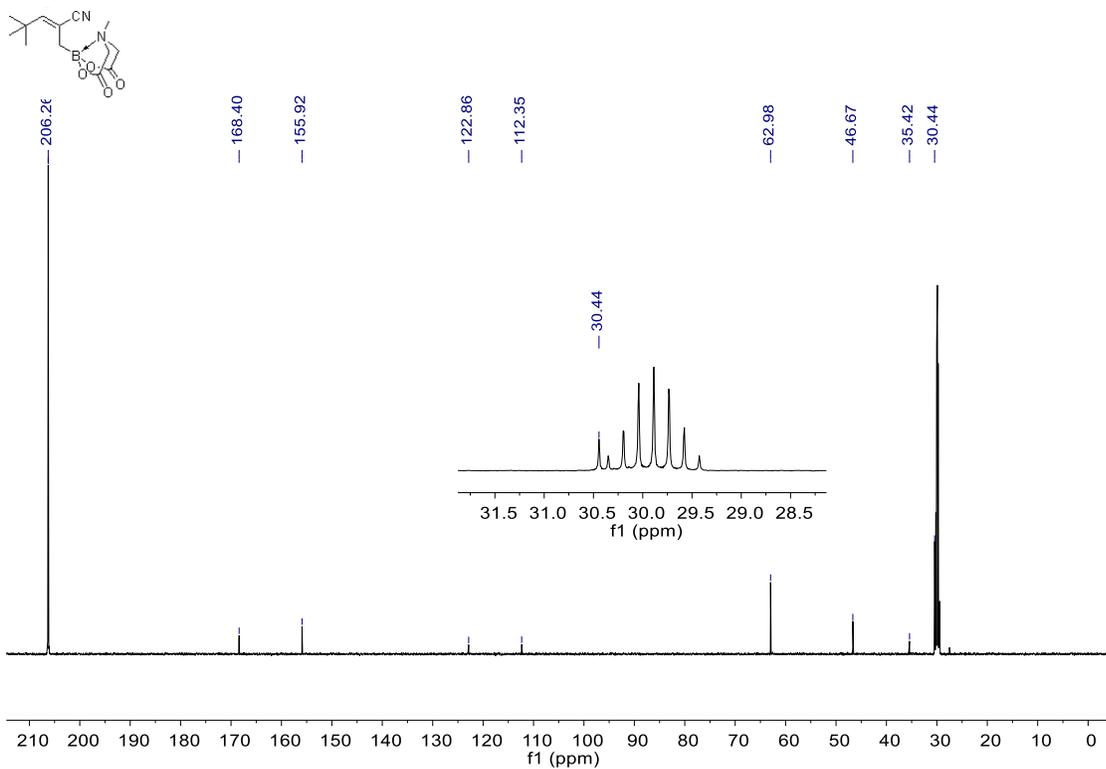
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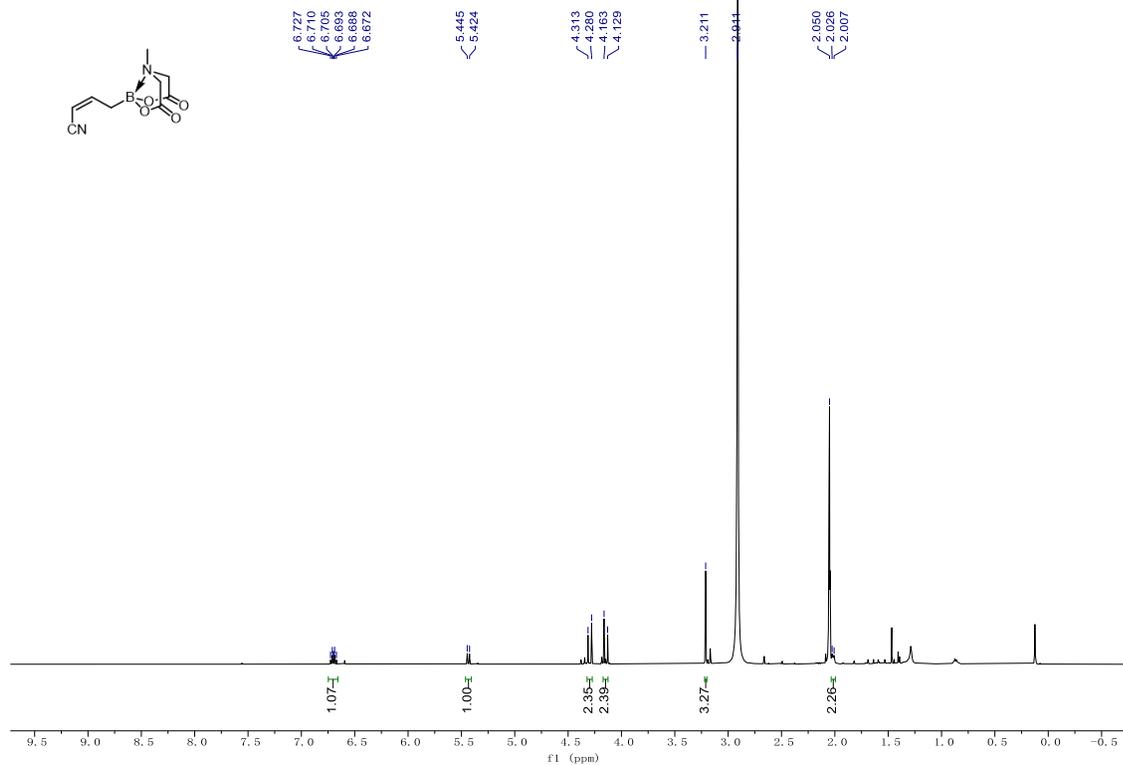
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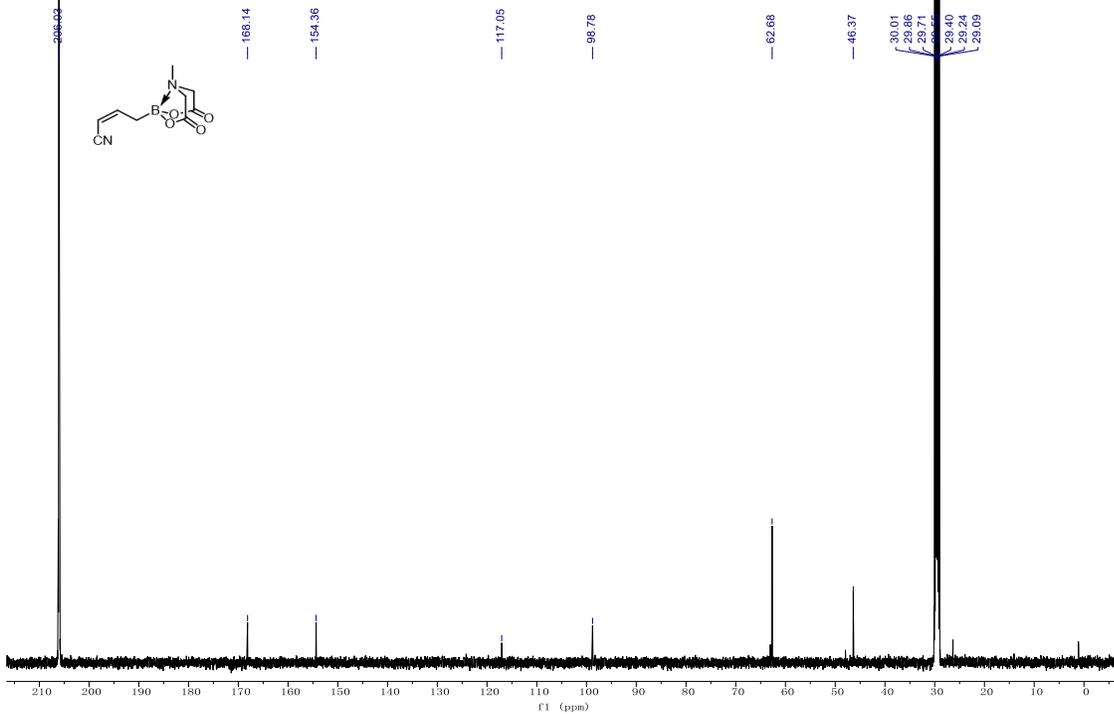


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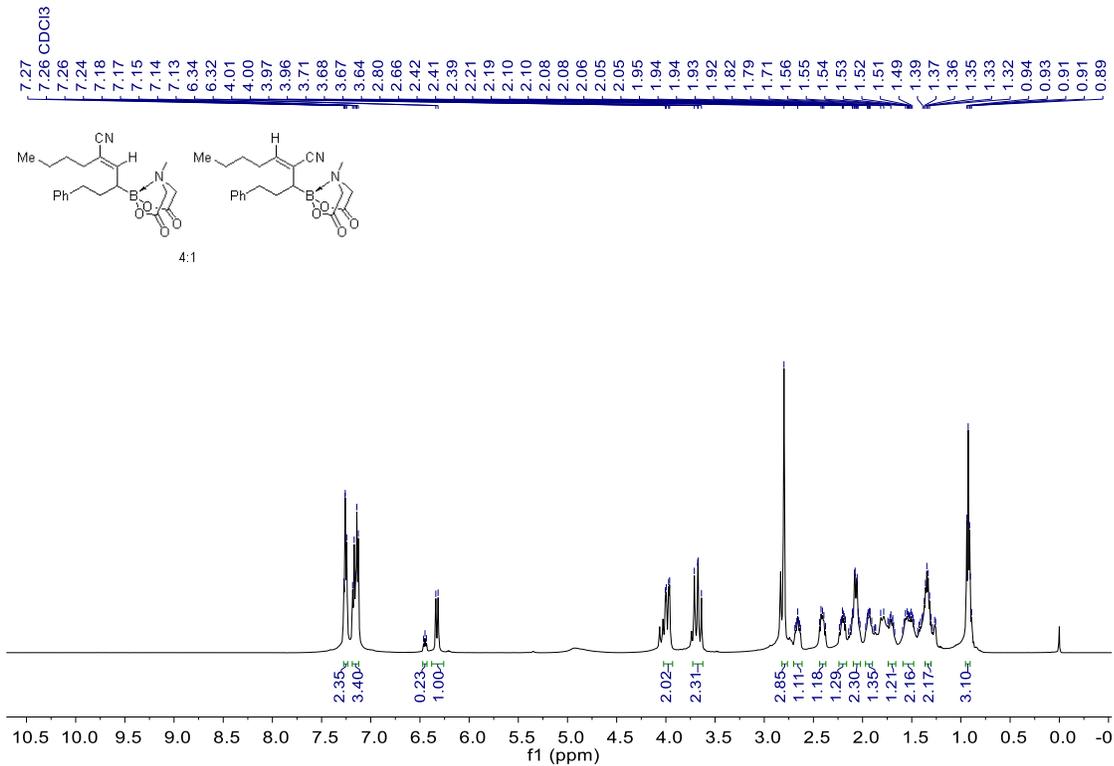
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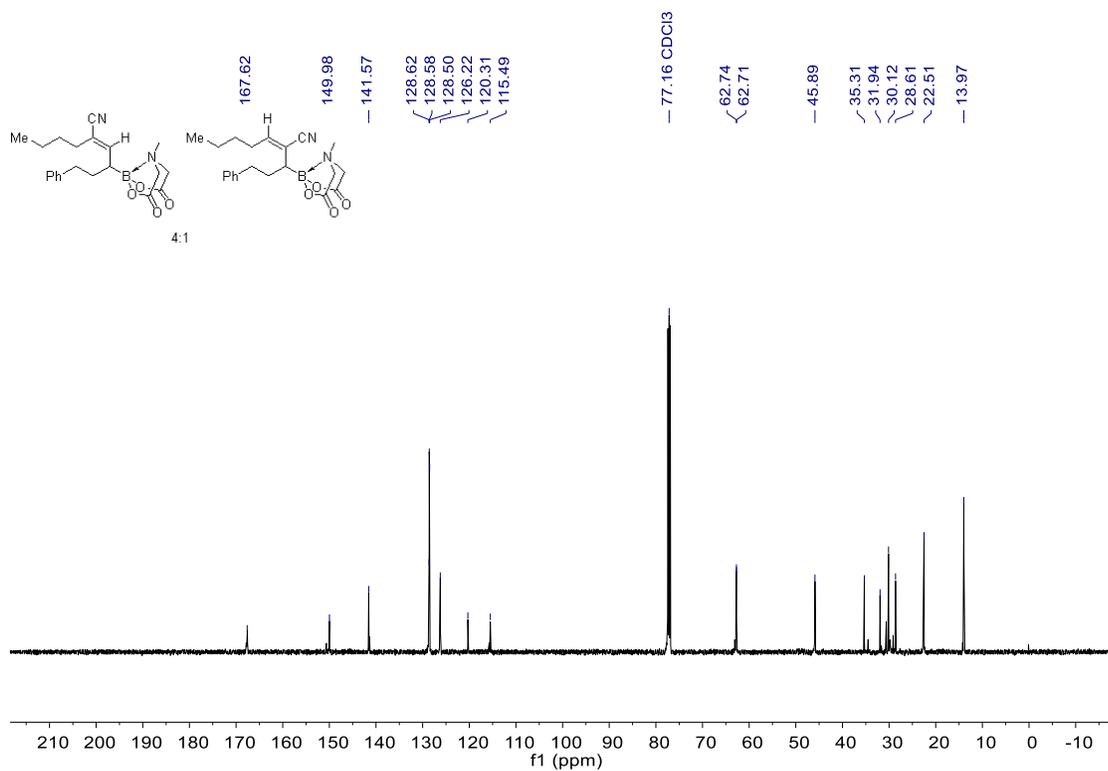


LS-H-93/PURE-C3. 1. F1d

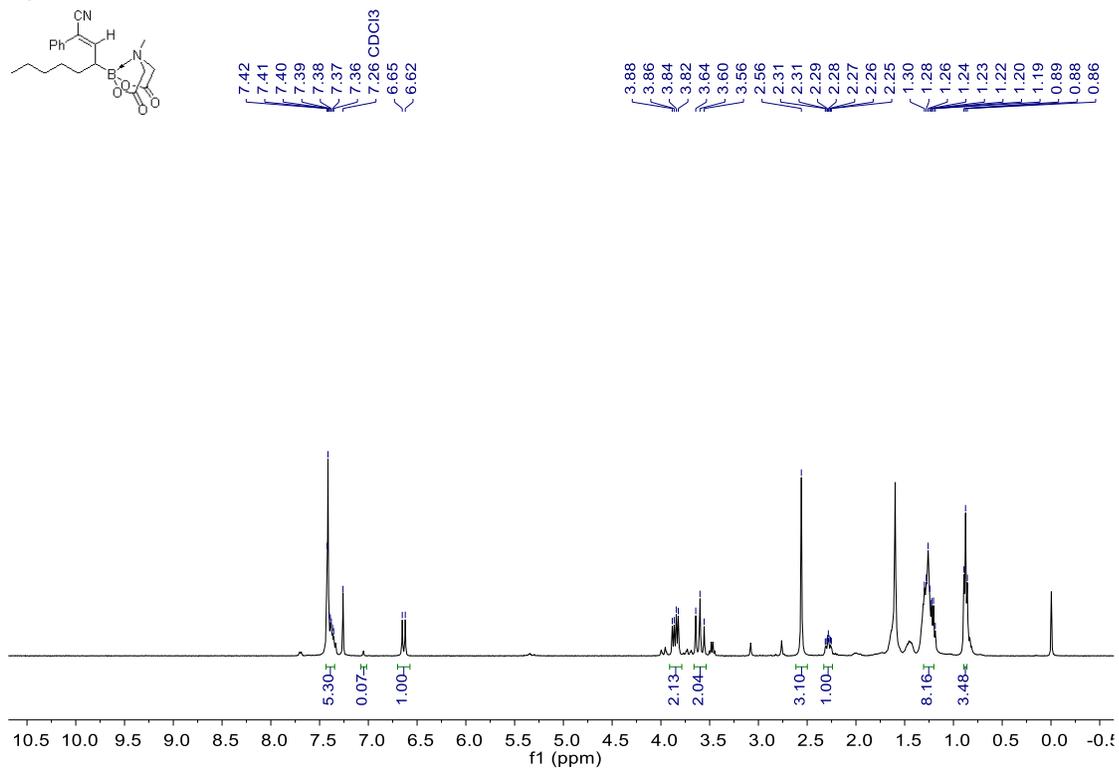


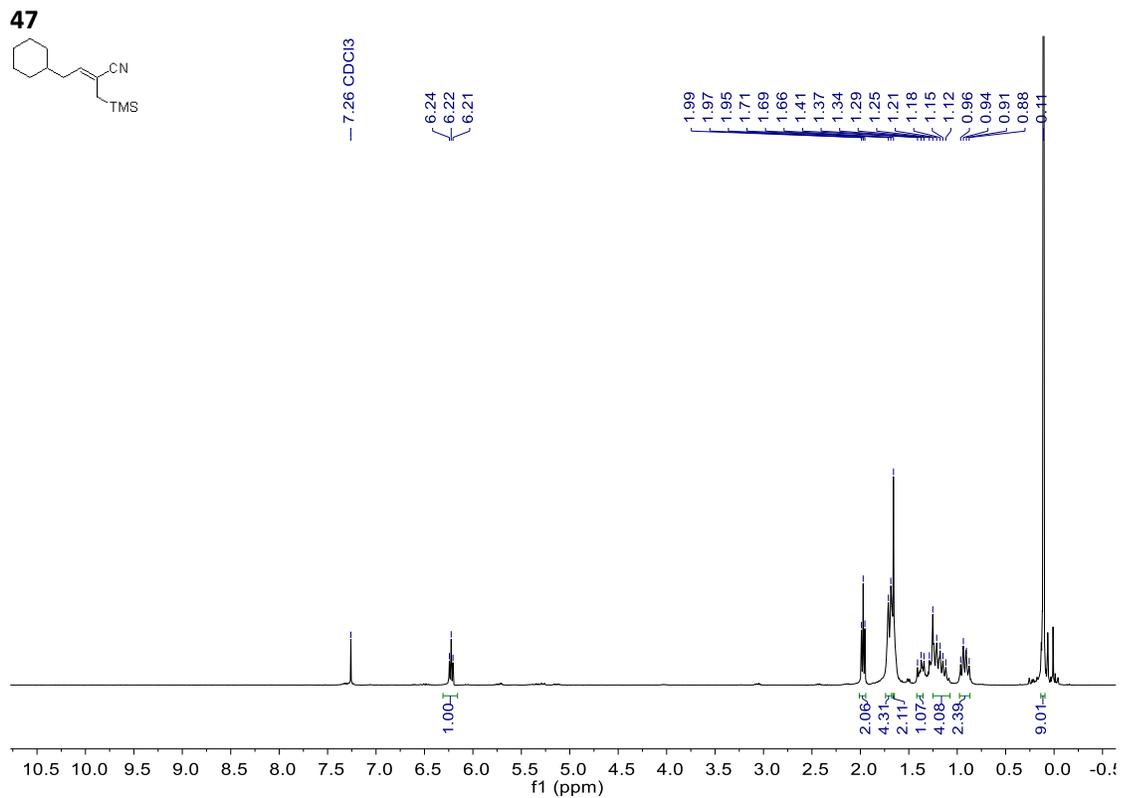
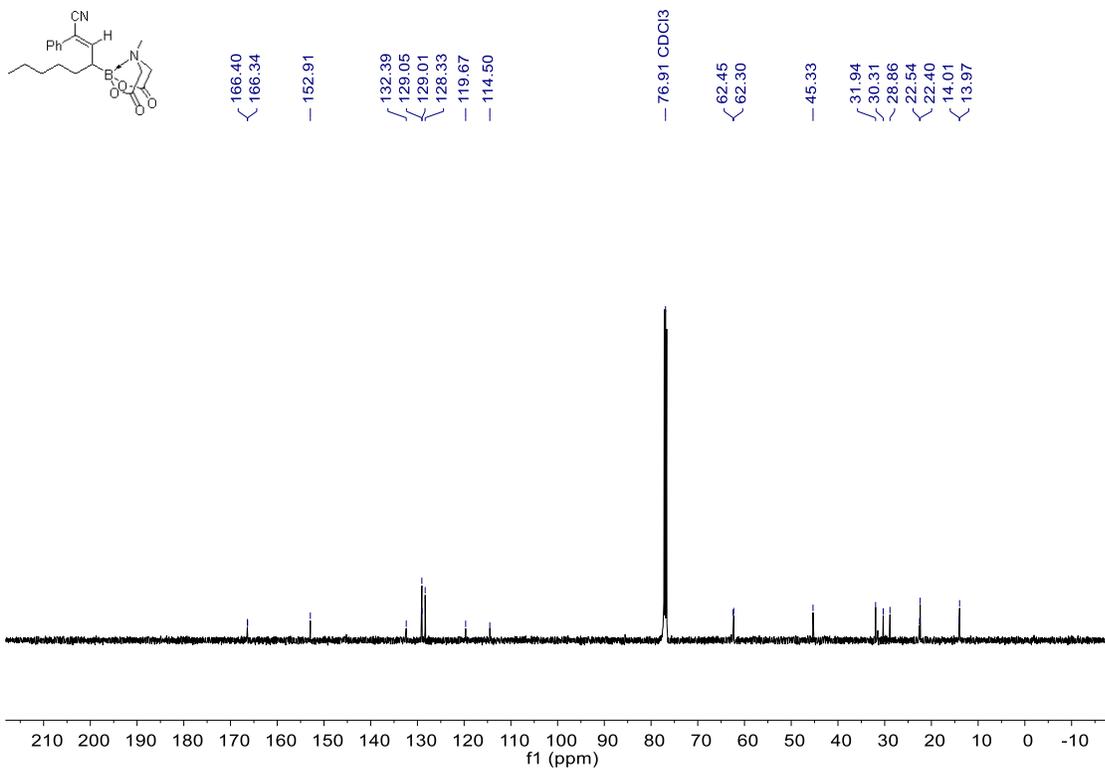
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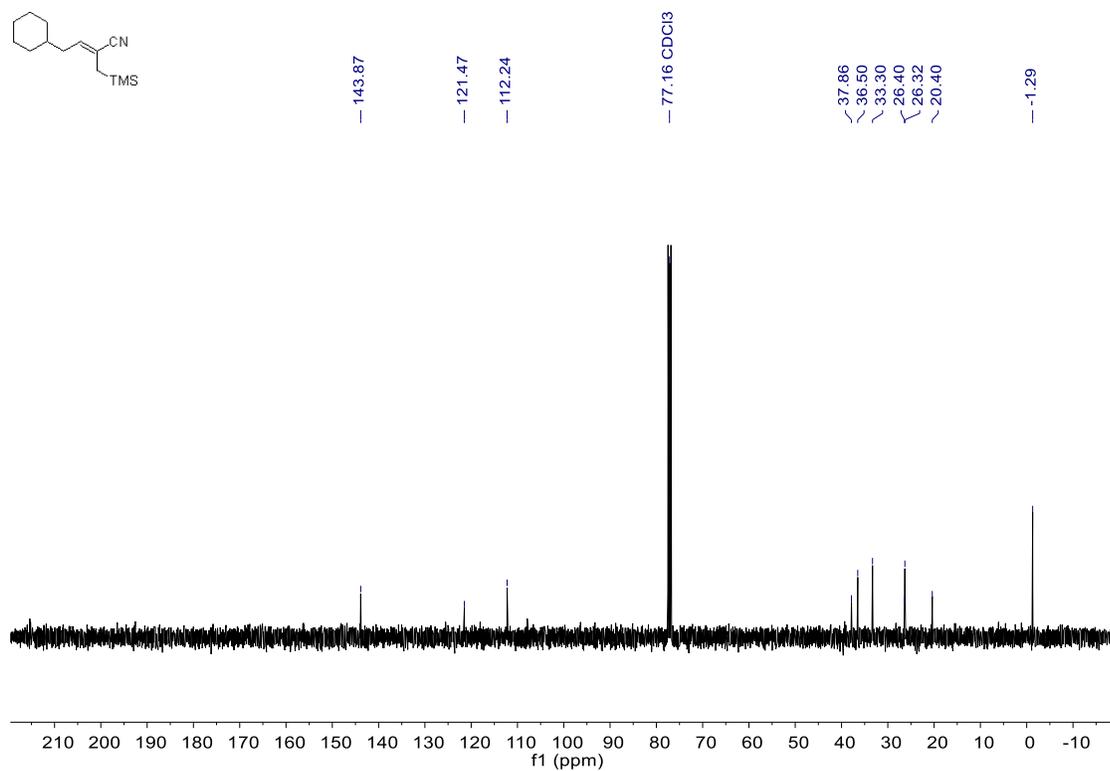
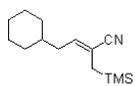




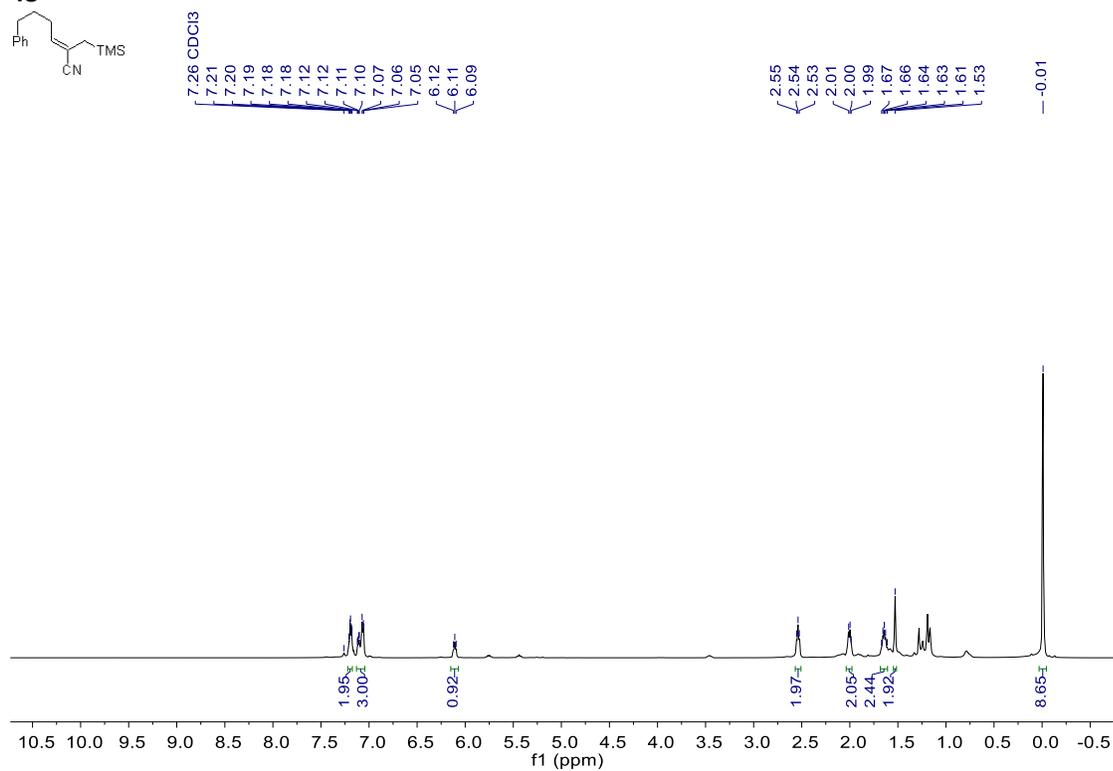
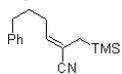
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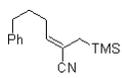






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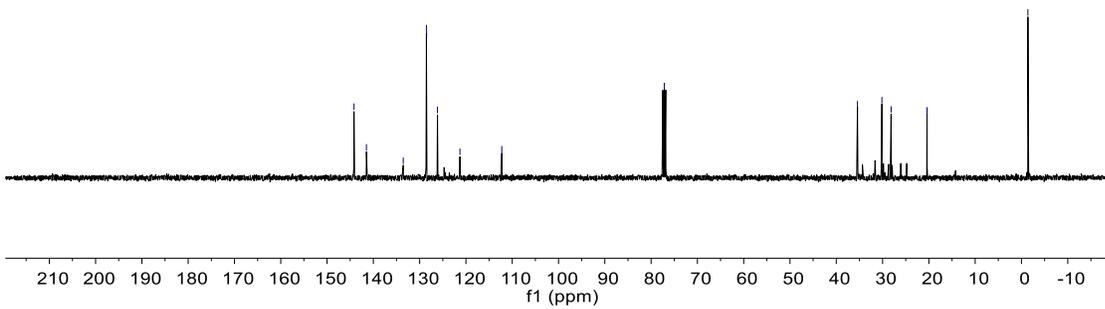


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141.49
133.54
128.54
128.49
126.15
121.30
112.26

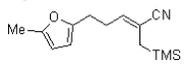
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35.42
30.14
28.16
20.40

-1.39



49

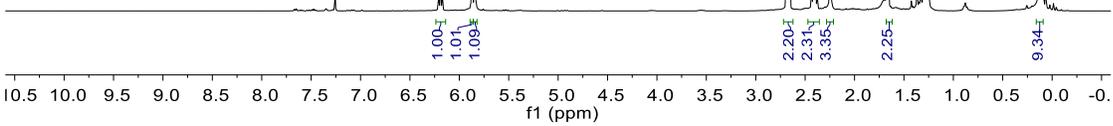


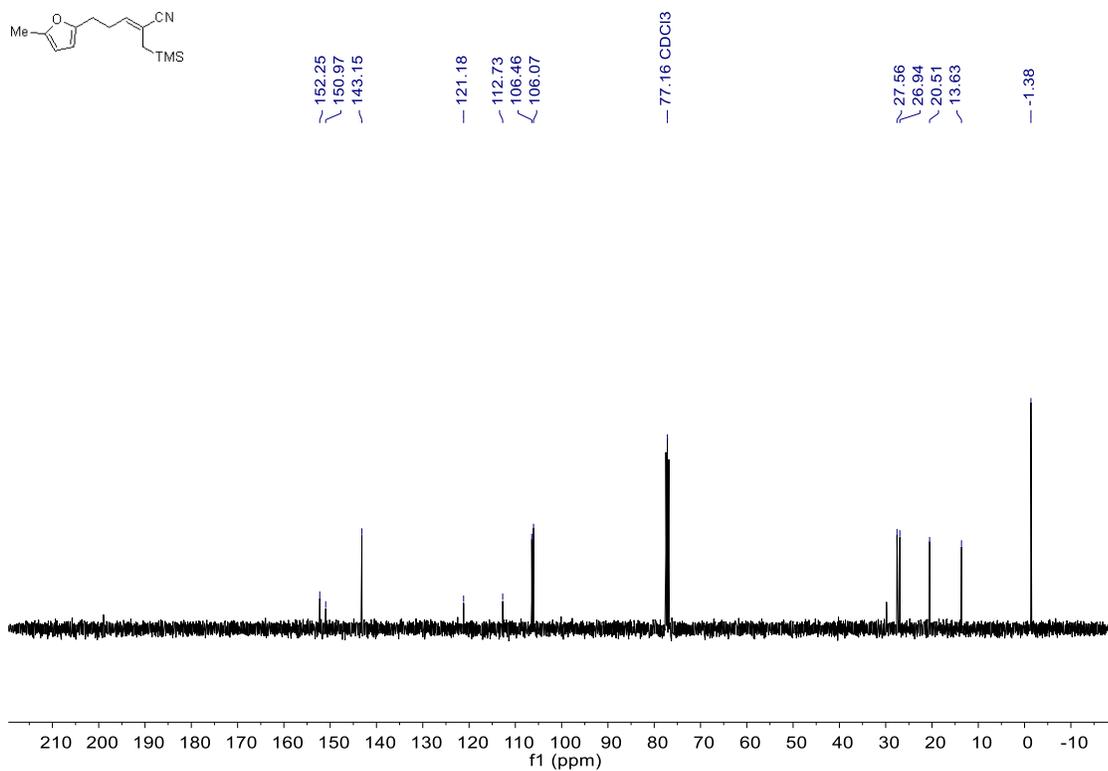
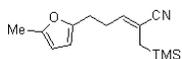
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6.17
5.87
5.85

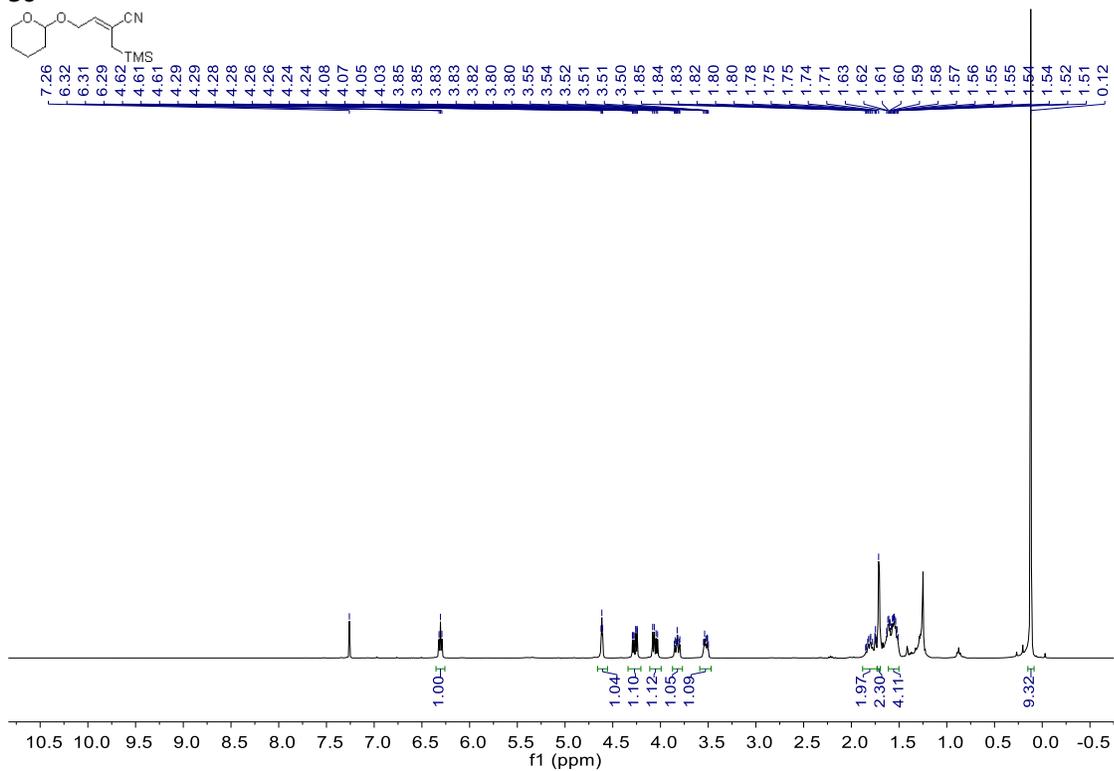
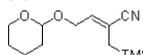
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1.66

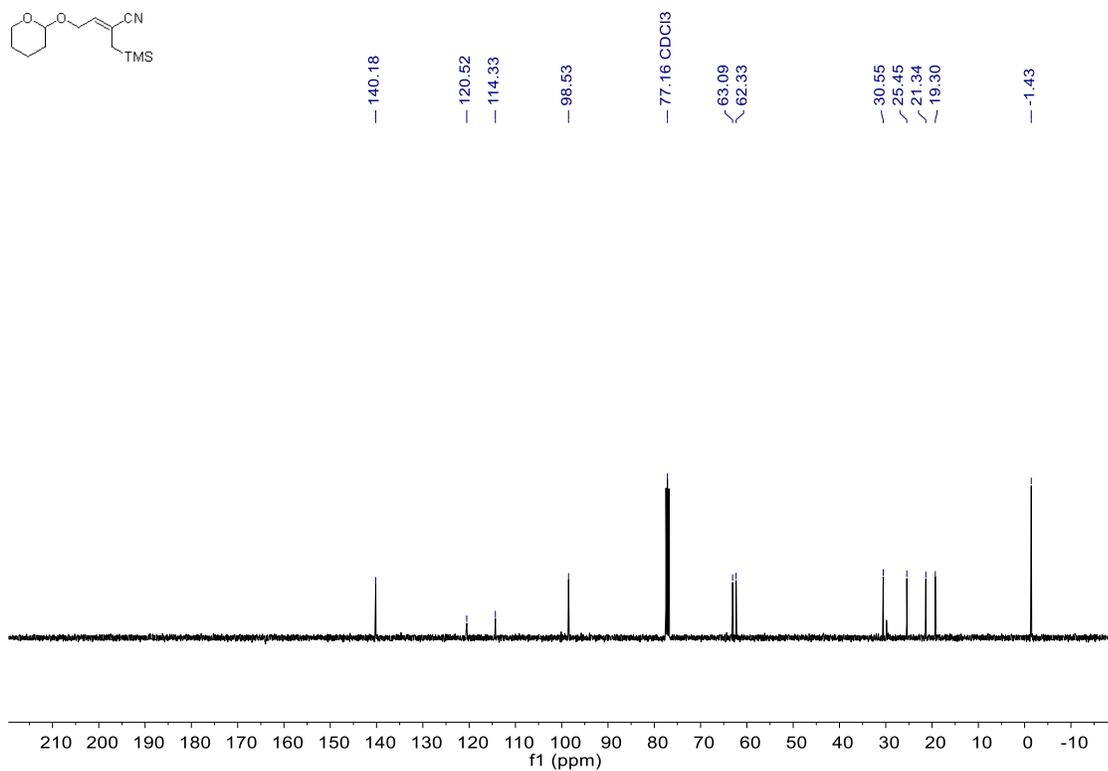
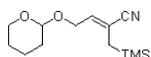
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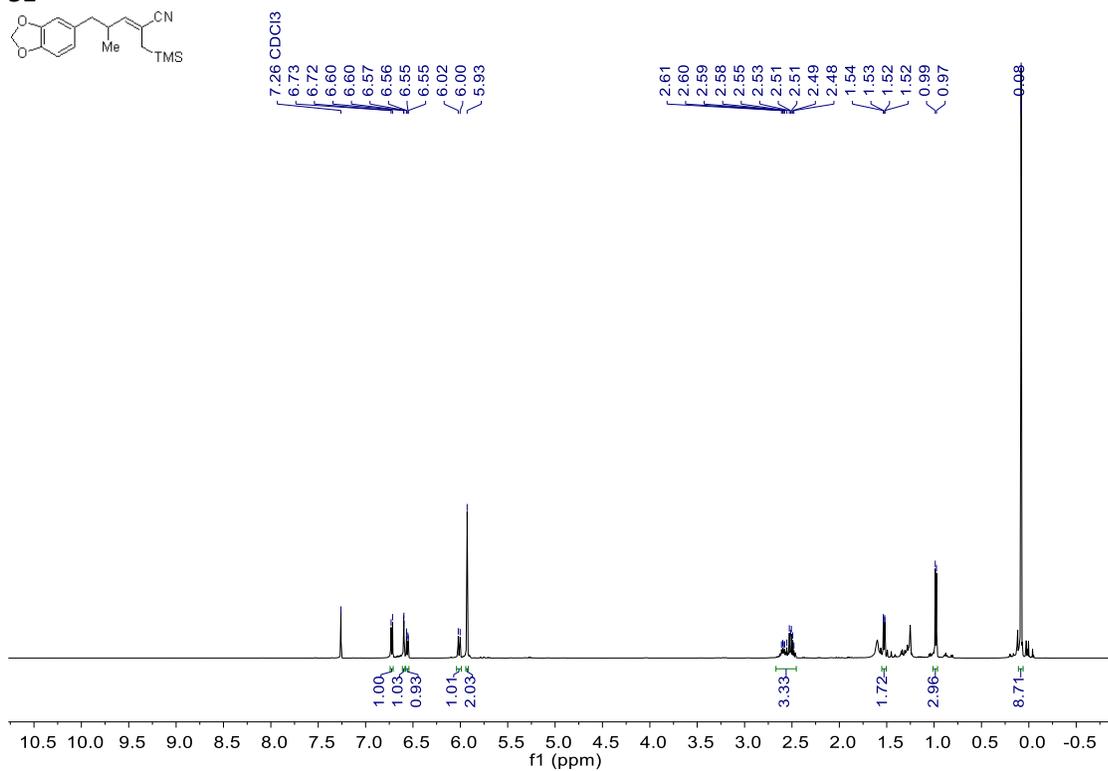
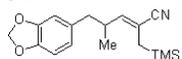


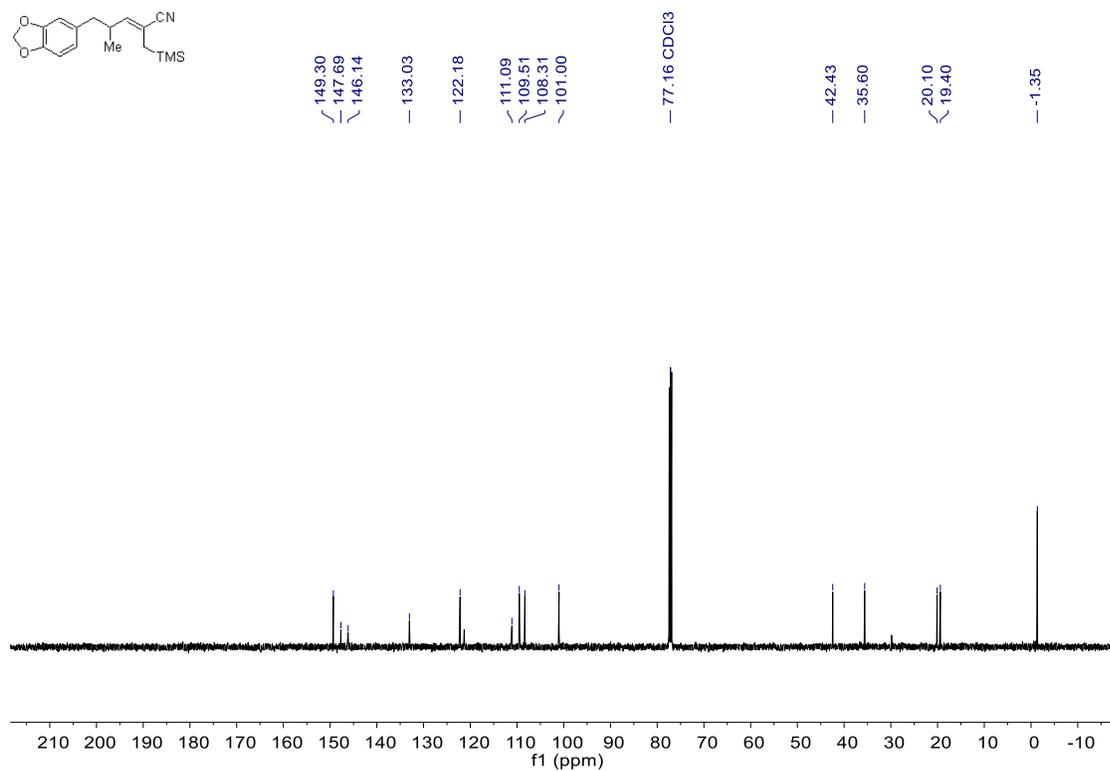
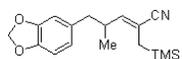
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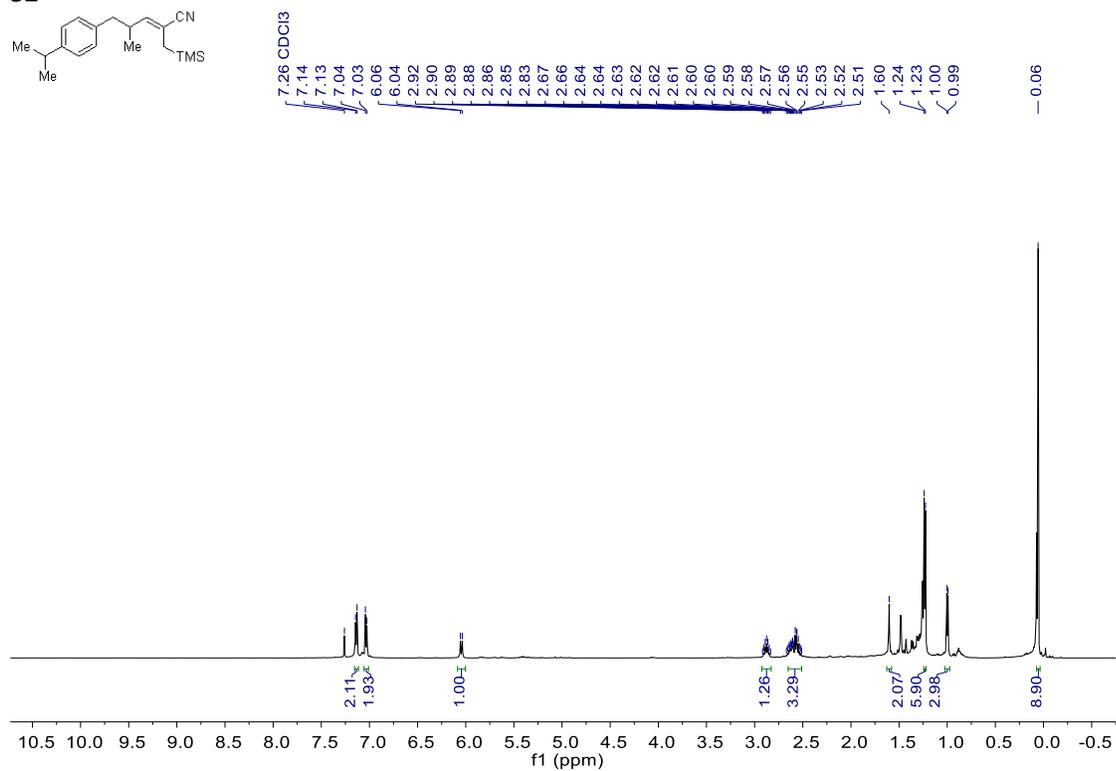
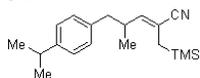


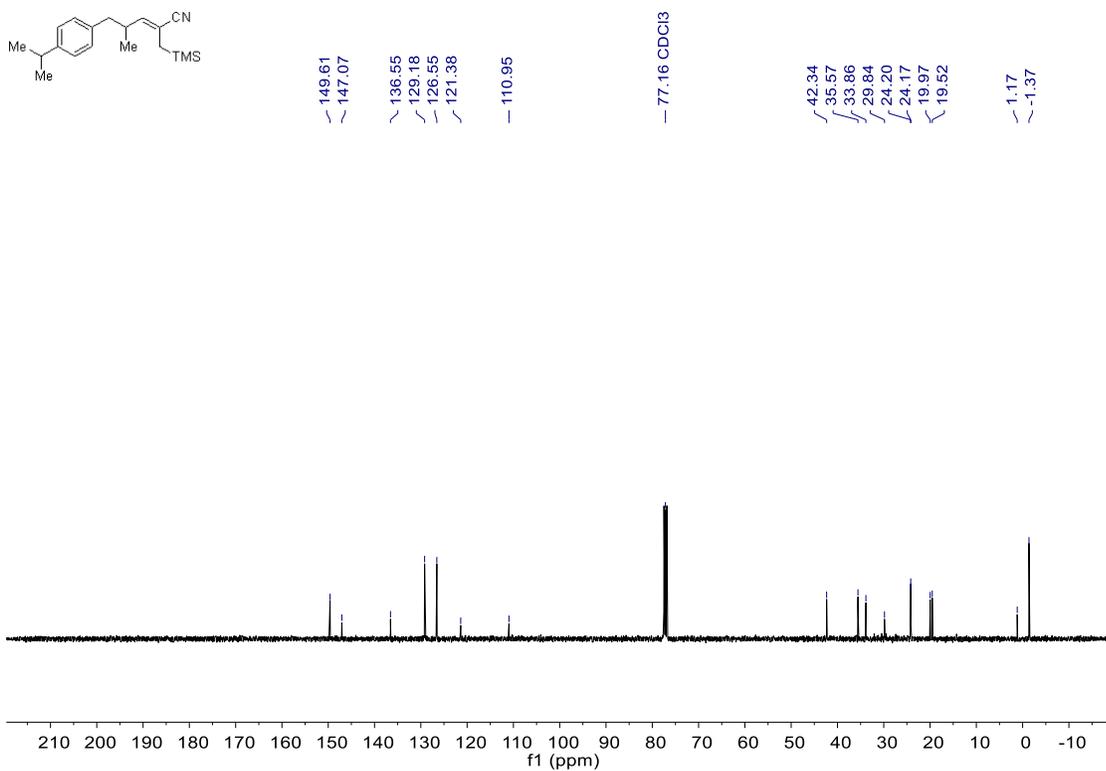
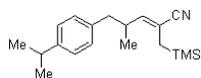
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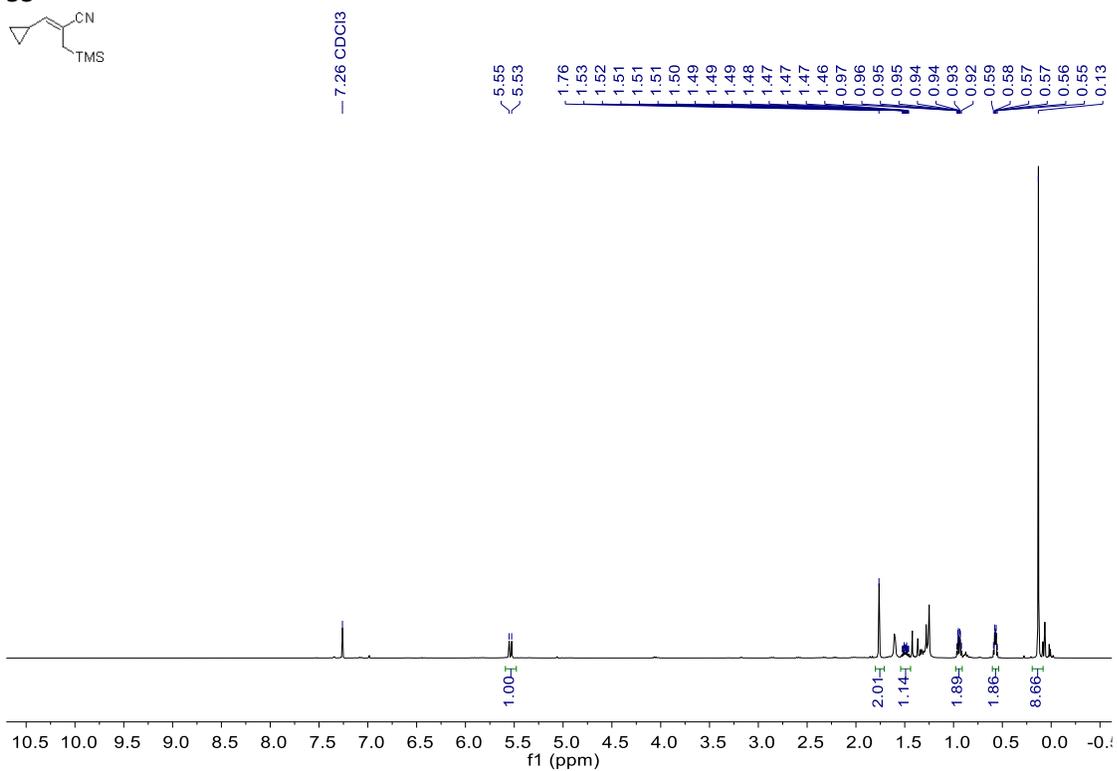
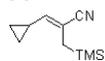


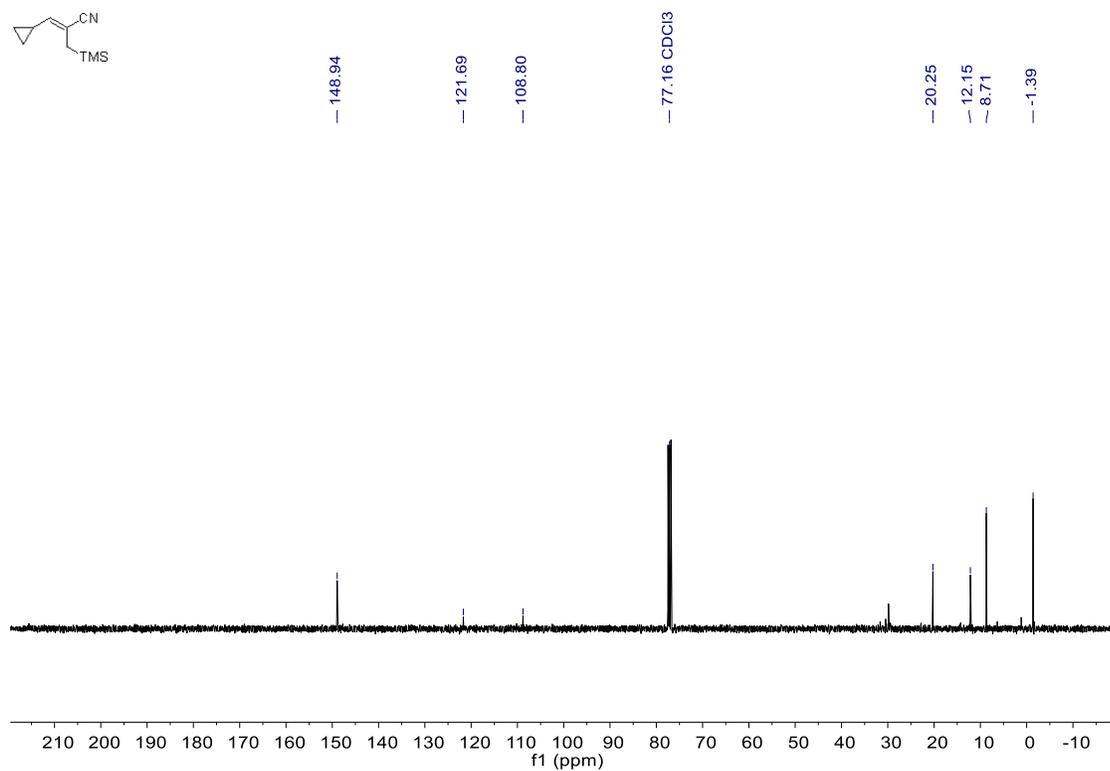
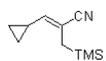
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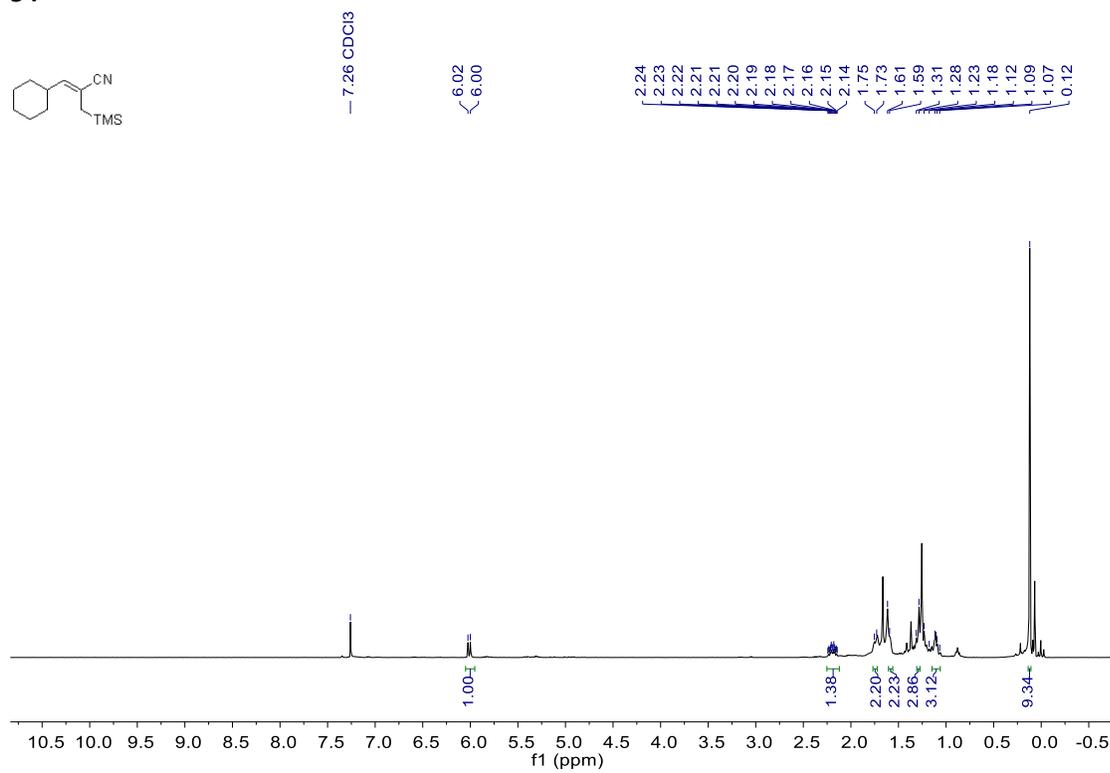
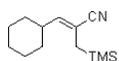


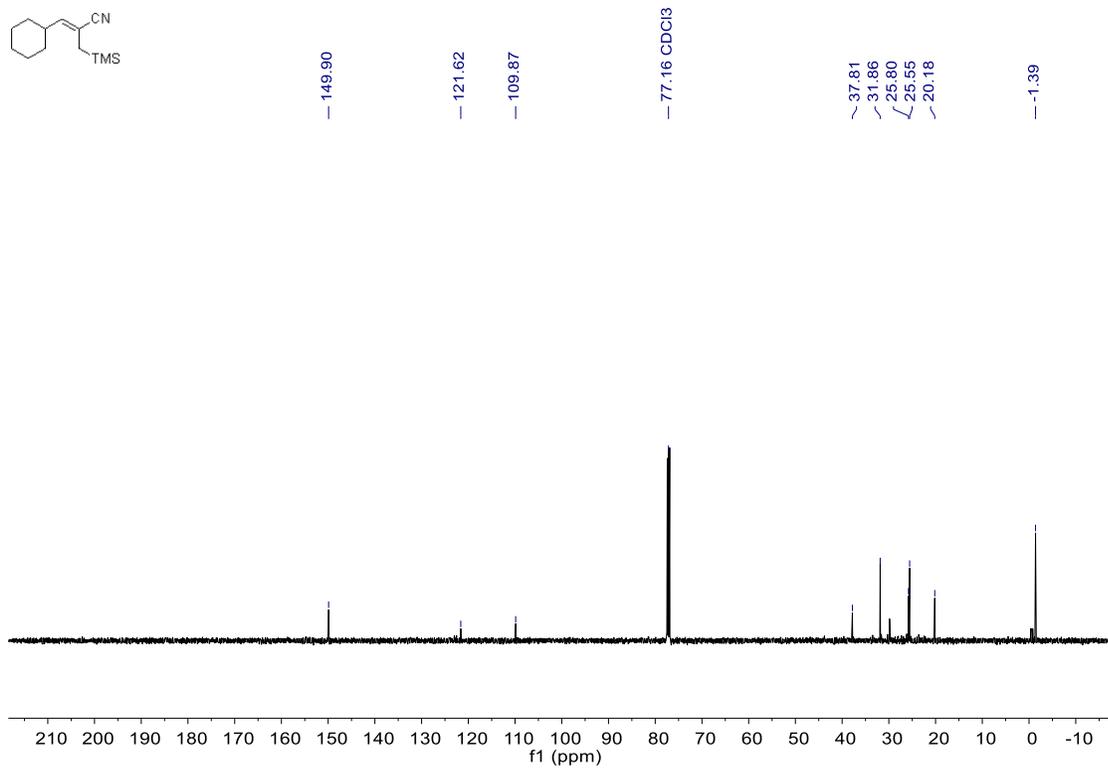
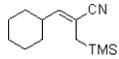
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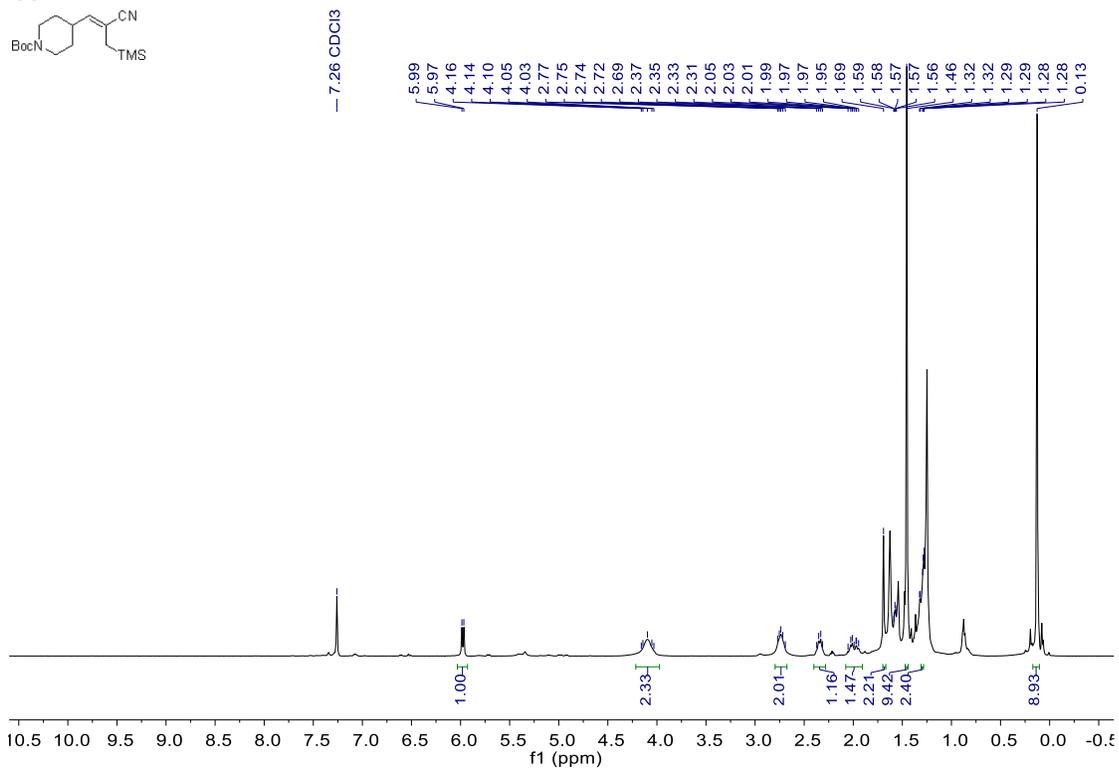
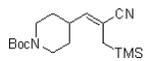


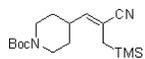
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55





154.83

147.26

121.10

111.54

79.85

77.16 CDCl₃

36.00

30.76

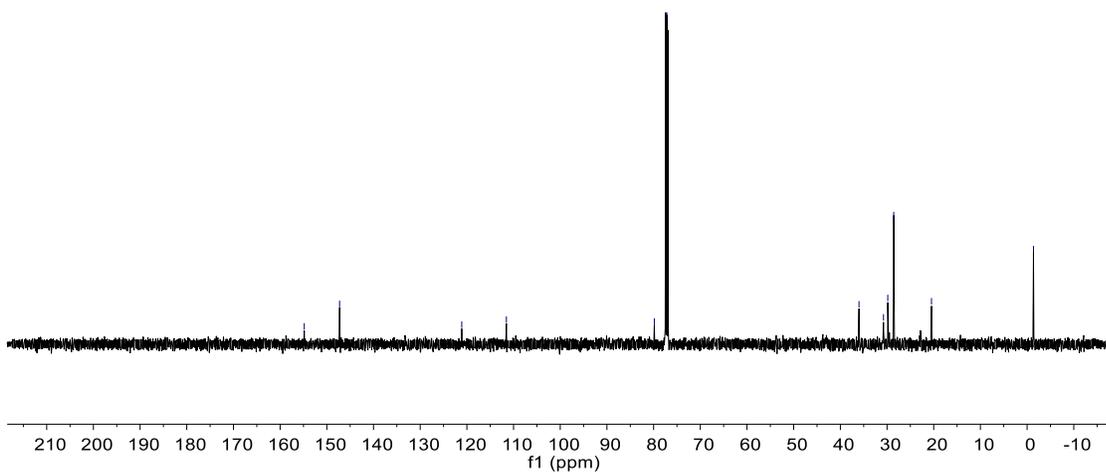
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28.57

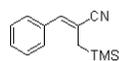
20.48

-1.37

¹³C NMR (126 MHz, CDCl₃) 154.8, 147.3, 121.1, 111.5, 79.9, 77.2, 36.0, 30.8, 29.8, 28.6, 20.5, -1.4.



56



7.41

7.41

7.40

7.40

7.39

7.38

7.38

7.37

7.37

7.36

7.35

7.35

7.34

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7.33

7.33

7.32

7.32

7.31

7.30

7.30

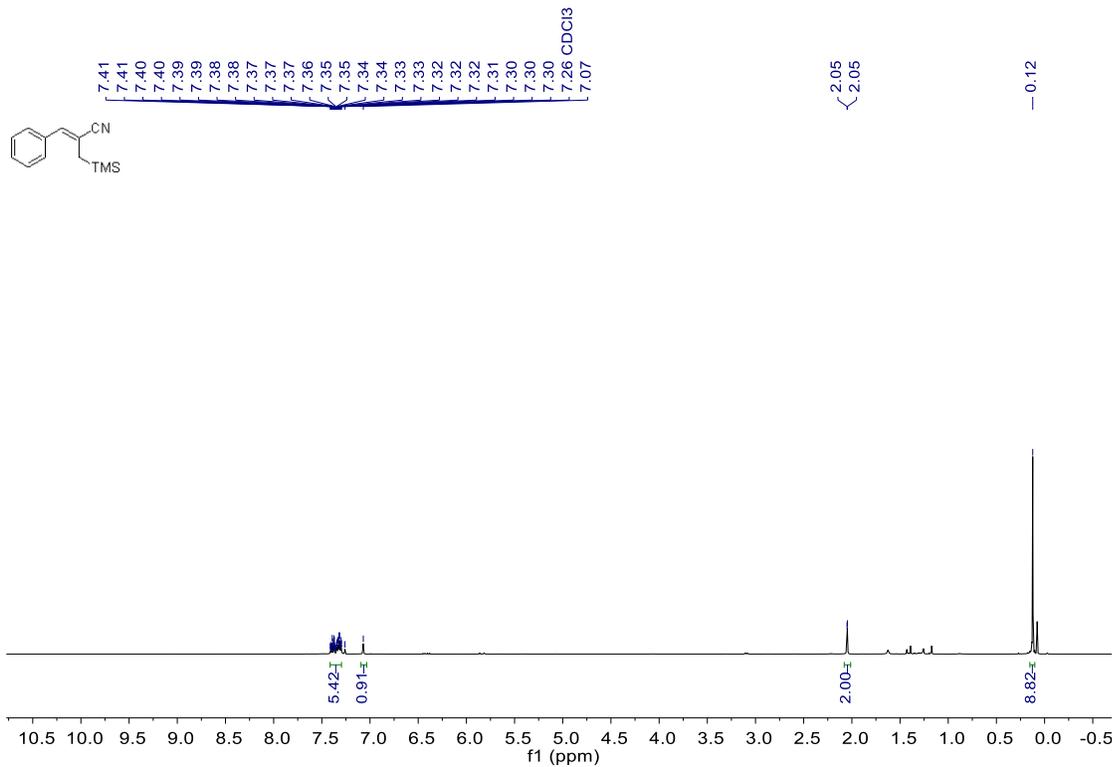
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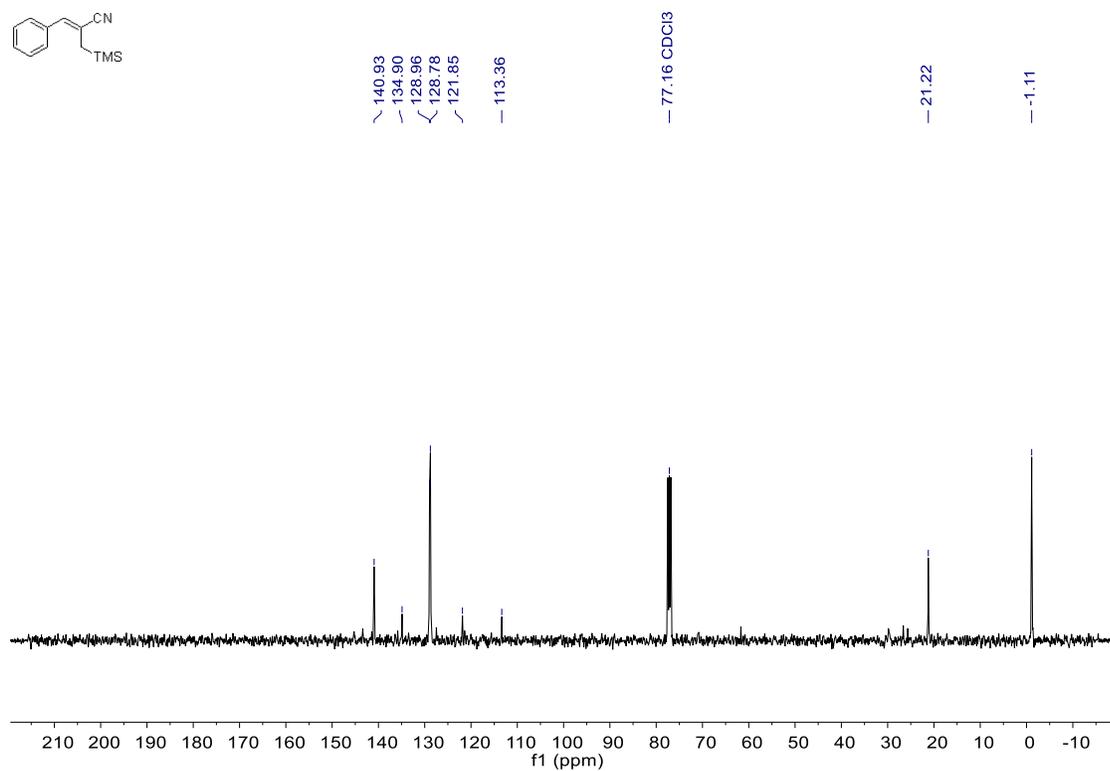
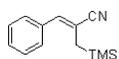
7.07

2.05

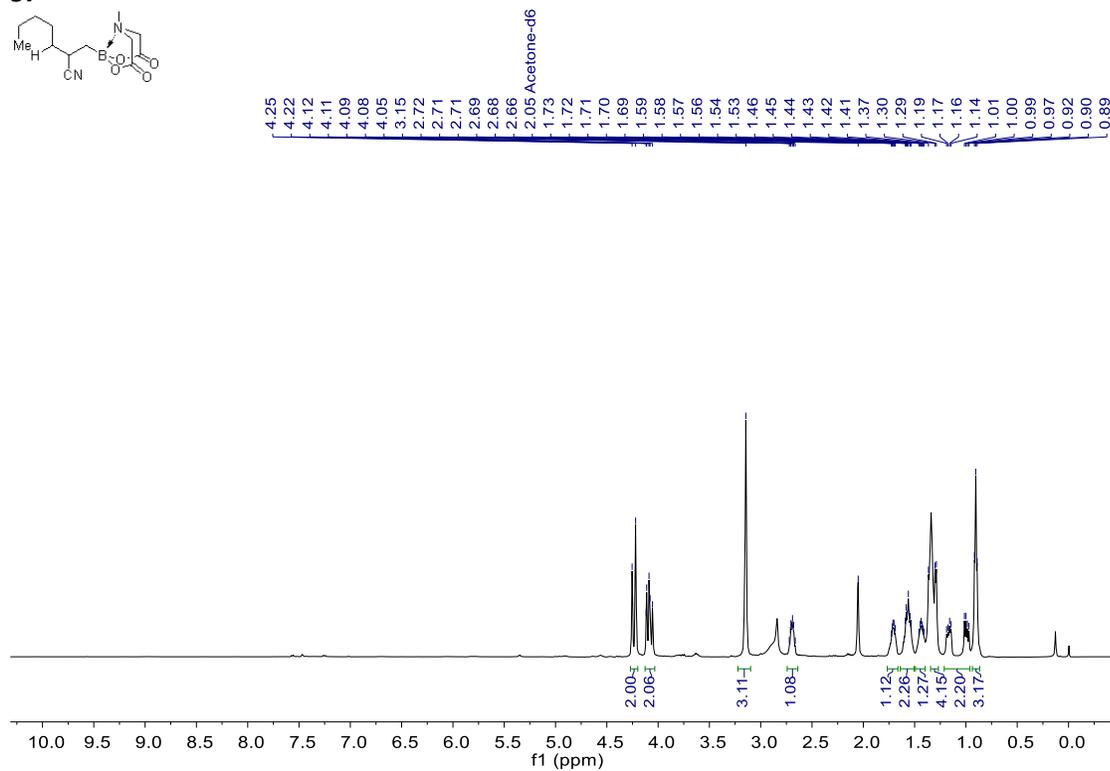
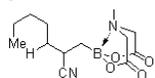
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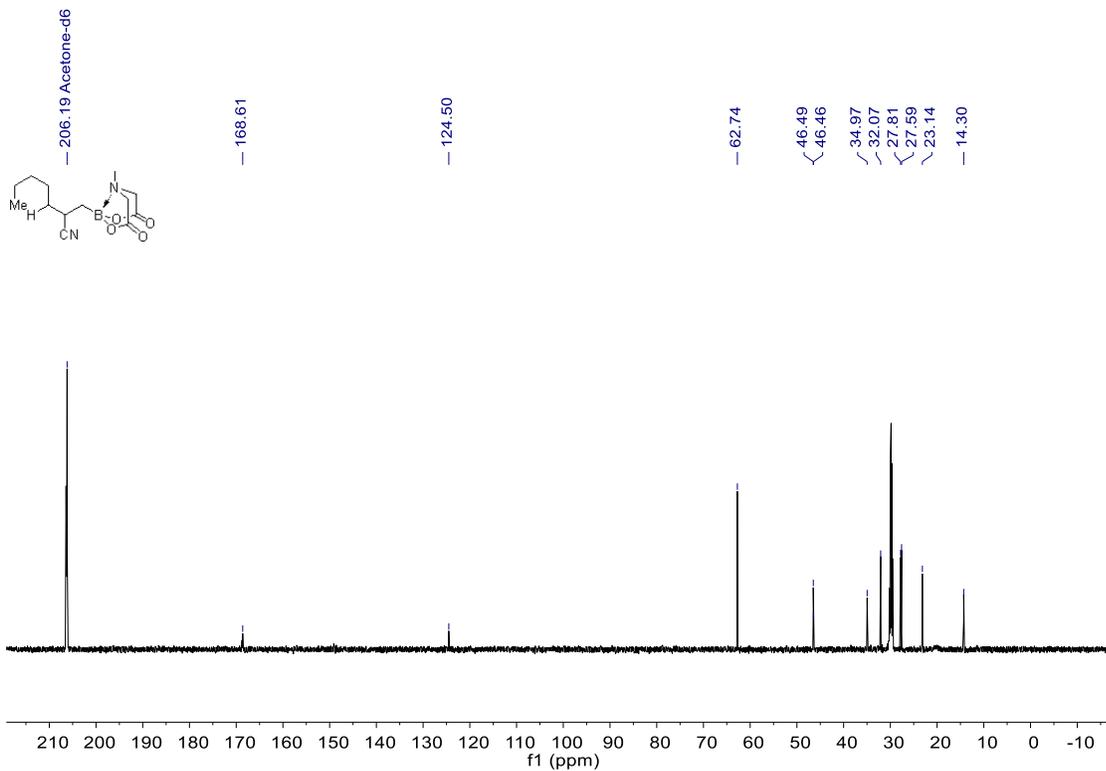
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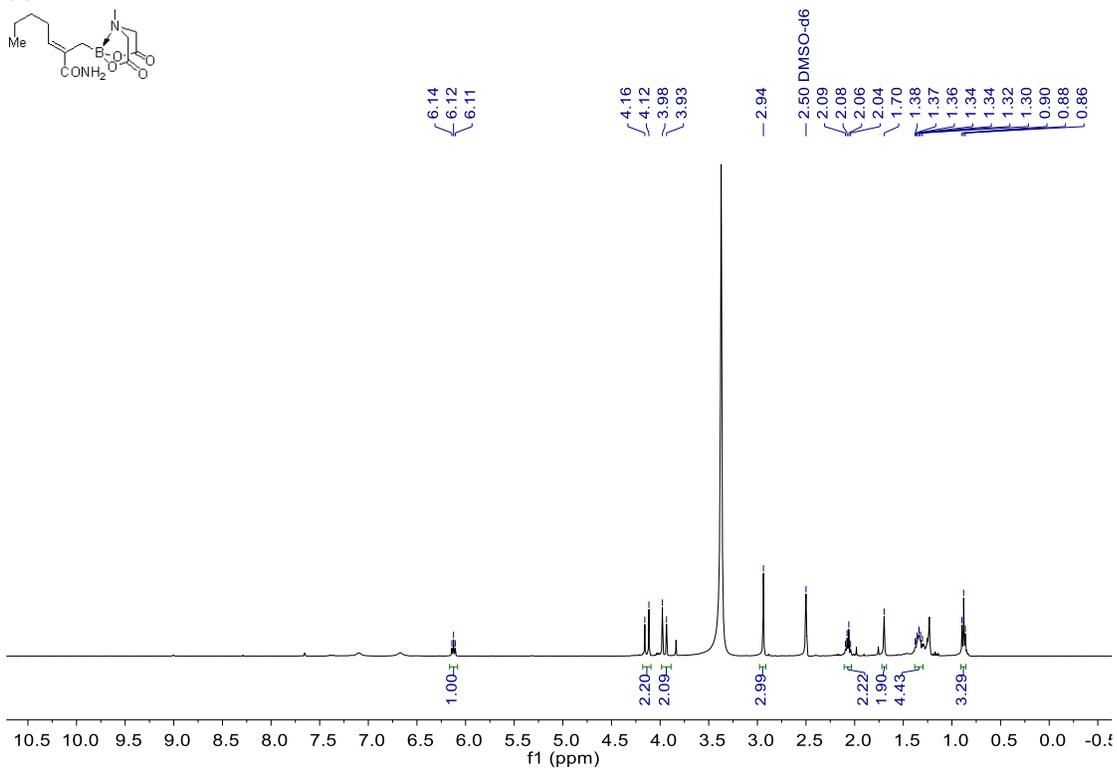


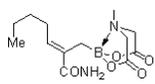
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58





171.29
168.75

133.63
133.39

61.67

45.56

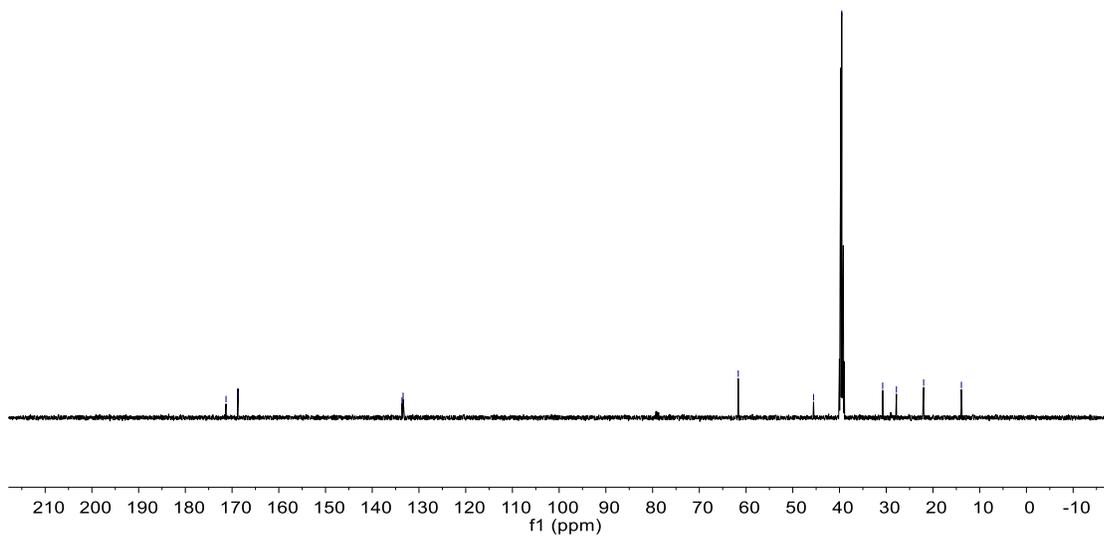
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30.76

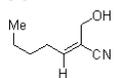
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21.99

13.92



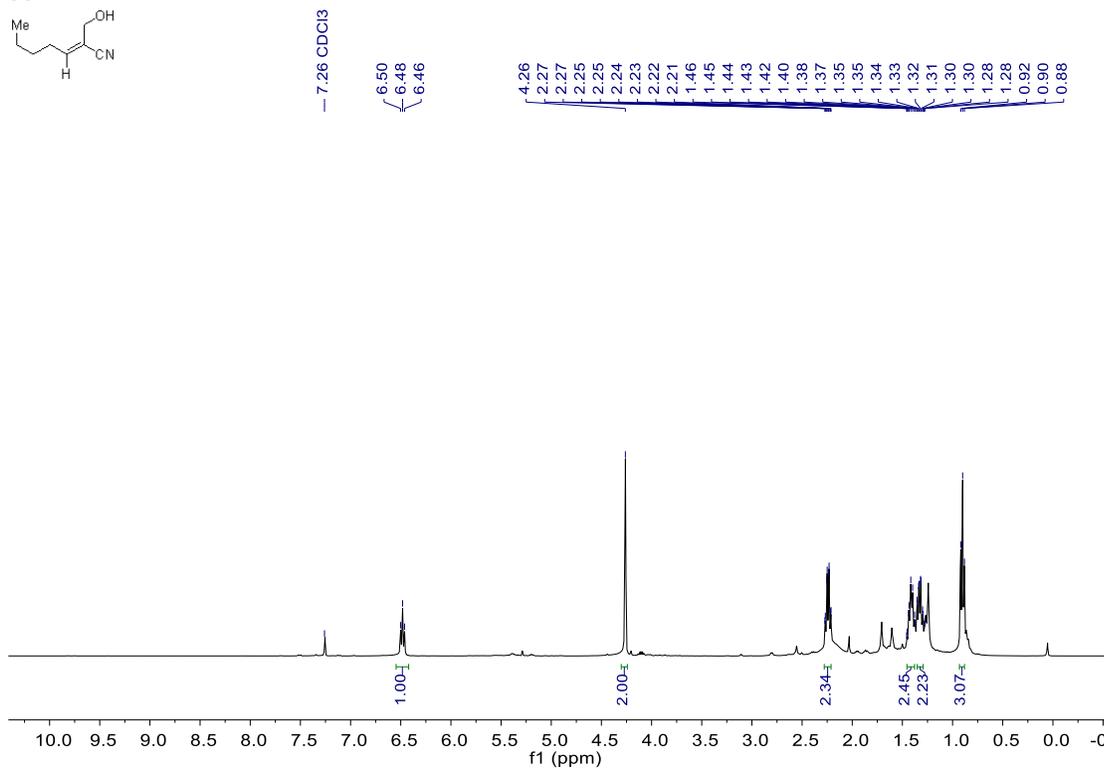
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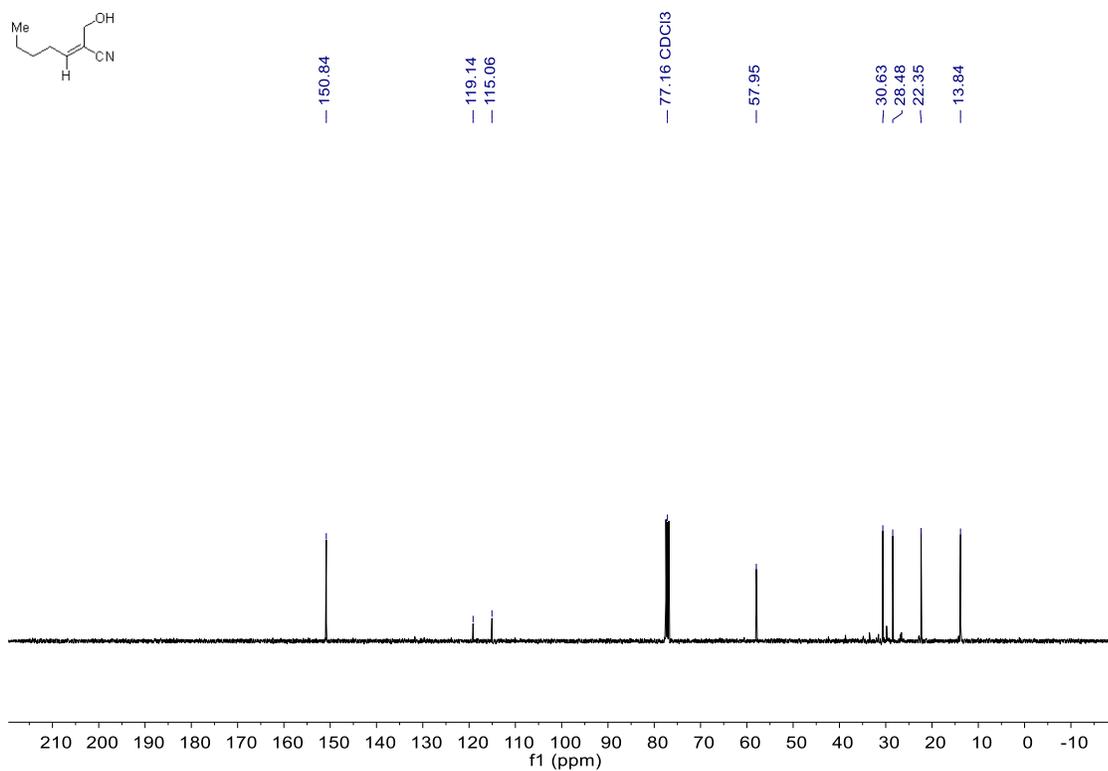
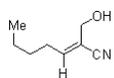


7.26 CDCl3

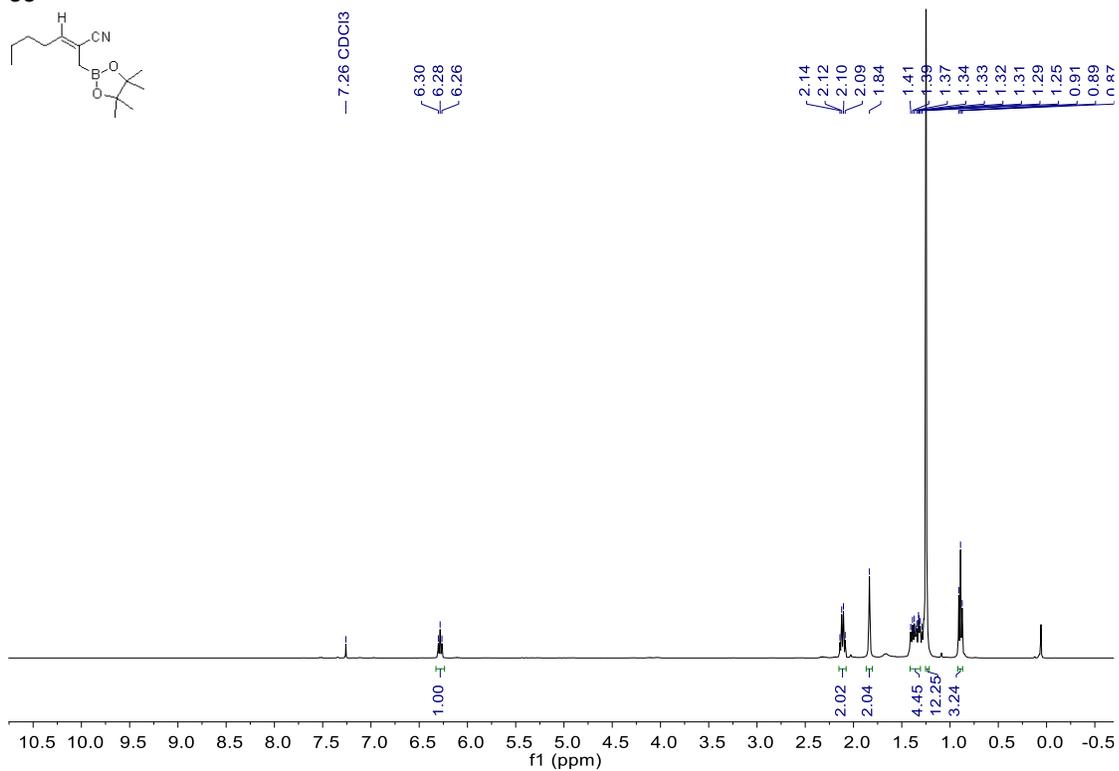
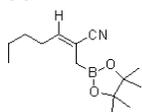
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6.48
6.46

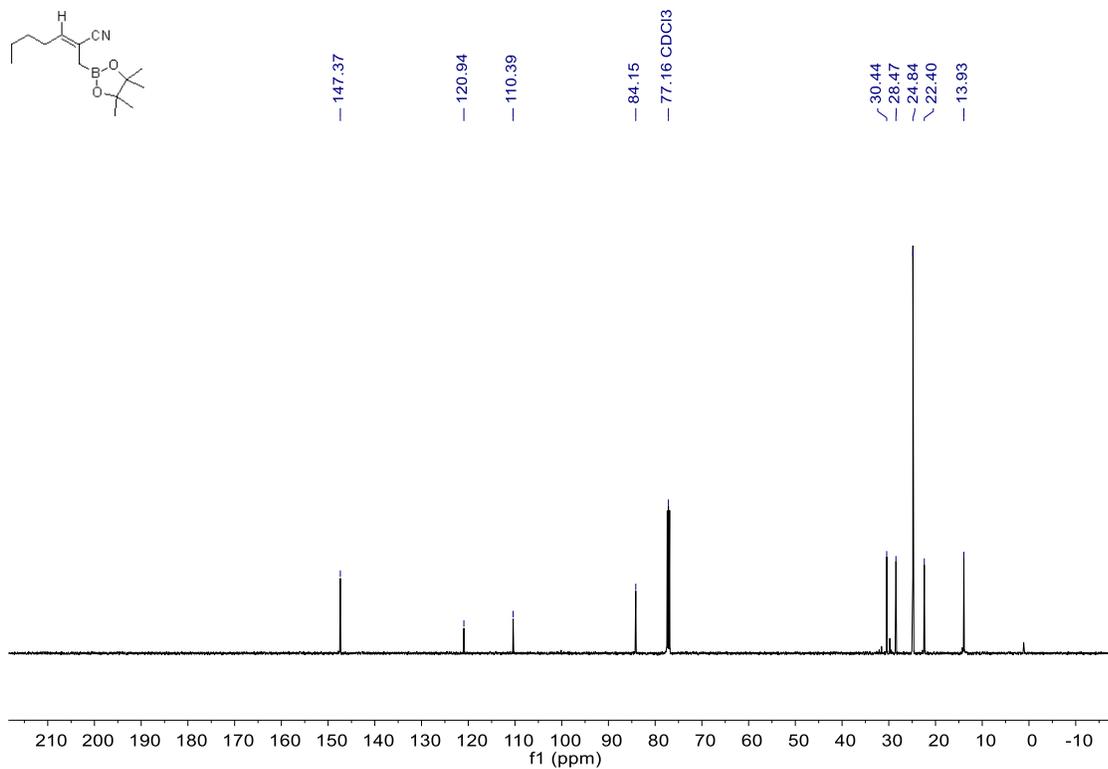
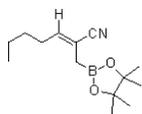
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2.27
2.27
2.25
2.25
2.24
2.23
2.22
2.21
1.46
1.45
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1.42
1.40
1.38
1.37
1.35
1.35
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1.30
1.30
1.28
1.28
0.92
0.90
0.88



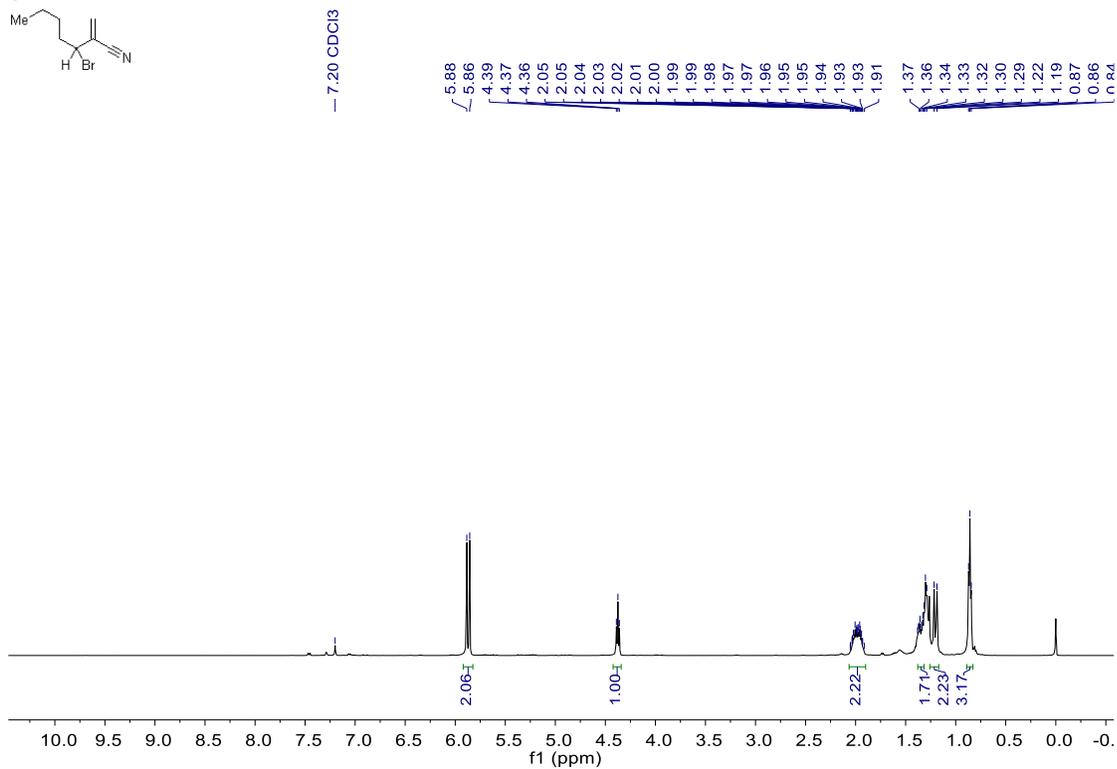
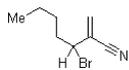


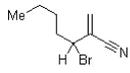
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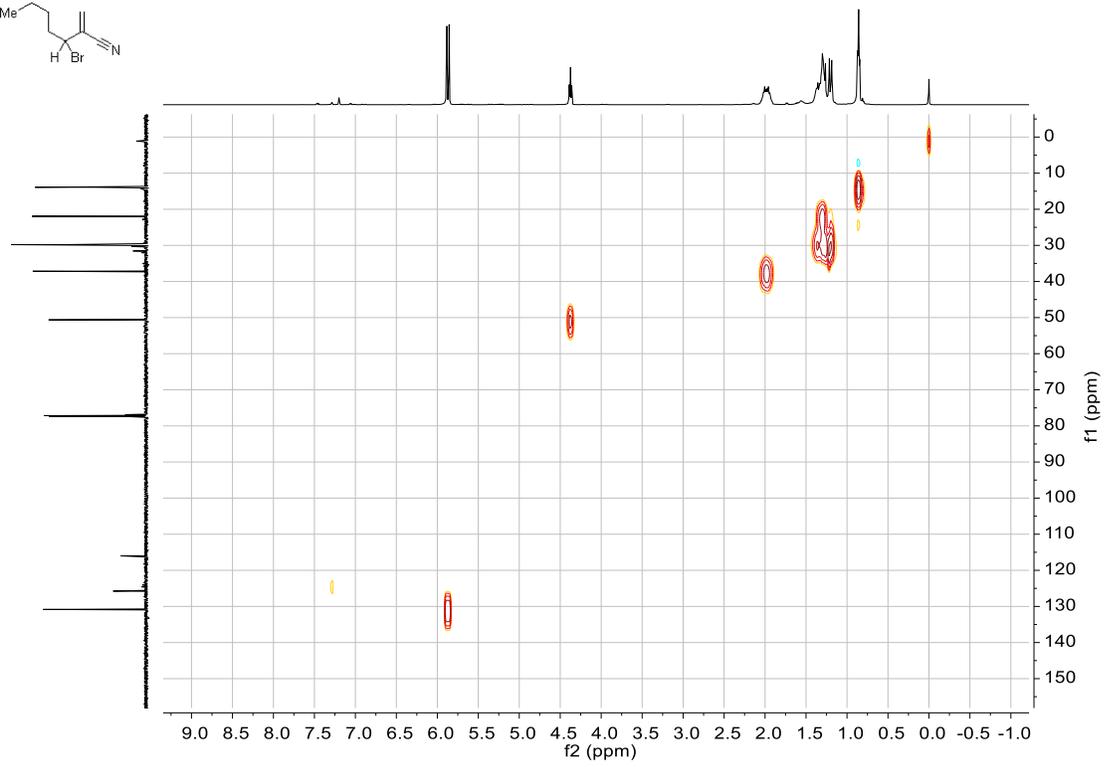
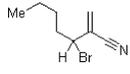
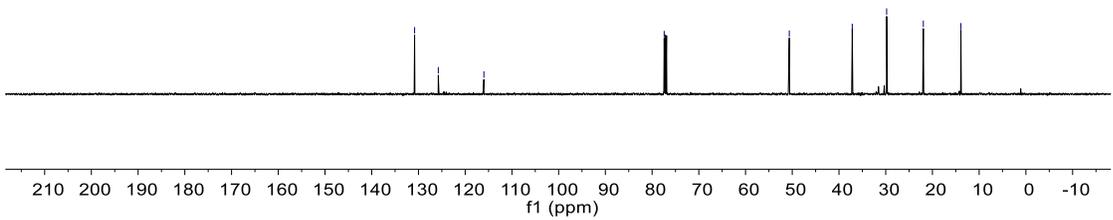


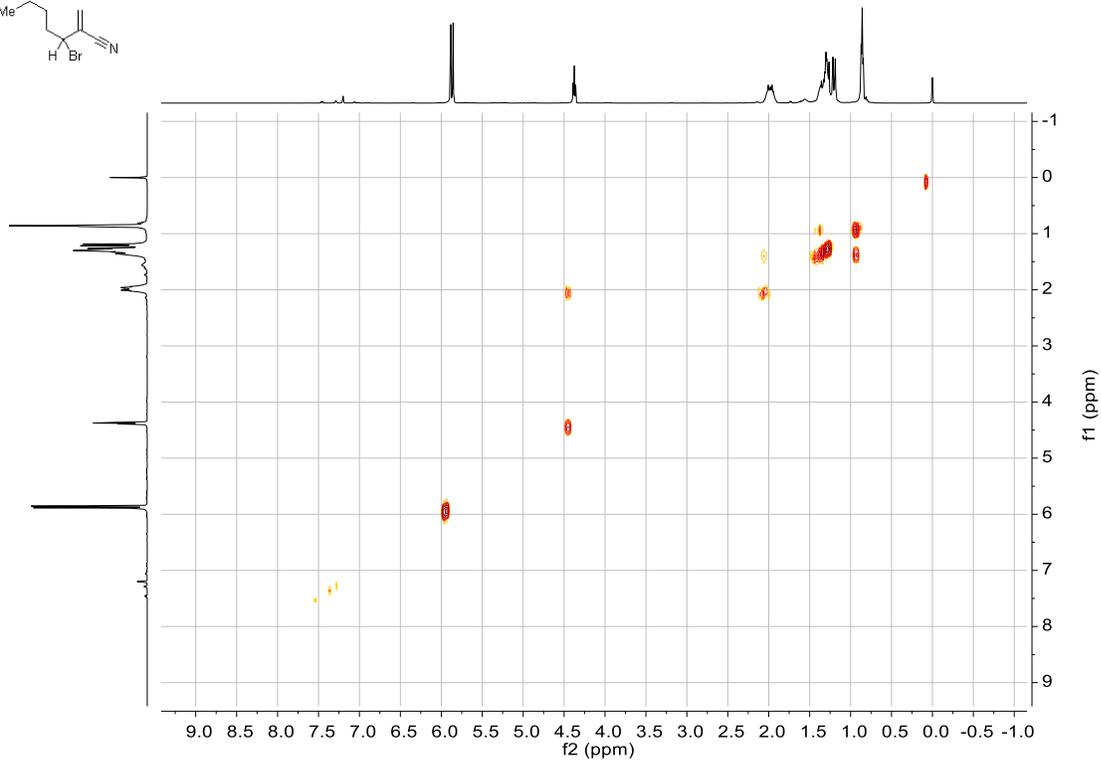
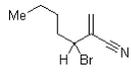
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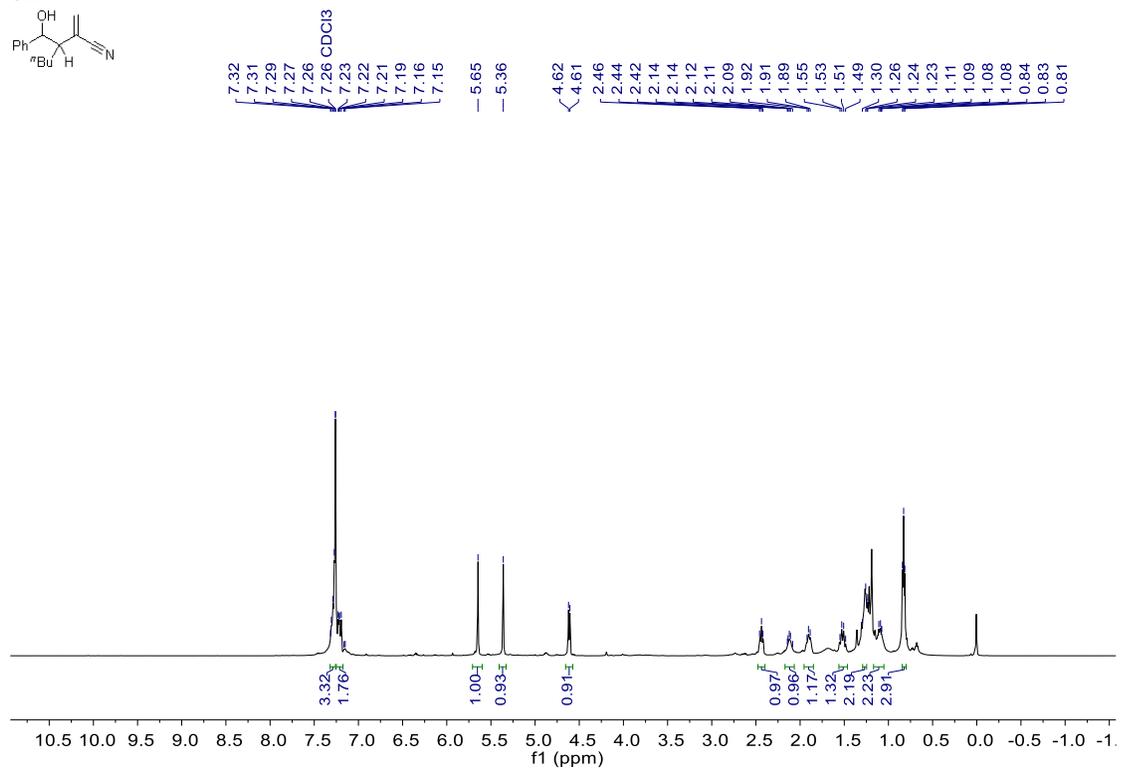
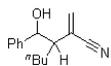


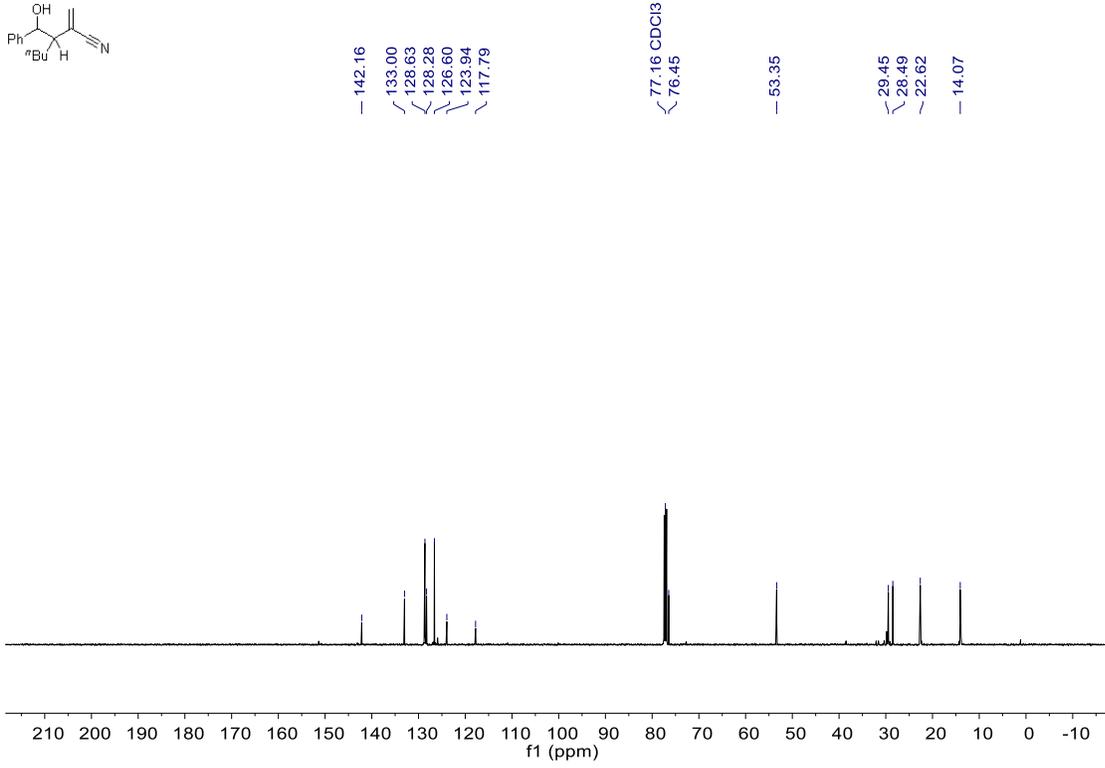
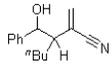
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— 125.76
— 116.00
— 77.41 CDCl₃
— 50.63
— 37.16
— 29.80
— 21.95
— 13.91



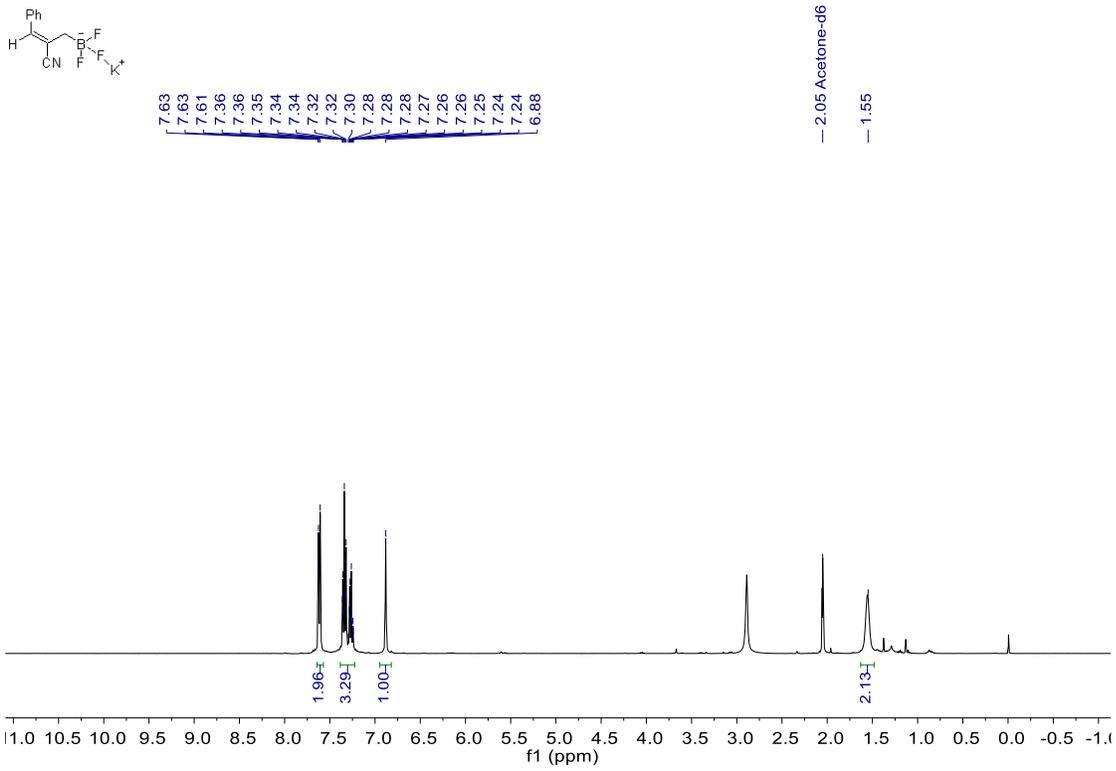
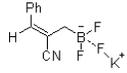


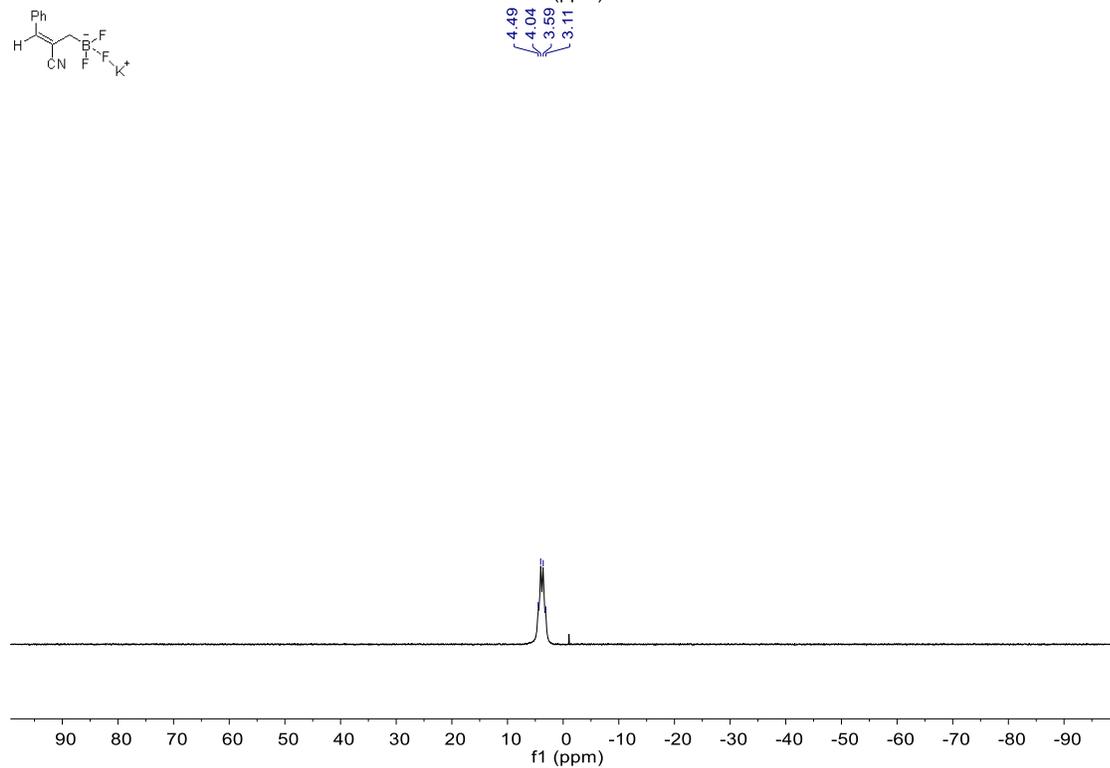
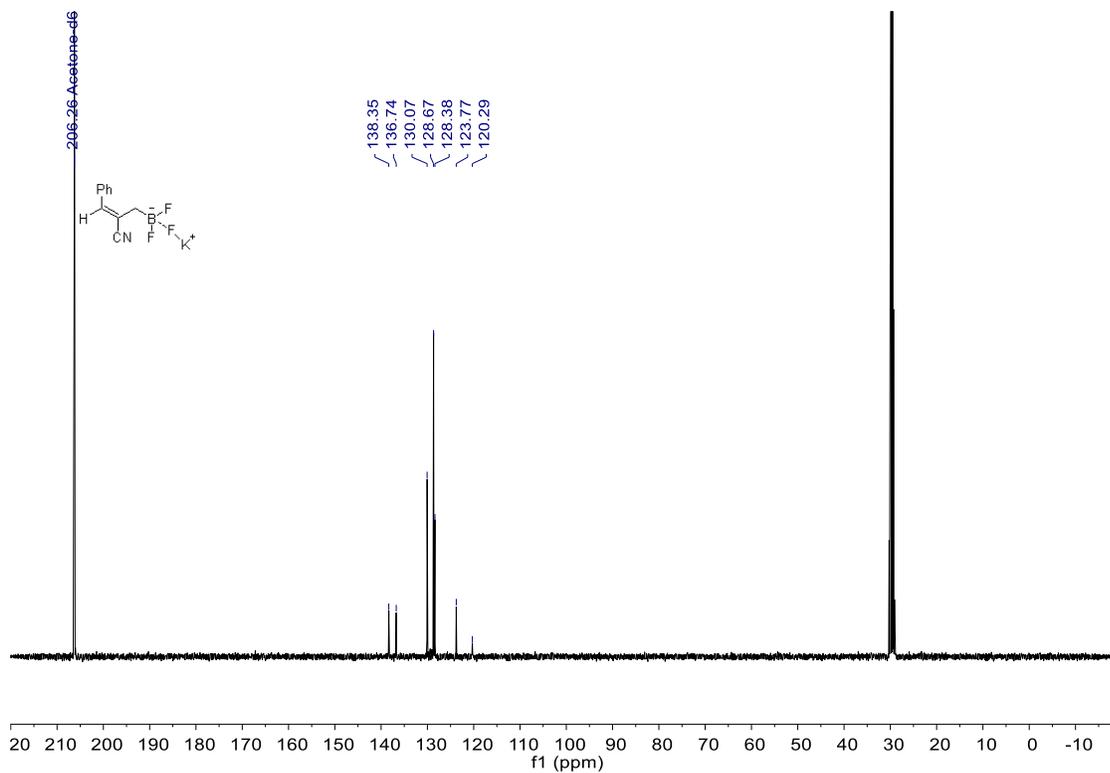
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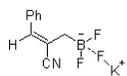




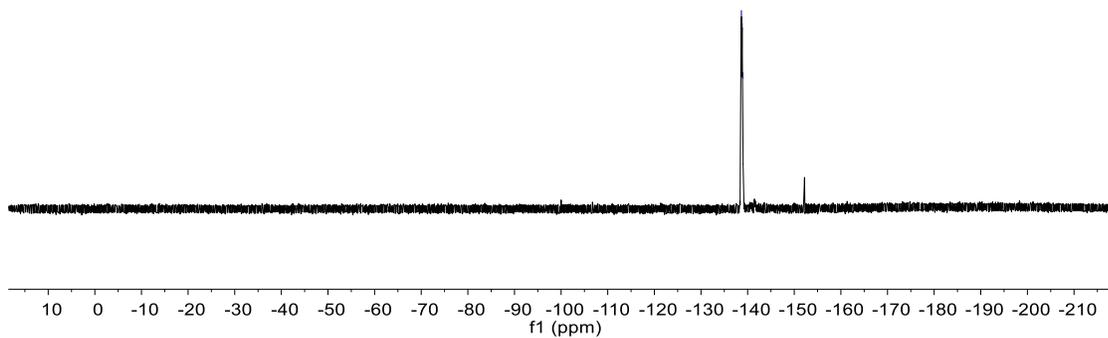
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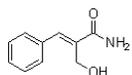




-138.66
-138.83
-138.96



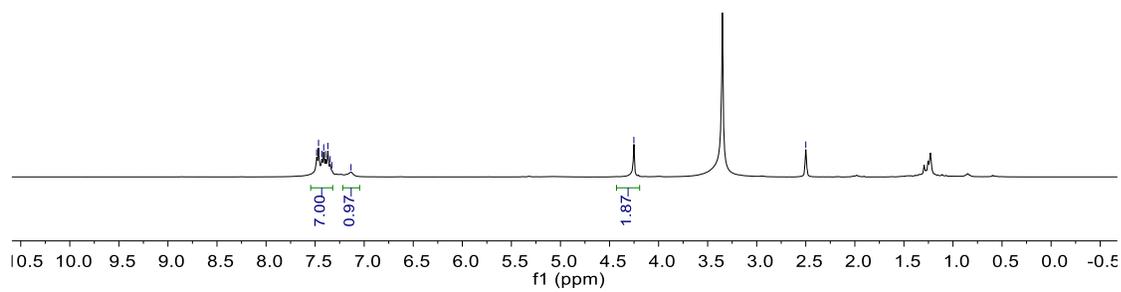
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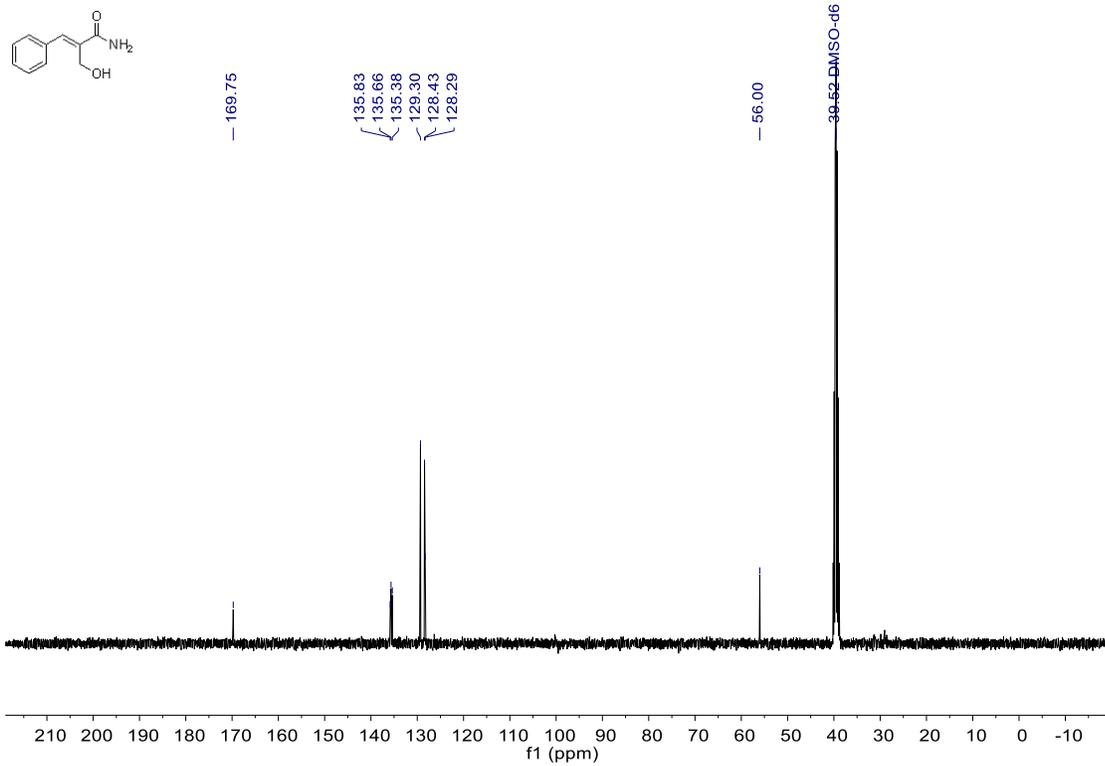


7.48
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7.41
7.39
7.37
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7.33
7.13

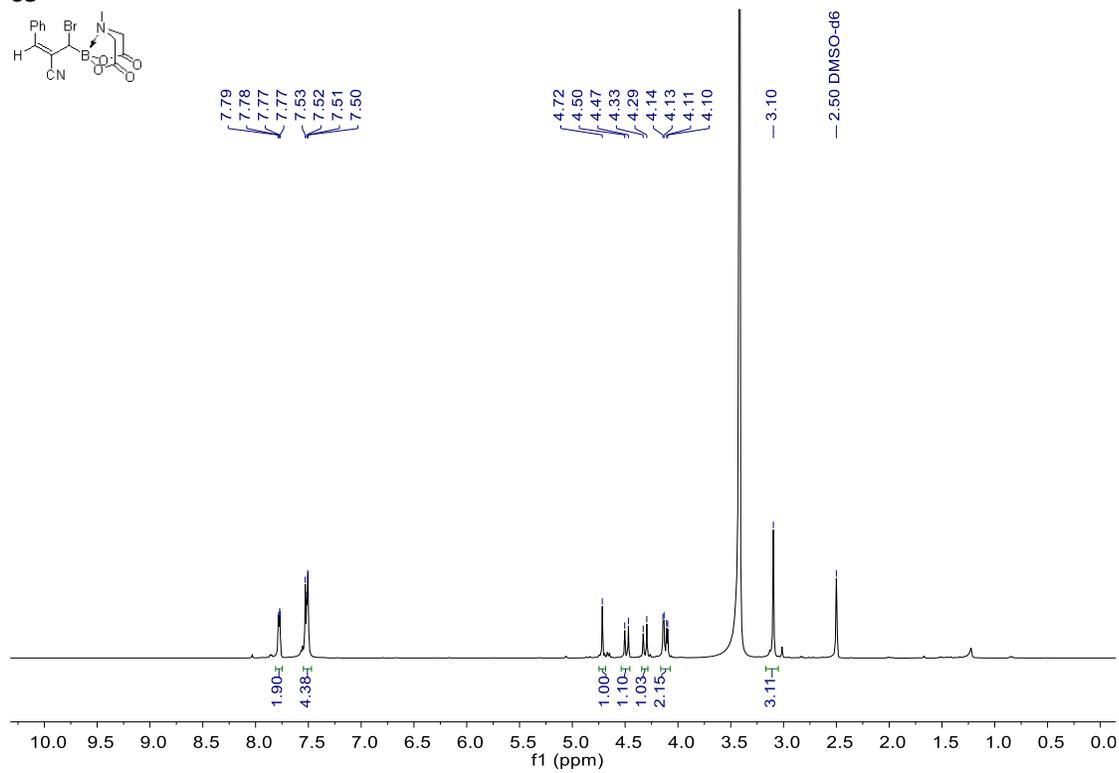
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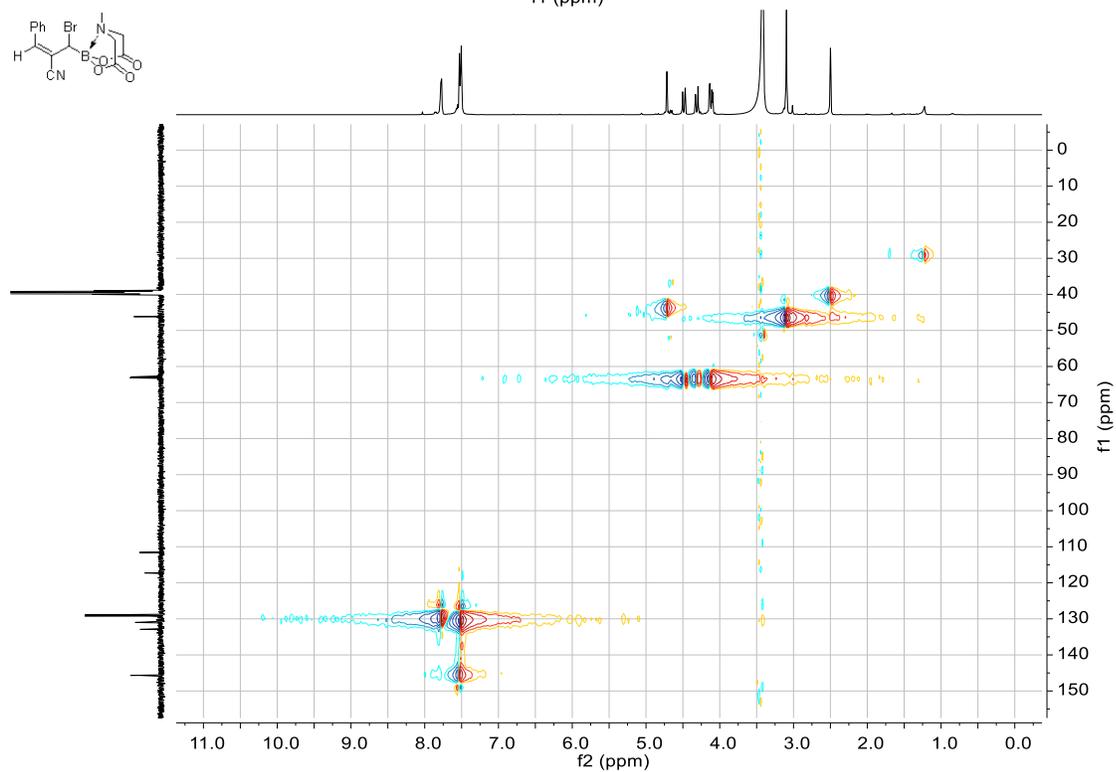
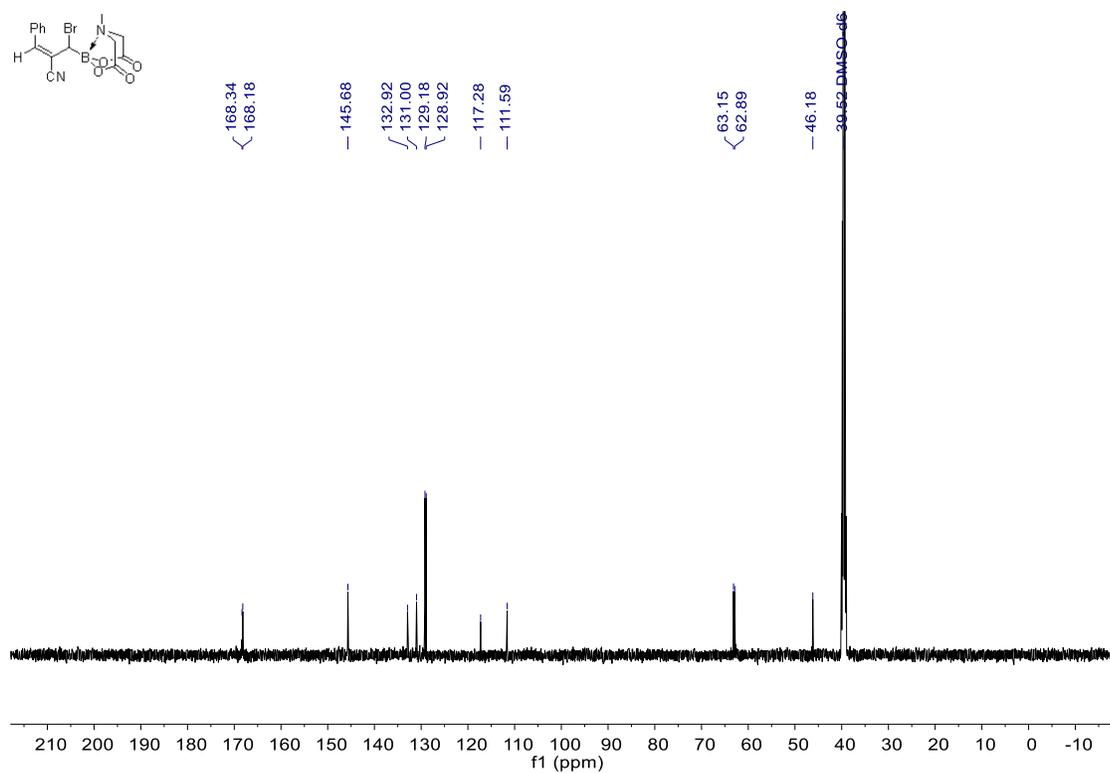
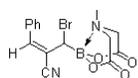
2.50 DMSO-d6



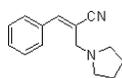


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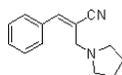
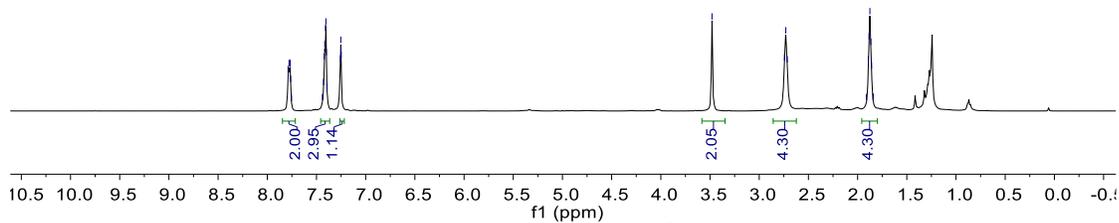
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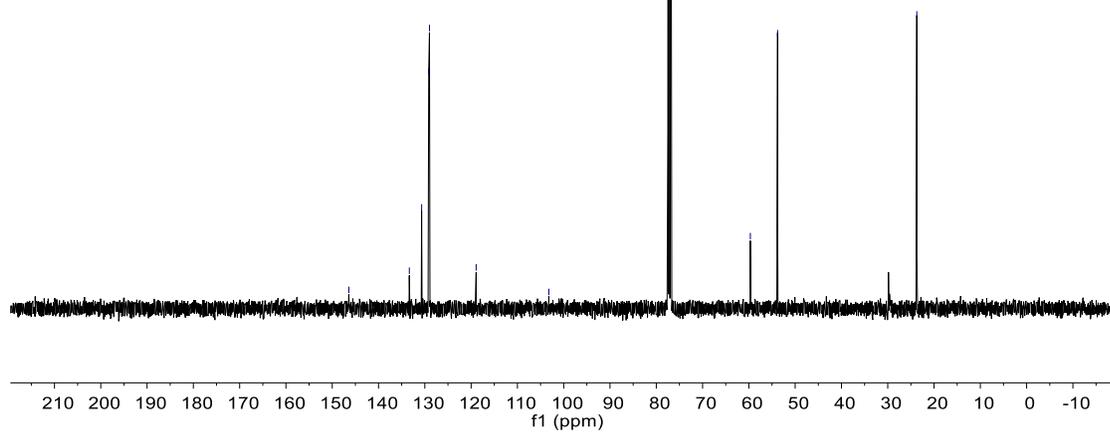
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7.726
7.725
7.725
7.725

— 3.48

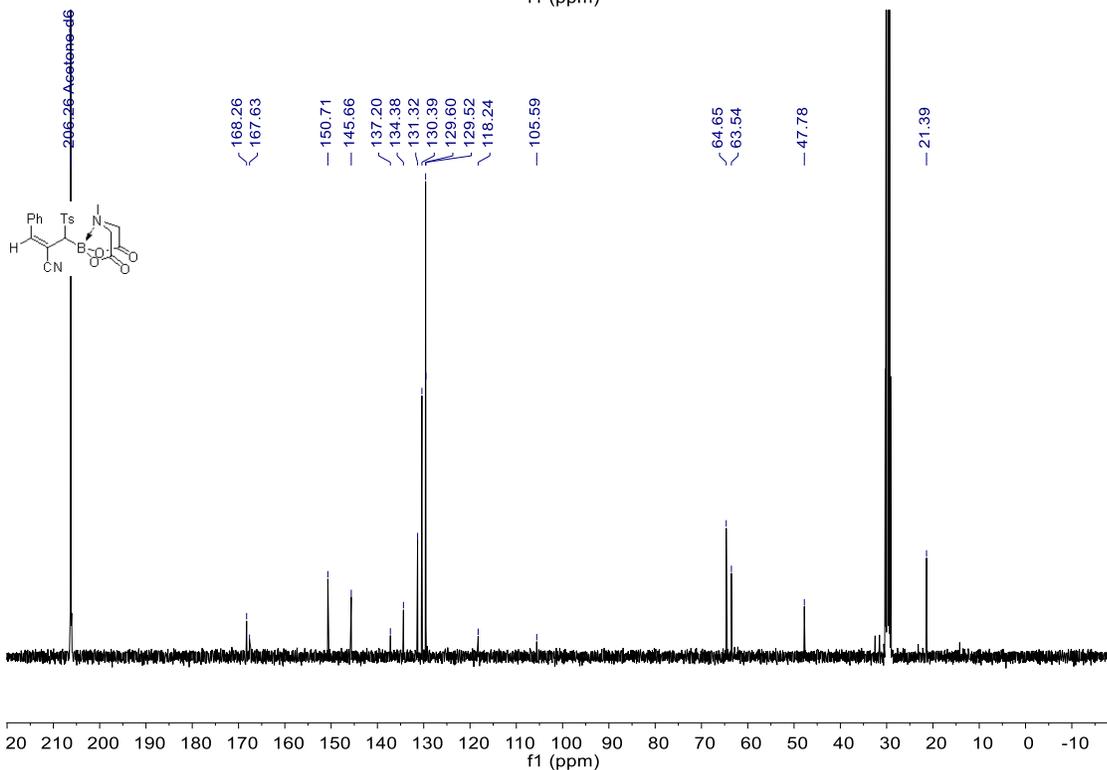
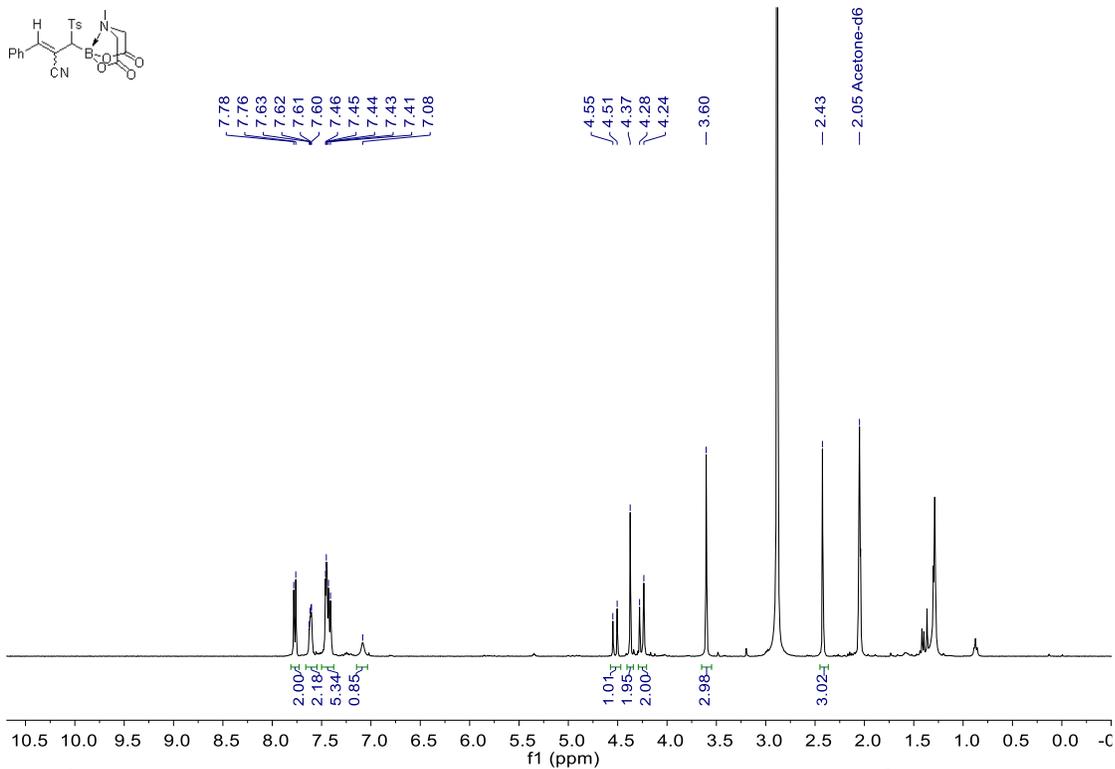
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1.88
1.87
1.86
1.84



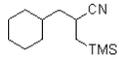
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— 103.22
77.16 CDCl₃
— 59.68
— 53.80
— 23.72



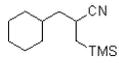
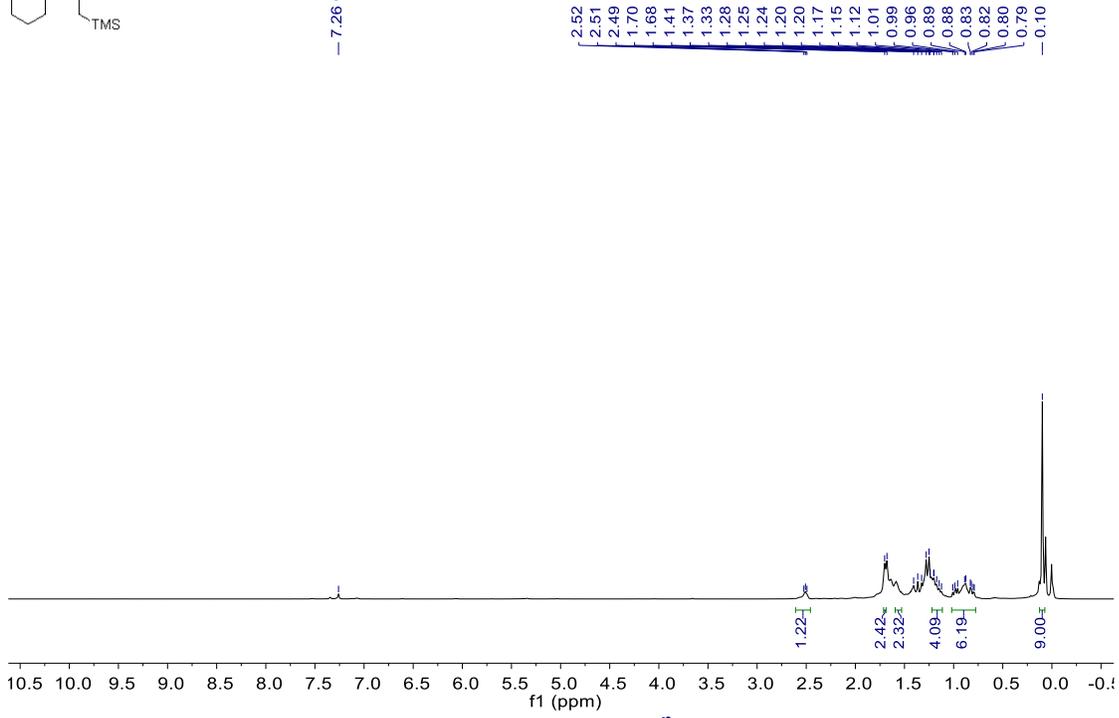
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68

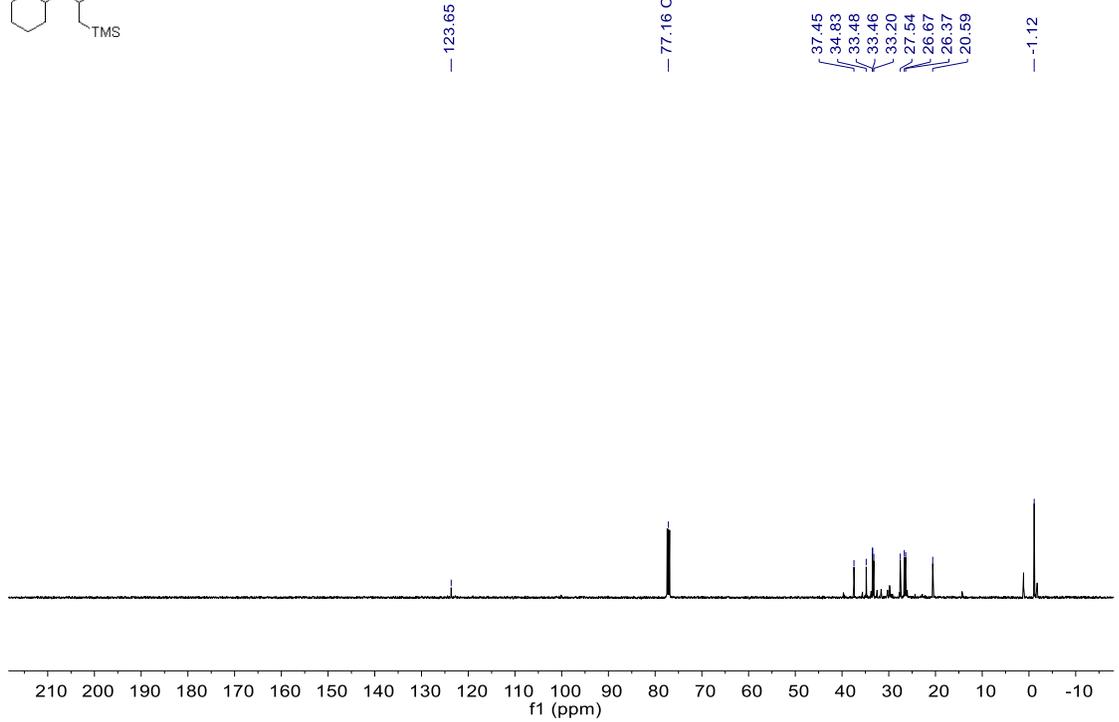


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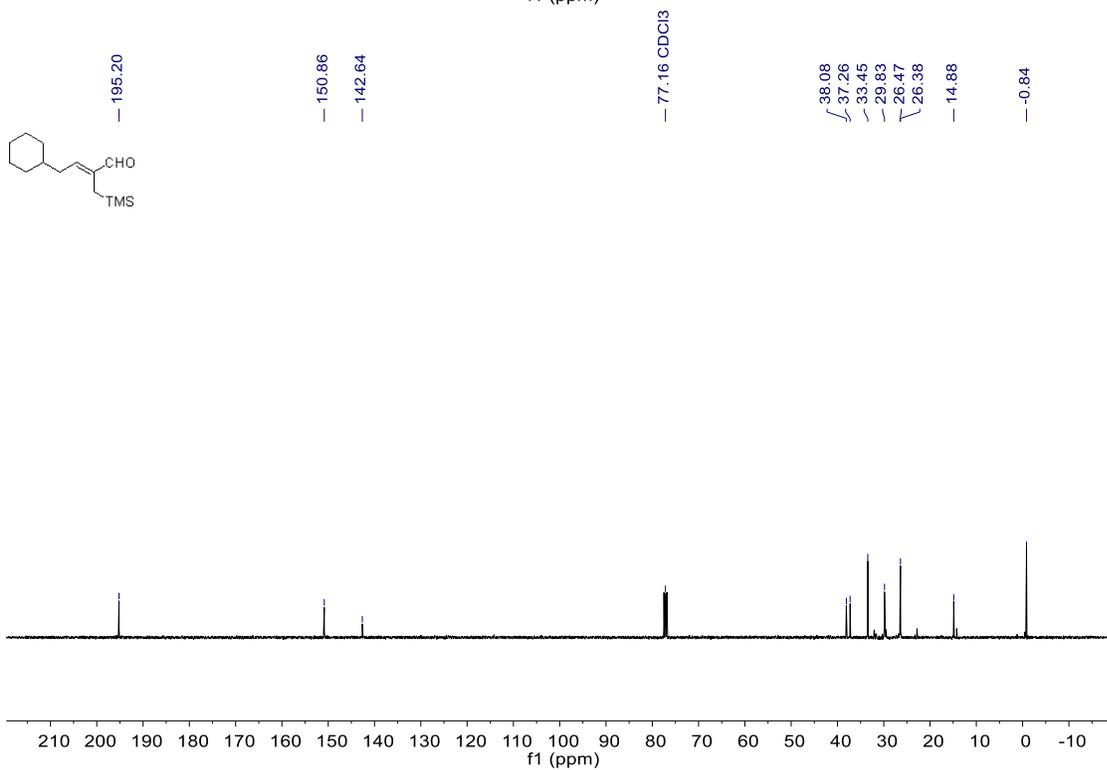
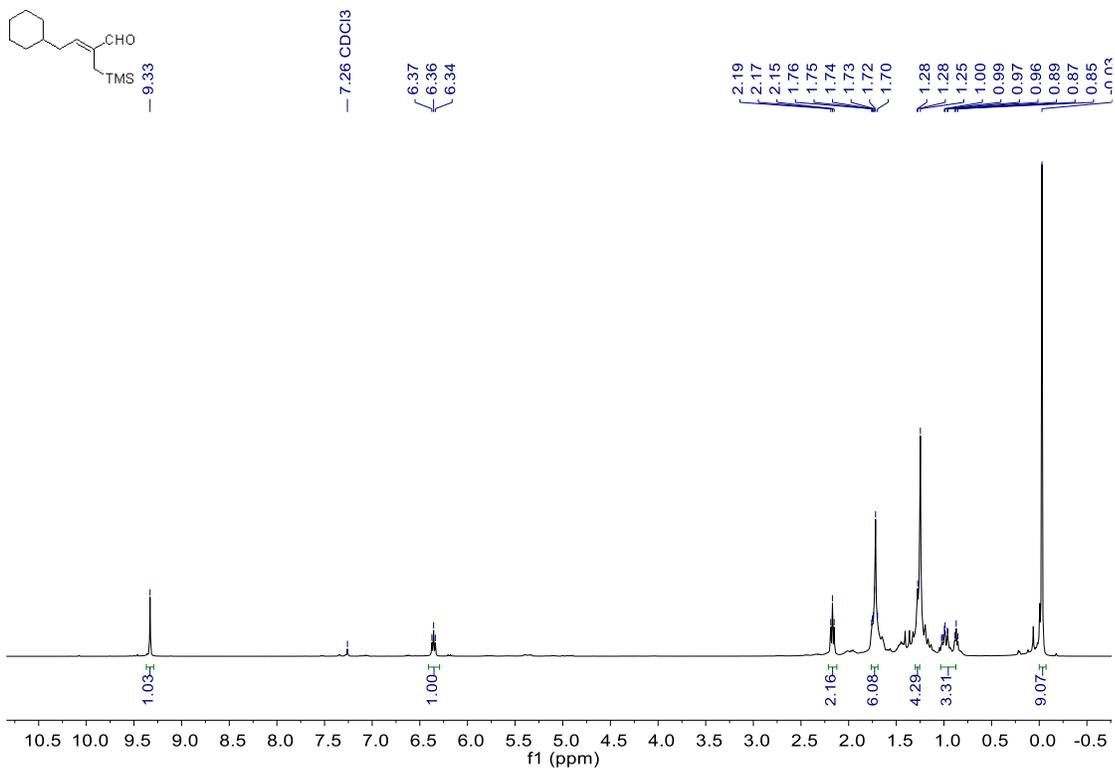


123.65

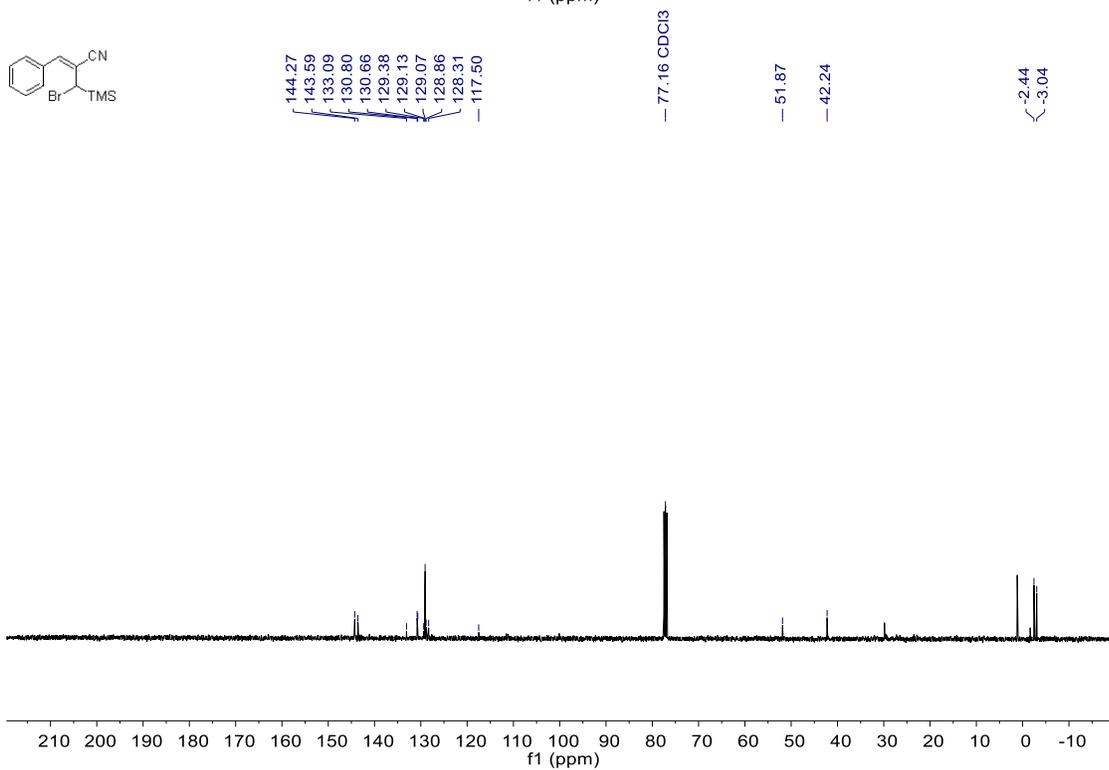
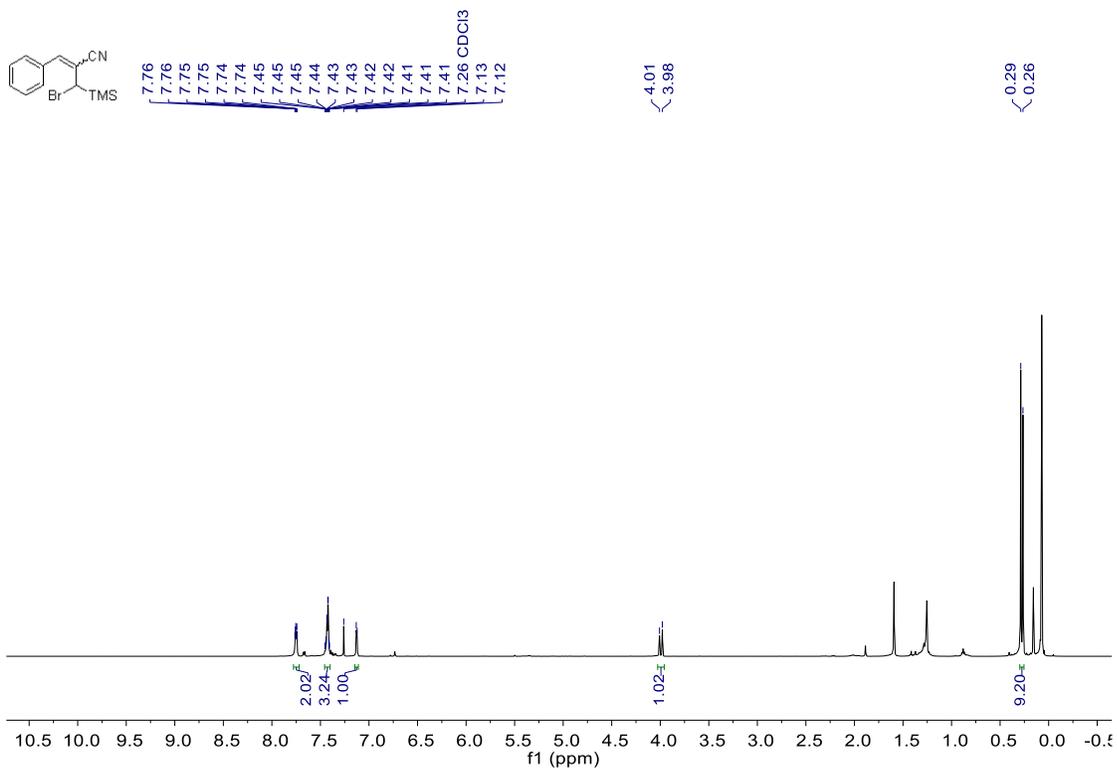
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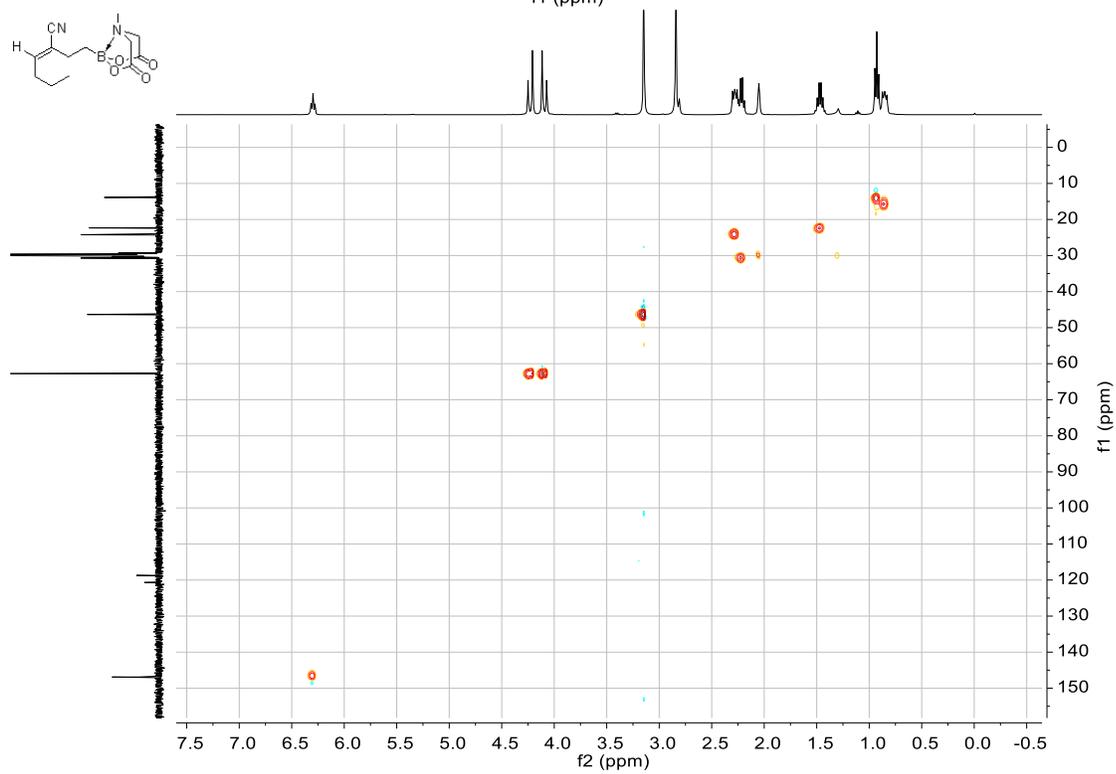
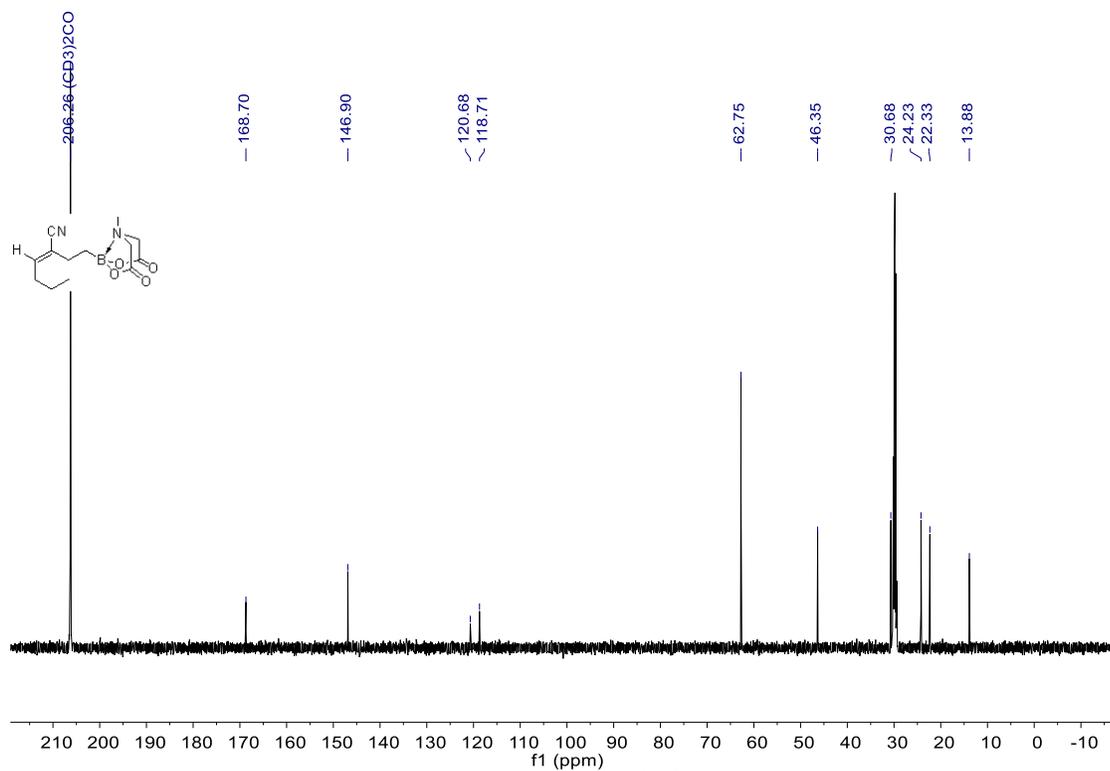
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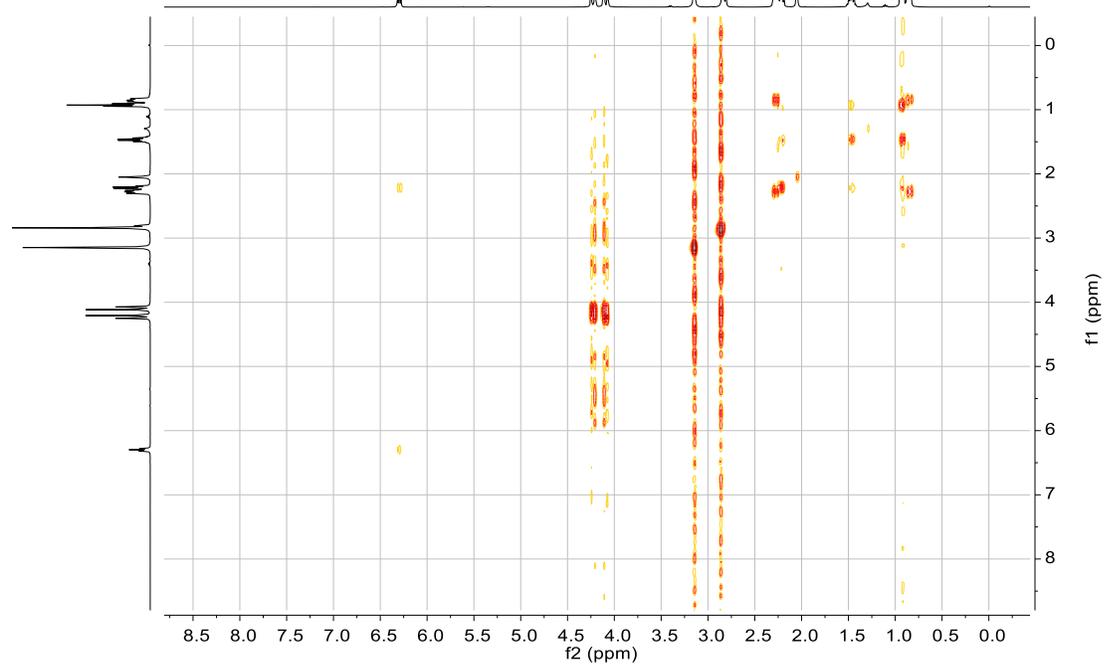
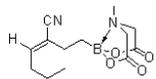


70



71





74

